UNIVERSITY OF CALIFORNIA

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Water as the Medium: Trace Metal Catalysis and Biocatalysis Enabled by Aqueous Micelles

A dissertation submitted in partial satisfaction of the

requirements for the degree Doctor of Philosophy

in Chemistry

by

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March 2021

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“It always seems impossible until it’s done.”

– Nelson Mandela

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Dobson, E. D., Jones, K. G., **Akporji, N**., Soika, D. Q. M., Nastiuk, K. L., Hornak, J. P., Schmitthenner, F. H "Modular Synthesis of DOTA-Metal based PSMA Targeted Imaging Agents for MRI and PET of Prostate Cancer" *Chem. Eur. J.* **2019** 25, 13848.

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Cortes-Clerget, M., Kincaid, J. R., **Akporji, N.**, Lipshutz, B. H. Supramolecular Catalysis: New Directions and Developments, *Surfactant Assemblies as Nanoreactors for Organic Transformations.* **2021**

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ABSTRACT

Water as the Medium: Trace Metal Catalysis and Biocatalysis Enabled by Aqueous Micelles

by

Nnamdi Akporji

I. A new biaryl phosphine-containing ligand from an active palladium catalyst for ppm level Suzuki-Miyaura couplings, enabled by aqueous micellar reaction medium is presented. A wide array of functionalized substrates including aryl/heteroaryl bromides are amenable, as are, notably, chlorides. The catalytic system is both general and highly effective at low palladium loadings (1000-2500 ppm or 0.10-0.25 mol%). Density functional theory calculations suggest that greater steric congestion in N_2Phos induces increased steric crowding around the Pd center, helping destabilize the 2:1 ligand-Pd^0 complex for N_2Phos then previously described ligands, and thereby favoring the formation of the 1:1 ligand-Pd^0 complex that is more reactive in the oxidative addition of aryl chlorides.

II. Previous studies have shown that aqueous solutions of designer surfactants enable a wide verity of valuable transformations in synthetic organic chemistry. Since reactions take place within the inner hydrophobic cores of the aggregate nanoreactors, and products made therein are in dynamic exchange between micelles through in water, opportunities exist to use enzymes to participate in multi-step chemo- and bio-catalytic processes. Herein, studies

conducted utilizing the oxidoreductase class of enzymes are presented. Most noteworthy is the finding that aqueous micelles present in the water appear to function not only as a medium for both chemo- and bio-catalysis, but as a reservoir for substrates, products and catalysts, decreasing noncompetitive enzyme inhibition.

III. Two new methods for selective deprotection of diphenylmethylsilyl (DPMS) ethers are described. Unmasking can be achieved with either catalytic amounts of perfluoro-1-butanesulfonyl fluoride (a SuFEx reagent) under mild, aqueous conditions, or using stoichiometric amounts of 18-crown-6 ether in aqueous ethanol.

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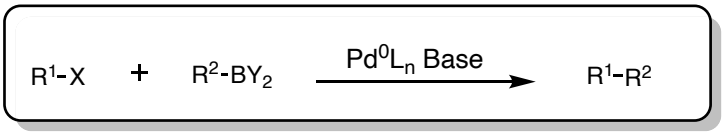
I. N_2Phos – An easily made, highly effective ligand designed for ppm level Pd-catalyzed Suzuki-Miyaura cross couplings in water

1.1 *Introduction and Background*

The Suzuki-Miyaura cross coupling reaction (SMC), first described in 1979,[1] has been integral to the field of organometallics and organic synthesis. The methodology involves the formation of new $C(sp^2)$-$C(sp^2)$ bond that utilized a ligated palladium catalyst (typically an organophosphine as the ligand), an aryl/alkenyl halide or psuedohalide, an organoboron species and a base. (Figure 1).

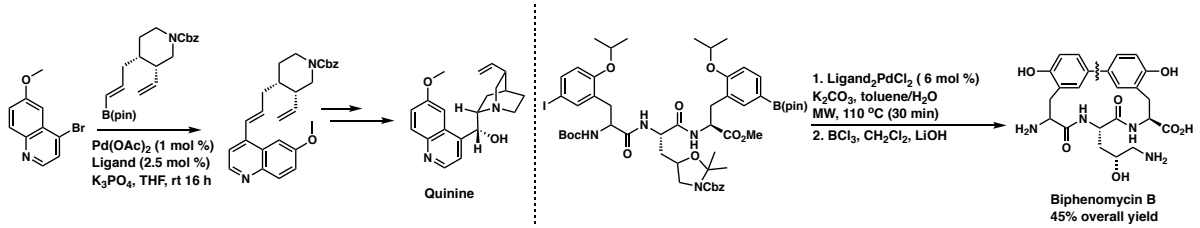
Figure 1. General reaction scheme for Suzuki-Miyaura cross-couplings



R^1 = alkenyl, aryl; R^2 = allyl, aryl, alkenyl;
Y = OH, O-alkyl, alkyl; X = Cl, Br, I, OTf

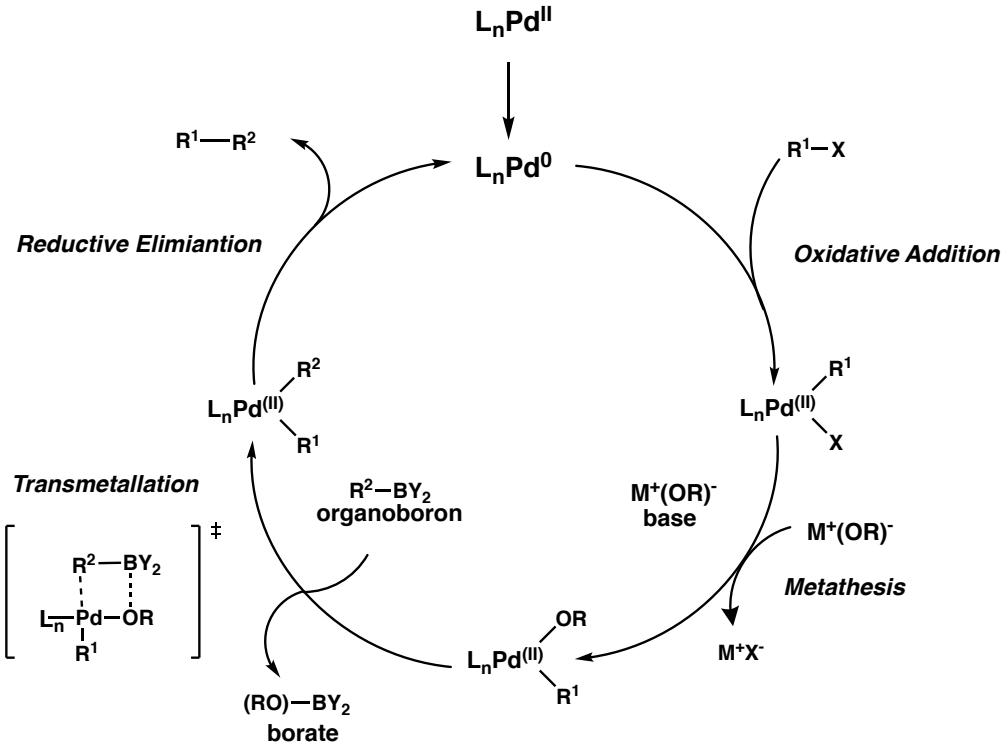
As a Nobel Prize-winning reaction, the SMC has been applied extensively to syntheses of natural products as well as a wide array of active pharmaceutical ingredients (APIs); including quinine, which is an anti-parasitic drug used to treat malaria among other ailments and biphenomycin, a compound known to inhibit protein synthesis (Figure 2). It's use in synthesis is attributed to several factors: the availability of various organoboron species, mild and robust reaction conditions, insensitivity of water and wide functional group tolerance. The prevalence of this methodology cannot be understated as it accounts for 22% of all C-C bond forming reactions in process chemistry and is utilized in greater than 20% of all APIs manufactured.[2-5]

Figure 2. Representative Examples of the Applications of the SMC



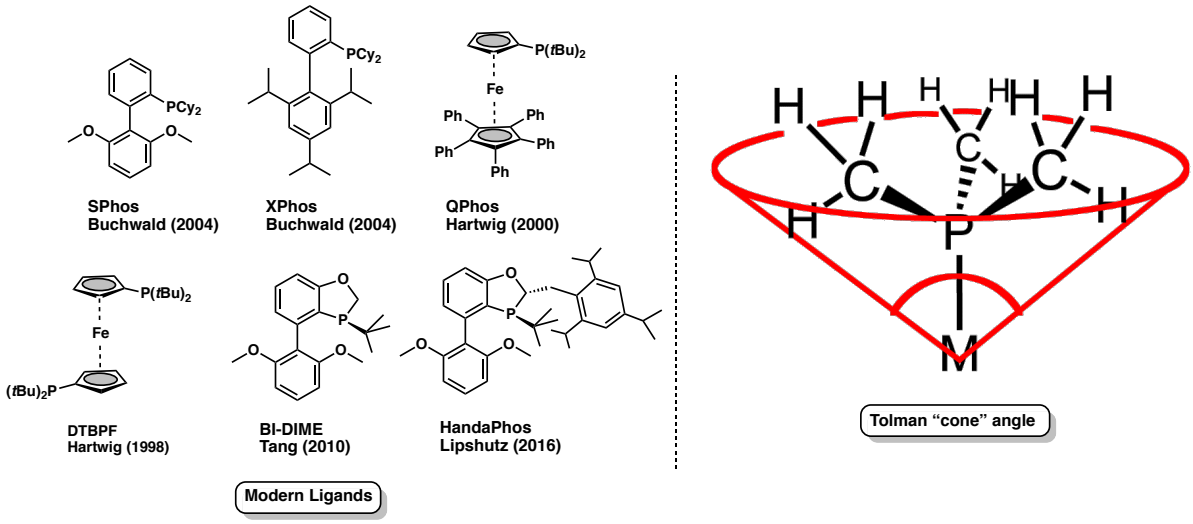
The mechanism of the SMC follows a similar pathway to other transition metal catalyzed processes (Figure 3).[6] The catalytic cycle firstly involves the reduction of a Pd^{II} species to a Pd^{0}, the active catalyst. This process can occur spontaneously in the presence of a monodentate phosphine ligand by reduction of Pd^{II} and forms phosphine oxide. Activation can also occur through higher temperatures, a base, another organometallic species or a hydride source. This species then undergoes oxidative addition of the aryl/alkenyl halide to generate an organopalladium halide complex. This intermediate participates in metathesis with hydroxide generated in solution to create an organo-oxo-palladium species. This is followed by transmetalation with the neutral organoboron species. Lastly, reductive elimination occurs yielding the new $C(sp^2)$-$C(sp^2)$ bond and the regenerated Pd^{0} species.

Figure 3. Suzuki Miyaura Catalytic Cycle



The overall efficacy of the reaction is greatly dictated by the nature of the catalytic palladium species. Early iterations of the methodology exhibited limited reactivity towards the crucial oxidative addition step which is beholden to the known reactivities of organohalides and psuedohalides (I > Br = OTf > Cl). However, extensive studies into the nature of the catalyst have revealed that the ligand (Figure 4) can greatly increase the reactivity of the active catalyst and aid in the ease of the initial oxidative addition step in addition to the reductive elimination step, increasing the overall rate of the reaction. Various steric and electronic effects of the ligand play a significant role in the activity of the ligated Pd complex. John Osbourne in 1989 discovered that significant catalytic activity is found only with phosphines which are both highly basic (i.e. electron-rich) and with a well-defined steric volume.[7] In the case of the least reactive aryl/alkenyl chlorides, the optimal basicity of the Pd complex must exhibit a pKa >

Figure 4. Highly Active Ligands Employed in SMC



6.5 and a large steric volume greater than 160°. The steric volume is sometimes termed as the Tolman angle or the cone angle.[8]

The "cone" describes the angle formed with the palladium metal at the vertex and the hydrogen atoms at the perimeter of the cone. Tertiary phosphine ligands are commonly classified using this parameter, but this method can easily be applied to any ligand. Sterically demanding ligands shift the equilibrium of ligated palladium from a *bis*-ligated species to a mono-ligated complex. The latter, a 12-electron complex, poses the highest reactivity towards oxidative addition; especially in the case of the less reactive aryl/alkenyl chlorides. Steric pressure of the ligand readily promotes reductive elimination.

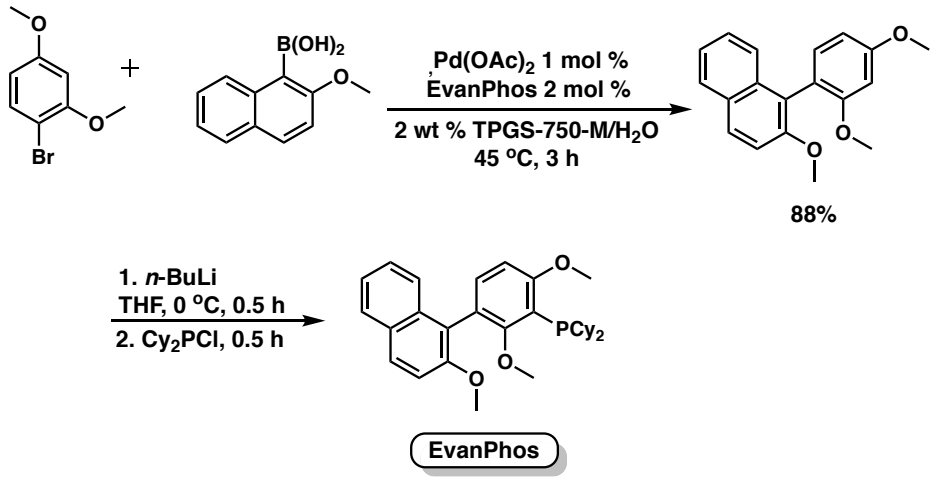
As powerful as these ligands are, they still face some limitations. For the ligands showcased (Figure 4) many of them are not bench stable and often suffer from oxidation over time. The BI-DIME series, including HandaPhos which can facilitate SMCs at ≤ 1000 ppm loading of palladium, often require a lengthy (10+ step) synthesis with unstable intermediates.[9]

Oftentimes, these couplings are ran under high temperatures and employ the use of harsh organic solvents.

Additional limitations are also highlighted in some examples by the use of unsustainable loadings of palladium (1-5 mol %). Moreover, every active pharmaceutical ingredient (API) must adhere to strict FDA guidelines that require very low levels of residual Pd (≤10 ppm/dose),[10] which only adds cost in the form of clean-up (e.g., metal scavenging). Due to the high cost of palladium ($2,296 as of September 2020) in addition to its limited availability, we ventured to create a new catalytic system that is highly reactive, easily synthesized, employs low loadings of palladium, and adheres to the principles of green chemistry.

EvanPhos (Figure 5) developed in our lab, was the first generation of ligand design that adhered to the principles of green chemistry.[11] It offers a new biaryl substitution pattern containing a *meta*-oriented phosphine that could facilitate SMCs under mild conditions. The 2,6-dimethoxy-substituted upper ring bearing electron donating (methoxy) substituents aids in the overall basicity of the phosphine atom. The larger naphthyl moiety enhanced steric crowding around the palladium center.

Figure 5. Synthesis of EvanPhos

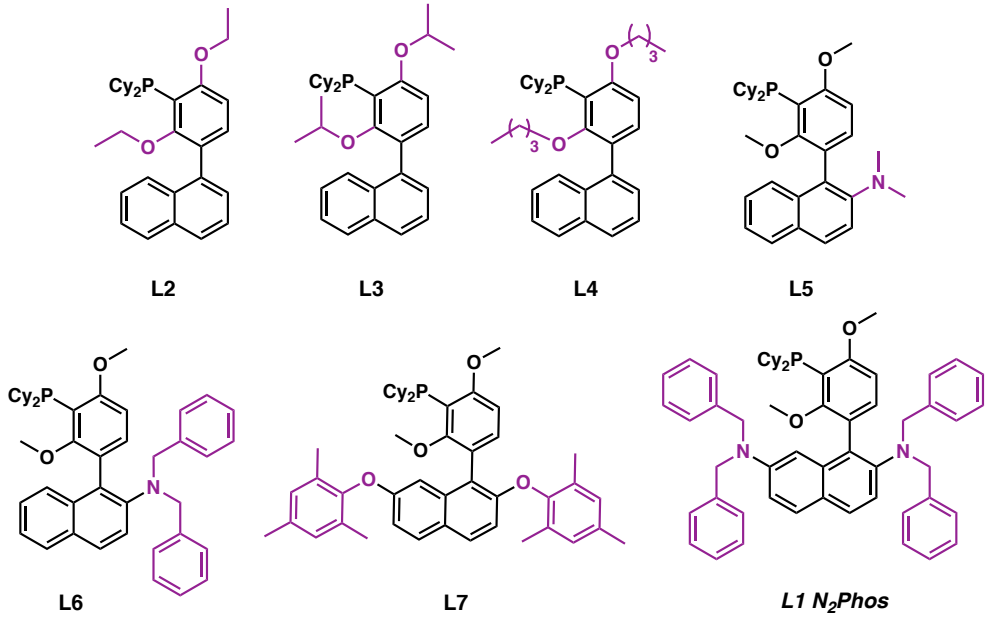


The synthesis was modular in nature and gave rise to a biaryl framework that could easily be assembled and avoided the use of cryogenic temperatures. The EvanPhos derived palladium catalyst could facilitate a wide variety of coupling partners leading to good yields of biaryl products. Although the complex exhibits impressive reactivity at ppm levels for highly functionalized substrates, the loading of palladium was typically within the 0.25-0.50 mol% range. It also lacked catalytic reactivity to participate in reactions with electronically demanding aryl/alkenyl halides. Therefore, we looked to create a new, easily fashioned ligand inspired from the same skeletal framework as EvanPhos, that also exhibits HandaPhos-like reactivity at similar 1000 ppm loadings. Moreover, the hope was that the new ligand may even extend the range of suitable reaction partners to both aryl and heteroaryl *chlorides* for use under mild, aqueous micellar conditions, using nanoreactors derived from the designer surfactant TPGS-750-M.[12]

1.2 Results and Discussion

Typically, ligand design for Pd-catalyzed cross coupling reactions takes, in large measure, steric and electronic factors into consideration, as they can weigh heavily on the activity of the active palladium catalyst.[13-16] While these factors are surely at play as well under micellar catalysis conditions, the switch from a traditional organic solvent medium to water presents new rules that must also be taken into account (e.g., ligand lipophilicity).[17] Thus, further derivatization of the biaryl skeletal of EvanPhos (Scheme 1), with the goal of increasing the activity of the resulting ligated Pd complex, focused on modifications ranging from increasing steric bulk around the phosphine moiety by altering the alkoxy residues (L2-L4) to enhancing steric interactions based on additional substitution on the naphthyl ring.

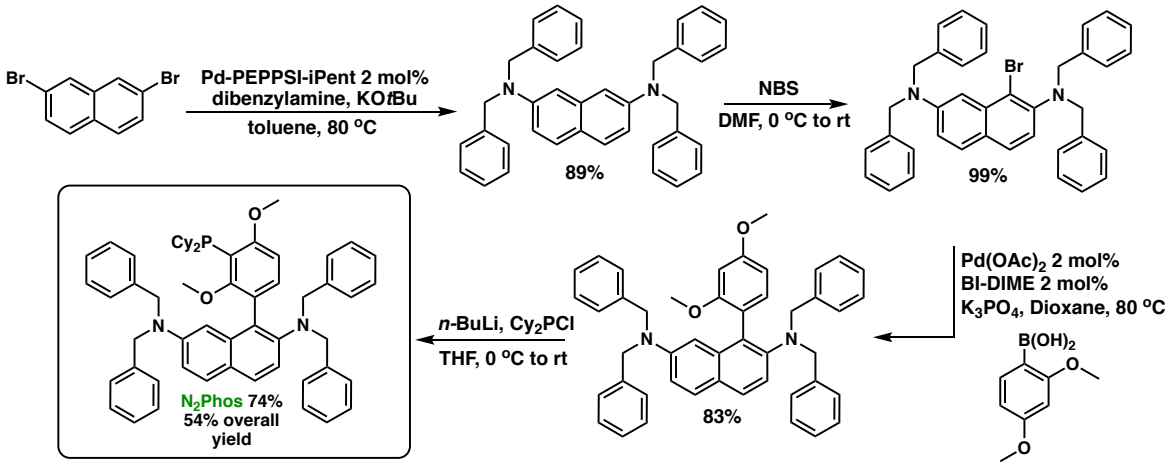
Scheme 1. Derivatization of EvanPhos Skeletal Structure



Results from the former changes showed no significant rate increase, while replacement of an alkoxy group at C-2 in the naphthyl ring showed significant improvements in reaction rates relative to those observed upon chelation of Pd with EvanPhos. Additional steric crowding by placement of two dialkylamino groups at the C-2 and C-7 locations afforded a catalyst, N_2Phos, with the highest activity. The final ratio of N_2Phos (L1) to $Pd(OAc)_2$ of 1.8:1 led to an active pre-catalyst capable of mediating SMCs at 1000 ppm of Pd under mild, aqueous conditions.

The synthesis of N_2Phos (L1) is short, robust, and attractive (Scheme 2). Starting with commercially available 2,7-dibromonaphthlene, double amination gives the *N*-2, *N*-7-dibenzylamine intermediate. Alternatively, the first steps can also be achieved using solventless mechanochemistry.[18] Subsequent bromination with NBS at 0 °C affords the second intermediate that can be isolated without chromatography. The penultimate Pd-catalyzed SMC leads to biaryl intermediate. Finally, lithiation at 0 °C with *n*-BuLi in THF followed by phosphine insertion leads to the targeted ligand in good overall chemical yield (4-steps, 54%).

Scheme 2. Synthesis of N_2Phos

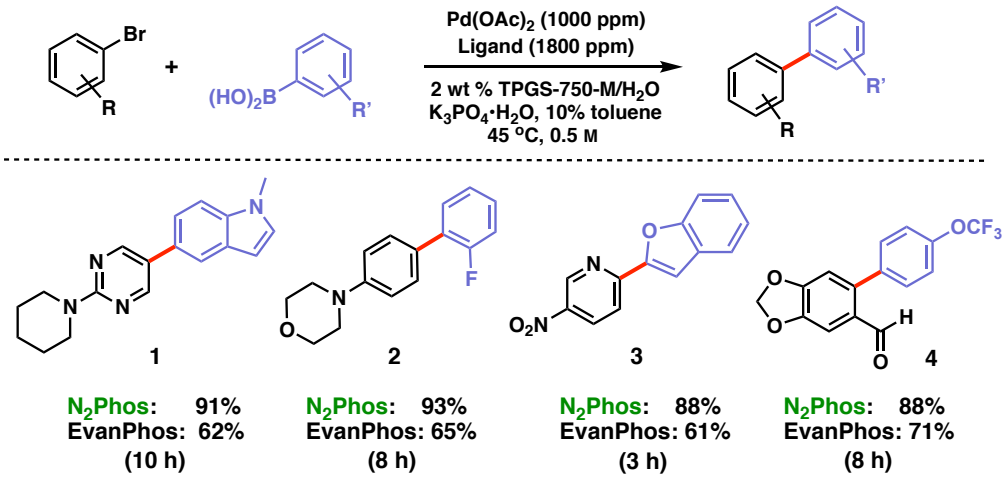


This synthesis of N_2Phos avoids both cryogenic conditions and unstable intermediates.

Initial screening of the catalyst derived from N_2Phos complexed with $Pd(OAc)_2$ (1.8:1) versus that formed using EvanPhos under otherwise identical micellar conditions showed a significant increase in reactivity for the former in all substrates tested (Scheme 3). At 45 °C, the new ligand system led to good, isolated yields of biaryl products, while the extent of conversion, and therefore, isolated yields of the same reactions, using EvanPhos was ca. 25% lower over the same time period. EvanPhos, however, showed comparable yields to N_2Phos when given longer reaction times (16-24 h) for the substrates tested. One notable advantage of the N_2Phos/$Pd(OAc)_2$-derived catalyst is that pre-activation using commercially available DIBAL in toluene is no longer needed, as is the case with the corresponding EvanPhos-derived catalyst.[11]

The same pre-catalyst combination of N_2Phos/$Pd(OAc)_2$ could also be applied to SMCs at the 1000 ppm level, run under traditional conditions involving an organic solvent such as dioxane[19] (Scheme 4). Relative to the corresponding reaction run under micellar catalysis

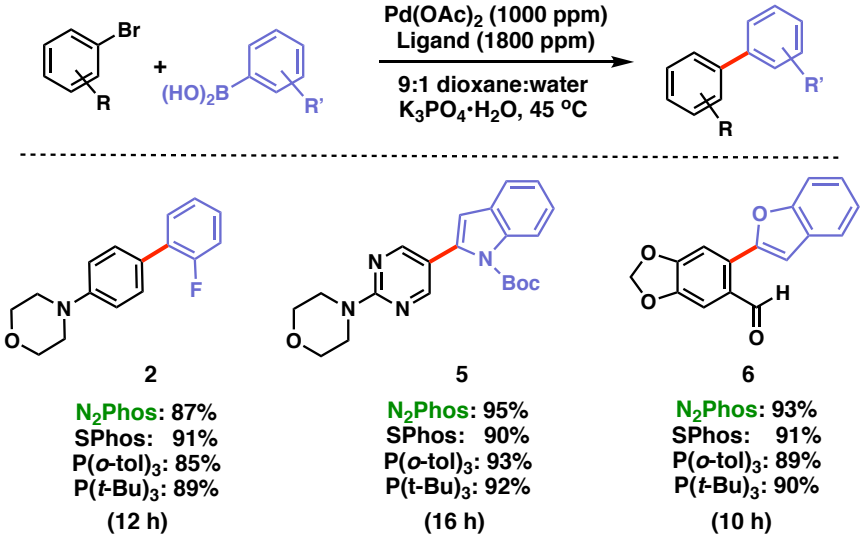
Scheme 3. N_2Phos vs. EvanPhos under micellar conditions.



conditions, these tended to require longer reaction times to reach completion (e.g., formation of biaryl **2**; 8 h *vs.* 12 h; see Scheme 3 *vs*. Scheme 4).

When compared to commercially available SPhos,[20] tri-*t*-butylphosphine (P(t-Bu)3), and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$), N_2Phos shows similar reactivity in dioxane for the substrates tested. Hence, under such conditions in organic media, there appears to be no real benefit to using this ligand over those currently readily available. In water, however, the choice of a 2 wt% aqueous solution of designer surfactant TPGS-750-M[21] was based on prior efforts that showed it to be an especially enabling and recyclable medium for several types of reactions, such as peptide couplings[22-24] SNAr[25] bio-catalytic processes,[26] as well as a wide variety of metal-catalyzed cross coupling reactions. In the case of SMCs, high reactivity can be achieved using this new catalytic system (L1/Pd(OAc)$_2$), with inclusion of K_3PO_4•H_2O (1.5 equiv). This salt exhibited superior performance compared to other commonly employed bases, such as Et_3N or K_2CO_3. Toluene was selected as co-solvent (10% by volume),[27] given the poor solubility of some of the chosen substrates.

Scheme 4. N_2Phos vs. SPhos, P(*o*-tol)$_3$ and P(*t*-Bu)$_3$ in organic solvent.



2

N_2Phos: 87%
SPhos: 91%
P(*o*-tol)$_3$: 85%
P(*t*-Bu)$_3$: 89%
(12 h)

5

N_2Phos: 95%
SPhos: 90%
P(*o*-tol)$_3$: 93%
P(t-Bu)$_3$: 92%
(16 h)

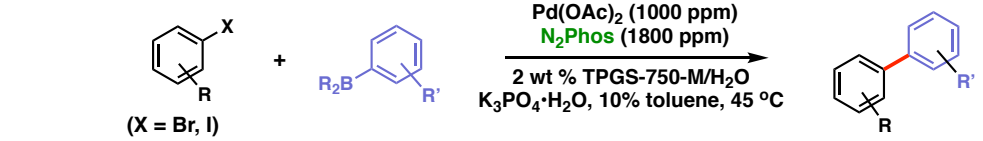
6

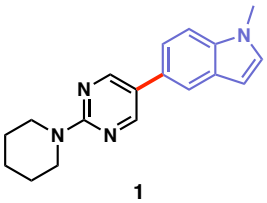
N_2Phos: 93%
SPhos: 91%
P(*o*-tol)$_3$: 89%
P(*t*-Bu)$_3$: 90%
(10 h)

Reactions run in the presence of this co-solvent appeared as nicely stirring emulsions. Broad functional group tolerance associated with either reaction partner is apparent, leading to good yields of coupled products. Hence, an assortment of challenging bromide partners can be coupled using this system at a loading of only 1000 ppm Pd (Scheme 5) including those bearing an ester (**12**), aldehyde (**4**), nitro (**3**, **8**), lactam (**13**), and sulfonamide (**7**) residues. Heteroaromatic bromides and boronic acids are also amenable, such as those containing pyridine, pyrimidine, benzofuran, indoles, furans, and benzothiophenes. Not surprisingly, aryl iodides are also converted quickly to the corresponding biaryls in excellent yields. Alternative boron-containing partners beyond boronic acids, including a Bpin derivative (leading to product **10**), a potassium trifluoroborate[30] (affording product **15**), and a MIDA boronate[31] (giving product **16**), could be used as well.

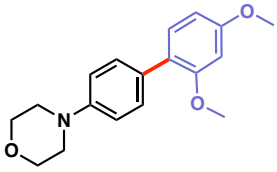
Although EvanPhos was designed as a quickly synthesized, alternative ligand to HandaPhos for Pd-catalyzed SMCs, it has shown limited, if any, applicability to aryl chlorides, especially at the ppm level of precious metal.[9,11]

Scheme 5. Substrate scope using N_2Phos

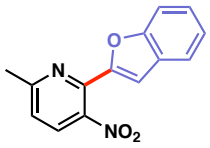




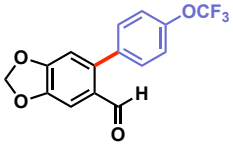
1
78% (12 h)



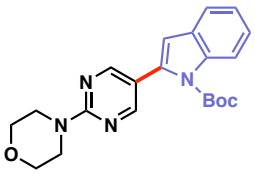
2
83% (12 h)



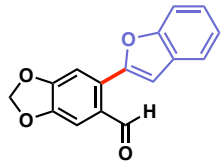
3
94% (8 h)



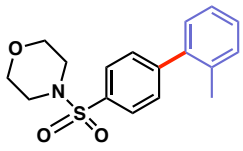
4
92% (16 h)



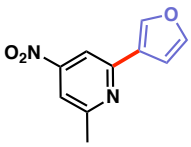
5
95% (16 h)



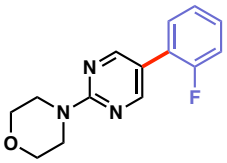
6
91% (8 h)



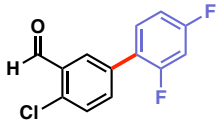
7
81% (16 h)



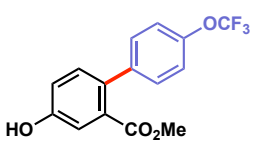
8
88% (8 h)



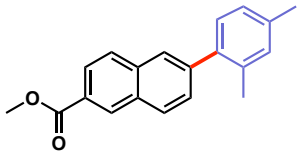
9
83% (22 h)



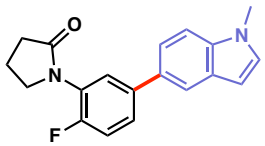
10
92% (8 h)
94% (12 h; Aryl-Bpin)



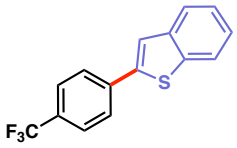
11
83% (1 h; X = I)



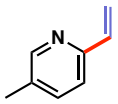
12
96% (1.5 h)



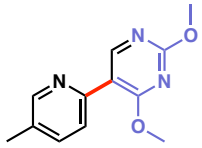
13
80% (36 h)



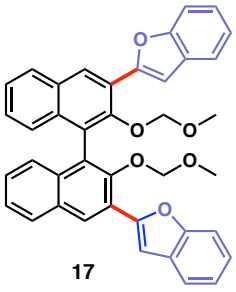
14
87% (16 h)



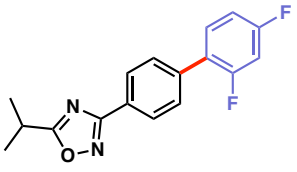
15
89% (16 h, vinyl-BF_3K)



16
87% (12 h, Ar-BMIDA)



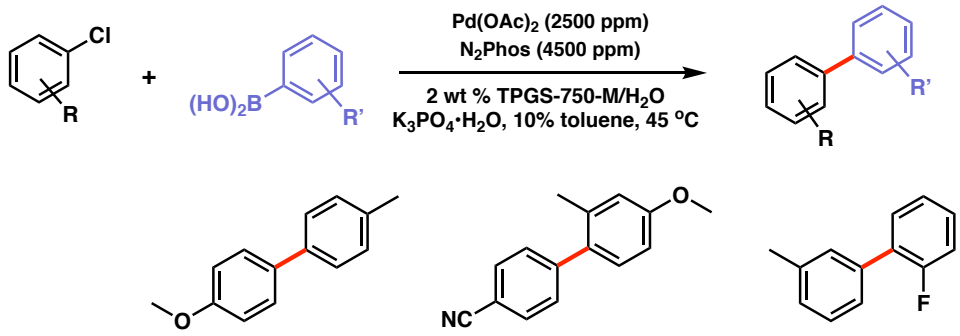
17
79% (24 h, Ar-I)



18
81% (24 h)

It is known to exist as a four-coordinate complex: $(EvanPhos)_2PdX_2$, based on both an X-ray crystal structure and computational work.[11] However, N_2Phos-complexed palladium can be used for couplings with aryl chlorides regardless of electronic influences on the ring. This may be a result of the differential modes of complexation, where EvanPhos can spatially form 2:1 complex with Pd. As shown, however, by modeling and calculations (vide infra), the far greater size of N_2Phos makes 2:1 complexation significantly less favorable. Thus, aryl chloride precursors reflecting both electron-rich, electron-poor, and neutral educts afford product biaryls **20**, **22**, and **23**, respectively, although an increase in Pd loading to 2500 ppm (0.25 mol %) was needed (Scheme 6a). Comparisons in each of these three cases were also made with EvanPhos, SPhos, P(*t*-Bu)3, and $P(o\text{-tol})_3$, the results from which indicate that N_2Phos affords a catalyst that is equal to or better than these others in terms of reactivity at this loading of Pd under micellar catalysis conditions. The difference in conversion of aryl chlorides is quite noticeable, leading, e.g., to biaryl **20**. Thus, while N_2Phos gave 88% of product **20** after eight hours, EvanPhos led to only 7% conversion after eight hours, and only 9% after 16 h (96% with N_2Phos), after which time there was both unreacted aryl chloride present, as well as the product of protodeborylation.

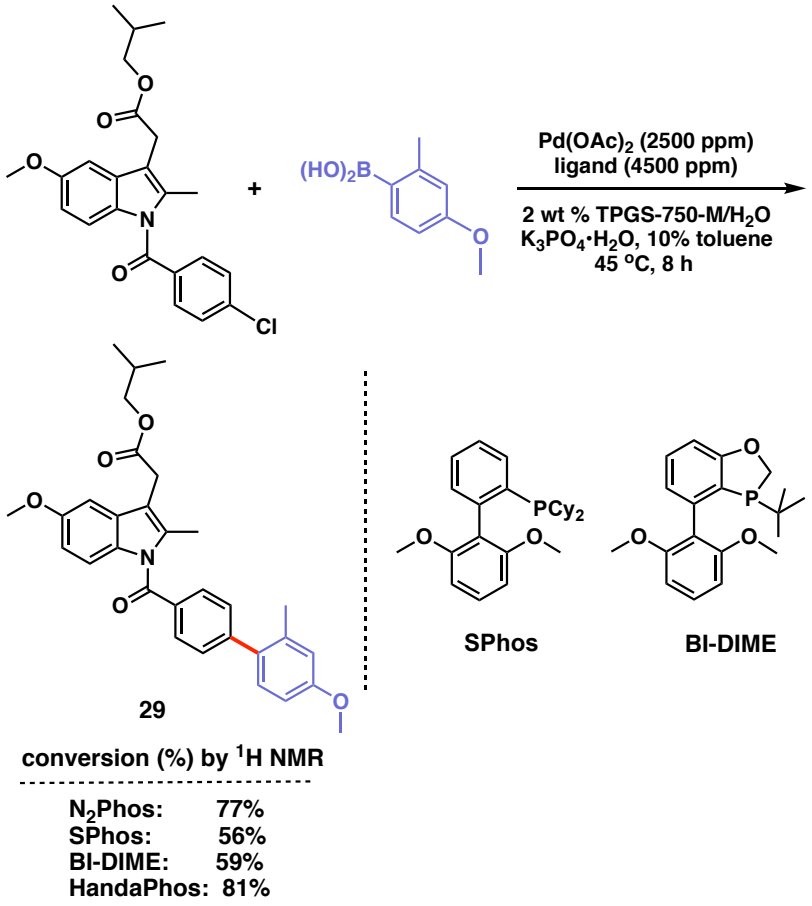
Scheme 6a. Comparison reactions between ligands and N_2Phos involving aryl chlorides



	20	**22**	**23**
Ligand	conversion (%)[a]	conversion (%)[a]	conversion (%)[a]
N_2Phos	**88**	**99**	**98**
EvanPhos	7	41	25
SPhos	71	99	93
P(*o*-tol)$_3$	70	96	95
P(*t*-Bu)$_3$	75	99	92

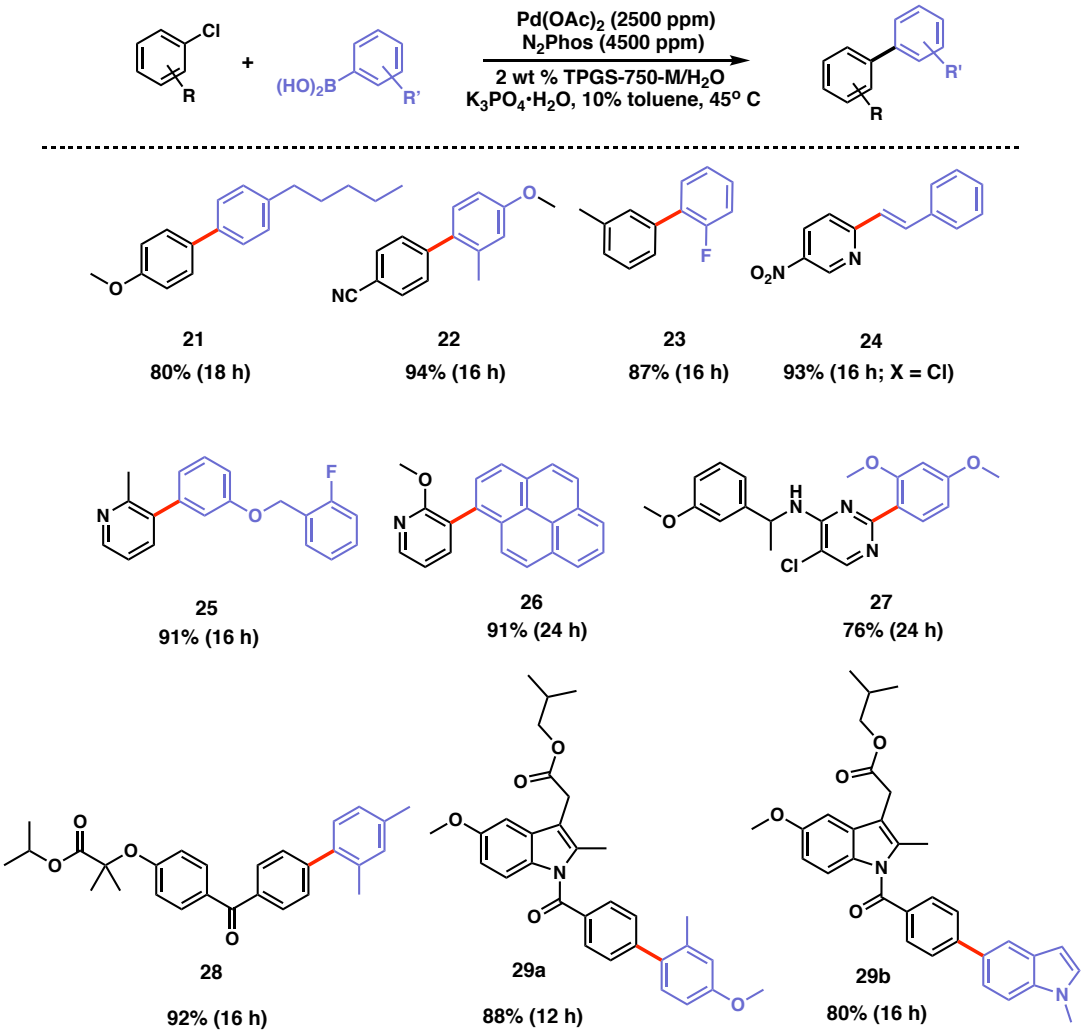
[a]By ^{1}H NMR.

Scheme 6b. Comparison reactions between ligands and N_2Phos involving aryl chlorides



The low yields with aryl chlorides appears, then, to be the result of a slow oxidative addition with EvanPhos compared to N_2Phos. How these two ligands differ in their behavior and the possible role of steric effects was explored computationally. A similar outcome was noted in the case of the ester of indomethacin (Scheme 6b), where a better result was observed in comparisons with catalysts derived from either SPhos or BI-DIME.[15,28] Moreover, that the results between N_2Phos and HandaPhos were within experimental error further suggests that the derived catalysts in each case are roughly comparable in activity imparted as their 1:1 complexes with Pd. The biaryls prepared and isolated from a more general study on the scope

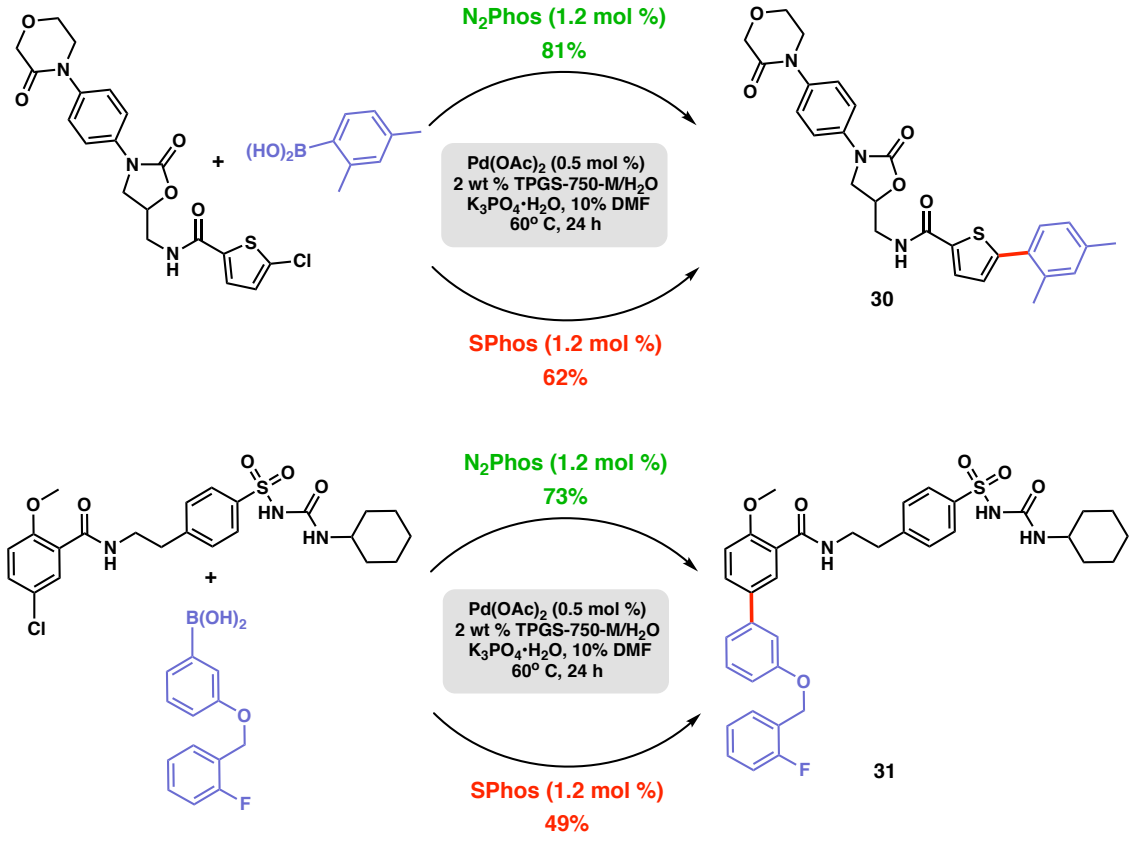
Scheme 7. Substrate Scope using N_2Phos with aryl chlorides



of these couplings with various aryl/heteroaryl chlorides are illustrated in Scheme 7. Several heterocyclic arrays, such as those in products **24**-**27** were formed under the same coupling conditions used for analogous bromides, although somewhat increased reaction times and catalyst loadings were needed to achieve high levels of conversion, and hence, good, isolated yields.Modified known targets that coupled smoothly included fenofibrate (leading to **28**), used to treat high cholesterol, and previously mentioned indomethacin (giving products **29a**-**b**), an anti-inflammatory drug. Very highly functionalized and especially challenging chloroarenes also participated, including rivaroxaban (a medication used to prevent blood

clots) affording product **30**, and glibenclamide (used to treat type 2 diabetes) leading to biaryl **31** (Scheme 8). Palladium loadings of 5000 ppm (0.50 mol %) together with a reaction temperature of 60 °C were required, along with water-miscible DMF (10%) as co-solvent. Direct comparisons with the most commonly used, state-of-the-art Pd/ligand combination (i.e., SPhos),[20] clearly indicated that under otherwise identical micellar conditions and ppm levels of Pd, (N_2Phos)Pd gave far better results.

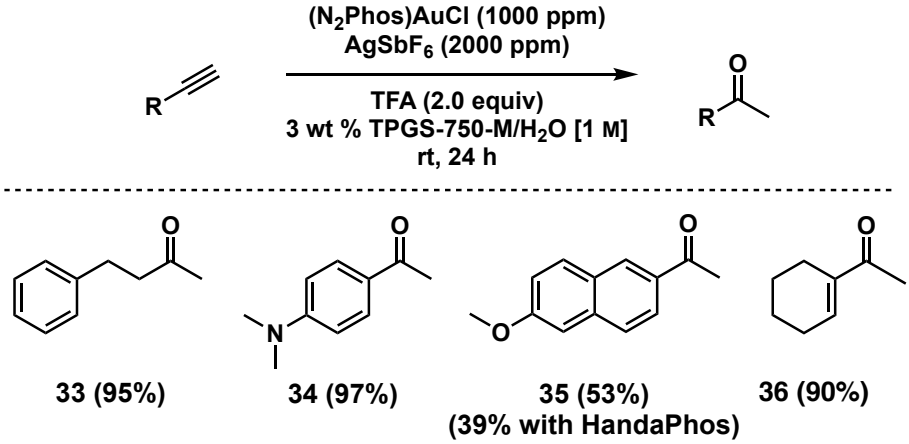
Scheme 8. Comparison of N_2Phos and SPhos with highly functionalized aryl/heteroaryl chlorides



Further investigations into the generality of the ligand are ongoing, including its use in other metal-catalyzed processes. For example, preliminary results (Scheme 9) indicate that the ligand that can also facilitate ppm level Au-catalyzed hydration of alkynes in the same aqueous

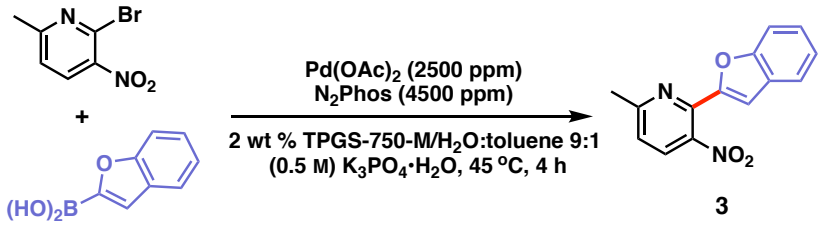
surfactant media at rt. Moreover, the combination of N_2Phos with AuCl may lead not only to competitive outcomes relative to those obtained previously with HandaPhos-complexed AuCl,[29] but also, on the basis of naphthyl-containing product **35**, a greater extent of conversion and thus, a higher-yielding reaction.

Scheme 9. N_2Phos employed in gold-catalyzed hydration of alkynes



Recycling of the 2 wt % aqueous surfactant media could be readily achieved as a means of reducing the amount of organic waste produced, as measured by E Factors (Scheme 10).[30,31] Each recycle was carried out starting with an in-flask extraction of the aqueous reaction with recyclable ethyl acetate, followed by introduction of additional catalyst (i.e., an additional 1000 ppm Pd) into the reaction medium. Based on this representative biaryl coupling, an E Factor of only 4.7 is indicative of the limited amounts of solvent waste generated. This value is far below those typically seen based on usage of organic solvents as both reaction medium and for extraction purposes.

Scheme 10. Recycle study and E Factor Determination



E Factor = $\frac{\text{wt of solvent used (waste)}}{\text{wt of product isolated}}$

E Factor = 4.7

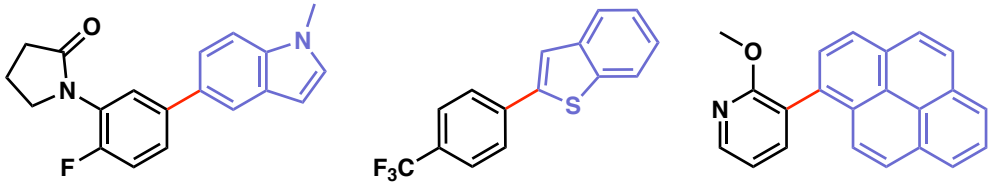
recycling: initial reaction: 93%

1st recycle: 92%

2nd recycle: 88%

Levels of residual Pd found in the products using ppm loadings of Pd catalysts enabled by aqueous nanomicellar technology are typically below the 10 ppm FDA allowed limit.[10] This is yet another major advantage associated with this chemistry in water which avoids the time and expense of scavenging metal impurities. In this case, analyses of three products via ICP-MS led to observed levels all within the targeted range (Figure 6).[10]

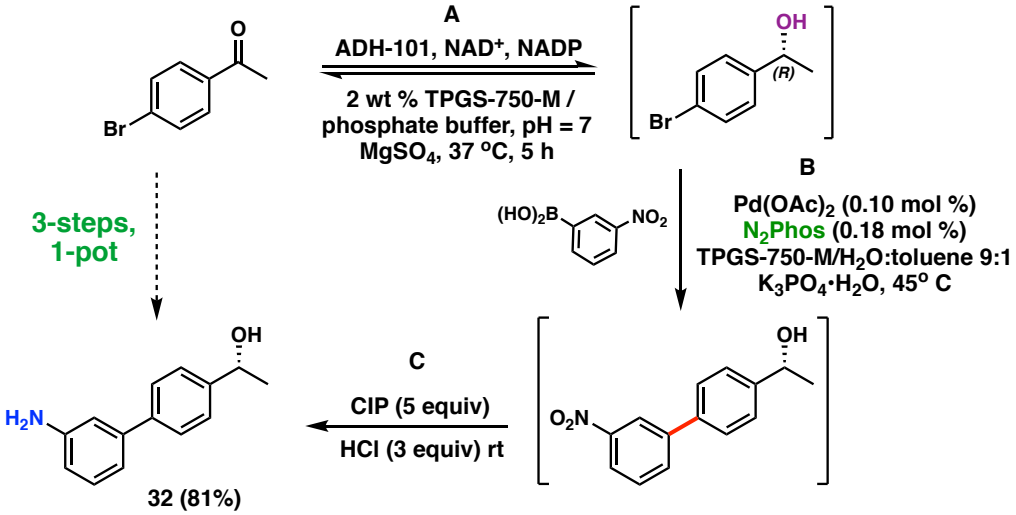
Figure 6. Residual levels of Pd in products



13 (4 ppm) **14** (2 ppm) **26** (9 ppm)

A representative 3-step, 1-pot sequence illustrative of the infinite opportunities now available for combining chemo- and bio-catalysis in water[26] is illustrated in Scheme 11. Thus, following an enzymatic reduction of *p*-bromoacetphenone in an aqueous buffered medium (step A), the product (without isolation) is then used for a 1000 ppm N_2Phos Pd-catalyzed Suzuki-Miyaura coupling (step B). Again, without processing the newly formed biaryl, nitro group reduction utilizing carbonyl iron powder (CIP)[32] (step C) ultimately affords nonracemic aminoalcohol **32** in 81% overall yield.

Scheme 11. 3-step, 1-pot sequence



Density functional theory (DFT) calculations and an X-ray crystal structure were obtained to gain insight into the structural factors that contribute to the greater reactivity of the N_2Phos/Pd(OAc)$_2$-derived species formed in solution relative to the corresponding catalyst derived from EvanPhos. The X-ray crystal structure of N_2Phos is shown in Figure 7. Two notable features include the dihedral angle between the biaryl groups of 79.47° and the orientation of the two N,N-dibenzyl moieties, the steric requirements for each forcing the aromatic rings of the biaryl unit to be almost perpendicular. Quantum-calculated geometry optimizations of the free ligand N_2Phos at the B3LYP/6-31G(d) level were completed for seventeen of the most reasonable conformations. The next most stable, by 0.60 kcal/mol, of these calculated structures had the same basic conformation as in the X-ray crystal structure. At the B3LYPD3/6-31+G(d,p) level with D3 empirical dispersion corrections and a larger basis set and at the M06/6-31+G(d,p) level, this structure was not always the lowest in energy but was within about 2 kcal/mol of being the lowest energy. Small computational inconsistencies and/or small crystal-packing effects could account for these differences between experiment and theory. Structural parameters for the X-ray structure and for the

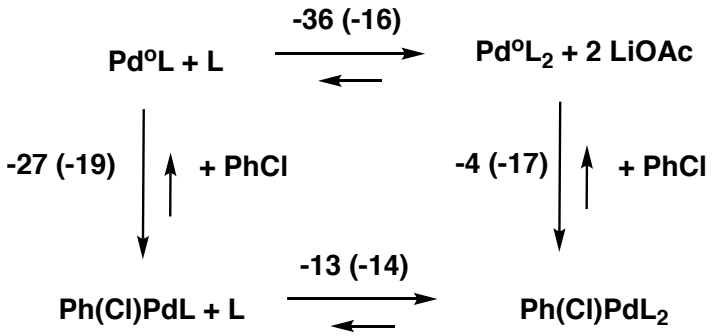
calculated structures at the three levels for the same basic conformation gave a close correlation between experiment and theory at all levels for bond distances and angles. Average errors were about 0.010 Å in some selected distances and 2.0-2.1° for selected angles. For selected dihedral angles that determine the exact conformation, the differences were larger, averaging 10-14°, as expected since these bond rotations have shallow energy wells. The B3LYPD3/6-31+G(d,p) level of theory gave slightly smaller geometry errors than the other two levels of theory. These geometry comparisons between theory and experiment suggest that the levels of theory chosen might also be expected to give reliable reaction energies for interconversion of the conformers.

The structures and relative energies of the pre-reductive elimination intermediates, Ph_2PdL, for SMCs between two simple phenyl rings to form biphenyl were calculated at the B3LYP/6-31G(d)-SDD(Pd) level using a conformation for the ligand close to the experimental conformation of the free ligand from the X-ray structure for N_2Phos and for a low-energy conformer for EvanPhos.[11] The calculations reveal that intermediates from both ligands form a square planar complex, as expected for Pd(II). Key distinguishing features, however, show a C-Pd-C angle of 82.17°, along with a bond length of 2.453 Å between palladium and the methoxy oxygen on the resorcinol ring of N_2Phos, well in the range of the van der Wall's radii of the two elements indicative of a weak interaction (Figure 8). The former observation highlights a notable difference as compared with the corresponding EvanPhos-containing intermediate possessing a greater C-Pd-C angle of 87.68° (Figure 8). The enhanced proximity of the two phenyl rings could translate into an increased rate of reductive elimination for the N_2Phos-containing intermediate compared with that with EvanPhos in this complex. The explanation can be attributed to the N,N-dibenzyl moieties of the naphthyl ring, such that the -NBn_2 residues significantly crowd the available space around palladium, thereby forcing the

two phenyl rings into closer proximity and increasing their rate of reductive elimination. No such phenomenon is in play with EvanPhos. The steric requirements of the N_2Phos ligand make the formation of a 2:1 complex with diphenylpalladium impossible, with no energy minimum found for the $Ph_2Pd(N_2Phos)_2$ complex, though less hindered versions lacking dibenzylamino substituents were able to form such 2:1 complex.

More important, however, than the reductive elimination step in our analysis as to why the N_2Phos ligand gives improved yields over EvanPhos with aryl chlorides is the possibly rate-limiting oxidative addition step.[33] Oxidative additions of ligated Pd^0 (LPd^0 and $L2Pd^0$) to chlorobenzene forming PhPd(Cl)L and $PhPd(Cl)L_2$, respectively, were studied with both EvanPhos and N_2Phos ligands. Oxidative addition was found to be much more downhill in free energy when carried out with monoligated species LPd^0 in accord with literature expectations.[34-36] The oxidative addition reaction Scheme 12 summarizes the computational results with M06D3/6-31+G(d,p)-SDD(Pd) level free energies. The free energies for the oxidative addition are 8 kcal/mol more downhill for the monoligated species LPd^0 for EvanPhos than for N_2Phos. This seems to contradict our presumption that catalysis by the Pd-complexing N_2Phos ligand would be favored, although it does follow based on steric arguments. The equilibria for further ligation of LPd^0 to form L_2Pd^0 have free energies of reaction of -36 and -16 kcal/mol for the EvanPhos and N_2Phos ligands, respectively. Thus, the di-ligated L_2Pd^0 is the predominant form of the LPd^0 catalyst, and the overall reaction to form PhPd(Cl)L from L_2Pd^0 is predicted to be downhill by 3 kcal/mol for N_2Phos and uphill by 9 kcal/mol for EvanPhos, leading to a strong 12 kcal/mol overall preference for the N_2Phos reaction. Inclusion of solvation by toluene computationally using a continuum model makes little difference, showing the same 12 kcal/mol preference.

Scheme 12. Reaction Scheme for oxidative addition with free energies in kcal/mol



Electron-donating effects of the dibenzylamino nitrogens were also considered as a possible influence on the electron density in the vicinity of the phosphine group and perhaps, catalyst reactivity. Natural population analysis calculations at several levels of theory on the free ligands and diphenylpalladium complexes for EvanPhos, N_2Phos, and an N_2Phos with the nitrogens replaced with -CH groups showed little or no regular variation of charge densities at phosphorus or palladium. The fact that the dihedral angles between the planes of the biaryl groups in the ligands is near 80° for the free ligands and palladium complexes would certainly be expected to seriously diminish any putative π-donating electronic effect. This suggests that the efficacy of N_2Phos is likely the result of steric, rather than any significant electronic effects.

Figure 7. X-ray (left) and B3LYP/6-31G(d) calculated (right) structures of N_2Phos

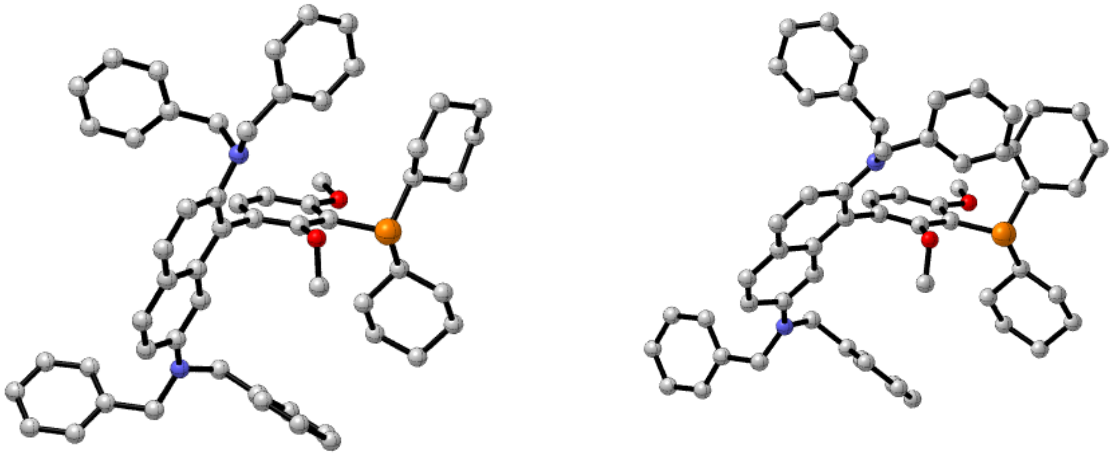
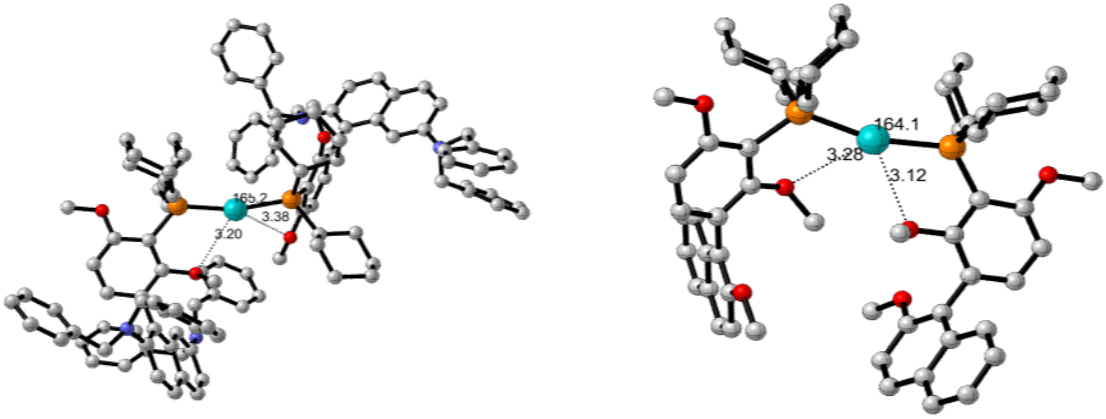


Figure 8. B3LYP/6-31G(d)-SDD(Pd) calculated structures of sterically hindered, but lowest-energy palladium zero intermediates for (N2Phos)2Pd (left) and (EvanPhos)2Pd (right)



1.3 Conclusion

In summary, a next-generation ligand, N_2Phos, featuring judiciously positioned *N*,*N*-dibenzylamine substituents on a naphthalene ring as part of a biaryl array, has been found to impart considerable catalytic activity to its derived palladium complex. This new catalyst facilitates Suzuki-Miyaura reactions at low loadings of palladium of both aryl bromides and iodides, and, most notably, on aryl chlorides. This represents a significant advance in cross-

coupling chemistry, given that such critical reactions can involve complex educts, take place at the ppm level of Pd, and are uniquely positioned for use under environmentally responsible conditions (i.e., in water under ambient-like conditions). Modeling studies suggest that the observed facile participation of aryl chlorides towards a Pd catalyst containing the N_2Phos ligand may be due to steric effects stemming from the locations of the two NBn_2 residues within this biaryl ligand, thereby destabilizing the 2:1 L_2Pd^0 complex and making formation of the more reactive 1:1 LPd^0 complex more accessible when compared to EvanPhos. The monoligated 12-electron (N_2Phos)Pd catalyst is then especially prone towards oxidative addition to aryl chlorides.[37]

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37. The new ligand, N_2Phos, will soon be available from MilliporeSigma (Sigma-Aldrich) under catalog number 915068.

