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Author
Qiu, Yehao

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Formation of C–O and C–C Bonds Catalyzed by Transition Metal Complexes

By

Yehao Qiu

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Committee in charge:

Professor John F. Hartwig, Chair
Professor Richmond Sarpong
Professor Alexis T. Bell

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Abstract

Formation of C–O and C–C Bonds Catalyzed by Transition Metal Complexes

By

Yehao Qiu

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor John F. Hartwig, Chair

The following dissertation discusses the development, mechanism, and computational studies of reactions involving transition metal complexes that form C–O and C–C bonds. These reactions include Ni-catalyzed oxidation of unactivated C(sp^3)–H bonds, stereoselective synthesis of vicinal difluorides by the combination of Cu and Ir catalysts, and reductive elimination from Pd(aryl)(fluoroalkyl) complexes to form fluoroalkylarenes. Oxidative additions of C–H and C–Cl bonds to Ir and Pd complexes are also discussed.

Chapter 1 is an overview of direct oxidations of unactivated, aliphatic C–H bonds involving metal-free organic oxidants, transition metal complexes, and enzymes. The synthetic applications and the mechanism of each oxidation are discussed in detail.

Chapter 2 describes the mechanistic studies of Ni-catalyzed oxidation of unactivated C(sp^3)–H bonds with *meta*-chloroperbenzoic acid (*m*CPBA) as the oxidant. Comparison of the selectivity of different oxidation reactions and deuterium-labelling experiments suggest that this Ni-catalyzed reaction occurs by a free-radical chain mechanism.

Chapter 3 describes the development of a strategy to control the conformation of acyclic C(sp^3)–C(sp^3) bonds by synthesizing all four stereoisomers of vicinal difluorides with the combination of a chiral Cu catalyst and a chiral Ir catalyst. These vicinal difluoride products were synthesized in good yields and with high stereoselectivity. Due to the 1,2-gauche effect of the vicinal difluoride motif, each stereoisomer corresponds to a unique conformer of the acyclic C(sp^3)–C(sp^3) bond between the two C–F bonds. Chemical proteomic experiments suggest that biologically active molecules containing different stereoisomers of the vicinal difluorides bind differently to proteins.

Chapter 4 describes the computational studies of reductive elimination from Pd(aryl)(fluoroalkyl) complexes to form fluoroalkylarenes. This work focuses on understanding the features of the fluoroalkyl ligand that affect the barriers to reductive elimination. Results from DFT calculations suggest that secondary orbital interactions between the Pd center and a π-acid or a hydrogen atom attached to the α-carbon of the fluoroalkyl ligand significantly stabilize the transition state for reductive elimination. In the absence of such orbital interactions, a more electron-withdrawing fluoroalkyl ligand leads to a higher barrier to reductive elimination than a less electron-withdrawing fluoroalkyl ligand.

Chapter 5 explains the selectivity of Ir and Pd complexes for oxidative additions of aromatic C–H and C–Cl bonds. DFT calculations and energy decomposition analysis suggest that oxidative

addition of a C–Cl bond to Ir and Pd complexes is more exergonic than that of a C–H bond whereas the barrier to oxidative addition of a C–H bond to Ir complexes is lower than that of a C–Cl bond. Palladium(0) complexes are highly selective for oxidative addition of C–Cl bonds over C–H bonds because oxidative addition of C–H bonds is endergonic. Such endergonicity is closely related to the weakness of Pd–H bonds. Iridium(I) complexes are highly selective for oxidative addition of C–H bonds over C–Cl bonds because charge transfer between Ir and the C–H bond in the transition state is more stabilizing than that between Ir and the C–Cl bond.

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Chapter One

Overview of Direct Oxidation of Aliphatic C–H Bonds

1.1. Introduction

Oxidation of aliphatic C–H bonds occurs commonly in biological systems and is widely practiced in chemical synthesis. In many living organisms, enzymes, such as cytochrome P450s and methane monooxygenases, catalyze the hydroxylation of saturated C–H bonds.[1-2] In synthetic chemistry, direct oxidation of unactivated C(sp^3)–H bonds is a promising way to synthesize valuable products, such as alcohols and ketones, from abundant, inexpensive feedstock alkanes, and many examples of selective oxidation of C–H bonds have been reported for the synthesis of complex molecules and natural products.[3] More recently, direct oxidation of unactivated C(sp^3)–H bonds in polymers has enabled the synthesis of functional materials from virgin polyolefins.[4-6]

However, several challenges must be addressed for a high-yielding and selective oxidation reaction to be developed: (1) unactivated, aliphatic C–H bonds are strong (bond dissociation energy around 100 kcal/mol)[7-8] and usually require potent oxidants to cleave them; (2) C–H bonds are ubiquitous in organic molecules and often occupy similar chemical environments, so selective oxidation of one type of C–H bonds among many similar but inequivalent ones can be difficult; (3) oxidized products, e.g., alcohols, are generally more reactive than unfunctionalized aliphatic C–H bonds, so overoxidation may occur and form undesired byproducts.[9]

Despite these challenges, chemists have discovered many methods for the direct oxidation of aliphatic C–H bonds with metal-free organic oxidants, transition metal complexes, or enzymes (*vide infra*). Many of these methods require mild reaction conditions, form the desired oxidized products in good yield and high selectivity, and tolerate a broad scope of substrates. Meanwhile, mechanistic investigations provided insight into the pathways by which C–H bonds were oxidized by different systems and guided the development of novel methods for oxidation.

This chapter provides an overview of representative examples of direct oxidation of aliphatic C–H bonds involving (1) metal-free organic oxidants, (2) cytochrome P450 enzymes, and (3) transition metal complexes. Synthetic applications as well as mechanistic studies are discussed for each example.

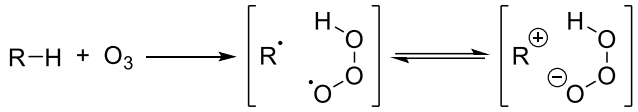
1.2. Oxidation of C(sp^3)–H Bonds by Metal-Free Organic Oxidants

1.2.1. Ozone (O_3)

In as early as 1898, ozone was reported to react with methane to form formaldehyde and formic acid at temperatures as low as 15 ˚C. Years later, the reaction of ozone with ethane to form a mixture of products including ethanol, acetaldehyde, and acetic acid was also disclosed.[10] In 1956, Schubert, Schubert, and Pease reported that propane reacted with O_3 to afford acetone as one of the major products, whereas isobutane reacted with O_3 to give *tert*-butanol as the major product.[11-12] They also measured the rates of the reactions between ozonized oxygen (*circa* 3 mol% O_3) and methane, propane, *n*-butane, and isobutane at temperatures between 25 and 50 ˚C and calculated the activation energies to be 14.9, 12.1, 11.1, and 10.3 kcal/mol for the reactions with those four alkanes, respectively.[11-12] These low activation energies of the reactions between O_3 and saturated hydrocarbons were attributed to the high reactivity of a low-lying triplet electronic state of O_3.[11-12] In agreement with these results, Williamson and Cvetanovic measured the second-order rate constants of the ozonation of a series of saturated alkanes containing five to six carbon atoms at 25 ˚C and determined that tertiary C–H bonds reacted faster with O_3 than secondary C–H bonds, which, in turn, reacted faster than primary C–H bonds.[13]

At 22 ˚C, oxidation of the tertiary C–H bonds in *cis*- or *trans*-1,2-dimethylcyclohexane and in *cis*- or *trans*-decalin by O_3 afforded the corresponding tertiary alcohols with 79% – 85% retention and 15% – 21% inversion of configuration at the tertiary carbon atom.[14-15] Based on these results,

Hamilton, Ribner, and Hellman proposed the following mechanism for the oxidation of aliphatic C–H bonds by O_3 at low temperatures (< 50 ˚C):[14-15]



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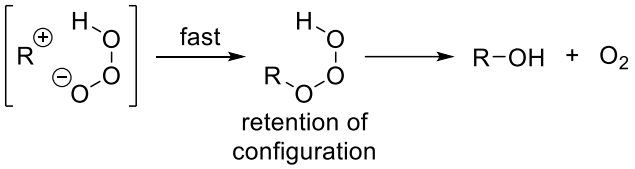

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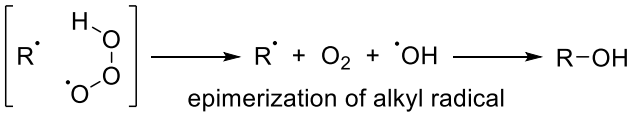


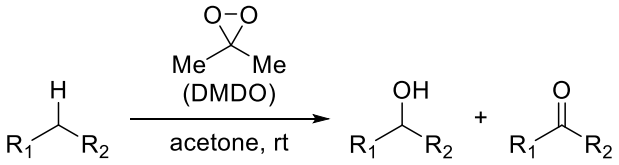
(1.2.1.3)

In this proposed mechanism, the alkane first reacts with O_3 to form an alkyl radical and a HO_3· radical within the solvent cage; this radical pair equilibrates with the ionic pair consisting of a carbocation and a HO_3^- anion (eq 1.2.1.1). The HO_3^- anion is proposed to react rapidly with the carbocation to generate an alkyl hydrotrioxide intermediate with retention of configuration at the carbon center, which then decomposes to the alcohol product and the O_2 byproduct (eq 1.2.1.2). In contrast, since cleavage of the O–O bond in the HO_3· radical is exothermic by 15 kcal/mol, the HO_3· radical is expected to release O_2 first, generate a hydroxy radical, which combines with the alkyl radical to form the alcohol product with epimerization at the carbon atom (eq 1.2.1.3).

1.2.2. Dioxiranes

Dioxiranes oxidize alkanes to form the corresponding alcohol and ketone products. In 1985, Murray reported the oxidation of various saturated hydrocarbons by dimethyldioxirane (DMDO).[17-18] As shown in Table 1.1, oxidation occurring at secondary carbons formed ketone as the major product and alcohol as the minor product (entries 3–5). Tertiary C–H bonds were more prone to oxidation by DMDO than secondary C–H bonds, which in turn were more reactive than primary C–H bonds, as evident in the oxidations of adamantane and *n*-decane (Table 1.1, entries 1 and 5). A few years later, Curci reported the oxidation of alkanes by methyl(trifluoromethyl)dioxirane (TFDO), which occurred with similar selectivity but significantly higher rate than did the reaction with DMDO.[19-21]

Table 1.1. Oxidation of alkanes by dimethyldioxirane.



Entry	Substrate	Products	Yield (%)[a]
1	adamantane	1-adamantanol	87
		2-adamantanol + 2-adamantanone	2.6
2	toluene	benzaldehyde	3.3
		benzoic acid	1.8
3	cyclohexane	cyclohexanol	23
		cyclohexanone	41
4	cyclododecane	cyclododecanone	60

		cyclododecanol	3
5	*n*-decane	2-decanone	20.3
		3-decanone + others	9.5

[a]Yield was determined by gas chromatography (GC) with respect to DMDO.

Since the initial reports by Murray and Curci, dioxiranes have been widely used for the selective oxidation of aliphatic C–H bonds in alkanes and in complex molecules.[22-29] Figure 1.1 shows the selectivity of TFDO for the oxidation of C(sp^3)–H bonds in representative substrates.[25, 27-29] In general, TFDO is selective for weak, tertiary C–H bonds, as well as those α to an oxygen atom or a cyclopropyl group (Figure 1.1(a) and (b)), which are weaker than other secondary C–H bonds. Due to its electrophilicity, TFDO is also selective for the C–H bonds that are 3 or 4 bonds away from an electron-withdrawing group (Figure 1.1(d), (e), and (f)) because these bonds are more electron rich than those proximal to the electron-withdrawing group. Due to their small sizes, dioxiranes are generally less sensitive to the steric environment of the substrate than are larger oxidants.

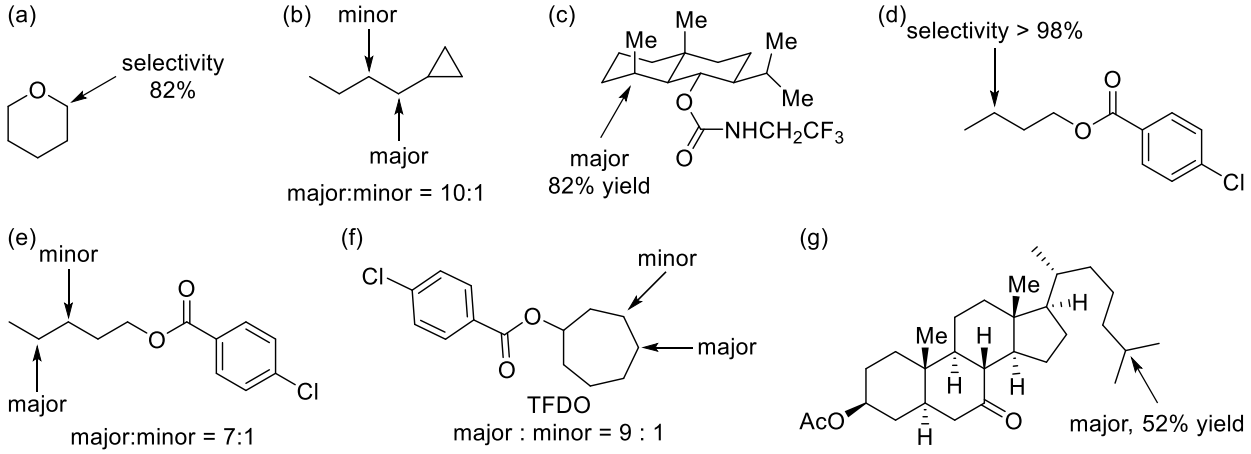
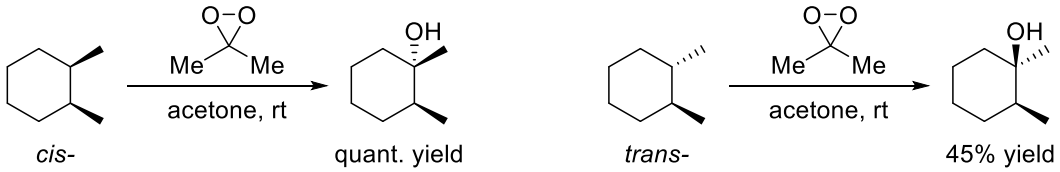


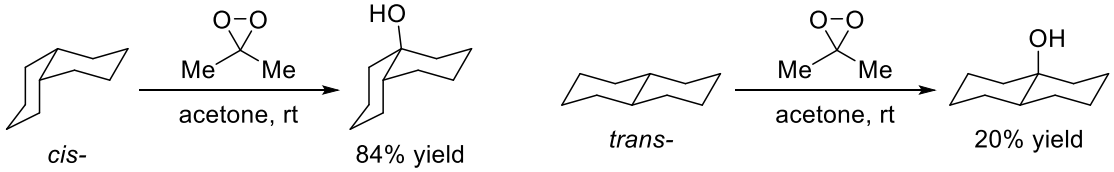
Figure 1.1. Selectivity of TFDO for the oxidation of C(sp^3)–H bonds in model compounds and complex molecules.

To understand the mechanism of the oxidation of alkanes by dioxiranes, Murray and coworkers conducted the following experiments:[17-18] (1) oxidation of the tertiary C–H bonds in *cis*- and *trans*-1,2-dimethylcyclohexane as well as in *cis*- and *trans*-decalin by DMDO formed the corresponding tertiary alcohol with retention of configuration as the only product (Figure 1.2(a) and (b)); (2) relative rates for benzylic oxidations of toluene, ethylbenzene and cumene by DMDO were compared to those by *tert*-butoxy radical (Figure 1.2(c)), and these rates indicated that DMDO is much more selective than an alkoxy radical towards tertiary C–H bonds; (3) a mixture of equimolar amounts of cyclododecane and fully deuterated cyclododecane-d_{24} was treated with DMDO, and a large kinetic isotope effect (KIE, k_H/k_D = 4.97, Figure 1.2(d)) was observed. Based on these mechanistic results, the authors proposed that oxidation of saturated C–H bonds by dioxiranes did not involve radical intermediates and likely proceeded by a concerted pathway by which oxygen inserted into the C–H bond (Scheme 1.1(a)).[17]

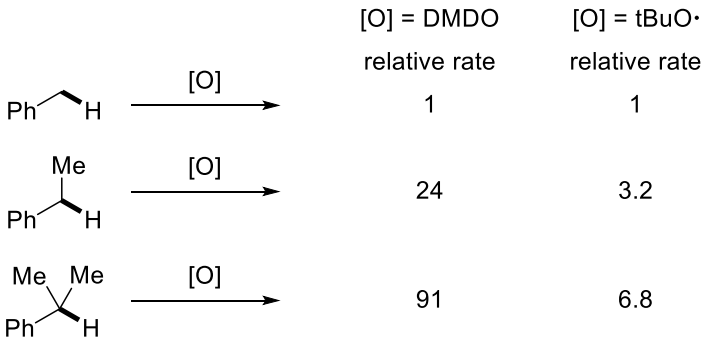
(a) Stereoretentive oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane by DMDO



(b) Stereoretentive oxidation of *cis*- and *trans*-decalin by DMDO



(c) Relative rates of benzylic oxidation by DMDO and by *tert*-butoxy radical



Note: relative rates were normalized based on the number of H atoms.

(d) Kinetic isotope effect for the oxidation of cyclododecane by DMDO

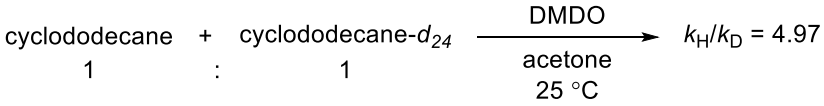
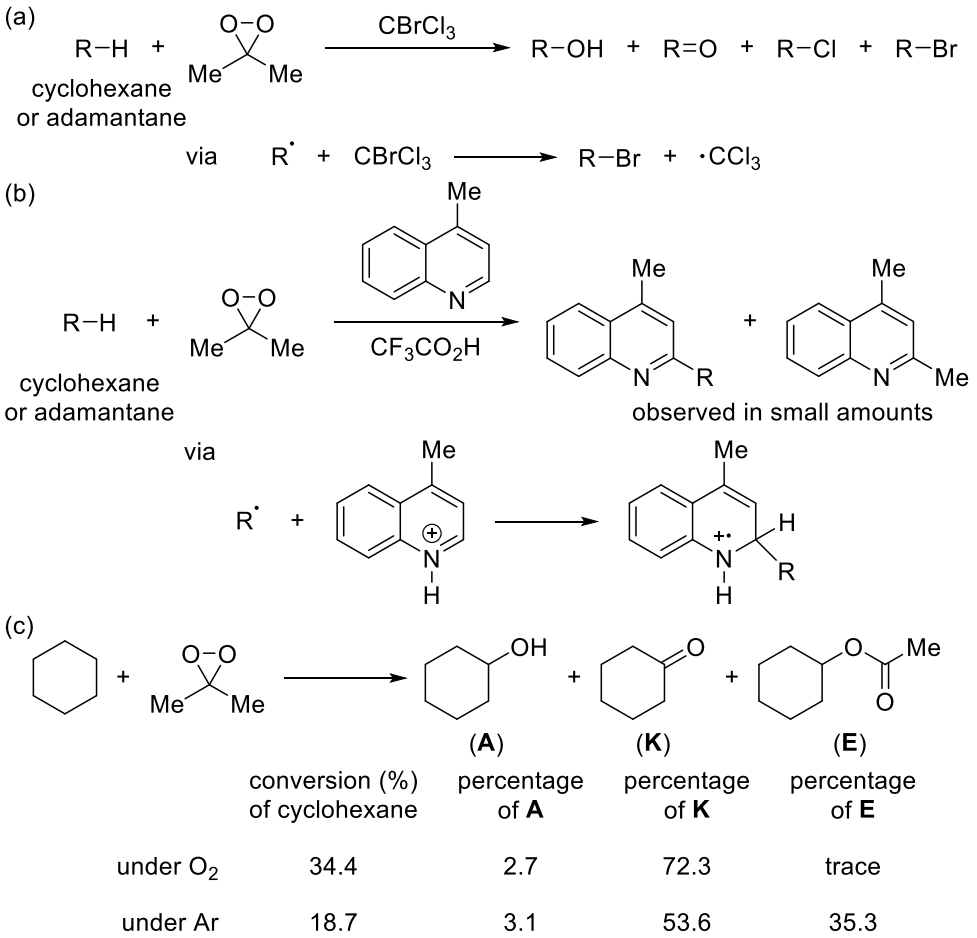


Figure 1.2. Mechanistic experiments of the oxidation of alkanes by DMDO conducted by Murray.

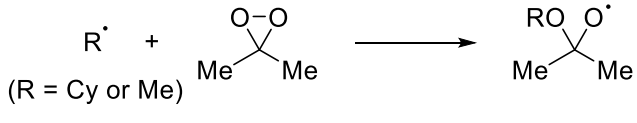
In contrast to Murray's proposed mechanism, Minisci published in 1998 a series of results that supported the formation of radical intermediates in the oxidation of alkanes by DMDO:[30] (1) oxidation of cyclohexane or adamantane by DMDO in the presence of varying amounts of $CBrCl_3$ afforded the corresponding alkyl bromide and alkyl chloride in addition to the alcohol and ketone products. These alkyl halide products were likely formed from the reaction of $CBrCl_3$ with an alkyl radical (Figure 1.3(a)). (2) Oxidation of cyclohexane or adamantane by DMDO in the presence of 4-methylquinoline and trifluoroacetic acid afforded small amounts of quinoline byproducts that were substituted at the 2-position, most likely from alkylation of the protonated quinoline by an alkyl radical (Figure 1.3(b)). (3) Oxidation of cyclohexane by DMDO in the absence of atmospheric O_2 afforded cyclohexyl acetate as a byproduct in much higher yield than the reaction in the presence of O_2; also, the conversion of the alkane substrate for the reaction in the absence of O_2 was lower than that in the presence of O_2 (Figure 1.3(c)). The authors attributed the formation of cyclohexyl acetate to the process described in eq 1.2.2.1 and eq 1.2.2.2, in which the cyclohexyl radical reacted with DMDO to form an oxygen-based radical intermediate, which subsequently underwent β-scission to form the cyclohexyl acetate byproduct and a methyl radical. The methyl radical then reacted with another equivalent of DMDO (eq 1.2.2.1), thus propagating the chain reaction, consuming the oxidant in this unproductive pathway, and resulting in the low conversion

of the cyclohexane substrate. In the presence of O_2, however, the alkyl radicals reacted rapidly with O_2 (eq 1.2.2.3) and did not engage in this unproductive radical chain reaction, hence leading to higher conversion of cyclohexane.



	conversion (%) of cyclohexane	percentage of **A**	percentage of **K**	percentage of **E**
under O_2	34.4	2.7	72.3	trace
under Ar	18.7	3.1	53.6	35.3

Figure 1.3. Minisci's results that supported the involvement of radical intermediates: (a) oxidation of alkanes with DMDO in the presence of $CBrCl_3$; (b) oxidation of alkanes with DMDO in the presence of 4-methylquinoline and CF_3CO_2H; (c) the effect of atmospheric O_2 on the oxidation of cyclohexane with DMDO.



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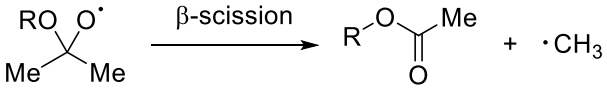
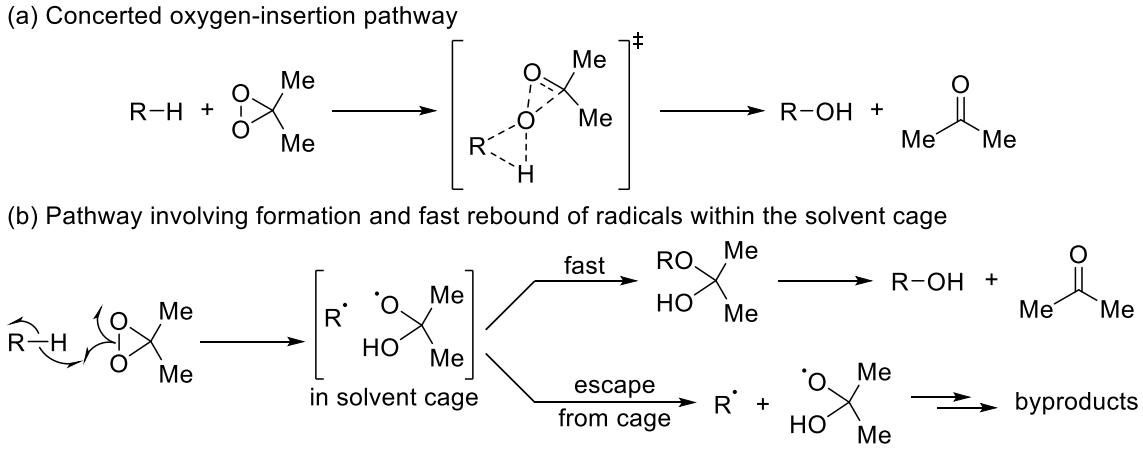


(1.2.2.2)

(1.2.2.3)

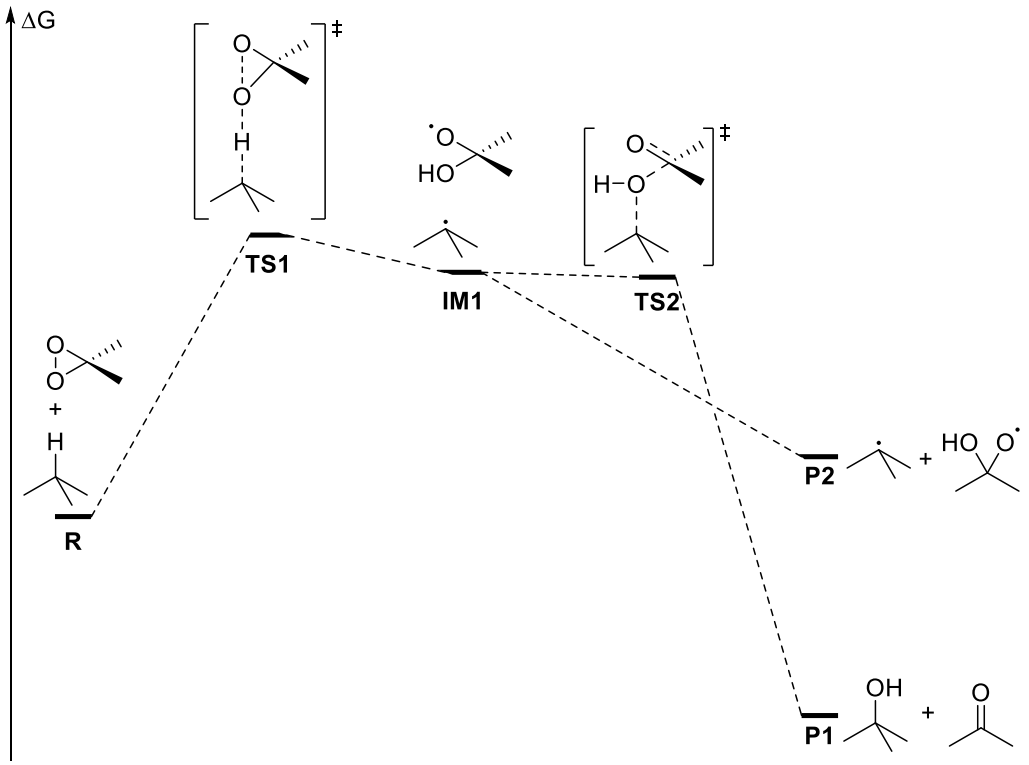
Based on these results, Minisci proposed a radical pathway for the oxidation of alkanes by dioxiranes (Scheme 1.1(b)).[30] In this proposed mechanism, hydrocarbon-induced homolysis of the O–O bond in dioxirane followed by HAT from the alkane formed an alkyl radical and an *α*-

hydroxyalkoxyl radical within the solvent cage. In most cases, these two radicals underwent fast recombination within the cage to afford the hemiacetal intermediate, which was subsequently converted to the alcohol product and acetone. The rate of radical recombination was expected to be faster than the rate of epimerization of a tertiary carbon-centered radical (first-order rate constant $k \approx 10^9$ s^{-1}),[31] so as to be consistent with the stereoretentive hydroxylations of tertiary C–H bonds (Figures 1.2(a) and (b)). However, there was a small possibility that the alkyl radical escaped the solvent cage and initiated radical chain reactions, as depicted in Figure 1.2.



Scheme 1.1. (a) The concerted oxygen-insertion pathway proposed by Murray; (b) the radical pathway proposed by Minisci.

Given the two conflicting pathways (concerted *vs.* radical), many research groups have conducted computational studies[32-38] to elucidate the mechanism of oxidation of aliphatic C–H bonds by dioxiranes. These studies, in which isobutane was used as the alkane, generally supported the reaction pathway outlined in Scheme 1.2: first, isobutane reacted with DMDO to form a *tert*-butyl radical and an *α*-hydroxyisopropoxyl radical (**IM1**) by a concerted, asynchronous transition state (**TS1**). The relative free-energy barrier corresponding to **TS1** ranged from 18 to 30 kcal/mol,[32, 39] depending on the level of theory and on whether an implicit solvation model was implemented in the calculations. The radical pair **IM1** was a bifurcation point, from which the two radicals could either combine through transition state **TS2** to form the *tert*-butanol and acetone products (**P1**) or dissociate from each other and initiate free radical reactions. Studies by Houk[35, 39] showed that both pathways after the bifurcation point were essentially barrierless and the distribution between the two was highly dependent on the polarity of the solvent. In acetone, molecular dynamic studies predicted that 90% of radical pair **IM1** would recombine and the other 10% would dissociate.[39] The authors also estimated the lifetime of **IM1** to be 30 – 150 fs, consistent with the experimental value (<200 fs) determined by radical clock experiments with *trans*-1-phenyl-2-ethylcyclopropane.[40] The mechanism supported by computational studies was similar to the one proposed by Minisci, except that computations predicted that the C–O bond in the alcohol product was formed directly by reaction of the tertiary radical with the hydroxy group (Scheme 1.2, **IM1** to **TS2**), rather than indirectly by a hemiacetal intermediate, as proposed by Minisci (Scheme 1.1(b)).

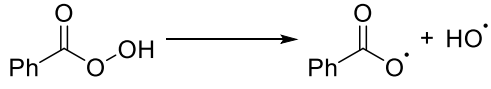


Scheme 1.2. A representative energy diagram for the oxidation of isobutane by DMDO based on computational studies. Heights of barriers are not to scale.

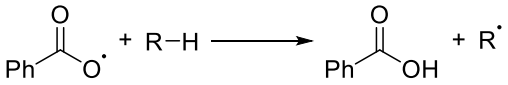
1.2.3. Aromatic Peracids

Aromatic peracids, such as *meta*-chloroperbenzoic acid (*m*CPBA) and *para*-nitroperbenzoic acid, oxidize C(sp^3)–H bonds to form the corresponding alcohol and ketone products.[41-44] This transformation has been utilized for the oxidation of aliphatic C–H bonds in complex molecules such as triterpenoids.[45-48]

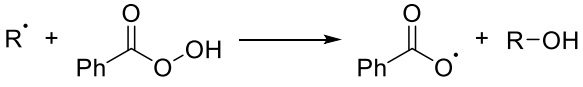
Like the case of dioxiranes, there have been long-standing debates between a concerted oxygen-insertion mechanism and a free radical mechanism for the oxidation of C(sp^3)–H bonds by aromatic peracids. In an early report, Tokumaru and Simamura proposed a free radical mechanism,[44] which involved homolysis of the O–O bond in the peracid (eq 1.2.3.1), abstraction of a hydrogen atom in the alkane by the benzoyloxy radical (eq 1.2.3.2), and reaction of the alkyl radical with an oxygen-donor to form the C–O bond (eq 1.2.3.3 and 1.2.3.4).



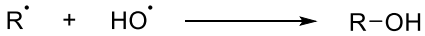
(1.2.3.1)



(1.2.3.2)

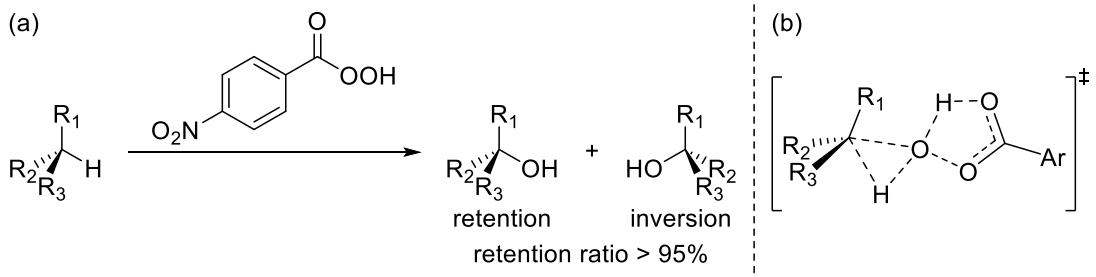


(1.2.3.3)



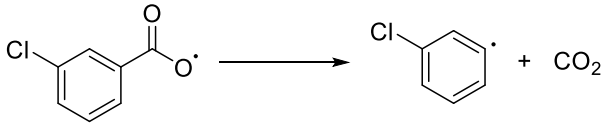
(1.2.3.4)

However, this free radical mechanism was inconsistent with the retention of configuration at the tertiary carbon observed from the oxidation of tertiary C–H bonds by aromatic peracids (Scheme 1.3(a))[41] because a free alkyl radical (eq 1.2.3.2) would epimerize rapidly and lead to racemization at the tertiary center. Such retention of configuration prompted some researchers to propose the concerted oxygen-insertion pathway (Scheme 1.3(b)).[42]



Scheme 1.3. (a) High ratio of retention of configuration at the tertiary carbon oxidized by *p*-nitroperbenzoic acid; (b) the proposed transition state for the concerted oxygen-insertion pathway.

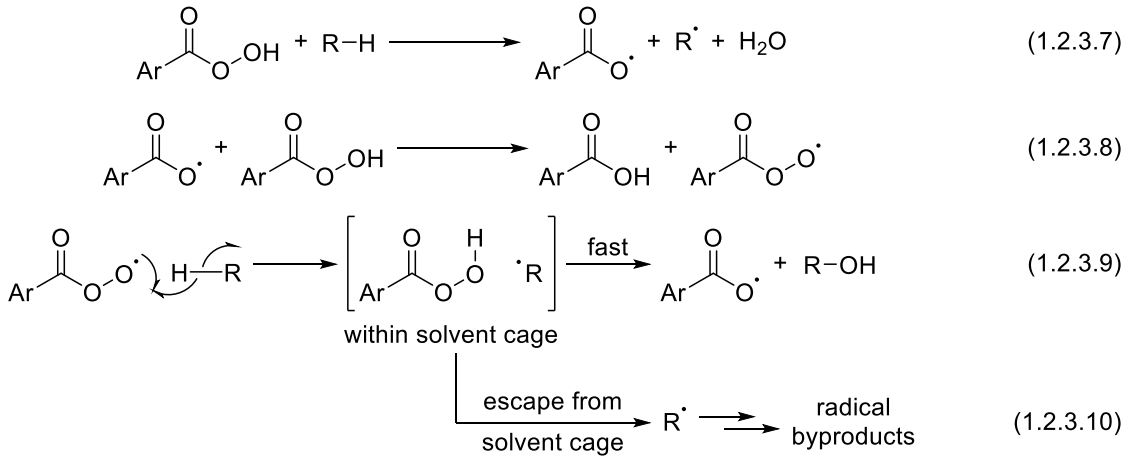
In 1996, Minisci disclosed mechanistic studies[42-43] that contradicted the concerted oxygen-insertion mechanism and proposed a modified radical mechanism for the oxidation of alkanes by aromatic peracids. The authors conducted oxidations of adamantane and cyclohexane by *m*CPBA and observed the formation of chlorobenzene, which was generated by decarboxylation of the *m*-chlorobenzoyloxy radical (eq 1.2.3.5). The oxidation of adamantane by *m*CPBA in CCl_4 as the solvent afforded chloroadamantanes as major products, which were likely formed by the reaction of adamantyl radicals with CCl_4 (eq 1.2.3.6).



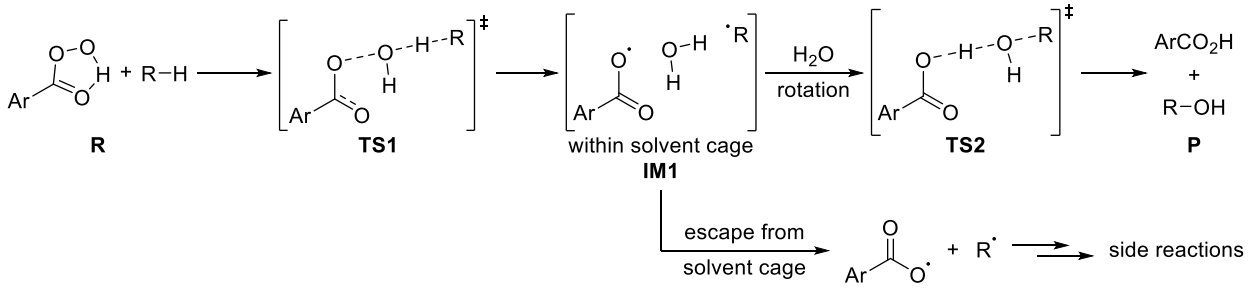
(1.2.3.5)

(1.2.3.6)

Based on these results, which clearly indicated that radical intermediates were formed in the oxidation of alkanes by peracids, Minisci proposed the following mechanism for this transformation:[42-43] as the initiation step, the presence of alkane induced the breaking of the O–O bond in the peracid and the formation of the aroyloxy radical ($ArCO_2$·, eq 1.2.3.7), which abstracted a hydrogen atom from *m*CPBA to form the carboxylic acid byproduct and the aroylperoxy radical ($ArCO_3$·, eq 1.2.3.8). The aroylperoxy radical then abstracted a hydrogen atom from the alkane, generated an alkyl radical and *m*CPBA within the solvent cage, which rapidly recombined to form the alcohol product and the aroyloxy radical (eq 1.2.3.9). This aroyloxy radical would subsequently undergo the reaction described in eq 1.2.3.8, propagating the radical chain. The rate of recombination within the solvent cage was expected to be faster than the rate of epimerization of a tertiary carbon radical, consistent with the high ratio of retention shown in Scheme 1.3(a). It was also possible that a small portion of alkyl radicals escaped from the solvent cage and underwent side reactions (eq 1.2.3.10). However, the authors did not provide experimental evidence to support the hypothesis that an aroyloxy radical would selectively react with an aromatic peracid in the presence of excess alkane (eq 1.2.3.8), even though aroyloxy radicals have been known to cleave unactivated C(sp^3)–H bonds.[49-51] In addition, some key results reported by Minisci[42] could not be reproduced in our laboratory, thus decreasing the credibility of this proposed radical chain mechanism.



Computational studies provided an alternative mechanism for the oxidation of C(sp^3)–H bonds by peracids (Scheme 1.4).[52-53] By this mechanism, the peracid reacts first with the alkane by a concerted, asynchronous pathway (**TS1**) to form the aroyloxy radical, the alkyl radical, and a water molecule within the solvent cage (**IM1**). In most cases, the water molecule in **IM1** undergoes barrierless rotation (**IM1** to **TS2**) so that the O–H bond is pointed towards the oxygen atom in the aroyloxy radical (**TS2**). Subsequent trimolecular reaction between the aroyloxy radical, the rotated water molecule, and the alkyl radical affords the alcohol product and the carboxylic acid byproduct (**TS2** to **P**). Meanwhile, there is a small possibility that radical species in **IM1** escapes the solvent cage and undergoes radical-mediated side reactions (such as chlorination of the alkyl radical and decarboxylation of the aroyloxy radical). DFT calculations suggested that the pathway depicted in Scheme 1.4 (from **R** to **P**) was exergonic and kinetically feasible ($\Delta G^{\ddagger}$(**TS1**) = 20.2 kcal/mol with respect to **R**) and was more energetically favorable than free radical pathways.[53]



Scheme 1.4. An alternative mechanism for the oxidation of alkanes by aromatic peracids supported by computational studies.

1.3. Oxidation of Aliphatic C–H Bonds Catalyzed by Cytochrome P450 Enzymes

The cytochromes P450 are a large family of cysteinato-heme enzymes that are present in many living organisms. They catalyze oxidative transformations, such as the hydroxylation of aliphatic C–H bonds, the epoxidation of double bonds, and the oxidation of heteroatoms in endogenous and exogenous molecules.[54-55] The common key component of all P450 enzymes is an iron(III) protoporphyrin-IX complex that is linked to the protein by a cysteine ligand (Figure 1.4).[1] The typical hydroxylation of aliphatic C–H bonds catalyzed by a P450 enzyme is depicted in eq 1.3.1. The enzyme inserts one oxygen atom from molecular O_2 into the C–H bond of the substrate to afford the hydroxylated product. Two electrons provided by NAD(P)H via a reductase protein are used in this process to reduce the other oxygen atom of O_2 to water.

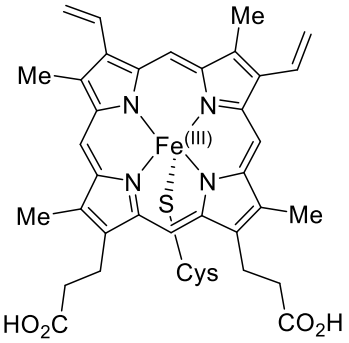
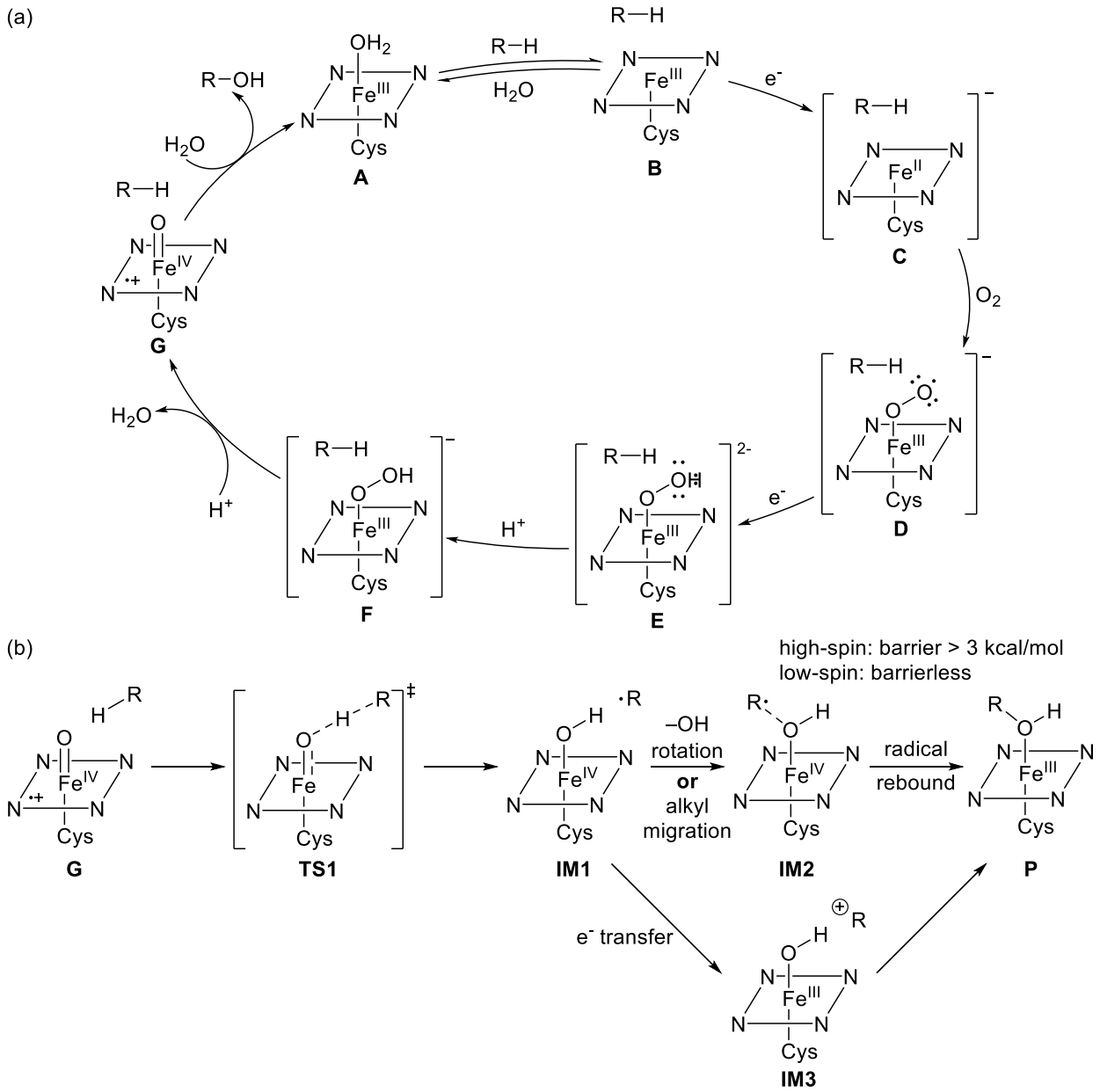


Figure 1.4. The prosthetic group of cytochrome P450 enzymes: an iron(III) protoporphyrin-IX complex linked to a cysteine ligand.

$$R{-}H + O_2 + 2e^- + 2H^+ \xrightarrow[\text{enzyme}]{\text{cytochrome P450}} R{-}OH + H_2O \qquad (1.3.1)$$

The general catalytic cycle for the oxidation of saturated C–H bonds catalyzed by cytochromes P450 is presented in Scheme 1.5.[1] The resting state of the catalyst is a Fe(III) porphyrin hydrate complex **A**. Reversible displacement of water molecules by the hydrocarbon leads to the formation of intermediate **B**, which, after accepting one electron from the reductase, forms an anionic, highly reductive Fe(II) species **C**. Binding of O_2 to compound **C** affords a Fe(III)-superoxide intermediate **D** with an unpaired electron on the terminal oxygen atom. Subsequent transfer of another electron from the reductase to compound **D** forms the dianionic Fe(III)-peroxo species **E**, which after fast protonation affords the Fe(III)-hydroperoxo intermediate **F**. Protonation of species **F** followed by dissociation of H_2O generates a hypervalent Fe(IV)-oxo species **G** containing a porphyrin radical cation, which is the active oxidant in the catalytic cycle responsible for the hydroxylation of C–H bonds.

The mechanism by which the Fe(IV)-oxo intermediate **G** oxidizes C–H bonds remains a subject of debate, but extensive experimental studies, including KIE experiments[56-58] and reactions with cyclopropane-based radical clocks,[59-60] as well as computational studies[61-63] generally support a two-state reactivity (TSR) pathway based on a "radical rebound" mechanism,[1, 56] as illustrated in Scheme 1.5(b). First, the intermediate **G** abstracts a hydrogen atom from the alkane via transition state **TS1** to form an Fe(IV)-hydroxy species and an alkyl radical (**IM1**). The hydroxy group in the intermediate **IM1** undergoes facile rotation (or the alkyl radical in **IM1** migrates to the other side of the hydroxy group) so that the carbon-centered radical is pointed towards the oxygen atom and away from the hydrogen atom (**IM2**). Then, radical rebound occurs to form the alcohol product and the Fe(III) complex (**P**). DFT studies[1, 61-63] suggested that all intermediates in the aforementioned pathway could adopt either a high-spin quartet state or a low-spin doublet state. Before the radical rebound step (from **G** to **IM2**), the relative energies of the different spin states of the same intermediate were similar. In the radical rebound step (**IM2** to **P**), however, the barrier corresponding to the high-spin pathway (**^{4}IM2** and **^{4}P**) was calculated to be around 3 kcal/mol, whereas the low-spin pathway (**^{2}IM2** and **^{2}P**) was barrierless. Despite this radical pathway, observation of rearranged products derived from carbocations of cyclopropane-based hydrocarbons[59, 64-65] supported an alternative cation pathway, in which the Fe(IV)-hydroxy species in **IM1** oxidized the alkyl radical to form a carbocation (**IM3**, Scheme 1.5(b)), which, after potential rearrangement, recombined with the Fe species to afford the alcohol product (**P**).



Scheme 1.5. (a) The general catalytic cycle of the oxidation of saturated C–H bonds mediated by cytochrome P450 enzymes; (b) the two-state radical pathway and the cation pathway proposed for the oxidation of C(sp^3)–H bonds by the Fe(V)-oxo species.

1.4. Transition-Metal Mediated Oxidation of C(sp^3)–H Bonds

1.4.1. Fenton Oxidation

In 1894, Fenton disclosed the oxidation of tartaric acid in the presence of hydrogen peroxide (H_2O_2) and a catalytic amount of Fe(II) salt.[66] It was perhaps the earliest reported example of transition-metal catalyzed oxidation of C–H bonds and the combination of H_2O_2 and a Fe(II) salt was later referred to as "Fenton's reagent".[67] In the following century, the mechanism of Fenton oxidation was studied extensively and elucidated:[67-71] first, the Fe(II) cation is oxidized by H_2O_2 to generate an Fe(III) cation, a hydroxide anion, and a hydroxy radical (eq 1.4.1.1). In the presence

of an organic substrate containing aliphatic or aromatic C–H bonds, the hydroxy radical can abstract a hydrogen atom from the substrate and form H_2O as well as the corresponding alkyl or aryl radical, which is subsequently oxidized (by O_2 or hydroxy radicals) to the alcohol or phenol product (eq 1.4.1.2). The hydroxy radical can also react with H_2O_2 to form water and a hydroperoxyl radical (eq 1.4.1.3), which can either react with H_2O_2 to form water, dioxygen, and a hydroxy radical (eq 1.4.1.4), or react with the Fe(III) cation to regenerate the Fe(II) catalyst (eq 1.4.1.5).

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + HO^{\bullet} + HO^{\ominus} \quad (1.4.1.1)$$

$$HO^{\bullet} + R{-}H \longrightarrow H_2O + R^{\bullet} \xrightarrow{[O]} R{-}OH \quad (1.4.1.2)$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HOO^{\bullet} \quad (1.4.1.3)$$

$$HOO^{\bullet} + H_2O_2 \longrightarrow H_2O + O_2 + HO^{\bullet} \quad (1.4.1.4)$$

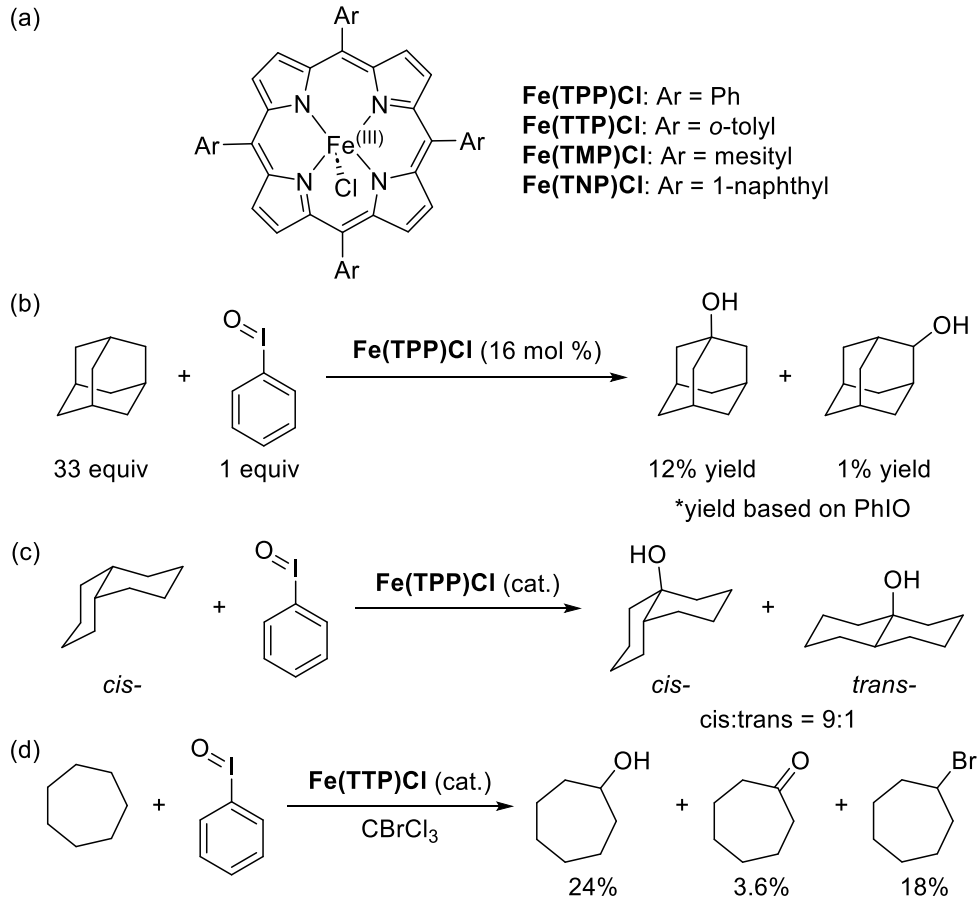
$$Fe(III) + HOO^{\bullet} \longrightarrow Fe(II) + O_2 + H^{\oplus} \quad (1.4.1.5)$$

Fenton oxidation is rarely used in organic synthesis but is widely used in industrial processes such as the treatment of wastewater[72] because the hydroxy radical generated *in situ* readily reacts with organic pollutants from toxic wastewater.

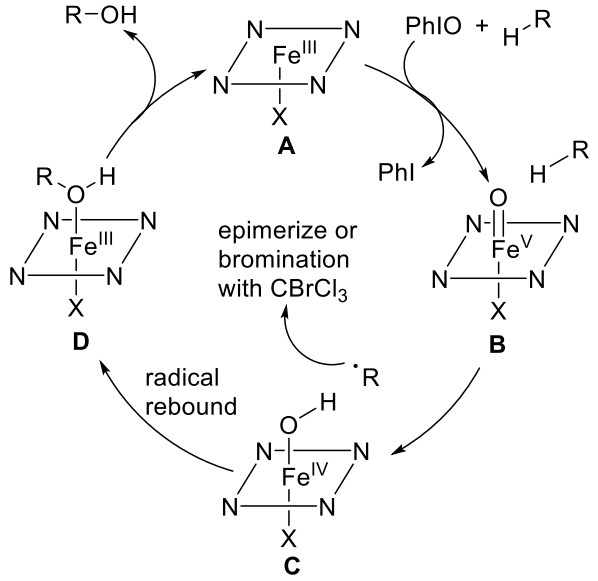
1.4.2. Transition Metal Complexes Containing Porphyrin Ligands

Transition metal complexes containing porphyrin ligands that model the active site of cytochromes P450 catalyze the oxidation of aliphatic C–H bonds, as well as the epoxidation of double bonds in the presence of an oxidant. This section focuses on the reactivity of Fe-, Mn-, and Ru-porphyrin complexes and the mechanisms of these reactions.

In 1979, Groves reported that Fe(III) complexes containing substituted porphyrin ligands catalyzed the oxidation of C(sp^3)–H bonds in the presence of iodosylbenzene as the oxidant.[73-74] These reactions were selective for the oxidation of tertiary C–H bonds over secondary or primary C–H bonds (Scheme 1.6(b)). Oxidation of *cis*-decalin catalyzed by these Fe-porphyrin complexes formed *cis*-9-decalol as the major product and *trans*-9-decalol as the minor product (Scheme 1.6(c)). The catalytic oxidation of cycloheptane in the presence of $CBrCl_3$ afforded significant amounts of bromocycloheptane (Scheme 1.6(d)). Based on these results, the authors proposed the "radical rebound" pathway for the oxidation of C(sp^3)–H bonds catalyzed by Fe-porphyrin complexes (Scheme 1.7).[73] The Fe(III) precatalyst reacted with iodosylbenzene to form the active Fe(V)-oxo intermediate (**B**), which abstracted a hydrogen atom from the alkane to form an Fe(IV)-hydroxy species and an alkyl radical (**C**). Recombination of the alkyl radical and the Fe(IV)-hydroxy intermediate afforded the alcohol product and regenerated the Fe(III) catalyst. Meanwhile, the alkyl radical in **C** could also epimerize or undergo bromination in the presence of $CBrCl_3$, consistent with the results shown in Scheme 1.6(c) and (d).



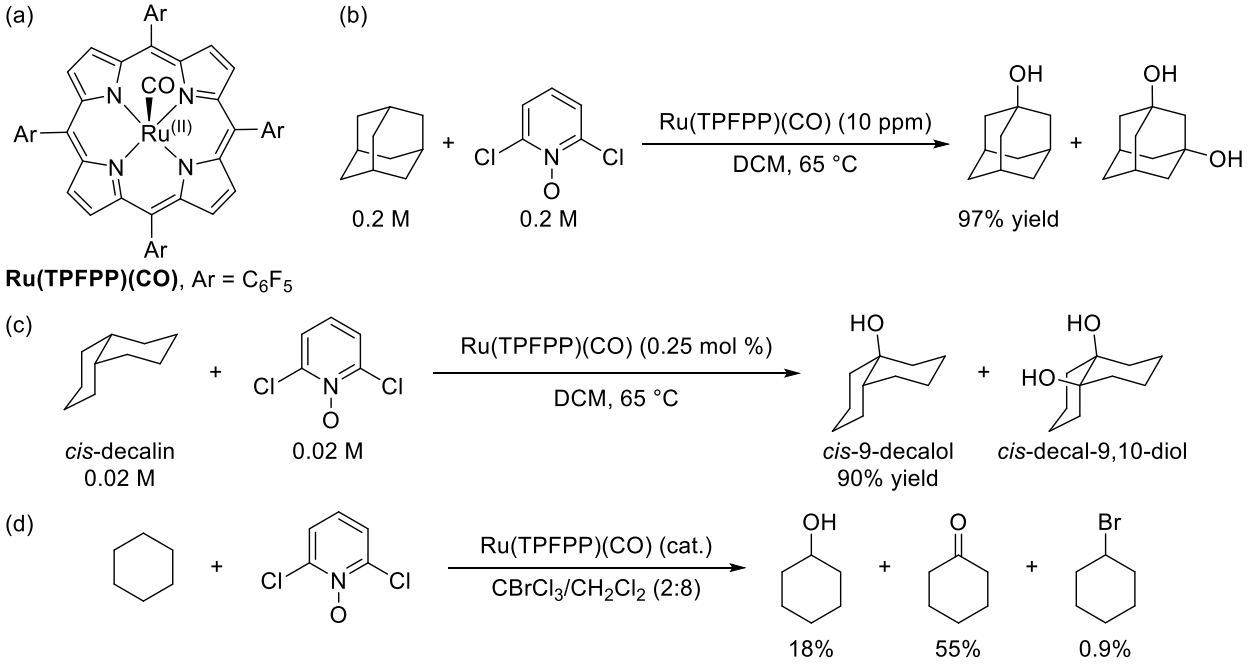
Scheme 1.6. (a) Abbreviations for Fe-porphyrin complexes; Fe-porphyrin catalyzed oxidations of (b) adamantane, (c) *cis*-decalin, and (d) cycloheptane in the presence of $CBrCl_3$.



Scheme 1.7. The proposed radical rebound mechanism for the oxidation of C(sp^3)–H bonds catalyzed by Fe-porphyrin complexes.

Groves reported that a mixture of iodosylbenzene and catalytic amounts of Mn^{III}(TPP)Cl (TPP = tetraphenylporphinato, Scheme 1.6(a)) oxidized cyclohexane in DCM to form cyclohexanol, cyclohexanone, and chlorocyclohexane in 70% combined yield based on the oxidant,[75] much higher than those from similar reactions with Fe(III)-porphyrin catalysts.[73-74] Formation of both ring-opening and unrearranged products from the reaction of norcarane, iodosylbenzene, and Mn^{III}(TPP)Cl indicated the generation of alkyl radicals during the reaction.[75] The proposed mechanism for Mn-porphyrin catalyzed oxidation of C(sp^3)–H bonds was very similar to that for the Fe-catalyzed reaction (Scheme 1.7), in which a Mn(V)-oxo intermediate was believed to be the active oxidizing species.

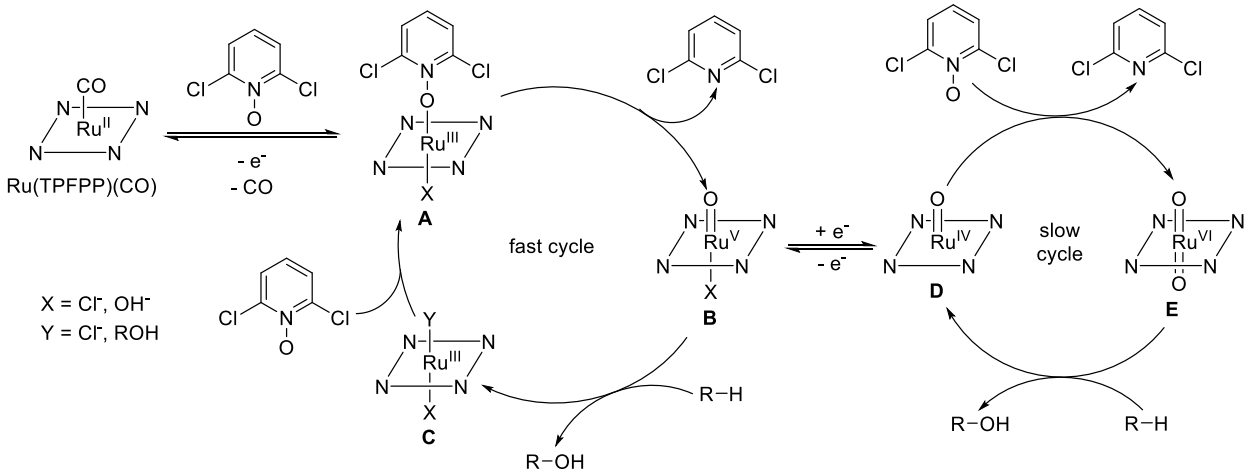
In addition to Fe- and Mn-porphyrin catalysts, Groves also disclosed the oxidation of alkanes catalyzed by a ruthenium porphyrin complex, Ru(TPFPP)(CO), (TPFPP = tetrakis(pentafluorophenyl)porphyrin, Scheme 1.8(a)) in the presence of 2,6-dichloropyridine *N*-oxide as the oxidant.[76-78] This transformation was different from its Fe or Mn counterparts (*vide supra*) in the following aspects: (1) the Ru-catalyzed reaction occurred with equimolar amount of alkane and oxidant, required very low loading of the catalyst (as low as 10 ppm), and formed the oxidized products in high yields (Scheme 1.8(b)),[77] whereas the Fe- or Mn-catalyzed reactions required superstoichiometric amounts of alkane, high loadings of catalysts, and formed the products in low yields.[73-75] (2) The Ru-catalyzed oxidation of *cis*-decalin afforded *cis*-9-decalol and *cis*-decal-9,10-diol as the only products, suggesting that epimerization at the tertiary carbons did not occur.[76-78] (3) Ru-catalyzed oxidation of cyclohexane in the presence of $CBrCl_3$ formed bromocyclohexane in very low yield (0.9%, Scheme 1.8(c)),[78] whereas a similar reaction catalyzed by Fe(TTP)Cl formed the bromoalkane in 18% yield (Scheme 1.6(d)).[74]



Scheme 1.8. (a) The structure of Ru(TPFPP)(CO); (b) Ru-catalyzed oxidation of adamantane in the presence of 2,6-dichloropyridine *N*-oxide; (c) oxidation of *cis*-decalin; (d) oxidation of cyclohexane in the presence of $CBrCl_3$.

Based on these results, as well as kinetic studies and Electron Paramagnetic Resonance (EPR) spectroscopy, the authors proposed the following catalytic cycle for the oxidation of alkanes

catalyzed by Ru(TPFPP) complexes (Scheme 1.9).[78] Single electron oxidation of the precatalyst Ru(TPFPP)(CO) and dissociation of CO led to the formation of intermediate **A**, which, after extrusion of 2,6-dichloropyridine formed the Ru(V)-oxo species **B**. Intermediate **B** was proposed as the major active species that oxidized the C(sp^3)–H bonds, and the lifetime of the alkyl radical generated in the oxidation step should be very short, based on the results shown in Scheme 1.8. After oxidation of the substrate, the Ru(V)-oxo species **B** was reduced to a Ru(III) intermediate **C**, which regenerated intermediate **A** upon reaction with 2,6-dichloropyridine *N*-oxide. The turnover rate of this Ru(III)-Ru(V) catalytic cycle (species **A**, **B**, and **C**) was fast and, therefore, was the major pathway for oxidation, but a separate cycle involving a Ru(IV)-oxo and a Ru(VI)-dioxide species (**D** and **E**, respectively) also could catalyze the oxidation of the alkane, albeit at a slower rate.



Scheme 1.9. Proposed catalytic cycle for the oxidation of alkanes catalyzed by Ru(TPFPP)(CO) in the presence of 2,6-dichloropyridine *N*-oxide.

Taking advantage of the high yield of oxidized products and the low loading of catalyst in this Ru-catalyzed reaction, as well as the very short lifetime of the alkyl radical intermediate, Hartwig developed Ru-catalyzed oxidations of unfunctionalized polyolefins for the synthesis of functional polymers.[5-6] These reactions occurred without deleterious, radical-mediated chain cleavage, and the adhesive property, wettability, and paintability of the resulting functional polymers were significantly better than those of the unfunctionalized polyolefins.

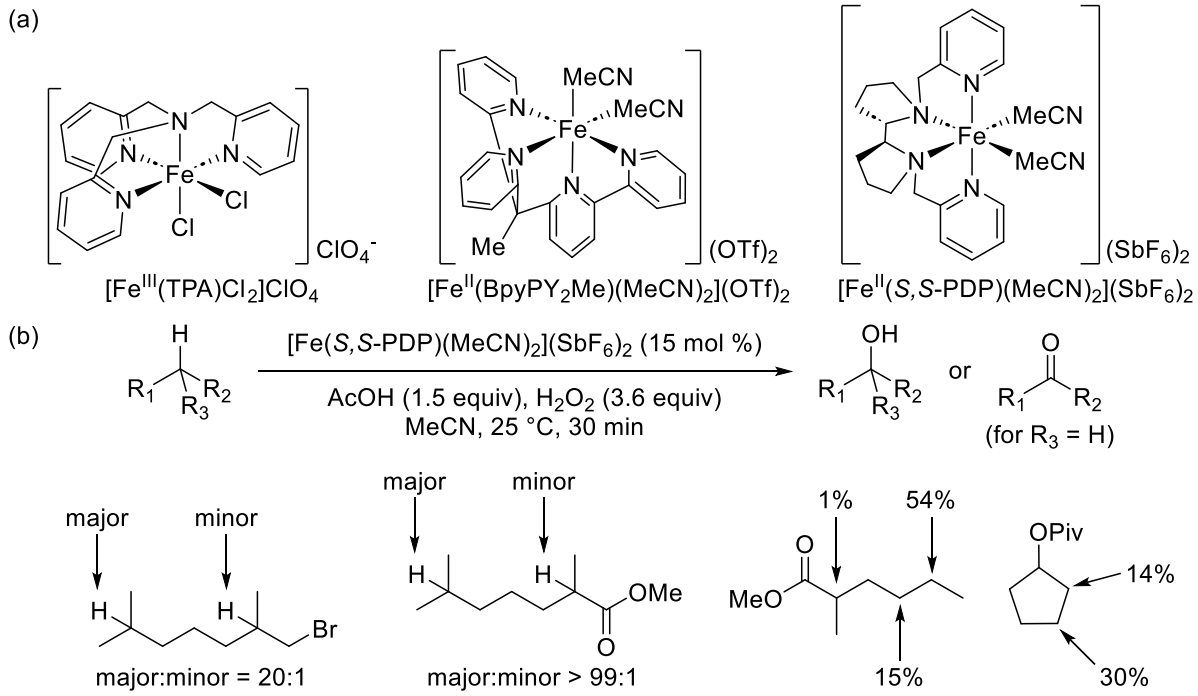
1.4.3. Iron Complexes Containing Non-Porphyrin Ligands

Fe complexes containing tetradentate nitrogen-based ligands other than porphyrins have also been found to catalyze the direct oxidation of aliphatic C–H bonds. In 1990, Que disclosed that Fe(III) complexes containing the TPA ligand (TPA = tris(2-pyridylmethyl)amine, Scheme 1.10(a)) catalyze the oxidation of cyclohexane in the presence of *tert*-butyl hydroperoxide (TBHP) or *m*CPBA as the oxidants.[79-80]

In 2018, Jurss reported a Fe(II) complex containing the tetradentate BpyPY2Me ligand (BpyPY2Me = 6-(1,1-di(pyridin-2-yl)ethyl)-2,2′-bipyridine, Scheme 1.10(a)) that catalyzes the oxidation of strong, unactivated C(sp^3)–H bonds in the presence of *m*CPBA as the oxidant.[81] These catalytic reactions were selective for the alcohol product over the ketone product and were more reactive towards tertiary C–H bonds than towards secondary or primary ones. Oxidation of *cis*-1,2-dimethylcyclohexane in the presence of a catalytic amount of Fe(BpyPY2Me)$(OTf)_2$ afforded

the corresponding tertiary alcohol with retention of configuration, suggesting that the rate of formation of the C–O bond was higher than the rate of epimerization of the alkyl radical.

Since 2007, White has published a series of papers[82-89] disclosing the oxidation of aliphatic C–H bonds that are remote to an electron-withdrawing group. These reactions are catalyzed by the iron(II) complex, [Fe(*S*,*S*-PDP)(MeCN)$_2$](SbF$_6$)$_2$, in the presence of H_2O_2 as the oxidant (Scheme 1.10(a)). These reactions occurred with the substrate as the limiting reagent, were selective for the C–H bonds distal from an electron-withdrawing group, formed the oxidized products in good yields, and tolerated a broad scope of functional groups (Scheme 1.10(b)). This method has also been applied to the late-stage functionalization of C–H bonds in complex molecules and to the total synthesis of natural products.[85-86, 89]



Scheme 1.10. (a) Structures of Fe catalysts; (b) oxidation of C(*sp*^{3})–H bonds catalyzed by the Fe(*S*,*S*-PDP) complex is selective for the position distal from an electron-withdrawing group.

1.4.4. Nickel Complexes Containing Nitrogen-based Ligands

For the past two decades, Ni(II) complexes containing various nitrogen-based ligands have been shown to catalyze the oxidation of strong, unactivated C(*sp*^{3})–H bonds in the presence of an oxidant, such as *m*CPBA. Representative examples of these nitrogen-based ligands are shown in Figure 1.5. Itoh,[90-93] Palaniandavar,[94-96] Hikichi,[97-98] and Hartwig[4, 51] reported the catalytic oxidations of unactivated alkanes using *m*CPBA as the oxidant in the presence of Ni complexes containing ligand **L1**–**L11**. These reactions generally required mild conditions (< 65 ˚C) and low loadings of the Ni catalyst (on the order of 0.1 mol %), and they occurred with high turnover numbers (TONs, on the order of 10^2–10^3 s^{-1}). Under these conditions, oxidation of an alkane that contained tertiary, secondary, and primary C–H bonds was usually selective for the tertiary positions, and the oxidation of secondary C–H bonds (e.g., cyclohexane) formed alcohol as the major product, along with ketone and lactone as minor products. In addition, a hexanuclear Ni(II) silsesquioxane has been reported to catalyze the oxidation of aliphatic C–H bonds in the presence of *m*CPBA as the oxidant.[99]

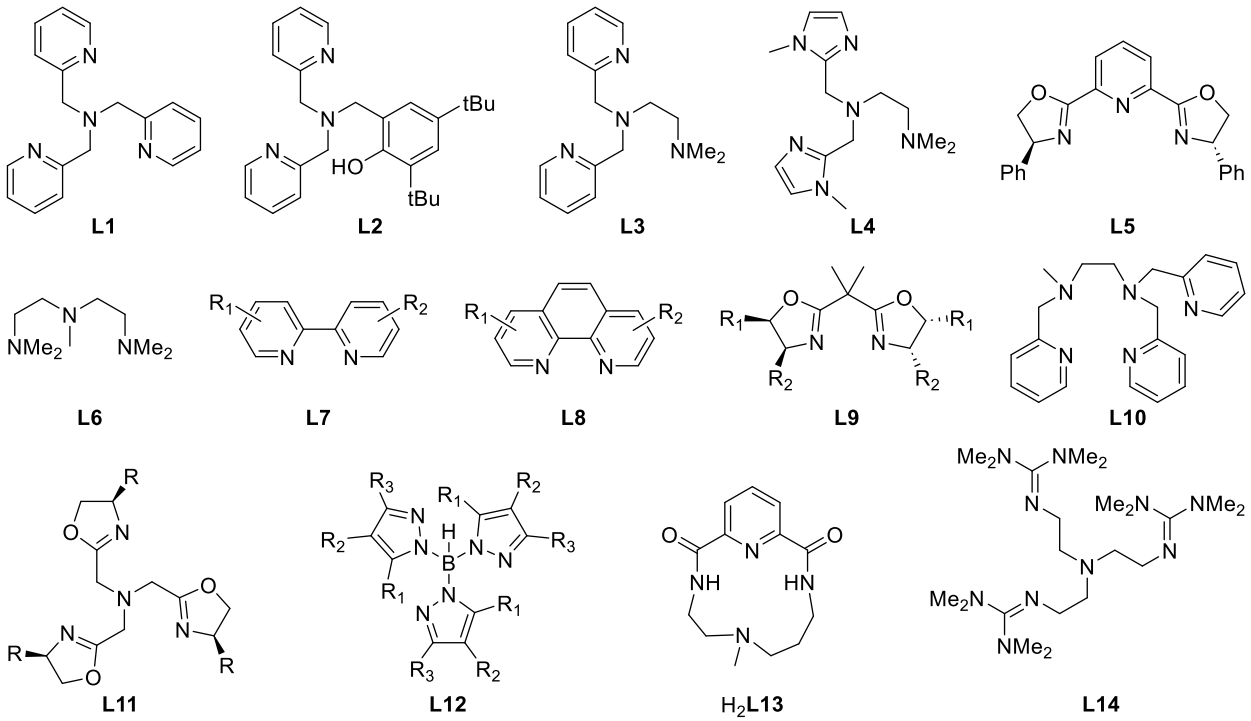
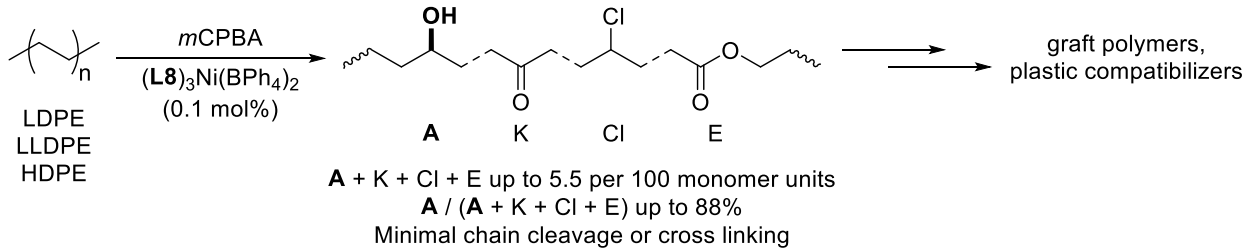


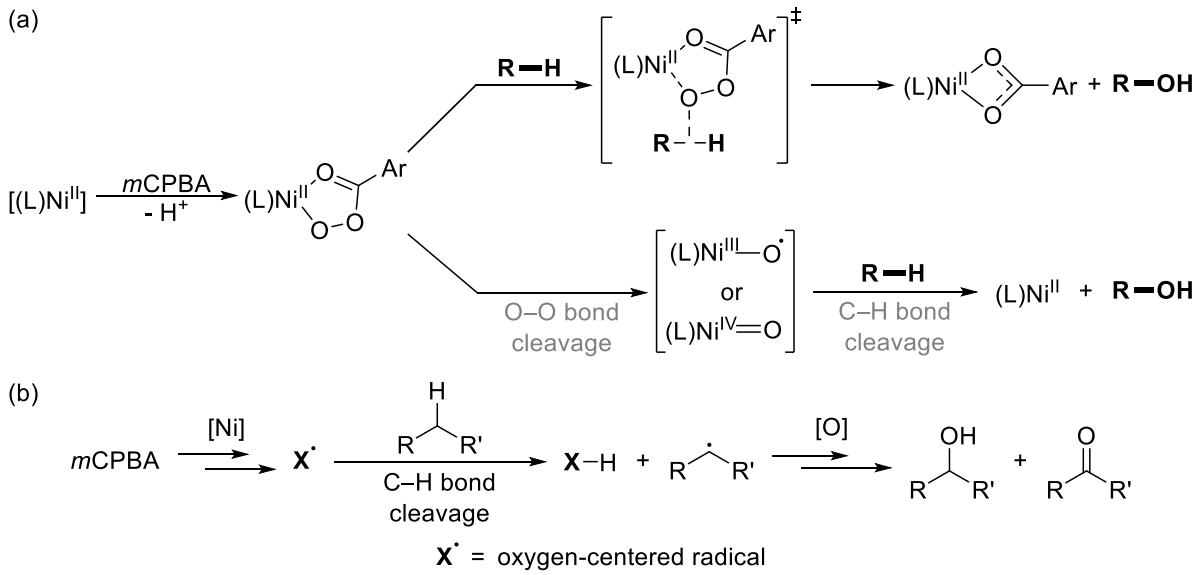
Figure 1.5. Representative nitrogen-based ligands for Ni complexes that catalyze the oxidation of unactivated C(sp^3)– H bonds.

Besides the oxidation of small-molecule alkanes, Ni complexes containing phenanthroline ligands (**L8**) also catalyzed the hydroxylation of polyethylenes in the presence of *m*CPBA.[4] This method allowed for the synthesis of hydroxylated polyethylenes with good levels of incorporation of functional groups (5.5 per 100 monomer units), good selectivity for the hydroxy group (up to 88%), and minimal chain cleavage or loss of molecular weight. The hydroxylated polyethylenes can react as macroinitiators for the polymerization of ε-caprolactone to synthesize graft polymers of low-density polyethylene (LDPE) and poly(ε-caprolactone), which are plastic compatibilizers between polyethylenes and polar materials (Scheme 1.11).



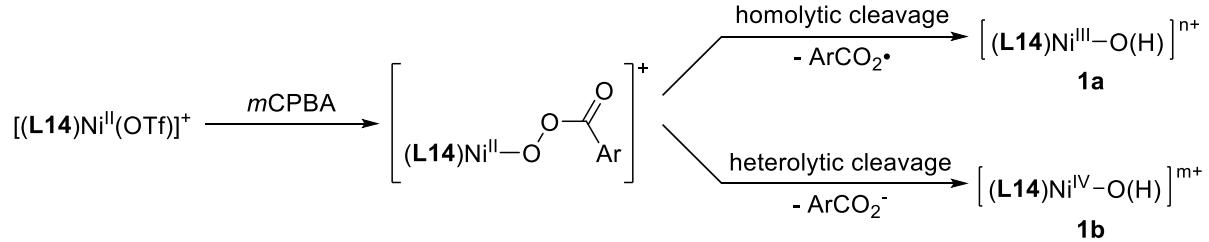
Scheme 1.11. Ni-catalyzed hydroxylation of polyethylenes in the presence of *m*CPBA.

The mechanism of Ni-catalyzed oxidation of unactivated C(sp^3)–H bonds has been a subject of debate. Many papers proposed that high-valent Ni-oxo or Ni-oxyl intermediates cleave the C–H bonds in the catalytic reactions (Scheme 1.12(a)).[90-96] Several such Ni-oxygen species have been synthesized and characterized, and their reactivities towards C(sp^3)–H bonds have been studied in detail.[99-109]



Scheme 1.12. (a) Proposed mechanism: Ni-oxygen intermediates cleave the C–H bonds in the alkane substrate; (b) proposed mechanism: oxygen-centered radicals derived from *m*CPBA cleave the C–H bonds in the alkane substrate.

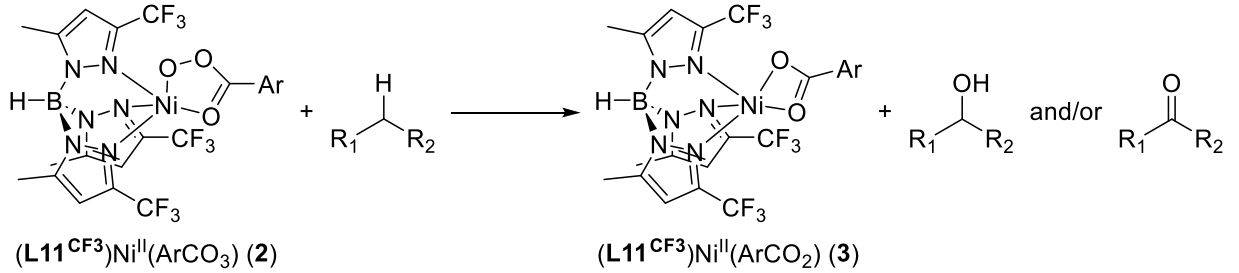
Ray reported[103] that the reaction of *m*CPBA and a cationic Ni(II) complex containing the tetradentate ligand **L14** (see Figure 1.5) at low temperature afforded two high-valent Ni species **1a** and **1b**. Data obtained from EPR spectroscopy and electrospray mass spectrometry (ESI MS) suggested that intermediates **1a** and **1b** were the Ni(III)-oxygen and the Ni(IV)-oxygen species generated from the homolytic and the heterolytic cleavage of the O–O bond in the Ni(II)-acylperoxo adduct, respectively (Scheme 1.13). Reactions of **1a** and **1b** with hydrocarbons at low temperature (< -30 ˚C) indicated that these Ni intermediates oxidize the weak C(sp^3)–H bonds in 1-benzyl-1,4-dihydronicotinamide (BNAH), xanthene, 9,10-dihydroanthracene (DHA), and 1,4-cyclohexadiene (1,4-CHD). A strong linear correlation was observed between the bond dissociation energies (BDEs) of the activated C–H bonds in these hydrocarbons and the natural logarithms of the second-order rate constants of the oxidation of these substrates. However, the authors did not investigate the reactivity of intermediates **1a** and **1b** towards strong, unactivated C(sp^3)–H bonds, such as those in cyclohexane.



Scheme 1.13. Formation of high-valent Ni-oxygen species containing ligand **L14**.

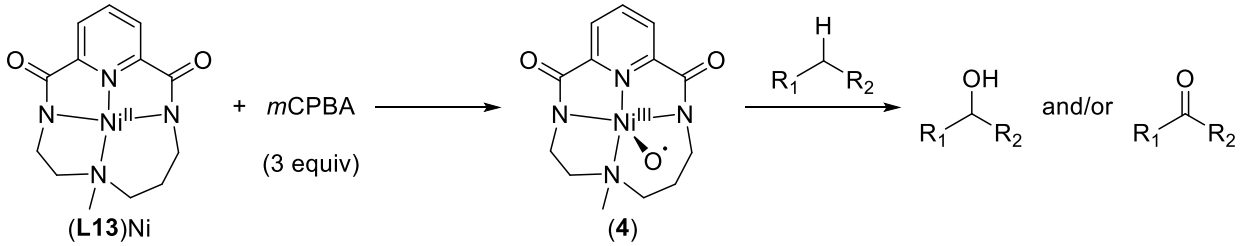
In 2013, Hikichi reported[101-102] the first example of the isolation and the crystallographic characterization of a stable Ni(II)-acylperoxo complex (**2**, Scheme 1.14) containing the CF_3-substituted Tp ligand $\mathbf{L11^{CF3}}$. Reactions of the isolated complex **2** with hydrocarbons containing weak C–H bonds, such as 1,4-CHD, DHA, xanthene, and fluorene, afforded the corresponding Ni(II)-carboxylate complex **3**, as well as the alcohol and/or ketone product (Scheme 1.14). These

reactions obeyed second-order kinetics. Analysis by UV-vis spectroscopy indicated that high-valent Ni-oxo or Ni-oxyl species did not accumulate during these reactions, suggesting that complex **2** directly oxidized the substrates in these transformations. Different from reactions with hydrocarbons containing activated C–H bonds, the reaction of complex **2** with cyclohexane, which contained only unactivated C–H bonds, did not follow second-order kinetics; the addition of 1000 equivalents of cyclohexane did not accelerate the consumption of complex **2**. Based on this observation, the authors proposed that strong, unactivated C–H bonds (like the ones in cyclohexane) were oxidized by high-valent Ni-oxygen species formed from the first-order cleavage of the O–O bond in complex **2**, a pathway different from that for weak C–H bonds.



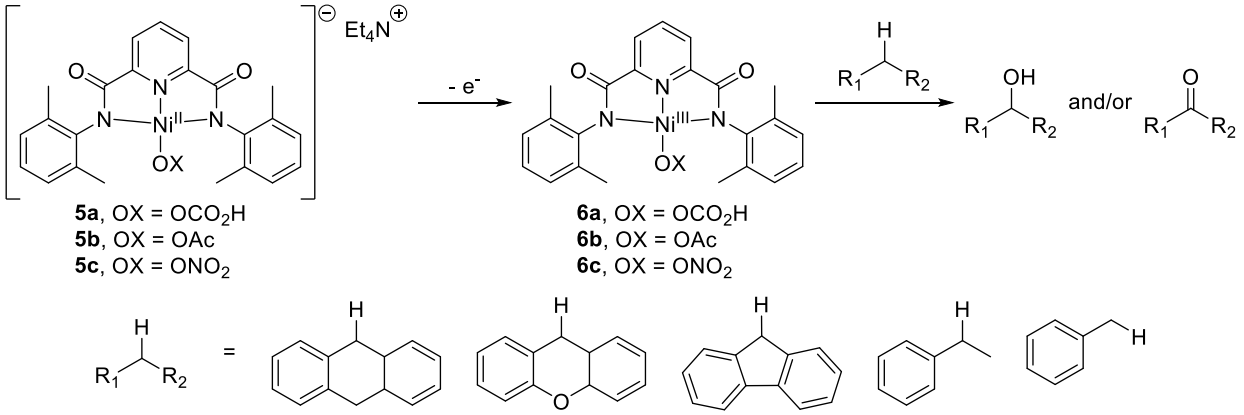
Scheme 1.14. Oxidation of aliphatic C–H bonds by the isolated Ni-acylperoxo complex **2**.

Company reported[107] that the reaction of three equivalents of *m*CPBA with a nickel(II) complex containing the cyclic, bis(amidate) ligand **L13** at -30 ˚C in acetonitrile formed the intermediate **4**. Analysis by EPR spectroscopy, mass spectrometry, X-ray absorption spectroscopy (XAS), resonance Raman spectroscopy, as well as DFT calculations, suggested that intermediate **4** was most likely a Ni(III)-oxyl species (Scheme 1.15). Species **4** oxidized activated C(sp^3)–H bonds in fluorene, 1,4-CHD, DHA, and xanthene. These oxidation reactions exhibited pseudo-first-order kinetics in the presence of excess alkanes, and the logarithms of the second-order rate constants correlated linearly with the BDEs of the C(sp^3)–H bonds. The *in situ* generated intermediate **4** also oxidized the C(sp^3)–H bonds in toluene, ethylbenzene, and cyclohexane at low temperature, but these reactions did not follow pseudo-first-order kinetics. The authors attributed such deviation from pseudo-first-order kinetics to the interference from background, catalytic reactions. Reaction of (**L13**)Ni with 150 equivalents of *m*CPBA and *cis*-1,2-dimethylcyclohexane afforded the tertiary alcohol product with 84% retention of configuration at the tertiary carbons, indicating that the rate of formation of the C–O bond in this reaction was higher than the rate of epimerization of the alkyl radical. A related system involving (**L13**)Ni and NaOCl in place of *m*CPBA as the oxidant has also been reported.[106]



Scheme 1.15. Oxidation of C(sp^3)–H bonds by the Ni(III)-oxyl species **4** generated from (**L13**)Ni and *m*CPBA.

McDonald reported[109] the synthesis of several Ni(II) complexes (**5a**–**5c**) containing the acyclic, bis(amidate) ligand **L15** and different counteranions. These Ni(II) complexes were further converted via one-electron oxidations to the corresponding Ni(III) species (**6a**–**6c**, Scheme 1.16), whose identities were confirmed by EPR spectroscopy, ESI-MS, XAS, as well as DFT calculations. These Ni(III) species oxidized a series of hydrocarbons containing activated C(sp^3)–H bonds with BDEs ranging from 68 to 90 kcal/mol (Scheme 1.16). A strong linear correlation was established between the logarithms of the second-order rate constants of these oxidation reactions and the BDEs of these substrates, consistent with a hydrogen atom transfer (HAT) mechanism. However, the reactivity of these Ni(III) species with strong C(sp^3)–H bonds (such as adamantane or cyclohexane) whose BDEs were close to 100 kcal/mol was not discussed in the paper.



Scheme 1.16. Formation of Ni(III)-bis(amidate) species and their reactivity towards activated, aliphatic C–H bonds.

These aforementioned reports[101-103, 106-107, 109] clearly demonstrated that high-valent Ni-oxygen intermediates bearing various nitrogen-based ligands could oxidize alkanes containing activated C(sp^3)–H bonds to the corresponding alcohol and/or ketone products. However, evidence that supported such reactivity towards strong, unactivated C(sp^3)–H bonds with BDEs close to 100 kcal/mol was rather scarce. Some reports[103, 109] did not discuss the reactivity of high-valent Ni-oxygen species towards unactivated C–H bonds; others[102, 107] noted that reactions of Ni-oxygen species with unactivated C–H bonds exhibited different kinetics compared to those with weak C–H bonds, suggesting that oxidations of these two types of C–H bonds might occur through different mechanisms. In addition, high-valent Ni-oxo or Ni-oxyl intermediates were often generated *in situ* by mixing the Ni precursors with superstoichiometric amounts of *m*CPBA,[103, 107] so oxygen-centered radicals derived from *m*CPBA might be present in the reaction mixture and cleave C–H bonds in the alkane substrate.

In the late 1980s, Ingold measured the rate constants of hydrogen atom abstraction and decarboxylation for substituted benzoyloxy radicals and determined that the rates of these two reactions were comparable in the presence of alkane substrates.[49-50] In many examples of Ni-catalyzed oxidations of unactivated alkanes by *m*CPBA,[4, 51, 90-94, 96] chlorobenzene was observed as a major byproduct, which was most likely formed via decarboxylation of the *m*-chlorobenzoyloxy radical. These results strongly suggested that oxygen-centered radicals derived from *m*CPBA were present in the Ni-catalyzed reactions and might participate in the oxidation of C–H bonds (Scheme 1.12(b)).

Indeed, based on detailed selectivity experiments and deuterium labelling experiments, Hartwig proposed a free radical mechanism for Ni-catalyzed oxidations of unactivated, aliphatic

C–H bonds (see Chapter 2 of this dissertation for details).[51] In this proposed mechanism, Ni complexes catalyzed the decomposition of *m*CPBA to form the aroyloxy radical (eq 1.4.4.1), which cleaved the C–H bonds in the alkane substrate to generate an alkyl radical and the *m*-chlorobenzoic acid byproduct (eq 1.4.4.2). The alkyl radical then reacted with *m*CPBA to afford the alcohol product and regenerated the aroyloxy radical (eq 1.4.4.3), thus propagating the radical chain reaction. As a side reaction, decarboxylation of the aroyloxy radical generated the *m*-chlorophenyl radical, which mostly led to pathways that did not form the alcohol or ketone products. When the reaction was conducted under air, approximately 10% of the generated alkyl radicals reacted with O_2 and afford a mixture of alcohol and ketone (eq 1.4.4.4). Combination of the alkyl radical with a putative Ni-oxyl or Ni-oxo intermediate was also possible (eq 1.4.4.5) but not directly observed. A follow-up study by Itoh[93] proposed that abstraction of hydrogen atoms from C(sp^3)–H bonds by Ni(II)-oxyl species might also occur concomitantly with the free radical pathways depicted in eq 1.4.4.1–1.4.4.5.

Free Radical Formation: $ArCO_3H \xrightarrow{\text{cat. [Ni]}} ArCO_2\bullet$ + other radicals (1.4.4.1)

C–H Bond Cleavage: $ArCO_2\bullet + H{-}R \longrightarrow R\bullet + ArCO_2H$ (1.4.4.2)

C–O Bond Formation (major): $ArCO_3H + R\bullet \longrightarrow R{-}OH + ArCO_2\bullet$ (1.4.4.3)

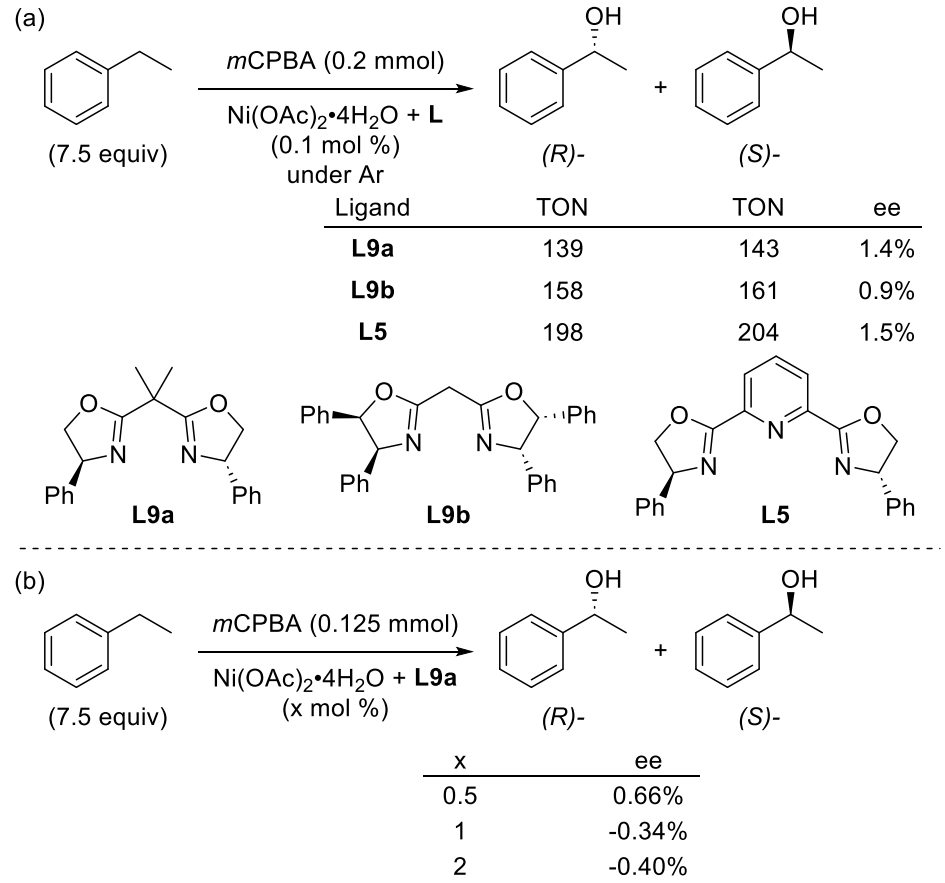
C–O Bond Formation (minor): $R\bullet + O_2 \longrightarrow R{-}OO\bullet \longrightarrow R{-}OH + R{=}O$ (1.4.4.4)

C–O Bond Formation (possible): $R^{\cdot} \xrightarrow[\text{or [Ni]=O}]{\text{[Ni]}{-}O^{\cdot}} \text{[Ni]}{-}O{-}R \longrightarrow R{-}OH$ (1.4.4.5)

The reaction of an alkyl radical with *m*CPBA (eq 1.4.4.3) was proposed as the major pathway for the formation of the C–O bond in the alcohol product because such reactions were known to be highly exothermic (calculated $\Delta H \approx$ -40 kcal/mol) and kinetically feasible (calculated activation barrier $\approx$ 4 kcal/mol)[110] and because the concentration of *m*CPBA was much higher than that of the Ni catalyst in the reaction mixture.[51] However, reaction of the alkyl radical with a Ni-oxygen species (eq 1.4.4.5) was also a possible step to form the C–O bond. Due to the transient nature of both the alkyl radical and the Ni-oxo or Ni-oxyl intermediate, this reaction is very difficult to study directly.

One way to investigate whether the alkyl radical reacts with the Ni-oxygen species to form the C–O bond is to measure the enantioselectivity for the oxidation at a prochiral methylene position in the presence of a Ni catalyst containing a chiral ligand. If the alcohol product were formed enantioselectively, then the alkyl radical would, most likely, have reacted with the chiral Ni-oxygen species. Hikichi conducted catalytic oxidations of ethylbenzene in the presence of *m*CPBA and Ni complexes containing chiral bisoxazoline and PyBox ligands.[97] In these reactions, 1-phenylethanol was formed as the major product with reported ee values of 0.9% – 1.5% (Scheme 1.17(a)). If these values of enantiomeric excess were not simply experimental error in the measurements, then reactions in the presence of higher loadings of the chiral Ni catalyst should generate the chiral Ni-oxygen intermediates in higher concentration and form 1-phenylethanol with higher enantioselectivity. Thus, we conducted catalytic oxidation of ethylbenzene with varying loadings of the Ni catalyst containing the chiral ligand **L9a** (Scheme 1.17(b)). The measured enantiomeric excess of 1-phenylethanol formed from these reactions was very low (less than 1%) regardless of the loading of the chiral Ni catalyst, suggesting that the ee values observed by Hikichi and in our experiment were simply in the range of normal experimental error. These

results do not support the pathway in which an alkyl radical reacts with a Ni-oxygen species to form the C–O bond (eq 1.4.4.5).



Ligand	TON	TON	ee
L9a	139	143	1.4%
L9b	158	161	0.9%
L5	198	204	1.5%

x	ee
0.5	0.66%
1	-0.34%
2	-0.40%

Scheme 1.17. (a) Catalytic oxidation of ethylbenzene in the presence of Ni complexes and chiral bisoxazoline and PyBox ligands reported by Hikichi; (b) catalytic oxidation of ethylbenzene in the presence of varying loadings of the Ni catalyst containing a chiral bisoxazoline ligand conducted in our laboratory.

Overall, nickel complexes containing various nitrogen-based ligands catalyze the oxidation of unactivated C(sp^3)–H bonds in the presence of *m*CPBA as the oxidant. These reactions typically require mild conditions, low loadings of catalysts, and form oxidized products with high turnover numbers. These reactions are selective for the alcohol product over the ketone and lactone byproducts, and they are selective for tertiary over secondary or primary C–H bonds. High-valent Ni-oxygen intermediates readily oxidize weak, activated C(sp^3)–H bonds with BDEs less than 90 kcal/mol, but evidence that unequivocally supports the reactions of strong C–H bonds (BDEs around 100 kcal/mol) with a Ni-oxygen intermediate is scarce. During Ni-catalyzed reactions, the aroyloxy radical derived from *m*CPBA cleaves the C–H bonds of alkanes to generate alkyl radicals, which subsequently react with *m*CPBA to form the alcohol products. Trapping of the alkyl radical by O_2 occurs as a minor pathway to form the C–O bond during reactions conducted under air. Reaction of the alkyl radical with a Ni-oxygen species is possible but poorly understood. Despite extensive studies, questions remain to be answered regarding the mechanism of Ni-catalyzed oxidations of aliphatic C–H bonds, and the specific mechanism of a catalytic system likely depends on the identity of the ligand and the strength of the C–H bonds in the alkane.

1.5. Summary

Direct oxidation of aliphatic C–H bonds is an important transformation in both nature and synthetic chemistry. This chapter has described various methods for the direct oxidation of C(sp^3)–H bonds involving metal-free organic oxidants, cytochrome P450 enzymes, as well as transition metal complexes, along with the mechanisms of these transformations. Many examples have shown that high-yielding, chemo- and regioselective oxidations of C–H bonds can be achieved by meticulous design of catalysts and oxidants. In mechanistic studies of these oxidation reactions, the dichotomy between concerted oxygen insertion and stepwise reactions, the involvement and lifetime of alkyl radicals, the role of metal-oxo or metal-oxyl intermediates, and the origin of chemo-/regioselectivity are important to investigate. Experiments in the presence of reagents that rapidly react with alkyl radicals (e.g., $CBrCl_3$) and reactions with alkanes containing epimerizable tertiary carbons (e.g., *cis*-1,2-dimethylcyclohexane) or cyclopropane motifs can provide valuable information about the formation and lifetime of alkyl radicals. X-ray crystallography, mass spectrometry, various spectroscopic techniques, and DFT calculations have been used to identify key reactive intermediates, especially for reactions catalyzed by transition metals. It is safe to say that the field of direct oxidation of C(sp^3)–H bonds will continue to grow, and deeper mechanistic understanding of such reactions will guide chemists to develop more high-yielding and more selective methods for the oxidations of aliphatic C–H bonds.

1.6. References

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Chapter Two

Mechanism of Ni-catalyzed Oxidations of Unactivated C(sp^3)–H Bonds

2.1. Introduction

Oxidation of aliphatic C–H bonds is an important chemical transformation that is widely practiced in nature and in synthetic chemistry. In most living organisms, cytochrome P450 enzymes catalyze the hydroxylation of saturated C–H bonds,[1] and, in methanotrophic bacteria, methane monooxygenases (MMOs) catalyze the hydroxylation of methane to produce methanol.[2] In synthetic chemistry, oxidation of feedstock alkanes is a promising way to make valuable products, such as alcohols and ketones, from inexpensive starting materials. However, high-yielding, selective oxidation of unactivated aliphatic C–H bonds is challenging because the large bond dissociation energies (BDEs) near 100 kcal/mol[3-4] and high HOMO-LUMO gaps make them inert to many chemical reactions and because the ubiquity of C(sp^3)–H bonds in organic molecules makes reactions at similar, but inequivalent sites common. In addition, oxidized products, such as alcohols and alkyl halides, are generally more reactive than the starting unfunctionalized alkanes, so overoxidation may occur, leading to undesired byproducts.[5]

Despite these challenges, many methods have been developed in the past century for the oxidation of aliphatic C–H bonds. Several organic reagents, such as ozone,[6] dioxiranes,[7-8] and aromatic peracids,[9-10] were found to oxidize saturated hydrocarbons with high selectivity for tertiary C–H bonds. Transition-metal-catalyzed oxidation of aliphatic C–H bonds also has been developed extensively. As early as the 1890s, Fenton reported iron(II)-catalyzed oxidation of tartaric acid by hydrogen peroxide.[11] Later, the Gif-Barton system[12] which utilizes iron catalysts and tBuOOH or H_2O_2 as oxidants, the Pt(II) catalytic system by Shilov and Periana[3, 13-14], and the Ru porphyrin system by Groves and others[15-17] were developed to achieve oxidation of alkanes with high turnover numbers (TONs). White reported selective oxidation of aliphatic C–H bonds in complex molecules with H_2O_2 and iron catalysts with nitrogen-based ligands.[18-19]

Compared to these methods that involve Group 8 transition metal catalysts, Ni-catalyzed oxidation of alkanes is less explored but occurs with high TONs. Itoh and others have reported hydroxylation of cyclohexane and adamantane with *m*CPBA and nickel catalysts containing tetradentate, nitrogen-based ligands, such as tris(2-pyridylmethyl)amine (TPA).[20-22] Our group achieved selective hydroxylation of polyethylenes with *m*CPBA and Ni-catalysts containing phenanthroline-based (Phen-based) ligands.[23] This oxidation occurred with loadings of nickel as low as 0.1 mol %, required mild conditions (50 ˚C under air), and afforded the mono-oxidized product (alcohol rather than ketone or ester) with hundreds of TONs (Figure 2.1(A)).

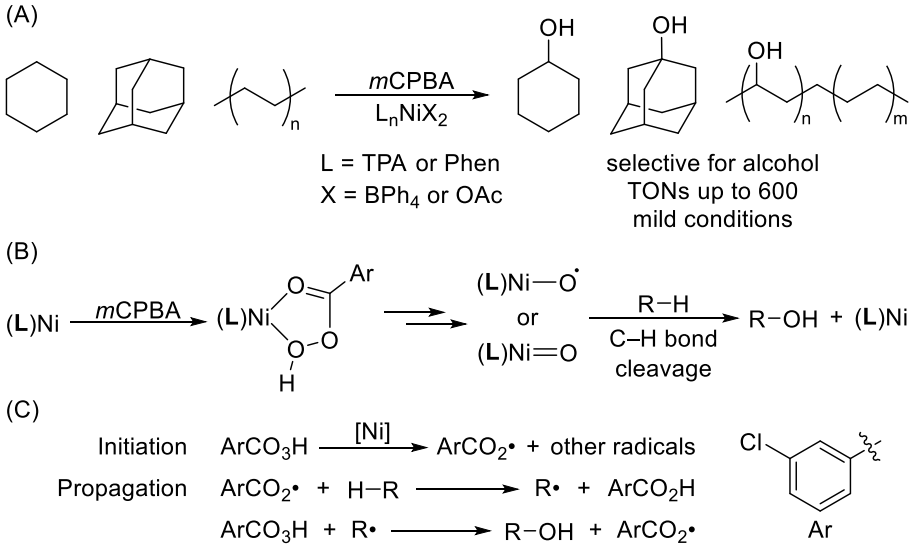


Figure 2.1. (A) Ni-catalyzed hydroxylation of cyclohexane, adamantane and polyethylenes by *m*CPBA. (B) Previously proposed pathway for Ni-catalyzed oxidation of aliphatic C–H bonds. (C) This work: free radical chain mechanism of Ni-catalyzed oxidation of C(sp^3)–H bonds by *m*CPBA.

Ni-catalyzed oxidation of saturated hydrocarbons by *m*CPBA has been proposed to occur by forming a transient Ni-oxyl or Ni-oxo intermediate[24] (hereafter called a Ni-oxygen species) that cleaves the C–H bond (Figure 2.1(B)).[20, 25-26] Hikichi reported the isolation and characterization of a Ni complex of *m*CPBA containing a trispyrazolylborate-based (Tp-based) ligand.[27] Several other Ni-oxygen species containing macrocyclic, nitrogen-based ligands also have been characterized spectroscopically.[26, 28-34] These nickel intermediates oxidize activated C–H bonds (BDE < 90 kcal/mol) in substrates such as 9,10-dihydroanthracene (DHA) and xanthene,[27-28, 33] but the reactivity of such intermediates with unactivated C–H bonds (BDE ~ 100 kcal/mol) has not been convincingly established.[35] This trend in reactivity is inconsistent with the results of the catalytic reactions, in which the strong C–H bonds in cyclohexane and polyethylenes undergo hydroxylation under mild conditions. Studies that address this issue of the reactivity of Ni-oxo or Ni-oxyl complexes with C–H bonds and mechanisms of Ni-catalyzed oxidation reactions are crucial to understanding the role of Ni in the catalytic system and to improving the efficiency and selectivity of these reactions further.

In this work, we report mechanistic investigations of Ni-catalyzed oxidation of unactivated aliphatic C–H bonds. We provide evidence that, contrary to the previously proposed reaction pathways, Ni complexes are not involved in the cleavage of C–H bonds; rather, they catalyze the decomposition of *m*CPBA to generate an aroyloxy radical that cleaves the C–H bond via hydrogen atom abstraction (HAA). The resulting alkyl radical then reacts with *m*CPBA to form the hydroxylated product and regenerates the aroyloxy radical. Thus, the catalytic reaction proceeds via a free radical chain mechanism (Figure 2.1(C)) in which the rate of initiation is determined by the concentration and identity of the nickel complex; the nickel complex does not control the regioselectivity of the oxidations.

2.2 Results and Discussions

2.2.1. Effect of Ligands on Selectivity

To understand the role of Ni complexes in the catalytic reaction, we studied the effect of varying the ligands on the selectivity of oxidation. If a transient Ni-oxygen intermediate cleaved the C–H bonds in hydrocarbons, the identity of the ancillary ligands that possess varied electronic and steric properties should affect the selectivity of the catalytic reaction. Therefore, Ni complexes (**1a**–**1h**, Figure 2.2) that contain a series of nitrogen-based, bidentate or tetradentate ligands (**L1**–**L8**) were synthesized and used for the catalytic oxidation of cyclohexane (**2**) and adamantane (**3**).

Results of the oxidation of cyclohexane (**2**) catalyzed by this series of nickel complexes are shown in Table 1A. Cyclohexanol (**4a**) was formed as the major product together with small amounts of cyclohexanone (**4b**), ε-caprolactone (**4c**) and chlorocyclohexane (**4d**). The formation of **4c** can be attributed to the uncatalyzed Baeyer–Villiger oxidation of **4b**. The alcohol to ketone and lactone ratio, i.e., A/(K+E), defined as the ratio of the yield of **4a** to the combined yield of **4b** and **4c**, reflects the selectivity for mono-oxidation.

Our data show that the identity of the ligand affects the rate of the oxidation process. Reactions in the presence of complexes **1a**-**1e**, which contain sterically unhindered ligands **L1**-**L5**, reached full conversion of *m*CPBA within 1–1.5 h (Table 2.1(A), entries 1–5), whereas those in the presence of **1f** and **1g**, which contain sterically encumbered ligands **L6** and **L7**, required 2 and 3 h to reach greater than 90% conversion, respectively (Table 2.1(A), entries 6–7). The conversion of

the reaction with complex **1h**, which contains the most sterically hindered ligand **L8**, in which two methyl groups flank the phenanthroline moiety, was low even after 4 hours of heating (Table 2.1(A), entries 8). Time courses further confirmed that the rate of reaction in the presence of complex **1a** was significantly higher than those in the presence of Ni complexes containing sterically hindered ligands, such **1h** (see Experimental Section).

However, the data in Table 1 also show the lack of a pronounced effect of the ligand on the yield of oxidized products or on the A/(K+E) ratio. All reactions in the presence of complexes **1a-1g** gave product **4a** in 31%–39% yield and products **4b**, **4c** in 10%–11% combined yield; the A/(K+E) ratios of these reactions range from 3.1 to 3.5, which is well within experimental error. The oxidation of cyclohexane in the presence of ligandless $NiCl_2$ (Table 2.1(A), entry 9) formed product **4a** in 31% yield and products **4b**, **4c** in 13% combined yield, corresponding to an A/(K+E) ratio of 2.4±0.6. This ratio is comparable to those of reactions catalyzed by ligated Ni complexes **1a**-**1g**. Similar results were observed for the oxidation of **2** catalyzed by $CoCl_2$, although the cobalt-catalyzed reaction was faster than the nickel-catalyzed one and reached full conversion within 1.5 h (Table 2.1(A), entry 10). The negligible effect of ligands on both product distribution and selectivity for mono-oxidation, along with the similar yield of products and selectivity of the catalytic reactions conducted without ligands, is inconsistent with the previously proposed pathway in which a Ni-oxygen species cleaves the C–H bond.

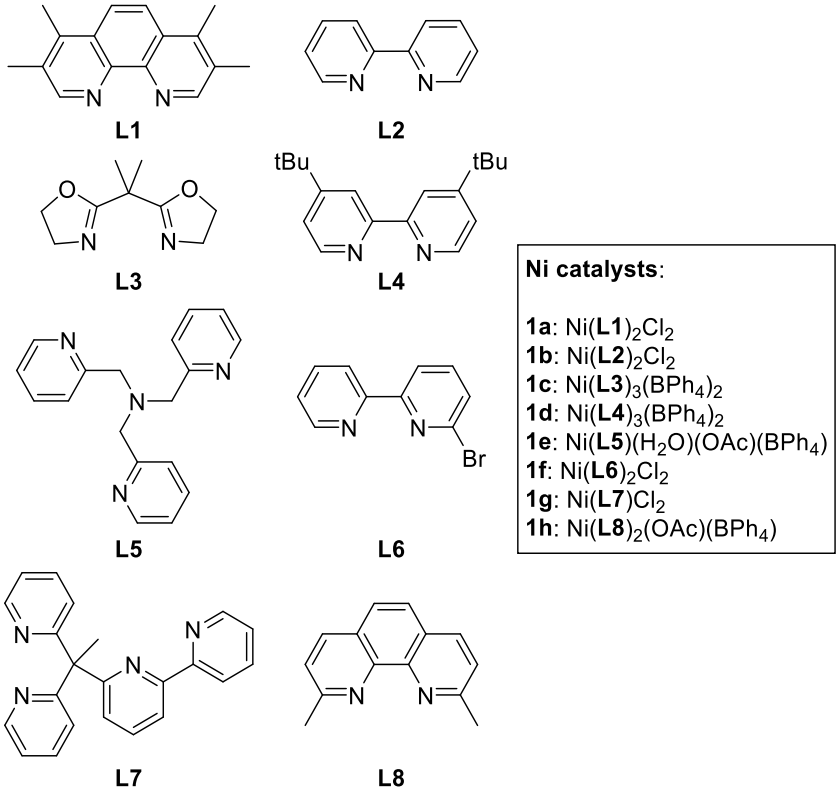


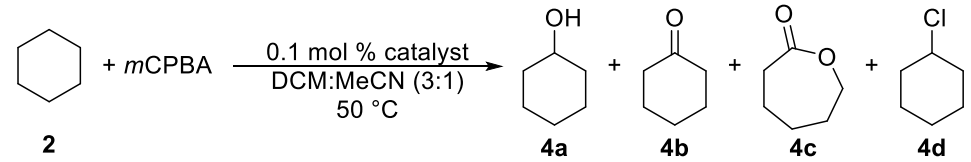
Figure 2.2. Structures of ligands **L1**–**L8** and Ni catalysts **1a–h**.

Although the chemoselectivity for formation of alcohol, ketone and lactone products **4a-c** provided preliminary evidence that a ligated nickel complex is not involved in the cleavage of C–H bonds, the ketone and ester are likely to be secondary products. Therefore, the distribution of these products could be envisioned to depend on several factors besides the identity of the species that cleaves the C–H bond. A more rigorous test would involve the measurement of initial products.

In addition, measuring the selectivity for tertiary versus secondary (or primary) C–H bonds in a model alkane is important to identify the species that cleaves the C–H bond and to understand the mechanism of Ni-catalyzed oxidations of hydrocarbons. Thus, we measured the regioselectivity for the oxidation of adamantane.

Table 2.1. Results of oxidation of (A) cyclohexane and (B) adamantane in the presence of different catalysts

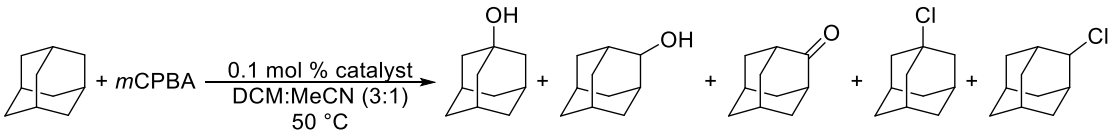
(A)



2 **4a** **4b** **4c** **4d**

Entry	Catalyst	Time (h)[a]	**4a** (%)	**4b** (%)	**4c** (%)	**4d** (%)	A/(K+E)
1	**1a**	1	33.8±6.0	10.9±0.3	0.0±0.0	12.8±3.2	3.1±0.6
2	**1b**	1	38.1±2.5	10.3±1.0	1.1±1.0	11.4±2.9	3.3±0.6
3	**1c**	1	39.1±2.1	10.4±0.6	1.0±1.0	12.4±3.0	3.4±0.5
4	**1d**	1.5	31.1±1.7	6.3±0.5	3.3±0.2	8.3±0.8	3.2±0.3
5	**1e**	1.5	32.9±2.3	8.3±1.4	2.1±1.3	13.0±3.8	3.2±0.9
6	**1f**	2	34.6±1.9	5.2±0.7	4.8±0.7	9.5±1.5	3.5±0.5
7	**1g**	3	33.7±2.1	4.7±1.4	5.4±0.8	10.6±0.5	3.3±0.7
8	**1h**	4[b]	10.0±2.3	2.3±0.4	5.1±0.3	5.8±1.1	-[c]
9	$NiCl_2$	4	30.7±1.0	8.3±1.6	4.4±1.8	9.7±0.8	2.4±0.6
10	$CoCl_2$	1.5	24.7±5.1	10.7±0.4	0.0±0.0	9.1±1.0	2.3±0.5
11	none	4[b]	1.3±2.2	0.9±1.5	0.6±1.1	0.0±0.0	-[c]

(B)



3 **5a** **5b** **5c** **5d** **5e**

Entry	Catalyst	Time (h)[a]	**5a** (%)	**5b**+**5c** (%)	**5d** (%)	**5e** (%)	3˚/2˚
1	**1a**	1	36.7±6.4	3.1±0.7	2.7±0.4	3.9±3.6	5.6±3.1
2	**1b**	1	30.6±3.8	2.6±0.2	2.8±0.5	2.7±2.3	6.3±2.8
3	**1c**	1	30.6±5.7	2.4±0.3	2.4±0.2	2.4±2.1	6.9±3.3
4	**1d**	1.5	24.9±2.1	2.5±0.7	4.0±0.7	4.0±0.6	4.4±0.7
5	**1e**	1.5	30.0±1.2	2.5±0.1	4.8±0.1	4.9±0.6	4.7±0.4
6	**1f**	2	38.5±6.0	3.0±0.3	3.5±0.9	4.1±0.4	5.9±0.9
7	**1g**	3	29.0±1.2	2.6±0.5	5.2±0.6	5.0±0.7	4.5±0.5
8	**1h**	4[b]	20.7±2.1	1.4±0.2	4.0±0.4	2.6±0.3	6.2±0.8
9	$NiCl_2$	4	28.2±1.8	2.4±0.1	4.4±0.3	3.5±0.1	5.5±0.3
10	$CoCl_2$	1.5	27.9±0.7	2.8±0.1	2.0±0.5	2.1±1.8	6.1±2.3
11	none	4[b]	8.8±5.0	0.6±1.1	0.4±0.7	0.2±0.3	-[c]
12	**1a**[d]	1	6.5	5.0	53.8	13.4	

Conditions: 0.125 mmol *m*CPBA, 7.5 equiv **2** or 2 equiv **3**, 0.1 mol % catalyst, DCM:MeCN (3:1, 0.125 M), 50 ˚C under air. All yields were based on *m*CPBA and reported as the arithmetic mean of three repeated experiments. [a]Time required to reach greater than 90% conversion of *m*CPBA unless noted otherwise. [b]Low conversion of *m*CPBA even after 4 h of reaction. [c]Conversion too low to determine. [d]In the presence of CCl_4 (1 equiv).

The results of the oxidations of adamantane (**3**) catalyzed by a series of nickel complexes are shown in Table 2.1(B). 1-Adamantanol (**5a**) was the major product; 2-adamantanol (**5b**), 2-adamantanone (**5c**), 1- and 2-chloroadamantane (**5d** and **5e**) were the minor products. Like the reactions of cyclohexane, the rates of the reactions of adamantane depended on the ligand bound to nickel. Reactions catalyzed by Ni complexes **1a**-**1e** reached greater than 90% conversion of *m*CPBA within 1–1.5 h (Table 2.1(B), entries 1-5), whereas those catalyzed by **1f** and **1g**, which contain sterically encumbered ligands **L6** and **L7**, required 2 and 3 h to reach similar levels of conversion (Table 2.1(B), entries 6–7). The reaction in the presence of complex **1h**, which contains the most sterically hindered ligand **L8**, did not reach 90% conversion even after 4 h of heating (Table 2.1(B), entry 8).

Despite the different rates of reactions catalyzed by these complexes, all of the reactions catalyzed by complexes **1a**–**1g** furnished product **5a** in 24.9%–38.5% yield, the combination of products **5b** and **5c** in 2.4%–3.1% yield, product **5d** in 2.4%–5.2% yield, and product **5e** in 2.4%–5.0% yield. The ratio of the combination of products from functionalization at the tertiary positions (**5a** and **5d**) to the combination of those at the secondary position (**5b**, **5c** and **5e**), which is denoted 3˚/2˚, reflects the regioselectivity of this reaction. These 3˚/2˚ ratios were between 4.4 and 6.9, and all the ratios were well within experimental error of each other. In addition, oxidation of adamantane catalyzed by ligandless $NiCl_2$ and $CoCl_2$ furnished the combination of products **5a** and **5d** in 32.6% and 29.9% yield and the combination of products **5b**, **5c** and **5e** in 5.9% and 4.9% yield, corresponding to 3˚/2˚ ratios of 5.5 and 6.1, respectively, which are indistinguishable from those of reactions catalyzed by ligated Ni complexes **1a**-**1g**. The lack of dependence of the product distribution and regioselectivity of the oxidation of adamantane on this series of Ni complexes containing different ligands and on ligandless metal chlorides, again, is inconsistent with the hypothesis that a Ni-oxygen species cleaves the C–H bonds in hydrocarbons.

2.2.2. Formation of Carbon-centered Radicals with Long Lifetimes

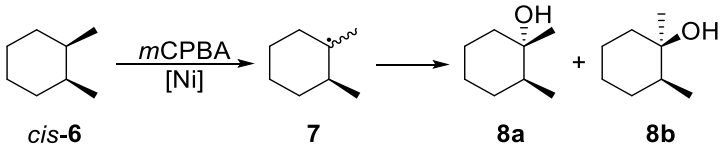
Determining whether carbon-centered radicals are formed and, if so, estimating the lifetime of these radicals is crucial to understanding the mechanism of oxidations of C–H bonds. The formation of chlorinated products **5d** and **5e** in high yields in Ni-catalyzed oxidation of adamantane with one equivalent of CCl_4 (Table 2.1(B), entry 12) strongly suggests the formation of carbon-centered radicals and subsequent trapping by CCl_4. Substrates that react as radical clocks are often employed to study the lifetime of carbon-centered radicals and the rate of the formation of C–O bonds during the oxidation of C–H bonds.[36] For example, several radical clocks based on cyclopropanes were used to study the mechanism of the hydroxylation of saturated C–H bonds catalyzed by P450 enzymes.[1] In this work, we used the well-known *cis*- and *trans*-1,2-dimethylcyclohexane (*cis*- and *trans*-**6**) as radical clocks[37] to investigate the lifetime of carbon-centered radicals formed in the Ni-catalyzed oxidation reaction.

Ni-catalyzed oxidation of *cis*-**6**, which occurred predominantly at the tertiary position, generated the tertiary alkyl radical **7**, which is known to epimerize rapidly (first-order rate constant $k \sim 10^9$ s^{-1}),[36] and afforded tertiary alcohols **8a** and **8b** as major products (Table 2.2(A)). The fraction of *cis* product (ratio of the yield of **8a** to the combined yield of **8a** and **8b**), reflects the rate of the epimerization of **7** versus that of the formation of a C–O bond. If the formation of the C–O bond occurs much faster than epimerization, then the *cis* product **8a** would be formed predominantly. In cases where the step that forms the C–O bond occurs more slowly than epimerization of **7**, products **8a** and **8b** have been observed in similar amounts, corresponding to a *cis*-fraction close to 50%.[36, 38] As shown in Table 2.2(A), oxidation of *cis*-**6** in the presence of a

series of Ni complexes, including the ligandless $NiCl_2$, formed the tertiary alcohols with a *cis*-fraction ranging from 42.6% to 48.9%. These results indicate that the lifetime of the carbon-centered radical formed in these reactions is long enough that complete epimerization occurs before the formation of the C–O bond.

Table 2.2. Results of Ni-catalyzed oxidation of (A) *cis*-**6** and (B) *trans*-**6**.

(A)

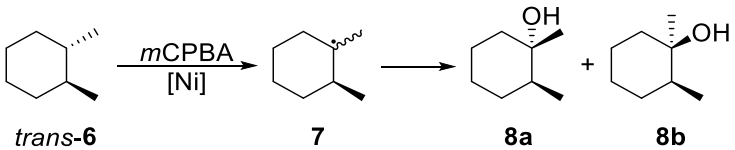


cis-**6** **7** **8a** **8b**

$$cis\text{-fraction} = \frac{\text{yield}(\mathbf{8a})}{\text{yield}(\mathbf{8a}) + \text{yield}(\mathbf{8b})}$$

Entry	[Ni]	Yield of **8a** (%)	Yield of **8b** (%)	*cis*-fraction (%)
1	**1a**	22.9±5.4	30.7±6.8	42.6±0.6
2	**1b**	20.3±2.7	26.2±3.5	43.7±0.5
3	**1c**	17.8±1.9	23.5±2.5	43.1±0.2
4	**1e**	17.9±2.1	18.8±3.0	48.9±1.8
5	**1f**	23.8±4.1	26.8±2.4	46.8±2.3
6	**1g**	17.5±4.1	19.9±6.5	47.3±2.5
7	$NiCl_2$	22.7±2.5	24.6±1.5	47.9±3.4

(B)



trans-**6** **7** **8a** **8b**

Entry	[Ni]	Yield of **8a** (%)	Yield of **8b** (%)	*cis*-fraction (%)
1	**1a**	11.4±0.9	16.0±1.2	41.7±0.1
2	**1b**	11.7±1.4	16.5±2.2	41.6±0.3
3	**1c**	11.2±1.6	15.8±2.6	41.4±0.4
4	**1e**	8.2±1.0	14.0±1.8	36.9±0.2
5	**1f**	10.2±0.7	15.8±1.0	39.3±0.1
6	**1g**	5.9±2.7	10.0±4.6	37.2±0.3
7	$NiCl_2$	8.1±3.3	12.8±5.5	39.1±1.0

Conditions: 0.125 mmol mCPBA, 7.5 equiv cis- or trans-**6**, 0.1 mol % [Ni], DCM:MeCN (3:1, 0.125 M), 50 ˚C under air, 1-4 h. All yields were based on *m*CPBA and reported as the arithmetic mean of three repeated experiments.

The *cis*-fraction from Ni-catalyzed oxidation of *trans*-**6**, summarized in Table 2.2(B) ranged from 36.9% to 41.7%. The lower fraction of *cis* product from reactions catalyzed by **1e**–**1g** and $NiCl_2$, which are slower than the reactions catalyzed by **1a**-**1c** (Table 2.2(B), entries 4-7) is likely due to competing background, uncatalyzed hydroxylation by *m*CPBA. Oxidation of alkanes by *m*CPBA is known to occur with retention of configuration.[9] These results are also consistent with reaction through a long-lived alkyl radical before the step that forms the C–O bond in Ni-catalyzed oxidations.

2.2.3. Ni-catalyzed Decomposition of mCPBA and a Callback to Fenton Chemistry

Our attempts to isolate Ni-oxygen intermediates or Ni-*m*CPBA adducts with phenanthroline-based ligands have simply led to decomposition of *m*CPBA. In the absence of alkanes, *m*CPBA was consumed completely to form *meta*-chlorobenzoic acid (*m*CBA) in 72% yield and chlorobenzene (**9**) in 15% yield in the presence of Ni complex **1a** under standard conditions (Figure 2.3(A)). Chlorobenzene, which was formed in approximately 51% yield in the catalytic oxidation of cyclohexane (Figure 2.3(B)) would arise from decarboxylation of *meta*-chlorobenzoyloxy radical (**10**). Moreover, our data show that the rate of decomposition of *m*CPBA is dependent on the identity of the ligand in the Ni catalyst. Time courses indicate that the rate of decomposition in the presence of complex **1a** is significantly higher than that in the presence of complex **1h**, which contains sterically hindered ligands (see Experimental Section).

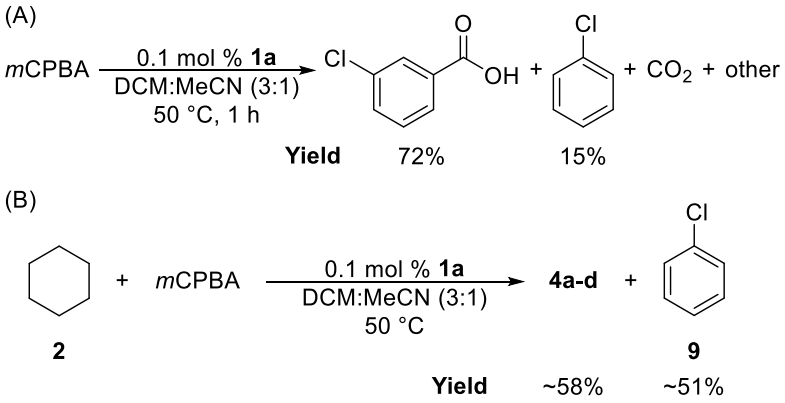


Figure 2.3. (A) Results of Ni-catalyzed decomposition of *m*CPBA in the absence of alkanes. (B) Formation of chlorobenzene in Ni-catalyzed oxidation of **2** by *m*CPBA.

This Ni-catalyzed decomposition of an aromatic peracid that involves free radical intermediates is reminiscent of the classic Fenton chemistry (Scheme 2.1),[39-40] in which an iron(II) cation catalyzes the decomposition of hydrogen peroxide to generate the hydroxyl radical (**11**) (eq 2.1.1). If an alkane is present in the reaction system, the highly reactive radical **11** will abstract a hydrogen atom from a C–H bond to form water and an alkyl radical, which can subsequently form alcohol (eq 2.1.2). If no alkane is present, H_2O_2 will decompose to release O_2 and water through either a radical chain (eq 2.1.3, 2.1.4) or a non-chain pathway (eq 2.1.1, 2.1.3, 2.1.5). The decomposition of *m*CPBA in the presence of Ni complexes, the lack of effect of the ligands on the selectivity of catalytic reactions, and the formation of long-lived carbon-centered radicals led us to propose an alternative reaction pathway in which the Ni species does not cleave the C–H bond; instead, it reacts with *m*CPBA to generate free radicals that abstract a hydrogen atom from the C(sp^3)–H bond. However, because the nickel-catalyzed reaction occurs with *m*CPBA instead of H_2O_2, the identity of the species that cleaves the C–H bond in such a scenario was unclear.

Scheme 2.1. Mechanism of Fenton reactions of H_2O_2

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + HO^{\bullet} + HO^{\ominus} \quad (2.1.1)$$

$$HO^{\bullet} + R{-}H \longrightarrow H_2O + R^{\bullet} \xrightarrow{[O]} R{-}OH \quad (2.1.2)$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HOO^{\bullet} \quad (2.1.3)$$

$$HOO^{\bullet} + H_2O_2 \longrightarrow H_2O + O_2 + HO^{\bullet} \quad (2.1.4)$$

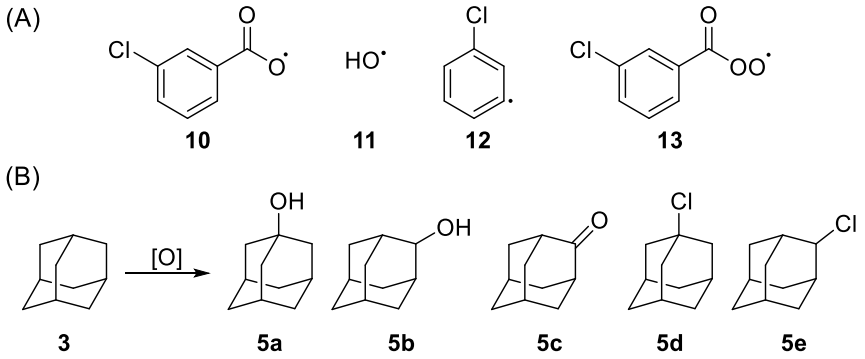
$$Fe(III) + HOO^{\bullet} \longrightarrow Fe(II) + O_2 + H^{\oplus} \quad (2.1.5)$$

2.2.4. Identity of the Free Radical Responsible for C–H Bond Cleavage

To identify the radical that cleaves the C–H bond during the reactions with *m*CPBA containing catalytic amounts of nickel complex, we conducted the reactions of *m*CPBA and Ni complexes with deuterium labelled cyclohexane (**2**-d_{12}) and adamantane (**3**) and compared the selectivity of these reactions to the known selectivities for the reactions involving abstraction of the hydrogen atom in a C–H bond by various radicals. Figure 4A shows four *m*CPBA-derived free radicals that might be formed in the reaction system containing nickel: the 3-chlorobenzoyloxy radical (**10**), the hydroxyl radical (**11**), the 3-chlorophenyl radical (**12**), which can be formed by decarboxylation of **10**, and the 3-chlorobenzoylperoxy radical (**13**).

The selectivity of hydroxyl radical (**11**) for the oxidation of adamantane is low. The 3˚/2˚ ratios from oxidations of **3** that involve cleavage of C–H bonds by radical **11** range from 0.4 to 1.3 (Figure 2.4(B), entries 1–3).[41] These values are much smaller than those of Ni-catalyzed oxidation of **3** by *m*CPBA, which range from 4.4 to 6.9. Thus, hydroxyl radical **11** is unlikely to be the species that cleaves the C–H bond in this reaction.

If 3-chlorophenyl radical (**12**) were the major species that cleaves the C–H bond in Ni-catalyzed oxidations of alkanes, then the oxidation of deuterated cyclohexane (**2**-d_{12}) would afford deuterated cyclohexanol (**4a**-d_{11}) and deuterated cyclohexanone (**4b**-d_{10}) as the major products, along with a stoichiometric amount of deuterated chlorobenzene (**9**-d_1). However, ^{2}H NMR spectra of the reaction of **2**-d_{12} with *m*CPBA and a catalytic amount of Ni complex **1a** showed that this reaction formed **4a**-d_{11} and **4b**-d_{10} in 26% and 8% yield, respectively, but produced **9**-d_1 in only 2% yield (Figure 2.4(D)). This result indicates that aryl radical **12** cannot be the major intermediate that cleaves C–H bonds in hydrocarbons. The large amount of byproduct **9** observed in the catalytic oxidations of **2** and **3** (Figure 2.3(B)) was most likely formed by hydrogen atom transfer (HAT) from solvent molecules, such as DCM, to **12**. This hypothesis is supported by the detection of 1,1,2,2-tetrachloroethane in the reaction mixture, which is the homocoupling product of dichloromethyl radicals ($CHCl_2\cdot$) that would form by hydrogen-atom transfer from DCM to **12**. We also conducted Ni-catalyzed oxidation of cyclohexane by *m*CPBA with DCM-d_2 as the solvent and observed that 87% of the chlorobenzene that formed contained the deuterium label (see Experimental Section). These results further support our hypothesis that chlorobenzene (**9**) is formed primarily by hydrogen atom transfer from solvent molecules to radical **12**.



Entry	[O]	Free radical	3˚/2˚
1	O_2-H_2O_2-^{n}Bu$_4$NVO$_3$-PCA	**11**	0.4
2	O_2-H_2O_2-*hv*	**11**	0.5
3	O_2-H_2O_2-Fe(ClO$_4$)$_3$	**11**	1.3
4	benzil-O_2-*hv* in DCE[a]	**13'**	11.2-12.1
5	Ni-*m*CPBA[b]	TBD	4.4-6.9

[a]DCE instead of DCM/MeCN was used to reduce evaporation of solvent while the solution was sparged with O_2. [b]Similar selectivity in DCE and DCM/MeCN.

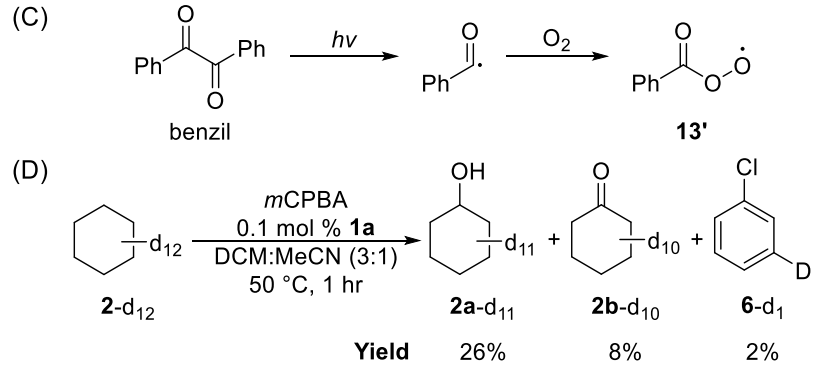


Figure 2.4. (A) Free radicals derived from *m*CPBA that might cleave C–H bonds in the catalytic reaction. (B) Tertiary to secondary selectivity of free radicals for the oxidation of **3**. (C) Photomediated formation of benzoylperoxy radical from benzil under an atmosphere of O_2. (D) Results of Ni-catalyzed oxidation of **2**-d_{12}.

The benzoylperoxy radical (**13'**) can be generated by the photo-mediated homolysis of benzil under an atmosphere of O_2 (Figure 2.4(C)).[42-43] To measure the selectivity of radical **13'** for the oxidation of adamantane (**3**), we conducted the photochemical oxidation of **3** with benzil and O_2 in 1,2-dichloroethane (DCE). The 3˚/2˚ ratios derived from the products of these reactions range from 11.2 to 12.1 (Figure 2.4(B), entry 4), which is higher than those from Ni-catalyzed oxidations of **3** conducted in the same solvent (Figure 2.4(B), entry 5). Given the similar structures of radicals **13** and **13'**, it is likely that the 3˚/2˚ selectivity for the oxidation of **3** by these two radicals is similar. Therefore, the 3-chlorobenzoylperoxy radical (**13**) is unlikely to be the species that cleaves C–H bonds in Ni-catalyzed oxidations of alkanes.

Thus, the aroyloxy radical **10** is the most likely radical to cleave the C–H bond. The BDE of the O–H bond in *m*CBA was reported to be 107.3 kcal/mol,[4] which is higher than those of unactivated C–H bonds in alkanes and makes HAT from alkanes to radical **10** thermodynamically favorable. The second-order rate constant for abstraction of a hydrogen atom from **2** by 4-

methoxybenzoyloxy radical (**14**) was measured to be on the order of 10^5 M^{-1} s^{-1}, whereas the first-order rate constant for decarboxylation of **14** was measured to be 10^4-10^5 s^{-1}.[44] Given the similarity between the structures of *m*-chloro and *p*-methoxy substituted benzoyloxy radicals **10** and **14**, it is likely that the rate constants for abstraction of a hydrogen atom from an unactivated C(sp^3)–H bond by these two radicals are similar and that the rate of abstraction of a hydrogen atom by **10** would be similar to that of the decarboxylation. This prediction based on the literature values fits with the observed oxidation process and formation of chlorobenzene.

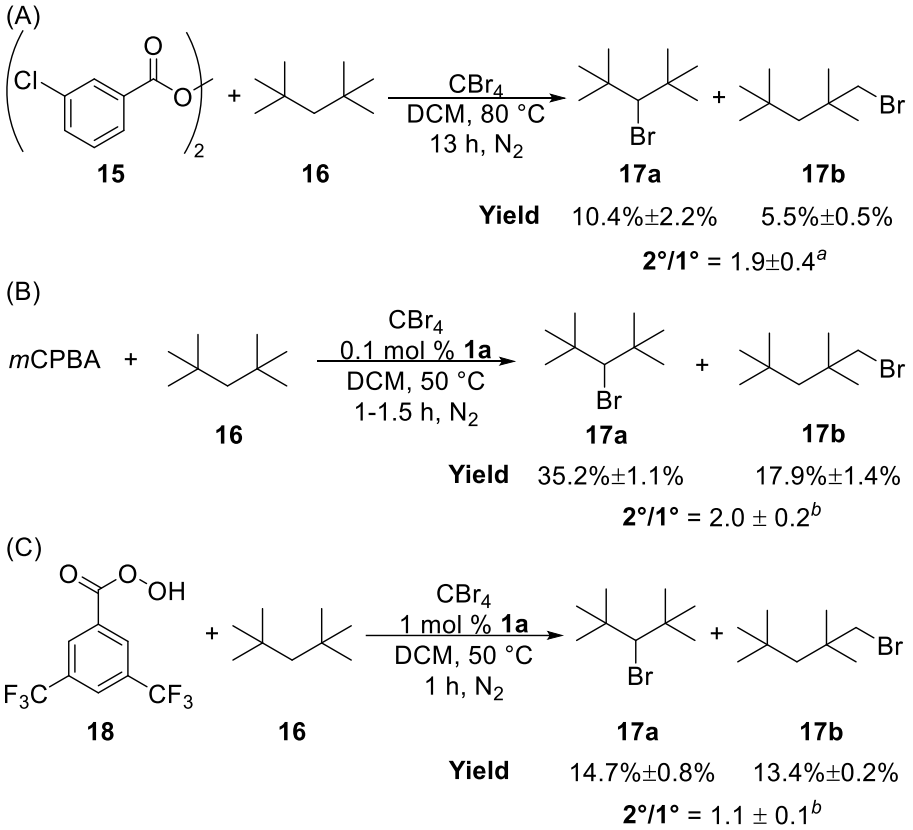


Figure 2.5. Bromination of alkane **16** by (A) peroxide **15**, (B) *m*CPBA and Ni complex **1a**, and (C) peracid **18** and Ni complex **1a**. Conditions: (A) 0.0625 mmol **15**, 10 equiv **16**, 4 equiv CBr_4, DCM (0.0625 M), 80 ˚C under N_2; (B) 0.125 mmol *m*CPBA, 5 equiv **16**, 2 equiv CBr_4, 0.1 mol% **1a**, DCM (0.125 M), 50 ˚C under N_2. (C) 0.125 mmol **18**, 5 equiv **16**, 2 equiv CBr_4, 1 mol% **1a**, DCM (0.125 M), 50 ˚C under N_2. [a]Average of eight repeated experiments. [b]Average of three repeated experiments.

However, reliable data on the selectivity of aroyloxy radical **10** for abstraction of hydrogen atoms from alkanes were needed to assess more precisely whether this radical cleaves the C–H bonds in Ni-catalyzed oxidations. Thus, we generated radical **10** in situ via thermal decomposition of bis(3-chlorobenzoyl)peroxide (**15**), measured its selectivity for hydrogen-atom abstraction of an model alkane, 2,2,4,4-tetramethylpentane (**16**), and compared the selectivity of metal-free bromination of **16** by peroxide **15** to that of Ni-catalyzed reactions (Figure 2.5). All reactions were conducted in the presence of CBr_4, which is well known to trap carbon-centered radicals rapidly. In this case, the distribution of products **17a** and **17b** from bromination at the secondary and primary C–H bonds accurately reflects the selectivity in the hydrogen-atom transfer step. The model substrate **16** was chosen because radicals derived from CBr_4, such as CBr_3·, do not cleave

the strong primary and secondary C–H bonds in alkane **16** and, therefore, do not interfere with the measurement of the selectivity of hydrogen-atom abstraction by aroyloxy radical **10**. The tertiary C–H bonds in adamantane, however, can be cleaved by these radicals derived from CBr_4, so adamantane is not a suitable substrate for this experiment (see Experimental Section).

Reaction of peroxide **15** with alkane **16** in the presence of two equivalents of CBr_4 furnished **17a** in 10.4% yield and **17b** in 5.5% yield, corresponding to a 2˚/1˚ ratio of 1.9±0.4 (Figure 2.6(A)). The Ni-catalyzed bromination of **16** by *m*CPBA formed **17a** in 35.2% yield and **17b** in 17.9% yield, corresponding to a 2˚/1˚ ratio of 2.0±0.2 (Figure 2.6(B)). The similarity between the selectivity of the bromination reactions with diaroyl peroxide **15** and the process with the nickel complex and *m*CPBA strongly suggests that radical **10** is the species that cleaves the C–H bond in the catalytic system.

To assess further our proposal that the aroyloxy radical derived from the aromatic peracid is the species that cleaves the C–H bond in the catalytic reaction, we envisioned that the selectivity for Ni-catalyzed bromination of **16** would be different for reactions with aromatic peracids bearing different substituents than the chloride in *m*CPBA. Indeed, Ni-catalyzed bromination of **16** by 3,5-bis(trifluoromethyl)perbenzoic acid (**18**) furnished **17a** in 14.7% yield and **17b** in 13.4% yield, corresponding to a 2˚/1˚ ratio of 1.1±0.1 (Figure 2.6(C)). This ratio is lower than those from reactions involving *m*-chlorobenzoyloxy radical **10** (Figure 2.6(A), 2.6(B)) and further corroborates our hypothesis that aroyloxy radicals derived from aromatic peracids cleave the C–H bonds of alkanes in the catalytic system.

2.2.5. The C–O Bond Formation Step

Having identified the free radical responsible for C–H bond cleavage, we investigated the step that forms the C–O bond. Three possible pathways can lead to formation of a C–O bond from the carbon-centered radical generated by hydrogen-atom abstraction by aroyloxy radical **10** (Scheme 2.2): 1) trapping by O_2 to generate an alkylperoxy radical, which subsequently decomposes to form alcohol and ketone products (eq 2.2.1); 2) trapping by a putative nickel(III) hydroxide species, which would be generated by oxidation of the Ni(II) complex by *m*CPBA, to form the alcohol product and a Ni(II) species (eq 2.2.2); 3) trapping by *m*CPBA to afford the alcohol product and radical **10** (eq 2.2.3).

Scheme 2.2. Three possible pathways for the formation of C–O bonds

$$R^{\bullet} + O_2 \longrightarrow R{-}OO^{\bullet} \longrightarrow R{-}OH + R{=}O \qquad (2.2.1)$$

$$R^{\bullet} + [Ni^{III}]{-}OH \longrightarrow R{-}OH + [Ni^{II}] \qquad (2.2.2)$$

$$R^{\bullet} + ArCO_3H \longrightarrow R{-}OH + ArCOO^{\bullet} \qquad (2.2.3)$$

Decomposition of alkylperoxy radicals usually forms the corresponding alcohol and ketone products in approximately 1:1 ratio,[45] whereas Ni-catalyzed oxidation of **2** gave A/(K+E) ratios between 3.1 and 3.5 (Table 2.1(A)). Furthermore, the yield and selectivity of the catalytic oxidations of **2** and **3** under an atmosphere of N_2 was similar to that of the reactions under air. These straightforward observations suggest that the formation of the C–O bond does not involve O_2 and that the steps in eq 2.2.1 are unlikely to be the major ones forming the C–O bond in the Ni-catalyzed oxidations. Nonetheless, we decided to assess more precisely whether trapping of alkyl radicals by O_2 occurred and, if so, what percentage of the oxidized products were formed from O_2.

To assess this pathway further, we determined the amount of alkylperoxy intermediates in the product mixture that would form by trapping of the alkyl radical with O_2. Shul'pin et al. reported

an experiment for this purpose (Figure 2.6).[46-47] Alkylperoxy intermediates, such as cyclohexyl hydroperoxide (**19**), decompose by gas chromatography (GC) to generate the corresponding alcohol and ketone products **4a** and **4b** in approximately 1:1 ratio. Treatment of a reaction mixture containing alcohol **4a**, ketone **4b** and intermediate **19** with an excess of reductants, such as PPh_3, reduces **19** to **4a** in quantitative yield without affecting the amount of alcohol or ketone formed before addition of PPh_3. Thus, if intermediate **19** is present in a reaction mixture, the ratios of alcohol to ketone (A/K) derived from the GC trace of the mixture before and after the treatment with PPh_3 will be different. Moreover, the percentage of **19** in the total amount of oxidized products can be calculated from these ratios.

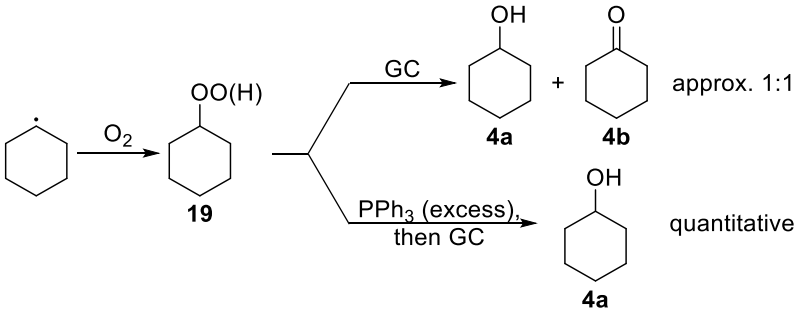
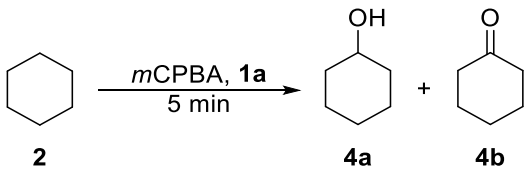


Figure 2.6. Illustration of the GC experiment for detection of alkyl hydroperoxide intermediates designed by Shul'pin.

Table 2.3. GC results of Ni-catalyzed oxidation of cyclohexane under N_2 and air.



Entry	N_2/air	Treatment with PPh_3	A/K[a]
1	N_2	yes	4.6±0.1
2		no	4.5±0.0
3	air	yes	6.1±0.8
4		no	4.2±0.7

Conditions: 0.125 mmol *m*CPBA, 7.5 equiv **2**, 0.1 mol % **1a**, DCM:MeCN (3:1, 0.125 M), 50 ˚C, 5 min.
[a]Arithmetic mean of three repeated experiments.

The A/K ratio derived from GC traces of the mixture from the Ni-catalyzed oxidation of **2** under an atmosphere of N_2 after 5 min before addition of PPh_3 was identical to that after addition of PPh_3 (Table 2.3, entries 1–2). This result indicates that intermediate **19** was not formed and that molecular O_2 was not generated in situ during the reaction under N_2. On the other hand, the A/K ratio derived from GC traces of the reaction conducted under air before addition of PPh_3 was 4.2±0.7 and the ratio after addition of PPh_3 was 6.1±0.8 (Table 2.3, entries 3–4). The small difference between these ratios suggested that some amount of intermediate **19** was formed under air by the pathway depicted by eq 2.2.1. However, the percentage of **19** in the total amount of oxidized species (**4a** + **4b** + **19**) was estimated to be only 10% based on these two ratios (see Experimental Section for details of calculation). Thus, trapping of alkyl radicals by O_2, even under air, was not the major pathway for formation of the C–O bond in the catalytic reactions.

The lack of effect of the ligands on the yield and selectivity of Ni-catalyzed oxidation of alkanes does not support the potential formation of alcohol by reaction of the alkyl radical with a nickel hydroxide species (Scheme 2.2, eq 2.2.2). If the C–O bond is formed by this species, then the *cis* fraction of the alcohols formed from the reactions of 1,2-dimethylcyclohexanes would be expected to depend on the electronic and steric properties of the nickel species, which in turn would depend on the identity of the ligand.

Having ruled out the two pathways described above, we considered that trapping of carbon-centered radicals by *m*CPBA (Scheme 2.2, eq 2.2.3) would be the major pathway for formation of the C–O bond. Indeed, the reaction of an alkyl radical with an aliphatic peracid by a free-radical chain process has been well established by many examples of decarboxylative formation of alcohols from aliphatic peracids.[48]

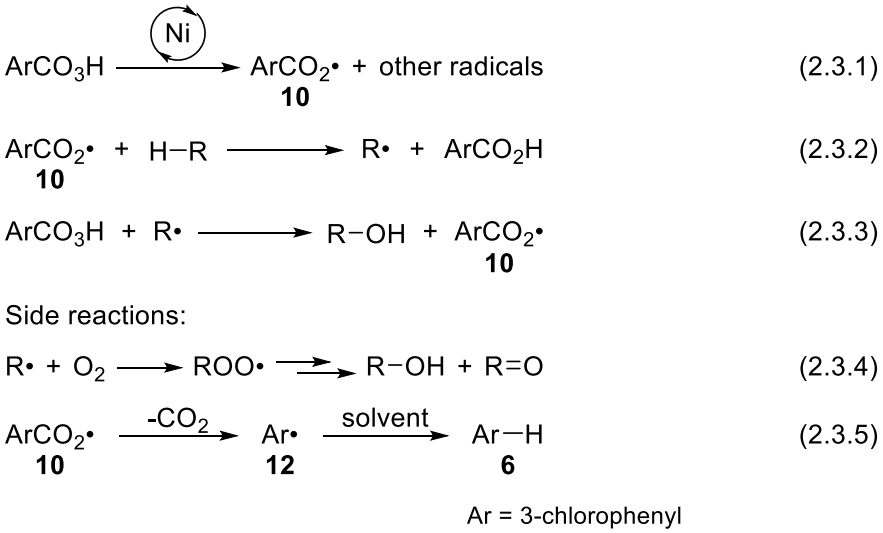
2.2.6. The Free Radical Chain Mechanism

Having investigated both the C–H bond-cleaving and the C–O bond-forming steps, we propose a free-radical chain mechanism for the Ni-catalyzed oxidation of unactivated C(sp^3)–H bonds by *m*CPBA (Scheme 2.3). Contrary to the hypotheses in the literature[20, 25-26] that Ni-oxygen intermediates cleave C–H bonds, our data suggest that the Ni complex catalyzes the reaction of *m*CPBA to generate the 3-chlorobenzoyloxy radical (**10**) among other products (eq 2.3.1). Eq 2.3.1 likely consists of several redox reactions, but our data do not allow conclusions about the mechanism of this step. Radical **10** abstracts a hydrogen atom from the alkane to form the *m*CBA byproduct and a carbon-centered radical (eq 2.3.2), which then reacts with *m*CPBA to afford the alcohol product and regenerate radical **10** (eq 2.3.3), thus propagating the radical chain. As discussed previously, trapping of alkyl radicals by O_2 is a minor side reaction under air (eq 2.3.4). Decarboxylation of radical **10** to generate the 3-chlorophenyl radical **12**, which captures a hydrogen atom from solvent molecules to form the chlorobenzene byproduct (eq 2.3.5), competes with the reaction of **10** with a C–H bond (eq 2.3.2).

Based on this mechanism, the identity of the Ni complex influences the rate of decomposition of *m*CPBA and hence the rate of formation of radical **10**, but it does not change the selectivity for reaction at one C–H bond over another. This conclusion is consistent with our observation that reactions catalyzed by Ni complexes with more sterically hindered ligands are slower but the selectivities of these reactions are similar to those catalyzed by complexes with less hindered ligands. This radical chain mechanism, in which the C–H bond is not cleaved by a nickel complex, reconciles the combination of low reactivity of Ni-oxygen species towards strong C(sp^3)–H bonds and the well documented formation of oxidation products in high yield from Ni-catalyzed oxidations occurring at strong aliphatic C–H bonds.

Alexanian and coworkers achieved tunable, selective chlorination of C(sp^3)–H bonds via free radical pathways by modifying the substituents on the *N*-chloroamide reagents.[49-50] Our free radical mechanism for Ni-catalyzed oxidation of unactivated alkanes suggests that novel, substituted aromatic peracids, likewise, could modify the selectivity for oxidation of C(sp^3)–H bonds in complex molecules and polymers.

Scheme 2.3. The free radical chain mechanism of Ni-catalyzed oxidation of unactivated C(sp^3)–H bonds.



2.3. Conclusion

In conclusion, we report detailed mechanistic investigations of the oxidation of unactivated C(sp^3)–H bonds by *m*CPBA catalyzed by Ni complexes coordinated by nitrogen-based ligands. We show the absence of an effect of the ligand on the yield and selectivity of this reaction, as well as a clear correlation between reaction rates and the steric hindrance of the ligands. Experiments with radical clocks indicate that this reaction generates a carbon-centered radical that is sufficiently long-lived to epimerize before the formation of the C–O bond.

Based on these results and the observation of Ni-catalyzed decomposition of *m*CPBA, we propose an alternative pathway for oxidation that does not involve a nickel-oxo or -oxyl species. We conclude that the nickel facilitates the generation of 3-chlorobenzoyloxy radical, which cleaves the C–H bonds in alkanes, as evidenced by a series of experiments on the selectivity for reactions of adamantane and 2,2,4,4-tetramethylpentane and on the oxidation of deuterium labelled cyclohexane. We also conclude that trapping of alkyl radicals by *m*CPBA is the major pathway to form the C–O bond. Finally, we propose that the oxidation occurs by a free radical chain mechanism. Our results and this proposed mechanism reconcile the lack of strong evidence for the reactivities of Ni-oxo or Ni-oxyl complexes towards strong C(sp^3)–H bonds and the formation of oxidized products in good yield from Ni-catalyzed oxidations of unactivated alkanes with aromatic peracids. We envision that such mechanistic understanding can guide us to design more effective and selective organic oxidants, e.g., substituted aromatic peracids, for the oxidation of unactivated C(sp^3)–H bonds in complex molecules and polymers.

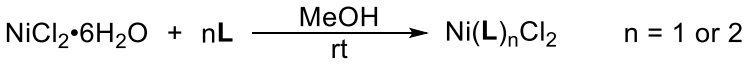
2.4. Experimental Section

2.4.1. General Procedures

Unless otherwise specified, all reactions were performed in oven-dried glassware under air. Reagents and solvents were used as received from commercial sources without further purification. Reaction temperatures refer to the temperatures of aluminum heating blocks or silicone oil baths. ^{1}H and ^{2}H NMR spectra were obtained on Bruker AV and NEO spectrometers operating at 300, 500, 600, or 700 MHz. Chemical shifts (δ) were reported relative to the residual solvent signal (δ 7.26 for $CDCl_3$, δ 1.94 for CD_3CN). Infrared (IR) spectra were obtained on a Bruker Vertex 80

spectrometer and were reported in frequency of absorption (cm^{-1}). Electrospray ionization high-resolution mass spectra (ESI HRMS) were obtained on a PerkinElmer AxION 2 TOF mass spectrometer. Low-temperature X-band EPR spectra were recorded using a Varian E109 EPR spectrometer equipped with a Model 102 Microwave bridge. Sample temperature was maintained at 8K using an Air Products LTR liquid helium cryostat. The following spectrometer conditions were used: microwave frequency, 9.22 GHz; field modulation amplitude, 32 G at 100 kHz; microwave power, 2 mW. X-ray diffraction data were obtained at the Small Molecule X-ray Crystallography Facility (CheXray) at the University of California, Berkeley. Elemental analyses were performed by the Microanalytical Facility at University of California, Berkeley.

*2.4.2. Synthesis and Characterization of Ni Complexes **1a-1h***



Complexes **1c**–**1e** were synthesized according to reported literature.[21, 23]

2.4.2.1. Synthesis of $Ni(Me4Phen)_2Cl_2$ (**1a**)

To a round bottom flask equipped with a stir bar was charged $NiCl_2 \cdot 6H_2O$ (118.8 mg, 0.5000 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen, **L1**, 236.3 mg, 1.000 mmol), and methanol (10.0 mL). The resulting dark red solution was stirred at room temperature for 3 h. Acetonitrile (5.0 mL) was added, and the solvent was evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and subsequently dried under high vacuum overnight. Product **1a** was collected as a blue-green powder (150.9 mg, 50.11% yield). Vapor diffusion of diethyl ether into a saturated solution of **1a** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3296, 1617, 1525, 1428, 1385, 1245, 1180, 1015, 946, 915, 888, 864, 824, 730, 620, 572, 554, 525, 467. ESI HRMS (m/z, amu): $[Ni(Me_4Phen)_2]^{2+}$: calculated 265.0985, found 265.0933; $[Ni(Me_4Phen)_2Cl]^{+}$: calculated 565.1663, found 565.1589.

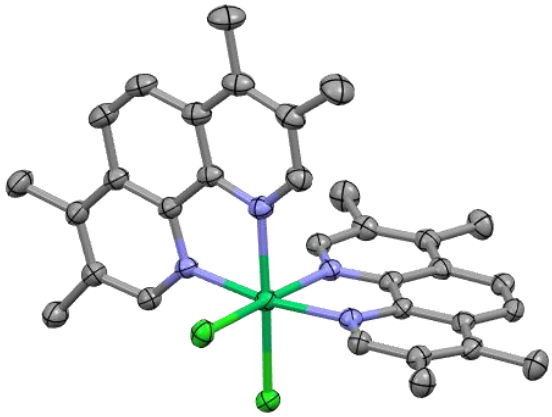


Figure 2.7. X-ray crystal structure of complex **1a**. Hydrogen atoms are omitted for clarity.

2.4.2.2. Synthesis of $Ni(bpy)_2Cl_2$ (**1b**)

To a round-bottom flask equipped with a stir bar was charged $NiCl_2 \cdot 6H_2O$ (47.5 mg, 0.200 mmol), 2,2'-bipyridine (bpy, **L2**, 62.5 mg, 0.400 mmol), and methanol (2.0 mL). The reaction mixture was stirred at room temperature for 100 min. During the course of the reaction, the solution turned from pink to dark blue. Acetonitrile (3.0 mL) was added, and the solvent was evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and subsequently dried under high vacuum overnight. Product **1b** was collected as a blue-green powder.

IR (neat, cm^{-1}): 3429, 3026, 1599, 1565, 1493, 1473, 1440, 1314, 1249, 1172, 1153, 1104, 1057, 1041, 1020, 917, 770, 736, 652, 631, 530, 439, 420. ESI HRMS (m/z, amu): $[Ni(bpy)_2]^{2+}$: calculated 185.0359, found 185.0264; $[Ni(bpy)_2Cl]^+$: calculated 405.0411, found 405.0228. Elemental analysis (%): calculated for $C_{22}H_{24}Cl_2N_4NiO_2$ (**1b**·2MeOH): C 52.22, H 4.78, N, 11.07; found: C 52.41, H 4.60, N 11.39.

2.4.2.3.Synthesis of $Ni(Brbpy)_2Cl_2$ (**1f**)

To a round-bottom flask equipped with a stir bar was charged $NiCl_2 \cdot 6H_2O$ (23.8 mg, 0.100 mmol), 6-bromo-2,2'-bipyridine (Brbpy, **L6**, 47.0 mg, 0.200 mmol), and methanol (2.0 mL). The blue-green solution was stirred at room temperature for 80 min. The solvent was then evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and subsequently dried under high vacuum. Product **1f** was collected as a green powder (44 mg, 73% yield). Vapor diffusion of diethyl ether into a saturated solution of **1f** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3063, 1653, 1602, 1587, 1571, 1554, 1484, 1451, 1427, 1393, 1293, 1262, 1230, 1186, 1161, 1131, 1115, 1102, 1077, 1021, 995, 917, 817, 788, 770, 731, 685, 645, 634, 600. ESI HRMS (m/z, amu): $[Ni(Brbpy)_2Cl]^+$: calculated 562.8601, found 562.8567. Elemental analysis (%): calculated for $C_{20}H_{14}Br_2Cl_2N_4Ni$: C 40.05, H 2.35, N 9.34; found: C 39.83, H 2.06, N 9.03.

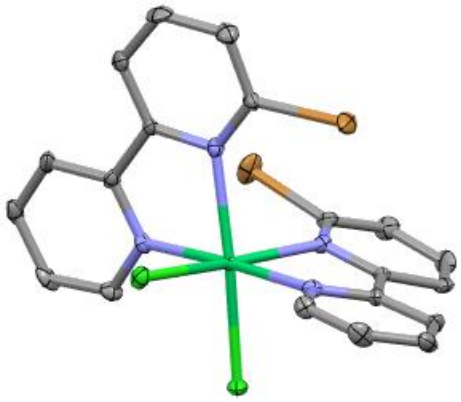


Figure 2.8. X-ray crystal structure of complex **1f**. Hydrogen atoms are omitted for clarity.

2.4.2.4.Synthesis of $Ni(bpyPY2Me)Cl_2$ (**1g**)

The ligand bpyPY2Me (**L7**) was synthesized based on reported literature.[51]

To a round-bottom flask equipped with a stir bar was charged $NiCl_2 \cdot 6H_2O$ (118.8 mg, 0.5000 mmol), ligand **L7** (169.2 mg, 0.5000 mmol), and a mixture of acetonitrile and methanol (10.0 mL).

The clear brown solution was stirred at room temperature for 1 h. The solution was then concentrated *in vacuo* until precipitate formed. The precipitate was collected by filtration, washed with acetonitrile, and subsequently dried under high vacuum. Product **1g** was obtained as a gray-green powder (84 mg, 36% yield). Vapor diffusion of diethyl ether into a saturated solution of **1g** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3066, 1593, 1566, 1471, 1452, 1408, 1389, 1329, 1303, 1287, 1257, 1160, 1117, 1104, 1076, 1051, 1024, 1014, 972, 905, 885, 870, 853, 811, 804, 780, 765, 756, 748, 707, 662, 639, 591, 570, 509, 494, 475, 436, 415. ESI HRMS (m/z, amu): $[Ni(\mathbf{L7})Cl]^+$: calculated 431.0568, found 431.7147. Elemental analysis (%): calculated for $C_{24}H_{26}Cl_2N_4NiO_2$ (**1g**·2MeOH): C 54.18, H 4.93, N 10.53; found: C 53.84, H 4.85, N 10.36.

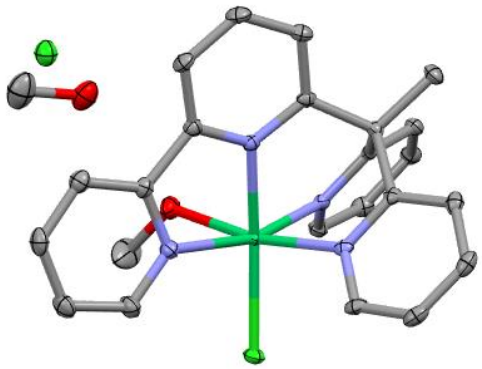


Figure 2.9. X-ray crystal structure of complex **1g**·2MeOH. Hydrogen atoms are omitted for clarity.

2.4.2.5.Synthesis of $Ni(Me_2Phen)_2(OAc)(BPh_4)$ (**1h**)

To a round bottom flask equipped with a stir bar was added $Ni(OAc)_2{\cdot}4H_2O$ (29.9 mg, 0.120 mmol) and methanol (3 mL). Then 2,9-dimethyl-1,10-phenanthroline (Me_2Phen, **L8**, 50.0 mg, 0.240 mmol), dissolved in 2 mL methanol, was added slowly and the reaction mixture was stirred at room temperature for 2 h. $NaBPh_4$ (41.1 mg, 0.120 mmol) was then added in one portion and the reaction mixture was stirred at room temperature overnight. The resulting light blue precipitate was collected by filtration, washed with water, methanol and hexanes, then redissolved in DCM and filtered with a syringe filter. The filtrate was concentrated to ~ 2 mL and added dropwise to a 100 mL mixture of diethyl ether and hexanes (1:1 v/v). The resulting precipitate was collected by filtration and dried under high vacuum overnight. Product **1h** was obtained as a pale blue powder (47.5 mg, 46% yield). Vapor diffusion of diethyl ether into a concentrated solution of complex **1h** in DCM afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3054, 1594, 1543, 1499, 1453, 1425, 1380, 1293, 1154, 1032, 939, 855, 814, 775, 732, 704, 679, 656, 624, 612, 551, 468, 437, 408. ESI HRMS (m/z, amu): $[Ni(\mathbf{L8})_2(OAc)]^+$: calculated 533.1482, found 533.1277. Elemental analysis (%): calculated for $C_{55}H_{51}BN_4NiO_3$ (**1h**·MeOH): C 74.60, H 5.81, N 6.33; found: C 74.44, H 5.84, N 6.26.

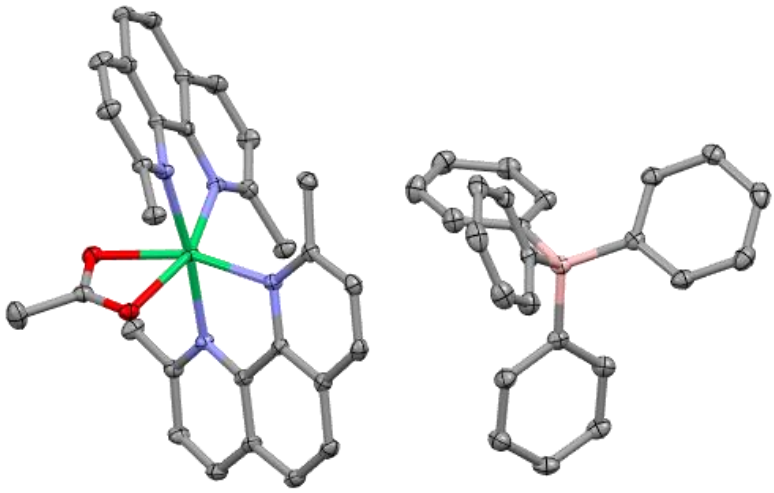


Figure 2.10. X-ray crystal structure of complex **1h**. Hydrogen atoms and DCM molecules are omitted for clarity.

*2.4.3. Ni-catalyzed Oxidation of Cyclohexane (**2**)*

2.4.3.1. General procedure for Ni-catalyzed oxidation of **2** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a**-**1h** were added as stock solutions or suspensions in DCM. $NiCl_2$ and $CoCl_2$ were added as stock solutions in a mixture of methanol-d_4 and acetonitrile (1:9 v/v). Methanol-d_4 was used to avoid overlapping of peaks with product **4a** in the ^{1}H NMR spectra. The vial was sealed, and the reaction mixture was stirred at 50 ˚C. The reaction was monitored by ^{1}H NMR spectroscopy until greater than 90% conversion of *m*CPBA was achieved. After cooling to room temperature, dibromomethane (4.4 μL, 0.50 equiv) was added as an internal standard. An aliquot (~ 30 μL) of the mixture was taken, diluted with chloroform-d_1, and subjected to analysis by ^{1}H NMR spectroscopy.

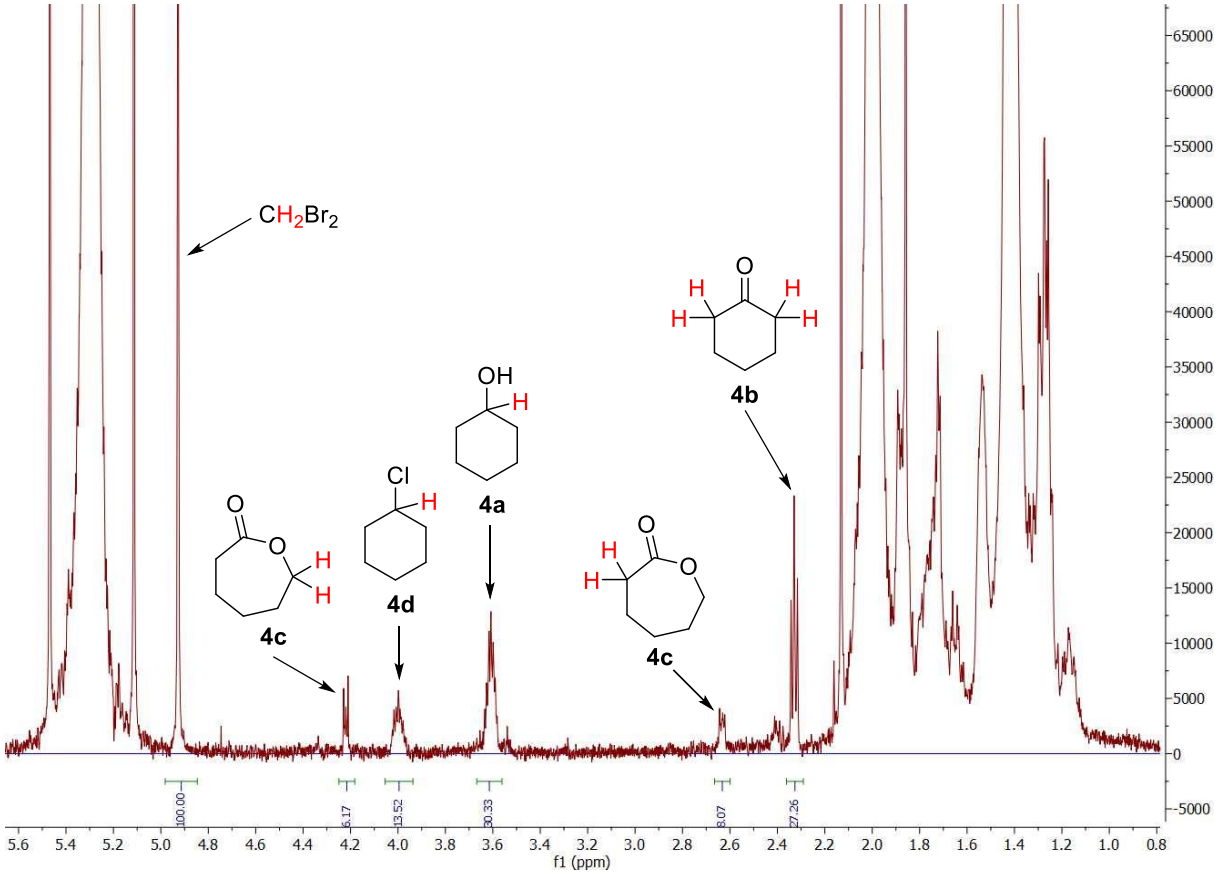
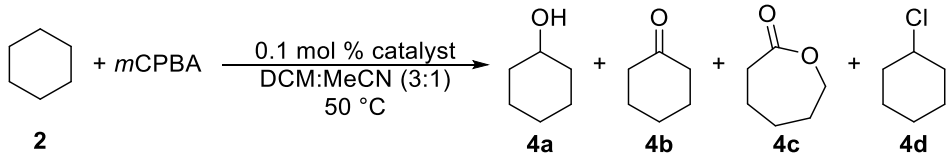


Figure 2.11. A typical ^{1}H NMR spectrum of the reaction mixture from the Ni-catalyzed oxidation of **2**.

2.4.3.2. Results of transition metal catalyzed oxidation of **2**

Table 2.4. Results of oxidation of cyclohexane in the presence of different catalysts



Entry	Catalyst	Time (h)	**4a** (%)	**4b** (%)	**4c** (%)	**4d** (%)	Conversion of *m*CPBA (%)
1	$Ni(Me_4Phen)_2Cl_2$ (**1a**)	1	27.6	10.7	0	14.3	100
2			34.1	10.7	0	15.0	100
3			39.6	11.3	0	9.2	100
4	$Ni(bpy)_2Cl_2$ (**1b**)	1	36.0	9.4	2.0	13.8	100
5			37.3	10.0	1.4	12.2	100
6			40.9	11.4	0	8.2	100

7	$Ni(box)_3(BPh_4)_2$ (**1c**)	1	37.9	9.9	1.1	15.0	100
8			38.0	10.2	0	13.1	100
9			41.5	11.1	2.0	9.2	100
10	$Ni(tBubpy)_3(BPh_4)_2$ (**1d**)	1.5	30.1	6.0	3.4	7.8	96
11			33.1	6.8	3.1	9.2	96
12			30.1	6.0	3.4	7.8	96
13	$Ni(TPA)(H_2O)(OAc)(BPh_4)$ (**1e**)	1.5	33.6	9.6	1.5	16.5	100
14			30.3	6.8	3.6	13.5	100
15			34.8	8.6	1.2	8.9	100
16	$Ni(Brbpy)_2Cl_2$ (**1f**)	2	32.5	6.0	4.1	11.2	100
17			36.1	4.8	5.5	8.6	90
18			35.1	4.8	4.7	8.6	85
19	$Ni(bpyPY2Me)Cl_2$ (**1g**)	3	32.0	5.7	5.0	10.4	96
20			33.1	3.1	6.3	10.2	94
21			36.1	5.4	4.9	11.2	96
22	$Ni(Me_2Phen)_2(OAc)(BPh_4)$ (**1h**)	4	8.7	2.7	5.0	5.7	31
23			8.6	2.0	4.9	4.8	36
24			12.6	2.3	5.5	7.0	45
25	$NiCl_2$	4	31.8	6.6	6.5	10.5	100
26			30.2	8.5	3.5	8.9	100
27			30.0	9.8	3.2	9.7	100
28	$CoCl_2$	1.5	21.7	11.0	0	9.6	100
29			30.6	10.2	0	8.0	100
30			21.9	10.9	0	9.7	100
31	none	4	0	0	0	0	0
32			0	0	0	0	0
33			3.8	2.6	1.9	0	< 10

2.4.3.3. Time courses of Ni-catalyzed oxidation of **2**

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv), dibromomethane (4.4 μL, 0.50 equiv) as the internal standard and chloroform-d_1 (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a** and **1h** were added as stock solutions or suspensions in $CDCl_3$. The vial was capped, and the reaction mixture was stirred at 50 ˚C. Aliquots (~ 15 μL) were periodically taken from the reaction mixture, diluted with chloroform-d_1, and subjected to analysis by ^{1}H NMR spectroscopy.

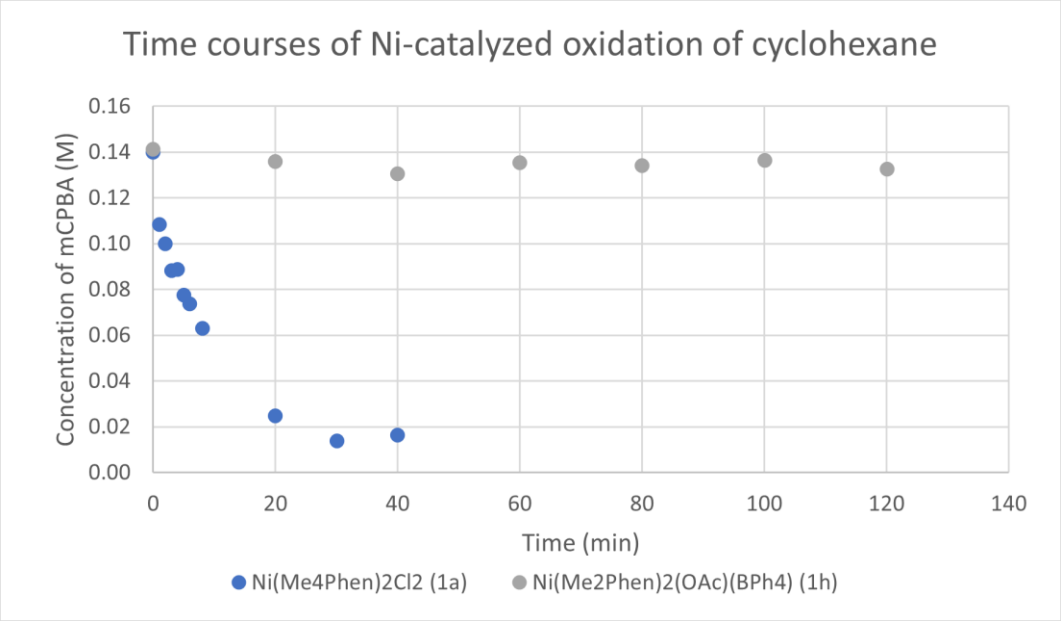


Figure 2.12. Time courses of the oxidation of cyclohexane catalyzed by Ni complexes **1a** and **1h**.

2.4.4. Ni-catalyzed Oxidation of Adamantane (3)

2.4.4.1. General procedure for Ni-catalyzed oxidation of **3** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **3** (34.1 mg, 2.00 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a**–**1h** were added as stock solutions or suspensions in DCM. $NiCl_2$ and $CoCl_2$ were added as stock solutions in a mixture of methanol and acetonitrile (1:9 v/v). The vial was sealed, and the reaction mixture was stirred at 50 ˚C for 1–4 h. After cooling to room temperature, n-dodecane (28.0 µL, 0.123 mmol) was added as an internal standard. An aliquot (~ 60 µL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

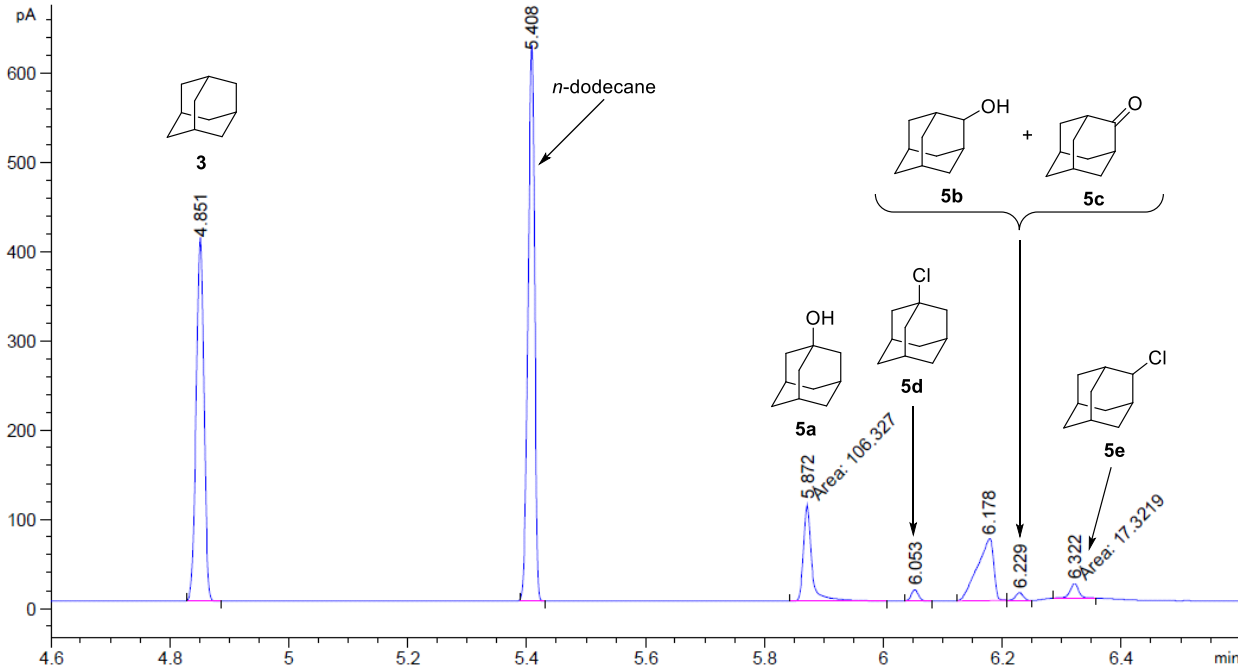


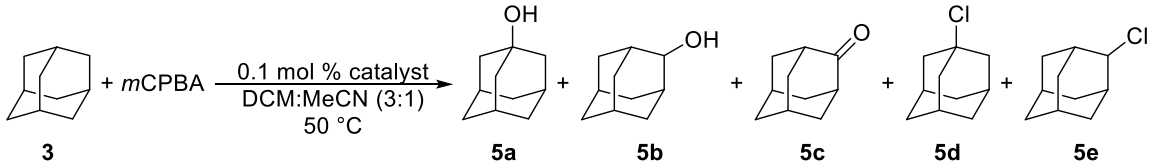
Figure 2.13. A typical GC trace of the reaction mixture from the Ni-catalyzed oxidation of **3**.

2.4.4.2.Results of transition metal catalyzed oxidation of **3**

$$\frac{A_{pdt}}{A_{I.S.}} = R_f \frac{m_{pdt}}{m_{I.S.}} \qquad (2.4.1)$$

The response factor (R_f) for the products of oxidation with respect to the internal standard (n-dodecane) is defined in eq 2.4.1. A_{pdt} and $A_{I.S.}$ represent the area under the peak of the product and the internal standard in the GC trace, respectively. m_{pdt} and $m_{I.S.}$ represent the mass (measured in milligrams) of the product and the internal standard, respectively. The response factors for 1-adamantanol (**5a**), 2-adamantanol (**5b**), 2-adamantanone (**5c**), 1-chloroadamantane (**5d**) and 2-chloroadamantane (**5e**) were measured to be 0.9255 (R^2 = 0.9907), 0.9515 (R^2 = 0.9942), 0.8936 (R^2 = 0.9961), 0.8259 (R^2 = 0.9962) and 0.8425 (R^2 = 0.9966), respectively.

Table 2.5. Results of oxidation of adamantane in the presence of different catalysts



Entry	Catalyst	Time (h)[a]	**5a** (%)	**5b**+**5c** (%)	**5d** (%)	**5e** (%)
1	$Ni(Me_4Phen)_2Cl_2$ (**1a**)	1	32.7	2.6	3.0	7.1
2			44.1	2.9	2.2	0
3			33.3	3.9	2.8	4.5

4	$Ni(bpy)_2Cl_2$ (**1b**)	1	28.1	2.4	2.9	4.4
5			35.0	2.7	2.3	0
6			28.7	2.7	3.2	3.6
7	$Ni(box)_3(BPh_4)_2$ (**1c**)	1	27.3	2.1	2.5	4.1
8			37.2	2.7	2.2	0
9			27.2	2.4	2.5	3.1
10	$Ni(tBubpy)_3(BPh_4)_2$ (**1d**)	1.5	27.3	3.2	4.6	3.9
11			23.4	2.4	4.2	3.4
12			24.1	1.9	3.2	4.6
13	$Ni(TPA)(H_2O)(OAc)(BPh_4)$ (**1e**)	1.5	31.2	2.5	4.9	5.5
14			28.8	2.4	4.8	5.0
15			30.0	2.6	4.7	4.3
16	$Ni(Brbpy)_2Cl_2$ (**1f**)	2	34.2	2.8	4.3	4.1
17			45.3	3.0	3.7	4.5
18			35.9	3.3	2.5	3.8
19	$Ni(bpyPY2Me)Cl_2$ (**1g**)	3	29.2	3.1	5.2	5.1
20			30.1	2.5	5.8	5.6
21			27.8	2.1	4.6	4.2
22	$Ni(Me_2Phen)_2(OAc)(BPh_4)$ (**1h**)	4	22.8	1.6	4.4	2.9
23			20.6	1.3	3.9	2.6
24			18.7	1.3	3.6	2.3
25	$NiCl_2$	4	27.6	2.5	4.1	3.6
26			26.7	2.3	4.5	3.5
27			30.2	2.5	4.6	3.5
28	$CoCl_2$	1.5	27.6	2.9	2.3	3.2
29			27.4	2.8	2.3	3.2
30			28.7	2.8	1.4	0
31	none	4	5.9	0	0	0
32			14.6	1.9	1.2	0.6
33			6.0	0	0	0

2.4.5. Ni-catalyzed Oxidation of Adamantane in the Presence of CCl_4

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **3** (34.1 mg, 2.00 equiv), CCl_4 (1.0 equiv, 12 μL) and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was sealed, and the reaction mixture was stirred at 50 ˚C for 1 h. After cooling to room temperature, n-dodecane (28.0 μL, 0.123 mmol) was added as an internal standard. An

aliquot (~ 60 µL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

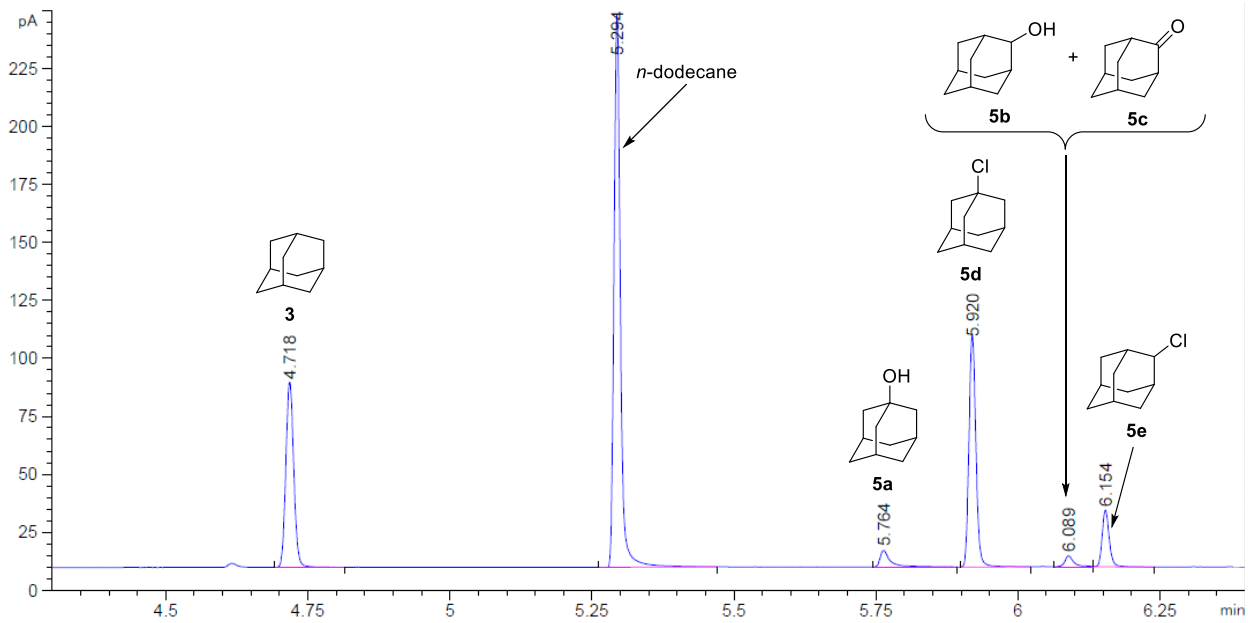


Figure 2.14. The GC trace of the reaction mixture from Ni-catalyzed oxidation of **3** in the presence of CCl_4.

*2.4.6. Ni-catalyzed Oxidation of cis- and trans-1,2-Dimethylcyclohexane (cis- and trans-**6**)*

2.4.6.1. General procedure for Ni-catalyzed oxidation of *cis*- or *trans*-**6** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane *cis*- or *trans*-**6** (7.50 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a**-**1g** were added as stock solutions or suspensions in DCM. $NiCl_2$ was added as a stock solution in a mixture of methanol and acetonitrile (1:9 v/v). The vial was sealed, and the reaction mixture was stirred at 50 ˚C for 1–4 h. After cooling to room temperature, n-dodecane (28.0 µL, 0.123 mmol) was added as an internal standard. An aliquot (~ 60 µL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

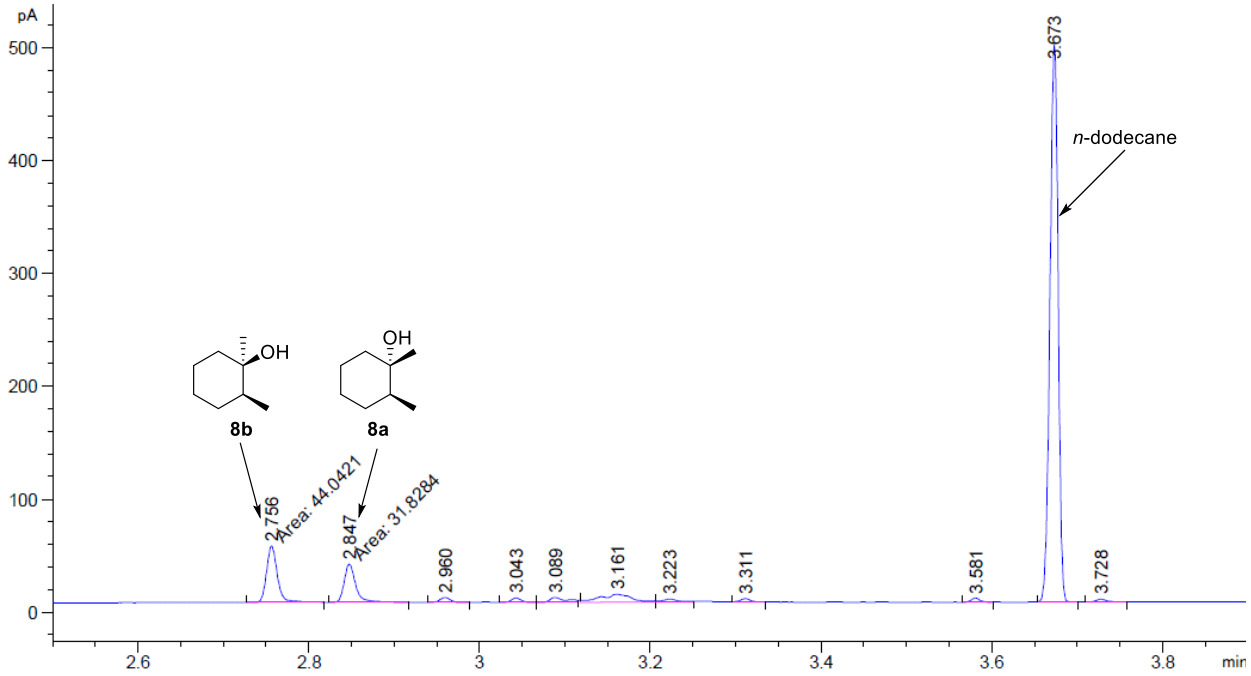
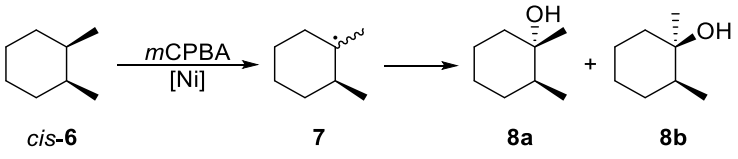


Figure 2.15. A typical GC trace of the reaction mixture from Ni-catalyzed oxidation of *cis*- or *trans*-**6**.

2.4.6.2. Results of Ni-catalyzed oxidation of *cis*-**6**

The GC response factor (R_f), defined in eq 2.4.1, of alcohol **8a** with respect to n-dodecane was determined to be 0.7457 ($R^2 = 0.9936$). The response factor of alcohol **8b**, which is a diastereomer of **8a**, was assumed to be identical to that of **8a**.

Table 2.6. Results of Ni-catalyzed oxidation of *cis*-6



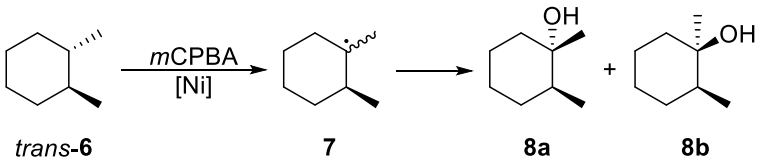
$$\textit{cis}\text{-fraction} = \frac{\text{yield}(\mathbf{8a})}{\text{yield}(\mathbf{8a}) + \text{yield}(\mathbf{8b})}$$

Entry	[Ni]	**8a** (%)	**8b** (%)	*cis*-fraction (%)
1	**1a**	28.0	37.4	42.7
2		23.4	30.9	43.1
3		17.3	23.9	42.0
4	**1b**	17.3	22.2	43.8
5		22.4	28.5	44.1
6		21.1	27.8	43.1
7	**1c**	18.2	23.9	43.3
8		15.7	20.8	43.0
9		19.5	25.8	43.0
10	**1e**	15.7	15.3	50.6

11		19.8	20.6	49.0
12		18.2	20.5	47.0
13	**1f**	26.0	28.6	47.6
14		26.4	27.8	48.7
15		19.1	24.1	44.2
16	**1g**	13.7	13.8	49.8
17		17.1	19.2	47.2
18		21.8	26.7	44.9
19	$NiCl_2$	23.2	26.2	46.9
20		24.9	23.3	51.6
21		20.0	24.4	45.1

2.4.6.3. Results of Ni-catalyzed oxidation of *trans*-**6**

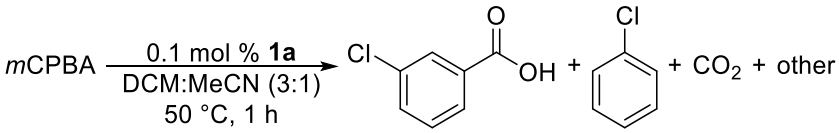
Table 2.7. Results of Ni-catalyzed oxidation of *trans*-6



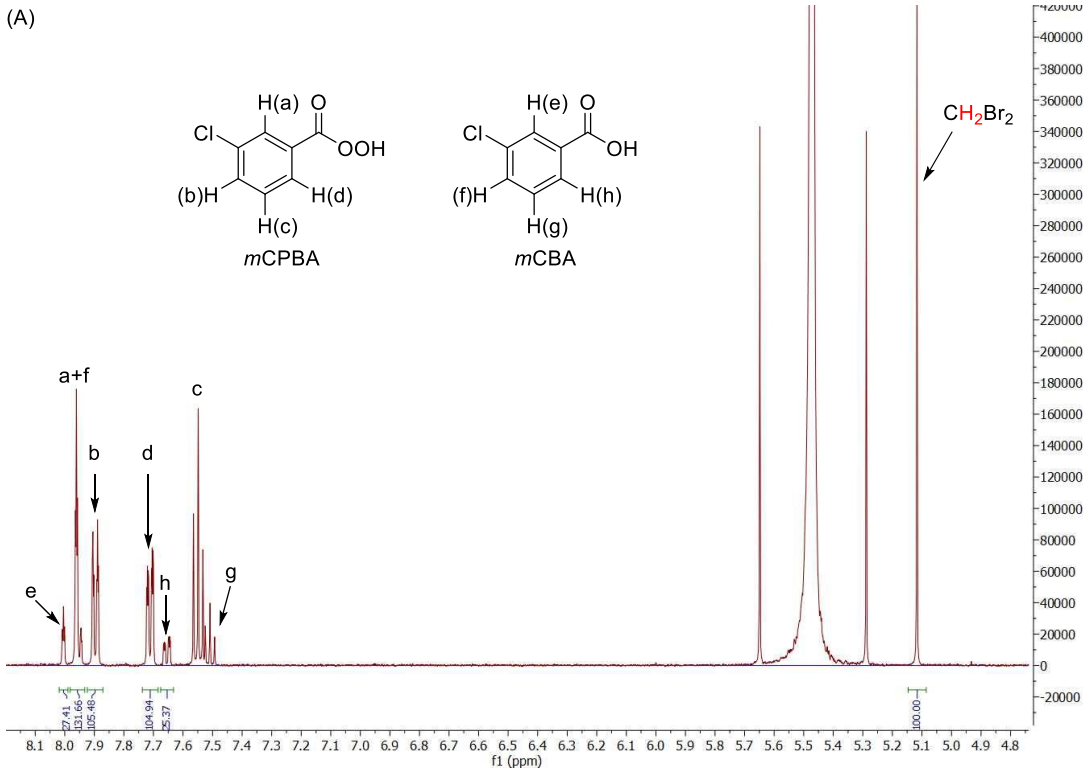
trans-**6** **7** **8a** **8b**

Entry	[Ni]	**8a** (%)	**8b** (%)	*cis*-fraction (%)
1	**1a**	10.8	15.0	41.8
2		11.1	15.6	41.7
3		12.4	17.3	41.6
4	**1b**	11.1	15.5	41.8
5		10.8	15.0	41.8
6		13.3	19.0	41.3
7	**1c**	9.6	13.3	41.8
8		11.1	15.8	41.3
9		12.8	18.4	41.1
10	**1e**	7.5	12.7	37.1
11		7.7	13.3	36.7
12		9.3	16.0	36.9
13	**1f**	10.7	16.5	39.3
14		9.7	15.1	39.2
15	**1g**	3.7	6.2	37.5
16		5.1	8.7	37.1
17		8.9	15.2	36.9
18	$NiCl_2$	10.4	17.0	38.1
19		4.4	6.6	40.1
20		9.6	14.9	39.1

2.4.7. Ni-catalyzed Decomposition of mCPBA



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), dibromomethane (4.4 µL, 0.50 equiv) as the internal standard. and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was sparged with N_2 for 5 min, sealed, and the reaction mixture was stirred at 50 ˚C for 1 h. An aliquot (~ 30 µL) of the mixture was taken, diluted with acetonitrile-d_3, and subjected to analysis by ^{1}H NMR spectroscopy.



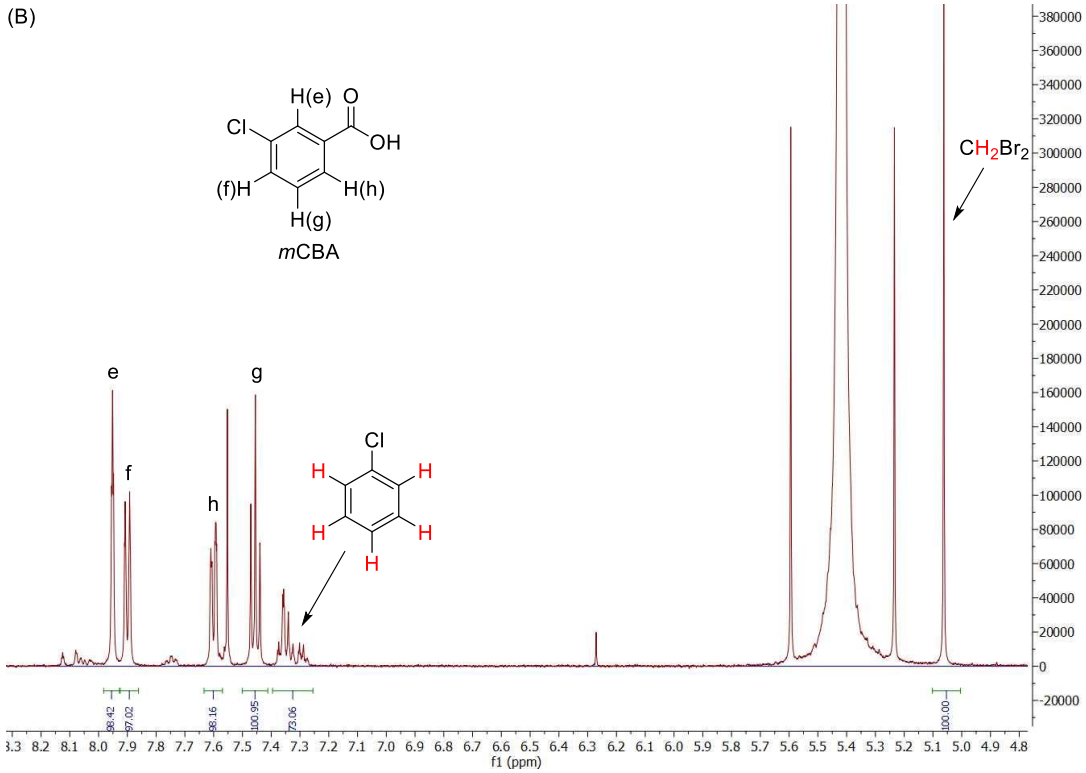


Figure 2.16. ^{1}H NMR spectra of the reaction mixture from Ni-catalyzed decomposition of *m*CPBA in the absence of alkane (A) at t = 0 and (B) at t = 1 h.

2.4.7.1.Time courses of Ni-catalyzed decomposition of *m*CPBA.

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), dibromomethane (4.4 µL, 0.50 equiv) as the internal standard and chloroform-d_1 (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a** and **1h** were added as stock solutions or suspensions in $CDCl_3$. The vial was capped, and the reaction mixture was stirred at 50 ˚C. Aliquots (~ 15 µL) were periodically taken from the reaction mixture, diluted with chloroform-d_1, and subjected to analysis by ^{1}H NMR spectroscopy.

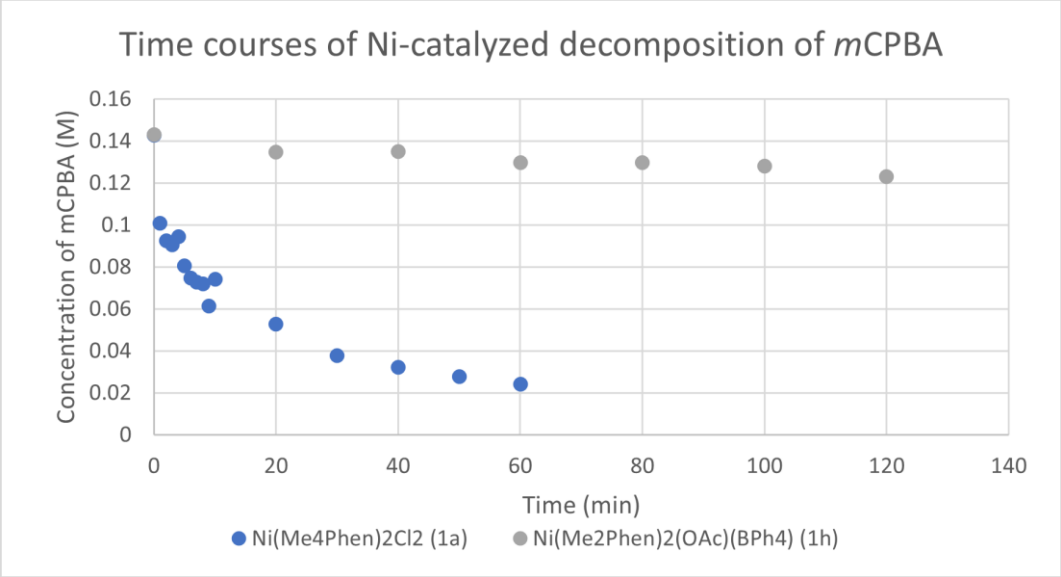


Figure 2.17. Time courses of the decomposition of *m*CPBA catalyzed by Ni complexes **1a** and **1h**.

*2.4.8. EPR Spectra of Stoichiometric Reactions of Ni Complex **1a***

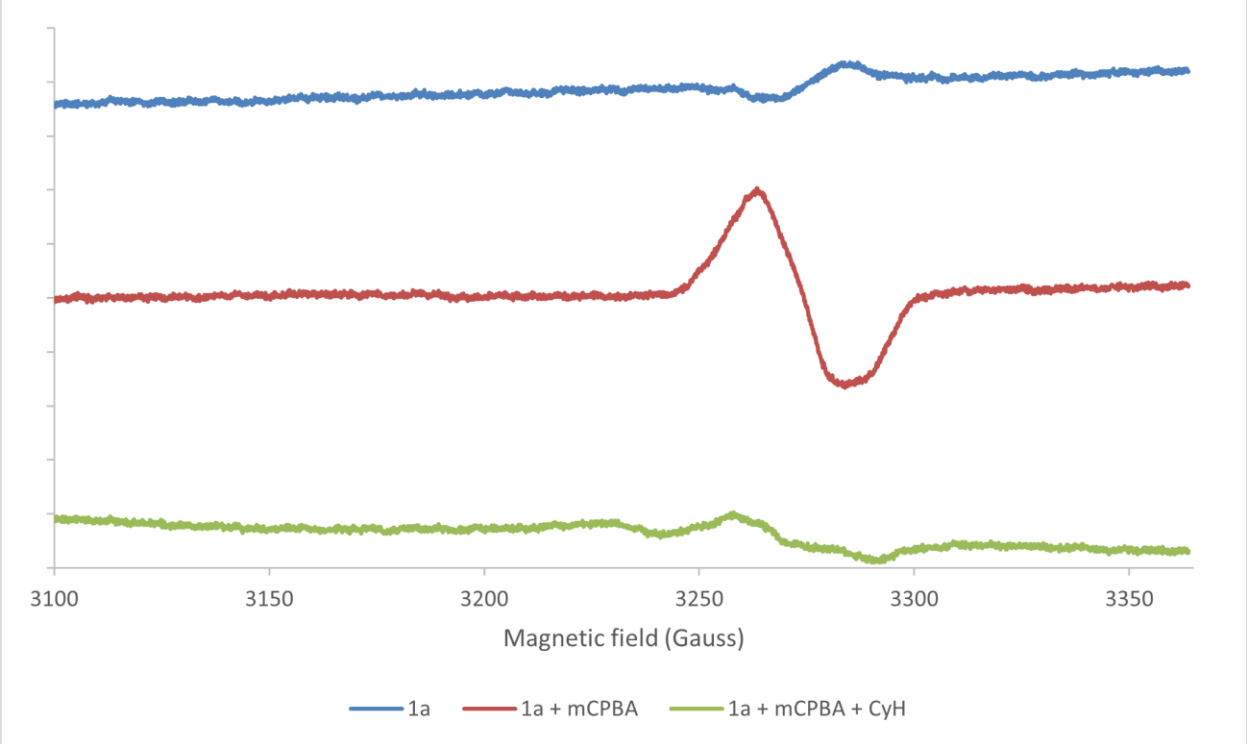
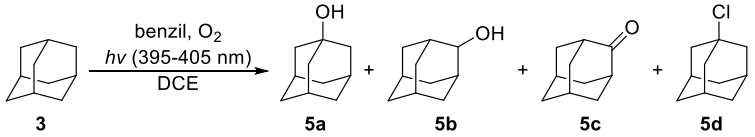


Figure 2.18. Overlaid EPR spectra of (a) 10 mM methanol solution of complex **1a** (1a, blue); (b) 10 mM methanol solution of complex **1a** with 5 equiv of *m*CPBA after heating at 50 ˚C for 30 s (1a + mCPBA, red); (c) 10 mM methanol solution of complex **1a** with 5 equiv of *m*CPBA and 10 equiv of cyclohexane after heating at 50 ˚C for 30 s (1a + mCPBA + CyH, green).

Complex **1a**, which is a Ni(II) compound with d^8 electron configuration, is EPR-silent (Figure 2.18, blue curve). Reaction of **1a** with 5 equivalents of *m*CPBA resulted in an isotropic signal (g = 2.007) at 3282 Gauss (Figure 2.18, red curve), which likely corresponds to an oxygen-centered free radical rather than a Ni-oxygen species because the signals of reported Ni-oxygen species are generally centered around 3100 Gauss and have more sophisticated peak shapes.[29-30, 33] Addition of 10 equivalents (with respect to Ni) of cyclohexane likely quenched the oxygen-centered free radical and resulted in the disappearance of the isotropic signal (Figure 2.18, green curve).

*2.4.9. Photo-mediated Oxidation of Adamantane (**3**) by Benzil and Oxygen*



To a 4 mL vial equipped with a stir bar was added benzil (26.3 mg, 0.125 mmol), adamantane (34.1 mg, 0.250 mmol) and 1,2-dichloroethane (DCE, 1.5 mL) as the solvent. The solution was sparged with O_2 for 10 min. Then a UV lamp (395–405 nm) was turned on and the solution was sparged with O_2 for another 10 min. Sparging was then stopped to prevent extensive evaporation of solvent and the solution was stirred under an atmosphere of O_2 and UV irradiation for the required time. After the UV lamp was turned off, n-dodecane (28.0 μL, 0.123 mmol) was added to the reaction mixture as an internal standard. An aliquot (40–50 μL) of this mixture was transferred to a GC vial, diluted with ethyl acetate, and subjected to analysis by GC.

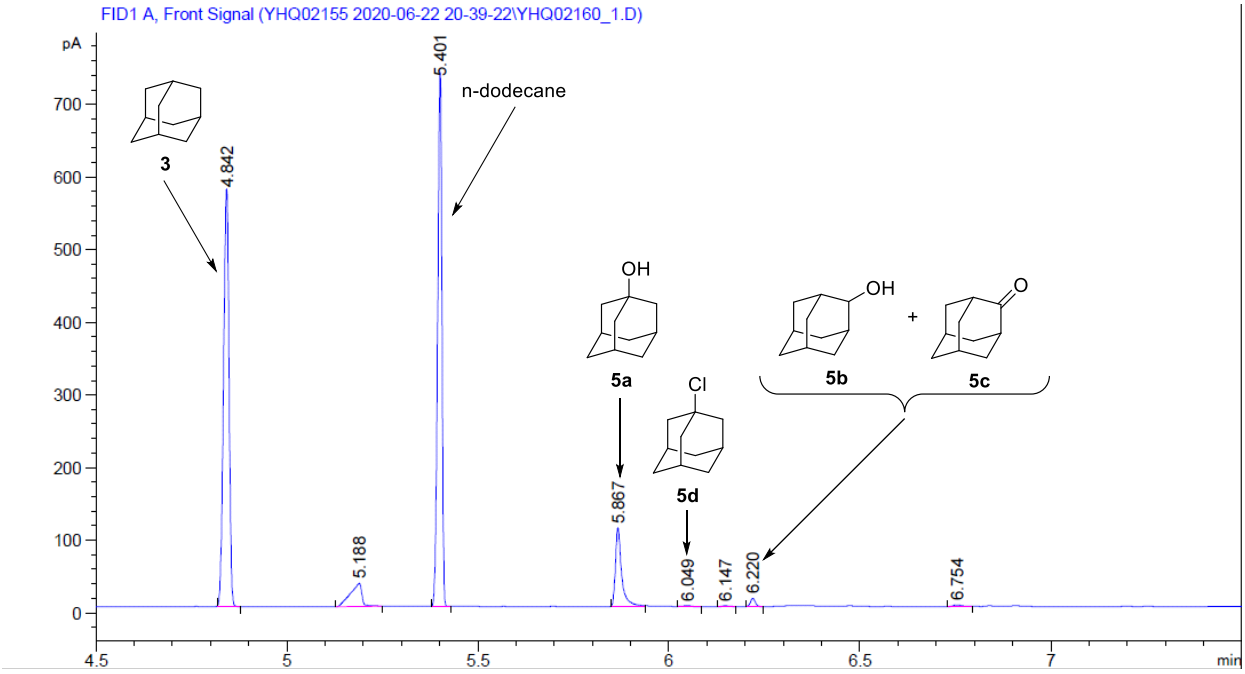


Figure 2.19. A typical GC trace of the reaction mixture from the photo-mediated oxidation of **3** by benzil and O_2.

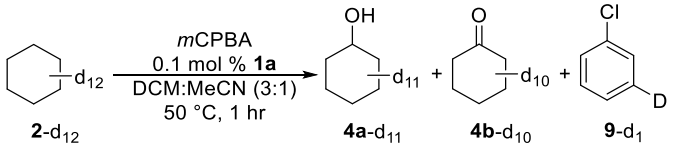
1-Adamantanol (**5a**) was formed as the major product and byproducts **3b**, **3c** and **3d** were formed in less than 3% yield. 2-Chloroadamantane (**5e**) was not observed. The results of this experiment were summarized in Table 2.8.

Table 2.8. Results of the photo-mediated oxidation of adamantane by benzil and O_2

Entry	Time (min)	Temperature	**5a** (%)[a]	**5b + 5c** (%)[a]	**5d** (%)[a]	3˚/2˚[b]
1	75	rt	20.9	1.9	0.3	11.3
2	133	rt	25.8	2.3	0.3	11.5
3	133	rt	28.4	2.4	0.4	12.1
4	128	50 ˚C	31.8	2.9	0.5	11.2
5	128	50 ˚C	31.3	2.8	0.5	11.4

[a]All yields were calculated based on benzil. [b]Defined as the ratio of the combined yield of **5a**+**5d** to the combined yield of **5b**+**5c**.

*2.4.10. Ni-catalyzed Oxidation of Cyclohexane-d_{12} (**2**-d_{12})*



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), deuterated alkane **2**-d_{12} (5.00 equiv) and acetonitrile (1.0 mL) as solvent. Ni complex **1a** was added as a suspension in DCM. The vial was sealed, and the reaction mixture was stirred at 50 ˚C for 75 min. After cooling to room temperature, saturated aqueous solution of Na_2CO_3 (2.0 mL) was added, and the mixture was extracted three times with DCM. The organic layer was separated, concentrated *in vacuo* to remove unreacted **2**-d_{12}, then diluted to ~0.6 mL with DCM. CD_2Cl_2 (2.4 μL, 0.30 equiv) was added as an internal standard, and the mixture was subjected to analysis by ^2H NMR spectroscopy.

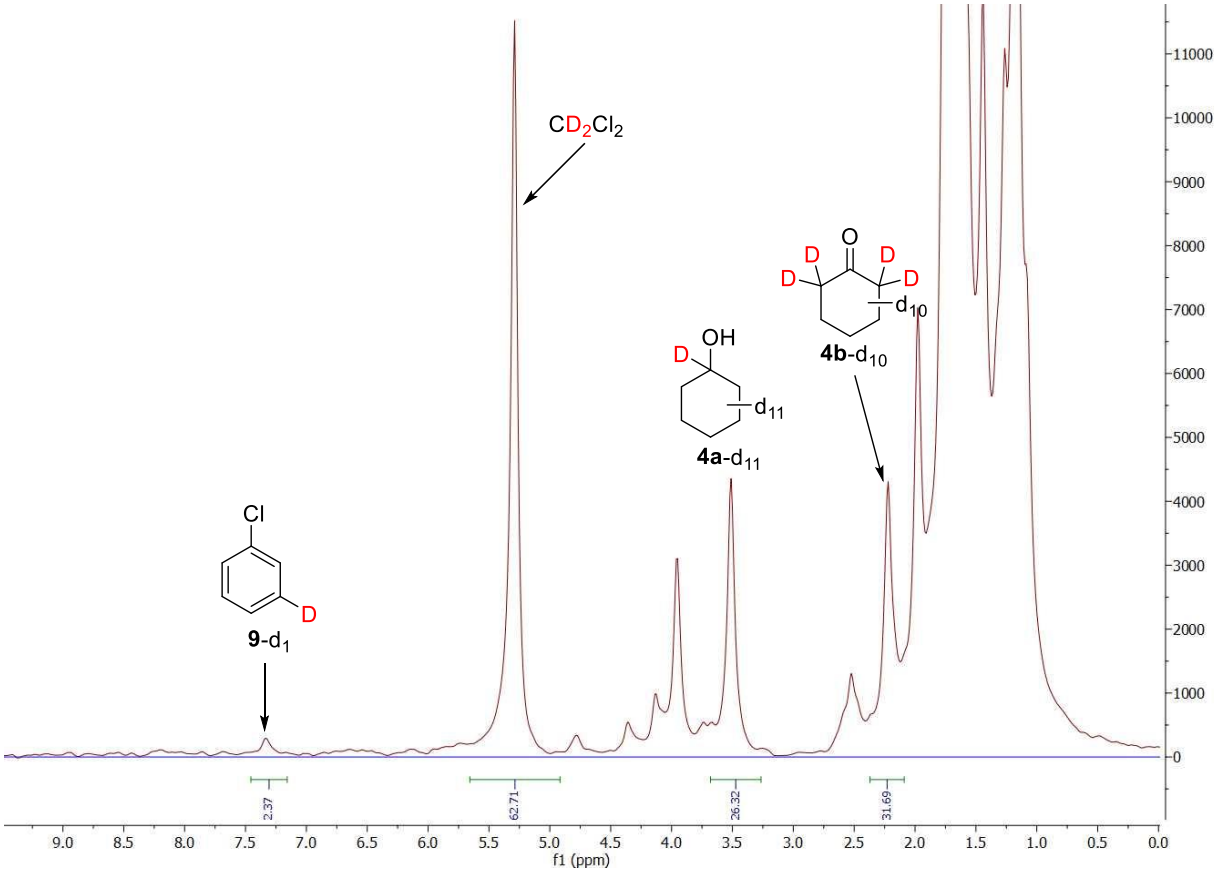
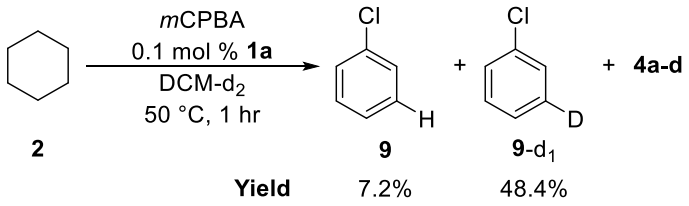


Figure 2.20. ^{2}H NMR spectrum of Ni-catalyzed oxidation of **2**-d_{12} by *m*CPBA.

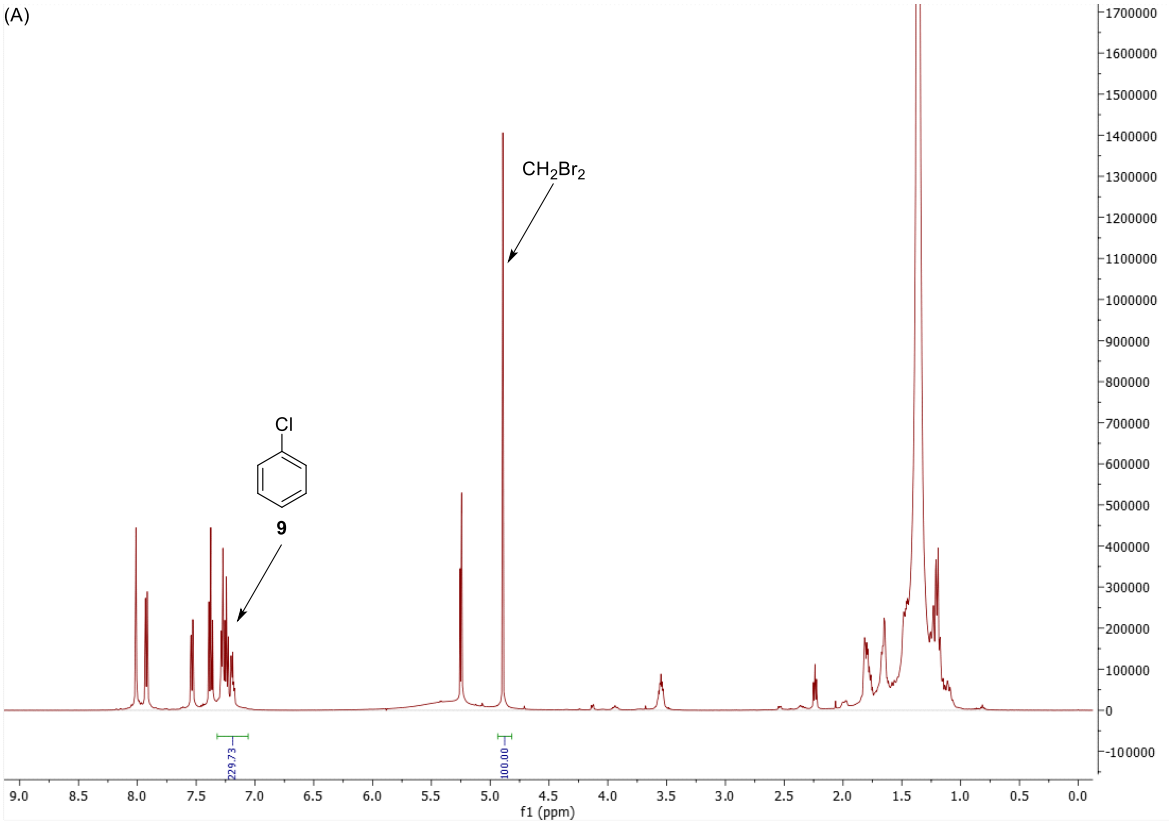
2.4.10.1. Hydrogen atom transfer (HAT) from solvent molecules to 3-chlorophenyl radical (**12**)



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), cyclohexane (68.0 µL, 0.625 mmol), catalyst **1a** (0.1 mol %), and DCM-d_2 (1 mL). The vial was sealed, and the reaction mixture was stirred at 50 ℃ for 1 h. After cooling to room temperature, dibromomethane (4.4 µL, 0.5 equiv) was added to the reaction mixture as an internal standard. Half of this solution (0.5 mL) was then transferred to an NMR tube and subjected to analysis by ^{1}H NMR spectroscopy. The remaining half of the solution was evaporated under reduced pressure (340 mbar) until it was almost dry, then diluted with CH_2Cl_2 (0.6 mL) and CD_3CN (1.1 µL, 0.17 equiv) was added as the internal standard. This mixture was transferred to another NMR tube and subjected to analysis by ^{2}H NMR spectroscopy.

The yields (based on *m*CPBA) of chlorobenzene (**9**) and deuterated chlorobenzene (**9**-d_1) were determined, from ^{1}H and ^{2}H NMR spectra, to be 7.2% and 48.4%, respectively. This result shows that 87% of product **9** is labelled by deuterium for the reaction conducted in DCM-d_2 and strongly

supports our hypothesis that most of the chlorobenzene byproduct is formed by hydrogen atom transfer from solvent molecules to radical **12** in Ni-catalyzed oxidation of alkanes.



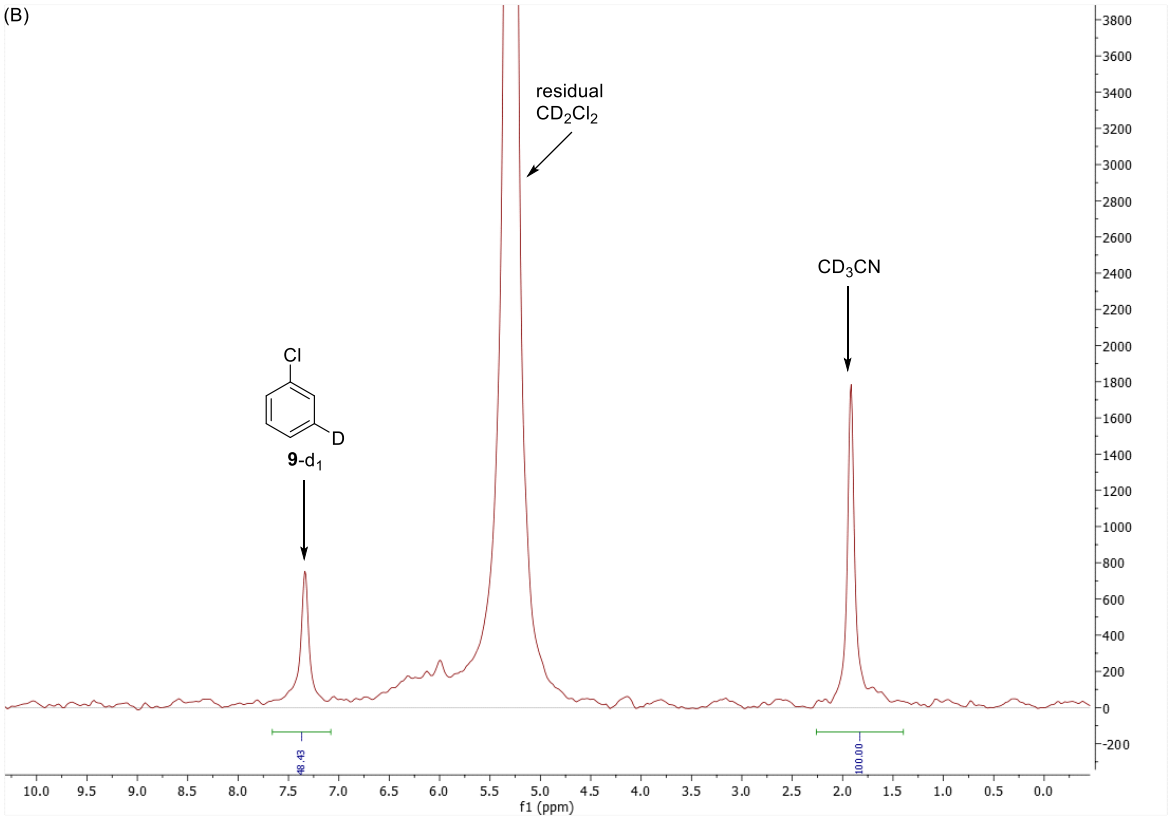
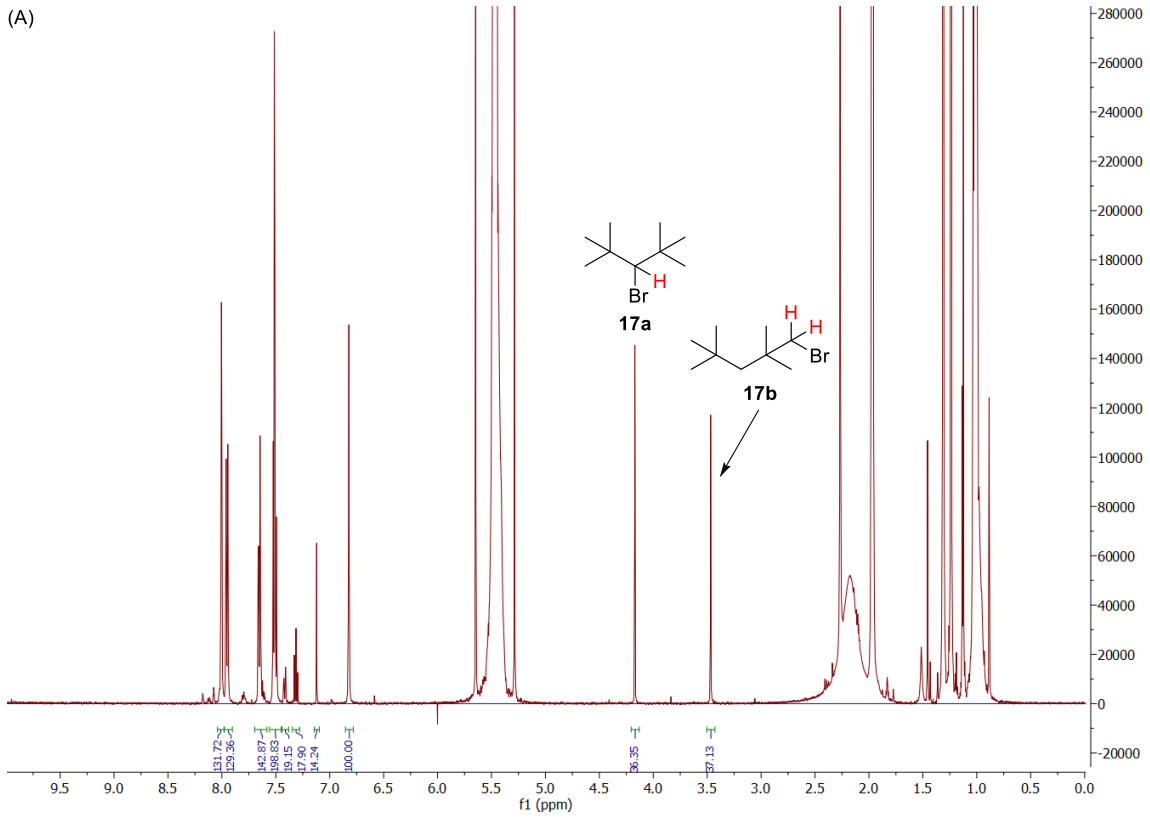


Figure 2.21. (A) ^{1}H NMR spectrum and (B) ^{2}H NMR spectrum from Ni-catalyzed oxidation of cyclohexane by *m*CPBA in DCM-d_2.

*2.4.11. Bromination of 2,2,4,4-Tetramethylpentane (**16**)*

2.4.11.1. General procedure for Ni-catalyzed bromination of **16** by *m*CPBA

In a N_2-filled dry box, *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **16** (111 µL, 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added to a 4 mL vial equipped with a stir bar. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was capped, sealed with electrical tape, and the reaction mixture was stirred at 50 ˚C for 1 h. After cooling to room temperature, mesitylene (5.8 µL, 0.33 equiv) was added as an internal standard. An aliquot (~ 30 µL) of the mixture was taken, diluted with acetonitrile-d_3, and subjected to analysis by ^{1}H NMR spectroscopy.


(A)
Br
H
17a
H
H
Br
17b
f1 (ppm)

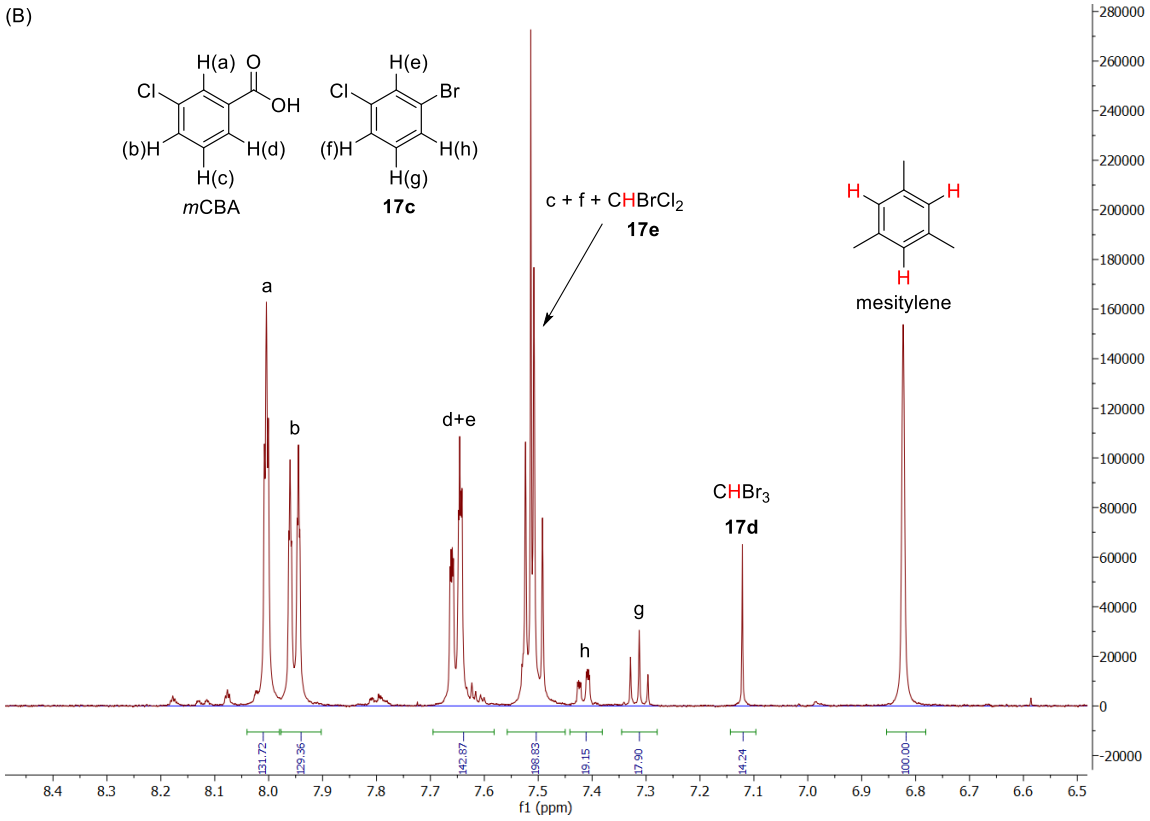
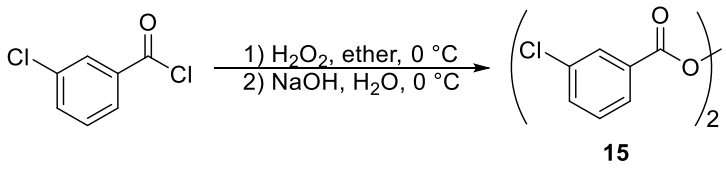

(B)
H(a)
O
Cl
OH
(b)H
H(d)
H(c)
mCBA
H(e)
Cl
Br
(f)H
H(h)
H(g)
17c
c + f + CHBrCl2
17e
H
H
H
mesitylene
a
b
d+e
h
g
CHBr3
17d
f1 (ppm)

Figure 2.22. (A) A typical ^{1}H NMR spectrum of the reaction mixture from Ni-catalyzed bromination of **16** by *m*CPBA; (B) the aromatic region of the spectrum in (A).

2.4.11.2. Synthesis of Bis(3-chlorobenzoyl)peroxide (**15**)



15

The following procedure was adapted from reported literature.[52]

In a 50 mL round bottom flask equipped with a stir bar, 3-chlorobenzoyl chloride (5.0 mmol, 0.88 g, 0.64 mL) was dissolved in ethyl ether (2.5 mL) and cooled to 0 ˚C. Hydrogen peroxide (2.90 mmol, 162 µL, 50% w/w aqueous solution) was added to the stirring solution by slow addition over 10 min. Sodium hydroxide (6.300 mmol, 252.8 mg, dissolved in 2 mL H_2O) was then added to the stirring solution by slow addition over 20 min. The resulting white precipitate was collected by filtration, washed with H_2O (5.0 mL × 2 times) and ethyl ether (5.0 mL × 2 times), and dried under high vacuum for 4 h. Product **15** was obtained as a white powder (339.2 mg, 43.61% yield) and stored at -20 ˚C.

^{1}H NMR (500 MHz, CDCl3): δ 8.06 (t, J = 1.9 Hz, 1H), 7.96 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.65 (ddd, J = 8.1, 2.2, 1.1 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H).

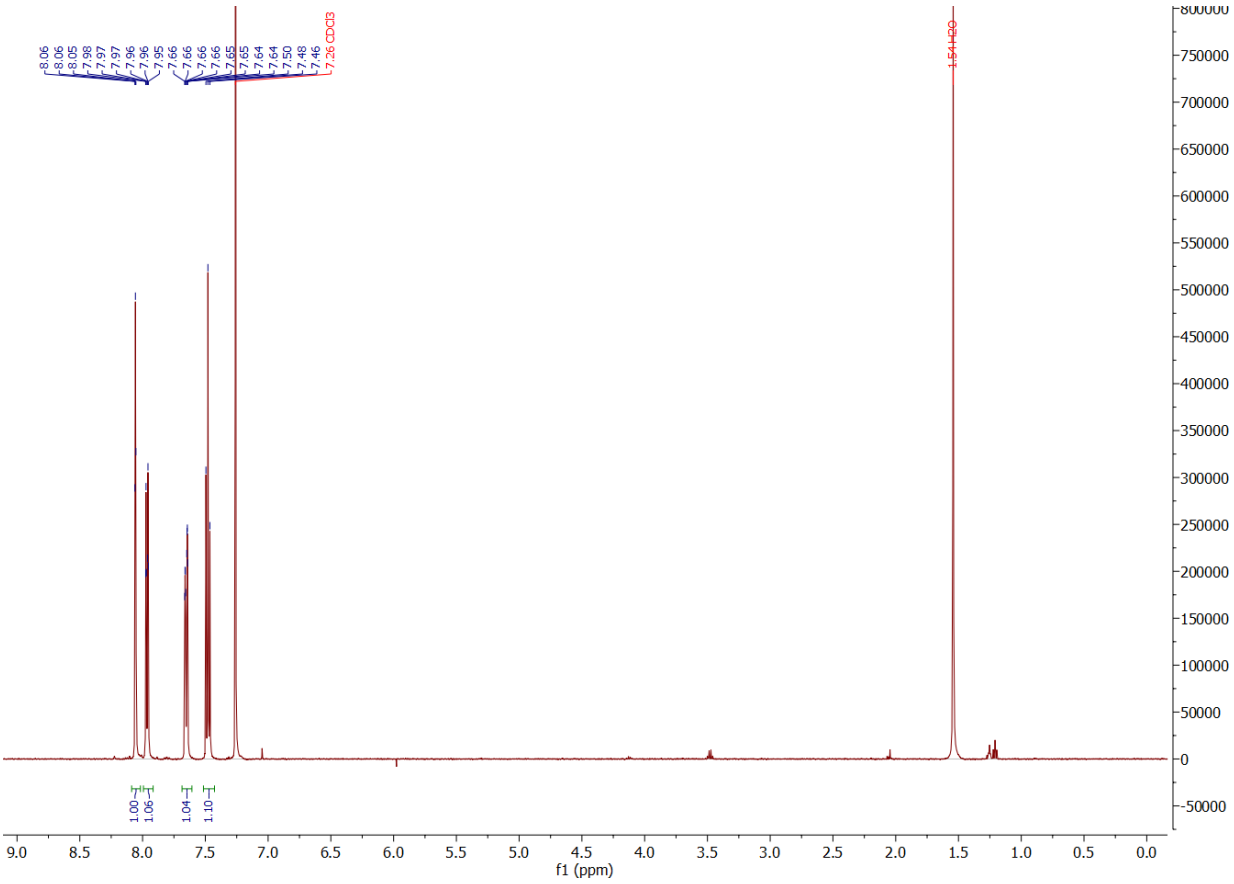


Figure 2.23. ^{1}H NMR spectrum of compound **15**.

2.4.11.3. General procedure for bromination of **16** by peroxide **15**

In a N_2-filled dry box, peroxide **15** (19.4 mg, 0.0625 mmol), alkane **16** (111 µL, 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added to a 4 mL vial equipped with a stir bar. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was capped, sealed with electrical tape, and the reaction mixture was stirred at 80 ˚C for 13 h. After cooling to room temperature, mesitylene (5.8 µL, 0.33 equiv) was added as an internal standard. An aliquot (~ 30 µL) of the mixture was taken, diluted with acetonitrile-d_3, and subjected to analysis by ^{1}H NMR spectroscopy.

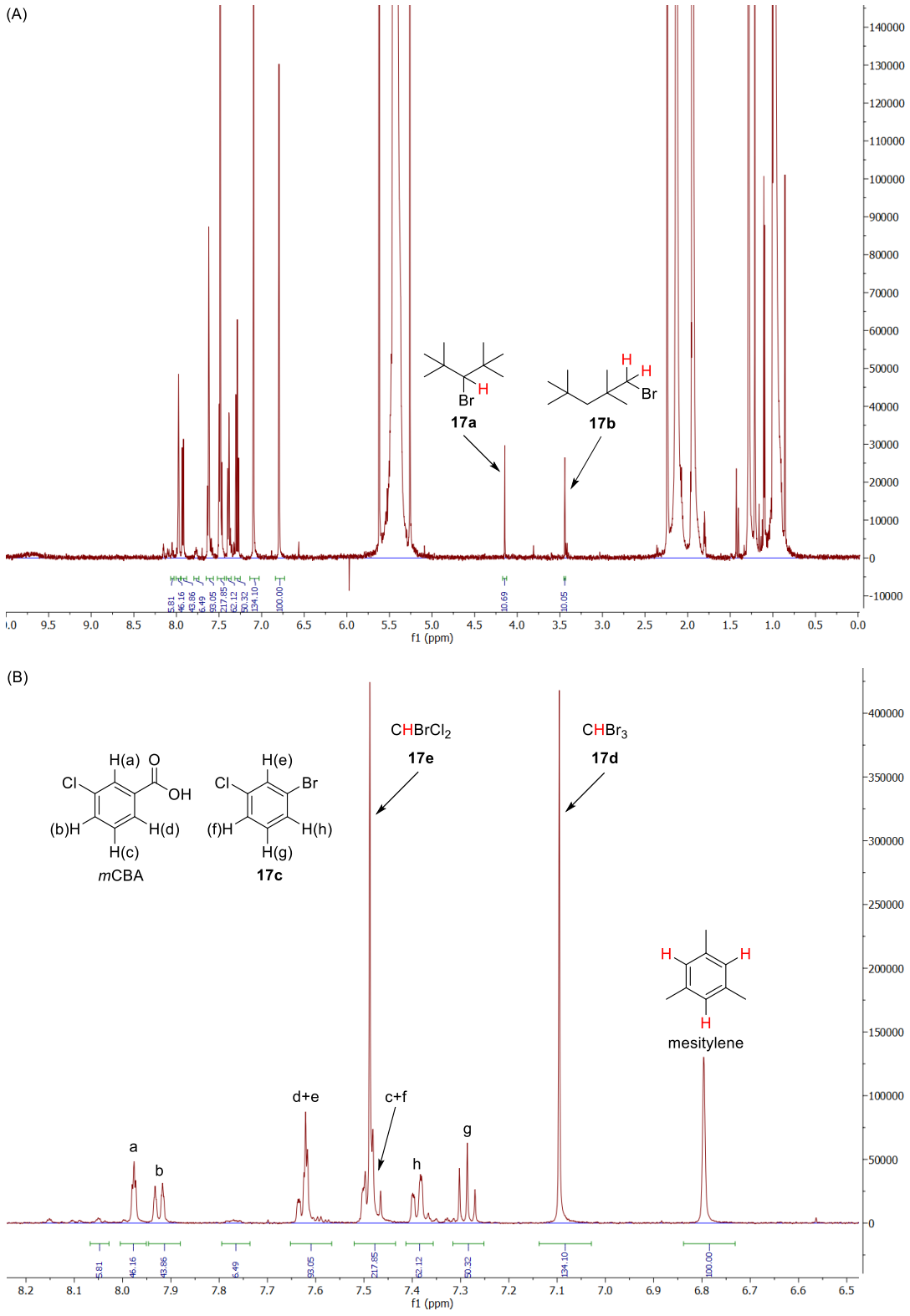
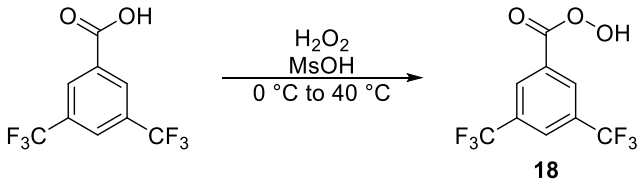


Figure 2.24. (A) A typical ^{1}H NMR spectrum of the reaction mixture from the bromination of **16** by peroxide **15**; (B) the aromatic region of the spectrum in (A).

2.4.11.4. Synthesis of 3,5-bis(trifluoromethyl)perbenzoic acid (**18**)



18

The following procedure was adapted from reported literature.[53]

Concentrated H_2O_2 (approx. 90% w/w in H_2O) was prepared by subjecting commercial H_2O_2 solution (50 % w/w in H_2O) to high vacuum for 8 h. **CAUTION**: Concentrated hydrogen peroxide should be stored in the freezer and handled with care due to potential hazard of explosion.

To a 25 mL pear-shaped flask equipped with a stir bar was added 3,5-bis(trifluoromethyl)benzoic acid (774.4 mg, 3.000 mmol, 1.000 equiv) and methanesulfonic acid (1.0 mL). The resulting slurry was stirred at 0 ℃ for 30 min, then H_2O_2 (0.24 mL, 3 equiv, approx. 90% w/w in H_2O) was added dropwise. The reaction mixture was stirred at 40 ℃ for 1.5 h, and subsequently quenched with 5 mL ice water. The white precipitate was collected by filtration and washed with 25 mL ice water. The crude product was obtained as a white solid (736.3 mg, approx. 85% purity by NMR) and used for Ni-catalyzed bromination of **16** without further purification. The major impurities in the crude product are water and the unreacted 3,5-bis(trifluoromethyl)benzoic acid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (s, 2H), 8.16 (s, 1H).

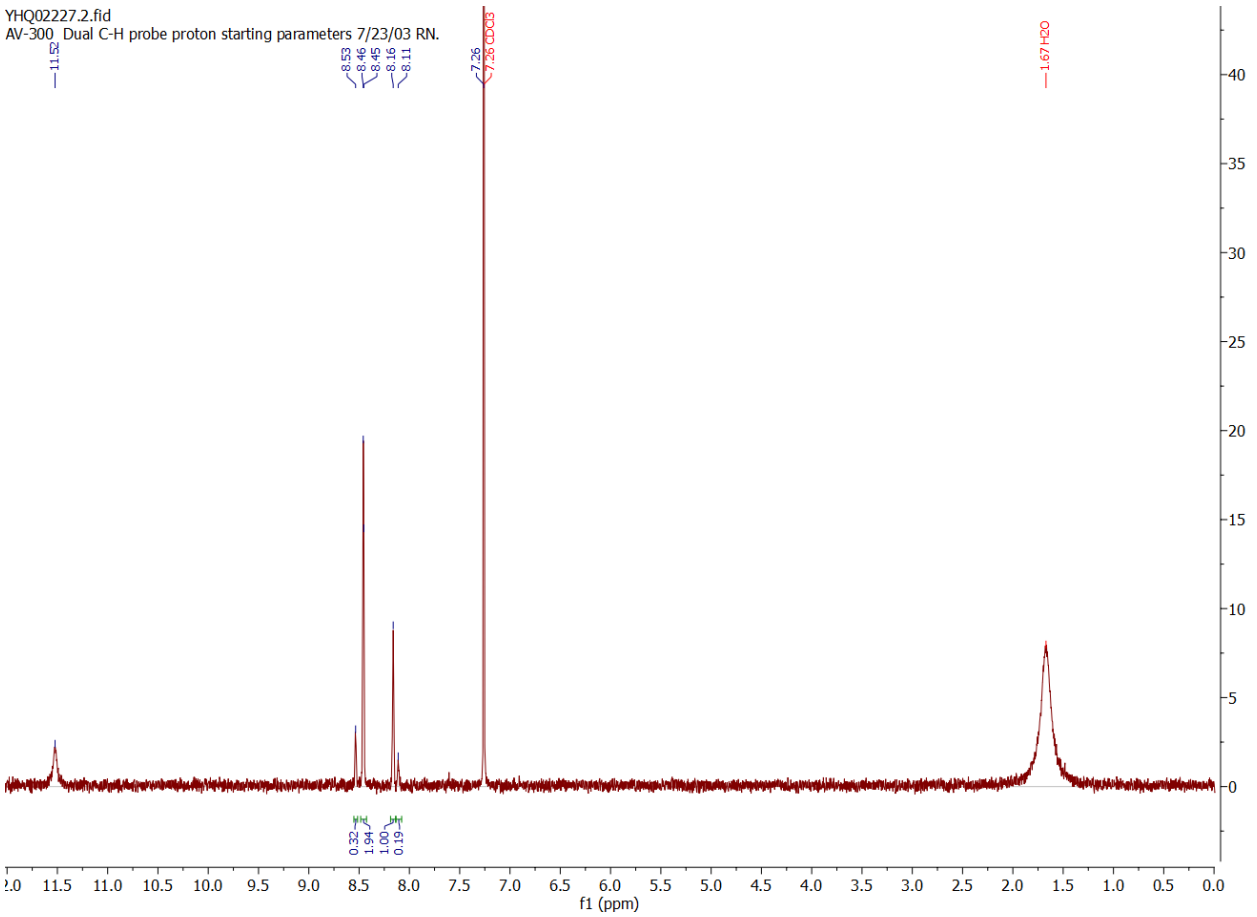


Figure 2.25. ^{1}H NMR spectrum of the crude product of peracid **18**.

2.4.11.5. General procedure for Ni-catalyzed bromination of **16** by peracid **18**

To a 4 mL vial equipped with a stir bar, peracid **18** (40.3 mg, 0.125 mmol, ~85% purity), alkane **16** (111 µL, 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added. Ni complex **1a** (1 mol %) was added as a suspension in DCM. The vial was sparged with N_2 for 1 min, capped, sealed with electrical tape, and the reaction mixture was stirred at 50 ˚C for 1 h. After cooling to room temperature, mesitylene (5.8 µL, 0.33 equiv) was added as an internal standard. An aliquot (~ 25 µL) of the mixture was taken, diluted with acetonitrile-d_3, and subjected to analysis by ^{1}H NMR spectroscopy.

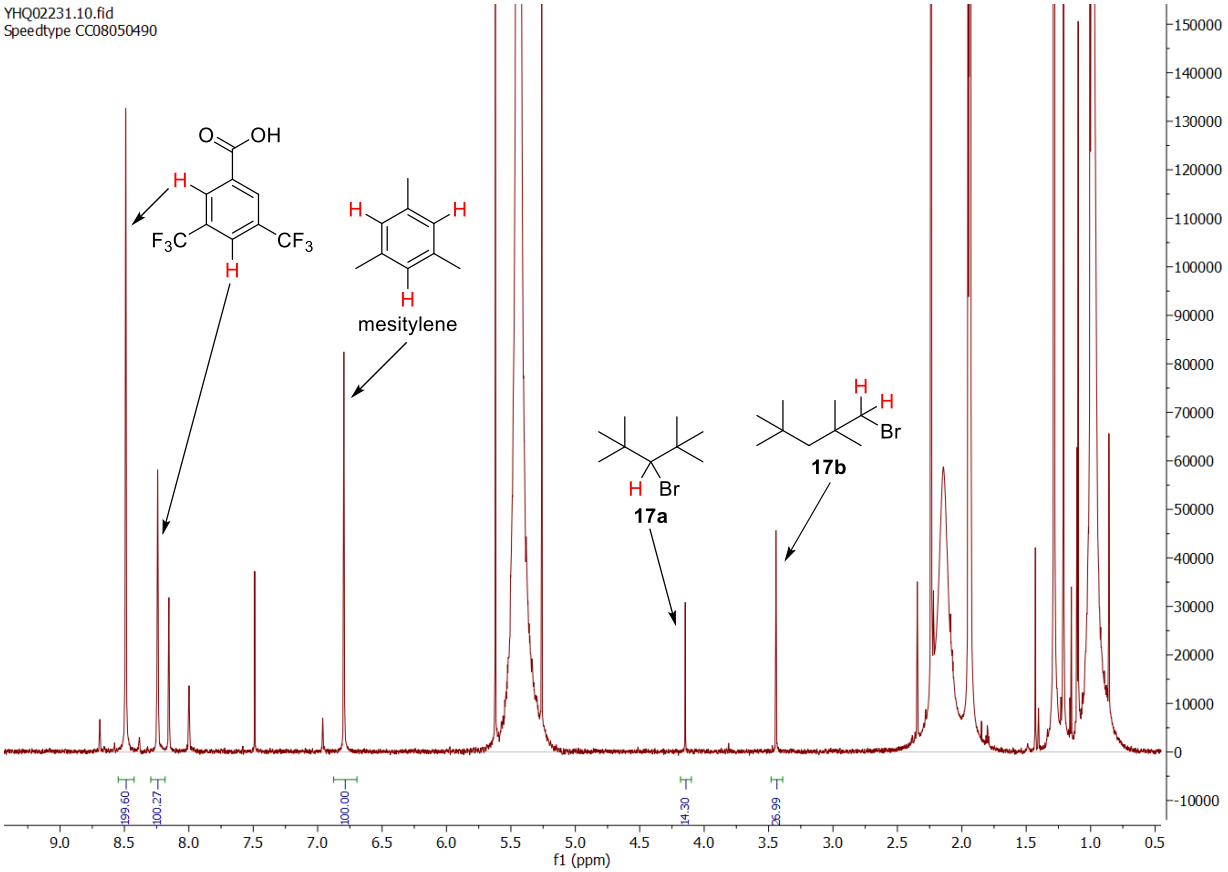
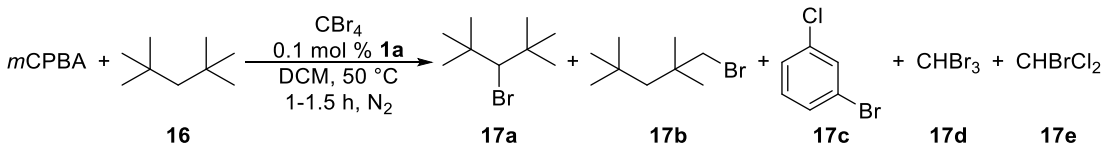


Figure 2.26. A typical ^{1}H NMR spectrum of the reaction mixture from the Ni-catalyzed bromination of **16** by peracid **18**.

2.4.11.6. Results and discussions

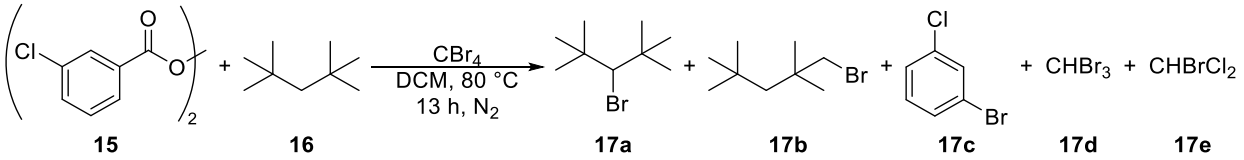
Results of three repeated experiments of Ni-catalyzed bromination of **16** by *m*CPBA and those of eight repeated experiments of bromination of **16** by peroxide **15** are summarized in Table S6 and S7, respectively. In both reactions, byproducts *meta*-bromochlorobenzene (**17c**), bromoform (**17d**) and bromodichloromethane (**17e**) were formed together with brominated alkanes **17a** and **17b**. Compound **17c** was likely formed by decarboxylation of radical **10**, followed by trapping with CBr_4. Byproduct **17e** can be formed by the reaction of $CHCl_2\cdot$ radical and CBr_4. The formation of **17a** and **17b** in low yields in the nickel-free reaction can be attributed to acceleration of decarboxylation of the 3-chlorobenzoyloxy radical **10** at elevated temperature (80 ˚C), which is supported by the formation of **17c** in higher yield in the nickel-free reaction (~50%, Table 2.10) than in the Ni-catalyzed reaction (~20%, Table 2.9).

Table 2.9. Results of Ni-catalyzed Bromination of 16 by *m*CPBA



Entry	**17a** (%)	**17b** (%)	2˚/1˚	**17c** (%)	**17d** (%)	**17e** (%)
1	35.0	18.9	1.9	17	13.7	55
2	36.4	18.6	2.0	19	14.2	56
3	34.3	16.3	2.1	19	11.5	54

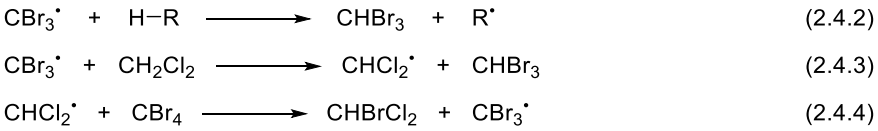
Table 2.10. Results of Bromination of 16 by Peroxide 15



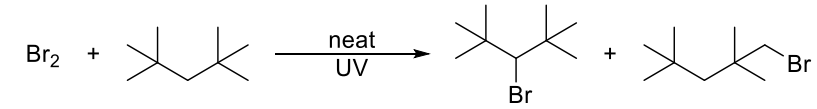
15 **16** **17a** **17b** **17c** **17d** **17e**

Entry	**17a** (%)	**17b** (%)	2˚/1˚	*m*CBA (%)	**17c** (%)	**17d** (%)	**17e** (%)
1	7.0	5.5	1.3	47	50	130	120
2	13.5	6.5	2.1	43	50	131	123
3	10.7	5.0	2.1	44	50	134	118
4	11.5	5.6	2.1	38	52	132	110
5	10.5	5.3	2.0	41	50	125	100
6	11.6	4.7	2.5	39	48	131	115
7	6.7	5.7	1.2	44	49	123	110
8	11.9	5.5	2.2	41	49	128	109

In the Ni-catalyzed reactions, tribromomethyl radical ($CBr_3\cdot$) cannot be the major species that cleaves C–H bonds in alkane **16** (eq 2.4.2) because byproduct **17d** was formed in only 11%-15% yield, which is much lower than the yield of products **17a** and **17b** (Table 2.9). The large amount of **17d** and **17e** formed in the nickel-free reaction (Table 2.10) can be explained by a radical chain pathway that would occur at elevated temperature (eq 2.4.3–2.4.4).



Bromine radical ($Br\cdot$) cannot be the major species that cleaves C–H bonds, because the solutions of both Ni-catalyzed and Ni-free reactions were either colorless or very slightly orange, indicating that Br_2 was either not formed or formed in only trace amount. In addition, the selectivity of $Br\cdot$ for the secondary C–H bonds in the photo-mediated reaction of **16** and Br_2 was high (2˚/1˚ ratio = 31, Figure S21). This ratio, which is much larger than those presented in Tables S6 and S7, suggests that $Br\cdot$ does not cleave the C–H bonds in **16** in these reactions. Thus, we have demonstrated that radicals such as $Br\cdot$ and $CBr_3\cdot$ do not interfere with abstraction of hydrogen atoms from substrate **16**.



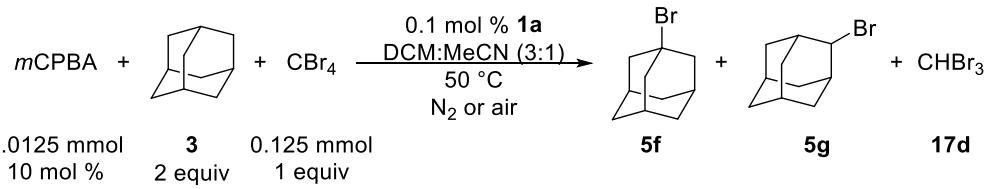
1 mmol **16** (7.5 equiv) **17a** **17b**

2°/1° = 31

Figure 2.27. Photoinduced bromination of **16** by Br_2.

Bromination of adamantane (**3**) with substoichiometric amounts (10 mol % with respect to CBr_4) of *m*CPBA and catalytic amounts of Ni complex **1a** was conducted under an atmosphere of N_2 or air (Table 2.11) to assess whether CBr_3· or Br· cleaves the C–H bonds in adamantane. 1- and 2-bromoadamantane (**5f** and **5g**) were formed as the major products. The formation of the combination of **5f** and **5g** in higher than 10% yield in the reactions under air, along with the orange color of the reaction mixture (Table 2.11, Entries 1–2) suggests that Br· abstracts hydrogen atoms from adamantane in reactions conducted under air. The formation of the combination of **5f** and **5g** in approximately 30% yield in the reactions under nitrogen, the formation of bromoform (**17d**), and the colorlessness of the reaction mixture (Table 2.11, Entries 3–4) indicate that CBr_3· abstracts hydrogen atoms from adamantane in reactions conducted under nitrogen. Due to such interference from CBr_3· and Br· in hydrogen-atom abstraction, adamantane is not a suitable substrate for the measurement of the selectivity of aroyloxy radical **10**.

Table 2.11. Results of Bromination of Adamantane

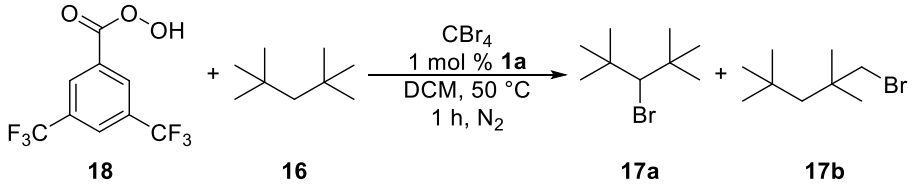


Entry	N_2 or air	**5f** (%)	**5g** (%)	**17d** (%)	Color of reaction mixture
1	Air	12.0	2.0	0	Orange
2	Air	9.8	1.6	0	Orange
3	N_2	24.6	2.1	14	Colorless
4	N_2	27.2	2.3	18	Colorless

All yields were determined based on CBr_4.

Results of three repeated experiments of Ni-catalyzed bromination of **16** by aromatic peracid **18**, along with those of a control experiment conducted in the absence of Ni, are summarized in Table 2.12.

Table 2.12. Results of Ni-catalyzed Bromination of 16 by peracid 18



Entry	**17a** (%)	**17b** (%)	2˚/1˚
1	14.3	13.5	1.1
2	15.6	13.5	1.2
3	14.2	13.1	1.1
4[a]	0	0	-

[a]In the absence of Ni.

2.4.12. Assay for the Alkylperoxy Intermediate by GC

2.4.12.1. General procedure for the assay for alkylperoxy intermediates by GC

To a set of two 4 mL vials, each equipped with a stir bar, was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv) and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complex **1a** was added as a suspension in DCM. One of these two vials was sparged with N_2 for 30-60 s before both were sealed and heated at 50 ˚C for 5 min. After cooling to room temperature, half of the reaction mixture in each vial was transferred to a clean GC vial, diluted with ethyl acetate, and immediately subjected to analysis by GC. The remaining mixture in each vial was treated with PPh_3 (18.1 mg, 0.0700 mmol), diluted with ethyl acetate, and then subjected to analysis by GC.

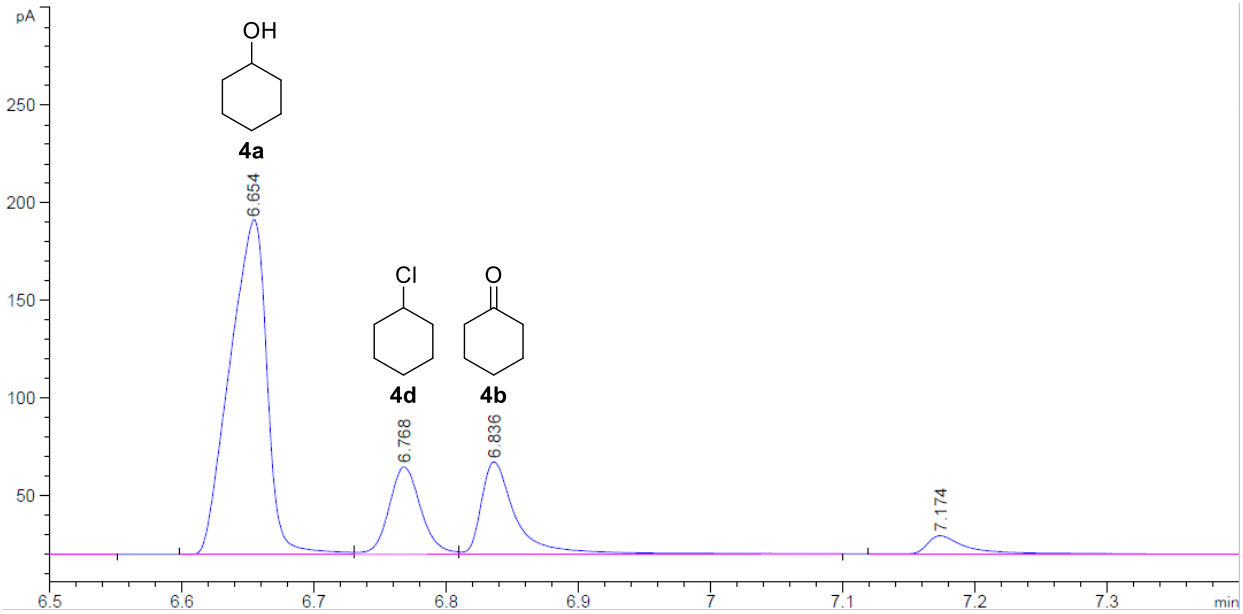
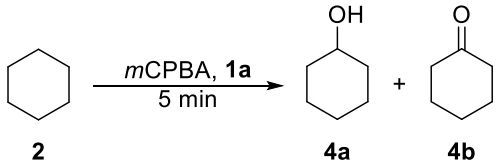


Figure 2.28. A typical GC trace of the reaction mixture from Ni-catalyzed oxidation of **2** after 5 min.

2.4.12.2. Results and derivation of the percentage of alkylperoxy intermediate **19**

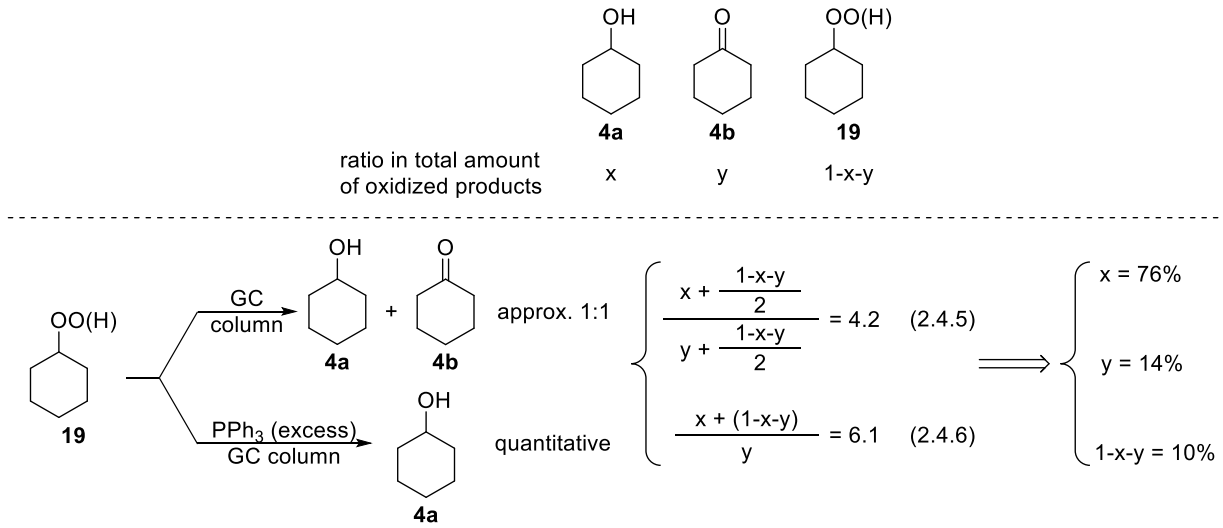
Table 2.13. Results of the Assay for Alkylperoxy Intermediate 19



Entry	N_2/air	Treatment with PPh_3	A/K[a]	Average A/K
1	N_2	yes	4.5	4.6±0.1

2			4.6	
3			4.6	
4		no	4.5	4.5±0.0
5			4.5	
6			4.5	
7	air	yes	6.8	6.1±0.8
8			5.2	
9			6.2	
10		no	4.5	4.2±0.7
11			3.4	
12			4.8	

Results of the assay for intermediate **19** in Ni-catalyzed oxidation of **2** by GC before and after addition of PPh_3 are summarized in Table 2.13. All reactions were repeated three times and the average A/K ratio was calculated as the arithmetic mean of the ratios from the three reactions. The derivation of the percentage of **19** in the total amount of oxidized products is presented in Scheme 2.4. The ratio of alcohol **4a** in the total amount of oxidized products is assumed to be *x* and that of ketone **4b** is assumed to be *y*; in this case the ratio of intermediate **19** would be *1-x-y*. Because intermediate **19** decomposes in the GC to afford **4a** and **4b** in roughly 1:1 ratio, eq 2.4.5 can be established based on experimental data from Table 2.13, Entries 10–12. Because treatment of **19** with PPh_3 results in quantitative formation of **4a**, eq 2.4.6 can be established based on data from Table 2.13, Entries 7–9. Solving for equations 2.4.5, 2.4.6 gives x = 76%, y = 14%, and *1-x-y* = 10%, indicating that intermediate **19** only accounts for 10% of the total amount of oxidized products and that trapping of alkyl radicals by O_2 is not the major pathway for the formation of C–O bonds.



Scheme 2.4. Derivation of the percentage of **19** in the total amount of oxidized products.

2.4.13. X-ray Crystallographic Data

2.4.13.1. $Ni(Me_4Phen)_2Cl_2$ (**1a**)

A light blue block 0.23 x 0.14 x 0.07 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 30.23 mm and exposure time was 0.50 seconds per frame at low angles and 1.50 seconds per frame at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 37258 reflections were collected covering the indices -14<=h<=14, -20<=k<=32, -15<=l<=15. 6886 reflections were found to be symmetry independent, with an R_{int} of 0.0585. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.40.50a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Electron density most likely corresponding to one or (possibly) more highly disordered methanol molecules was masked using the SQUEEZE function.

Table 2.14. Crystal data and structure refinement for Yehao003_Hartwig.

Identification code	Yehao003_Hartwig	
Empirical formula	C34 H35 Cl2 N5 Ni	
Formula weight	643.28	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.4248(2) Å	α= 90°.
	b = 25.6713(3) Å	β= 115.298(2)°.
	c = 12.7082(2) Å	γ = 90°.
Volume	3369.73(10) $Å^3$	
Z	4	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	2.515 mm^{-1}	
F(000)	1344	
Crystal size	0.230 x 0.140 x 0.070 mm^3	
Theta range for data collection	3.443 to 74.502°.	
Index ranges	-14<=h<=14, -20<=k<=32, -15<=l<=15	
Reflections collected	37258	
Independent reflections	6886 [R(int) = 0.0585]	
Completeness to theta = 74.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.78221	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6886 / 0 / 388	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1227	

R indices (all data)	R1 = 0.0461, wR2 = 0.1252
Extinction coefficient	n/a
Largest diff. peak and hole	0.415 and -0.493 e.Å^{-3}

2.4.13.2. Ni(Brbpy)$_2$Cl$_2$ **(1f)**

A green block 0.29 x 0.23 x 0.17 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 1.00 seconds per frame at low and high angles using a scan width of 0.5°. Data collection was 100% complete to 26.359° in θ. A total of 24612 reflections were collected covering the indices -19<=h<=20, -15<=k<=15, -15<=l<=15. 2418 reflections were founded to be symmetry independent, with an R_{int} of 0.1056. Indexing and unit cell refinement indicated a centered, monoclinic lattice. The space group was found to be C 2/c (No. 15). The data were integrated using the CrysAlis^{Pro} 1.171.40.79a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Electron density attributable to outer sphere solvent (unidentifiable amongst the solvents used: methanol, acetonitrile and diethyl ether) was treated using the solvent mask option included within the OLEX2 software.

Table 2.15. Crystal data and structure refinement for Yehao005_Hartwig.

Identification code	Yehao005_Hartwig	
Empirical formula	C20 H14 Br2 Cl2 N4 Ni	
Formula weight	599.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 16.1864(6) Å	α= 90°.
	b = 12.0596(4) Å	β= 106.161(4)°.
	c = 12.6122(4) Å	γ = 90°.
Volume	2364.63(15) Å^3	
Z	4	
Density (calculated)	1.685 Mg/m^3	
Absorption coefficient	4.439 mm^{-1}	
F(000)	1176	
Crystal size	0.29 x 0.23 x 0.17 mm^3	
Theta range for data collection	2.937 to 26.359°.	
Index ranges	-19<=h<=20, -15<=k<=15, -15<=l<=15	
Reflections collected	24612	
Independent reflections	2418 [R(int) = 0.1056]	
Completeness to theta = 26.359°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64989	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	2418 / 0 / 132
Goodness-of-fit on F^2	1.267
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1174
R indices (all data)	R1 = 0.0485, wR2 = 0.1179
Extinction coefficient	n/a
Largest diff. peak and hole	0.620 and -0.731 e.Å^{-3}

2.4.13.3. Ni(bpyPY2Me)Cl_2 (**1g**)

A red block 0.43 x 0.31 x 0.24 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame at low and high angles using a scan width of 0.5°. Data collection was 100% complete to 26.372° in θ. A total of 23753 reflections were collected covering the indices -12<=h<=11, -13<=k<=13, -15<=l<=15. 4753 reflections were founded to be symmetry independent, with an R_{int} of 0.0873. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the CrysAlis^{Pro} 1.171.40.79a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 2.16. Crystal data and structure refinement for Yehao004_Hartwig.

Identification code	Yehao004_Hartwig	
Empirical formula	C24 H26 Cl2 N4 Ni O2	
Formula weight	532.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6088(2) Å	α= 102.911(2)°.
	b = 10.9517(3) Å	β= 95.301(2)°.
	c = 12.2940(2) Å	γ = 109.822(2)°.
Volume	1166.19(5) Å^3	
Z	2	
Density (calculated)	1.515 Mg/m^3	
Absorption coefficient	1.091 mm^{-1}	
F(000)	552	
Crystal size	0.43 x 0.31 x 0.24 mm^3	
Theta range for data collection	2.915 to 26.372°.	
Index ranges	-12<=h<=11, -13<=k<=13, -15<=l<=15	
Reflections collected	23753	
Independent reflections	4753 [R(int) = 0.0873]	
Completeness to theta = 26.372°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.71519	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4753 / 0 / 309
Goodness-of-fit on F^2	1.101
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0960
R indices (all data)	R1 = 0.0374, wR2 = 0.0974
Extinction coefficient	n/a
Largest diff. peak and hole	0.437 and -0.420 e.Å^{-3}

2.4.13.4. Ni(Me_2Phen)$_2$(OAc)(BPh_4) (**1h**)

A colorless rod 0.26 x 0.09 x 0.06 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 30.23 mm and exposure time was 1.00 seconds per frame at low angles and 2.50 seconds per frame at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 63840 reflections were collected covering the indices -23<=h<=23, -22<=k<=18, -34<=l<=40. 11084 reflections were found to be symmetry independent, with an R_{int} of 0.0438. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P b c a (No. 61). The data were integrated using the CrysAlis^{Pro} 1.171.40.50a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 2.17. Crystal data and structure refinement for Yehao002_Hartwig.

Identification code	Yehao002_Hartwig	
Empirical formula	C57.50 H54 B Cl7 N4 Ni O2	
Formula weight	1150.71	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 18.9478(2) Å	α= 90°.
	b = 17.9054(2) Å	β= 90°.
	c = 32.0064(2) Å	γ = 90°.
Volume	10858.75(18) Å^3	
Z	8	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	4.051 mm^{-1}	
F(000)	4760	
Crystal size	0.260 x 0.090 x 0.060 mm^3	
Theta range for data collection	3.666 to 74.502°.	
Index ranges	-23<=h<=23, -22<=k<=18, -34<=l<=40	
Reflections collected	63840	
Independent reflections	11084 [R(int) = 0.0438]	
Completeness to theta = 74.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58443	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11084 / 0 / 672
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0860
R indices (all data)	R1 = 0.0391, wR2 = 0.0893
Extinction coefficient	n/a
Largest diff. peak and hole	0.664 and -0.481 e.Å^{-3}

2.5. References

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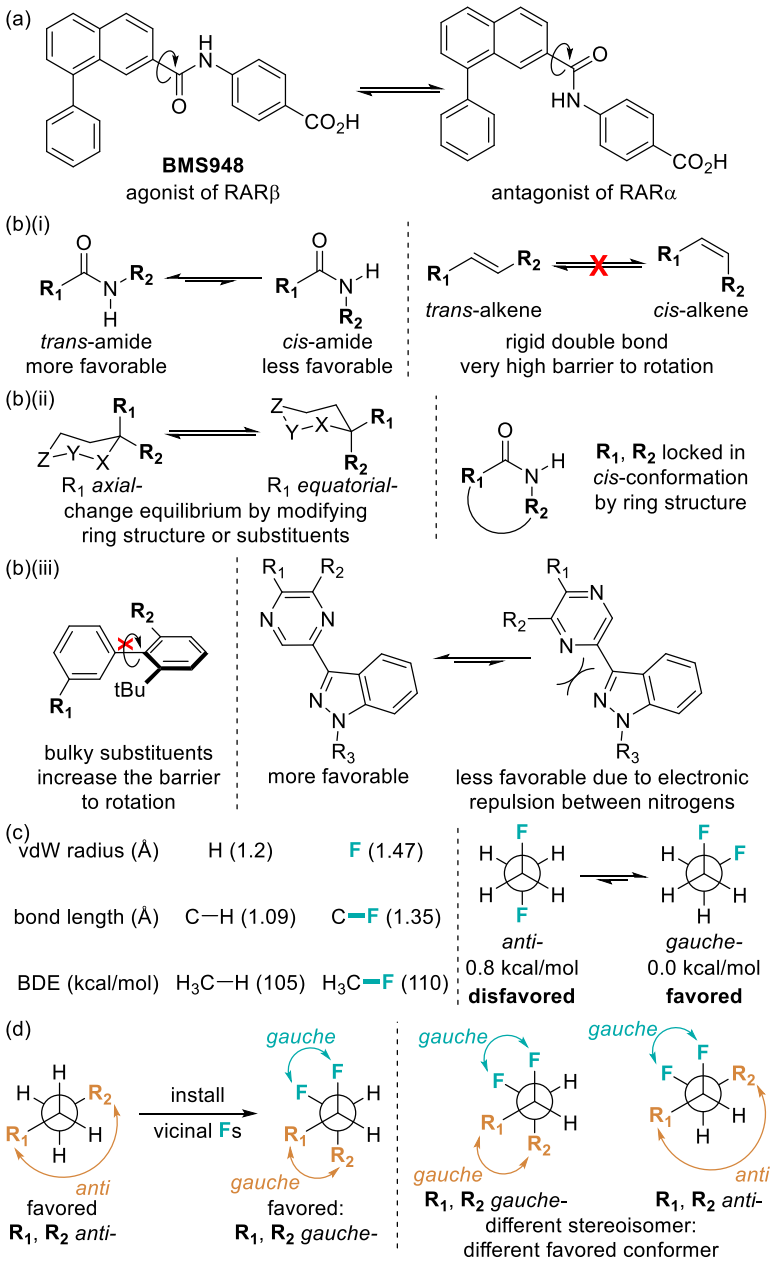
Chapter Three

Synthesis of All Stereoisomers of Vicinal Difluorides by Synergistic Catalysis Enables Conformational Control and Enhanced Protein Binding of Molecules Containing Acyclic C(sp^3)–C(sp^3) Bonds

3.1.Introduction

The absolute and relative configuration of stereogenic centers and the conformations around rotatable bonds define the specific overall structure of a molecule with a specific connectivity. This overall structure, in turn, dictates the properties and function of the molecule, such as the ability of a molecule to bind to proteins, nucleic acids and carbohydrates.[1-4] For example, one conformer of the compound BMS948 has been reported to be an antagonist of retinoic acid receptor α (RARα), whereas a different conformer, in which the C(aryl)–C(amide) bond is rotated by 180˚, is an agonist of RARβ (Scheme 3.1(a)).[5] Many strategies have been developed to control the conformations of molecules that contain planar functional groups, such as amides, alkenes (Scheme 3.1(b)(i)),[1, 6-9] saturated rings (Scheme 3.1(b)(ii)),[10-18] or arenes connected by a single bond (Scheme 3.1(b)(iii)).[19-23] However, strategies to control the conformation about acyclic C(sp^3)–C(sp^3) bonds are more limited because the barrier to rotation around a C(sp^3)–C(sp^3) bond is usually low[24] and because conformers resulting from rotation around a C(sp^3)–C(sp^3) bond are often similar in energy.[25-26] Indeed, guidelines for designing molecules for medicinal chemistry recommend limiting the number of rotatable bonds in a molecule.[27-28]

The vicinal difluoride motif, defined as a C(F)–C(F) unit in which both carbon atoms are sp^3-hybridized, provides a solution to this longstanding challenge of controlling the conformation around an acyclic C(sp^3)–C(sp^3) bond.[29-31] The size of a fluorine atom is similar to that of a hydrogen atom,[32] so the vicinal difluoride motif is sterically similar to two adjacent methine units. In addition, most C(sp^3)–F bonds are stable, (bond dissociation energy > 110 kcal/mol, Scheme 3.1(c), left)[33] making the C–F bond resistant to most chemical transformations. As a result, replacement of a C(H)–C(H) unit, in which both carbons are sp^3-hybridized, by a vicinal difluoride motif does not significantly change the steric properties or the chemical reactivity of the compound. Yet, the stabilizing hyperconjugation between the σ^* orbital of the C–F bond and an adjacent, occupied σ orbital causes the vicinal difluoride motif to favor the conformer in which the two F atoms are positioned *gauche* to each other (Scheme 3.1(c), right, 1,2-difluoroethane as an example).[34-37] In this way, the two adjacent C–F bonds can control the most favorable conformer about an acyclic C(sp^3)–C(sp^3) bond (Scheme 3.1(d), left). This stable *gauche* conformer of two adjacent fluorine atoms allows one to predict the relative position (*e.g.*, *gauche*- or *anti*-) of substituents (R_1, R_2, Scheme 3.1(d)) in the most favorable conformation about the C(sp^3)–C(sp^3) bond, due to the configurations of the two fluorine-substituted carbon atoms. Since the most favorable conformer of each stereoisomer of a given vicinal difluoride compound is different, one can control the relative position of substituents about the C–C bond by synthesizing the corresponding stereoisomer (Scheme 3.1(d), right). This strategy has been implemented to identify the active conformation of γ-aminobutyric acid (GABA) in GABA receptors[38] as well as to modify the conformations of peptides and cyclic polypeptides.[29, 39] Given such precedence, we envision that this strategy would be valuable to biochemistry and drug discovery if stereoselective synthesis of all stereoisomers of vicinal difluoride compounds could be readily achieved.

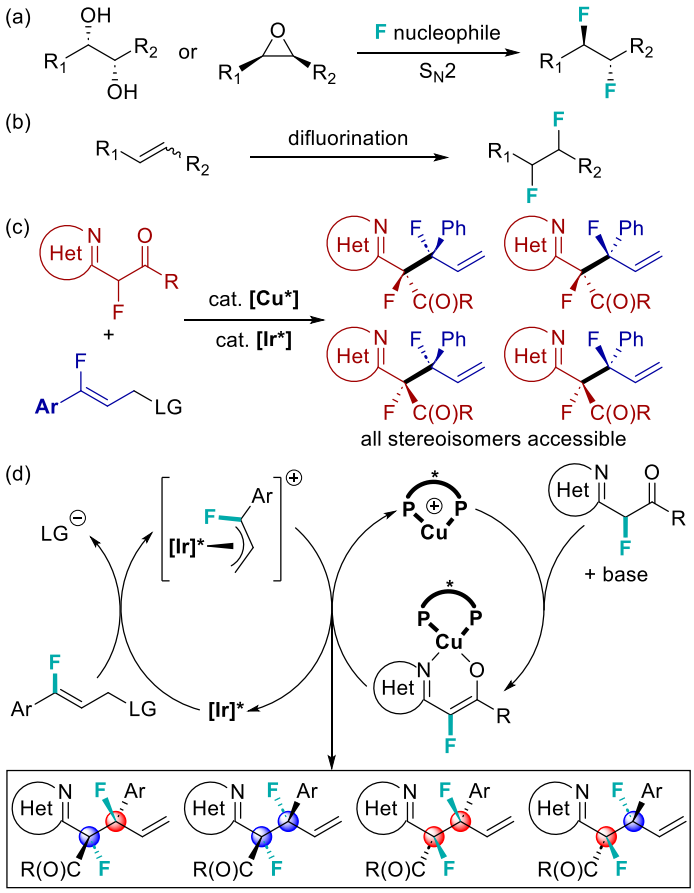


Scheme 3.1. (a) Different conformers affect the bioactivity of BMS948; (b) strategies to control the conformation of molecules that contain (i) planar functional groups, (ii) ring structures, and (iii) arenes connected by a single bond; (c) comparison between the hydrogen and the fluorine atom (left) and the *gauche* effect (right); (d) the vicinal difluoride motif as a strategy to control the favored conformer about an acyclic C(sp^3)–C(sp^3) bond.

However, methods for the selective synthesis of all stereoisomers of vicinal difluoride compounds are currently lacking. Conventional syntheses of vicinal difluorides follow two strategies: (1) two sequential nucleophilic substitution reactions between fluorine nucleophiles and an epoxide or a diol[40-42] (Scheme 3.2(a)); and (2) the difluorination of alkenes[43-49] (Scheme 3.2(b)). The nucleophilic substitution strategy often requires harsh, toxic reagents (*e.g.*, HF, SF_4),[41-42] which limit the tolerance of functional groups in these reactions, and the synthesis of all

stereoisomers of the vicinal difluoride product requires the tedious preparation of all stereoisomers of the starting material or synthetic intermediates[50] because these substitution reactions are stereospecific. The development of methods for enantioselective difluorination of alkenes is challenging, and only a few examples have been reported.[51-53]

To address these limitations, we proposed to construct the vicinal difluoride motif by the stereoselective formation of a C(sp^3)–C(sp^3) bond between two mono-fluorinated building-blocks. Specifically, we proposed to exploit the synergistic combination of Cu and Ir catalysts, which was developed by our group for the synthesis of stereoisomers that contain just one or no fluorines on adjacent stereogenic centers,[54-55] to access all stereoisomers of vicinal difluorides by allylic substitution between a 3-fluoroallylic electrophile and an α-fluoro pronucleophile that contains a heteroaryl and a carbonyl fragment (Scheme 3.2(c)). Based on our design, the Lewis acidic copper catalyst, which is ligated by a chiral bisphosphine, coordinates to the nitrogen and the oxygen atom in the 2-fluoro-2-azaarylcarbonyl compound and generates the chiral Cu-enolate intermediate in the presence of a base. This Cu-enolate then reacts with the chiral, cationic (3-fluoroallyl)iridium species to generate the vicinal difluoride product by enantioselective and diastereoselective formation of the C(sp^3)–C(sp^3) bond. Ideally, permutations of the enantiomers of the Cu and the Ir catalysts would catalyze the formation of all four stereoisomers of a vicinal difluoride product (Scheme 3.2(d)).



Scheme 3.2. (a)(b) Conventional strategies to synthesize vicinal difluoride compounds; (c) our strategy to access all four stereoisomers of the vicinal difluoride compound; (d) proposed catalytic cycle for the stereodivergent synthesis of vicinal difluoride compounds.

Here, we report the realization of the strategy to form all four stereoisomers of vicinal difluoride compounds catalyzed by the combination of a Lewis acidic copper catalyst containing a chiral bisphosphine ligand and an iridium catalyst containing a chiral phosphoramidite ligand. The Cu catalyst controls the configuration of the stereogenic center that is α to the heteroarene in the product, whereas the Ir catalyst dictates the configuration of the allylic stereogenic center in the product. Permutation of the enantiomers of these catalysts allows for the synthesis of all four stereoisomers of the vicinal difluoride compound from the same, optically inactive starting materials. This method affords the vicinal difluoride product with good yield and high stereoselectivity and tolerates a broad scope of heteroarenes and functional groups that are commonly found in medicinally active compounds. Attachment of a photoreactive chemical probe to these products and analysis of binding to proteins of human kidney cells by proteomic methods shows the ability of the absolute and relative configuration of the vicinal difluoride unit to influence binding to protein targets.

3.2.Results and Discussions

3.2.1. Development of Reaction Conditions

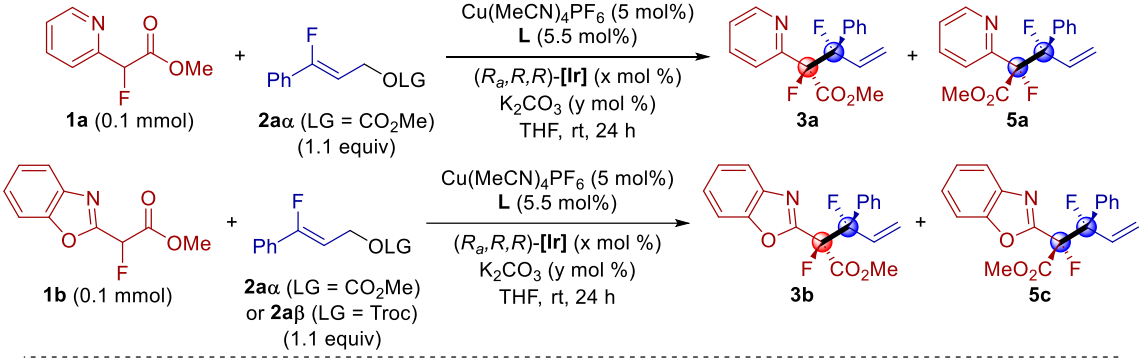
We began the development of conditions for the diastereo- and enantioselective synthesis of vicinal difluoride compounds by investigating the effect of bisphosphine ligands on the yield and stereoselectivity of the catalytic allylic substitution between methyl 2-fluoro-2-(pyridin-2-yl)acetate (**1a**) and (*Z*)-3-fluoro-3-phenylallyl methyl carbonate (**2aα**) with K_2CO_3 as the base, $[Cu(MeCN)_4](PF_6)$ as the precursor for copper and (R_a,*R*,*R*)-[**Ir**] as the iridium catalyst. As shown in Table 3.1, reactions with the ligand **L1** or **L3**–**L5** on copper formed the vicinal difluoride product **3a** or **5a** with low diastereoselectivity (dr ≤ 4:1, entries 1, 4–6). Reaction with the WALPHOS ligand **L2** formed product **5a** in high yield (88%) and high stereoselectivity (dr 1:12, ee >99%, entry 2), but the reaction with the enantiomer of **L2** (*ent*-**L2**) afforded the diastereomer of product **5a**, *i.e.*, **3a**, with low diastereoselectivity (dr 3:1, entry 3), suggesting a mismatch of selectivity between the ligand *ent*-**L2** and the catalyst (R_a,*R*,*R*)-**[Ir]**. These results indicate that Cu complexes containing ligands **L1**–**L5** are not suitable catalysts for the synthesis of all stereoisomers of vicinal difluorides.

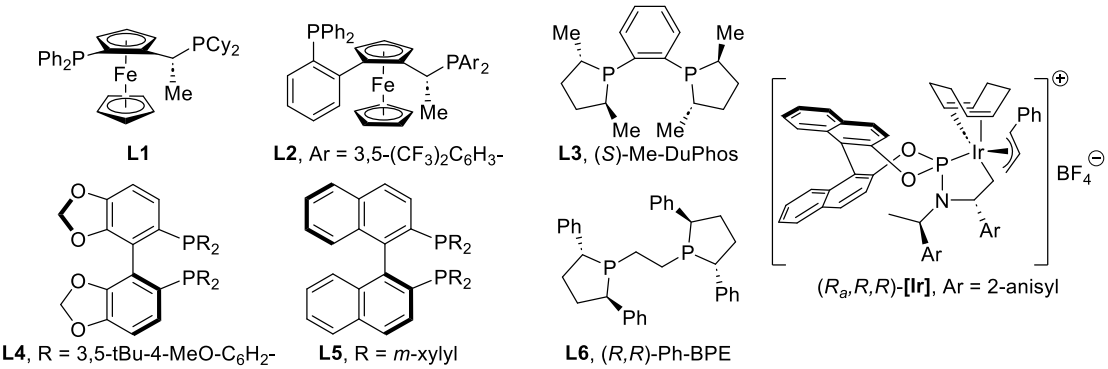
In contrast, reactions with the ligand (*R*,*R*)-Ph-BPE (**L6**) or its enantiomer (*ent*-**L6**) afforded the desired vicinal difluoride product **3a** or **5a** in high yield and excellent stereoselectivity (entries 7–8). The reactions with this ligand occurred even in the presence of substoichiometric amounts of base (see the Experimental Section for the effect of base on this reaction). Control experiments indicated that both the Cu/bisphosphine catalyst and the Ir catalyst were necessary for this reaction (entries 9–10).

Having identified the conditions for the fluoroallylation of compound **1a**, which contained a six-membered pyridine substituent, we tested these conditions for the fluoroallylation of substrates containing five-membered heteroarenes and found that reaction with compound **1b**, which possessed a benzoxazole substituent, formed the product **3b** with low yield (43%) and poor stereoselectivity (dr 3:1, entry 11). To increase the yield and stereoselectivity, we investigated the effect of the leaving group in the 3-fluoroallylic electrophile on the yield and stereoselectivity of this reaction. We found that reactions between **1b** and electrophile **2aβ**, which contained the -OTroc leaving group (Troc = 2,2,2-trichloroethoxycarbonyl), afforded the vicinal difluoride

products **3b** or **5c** in good yields and with high or synthetically useful stereoselectivities (entries 12–13).

Table 3.1. Development of reaction conditions for the allylic substitution between 2-fluoro-2-azaarylacetates **1a**, **1b** and (*Z*)-3-fluoro-3-phenylallylic electrophile **2aα** or **2aβ**.





entry	substrates	ligand	x	y	yield (%)[a]	dr[b]	ee (%)[c]
1	**1a** + **2aα**	**L1**	5	120	90	1:2	*n.d.*
2	**1a** + **2aα**	**L2**	5	120	88	1:12	>99
3	**1a** + **2aα**	*ent*-**L2**	5	120	85	3:1	*n.d.*
4	**1a** + **2aα**	**L3**	5	120	16	1:1	*n.d.*
5	**1a** + **2aα**	**L4**	5	120	53	2:1	*n.d.*
6	**1a** + **2aα**	**L5**	5	120	88	1:4	*n.d.*
7	**1a** + **2aα**	**L6**	5	50	83[d]	15:1	99
8	**1a** + **2aα**	*ent*-**L6**	5	50	80[d]	1:20	97
9	**1a** + **2aα**	**L6**	0	50	0	-	-
10	**1a** + **2aα**	none[e]	5	50	0	-	-
11	**1b** + **2aα**	**L6**	3	100	43	3:1	*n.d.*
12	**1b** + **2aβ**	**L6**	3	100	83[d]	12:1	>99
13	**1b** + **2aβ**	*ent*-**L6**	3	100	73[d]	1:5	>99

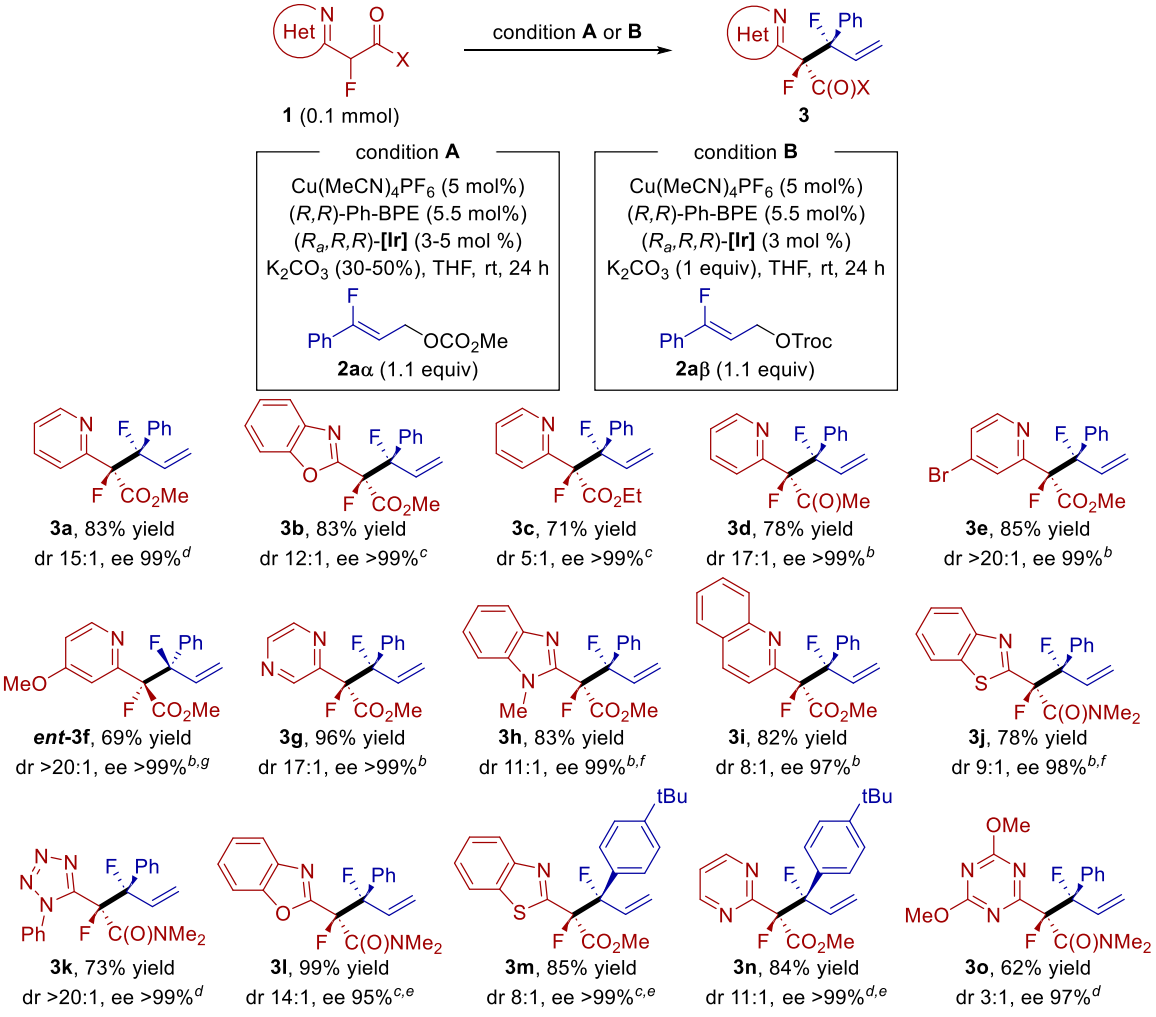
[a]Combined NMR yield of both diastereomers, unless specified otherwise; [b]the ratio of **3a** to **5a** or **3b** to **5c**; [c]*n.d.* stands for not determined; [d]isolated yield of one diastereomer; [e]in the absence of $Cu(MeCN)_4PF_6$ and ligand.

3.2.2. Scope of the α-Fluoro-α-azaaryl Acetates, Ketones, and Acetamides

Having identified the reaction conditions to synthesize vicinal difluorides by formation of the C–C bond between a fluoroallyl electrophile and an α-fluorinated pronucleophile that contains either a five-membered or a six-membered heteroarene, we explored the scope of these

pronucleophiles for this catalytic reaction (Table 3.2). A series of α-fluoroacetates and α-fluoroketones that contained six-membered heteroarenes, such as pyridines, pyrazines, pyrimidines, and quinolines, underwent the catalytic fluoroallylation with the electrophile **2aα** or **2aβ** to form the corresponding vicinal difluoride products **3a**, **3c**–**3g**, **3i**, and **3n** in good yields (69–96%), with acceptable to high diastereoselectivity (dr 5:1–20:1) and excellent enantioselectivity (ee 97–99%). α-Fluoroacetates containing five-membered heteroarenes, such as benzoxazole, benzothiazole, and benzimidazole, also underwent the catalytic reaction to afford products **3b**, **3m**, and **3h** with 83–85% yield, 8:1–12:1 diastereomeric ratio, and >99% enantiomeric excess. In addition to α-fluoro-α-azaaryl acetates and ketones, α-fluoroacetamides containing the benzoxazole and the benzothiazole moieties underwent the allylic substitution to form products **3l** and **3j** with good yields (78% for **3j**, 99% for **3l**) and high stereoselectivity (dr 9:1, ee 98% for **3j**; dr 14:1, ee 95% for **3l**). Heteroaryl groups that contain three or four nitrogen atoms, such as triazine (**3o**) and tetrazole (**3k**), were also compatible with this reaction, even though compound **3o** was formed with moderate diastereoselectivity (dr 3:1), presumably because the steric effect of the methoxy substituents on the triazine led to poor binding of the nitrogen atom to the Lewis-acidic, copper catalyst.