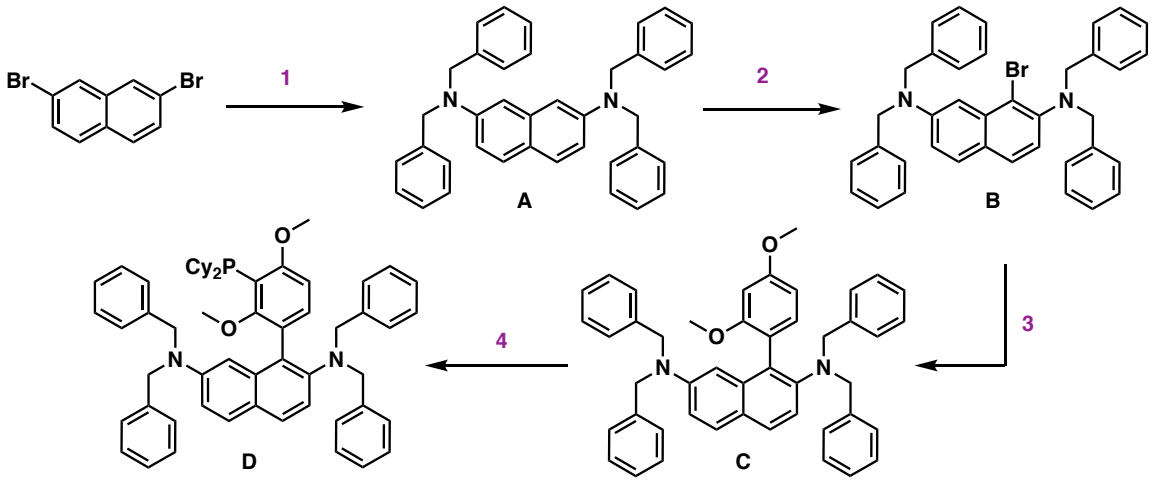
1.5 Experimental Data

1. General Information

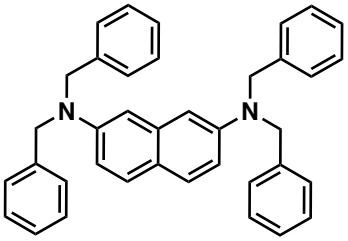
Unless otherwise specified, all of the reactions were run under and inert atmosphere of argon. Silica gel TLC plates (UV 254 indicator, thickness 200 mm standard grade, glass backed and 230-400 mesh from Merck) or Aluminum Oxide 60 F254 polyester basked plates (Sigma-Aldrich, 0.2 mm thick) were used. The developed TLC plate was analyzed by a UV lamp (254 nm). The plates were further analyzed with the use of an aqueous potassium permanganate stain or butanolic vanillin and developed with a heat gun. All commercially available reagents were used without further purification. A 2 wt % TPGS-750-M/H_2O solution was prepared by dissolving TPGS-750-M in degassed HPLC grade water. TPGS-750-M was made as described previously1 and is also commercially available. Tetrahydrofuran (THF) and toluene were all taken from an Innovative Technologies Solvent Purification System (SOS) and used immediately. *N*,*N*-Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were stored over activated 4Å molecular sieves and were purchased from Fisher Scientific. K_3PO_4 tribasic was purchased from Sigma-Aldrich and used without further purification. The source of $Pd(OAc)_2$ was either Spectrum Chemicals or Johnson Matthey. Reagents were purchased from Sigma-Aldrich, Combi-Blocks, Alfa Aesar, or Acros Organics. n-Butyllithium was purchased from Sigma-Aldrich and was titrated with diphenylacetic acid prior to use. Flash chromatography was performed using Silicycle Silicaflash® P60 unbonded grade silica. 1H and 13C NMR were recorded at 25 ºC on either a Varian Unity Inova 500 MHz or a Varian Unity Inova 600 MHz spectrometers in CDCl3 with residual CHCl3 (1H = 7.26 ppm, 13C = 77.16 ppm) as the internal standard. Chemical shifts are reported in parts per million (ppm). The data presented will be reported as follows; chemical shift, multiplicity (s = singlet, bs =

broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (if applicable) and integration. HRMS data were recorded on a Waters Micromass LCT TOF ES+ Premier mass spectrometer using ESI ionization.

2. Synthesis of N_2Phos



N^2,*N*^{2},*N*^{7},*N*^{7}-Tetrabenzylnaphthalene-2,7-diamine (A)



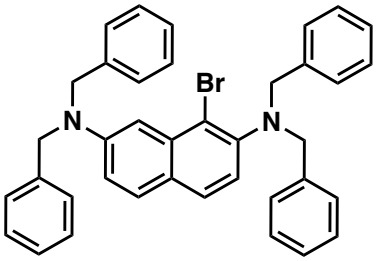
In solution: To an oven dried 3-neck round bottom flask equipped with a stir bar under argon were added 2,7-dibromonaphthlene (1 equiv.), potassium *t*-butoxide (3 equiv.), and Pd-PEPPSI-*i*Pent (0.02 equiv.). The reaction flask was evacuated and backfilled three times with argon. The flask was sealed with a rubber septum after which *N,N*-dibenzylamine (2.05 equiv.) was added via syringe followed by anhydrous toluene (0.5 M). The reaction flask was

sealed with a rubber septum and a water jacketed condenser was attached. The reaction was set to stir at 80 ºC for 16 h. Upon completion, the reaction was cooled to rt. The solvent was removed under reduced pressure. The crude reaction mixture was added to a beaker and distilled H_2O was added. The suspension was set to stir for 30 min. The beakers' contents were then vacuum filtered, and the filtered material was allowed to dry. The dried mixture was transferred to a flask and sonicated with several portions of hexanes. The material was vacuum filtered and washed with hexanes and allowed to dry. The product (86% yield) was obtained as a white solid and used without any further purification.

Using Mechanochemistry: The amination was run in a 30 mL stainless steel Form Tech Scientific grinding jar (https://www.FormTechScientific.com). To the jar was added 1.72 g (6.00 mmol, 1 equiv.) of 2,7-dibromonaphthalene, 2.02 g (18.0 mmol, 3 equiv.) potassium *t*-butoxide, and 95.0 mg (0.120 mmol, 0.02 equiv.) Pd-PEPPSI-*i*Pent, and a 1/2" stainless steel ball. The jar was closed, leaving a slight gap where the two halves join together. The middle of the jar was wrapped with Parafilm and flushed with argon for several min. After this, 2.48 mL (12.3 mmol, 2.05 equiv.) *N,N*-dibenzylamine was added by syringe through the Parafilm. The Parafilm was removed and the jar was fully sealed. The reaction vessel was placed in a modified SPEX 8000M Mixer/mill and run for 10 h at 40 °C. Afterwards, the dry, yellow-orange reaction mixture was scraped out of the vial onto a watch glass using a metal spatula. The dry reaction mixture was finely divided up using the metal spatula. This was then added to a beaker and suspended with stirring in distilled H_2O for 30 min to remove salt. The beaker's contents were then vacuum filtered and allowed to dry. The dried mixture was transferred to a recovery flask. This was sonicated in several portions of hexanes and transferred to a Buchner funnel, washed a final time with hexanes, and allowed to dry. The product (2.806 g, 90% yield)

was obtained as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, J = 9.0 Hz, 2H), 7.33-7.29 (m, 8H), 7.25-7.22 (m, 12H), 6.85 (dd, *J* = 9.0, 2.4 Hz, 2H), 6.74 (d, *J* = 2.4 Hz, 2H), 4.68 (s, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.87, 138.82, 136.69, 128.73, 126.99, 126.96, 120.69, 112.38, 104.70, 53.96. **Chemical Formula:** $C_{38}H_{34}N_2$; EI-MS [M^+] calcd: 518.2722; found: 518.2720.

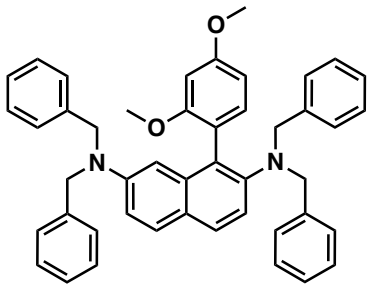
***N*^{2},*N*^{2},*N*^{7},*N*^{7}-Tetrabenzyl-1-bromonaphthalene-2,7-diamine (B)**



To an oven-dried round-bottom flask under a continuous flow of argon was added the substrate. The reaction vessel was evacuated and backfilled with argon two to three times. The substrate was dissolved in DMF (0.5 M) and cooled to 0 °C with an ice bath. A solution of *N*-bromosuccinimide (1 equiv.) in DMF (0.5 M relative to substrate) was added dropwise slowly into the solution with the use of an addition funnel over a period of 10 min. The resulting mixture was removed from the ice bath and set to stir for an additional 3 h. Upon completion the reaction was diluted with ether and washed with brine (4x the volume of organic solvent) to remove DMF. The resulting organic mixture was dried with anhydrous Na_2SO_4 and reduced under pressure. The compound was used without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (s, 1H) 7.43– 7.41 (d, J = 9.0 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.28 (m, 7H), 7.28 - 7.26 (m, 4H), 7.22 – 7.16 (m, 7H), 7.14 – 7.10 (m, 2H), 6.96 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 4.73 (s, 4H), 4.17 (s, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.15, 147.62, 138.56, 138.44, 135.09, 129.32, 128.84, 128.83, 128.80, 128.28, 127.25, 127.21,

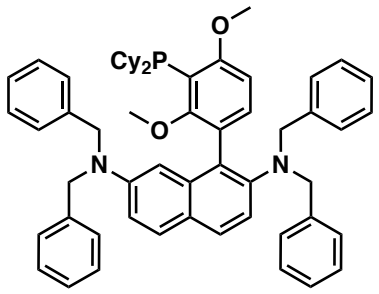
127.04, 127.02, 125.05, 119.09, 118.41, 115.21, 106.19, 57.03, 54.81. **Yield:** 96% as a tan solid. **Chemical Formula**: $C_{38}H_{33}BrN_2$; EI-MS [M^+] calcd: 596.1827; found: 596.1824

***N*²,*N*²,*N*⁷,*N*⁷-Tetrabenzyl-1-(2,4-dimethoxyphenyl)naphthalene-2,7-diamine (C)**



Aryl bromide (1 equiv.), base (2 equiv.), aryl boronic acid (1.5 equiv.) and $Pd(dppf)Cl_2$ (2 mol %) were charged into a 3-neck round bottom flask under a continuous flow of argon. Upon addition of solids the flask was evacuated and then refilled with argon 3 times. Degassed toluene and water were then added to the reaction vessel in a 10:1 ratio of toluene to water. A reflux condenser was attached and the reaction was set to stir for 16 h at 80 °C. Upon completion, the reaction was diluted with EtOAc and the organic mixture was washed with water, and then brine. The resulting organic layer was dried over anhydrous Na_2SO_4 and the solvent was reduced under vacuum. The resulting crude mixture was purified via flash chromatography. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 12.1, 8.8 Hz, 2H), 7.26 (d, *J* = 4.5 Hz, 2H), 7.24 (d, *J* = 0.8 Hz, 2H), 7.22 – 7.13 (m, 12H), 7.06 – 7.02 (m, 5H), 6.98 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.55 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 4.64 – 4.50 (m, 4H), 4.01 – 3.92 (m, 4H), 3.91 (s, 3H), 3.33 (s, 3H)**. ^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.36, 139.27, 138.96, 135.72, 132.68, 129.05, 128.82, 128.64, 127.95, 127.34, 126.85, 126.80, 126.66, 118.53, 114.35, 105.45, 104.79, 98.57, 56.96, 55.62, 55.12, 55.10. **Yield:** 83% as a yellow solid. **R_f:** 0.14 (10% EtOAc/hexanes) **Chemical Formula**: $C_{58}H_{63}N_2O_2P$ EI-MS [M^+] calcd: 859.4627; found: 850.4628.

N^2,N^2,N^7,N^7-Tetrabenzyl-1-(3-(dicyclohexylphosphaneyl)-2,4-dimethoxyphenyl)naphthalene-2,7-diamine L1 (D; N_2Phos)

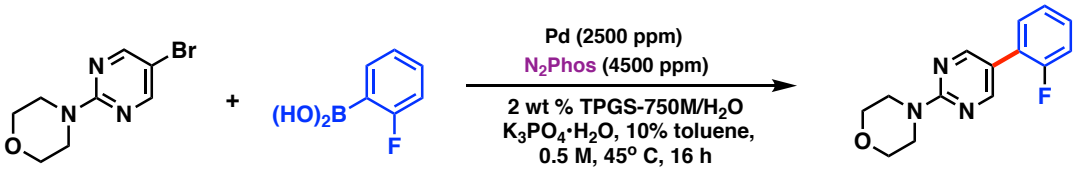


An oven dried round bottom flask was charged with substrate under a continuous flow of argon. The reaction vessel was evacuated and back-filled with argon three times. Anhydrous THF [0.2 M] was added to the reaction vessel and the reaction was cooled to 0 °C using an ice bath. *n*-Butyllithium ([2.3 M] in hexanes 1.2 equiv.) was added to reaction dropwise via syringe over a period of 15 min. The resulting mixture was set to stir for an additional 30 min. Neat chlorodicyclohexylphosphine (1.05 equiv.) was added dropwise via syringe over a period of 10 min. The reaction vessel was removed from the ice bath and set to stir for an additional 2 h. The solution was quenched with water and diluted with diethyl ether. The organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The resulting ether was concentrated under vacuum. The mixture was purified via flash chromatography utilizing basic alumina (5% EtOAc/hexanes) to afford a white solid 75% yield. $\mathbf{R_f}$ = 0.28 (5% EtOAc/hexanes) on aluminum oxide plates**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.22 (m, 5H), 7.16 – 7.13 (m, 5H), 7.12 – 7.10 (m, 5H), 7.08 – 7.04 (m, 5H), 7.03 – 7.01 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 4.56 – 4.48 (m, 4H), 3.99 (d, *J* = 14.2 Hz, 2H), 3.92 (d, *J* = 14.3 Hz, 2H), 3.81 (s, 3H), 3.19 (s, 3H), 2.44 (m, 1H), 1.96 (d, *J* = 8.4 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.63 (q, *J* = 10.7, Hz, 3H), 1.37 – 1.27 (m, 5H), 1.24 – 1.19 (m,

2H), 1.07 – 0.95 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.36, 139.27, 138.96, 135.72, 132.68, 129.05, 128.82, 128.64, 127.95, 127.34, 126.85, 126.80, 126.66, 118.53, 114.35, 105.45, 104.79, 98.57, 56.96, 55.62, 55.12, 55.10. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -9.69. **Chemical Formula:** $C_{58}H_{63}N_2O_2P$. EI-MS [M^+] calcd: 851.4705; found: 851.4692.

3. Reaction Optimization

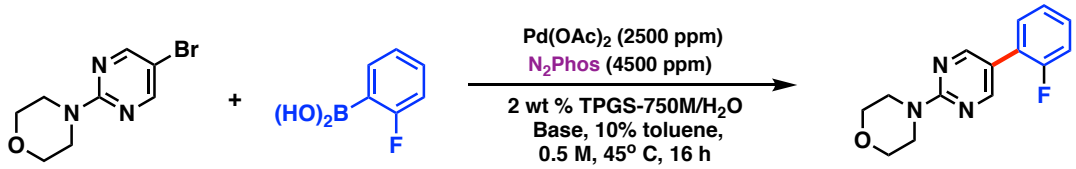
Palladium Source Screen



Entry	Pd Source	Conv (%)[1]
1	**$Pd(OAc)_2$**	**96**
2	$[Pd(cinnamyl)Cl_2]_2$	87
3	$[Pd(allyl)Cl_2]_2$	63
4	$Pd(PhCN)_2Cl_2$	71

[1]Conversion based on ^{1}H NMR

Choice of Base



Entry	Base	Conv (%)[1]
1	Et_3N	88
2	**$K_3PO_4·H_2O$**	**96**
3	K_2CO_3	79
4	DIPEA	89
5	NaO*t*-Bu	82

[1]Conversion based on ^{1}H NMR.

4. Recycle Study

The initial reaction was set up according to the general procedure. After 4 h, the reaction media was extracted three times with MTBE and the combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude reaction mixture was purified via flash chromatography.

Recycling of the surfactant solution involved first sparging the reaction vial with argon followed by addition of aryl bromide (0.5 mmol), aryl boronic acid (0.625 mmol), the base (0.5 mmol) and fresh catalyst solution (0.1 mL). The reaction vial was then flushed with argon, capped, and sealed with Teflon tape

5. General Procedure for catalyst solution preparation

To an oven dried 1-dram vile equipped with a stir bar was added $Pd(OAc)_2$ (2.25 mg, 0.01 mmol) and N_2Phos (14.8 mg, 0.018 mmol). The vial was capped with a 14/20 rubber septum sealed with Teflon tape. The vial was evacuated and backfilled with argon three times and left under a continuous flow of argon. Anhydrous toluene (1 mL) was added to the vile to achieve the desired Pd concentration (50 μL of stock solution equates to 1000 ppm loading for a 0.5 mmol reaction). The mixture was set to stir for 15 min. DIBAL-H ([1.0 M in toluene], 2.0 equiv relative to Pd) was added dropwise if needed. The resulting mixture was stirred for additional 5 min. At this point the catalyst is ready and may be added to the reaction mixture.

6. General Procedure for Suzuki-Miyaura Couplings

General Procedure for SMC reactions in aqueous TPGS-750-M:

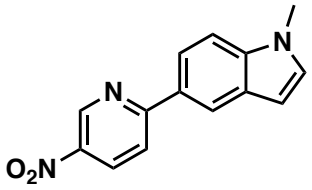
To an oven dried, 1-dram vial equipped with a magnetic stir bar was charged aryl bromide (0.5 mmol), organoboron (0.75 mmol), and potassium phosphate (0.75 mmol). The vial was fitted with a rubber septum and sealed with Teflon tape. The reaction vial was purged with argon

with the use of a vent needle. At this point, a solution of 2 wt % TPGS-750-M in (0.9 mL) and toluene (50 μL) were added, followed by the catalyst solution via syringe. The vial was placed in an aluminum heating block over a stir plate with a stir rate set to >1000 rpm with a thermocouple probe in the aluminum block set to 48 ºC (this gives a temperature of 45 ºC in the reaction vial). The reactions were monitored by either GC/MS or TLC analysis. Upon completion of the reaction, the vial was cooled to rt. The mixture was extracted with EtOAc and the organic layer was washed with brine three times. The layers were then separated and the organic layer was dried over anhydrous Na_2SO_4. The mixture was concentrated under vacuum and the crude mixture was purified via flash chromatography.

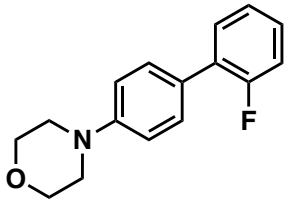
General Procedure for SMC Reactions in Organic Solvent:

To an oven dried 1-dram vial equipped with a magnetic stir bar was charged aryl bromide (0.5 mmol), organoboron (0.75 mmol), and potassium phosphate (0.75 mmol). The vial was fitted with a rubber septum and sealed with Teflon tape. The reaction vial was purged with argon with the use of a vent needle. Degassed organic solvent (either EtOAc or toluene) (0.8 mL), DI water (0.1 mL) and the catalyst solution were added via syringe. The vial was placed in an aluminum heating block over a stir plate with a stir rate set to >1000 rpm with a thermocouple probe in the aluminum block set to 48 ºC (this gives a temperature of 45 ºC in the reaction vial). The reactions were monitored by either GC/MS or TLC analysis. Upon completion of the reaction, the vial was cooled to rt. The mixture was extracted with EtOAc and the organic layer was washed with brine three times. The layers were then separated and the organic layer was dried over anhydrous Na_2SO_4. The mixture was concentrated under vacuum and the crude mixture was purified via flash chromatography.

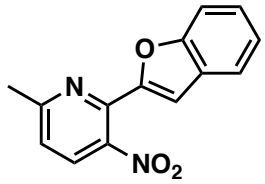
6. Analytica data for products from Suzuki-Miyaura couplings



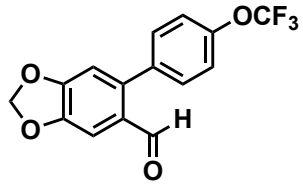
1-Methyl-5-(5-nitropyridin-2-yl)-1*H*-indole (1). Prepared from 5-bromo-5-nitropyridine and 1-methylindole-5-boronic acid according to the general procedure**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.48 (dd, *J* = 2.7, 0.7 Hz, 1H), 8.48 (dd, *J* = 8.8, 2.7 Hz, 1H), 8.41 (dd, *J* = 1.8, 0.6 Hz, 1H), 8.01 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.94 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.44 (dt, *J* = 8.7, 0.8 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.61 (dd, *J* = 3.2, 0.9 Hz, 1H), 3.85 (s, 3H**). ^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.02, 145.40, 131.82, 130.49, 128.76, 121.53, 121.45, 119.54, 110.02, 102.66, 77.36, 33.22. **Yield**: 89%, 12 h; as a yellow solid. **R_f**: 0.31 (25% EtOAc/hexanes).



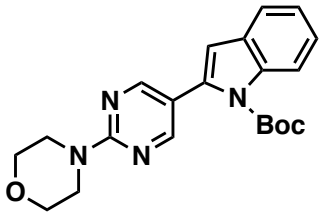
4-(2'-Fluoro-[1,1'-biphenyl]-4-yl)morpholine (2). Prepared from 4-bromophenylmorpholine and 2-fluorophenylboronic acid according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.42 (td, *J* = 7.8, 1.9 Hz, 1H), 7.24 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.13 (ddd, *J* = 10.9, 8.0, 1.3 Hz, 1H), 7.02 – 6.95 (m, 2H), 3.91 – 3.86 (m, 4H), 3.24 – 3.20 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.76, 130.48, 129.95, 129.92, 128.37, 128.29, 124.43, 116.29, 116.06, 115.43, 67.03, 49.13. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.30 (dddt, *J* = 11.2, 8.3, 4.9, 1.7 Hz). **Yield**: 93%, as a white solid. **R_f**: 0.24 (15% EtOAc/hexanes).



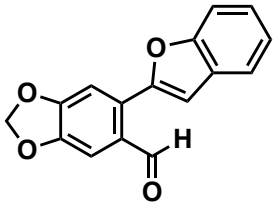
2-(Benzofuran-2-yl)-6-methyl-3-nitropyridine (3). Synthesized with 2-bromo-3-nitro-6-methyl-pyridine and benzofuran-2-phenyl boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.68 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.38 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 2.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.12, 155.82, 151.26, 141.09, 134.18, 132.24, 128.03, 126.27, 123.60, 122.71, 122.69, 122.15, 112.01, 109.33, 24.83, 24.50. **Yield:** 94%, as a yellow solid. **R_f:** 0.35 (25% EtOAc/hexanes).



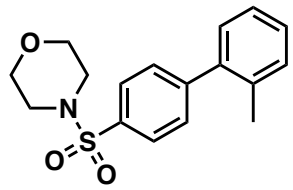
6-(4-(Trifluoromethoxy)phenyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (4). Synthesized with 5-Bromopiperonal and 4-trifluoromethoxypehnyl boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.47 (s, 1H), 7.38 – 7.36 (m, 2H), 7.31 – 7.29 (m, 2H), 6.82 (s, 1H), 6.10 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.15, 152.35, 149.35, 148.27, 142.04, 136.37, 131.62, 129.04, 121.62, 120.96, 120.95, 110.33, 106.64, 102.39, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.85; **Yield**: 92%, as a white solid. **R_f:** 0.30 (15% EtOAc/hexanes).



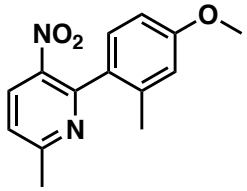
***t*-Butyl 2-(2-morpholinopyrimidin-5-yl)-1*H*-indole-1-carboxylate (5).** Synthesized with 4-(5-bromo-pyrimidin-2-yl)morpholine and (1-(*t*-butoxycarbonyl)-1H-indol-2-yl) boronic acid according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 2H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.21 (m, 2H), 6.55 (s, 1H), 3.90 – 3.82 (m, 4H), 3.83 – 3.75 (m, 4H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.84, 157.27, 150.23, 137.27, 135.08, 129.25, 124.67, 123.27, 120.56, 117.87, 115.85, 110.63, 84.28, 66.96, 44.49, 28.11. **Yield:** 78%, 24 h as a white solid; **R_f:** 0.20 (15% EtOAc/hexanes).



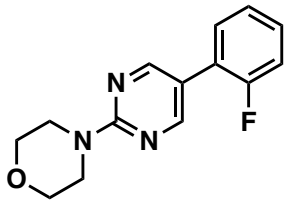
6-(Benzofuran-2-yl)benzo[*d*][1,3]dioxole-5-carbaldehyde (6). Synthesized from 5-bromopiperanal and benzofuran-2-phenylboronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.64 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.54 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.50 (s, 1H), 7.36 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 7.29 (td, *J* = 7.5, 1.0 Hz, 1H), 7.23 (s, 1H), 6.87 (d, *J* = 1.0 Hz, 1H), 6.12 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.21, 155.47, 152.43, 152.36, 149.01, 130.65, 129.86, 128.69, 125.31, 123.53, 121.42, 111.54, 108.89, 108.13, 107.05, 102.55. **Yield**: 91%, 8 h, as a white solid. **R_f**: 0.31 (15% EtOAc/hexanes).



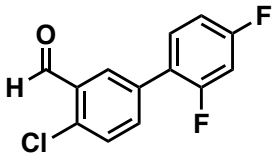
4-((2'-Methyl-[1,1'-biphenyl]-4-yl)sulfonyl)morpholine (7). Synthesized with 4-((4-bromophenyl)-sulfonyl)morpholine and methyl phenyboronic acid according to the general procedure**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (d, 2H), 7.52 – 7.49 (d, 2H), 7.34 – 7.27 (m, 3H), 7.22 (dd, *J* = 7.2, 1.3 Hz, 1H), 3.80 – 3.76 (m, 4H), 3.10 – 3.04 (m, 4H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.22, 140.08, 135.28, 130.79, 130.07, 129.64, 128.39, 127.88, 126.21, 105.14, 66.30, 46.20, 20.51. **Yield**: 81%, 16 h, as a white solid. **R_f**: 0.55 (40% EtOAc/hexanes). **Chemical Formula:** $C_{17}H_{19}NO_3S$ EI-MS $[M]^+$ calcd: 317.1086; found: 372.1253 $[M+Na+MeOH]^+$.



2-(4-Methoxy-2-methylphenyl)-6-methyl-3-nitropyridine (8). Synthesized with 2-Bromo-6-methyl-3-nitropyridine and 2-methyl-4-methoxyphenyl boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.82 (dt, *J* = 2.8, 0.6 Hz, 1H), 6.79 (ddd, *J* = 8.3, 2.6, 0.6 Hz, 1H), 3.83 (s, 3H), 2.69 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.72, 160.17, 153.79, 137.51, 132.52, 129.69, 129.49, 122.13, 116.14, 111.47, 55.39, 24.95, 19.90. **Yield**: 91%, 8 h, as a yellow solid **R_f:** 0.20 (25% EtOAc/hexanes).

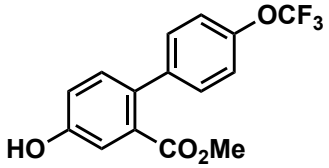


4-(5-(2-Fluorophenyl)pyrimidin-2-yl)morpholine (9). Synthesized with 4-(5-bromopyrimidin-2-yl)morpholine and 2-fluorophenyl boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.9 Hz, 2H), 8.54 (d, *J* = 1.6 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.34 – 7.30 (m, 1H), 7.23 – 7.20 (m, 1H), 7.16 (m, 1H), 3.87 (dd, *J* = 5.7, 3.9 Hz, 4H), 3.79 (dd, *J* = 5.6, 3.9 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.48, 157.45, 129.47, 129.44, 129.32, 129.25, 124.88, 124.85, 116.49, 116.31, 105.14, 66.98, 44.46. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.81 (dt, *J* = 7.7, 2.8 Hz). **Yield**: 83%, 22 h, as a white solid. **R_f**: 0.50 (25% EtOAc/hexanes). **Chemical Formula:** $C_{14}H_{14}FN_3O$ EI-MS $[M]^+$ calcd: 259.1121; found: 260.1196.

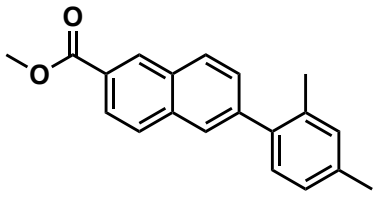


4-Chloro-2',4'-difluoro-[1,1'-biphenyl]-3-carbaldehyde (10) Synthesized with 3-bromo-6-chlorobenzalsehyde and 2,4-difluorophenyl boronic acid according to the general procedure. The pinacol ester of the boronic acid was also employed. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.84 (d, *J* = 3.0 Hz, 1H), 8.00 (d, *J* = 2.3 Hz, 1H), 7.63 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.03 (m, 1H), 6.98 – 6.94 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.02, 136.18, 135.47, 133.89, 132.96, 132.74, 132.71, 132.67, 132.63, 128.13, 112.24, 112.21, 112.07, 112.04, 104.74, 104.54, 104.33. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

108.22 (qd, J = 8.3, 6.2 Hz), -110.85 (dd, J = 9.0, 2.9 Hz). **Yield:** 92% with the boronic acid. 94% as the pinacol ester as a white solid. **R_f**: 0.54 (15% EtOAc/hexanes).

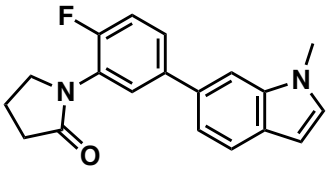


Methyl 4-hydroxy-4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-carboxylate (11). Synthesized with methyl 5-hydroxy-2-iodobenzoate and 4-trifluoromethoxyphenylboronic acid according to the general procedure**. ^{1}H NMR** (500 MHz, MeOH-d_4) δ 7.71 – 7.68 (m, 2H), 7.58 – 7.55 (m, 2H), 7.40 – 7.37 (m, 1H), 7.31 (dq, J = 7.8, 1.0 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, MeOH-d_4) δ 166.90, 154.27, 136.93, 130.64, 130.33, 130.25, 120.55, 120.13, 116.34, 106.82, 51.20**. ^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.79. **Yield:** 83%, as a pale yellow solid. **R_f:** 0.45 (40% EtOAc/hexanes).

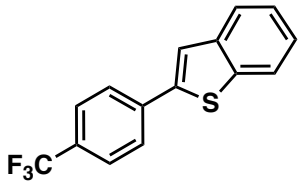


Methyl 6-(2,4-dimethylphenyl)-2-naphthoate (12). Synthesized with methyl 6-bromo-2-naphthoate and 2,4-methylphenylbornoc acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 – 8.62 (m, 1H), 8.08 (dd, J = 8.6, 1.7 Hz, 1H), 7.99 – 7.96 (m, 1H), 7.89 (dt, J = 8.6, 0.7 Hz, 1H), 7.79 (t, J = 1.1 Hz, 1H), 7.53 (dd, J = 8.4, 1.7 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.11 (m, 1H), 4.00 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.42, 142.21, 138.60, 137.56, 135.60, 135.39, 131.39, 130.99,

129.98, 129.04, 128.89, 128.32, 127.80, 127.39, 126.79, 125.66, 77.41, 77.16, 76.91, 52.37, 21.24, 20.57. **Yield:** 96%, 1.5 h as a white solid. **R_f**: 0.50 (25% EtOAc/hexanes).

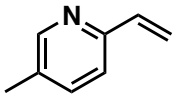


1-(2-Fluoro-5-(1-methyl-1*H*-indol-6-yl)phenyl)pyrrolidin-2-one (13). Synthesized from 1-(5-bromo-2-fluorophenyl)pyrrolidine-2-one and 1-methylindole-5-boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 1H), 7.65 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.50 (ddd, *J* = 8.4, 4.6, 2.3 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.20 (dd, *J* = 10.5, 8.6 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 3.88 (t, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.24 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.91, 139.53, 132.69, 131.36, 129.76, 129.06, 127.20, 127.14, 126.73, 126.71, 121.36, 119.56, 116.90, 109.61, 101.48, 50.30, 33.09, 31.32, 19.22. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.22 (ddd, *J* = 11.1, 7.3, 4.7 Hz). **Yield:** 80% 36 h as a tan solid. **R_f:** 0.24 (40% EtOAc/hexanes).

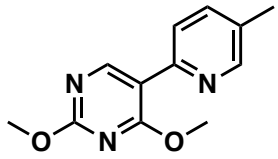


2-(4-(Trifluoromethyl)phenyl)benzo[*b*]thiophene (14) Synthesized with benzothiophene-2-bornic acid and 4-trifluoromethylphenyl boronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 1H), 7.82 (m, 3H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 0.7 Hz, 1H), 7.37 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.57, 126.75, 126.11,

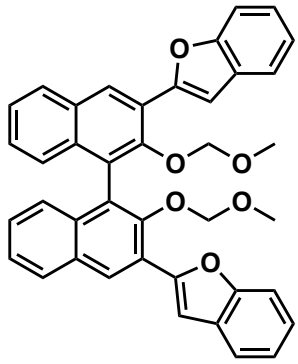
126.08, 125.14, 124.96, 124.11, 123.80, 122.52, 121.41, 121.19. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.64. **Yield:** 87%, 16 h, as a white solid. **R_f:** 0.60 (25% EtOAc/hexanes).



5-Methyl-2-vinylpyridine (15). Prepared from 2-boromo-5-methylpyridine and potassium vinyltrifluoroborate according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.41 (d, *J* = 9.0, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 6.78 (dd, *J* = 11.0, 17.5, 1H), 6.12 (dd, *J* = 17.5, 1H), 5.41 (d, *J* = 11.0 Hz, 1H) 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.51, 149.69, 138.03, 137.03, 132.38, 121.40, 117.15, 20.22. **Yield**: 89%, as a colorless oil. **R_f**: 0.20 (10% EtOAc/hexanes).

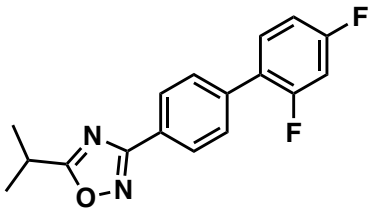


2,4-Dimethoxy-5-(5-methylpyridin-2-yl)pyrimidine (16). Prepared from 2-bromo-5-methylpyridine and (2,4-dimethoxypyrimidin-5-yl)boronic acid MIDA ester according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.52 – 8.48 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1, Hz, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.96, 159.54, 150.18, 149.16, 136.94, 131.93, 123.56, 114.90, 110.16, 55.13, 54.32, 29.86. **Yield**: 87%, as a white solid. **R_f**: 0.30 (40% EtOAc/hexanes).

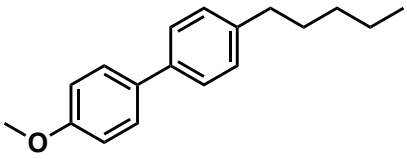


2,2'-(2,2'-bis(Methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(benzofuran) (17)

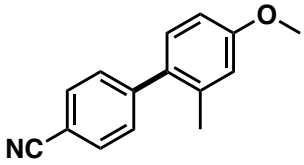
Synthesized with 3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene and benzofuran-2-boronic acid according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.55 (m, 6H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.29 (m, 8H), 4.81-4.53 (m, 4H), 2.56 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6,152.3, 150.0, 134.0, 130.9, 129.2, 128.7, 128.1, 127.4, 126.7, 126.5, 125.9, 124.9, 124.2, 123.1, 121.6,111.1, 107.1, 98.7, 56.7. **Yield**: 79%, 24 h as a white solid. **R_f:** 0.40 (25% EtOAc/hexanes).



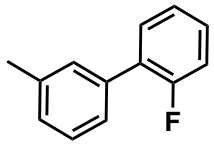
3-(2',4'-Difluoro-[1,1'-biphenyl]-4-yl)-5-isopropyl-1,2,4-oxadiazole (18). Prepared from 3-(4-bromophenyl)-5-isopropyl-1,2,4-oxadiazole and 2,4-difluorophenylbornic acid according to the general procedure**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.13 (d, *J* = 8.4 2H), 7.64 (d, *J* = 1.7 Hz, 2H), 7.48 (td, *J* = 8.7, 6.4 Hz, 1H), 7.04 – 6.93 (m, 2H), 3.33 (hept, *J* = 7.0 Hz, 1H), 1.50 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.17, 168.00, 131.60, 129.45, 129.42, 127.73, 126.52, 112.03, 111.81, 104.71, 27.73, 20.39. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.51 (p, *J* = 7.8 Hz), -113.12 (q, *J* = 9.1 Hz). **Yield**: 81%, as a white solid. **R_f:** 0.25 (5% EtOAc/hexanes).



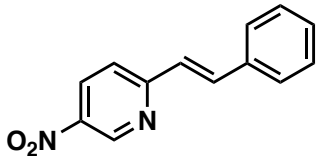
4-Methoxy-4'-pentyl-1,1'-biphenyl (21). Synthesized from 4-chloroanisole and 4-pentylphenylboronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.65 – 2.62 (m, 2H), 1.67 – 1.63 (m, 2H), 1.38 – 1.34 (m, 4H), 0.93 – 0.90 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.60, 138.29, 133.92, 128.92, 128.11, 126.70, 114.28, 108.93, 77.37, 77.16, 76.95, 55.48, 35.70, 31.72, 31.37, 22.73, 14.20. **Yield**: 83%, as a white solid. **R_f**: 0.30 (5% EtOAc/hexanes).



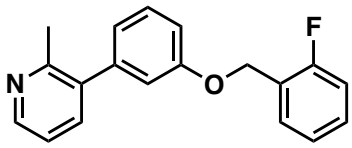
4'-Methoxy-2'-methyl-[1,1'-biphenyl]-4-carbonitrile (22). Synthesied from 4-chlorobenzonitrole and 2-methyl-4-methoxyphenyl boronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.81 (m, 2H), 3.84 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.63, 146.69, 136.70, 132.74, 132.04, 130.79, 130.29, 119.19, 116.20, 111.63, 110.42, 77.37, 77.16, 76.95, 55.44, 20.79. **Yield**: 94%, as a yellow solid. **R_f:** 0.25 (10% EtOAc/hexanes).



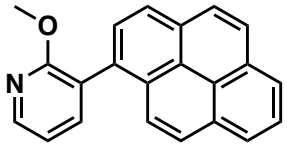
2-Fluoro-3'-methyl-1,1'-biphenyl (23). Synthesized from 3-chlorotoluene and 2-fluorophenyl boronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (m, *J* = 7.8, 1.8 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.33 – 7.29 (m, 1H), 7.21 (m, *J* = 7.5, 1.4 Hz, 2H), 7.15 (m, *J* = 11.0, 8.2, 1.5 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.16, 135.90, 130.96, 129.91, 129.00, 128.46, 126.28, 124.42, 116.27, 116.09, 21.65. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.96 (m). **Yield**: 87%, as a colorless oil. **R_f:** 0.35 (5% Et_2O/hexanes).



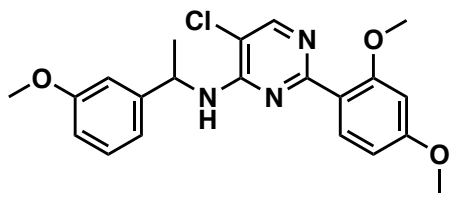
(*E*)-5-Nitro-2-styrylpyridine (24). Synthesized with 2-chloro-5-nitropyridine and (*E*)-phenethylboronic acid according to the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 – 9.40 (m, 1H), 8.44 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.87 (d, *J* = 16.0 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.50 (dd, *J* = 8.7, 0.7 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.24 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.09, 145.59, 138.26, 131.92, 129.78, 129.10, 127.89, 125.92, 121.78, 105.15. **Yield**: 93%, 16 h, as a yellow solid. **R_f**: 0.40 (25% EtOAc/hexanes).



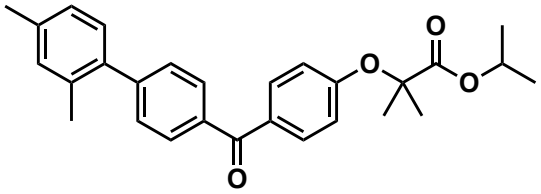
3-(3-((2-Fluorobenzyl)oxy)phenyl)-2-methylpyridine (25). Synthesized from 3-chloro-2-methyl-pyridine and 3-((2-fluorobenzyl)oxy)phenyl boronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.39 – 7.29 (m, 2H), 7.20 – 7.15 (m, 2H), 7.09 (ddd, *J* = 9.6, 8.2, 1.1 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.95 – 6.91 (m, 2H), 5.17 (s, 2H), 2.49 (s, 3H). ^{13}C **NMR** (101 MHz, $CDCl_3$) δ 161.81, 158.58, 155.96, 148.16, 141.55, 137.20, 136.87, 129.97, 124.45, 124.41, 122.06, 121.09, 115.83, 113.94, 110.15, 63.94, 23.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.53 (ddd, *J* = 10.3, 7.4, 5.5 Hz). **Yield**: 91%, 16 h, as a yellow oil. **R_f**: 0.21 (25% EtOAc/hexanes).



2-Methoxy-3-(pyren-1-yl)pyridine (26). Synthesized from and pyrene boronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 5.1, 1.9 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.19 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.16 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.09 (s, 2H), 8.02 – 7.98 (m, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.71 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.10 (dd, *J* = 7.1, 5.1 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.91, 146.59, 140.74, 132.31, 131.51, 131.17, 131.07, 129.24, 127.99, 127.72, 127.59, 127.54, 126.13, 125.36, 125.33, 125.18, 124.93, 124.70, 124.13, 116.94, 53.74. **Yield:** 91%, as a white solid. **R_f**: 0.25 (10% EtOAc/hexanes) **Chemical Formula**: $C_{22}H_{15}NO$ EI-MS $[M]^+$ calcd: 310.1232; found: 310.1227.

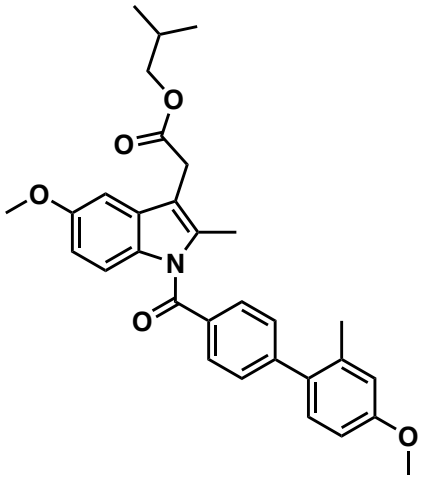


5-Chloro-2-(2,4-dimethoxyphenyl)-*N*-(1-(3-methoxyphenyl)ethyl)pyrimidin-4-amine (27). Synthesized from 2,5-dichloro-*N*-(1-(3-methoxyphenyl)ethyl)pyrimidin-4-amine and 2,4-dimethoxy-phenylboronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.67 – 7.62 (m, 1H), 7.36 – 7.30 (m, 2H), 6.92 – 6.87 (m, 2H), 6.54 (m, 2H), 5.43 (dt, *J* = 13.6, 7.3 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 1.62 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.00, 162.09, 159.29, 158.96, 156.66, 152.59, 135.82, 133.12, 127.61, 121.32, 114.11, 111.79, 104.72, 99.40, 77.36, 56.14, 55.56, 55.45, 49.59, 22.09. **Yield**: 76%, as a tan solid. **R_f**: 0.25 (30% Et_2O in hexanes) **Chemical Formula:** $C_{21}H_{22}ClN_3O_3$ EI-MS $[M]^+$ calcd: 399.1350; found: 401.1360 [M+2H].



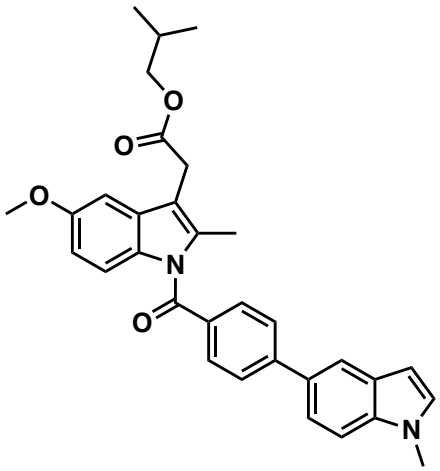
Isopropyl-2-(4-(2',4'-dimethyl-[1,1'-biphenyl]-4-carbonyl)phenoxy)-2-methylpropanoate (28). Synthesized from isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate and 2,4-dimethyl-phenylboronic acid according to the general procedure ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 4H), 7.42 – 7.39 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.84 (d, *J* = 2.6 Hz, 1H), 6.82 (dd, *J* =

8.2, 2.7 Hz, 1H), 5.10 (h, *J* = 6.2 Hz, 1H), 3.85 (s, 3H), 2.30 (s, 3H), 1.67 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.42, 173.33, 159.63, 159.31, 145.80, 136.86, 136.33, 133.69, 132.15, 130.93, 130.89, 129.84, 129.40, 117.35, 116.07, 111.45, 105.14, 79.52, 69.45, 55.43, 25.54, 21.68, 20.93. **Yield**: 92%, 12 h, as a white solid. **R_f:** 0.45 (25% EtOAc/hexanes). **Chemical Formula:** $C_{28}H_{30}O_4$ EI-MS [M^+ calcd: 430.2144. found: 430.2143.

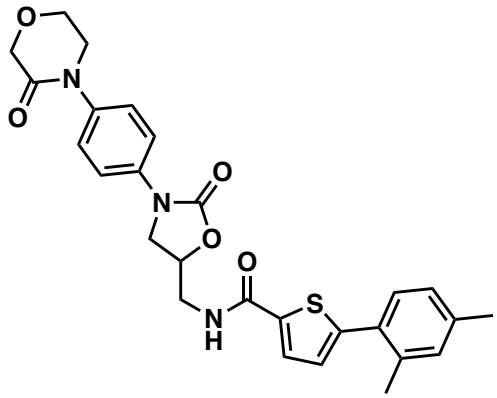


Isobutyl 2-(5-methoxy-1-(4'-methoxy-2'-methyl-[1,1'-biphenyl]-4-carbonyl)-2-methyl-1*H*-indol-3-yl)acetate (29a). Synthesized from isobutyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate and 2-methyl-4-methoxyphenyl boronic acid ($Pd(OAc)_2$ 0.25 mol %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.44 – 7.40 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.99 (s, 1H), 6.86 – 6.82 (m, 2H), 6.69 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.89 (d, *J* = 6.6 Hz, 2H), 3.85 (d, *J* = 2.1 Hz, 6H), 3.69 (s, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 1.92 (dp, *J* = 13.4, 6.7 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.17, 169.52, 159.46, 156.06, 146.68, 136.79, 136.04, 133.71, 133.32, 131.20, 130.88, 130.70, 129.89, 129.80, 116.14, 115.18, 112.51, 111.81, 111.54, 101.23, 71.20, 55.85, 55.44,

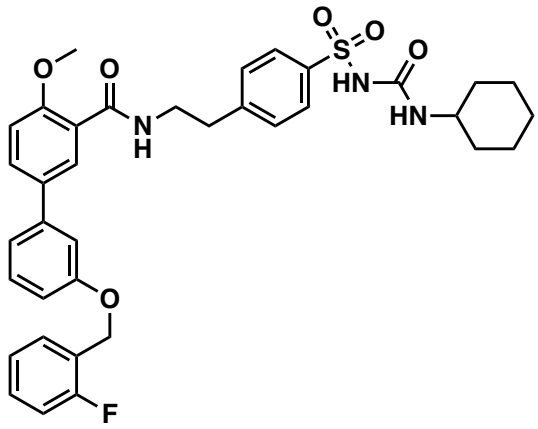
30.64, 27.87, 20.92, 19.18, 13.49. **Yield**: 88%, 12 h, as a yellow solid. **R_f:** 0.43 (25% EtOAc/hexanes). **Chemical Formula**: $C_{31}H_{33}NO_5$ EI-MS $[M]^+$ calcd: 499.2359, found: 499.2351.



Isobutyl 2-(5-methoxy-2-methyl-1-(4-(1-methyl-1*H*-indol-5-yl)benzoyl)-1*H*-indol-3-yl)acetate (29b). Synthesized from isobutyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate and 1-methylindole-5-boronic acid ($Pd(OAc)_2$ 0.25 mol%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.78 – 7.73 (m, 4H), 7.53 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.11 – 7.08 (m, 1H), 7.01 – 6.97 (m, 2H), 6.67 (dt, *J* = 9.0, 1.9 Hz, 1H), 6.57 – 6.54 (m, 1H), 3.88 (dd, *J* = 6.6, 1.5 Hz, 2H), 3.83 (d, *J* = 1.5 Hz, 6H), 3.68 (s, 2H), 2.43 (d, *J* = 1.5 Hz, 3H), 1.91 (hept, *J* = 13.4, 6.7, 1.4 Hz, 1H), 0.89 (d, *J* = 6.7, 1.4 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.24, 169.58, 155.97, 147.36, 136.15, 133.10, 131.24, 130.61, 130.03, 129.19, 127.43, 121.32, 119.99, 115.20, 112.27, 111.75, 109.88, 108.92, 101.77, 101.17, 71.19, 55.85, 33.15, 30.67, 27.88, 19.19, 13.45. **Yield**: 80%, 16 h, as a yellow solid. **R_f:** 0.40 (20% EtOAc/hexanes). **Chemical Formula:** $C_{32}H_{32}N_2O_4$ EI-MS $[M]^+$ calcd: 508.2362; found: 509.2369 [M+H].



5-(2,4-Dimethylphenyl)-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)thiophene-2-carboxamide (30). Synthesized from rivaroxaban and 2,4-dimethylphenyl-boronic acid. DMSO 10% v/v used as a co-solvent at 60 °C with 0.5 mol % loading of palladium. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.86 (t, J = 5.9 Hz, 1H), 7.76 (d, J = 3.8 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.39 – 7.36 (m, 2H), 7.26 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 3.8 Hz, 1H), 7.11 (s, 1H), 7.04 (dd, J = 8.0, 1.7 Hz, 1H), 4.83 (dd, J = 8.9, 5.5 Hz, 1H), 4.16 (s, 2H), 3.94 – 3.91 (m, 2H), 3.68 – 3.65 (m, 2H), 3.60 (t, J = 5.6 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.95, 161.73, 154.14, 147.14, 138.31, 137.95, 137.04, 136.51, 135.10, 131.66, 130.00, 129.72, 128.75, 127.20, 126.92, 125.93, 118.32, 71.41, 67.72, 63.46, 49.00, 47.46, 42.18, 20.77, 20.63. **Yield**: 68%, as a white solid. **R_f:** 0.20 (5% methanol in DCM). **Chemical Formula:** $C_{27}H_{27}N_3O_5S$ EI-MS $[M]^+$ calcd: 505.1671; found: 538.2104 [M+MeOH+H].



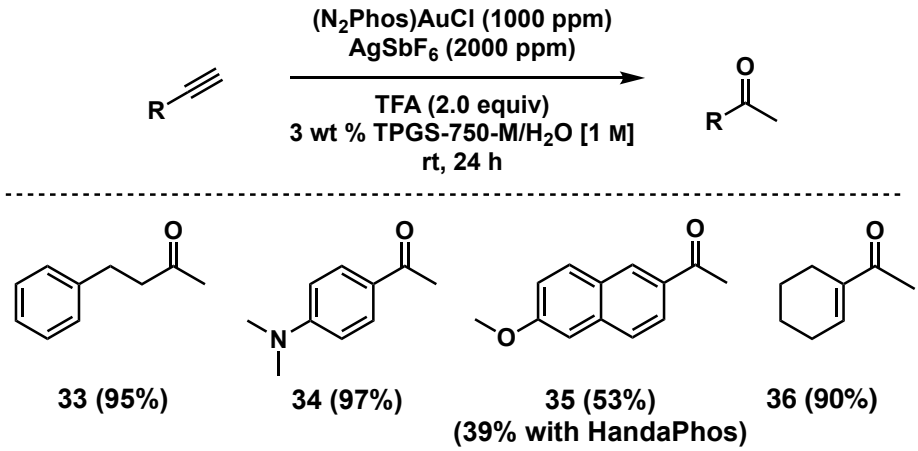
***N*-(4-(*N*-(Cyclohexylcarbamoyl)sulfamoyl)phenethyl)-3'-((2-fluorobenzyl)oxy)-4-methoxy-[1,1'-biphenyl]-3-carboxamide (31).** Prepared from glibenclamide and (3-((2-fluorobenzyl)oxy)phenyl) boronic acid. DMSO was used as a co-solvent at 55 °C with 0.5 mol % loading of palladium. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.30 (bs, 3H), 8.23 (t, J = 5.7 Hz, 1H), 8.03 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 2.8 Hz, 1H), 7.50 (d, J = 1.7 Hz, 1H), 7.45 (m, 3H), 7.42 – 7.34 (m, 2H), 7.22 (m, 2H), 7.11 (d, J = 8.9 Hz, 1H), 6.34 (d, J = 7.8 Hz, 1H), 5.09 (s, 1H), 3.76 (s, 3H), 3.51 (q, J = 6.7 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 1.56 (m, 4H), 1.46 – 1.41 (m, 1H), 1.23 – 0.99 (m, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.67, 157.58, 155.70, 150.52, 145.20, 138.24, 131.53, 130.59, 130.33, 130.24, 129.52, 129.30, 128.66, 127.32, 126.86, 124.82, 124.55, 124.34, 124.00, 119.87, 116.54, 115.48, 115.28, 114.15, 109.59, 63.27, 56.23, 48.08, 40.20, 34.68, 32.30, 25.01, 24.20. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -118.53 (ddd, J = 10.3, 7.4, 5.5 Hz). **Yield:** 61%, as a white solid. **R_f:** 0.15 (10% methanol in DCM). **Chemical Formula**: $C_{36}H_{38}FN_3O_6S$ EI-MS $[M]^+$ calcd: 659.2465; found: 692.3128 [M+H+MeOH].

6. General Procedure for Hydration of Alkynes

Precatalyst N_2Phos-gold(I) chloride synthesis was performed as previously described.[1]

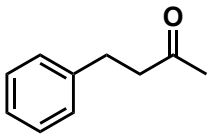
Gold pre-catalyst synthesis. N_2Phos-gold(I) chloride (0.9 mg, 0.001 mmol) and silver(I)hexafluoro-antimonate (0.7 mg, 0.002 mmol) were charged under an inert atmosphere (glovebox) into a 1-dram vial containing a Teflon-coated magnetic stir bar and a rubber septum. The vial was covered with aluminum foil to protect it from light. Anhydrous DCM (1 mL) was added and the solution was stirred for 15 min.

1-Pot reaction set-up. To a dried 1-dram vial was added, under an argon atmosphere, 0.2 mL of the gold pre-catalyst solution (1000 ppm or 0.1 mol %). DCM was evaporated under argon. Alkyne (0.2 mmol, 1.0 equiv) was added to the vial, followed by toluene (20 μL), a 3 wt % TPGS-750-M/H_2O solution (0.2 mL, 1.0 M), and trifluoroacetic acid (46 mg, 0.4 mmol, 2.0 equiv). The resulting mixture was stirred at rt for 24 h. The reaction was then extracted with EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The products were purified by flash chromatography (100:0 → 80:20 hexanes/EtOAc).

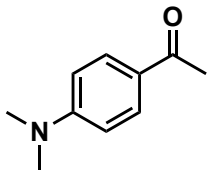


[1] Klumphu, P. *et al.* Micellar catalysis-enabled sustainable ppm Au-catalyzed reactions in water at room temperature. *Chem. Sci.* **8,** 6354–6358 (2017).

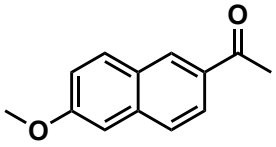
7. Analytical Data for Products from Hydration of Alkynes



Benzylacetone. Synthesized according to general procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.6, 6.6 Hz, 2H), 7.23 – 7.18 (m, 3H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.78 (dd, *J* = 8.3, 7.0 Hz, 2H), 2.15 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.1, 141.1, 128.6, 128.4, 126.2, 45.3, 30.2, 29.9, 6.6. **Yield:** 95%, as a colorless oil. **R_f:** 0.65 (20% EtOAc/hexanes) – UV + CAM stain.

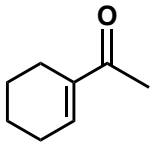


***N,N*-Dimethylaminoacetophenone.** Synthesized according to general procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 6.69 – 6.62 (m, 2H), 3.08 – 3.04 (m, 6H), 2.51 (t, *J* = 0.9 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.4, 153.5, 130.6, 125.4, 110.7, 40.1, 26.1. **Yield:** 97%, as a white powder. **R_f**: 0.35 (8:2 hexanes/EtOAc) – UV + CAM stain.



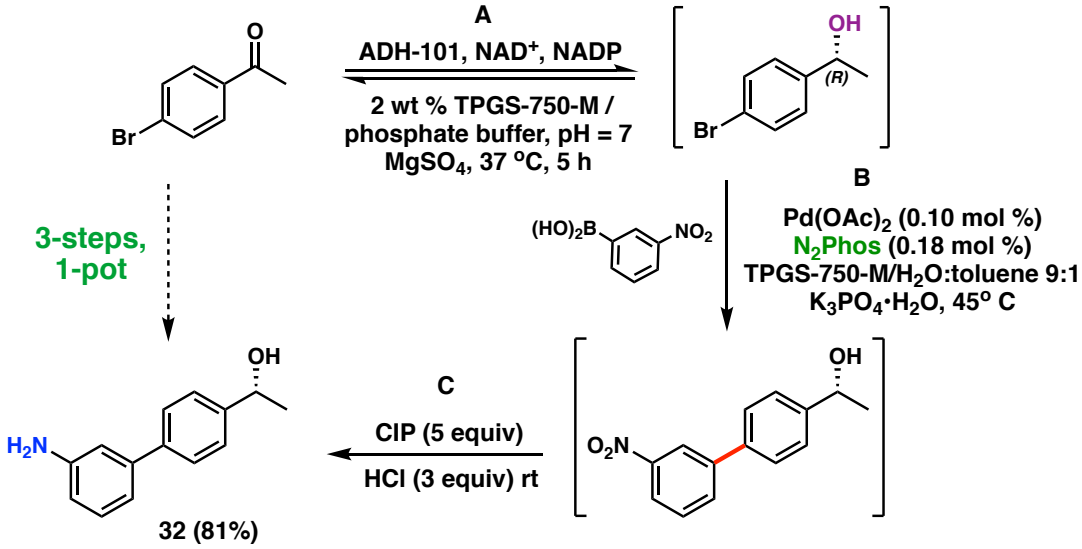
1-(6-Methoxynaphthalen-2-yl)ethan-1-one. Synthesized according to general procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.01 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.85 (d, *J* = 8.9 Hz,

1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.21 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 3.95 (s, 3H), 2.70 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.0, 159.9, 137.4, 132.8, 131.2, 130.2, 128.0, 127.2, 124.8, 119.9, 105.9, 55.6, 26.7. **Yield:** 53%, as a beige solid. **R_f:** 0.46 (20% EtOAc/hexanes) – UV + CAM stain.



1-Acetyl-1-cyclohexene. Synthesized according to general procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.93 – 6.87 (m, 1H), 2.27 (t, *J* = 1.1 Hz, 3H), 2.27 – 2.18 (m, 4H), 1.68 – 1.55 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.6, 141.1, 139.8, 26.2, 25.3, 23.1, 22.0, 21.6. **Yield:** 90%, as a colorless oil. **R_f**: 0.33 (15% EtOAc/hexanes) CAM stain.