Table 3.2. Scope of the α-fluoro-α-azaaryl acetates, ketones, and acetamides for the catalytic fluoroallylation reaction[a]

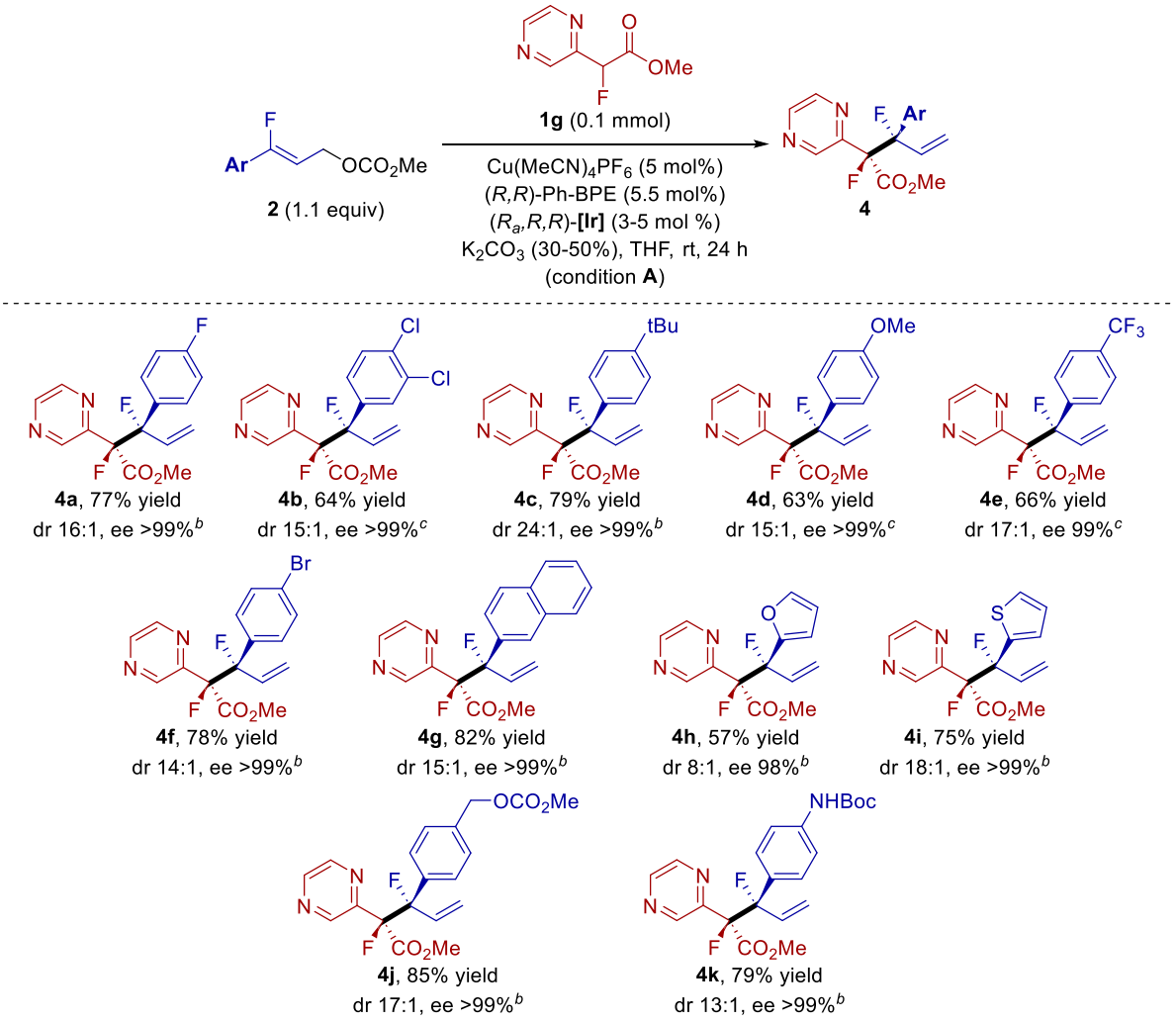


[a]Isolated yield of single diastereomer unless noted otherwise. Diastereomeric ratio (dr) was determined by ^{19}F NMR spectroscopy of the crude reaction mixture. Enantiomeric excess (ee) was determined by chiral HPLC analysis of the isolated major diastereomer. [b]Condition **A**, 3% **[Ir]** and 30% K_2CO_3; [c]condition **B**; [d]condition **A**, 5% **[Ir]** and 50% K_2CO_3; [e]combined yield of both diastereomers; [f]48 h instead of 24 h; [g](*S,S*)-Ph-BPE and (S_a,*S,S*)-**[Ir]** were used.

3.2.3. Scope of the (Z)-3-Fluoro-3-arylallylic Electrophiles

As shown in Table 3.3, a series of (*Z*)-3-fluoro-3-arylallyl methyl carbonates containing substituted aryl or heteroaryl groups underwent the catalytic allylic substitution with α-fluoroacetate **1g** and formed the corresponding vicinal difluoride products in good yields (57–85%) and with high stereoselectivity (dr 8:1–24:1, ee 98–99%). Reactions of (*Z*)-3-fluoro-3-arylallyl methyl carbonates containing electron-rich, electron-neutral, and electron-poor arenes (**4a**–**4g**) afforded the products with good yield and excellent diastereo- and enantioselectivity. This catalytic method tolerated versatile synthetic handles, such as mono- or di-halogenated arenes (**4a**, **4b**, **4f**), Boc-protected aniline (**4k**), and carbonate-masked benzylic alcohol (**4j**). Simple heteroarenes, such as furan (**4h**) and thiophene (**4i**), also were compatible with this transformation.

Table 3.3. Scope of the (*Z*)-3-fluoro-3-arylallyl methyl carbonates that undergo the catalytic allylic substitution with methyl 2-pyrazinyl α-fluoroacetate (**1g**)[a]



[a]Isolated yield of single diastereomer. Diastereomeric ratio (dr) was determined by ^{19}F NMR spectroscopy of the crude reaction mixture. Enantiomeric excess (ee) was determined by chiral HPLC analysis of the isolated major diastereomer. [b]3% **[Ir]** and 30% K_2CO_3; [c]5% **[Ir]** and 50% K_2CO_3.

3.2.4. Demonstration of Stereodivergent Synthesis

Results from Figure 3.1 show that the reaction catalyzed by a combination of Cu and Ir complexes to form the C–C bond between vicinal fluorides stereoselectively can be used to synthesize each of the four stereoisomers. These reactions can be conducted in this stereodivergent fashion to form products containing a six-membered (Figure 3.1(a), 3.1(b)) or a five-membered heteroarene (Figure 3.1(c)), as well as those containing various unsubstituted or substituted arenes (Figure 3.1(d), 3.1(e)). Any stereoisomer of a given vicinal difluoride product in Figure 3.1 can be synthesized in good yield (56–96%), with synthetically useful to high diastereoselectivity (dr 4:1–18:1), and excellent enantioselectivity (ee 97–99%) from the same, optically inactive starting materials by simple permutation of the enantiomers of the Cu and the Ir catalysts. The heteroaryl group on the azaaryl ester unit provides a defined structure to the copper-substrate complex, and is the type of subunit in a wide range of small molecules with biological activities.[56-61]

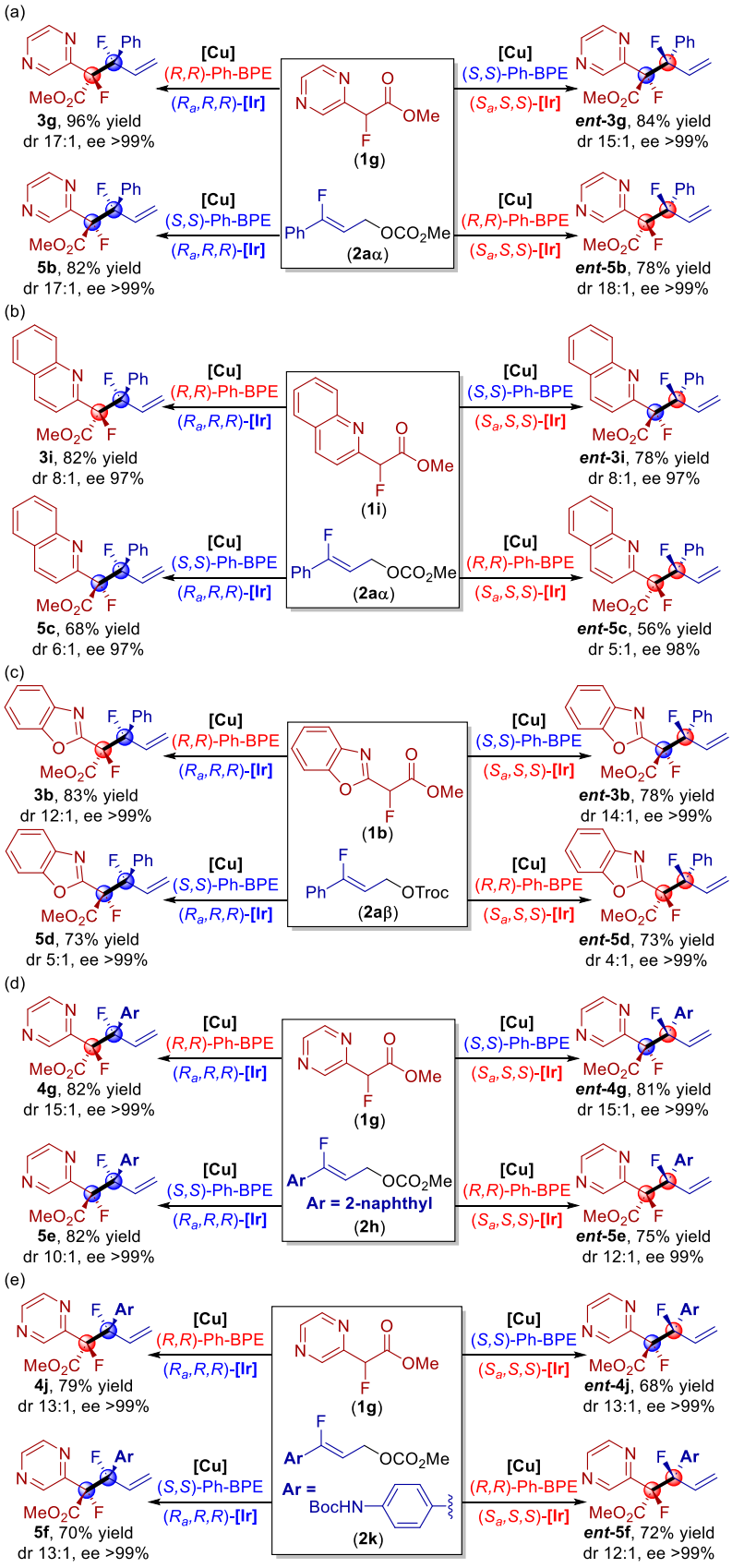

(a)
[Cu]
(R,R)-Ph-BPE
(Ra,R,R)-[Ir]
[Cu]
(S,S)-Ph-BPE
(Sa,S,S)-[Ir]
3g, 96% yield
dr 17:1, ee >99%
ent-3g, 84% yield
dr 15:1, ee >99%
(1g)
(2aα)
5b, 82% yield
dr 17:1, ee >99%
ent-5b, 78% yield
dr 18:1, ee >99%
(b)
3i, 82% yield
dr 8:1, ee 97%
ent-3i, 78% yield
dr 8:1, ee 97%
(1i)
5c, 68% yield
dr 6:1, ee 97%
ent-5c, 56% yield
dr 5:1, ee 98%
(c)
3b, 83% yield
dr 12:1, ee >99%
ent-3b, 78% yield
dr 14:1, ee >99%
(1b)
(2aβ)
5d, 73% yield
dr 5:1, ee >99%
ent-5d, 73% yield
dr 4:1, ee >99%
(d)
4g, 82% yield
dr 15:1, ee >99%
ent-4g, 81% yield
dr 15:1, ee >99%
(1g)
Ar = 2-naphthyl
(2h)
5e, 82% yield
dr 10:1, ee >99%
ent-5e, 75% yield
dr 12:1, ee 99%
(e)
4j, 79% yield
dr 13:1, ee >99%
ent-4j, 68% yield
dr 13:1, ee >99%
(1g)
Ar =
BocHN
(2k)
5f, 70% yield
dr 13:1, ee >99%
ent-5f, 72% yield
dr 12:1, ee >99%

Figure 3.1. Selected examples of stereodivergent synthesis of all four stereoisomers of vicinal difluoride compounds.

3.2.5. Evidence for a gauche Relationship between Fluorines in the Vicinal Difluoride Products

X-ray crystallographic data of the vicinal difluoride compound **4g**, which was synthesized from the allylic substitution in the presence of catalytic amounts of (*R,R*)-Ph-BPE (**L6**) and (R_a,*R,R*)-**[Ir]**, indicated that the two C–F bonds in **4g** adopted the *gauche* conformation in the solid-state structure of the compound (Figure 3.2(a)). Similarly, X-ray crystallographic data of compound *ent*-**5d**, which was synthesized from the reaction with (*R,R*)-Ph-BPE and (S_a,*S,S*)-**[Ir]**, show that the two C–F bonds in *ent*-**5d** are located *gauche* to each other in the solid state (Figure 3.2(b)).

DFT calculations of the relative free energies of the *anti*- and the *gauche*- conformers of the two pairs of diastereomers **3a**, **5a** and **3b**, **5d** in the solution phase (see the Experimental Section for computational details) suggest that the *gauche* conformers are thermodynamically more stable than the other conformers (1.2 – 1.9 kcal/mol lower in energy than the *anti*- conformers) in all cases (Figure 3.3). These results indicate that the *gauche* conformation of the two adjacent C–F bonds dictates the most stable structure of these molecules despite the apparent steric repulsion between the heteroarene and the arene attached to the two adjacent carbons.

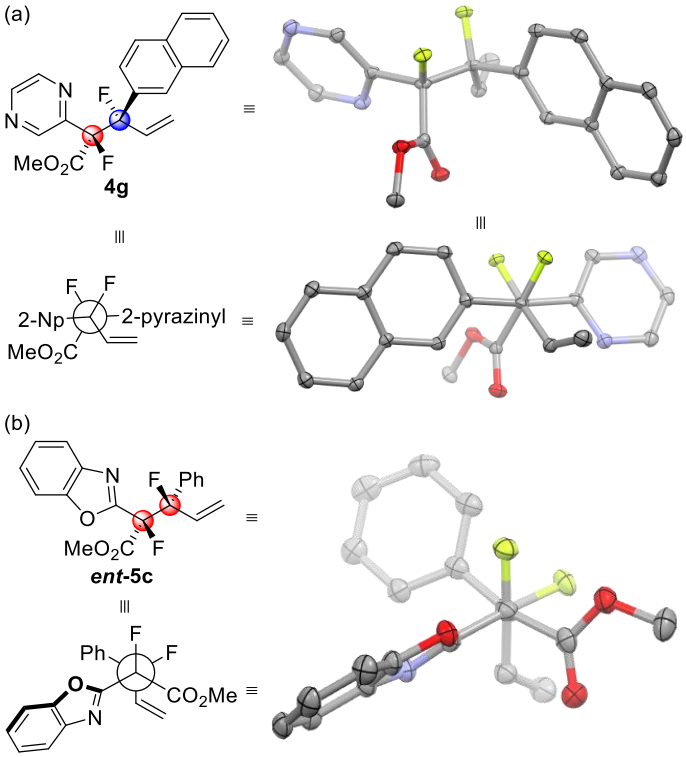


Figure 3.2. The *gauche* conformation of the two C(sp^3)–F bonds in vicinal difluoride compounds (a) **4g** and (b) *ent*-**5d** in the crystal structures.

The ability to synthesize all four stereoisomers of the vicinal difluoride compounds (Figure 3.1) and the low energy of the conformation with the two C–F bonds *gauche* to each other (Figures 2 and 3) demonstrates that one can generate a range of molecular structures containing an acyclic C(sp^3)–C(sp^3) bond from the same reactants by synthesizing the corresponding stereoisomers of a vicinal difluoride. For example, if one considers the structures of diastereomers **3a** and **5a** and

seeks a structure in which the pyridyl and the phenyl groups are located *anti* to each other, then one should synthesize diastereomer **3a**; likewise, if one seeks a structure in which the pyridyl and the phenyl groups are located *gauche* to each other, then stereoisomer **5a** should be synthesized. Thus, we have developed a working strategy to control the conformation of acyclic C(sp^3)–C(sp^3) bonds by synthesizing the desired stereoisomer of the vicinal difluoride motif.

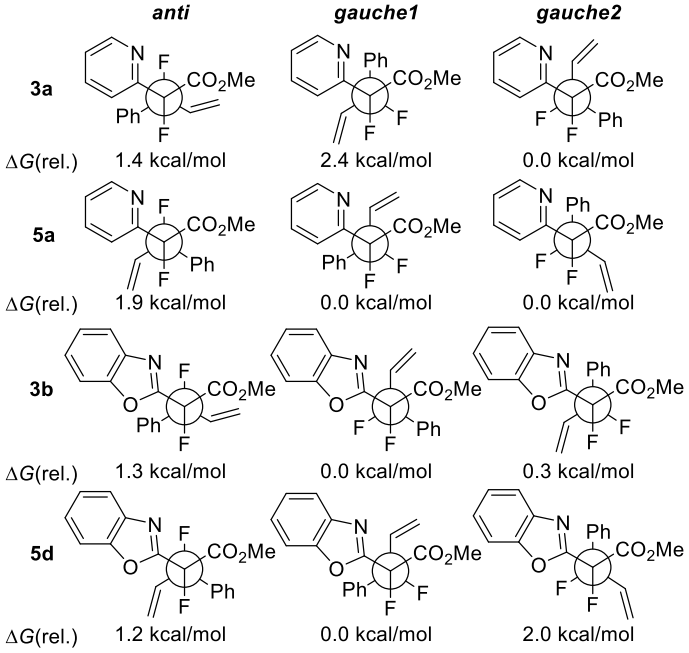


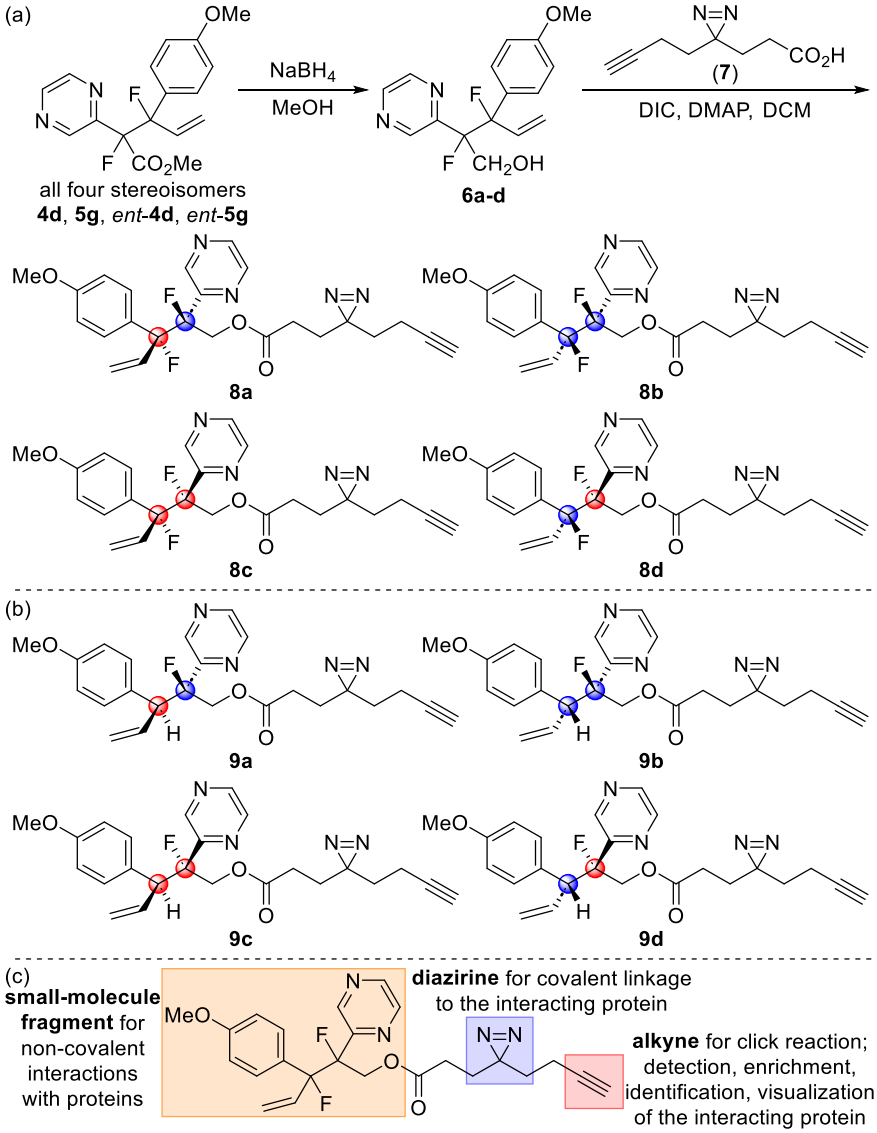
Figure 3.3. Calculated relative Gibbs free energies (Δ*G*(rel.)) of the *anti*- and *gauche*- conformers of vicinal difluoride compounds **3a**, **5a**, **3b**, and **5d**.

3.2.6. Chemical Proteomic Experiments to Assess Binding of Vicinal Difluoride Stereoisomers

We hypothesized that this strategy could be implemented to control the lowest-energy conformer of biologically active molecules and, thus, modify their activity. To test this hypothesis, we synthesized compounds **8a-d**, which constitute a set of four stereoisomers containing photoreactive probes, from the vicinal difluoride compound **4d** and its three stereoisomers *ent*-**4d**, **5g**, and *ent*-**5g**, all of which contain a pyrazine and a methoxy substituent that could assist binding to proteins by hydrogen bonds (see Scheme 3.3(a) and the Experimental Section for details of the synthesis).

Compounds **8a-d** were designed to contain components of probes used for fragment-based chemical proteomics.[62-63] Each compound possesses a small-molecule fragment that engages in non-covalent interactions with proteins (the vicinal difluoride moiety containing the pyrazine and the 4-methoxyphenyl group shown in the orange box of Scheme 3.3(c)), a photoreactive diazirine group (blue box of Scheme 3.3(c)), which forms, by photoirradiation, a carbene intermediate that covalently binds to the protein interacting with the probe, and a terminal alkyne, which can undergo click reactions for the detection, enrichment, identification, or visualization of the interacting protein (red box of Scheme 3.3(c)).[64] Because the lowest-energy conformers of probes **8a-d** are different, we envisioned that the identity of the proteins to which they bind and the strength of such binding will be different and such differences would become evident in chemical proteomic experiments.

Based on preliminary results from chemical proteomic experiments with compounds **8a–d**, we have identified 34 proteins that bind more strongly to at least one stereoisomer of **8a–d** than to the other stereoisomers. Quantitative assessment of the binding affinities of these proteins to compounds **8a–d** and control experiments with mono-fluorinated compounds **9a–d** are ongoing.



Scheme 3.3. (a) Synthesis of probes **8a–d** from all four stereoisomers of the vicinal difluoride compound **4d**; (b) the mono-fluorinated analogues **9a–d** for control experiments; (c) the three important components of a probe for fragment-based chemical proteomics.

3.3.Conclusion

We have developed a method for the diastereoselective and enantioselective synthesis of all four stereoisomers of vicinal difluoride compounds by a reaction that forms the C–C bond connecting the two fluorides catalyzed by a synergistic combination of Cu and Ir catalysts. This method furnishes the vicinal difluoride products in good yields and with high stereoselectivity, and

it tolerates a broad scope of heteroarenes and functional groups that are commonly found in medicinally active molecules. All four stereoisomers of the vicinal difluoride compounds can be synthesized from the same, optically inactive starting materials by permutation of the enantiomers of the Cu and the Ir catalysts. X-ray crystallographic data and DFT calculations reveal that the two C–F bonds are located *gauche* to each other in the lowest-energy conformers of these vicinal difluoride compounds, regardless of the position of the ancillary groups and consistent with the reported stabilizing "*gauche* effect" of the vicinal difluoride motif.

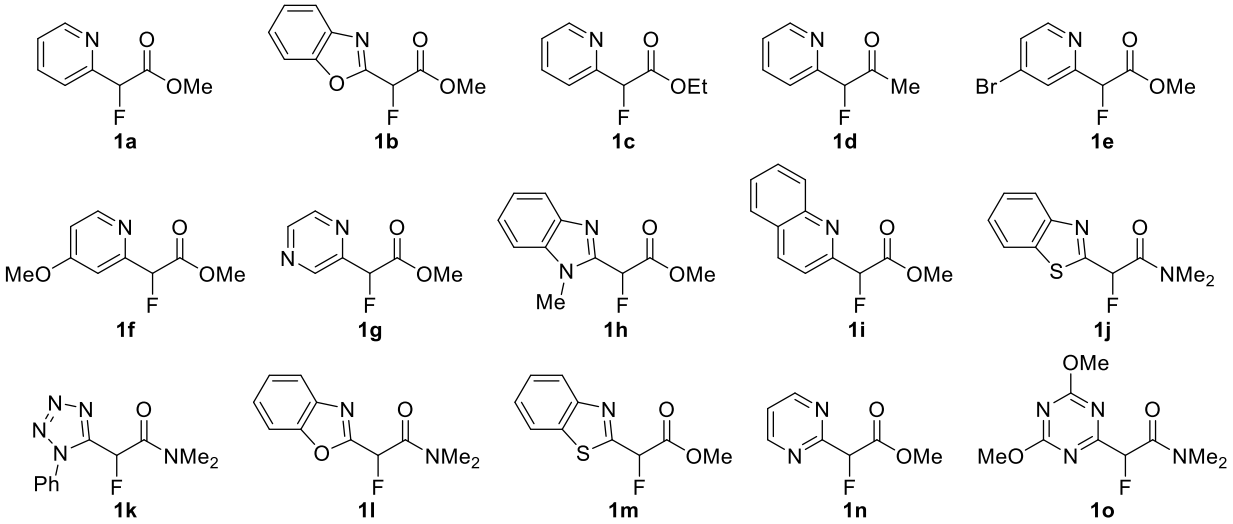
A set of four probes that contain all four stereoisomers of the vicinal difluoride fragment were synthesized and protein binding was evaluated by chemical proteomic experiments. Preliminary results from these experiments suggest that stereoisomers of these probes, which adopt different conformations, bind differently to a series of proteins. We envision that the strategy to form vicinal difluorides by formation of C–C bonds will be valuable for achieving conformational control in molecules containing highly substituted, tertiary carbon–carbon bonds.

3.4.Experimental Section

General Information

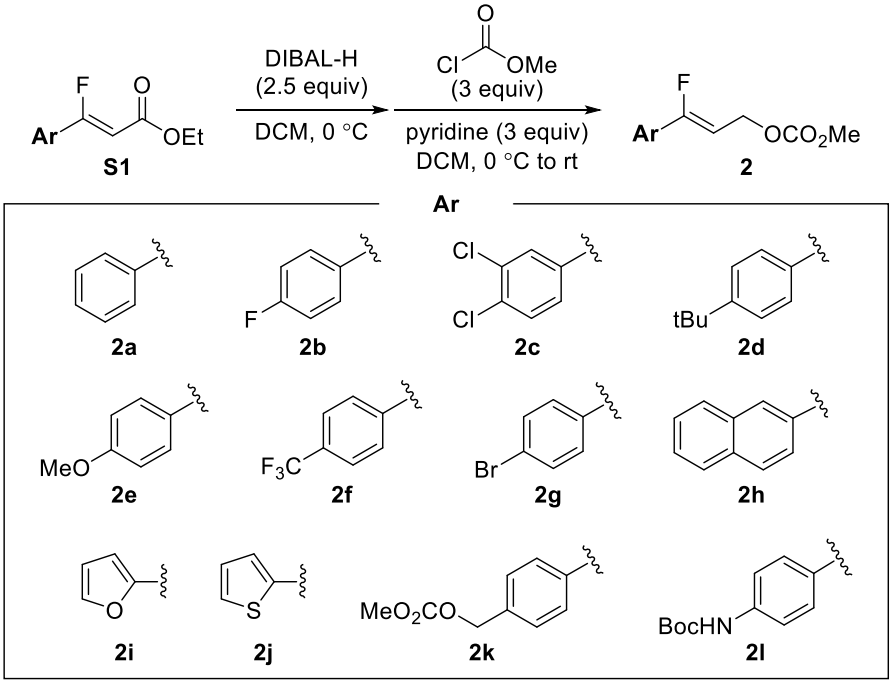
All air-sensitive procedures were conducted in a nitrogen-filled glovebox or by Schlenk techniques under nitrogen. All dry solvents were obtained by passing them through a solvent column composed of activated A-1 alumina and further degassing them by freeze-pump-thaw methods. Unless otherwise indicated, all commercially available starting materials were purchased and used directly without further purification. Column chromatography was performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns. EA is the abbreviation for ethyl acetate. ^{1}H, ^{13}C, ^{19}F NMR spectra were acquired on 500 MHz, 600 MHz or 700 MHz Bruker instruments at the University of California, Berkeley. Chemical shifts are reported in δ (ppm) with reference to residual solvent peaks or internal standard peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR, $CFCl_3$: 0 ppm for ^{19}F NMR). Coupling constants (*J*) are reported in Hz. Chiral high-performance liquid chromatography (HPLC) analysis was conducted on a Waters e2695 separations module equipped with a 2998 PDA detector. Optical rotations were measured on a Perkin Elmer 241 Polarimeter. The high-resolution mass spectra (HRMS) were obtained on a Perkin Elmer AxION2 TOF mass spectrometer in the LBNL Catalysis Facility or on a high-resolution mass spectrometer at the QB3/Chemistry Mass Spectrometry Facility at UC Berkeley. X-ray diffraction data were obtained at the Small Molecule X-ray Crystallography Facility (CheXray) at the University of California, Berkeley. Density functional theory (DFT) computations were conducted at the Molecular Graphics and Computational Facility (MGCF) at the University of California, Berkeley.

Synthesis of the α-Fluorinated Pronucleophiles



All α-fluorinated pronucleophiles were synthesized based on reported procedures.[55, 65-66] NMR spectra of the synthesized compounds match those in the literature: **1e**,[65] **1n**,[66] all others.[55]

General Procedure for the Synthesis of 3-Fluoroallylic Electrophiles

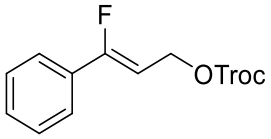


Intermediates **S1** were synthesized based on a reported procedure.[67]

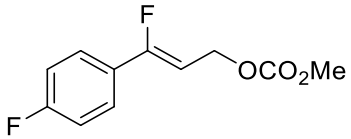
General procedure for converting intermediates **S1** into 3-fluoroallylic electrophiles **2**:
Under an atmosphere of N_2, to a solution of compound **S1** (2.0 mmol, 1.0 equiv) in dry DCM (5 mL) was added a solution of DIBAL-H in hexanes (1.0 M, 5.0 mL, 5.0 mmol, 2.5 equiv) dropwise at 0 ˚C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. The mixture was then cooled to 0 ˚C and quenched slowly with an aqueous solution of HCl (1 M). The organic layer was separated, and the aqueous layer was extracted with DCM (10 mL × 3). The

combined organic layer was then washed twice with a saturated aqueous solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. After evaporation of the organic solvent *in vacuo*, the crude product mixture was redissolved in dry DCM (10 mL). To this solution was added sequentially pyridine (0.48 mL, 6.0 mmol, 3.0 equiv) and methyl chloroformate (0.46 mL, 6.0 mmol, 3.0 equiv) at 0 ˚C. The reaction mixture was then warmed to room temperature and stirred overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (10 mL × 3). The combined organic layer was then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EA/hexanes) to afford the corresponding 3-fluoroallylic methyl carbonate **2**.

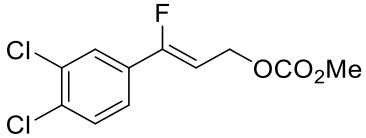
Compound **2aα** has been previously reported in the literature.[67]



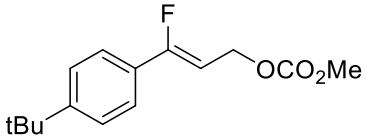
2aβ. Eluent: 0–5% EA/hexanes. White solid, 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.50 (m, 2H), 7.45 – 7.34 (m, 3H), 5.68 (dt, *J* = 34.6, 7.5 Hz, 1H), 5.02 (dd, *J* = 7.5, 1.9 Hz, 2H), 4.79 (s, 2H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.44 (d, *J* = 34.2 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.63 (d, *J* = 256.5 Hz), 154.05, 131.15 (d, *J* = 27.8 Hz), 130.13, 128.77 (d, *J* = 2.1 Hz), 124.90 (d, *J* = 7.2 Hz), 98.78 (d, *J* = 14.6 Hz), 94.50, 77.05, 62.28 (d, *J* = 8.5 Hz). HRMS (ESI): *m/z* for $C_{12}H_{10}Cl_3FO_3$ $[M]^+$ calcd.: 325.9680, found: 325.9651.



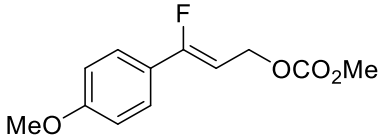
2b. Eluent: 5–10% EA/hexanes. Colorless oil, 91% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.48 (m, 2H), 7.12 – 7.02 (m, 2H), 5.58 (dt, *J* = 34.8, 7.4 Hz, 1H), 4.91 (dd, *J* = 7.4, 1.9 Hz, 2H), 3.81 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -111.07, -113.53 (d, *J* = 34.9 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.72 (d, *J* = 250.4 Hz), 159.32 (d, *J* = 255.2 Hz), 155.86, 127.58 (dd, *J* = 28.8, 3.3 Hz), 127.07 – 126.66 (m), 117.59 – 112.22 (m), 99.37 (d, *J* = 14.6 Hz), 61.09 (d, *J* = 8.3 Hz), 55.03. HRMS (ESI): *m/z* for $C_{11}H_{10}F_2O_3$ $[M]^+$ calcd.: 228.0598, found: 228.0605.



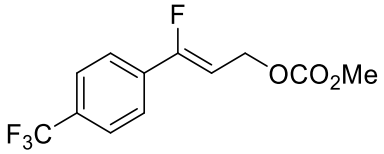
2c. Eluent: 5–10% EA/hexanes. White solid, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.1 Hz, 1H), 7.46 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.66 (dt, *J* = 34.7, 7.3 Hz, 1H), 4.91 (dd, *J* = 7.3, 2.0 Hz, 2H), 3.81 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.67 (d, *J* = 34.5 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.82 (d, *J* = 255.1 Hz), 155.81, 134.12, 133.29 (d, *J* = 2.2 Hz), 131.29 (d, *J* = 29.3 Hz), 130.82 (d, *J* = 1.9 Hz), 126.74 (d, *J* = 7.6 Hz), 123.95 (d, *J* = 7.0 Hz), 101.42 (d, *J* = 14.3 Hz), 60.86 (d, *J* = 8.2 Hz), 55.13. HRMS (ESI): *m/z* for $C_{11}H_9Cl_2FO_3$ $[M]^+$ calcd.: 277.9913, found: 277.9931.



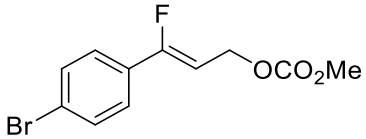
2d. Eluent: 5–10% EA/hexanes. Colorless oil, 67% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 5.60 (dt, *J* = 35.0, 7.4 Hz, 1H), 4.92 (dd, *J* = 7.4, 1.9 Hz, 2H), 3.80 (s, 3H), 1.32 (s, 9H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.82 (d, *J* = 34.8 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.33 (d, *J* = 255.3 Hz), 155.90, 153.29, 128.55 (d, *J* = 28.4 Hz), 125.65 (d, *J* = 2.0 Hz), 124.64 (d, *J* = 7.1 Hz), 98.71 (d, *J* = 14.8 Hz), 61.30 (d, *J* = 8.3 Hz), 54.98, 34.92, 31.30. HRMS (ESI): *m/z* for $C_{15}H_{19}FO_3Na$ $[M+Na]^+$ calcd.: 289.1210, found: 289.1216.



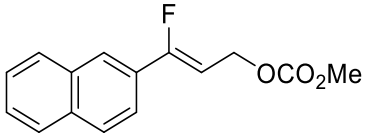
2e. Eluent: 10% EA/hexanes. Colorless oil, 83% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 6.92 – 6.87 (m, 2H), 5.51 (dt, *J* = 35.1, 7.5 Hz, 1H), 4.90 (dd, *J* = 7.5, 1.9 Hz, 2H), 3.83 (s, 3H), 3.80 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.77 (d, *J* = 34.8 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.97, 160.30 (d, *J* = 254.9 Hz), 155.92, 126.42 (d, *J* = 7.2 Hz), 123.92 (d, *J* = 28.4 Hz), 114.11, 97.50 (d, *J* = 14.9 Hz), 61.37, 55.48, 54.96. HRMS (ESI): *m/z* for $C_{12}H_{13}FO_4K$ $[M+K]^+$ calcd.: 279.0430, found: 279.0429.



2f. Eluent: 5–10% EA/hexanes. White solid, 77% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (apparent s, 4H), 5.76 (dt, *J* = 34.7, 7.3 Hz, 1H), 4.95 (dd, *J* = 7.2, 2.1 Hz, 2H), 3.82 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -63.44, -114.84 (d, *J* = 34.8 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.55 (d, *J* = 255.1 Hz), 155.82, 134.68 (d, *J* = 28.8 Hz), 131.74 (q, *J* = 32.8 Hz), 126.62, 125.77 (d, *J* = 2.6 Hz), 125.09 (d, *J* = 7.2 Hz), 124.81, 123.01, 121.20, 102.02 (d, *J* = 14.4 Hz), 60.93 (d, *J* = 8.1 Hz), 55.13. HRMS (ESI): *m/z* for $C_{12}H_{10}F_4O_3$ $[M]^+$ calcd.: 278.0566, found: 278.0597.

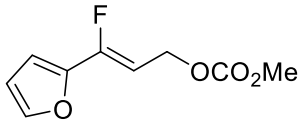


2g. Eluent: 10% EA/hexanes. Colorless oil, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.46 (m, 2H), 7.46 – 7.34 (m, 2H), 5.65 (dt, *J* = 34.8, 7.4 Hz, 1H), 4.91 (dd, *J* = 7.3, 2.0 Hz, 2H), 3.81 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.63 (d, *J* = 35.2 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.16 (d, *J* = 255.1 Hz), 155.84, 131.98, 130.28 (d, *J* = 28.9 Hz), 126.34 (d, *J* = 7.0 Hz), 124.22, 100.28 (d, *J* = 14.6 Hz), 61.04 (d, *J* = 8.3 Hz), 55.08. HRMS (ESI): *m/z* for $C_{11}H_{10}BrFO_3$ $[M]^+$ calcd.: 287.9797, found: 287.9790.

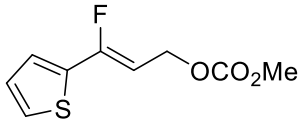


2h. Eluent: 5–10% EA/hexanes. Faint yellow solid, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.91 – 7.79 (m, 3H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.52 (dt, *J* = 6.3, 3.5 Hz, 2H), 5.79 (dt, *J* = 35.1, 7.4 Hz, 1H), 4.99 (dd, *J* = 7.4, 2.0 Hz, 2H), 3.82 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.63 (d, *J* = 35.3 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.14 (d, *J* =

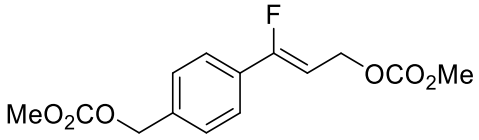
255.0 Hz), 155.93, 133.90, 128.78, 128.58 (m, J = 2.9 Hz), 128.42, 127.85, 127.24, 126.91, 124.58 (d, J = 7.6 Hz), 121.94 (d, J = 6.8 Hz), 100.10 (d, J = 14.9 Hz), 61.31 (d, J = 8.7 Hz), 55.05. HRMS (ESI): m/z for $C_{15}H_{13}FO_3K$ $[M+K]^+$ calcd.: 299.0481, found: 299.0498.



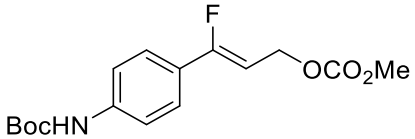
2i. Eluent: 5% EA/hexanes. Colorless oil, 76% yield. **NOTE**: due to its instability, this compound is stored as a dilute DCM solution in the freezer. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, J = 2.6 Hz, 1H), 6.59 (d, J = 3.4 Hz, 1H), 6.44 (dd, J = 3.5, 1.8 Hz, 1H), 5.57 (dt, J = 35.1, 7.7 Hz, 1H), 4.88 (dd, J = 7.7, 1.8 Hz, 2H), 3.80 (d, J = 0.9 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.36 (d, J = 35.0 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.78, 152.38 (d, J = 245.4 Hz), 145.98 (d, J = 49.4 Hz), 143.97, 111.56, 109.26, 98.21 (d, J = 10.5 Hz), 60.44 (d, J = 7.1 Hz), 54.95. HRMS (ESI): m/z for $C_9H_9FO_4Na$ $[M+Na]^+$ calcd.: 223.0377, found: 223.0375.



2j. Eluent: 10% EA/hexanes. Faint yellow oil, 87% yield. **NOTE**: due to its instability, this compound is stored as a dilute DCM solution in the freezer. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (ddd, J = 5.1, 2.7, 1.3 Hz, 1H), 7.27 (dd, J = 3.7, 1.2 Hz, 1H), 7.03 (ddd, J = 5.0, 3.7, 1.2 Hz, 1H), 5.49 (dt, J = 34.3, 7.6 Hz, 1H), 4.87 (dd, J = 7.6, 1.9 Hz, 2H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.92 (d, J = 34.0 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.72, 155.82, 155.04, 134.37 (d, J = 34.0 Hz), 127.77, 127.09, 126.06 (d, J = 3.8 Hz), 98.76 (d, J = 14.1 Hz), 60.91 (d, J = 7.2 Hz), 55.08. HRMS (ESI): m/z for $C_9H_9FO_3SK$ $[M+K]^+$ calcd.: 254.9888, found: 254.9901.

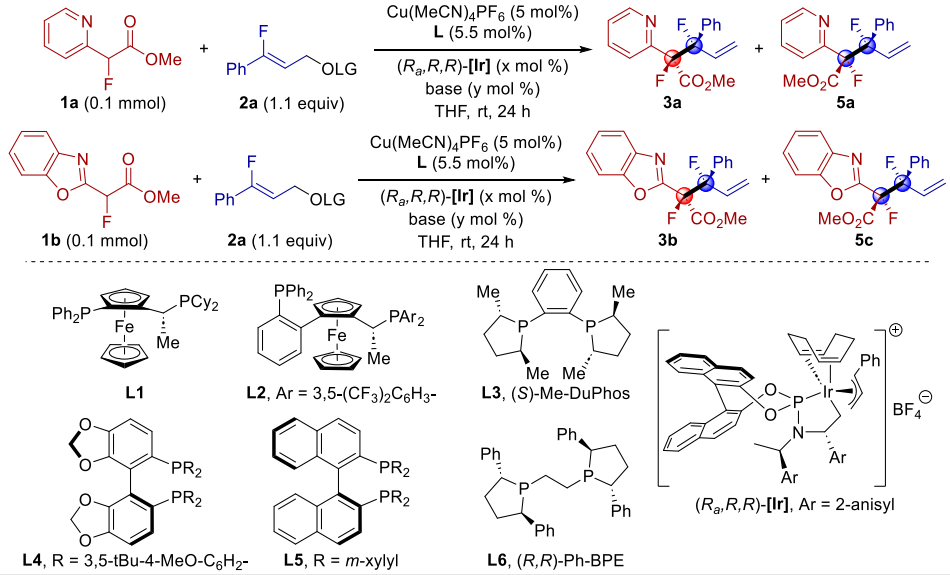


2k. Eluent: 15–20% EA/pentane. White powder, 35% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.47 (m, 2H), 7.38 (d, J = 8.1 Hz, 2H), 5.65 (dt, J = 34.9, 7.3 Hz, 1H), 5.16 (s, 2H), 4.91 (dd, J = 7.4, 1.9 Hz, 2H), 3.79 (d, J = 2.3 Hz, 6H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.47 (d, J = 34.9 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.55 (d, J = 255.4 Hz), 155.77 (d, J = 10.8 Hz), 137.06, 131.45 (d, J = 28.4 Hz), 128.40, 125.00 (d, J = 7.1 Hz), 100.05 (d, J = 14.5 Hz), 69.00, 61.07 (d, J = 8.3 Hz), 55.02 (apparent d, J = 11.0 Hz). HRMS (ESI): *m/z* for $C_{14}H_{15}FO_6Na$ $[M+Na]^+$ calcd.: 321.0745, found: 321.0765.



2l. Eluent: 10–15% EA/hexanes. White solid, 78% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.55 (s, 1H), 5.54 (dt, J = 35.2, 7.5 Hz, 1H), 4.90 (dd, J = 7.5, 1.7 Hz, 2H), 3.80 (d, J = 0.8 Hz, 3H), 1.52 (s, 9H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.41 (d, J = 35.0 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.02 (d, J = 254.8 Hz), 155.91, 152.50, 139.96, 125.98, 125.77 (d, J = 7.2 Hz), 118.18, 98.14 (d, J = 14.9 Hz), 81.16, 61.29 (d, J = 8.4 Hz), 55.00, 28.45. HRMS (ESI): *m/z* for $C_{16}H_{20}FNO_5Na$ $[M+Na]^+$ calcd.: 348.1218, found: 348.1215.

Table 3.4. Development of reaction conditions for the allylic substitution between 2-fluoro-2-azaarylacetates **1a**, **1b** and (*Z*)-3-fluoro-3-phenylallylic electrophile **2a**.



entry	Nu	–OLG	ligand	x	base	y	yield (%)[a]	dr[b]	ee (%)[c]
1	**1a**	–OCO_2Me	**L1**	5	K_2CO_3	120	90	1:2	*n.d.*
2	**1a**	–OCO_2Me	**L2**	5	K_2CO_3	120	88	1:12	>99
3	**1a**	–OCO_2Me	*ent*-**L2**	5	K_2CO_3	120	85	3:1	*n.d.*
4	**1a**	–OCO_2Me	**L3**	5	K_2CO_3	120	16	1:1	*n.d.*
5	**1a**	–OCO_2Me	**L4**	5	K_2CO_3	120	53	2:1	*n.d.*
6	**1a**	–OCO_2Me	**L5**	5	K_2CO_3	120	88	1:4	*n.d.*
7	**1a**	–OCO_2Me	**L6**	5	K_2CO_3	120	77[d]	13:1	>99
8	**1a**	–OCO_2Me	**L6**	5	K_2CO_3	50	83[d]	15:1	99
9	**1a**	–OCO_2Me	*ent*-**L6**	5	K_2CO_3	50	80[d]	1:20	97
10	**1a**	–OCO_2Me	**L6**	0	K_2CO_3	50	0	-	-
11	**1a**	–OCO_2Me	none[e]	5	K_2CO_3	50	0	-	-
12	**1a**	–OCO_2Me	**L6**	5	Li_2CO_3	120	0	-	-
13	**1a**	–OCO_2Me	**L6**	5	Na_2CO_3	120	65	4:1	*n.d.*
14	**1a**	–OCO_2Me	**L6**	5	K_3PO_4	120	71	16:1	*n.d.*
15	**1a**	–OCO_2Me	**L6**	5	Cs_2CO_3	120	15	>20:1	*n.d.*
16	**1a**	–OCO_2Me	**L6**	5	DBU	120	0	-	-
17	**1a**	–OCO_2Me	**L6**	5	DBN	120	0	-	-
18	**1a**	–OCO_2Me	**L6**	5	DIPEA	120	66	5:1	*n.d.*
19	**1a**	–OCO_2Me	**L6**	5	TBD	120	0	-	-
20	**1a**	–OBz	**L6**	5	K_2CO_3	120	11	10:1	*n.d.*
21	**1a**	–OBoc	**L6**	5	K_2CO_3	120	16	12:1	*n.d.*
22	**1a**	–OTFA	**L6**	5	K_2CO_3	120	<10	*n.d.*	*n.d.*
23	**1a**	–OPO_3Et_2	**L6**	5	K_2CO_3	120	<10	*n.d.*	*n.d.*
24	**1a**	–OTroc	**L6**	3	K_2CO_3	120	81[d]	13:1	>99
25	**1a**	–OTroc	*ent*-**L6**	5	K_2CO_3	120	87[d]	1:16	>99
26	**1a**	–OTroc	**L6**	3	K_2CO_3	50	84[d]	10:1	>99
27	**1b**	–OCO_2Me	**L6**	3	K_2CO_3	100	43	3:1	*n.d.*

28	**1b**	–OTroc	**L6**	3	K_2CO_3	100	83[d]	12:1	>99
29	**1b**	–OTroc	*ent*-**L6**	3	K_2CO_3	100	73[d]	1:5	>99

[a]Combined NMR yield of both diastereomers, unless specified otherwise; [b]the ratio of **3a** to **5a** or **3b** to **5c**; [c]*n.d.* stands for not determined; [d]isolated yield of one diastereomer; [e]in the absence of $Cu(MeCN)_4PF_6$ and ligand.

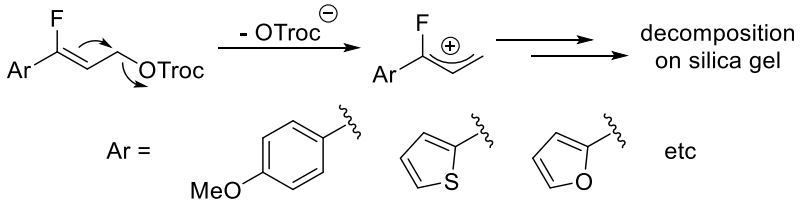
The Effect of Base

The effect of a series of inorganic and organic bases on the yield and the stereoselectivity of the catalytic reaction between substrates **1a** and **2aα** (-OLG = -OCO_2Me, Table 3.4, entries 7, 12–19) was analyzed. The reaction with K_2CO_3 formed the product **3a** with better yield and higher stereoselectivity than those with any other base tested. Since the dissociated leaving group, methyl carbonate, undergoes decarboxylation and generates one equivalent of methoxide anion *in situ*, only 50 mol % (30 mol % for some pronucleophiles, see Table 3.2) of K_2CO_3 is required for this reaction (Table 3.4, entries 8–9).

*The Effect of Leaving Group on the Electrophile **2a***

The effect of a series of leaving groups in the electrophile **2a** on the yield and the stereoselectivity for the fluoroallylation of substrates **1a** and **1b** was tested (entries 8–9, 20–29). Reactions with leaving groups other than -OCO_2Me or -OTroc (Troc = 2,2,2-trichloroethoxycarbonyl) formed the product **3a** in very poor yields. For substrate **1a**, which contained the six-membered pyridine substituent, reactions with **2aα** (-OLG = -OCO_2Me) or **2aβ** (-OLG = -OTroc) afforded the product **3a** or **5a** with comparable yield and stereoselectivity (Table 3.4, entries 8–9, 24–25). In contrast, for substrate **1b**, which contained the five-membered benzoxazole substituent, the reaction with **2aβ** formed the product **3b** with much higher yield and diastereoselectivity than that with **2aα**.

Since -OTroc is a better leaving group than -OCO_2Me, several (*Z*)-3-fluoro-3-arylallylic electrophiles that contain the -OTroc leaving group and an electron-donating arene undergo spontaneous decomposition on silica gel, presumably through a stabilized, cationic allyl intermediate (eq 3.4.1). As a result, we chose methyl carbonate as the leaving group on substrates **2b-l** for the fluoroallylation of pronucleophile **1g** (Table 3.3).

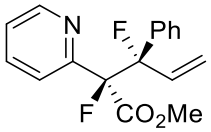


(3.4.1)

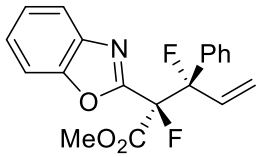
General Procedure for the Synthesis of Compounds Containing the Vicinal Difluoride Motif

In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with $[Cu(MeCN)_4]PF_6$ (9.3 mg, 0.025 mmol), (*R,R*)-Ph-BPE (13.9 mg, 0.0275 mmol) and THF (1.5 mL) and stirred at room temperature for 30 min to prepare the stock solution of the copper complex (solution **A**). Another 4 mL vial equipped with a magnetic stir bar was charged with the pronucleophile (0.11 mmol) and solution **A** (0.33 mL), and the resulting solution was stirred at room temperature for 15 min (solution **B**). To a third 4 mL vial equipped with a magnetic stir bar was added sequentially the **[Ir]** catalyst (3.3 mg, 0.0030 mmol, 3 mol % or 5.5 mg, 0.0050 mmol, 5 mol %), K_2CO_3 (4.1 mg, 0.030 mmol, 0.30 equiv or 13.8 mg, 0.100 mmol, 1.000 equiv), the electrophile (0.11 mmol), THF (0.3 mL) and finally solution **B** (0.3 mL). The vial was capped, and

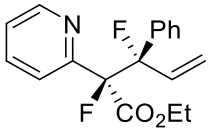
the reaction mixture was stirred at room temperature in the glovebox for 24 h. The reaction vial was then removed from the glovebox, and hexane (approx. 1.5 mL) was added to the reaction mixture and stirred for 30 min. The mixture was then filtered through a plug (approx. 3 cm) of silica gel, eluted with 1:1 (v/v) hexanes/EtOAc (100% EtOAc was used for highly polar products), and the filtrate was concentrated *in vacuo*. To this crude mixture was added a stock solution of 1,3,5-trimethoxybenzene (TMB) in $CDCl_3$ (0.05 mL, 0.67 M, 0.33 equiv) as the internal standard. This mixture was further diluted with $CDCl_3$ (approx. 0.55 mL) and subjected to analysis by ^1H and ^{19}F NMR to determine the diastereomeric ratio (dr) of the reaction. Finally, the crude mixture was purified by column chromatography to afford the vicinal difluoride product as either a single diastereomer or a mixture of diastereomers.



3a. Eluent: 5–15% EA/hexanes. Colorless oil, 83% yield, dr 15:1, ee 99%. $[\alpha]_D^{26}$ = +64.5; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.59 – 8.53 (m, 1H), 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.45 (dd, *J* = 6.2, 2.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.25 (ddd, *J* = 7.5, 5.0, 1.3 Hz, 1H), 6.91 (ddd, *J* = 21.7, 17.2, 11.2 Hz, 1H), 5.36 – 5.24 (m, 2H), 3.77 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -164.07 (d, *J* = 21.7 Hz), -164.74 (d, *J* = 6.9 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.88 (dd, *J* = 22.5, 5.0 Hz), 153.77 (d, *J* = 26.5 Hz), 148.35, 137.44 (d, *J* = 22.8 Hz), 136.44, 134.95 (dd, *J* = 17.4, 3.0 Hz), 127.95, 127.17 (dd, *J* = 9.2, 2.6 Hz), 123.96, 122.69 (dd, *J* = 6.6, 3.7 Hz), 117.13 (d, *J* = 13.8 Hz), 99.03 (d, *J* = 25.4 Hz), 97.69 (d, *J* = 24.5 Hz), 96.42 (d, *J* = 23.7 Hz), 53.02. HRMS (ESI): *m/z* for $C_{17}H_{15}F_2NO_2Na$ $[M+Na]^+$ calcd.: 326.0963, found: 326.0955.

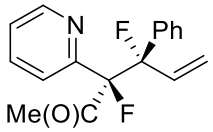


3b. Eluent: 0–10% EA/hexanes. Colorless oil, 83% yield, dr 12:1, ee >99%. $[\alpha]_D^{26}$ = +2.1; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 1H), 7.59 – 7.54 (m, 1H), 7.48 (ddd, *J* = 6.5, 3.2, 1.3 Hz, 2H), 7.38 (dtd, *J* = 18.1, 7.4, 1.3 Hz, 2H), 7.32 (dd, *J* = 5.1, 2.0 Hz, 3H), 6.86 (ddd, *J* = 21.1, 17.1, 11.2 Hz, 1H), 5.55 (dd, *J* = 17.1, 0.8 Hz, 1H), 5.46 – 5.38 (m, 1H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.23 (dd, *J* = 23.4, 3.8 Hz), 157.05 (d, *J* = 25.7 Hz), 150.70, 140.05, 136.16 (d, *J* = 22.2 Hz), 133.28 (dd, *J* = 17.2, 2.8 Hz), 129.02, 128.18, 126.38 (d, *J* = 9.0 Hz), 124.99, 121.12, 118.29 (d, *J* = 13.9 Hz), 111.16, 97.32 (d, *J* = 23.5 Hz), 95.76 (d, *J* = 23.5 Hz), 95.03 (d, *J* = 28.3 Hz), 93.40 (d, *J* = 28.1 Hz), 53.66. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -162.98 – -165.52 (m). HRMS (ESI): *m/z* for $C_{19}H_{16}F_2NO_3$ $[M+H]^+$ calcd.: 344.1093, found: 344.1090.

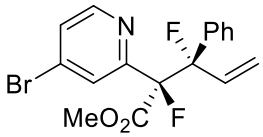


3c. Eluent: 0–15% EA/hexanes. Colorless oil, 71% yield, dr 5:1, ee >99%. $[\alpha]_D^{26}$ = +53.7; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.54 – 8.38 (m, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.44 – 7.31 (m, 2H), 7.27 – 7.19 (m, 3H), 7.19 – 7.14 (m, 1H), 6.84 (ddd, *J* = 21.8, 17.2, 11.2 Hz, 1H), 5.27 – 5.12 (m, 2H), 4.24 – 4.09 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.25 (dd, *J* = 22.1, 5.0 Hz), 153.78 (d, *J* = 26.5 Hz), 148.20,

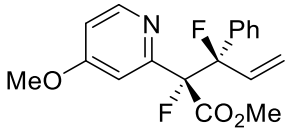
137.46 (d, *J* = 23.0 Hz), 136.25, 134.95 (dd, *J* = 17.5, 3.0 Hz), 128.45, 127.78, 127.14 (dd, *J* = 9.0, 2.6 Hz), 123.75, 122.63 (dd, *J* = 6.5, 3.8 Hz), 116.88 (d, *J* = 14.1 Hz), 98.63 (d, *J* = 25.0 Hz), 97.65 (d, *J* = 23.4 Hz), 97.30 (d, *J* = 25.2 Hz), 96.38 (d, *J* = 23.5 Hz), 62.16, 13.89. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.14 – -163.58 (m), -164.24 (d, *J* = 6.8 Hz). HRMS (ESI): *m/z* for $C_{18}H_{17}F_2NO_2Na$ $[M+Na]^+$ calcd.: 340.1119, found: 340.1110.



3d. Eluent: 0 – 10% EA/hexanes. White solid, 78% yield, dr 17:1, ee >99%. $[\alpha]_D^{26}$ = +105.0; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 – 8.54 (m, 1H), 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.56 (dt, *J* = 8.1, 1.4 Hz, 1H), 7.41 (dt, *J* = 7.5, 1.6 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.26 – 7.23 (m, 1H), 6.87 (ddd, *J* = 22.3, 17.3, 11.1 Hz, 1H), 5.30 – 5.23 (m, 2H), 2.16 (dd, *J* = 5.6, 0.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.41 (dd, *J* = 26.6, 2.3 Hz), 153.26 (d, *J* = 26.1 Hz), 148.26 (d, *J* = 2.3 Hz), 137.65 (d, *J* = 23.4 Hz), 136.41 (d, *J* = 1.6 Hz), 134.83 (dd, *J* = 17.1, 3.6 Hz), 128.35 (d, *J* = 1.5 Hz), 127.81, 127.04 (dd, *J* = 9.4, 2.5 Hz), 123.71, 122.80 (dd, *J* = 7.0, 3.1 Hz), 116.71 (dd, *J* = 14.4, 1.8 Hz), 102.03 (d, *J* = 23.6 Hz), 100.47 (d, *J* = 23.6 Hz), 97.92 (d, *J* = 23.0 Hz), 96.40 (d, *J* = 23.2 Hz), 27.93 (d, *J* = 3.2 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.24 (d, *J* = 21.9 Hz), -163.59 (t, *J* = 6.1 Hz). HRMS (ESI): *m/z* for $C_{17}H_{16}F_2NO$ $[M+H]^+$ calcd.: 288.1195, found: 288.1187.

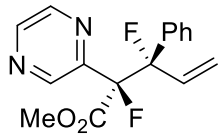


3e. Eluent: 5–15% EA/hexanes. Colorless oil, 85% yield, dr >20:1, ee 99%. $[\alpha]_D^{26}$ = +67.6; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 5.2 Hz, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.44 (ddd, *J* = 12.2, 5.9, 2.4 Hz, 4H), 7.32 (d, *J* = 1.9 Hz, 2H), 6.90 (ddd, *J* = 21.8, 17.2, 11.2 Hz, 1H), 5.42 – 5.19 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.20 (dd, *J* = 22.3, 5.2 Hz), 154.90 (d, *J* = 26.9 Hz), 148.89 (d, *J* = 2.3 Hz), 136.93 (d, *J* = 23.0 Hz), 134.47 (dd, *J* = 17.4, 3.0 Hz), 133.18, 128.70, 127.94, 127.30, 127.01 (dd, *J* = 9.2, 2.4 Hz), 126.08 (dd, *J* = 7.5, 3.8 Hz), 117.31 (dd, *J* = 13.9, 1.7 Hz), 98.58 (d, *J* = 25.4 Hz), 97.66 (d, *J* = 23.3 Hz), 96.97 (d, *J* = 25.3 Hz), 96.14 (d, *J* = 23.4 Hz), 53.05. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.31 – -163.76 (m), -164.53 (d, *J* = 7.2 Hz). HRMS (ESI): *m/z* for $C_{17}H_{14}BrF_2NO_2K$ $[M+K]^+$ calcd.: 419.9808, found: 419.9809.

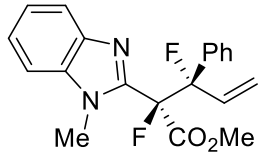


***ent*-3f**. Eluent: 10–20% EA/hexanes. Colorless oil, 69% yield, dr >20:1, ee >99%. $[\alpha]_D^{26}$ = -56.0; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 5.7 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.05 – 7.00 (m, 1H), 6.91 (ddd, *J* = 21.6, 17.2, 11.2 Hz, 1H), 6.76 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.37 – 5.25 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.68 (dd, *J* = 22.4, 4.9 Hz), 165.93, 155.25 (d, *J* = 26.2 Hz), 149.40 (d, *J* = 2.3 Hz), 137.39 (d, *J* = 23.1 Hz), 134.81 (dd, *J* = 17.5, 3.0 Hz), 128.48 (d, *J* = 1.5 Hz), 127.82, 127.12 (dd, *J* = 9.3, 2.5 Hz), 116.99 (dd, *J* = 13.8, 1.7 Hz), 110.63, 108.29 (dd, *J* = 7.3, 3.4 Hz), 98.94 (d, *J* = 25.4 Hz), 97.83 – 97.13 (m), 96.13 (d, *J* = 22.6 Hz), 55.25, 52.92. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -

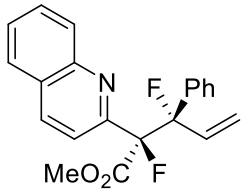
163.34 (d, J = 21.5 Hz), -163.68 (d, J = 6.9 Hz). HRMS (ESI): *m/z* for $C_{18}H_{17}F_2NO_3Na$ $[M+Na]^+$ calcd.: 356.1068, found: 356.1079.



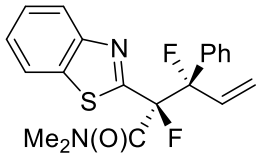
3g. Eluent: 10–20% EA/hexanes. White solid, 96% yield, dr 17:1, ee >99%. $[\alpha]_D^{26}$ = +40.1; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 8.61 – 8.39 (m, 2H), 7.52 – 7.37 (m, 2H), 7.31 (dd, J = 5.1, 2.0 Hz, 3H), 6.85 (ddd, J = 21.9, 17.2, 11.1 Hz, 1H), 5.71 – 4.57 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.10 (dd, J = 22.5, 4.6 Hz), 149.52 (d, J = 25.8 Hz), 144.76, 144.37 (dd, J = 7.1, 4.9 Hz), 142.78, 136.70 (d, J = 22.8 Hz), 134.27 (dd, J = 17.7, 2.8 Hz), 128.95 (d, J = 1.5 Hz), 128.20, 126.86 (dd, J = 9.3, 2.6 Hz), 117.70 (dd, J = 13.9, 1.7 Hz), 98.29 (d, J = 26.2 Hz), 97.65 (d, J = 23.7 Hz), 96.69 (d, J = 26.1 Hz), 96.12 (d, J = 23.7 Hz), 53.28. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -164.58 (dd, J = 21.8, 7.0 Hz), -167.04 (d, J = 6.9 Hz). HRMS (ESI): *m/z* for $C_{16}H_{15}F_2N_2O_2$ $[M+H]^+$ calcd.: 305.1096, found: 305.1080.



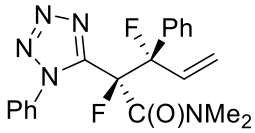
3h. Eluent: 5–15% EA/hexanes. Opaque oil, 83% yield, dr 11:1, ee 99%. $[\alpha]_D^{26}$ = +62.4; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, J = 8.0 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.36 (dt, J = 9.6, 6.3 Hz, 5H), 7.32 – 7.27 (m, 1H), 7.05 (ddd, J = 21.4, 17.1, 11.2 Hz, 1H), 5.35 – 5.27 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -157.32, -167.43 (d, J = 13.5 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.04 (dd, J = 22.4, 7.7 Hz), 145.10 (d, J = 25.2 Hz), 141.56, 136.77, 136.60 (d, J = 2.5 Hz), 134.36 (d, J = 2.7 Hz), 134.23 (d, J = 2.7 Hz), 129.03 (d, J = 1.8 Hz), 128.09, 127.49 (dd, J = 8.7, 2.2 Hz), 123.70, 122.53, 120.83, 117.78 (d, J = 14.4 Hz), 109.65, 99.05 – 98.20 (m), 97.64 – 96.49 (m), 53.42, 31.76 (dd, J = 10.5, 8.4 Hz). HRMS (ESI): *m/z* for $C_{20}H_{19}F_2N_2O_2$ $[M+H]^+$ calcd.: 357.1409, found: 357.1420.



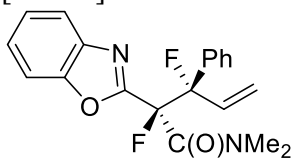
3i. Eluent: 0–10% EA/hexanes. Colorless oil, 82% yield, dr 8:1, ee 97%. $[\alpha]_D^{26}$ = +87.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, J = 8.7 Hz, 1H), 8.10 (dd, J = 8.5, 1.0 Hz, 1H), 7.81 (dd, J = 8.2, 1.4 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.60 – 7.50 (m, 3H), 7.32 (dd, J = 5.0, 2.4 Hz, 3H), 6.98 (ddd, J = 21.4, 17.2, 11.2 Hz, 1H), 5.31 (dd, J = 17.4, 1.1 Hz, 1H), 5.27 – 5.21 (m, 1H), 3.80 (s, 3H). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -161.62 (d, J = 13.8 Hz), -163.57 (d, J = 7.7 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.81 (dd, J = 22.4, 5.6 Hz), 154.08 (d, J = 26.6 Hz), 146.66 (d, J = 2.0 Hz), 137.59 (d, J = 23.1 Hz), 136.36, 135.15 (dd, J = 17.4, 3.0 Hz), 130.16, 129.70, 128.67, 127.96, 127.89, 127.56, 127.44, 127.37 (d, J = 2.6 Hz), 119.82 (t, J = 5.0 Hz), 117.22 (dd, J = 13.7, 1.6 Hz), 99.88 (d, J = 24.8 Hz), 98.53 – 97.63 (m), 96.62 (d, J = 23.1 Hz), 52.92. HRMS (ESI): *m/z* for $C_{21}H_{18}F_2NO_2$ $[M+H]^+$ calcd.: 354.1300, found: 354.1290.



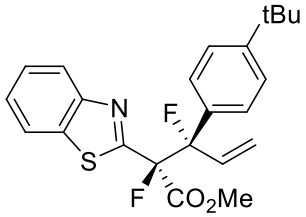
3j. Eluent: 5–20% EA/hexanes. White solid, 78% yield, dr 9:1, ee 98%. $[\alpha]_D^{26}$ = +115.8; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.66 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.44 (td, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.15 (ddd, *J* = 22.3, 17.5, 11.4 Hz, 1H), 5.26 – 5.17 (m, 2H), 2.92 (d, *J* = 1.3 Hz, 3H), 2.74 (d, *J* = 4.9 Hz, 3H). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -150.46, -157.50 (dd, *J* = 22.1, 6.5 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.87 (dd, *J* = 18.8, 6.0 Hz), 163.74 (d, *J* = 27.2 Hz), 151.97, 137.42 (d, *J* = 23.0 Hz), 135.86, 135.19 (dd, *J* = 16.6, 2.8 Hz), 128.60 (d, *J* = 1.7 Hz), 127.94 (dd, *J* = 9.2, 2.2 Hz), 127.75, 126.03 (d, *J* = 29.1 Hz), 124.26, 121.45, 117.09 (dd, *J* = 14.6, 1.6 Hz), 100.71 (d, *J* = 23.9 Hz), 99.64 – 98.66 (m), 97.55 (d, *J* = 22.5 Hz), 37.71, 37.49, 37.37. HRMS (ESI): *m/z* for $C_{20}H_{18}F_2N_2OSNa$ $[M+Na]^+$ calcd.: 395.1000, found: 395.1022.



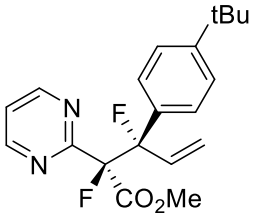
3k. Eluent: 10–25% EA/hexanes. White solid, 73% yield, dr >20:1, ee >99%. $[\alpha]_D^{26}$ = +12.0; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.48 (m, 5H), 7.43 – 7.37 (m, 2H), 7.33 – 7.28 (m, 3H), 7.19 (ddd, *J* = 20.9, 17.2, 11.1 Hz, 1H), 5.54 – 5.43 (m, 2H), 2.55 (s, 3H), 2.49 (d, *J* = 4.7 Hz, 3H). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -149.41 (br), -155.15. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.37 (dd, *J* = 19.9, 4.8 Hz), 151.30 (dd, *J* = 26.9, 2.4 Hz), 136.63 (d, *J* = 23.1 Hz), 134.97 (dd, *J* = 16.3, 2.4 Hz), 134.18, 130.83, 128.94, 127.80 (d, *J* = 9.2 Hz), 127.67, 126.95 (d, *J* = 2.5 Hz), 118.50 (d, *J* = 13.8 Hz), 99.17 (d, *J* = 21.0 Hz), 97.65 (d, *J* = 20.9 Hz), 96.53 (d, *J* = 26.7 Hz), 94.86 (d, *J* = 26.4 Hz), 37.69, 36.74 (dd, *J* = 15.6, 2.9 Hz). HRMS (ESI): *m/z* for $C_{20}H_{19}F_2N_5ONa$ $[M+Na]^+$ calcd.: 406.1450, found: 406.1467.



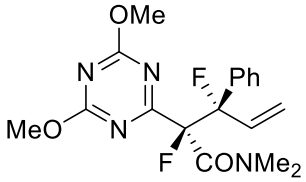
3l. Eluent: 5–20% EA/hexanes. White solid, 99% yield (sum of both diastereomers), dr 14:1, ee 95%. $[\alpha]_D^{26}$ = +66.2; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 – 7.79 (m, 1H), 7.74 – 7.67 (m, 2H), 7.66 – 7.61 (m, 1H), 7.46 – 7.32 (m, 5H), 7.22 – 7.11 (m, 1H), 5.36 – 5.12 (m, 2H), 2.92 (d, *J* = 1.4 Hz, 3H), 2.76 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.41 (dd, *J* = 18.9, 6.3 Hz), 158.56 (d, *J* = 26.1 Hz), 150.80, 140.28, 137.21 (d, *J* = 22.6 Hz), 135.47 (dd, *J* = 16.6, 2.6 Hz), 128.81 (d, *J* = 1.6 Hz), 128.15 (dd, *J* = 9.0, 2.3 Hz), 127.86, 126.29, 125.08, 121.19, 117.27 (d, *J* = 15.0 Hz), 111.36, 99.13 (d, *J* = 21.9 Hz), 97.55 (dd, *J* = 22.9, 16.9 Hz), 95.81 (d, *J* = 24.0 Hz), 37.68, 37.37 (d, *J* = 14.2 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -157.32 (d, *J* = 22.7 Hz), -160.07. HRMS (ESI): *m/z* for $C_{20}H_{19}F_2N_2O_2$ $[M+H]^+$ calcd.: 357.1409, found: 357.1400.



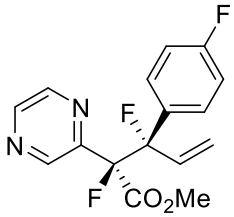
3m. Eluent: 0–10% EA/hexanes. Colorless oil, 85% yield (sum of both diastereomers), dr 8:1, ee >99%. $[\alpha]_D^{26}$ = +35.2; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.40 – 7.30 (m, 4H), 6.88 (ddd, *J* = 21.8, 17.1, 11.2 Hz, 1H), 5.50 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.41 – 5.35 (m, 1H), 3.85 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.35 (dd, *J* = 23.2, 3.8 Hz), 162.45 (d, *J* = 28.6 Hz), 152.15, 151.90, 135.53, 133.69 (dd, *J* = 17.5, 2.5 Hz), 133.17 (d, *J* = 22.8 Hz), 126.37 (dd, *J* = 9.1, 2.4 Hz), 126.19, 125.94, 125.07, 124.24, 121.41, 117.82 (d, *J* = 13.5 Hz), 97.94 (d, *J* = 26.6 Hz), 97.36 (d, *J* = 23.7 Hz), 96.60 (d, *J* = 26.6 Hz), 96.07 (d, *J* = 23.8 Hz), 53.47, 34.56, 31.21. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -155.15 (d, *J* = 7.5 Hz), -163.47 (dd, *J* = 22.1, 7.3 Hz). HRMS (ESI): *m/z* for $C_{23}H_{24}F_2NO_2S$ $[M+H]^+$ calcd.: 416.1491, found: 416.1497.



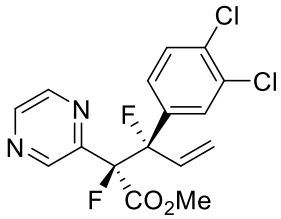
3n. Eluent: 10–40% EA/hexanes. Colorless oil, 84% yield (sum of both diastereomers), dr 11:1, ee >99%. $[\alpha]_D^{26}$ = +4.2; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.9 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 4.9 Hz, 1H), 6.98 (ddd, *J* = 21.8, 17.2, 11.2 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.29 – 5.23 (m, 1H), 3.76 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.14 (dd, *J* = 23.2, 5.3 Hz), 162.43 (d, *J* = 23.0 Hz), 156.91 (d, *J* = 1.9 Hz), 151.37, 134.99 (d, *J* = 17.1 Hz), 134.25 (d, *J* = 23.0 Hz), 126.66 (dd, *J* = 8.8, 2.3 Hz), 124.83, 120.98, 116.66 (d, *J* = 14.1 Hz), 98.77 – 97.66 (m), 97.17 – 96.15 (m), 53.03, 34.51, 31.24. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.44 (dd, *J* = 21.7, 9.4 Hz), -164.31. HRMS (ESI): *m/z* for $C_{20}H_{22}F_2N_2O_2K$ $[M+K]^+$ calcd.: 399.1281, found: 399.1274.



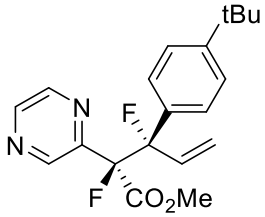
3o. Eluent: 15–35% EA/hexanes. White solid, 62% yield, dr 3:1, ee 97%. $[\alpha]_D^{26}$ = +110.1; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.33 (q, *J* = 8.3 Hz, 4H), 5.21 (dd, *J* = 14.6, 8.9 Hz, 2H), 4.06 (s, 6H), 2.84 (s, 3H), 2.74 (d, *J* = 3.8 Hz, 3H). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -157.48 – -158.06 (m), -164.45. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.11 (d, *J* = 22.7 Hz), 172.25 (d, *J* = 3.1 Hz), 163.98 (dd, *J* = 19.8, 6.7 Hz), 138.30 (d, *J* = 23.2 Hz), 137.06 (dd, *J* = 16.5, 3.2 Hz), 128.53 – 128.26 (m), 127.46, 115.64 (d, *J* = 14.7 Hz), 99.17 (dd, *J* = 40.1, 22.3 Hz), 97.83 (d, *J* = 21.5 Hz), 97.32 (d, *J* = 23.9 Hz), 55.69, 36.98, 29.71. HRMS (ESI): *m/z* for $C_{18}H_{21}F_2N_4O_3$ $[M+H]^+$ calcd.: 379.1576, found: 379.1569.



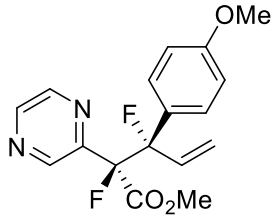
4a. Eluent: 10–20% EA/hexanes. Colorless oil, 77% yield, dr 16:1, ee >99%. $[\alpha]_D^{26}$ = +50.8; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.56 (d, *J* = 2.5 Hz, 1H), 8.51 (t, *J* = 2.0 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.84 (ddd, *J* = 21.9, 17.2, 11.1 Hz, 1H), 5.37 – 5.27 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.89 (dd, *J* = 22.4, 5.2 Hz), 163.71 (d, *J* = 2.0 Hz), 162.06 (d, *J* = 2.1 Hz), 149.33 (d, *J* = 26.1 Hz), 144.76, 144.21 (dd, *J* = 7.1, 5.0 Hz), 142.67 (d, *J* = 2.1 Hz), 134.00 (dd, *J* = 17.4, 2.8 Hz), 132.52 (dd, *J* = 23.3, 3.3 Hz), 128.99 (td, *J* = 8.6, 2.7 Hz), 117.86 (d, *J* = 13.4 Hz), 115.04 (d, *J* = 21.6 Hz), 98.91 – 95.07 (m), 53.18. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -112.70, -161.97 – -163.48 (m), -167.24. HRMS (ESI): *m/z* for $C_{16}H_{14}F_3N_2O_2$ $[M+H]^+$ calcd.: 323.1002, found: 323.1024.



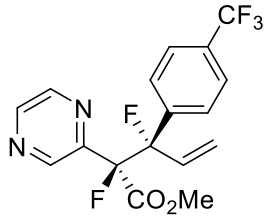
4b. Eluent: 10–25% EA/hexanes. White solid, 64% yield, dr 15:1, ee >99%. $[\alpha]_D^{26}$ = +43.5; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 8.53 (t, *J* = 2.0 Hz, 1H), 7.59 (t, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.31 (dt, *J* = 8.6, 1.7 Hz, 1H), 6.81 (ddd, *J* = 21.8, 17.2, 11.2 Hz, 1H), 5.37 – 5.25 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.67 (dd, *J* = 22.1, 5.9 Hz), 149.06 (d, *J* = 26.5 Hz), 144.97, 144.14 (dd, *J* = 7.0, 4.8 Hz), 142.72 (d, *J* = 2.2 Hz), 136.89 (d, *J* = 24.0 Hz), 133.63 – 132.99 (m), 132.48, 130.02, 129.32 (dd, *J* = 10.0, 2.7 Hz), 126.49 (dd, *J* = 8.9, 2.7 Hz), 118.52 (d, *J* = 13.4 Hz), 98.63 – 94.81 (m), 53.31. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.07 (dd, *J* = 22.4, 7.8 Hz), -167.31 (d, *J* = 7.4 Hz). HRMS (ESI): *m/z* for $C_{16}H_{13}Cl_2F_2N_2O_2$ $[M+H]^+$ calcd.: 373.0317, found: 373.0322.



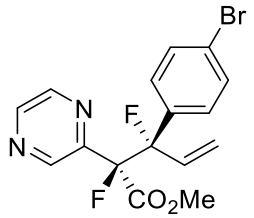
4c. Eluent: 5–20% EA/hexanes. White solid, 79% yield, dr 24:1, ee >99%. $[\alpha]_D^{26}$ = +34.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 1.8 Hz, 1H), 8.63 – 8.43 (m, 2H), 7.44 – 7.28 (m, 4H), 6.85 (ddd, *J* = 22.2, 17.2, 11.2 Hz, 1H), 5.39 – 5.18 (m, 2H), 3.78 (s, 3H), 1.29 (d, *J* = 0.8 Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.07 (dd, *J* = 22.3, 4.9 Hz), 149.56 (d, *J* = 26.1 Hz), 144.59, 144.34 (dd, *J* = 7.0, 5.0 Hz), 142.60 (d, *J* = 2.1 Hz), 134.36 (dd, *J* = 17.6, 2.8 Hz), 133.54 (d, *J* = 22.9 Hz), 126.51 (dd, *J* = 8.9, 2.4 Hz), 125.03, 117.22 (d, *J* = 13.9 Hz), 98.97 – 95.36 (m), 77.83 – 76.27 (m), 53.11, 34.55, 31.21. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -164.09 (dd, *J* = 22.6, 7.5 Hz), -166.86 (d, *J* = 7.4 Hz). HRMS (ESI): *m/z* for $C_{20}H_{22}F_2N_2O_2K$ $[M+K]^+$ calcd.: 399.1281, found: 399.1251.



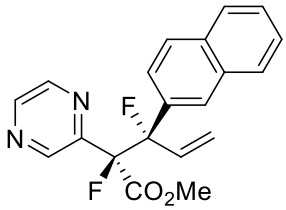
4d. Eluent: 10–20% EA/hexanes. White solid, 63% yield, dr 15:1, ee >99%. $[\alpha]_D^{26}$ = +30.8; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 8.55 (d, *J* = 2.5 Hz, 1H), 8.51 (t, *J* = 1.9 Hz, 1H), 7.35 (dd, *J* = 8.9, 1.6 Hz, 2H), 6.92 – 6.74 (m, 3H), 5.36 – 5.23 (m, 2H), 3.78 (d, *J* = 4.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.09 (dd, *J* = 22.5, 4.8 Hz), 159.85 (d, *J* = 1.7 Hz), 149.55 (d, *J* = 26.1 Hz), 144.62, 144.32 (dd, *J* = 7.0, 5.0 Hz), 142.63 (d, *J* = 2.1 Hz), 134.33 (dd, *J* = 17.4, 2.7 Hz), 128.61 (d, *J* = 23.5 Hz), 128.27 (dd, *J* = 8.8, 2.7 Hz), 117.35 (d, *J* = 13.8 Hz), 113.43, 98.70 – 97.20 (m), 97.06 – 95.79 (m), 55.23, 53.14. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -162.19 – -163.37 (m), -166.88 (d, *J* = 6.9 Hz). HRMS (ESI): *m/z* for $C_{17}H_{16}F_2N_2O_3$ $[M]^+$ calcd.: 334.1129, found: 334.1125.



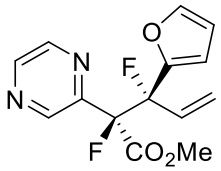
4e. Eluent: 10–20% EA/hexanes. Colorless oil, 66% yield, dr 17:1, ee 99%. $[\alpha]_D^{26}$ = +35.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.58 (d, *J* = 2.5 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 7.60 (s, 4H), 6.88 (ddd, *J* = 21.9, 17.1, 11.2 Hz, 1H), 5.44 – 5.24 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.73 (dd, *J* = 22.2, 5.4 Hz), 149.07 (d, *J* = 26.3 Hz), 144.93, 144.17, 142.73, 140.58 (d, *J* = 23.1 Hz), 133.56 (dd, *J* = 17.4, 2.9 Hz), 131.62 – 130.19 (m), 127.49 (dd, *J* = 9.4, 2.6 Hz), 125.03 (d, *J* = 4.3 Hz), 122.73, 118.39 (d, *J* = 14.2 Hz), 98.49 – 97.03 (m), 96.80 – 95.56 (m), 53.30. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.84, -164.07 (dd, *J* = 22.0, 7.6 Hz), -167.43 (d, *J* = 7.5 Hz). HRMS (ESI): *m/z* for $C_{17}H_{14}F_5N_2O_2$ $[M+H]^+$ calcd.: 373.0970, found: 373.0946.



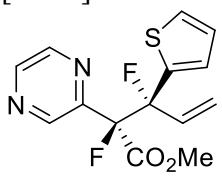
4f. Eluent: 10–20% EA/hexanes. White solid, 78% yield, dr 14:1, ee >99%. $[\alpha]_D^{26}$ = +34.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.56 (s, 1H), 8.51 (s, 1H), 7.46 (dd, *J* = 8.7, 0.8 Hz, 2H), 7.37 – 7.28 (m, 2H), 6.82 (ddd, *J* = 21.8, 17.1, 11.2 Hz, 1H), 5.35 – 5.26 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.81 (dd, *J* = 22.2, 5.2 Hz), 149.21 (d, *J* = 26.2 Hz), 144.83, 144.18 (dd, *J* = 7.1, 4.9 Hz), 142.71 (d, *J* = 2.2 Hz), 135.74 (d, *J* = 23.4 Hz), 133.72 (dd, *J* = 17.4, 2.8 Hz), 131.25, 128.71 (dd, *J* = 9.2, 2.7 Hz), 123.37 (d, *J* = 1.9 Hz), 118.07 (dd, *J* = 13.9, 1.7 Hz), 98.90 – 96.91 (m), 96.82 – 95.37 (m), 53.25. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.78 (d, *J* = 14.7 Hz), -167.31 (d, *J* = 7.1 Hz). HRMS (ESI): *m/z* for $C_{16}H_{14}BrF_2N_2O_2$ $[M+H]^+$ calcd.: 383.0201, found: 383.0186.



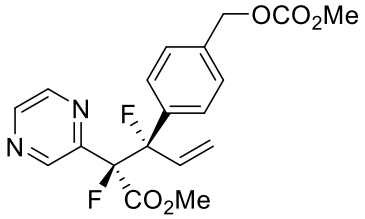
4g. Eluent: 10–20% EA/hexanes. White solid, 82% yield, dr 15:1, ee >99%. $[\alpha]_D^{26}$ = +17.6; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.53 (dd, *J* = 10.7, 2.1 Hz, 2H), 7.93 (s, 1H), 7.87 – 7.75 (m, 3H), 7.55 (dt, *J* = 8.7, 1.8 Hz, 1H), 7.50 (apparent hept, *J* = 4.9 Hz, 2H), 6.99 (ddd, *J* = 21.8, 17.2, 11.2 Hz, 1H), 5.45 – 5.30 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.02 (dd, *J* = 22.5, 4.7 Hz), 149.46 (d, *J* = 26.0 Hz), 144.70, 144.29 (dd, *J* = 7.1, 5.0 Hz), 142.71 (d, *J* = 2.1 Hz), 134.26 (dd, *J* = 17.5, 2.8 Hz), 134.05 (d, *J* = 22.9 Hz), 133.12, 132.62, 128.60, 127.78, 127.52, 126.86, 126.75 (dd, *J* = 10.0, 2.1 Hz), 126.38, 124.02 (dd, *J* = 8.6, 3.1 Hz), 118.14 – 117.32 (m), 98.69 – 97.49 (m), 97.13 – 95.95 (m), 53.20. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.39 (dd, *J* = 22.1, 6.7 Hz), -166.68 (d, *J* = 7.3 Hz). HRMS (ESI): *m/z* for $C_{20}H_{16}F_2N_2O_2Na$ $[M+Na]^+$ calcd.: 377.1072, found: 377.1044.



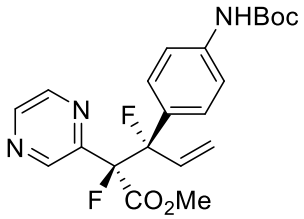
4h. Eluent: 10–20% EA/hexanes. **NOTE**: the column chromatography should be performed rapidly because this compound decomposes gradually on silica gel. This compound decomposes slowly at room temperature and should be stored in a freezer. Colorless liquid, 57% yield, dr 8:1, ee 98%. $[\alpha]_D^{26}$ = +26.8; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.60 (d, *J* = 2.6 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 7.49 – 7.37 (m, 1H), 6.61 (ddd, *J* = 20.4, 17.2, 11.3 Hz, 1H), 6.53 (dt, *J* = 3.5, 1.9 Hz, 1H), 6.45 – 6.35 (m, 1H), 5.39 – 5.23 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.81 (dd, *J* = 22.1, 5.6 Hz), 149.37 (d, *J* = 26.6 Hz), 148.90 (d, *J* = 27.7 Hz), 144.90, 144.51 – 144.33 (m), 143.57 (d, *J* = 3.1 Hz), 142.57 (d, *J* = 2.1 Hz), 132.04 (dd, *J* = 18.8, 2.7 Hz), 118.40 (d, *J* = 12.1 Hz), 111.48 (dd, *J* = 4.7, 2.5 Hz), 110.74 (d, *J* = 2.2 Hz), 97.29 (dd, *J* = 204.0, 24.9 Hz), 93.19 (dd, *J* = 189.3, 22.4 Hz), 53.24. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -157.98 (dd, *J* = 20.1, 12.0 Hz), -165.24 (d, *J* = 12.0 Hz). HRMS (ESI): *m/z* for $C_{14}H_{13}F_2N_2O_3$ $[M+H]^+$ calcd.: 295.0889, found: 295.0870.



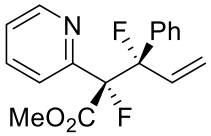
4i. Eluent: 10–20% EA/hexanes. White solid, 75% yield, dr 18:1, ee >99%. $[\alpha]_D^{26}$ = +50.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.59 (s, 1H), 8.52 (s, 1H), 7.36 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.24 – 7.15 (m, 1H), 7.00 (ddd, *J* = 5.3, 3.6, 1.8 Hz, 1H), 6.77 (ddd, *J* = 21.1, 17.2, 11.1 Hz, 1H), 5.37 – 5.23 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.82 (dd, *J* = 22.0, 5.6 Hz), 149.39 (d, *J* = 26.8 Hz), 144.88, 144.56 – 144.14 (m), 142.59 (d, *J* = 2.1 Hz), 138.77 (d, *J* = 25.4 Hz), 133.96 (dd, *J* = 18.0, 2.8 Hz), 128.16 – 127.66 (m), 127.31, 126.77, 117.82 (d, *J* = 13.2 Hz), 97.85 (dd, *J* = 202.9, 25.2 Hz), 95.62 (dd, *J* = 190.7, 22.7 Hz), 53.20. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -148.07 – -151.12 (m), -164.95 (d, *J* = 9.0 Hz). HRMS (ESI): *m/z* for $C_{14}H_{12}F_2N_2O_2SNa$ $[M+Na]^+$ calcd.: 333.0480, found: 333.0497.



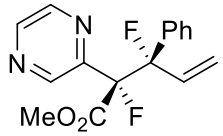
4j. Eluent: 15–35% EA/hexanes. White solid, 85% yield, dr 17:1, ee >99%. $[\alpha]_D^{26}$ = +33.6; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.56 (d, *J* = 2.5 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.85 (ddd, *J* = 21.9, 17.3, 11.1 Hz, 1H), 5.36 – 5.27 (m, 2H), 5.14 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.90 (dd, *J* = 22.4, 5.0 Hz), 155.66, 149.32 (d, *J* = 26.2 Hz), 144.75, 144.25 (dd, *J* = 7.1, 5.0 Hz), 142.68 (d, *J* = 2.1 Hz), 136.94 (d, *J* = 23.0 Hz), 134.02 (dd, *J* = 17.4, 3.0 Hz), 127.79, 127.17 (dd, *J* = 9.2, 2.5 Hz), 117.77 (d, *J* = 13.0 Hz), 98.49 – 97.17 (m), 96.84 – 95.73 (m), 68.93, 54.97, 53.21. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -164.08 (dd, *J* = 21.9, 7.4 Hz), -167.14 (d, *J* = 7.2 Hz). HRMS (ESI): *m/z* for $C_{19}H_{18}F_2N_2O_5K$ $[M+K]^+$ calcd.: 431.0816, found: 431.0811.



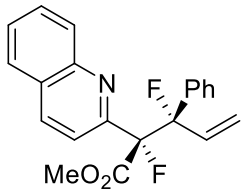
4k. On Et_3N/MeOH deactivated silica gel, eluent: 15–40% EA/hexanes. Colorless oil, 79% yield, dr 13:1, ee >99%. $[\alpha]_D^{26}$ = -32.9 (measured for ***ent*-4k**); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.54 (d, *J* = 2.5 Hz, 1H), 8.51 (t, *J* = 1.9 Hz, 1H), 7.38 – 7.28 (m, 4H), 6.81 (ddd, *J* = 21.7, 17.1, 11.2 Hz, 1H), 6.59 (s, 1H), 5.35 – 5.25 (m, 2H), 3.77 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.99 (dd, *J* = 22.5, 4.7 Hz), 152.51, 149.49 (d, *J* = 26.1 Hz), 144.64, 144.26 (dd, *J* = 7.1, 4.9 Hz), 142.65 (d, *J* = 2.2 Hz), 138.97 (d, *J* = 1.6 Hz), 134.19 (dd, *J* = 17.4, 2.7 Hz), 130.83 (d, *J* = 23.4 Hz), 127.71 (dd, *J* = 9.1, 2.6 Hz), 117.63, 117.51 (d, *J* = 13.6 Hz), 98.28 (d, *J* = 26.3 Hz), 96.95 – 95.69 (m), 80.80, 53.15, 28.31. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.32 (d, *J* = 19.5 Hz), -166.88 (d, *J* = 7.1 Hz). HRMS (ESI): *m/z* for $C_{21}H_{24}F_2N_3O_4$ $[M+H]^+$ calcd.: 420.1730, found: 420.1739.



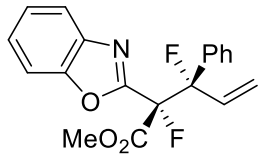
5a. Eluent: 5–15% EA/hexanes. White solid, 80% yield, dr 20:1, ee 97%. $[\alpha]_D^{26}$ = -79.8; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.70 (td, *J* = 7.8, 1.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.25 (m, 6H), 6.77 (dddd, *J* = 20.7, 17.2, 11.1, 1.3 Hz, 1H), 5.42 – 5.30 (m, 2H), 3.71 (s, 3H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -164.17 (d, *J* = 20.7 Hz), -165.51 (d, *J* = 6.9 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.72 (d, *J* = 24.7 Hz), 153.29 (dd, *J* = 25.0, 2.4 Hz), 148.72, 138.08 (d, *J* = 22.8 Hz), 136.45, 134.72 (dd, *J* = 17.7, 3.8 Hz), 128.41, 127.88, 126.51 – 125.97 (m), 124.01, 122.56 (dd, *J* = 8.2, 2.9 Hz), 117.13 (d, *J* = 13.3 Hz), 98.27 (d, *J* = 26.9 Hz), 97.76 (d, *J* = 24.7 Hz), 96.95 (d, *J* = 26.6 Hz), 96.48 (d, *J* = 24.6 Hz), 52.91. HRMS (ESI): *m/z* for $C_{17}H_{16}F_2NO_2$ $[M+H]^+$ calcd.: 304.1144, found: 304.1153.



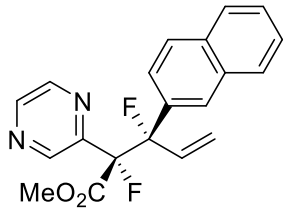
5b. Eluent: 5–20% EA/hexanes. Colorless oil, 82% yield, dr 17:1, ee >99%. $[\alpha]_D^{26}$ = -39.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.60 (s, 2H), 7.39 (dt, *J* = 7.2, 1.5 Hz, 2H), 7.33 (dd, *J* = 5.1, 2.2 Hz, 3H), 6.60 (dddd, *J* = 21.0, 17.0, 11.2, 2.1 Hz, 1H), 5.38 – 5.25 (m, 2H), 3.66 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.90 (d, *J* = 24.3 Hz), 148.95 (d, *J* = 23.9 Hz), 144.82, 144.16 (dd, *J* = 7.9, 4.1 Hz), 143.01 (d, *J* = 2.3 Hz), 137.36 (d, *J* = 22.6 Hz), 133.66 (dd, *J* = 18.2, 3.6 Hz), 128.69, 128.12 (d, *J* = 1.8 Hz), 125.79 (dd, *J* = 9.7, 2.7 Hz), 117.88 (dd, *J* = 13.4, 1.8 Hz), 97.83 – 96.67 (m), 96.22 – 95.16 (m), 53.04. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -165.30 (d, *J* = 4.7 Hz), -167.42. HRMS (ESI): *m/z* for $C_{16}H_{14}F_2N_2O_2K$ $[M+K]^+$ calcd.: 343.0655, found: 343.0636.



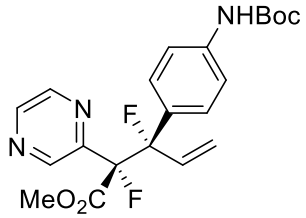
5c. Eluent: 0–10% EA/hexanes. Colorless oil, 68% yield, dr 6:1, ee 97%. $[\alpha]_D^{26}$ = +117.6 (measured for ***ent*-5c**); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.44 – 7.35 (m, 2H), 7.29 (dd, *J* = 5.4, 1.9 Hz, 3H), 6.99 (dddd, *J* = 20.5, 17.2, 11.2, 1.1 Hz, 1H), 5.45 – 5.26 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.63 (d, *J* = 24.8 Hz), 153.32 (dd, *J* = 24.4, 2.8 Hz), 146.81 (d, *J* = 2.1 Hz), 138.19 (d, *J* = 23.2 Hz), 136.32, 135.10 (dd, *J* = 17.5, 3.7 Hz), 130.05, 129.82, 128.31, 127.76, 127.71, 127.48 (d, *J* = 4.2 Hz), 126.43 (dd, *J* = 9.3, 2.6 Hz), 119.45 (dd, *J* = 6.9, 4.0 Hz), 116.97 (dd, *J* = 13.3, 1.8 Hz), 99.15 – 97.66 (m), 97.61 – 96.06 (m), 52.79. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -161.67 – -162.18 (m), -164.93 (d, *J* = 7.1 Hz). HRMS (ESI): *m/z* for $C_{21}H_{17}F_2NO_2Na$ $[M+Na]^+$ calcd.: 376.1119, found: 376.1137.



5d. On amine-coated silica gel, eluent: 0–15% EA/hexanes. White solid, 73% yield, dr 5:1, ee >99%. $[\alpha]_D^{26}$ = -2.6; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.40 (m, 5H), 6.89 (dddd, *J* = 19.2, 17.1, 11.1, 1.8 Hz, 1H), 5.49 (d, *J* = 17.1 Hz, 1H), 5.44 (dd, *J* = 11.1, 2.2 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.16 (d, *J* = 25.6 Hz), 157.59 – 156.54 (m), 150.79, 140.39, 136.76 (d, *J* = 22.4 Hz), 133.66 (dd, *J* = 18.1, 3.3 Hz), 129.07, 128.35, 126.53, 126.14 (dd, *J* = 9.5, 2.6 Hz), 125.20, 121.31, 118.58 (d, *J* = 13.1 Hz), 111.34, 96.57 (dd, *J* = 194.0, 25.0 Hz), 94.02 (dd, *J* = 200.9, 29.7 Hz), 53.56. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -163.24 (dd, *J* = 20.0, 9.1 Hz), -163.36 (d, *J* = 8.9 Hz). HRMS (ESI): *m/z* for $C_{19}H_{16}F_2NO_3$ $[M+H]^+$ calcd.: 344.1093, found: 344.1078.

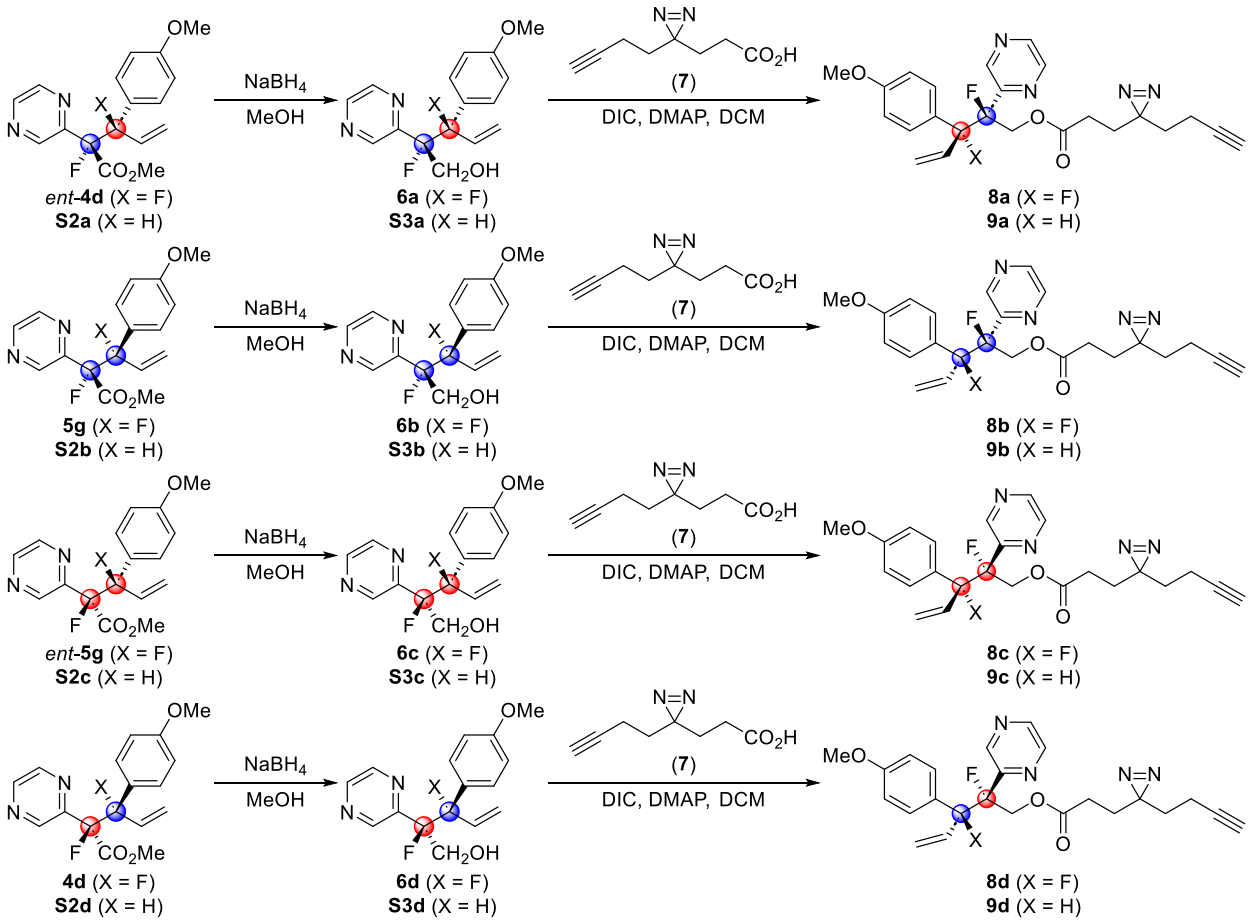


5e. Eluent: 10–20% EA/hexanes. Colorless oil, 82% yield, dr 10:1, ee >99%. $[\alpha]_D^{26}$ = -63.2; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 8.62 (s, 2H), 7.90 (s, 1H), 7.87 – 7.71 (m, 3H), 7.58 – 7.39 (m, 3H), 6.84 – 6.59 (m, 1H), 5.47 – 5.24 (m, 2H), 3.64 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.94 (d, *J* = 24.1 Hz), 149.02 (d, *J* = 23.4 Hz), 144.86, 144.16 (dd, *J* = 8.1, 4.0 Hz), 143.07, 134.81 (d, *J* = 22.5 Hz), 133.73 (dd, *J* = 18.0, 3.6 Hz), 133.05, 132.65 (d, *J* = 1.6 Hz), 128.53, 127.82 (d, *J* = 1.9 Hz), 127.57, 126.79, 126.44, 125.54 (dd, *J* = 10.4, 2.4 Hz), 123.23 (dd, *J* = 8.9, 3.0 Hz), 118.14 (dd, *J* = 13.4, 1.8 Hz), 97.94 – 96.91 (m), 95.97 (dd, *J* = 26.7, 4.6 Hz), 53.09. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -164.02 (d, *J* = 20.8 Hz), -166.94 (d, *J* = 5.2 Hz). HRMS (ESI): *m/z* for $C_{20}H_{17}F_2N_2O_2$ $[M+H]^+$ calcd.: 355.1253, found: 355.1220.



5f. On Et_3N/MeOH deactivated silica gel, eluent: 15–40% EA/hexanes. Colorless oil, 70% yield, dr 13:1, ee >99%. $[\alpha]_D^{26}$ = -35.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.52 (s, 2H), 7.31 – 7.16 (m, 4H), 6.59 – 6.41 (m, 2H), 5.30 – 5.19 (m, 2H), 3.62 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.05 (d, *J* = 24.3 Hz), 152.61, 149.15 (d, *J* = 24.1 Hz), 144.91, 144.24 (dd, *J* = 8.2, 4.1 Hz), 143.11 (d, *J* = 2.3 Hz), 138.93, 133.82 (dd, *J* = 17.8, 3.6 Hz), 131.68 (d, *J* = 23.3 Hz), 126.96 (dd, *J* = 9.6, 2.6 Hz), 117.93 (d, *J* = 13.4 Hz), 117.76, 97.91 – 97.13 (m), 95.87 (d, *J* = 25.1 Hz), 80.95, 53.22, 28.44. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -164.00 (d, *J* = 20.5 Hz), -167.58. HRMS (ESI): *m/z* for $C_{21}H_{24}F_2N_3O_4$ $[M+H]^+$ calcd.: 420.1730, found: 420.1748.

General Procedures for the Conjugation of Probes to the Vicinal Difluorides for Chemical Proteomics

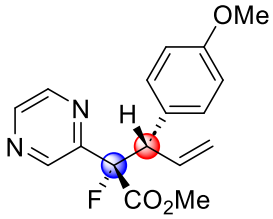


The procedure for the synthesis of **8a**, a vicinal difluoride compound conjugated to the crosslinking unit, is reported as a representative example:

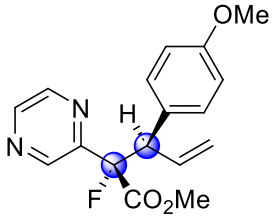
Compound *ent*-**4d** (0.0730 mmol, 24.4 mg, 1.00 equiv) was dissolved in MeOH (2 mL), and to this stirring solution was added $NaBH_4$ (3.65 mmol, 138 mg, 50.0 equiv) portion-wise at 0 ˚C. The resulting suspension was warmed to room temperature and stirred for 21 h. The reaction mixture was then concentrated *in vacuo*, dissolved in H_2O (4 mL), and extracted with DCM (5 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (50% – 60% EA/hexanes) to afford the primary alcohol **6a**.

To a 4 mL scintillation vial equipped with a magnetic stir bar was added primary alcohol **6a** (0.0263 mmol, 8.0 mg, 1.05 equiv), carboxylic acid **7** (0.025 mmol, 4.2 mg, 1.0 equiv), dicyclohexylcarbodiimide (DIC, 0.025 mmol, 3.2 mg, 1.0 equiv), 4-dimethylaminopyridine (DMAP, 0.013 mmol, 1.5 mg, 0.50 equiv), and anhydrous DCM (0.1 M). The reaction mixture was stirred at room temperature for 12 h and subsequently purified by column chromatography (15% – 35% EA/hexanes) to afford product **8a** as a colorless oil.

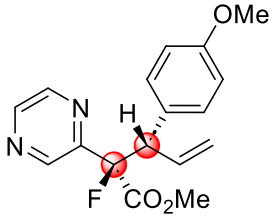
Mono-fluorinated compounds **S2a-d** were synthesized based on published procedures.[55]



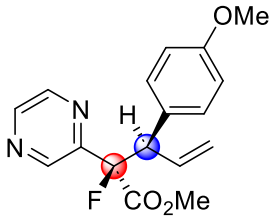
S2a. White solid, 82% yield, mixture of diastereomers (dr 11.2:1). Characterizations consistent with those of its enantiomer, **S2d**.



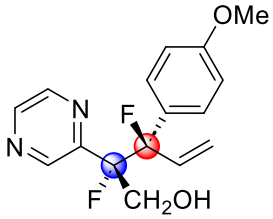
S2b. White solid, 70% yield, mixture of diastereomers (dr 5.3:1). Characterizations consistent with those of its enantiomer, **S2c**.



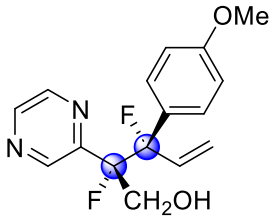
S2c. White solid, 88% yield, mixture of diastereomers (dr 3.7:1). $[\alpha]_D^{25}$ = 10.9; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.69 – 8.63 (m, 1H), 8.58 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.91 (ddd, *J* = 16.7, 10.2, 8.5 Hz, 1H), 5.01 – 4.84 (m, 2H), 4.68 (dd, *J* = 34.2, 8.6 Hz, 1H), 3.79 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.80 (d, *J* = 26.5 Hz), 159.10, 151.56 (d, *J* = 27.6 Hz), 144.63, 143.74 (d, *J* = 2.5 Hz), 142.72 (d, *J* = 11.7 Hz), 134.29 (d, *J* = 5.2 Hz), 130.52 (d, *J* = 2.4 Hz), 129.76, 119.45, 114.10, 99.27 (d, *J* = 195.2 Hz), 55.33, 54.63 (d, *J* = 17.9 Hz), 53.05. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -178.92 (d, *J* = 34.3 Hz). HRMS (ESI): *m/z* for $C_{17}H_{18}FN_2O_3$ $[M+H]^+$ calcd.: 317.1296, found: 317.1296.



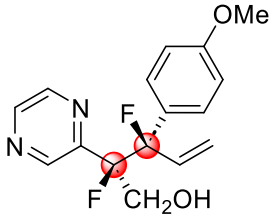
S2d. White solid, 86% yield, mixture of diastereomers (dr 12.5:1). $[\alpha]_D^{25}$ = 11.5; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.53 (s, 2H), 8.41 (s, 1H), 7.09 – 7.00 (m, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.26 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.34 – 5.20 (m, 2H), 4.62 (dd, *J* = 34.3, 8.8 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.26 (d, *J* = 25.7 Hz), 158.77, 151.45 (d, *J* = 27.6 Hz), 144.25, 143.35 (d, *J* = 2.7 Hz), 142.41 (d, *J* = 10.9 Hz), 134.94 (d, *J* = 4.8 Hz), 130.62 (d, *J* = 2.3 Hz), 128.83, 119.07, 113.81, 99.47 (d, *J* = 195.9 Hz), 55.19, 54.88 (d, *J* = 17.9 Hz), 53.35. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -179.70 (d, *J* = 34.6 Hz). HRMS (ESI): *m/z* for $C_{17}H_{18}FN_2O_3$ $[M+H]^+$ calcd.: 317.1296, found: 317.1293.



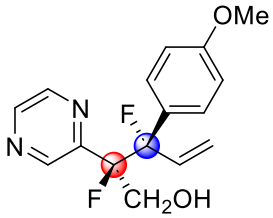
6a. Colorless oil, 87% yield. Characterizations consistent with those of its enantiomer, **6d**.



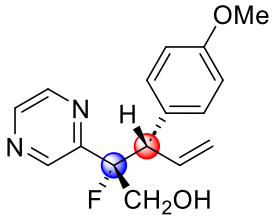
6b. Faint yellow solid, 64% yield. Characterizations consistent with those of its enantiomer, **6c**.



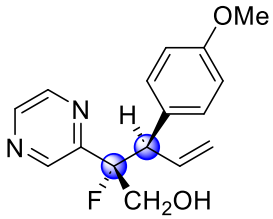
6c. Faint yellow solid, 83% yield. $[\alpha]_D^{25}$ = 55.1; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 1.4 Hz, 1H), 8.51 (d, *J* = 2.5 Hz, 1H), 8.45 (s, 1H), 7.13 – 7.07 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.50 (ddd, *J* = 22.4, 17.1, 11.2 Hz, 1H), 5.38 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.31 (dd, *J* = 11.2, 2.8 Hz, 1H), 4.46 (ddd, *J* = 31.7, 13.1, 5.3 Hz, 1H), 4.12 (t, *J* = 12.9 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.70, 152.14 (dd, *J* = 26.9, 2.5 Hz), 145.05 (dd, *J* = 10.4, 1.7 Hz), 144.04, 142.71 (d, *J* = 2.7 Hz), 134.03 (dd, *J* = 17.5, 3.7 Hz), 129.57 (d, *J* = 23.5 Hz), 127.41 (dd, *J* = 9.5, 2.5 Hz), 117.03 – 116.19 (m), 113.53, 100.62 (d, *J* = 25.3 Hz), 99.14 (d, *J* = 25.3 Hz), 97.86 (d, *J* = 22.9 Hz), 96.34 (d, *J* = 22.9 Hz), 63.72 (dd, *J* = 21.3, 2.4 Hz), 55.34. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -166.16 – -166.36 (m), -178.70 – -179.08 (m). HRMS (ESI): *m/z* for $C_{16}H_{17}F_2N_2O_2$ $[M+H]^+$ calcd.: 307.1253, found: 307.1253



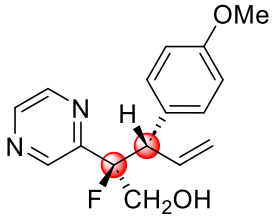
6d. Colorless oil, 86% yield. $[\alpha]_D^{25}$ = 14.3; ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.49 (d, *J* = 2.5 Hz, 1H), 8.41 (s, 1H), 7.20 – 7.13 (m, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.61 (dddd, *J* = 22.7, 17.1, 11.2, 1.4 Hz, 1H), 5.37 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.33 – 5.27 (m, 1H), 4.42 (ddd, *J* = 26.9, 12.7, 1.7 Hz, 1H), 4.18 (ddd, *J* = 13.0, 10.8, 2.4 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.72, 152.59 (d, *J* = 27.5 Hz), 144.99 (dd, *J* = 8.3, 2.2 Hz), 144.07, 142.36 (d, *J* = 2.3 Hz), 134.29 (dd, *J* = 17.6, 3.0 Hz), 129.73 (d, *J* = 23.3 Hz), 127.30 (dd, *J* = 9.7, 2.3 Hz), 116.43 (d, *J* = 14.2 Hz), 113.59 (d, *J* = 1.4 Hz), 99.03 (d, *J* = 26.4 Hz), 98.01 (d, *J* = 24.7 Hz), 97.57 (d, *J* = 26.5 Hz), 96.50 (d, *J* = 24.8 Hz), 63.97 (dd, *J* = 23.0, 2.8 Hz), 55.34. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -167.75 (d, *J* = 22.4 Hz), -174.51 (dd, *J* = 26.9, 10.8 Hz). HRMS (ESI): *m/z* for $C_{16}H_{17}F_2N_2O_2$ $[M+H]^+$ calcd.: 307.1253, found: 307.1253.



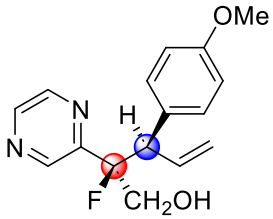
S3a. White solid, 67% yield. Characterizations consistent with those of its enantiomer, **S3d**.



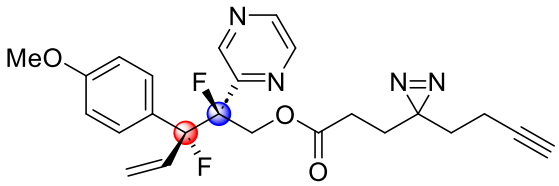
S3b. White solid, 77% yield. Characterizations consistent with those of its enantiomer, **S3c**.



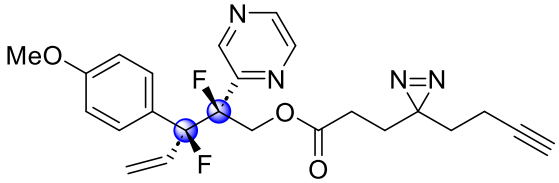
S3c. White solid, 77% yield, mixture of diastereomers (dr 3.3:1). $[\alpha]_D^{25}$ = 22.7; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.56 – 8.52 (m, 2H), 7.25 – 7.22 (m, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.07 (ddd, *J* = 17.0, 10.2, 9.2 Hz, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 4.76 (d, *J* = 17.0 Hz, 1H), 4.01 (dd, *J* = 31.0, 9.2 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.83 – 3.75 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.99, 155.67 (d, *J* = 27.7 Hz), 143.79, 143.64 (d, *J* = 11.3 Hz), 143.00 (d, *J* = 2.8 Hz), 135.30 (d, *J* = 6.3 Hz), 130.44, 130.34 (d, *J* = 2.1 Hz), 118.42, 114.14, 100.25 (d, *J* = 182.4 Hz), 66.32 (d, *J* = 24.8 Hz), 55.39, 54.67 (d, *J* = 19.2 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -183.06 – -183.58 (m). HRMS (ESI): *m/z* for $C_{16}H_{18}FN_2O_2$ $[M+H]^+$ calcd.: 289.1347, found: 289.1347.



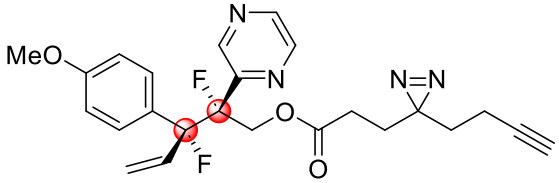
S3d. White solid, 58% yield, mixture of diastereomers (dr 11.1:1). $[\alpha]_D^{25}$ = -4.4; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 1.3 Hz, 1H), 8.38 (dd, *J* = 2.5, 1.0 Hz, 1H), 8.27 (s, 1H), 6.92 – 6.87 (m, 2H), 6.67 – 6.62 (m, 2H), 6.38 – 6.27 (m, 1H), 5.33 – 5.24 (m, 2H), 4.27 – 4.11 (m, 2H), 3.97 (dd, *J* = 32.9, 9.6 Hz, 1H), 3.70 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.62, 155.79 (d, *J* = 28.1 Hz), 143.49, 143.38 (d, *J* = 10.3 Hz), 142.54 (d, *J* = 2.8 Hz), 135.26 (d, *J* = 4.6 Hz), 130.52, 129.96 (d, *J* = 2.1 Hz), 118.84, 113.85, 99.58 (d, *J* = 182.5 Hz), 66.16 (d, *J* = 26.0 Hz), 55.22, 54.75 (d, *J* = 18.8 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -183.91 (ddd, *J* = 32.2, 21.8, 8.7 Hz). HRMS (ESI): *m/z* for $C_{16}H_{18}FN_2O_2$ $[M+H]^+$ calcd.: 289.1347, found: 289.1346.



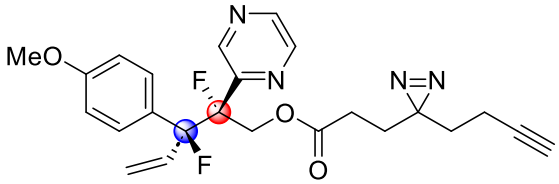
8a. Colorless oil, 88% yield. Characterizations consistent with those of its enantiomer, **8d**.



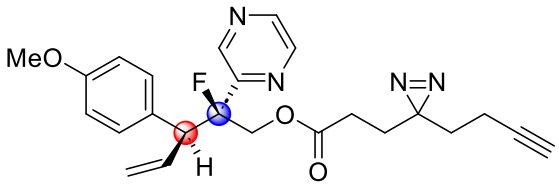
8b. Colorless oil, 75% yield. Characterizations consistent with those of its enantiomer, **8c**.



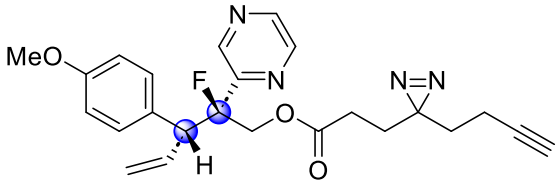
8c. Colorless oil, 82% yield. $[\alpha]_D^{25}$ = 52.0; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.58 – 8.55 (m, 1H), 8.53 (d, *J* = 2.5 Hz, 1H), 8.39 (s, 1H), 7.08 (dd, *J* = 8.9, 1.5 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.50 (ddd, *J* = 22.3, 17.1, 11.2 Hz, 1H), 5.46 – 5.40 (m, 1H), 5.36 – 5.30 (m, 1H), 5.03 (ddd, *J* = 34.4, 12.3, 2.0 Hz, 1H), 4.65 (td, *J* = 12.2, 1.7 Hz, 1H), 3.78 (s, 3H), 1.97 – 1.80 (m, 5H), 1.62 – 1.57 (m, 2H), 1.53 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.50, 159.87, 151.38 (dd, *J* = 26.8, 2.5 Hz), 144.48 (d, *J* = 10.8 Hz), 144.21, 142.78 (d, *J* = 2.7 Hz), 133.59 (dd, *J* = 17.3, 3.6 Hz), 129.13 (d, *J* = 23.6 Hz), 127.48 (dd, *J* = 9.2, 2.4 Hz), 117.15 (d, *J* = 14.4 Hz), 113.62, 99.19 (d, *J* = 25.3 Hz), 97.92 (d, *J* = 25.3 Hz), 97.53 (d, *J* = 22.2 Hz), 96.26 (d, *J* = 22.1 Hz), 82.65, 69.39, 64.60 (dd, *J* = 18.8, 2.5 Hz), 55.36, 32.22, 28.17, 27.93, 27.47, 13.32. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -166.57 (d, *J* = 22.1 Hz), -179.03 (d, *J* = 33.1 Hz). HRMS (ESI): *m/z* for $C_{24}H_{25}F_2N_4O_3$ $[M+H]^+$ calcd.: 455.1889, found: 455.1885.



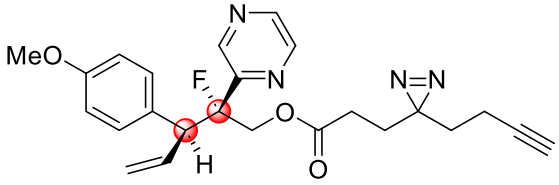
8d. Colorless oil, 81% yield. $[\alpha]_D^{25}$ = 34.6; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.54 – 8.50 (m, 1H), 8.44 (d, *J* = 2.5 Hz, 1H), 8.21 (s, 1H), 7.05 – 6.97 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.58 (dddd, *J* = 22.1, 17.1, 11.2, 2.3 Hz, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.44 (dd, *J* = 11.1, 3.2 Hz, 1H), 5.12 (ddd, *J* = 34.9, 12.4, 3.0 Hz, 1H), 4.82 (t, *J* = 12.2 Hz, 1H), 3.74 (s, 3H), 1.99 – 1.84 (m, 5H), 1.61 (td, *J* = 7.6, 2.3 Hz, 2H), 1.53 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.58, 159.75, 151.27 (d, *J* = 27.1 Hz), 144.00 (d, *J* = 9.5 Hz), 143.91, 142.79 (d, *J* = 2.5 Hz), 133.99 – 133.42 (m), 129.51 (d, *J* = 22.7 Hz), 126.96 (dd, *J* = 9.9, 2.4 Hz), 117.12 (d, *J* = 13.9 Hz), 113.59, 98.58 (d, *J* = 28.9 Hz), 97.35 (d, *J* = 28.4 Hz), 96.08 (d, *J* = 25.8 Hz), 82.65, 69.39, 64.42 (dd, *J* = 17.9, 3.2 Hz), 55.32, 32.23, 28.21, 27.95, 27.48, 13.33. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -169.62 (d, *J* = 22.0 Hz), -176.44 (dd, *J* = 34.7, 12.3 Hz). HRMS (ESI): *m/z* for $C_{24}H_{24}F_2N_4O_3Na$ $[M+Na]^+$ calcd.: 477.1708, found: 477.1704.



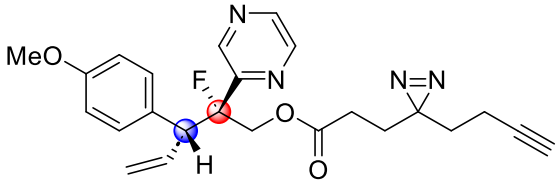
9a. Colorless oil, 48% yield, mixture of diastereomers (dr >20:1). Characterizations consistent with those of its enantiomer, **9d**.



9b. Colorless oil, 63% yield, mixture of diastereomers (dr 13.6:1). $[\alpha]_D^{25}$ = -21.4; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.70 (t, *J* = 1.5 Hz, 1H), 8.57 (dt, *J* = 2.5, 1.3 Hz, 1H), 8.53 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.02 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 4.93 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.78 (d, *J* = 17.1 Hz, 1H), 4.56 (dd, *J* = 33.0, 12.3 Hz, 1H), 4.22 (t, *J* = 12.6 Hz, 1H), 4.02 (dd, *J* = 29.9, 8.9 Hz, 1H), 3.80 (s, 3H), 1.97 – 1.80 (m, 5H), 1.60 – 1.55 (m, 2H, overlaps with H_2O peak), 1.52 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.37, 159.18, 154.27 (d, *J* = 28.0 Hz), 143.80, 143.37 (dd, *J* = 7.2, 4.4 Hz), 134.92 (d, *J* = 6.5 Hz), 130.21 (d, *J* = 2.3 Hz), 129.95, 118.70, 114.36, 99.67 (d, *J* = 186.0 Hz), 82.65, 69.40, 67.68 (d, *J* = 20.6 Hz), 55.39, 55.20 (d, *J* = 18.9 Hz), 32.22, 28.15, 27.90, 27.46, 13.32. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -181.58 (d, *J* = 12.9 Hz). HRMS (ESI): *m/z* for $C_{24}H_{26}FN_4O_3$ $[M+H]^+$ calcd.: 437.1984, found: 437.1982.

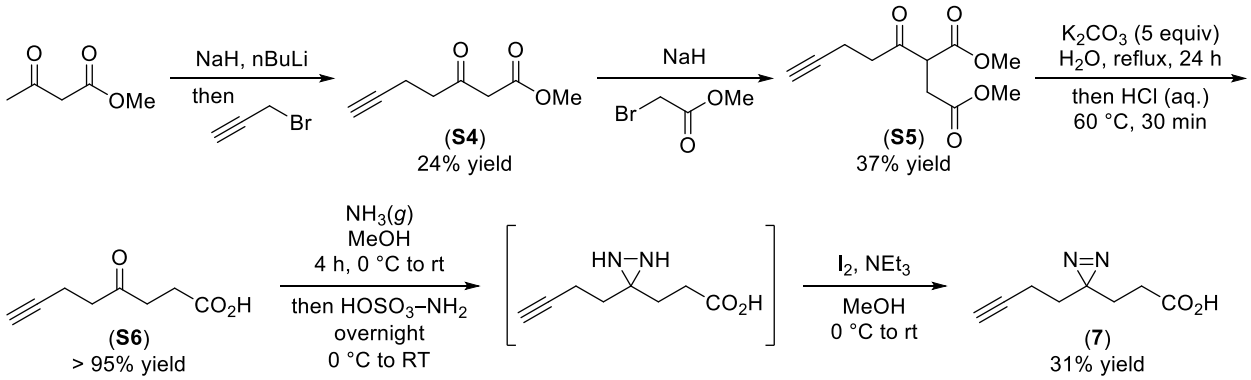


9c. Colorless oil, 48% yield, mixture of diastereomers (dr >20:1). Characterizations consistent with those of its enantiomer, **9b**.



9d. Colorless oil, 86% yield, single diastereomer. $[\alpha]_D^{25}$ = 5.3; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.50 – 8.46 (m, 1H), 8.37 (d, *J* = 2.5 Hz, 1H), 8.32 (s, 1H), 6.88 (dd, *J* = 8.7, 1.5 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.34 (dt, *J* = 17.3, 9.8 Hz, 1H), 5.33 – 5.25 (m, 2H), 4.82 – 4.67 (m, 2H), 3.91 (dd, *J* = 31.9, 9.8 Hz, 1H), 3.69 (s, 3H), 1.98 – 1.84 (m, 5H), 1.63 – 1.59 (m, 2H), 1.54 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.54, 158.66, 154.19 (d, *J* = 28.2 Hz), 143.40, 143.13 – 142.97 (m), 134.94 (d, *J* = 4.2 Hz), 130.03, 129.93 (d, *J* = 2.3 Hz), 119.10, 113.83, 99.31 (d, *J* = 186.3 Hz), 82.66, 69.40, 67.58 (d, *J* = 20.5 Hz), 55.49 (d, *J* = 18.5 Hz), 55.21, 32.23, 28.24, 27.95, 27.49, 13.33. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -184.03 (td, *J* = 32.6, 12.3 Hz). HRMS (ESI): *m/z* for $C_{24}H_{26}FN_4O_3$ $[M+H]^+$ calcd.: 437.1984, found: 437.1982.

*Procedures for the Synthesis of the Carboxylic Acid **7***



Scheme 3.4. Synthesis of the photoreactive carboxylic acid **7**.

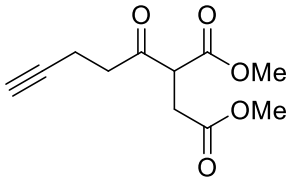
To a flame-dried, 100 mL round-bottom flask equipped with a magnetic stir bar under an atmosphere of N_2 was added NaH (480 mg, 20.0 mmol, 2.00 equiv) and anhydrous THF (20 mL). Methyl acetoacetate (1.16 g, 10.0 mmol, 1.00 equiv) was dissolved in anhydrous THF (3 mL) and added slowly to this stirring suspension at 0 ˚C. After the reaction mixture was stirred at 0 ˚C for 30 min, n-butyl lithium (4.4 mL, 2.5 M solution in hexanes, 11 mmol, 1.1 equiv) was added slowly at 0 ˚C, and the mixture was stirred for 20 min at 0 ˚C. Propargyl bromide (1.4 mL, 9.2 M solution in toluene, 13 mmol, 1.3 equiv) was then added slowly at 0 ˚C, and the resulting mixture was gradually warmed to room temperature and stirred for 2 h. The reaction was subsequently quenched with a saturated, aqueous solution of NH_4Cl (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (with 100% DCM as the eluent) to afford compound **S4** as a yellow oil in 24% yield.

To a flame-dried, 100 mL round-bottom flask equipped with a magnetic stir bar under an atmosphere of N_2 was added NaH (153 mg, 6.35 mmol, 1.10 equiv) and anhydrous THF (10 mL). To this stirring suspension was added compound **S4** (890 mg, 5.77 mmol, 1.00 equiv, dissolved in 5 mL of anhydrous THF) slowly at 0 ˚C, and the mixture was stirred at 0 ˚C for 1 h. Methyl 2-bromoacetate (971 mg, 6.35 mmol, 1.10 equiv, dissolved in 5 mL of anhydrous THF) was then added at 0 ˚C, and the resulting mixture was slowly warmed to room temperature and stirred for 4 h. The reaction was subsequently quenched with a saturated, aqueous solution of NH_4Cl (20 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (0% – 5% EA/DCM) to afford compound **S5** as colorless liquid in 37% yield.

To a 25 mL round-bottom flask equipped with a magnetic stir bar was added compound **S5** (470 mg, 2.07 mmol, 1.00 equiv), water (9 mL) and K_2CO_3 (1.38 g, 10.4 mmol, 5.00 equiv). The mixture was stirred at reflux for 24 h and then cooled to room temperature. An aqueous solution of HCl (2 M) was added dropwise to the stirring mixture until effervescence stopped. The solution was then stirred at 60 ˚C for 30 min, cooled to room temperature, and extracted with Et_2O (15 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to afford the γ-ketocarboxylic acid **S6** as a beige solid in quantitative yield.

To a flame-dried, 50 mL round-bottom flask equipped with a magnetic stir bar under an atmosphere of N_2 was added compound **S6** (165 mg, 1.07 mmol, 1.00 equiv) and anhydrous methanol (2 mL). This stirring solution was sparged with gaseous ammonia at 0 ˚C for 4 h. Hydroxylamine-O-sulfonic acid (HOSA, 170 mg, 1.50 mmol, 1.40 equiv, dissolved in 2.5 mL of anhydrous MeOH) was then added dropwise at 0 ˚C, and the resulting mixture was warmed to room temperature and stirred for 14 h. This suspension was filtered through a plug of Celite, washed with anhydrous MeOH, and the filtrate was concentrated *in vacuo* to approximately 5 mL. To this stirring solution was added diisopropylethylamine (DIPEA, 0.42 mL, 2.40 mmol, 2.24 equiv) in one portion and I_2 portionwise at room temperature, until the dark brown color persisted. The mixture was then stirred at room temperature for 1 h, diluted with ethyl acetate (20 mL), washed with an aqueous solution of HCl (1 M, 10 mL) and subsequently with a saturated, aqueous solution of $Na_2S_2O_3$ until the color of the organic layer stopped changing. The organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (100% hexanes, then 30% – 45% (1% AcOH in EA)/hexanes) to afford the photoreactive carboxylic acid **7** as a faint green oil in 31% yield.

The characterizations of compounds **S4**, **S6**, and **7** are consistent with those from reported literature.[62, 68]



S5. Colorless liquid, 37% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.99 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.08 – 2.95 (m, 2H), 2.93 – 2.80 (m, 2H), 2.47 (td, *J* = 7.2, 2.6 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.94, 171.85, 168.62, 82.73, 68.93, 53.64, 52.96, 52.22, 41.79, 32.22, 12.97. HRMS (ESI): *m/z* for $C_{11}H_{15}O_5$ $[M+H]^+$ calcd.: 227.0914, found: 227.0915.

Computational Details

DFT calculations were conducted at the Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley using the Gaussian 16[69] program package. Initial geometries were constructed in GaussView[70] and optimized to ground states using the B3LYP functional[71-72] with Grimme's D3 dispersion correction with Becke-Johnson damping (GD3BJ)[73] and the basis set def2-SVP for all atoms (**BS1**). The nature of these ground states was confirmed by accompanying frequency calculations (all positive eigenvalues). Further single-point energy calculations were performed on the optimized geometries with the def2-TZVPP basis set on all atoms (**BS2**). Gibbs free energies for **BS2** were approximated by adding the thermal corrections obtained from frequency calculations using **BS1** to the **BS2** electronic energies. All calculations, including geometry optimizations, were performed in THF solvent using the SMD solvent continuum model. For any given vicinal difluoride compound, three sets of conformers, which were categorized by the relative position of the two C–F bonds (*anti*, *gauche1*, and *gauche2*, see

Figure 3.3), were computed. Within each set, several rotamers formed by rotation of the C(heteroaryl)–C(F) and C(F)–C(ester) bonds were computed, and their relative Gibbs free energies (ΔG) were compared, but only the lowest-energy rotamer was reported in this document.

Energies of Optimized Structures

structure	E(BS1) (a.u.)	Thermal Correction to Free Energy (a.u.)	G(BS1) (a.u.)	E(BS2) (a.u.)	G(BS2) (a.u.)
3a(*anti*)	-1061.00045539	0.236310	-1060.764145	-1062.19389528	-1061.957585
3a(*gauche1*)	-1060.99854392	0.236572	-1060.761972	-1062.19259775	-1061.956026
3a(*gauche2*)	-1061.00345149	0.236586	-1060.766865	-1062.19642073	-1061.959835
5a(*anti*)	-1060.99880777	0.236306	-1060.762502	-1062.19211839	-1061.955812
5a(*gauche1*)	-1061.00097568	0.235422	-1060.765554	-1062.19420972	-1061.958788
5a(*gauche2*)	-1061.00186654	0.236679	-1060.765188	-1062.19547910	-1061.958800
3b(*anti*)	-1212.33366393	0.250941	-1212.082723	-1213.69439246	-1213.443451
3b(*gauche1*)	-1212.33409335	0.250482	-1212.083611	-1213.69600750	-1213.445526
3b(*gauche2*)	-1212.33471764	0.251308	-1212.083410	-1213.69636683	-1213.445059
5d(*anti*)	-1212.33440534	0.251177	-1212.083228	-1213.69502880	-1213.443852
5d(*gauche1*)	-1212.33550086	0.250852	-1212.084649	-1213.69655239	-1213.445700
5d(*gauche2*)	-1212.33247612	0.251343	-1212.081133	-1213.69382840	-1213.442485

Atomic Coordinates of Optimized Structures

37
3a(anti)

C	0.7282400000	-0.1107170000	0.6313160000
C	0.0134660000	-1.1349800000	-0.3326300000
C	0.4726640000	-2.5394830000	-0.0260810000
H	0.2367500000	-2.8984730000	0.9781630000
C	1.1288770000	-3.3071270000	-0.8937350000
H	1.4364340000	-4.3213680000	-0.6267030000
H	1.3753300000	-2.9449080000	-1.8940090000
F	0.3882520000	-0.7912050000	-1.6181870000
C	-1.5033400000	-0.9983560000	-0.2275190000
C	-2.2104580000	-1.4794030000	0.8840540000
C	-2.2044740000	-0.3430760000	-1.2478190000
C	-3.5911880000	-1.2967480000	0.9753090000
H	-1.6844670000	-1.9799790000	1.6962760000
C	-3.5865220000	-0.1667970000	-1.1566140000
H	-1.6587940000	0.0331360000	-2.1124040000
C	-4.2846760000	-0.6394150000	-0.0440910000
H	-4.1278960000	-1.6726790000	1.8496050000
H	-4.1188340000	0.3476130000	-1.9603390000
H	-5.3656780000	-0.4984350000	0.0288610000
F	0.2681910000	-0.4140460000	1.9021690000
C	2.2617370000	-0.2682100000	0.6820120000
O	2.8780580000	-0.1791510000	1.7108710000
O	2.7986720000	-0.4946580000	-0.5118190000
C	4.2204610000	-0.5763290000	-0.5526410000
H	4.4844280000	-0.7659040000	-1.6003690000
H	4.6722850000	0.3680030000	-0.2131190000
H	4.5859430000	-1.3947760000	0.0860670000

C	0.3618800000	1.3308890000	0.3108800000
C	-0.8107230000	1.8897070000	0.8356230000
N	1.1924270000	2.0007290000	-0.4880080000
C	-1.1282650000	3.2005270000	0.4840920000
H	-1.4497570000	1.3081370000	1.4981370000
C	0.8822090000	3.2535560000	-0.8202450000
C	-0.2704320000	3.8996130000	-0.3664230000
H	-2.0369740000	3.6691150000	0.8691760000
H	1.5885830000	3.7736790000	-1.4770540000
H	-0.4829200000	4.9275600000	-0.6674140000

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3a(gauche1)

C	0.6939900000	-1.0653240000	0.1223920000
C	-0.5390340000	-0.7386530000	1.0447160000
C	-0.0825330000	-0.5270150000	2.4710200000
H	0.3817560000	0.4394800000	2.6781310000
C	-0.2413340000	-1.4277720000	3.4381660000
H	0.0862610000	-1.2191670000	4.4598270000
H	-0.7091230000	-2.3943030000	3.2403010000
F	-1.2986860000	-1.9079900000	0.9988970000
C	-1.4036600000	0.4340850000	0.5965620000
C	-0.9343230000	1.7523180000	0.6711510000
C	-2.7110440000	0.2050630000	0.1513580000
C	-1.7478820000	2.8181160000	0.2828330000
H	0.0729990000	1.9642490000	1.0306150000
C	-3.5257000000	1.2713800000	-0.2299230000
H	-3.0820710000	-0.8173780000	0.0992840000
C	-3.0462860000	2.5821470000	-0.1715960000
H	-1.3619660000	3.8386170000	0.3401050000
H	-4.5434630000	1.0753890000	-0.5764330000
H	-3.6838980000	3.4164580000	-0.4735660000
F	1.4095260000	-2.0433910000	0.7855900000
C	0.2859220000	-1.6796570000	-1.2324860000
O	0.9062800000	-2.5660380000	-1.7538410000
O	-0.7900980000	-1.0928160000	-1.7463490000
C	-1.1719130000	-1.4939420000	-3.0586020000
H	-2.0815430000	-0.9280610000	-3.2949040000
H	-0.3768180000	-1.2514740000	-3.7799980000
H	-1.3723400000	-2.5750800000	-3.0979370000
C	1.6237560000	0.1157210000	-0.1161050000
C	2.6409020000	0.4027280000	0.8026530000
N	1.4125580000	0.8392490000	-1.2159290000
C	3.4404030000	1.5216260000	0.5701810000
H	2.7948750000	-0.2417880000	1.6676190000
C	2.1843870000	1.9028190000	-1.4363420000
C	3.2059170000	2.2959020000	-0.5676820000
H	4.2401470000	1.7832720000	1.2671490000
H	1.9817010000	2.4719010000	-2.3503510000
H	3.8091520000	3.1791480000	-0.7869770000

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3a(gauche2)

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C	-0.4901960000	-0.9013130000	0.2714610000
C	-0.0861300000	-1.1403950000	1.7043230000

H	-0.1579500000	-0.2724840000	2.3594950000
C	0.3575300000	-2.3152630000	2.1475880000
H	0.6416180000	-2.4445810000	3.1950620000
H	0.4534900000	-3.1781820000	1.4852300000
F	-0.1768230000	-2.0444200000	-0.4717370000
C	-1.9799460000	-0.6319050000	0.0803980000
C	-2.7518060000	0.0090460000	1.0582510000
C	-2.5905530000	-1.0312660000	-1.1171180000
C	-4.1099630000	0.2483890000	0.8391290000
H	-2.2929400000	0.3375830000	1.9889530000
C	-3.9481840000	-0.7925320000	-1.3319750000
H	-1.9954580000	-1.5348680000	-1.8777380000
C	-4.7130640000	-0.1509280000	-0.3550260000
H	-4.6992770000	0.7492780000	1.6109490000
H	-4.4109520000	-1.1110120000	-2.2693090000
H	-5.7764850000	0.0359160000	-0.5235160000
F	-0.0019320000	0.2745310000	-1.7285560000
C	0.1561590000	1.6118490000	0.2239670000
O	-0.2975740000	1.8280640000	1.3188250000
O	0.5538390000	2.5560120000	-0.6251800000
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H	0.8276170000	4.5356000000	-0.9698230000
H	-0.5768490000	4.1589830000	0.0953120000
H	1.0867050000	4.0370430000	0.7437850000
C	1.8601540000	-0.1186840000	-0.3323780000
C	2.4442870000	-0.9549600000	-1.2885470000
N	2.5311990000	0.4015980000	0.6950330000
C	3.7963290000	-1.2627860000	-1.1463120000
H	1.8466800000	-1.3483480000	-2.1094620000
C	3.8236550000	0.1023130000	0.8258380000
C	4.5040910000	-0.7280810000	-0.0676510000
H	4.2929340000	-1.9145230000	-1.8691920000
H	4.3448390000	0.5472610000	1.6806870000
H	5.5641420000	-0.9454050000	0.0783560000

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5a(anti)

C	-0.5729700000	-0.0396000000	0.5701000000
C	0.3233670000	-0.8333070000	-0.4555560000
C	0.0083620000	-2.3113790000	-0.3873500000
H	-0.9906840000	-2.5572790000	-0.7606400000
C	0.8169650000	-3.2759890000	0.0482500000
H	0.4897090000	-4.3192490000	0.0472710000
H	1.8233840000	-3.0695140000	0.4196770000
F	-0.4438670000	-0.6832190000	1.7900400000
C	-0.1106510000	1.4144230000	0.7842300000
O	-0.1375550000	1.9526880000	1.8589570000
O	0.3022430000	1.9754410000	-0.3468270000
C	0.7317750000	3.3312030000	-0.2593590000
H	1.0544460000	3.6134090000	-1.2688770000
H	-0.0942820000	3.9790400000	0.0708480000
H	1.5683870000	3.4297560000	0.4487500000
C	-2.0485460000	-0.0532680000	0.1863920000
C	-2.8869830000	-1.0683310000	0.6644310000
N	-2.4791680000	0.9361340000	-0.5956830000
C	-4.2261470000	-1.0540070000	0.2750440000

H	-2.4941880000	-1.8363730000	1.3298790000
C	-3.7597050000	0.9445530000	-0.9625670000
C	-4.6756050000	-0.0319800000	-0.5619250000
H	-4.9109060000	-1.8300730000	0.6253560000
H	-4.0782210000	1.7742510000	-1.6037490000
H	-5.7159940000	0.0173160000	-0.8896540000
F	-0.0881800000	-0.4185930000	-1.7204700000
C	1.8022760000	-0.5198000000	-0.2877220000
C	2.5793590000	-0.2595360000	-1.4226840000
C	2.4081400000	-0.5015630000	0.9769470000
C	3.9412400000	0.0165540000	-1.2967990000
H	2.1042280000	-0.2621940000	-2.4032860000
C	3.7721880000	-0.2229720000	1.0982090000
H	1.8137720000	-0.6941260000	1.8695830000
C	4.5434500000	0.0357500000	-0.0361320000
H	4.5355790000	0.2216760000	-2.1906550000
H	4.2312140000	-0.2070030000	2.0896110000
H	5.6095570000	0.2541900000	0.0614590000

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5a(gauche1)

C	-0.7918880000	-0.1258310000	-0.3799160000
C	0.0456000000	-1.1803320000	0.4320150000
C	-0.2194130000	-1.1675690000	1.9164020000
H	-0.2149690000	-0.1819520000	2.3818340000
C	-0.4548830000	-2.2780330000	2.6125000000
H	-0.6306400000	-2.2326400000	3.6902150000
H	-0.4919840000	-3.2594640000	2.1343820000
F	-0.5422970000	-0.3979660000	-1.7109080000
C	-2.2930040000	-0.3281530000	-0.1042250000
O	-2.7884200000	-0.1756320000	0.9809020000
O	-2.9604330000	-0.6701840000	-1.2059670000
C	-4.3620260000	-0.8868230000	-1.0362910000
H	-4.7499590000	-1.1593870000	-2.0254670000
H	-4.5461880000	-1.6995610000	-0.3176180000
H	-4.8578570000	0.0250100000	-0.6700550000
C	-0.3990690000	1.3285620000	-0.1232430000
C	-0.0473890000	2.1459720000	-1.2047890000
N	-0.4146220000	1.7671420000	1.1354880000
C	0.2980180000	3.4718830000	-0.9453700000
H	-0.0407170000	1.7427960000	-2.2156080000
C	-0.0863090000	3.0357440000	1.3768100000
C	0.2777900000	3.9334670000	0.3707220000
H	0.5808680000	4.1365490000	-1.7651450000
H	-0.1097860000	3.3539250000	2.4249840000
H	0.5404950000	4.9641680000	0.6169170000
F	-0.3847780000	-2.4052560000	-0.0838550000
C	1.5212580000	-1.0112060000	0.0891570000
C	2.0579320000	-1.6974210000	-1.0072710000
C	2.3412980000	-0.1433120000	0.8228480000
C	3.3964650000	-1.5206900000	-1.3612850000
H	1.4191550000	-2.3701910000	-1.5783580000
C	3.6777000000	0.0368670000	0.4617680000
H	1.9370690000	0.3982100000	1.6778070000
C	4.2099670000	-0.6516540000	-0.6305170000
H	3.8055270000	-2.0647530000	-2.2162170000

H 4.3064900000 0.7166550000 1.0417510000
H 5.2570640000 -0.5126490000 -0.9103310000

37
5a(gauche2)
C 1.0695660000 -0.1757220000 0.4628700000
C -0.0742240000 -1.1897830000 0.8470850000
C 0.4213660000 -2.6144070000 0.8436860000
H 0.5409250000 -3.0670030000 -0.1406570000
C 0.7163620000 -3.2869160000 1.9548750000
H 1.0702080000 -4.3200490000 1.9059390000
H 0.6102340000 -2.8325020000 2.9419480000
F 2.0256470000 -0.2832100000 1.4607070000
C 1.7897750000 -0.4869490000 -0.8631850000
O 1.5228440000 -1.3747950000 -1.6334280000
O 2.8078520000 0.3556850000 -1.0199880000
C 3.5658520000 0.2133520000 -2.2209950000
H 4.3549080000 0.9738150000 -2.1751150000
H 4.0089010000 -0.7915910000 -2.2889930000
H 2.9267530000 0.3806740000 -3.1010660000
C 0.5285080000 1.2401450000 0.4281980000
C 0.4441470000 2.0126150000 1.5886030000
N 0.0870480000 1.6484170000 -0.7625240000
C -0.1469840000 3.2722990000 1.4896660000
H 0.8250950000 1.6244330000 2.5323860000
C -0.4787710000 2.8510170000 -0.8494580000
C -0.6237220000 3.7019570000 0.2499460000
H -0.2375890000 3.9106070000 2.3719190000
H -0.8343580000 3.1542910000 -1.8402300000
H -1.0958860000 4.6794370000 0.1323910000
F -0.3563800000 -0.8316470000 2.1683690000
C -1.3479570000 -0.9862150000 0.0308880000
C -2.4003600000 -0.2507910000 0.5936760000
C -1.4891740000 -1.4870180000 -1.2699250000
C -3.5681820000 -0.0140670000 -0.1326250000
H -2.3001520000 0.1388650000 1.6056590000
C -2.6591800000 -1.2493390000 -1.9928130000
H -0.6714750000 -2.0335670000 -1.7349910000
C -3.7022740000 -0.5112320000 -1.4301820000
H -4.3774650000 0.5634830000 0.3209600000
H -2.7512440000 -1.6421680000 -3.0083090000
H -4.6156540000 -0.3247490000 -2.0003910000

40
3b_anti
C -0.7214840000 -0.7753980000 0.6332590000
C -1.6468770000 0.0343590000 -0.3536410000
C -3.0757640000 -0.4288720000 -0.1947250000
H -3.5341370000 -0.1971350000 0.7695420000
C -3.7464900000 -1.0835520000 -1.1409720000
H -4.7820320000 -1.3943270000 -0.9819420000
H -3.2847520000 -1.3173500000 -2.1026150000
F -1.1936920000 -0.2909400000 -1.6221310000
C -1.5460940000 1.5466910000 -0.1721750000
C -1.9977160000 2.1746170000 0.9972530000
C -1.0243700000 2.3297590000 -1.2091340000

C	-1.9122840000	3.5612550000	1.1295830000
H	-2.4024500000	1.5836870000	1.8180310000
C	-0.9452380000	3.7166100000	-1.0750700000
H	-0.6749970000	1.8465590000	-2.1206570000
C	-1.3857030000	4.3377610000	0.0952390000
H	-2.2620580000	4.0364830000	2.0490900000
H	-0.5349460000	4.3145800000	-1.8925080000
H	-1.3218450000	5.4234410000	0.2002320000
F	-0.9928860000	-0.3284920000	1.9111370000
C	-1.0741350000	-2.2797590000	0.6096150000
O	-1.4692690000	-2.8687750000	1.5775860000
O	-0.9189590000	-2.7973270000	-0.6041660000
C	-1.2546760000	-4.1768940000	-0.7444460000
H	-1.0703940000	-4.4292720000	-1.7957270000
H	-0.6261670000	-4.7975590000	-0.0886880000
H	-2.3124370000	-4.3455680000	-0.4914990000
C	0.7429040000	-0.5908290000	0.3663070000
C	2.8343460000	-0.8429050000	0.0774720000
C	2.5661660000	0.5379490000	0.1063260000
C	3.5402540000	1.5175060000	-0.0404810000
C	4.8438640000	1.0487240000	-0.2229440000
C	5.1400590000	-0.3297270000	-0.2546320000
C	4.1459650000	-1.2964210000	-0.1062420000
H	3.2974890000	2.5803860000	-0.0150210000
H	5.6555370000	1.7694470000	-0.3446760000
H	6.1760510000	-0.6436500000	-0.3999240000
H	4.3692350000	-2.3640280000	-0.1308930000
N	1.6319560000	-1.5213870000	0.2527690000
O	1.2216090000	0.6853110000	0.2957390000

40

3b_gauche1

C	-0.2791200000	0.2672620000	-0.4120930000
C	-0.9966100000	-0.9714130000	0.2418220000
C	-0.5020410000	-1.1932220000	1.6491860000
H	-0.6735910000	-0.3688580000	2.3414410000
C	0.1485740000	-2.2944170000	2.0222430000
H	0.5018560000	-2.4118720000	3.0498350000
H	0.3470530000	-3.1065270000	1.3197210000
F	-0.6077180000	-2.0488500000	-0.5446820000
C	-2.5093010000	-0.8249000000	0.1127930000
C	-3.2969350000	-0.2882870000	1.1398820000
C	-3.1208410000	-1.2126020000	-1.0880110000
C	-4.6748670000	-0.1407020000	0.9661800000
H	-2.8392760000	0.0271200000	2.0764080000
C	-4.4977350000	-1.0657670000	-1.2568000000
H	-2.5094000000	-1.6312670000	-1.8864640000
C	-5.2793420000	-0.5284830000	-0.2310750000
H	-5.2779650000	0.2773750000	1.7756020000
H	-4.9626710000	-1.3733100000	-2.1965580000
H	-6.3577780000	-0.4136200000	-0.3642310000
F	-0.5764970000	0.2401830000	-1.7585690000
C	-0.7737880000	1.5908220000	0.2078410000
O	-0.9163190000	1.7628820000	1.3916810000
O	-1.0200890000	2.4951600000	-0.7286850000
C	-1.4748950000	3.7681030000	-0.2610540000

H -1.6277910000 4.3825820000 -1.1562780000
H -2.4181680000 3.6607280000 0.2947690000
H -0.7227010000 4.2280660000 0.3967500000
C 1.2159680000 0.2147940000 -0.2623130000
C 3.2562720000 0.6200920000 0.1730560000
C 3.1899440000 -0.6266080000 -0.4755880000
C 4.3028610000 -1.4105310000 -0.7532520000
C 5.5305230000 -0.8848960000 -0.3415900000
C 5.6234890000 0.3616080000 0.3106490000
C 4.4933620000 1.1338230000 0.5784760000
H 4.2193880000 -2.3735420000 -1.2582160000
H 6.4426150000 -1.4556390000 -0.5298230000
H 6.6073470000 0.7277690000 0.6121800000
H 4.5586400000 2.0990690000 1.0827680000
N 1.9617230000 1.1203440000 0.2794910000
O 1.8745600000 -0.8731080000 -0.7513940000

40
3b_gauche2
C 0.3605920000 -1.2664660000 0.1819260000
C 1.4964860000 -0.9041310000 -0.8524810000
C 1.0615900000 -1.2028850000 -2.2661550000
H 0.3374210000 -0.5077390000 -2.6908220000
C 1.5064410000 -2.2530840000 -2.9536290000
H 1.1709860000 -2.4314610000 -3.9785400000
H 2.2163780000 -2.9604330000 -2.5204430000
F 2.5046970000 -1.7977560000 -0.5053250000
C 2.0447020000 0.5093260000 -0.6705460000
C 1.3828190000 1.6364910000 -1.1745070000
C 3.2375710000 0.6821830000 0.0457100000
C 1.9008240000 2.9136080000 -0.9523360000
H 0.4435270000 1.5210190000 -1.7129300000
C 3.7514840000 1.9612470000 0.2664020000
H 3.7615670000 -0.1915560000 0.4322610000
C 3.0835650000 3.0827430000 -0.2293440000
H 1.3711710000 3.7839210000 -1.3472390000
H 4.6822870000 2.0794850000 0.8266290000
H 3.4851110000 4.0841650000 -0.0566660000
F 0.1513880000 -2.6233870000 0.0832700000
C 0.8670420000 -0.9835670000 1.6133510000
O 1.3926840000 -1.7945490000 2.3206250000
O 0.6613460000 0.3006680000 1.9190050000
C 1.2183730000 0.7651890000 3.1488420000
H 0.9840650000 1.8348640000 3.2028750000
H 0.7759380000 0.2308990000 4.0026500000
H 2.3082190000 0.6169000000 3.1567310000
C -0.9651160000 -0.5959560000 -0.0464350000
C -2.7027180000 0.4358740000 -0.7231030000
C -3.0215820000 -0.1883130000 0.4956980000
C -4.2696860000 -0.1044450000 1.0997290000
C -5.2218210000 0.6568090000 0.4162520000
C -4.9260820000 1.2926510000 -0.8066170000
C -3.6662380000 1.1940970000 -1.3970640000
H -4.4884760000 -0.6005260000 2.0459220000
H -6.2223330000 0.7618460000 0.8415100000
H -5.7060040000 1.8756550000 -1.3011460000

H -3.4327110000 1.6826510000 -2.3442130000
N -1.3768420000 0.1365310000 -1.0266460000
O -1.9019680000 -0.8477870000 0.9171530000

40
5d(anti)
C 0.1516160000 -0.0216030000 0.7037100000
C 0.9635840000 -0.9378640000 -0.2916300000
C 0.7259080000 -2.4003040000 0.0156420000
H -0.3283140000 -2.6829660000 0.0483870000
C 1.6734020000 -3.3215250000 0.1867120000
H 1.4031110000 -4.3656850000 0.3662180000
H 2.7386290000 -3.0818150000 0.1585620000
F 0.2744320000 -0.5691130000 1.9659520000
C 0.7216730000 1.4114890000 0.7662250000
O 1.0490400000 1.9492790000 1.7870650000
O 0.8184380000 1.9272890000 -0.4549450000
C 1.3933650000 3.2299360000 -0.5468160000
H 1.4080760000 3.4808820000 -1.6142070000
H 0.7867490000 3.9606820000 0.0083180000
H 2.4167170000 3.2282920000 -0.1423470000
F 0.4000470000 -0.6943360000 -1.5474690000
C 2.4324250000 -0.5516930000 -0.3189160000
C 3.0549490000 -0.2373460000 -1.5313620000
C 3.1718890000 -0.4995550000 0.8715390000
C 4.4038490000 0.1225270000 -1.5549010000
H 2.4729740000 -0.2681260000 -2.4520000000
C 4.5195790000 -0.1360990000 0.8436280000
H 2.6888140000 -0.7318850000 1.8211970000
C 5.1399680000 0.1744200000 -0.3688190000
H 4.8813680000 0.3664940000 -2.5069900000
H 5.0857030000 -0.0938160000 1.7769570000
H 6.1948080000 0.4584150000 -0.3887200000
C -3.3075660000 -0.6868030000 0.0147850000
C -4.4481520000 -1.4560710000 -0.1764940000
C -5.6231740000 -0.7416450000 -0.4259430000
C -5.6391330000 0.6670810000 -0.4769970000
C -4.4815050000 1.4198940000 -0.2813340000
C -3.2964780000 0.7187410000 -0.0310510000
H -4.4258350000 -2.5456470000 -0.1351290000
H -6.5540880000 -1.2901010000 -0.5858450000
H -6.5840970000 1.1775990000 -0.6751470000
H -4.4870460000 2.5101590000 -0.3194310000
C -1.3104720000 0.0678200000 0.3663000000
N -1.9946700000 1.1501920000 0.2054810000
O -2.0274210000 -1.0929660000 0.2741040000

40
5d(gauche1)
C -0.5221170000 0.8290100000 -0.6008750000
C -1.7225620000 0.4477290000 0.3401880000
C -1.4730310000 0.7865210000 1.7891990000
H -0.5942130000 0.3195200000 2.2340080000
C -2.2633000000 1.5999450000 2.4876870000
H -2.0568520000 1.8076410000 3.5407080000
H -3.1348820000 2.0795980000 2.0370840000

F	-0.8600690000	0.4539810000	-1.8801830000
C	-0.3449000000	2.3654490000	-0.6310840000
O	-0.7469540000	3.0748470000	-1.5072000000
O	0.3171190000	2.7686010000	0.4567920000
C	0.4786290000	4.1792690000	0.6171320000
H	1.0435660000	4.3173550000	1.5467630000
H	1.0299560000	4.6068240000	-0.2332800000
H	-0.5020390000	4.6724250000	0.6918990000
F	-2.7561470000	1.2610280000	-0.1280270000
C	-2.1375950000	-1.0036800000	0.1167350000
C	-3.0400190000	-1.2944930000	-0.9157990000
C	-1.6395650000	-2.0485450000	0.9060210000
C	-3.4395300000	-2.6100140000	-1.1524080000
H	-3.4287260000	-0.4827670000	-1.5294670000
C	-2.0394890000	-3.3642160000	0.6634570000
H	-0.9243400000	-1.8418740000	1.7000320000
C	-2.9403500000	-3.6496440000	-0.3642820000
H	-4.1452320000	-2.8232210000	-1.9589560000
H	-1.6437060000	-4.1702890000	1.2858810000
H	-3.2533020000	-4.6799230000	-0.5504690000
C	2.8433620000	-0.3403180000	-0.6677130000
C	4.1127400000	-0.5076660000	-1.2060330000
C	5.0131450000	-1.2296990000	-0.4175990000
C	4.6461350000	-1.7526350000	0.8388140000
C	3.3642040000	-1.5754840000	1.3596290000
C	2.4529580000	-0.8529440000	0.5820050000
H	4.3858280000	-0.1001260000	-2.1799960000
H	6.0284670000	-1.3930890000	-0.7854630000
H	5.3868930000	-2.3105260000	1.4157180000
H	3.0745200000	-1.9795020000	2.3307800000
C	0.7796070000	0.1613440000	-0.2574210000
N	1.1216400000	-0.5033610000	0.7948890000
O	1.7621590000	0.3099060000	-1.1947800000

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5d(gauche2)

C	0.3769200000	-1.2569740000	-0.0865890000
C	1.4950530000	-0.6570440000	-1.0145310000
C	2.6135440000	-1.6701990000	-1.1399960000
H	3.0032170000	-2.0665920000	-0.2007570000
C	3.0958770000	-2.0739420000	-2.3125970000
H	3.9134770000	-2.7975160000	-2.3612170000
H	2.6908510000	-1.7001370000	-3.2554470000
F	0.2239910000	-2.5892660000	-0.4121490000
C	0.8368340000	-1.2141250000	1.3890740000
O	1.5950100000	-2.0138050000	1.8700600000
O	0.3108150000	-0.1713790000	2.0251060000
C	0.7550210000	0.0567230000	3.3649630000
H	0.1932030000	0.9262880000	3.7253890000
H	0.5541130000	-0.8212320000	3.9956930000
H	1.8334590000	0.2729340000	3.3763490000
F	0.9162290000	-0.4903540000	-2.2622760000
C	2.0028290000	0.6954630000	-0.5175290000
C	1.5009410000	1.8774410000	-1.0743740000
C	2.9740160000	0.7728780000	0.4917150000
C	1.9566700000	3.1159910000	-0.6196830000

H	0.7395340000	1.8162370000	-1.8487380000
C	3.4195840000	2.0136140000	0.9512290000
H	3.3926820000	-0.1350230000	0.9266120000
C	2.9112630000	3.1902620000	0.3969080000
H	1.5566390000	4.0316210000	-1.0619550000
H	4.1762160000	2.0580590000	1.7383010000
H	3.2626740000	4.1617780000	0.7526080000
C	-3.0919790000	-0.4901290000	0.1433710000
C	-4.4104590000	-0.7006930000	0.5267170000
C	-5.3119300000	0.3077580000	0.1739870000
C	-4.9006590000	1.4576720000	-0.5296660000
C	-3.5717460000	1.6469330000	-0.9097170000
C	-2.6572160000	0.6472530000	-0.5606680000
H	-4.7187790000	-1.5949730000	1.0695640000
H	-6.3630660000	0.2013850000	0.4512540000
H	-5.6443200000	2.2166580000	-0.7823990000
H	-3.2477710000	2.5336300000	-1.4566440000
C	-0.9670330000	-0.6002810000	-0.2417600000
N	-1.2888550000	0.5231170000	-0.7840320000
O	-1.9992370000	-1.2848140000	0.3428730000

X-ray Crystallographic Data

3.4.11.1. Compound **4g**

A colorless needle 0.31 x 0.10 x 0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 17727 reflections were collected covering the indices -28<=h<=23, -7<=k<=7, -14<=l<=14. 3342 reflections were founded to be symmetry independent, with an R_{int} of 0.0389. Indexing and unit cell refinement indicated a centered, monoclinic lattice. The space group was found to be C 2 (No. 5). The data were integrated using the CrysAlis^{Pro} 1.171.41.109a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 3.5. Crystal data and structure refinement for Yehao06_Hartwig.