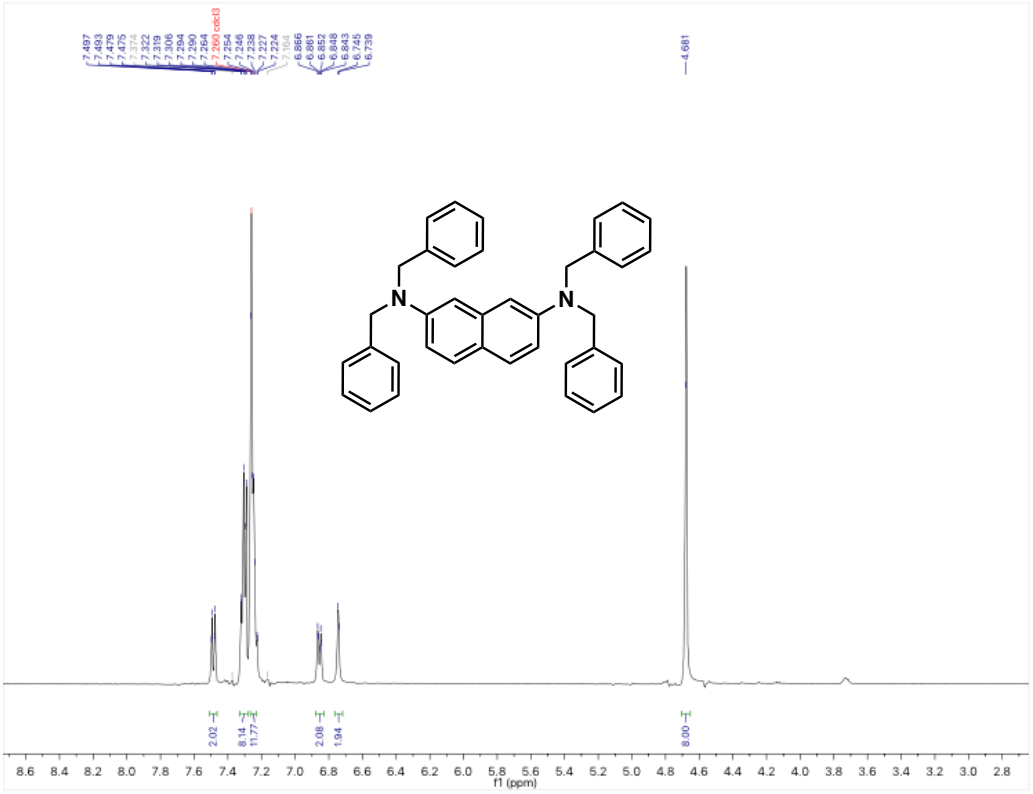
8. Procedure for the 1-pot Process

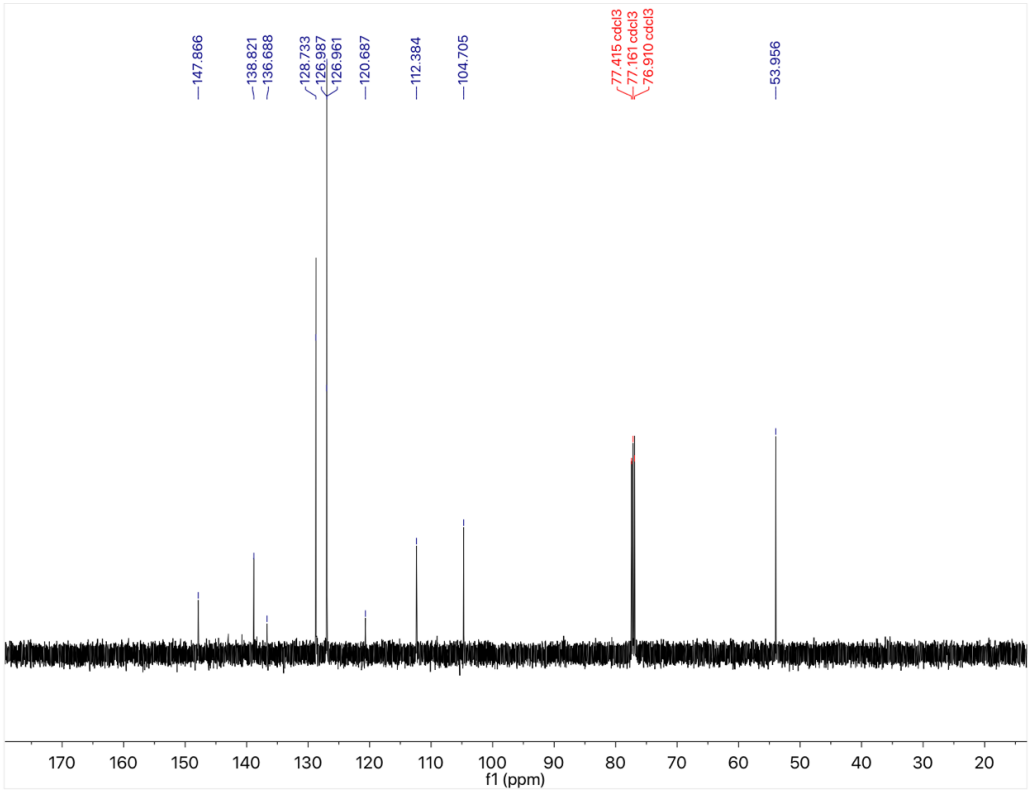


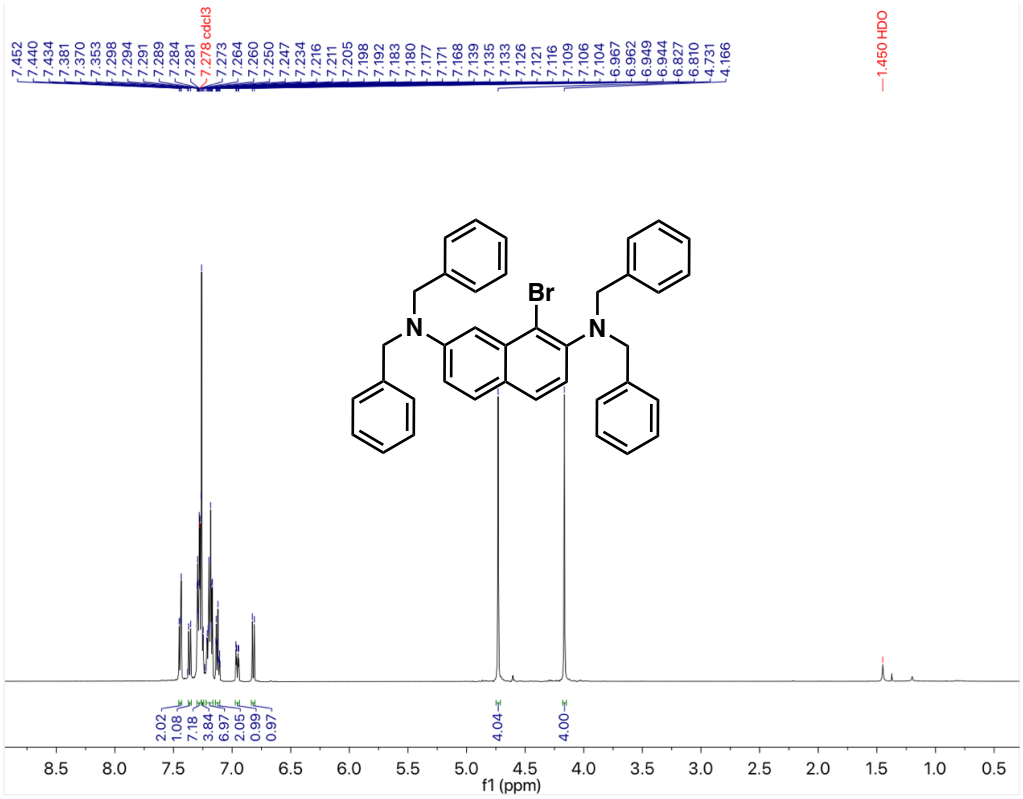
ADH-101[1-3] is commercially available within the enzyme kit EZK-001 from Johnson Matthey. NAD^+ was purchased from Bioworld and $NADP^+$ was purchased from Chem-Impes. Isopropanol was purchased from VWR. All other commercially available reagents were used without further purification. To a 2-dram vial equipped with a stir bar was added the ketone (0.2 mmol, 1 equiv), $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg) and $NADP^+$ (2.4 mg). *i*-PrOH (0.1 mL) and a [0.2 M] phosphate buffer solution at pH = 7 (0.7 mL) and 2 wt % aqueous TPGS-750-M were added. ADH-101 (20 mg) was then added. The reaction was set to stir at 37 °C for 16 h. The reaction was monitored by HPLC. Upon completion, the reaction was charged with the arylboronic acid (0.3 mmol, 1.5 equiv) and potassium phosphate (0.3 mmol, 1.5 equiv). The reaction vial was fitted with a rubber septum and sealed with Teflon tape. The reaction vial was purged with argon with the use of a vent needle. At this point a solution of $Pd(OAc)_2$ and N_2Phos in toluene (0.05 mL) was added via syringe. The reaction was set to stir at 45 °C and monitored by either GC/MS or TLC analysis. Upon completion of the reaction, carbonyl Fe powder (CIP, 5 equiv) and HCl (3 equiv) was added to the reaction vial. The reaction was set

to stir at rt and monitored by TLC analysis. Upon completion, the reaction was extracted with EtOAc and the organic layer was washed with brine three times. The layers were then separated and the organic layer was dried over anhydrous Na_2SO_4. The mixture was concentrated under vacuum and then purified via flash chromatography (40% EtOAc in hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.90 (t, *J* = 2.0 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.95 (q, *J* = 6.5 Hz, 1H), 3.74 (s, 2H), 1.54 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.84, 144.88, 142.20, 140.77, 129.83, 127.35, 125.87, 117.75, 114.24, 113.94, 70.35, 25.27. **Yield**: 81%**,** as a yellow solid. **R_f:** 0.33 (40% EtOAc in hexanes). **Chemical Formula**: $C_{14}H_{15}NO$ EI-MS $[M]^+$ calcd: 213.1154; found: 213.1147.

9. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR of Spectra for Products



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7.294
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7.281
7.278 cdcl3
7.273
7.264
7.260
7.250
7.247
7.234
7.216
7.211
7.205
7.198
7.192
7.183
7.180
7.177
7.171
7.168
7.139
7.135
7.133
7.126
7.121
7.116
7.109
7.106
7.104
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6.949
6.944
6.827
6.810
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Br
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7.18
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0.97
4.04
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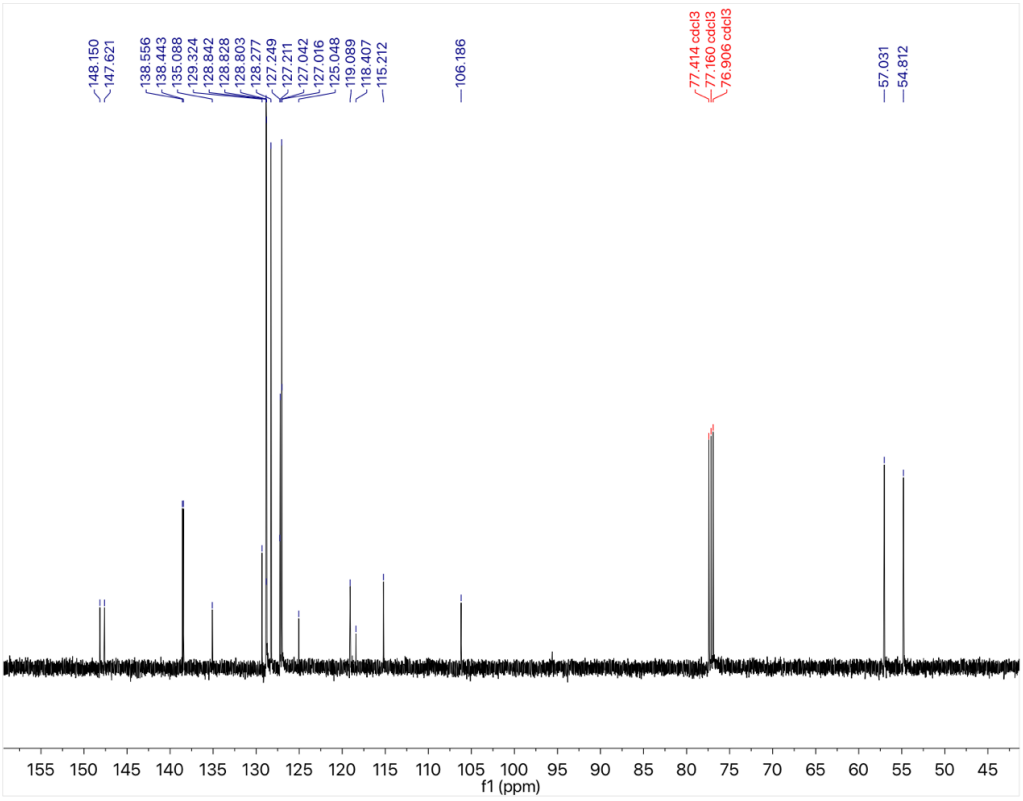
f1 (ppm)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128.828
128.803
128.277
127.249
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127.042
127.016
125.048
119.089
118.407
115.212
106.186
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76.906 cdcl3
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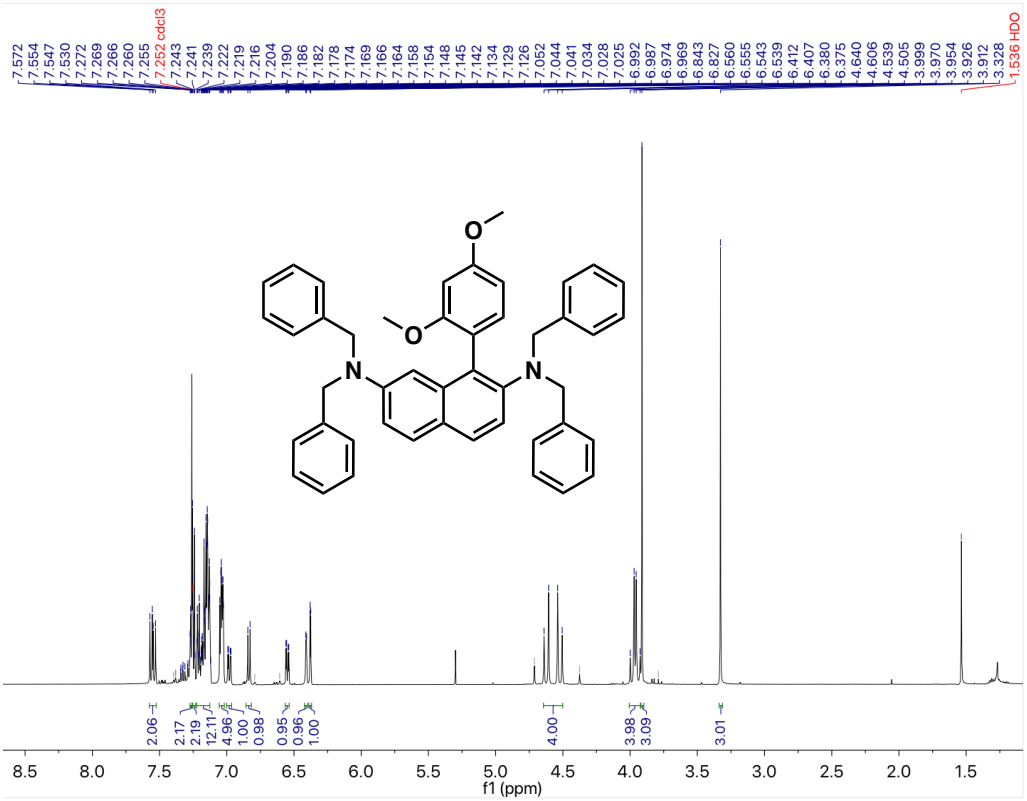
54.812
f1 (ppm)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7.241
7.239
7.222
7.219
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7.204
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7.186
7.182
7.178
7.174
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7.154
7.148
7.145
7.142
7.134
7.129
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7.044
7.041
7.034
7.028
7.025
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6.987
6.974
6.969
6.843
6.827
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6.543
6.539
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6.407
6.380
6.375
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4.505
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3.970
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3.912
3.328
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O
N
N
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2.17
2.19
12.11
4.96
1.00
0.98
0.95
0.96
1.00
4.00
3.98
3.09
3.01
8.5
8.0
7.5
7.0
6.5
6.0
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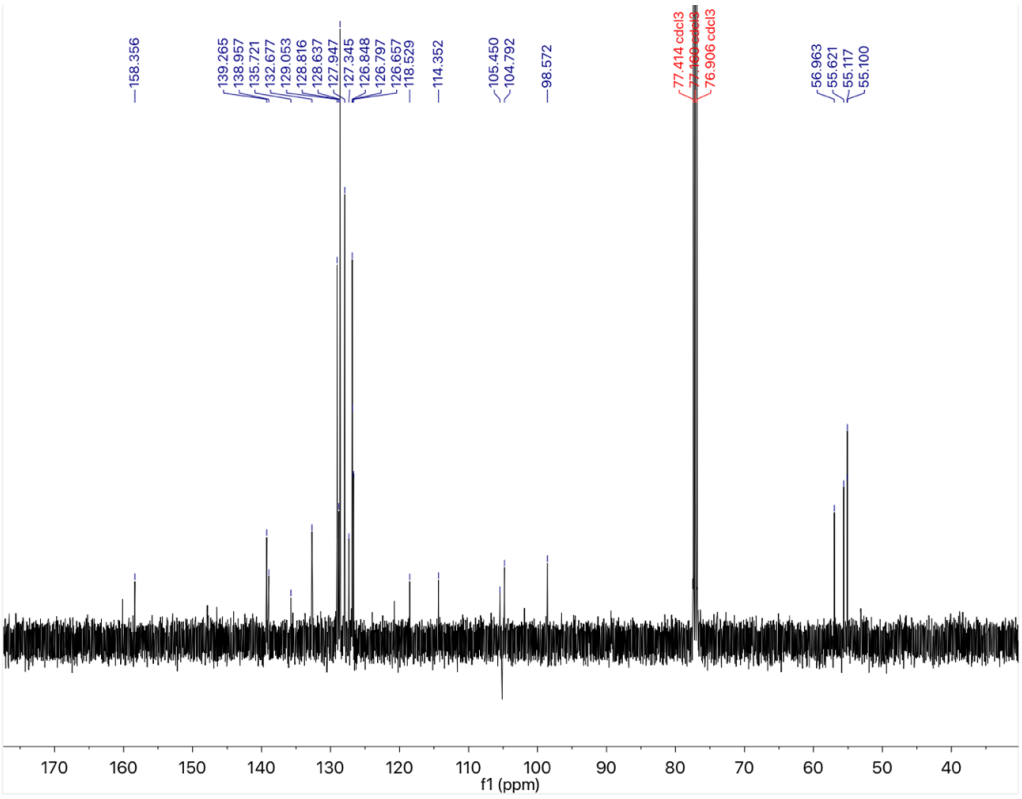
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126.797
126.657
118.529
114.352
105.450
104.792
98.572
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
56.963
55.621
55.117
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150
140
130
120
110
100
90
80
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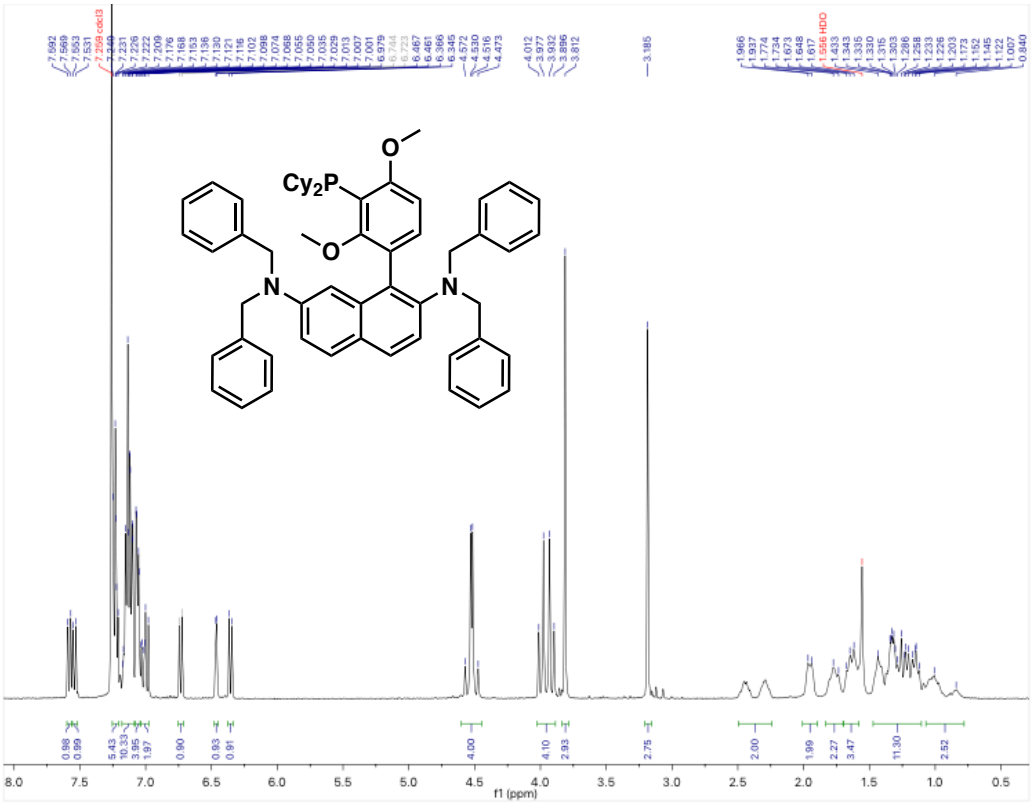
60
50
40
f1 (ppm)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O
O
N
N
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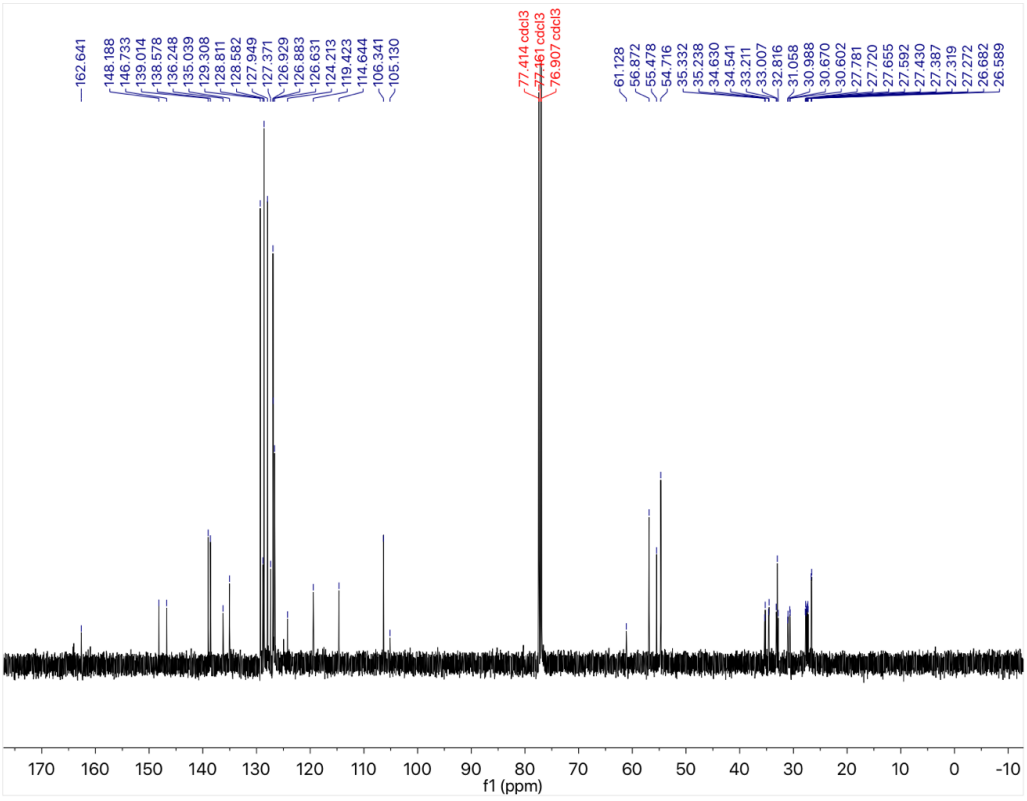
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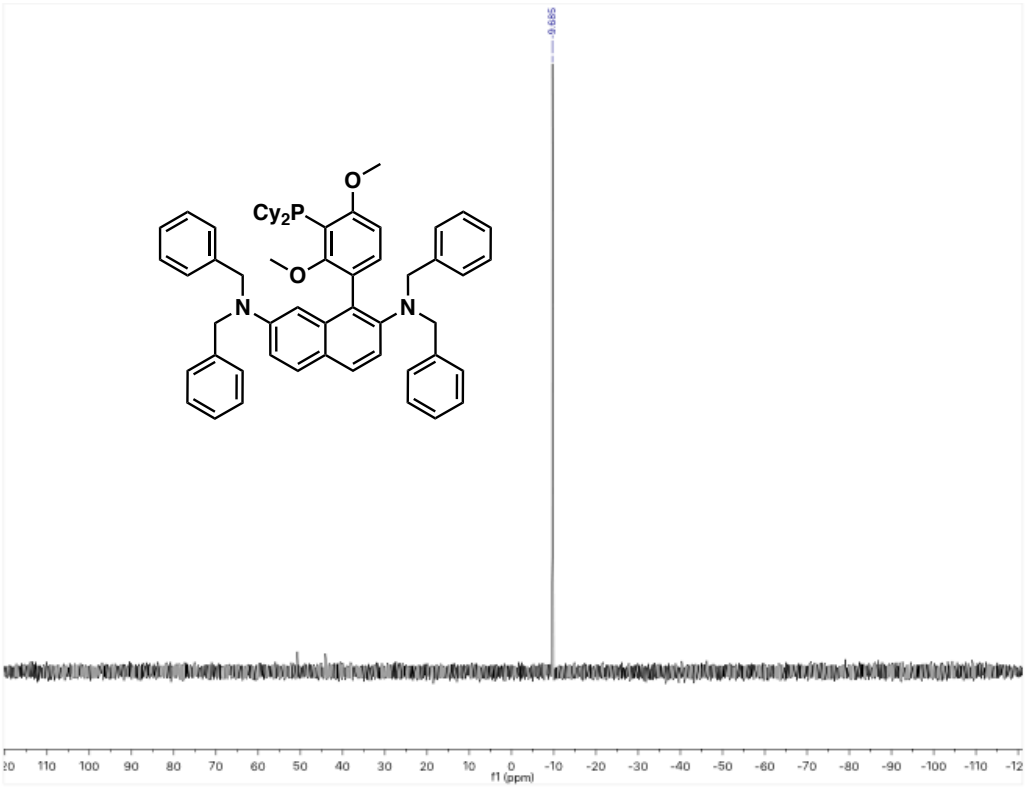
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O
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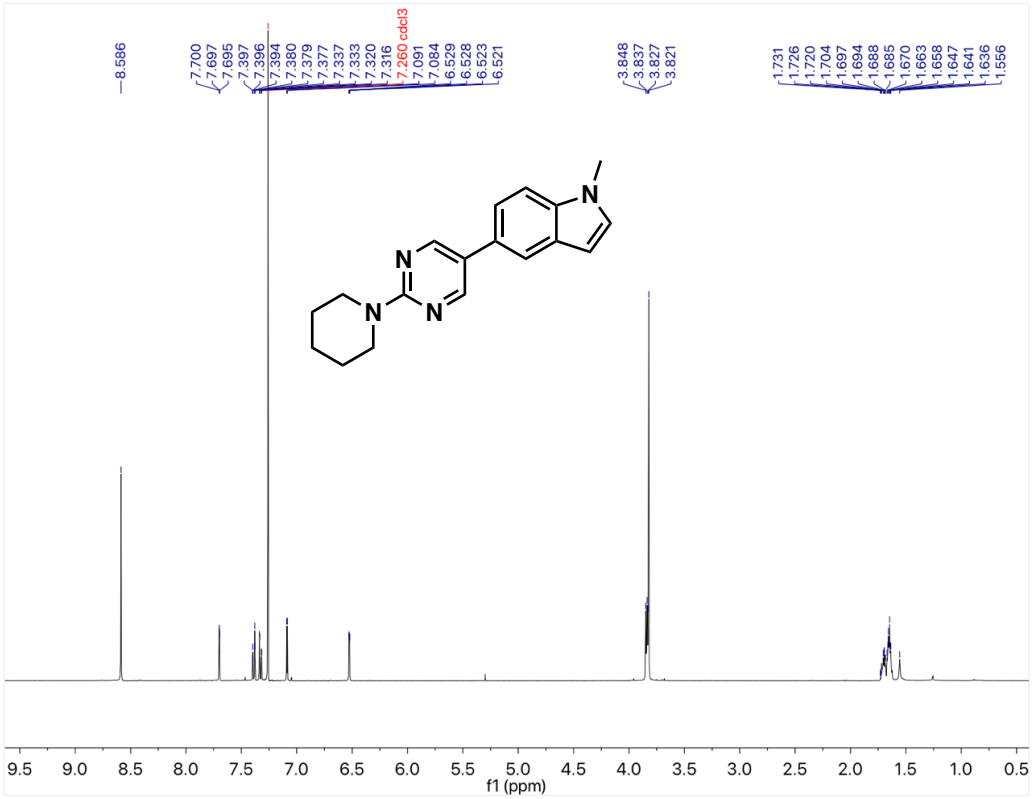
f1 (ppm)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7.320
7.316
7.260 cdcl3
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7.084
6.529
6.528
6.523
6.521
3.848
3.837
3.827
3.821
1.731
1.726
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1.694
1.688
1.685
1.670
1.663
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N
N
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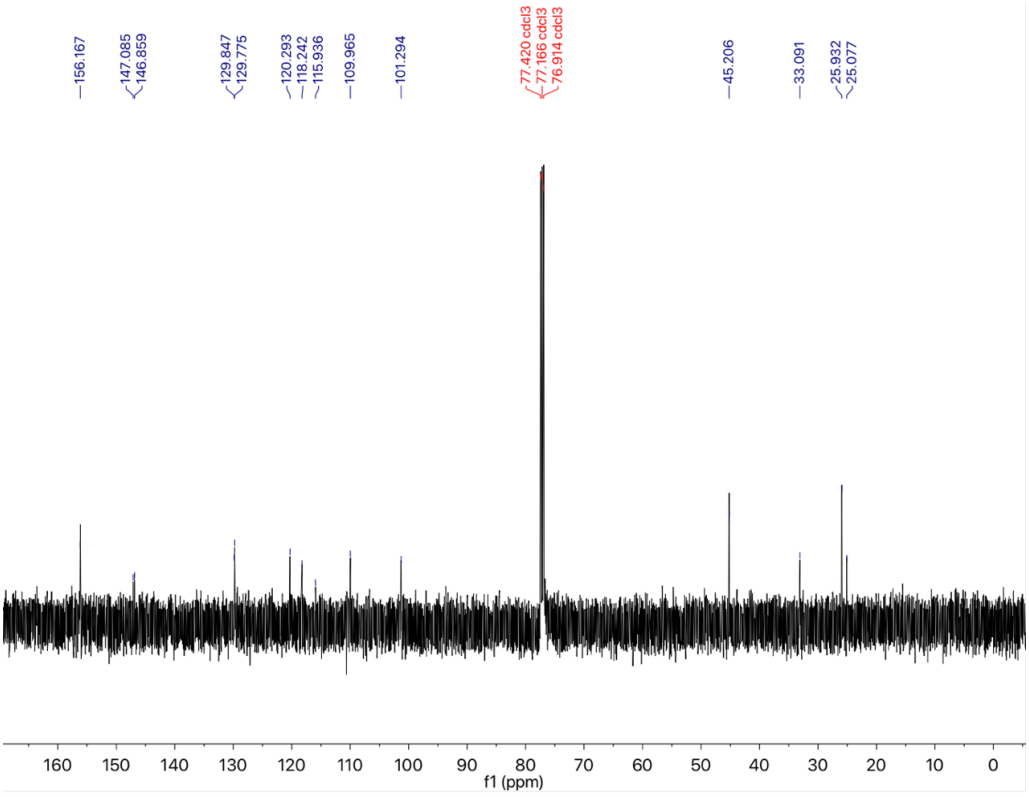
f1 (ppm)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101.294
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77.166 cdcl3
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45.206
33.091
25.932
25.077
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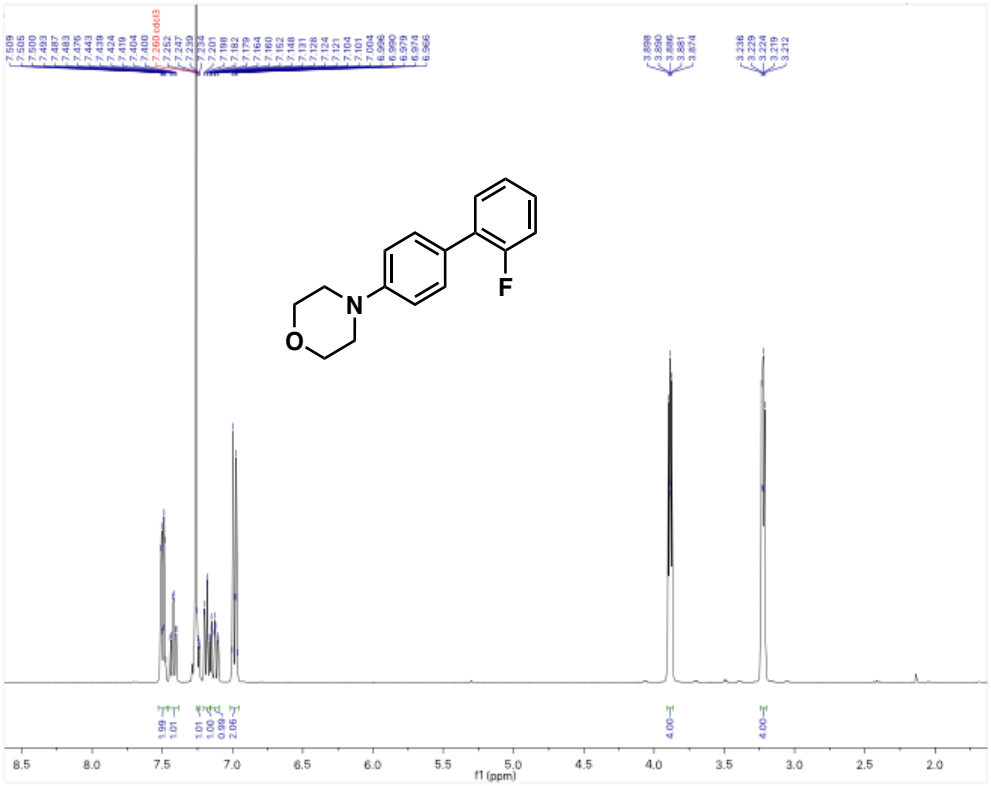
f1 (ppm)


F
N
O
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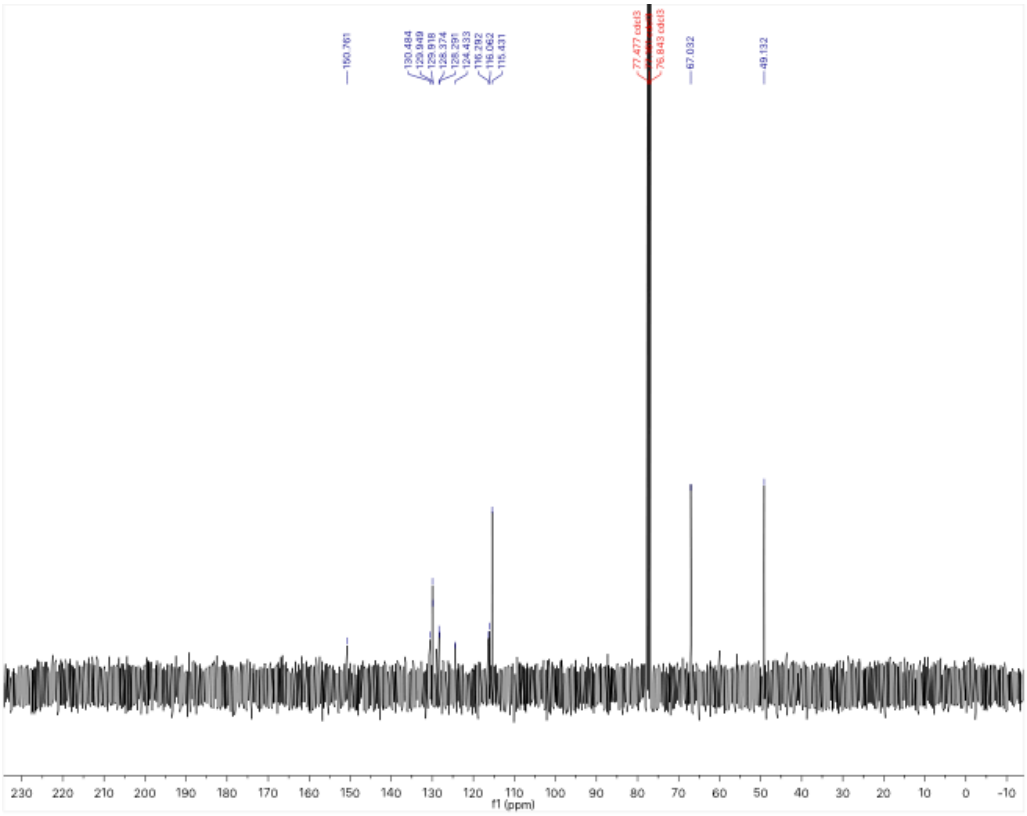
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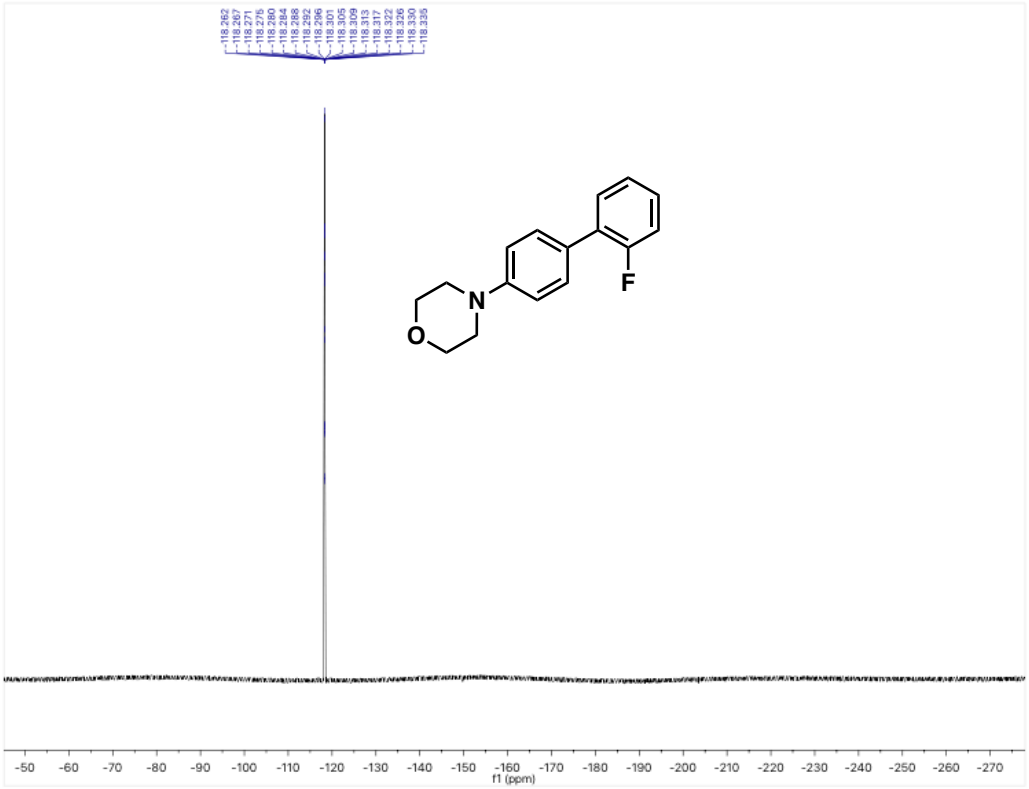
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118.322
118.326
118.330
118.335
N
O
F
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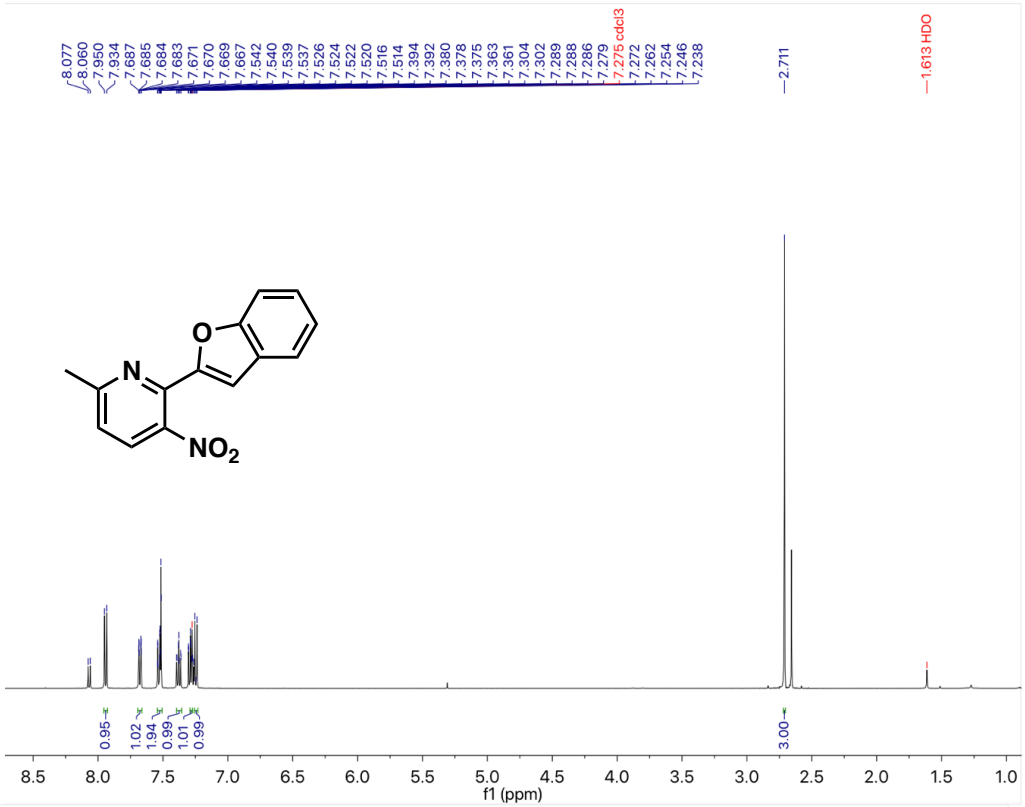
f1 (ppm)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7.279
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7.272
7.262
7.254
7.246
7.238
2.711
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O
N
NO2
0.95
1.02
1.94
0.99
1.01
0.99
3.00
8.5
8.0
7.5
7.0
6.5
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3.5
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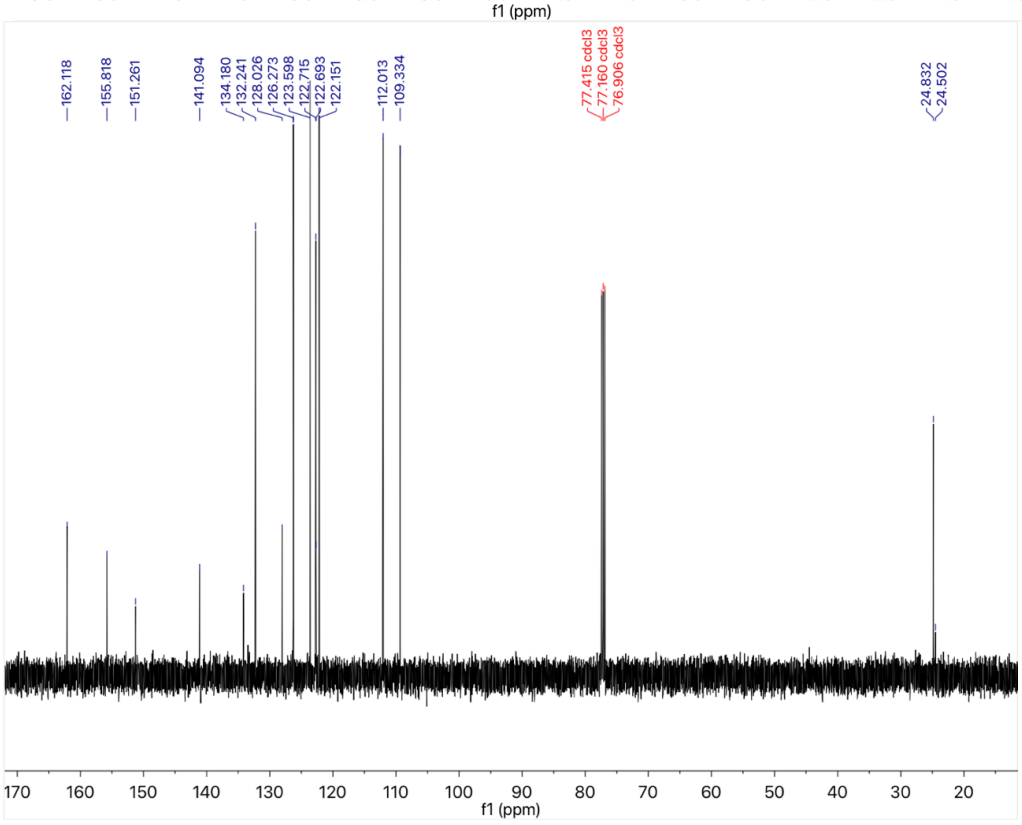
1.0
f1 (ppm)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109.334
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77.160 cdcl3
76.906 cdcl3
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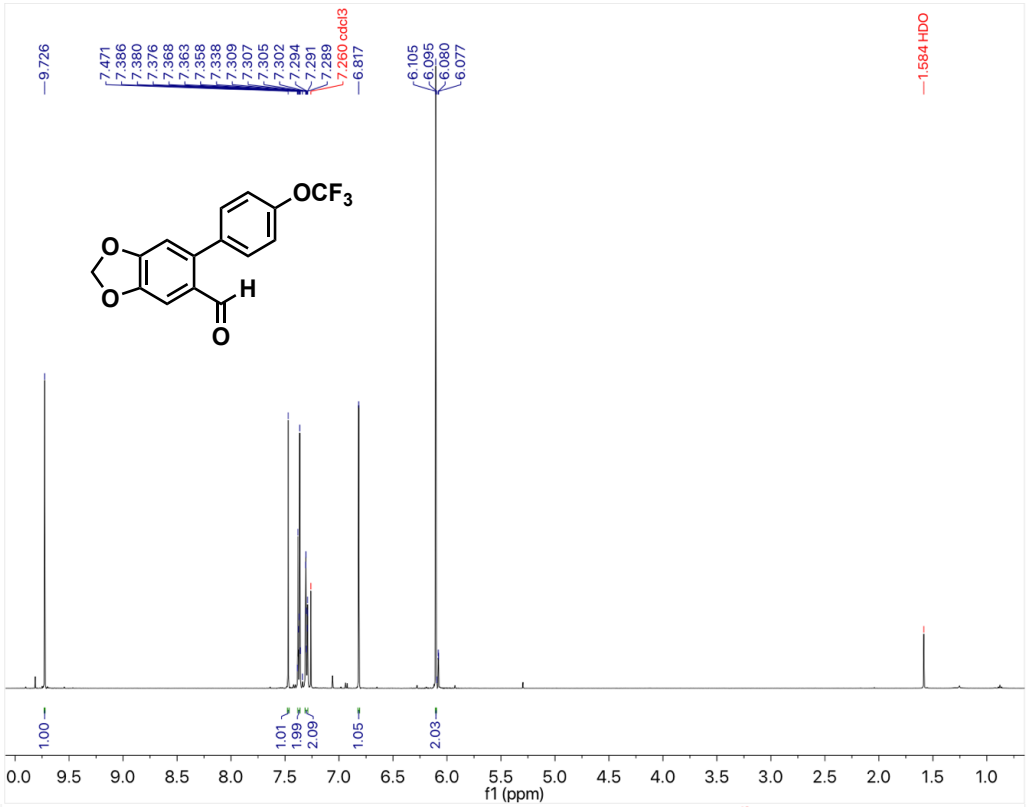
f1 (ppm)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7.294
7.291
7.289
7.260 cdcl3
6.817
6.105
6.095
6.080
6.077
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O
O
H
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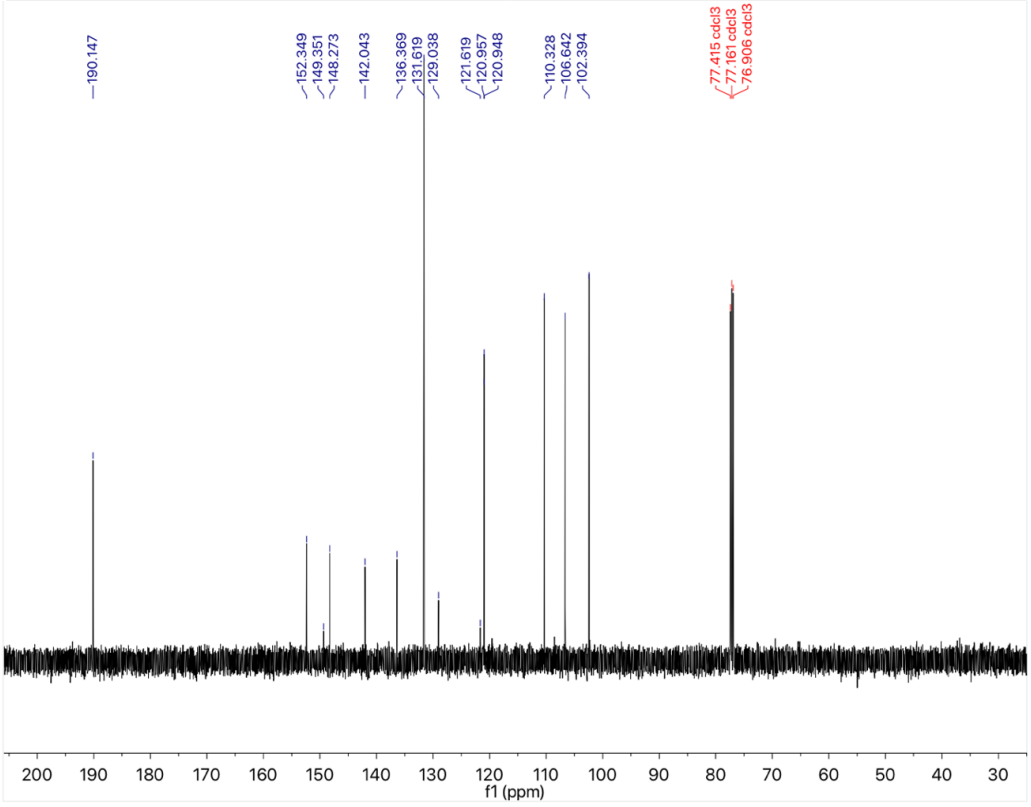
f1 (ppm)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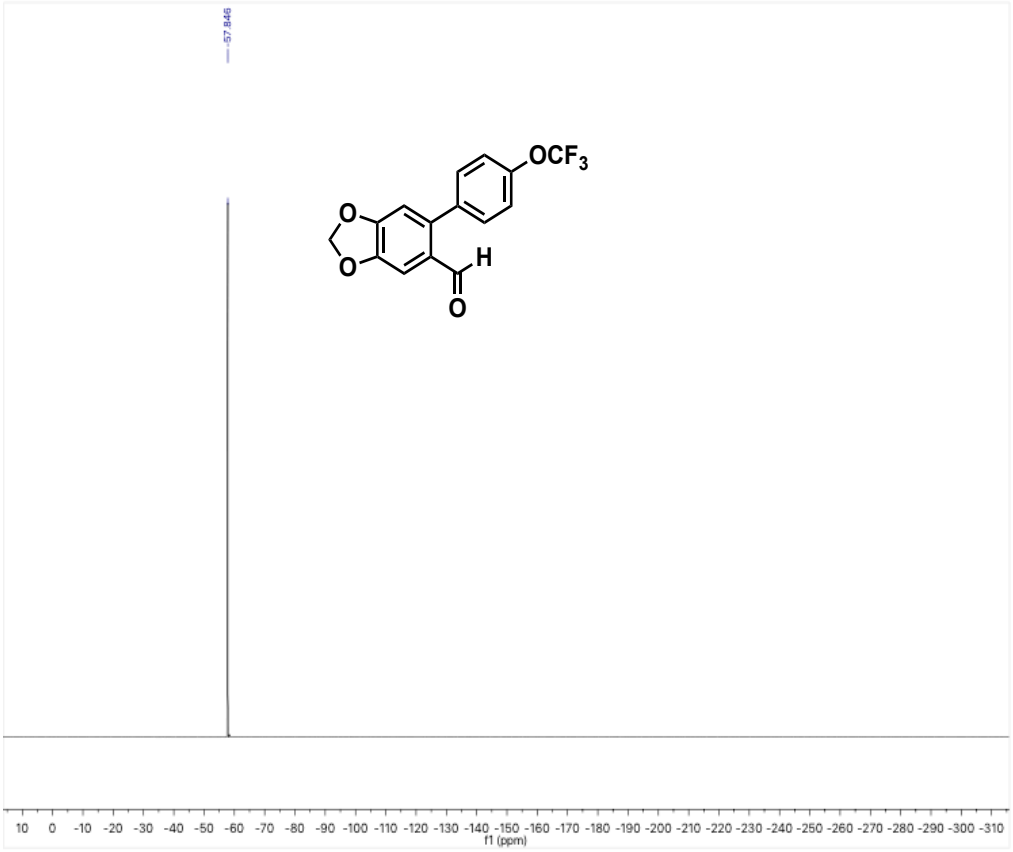
102.394
77.415 cdcl3
77.161 cdcl3
76.906 cdcl3
f1 (ppm)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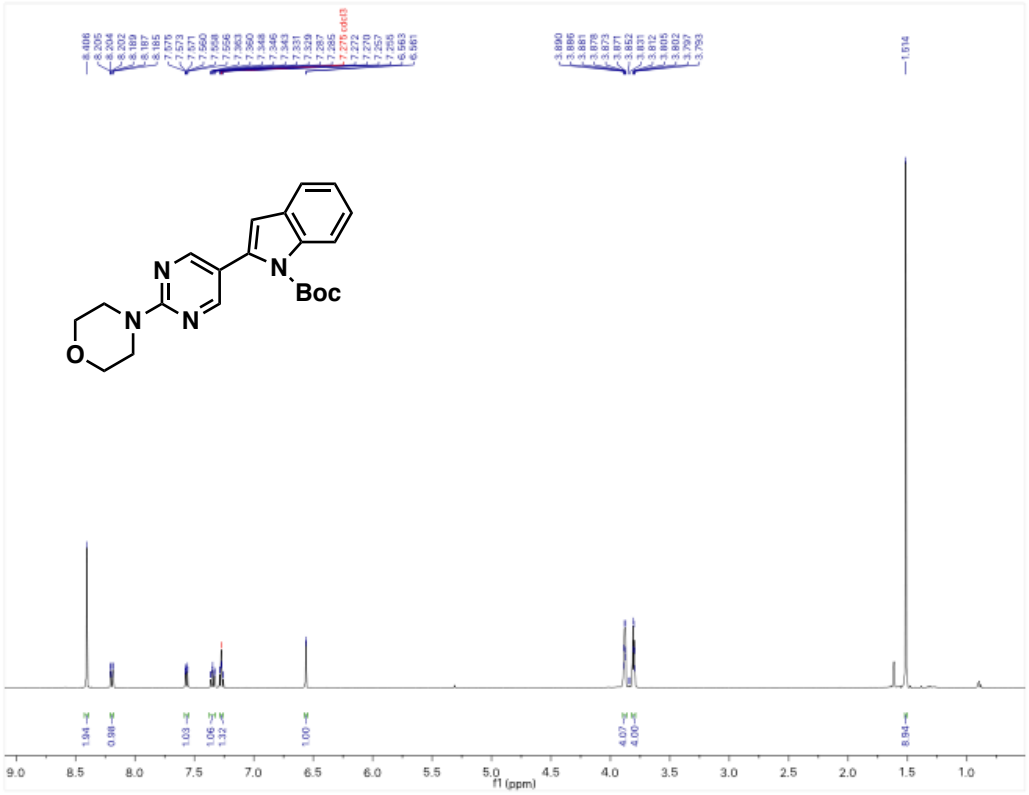
OCF3
O
O
H
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)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N
N
Boc
O
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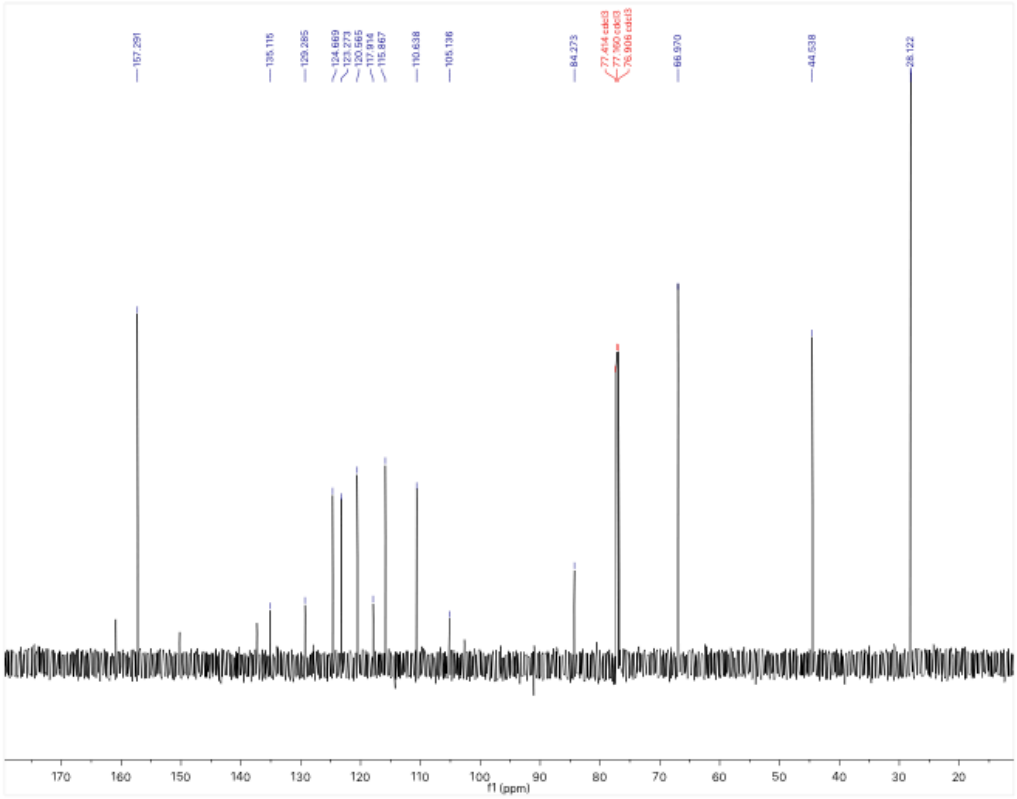
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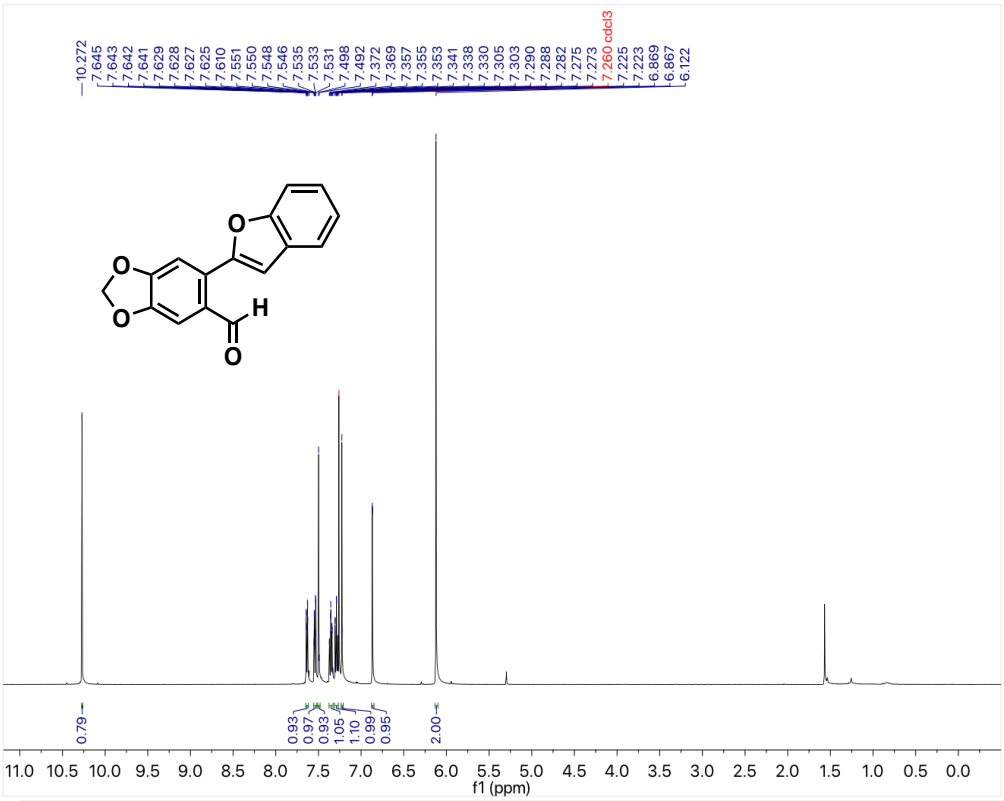
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7.610
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7.548
7.546
7.535
7.533
7.531
7.498
7.492
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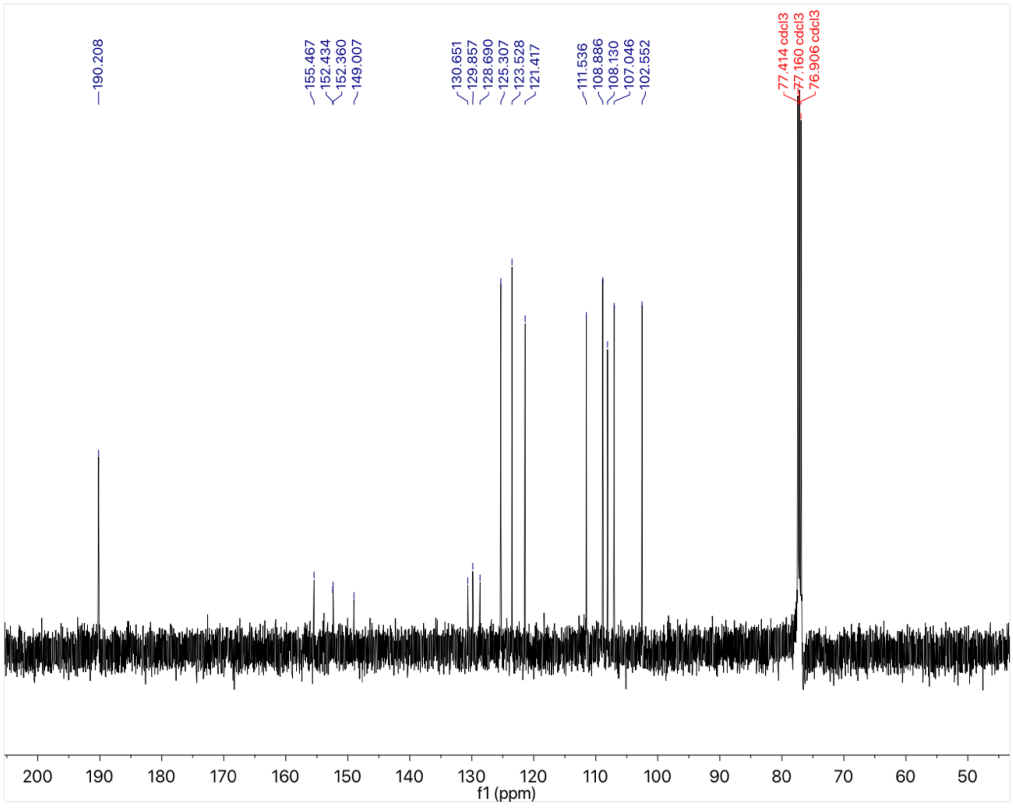
7.355
7.353
7.341
7.338
7.330
7.305
7.303
7.290
7.288
7.282
7.275
7.273
7.260 cdcl3
7.225
7.223
6.869
6.867
6.122
O
O
O
H
O
0.79
0.93
0.97
0.93
1.05
1.10
0.99
0.95
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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111.536
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108.130
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77.414 cdcl3
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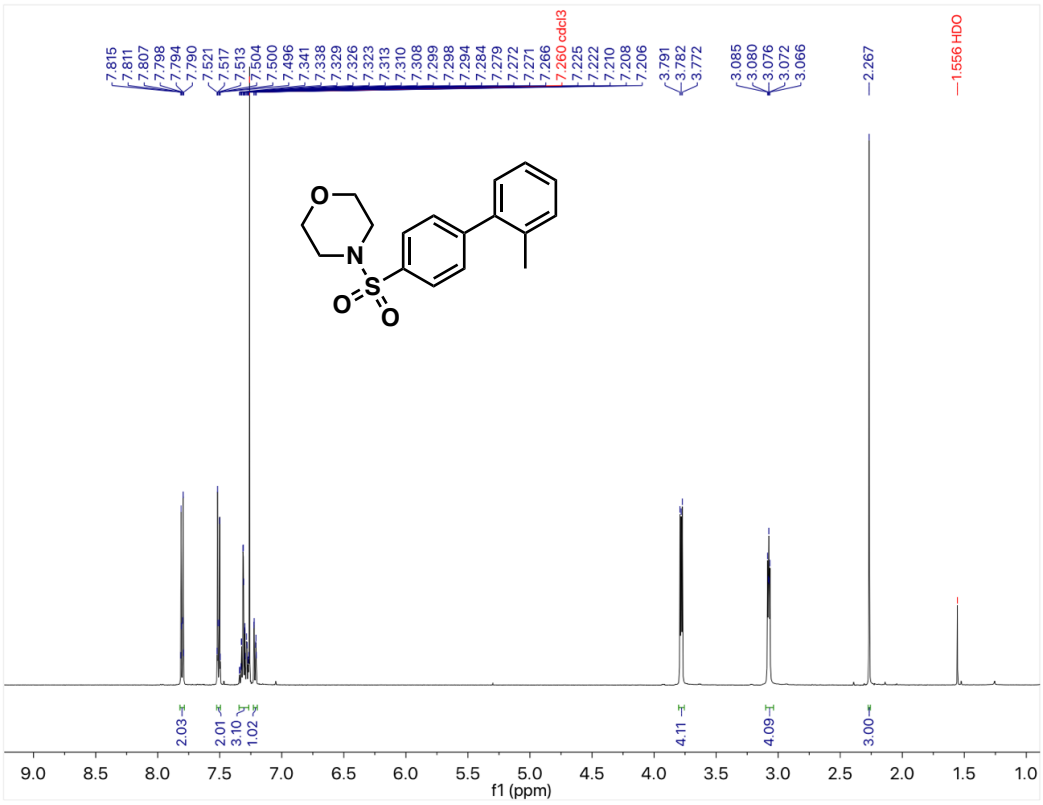
76.906 cdcl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
f1 (ppm)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7.517
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7.504
7.500
7.496
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7.338
7.329
7.326
7.323
7.313
7.310
7.308
7.299
7.298
7.294
7.284
7.279
7.272
7.271
7.266
7.260 cdcl3
7.225
7.222
7.210
7.208
7.206
3.791
3.782
3.772
3.085
3.080
3.076
3.072
3.066
2.267
1.556 HDO
O
N
S
O
O
2.03
2.01
3.10
1.02
4.11
4.09
3.00
9.0
8.5
8.0
7.5
7.0
6.5
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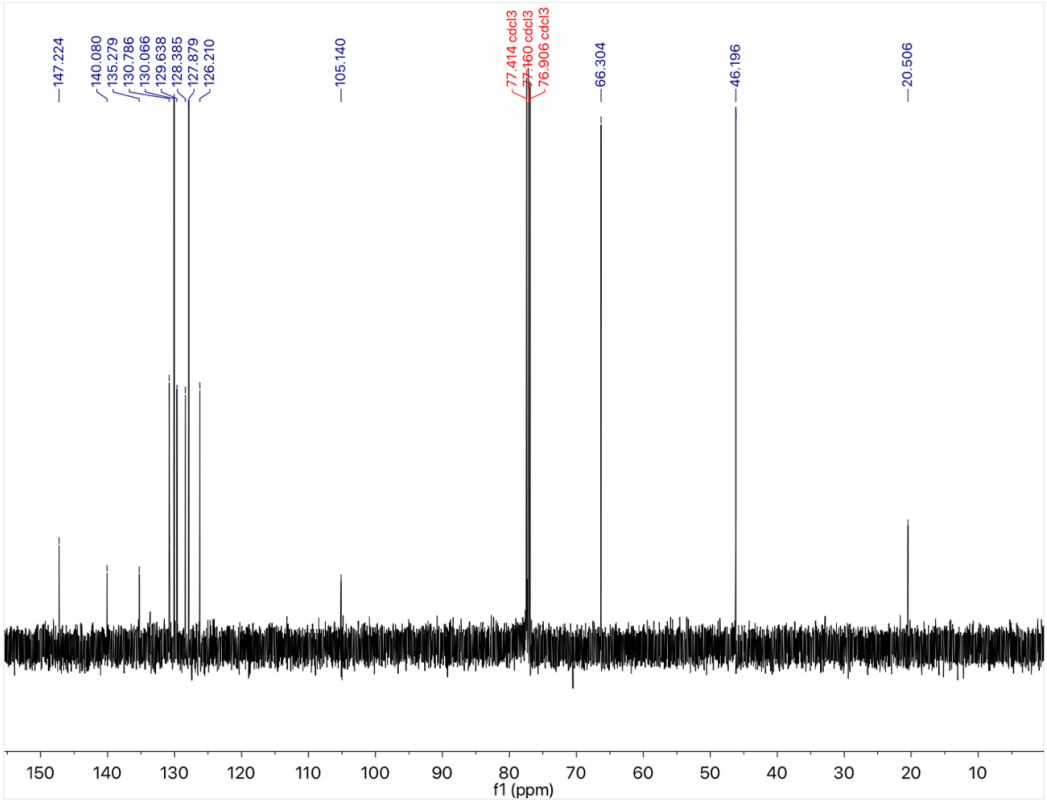
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