Identification code	Yehao06_Hartwig	
Empirical formula	C20 H16 F2 N2 O2	
Formula weight	354.35	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 23.3475(3) Å	a= 90°.
	b = 5.99340(10) Å	b= 103.1160(10)°.
	c = 11.9565(2) Å	g = 90°.
Volume	1629.44(4) Å^3	

Z	4
Density (calculated)	1.444 Mg/m^3
Absorption coefficient	0.923 mm^{-1}
F(000)	736
Crystal size	0.310 x 0.100 x 0.040 mm^3
Theta range for data collection	3.796 to 74.434°.
Index ranges	-28<=h<=23, -7<=k<=7, -14<=l<=14
Reflections collected	17727
Independent reflections	3342 [R(int) = 0.0389]
Completeness to theta = 74.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.92950
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3342 / 1 / 236
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0775
R indices (all data)	R1 = 0.0303, wR2 = 0.0785
Absolute structure parameter	0.01(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.235 and -0.218 $e.Å^{-3}$

3.4.11.2. Compound *ent*-**5c**

A colorless block 0.177 x 0.033 x 0.026 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected on a ROD, Synergy Custom DW system, Pilatus 200K diffractometer in a nitrogen gas stream at 100.00(10) K during data collection using omega scans. Crystal-to-detector distance was 30.23 mm and exposure time was 4 seconds per frame at low angles and 17 seconds per frame at high angles using a scan width of 0.5°. Data collection was 100% complete to 67.7° in θ. A total of 55939 reflections were collected covering the indices -7<=h<=7, -20<=k<=20, -40<=l<=39. 6901 reflections were founded to be symmetry independent, with an Rint of 0.0792. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 212121 (No. 19). The data were integrated using the CrysAlisPro 1.171.39.46e software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute configuration was determined by anomalous dispersion.

Table 3.6. Crystal data and structure refinement for JFH2022002

Identification code	JFH2022002
Empirical formula	$C_{19}H_{15}F_2NO_3$
Formula weight	343.32
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	6.07900(10)
b/Å	16.4760(3)
c/Å	32.3026(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3235.35(11)
Z	8
ρ_{calc}g/cm^3	1.410
μ/mm^{-1}	0.939
F(000)	1424.0
Crystal size/mm^3	0.177 × 0.033 × 0.026
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.472 to 158.378
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -40 ≤ l ≤ 39
Reflections collected	55939
Independent reflections	6901 [R_{int} = 0.0792, R_{sigma} = 0.0376]
Data/restraints/parameters	6901/0/453
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0973
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1016
Largest diff. peak/hole / e Å^{-3}	0.24/-0.22
Flack parameter	-0.04(5)

3.5.References

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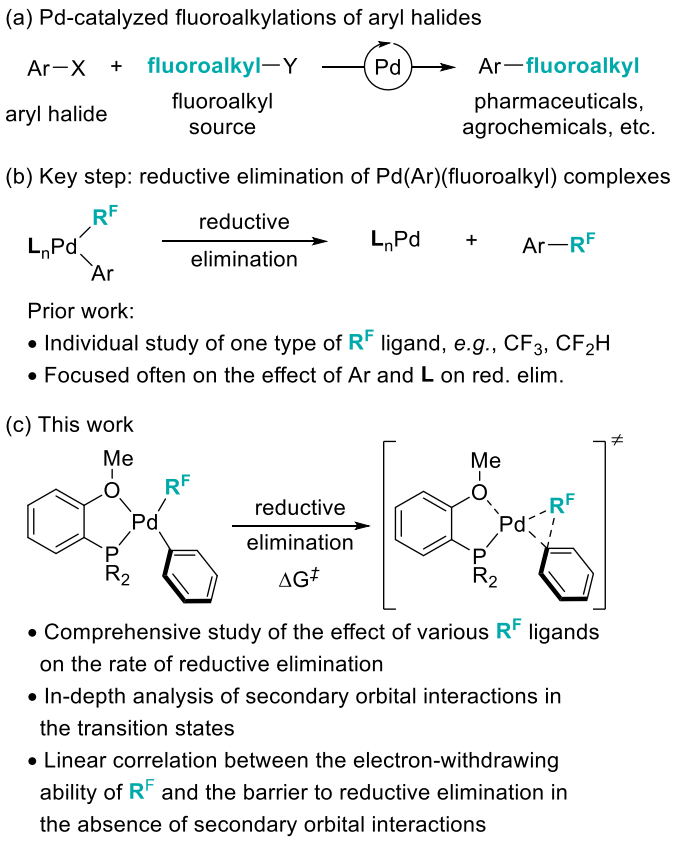
Chapter Four

Transition-State Stabilization by Secondary Orbital Interactions between Fluoroalkyl Ligands and Palladium During Reductive Elimination from Palladium(aryl)(fluoroalkyl) Complexes

4.1.Introduction

The construction of organic molecules containing fluorine is important for the development of biologically active compounds, including pharmaceuticals and agrochemicals, because fluorinated functional groups alter the lipophilicity, acidity, and metabolic stability of these molecules.[1-10] Pd-catalyzed fluoroalkylations of aryl halides are attractive reactions to introduce fluorinated motifs at late stages in the synthesis of these molecules because of the high selectivity and functional-group tolerance of Pd catalysts (Scheme 4.1a).[11] The C–C bond-forming step of these catalytic fluoroalkylation reactions is reductive elimination from an intermediate palladium(aryl)(fluoroalkyl) complex to form fluoroalkylarenes. While the reductive elimination step is not always rate-limiting in the catalytic reactions,[12-13] the reductive elimination of fluoroalkylarenes, nevertheless, is often much slower than the reductive elimination of non-fluorinated alkylarenes from analogous palladium(aryl)(alkyl) complexes.[11, 14-16] As such, the rate of this step imposes a lower bound on the rate of the reaction overall and affects the partitioning of the reaction between the steps on the catalytic cycle and those occurring off of the cycle to form side products or induce decomposition of the catalyst. Thus, understanding how structural and electronic effects of the Pd(aryl)(fluoroalkyl) complexes affect the rate of reductive elimination is key for the development of new, milder Pd-catalyzed fluoroalkylation reactions.

Many experimental and computational studies on the reductive elimination from Pd complexes of perfluoroalkyl, difluoromethyl, and α-fluoroenolate ligands have been reported.[15-33] However, most of these studies have focused on a single fluoroalkyl ligand, *e.g.*, the CF_3 group, and have not compared this reductive elimination to those of other fluoroalkyl, and non-fluorinated ligands (Scheme 4.1b). A comparison of reductive elimination from complexes containing various types of fluoroalkyl ligands would provide insight into structural and electronic effects that influence the rate of reductive elimination step and aid the future development of Pd-catalyzed fluoroalkylations of aryl halides (Scheme 4.1c). To this end, we report computational investigations into the reductive elimination of fluoroalkylarenes from (**L**)Pd(aryl)(R^F) complexes (**L** = di-tert-butyl(2-methoxyphenyl)phosphine), containing a series of alkyl and fluoroalkyl ligands R^F (R^F = CF_3, C_2F_5, CF_2H, CF_2CH_3, $CF_2CF(CH_3)_2$, CFH_2, CH_3, CF_2Ph, CF_2CN, $CF_2C(O)F$, $CF_2C(O)H$, $CF_2C(O)Me$, CF_2CO_2Me, or CHFC(O)Me), leading to new insights into the factors controlling reductive elimination. We find that the barriers to reductive elimination from complexes of fluoroalkyl ligands containing electron-withdrawing π-acids (carbonyl, nitrile, or aryl moieties) or containing hydrogen atoms attached to the α-carbon are significantly lower than those of fluoroalkyl ligands that do not contain these moieties. Analyses of these structures by Natural Bond Orbital (NBO)[34] and the Independent Gradient Model based on Hirshfeld partition (IGMH)[35-37] reveal that the lower barriers for the complexes containing π-acids or α-hydrogens result from stabilizing, secondary orbital interactions between the Pd center and the π-acidic or α-hydrogen substituents in the fluoroalkyl ligand.



Scheme 4.1. (a) Palladium-catalyzed fluoroalkylations of aryl halides to access fluorinated, biologically active molecules; (b) reductive elimination from Pd(aryl)(fluoroalkyl) complexes is a key step in the catalytic cycle; (c) this work.

4.2.Results and Discussions

4.2.1.Validation of the Computational Methods

The computational methods chosen for this work (see Section 4.4 for details) closely reproduce higher-level computations of closed-shell organometallic complexes in established DFT benchmarks[38-40] as well as experimentally determined energetic barriers to reductive elimination from arylpalladium fluorooxindole complexes.[12] Nevertheless, we calculated the barriers to reductive elimination from Pd complexes containing various bisphosphine ligands and fluoroalkyl groups and compared the computed barriers to those derived from published experimental measurements.[12, 15, 24] The barrier to reductive elimination from the complex (dfmpe)Pd(Ph)(CF_3) (dfmpe = 1,2-bis(bis(trifluoromethyl)phosphino)ethane) reported by Schoenebeck and co-workers was calculated to be 24.5 kcal/mol, which is only 0.9 kcal/mol higher than the value measured from experiments (Figure 4.1(a)).[24] This difference is similar to that between computed and experimental barriers to reductive elimination from the (aryl)Pd(fluorooxindole) complex containing the (*S*)-SEGPHOS ligand (1.2 kcal/mol, Figure 4.1(b)) that we published previously.[12] Similarly, the computed barriers to reductive elimination from (dppf)Pd(phenyl)(fluoroalkyl) complexes (dppf = 1,1'-bis(diphenylphosphino)ferrocene) agree with experimental values (Figure 4.1(c), (d), $|\Delta G^{\ddagger}_{calc} - \Delta G^{\ddagger}_{expt}| < 1.8$ kcal/mol).[15] The calculated barrier to reductive elimination

from (dppf)Pd(Ph)(CF_2CN) was 1.9 kcal/mol higher than that from (dppf)Pd(Ph)(CF_2CO_2Et) ($\Delta G^{\ddagger}_{calc}(CF_2CN) - \Delta G^{\ddagger}_{calc}(CF_2CO_2Et)$ = 1.9 kcal/mol), consistent with barriers calculated from experimentally determined rate constants ($\Delta G^{\ddagger}_{expt}(CF_2CN) - \Delta G^{\ddagger}_{expt}(CF_2CO_2Et)$ = 1.0 kcal/mol).[15] These small differences between computation and experiment show that our computational method accurately predicts the relative free-energy barriers to reductive elimination from Pd(aryl)(fluoroalkyl) complexes.

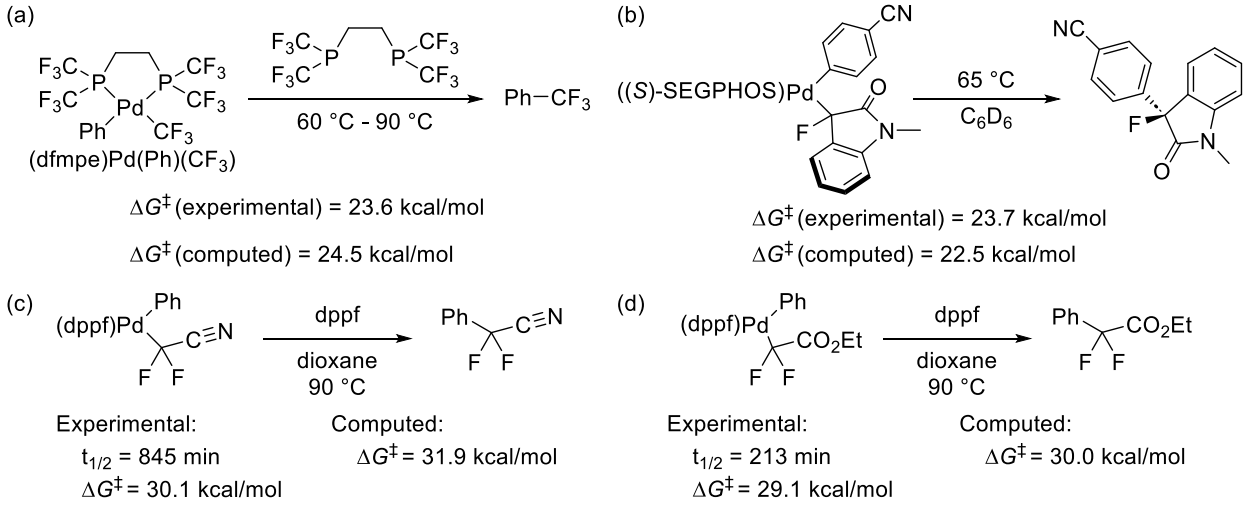
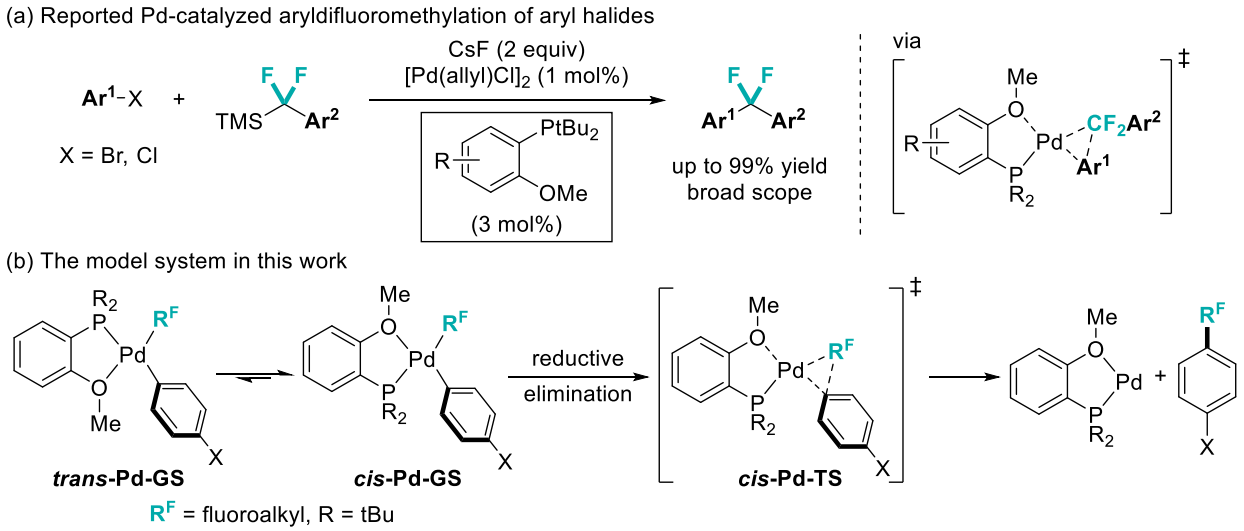


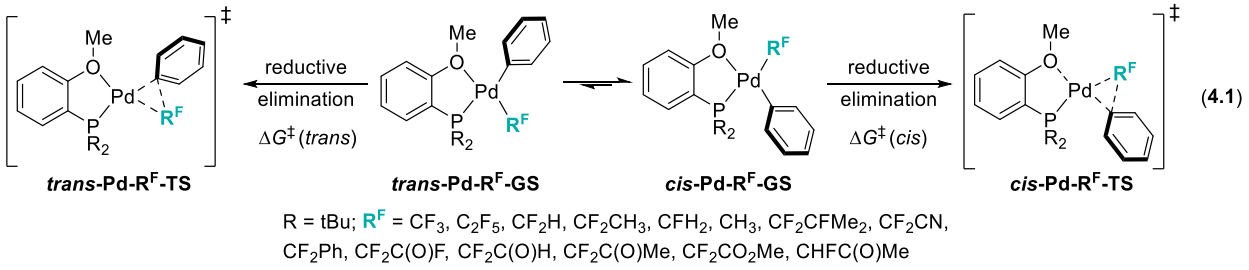
Figure 4.1. Comparison of experimentally determined and computed barriers to reductive elimination from (a) (dfmpe)Pd(Ph)(CF_3),[24] (b) ((*S*)-SEGPHOS)Pd(4-CN-C_6H_4)(fluorooxindole)[12] (c) (dppf)Pd(Ph)(CF_2CN), and (d) (dppf)Pd(Ph)(CF_2CO_2Et).[15]

4.2.2.Geometries and Energies of Optimized Structures

Having confirmed that our computational method accurately predicts the barriers to reductive eliminations from Pd(aryl)(fluoroalkyl) complexes, we investigated the effect of the identity of the fluoroalkyl ligand on the barrier to reductive elimination. We selected Pd complexes containing the aryldialkylphosphine ligand di-*tert*-butyl(2-methoxyphenyl)phosphine (**L**) as the model system because we recently showed that Pd complexes of **L** catalyzed the aryldifluoromethylation of aryl halides with high yields and a broad scope (Scheme 4.2(a)).[32, 41] Other aryldialkylphoshines containing alkoxyaryl moieties such as BrettPhos, RuPhos, and SPhos also have been reported to facilitate a variety of Pd-catalyzed fluoroalkylation reactions;[13, 18, 42] however, we did not investigate systems containing these ligands due to their large sizes and accompanying high computational costs.



Scheme 4.2. (a) The reported Pd-catalyzed aryldifluoromethylation of aryl halides; (b) the model system studied in this work.



We optimized ground-state and transition-state geometries for a series of palladium complexes **Pd-R^F** (eq 4.1, ***trans*-/*cis*-Pd-R^F-GS** and ***trans*-/*cis*-Pd-R^F-TS**, respectively). The calculated relative Gibbs free energies (ΔG) and selected geometric parameters of representative **Pd-R^F** structures are shown in Table 4.1 (see Tables 4.2 and 4.7 for the data of all other **Pd-R^F** structures). Structures in which the fluoroalkyl ligand was either *cis* to the methoxy fragment of the ligand **L** (***cis*-Pd-R^F**) or *trans* to it (***trans*-Pd-R^F**) were considered (Figure2(a), 2(c), R^F = CF_2Ph as an example); in most cases the ground-state free energy of the *cis* isomer was lower than that of the *trans* isomer ($\Delta G_{trans} - \Delta G_{cis}$ = 0.2 – 2.1 kcal/mol). The exception was the system in which R^F = CF_2H; in this case, the *trans* isomer was slightly more stable ($\Delta G_{trans} - \Delta G_{cis}$ = -0.3 kcal/mol). Both *cis* and *trans* ground-state complexes adopted slightly distorted square-planar structures, with φ = 170˚– 180˚, in which φ is defined as the dihedral angle formed by C(Ph)–Pd–P–O or C(R^F)–Pd–P–O for *cis*- or *trans*-complexes, respectively (Figure 4.2(a), 2(c), R^F = CF_2Ph as an example). In these computed ground-state structures, the distances from the Pd center to either the phosphine or the methoxy fragment of the bidentate ligand **L** (r(Pd–P) = 2.36 – 2.41 Å and r(Pd–O) = 2.27 – 2.32 Å) were in close agreement to values obtained from reported crystal structures of similar (**L**)Pd complexes (r(Pd–P) = 2.29 – 2.32 Å and r(Pd–O) = 2.27 – 2.30 Å).[43-44]

The lowest-energy transition-state structures for reductive elimination from the *cis* and *trans* complexes (***cis*-** and ***trans*-Pd-R^F-TS**) were also computed. As was the case for the ground-

state structures, the transition-state geometries were calculated to be lower in energy for the *cis* structures than for the *trans* structures for most fluoroalkyl ligands ($\Delta G^{\ddagger}_{trans} - \Delta G^{\ddagger}_{cis}$ = 0.7 – 5.7 kcal/mol). Exceptions to this trend were complexes with $R^F = CF_3$, C_2F_5, $CF_2C(O)H$, for which the *trans* transition-state structures were slightly lower in energy than the *cis* analogs ($\Delta G^{\ddagger}_{trans} - \Delta G^{\ddagger}_{cis}$ = -0.9, -0.1, and -0.5 kcal/mol, respectively). The Pd–O bonds in the transition-state structures ***trans*-Pd-R^F-TS** were moderately longer than those in the ground states (Δr(Pd–O) = 0.2 – 0.3 Å), and the degrees of distortion from square planar in the transition states were only slightly larger ($|\Delta\varphi| < 6$˚) than in the ground-states (Table 4.1 and Figure 4.2(d)). In contrast, larger changes in the structures were computed to occur during reductive elimination from the ***cis*-Pd-R^F** isomers. As the reaction proceeds from ***cis*-Pd-R^F-GS** to ***cis*-Pd-R^F-TS**, the methoxy fragment of the ligand **L** twists significantly out of the plane defined by other ligated groups on the Pd center (Table 4.1 and Figure 4.2(b)), the Pd–O bond lengthens (Δr(Pd–O) = 0.2 – 0.6 Å), and the deviation from the square-planar geometry ($\Delta\varphi$ = 14 – 48˚ except for $R^F = CF_3$ ($\Delta\varphi$ = -1˚)) is larger than it is during reductive elimination from the ***trans*-Pd-R^F** isomers. These changes in structure suggest that the Pd–O bond is weaker in the transition state ***cis*-Pd-R^F-TS** than in ***trans*-Pd-R^F-TS**. We note that similar elongation of the Pd–O bond in the transition state was observed in a previous DFT study on the reductive elimination from alkylpalladium amido complexes containing similar methoxy-substituted aryldialkylphosphine ligands.[44] We hypothesized that the greater degree of dissociation of the methoxy substituent on the ligand in ***cis*-Pd-R^F-TS**, relative to that of the same group in the ligand of ***trans*-Pd-R^F-TS**, might reduce the destabilizing steric interaction of the methoxy group with the adjacent migrating R^F ligand and allow for stabilizing interactions between the R^F ligand and the Pd center (*vide infra*), ultimately leading to lower barriers to reductive elimination.

Table 4.1. Calculated relative Gibbs free energies (ΔG) and selected geometric parameters of the lowest-energy ground-state and transition-state structures of representative ***cis*-** and ***trans*-Pd-R^F** complexes

R^F	structure	ΔG (kcal/mol)	*r*(Pd-P) (Å)	*r*(Pd-O) (Å)	φ(C(Ph),Pd, P, O) (˚)	φ(C(R^F),Pd, P, O) (˚)
CF_3	*cis*-GS	0.0	2.39	2.29	175	
	cis-TS	28.2	2.33	2.47	176	
	trans-GS	1.1	2.40	2.29		176
	trans-TS	27.3	2.34	2.54		178
CF_2CN	*cis*-GS	0.0	2.36	2.29	179	
	cis-TS	21.0	2.34	2.77	147	
	trans-GS	2.1	2.40	2.30		179
	trans-TS	24.7	2.38	2.53		173
CF_2Ph	*cis*-GS	0.0	2.39	2.31	171	
	cis-TS	17.3	2.33	2.92	123	
	trans-GS	0.2	2.40	2.32		180
	trans-TS	23.0	2.37	2.61		176
CF_2H	*cis*-GS	0.3	2.40	2.29	176	
	cis-TS	18.5	2.34	2.66	156	
	trans-GS	0.0	2.39	2.29		176
	trans-TS	19.7	2.35	2.58		180
CFH_2	*cis*-GS	0.0	2.39	2.30	173	

	cis-TS	16.0	2.33	2.60	154	
	trans-GS	1.5	2.37	2.31		172
	trans-TS	17.2	2.35	2.57		174
CH_3	*cis*-GS	0.0	2.37	2.30	180	
	cis-TS	14.0	2.33	2.59	166	
	trans-GS	1.1	2.36	2.31		177
	trans-TS	15.6	2.35	2.57		178
$CF_2C(O)Me$	*cis*-GS	0.0	2.40	2.30	173	
	cis-TS	21.6	2.35	2.72	140	
	trans-GS	1.8	2.39	2.30		179
	trans-TS	23.2	2.38	2.54		175
$CF_2C(O)H$	*cis*-GS	0.0	2.40	2.31	175	
	cis-TS	20.6	2.37	2.74	133	
	trans-GS	1.0	2.38	2.31		178
	trans-TS	20.1	2.38	2.51		176

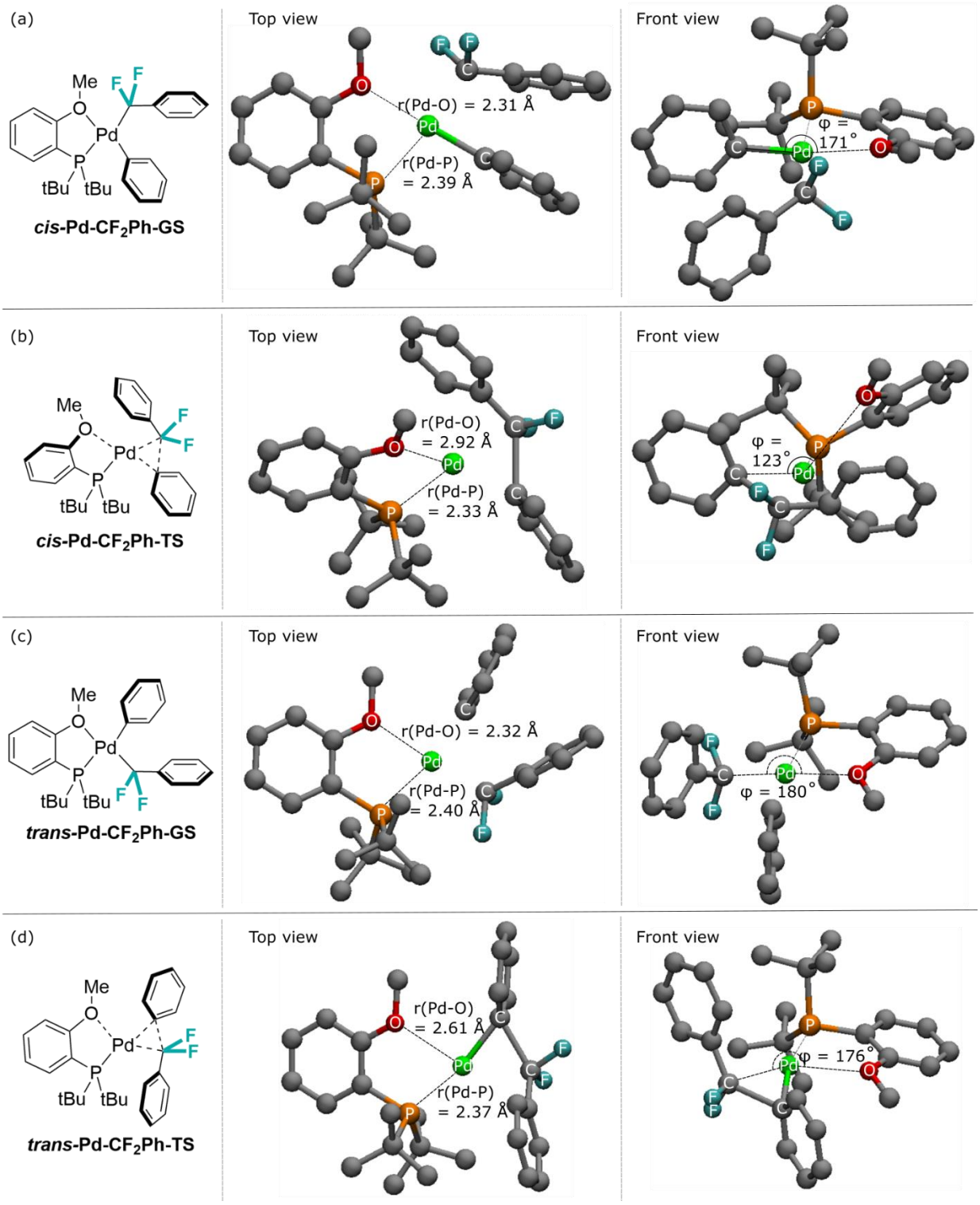
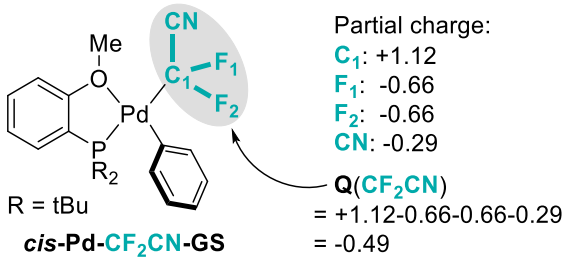


Figure 4.2. Optimized structures and selected geometric parameters of (a) ***cis*-Pd-CF$_2$Ph-GS**; (b) ***cis*-Pd-CF$_2$Ph-TS**; (c) ***trans*-Pd-CF$_2$Ph-GS**; (d) ***trans*-Pd-CF$_2$Ph-TS**. Hydrogen atoms are omitted for clarity.

Overall, the calculated barriers indicate that reductive elimination from ten of the fourteen **Pd-R^F** complexes studied would proceed quickly, even at 25 °C ($\Delta G^{\ddagger} \leq 22.3$ kcal/mol, corresponding to predicted $t_{1/2} < 45$ min for $R^F \neq CF_3$, C_2F_5, CF_2Me, or CF_2CFMe_2). The four exceptions are **Pd-CF$_3$**, **Pd-C$_2$F$_5$**, **Pd-CF$_2$Me**, and **Pd-CF$_2$CFMe$_2$**. The computed barriers to reductive elimination from these four Pd complexes suggest that reductive elimination would be slow at room temperature; reductive elimination from ***cis*-Pd-CF$_3$**, ***cis*-Pd-C$_2$F$_5$**, ***cis*-Pd-CF$_2$Me**, or ***cis*-Pd-CF$_2$CFMe$_2$** would proceed with a reasonable rate at 100 °C ($t_{1/2}$ = 55 min and 106 min for $R^F = CF_3$ and C_2F_5, respectively) or at 60 ˚C ($t_{1/2}$ = 5 min and 123 min for $R^F = CF_2Me$ and CF_2CFMe_2, respectively). These computational results are consistent with the high temperatures required in experimental work for reductive elimination from related monophosphine-ligated aryl(perfluoroalkyl)palladium complexes to form trifluoromethylarenes.[13, 18-19, 22]



Scheme 4.3. Illustration of the definition of Q(R^F) using $R^F = CF_2CN$ as an example. Q(CF_2CN) is equal to the sum of the QTAIM partial charge of each atom of the CF_2CN fragment in the lowest-energy ground-state structure ***cis*-Pd-CF$_2$CN-GS**.

4.2.3.Quantification of the Electronic Properties of Fluoroalkyl Ligands and Analysis of the Features of Fluoroalkyl Ligands that Affect the Barriers to Reductive Elimination

To determine the factors that affect the barriers to reductive elimination, we first quantitatively assessed the effect of the electronic properties of the fluoroalkyl ligands on the Gibbs free energy of activation ($\Delta G^{\ddagger}$). It was not possible to simply compare $\Delta G^{\ddagger}$ values to the Hammett substituent constants of the R^F ligands of ***cis*-Pd-R^F** structures,[45] as was done in previous studies on the reductive eliminations from arylpalladium thiolate,[46] amide,[47] and alkoxide species,[48 49] because of the lack of published substituent constants for several of the R^F ligands. Thus, we developed a new descriptor for the electronic properties of the R^F ligands: Q(R^F), which is the sum of the QTAIM atomic charges[50, 51] of the fluoroalkyl (R^F) fragment in the ground-state structures ***cis*-Pd-R^F-GS** (Scheme 4.3, $R^F = CF_2CN$ as an example). We reasoned that a more electron-withdrawing R^F fragment in the ground-state complex ***cis*-Pd-R^F-GS** would contain a greater share of the electron density of the molecule, leading to a more negative Q(R^F) value. To evaluate this new descriptor, we plotted the Q(R^F) values of the difluoroalkyl ($R^F = CF_2X$) ligands against the σ_m substituent constant of the X group, a parameter commonly used to quantify inductive effects in linear free-energy relationships (Figure 4.3).[52] The strong linear correlation ($R^2 = 0.93$) between Q(CF_2X) and σ_m(X) demonstrates that Q(R^F) does reflect quantitatively the electron-withdrawing properties of the R^F ligands.

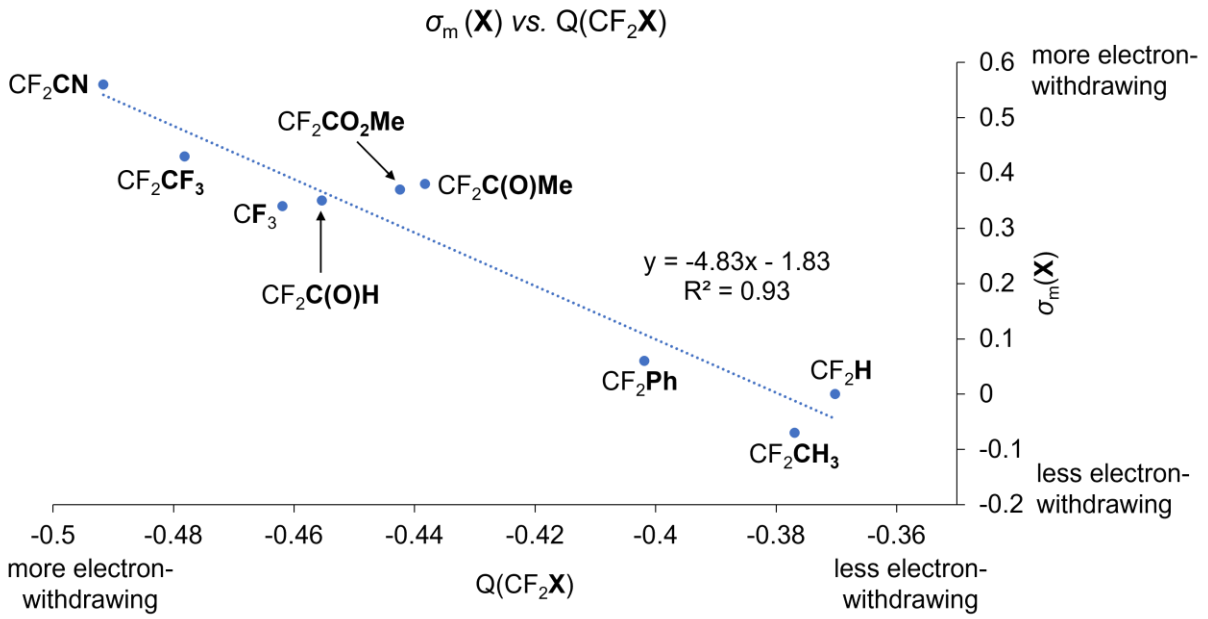


Figure 4.3. The linear relationship between the Q(CF_2X) and the σ_m (X) values for a series of difluoroalkyl ligands.

We next plotted the free-energy barriers ($\Delta G^{\ddagger}$) to reductive elimination from complexes ***cis*-Pd-R^F** against the Q(R^F) values of the R^F fragments (Figure 4.4 and Table 4.2). A high degree of scatter in this plot (R^2 = 0.45, Figure 4.4(a)) can be seen. For example, the Q(R^F) values, and, hence, the electron-withdrawing abilities, of R^F = C_2F_5 and R^F = CF_2CN are similar (Q(C_2F_5) = -0.478, Q(CF_2CN) = -0.492), but the barrier to reductive elimination from ***cis*-Pd-C$_2$F$_5$** is 7.9 kcal/mol higher than the corresponding barrier to elimination from ***cis*-Pd-CF$_2$CN** ($\Delta G^{\ddagger}$(C_2F_5) = 28.9 kcal/mol, $\Delta G^{\ddagger}$(CF_2CN) = 21.0 kcal/mol). Likewise, the Q(R^F) values of R^F = CF_2Me and R^F = CF_2H are similar (Q(CF_2Me) = -0.377, Q(CF_2H) = -0.370), but the barrier to reductive elimination from ***cis*-Pd-CF$_2$Me** is 5.1 kcal/mol higher than that from ***cis*-Pd-CF$_2$H** ($\Delta G^{\ddagger}$(CF_2Me) = 23.3 kcal/mol, $\Delta G^{\ddagger}$(CF_2H) = 18.2 kcal/mol). Thus, the barriers to reductive elimination depend on more than the Q(R^F) values.

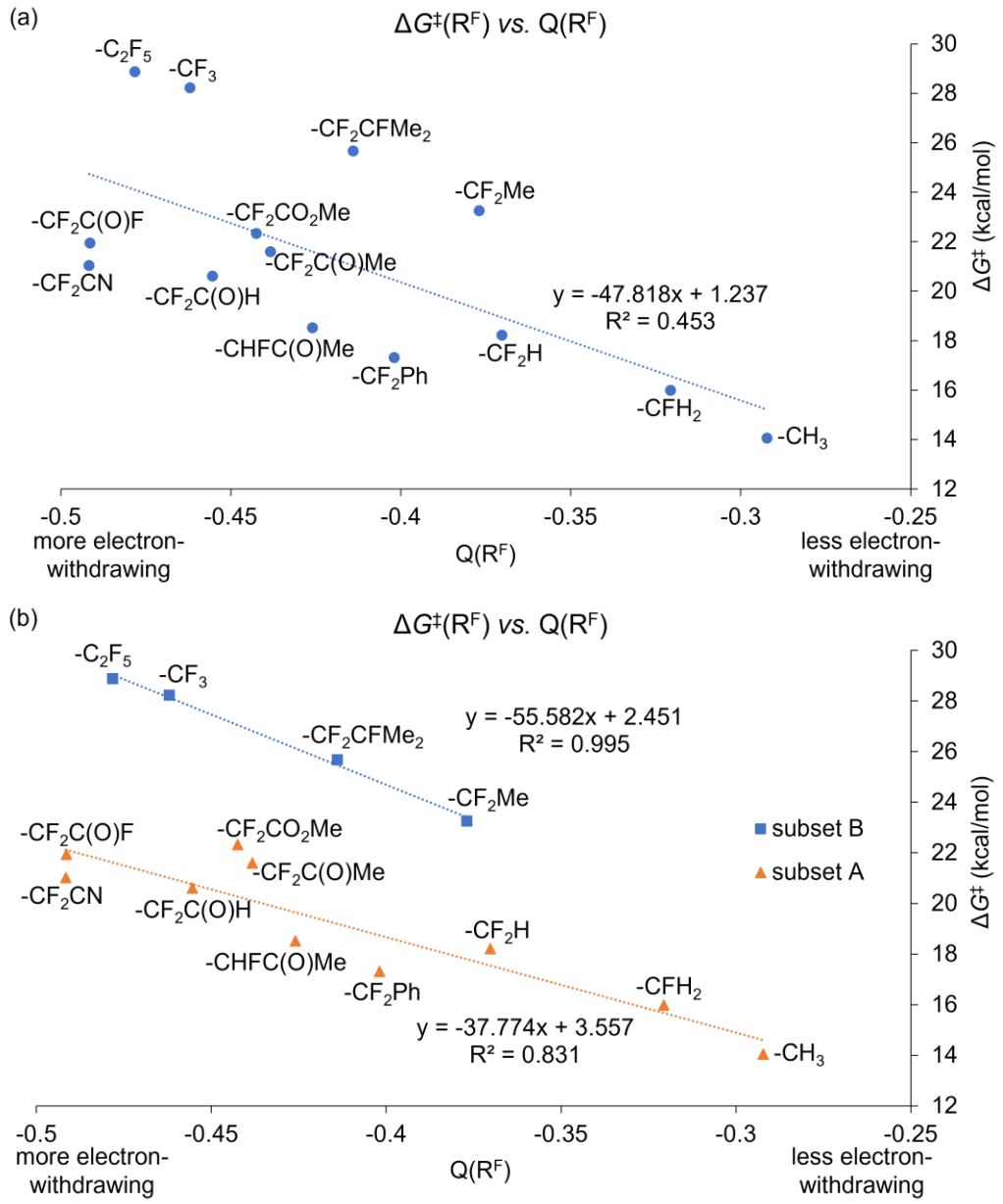


Figure 4.4. Plots of computed barriers to reductive elimination ($\Delta G^{\ddagger}(R^F)$) against $Q(R^F)$ values (a) without partitioning of R^F ligands into subsets; and (b) with partitioning of R^F ligands into subsets.

Table 4.2. $Q(R^F)$ values for a series of fluoroalkyl ligands and calculated free energies related to the reductive elimination of ***cis*-Pd-R^F** complexes.

R^F	$Q(R^F)$	$\Delta G^{\ddagger}(R^F)$ (kcal/mol)	$\Delta G^{\ddagger}_{rot}(R^F)$ (kcal/mol)	$\Delta\Delta G^{\ddagger}(R^F)$ (kcal/mol)	$\Delta E_{orb}(R^F)$ (kcal/mol)	$\Delta G^{\ddagger}_{no\text{-}orb}(R^F)$ (kcal/mol)
CF_2CN	-0.492	21.0	33.1	-12.1	-9.9	30.9
CF_2Ph	-0.402	17.3	28.4	-11.1	-7.3	24.6
CF_2H	-0.370	18.2	25.1	-6.9	-4.7	22.9
$CF_2C(O)Me$	-0.438	21.6	30.7	-9.1	-6.6	28.2
$CF_2C(O)H$	-0.455	20.6	29.5	-8.9	-6.7	27.3
CF_2CO_2Me	-0.442	22.3	30.9	-8.6	-4.8	27.1

$CF_2C(O)F$	-0.491	21.9	32.1	-10.1	-7.9	29.9
C_2F_5[a]	-0.478	28.9	31.3	-2.5	*n/a*	28.9
CF_2CH_3[a]	-0.377	23.3	25.5	-2.2	*n/a*	23.3
CF_2CFMe_2[a]	-0.414	25.7	29.5	-3.8	*n/a*	25.7
CF_3[a,b]	-0.462	28.2	*n/a*	*n/a*	*n/a*	28.2
CFH_2[c]	-0.321	16.0	*not found*	*n/a*	*n/a*	*n/a*
CH_3[b]	-0.292	14.0	*n/a*	*n/a*	*n/a*	*n/a*
CFHC(O)Me[c]	-0.426	20.6	*not found*	*n/a*	*n/a*	*n/a*

Definitions of energetic terms: $\Delta G^{\ddagger}(R^F)$, the barrier to reductive elimination involving the lowest-energy transition state ***cis*-Pd-R^F-TS**; $\Delta G^{\ddagger}_{rot}(R^F)$, the barrier to reductive elimination involving the transition states ***cis*-Pd-R^F-TS-rot**, in which the α-H or the α-π-acceptor is oriented away from the Pd center; $\Delta\Delta G^{\ddagger}(R^F) = \Delta G^{\ddagger}(R^F) - \Delta G^{\ddagger}_{rot}(R^F)$; $\Delta E_{orb}(R^F) = \Delta\Delta G^{\ddagger}(R^F) - \Delta E_{se}(R^F)$, the energy attributable to solely secondary orbital interactions, where $\Delta E_{se}(R^F)$ is the estimated energetic penalty attributed to changing steric and electronic interactions caused by the rotation of the R^F ligand (see Table 4.4); $\Delta G^{\ddagger}_{no\text{-}orb}(R^F) = \Delta G^{\ddagger}(R^F) - \Delta E_{orb}(R^F)$, the estimated barrier for the hypothetical scenario in which secondary orbital interactions are absent in ***cis*-Pd-R^F-TS** structures.

[a]Since these R^F ligands do not engage in secondary orbital interactions with the Pd center in ***cis*-Pd-R^F-TS** structures, $\Delta G^{\ddagger}(R^F) = \Delta G^{\ddagger}_{no\text{-}orb}(R^F)$ by definition.

[b]Due to the symmetric nature of these R^F ligands, the ***cis*-Pd-R^F-TS-rot** structures are identical to the ***cis*-Pd-R^F-TS** structures. Therefore, analysis based on $\Delta G^{\ddagger}_{rot}(R^F)$ is not applicable to these structures.

[c]We were unable to locate the transition-state structures ***cis*-Pd-R^F-rot** in which the α-hydrogens or the α-π-acceptor were oriented away from the Pd for these R^F ligands. Therefore, we have omitted analyses of $\Delta G^{\ddagger}_{rot}(R^F)$ for these structures.

We recently suggested that a donor-acceptor interaction between the *d* orbitals of Pd and the π^* orbital of the R^F fragment was present in the transition states for reductive elimination from aryl(3-fluorooxindolyl)- and aryl(difluoromethylaryl)palladium complexes.[12, 41] Thus, we hypothesized that the lack of correlation between $\Delta G^{\ddagger}(R^F)$ and $Q(R^F)$ could result from the presence or absence and varying strengths of such interactions within ***cis*-Pd-TS-R^F** complexes containing different R^F ligands. Indeed, the data points can be partitioned into two subsets that individually correlate $\Delta G^{\ddagger}(R^F)$ more strongly with $Q(R^F)$: a lower-energy subset **A** ($R^2 = 0.831$), in which the R^F ligands contain unsaturated groups or hydrogen atoms attached to the α-carbon atom (Figure 4.4(b), orange triangles), and a higher energy subset **B** ($R^2 = 0.995$), in which the R^F ligands are saturated and do not contain α-hydrogen atoms (Figure 4.4(b), blue squares). Within each subset, the correlation between $\Delta G^{\ddagger}(R^F)$ and $Q(R^F)$ is negative, indicating that the barriers to reductive elimination from aryl(fluoroalkyl)palladium complexes containing more electron-withdrawing fluoroalkyl ligands are higher than those containing less electron-withdrawing fluoroalkyl ligands, a trend which matches the well-established trend for reductive eliminations from arylpalladium complexes containing non-fluorinated alkyl ligands.[16, 53-55]

*4.2.4.Analysis of the Stabilizing Secondary Orbital Interactions between Pd and the Fluoroalkyl Ligands in the Transition States of Subset **A***

Further analysis of metal-ligand bonding in the ground and transition states provides strong evidence that the two subsets lie on distinct correlation lines because the transition states of subset **A** are stabilized by secondary orbital interactions between Pd and the unsaturated group or the α-hydrogen atom in the fluoroalkyl ligand, but the transition states of subset **B** are not. The fluoroalkyl ligands in the transition states for reductive elimination from the complexes in subset

A are oriented such that the π^* orbitals of the electrophilic aryl, nitrile, or carbonyl groups (R^F = CF_2Ph, CF_2CN, and $CF_2C(O)R$) can interact with the Pd center (Figure 4.5). To determine whether bonding interactions were present in such structures, we conducted IGMH (Independent Gradient Model based on Hirshfeld partition)[35-37] and NBO (Natural Bond Orbital)[34] analyses of these transition-state structures. IGMH analysis classifies interactions in specific regions of molecular space and assigns colors to these regions, based on whether the interactions are attractive and stabilizing (blue), repulsive and destabilizing (red), or result from van der Waals interactions (green). The IGMH plots of transition-state structures ***cis*-Pd-R^F-TS** possessing unsaturated groups in the R^F fragments clearly contain blue isosurfaces between the Pd center and the sp^2 or *sp* carbon in the carbonyl, nitrile, or phenyl groups (pointed by black arrows in Figure 4.5(a)(ii), 5(b)(ii), and 5(c)(ii), R^F = $CF_2C(O)Me$, CF_2CN, CF_2Ph, respectively), indicating stabilizing, bonding-like interactions between them. Furthermore, NBO analysis, which determines the presence of stabilizing interactions by electron donation from filled NBOs into vacant acceptor NBOs, reveals a stabilizing donor-acceptor interaction from a mostly filled *d* orbital of the Pd center into the mostly vacant π^* orbital of the carbonyl, nitrile, and phenyl fragments (Figure 4.5(a)(i), 5(b)(i), 5(c)(i)).

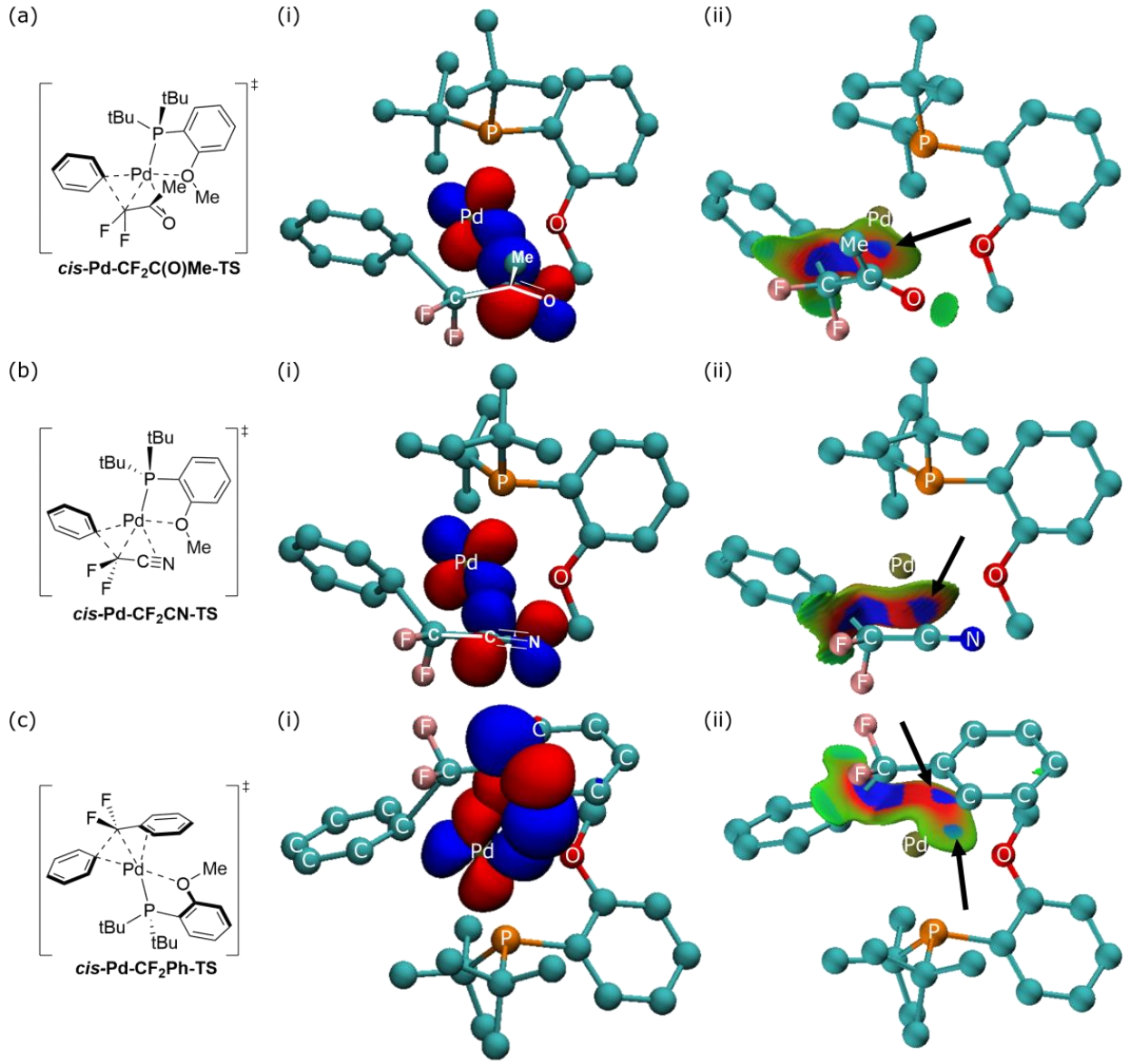


Figure 4.5. NBO and IGMH analyses of the stabilizing secondary orbital interactions in ***cis*-Pd-R^F-TS** structures between the Pd center and (a) the α-carbonyl group for R^F = $CF_2C(O)Me$, (b) the α-nitrile group for R^F = CF_2CN, (c) the α-phenyl group for R^F = CF_2Ph. NBO isosurfaces depict the leading orbitals involved in the d(Pd) → π^*(R^F) interactions. Blue isosurfaces labeled with black arrows in the IGMH plots indicate stabilizing interactions between the R^F ligand and the Pd center.

A similar examination of the structures ***cis*-Pd-R^F-TS**, in which R^F = CH_3, CFH_2, CF_2H, and CHFC(O)Me, reveals that the α-C–H bond is oriented so that the σ and σ* orbital of the C–H bond interact with the Pd center (Figure 4.6, R^F = CF_2H as an example). IGMH plots of the transition states contain blue regions between the Pd atom and the α-hydrogen atom of the methyl or fluoroalkyl ligands, suggesting the presence of stabilizing interactions between them (Figure 4.6(c) and 6(d)). NBO analysis revealed two stabilizing interactions between the C–H bond and the Pd center in these transition-state structures: (1) a stabilizing donor-acceptor interaction from a mostly filled d orbital of the Pd center into the mostly vacant σ* orbital of the C–H bond (Figure 4.6(a)), and (2) a stabilizing donor-acceptor interaction from the mostly filled σ orbital of the C–

H bond to the mostly vacant 5*s* orbital of the Pd center (Figure 4.6(b)). Similar C–H agostic interactions also have been proposed to be present in the transition states for reductive eliminations from Pt(IV) and Pd(IV) methyl complexes[56-57] and are in agreement with early theoretical studies on reductive elimination reactions.[58-59] These results support our hypothesis that transition states in subset **A** containing unsaturated groups or α-hydrogens in the R^F ligands are stabilized by secondary orbital interactions between the Pd center and the π-accepting groups or the α-hydrogens.

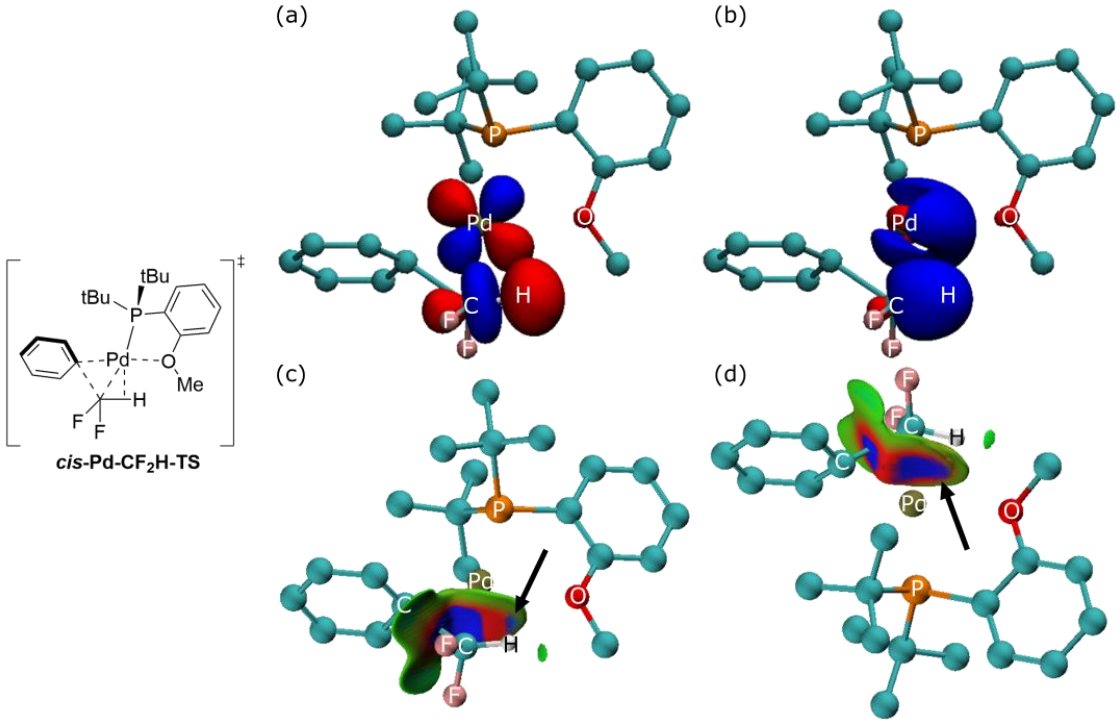
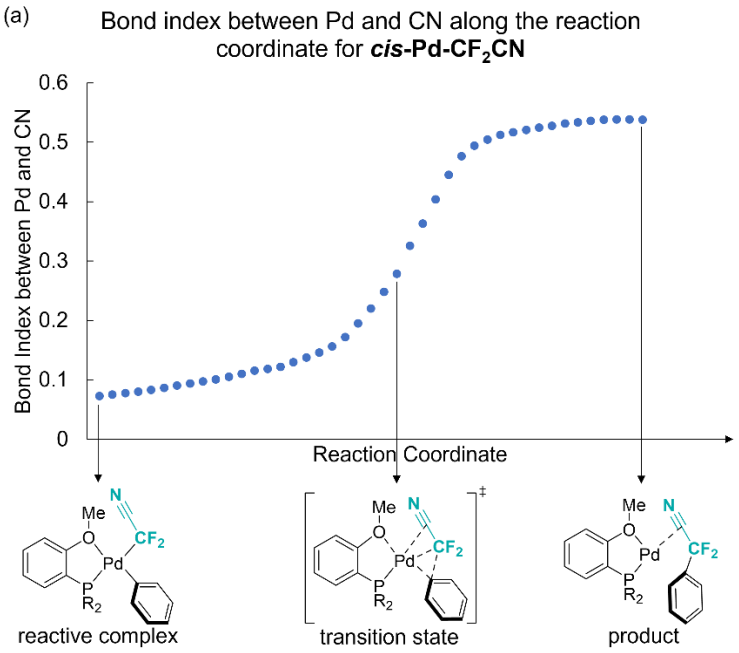


Figure 4.6. NBO and IGMH analyses of the stabilizing secondary orbital interactions between the Pd center and the C(α)–H bond in the transition state ***cis*-Pd-CF$_2$H-TS**; (a) visualization of the *d*(Pd) → σ*(C–H) orbital interaction; (b) visualization of the σ(C–H) → *s*(Pd) orbital interaction; (c)(d) IGMH plots; blue isosurfaces labelled with black arrows indicate stabilizing interactions between the R^F ligand and the Pd center.

Analysis of the Wiberg bond indices[60] (calculated in the NAO basis) between Pd and the π-acid or the α-hydrogen in the structures lying on the intrinsic reaction coordinates (IRCs) for reductive elimination from ***cis*-Pd-R^F** complexes in subset **A** suggests that the Pd-H and the Pd-π^* interactions are absent in the ground-state structures ***cis*-Pd-R^F-GS**. Therefore, these interactions are specific to the transition states. Figures 4.7(a) and 4.7(b) show the Wiberg bond index between Pd and the cyano group as well as the index between Pd and the α–H along the reaction coordinates for the reductive elimination from ***cis*-Pd-CF$_2$CN** and ***cis*-Pd-CF$_2$H** complexes (as representative examples for Pd-π^* and Pd-H interactions, respectively). In the reactive complex, which is similar in structure to the lowest-energy ground state, the bond index between Pd and the substituent in the fluoroalkyl ligand is small (0.072 for Pd···CN, less than 0.02 for Pd···H), suggesting that the bonding interactions between the metal and the substituent in the R^F fragment are absent. As the reaction progresses to the transition state, the bond index between Pd and the substituent increases (Pd···CN: from 0.072 to 0.278; Pd···H: from < 0.02 to 0.0412), indicating the emergence of orbital interactions between the metal and the π-acceptor or the α-hydrogen in the transition state. After the C–C bond has formed between the phenyl and the CF_2CN fragments, the phenyl ring moves

farther from the Pd, whereas the cyano group moves closer to the metal, leading to a larger Wiberg bond index between Pd and CN in the product than in the transition state (Figure 4.7(a)). In contrast, after the C–C bond has formed between the phenyl and the difluoromethyl fragments, the C(sp^3)–H bond rotates away from the Pd, resulting in a smaller bond index between Pd and H in the product than in the transition state (Figure 4.7(b)). Although the bond index in the product may be smaller or larger than that in the transition state, depending on the identity of the R^F ligand, such changes in this bonding interaction occur after the transition state and, therefore, do not affect our analysis of the orbital interactions in the ground state versus the transition state. The small Wiberg bond indices between the metal and the substituent in the fluoroalkyl ligand in the reactive complexes versus the significantly larger bond indices in the transition states strongly suggest that the stabilizing secondary orbital interactions are specific to the transition-state structures and, therefore, influence the free energy barriers to reductive elimination.

We propose that the secondary orbital interactions are absent in the ground-state structures ***cis*-Pd-R^F-GS** for the following reasons: (1) the distance between Pd and the methoxy fragment of ligand **L** is short, and the coordination site on the metal is occupied; (2) the bond angle θ formed by C(R^F)–Pd–C(Ph) is close to 90˚, so the distance between Pd and the substituent in the fluoroalkyl ligand is long; (3) the π-acceptor lies out of the plane defined by the atoms bound to Pd in complexes containing large R^F ligands, due to steric repulsions (Figure 4.7(c), left). In contrast, the secondary orbital interactions can be present in the transition states ***cis*-Pd-R^F-TS** because (1) the methoxy group of ligand **L** dissociates from the metal center to open a coordination site; (2) the R^F ligand migrates closer to the phenyl ligand, decreasing the bond angle θ (from ~ 90˚ to ~ 55˚) and the distance between Pd and the π-acceptor or the α-H; and (3) the substituent in the migrating fluoroalkyl ligand is coplanar with the Pd center, enabling favorable overlap between the orbitals. All of these factors lead to the presence of stabilizing orbital interactions between Pd and the fluoroalkyl ligand in the transition state, but not in the ground state.



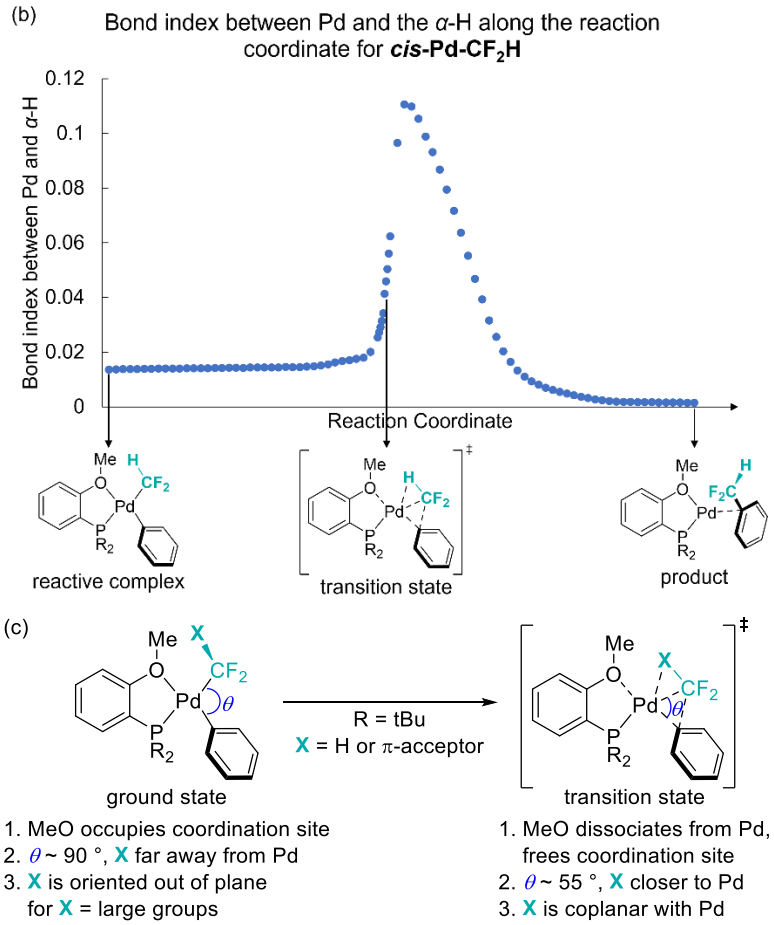


Figure 4.7. (a) Wiberg bond index between Pd and CN along the reaction coordinate for the reductive elimination from ***cis*-Pd-CF$_2$CN** complex; (b) Wiberg bond index between Pd and α-H along the reaction coordinate for the reductive elimination from ***cis*-Pd-CF$_2$H** complex; (c) rationalizations for why secondary orbital interactions are specific to the transition states.

4.2.5.Determination of the Energetic Stabilizations Resulting from Secondary Orbital Interactions

Having identified features in the R^F ligands that engage in secondary orbital interactions with the Pd center, as well as the causes for such stabilizations, we sought to estimate the energetic stabilization resulting from these features. To do so, we compared the ***cis*-Pd-R^F-TS** structures to higher-energy transition-state structures in which stabilizing groups of the fluoroalkyl ligand were oriented away from the Pd center by rotation about the Pd–R^F bond (***cis*-Pd-R^F-TS-rot**) (Figure 4.8). The free energies of ***cis*-Pd-R^F-TS-rot**, relative to the corresponding ground-state structures ***cis*-Pd-R^F-GS** ($\Delta G^{\ddagger}_{rot}$(R^F)), are reported in Table 4.2, and representative geometries for ***cis*-Pd-R^F-TS** and ***cis*-Pd-R^F-TS-rot** are compared in Figure 4.8 (R^F = CF$_2$H and CF$_2$CN as examples) and Table 4.3. By separating the Pd center from the unsaturated groups or α-hydrogen atoms of the R^F ligand, we reasoned that the secondary orbital interactions would be much weaker or absent. Indeed, in the rotameric transition-state structures ***cis*-Pd-R^F-TS-rot**, the distances between the Pd center and the α-hydrogen or the α-π-acid are greater than the sum of the van der Waals radii of the corresponding atoms (Table 4.3), demonstrating that the Pd center does not interact directly with the α-hydrogen or the α-π-acid in the R^F ligand.

The energies of ***cis*-Pd-R^F-TS-rot** are higher than those of ***cis*-Pd-R^F-TS** by 6.9 – 12.1 kcal/mol for the complexes of R^F in subset **A** and by 2.2 – 3.8 kcal/mol for the complexes of R^F in subset **B** (Table 4.2). We recognize that the difference in energy between ***cis*-Pd-R^F-TS** and ***cis*-Pd-R^F-TS-rot** ($\Delta\Delta G^{\ddagger}(R^F)$) does not arise solely from the aforementioned donor-acceptor interactions ($\Delta E_{orb}(R^F)$). Other differences in the steric and electronic properties ($\Delta E_{se}(R^F)$) caused by the rotation of the R^F fragment exist between these two structures. Thus, we decomposed $\Delta\Delta G^{\ddagger}(R^F)$ into a term representing the stabilization energy arising from the secondary orbital interactions ($\Delta E_{orb}(R^F)$) and a term representing the energetic penalty resulting from other differences between the steric and electronic properties of the structures ($\Delta E_{se}(R^F)$). That is,

$$\Delta\Delta G^{\ddagger}(R^F) = \Delta G^{\ddagger}(R^F) - \Delta G^{\ddagger}_{rot}(R^F) = \Delta E_{orb}(R^F) + \Delta E_{se}(R^F) \quad (4.2)$$

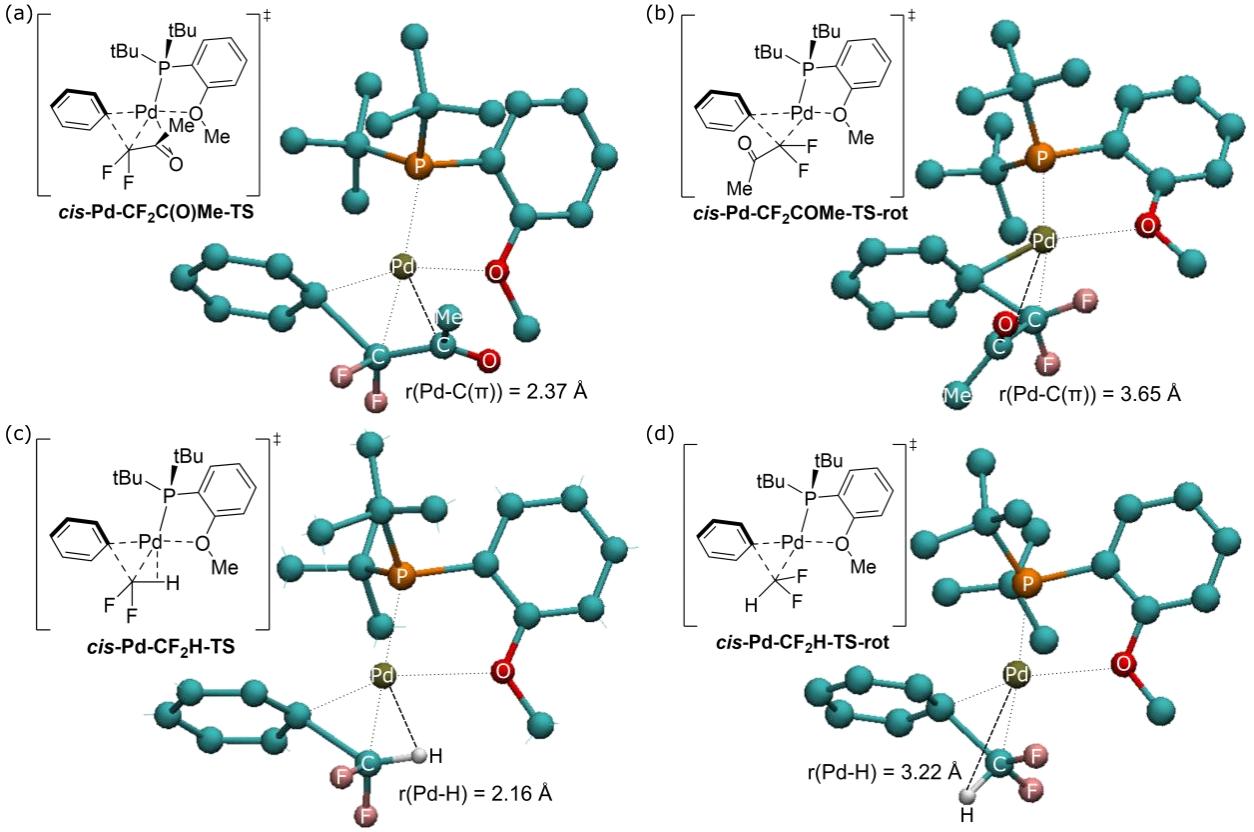


Figure 4.8. Optimized transition-state structures of (a) ***cis*-Pd-CF$_2$C(O)Me-TS**, (b) ***cis*-Pd-CF$_2$C(O)Me-TS-rot**, (c) ***cis*-Pd-CF$_2$H-TS**, (d) ***cis*-Pd-CF$_2$H-TS-rot**.

Table 4.3. The distances between the Pd center and the α-H or the electrophilic atom of the α-π-acid in optimized transition-state structures ***cis*-Pd-R^F-TS** and ***cis*-Pd-R^F-TS-rot**.

Entry	R^F	r(Pd···X)^a in ***cis*-Pd-R^F-TS** (Å)	r(Pd···X)^a in ***cis*-Pd-R^F-TS-rot** (Å)	r_{vdW}(Pd) + r_{vdW}(X)^a (Å)[61]
1	CF_2CN	2.22	3.64	3.33
2	$CF_2C(O)Me$	2.37	3.65	
3	$CF_2C(O)H$	2.24	3.63	

4	CF_2CO_2Me	2.41	3.66	
5	$CF_2C(O)F$	2.30	3.66	
6	CF_2Ph	2.29	3.66	
7	CF_2H	2.16	3.22	2.83

[a]X refers to the atom that is α to the difluoromethylene moiety. X = H(α) for $R^F = CF_2H$; X = C(π) for any other R^F.

To estimate $\Delta E_{se}(R^F)$, we first considered that $\Delta E_{se}(R^F) = \Delta\Delta G^{\ddagger}(R^F)$ for R^F ligands that did *not* participate in donor-acceptor orbital interactions (*i.e.*, those in subset **B**: $R^F_{\mathbf{B}} = C_2F_5$, CF_2CH_3 and CF_2CFMe_2, for which $\Delta E_{orb}(R^F_{\mathbf{B}}) = 0$; see Table 4.2). Then, we reasoned that $\Delta E_{se}(R^F)$ would be similar for R^F ligands of similar sizes (see Section 4.4 for details regarding the volumes of R^F ligands) and assigned the $\Delta E_{se}(R^F_{\mathbf{A}})$ value of any remaining fluoroalkyl ligand to the $\Delta E_{se}(R^F_{\mathbf{B}})$ value of the $R^F_{\mathbf{B}}$ ligand whose volume is closest to that of the $R^F_{\mathbf{A}}$ (Table 4.4). By solving eq 4.2 for ΔE_{orb}, we obtained a quantitative estimate of the magnitude of the stabilizing secondary orbital interactions, $\Delta E_{orb}(R^F)$ in the transition state ***cis*-Pd-R^F-TS** for each R^F ligand (eq 4.3). From this analysis, we determined that the secondary orbital interactions stabilized the lowest-energy transition states to reductive elimination by 4.7 – 9.9 kcal/mol (Table 4.2, column "$\Delta E_{orb}(R^F)$").

Table 4.4. Calculated volumes of protonated fluoroalkyl fragments and estimates of the energetic penalties (E_p) associated with reorienting the R^F ligands in ***cis*-Pd-R^F-TS-rot** structures.

$R^F_{\mathbf{B}}$	Calculated volume of $R^F_{\mathbf{B}}$ (Å^3)[a]	$\Delta E_{se}(R^F_{\mathbf{B}}) = \Delta\Delta G^{\ddagger}(R^F_{\mathbf{B}})$ (kcal/mol)	$R^F_{\mathbf{A}}$	Calculated volume of $R^F_{\mathbf{A}}$ (Å^3)[a]	$R^F_{\mathbf{B}}$ most similar in volume	$\Delta E_{se}(R^F_{\mathbf{A}})$ (kcal/mol)
C_2F_5	90.6	-2.5	CF_2CN	76.1	CF_2Me	-2.2
CF_2Me	75.5	-2.2	CF_2CO_2Me	111.6	CF_2CFMe_2	-3.8
CF_2CFMe_2	125.8	-3.8	$CF_2C(O)F$	82.5	CF_2Me	-2.2
			$CF_2C(O)H$	78.3	CF_2Me	-2.2
			$CF_2C(O)Me$	100.8	C_2F_5	-2.5
			CF_2H	52.0	CF_2Me	-2.2
			CF_2Ph	148.7	CF_2CFMe_2	-3.8

[a]See Section 4.4 for calculations of the volumes of R^F fragments.

$$\Delta E_{orb}(R^F) = \Delta\Delta G^{\ddagger}(R^F) - \Delta E_{se}(R^F) \tag{4.3}$$

$$\Delta\Delta G^{\ddagger}_{no-orb}(R^F) = \Delta G^{\ddagger}(R^F) - \Delta E_{orb}(R^F) \tag{4.4}$$

Subtracting $\Delta E_{orb}(R^F)$ from the barrier to reductive elimination corresponding to the lowest-energy transition state ($\Delta G^{\ddagger}(R^F)$) affords a new parameter $\Delta G^{\ddagger}_{no\text{-}orb}(R^F)$ (eq 4.4), which estimates the hypothetical barrier to reductive elimination through the lowest-energy transition-state structure ***cis*-Pd-R^F-TS** in the absence of secondary orbital interactions between the Pd center and the R^F ligand. By plotting the $\Delta G^{\ddagger}_{no\text{-}orb}(R^F)$ *vs* the $Q(R^F)$ values, we observed that subsets **A** and **B** no longer constitute distinct groups. Instead, these new transition-state energies for all complexes together correlate well with the corresponding $Q(R^F)$ values (Figure 4.9, $R^2 = 0.96$). Thus, in the absence of secondary orbital interactions, complexes of more electron-withdrawing fluoroalkyl ligands generally undergo reductive elimination more slowly than those with a less electron-withdrawing fluoroalkyl ligand, and this result is consistent with general trends for reductive elimination from palladium(alkyl)(aryl) complexes in which complexes containing more

electron-withdrawing alkyl ligands undergo reductive elimination to form alkylarenes more slowly than complexes containing less electron-withdrawing alkyl ligands.[16, 53-55] Furthermore, the absence of the distinction between subsets **A** and **B** after the orbital stabilizations are removed strongly suggests that these orbital interactions are the primary, if not the sole, features distinguishing subset **A** from subset **B**.

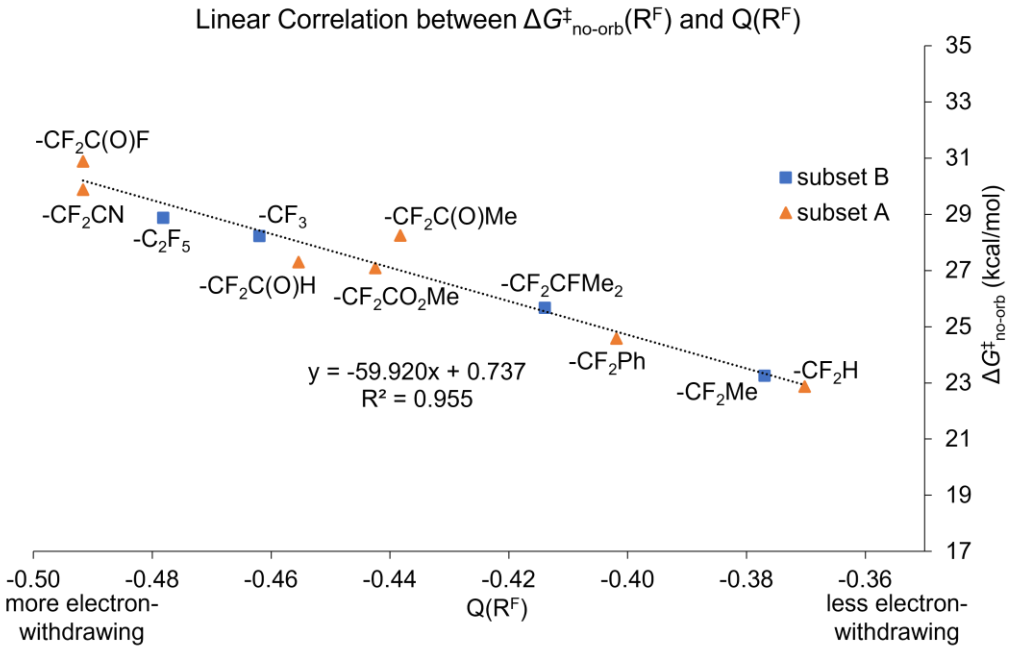


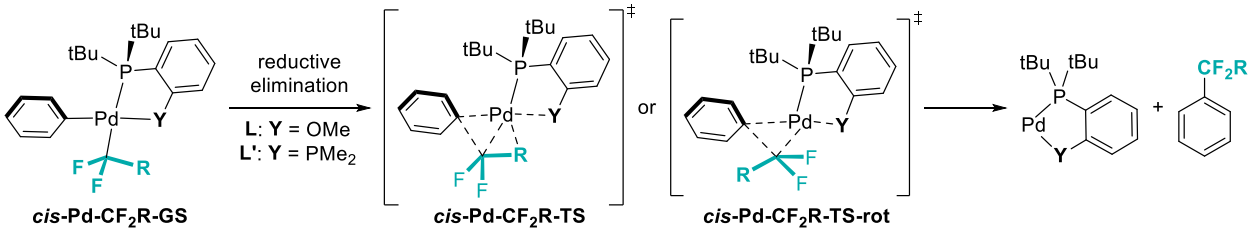
Figure 4.9. The linear correlation between $\Delta G^{\ddagger}_{\text{no-orb}}(R^F)$ and $Q(R^F)$. $\Delta G^{\ddagger}_{\text{no-orb}}(R^F)$ is the estimated hypothetical barrier to reductive elimination through the lowest-energy transition-state structure ***cis*-Pd-R^F-TS** in the absence of secondary orbital interactions between the Pd center and the R^F ligand; "no-orb" stands for "no orbital".

4.2.6.Effect of the Hemilabile Ligand on the Secondary Orbital Interactions

As illustrated in Figure 4.7(c), dissociation of the methoxy group of ligand **L** from the Pd center in transition states ***cis*-Pd-R^F-TS** accompanies the secondary orbital interactions. To investigate the impact of this dissociation on the stabilization from these secondary interactions, we computed the barriers to reductive elimination from palladium(phenyl)(fluoroalkyl) complexes (fluoroalkyl = CF_2H, CF_2CN, and CF_2Ph) containing the nonlabile bisphosphine ligand **L'** (**L'** = di-*tert*-butyl(2-dimethylphosphinophenyl)phosphine) and compared the results to those for reductive elimination from (**L**)Pd(aryl)(fluoroalkyl) complexes (Table 4.5). Barriers to reductive elimination from (**L'**)Pd complexes are significantly higher than those from (**L**)Pd complexes ($\Delta G^{\ddagger}$(**L'**, R^F) – $\Delta G^{\ddagger}$(**L**, R^F) = 11.7 – 13.5 kcal/mol). This difference in barrier is consistent with the well-established trend that reductive elimination from three-coordinate complexes is faster than from closely related four-coordinate complexes.[62] At the same time, this study shows that the stabilization from secondary orbital interactions in the transition states for reductive elimination from (**L'**)Pd complexes is smaller than that from (**L**)Pd complexes ($|\Delta E_{\text{orb}}$(**L**, R^F)| – $|\Delta E_{\text{orb}}$(**L'**, R^F)| = 3.4 – 4.6 kcal/mol, see Section 4.4 for details of calculation). Such differences in energy suggest

that dissociation of the methoxy fragment of the hemilabile ligand **L** in the transition state enhances the stabilizing secondary orbital interactions between the fluoroalkyl ligand and the Pd center and that enhancement of these interactions is one reason that complexes containing hemilabile or monodentate ligands generate catalysts that are particularly active for coupling of aryl halides with partially fluorinated alkyl groups.

Table 4.5. Comparison of reductive elimination from palladium(phenyl)(fluoroalkyl) complexes containing the hemilabile ligand **L** and the nonlabile bisphosphine ligand **L'**



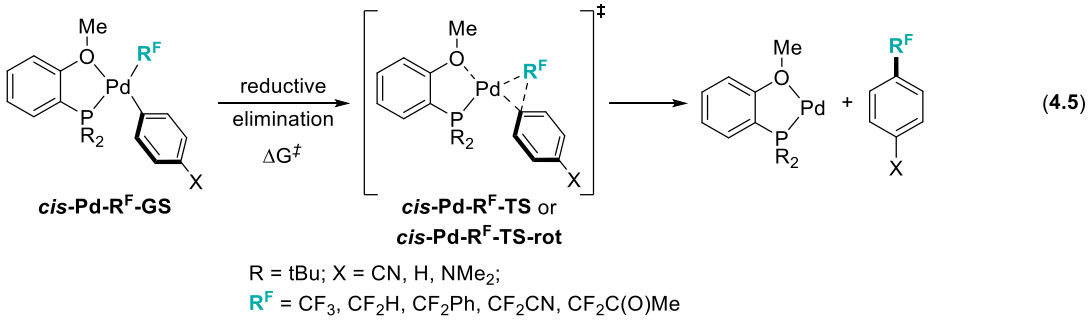
CF_2R	Ligand = **L** (Y = OMe)			Ligand = **L'** (Y = PMe_2)		
	$\Delta G^{\ddagger}$(**L**, R^F) (kcal/mol)	$\Delta G^{\ddagger}_{rot}$(**L**, R^F) (kcal/mol)	ΔE_{orb}(**L**, R^F) (kcal/mol)	$\Delta G^{\ddagger}$(**L'**, R^F) (kcal/mol)	$\Delta G^{\ddagger}_{rot}$(**L'**, R^F) (kcal/mol)	ΔE_{orb}(**L'**, R^F) (kcal/mol)
CF_2H	18.2	25.1	-4.7	31.0	33.9	-0.6
CF_2CN	21.0	33.1	-9.9	32.7	41.5	-6.5
CF_2Ph	17.3	28.4	-7.3	30.8	38.3	-2.7

4.2.7.Effect of the Electronic Properties of the Pd-bound Aryl Ligand

Finally, to conduct a systematic study of the effect of the electronic properties of the palladium-bound aryl group that couples with the fluoroalkyl group during reductive elimination from ***cis*-Pd-R^F** complexes, we computed the barriers to reductive elimination from a set of complexes with varying substituents on the palladium-bound aryl group (eq 4.5). We obtained the lowest-energy ground-state, transition-state, and rotated transition-state structures of a representative series of ***cis*-Pd-R^F** complexes (R^F = CF_3, CF_2H, CF_2CN, CF_2Ph, and $CF_2C(O)Me$) that contained electron-poor 4-cyanophenyl or electron-rich 4-*N,N*-dimethylaminophenyl ligands and compared the computed barriers to reductive elimination from these complexes to those from ***cis*-Pd-R^F** complexes containing unsubstituted phenyl ligands (Table 4.5). For complexes containing R^F ligands that can participate in secondary orbital interactions, *i.e.*, R^F = CF_2H, CF_2CN, CF_2Ph, and $CF_2C(O)Me$, the barriers to reductive elimination from species containing the more electron-donating 4-*N,N*-dimethylaminophenyl ligand were lower than the barriers for those containing the less electron-rich phenyl or 4-cyanophenyl ligands (see entries 1–4 in Table 4.6). This trend matches that observed experimentally for bisphosphine-ligated arylpalladium fluoroenolate and difluoromethyl complexes,[12, 15, 30] but is the *opposite* of that commonly observed for the reductive elimination of non-fluorinated alkylarenes and biaryls from Pd centers. It is most common that the barriers to reductive elimination from complexes containing more electron-poor aryl ligands are lower than those from complexes containing more electron-rich aryl ligands.[16, 46-48, 55] This unusual electronic effect on reductive elimination from ***cis*-Pd-R^F** complexes for which the transition states contain secondary orbital interactions was absent for reductive elimination from complexes lacking such secondary orbital interactions. No consistent trend was observed between the $\Delta G^{\ddagger}$ values for reductive elimination from complexes that lack the secondary orbital interactions (***cis*-Pd-CF_3-TS** and all ***cis*-Pd-R^F-TS-rot**) and the electronic properties of the palladium-bound aryl group (entries 5–9, Table 4.6). We note that previous experimental and

computational studies investigating the rates of reductive elimination from several aryl(trifluoromethyl)palladium complexes also revealed no systematic effect of the electronic properties of the palladium-bound aryl group on the barriers to reductive elimination of trifluoromethylarenes.[18, 63]

We propose that the greater electron density on the Pd center in the transition states ***cis*-Pd-R^F-TS** of complexes containing the more electron-donating aryl ligand enhances the stabilizing donor-acceptor interaction between *d*(Pd) and the π^* orbital of the unsaturated group or the σ^* orbital of the α-C–H bond of the R^F ligand. This enhanced stabilizing secondary orbital interaction results in a lower barrier to reductive elimination. However, the electron density around Pd resulting from the electron-donating ability of the phenyl ligand has less impact on the barrier to reductive elimination for complexes undergoing reductive elimination through transition states ***cis*-Pd-CF$_3$-TS** and all ***cis*-Pd-R^F-TS-rot** that lack the donor-acceptor interaction.



(4.5)

Table 4.6. Free energy barriers to reductive elimination ($\Delta G^{\ddagger}$) from transition-state structures containing unsubstituted or *para*-substituted phenyl groups.

Entry	Transition-state structure	$\Delta G^{\ddagger}$ (kcal/mol)		
		p-CN	*p*-H	*p*-NMe$_2$
1	***cis*-Pd-CF$_2$H-TS**	19.0	18.5	17.5
2	***cis*-Pd-CF$_2$CN-TS**	22.5	21.0	19.2
3	***cis*-Pd-CF$_2$Ph-TS**	18.7	17.3	16.9
4	***cis*-Pd-CF$_2$C(O)Me-TS**	21.6	21.6	20.3
5	***cis*-Pd-CF$_3$-TS**	27.2	28.2	27.3
6	***cis*-Pd-CF$_2$H-TS-rot**	24.3	25.1	25.2
7	***cis*-Pd-CF$_2$CN-TS-rot**	32.2	33.1	31.5
8	***cis*-Pd-CF$_2$Ph-TS-rot**	27.7	28.4	27.8
9	***cis*-Pd-CF$_2$C(O)Me-TS-rot**	30.3	30.7	30.2

4.3.Conclusion

In-depth DFT calculations investigating the effect of the fluoroalkyl ligand on the barrier to reductive elimination from (**L**)Pd(aryl)(fluoroalkyl) (**L** = di-tert-butyl(2-methoxyphenyl)phosphine) complexes to form fluoroalkylarenes have revealed the strong influence of secondary orbital interactions between the metal and the substituents in the fluoroalkyl ligand on the barriers to reductive elimination. The energies of ground-state and transition-state structures in which the fluoroalkyl group is *cis*- to the methoxy fragment of the ligand **L** are generally lower than those for structures in which the fluoroalkyl group is *trans*- to the methoxy fragment. A descriptor Q(R^F), defined as the sum of QTAIM atomic charges of the fluoroalkyl (R^F)

fragment in the ground-state structure ***cis*-Pd-R^F-GS** was developed to describe the electron-withdrawing ability of the R^F ligand quantitatively and correlated strongly with the barrier to reductive elimination in the absence of the secondary orbital interactions. The barriers to reductive elimination from complexes containing more electron-withdrawing fluoroalkyl ligands are generally higher than those containing less electron-withdrawing fluoroalkyl ligands in the absence of this secondary orbital interaction.

However, analyses of the lowest-energy transition-state structures ***cis*-Pd-R^F-GS-TS** by IGMH, NBO, and Wiberg bond indices revealed the presence of stabilizing secondary orbital interactions between the Pd center and the α-π-acceptors or the α-hydrogens in the R^F fragment in the transition states that were absent in the ground states. These secondary orbital interactions exist in the transition states because (1) the methoxy fragment of the ligand **L** dissociates from Pd and opens a free coordination site; (2) the distance between Pd and the π-acceptor or the α-hydrogen in the migrating fluoroalkyl ligand is short; (3) the substituent in the R^F ligand and the metal center are coplanar in the transition states. The magnitude of such stabilization was estimated to be 4.7 – 9.9 kcal/mol, and this stabilization accounts for the much lower barriers to reductive elimination from arylpalladium difluoroenolates, difluorocyanomethyl, difluorobenzyl, and difluoromethyl complexes than from perfluoroalkyl complexes. These secondary interactions account for the poor correlation between the experimental rates of reductive elimination from palladium(aryl)(fluoroalkyl) complexes and common parameters of the fluoroalkyl ligands (*e.g.*, steric or electronic properties). In the absence of these interactions, computed barriers to reductive elimination correlate linearly with the electronic property of the fluoroalkyl ligands. Finally, the barrier to reductive elimination from a palladium complex containing a more electron-donating aryl ligand that couples with the fluoroalkyl fragment in the transition state is lower than that containing a less electron-donating aryl ligand if the fluoroalkyl ligand can participate in stabilizing secondary orbital interactions with the Pd in the transition state because such stabilizations are enhanced by a more electron-rich metal center. This work rationalizes the scope and effects of ancillary ligands on a wide range of coupling reactions involving fluoroalkyl ligands, and can facilitate future development of novel, Pd-catalyzed fluoroalkylations of aryl halides.

4.4.Computational Details

4.4.1. Computational Methods

DFT calculations were conducted at the Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley using the Gaussian 16[64] software package. Initial geometries were constructed in GaussView[65] and optimized to stationary points (minima for ground states and first-order saddle points for transition states) using the PBE0 functional (the hybrid functional based on the Perdew-Burke-Ernzerhof functional [PBE][66] as described by Adamo[67]) with Grimme's D3 dispersion correction with Becke-Johnson damping (GD3BJ)[68] and the basis sets def2-TZVP (with ECP) for Pd and def2-SVP for all light atoms (**BS1**). This functional has been shown to accurately reproduce thermochemical energies[38] and kinetic barriers[39-40] calculated at the CCSD(T) level for closed-shell transition metal systems as well as experimentally determined barriers for isomerization and reductive elimination of arylpalladium fluoroenolate complexes.[12] The nature of each stationary point was evaluated by accompanying frequency calculations (all positive eigenvalues for minima and exactly one negative eigenvalue for transition states). Several conformers were considered, but only those representing the

minimum-energy paths are presented here. Transition states were connected to ground states by following the intrinsic reaction coordinate downhill from the transition state. While in most cases this corresponded to **Pd-R^F-GS**, intermediate ground state structures that were slightly higher in energy than **Pd-R^F-GS** were connected to the transition state **Pd-R^F-TS** for R^F = CF_2CN, CF_2Ph. These structures were labeled **Pd-R^F-GS'**.

Further single-point energy calculations were performed on the optimized geometries with a larger def2-QZVP basis set (with ECP) for Pd (obtained through the Basis Set Exchange,[69] accessed October 2019) and Truhlar's minimally-augmented version of the def2-TZVP basis set ("ma-TZVP") on all light atoms (**BS2**).[70] In all cases, Gibbs free energies for **BS2** were approximated by adding the thermal corrections obtained from frequency calculations using **BS1** to the **BS2** electronic energies. For calculations of reactions occurring at temperatures higher than 25 ˚C, thermodynamic data were corrected based on the method reported by Grimme[71] using the script GoodVibes v2.0.3 published by Luchini and co-workers.[72]

All calculations for Pd complexes containing the ligand di-*tert*-butyl(2-methoxyphenyl)phosphine (**L**), including geometry optimizations, were performed in THF solvent using the SMD solvent continuum model reported by Truhlar and co-workers according to the Solvent-Accessible Surface (scrf=sas).[73] All calculations for (dfmpe)Pd(Ph)(CF_3) (dfmpe = 1,2-bis(bis(trifluoromethyl)phosphino)ethane), including geometry optimizations, were performed with toluene as solvent, based on reported literature.[24] Geometry optimizations for (dppf)Pd and (**L'**)Pd complexes (dppf = 1,1'-bis(diphenylphosphino)ferrocene, **L'** = di-*tert*-butyl(2-dimethylphosphinophenyl)phosphine) were performed in the gas phase, due to difficulty in convergence with the solvation model. Single-point energy calculations for (dppf)Pd complexes were performed in dioxane solvent, consistent with reported literature.[15]

Natural Bond Orbital (NBO) and Natural Atomic Orbital (NAO) analyses were conducted with the NBO 6.0 program.[74] IGMH analysis[36] was conducted with Multiwfn 3.8(dev)[75] using the default parameters and a grid resolution of 0.1 Bohr. Complexes **Pd-R^F** were partitioned into fragments corresponding to the fluoroalkyl ligand (CF_3, CF_2H, CF_2CN, or CF_2Ph, etc.) and the rest of the molecule. Grid data were visualized with VMD.[76] AIM analyses were conducted on **BS2** wavefunctions using AIMALL[77] with Simple connectivity searching and the VeryFine integration mesh. All other parameters were left as their defaults.

Optimized structures for free fluoroalkanes R^F–H were calculated at the PBE0-D3BJ/def2-SVP level followed by final single-point energy calculations at the PBE0-D3BJ/ma-TZVP level. Molecular volumes (ρ > 0.001 au) were obtained using the molecular surface analysis feature of Multiwfn 3.8(dev) with a grid spacing of 0.12 Bohr (input: 12 2 11 3 0.12 0).

4.4.2. Geometries and Energies of Optimized Structures

Table 4.7. Calculated relative Gibbs free energies (ΔG) and selected geometric parameters of the lowest-energy ground-state and transition-state structures of ***cis-*** and ***trans*-Pd-R^F** complexes.

R^F	**structure**	**Δ*G* (kcal/mol)**	***r*(Pd-P) (Å)**	***r*(Pd-O) (Å)**	***φ*(C(Ph),Pd, P, O) (°)**	***φ*(C(R^F),Pd, P, O) (°)**
CF_3	*cis*-GS	0.0	2.39	2.29	175	
	cis-TS	28.2	2.33	2.47	176	
	trans-GS	1.1	2.40	2.29		176
	trans-TS	27.3	2.34	2.54		178
CF_2CN	*cis*-GS	0.0	2.36	2.29	179	
	cis-TS	21.0	2.34	2.77	147	
	trans-GS	2.1	2.40	2.30		179
	trans-TS	24.7	2.38	2.53		173
CF_2Ph	*cis*-GS	0.0	2.39	2.31	171	
	cis-TS	17.3	2.33	2.92	123	
	trans-GS	0.2	2.40	2.32		180
	trans-TS	23.0	2.37	2.61		176
CF_2H	*cis*-GS	0.3	2.40	2.29	176	
	cis-TS	18.5	2.34	2.66	156	
	trans-GS	0.0	2.39	2.29		176
	trans-TS	19.7	2.35	2.58		180
CFH_2	*cis*-GS	0.0	2.39	2.30	173	
	cis-TS	16.0	2.33	2.60	154	
	trans-GS	1.5	2.37	2.31		172
	trans-TS	17.2	2.35	2.57		174
CH_3	*cis*-GS	0.0	2.37	2.30	180	
	cis-TS	14.0	2.33	2.59	166	
	trans-GS	1.1	2.36	2.31		177
	trans-TS	15.6	2.35	2.57		178
C_2F_5	*cis*-GS	0.0	2.39	2.30	176	
	cis-TS	28.9	2.33	2.54	158	
	trans-GS	2.4	2.41	2.30		176
	trans-TS	28.8	2.37	2.53		175
CF_2CH_3	*cis*-GS	0.2	2.40	2.31	176	
	cis-TS	23.5	2.32	2.58	159	
	trans-GS	0.0	2.40	2.32		173
	trans-TS	24.5	2.35	2.57		175
$CF_2C(O)Me$	*cis*-GS	0.0	2.40	2.30	173	
	cis-TS	21.6	2.35	2.72	140	
	trans-GS	1.8	2.39	2.30		179

	trans-TS	23.2	2.38	2.54		175
CFHC(O)Me	*cis*-GS	0.0	2.39	2.31	178	
	cis-TS	18.5	2.34	2.64	144	
	trans-GS	2.5	2.36	2.30		176
	trans-TS	21.8	2.37	2.58		173
$CF_2C(O)H$	*cis*-GS	0.0	2.40	2.31	175	
	cis-TS	20.6	2.37	2.74	133	
	trans-GS	1.0	2.38	2.31		178
	trans-TS	20.1	2.38	2.51		176
CF_2CO_2Me	*cis*-GS	0.0	2.39	2.30	170	
	cis-TS	22.3	2.35	2.70	144	
	trans-GS	1.6	2.39	2.30		178
	trans-TS	24.0	2.37	2.51		175
$CF_2P(O)(OMe)_2$	*cis*-GS	0.0	2.40	2.27	174	
	cis-TS	22.0	2.35	2.74	128	
	trans-GS	1.5	2.40	2.30		176
	trans-TS	26.9	2.39	2.56		176
$CF_2C(O)F$	*cis*-GS	0.0	2.39	2.31	176	
	cis-TS	21.9	2.36	2.69	140	
	trans-GS	1.3	2.39	2.30		177
	trans-TS	22.6	2.37	2.50		177
CF_2CFMe_2	*cis*-GS	0.0	2.41	2.31	175	
	cis-TS	25.7	2.32	2.57	154	

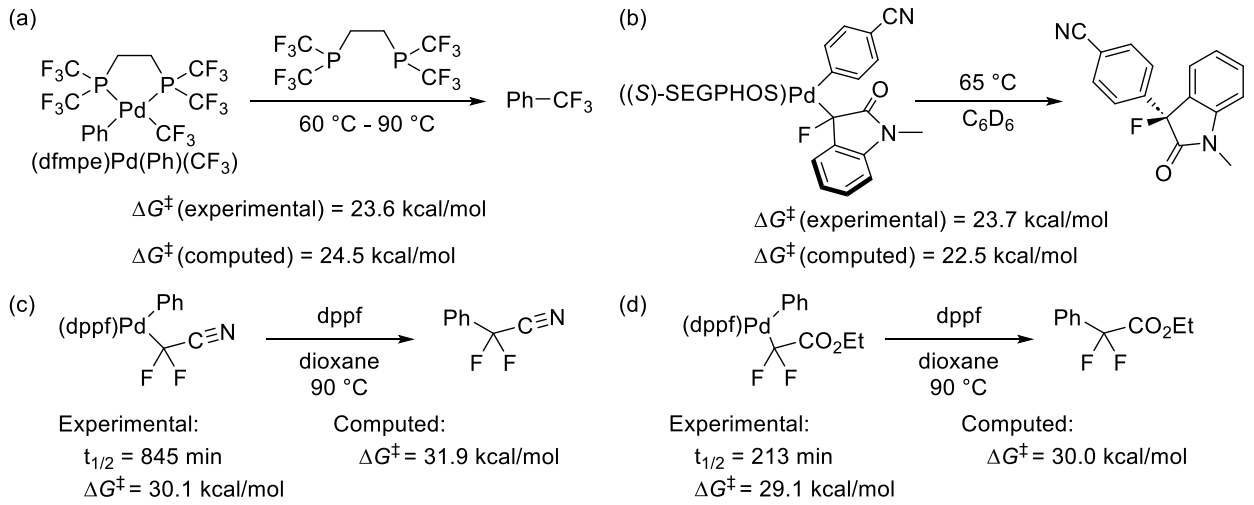


Figure 4.1. Comparison of experimentally measured and computed barriers to reductive elimination from (a) (dfmpe)Pd(Ph)(CF_3),[24] (b) ((*S*)-SEGPHOS)Pd(4-CN-C_6H_4)(fluorooxindole)[12] (c) (dppf)Pd(Ph)(CF_2CN), and (d) (dppf)Pd(Ph)(CF_2CO_2Et).[15]

Table 4.8. Energies of optimized structures in **Figure 4.1**

Structure	E(BS1) (a.u.)	Thermal Correction to Free Energy (a.u.)	G(BS1) (a.u.)	E(BS2) (a.u.)	G(BS2) (a.u.)
(dfmpe)Pd(Ph)(CF_3)-GS	-2805.20797248	0.155351	-2805.052621	-2807.80127774	-2807.645927
(dfmpe)Pd(Ph)(CF_3)-TS	-2805.1672623	0.153692	-2805.01357	-2807.7605712	-2807.606879
(dppf)Pd(Ph)(CF_2CN)-GS	-3945.12925999	0.541523	-3944.587737	-3947.37552397	-3946.834001
(dppf)Pd(Ph)(CF_2CN)-TS	-3945.08055147	0.539701	-3944.54085	-3947.32292934	-3946.783228
(dppf)Pd(Ph)(CF_2CO_2Et)-GS	-4119.78300734	0.610126	-4119.172881	-4122.22367068	-4121.613545
(dppf)Pd(Ph)(CF_2CO_2Et)-TS	-4119.73693948	0.609364	-4119.127575	-4122.17503777	-4121.565674

Note: Calculations of ((*S*)-SEGPHOS)Pd(4-CN-C_6H_4)(fluorooxindole) complexes have been reported in the literature.[12]

Table 4.9. Energies of optimized structures **Pd-R^F**

Note: In this table, names of structures follow the general format: **Pd-R$^{F(X)}$-GS** or **Pd-R$^{F(X)}$-TS**, in which **GS** indicates ground-state structures and **TS** indicates transition-state structures. The superscripted $^{(X)}$ indicates the *para*-substituent of the phenyl ligand in the Pd complex; the absence of the superscripted $^{(X)}$ indicates an unsubstituted phenyl ligand. The suffix ***-trans*** indicates ***trans*-Pd-R^F** structures in the main text, whereas the absence of the ***-trans*** suffix indicates ***cis*-Pd-R^F** structures. The suffix **-rot** indicates transition-state structures in which the group capable of engaging in secondary orbital interactions with the Pd center is rotated away from Pd. The parenthesized (**L'**) indicates complexes containing the nonlabile bisphosphine ligand di-*tert*-butyl(2-dimethylphosphinophenyl)phosphine. The atomic coordinates for each structure can be found in the accompanying XYZ file(s) with the structure's name in the comment line.

Structure	E(BS1) (Hartree)	Thermal Correction to Free Energy (Hartree)	G(BS1) (Hartree)	E(BS2) (Hartree)	G(BS2) (Hartree)	Q(R^F)
Pd-CF$_3$-GS	-1698.01917984	0.416122	-1697.60305784	-1699.4812436	-1699.0651216	-0.46194
Pd-CF$_3$-GS-*trans*	-1698.01924144	0.41721	-1697.60203144	-1699.48056496	-1699.06335496	
Pd-CF$_3$-TS	-1697.97296375	0.413891	-1697.55907275	-1699.43404082	-1699.02014982	
Pd-CF$_3^{(CN)}$-GS	-1790.09297239	0.412966	-1789.68000639	-1791.65900602	-1791.24604002	
Pd-CF$_3^{(CN)}$-TS	-1790.04766994	0.41005	-1789.63761994	-1791.61267497	-1791.20262497	
Pd-CF$_3^{(NMe2)}$-GS	-1831.74135814	0.483613	-1831.25774514	-1833.34419781	-1832.86058481	
Pd-CF$_3^{(NMe2)}$-TS	-1831.6960795	0.480578	-1831.2155015	-1833.29772966	-1832.81715166	
Pd-CF$_2$H-GS	-1598.92540373	0.425659	-1598.49974473	-1600.26785113	-1599.84219213	-0.370227
Pd-CF$_2$H-GS-*trans*	-1598.92687099	0.425998	-1598.50087299	-1600.26864855	-1599.84265055	
Pd-CF$_2$H-TS	-1598.88990875	0.420455	-1598.46945375	-1600.23361337	-1599.81315837	
Pd-CF$_2$H-TS-rot	-1598.8834911	0.422151	-1598.46134	-1600.22484729	-1599.8027	
Pd-CF$_2$H-TS-*trans*	-1598.89033169	0.422637	-1598.46769469	-1600.23383574	-1599.81119874	
Pd-CF$_2$H$^{(CN)}$-GS	-1690.99922488	0.421851	-1690.57737388	-1692.44566866	-1692.02381766	
Pd-CF$_2$H$^{(CN)}$-TS	-1690.9640133	0.417923	-1690.5460903	-1692.41141704	-1691.99349404	
Pd-CF$_2$H$^{(CN)}$-TS-rot	-1690.9591041	0.419272	-1690.53983	-1692.40438429	-1691.98511	
Pd-CF$_2$H$^{(NMe2)}$-GS	-1732.64737074	0.492358	-1732.15501274	-1734.13055305	-1733.63819505	
Pd-CF$_2$H$^{(NMe2)}$-TS	-1732.61328882	0.487434	-1732.12585482	-1734.0977065	-1733.6102725	
Pd-CF$_2$H$^{(NMe2)}$-TS-rot	-1732.60572651	0.489573	-1732.11615	-1734.08768382	-1733.59811	
Pd-CFH$_2$-GS	-1499.83866046	0.431896	-1499.40676446	-1501.06160835	-1500.62971235	-0.320609
Pd-CFH$_2$-GS-*trans*	-1499.83885753	0.434013	-1499.40484453	-1501.06127298	-1500.62725998	
Pd-CFH$_2$-TS	-1499.8124755	0.430428	-1499.3820475	-1501.03467236	-1500.60424436	
Pd-CFH$_2$-TS-*trans*	-1499.81069384	0.430827	-1499.37986684	-1501.03320315	-1500.60237615	
Pd-CFH$_2^{(CN)}$-GS	-1591.91321654	0.429768	-1591.48344854	-1593.24019838	-1592.81043038	
Pd-CFH$_2^{(CN)}$-TS	-1591.88821652	0.42758	-1591.46063652	-1593.21419093	-1592.78661093	
Pd-CFH$_2^{(NMe2)}$-GS	-1633.56069991	0.500318	-1633.06038191	-1634.92434609	-1634.42402809	
Pd-CFH$_2^{(NMe2)}$-TS	-1633.53447007	0.497438	-1633.03703207	-1634.89748371	-1634.40004571	
Pd-CH$_3$-GS	-1400.77013308	0.438211	-1400.33192208	-1401.87249526	-1401.43428426	-0.292233

Structure	E(BS1) (Hartree)	Thermal Correction to Free Energy (Hartree)	G(BS1) (Hartree)	E(BS2) (Hartree)	G(BS2) (Hartree)	$Q(R^F)$
Pd-CH_3-GS-*trans*	-1400.77058701	0.440447	-1400.33014001	-1401.87298367	-1401.43253667	
Pd-CH_3-TS	-1400.74710362	0.437442	-1400.30966162	-1401.84933713	-1401.41189513	
Pd-CH_3-TS-*trans*	-1400.74608615	0.438647	-1400.30743915	-1401.84813045	-1401.40948345	
Pd-$CH_3^{(CN)}$-GS	-1492.8453811	0.437598	-1492.4077831	-1494.05183709	-1493.61423909	
Pd-$CH_3^{(CN)}$-TS	-1492.82415079	0.434304	-1492.38984679	-1494.03000186	-1493.59569786	
Pd-$CH_3^{(NMe2)}$-GS	-1534.49129711	0.504449	-1533.98684811	-1535.73450086	-1535.23005186	
Pd-$CH_3^{(NMe2)}$-TS	-1534.46841356	0.50482	-1533.96359356	-1535.71105774	-1535.20623774	
Pd-CF_2CN-GS	-1690.99013764	0.420518	-1690.56961964	-1692.43488837	-1692.01437037	-0.491634
Pd-CF_2CN-GS'	-1690.98893894	0.42169	-1690.56724894	-1692.43360756	-1692.01191756	
Pd-CF_2CN-GS-*trans*	-1690.9886694	0.421971	-1690.5666984	-1692.43302078	-1692.01104978	
Pd-CF_2CN-TS	-1690.95421954	0.418819	-1690.53540054	-1692.39968294	-1691.98086394	
Pd-CF_2CN-TS-rot	-1690.93649892	0.418309	-1690.51819	-1692.3799563	-1691.96165	
Pd-CF_2CN-TS-*trans*	-1690.95165145	0.420908	-1690.53074345	-1692.39588271	-1691.97497471	
Pd-$CF_2CN^{(CN)}$-GS	-1783.06310284	0.417129	-1782.64597384	-1784.61180975	-1784.19468075	
Pd-$CF_2CN^{(CN)}$-TS	-1783.02519909	0.415536	-1782.60966309	-1784.57428785	-1784.15875185	
Pd-$CF_2CN^{(CN)}$-TS-rot	-1783.01039685	0.414319	-1782.59608	-1784.55768971	-1784.14337	
Pd-$CF_2CN^{(NMe2)}$-GS	-1824.71273392	0.487287	-1824.22544692	-1826.29821627	-1825.81092927	
Pd-$CF_2CN^{(NMe2)}$-TS	-1824.67976005	0.485588	-1824.19417205	-1826.26590396	-1825.78031596	
Pd-$CF_2CN^{(NMe2)}$-TS-rot	-1824.66075886	0.484254	-1824.1765	-1826.24497619	-1825.76072	
Pd-CF_2Ph-GS	-1829.56765022	0.501121	-1829.06652922	-1831.14484737	-1830.64372637	-0.401886
Pd-CF_2Ph-GS'	-1829.56049309	0.499557	-1829.06093609	-1831.13956335	-1830.64000635	
Pd-CF_2Ph-GS-*trans*	-1829.56743184	0.500749	-1829.06668284	-1831.14410393	-1830.64335493	
Pd-CF_2Ph-TS	-1829.53662346	0.499538	-1829.03708546	-1831.11567441	-1830.61613641	
Pd-CF_2Ph-TS-rot	-1829.5199212	0.498059	-1829.02186	-1831.0965512	-1830.59849	
Pd-CF_2Ph-TS-*trans*	-1829.52037907	0.497414	-1829.02296507	-1831.09736497	-1830.59995097	
Pd-$CF_2Ph^{(CN)}$-GS	-1921.64253949	0.497157	-1921.14538249	-1923.32371844	-1922.82656144	
Pd-$CF_2Ph^{(CN)}$-TS	-1921.61024786	0.496388	-1921.11385986	-1923.29316482	-1922.79677682	
Pd-$CF_2Ph^{(CN)}$-TS-rot	-1921.59655482	0.494316	-1921.10224	-1923.2767823	-1922.78247	
Pd-$CF_2Ph^{(NMe2)}$-GS	-1963.29094662	0.568868	-1962.72207862	-1965.00916054	-1964.44029254	
Pd-$CF_2Ph^{(NMe2)}$-TS	-1963.26026177	0.566656	-1962.69360577	-1964.97999326	-1964.41333726	
Pd-$CF_2Ph^{(NMe2)}$-TS-rot	-1963.24286637	0.564374	-1962.67849	-1964.9603145	-1964.39594	
Pd-CF_2C(O)Me-GS	-1751.30634646	0.459295	-1750.847051	-1752.81517993	-1752.355885	-0.438256
Pd-CF_2C(O)Me-GS-*trans*	-1751.30391908	0.459605	-1750.844314	-1752.81258288	-1752.352978	

Structure	E(BS1) (Hartree)	Thermal Correction to Free Energy (Hartree)	G(BS1) (Hartree)	E(BS2) (Hartree)	G(BS2) (Hartree)	Q(R^F)
Pd-$CF_2C(O)Me$-TS	-1751.26797718	0.456603	-1750.811374	-1752.77807382	-1752.321471	
Pd-$CF_2C(O)Me$-TS-rot	-1751.25324561	0.455133	-1750.798113	-1752.76202541	-1752.306892	
Pd-$CF_2C(O)Me$-TS-*trans*	-1751.26783143	0.45891	-1750.808921	-1752.77777028	-1752.31886	
Pd-$CF_2C(O)Me^{(CN)}$-GS	-1843.37931277	0.45609	-1842.923223	-1844.99209335	-1844.536003	
Pd-$CF_2C(O)Me^{(CN)}$-TS	-1843.34072392	0.452956	-1842.887768	-1844.95448785	-1844.501532	
Pd-$CF_2C(O)Me^{(CN)}$-TS-rot	-1843.32764138	0.452356	-1842.875285	-1844.94009809	-1844.487742	
Pd-$CF_2C(O)Me^{(NMe2)}$-GS	-1885.0290741	0.525363	-1884.503711	-1886.67854034	-1886.153177	
Pd-$CF_2C(O)Me^{(NMe2)}$-TS	-1884.99267574	0.522432	-1884.470244	-1886.64319028	-1886.120758	
Pd-$CF_2C(O)Me^{(NMe2)}$-TS-rot	-1884.97746294	0.522103	-1884.45536	-1886.62709006	-1886.104987	
Pd-$CF_2C(O)H$-GS	-1712.05166728	0.433064	-1711.618603	-1713.52127002	-1713.088206	-0.455363
Pd-$CF_2C(O)H$-GS-*trans*	-1712.04993357	0.432955	-1711.616979	-1713.51962648	-1713.086671	
Pd-$CF_2C(O)H$-TS	-1712.0142613	0.429856	-1711.584405	-1713.48521957	-1713.055364	
Pd-$CF_2C(O)H$-TS-*trans*	-1712.01697345	0.432326	-1711.584647	-1713.48856958	-1713.056244	
Pd-$CF_2C(O)H$-TS-rot	-1712.00029563	0.428726	-1711.57157	-1713.46992786	-1713.041202	
Pd-CF_2CO_2Me-GS	-1826.40112222	0.462834	-1825.938288	-1827.99870641	-1827.535872	-0.442447
Pd-CF_2CO_2Me-GS-*trans*	-1826.4002185	0.463781	-1825.936438	-1827.99704316	-1827.533262	
Pd-CF_2CO_2Me-TS	-1826.36229499	0.460244	-1825.902051	-1827.96054153	-1827.500298	
Pd-CF_2CO_2Me-TS-*trans*	-1826.36218759	0.462268	-1825.89992	-1827.95985666	-1827.497589	
Pd-CF_2CO_2Me-TS-rot	-1826.34920401	0.459591	-1825.889613	-1827.94624106	-1827.48665	
Pd-$CF_2C(O)F$-GS	-1811.14842313	0.424445	-1810.723978	-1812.73854992	-1812.314105	-0.491374
Pd-$CF_2C(O)F$-GS-*trans*	-1811.14602612	0.423652	-1810.722374	-1812.7357313	-1812.312079	
Pd-$CF_2C(O)F$-TS	-1811.11009046	0.421144	-1810.688946	-1812.70029138	-1812.279147	
Pd-$CF_2C(O)F$-TS-*trans*	-1811.11181848	0.423935	-1810.687883	-1812.70194706	-1812.278012	
Pd-$CF_2C(O)F$-TS-rot	-1811.09482746	0.421056	-1810.673771	-1812.68404166	-1812.262986	
Pd-C_2F_5-GS	-1935.40812804	0.426452	-1934.981676	-1937.1507538	-1936.724302	-0.478135
Pd-C_2F_5-GS-*trans*	-1935.40563868	0.426598	-1934.979041	-1937.14715397	-1936.720556	
Pd-C_2F_5-TS	-1935.36096183	0.424037	-1934.936925	-1937.10232902	-1936.678292	
Pd-C_2F_5-TS-*trans*	-1935.36207673	0.425059	-1934.937018	-1937.10343911	-1936.67838	
Pd-C_2F_5-TS-rot	-1935.356452	0.423572	-1934.93288	-1937.09793351	-1936.674362	
Pd-CF_2CH_3-GS	-1638.17465145	0.452117	-1637.722534	-1639.55621742	-1639.1041	-0.376931
Pd-CF_2CH_3-GS-*trans*	-1638.17516697	0.451915	-1637.723252	-1639.55638251	-1639.104468	
Pd-CF_2CH_3-TS	-1638.13241436	0.448167	-1637.684247	-1639.51521	-1639.067043	

Structure	E(BS1) (Hartree)	Thermal Correction to Free Energy (Hartree)	G(BS1) (Hartree)	E(BS2) (Hartree)	G(BS2) (Hartree)	Q(R^F)
Pd-CF_2CH_3-TS-*trans*	-1638.1330546	0.45037	-1637.682685	-1639.51584174	-1639.065472	
Pd-CF_2CH_3-TS-rot	-1638.13148605	0.448919	-1637.682567	-1639.51239351	-1639.063475	
Pd-CF_2CFMe_2-GS	-1815.73535053	0.498072	-1815.237279	-1817.31511754	-1816.817046	-0.413921
Pd-CF_2CFMe_2-TS	-1815.69155971	0.495321	-1815.196239	-1817.27146459	-1816.776144	
Pd-CF_2CFMe_2-TS-rot	-1815.68109069	0.493874	-1815.187217	-1817.26391808	-1816.770044	
Pd-CHFC(O)Me-GS	-1652.22937783	0.468753	-1651.760625	-1653.62006155	-1653.151309	-0.425972
Pd-CHFC(O)Me-GS-*trans*	-1652.22461577	0.467262	-1651.757354	-1653.61459957	-1653.147338	
Pd-CHFC(O)Me-TS	-1652.1963396	0.463824	-1651.732516	-1653.58562235	-1653.121798	
Pd-CHFC(O)Me-TS-*trans*	-1652.1941046	0.46766	-1651.726445	-1653.58421283	-1653.116553	
(L')Pd-CF_2H-GS	-1904.84635977	0.553501	-1904.292859	-1906.27101581	-1905.717515	
(L')Pd-CF_2H-TS	-1904.79501271	0.551009	-1904.244004	-1906.21918094	-1905.668172	
(L')Pd-CF_2H-TS-rot	-1904.79267204	0.551205	-1904.241467	-1906.21474720	-1905.663542	
(L')Pd-CF_2CN-GS	-1996.91399749	0.553335	-1996.360662	-1998.43906600	-1997.885731	
(L')Pd-CF_2CN-TS	-1996.86191903	0.550968	-1996.310951	-1998.38458758	-1997.83362	
(L')Pd-CF_2CN-TS-rot	-1996.84718100	0.550526	-1996.296655	-1998.37005857	-1997.819533	
(L')Pd-CF_2Ph-GS	-2135.48766498	0.638986	-2134.848679	-2137.14890120	-2136.509915	
(L')Pd-CF_2Ph-TS	-2135.43748827	0.636701	-2134.800787	-2137.09757578	-2136.460875	
(L')Pd-CF_2Ph-TS-rot	-2135.42573398	0.636275	-2134.789459	-2137.08512814	-2136.448853	
(L')Pd-CF_2CH_3-GS	-1944.09483034	0.582217	-1943.512613	-1945.55887229	-1944.976655	
(L')Pd-CF_2CH_3-TS	-1944.04037090	0.579546	-1943.460825	-1945.50406631	-1944.92452	
(L')Pd-CF_2CH_3-TS-rot	-1944.03875651	0.579703	-1943.459054	-1945.50048148	-1944.920778	
(L')Pd-CF_2CFMe_2-GS	-2121.65177440	0.63431	-2121.017464	-2123.31497864	-2122.680669	
(L')Pd-CF_2CFMe_2-TS	-2121.59878977	0.631827	-2120.966963	-2123.25928705	-2122.62746	
(L')Pd-CF_2CFMe_2-TS-rot	-2121.58781168	0.631717	-2120.956095	-2123.25144910	-2122.619732	

4.4.3. Examining Different Descriptors of Fragment Charges to Assess the Electron-withdrawing Ability of the R^F Ligand

Table 4.9. Partial charges of the R^F fragments in the ground-state structures ***cis*-Pd-R^F-GS** determined by QTAIM, Hirshfeld, and NPA analyses.

Entry	R^F Ligand	Q(R^F)	Hirshfeld Charge of R^F	NPA Charge of R^F	σ_m(X) for R^F = CF_2X[52]
1	CF_3	-0.461945	-0.332597	-0.37790	0.34
2	CF_2H	-0.370227	-0.326393	-0.32275	0
3	CFH_2	-0.320609	-0.413828	-0.32533	*n/a*
4	CH_3	-0.292234	-0.528902	-0.36326	*n/a*
5	CF_2CN	-0.491635	-0.423294	-0.46168	0.56
6	CF_2Ph	-0.401887	-0.334391	-0.36987	0.06
7	$CF_2C(O)Me$	-0.438256	-0.342611	-0.39726	0.38
8	$CF_2C(O)H$	-0.455363	-0.358113	-0.41400	0.35
9	CF_2CO_2Me	-0.442447	-0.333056	-0.39808	0.37
10	$CF_2C(O)F$	-0.491374	-0.374218	-0.44387	0.55
11	CF_2CF_3	-0.478135	-0.583894	-0.41730	0.43
12	CF_2CH_3	-0.376931	-0.301684	-0.33499	-0.07
13	CF_2CFMe_2	-0.413921	*n.d.*	*n.d.*	*not reported*
14	CFHC(O)Me	-0.425972	-0.359447	-0.43068	*n/a*

n.d. stands for not determined; *n/a* stands for not applicable.

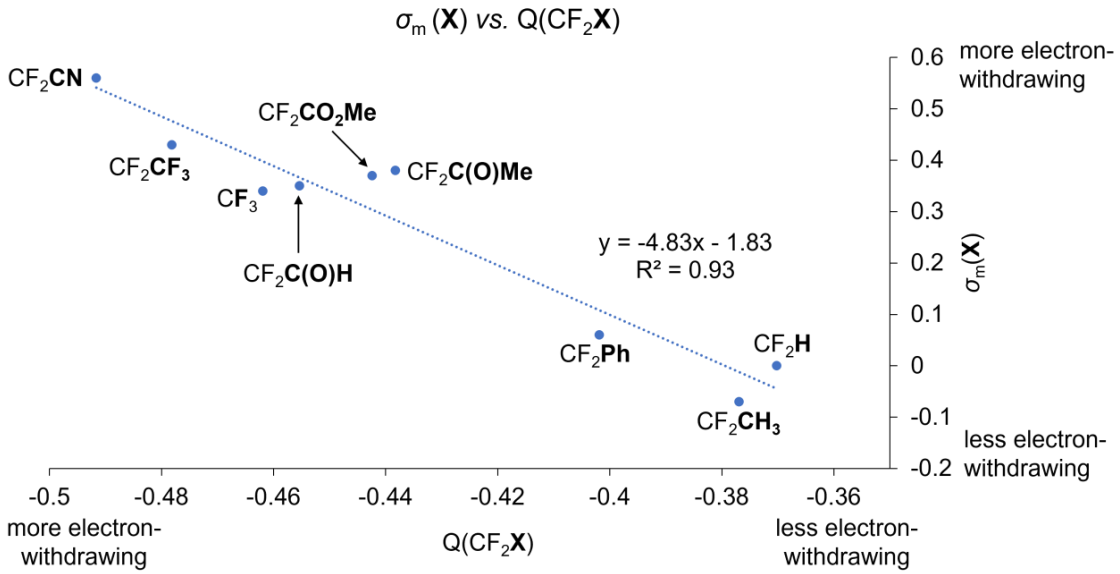


Figure 4.3 The linear relationship between the Q(CF_2X) and the σ_m (X) values for a series of difluoroalkyl ligands.

In addition to the descriptor Q(R^F), we attempted to quantify the electron-withdrawing ability of R^F ligands by the sum of Hirshfeld[78] or Natural Population Analysis (NPA) charges[79-80] of the R^F fragment in the ground-state structures ***cis*-Pd-R^F-GS**. These results are shown in Table 4.9. Hirshfeld charges of difluoroalkyl ligands ($R^F = CF_2X$) correlate poorly with the corresponding σ_m (X) values ($R^2 = 0.30$, Figure 4.10), which are commonly used as a measure of inductive effects.[52] These results suggest that Hirshfeld charge is not a good descriptor of the electron-withdrawing ability of R^F ligands in this system.

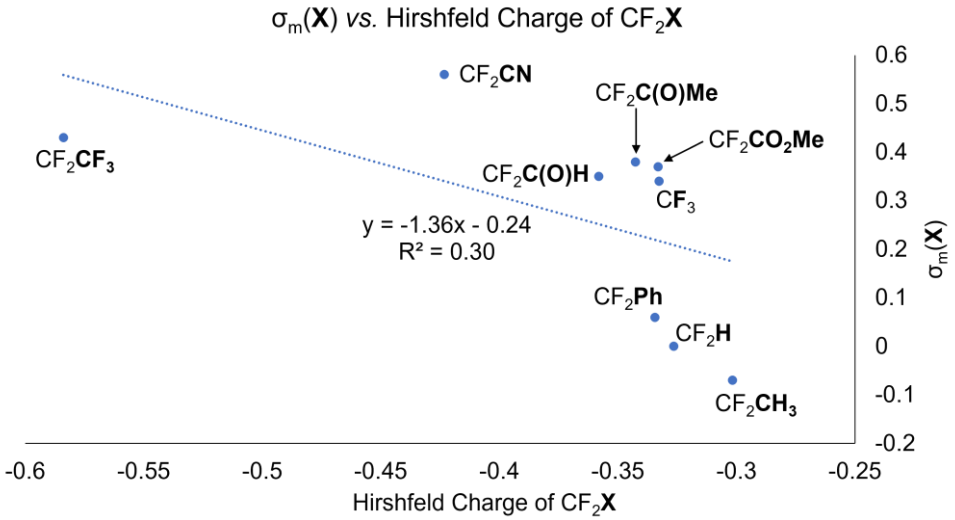


Figure 4.10. Plot of the σ_m (X) values against the Hirshfeld partial charges of CF_2X fragments for a series of difluoroalkyl ligands.

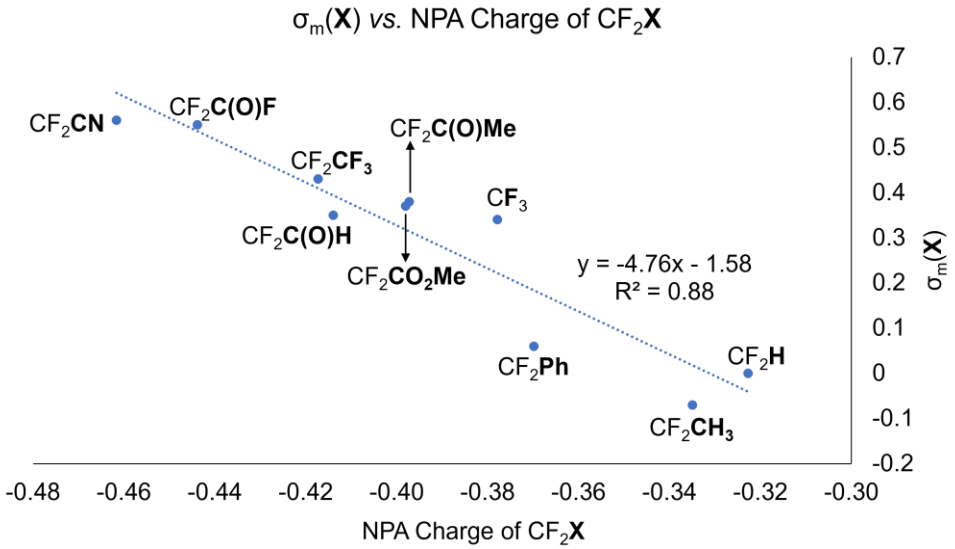


Figure 4.11. Plot of the σ_m (X) values against the NPA partial charges of CF_2X fragments for a series of difluoroalkyl ligands.

Even though NPA charges of difluoroalkyl ligands ($R^F = CF_2X$) correlate linearly with the corresponding σ_m (X) values ($R^2 = 0.88$, Figure 4.11), they do not reflect the effect of different levels of fluorination on the electron-withdrawing ability of R^F ligands. For example, the NPA charges of the CF_3 and the CH_3 fragments are similar (-0.378 for CF_3, -0.363 for CH_3, Table 4.9, entries 1 and 4), and the NPA charge of CF_2H (-0.323, Table 4.9, entry 2) is less negative than that

of either CF_3 or CH_3. These values contradict both the intuitive notion that a greater degree of fluorination leads to a more electron-withdrawing fragment and the trend in Hammett σ_m parameters for these R^F groups (σ_m = -0.07, 0.29, and 0.43 for R^F = CH_3, CF_2H, and CF_3, respectively). As a result, the computed barriers to reductive elimination ($\Delta G^{\ddagger}$) do not correlate linearly with the NPA charges of R^F ligands for both subsets **A** and **B** (Figure 4.12, R^2 = 0.362 for subset **A**, R^2 = 0.853 for subset **B**) compared to the $Q(R^F)$ values (see Figure 4.4, R^2 = 0.831 for subset **A**, R^2 = 0.995 for subset **B**). These data suggest that NPA charge is not a good measure of the electron-withdrawing ability of R^F ligands in this system either.

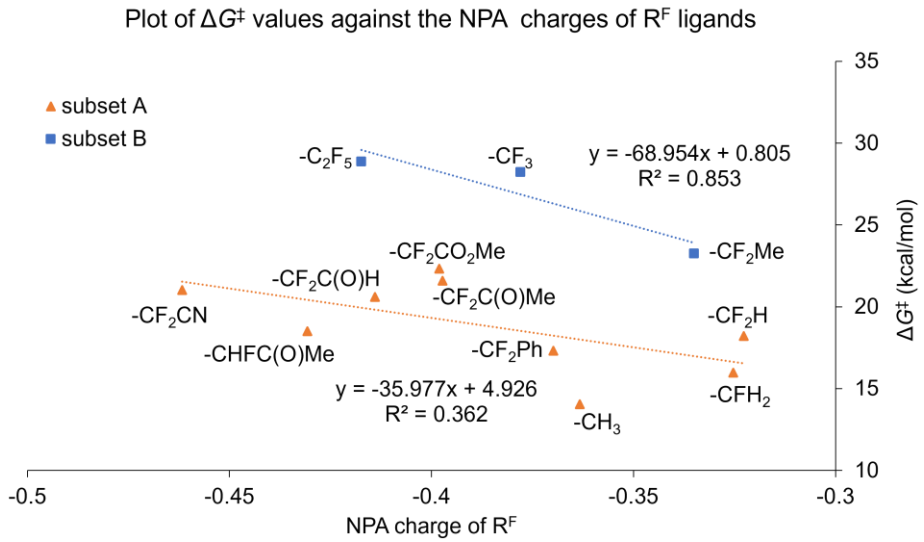


Figure 4.12. Plot of computed barriers to reductive elimination ($\Delta G^{\ddagger}$) against the NPA charges of R^F ligands.

Overall, the descriptor $Q(R^F)$ correlates well with the well-established Hammett substituent constant σ_m across a series of difluoroalkyl ligands and reflects the effect of different levels of fluorination on the electron-withdrawing ability of R^F ligands. Therefore, among the descriptors that we have examined, $Q(R^F)$ is the best option for quantifying the electron-withdrawing ability of R^F ligands.

4.4.4. *Evaluation of ΔE_{se} Values and Calculation of the Volumes of R^F Fragments*

Definitions:

ΔE_{se}: the portion of the difference in energy between the lowest-energy and rotated transition states (***cis*-Pd-R^F-TS** and ***cis*-Pd-R^F-TS-rot**, respectively) not attributable to secondary orbital interactions of the R^F fragment with the Pd center; "se" for "steric and electronic"

R^F_B: a fluoroalkyl fragment that does not engage in secondary orbital interactions with the Pd center in the transition state ***cis*-Pd-$R^F_{no\text{-}orb}$-TS** (*i.e.*, $R^F_{no\text{-}orb}$ = C_2F_5, CF_2Me, or CF_2CFMe_2)

R^F_A: a fluoroalkyl fragment that engages in secondary orbital interactions in the transition state ***cis*-Pd-R^F_{orb}-TS** (*i.e.*, R^F_{orb} = CF_2CN, CF_2CO_2Me, $CF_2C(O)F$, $CF_2C(O)H$, $CF_2C(O)Me$, CF_2H, or CF_2Ph) for which a rotated transition state ***cis*-Pd-R^F_{orb}-TS-rot** could be located

$\Delta\Delta G^{\ddagger}(R^F) = \Delta G^{\ddagger}$(***cis*-Pd-$R^F$-TS**) – $\Delta G^{\ddagger}$(***cis*-Pd-R^F-TS-rot**) = $\Delta E_{orb}(R^F) + \Delta E_{se}(R^F)$

$\Delta E_{orb}(R^F_{orb})$: the energetic stabilization in ***cis*-Pd-R^F_{orb}-TS** attributable to secondary orbital interactions of the R^F ligand with the Pd center; $\Delta E_{orb}(R^F_{orb}) = \Delta\Delta G^{\ddagger}(R^F_{orb}) - \Delta E_{se}(R^F_{orb})$

To determine the energetic stabilizations attributable to the interactions between *d*(Pd) and $\pi^*(R^F)$ or those between Pd and α-C–H bonds in the transition-state structures (ΔE_{orb}), we compared the transition state structures ***cis*-Pd-R^F-TS** to rotameric structures in which such orbital interactions were absent (***cis*-Pd-R^F-TS-rot**). The difference in energy between these two structures, $\Delta\Delta G^{\ddagger}(R^F)$, can be split into two terms: $\Delta E_{orb}(R^F)$ (the desired secondary orbital contributions) and $\Delta E_{se}(R^F)$ (all other contributions, labeled here "se" for "steric and electronic"). While we could not calculate $\Delta E_{se}(R^F)$ directly for all R^F ligands, the lowest-energy transition states for three R^F ligands (R^F = C_2F_5, CF_2Me, or CF_2CFMe_2) did not exhibit secondary orbital interactions (*i.e.*, $\Delta E_{orb}(R^F) = 0$). For this $R^F_{no\text{-}orb}$ subset, $\Delta E_{se}(R^F_B) = \Delta\Delta G^{\ddagger}(R^F_B)$. We then assumed that $\Delta E_{se}(R^F)$ values would vary little for R^F ligands possessing similar steric properties.

As a measure of the steric bulk of a given R^F ligand, we calculated the molecular volumes (within ρ = 0.001 au) of R^F–H, the isolated protonated fluoroalkyl ligands. Then, we assigned each $\Delta E_{se}(R^F_A)$ value to the $\Delta E_{se}(R^F_B)$ value corresponding to the R^F_B with the closest R^F_B–H volume to that of R^F_A–H, that is,

$$\Delta E_{se}\left(R^F_A\right) = \Delta E_{se}\left(\underset{R^F \in \{R^F_B\}}{\operatorname{argmin}} \left| Volume(R^F_A\text{-H}) - Volume(R^F\text{-H}) \right|\right)$$

For example, the calculated volume of the H–$CF_2C(O)Me$ fragment is 100.8 Å^3, which is numerically closer to that of H–C_2F_5 (90.6 Å^3) than to those of the other $R^F_{no\text{-}orb}$ fragments (75.5 Å^3 for CF_2Me, 125.8 Å^3 for CF_2CFMe_2). Therefore, $\Delta E_{se}(CF_2C(O)Me)$ was assigned the same value as $\Delta\Delta G^{\ddagger}(C_2F_5)$, *i.e.*, 2.5 kcal/mol. The $\Delta E_{se}(R^F)$ values are shown in Table 4.4. The energies of optimized H–R^F fragments are summarized in Table S6, and the atomic coordinates of these structures can be found in the accompanying XYZ file with the fragment's name in the comment line.

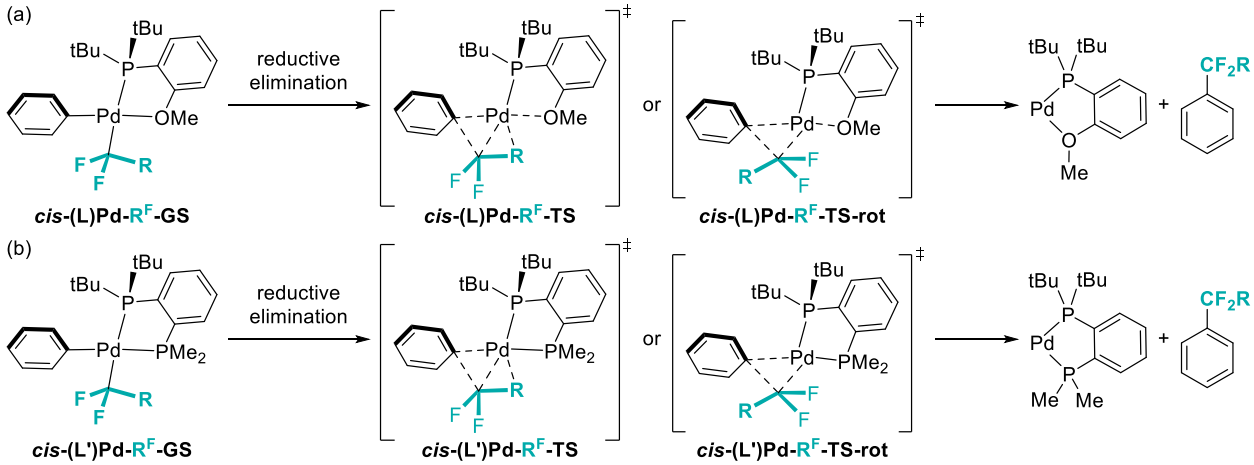
Table 4.4. Calculated volumes of protonated fluoroalkyl fragments and estimates of the energetic penalties (ΔE_{se}) associated with reorienting the R^F ligands in ***cis*-Pd-TS-rot** structures.

R^F_B	Calculated volume of R^F_B (Å^3)	$\Delta E_{se}(R^F_B) = \Delta\Delta G^{\ddagger}(R^F_B)$ (kcal/mol)	R^F_A	Calculated volume of R^F_A (Å^3)	R^F_B most similar in volume	$\Delta E_{se}(R^F_A)$ (kcal/mol)
C_2F_5	90.6	-2.5	CF_2CN	76.1	CF_2Me	-2.2
CF_2Me	75.5	-2.2	CF_2CO_2Me	111.6	CF_2CFMe_2	-3.8
CF_2CFMe_2	125.8	-3.8	$CF_2C(O)F$	82.5	CF_2Me	-2.2
			$CF_2C(O)H$	78.3	CF_2Me	-2.2
			$CF_2C(O)Me$	100.8	C_2F_5	-2.5
			CF_2H	52.0	CF_2Me	-2.2
			CF_2Ph	148.7	CF_2CFMe_2	-3.8

Table 4.10. Energies of optimized structures of H–R^F fragments

Structure	E(BS1) (a.u.)	Thermal Correction to Free Energy (a.u.)	G(BS1) (a.u.)	E(BS2) (a.u.)	G(BS2) (a.u.)
H–C_2F_5	-575.0374715	0.007809	-575.0296625	-575.7342672	-575.7264582
H–CF_2CFMe_2	-455.3667888	0.077871	-455.2889178	-455.9028585	-455.8249875
H–CF_2CN	-330.6164055	0.003806	-330.6125995	-331.0108458	-331.0070398
H–CF_2CO_2Me	-466.024204	0.043158	-465.981046	-466.5759001	-466.5327421
H–$CF_2C(O)F$	-450.7673119	0.005365	-450.7619469	-451.3104894	-451.3051244
H–$CF_2C(O)H$	-351.6719836	0.013347	-351.6586366	-352.0943165	-352.0809695
H–$CF_2C(O)Me$	-390.9280916	0.039122	-390.8889696	-391.3898643	-391.3507423
H–CF_2H	-238.5628594	0.00862	-238.5542394	-238.8569102	-238.8482902
H–CF_2Me	-277.8156278	0.034345	-277.7812828	-278.1486217	-278.1142767
H–CF_2Ph	-469.1999701	0.082064	-469.1179061	-469.7280309	-469.6459669
H–CF_3	-337.6553341	-0.00019	-337.6555261	-338.068443	-338.068635
H–CFH_2	-139.4841377	0.016945	-139.4671927	-139.6558655	-139.6389205
H–CFHC(O)Me	-291.8520382	0.047729	-291.8043092	-292.1927353	-292.1450063
H–CH_3	-40.42946622	0.025033	-40.40443322	-40.47483952	-40.44980652

4.4.5. *Reductive Elimination from Palladium(phenyl)(fluoroalkyl) Complexes Containing the Nonlabile Bisphosphine Ligand **L'***



Scheme 4.4. Reductive elimination from (a) ***cis*-(L)Pd-R^F** and (b) ***cis*-(L')Pd-R^F** complexes.

We optimized the structures of ground states (***cis*-(L')Pd-R^F-TS**) and transition states (***cis*-(L')Pd-R^F-TS** and ***cis*-(L')Pd-R^F-TS-rot**) for reductive elimination from palladium(phenyl)(fluoroalkyl) complexes (fluoroalkyl = CF_2H, CF_2CN, CF_2Ph, CF_2CH_3, and CF_2CFMe_2) containing the bisphosphine ligand di-*tert*-butyl(2-dimethylphosphinophenyl)phosphine (**L'**) and calculated the free-energies of the transition states ***cis*-(L')Pd-R^F-TS** ($\Delta G^{\ddagger}$(**L'**, R^F)) and ***cis*-(L')Pd-R^F-TS-rot** ($\Delta G^{\ddagger}_{rot}$(**L'**, R^F)). As discussed in the main article, the distance between Pd and the oxygen atom of the methoxy fragment of ligand **L** in transition states ***cis*-(L)Pd-R^F-TS** is significantly longer than that in ground states ***cis*-(L)Pd-R^F-GS**, suggesting that the labile methoxy group dissociates from the metal center during reductive elimination. In contrast, the distance between Pd and the phosphorus atom of the dimethylphosphino group of ligand **L'** in transition states ***cis*-(L')Pd-R^F-TS** is nearly identical to that in ground states ***cis*-(L')Pd-R^F-GS** (Table 4.11, Δr(Pd–PMe$_2$) $\leqslant$ 0.05 Å). This result indicates that both phosphino groups of the bisphosphine ligand **L'** remain bound to Pd during the reductive elimination.

Table 4.11. Comparison of the distance between Pd and the O atom of the methoxy group of ligand **L** and the distance between Pd and the P atom of the dimethylphosphino group of ligand **L'** in the ground state and transition state.

Entry	**R^F**	Ligand = **L**			Ligand = **L'**		
		r(Pd–OMe) in **GS** (Å)	r(Pd–OMe) in **TS** (Å)	Δr(Pd–OMe) (Å)	r(Pd–PMe$_2$) in **GS** (Å)	r(Pd–PMe$_2$) in **TS** (Å)	Δr(Pd–PMe$_2$) (Å)
1	CF_2H	2.29	2.66	0.37	2.29	2.34	0.05
2	CF_2CN	2.29	2.77	0.48	2.30	2.33	0.03
3	CF_2Ph	2.31	2.92	0.61	2.30	2.35	0.05

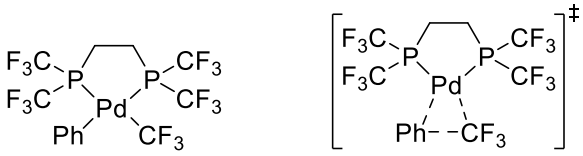
The calculated barriers to reductive elimination and the estimated stabilization caused by secondary orbital interactions in the lowest-energy transition states (ΔE_{orb}(R^F)) for ***cis*-(L)Pd-R^F** and ***cis*-(L')Pd-R^F** are summarized in Table 4.12. Values of ΔE_{se}(R^F) and ΔE_{orb}(R^F) for ***cis*-(L')Pd-R^F** complexes were determined by the method described in Sections 4.2.5 and 4.4.4. The barriers to reductive elimination from ***cis*-(L')Pd-R^F** complexes are significantly higher than those to

reductive elimination from ***cis*-(L)Pd-R^F** complexes ($\Delta G^{\ddagger}$(**L'**, R^F) – $\Delta G^{\ddagger}$(**L**, R^F) = 11.7 – 13.5 kcal/mol, Table 4.12, entries 1–6), and the stabilization from secondary orbital interactions in the transition states for reductive elimination from ***cis*-(L')Pd-R^F** complexes is smaller than that for reductive elimination from ***cis*-(L)Pd-R^F** complexes ($|\Delta E_{orb}$(**L**, $R^F)|$ – $|\Delta E_{orb}$(**L'**, $R^F)|$ = 3.4 – 4.6 kcal/mol, Table 4.12, entries 1–6). These differences in energy suggest that dissociation of the methoxy fragment of the hemilabile ligand **L** in the transition state enhances the stabilizing secondary orbital interactions between the fluoroalkyl ligand and the Pd center. Such enhancement of orbital interactions is one reason that these fluoroalkyl complexes containing hemilabile or monodentate ligands generate catalysts that are particularly active for coupling of aryl halides with partially fluorinated alkyl groups.

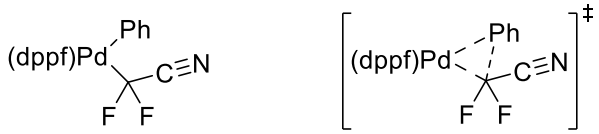
Table 4.12. Calculated free-energy barriers and estimated stabilization caused by secondary orbital interactions for reductive elimination from ***cis*-(L)Pd-R^F** and ***cis*-(L')Pd-R^F** complexes.

Entry	Ligand	R^F	$\Delta G^{\ddagger}(R^F)$ (kcal/mol)	$\Delta G^{\ddagger}_{rot}(R^F)$ (kcal/mol)	$\Delta\Delta G^{\ddagger}(R^F)$ (kcal/mol)	$\Delta E_{se}(R^F)$ (kcal/mol)	$\Delta E_{orb}(R^F)$ (kcal/mol)
1	**L**	CF_2H	18.2	25.1	-6.9	-2.2	-4.7
2		CF_2CN	21.0	33.1	-12.1	-2.2	-9.9
3		CF_2Ph	17.3	28.4	-11.1	-3.8	-7.3
4	**L'**	CF_2H	31.0	33.9	-2.9	-2.4	-0.5
5		CF_2CN	32.7	41.5	-8.8	-2.4	-6.4
6		CF_2Ph	30.8	38.3	-7.5	-4.8	-2.7
7		CF_2CH_3	32.7	35.1	-2.4	-2.4	–
8		CF_2CFMe_2	33.4	38.2	-4.8	-4.8	–

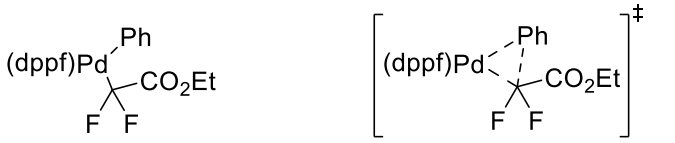
4.4.6. Cartoons of Optimized Structures



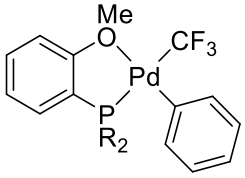
(dfmpe)Pd(Ph)(CF_3)-GS **(dfmpe)Pd(Ph)(CF_3)-TS**



(dppf)Pd(Ph)(CF_2CN)-GS **(dppf)Pd(Ph)(CF_2CN)-TS**



(dppf)Pd(Ph)(CF_2CO_2Et)-GS **(dppf)Pd(Ph)(CF_2CO_2Et)-TS**



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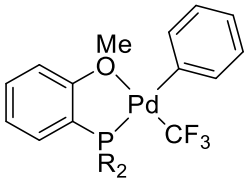

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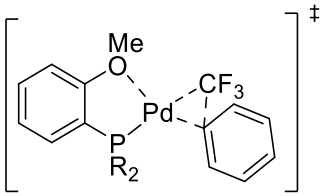

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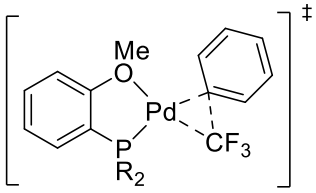

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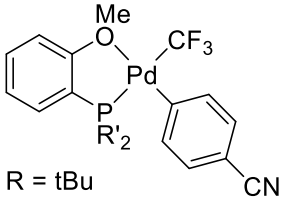

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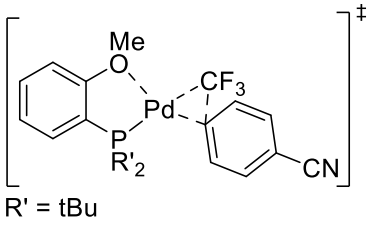

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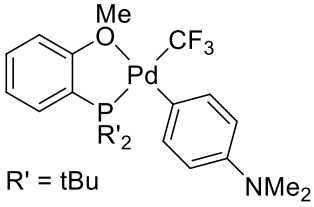

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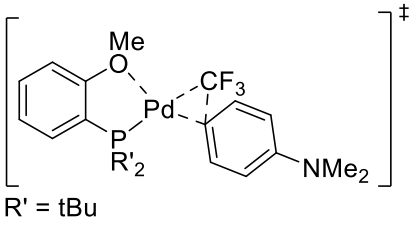

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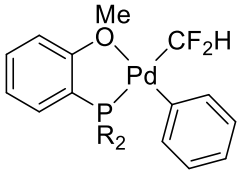

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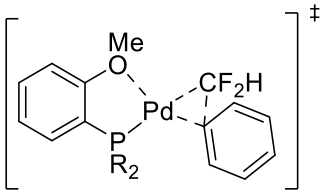

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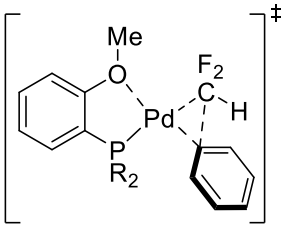

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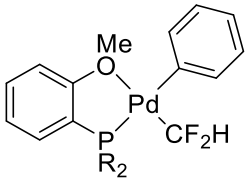

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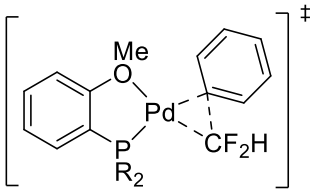

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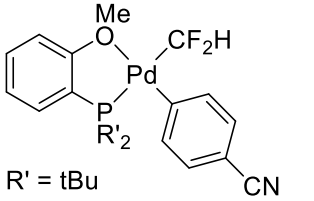

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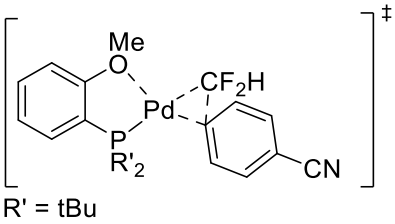

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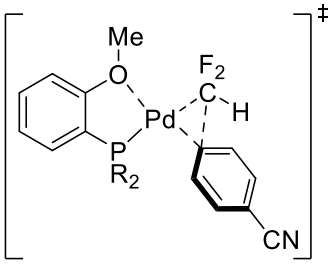

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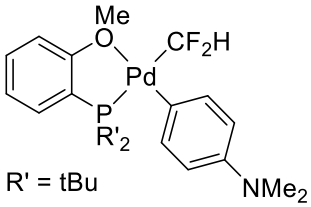

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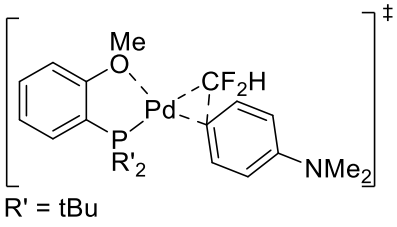

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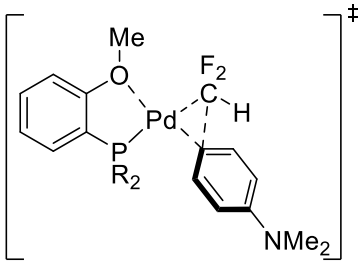

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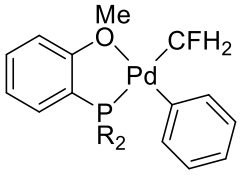

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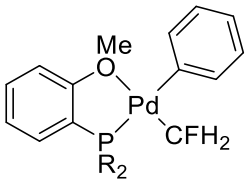

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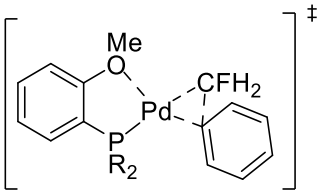

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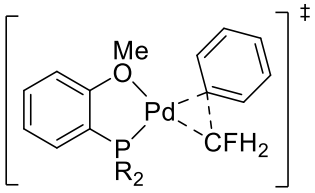

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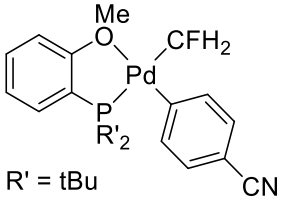

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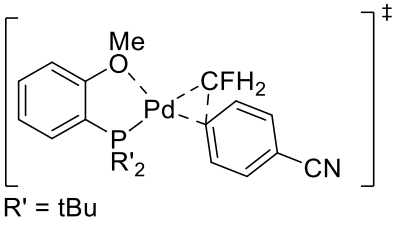

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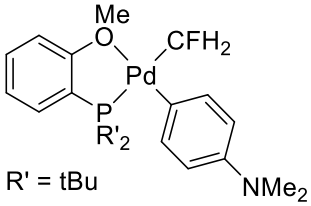

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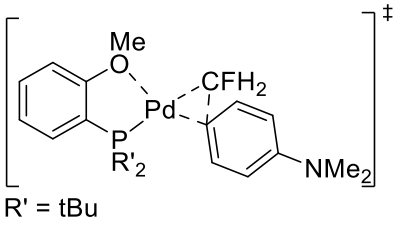

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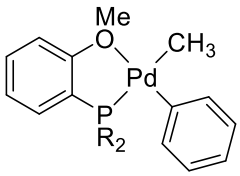

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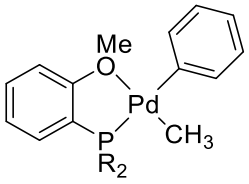

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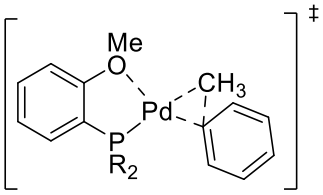

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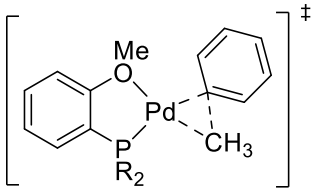

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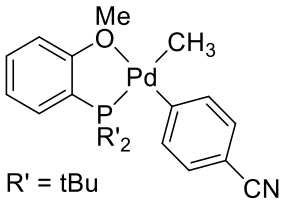

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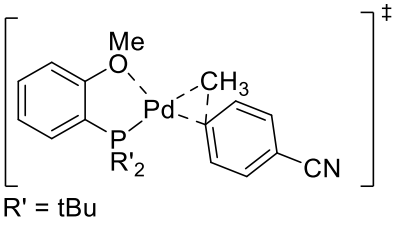

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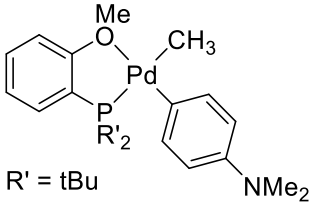

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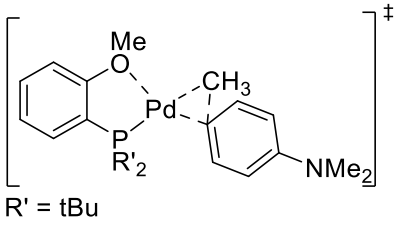

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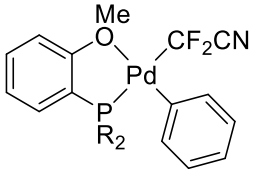

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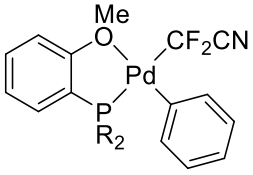

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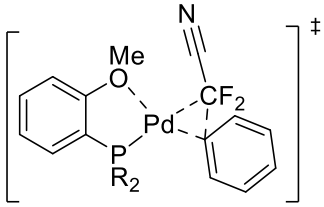

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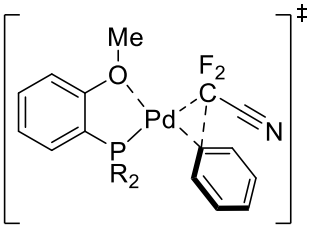

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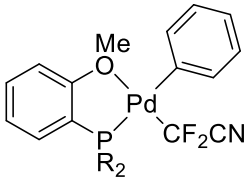

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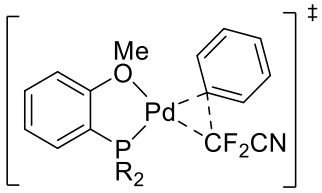

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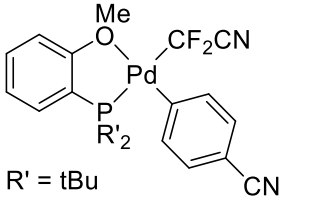

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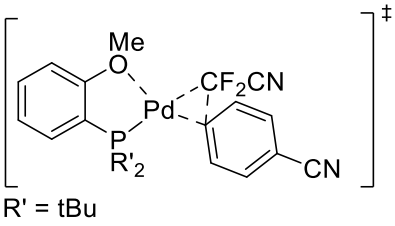

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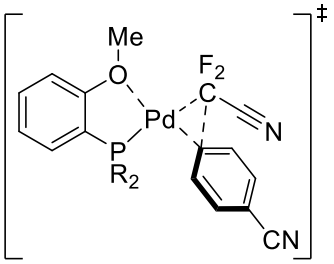

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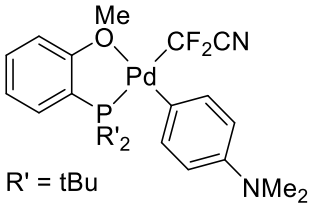

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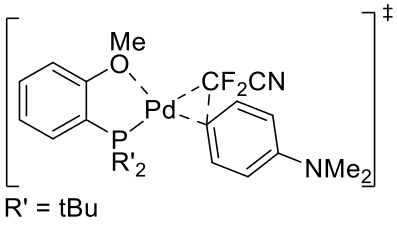

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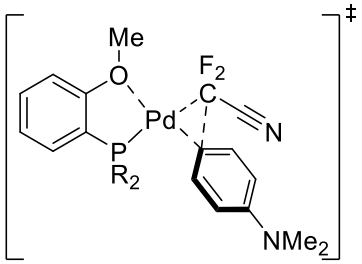

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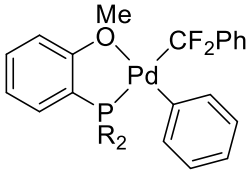

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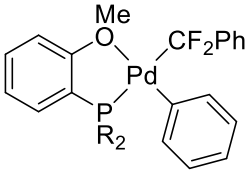

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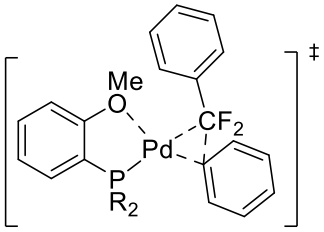

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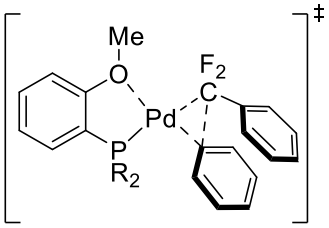

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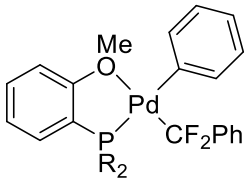

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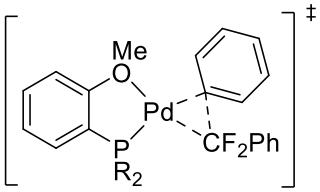

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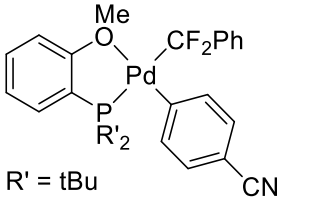

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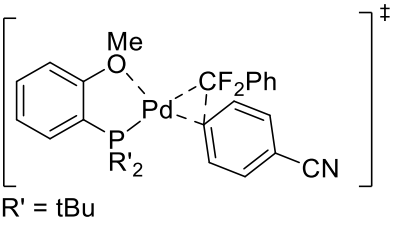

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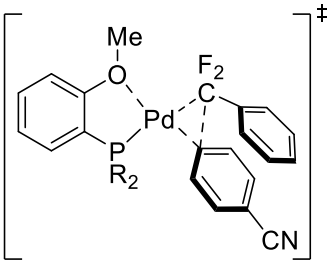

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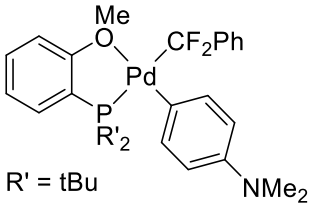

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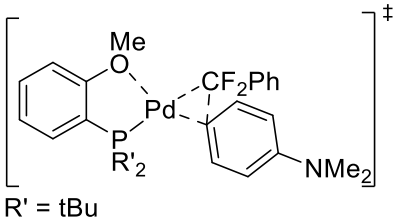

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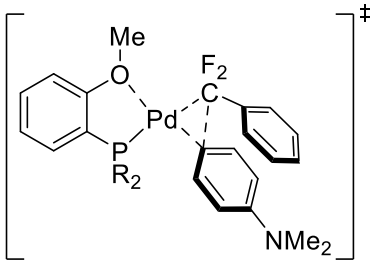

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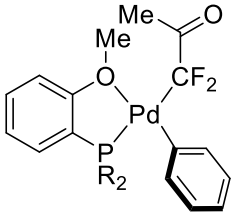

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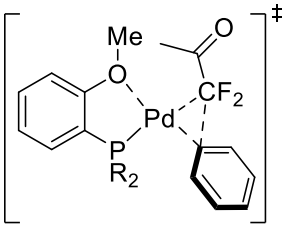

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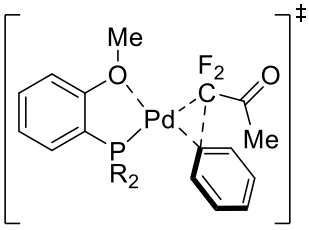

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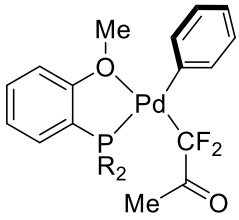

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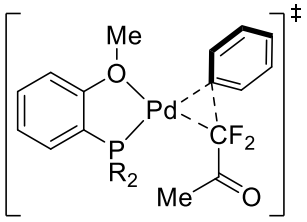

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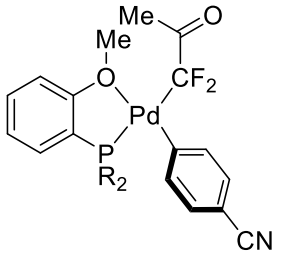

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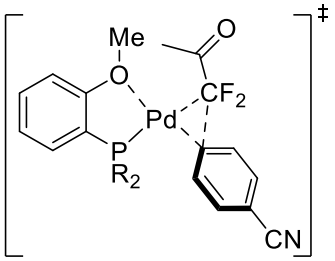

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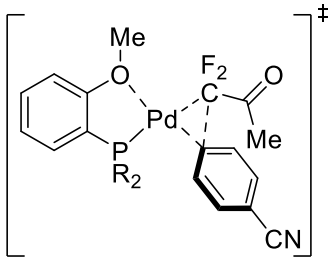

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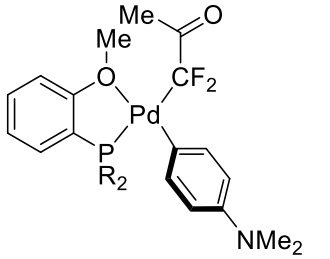

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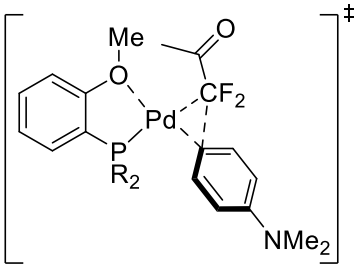

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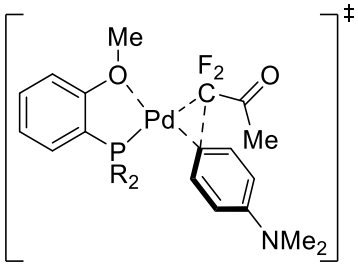

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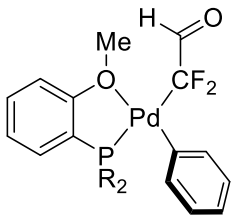

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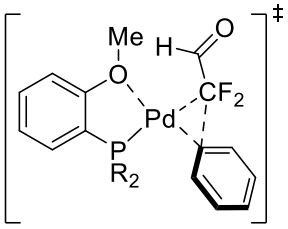

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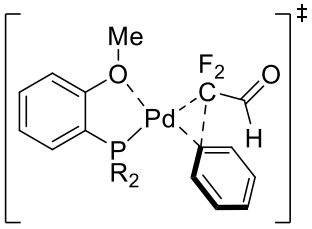

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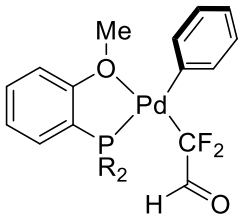

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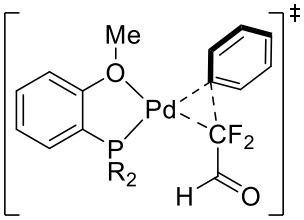

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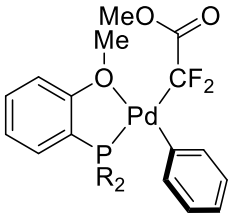

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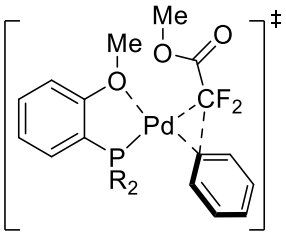

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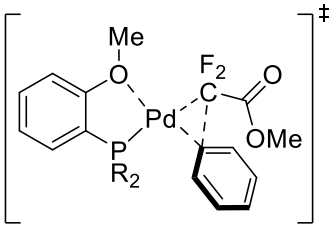

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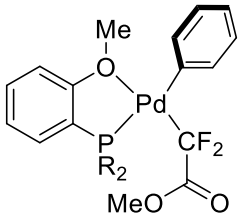

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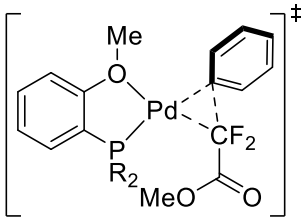

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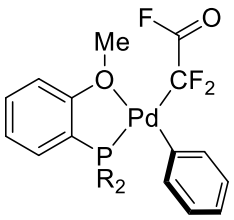

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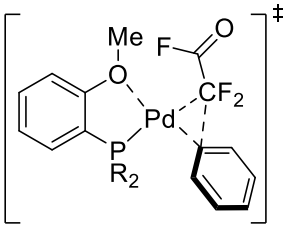

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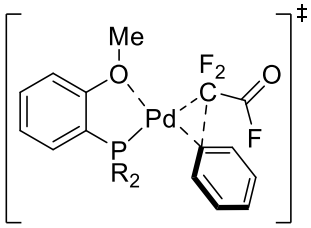

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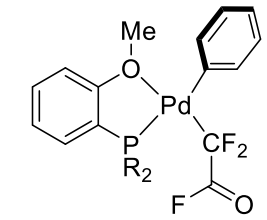
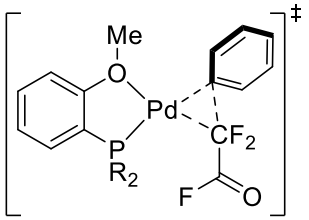


***trans*-Pd-$CF_2C(O)F$-GS**



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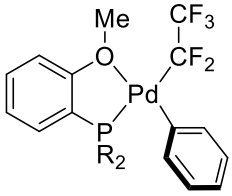
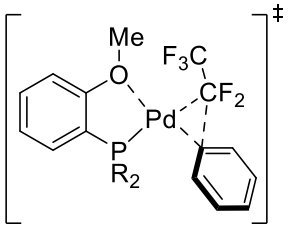


***cis*-Pd-C_2F_5-GS**



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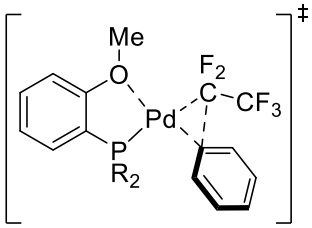

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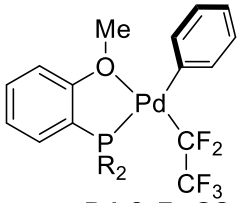

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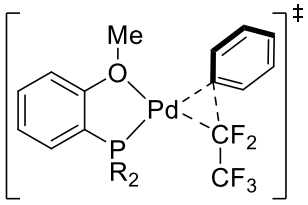

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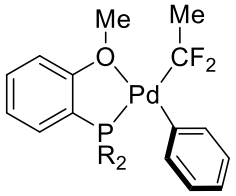

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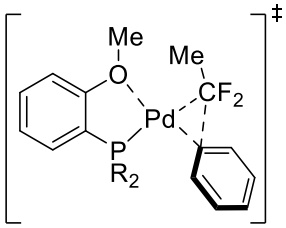

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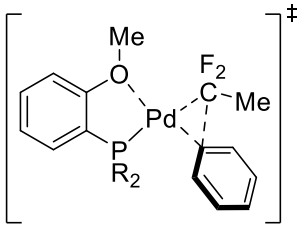

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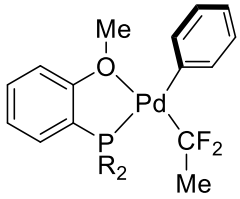

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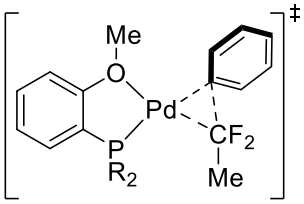

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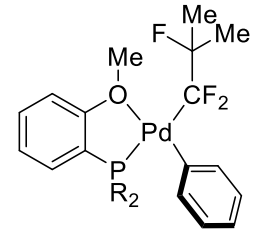

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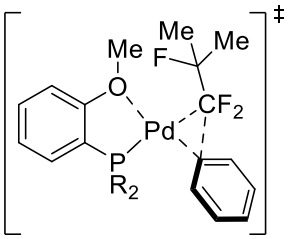
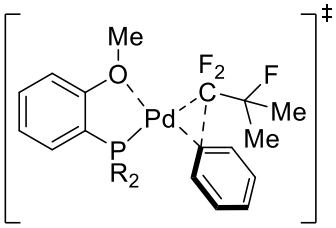


***cis*-Pd-CF_2CFMe_2-TS**



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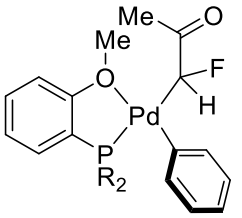

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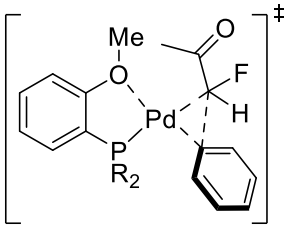

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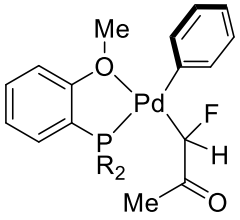

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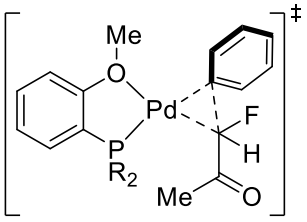

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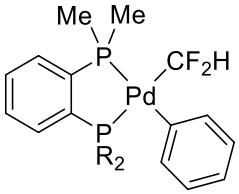

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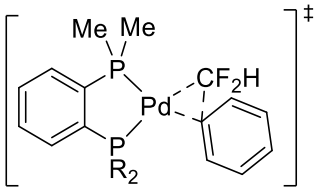

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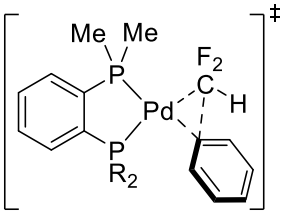

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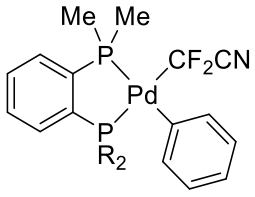

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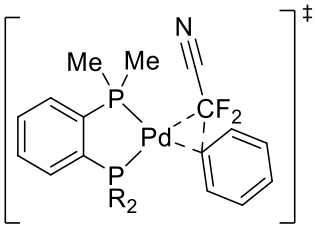

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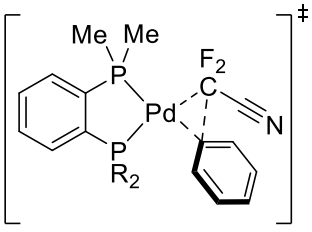

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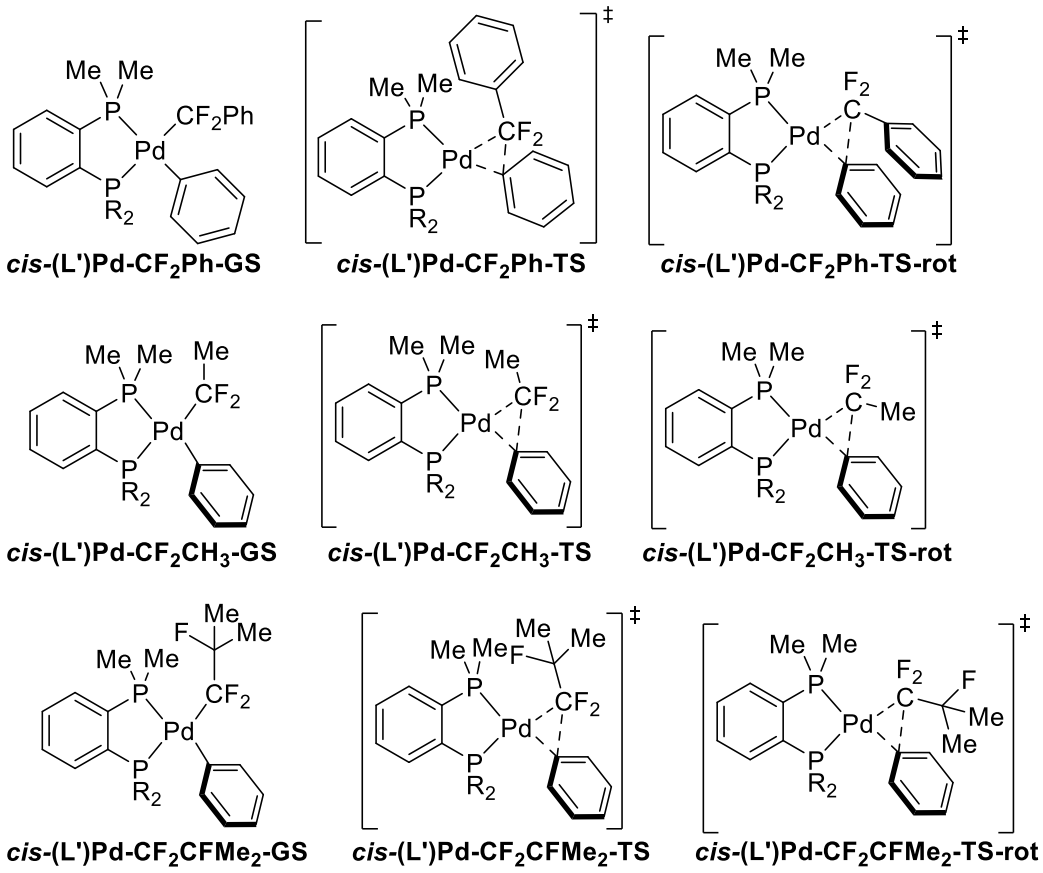

4.4.7. Atomic Coordinates of Optimized Structures

40

(dfmpe)Pd(Ph)(CF3)-GS

C	-0.3747620000	-2.5794890000	0.6064100000
H	-0.0960860000	-3.6213970000	0.3885540000
H	-0.4390820000	-2.4776930000	1.7020640000
C	-1.7042940000	-2.2006460000	-0.0462160000
H	-1.6987660000	-2.4688380000	-1.1153480000
H	-2.5493730000	-2.7311610000	0.4173030000
P	0.9532280000	-1.4085320000	0.0786910000
P	-1.9654830000	-0.3692400000	0.0038720000
C	2.3485660000	-1.8191010000	1.2785010000
C	1.5827370000	-2.2437490000	-1.4896040000
C	-2.8344020000	-0.1758830000	1.6655240000

C -3.4333260000 -0.1672700000 -1.1718950000

F 2.0894960000 -1.2297140000 2.4414060000

F 2.4435350000 -3.1306050000 1.4969020000

F 3.5068270000 -1.3855880000 0.8154100000

F 1.9452420000 -3.5083940000 -1.2882030000

F 2.6055810000 -1.5917420000 -2.0112310000

F 0.5779050000 -2.2432010000 -2.3736800000

F -2.9674250000 -0.0190670000 -2.4072920000

F -4.1638010000 0.8850260000 -0.8513120000

F -4.2207500000 -1.2439140000 -1.1592800000

F -3.1204110000 1.0847280000 1.9229920000

F -3.9544740000 -0.8925910000 1.7428600000

F -1.9969670000 -0.6268810000 2.6084400000

Pd 0.0828700000 0.7061030000 -0.1267880000

C -0.6323610000 2.6229090000 -0.2570260000

F -0.1489750000 3.3312150000 -1.2875850000

F -1.9889850000 2.6284450000 -0.4287330000

F -0.4143370000 3.3487560000 0.8516480000

C 1.9286550000 1.5489640000 -0.0755900000

C 2.4732670000 1.9757720000 1.1390470000

C 2.6931700000 1.6616640000 -1.2407880000

C 3.7669810000 2.4976220000 1.1881550000

H 1.8870010000 1.9144830000 2.0597400000

C 3.9855120000 2.1860530000 -1.1893170000

H 2.2846780000 1.3459440000 -2.2045880000

C 4.5269530000 2.6022240000 0.0251970000

H 4.1801160000 2.8294950000 2.1445580000

H 4.5717270000 2.2704140000 -2.1084190000

H 5.5392620000 3.0119150000 0.0644750000

40

(dfmpe)Pd(Ph)(CF3)-TS

Pd 0.1105520000 0.6731680000 -0.0004370000

C	1.7534340000	1.8970820000	0.0589530000
C	2.2377560000	2.1625780000	1.3446770000
C	2.6349780000	1.8578480000	-1.0296370000
C	3.6099110000	2.3021040000	1.5494930000
H	1.5443520000	2.2492950000	2.1851640000
C	4.0016200000	1.9991580000	-0.8121290000
H	2.2535350000	1.6964670000	-2.0409170000
C	4.4942660000	2.2151660000	0.4763180000
H	3.9875910000	2.4876850000	2.5581550000
H	4.6903360000	1.9409030000	-1.6587560000
H	5.5680010000	2.3311130000	0.6397340000
C	0.0637650000	2.9085820000	-0.2705820000
F	-0.8240130000	2.8271800000	-1.2928350000
F	0.7709160000	4.0079280000	-0.5674340000
F	-0.6086060000	3.2115820000	0.8526350000
C	-1.8436950000	-2.0621870000	-0.3717720000
H	-2.7405900000	-2.6097110000	-0.0459130000
H	-1.7979110000	-2.1298240000	-1.4711670000
C	-0.5769180000	-2.6449910000	0.2534090000
H	-0.6956120000	-2.7428110000	1.3450400000
H	-0.3587300000	-3.6474860000	-0.1440690000
P	-2.0071570000	-0.2535800000	-0.0010380000
P	0.8674930000	-1.5090110000	0.0186800000
C	-3.4786720000	0.1787310000	-1.1016300000
C	-2.8812480000	-0.3326750000	1.6691180000
C	1.4815830000	-2.0873460000	-1.6691500000
C	2.1476980000	-2.3637030000	1.1134550000
F	-3.0464950000	0.2660400000	-2.3587830000
F	-4.4503400000	-0.7336960000	-1.0713780000
F	-3.9953330000	1.3460210000	-0.7433240000
F	-3.9614770000	-1.1127670000	1.6731740000
F	-3.2414950000	0.8747670000	2.0771900000

F -2.0164610000 -0.8400520000 2.5573720000

F 1.8614580000 -2.0798050000 2.3843680000

F 3.3628840000 -1.9088360000 0.8379080000

F 2.1609450000 -3.6906610000 0.9902000000

F 2.6202880000 -1.4890720000 -1.9903900000

F 1.6654260000 -3.4041980000 -1.7569460000

F 0.5569420000 -1.7504940000 -2.5778610000

82

(dppf)Pd(Ph)(CF2CN)-GS

C -0.3820560000 -3.1335340000 -0.0153580000

C -0.1071730000 -3.6456750000 -1.3660960000

C 2.1579140000 -2.0492970000 0.1210320000

C 2.6905550000 -2.3208280000 1.3874460000

H 2.1057950000 -2.1063660000 2.2873360000

C 3.9645020000 -2.8752780000 1.5244040000

H 4.3620470000 -3.0819510000 2.5222590000

C 4.7254150000 -3.1703220000 0.3941060000

H 5.7230920000 -3.6042510000 0.4988810000

C 4.1992860000 -2.9150370000 -0.8713000000

H 4.7835970000 -3.1489300000 -1.7652060000

C 2.9261450000 -2.3591070000 -1.0053950000

H 2.5332500000 -2.1703950000 -2.0084780000

C -3.0426040000 -1.0411150000 -1.0499820000

C -2.5405550000 -1.4464080000 -2.2902880000

H -1.4695410000 -1.3697650000 -2.4954710000

C -3.3921700000 -1.9894170000 -3.2496130000

H -2.9852060000 -2.3191950000 -4.2079270000

C -4.7499450000 -2.1352650000 -2.9710590000

H -5.4178270000 -2.5708740000 -3.7180150000

C -5.2524340000 -1.7419300000 -1.7304500000

H -6.3137210000 -1.8694810000 -1.5041500000

C -4.4032470000 -1.1956730000 -0.7707870000

H	-4.8000820000	-0.9032930000	0.2038510000
C	-2.5660400000	-0.5119140000	1.8063550000
C	-2.0121310000	-1.4870820000	2.6463360000
H	-1.1966760000	-2.1171010000	2.2858120000
C	-2.4964470000	-1.6547870000	3.9418060000
H	-2.0557770000	-2.4189600000	4.5861350000
C	-3.5357810000	-0.8532430000	4.4118870000
H	-3.9132020000	-0.9858910000	5.4287150000
C	-4.0894080000	0.1218650000	3.5830350000
H	-4.9004150000	0.7567440000	3.9477570000
C	-3.6047750000	0.2959090000	2.2885460000
H	-4.0272610000	1.0773730000	1.6525570000
C	-2.2445780000	1.4829630000	-0.1586430000
C	-1.7948700000	2.5854250000	0.6410880000
H	-1.1845760000	2.5146660000	1.5390570000
C	-2.2579080000	3.7857210000	0.0360880000
H	-2.0510270000	4.7947010000	0.3892850000
C	-2.9897050000	3.4406380000	-1.1354980000
H	-3.4438970000	4.1388800000	-1.8366380000
C	-2.9916330000	2.0236220000	-1.2546430000
H	-3.4458980000	1.4406530000	-2.0534060000
C	0.8112760000	3.4673030000	-1.2580310000
H	1.2205460000	4.1012490000	-0.4746410000
C	0.1142260000	3.9138540000	-2.4143940000
H	-0.0953060000	4.9517090000	-2.6687880000
C	-0.3101690000	2.7710000000	-3.1504430000
H	-0.8979930000	2.7805100000	-4.0667160000
C	0.1196890000	1.6115910000	-2.4502760000
H	-0.0701340000	0.5750220000	-2.7260490000
C	0.8136040000	2.0348660000	-1.2676120000
C	3.2602020000	0.8072800000	-0.5642540000
C	3.6316570000	0.9973020000	-1.8990960000

H 2.8796220000 1.2646980000 -2.6446420000

C 4.9621120000 0.8417640000 -2.2832770000

H 5.2438080000 0.9904690000 -3.3283510000

C 5.9266380000 0.4933600000 -1.3404640000

H 6.9677030000 0.3620800000 -1.6447880000

C 5.5597890000 0.3092120000 -0.0076620000

H 6.3089440000 0.0263110000 0.7348920000

C 4.2340750000 0.4669960000 0.3818100000

H 3.9514310000 0.3014300000 1.4229220000

C 1.5264650000 1.6948820000 1.5371700000

C 0.7710440000 1.1552560000 2.5841170000

H 0.2044190000 0.2349630000 2.4188350000

C 0.7370800000 1.7849270000 3.8274460000

H 0.1374930000 1.3553090000 4.6332320000

C 1.4689960000 2.9524920000 4.0348090000

H 1.4448940000 3.4480500000 5.0083200000

C 2.2478730000 3.4805910000 3.0032790000

H 2.8376660000 4.3848760000 3.1712500000

C 2.2839120000 2.8519220000 1.7614280000

H 2.9192310000 3.2493130000 0.9659330000

N 0.1072710000 -3.9218850000 -2.4715120000

F 0.1800710000 -3.9549160000 0.9137720000

F -1.7395460000 -3.2630220000 0.1922020000

P -1.8700820000 -0.2778200000 0.1268780000

P 1.4998340000 0.8522320000 -0.0817680000

Fe -1.0753430000 2.7170350000 -1.2482210000

Pd 0.3310660000 -1.1738260000 0.0027120000

82

(dppf)Pd(Ph)(CF2CN)-TS

C 0.1999050000 -3.3254710000 -0.5009580000

C -0.2787550000 -2.9457680000 -1.8324080000

C 1.8275620000 -2.4478630000 0.0860700000

C	2.1448210000	-2.7853350000	1.4137740000
H	1.3632260000	-2.7778640000	2.1786380000
C	3.4496290000	-3.1324470000	1.7589150000
H	3.6845670000	-3.3716340000	2.7995760000
C	4.4446910000	-3.2010020000	0.7840320000
H	5.4623800000	-3.4908190000	1.0552750000
C	4.1277790000	-2.9032430000	-0.5426150000
H	4.9005390000	-2.9468030000	-1.3137900000
C	2.8346280000	-2.5328910000	-0.8929340000
H	2.5999650000	-2.2995670000	-1.9350860000
C	-3.3257310000	-1.0862250000	-0.6744560000
C	-3.2606670000	-1.2265040000	-2.0675170000
H	-2.3892270000	-0.8612560000	-2.6145660000
C	-4.2893630000	-1.8595670000	-2.7596680000
H	-4.2213020000	-1.9686630000	-3.8444280000
C	-5.3855020000	-2.3733460000	-2.0675110000
H	-6.1877480000	-2.8796520000	-2.6095860000
C	-5.4478510000	-2.2505650000	-0.6805310000
H	-6.3004100000	-2.6583390000	-0.1319670000
C	-4.4248180000	-1.6090400000	0.0155390000
H	-4.4812530000	-1.5171940000	1.1021700000
C	-2.3738560000	-0.3607400000	1.9415610000
C	-1.8295270000	-1.4148490000	2.6880220000
H	-1.1857870000	-2.1455410000	2.1907520000
C	-2.1117290000	-1.5359130000	4.0469660000
H	-1.6819720000	-2.3623680000	4.6178540000
C	-2.9349630000	-0.6016640000	4.6753130000
H	-3.1495080000	-0.6907840000	5.7430620000
C	-3.4872060000	0.4445140000	3.9365820000
H	-4.1385200000	1.1746190000	4.4232210000
C	-3.2128010000	0.5635760000	2.5751770000
H	-3.6487450000	1.3844040000	2.0017620000

C	-2.2645730000	1.4959270000	-0.2198590000
C	-1.7506740000	2.6164440000	0.5138270000
H	-1.1271170000	2.5637570000	1.4033480000
C	-2.1779760000	3.8066290000	-0.1367110000
H	-1.9253260000	4.8212290000	0.1671230000
C	-2.9429060000	3.4363330000	-1.2783460000
H	-3.3832740000	4.1173250000	-2.0048560000
C	-3.0029120000	2.0158200000	-1.3290790000
H	-3.5048340000	1.4208730000	-2.0891040000
C	0.8208280000	3.4203280000	-1.4918040000
H	1.2310950000	4.1183210000	-0.7653180000
C	0.0928300000	3.7676440000	-2.6635370000
H	-0.1422910000	4.7798190000	-2.9895460000
C	-0.3220380000	2.5652420000	-3.3047580000
H	-0.9253300000	2.4963110000	-4.2084080000
C	0.1436820000	1.4691980000	-2.5301260000
H	-0.0293280000	0.4094710000	-2.7232980000
C	0.8566790000	1.9912280000	-1.3982270000
C	3.2870990000	0.7432270000	-0.5465040000
C	3.7189810000	0.8201210000	-1.8754680000
H	3.0079140000	1.0758320000	-2.6650140000
C	5.0538820000	0.5767880000	-2.1936960000
H	5.3827530000	0.6440140000	-3.2336110000
C	5.9659670000	0.2515920000	-1.1908510000
H	7.0119700000	0.0603830000	-1.4422250000
C	5.5372940000	0.1662770000	0.1334850000
H	6.2434320000	-0.1018110000	0.9227450000
C	4.2052440000	0.4054180000	0.4553910000
H	3.8727420000	0.3163080000	1.4925580000
C	1.5628340000	1.8575440000	1.4267700000
C	0.8260580000	1.3873310000	2.5193820000
H	0.2600710000	0.4571860000	2.4217740000

C 0.8048820000 2.1001160000 3.7178290000

H 0.2178730000 1.7239300000 4.5589530000

C 1.5316450000 3.2833320000 3.8346870000

H 1.5169690000 3.8450400000 4.7718940000

C 2.2928330000 3.7437880000 2.7582840000

H 2.8781300000 4.6614330000 2.8554990000

C 2.3157920000 3.0313380000 1.5620120000

H 2.9365750000 3.3778310000 0.7318580000

N -0.5560000000 -2.6269750000 -2.9152340000

F 0.8522290000 -4.5151950000 -0.6438660000

F -0.8200130000 -3.6228710000 0.3557900000

P -1.9258730000 -0.2573900000 0.1664900000

P 1.5195840000 0.8886430000 -0.1231270000

Fe -1.0564440000 2.6486780000 -1.3900340000

Pd 0.2975120000 -1.0931030000 -0.0950830000

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(dppf)Pd(Ph)(CF2CO2Et)-GS

C 2.6713560000 0.2495520000 -0.2989340000

C 3.3739120000 -0.0234590000 -1.4785770000

H 2.8459820000 -0.0463310000 -2.4359050000

C 4.7474780000 -0.2637950000 -1.4567470000

H 5.2750430000 -0.4775420000 -2.3904290000

C 5.4490480000 -0.2353650000 -0.2506930000

H 6.5250770000 -0.4271250000 -0.2340840000

C 4.7641700000 0.0406030000 0.9309660000

H 5.3024830000 0.0714970000 1.8829580000

C 3.3877350000 0.2809960000 0.9050440000

H 2.8733980000 0.5160430000 1.8419530000

C 1.0923910000 2.5198260000 -0.7018760000

C 2.2592880000 3.0470420000 0.1070090000

C 4.5511060000 3.5480450000 0.1009640000

H 5.3663120000 3.1494960000 -0.5182610000

H	4.5493470000	3.0153540000	1.0627470000
C	4.6707450000	5.0410110000	0.3009620000
H	4.6262990000	5.5714130000	-0.6619420000
H	5.6305350000	5.2812730000	0.7833280000
H	3.8598340000	5.4092790000	0.9453500000
C	1.9613850000	-2.7997090000	-0.4912970000
C	2.0326020000	-3.3270410000	-1.7851120000
H	1.1866110000	-3.2189500000	-2.4674070000
C	3.1821330000	-3.9903990000	-2.2091240000
H	3.2282480000	-4.3987420000	-3.2215210000
C	4.2682910000	-4.1291310000	-1.3476450000
H	5.1725790000	-4.6419700000	-1.6838000000
C	4.1983490000	-3.6100840000	-0.0554620000
H	5.0486030000	-3.7078100000	0.6230520000
C	3.0511500000	-2.9505010000	0.3737810000
H	3.0105260000	-2.5337300000	1.3815090000
C	0.2577330000	-2.2651340000	1.7558380000
C	0.2847670000	-3.5984070000	2.1850890000
H	0.5138740000	-4.3950540000	1.4728150000
C	0.0447240000	-3.9068840000	3.5215340000
H	0.0629740000	-4.9488100000	3.8501050000
C	-0.2095020000	-2.8880380000	4.4419080000
H	-0.3960850000	-3.1343210000	5.4900040000
C	-0.2090450000	-1.5576810000	4.0269380000
H	-0.3922260000	-0.7525860000	4.7421810000
C	0.0298290000	-1.2470360000	2.6890070000
H	0.0367850000	-0.2038090000	2.3600820000
C	-0.8126680000	-2.5626830000	-0.9400650000
C	-1.2841870000	-2.0024710000	-2.1744900000
H	-0.9132000000	-1.0818910000	-2.6235610000
C	-2.3433960000	-2.8190230000	-2.6555360000
H	-2.9344550000	-2.6342750000	-3.5509530000

C	-2.5327640000	-3.8859490000	-1.7312790000
H	-3.2962680000	-4.6596510000	-1.7963530000
C	-1.5896480000	-3.7368960000	-0.6771850000
H	-1.5105410000	-4.3705420000	0.2033900000
C	-3.0792580000	-1.2850790000	1.0466570000
H	-2.4379260000	-1.4276580000	1.9138760000
C	-4.1814630000	-2.1036940000	0.6776420000
H	-4.5194790000	-2.9906770000	1.2111380000
C	-4.7286450000	-1.5936650000	-0.5338650000
H	-5.5610820000	-2.0202380000	-1.0911520000
C	-3.9724130000	-0.4505030000	-0.9135280000
H	-4.1192980000	0.1565300000	-1.8046090000
C	-2.9388300000	-0.2550000000	0.0587030000
C	-2.3417030000	2.1145210000	-1.2780440000
C	-3.4055400000	2.9894620000	-1.0425130000
H	-3.8096350000	3.1007500000	-0.0338670000
C	-3.9422140000	3.7324980000	-2.0915140000
H	-4.7683560000	4.4214870000	-1.9000080000
C	-3.4236700000	3.6031950000	-3.3800500000
H	-3.8449640000	4.1892200000	-4.2004330000
C	-2.3557770000	2.7389560000	-3.6158060000
H	-1.9304770000	2.6506690000	-4.6181420000
C	-1.8116640000	2.0013320000	-2.5666130000
H	-0.9430110000	1.3600710000	-2.7379710000
C	-1.9571780000	1.8571970000	1.6329330000
C	-0.8993910000	2.5000280000	2.2892180000
H	0.0956980000	2.5509500000	1.8395520000
C	-1.1095220000	3.0951620000	3.5321420000
H	-0.2742690000	3.5939550000	4.0291380000
C	-2.3676900000	3.0560110000	4.1303310000
H	-2.5271960000	3.5228230000	5.1055640000
C	-3.4236440000	2.4154860000	3.4820960000

H -4.4119740000 2.3768850000 3.9466190000

C -3.2196600000 1.8147700000 2.2421320000

H -4.0459820000 1.2951720000 1.7514900000

O 2.1738950000 3.2519850000 1.2966470000

O 3.3599950000 3.2105990000 -0.6085730000

F 1.3379420000 2.6304670000 -2.0393250000

F 0.0516820000 3.3905740000 -0.4505330000

P 0.5207560000 -1.7941640000 0.0123980000

P -1.6465240000 1.0339630000 0.0247040000

Fe -2.7543290000 -2.0773370000 -0.7893290000

Pd 0.6590270000 0.5307440000 -0.2636070000

90

(dppf)Pd(Ph)(CF2CO2Et)-TS

C 1.3621650000 2.5978460000 0.2718760000

C 1.9439080000 3.0957110000 -0.9098170000

H 1.4211760000 2.9663020000 -1.8606270000

C 3.1558950000 3.7744370000 -0.8680880000

H 3.5976900000 4.1418600000 -1.7977750000

C 3.8053140000 3.9946130000 0.3483790000

H 4.7517250000 4.5394530000 0.3768220000

C 3.2343820000 3.5119540000 1.5245760000

H 3.7312860000 3.6785650000 2.4843840000

C 2.0206700000 2.8269310000 1.4923520000

H 1.5633810000 2.4868560000 2.4250330000

C -0.5054830000 3.1356040000 0.4715070000

C -1.6615720000 2.9716730000 -0.4904670000

C -4.0123260000 2.8013970000 -0.6606490000

H -4.7254140000 2.1764050000 -0.1064420000

H -3.8032810000 2.3260600000 -1.6277690000

C -4.5215290000 4.2118080000 -0.8416820000

H -4.6899220000 4.6988570000 0.1301310000

H -5.4737000000 4.1985440000 -1.3933800000

H	-3.8016560000	4.8120360000	-1.4168070000
C	3.5072040000	0.1309130000	-0.7829980000
C	3.6934550000	0.2201700000	-2.1687650000
H	2.9420710000	-0.1894800000	-2.8479860000
C	4.8365440000	0.8203430000	-2.6885610000
H	4.9723970000	0.8788250000	-3.7712010000
C	5.8040150000	1.3443290000	-1.8314210000
H	6.7005800000	1.8170110000	-2.2395690000
C	5.6194050000	1.2660940000	-0.4532220000
H	6.3654510000	1.6862430000	0.2252640000
C	4.4770090000	0.6664170000	0.0707850000
H	4.3349290000	0.6264870000	1.1521200000
C	2.4543550000	-1.2604510000	1.4827720000
C	3.5893000000	-2.0696670000	1.6261200000
H	4.2274470000	-2.2682660000	0.7615320000
C	3.9216520000	-2.5990630000	2.8705810000
H	4.8062940000	-3.2323430000	2.9728270000
C	3.1332460000	-2.3140430000	3.9867370000
H	3.3980090000	-2.7285540000	4.9624970000
C	2.0177490000	-1.4888040000	3.8581150000
H	1.4057740000	-1.2492340000	4.7307800000
C	1.6829240000	-0.9607520000	2.6116810000
H	0.8119670000	-0.3064210000	2.4984890000
C	1.6672080000	-1.9775950000	-1.2071510000
C	0.8134580000	-1.8939330000	-2.3570820000
H	0.2856810000	-0.9989310000	-2.6808360000
C	0.7302300000	-3.1837480000	-2.9475770000
H	0.1275490000	-3.4508490000	-3.8140170000
C	1.5264960000	-4.0737810000	-2.1722280000
H	1.6384910000	-5.1437140000	-2.3415220000
C	2.1081200000	-3.3364670000	-1.1036840000
H	2.7302680000	-3.7465970000	-0.3115690000

C	-0.5709060000	-3.1032750000	0.9134140000
H	0.0085300000	-2.7170570000	1.7493830000
C	-0.5999680000	-4.4538140000	0.4701110000
H	-0.0351710000	-5.2770520000	0.9047960000
C	-1.4465100000	-4.5278180000	-0.6727060000
H	-1.6449890000	-5.4187380000	-1.2665190000
C	-1.9520590000	-3.2235420000	-0.9333840000
H	-2.6067630000	-2.9357200000	-1.7535010000
C	-1.4071390000	-2.3293280000	0.0441200000
C	-2.8842460000	-0.3042590000	-1.1824210000
C	-4.2426520000	-0.6323910000	-1.1010150000
H	-4.6554540000	-1.0101790000	-0.1626110000
C	-5.0710670000	-0.4672950000	-2.2086700000
H	-6.1318810000	-0.7190820000	-2.1346850000
C	-4.5500240000	0.0207750000	-3.4083200000
H	-5.2027430000	0.1527000000	-4.2746870000
C	-3.1989710000	0.3522000000	-3.4946240000
H	-2.7885210000	0.7574520000	-4.4220750000
C	-2.3713080000	0.1971250000	-2.3837910000
H	-1.3256670000	0.5108610000	-2.4319320000
C	-2.7977060000	-0.5550340000	1.6993240000
C	-2.9604280000	0.6266640000	2.4329590000
H	-2.4463530000	1.5348510000	2.1187210000
C	-3.7831670000	0.6467820000	3.5580630000
H	-3.9012120000	1.5762330000	4.1202740000
C	-4.4432760000	-0.5100850000	3.9686350000
H	-5.0830440000	-0.4927400000	4.8544610000
C	-4.2772760000	-1.6930200000	3.2492150000
H	-4.7856980000	-2.6061100000	3.5686280000
C	-3.4582450000	-1.7176600000	2.1222710000
H	-3.3264860000	-2.6510030000	1.5704640000
O	-1.5256160000	3.0726440000	-1.6864070000

O -2.8244910000 2.7923010000 0.1354800000

F -0.8815680000 3.0548940000 1.7729200000

F -0.1371160000 4.4423140000 0.2943380000

P 1.9431530000 -0.5488090000 -0.1237440000

P -1.7145150000 -0.5385270000 0.2120060000

Fe 0.0835340000 -3.2092610000 -1.0029040000

Pd 0.1443860000 0.9501100000 0.1384990000

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cis-Pd-CF3-GS

C 2.38723100 1.41225500 0.14370000

C 2.45068300 0.01211400 0.28686400

C 3.68043500 -0.54011000 0.66425600

C 4.80000500 0.24846900 0.91320400

C 4.70589900 1.62874400 0.77609700

C 3.50492400 2.21342900 0.38706300

H 3.77360800 -1.62002400 0.75998200

H 5.74114900 -0.21826000 1.20965700

H 5.57235700 2.26469300 0.97094400

H 3.43997400 3.29627000 0.28638000

P 0.93034500 -0.97304700 -0.06566100

O 1.20065100 1.95349000 -0.25293500

C 1.18941000 3.26262000 -0.80153700

H 1.98321300 3.35983800 -1.55849800

C 0.84797200 -2.34045100 1.24037000

C 1.25857200 -1.63103200 -1.80680100

C 2.65854700 -2.20275400 -2.01320100

H 2.87094600 -3.06076200 -1.36122900

H 2.75238900 -2.55554600 -3.05411700

H 3.43999800 -1.44602500 -1.85420600

C 0.20062100 -2.68105800 -2.14650300

H -0.81678600 -2.33948100 -1.90573600

H 0.23625900 -2.89665900 -3.22729400

H	0.37777900	-3.63110200	-1.62212600
C	1.07921500	-0.41399500	-2.72052000
H	0.07256100	0.02320500	-2.62868200
H	1.81193200	0.37702600	-2.49762500
H	1.22983800	-0.71688900	-3.77002900
C	-0.55535300	-2.95285600	1.17817100
H	-1.34378800	-2.20017100	1.29201600
H	-0.74372100	-3.49229600	0.24090600
H	-0.65801400	-3.68001600	2.00064600
C	1.00030800	-1.61396100	2.58033800
H	0.30690600	-0.75990600	2.65133400
H	0.76117700	-2.30877700	3.40193800
H	2.01988900	-1.23635400	2.74310500
C	1.85984600	-3.47978600	1.12584000
H	2.90713700	-3.16407400	1.21015800
H	1.67978400	-4.18897900	1.95088100
H	1.74262000	-4.04538600	0.19091300
Pd	-0.72605100	0.74611000	0.01740200
C	-2.39064400	-0.30590100	0.07152300
C	-2.90876200	-0.86834400	-1.10188800
C	-3.07728400	-0.53101700	1.27311300
C	-4.05037800	-1.67235100	-1.06838500
H	-2.42570900	-0.67570600	-2.06371800
C	-4.21426800	-1.33792200	1.30634900
H	-2.72072700	-0.07401600	2.19955100
C	-4.70208900	-1.92022800	0.13729000
H	-4.43298600	-2.10481000	-1.99732500
H	-4.72633800	-1.50930000	2.25746800
H	-5.59293200	-2.55258700	0.16438200
C	-1.90178900	2.40173900	0.13609800
F	-1.23034500	3.34873000	0.86834500
F	-3.12555500	2.36044600	0.68094000

F -2.07559700 2.98621100 -1.08925300

H 0.21083600 3.39468800 -1.27311900

H 1.31349700 4.02402200 -0.01757400

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trans-Pd-CF3-GS

C -1.03254200 2.32797800 -0.13928400

C -2.01928500 1.33133200 -0.00102100

C -3.34230000 1.75440300 0.18390900

C -3.69166500 3.09975800 0.23695900

C -2.69853600 4.06293200 0.10310800

C -1.37391000 3.68333800 -0.08510500

H -4.12844000 1.00962400 0.29107400

H -4.73372100 3.38945600 0.38403000

H -2.94784300 5.12557500 0.14644300

H -0.60926600 4.45226900 -0.18045500

P -1.51934200 -0.44391600 -0.00826700

O 0.25928700 1.93180300 -0.32515000

C 1.23491800 2.91591200 -0.63810700

H 0.90944100 3.51144500 -1.50478200

C -2.35735800 -1.15096500 -1.55228200

C -2.20533800 -1.12751200 1.62361100

C -3.71141500 -1.37511600 1.66648900

H -3.97836200 -1.76861100 2.66165000

H -4.30617700 -0.46378800 1.52151300

H -4.03360600 -2.12476900 0.92995600

C -1.47849700 -2.44074300 1.92710100

H -1.84064900 -2.82799300 2.89404700

H -1.65748700 -3.21536600 1.17046300

H -0.39311700 -2.29609300 2.00614500

C -1.80579400 -0.10752400 2.69428300

H -2.37179300 0.83146600 2.61745600

H -1.99542800 -0.53654200 3.69191200

H -0.73116500 0.13312300 2.63653900

C -1.47962600 -0.64846500 -2.70385400

H -0.44745300 -1.02169100 -2.61793300

H -1.89424900 -0.99755600 -3.66431600

H -1.44185000 0.45216000 -2.74002900

C -3.79505700 -0.69585900 -1.78993700

H -3.86716300 0.38770900 -1.95607200

H -4.17363100 -1.18861800 -2.70116800

H -4.47384900 -0.97253400 -0.97113600

C -2.30474200 -2.67789000 -1.50611300

H -2.97546200 -3.09461100 -0.74037400

H -2.63937100 -3.07542400 -2.47871100

H -1.28963500 -3.04939100 -1.32126100

Pd 0.87011000 -0.26010900 -0.06880700

C 2.81437100 0.24658900 0.05245200

C 3.68205900 0.25743800 -1.04886800

C 3.27096000 0.81103800 1.25337700

C 4.94345700 0.85058000 -0.96666000

H 3.37120400 -0.20601700 -1.98911500

C 4.53398500 1.39932800 1.34104100

H 2.62955900 0.80132700 2.14061900

C 5.37233300 1.42795800 0.22768300

H 5.59920200 0.85652000 -1.84226300

H 4.86615700 1.83663100 2.28714900

H 6.36075500 1.89010400 0.29326900

C 1.53396300 -2.12593400 -0.00225700

F 2.08475600 -2.46747400 1.18146500

F 2.44897800 -2.42549600 -0.94542700

F 0.55131300 -3.05445500 -0.20010300

H 1.42408700 3.57016000 0.22674900

H 2.15475900 2.37613200 -0.88365700

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cis-Pd-CF3-TS

C	-2.46084100	-1.57327300	0.26946600
C	-2.57076200	-0.16342600	0.29362700
C	-3.80789100	0.38230700	0.65299100
C	-4.89847700	-0.41273700	0.99658800
C	-4.76226500	-1.79590000	0.97715700
C	-3.55117700	-2.37817800	0.61425900
H	-3.92633200	1.46508300	0.66524900
H	-5.84724800	0.04972300	1.27531500
H	-5.60495300	-2.43818800	1.24363300
H	-3.46250400	-3.46407200	0.60178100
P	-1.08466900	0.83956200	-0.13332000
O	-1.27100400	-2.09942400	-0.10748700
C	-1.09583800	-3.49625200	-0.14707800
H	-1.80241800	-3.96860500	-0.84955400
C	-1.00771600	2.27656100	1.10016800
C	-1.46539900	1.41238500	-1.89703500
C	-2.85752000	2.00418300	-2.09826600
H	-3.03169300	2.90531400	-1.49544500
H	-2.97977000	2.29304600	-3.15616700
H	-3.64839700	1.27589100	-1.86759900
C	-0.38884300	2.41046900	-2.32298100
H	0.62208300	2.03418700	-2.10165900
H	-0.45660200	2.58311400	-3.41021400
H	-0.50844400	3.38740100	-1.83246000
C	-1.33723400	0.14794300	-2.75216000
H	-0.33080600	-0.29290200	-2.67058600
H	-2.06887300	-0.62148600	-2.46105400
H	-1.52166400	0.39863600	-3.81039300
C	0.41056900	2.85162700	0.99980500
H	1.17515000	2.07732000	1.14327400
H	0.60493400	3.33698300	0.03424000

H 0.54505800 3.61512400 1.78431900

C -1.16439000 1.63138300 2.47967400

H -0.47680000 0.77757000 2.59646200

H -0.91731900 2.37024500 3.25990000

H -2.18665600 1.27191800 2.66522000

C -2.00561200 3.41925400 0.92728600

H -3.05573100 3.10872900 1.00893400

H -1.83410100 4.16393600 1.72294500

H -1.87409100 3.94251400 -0.03043900

Pd 0.71482800 -0.63241700 -0.05984500

C 2.59295100 0.00772000 0.12729800

C 3.13627200 0.73031900 -0.95632300

C 3.03054300 0.32540200 1.42943400

C 3.98221900 1.80875700 -0.72814100

H 2.86712700 0.45367700 -1.97885500

C 3.88576800 1.40320100 1.64319100

H 2.67512100 -0.26699000 2.27583400

C 4.35592000 2.16061600 0.57145900

H 4.36032900 2.38276300 -1.57859300

H 4.18672100 1.65405900 2.66399600

H 5.02640700 3.00552800 0.74325100

C 2.57948400 -1.87022500 -0.09934300

F 2.31461000 -2.58094300 1.01859700

F 3.90701000 -1.97370400 -0.27152400

F 2.07972400 -2.58861900 -1.15455500

H -0.07242400 -3.66511400 -0.50120300

H -1.21082400 -3.94566900 0.85331100

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trans-Pd-CF3-TS

C -1.4715110000 2.2430920000 -0.0597790000

C -2.2735530000 1.0802810000 -0.1419510000

C -3.6367240000 1.2503500000 -0.4081760000

C	-4.2043270000	2.5066540000	-0.6049990000
C	-3.3942510000	3.6343280000	-0.5324640000
C	-2.0352710000	3.5083150000	-0.2610300000
H	-4.2786780000	0.3718600000	-0.4681550000
H	-5.2717200000	2.5995520000	-0.8142570000
H	-3.8181870000	4.6296490000	-0.6857760000
H	-1.4150600000	4.4024790000	-0.2046310000
P	-1.4749510000	-0.5667780000	0.0711630000
O	-0.1626120000	2.0780850000	0.2264880000
C	0.7078020000	3.1826200000	0.2471520000
H	0.7485850000	3.6837380000	-0.7343170000
C	-2.1382190000	-1.6633590000	-1.3294530000
C	-2.0781320000	-1.1121900000	1.7806780000
C	-3.5793540000	-0.9887980000	2.0234100000
H	-3.8078760000	-1.3161590000	3.0520290000
H	-3.9239910000	0.0511490000	1.9313250000
H	-4.1768100000	-1.6134260000	1.3463430000
C	-1.6108970000	-2.5486310000	2.0150560000
H	-1.7680340000	-2.8190610000	3.0727910000
H	-2.1735150000	-3.2741870000	1.4091350000
H	-0.5394510000	-2.6662010000	1.7905330000
C	-1.3439120000	-0.1837340000	2.7535170000
H	-1.6241560000	0.8706570000	2.6042760000
H	-1.6043690000	-0.4545940000	3.7906340000
H	-0.2510820000	-0.2641700000	2.6382490000
C	-2.0352790000	-0.8183600000	-2.6017820000
H	-1.0406560000	-0.3502880000	-2.6878660000
H	-2.1776250000	-1.4648700000	-3.4836960000
H	-2.7893400000	-0.0197560000	-2.6419290000
C	-3.5495940000	-2.2252130000	-1.1776310000
H	-4.3236210000	-1.4506760000	-1.0924560000
H	-3.7965390000	-2.8214870000	-2.0723930000

H -3.6380780000 -2.8978050000 -0.3125310000

C -1.1544480000 -2.8330700000 -1.4554250000

H -1.1204310000 -3.4589940000 -0.5531560000

H -1.4645730000 -3.4774140000 -2.2955500000

H -0.1324200000 -2.4798490000 -1.6507310000

Pd 0.8438370000 -0.2441470000 0.0166400000

C 2.7801270000 0.1518760000 -0.0222710000

C 3.2065490000 0.7591510000 -1.2137240000

C 3.3080160000 0.5880000000 1.2062650000

C 4.0867650000 1.8400010000 -1.1673860000

H 2.8401570000 0.3835980000 -2.1721130000

C 4.1852230000 1.6683460000 1.2406470000

H 3.0223970000 0.0805640000 2.1312360000

C 4.5739230000 2.2990930000 0.0558840000

H 4.3979060000 2.3244770000 -2.0966400000

H 4.5747040000 2.0194760000 2.1998330000

H 5.2705070000 3.1402470000 0.0873250000

C 2.4884470000 -1.7387920000 -0.2054310000

F 2.3893210000 -2.0508800000 -1.5113370000

F 3.7730840000 -2.0156840000 0.1267890000

H 0.4156480000 3.9107000000 1.0224900000

H 1.7018880000 2.7855000000 0.4868310000

F 1.8136840000 -2.7019630000 0.4858550000

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cis-Pd-CF3(CN)-GS

C -2.95041900 0.90941400 -0.16181500

C -2.70456800 -0.47065700 -0.29549400

C -3.78068300 -1.28285700 -0.67314400

C -5.04469400 -0.76030600 -0.92973800

C -5.25649100 0.60788900 -0.80123000

C -4.21506100 1.44474800 -0.41318900

H -3.63371700 -2.35738600 -0.76359500

H	-5.85929800	-1.42362100	-1.22598700
H	-6.24061800	1.03666200	-1.00282300
H	-4.38968800	2.51611800	-0.32010300
P	-1.00851900	-1.09576500	0.06805300
O	-1.91201600	1.70158100	0.23405400
C	-2.19488100	2.97329400	0.80128400
H	-2.99432700	2.87923900	1.55224800
C	-0.61954400	-2.41581600	-1.23041500
C	-1.18359500	-1.79737100	1.81357900
C	-2.41810200	-2.67091000	2.01935500
H	-2.42454600	-3.56129100	1.37667400
H	-2.43665700	-3.02498400	3.06371500
H	-3.35005400	-2.11350100	1.84822800
C	0.08414900	-2.57679500	2.16313900
H	0.99758100	-2.01034500	1.92984400
H	0.09136100	-2.79426500	3.24393100
H	0.13501600	-3.54230200	1.63978200
C	-1.28982900	-0.56594500	2.71937600
H	-0.40654300	0.08626500	2.63289200
H	-2.18038900	0.03828800	2.48724100
H	-1.37619100	-0.88958700	3.76976000
C	0.88779300	-2.68440100	-1.17648200
H	1.47539200	-1.77392500	-1.33753500
H	1.21063800	-3.12531300	-0.22435400
H	1.14741100	-3.40023700	-1.97365000
C	-0.94558900	-1.76015800	-2.57588300
H	-0.47593400	-0.76633300	-2.66051500
H	-0.55100900	-2.38675400	-3.39222700
H	-2.02597400	-1.63761500	-2.73656700
C	-1.33985400	-3.75662800	-1.09382100
H	-2.43319200	-3.68948300	-1.15356900
H	-1.02038600	-4.40944900	-1.92296000

H -1.07592700 -4.27574600 -0.16189300

Pd 0.22708700 0.94967800 -0.01823400

C 2.08438100 0.30987200 -0.04979000

C 2.71815800 -0.08841600 1.13695100

C 2.81792200 0.23562300 -1.24560700

C 4.01589800 -0.58888700 1.12983000

H 2.19720600 -0.00204000 2.09359400

C 4.11233700 -0.26676000 -1.26662500

H 2.37015200 0.57580800 -2.18196500

C 4.72245800 -0.69442900 -0.07680400

H 4.49163700 -0.89991700 2.06248100

H 4.66400600 -0.32922600 -2.20713100

C 1.00435100 2.82747400 -0.14263700

F 0.13675300 3.59790300 -0.86956500

F 2.20390700 3.04850400 -0.69950400

F 1.05770800 3.43317700 1.08017200

H -1.27330100 3.31249900 1.28405400

H -2.48072200 3.69947700 0.02657500

C 6.05176600 -1.22054400 -0.09315200

N 7.12932100 -1.65046600 -0.10666800

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cis-Pd-CF3(CN)-TS

C -3.02248900 1.04581600 -0.34025000

C -2.80901000 -0.35087400 -0.31567400

C -3.88906700 -1.17687100 -0.64671800

C -5.13144400 -0.66200500 -1.00720900

C -5.31348600 0.71578500 -1.03407100

C -4.26670000 1.57054500 -0.70084300

H -3.75893100 -2.25806700 -0.62207600

H -5.95028300 -1.33690600 -1.26314100

H -6.28018200 1.14011100 -1.31482800

H -4.42772000 2.64774400 -0.72608700

P	-1.13878800	-0.97730100	0.14157100
O	-1.98032700	1.84419100	0.00626600
C	-2.14122500	3.24575400	0.02807700
H	-2.94303400	3.54276500	0.72339000
C	-0.71390800	-2.37686700	-1.05973300
C	-1.38278500	-1.57388400	1.91980300
C	-2.59802200	-2.47216600	2.13373600
H	-2.55107600	-3.40351600	1.55416000
H	-2.65416900	-2.75563400	3.19837300
H	-3.53699200	-1.95651500	1.88618900
C	-0.10541600	-2.28013000	2.37417000
H	0.79265100	-1.68494800	2.14749400
H	-0.14107300	-2.43577400	3.46524300
H	0.01092800	-3.27050600	1.91075000
C	-1.56589100	-0.29271200	2.73941400
H	-0.69335600	0.37392000	2.64975400
H	-2.45794600	0.27169100	2.42670000
H	-1.69406500	-0.55231300	3.80349800
C	0.79639600	-2.60894900	-0.93571500
H	1.36491800	-1.68386800	-1.09420400
H	1.08517700	-3.01558600	0.04246200
H	1.11202100	-3.33832800	-1.70004900
C	-1.00172700	-1.81234100	-2.45337400
H	-0.52965500	-0.82508100	-2.58736100
H	-0.58382800	-2.48987800	-3.21596000
H	-2.07763100	-1.70323200	-2.65096500
C	-1.42662300	-3.71324200	-0.86608800
H	-2.51861200	-3.65170100	-0.96218600
H	-1.08067000	-4.41448700	-1.64394400
H	-1.18952300	-4.17315900	0.10356500
Pd	0.22695200	0.89722200	0.04000800
C	2.18787300	0.68436100	-0.03596800

C 2.85127400 0.19104300 1.11471500

C 2.77210200 0.41636200 -1.29849000

C 3.95168100 -0.63796600 0.99933800

H 2.47115300 0.44611300 2.10669800

C 3.87878900 -0.40716200 -1.41141100

H 2.32657800 0.84645800 -2.19838800

C 4.47620700 -0.96230800 -0.26639300

H 4.42303900 -1.04728000 1.89551300

H 4.29202400 -0.63400200 -2.39654700

C 1.78159900 2.53866300 0.07805900

F 1.32971500 3.14351700 -1.04262600

F 3.05648100 2.92897400 0.19468300

F 1.16153200 3.13254800 1.13623200

H -1.18981300 3.65753700 0.38315900

H -2.35398300 3.64121100 -0.97857600

C 5.60700800 -1.82342500 -0.38318400

N 6.52547600 -2.52756000 -0.47778200

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cis-Pd-CF3(NMe2)-GS

C -3.30611300 0.69420000 -0.15228600

C -2.93003400 -0.65631200 -0.29599700

C -3.92653700 -1.56328300 -0.67581500

C -5.23520700 -1.16231000 -0.92898000

C -5.57537800 0.17878300 -0.79316900

C -4.61713100 1.10763700 -0.40019100

H -3.67935900 -2.61888800 -0.76829500

H -5.98369500 -1.89875100 -1.22727000

H -6.59596000 0.51395400 -0.99143400

H -4.89281100 2.15681000 -0.29964700

P -1.17817900 -1.12044500 0.05737800

O -2.34968800 1.57746900 0.24964300

C -2.74872900 2.82676600 0.79147700

H	-3.53725400	2.67528600	1.54517100
C	-0.66305900	-2.36172200	-1.27602100
C	-1.29325400	-1.88555200	1.78159100
C	-2.45048600	-2.86276200	1.96808500
H	-2.39330900	-3.72668300	1.29206100
H	-2.42686100	-3.25533000	2.99875400
H	-3.42667100	-2.37747500	1.82655800
C	0.03471200	-2.56878000	2.10860700
H	0.89985000	-1.93153400	1.87373100
H	0.06889200	-2.80042400	3.18622600
H	0.15198400	-3.52025600	1.57005800
C	-1.49619200	-0.68983600	2.71827400
H	-0.67069100	0.03511000	2.64182300
H	-2.43427300	-0.15531400	2.50158700
H	-1.55115600	-1.04385100	3.76124500
C	0.85815400	-2.52792600	-1.19041800
H	1.38602000	-1.56751100	-1.22288700
H	1.17680400	-3.05273400	-0.28059900
H	1.19388900	-3.13123800	-2.05017800
C	-1.00208700	-1.66865100	-2.59944700
H	-0.58226100	-0.64990000	-2.63312600
H	-0.56452900	-2.24009600	-3.43438600
H	-2.08572600	-1.59481800	-2.77131900
C	-1.28952000	-3.75415400	-1.22185700
H	-2.37842400	-3.76306800	-1.35603900
H	-0.86935100	-4.35642700	-2.04468800
H	-1.04873200	-4.28220700	-0.28849700
Pd	-0.13894100	1.02925800	0.00455100
C	1.76936100	0.52984200	-0.02181800
C	2.41809800	0.11466100	1.14450200
C	2.52994600	0.54573600	-1.19627700
C	3.74183400	-0.32438300	1.13692000

H 1.89287900 0.13608000 2.10363600

C 3.85040500 0.10463800 -1.22331000

H 2.08891600 0.90845200 -2.12828000

C 4.48835400 -0.36642300 -0.05723100

H 4.19139800 -0.63294700 2.08111400

H 4.38813800 0.13648300 -2.17122900

C 0.47163700 2.96355700 -0.10699300

F -0.45457400 3.65934700 -0.84689700

F 1.65160200 3.30392600 -0.64371900

F 0.44680400 3.57596700 1.11754800

H -1.86193600 3.25815000 1.26579500

H -3.09948800 3.50930400 0.00342500

N 5.78986000 -0.83648200 -0.08269300

C 6.45226800 -1.14891400 1.15033200

H 7.45425800 -1.54419200 0.93769400

H 6.57050700 -0.27227700 1.81906000

H 5.91130600 -1.92583200 1.71835700

C 6.56509000 -0.70734700 -1.28255200

H 6.08970900 -1.22638500 -2.13302900

H 6.72915400 0.34601600 -1.58751100

H 7.54998200 -1.16899400 -1.13311900

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cis-Pd-CF3(NMe2)-TS

C -3.39443700 0.74950500 -0.48788800

C -3.00498800 -0.60752700 -0.39457700

C -3.94027800 -1.57573900 -0.77567700

C -5.20588100 -1.24075000 -1.25094200

C -5.56129100 0.09972400 -1.34541500

C -4.66385300 1.09331400 -0.96518100

H -3.67380000 -2.62915800 -0.69870800

H -5.90713700 -2.02512200 -1.54225300

H -6.54894600 0.38514700 -1.71543200

H	-4.96017600	2.13904800	-1.04171700
P	-1.30291900	-0.99055700	0.20059100
O	-2.50023100	1.68298700	-0.09035900
C	-2.81692300	3.05061900	-0.18830900
H	-3.69135700	3.30622400	0.43349200
C	-0.63358600	-2.38428500	-0.89884500
C	-1.61181300	-1.56025900	1.98074900
C	-2.72936100	-2.58516600	2.15164600
H	-2.53571500	-3.52417500	1.61624000
H	-2.83210100	-2.83675200	3.22124000
H	-3.69957600	-2.19077500	1.81668800
C	-0.29915400	-2.09697300	2.55146200
H	0.53705900	-1.40604400	2.36165600
H	-0.39600100	-2.22166400	3.64318100
H	-0.03478200	-3.08031700	2.13577900
C	-1.99447000	-0.28177600	2.73285600
H	-1.19741100	0.47620400	2.66756500
H	-2.91962500	0.16569100	2.33787300
H	-2.16608500	-0.51637600	3.79709100
C	0.88294100	-2.41755600	-0.67059500
H	1.34029800	-1.43358000	-0.83697700
H	1.15225300	-2.74271800	0.34311100
H	1.33764500	-3.13205400	-1.37747400
C	-0.88767100	-1.91990700	-2.33539500
H	-0.53050800	-0.88756900	-2.48438200
H	-0.33584700	-2.57028000	-3.03434700
H	-1.95191200	-1.95402300	-2.60924500
C	-1.18484100	-3.79209700	-0.68651500
H	-2.26658700	-3.87580500	-0.85573700
H	-0.69963500	-4.47638500	-1.40325800
H	-0.96243200	-4.17642100	0.31902900
Pd	-0.08130900	0.99528200	0.11314400

C 1.92065300 1.04770600 0.02588700

C 2.61875400 0.57657400 1.15316300

C 2.50973800 0.83399400 -1.23065600

C 3.77608400 -0.17503600 1.02373800

H 2.22935300 0.78062100 2.15386700

C 3.67556500 0.08833300 -1.36797100

H 2.03029400 1.23677500 -2.12568700

C 4.33793500 -0.44895700 -0.24507100

H 4.25385100 -0.54985000 1.92895800

H 4.06965600 -0.07435100 -2.37103500

C 1.21657000 2.79158100 0.14619300

F 0.96493200 3.29878600 -1.07670500

F 2.37229700 3.35910400 0.54207500

F 0.30874500 3.39289900 1.00162700

H -1.93990200 3.59222500 0.18383400

H -3.00776600 3.34700300 -1.23342700

N 5.49140800 -1.19441800 -0.37430100

C 5.96576500 -1.54468300 -1.68254000

H 5.24084700 -2.15758700 -2.25408500

H 6.19536200 -0.65158600 -2.29032700

H 6.89412300 -2.12307600 -1.59291300

C 6.07042300 -1.81733300 0.78172300

H 6.98379600 -2.35145300 0.49034600

H 6.35745800 -1.07696900 1.54924700

H 5.39224900 -2.54938500 1.26330000

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cis-Pd-CF2H-GS

C 2.42480200 -1.27867000 0.11363100

C 2.38099300 0.12707700 0.21192500

C 3.57671600 0.79016800 0.51305600

C 4.76800600 0.10535400 0.73429500

C 4.78007500 -1.28206400 0.64814100

C	3.61571100	-1.97587200	0.33432900
H	3.58194100	1.87704600	0.57123900
H	5.67990000	0.65662500	0.97109700
H	5.70296300	-1.83942300	0.82399200
H	3.63931000	-3.06301000	0.27287400
P	0.76944500	0.97820600	-0.06846900
O	1.27358900	-1.92867700	-0.21562700
C	1.34056800	-3.28855500	-0.61853200
H	0.35831200	-3.53812300	-1.02988500
C	0.98180500	1.73893600	-1.78479400
C	0.59973100	2.26838400	1.30668500
C	0.85527200	1.49293400	2.60275300
H	1.90890800	1.19994800	2.71711700
H	0.58266100	2.12232500	3.46577900
H	0.24143300	0.57811700	2.64703100
C	1.50352000	3.49726000	1.23120100
H	1.27716200	4.15241000	2.08913600
H	2.57464500	3.26593800	1.29048600
H	1.32424200	4.09045400	0.32339700
C	-0.85630600	2.74576100	1.30681500
H	-1.11321700	3.32515600	0.41042200
H	-1.56656500	1.91312800	1.37800700
H	-1.01300500	3.40367800	2.17779000
C	2.30862100	2.45667700	-2.01524600
H	2.46228300	3.30291300	-1.33190000
H	3.16658500	1.77580700	-1.92224200
H	2.32418700	2.86190300	-3.04119500
C	-0.18635500	2.68984000	-2.04649200
H	-0.08483300	3.63171300	-1.48798800
H	-0.21190800	2.94998700	-3.11782300
H	-1.15540300	2.23856900	-1.78722500
C	0.89170000	0.54397100	-2.73999200

H 0.97857200 0.89599200 -3.78149800

H 1.70457400 -0.17863100 -2.56679500

H -0.06383600 0.00655600 -2.63473600

Pd -0.74289900 -0.87847500 0.01974200

C -2.51520300 -0.01142500 0.08856700

C -3.23423800 0.09574400 1.29014900

C -3.09880600 0.52469800 -1.06899600

C -4.45995500 0.76113100 1.34252600

H -2.82747500 -0.33898800 2.20818700

C -4.32866100 1.18399500 -1.01922800

H -2.59333900 0.42398600 -2.03339300

C -5.01087600 1.31559400 0.18861500

H -4.99010500 0.84316300 2.29581100

H -4.75754000 1.59597900 -1.93734000

H -5.97104000 1.83592500 0.22809000

C -1.80601700 -2.59444600 0.18656700

F -1.83695100 -3.28029600 -1.01198900

F -1.13161400 -3.42601500 1.05869900

H 2.11231400 -3.41398200 -1.39392500

H 1.54947600 -3.94549700 0.23885200

H -2.84777100 -2.54565800 0.54429900

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trans-Pd-CF2H-GS

C 0.83343000 2.31067100 0.04084100

C 1.86290200 1.36014100 -0.11188800

C 3.14834100 1.84218500 -0.38889200

C 3.41929900 3.20040100 -0.52314500

C 2.38441000 4.11641600 -0.37422900

C 1.09507900 3.67789200 -0.09087800

H 3.96778700 1.13478100 -0.50184700

H 4.43430900 3.53686800 -0.74236200

H 2.57333200 5.18724500 -0.47886800

H	0.29440700	4.40801100	0.01732100
P	1.46021000	-0.43507600	0.04147300
O	-0.41838600	1.85277200	0.32294100
C	-1.42192200	2.78070400	0.70218300
H	-2.28230500	2.18891300	1.03112900
C	2.30585400	-0.92883400	1.66205000
C	2.22913800	-1.24811100	-1.48941200
C	1.80592200	-0.37428900	-2.67376500
H	2.32396300	0.59502100	-2.69214600
H	2.03803300	-0.90052600	-3.61430600
H	0.72010200	-0.18305900	-2.65992500
C	3.74555400	-1.42935100	-1.47855500
H	4.04995000	-1.91183800	-2.42250500
H	4.30198000	-0.48497800	-1.41797000
H	4.08190300	-2.08486100	-0.66291200
C	1.57337900	-2.62259000	-1.65452800
H	1.76441400	-3.29292700	-0.80648600
H	0.48636500	-2.54456500	-1.77835900
H	1.98540200	-3.10240000	-2.55813800
C	3.72077200	-0.38861800	1.85129400
H	4.41814800	-0.73164600	1.07480300
H	3.74524000	0.70952800	1.88284100
H	4.11159500	-0.74958700	2.81761400
C	2.30844100	-2.45236100	1.78340200
H	3.01702100	-2.92349900	1.08640000
H	2.62455700	-2.73103800	2.80254000
H	1.31187700	-2.87728300	1.60789200
C	1.39842600	-0.33795000	2.74631500
H	1.81149500	-0.57192400	3.74184000
H	1.32579500	0.75851600	2.66767900
H	0.37962500	-0.75142000	2.68842600
Pd	-0.92825000	-0.36732600	0.08013200

H -1.06326600 3.41290800 1.52939500

H -1.72640300 3.40646000 -0.15100200

C -1.50795800 -2.25747900 0.01671900

H -2.42831700 -2.44849400 0.59272900

F -0.56236700 -3.11192200 0.53272200

F -1.73390900 -2.69025800 -1.25811100

C -2.90506300 0.02596900 -0.02154700

C -3.78891600 -0.16966400 1.05071800

C -3.40969200 0.66838500 -1.16480100

C -5.10946000 0.28355900 1.00089400

H -3.44302100 -0.68199900 1.95540500

C -4.73075700 1.11454100 -1.22530000

H -2.75886000 0.82915700 -2.03063200

C -5.58501500 0.92941200 -0.13862700

H -5.77179700 0.12835900 1.85769400

H -5.09748600 1.60922200 -2.12960700

H -6.61891900 1.28144800 -0.18292700

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cis-Pd-CF2H-TS

C -2.60872700 -1.52431000 0.19183900

C -2.60937100 -0.11497300 0.07072800

C -3.84907700 0.53452100 0.05481700

C -5.05242700 -0.15914900 0.15380600

C -5.02737600 -1.54373900 0.27669500

C -3.81502500 -2.22660400 0.29627500

H -3.87807700 1.61987200 -0.03761000

H -6.00043600 0.38187200 0.13691400

H -5.95945000 -2.10805600 0.35783900

H -3.81499200 -3.31241700 0.38909300

P -1.00209500 0.77130200 -0.07696900

O -1.41152900 -2.14865400 0.20124300

C -1.33907200 -3.53440600 0.40341300

H	-0.27014600	-3.78563200	0.43302000
C	-0.86486500	1.72086500	1.55420700
C	-1.17956600	1.90975600	-1.58563200
C	-1.81500900	1.05195900	-2.68283500
H	-2.87791700	0.84530700	-2.49402500
H	-1.73783100	1.57723700	-3.64934700
H	-1.29462200	0.08542500	-2.78609200
C	-1.97669600	3.19774100	-1.39738700
H	-2.00904300	3.74260600	-2.35613400
H	-3.01950600	3.02493400	-1.09858400
H	-1.51197900	3.87089200	-0.66311900
C	0.24498000	2.26729800	-2.02396100
H	0.79923500	2.83012000	-1.26040200
H	0.82677600	1.36138100	-2.24658000
H	0.20175600	2.88879600	-2.93442100
C	-2.09111300	2.52935100	1.96718100
H	-2.35822200	3.30968600	1.24255200
H	-2.96931200	1.88845700	2.12976900
H	-1.88008200	3.03570800	2.92439800
C	0.36832600	2.62142400	1.46806800
H	0.20841700	3.48181000	0.80138900
H	0.59734100	3.02504000	2.46847500
H	1.25453700	2.06814200	1.12085600
C	-0.62126700	0.63069300	2.60265600
H	-0.48115400	1.09570800	3.59296300
H	-1.47457700	-0.06182500	2.67689600
H	0.27874100	0.04225600	2.36692000
Pd	0.78140400	-0.72049400	-0.29746100
C	2.71375100	-0.21559700	0.00627600
C	3.37201300	0.58209100	-0.94449200
C	3.11755400	-0.12172200	1.34863000
C	4.33241400	1.50898200	-0.54987300

H 3.12194500 0.47992200 -2.00244900

C 4.07836500 0.80949500 1.73923500

H 2.67206200 -0.78391700 2.09424600

C 4.68299800 1.63702200 0.79492800

H 4.81518100 2.13743300 -1.30329300

H 4.36004700 0.88244900 2.79321100

H 5.43796500 2.36504500 1.10128800

C 2.35366400 -2.05919900 -0.55988600

F 3.25304200 -2.10402400 -1.57150400

F 2.85638500 -2.74543500 0.49475000

H -1.79569400 -3.83016400 1.36301500

H -1.81519300 -4.09650500 -0.41811400

H 1.48160600 -2.66297500 -0.93220700

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cis-Pd-CF2H-TS-rot

C 2.4872230000 1.4265500000 -0.2099290000

C 2.4767290000 0.0127180000 -0.2589190000

C 3.6723540000 -0.6307970000 -0.5962590000

C 4.8362510000 0.0733480000 -0.8954840000

C 4.8182210000 1.4626460000 -0.8529810000

C 3.6517450000 2.1405450000 -0.5106950000

H 3.6985910000 -1.7194480000 -0.6268200000

H 5.7494120000 -0.4641410000 -1.1582780000

H 5.7198750000 2.0344670000 -1.0849990000

H 3.6550610000 3.2297460000 -0.4793370000

P 0.8961240000 -0.8648710000 0.1057660000

O 1.3377350000 2.0448080000 0.1456590000

C 1.2733150000 3.4497890000 0.2022450000

H 1.4509400000 3.9021130000 -0.7877230000

C 1.1882130000 -1.5347410000 1.8524960000

C 0.7223350000 -2.2433610000 -1.1855750000

C 1.6131240000 -3.4747070000 -1.0401630000

H	1.4138720000	-4.0224480000	-0.1081030000
H	1.3982850000	-4.1696100000	-1.8697690000
H	2.6874160000	-3.2523780000	-1.0869450000
C	-0.7423630000	-2.6948020000	-1.1363060000
H	-1.4342250000	-1.8499720000	-1.2533130000
H	-0.9271970000	-3.4082930000	-1.9570220000
H	-0.9976490000	-3.2033350000	-0.1969300000
C	0.9666950000	-1.5616240000	-2.5344060000
H	0.3612230000	-0.6449100000	-2.6279720000
H	2.0210180000	-1.2887680000	-2.6852560000
H	0.6723100000	-2.2438370000	-3.3491720000
C	0.0129000000	-2.4394380000	2.2224120000
H	-0.9530150000	-1.9590890000	2.0007360000
H	0.0477840000	-3.4040580000	1.6953180000
H	0.0433830000	-2.6592510000	3.3029020000
C	1.1624780000	-0.2934200000	2.7497650000
H	0.2072690000	0.2481450000	2.6592890000
H	1.2932980000	-0.5962440000	3.8024400000
H	1.9741830000	0.4082570000	2.5025890000
C	2.5131650000	-2.2630140000	2.0589900000
H	3.3741930000	-1.6054790000	1.8710290000
H	2.5834550000	-2.5986690000	3.1078380000
H	2.6157240000	-3.1551730000	1.4271380000
Pd	-0.7711630000	0.7415410000	0.0527100000
C	-2.7201970000	0.3172280000	-0.0958500000
C	-3.2271900000	0.0087060000	-1.3781310000
C	-3.3339390000	-0.2985370000	1.0191650000
C	-4.2217610000	-0.9518070000	-1.5386580000
H	-2.8148690000	0.5169470000	-2.2535700000
C	-4.3224610000	-1.2603070000	0.8447050000
H	-3.0080220000	-0.0311330000	2.0280990000
C	-4.7699260000	-1.6030900000	-0.4336120000

H -4.5720870000 -1.1960080000 -2.5455180000

H -4.7533860000 -1.7501970000 1.7225220000

H -5.5509010000 -2.3553510000 -0.5638990000

C -2.4925830000 2.1647770000 0.0815390000

F -2.0915150000 2.8612050000 -1.0224940000

F -1.9845350000 2.8095730000 1.1930750000

H 0.2566870000 3.6933390000 0.5317920000

H 1.9959770000 3.8552500000 0.9300130000

H -3.5803530000 2.3162710000 0.1551780000

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trans-Pd-CF2H-TS

C 1.18000000 2.29182000 -0.06025700

C 2.07222100 1.19595500 -0.13894500

C 3.41902900 1.47478200 -0.39602600

C 3.88621500 2.77271100 -0.58833200

C 2.98876900 3.83240900 -0.52018900

C 1.64244800 3.59822400 -0.25718100

H 4.12968700 0.65063800 -0.45213200

H 4.94421600 2.95037000 -0.79062600

H 3.33326000 4.85848700 -0.67013000

H 0.95228400 4.43985500 -0.20355400

P 1.40239100 -0.50981100 0.06783000

O -0.11204900 2.02229600 0.21867100

C -1.07118300 3.04954300 0.23121400

H -2.03103400 2.56950200 0.46026200

C 2.03801000 -1.00809900 1.78005400

C 2.16105200 -1.55033000 -1.32787900

C 1.98291300 -0.72138500 -2.60236500

H 2.65831400 0.14499100 -2.64145600

H 2.18872700 -1.35302100 -3.48262800

H 0.94833300 -0.35058700 -2.69123000

C 3.61609800 -1.98694600 -1.17744400

H	3.91061600	-2.56718900	-2.06846800
H	4.32112800	-1.14818500	-1.10161000
H	3.76488200	-2.64242800	-0.30752500
C	1.28332400	-2.80220200	-1.44899600
H	1.32130200	-3.43415400	-0.55095700
H	0.22994900	-2.54253300	-1.62436500
H	1.63771600	-3.41108300	-2.29821300
C	3.52370400	-0.77037300	2.03291700
H	4.17172600	-1.34173700	1.35522800
H	3.78736700	0.29378300	1.94974100
H	3.77155000	-1.08613700	3.06080600
C	1.68033500	-2.47667400	2.00901900
H	2.30885000	-3.15564200	1.41382400
H	1.84011100	-2.73392300	3.06974700
H	0.62525100	-2.67702300	1.76513000
C	1.22833500	-0.14123500	2.74975000
H	1.50267900	-0.39308100	3.78818900
H	1.42674500	0.93202800	2.60345100
H	0.14601900	-0.30610900	2.62585100
Pd	-0.92725300	-0.38553100	0.00099700
H	-0.84932300	3.79901600	1.00971200
H	-1.14433100	3.54728700	-0.75027500
C	-2.45940500	-1.99889300	-0.19924300
H	-3.52309000	-2.22691600	-0.02026500
F	-1.80780800	-2.87324300	0.64013600
F	-2.21931600	-2.37598100	-1.48521700
C	-2.89504500	-0.15024200	-0.02378200
C	-3.46301000	0.23837200	1.20556000
C	-3.40172400	0.40578700	-1.21244800
C	-4.45492000	1.21518000	1.24350800
H	-3.11309900	-0.22334800	2.13335600
C	-4.39502800	1.38291600	-1.16353900

H -3.00308100 0.07255700 -2.17422600

C -4.92201300 1.79410500 0.06096000

H -4.87049900 1.52730400 2.20547900

H -4.76253800 1.82689900 -2.09271200

H -5.70618200 2.55408000 0.09450600

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cis-Pd-CF2H(CN)-GS

C 2.92223400 0.91485300 -0.15560800

C 2.65291100 -0.46555200 -0.24441500

C 3.72057800 -1.31287300 -0.56490300

C 5.00110700 -0.82699300 -0.81134600

C 5.23650500 0.54088400 -0.73168900

C 4.20426100 1.41290000 -0.40053700

H 3.55157900 -2.38692100 -0.61926900

H 5.80858500 -1.51707200 -1.06266600

H 6.23319300 0.94290300 -0.92695500

H 4.40217800 2.48251100 -0.34531500

P 0.93430400 -1.04583700 0.07740800

O 1.89407800 1.74229300 0.18902100

C 2.18853400 3.06713700 0.61023600

H 1.26666000 3.46751800 1.04168500

C 1.05001700 -1.79040200 1.80905700

C 0.53425800 -2.32084400 -1.26292300

C 0.91215100 -1.64086600 -2.58241800

H 1.99972900 -1.54775900 -2.71250800

H 0.51971800 -2.23374300 -3.42474400

H 0.47489000 -0.63100100 -2.65127800

C 1.21036600 -3.68590100 -1.14959500

H 0.88485700 -4.31011600 -1.99841100

H 2.30604800 -3.64562400 -1.19426800

H 0.91933600 -4.21911800 -0.23364800

C -0.98249100 -2.53714500 -1.24784000

H	-1.33809300	-3.00450500	-0.32008600
H	-1.53393300	-1.59893000	-1.37989200
H	-1.25336300	-3.21008000	-2.07812700
C	2.24394600	-2.71468100	2.03031300
H	2.23726700	-3.58888900	1.36559100
H	3.20063000	-2.18865300	1.90220400
H	2.21730900	-3.09432300	3.06561500
C	-0.25446700	-2.52644200	2.11462800
H	-0.32923700	-3.47985900	1.57200300
H	-0.29681500	-2.76272000	3.19075800
H	-1.13950300	-1.92100600	1.86975300
C	1.18144200	-0.57787200	2.73679600
H	1.23123800	-0.91873700	3.78423100
H	2.09941700	-0.00507800	2.53250900
H	0.32653500	0.10963900	2.63838500
Pd	-0.26178100	1.03132800	-0.02106500
C	-2.14929300	0.47583600	-0.06117200
C	-2.89152200	0.47154900	-1.25654200
C	-2.80985000	0.07597800	1.11317600
C	-4.21062500	0.03571300	-1.29288400
H	-2.42582700	0.80838300	-2.18682000
C	-4.13142200	-0.35554400	1.09316100
H	-2.28649000	0.10564200	2.07204100
C	-4.84334400	-0.39159300	-0.11537400
H	-4.76288800	0.02516700	-2.23523100
H	-4.62363900	-0.66705200	2.01720300
C	-1.02641400	2.90159500	-0.19475100
F	-0.95141600	3.57855400	1.00341500
F	-0.21600500	3.60199800	-1.06155600
H	2.98101100	3.05065700	1.37428200
H	2.48988100	3.69503500	-0.24107100
H	-2.05898800	3.02671200	-0.56127600

C -6.19840300 -0.84627300 -0.14466500

N -7.29751400 -1.21722900 -0.16856300

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cis-Pd-CF3(CN)-TS

C -3.11994100 1.11441100 -0.22500300

C -2.87592600 -0.27101800 -0.08883900

C -3.98307800 -1.12767500 -0.07104600

C -5.28757400 -0.65558500 -0.18599700

C -5.50308000 0.71061900 -0.32637300

C -4.42853900 1.59455000 -0.34618500

H -3.82277400 -2.19991200 0.03635400

H -6.12693000 -1.35319400 -0.16745000

H -6.51835700 1.10294700 -0.42029600

H -4.61903700 2.66216000 -0.45131600

P -1.14222400 -0.86210200 0.07898100

O -2.04927500 1.94374200 -0.23031000

C -2.23128000 3.31718100 -0.46139100

H -1.22814600 3.76338300 -0.49107200

C -0.83151600 -1.83274100 -1.51338900

C -1.11699600 -1.94286000 1.63680400

C -1.88307500 -1.15193400 2.70046300

H -2.96543300 -1.13007900 2.51040500

H -1.72126700 -1.61519100 3.68777100

H -1.52713200 -0.10996700 2.75891100

C -1.69510200 -3.34961800 1.50945800

H -1.63689700 -3.85000800 2.49074800

H -2.75289100 -3.35978700 1.21377500

H -1.12886400 -3.97048200 0.80086800

C 0.34736200 -2.04228400 2.07562600

H 0.98543800 -2.54121700 1.33342400

H 0.77303200 -1.04579400 2.25637500

H 0.40863500 -2.62163700 3.01209600

C	-1.89447400	-2.85922000	-1.89477100
H	-2.03017100	-3.64297400	-1.13787600
H	-2.86844800	-2.38908800	-2.09070900
H	-1.58642900	-3.36137500	-2.82737400
C	0.53784700	-2.50279600	-1.39213000
H	0.52302100	-3.35489000	-0.69688800
H	0.84242700	-2.89416400	-2.37695900
H	1.31226600	-1.79440600	-1.06067200
C	-0.77583700	-0.75791400	-2.60389800
H	-0.55735500	-1.22936200	-3.57661300
H	-1.73444100	-0.22410200	-2.70031400
H	0.00938600	-0.01410500	-2.39701800
Pd	0.29106900	0.97602300	0.21272500
C	2.28086700	0.79279600	0.11396800
C	2.99801200	0.28706400	1.21801800
C	2.82227300	0.58275600	-1.17166000
C	4.13525600	-0.48340300	1.04238500
H	2.64748200	0.49715300	2.23006100
C	3.95961400	-0.18911300	-1.35502300
H	2.33538700	1.02870900	-2.04103300
C	4.62371600	-0.74501800	-0.24972700
H	4.65955500	-0.89211800	1.90872900
H	4.34575700	-0.36588700	-2.36106700
C	1.63408000	2.59969500	0.36697200
F	2.43013500	2.93193300	1.40961800
F	2.10684300	3.19957500	-0.74950900
H	-2.72464700	3.50298600	-1.42969200
H	-2.80945700	3.79609800	0.34647600
H	0.65515800	3.09368400	0.59370000
C	5.78995400	-1.54795600	-0.43405200
N	6.73591000	-2.20371700	-0.58388100

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cis-Pd-CF2H(CN)-TS-rot

C	3.0058960000	0.9784030000	-0.2676460000
C	2.7249470000	-0.4068360000	-0.2701360000
C	3.7756120000	-1.2802910000	-0.5726650000
C	5.0542680000	-0.8223340000	-0.8795890000
C	5.3032100000	0.5453030000	-0.8806160000
C	4.2870450000	1.4459760000	-0.5748200000
H	3.5922570000	-2.3541030000	-0.5683870000
H	5.8487400000	-1.5330920000	-1.1145470000
H	6.2991800000	0.9253660000	-1.1195630000
H	4.5001100000	2.5144440000	-0.5791930000
P	1.0084760000	-0.9557930000	0.1124690000
O	1.9916690000	1.8210270000	0.0497590000
C	2.2122700000	3.2134800000	0.0893480000
H	2.4810360000	3.6059090000	-0.9051150000
C	1.1596710000	-1.6382690000	1.8697040000
C	0.5535050000	-2.2799900000	-1.1635210000
C	1.1902790000	-3.6588620000	-1.0081680000
H	0.8965740000	-4.1482060000	-0.0688000000
H	0.8377260000	-4.3067080000	-1.8283460000
H	2.2867140000	-3.6484050000	-1.0655320000
C	-0.9699390000	-2.4368060000	-1.1013150000
H	-1.4840710000	-1.4751570000	-1.2277320000
H	-1.2963260000	-3.1094040000	-1.9119770000
H	-1.3134170000	-2.8753860000	-0.1549190000
C	0.9199390000	-1.6713350000	-2.5196480000
H	0.5025780000	-0.6562090000	-2.6245460000
H	2.0066460000	-1.6088500000	-2.6740430000
H	0.4976130000	-2.2929670000	-3.3262600000
C	-0.1740510000	-2.2801370000	2.2521310000
H	-1.0249180000	-1.6204380000	2.0208420000
H	-0.3341100000	-3.2417940000	1.7432630000

H -0.1868450000 -2.4816450000 3.3362600000

C 1.3923060000 -0.4035960000 2.7461390000

H 0.5665190000 0.3197030000 2.6538700000

H 1.4669790000 -0.7110290000 3.8026500000

H 2.3280040000 0.1146610000 2.4848430000

C 2.3092840000 -2.6181220000 2.0871450000

H 3.2864060000 -2.1506580000 1.8988480000

H 2.3062200000 -2.9507580000 3.1390160000

H 2.2299900000 -3.5184850000 1.4638510000

Pd -0.2657630000 0.9744370000 0.0401910000

C -2.2423570000 0.9089800000 -0.0253100000

C -2.8663580000 0.6634520000 -1.2770870000

C -2.9364610000 0.4832110000 1.1383050000

C -4.0393420000 -0.0649650000 -1.3649850000

H -2.3967690000 1.0369170000 -2.1903750000

C -4.1051900000 -0.2499510000 1.0480630000

H -2.5253530000 0.7161890000 2.1237720000

C -4.6727240000 -0.5489580000 -0.2057660000

H -4.4791120000 -0.2737080000 -2.3428490000

H -4.5973930000 -0.6047650000 1.9564290000

C -1.7055600000 2.7052390000 0.0673290000

F -1.1824750000 3.2898790000 -1.0489790000

F -1.0917710000 3.2607080000 1.1647830000

H 1.2656590000 3.6626150000 0.4103760000

H 2.9988450000 3.4710040000 0.8173020000

H -2.7524480000 3.0403280000 0.1257740000

C -5.8753600000 -1.3086040000 -0.2966960000

N -6.8542220000 -1.9294280000 -0.3703140000

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cis-Pd-CF2H(NMe2)-GS

C 3.28122400 0.72381800 -0.16406400

C 2.88997300 -0.62762700 -0.26138500

C	3.87671800	-1.56103300	-0.60071700
C	5.19262400	-1.18828700	-0.85931300
C	5.54817500	0.15272100	-0.77239100
C	4.60004700	1.10853300	-0.42153200
H	3.61317900	-2.61540100	-0.65922900
H	5.93322600	-1.94486300	-1.12524400
H	6.57404700	0.46776500	-0.97664300
H	4.89208500	2.15596800	-0.35988600
P	1.12699200	-1.05889900	0.07067100
O	2.33614900	1.63403400	0.20053500
C	2.74433600	2.93705500	0.58760300
H	1.86448700	3.41965800	1.02288900
C	1.20305300	-1.87242500	1.77478900
C	0.59937100	-2.24973900	-1.30361800
C	0.97530200	-1.52981300	-2.60244300
H	2.06319500	-1.48110400	-2.75606100
H	0.53528600	-2.06615800	-3.45926300
H	0.58351000	-0.49930400	-2.61313400
C	1.19178400	-3.65720000	-1.28206000
H	0.76915900	-4.22855300	-2.12566000
H	2.28210400	-3.68210800	-1.40497300
H	0.93019900	-4.20502300	-0.36565000
C	-0.92712200	-2.37291700	-1.24157500
H	-1.27187700	-2.91855700	-0.35353900
H	-1.42400800	-1.39481600	-1.24475100
H	-1.27204900	-2.93544700	-2.12516400
C	2.32708700	-2.88759300	1.96060000
H	2.25653800	-3.73566700	1.26573900
H	3.31965500	-2.42888800	1.84782500
H	2.27310900	-3.30065500	2.98222800
C	-0.14861100	-2.52370200	2.06836200
H	-0.28629800	-3.45871600	1.50606600

H	-0.20521300	-2.77889700	3.13980400
H	-0.99128800	-1.85599100	1.83659700
C	1.42581800	-0.70187200	2.73843000
H	1.46110700	-1.07708100	3.77496600
H	2.37908900	-0.18687600	2.54060600
H	0.61995400	0.04539800	2.66691800
Pd	0.11651600	1.11385000	0.02582500
C	-1.81492100	0.69187100	-0.00379200
C	-2.58001300	0.78719600	-1.17390100
C	-2.48568800	0.24860600	1.14226800
C	-3.91964800	0.40531800	-1.21993800
H	-2.12026800	1.15367700	-2.09712900
C	-3.82742300	-0.12944100	1.11882500
H	-1.95699000	0.18965600	2.09799600
C	-4.58329900	-0.06582000	-0.06911500
H	-4.45038500	0.48372500	-2.16929900
H	-4.28586500	-0.47437300	2.04619800
C	-0.50093800	3.03363500	-0.12392300
F	-0.33014800	3.70946000	1.06978400
F	0.32963100	3.67957700	-1.02084700
H	3.54578800	2.87345300	1.34026300
H	3.08199800	3.52078000	-0.28175900
H	-1.53336300	3.23818800	-0.45195600
N	-5.91528700	-0.43989400	-0.10189400
C	-6.50720400	-1.04740900	1.05444800
H	-6.02083600	-2.00114700	1.34329300
H	-6.47030600	-0.38007900	1.93351900
H	-7.56575800	-1.25965700	0.85537500
C	-6.60167800	-0.49883800	-1.35971700
H	-6.15430000	-1.22617800	-2.06706600
H	-7.64596800	-0.79396900	-1.19363500
H	-6.61887500	0.48303600	-1.86475800

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cis-Pd-CF2H(NMe2)-TS

C	-3.46315100	0.91304300	-0.53084600
C	-3.12841800	-0.42842400	-0.22972800
C	-4.16197600	-1.37190500	-0.23548800
C	-5.48071800	-1.02796900	-0.52239400
C	-5.78591200	0.29572700	-0.81823600
C	-4.78630200	1.26394500	-0.82403200
H	-3.93127100	-2.41262600	-0.00884400
H	-6.26064500	-1.79183200	-0.51628900
H	-6.81344400	0.58751300	-1.04836200
H	-5.04416300	2.29727800	-1.05533500
P	-1.37794700	-0.84346000	0.16538100
O	-2.46410900	1.81924500	-0.52261500
C	-2.71329400	3.15225100	-0.87593500
H	-1.74283400	3.66563400	-0.83944600
C	-0.81975100	-1.85874400	-1.33170800
C	-1.43648300	-1.86098800	1.76730300
C	-2.39211300	-1.11480000	2.70185900
H	-3.44354300	-1.21452400	2.39738500
H	-2.29498300	-1.51787200	3.72377900
H	-2.15165600	-0.03956800	2.74300500
C	-1.84928400	-3.32618300	1.65384000
H	-1.85330500	-3.77700300	2.66087700
H	-2.85870100	-3.46475200	1.24321700
H	-1.14436900	-3.91030000	1.04544500
C	-0.02813800	-1.78906500	2.36908600
H	0.73592800	-2.24554100	1.72490800
H	0.27297100	-0.74515600	2.53987400
H	-0.01611700	-2.32144100	3.33543600
C	-1.74510800	-2.99498100	-1.75647800
H	-1.87699800	-3.75861800	-0.97870500

H	-2.73683600	-2.62656900	-2.05544900
H	-1.31077900	-3.50097300	-2.63556300
C	0.58512600	-2.38915900	-1.04083700
H	0.57626700	-3.20254600	-0.29999100
H	1.02050000	-2.79942900	-1.96738700
H	1.25528400	-1.59306500	-0.68131100
C	-0.74613400	-0.83549800	-2.46956900
H	-0.37519700	-1.32723300	-3.38463100
H	-1.73506400	-0.40748800	-2.69771400
H	-0.06343400	-0.00887400	-2.21983900
Pd	-0.03099900	1.05572100	0.38077400
C	1.98860200	1.02033000	0.22886400
C	2.74591600	0.45478700	1.26355800
C	2.52383200	0.95494600	-1.06437800
C	3.93007000	-0.22653900	1.01147900
H	2.39858400	0.53530400	2.29595700
C	3.70692000	0.27431000	-1.33279300
H	2.00134000	1.44237500	-1.89082400
C	4.44026700	-0.34667300	-0.30014000
H	4.46483500	-0.66684700	1.85323300
H	4.06255900	0.23719100	-2.36251100
C	1.11306000	2.75436500	0.63315800
F	1.87972900	3.07823600	1.70324800
F	1.53270600	3.48119600	-0.43271100
H	-3.11668400	3.23455200	-1.89958600
H	-3.40425100	3.64427400	-0.16989100
H	0.09112500	3.15441100	0.88906900
N	5.61156800	-1.02846800	-0.55707900
C	6.29128600	-1.70673100	0.50885800
H	5.67406400	-2.49876600	0.97625600
H	7.20092300	-2.18163000	0.11958600
H	6.60189200	-1.01368300	1.31161000

C 6.05535800 -1.19557500 -1.91103200

H 6.24646800 -0.22757200 -2.40890400

H 6.99751400 -1.75833700 -1.92126600

H 5.32724200 -1.74992000 -2.53495500

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cis-Pd-CF2H(NMe2)-TS-rot

C 3.3551370000 0.7644180000 -0.4441530000

C 2.9331200000 -0.5862380000 -0.4101170000

C 3.8393560000 -1.5568560000 -0.8499770000

C 5.1063170000 -1.2293540000 -1.3277250000

C 5.4926500000 0.1054410000 -1.3654370000

C 4.6249850000 1.1009520000 -0.9254230000

H 3.5483340000 -2.6062990000 -0.8198060000

H 5.7843840000 -2.0153610000 -1.6659330000

H 6.4815810000 0.3843840000 -1.7371460000

H 4.9440560000 2.1424680000 -0.9572330000

P 1.2253500000 -0.9509370000 0.1843150000

O 2.4901850000 1.6951860000 0.0140320000

C 2.8187090000 3.0613750000 -0.0403770000

H 2.9852720000 3.3961440000 -1.0781310000

C 1.5364200000 -1.5962650000 1.9385360000

C 0.5167520000 -2.2903240000 -0.9595390000

C 1.0322350000 -3.7184800000 -0.7986910000

H 0.8046400000 -4.1312670000 0.1944220000

H 0.5268830000 -4.3655830000 -1.5358860000

H 2.1109560000 -3.8237850000 -0.9757320000

C -0.9993080000 -2.2929230000 -0.7243560000

H -1.4320850000 -1.2917400000 -0.8525380000

H -1.4756000000 -2.9712370000 -1.4525290000

H -1.2712640000 -2.6458390000 0.2794950000

C 0.7748080000 -1.7843100000 -2.3811760000

H 0.4460470000 -0.7377120000 -2.4910310000

H	1.8359290000	-1.8382420000	-2.6637040000
H	0.2006130000	-2.3946010000	-3.0981480000
C	0.2153630000	-2.1195380000	2.5021940000
H	-0.6022470000	-1.3976910000	2.3491540000
H	-0.0811240000	-3.0773160000	2.0499280000
H	0.3194450000	-2.2912930000	3.5869340000
C	1.9587440000	-0.3574890000	2.7344830000
H	1.1840100000	0.4251680000	2.6987830000
H	2.1270910000	-0.6353920000	3.7888720000
H	2.8950990000	0.0766250000	2.3513250000
C	2.6286840000	-2.6549750000	2.0593350000
H	3.6042220000	-2.2743920000	1.7235760000
H	2.7394990000	-2.9457670000	3.1182250000
H	2.4034680000	-3.5697160000	1.4951390000
Pd	0.0418060000	1.0443480000	0.1625280000
C	-1.9604100000	1.2092710000	0.0690560000
C	-2.5664660000	1.0359340000	-1.1885000000
C	-2.6926260000	0.7726890000	1.1909750000
C	-3.7767080000	0.3654320000	-1.3304530000
H	-2.0621410000	1.4103010000	-2.0828200000
C	-3.8973490000	0.0976310000	1.0567600000
H	-2.2906060000	0.9375550000	2.1946860000
C	-4.4763430000	-0.1324520000	-0.2120430000
H	-4.1762170000	0.2291250000	-2.3355520000
H	-4.3957850000	-0.2546660000	1.9601090000
C	-1.1784940000	2.8990990000	0.2010010000
F	-0.7663310000	3.4102280000	-0.9922440000
F	-0.3407020000	3.4221880000	1.1852800000
H	1.9560810000	3.5951820000	0.3750690000
H	3.7117000000	3.2855590000	0.5674640000
H	-2.1471190000	3.3735060000	0.4233850000
N	-5.6795210000	-0.7990780000	-0.3465880000

C -6.1548880000 -1.1380630000 -1.6571420000

H -5.4675910000 -1.8114930000 -2.2078540000

H -7.1252200000 -1.6445850000 -1.5751050000

H -6.3090920000 -0.2409180000 -2.2819250000

C -6.2798770000 -1.4157530000 0.8014750000

H -5.6450110000 -2.2038330000 1.2541910000

H -6.5062180000 -0.6789000000 1.5918950000

H -7.2316890000 -1.8793530000 0.5116920000

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cis-Pd-CFH2-GS

C 2.50554300 -1.17334300 -0.00498800

C 2.34043900 0.22260900 0.10495300

C 3.49254900 1.00056100 0.28006900

C 4.76057600 0.43368800 0.37117600

C 4.89481200 -0.94693500 0.28164600

C 3.77571700 -1.75061800 0.08867800

H 3.39975800 2.08326300 0.33898300

H 5.63627300 1.07066200 0.50953800

H 5.87986700 -1.41314200 0.35747000

H 3.89932200 -2.83038900 0.01898700

P 0.63931000 0.91491400 -0.01891500

O 1.39693700 -1.93657800 -0.22066200

C 1.57878500 -3.25724600 -0.70865400

H 0.59108900 -3.62149200 -0.99800200

C 0.66506400 1.87451300 -1.64797600

C 0.42179400 1.97784900 1.53278200

C 1.46658200 3.05527700 1.81247400

H 1.57923800 3.76840600 0.98348300

H 1.14379700 3.63693800 2.69242800

H 2.45112100 2.63525200 2.05681700

C -0.96105200 2.63209500 1.47137400

H -1.74288200 1.93712800 1.13586200

H	-1.23655800	2.98063300	2.48068500
H	-0.97176200	3.51131900	0.81332400
C	0.44544900	0.95253300	2.67220600
H	-0.33027100	0.18203300	2.53883200
H	1.41886500	0.44255700	2.74480500
H	0.26290100	1.46503600	3.63145700
C	-0.68329900	2.57468000	-1.82647900
H	-1.53092700	1.92385700	-1.56723000
H	-0.75588700	3.48967600	-1.22333400
H	-0.79842300	2.87307800	-2.88191300
C	0.80257300	0.77474500	-2.70702200
H	-0.02103500	0.04638100	-2.64204200
H	0.78375800	1.22781800	-3.71223700
H	1.75209500	0.22559000	-2.60808400
C	1.79729600	2.88098700	-1.82422000
H	2.78660400	2.40278800	-1.81160200
H	1.68974900	3.37295300	-2.80583100
H	1.78042100	3.67586100	-1.06501200
Pd	-0.71694100	-1.05229200	0.00675400
C	-2.53955800	-0.29612100	-0.00343400
C	-3.25617300	-0.04505600	1.17802000
C	-3.17473800	0.00107400	-1.22046600
C	-4.53208400	0.51974900	1.14667700
H	-2.81254800	-0.29096300	2.14704000
C	-4.45259400	0.56279700	-1.25365700
H	-2.66676400	-0.20775700	-2.16629600
C	-5.13570800	0.83308400	-0.06969700
H	-5.05996300	0.71287600	2.08510900
H	-4.91780700	0.78867800	-2.21761100
H	-6.13493000	1.27488300	-0.09505100
C	-1.76096500	-2.79217100	0.18227200
F	-0.89137200	-3.82134000	0.57637000

H 2.25811900 -3.24894800 -1.57537100

H 1.97209900 -3.91935000 0.07754500

H -2.55182200 -2.73529300 0.94724200

H -2.22307900 -3.10243100 -0.77339000

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trans-Pd-CFH2-GS

C 0.92424000 2.22624000 -0.25835900

C 1.91800600 1.23025500 -0.15387700

C 3.25681100 1.63979400 -0.19907700

C 3.61873600 2.97443500 -0.35313200

C 2.62182100 3.93672100 -0.46498200

C 1.28081800 3.56975200 -0.41757400

H 4.04417300 0.89294700 -0.10905800

H 4.67266900 3.25686600 -0.38462200

H 2.88166800 4.99078300 -0.58682200

H 0.51624000 4.34072800 -0.49737900

P 1.40264200 -0.51883900 0.09626400

O -0.38120300 1.84257400 -0.19177700

C -1.39076800 2.80680600 -0.43990000

H -2.34204100 2.26433000 -0.43630800

C 2.22189800 -1.01792100 1.73344800

C 2.08137800 -1.44756000 -1.40463500

C 1.90418500 -2.94794500 -1.16292800

H 0.86415800 -3.20103800 -0.91561000

H 2.15630500 -3.49069900 -2.08922500

H 2.57045500 -3.32987000 -0.37541500

C 1.15898000 -1.01661000 -2.55099200

H 1.48499700 -1.50393800 -3.48534100

H 0.11664500 -1.30941500 -2.35511500

H 1.19332600 0.07217300 -2.71620000

C 3.52719600 -1.14868700 -1.79132400

H 3.66197800 -0.10437300 -2.10508800

H	4.24598300	-1.37137000	-0.99092400
H	3.79967800	-1.78011800	-2.65377100
C	3.71395000	-1.33169400	1.67452900
H	4.06984900	-1.58016100	2.68875700
H	3.93470300	-2.19896100	1.03605500
H	4.31696900	-0.48127800	1.32848200
C	1.46714100	-2.24132400	2.26209500
H	1.89409700	-2.53936400	3.23426100
H	0.40267300	-2.01164300	2.41510200
H	1.53896200	-3.11017000	1.59286600
C	1.96742400	0.14514000	2.69649300
H	2.23036300	-0.16604200	3.72110200
H	2.56539500	1.03366500	2.44983100
H	0.90445500	0.43797100	2.70024800
Pd	-0.95713700	-0.36679700	0.14593900
C	-2.94395500	-0.03622500	0.16597600
C	-3.76908700	-0.37109100	-0.92060800
C	-3.53928400	0.65239900	1.23778900
C	-5.11522200	-0.00297400	-0.95435600
H	-3.35103500	-0.94040600	-1.75685500
C	-4.88815500	1.01477600	1.21413000
H	-2.93819800	0.92489900	2.11219900
C	-5.68058100	0.69364600	0.11313900
H	-5.73044600	-0.26719400	-1.81983100
H	-5.32353000	1.55090800	2.06289400
H	-6.73581600	0.97852600	0.09049400
C	-1.46080200	-2.30279800	0.17356600
F	-1.44713800	-2.78455900	-1.13627900
H	-1.40654500	3.57180300	0.35247100
H	-1.23902600	3.28177100	-1.42176500
H	-0.72164500	-2.88919400	0.74148100
H	-2.46331000	-2.49728400	0.58016400

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cis-Pd-CFH2-TS

C	-2.54231700	1.44009900	0.09714900
C	-2.47947300	0.02670600	0.10060100
C	-3.68506200	-0.67587600	0.20568000
C	-4.91461700	-0.02926600	0.30574100
C	-4.95124800	1.36065900	0.30617600
C	-3.77409200	2.09585300	0.20272600
H	-3.66538000	-1.76550000	0.21037300
H	-5.83511500	-0.61076400	0.38536700
H	-5.90501900	1.88775200	0.38609800
H	-3.82061200	3.18477600	0.19871600
P	-0.83306500	-0.78843500	-0.04383700
O	-1.37736200	2.11243400	-0.01284100
C	-1.34395300	3.51114400	0.10312500
H	-0.28242200	3.79153700	0.08293600
C	-1.01794600	-2.08986700	-1.41332200
C	-0.56884000	-1.55305300	1.66766500
C	-1.72226200	-2.38664000	2.21813500
H	-1.96268900	-3.25772500	1.59456200
H	-1.44345200	-2.76974200	3.21458100
H	-2.63510700	-1.78800000	2.34850200
C	0.71617900	-2.38092800	1.61654100
H	1.54994000	-1.81453400	1.17351500
H	1.01105100	-2.66257900	2.64123900
H	0.58577500	-3.31484400	1.04981200
C	-0.35439000	-0.34671600	2.58746100
H	0.49113400	0.27088300	2.24768000
H	-1.24997300	0.29260200	2.63666300
H	-0.13796500	-0.69744200	3.61061800
C	0.40339600	-2.41432800	-1.88635700
H	0.91974500	-1.50486500	-2.22564200

H 1.02308300 -2.86584600 -1.09938400

H 0.35560800 -3.12709300 -2.72718500

C -1.75347100 -1.38925600 -2.55838500

H -1.29590900 -0.41267600 -2.78762700

H -1.69146600 -2.00944100 -3.46817000

H -2.81651200 -1.22047600 -2.33561000

C -1.72793500 -3.39122000 -1.05068400

H -2.76150600 -3.24277000 -0.70955000

H -1.77925300 -4.03410300 -1.94590400

H -1.18672400 -3.95879000 -0.28052900

Pd 0.81692900 0.79855700 -0.49453100

C 2.77868200 0.45589000 -0.20350500

C 3.24721900 0.56009500 1.11858900

C 3.46170400 -0.41628100 -1.07591600

C 4.29249500 -0.24348800 1.57353100

H 2.78180900 1.27937700 1.79647400

C 4.50584100 -1.21195400 -0.61656000

H 3.15731300 -0.48301400 -2.12397800

C 4.92327700 -1.14083500 0.71480400

H 4.61821600 -0.16088000 2.61434400

H 5.00069100 -1.89979800 -1.30816200

H 5.74302800 -1.76840700 1.07207200

C 2.28468300 2.22762600 -0.89552400

F 2.38370000 3.12475300 0.14310500

H -1.86668400 4.00531100 -0.73367500

H -1.78098500 3.84811300 1.05821200

H 3.21838700 2.25026600 -1.47075800

H 1.47663500 2.57916700 -1.59083000

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trans-Pd-CFH2-TS

C -1.05039900 2.24792800 0.11441300

C -1.99553100 1.19849200 0.02193600

C	-3.34895500	1.54733800	-0.04639500
C	-3.77575100	2.87298200	-0.03455200
C	-2.82908500	3.88793900	0.05099100
C	-1.47358600	3.58247800	0.12545100
H	-4.09748000	0.75817700	-0.11505900
H	-4.84047900	3.10716300	-0.09217000
H	-3.14188300	4.93487800	0.06112700
H	-0.74444600	4.38957200	0.19220400
P	-1.38516800	-0.53921100	-0.03370400
O	0.25032400	1.90565200	0.19548500
C	1.24978900	2.89222600	0.26522200
H	2.20526400	2.35609400	0.32956900
C	-2.29063200	-1.35162500	-1.49420100
C	-1.92065500	-1.23876300	1.64322500
C	-1.58891000	-2.73117600	1.65890000
H	-0.54720100	-2.91358900	1.35106300
H	-1.71074500	-3.12515400	2.68188200
H	-2.25509100	-3.31527800	1.00642900
C	-1.02005500	-0.51849100	2.65238900
H	-1.22361400	-0.89994200	3.66727300
H	0.04633600	-0.68202700	2.42746800
H	-1.20386000	0.56730000	2.66131500
C	-3.37675100	-1.01028400	2.03748700
H	-3.61634000	0.05991200	2.11411300
H	-4.08978300	-1.47773600	1.34580700
H	-3.55473500	-1.45219500	3.03276600
C	-3.73816200	-1.78294700	-1.27420100
H	-4.13254200	-2.21394400	-2.21021600
H	-3.82764900	-2.56046400	-0.50215000
H	-4.40384100	-0.95174500	-1.00521600
C	-1.46180700	-2.58370300	-1.87567500
H	-1.92141800	-3.08099100	-2.74657500

H -0.43478700 -2.29572100 -2.14483400

H -1.40135300 -3.32336900 -1.06460100

C -2.20579400 -0.34962600 -2.64830400

H -2.49165100 -0.84786200 -3.58979700

H -2.87104500 0.51350800 -2.50658300

H -1.17834600 0.03182700 -2.76946800

Pd 0.96161000 -0.52788500 -0.20716400

C 2.93415700 -0.31815100 -0.22047000

C 3.55318800 -0.05882300 1.01452800

C 3.45280400 0.30396700 -1.37435000

C 4.61575400 0.84103500 1.10034500

H 3.19233900 -0.57002700 1.91013600

C 4.51027800 1.20509600 -1.28016500

H 3.01549900 0.08138900 -2.35226800

C 5.09519600 1.48147400 -0.04211100

H 5.07406300 1.04374500 2.07242600

H 4.88505100 1.69553800 -2.18296000

H 5.92977900 2.18319400 0.02811600

C 2.32052200 -2.18158100 -0.36068300

F 2.54262900 -2.71730600 0.88411000

H 1.25395400 3.52759300 -0.63633300

H 1.12951200 3.52360700 1.16162800

H 1.47644300 -2.72465100 -0.82712400

H 3.20356400 -2.37208500 -0.98643900

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cis-Pd-CFH2(CN)-GS

C 2.91041400 0.94692800 -0.11991000

C 2.60264900 -0.41791800 -0.28106400

C 3.64180300 -1.27267500 -0.66789300

C 4.93135800 -0.80579600 -0.90471400

C 5.20641800 0.54802100 -0.74557800

C 4.20228400 1.42565000 -0.34931800

H	3.44373800	-2.33717500	-0.78132200
H	5.71648600	-1.50059400	-1.20861000
H	6.21175400	0.93341200	-0.92979400
H	4.42701700	2.48540600	-0.23314600
P	0.87311600	-0.95567500	0.05732800
O	1.90640600	1.78071300	0.27804600
C	2.25242300	3.00953800	0.89866400
H	1.33998500	3.39440600	1.36142800
C	1.00719800	-1.72963500	1.77752800
C	0.42517800	-2.21649900	-1.28268100
C	1.05721100	-3.60341500	-1.17689600
H	0.74365500	-4.13385700	-0.26688500
H	0.71678600	-4.21056400	-2.03231200
H	2.15396900	-3.59978800	-1.21272200
C	-1.09756800	-2.38500100	-1.25407200
H	-1.61968000	-1.43123700	-1.39379400
H	-1.39635500	-3.05932300	-2.07371000
H	-1.46111700	-2.82849500	-0.31763800
C	0.80954600	-1.55014200	-2.60722500
H	0.40666600	-0.52587900	-2.67096300
H	1.89757100	-1.49458200	-2.75304300
H	0.38533000	-2.12922400	-3.44382500
C	-0.30953300	-2.43532600	2.10212300
H	-1.18260600	-1.79920700	1.89378500
H	-0.42698000	-3.37412200	1.54193800
H	-0.33105500	-2.69383300	3.17385200
C	1.18834400	-0.53755300	2.72294000
H	0.35172400	0.17475600	2.64734000
H	1.24321000	-0.89777600	3.76370400
H	2.12024400	0.01091900	2.51515700
C	2.18211100	-2.68622700	1.95938800
H	3.14793000	-2.18434800	1.80450400

H 2.17684500 -3.07112600 2.99318300

H 2.13342500 -3.55595500 1.29097000

Pd -0.26860700 1.15809900 -0.00103400

C -2.16786900 0.65415300 -0.04217100

C -2.92252000 0.66021300 -1.23008000

C -2.82747200 0.26737600 1.13846700

C -4.25148200 0.25479100 -1.25254300

H -2.45798600 0.98100400 -2.16608300

C -4.15813400 -0.13501100 1.13273900

H -2.29264300 0.28023800 2.09151900

C -4.88332600 -0.15526700 -0.06841400

H -4.81250700 0.25457300 -2.18978600

H -4.64709400 -0.43678000 2.06177500

C -1.03135200 3.03677600 -0.15519700

F 0.00411300 3.90597600 -0.51029100

H 3.02309200 2.83670500 1.66608600

H 2.60333000 3.74527300 0.16095600

H -1.80716200 3.12316500 -0.93300400

H -1.45336300 3.39524800 0.80211300

C -6.24878000 -0.57785500 -0.08348600

N -7.35666700 -0.92269900 -0.09563000

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cis-Pd-CFH2(CN)-TS

C 3.03246000 1.09492900 -0.11702200

C 2.76382200 -0.29242400 -0.09383400

C 3.85469000 -1.16648400 -0.16389500

C 5.16622100 -0.70746400 -0.25300800

C 5.40544100 0.66201200 -0.27768600

C 4.34697000 1.56317000 -0.21063000

H 3.67602600 -2.24138400 -0.14999400

H 5.99324800 -1.41804700 -0.30483900

H 6.42703700 1.04273300 -0.34823000

H	4.55295800	2.63320900	-0.22483000
P	1.01490300	-0.85266300	0.03577100
O	1.97430600	1.93658800	-0.04409800
C	2.15313500	3.32015800	-0.22675800
H	1.14657700	3.75706700	-0.26063700
C	0.97654700	-2.13340800	1.43256300
C	0.65595600	-1.59455400	-1.66623800
C	1.68332100	-2.59494200	-2.18767700
H	1.78707600	-3.48071600	-1.54759900
H	1.36397000	-2.95051200	-3.18191600
H	2.67458100	-2.13672900	-2.31373100
C	-0.73523300	-2.22777200	-1.61908500
H	-1.48402600	-1.53857900	-1.19898400
H	-1.05518300	-2.48471500	-2.64261600
H	-0.74908500	-3.15900800	-1.03375400
C	0.62868000	-0.38514900	-2.60644900
H	-0.12365900	0.35400500	-2.29006300
H	1.60656300	0.11960700	-2.65106500
H	0.37865200	-0.71774500	-3.62777200
C	-0.48484200	-2.23488300	1.88187200
H	-0.86626500	-1.25679000	2.20540500
H	-1.15265900	-2.59982700	1.08952400
H	-0.55803300	-2.93602600	2.73016700
C	1.78844700	-1.52505300	2.57888300
H	1.47741400	-0.48702800	2.78232800
H	1.61917500	-2.11038700	3.49781700
H	2.86846800	-1.52075000	2.37503400
C	1.49312000	-3.53189900	1.10502900
H	2.54262300	-3.54401300	0.78128200
H	1.43458100	-4.15644700	2.01239100
H	0.88661000	-4.02975300	0.33532400
Pd	-0.30971200	1.02907900	0.41976400

C -2.29856300 0.95485500 0.33272500

C -2.87999600 0.95340600 -0.95543800

C -3.03436300 0.34086700 1.37580600

C -4.07012600 0.28864600 -1.20986400

H -2.37850000 1.48142800 -1.76922000

C -4.22320900 -0.32026800 1.12688400

H -2.64979400 0.37301700 2.39850200

C -4.75538900 -0.36999500 -0.17599300

H -4.48222900 0.27528400 -2.22138100

H -4.75597500 -0.81333800 1.94306500

C -1.55219200 2.70380800 0.73453900

F -1.56227600 3.46838700 -0.40753700

H 2.71922200 3.77225000 0.60486600

H 2.66261600 3.53580700 -1.18028300

H -2.44991400 2.93533100 1.32098900

H -0.68291100 3.01233400 1.36728900

C -5.97560700 -1.06134400 -0.43615600

N -6.96795200 -1.62620400 -0.64764700

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cis-Pd-CFH2(NMe)2-GS

C 3.26768000 0.83920000 -0.13613800

C 2.88258200 -0.50625000 -0.30200400

C 3.87023400 -1.41433400 -0.70130200

C 5.18268900 -1.02039200 -0.94632000

C 5.53492500 0.31438500 -0.78068100

C 4.58435400 1.24410000 -0.37137400

H 3.61197700 -2.46547800 -0.81629600

H 5.92491200 -1.75695100 -1.25990400

H 6.55928000 0.64397200 -0.96906100

H 4.87040700 2.28816300 -0.24897700

P 1.12667100 -0.94889700 0.05086300

O 2.31666500 1.72549900 0.27167800

C	2.73540500	2.94136200	0.86906000
H	1.84397500	3.39399400	1.30990200
C	1.24691900	-1.75289000	1.75992800
C	0.59858200	-2.17498400	-1.29391100
C	1.17920500	-3.58674200	-1.23246800
H	0.88883900	-4.11488600	-0.31339200
H	0.77257300	-4.16990200	-2.07593100
H	2.27211400	-3.62723300	-1.32399200
C	-0.92858500	-2.28874600	-1.22907300
H	-1.42085600	-1.31069600	-1.29228400
H	-1.27405000	-2.90252300	-2.07779200
H	-1.27956200	-2.77614300	-0.31002200
C	0.97464700	-1.49723300	-2.61501500
H	0.59680600	-0.46223000	-2.65158400
H	2.06130600	-1.46745800	-2.78022200
H	0.51954500	-2.05086400	-3.45286000
C	-0.09517200	-2.40698800	2.08914000
H	-0.94372400	-1.73748100	1.88415100
H	-0.25000100	-3.33941300	1.52713200
H	-0.12176000	-2.66690400	3.16070700
C	1.48494800	-0.58011400	2.71675800
H	0.67684200	0.16553300	2.65421700
H	1.53561200	-0.95325500	3.75349000
H	2.43566500	-0.06641800	2.50438000
C	2.38152100	-2.76030700	1.92174100
H	3.36708700	-2.29676700	1.77162300
H	2.36322400	-3.16319500	2.94880300
H	2.29501900	-3.61527600	1.23782600
Pd	0.09232500	1.21746800	0.01809700
C	-1.83253300	0.77250100	-0.02065700
C	-2.60466000	0.83121200	-1.18855700
C	-2.49755200	0.35250600	1.13861100

C -3.94153000 0.43753400 -1.21903600

H -2.15473100 1.18420100 -2.12128600

C -3.83564100 -0.03873100 1.13043200

H -1.96677800 0.32815300 2.09492700

C -4.59104900 -0.03050000 -0.05938400

H -4.48011700 0.50148200 -2.16505000

H -4.29050200 -0.35274500 2.07048500

C -0.62513100 3.11104300 -0.11744000

F 0.43652800 3.99873200 -0.35395000

H 3.49024300 2.73829900 1.64528700

H 3.13756800 3.63785600 0.11848700

H -1.33112100 3.22684500 -0.95597500

H -1.12726000 3.44274200 0.80944100

N -5.90982500 -0.45309600 -0.08522700

C -6.57847800 -0.75499300 1.14690400

H -6.06434700 -1.55772700 1.70363900

H -6.66235000 0.11732500 1.82680000

H -7.59501200 -1.11127100 0.93396000

C -6.68716900 -0.26666200 -1.27582500

H -6.23659300 -0.78247000 -2.14156100

H -7.68758700 -0.69527300 -1.13063200

H -6.81410600 0.79911600 -1.55543500

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cis-Pd-CFH2(NMe)2-TS

C -3.35920500 0.98443100 0.45680900

C -3.02546500 -0.38189700 0.29768500

C -4.04760900 -1.32247300 0.46445300

C -5.35450500 -0.95233000 0.77375100

C -5.65832900 0.39560100 0.92859900

C -4.66940800 1.36245900 0.77241800

H -3.81749600 -2.38166300 0.35016700

H -6.12630300 -1.71487400 0.89519700

H	-6.67651100	0.70735500	1.17383700
H	-4.92416000	2.41533600	0.89358100
P	-1.28672800	-0.82447600	-0.12472100
O	-2.36959400	1.88399800	0.29265200
C	-2.59257300	3.24929300	0.52278300
H	-1.61861900	3.73967400	0.39161700
C	-1.39553600	-2.07303900	-1.55130400
C	-0.64036500	-1.60175100	1.47721400
C	-1.51997700	-2.68212600	2.09938600
H	-1.65787900	-3.55554400	1.44871300
H	-1.04344400	-3.04251600	3.02710500
H	-2.51083500	-2.29444700	2.37671400
C	0.76491200	-2.14061900	1.20480000
H	1.39939700	-1.39057000	0.70766200
H	1.24724100	-2.40572500	2.16059700
H	0.74746500	-3.05138100	0.58774500
C	-0.54584500	-0.42551200	2.45413600
H	0.10503700	0.36974900	2.06016900
H	-1.53526700	0.01016100	2.66474900
H	-0.12436500	-0.77580600	3.41148800
C	-0.01863200	-2.06101900	-2.22616000
H	0.24241700	-1.04663400	-2.56218800
H	0.78622400	-2.39954800	-1.55907500
H	-0.03447200	-2.73088700	-3.10291500
C	-2.41331500	-1.49556200	-2.53816400
H	-2.20702700	-0.43276400	-2.74660800
H	-2.34953600	-2.04251100	-3.49376900
H	-3.44692000	-1.57308600	-2.17246600
C	-1.75970600	-3.51417000	-1.20351200
H	-2.74029800	-3.61234600	-0.71810200
H	-1.80560700	-4.10752300	-2.13270200
H	-1.00632500	-3.98865900	-0.55886000