147.224
140.080
135.279
130.786
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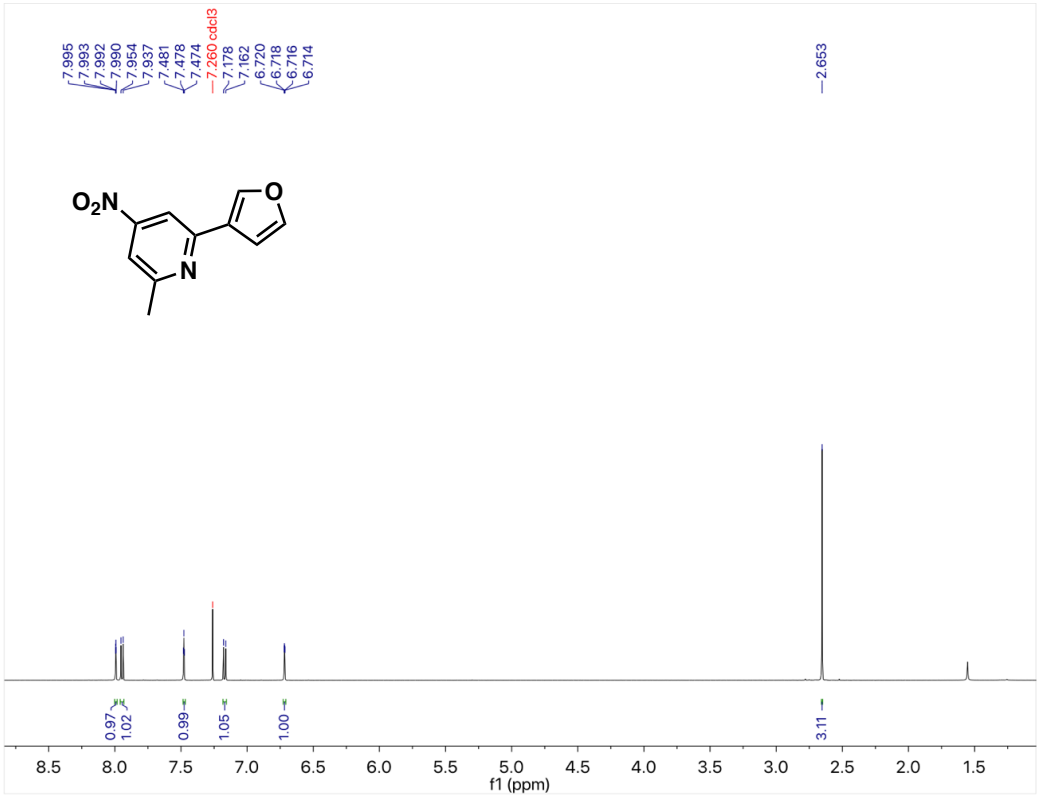
129.638
128.385
127.879
126.210
105.140
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
66.304
46.196
20.506
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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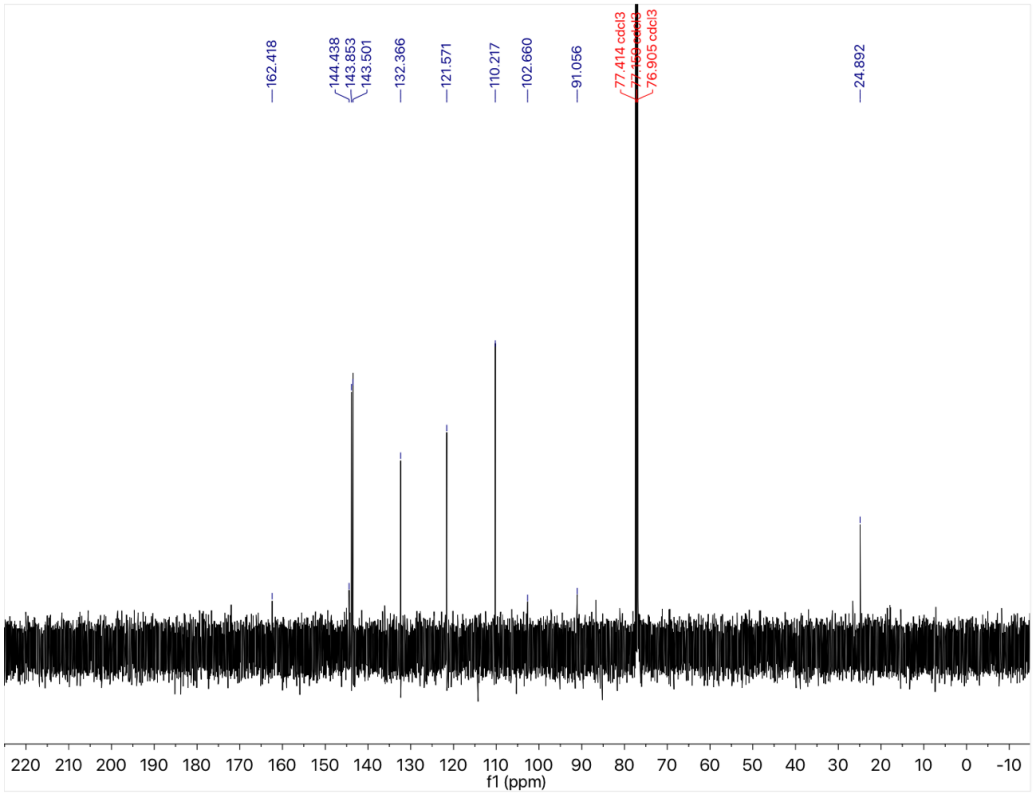
7.993
7.992
7.990
7.954
7.937
7.481
7.478
7.474
7.260 cdcl3
7.178
7.162
6.720
6.718
6.716
6.714
2.653
O2N
O
N
0.97
1.02
0.99
1.05
1.00
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)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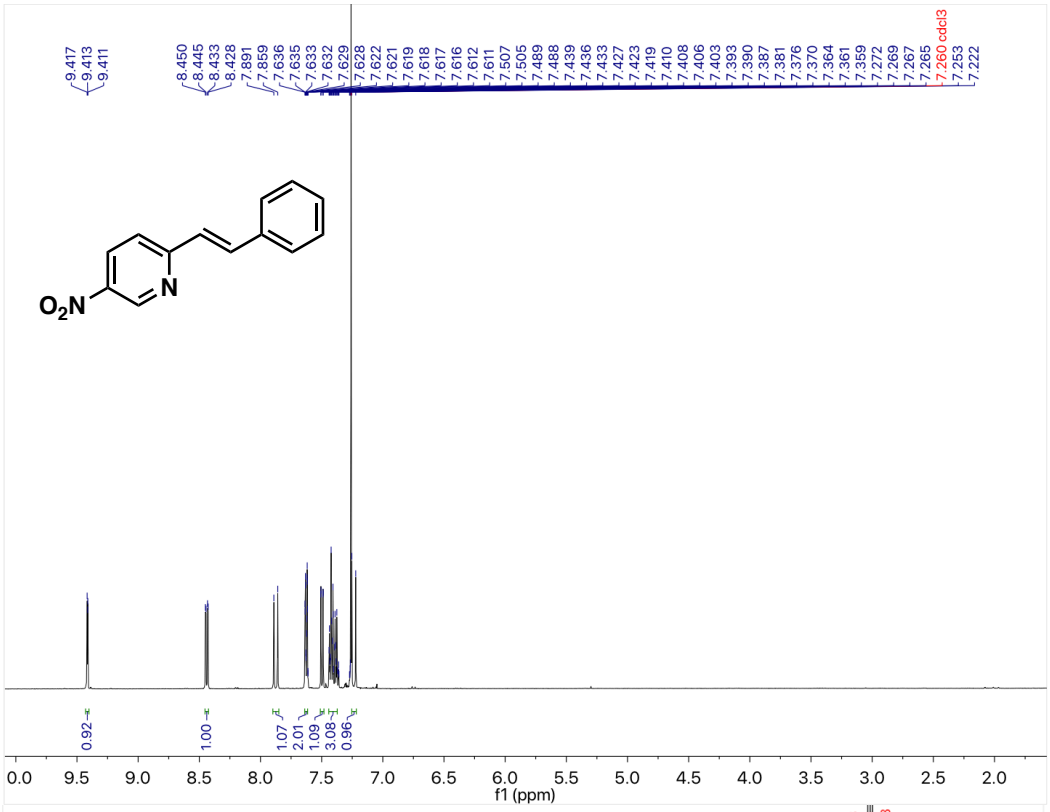
143.853
143.501
132.366
121.571
110.217
102.660
91.056
77.414 cdcl3
77.159 cdcl3
76.905 cdcl3
24.892
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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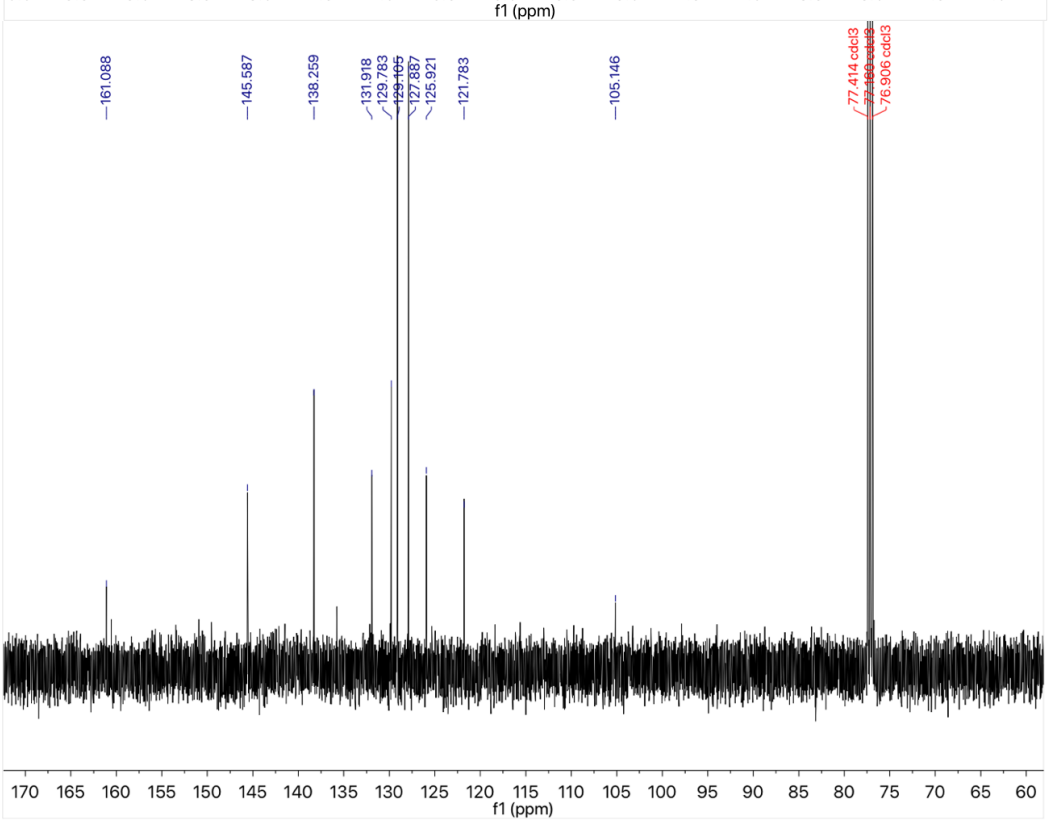
9.411
8.450
8.445
8.433
8.428
7.891
7.859
7.636
7.635
7.633
7.632
7.629
7.628
7.622
7.621
7.619
7.618
7.617
7.616
7.612
7.611
7.507
7.505
7.489
7.488
7.439
7.436
7.433
7.427
7.423
7.419
7.410
7.408
7.406
7.403
7.393
7.390
7.387
7.381
7.376
7.370
7.364
7.361
7.359
7.272
7.269
7.267
7.265
7.260 cdcl3
7.253
7.222
O_2N
N
0.92
1.00
1.07
2.01
1.09
3.08
0.96
f1 (ppm)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129.105
127.887
125.921
121.783
105.146
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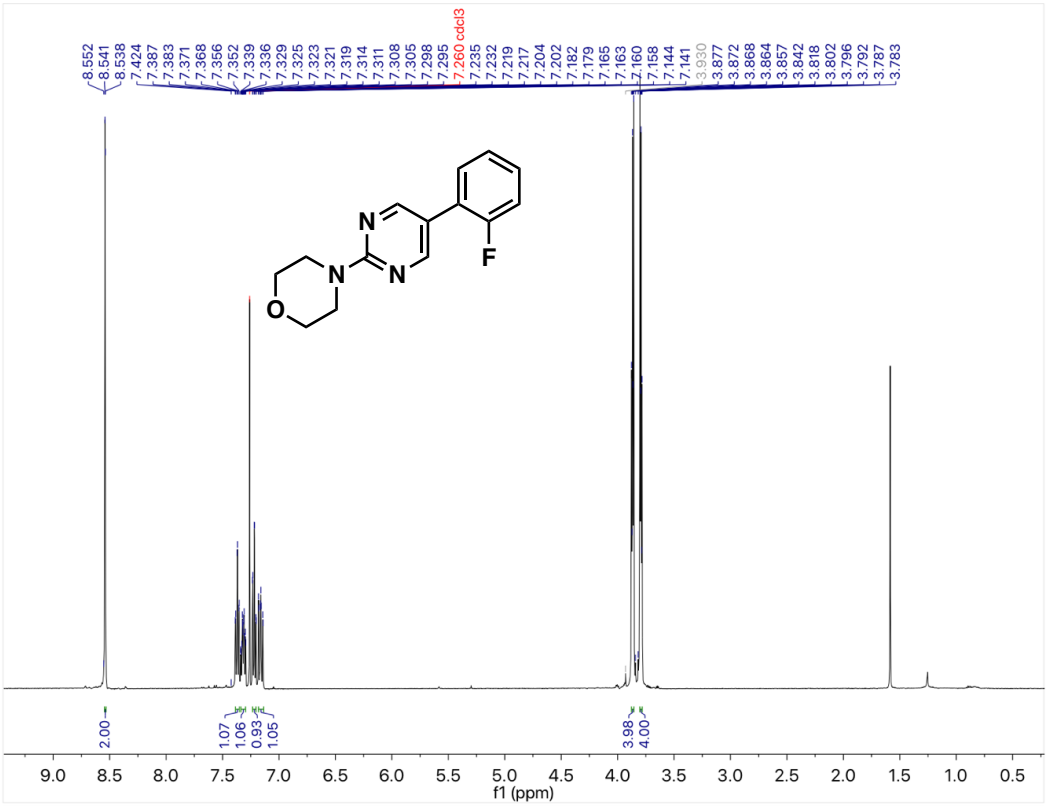
77.180 cdcl3
76.906 cdcl3
f1 (ppm)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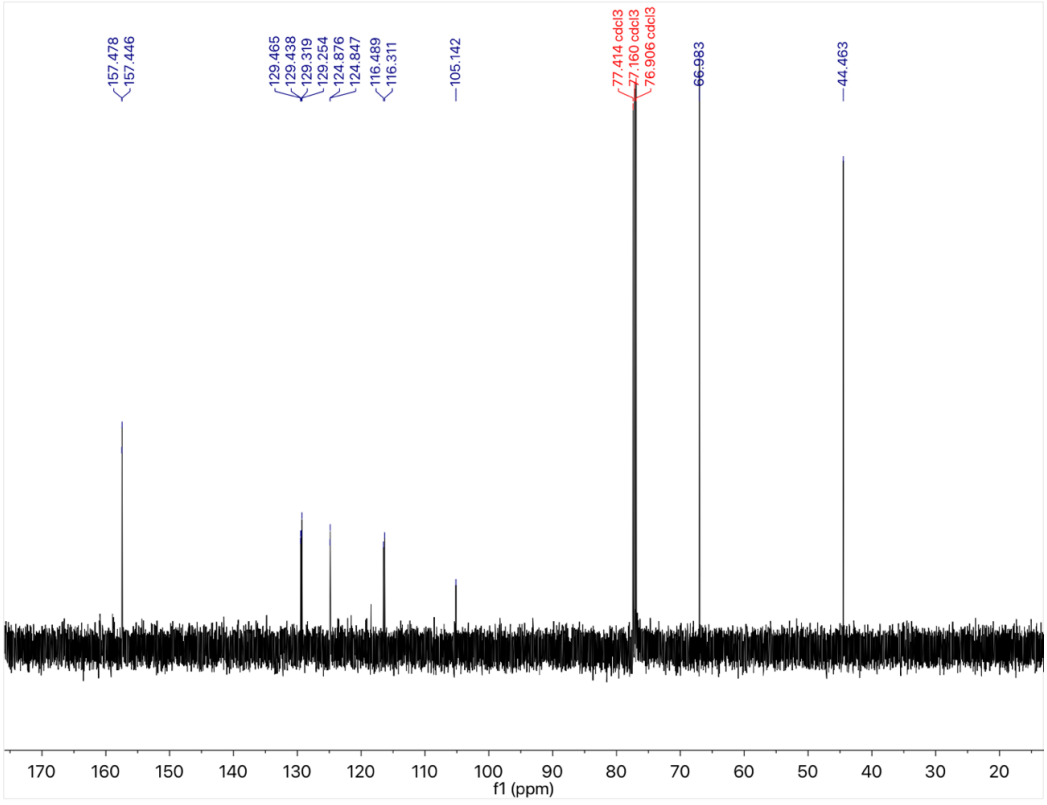
7.329
7.325
7.323
7.321
7.319
7.314
7.311
7.308
7.305
7.298
7.295
7.260 cdcl3
7.235
7.232
7.219
7.217
7.204
7.202
7.182
7.179
7.165
7.163
7.160
7.158
7.144
7.141
3.930
3.877
3.872
3.868
3.864
3.857
3.842
3.818
3.802
3.796
3.792
3.787
3.783
N
N
N
O
F
2.00
1.07
1.06
0.93
1.05
3.98
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.438
129.319
129.254
124.876
124.847
116.489
116.311
105.142
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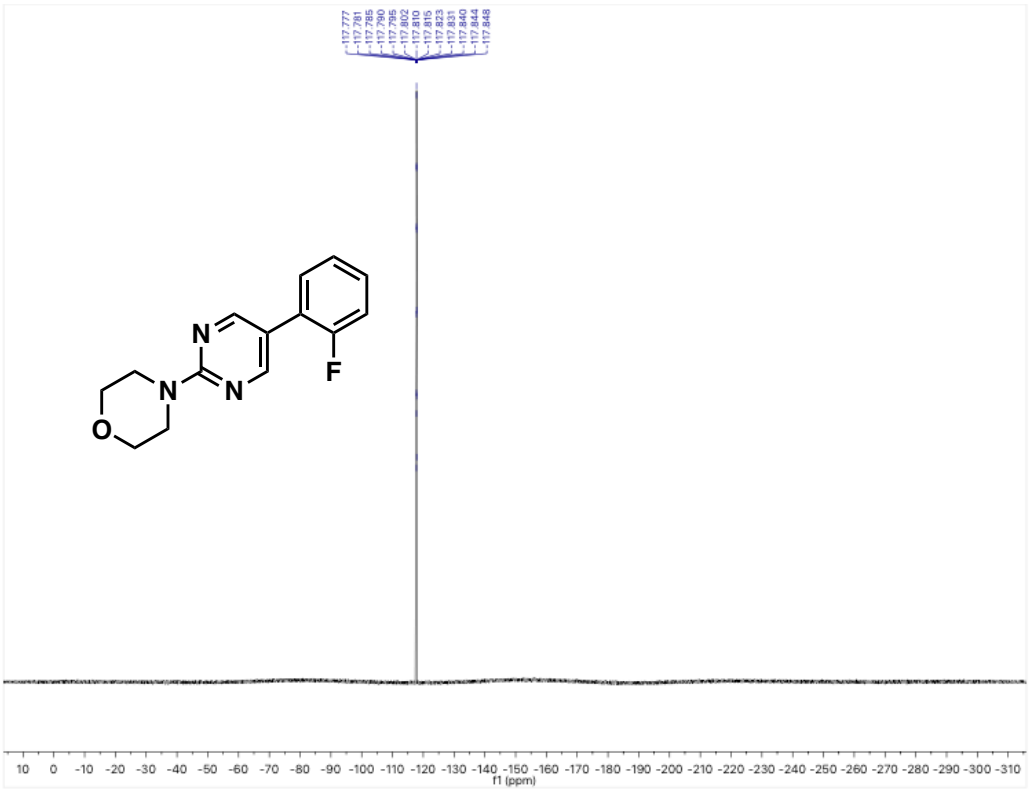
77.160 cdcl3
76.906 cdcl3
66.983
44.463
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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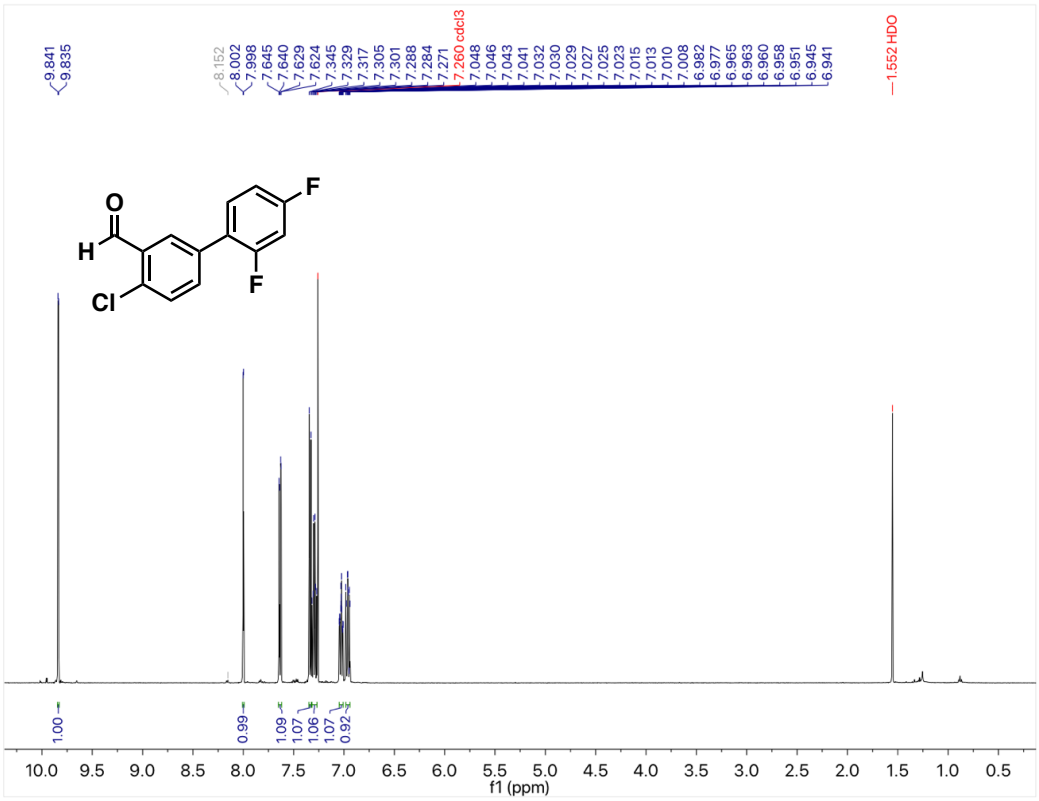
-117.810
-117.815
-117.823
-117.831
-117.840
-117.844
-117.848
N
N
N
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)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7.629
7.624
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7.329
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7.305
7.301
7.288
7.284
7.271
7.260 cdcl3
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7.046
7.043
7.041
7.032
7.030
7.029
7.027
7.025
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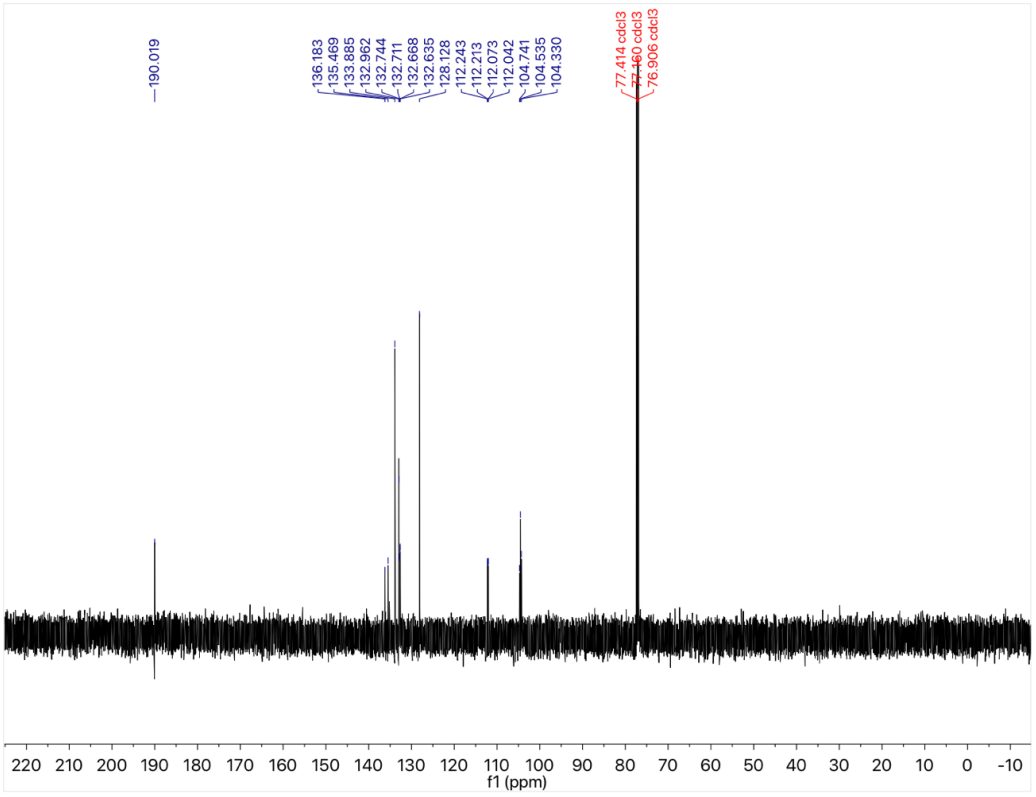
7.015
7.013
7.010
7.008
6.982
6.977
6.965
6.963
6.960
6.958
6.951
6.945
6.941
1.552 HDO
O
H
Cl
F
F
1.00
0.99
1.09
1.07
1.06
1.07
0.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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132.668
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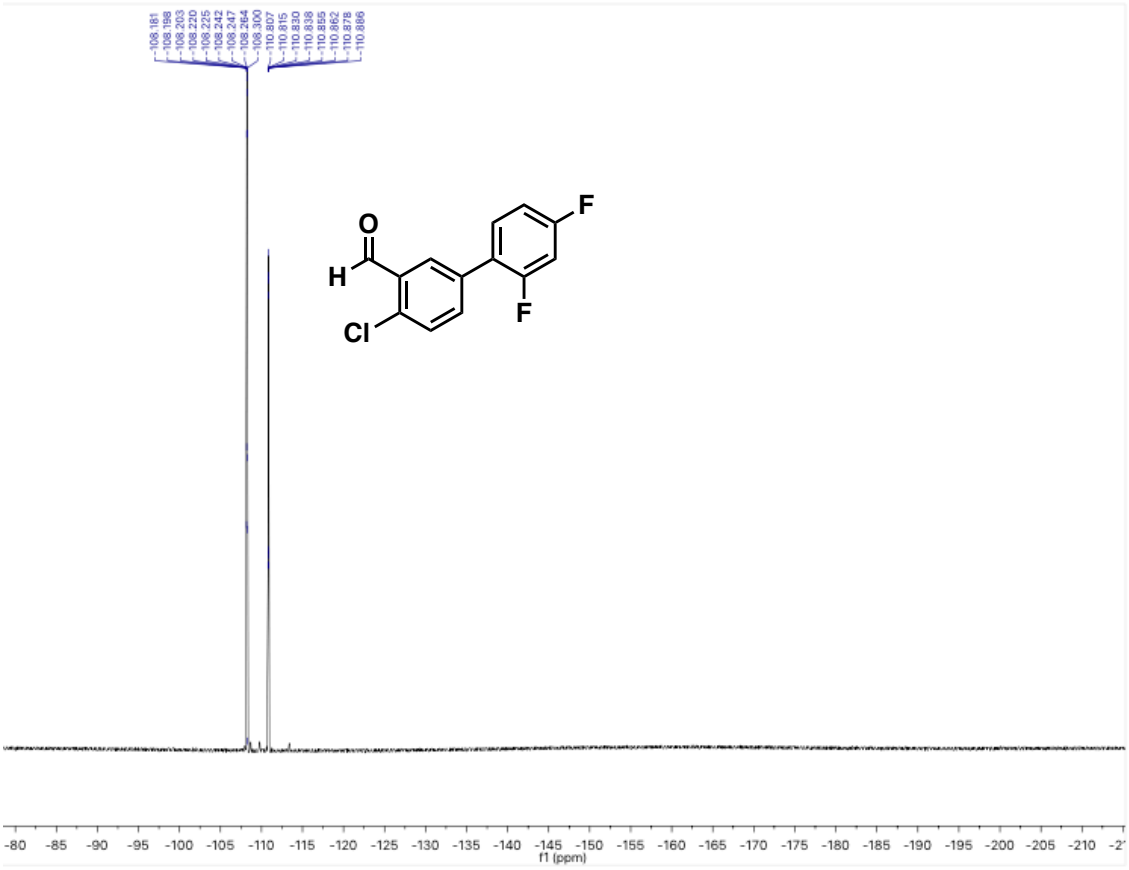
112.213
112.073
112.042
104.741
104.535
104.330
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-108.203
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-108.247
-108.264
-108.300
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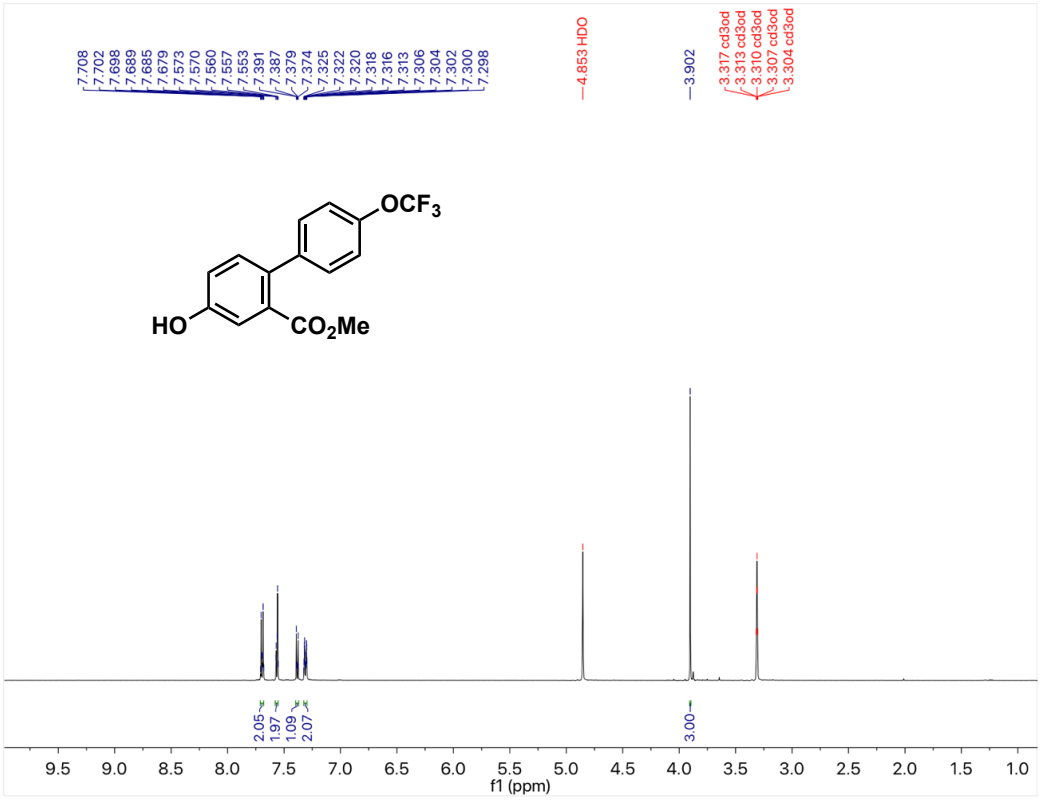
-110.815
-110.830
-110.838
-110.855
-110.862
-110.878
-110.886
O
H
Cl
F
F
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210
f1 (ppm)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7.374
7.325
7.322
7.320
7.318
7.316
7.313
7.306
7.304
7.302
7.300
7.298
4.853 HDO
3.902
3.317 cd3od
3.313 cd3od
3.310 cd3od
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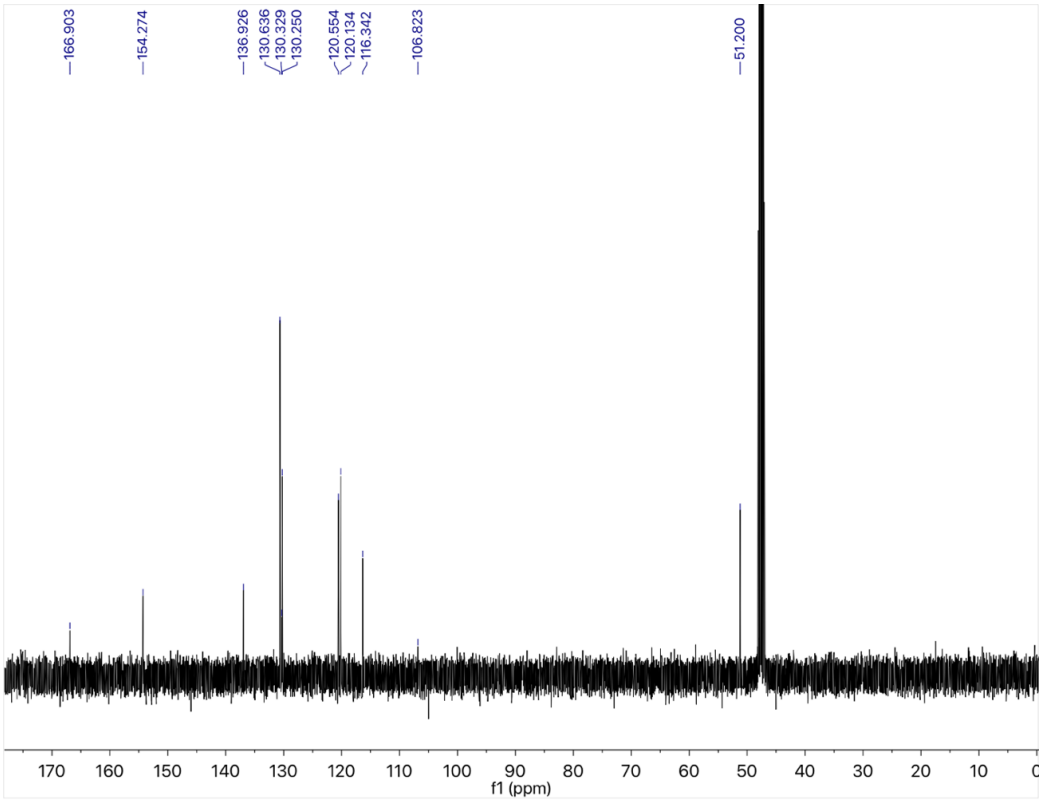
OCF3
HO
CO2Me
2.05
1.97
1.09
2.07
3.00
f1 (ppm)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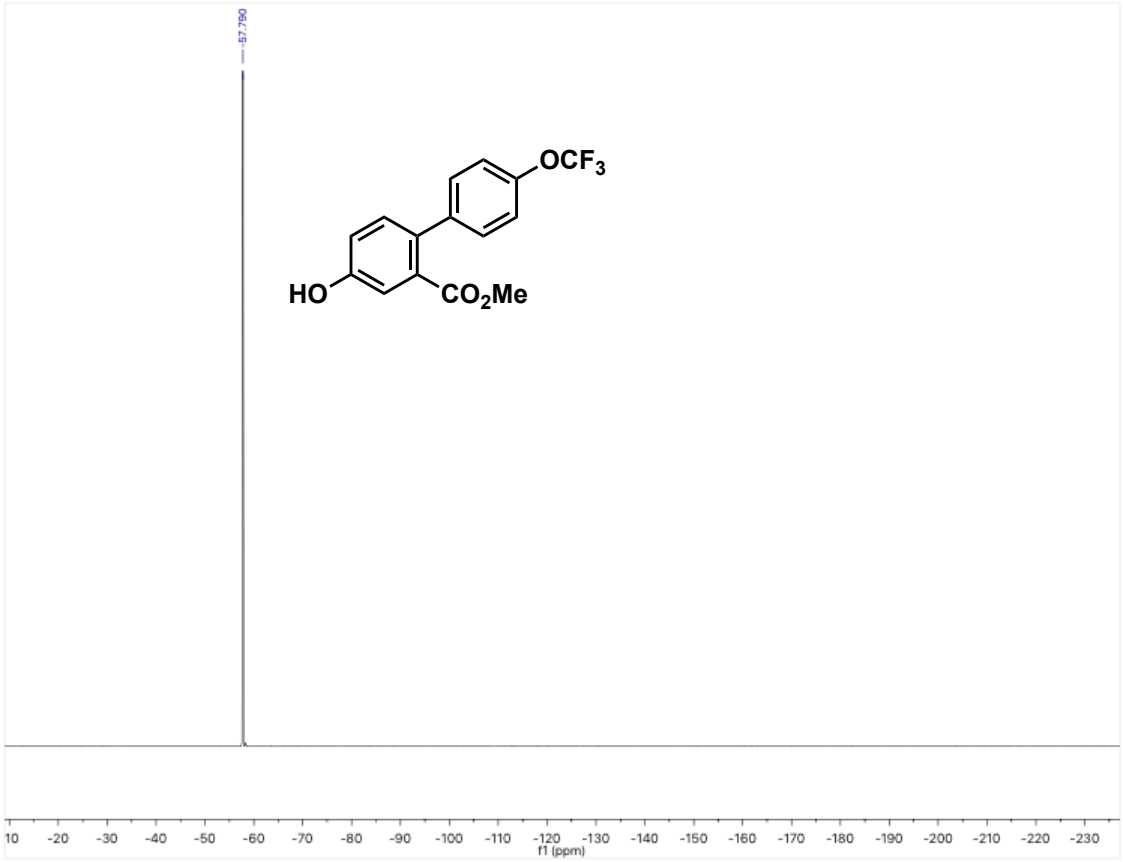
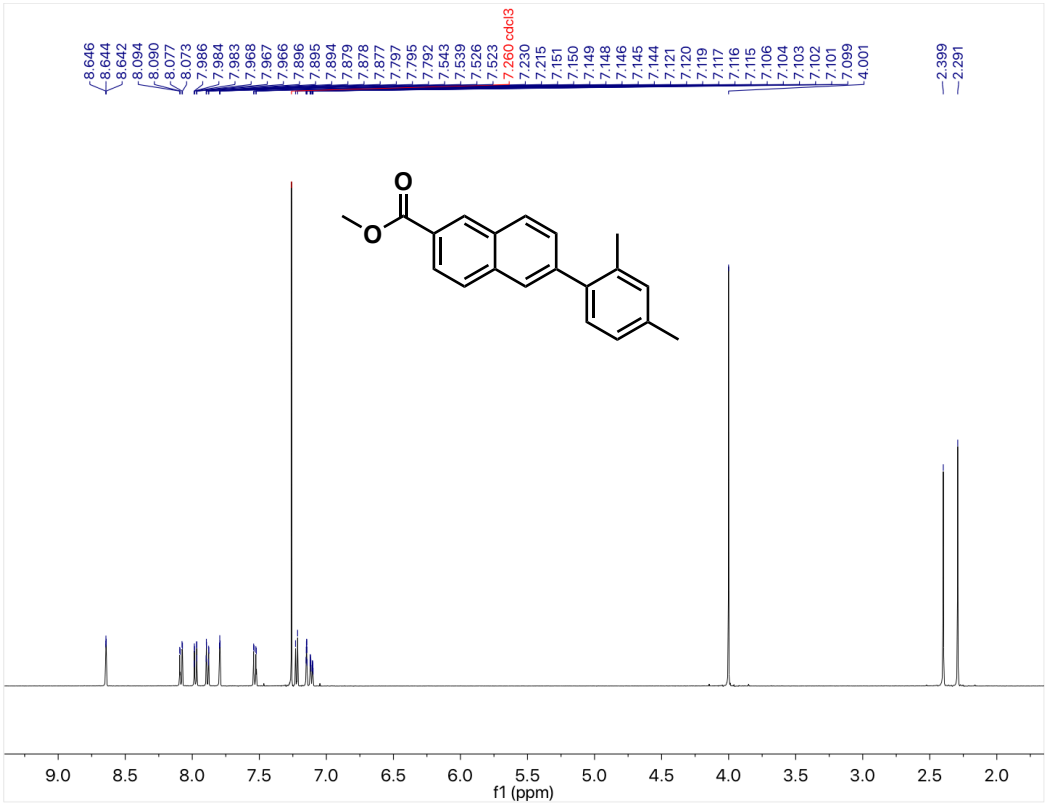
51.200
f1 (ppm)