Pd -0.02127800 1.06329700 -0.66148400

C 1.99313300 1.11029400 -0.51547000

C 2.54803900 1.30153000 0.75746500

C 2.76155700 0.37824100 -1.43624100

C 3.75611000 0.71646700 1.12867600

H 2.01687500 1.91786700 1.48678100

C 3.97045800 -0.20700000 -1.07980700

H 2.39754100 0.23600600 -2.45748500

C 4.50269300 -0.05971900 0.22019100

H 4.11780100 0.87720400 2.14450500

H 4.50435700 -0.78983400 -1.83083100

C 1.06787600 2.76359000 -1.12752000

F 1.12354500 3.64698500 -0.07290600

H -3.31309600 3.67581800 -0.19636600

H -2.94919600 3.43489100 1.55035600

H 1.90293900 2.97186300 -1.80770200

H 0.12336700 2.96901300 -1.70419400

N 5.70593500 -0.64096400 0.57876900

C 6.12839200 -0.59659000 1.94877200

H 7.10570900 -1.08688700 2.04688900

H 6.24870800 0.44081300 2.30690300

H 5.42438700 -1.10493300 2.63844700

C 6.35141900 -1.54716100 -0.32662800

H 5.74068400 -2.44364100 -0.55685200

H 6.59840100 -1.06110700 -1.28665300

H 7.29710500 -1.89112300 0.11218500

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cis-Pd-CH3-GS

C 2.52900400 1.20488100 -0.00004300

C 2.29789500 -0.18686400 -0.00003300

C 3.41764200 -1.02891700 0.00000200

C 4.71874900 -0.53397500 0.00005000

C	4.91976900	0.84071400	0.00007300
C	3.83326600	1.71017800	0.00002400
H	3.27053700	-2.10698400	-0.00000600
H	5.56656700	-1.22164900	0.00007500
H	5.93159000	1.25255400	0.00012700
H	4.01493000	2.78353900	0.00004400
P	0.56140900	-0.80474900	-0.00002500
O	1.44718900	2.03543500	-0.00012100
C	1.66573600	3.43271500	-0.00044700
H	0.67740900	3.90141500	-0.00069400
C	0.42612100	-1.81463200	1.59585200
C	0.42607700	-1.81471700	-1.59582900
C	0.54770500	-0.75594100	-2.69769200
H	-0.22393900	0.02322100	-2.59558200
H	1.53213500	-0.26205300	-2.68491400
H	0.42751800	-1.23571800	-3.68341700
C	1.47483800	-2.89777000	-1.83064200
H	1.23129100	-3.42941200	-2.76613600
H	2.48518300	-2.48471000	-1.95368300
H	1.49500000	-3.65241100	-1.03140600
C	-0.96958000	-2.44032300	-1.65246800
H	-1.04467100	-3.33736600	-1.02323700
H	-1.75866400	-1.73770700	-1.34922800
H	-1.18061800	-2.75388500	-2.68855100
C	-0.96953300	-2.44023200	1.65259500
H	-1.75863200	-1.73763100	1.34936000
H	-1.04467200	-3.33729800	1.02340200
H	-1.18050800	-2.75375200	2.68870400
C	0.54779900	-0.75580400	2.69766000
H	-0.22383700	0.02336500	2.59553000
H	0.42762500	-1.23553500	3.68341000
H	1.53223800	-0.26193700	2.68483900

C	1.47488500	-2.89768200	1.83065400
H	2.48524400	-2.48463200	1.95360100
H	1.23140200	-3.42927400	2.76619500
H	1.49497700	-3.65236700	1.03145800
Pd	-0.69625100	1.20418500	0.00006100
C	-2.54379400	0.53768500	0.00003000
C	-3.22789600	0.28559800	-1.20024000
C	-3.22800300	0.28552500	1.20021800
C	-4.51981500	-0.24300800	-1.20081300
H	-2.74702400	0.50586400	-2.15728600
C	-4.51992100	-0.24308700	1.20064100
H	-2.74721800	0.50574300	2.15732000
C	-5.17137100	-0.51883900	-0.00012300
H	-5.02252300	-0.43719400	-2.15292100
H	-5.02271300	-0.43733700	2.15269200
H	-6.18264900	-0.93320100	-0.00018000
C	-1.60232400	3.04230400	0.00032900
H	2.21579700	3.74437100	0.90166300
H	2.21603900	3.74390100	-0.90257100
H	-1.26574000	3.58592100	-0.90316700
H	-1.26514700	3.58591500	0.90360800
H	-2.70153500	3.05463200	0.00068700

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trans-Pd-CH3-GS

C	-0.77442100	2.17948900	0.03106900
C	-1.81364100	1.22526800	0.00359700
C	-3.13031400	1.69914300	-0.05295400
C	-3.42893800	3.05816100	-0.07469600
C	-2.38867200	3.97946900	-0.03788200
C	-1.06718700	3.54771500	0.01422200
H	-3.95120100	0.98416100	-0.08378800
H	-4.46755300	3.39103800	-0.12015400

H	-2.59859900	5.05147800	-0.05286000
H	-0.26748100	4.28621400	0.03570400
P	-1.37607700	-0.56376100	-0.00267100
O	0.50860600	1.72778000	0.06929600
C	1.56652200	2.66765700	0.14443800
H	1.46538800	3.29578000	1.04356300
C	-2.21455000	-1.26196300	-1.55392400
C	-2.10779400	-1.22277800	1.61355900
C	-1.96875900	-2.74555300	1.61274900
H	-0.94312300	-3.06177000	1.37316200
H	-2.21070200	-3.13343000	2.61635000
H	-2.65909600	-3.22843900	0.90526200
C	-1.19775100	-0.63638000	2.69822300
H	-1.23831100	0.46440800	2.71243200
H	-1.52581200	-0.99424500	3.68865200
H	-0.14819900	-0.93494700	2.54836500
C	-3.55079800	-0.83127200	1.92011300
H	-4.26208100	-1.16492800	1.15268300
H	-3.85381200	-1.30540700	2.86907200
H	-3.66273300	0.25340300	2.05484300
C	-1.52388000	-2.58986700	-1.87960500
H	-0.44102500	-2.45509100	-2.01028900
H	-1.67878400	-3.35141500	-1.10249600
H	-1.93842300	-2.99134800	-2.81953300
C	-1.88786900	-0.27093900	-2.67470900
H	-2.43281800	0.67780700	-2.56913500
H	-0.80930800	-0.04456000	-2.70623400
H	-2.16428100	-0.71448000	-3.64562600
C	-3.72142300	-1.48858300	-1.47518200
H	-3.99162600	-2.23904700	-0.71854900
H	-4.28611100	-0.56875000	-1.27147200
H	-4.07824300	-1.87028800	-2.44682700

Pd 0.98014000 -0.53052900 -0.02788100

C 2.97395600 -0.28017100 -0.03481500

C 3.66451500 -0.03756200 -1.23495800

C 3.71340900 -0.19388700 1.15732100

C 5.01807500 0.30555500 -1.24389600

H 3.13437400 -0.11319200 -2.19000400

C 5.06698600 0.14988600 1.15590200

H 3.22244500 -0.39490600 2.11521200

C 5.72517400 0.40493300 -0.04636200

H 5.52594400 0.49412500 -2.19466600

H 5.61323200 0.21599900 2.10178400

H 6.78504000 0.67298400 -0.05055200

C 1.47049800 -2.48881500 -0.02060300

H 2.49157000 2.08460300 0.20752700

H 1.59384100 3.29967900 -0.75734700

H 0.57577300 -3.12677900 -0.04622000

H 2.04766700 -2.72104000 0.88886900

H 2.10110100 -2.73614900 -0.88913600

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cis-Pd-CH3-TS

C 2.62958800 -1.29147700 0.07967600

C 2.39895700 0.10359700 0.07187700

C 3.51669500 0.94444100 0.12484900

C 4.81710800 0.45031800 0.19005800

C 5.01848800 -0.92496500 0.20630700

C 3.93377300 -1.79496600 0.15120300

H 3.36895800 2.02360300 0.11449100

H 5.66391900 1.13822700 0.22945300

H 6.02982800 -1.33506500 0.25995700

H 4.11150500 -2.86999400 0.15920700

P 0.66388400 0.71818400 -0.03952700

O 1.55131000 -2.10376500 0.01170700

C	1.71562300	-3.49503100	0.07499800
H	0.70613700	-3.92594500	0.04030300
C	0.65994700	1.90761100	-1.52097600
C	0.39470800	1.60816900	1.61109000
C	0.32522200	0.47531400	2.64007800
H	-0.47906600	-0.23612000	2.39721700
H	1.27233700	-0.08479400	2.69401600
H	0.12807900	0.89603700	3.64065600
C	1.47734200	2.59161400	2.04743400
H	1.17815300	3.04820600	3.00635700
H	2.44167000	2.09259100	2.21802100
H	1.62986500	3.41317000	1.33500500
C	-0.96277800	2.30975800	1.54327000
H	-0.93585000	3.20375000	0.90274700
H	-1.75327900	1.63759200	1.17576200
H	-1.25212800	2.64460200	2.55361000
C	-0.80356800	2.07115600	-1.94210400
H	-1.25659600	1.09821200	-2.17649300
H	-1.42381700	2.53832000	-1.16504900
H	-0.85602600	2.70843700	-2.84128900
C	1.39973200	1.17244100	-2.64148100
H	1.01611800	0.14618100	-2.76510300
H	1.24419700	1.70482400	-3.59473000
H	2.48244100	1.11110100	-2.46082700
C	1.27337800	3.28847300	-1.30759600
H	2.33224600	3.25263100	-1.01750800
H	1.22372900	3.85351300	-2.25407600
H	0.72567900	3.87533700	-0.55664900
Pd	-0.80739700	-1.07584800	-0.26304300
C	-2.78695500	-0.82027100	-0.09363800
C	-3.30639700	-0.65709200	1.20749800
C	-3.50185500	-0.21408000	-1.14980300

C -4.42860400 0.13518700 1.44646900

H -2.81346900 -1.15023700 2.04945500

C -4.62001100 0.57554800 -0.90612600

H -3.16519200 -0.36219000 -2.17936900

C -5.09021600 0.76621900 0.39532300

H -4.78839700 0.25746500 2.47220700

H -5.13486700 1.04863400 -1.74738400

H -5.97006100 1.38590400 0.58314100

C -2.18344100 -2.66003700 -0.42911500

H 2.29581100 -3.87906600 -0.78125600

H 2.20079900 -3.80480800 1.01599500

H -1.30104500 -3.13982400 -0.92247700

H -3.02784900 -2.82776300 -1.10650500

H -2.38273700 -3.16774200 0.52460000

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trans-Pd-CH3-TS

C -0.73243000 2.21337400 0.03928300

C -1.77120400 1.26319800 -0.10456600

C -3.05658400 1.74381200 -0.37723900

C -3.32597900 3.10203800 -0.52657100

C -2.28641000 4.01648300 -0.39783000

C -0.99572200 3.57965200 -0.11583100

H -3.87709900 1.03443300 -0.48138100

H -4.34150600 3.43916500 -0.74312800

H -2.47479800 5.08654700 -0.51403500

H -0.19252200 4.30892500 -0.01370400

P -1.35470200 -0.52667400 0.04162100

O 0.49606400 1.74686200 0.33876500

C 1.59649900 2.62128400 0.39907200

H 1.46868300 3.37167600 1.19743700

C -2.26403200 -1.39760100 -1.38325800

C -2.06796000 -0.97810300 1.73810900

C	-1.94563900	-2.48987200	1.92472000
H	-0.92657700	-2.84008100	1.69749500
H	-2.16656400	-2.75265500	2.97297000
H	-2.65350200	-3.04873400	1.29489000
C	-1.13800800	-0.27729500	2.73386500
H	-1.17666100	0.81793100	2.62799500
H	-1.44535400	-0.52409900	3.76426500
H	-0.09153500	-0.59355100	2.59631400
C	-3.50046300	-0.52193700	1.99918500
H	-4.22821500	-0.97363100	1.31209300
H	-3.79441300	-0.81644700	3.02125400
H	-3.59816300	0.57144400	1.93763800
C	-1.57097500	-2.75432400	-1.55785200
H	-0.49285500	-2.62802100	-1.73401000
H	-1.69133200	-3.40697000	-0.68159300
H	-2.00795200	-3.27911100	-2.42432300
C	-1.97973700	-0.55891900	-2.63185900
H	-2.53225800	0.39101200	-2.63776300
H	-0.90525000	-0.32586700	-2.71598100
H	-2.27178700	-1.12723500	-3.53077400
C	-3.76463000	-1.63489500	-1.23286900
H	-3.99822300	-2.29616500	-0.38624300
H	-4.34582500	-0.71038300	-1.11682000
H	-4.14288000	-2.13363500	-2.14150900
Pd	0.98707900	-0.74199000	-0.05582200
C	2.96032900	-0.66088600	-0.13805900
C	3.51023200	-0.09392500	-1.30375600
C	3.62684100	-0.43036900	1.08435400
C	4.64837000	0.71026500	-1.24171000
H	3.03013800	-0.27685600	-2.26890300
C	4.76238100	0.37392000	1.13993900
H	3.24261600	-0.88773000	2.00051200

C 5.27916100 0.95227800 -0.02204500

H 5.04560900 1.15401700 -2.15911200

H 5.25152800 0.55141300 2.10202300

H 6.17330700 1.57856800 0.02351000

C 2.19863000 -2.47585900 -0.41833100

H 2.47099500 1.99882100 0.62683400

H 1.76067100 3.13034000 -0.56511600

H 1.40897000 -3.08897700 0.05345400

H 3.15318500 -2.83754700 -0.01699000

H 2.19993300 -2.64373000 -1.50441800

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cis-Pd-CH3(CN)-GS

C -2.95864900 -1.04544700 -0.00011000

C -2.62959600 0.32588500 -0.00000500

C -3.68579100 1.24668300 0.00028500

C -5.01846000 0.84543300 0.00044600

C -5.31665100 -0.51154100 0.00033100

C -4.29520100 -1.45659200 0.00005900

H -3.46217700 2.31162000 0.00039900

H -5.81526800 1.59150100 0.00066900

H -6.35515900 -0.85025700 0.00046800

H -4.55378200 -2.51395300 -0.00000800

P -0.85622000 0.81934400 -0.00017000

O -1.93753900 -1.95235000 -0.00037500

C -2.26023700 -3.33084300 -0.00067000

H -1.31079400 -3.87341600 -0.00099300

C -0.64413600 1.81263500 1.59692400

C -0.64435100 1.81254500 -1.59735500

C -0.85253700 0.76688500 -2.69876600

H -0.14455200 -0.07116500 -2.60114800

H -1.87267300 0.35214400 -2.68319900

H -0.69827600 1.23611800 -3.68462100

C	-1.60654500	2.97421600	-1.82756300
H	-1.32674100	3.48482800	-2.76442400
H	-2.64635400	2.64095200	-1.94593900
H	-1.56417300	3.72828500	-1.02885000
C	0.79522500	2.32816800	-1.65811000
H	0.94406700	3.21254900	-1.02424200
H	1.52844600	1.56462800	-1.36300600
H	1.02544200	2.63036100	-2.69327800
C	0.79544200	2.32828600	1.65744100
H	1.52863400	1.56474400	1.36227200
H	0.94417800	3.21263600	1.02350700
H	1.02580200	2.63053500	2.69256000
C	-0.85215200	0.76703500	2.69842300
H	-0.14416100	-0.07100600	2.60075800
H	-0.69776700	1.23632800	3.68423000
H	-1.87228200	0.35227000	2.68301600
C	-1.60631600	2.97430700	1.82719100
H	-2.64610700	2.64103600	1.94571800
H	-1.32639900	3.48497500	2.76398700
H	-1.56405800	3.72833100	1.02843000
Pd	0.24934800	-1.27927300	-0.00018400
C	2.13722700	-0.76891400	0.00016400
C	2.84434800	-0.57704500	-1.20134500
C	2.84404200	-0.57745000	1.20191800
C	4.17214900	-0.16746000	-1.20853700
H	2.34738600	-0.75315200	-2.15844900
C	4.17184100	-0.16786700	1.20958500
H	2.34683700	-0.75388300	2.15883500
C	4.85033900	0.05168800	0.00064700
H	4.69684800	-0.01611900	-2.15463800
H	4.69630000	-0.01684500	2.15587100
C	1.01675900	-3.18191800	-0.00015200

H -2.83171700 -3.59933400 0.90167500

H -2.83206700 -3.59885700 -0.90293400

H 0.63711500 -3.69398900 -0.90424000

H 0.63661800 -3.69412700 0.90364900

H 2.11111200 -3.28547600 0.00013900

C 6.21390900 0.47902800 0.00089300

N 7.32076600 0.82809000 0.00109200

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cis-Pd-CH3(CN)-TS

C -3.03145900 -1.05651100 0.15647900

C -2.68111300 0.31215200 0.15184000

C -3.71158700 1.24426700 0.32202800

C -5.03815500 0.85996500 0.49836000

C -5.35739500 -0.49280500 0.50069700

C -4.36219900 -1.45056500 0.32982900

H -3.47264200 2.30677000 0.31617400

H -5.81458900 1.61576100 0.63085700

H -6.39203100 -0.81655300 0.63577500

H -4.63254000 -2.50592300 0.33360600

P -0.90839900 0.77037500 -0.05582700

O -2.03437800 -1.96057000 -0.01562000

C -2.32681800 -3.33590800 0.00833000

H -1.37210800 -3.85794400 -0.13457000

C -0.50933000 1.96375700 1.36254800

C -0.86372500 1.59921600 -1.75697300

C -1.07200300 0.44914900 -2.74730300

H -0.29546900 -0.32415400 -2.63561100

H -2.05305800 -0.03334500 -2.61282400

H -1.03103100 0.83744300 -3.77885900

C -1.92978800 2.66090700 -2.01372300

H -1.78064400 3.08128900 -3.02278400

H -2.94448700 2.23918200 -1.98843200

H	-1.88306400	3.49942400	-1.30622000
C	0.53228900	2.19012400	-1.95751000
H	0.68280300	3.10604800	-1.36761600
H	1.32426600	1.47291500	-1.69156400
H	0.66561000	2.46311200	-3.01771100
C	1.01746900	2.05783500	1.44566700
H	1.48494400	1.06637000	1.51283500
H	1.45883100	2.57164300	0.58125200
H	1.29539800	2.63189400	2.34540400
C	-1.02003900	1.26290500	2.62433500
H	-0.64890000	0.22623700	2.68145900
H	-0.65456800	1.79946700	3.51548100
H	-2.11825000	1.23453500	2.67319300
C	-1.08401200	3.37495600	1.27510200
H	-2.18158400	3.39891900	1.25084300
H	-0.77630400	3.94046600	2.17089800
H	-0.70200800	3.92699200	0.40467800
Pd	0.30172800	-1.21874800	-0.03969300
C	2.28167800	-1.19346100	-0.01515300
C	2.96126200	-0.75523900	-1.18269000
C	2.95381000	-1.00758600	1.22026400
C	4.18327900	-0.11179300	-1.11219800
H	2.50406600	-0.91991700	-2.16147200
C	4.17931600	-0.36739600	1.29200800
H	2.48734400	-1.36459500	2.14159600
C	4.81335400	0.10329700	0.12864400
H	4.66777200	0.23917700	-2.02639400
H	4.65963000	-0.21785300	2.26179700
C	1.50422200	-2.96759300	-0.13470200
H	-2.75729700	-3.64133800	0.97635400
H	-3.01260800	-3.61751600	-0.80768200
H	1.22362500	-3.42763300	0.82803800

H 2.51976200 -3.30324700 -0.36870400

H 0.86891800 -3.34318900 -0.96235500

C 6.06957000 0.77236700 0.20172400

N 7.09285300 1.31924000 0.26074300

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cis-Pd-CH3(NMe2)-GS

C 3.31498600 -0.97015000 -0.00226300

C 2.93063300 0.38765600 -0.00229800

C 3.95025600 1.34843600 -0.00429900

C 5.29843400 1.00111100 -0.00672300

C 5.65081000 -0.34276900 -0.00709300

C 4.66744200 -1.32740300 -0.00479300

H 3.68405700 2.40354000 -0.00381700

H 6.06470400 1.77866700 -0.00828400

H 6.70211600 -0.63980200 -0.00910100

H 4.96679800 -2.37411700 -0.00507900

P 1.13522600 0.80818900 0.00104400

O 2.33251700 -1.91525800 0.00061000

C 2.70249300 -3.27963900 0.00515000

H 1.77078900 -3.85304300 0.01001200

C 0.88762500 1.80284600 -1.59141700

C 0.89343100 1.79618500 1.59853700

C 1.13365300 0.75592100 2.69847500

H 0.45167900 -0.10282200 2.59584500

H 2.16637000 0.37302300 2.68252700

H 0.96388200 1.21823600 3.68534000

C 1.81634900 2.98839600 1.83268200

H 1.51853800 3.48847200 2.77000200

H 2.86668300 2.68951900 1.95154500

H 1.75039900 3.74182700 1.03471600

C -0.56318500 2.26230700 1.65956300

H -0.73932000 3.14581600 1.03131400

H	-1.26971700	1.47615800	1.35707100
H	-0.80489000	2.54977500	2.69661700
C	-0.56889200	2.27036800	-1.64381300
H	-1.27455200	1.48373300	-1.34052600
H	-0.74109400	3.15206500	-1.01191100
H	-0.81542100	2.56132900	-2.67875200
C	1.12205300	0.76692900	-2.69667500
H	0.43866400	-0.09080700	-2.59557700
H	0.94995100	1.23395400	-3.68092200
H	2.15403500	0.38184800	-2.68582500
C	1.81030100	2.99534600	-1.82522700
H	2.85951900	2.69600900	-1.95240200
H	1.50701700	3.50044100	-2.75808800
H	1.75028800	3.74480000	-1.02307000
Pd	0.10681600	-1.32662600	-0.00144300
C	-1.80265100	-0.84947600	-0.00136900
C	-2.52134100	-0.67016700	1.18779100
C	-2.52111100	-0.66690300	-1.19016500
C	-3.85668600	-0.26863900	1.19820100
H	-2.03493200	-0.84953000	2.15096500
C	-3.85644300	-0.26533500	-1.19976400
H	-2.03449700	-0.84357700	-2.15372900
C	-4.55700800	-0.02954700	-0.00052600
H	-4.35313500	-0.14519000	2.16130500
H	-4.35268200	-0.13923300	-2.16263200
C	-0.59414800	-3.24987200	-0.00465300
H	3.28108800	-3.53332000	-0.89742900
H	3.28605700	-3.52574400	0.90661200
H	-0.20769100	-3.75564300	0.90126300
H	-0.19578500	-3.75633400	-0.90500600
H	-1.68616300	-3.37611000	-0.01169900
N	-5.87441900	0.40592400	-0.00004900

C -6.60316300 0.43636000 1.23441100

H -6.11445500 1.08923900 1.97787900

H -7.60639000 0.84649800 1.05708300

H -6.72406900 -0.56308000 1.70114300

C -6.60296800 0.43975400 -1.23453500

H -6.11419900 1.09473800 -1.97611000

H -6.72372700 -0.55839000 -1.70406500

H -7.60626100 0.84930800 -1.05622600

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cis-Pd-CH3(NMe2)-TS

C 3.42742800 -0.85654700 -0.41709700

C 2.91980100 0.46340600 -0.38972000

C 3.77689900 1.49094900 -0.79756800

C 5.07599100 1.24805700 -1.23763200

C 5.54773200 -0.05881900 -1.26821100

C 4.73125900 -1.10895800 -0.85852800

H 3.42072000 2.51954200 -0.76993600

H 5.71237800 2.07806600 -1.55076200

H 6.56340400 -0.27291800 -1.60947100

H 5.11828700 -2.12726600 -0.88384800

P 1.17873800 0.72250600 0.16506500

O 2.60896200 -1.84374200 0.00844700

C 3.05337500 -3.17253400 0.00003900

H 2.22096900 -3.77880100 0.38204600

C 0.44267600 2.06358000 -0.96331000

C 1.41810300 1.34728700 1.93978500

C 1.86544300 0.11263300 2.72842900

H 1.12044300 -0.69637000 2.66014600

H 2.82688800 -0.28070500 2.36387300

H 1.99621400 0.38022800 3.79082500

C 2.46699400 2.44282900 2.10805600

H 2.53721800 2.71820800 3.17447100

H	3.46494300	2.10470700	1.79351900
H	2.22386200	3.35895800	1.55372800
C	0.06482200	1.81361800	2.47634000
H	-0.25039500	2.77091000	2.03624900
H	-0.72490400	1.07044300	2.28530100
H	0.13365200	1.96488200	3.56694400
C	-1.07793100	2.00886600	-0.76975600
H	-1.47823200	1.00282800	-0.94941700
H	-1.38965000	2.31237400	0.23848500
H	-1.55418700	2.70164900	-1.48409900
C	0.75440400	1.60607200	-2.39086000
H	0.47006600	0.55091200	-2.53633900
H	0.17293600	2.21202600	-3.10564300
H	1.81857500	1.70912400	-2.64701600
C	0.89414900	3.50788300	-0.75449100
H	1.97053800	3.66796100	-0.89993200
H	0.37893600	4.14946100	-1.48954300
H	0.62219800	3.88599700	0.24114100
Pd	0.02097300	-1.30908000	0.11966400
C	-1.98279900	-1.40109900	0.04028600
C	-2.70468800	-0.96633800	1.16609300
C	-2.62434700	-1.25133700	-1.20114100
C	-3.94511700	-0.34773200	1.05641200
H	-2.27518200	-1.09590800	2.16347600
C	-3.86753600	-0.63767400	-1.32476600
H	-2.12543500	-1.60079900	-2.10927200
C	-4.56622700	-0.16305900	-0.19676700
H	-4.43469800	-0.00723200	1.96928900
H	-4.29321500	-0.53033300	-2.32280400
C	-1.02602100	-3.12320500	0.21623000
H	3.30166400	-3.51635600	-1.01852900
H	3.92694900	-3.31413100	0.65889200

H -1.61348900 -3.45873400 1.07923900

H 0.01787200 -3.50327800 0.37315800

H -1.41510500 -3.59751800 -0.69340900

N -5.80732700 0.44359900 -0.31061700

C -6.30442700 0.78099800 -1.61298700

H -7.30196000 1.23017600 -1.51910000

H -5.65823400 1.50079400 -2.15649700

H -6.41184100 -0.11240000 -2.25190800

C -6.38562400 1.07894900 0.83791800

H -7.37263600 1.48184800 0.57495800

H -6.53920500 0.36422800 1.66462200

H -5.77273400 1.91528600 1.23284200

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cis-Pd-CF2CN-GS

C -2.34950500 1.49181800 -0.25290900

C -2.49436500 0.09244200 -0.31602700

C -3.75020800 -0.40677000 -0.68065000

C -4.81649100 0.43335300 -0.98884700

C -4.64175000 1.81156000 -0.92822000

C -3.41149200 2.34471700 -0.55672700

H -3.90803400 -1.48274600 -0.71931600

H -5.78077200 0.00775300 -1.27253200

H -5.46635800 2.48508100 -1.17197400

H -3.27707600 3.42569000 -0.51897300

P -1.03413600 -0.94853700 0.12172000

O -1.13424600 1.98205500 0.12536200

C -1.06290500 3.27224100 0.71177100

H -1.89768400 3.41239100 1.41554800

C -1.06466100 -2.46048100 -1.01600100

C -1.36377200 -1.38424800 1.93241100

C -2.79147800 -1.84797700 2.20921900

H -3.05592000 -2.76715100 1.67012900

H	-2.89722400	-2.06157200	3.28611500
H	-3.53102600	-1.07466900	1.95607000
C	-0.35898100	-2.44740800	2.37620000
H	0.67259500	-2.18420200	2.09931200
H	-0.39697900	-2.54691600	3.47356200
H	-0.58756600	-3.43656700	1.95456900
C	-1.10463100	-0.09000600	2.71076300
H	-0.08124900	0.28739500	2.55765900
H	-1.80875700	0.70664200	2.42672700
H	-1.24182200	-0.27955100	3.78813000
C	0.30157000	-3.14727500	-0.91135600
H	1.12790200	-2.47008100	-1.15487200
H	0.49550700	-3.56373600	0.08541500
H	0.32741000	-3.98547600	-1.62712900
C	-1.21074300	-1.89415200	-2.43192400
H	-0.47104300	-1.09942300	-2.62203600
H	-1.03254500	-2.69764400	-3.16501700
H	-2.21002000	-1.47865500	-2.62367700
C	-2.13646900	-3.51491200	-0.74014000
H	-3.16708400	-3.14449400	-0.80327700
H	-2.04186700	-4.31182000	-1.49631800
H	-2.00280900	-3.99207200	0.24071700
Pd	0.71628900	0.64741200	-0.15341600
C	2.31211100	-0.50866900	-0.19129100
C	2.86797400	-0.97410800	1.00620300
C	2.91541200	-0.88396500	-1.39904400
C	3.96977100	-1.83262400	0.99456400
H	2.45102200	-0.65909800	1.96676000
C	4.01337700	-1.74386700	-1.40833800
H	2.52733900	-0.50279700	-2.34689800
C	4.54004000	-2.22977700	-0.21232500
H	4.38621100	-2.18783800	1.94130500

H 4.46359900 -2.03330000 -2.36199900

H 5.40004900 -2.90385600 -0.22118800

C 2.02379200 2.21073900 -0.43036700

F 1.30898700 3.25577900 -0.98293900

F 3.09607300 2.04042200 -1.23887500

H -0.11726300 3.32064200 1.26349700

H -1.07325100 4.06102400 -0.05408000

C 2.47443300 2.64588200 0.90000800

N 2.71710300 2.92326100 1.99953100

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cis-Pd-CF2CN-GS'

C -2.36095700 1.39582100 0.12913300

C -2.43302400 0.00271200 0.32632200

C -3.64154400 -0.51706600 0.80459800

C -4.73026400 0.29643400 1.10371200

C -4.62568500 1.66977900 0.91718800

C -3.44705000 2.22182300 0.42583400

H -3.74280700 -1.59103900 0.94467200

H -5.65461900 -0.14583700 1.47965800

H -5.46617200 2.32639700 1.15267600

H -3.37511300 3.29974000 0.28804700

P -0.95188700 -1.01872100 -0.08049100

O -1.20070800 1.90493600 -0.37800700

C -1.21447500 3.21862000 -0.91839000

H -1.28391600 3.97399700 -0.12195100

C -1.35826100 -1.66893000 -1.80957700

C -0.85164900 -2.39441800 1.21721400

C -1.89150000 -3.51149000 1.12381000

H -1.79826900 -4.08534600 0.19129600

H -1.71358200 -4.21877700 1.95071600

H -2.93173000 -3.17723100 1.21865700

C 0.53230400 -3.04496600 1.11011400

H	1.34363200	-2.32287800	1.25144600
H	0.61852000	-3.80909600	1.90013200
H	0.69528000	-3.54991800	0.14951500
C	-0.94280900	-1.67662300	2.56740200
H	-0.23032200	-0.83752100	2.62120500
H	-1.94736400	-1.28033000	2.77193100
H	-0.68724000	-2.38370000	3.37329400
C	-0.34474200	-2.74778300	-2.19093400
H	0.69104200	-2.42953600	-2.00267900
H	-0.51802300	-3.69031500	-1.65229400
H	-0.43768300	-2.96851900	-3.26714700
C	-1.18453200	-0.46262800	-2.73834500
H	-0.16216200	-0.05471200	-2.69512800
H	-1.38831000	-0.76928200	-3.77764400
H	-1.88382500	0.35067400	-2.49176300
C	-2.78154600	-2.20182700	-1.95300500
H	-3.53345500	-1.42477300	-1.75426700
H	-2.93288100	-2.54635600	-2.98978700
H	-2.98716700	-3.05683900	-1.29537500
Pd	0.72824200	0.66571500	-0.11153300
C	2.34846600	-0.42785000	0.09529000
C	2.97395500	-0.54620500	1.34370800
C	2.90008800	-1.10617200	-0.99697200
C	4.09345600	-1.36279800	1.50273200
H	2.58370400	-0.00126400	2.20739600
C	4.02182700	-1.92206500	-0.83525600
H	2.46032100	-0.99809100	-1.99196800
C	4.61694400	-2.06234600	0.41634200
H	4.56145900	-1.45065500	2.48719000
H	4.43392000	-2.44985400	-1.69995000
H	5.49235800	-2.70396900	0.54257700
C	2.00052600	2.29582700	-0.16044500

F 1.88721700 2.92245300 -1.38893700

F 3.33009500 2.15298900 0.04895600

H -0.26609000 3.34387600 -1.44949900

H -2.05067000 3.32617400 -1.62662200

C 1.47134500 3.21978700 0.85892100

N 0.94784900 3.86551700 1.66729700

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trans-Pd-CF2CN-GS

C -1.19287100 2.32377000 -0.13989900

C -2.12959100 1.27054700 -0.15045900

C -3.48276100 1.61082700 -0.28304000

C -3.90692400 2.92720900 -0.43168500

C -2.96049400 3.94432300 -0.45314700

C -1.60952600 3.64884600 -0.30522900

H -4.23326400 0.82359000 -0.26899700

H -4.97027000 3.15155900 -0.53334700

H -3.26762700 4.98488400 -0.57995100

H -0.88580100 4.46155500 -0.31765200

P -1.54728500 -0.46424400 0.06808700

O 0.12340700 2.01697800 0.05173000

C 1.05276300 3.08460900 0.18100200

H 1.14573600 3.63754300 -0.76625300

C -2.15500800 -1.36656300 -1.48609900

C -2.38242300 -1.02569000 1.67362200

C -3.87724800 -1.31525700 1.57364900

H -4.25124600 -1.61162200 2.56802400

H -4.46408700 -0.43965000 1.26511500

H -4.09683500 -2.14646800 0.88853900

C -1.65739600 -2.27612200 2.17590100

H -2.09232600 -2.57319600 3.14467100

H -1.75419300 -3.12974200 1.49272500

H -0.58542600 -2.09016400 2.32506300

C	-2.13169100	0.10614900	2.67477400
H	-2.70277500	1.01448900	2.43560900
H	-2.43288100	-0.22718500	3.68143600
H	-1.06295500	0.37318700	2.72112800
C	-1.19827300	-0.89828800	-2.58859400
H	-0.15848200	-1.19972600	-2.39347700
H	-1.50237500	-1.34461100	-3.54996700
H	-1.22049200	0.19659200	-2.71136400
C	-3.58609200	-1.06490500	-1.92738400
H	-3.71187700	-0.02312500	-2.25102900
H	-3.82121400	-1.70096500	-2.79696000
H	-4.33510400	-1.29018300	-1.15556200
C	-2.00321200	-2.87411700	-1.28228700
H	-2.74239800	-3.27194400	-0.57112300
H	-2.17586900	-3.38174500	-2.24552800
H	-1.00141500	-3.15135200	-0.93391300
Pd	0.83400200	-0.17193800	0.14977700
C	2.76395400	0.40396500	0.09996800
C	3.36457900	0.74186600	-1.11977700
C	3.46783800	0.66729000	1.28372800
C	4.61226100	1.36813600	-1.15466600
H	2.85994500	0.50882000	-2.06273800
C	4.71385200	1.29561800	1.25093400
H	3.04056900	0.37977700	2.24898400
C	5.28653000	1.65446700	0.03093200
H	5.06231700	1.62839500	-2.11685200
H	5.24410600	1.50090500	2.18528200
H	6.26311800	2.14461900	0.00455700
C	1.60094200	-2.01753000	0.19126000
F	2.55825100	-2.22325400	1.12970800
F	0.66128700	-2.98914000	0.44591600
H	0.74420200	3.76312000	0.99093700

H 2.01708500 2.63178900 0.42914900

C 2.14655100 -2.30973600 -1.14650900

N 2.50848100 -2.48101300 -2.23342400

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C 2.58407600 -1.40837500 -0.66213200

C 2.64193000 -0.07645300 -0.18768100

C 3.90536000 0.48539200 0.02866000

C 5.08069300 -0.22966700 -0.18392900

C 5.00097700 -1.54600400 -0.62550200

C 3.76375900 -2.13522600 -0.86478500

H 3.97627000 1.51435000 0.38051600

H 6.04902800 0.24000200 -0.00140900

H 5.91062800 -2.12796900 -0.79203900

H 3.72005800 -3.16619200 -1.21485500

P 1.07655500 0.81944500 0.16263100

O 1.36709200 -1.92121100 -0.91869100

C 1.23251300 -3.27157700 -1.28022500

H 1.60461600 -3.94369200 -0.49011100

C 0.92738900 2.02384800 -1.28718500

C 1.31586000 1.69368900 1.83115200

C 2.12327000 2.98973400 1.83336900

H 1.64187400 3.77963100 1.23970800

H 2.19425800 3.36454700 2.86835200

H 3.15284300 2.86697200 1.47173300

C -0.09260900 1.99622800 2.35825400

H -0.67442000 1.06989200 2.47864800

H -0.01547300 2.48674600 3.34320100

H -0.66376000 2.66168000 1.69617700

C 1.95825500 0.66335300 2.76412600

H 1.43069300 -0.30381600 2.72035000

H 3.01550400 0.47954100 2.52858100

H	1.90117900	1.02771700	3.80325600
C	-0.27087200	2.93874000	-1.03489600
H	-1.17493700	2.36807500	-0.77504600
H	-0.07672800	3.66851600	-0.23493800
H	-0.49248600	3.51266600	-1.94988800
C	0.63408300	1.12905900	-2.49531900
H	-0.28024500	0.53668500	-2.34523700
H	0.49163200	1.75764500	-3.39021300
H	1.46397600	0.43611200	-2.70251500
C	2.18151500	2.84303800	-1.57738800
H	3.04181900	2.20269000	-1.81988100
H	1.99586600	3.48364000	-2.45612200
H	2.46423700	3.50618600	-0.74953000
Pd	-0.77647300	-0.63438100	0.29912400
C	-2.64881900	0.03454900	-0.17314900
C	-3.24228900	0.97614400	0.68146600
C	-2.92969100	0.09115200	-1.54657400
C	-4.02395200	2.00238100	0.15879000
H	-3.07903700	0.91239200	1.75870300
C	-3.71037600	1.12349000	-2.06301700
H	-2.53019300	-0.67485100	-2.21433100
C	-4.25255900	2.08749000	-1.21520100
H	-4.46041200	2.74314800	0.83370100
H	-3.89961400	1.16889900	-3.13851300
H	-4.86691800	2.89436800	-1.62126200
C	-2.56356800	-1.75761900	0.51751100
F	-3.10627000	-2.43815100	-0.51866200
F	-3.49821400	-1.62340800	1.48678700
H	0.15806700	-3.44867900	-1.41163700
H	1.74765800	-3.48881500	-2.23154400
C	-1.47476300	-2.59378200	1.07701700
N	-0.64486300	-3.29600300	1.50474300

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C	-2.4725310000	-1.6905600000	-0.2539450000
C	-2.6611360000	-0.2890780000	-0.2678030000
C	-3.9347670000	0.1879550000	-0.5968260000
C	-4.9866510000	-0.6654340000	-0.9200200000
C	-4.7732810000	-2.0389100000	-0.9105330000
C	-3.5237100000	-2.5538660000	-0.5778630000
H	-4.1142710000	1.2622970000	-0.6004090000
H	-5.9657230000	-0.2555440000	-1.1751070000
H	-5.5846480000	-2.7262350000	-1.1612400000
H	-3.3744140000	-3.6331530000	-0.5729290000
P	-1.2276460000	0.7981530000	0.1327420000
O	-1.2463580000	-2.1518280000	0.0919800000
C	-0.9959040000	-3.5372500000	0.1295310000
H	-1.1093840000	-3.9954200000	-0.8670200000
C	-1.6055500000	1.3458390000	1.9054300000
C	-1.2588320000	2.2384390000	-1.0987490000
C	-2.3160700000	3.3219830000	-0.8996390000
H	-2.1949180000	3.8485410000	0.0575420000
H	-2.2034540000	4.0778650000	-1.6951930000
H	-3.3481820000	2.9524330000	-0.9618300000
C	0.1264210000	2.8925920000	-1.0265020000
H	0.9300360000	2.1637440000	-1.1924810000
H	0.1998100000	3.6666240000	-1.8087040000
H	0.3150680000	3.3828360000	-0.0623180000
C	-1.4096910000	1.5892510000	-2.4769790000
H	-0.6783900000	0.7756740000	-2.6137020000
H	-2.4140600000	1.1735770000	-2.6413470000
H	-1.2222380000	2.3432230000	-3.2592780000
C	-0.5848790000	2.4089840000	2.3111180000
H	0.4433770000	2.0967460000	2.0713520000

H -0.7741210000 3.3763340000 1.8235700000

H -0.6429840000 2.5778640000 3.3994380000

C -1.3838120000 0.0917640000 2.7565940000

H -0.3541070000 -0.2870050000 2.6562420000

H -1.5633940000 0.3307800000 3.8182770000

H -2.0724800000 -0.7209460000 2.4785110000

C -3.0272630000 1.8506900000 2.1353620000

H -3.7762660000 1.0744680000 1.9222600000

H -3.1443770000 2.1334480000 3.1954160000

H -3.2695240000 2.7382430000 1.5360930000

Pd 0.6465160000 -0.5771770000 0.0255240000

C 2.4821140000 0.1846940000 -0.1479550000

C 2.9032990000 0.5476270000 -1.4464390000

C 2.9638930000 0.9381250000 0.9472940000

C 3.6735130000 1.6900770000 -1.6434700000

H 2.6038540000 -0.0644590000 -2.3005340000

C 3.7238290000 2.0799920000 0.7326060000

H 2.7171810000 0.6291270000 1.9663250000

C 4.0784150000 2.4706020000 -0.5617680000

H 3.9616730000 1.9719810000 -2.6596580000

H 4.0532920000 2.6724020000 1.5903700000

H 4.6876520000 3.3627050000 -0.7210630000

C 2.6340880000 -1.6861530000 0.0416700000

F 2.3745360000 -2.3829550000 -1.1005860000

F 2.1659820000 -2.4463510000 1.1006830000

H 0.0430560000 -3.6504460000 0.4603500000

H -1.6593920000 -4.0449140000 0.8490500000

C 4.1041140000 -1.6983160000 0.2134010000

N 5.2512590000 -1.7215480000 0.3570010000

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trans-Pd-CF2CN-TS

C 1.34206000 2.30457800 0.08356500

C	2.19462100	1.19976900	-0.13922200
C	3.51679200	1.46793900	-0.51236100
C	3.99275400	2.76470700	-0.68370300
C	3.13101100	3.83536800	-0.47399600
C	1.81252600	3.61118400	-0.09104200
H	4.20041800	0.63626500	-0.67708200
H	5.03000100	2.93304300	-0.97931100
H	3.48215800	4.86164900	-0.60498000
H	1.15149800	4.46137000	0.07326900
P	1.52622300	-0.50804200	0.04416800
O	0.07475300	2.04582200	0.47608200
C	-0.83920900	3.10447300	0.64186200
H	-0.50641900	3.79837600	1.43152600
C	2.28910900	-1.08368600	1.67817600
C	2.16352200	-1.48232600	-1.45505900
C	3.61675400	-1.95064500	-1.41444500
H	3.84145000	-2.49665200	-2.34614000
H	4.34264600	-1.12928800	-1.35023900
H	3.80752300	-2.64443400	-0.58386600
C	1.25583600	-2.71108700	-1.58458800
H	1.58249800	-3.31109700	-2.45053400
H	1.27944700	-3.36109000	-0.69947000
H	0.21037900	-2.41654400	-1.75253800
C	1.92515900	-0.58800500	-2.67442300
H	2.62272900	0.25960500	-2.72353800
H	2.04967100	-1.18395600	-3.59371000
H	0.89942900	-0.18320000	-2.67642300
C	1.49925300	-0.32174000	2.74730800
H	0.42566000	-0.56355900	2.70180300
H	1.87194700	-0.59755400	3.74802900
H	1.60775200	0.76895400	2.64058300
C	3.77367900	-0.77000000	1.84214400

H 3.97379500 0.31057600 1.81725900

H 4.11097900 -1.14153200 2.82462100

H 4.40020400 -1.25700800 1.08256500

C 2.04223800 -2.58225000 1.84594100

H 2.65581200 -3.18495900 1.16038000

H 2.32075600 -2.88012600 2.87085200

H 0.98760700 -2.85679900 1.69610400

Pd -0.83833100 -0.27936400 0.08895300

C -2.75715000 0.22758600 -0.06282300

C -3.40939100 0.56774600 1.13381900

C -3.07891300 0.90458100 -1.24600000

C -4.31525600 1.62504500 1.15380800

H -3.20241300 0.00400900 2.04704900

C -3.98621100 1.96397000 -1.21538400

H -2.61396000 0.60078500 -2.18692200

C -4.60117600 2.32867500 -0.01860600

H -4.80686000 1.89966700 2.09065100

H -4.21930800 2.50334000 -2.13707200

H -5.31843100 3.15262100 -0.00050300

C -2.45592900 -1.68424200 -0.33607100

F -3.74569500 -1.95869200 0.03761100

F -2.39872900 -1.88735500 -1.67433300

H -0.99129200 3.65760800 -0.29925600

H -1.78875200 2.64780100 0.94411800

C -1.65484100 -2.69167700 0.36677900

N -1.11124000 -3.54406300 0.94088400

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C -2.95205600 0.92699700 -0.27250000

C -2.74682900 -0.46465600 -0.31781600

C -3.84098000 -1.26503300 -0.66756800

C -5.08249200 -0.71836800 -0.97861300

C	-5.25349600	0.66121800	-0.93663300
C	-4.19230300	1.48723200	-0.58004800
H	-3.72774100	-2.34715200	-0.69206200
H	-5.91281600	-1.37257600	-1.25044700
H	-6.21980100	1.10640600	-1.18349200
H	-4.32914300	2.56832600	-0.55658200
P	-1.07568000	-1.10744700	0.12231900
O	-1.89409200	1.70921200	0.09320000
C	-2.14908600	2.97202700	0.69207700
H	-2.99315000	2.89083400	1.39361000
C	-0.72767700	-2.58023000	-1.01274100
C	-1.27732000	-1.59985600	1.93618700
C	-2.53814300	-2.41208800	2.22010200
H	-2.55777500	-3.37316200	1.68995300
H	-2.58496300	-2.63586000	3.29893200
H	-3.45134200	-1.85640000	1.96289200
C	-0.03283300	-2.36730000	2.38240300
H	0.89640900	-1.84679400	2.10739900
H	-0.04511100	-2.47208400	3.47968700
H	0.00312300	-3.38244800	1.96221100
C	-1.35852000	-0.27686500	2.70522100
H	-0.46725700	0.35094100	2.54770400
H	-2.24494300	0.30930600	2.41914000
H	-1.44040300	-0.48781300	3.78406300
C	0.76999800	-2.89117600	-0.92147200
H	1.38887900	-2.03171500	-1.20114400
H	1.08099000	-3.21383100	0.08061300
H	1.00120800	-3.71448700	-1.61704800
C	-1.03046900	-2.08159800	-2.42925400
H	-0.53094800	-1.12002100	-2.63156900
H	-0.65173200	-2.81375600	-3.16072100
H	-2.10556800	-1.94781800	-2.61299500

C -1.49052000 -3.87179500 -0.71809400

H -2.58226800 -3.77507500 -0.76376000

H -1.20917600 -4.62174300 -1.47566500

H -1.22407800 -4.29467400 0.26054900

Pd 0.22270000 0.87538500 -0.15832000

C 2.05875700 0.17179000 -0.16581000

C 2.71327200 -0.09461600 1.04537000

C 2.75652400 -0.05531800 -1.36264300

C 4.00216600 -0.61784100 1.06601200

H 2.22021000 0.12015800 1.99674600

C 4.04239200 -0.58011200 -1.35422800

H 2.29050400 0.18268500 -2.32144400

C 4.67467800 -0.87732600 -0.13657700

H 4.49709200 -0.82471000 2.01723700

H 4.56940200 -0.76190200 -2.29328100

C 1.10012400 2.71811500 -0.43550100

F 0.15268400 3.54994900 -0.99049400

F 2.18256000 2.80958800 -1.24346500

H -1.24737300 3.25168600 1.24839100

H -2.35629800 3.73925700 -0.06739200

C 1.43297300 3.24601200 0.89571000

N 1.60995500 3.56030200 1.99764900

C 5.99494800 -1.42662800 -0.12269900

N 7.06461100 -1.87553400 -0.11177300

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cis-Pd-CF2CN(CN)-TS

C -3.04841600 0.80976100 -0.88011500

C -2.83140600 -0.45681100 -0.28880600

C -3.93974000 -1.29186700 -0.10481300

C -5.22665800 -0.90404100 -0.46580800

C -5.42121000 0.35316800 -1.02757700

C -4.34302700 1.20718700 -1.23555700

H	-3.79565800	-2.27654200	0.33913900
H	-6.06854100	-1.57997700	-0.30537800
H	-6.42373800	0.68048300	-1.31305200
H	-4.51515400	2.18751500	-1.67868600
P	-1.13765700	-0.92608600	0.24175000
O	-1.97066700	1.59016900	-1.09158600
C	-2.13248700	2.88370400	-1.61821800
H	-2.72804900	3.52452200	-0.94828100
C	-0.60452300	-2.20400400	-1.04376500
C	-1.30081700	-1.64322900	1.99143800
C	-1.79506300	-3.08328800	2.10754700
H	-1.10351300	-3.79927000	1.64157500
H	-1.86305200	-3.35157200	3.17513600
H	-2.79415800	-3.23991400	1.67971900
C	0.09233400	-1.55111200	2.62533000
H	0.43505200	-0.50647400	2.66869800
H	0.05048700	-1.94259600	3.65545700
H	0.85032800	-2.12916600	2.07863500
C	-2.23276300	-0.69668000	2.75298600
H	-1.93570500	0.35672600	2.61922700
H	-3.28123500	-0.79213200	2.43896600
H	-2.17992800	-0.92323300	3.83064600
C	0.74912600	-2.77585900	-0.62264500
H	1.47218000	-1.98240000	-0.38315100
H	0.66659600	-3.44522000	0.24625600
H	1.17026100	-3.37027700	-1.45006000
C	-0.43712500	-1.39583000	-2.33419600
H	0.29582200	-0.58505100	-2.21204500
H	-0.08148600	-2.06002700	-3.13931300
H	-1.38890800	-0.95178400	-2.66415100
C	-1.60705800	-3.32611500	-1.29712400
H	-2.56813200	-2.94127500	-1.66687500

H -1.20471500 -3.99490700 -2.07650800

H -1.79668100 -3.94366700 -0.40973200

Pd 0.28903200 0.94763400 0.28106300

C 2.28104500 0.66875600 0.04551400

C 2.99784800 0.00826700 1.06081800

C 2.70646700 0.51308000 -1.28684100

C 4.03122900 -0.86000000 0.74745000

H 2.72760900 0.16385300 2.10614700

C 3.73821000 -0.35800900 -1.60614400

H 2.21474200 1.07591400 -2.08220700

C 4.40382600 -1.06381500 -0.59231300

H 4.55959700 -1.39196000 1.54101700

H 4.03738800 -0.49561300 -2.64696300

C 1.80000200 2.47075100 0.46137800

F 2.25603000 3.11606200 -0.63445600

F 2.67444800 2.66063000 1.47467100

H -1.12569400 3.30954400 -1.70487100

H -2.59392800 2.85510300 -2.61967600

C 0.52498500 3.10159000 0.86255100

N -0.46309400 3.64367400 1.16672000

C 5.45897000 -1.97099100 -0.91753200

N 6.31254600 -2.71077600 -1.18177700

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cis-Pd-CF2CN(CN)-TS-rot

C -3.0385530000 -1.1814830000 -0.3500100000

C -2.9033540000 0.2243170000 -0.3092840000

C -4.0292740000 0.9921780000 -0.6274800000

C -5.2418480000 0.4126070000 -0.9907340000

C -5.3464860000 -0.9728120000 -1.0334050000

C -4.2522880000 -1.7712380000 -0.7130620000

H -3.9597240000 2.0784220000 -0.5895550000

H -6.0980710000 1.0434620000 -1.2363340000

H	-6.2887600000	-1.4474080000	-1.3165520000
H	-4.3526670000	-2.8554230000	-0.7505500000
P	-1.2719300000	0.9431890000	0.1521420000
O	-1.9515000000	-1.9246970000	-0.0165930000
C	-2.0346570000	-3.3332620000	-0.0043890000
H	-2.2296630000	-3.7331460000	-1.0128320000
C	-1.5430500000	1.4990030000	1.9400220000
C	-0.9346610000	2.3829480000	-1.0294360000
C	-1.7237590000	3.6718740000	-0.8106760000
H	-1.5104790000	4.1290000000	0.1657570000
H	-1.4217000000	4.4046010000	-1.5776360000
H	-2.8106030000	3.5489220000	-0.9054090000
C	0.5598060000	2.7017910000	-0.9069180000
H	1.1812610000	1.8161350000	-1.0885840000
H	0.8270900000	3.4639790000	-1.6574350000
H	0.8296780000	3.1050110000	0.0779390000
C	-1.1956990000	1.8259320000	-2.4313460000
H	-0.6663730000	0.8712990000	-2.5857560000
H	-2.2641140000	1.6562740000	-2.6265350000
H	-0.8230490000	2.5404850000	-3.1834360000
C	-0.3125190000	2.2814240000	2.3986880000
H	0.6216440000	1.7480160000	2.1649450000
H	-0.2613740000	3.2818520000	1.9453300000
H	-0.3555030000	2.4233260000	3.4912990000
C	-1.6403490000	0.1994340000	2.7449680000
H	-0.7263860000	-0.4077830000	2.6473610000
H	-1.7829710000	0.4381150000	3.8120220000
H	-2.4944030000	-0.4183330000	2.4271780000
C	-2.8130250000	2.3142580000	2.1689740000
H	-3.7179030000	1.7423840000	1.9181980000
H	-2.8824330000	2.5799330000	3.2373300000
H	-2.8284470000	3.2540270000	1.6015830000

Pd 0.1901760000 -0.8548300000 0.0198950000

C 2.1332230000 -0.5012370000 -0.0537070000

C 2.6953570000 -0.1884540000 -1.3190230000

C 2.7553930000 0.0501220000 1.0970090000

C 3.7325600000 0.7201760000 -1.4325510000

H 2.2887690000 -0.6572620000 -2.2181790000

C 3.7849430000 0.9634870000 0.9776270000

H 2.3999230000 -0.2338320000 2.0904290000

C 4.2845600000 1.3237560000 -0.2891440000

H 4.1272150000 0.9755240000 -2.4182170000

H 4.2221710000 1.4110610000 1.8726730000

C 1.9056280000 -2.3875440000 0.0473210000

F 1.4725330000 -2.9903390000 -1.0962000000

F 1.2978350000 -3.0209030000 1.1069850000

H -1.0601880000 -3.6946700000 0.3437610000

H -2.8150920000 -3.6793630000 0.6923830000

C 3.3415900000 -2.7088700000 0.1764700000

N 4.4643240000 -2.9624180000 0.2846300000

C 5.3454780000 2.2688160000 -0.4077770000

N 6.2053350000 3.0431560000 -0.5040040000

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cis-Pd-CF2CN(NMe2)-GS

C -3.30640600 0.66810100 -0.28973800

C -2.94480100 -0.69232200 -0.34533100

C -3.93553800 -1.60362700 -0.72874500

C -5.22420400 -1.19596600 -1.06236900

C -5.55031000 0.15463800 -1.00818900

C -4.59595900 1.08901300 -0.61826600

H -3.70174000 -2.66589500 -0.76140300

H -5.96952500 -1.93576600 -1.36022800

H -6.55528400 0.49230600 -1.27105900

H -4.85413100 2.14740300 -0.58512300

P	-1.21830500	-1.14702600	0.12748800
O	-2.35147400	1.55704500	0.10620900
C	-2.75112900	2.79402400	0.67333600
H	-3.59165800	2.63665300	1.36678800
C	-0.68561600	-2.57057200	-1.00025200
C	-1.41320400	-1.67482000	1.93334100
C	-2.59212000	-2.61144400	2.18390700
H	-2.50771900	-3.56134700	1.63956500
H	-2.63544000	-2.85574100	3.25869400
H	-3.55130400	-2.14518600	1.91639000
C	-0.10861500	-2.31761100	2.40429200
H	0.77063400	-1.71131700	2.14109900
H	-0.13024200	-2.42040800	3.50187500
H	0.03108200	-3.32565600	1.98852700
C	-1.64123700	-0.37277500	2.70836800
H	-0.81261300	0.33985200	2.57147000
H	-2.57396100	0.12638900	2.40491900
H	-1.72547300	-0.59892500	3.78420300
C	0.83157000	-2.73464400	-0.85492800
H	1.37301200	-1.80479400	-1.06356300
H	1.12987700	-3.07580100	0.14460600
H	1.17107300	-3.49654500	-1.57602700
C	-0.98196900	-2.08444200	-2.42243200
H	-0.55362800	-1.08420300	-2.59798700
H	-0.52146800	-2.77624900	-3.14648700
H	-2.05824700	-2.03537200	-2.64049900
C	-1.32627600	-3.93538200	-0.74905600
H	-2.41837700	-3.95207200	-0.85184400
H	-0.92979000	-4.64693600	-1.49234400
H	-1.06819700	-4.33581200	0.24121800
Pd	-0.14194100	0.96514800	-0.13438700
C	1.75801500	0.43144800	-0.13914100

C 2.42405000 0.15814400 1.05818700

C 2.49123300 0.29921500 -1.32258700

C 3.74486300 -0.28821000 1.07809100

H 1.91774100 0.30390100 2.01672700

C 3.80917000 -0.14977800 -1.32024600

H 2.03253100 0.54972300 -2.28260100

C 4.46745500 -0.47914100 -0.11678900

H 4.21219200 -0.48168800 2.04383700

H 4.32866700 -0.23732900 -2.27469700

C 0.54106600 2.88098600 -0.41499200

F -0.49220000 3.61373200 -0.97123300

F 1.60557000 3.09264300 -1.22443900

H -1.89171800 3.18082400 1.23249800

H -3.02930200 3.52008000 -0.10417500

C 0.80975600 3.45313300 0.91278300

N 0.93630500 3.80846800 2.00945500

N 5.76526800 -0.95524000 -0.10946700

C 6.51286200 -0.99553700 -1.33311700

H 7.50037900 -1.43622600 -1.14405000

H 6.01755400 -1.62336900 -2.09449200

H 6.67133900 0.00574700 -1.78146600

C 6.44635500 -1.13604700 1.13995900

H 6.57692200 -0.19242600 1.70680000

H 5.91292300 -1.84472100 1.79764000

H 7.44412000 -1.55512800 0.95563700

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cis-Pd-CF2CN(NMe2)-TS

C -3.32508700 0.49382800 -1.04990700

C -3.01897400 -0.70039400 -0.35464300

C -4.05382300 -1.61998000 -0.15063000

C -5.35549400 -1.37906100 -0.58212400

C -5.64099200 -0.18642600 -1.23801500

C	-4.63589500	0.74625600	-1.47318900
H	-3.84006700	-2.55449000	0.36771400
H	-6.13853900	-2.11807100	-0.40215100
H	-6.65727300	0.02632100	-1.57844500
H	-4.87544500	1.67329800	-1.99348100
P	-1.31182800	-0.94954900	0.27874800
O	-2.31118200	1.34291800	-1.29287500
C	-2.56436500	2.60251100	-1.85853700
H	-3.23411400	3.20628200	-1.22493900
C	-0.57455500	-2.19321400	-0.94062200
C	-1.48029400	-1.65206600	2.03509900
C	-1.80979400	-3.13682800	2.17133500
H	-1.01776500	-3.77686200	1.75746300
H	-1.89753300	-3.38698500	3.24217700
H	-2.76098100	-3.42155600	1.70212400
C	-0.13674200	-1.38648200	2.72670700
H	0.08898400	-0.30948100	2.74674900
H	-0.18449500	-1.75027200	3.76706000
H	0.70582800	-1.89032300	2.23320600
C	-2.54570900	-0.80219200	2.73333200
H	-2.36362200	0.27458700	2.58151600
H	-3.56259800	-1.02302500	2.38087000
H	-2.51370500	-0.99669000	3.81829200
C	0.81132200	-2.59920100	-0.43943100
H	1.42934100	-1.72297100	-0.19245000
H	0.75995900	-3.25166300	0.44477500
H	1.33500900	-3.16387300	-1.22868800
C	-0.42560200	-1.40420600	-2.24500700
H	0.20778900	-0.51590100	-2.10686100
H	0.04535800	-2.04583600	-3.00854300
H	-1.39972000	-1.07590000	-2.63864200
C	-1.43675800	-3.42349600	-1.20708800

H -2.42010300 -3.15294500 -1.61834700

H -0.93476600 -4.05866700 -1.95664300

H -1.59254900 -4.04180000 -0.31344400

Pd -0.05726500 1.05040100 0.35154200

C 1.97754700 0.98768700 0.14073700

C 2.73007700 0.41290000 1.17291200

C 2.45946500 0.85496300 -1.16738900

C 3.86392100 -0.34190600 0.90543700

H 2.41779900 0.54151900 2.21118900

C 3.59175200 0.10065200 -1.44925200

H 1.93556300 1.34495300 -1.99108900

C 4.32047500 -0.53318900 -0.41890500

H 4.40164100 -0.78488500 1.74344000

H 3.91172500 0.01267500 -2.48718200

C 1.19846100 2.72556700 0.52359700

F 1.63469100 3.41140600 -0.56079100

F 1.98258900 3.04064000 1.58245300

H -1.59412400 3.11018600 -1.92315700

H -2.98756900 2.51289100 -2.87386300

C -0.16683700 3.21885900 0.83543000

N -1.24039000 3.62260800 1.05902200

N 5.43338100 -1.29326200 -0.68995400

C 5.85467200 -1.48594700 -2.04921500

H 6.11638000 -0.53389400 -2.54638500

H 6.74802400 -2.12247400 -2.06885000

H 5.07985100 -1.98064800 -2.66458500

C 6.13883000 -1.93927000 0.38124400

H 6.54099500 -1.21660600 1.11470200

H 5.50250300 -2.65564200 0.93409700

H 6.98921700 -2.49984400 -0.02647200

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cis-Pd-CF2CN(NMe2)-TS-rot

C	3.4407430000	0.8627620000	-0.4515860000
C	3.1170270000	-0.5104000000	-0.3439310000
C	4.1128450000	-1.4365480000	-0.6732890000
C	5.3762600000	-1.0464830000	-1.1104650000
C	5.6674200000	0.3084020000	-1.2183950000
C	4.7080620000	1.2616970000	-0.8900320000
H	3.8970390000	-2.5005660000	-0.5848320000
H	6.1258620000	-1.7994060000	-1.3614890000
H	6.6523920000	0.6369460000	-1.5585140000
H	4.9544120000	2.3195290000	-0.9767080000
P	1.4185000000	-0.9733750000	0.2026620000
O	2.4868140000	1.7576560000	-0.1071500000
C	2.7398780000	3.1373670000	-0.2198320000
H	2.9599370000	3.4241990000	-1.2618810000
C	1.6978550000	-1.5081680000	1.9988680000
C	0.8579270000	-2.4120480000	-0.9002500000
C	1.4707970000	-3.7876130000	-0.6486350000
H	1.2334870000	-4.1696720000	0.3543280000
H	1.0454780000	-4.5046400000	-1.3713310000
H	2.5604970000	-3.8186790000	-0.7801390000
C	-0.6619460000	-2.5186360000	-0.7236210000
H	-1.1615130000	-1.5613650000	-0.9215480000
H	-1.0557310000	-3.2653330000	-1.4337260000
H	-0.9499390000	-2.8419490000	0.2855290000
C	1.1392830000	-1.9547240000	-2.3338850000
H	0.7362270000	-0.9441060000	-2.5119900000
H	2.2129920000	-1.9381320000	-2.5695380000
H	0.6466680000	-2.6420080000	-3.0416570000
C	0.3973240000	-2.1088840000	2.5323450000
H	-0.4678080000	-1.4657120000	2.3079520000
H	0.1993820000	-3.1088280000	2.1193670000
H	0.4644380000	-2.2180360000	3.6279140000

C	1.9877450000	-0.2043240000	2.7487690000
H	1.1539330000	0.5093670000	2.6511570000
H	2.1382320000	-0.4196570000	3.8201870000
H	2.8996240000	0.2885250000	2.3775900000
C	2.8615560000	-2.4707140000	2.2180330000
H	3.8206680000	-2.0277730000	1.9133920000
H	2.9395630000	-2.7080270000	3.2929120000
H	2.7367990000	-3.4228850000	1.6854430000
Pd	0.0989030000	0.9471930000	0.0566540000
C	-1.9070520000	0.8962670000	-0.0345510000
C	-2.4921820000	0.6227150000	-1.2840260000
C	-2.5635760000	0.3942100000	1.1084270000
C	-3.6030010000	-0.2041140000	-1.3981070000
H	-2.0542140000	1.0501740000	-2.1885860000
C	-3.6631130000	-0.4387900000	1.0004890000
H	-2.1897050000	0.6508900000	2.1030610000
C	-4.2114710000	-0.7758860000	-0.2607830000
H	-3.9985480000	-0.4030540000	-2.3938800000
H	-4.1110520000	-0.8255640000	1.9156060000
C	-1.3401900000	2.6767430000	0.0221790000
F	-1.0999960000	3.1277420000	-1.2364110000
F	-0.4424060000	3.3622720000	0.8590420000
H	1.8221450000	3.6411810000	0.1044720000
H	3.5733830000	3.4482340000	0.4322150000
C	-2.6489560000	3.2311150000	0.4393220000
N	-3.6655780000	3.6703480000	0.7741440000
N	-5.3024600000	-1.6061580000	-0.3676800000
C	-5.9086720000	-2.1518610000	0.8139720000
H	-6.7519990000	-2.7932800000	0.5292450000
H	-5.2042600000	-2.7721740000	1.3987420000
H	-6.3012250000	-1.3680180000	1.4882450000
C	-5.8406350000	-1.9147960000	-1.6622450000

H -5.0988900000 -2.4099890000 -2.3161520000

H -6.6909250000 -2.5992780000 -1.5519560000

H -6.2046010000 -1.0156450000 -2.1937920000

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cis-Pd-CF2Ph-GS

C -2.56243100 -1.86969400 0.06243900

C -2.95472000 -0.55555900 0.38444200

C -4.24776900 -0.37538600 0.89020700

C -5.11749800 -1.44268000 1.09402800

C -4.70037700 -2.73137500 0.77954400

C -3.42860600 -2.94810200 0.25946500

H -4.59344300 0.62954800 1.12431800

H -6.11750500 -1.26345800 1.49334300

H -5.36695700 -3.58247900 0.93629800

H -3.10872700 -3.96155400 0.01923000

P -1.75264800 0.81129400 0.08434200

O -1.31748200 -2.04919500 -0.45869100

C -1.05781700 -3.21968900 -1.21911500

H -0.92456400 -4.09638200 -0.56850800

C -1.88993700 1.98141600 1.56714100

C -2.38390000 1.57641600 -1.52407600

C -3.88842200 1.82888400 -1.56448300

H -4.46459900 0.89852400 -1.45844300

H -4.22564600 2.53385400 -0.79281500

H -4.15317100 2.26693200 -2.54171900

C -1.61702500 2.87392800 -1.78074400

H -1.79760900 3.20487000 -2.81706000

H -1.94986500 3.68756400 -1.12010100

H -0.53145900 2.74662400 -1.65327600

C -2.02463300 0.55093100 -2.60468200

H -2.54759900 -0.40573300 -2.45043300

H -2.32674600 0.93682800 -3.59250400

H	-0.94316200	0.34463200	-2.62982600
C	-0.68563100	2.92604500	1.51590600
H	-0.67698200	3.53939600	2.43227800
H	0.26556200	2.38529700	1.45907600
H	-0.72208800	3.61494400	0.66196000
C	-1.74401100	1.07693300	2.79473500
H	-1.60613900	1.69950700	3.69394400
H	-2.62480500	0.43932300	2.95683300
H	-0.86298900	0.42046400	2.70284100
C	-3.15031200	2.83827200	1.67593100
H	-3.25486100	3.52966000	0.82801600
H	-4.08006500	2.26362800	1.77106200
H	-3.07215000	3.45900100	2.58421700
Pd	0.28384500	-0.41114900	-0.19062800
C	1.62152900	1.04031000	-0.24755500
C	1.89972700	1.67430500	-1.46632000
C	2.34996900	1.44036300	0.88207300
C	2.86199700	2.68400400	-1.54917400
H	1.37659800	1.36886300	-2.37697200
C	3.30745600	2.45015500	0.80096500
H	2.18936800	0.94149600	1.84104800
C	3.56813500	3.07911500	-0.41580500
H	3.06307500	3.15961700	-2.51354800
H	3.86494100	2.73700500	1.69677500
H	4.32451500	3.86514200	-0.48147500
C	1.84658500	-1.73233700	-0.40354400
F	1.94661900	-2.07990000	-1.74095600
F	1.39194100	-2.88723900	0.22116700
H	-1.87997300	-3.39375300	-1.93089500
H	-0.12574500	-3.03860500	-1.76249100
C	3.20793500	-1.42080900	0.12550200
C	3.49413300	-1.62938200	1.47777300

C 4.17714700 -0.83942400 -0.69691900

C 4.72593200 -1.24797000 2.00262100

H 2.73636600 -2.08430300 2.11906500

C 5.40505500 -0.45445200 -0.16849200

H 3.95154700 -0.66991500 -1.75036800

C 5.68357600 -0.65281700 1.18309900

H 4.93876700 -1.41396700 3.06188500

H 6.14912500 0.01348100 -0.81767200

H 6.64617100 -0.34317100 1.59751300

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cis-Pd-CF2Ph-GS'

C 2.48681200 0.09109500 -1.16030500

C 2.30018900 -0.97819500 -0.25490800

C 3.43738300 -1.67040700 0.17469100

C 4.71835500 -1.32262300 -0.24721300

C 4.87831000 -0.26358800 -1.13435200

C 3.76962400 0.43913700 -1.59582600

H 3.32315100 -2.51590800 0.85231300

H 5.58301500 -1.88515800 0.10997100

H 3.90522000 1.26584000 -2.29318900

P 0.58264600 -1.41068000 0.25152300

O 1.38048300 0.73432800 -1.58015700

C 1.42938900 1.54454500 -2.72259500

H 2.03746900 2.44994600 -2.56770200

C 0.68077000 -2.04164000 2.04114500

C 0.14279500 -2.79123800 -0.96643000

C 1.20423900 -3.88106400 -1.09182800

H 2.17898600 -3.47321500 -1.39687800

H 1.34343700 -4.45588300 -0.16748000

H 0.89052600 -4.59496300 -1.87214400

C -1.20448300 -3.39410900 -0.56755700

H -1.54353900 -4.07833700 -1.36293700

H	-1.13982400	-3.98438700	0.35828100
H	-1.97837700	-2.62369500	-0.43950400
C	-0.00048200	-2.09214400	-2.32163300
H	0.95942000	-1.68664600	-2.67442600
H	-0.34634600	-2.82448600	-3.06997400
H	-0.73314300	-1.27528900	-2.28107700
C	-0.74296400	-1.91894200	2.59852000
H	-0.75588400	-2.26218500	3.64662000
H	-1.08673100	-0.87384200	2.57197200
H	-1.47317500	-2.51930900	2.03904400
C	1.56968900	-1.06292500	2.81379100
H	1.43921400	-1.23105200	3.89568100
H	2.63710700	-1.17598300	2.58287300
H	1.29346500	-0.01869700	2.60278800
C	1.16316300	-3.47459400	2.25890000
H	0.48330700	-4.21292600	1.81177200
H	2.17350400	-3.66668600	1.87377200
H	1.19049600	-3.67905500	3.34253000
Pd	-0.79631600	0.56657100	0.21275500
C	-2.60858600	-0.12618100	-0.25521300
C	-3.02820500	-0.12764900	-1.59392100
C	-3.48978900	-0.63714500	0.70734200
C	-4.25646100	-0.67710200	-1.96442700
H	-2.39162000	0.30857400	-2.36864300
C	-4.72054000	-1.18305900	0.33795900
H	-3.22113400	-0.61534400	1.76569800
C	-5.10564400	-1.21740600	-1.00078700
H	-4.55233700	-0.67683700	-3.01754300
H	-5.38534700	-1.58347900	1.10895200
H	-6.06708800	-1.64943000	-1.28958300
C	-1.63801700	2.38567100	0.42138000
F	-2.41752800	2.52388000	1.52712900

F -2.31493100 2.94789200 -0.60818800

H 1.81921100 0.98601400 -3.59138500

H 0.39500400 1.84971200 -2.92618700

C -0.27998600 2.97564700 0.59163900

C 0.31894100 3.76224900 -0.40584500

C 0.49836800 2.55308400 1.68824500

C 1.65855300 4.11284400 -0.30729100

H -0.28861400 4.09242000 -1.25028800

C 1.85124100 2.89032600 1.76372500

H 0.01857900 1.99704800 2.49808300

C 2.43481300 3.66316300 0.76562300

H 2.11094800 4.74502400 -1.07601300

H 2.44718600 2.55121500 2.61419400

H 3.49319200 3.92663000 0.82435300

H 5.87497300 0.02123100 -1.47969000

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trans-Pd-CF2Ph-GS

C 2.24326500 2.03602300 -0.53682900

C 2.87287300 0.79208500 -0.32924100

C 4.27216700 0.75802800 -0.39589900

C 5.03350500 1.89197800 -0.65933900

C 4.38863300 3.10542100 -0.86592100

C 3.00142600 3.18147800 -0.80533500

H 4.78836900 -0.18589000 -0.23447900

H 6.12210700 1.82346300 -0.70123400

H 4.96362000 4.01054700 -1.07449600

H 2.51717200 4.14305700 -0.96425100

P 1.84930600 -0.68972300 0.07072200

O 0.88370100 2.08952600 -0.46372300

C 0.24591900 3.33766600 -0.68574600

H 0.48644200 3.72086800 -1.68964100

C 2.55613000 -1.29891600 1.72516300

C	2.18160200	-1.85993800	-1.38519300
C	3.63665200	-1.98622200	-1.83129900
H	4.29994200	-2.35794700	-1.03823400
H	3.68670300	-2.71402300	-2.65863500
H	4.03981900	-1.03865700	-2.21337000
C	1.63287600	-3.24721200	-1.05259900
H	1.67107300	-3.87419000	-1.95903700
H	2.23386900	-3.75580100	-0.28409200
H	0.59310700	-3.20939100	-0.70717600
C	1.37193100	-1.24933000	-2.53413700
H	1.72607000	-0.23775300	-2.78962900
H	1.47699600	-1.87557300	-3.43587700
H	0.30223200	-1.17623800	-2.28513200
C	3.90066400	-2.01898300	1.65821600
H	4.71165100	-1.39269100	1.26416900
H	4.19781000	-2.31082400	2.67958400
H	3.85018500	-2.94298500	1.06477700
C	1.52839400	-2.23447200	2.36690900
H	1.91323300	-2.55711100	3.34890700
H	0.56455000	-1.73459300	2.52653000
H	1.33924700	-3.13621700	1.77044500
C	2.66899000	-0.04824700	2.60243600
H	2.88508500	-0.35220200	3.63990700
H	3.47068700	0.62852400	2.27471400
H	1.72312600	0.51839100	2.61353900
Pd	-0.35881900	0.24486500	0.18985200
C	-2.04520300	1.33931900	0.31770400
C	-2.41832100	1.92764600	1.53418700
C	-2.81620900	1.63534500	-0.81768900
C	-3.51229900	2.79295300	1.61189200
H	-1.85680800	1.69693300	2.44449300
C	-3.90711600	2.50165900	-0.74546700

H -2.57726400 1.16411100 -1.77643600

C -4.25934900 3.08446200 0.47194800

H -3.78589600 3.23892900 2.57272200

H -4.49475600 2.71241900 -1.64354800

H -5.11875000 3.75726200 0.53301500

C -1.54494000 -1.27295500 0.74888800

F -1.82578700 -1.16231100 2.08478200

F -0.86072100 -2.46945700 0.64140100

H -0.83030200 3.15450100 -0.61237800

H 0.54349700 4.06903900 0.08178400

C -2.82143900 -1.43538200 -0.02991100

C -4.05739300 -1.10530000 0.52892200

C -2.76657300 -1.89311800 -1.34947300

C -5.21955400 -1.21352600 -0.22984700

H -4.09772300 -0.73698600 1.55442800

C -3.92931200 -2.00015900 -2.10640700

H -1.80115100 -2.15739300 -1.78669200

C -5.16084600 -1.65573700 -1.54988100

H -6.18010700 -0.94032700 0.21371500

H -3.87404300 -2.35472500 -3.13874700

H -6.07359200 -1.73219100 -2.14584400

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cis-Pd-CF2Ph-TS

C 2.60415800 0.91569300 -1.08217600

C 2.67451000 -0.18848400 -0.20040300

C 3.93915900 -0.56687300 0.26209300

C 5.09845500 0.11692300 -0.09655600

C 5.00392300 1.20884800 -0.95149600

C 3.76590800 1.60624600 -1.44729600

H 4.02803200 -1.42952200 0.92114900

H 6.06705100 -0.20900400 0.28736100

H 3.70789300 2.45990600 -2.12220900

P	1.11690300	-1.05589300	0.26776300
O	1.38852000	1.24647300	-1.55441500
C	1.26908300	2.22243400	-2.55021800
H	1.59767300	3.21501300	-2.20058200
C	1.34230600	-1.64407100	2.06480000
C	1.09435400	-2.50574400	-0.95323700
C	2.41078700	-3.27037300	-1.05521300
H	3.24202800	-2.61709300	-1.35817000
H	2.69000600	-3.77243300	-0.11997400
H	2.31291500	-4.05362400	-1.82614300
C	-0.05183500	-3.44421800	-0.57909300
H	-0.19539300	-4.18448100	-1.38366800
H	0.15185500	-4.00688000	0.34397500
H	-0.99991900	-2.90096600	-0.45550400
C	0.78824200	-1.86909400	-2.31191100
H	1.59271900	-1.19402600	-2.63955500
H	0.68885300	-2.66363600	-3.07043800
H	-0.15287400	-1.30150400	-2.28521600
C	-0.06953500	-1.93342700	2.59153900
H	-0.00662600	-2.25256100	3.64573300
H	-0.70231800	-1.03452300	2.53638500
H	-0.57888900	-2.72815600	2.02975800
C	1.89613500	-0.45092800	2.84964200
H	1.79816400	-0.64828600	3.93022400
H	2.95583800	-0.25380800	2.63946700
H	1.33414500	0.46935100	2.62296600
C	2.20064900	-2.88482500	2.30658400
H	1.76785200	-3.78260900	1.84360300
H	3.23602700	-2.78777200	1.95439300
H	2.25137400	-3.07704900	3.39174700
Pd	-0.75747800	0.31983100	0.19256800
C	-2.53407700	-0.59924000	-0.28966800

C -2.76665400 -0.72081900 -1.66999500

C -3.10475600 -1.54940800 0.56834100

C -3.46558000 -1.81208100 -2.18064400

H -2.38887500 0.04533300 -2.35249100

C -3.81760700 -2.63188800 0.05525700

H -2.98201300 -1.44686600 1.64800600

C -3.98933700 -2.77757900 -1.32082100

H -3.60899800 -1.90394700 -3.26068600

H -4.24038400 -3.37128800 0.74097000

H -4.54324800 -3.63016800 -1.72078200

C -2.70170300 1.27502600 0.41616500

F -3.30243700 1.01255800 1.59953100

F -3.65639600 1.62797500 -0.47343500

H 1.83768400 1.94623700 -3.45578900

H 0.20245000 2.27767600 -2.80072000

C -1.70151500 2.37111700 0.54875500

C -1.49491300 3.28785900 -0.50305800

C -0.89069100 2.46270300 1.70523700

C -0.51016800 4.25983300 -0.39899700

H -2.13287800 3.23054500 -1.38635600

C 0.11087400 3.43393500 1.77929000

H -1.10039700 1.81960300 2.56197800

C 0.30661100 4.33041900 0.73394600

H -0.37712600 4.97899300 -1.21133200

H 0.73255500 3.49282200 2.67580200

H 1.08554600 5.09292100 0.80319300

H 5.90036400 1.75947100 -1.24640000

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cis-Pd-CF2PH-TS-rot

C -2.7746580000 -1.9988010000 -0.1935740000

C -3.1548300000 -0.6481300000 -0.3744060000

C -4.4476760000 -0.3995000000 -0.8472920000

C	-5.3377610000	-1.4260930000	-1.1537840000
C	-4.9375740000	-2.7455300000	-0.9783400000
C	-3.6634600000	-3.0350910000	-0.4985540000
H	-4.7753500000	0.6307440000	-0.9792560000
H	-6.3377800000	-1.1914470000	-1.5235760000
H	-5.6200840000	-3.5661970000	-1.2117530000
H	-3.3659320000	-4.0746170000	-0.3637380000
P	-1.9237120000	0.6674100000	0.0189130000
O	-1.5345140000	-2.2343230000	0.2904910000
C	-1.1123020000	-3.5528190000	0.5388170000
H	-1.0725710000	-4.1475620000	-0.3892690000
C	-2.4936690000	1.2503630000	1.7300580000
C	-2.1136430000	2.0208470000	-1.2977520000
C	-3.3345680000	2.9347630000	-1.2144100000
H	-3.3445670000	3.5277010000	-0.2889710000
H	-3.2975000000	3.6524730000	-2.0515110000
H	-4.2946390000	2.4081820000	-1.2945810000
C	-0.8549230000	2.8915110000	-1.2011580000
H	0.0617350000	2.2943580000	-1.2875200000
H	-0.8638430000	3.6277300000	-2.0225170000
H	-0.7971210000	3.4523870000	-0.2590470000
C	-2.0819450000	1.2876430000	-2.6414480000
H	-1.2280700000	0.5920810000	-2.6905830000
H	-2.9986430000	0.7120620000	-2.8331380000
H	-1.9650800000	2.0211140000	-3.4564640000
C	-1.6858860000	2.4893810000	2.1155540000
H	-0.6076940000	2.3354690000	1.9546710000
H	-1.9949360000	3.3814530000	1.5516910000
H	-1.8417860000	2.7116040000	3.1846770000
C	-2.1265270000	0.1051700000	2.6787810000
H	-1.0464860000	-0.1109260000	2.6496130000
H	-2.3988370000	0.3817990000	3.7114070000

H	-2.6645500000	-0.8225010000	2.4307920000
C	-3.9901030000	1.5250190000	1.8484040000
H	-4.5880820000	0.6261910000	1.6392170000
H	-4.2214810000	1.8380560000	2.8809660000
H	-4.3325820000	2.3284780000	1.1831910000
Pd	0.1585380000	-0.3419390000	0.1219800000
C	1.8465540000	0.7171020000	0.0240870000
C	2.2932860000	1.0872580000	-1.2657110000
C	2.1006050000	1.6087900000	1.0873330000
C	2.8811290000	2.3252610000	-1.4884300000
H	2.1717530000	0.3900310000	-2.0984350000
C	2.6896380000	2.8484970000	0.8515570000
H	1.8178610000	1.3243090000	2.1033740000
C	3.0799070000	3.2206110000	-0.4344500000
H	3.1961070000	2.5939350000	-2.5004130000
H	2.8473920000	3.5333010000	1.6896780000
H	3.5515300000	4.1895090000	-0.6121850000
C	2.3085390000	-1.0737610000	0.5214060000
F	1.7993150000	-2.2981910000	0.0676730000
F	2.2339310000	-1.1307100000	1.8778180000
H	-0.1005640000	-3.4759960000	0.9521280000
H	-1.7699520000	-4.0530540000	1.2694510000
C	3.7524240000	-1.0565240000	0.0961530000
C	4.7072870000	-0.3935800000	0.8705870000
C	4.1392180000	-1.6767410000	-1.0940250000
C	6.0333310000	-0.3461270000	0.4531410000
H	4.4026200000	0.0924700000	1.7983830000
C	5.4664440000	-1.6218990000	-1.5113710000
H	3.3951190000	-2.2031590000	-1.6939700000
C	6.4164810000	-0.9548820000	-0.7411330000
H	6.7740800000	0.1742410000	1.0649180000
H	5.7604910000	-2.1075870000	-2.4450020000

H 7.4573460000 -0.9102980000 -1.0705580000

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trans-Pd-CF2Ph-TS

C 2.68279600 1.92703600 -0.25312700

C 3.16901500 0.60697100 -0.09471800

C 4.55214200 0.43705300 0.03402400

C 5.43827000 1.51137700 0.02363000

C 4.93710000 2.80020800 -0.12139500

C 3.56876700 3.01143000 -0.25926400

H 4.95353600 -0.56913800 0.15173000

H 6.51101700 1.33881600 0.12994100

H 5.61373100 3.65820700 -0.13010900

H 3.19223200 4.02751000 -0.37476500

P 1.96346400 -0.78613500 -0.02271900

O 1.35314800 2.08723900 -0.40308400

C 0.78971600 3.37305200 -0.45939900

H 1.14862400 3.93404800 -1.33907500

C 2.45842700 -1.82174200 1.49148100

C 2.25542000 -1.69303200 -1.65924000

C 3.70845700 -2.00224300 -2.00676100

H 4.19658500 -2.65630000 -1.27202000

H 3.74533200 -2.52339900 -2.97875500

H 4.30795900 -1.08639500 -2.10910900

C 1.42161500 -2.97422400 -1.64290200

H 1.39952100 -3.41278300 -2.65489600

H 1.84143200 -3.73621100 -0.96953100

H 0.38356800 -2.77430900 -1.33488900

C 1.68681500 -0.74348100 -2.71874600

H 2.22847000 0.21510100 -2.74318600

H 1.77764700 -1.20456400 -3.71689800

H 0.62290300 -0.52673900 -2.53071400

C 3.66950700 -2.74056700 1.35476600

H	4.59971600	-2.20557900	1.12035800
H	3.83717700	-3.26026100	2.31353800
H	3.51678200	-3.51870300	0.59335000
C	1.23186900	-2.67139700	1.84522200
H	1.44124600	-3.24524900	2.76409900
H	0.34587000	-2.04477600	2.02161900
H	0.97219100	-3.39085300	1.05666800
C	2.68049300	-0.81604000	2.62395300
H	2.74397700	-1.35358000	3.58482300
H	3.60532800	-0.23535900	2.49844500
H	1.83986100	-0.10582600	2.69314400
Pd	-0.20477200	0.07940500	0.12100200
C	-1.96582800	0.95283400	0.22463100
C	-2.13426400	1.71281100	1.39528600
C	-2.43934500	1.46704900	-0.99831100
C	-2.71484400	2.97979600	1.33201900
H	-1.80876600	1.30171500	2.35378500
C	-3.01569300	2.73188800	-1.05096600
H	-2.36470500	0.86360900	-1.90630900
C	-3.15878900	3.49175400	0.11353800
H	-2.82573400	3.56978100	2.24586300
H	-3.36712200	3.12656200	-2.00791700
H	-3.62831000	4.47733900	0.07038000
C	-2.23593900	-0.95955300	0.56005000
F	-2.19319800	-1.06287900	1.91461500
F	-1.68842100	-2.13819700	0.07599300
H	-0.29449800	3.22864200	-0.54637900
H	1.00275400	3.94888600	0.45692200
C	-3.67101100	-0.97441700	0.09587600
C	-4.68753200	-0.45451200	0.90039100
C	-3.98306300	-1.48144400	-1.16788700
C	-6.00010900	-0.43466900	0.44030000

H -4.44135400 -0.05637300 1.88606800

C -5.29685800 -1.45185200 -1.62836600

H -3.18896600 -1.89925900 -1.78944700

C -6.30878200 -0.92668500 -0.82745900

H -6.78979500 -0.02801500 1.07669200

H -5.53210700 -1.84722500 -2.61958000

H -7.33931800 -0.90255800 -1.18973800

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cis-Pd-CF2PH(CN)-GS

C -3.08024300 -1.51625700 0.02533500

C -3.23571900 -0.16286100 0.38200900

C -4.47273000 0.22689000 0.90936300

C -5.51250400 -0.67863200 1.09807600

C -5.32882800 -2.01149300 0.74652200

C -4.11830400 -2.43285000 0.20597800

H -4.63628600 1.26965900 1.17456600

H -6.46249100 -0.33936500 1.51504200

H -3.98121200 -3.47995300 -0.06226700

P -1.81810300 0.97894300 0.09279600

O -1.88693000 -1.89590900 -0.51307300

C -1.84299200 -3.06545200 -1.31863100

H -1.86224400 -3.97505600 -0.70108000

C -1.76079100 2.16072700 1.57054600

C -2.29462600 1.83743000 -1.52205500

C -3.73388700 2.34287000 -1.56794700

H -4.46016600 1.52540600 -1.45353700

H -3.94592800 3.10276900 -0.80438500

H -3.91968400 2.80943700 -2.54998600

C -1.31598800 2.98408200 -1.77666500

H -1.44011200 3.34586300 -2.81077000

H -1.49836100 3.84074100 -1.11200600

H -0.26844900 2.67004300 -1.65566900

C	-2.11196300	0.76617800	-2.60246200
H	-2.79405700	-0.08513800	-2.45461100
H	-2.33675400	1.20042800	-3.59064300
H	-1.08228200	0.37588700	-2.62385200
C	-0.39946400	2.86199400	1.54039700
H	-0.30980300	3.50167100	2.43390700
H	0.43218300	2.14927300	1.54990900
H	-0.26987200	3.50762200	0.66183100
C	-1.81037500	1.25808400	2.80724400
H	-1.56123800	1.85101000	3.70239000
H	-2.80092500	0.80894300	2.96522700
H	-1.07621200	0.43884600	2.73359700
C	-2.84087100	3.23919000	1.64467400
H	-2.78102100	3.94247600	0.80242400
H	-3.86540100	2.85028300	1.69597700
H	-2.68252700	3.82868300	2.56306900
Pd	-0.02704200	-0.58397000	-0.18727500
C	1.55408300	0.58783800	-0.17318600
C	1.98506400	1.19024500	-1.36607000
C	2.31992700	0.80687600	0.98434300
C	3.12749500	1.98306000	-1.40548700
H	1.43492200	1.02293900	-2.29558900
C	3.46114200	1.59648400	0.95990600
H	2.03776100	0.32827700	1.92459000
C	3.87741400	2.19531800	-0.23985900
H	3.45113300	2.43714100	-2.34475800
H	4.04803500	1.74427100	1.86865000
C	1.27253400	-2.16517000	-0.43102400
F	1.32690300	-2.47490400	-1.77787400
F	0.60481900	-3.23314900	0.14840200
H	-2.68769600	-3.06483200	-2.02492500
H	-0.89742800	-3.03185200	-1.86787900

C 2.65863200 -2.11874700 0.12310600

C 2.87608200 -2.39814600 1.47558300

C 3.73219500 -1.70825500 -0.67252000

C 4.14527100 -2.24970900 2.02816900

H 2.03757300 -2.72311800 2.09517000

C 4.99819500 -1.55461800 -0.11585000

H 3.56316000 -1.49117000 -1.72799900

C 5.20895700 -1.81871300 1.23682100

H 4.30465400 -2.46933800 3.08693400

H 5.82741900 -1.21872800 -0.74315800

H 6.20245400 -1.69047300 1.67314300

H -6.13222700 -2.73732200 0.89085100

C 5.05946300 2.99810200 -0.27616600

N 6.01935600 3.64944200 -0.30607700

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cis-Pd-CF2PH(CN)-TS

C 2.89500200 -0.19812800 -1.27202600

C 2.60463500 -1.18420300 -0.30045300

C 3.65003900 -2.01929900 0.10798200

C 4.94362000 -1.88903500 -0.39089900

C 5.20981500 -0.90374200 -1.33467500

C 4.19294200 -0.06410100 -1.77860600

H 3.45057200 -2.80462500 0.83588200

H 5.73319700 -2.55933800 -0.04613300

H 4.41564100 0.69936700 -2.52363000

P 0.88562800 -1.32468900 0.34493400

O 1.87419600 0.57584600 -1.68673200

C 2.05380300 1.43997900 -2.77399500

H 2.78477300 2.23577800 -2.55578100

C 1.02641300 -1.83863800 2.17151700

C 0.16788700 -2.70671400 -0.73364100

C 1.05055400 -3.94652300 -0.84547300

H	2.04216100	-3.70846000	-1.25703900
H	1.18907500	-4.46431800	0.11223700
H	0.57473900	-4.66421100	-1.53501400
C	-1.21737100	-3.07387100	-0.20380500
H	-1.72088500	-3.73933700	-0.92430800
H	-1.17054500	-3.61244500	0.75405100
H	-1.85176400	-2.18560900	-0.07314200
C	0.01976400	-2.08279400	-2.12437000
H	0.99459100	-1.82318400	-2.56313100
H	-0.46656800	-2.80831900	-2.79755400
H	-0.59935400	-1.17491300	-2.09454700
C	-0.32548200	-1.49708500	2.81156400
H	-0.29501800	-1.75170100	3.88433200
H	-0.54591500	-0.42299900	2.71563800
H	-1.16174300	-2.04826700	2.36010200
C	2.08427300	-0.92790600	2.80219600
H	2.02109000	-1.00284000	3.90047900
H	3.10843700	-1.19149300	2.50652100
H	1.91851600	0.12628400	2.52719900
C	1.33616800	-3.30425000	2.47224300
H	0.53832100	-3.97471600	2.12369000
H	2.28498300	-3.65663900	2.04709600
H	1.41009100	-3.43532400	3.56494700
Pd	-0.27342900	0.68962000	0.25131500
C	-2.29000000	0.54124200	-0.00128000
C	-2.70619900	0.42392400	-1.34244600
C	-3.10756200	-0.02033100	0.99489100
C	-3.82842600	-0.31525000	-1.68362100
H	-2.13057300	0.91306300	-2.13200900
C	-4.24110700	-0.74866500	0.66403400
H	-2.84226900	0.10430900	2.04562200
C	-4.60572200	-0.92001900	-0.68151900

H -4.11665500 -0.42703800 -2.73089700

H -4.85244800 -1.19877200 1.44902700

C -1.65689700 2.37299100 0.49142000

F -2.20507100 2.46745100 1.72304300

F -2.46911300 3.00347600 -0.38426200

H 2.36975500 0.88964600 -3.67751100

H 1.07850400 1.90558200 -2.96222900

C -0.29690900 2.98268700 0.45791800

C 0.15788500 3.65984300 -0.69123800

C 0.57735400 2.83644400 1.55993000

C 1.44846200 4.16892400 -0.73507200

H -0.52426000 3.79369600 -1.53221100

C 1.87934700 3.33549900 1.48635200

H 0.20821900 2.39126300 2.48573300

C 2.31937100 3.99812900 0.34473600

H 1.78175000 4.71265500 -1.62259900

H 2.54740600 3.21459700 2.34220600

H 3.33597000 4.39455500 0.29822400

H 6.21731400 -0.78461600 -1.74025800

C -5.75891600 -1.68910600 -1.02624600

N -6.69373500 -2.31699300 -1.30674100

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cis-Pd-CF2PH(CN)-TS-rot

C -3.2435930000 -1.6549520000 -0.4460670000

C -3.4274200000 -0.2738340000 -0.2082660000

C -4.7220480000 0.2396560000 -0.3469670000

C -5.8006300000 -0.5576780000 -0.7201000000

C -5.5930270000 -1.9115750000 -0.9566760000

C -4.3224560000 -2.4625010000 -0.8196310000

H -4.8969270000 1.2973350000 -0.1555060000

H -6.7956120000 -0.1203460000 -0.8216990000

H -6.4253650000 -2.5556380000 -1.2497920000

H	-4.1787250000	-3.5261140000	-1.0064250000
P	-1.9667800000	0.7483410000	0.2581770000
O	-1.9938940000	-2.1572670000	-0.2907780000
C	-1.7508250000	-3.5266280000	-0.5252890000
H	-1.9734500000	-3.8004480000	-1.5697250000
C	-2.2366350000	1.0506000000	2.1075220000
C	-2.0556020000	2.3375350000	-0.7694820000
C	-3.1124230000	3.3706740000	-0.3857690000
H	-2.9600540000	3.7633500000	0.6294100000
H	-3.0329370000	4.2290520000	-1.0739090000
H	-4.1432510000	3.0010870000	-0.4643500000
C	-0.6755500000	2.9974590000	-0.6728290000
H	0.1269250000	2.3072300000	-0.9611170000
H	-0.6424970000	3.8623400000	-1.3560780000
H	-0.4519870000	3.3697300000	0.3354940000
C	-2.2658230000	1.8683830000	-2.2115440000
H	-1.5325830000	1.0926840000	-2.4873090000
H	-3.2724290000	1.4590350000	-2.3791290000
H	-2.1269660000	2.7200740000	-2.8976410000
C	-1.1902880000	2.0543740000	2.5916770000
H	-0.1792780000	1.7883990000	2.2469050000
H	-1.4099120000	3.0786710000	2.2573010000
H	-1.1791950000	2.0692130000	3.6943250000
C	-1.9722340000	-0.3068250000	2.7661300000
H	-0.9500050000	-0.6625870000	2.5606890000
H	-2.0953550000	-0.2167040000	3.8584350000
H	-2.6760680000	-1.0776890000	2.4155570000
C	-3.6392490000	1.5157200000	2.4898060000
H	-4.4030630000	0.7676530000	2.2339290000
H	-3.6839660000	1.6647590000	3.5820250000
H	-3.9182080000	2.4696120000	2.0228550000
Pd	-0.1283460000	-0.6035680000	-0.1245870000

C 1.6622720000 0.2189830000 -0.2439500000

C 2.0216740000 0.7555470000 -1.5073270000

C 2.2130620000 0.8464630000 0.9048520000

C 2.8057590000 1.8922670000 -1.6116480000

H 1.6592720000 0.2698530000 -2.4158330000

C 2.9884750000 1.9833760000 0.8004320000

H 2.0144920000 0.4264490000 1.8935720000

C 3.2966890000 2.5323740000 -0.4612030000

H 3.0429680000 2.3017150000 -2.5961810000

H 3.3745030000 2.4641670000 1.7018880000

C 1.9236600000 -1.6936150000 -0.3163390000

F 1.7687270000 -2.0897790000 -1.6079260000

F 1.2967090000 -2.6644190000 0.4627820000

H -0.6840070000 -3.6831230000 -0.3308650000

H -2.3400030000 -4.1592390000 0.1587090000

C 3.3779420000 -1.7301630000 0.0570200000

C 3.7542340000 -2.0366170000 1.3671800000

C 4.3575220000 -1.4212450000 -0.8895000000

C 5.0983010000 -2.0208510000 1.7286990000

H 2.9898470000 -2.2892330000 2.1038890000

C 5.7000040000 -1.4097200000 -0.5243630000

H 4.0624010000 -1.1853560000 -1.9126780000

C 6.0739000000 -1.7034780000 0.7858640000

H 5.3853910000 -2.2605930000 2.7552450000

H 6.4606700000 -1.1664580000 -1.2697540000

H 7.1282260000 -1.6867550000 1.0718140000

C 4.1007880000 3.7040080000 -0.5673350000

N 4.7537300000 4.6609160000 -0.6532240000

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cis-Pd-CF2PH(NMe2)-GS

C -3.52859600 -1.18699600 -0.22742900

C -3.50778200 0.16379300 0.17780200

C	-4.72902200	0.75156000	0.53361400
C	-5.92433600	0.03811600	0.52053800
C	-5.91366500	-1.29953100	0.14206500
C	-4.72347300	-1.91258300	-0.23603000
H	-4.75105000	1.80023500	0.82293700
H	-6.85704100	0.52867700	0.80534300
H	-4.72938000	-2.96126400	-0.53091800
P	-1.89888800	1.06187900	0.17350300
O	-2.35672100	-1.75376400	-0.62456900
C	-2.40179800	-2.93495500	-1.41150400
H	-2.63468700	-3.81494800	-0.79356900
C	-1.72387600	1.77700300	1.91614000
C	-2.09356500	2.33705700	-1.20663600
C	-3.29023500	3.27473600	-1.08919100
H	-4.24867600	2.73788400	-1.11667800
H	-3.25501000	3.88977700	-0.17833900
H	-3.28644600	3.96999800	-1.94572600
C	-0.80326800	3.15304700	-1.31077800
H	-0.79053200	3.68090100	-2.27895900
H	-0.73096200	3.91698400	-0.52576400
H	0.09585600	2.52232800	-1.25884200
C	-2.24024200	1.47606800	-2.46666600
H	-3.15707300	0.86663400	-2.44551800
H	-2.29433100	2.12954000	-3.35305700
H	-1.38105300	0.79806800	-2.59301700
C	-0.48636000	2.67754800	1.93981600
H	-0.17370700	2.82894500	2.98643700
H	0.36537800	2.24279300	1.39820500
H	-0.69723200	3.67086000	1.51981300
C	-1.47517000	0.53856300	2.78531200
H	-1.32380800	0.84867800	3.83277100
H	-2.33056900	-0.15522900	2.76215200

H	-0.58382600	-0.01723700	2.45512800
C	-2.91097900	2.54759000	2.48922200
H	-3.22497400	3.38868000	1.85457600
H	-3.77874900	1.90195700	2.67879800
H	-2.61345200	2.97459400	3.46180100
Pd	-0.34631000	-0.68381000	-0.24294100
C	1.35143300	0.33103700	-0.22368100
C	1.90081000	0.78841800	-1.42690000
C	2.10590800	0.55253600	0.93358500
C	3.13170600	1.44258500	-1.47737800
H	1.37551000	0.61603900	-2.37103300
C	3.33460400	1.20550800	0.90232200
H	1.75569400	0.17812300	1.89909800
C	3.88125100	1.67639500	-0.30823000
H	3.50953700	1.76089500	-2.44935800
H	3.87957100	1.32544200	1.83848700
C	0.79418700	-2.38347000	-0.45400700
F	0.87697000	-2.72213000	-1.79458200
F	0.00565400	-3.38485600	0.10634500
H	-3.14780100	-2.82375000	-2.21386100
H	-1.40601700	-3.05883600	-1.84647900
C	2.15325700	-2.46506700	0.16158200
C	2.28239000	-2.74147200	1.52615300
C	3.29778300	-2.17853900	-0.58772900
C	3.53439800	-2.71634800	2.13429300
H	1.38771900	-2.96517400	2.11106500
C	4.54708700	-2.14753300	0.02415600
H	3.19808200	-1.95617200	-1.65054600
C	4.67140000	-2.41255600	1.38717000
H	3.62277600	-2.93248200	3.20224500
H	5.43241800	-1.90630700	-0.56957800
H	5.65294900	-2.38129700	1.86677300

H -6.83937000 -1.87957300 0.13428900

N 5.10688900 2.32397800 -0.34551600

C 5.71530900 2.59472100 -1.61583400

H 6.65164000 3.14782000 -1.46281900

H 5.95278000 1.67880400 -2.19598300

H 5.06791100 3.22607800 -2.24743200

C 5.93941100 2.30717500 0.82357300

H 5.44356900 2.79069100 1.68225500

H 6.22878400 1.28422600 1.14042200

H 6.85967900 2.87240800 0.62481200

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cis-Pd-CF2Ph(NMe2)-TS

C 3.02901400 -0.57270600 -1.36888400

C 2.65330200 -1.48309600 -0.35280600

C 3.59580600 -2.43949200 0.03830700

C 4.87213700 -2.49815300 -0.51689700

C 5.22523400 -1.58320400 -1.50191900

C 4.30981400 -0.62711300 -1.93149400

H 3.32645900 -3.17066600 0.79941500

H 5.57991600 -3.25924700 -0.18269600

H 4.59782900 0.07940100 -2.70967000

P 0.96412000 -1.35408800 0.37483600

O 2.10122300 0.31532200 -1.76802800

C 2.35497600 1.14593800 -2.86465600

H 3.19651100 1.83355600 -2.67886700

C 1.12178200 -1.86073500 2.20387800

C 0.00705400 -2.64505100 -0.63222600

C 0.70251800 -3.99727300 -0.75861400

H 1.69594800 -3.90586000 -1.22169600

H 0.81712400 -4.51356400 0.20328300

H 0.09820300 -4.65362300 -1.40796000

C -1.38651000 -2.80466100 -0.02642000

H	-2.01407100	-3.40374600	-0.70726300
H	-1.36556300	-3.33093200	0.93935100
H	-1.88277700	-1.83360000	0.11501400
C	-0.13035000	-2.02924300	-2.02753600
H	0.84483400	-1.91408700	-2.52345100
H	-0.74984700	-2.69063200	-2.65645700
H	-0.61660300	-1.04427600	-1.98296100
C	-0.13750300	-1.32179900	2.89574300
H	-0.08895900	-1.55385300	3.97332800
H	-0.21554100	-0.23028900	2.77601400
H	-1.06246000	-1.76119600	2.49821200
C	2.32408400	-1.09708400	2.76747900
H	2.30165900	-1.14307800	3.86918500
H	3.28711000	-1.50649100	2.43428200
H	2.29316500	-0.03560600	2.47356400
C	1.23798200	-3.34979800	2.52567100
H	0.33864400	-3.90685600	2.22816000
H	2.10666300	-3.84006500	2.06664000
H	1.34420000	-3.47201600	3.61704600
Pd	0.06594400	0.79360600	0.29481600
C	-1.98593400	0.89673500	0.10672600
C	-2.47581200	0.81481400	-1.20411700
C	-2.82528600	0.44563600	1.13063400
C	-3.69869700	0.22054100	-1.49274400
H	-1.88174500	1.21404000	-2.03102200
C	-4.05823300	-0.13910800	0.86026100
H	-2.50723900	0.53626500	2.17123000
C	-4.52570700	-0.28039000	-0.46396500
H	-4.01310300	0.15659200	-2.53447800
H	-4.66042000	-0.49057500	1.69818300
C	-1.04255400	2.63217900	0.55691600
F	-1.51194500	2.80998200	1.81473200

F -1.80104700 3.37015800 -0.28568000

H 2.55663300 0.55840600 -3.77796300

H 1.44620800 1.74172000 -3.01531100

C 0.38334100 3.04700400 0.44743700

C 0.87197600 3.64642100 -0.73302700

C 1.29309600 2.76205500 1.49456100

C 2.21945600 3.95166300 -0.85664500

H 0.16963400 3.88109100 -1.53438500

C 2.65068200 3.05626500 1.33952500

H 0.91554000 2.38510300 2.44698500

C 3.11869100 3.64702900 0.17090200

H 2.57857700 4.43912600 -1.76682800

H 3.34244800 2.82940400 2.15430900

H 4.17968000 3.88194400 0.06071000

H 6.22078300 -1.61122600 -1.95147000

N -5.74100300 -0.87201100 -0.74070400

C -6.50253300 -1.46231800 0.32251100

H -5.96680700 -2.28956800 0.82878000

H -6.77396500 -0.72224100 1.09617200

H -7.43923100 -1.86884400 -0.07985200

C -6.12783700 -1.09754900 -2.10393300

H -7.11999000 -1.56603000 -2.13034300

H -6.19710400 -0.15483600 -2.67539400

H -5.42734300 -1.76301200 -2.64620500

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cis-Pd-CF2Ph(NMe2)-TS-rot

C -3.6042070000 -1.4935680000 -0.3250690000

C -3.6053000000 -0.0839400000 -0.4535840000

C -4.7609350000 0.5158420000 -0.9646850000

C -5.8729170000 -0.2250260000 -1.3587160000

C -5.8434780000 -1.6091480000 -1.2354280000

C -4.7173680000 -2.2442060000 -0.7196460000

H	-4.7982860000	1.6003800000	-1.0572310000
H	-6.7553490000	0.2807170000	-1.7556110000
H	-6.7045960000	-2.2099090000	-1.5379770000
H	-4.7109530000	-3.3298430000	-0.6257220000
P	-2.0877700000	0.8391790000	0.0453670000
O	-2.4995460000	-2.0656050000	0.1986890000
C	-2.4451640000	-3.4572420000	0.3845460000
H	-2.5110140000	-3.9983820000	-0.5746960000
C	-2.5636710000	1.4836480000	1.7643600000
C	-1.8653560000	2.2522830000	-1.2046910000
C	-2.8043690000	3.4531550000	-1.1086280000
H	-2.6941340000	3.9885140000	-0.1549320000
H	-2.5471820000	4.1699530000	-1.9071310000
H	-3.8655870000	3.2040320000	-1.2402220000
C	-0.4266850000	2.7544820000	-1.0296090000
H	0.3030010000	1.9397500000	-1.1226800000
H	-0.2097740000	3.5038440000	-1.8097020000
H	-0.2599770000	3.2355660000	-0.0567020000
C	-1.9718710000	1.5962220000	-2.5839560000
H	-1.3308380000	0.7012580000	-2.6435110000
H	-2.9988790000	1.2936450000	-2.8329520000
H	-1.6306670000	2.3064340000	-3.3555650000
C	-1.4787800000	2.4503060000	2.2384870000
H	-0.4724540000	2.0244630000	2.1034300000
H	-1.5188650000	3.4144330000	1.7109940000
H	-1.6180500000	2.6620560000	3.3121670000
C	-2.5481410000	0.2445960000	2.6648080000
H	-1.5610430000	-0.2449970000	2.6555320000
H	-2.7824330000	0.5401020000	3.7016910000
H	-3.2974460000	-0.4990050000	2.3533270000
C	-3.9404330000	2.1361300000	1.8498360000
H	-4.7416060000	1.4367410000	1.5699020000

H	-4.1304180000	2.4510030000	2.8904140000
H	-4.0301990000	3.0312680000	1.2203660000
Pd	-0.3066080000	-0.6430460000	0.1630720000
C	1.6164420000	-0.0695210000	0.1756470000
C	2.2028060000	0.2283570000	-1.0713610000
C	2.0515030000	0.6909330000	1.2745380000
C	3.0941240000	1.2772600000	-1.2290550000
H	1.9542550000	-0.3813880000	-1.9434550000
C	2.9486110000	1.7432450000	1.1269660000
H	1.6724360000	0.4562660000	2.2716120000
C	3.4855800000	2.0796260000	-0.1332960000
H	3.5007050000	1.4648990000	-2.2226780000
H	3.2328240000	2.3075680000	2.0153570000
C	1.5367020000	-1.9213760000	0.5982200000
F	0.6983740000	-2.9761690000	0.1781810000
F	1.4963350000	-1.9718450000	1.9558930000
H	-1.4707570000	-3.6648880000	0.8403290000
H	-3.2472510000	-3.8048670000	1.0577490000
C	2.9115570000	-2.3079970000	0.1164050000
C	4.0425590000	-1.9536280000	0.8562240000
C	3.0653060000	-2.9875290000	-1.0939240000
C	5.3122990000	-2.2685910000	0.3843380000
H	3.9199770000	-1.4167960000	1.7980890000
C	4.3390280000	-3.2939110000	-1.5671420000
H	2.1810470000	-3.2733920000	-1.6660340000
C	5.4658560000	-2.9343980000	-0.8314440000
H	6.1912960000	-1.9874440000	0.9694470000
H	4.4504980000	-3.8221630000	-2.5172990000
H	6.4647460000	-3.1739570000	-1.2040460000
N	4.3685470000	3.1289670000	-0.2876080000
C	4.9900780000	3.3548390000	-1.5609560000
H	4.2449570000	3.5425100000	-2.3543380000

H 5.6314510000 4.2436140000 -1.5024300000

H 5.6206430000 2.5059840000 -1.8917970000

C 4.8359320000 3.8393130000 0.8675510000

H 5.5000940000 4.6544240000 0.5526520000

H 4.0044000000 4.2962110000 1.4330660000

H 5.4018730000 3.1971060000 1.5714350000

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cis-Pd-CF2C(O)Me-GS

C 2.2947060000 -1.6901000000 -0.2070310000

C 2.6042230000 -0.3174960000 -0.2806820000

C 3.9183080000 0.0308380000 -0.6148560000

C 4.8909330000 -0.9278680000 -0.8824160000

C 4.5586100000 -2.2760220000 -0.8053800000

C 3.2665600000 -2.6605750000 -0.4630290000

H 4.1984460000 1.0813300000 -0.6586240000

H 5.9047010000 -0.6185890000 -1.1434600000

H 5.3084620000 -3.0430950000 -1.0118570000

H 3.0131410000 -3.7186160000 -0.4081790000

P 1.2707770000 0.8917020000 0.1194900000

O 1.0230530000 -2.0337710000 0.1332610000

C 0.7820060000 -3.3288190000 0.6742740000

H 1.5091920000 -3.5352180000 1.4753050000

C 1.4735620000 2.3495510000 -1.0720180000

C 1.6587930000 1.3502630000 1.9135540000

C 3.1350460000 1.6287400000 2.1840240000

H 3.5235470000 2.4774570000 1.6050960000

H 3.2636870000 1.8777750000 3.2509330000

H 3.7642200000 0.7517340000 1.9755130000

C 0.8103150000 2.5560370000 2.3168510000

H -0.2474400000 2.4300170000 2.0445200000

H 0.8622270000 2.6871420000 3.4104570000

H 1.1731510000 3.4890400000 1.8623880000

C	1.2258910000	0.1281150000	2.7300230000
H	0.1597240000	-0.1072690000	2.5869800000
H	1.8060820000	-0.7685150000	2.4638860000
H	1.3950830000	0.3239680000	3.8018750000
C	0.1971090000	3.1941720000	-0.9962750000
H	-0.7014540000	2.6090170000	-1.2217580000
H	0.0517460000	3.6627500000	-0.0143410000
H	0.2690920000	4.0057380000	-1.7391980000
C	1.5496010000	1.7179940000	-2.4654730000
H	0.7188470000	1.0118180000	-2.6279440000
H	1.4701030000	2.5090090000	-3.2290540000
H	2.4914240000	1.1774110000	-2.6357610000
C	2.6621240000	3.2812010000	-0.8353200000
H	3.6419250000	2.7935130000	-0.9094460000
H	2.6454440000	4.0690980000	-1.6066720000
H	2.6028560000	3.7889510000	0.1374890000
Pd	-0.6628330000	-0.4941330000	-0.1649990000
C	-2.0979710000	0.8581840000	-0.1877480000
C	-2.5140190000	1.4515870000	1.0133900000
C	-2.7204990000	1.2682370000	-1.3749490000
C	-3.4945950000	2.4459280000	1.0242480000
H	-2.0803510000	1.1282050000	1.9638120000
C	-3.6955290000	2.2663030000	-1.3646600000
H	-2.4468620000	0.7989250000	-2.3223780000
C	-4.0838780000	2.8646950000	-0.1668850000
H	-3.8003250000	2.8926210000	1.9745960000
H	-4.1595680000	2.5758690000	-2.3053710000
H	-4.8485860000	3.6452240000	-0.1607970000
C	-2.1097220000	-1.8964620000	-0.5898910000
F	-1.4285310000	-3.0045420000	-1.0357280000
F	-2.9762310000	-1.5802170000	-1.5953190000
H	-0.2384360000	-3.3166970000	1.0762440000

H 0.8485500000 -4.1004360000 -0.1065060000

C -2.8629590000 -2.2443890000 0.6687500000

O -2.3434410000 -2.9336170000 1.5255830000

C -4.2357640000 -1.6612310000 0.8124320000

H -4.2201040000 -0.5745630000 0.6428920000

H -4.8917620000 -2.0917260000 0.0390930000

H -4.6292250000 -1.8886700000 1.8109360000

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trans-Pd-CF2C(O)Me-GS

C -1.5947320000 2.2693930000 -0.1600010000

C -2.4022120000 1.1136460000 -0.1550500000

C -3.7876150000 1.2968080000 -0.2614520000

C -4.3649960000 2.5555650000 -0.3932530000

C -3.5442670000 3.6762960000 -0.4251150000

C -2.1655210000 3.5382530000 -0.3068880000

H -4.4411540000 0.4276720000 -0.2410030000

H -5.4490550000 2.6547360000 -0.4737250000

H -3.9727890000 4.6747960000 -0.5376900000

H -1.5403860000 4.4290170000 -0.3280670000

P -1.6173020000 -0.5437570000 0.0556890000

O -0.2486420000 2.1170800000 -0.0023760000

C 0.5538460000 3.2802480000 0.1288530000

H 0.5628430000 3.8576800000 -0.8086460000

C -2.1266680000 -1.5091120000 -1.4984330000

C -2.3784480000 -1.2002710000 1.6624750000

C -3.8334960000 -1.6511520000 1.5683070000

H -4.1615330000 -2.0129620000 2.5573820000

H -4.5161230000 -0.8371100000 1.2897770000

H -3.9699970000 -2.4820120000 0.8615550000

C -1.5165560000 -2.3658380000 2.1543270000

H -1.9098710000 -2.7117400000 3.1249100000

H -1.5228190000 -3.2219490000 1.4676950000

H	-0.4703330000	-2.0639630000	2.2976330000
C	-2.2477960000	-0.0543170000	2.6703130000
H	-2.9134560000	0.7892940000	2.4381050000
H	-2.5084910000	-0.4237320000	3.6758220000
H	-1.2132710000	0.3244300000	2.7140080000
C	-1.1676630000	-0.9950280000	-2.5787900000
H	-0.1216900000	-1.2546220000	-2.3533530000
H	-1.4309810000	-1.4540450000	-3.5467370000
H	-1.2396080000	0.0979810000	-2.7033460000
C	-3.5639810000	-1.3001690000	-1.9706740000
H	-3.7555710000	-0.2658230000	-2.2862310000
H	-3.7343880000	-1.9419000000	-2.8512000000
H	-4.3128470000	-1.5866170000	-1.2182570000
C	-1.8874890000	-3.0038640000	-1.2842780000
H	-2.5953240000	-3.4415520000	-0.5646930000
H	-2.0410220000	-3.5234140000	-2.2446330000
H	-0.8651320000	-3.2148010000	-0.9525570000
Pd	0.6976730000	0.0223530000	0.1506190000
C	2.5671890000	0.7893110000	0.1203660000
C	3.1250870000	1.2163900000	-1.0951720000
C	3.2821980000	1.0529270000	1.2985910000
C	4.3397870000	1.9039830000	-1.1313600000
H	2.6106530000	0.9978010000	-2.0365060000
C	4.4948190000	1.7449410000	1.2672130000
H	2.8927440000	0.7024340000	2.2587280000
C	5.0272770000	2.1735620000	0.0512780000
H	4.7556440000	2.2247500000	-2.0908210000
H	5.0320090000	1.9448050000	2.1989190000
H	5.9800630000	2.7085850000	0.0252930000
C	1.6373390000	-1.7278280000	0.3116880000
F	2.2785410000	-1.8443110000	1.5149440000
F	0.7743870000	-2.7980110000	0.2871440000

H 0.1897030000 3.9067110000 0.9578360000

H 1.5685860000 2.9349610000 0.3479700000

C 2.6227370000 -1.9571530000 -0.8360550000

C 4.0759100000 -2.0677640000 -0.4840700000

H 4.4107420000 -1.1944690000 0.0930070000

H 4.2237940000 -2.9523090000 0.1566190000

H 4.6646360000 -2.1675590000 -1.4041290000

O 2.2006610000 -2.0782070000 -1.9630220000

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cis-Pd-CF2C(O)Me-TS

C 2.5896340000 -1.4474070000 -0.7365920000

C 2.7206550000 -0.1569860000 -0.1693840000

C 4.0130140000 0.3210910000 0.0754240000

C 5.1487660000 -0.4308800000 -0.2125450000

C 4.9981010000 -1.6972980000 -0.7673920000

C 3.7302390000 -2.2056020000 -1.0304780000

H 4.1394950000 1.3138170000 0.5068250000

H 6.1414700000 -0.0266100000 -0.0058030000

H 5.8758540000 -2.3039560000 -1.0030870000

H 3.6298380000 -3.1991060000 -1.4665440000

P 1.2035140000 0.8038360000 0.2243840000

O 1.3454320000 -1.8932480000 -0.9799560000

C 1.1394470000 -3.1772770000 -1.5172970000

H 1.5606560000 -3.9601640000 -0.8657830000

C 1.1863580000 2.1502080000 -1.1045220000

C 1.4516440000 1.4949210000 1.9764330000

C 2.3450130000 2.7245610000 2.1218740000

H 1.9356600000 3.5993590000 1.5972780000

H 2.4129610000 2.9934930000 3.1895900000

H 3.3732030000 2.5625620000 1.7718230000

C 0.0539130000 1.8403410000 2.5037760000

H -0.5882370000 0.9472280000 2.5201240000

H	0.1368870000	2.2287890000	3.5329220000
H	-0.4564210000	2.6011830000	1.8971060000
C	2.0022450000	0.3383570000	2.8148640000
H	1.4118160000	-0.5810170000	2.6668250000
H	3.0495330000	0.1051390000	2.5780420000
H	1.9463390000	0.6023150000	3.8840620000
C	0.0389640000	3.1125760000	-0.7970610000
H	-0.9059260000	2.5802100000	-0.6146880000
H	0.2539610000	3.7508620000	0.0728240000
H	-0.1182680000	3.7820800000	-1.6588510000
C	0.8815940000	1.3947510000	-2.4018030000
H	-0.0724410000	0.8517640000	-2.3383760000
H	0.8111860000	2.1130110000	-3.2357360000
H	1.6748720000	0.6724380000	-2.6494170000
C	2.4949800000	2.9147360000	-1.2829110000
H	3.3211510000	2.2515900000	-1.5766260000
H	2.3685490000	3.6524300000	-2.0934350000
H	2.7967470000	3.4714420000	-0.3861440000
Pd	-0.7330310000	-0.5312660000	0.1348990000
C	-2.4963800000	0.3607480000	-0.3244930000
C	-3.0674110000	1.2465460000	0.6065310000
C	-2.7319610000	0.5833630000	-1.6909020000
C	-3.7660040000	2.3701190000	0.1766180000
H	-2.9462640000	1.0676380000	1.6769670000
C	-3.4340080000	1.7107030000	-2.1148060000
H	-2.3604520000	-0.1334950000	-2.4262610000
C	-3.9441710000	2.6154180000	-1.1861980000
H	-4.1767670000	3.0630260000	0.9157900000
H	-3.5863840000	1.8776110000	-3.1843950000
H	-4.4938810000	3.4984290000	-1.5200130000
C	-2.6915170000	-1.5624560000	0.0961040000
F	-2.8590020000	-2.1422910000	-1.1031430000

F -3.9178130000 -1.3875030000 0.6557140000

H 0.0532590000 -3.3144750000 -1.5586990000

H 1.5731530000 -3.2596230000 -2.5285720000

C -1.8612800000 -2.4219950000 1.0205580000

O -1.1282240000 -3.2983220000 0.5846250000

C -2.0531170000 -2.1886510000 2.4958910000

H -2.3637800000 -1.1627220000 2.7319260000

H -2.8466150000 -2.8660640000 2.8542050000

H -1.1230590000 -2.4371100000 3.0243800000

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cis-Pd-CF2C(O)Me-TS-rot

C -2.6184700000 -1.7710900000 0.2380780000

C -2.8594840000 -0.3816290000 0.1223030000

C -4.1908740000 0.0500880000 0.1554040000

C -5.2549360000 -0.8340410000 0.3152150000

C -4.9923090000 -2.1927300000 0.4463160000

C -3.6833430000 -2.6633740000 0.4066810000

H -4.4074630000 1.1122550000 0.0496510000

H -6.2802800000 -0.4598680000 0.3368420000

H -5.8114950000 -2.9039100000 0.5766980000

H -3.4973330000 -3.7326340000 0.5027790000

P -1.4268260000 0.7529480000 -0.1162420000

O -1.3363910000 -2.1947400000 0.1691840000

C -1.0363750000 -3.5655930000 0.2749510000

H -1.5129280000 -4.1461800000 -0.5326310000

C -1.5131450000 1.9580300000 1.3405540000

C -1.7554680000 1.5800540000 -1.7931570000

C -2.8244150000 2.6679230000 -1.8191290000

H -2.5469620000 3.5389540000 -1.2083320000

H -2.9476660000 3.0286820000 -2.8546080000

H -3.8091580000 2.3080880000 -1.4901970000

C -0.4234270000 2.1627420000 -2.2729940000

H	0.3473560000	1.3817840000	-2.3318960000
H	-0.5557090000	2.5986510000	-3.2777910000
H	-0.0391850000	2.9537040000	-1.6147510000
C	-2.1463780000	0.4406560000	-2.7381660000
H	-1.4252640000	-0.3915380000	-2.6807720000
H	-3.1470940000	0.0408230000	-2.5203550000
H	-2.1472940000	0.8105750000	-3.7770120000
C	-0.4408210000	3.0245600000	1.1080330000
H	0.5259600000	2.5800550000	0.8276480000
H	-0.7359800000	3.7440550000	0.3297990000
H	-0.2868990000	3.5977980000	2.0375180000
C	-1.1260640000	1.1052090000	2.5529730000
H	-0.1282790000	0.6590560000	2.4269440000
H	-1.1135930000	1.7345810000	3.4588420000
H	-1.8458310000	0.2885290000	2.7219830000
C	-2.8579390000	2.6214340000	1.6278600000
H	-3.6164590000	1.8927240000	1.9456140000
H	-2.7308780000	3.3333520000	2.4611780000
H	-3.2531220000	3.1915480000	0.7766670000
Pd	0.5111760000	-0.5151890000	-0.0643770000
C	2.2977360000	0.3541110000	0.1152590000
C	2.8121380000	1.1012000000	-0.9720500000
C	2.6086800000	0.8031280000	1.4207250000
C	3.5036800000	2.2862270000	-0.7578930000
H	2.6636840000	0.7370410000	-1.9907890000
C	3.2972730000	1.9956670000	1.6221600000
H	2.2964590000	0.2063950000	2.2800780000
C	3.7468810000	2.7503530000	0.5384320000
H	3.8658660000	2.8555000000	-1.6181620000
H	3.4911160000	2.3348820000	2.6434110000
H	4.2973200000	3.6796600000	0.6996940000
C	2.5685400000	-1.5032530000	0.0029450000

F 1.9685200000 -2.4828580000 -0.7745280000

F 2.5916270000 -2.0004080000 1.2703660000

H 0.0524180000 -3.6452590000 0.1762490000

H -1.3442260000 -3.9716930000 1.2530690000

C 4.0156010000 -1.4252540000 -0.5383720000

O 4.2082140000 -1.6520390000 -1.7050420000

C 5.1039920000 -1.0601690000 0.4273630000

H 4.9474010000 -1.5168900000 1.4133160000

H 6.0664350000 -1.3710060000 0.0015240000

H 5.1150150000 0.0329250000 0.5661300000

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trans-Pd-CF2C(O)Me-TS

C -1.6011780000 2.2843040000 -0.3397330000

C -2.3754520000 1.1263450000 -0.1007520000

C -3.7557060000 1.2962400000 0.0677730000

C -4.3671310000 2.5448610000 0.0005180000

C -3.5854310000 3.6685950000 -0.2404540000

C -2.2105470000 3.5433270000 -0.4082830000

H -4.3780810000 0.4254030000 0.2636870000

H -5.4463010000 2.6343790000 0.1385860000

H -4.0426400000 4.6593420000 -0.2969240000

H -1.6122990000 4.4348990000 -0.5913630000

P -1.5454710000 -0.5138160000 0.0590260000

O -0.2678210000 2.1302660000 -0.4909750000

C 0.5532260000 3.2663230000 -0.6295500000

H 0.3030410000 3.8322740000 -1.5422800000

C -2.3140220000 -1.5600970000 -1.3197310000

C -2.0164110000 -1.0992840000 1.8028590000

C -3.4516770000 -1.5815470000 1.9918380000

H -3.5899710000 -1.8886990000 3.0423380000

H -4.1990740000 -0.8019710000 1.7917690000

H -3.6823280000 -2.4588180000 1.3706520000

C	-1.0516170000	-2.2260820000	2.1799330000
H	-1.2454400000	-2.5296310000	3.2227120000
H	-1.1606400000	-3.1164280000	1.5482480000
H	-0.0025640000	-1.9072190000	2.1038000000
C	-1.7384330000	0.0949730000	2.7198070000
H	-2.4509960000	0.9187280000	2.5697510000
H	-1.8099270000	-0.2296760000	3.7710860000
H	-0.7202850000	0.4883970000	2.5623740000
C	-1.6399020000	-1.0357730000	-2.5916000000
H	-0.5461870000	-1.1392420000	-2.5426820000
H	-2.0042330000	-1.5997280000	-3.4667650000
H	-1.8681190000	0.0287260000	-2.7614460000
C	-3.8267170000	-1.4597520000	-1.5014490000
H	-4.1428160000	-0.4544730000	-1.8118730000
H	-4.1314580000	-2.1552710000	-2.3017890000
H	-4.3881030000	-1.7434680000	-0.6005530000
C	-1.9261010000	-3.0208660000	-1.0855470000
H	-2.5277210000	-3.4767860000	-0.2851270000
H	-2.1231240000	-3.5998080000	-2.0036620000
H	-0.8675160000	-3.1537650000	-0.8200250000
Pd	0.7951950000	-0.1394520000	-0.0883330000
C	2.6555730000	0.5571340000	0.0976160000
C	3.3052370000	1.0448760000	-1.0478020000
C	2.8925970000	1.1738740000	1.3335620000
C	4.1204620000	2.1714480000	-0.9652330000
H	3.1712370000	0.5422560000	-2.0087100000
C	3.7033900000	2.3065790000	1.4083810000
H	2.4406560000	0.7585800000	2.2376310000
C	4.3154790000	2.8099820000	0.2611710000
H	4.6093080000	2.5533330000	-1.8653070000
H	3.8663900000	2.7923330000	2.3739810000
H	4.9589840000	3.6907250000	0.3240920000

C 2.5509360000 -1.4331340000 0.2412720000

F 3.8091720000 -1.5327890000 -0.2998150000

F 2.6692520000 -1.6563560000 1.5588280000

H 0.4759040000 3.9265420000 0.2497170000

H 1.5811510000 2.8973720000 -0.7118980000

C 1.7340450000 -2.5165030000 -0.4316170000

C 1.8675300000 -2.5810490000 -1.9325490000

H 2.0074260000 -1.5961950000 -2.3981590000

H 2.7586430000 -3.1884910000 -2.1631830000

H 0.9923110000 -3.0826630000 -2.3642540000

O 1.1482170000 -3.3659260000 0.2097030000

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cis-Pd-CF2C(O)Me(CN)-GS

C -2.9754740000 0.9933370000 -0.2725250000

C -2.8471470000 -0.4082490000 -0.3181990000

C -3.9809730000 -1.1507120000 -0.6691440000

C -5.1932020000 -0.5416910000 -0.9785130000

C -5.2926200000 0.8446100000 -0.9283320000

C -4.1904080000 1.6140880000 -0.5710220000

H -3.9233140000 -2.2370760000 -0.6940270000

H -6.0561300000 -1.1517600000 -1.2515490000

H -6.2360680000 1.3400840000 -1.1682290000

H -4.2754570000 2.6996110000 -0.5377510000

P -1.2191330000 -1.1393420000 0.1380560000

O -1.8784070000 1.7174520000 0.0848210000

C -2.0658540000 3.0256980000 0.6186720000

H -2.8436380000 2.9974060000 1.3976110000

C -0.9418130000 -2.6279420000 -0.9985710000

C -1.4793410000 -1.6331730000 1.9459310000

C -2.8025750000 -2.3466380000 2.2108400000

H -2.8929050000 -3.2968440000 1.6680380000

H -2.8752040000 -2.5794940000 3.2864750000

H	-3.6671820000	-1.7182330000	1.9539950000
C	-0.3081680000	-2.5025080000	2.4026960000
H	0.6641200000	-2.0570990000	2.1479470000
H	-0.3465070000	-2.6169940000	3.4985320000
H	-0.3463570000	-3.5128540000	1.9712370000
C	-1.4643050000	-0.3122010000	2.7221970000
H	-0.5232550000	0.2420500000	2.5801460000
H	-2.2923350000	0.3481940000	2.4235020000
H	-1.5812730000	-0.5193020000	3.7987260000
C	0.5351010000	-3.0238590000	-0.8966730000
H	1.2018670000	-2.2028210000	-1.1818820000
H	0.8231480000	-3.3554980000	0.1094090000
H	0.7220490000	-3.8646870000	-1.5846800000
C	-1.2017350000	-2.1093670000	-2.4163370000
H	-0.6437700000	-1.1785670000	-2.6100410000
H	-0.8603630000	-2.8607770000	-3.1468560000
H	-2.2653280000	-1.9110920000	-2.6086370000
C	-1.7790220000	-3.8755710000	-0.7161400000
H	-2.8626520000	-3.7185940000	-0.7813280000
H	-1.5266660000	-4.6415520000	-1.4680000000
H	-1.5542490000	-4.3107540000	0.2675850000
Pd	0.1993080000	0.7709960000	-0.1597070000
C	1.9782720000	-0.0656610000	-0.1717550000
C	2.5691080000	-0.4881630000	1.0310480000
C	2.6948970000	-0.2722100000	-1.3621770000
C	3.8056270000	-1.1245710000	1.0476670000
H	2.0623170000	-0.3099950000	1.9828530000
C	3.9283100000	-0.9117780000	-1.3600510000
H	2.2845550000	0.0786340000	-2.3109670000
C	4.4942400000	-1.3521150000	-0.1531590000
H	4.2471140000	-1.4477280000	1.9929270000
H	4.4662800000	-1.0732190000	-2.2967130000

C 1.1483250000 2.5528220000 -0.5790700000

F 0.1683800000 3.3883640000 -1.0531060000

F 2.0925310000 2.5098440000 -1.5626250000

H -1.1042240000 3.3311650000 1.0480300000

H -2.3459330000 3.7364510000 -0.1721160000

C 1.7307050000 3.1287290000 0.6888280000

O 1.0024730000 3.6125320000 1.5327900000

C 3.2163760000 3.0260710000 0.8545690000

H 3.5645790000 1.9981070000 0.6783080000

H 3.7060200000 3.6578680000 0.0963010000

H 3.4985100000 3.3595450000 1.8608120000

C 5.7614540000 -2.0142490000 -0.1461140000

N 6.7888090000 -2.5531170000 -0.1401850000

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cis-Pd-CF2C(O)Me(CN)-TS

C -3.0753290000 0.7301410000 -0.9262030000

C -2.8867470000 -0.5053350000 -0.2633330000

C -4.0084830000 -1.3180830000 -0.0602890000

C -5.2792550000 -0.9454600000 -0.4885660000

C -5.4420860000 0.2701150000 -1.1444830000

C -4.3513960000 1.1047690000 -1.3648720000

H -3.8882230000 -2.2743720000 0.4480950000

H -6.1323710000 -1.6032110000 -0.3124720000

H -6.4301930000 0.5807530000 -1.4922720000

H -4.4985430000 2.0547400000 -1.8775210000

P -1.2008240000 -0.9707700000 0.2961060000

O -1.9928160000 1.5093950000 -1.1130370000

C -2.1073840000 2.7224710000 -1.8216150000

H -2.7860570000 3.4248820000 -1.3113150000

C -0.7218070000 -2.3924950000 -0.8540580000

C -1.3731470000 -1.4993270000 2.1108960000

C -1.9256180000 -2.8983600000 2.3719310000

H	-1.2687190000	-3.6855620000	1.9759710000
H	-1.9963850000	-3.0573050000	3.4611040000
H	-2.9341050000	-3.0510640000	1.9651700000
C	0.0250420000	-1.3976200000	2.7300350000
H	0.4090870000	-0.3696860000	2.6556660000
H	-0.0261620000	-1.6724400000	3.7968860000
H	0.7563430000	-2.0610430000	2.2477650000
C	-2.2659230000	-0.4464070000	2.7727310000
H	-1.9245390000	0.5756710000	2.5386600000
H	-3.3165690000	-0.5283770000	2.4616300000
H	-2.2252940000	-0.5684790000	3.8677430000
C	0.6152330000	-2.9606260000	-0.3773580000
H	1.3615400000	-2.1704450000	-0.2111530000
H	0.5118170000	-3.5427410000	0.5502850000
H	1.0185050000	-3.6425080000	-1.1439150000
C	-0.5365180000	-1.7256970000	-2.2205520000
H	0.2316380000	-0.9396830000	-2.1871260000
H	-0.2190440000	-2.4818870000	-2.9576400000
H	-1.4735080000	-1.2770360000	-2.5856570000
C	-1.7554090000	-3.5065900000	-0.9934050000
H	-2.6987670000	-3.1401900000	-1.4221790000
H	-1.3620130000	-4.2710010000	-1.6844900000
H	-1.9758430000	-4.0136440000	-0.0450800000
Pd	0.2688160000	0.8534260000	0.1031250000
C	2.2215380000	0.4400940000	-0.1080320000
C	2.9400300000	-0.1352290000	0.9609850000
C	2.6363600000	0.1381600000	-1.4207540000
C	3.9485140000	-1.0550980000	0.7295950000
H	2.6879910000	0.1240710000	1.9906790000
C	3.6462030000	-0.7827800000	-1.6584160000
H	2.1531350000	0.6334420000	-2.2650370000
C	4.3053030000	-1.4029110000	-0.5855570000

H 4.4704820000 -1.5183610000 1.5693500000

H 3.9340830000 -1.0272760000 -2.6828710000

C 1.9025320000 2.3682470000 0.0592400000

F 2.0213660000 2.8373820000 -1.1917900000

F 3.0784860000 2.5831110000 0.7055090000

H -1.1039400000 3.1612740000 -1.8312870000

H -2.4570270000 2.5456550000 -2.8525500000

C 0.8066330000 3.0830390000 0.8206780000

O -0.0653620000 3.7032610000 0.2346670000

C 0.9134690000 3.0524170000 2.3213180000

H 1.4014960000 2.1444790000 2.6989420000

H 1.5237210000 3.9129850000 2.6432740000

H -0.0887620000 3.1565270000 2.7573350000

C 5.3337760000 -2.3641180000 -0.8252440000

N 6.1666600000 -3.1485430000 -1.0194090000

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cis-Pd-CF2C(O)Me(CN)-TS-rot

C 3.1315530000 -1.2950730000 -0.4090630000

C 3.0785020000 0.1050530000 -0.2199200000

C 4.2814500000 0.8174210000 -0.2969070000

C 5.4946690000 0.1933190000 -0.5750900000

C 5.5183370000 -1.1811540000 -0.7806240000

C 4.3458930000 -1.9263290000 -0.6962920000

H 4.2743490000 1.8936520000 -0.1307190000

H 6.4131700000 0.7806690000 -0.6294380000

H 6.4587780000 -1.6901910000 -1.0042010000

H 4.3867280000 -3.0039850000 -0.8506360000

P 1.4593480000 0.8856830000 0.1743500000

O 1.9750800000 -1.9924450000 -0.2877270000

C 1.9747660000 -3.3922770000 -0.4588970000

H 2.6263890000 -3.8859660000 0.2805620000

C 1.2033530000 2.2314480000 -1.1277580000

C	1.6836520000	1.5571960000	1.9334390000
C	2.5279490000	2.8209130000	2.0606130000
H	2.0561120000	3.6876220000	1.5761150000
H	2.6413380000	3.0730070000	3.1285970000
H	3.5416770000	2.6982410000	1.6542710000
C	0.2888630000	1.8080350000	2.5109460000
H	-0.3115770000	0.8879390000	2.4973790000
H	0.3822880000	2.1440270000	3.5572600000
H	-0.2709930000	2.5782810000	1.9637180000
C	2.3308220000	0.4159180000	2.7230470000
H	1.7804020000	-0.5297800000	2.5869610000
H	3.3779720000	0.2478760000	2.4333640000
H	2.3118540000	0.6600940000	3.7979850000
C	-0.0629560000	2.9962060000	-0.7348810000
H	-0.8880160000	2.3196230000	-0.4677480000
H	0.1148350000	3.6815980000	0.1069920000
H	-0.3994240000	3.6098640000	-1.5866920000
C	0.9536010000	1.4558180000	-2.4249740000
H	0.0875240000	0.7843860000	-2.3334580000
H	0.7554310000	2.1650790000	-3.2459140000
H	1.8276930000	0.8492180000	-2.7101780000
C	2.3496350000	3.2119300000	-1.3660810000
H	3.2254740000	2.7212800000	-1.8121220000
H	2.0136340000	3.9774880000	-2.0856650000
H	2.6659800000	3.7419960000	-0.4582550000
Pd	-0.1246320000	-0.7945670000	0.0356260000
C	-2.0272900000	-0.2689330000	-0.0531030000
C	-2.6641500000	0.3133920000	1.0763110000
C	-2.4671950000	0.1657130000	-1.3331000000
C	-3.5755680000	1.3422130000	0.9363270000
H	-2.4242050000	-0.0547590000	2.0753120000
C	-3.3747570000	1.2018470000	-1.4718680000

H -2.0695740000 -0.3182370000 -2.2270620000

C -3.9378390000 1.8176290000 -0.3398850000

H -4.0230970000 1.7947240000 1.8237350000

H -3.6597380000 1.5452610000 -2.4687160000

C -1.9780210000 -2.1698560000 -0.0307930000

F -1.1559500000 -3.0453480000 0.6583070000

F -1.9762080000 -2.5914850000 -1.3223570000

H 0.9407750000 -3.7173950000 -0.2973400000

H 2.2895940000 -3.6718010000 -1.4777360000

C -3.3759600000 -2.3902200000 0.5846780000

O -3.4536160000 -2.6258920000 1.7623420000

C -4.5520890000 -2.3014840000 -0.3371890000

H -4.4301540000 -2.9947590000 -1.1824890000

H -5.4645080000 -2.5372350000 0.2233110000

H -4.6258030000 -1.2882320000 -0.7613570000

C -4.8707800000 2.8859270000 -0.4812130000

N -5.6290010000 3.7579330000 -0.5966700000

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cis-Pd-CF2C(O)Me(NMe2)-GS

C -3.3530510000 0.6590040000 -0.2251730000

C -3.0318550000 -0.7116150000 -0.2935650000

C -4.0604910000 -1.5987590000 -0.6320460000

C -5.3522720000 -1.1616180000 -0.9098520000

C -5.6419810000 0.1965880000 -0.8387170000

C -4.6495110000 1.1070800000 -0.4916040000

H -3.8541260000 -2.6663640000 -0.6702130000

H -6.1276480000 -1.8831600000 -1.1740020000

H -6.6499030000 0.5591710000 -1.0532410000

H -4.8835920000 2.1697660000 -0.4409930000

P -1.3056860000 -1.2175110000 0.1172880000

O -2.3622220000 1.5240170000 0.1203400000

C -2.7132680000 2.7998330000 0.6450310000

H	-3.4652220000	2.6777440000	1.4406250000
C	-0.8401440000	-2.6085430000	-1.0808560000
C	-1.4713870000	-1.8138170000	1.9050290000
C	-2.6853380000	-2.7029310000	2.1615710000
H	-2.6711690000	-3.6274710000	1.5685530000
H	-2.6959210000	-2.9988770000	3.2242820000
H	-3.6298840000	-2.1782640000	1.9592500000
C	-0.1893150000	-2.5405480000	2.3112910000
H	0.7136260000	-1.9740710000	2.0416990000
H	-0.1834460000	-2.6828210000	3.4048120000
H	-0.1171120000	-3.5385300000	1.8555240000
C	-1.6116700000	-0.5299240000	2.7293940000
H	-0.7479860000	0.1402180000	2.5973990000
H	-2.5172310000	0.0339820000	2.4579130000
H	-1.6906900000	-0.7860620000	3.7990790000
C	0.6745520000	-2.8214970000	-0.9825430000
H	1.2367420000	-1.8968910000	-1.1567550000
H	0.9862640000	-3.2218390000	-0.0091900000
H	0.9755960000	-3.5542330000	-1.7496260000
C	-1.1586310000	-2.0521870000	-2.4720400000
H	-0.7058260000	-1.0571580000	-2.6143050000
H	-0.7392970000	-2.7240160000	-3.2388600000
H	-2.2389180000	-1.9623210000	-2.6552770000
C	-1.5143550000	-3.9645280000	-0.8738070000
H	-2.6059070000	-3.9483020000	-0.9820950000
H	-1.1347410000	-4.6621000000	-1.6390310000
H	-1.2704130000	-4.4035700000	0.1037160000
Pd	-0.1691210000	0.8730480000	-0.1558020000
C	1.7123770000	0.2720460000	-0.1524590000
C	2.3297170000	-0.1065830000	1.0452930000
C	2.4834550000	0.1743730000	-1.3159490000
C	3.6357350000	-0.5935140000	1.0851490000

H 1.7912550000 -0.0156690000 1.9931480000

C 3.7862210000 -0.3182120000 -1.2971300000

H 2.0643930000 0.4893250000 -2.2743220000

C 4.4010480000 -0.7187790000 -0.0923550000

H 4.0567300000 -0.8742290000 2.0509540000

H 4.3297510000 -0.3828930000 -2.2401140000

C 0.5318570000 2.7595310000 -0.5775290000

F -0.5563210000 3.4651520000 -1.0379010000

F 1.4627450000 2.8505200000 -1.5714930000

H -1.7925550000 3.2365140000 1.0511000000

H -3.1015950000 3.4579900000 -0.1459910000

C 1.0433240000 3.3973010000 0.6878700000

O 0.2657350000 3.8051200000 1.5301580000

C 2.5310900000 3.4472120000 0.8590110000

H 2.9736740000 2.4514360000 0.7074680000

H 2.9607820000 4.1047500000 0.0866210000

H 2.7737000000 3.8285420000 1.8587140000

N 5.6940170000 -1.2036300000 -0.0659360000

C 6.2453500000 -1.6890750000 1.1658340000

H 5.6807550000 -2.5461650000 1.5835890000

H 7.2781990000 -2.0211350000 0.9996170000

H 6.2762130000 -0.9047500000 1.9435780000

C 6.4009770000 -1.4107580000 -1.2967130000

H 5.9047910000 -2.1456270000 -1.9611090000

H 6.5172270000 -0.4738130000 -1.8705960000

H 7.4096720000 -1.7858870000 -1.0810240000

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cis-Pd-CF2C(O)Me(NMe2)-TS

C -3.2871530000 0.2554990000 -1.1969190000

C -3.0050730000 -0.8368540000 -0.3407410000

C -4.0440310000 -1.7306950000 -0.0589730000

C -5.3267110000 -1.5632640000 -0.5746470000

C	-5.5866930000	-0.4755180000	-1.4016650000
C	-4.5773090000	0.4291920000	-1.7144960000
H	-3.8485560000	-2.5860280000	0.5876260000
H	-6.1138430000	-2.2792480000	-0.3305510000
H	-6.5863980000	-0.3250580000	-1.8165610000
H	-4.7945260000	1.2728400000	-2.3693260000
P	-1.3131960000	-0.9949270000	0.3625980000
O	-2.2734660000	1.0843350000	-1.4902040000
C	-2.5012320000	2.2637580000	-2.2198150000
H	-3.2681480000	2.8933770000	-1.7405510000
C	-0.5599040000	-2.3923410000	-0.6677180000
C	-1.5266190000	-1.4692420000	2.1903340000
C	-1.8635950000	-2.9243170000	2.5074340000
H	-1.0648370000	-3.6116480000	2.1951860000
H	-1.9754440000	-3.0369730000	3.5992370000
H	-2.8053150000	-3.2653760000	2.0570740000
C	-0.2003060000	-1.1169210000	2.8762050000
H	0.0289650000	-0.0470240000	2.7582990000
H	-0.2747500000	-1.3418280000	3.9537650000
H	0.6521860000	-1.6808940000	2.4726850000
C	-2.6085710000	-0.5404920000	2.7477970000
H	-2.4215170000	0.5080910000	2.4631940000
H	-3.6158630000	-0.8056840000	2.3983110000
H	-2.6062330000	-0.5943820000	3.8492850000
C	0.8147650000	-2.7296560000	-0.0908810000
H	1.4278280000	-1.8284500000	0.0563080000
H	0.7437210000	-3.2645690000	0.8680460000
H	1.3545420000	-3.3893690000	-0.7905180000
C	-0.3860870000	-1.7825420000	-2.0619330000
H	0.2445640000	-0.8827890000	-2.0321320000
H	0.0993930000	-2.5184700000	-2.7247440000
H	-1.3530920000	-1.5125970000	-2.5132750000

C	-1.4182640000	-3.6479970000	-0.7885000000
H	-2.3917640000	-3.4355910000	-1.2535750000
H	-0.9002120000	-4.3746870000	-1.4373850000
H	-1.5944570000	-4.1448750000	0.1743520000
Pd	-0.0737500000	1.0088200000	0.2095240000
C	1.9486180000	0.8770880000	-0.0399180000
C	2.7170260000	0.4234510000	1.0428060000
C	2.4064460000	0.5698680000	-1.3277750000
C	3.8253460000	-0.3904980000	0.8548010000
H	2.4331280000	0.6868480000	2.0643590000
C	3.5169140000	-0.2410470000	-1.5308840000
H	1.8790650000	0.9701140000	-2.1966780000
C	4.2508720000	-0.7592600000	-0.4420740000
H	4.3675880000	-0.7404520000	1.7330560000
H	3.8157670000	-0.4649440000	-2.5547350000
C	1.2715650000	2.7206900000	0.0651650000
F	1.2941340000	3.1539450000	-1.2057690000
F	2.3767370000	3.1989830000	0.6961340000
H	-1.5528150000	2.8125460000	-2.2078660000
H	-2.7972620000	2.0404940000	-3.2596130000
C	0.0393110000	3.1631970000	0.8023400000
O	-0.9804270000	3.5005270000	0.1990530000
C	0.1526300000	3.2671870000	2.3016790000
H	0.9159830000	2.6013510000	2.7240890000
H	0.4337150000	4.3023500000	2.5598750000
H	-0.8272210000	3.0559460000	2.7513210000
N	5.3405600000	-1.5775420000	-0.6335440000
C	6.0417790000	-2.1132980000	0.4987570000
H	5.3961290000	-2.7460660000	1.1371730000
H	6.8756250000	-2.7362690000	0.1516590000
H	6.4682070000	-1.3206180000	1.1402560000
C	5.7166770000	-1.9665010000	-1.9632070000