-57.790
OCF3
HO
CO2Me
10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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8.090
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7.966
7.896
7.895
7.894
7.879
7.878
7.877
7.797
7.795
7.792
7.543
7.539
7.526
7.523
7.260 cdcl3
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7.215
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7.150
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7.148
7.146
7.145
7.144
7.121
7.120
7.119
7.117
7.116
7.115
7.106
7.104
7.103
7.102
7.101
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4.001
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2.291
O
O
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8.5
8.0
7.5
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2.0
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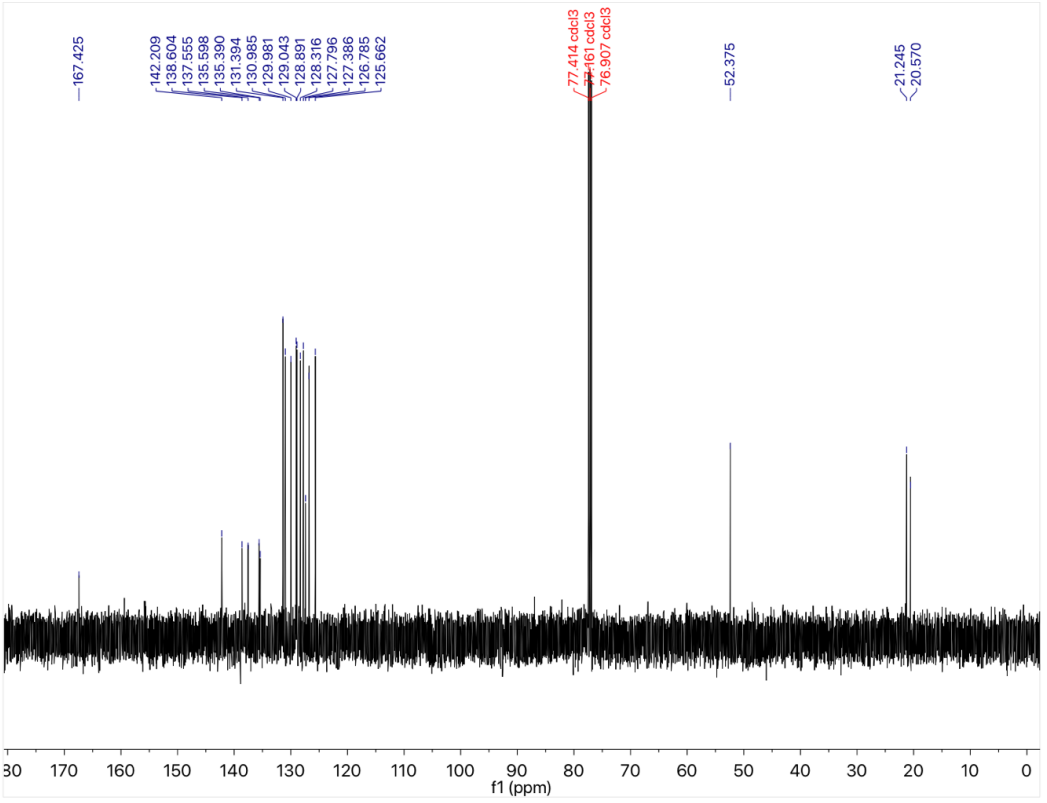
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128.891
128.316
127.796
127.386
126.785
125.662
77.414 cdcl3
77.161 cdcl3
76.907 cdcl3
52.375
21.245
20.570
30
170
160
150
140
130
120
110
100
90
80
70
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50
40
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20
10
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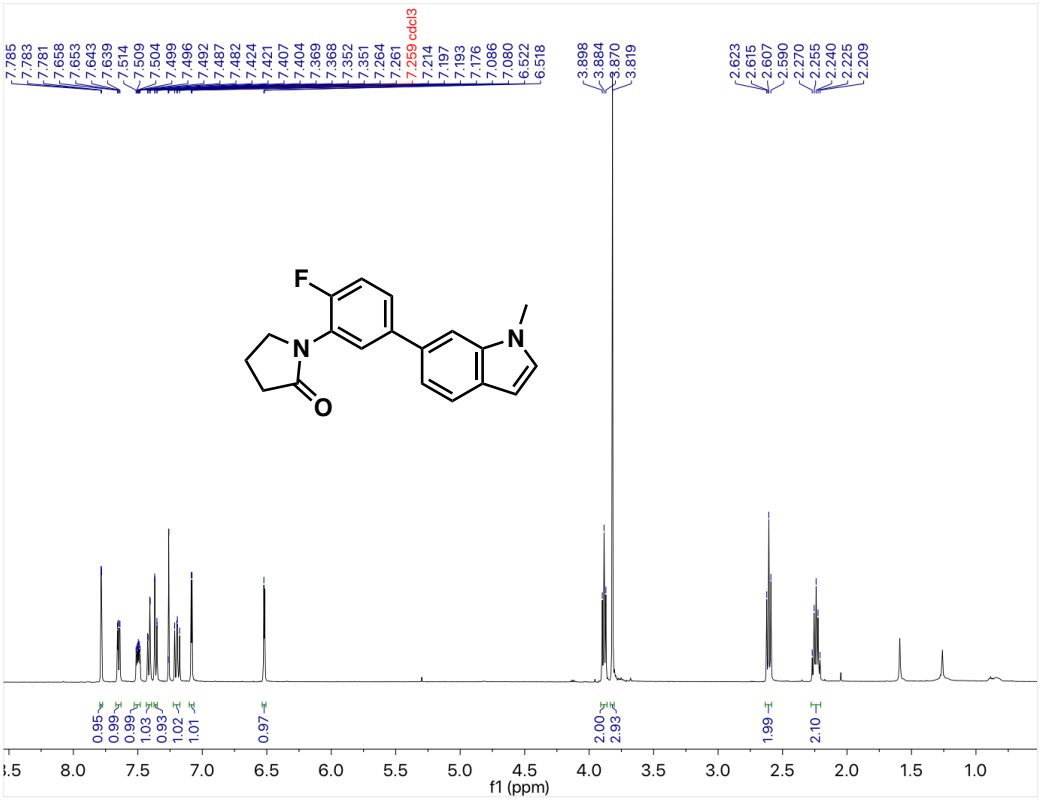
f1 (ppm)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7.424
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7.368
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7.351
7.264
7.261
7.259 cdcl3
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7.197
7.193
7.176
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7.080
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6.518
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3.870
3.819
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2.255
2.240
2.225
2.209
F
N
O
N
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0.93
1.02
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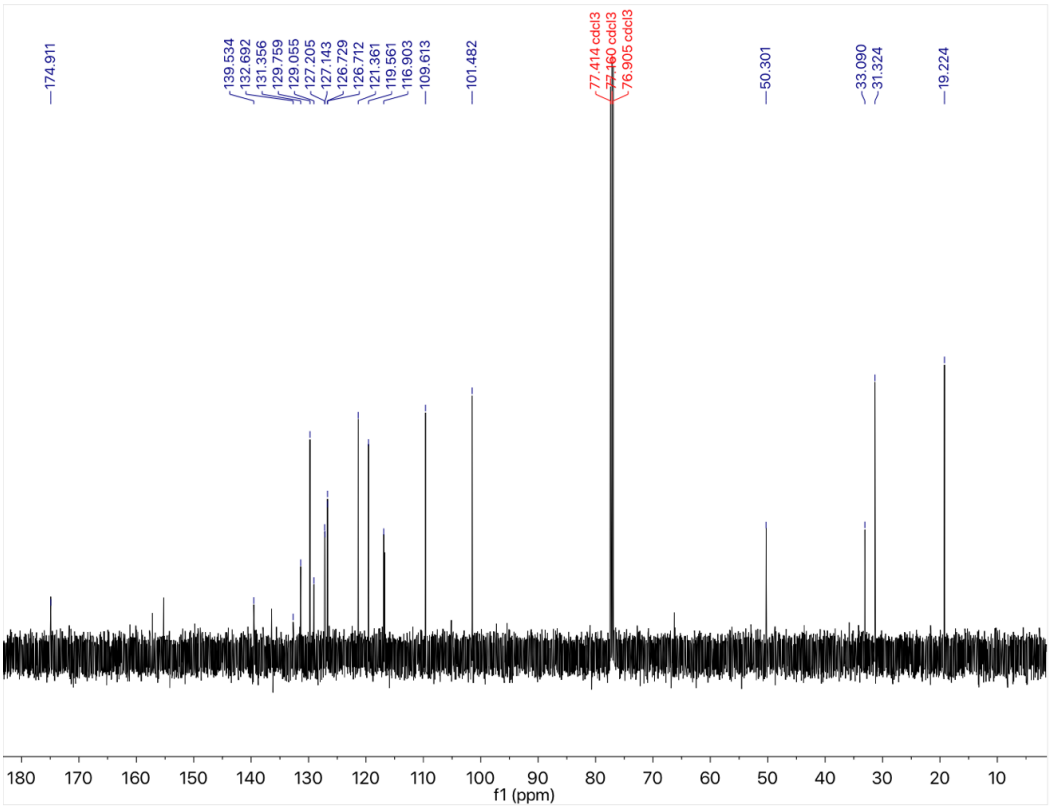
2.93
1.99
2.10
f1 (ppm)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127.143
126.729
126.712
121.361
119.561
116.903
109.613
101.482
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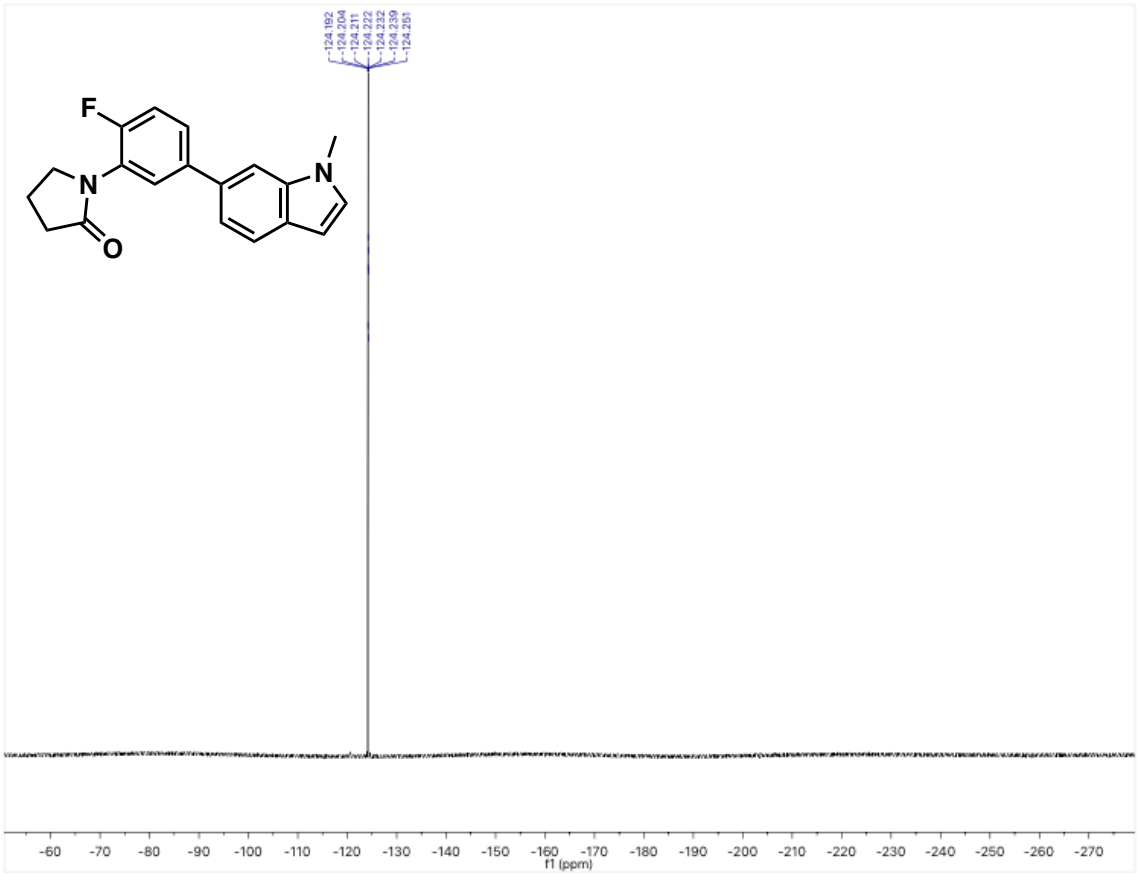
77.160 cdcl3
76.905 cdcl3
50.301
33.090
31.324
19.224
f1 (ppm)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-124.204
-124.211
-124.222
-124.232
-124.239
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F
N
N
O
-60
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-80
-90
-100
-110
-120
-130
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-200
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-220
-230
-240
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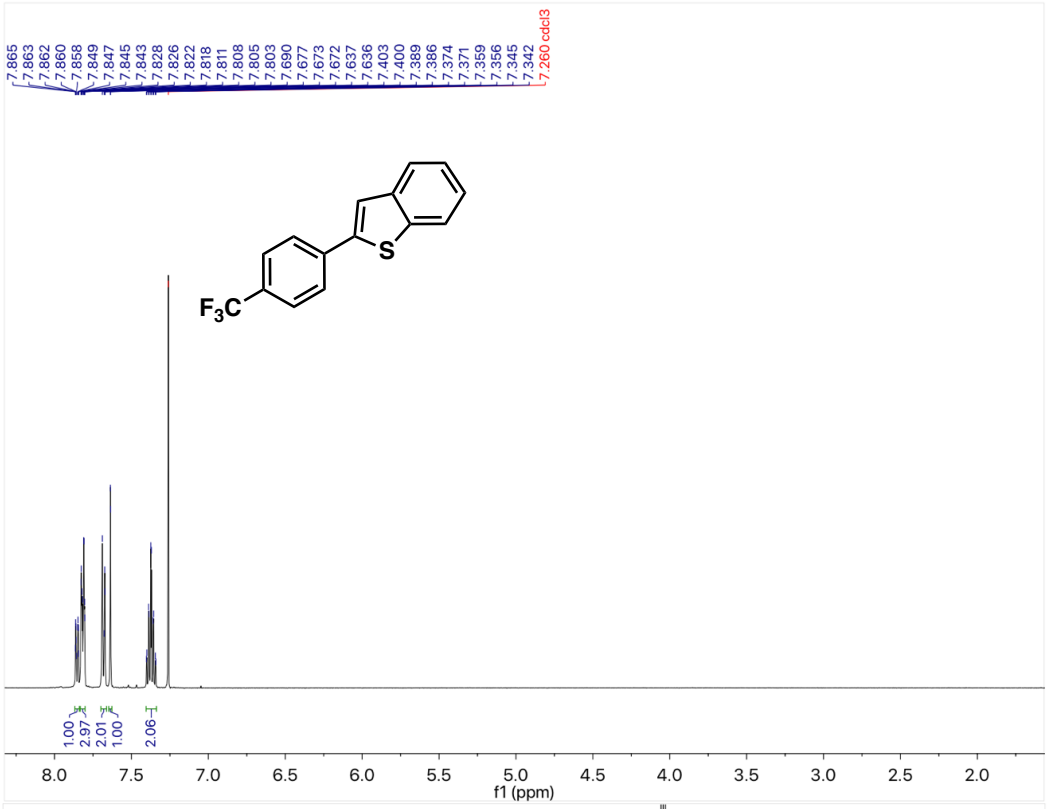
f1 (ppm)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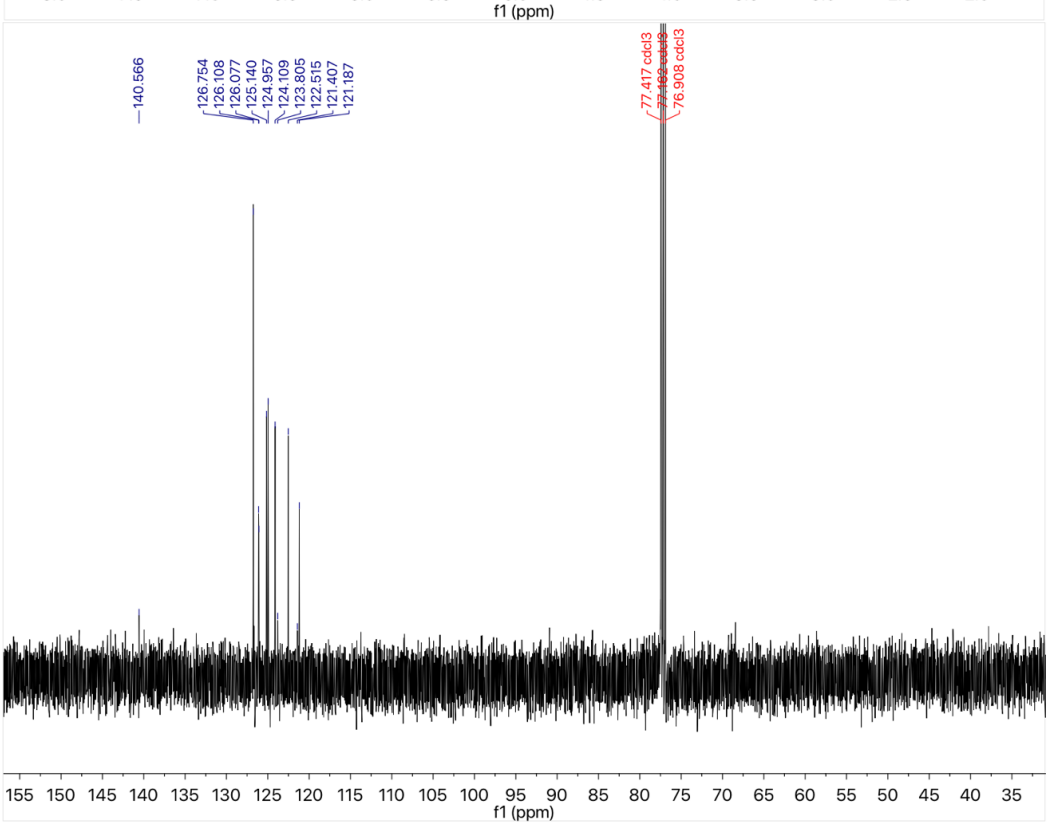
7.818
7.811
7.808
7.805
7.803
7.690
7.677
7.673
7.672
7.637
7.636
7.403
7.400
7.389
7.386
7.374
7.371
7.359
7.356
7.345
7.342
7.260 cdcl3
S
F3C
1.00
2.97
2.01
1.00
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)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124.109
123.805
122.515
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77.417 cdcl3
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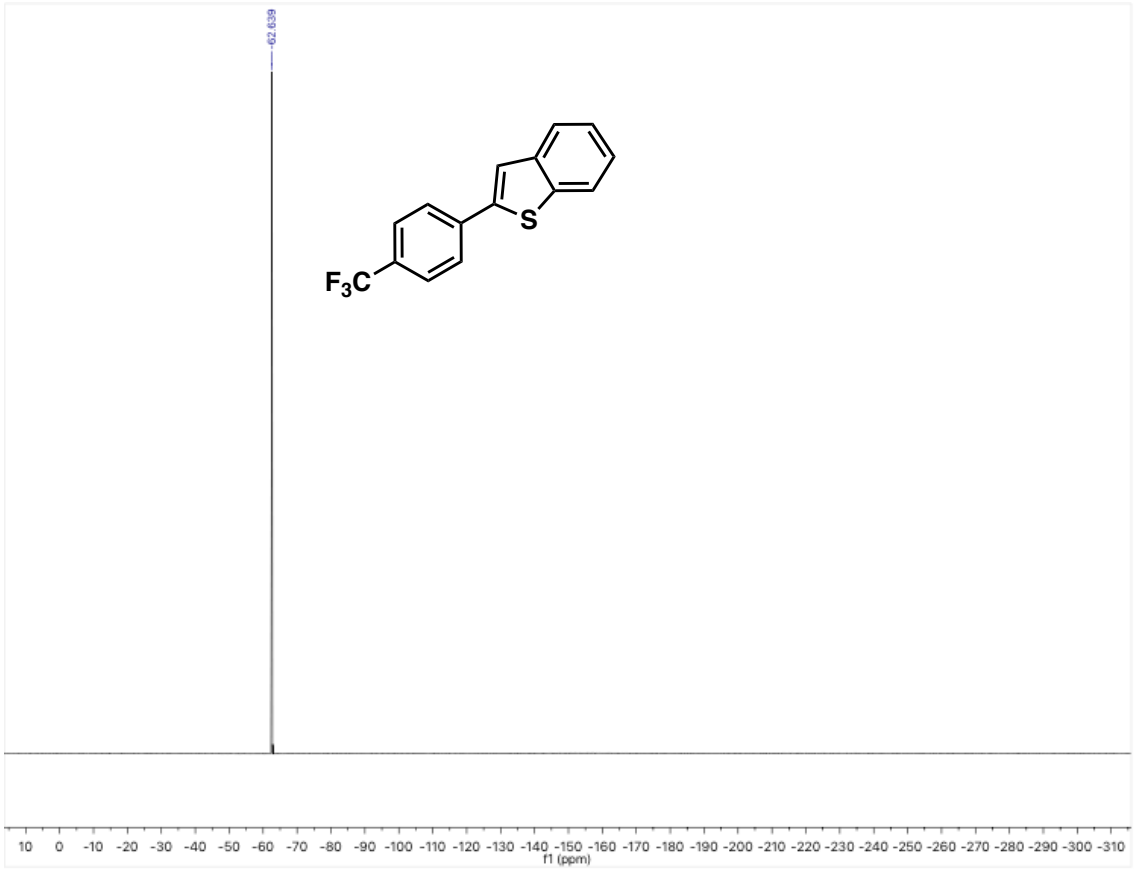
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)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S
F3C
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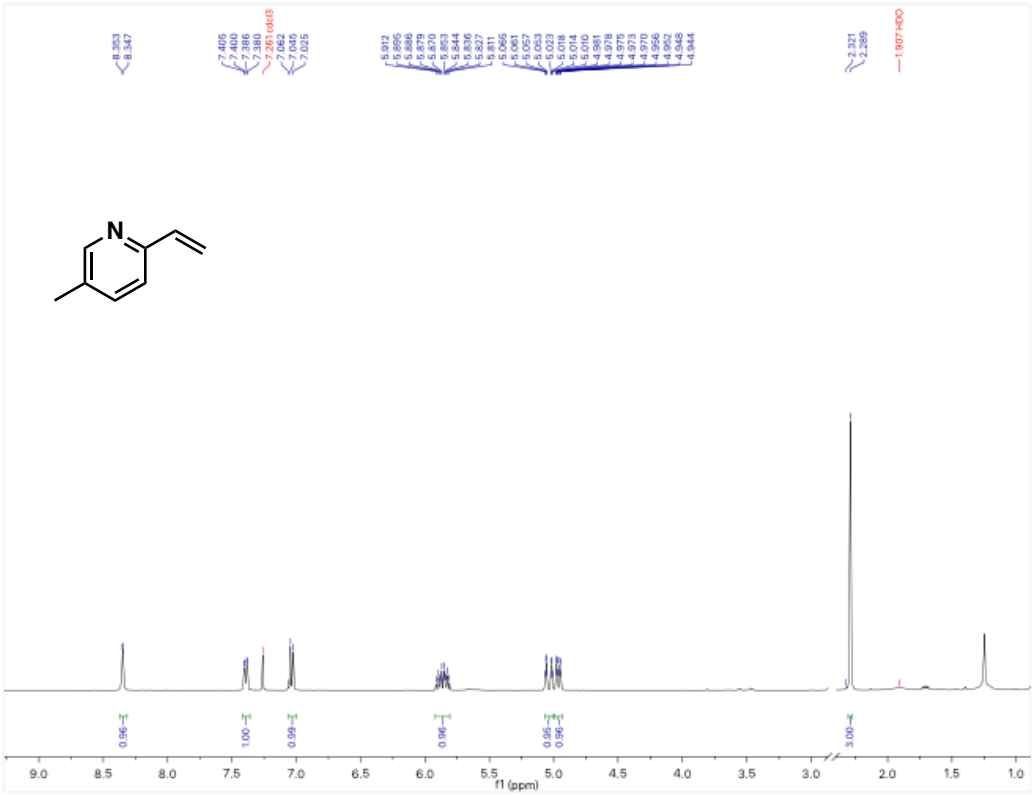
f1 (ppm)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8.347
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7.400
7.396
7.380
7.261 cdcl3
7.062
7.045
7.025
5.912
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5.886
5.879
5.870
5.853
5.844
5.836
5.827
5.811
5.065
5.061
5.057
5.053
5.023
5.018
5.014
5.010
4.981
4.978
4.975
4.973
4.970
4.956
4.953
4.948
4.944
2.321
2.269
1.907 HDO
0.96
1.00
0.99
0.96
0.95
0.96
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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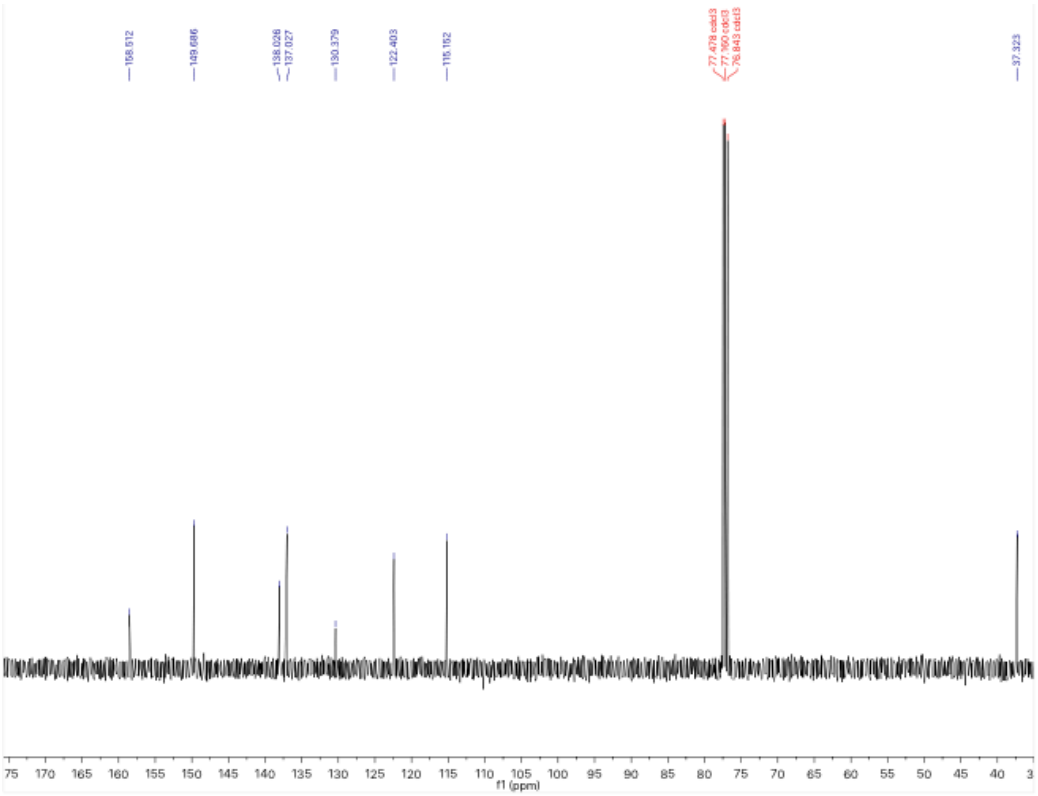
5.0
4.5
4.0
3.5
3.0
2.0
1.5
1.0
f1 (ppm)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115.152
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77.160 cdcl3
76.843 cdcl3
37.323
75
170
165
160
155
150
145
140
135
130
125
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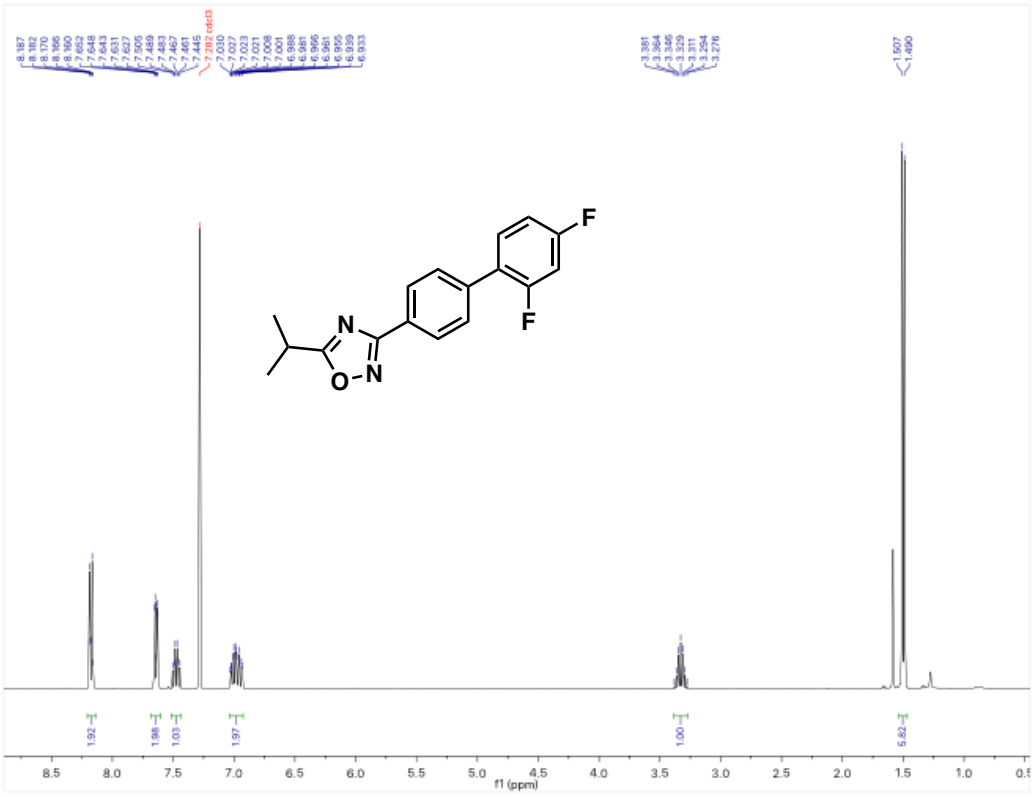
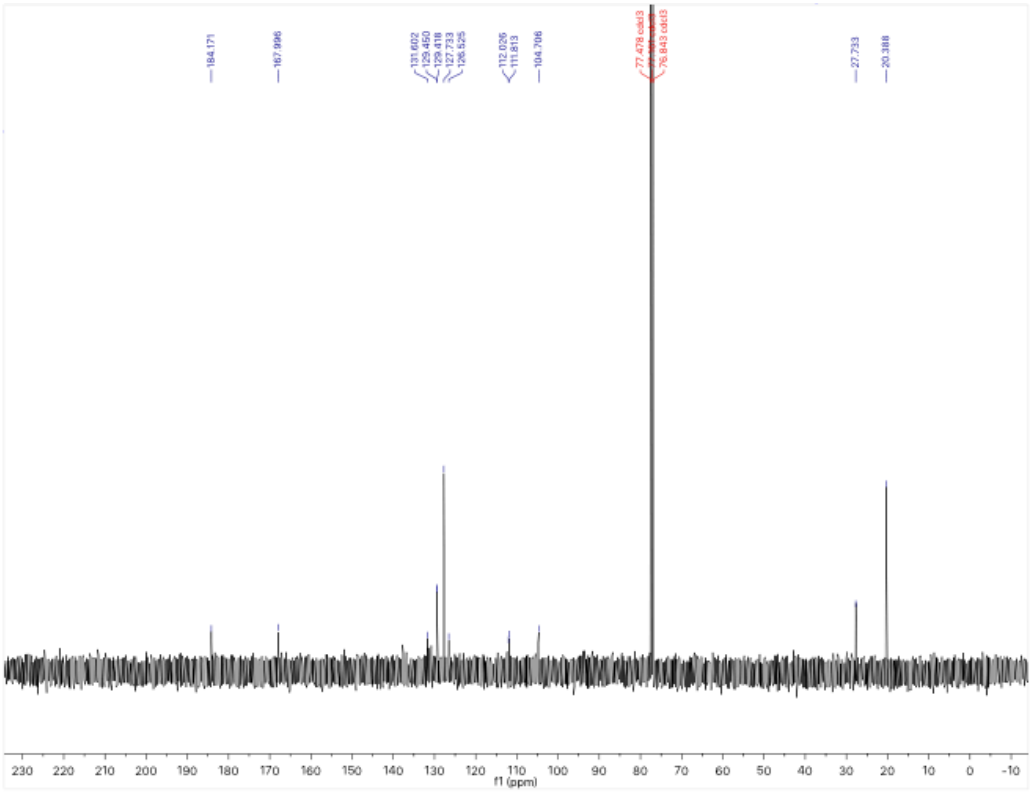
65
60
55
50
45
40
3
f1 (ppm)


F
F
N
O
N
f1 (ppm)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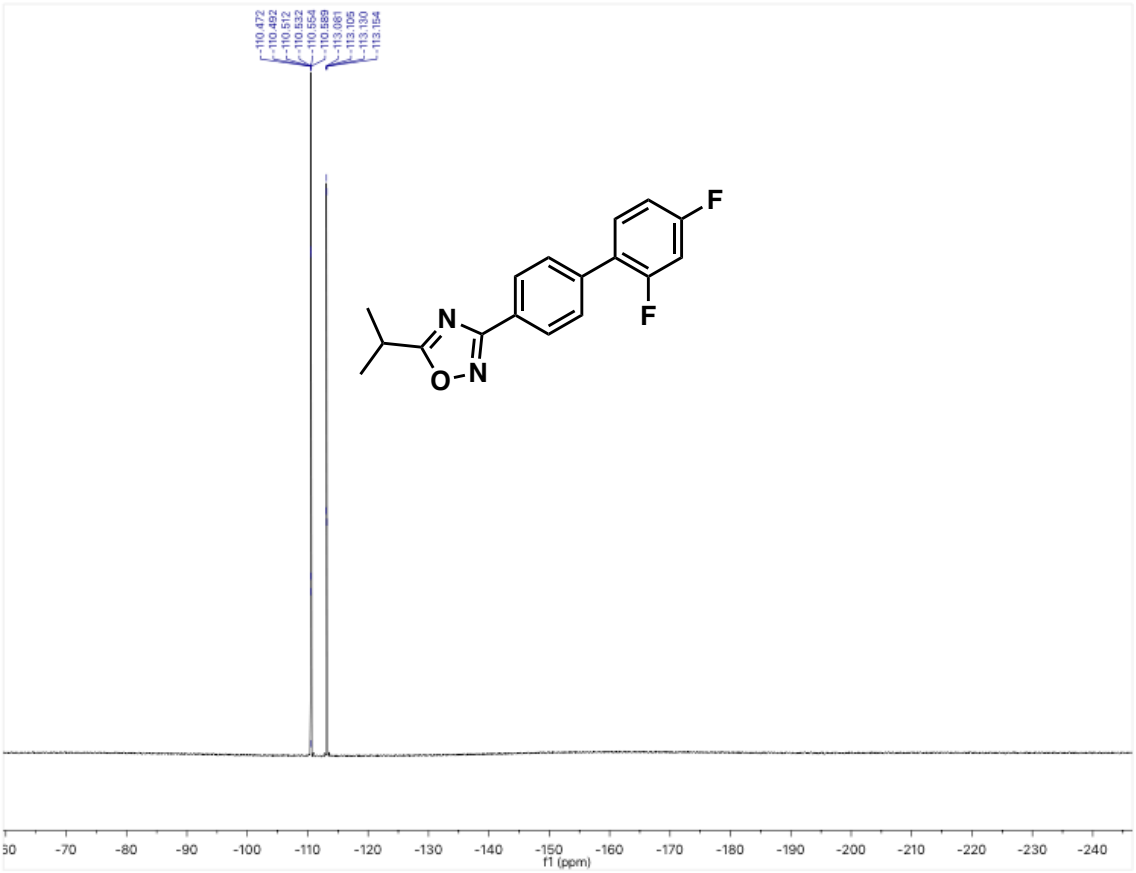
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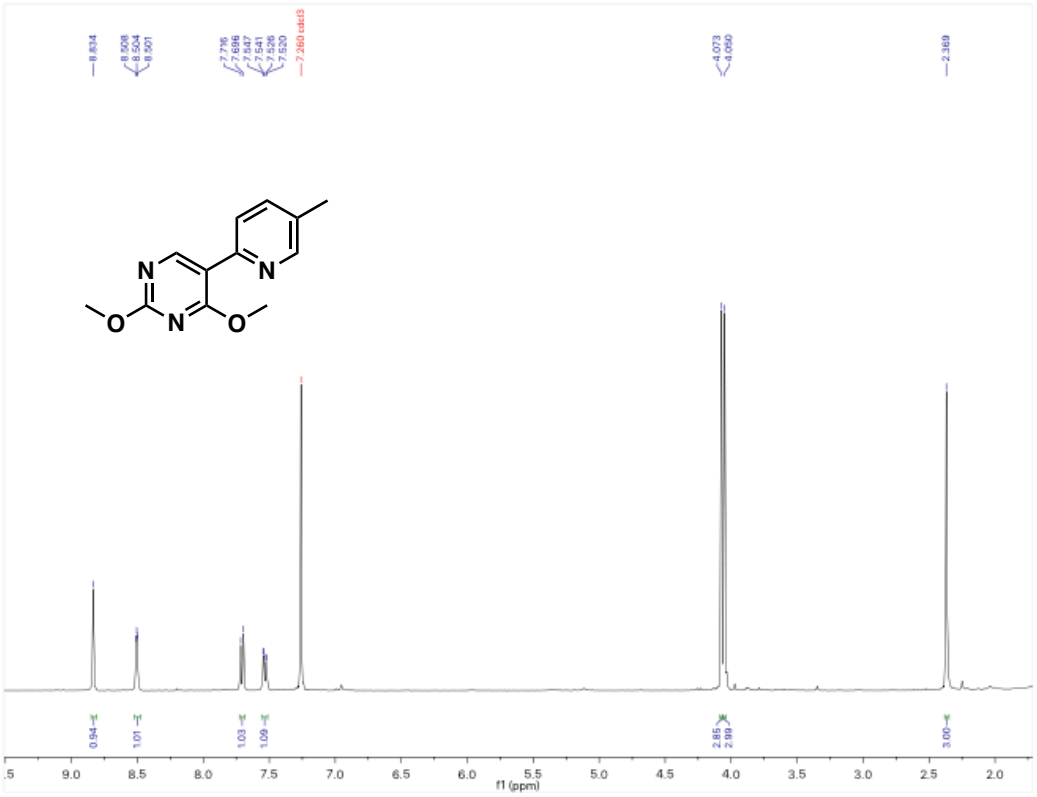
-110.512
-110.532
-110.554
-110.569
-113.081
-113.105
-113.130
-113.154
F
F
N
O
N
-50
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)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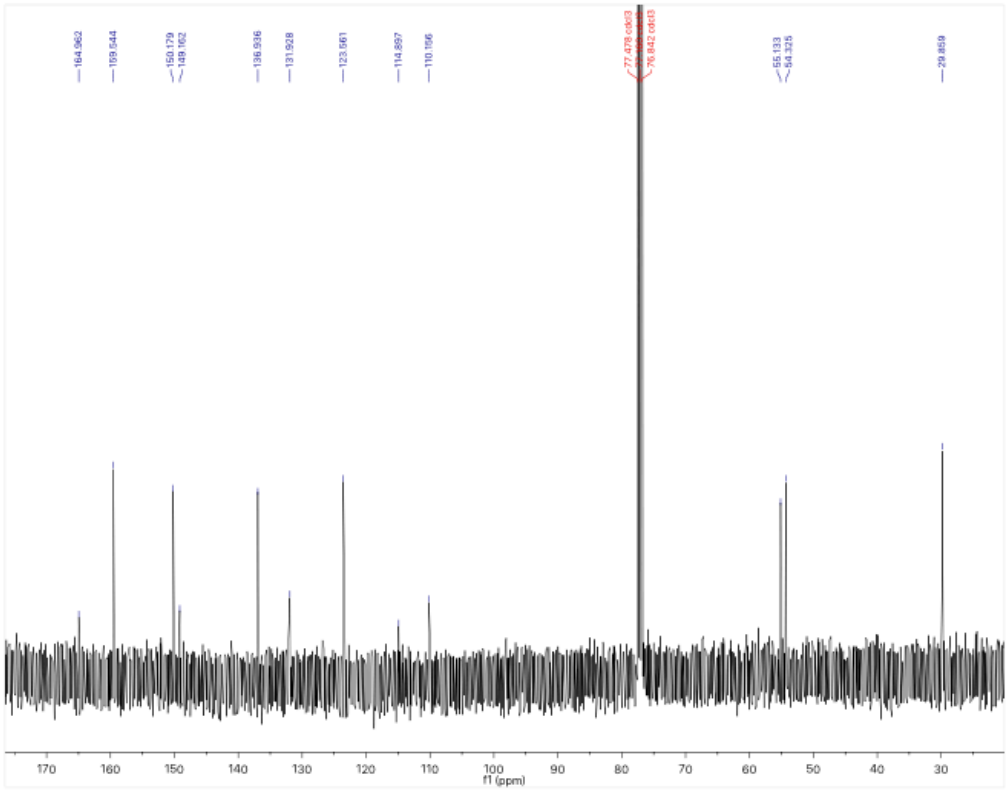
8.504
8.501
7.726
7.696
7.547
7.541
7.526
7.520
7.260 cdcl3
4.073
4.050
2.369
N
N
O
N
O
0.94
1.01
1.03
1.09
2.85
2.99
3.00
f1 (ppm)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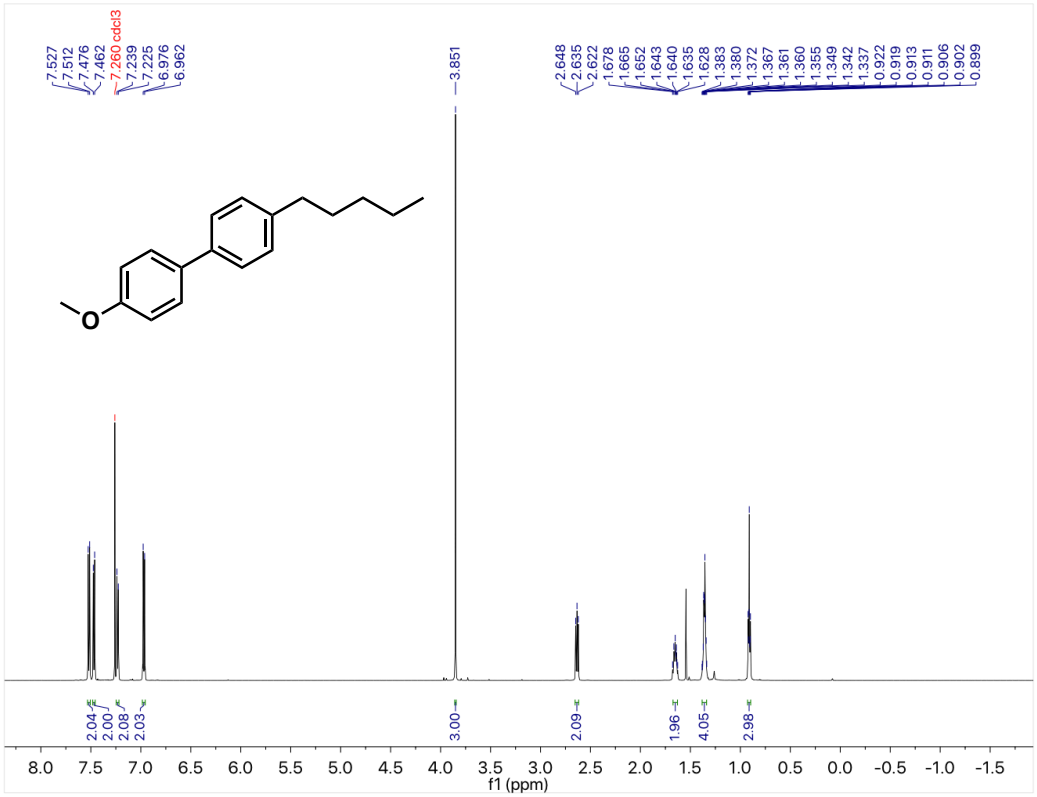
150.179
149.162
136.936
131.928
123.561
114.897
110.196
77.478 cdcl3
76.842 cdcl3
55.133
54.325
29.859
f1 (ppm)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7.512
7.476
7.462
7.260 cdcl3
7.239
7.225
6.976
6.962
3.851
2.648
2.635
2.622
1.678
1.665
1.652
1.643
1.640
1.635
1.628
1.383
1.380
1.372
1.367
1.361
1.360
1.355
1.349
1.342
1.337
0.922
0.919
0.913
0.911
0.906
0.902
0.899
O
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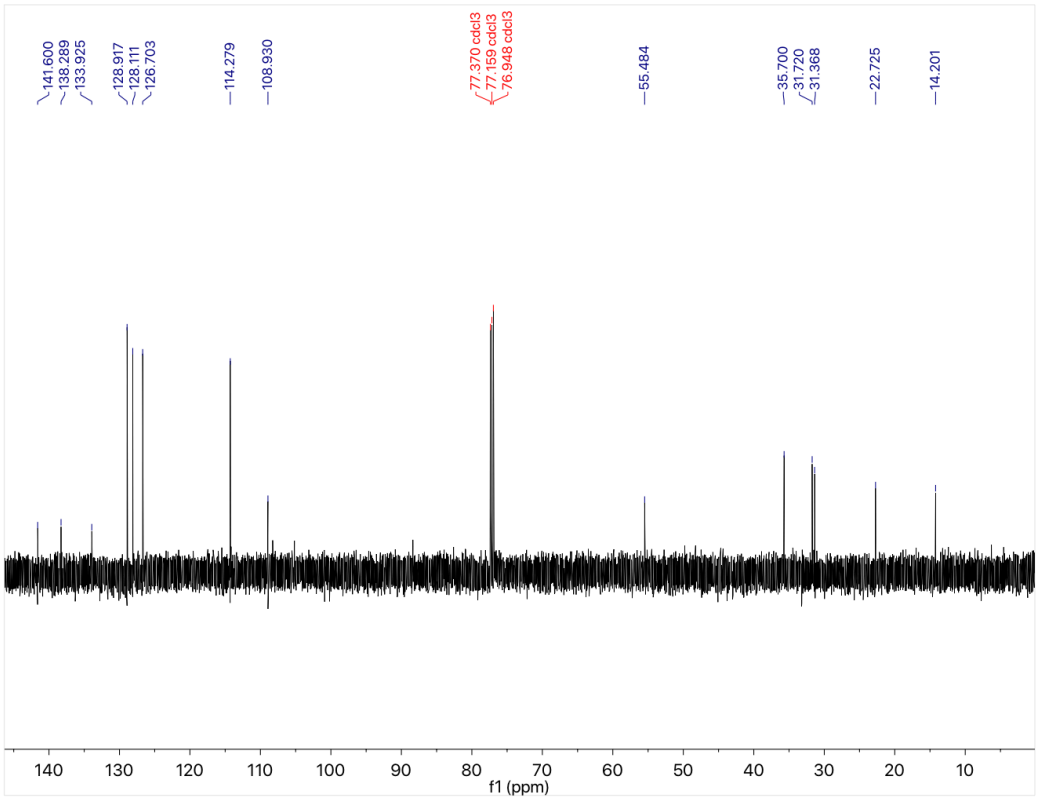
2.00
2.08
2.03
3.00
2.09
1.96
4.05
2.98
f1 (ppm)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138.289
133.925
128.917
128.111
126.703
114.279
108.930
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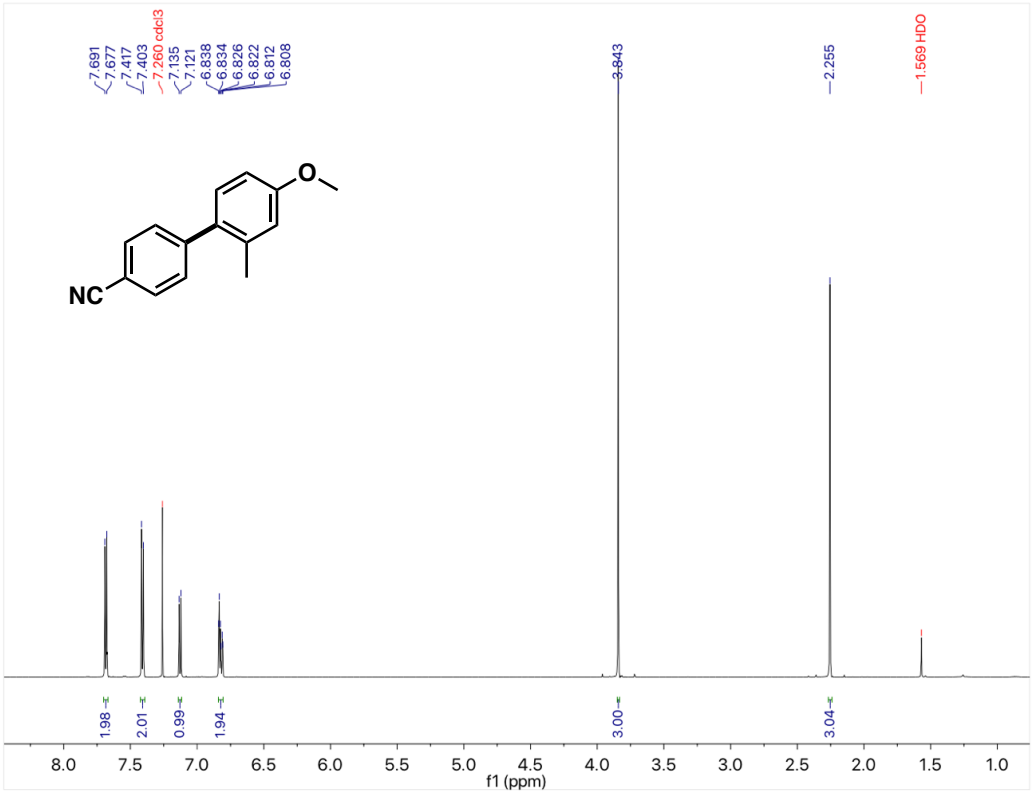
76.948 cdcl3
55.484
35.700
31.720
31.368
22.725
14.201
f1 (ppm)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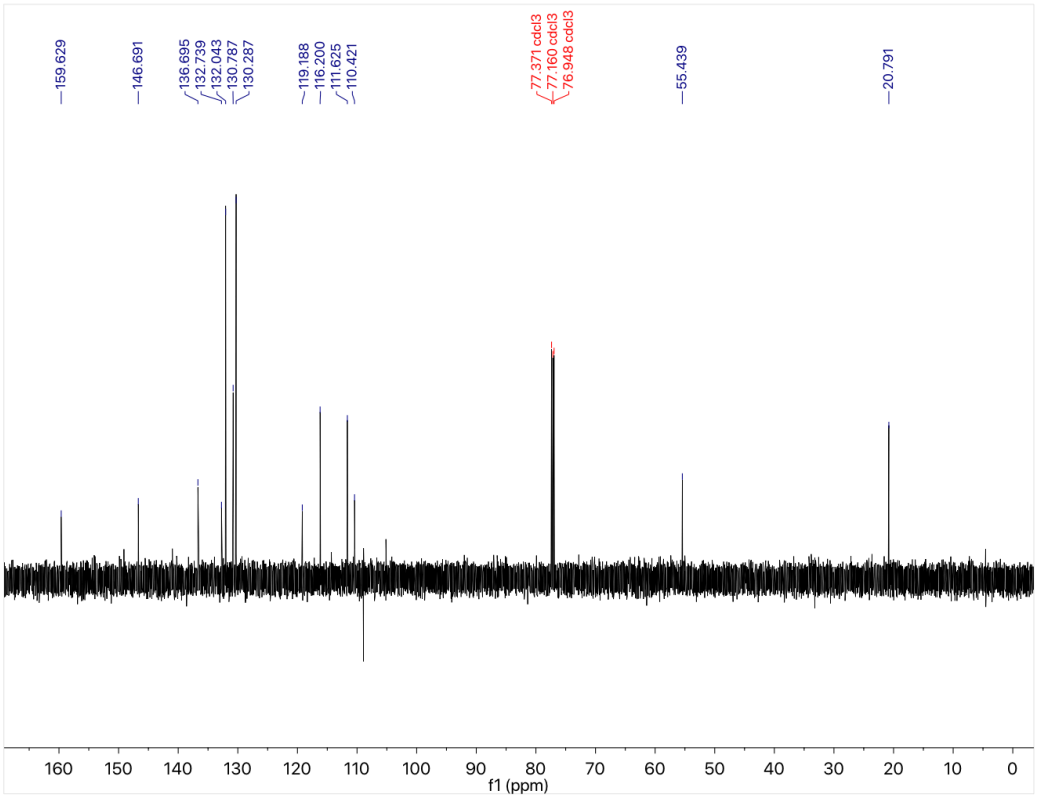
7.417
7.403
7.260 cdcl3
7.135
7.121
6.838
6.834
6.826
6.822
6.812
6.808
3.843
2.255
1.569 HDO
O
NC
1.98
2.01
0.99
1.94
3.00
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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136.695
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130.287
119.188
116.200
111.625
110.421
77.371 cdcl3
77.160 cdcl3
76.948 cdcl3
55.439
20.791
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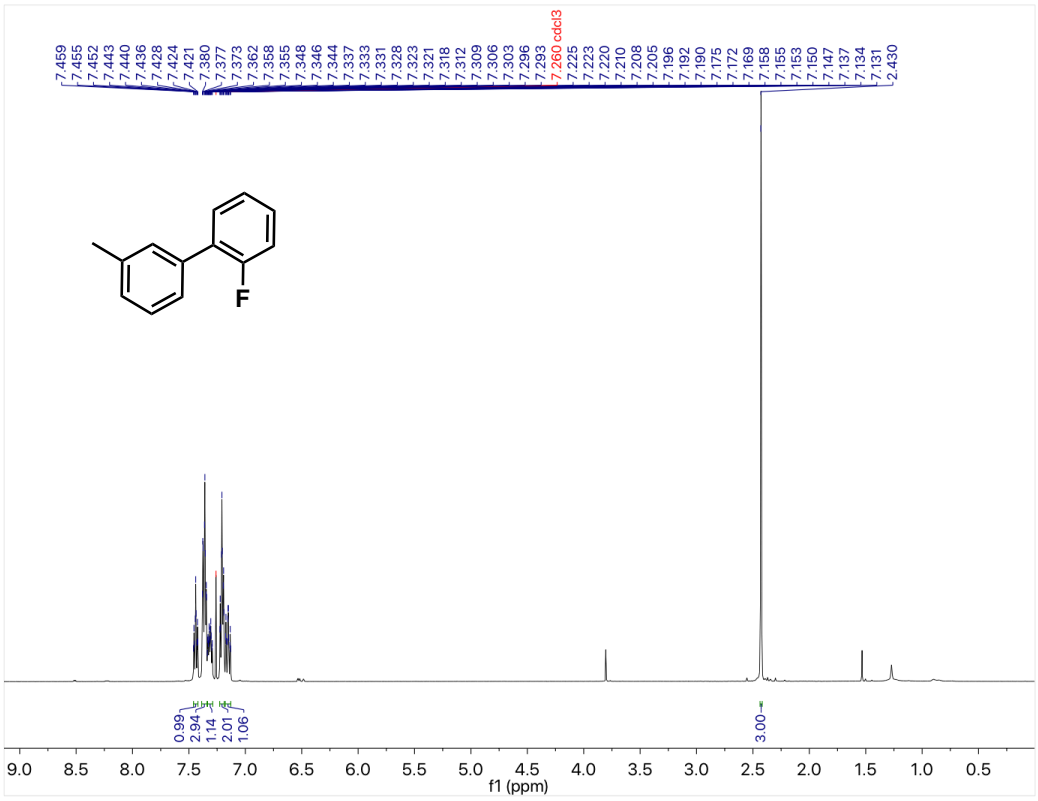
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.362
7.358
7.355
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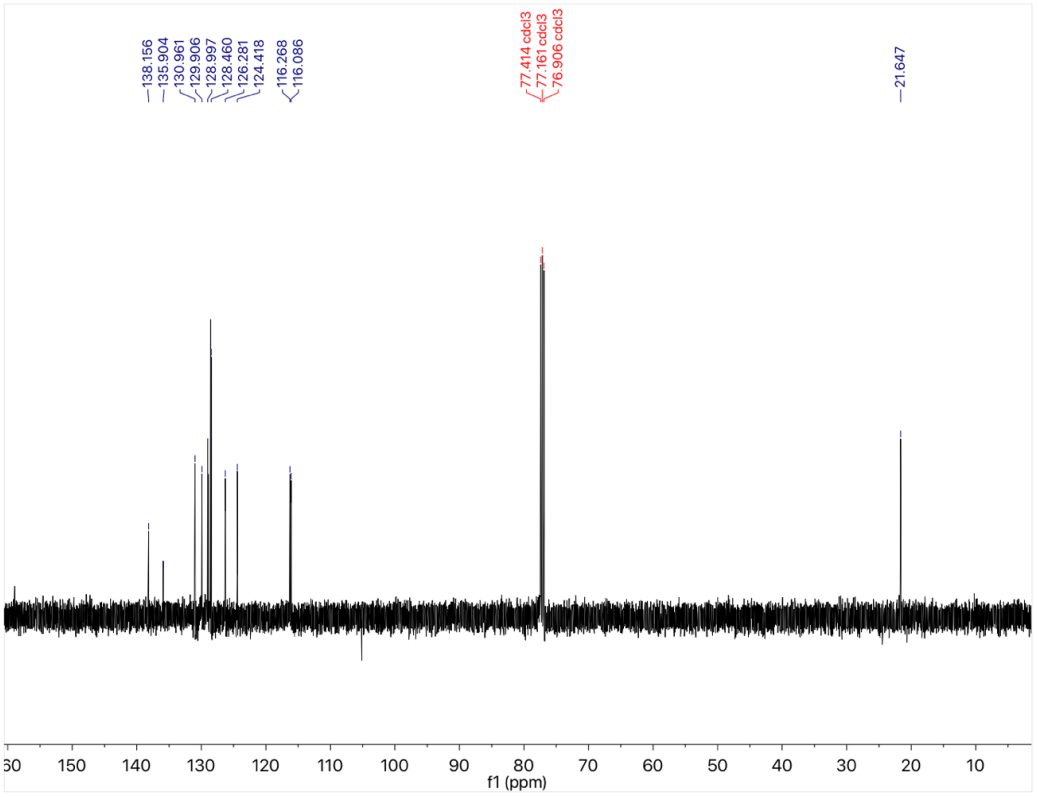
7.346
7.344
7.337
7.333
7.331
7.328
7.323
7.321
7.318
7.312
7.309
7.306
7.303
7.296
7.293
7.260 cdcl3
7.225
7.223
7.220
7.210
7.208
7.205
7.196
7.192
7.190
7.175
7.172
7.169
7.158
7.155
7.153
7.150
7.147
7.137
7.134
7.131
2.430
F
0.99
2.94
1.14
2.01
1.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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124.418
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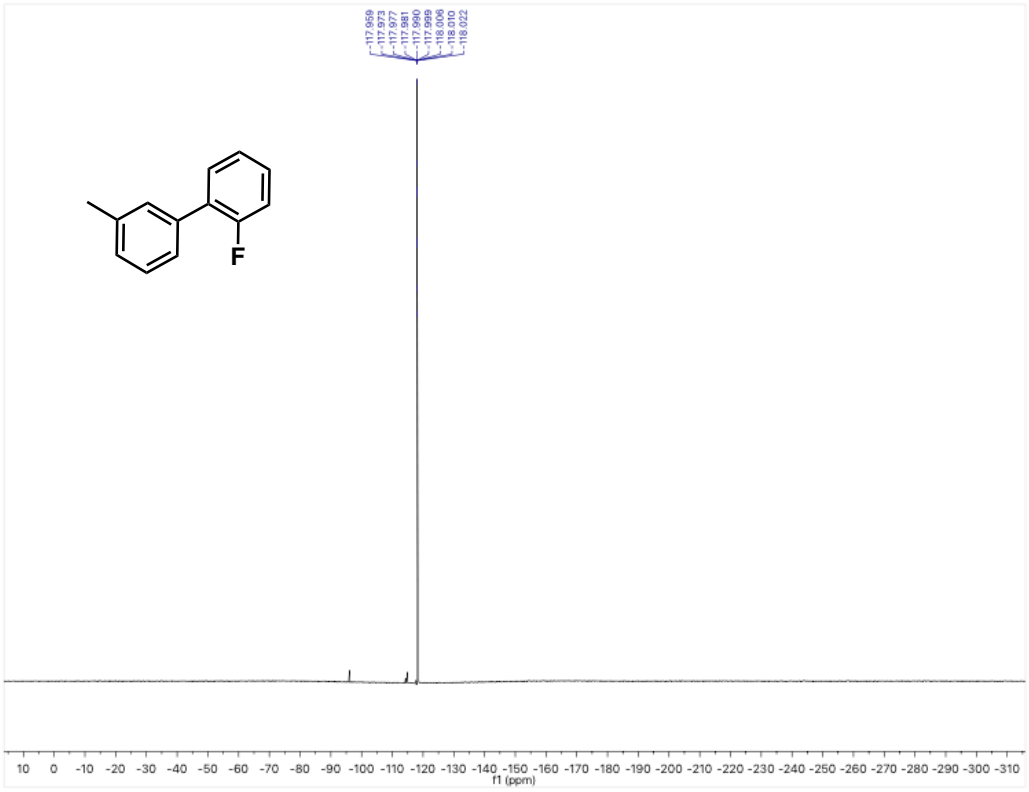
77.161 cdcl3
76.906 cdcl3
21.647
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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-117.973
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-118.006
-118.010
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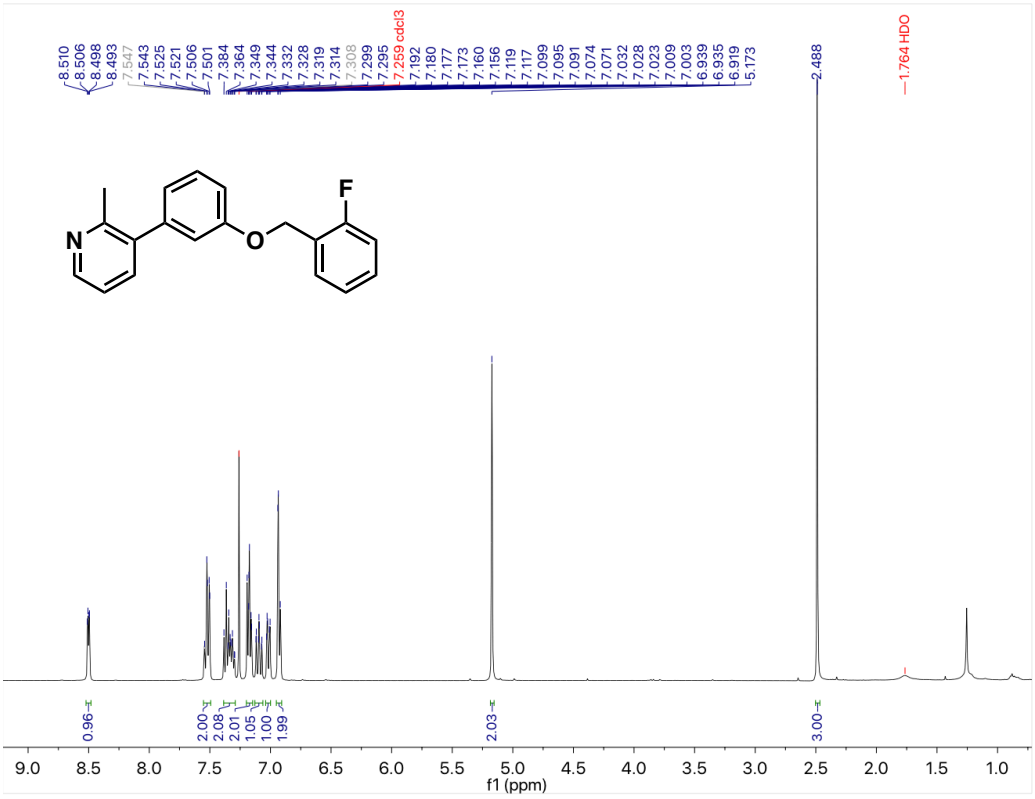
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)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7.349
7.344
7.332
7.328
7.319
7.314
7.308
7.299
7.295
7.259 cdcl3
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7.180
7.177
7.173
7.160
7.156
7.119
7.117
7.099
7.095
7.091
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7.023
7.009
7.003
6.939
6.935
6.919
5.173
2.488
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F
N
O
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2.00
2.08
2.01
1.05
1.00
1.99
2.03
3.00
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8.5
8.0
7.5
7.0
6.5
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3.5
3.0
2.5
2.0
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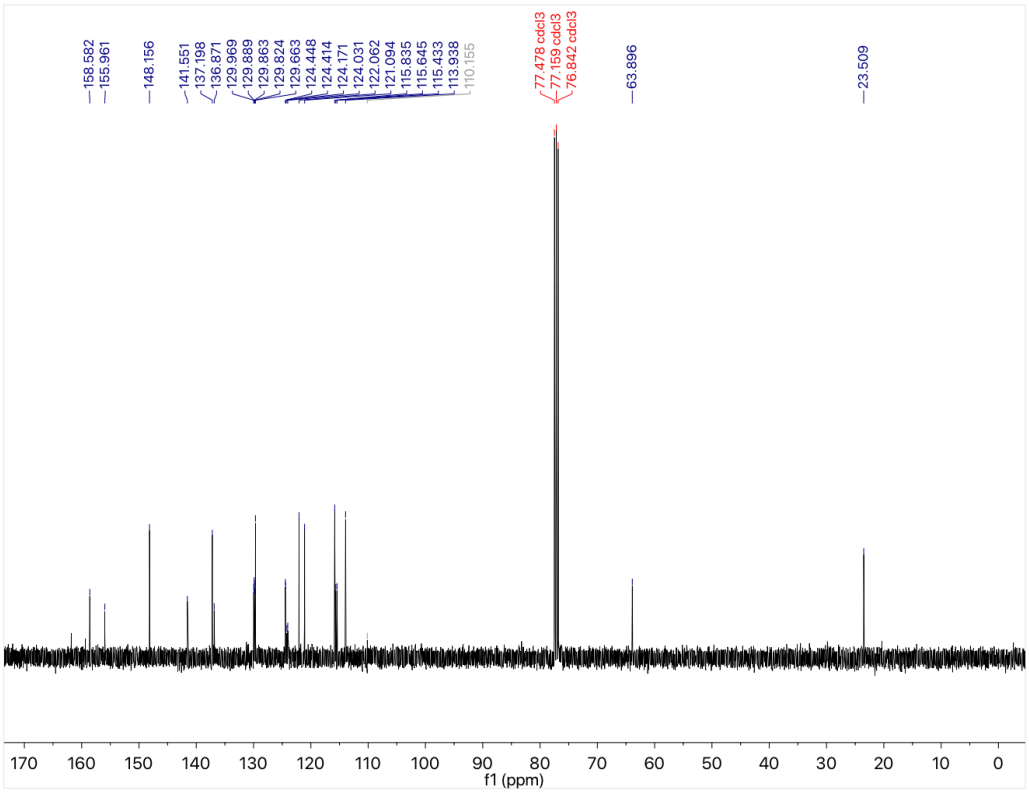
1.0
f1 (ppm)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129.663
124.448
124.414
124.171
124.031
122.062
121.094
115.835
115.645
115.433
113.938
110.155
77.478 cdcl3
77.159 cdcl3
76.842 cdcl3
63.896
23.509
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130
120
110
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90
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70
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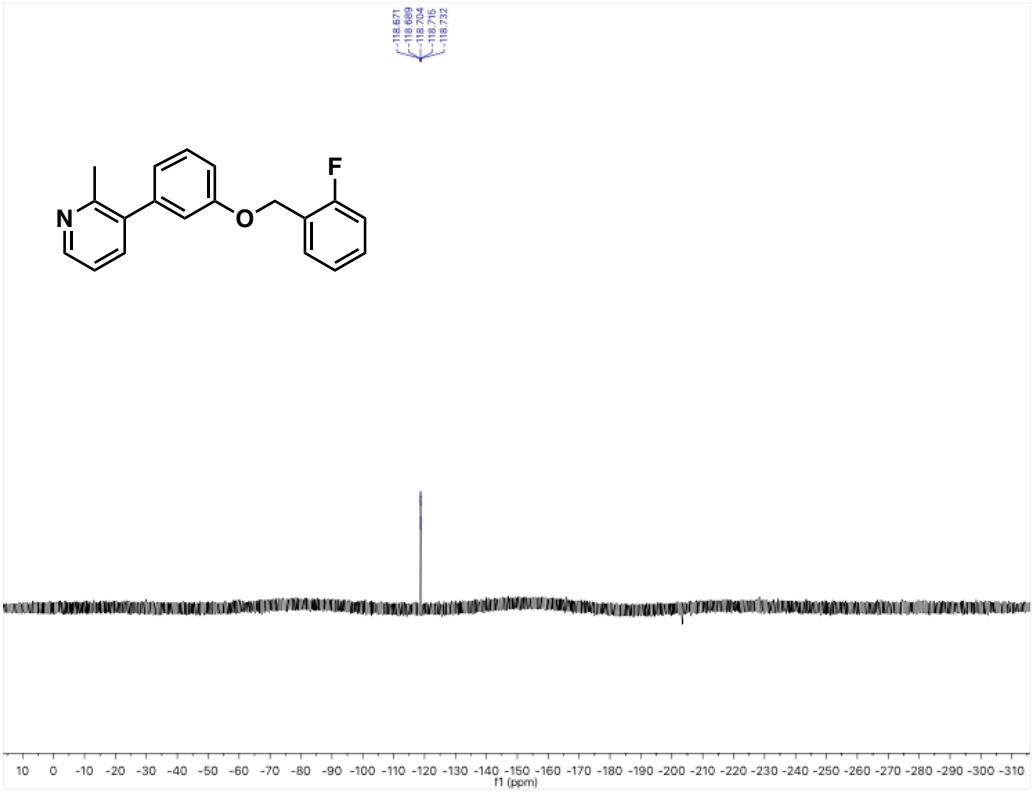
50
40
30
20
10
0
f1 (ppm)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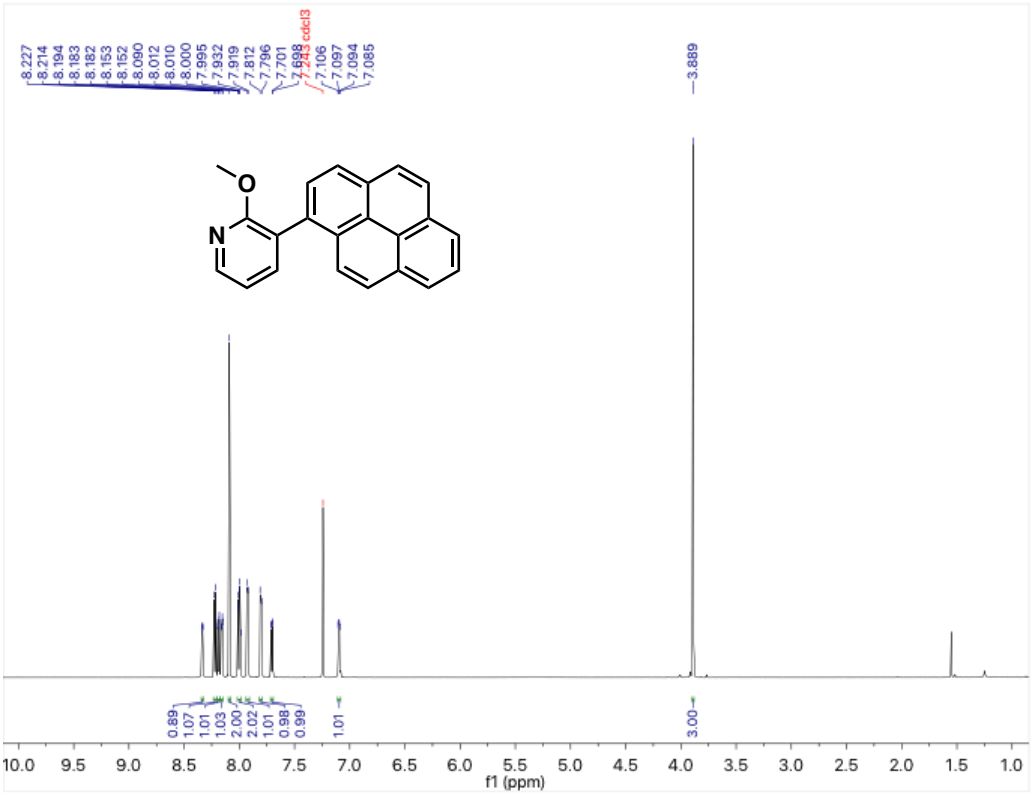
-118.689
-118.704
-118.715
-118.732
F
N
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)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8.152
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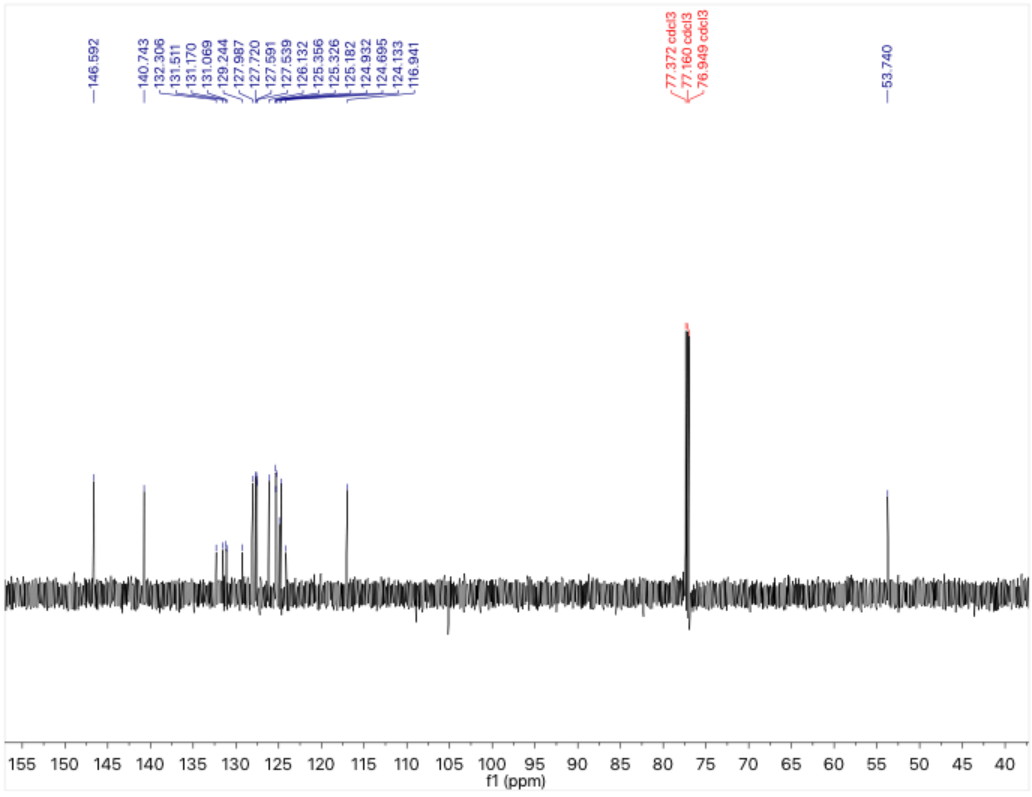
8.012
8.010
8.000
7.995
7.932
7.919
7.812
7.796
7.701
7.598 cdcl3
7.106
7.097
7.094
7.085
3.889
O
N
0.89
1.07
1.01
1.03
2.00
2.02
1.01
0.98
0.99
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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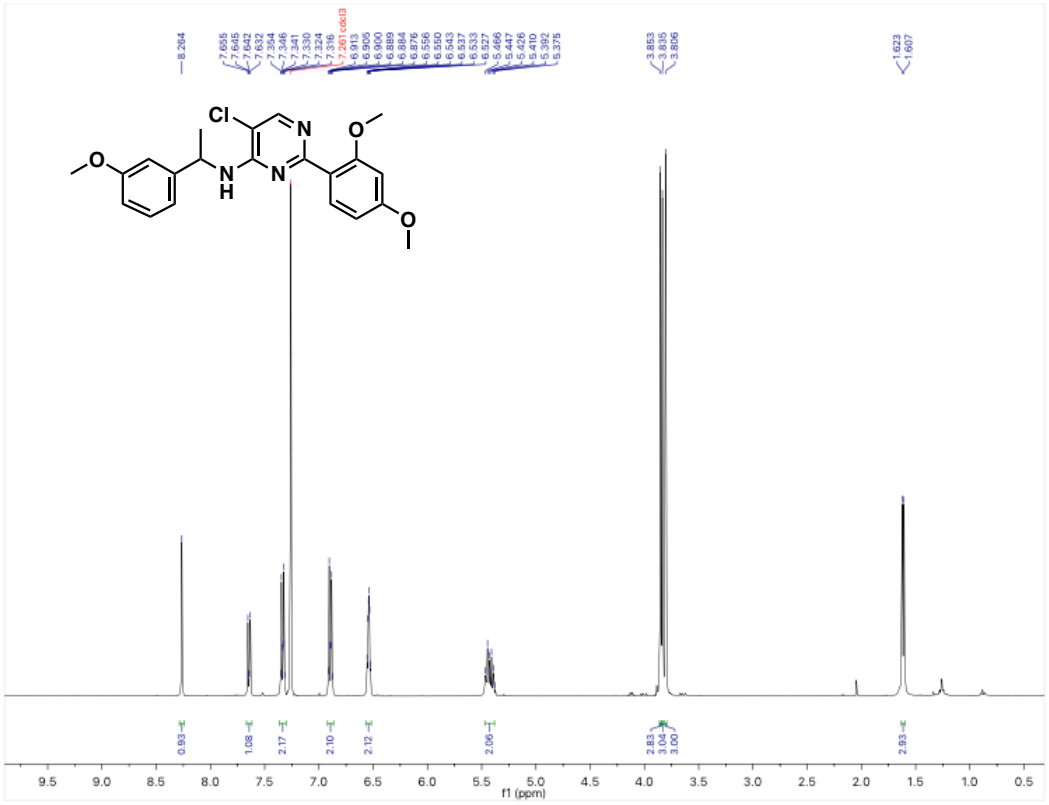
125.356
125.326
125.182
124.932
124.695
124.133
116.941
77.372 cdcl3
77.160 cdcl3
76.949 cdcl3
53.740
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)