H 6.5949960000 -2.6225450000 -1.9183430000

H 4.9130730000 -2.5198710000 -2.4853860000

H 5.9852070000 -1.0988340000 -2.5932650000

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cis-Pd-CF2C(O)Me(NMe2)-TS-rot

C -3.5707050000 1.0223160000 -0.2314710000

C -3.3428050000 -0.3621690000 -0.0461120000

C -4.4628880000 -1.1972720000 0.0391340000

C -5.7640560000 -0.7098580000 -0.0555250000

C -5.9634860000 0.6528230000 -0.2451450000

C -4.8766520000 1.5172310000 -0.3327500000

H -4.3164880000 -2.2667830000 0.1864490000

H -6.6125930000 -1.3929610000 0.0171370000

H -6.9753770000 1.0573710000 -0.3254460000

H -5.0520670000 2.5828170000 -0.4777640000

P -1.6070060000 -0.9664150000 0.1043880000

O -2.4923170000 1.8303660000 -0.3030080000

C -2.6558300000 3.2148680000 -0.4830020000

H -3.2219620000 3.6672440000 0.3488420000

C -1.3747430000 -2.0325680000 -1.4446670000

C -1.5719040000 -1.9858370000 1.7073800000

C -2.1841970000 -3.3832290000 1.6661920000

H -1.6532160000 -4.0501180000 0.9719340000

H -2.1079050000 -3.8387420000 2.6684180000

H -3.2503200000 -3.3830740000 1.4014210000

C -0.0987090000 -2.1002810000 2.1127670000

H 0.3573670000 -1.1071190000 2.2248630000

H -0.0249550000 -2.6314050000 3.0771420000

H 0.5050520000 -2.6534930000 1.3802100000

C -2.2883570000 -1.1277590000 2.7531630000

H -1.9073870000 -0.0930220000 2.7467190000

H -3.3751930000 -1.0899130000 2.5923530000

H	-2.1075890000	-1.5452540000	3.7578490000
C	-0.0170810000	-2.7272020000	-1.3303890000
H	0.7802910000	-2.0192790000	-1.0569230000
H	-0.0294040000	-3.5426020000	-0.5918890000
H	0.2495170000	-3.1750150000	-2.3027040000
C	-1.3264570000	-1.0180080000	-2.5915190000
H	-0.5227570000	-0.2806360000	-2.4386200000
H	-1.1443090000	-1.5430480000	-3.5446100000
H	-2.2760050000	-0.4681140000	-2.6885410000
C	-2.4689600000	-3.0529310000	-1.7448130000
H	-3.4368760000	-2.5706680000	-1.9414480000
H	-2.1972570000	-3.6125600000	-2.6563080000
H	-2.6033730000	-3.7906960000	-0.9427860000
Pd	-0.1467020000	0.8400780000	0.0883130000
C	1.8518030000	0.6560830000	0.0111270000
C	2.5323040000	0.2224170000	1.1690690000
C	2.3764320000	0.2272500000	-1.2246100000
C	3.5922090000	-0.6674620000	1.1031870000
H	2.2227950000	0.6004420000	2.1459050000
C	3.4361480000	-0.6675500000	-1.3000740000
H	1.9359660000	0.5998930000	-2.1516400000
C	4.0646350000	-1.1616000000	-0.1356160000
H	4.0630230000	-0.9786870000	2.0355050000
H	3.7774750000	-0.9815780000	-2.2864360000
C	1.4057710000	2.4704890000	-0.0462030000
F	0.4527640000	3.2627000000	0.5936220000
F	1.3438730000	2.8255310000	-1.3602960000
H	-1.6456470000	3.6395550000	-0.4963130000
H	-3.1608280000	3.4413870000	-1.4373760000
C	2.7463960000	2.9535580000	0.5503390000
O	2.7793090000	3.3028130000	1.7035710000
C	3.9535880000	2.9427830000	-0.3432750000

H 3.7040730000 3.2090250000 -1.3783730000

H 4.6969750000 3.6368940000 0.0695130000

H 4.3878040000 1.9296590000 -0.3548290000

N 5.1033570000 -2.0625630000 -0.2023200000

C 5.6197910000 -2.4615450000 -1.4808930000

H 6.4133530000 -3.2059760000 -1.3391400000

H 4.8420040000 -2.9277940000 -2.1113820000

H 6.0502750000 -1.6169310000 -2.0536230000

C 5.7827250000 -2.4609570000 0.9982490000

H 6.2853690000 -1.6165980000 1.5089130000

H 5.0943000000 -2.9266540000 1.7254500000

H 6.5502520000 -3.2060680000 0.7538210000

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cis-Pd-CF2C(O)H-GS

C -2.3553150000 1.4559800000 -0.2783200000

C -2.4827300000 0.0543340000 -0.3467140000

C -3.7261770000 -0.4625200000 -0.7290710000

C -4.8017090000 0.3607700000 -1.0485250000

C -4.6482740000 1.7408760000 -0.9769630000

C -3.4314670000 2.2911090000 -0.5877370000

H -3.8666470000 -1.5406080000 -0.7714430000

H -5.7555250000 -0.0786330000 -1.3462350000

H -5.4805930000 2.4035810000 -1.2245270000

H -3.3189070000 3.3734510000 -0.5380030000

P -1.0238010000 -0.9731690000 0.1180590000

O -1.1534120000 1.9640620000 0.1109920000

C -1.1039920000 3.2892900000 0.6291600000

H -1.8914050000 3.4194480000 1.3879490000

C -1.0128720000 -2.4773450000 -1.0320720000

C -1.4001380000 -1.4290670000 1.9159730000

C -2.8378040000 -1.8835350000 2.1541680000

H -3.0992770000 -2.7899940000 1.5921300000

H	-2.9678360000	-2.1165230000	3.2244600000
H	-3.5645000000	-1.0986650000	1.9002900000
C	-0.4188590000	-2.5073930000	2.3748750000
H	0.6222890000	-2.2529240000	2.1291760000
H	-0.4877910000	-2.6183870000	3.4697020000
H	-0.6452040000	-3.4895790000	1.9360710000
C	-1.1478020000	-0.1443740000	2.7118480000
H	-0.1150660000	0.2192650000	2.5933810000
H	-1.8273350000	0.6664810000	2.4089810000
H	-1.3231850000	-0.3376420000	3.7831080000
C	0.3572170000	-3.1524040000	-0.9027540000
H	1.1809990000	-2.4678880000	-1.1339850000
H	0.5376120000	-3.5663140000	0.0976260000
H	0.4026660000	-3.9909450000	-1.6171960000
C	-1.1322430000	-1.9011450000	-2.4463800000
H	-0.3958950000	-1.0979190000	-2.6126460000
H	-0.9295370000	-2.6966440000	-3.1819230000
H	-2.1308430000	-1.4931450000	-2.6569260000
C	-2.0801950000	-3.5446590000	-0.7895400000
H	-3.1124330000	-3.1860690000	-0.8851410000
H	-1.9533200000	-4.3398000000	-1.5429460000
H	-1.9720460000	-4.0212310000	0.1947590000
Pd	0.7287360000	0.6436120000	-0.1199000000
C	2.3230270000	-0.5198350000	-0.1530110000
C	2.8184050000	-1.0803020000	1.0320340000
C	2.9697510000	-0.8331040000	-1.3561600000
C	3.9004030000	-1.9630740000	1.0099890000
H	2.3624530000	-0.8267970000	1.9932220000
C	4.0455660000	-1.7209170000	-1.3777800000
H	2.6333230000	-0.3788720000	-2.2910290000
C	4.5116100000	-2.2962670000	-0.1965920000
H	4.2673220000	-2.3906180000	1.9473740000

H 4.5263270000 -1.9618850000 -2.3300390000

H 5.3546910000 -2.9911810000 -0.2153310000

C 2.0170030000 2.2273150000 -0.4321830000

F 1.2706770000 3.2629390000 -0.9241070000

F 3.0309840000 2.0362140000 -1.3141240000

H -0.1145010000 3.4162680000 1.0842100000

H -1.2249430000 4.0308130000 -0.1739590000

C 2.5311160000 2.5140650000 0.9299220000

O 1.9769300000 3.2186100000 1.7472080000

H 3.4540270000 1.9337890000 1.1768960000

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trans-Pd-CF2C(O)H-GS

C -1.1921170000 2.3472300000 -0.1135780000

C -2.1281720000 1.2928850000 -0.1393550000

C -3.4814220000 1.6383540000 -0.2586690000

C -3.9052200000 2.9575610000 -0.3826120000

C -2.9587080000 3.9748750000 -0.3932160000

C -1.6077120000 3.6752730000 -0.2558840000

H -4.2334050000 0.8526530000 -0.2537860000

H -4.9690990000 3.1839040000 -0.4742080000

H -3.2659560000 5.0174200000 -0.5025870000

H -0.8808940000 4.4857310000 -0.2596270000

P -1.5433100000 -0.4471090000 0.0567890000

O 0.1232020000 2.0390090000 0.0724520000

C 1.0393120000 3.0946610000 0.3219050000

H 1.1979000000 3.7006720000 -0.5834110000

C -2.1726740000 -1.3466470000 -1.4948060000

C -2.3569960000 -1.0168060000 1.6688160000

C -3.8578720000 -1.2801750000 1.5885450000

H -4.2197330000 -1.6039310000 2.5789530000

H -4.4332390000 -0.3835190000 1.3210930000

H -4.1055630000 -2.0819270000 0.8785040000

C	-1.6374050000	-2.2826340000	2.1412720000
H	-2.0527170000	-2.5831780000	3.1176750000
H	-1.7612370000	-3.1276430000	1.4521530000
H	-0.5592990000	-2.1128580000	2.2666820000
C	-2.0735890000	0.0981140000	2.6801090000
H	-2.6317120000	1.0190690000	2.4584770000
H	-2.3681290000	-0.2414430000	3.6867400000
H	-0.9996330000	0.3450190000	2.7145700000
C	-1.1544400000	-0.9696850000	-2.5774140000
H	-0.1552750000	-1.3735840000	-2.3544570000
H	-1.4794400000	-1.3879460000	-3.5448900000
H	-1.0718640000	0.1224550000	-2.7019180000
C	-3.5695940000	-0.9534770000	-1.9710900000
H	-3.6250340000	0.0956860000	-2.2907280000
H	-3.8205490000	-1.5713440000	-2.8492970000
H	-4.3501480000	-1.1382430000	-1.2189190000
C	-2.1351980000	-2.8595650000	-1.2766770000
H	-2.8950410000	-3.1976300000	-0.5566950000
H	-2.3575190000	-3.3551710000	-2.2361480000
H	-1.1501310000	-3.2061370000	-0.9468260000
Pd	0.8226790000	-0.1593950000	0.1240940000
C	2.7641080000	0.4155970000	0.0480230000
C	3.2687280000	0.9497600000	-1.1486980000
C	3.5605870000	0.5105690000	1.1981980000
C	4.5051400000	1.5965130000	-1.1854100000
H	2.6882770000	0.8613530000	-2.0730700000
C	4.7946860000	1.1637900000	1.1666190000
H	3.2136740000	0.0652290000	2.1348560000
C	5.2684750000	1.7129410000	-0.0242720000
H	4.8769960000	2.0080040000	-2.1281480000
H	5.3938050000	1.2391070000	2.0787020000
H	6.2365040000	2.2198500000	-0.0501290000

C 1.5413350000 -2.0143050000 0.2434390000

F 2.2085530000 -2.2146290000 1.4186160000

F 0.5716710000 -2.9765470000 0.2174020000

H 0.6759780000 3.7280430000 1.1457990000

H 1.9858360000 2.6256910000 0.6075380000

C 2.4805740000 -2.2418660000 -0.9147500000

O 2.1138480000 -2.5588510000 -2.0176510000

H 3.5536990000 -2.0649680000 -0.6626100000

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cis-Pd-CF2C(O)H-TS

C 2.5414170000 -1.4571740000 -0.6493380000

C 2.6478990000 -0.1227980000 -0.1887050000

C 3.9306190000 0.4117970000 -0.0229670000

C 5.0806760000 -0.3284660000 -0.2830540000

C 4.9544430000 -1.6405050000 -0.7271650000

C 3.6964380000 -2.2048050000 -0.9117420000

H 4.0381360000 1.4398510000 0.3225600000

H 6.0656320000 0.1198710000 -0.1400410000

H 5.8440600000 -2.2390100000 -0.9378200000

H 3.6150470000 -3.2327940000 -1.2639260000

P 1.1122870000 0.8161740000 0.1795060000

O 1.3049990000 -1.9511160000 -0.8286210000

C 1.1205120000 -3.2938080000 -1.2047350000

H 1.5869940000 -3.9834580000 -0.4829420000

C 0.9819030000 2.0162950000 -1.2760610000

C 1.3959000000 1.6912450000 1.8401500000

C 2.2420770000 2.9620410000 1.8264450000

H 1.7780380000 3.7628160000 1.2336200000

H 2.3368250000 3.3403080000 2.8583230000

H 3.2628600000 2.8046440000 1.4534130000

C 0.0037170000 2.0370770000 2.3831200000

H -0.6065400000 1.1292630000 2.5062360000

H	0.1057740000	2.5236760000	3.3677870000
H	-0.5530010000	2.7205950000	1.7270650000
C	2.0221320000	0.6466600000	2.7679700000
H	1.4655960000	-0.3048650000	2.7374970000
H	3.0688550000	0.4291360000	2.5144870000
H	1.9940850000	1.0162340000	3.8064750000
C	-0.1906010000	2.9625760000	-1.0185190000
H	-1.1065220000	2.4183580000	-0.7457080000
H	0.0310530000	3.6926160000	-0.2258150000
H	-0.4061890000	3.5358740000	-1.9352810000
C	0.6585670000	1.1206130000	-2.4757070000
H	-0.2652730000	0.5471340000	-2.3145290000
H	0.5189380000	1.7469040000	-3.3726360000
H	1.4737210000	0.4116160000	-2.6872700000
C	2.2517730000	2.8043840000	-1.5835570000
H	3.0935590000	2.1437320000	-1.8357950000
H	2.0691420000	3.4464780000	-2.4618760000
H	2.5604540000	3.4634280000	-0.7617350000
Pd	-0.7679850000	-0.6076590000	0.3672200000
C	-2.5726410000	0.1457040000	-0.1938350000
C	-3.1749980000	1.1093480000	0.6322570000
C	-2.8357120000	0.1790350000	-1.5712080000
C	-3.9377950000	2.1331780000	0.0788200000
H	-3.0324830000	1.0664590000	1.7141520000
C	-3.6060370000	1.2039600000	-2.1185130000
H	-2.4337740000	-0.6040750000	-2.2176790000
C	-4.1494720000	2.1918290000	-1.2997320000
H	-4.3750050000	2.8923860000	0.7326570000
H	-3.7848770000	1.2250730000	-3.1967080000
H	-4.7516020000	2.9950820000	-1.7305300000
C	-2.6556640000	-1.7164990000	0.4871760000
F	-2.8463360000	-2.4499280000	-0.6190150000

F -3.8471390000 -1.5212020000 1.0985330000

H 0.0384110000 -3.4647570000 -1.1903960000

H 1.5203320000 -3.4836780000 -2.2156500000

C -1.7034820000 -2.3359620000 1.4489130000

O -0.8843910000 -3.2030200000 1.1669560000

H -1.8428520000 -1.9702790000 2.4949200000

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cis-Pd-CF2C(O)H-TS-rot

C 2.4579590000 -1.7307000000 0.2265390000

C 2.6880020000 -0.3360970000 0.2785980000

C 3.9715280000 0.0946410000 0.6317630000

C 4.9947250000 -0.7974520000 0.9428280000

C 4.7408930000 -2.1633500000 0.8962440000

C 3.4802720000 -2.6326070000 0.5386460000

H 4.1819890000 1.1629420000 0.6650660000

H 5.9828190000 -0.4235170000 1.2177390000

H 5.5291310000 -2.8805490000 1.1370830000

H 3.2991530000 -3.7064960000 0.5044240000

P 1.2874390000 0.7996240000 -0.1041070000

O 1.2235070000 -2.1455930000 -0.1435540000

C 0.9252470000 -3.5208620000 -0.2013660000

H 1.0179880000 -3.9954540000 0.7896400000

C 1.7120690000 1.4105920000 -1.8449940000

C 1.3301220000 2.1848430000 1.1895740000

C 2.4197940000 3.2463290000 1.0608140000

H 2.3351940000 3.8153380000 0.1241930000

H 2.3099670000 3.9713120000 1.8850900000

H 3.4394420000 2.8446360000 1.1299250000

C -0.0355410000 2.8787610000 1.1192920000

H -0.8620930000 2.1641490000 1.2284310000

H -0.1079150000 3.6155880000 1.9368520000

H -0.1872730000 3.4203860000 0.1760990000

C	1.4352270000	1.4706690000	2.5396250000
H	0.6802250000	0.6716740000	2.6240900000
H	2.4248520000	1.0206440000	2.7034420000
H	1.2519690000	2.1932110000	3.3521050000
C	0.7166870000	2.5060160000	-2.2274620000
H	-0.3206250000	2.2024660000	-2.0163790000
H	0.9136990000	3.4510550000	-1.7004760000
H	0.7963170000	2.7148760000	-3.3075400000
C	1.4838780000	0.1930520000	-2.7462960000
H	0.4468290000	-0.1721830000	-2.6747030000
H	1.6842950000	0.4678840000	-3.7956010000
H	2.1545790000	-0.6408490000	-2.4874270000
C	3.1456270000	1.8992960000	-2.0319350000
H	3.8777500000	1.1026240000	-1.8362880000
H	3.2861420000	2.2198610000	-3.0783770000
H	3.3923140000	2.7593190000	-1.3952150000
Pd	-0.6291240000	-0.5147960000	-0.0813310000
C	-2.4689820000	0.2403830000	0.0705770000
C	-2.9167550000	0.5960580000	1.3658660000
C	-2.9604160000	0.9926900000	-1.0251680000
C	-3.7165550000	1.7150960000	1.5574060000
H	-2.6177740000	-0.0143760000	2.2206960000
C	-3.7548280000	2.1159900000	-0.8157920000
H	-2.6767220000	0.7102880000	-2.0424590000
C	-4.1325710000	2.4911750000	0.4732650000
H	-4.0226080000	1.9860380000	2.5713620000
H	-4.0863160000	2.7044910000	-1.6755630000
H	-4.7647530000	3.3675770000	0.6308080000
C	-2.5785980000	-1.6060710000	-0.1369620000
F	-2.3648670000	-2.3311190000	0.9874720000
F	-2.1277180000	-2.3629020000	-1.2221850000
H	-0.1152790000	-3.5918080000	-0.5381720000

H 1.5751140000 -4.0413410000 -0.9243520000

C -4.0944730000 -1.5686640000 -0.3754300000

O -4.9056460000 -1.8503050000 0.4558470000

H -4.3597480000 -1.2788610000 -1.4214010000

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trans-Pd-CF2C(O)H-TS

C -1.3722590000 2.3079500000 -0.1688110000

C -2.2437950000 1.1944710000 -0.1567840000

C -3.6182990000 1.4529980000 -0.2359000000

C -4.1272820000 2.7418180000 -0.3734880000

C -3.2474290000 3.8154830000 -0.4314050000

C -1.8765960000 3.6040080000 -0.3244740000

H -4.3207600000 0.6247290000 -0.1831150000

H -5.2056650000 2.8997390000 -0.4350160000

H -3.6235290000 4.8343400000 -0.5503710000

H -1.2005530000 4.4574110000 -0.3570810000

P -1.5406890000 -0.4992230000 0.0480140000

O -0.0513820000 2.0747400000 0.0003650000

C 0.8362510000 3.1616800000 0.1369780000

H 0.9281260000 3.7282960000 -0.8039320000

C -2.3316420000 -1.5569110000 -1.3139100000

C -2.0870930000 -0.9799450000 1.7978100000

C -3.5803520000 -1.2390980000 1.9625450000

H -3.7942090000 -1.4644480000 3.0211100000

H -4.1929410000 -0.3672650000 1.6924970000

H -3.9192550000 -2.1056010000 1.3765090000

C -1.2893270000 -2.2119090000 2.2280370000

H -1.5081170000 -2.4283040000 3.2873260000

H -1.5367890000 -3.1101890000 1.6493170000

H -0.2061800000 -2.0521380000 2.1269470000

C -1.6616820000 0.1972480000 2.6808610000

H -2.2463590000 1.1067910000 2.4798420000

H	-1.8090900000	-0.0720910000	3.7397180000
H	-0.5936460000	0.4344330000	2.5435320000
C	-1.5791270000	-1.1450100000	-2.5839130000
H	-0.4989930000	-1.3360980000	-2.5036750000
H	-1.9676680000	-1.7124460000	-3.4461510000
H	-1.7112730000	-0.0729740000	-2.8018570000
C	-3.8274970000	-1.3850020000	-1.5773130000
H	-4.0663700000	-0.4036310000	-2.0078570000
H	-4.1374860000	-2.1420980000	-2.3172030000
H	-4.4460780000	-1.5419740000	-0.6826760000
C	-2.0629940000	-3.0299020000	-0.9906070000
H	-2.7578070000	-3.4036200000	-0.2235890000
H	-2.2347680000	-3.6320930000	-1.8984050000
H	-1.0424350000	-3.2344700000	-0.6382840000
Pd	0.8249440000	-0.2766570000	-0.0814800000
C	2.7439640000	0.2926220000	-0.0402510000
C	3.2232620000	0.9724570000	-1.1685520000
C	3.2312210000	0.6353280000	1.2292270000
C	4.1245650000	2.0254180000	-1.0204070000
H	2.8872490000	0.6738720000	-2.1640340000
C	4.1318860000	1.6904730000	1.3710960000
H	2.9051330000	0.0693690000	2.1053050000
C	4.5772440000	2.3895130000	0.2482820000
H	4.4812000000	2.5614950000	-1.9037340000
H	4.4959600000	1.9616970000	2.3653810000
H	5.2906670000	3.2093670000	0.3611390000
C	2.5232100000	-1.6943160000	-0.3148870000
F	3.2405060000	-1.7154420000	-1.4668930000
F	3.3145880000	-2.0567600000	0.7045080000
H	0.5127330000	3.8351560000	0.9473530000
H	1.8117150000	2.7369970000	0.3947720000
C	1.3783950000	-2.6421650000	-0.4543270000

O 1.0162530000 -3.4279590000 0.4007850000

H 0.9675270000 -2.6473720000 -1.4924900000

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cis-Pd-CF2CO2Me-GS

C 2.3590530000 -1.7958400000 -0.1395720000

C 2.7603110000 -0.4457150000 -0.1671030000

C 4.1186700000 -0.1805610000 -0.3787320000

C 5.0476680000 -1.1992690000 -0.5691340000

C 4.6246350000 -2.5240200000 -0.5380820000

C 3.2848750000 -2.8262810000 -0.3186390000

H 4.4679270000 0.8502720000 -0.3848010000

H 6.0986740000 -0.9551430000 -0.7346080000

H 5.3400520000 -3.3362280000 -0.6857550000

H 2.9578150000 -3.8656290000 -0.3010020000

P 1.4749950000 0.8435200000 0.1311310000

O 1.0419610000 -2.0590540000 0.0767890000

C 0.6719060000 -3.3084950000 0.6491690000

H 1.3360280000 -3.5384220000 1.4970440000

C 1.8505310000 2.2762080000 -1.0469830000

C 1.7491200000 1.2855020000 1.9485860000

C 3.2096890000 1.5040390000 2.3335000000

H 3.6753900000 2.3371830000 1.7904140000

H 3.2655990000 1.7457640000 3.4083560000

H 3.8173550000 0.6025470000 2.1702830000

C 0.9187690000 2.5241870000 2.2848300000

H -0.1184680000 2.4381050000 1.9292410000

H 0.8892970000 2.6565030000 3.3791720000

H 1.3533180000 3.4408200000 1.8606920000

C 1.2067960000 0.0811310000 2.7255640000

H 0.1494480000 -0.1192730000 2.4925920000

H 1.7784450000 -0.8345600000 2.5097690000

H 1.2914180000 0.2742500000 3.8078710000

C	0.6163780000	3.1836350000	-1.0726910000
H	-0.2938690000	2.6370960000	-1.3452080000
H	0.4286770000	3.6768620000	-0.1099450000
H	0.7764030000	3.9765250000	-1.8221010000
C	1.9983840000	1.6270250000	-2.4265550000
H	1.1452730000	0.9643750000	-2.6474940000
H	2.0202450000	2.4129810000	-3.1991700000
H	2.9199790000	1.0351920000	-2.5202700000
C	3.0665530000	3.1434400000	-0.7246350000
H	4.0191220000	2.5990390000	-0.7175970000
H	3.1558080000	3.9219840000	-1.5005950000
H	2.9598420000	3.6649410000	0.2368280000
Pd	-0.5142970000	-0.4066890000	-0.3038090000
C	-1.9025420000	0.9984050000	-0.2975380000
C	-2.3778080000	1.4746420000	0.9328450000
C	-2.4578290000	1.5278520000	-1.4692180000
C	-3.3582050000	2.4673960000	0.9903650000
H	-1.9911850000	1.0607240000	1.8688930000
C	-3.4308910000	2.5256230000	-1.4116410000
H	-2.1383580000	1.1485530000	-2.4425790000
C	-3.8840660000	3.0033280000	-0.1830130000
H	-3.7120340000	2.8221480000	1.9627780000
H	-3.8452900000	2.9281530000	-2.3403260000
H	-4.6490770000	3.7825880000	-0.1406590000
C	-2.0310620000	-1.6840120000	-0.8433130000
F	-1.4364510000	-2.8833210000	-1.1651910000
F	-2.7463020000	-1.3297850000	-1.9379760000
H	-0.3628790000	-3.2024240000	0.9959570000
H	0.7178970000	-4.1143580000	-0.0978360000
C	-2.9177920000	-1.9075790000	0.3535050000
O	-2.5716520000	-2.5437800000	1.3239240000
O	-4.0656510000	-1.2495030000	0.2666980000

C -4.8469640000 -1.1990720000 1.4435910000

H -4.2737600000 -0.7654520000 2.2764670000

H -5.7074480000 -0.5596800000 1.2133110000

H -5.1884720000 -2.2032920000 1.7371110000

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trans-Pd-CF2CO2Me-GS

C -1.8606810000 2.2050410000 -0.2120800000

C -2.5971530000 1.0028210000 -0.2264350000

C -3.9841660000 1.1006140000 -0.4024470000

C -4.6279120000 2.3203390000 -0.5843950000

C -3.8744890000 3.4878240000 -0.5975430000

C -2.4975500000 3.4348930000 -0.4099480000

H -4.5856370000 0.1943200000 -0.3971540000

H -5.7107180000 2.3530430000 -0.7184430000

H -4.3554920000 4.4567670000 -0.7495220000

H -1.9253740000 4.3608620000 -0.4178000000

P -1.7252750000 -0.6012200000 0.0461510000

O -0.5177160000 2.1367960000 0.0147210000

C 0.2022370000 3.3466090000 0.1969480000

H 0.2431120000 3.9236500000 -0.7398820000

C -2.0918170000 -1.6080460000 -1.5223730000

C -2.5256670000 -1.2919190000 1.6184090000

C -3.9420050000 -1.8368170000 1.4564500000

H -4.2968620000 -2.2091510000 2.4322800000

H -4.6599970000 -1.0713800000 1.1326240000

H -3.9885070000 -2.6817980000 0.7548400000

C -1.6161340000 -2.3948710000 2.1659260000

H -2.0343640000 -2.7575150000 3.1198390000

H -1.5329960000 -3.2553520000 1.4897900000

H -0.5998380000 -2.0249360000 2.3574160000

C -2.5201640000 -0.1312110000 2.6178090000

H -3.2265880000 0.6650780000 2.3428780000

H	-2.8062460000	-0.5079940000	3.6136390000
H	-1.5159120000	0.3147920000	2.7077610000
C	-1.1144900000	-1.0409930000	-2.5589890000
H	-0.0663830000	-1.2260170000	-2.2770420000
H	-1.2952020000	-1.5264980000	-3.5328990000
H	-1.2527800000	0.0433270000	-2.7018120000
C	-3.5138670000	-1.4945960000	-2.0676660000
H	-3.7552120000	-0.4764710000	-2.4013320000
H	-3.5990870000	-2.1511020000	-2.9496580000
H	-4.2792860000	-1.8239120000	-1.3502930000
C	-1.7689530000	-3.0829470000	-1.2823990000
H	-2.4795190000	-3.5592990000	-0.5906480000
H	-1.8458500000	-3.6184250000	-2.2431960000
H	-0.7513910000	-3.2259340000	-0.9032710000
Pd	0.5467330000	0.1060690000	0.2307230000
C	2.3660400000	0.9859690000	0.2164680000
C	2.8812640000	1.4531890000	-1.0032760000
C	3.0745850000	1.2877570000	1.3878240000
C	4.0483720000	2.2195440000	-1.0484740000
H	2.3683630000	1.2106800000	-1.9399050000
C	4.2393830000	2.0558000000	1.3467270000
H	2.7198960000	0.9046250000	2.3486560000
C	4.7293770000	2.5263120000	0.1286730000
H	4.4292040000	2.5765860000	-2.0099600000
H	4.7740550000	2.2828660000	2.2736460000
H	5.6436900000	3.1245630000	0.0965670000
C	1.5792020000	-1.5809390000	0.4921140000
F	2.1295430000	-1.6383720000	1.7325570000
F	0.7905680000	-2.7030790000	0.4086140000
H	-0.2576450000	3.9492860000	0.9954030000
H	1.2182300000	3.0630380000	0.4879720000
C	2.6361750000	-1.7390190000	-0.5909710000

O 2.3558610000 -1.9325100000 -1.7478340000

O 3.8715650000 -1.6217400000 -0.1269090000

C 4.8946540000 -1.5735140000 -1.1029340000

H 4.7257070000 -0.7370850000 -1.7970960000

H 5.8325750000 -1.4188050000 -0.5564560000

H 4.9393700000 -2.5110570000 -1.6773510000

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cis-Pd-CF2CO2Me-TS

C 2.5830230000 -1.2980060000 -0.9554840000

C 2.7387150000 -0.1056410000 -0.2090000000

C 4.0387270000 0.2898170000 0.1261670000

C 5.1582240000 -0.4496410000 -0.2459380000

C 4.9832540000 -1.6175490000 -0.9802490000

C 3.7070450000 -2.0421920000 -1.3358000000

H 4.1845070000 1.2067030000 0.6966640000

H 6.1574380000 -0.1112500000 0.0346390000

H 5.8478170000 -2.2121740000 -1.2851310000

H 3.5882690000 -2.9603730000 -1.9102460000

P 1.2394410000 0.8392280000 0.2804440000

O 1.3305810000 -1.6704740000 -1.2774260000

C 1.1120890000 -2.8193920000 -2.0600790000

H 1.4777120000 -3.7289260000 -1.5560870000

C 1.3063340000 2.3725310000 -0.8248270000

C 1.4466690000 1.2413640000 2.1251040000

C 2.3891540000 2.3858280000 2.4889380000

H 2.0431520000 3.3499300000 2.0903260000

H 2.4234930000 2.4867900000 3.5869620000

H 3.4229050000 2.2248420000 2.1551060000

C 0.0461470000 1.5690110000 2.6554810000

H -0.6378200000 0.7215280000 2.5024500000

H 0.1056740000 1.7792430000 3.7368210000

H -0.4019880000 2.4455870000 2.1678240000

C	1.9093310000	-0.0587450000	2.7876980000
H	1.2682240000	-0.9052040000	2.4900300000
H	2.9478590000	-0.3164450000	2.5372500000
H	1.8384630000	0.0429680000	3.8834490000
C	0.1787060000	3.3145250000	-0.4017890000
H	-0.7861450000	2.7917490000	-0.3243320000
H	0.3875860000	3.8068490000	0.5596370000
H	0.0652630000	4.1110630000	-1.1557180000
C	1.0162300000	1.8354870000	-2.2299550000
H	0.0423290000	1.3259510000	-2.2731190000
H	0.9970040000	2.6740580000	-2.9460700000
H	1.7911390000	1.1283920000	-2.5649170000
C	2.6415660000	3.1107820000	-0.8503360000
H	3.4550440000	2.4745730000	-1.2273240000
H	2.5603870000	3.9716380000	-1.5355380000
H	2.9352720000	3.5073660000	0.1304580000
Pd	-0.7229220000	-0.3952400000	-0.0818620000
C	-2.4764950000	0.5705520000	-0.3469360000
C	-3.0226690000	1.3108330000	0.7160180000
C	-2.7020050000	1.0115450000	-1.6608070000
C	-3.6821970000	2.5103830000	0.4707650000
H	-2.9154640000	0.9493130000	1.7404030000
C	-3.3629400000	2.2164350000	-1.8979100000
H	-2.3534390000	0.4072390000	-2.5009730000
C	-3.8454540000	2.9771690000	-0.8354940000
H	-4.0758650000	3.0884470000	1.3111400000
H	-3.5054260000	2.5575130000	-2.9267530000
H	-4.3643770000	3.9200880000	-1.0227810000
C	-2.6837770000	-1.3689010000	-0.1972150000
F	-2.9583670000	-1.7518600000	-1.4589130000
F	-3.8546090000	-1.2801230000	0.4798670000
H	0.0262540000	-2.9052960000	-2.1757090000

H 1.5919290000 -2.7226860000 -3.0488580000

C -1.8528010000 -2.4560330000 0.4700740000

O -1.2387870000 -3.3123820000 -0.1257630000

O -1.9110460000 -2.3706230000 1.8045530000

C -1.1062920000 -3.2997170000 2.5069340000

H -1.1934230000 -3.0404540000 3.5688470000

H -1.4580240000 -4.3292920000 2.3421430000

H -0.0556630000 -3.2340890000 2.1867310000

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cis-Pd-CF2CO2Me-TS-rot

C -2.6151450000 -1.8987280000 -0.2558790000

C -2.9450290000 -0.5267570000 -0.3556260000

C -4.2429720000 -0.2020960000 -0.7644490000

C -5.1866340000 -1.1751400000 -1.0844060000

C -4.8361530000 -2.5167720000 -0.9882730000

C -3.5582750000 -2.8815170000 -0.5743460000

H -4.5301790000 0.8462900000 -0.8341590000

H -6.1889170000 -0.8823880000 -1.4030340000

H -5.5611620000 -3.2965550000 -1.2333430000

H -3.3010800000 -3.9377990000 -0.5013580000

P -1.6479130000 0.7181820000 0.0505230000

O -1.3676420000 -2.2098960000 0.1650560000

C -0.9850040000 -3.5572020000 0.3022200000

H -1.0206130000 -4.0880180000 -0.6638520000

C -2.1517450000 1.2778810000 1.7890090000

C -1.7930310000 2.1115360000 -1.2281690000

C -2.9638220000 3.0829640000 -1.0959740000

H -2.9270420000 3.6499700000 -0.1550860000

H -2.9073900000 3.8205660000 -1.9144840000

H -3.9496110000 2.6052370000 -1.1711780000

C -0.4878580000 2.9114220000 -1.1363880000

H 0.3929920000 2.2681950000 -1.2590680000

H	-0.4735290000	3.6703640000	-1.9366900000
H	-0.3800470000	3.4406950000	-0.1804150000
C	-1.8280430000	1.4113520000	-2.5891470000
H	-1.0133320000	0.6735560000	-2.6745810000
H	-2.7779490000	0.8894580000	-2.7729780000
H	-1.6905160000	2.1577660000	-3.3890420000
C	-1.2692120000	2.4591140000	2.1919380000
H	-0.2045750000	2.2516880000	2.0027390000
H	-1.5406960000	3.3832470000	1.6611660000
H	-1.3901090000	2.6571980000	3.2702480000
C	-1.8265050000	0.0843460000	2.6925580000
H	-0.7596420000	-0.1852050000	2.6354170000
H	-2.0654110000	0.3390650000	3.7389390000
H	-2.4157760000	-0.8061460000	2.4248510000
C	-3.6279680000	1.6288940000	1.9510610000
H	-4.2784480000	0.7690400000	1.7350450000
H	-3.8176940000	1.9263070000	2.9966050000
H	-3.9421720000	2.4669290000	1.3150640000
Pd	0.3843060000	-0.4033060000	0.0890290000
C	2.1347280000	0.5588160000	0.0160460000
C	2.5781640000	0.9363660000	-1.2733990000
C	2.4656870000	1.3975950000	1.1019500000
C	3.2204000000	2.1536330000	-1.4726320000
H	2.3984520000	0.2703950000	-2.1201400000
C	3.1057050000	2.6131440000	0.8874630000
H	2.2047690000	1.0882770000	2.1160970000
C	3.4803660000	3.0063420000	-0.3981170000
H	3.5212650000	2.4408870000	-2.4839550000
H	3.3219790000	3.2609610000	1.7412530000
H	3.9907440000	3.9585010000	-0.5586760000
C	2.4498320000	-1.2507380000	0.4614530000
F	2.0287060000	-2.4133670000	-0.1752400000

F 2.2838100000 -1.4485950000 1.7891830000

H 0.0505530000 -3.5454540000 0.6598530000

H -1.6200590000 -4.0813010000 1.0359120000

C 3.9626150000 -1.1827540000 0.2129870000

O 4.7616890000 -0.8743400000 1.0506390000

O 4.2526240000 -1.4921220000 -1.0454710000

C 5.6022540000 -1.2956570000 -1.4258940000

H 5.6722680000 -1.5920050000 -2.4792620000

H 5.8841980000 -0.2377270000 -1.3115550000

H 6.2791890000 -1.9103870000 -0.8147310000

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trans-Pd-CF2CO2Me-TS

C -1.8235320000 2.2108950000 -0.4955360000

C -2.5137530000 1.0205710000 -0.1711890000

C -3.9062770000 1.0972990000 -0.0417110000

C -4.6072000000 2.2871690000 -0.2159730000

C -3.9059420000 3.4454270000 -0.5305630000

C -2.5225800000 3.4116770000 -0.6700270000

H -4.4665120000 0.1978350000 0.2066850000

H -5.6929580000 2.3048650000 -0.1040230000

H -4.4342290000 4.3915990000 -0.6702540000

H -1.9882410000 4.3285940000 -0.9154320000

P -1.5626260000 -0.5326890000 0.1279520000

O -0.4810670000 2.1434390000 -0.6276420000

C 0.2607290000 3.3172830000 -0.8644520000

H -0.0273200000 3.7859490000 -1.8200870000

C -2.1545090000 -1.6980880000 -1.2425850000

C -2.0912900000 -1.0910160000 1.8633480000

C -3.4905940000 -1.6848340000 1.9996070000

H -3.6549580000 -1.9756830000 3.0509960000

H -4.2884870000 -0.9752120000 1.7430240000

H -3.6208100000 -2.5931060000 1.3942420000

C	-1.0597410000	-2.1194420000	2.3371900000
H	-1.2827180000	-2.3943830000	3.3820930000
H	-1.0674530000	-3.0421220000	1.7433110000
H	-0.0381780000	-1.7169170000	2.2985000000
C	-1.9604400000	0.1557820000	2.7424960000
H	-2.7289050000	0.9105160000	2.5216130000
H	-2.0606570000	-0.1323260000	3.8020800000
H	-0.9711860000	0.6271350000	2.6171660000
C	-1.4092110000	-1.2030810000	-2.4867610000
H	-0.3178850000	-1.2284210000	-2.3420910000
H	-1.6648090000	-1.8368060000	-3.3529850000
H	-1.6857880000	-0.1669090000	-2.7396060000
C	-3.6521190000	-1.6965910000	-1.5367840000
H	-4.0025980000	-0.7222210000	-1.9042390000
H	-3.8593070000	-2.4359070000	-2.3291560000
H	-4.2591430000	-1.9818720000	-0.6660970000
C	-1.7020400000	-3.1172570000	-0.8989230000
H	-2.3232810000	-3.5649600000	-0.1092820000
H	-1.8092460000	-3.7585880000	-1.7904400000
H	-0.6545420000	-3.1646220000	-0.5687310000
Pd	0.7274000000	0.0526260000	0.0544590000
C	2.5313260000	0.8746750000	0.1949970000
C	3.1790640000	1.2184000000	-1.0029770000
C	2.7109310000	1.6723160000	1.3328010000
C	3.9290490000	2.3897440000	-1.0756720000
H	3.0897730000	0.5614290000	-1.8714670000
C	3.4603880000	2.8462800000	1.2493330000
H	2.2582660000	1.3711530000	2.2810230000
C	4.0651960000	3.2102880000	0.0468110000
H	4.4154630000	2.6642900000	-2.0155240000
H	3.5788980000	3.4772140000	2.1342440000
H	4.6585200000	4.1258820000	-0.0129840000

C 2.5309150000 -1.0732400000 0.6125340000

F 3.8842200000 -1.0925690000 0.3818490000

F 2.3881360000 -1.2411550000 1.9415810000

H 0.1383260000 4.0419650000 -0.0429600000

H 1.3116490000 3.0123660000 -0.9201380000

C 1.9956850000 -2.2760590000 -0.1370590000

O 1.4313940000 -3.2176940000 0.3605750000

O 2.3241730000 -2.1918710000 -1.4334250000

C 1.9823090000 -3.3054960000 -2.2360110000

H 2.4134100000 -3.1134420000 -3.2260090000

H 2.3967570000 -4.2349890000 -1.8181780000

H 0.8917560000 -3.4164540000 -2.3239980000

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cis-Pd-CF2C(O)F-GS

C 2.3150370000 -1.6297450000 -0.3140300000

C 2.5846410000 -0.2471870000 -0.3307660000

C 3.8796640000 0.1519680000 -0.6813290000

C 4.8690910000 -0.7664630000 -1.0196620000

C 4.5744220000 -2.1251670000 -1.0010530000

C 3.3023520000 -2.5604630000 -0.6440190000

H 4.1312590000 1.2103770000 -0.6829330000

H 5.8669590000 -0.4173270000 -1.2913560000

H 5.3376310000 -2.8605680000 -1.2653090000

H 3.0774560000 -3.6264460000 -0.6360150000

P 1.2273490000 0.9037250000 0.1546850000

O 1.0620670000 -2.0248600000 0.0475930000

C 0.8788000000 -3.3430660000 0.5499210000

H 1.6559930000 -3.5673150000 1.2970110000

C 1.3997860000 2.4563820000 -0.9152520000

C 1.5989080000 1.2289420000 1.9815720000

C 3.0691990000 1.5213850000 2.2699920000

H 3.4348090000 2.4226470000 1.7601660000

H	3.1966130000	1.6868740000	3.3530320000
H	3.7184910000	0.6796450000	1.9895670000
C	0.7201900000	2.3786340000	2.4741370000
H	-0.3341320000	2.2458540000	2.1909650000
H	0.7687590000	2.4261900000	3.5745740000
H	1.0584870000	3.3529990000	2.0939350000
C	1.1978420000	-0.0587790000	2.7085300000
H	0.1378980000	-0.3115250000	2.5481370000
H	1.8037590000	-0.9184600000	2.3853330000
H	1.3599530000	0.0686100000	3.7916240000
C	0.1112490000	3.2739940000	-0.7698960000
H	-0.7800780000	2.6982770000	-1.0420610000
H	-0.0369390000	3.6617500000	0.2459040000
H	0.1723400000	4.1427060000	-1.4460180000
C	1.4818290000	1.9418630000	-2.3558320000
H	0.6608240000	1.2400330000	-2.5751480000
H	1.3881050000	2.7917240000	-3.0513590000
H	2.4306820000	1.4313570000	-2.5728600000
C	2.5721760000	3.3868040000	-0.6027020000
H	3.5619500000	2.9245420000	-0.7015260000
H	2.5461950000	4.2277050000	-1.3154470000
H	2.4959000000	3.8223420000	0.4033050000
Pd	-0.6640820000	-0.5153560000	-0.1869300000
C	-2.1149480000	0.8154110000	-0.2481560000
C	-2.6094260000	1.3827680000	0.9321740000
C	-2.6561430000	1.2353120000	-1.4699420000
C	-3.5862780000	2.3792370000	0.8896860000
H	-2.2407280000	1.0434920000	1.9040300000
C	-3.6290940000	2.2340590000	-1.5106320000
H	-2.3180400000	0.7794950000	-2.4035550000
C	-4.0917220000	2.8175120000	-0.3321720000
H	-3.9561220000	2.8122760000	1.8232840000

H -4.0310540000 2.5562760000 -2.4752550000

H -4.8530430000 3.6006690000 -0.3655360000

C -2.1155400000 -1.9334690000 -0.5697650000

F -1.4686460000 -3.0520210000 -1.0331810000

F -3.0604520000 -1.6373150000 -1.4913120000

H -0.1108070000 -3.3694100000 1.0185620000

H 0.9087540000 -4.0836610000 -0.2624630000

C -2.7294210000 -2.2588700000 0.7542050000

O -2.2720930000 -2.9650240000 1.5988550000

F -3.8453250000 -1.5648770000 0.9738550000

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trans-Pd-CF2C(O)F-GS

C 1.5444540000 2.2850950000 -0.1234810000

C 2.3735740000 1.1453200000 -0.1086920000

C 3.7584190000 1.3541310000 -0.1659110000

C 4.3162160000 2.6248740000 -0.2572050000

C 3.4757360000 3.7307400000 -0.2987660000

C 2.0966150000 3.5661850000 -0.2304290000

H 4.4265990000 0.4961760000 -0.1381360000

H 5.4002470000 2.7453240000 -0.2990660000

H 3.8890000000 4.7385880000 -0.3803920000

H 1.4568000000 4.4461230000 -0.2592720000

P 1.6160630000 -0.5287730000 0.0403610000

O 0.1955550000 2.1062670000 -0.0177410000

C -0.6281930000 3.2564280000 0.1149930000

H -0.2969810000 3.8680180000 0.9682280000

C 2.3608700000 -1.2382070000 1.6305050000

C 2.1592340000 -1.4275600000 -1.5419090000

C 3.6000370000 -1.1809340000 -1.9837610000

H 3.7928440000 -1.7805130000 -2.8890040000

H 3.7835310000 -0.1310750000 -2.2486880000

H 4.3399990000 -1.4914630000 -1.2324080000

C	1.9368340000	-2.9321990000	-1.3890910000
H	2.1065090000	-3.4140740000	-2.3662160000
H	2.6427530000	-3.3881120000	-0.6794480000
H	0.9153270000	-3.1696170000	-1.0725600000
C	1.2116360000	-0.8817220000	-2.6163420000
H	1.2877160000	0.2136110000	-2.7120020000
H	1.4750260000	-1.3175720000	-3.5946250000
H	0.1630070000	-1.1348150000	-2.3993550000
C	2.2077620000	-0.1310160000	2.6777460000
H	1.1701430000	0.2391460000	2.7217270000
H	2.4571590000	-0.5357190000	3.6723600000
H	2.8701480000	0.7252280000	2.4861340000
C	3.8198760000	-1.6774070000	1.5407900000
H	4.5027640000	-0.8506300000	1.3037460000
H	4.1346800000	-2.0743580000	2.5204750000
H	3.9721730000	-2.4807460000	0.8060870000
C	1.4984050000	-2.4266630000	2.0639220000
H	1.5165160000	-3.2542250000	1.3432220000
H	1.8825200000	-2.8113290000	3.0233490000
H	0.4497720000	-2.1355300000	2.2110500000
Pd	-0.7133930000	-0.0029410000	0.1225520000
C	-2.5909190000	0.7355130000	0.1061240000
C	-3.2981340000	0.9759940000	1.2920580000
C	-3.1416810000	1.1935900000	-1.1005740000
C	-4.4957280000	1.6925330000	1.2782840000
H	-2.9124420000	0.5948450000	2.2418450000
C	-4.3422280000	1.9054260000	-1.1168270000
H	-2.6295030000	0.9932590000	-2.0471330000
C	-5.0185580000	2.1631440000	0.0744330000
H	-5.0293530000	1.8778370000	2.2148090000
H	-4.7539280000	2.2570190000	-2.0670960000
H	-5.9595000000	2.7191510000	0.0634950000

C -1.6237940000 -1.7603660000 0.3399590000

F -0.7875300000 -2.8330730000 0.1097460000

F -2.0774590000 -1.9288050000 1.6062060000

H -0.6158840000 3.8536210000 -0.8097560000

H -1.6441150000 2.8939450000 0.2961930000

C -2.7899720000 -1.9659080000 -0.6055610000

O -3.9263000000 -2.1528950000 -0.3502910000

F -2.3522590000 -1.9374720000 -1.8779220000

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cis-Pd-CF2C(O)F-TS

C 2.5607220000 -1.4265600000 -0.7521830000

C 2.7031330000 -0.1360450000 -0.1891470000

C 3.9991990000 0.3355760000 0.0480800000

C 5.1282390000 -0.4248050000 -0.2436730000

C 4.9664220000 -1.6925330000 -0.7922500000

C 3.6940330000 -2.1940080000 -1.0475300000

H 4.1332380000 1.3285720000 0.4769720000

H 6.1247110000 -0.0266910000 -0.0434390000

H 5.8389600000 -2.3061860000 -1.0288850000

H 3.5863170000 -3.1892510000 -1.4777880000

P 1.1943130000 0.8290440000 0.2148300000

O 1.3104240000 -1.8640860000 -0.9918080000

C 1.0981590000 -3.1430890000 -1.5379460000

H 1.4947210000 -3.9351810000 -0.8826120000

C 1.1587010000 2.1725260000 -1.1141980000

C 1.4388400000 1.5092620000 1.9683210000

C 2.3324070000 2.7382170000 2.1161030000

H 1.9206200000 3.6158450000 1.5979540000

H 2.4052660000 3.0014360000 3.1847930000

H 3.3589320000 2.5775270000 1.7601160000

C 0.0395190000 1.8488700000 2.4964020000

H -0.5992740000 0.9533950000 2.5199690000

H	0.1235630000	2.2401550000	3.5242650000
H	-0.4742150000	2.6078920000	1.8902010000
C	1.9899660000	0.3474550000	2.7993580000
H	1.3955810000	-0.5695980000	2.6528190000
H	3.0361660000	0.1135380000	2.5581890000
H	1.9382880000	0.6083560000	3.8693840000
C	0.0028400000	3.1237470000	-0.8035140000
H	-0.9375790000	2.5822790000	-0.6227980000
H	0.2115910000	3.7610620000	0.0685100000
H	-0.1601000000	3.7944260000	-1.6632920000
C	0.8557190000	1.4139590000	-2.4101730000
H	-0.0948600000	0.8646450000	-2.3444720000
H	0.7778910000	2.1313330000	-3.2441070000
H	1.6530950000	0.6971320000	-2.6603250000
C	2.4605810000	2.9478790000	-1.2946900000
H	3.2919120000	2.2909620000	-1.5880520000
H	2.3281450000	3.6837360000	-2.1058190000
H	2.7580050000	3.5074020000	-0.3982010000
Pd	-0.7346950000	-0.5270250000	0.1283200000
C	-2.5239470000	0.3112140000	-0.3210890000
C	-3.0952000000	1.2071840000	0.5975440000
C	-2.7786020000	0.4840400000	-1.6890680000
C	-3.8198650000	2.3046310000	0.1448150000
H	-2.9553050000	1.0515690000	1.6690380000
C	-3.5068450000	1.5872530000	-2.1340120000
H	-2.4028310000	-0.2474320000	-2.4077650000
C	-4.0200230000	2.5068430000	-1.2224300000
H	-4.2347520000	3.0107380000	0.8688620000
H	-3.6774640000	1.7221400000	-3.2052190000
H	-4.5907200000	3.3698470000	-1.5729090000
C	-2.6225170000	-1.5802260000	0.1842040000
F	-2.8044680000	-2.2411120000	-0.9738270000

F -3.8229210000 -1.4437860000 0.7920740000

H 0.0117390000 -3.2659300000 -1.6099290000

H 1.5486860000 -3.2274780000 -2.5415060000

C -1.7182780000 -2.3698320000 1.0918960000

O -0.9855180000 -3.2718160000 0.8059990000

F -1.8823390000 -1.9907580000 2.3760210000

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cis-Pd-CF2C(O)F-TS-rot

C -2.5353360000 -1.7887510000 -0.2877130000

C -2.8078350000 -0.4011280000 -0.2672550000

C -4.1113110000 0.0057250000 -0.5728580000

C -5.1140250000 -0.9017090000 -0.9051630000

C -4.8190010000 -2.2598300000 -0.9286050000

C -3.5372450000 -2.7060980000 -0.6201800000

H -4.3549110000 1.0671540000 -0.5499140000

H -6.1186240000 -0.5456530000 -1.1411940000

H -5.5907890000 -2.9889120000 -1.1863450000

H -3.3238190000 -3.7743840000 -0.6405720000

P -1.4374680000 0.7604790000 0.1454380000

O -1.2803210000 -2.1826890000 0.0338840000

C -0.9461710000 -3.5504860000 0.0343780000

H -1.0530130000 -3.9928990000 -0.9701030000

C -1.8336670000 1.2492540000 1.9318300000

C -1.5676360000 2.2211490000 -1.0559160000

C -2.6871230000 3.2343210000 -0.8283700000

H -2.5909770000 3.7490580000 0.1380820000

H -2.6269740000 4.0108630000 -1.6096570000

H -3.6952850000 2.8038190000 -0.8911440000

C -0.2242940000 2.9570420000 -0.9804860000

H 0.6201890000 2.2812580000 -1.1666070000

H -0.2040900000 3.7492240000 -1.7476240000

H -0.0581160000 3.4388210000 -0.0079460000

C	-1.6900220000	1.5910760000	-2.4458100000
H	-0.9121300000	0.8259070000	-2.6034110000
H	-2.6687700000	1.1185570000	-2.6113100000
H	-1.5546950000	2.3699580000	-3.2144040000
C	-0.8773800000	2.3654730000	2.3514380000
H	0.1664770000	2.1210100000	2.1007160000
H	-1.1285200000	3.3279670000	1.8825410000
H	-0.9386390000	2.5108230000	3.4430130000
C	-1.5264380000	-0.0053610000	2.7553310000
H	-0.4764090000	-0.3178310000	2.6379590000
H	-1.7098000000	0.2008280000	3.8232900000
H	-2.1664590000	-0.8534020000	2.4666070000
C	-3.2815460000	1.6602450000	2.1839030000
H	-3.9829960000	0.8433890000	1.9611420000
H	-3.4059370000	1.9139730000	3.2504920000
H	-3.5840940000	2.5428060000	1.6049990000
Pd	0.5253600000	-0.4847680000	0.0049620000
C	2.3134570000	0.3839610000	-0.1695660000
C	2.6820490000	0.7775400000	-1.4755130000
C	2.7560120000	1.1764920000	0.9151600000
C	3.3511430000	1.9786290000	-1.6886640000
H	2.4208190000	0.1390630000	-2.3221730000
C	3.4187660000	2.3755390000	0.6856230000
H	2.5574220000	0.8489500000	1.9384800000
C	3.7120940000	2.7924340000	-0.6154010000
H	3.5949640000	2.2807750000	-2.7105910000
H	3.7174070000	2.9926470000	1.5371650000
H	4.2422150000	3.7315600000	-0.7873350000
C	2.5644630000	-1.4720570000	0.0248410000
F	2.4401130000	-2.1340920000	-1.1551560000
F	2.0859440000	-2.3049900000	1.0182980000
H	0.1045100000	-3.6063300000	0.3416750000

H -1.5625580000 -4.1137040000 0.7546180000

C 4.0578090000 -1.3687610000 0.3439540000

O 4.5457160000 -1.4206680000 1.4181610000

F 4.7823150000 -1.2103030000 -0.7582940000

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trans-Pd-CF2C(O)F-TS

C -1.5420200000 2.3136170000 -0.2379290000

C -2.3453920000 1.1636490000 -0.0693340000

C -3.7262870000 1.3555120000 0.0681480000

C -4.3099520000 2.6185380000 0.0397720000

C -3.4991510000 3.7346230000 -0.1301460000

C -2.1231310000 3.5872220000 -0.2674130000

H -4.3718700000 0.4903250000 0.2053480000

H -5.3905740000 2.7250860000 0.1516110000

H -3.9342630000 4.7365020000 -0.1550290000

H -1.5027540000 4.4731130000 -0.3955820000

P -1.5540190000 -0.4990930000 0.0415540000

O -0.2069730000 2.1384360000 -0.3633550000

C 0.6350980000 3.2638530000 -0.4684600000

H 0.3977350000 3.8569330000 -1.3669160000

C -2.2656120000 -1.4532950000 -1.4328020000

C -2.1146090000 -1.1698200000 1.7256600000

C -3.5627770000 -1.6417920000 1.8199130000

H -3.7526070000 -2.0125440000 2.8413500000

H -4.2902830000 -0.8396570000 1.6374540000

H -3.7769760000 -2.4733260000 1.1336790000

C -1.1812610000 -2.3293520000 2.0824620000

H -1.4356940000 -2.6985670000 3.0902700000

H -1.2599180000 -3.1754270000 1.3883350000

H -0.1286580000 -2.0126570000 2.0902610000

C -1.8647440000 -0.0328290000 2.7201320000

H -2.5624570000 0.8062980000 2.5872630000

H	-1.9840670000	-0.4150390000	3.7474250000
H	-0.8372920000	0.3575150000	2.6281070000
C	-1.4826690000	-0.9090720000	-2.6328040000
H	-0.4071360000	-1.1229890000	-2.5431160000
H	-1.8505360000	-1.3823880000	-3.5587110000
H	-1.6090430000	0.1799900000	-2.7436640000
C	-3.7580880000	-1.2691200000	-1.6958870000
H	-4.0094300000	-0.2332120000	-1.9617030000
H	-4.0445470000	-1.9017680000	-2.5529030000
H	-4.3854590000	-1.5772700000	-0.8476250000
C	-1.9597920000	-2.9409250000	-1.2587820000
H	-2.5864890000	-3.4037250000	-0.4822220000
H	-2.1806840000	-3.4635840000	-2.2044720000
H	-0.9082150000	-3.1382600000	-1.0112410000
Pd	0.7873540000	-0.1308670000	-0.0257910000
C	2.6769550000	0.5032300000	0.0926800000
C	3.2753060000	0.9512470000	-1.0958460000
C	3.0027650000	1.1177640000	1.3079310000
C	4.1321600000	2.0485490000	-1.0713370000
H	3.0653730000	0.4357650000	-2.0361950000
C	3.8593520000	2.2192410000	1.3229920000
H	2.5838230000	0.7304660000	2.2398660000
C	4.4212480000	2.6883110000	0.1364450000
H	4.5823460000	2.4055050000	-2.0012020000
H	4.0958500000	2.7079430000	2.2716450000
H	5.0995140000	3.5447080000	0.1530410000
C	2.5122330000	-1.4631900000	0.2397100000
F	3.7457650000	-1.6206970000	-0.3302140000
F	2.6413430000	-1.7126930000	1.5536960000
H	0.5648500000	3.9014930000	0.4277910000
H	1.6566870000	2.8803010000	-0.5575260000
C	1.6473580000	-2.5143380000	-0.3897180000

O 1.0746110000 -3.4157510000 0.1346040000

F 1.6964180000 -2.4117730000 -1.7362140000

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cis-Pd-C2F5-GS

C 2.1782380000 -1.9147590000 -0.2458040000

C 2.6741120000 -0.5965220000 -0.2235750000

C 4.0463150000 -0.4194500000 -0.4430570000

C 4.8931650000 -1.4891280000 -0.7188270000

C 4.3712410000 -2.7767560000 -0.7694530000

C 3.0191460000 -2.9945960000 -0.5252170000

H 4.4716770000 0.5797300000 -0.3814650000

H 5.9570220000 -1.3131480000 -0.8886530000

H 5.0184410000 -3.6278370000 -0.9930540000

H 2.6214170000 -4.0082410000 -0.5609040000

P 1.4978460000 0.7735220000 0.1429510000

O 0.8579650000 -2.1033760000 0.0390950000

C 0.4474610000 -3.3800380000 0.5076360000

H 1.1491420000 -3.7389130000 1.2765650000

C 1.8423350000 2.1313310000 -1.1295200000

C 1.9252160000 1.2266850000 1.9283700000

C 3.4151750000 1.3859840000 2.2152160000

H 3.8768470000 2.1916830000 1.6268060000

H 3.5487760000 1.6476120000 3.2784090000

H 3.9760050000 0.4578740000 2.0363560000

C 1.1814270000 2.5025330000 2.3233420000

H 0.1345410000 2.4996610000 1.9887950000

H 1.1842720000 2.5967330000 3.4219350000

H 1.6673670000 3.4018920000 1.9211500000

C 1.3805590000 0.0483440000 2.7439270000

H 0.2947230000 -0.0752960000 2.6077260000

H 1.8665490000 -0.9011160000 2.4700410000

H 1.5755980000 0.2219800000 3.8151620000

C	0.9014710000	3.3081380000	-0.8461210000
H	-0.1214960000	2.9912120000	-0.6084710000
H	1.2706550000	3.9421930000	-0.0297330000
H	0.8479870000	3.9394760000	-1.7481760000
C	1.4536870000	1.4799300000	-2.4614010000
H	0.4046250000	1.1485210000	-2.4559350000
H	1.5763990000	2.2125780000	-3.2760750000
H	2.0859480000	0.6090230000	-2.6945240000
C	3.2677650000	2.6727450000	-1.2291330000
H	3.9704930000	1.9489590000	-1.6611470000
H	3.2605370000	3.5431720000	-1.9061880000
H	3.6623390000	3.0241930000	-0.2650730000
Pd	-0.5988210000	-0.3330940000	-0.1610460000
C	-1.7859360000	1.2400900000	-0.1856220000
C	-2.1687920000	1.8570880000	1.0129860000
C	-2.2309460000	1.7996760000	-1.3901920000
C	-2.9297600000	3.0270700000	1.0053160000
H	-1.8811130000	1.4192150000	1.9724070000
C	-2.9883590000	2.9713910000	-1.3973410000
H	-1.9920830000	1.3151370000	-2.3395930000
C	-3.3325290000	3.5971950000	-0.2007500000
H	-3.2120030000	3.4931640000	1.9535520000
H	-3.3141910000	3.3964360000	-2.3508390000
H	-3.9240420000	4.5159900000	-0.2071770000
C	-2.2527070000	-1.4471850000	-0.6329450000
F	-1.7943050000	-2.6767260000	-1.0733690000
F	-3.0275370000	-0.9791940000	-1.6479080000
H	-0.5449920000	-3.2499570000	0.9456100000
H	0.3814970000	-4.1052360000	-0.3164220000
C	-3.2162550000	-1.7841290000	0.5075710000
F	-4.1026420000	-2.7207710000	0.1617350000
F	-2.5337900000	-2.2618650000	1.5648250000

F -3.8918120000 -0.7174480000 0.9111120000

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trans-Pd-C2F5-GS

C 1.7671500000 2.2359030000 -0.2201450000

C 2.5226750000 1.0461420000 -0.2115420000

C 3.9082190000 1.1627170000 -0.3890060000

C 4.5295130000 2.3877960000 -0.6093660000

C 3.7550680000 3.5404460000 -0.6603400000

C 2.3804010000 3.4695560000 -0.4623060000

H 4.5266540000 0.2689110000 -0.3518840000

H 5.6116290000 2.4358980000 -0.7442130000

H 4.2179610000 4.5119520000 -0.8478070000

H 1.7907920000 4.3839770000 -0.4974190000

P 1.6714120000 -0.5621850000 0.0903600000

O 0.4292780000 2.1538260000 0.0353300000

C -0.2792730000 3.3587950000 0.2952810000

H 0.2508010000 3.9516040000 1.0562710000

C 2.4178680000 -1.1628260000 1.7249940000

C 2.1318910000 -1.6247570000 -1.4155000000

C 3.5842930000 -1.5554870000 -1.8841560000

H 3.7103210000 -2.2634370000 -2.7202670000

H 3.8546190000 -0.5618060000 -2.2649440000

H 4.3054460000 -1.8479650000 -1.1080350000

C 1.7735240000 -3.0850970000 -1.1385500000

H 1.8887110000 -3.6596750000 -2.0725120000

H 2.4425400000 -3.5432010000 -0.3948810000

H 0.7388240000 -3.2025330000 -0.7988540000

C 1.2326780000 -1.0814830000 -2.5315400000

H 1.4139080000 -0.0102720000 -2.7167760000

H 1.4458750000 -1.6201150000 -3.4700710000

H 0.1668640000 -1.2127480000 -2.2957500000

C 2.3427690000 0.0432460000 2.6664620000

H	1.3258150000	0.4683390000	2.6935940000
H	2.5942490000	-0.2791760000	3.6902350000
H	3.0425960000	0.8424970000	2.3833280000
C	3.8532170000	-1.6731820000	1.6413570000
H	4.5583160000	-0.9076200000	1.2900800000
H	4.1874170000	-1.9725690000	2.6490070000
H	3.9448120000	-2.5592880000	0.9970250000
C	1.5169850000	-2.2638100000	2.2892690000
H	1.4783790000	-3.1550090000	1.6496610000
H	1.9099990000	-2.5742310000	3.2717750000
H	0.4860010000	-1.9125020000	2.4296390000
Pd	-0.6381820000	0.1206850000	0.1710130000
C	-2.4160310000	1.0475420000	0.1226840000
C	-3.1363050000	1.3416940000	1.2874720000
C	-2.8333080000	1.6346250000	-1.0814910000
C	-4.2137060000	2.2299650000	1.2589460000
H	-2.8564450000	0.8682380000	2.2325490000
C	-3.9131660000	2.5175910000	-1.1132450000
H	-2.3080200000	1.4042210000	-2.0138770000
C	-4.6023310000	2.8247170000	0.0596400000
H	-4.7572900000	2.4547440000	2.1811790000
H	-4.2206130000	2.9675370000	-2.0616930000
H	-5.4471990000	3.5178230000	0.0366570000
C	-1.6685160000	-1.5664160000	0.4255430000
F	-0.8258750000	-2.6509580000	0.4949540000
F	-2.3448960000	-1.5840220000	1.6080400000
H	-0.4075880000	3.9464340000	-0.6264360000
H	-1.2645700000	3.0695150000	0.6724020000
C	-2.6909260000	-1.9741800000	-0.6589440000
F	-2.1787580000	-1.7929320000	-1.8815510000
F	-3.8202840000	-1.2896080000	-0.5736450000
F	-3.0030740000	-3.2691370000	-0.5506590000

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cis-Pd-C2F5-TS

C	2.4481950000	-1.7401300000	-0.6074300000
C	2.7883880000	-0.4443320000	-0.1536540000
C	4.1464320000	-0.1510760000	0.0181610000
C	5.1463460000	-1.0820290000	-0.2504700000
C	4.7890870000	-2.3466080000	-0.7044800000
C	3.4495300000	-2.6784970000	-0.8825840000
H	4.4347010000	0.8369510000	0.3759160000
H	6.1955090000	-0.8179560000	-0.1047030000
H	5.5570880000	-3.0927560000	-0.9218140000
H	3.1888590000	-3.6776430000	-1.2303840000
P	1.4399540000	0.7509400000	0.2213970000
O	1.1359570000	-2.0305240000	-0.7564490000
C	0.7456630000	-3.2625590000	-1.3130890000
H	-0.3434220000	-3.2161380000	-1.4240190000
C	1.6986800000	2.1629530000	-1.0089740000
C	1.7284860000	1.2646940000	2.0258680000
C	2.0226630000	-0.0320620000	2.7845110000
H	3.0190060000	-0.4360730000	2.5559430000
H	1.9743540000	0.1596340000	3.8693570000
H	1.2779070000	-0.8109200000	2.5507380000
C	2.8355580000	2.2830760000	2.2812150000
H	2.9188740000	2.4597950000	3.3671000000
H	3.8225120000	1.9413870000	1.9402660000
H	2.6222010000	3.2553030000	1.8145610000
C	0.3981870000	1.8250690000	2.5386870000
H	0.0627840000	2.7117500000	1.9831950000
H	-0.3967870000	1.0696590000	2.4630290000
H	0.5062190000	2.1125920000	3.5982870000
C	3.1073080000	2.7424310000	-1.1073660000
H	3.4750260000	3.1554580000	-0.1588730000

H	3.8318740000	2.0006290000	-1.4716320000
H	3.1009180000	3.5692090000	-1.8379170000
C	0.6935910000	3.2621620000	-0.6595730000
H	0.9788170000	3.8092990000	0.2513340000
H	0.6542240000	3.9971910000	-1.4805690000
H	-0.3221810000	2.8615520000	-0.5239400000
C	1.3292700000	1.5501460000	-2.3634620000
H	1.4172870000	2.3172620000	-3.1510980000
H	2.0001840000	0.7182020000	-2.6303920000
H	0.2959190000	1.1730920000	-2.3645400000
Pd	-0.6096120000	-0.3132880000	-0.0946220000
C	-2.2580120000	0.7773670000	-0.3348010000
C	-2.7331870000	1.5669130000	0.7324750000
C	-2.4454100000	1.2485360000	-1.6507010000
C	-3.2475910000	2.8351580000	0.4912050000
H	-2.6727930000	1.1895750000	1.7547520000
C	-2.9604020000	2.5219410000	-1.8783280000
H	-2.1723530000	0.6113810000	-2.4952830000
C	-3.3521760000	3.3290990000	-0.8114520000
H	-3.5738530000	3.4490740000	1.3351710000
H	-3.0618730000	2.8833900000	-2.9051700000
H	-3.7585440000	4.3265560000	-0.9927290000
C	-2.7484930000	-1.0496800000	-0.2601570000
F	-4.0784960000	-0.7495880000	-0.2325160000
F	-2.5678850000	-1.7341850000	-1.4271290000
H	1.2016720000	-3.4160110000	-2.3052980000
H	1.0045160000	-4.1069600000	-0.6526280000
C	-2.6226520000	-2.0673980000	0.9008760000
F	-1.4927350000	-2.7787930000	0.8236740000
F	-3.6273780000	-2.9384520000	0.8911680000
F	-2.6379760000	-1.4361130000	2.0732190000

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cis-Pd-C2F5-TS-rot

C	2.5578930000	-1.9128490000	0.2550550000
C	2.9243340000	-0.5476360000	0.3008480000
C	4.2435140000	-0.2436310000	0.6538200000
C	5.1737050000	-1.2303690000	0.9708480000
C	4.7872800000	-2.5648770000	0.9290510000
C	3.4870510000	-2.9093560000	0.5711550000
H	4.5586960000	0.7986140000	0.6802860000
H	6.1935860000	-0.9538410000	1.2448960000
H	5.5010840000	-3.3550970000	1.1734210000
H	3.2017100000	-3.9604420000	0.5411540000
P	1.6448200000	0.7156430000	-0.1002790000
O	1.2883550000	-2.2047890000	-0.1132390000
C	0.8807300000	-3.5476700000	-0.2263320000
H	0.9237790000	-4.0665690000	0.7457730000
C	2.0876750000	1.1936690000	-1.8789620000
C	1.8758320000	2.1521680000	1.1151420000
C	3.0669460000	3.0841040000	0.9027100000
H	3.0109300000	3.6153600000	-0.0578870000
H	3.0599270000	3.8539810000	1.6928140000
H	4.0420220000	2.5828030000	0.9616800000
C	0.5912830000	2.9861500000	1.0388990000
H	-0.3021860000	2.3746440000	1.2175900000
H	0.6273890000	3.7739470000	1.8099890000
H	0.4640850000	3.4833120000	0.0682310000
C	1.9421270000	1.5042130000	2.5006970000
H	1.1094860000	0.7964990000	2.6463980000
H	2.8821570000	0.9599760000	2.6696840000
H	1.8582620000	2.2850450000	3.2746550000
C	1.2196830000	2.3814940000	-2.2936380000
H	0.1582550000	2.2109600000	-2.0560590000
H	1.5353870000	3.3176010000	-1.8106550000

H 1.3030420000 2.5346220000 -3.3827200000

C 1.6965530000 -0.0253010000 -2.7202800000

H 0.6271670000 -0.2661160000 -2.6085250000

H 1.8959470000 0.1831390000 -3.7849260000

H 2.2760490000 -0.9191760000 -2.4429950000

C 3.5643920000 1.4992740000 -2.1129630000

H 4.2023030000 0.6331560000 -1.8848090000

H 3.7194440000 1.7467140000 -3.1770320000

H 3.9232940000 2.3556940000 -1.5269670000

Pd -0.4173260000 -0.3649460000 -0.0016370000

C -2.1328290000 0.6504560000 0.1130910000

C -2.4972080000 1.1182950000 1.3949820000

C -2.4771640000 1.4374680000 -1.0057640000

C -3.0925720000 2.3655470000 1.5481000000

H -2.2905780000 0.5046490000 2.2742470000

C -3.0655210000 2.6861660000 -0.8375800000

H -2.2646190000 1.0642920000 -2.0098690000

C -3.3719050000 3.1627660000 0.4374360000

H -3.3393470000 2.7207170000 2.5521560000

H -3.2924750000 3.2939460000 -1.7176460000

H -3.8428840000 4.1400830000 0.5635150000

C -2.4906630000 -1.1800450000 -0.2187270000

F -2.0272280000 -2.3426920000 0.4031530000

F -2.4569010000 -1.4143040000 -1.5552880000

H -0.1599850000 -3.5242690000 -0.5671710000

H 1.4950500000 -4.0908500000 -0.9635520000

C -3.9999440000 -1.2578140000 0.1542390000

F -4.4834260000 -2.4287590000 -0.2638480000

F -4.1640620000 -1.2003550000 1.4717260000

F -4.7224150000 -0.3045050000 -0.4103250000

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trans-Pd-C2F5-TS

C	-2.0378950000	2.1289520000	0.1574410000
C	-2.6343690000	0.8640940000	-0.0472550000
C	-4.0101310000	0.8345840000	-0.3045830000
C	-4.7800460000	1.9918500000	-0.3799310000
C	-4.1678070000	3.2253560000	-0.1897540000
C	-2.8050710000	3.2976540000	0.0790410000
H	-4.5011730000	-0.1255310000	-0.4537760000
H	-5.8498870000	1.9255380000	-0.5866390000
H	-4.7510980000	4.1474550000	-0.2473260000
H	-2.3405160000	4.2715970000	0.2283020000
P	-1.5844210000	-0.6543960000	0.0005760000
O	-0.7172080000	2.1585160000	0.4357610000
C	-0.0623280000	3.3928930000	0.6064950000
H	-0.1039730000	4.0024570000	-0.3110030000
C	-2.1008370000	-1.6650270000	-1.5256810000
C	-2.1086130000	-1.4617030000	1.6339460000
C	-3.6125120000	-1.5129320000	1.8884640000
H	-3.7951390000	-1.9971430000	2.8628400000
H	-4.0566790000	-0.5089320000	1.9376050000
H	-4.1556430000	-2.0965760000	1.1327710000
C	-1.5163950000	-2.8681450000	1.7078910000
H	-1.6698580000	-3.2742640000	2.7218150000
H	-2.0003350000	-3.5630130000	1.0058370000
H	-0.4367660000	-2.8696680000	1.5067710000
C	-1.4529390000	-0.5858280000	2.7065810000
H	-1.8189810000	0.4521580000	2.6683330000
H	-1.6888380000	-0.9859700000	3.7070860000
H	-0.3575140000	-0.5639500000	2.5918930000
C	-2.1123070000	-0.6728040000	-2.6915840000
H	-1.1821670000	-0.0809660000	-2.7171700000
H	-2.1811430000	-1.2267680000	-3.6425050000
H	-2.9579380000	0.0274560000	-2.6453870000

C -3.4249370000 -2.4226750000 -1.4556740000

H -4.3000510000 -1.7729530000 -1.3253120000

H -3.5756750000 -2.9643290000 -2.4048180000

H -3.4315200000 -3.1760100000 -0.6551290000

C -0.9792160000 -2.6770500000 -1.7788530000

H -0.8858230000 -3.4150160000 -0.9709390000

H -1.1964340000 -3.2290900000 -2.7088200000

H -0.0062010000 -2.1804100000 -1.8913050000

Pd 0.6629370000 0.0922450000 -0.0351300000

C 2.4043140000 1.0042420000 -0.1439950000

C 2.5651530000 1.7793370000 -1.3031290000

C 2.9587920000 1.4451610000 1.0703710000

C 3.1943130000 3.0207290000 -1.2262670000

H 2.1908450000 1.4055220000 -2.2596160000

C 3.5910910000 2.6847680000 1.1328590000

H 2.8894100000 0.8147340000 1.9598130000

C 3.7057460000 3.4775890000 -0.0112290000

H 3.2946100000 3.6330030000 -2.1263360000

H 4.0024850000 3.0343330000 2.0834680000

H 4.2094970000 4.4455920000 0.0418300000

C 2.6478730000 -0.8969760000 -0.5090790000

F 2.4022350000 -1.2506350000 -1.7947760000

F 4.0052240000 -0.6863960000 -0.4672110000

H -0.4929700000 3.9595060000 1.4488680000

H 0.9836920000 3.1580260000 0.8325130000

C 2.5093190000 -2.1576780000 0.3820620000

F 1.4153000000 -2.8577490000 0.1008020000

F 2.4726840000 -1.8132190000 1.6717690000

F 3.5431660000 -2.9809570000 0.2170570000

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cis-Pd-CF2CH3-GS

C -2.3806710000 1.4180160000 -0.2212810000

C	-2.4575410000	0.0143260000	-0.3210800000
C	-3.6839310000	-0.5378450000	-0.7079410000
C	-4.7894020000	0.2527210000	-1.0088680000
C	-4.6829430000	1.6356920000	-0.9156470000
C	-3.4849990000	2.2207900000	-0.5177840000
H	-3.7853730000	-1.6194550000	-0.7708620000
H	-5.7286430000	-0.2142540000	-1.3111160000
H	-5.5376030000	2.2737850000	-1.1516440000
H	-3.4112100000	3.3055590000	-0.4510190000
P	-0.9491290000	-0.9631080000	0.0905600000
O	-1.1999910000	1.9591480000	0.1887260000
C	-1.1988530000	3.2848680000	0.6973250000
H	-2.0127050000	3.4055400000	1.4295030000
C	-0.9015900000	-2.4304410000	-1.1065880000
C	-1.2803020000	-1.4942670000	1.8761420000
C	-2.6813180000	-2.0482690000	2.1193310000
H	-2.8898620000	-2.9565550000	1.5385760000
H	-2.7846150000	-2.3135060000	3.1851950000
H	-3.4606150000	-1.3069210000	1.8907880000
C	-0.2199840000	-2.5147330000	2.2898080000
H	0.7963140000	-2.1818460000	2.0304690000
H	-0.2586610000	-2.6581540000	3.3825020000
H	-0.3886620000	-3.4986820000	1.8292170000
C	-1.1000490000	-0.2199790000	2.7078260000
H	-0.0942450000	0.2115710000	2.5829360000
H	-1.8360330000	0.5532350000	2.4397110000
H	-1.2444970000	-0.4568720000	3.7751480000
C	0.4964910000	-3.0510040000	-1.0120220000
H	1.2900470000	-2.3175610000	-1.1930420000
H	0.6910620000	-3.5156040000	-0.0367430000
H	0.5834290000	-3.8424930000	-1.7749370000
C	-1.0599490000	-1.8113310000	-2.4989190000

H -0.3664700000 -0.9662810000 -2.6400380000

H -0.8255980000 -2.5688100000 -3.2647590000

H -2.0791450000 -1.4452230000 -2.6871060000

C -1.9195540000 -3.5505910000 -0.8941100000

H -2.9673280000 -3.2335830000 -0.9672840000

H -1.7668600000 -4.3127570000 -1.6765580000

H -1.7803420000 -4.0563440000 0.0716350000

Pd 0.7425320000 0.7325640000 -0.0494830000

C 2.3911530000 -0.3425950000 -0.1321130000

C 2.9932370000 -0.8173930000 1.0426590000

C 2.9962530000 -0.6743150000 -1.3551170000

C 4.1347230000 -1.6205860000 0.9956640000

H 2.5752830000 -0.5493870000 2.0171160000

C 4.1374990000 -1.4756970000 -1.4030000000

H 2.5691690000 -0.3055800000 -2.2920800000

C 4.7102590000 -1.9587380000 -0.2275370000

H 4.5802390000 -1.9805200000 1.9276530000

H 4.5833420000 -1.7237210000 -2.3705950000

H 5.6035570000 -2.5871110000 -0.2642270000

C 1.9354200000 2.3937440000 -0.1024200000

F 1.8902450000 2.9583750000 1.1739480000

F 1.2292280000 3.3016980000 -0.8877030000

H -0.2304930000 3.4286820000 1.1843300000

H -1.3023840000 4.0212070000 -0.1131040000

C 3.3654050000 2.4509320000 -0.5523570000

H 3.7136780000 3.4963600000 -0.5040920000

H 3.4569200000 2.0869570000 -1.5836630000

H 3.9973340000 1.8233570000 0.0880560000

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trans-Pd-CF2CH3-GS

C -1.0913030000 2.3304440000 -0.1209930000

C -2.0568700000 1.3055230000 -0.0509260000

C	-3.4019080000	1.6933490000	0.0188160000
C	-3.7940350000	3.0278690000	0.0257240000
C	-2.8218070000	4.0189850000	-0.0376900000
C	-1.4764470000	3.6759190000	-0.1119610000
H	-4.1732940000	0.9280180000	0.0672820000
H	-4.8529460000	3.2870030000	0.0815040000
H	-3.1040590000	5.0742760000	-0.0285220000
H	-0.7287630000	4.4659790000	-0.1543120000
P	-1.5085570000	-0.4564590000	0.0195400000
O	0.2209510000	1.9741430000	-0.1946960000
C	1.1824440000	2.9828540000	-0.4626320000
H	0.8999870000	3.5513690000	-1.3622020000
C	-2.2412450000	-1.2354330000	-1.5496030000
C	-2.2899220000	-1.0991750000	1.6270670000
C	-3.7965320000	-1.3446970000	1.5931340000
H	-4.1163550000	-1.7334460000	2.5746720000
H	-4.3790960000	-0.4316170000	1.4149490000
H	-4.0825440000	-2.0958130000	0.8434190000
C	-1.5845320000	-2.4026790000	2.0089340000
H	-1.9776340000	-2.7460890000	2.9804630000
H	-1.7447260000	-3.2067220000	1.2795340000
H	-0.5009700000	-2.2590200000	2.1073210000
C	-1.9515340000	-0.0497010000	2.6903550000
H	-2.5049900000	0.8893620000	2.5487010000
H	-2.2074600000	-0.4460110000	3.6868650000
H	-0.8739500000	0.1843330000	2.6919280000
C	-1.2627130000	-0.8149400000	-2.6524340000
H	-0.2533200000	-1.2138840000	-2.4696260000
H	-1.6161080000	-1.1978660000	-3.6246780000
H	-1.1864750000	0.2812630000	-2.7362710000
C	-3.6446360000	-0.7667670000	-1.9255880000
H	-3.6818400000	0.3086220000	-2.1466950000

H -3.9572360000 -1.2969910000 -2.8408770000

H -4.3940790000 -0.9939660000 -1.1538530000

C -2.2349700000 -2.7593860000 -1.4283720000

H -2.9743570000 -3.1226560000 -0.6994910000

H -2.5071550000 -3.1922140000 -2.4055180000

H -1.2471980000 -3.1458770000 -1.1517590000

Pd 0.8777850000 -0.2350560000 0.0321410000

C 2.8193850000 0.3018420000 0.0777560000

C 3.6359050000 0.2900850000 -1.0636780000

C 3.3457830000 0.8787700000 1.2464480000

C 4.9114150000 0.8589270000 -1.0488860000

H 3.2708300000 -0.1793890000 -1.9812630000

C 4.6225810000 1.4431350000 1.2678500000

H 2.7478910000 0.8948910000 2.1638870000

C 5.4090860000 1.4404640000 0.1164510000

H 5.5240180000 0.8436960000 -1.9552520000

H 5.0063980000 1.8876990000 2.1909190000

H 6.4084770000 1.8831570000 0.1296640000

C 1.5657050000 -2.1100170000 -0.0258850000

F 0.5068530000 -3.0044920000 0.0166160000

F 2.1180020000 -2.3325210000 -1.2650020000

H 1.2908430000 3.6618220000 0.3975640000

H 2.1330120000 2.4691400000 -0.6351540000

C 2.5404410000 -2.5657180000 1.0282510000

H 2.7154850000 -3.6485330000 0.9125760000

H 2.1321110000 -2.3742140000 2.0302250000

H 3.4886620000 -2.0248070000 0.9326110000

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cis-Pd-CF2CH3-TS

C -2.5377280000 1.5704520000 -0.2386960000

C -2.6324020000 0.1691490000 -0.0713140000

C -3.9133690000 -0.3931580000 -0.0283760000

C	-5.0674120000	0.3772200000	-0.1466930000
C	-4.9494200000	1.7519600000	-0.3170870000
C	-3.6935250000	2.3495750000	-0.3636250000
H	-4.0151260000	-1.4702750000	0.1011390000
H	-6.0498730000	-0.0971760000	-0.1078930000
H	-5.8415560000	2.3752780000	-0.4139630000
H	-3.6193590000	3.4293380000	-0.4912810000
P	-1.0843070000	-0.8175530000	0.0938800000
O	-1.3009180000	2.1147650000	-0.2699980000
C	-1.1314600000	3.4724470000	-0.5918110000
H	-0.0489790000	3.6318960000	-0.6735120000
C	-1.0304390000	-1.8324690000	-1.5026580000
C	-1.3287580000	-1.8896970000	1.6424640000
C	-1.8974310000	-0.9534080000	2.7115410000
H	-2.9470190000	-0.6866420000	2.5235600000
H	-1.8433710000	-1.4454780000	3.6969520000
H	-1.3158140000	-0.0185400000	2.7723950000
C	-2.2117750000	-3.1271080000	1.5048510000
H	-2.2791370000	-3.6304860000	2.4843620000
H	-3.2410330000	-2.8964880000	1.1981350000
H	-1.7947470000	-3.8587710000	0.7984750000
C	0.0713430000	-2.3259870000	2.0865990000
H	0.5827820000	-2.9493580000	1.3403640000
H	0.7121680000	-1.4530460000	2.2734270000
H	-0.0063860000	-2.9120010000	3.0181400000
C	-2.3069840000	-2.5820640000	-1.8730390000
H	-2.6095570000	-3.3211960000	-1.1197400000
H	-3.1488700000	-1.8972850000	-2.0487290000
H	-2.1379670000	-3.1318710000	-2.8146200000
C	0.1489690000	-2.8005900000	-1.3963760000
H	-0.0551690000	-3.6283140000	-0.7010300000
H	0.3450240000	-3.2491130000	-2.3846570000

H 1.0689990000 -2.2893890000 -1.0737250000

C -0.7376760000 -0.7985670000 -2.5945290000

H -0.6411770000 -1.3079110000 -3.5681560000

H -1.5493190000 -0.0592080000 -2.6837390000

H 0.1989260000 -0.2570630000 -2.3922860000

Pd 0.7366130000 0.6109670000 0.2266710000

C 2.6166910000 -0.0214420000 -0.0294310000

C 3.2236480000 -0.8082420000 0.9679110000

C 3.0104570000 -0.2236140000 -1.3657490000

C 4.1029130000 -1.8305440000 0.6260000000

H 2.9873210000 -0.6319310000 2.0202680000

C 3.8887960000 -1.2518610000 -1.6996910000

H 2.6156560000 0.4301070000 -2.1472760000

C 4.4321260000 -2.0695280000 -0.7096980000

H 4.5374800000 -2.4509840000 1.4148620000

H 4.1557250000 -1.4106630000 -2.7482720000

H 5.1226680000 -2.8739720000 -0.9732550000

C 2.5325730000 1.8994850000 0.3607810000

F 3.8943680000 1.9441930000 0.4664780000

F 2.2624940000 2.6445620000 -0.7657330000

H -1.5999050000 3.7181530000 -1.5595730000

H -1.5411470000 4.1336150000 0.1909960000

C 2.0158450000 2.6123290000 1.5907880000

H 2.2829210000 2.0384310000 2.4877290000

H 0.9229460000 2.7429900000 1.5767760000

H 2.4990260000 3.6032170000 1.6493680000

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cis-Pd-CF2CH3-TS-rot

C 2.5221380000 1.5557640000 -0.2537020000

C 2.6054070000 0.1437030000 -0.2605660000

C 3.8484290000 -0.4289140000 -0.5504350000

C 4.9717700000 0.3411790000 -0.8419680000

C	4.8631480000	1.7269060000	-0.8382660000
C	3.6465830000	2.3357860000	-0.5440340000
H	3.9462020000	-1.5137400000	-0.5466800000
H	5.9243220000	-0.1426040000	-1.0665460000
H	5.7319420000	2.3501820000	-1.0630770000
H	3.5791050000	3.4232910000	-0.5428350000
P	1.0794460000	-0.8246560000	0.1055150000
O	1.3252120000	2.1062510000	0.0514910000
C	1.1847240000	3.5054740000	0.1066970000
H	0.1433160000	3.6958920000	0.3880820000
C	1.3646930000	-1.3663660000	1.8987340000
C	1.0543460000	-2.2917700000	-1.0968610000
C	1.2992760000	-1.6843810000	-2.4806710000
H	2.3364810000	-1.3465230000	-2.6173130000
H	1.0828110000	-2.4382730000	-3.2557410000
H	0.6353290000	-0.8218430000	-2.6557010000
C	2.0230750000	-3.4440940000	-0.8402950000
H	1.8861280000	-4.2047420000	-1.6276430000
H	3.0810650000	-3.1515690000	-0.8672910000
H	1.8279540000	-3.9427720000	0.1195990000
C	-0.3746030000	-2.8469740000	-1.0653840000
H	-0.6339200000	-3.2997670000	-0.0990970000
H	-1.1195890000	-2.0683870000	-1.2740580000
H	-0.4724190000	-3.6323910000	-1.8337420000
C	2.7373750000	-1.9698400000	2.1822900000
H	2.9301880000	-2.8866890000	1.6096840000
H	3.5480790000	-1.2564080000	1.9751650000
H	2.8028460000	-2.2355670000	3.2513190000
C	0.2556170000	-2.3426420000	2.2901310000
H	0.3853980000	-3.3299650000	1.8234270000
H	0.2694790000	-2.4961610000	3.3823710000
H	-0.7382340000	-1.9575850000	2.0141000000

C 1.2112130000 -0.0837120000 2.7221700000

H 1.3328260000 -0.3175530000 3.7933890000

H 1.9718530000 0.6670910000 2.4579870000

H 0.2191780000 0.3728390000 2.5761660000

Pd -0.7082600000 0.6331600000 -0.0565840000

C -2.5862620000 -0.0188450000 -0.1675980000

C -3.0473620000 -0.4347430000 -1.4385630000

C -3.1252620000 -0.6656890000 0.9664190000

C -3.9245400000 -1.5066800000 -1.5651620000

H -2.6885560000 0.0785950000 -2.3351300000

C -4.0012800000 -1.7381550000 0.8271160000

H -2.8372800000 -0.3238360000 1.9635550000

C -4.4030640000 -2.1744960000 -0.4364720000

H -4.2385380000 -1.8266140000 -2.5627790000

H -4.3776100000 -2.2407740000 1.7227700000

H -5.0945460000 -3.0135450000 -0.5398370000

C -2.5964240000 1.8923920000 0.0794010000

F -2.4211700000 2.1979350000 1.4020240000

F -1.8758630000 2.8642630000 -0.6301830000

H 1.8566790000 3.9452350000 0.8626360000

H 1.3778070000 3.9699000000 -0.8748310000

C -4.0365710000 2.1691660000 -0.2681960000

H -4.7095780000 1.5175920000 0.3013980000

H -4.2078240000 1.9991690000 -1.3383150000

H -4.2455530000 3.2238310000 -0.0281090000

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trans-Pd-CF2CH3-TS

C 1.3817620000 2.2583690000 -0.0251300000

C 2.2168410000 1.1255780000 -0.1670580000

C 3.5532150000 1.3472770000 -0.5183330000

C 4.0611060000 2.6233770000 -0.7470410000

C 3.2166900000 3.7206310000 -0.6198940000

C	1.8845750000	3.5438630000	-0.2600630000
H	4.2231060000	0.4947140000	-0.6212720000
H	5.1089360000	2.7547300000	-1.0237010000
H	3.5927180000	4.7309590000	-0.7981350000
H	1.2362140000	4.4137610000	-0.1598440000
P	1.4985530000	-0.5554300000	0.0839480000
O	0.1055380000	2.0447450000	0.3516760000
C	-0.8027870000	3.1169190000	0.4248040000
H	-0.4860910000	3.8590240000	1.1769170000
C	2.2162740000	-1.0551630000	1.7655350000
C	2.1701460000	-1.6207940000	-1.3423740000
C	3.6157430000	-2.1044060000	-1.2515550000
H	3.8508540000	-2.6995920000	-2.1502200000
H	4.3523640000	-1.2912210000	-1.2134610000
H	3.7817410000	-2.7592050000	-0.3842030000
C	1.2547970000	-2.8476080000	-1.4287000000
H	1.5622150000	-3.4699990000	-2.2860150000
H	1.3124440000	-3.4802490000	-0.5311660000
H	0.2058080000	-2.5549180000	-1.5780010000
C	1.9611160000	-0.7906830000	-2.6116190000
H	2.6607900000	0.0533600000	-2.6858270000
H	2.1064400000	-1.4316680000	-3.4970820000
H	0.9358960000	-0.3870510000	-2.6556360000
C	1.4607610000	-0.1791770000	2.7698620000
H	0.3725250000	-0.3372040000	2.7008690000
H	1.7853670000	-0.4255360000	3.7949540000
H	1.6564190000	0.8918390000	2.6064490000
C	3.7145610000	-0.8237170000	1.9391900000
H	3.9790680000	0.2382010000	1.8364320000
H	4.0135840000	-1.1357180000	2.9544390000
H	4.3234350000	-1.4023150000	1.2318400000
C	1.8730400000	-2.5204550000	2.0285460000

H 2.4403520000 -3.2078500000 1.3839680000

H 2.1210530000 -2.7759590000 3.0724250000

H 0.7995260000 -2.7145510000 1.8850880000

Pd -0.8428200000 -0.3226990000 0.0730710000

C -2.7486880000 0.1778690000 -0.0162290000

C -3.3458280000 0.5788910000 1.1914250000

C -3.1331020000 0.8053580000 -1.2112680000

C -4.2521570000 1.6375420000 1.2071520000

H -3.0935100000 0.0641800000 2.1224110000

C -4.0360420000 1.8674420000 -1.1858630000

H -2.7160260000 0.4574910000 -2.1597760000

C -4.5950240000 2.2894530000 0.0208390000

H -4.6967170000 1.9560640000 2.1540130000

H -4.3117880000 2.3660370000 -2.1191650000

H -5.3096860000 3.1158870000 0.0359360000

C -2.5029610000 -1.8003490000 -0.2520680000

F -3.8709440000 -1.9098310000 -0.1268130000

F -2.2735280000 -2.0804310000 -1.5698070000

H -0.9258470000 3.6095610000 -0.5537190000

H -1.7634310000 2.6848240000 0.7294350000

C -1.9670940000 -2.9061110000 0.6276020000

H -2.5501660000 -3.8220160000 0.4229610000

H -2.0958640000 -2.6396620000 1.6849440000

H -0.9060240000 -3.0905780000 0.4332660000

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cis-Pd-CF2CFMe2-GS

C 2.0223880000 -1.9947800000 -0.2714320000

C 2.5885980000 -0.7062170000 -0.3383140000

C 3.9229870000 -0.6114090000 -0.7490920000

C 4.6709710000 -1.7325250000 -1.0978040000

C 4.0856740000 -2.9916460000 -1.0286800000

C 2.7654970000 -3.1275020000 -0.6113360000

H	4.4013510000	0.3647230000	-0.7919990000
H	5.7085110000	-1.6179670000	-1.4171660000
H	4.6561000000	-3.8828520000	-1.3001080000
H	2.3123600000	-4.1170950000	-0.5646270000
P	1.5300230000	0.7221330000	0.1589760000
O	0.7322880000	-2.0912030000	0.1502740000
C	0.2667170000	-3.3357390000	0.6484120000
H	0.9873590000	-3.7391070000	1.3774320000
C	2.0126880000	2.1767800000	-0.9564800000
C	2.0473960000	0.9941030000	1.9610200000
C	3.5552040000	0.9407640000	2.1923650000
H	4.0993730000	1.7224930000	1.6454640000
H	3.7608890000	1.0919260000	3.2656580000
H	3.9796030000	-0.0339210000	1.9121210000
C	1.4848800000	2.3278900000	2.4518210000
H	0.4159360000	2.4379710000	2.2199770000
H	1.5985680000	2.3887240000	3.5469770000
H	2.0188000000	3.1879740000	2.0233840000
C	1.3834680000	-0.1475040000	2.7380520000
H	0.2897710000	-0.1542840000	2.6077260000
H	1.7647340000	-1.1312880000	2.4258480000
H	1.6030720000	-0.0352400000	3.8129210000
C	0.9398950000	3.2614240000	-0.8035460000
H	-0.0601720000	2.8929830000	-1.0571320000
H	0.8965680000	3.6820010000	0.2092000000
H	1.1805210000	4.0887690000	-1.4916690000
C	1.9345900000	1.6300930000	-2.3853840000
H	0.9741150000	1.1190480000	-2.5619140000
H	2.0039760000	2.4670750000	-3.0994260000
H	2.7426780000	0.9217770000	-2.6160980000
C	3.3696380000	2.8328990000	-0.6992160000
H	4.2298980000	2.1608330000	-0.8057980000

H 3.5098980000 3.6414650000 -1.4359400000

H 3.4212260000 3.2984820000 0.2949620000

Pd -0.6474080000 -0.2563120000 -0.1408850000

C -1.7529940000 1.3699540000 -0.2236630000

C -1.9877520000 2.1195840000 0.9394330000

C -2.2658850000 1.8582170000 -1.4331820000

C -2.6790730000 3.3308690000 0.8907790000

H -1.6329070000 1.7527000000 1.9066090000

C -2.9508450000 3.0733760000 -1.4833890000

H -2.1317070000 1.2821450000 -2.3508640000

C -3.1558810000 3.8197150000 -0.3243210000

H -2.8457200000 3.8957430000 1.8125360000

H -3.3299480000 3.4388560000 -2.4421000000

H -3.6919350000 4.7711140000 -0.3656690000

C -2.3114980000 -1.3579090000 -0.6154700000

F -1.7607320000 -2.5230390000 -1.1464260000

F -3.0924870000 -0.8810220000 -1.6332630000

H -0.6883510000 -3.1319520000 1.1404570000

H 0.1070710000 -4.0569230000 -0.1662590000

C -3.2748810000 -1.7796730000 0.5112980000

C -4.0253540000 -3.0510490000 0.1665810000

H -4.6090200000 -2.9010390000 -0.7528760000

H -3.3301480000 -3.8832820000 -0.0013340000

H -4.7137370000 -3.3178330000 0.9816760000

C -4.2082780000 -0.6573870000 0.8997790000

H -4.8700440000 -0.4025780000 0.0615040000

H -4.8222540000 -0.9737480000 1.7557870000

H -3.6478210000 0.2439780000 1.1745910000

F -2.4740440000 -2.0667920000 1.6319800000

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cis-Pd-CF2CFMe2-TS

C 2.4163130000 -1.7917260000 -0.6092000000

C	2.7814540000	-0.5071460000	-0.1412990000
C	4.1444370000	-0.2462940000	0.0414700000
C	5.1258940000	-1.1976260000	-0.2251330000
C	4.7443190000	-2.4506840000	-0.6912290000
C	3.3992460000	-2.7504020000	-0.8834130000
H	4.4527220000	0.7332210000	0.4055250000
H	6.1794720000	-0.9574790000	-0.0697170000
H	5.4973770000	-3.2121250000	-0.9082790000
H	3.1175870000	-3.7397980000	-1.2426970000
P	1.4549770000	0.7192360000	0.2240080000
O	1.1020370000	-2.0469890000	-0.7742160000
C	0.6808920000	-3.2690710000	-1.3277260000
H	-0.4078490000	-3.1974160000	-1.4226070000
C	1.7405860000	2.0908200000	-1.0478950000
C	1.7880540000	1.2858860000	2.0075010000
C	2.0587710000	0.0070450000	2.8042720000
H	3.0413080000	-0.4297420000	2.5762400000
H	2.0293950000	0.2329680000	3.8833580000
H	1.2928920000	-0.7600930000	2.6016370000
C	2.9205520000	2.2861220000	2.2220370000
H	3.0142940000	2.4975100000	3.3009960000
H	3.8980410000	1.9124320000	1.8882560000
H	2.7261710000	3.2466910000	1.7241230000
C	0.4811140000	1.8990520000	2.5198550000
H	0.1690180000	2.7836140000	1.9478630000
H	-0.3388770000	1.1694660000	2.4627290000
H	0.6066730000	2.2043690000	3.5726280000
C	3.1651530000	2.6233300000	-1.1766550000
H	3.5525220000	3.0588410000	-0.2461980000
H	3.8645400000	1.8469990000	-1.5177980000
H	3.1781230000	3.4232890000	-1.9365890000
C	0.7736140000	3.2300020000	-0.7205120000

H	1.0889310000	3.7971540000	0.1681120000
H	0.7433810000	3.9397710000	-1.5639280000
H	-0.2512590000	2.8645920000	-0.5580260000
C	1.3397190000	1.4516720000	-2.3809710000
H	1.4334770000	2.1962210000	-3.1894720000
H	1.9896570000	0.5990610000	-2.6343090000
H	0.2991610000	1.0966870000	-2.3580830000
Pd	-0.6210550000	-0.2955570000	-0.0267340000
C	-2.2240100000	0.8518110000	-0.3109990000
C	-2.6738440000	1.6964780000	0.7264990000
C	-2.3836310000	1.3034880000	-1.6386960000
C	-3.1450830000	2.9744550000	0.4484650000
H	-2.6245550000	1.3618270000	1.7641060000
C	-2.8551080000	2.5857250000	-1.9062150000
H	-2.1256210000	0.6368550000	-2.4645220000
C	-3.2284450000	3.4365430000	-0.8668600000
H	-3.4510930000	3.6221950000	1.2748350000
H	-2.9349970000	2.9208720000	-2.9440540000
H	-3.6002430000	4.4415760000	-1.0783180000
C	-2.7967840000	-0.9789730000	-0.2232360000
F	-4.1131420000	-0.5965840000	-0.1602550000
F	-2.6642660000	-1.5648310000	-1.4521180000
H	1.1268260000	-3.4319030000	-2.3233840000
H	0.9256330000	-4.1188480000	-0.6687190000
C	-2.7110320000	-2.0878380000	0.8623330000
C	-3.7574680000	-3.1585300000	0.6208950000
H	-3.6053820000	-3.9804740000	1.3354240000
H	-4.7684410000	-2.7536000000	0.7532260000
H	-3.6698080000	-3.5566480000	-0.3989960000
C	-2.7746470000	-1.5008780000	2.2537480000
H	-2.7399100000	-2.3069370000	3.0008100000
H	-1.9170950000	-0.8317270000	2.4191760000

H -3.7039680000 -0.9320930000 2.3908650000

F -1.4693630000 -2.7156860000 0.7209200000

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cis-Pd-CF2CFMe2-TS-rot

C -2.5841930000 -1.9189150000 0.2772520000

C -2.9524390000 -0.5589480000 0.1452610000

C -4.3160890000 -0.2477550000 0.2047350000

C -5.2919860000 -1.2200980000 0.4090770000

C -4.9047160000 -2.5467250000 0.5583970000

C -3.5601520000 -2.8990000000 0.4914030000

H -4.6300130000 0.7882520000 0.0847780000

H -6.3460160000 -0.9388630000 0.4510600000

H -5.6529470000 -3.3255820000 0.7239740000

H -3.2761780000 -3.9452090000 0.6005700000

P -1.6340650000 0.6955820000 -0.1461180000

O -1.2723020000 -2.2279200000 0.1764650000

C -0.8437370000 -3.5591840000 0.3371700000

H -1.2728930000 -4.2167720000 -0.4373860000

C -1.8173610000 1.9412490000 1.2675440000

C -2.0598590000 1.4267990000 -1.8463730000

C -3.2243980000 2.4107110000 -1.8921090000

H -3.0163560000 3.3280450000 -1.3230520000

H -3.3999720000 2.7149610000 -2.9381730000

H -4.1653010000 1.9764030000 -1.5264790000

C -0.7938010000 2.1093960000 -2.3700920000

H 0.0391170000 1.3943080000 -2.4214230000

H -0.9808730000 2.5015890000 -3.3842040000

H -0.4676720000 2.9492490000 -1.7416620000

C -2.3591630000 0.2231920000 -2.7441320000

H -1.5671710000 -0.5401410000 -2.6670930000

H -3.3180680000 -0.2545610000 -2.4973350000

H -2.4046190000 0.5525670000 -3.7956100000

C	-0.8409950000	3.0853440000	0.9845940000
H	0.1578190000	2.7150540000	0.7092540000
H	-1.2036860000	3.7479250000	0.1844410000
H	-0.7282930000	3.7031610000	1.8910330000
C	-1.3521160000	1.1696510000	2.5064830000
H	-0.3224110000	0.8021050000	2.3868920000
H	-1.3836800000	1.8327090000	3.3875070000
H	-2.0024170000	0.3049680000	2.7139100000
C	-3.2107560000	2.5002830000	1.5453160000
H	-3.9012000000	1.7244670000	1.9038440000
H	-3.1352540000	3.2543270000	2.3472680000
H	-3.6618910000	2.9993100000	0.6776740000
Pd	0.4133290000	-0.3793730000	-0.0829550000
C	2.0887050000	0.6723460000	0.1568970000
C	2.4854040000	1.5281390000	-0.8960880000
C	2.3477550000	1.1059150000	1.4774170000
C	3.0517750000	2.7710210000	-0.6352180000
H	2.3075670000	1.2290900000	-1.9308180000
C	2.9082080000	2.3550290000	1.7284200000
H	2.1007520000	0.4477890000	2.3126980000
C	3.2687870000	3.1978580000	0.6776830000
H	3.3206690000	3.4216610000	-1.4720930000
H	3.0710240000	2.6695700000	2.7629040000
H	3.7168960000	4.1738130000	0.8760770000
C	2.5232920000	-1.2141740000	0.0481620000
F	1.9912870000	-2.2188090000	-0.7748360000
F	2.4325350000	-1.7081400000	1.3134360000
H	0.2465780000	-3.5415990000	0.2279760000
H	-1.1031120000	-3.9473140000	1.3363270000
C	4.0349150000	-1.2400860000	-0.3269670000
C	4.9186570000	-0.4055730000	0.5724300000
H	4.7004670000	-0.6127510000	1.6283430000

H 5.9624850000 -0.6897530000 0.3731630000

H 4.8046240000 0.6695670000 0.3877940000

C 4.2826810000 -0.9830840000 -1.7983360000

H 5.3161670000 -1.2810520000 -2.0257990000

H 3.6050660000 -1.5834110000 -2.4195450000

H 4.1677130000 0.0769870000 -2.0505230000

F 4.3882670000 -2.5708760000 -0.0956980000

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cis-Pd-CHFC(O)Me-GS

C 2.3336040000 1.5123650000 -0.3041420000

C 2.5105390000 0.1147400000 -0.2599660000

C 3.7920780000 -0.3845540000 -0.5213300000

C 4.8611420000 0.4482700000 -0.8360160000

C 4.6591540000 1.8230010000 -0.8832390000

C 3.4039850000 2.3573690000 -0.6131120000

H 3.9673670000 -1.4570150000 -0.4704750000

H 5.8453530000 0.0216300000 -1.0379440000

H 5.4840140000 2.4952680000 -1.1303130000

H 3.2588260000 3.4355910000 -0.6538630000

P 1.0593800000 -0.9353040000 0.1714990000

O 1.0980070000 2.0065760000 -0.0224120000

C 0.9735530000 3.3949330000 0.2773590000

H 1.1428170000 4.0040210000 -0.6223550000

C 1.3569500000 -1.3147060000 2.0027300000

C 1.1626320000 -2.4825970000 -0.9189800000

C 2.2445160000 -3.5053680000 -0.5705220000

H 2.0980420000 -3.9400500000 0.4280380000

H 2.1809940000 -4.3372170000 -1.2916480000

H 3.2696260000 -3.1197400000 -0.6303730000

C -0.1909950000 -3.1983910000 -0.8491350000

H -1.0161550000 -2.5578400000 -1.1794690000

H -0.1566020000 -4.0766660000 -1.5148410000

H	-0.4323130000	-3.5617820000	0.1581430000
C	1.3555180000	-1.9580840000	-2.3450580000
H	0.6147640000	-1.1785220000	-2.5868940000
H	2.3564640000	-1.5350090000	-2.5097760000
H	1.2153760000	-2.7855040000	-3.0597860000
C	0.4082610000	-2.4254160000	2.4527150000
H	-0.6299190000	-2.2357070000	2.1459750000
H	0.7054860000	-3.4099630000	2.0642330000
H	0.4254080000	-2.4932340000	3.5531650000
C	1.0000560000	-0.0155270000	2.7323540000
H	-0.0446160000	0.2833950000	2.5530330000
H	1.1387540000	-0.1533790000	3.8175930000
H	1.6442780000	0.8208010000	2.4207590000
C	2.7988870000	-1.6891020000	2.3364660000
H	3.4995730000	-0.8746240000	2.1046230000
H	2.8757990000	-1.8895850000	3.4184730000
H	3.1379020000	-2.5945700000	1.8153360000
Pd	-0.7204670000	0.6033080000	-0.2236110000
C	-2.2520170000	-0.6294780000	-0.3257250000
C	-2.8473330000	-0.9492220000	-1.5559190000
C	-2.7684600000	-1.2366500000	0.8281530000
C	-3.8913200000	-1.8733230000	-1.6323110000
H	-2.4856630000	-0.4817980000	-2.4759330000
C	-3.8147810000	-2.1565200000	0.7530170000
H	-2.3584900000	-0.9836270000	1.8094150000
C	-4.3766930000	-2.4866800000	-0.4792450000
H	-4.3292160000	-2.1130170000	-2.6053910000
H	-4.1952260000	-2.6171480000	1.6691460000
H	-5.1934820000	-3.2099640000	-0.5387380000
C	-2.0487480000	2.1206590000	-0.7272240000
F	-1.2850240000	3.0644000000	-1.3922620000
H	-0.0532930000	3.5600440000	0.6279890000

H 1.6962460000 3.6652660000 1.0633740000

C -2.5680560000 2.6353340000 0.5528370000

O -2.0387730000 3.5540560000 1.1630210000

C -3.7959200000 1.9569260000 1.1122660000

H -4.5674550000 2.7300040000 1.2524960000

H -4.1898200000 1.1583940000 0.4717960000

H -3.5711840000 1.5413140000 2.1055030000

H -2.8308230000 1.7550760000 -1.4080510000

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trans-Pd-CHFC(O)Me-GS

C 1.5987800000 2.2080920000 -0.1431560000

C 2.3981460000 1.0463730000 -0.1107500000

C 3.7830190000 1.2057740000 -0.2460270000

C 4.3727450000 2.4557340000 -0.4065400000

C 3.5644700000 3.5862010000 -0.4332360000

C 2.1844070000 3.4683280000 -0.3024030000

H 4.4228220000 0.3248220000 -0.2273750000

H 5.4559100000 2.5418560000 -0.5104640000

H 4.0045520000 4.5780260000 -0.5595360000

H 1.5699370000 4.3665090000 -0.3320300000

P 1.5816890000 -0.5938480000 0.0606070000

O 0.2488000000 2.0644970000 -0.0167960000

C -0.5609230000 3.2277290000 0.0450470000

H -0.2403290000 3.8774360000 0.8741970000

C 2.1859820000 -1.2382870000 1.7338110000

C 2.1811300000 -1.6067470000 -1.4232420000

C 3.6105230000 -2.1359030000 -1.3496510000

H 3.8376340000 -2.6782010000 -2.2829050000

H 4.3642390000 -1.3426090000 -1.2554530000

H 3.7485460000 -2.8496980000 -0.5247960000

C 1.2173580000 -2.7854490000 -1.5964970000

H 1.5318530000 -3.3729680000 -2.4753810000

H	1.2248730000	-3.4702300000	-0.7361190000
H	0.1830250000	-2.4542780000	-1.7745690000
C	2.0164730000	-0.6830270000	-2.6336210000
H	2.7446320000	0.1405840000	-2.6389810000
H	2.1584630000	-1.2680530000	-3.5570840000
H	1.0028230000	-0.2512690000	-2.6698570000
C	1.4629990000	-0.3552950000	2.7571300000
H	0.3688010000	-0.4370290000	2.6604840000
H	1.7440390000	-0.6682570000	3.7766460000
H	1.7381430000	0.7057790000	2.6484570000
C	3.6894480000	-1.1531540000	1.9830200000
H	4.0461300000	-0.1139480000	1.9952660000
H	3.9099440000	-1.5795970000	2.9761820000
H	4.2818480000	-1.7189230000	1.2513230000
C	1.7109760000	-2.6824960000	1.8995880000
H	2.2313150000	-3.3770220000	1.2238950000
H	1.9199430000	-3.0151830000	2.9298680000
H	0.6272220000	-2.7799880000	1.7414510000
Pd	-0.7109480000	-0.0210620000	0.0732860000
C	-2.5948290000	0.6910350000	0.0803280000
C	-3.2846410000	0.9395930000	1.2769730000
C	-3.1988550000	1.0969470000	-1.1203520000
C	-4.5169720000	1.5963670000	1.2774070000
H	-2.8600730000	0.6009310000	2.2265610000
C	-4.4332660000	1.7498350000	-1.1249500000
H	-2.7058140000	0.8871180000	-2.0751420000
C	-5.0952120000	2.0047730000	0.0754170000
H	-5.0341740000	1.7839130000	2.2230270000
H	-4.8852470000	2.0539450000	-2.0735830000
H	-6.0635900000	2.5118890000	0.0741180000
C	-1.5849650000	-1.8303230000	0.2916570000
F	-2.1613110000	-1.9485210000	1.5475050000

H -0.5252180000 3.7804420000 -0.9068220000

H -1.5842140000 2.8819320000 0.2238970000

C -2.5744800000 -2.1070660000 -0.7992010000

C -4.0186310000 -2.2504270000 -0.4077300000

H -4.1291530000 -3.1057950000 0.2779020000

H -4.3673220000 -1.3599430000 0.1342400000

H -4.6231970000 -2.4102430000 -1.3091720000

O -2.1937750000 -2.2484980000 -1.9462850000

H -0.7906180000 -2.5883170000 0.2304550000

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cis-Pd-CHFC(O)Me-TS

C -2.4712930000 1.8236650000 0.2121770000

C -2.7504210000 0.4448740000 0.0548420000

C -4.0932230000 0.0535730000 0.0171530000

C -5.1357980000 0.9709310000 0.1241860000

C -4.8381570000 2.3202980000 0.2805090000

C -3.5149900000 2.7491050000 0.3258230000

H -4.3359590000 -1.0028370000 -0.0969160000

H -6.1720960000 0.6294560000 0.0891910000

H -5.6414980000 3.0556880000 0.3687920000

H -3.2967350000 3.8103460000 0.4449920000

P -1.3413010000 -0.7330940000 -0.0826990000

O -1.1758180000 2.1905610000 0.2469850000

C -0.8045250000 3.5119030000 0.5529880000

H -1.2341410000 3.8361010000 1.5158290000

C -1.7516970000 -1.8967600000 -1.5246980000

C -1.3464890000 -1.6077150000 1.5946170000

C -2.6933800000 -2.1672950000 2.0427910000

H -3.0838840000 -2.9429940000 1.3713010000

H -2.5761330000 -2.6297930000 3.0375870000

H -3.4523430000 -1.3779540000 2.1420370000

C -0.2891190000 -2.7118140000 1.5561610000

H	0.6770590000	-2.3408820000	1.1812970000
H	-0.1244620000	-3.0970020000	2.5762530000
H	-0.6019250000	-3.5645860000	0.9355070000
C	-0.9115760000	-0.5250090000	2.5872730000
H	0.0692250000	-0.1043370000	2.3215280000
H	-1.6388700000	0.3003340000	2.6353320000
H	-0.8362640000	-0.9622500000	3.5970390000
C	-0.4215090000	-2.5269150000	-1.9551000000
H	0.3106020000	-1.7526630000	-2.2282130000
H	0.0328830000	-3.1434330000	-1.1671860000
H	-0.5916250000	-3.1745680000	-2.8318470000
C	-2.2424100000	-0.9977770000	-2.6625010000
H	-1.5565080000	-0.1500650000	-2.8255240000
H	-2.2813600000	-1.5799340000	-3.5982270000
H	-3.2455880000	-0.5895040000	-2.4759830000
C	-2.7601270000	-3.0123370000	-1.2619000000
H	-3.7476490000	-2.6457370000	-0.9508160000
H	-2.9132900000	-3.5835760000	-2.1931960000
H	-2.4024610000	-3.7251500000	-0.5055960000
Pd	0.6580370000	0.4283900000	-0.4624420000
C	2.4508320000	-0.3681080000	0.0079600000
C	2.7384000000	-0.3290740000	1.3860790000
C	2.9994170000	-1.4092540000	-0.7594260000
C	3.4720490000	-1.3505290000	1.9866870000
H	2.3871400000	0.5121080000	1.9881860000
C	3.7332290000	-2.4242530000	-0.1505680000
H	2.8367820000	-1.4271650000	-1.8380940000
C	3.9670610000	-2.4082480000	1.2252170000
H	3.6628030000	-1.3117140000	3.0625530000
H	4.1270680000	-3.2407770000	-0.7620870000
H	4.5451140000	-3.2063220000	1.6967180000
C	2.4780670000	1.3483640000	-0.9655170000

F 3.1584030000 0.9597710000 -2.0929710000

H 0.2912520000 3.5052190000 0.6365060000

H -1.1111850000 4.2160410000 -0.2396080000

C 3.3071150000 2.1495430000 -0.0232740000

O 2.7649600000 2.7962670000 0.8525620000

C 4.7936690000 2.0775570000 -0.1975570000

H 5.1213340000 1.0293130000 -0.1116970000

H 5.0776340000 2.4165460000 -1.2054760000

H 5.2869710000 2.6925240000 0.5649220000

H 1.6384250000 2.0191040000 -1.3054380000

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trans-Pd-CHFC(O)Me-TS

C -1.3340430000 2.3534550000 -0.2918920000

C -2.1840680000 1.2474690000 -0.0608480000

C -3.5455510000 1.5093100000 0.1375200000

C -4.0681900000 2.7993340000 0.1118860000

C -3.2130630000 3.8709890000 -0.1174110000

C -1.8538900000 3.6537240000 -0.3172890000

H -4.2241250000 0.6788560000 0.3237170000

H -5.1357130000 2.9613550000 0.2728220000

H -3.6000580000 4.8925630000 -0.1407170000

H -1.1972210000 4.5049870000 -0.4927570000

P -1.4665820000 -0.4486130000 0.0433710000

O -0.0208880000 2.1071440000 -0.4807950000

C 0.8815160000 3.1787900000 -0.6113210000

H 0.6577640000 3.7861560000 -1.5043710000

C -2.2927590000 -1.3847580000 -1.3793830000

C -1.9834550000 -1.0753530000 1.7594920000

C -3.4447630000 -1.4811740000 1.9271350000

H -3.6048480000 -1.8195830000 2.9649120000

H -4.1468580000 -0.6542370000 1.7548080000

H -3.7214600000 -2.3201090000 1.2727070000

C	-1.0881880000	-2.2727920000	2.0892650000
H	-1.3083070000	-2.6117380000	3.1159270000
H	-1.2434620000	-3.1254840000	1.4166640000
H	-0.0211320000	-2.0150740000	2.0336310000
C	-1.6378260000	0.0602360000	2.7263990000
H	-2.2998740000	0.9306010000	2.6119870000
H	-1.7304290000	-0.3041900000	3.7629550000
H	-0.5976960000	0.3983600000	2.5848920000
C	-1.5899100000	-0.8418610000	-2.6278940000
H	-0.5009100000	-0.9907470000	-2.5769930000
H	-1.9716350000	-1.3574700000	-3.5252680000
H	-1.7734760000	0.2365580000	-2.7592130000
C	-3.7972070000	-1.1886080000	-1.5499750000
H	-4.0546940000	-0.1508910000	-1.8031180000
H	-4.1435510000	-1.8203070000	-2.3856500000
H	-4.3728230000	-1.4872780000	-0.6630420000
C	-1.9856770000	-2.8737410000	-1.2130910000
H	-2.6073200000	-3.3311440000	-0.4289710000
H	-2.2185760000	-3.4000040000	-2.1543080000
H	-0.9345710000	-3.0764290000	-0.9603390000
Pd	0.8935330000	-0.2673260000	-0.0867130000
C	2.8098670000	0.2736040000	0.0777900000
C	3.4681480000	0.7313700000	-1.0795070000
C	3.1017960000	0.8865900000	1.3077260000
C	4.3474790000	1.8098660000	-1.0111850000
H	3.2877230000	0.2464050000	-2.0428280000
C	3.9733950000	1.9735560000	1.3646820000
H	2.6416590000	0.4986440000	2.2196460000
C	4.5993190000	2.4404730000	0.2091020000
H	4.8390940000	2.1631160000	-1.9216040000
H	4.1725670000	2.4543520000	2.3261860000
H	5.2916480000	3.2839260000	0.2596000000

C 2.5503430000 -1.6646400000 0.2850990000

F 2.5747250000 -1.9097710000 1.6199830000

H 0.8759390000 3.8212430000 0.2845850000

H 1.8756540000 2.7323640000 -0.7254980000

C 1.7045000000 -2.6515260000 -0.4620930000

C 1.8757060000 -2.6500150000 -1.9663130000

H 2.2622660000 -1.7027120000 -2.3671260000

H 2.5825750000 -3.4550550000 -2.2294210000

H 0.9192210000 -2.8873550000 -2.4500630000

O 1.0694390000 -3.5276520000 0.0987900000

H 3.5770370000 -1.7273040000 -0.1066720000

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H-C2F5

C -0.8544060000 0.0000430000 -0.4342330000

C 0.6131770000 0.0001390000 -0.0028360000

F -1.4500700000 -1.0920370000 0.0595820000

F -1.4506610000 1.0917850000 0.0595480000

F 0.7257110000 -0.0001370000 1.3159910000

H -0.9270570000 0.0001350000 -1.5357560000

F 1.2194480000 1.0792150000 -0.4863690000

F 1.2193980000 -1.0789620000 -0.4867320000

14

H-CF2CFMe2

C 0.8521470000 -0.0000010000 -0.4656160000

C -0.5964470000 -0.0000160000 0.0172510000

F 1.4993410000 1.0895350000 -0.0057570000

F 1.4993870000 -1.0896120000 -0.0060320000

C -1.3020560000 1.2661550000 -0.4229010000

F -0.5451080000 -0.0000730000 1.4004600000

C -1.3022820000 -1.2660310000 -0.4228310000

H 0.9067960000 0.0001140000 -1.5700390000

H -0.7684690000 2.1450540000 -0.0369820000

H -2.3263890000 1.2705590000 -0.0253600000

H -1.3534640000 1.3340650000 -1.5195920000

H -1.3544280000 -1.3336800000 -1.5194960000

H -2.3263260000 -1.2703680000 -0.0245440000

H -0.7684700000 -2.1450400000 -0.0374460000

6

H-CF2CN

C -0.4350920000 -0.0001030000 0.3569680000

C 1.0169890000 -0.0009370000 0.0687120000

N 2.1564200000 -0.0001700000 -0.1180640000

F -0.9981170000 1.0919250000 -0.1763000000

F -0.9997040000 -1.0910560000 -0.1765450000

H -0.6059320000 -0.0003900000 1.4479690000

11

H-CF2CO2Me

C 0.2890860000 0.4803310000 -0.0004640000

C -1.2258030000 0.2812580000 -0.0004830000

F -1.5931280000 -0.4115210000 1.0917420000

F -1.5932550000 -0.4140760000 -1.0908460000

O 0.8061130000 1.5632840000 -0.0010100000

O 0.9249260000 -0.6794370000 0.0004770000

H -1.7249220000 1.2641360000 -0.0016970000

C 2.3438460000 -0.6109300000 0.0003940000

H 2.7004260000 -1.6465860000 0.0002680000

H 2.7054810000 -0.0811060000 0.8935310000

H 2.7053770000 -0.0807960000 -0.8925910000

7

H-CF2C(O)F

C 0.7695370000 -0.1778250000 0.0238180000

C -0.6960180000 0.1006920000 0.3495090000

F -1.4197010000 -0.9843390000 0.0742650000

F -1.1233730000 1.1313160000 -0.3989530000

O 1.2477810000 -1.2107790000 -0.2738010000

F 1.4747940000 0.9403950000 0.1616160000

H -0.8088480000 0.3626760000 1.4180950000

7

H-CF2C(O)H

C 0.9415330000 -0.0002770000 0.3804740000

C -0.4078450000 -0.0000610000 -0.3251310000

F -1.0905610000 1.0921820000 0.0696380000

F -1.0910070000 -1.0919060000 0.0694960000

O 1.9831390000 0.0000200000 -0.2073960000

H 0.8622560000 -0.0006500000 1.4973530000

H -0.2953780000 0.0000400000 -1.4224460000

10

H-CF2C(O)Me

C 0.7267220000 -0.4458800000 0.0007600000

C -0.7875990000 -0.2035850000 -0.0011620000

F 1.2707190000 0.1323100000 -1.0911810000

F 1.2682390000 0.1362830000 1.0918590000

H 0.9515290000 -1.5251570000 0.0029430000

O -1.5350480000 -1.1467070000 0.0013040000

C -1.2108420000 1.2330060000 -0.0019580000

H -0.7966780000 1.7384620000 0.8840470000

H -2.3049140000 1.3015670000 -0.0057020000

H -0.7898580000 1.7402030000 -0.8836600000

5

H-CF2H

C 0.0001610000 0.4906810000 0.0000390000

H 0.0002800000 1.1121750000 -0.9130870000

H 0.0009720000 1.1101510000 0.9142800000

F 1.0960340000 -0.2871500000 -0.0001110000

F -1.0962800000 -0.2868960000 -0.0000470000

8

H-CF2Me

C -0.0705640000 0.0000110000 0.3505780000

C 1.3641960000 -0.0000690000 -0.0873160000

F -0.7070530000 1.0921750000 -0.1347440000

F -0.7071920000 -1.0921100000 -0.1347370000

H -0.1925760000 -0.0000440000 1.4491050000

H 1.4050240000 -0.0017190000 -1.1858630000

H 1.8774610000 -0.8938520000 0.2925560000

H 1.8765120000 0.8953790000 0.2899490000

15

H-CF2Ph

C -1.6728990000 0.0001430000 0.3363800000

F -2.2245150000 -1.0948630000 -0.2345040000

F -2.2248230000 1.0947020000 -0.2347510000

C -0.1800020000 0.0001830000 0.1550390000

C 0.5159260000 -1.2083970000 0.0890740000

H -0.0350690000 -2.1502400000 0.1260710000

C 1.9030310000 -1.2068430000 -0.0382010000

H 2.4436860000 -2.1544910000 -0.0945760000

C 2.5986520000 -0.0001580000 -0.1001610000

H 3.6865600000 -0.0002660000 -0.2010490000

C 1.9033640000 1.2067240000 -0.0381200000

H 2.4442360000 2.1542630000 -0.0942450000

C 0.5162500000 1.2086050000 0.0890430000

H -0.0347890000 2.1504300000 0.1260550000

H -1.9665220000 0.0002000000 1.4027160000

5

H-CF3

C 0.0001870000 -0.0001800000 0.3328320000

H 0.0001800000 0.0001090000 1.4360420000

F -0.4811640000 1.1481970000 -0.1271130000

F -0.7544550000 -0.9904400000 -0.1271360000

F 1.2354750000 -0.1576490000 -0.1271990000

5

H-CFH2

C 0.6186480000 0.0000510000 -0.0000440000

F -0.7445210000 -0.0001120000 0.0000770000

H 0.9964860000 -0.7213760000 -0.7435660000

H 0.9972440000 -0.2829370000 0.9963510000

H 0.9950710000 1.0050110000 -0.2532170000

10

H-CFHC(O)Me

C 0.6054120000 -0.1523430000 0.0000280000

C -0.7985430000 -0.7343240000 0.0001200000

F -1.7667110000 0.2310250000 -0.0001230000

O 1.5483590000 -0.9037300000 -0.0000920000

C 0.7176640000 1.3437200000 0.0000560000

H -0.9088050000 -1.3738940000 0.8928110000

H -0.9088560000 -1.3744140000 -0.8921750000

H 0.2041700000 1.7619060000 0.8798900000

H 0.2044640000 1.7617360000 -0.8800460000

H 1.7753550000 1.6329620000 0.0001400000

5

H-CH3

C -0.0000300000 0.0000040000 -0.0000060000

H 0.4970230000 -0.5343540000 -0.8204570000

H 0.4911290000 -0.2497020000 0.9498190000

H -1.0558910000 -0.2980700000 0.0444160000

H 0.0679170000 1.0821030000 -0.1737400000

65

(L')Pd-CF2CH3-GS

C 2.6557300000 1.0378980000 -0.0067320000

C 2.5477340000 -0.3642610000 -0.0371660000

C 3.7313360000 -1.1181640000 -0.1063530000

C	4.9786310000	-0.5029980000	-0.1478940000
C	5.0748610000	0.8873660000	-0.1203410000
C	3.9149650000	1.6494860000	-0.0488620000
H	3.6877180000	-2.2044040000	-0.1285390000
H	5.8815380000	-1.1157740000	-0.2025610000
H	6.0520930000	1.3746900000	-0.1537720000
H	3.9910630000	2.7400710000	-0.0254590000
P	0.8513700000	-1.1222790000	0.0042110000
C	0.8752820000	-2.1894520000	1.5692090000
C	0.7607430000	-2.0840660000	-1.6261210000
C	0.6952670000	-0.9718690000	-2.6813660000
H	1.6015300000	-0.3456210000	-2.6721090000
H	0.6082960000	-1.4241250000	-3.6829100000
H	-0.1759870000	-0.3180970000	-2.5187940000
C	1.9328140000	-3.0100510000	-1.9422910000
H	1.7099730000	-3.5466920000	-2.8795330000
H	2.8713510000	-2.4623450000	-2.0994450000
H	2.0887190000	-3.7716240000	-1.1638410000
C	-0.5374330000	-2.8931770000	-1.6695160000
H	-0.4642370000	-3.8177060000	-1.0825210000
H	-1.4011570000	-2.3180940000	-1.3111610000
H	-0.7357910000	-3.1833500000	-2.7144820000
C	2.1158880000	-3.0478130000	1.8055330000
H	2.3013730000	-3.7567630000	0.9852990000
H	3.0194260000	-2.4446470000	1.9659080000
H	1.9565010000	-3.6449880000	2.7189380000
C	-0.3605060000	-3.0913490000	1.5815690000
H	-0.2207770000	-3.9754000000	0.9450120000
H	-0.5277980000	-3.4514130000	2.6102060000
H	-1.2690860000	-2.5682880000	1.2554710000
C	0.7683700000	-1.1518770000	2.6945810000
H	0.7401410000	-1.6672270000	3.6688550000

H 1.6346720000 -0.4708350000 2.6993720000

H -0.1426340000 -0.5417660000 2.5931330000

Pd -0.7260590000 0.6708480000 0.0791930000

C -2.4454020000 -0.4320470000 0.0349820000

C -3.1463980000 -0.6274940000 -1.1670720000

C -3.0387800000 -0.9403220000 1.2024200000

C -4.3619450000 -1.3132000000 -1.2067330000

H -2.7474890000 -0.2175750000 -2.0999840000

C -4.2547550000 -1.6271270000 1.1731940000

H -2.5543820000 -0.7861950000 2.1722680000

C -4.9216500000 -1.8222740000 -0.0352040000

H -4.8797630000 -1.4444490000 -2.1614460000

H -4.6865120000 -2.0072550000 2.1038320000

H -5.8743500000 -2.3572100000 -0.0625730000

C -1.9974440000 2.3063570000 -0.0285880000

F -1.3149450000 3.4891170000 0.3188750000

F -2.2888440000 2.4965640000 -1.3640170000

P 1.1232070000 2.0408070000 0.0986700000

C 1.2832670000 3.2138100000 -1.2926210000

H 1.2715120000 2.6443740000 -2.2325820000

H 0.4038740000 3.8706290000 -1.2676820000

H 2.2051860000 3.8111350000 -1.2338680000

C 1.4068890000 3.0585330000 1.5907210000

H 2.3299790000 3.6527180000 1.5190500000

H 0.5394050000 3.7207870000 1.7066360000

H 1.4669430000 2.3932080000 2.4635220000

C -3.2865160000 2.3635140000 0.7453450000

H -3.9746520000 1.5789730000 0.4121530000

H -3.0883700000 2.2182350000 1.8163460000

H -3.7498230000 3.3524180000 0.5932930000

65

(L')Pd-CF2CH3-TS

C	2.6259910000	-1.1727500000	-0.3162910000
C	2.5673080000	0.2282040000	-0.1639280000
C	3.7680990000	0.9537760000	-0.2220000000
C	4.9888440000	0.3244110000	-0.4443820000
C	5.0365720000	-1.0576740000	-0.6169380000
C	3.8596100000	-1.7944710000	-0.5493010000
H	3.7560190000	2.0341860000	-0.0864190000
H	5.9060230000	0.9170270000	-0.4831700000
H	5.9897030000	-1.5603380000	-0.7978840000
H	3.9048700000	-2.8795230000	-0.6777260000
P	0.9229280000	1.0312430000	0.1518240000
C	0.7247550000	2.2708970000	-1.2649890000
C	1.1595750000	1.8664850000	1.8428990000
C	1.8524470000	0.8264320000	2.7293100000
H	2.9043870000	0.6733460000	2.4495480000
H	1.8224850000	1.1637160000	3.7786590000
H	1.3377630000	-0.1469020000	2.6717550000
C	1.9480570000	3.1728080000	1.8593780000
H	2.0322520000	3.5297360000	2.9000970000
H	2.9713940000	3.0560420000	1.4769550000
H	1.4468840000	3.9643840000	1.2846220000
C	-0.2433240000	2.1098090000	2.4056810000
H	-0.8438020000	2.7830300000	1.7792290000
H	-0.7941070000	1.1619140000	2.4861420000
H	-0.1633980000	2.5569710000	3.4109150000
C	1.8966730000	3.1975970000	-1.5829450000
H	2.2031990000	3.8160240000	-0.7290600000
H	2.7712110000	2.6424590000	-1.9491610000
H	1.5902360000	3.8849730000	-2.3896930000
C	-0.5271790000	3.0970010000	-0.9595890000
H	-0.3483070000	3.8292690000	-0.1579520000
H	-0.8203410000	3.6609960000	-1.8602510000

H	-1.3775590000	2.4624860000	-0.6724240000
C	0.4643140000	1.3837650000	-2.4884850000
H	0.2812800000	2.0201090000	-3.3704050000
H	1.3310010000	0.7406250000	-2.7107460000
H	-0.4160870000	0.7430510000	-2.3364110000
Pd	-0.6878490000	-0.6825110000	0.1609320000
C	-2.5656700000	0.0890450000	-0.0756710000
C	-3.1758160000	0.9472420000	0.8612240000
C	-2.9183920000	0.2480770000	-1.4328220000
C	-4.0101400000	1.9801220000	0.4476750000
H	-2.9797980000	0.8161990000	1.9284980000
C	-3.7441790000	1.2912270000	-1.8429480000
H	-2.5404650000	-0.4663960000	-2.1696880000
C	-4.2890650000	2.1723010000	-0.9082400000
H	-4.4486840000	2.6482220000	1.1943780000
H	-3.9764960000	1.4077440000	-2.9051760000
H	-4.9449350000	2.9848870000	-1.2285090000
C	-2.6797800000	-1.7986750000	0.3959940000
F	-4.0490870000	-1.7093390000	0.3767770000
F	-2.4232110000	-2.7031740000	-0.6057570000
P	1.0807220000	-2.1777270000	-0.1888710000
C	1.5960080000	-3.5557900000	0.9165170000
H	1.7944090000	-3.1532590000	1.9204890000
H	0.7566740000	-4.2640560000	0.9881630000
H	2.4861810000	-4.0979910000	0.5620520000
C	1.0302150000	-3.0062730000	-1.8278950000
H	1.9570060000	-3.5537700000	-2.0602570000
H	0.1769080000	-3.7002660000	-1.8380250000
H	0.8557220000	-2.2416080000	-2.5982000000
C	-2.3518920000	-2.3726160000	1.7560640000
H	-1.3082040000	-2.7035740000	1.8168820000
H	-2.5242200000	-1.6091130000	2.5264470000

H -3.0304280000 -3.2209360000 1.9500800000

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(L')Pd-CF2CH3-TS-rot

C -2.6455650000 -1.1612790000 0.2753240000

C -2.5722380000 0.2454690000 0.1882370000

C -3.7646030000 0.9781180000 0.3081110000

C -4.9876580000 0.3497270000 0.5236490000

C -5.0498510000 -1.0389570000 0.6174090000

C -3.8822770000 -1.7827720000 0.4888660000

H -3.7450950000 2.0630530000 0.2281130000

H -5.8962040000 0.9498340000 0.6155900000

H -6.0058640000 -1.5404980000 0.7860080000

H -3.9359410000 -2.8731480000 0.5554930000

P -0.9223960000 1.0526830000 -0.1100830000

C -0.7423280000 2.3197590000 1.2886740000

C -1.1421510000 1.8137920000 -1.8353960000

C -1.2687440000 0.5945070000 -2.7574330000

H -2.1709430000 0.0042810000 -2.5325510000

H -1.3396290000 0.9332090000 -3.8044890000

H -0.3917340000 -0.0663540000 -2.6632440000

C -2.3453300000 2.7275080000 -2.0496820000

H -2.3227320000 3.1109660000 -3.0841120000

H -3.2986240000 2.1964850000 -1.9227120000

H -2.3349200000 3.5999450000 -1.3809660000

C 0.1436620000 2.5636070000 -2.1896950000

H 0.2031310000 3.5394460000 -1.6897100000

H 1.0382740000 1.9864440000 -1.9164850000

H 0.1684640000 2.7483250000 -3.2766500000

C -1.8633950000 3.3306840000 1.5181000000

H -2.0833790000 3.9302800000 0.6233600000

H -2.7908380000 2.8558170000 1.8647310000

H -1.5477150000 4.0327790000 2.3084960000

C	0.5720770000	3.0714960000	1.0565860000
H	0.4622320000	3.8611040000	0.3011200000
H	0.8792520000	3.5579300000	1.9970460000
H	1.3855540000	2.4014580000	0.7472250000
C	-0.6008860000	1.4383690000	2.5365020000
H	-0.4223040000	2.0768190000	3.4177390000
H	-1.5121580000	0.8484930000	2.7233090000
H	0.2453550000	0.7418700000	2.4352200000
Pd	0.6740470000	-0.6630200000	-0.0731840000
C	2.5689950000	0.0743940000	0.0549810000
C	3.1442520000	0.8247010000	-0.9984760000
C	2.9911860000	0.3845200000	1.3709920000
C	4.0080770000	1.8826410000	-0.7402620000
H	2.8897300000	0.5772140000	-2.0334380000
C	3.8584450000	1.4438780000	1.6204020000
H	2.6264080000	-0.2229230000	2.2042030000
C	4.3686790000	2.2101370000	0.5706180000
H	4.4085330000	2.4634990000	-1.5761560000
H	4.1419730000	1.6728330000	2.6516500000
H	5.0530320000	3.0380230000	0.7674640000
C	2.6869680000	-1.8339300000	-0.1944860000
F	2.3948380000	-2.5745580000	0.9261410000
F	2.1588950000	-2.5078450000	-1.2853200000
P	-1.1117760000	-2.1698460000	0.0864130000
C	-1.5541460000	-3.2982990000	-1.2940160000
H	-1.6583920000	-2.7056570000	-2.2139780000
H	-0.7209980000	-4.0025280000	-1.4357020000
H	-2.4837490000	-3.8606310000	-1.1146190000
C	-1.1834340000	-3.2888660000	1.5406810000
H	-2.1118180000	-3.8783980000	1.5963950000
H	-0.3205820000	-3.9686810000	1.4837570000
H	-1.0791590000	-2.6840220000	2.4527580000

C 4.1853030000 -1.9311630000 -0.3793120000

H 4.4890680000 -1.4292790000 -1.3053900000

H 4.7137260000 -1.4674480000 0.4616320000

H 4.4406570000 -3.0007590000 -0.4392100000

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(L')Pd-CF2CFMe2-GS

C 2.4482730000 -1.6495680000 -0.2206390000

C 2.7770370000 -0.3077550000 0.0410190000

C 4.1335130000 0.0214030000 0.2024760000

C 5.1291030000 -0.9456910000 0.1100460000

C 4.7922580000 -2.2737490000 -0.1454730000

C 3.4562260000 -2.6180640000 -0.3103800000

H 4.4267300000 1.0465960000 0.4130430000

H 6.1748030000 -0.6586370000 0.2432930000

H 5.5697940000 -3.0379080000 -0.2167350000

H 3.1936710000 -3.6590260000 -0.5156830000

P 1.4004380000 0.9345520000 0.1718360000

C 1.8181320000 2.2159850000 -1.1625280000

C 1.5586090000 1.5640330000 1.9570380000

C 0.8743620000 0.4649530000 2.7801810000

H 1.3769990000 -0.5074340000 2.6553890000

H 0.9116930000 0.7292760000 3.8499700000

H -0.1782840000 0.3329040000 2.4869290000

C 2.9758560000 1.7608310000 2.4908190000

H 2.9041860000 2.1555440000 3.5180770000

H 3.5414390000 0.8209660000 2.5408280000

H 3.5514300000 2.4923500000 1.9047690000

C 0.7963660000 2.8809690000 2.1072470000

H 1.3811320000 3.7290320000 1.7246280000

H -0.1734520000 2.8701620000 1.5950560000

H 0.6130870000 3.0657500000 3.1787360000

C 3.2393950000 2.7751860000 -1.1473140000

H	3.4973550000	3.2396070000	-0.1835980000
H	3.9941780000	2.0169010000	-1.3930710000
H	3.3113800000	3.5634180000	-1.9150610000
C	0.8310520000	3.3850590000	-1.0963520000
H	1.0800400000	4.0885660000	-0.2924560000
H	0.8877670000	3.9403880000	-2.0469820000
H	-0.2066580000	3.0539390000	-0.9657250000
C	1.5887830000	1.4433210000	-2.4678540000
H	1.7857470000	2.1084770000	-3.3244710000
H	2.2625480000	0.5759230000	-2.5534310000
H	0.5494410000	1.0878000000	-2.5408140000
Pd	-0.6581370000	-0.2393780000	-0.1684810000
C	-1.8694400000	1.4084060000	-0.2419470000
C	-2.3214640000	2.1771950000	0.8395360000
C	-2.2847600000	1.8207960000	-1.5213680000
C	-3.1158040000	3.3137280000	0.6606580000
H	-2.0604090000	1.8940200000	1.8631600000
C	-3.0723400000	2.9554800000	-1.7128340000
H	-1.9943410000	1.2363130000	-2.3997000000
C	-3.4879250000	3.7159300000	-0.6195510000
H	-3.4453530000	3.8864490000	1.5326470000
H	-3.3689090000	3.2451000000	-2.7251370000
H	-4.1062560000	4.6054430000	-0.7642640000
C	-2.3801500000	-1.3877400000	-0.3736300000
F	-3.4056320000	-0.8062370000	-1.0643770000
F	-2.0937900000	-2.5270480000	-1.1388260000
P	0.6901950000	-2.0900460000	-0.5021060000
C	0.4774990000	-3.6638890000	0.3950240000
H	0.6302370000	-3.4889040000	1.4682850000
H	-0.5609300000	-3.9837430000	0.2489000000
H	1.1696830000	-4.4394440000	0.0362680000
C	0.7177060000	-2.5980130000	-2.2617810000

H 1.4458610000 -3.4041040000 -2.4372390000

H -0.2919860000 -2.9306200000 -2.5346910000

H 0.9823090000 -1.7266890000 -2.8766900000

C -2.9975230000 -1.9185490000 0.9384650000

F -1.9765460000 -2.6071390000 1.6053780000

C -3.4523440000 -0.8008530000 1.8460070000

H -2.5885280000 -0.2041490000 2.1627160000

H -4.1524100000 -0.1355460000 1.3239980000

H -3.9417770000 -1.2202210000 2.7370250000

C -4.1041380000 -2.9199970000 0.6631780000

H -3.7337000000 -3.7420240000 0.0380310000

H -4.4782050000 -3.3285790000 1.6128020000

H -4.9314600000 -2.4267550000 0.1355520000

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(L')Pd-CF2CFMe2-TS

C 2.4675330000 -1.6773520000 -0.4419920000

C 2.8062290000 -0.3325890000 -0.1807090000

C 4.1657390000 0.0199600000 -0.1792210000

C 5.1604270000 -0.9121160000 -0.4586900000

C 4.8163200000 -2.2318610000 -0.7444680000

C 3.4773430000 -2.6053800000 -0.7269160000

H 4.4617120000 1.0424030000 0.0474980000

H 6.2089190000 -0.6044980000 -0.4519920000

H 5.5902420000 -2.9695680000 -0.9698580000

H 3.2129260000 -3.6464490000 -0.9326560000

P 1.4530500000 0.8845630000 0.1972790000

C 1.7307300000 2.3063640000 -1.0239490000

C 1.8218240000 1.3818410000 1.9967150000

C 2.0668680000 0.0712790000 2.7507250000

H 3.0129220000 -0.4079420000 2.4606650000

H 2.1036570000 0.2751140000 3.8337430000

H 1.2483330000 -0.6444110000 2.5702930000

C	2.9993420000	2.3281590000	2.2104860000
H	3.1273580000	2.5064550000	3.2919840000
H	3.9468310000	1.9141630000	1.8387950000
H	2.8327720000	3.3065470000	1.7382130000
C	0.5459650000	2.0156090000	2.5561620000
H	0.2524580000	2.9298310000	2.0236740000
H	-0.2963960000	1.3138530000	2.4865290000
H	0.6998980000	2.2728400000	3.6177900000
C	3.1390540000	2.8732100000	-1.1982290000
H	3.5828780000	3.2325510000	-0.2602580000
H	3.8217760000	2.1457460000	-1.6576120000
H	3.0826870000	3.7368100000	-1.8826500000
C	0.7742720000	3.4275300000	-0.6113020000
H	1.1410130000	3.9698040000	0.2730960000
H	0.6900830000	4.1574580000	-1.4330880000
H	-0.2354240000	3.0504780000	-0.3985190000
C	1.2832540000	1.7149340000	-2.3661210000
H	1.3522470000	2.4879780000	-3.1497450000
H	1.9239080000	0.8703430000	-2.6661470000
H	0.2440840000	1.3608030000	-2.3199910000
Pd	-0.5937850000	-0.2855500000	-0.0862620000
C	-2.1430250000	1.0487710000	-0.2511550000
C	-2.5108330000	1.8540870000	0.8528760000
C	-2.2911240000	1.6166120000	-1.5377260000
C	-2.8948850000	3.1772500000	0.6815130000
H	-2.4763400000	1.4383640000	1.8623230000
C	-2.6793360000	2.9429590000	-1.7028780000
H	-2.1074360000	0.9942040000	-2.4168110000
C	-2.9746400000	3.7394160000	-0.5967720000
H	-3.1409300000	3.7817910000	1.5591090000
H	-2.7593760000	3.3561650000	-2.7121460000
H	-3.2862900000	4.7780420000	-0.7268930000