Cl
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O
N
H
N
O
O
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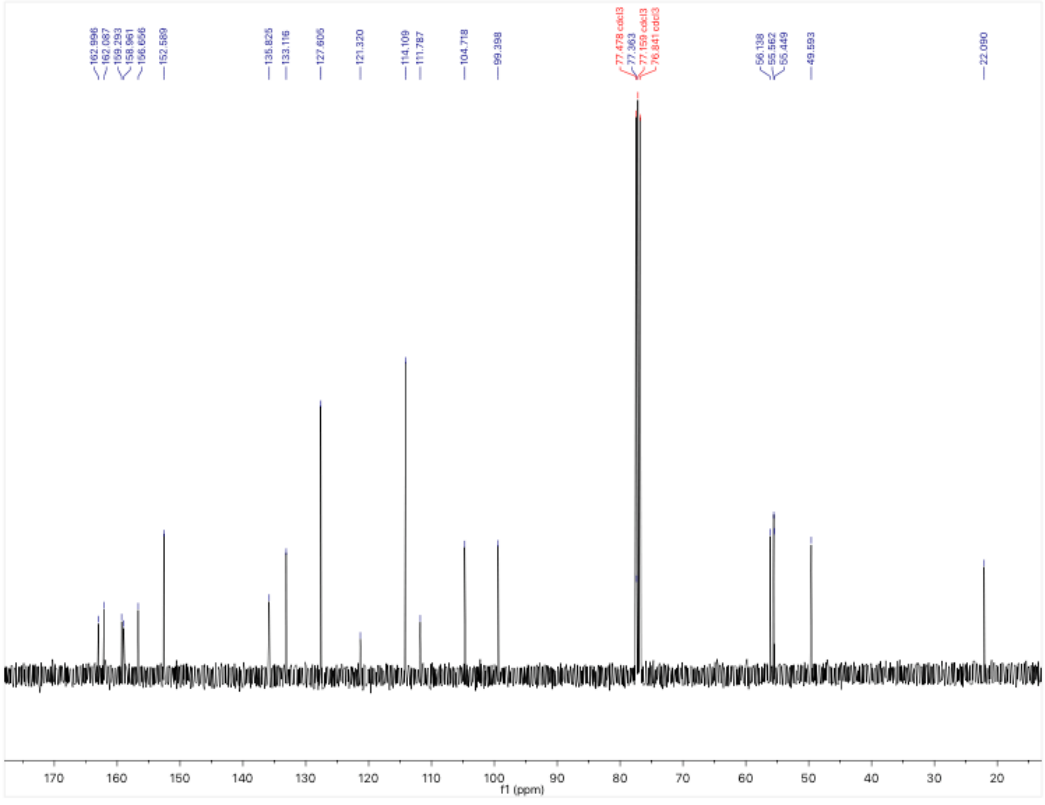
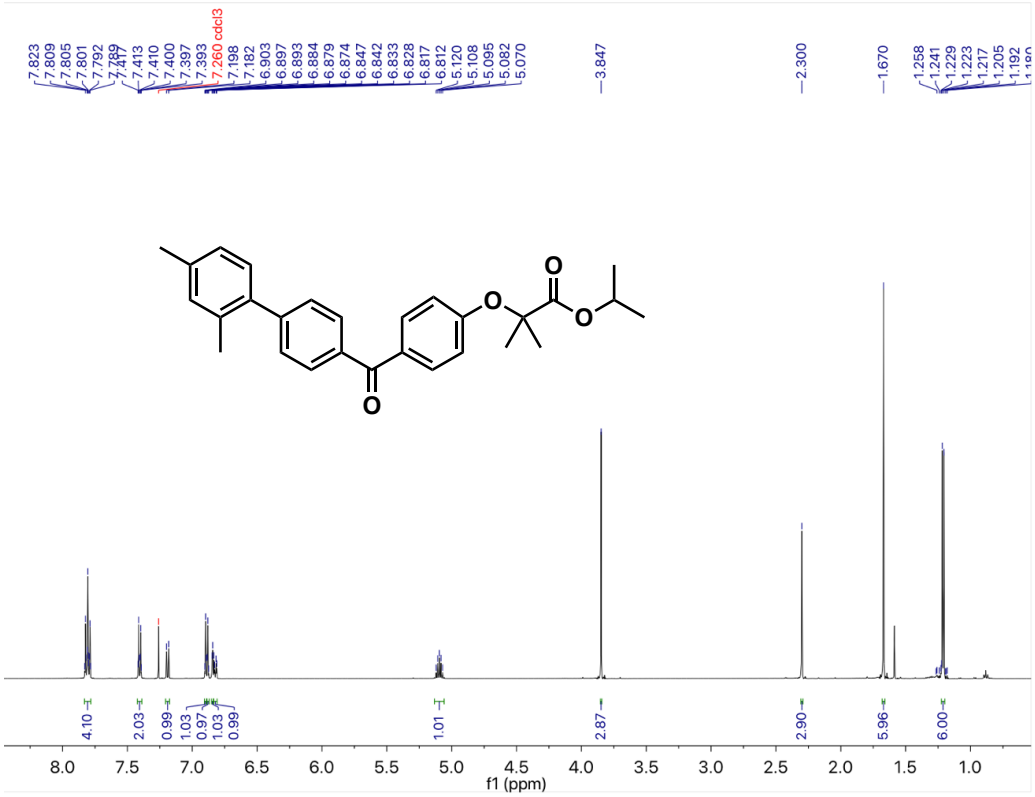

f1 (ppm)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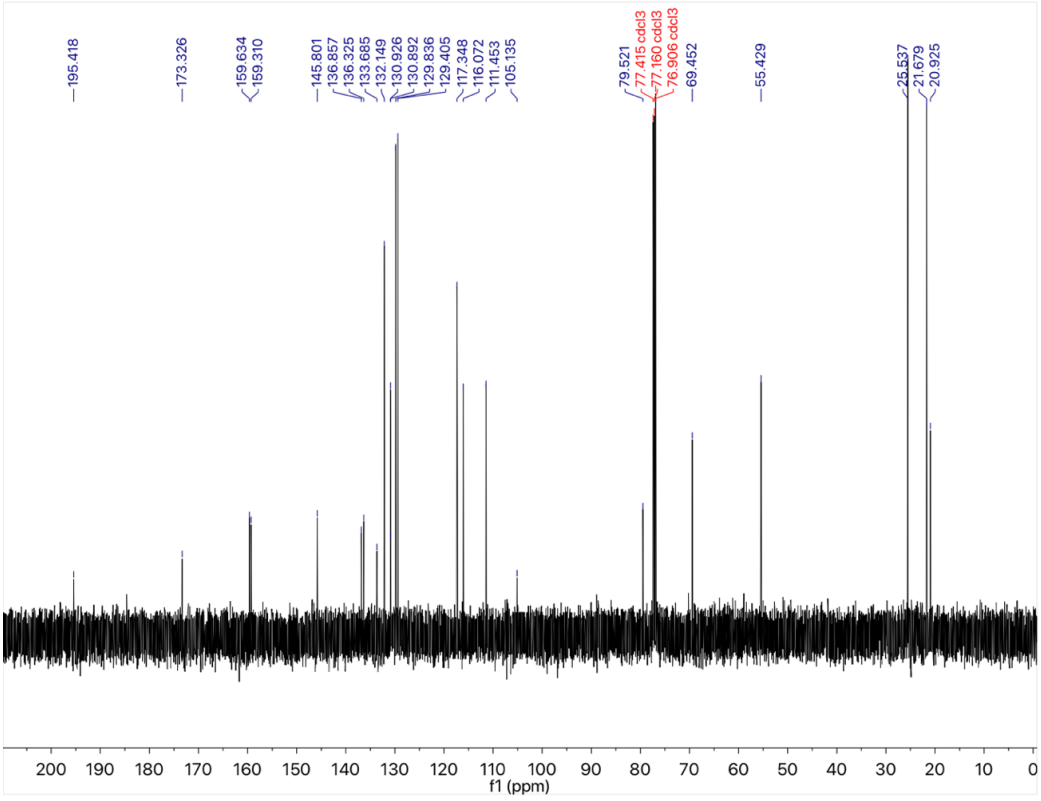
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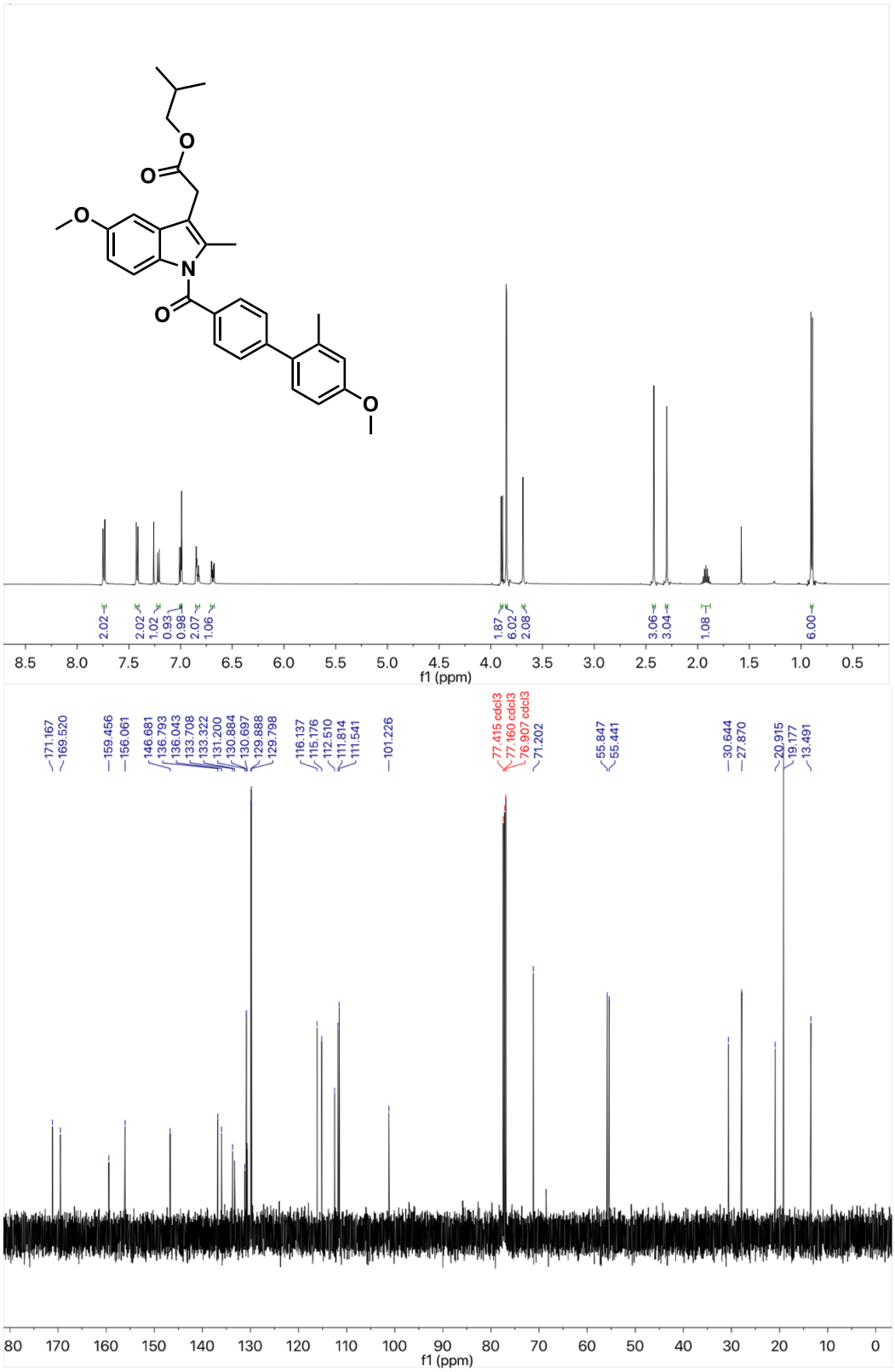
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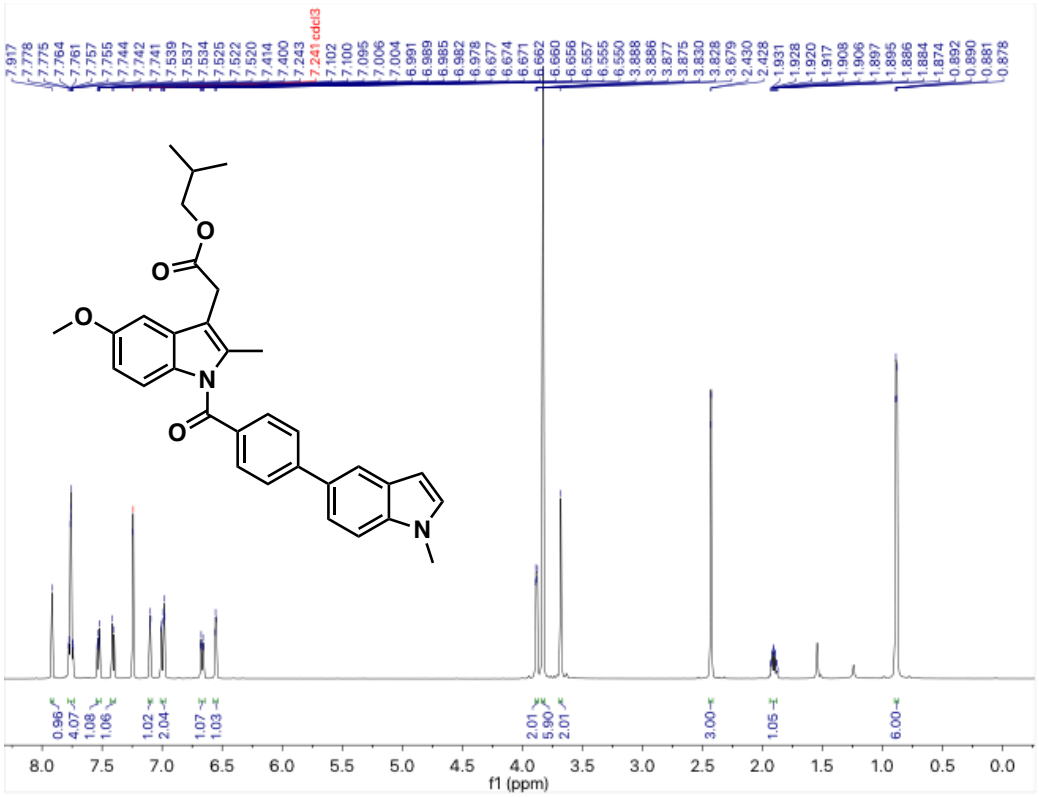
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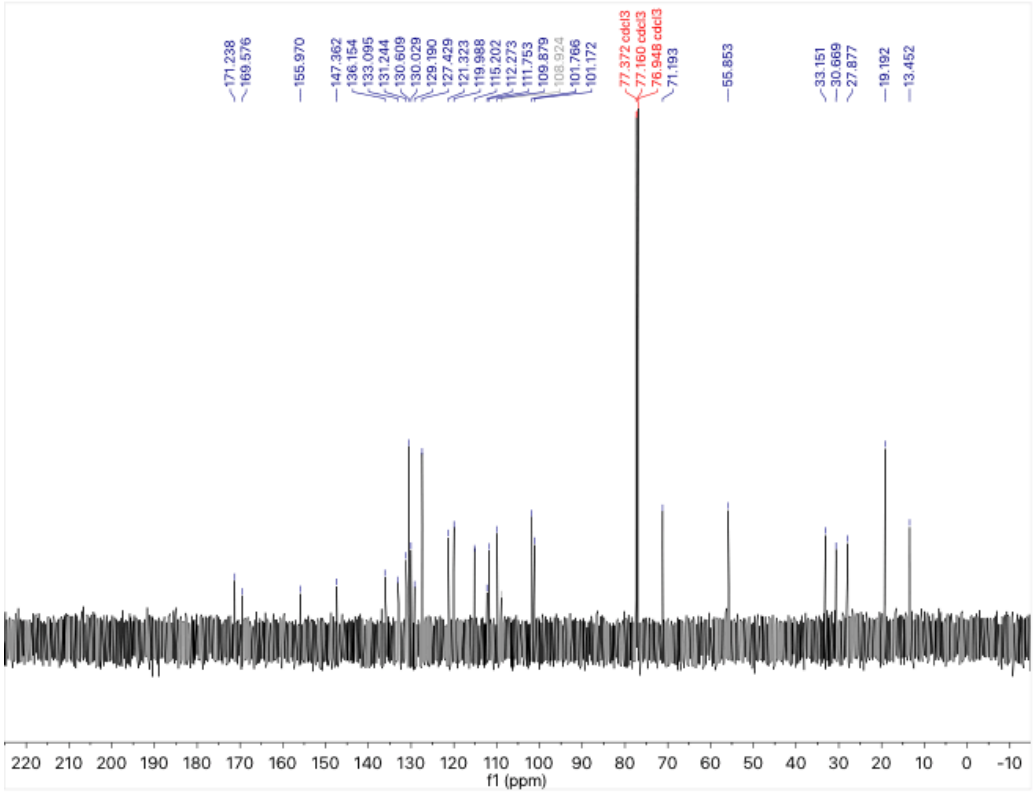
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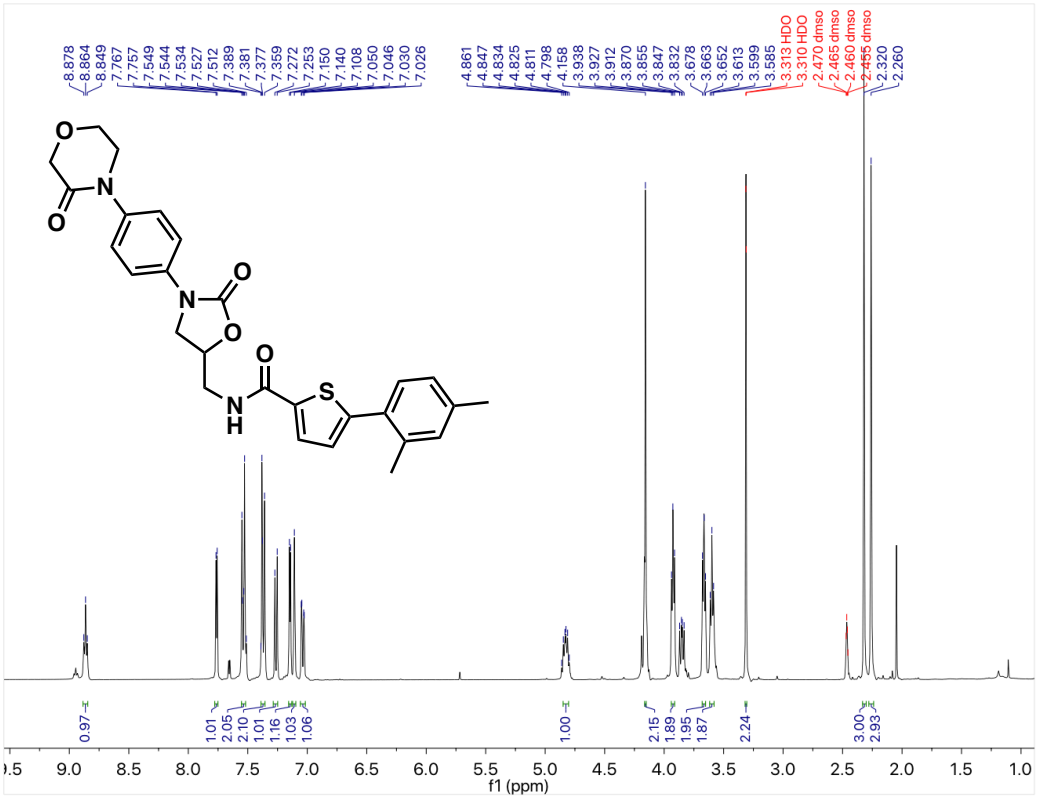
f1 (ppm)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3.310 HDO
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2.465 dmso
2.460 dmso
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O
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N
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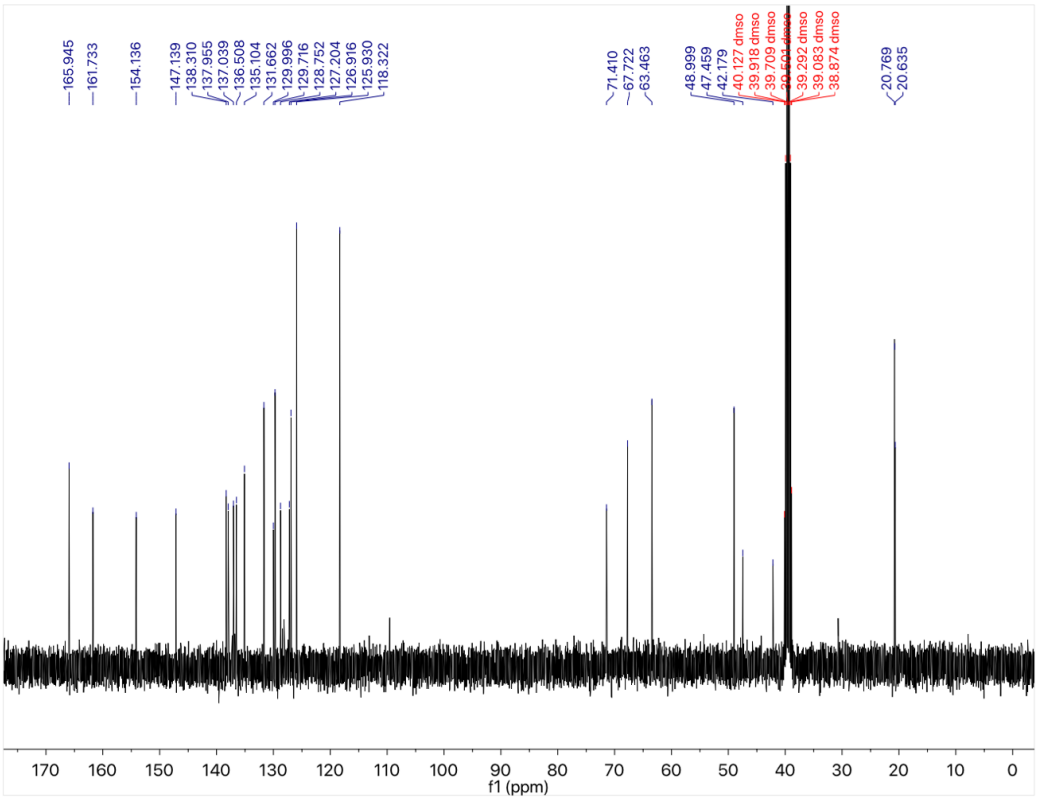
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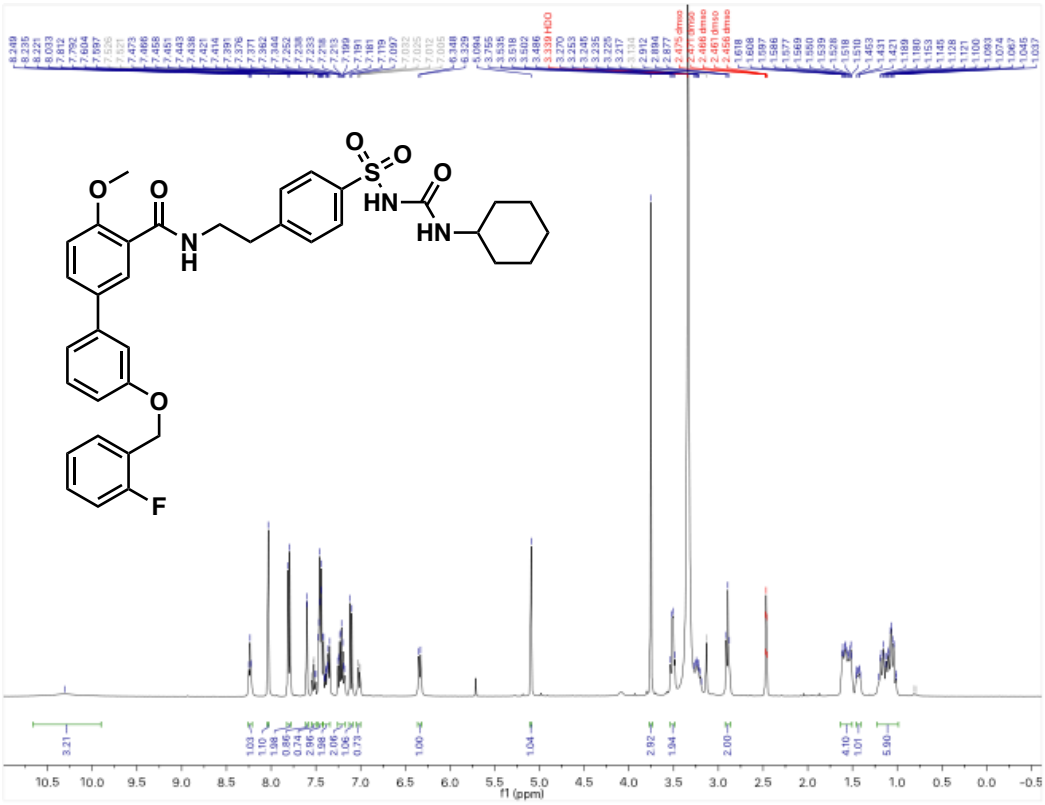
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O
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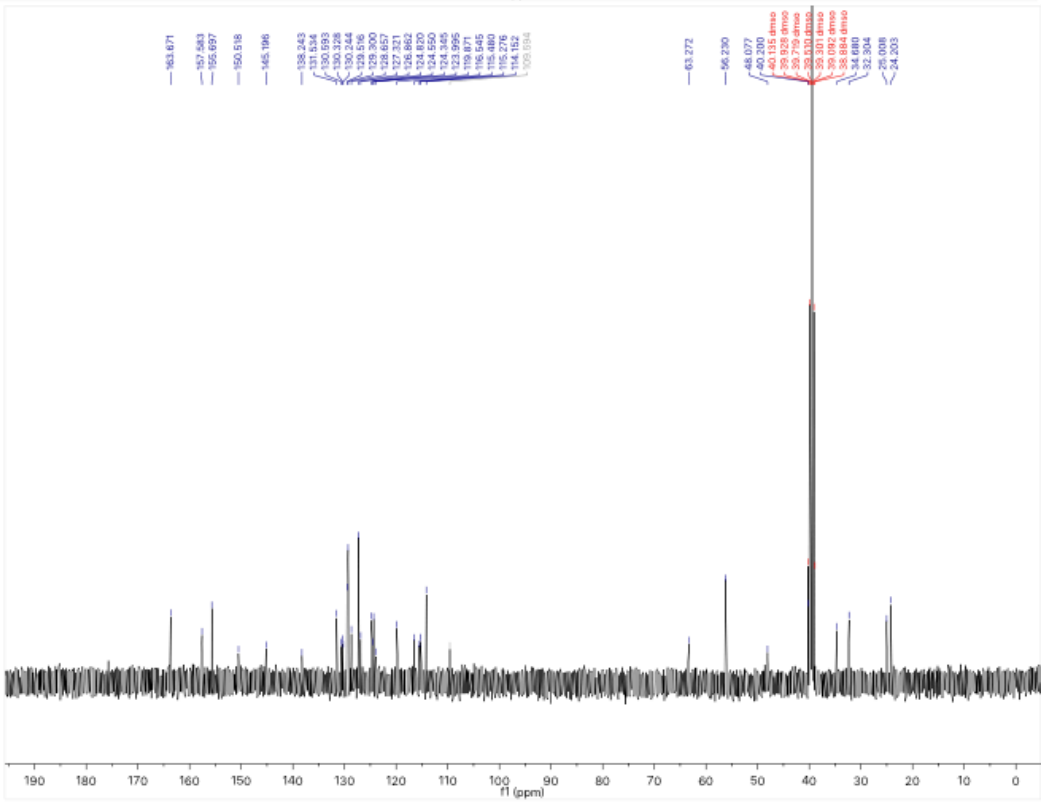
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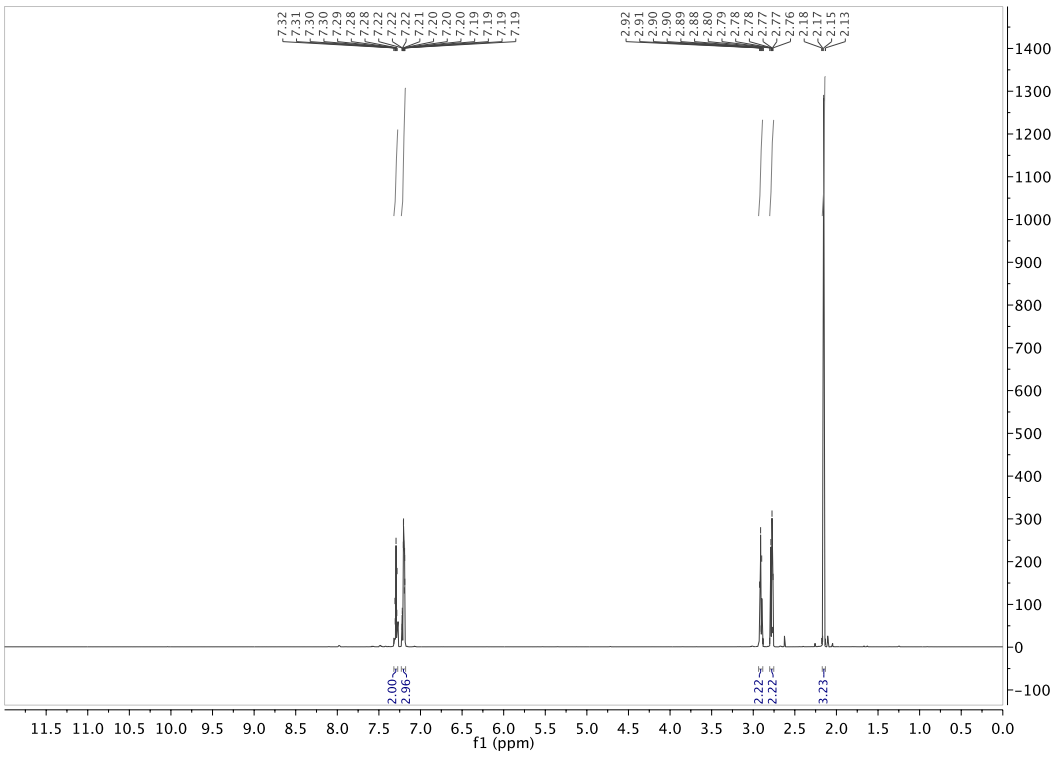


Fig. 1: [1]H NMR spectra of benzylacetone

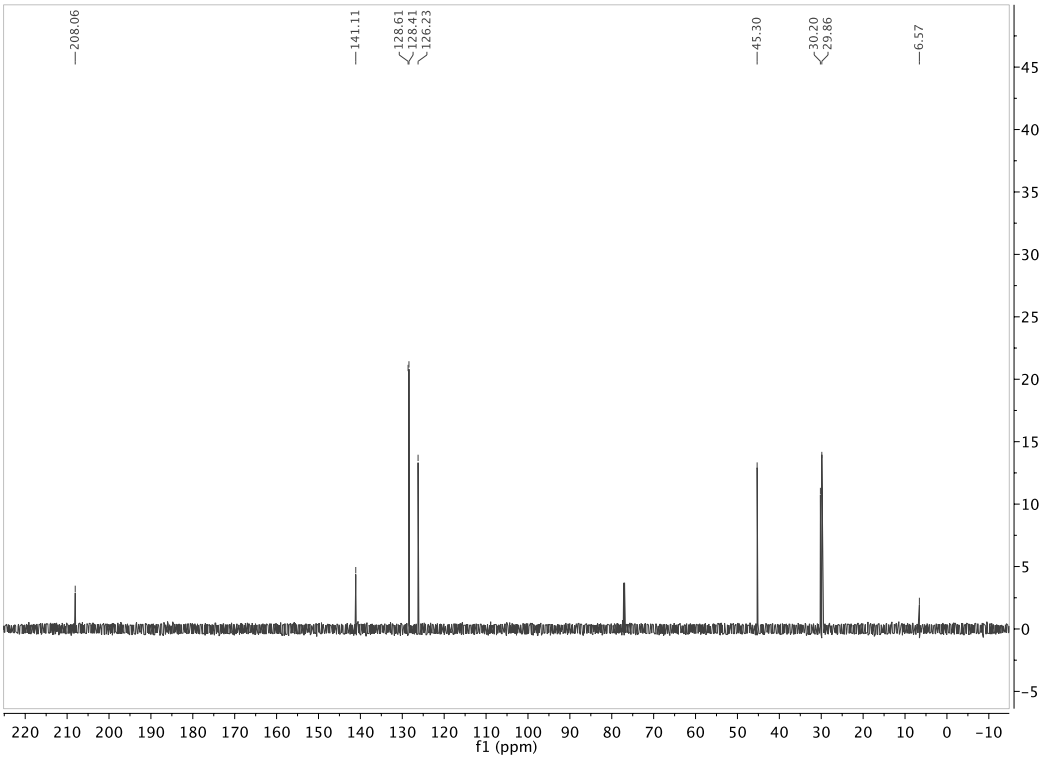


Fig. 2: [13]C NMR spectra of benzylacetone

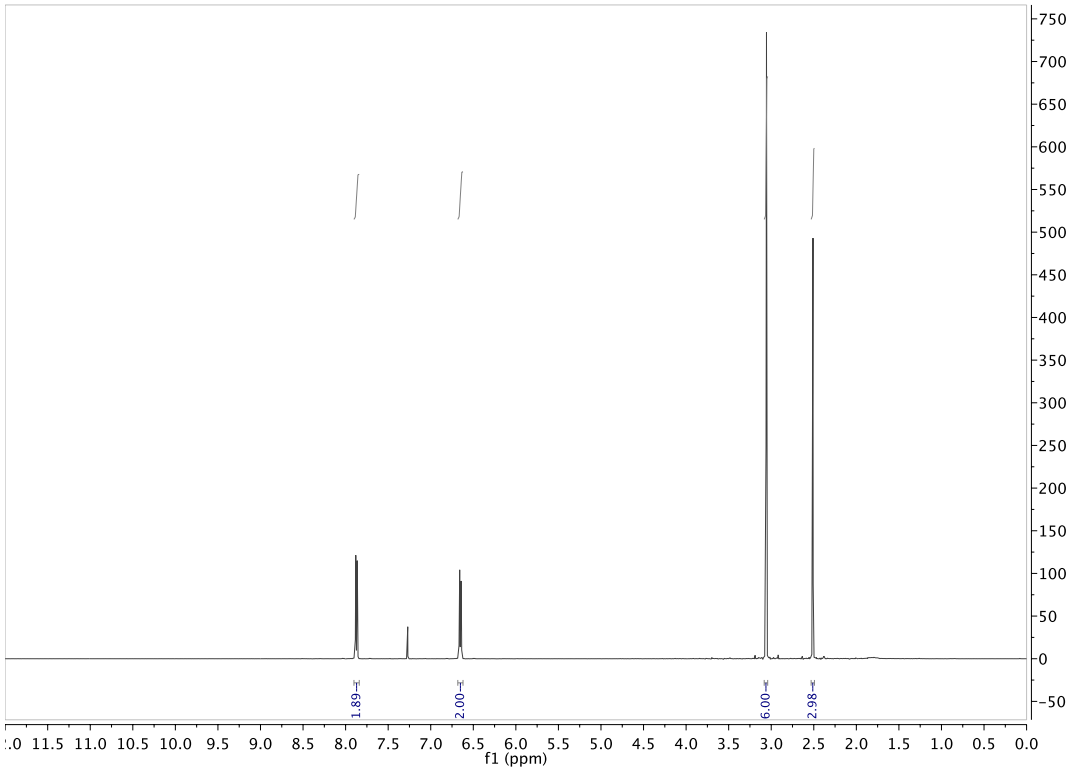


Fig. 3: [1]H NMR spectra of N-dimethylaminoacetophenone

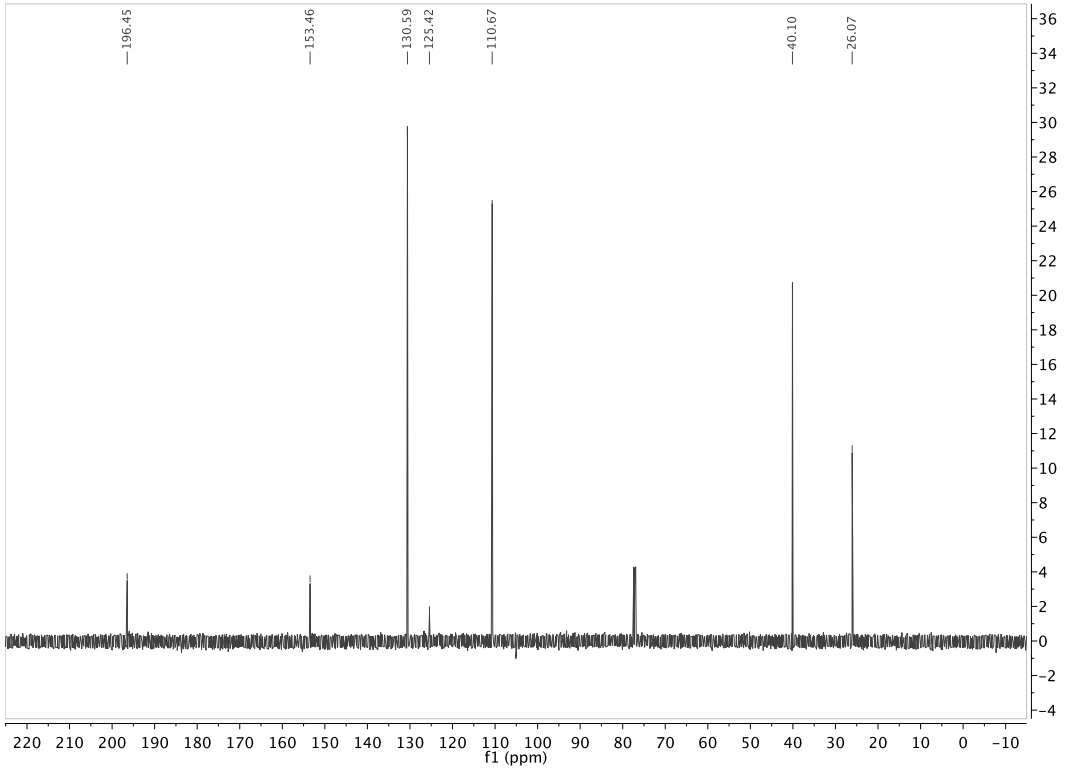


Fig. 4: [13]C NMR spectra of N-dimethylaminoacetophenon

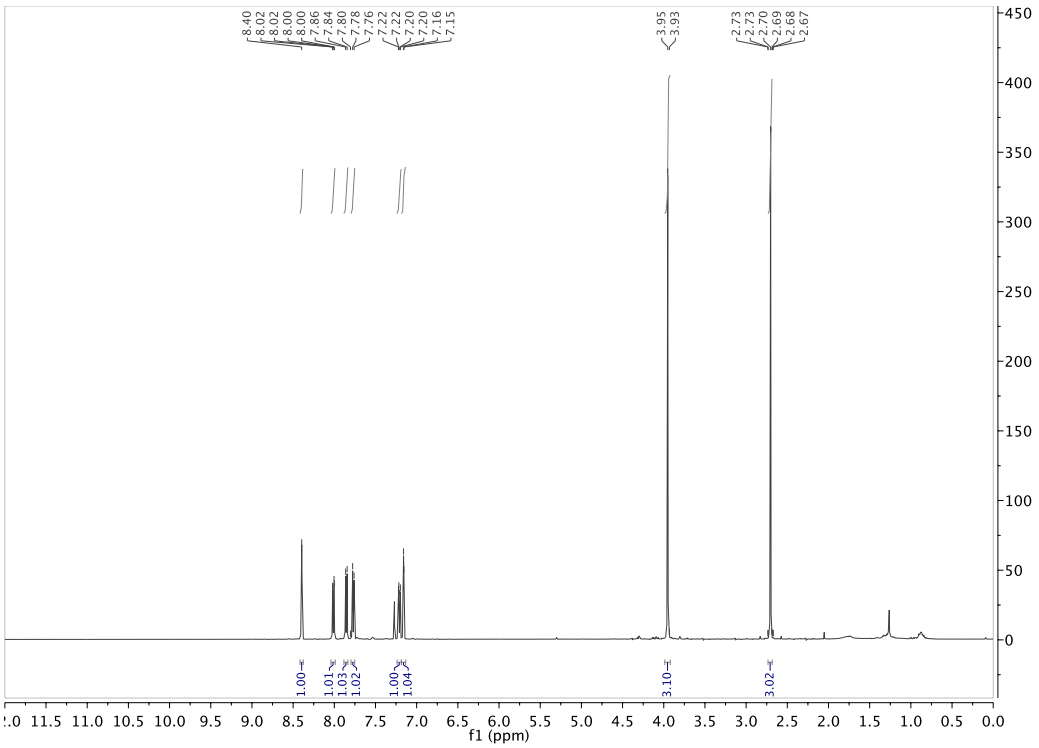


Fig. 5: 1H NMR spectra of 1-(6-methoxynaphthalen-2-yl)ethan-1-one

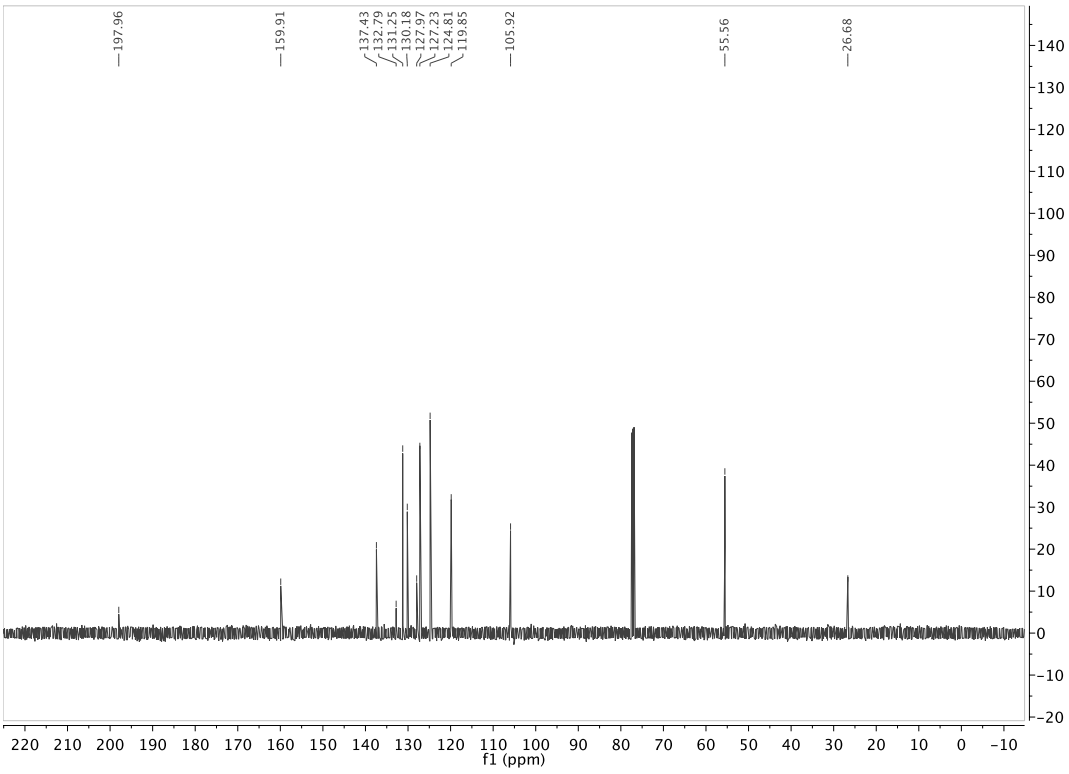


Fig. 6: ^{13}C NMR spectra of 1-(6-methoxynaphthalen-2-yl)ethan-1-one

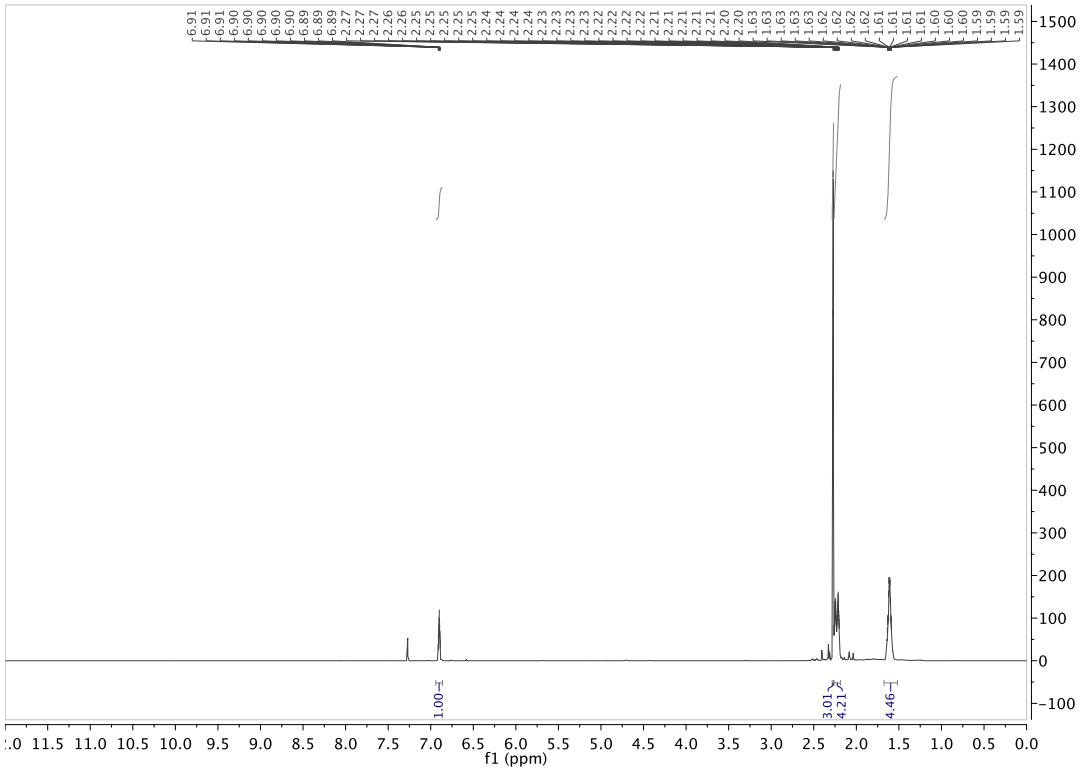


Fig. 7 :[1]H NMR spectra of 1-acetyl-1-cyclohexene

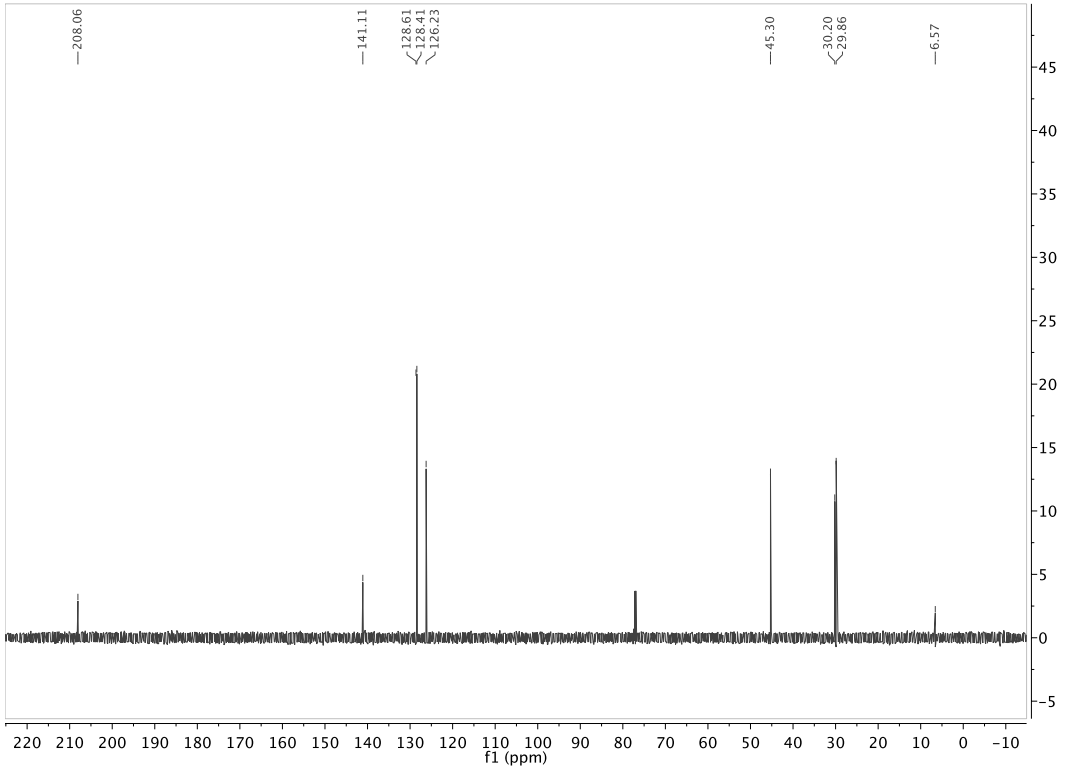
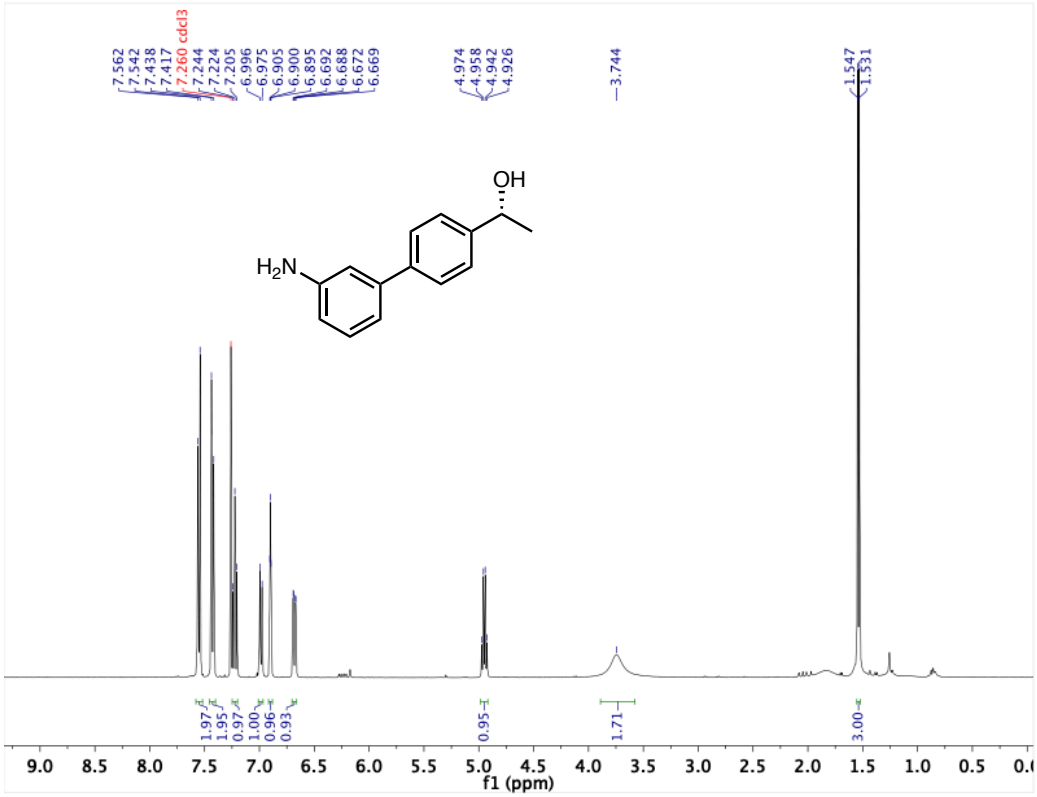


Fig. 8: [13]C NMR spectra of 1-acetyl-1-cyclohexene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1.531
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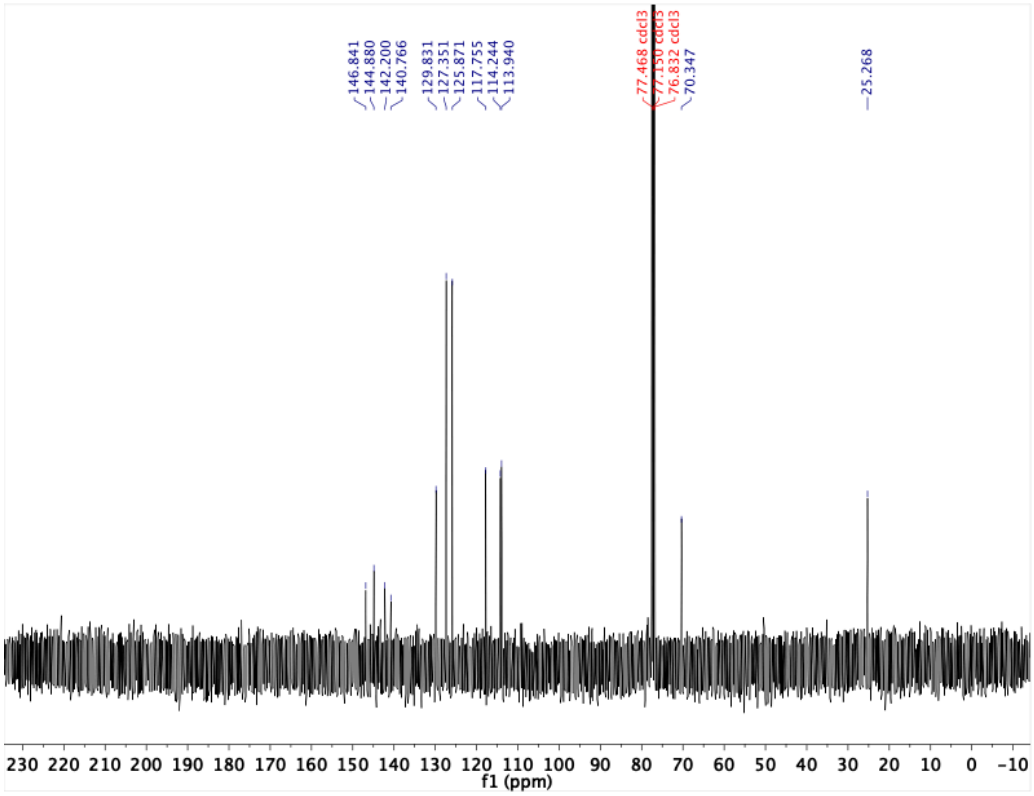
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76.832 cdcl3
70.347
25.268
f1 (ppm)

1.6 Computational Work

1. Theoretical Methods

For molecules with no palladium, complete geometry optimizations were carried out using density functional theory (DFT) methods at B3LYP/6-31G(d), B3LYPD3/6-31+G(d,p) with Grimme's D3 empirical dispersion corrections, and M06/6-31+G(d,p) levels[1-3]. The basis set used for palladium was the SDD[4,5] effective core potential. B3LYP/6-31G(d)(C,H,N,O,Cl)-SDD(Pd) level geometry optimizations along with frequency calculations were carried out in order to verify that the stationary points thus obtained were true minima and to determine thermodynamic parameters for the determination of reaction energetics. B3LYPD3/6-31+G(d,p)(C,H,N,O,Cl)-SDD(Pd,Zn) with D3 empirical dispersion corrections single-point calculations, scf=tight, were also done to get reaction energies. B3LYP/6-31G(d) and M06/6-31+G(d,p) calculations were done with the 5d option to match the SDD calculations with 5 d orbitals and done with the default Gaussian 'int=ultrafine' option.

Thermochemical data were calculated with zero-point energy corrections from scaled frequencies using a scaling factor of 0.99 for zero-point energies.[6] A scaling factor of 1.00 for frequencies for the thermal and entropy terms was used. [6ab] The quasiharmonic approximation was used for low frequencies to calculate entropies to avoid the large distortions found when many low-frequency vibrations are present in organometallic compounds.[6cd] Thus, frequencies below 100 cm^{-1} were treated as free rotors rather than by the harmonic approximation in calculating entropies. All calculations were performed using the Gaussian 16 program suite.[7]

Thermochemical data and Cartesian coordinates are found in Tables S3 and S4 at the end of this document.

2. Theoretical Results

Density functional theory (DFT) calculations and an X-ray crystal structure were obtained to gain insight into the structural factors that contribute to the greater reactivity of the N_2Phos/Pd(OAc)$_2$ derived species formed in solution relative to the corresponding catalyst derived from EvanPhos. The X-ray crystal structure of N_2Phos is shown in Figure S1. Two features that are notable from the crystal structure are the dihedral angle between the biaryl groups of 79.47º and the orientation of the two *N,N*-dibenzyl moieties whose steric requirements force the aromatic rings of the biaryl system to be almost perpendicular. Geometry optimizations of the free ligand N_2Phos at the B3LYP/6-31G(d) level were completed for 15 of the most reasonable-looking conformations, **A**-**O**. The most stable of these calculated structures had the same basic conformation **A** as in the X-ray crystal structure. See Table S1 for a quantitative comparison of structural parameters. At the B3LYPD3/6-31+G(d,p) level with D3 empirical dispersion corrections and a larger basis set and at the M06/6-31+G(d,p) level, structure **A** was not always the lowest in energy, but within about 2 kcal/mol as shown in Table S2. Three other conformers, **B**, **C**, **D** and **H** were as much as 2.4 kcal/mol lower in energy than conformer **A**. Small computational inconsistencies and/or small crystal-packing effects could account for these differences between experiment and theory.

Comparison of the drawings for the X-ray structure and the B3LYP/6-31G(d) optimized structure for conformer **A** are shown in Figure S1. The geometries are very similar but differ some in the rotational angles about some sigma bonds of the benzyl and cyclohexyl groups. Structural parameters for the X-ray structure and for the calculated structure are shown in Table S1. At the three levels of theory for the same basic conformation **A**, close correlation between experiment and theory was found at all levels for bond distances and angles. Average errors

were about 0.010 Å in some selected distances and 2.0-2.1º for selected angles. For selected dihedral angles that determine the exact conformation, the differences were larger, averaging 10-14º, as expected since these bond rotations have shallow energy wells. The B3LYPD3/6-31+G(d,p) level of theory gave slightly smaller geometry errors than the other two levels of theory. These geometry comparisons with between theory and experiment suggest that the levels of theory chosen might also be expected to give reliable reaction energies for the interconversion of the conformers in Table S2.

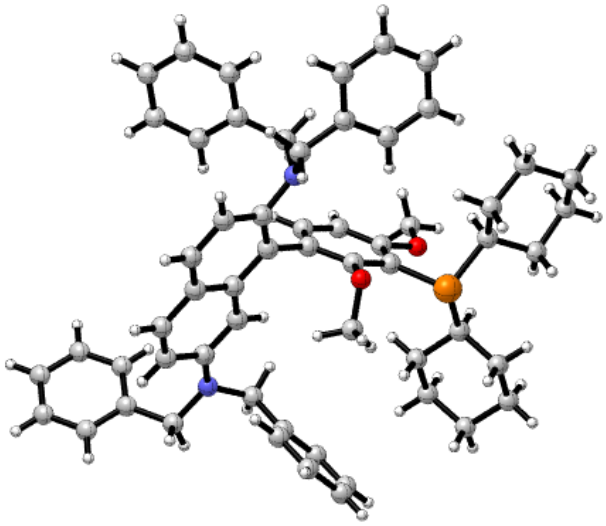
Table S1. Structural parameters for X-ray and optimized structures at B3LYP/6-31G(d) [5d], B3LYPD3/6-311+G(d,p), and M06/6-311+G(d,p) [5d] levels for conformer A of N_2Phos.