C -2.9752870000 -0.6580010000 -0.2966690000

F -4.2095960000 -0.0706470000 -0.1332960000

F -2.9767770000 -1.1178000000 -1.5741120000

P 0.7056780000 -2.2147650000 -0.3233310000

C 0.8096790000 -3.4948070000 0.9919360000

H 1.1008530000 -3.0127620000 1.9360430000

H -0.1918720000 -3.9288070000 1.1154970000

H 1.5349570000 -4.2885850000 0.7556720000

C 0.4686220000 -3.2319700000 -1.8312740000

H 1.1912150000 -4.0577050000 -1.9229840000

H -0.5513070000 -3.6407620000 -1.7907390000

H 0.5428620000 -2.5795280000 -2.7127770000

C -3.0634180000 -1.8825550000 0.6669910000

C -2.7288020000 -1.4944280000 2.0896580000

H -3.4298500000 -0.7306790000 2.4532640000

H -2.7949570000 -2.3755290000 2.7438480000

H -1.7039890000 -1.0894270000 2.1337030000

C -4.4151660000 -2.5667330000 0.5408180000

H -4.6260660000 -2.7942170000 -0.5129740000

H -4.3852500000 -3.5091180000 1.1065630000

H -5.2204240000 -1.9352240000 0.9333830000

F -2.1366900000 -2.8337050000 0.2469780000

71

(L')Pd-CF2CFMe2-TS-rot

C -2.7370920000 -1.5973630000 -0.3156510000

C -2.9697030000 -0.2203190000 -0.1171530000

C -4.2984370000 0.2342270000 -0.1141380000

C -5.3653830000 -0.6343410000 -0.3220860000

C -5.1265040000 -1.9901890000 -0.5385850000

C -3.8186440000 -2.4613990000 -0.5299370000

H -4.5117420000 1.2878180000 0.0584600000

H -6.3878700000 -0.2491070000 -0.3138320000

H	-5.9579860000	-2.6788950000	-0.7065520000
H	-3.6362790000	-3.5280820000	-0.6886050000
P	-1.5240980000	0.9080090000	0.1860920000
C	-1.8638370000	1.5860200000	1.9299060000
C	-1.6643420000	2.2285650000	-1.1642220000
C	-1.2782990000	1.4779010000	-2.4446010000
H	-1.9998660000	0.6774990000	-2.6738520000
H	-1.2712160000	2.1808460000	-3.2943720000
H	-0.2789770000	1.0278290000	-2.3581710000
C	-3.0188860000	2.8977330000	-1.3894060000
H	-2.8995870000	3.6780620000	-2.1602080000
H	-3.7694320000	2.1887620000	-1.7645730000
H	-3.4141720000	3.3878480000	-0.4899740000
C	-0.6053960000	3.2894560000	-0.8551950000
H	-0.9016030000	3.9272320000	-0.0088200000
H	0.3718270000	2.8399100000	-0.6299450000
H	-0.4782240000	3.9451340000	-1.7322770000
C	-2.9309710000	2.6700520000	2.0484980000
H	-2.6533680000	3.5834960000	1.5036460000
H	-3.9162720000	2.3360330000	1.6954680000
H	-3.0465930000	2.9470130000	3.1103460000
C	-0.5300550000	2.1216690000	2.4567480000
H	-0.1311930000	2.9452870000	1.8491350000
H	-0.6643920000	2.4908200000	3.4875200000
H	0.2251540000	1.3231270000	2.4670950000
C	-2.2536880000	0.3722660000	2.7797390000
H	-2.2615260000	0.6603870000	3.8439910000
H	-3.2499270000	-0.0152210000	2.5232900000
H	-1.5239200000	-0.4450020000	2.6572950000
Pd	0.4081770000	-0.4079820000	0.0405320000
C	2.0872110000	0.7271930000	-0.1824200000
C	2.3181240000	1.0214460000	-1.5482800000

C 2.5076360000 1.6924020000 0.7609950000

C 2.8583880000 2.2408100000 -1.9470790000

H 2.0694770000 0.2708470000 -2.3028700000

C 3.0701800000 2.8980580000 0.3572880000

H 2.3532200000 1.5092430000 1.8259490000

C 3.2477200000 3.1882930000 -0.9997850000

H 2.9941310000 2.4441840000 -3.0128310000

H 3.3633260000 3.6316130000 1.1138110000

H 3.6893420000 4.1374680000 -1.3104910000

C 2.6123890000 -1.1364520000 0.1061100000

F 2.1754670000 -1.9970250000 1.1038360000

F 2.5360160000 -1.8179490000 -1.0748450000

P -1.0135780000 -2.2549710000 -0.2521320000

C -0.8722020000 -3.1580420000 -1.8447000000

H -0.9150620000 -2.4281180000 -2.6656720000

H 0.1143590000 -3.6439250000 -1.8719490000

H -1.6593170000 -3.9149530000 -1.9868890000

C -1.1554770000 -3.6257080000 0.9617560000

H -1.9244460000 -4.3677140000 0.6962460000

H -0.1752020000 -4.1210930000 1.0233670000

H -1.3848930000 -3.2014740000 1.9496990000

C 4.1458320000 -1.0319290000 0.4098630000

F 4.5549470000 -2.3647510000 0.3323850000

C 4.4528030000 -0.5843630000 1.8246290000

H 5.5121680000 -0.8014150000 2.0216510000

H 4.2894200000 0.4905140000 1.9557380000

H 3.8433500000 -1.1423010000 2.5468930000

C 4.9509680000 -0.2822260000 -0.6278220000

H 4.8044050000 0.8024770000 -0.5618020000

H 6.0123510000 -0.5091870000 -0.4506570000

H 4.6876570000 -0.6203930000 -1.6383440000

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(L')Pd-CF2H-GS

C	2.6454070000	0.8606610000	-0.0535070000
C	2.4147190000	-0.5278920000	-0.0794630000
C	3.5260750000	-1.3813230000	-0.1764750000
C	4.8202770000	-0.8759100000	-0.2582700000
C	5.0369230000	0.5009430000	-0.2429090000
C	3.9502440000	1.3613490000	-0.1370250000
H	3.3873470000	-2.4600600000	-0.1915080000
H	5.6650990000	-1.5643590000	-0.3360340000
H	6.0510890000	0.9016030000	-0.3099620000
H	4.1207630000	2.4413150000	-0.1173900000
P	0.6605240000	-1.1376400000	0.0053840000
C	0.6154380000	-2.1730270000	1.5881730000
C	0.4461140000	-2.1092880000	-1.6055070000
C	0.4391010000	-1.0094570000	-2.6756520000
H	1.3957290000	-0.4640020000	-2.7061620000
H	0.2787730000	-1.4651980000	-3.6665580000
H	-0.3648740000	-0.2790160000	-2.4945190000
C	1.5262070000	-3.1327770000	-1.9474400000
H	1.2280180000	-3.6587270000	-2.8697080000
H	2.5003910000	-2.6656540000	-2.1434690000
H	1.6469180000	-3.8965010000	-1.1652190000
C	-0.9157670000	-2.8069830000	-1.5883860000
H	-0.8958500000	-3.7258980000	-0.9876780000
H	-1.7145080000	-2.1560110000	-1.2084570000
H	-1.1780090000	-3.0954670000	-2.6196370000
C	1.7272720000	-3.2025730000	1.7730620000
H	1.7566690000	-3.9413910000	0.9588700000
H	2.7175540000	-2.7369300000	1.8667660000
H	1.5397300000	-3.7577880000	2.7073600000
C	-0.7420640000	-2.8730190000	1.6830480000
H	-0.7825330000	-3.7703730000	1.0516950000

H -0.9030940000 -3.1974930000 2.7243840000

H -1.5744100000 -2.2139930000 1.4005490000

C 0.7185260000 -1.1175380000 2.6971060000

H 0.6557830000 -1.6117560000 3.6805890000

H 1.6767430000 -0.5754190000 2.6542210000

H -0.0970610000 -0.3805030000 2.6245940000

Pd -0.7432510000 0.7854870000 0.0839210000

C -2.5897710000 -0.0939470000 0.0497200000

C -3.3014530000 -0.2660970000 -1.1497910000

C -3.2599750000 -0.4381440000 1.2361560000

C -4.5950870000 -0.7917900000 -1.1698700000

H -2.8418780000 0.0208280000 -2.1012040000

C -4.5537520000 -0.9653140000 1.2259870000

H -2.7673190000 -0.2900490000 2.2030190000

C -5.2265460000 -1.1523660000 0.0196650000

H -5.1155090000 -0.9156030000 -2.1242030000

H -5.0406600000 -1.2272630000 2.1701070000

H -6.2390700000 -1.5637230000 0.0075760000

C -1.8442770000 2.5084500000 -0.0051730000

F -1.2966440000 3.5538580000 0.7261190000

F -1.8624470000 2.9598870000 -1.3035560000

H -2.8925730000 2.4354620000 0.3236810000

P 1.2099780000 1.9861310000 0.1354460000

C 1.4261790000 3.2469250000 -1.1661280000

H 1.3524120000 2.7585420000 -2.1477150000

H 0.5914220000 3.9549290000 -1.0703300000

H 2.3847120000 3.7807160000 -1.0855530000

C 1.5861500000 2.8829000000 1.6827050000

H 2.5564580000 3.3995860000 1.6371620000

H 0.7762710000 3.6071270000 1.8423660000

H 1.5896620000 2.1668790000 2.5163390000

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(L')Pd-CF2H-TS

C	2.6245090000	-1.1149570000	-0.2577020000
C	2.4972290000	0.2850380000	-0.1403720000
C	3.6626830000	1.0631910000	-0.2378770000
C	4.9118250000	0.4858330000	-0.4422060000
C	5.0291970000	-0.8985340000	-0.5489030000
C	3.8880920000	-1.6866050000	-0.4565670000
H	3.6005520000	2.1460560000	-0.1499250000
H	5.7973670000	1.1217240000	-0.5154470000
H	6.0062560000	-1.3615630000	-0.7062780000
H	3.9841500000	-2.7722850000	-0.5468680000
P	0.8103210000	1.0238840000	0.1251540000
C	0.6123630000	2.2777780000	-1.2850160000
C	0.9612720000	1.8382340000	1.8318730000
C	0.9247070000	0.6593170000	2.8117340000
H	1.7775450000	-0.0211070000	2.6577840000
H	0.9770930000	1.0368570000	3.8467030000
H	-0.0022450000	0.0752540000	2.6964120000
C	2.2178910000	2.6609100000	2.1065330000
H	2.1383480000	3.1042210000	3.1137580000
H	3.1254270000	2.0418000000	2.0956530000
H	2.3492220000	3.4888690000	1.3963040000
C	-0.2810770000	2.7050320000	2.0438100000
H	-0.2292040000	3.6423780000	1.4710730000
H	-1.2000950000	2.1750360000	1.7545620000
H	-0.3603640000	2.9747940000	3.1101230000
C	1.4929570000	3.5241300000	-1.2571430000
H	1.3219910000	4.1309990000	-0.3564390000
H	2.5643200000	3.2952410000	-1.3312890000
H	1.2411000000	4.1571940000	-2.1249340000
C	-0.8585570000	2.7079410000	-1.3042110000
H	-1.1233940000	3.3396020000	-0.4469410000

H -1.0467090000 3.2951050000 -2.2184220000

H -1.5367280000 1.8449090000 -1.3083000000

C 0.8893470000 1.4641750000 -2.5542990000

H 0.6439880000 2.0735070000 -3.4396520000

H 1.9432150000 1.1579330000 -2.6314220000

H 0.2612350000 0.5587330000 -2.5838510000

Pd -0.7263730000 -0.7893010000 0.1366950000

C -2.6683490000 -0.1700230000 -0.0241380000

C -3.2886430000 0.7923880000 0.7944800000

C -3.0804690000 -0.2582480000 -1.3671380000

C -4.2010240000 1.6962090000 0.2637200000

H -3.0430160000 0.8330010000 1.8578490000

C -3.9873470000 0.6588790000 -1.8992620000

H -2.6846990000 -1.0580310000 -1.9987830000

C -4.5452770000 1.6470880000 -1.0909400000

H -4.6518810000 2.4510370000 0.9139660000

H -4.2711350000 0.5868100000 -2.9527000000

H -5.2644760000 2.3584640000 -1.5034420000

C -2.4816590000 -1.9362380000 0.7641820000

F -3.4584360000 -1.7200610000 1.6935360000

F -2.9865440000 -2.7605600000 -0.1832400000

H -1.7220720000 -2.5081210000 1.3292270000

P 1.1233030000 -2.1872910000 -0.1871530000

C 1.6070510000 -3.4727210000 1.0349610000

H 1.7048550000 -3.0011500000 2.0235570000

H 0.7971140000 -4.2162310000 1.0892100000

H 2.5470520000 -3.9877840000 0.7838780000

C 1.2446120000 -3.1014880000 -1.7772730000

H 2.2129480000 -3.6086510000 -1.9100620000

H 0.4347760000 -3.8451380000 -1.8148670000

H 1.0930950000 -2.3888970000 -2.6005730000

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(L')Pd-CF2H-TS-rot

C	2.6435060000	0.9307760000	-0.2422670000
C	2.4164930000	-0.4608580000	-0.1794790000
C	3.5230790000	-1.3176390000	-0.2986170000
C	4.8105180000	-0.8236070000	-0.4872970000
C	5.0251470000	0.5513100000	-0.5549930000
C	3.9438620000	1.4162200000	-0.4290110000
H	3.3834050000	-2.3952130000	-0.2402980000
H	5.6493330000	-1.5178750000	-0.5789910000
H	6.0325340000	0.9480950000	-0.7021530000
H	4.1175990000	2.4950170000	-0.4764610000
P	0.6846310000	-1.0861060000	0.0858770000
C	0.7943860000	-1.9067070000	1.7939880000
C	0.3795250000	-2.2895130000	-1.3464650000
C	0.3503370000	-1.3672010000	-2.5722920000
H	1.3241670000	-0.8800860000	-2.7384050000
H	0.1083840000	-1.9588800000	-3.4709160000
H	-0.4117560000	-0.5808700000	-2.4581460000
C	1.3834710000	-3.4130700000	-1.5930570000
H	1.0041960000	-4.0525860000	-2.4082460000
H	2.3633750000	-3.0348550000	-1.9134340000
H	1.5217510000	-4.0589310000	-0.7142740000
C	-1.0137140000	-2.8928770000	-1.1440530000
H	-1.0036200000	-3.7048480000	-0.4044720000
H	-1.7491280000	-2.1402090000	-0.8279170000
H	-1.3624400000	-3.3225800000	-2.0976870000
C	1.8734360000	-2.9663120000	1.9956030000
H	1.7600030000	-3.8166570000	1.3082130000
H	2.8860960000	-2.5550440000	1.8849030000
H	1.7957920000	-3.3652880000	3.0214490000
C	-0.5777650000	-2.4988550000	2.1227760000
H	-0.7545930000	-3.4472800000	1.5983660000

H -0.6338620000 -2.7055140000 3.2046130000

H -1.3915290000 -1.8078410000 1.8605530000

C 1.0600590000 -0.7314540000 2.7433940000

H 1.0780900000 -1.0976520000 3.7834120000

H 2.0294920000 -0.2509400000 2.5382070000

H 0.2707840000 0.0330310000 2.6570960000

Pd -0.7061100000 0.8053170000 0.0716140000

C -2.6957900000 0.3156450000 -0.0325840000

C -3.1807410000 0.0325600000 -1.3317060000

C -3.3384130000 -0.3254430000 1.0529030000

C -4.1723550000 -0.9218590000 -1.5364450000

H -2.7611290000 0.5692090000 -2.1874740000

C -4.3264480000 -1.2790220000 0.8385020000

H -3.0380920000 -0.0768970000 2.0750250000

C -4.7464990000 -1.5960380000 -0.4571500000

H -4.5027920000 -1.1414770000 -2.5555680000

H -4.7790910000 -1.7842820000 1.6964740000

H -5.5278420000 -2.3414120000 -0.6197250000

C -2.5526890000 2.1545070000 0.2118360000

F -2.1180710000 2.7141100000 1.3862770000

F -2.1980400000 2.9640390000 -0.8321320000

H -3.6497550000 2.2315260000 0.2630370000

P 1.2269630000 2.1016920000 -0.0602170000

C 1.4438570000 3.2187780000 -1.5014890000

H 1.2808360000 2.6386140000 -2.4209540000

H 0.6649180000 3.9934180000 -1.4460600000

H 2.4348350000 3.6971210000 -1.5412590000

C 1.7763140000 3.1594820000 1.3377410000

H 2.7656070000 3.6147880000 1.1748520000

H 1.0269390000 3.9523800000 1.4789500000

H 1.8021730000 2.5493780000 2.2518090000

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(L')Pd-CF2CN-GS

C	2.6674120000	-1.0730400000	-0.0497910000
C	2.5842250000	0.3271100000	0.0552290000
C	3.7811570000	1.0525740000	0.1761030000
C	5.0157620000	0.4109560000	0.1933500000
C	5.0863500000	-0.9773790000	0.0910220000
C	3.9130990000	-1.7121950000	-0.0305730000
H	3.7589800000	2.1362870000	0.2611500000
H	5.9295440000	1.0020240000	0.2892730000
H	6.0538660000	-1.4843860000	0.1056320000
H	3.9682520000	-2.8011620000	-0.1128330000
P	0.9049860000	1.1241890000	0.0430300000
C	0.9599950000	2.2805640000	-1.4548930000
C	0.8080150000	1.9750310000	1.7326450000
C	2.0292720000	2.7916220000	2.1498290000
H	2.2657200000	3.5933720000	1.4346570000
H	1.8074790000	3.2753640000	3.1154160000
H	2.9216900000	2.1691830000	2.2974220000
C	-0.4291720000	2.8734100000	1.7843280000
H	-1.3158440000	2.3958690000	1.3480730000
H	-0.6547120000	3.0999070000	2.8392730000
H	-0.2585240000	3.8303610000	1.2739040000
C	0.6325210000	0.8035930000	2.7083900000
H	-0.2792060000	0.2258950000	2.4915520000
H	1.4912210000	0.1139420000	2.6759440000
H	0.5563550000	1.1948080000	3.7359520000
C	-0.2834270000	3.1723130000	-1.4560330000
H	-1.1988610000	2.6219690000	-1.2024380000
H	-0.1788430000	4.0148490000	-0.7602050000
H	-0.4128050000	3.5949020000	-2.4659700000
C	0.8974070000	1.3118740000	-2.6432860000
H	-0.0163520000	0.6981990000	-2.6134070000

H	0.8998490000	1.8862930000	-3.5840810000
H	1.7660650000	0.6341630000	-2.6610430000
C	2.2001470000	3.1605410000	-1.5942820000
H	3.1130050000	2.5762310000	-1.7701260000
H	2.0619620000	3.8184310000	-2.4682600000
H	2.3545730000	3.8122800000	-0.7217150000
Pd	-0.6939480000	-0.6127410000	-0.1633760000
C	-2.3855710000	0.5361540000	-0.1335850000
C	-3.0848680000	0.8053210000	1.0513870000
C	-2.9566920000	0.9876610000	-1.3335690000
C	-4.2827040000	1.5246110000	1.0449800000
H	-2.7051320000	0.4371310000	2.0095910000
C	-4.1513320000	1.7088790000	-1.3477580000
H	-2.4702970000	0.7669170000	-2.2890420000
C	-4.8174070000	1.9880400000	-0.1549610000
H	-4.8033250000	1.7158640000	1.9875870000
H	-4.5684650000	2.0487580000	-2.3001050000
H	-5.7546710000	2.5500820000	-0.1630910000
C	-2.0250540000	-2.2005800000	-0.1732640000
F	-1.4661720000	-3.3962690000	-0.6140670000
F	-3.1590870000	-2.0722430000	-0.8973980000
C	-2.3499610000	-2.3946430000	1.2481410000
N	-2.4928750000	-2.4855310000	2.3953940000
P	1.1199310000	-2.0326260000	-0.2350270000
C	1.2195810000	-3.3082500000	1.0671610000
H	0.3503330000	-3.9702630000	0.9532250000
H	2.1460460000	-3.8976920000	1.0039500000
H	1.1570340000	-2.8189210000	2.0492310000
C	1.3740910000	-2.9497500000	-1.7946220000
H	0.4827370000	-3.5671740000	-1.9685310000
H	1.4693870000	-2.2264470000	-2.6166420000
H	2.2711590000	-3.5855840000	-1.7593480000

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(L')Pd-CF2CN-TS

C	-2.6351710000	1.2058670000	0.1983400000
C	-2.6105440000	-0.2016630000	0.1164460000
C	-3.8353850000	-0.8868680000	0.1726530000
C	-5.0432910000	-0.2105810000	0.3102870000
C	-5.0582540000	1.1809240000	0.3858020000
C	-3.8573850000	1.8780580000	0.3281410000
H	-3.8543650000	-1.9724950000	0.1015130000
H	-5.9777310000	-0.7751040000	0.3542910000
H	-6.0028300000	1.7198570000	0.4907420000
H	-3.8704160000	2.9697550000	0.3913250000
P	-0.9800180000	-1.0760850000	-0.0717810000
C	-1.1045750000	-1.8193020000	-1.8119330000
C	-0.9568990000	-2.3836630000	1.3009950000
C	-1.9373480000	-3.5493250000	1.1959570000
H	-1.7924980000	-4.1307330000	0.2742520000
H	-1.7621420000	-4.2360250000	2.0413900000
H	-2.9877010000	-3.2358950000	1.2555110000
C	0.4688460000	-2.9423190000	1.3635150000
H	1.2201820000	-2.1434420000	1.4025430000
H	0.5725560000	-3.5541500000	2.2749730000
H	0.7066090000	-3.5855540000	0.5069570000
C	-1.2188950000	-1.5849640000	2.5828060000
H	-0.5166200000	-0.7397200000	2.6695750000
H	-2.2435840000	-1.1866220000	2.6225800000
H	-1.0714660000	-2.2387570000	3.4580170000
C	0.0438140000	-2.8133650000	-1.9880890000
H	0.9995430000	-2.4004200000	-1.6359880000
H	-0.1441930000	-3.7550350000	-1.4522930000
H	0.1504000000	-3.0595760000	-3.0576600000
C	-0.8887310000	-0.6238590000	-2.7479770000

H	0.0874150000	-0.1440630000	-2.5739930000
H	-0.9291020000	-0.9650420000	-3.7959100000
H	-1.6710090000	0.1402350000	-2.6140430000
C	-2.4270300000	-2.4910950000	-2.1745650000
H	-3.2633130000	-1.7786640000	-2.1821850000
H	-2.3436150000	-2.9084520000	-3.1923360000
H	-2.6808110000	-3.3222310000	-1.5019500000
Pd	0.6905070000	0.6138930000	0.0210990000
C	2.5637170000	-0.2218820000	0.0820400000
C	3.0255630000	-0.3778390000	1.4066680000
C	3.0619660000	-1.0945900000	-0.9033130000
C	3.8526760000	-1.4430770000	1.7488410000
H	2.7223710000	0.3422390000	2.1729740000
C	3.8942390000	-2.1530090000	-0.5543030000
H	2.7826780000	-0.9395510000	-1.9482040000
C	4.2826280000	-2.3447720000	0.7738530000
H	4.1740420000	-1.5644880000	2.7866600000
H	4.2479830000	-2.8375720000	-1.3301340000
H	4.9403350000	-3.1747000000	1.0413310000
C	2.6892010000	1.5824820000	-0.5001990000
F	2.4474540000	1.6529840000	-1.8367470000
F	4.0490160000	1.5887800000	-0.3663170000
C	2.2396540000	2.8063390000	0.1639450000
N	1.9628580000	3.7975640000	0.7086160000
P	-1.0568460000	2.1499310000	0.1727800000
C	-1.1466330000	3.1526800000	1.7004760000
H	-0.2222750000	3.7491480000	1.7544660000
H	-2.0206870000	3.8211130000	1.7190180000
H	-1.1837700000	2.4757010000	2.5656690000
C	-1.3127340000	3.3978940000	-1.1442020000
H	-0.4407020000	4.0688770000	-1.1356120000
H	-1.3528800000	2.8905970000	-2.1184090000

H -2.2275860000 3.9927430000 -1.0004290000

63

(L')Pd-CF2CN-TS-rot

C -2.6735890000 -1.2784530000 -0.2508620000

C -2.6705540000 0.1309080000 -0.1740970000

C -3.8998920000 0.8013240000 -0.2840260000

C -5.0921590000 0.1106550000 -0.4800560000

C -5.0851850000 -1.2799370000 -0.5633410000

C -3.8800800000 -1.9629070000 -0.4442770000

H -3.9341190000 1.8863960000 -0.2119820000

H -6.0307890000 0.6635310000 -0.5648580000

H -6.0164060000 -1.8305290000 -0.7163980000

H -3.8802130000 -3.0550170000 -0.5022460000

P -1.0658370000 1.0292050000 0.1011460000

C -1.3029040000 1.7846040000 1.8261610000

C -0.9660250000 2.2946120000 -1.3060380000

C -2.1462170000 3.2354730000 -1.5371560000

H -2.4009300000 3.8244280000 -0.6447010000

H -1.8743810000 3.9516710000 -2.3310210000

H -3.0435780000 2.7038640000 -1.8804370000

C 0.3017620000 3.1241720000 -1.0810110000

H 1.1532300000 2.5058530000 -0.7661740000

H 0.5801770000 3.6205690000 -2.0251180000

H 0.1453890000 3.9116580000 -0.3315010000

C -0.7781030000 1.4160540000 -2.5496830000

H 0.1071790000 0.7696840000 -2.4496140000

H -1.6543380000 0.7733590000 -2.7295100000

H -0.6406460000 2.0586700000 -3.4351390000

C -0.0444360000 2.5831920000 2.1721300000

H 0.8701360000 2.0363990000 1.9030960000

H -0.0197190000 3.5566440000 1.6649420000

H -0.0250650000 2.7767990000 3.2574980000

C	-1.3776260000	0.5640540000	2.7522110000
H	-0.4769680000	-0.0637620000	2.6548330000
H	-1.4521620000	0.9033940000	3.7986310000
H	-2.2590830000	-0.0599260000	2.5370430000
C	-2.5384990000	2.6531160000	2.0434990000
H	-3.4720870000	2.0877580000	1.9187430000
H	-2.5274290000	3.0365720000	3.0779700000
H	-2.5610800000	3.5258500000	1.3755300000
Pd	0.6144490000	-0.6202370000	0.0462830000
C	2.4805040000	0.2159100000	-0.0777680000
C	2.8880220000	0.5782800000	-1.3833140000
C	3.0080540000	0.9531490000	1.0079210000
C	3.6879020000	1.6961700000	-1.5932200000
H	2.5693060000	-0.0308980000	-2.2337430000
C	3.8041810000	2.0686590000	0.7851180000
H	2.7787290000	0.6428890000	2.0310990000
C	4.1444710000	2.4555330000	-0.5148450000
H	3.9674940000	1.9720330000	-2.6133810000
H	4.1752560000	2.6418480000	1.6388900000
H	4.7854620000	3.3235000000	-0.6818990000
C	2.6967360000	-1.6438490000	0.1428770000
F	2.4286700000	-2.4720260000	-0.9132440000
F	2.3449250000	-2.2809090000	1.3058120000
C	4.1804570000	-1.5824050000	0.1962650000
N	5.3362190000	-1.5641740000	0.2393090000
P	-1.0937040000	-2.2144340000	-0.0737510000
C	-1.1345510000	-3.3574530000	-1.5097240000
H	-0.2459070000	-4.0032650000	-1.4534430000
H	-2.0389750000	-3.9842890000	-1.5440230000
H	-1.0661510000	-2.7642810000	-2.4327480000
C	-1.4613000000	-3.3379930000	1.3317660000
H	-0.6004380000	-4.0090530000	1.4689760000

H -1.5738840000 -2.7365190000 2.2449100000

H -2.3712520000 -3.9380490000 1.1763670000

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(L')Pd-CF2Ph-GS

C 2.8200550000 -1.5634610000 -0.0368540000

C 3.0503310000 -0.1942210000 -0.2631140000

C 4.3648310000 0.2190230000 -0.5370710000

C 5.4144460000 -0.6932520000 -0.5832440000

C 5.1757270000 -2.0477780000 -0.3566580000

C 3.8816130000 -2.4755580000 -0.0853550000

H 4.5815810000 1.2688050000 -0.7196300000

H 6.4263140000 -0.3417750000 -0.7983450000

H 5.9970030000 -2.7673710000 -0.3916210000

H 3.6947840000 -3.5381510000 0.0928330000

P 1.6063030000 0.9730890000 -0.1783220000

C 1.5469330000 1.7386730000 -1.9100500000

C 2.0771010000 2.1620660000 1.2189620000

C 3.4694710000 2.7849330000 1.1493120000

H 4.2696140000 2.0408600000 1.2577120000

H 3.6306330000 3.3515380000 0.2201220000

H 3.5746030000 3.4974390000 1.9843520000

C 1.0357380000 3.2799060000 1.3097090000

H 1.1294270000 3.7678420000 2.2938820000

H 1.1953190000 4.0520180000 0.5462280000

H 0.0083420000 2.9039610000 1.2169480000

C 1.9777760000 1.2809210000 2.4714620000

H 2.6974450000 0.4472630000 2.4431200000

H 2.2010810000 1.8886040000 3.3636250000

H 0.9661280000 0.8595150000 2.5829110000

C 0.5861150000 2.9290040000 -1.9025650000

H 0.3006470000 3.1610310000 -2.9419090000

H -0.3338900000 2.7258280000 -1.3387290000

H	1.0607010000	3.8275910000	-1.4858830000
C	0.9631640000	0.6094190000	-2.7698000000
H	0.8609350000	0.9572300000	-3.8109570000
H	1.6198260000	-0.2755470000	-2.7743880000
H	-0.0281490000	0.2967060000	-2.4067800000
C	2.8781450000	2.1807320000	-2.5134570000
H	3.3932690000	2.9308110000	-1.8954800000
H	3.5589830000	1.3377150000	-2.6916230000
H	2.6773670000	2.6500770000	-3.4909680000
Pd	-0.3198440000	-0.3249450000	0.3406110000
C	-1.6969700000	1.1910550000	0.4181530000
C	-2.0873600000	1.7528350000	1.6437620000
C	-2.3801600000	1.6272080000	-0.7277710000
C	-3.0980340000	2.7137220000	1.7209070000
H	-1.6095530000	1.4226990000	2.5712970000
C	-3.3875400000	2.5907230000	-0.6618110000
H	-2.1522650000	1.1834750000	-1.7020480000
C	-3.7506270000	3.1421970000	0.5658390000
H	-3.3807090000	3.1265750000	2.6938270000
H	-3.9027620000	2.8994710000	-1.5758000000
H	-4.5442180000	3.8916020000	0.6237900000
C	-1.9425490000	-1.5152100000	0.8463420000
F	-2.3249040000	-1.2676320000	2.1357850000
F	-1.6006260000	-2.8779220000	0.8634180000
C	-3.1149840000	-1.3788300000	-0.0774940000
C	-2.9864060000	-1.7912170000	-1.4081660000
C	-4.3101640000	-0.7949090000	0.3442310000
C	-4.0344940000	-1.6143700000	-2.3057870000
H	-2.0450010000	-2.2351300000	-1.7423620000
C	-5.3573910000	-0.6137330000	-0.5567090000
H	-4.3998570000	-0.4555890000	1.3767130000
C	-5.2247830000	-1.0200460000	-1.8827620000

H -3.9224330000 -1.9376650000 -3.3439110000

H -6.2827430000 -0.1405380000 -0.2192260000

H -6.0453620000 -0.8711230000 -2.5889080000

P 1.1117490000 -2.1227520000 0.3268450000

C 0.8267150000 -3.4332410000 -0.9159610000

H -0.1659410000 -3.8606340000 -0.7223330000

H 0.8322330000 -2.9782930000 -1.9166230000

H 1.5899860000 -4.2241040000 -0.8701480000

C 1.2873250000 -3.0282140000 1.9039460000

H 2.0158260000 -3.8497910000 1.8364890000

H 1.6025220000 -2.3190100000 2.6821470000

H 0.2960030000 -3.4218260000 2.1649360000

72

(L')Pd-CF2Ph-TS

C -2.1750450000 -1.8461360000 -0.7784430000

C -2.7277550000 -0.6997690000 -0.1712660000

C -4.1192940000 -0.6511530000 0.0114820000

C -4.9465350000 -1.6809870000 -0.4257720000

C -4.3962580000 -2.7938040000 -1.0589280000

C -3.0179320000 -2.8731820000 -1.2218850000

H -4.5730140000 0.2059230000 0.5056360000

H -6.0260440000 -1.6119800000 -0.2715290000

H -5.0389790000 -3.6035250000 -1.4126680000

H -2.5887630000 -3.7603390000 -1.6957490000

P -1.5910340000 0.6649830000 0.3679760000

C -1.8202500000 0.7246630000 2.2527100000

C -2.2643550000 2.2005960000 -0.5136280000

C -3.7628910000 2.4908970000 -0.4389460000

H -4.3566510000 1.7357340000 -0.9712180000

H -4.1388900000 2.5774110000 0.5891560000

H -3.9523890000 3.4570510000 -0.9366470000

C -1.4835160000 3.4018360000 0.0236570000

H	-1.6457930000	4.2676490000	-0.6388230000
H	-1.8235840000	3.6904860000	1.0296790000
H	-0.4027590000	3.2094200000	0.0603420000
C	-1.8951580000	1.9609880000	-1.9825260000
H	-2.4078100000	1.0735110000	-2.3865200000
H	-2.2028140000	2.8328540000	-2.5836770000
H	-0.8123260000	1.8227480000	-2.1053870000
C	-0.6371910000	1.5114510000	2.8225240000
H	-0.6969010000	1.5155420000	3.9238860000
H	0.3116370000	1.0430100000	2.5262230000
H	-0.6112220000	2.5541170000	2.4793830000
C	-1.6938460000	-0.7257080000	2.7292240000
H	-1.6568250000	-0.7449030000	3.8310360000
H	-2.5409720000	-1.3477860000	2.4056400000
H	-0.7628990000	-1.1810330000	2.3534300000
C	-3.1272820000	1.3278380000	2.7578020000
H	-3.2216490000	2.3895040000	2.4892340000
H	-4.0112550000	0.7905220000	2.3875110000
H	-3.1509500000	1.2673610000	3.8592760000
Pd	0.5927860000	0.0283810000	-0.2600690000
C	1.7769800000	1.7088310000	-0.3540890000
C	1.6999020000	2.3573850000	-1.6029920000
C	2.0907440000	2.5037920000	0.7692260000
C	1.8227150000	3.7419600000	-1.7077200000
H	1.5532600000	1.7596230000	-2.5059760000
C	2.2234940000	3.8821510000	0.6595420000
H	2.2244120000	2.0389420000	1.7485050000
C	2.0770360000	4.5168480000	-0.5778940000
H	1.7323070000	4.2161940000	-2.6888180000
H	2.4445980000	4.4725120000	1.5530770000
H	2.1846140000	5.6006660000	-0.6602770000
C	2.8542320000	0.1069530000	-0.5614210000

F 3.9896110000 0.8135670000 -0.2477360000

F 2.9699150000 -0.1619060000 -1.8902710000

C 2.9336050000 -1.1525760000 0.2540530000

C 3.3151270000 -2.3644070000 -0.3399650000

C 2.7442960000 -1.1055590000 1.6445050000

C 3.4732850000 -3.5078080000 0.4382020000

H 3.4947930000 -2.3952380000 -1.4157270000

C 2.8834200000 -2.2583730000 2.4122710000

H 2.4950040000 -0.1576660000 2.1246240000

C 3.2496570000 -3.4652710000 1.8156240000

H 3.7828300000 -4.4429250000 -0.0359750000

H 2.7209160000 -2.2086250000 3.4917350000

H 3.3708940000 -4.3656010000 2.4220340000

P -0.3415350000 -2.0352440000 -0.8675870000

C -0.1141100000 -3.5340790000 0.1677120000

H 0.9516640000 -3.8002940000 0.1696280000

H -0.4073510000 -3.2962930000 1.1995120000

H -0.7122960000 -4.3849100000 -0.1930170000

C -0.0519700000 -2.6836710000 -2.5599170000

H -0.6170880000 -3.6018060000 -2.7833230000

H -0.3135550000 -1.9034980000 -3.2886420000

H 1.0238470000 -2.8931430000 -2.6550160000

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(L')Pd-CF2Ph-TS-rot

C 3.0793710000 -1.5117490000 -0.2306120000

C 3.2297260000 -0.1283840000 0.0009030000

C 4.5310180000 0.3910170000 0.0960820000

C 5.6516450000 -0.4201930000 -0.0522210000

C 5.4954160000 -1.7825800000 -0.3006360000

C 4.2150090000 -2.3175000000 -0.3841670000

H 4.6788160000 1.4512780000 0.2950370000

H 6.6508150000 0.0148430000 0.0276280000

H	6.3694200000	-2.4269730000	-0.4222660000
H	4.0980130000	-3.3891860000	-0.5685910000
P	1.7130390000	0.9231550000	0.2217910000
C	1.8649280000	2.2542330000	-1.1167460000
C	1.9132610000	1.6119840000	1.9829740000
C	2.9115020000	2.7511650000	2.1679070000
H	3.9331870000	2.4732520000	1.8746470000
H	2.6181870000	3.6513770000	1.6093900000
H	2.9475310000	3.0283170000	3.2354030000
C	0.5235100000	2.0738730000	2.4289110000
H	0.5758450000	2.4449820000	3.4664290000
H	0.1183700000	2.8776620000	1.7993930000
H	-0.1884270000	1.2374630000	2.3917360000
C	2.3154270000	0.4161660000	2.8522040000
H	3.3458530000	0.0858900000	2.6582880000
H	2.2396920000	0.6968100000	3.9158100000
H	1.6414360000	-0.4392180000	2.6798470000
C	0.7367610000	3.2592220000	-0.8721130000
H	0.6326810000	3.9126790000	-1.7538990000
H	-0.2292840000	2.7606200000	-0.7100890000
H	0.9467080000	3.9062790000	-0.0073100000
C	1.5944720000	1.4913000000	-2.4192530000
H	1.6065910000	2.1969160000	-3.2667890000
H	2.3658050000	0.7267500000	-2.6049710000
H	0.6135080000	0.9953820000	-2.3948910000
C	3.1960180000	2.9900370000	-1.2572100000
H	3.5090940000	3.4963820000	-0.3347080000
H	4.0028710000	2.3196960000	-1.5835990000
H	3.0870630000	3.7656460000	-2.0343100000
Pd	-0.1281460000	-0.4942730000	-0.0444880000
C	-1.8424510000	0.5820200000	-0.3380200000
C	-2.3839580000	1.5223830000	0.5686650000

C	-2.0229520000	0.8371180000	-1.7171760000
C	-2.9898380000	2.6860880000	0.1186470000
H	-2.3293830000	1.3306840000	1.6425410000
C	-2.6192370000	2.0158080000	-2.1619380000
H	-1.6942390000	0.0904390000	-2.4454850000
C	-3.1068160000	2.9513070000	-1.2511910000
H	-3.3832890000	3.4005440000	0.8470410000
H	-2.7161460000	2.1951330000	-3.2364470000
H	-3.5921160000	3.8656620000	-1.5990180000
C	-2.3673660000	-1.2578440000	-0.0024650000
F	-1.9455990000	-2.0604480000	1.0425930000
F	-2.2811370000	-1.9960050000	-1.1464590000
C	-3.8270410000	-0.9746560000	0.2619870000
C	-4.7010560000	-0.7233220000	-0.7986510000
C	-4.3099590000	-0.9459050000	1.5723950000
C	-6.0379410000	-0.4303350000	-0.5487090000
H	-4.3242250000	-0.7475840000	-1.8218010000
C	-5.6479780000	-0.6482450000	1.8196420000
H	-3.6316270000	-1.1582320000	2.4000090000
C	-6.5151010000	-0.3853450000	0.7610450000
H	-6.7130350000	-0.2327250000	-1.3847350000
H	-6.0159420000	-0.6256760000	2.8483260000
H	-7.5638890000	-0.1484550000	0.9555540000
P	1.3900410000	-2.2579270000	-0.2956380000
C	1.4116290000	-3.1248270000	-1.9157500000
H	0.4654130000	-3.6760990000	-2.0206140000
H	1.4577600000	-2.3710960000	-2.7148180000
H	2.2563760000	-3.8230780000	-2.0236930000
C	1.5339430000	-3.6537060000	0.8908700000
H	2.3623030000	-4.3416230000	0.6607050000
H	1.6714490000	-3.2445490000	1.9020010000
H	0.5842910000	-4.2087670000	0.8749580000

4.5.References

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Chapter Five

Explaining the Selectivity of Late Transition Metals from Group 9 and Group 10 for Oxidative Addition of C–H vs C–Cl Bonds by Computation

5.1. Introduction

The oxidative addition of a C–X bond (X = H or halogen) to a transition metal center M is defined as the reaction that forms a new M–C and a new M–X bond by cleavage of the C–X bond. The formal oxidation state of the metal center is increased by +2 in this process.[1] The oxidative additions of C–H and C–halogen bonds to transition-metal complexes are key steps in many important catalytic reactions, such as the functionalization of C–H bonds[2-7] and cross-coupling reactions.[8-14] Iridium complexes are well-known to activate or functionalize C–H bonds but are rarely reported to undergo oxidative addition of carbon–halogen bonds.[4, 15-18] In contrast, palladium complexes readily undergo oxidative additions of carbon–halogen or carbon–pseudohalogen bonds and catalyze a large variety of cross-coupling reactions, but they rarely undergo oxidative addition of C–H bonds.[8-14] Although many Pd-catalyzed functionalizations of C–H bonds have been reported, the Pd complexes cleave the C–H bonds, in almost all cases, by electrophilic activation or a concerted-metalation-deprotonation (CMD) step,[19-26] during which the formal oxidation state of the Pd center does not change. Investigation of the reasons behind the high selectivity of Pd complexes to oxidatively add carbon–halogen bonds over C–H bonds, as well as the high selectivity of Ir complexes to oxidatively add C–H bonds over carbon–halogen bonds is valuable for understanding the fundamental reactivity of these transition metals and for the future development of Pd and Ir catalysts.

The Activation Strain Model (ASM)[27-29] or the Distortion/Interaction Model[30-31] decomposes the potential energy surface $\Delta E(\zeta)$ along the reaction coordinate ζ of a given chemical reaction into two terms: the reaction strain or distortion energy, $\Delta E_{\text{strain}}(\zeta)$, and the interaction energy, $\Delta E_{\text{int}}(\zeta)$;[32] that is,

$$\Delta E(\zeta) = \Delta E_{\text{strain}}(\zeta) + \Delta E_{\text{int}}(\zeta) \tag{5.1.1}$$

The distortion energy, $\Delta E_{\text{strain}}(\zeta)$, refers to the energy required to distort the geometries of the reactants from their lowest-energy ground states to the reactive conformations. By definition, the distortion energy is destabilizing, *i.e.*, $\Delta E_{\text{strain}}(\zeta) > 0$. The interaction energy, $\Delta E_{\text{int}}(\zeta)$, refers to the change in energy caused by electronic interactions between the distorted reactive fragments and is usually stabilizing, *i.e.*, $\Delta E_{\text{int}}(\zeta) < 0$. Therefore, the sum of $\Delta E_{\text{strain}}(\zeta)$ and $\Delta E_{\text{int}}(\zeta)$ determines the energy profile of a chemical reaction along the reaction coordinate. At the transition state, the potential energy surface reaches a first-order saddle point; that is, for $\zeta = \zeta(\text{TS})$,

$$\frac{\partial \Delta E(\zeta)}{\partial \zeta} = \frac{\partial \Delta E_{strain}(\zeta)}{\partial \zeta} + \frac{\partial \Delta E_{int}(\zeta)}{\partial \zeta} = 0 \tag{5.1.2}$$

Rearrangement of eq 5.1.2 gives the following equation:

$$\frac{\partial \Delta E_{strain}(\zeta)}{\partial \zeta} = -\frac{\partial \Delta E_{int}(\zeta)}{\partial \zeta} \tag{5.1.3}$$

This equation shows that the rate by which $\Delta E_{\text{strain}}(\zeta)$ increases is equal to the rate by which $\Delta E_{\text{int}}(\zeta)$ decreases at the transition state.

According to Energy Decomposition Analysis based on Absolutely Localized Molecular Orbitals (ALMO EDA) developed by the Head-Gordon group,[33-34] the interaction energy, ΔE_{int}, can be further decomposed into three terms: the frozen density term (ΔE_{FRZ}), the polarization term,

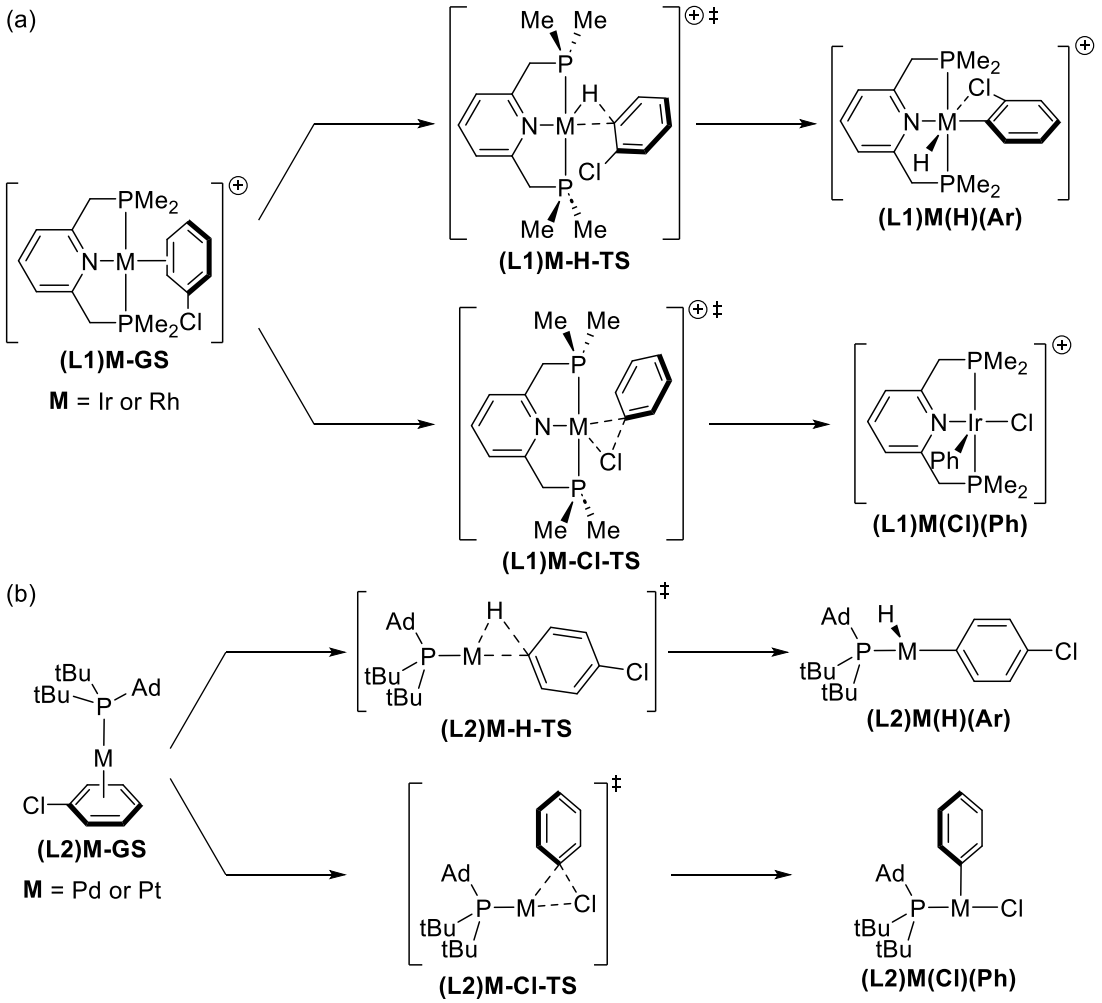
(ΔE_{POL}), and the charge transfer term, (ΔE_{CT}). The frozen density term (ΔE_{FRZ}) is defined as the change in energy caused by bringing infinitely separated, distorted reactive fragments into the reactive complex without any relaxation of the molecular orbitals (MOs) on those fragments. The polarization term (ΔE_{POL}) refers to the stabilization energy attributable to relaxation of localized MOs on each reactive fragment in the field of all other fragments. Lastly, the charge transfer term (ΔE_{CT}) takes into account the stabilization energy caused by charge transfer from occupied orbitals on one reactive fragment into virtual orbitals on another fragment. EDA allows the interaction energy (ΔE_{int}) to be interpreted in chemically meaning terms, such as electrostatic interactions and orbital interactions,[33] and has been used for the analysis of many chemical systems.[33-40]

In this chapter, we report computational investigations of the origin of the high selectivity of Pd complexes for oxidative addition of C–Cl bonds over C–H bonds and the origin of the high selectivity of Ir complexes for oxidative addition of C–H bonds over C–Cl bonds. DFT calculations and EDA were performed on the (**L1**)iridium complexes (**L1** = 2,6-bis((dimethylphosphino)methyl)pyridine) and (**L2**)palladium complexes (**L2** = (1-adamantyl)-di-*tert*-butylphosphine) undergoing oxidative addition of the C–H or the C–Cl bond in chlorobenzene (PhCl). Computations suggest that oxidative addition of an aryl C–H bond by the (**L2**)Pd(0) complex is endergonic, whereas oxidative addition of an aryl C–Cl bond to (**L2**)Pd(0) is exergonic. Oxidative addition of a C–H bond to the (**L1**)Ir(I) complex is less exergonic than that of a C–Cl bond, but the barrier to oxidative addition of a C–H bond to Ir is lower than that of a C–Cl bond. EDA indicates that the cationic (**L1**)iridium(I) complex is highly selective for oxidative addition of C–H bonds over that of C–Cl bonds because the stabilization afforded by charge transfer between the *d* orbitals on Ir and the σ or σ^* orbitals of the C–H bond is greater than that between Ir and the C–Cl bond.

5.2. Results and Discussions

5.2.1. Model Systems

We chose oxidative addition of the C–X (X = H or Cl) bond in chlorobenzene (PhCl) to the Ir complex containing the tridentate PNP pincer ligand **L1** (**L1** = 2,6-bis((dimethylphosphino)methyl)pyridine, Scheme 5.1(a)) and oxidative addition of the same arene to the Pd complex containing the trialkylphosphine ligand **L2** (**L2** = (1-adamantyl)-di-*tert*-butylphosphine, Scheme 5.1(b)) as model reactions for this study because activation of aromatic C–H bonds by (**L1**)Ir(I) complexes and oxidative addition of aryl halides to (**L2**)Pd(0) complexes are well-documented.[41-43] We also computed oxidative addition of the C–H or C–Cl bonds in PhCl to (**L1**)Rh(I) and (**L2**)Pt(0) complexes (Scheme 5.1) to assess the effect of second-row versus third-row transition metals on the oxidative addition by comparing the reactivity of (**L1**)Rh with that of (**L1**)Ir and by comparing the reactivity of (**L2**)Pd with that of (**L2**)Pt. Likewise, we assessed the effect of Group 9 versus Group 10 metals on the oxidative addition by comparing the reactivity of (**L1**)Rh with that of (**L2**)Pd and by comparing the reactivity of (**L1**)Ir with that of (**L2**)Pt.



Scheme 5.1. Oxidative addition of C–H and C–Cl bonds in chlorobenzene to complexes of (a) Group 9 transition metals and (b) Group 10 transition metals.

5.2.2. Geometries and Energies

We optimized the geometries and calculated the relative Gibbs free energies (*G*) of the ground-state and the transition-state structures for these model oxidative additions. The free-energy diagrams of these reactions are shown in Figures 5.1–5.4. For reactions with (**L1**)Ir complexes, the η^2-complex between the iridium center and the C(2)–C(3) double bond of PhCl is the lowest-energy ground state (**Ir-GS-1**, Figure 5.1). The σ-complex between the Ir center and the C–Cl bond of PhCl (**Ir-GS-2**, Figure 5.1), which is 3.0 kcal/mol higher in energy than **Ir-GS-1**, was located as another ground state of this system. The reactive complex **Ir-GS-1** undergoes oxidative addition of the *ortho*-C–H bond in PhCl to form product **Ir(H)(Ar)**, in which the chlorine atom in the aryl ligand partially occupies the coordination site on Ir that is *trans* to the hydride. The interaction between Ir and Cl in **Ir(H)(Ar)** was computed to be stabilizing. The reactive complex **Ir-GS-2** undergoes oxidative addition of the C–Cl bond to form product **Ir(Cl)(Ph)**, in which the phenyl ligand is perpendicular to the plane defined by the other atoms bound to Ir. The oxidative addition of the C–Cl bond to the cationic (**L1**)Ir complex (ΔG(Ir-Cl) = -23.2 kcal/mol) is more exergonic than that of the C–H bond (ΔG(Ir-H) = -13.3 kcal/mol), but the barrier to oxidative addition of the

C–Cl bond to (**L1**)Ir is higher than that of the C–H bond ($\Delta G^{\ddagger}$(Ir-Cl) = 18.9 kcal/mol, $\Delta G^{\ddagger}$(Ir-H) = 11.4 kcal/mol, $\Delta\Delta G^{\ddagger}$(Ir) = 7.5 kcal/mol, Figure 5.1). These results agree with the high selectivity of Ir complexes for oxidative addition of C–H bonds over C–halogen bonds and are consistent with previously reported computational studies on similar Ir complexes containing pincer ligands.[42, 44-45]

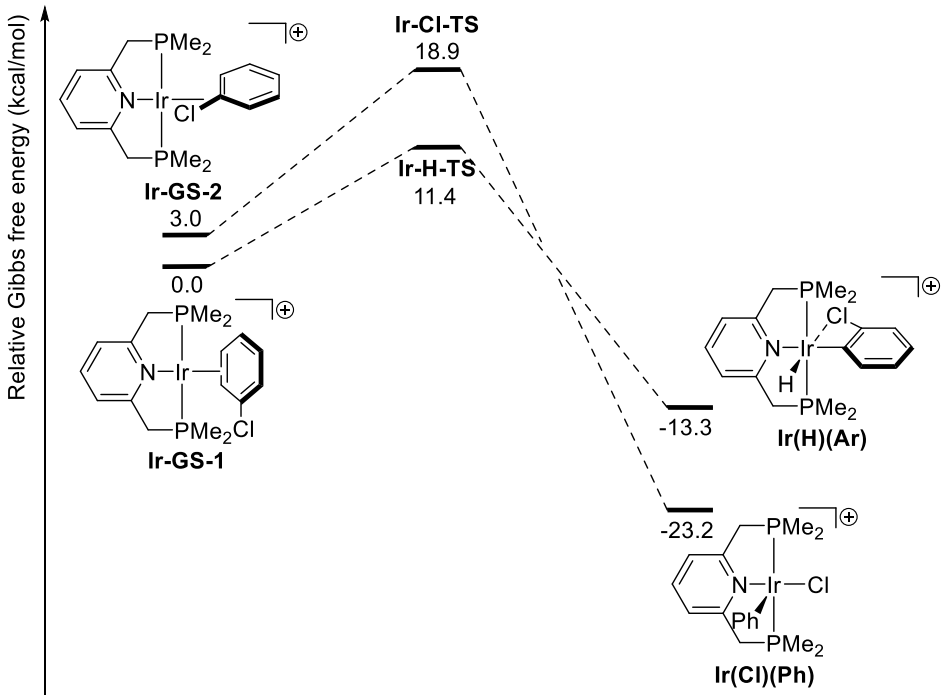


Figure 5.1. Free-energy diagram of the oxidative addition of the *ortho*-C–H bond and the C–Cl bond in PhCl to (**L1**)Ir(I) complexes.

The computed energies for the oxidative addition of the C–H and C–Cl bonds of chlorobenzene to (**L1**)Rh(I) are shown in Figure 5.2. Like the ground states **Ir-GS-1** and **Ir-GS-2**, the π-complex between the Rh center and PhCl (**Rh-GS-1**) as well as the σ-complex between Rh and the C–Cl bond in PhCl (**Rh-GS-2**, Figure 5.2) were computed to be ground states for the reactions with (**L1**)Rh complexes. In addition, the σ-complex between Rh and the *ortho*-C–H bond in PhCl (**Rh-GS-3**) was located as the third ground-state reactive complex and is 6.4 kcal/mol higher in free energy than **Rh-GS-1**. The structures of the transition states and the products for the oxidative addition of C–H or C–Cl bond to (**L1**)Rh complexes are similar to their Ir analogues. The oxidative addition of C–H and C–Cl bond to (**L1**)Rh is less exergonic than the oxidative addition to (**L1**)Ir (ΔG(Ir-H) = -13.3 kcal/mol, ΔG(Rh-H) = -0.7 kcal/mol; ΔG(Ir-Cl) = -23.2 kcal/mol, ΔG(Rh-Cl) = -13.8 kcal/mol). These thermodynamics are consistent with the known trend that the metal–hydrogen or metal–halogen bonds to second-row late transition metals are weaker than those to third-row late transition metals.[1] The computed barrier to oxidative addition of the aromatic C–H bond to the cationic (**L1**)Rh(I) is higher than that for (**L1**)Ir(I) ($\Delta G^{\ddagger}$(Ir-H) = 11.4 kcal/mol, $\Delta G^{\ddagger}$(Rh-H) = 15.1 kcal/mol), whereas the barrier to oxidative addition of the C–Cl bond to (**L1**)Rh(I) is similar to that for (**L1**)Ir(I) ($\Delta G^{\ddagger}$(Ir-Cl) = 18.9 kcal/mol, $\Delta G^{\ddagger}$(Rh-Cl) = 18.5 kcal/mol).

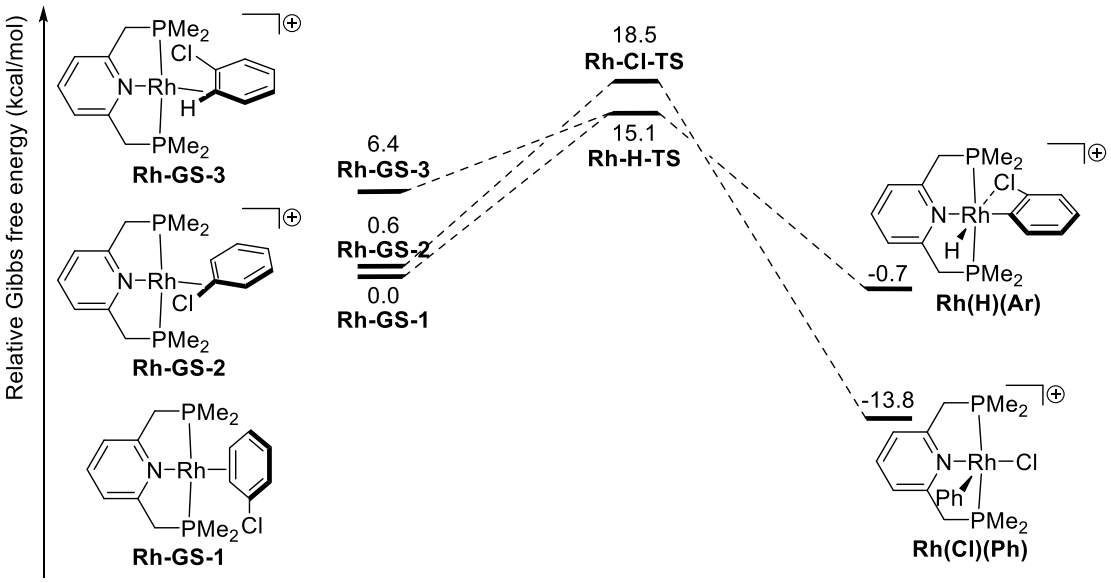


Figure 5.2. Free-energy diagram of the oxidative addition of the *ortho*-C–H bond and the C–Cl bond in PhCl to (**L1**)Rh(I) complexes.

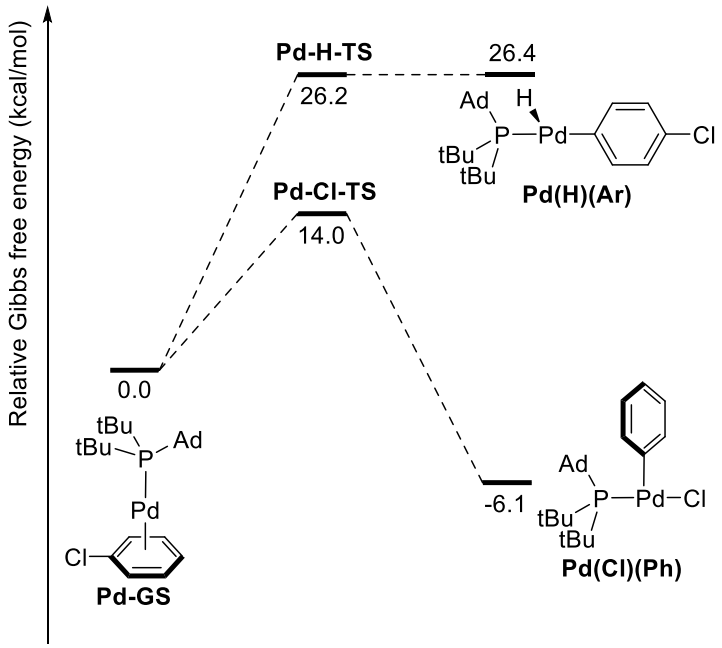


Figure 5.3. Free-energy diagram of the oxidative addition of the *para*-C–H bond and the C–Cl bond in PhCl to (**L2**)Pd(0) complexes.

The computed energies for oxidative addition of the *para*-C–H bond and the C–Cl bond in PhCl to (**L2**)Pd(0) are shown in Figure 5.3. The π-complex between (**L2**)Pd and the arene in PhCl (**Pd-GS**) was computed to be the lowest-energy ground state for both oxidative additions. Oxidative addition of the C–Cl bond to Pd forms the three-coordinate, T-shaped product **Pd(Cl)(Ph)**, in which the phosphine and the chloride ligands are *trans* to each other. This reaction is exergonic (ΔG(Pd-Cl) = -6.1 kcal/mol) and is computed to occur with a low barrier ($\Delta G^{\ddagger}$(Pd-Cl) = 14.0 kcal/mol). In contrast, the oxidative addition of the *para* C–H bond to (**L2**)Pd(0) is

endergonic (ΔG(Pd-H) = 26.4 kcal/mol) and the barrier to oxidative addition of the C–H bond ($\Delta G^{\ddagger}$(Pd-H) = 26.2 kcal/mol) is significantly higher than that of the C–Cl bond. In agreement with Hammond's postulate, the structure of transition state **Pd-H-TS** is similar to that of the product **Pd(H)(Ar)**. We recognize that the relative free energy of product **Pd(H)(Ar)** is 0.2 kcal/mol higher than that of the transition state **Pd-H-TS**. Although this result must reflect a small error in the energies, the results make clear that oxidative addition of C–H bonds to Pd(0) complexes is less favorable thermodynamically than the oxidative addition of C–Cl bonds and the resulting barrier for oxidative addition of the C–H bond is much higher than that for the more thermodynamically favorable oxidative addition of the C–Cl bond. It also implies that reductive elimination to form the C–H bond from the arylpalladium hydride is nearly barrierless.

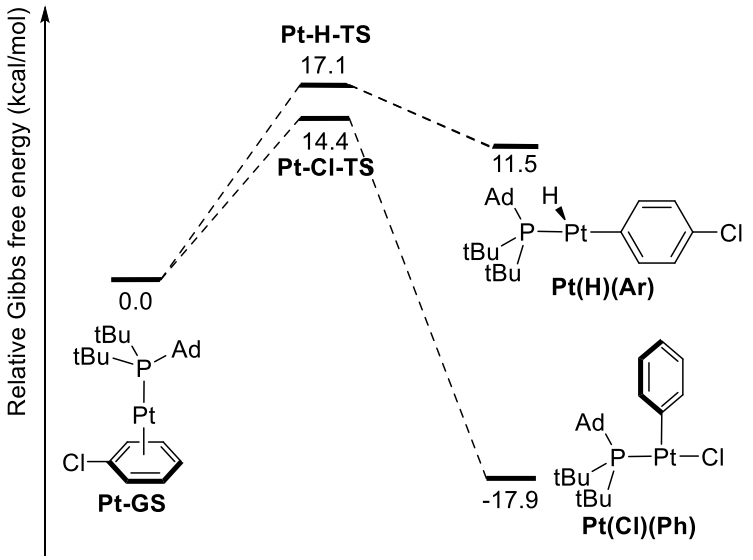


Figure 5.4. Free-energy diagram of the oxidative addition of the *para*-C–H bond and the C–Cl bond in PhCl to (**L2**)Pt(0) complexes.

The structures of ground states, transition states, and products of the oxidative addition of C–H and C–Cl bond in PhCl to the (**L2**)Pt(0) complex (Figure 5.4) are similar to their Pd counterparts (shown in Figure 5.3). Oxidative addition of the C–H bond to (**L2**)Pt(0) is less endergonic than that to (**L2**)Pd(0) (ΔG(Pt-H) = 11.5 kcal/mol, ΔG(Pd-H) = 26.4 kcal/mol), and oxidative addition of the C–Cl bond to Pt is more exergonic than that to Pd (ΔG(Pt-Cl) = -17.9 kcal/mol, ΔG(Pd-Cl) = -6.1 kcal/mol). Like the energetic differences between reactions with Rh and Ir complexes (*vide supra*), these data agree with the trend that the metal–hydrogen and metal–halogen bonds to second-row, late transition metals are weaker than those to third-row late transition metals.[1] The computed barrier for oxidative addition of the C–H bond to the (**L2**)Pt(0) complex is lower than that for (**L2**)Pd(0) ($\Delta G^{\ddagger}$(Pt-H) = 17.1 kcal/mol, $\Delta G^{\ddagger}$(Pd-H) = 26.2 kcal/mol), whereas the barrier for oxidative addition of the C–Cl bond to (**L2**)Pt(0) is similar to that for (**L2**)Pd(0) ($\Delta G^{\ddagger}$(Pt-Cl) = 14.4 kcal/mol, $\Delta G^{\ddagger}$(Pd-Cl) = 14.0 kcal/mol).

5.2.3. Thermodynamics of Oxidative Addition and Correlation with Bond Dissociation Energies

The bond dissociation energies (BDEs) of the bonds that are broken or formed during the oxidative addition of C–H or C–Cl bond in PhCl to complexes of Rh, Ir, Pd, and Pt agree well with

the thermodynamics of these reactions. Table 5.1 summarizes the BDEs of C–H, C–Cl, M–H, and M–Cl bonds reported in the literature.[46] We recognize that the complexes containing these bonds are different from those in our system and, therefore, the BDEs reported in Table 5.1 do not precisely reflect the strengths of the chemical bonds in our system. Nonetheless, these BDE values from the literature provide an acceptable estimate for the thermodynamics of reactions in our study.

Table 5.1. Bond Dissociation Energies of C–H, C–Cl, M–H, and M–Cl Bonds Reported in the Literature.[46]

Entry	Compound	Bond	BDE (kcal/mol)
1	$(\eta^5\text{-}C_5H_5)Rh(CO)_2(H)^+$	cationic Rh–H	68.6±2.9
2	$Rh–CH_3^+$ (*g*)	cationic Rh–C	33.9±1.4
3	$(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(H)(Ph)$	Ir–C(Ph)	80.6±3.6
4	$(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(Cl)_2$	Ir–Cl	90.3±5
5	$(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(H)_2$	Ir–H	74.2±5.0
6	Pd–H (*g*)	Pd–H	56±6
7	$PdCl_2$ (surface of single crystal)	Pd–Cl	65
8	Pt–H (*g*)	Pt–H	79
9[a]	$(COD)Pt(Cl)_2$	Pt–Cl	95.1±5.7
10	benzene	C–H	112.9±0.5
11	PhCl	C–Cl	95.5±1.5

[a]COD = 1,5-cyclooctadiene

The trends in computed thermodynamics of oxidative additions of C–H and C–Cl bonds to metal complexes are consistent with the trends in BDEs of chemical bonds in Table 5.1. The BDE of a C(aryl)–H bond is higher than that of a C(aryl)–Cl bond (entries 10–11) and the BDE of a metal–hydrogen bond is lower than that of a metal–chlorine bond for each metal. These data are consistent with our computational results showing that oxidative addition of a C(aryl)–H bond to a metal center is less exergonic than that of a C(aryl)–Cl bond. The BDEs of M–H and M–Cl bonds for third-row transition metals (Ir, Pt) are higher than those for second-row metals (Rh, Pd), and this trend is consistent with our computations and shows that oxidative addition of C–H or C–Cl bonds to (**L1**)Ir is more exergonic than to (**L1**)Rh and oxidative addition of these bonds to (**L2**)Pt is more exergonic than to (**L2**)Pd.

5.2.4.Energy Decomposition Analysis of Transition States and Ground States

To investigate the factors that influence the barriers to oxidative addition of C–H and C–Cl bonds in PhCl to complexes containing Rh, Ir, Pd, and Pt, we conducted energy decomposition analysis (EDA) of the transition states and ground states of these reactions by partitioning each structure into two fragments: one containing chlorobenzene and the other one containing the metal center and the ligand **L1** or **L2**. The results are summarized in Table 5.2. In the following subsections, we will rationalize the trends in barriers to oxidative addition (see Section 5.2.2) based on the data from EDA.

Table 5.2. Results from Energy Decomposition Analysis of the Ground States and Transition States of Oxidative Addition of the C–H and C–Cl Bonds in Chlorobenzene to Complexes of Ir, Rh, Pd, and Pt.[a]

structure	ΔE_{FRZ}	ΔE_{POL}	ΔE_{CT}	ΔE_{M2L}	ΔE_{L2M}	ΔE_{INT}	ΔE_{GD}^{PhCl}	$\Delta E_{GD}^{(L)M}$	$\Delta E_{GD} + \Delta E_{INT}$

Ir-GS-1	74.6	-54.8	-76.7	-37.0	-33.1	-56.9	12.3	4.7	-39.9
Ir-H-TS	89.0	-67.0	-89.4	-41.0	-39.1	-67.3	38.0	4.1	-25.2
Ir-Cl-TS	67.2	-41.2	-63.6	-33.4	-26.5	-37.6	13.4	4.4	-19.7
Rh-GS-1	30.2	-21.6	-51.4	-25.9	-21.9	-42.8	7.8	2.7	-32.3
Rh-H-TS	54.9	-36.9	-89.4	-47.0	-33.7	-71.5	54.9	2.6	-14.0
Rh-Cl-TS	51.1	-26.8	-64.3	-40.2	-20.3	-40.0	24.1	3.5	-12.5
Pd-GS	29.3	-15.9	-44.4	-30.8	-11.6	-31.0	3.7	1.6	-25.8
Pd-H-TS	60.9	-58.9	-94.7	-63.0	-24.7	-92.6	93.0	3.9	4.3
Pd-Cl-TS	43.6	-18.7	-55.5	-42.4	-10.9	-30.6	16.2	1.6	-12.8
Pt-GS	64.0	-37.7	-65.3	-38.2	-22.6	-38.9	5.9	3.9	-29.1
Pt-H-TS	108.4	-82.9	-102.5	-56.5	-36.4	-77.0	59.3	7.8	-9.9
Pt-Cl-TS	39.3	-20.7	-42.1	-24.3	-15.9	-23.4	5.3	1.4	-16.7

[a]All energies are reported in kcal/mol. Abbreviations: ΔE_{FRZ} = change in energy attributable to the frozen density term; ΔE_{POL} = change in energy attributable to the polarization term; ΔE_{CT} = change in energy attributable to the charge transfer term; ΔE_{M2L} = the part of ΔE_{CT} caused by charge transfer from the metal center to the PhCl fragment; ΔE_{L2M} = the part of ΔE_{CT} caused by charge transfer from PhCl to the metal center; $\Delta E_{INT} = \Delta E_{FRZ} + \Delta E_{POL} + \Delta E_{CT}$, the total interaction energy; ΔE_{GD}^{PhCl} = destabilization caused by distorting the geometry of the PhCl fragment from its isolated, lowest-energy ground-state structure; "GD" stands for geometry distortion; $\Delta E_{GD}^{(\mathbf{L})M}$ = destabilization caused by distorting the geometry of the (**L**)M (**L** = **L1** or **L2**, M = Ir, Rh, Pt, or Pd) fragment from its isolated, lowest-energy ground-state structure.

5.2.4.1. Explanation for the Higher Barrier to Oxidative Addition of C(aryl)–H Bonds to Complexes of Second-row Transition Metals than to Complexes of Third-row Transition Metals

As discussed in Section 5.2.2, comparison between Figures 5.1 and 5.2 indicates that the barrier to oxidative addition of a C(aryl)–H bond to the cationic (**L1**)Rh is 3.7 kcal/mol higher than that for (**L1**)Ir. Likewise, comparison between Figure 5.3 and 5.4 indicates that the barrier to oxidative addition of a C(aryl)–H bond to (**L2**)Pd is 9.1 kcal/mol higher than that for (**L2**)Pt. Energy decomposition analysis of the transition states suggests that the PhCl fragment in the transition states for reactions with second-row metals is more distorted than that with third-row metals and that this relative degree of distortion is the primary cause of the difference in barrier to oxidative addition for second-row versus third-row transition metals. For example, the interaction energies of transition states **Ir-H-TS** and **Rh-H-TS** are similar (ΔE_{INT}(**Ir-H-TS**) = -67.3 kcal/mol, ΔE_{INT}(**Rh-H-TS**) = -71.5 kcal/mol, different by only 4.2 kcal/mol) whereas the PhCl fragment in **Rh-H-TS** is significantly more distorted than that in **Ir-H-TS** (ΔE_{GD}^{PhCl}(**Rh-H-TS**) = 54.9 kcal/mol, ΔE_{GD}^{PhCl}(**Ir-H-TS**) = 38.0 kcal/mol, different by 16.9 kcal/mol). The interaction energy between the PhCl fragment and the (**L2**)M fragment in **Pd-H-TS** is 15.6 kcal/mol more stabilizing than that in **Pt-H-TS** (ΔE_{INT}(**Pd-H-TS**) = -92.6 kcal/mol, ΔE_{INT}(**Pt-H-TS**) = -77.0 kcal/mol) but the destabilization caused by distortion of the PhCl fragment in **Pd-H-TS** is 33.7 kcal/mol larger than that in **Pt-H-TS** (ΔE_{GD}^{PhCl}(**Pd-H-TS**) = 93.0 kcal/mol, ΔE_{GD}^{PhCl}(**Pt-H-TS**) = 59.3 kcal/mol). For transition metals from either Group 9 or Group 10, the difference in ΔE_{GD}^{PhCl} between second-row and third-row metals is much larger than the difference in ΔE_{INT} or $\Delta E_{GD}^{(\mathbf{L})M}$ and is, therefore, the main contributor to the difference in barrier to oxidative addition for second-row versus third-row transition metals.

Table 5.3. Bond Lengths of C(aryl)–H Bonds in Computed Structures

Entry	Structure	Bond	Bond Length (Å)
1	PhCl	*ortho*-C–H	1.091
2	**Rh-H-TS**	*ortho*-C(aryl)–H	1.512

3	**Ir-H-TS**	*ortho*-C(aryl)–H	1.413
4	PhCl	*para*-C–H	1.092
5	**Pd-H-TS**	*para*-C(aryl)–H	1.951
6	**Pt-H-TS**	*para*-C(aryl)–H	1.616

As shown in Table 5.3, the *ortho*-C–H bond that is being cleaved in transition state **Rh-H-TS** is longer than that in **Ir-H-TS** (entries 2–3) and the *para*-C–H bond that is being cleaved in transition state **Pd-H-TS** is longer than that in **Pt-H-TS** (entries 5–6). The greater distance between the carbon and the hydrogen atom undergoing oxidative addition in transition states containing second-row metals is consistent with the greater degree of distortion of the PhCl fragment in these structures, as determined from energy decomposition analysis. This result is consistent with the periodic trend in polarizability of late transition metals. We propose that less elongation of the C–H bond in PhCl is required to achieve good overlapping between the σ^* orbital of the C–H bond and the *d* orbitals on an Ir or Pt center than that for a Rh or Pd center since a third-row transition metal is more polarizable than a second-row transition metal.

5.2.4.2. Explanation for the High Selectivity of Ir Complexes to Undergo Oxidative Addition of C–H Bonds over C–Cl Bonds

Energy decomposition analysis of transition states **Ir-H-TS** and **Ir-Cl-TS** suggests that the PhCl fragment in **Ir-H-TS** is more distorted than that in **Ir-Cl-TS** (ΔE_{GD}^{PhCl}(**Ir-H-TS**) = 38.0 kcal/mol, ΔE_{GD}^{PhCl}(**Ir-Cl-TS**) = 13.4 kcal/mol) whereas the total interaction energy between the PhCl fragment and the (**L1**)Ir fragment in **Ir-H-TS** is more negative, *i.e.*, more stabilizing, than that in **Ir-Cl-TS** (ΔE_{INT}(**Ir-H-TS**) = -67.3 kcal/mol, ΔE_{INT}(**Ir-Cl-TS**) = -37.6 kcal/mol). The difference in interaction energy between these two transition states ($|\Delta\Delta E_{INT}$(**Ir-H-TS** – **Ir-Cl-TS**)| = $|\Delta E_{INT}$(**Ir-H-TS**) – ΔE_{INT}(**Ir-Cl-TS**)| = 29.7 kcal/mol) is larger than the difference in distortion energy between these transition states ($|\Delta\Delta E_{GD}^{PhCl}$(**Ir-H-TS** – **Ir-Cl-TS**)| = $|\Delta E_{GD}^{PhCl}$(**Ir-H-TS**) – ΔE_{GD}^{PhCl}(**Ir-Cl-TS**)| = 24.6 kcal/mol). Therefore, significant stabilization afforded by electronic interactions between the Ir center and the C(aryl)–H bond that is being cleaved in the transition state contributes to the low barrier to oxidative addition of C(aryl)–H bonds to Ir complexes. Such stabilizing electronic interactions are partially reflected in ΔE_{M2L} and ΔE_{L2M}, which represent stabilization caused by charge transfer from the metal to the arene and from the arene to the metal, respectively. As shown in Table 5.2, ΔE_{M2L}(**Ir-H-TS**) is 7.6 kcal/mol more negative than ΔE_{M2L}(**Ir-Cl-TS**), and ΔE_{L2M}(**Ir-H-TS**) is 12.6 kcal/mol more negative than ΔE_{L2M}(**Ir-Cl-TS**). This comparison indicates that the interactions between *d* orbitals on Ir and the σ or σ^* orbitals of the C–H bond are more stabilizing than those between *d* orbitals on Ir and the orbitals of the C–Cl bond in the two transition states.

Analysis by Natural Bond Orbitals (NBOs) of ground states and transition states for the oxidative addition of a C–H bond to the cationic (**L1**)Ir complex indicates that the partial charge on Ir changes from -0.02 (**Ir-GS-1**) to -0.15 (**Ir-H-TS**), then to +0.07 (**Ir(H)(Ar)**) during the reaction and the sum of partial charges on the carbon and hydrogen atoms of the C–H bond that is being cleaved changes from -0.10 (**Ir-GS-1**) to 0.00 (**Ir-H-TS**), then to -0.16 (**Ir(H)(Ar)**, Table 5.4, left). These results suggest that transfer of electron density from the occupied σ orbital of the C–H bond to the vacant orbitals of Ir occurs before the transfer of electron density from the occupied *d* orbital of Ir to the vacant σ^* orbital of the C–H bond and the Ir center contains partial negative charge in the transition state despite the overall +1 charge of the entire complex. We

propose that such transfer of electron density from the C–H bond to the positively charged (**L1**)Ir fragment stabilizes the transition state for oxidative addition of the C–H bond.

Table 5.4. Natural charges of atoms in the ground states and transition states for oxidative addition of C–H and C–Cl bonds to (**L1**)Ir complexes.

Structure	Atom[a]	Charge[b]	Structure	Atom[a]	Charge[b]
	Ir	-0.02		Ir	-0.24
Ir-GS-1	*α*-H	0.25	**Ir-GS-2**	Cl	0.17
	α-C(Ar)	-0.35		*α*-C(Ar)	-0.05
	Ir	-0.15		Ir	0.00
Ir-H-TS	*α*-H	0.25	**Ir-Cl-TS**	Cl	0.03
	α-C(Ar)	-0.25		*α*-C(Ar)	-0.02
	Ir	0.07		Ir	0.37
Ir(H)(Ar)	*α*-H	0.07	**Ir(Cl)(Ph)**	Cl	-0.46
	α-C(Ar)	-0.23		*α*-C(Ar)	-0.07

[a]*α*-C(Ar) refers to the carbon atom in PhCl that is bound to Ir in the product **Ir(H)(Ar)** or **Ir(Cl)(Ph)**; *α*-H refers to the hydrogen atom that is bound to *α*-C(Ar) in PhCl; [b]charge is determined by natural population analysis.

Similar analysis of the oxidative addition of a C–Cl bond to (**L1**)Ir shows that the partial charge on Ir increases monotonically from -0.24 (**Ir-GS-2**) to 0.00 (**Ir-Cl-TS**), then to 0.37 (**Ir(Cl)(Ph)**) during the reaction whereas the partial charge on Cl decreases monotonically from 0.17 (**Ir-GS-2**) to 0.03 (**Ir-Cl-TS**), then to -0.46 (**Ir(Cl)(Ph)**) and the partial charge on carbon undergoes little change (Table 5.4, right). The partial negative charge on Ir (-0.24) and the partial positive charge on Cl (+0.17) in the σ-complex **Ir-GS-2** are attributed to coordination of Cl to the Ir center. The large difference in partial charges on Ir and Cl in the product **Ir(Cl)(Ph)** (+0.37 for Ir, -0.46 for Cl) suggests that this Ir-Cl bond is highly ionic, consistent with the large BDE of Ir-Cl bonds (Table 5.1, entry 4) and the exergonicity of oxidative addition of C–Cl bonds. Such changes in partial charges suggest that transfer of electron density from Ir to the C–Cl bond is not accompanied by transfer of electron density to Ir during oxidative addition and we propose that this donation of electron density from the electrophilic (**L1**)Ir fragment destabilizes the transition state and accounts for the high barrier to oxidative addition of C–Cl bonds to (**L1**)Ir complexes.

5.2.4.3. Explanation for the High Selectivity of Pd Complexes to Undergo Oxidative Addition of C–Cl Bonds over C–H Bonds

Energy decomposition analysis suggests that the PhCl fragment in transition state **Pd-H-TS** is significantly more distorted than that in **Pd-Cl-TS** (ΔE_{GD}^{PhCl}(**Pd-H-TS**) = 93.0 kcal/mol, ΔE_{GD}^{PhCl}(**Pd-Cl-TS**) = 16.2 kcal/mol). The difference in distortion energy (76.8 kcal/mol) between **Pd-H-TS** and **Pd-Cl-TS** is greater than the difference in interaction energy between these two structures (ΔE_{INT}(**Pd-H-TS**) = -92.6 kcal/mol, ΔE_{INT}(**Pd-Cl-TS**) = -30.6 kcal/mol, different by 62 kcal/mol). Therefore, significant destabilization caused by distortion in the transition state **Pd-H-TS** is a major contributor to the high barrier to oxidative addition of C–H bonds to Pd species. We recognize that this conclusion does not offer much insight into the high selectivity of Pd complexes to oxidatively add C–Cl bonds over C–H bonds because this difference in distortion energy results from the endergonicity of the oxidative addition of C–H bonds to Pd species (see Sections 5.2.2 and 5.2.3). In agreement with Hammond's postulate, which states that the transition state of an endergonic reaction is more similar in structure to the product than to the reactant, the structure of

Pd-H-TS is similar to that of the product **Pd(H)(Ar)**, and the C–H bond is broken in the transition state (bond length = 1.951 Å, Table 5.3, entry 5). Such a long distance between the carbon and the hydrogen atom, by definition, leads to large distortion energy. In this case, the conclusion derived from EDA also can be derived from conventional analysis of structures and thermodynamics. Therefore, to understand the high selectivity of Pd complexes to undergo oxidative addition of C–Cl bonds over C–H bonds, we must first understand the reasons for endergonicity of oxidative addition of C–H bonds (or exergonicity of oxidative addition of C–Cl bonds). These reasons stem from the well-established, low BDE of a Pd–H bond.[46-49]

5.3. Summary and Future Directions

We conducted DFT calculations and energy decomposition analysis of (**L1**)Ir, (**L1**)Rh, (**L2**)Pd, and (**L2**)Pt complexes (**L1** = 2,6-bis((dimethylphosphino)methyl)pyridine, **L2** = (1-adamantyl)-di-*tert*-butylphosphine) to investigate the reasons for the high selectivity of Pd complexes to undergo oxidative addition of C–Cl bonds over C–H bonds, as well as the high selectivity of Ir complexes to oxidative add C–H bonds over C–Cl bonds. Computations suggest that oxidative addition of a C–H bond to the (**L2**)Pd(0) complex is endergonic, whereas oxidative addition of a C–Cl bond to (**L2**)Pd(0) is exergonic. Oxidative addition of a C–H bond to the cationic (**L1**)Ir(I) complex is less exergonic than that of a C–Cl bond, but the barrier to oxidative addition of a C–H bond to Ir is lower than that of a C–Cl bond. Consistent with bond dissociation energies of metal–hydrogen and metal–chlorine bonds for transition metals from Groups 9 and 10, the oxidative addition of C–H or C–Cl bonds to third-row metals is more exergonic (or less endergonic) than that to second-row metals. Energy decomposition analysis of the transition states suggests that the barriers to oxidative addition of C–H or C–Cl bonds to second-row transition metals are higher than those to third-row transition metals primarily because the degree of distortion of the PhCl fragment in transition states of reactions with second-row metals is greater than that for third-row transition metals. Iridium complexes of the ligand **L1** are highly selective towards oxidative addition of C–H bonds because the stabilization afforded by charge transfer between the *d* orbitals on Ir and the σ or σ^* orbitals of the C–H bond is greater than that between Ir and the C–Cl bond.

The high selectivity of a palladium(0) complex to undergo oxidative addition of a C–Cl bond over a C–H bond is closely related to the endergonicity of the reaction with a C–H bond, which, in turn, can be primarily attributed to the lower bond dissociation energy of the Pd–H bond than that of the Pd–Cl bond. As one future direction for this study, analysis by Natural Bond Orbital or bonded energy decomposition analysis[50-51] of the energies and orientations of atomic orbitals around the Pd–H bond versus the Pd–Cl bond would be helpful for understanding the reasons for the weakness of a Pd–H bond.

Another future direction for this study would be comparing complexes of Group 9 and Group 10 transition metals that contain the same ligands, charge, or oxidation state. Control of variables and identification of the factors that affect the reactivity of (**L1**)Ir and (**L2**)Pd complexes is difficult because the ligand, charge, oxidation state, and number of valence electrons of these two complexes are all different. Potential solutions to this problem include comparing the reactivities of an iridium and a palladium complex containing the same phosphine ligand or comparing the reactivity of an Ir(I) complex with a negatively charged ligand with that of a neutral Pd(0) complex so that both complexes contain the same charge. These proposed complexes may not be reported in the literature but may facilitate our study by controlling some variables.

5.4. Computational Details

Note: This section was written in collaboration with Dr. Kevin Ikeda.

5.4.1. Computational Methods

All calculations were performed with the Q-Chem (Version 5.4.1) program package.[52] Geometry optimizations were conducted with the PBE0 functional[53] and the basis sets def2-SVP for H atoms, def2-SVPD for O, Cl, and P atoms, and def2-TZVP (with effective core potential) for metal centers (**BS1**),[54] with Grimme's D3 dispersion correction with Becke-Johnson damping (GD3BJ)[55] in the gas phase. The nature of each stationary point was evaluated by accompanying frequency calculations (all positive eigenvalues for ground states and precisely one negative eigenvalue for transition states). Further single-point energy calculations were performed on the optimized structures with the def2-TZVPD basis set (with effective core potential for metal centers) for all atoms (**BS2**). In all cases, Gibbs free energies for **BS2** were approximately by adding the thermal corrections obtained from frequency calculations using **BS1** to the electronic energies computed at **BS2**.

Energy decomposition analysis was performed using the second-generation absolutely localized molecular orbital energy decomposition analysis (ALMO-EDA).[56] Natural Bond Orbital (NBO) and Natural Population Analysis (NPA) were conducted with the NBO 5.0 program.[57]

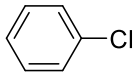
5.4.2. Energies of Optimized Structures

Table 5.4. Energies of Optimized Structures.

Structure	E(BS1) (Hartree)	Thermal Correction to Enthalpy (kcal/mol)	Thermal Correction to Entropy (cal mol^{-1} K^{-1})	E(BS2) (Hartree)
PhCl	-691.129164	61.607	76.062	-691.525282
Ir-GS-1	-1962.181526	251.223	165.752	-1963.321792
Ir-GS-2	-1962.170445	251.463	172.489	-1963.314187
Ir-H-TS	-1962.157550	248.317	168.177	-1963.297849
Ir-Cl-TS	-1962.146672	250.201	167.072	-1963.289482
Ir(H)(Ar)	-1962.201173	249.517	166.486	-1963.339904
Ir(Cl)(Ph)	-1962.222598	251.358	169.023	-1963.357374
Rh-GS-1	-1968.379119	251.145	166.474	-1969.518568
Rh-GS-2	-1968.373452	251.398	171.036	-1969.515776
Rh-GS-3	-1968.366137	250.749	169.508	-1969.506221
Rh-H-TS	-1968.351146	248.173	167.493	-1969.489318
Rh-Cl-TS	-1968.346519	250.075	167.555	-1969.486926
Rh(H)(Ar)	-1968.378926	249.191	166.770	-1969.516407
Rh(Cl)(Ph)	-1968.405346	251.238	168.352	-1969.539832
Pd-GS	-1864.760693	379.232	185.012	-1865.996362
Pd-H-TS	-1864.712937	376.132	187.779	-1865.948236
Pd-Cl-TS	-1864.739286	378.877	180.220	-1865.975731
Pd(H)(Ar)	-1864.713222	376.862	189.243	-1865.948477
Pd(Cl)(Ph)	-1864.776740	380.118	182.106	-1866.008762
Pt-GS	-1856.208349	379.190	188.052	-1857.445597
Pt-H-TS	-1856.178406	376.548	186.891	-1857.414707

Pt-Cl-TS	-1856.185409	379.160	181.569	-1857.425724
Pt(H)(Ar)	-1856.187422	377.478	190.508	-1857.423338
Pt(Cl)(Ph)	-1856.245618	380.247	182.265	-1857.478595

5.4.3. Atomic Coordinates of Optimized Structures



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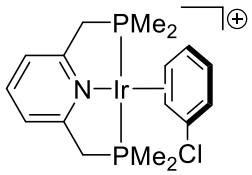
PhCl

H	-2.1061947027	-2.1572311959	0.0025503860
C	-1.5656771096	-1.2078321649	0.0015922233
C	-0.1722221293	-1.2150088364	-0.0020815730
H	0.3874967102	-2.1515391852	-0.0039374734
C	0.5093504087	0.0001702929	-0.0032438303
Cl	2.2480910851	0.0022044978	-0.0079395517
C	-0.1747642572	1.2140271194	-0.0010278469
H	0.3828897468	2.1517832857	-0.0022376803
C	-1.5681473663	1.2039547160	0.0025319143
H	-2.1107184647	2.1521801908	0.0043845697
C	-2.2665996069	-0.0027020663	0.0038499480
H	-3.3586529638	-0.0037927604	0.0065420621

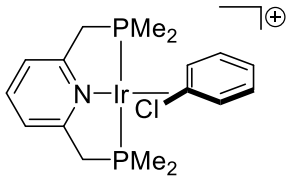


Ir-GS-1

46
Ir-GS-1

Ir	-0.00971	-0.20592	0.30374
P	0.69112	2.00314	0.19707
P	-1.27833	-2.09856	0.23783
N	-1.87737	0.71131	0.10427
C	-0.84082	2.77882	0.87328
C	-2.03497	2.03051	0.39093
C	-3.27416	2.65325	0.26191
C	-4.37921	1.91614	-0.14277
C	-4.21262	0.56713	-0.42772
C	-2.95251	-0.00985	-0.31200
C	-2.73969	-1.44748	-0.67247
C	1.97390	2.94386	1.08855
H	1.73265	4.01595	1.03095
H	2.01436	2.62697	2.13834
H	2.95489	2.77972	0.62851
C	0.79344	2.64824	-1.50601
H	-0.07571	2.29442	-2.07776
H	0.82803	3.74758	-1.51985
H	1.69716	2.24342	-1.98393
C	-1.95262	-2.75279	1.80284
H	-2.41367	-1.93392	2.37176
H	-2.69799	-3.54013	1.61603

H	-1.13413	-3.17036	2.40639
C	-0.78977	-3.59641	-0.67926
H	-1.61900	-4.31749	-0.72554
H	0.06039	-4.07545	-0.17200
H	-0.48342	-3.32714	-1.69950
H	-0.76994	2.67960	1.97029
H	-0.92143	3.85100	0.64141
H	-3.36525	3.71399	0.49821
H	-5.36055	2.38616	-0.23581
H	-5.05227	-0.04758	-0.75562
H	-3.65361	-2.04047	-0.51802
H	-2.48196	-1.51478	-1.74374
H	4.30811	0.77382	1.97753
C	3.59482	0.22469	1.35893
C	3.71464	0.29907	-0.05654
H	4.50767	0.89157	-0.51640
C	2.83799	-0.39594	-0.84595
Cl	2.97710	-0.34647	-2.57011
C	1.80803	-1.23176	-0.28963
H	1.48422	-2.06202	-0.92116
C	1.70472	-1.29249	1.13729
H	1.26539	-2.17428	1.61219
C	2.61480	-0.53155	1.94356
H	2.55676	-0.61835	3.03047



Ir-GS-2

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Ir-GS-2

Ir	0.05050	0.65815	-0.60486
P	0.05242	2.90417	-0.97108
P	0.54469	-1.52288	-0.11657
N	1.96245	0.98420	-0.02433
C	1.86696	3.13060	-1.20236
C	2.60728	2.14291	-0.35452
C	3.91510	2.38482	0.04727
C	4.60793	1.42444	0.77271
C	3.95652	0.24100	1.09144
C	2.63695	0.04577	0.70021
C	1.90183	-1.19995	1.08807
C	-0.71343	3.67205	-2.43499
H	-0.42903	4.73046	-2.52998
H	-0.41020	3.12489	-3.33796
H	-1.80690	3.60645	-2.33935
C	-0.40775	4.01844	0.39884
H	0.11658	3.70602	1.31217
H	-0.15777	5.06445	0.16627
H	-1.48928	3.93763	0.57805
C	1.30265	-2.53028	-1.43638
H	2.10167	-1.95343	-1.92139
H	1.71136	-3.47111	-1.03849

H	0.53923	-2.75854	-2.19348
C	-0.54851	-2.70102	0.74331
H	0.00588	-3.60481	1.03678
H	-1.37130	-2.98672	0.07297
H	-0.98439	-2.22510	1.63149
H	2.05244	2.89617	-2.26511
H	2.21698	4.15804	-1.02449
H	4.38596	3.32735	-0.23408
H	5.64028	1.59485	1.08288
H	4.45772	-0.54261	1.66107
H	2.59048	-2.04788	1.21903
H	1.39621	-1.03284	2.05502
H	-3.98466	-1.82303	-1.72083
C	-3.92757	-1.58586	-0.65704
C	-3.10379	-0.56543	-0.20127
Cl	-2.15275	0.32447	-1.39438
C	-2.99577	-0.22150	1.14032
H	-2.32280	0.58288	1.44346
C	-3.75089	-0.94378	2.06257
H	-3.68779	-0.69166	3.12339
C	-4.58514	-1.97853	1.63745
H	-5.17306	-2.53884	2.36712
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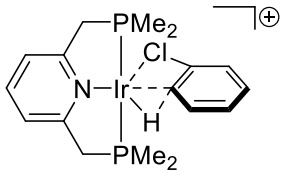
H	-5.32915	-3.10369	-0.05124



Ir-H-TS

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Ir-H-TS

Ir	0.0731194393	0.1583378132	0.1132008161
P	-0.2250197147	-2.1156774593	-0.1858212144
P	0.9362681706	2.2544564152	0.3396088371
N	2.0896693600	-0.3643786107	-0.1004417659
C	1.4443686240	-2.6840235817	0.3556021072
C	2.4818649643	-1.6616346311	0.0094203026
C	3.8142032788	-2.0266490423	-0.1626396237
C	4.7678059584	-1.0495120621	-0.4173276183
C	4.3618777942	0.2759715545	-0.5125811025
C	3.0153265411	0.5962124592	-0.3685816638
C	2.5419931916	2.0091053868	-0.5370043459
C	-1.3771070245	-3.2363565458	0.6601236720
H	-1.1420103519	-4.2785796521	0.3976460514
H	-1.3123317775	-3.0940630997	1.7456141337
H	-2.4029978224	-3.0052360039	0.3435162745
C	-0.3506322141	-2.6091026629	-1.9381953563
H	0.4427759260	-2.1189899822	-2.5192533743
H	-0.2766129300	-3.7002414455	-2.0572825184
H	-1.3199388996	-2.2643205075	-2.3264222788
C	1.3891798252	2.7938763300	2.0208114690
H	1.9592378588	1.9963636069	2.5165718202
H	1.9856223293	3.7179294275	1.9949199301

H	0.4721362716	2.9692983823	2.6006414672
C	0.2021613982	3.7367864837	-0.4200945496
H	0.8594357221	4.6101198221	-0.2971828709
H	-0.7627159279	3.9431875684	0.0648125072
H	0.0205234695	3.5625193488	-1.4891204873
H	1.3845203258	-2.7708088733	1.4547928124
H	1.7157878259	-3.6757956317	-0.0359524075
H	4.0954732947	-3.0770804999	-0.0770367925
H	5.8190130288	-1.3183917431	-0.5407847898
H	5.0813676858	1.0702352954	-0.7158591006
H	3.3186567592	2.7274260200	-0.2341967567
H	2.3332570650	2.1897129403	-1.6059714485
H	-5.5560528085	0.6834516405	-1.8327777570
C	-4.5621196913	0.6428628387	-1.3826731851
C	-3.4669078709	1.2149183215	-2.0309581349
H	-3.5959804963	1.7062179244	-2.9977872226
C	-2.2058529208	1.1702748945	-1.4455568645
H	-1.3587522727	1.6211788633	-1.9666683661
C	-1.9831644055	0.5089934285	-0.2210733687
C	-3.1202833183	-0.0034149388	0.4306253533
Cl	-2.9670909450	-0.6638935100	2.0359931185
C	-4.3920391490	0.0444442524	-0.1392907995
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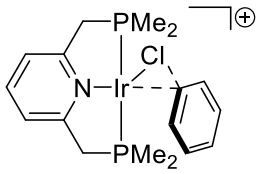
H	-1.1833130582	0.7791010236	0.9115164795



Ir-Cl-TS

46

Ir-Cl-TS

Ir	-0.1286887046	-0.0351098356	-0.4871899343
P	0.4174162963	-2.2723668774	-0.6262554990
P	0.1414731467	2.2459504355	-0.4337544435
N	1.6776455094	-0.0043136968	0.4591629858
C	1.3094541914	-2.3575694562	0.9874049176
C	2.1364294332	-1.1174369046	1.1001149509
C	3.3403132991	-1.1027407281	1.7969812945
C	4.0989829148	0.0597993409	1.8444585832
C	3.6506258525	1.1754900451	1.1462365154
C	2.4537425876	1.1176605406	0.4423833057
C	1.9844510435	2.2545013363	-0.4070767394
C	-0.6220437308	-3.7712493329	-0.6813965113
H	0.0090557339	-4.6578135904	-0.8384178895
H	-1.1774654424	-3.8973848995	0.2568054452
H	-1.3381177543	-3.6921357945	-1.5119147211
C	1.6907772833	-2.6140517397	-1.8883627232
H	2.4512074756	-1.8218976890	-1.8637644949
H	2.1661686303	-3.5926475167	-1.7242971843
H	1.2179224503	-2.6016819547	-2.8806587182
C	-0.2605681458	3.2610779617	1.0319715021
H	0.0602502038	2.7297203073	1.9389124741
H	0.2515424274	4.2330818967	0.9733194890

H	-1.3417982910	3.4305789051	1.1013760912
C	-0.3323947026	3.2906206230	-1.8458551063
H	0.0928183204	4.3009822575	-1.7558391098
H	-1.4285419544	3.3669849976	-1.8831416939
H	0.0102771629	2.8213009063	-2.7777933131
H	0.5160595188	-2.3592267059	1.7560340383
H	1.9240915150	-3.2596024696	1.1241293092
H	3.6698095196	-2.0107811992	2.3036554206
H	5.0381812894	0.0906434450	2.4001737330
H	4.2350276125	2.0962170172	1.1225930791
H	2.4162495590	3.2118083143	-0.0812190518
H	2.3079670526	2.0745085703	-1.4470291679
H	-3.2393200458	-2.1701765341	2.7606438009
C	-3.0856390848	-1.2386044144	2.2108751099
C	-2.5380064139	-1.2907808242	0.9317817025
H	-2.3170437982	-2.2434296807	0.4583839598
C	-2.2969611392	-0.0909939839	0.2435610998
Cl	-2.1907986361	-0.1648363791	-1.6612679531
C	-2.7980040620	1.1212209299	0.7480152048
H	-2.7661905052	2.0190099522	0.1301981786
C	-3.3475510237	1.1500584718	2.0231846940
H	-3.7094852037	2.0990234647	2.4260976208
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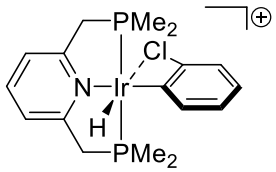
H	-3.9127698740	0.0075722919	3.7703799828



Ir(H)(Ar)

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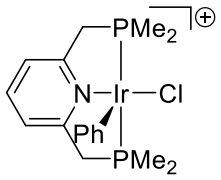
Ir(H)(Ar)

H	-0.2677536641	-0.0525582217	1.8489713440
Ir	-0.0286199203	-0.0372176884	0.3150948296
P	-0.2026042854	-2.3294646291	0.2860529895
P	-0.4719234338	2.2084594725	0.4032737097
N	-2.1210859401	-0.1588080935	-0.0872650357
C	-1.6941054438	-2.4611520091	-0.8011251014
C	-2.6342232538	-1.3118892961	-0.5697268347
C	-3.9892900066	-1.4158123564	-0.8778417139
C	-4.8124808358	-0.3082953357	-0.7150939089
C	-4.2674548284	0.8750543601	-0.2289512078
C	-2.9138516595	0.9216985299	0.0961778458
C	-2.2955870857	2.1424797492	0.7128613800
C	1.0560508955	-3.3882300497	-0.4819630855
H	0.7039308210	-4.4248615265	-0.5829850807
H	1.3188801852	-2.9835131000	-1.4687356623
H	1.9562465573	-3.3675060734	0.1484778026
C	-0.6578720830	-3.1671368065	1.8348302881
H	-1.5233131800	-2.6583224863	2.2812164111
H	-0.9023392752	-4.2244430006	1.6564480490
H	0.1839139493	-3.1017881322	2.5382213278
C	-0.2672327192	3.1958986820	-1.1116734195
H	-0.7862939239	2.7020696117	-1.9446369336

H	-0.6640884961	4.2130896735	-0.9793043969
H	0.8027334718	3.2509449218	-1.3578287150
C	0.2113656031	3.2366436005	1.7335265462
H	-0.2275878177	4.2447970036	1.7334186557
H	1.2980993751	3.3115534715	1.5857253650
H	0.0284088243	2.7487252666	2.7002720034
H	-1.3074806147	-2.4005198652	-1.8342082244
H	-2.2153645660	-3.4261954568	-0.7111442157
H	-4.3864422265	-2.3584662141	-1.2576908349
H	-5.8743788264	-0.3676728538	-0.9636816337
H	-4.8898940279	1.7590292669	-0.0831413284
H	-2.8176568105	3.0580968438	0.3980751877
H	-2.4068318881	2.0692381958	1.8093380928
H	5.0815468791	0.2392230531	1.8350927195
C	4.3295831951	0.1847277581	1.0442805895
C	2.9743124227	0.1394179239	1.3862342194
H	2.6810891797	0.1564415986	2.4391840853
C	1.9917972181	0.0671773677	0.3908889427
C	2.4731526394	0.0483385608	-0.9167802783
Cl	1.1230104578	-0.0437913193	-2.0953983070
C	3.7955006639	0.0901664163	-1.3151888894
H	4.0823320168	0.0710650205	-2.3680540108
C	4.7413517818	0.1603519010	-0.2895159086
H	5.8034337815	0.1963405827	-0.5394104734



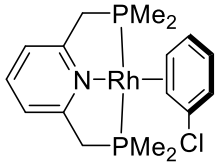
Ir(Cl)(Ph)

46

Ir(Cl)(Ph)

Ir	0.3768427002	0.2013618634	0.3009567185
P	-0.8654413731	2.0902487239	0.7776118296
P	1.2796285537	-1.9022716169	0.0057228422
N	-1.2301054460	-0.8216764583	1.0582469298
C	-2.0541705808	1.3212271524	1.9648579505
C	-2.2000911963	-0.1552914627	1.7401358779
C	-3.2993470772	-0.8376182570	2.2554267559
C	-3.3944629494	-2.2151590617	2.1058765670
C	-2.3834265367	-2.8849995647	1.4293290616
C	-1.3163547046	-2.1696196000	0.8950077090
C	-0.2895995660	-2.8617215944	0.0485737863
C	-0.0919451802	3.4606765235	1.6797422095
H	-0.8412761717	4.1887433676	2.0228185400
H	0.4702834327	3.0665518245	2.5371341548
H	0.6226453491	3.9541699006	1.0062327375
C	-1.8559411819	2.8644869607	-0.5319488058
H	-2.4594352248	2.1040798836	-1.0444044545
H	-2.5050256664	3.6459009603	-0.1114529307
H	-1.1728695553	3.3097805120	-1.2690798576
C	2.3120674798	-2.5402891640	1.3588187478
H	1.7794400112	-2.4309403938	2.3141043583
H	2.5614899080	-3.5995951977	1.1992506366

H	3.2372426923	-1.9480913647	1.4047525123
C	2.1254323943	-2.3510635200	-1.5301501238
H	2.3275128499	-3.4309538649	-1.5717530419
H	3.0745500554	-1.7978233916	-1.5709910581
H	1.5060145627	-2.0474451200	-2.3849750061
H	-4.0737346689	-0.2785582540	2.7824730284
H	-4.2496778813	-2.7613826071	2.5094011214
H	-2.4265690950	-3.9653313518	1.2833678526
H	-0.1594142747	-3.9096151581	0.3546792801
H	-0.6565472520	-2.8665048412	-0.9936815721
H	0.5109412149	0.8539359224	-4.7163450899
C	-0.1308906482	0.4933491659	-3.9086392304
C	-1.4079911176	0.0110942099	-4.1883885177
H	-1.7776817418	-0.0141305928	-5.2154165178
C	-2.2070552206	-0.4315457339	-3.1395275774
H	-3.2142814972	-0.8066300494	-3.3379785779
C	-1.7399518697	-0.3980993650	-1.8219853831
H	-2.4146247714	-0.7395356691	-1.0359656058
C	-0.4524234246	0.0766010693	-1.5360980064
C	0.3464969727	0.5279581962	-2.5991296407
H	1.3467280007	0.9144926020	-2.4032156565
H	-3.0383960831	1.8130182086	1.9646077808
H	-1.6262979969	1.4780979358	2.9707686072
Cl	2.3921821180	1.3218310932	0.0405506085



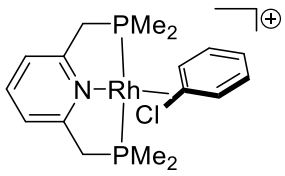
Rh-GS-1

46

Rh-GS-1

Rh	-0.0018574783	0.2997037345	0.2837914084
P	-0.7014496717	-1.9066835060	0.2229041213
P	1.2825079981	2.1758115899	0.1615992433
N	1.8571694760	-0.6154709942	-0.0782568808
C	0.8856740553	-2.6692834179	0.7862468653
C	2.0420387205	-1.9283150604	0.2004224832
C	3.2628534554	-2.5554957542	-0.0389174847
C	4.3218620658	-1.8187796661	-0.5537170998
C	4.1279203078	-0.4708028376	-0.8320730200
C	2.8824894056	0.1053594009	-0.5987346304
C	2.6119071021	1.5370271816	-0.9406276716
C	-1.9123632275	-2.8574957018	1.2029336137
H	-1.6741963472	-3.9294986189	1.1310958563
H	-1.8835267624	-2.5406299540	2.2534241306
H	-2.9239293445	-2.6966967836	0.8128166277
C	-0.9226777823	-2.5615119396	-1.4665104528
H	-0.0950540077	-2.2141897276	-2.1004908560
H	-0.9587851133	-3.6610096277	-1.4722448108
H	-1.8570463534	-2.1604342071	-1.8849316340
C	2.1493251881	2.6965544415	1.6808559242
H	2.6181228273	1.8197193041	2.1486915275
H	2.9170085053	3.4543299162	1.4639808344

H	1.4221505812	3.1149528908	2.3912920396
C	0.7594795762	3.7437620607	-0.6082526235
H	1.6015652514	4.4472449285	-0.6854142865
H	-0.0290852830	4.2081155618	0.0018211087
H	0.3567009895	3.5515908018	-1.6125287460
H	0.8991841919	-2.5580896760	1.8845888187
H	0.9435909641	-3.7456774409	0.5645586595
H	3.3750369225	-3.6154715842	0.1930443683
H	5.2892571023	-2.2903908421	-0.7388989408
H	4.9321462350	0.1394078741	-1.2454077092
H	3.5308130497	2.1418939978	-0.9191555970
H	2.2024965819	1.5902720507	-1.9645355927
H	-4.2253365521	-0.6847397446	2.1493949008
C	-3.5465661949	-0.1267364229	1.5006058616
C	-3.7280402921	-0.1934115697	0.0990822381
H	-4.5344298524	-0.7902330570	-0.3310232052
C	-2.8878911888	0.5169583421	-0.7257386206
Cl	-3.1006483228	0.4683434292	-2.4418620218
C	-1.8579438685	1.3573478455	-0.2045006555
H	-1.4979538694	2.1527085907	-0.8591280552
C	-1.6924103280	1.4123853557	1.2060274972
H	-1.1717396581	2.2552571308	1.6667315964
C	-2.5415852017	0.6368024365	2.0467120778
H	-2.4322912612	0.7132629401	3.1304301442



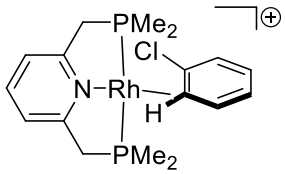
Rh-GS-2

46

Rh-GS-2

Rh	0.3021720417	0.3888920612	-0.0969682613
P	1.7075105555	2.1763424881	0.0388439796
P	-0.6132547579	-1.7095710537	-0.1633414954
N	2.0357737730	-0.6605315022	0.1030834514
C	3.0172554278	1.3608262642	1.0507859680
C	3.1461475984	-0.0643399790	0.6126860148
C	4.3469275173	-0.7572138636	0.7378224980
C	4.4133087743	-2.0938701151	0.3637655530
C	3.2717898721	-2.7010077766	-0.1446035127
C	2.0993729625	-1.9626150427	-0.2808251384
C	0.8633896014	-2.5603802638	-0.8750757307
C	2.5752066044	2.7391083183	-1.4647393050
H	3.3940726442	3.4321059392	-1.2197688281
H	2.9773894550	1.8658894673	-1.9969881679
H	1.8595920446	3.2436791501	-2.1289646281
C	1.3159922184	3.7151106580	0.9328058081
H	0.8622197122	3.4695462831	1.9025878584
H	2.2151202418	4.3295440504	1.0894054139
H	0.5877958633	4.2954292734	0.3480653584
C	-1.9956901063	-2.2468764106	-1.2227854355
H	-1.8919458301	-1.8024261472	-2.2218776526
H	-2.0199409540	-3.3437013806	-1.3066209396

H	-2.9421970409	-1.9022291497	-0.7835777996
C	-0.9011948603	-2.6023232074	1.4046106189
H	-1.0436459455	-3.6788682629	1.2263293544
H	-1.7978883920	-2.1986207146	1.8936785344
H	-0.0415066649	-2.4504593560	2.0719287075
H	3.9864805252	1.8813983014	1.0270771691
H	2.6489779417	1.3879659688	2.0909308736
H	5.2191918214	-0.2429258087	1.1436484534
H	5.3441865519	-2.6552453279	0.4661529929
H	3.2818191509	-3.7465051047	-0.4559046380
H	0.8410573208	-2.3441319095	-1.9572322062
H	0.8444090827	-3.6539970362	-0.7536832927
H	-6.0413855980	-0.1160620330	-1.3081576860
C	-5.2409029420	-0.0039976512	-0.5737753934
C	-5.3630009516	-0.5794963338	0.6903909686
H	-6.2624290368	-1.1422817435	0.9480575587
C	-4.3430608050	-0.4277215239	1.6312003258
C	-3.1923071005	0.2912064754	1.3121557278
H	-2.3814386101	0.4249824451	2.0303665308
C	-3.0932560273	0.8418713467	0.0394381411
Cl	-1.6338625884	1.7262158188	-0.3877140243
C	-4.0960711863	0.7178620292	-0.9136079892
H	-3.9822809500	1.1677843394	-1.9011802414
H	-4.4460509363	-0.8644028452	2.6272048773



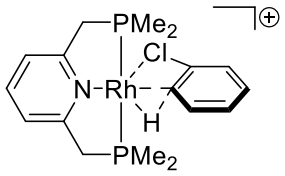
Rh-GS-3

46

Rh-GS-3

Rh	0.0928965078	0.2729141443	0.1163773358
P	-0.3690909839	-1.9667018182	-0.0990410561
P	1.1344685244	2.2893699094	0.3251795188
N	2.0184450970	-0.3916884664	-0.1382583159
C	1.0638008140	-2.3641462854	-1.1977364312
C	2.2551591443	-1.5871790944	-0.7363667516
C	3.5527449273	-2.0574849552	-0.9224370575
C	4.6303688645	-1.2810052782	-0.5152836421
C	4.3807656366	-0.0516997941	0.0832339489
C	3.0671145274	0.3672444801	0.2730502806
C	2.7484158867	1.6583731216	0.9587100952
C	-0.1174971676	-3.0579762736	1.3403103816
H	-0.1019106289	-4.1151360395	1.0357904989
H	0.8334558663	-2.8008382972	1.8272310892
H	-0.9306088652	-2.8949612890	2.0597102737
C	-1.7970041037	-2.6835954380	-0.9738742052
H	-2.0082390723	-2.0962152154	-1.8778848832
H	-1.5981927136	-3.7302750599	-1.2478568844
H	-2.6778928247	-2.6487921233	-0.3191251355
C	0.6377532450	3.5763562988	1.5155607892
H	0.4571115299	3.1184058486	2.4977329973
H	1.4089333075	4.3554229947	1.6080400314

H	-0.2976418932	4.0420196945	1.1729440271
C	1.5791271262	3.2252209613	-1.1794233116
H	2.3004736160	4.0242074810	-0.9507589383
H	0.6761700818	3.6759542598	-1.6151055250
H	2.0128408263	2.5383716171	-1.9194223625
H	1.2825634438	-3.4407908798	-1.2618382059
H	0.7748801683	-2.0225595254	-2.2067434049
H	3.7058011086	-3.0262200736	-1.4000313872
H	5.6545324702	-1.6298256131	-0.6626544319
H	5.1991314216	0.5855870533	0.4211470213
H	2.5938719789	1.4674989706	2.0348679071
H	3.5714536197	2.3827019550	0.8648964465
H	-1.3142332857	1.1341139932	0.8421752946
C	-2.0935574440	0.8473437344	0.0456585124
C	-2.2595157392	1.5868073142	-1.1332717634
H	-1.4691678702	2.2687972872	-1.4515106815
C	-3.4145289793	1.4472836084	-1.8986263728
C	-4.4411179480	0.6144994764	-1.4548290131
H	-5.3584300524	0.5170227723	-2.0397040673
C	-4.3239032604	-0.0792471848	-0.2501366272
H	-5.1365445470	-0.7072036029	0.1184096481
C	-3.1532473674	0.0432478424	0.4895513250
Cl	-2.9995926183	-0.8173650477	1.9853862047
H	-3.5245799324	2.0062001917	-2.8297420498



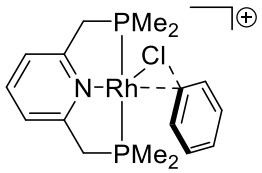
Rh-H-TS

46

Rh-H-TS

Rh	0.0225154872	-0.0209935020	-0.4248325744
P	0.1467956036	-2.2819886254	-0.1771704375
P	-0.7291756352	2.1258533162	-0.7402996289
N	-1.9864476304	-0.3227253235	0.1332599161
C	-1.6481692067	-2.6944570686	-0.3530162021
C	-2.5044699578	-1.5743532710	0.1596716864
C	-3.8021542302	-1.7990859285	0.6123762101
C	-4.5816273118	-0.7191377114	1.0122442909
C	-4.0448037813	0.5621760560	0.9642577342
C	-2.7317701835	0.7361623353	0.5325281781
C	-2.0834474593	2.0897605120	0.5178169044
C	0.9983794267	-3.3979551080	-1.3322368852
H	0.7304196222	-4.4463952065	-1.1345193262
H	0.7352142222	-3.1357583172	-2.3658276860
H	2.0827112070	-3.2768680054	-1.2025538485
C	0.6236191343	-2.8876052849	1.4738617502
H	0.0287442813	-2.3693226535	2.2388580658
H	0.4817717552	-3.9745393458	1.5666829196
H	1.6819825443	-2.6396400901	1.6400865729
C	-1.5938297877	2.4146902637	-2.3195440493
H	-2.2707230847	1.5736443157	-2.5237386600
H	-2.1668215233	3.3536301437	-2.2933803105

H	-0.8542732751	2.4639227860	-3.1310088158
C	0.1822493099	3.6685242773	-0.4352075256
H	-0.4843043311	4.5406709055	-0.5045830138
H	0.9752531176	3.7620715883	-1.1907625313
H	0.6512164516	3.6284011926	0.5561517264
H	-1.8257283111	-2.8034721540	-1.4375141506
H	-1.9181600864	-3.6530761692	0.1154799428
H	-4.1983000839	-2.8152468729	0.6340713814
H	-5.6051165281	-0.8762664759	1.3597186980
H	-4.6305339761	1.4287452770	1.2739579545
H	-2.8272350611	2.8889362543	0.3783680374
H	-1.5905450946	2.2648641511	1.4902227939
H	5.8883491360	0.1244670121	0.6179456525
C	4.8314980699	0.1096618594	0.3445252066
C	3.8905149515	0.6914904699	1.1909270986
H	4.1899568805	1.1466504469	2.1368830776
C	2.5450682885	0.6782848523	0.8347970586
Cl	1.4082401116	1.3481815324	1.9893460802
C	2.0788582977	0.0856842227	-0.3534549691
C	3.0595183458	-0.4970234922	-1.1777343073
H	2.7512670751	-0.9539609606	-2.1215250719
C	4.4119344780	-0.4896579526	-0.8397181185
H	5.1394734364	-0.9477810904	-1.5131247184
H	1.0990700229	0.3867904948	-1.4645282205



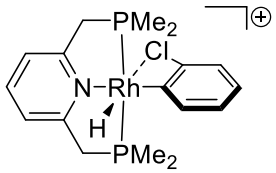
Rh-Cl-TS

46

Rh-Cl-TS

Rh	-0.1199999619	-0.0493190752	-0.5791059514
P	0.6457235243	-2.2253516184	-0.6223980851
P	-0.0551598592	2.2523504353	-0.5677034710
N	1.6968324335	0.1848131840	0.3854239658
C	1.5103030740	-2.1603159644	1.0091035341
C	2.2351855317	-0.8525149228	1.0759946508
C	3.4279230112	-0.7038346498	1.7788962617
C	4.0812244484	0.5227985640	1.7683048014
C	3.5467357823	1.5646350526	1.0177161870
C	2.3613308268	1.3665557361	0.3165318350
C	1.7840276180	2.4121389946	-0.5846174903
C	-0.2165960434	-3.8315975267	-0.6652617139
H	0.5144317685	-4.6475064939	-0.7601367307
H	-0.8045361281	-3.9924187147	0.2472684023
H	-0.8940407990	-3.8544856787	-1.5308432266
C	1.9820232599	-2.4485567434	-1.8464918539
H	2.6546468809	-1.5803944296	-1.8230158111
H	2.5568954635	-3.3662655609	-1.6516097131
H	1.5346692544	-2.5071665719	-2.8490216089
C	-0.4943427457	3.2242005695	0.9149092106
H	-0.0948295316	2.7211016002	1.8067877183
H	-0.0740166530	4.2385463057	0.8444657804

H	-1.5833485953	3.2920788534	1.0234094925
C	-0.6459819309	3.2473586624	-1.9707139219
H	-0.3108843826	4.2920859013	-1.8934382562
H	-1.7449186137	3.2232706035	-1.9880093518
H	-0.2827900744	2.8050921961	-2.9082305994
H	0.7092088263	-2.1892389896	1.7690576622
H	2.1900066785	-3.0052417221	1.1949998048
H	3.8330297848	-1.5525347358	2.3316288687
H	5.0106509223	0.6605982934	2.3247843376
H	4.0521112465	2.5292879023	0.9549111348
H	2.1357018650	3.4201474134	-0.3199160775
H	2.1076964688	2.2059929412	-1.6197703991
H	-3.0493700794	-2.3049423908	2.7499274613
C	-2.9644698089	-1.3906375749	2.1576578956
C	-2.2977120055	-1.4363876359	0.9333301475
H	-1.9230113348	-2.3803991352	0.5477889252
C	-2.1509497357	-0.2583474213	0.1922124675
Cl	-2.0638424762	-0.4303398683	-1.8244766612
C	-2.8310992052	0.9045790375	0.5803064060
H	-2.8562106368	1.7672122698	-0.0860918802
C	-3.4987625792	0.9299917399	1.7992044565
H	-4.0086026732	1.8455559110	2.1090142503
C	-3.5482755759	-0.2083215584	2.6069191042
H	-4.0826883696	-0.1849884177	3.5582525450



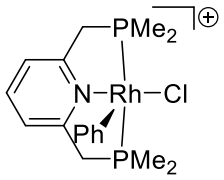
Rh(H)(Ar)

46

Rh(H)(Ar)

H	-0.0881399767	0.1262491999	1.7765178579
Rh	0.0719579578	0.0291879584	0.2695637209
P	-0.1669253995	-2.2401533595	0.4444272526
P	-0.2585247686	2.2823321859	0.2370523410
N	-2.0375166802	-0.0427310026	-0.0480339213
C	-1.7140143152	-2.4082140734	-0.5637340267
C	-2.6138383572	-1.2141960666	-0.3924378564
C	-3.9868143833	-1.2914162125	-0.6187406267
C	-4.7571611365	-0.1380983496	-0.5136663223
C	-4.1462810528	1.0615401311	-0.1637642614
C	-2.7749104251	1.0799292713	0.0843029814
C	-2.0799387356	2.3231786237	0.5697810597
C	1.0241975180	-3.3971359676	-0.2900804254
H	0.6354357040	-4.4256286899	-0.3052868034
H	1.2651599034	-3.0704398015	-1.3108906236
H	1.9469546599	-3.3641740975	0.3064309544
C	-0.5792018044	-2.9368014732	2.0728692964
H	-1.3981926265	-2.3552571333	2.5182252518
H	-0.8773907178	-3.9921628969	1.9895850943
H	0.2991851872	-2.8567958841	2.7284502432
C	-0.0219090453	3.1523829609	-1.3440527928
H	-0.5697085070	2.6282029658	-2.1390496102

H	-0.3668798036	4.1950668272	-1.2818598355
H	1.0478043528	3.1354610387	-1.5968977873
C	0.4920125982	3.3636135884	1.4871397412
H	0.1043935655	4.3906059648	1.4232041998
H	1.5788918567	3.3728934287	1.3221607664
H	0.2999357599	2.9531589168	2.4875590933
H	-1.3752005217	-2.4480240600	-1.6145962671
H	-2.2531982898	-3.3473886849	-0.3669672899
H	-4.4398937096	-2.2462481766	-0.8895395965
H	-5.8326040062	-0.1746617490	-0.7004704090
H	-4.7285736189	1.9788290124	-0.0639865290
H	-2.5608698160	3.2313102110	0.1758058111
H	-2.1788099668	2.3637539383	1.6692109302
H	5.1342473661	0.2937068012	1.8339124792
C	4.3930833697	0.1978703514	1.0368120100
C	3.0315055617	0.2031532221	1.3582020985
H	2.7231066426	0.3022821278	2.4023374122
C	2.0675987962	0.0794002405	0.3519473084
C	2.5538431496	-0.0421421865	-0.9468518541
Cl	1.2395662719	-0.1886945932	-2.1486539142
C	3.8879122195	-0.0536921846	-1.3173403975
H	4.1920589835	-0.1534010887	-2.3609536211
C	4.8215553418	0.0705042194	-0.2855727259
H	5.8876455944	0.0673484135	-0.5213385600



Rh(Cl)(Ph)

46

Rh(Cl)(Ph)

Rh	0.2089899715	-0.1921974227	-0.7231371087
P	-0.9653975184	-2.1541580724	-0.4424522762
P	1.0538769958	1.9369028196	-0.8532066831
N	-1.4499517855	0.7213872862	0.0636630798
C	-2.6515412468	-1.4020990585	-0.2970608611
C	-2.6067776171	0.0229704776	0.1834069275
C	-3.7497510803	0.6295807502	0.6998043807
C	-3.7124653457	1.9694113159	1.0655462134
C	-2.5239385749	2.6755155468	0.9214289219
C	-1.3923520156	2.0268857102	0.4347217847
C	-0.0666511317	2.7298376010	0.3769846886
C	-1.0612367053	-3.3283749883	-1.8215416816
H	-1.8146485404	-4.1074413635	-1.6353157087
H	-1.2944623235	-2.7914161350	-2.7508346699
H	-0.0705560601	-3.7893606181	-1.9409690398
C	-0.7036343485	-3.1646011333	1.0422913889
H	-0.7645276792	-2.5358916144	1.9399287024
H	-1.4442421292	-3.9757006792	1.0934800732
H	0.3087589659	-3.5907666498	0.9959505184
C	0.7813522167	2.7859822093	-2.4369966840
H	-0.2734436395	2.6926652789	-2.7318238409
H	1.0504144118	3.8504594398	-2.3706756457

H	1.4008073720	2.2957926522	-3.2018577217
C	2.7472725331	2.3280352390	-0.3506409348
H	2.9174936843	3.4142217832	-0.3380733579
H	3.4316648732	1.8562648832	-1.0701486440
H	2.9380873623	1.9016995260	0.6434763072
H	-4.6669081846	0.0467537842	0.7971821216
H	-4.6039678939	2.4603002123	1.4614887157
H	-2.4581088060	3.7269339285	1.2046177522
H	-0.1932373254	3.8114010287	0.2231552835
H	0.4330822694	2.5937995813	1.3530945819
H	4.0147209806	-1.2651817113	2.4363266298
C	2.9735051458	-0.9346258868	2.4045108821
C	2.2865658348	-0.6655791101	3.5868438132
H	2.7823612894	-0.7792990603	4.5529792533
C	0.9585561273	-0.2557721161	3.5204594471
H	0.4003892113	-0.0472081850	4.4367325702
C	0.3187568193	-0.1102479382	2.2855766679
H	-0.7280380126	0.1945464582	2.2832110290
C	1.0130021123	-0.3702933265	1.0981419742
C	2.3482607410	-0.7904127347	1.1645220789
H	2.9005620102	-1.0093387755	0.2507970615
H	-3.3342215422	-2.0017379415	0.3239846981
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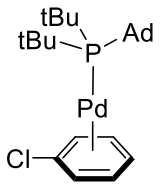
Cl	1.8018532835	-1.1100735516	-2.1301862442



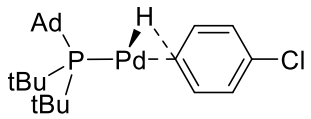
Pd-GS

65

Pd-GS

P	-0.573296	-1.209615	0.085261
C	-1.453366	-2.656565	-0.835083
C	-0.350596	-1.717356	1.933760
C	-2.625254	-3.319613	-0.091527
H	-3.071454	-4.087525	-0.735860
H	-2.306810	-3.817190	0.825920
H	-3.412373	-2.608303	0.164590
C	-1.956179	-2.153372	-2.202506
H	-1.157768	-1.654212	-2.758570
H	-2.284516	-3.017893	-2.791595
H	-2.806115	-1.475099	-2.122607
C	-0.381055	-3.720424	-1.161899
H	-0.828100	-4.486297	-1.807752
H	0.459826	-3.265013	-1.694036
H	0.012329	-4.223046	-0.280774
C	0.735098	-0.804988	2.550948
H	0.441153	0.240150	2.616296
H	0.948092	-1.155132	3.568823
H	1.656431	-0.853606	1.963710
C	-1.620448	-1.672033	2.800975
H	-2.012732	-0.660059	2.912361
H	-2.418558	-2.301411	2.404055

H	-1.381241	-2.037861	3.807376
C	0.237954	-3.140460	1.995005
H	-0.477692	-3.912615	1.710638
H	1.125395	-3.228936	1.361907
H	0.542674	-3.346284	3.027811
Pd	1.498802	-0.682333	-0.798858
C	-1.698798	0.345314	0.009539
C	-1.193695	1.378442	1.050398
C	-3.209880	0.115027	0.241046
C	-1.495395	1.006022	-1.384779
H	-1.321451	0.994228	2.063507
H	-0.125097	1.557892	0.895479
C	-1.969549	2.705075	0.947469
H	-3.384945	-0.331374	1.224115
H	-3.610660	-0.580632	-0.500660
C	-3.982632	1.447384	0.135487
H	-0.424558	1.188422	-1.529587
H	-1.809606	0.337717	-2.185493
C	-2.286068	2.322699	-1.497253
H	-1.584120	3.390456	1.712144
C	-3.464120	2.436154	1.193747
C	-1.775434	3.319055	-0.446411
H	-5.048377	1.249040	0.304688
C	-3.782743	2.046643	-1.267623
H	-2.137149	2.733859	-2.503416
H	-4.031851	3.373884	1.143645
H	-3.612830	2.022970	2.199984
H	-0.714189	3.535163	-0.615580
H	-2.320126	4.269019	-0.522340
H	-4.160105	1.352663	-2.030005
H	-4.358111	2.975974	-1.365412
C	3.020908	1.810569	0.124973
C	3.817825	1.238750	1.105644
C	4.444967	0.010406	0.843596
C	4.301976	-0.609529	-0.393734
C	3.532742	0.000257	-1.414916
C	2.852228	1.215142	-1.140392
H	3.578397	-0.376493	-2.433364
H	2.341969	1.759106	-1.926082
H	5.051622	-0.451683	1.615871
H	4.813913	-1.543637	-0.599810
H	3.935980	1.730688	2.064078
Cl	2.197436	3.330530	0.453278



Pd-H-TS

65

Pd-H-TS

Pd	-1.0993756209	-0.2935143054	-0.1158158061
P	1.1627196404	-0.9600547194	0.0329523457
C	1.2924697740	-1.8262967119	1.7369335329
C	1.6061333938	-2.2165977674	-1.3369710510
C	2.4985062415	-2.7434330229	1.9371206703

C	1.2819657009	-0.7745127139	2.8521790715
C	-0.0106713798	-2.6218684569	1.9197521256
C	1.0497510162	-1.6720690517	-2.6626222576
C	3.0961549188	-2.5287630361	-1.4844559654
C	0.8442785651	-3.5214553760	-1.0811123098
C	2.3714516725	0.5072327217	-0.0249565801
C	2.5368980959	0.9781213713	-1.4844032759
C	3.7681666195	0.2469223553	0.5643546249
C	1.7072348918	1.6811408117	0.7328594275
C	3.4023681234	2.2405598315	-1.5642420726
C	4.6248116602	1.5175771520	0.4864785463
C	2.5779347377	2.9391499099	0.6688618773
C	4.7826424637	1.9435396829	-0.9737690767
C	2.7415115537	3.3755377262	-0.7851692340
C	3.9508161924	2.6413138929	1.2769338607
H	2.4731116095	-3.1602190176	2.9580403922
H	2.5024262183	-3.5923183924	1.2419890388
H	3.4505437522	-2.2080907077	1.8235894165
H	0.4273241279	-0.0880568856	2.7566349528
H	1.1808658988	-1.2958193224	3.8181395135
H	2.2037435274	-0.1823087170	2.8980996444
H	-0.0406186197	-3.0353439176	2.9415915852
H	-0.8977767118	-1.9704572025	1.8128664940
H	-0.1230684880	-3.4565736508	1.2212972887
H	1.5482008815	-0.7595859369	-3.0037012276
H	1.1871104232	-2.4386101371	-3.4431747118
H	-0.0247455878	-1.4530998554	-2.5738604755
H	3.6803212069	-1.6508018483	-1.7897931143
H	3.5377055027	-2.9245844836	-0.5606143024
H	3.2289565662	-3.2931137154	-2.2683056598
H	1.2195978420	-4.0821902104	-0.2159797496
H	-0.2330738775	-3.3390379100	-0.9488955592
H	0.9624608713	-4.1704220868	-1.9638731143
H	3.0168075684	0.1980532945	-2.0907277127
H	1.5423764205	1.1708436298	-1.9193852937
H	4.2688530610	-0.5701786798	0.0238568715
H	3.6926108285	-0.0673086547	1.6151081826
H	0.7157359406	1.8724487218	0.2904028573
H	1.5342295455	1.4250797364	1.7837354725
H	3.5045210552	2.5242649943	-2.6247827706
H	5.6154842854	1.3009749249	0.9196400013
H	2.0811245582	3.7370129329	1.2450635416
H	5.4264309120	2.8364921603	-1.0426723424
H	5.2802088670	1.1449663728	-1.5504746725
H	1.7578248690	3.6147059486	-1.2221381549
H	3.3546651392	4.2905314144	-0.8479691367
H	3.8421472303	2.3483770619	2.3353745237
H	4.5805390966	3.5468097879	1.2596387825
C	-3.0066083046	0.2909624138	-0.2269963021
C	-3.9538740116	-0.4598634454	-0.9442907437
C	-3.4882862731	1.3189333410	0.6019650746
C	-5.3235050040	-0.2419920516	-0.7984070419
C	-4.8537710563	1.5524136799	0.7611358566
C	-5.7614308484	0.7630837688	0.0598965913
Cl	-7.4712590119	1.0479428354	0.2477288082
H	-2.7840533921	1.9537369262	1.1468633494

H	-5.2167385767	2.3444931300	1.4188853355
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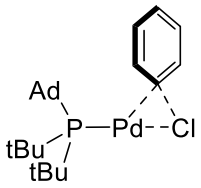
H	-3.6214802077	-1.2427896215	-1.6314818701
H	-6.0506857014	-0.8414294997	-1.3494729319



Pd-Cl-TS

65

Pd-Cl-TS

Pd	-1.7581152269	0.7883025392	-0.6802556199
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C	1.1132016587	2.4197956493	-1.7115488610
C	0.4143830649	2.5765624331	1.3146291264
C	2.3485435018	3.2721749339	-1.4169549401
C	1.4373955026	1.4459977473	-2.8495663106
C	-0.0105085879	3.3179320446	-2.2519318479
C	-0.5619230361	1.9834355256	2.3413548169
C	1.7811344900	2.8025217054	1.9640911198
C	-0.1826053397	3.9353771983	0.9333818449
C	1.5467822864	-0.0623854609	0.1156462076
C	1.2143062712	-0.6478833968	1.5044717546
C	3.0578600166	0.2228338358	0.0500476314
C	1.2016145426	-1.1695351737	-0.9067592768
C	2.0296867055	-1.9165626664	1.7793715488
C	3.8607797578	-1.0551151033	0.3237705042
C	2.0223984345	-2.4367454393	-0.6455926935
C	3.5217812731	-1.5861711463	1.7175448300
C	1.6959073957	-2.9849595848	0.7416541287
C	3.5148158609	-2.1100554737	-0.7292132024
H	2.6863081055	3.7505340274	-2.3515953116
H	2.1398183732	4.0779357815	-0.7019870566
H	3.1877914157	2.6819902344	-1.0278570714
H	0.5821225185	0.7888785220	-3.0683727404
H	1.6501379959	2.0319872948	-3.7585535629
H	2.3188799514	0.8244840160	-2.6493254308
H	0.3387572063	3.8005929831	-3.1800276211
H	-0.9068466064	2.7231006211	-2.4896317583
H	-0.3090597771	4.1109863182	-1.5593217906
H	-0.2805849566	0.9884358259	2.6991223833
H	-0.6095438543	2.6567543291	3.2136631645
H	-1.5687975742	1.9052237539	1.9061159778
H	2.2037457387	1.8817163017	2.3853492049
H	2.5145816497	3.2239248678	1.2649288767
H	1.6693446852	3.5174410063	2.7965296512
H	0.4769213601	4.5358661143	0.2948256623
H	-1.1545600446	3.8175136536	0.4309435285
H	-0.3522462948	4.5108757615	1.8580607617
H	1.4417949719	0.0790509206	2.2951585870
H	0.1369427522	-0.8742278266	1.5610564320
H	3.3412785142	0.9967892345	0.7778706481
H	3.3354010303	0.6026783844	-0.9436372977

H	0.1253373216	-1.3897923330	-0.8374364532
H	1.3894348133	-0.8328947418	-1.9321857491
H	1.7693203276	-2.2815199911	2.7869076370
H	4.9353562146	-0.8129743284	0.2688189017
H	1.7611346771	-3.1838497190	-1.4136445694
H	4.1211908776	-2.4852037271	1.9399642866
H	3.7784821621	-0.8328800531	2.4824235116
H	0.6284610308	-3.2453260715	0.8042274184
H	2.2726838687	-3.9048549275	0.9392808667
H	3.7678276888	-1.7359068204	-1.7362317498
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C	-2.0831835150	-3.0585061350	1.7232109852
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C	-2.9283555569	-0.7940796157	1.5205138440
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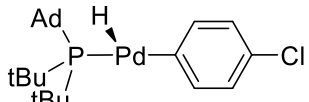

Pd(H)(Ar)

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Pd(H)(Ar)

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C	-2.4686461937	-2.7460511512	-1.9343775900
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H	-2.4626965254	-3.5954345404	-1.2400475432
H	-3.4285507305	-2.2243255406	-1.8233969390
C	-1.2785676609	-0.7607134627	-2.8458444973
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H	-2.2089544497	-0.1825864066	-2.8969397033
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H	0.0787015525	-3.0095262742	-2.9191015264
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H	0.1705220158	-3.4069770809	-1.1932924471
C	-1.0606661957	-1.6600462554	2.6720265309
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H	-3.2263151769	-3.2953353880	2.2652897030
C	-0.8322805535	-3.5058724724	1.0908579702
H	-1.1933602705	-4.0670907370	0.2200750624

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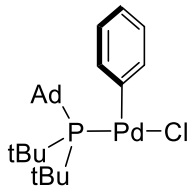

Pd(Cl)(Ph)

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Pd(Cl)(Ph)

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H	-1.6108479296	3.6553988097	0.8111734212
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H	0.1592047474	2.7684255906	3.2824474191
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C	1.7561668058	2.8396716398	1.2271815458
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H	2.3413184768	1.9435161762	1.5187659764
H	2.1816426801	3.2475382237	0.3062889631
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C	-1.1739730065	2.6565504453	-2.3326596505
H	-2.0207373818	1.9698846067	-2.4548991190
H	-1.4737039438	3.4457186313	-1.6317330022
H	-0.9994577353	3.1323885093	-3.3116412374
C	1.2773189315	2.9255818396	-1.9715954669
H	1.1214323418	3.8326280111	-1.3764833383
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C	1.2726225118	-2.6557027223	0.9186427473
C	1.2676341278	-2.2679258861	-1.4648001111
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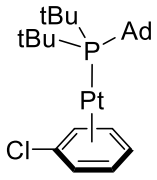

Pt-GS

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Pt-GS

P	-0.6300453193	1.1291538827	-0.2443132354
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C	-1.7045169973	2.2907926675	2.0814122888
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H	-2.6505442344	1.7357817089	2.0688305107
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H	-0.2916223351	4.4297700319	1.5720471333
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H	-2.2836519928	0.7081413955	-2.9443366108
H	-2.4259224131	2.4132344328	-2.4694372294
H	-1.5179258334	1.9650211750	-3.9258941158
C	0.3388352970	2.8651155367	-2.2317967188
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C	3.7179256640	-1.5959628824	-1.1220663319
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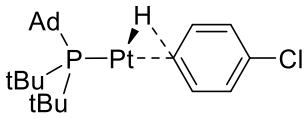

Pt-H-TS

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Pt-H-TS

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C	-2.7152196386	0.8875572657	1.4374099488
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C	-2.9686013200	3.3117051427	0.8529083476
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C	2.8978926271	0.3865957664	0.3501392490
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H	5.1008871883	2.4174561031	-1.3290321096
H	1.6307213903	0.7952501019	1.2668090847
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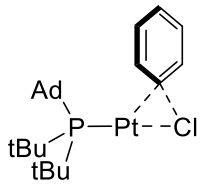
H	5.9441254546	-0.8830513374	1.3005732836



Pt-Cl-TS

65

Pt-Cl-TS

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Cl	3.7355762610	-0.0602403595	-0.8024464983
P	-0.6286766047	-1.1835358335	0.1627546873
C	-1.3112703649	-2.6099928416	-0.9304555314
C	-0.6958995697	-1.7433358175	1.9989211608
C	-2.5734970428	-3.2941390162	-0.4024238504

C	-1.5839734126	-2.0652888236	-2.3366875581
C	-0.1992753487	-3.6553368926	-1.1041115769
C	0.2571044981	-0.8492039988	2.8062277434
C	-2.0853387620	-1.7312826624	2.6407199874
C	-0.1121912077	-3.1562191502	2.1096171941
C	-1.7529654827	0.3474991154	-0.0518847759
C	-1.4498994021	1.3521704065	1.0790934075
C	-3.2643312679	0.0607967537	-0.0653328200
C	-1.3682928708	1.0562142799	-1.3707240496
C	-2.2530660478	2.6453996587	0.9026742691
C	-4.0572658787	1.3622330262	-0.2429830638
C	-2.1784726685	2.3435256290	-1.5593494127
C	-3.7472302847	2.3180491899	0.9102750731
C	-1.8798932408	3.3130228099	-0.4182487056
C	-3.6726129698	2.0144662326	-1.5724836416
C	1.8519560708	3.4969249169	-0.3985087920
C	1.8622414570	3.7054513280	0.9818326073
C	2.3665338974	2.7114038946	1.8240037651
C	2.8465487345	1.5138942843	1.3056937836
C	2.7530447899	1.2926901539	-0.0762269833
C	2.3111394044	2.3021164699	-0.9432230331
H	-2.8968628386	-4.0555697263	-1.1318372968
H	-2.4016288093	-3.8154191341	0.5480226610
H	-3.4110590930	-2.5990706948	-0.2622178645
H	-0.7064739553	-1.5308904038	-2.7306192100
H	-1.7880279750	-2.9171703784	-3.0056850055
H	-2.4549377530	-1.3998359260	-2.3811375328
H	-0.5394055975	-4.4087378949	-1.8343226577
H	0.7189686380	-3.1815979266	-1.4837341775
H	0.0546462250	-4.1807228804	-0.1781804763
H	-0.0224485557	0.2091848666	2.8114111332
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H	-2.0076668130	-2.1367593545	3.6634437292
H	-0.7644835640	-3.9294259765	1.6854919127
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H	2.3990878670	2.8725561388	2.9042587494
H	3.2595354435	0.7397348414	1.9527297635

H	1.4980541522	4.6466038225	1.3983686479
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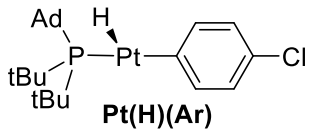
H	2.3108429084	2.1300368368	-2.0199868817



Pt(H)(Ar)

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Pt(H)(Ar)

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C	-1.7243213980	-2.1872344105	1.2914983577
C	-2.3973193667	-2.6660555257	-2.0361970107
H	-2.2884774179	-3.0531264707	-3.0632772391
H	-2.3845369616	-3.5307396320	-1.3616051638
H	-3.3873390980	-2.1952019608	-1.9656530281
C	-1.2868111719	-0.5946478372	-2.8400492100
H	-0.4849688742	0.1438061172	-2.6940830001
H	-1.1116367702	-1.0858788671	-3.8112326591
H	-2.2444825206	-0.0654746322	-2.9131732101
C	0.0995523918	-2.3575158558	-1.8748806662
H	0.2235428533	-2.7507272401	-2.8977120015
H	0.9293232054	-1.6290092500	-1.7371447379
H	0.2545292135	-3.1849559523	-1.1761783947
C	-1.2537701393	-1.6712037010	2.6610981132
H	-1.7976118517	-0.7871627849	3.0077929149
H	-1.4064382687	-2.4688545473	3.4066769141
H	-0.1829894286	-1.4216593377	2.6349156057
C	-3.2069359495	-2.5578155398	1.3524560804
H	-3.8370281076	-1.7135957378	1.6622536804
H	-3.5887874150	-2.9322979463	0.3935585247
H	-3.3477059603	-3.3571420092	2.0989222197
C	-0.8957770516	-3.4502704509	1.0305383524
H	-1.1893921664	-3.9866074716	0.1199286359
H	0.1781467205	-3.2162878158	0.9779920304
H	-1.0427887793	-4.1417758341	1.8758376099
C	-2.5229703007	0.5559594154	0.0401168274
C	-2.7621928370	0.9777475523	1.5044128234
C	-3.8876078102	0.2601609436	-0.6075740808
C	-1.8762888800	1.7717121357	-0.6649742592
H	-3.2390777483	0.1638209250	2.0669705739
H	-1.7954929711	1.1915829929	1.9888809144
C	-3.6730030309	2.2075413006	1.5833964872
H	-4.3782588429	-0.5873946198	-0.1062303937
H	-3.7619687611	-0.0246037195	-1.6619854311
C	-4.7920906608	1.4973227473	-0.5293154379
H	-0.9060546854	1.9868737921	-0.1898989069
H	-1.6611459651	1.5480841214	-1.7153918777
C	-2.7941900310	2.9955772345	-0.5997798790
H	-3.8239582604	2.4593153549	2.6461344596
C	-5.0190215579	1.8780970585	0.9346545759
C	-3.0252130216	3.3852177349	0.8583309969
H	-5.7576828239	1.2566590915	-1.0043319363
C	-4.1322965100	2.6652487215	-1.2653721735

H	-2.3064120359	3.8259980648	-1.1360952376
H	-5.6968041368	2.7456058898	1.0017613394
H	-5.5080796666	1.0472636427	1.4716532627
H	-2.0668195959	3.6461419479	1.3371342294
H	-3.6718920981	4.2765600739	0.9236704265
H	-3.9748162060	2.4052502655	-2.3261992802
H	-4.7955010438	3.5464872278	-1.2480478747
Pt	0.9671831585	-0.2361770791	0.1578271139
C	2.9423802211	0.2052436082	0.1330333728
C	3.8849758025	-0.5588676761	0.8488156996
C	3.4554880827	1.2262101879	-0.6913735439
C	5.2578634729	-0.3442906574	0.7335934539
C	4.8237110360	1.4597012569	-0.8223915889
H	2.7672102881	1.8635984707	-1.2540486166
C	5.7161883680	0.6664606965	-0.1067722371
H	5.2009212786	2.2530083249	-1.4707645836
H	0.8616280368	0.7563098660	1.3075167276
H	3.5418087389	-1.3508770627	1.5206899899
Cl	7.4311430021	0.9485886307	-0.2587484473
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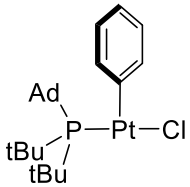

Pt(Cl)(Ph)

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Pt(Cl)(Ph)

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C	-0.1294100425	1.9137860666	-1.9213666992
C	-0.7099254263	3.8536507742	0.8262186453
H	-0.5163161212	4.5696744427	1.6420225465
H	-0.3987203840	4.3375794024	-0.1074238026
H	-1.7949819511	3.6914206082	0.7824970945
C	-0.3290370650	2.0670930152	2.5131287767
H	0.1880502844	1.1299506764	2.7653740654
H	-0.0139317871	2.8295697296	3.2438061524
H	-1.4091977526	1.9239540237	2.6378122829
C	1.5666130249	2.8338017770	1.1686851562
H	1.7740936967	3.5641225490	1.9684231131
H	2.1391299783	1.9256024316	1.4629538164
H	1.9883291776	3.2287899807	0.2407366102
C	0.2000538611	0.8006404107	-2.9236490831
H	-0.5176140793	-0.0256521058	-2.9268384391
H	0.2175166487	1.2368989216	-3.9357319843
H	1.1967621744	0.3901604909	-2.7137170724
C	-1.4169238130	2.6268735582	-2.3387527995
H	-2.2624891572	1.9366192676	-2.4493151504
H	-1.7112216818	3.4183666623	-1.6380033382
H	-1.2550489762	3.0993352212	-3.3214392055
C	1.0418478414	2.8980487176	-2.0247705485
H	0.8951664378	3.8167568338	-1.4452971254

H	1.9885390037	2.4276088806	-1.7207239616
H	1.1461330760	3.1937204220	-3.0809224206
C	-1.8453554180	0.2835827917	0.1129135383
C	-2.1595867823	-0.6152366475	-1.1024727017
C	-3.0310764712	1.2403178139	0.3402413915
C	-1.7217909880	-0.6452876083	1.3409484591
H	-2.2839329538	-0.0073110839	-2.0085896198
H	-1.3247295696	-1.3104522031	-1.2793116608
C	-3.4525058779	-1.4049960619	-0.8779041752
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H	-2.8498749720	1.8699267675	1.2233586352
C	-4.3241406318	0.4406177342	0.5573193945
H	-0.8921516726	-1.3446213792	1.1858662203
H	-1.4931833690	-0.0728863214	2.2458780401
C	-3.0182943929	-1.4292610404	1.5647614302
H	-3.6396366377	-2.0198814316	-1.7735041614
C	-4.6096704215	-0.4271488386	-0.6698926841
C	-3.3003878001	-2.3058317440	0.3460078614
H	-5.1516973804	1.1530166566	0.7110008337
C	-4.1752412559	-0.4548655535	1.7885639296
H	-2.8861504561	-2.0631216314	2.4569627143
H	-5.5556739693	-0.9771616988	-0.5320890818
H	-4.7367589263	0.2077355590	-1.5637852130
H	-2.4720625116	-3.0171100134	0.1915766161
H	-4.2179084665	-2.8983252871	0.5013037091
H	-3.9860350534	0.1600942505	2.6851550178
H	-5.1127112323	-1.0067012422	1.9710744291
Pt	1.7369538495	0.0158676164	0.2706359524
Cl	3.8655474210	-0.6377099622	0.8871652976
C	1.1891219289	-1.8071491236	-0.2231134091
C	0.9568832073	-2.7160275964	0.8194886416
C	1.0913488267	-2.2554349614	-1.5433275769
C	0.5625062957	-4.0242109819	0.5402336472
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C	0.6993406305	-3.5681701755	-1.8149167012
H	1.3215564306	-1.5886926188	-2.3722729370
C	0.4166287055	-4.4542155208	-0.7781463390
H	0.3777954077	-4.7147659518	1.3673282678
H	0.6217947321	-3.8971966925	-2.8546433314
H	0.1069724641	-5.4791044443	-0.9949278604

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