	B3LYP	B3LYPD3	M06	X-Ray
distances:				
C1-C1' (biaryl)	1.496	1.491	1.483	1.489
=C-P	1.870	1.865	1.856	1.840
=C2-N	1.423	1.422	1.414	1.426
=C7-N	1.397	1.393	1.389	1.394
angles:				
CH-P-CH	101.69	102.57	103.17	105.64
=C-P-CH	100.75	98.28	98.08	101.24
=C-P-CH	104.23	103.70	103.18	103.30
CH2-N-CH2	114.08	113.70	113.32	111.86
=C2-N-CH2	118.00	117.65	118.88	115.39
=C2-N-CH2	116.32	115.99	116.56	113.17
CH2-N-CH2	115.01	115.36	115.54	115.15
=C7-N-CH2	122.78	122.39	122.21	120.35
=C7-N-CH2	122.18	121.77	121.70	119.40
dihedral angles:				
(N)C-C-C-C(O)	69.12	75.76	74.64	79.47
=C1-C2-N-CH2	68.36	69.36	64.70	72.90
=C-CH2-N-C2=	151.82	155.47	153.61	163.61
=C-CH2-N-C2=	77.00	74.35	76.70	61.21
=C-CH2-N-C7=	103.82	95.05	93.43	78.69
=C-CH2-N-C7=	98.37	94.54	94.98	70.13
H-C-P-C=	-61.99	-50.08	-55.31	-27.58
H-C-P-C=	83.16	79.85	79.41	78.23
(P)C-C2'-O-CH3	-93.40	-97.63	-93.45	-89.82
(P)C-C4'-O-CH3	-179.96	-175.26	164.21	-175.54

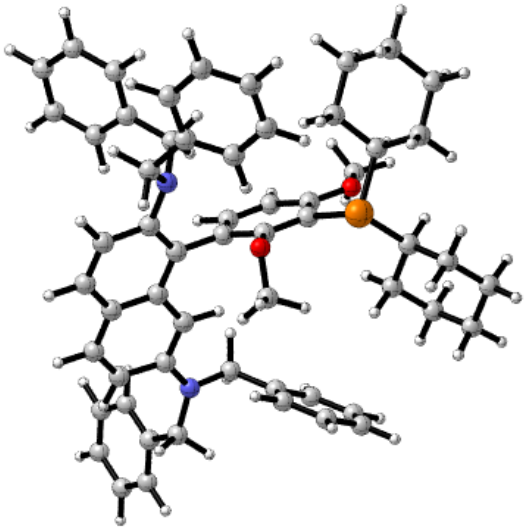
Table S2. Calculated relative electronic energies, enthalpies, and free energies at 298 K for selected conformers of N_2Phos optimized at B3LYP/6-31G(d) [5d], B3LYPD3/6-31+G(d,p), and M06/6-31+G(d,p) [5d] levels of theory.

Conformer:	B3LYP			B3LYPD3		
	$\Delta E^o e$	ΔH^o_{298K}	ΔG^o_{298K}	$\Delta E^o e$	ΔH^o_{298K}	ΔG^o_{298K}
A	0.00	0.00	0.00	0.00	0.00	0.00
B	0.24	0.06	0.05	-1.16		
C	1.13	0.80	0.90	-1.58	-1.92	-1.98
D	1.29	1.12	1.14	0.50	0.24	0.06
E	1.51	1.39	1.53	1.56	1.36	1.29
F	1.60	1.39	1.48	1.85		
G	1.75	1.73	1.57	0.00	0.00	0.00
H	2.11	1.90	2.12	-1.46	-1.66	-1.45
I	3.85	3.62	3.64	2.24		
J	3.91	3.78	3.81	4.01	3.69	3.68
K	3.91	3.78	3.81	4.29		
L	4.46	4.29	4.17	2.01	1.90	1.62
M				2.24	2.15	2.03
N				4.88	4.34	3.91
O	8.54	8.25	8.25	6.01		

Figure S1. Structures of ligands. Atom colors: nitrogen, blue; oxygen, red; palladium, teal

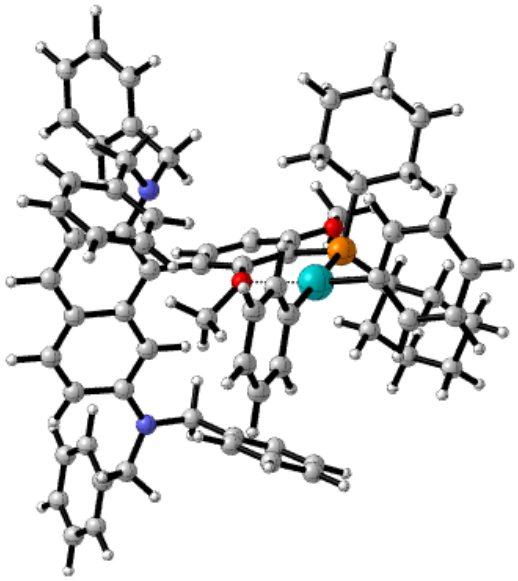


X-ray crystal structure of N_2Phos

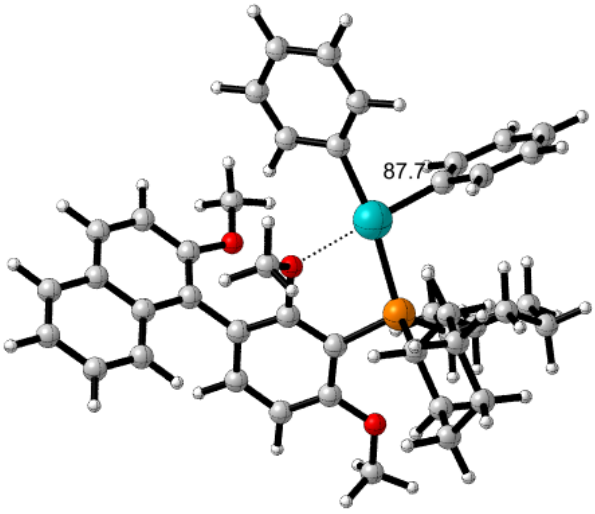


B3LYP/6-31G(d) [5d] optimized structure for conformer **A** of N_2Phos.

Figure S2. Structures for $PdPh_2$ pre-reductive elimination intermediates. Atom colors: nitrogen, blue; oxygen, red; palladium, teal.



B3LYP/6-31G(d)(SDD) [5d] optimized structure for conformer **APdPh2** of N_2Phos. O-Pd distance=2.453 Å, C-Pd-C angle=82.17°.



B3LYP/6-31G(d)(SDD) [5d] optimized structure for a low-energy conformer of EvanPhos., **EvanPhosPdPh2**, O-Pd distance=2.330 Å, C-Pd-C angle=87.68°.

The structures and relative energies of the pre-reductive elimination intermediates for Suzuki-Miyaura couplings between two simple phenyl rings to form biphenyl were examined. The first calculation at the B3LYP/6-31G(d)-SDD(Pd) level was optimized using conformation **A** for the ligand N_2Phos, close to the X-ray structure of the free ligand. The resulting optimized structure, **APdPh$_2$** for N_2Phos, is shown in Figure S2. **APdPh$_2$** has a C-Pd-C angle of 82.17º, along with a bond length of 2.453 Å between palladium and a methoxy oxygen on the resorcinol ring of N_2Phos, well in the range of the van der Wall's radii of the two elements indicative of a weak bonding interaction. This structure was the lowest energy found for a diphenylpalladium complex with N2Phos, but no systematic search was carried out for all conformers. Two other higher-energy structures were found with ligand conformations close to that for the calculated structure **J** for N2Phos and are shown in Table S3. The first of these was 2.95 kcal/mol higher in electronic energy than **APdPh$_2$**, and the other 17.67 kcal/mol higher. The first had a C-Pd-C angle of 82.45º and the second was a dramatically different structure with a C-Pd-C angle of 160.0º and an O-Pd distance of 3.065 Å, very near the sum of the van der Waals radii.

A corresponding calculation was done for the low-energy conformer shown in Figure S2 for EvanPhos, **EvanPhosPdPh$_2$**.[9] The calculations reveal that intermediates from both ligands form a square planar complexes, as expected for Pd(II). The more sterically encumbered N_2Phos intermediate has a C-Pd-C angle substantially smaller than the corresponding angle of 87.68º in the EvanPhos-containing intermediate (Figure S2). Both show coordination to a methoxy group, but with a shorter O-Pd distance of 2.330 Å. The enhanced proximity of the two phenyl rings in **APdPh$_2$** would be expected to result in an increased rate of reductive elimination as previously noted in our prior work.[9] This difference between the ligands can be

attributed to the two *N,N*-dibenzyl moieties of the naphthyl ring, such that one -NBn_2 residue significantly crowds the available space around palladium, thereby forcing the two phenyl rings into closer proximity and likely increasing their rate of reductive elimination.

Several alternative ligands seen in Figure S3 were screened for use as potential catalysts by calculation of structures for additional pre-reductive elimination intermediates with optimizations at the B3LYP/6-31G(d)-SDD(Pd) level. The first of those structures, **$QPdPh_2$** (***N,N*-dibenzyl-2-aminoNPhosPdPh_2**) has an NPhos ligand with a single dibenzylamino group in the 2 position of the naphthyl ring. The most stable structure found for this intermediate, shown in Figure S4 is similar to that of the N_2Phos intermediate **APdPh2** in Figure S2, but not exactly the same conformation as **A**. It has a larger 86.28° C-Pd-C bond angle and a shorter O-Pd distance, 2.338 Å, akin to that in **EvanPhosPdPh_2**. This suggests again that the rate of the coupling reaction between the phenyl groups might be more like that for the EvanPhos than for the N_2Phos ligands. Another much higher energy structure calculated for **$QPdPh_2$** (***N,N*-dibenzyl-2-aminoNPhosPdPh_2**) a adopted the same new T-shaped square planar Pd shape, see Figure S4, with a C-Pd-C angle of 161.23° and an O-Pd distance of 3.055 Å, as found above for N_2Phos and now 19.38 kcal/mol less stable in its electronic energy. Two other similar structures with electronic energies now higher by 21.20 and 25.26 kcal/mol and with somewhat different conformations also had large C-Pd-C angles (161.02° and 160.59°, respectively). Curiously, the extra steric bulk of the extra 7-NBn_2 group in **$APdPh_2$** with the N_2Phos ligand does not make formation of these near 160° forms substantially less stable than for the **$QPdPh_2$** structures, apparently because the 7-NBn_2 is far enough from the phenyl groups in the 160° forms that it has little steric effect.

Figure S3. Structures for various alternative ligands.

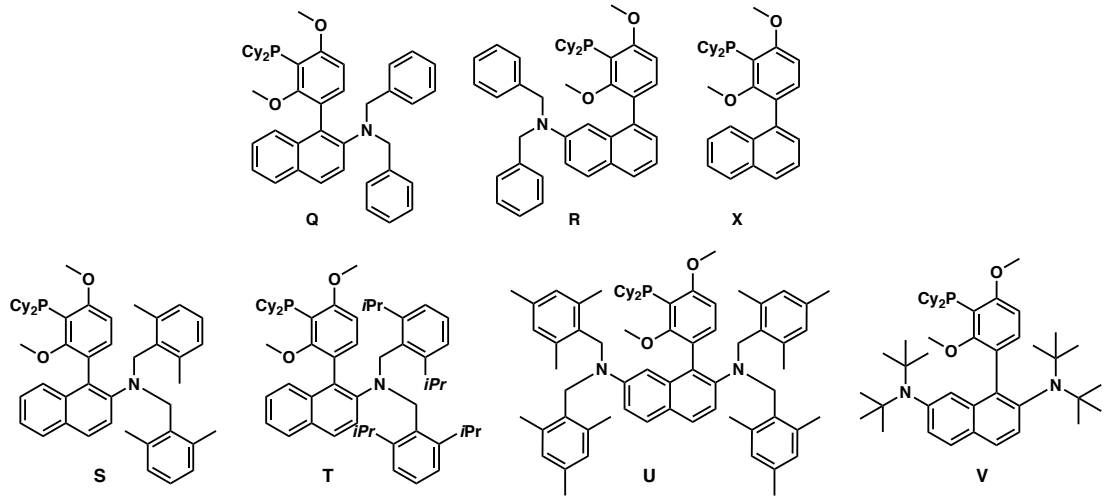


Figure S4. B3LYP/6-31G(d)(SDD) [5d] optimized structure for more stable conformer QPdPh$_2$ of *N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$. O-Pd distance=2.338 Å, C-Pd-C angle=86.28^o. Atom colors: nitrogen, blue; oxygen, red; palladium, teal. Cartesian coordinates in Table S4 below are for enantiomer.

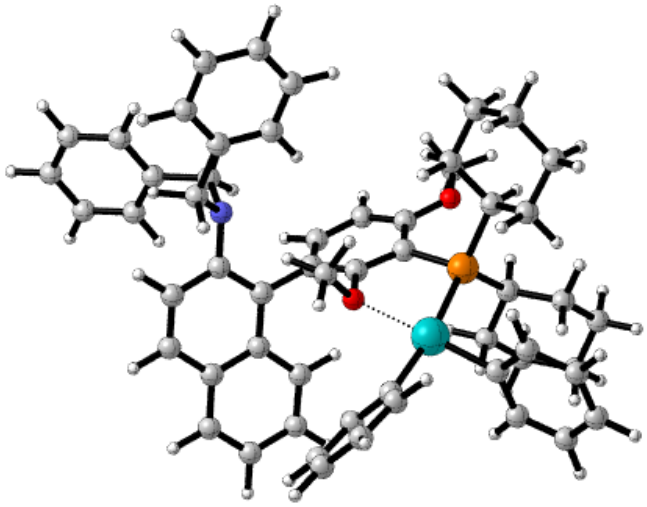
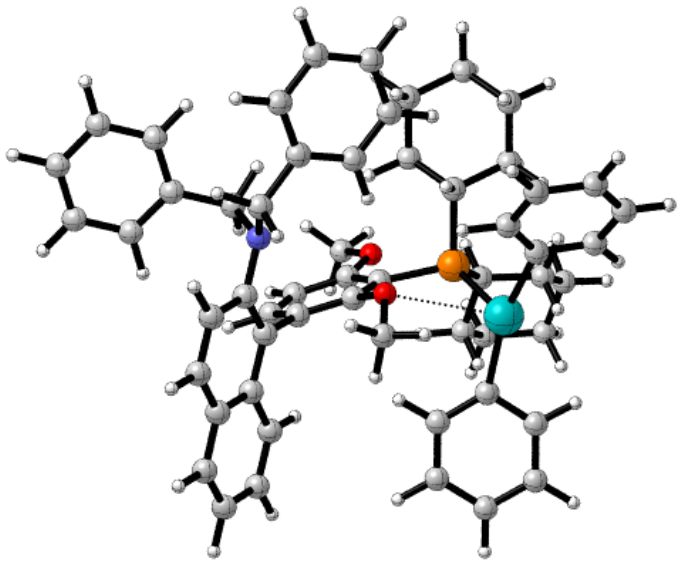


Figure S5. B3LYP/6-31G(d)(SDD) [5d] optimized structure for a less stable form of QPdPh$_2$ of *N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$. O-Pd distance=3.055 Å, C-Pd-C angle=161.23°. Atom colors: nitrogen, blue; oxygen, red; palladium, teal. Cartesian coordinates in Table S4 below are for enantiomer.



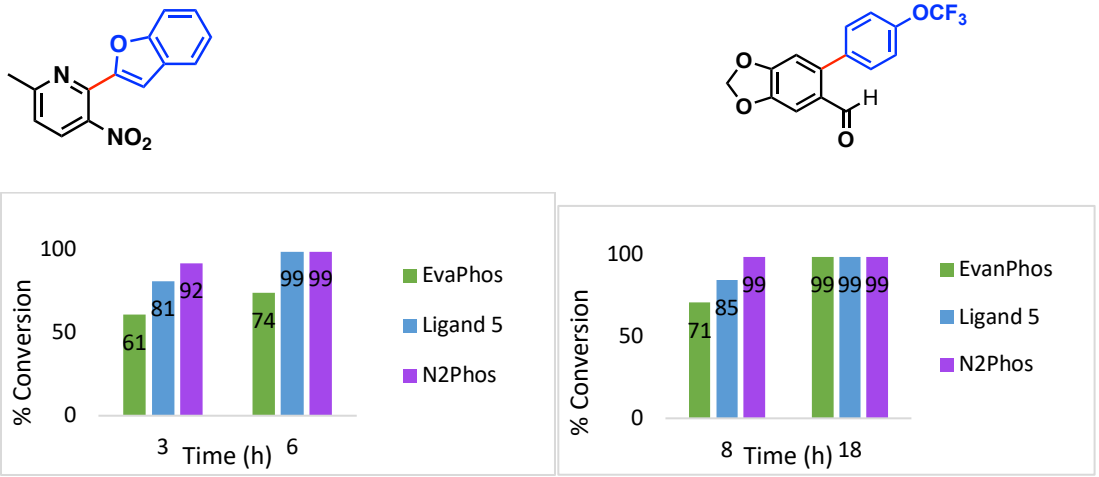
As with **QPdPh$_2$** with a single 2-NBn$_2$ group, the single 7-NBn$_2$ group in **RPdPh$_2$** (***N*,*N*-dibenzyl-7-aminoNPhosPdPh$_2$**) leads to a structures with an 87.36° C-Pd-C bond angle substantially larger than for the N$_2$Phos intermediate **APdPh$_2$**. Two higher-energy structures calculated for **RPdPh$_2$** are 0.46 and 10.04 kcal/mol above the lowest energy form found and have similar C-Pd-C angles (85.60° and 85.48°, respectively). A third form is 22.78 kcal/mol higher with a C-Pd-C angle of 161.67°. This suggests that NBn$_2$ groups in both the 2- and 7-positions are needed to maximally compress the C-Pd-C angle in N$_2$Phos.

Other, rather different, substitutions in **S**, **T**, **U,** and **V** in Figure S3 lead to C-Pd-C angles of 82.23, 83.63, 82.64, and 83.28°, almost as low as for N$_2$Phos. For **S** and **T**, high-energy (by 16-25 kcal/mole) near-160° forms were also found. To test the effect of aryl groups larger than phenyl for the coupling partners, a structure was calculated for N$_2$Phos ligated to 2-naphthyl,

o-tolylpalladium. In this case the C-Pd-C angle was 82.87°, only slightly larger than for diphenylpalladium.

Experimental data reflecting upon the rates of reaction that might be interpreted in the light of the computational results are discussed briefly here. Coupling reactions of aryl bromides generally occur smoothly and rapidly with a number of ligands studied at low catalyst concentrations. Some rather qualitative 'rate' data on this point are shown in Figure S6. In these two cases, the conversions appear to be slightly faster for N_2Phos

Figure S6. Relative Rates of Conversion between ligands [EvanPhos, Ligand 5 (NPhos with a 2-N,N-dimethylamino substituent in main text), and N_2Phos].



Conditions: Pd (0.25 mol %) ligand (0.5 mol %) Ar-Br (0.5 mmol) Ar-B(OH)$_2$ (0.75 mmol) K$_3$PO$_4$ (0.75 mol%) 2wt% TPGS-750-M/H2O with toluene 10% co-solvent) 45 ° C

than for EvanPhos or NPhos with a single 2-*N*,*N*-dimethylamino substituent. These data would be consistent with the C-Pd-C bond angle data in the pre-reductive intermediate structure if that were the rate-determining step, but again the effect appears to be small. For aryl chlorides, the conversions for are much slower than for aryl bromides, requiring higher catalyst concentrations. Furthermore, the difference in conversion is much more pronounced when changing from the EvanPhos to the N_2Phos ligand. For compound **20** for the coupling

of p-chloroanisole and *p*-tolylboronic acid in the main text**,** the reaction is 88% complete with N_2Phos after 8 hours, while only 7% with EvanPhos over the same 8 h reaction time. After 16 h, N_2Phos went to 96% while EvanPhos went to approximately 9%. The concentration of catalyst and surfactant were identical for both examples (0.25 mol% Pd, and 0.45 mol% ligand and 2wt% TPGS-750-M/H2O). For the aryl chlorides showing low conversions with EvanPhos, the final reaction mixtures showed substantial amounts of unreacted aryl chlorides and often protodeborylation of the boronic acid. In the case of aryl chlorides, the C-Pd-C bond angle data does not provide a very good explanation for why N_2Phos gives better conversions, since rate difference in the reductive elimination steps should be the same for aryl chlorides or bromides. A possibly better explanation for the increased efficacy of N_2Phos might lie in the considering that the palladium catalyst might be ligated to two ligands tying up a binding site on Pd needed for oxidative addition to the aryl chloride.

Thus, we tested whether two phosphine ligands might fit around a palladium using the pre-reductive elimination intermediates as models. When we tried to find an energy minimum for such a structure with two N_2Phos ligands **$(N_2Phos)PdPh_2$** at the B3LYP/6-31G(d)-SDD(Pd) level, one ligand separated from the palladium with a Pd-P distance of 6.3 Å before the geometry optimization was terminated unconverged, indicating that a structure with two ligands is too sterically hindered to stay bonded. The electronic energy of this separated-ligand structure was about 12 kcal/mol higher in energy than if the ligand were fully dissociated. For the 2-substituted ligand **Q** and diphenyl palladium, a 2:1 complex **Q_2PdPh_2**, was found as an energy minimum with Pd-P distances of 2.547 and 2.625 Å. A more stable minimum was found, however, for a structure **Q--QPdPh2** with one ligand only loosely bound with one Pd-P distance at 6.396 Å. This structure was lower in electronic energy by 5.98 kcal/mole and in

free energy by 8.99 kcal/mole. Incidentally, a remarkably larger difference in the free energy (17.45 kcal/mol!) was calculated when the distorted harmonic energy approximation was used instead of the preferred quasiharmonic approximation.[10] A second conformation of the loose complex **Q--QPdPh2** was also found that was to be higher than the first loose complex by 3.81 kcal/mole in electronic energy and by 3.96 kcal/mole in free energy. When as much less hindered ligand **X** with no dibenzylamino substituents was tested, we found that the 2:1 complex **X_2PdPh_2** existed as a minimum with Pd-P distances of 2.557 and 2.621 Å. These model studies clearly show that N_2Phos is not be able to form a 2:1 complex to diphenylpalladium

and formation of such a complex with the less hindered ligand **Q** would be substantially uphill in free energy. The much less hindered EvanPhos, on the other hand, is known to favor a 2:1complex with palladium dichloride based upon our X-ray crystal structure and computational work.[8] On the basis of this analysis, we think that the formation of an unreactive 2:1 complex between EvanPhos and other ligands much less sterically hindered than N_2Phos may well be the reason that N_2Phos is so effective as a catalyst. For EvanPhos, we think that tying the Pd up in an unreactive 2:1 complex slows the oxidative addition reaction with aryl chlorides to the point that irreversible protodeborylation of the boronic acid becomes faster and thereby interferes with the desired Suzuki-Miyaura cross coupling.

Electron-donating effects of the dibenzylamino nitrogens were considered as a possible avenue to influence the electron density in the vicinity of the phosphine group and catalyst reactivity. Natural population analysis calculations on the free ligands and diphenyl palladium complexes for EvanPhos, N_2Phos, and an N_2Phos with the nitrogens replaced with CH groups at several levels of theory showed little or no regular variation of charge densities at

phosphorus or palladium. The fact that the dihedral angles between the planes of the biaryl groups in the ligands is near 70º for these ligands and palladium complexes would certainly be expected to seriously diminish any putative pi-donating electronic effect. This suggests that the efficacy of N_2Phos is likely the result of steric effects, rather than any significant electronic effects.

Acknowledgments. Use was made of computational facilities purchased with funds from the National Science Foundation (CNS-1725797) and administered by the Center for Scientific Computing (CSC). The CSC is supported by the California NanoSystems Institute and the Materials Research Science and Engineering Center (MRSEC; NSF DMR 1720256) at UC Santa Barbara. The software used for 3-D drawings was from CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

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Grimme *Chem. Eur. J.* **2012**, *18*, 9955-9964. (e) D. H. Aue, to be published. We have evaluated optimum scale factors for experimental fundamental frequencies for numerous organic molecules and find that the DFT scale factors differ with basis set between 0.96 for the B3LYP/6-31G(d) and 0.954 for M06-2X/ 6-311+G(d,p) levels to 0.967 for the B3LYP/ 6-311G(d,p) level. For thermal terms and entropies, such variation has little effect, and one may argue that a scaling factor close to 1.00 might be best for the dominant low frequencies (we get 1.005 for 111 frequencies below 150 cm^{-1})(see also ref. 6a). For zero point energies determined from experimental values and CCSD(T)-F12/cc-aug-pVDZ values, the scale factors 1.00 (B3LYP/6-311G(d,p)), 0.984 (M06-2X/6-311+G(d,p)), 0.991 (M06/6-31G(d)), 0.996 (M06/6-31+G(d,p)) give the best fit for large variety of organic molecules.

7. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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10. This is the largest such difference we have ever seen between the quasiharmonic and harmonic approximations and emphasizes how important it is for workers in the field of computational chemistry to pay attention to this problem of low frequency distortions on entropy effects.[6c,d] Grimme has found examples of supermolecular complexes where differences in free energies of 3-4 kcal/mole can occur. Clearly, we see that organometallic complexes can show much larger discrepancies.

Table S3. Thermodynamic parameters and Cartesian coordinates from an X-ray structure and optimized structures at various levels of theory.

Conformer **A**: X-ray crystal structure:

C	-4.385022	-2.246773	0.474766
C	-4.189278	-1.730643	1.744038
C	-4.735198	-2.411401	2.809782
C	-5.476337	-3.567427	2.618240
C	-5.662001	-4.061298	1.363048
C	-5.117855	-3.403149	0.293166
C	-3.408561	-0.455560	1.983837
N	-2.442811	-0.129962	0.953397
C	-1.212563	-0.925344	0.979279
C	0.035305	-0.112267	0.809497
C	1.166804	-0.680843	0.242654
C	2.319570	0.060709	0.086731
C	2.380768	1.360290	0.495444
C	1.266061	1.926787	1.076162
C	0.108843	1.206246	1.226834
C	-2.859217	0.447482	-0.244827

C	-2.081254	0.288011	-1.417162
C	-2.480931	0.820130	-2.599568
C	-3.666691	1.580632	-2.713526
C	-4.448705	1.772753	-1.556857
C	-4.032646	1.180760	-0.338225
C	-5.653428	2.540494	-1.654190
C	-5.999676	3.119044	-2.865911
C	-5.210760	2.881629	-4.017005
C	-4.082898	2.122217	-3.937777
C	-6.512175	2.697775	-0.447645
C	-7.661471	1.925846	-0.268651
C	-8.441562	1.996068	0.884939
C	-8.050164	2.920031	1.873852
C	-6.935415	3.717711	1.714764
C	-6.185300	3.586065	0.558412
P	-9.899087	0.884931	1.051488
C	-9.635144	0.079003	2.703117
C	-8.183943	-0.344803	2.916293
C	-8.001013	-1.072728	4.242482
C	-8.887604	-2.300762	4.328044
C	-10.341410	-1.915869	4.102327
C	-10.524560	-1.166943	2.788126
O	-8.041522	1.078786	-1.291314
C	-7.496647	-0.240771	-1.179130
O	-8.826897	2.960798	2.999042
C	-8.516944	3.954218	3.980272
N	-7.134702	3.980052	-2.928672
C	-7.746403	4.113265	-4.245930
C	-9.132794	4.698324	-4.148534
C	-10.019445	4.239092	-3.198329
C	-11.294380	4.759888	-3.120651
C	-11.692477	5.755002	-3.992051
C	-10.819189	6.225380	-4.923253
C	-9.538010	5.701601	-5.010678
C	-6.903246	5.295399	-2.293487
C	-5.813410	6.119194	-2.897679
C	-4.488050	5.957527	-2.507925
C	-3.488854	6.721614	-3.061240
C	-3.787012	7.672622	-4.015239
C	-5.090733	7.841562	-4.423346

C	-6.090858	7.065583	-3.871564
C	-11.270379	2.120730	1.308849
C	-12.391705	1.624358	2.202663
C	-13.457783	2.709353	2.346979
C	-14.052215	3.040855	0.999609
C	-12.999669	3.494312	0.014173
C	-11.828046	2.521702	-0.064538
H	-10.874408	2.935841	1.732019
H	-12.030079	1.391994	3.095651
H	-12.795400	0.810060	1.811535
H	-14.172075	2.396351	2.957987
H	-13.052530	3.523120	2.739490
H	-14.728301	3.757576	1.107931
H	-14.513694	2.240868	0.640421
H	-12.662967	4.385335	0.284471
H	-13.408385	3.583559	-0.882266
H	-11.102125	2.936121	-0.596366
H	-12.121403	1.705290	-0.541636
H	-9.898750	0.719503	3.423864
H	-7.903185	-0.939260	2.175987
H	-7.603666	0.457052	2.901914
H	-7.054113	-1.345640	4.339510
H	-8.220865	-0.458958	4.987309
H	-8.789061	-2.720903	5.219717
H	-8.608748	-2.960718	3.644357
H	-10.648882	-1.344126	4.850619
H	-10.900698	-2.732865	4.093417
H	-11.472844	-0.895883	2.697047
H	-10.307922	-1.772371	2.035996
H	-5.412147	4.130187	0.452826
H	-6.687608	4.343614	2.385672
H	-6.523882	-0.203727	-1.298390
H	-7.887633	-0.816753	-1.867817
H	-7.702491	-0.604801	-0.292541
H	-7.610137	3.804323	4.321064
H	-9.157146	3.893847	4.720600
H	-8.569777	4.843996	3.574013
H	-5.472082	3.253742	-4.851203
H	-3.571767	1.958162	-4.721571
H	-1.949846	0.676598	-3.373230

H	-1.265948	-0.200059	-1.373875
H	-4.573188	1.288607	0.434544
H	-6.689321	5.147563	-1.337509
H	-7.745359	5.813183	-2.331922
H	-4.270019	5.310153	-1.848347
H	-2.588544	6.593108	-2.785411
H	-3.095331	8.207240	-4.387728
H	-5.303749	8.492032	-5.083074
H	-6.986028	7.181599	-4.166004
H	-7.794142	3.223222	-4.677164
H	-7.183001	4.697007	-4.812836
H	-9.751114	3.558370	-2.592591
H	-11.900982	4.434371	-2.465795
H	-12.572428	6.108974	-3.940851
H	-11.088671	6.917077	-5.516604
H	-8.934450	6.033077	-5.665507
H	-1.253177	-1.602411	0.257967
H	-1.162021	-1.408186	1.842097
H	1.145938	-1.587819	-0.040922
H	3.083794	-0.340667	-0.310914
H	3.176155	1.867148	0.383470
H	1.299741	2.827615	1.374041
H	-0.651758	1.615454	1.622734
H	-4.048077	0.295316	2.065133
H	-2.931454	-0.537272	2.848250
H	-4.600710	-2.083398	3.692158
H	-5.855606	-4.016686	3.364063
H	-6.165165	-4.856276	1.230801
H	-5.245480	-3.745697	-0.583835
H	-4.012755	-1.801211	-0.276398

Conformer **A**: B3LYP/6-31G(d) [5d]
Processing: namphos-h5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3619586

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
678.17688	714.264	336.475	285.949	714.471	46.099	40.619

Processing: namphos-h5dbe.log
126

C	3.894368	-2.272526	-1.227324
C	4.494421	-2.122183	0.029652
C	4.906855	-3.268955	0.719884
C	4.718111	-4.539803	0.174233
C	4.119045	-4.679868	-1.079663
C	3.707763	-3.541796	-1.777811
C	4.701181	-0.746251	0.654819
N	4.987120	0.322959	-0.290166
C	6.326092	0.299874	-0.858028
C	7.418049	0.956148	-0.016471
C	8.761393	0.662863	-0.290734
C	9.787216	1.264882	0.436753
C	9.483646	2.167509	1.459816
C	8.149811	2.460030	1.744839
C	7.123626	1.858623	1.010748
C	4.035623	1.273793	-0.666895
C	4.459748	2.473272	-1.322175
C	3.540683	3.409949	-1.720458
C	2.153418	3.253099	-1.473622
C	1.705130	2.086422	-0.771756
C	2.673886	1.105421	-0.415573
C	0.300470	1.921734	-0.496969
C	-0.610791	2.898629	-0.926682
C	-0.129741	4.042494	-1.629809
C	1.206152	4.213931	-1.891843
C	-0.143775	0.724556	0.283330
C	-0.924513	-0.312430	-0.274451
C	-1.357343	-1.426450	0.474182
C	-0.956728	-1.494788	1.830651
C	-0.167786	-0.492555	2.401926
C	0.221862	0.598584	1.627019
P	-2.474706	-2.664380	-0.370996
C	-1.661862	-4.351065	-0.011466
C	-0.120733	-4.313696	-0.022789
C	0.482020	-5.708324	0.221555

C	-0.026048	-6.739651	-0.795426
C	-1.560187	-6.773548	-0.826567
C	-2.148576	-5.372795	-1.066883
O	-1.309021	-0.194842	-1.592769
C	-0.391533	-0.729222	-2.544710
O	-1.374560	-2.591737	2.533564
C	-1.004044	-2.713603	3.897420
N	-2.008182	2.768139	-0.689778
C	-2.896047	3.397081	-1.673323
C	-4.250202	2.717767	-1.798984
C	-4.338946	1.341141	-2.051935
C	-5.582663	0.742090	-2.256337
C	-6.754127	1.504296	-2.204262
C	-6.674135	2.872779	-1.946247
C	-5.427705	3.472954	-1.746036
C	-2.487110	2.865965	0.703658
C	-2.555171	4.278367	1.269972
C	-1.390236	4.955135	1.663826
C	-1.454315	6.252295	2.173384
C	-2.687641	6.896646	2.302686
C	-3.854348	6.233763	1.919828
C	-3.785143	4.935668	1.407634
C	-3.952507	-2.685117	0.827684
C	-5.049993	-3.646371	0.322824
C	-6.291656	-3.632968	1.232734
C	-6.853687	-2.216187	1.409122
C	-5.768740	-1.258275	1.919426
C	-4.531143	-1.266145	1.006208
H	-3.601401	-3.040761	1.803573
H	-4.665336	-4.670836	0.260832
H	-5.344497	-3.359471	-0.697660
H	-7.059010	-4.302377	0.821658
H	-6.019758	-4.038598	2.218855
H	-7.710804	-2.227762	2.095245
H	-7.230524	-1.851929	0.441856
H	-5.472784	-1.556449	2.936708
H	-6.165484	-0.237527	1.995409
H	-3.767730	-0.595307	1.415836
H	-4.808093	-0.855510	0.025643
H	-1.984864	-4.685729	0.983929

H	0.231729	-3.937806	-0.995522
H	0.254190	-3.618011	0.732438
H	1.576927	-5.645712	0.190082
H	0.214424	-6.039849	1.236357
H	0.375222	-7.735602	-0.565414
H	0.348158	-6.474557	-1.795810
H	-1.934467	-7.164508	0.131536
H	-1.912253	-7.464763	-1.603848
H	-3.242632	-5.430412	-1.084678
H	-1.848314	-5.018684	-2.063879
H	0.824712	1.380820	2.080861
H	0.137898	-0.542662	3.440261
H	0.603498	-0.282412	-2.429068
H	-0.791752	-0.477835	-3.529523
H	-0.320906	-1.820672	-2.451241
H	0.086079	-2.762958	4.016997
H	-1.446868	-3.649511	4.243086
H	-1.396078	-1.883120	4.498769
H	-0.832025	4.812718	-1.926557
H	1.551762	5.105347	-2.411024
H	3.879079	4.312299	-2.225175
H	5.514644	2.663710	-1.482348
H	2.322046	0.191273	0.043730
H	-1.836720	2.247761	1.324606
H	-3.483878	2.413361	0.735483
H	-0.427068	4.460301	1.571515
H	-0.541299	6.759025	2.475975
H	-2.737697	7.905894	2.703169
H	-4.819208	6.724389	2.021614
H	-4.697470	4.420913	1.114580
H	-2.390991	3.331927	-2.642719
H	-3.057304	4.469195	-1.469467
H	-3.429714	0.746988	-2.081320
H	-5.635959	-0.323970	-2.462787
H	-7.720721	1.033564	-2.364927
H	-7.578172	3.474954	-1.901089
H	-5.367619	4.542025	-1.552674
H	6.297182	0.758762	-1.852574
H	6.598853	-0.749592	-1.032053
H	9.004799	-0.045540	-1.080725

H 10.823054 1.025154 0.210576
H 10.281331 2.634813 2.031016
H 7.903321 3.158488 2.540478
H 6.086443 2.088336 1.236042
H 3.826553 -0.461007 1.247979
H 5.537174 -0.807233 1.365736
H 5.388146 -3.165265 1.690570
H 5.050736 -5.418156 0.721329
H 3.981603 -5.666877 -1.512998
H 3.245848 -3.641794 -2.756646
H 3.582297 -1.389736 -1.777906
Conformer **A**: B3LYPD3/6-31+G(d,p) [5d]
Processing: namphos-h6pbed3.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-2849.7494763

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
676.51623	712.182	328.162	283.537	712.375	46.099	40.530

Processing: namphos-h6pbed3.log
126
C 3.434859 -1.703811 -1.620412
C 4.125394 -1.844376 -0.408724
C 4.488591 -3.129874 0.013409
C 4.165741 -4.253108 -0.752402
C 3.471869 -4.103911 -1.955405
C 3.107732 -2.825037 -2.386190
C 4.487496 -0.631091 0.441723
N 4.772492 0.577352 -0.317088
C 6.080138 0.620920 -0.950477
C 7.173462 1.297331 -0.131404
C 8.506440 1.206285 -0.557316
C 9.529036 1.826809 0.161988
C 9.230886 2.547740 1.323800
C 7.905946 2.640363 1.755241

C	6.883071	2.019212	1.030685
C	3.805309	1.548162	-0.564579
C	4.186009	2.801833	-1.144202
C	3.233122	3.737082	-1.468909
C	1.852288	3.518085	-1.221906
C	1.462291	2.307378	-0.564468
C	2.460566	1.341223	-0.265735
C	0.073790	2.058077	-0.302811
C	-0.894589	2.964030	-0.742302
C	-0.479910	4.164420	-1.392972
C	0.849931	4.436313	-1.614170
C	-0.284985	0.827647	0.459316
C	-0.847032	-0.311371	-0.147353
C	-1.126649	-1.488103	0.573563
C	-0.898766	-1.468869	1.970130
C	-0.333623	-0.352346	2.594719
C	-0.020509	0.770257	1.829989
P	-1.757326	-2.965669	-0.374283
C	-0.790319	-4.419420	0.364901
C	0.693096	-4.103301	0.643722
C	1.421325	-5.330736	1.215832
C	1.313718	-6.542574	0.279970
C	-0.152831	-6.852699	-0.053548
C	-0.871983	-5.614192	-0.614126
O	-1.172941	-0.256143	-1.486056
C	-0.099056	-0.530943	-2.393597
O	-1.246130	-2.600351	2.657658
C	-0.951693	-2.689515	4.045165
N	-2.278848	2.694388	-0.560154
C	-3.183307	3.281260	-1.552132
C	-4.490366	2.522465	-1.675242
C	-4.489075	1.137780	-1.900189
C	-5.694286	0.459762	-2.092182
C	-6.912541	1.146789	-2.045155
C	-6.920333	2.522344	-1.805203
C	-5.712237	3.203494	-1.623107
C	-2.808102	2.727263	0.818991
C	-2.957058	4.128553	1.383421
C	-1.827455	4.848205	1.803812
C	-1.950063	6.155344	2.278731

C	-3.208105	6.764635	2.342041
C	-4.339882	6.057176	1.928367
C	-4.211540	4.749098	1.450491
C	-3.446461	-3.126259	0.463470
C	-4.169640	-4.435442	0.095028
C	-5.581498	-4.492268	0.706286
C	-6.424804	-3.271908	0.308853
C	-5.709534	-1.966659	0.684947
C	-4.303928	-1.908245	0.070691
H	-3.286837	-3.115009	1.548242
H	-3.592779	-5.300618	0.440312
H	-4.245354	-4.518820	-0.999506
H	-6.081122	-5.420619	0.401385
H	-5.494880	-4.526143	1.802335
H	-7.413764	-3.320553	0.781553
H	-6.593035	-3.289052	-0.778434
H	-5.628508	-1.900215	1.779828
H	-6.291574	-1.097291	0.356574
H	-3.807095	-0.976961	0.362850
H	-4.388918	-1.880783	-1.023552
H	-1.264974	-4.702812	1.313016
H	1.186393	-3.794574	-0.287702
H	0.791802	-3.267636	1.339550
H	2.473243	-5.082360	1.399052
H	0.979395	-5.585879	2.190637
H	1.800299	-7.419062	0.726699
H	1.852640	-6.319196	-0.651683
H	-0.669680	-7.187434	0.857980
H	-0.215240	-7.679723	-0.772283
H	-1.912286	-5.863676	-0.848258
H	-0.404671	-5.323546	-1.565853
H	0.426397	1.635580	2.311677
H	-0.139727	-0.340481	3.660045
H	0.715888	0.190408	-2.267228
H	-0.519374	-0.439320	-3.396957
H	0.279460	-1.549562	-2.245781
H	0.125866	-2.595387	4.232384
H	-1.286902	-3.680842	4.354014
H	-1.491926	-1.928078	4.622100
H	-1.225318	4.894837	-1.683671

H	1.142904	5.367400	-2.093570
H	3.538957	4.675131	-1.926016
H	5.231625	3.027194	-1.317184
H	2.138497	0.397326	0.151588
H	-2.148978	2.134023	1.451966
H	-3.778885	2.222452	0.807274
H	-0.848104	4.381207	1.749398
H	-1.065693	6.698137	2.601049
H	-3.304297	7.781005	2.713381
H	-5.320968	6.521865	1.976937
H	-5.092456	4.200727	1.126102
H	-2.671190	3.241504	-2.518878
H	-3.404975	4.341939	-1.346824
H	-3.541525	0.604646	-1.914204
H	-5.686748	-0.609286	-2.279058
H	-7.846372	0.611383	-2.192288
H	-7.860726	3.064720	-1.759564
H	-5.717832	4.275506	-1.440724
H	5.997649	1.108842	-1.928745
H	6.382436	-0.411185	-1.167666
H	8.744658	0.642860	-1.457412
H	10.556953	1.745744	-0.180300
H	10.025040	3.030081	1.886237
H	7.664199	3.198404	2.655504
H	5.852988	2.093928	1.364648
H	3.689139	-0.420788	1.160626
H	5.374478	-0.868311	1.042729
H	5.035319	-3.253490	0.945861
H	4.454109	-5.242489	-0.409711
H	3.215663	-4.975351	-2.550474
H	2.566700	-2.699002	-3.319745
H	3.157293	-0.714167	-1.966539

Conformer **A**: M06/6-31+G(d,p) [5d] optimized

Method	Basis Set	Imaginary Freqs
RM06	6-31+G(d,p)	

HF

-2847.60921910

Processing: namphos-h5pm6.log
Frequency job incomplete: namphos-h5pm6.log
126
C 3.544503 -1.688400 -1.683081
C 4.112939 -1.840886 -0.416384
C 4.336010 -3.132208 0.068190
C 3.991877 -4.247546 -0.690536
C 3.413560 -4.086111 -1.947765
C 3.192946 -2.802660 -2.441534
C 4.502472 -0.643399 0.426169
N 4.798628 0.556461 -0.325570
C 6.102434 0.595701 -0.948706
C 7.188584 1.261181 -0.131570
C 8.504882 1.231709 -0.601309
C 9.530173 1.833888 0.119360
C 9.251483 2.474402 1.326520
C 7.943844 2.506400 1.801085
C 6.917183 1.903305 1.075450
C 3.836894 1.524501 -0.583933
C 4.219415 2.765712 -1.175006
C 3.269562 3.697291 -1.503313
C 1.893981 3.482290 -1.251203
C 1.503046 2.282346 -0.590642
C 2.497350 1.319535 -0.285392
C 0.120076 2.036379 -0.327977
C -0.847633 2.938228 -0.768707
C -0.430062 4.132473 -1.421256
C 0.896443 4.399490 -1.642560
C -0.229234 0.816111 0.439154
C -0.810299 -0.314936 -0.151366
C -1.112006 -1.471276 0.582277
C -0.865464 -1.449697 1.969019
C -0.258151 -0.349982 2.575449
C 0.057803 0.760617 1.801900
P -1.811257 -2.918513 -0.346389
C -0.910113 -4.388933 0.408450
C 0.578361 -4.124288 0.649867
C 1.259707 -5.357047 1.236880

C	1.093087	-6.574567	0.334850
C	-0.377917	-6.830448	0.025792
C	-1.044637	-5.582663	-0.546469
O	-1.114611	-0.277063	-1.486709
C	-0.053429	-0.668977	-2.339927
O	-1.239335	-2.552746	2.670453
C	-0.725952	-2.734045	3.969020
N	-2.226646	2.680470	-0.593532
C	-3.132935	3.313496	-1.541452
C	-4.422061	2.551917	-1.715668
C	-4.397760	1.183595	-2.000750
C	-5.584251	0.497788	-2.239821
C	-6.809176	1.162306	-2.181408
C	-6.840672	2.521694	-1.884252
C	-5.650271	3.210871	-1.655351
C	-2.767245	2.610833	0.769385
C	-2.951784	3.960814	1.417925
C	-1.842477	4.715383	1.816389
C	-2.008158	5.973697	2.386950
C	-3.287676	6.496490	2.571147
C	-4.398554	5.752800	2.182344
C	-4.228018	4.494458	1.607895
C	-3.497313	-2.976313	0.485074
C	-4.318394	-4.173708	0.004728
C	-5.741167	-4.144876	0.560005
C	-6.448745	-2.837856	0.220375
C	-5.644487	-1.645627	0.724191
C	-4.226584	-1.669460	0.167271
H	-3.352754	-3.055034	1.575169
H	-3.829562	-5.115041	0.294369
H	-4.356354	-4.165286	-1.099389
H	-6.309570	-5.004690	0.179705
H	-5.701222	-4.256642	1.656291
H	-7.463684	-2.828786	0.640194
H	-6.561401	-2.760184	-0.874751
H	-5.603172	-1.675001	1.825672
H	-6.133798	-0.699221	0.451860
H	-3.657955	-0.806854	0.545433
H	-4.265360	-1.548421	-0.929588
H	-1.383185	-4.644179	1.371928

H	1.063010	-3.856470	-0.307452
H	0.734145	-3.266029	1.315876
H	2.325032	-5.149295	1.412807
H	0.814749	-5.569841	2.224681
H	1.553157	-7.461881	0.791236
H	1.630057	-6.392620	-0.611544
H	-0.899067	-7.124310	0.952231
H	-0.483917	-7.672539	-0.671691
H	-2.099003	-5.788174	-0.778529
H	-0.569090	-5.317756	-1.507112
H	0.525320	1.626737	2.271401
H	-0.047262	-0.339851	3.640856
H	0.809945	0.005481	-2.233019
H	-0.433654	-0.615564	-3.363268
H	0.260131	-1.703196	-2.124041
H	0.373125	-2.675479	3.972484
H	-1.033887	-3.734820	4.282949
H	-1.131134	-1.998324	4.677899
H	-1.176013	4.867485	-1.711559
H	1.194481	5.330112	-2.124994
H	3.572634	4.633966	-1.970597
H	5.268623	2.984614	-1.356703
H	2.175041	0.372160	0.137815
H	-2.109028	1.983186	1.378248
H	-3.733604	2.088537	0.717456
H	-0.839878	4.309919	1.675504
H	-1.136023	6.547500	2.693579
H	-3.416742	7.479178	3.019597
H	-5.400461	6.152295	2.326024
H	-5.097103	3.910445	1.302326
H	-2.619420	3.343962	-2.511856
H	-3.367612	4.361890	-1.270251
H	-3.436975	0.666549	-2.022632
H	-5.555492	-0.565671	-2.473453
H	-7.734195	0.619415	-2.364863
H	-7.791418	3.048103	-1.830555
H	-5.672547	4.277131	-1.427431
H	6.026178	1.080442	-1.933408
H	6.403733	-0.441191	-1.167948
H	8.724960	0.727528	-1.543297

H 10.549765 1.802246 -0.258897
H 10.051590 2.945329 1.893080
H 7.717556 3.005400 2.741007
H 5.892257 1.931901 1.443233
H 3.716303 -0.421794 1.161937
H 5.394060 -0.900688 1.020336
H 4.794079 -3.263763 1.049416
H 4.180080 -5.247024 -0.301663
H 3.141522 -4.956445 -2.541627
H 2.746965 -2.665636 -3.424945
H 3.383670 -0.686939 -2.080558
Conformer **B**: B3LYP/6-31G(d) [5d]

Processing: namphos-n5dbe.log
PG=C01

Method BasisSet Imaginary Freqs
RB3LYP 6-31G(d) 0

HF Energy
-2849.3615792

ZPE E298 S298 Squasihar Equasihar Strans Srot
677.88400 714.083 340.586 285.997 714.297 46.099 40.581
ccl00:/aue/chem126/aue/ark/pj/nam> gtg namphos-n5dbe.log
Processing: namphos-n5dbe.log
126
C 1.398856 3.795292 -1.083479
C -0.064830 4.285387 -1.059588
C -0.252323 5.441706 -2.063916
C 0.748832 6.584904 -1.817489
C 2.200280 6.086868 -1.833384
C 2.395882 4.939276 -0.833205
P -1.233063 2.840290 -1.456513
C -2.954892 3.568326 -1.092411
C -3.912375 2.544492 -0.447935
C -5.319503 3.130680 -0.237149
C -5.920072 3.670555 -1.542332
C -4.972222 4.678388 -2.206804
C -3.572037 4.077361 -2.416755

C	-0.929912	1.706105	-0.003182
C	-0.683022	0.344880	-0.276887
C	-0.460974	-0.609430	0.737822
C	-0.470462	-0.158795	2.058972
C	-0.717955	1.174928	2.379564
C	-0.960619	2.097035	1.357196
C	-0.203003	-2.058266	0.456217
C	1.153761	-2.521273	0.349109
C	1.405575	-3.920482	0.171916
C	0.314522	-4.818994	0.108988
C	-0.975951	-4.361756	0.220939
C	-1.253507	-2.976402	0.400164
C	2.263704	-1.640015	0.465207
C	3.580554	-2.087943	0.376780
C	3.807434	-3.484735	0.164738
C	2.752330	-4.357996	0.078002
N	4.664414	-1.212269	0.471621
C	6.003213	-1.667373	0.813275
C	6.970686	-1.823755	-0.357108
C	8.349211	-1.864467	-0.105451
C	9.260441	-2.040180	-1.146137
C	8.804992	-2.170125	-2.461041
C	7.435372	-2.122980	-2.722114
C	6.524065	-1.951428	-1.676484
N	-2.605353	-2.531984	0.561578
C	-3.280665	-2.023829	-0.656734
C	-3.726976	-3.086193	-1.650907
C	-2.837855	-3.574617	-2.620409
C	-3.235423	-4.558960	-3.526102
C	-4.534311	-5.071828	-3.479785
C	-5.432169	-4.589841	-2.525794
C	-5.029800	-3.604027	-1.621467
O	-0.765715	-0.109488	-1.579758
C	0.431719	-0.078236	-2.357038
O	-1.266213	3.407632	1.608503
C	-1.313910	3.853203	2.954380
C	4.508728	0.224500	0.317632
C	4.375973	1.028470	1.609018
C	3.979533	0.439259	2.814433
C	3.847954	1.209877	3.972731

C	4.109073	2.580140	3.940580
C	4.507393	3.177093	2.741518
C	4.643756	2.404478	1.588418
C	-3.447385	-3.368544	1.418242
C	-4.576722	-2.590564	2.079260
C	-4.375713	-1.290116	2.562241
C	-5.404728	-0.608738	3.212989
C	-6.649936	-1.216557	3.395929
C	-6.859658	-2.510738	2.918089
C	-5.829717	-3.188479	2.260970
H	-0.287982	4.659818	-0.055043
H	-1.270976	5.840902	-2.000461
H	-0.126107	5.062743	-3.089322
H	0.606125	7.371851	-2.569789
H	0.536282	7.044575	-0.840685
H	2.889975	6.911804	-1.611532
H	2.450460	5.732250	-2.844476
H	2.259309	5.320368	0.189644
H	3.423841	4.556110	-0.887567
H	1.546895	3.007033	-0.335660
H	1.612742	3.344914	-2.065147
H	-2.840440	4.414027	-0.399819
H	-3.983586	1.656967	-1.094391
H	-3.515688	2.198511	0.510696
H	-5.975901	2.365993	0.198646
H	-5.260548	3.947811	0.497882
H	-6.898601	4.130809	-1.352323
H	-6.096226	2.832598	-2.232948
H	-4.892187	5.575110	-1.573792
H	-5.382257	5.012041	-3.169248
H	-2.920396	4.816686	-2.895915
H	-3.641284	3.233455	-3.118084
H	-0.290339	-0.872789	2.857855
H	-0.727883	1.477021	3.419937
H	0.765753	0.953827	-2.515875
H	0.175296	-0.521831	-3.321952
H	1.226885	-0.664390	-1.883228
H	-2.081685	3.319587	3.529617
H	-1.570957	4.913141	2.907397
H	-0.343058	3.736910	3.453214

H	-1.805184	-5.058344	0.157927
H	0.511824	-5.879442	-0.033051
H	2.945070	-5.416671	-0.081551
H	4.817856	-3.857894	0.039262
H	2.062399	-0.596791	0.671987
H	-2.593555	-1.333852	-1.147421
H	-4.150402	-1.447323	-0.323147
H	-1.830045	-3.170348	-2.666607
H	-2.533822	-4.920713	-4.273729
H	-4.845999	-5.835773	-4.187505
H	-6.448033	-4.975665	-2.489144
H	-5.737479	-3.221771	-0.888777
H	-2.797324	-3.780089	2.200173
H	-3.881584	-4.233233	0.887845
H	-3.410153	-0.817065	2.408848
H	-5.234647	0.400932	3.579059
H	-7.450595	-0.683606	3.902265
H	-7.825848	-2.991560	3.048921
H	-6.000021	-4.195376	1.884886
H	5.923540	-2.615170	1.357531
H	6.430921	-0.955299	1.532352
H	8.711262	-1.755527	0.915425
H	10.325891	-2.068519	-0.932713
H	9.513484	-2.302491	-3.274318
H	7.071590	-2.219175	-3.741904
H	5.458685	-1.912462	-1.883391
H	3.641307	0.410369	-0.326104
H	5.377862	0.598417	-0.240587
H	4.966316	2.874119	0.660943
H	4.721394	4.242205	2.706344
H	4.009797	3.178267	4.842589
H	3.541855	0.735269	4.901610
H	3.772814	-0.626256	2.844293

Conformer **C**: B3LYP/6-31G(d) [5d]

Processing: namphos-m5dbe.log
PG=C01

Method BasisSet Imaginary Freqs
RB3LYP 6-31G(d) 0

HF Energy
-2849.3601616

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.82580	713.937	338.261	285.613	714.148	46.099	40.436

Processing: namphos-m5dbe.log
126

C	2.595597	3.730532	2.223319
C	2.439705	4.631334	1.159920
C	1.814180	5.857730	1.407734
C	1.355862	6.184483	2.686789
C	1.517332	5.281799	3.737816
C	2.139153	4.051884	3.501306
C	2.978758	4.291773	-0.214828
N	2.372571	3.082037	-0.797878
C	3.092795	2.621890	-2.003104
C	4.530206	2.222840	-1.727228
C	5.565116	2.675586	-2.553817
C	6.887547	2.284155	-2.329678
C	7.193968	1.440474	-1.261879
C	6.168970	0.987717	-0.425933
C	4.848037	1.370508	-0.659706
C	0.950446	3.194616	-1.033202
C	0.083855	2.200129	-0.594074
C	-1.335534	2.358447	-0.795429
C	-1.824386	3.519990	-1.475221
C	-0.903730	4.485652	-1.947119
C	0.442236	4.327622	-1.728990
C	-3.225319	3.661179	-1.651524
C	-4.114375	2.726748	-1.181663
C	-3.649720	1.571662	-0.478216
C	-2.275726	1.411013	-0.308780
C	0.562590	0.975511	0.124414
C	0.987737	-0.183197	-0.561587
C	1.310992	-1.385824	0.102774
C	1.230496	-1.384946	1.516915

C	0.834320	-0.242685	2.217497
C	0.497179	0.914338	1.516792
P	1.752434	-2.867890	-0.946265
C	3.396974	-3.500637	-0.227123
C	4.330833	-2.375426	0.259246
C	5.671749	-2.934282	0.768290
C	6.380700	-3.787149	-0.292870
C	5.457389	-4.898353	-0.810815
C	4.122319	-4.326663	-1.316596
O	1.157371	-0.098492	-1.929998
C	0.032672	-0.424531	-2.748136
O	1.574473	-2.551015	2.148025
C	1.434546	-2.629338	3.558144
N	-4.562250	0.631126	0.004903
C	-4.146090	-0.702323	0.404992
C	-3.816154	-0.894537	1.884316
C	-3.566638	0.183898	2.739512
C	-3.242325	-0.032760	4.081624
C	-3.162044	-1.331203	4.586165
C	-3.413511	-2.414992	3.739722
C	-3.742049	-2.195455	2.402159
C	0.511648	-4.149817	-0.283056
C	-0.929010	-3.724945	-0.636612
C	-1.968571	-4.756968	-0.167334
C	-1.671460	-6.153054	-0.731645
C	-0.241096	-6.588797	-0.387067
C	0.800966	-5.554900	-0.850995
C	-5.961536	0.954631	0.236367
C	-6.937117	0.491201	-0.842378
C	-8.303226	0.405200	-0.539594
C	-9.226742	0.017684	-1.509728
C	-8.794893	-0.298597	-2.800788
C	-7.436457	-0.223139	-3.109223
C	-6.513525	0.169798	-2.136055
H	0.602708	-4.193412	0.808085
H	1.797465	-5.893036	-0.545464
H	0.805765	-5.513003	-1.950732
H	-0.020290	-7.565858	-0.836733
H	-0.156688	-6.720190	0.702093
H	-2.396655	-6.883899	-0.350479

H	-1.791025	-6.133603	-1.825168
H	-1.963305	-4.800449	0.931989
H	-2.975865	-4.433415	-0.463737
H	-1.152606	-2.746402	-0.194185
H	-1.013658	-3.605871	-1.727508
H	3.174657	-4.152358	0.629393
H	4.521060	-1.674356	-0.565687
H	3.850575	-1.800471	1.056130
H	6.321921	-2.108294	1.087113
H	5.488134	-3.548017	1.663229
H	7.305849	-4.215330	0.115056
H	6.676233	-3.142981	-1.134013
H	5.261967	-5.616870	-0.000364
H	5.950529	-5.461443	-1.614255
H	3.486025	-5.140246	-1.682908
H	4.310742	-3.675349	-2.181993
H	0.175915	1.793826	2.066233
H	0.770805	-0.243423	3.298910
H	-0.183828	-1.497940	-2.697765
H	0.318003	-0.164787	-3.770237
H	-0.852690	0.151111	-2.457736
H	2.096222	-1.918917	4.070676
H	1.723163	-3.646855	3.828899
H	0.397631	-2.447963	3.869503
H	1.136415	5.077772	-2.094630
H	-1.278787	5.357157	-2.479621
H	-3.596873	4.531949	-2.187273
H	-5.173332	2.854417	-1.377846
H	-1.900245	0.566366	0.252627
H	2.540528	1.756296	-2.382331
H	3.082495	3.390233	-2.799366
H	5.333082	3.342805	-3.381380
H	7.676522	2.646111	-2.984137
H	8.222287	1.139638	-1.078984
H	6.399891	0.333137	0.410607
H	4.049867	1.019025	-0.012637
H	4.051676	4.086345	-0.136355
H	2.886143	5.174364	-0.872926
H	1.682967	6.563923	0.591145
H	0.871620	7.142365	2.858934

H 1.163571 5.533169 4.734447
H 2.273665 3.344978 4.316539
H 3.073871 2.773025 2.038358
H -6.052831 2.037618 0.377629
H -6.259181 0.511175 1.196491
H -8.645548 0.642370 0.466258
H -10.282136 -0.044541 -1.257129
H -9.512241 -0.605278 -3.557263
H -7.090359 -0.470884 -4.109420
H -5.456343 0.224616 -2.378365
H -3.282226 -0.992322 -0.205028
H -4.949517 -1.398784 0.130045
H -3.944867 -3.044068 1.751716
H -3.365007 -3.430692 4.124222
H -2.915224 -1.498924 5.631307
H -3.053780 0.817394 4.732296
H -3.622214 1.196270 2.351401

Conformer **D**: B3LYP/6-31G(d) [5d]

Processing: namphos-o5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3599074

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.93302	714.097	339.798	285.883	714.311	46.099	40.599

Processing: namphos-o5dbe.log
126
C -0.819401 5.446083 -2.116365
C -0.557724 4.474803 -0.943104
C 0.952879 4.435880 -0.625367
C 1.514339 5.838459 -0.337328
C 1.237633 6.808261 -1.494716

C	-0.259644	6.850868	-1.830465
P	-1.148103	2.745692	-1.422820
C	-3.049755	2.799078	-1.392513
C	-3.720568	3.724017	-0.359050
C	-5.253912	3.584608	-0.390479
C	-5.818270	3.831019	-1.797289
C	-5.149591	2.913716	-2.831873
C	-3.617455	3.051085	-2.807289
C	-0.827195	1.659459	0.068922
C	-0.608432	0.295195	-0.222982
C	-0.356256	-0.674116	0.766835
C	-0.315383	-0.238132	2.093364
C	-0.532188	1.094081	2.433285
C	-0.795445	2.035900	1.432323
C	-0.077897	-2.115422	0.465847
C	-1.102054	-3.063430	0.431108
C	-0.786091	-4.440385	0.246042
C	0.515311	-4.861276	0.117174
C	1.581576	-3.932212	0.163369
C	1.289801	-2.540569	0.336638
C	2.373369	-1.625259	0.428502
C	3.701369	-2.033317	0.327943
C	3.969851	-3.424250	0.128548
C	2.940200	-4.329678	0.058699
N	-2.461368	-2.661060	0.626862
C	-3.174520	-2.138054	-0.562380
C	-3.626920	-3.187897	-1.567250
C	-4.924976	-3.716595	-1.526428
C	-5.333455	-4.691124	-2.440220
C	-4.446367	-5.151040	-3.414900
C	-3.152084	-4.627671	-3.472081
C	-2.748501	-3.654465	-2.557083
N	4.752779	-1.116117	0.396682
C	4.531185	0.307849	0.212667
C	4.282020	1.128295	1.477232
C	4.030637	0.533572	2.717215
C	3.792494	1.319956	3.848245
C	3.800241	2.711554	3.752526
C	4.051038	3.315182	2.516422
C	4.292970	2.528045	1.391314

O	-0.748387	-0.125501	-1.535602
C	0.442035	-0.165896	-2.328637
O	-1.043859	3.350539	1.723249
C	-0.908200	3.792954	3.064260
C	-3.265748	-3.535782	1.481478
C	-4.391695	-2.797356	2.191677
C	-4.199765	-1.509354	2.710272
C	-5.223072	-0.866300	3.407253
C	-6.453250	-1.500679	3.601101
C	-6.654060	-2.782547	3.087499
C	-5.629970	-3.421897	2.384446
C	6.113248	-1.513477	0.723609
C	7.069823	-1.643852	-0.458944
C	8.452316	-1.612448	-0.229130
C	9.354956	-1.763435	-1.281217
C	8.886161	-1.940697	-2.585793
C	7.511952	-1.965404	-2.825282
C	6.609596	-1.818337	-1.768332
H	-0.498974	1.385238	3.476078
H	-0.111230	-0.961751	2.877541
H	-1.087570	4.840843	-0.059524
H	-0.354487	5.048472	-3.030628
H	-1.893737	5.520389	-2.322179
H	-0.438751	7.505588	-2.693525
H	-0.807514	7.292482	-0.984640
H	1.797571	6.479333	-2.382909
H	1.603206	7.813993	-1.249073
H	2.593561	5.775899	-0.141830
H	1.052969	6.229897	0.581735
H	1.489564	4.005504	-1.484944
H	1.147739	3.777469	0.227741
H	-3.303070	1.761480	-1.128310
H	-3.344447	4.061024	-3.145234
H	-3.163019	2.352887	-3.520273
H	-5.529246	3.132867	-3.838617
H	-5.419571	1.869139	-2.616795
H	-5.643318	4.880756	-2.078003
H	-6.906147	3.683600	-1.803480
H	-5.707069	4.279879	0.329078
H	-5.530134	2.571619	-0.062041

H	-3.456580	4.769156	-0.576598
H	-3.340957	3.510356	0.645023
H	0.133656	-0.524716	-3.313378
H	0.870644	0.837643	-2.431050
H	1.179023	-0.852322	-1.899942
H	-1.099280	4.867687	3.042431
H	-1.638981	3.311188	3.727003
H	0.104229	3.609734	3.446599
H	0.739990	-5.916287	-0.024808
H	-1.595441	-5.161028	0.195973
H	2.144789	-0.586245	0.625604
H	3.163201	-5.383315	-0.094714
H	4.990194	-3.767755	-0.002550
H	-2.588882	-3.955288	2.235780
H	-3.697080	-4.393914	0.938406
H	-4.046048	-1.584504	-0.195825
H	-2.510816	-1.426324	-1.054497
H	-5.623938	-3.352406	-0.776368
H	-6.345575	-5.085661	-2.394292
H	-4.762740	-5.906249	-4.129860
H	-2.458861	-4.972525	-4.235335
H	-1.744233	-3.242562	-2.611839
H	-5.793071	-4.419310	1.980915
H	-7.608862	-3.283427	3.226470
H	-7.249505	-0.997534	4.143587
H	-5.060427	0.134313	3.800462
H	-3.246161	-1.015167	2.548419
H	6.523415	-0.778589	1.429959
H	6.077848	-2.458582	1.277374
H	8.824361	-1.466313	0.783476
H	10.423671	-1.735382	-1.084805
H	9.587625	-2.053745	-3.408022
H	7.137665	-2.098591	-3.837071
H	5.540569	-1.834862	-1.958794
H	5.409404	0.716653	-0.304991
H	3.691103	0.440575	-0.479647
H	4.494252	3.005175	0.433815
H	4.065763	4.398715	2.430660
H	3.620267	3.322807	4.633085
H	3.601070	0.840496	4.804921

H 4.015086 -0.549332 2.794656

Conformer **E**: B3LYP/6-31G(d) [5d]

Processing: namphos-i5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3595476

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
678.06249	714.138	337.337	285.485	714.348	46.099	40.626

ccl00:/aue/chem126/aue/ark/pj/nam> gtg namphos-i5dbe.log
Processing: namphos-i5dbe.log
126
C 4.878139 -0.977535 -0.343118
C 4.324580 -2.399102 -0.583240
C 5.395288 -3.451051 -0.231927
C 6.711675 -3.202778 -0.991476
C 7.248868 -1.783912 -0.759802
C 6.187678 -0.731819 -1.110926
P 2.724887 -2.612669 0.422614
C 2.141674 -4.366378 -0.021758
C 0.604105 -4.485747 -0.061807
C 0.151087 -5.929815 -0.338508
C 0.730253 -6.919148 0.682185
C 2.258292 -6.798100 0.761432
C 2.693504 -5.349148 1.039370
C 1.616954 -1.483110 -0.573720
C 1.114433 -0.336553 0.072507
C 0.302327 0.617191 -0.579446
C -0.041692 0.357087 -1.909536
C 0.434184 -0.761764 -2.592532
C 1.280217 -1.661494 -1.937075
C -0.179351 1.863762 0.097130
C -1.576631 1.970968 0.426064

C	-2.062877	3.161354	1.058195
C	-1.155353	4.202319	1.354625
C	0.173477	4.091595	1.031695
C	0.688701	2.930374	0.386074
C	-2.499307	0.912692	0.188257
C	-3.855138	1.021372	0.495661
C	-4.321018	2.238891	1.085732
C	-3.443756	3.255597	1.365514
N	-4.762098	-0.008546	0.232534
C	-6.060974	-0.082576	0.882929
C	-7.244280	0.432726	0.067238
C	-8.543815	0.053835	0.432242
C	-9.650706	0.529728	-0.269534
C	-9.473491	1.389239	-1.357289
C	-8.183758	1.765838	-1.732676
C	-7.076356	1.291079	-1.024386
N	2.073367	2.874167	0.049255
C	2.418833	2.815949	-1.388151
C	2.356641	4.144294	-2.131561
C	1.123677	4.726153	-2.466322
C	1.069140	5.946378	-3.140271
C	2.248071	6.606317	-3.497445
C	3.480577	6.036860	-3.175470
C	3.529929	4.816791	-2.497006
O	1.477388	-0.101858	1.378866
C	0.542605	-0.534084	2.367214
O	1.817564	-2.754870	-2.560488
C	1.502268	-2.990036	-3.923357
C	-4.455018	-1.113088	-0.662761
C	-4.087572	-2.426119	0.022120
C	-3.447398	-2.451349	1.267491
C	-3.109278	-3.665846	1.868117
C	-3.407198	-4.873144	1.232248
C	-4.046762	-4.857852	-0.009647
C	-4.386683	-3.642402	-0.605268
C	3.002716	3.738079	0.788361
C	3.045690	3.529573	2.291611
C	3.113841	4.637178	3.145336
C	3.244107	4.472722	4.526126
C	3.305490	3.190047	5.071637

C	3.236302	2.078902	4.226776
C	3.109201	2.244617	2.846855
H	4.076892	-2.505806	-1.646980
H	5.032966	-4.458410	-0.466577
H	5.592101	-3.428839	0.850613
H	7.459137	-3.949055	-0.691188
H	6.537725	-3.351029	-2.067819
H	8.161724	-1.621004	-1.347614
H	7.532124	-1.671886	0.297360
H	5.987804	-0.765195	-2.192550
H	6.563804	0.276727	-0.893610
H	4.131197	-0.227067	-0.628087
H	5.060389	-0.840258	0.732763
H	2.533678	-4.645104	-1.008414
H	0.185993	-4.158319	0.902284
H	0.183879	-3.821404	-0.821435
H	-0.945367	-5.976271	-0.337899
H	0.478051	-6.220188	-1.348534
H	0.439018	-7.947134	0.428659
H	0.301428	-6.707296	1.673260
H	2.699495	-7.133920	-0.189123
H	2.654675	-7.462652	1.540627
H	3.786237	-5.297026	1.095452
H	2.323592	-5.043233	2.028807
H	-0.680693	1.063620	-2.433310
H	0.157360	-0.907202	-3.630007
H	-0.456182	-0.127303	2.172495
H	0.910259	-0.149913	3.321051
H	0.498988	-1.630257	2.404301
H	0.425480	-3.147156	-4.067846
H	2.038978	-3.899443	-4.199889
H	1.835539	-2.163173	-4.563956
H	0.839388	4.915498	1.252558
H	-1.526244	5.105719	1.833968
H	-3.812800	4.172451	1.820131
H	-5.376986	2.377845	1.287444
H	-2.114938	-0.011706	-0.222294
H	1.757654	2.094722	-1.867007
H	3.435847	2.410821	-1.460987
H	0.201566	4.218981	-2.195903

H	0.104869	6.380490	-3.392295
H	2.204898	7.555020	-4.026047
H	4.403719	6.539787	-3.452349
H	4.494479	4.375767	-2.253031
H	3.996640	3.504404	0.383116
H	2.848588	4.808723	0.573877
H	3.067096	5.640318	2.725273
H	3.293595	5.345511	5.172386
H	3.405523	3.056461	6.145817
H	3.287671	1.075843	4.643640
H	3.035268	1.379555	2.196711
H	-6.008303	0.450970	1.838502
H	-6.246191	-1.132421	1.147474
H	-8.688625	-0.622033	1.273300
H	-10.650968	0.224882	0.027352
H	-10.334372	1.758027	-1.908509
H	-8.035339	2.431449	-2.579196
H	-6.073776	1.585535	-1.320058
H	-3.651184	-0.798915	-1.336729
H	-5.330996	-1.286276	-1.303562
H	-4.897830	-3.637576	-1.566244
H	-4.293092	-5.791920	-0.508034
H	-3.150961	-5.817971	1.703906
H	-2.617547	-3.668545	2.837510
H	-3.221406	-1.515047	1.769320

Conformer **F**: B3LYP/6-31G(d) [5d]

Processing: namphos-p5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3594087

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.88534	714.048	340.168	285.625	714.263	46.099	40.569

Processing: namphos-p5dbe.log
126
C -2.944930 -2.845887 3.239925
C -3.204961 -3.827901 2.273385
C -3.010864 -5.170574 2.612607
C -2.567722 -5.531242 3.888054
C -2.311004 -4.546788 4.842090
C -2.501016 -3.201001 4.513180
C -3.737202 -3.436385 0.907652
N -2.897045 -2.455059 0.213979
C -3.608703 -1.736963 -0.868628
C -4.105048 -2.600697 -2.020512
C -3.253130 -2.917666 -3.089566
C -3.691715 -3.725113 -4.139743
C -4.995241 -4.227984 -4.141742
C -5.856871 -3.913583 -3.089420
C -5.412384 -3.105707 -2.040436
C -1.549707 -2.855646 -0.076667
C -0.500880 -1.945601 0.072214
C 0.850872 -2.370425 -0.174435
C 1.098711 -3.717376 -0.593506
C 0.008159 -4.603874 -0.752326
C -1.275244 -4.187541 -0.497728
C 2.439865 -4.118485 -0.825135
C 3.495806 -3.260483 -0.645630
C 3.275562 -1.921663 -0.191753
C 1.963328 -1.508732 0.032185
C -0.740230 -0.554912 0.577729
C -0.989091 0.540616 -0.275751
C -1.199409 1.850182 0.204615
C -1.165620 2.037166 1.607575
C -0.895512 0.972200 2.471573
C -0.683594 -0.302456 1.949404
P -1.526195 3.193654 -1.051401
C -3.201539 3.915295 -0.505590
C -4.173381 2.838676 0.020092
C -5.546299 3.434787 0.378507
C -6.174812 4.187301 -0.802561
C -5.213117 5.250559 -1.350183
C -3.848574 4.639165 -1.710308

O	-1.136702	0.284572	-1.626677
C	0.024753	0.413976	-2.447638
O	-1.436526	3.300652	2.061384
C	-1.417073	3.543967	3.458740
N	4.361186	-1.063322	-0.001454
C	4.196649	0.377232	0.099972
C	4.136144	0.947397	1.515149
C	3.771194	0.164576	2.616132
C	3.703132	0.724279	3.894598
C	3.997267	2.074429	4.089222
C	4.365024	2.863344	2.996182
C	4.438171	2.300601	1.721996
C	-0.287158	4.525538	-0.500367
C	1.153808	4.011105	-0.705708
C	2.205272	5.070469	-0.334671
C	1.988074	6.376454	-1.111112
C	0.559296	6.899771	-0.912471
C	-0.495657	5.840514	-1.279986
C	5.715042	-1.556488	0.197873
C	6.627878	-1.502764	-1.024501
C	8.016764	-1.569830	-0.846136
C	8.879173	-1.557463	-1.941760
C	8.363499	-1.469098	-3.237734
C	6.983033	-1.394108	-3.424734
C	6.120832	-1.411472	-2.324948
H	-0.433985	4.729122	0.565586
H	-1.493202	6.248126	-1.080735
H	-0.447298	5.639817	-2.360993
H	0.397709	7.807144	-1.509300
H	0.425067	7.190420	0.140199
H	2.719426	7.134234	-0.800799
H	2.161179	6.193635	-2.182213
H	2.148246	5.274123	0.744800
H	3.213164	4.677119	-0.524182
H	1.319541	3.103472	-0.112765
H	1.289265	3.729546	-1.761358
H	-3.027319	4.641828	0.300336
H	-4.305184	2.062469	-0.748748
H	-3.752613	2.339213	0.897384
H	-6.217957	2.637230	0.723265

H	-5.425502	4.127782	1.224870
H	-7.125372	4.646914	-0.501496
H	-6.412226	3.470635	-1.602739
H	-5.071456	6.037540	-0.594055
H	-5.646667	5.740223	-2.232207
H	-3.186121	5.418552	-2.103072
H	-3.980543	3.913422	-2.525630
H	-0.484142	-1.128650	2.625165
H	-0.855085	1.118882	3.544292
H	0.368532	1.454584	-2.474193
H	-0.283273	0.115444	-3.452484
H	0.830681	-0.241498	-2.100404
H	-2.168591	2.940551	3.984306
H	-1.656553	4.602235	3.579365
H	-0.427576	3.344255	3.889959
H	-2.099771	-4.877993	-0.634222
H	0.200188	-5.623472	-1.079749
H	2.626892	-5.133819	-1.167990
H	4.499767	-3.596310	-0.880679
H	1.770359	-0.516661	0.419362
H	-2.934198	-0.973792	-1.257261
H	-4.461412	-1.224468	-0.404935
H	-2.242183	-2.519198	-3.096920
H	-3.018117	-3.956095	-4.961245
H	-5.338902	-4.853434	-4.961625
H	-6.876297	-4.291439	-3.087362
H	-6.094132	-2.853924	-1.230344
H	-4.714062	-2.950992	1.037883
H	-3.937907	-4.345894	0.317331
H	-3.207694	-5.942308	1.871746
H	-2.420431	-6.580161	4.132364
H	-1.965721	-4.823648	5.834865
H	-2.307652	-2.428430	5.253605
H	-3.085355	-1.800769	2.978987
H	5.662581	-2.583502	0.576464
H	6.173950	-0.972201	1.007274
H	8.425569	-1.630352	0.161016
H	9.953508	-1.609382	-1.784670
H	9.033828	-1.454542	-4.092938
H	6.572485	-1.321288	-4.428599

H 5.046795 -1.350481 -2.473661
H 3.294645 0.661045 -0.454173
H 5.033202 0.849585 -0.432900
H 4.737409 2.918316 0.877273
H 4.605172 3.914078 3.137134
H 3.947456 2.508197 5.084535
H 3.420640 0.100930 4.739218
H 3.539301 -0.886055 2.470146

Conformer **G**: B3LYP/6-31G(d) [5d]

Processing: namphos-k5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3591746

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
678.10952	714.245	339.037	286.491	714.452	46.099	40.669

Processing: namphos-k5dbe.log
126
C 4.249059 2.341319 0.922584
C 3.295155 3.543637 0.763138
C 4.056967 4.750001 0.173477
C 5.305605 5.103673 1.001338
C 6.243408 3.899705 1.160421
C 5.494079 2.698127 1.752035
P 1.815646 3.079267 -0.338419
C 0.566601 4.465635 0.058042
C -0.895522 3.975288 0.094545
C -1.880292 5.129781 0.351707
C -1.726996 6.256651 -0.679068
C -0.273246 6.743525 -0.748471
C 0.697753 5.579201 -1.008203
C 1.135437 1.598930 0.578079

C	0.956887	0.401722	-0.144550
C	0.482189	-0.786241	0.455237
C	0.184366	-0.741601	1.819955
C	0.342307	0.420006	2.574462
C	0.811879	1.582110	1.956920
C	0.255334	-2.045589	-0.320383
C	-1.101146	-2.471590	-0.557495
C	-1.347592	-3.678076	-1.294245
C	-0.246166	-4.424566	-1.775311
C	1.039448	-4.008922	-1.540058
C	1.319099	-2.813308	-0.811028
C	-2.225422	-1.729524	-0.105862
C	-3.535523	-2.127972	-0.352819
C	-3.753251	-3.334915	-1.079556
C	-2.686184	-4.079807	-1.524645
N	-4.614053	-1.352516	0.137816
C	-5.925437	-1.985398	0.267852
C	-6.765234	-1.378453	1.381538
C	-8.110679	-1.060510	1.166311
C	-8.901411	-0.556797	2.202891
C	-8.350276	-0.359141	3.469179
C	-7.005311	-0.668789	3.692543
C	-6.220521	-1.175814	2.657396
N	2.670767	-2.415439	-0.617347
C	3.213429	-2.451048	0.755496
C	3.580455	-3.835882	1.272794
C	2.588021	-4.740319	1.681822
C	2.926401	-6.011586	2.146286
C	4.266721	-6.401357	2.214317
C	5.264045	-5.510471	1.815796
C	4.920366	-4.239203	1.348954
O	1.296025	0.360222	-1.479942
C	0.241996	0.653714	-2.394878
O	0.971833	2.760755	2.632884
C	0.665897	2.803359	4.017611
C	-4.652241	0.082464	-0.201261
C	-5.283917	0.403983	-1.550478
C	-4.637479	0.064503	-2.749271
C	-5.222155	0.356323	-3.981504
C	-6.463701	0.996152	-4.037212

C	-7.115517	1.339883	-2.852633
C	-6.528197	1.043063	-1.619857
C	3.627494	-2.822862	-1.651583
C	4.806622	-1.874375	-1.796217
C	4.598342	-0.504417	-2.013378
C	5.683062	0.345937	-2.230821
C	6.988905	-0.154865	-2.226635
C	7.204036	-1.514958	-2.004621
C	6.116679	-2.367293	-1.792103
H	2.918722	3.820434	1.754861
H	3.404313	5.628801	0.120912
H	4.358465	4.521115	-0.859474
H	5.834984	5.943649	0.532294
H	4.991100	5.450198	1.997261
H	7.102893	4.165093	1.789935
H	6.649046	3.623351	0.175777
H	5.188767	2.934687	2.782607
H	6.158418	1.826485	1.814691
H	3.724269	1.500800	1.389939
H	4.568110	1.991318	-0.068999
H	0.809625	4.884191	1.044125
H	-1.144619	3.501187	-0.867409
H	-1.024117	3.207949	0.863249
H	-2.909709	4.747414	0.348271
H	-1.700848	5.534229	1.359232
H	-2.400542	7.089580	-0.438574
H	-2.030156	5.884443	-1.668998
H	-0.007537	7.232984	0.200583
H	-0.161962	7.503746	-1.532892
H	1.724036	5.959583	-1.055812
H	0.488936	5.146383	-1.997399
H	-0.184899	-1.640997	2.305856
H	0.097964	0.404634	3.629903
H	-0.621237	-0.001649	-2.227299
H	0.646281	0.475333	-3.393806
H	-0.067315	1.703517	-2.313678
H	-0.390187	2.569924	4.205365
H	0.870577	3.827271	4.335723
H	1.296102	2.112290	4.592197
H	1.866004	-4.618727	-1.886301

H	-0.431400	-5.346498	-2.322254
H	-2.864069	-4.992183	-2.089859
H	-4.761726	-3.656246	-1.314464
H	-2.055616	-0.831556	0.475120
H	2.478635	-1.989037	1.416892
H	4.101814	-1.810846	0.768715
H	1.543218	-4.444455	1.637432
H	2.143697	-6.696915	2.461838
H	4.530361	-7.390462	2.579819
H	6.309943	-5.802225	1.870213
H	5.701312	-3.546164	1.043963
H	3.081544	-2.836936	-2.600708
H	4.012723	-3.843778	-1.489708
H	3.584392	-0.113598	-2.007188
H	5.507087	1.403412	-2.411479
H	7.830776	0.511402	-2.396884
H	8.214818	-1.915157	-1.997353
H	6.286661	-3.429277	-1.627255
H	-6.501412	-1.960584	-0.672153
H	-5.752030	-3.040064	0.506673
H	-8.542235	-1.207513	0.178685
H	-9.944894	-0.315145	2.017763
H	-8.961690	0.035329	4.276462
H	-6.568941	-0.517251	4.676645
H	-5.172982	-1.410985	2.825989
H	-3.628207	0.460265	-0.172019
H	-5.205269	0.600960	0.588495
H	-7.040824	1.311213	-0.698772
H	-8.080453	1.839474	-2.885546
H	-6.916660	1.226674	-4.997911
H	-4.705862	0.089789	-4.900229
H	-3.670535	-0.430255	-2.715091

Conformer **H**: B3LYP/6-31G(d) [5d]

Processing: namphos-j5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs

RB3LYP 6-31G(d) 0

HF Energy
-2849.3586009

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
678.06400	714.052	333.824	285.208	714.256	46.099	40.508

Processing: namphos-j5dbe.log
126

C	-4.698431	1.133198	0.474168
C	-3.999242	2.447875	0.064619
C	-4.817890	3.657947	0.557963
C	-6.279908	3.597611	0.079255
C	-6.961518	2.285348	0.489000
C	-6.157775	1.076052	-0.007264
P	-2.226336	2.434394	0.751777
C	-1.530223	4.128846	0.238824
C	-0.021448	4.087752	-0.080336
C	0.526532	5.485615	-0.417559
C	0.255437	6.494898	0.706418
C	-1.235096	6.529091	1.070463
C	-1.765209	5.123663	1.401830
C	-1.427978	1.231698	-0.437522
C	-0.927255	0.027192	0.096783
C	-0.241939	-0.930774	-0.684649
C	-0.049687	-0.631200	-2.035179
C	-0.562365	0.529131	-2.617360
C	-1.269558	1.441504	-1.829153
C	0.280383	-2.212994	-0.107764
C	1.683427	-2.327424	0.193367
C	2.185009	-3.559769	0.725064
C	1.292963	-4.631075	0.955014
C	-0.039740	-4.512304	0.647602
C	-0.562610	-3.309594	0.097890
C	2.594823	-1.250743	0.004435
C	3.959321	-1.373809	0.269412
C	4.439215	-2.629375	0.762799
C	3.573297	-3.667190	0.993201
N	4.862611	-0.329936	0.059116

C	6.197170	-0.332965	0.638151
C	7.318600	-0.827095	-0.272811
C	8.649371	-0.551366	0.072369
C	9.702104	-1.006801	-0.720093
C	9.438725	-1.742052	-1.879332
C	8.117816	-2.015734	-2.234192
C	7.064421	-1.561694	-1.435364
N	-1.939715	-3.245117	-0.318256
C	-2.069233	-3.511529	-1.769858
C	-3.401459	-3.102440	-2.366965
C	-4.215395	-4.043607	-3.008142
C	-5.416552	-3.661946	-3.611617
C	-5.818422	-2.326679	-3.579163
C	-5.013630	-1.378830	-2.939821
C	-3.816008	-1.762979	-2.337311
O	-1.183132	-0.261407	1.416661
C	-0.154132	0.047477	2.356624
O	-1.829378	2.580893	-2.340618
C	-1.699012	2.842837	-3.728735
C	4.530003	0.862988	-0.706310
C	4.272796	2.110548	0.132820
C	3.652364	2.032708	1.386521
C	3.422552	3.186554	2.138304
C	3.810665	4.435781	1.647665
C	4.430587	4.523174	0.399238
C	4.662100	3.366850	-0.348297
C	-2.894615	-4.080608	0.429397
C	-2.956715	-3.832763	1.923075
C	-2.939393	-4.912053	2.815049
C	-3.072264	-4.710350	4.190679
C	-3.219889	-3.417422	4.693721
C	-3.235866	-2.333454	3.811682
C	-3.109686	-2.538501	2.437435
H	-3.943672	2.496623	-1.030540
H	-4.365948	4.593180	0.208742
H	-4.801686	3.688659	1.657995
H	-6.834470	4.458646	0.475429
H	-6.303008	3.689204	-1.017083
H	-7.988082	2.250625	0.101272
H	-7.038803	2.243766	1.585720

H	-6.178918	1.057319	-1.107053
H	-6.623139	0.140182	0.327525
H	-4.145336	0.270017	0.085788
H	-4.679013	1.045542	1.570249
H	-2.059705	4.487169	-0.653375
H	0.526656	3.688733	0.786060
H	0.180786	3.409585	-0.913403
H	1.603434	5.419181	-0.617136
H	0.053509	5.841735	-1.345450
H	0.603083	7.495416	0.416392
H	0.836579	6.205899	1.594871
H	-1.806662	6.942769	0.225926
H	-1.405867	7.202272	1.921172
H	-2.826857	5.183186	1.663613
H	-1.251871	4.744568	2.297456
H	0.500306	-1.333416	-2.656704
H	-0.415431	0.699731	-3.677222
H	0.793863	-0.425609	2.079115
H	-0.493592	-0.353600	3.313971
H	-0.022279	1.133646	2.439886
H	-0.647335	2.958234	-4.021702
H	-2.226502	3.782164	-3.904776
H	-2.157243	2.049762	-4.333756
H	-0.699840	-5.355260	0.811948
H	1.680567	-5.561294	1.364847
H	3.958023	-4.611621	1.371823
H	5.499578	-2.780384	0.927590
H	2.193136	-0.307587	-0.342714
H	-1.271181	-2.959677	-2.271499
H	-1.893941	-4.583200	-1.980250
H	-3.903918	-5.085706	-3.037083
H	-6.035670	-4.407781	-4.103585
H	-6.751606	-2.024579	-4.047470
H	-5.318886	-0.336145	-2.914353
H	-3.190653	-1.025977	-1.842812
H	-3.876778	-3.861152	-0.005353
H	-2.727480	-5.159037	0.247247
H	-2.824431	-5.923261	2.429215
H	-3.055935	-5.562146	4.865996
H	-3.321058	-3.254834	5.763819

H -3.352352 -1.321958 4.192932
H -3.104182 -1.690863 1.762871
H 6.183382 -0.920420 1.563053
H 6.425946 0.693653 0.952999
H 8.861516 0.027436 0.969699
H 10.727589 -0.783145 -0.437356
H 10.257497 -2.094766 -2.500734
H 7.902433 -2.584750 -3.134995
H 6.037458 -1.776960 -1.714908
H 3.666017 0.641921 -1.340361
H 5.360282 1.070020 -1.396011
H 5.159335 3.439780 -1.313676
H 4.747276 5.488818 0.013616
H 3.638399 5.332584 2.236588
H 2.945135 3.108921 3.111716
H 3.359150 1.062460 1.776986

Conformer **I**: B3LYP/6-31G(d) [5d]

Processing: namphos-l5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3558265

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.99608	714.038	334.160	285.887	714.243	46.099	40.560

Processing: namphos-l5dbe.log
126
C -4.862286 3.647091 0.662252
C -3.933170 2.841136 -0.274323
C -4.732768 1.713535 -0.956996
C -5.958113 2.262240 -1.708689
C -6.872180 3.081319 -0.786622
C -6.087868 4.199588 -0.086182

P	-2.508946	2.132467	0.748049
C	-1.339031	3.616467	1.053251
C	-1.375787	4.794617	0.059571
C	-0.356339	5.887068	0.431704
C	-0.557201	6.387072	1.869227
C	-0.517889	5.221001	2.867247
C	-1.533047	4.125169	2.501235
C	-1.506313	1.086348	-0.441906
C	-0.977611	-0.117525	0.077358
C	-0.195006	-1.009461	-0.690318
C	0.063409	-0.652485	-2.015620
C	-0.444470	0.517817	-2.577110
C	-1.224341	1.378500	-1.799184
C	0.391765	-2.266309	-0.120059
C	-0.385072	-3.408533	0.111166
C	0.222983	-4.573768	0.657307
C	1.566094	-4.613986	0.936168
C	2.390794	-3.496256	0.681925
C	1.806187	-2.299826	0.153018
C	2.652611	-1.174293	-0.056455
C	4.027515	-1.221258	0.174024
C	4.589599	-2.440773	0.668808
C	3.787550	-3.523024	0.925096
N	-1.775672	-3.432077	-0.249000
C	-1.969688	-3.559100	-1.709547
H	-1.690469	-4.574136	-2.048759
N	4.862892	-0.129952	-0.076523
C	4.450529	1.005139	-0.887554
C	4.098306	2.265656	-0.103872
C	3.566838	2.200031	1.190090
C	3.253596	3.367672	1.889058
C	3.463659	4.617766	1.302195
C	3.989036	4.692618	0.009990
C	4.308133	3.523944	-0.682649
O	-1.277869	-0.472578	1.371687
C	-0.306026	-0.152379	2.364879
O	-1.747826	2.538180	-2.301773
C	-1.542965	2.847945	-3.671107
C	-2.625835	-4.401085	0.461281
C	-2.680480	-4.251467	1.969077

C	-2.649159	-5.390286	2.783545
C	-2.785990	-5.287192	4.169508
C	-2.953099	-4.034915	4.761598
C	-2.982773	-2.892699	3.957046
C	-2.850141	-2.997564	2.571589
C	6.202137	-0.033721	0.482947
C	7.342444	-0.461181	-0.438184
C	8.651766	-0.061898	-0.134777
C	9.722853	-0.456419	-0.935443
C	9.498839	-1.253261	-2.061670
C	8.198705	-1.649428	-2.375702
C	7.127408	-1.256435	-1.568529
H	-0.226779	0.744980	-3.613760
H	0.677527	-1.309128	-2.626834
H	-3.552481	3.508469	-1.053253
H	-5.199383	2.997244	1.482871
H	-4.316808	4.476109	1.129452
H	-6.738027	4.742007	0.612878
H	-5.754379	4.932802	-0.835757
H	-7.308649	2.416153	-0.026721
H	-7.712506	3.501299	-1.354821
H	-6.519315	1.435894	-2.165367
H	-5.615140	2.899098	-2.537831
H	-5.068468	0.994239	-0.194267
H	-4.091730	1.159456	-1.650701
H	-0.337028	3.165358	0.997351
H	-2.550593	4.526314	2.616950
H	-1.455622	3.287898	3.205715
H	-0.707899	5.582075	3.886832
H	0.492421	4.785505	2.870877
H	-1.530361	6.895417	1.944623
H	0.205121	7.135043	2.125113
H	-0.434737	6.723513	-0.276247
H	0.660771	5.482558	0.328015
H	-2.380374	5.240991	0.055752
H	-1.188304	4.434625	-0.955281
H	-0.633949	-0.650084	3.279842
H	0.687190	-0.521415	2.086738
H	-0.263032	0.931872	2.534585
H	-2.069321	3.788472	-3.844179

H	-0.478011	2.982470	-3.901216
H	-1.959498	2.072114	-4.326099
H	2.013168	-5.518385	1.343151
H	-0.379441	-5.453028	0.845293
H	2.195560	-0.253193	-0.393050
H	4.230943	-4.441281	1.303971
H	5.660226	-2.528920	0.812770
H	-2.362768	-5.444510	0.205863
H	-3.635372	-4.251493	0.063079
C	-3.378603	-3.253957	-2.182697
H	-1.276157	-2.866881	-2.192549
H	-2.853354	-2.104526	1.956970
H	-3.116830	-1.912642	4.408625
H	-3.058551	-3.948985	5.840123
H	-2.758053	-6.183908	4.783539
H	-2.519706	-6.370496	2.328139
H	6.365516	1.009596	0.784188
H	6.239553	-0.611217	1.413390
H	8.832454	0.565658	0.736253
H	10.731270	-0.136991	-0.685185
H	10.331519	-1.558557	-2.689659
H	8.013796	-2.266830	-3.251052
H	6.116757	-1.566666	-1.816684
H	5.267326	1.243436	-1.583459
H	3.607138	0.697382	-1.513914
H	4.734066	3.589071	-1.682173
H	4.164366	5.660531	-0.452375
H	3.228265	5.525905	1.850370
H	2.851931	3.300876	2.896904
H	3.410704	1.229886	1.652934
C	-4.065587	-2.117166	-1.733974
C	-5.345204	-1.830398	-2.209837
C	-5.953993	-2.666509	-3.150027
C	-5.276031	-3.797217	-3.606179
C	-4.000161	-4.089546	-3.118481
H	-3.593926	-1.469278	-1.001184
H	-5.869589	-0.952030	-1.843972
H	-6.950863	-2.439788	-3.519178
H	-5.741717	-4.458506	-4.332535
H	-3.480363	-4.979579	-3.467254

Conformer **J**: B3LYP/6-31G(d) [5d]

Processing: namphos5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3557236

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
678.02005	714.125	337.717	285.838	714.334	46.099	40.652

Processing: namphos5dbe.log
126

C	-3.075884	-2.731290	1.102888
C	-3.658502	-2.736288	-0.169831
C	-3.680344	-3.935185	-0.895223
C	-3.125366	-5.101193	-0.367727
C	-2.546633	-5.087098	0.904130
C	-2.524445	-3.898698	1.636758
C	-4.255763	-1.474793	-0.787896
N	-4.701087	-0.460269	0.153042
C	-5.974169	-0.728114	0.803318
C	-7.220265	-0.357675	0.002827
C	-8.451192	-0.934816	0.344904
C	-9.615741	-0.594316	-0.342339
C	-9.565051	0.326439	-1.392490
C	-8.343276	0.900140	-1.745357
C	-7.178519	0.560617	-1.051647
C	-3.930326	0.665721	0.455884
C	-4.542086	1.799590	1.077451
C	-3.794674	2.907987	1.386586
C	-2.412059	2.990179	1.082546
C	-1.783120	1.883990	0.424047
C	-2.571172	0.729439	0.153553
C	-1.636485	4.124758	1.409457
C	-0.302596	4.181621	1.093257
C	0.352556	3.105999	0.425326

C	-0.381021	1.951099	0.104793
C	0.244456	0.779385	-0.587628
C	1.153275	-0.087756	0.058120
C	1.768953	-1.179953	-0.592011
C	1.426372	-1.396552	-1.949075
C	0.504136	-0.573122	-2.602377
C	-0.072990	0.495126	-1.918538
P	2.978677	-2.178599	0.431148
C	4.436382	-2.494413	-0.730625
C	4.977626	-1.160908	-1.287613
C	6.235181	-1.370771	-2.148455
C	7.334002	-2.117451	-1.378696
C	6.806354	-3.442028	-0.809538
C	5.550405	-3.225241	0.052383
O	1.482831	0.182683	1.365581
C	0.595889	-0.336343	2.354056
O	2.040114	-2.443368	-2.580450
C	1.759597	-2.679604	-3.950830
N	1.735005	3.222999	0.103343
C	2.108275	3.208806	-1.327073
C	1.915117	4.527562	-2.065320
C	3.016129	5.314259	-2.427276
C	2.846460	6.525854	-3.101616
C	1.563815	6.971678	-3.422455
C	0.455838	6.197004	-3.068268
C	0.630658	4.985806	-2.398652
C	2.084341	-3.861095	0.605058
C	2.277040	-4.923464	-0.495251
C	1.458059	-6.195116	-0.205020
C	1.789743	-6.784560	1.173039
C	1.605901	-5.735136	2.278536
C	2.416596	-4.459963	1.992259
C	2.549657	4.178090	0.864166
C	2.613052	3.942390	2.362807
C	2.529397	5.027654	3.243215
C	2.673554	4.847666	4.620771
C	2.902711	3.571454	5.135774
C	2.986556	2.482207	4.263971
C	2.844852	2.663769	2.887506
H	0.236217	-0.745577	-3.637863

H	-0.780455	1.136339	-2.438268
H	4.128948	-3.119372	-1.574994
H	5.816460	-2.631827	0.939214
H	5.190640	-4.192447	0.424972
H	7.584659	-3.939523	-0.215902
H	6.563565	-4.122460	-1.639474
H	7.688384	-1.485233	-0.550994
H	8.200887	-2.298233	-2.027729
H	6.610140	-0.401592	-2.503501
H	5.965634	-1.948671	-3.045282
H	5.220657	-0.489789	-0.450097
H	4.205272	-0.655424	-1.877704
H	1.019929	-3.582199	0.615944
H	3.489757	-4.697522	2.040866
H	2.235615	-3.713913	2.775665
H	1.892719	-6.151044	3.253578
H	0.539810	-5.471824	2.351204
H	2.833282	-7.133854	1.175980
H	1.165866	-7.665619	1.374148
H	1.638395	-6.940880	-0.991279
H	0.386561	-5.949308	-0.245890
H	3.339719	-5.197928	-0.560134
H	1.998070	-4.510523	-1.467322
H	0.915191	0.095494	3.304848
H	-0.440902	-0.044549	2.152412
H	0.667724	-1.431092	2.407208
H	2.370057	-3.538906	-4.234651
H	0.700578	-2.919585	-4.111954
H	2.033674	-1.817895	-4.572996
H	-2.114270	4.965487	1.907848
H	0.258328	5.073911	1.338516
H	-2.079199	-0.132539	-0.276857
H	-4.272488	3.761046	1.863554
H	-5.607310	1.802422	1.279462
H	3.565771	4.075987	0.459948
H	2.266851	5.226334	0.671194
H	3.163684	2.915329	-1.385296
H	1.536146	2.423627	-1.819645
H	4.019503	4.970276	-2.183721
H	3.715380	7.118826	-3.375772

H 1.427094 7.913409 -3.947597
H -0.546601 6.534573 -3.319211
H -0.236805 4.388974 -2.130411
H 2.352000 6.025864 2.846917
H 2.603335 5.702949 5.288173
H 3.014764 3.425778 6.207200
H 3.170355 1.485004 4.656794
H 2.890622 1.812818 2.216329
H -6.014488 -1.799712 1.042119
H -5.989143 -0.215363 1.771558
H -8.496398 -1.659166 1.156316
H -10.561351 -1.052357 -0.063774
H -10.470480 0.590007 -1.932572
H -8.293010 1.614716 -2.562980
H -6.228856 1.007774 -1.330143
H -5.116044 -1.762983 -1.408009
H -3.535137 -1.016322 -1.474093
H -4.142534 -3.956356 -1.880581
H -3.156097 -6.023170 -0.942640
H -2.125827 -5.996839 1.323648
H -2.082466 -3.880042 2.629718
H -3.061078 -1.810036 1.677694

Conformer **K**: B3LYPD3/6-31+G(d,p)

Processing: namphos-e6pbed3.log
Method Basis Set Imaginary Freqs
RB3LYP 6-31+G(d,p)

HF
-2849.74264110

Processing: namphos-e6pbed3.log
Frequency job incomplete: namphos-e6pbed3.log
126
C -6.844865 -1.360505 -1.378844
C -6.989198 -2.176486 -0.252684
C -8.265280 -2.652156 0.080988
C -9.375870 -2.321405 -0.697012

C	-9.223555	-1.506012	-1.824066
C	-7.955797	-1.027241	-2.160914
C	-5.797349	-2.568163	0.616586
N	-4.512424	-2.035260	0.204368
C	-3.688965	-2.833437	-0.693055
C	-2.412747	-3.380299	-0.062344
C	-2.400308	-3.799683	1.273102
C	-1.233783	-4.310313	1.845612
C	-0.061194	-4.398567	1.089426
C	-0.060888	-3.967411	-0.239329
C	-1.232001	-3.462732	-0.809452
C	-4.114523	-0.739937	0.534559
C	-2.852078	-0.270097	0.181810
C	-2.406385	1.032386	0.522001
C	-3.279512	1.887855	1.266638
C	-4.574649	1.405236	1.592829
C	-4.993053	0.144114	1.238933
C	-1.087533	1.483237	0.187520
C	-0.663122	2.754073	0.584994
C	-1.548594	3.586741	1.325095
C	-2.815950	3.167213	1.655629
C	-0.172755	0.587813	-0.578691
C	0.982671	0.048546	0.019848
C	1.960555	-0.664387	-0.703216
C	1.668279	-0.953452	-2.057333
C	0.492215	-0.490903	-2.659540
C	-0.400697	0.288709	-1.922382
P	3.562376	-0.973285	0.210902
C	3.465348	-2.831729	0.590070
C	3.825763	-3.811804	-0.542617
C	3.654424	-5.278247	-0.107505
C	4.454620	-5.588591	1.165807
C	4.084804	-4.620689	2.299442
C	4.265646	-3.155008	1.871414
O	1.195625	0.272366	1.355303
C	0.451610	-0.563234	2.249435
O	2.585607	-1.711708	-2.735413
C	2.409786	-1.942614	-4.126452
N	0.636837	3.217817	0.214284
C	1.292445	4.183000	1.107958

C	1.550964	3.632098	2.495151
C	2.420769	2.545697	2.660101
C	2.679936	2.030319	3.929783
C	2.077241	2.600387	5.057304
C	1.215310	3.688972	4.904084
C	0.956273	4.199274	3.627629
C	4.881086	-0.817470	-1.127089
C	6.275858	-1.013262	-0.494927
C	7.394490	-0.827057	-1.534457
C	7.301994	0.543253	-2.221325
C	5.913240	0.755293	-2.841727
C	4.796380	0.567051	-1.802208
C	0.795046	3.565241	-1.215476
C	0.056783	4.825368	-1.629571
C	0.707844	6.065518	-1.675182
C	0.008250	7.232568	-1.996639
C	-1.360018	7.172622	-2.275076
C	-2.020990	5.940512	-2.233374
C	-1.316959	4.777959	-1.913853
H	0.271155	-0.710279	-3.696738
H	-1.292932	0.678700	-2.404652
H	4.738212	-1.579200	-1.897718
H	6.412658	-0.289056	0.320944
H	6.358736	-2.009059	-0.045053
H	8.374053	-0.949657	-1.055351
H	7.313686	-1.618117	-2.294589
H	7.486426	1.331343	-1.476596
H	8.083138	0.642076	-2.985452
H	5.843263	1.754367	-3.290530
H	5.767959	0.031819	-3.657754
H	4.880354	1.350844	-1.034781
H	3.819640	0.699259	-2.278806
H	2.402628	-2.968818	0.830016
H	5.334084	-2.964973	1.698833
H	3.959316	-2.482065	2.680656
H	4.687890	-4.828088	3.192289
H	3.035492	-4.784055	2.586569
H	5.528604	-5.491862	0.948259
H	4.288781	-6.626968	1.478738
H	3.960912	-5.945717	-0.923196

H	2.590739	-5.482963	0.076862
H	4.872451	-3.657222	-0.837728
H	3.220660	-3.600471	-1.428237
H	0.708888	-0.221602	3.253630
H	-0.626888	-0.460015	2.089052
H	0.735089	-1.616178	2.124116
H	3.283224	-2.515624	-4.442292
H	1.502423	-2.526799	-4.327904
H	2.369923	-1.000188	-4.687378
H	-3.479130	3.824135	2.213417
H	-1.229046	4.581094	1.608478
H	-2.154602	-0.916444	-0.326347
H	-5.254151	2.060285	2.132765
H	-6.003528	-0.162004	1.480489
H	2.255847	4.414528	0.638838
H	0.755345	5.143134	1.174476
H	1.868518	3.676127	-1.405493
H	0.452911	2.718134	-1.811221
H	1.772655	6.116737	-1.459382
H	0.530183	8.184970	-2.030215
H	-1.906633	8.077480	-2.525191
H	-3.084383	5.885483	-2.449408
H	-1.835728	3.824310	-1.871691
H	0.280946	5.043549	3.513474
H	0.742130	4.138484	5.772717
H	2.279275	2.199388	6.046898
H	3.350405	1.181925	4.035177
H	2.867741	2.079867	1.789168
H	-5.995739	-2.281109	1.656967
H	-5.715460	-3.661074	0.629693
H	-8.389797	-3.285964	0.957043
H	-10.358064	-2.698037	-0.425411
H	-10.086088	-1.246049	-2.430738
H	-7.828208	-0.389130	-3.030816
H	-5.863005	-0.976943	-1.636940
H	-4.303905	-3.666922	-1.048250
H	-3.427964	-2.247276	-1.585920
H	-1.215283	-3.096128	-1.833026
H	0.851856	-3.999819	-0.825683
H	0.847826	-4.785349	1.538441

H -1.235966 -4.629384 2.884147
H -3.301951 -3.700281 1.870658

Conformer **L**: B3LYP/6-31G(d) [5d]

Processing: namphos-b5dbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31G(d)	0

HF Energy
-2849.3548478

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.99792	714.094	335.717	286.374	714.298	46.099	40.523

Processing: namphos-b5dbe.log
126
C 3.636620 4.665278 -0.369158
C 2.816858 3.642226 0.449956
C 3.751810 2.548865 1.006615
C 4.903265 3.153374 1.829631
C 5.702748 4.187451 1.024188
C 4.781642 5.276309 0.456187
P 1.477358 2.913705 -0.678363
C 0.003630 4.142357 -0.588104
C 0.126518 5.352949 0.357197
C -1.130759 6.240764 0.307158
C -1.439092 6.713399 -1.120308
C -1.554508 5.521766 -2.081239
C -0.307402 4.623972 -2.024168
C 0.830537 1.455330 0.292132
C 0.782529 0.204119 -0.355411
C 0.352943 -0.975015 0.294234
C -0.046753 -0.862537 1.628376
C -0.034823 0.356729 2.303599
C 0.398429 1.506832 1.638991
C 0.285255 -2.292483 -0.410022

C	1.444989	-2.966878	-0.815553
C	1.326828	-4.204227	-1.516688
C	0.102010	-4.751520	-1.803119
C	-1.090217	-4.110123	-1.393812
C	-1.007560	-2.869593	-0.679792
C	-2.222455	-2.234368	-0.302116
C	-3.474420	-2.788423	-0.567010
C	-3.526806	-4.034176	-1.264304
C	-2.368631	-4.655524	-1.665135
N	2.736705	-2.432552	-0.554732
C	3.185546	-2.371505	0.850576
C	3.642284	-3.697754	1.444721
C	5.005084	-3.968394	1.627309
C	5.431775	-5.185253	2.165310
C	4.496117	-6.154310	2.529437
C	3.133554	-5.896833	2.355713
C	2.711951	-4.679383	1.820581
N	-4.647330	-2.131251	-0.147810
C	-4.588675	-1.362014	1.097757
C	-4.427706	0.147376	0.955898
C	-4.093871	0.759102	-0.255317
C	-3.941583	2.146389	-0.333864
C	-4.120895	2.940142	0.799410
C	-4.451667	2.336535	2.016218
C	-4.602825	0.952618	2.090394
O	1.201753	0.104899	-1.664868
C	0.175419	0.241803	-2.645147
O	0.437872	2.733198	2.242134
C	-0.068788	2.859084	3.561655
C	3.795048	-2.774842	-1.510164
C	4.891590	-1.725794	-1.602266
C	4.577416	-0.387018	-1.879426
C	5.594138	0.555125	-2.040482
C	6.935833	0.178293	-1.921518
C	7.255524	-1.150132	-1.641320
C	6.236736	-2.094353	-1.484043
C	-5.943517	-2.739901	-0.473480
C	-7.128259	-1.802779	-0.331069
C	-7.253674	-0.673711	-1.152847
C	-8.365844	0.160101	-1.050714

C	-9.375012	-0.124077	-0.125957
C	-9.263149	-1.246462	0.694260
C	-8.145194	-2.078509	0.590115
H	-0.357897	0.394198	3.336947
H	-0.380427	-1.754024	2.153220
H	2.356034	4.156718	1.299926
H	4.055316	4.160384	-1.251944
H	2.989658	5.464162	-0.753730
H	5.355349	5.978457	-0.163295
H	4.359043	5.863907	1.284983
H	6.215526	3.679159	0.194143
H	6.486528	4.636292	1.648517
H	5.565504	2.352324	2.183382
H	4.489818	3.637075	2.727629
H	4.170836	1.960856	0.177806
H	3.185726	1.847447	1.628436
H	-0.846714	3.537826	-0.243478
H	0.558794	5.180440	-2.413035
H	-0.434810	3.762386	-2.691739
H	-1.718053	5.872926	-3.108724
H	-2.439882	4.925920	-1.811160
H	-0.630727	7.376594	-1.462932
H	-2.360542	7.310202	-1.136724
H	-1.004115	7.103524	0.975114
H	-1.988766	5.670089	0.693718
H	0.994347	5.963844	0.071587
H	0.298295	5.012622	1.381303
H	0.648918	0.056377	-3.611889
H	-0.627152	-0.487753	-2.483725
H	-0.241817	1.257290	-2.637367
H	0.021606	3.917017	3.815629
H	-1.123587	2.560351	3.614384
H	0.514108	2.265629	4.277985
H	0.036578	-5.700477	-2.331134
H	2.226915	-4.737211	-1.800772
H	-2.165669	-1.273343	0.191030
H	-2.426036	-5.605143	-2.192901
H	-4.473721	-4.519496	-1.464808
H	3.319000	-2.861081	-2.492558
H	4.258690	-3.752046	-1.292708

H	4.008045	-1.650160	0.896715
H	2.367817	-1.959077	1.444082
H	5.737654	-3.213862	1.349512
H	6.493818	-5.373579	2.301835
H	4.824164	-7.101461	2.949886
H	2.397672	-6.643480	2.643720
H	1.650014	-4.486195	1.694177
H	6.489202	-3.131347	-1.272418
H	8.294820	-1.454455	-1.545422
H	7.724516	0.915572	-2.048535
H	5.336759	1.586724	-2.267310
H	3.535042	-0.092621	-1.966200
H	-6.127523	-3.642578	0.135258
H	-5.896673	-3.067163	-1.516701
H	-6.471257	-0.448505	-1.872053
H	-8.447216	1.032080	-1.694157
H	-10.242429	0.525885	-0.047933
H	-10.043260	-1.477131	1.414961
H	-8.063779	-2.955541	1.228820
H	-5.506411	-1.555088	1.664889
H	-3.763730	-1.751068	1.710514
H	-4.870355	0.490511	3.039269
H	-4.603459	2.945730	2.903905
H	-4.011840	4.019464	0.735448
H	-3.686398	2.606587	-1.285193
H	-3.958104	0.141200	-1.137465

Conformer **M**: B3LYPD3/6-31+G(d,p)

Processing: namphos-c6pbed3.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-2849.7459130

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot

676.38169 712.094 328.177 283.952 712.282 46.099 40.332

Processing: namphos-c6pbed3.log
126
C -4.138969 -3.722487 -1.020010
C -3.226800 -2.985514 -0.015374
C -3.910422 -1.689848 0.472104
C -5.308345 -1.968677 1.048992
C -6.202758 -2.709305 0.044950
C -5.530422 -4.005140 -0.430602
P -1.566009 -2.624039 -0.859901
C -0.459392 -4.148565 -0.526869
C -1.140198 -5.396816 0.060268
C -0.126946 -6.534534 0.277323
C 0.613909 -6.890385 -1.019882
C 1.289074 -5.651674 -1.626581
C 0.282152 -4.507836 -1.832314
C -0.832111 -1.400166 0.333820
C -0.478908 -0.126437 -0.141353
C -0.057723 0.912044 0.712856
C 0.049037 0.625592 2.075246
C -0.236662 -0.641350 2.585072
C -0.677750 -1.645186 1.718243
C 0.316135 2.242517 0.156209
C -0.634723 3.072986 -0.446676
C -0.203177 4.289548 -1.059530
C 1.127524 4.634529 -1.111510
C 2.117395 3.802392 -0.533129
C 1.703000 2.608089 0.138446
C 2.698715 1.762399 0.689357
C 4.058600 2.034439 0.581119
C 4.456494 3.223937 -0.105088
C 3.507137 4.073785 -0.627261
N -1.995930 2.698860 -0.497093
C -2.744200 2.499138 0.752709
C -3.379325 3.769798 1.294816
C -4.770178 3.892784 1.395496
C -5.352824 5.069109 1.879354
C -4.545664 6.143013 2.261997
C -3.153925 6.031895 2.161112

C	-2.576936	4.854414	1.682508
N	4.996994	1.149295	1.131836
C	4.590797	0.323324	2.266067
C	4.005807	-1.050877	1.954225
C	3.566734	-1.419367	0.677787
C	2.968288	-2.664657	0.462751
C	2.810130	-3.562585	1.519720
C	3.254607	-3.207569	2.797022
C	3.845313	-1.960853	3.009436
O	-0.558707	0.136220	-1.493532
C	0.659402	-0.089065	-2.209911
O	-1.001316	-2.905161	2.143471
C	-0.732330	-3.266664	3.492423
C	-2.804645	3.196265	-1.611814
C	-3.931384	2.245248	-1.974054
C	-3.636729	0.933854	-2.375347
C	-4.662097	0.065598	-2.752178
C	-5.995627	0.489018	-2.720394
C	-6.296515	1.790449	-2.311585
C	-5.266465	2.663113	-1.942272
C	6.426677	1.392063	0.950395
C	6.928303	1.201679	-0.473315
C	7.830689	2.111717	-1.035147
C	8.329806	1.919357	-2.327030
C	7.925449	0.810454	-3.073967
C	7.024960	-0.104785	-2.518341
C	6.532211	0.089483	-1.226961
H	-0.121916	-0.825138	3.645949
H	0.376715	1.410351	2.751466
H	-3.065623	-3.626149	0.857704
H	-4.250401	-3.102236	-1.920141
H	-3.675754	-4.660417	-1.347810
H	-6.155807	-4.511683	-1.176798
H	-5.430537	-4.695987	0.419637
H	-6.383247	-2.056812	-0.821082
H	-7.181973	-2.925776	0.490242
H	-5.776023	-1.023131	1.351469
H	-5.207886	-2.577827	1.959786
H	-4.000435	-0.982684	-0.360904
H	-3.295451	-1.198912	1.232095

H	0.283412	-3.813158	0.203609
H	-0.452363	-4.801222	-2.596313
H	0.795239	-3.623174	-2.231025
H	1.769454	-5.905724	-2.579809
H	2.090204	-5.313423	-0.953934
H	-0.107410	-7.297451	-1.743546
H	1.354216	-7.678716	-0.835113
H	-0.638096	-7.418458	0.679914
H	0.604092	-6.222099	1.037870
H	-1.925958	-5.752109	-0.620041
H	-1.623743	-5.148956	1.008898
H	0.464941	0.201365	-3.244129
H	1.473332	0.521657	-1.801428
H	0.938726	-1.150389	-2.175859
H	-0.996297	-4.322715	3.572000
H	0.330334	-3.135205	3.731621
H	-1.345273	-2.687206	4.194665
H	1.430645	5.559244	-1.597052
H	-0.942694	4.960780	-1.480822
H	2.373973	0.851405	1.166360
H	3.827411	4.976419	-1.142268
H	5.502755	3.468269	-0.229169
H	-2.143303	3.289703	-2.477883
H	-3.224119	4.195492	-1.408887
H	-3.519050	1.746624	0.571770
H	-2.067141	2.078163	1.494918
H	-5.400505	3.063675	1.084202
H	-6.434265	5.146986	1.951847
H	-4.994702	7.059037	2.635331
H	-2.519089	6.862225	2.458194
H	-1.496693	4.774416	1.600316
H	-5.501929	3.674327	-1.620107
H	-7.329041	2.127412	-2.277998
H	-6.792197	-0.191494	-3.008394
H	-4.417458	-0.946818	-3.059981
H	-2.605369	0.594499	-2.364564
H	6.711388	2.394863	1.307856
H	6.952508	0.678682	1.591663
H	8.140650	2.983398	-0.462444
H	9.025280	2.638629	-2.750244

H 8.305668 0.661055 -4.080342
H 6.707197 -0.971377 -3.091428
H 5.833258 -0.620329 -0.797218
H 5.460116 0.186138 2.918043
H 3.852631 0.878945 2.863303
H 4.183692 -1.689093 4.007578
H 3.144965 -3.902575 3.625226
H 2.342271 -4.527286 1.352334
H 2.613987 -2.926167 -0.529801
H 3.670384 -0.718949 -0.143481

Conformer **N**: B3LYPD3/6-31+G(d,p)

Processing: namphos-f6pbed3.log
PG=C01

Method BasisSet Imaginary Freqs
RB3LYP 6-31+G(d,p) 0

HF Energy
-2849.7417005

ZPE E298 S298 Squasihar Equasihar Strans Srot
675.79827 711.634 326.542 284.986 711.832 46.099 40.534

Processing: namphos-f6pbed3.log
126
C -7.311688 -2.384395 0.742818
C -7.560197 -1.417108 -0.236922
C -8.879021 -1.213642 -0.667364
C -9.927768 -1.966287 -0.136080
C -9.670718 -2.933341 0.841926
C -8.360438 -3.138103 1.279793
C -6.435809 -0.590370 -0.854503
N -5.157986 -0.650431 -0.169310
C -5.016598 0.150186 1.037004
C -4.265376 1.471752 0.903859
C -3.664313 1.879255 -0.290823
C -2.942114 3.075975 -0.350482

C	-2.821721	3.882181	0.782832
C	-3.426970	3.485451	1.979639
C	-4.140590	2.287960	2.037404
C	-4.177736	-1.586065	-0.510244
C	-2.861864	-1.396560	-0.101926
C	-1.831066	-2.314652	-0.419972
C	-2.159828	-3.483987	-1.175715
C	-3.509264	-3.667858	-1.577685
C	-4.493543	-2.755443	-1.268294
C	-0.458825	-2.041588	-0.086223
C	0.532775	-2.959197	-0.428756
C	0.175790	-4.139222	-1.146161
C	-1.121927	-4.387950	-1.522724
C	-0.133732	-0.697096	0.473647
C	0.446750	0.280554	-0.357407
C	0.786955	1.565039	0.100669
C	0.505150	1.863973	1.453235
C	-0.105680	0.923607	2.290287
C	-0.412555	-0.342707	1.793473
P	1.636791	2.714578	-1.095590
C	0.704064	4.350549	-0.784430
C	1.451807	5.485325	-0.062543
C	0.533609	6.702123	0.147355
C	-0.037755	7.212119	-1.184098
C	-0.759860	6.089468	-1.944240
C	0.144194	4.859271	-2.130891
O	0.746672	-0.069491	-1.658474
C	-0.307900	0.152431	-2.602154
O	0.877613	3.107419	1.885327
C	0.479367	3.536929	3.181387
N	1.920184	-2.803647	-0.128406
C	2.757130	-2.369624	-1.269589
C	4.107367	-3.053494	-1.358103
C	4.198897	-4.404147	-1.719596
C	5.436757	-5.043483	-1.792079
C	6.608291	-4.335818	-1.500403
C	6.529582	-2.986868	-1.147465
C	5.286094	-2.352283	-1.083227
C	3.324607	2.886025	-0.254934
C	4.293468	3.642238	-1.188579

C	5.702272	3.749396	-0.581149
C	6.270503	2.362366	-0.247071
C	5.317007	1.586535	0.672367
C	3.902578	1.493873	0.078113
C	2.287266	-2.223731	1.164955
C	3.586530	-2.757589	1.742895
C	4.483722	-1.877305	2.357673
C	5.672420	-2.346216	2.925045
C	5.977249	-3.708217	2.878237
C	5.082271	-4.595413	2.269175
C	3.894558	-4.122966	1.711178
H	-0.333004	1.157356	3.322751
H	-0.869762	-1.077353	2.450342
H	3.214369	3.442608	0.683257
H	4.353948	3.104440	-2.145609
H	3.912005	4.642847	-1.419336
H	6.368061	4.279211	-1.273926
H	5.655720	4.353333	0.337008
H	6.409413	1.796889	-1.180147
H	7.260208	2.453704	0.217353
H	5.704393	0.578096	0.864165
H	5.262909	2.093213	1.647279
H	3.932659	0.886038	-0.837791
H	3.244446	0.969308	0.776950
H	-0.145660	4.069952	-0.153866
H	0.980181	5.116799	-2.797608
H	-0.410106	4.058263	-2.636407
H	-1.108563	6.451651	-2.919499
H	-1.657721	5.794537	-1.382420
H	0.787864	7.592092	-1.803472
H	-0.717261	8.056245	-1.012713
H	1.082861	7.503477	0.658154
H	-0.294754	6.415292	0.812548
H	2.317492	5.802110	-0.658804
H	1.834166	5.135215	0.899022
H	0.058411	-0.219595	-3.560776
H	-1.213424	-0.393040	-2.313751
H	-0.527278	1.224412	-2.687338
H	0.813074	4.572901	3.263259
H	-0.611027	3.493108	3.294172

H	0.957205	2.939797	3.968502
H	-1.368079	-5.287783	-2.081386
H	0.965902	-4.844797	-1.381461
H	-2.596606	-0.496908	0.432672
H	-3.767768	-4.560153	-2.142865
H	-5.516120	-2.950911	-1.570754
H	2.893456	-1.280327	-1.236783
H	2.188257	-2.572816	-2.179877
H	2.354526	-1.127579	1.121298
H	1.478019	-2.456763	1.863557
H	4.258597	-0.813751	2.377856
H	6.362629	-1.647194	3.389762
H	6.906000	-4.076253	3.305085
H	5.317521	-5.654871	2.218839
H	3.212454	-4.802228	1.209800
H	5.227359	-1.307172	-0.791731
H	7.432575	-2.430546	-0.912315
H	7.572957	-4.833151	-1.547862
H	5.490030	-6.091866	-2.073115
H	3.289609	-4.959671	-1.933872
H	-6.288741	-0.891925	-1.897988
H	-6.749707	0.460894	-0.894581
H	-9.086027	-0.458098	-1.422783
H	-10.944068	-1.795902	-0.480169
H	-10.485116	-3.518386	1.259124
H	-8.150426	-3.886127	2.039092
H	-6.294395	-2.550192	1.082951
H	-6.022522	0.350973	1.425563
H	-4.514699	-0.455810	1.803936
H	-4.602129	1.979205	2.973468
H	-3.343405	4.109188	2.865682
H	-2.258353	4.808650	0.737658
H	-2.463184	3.371679	-1.279236
H	-3.745971	1.243000	-1.166636

Conformer **O**: B3LYP/6-31G(d) [5d]

Processing: namphos-g5dbe.log
PG=C01

Method BasisSet Imaginary Freqs
RB3LYP 6-31G(d) 0

HF Energy
-2849.3483494

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
677.86646	713.968	337.224	285.928	714.176	46.099	40.590

ccl00:/aue/chem126/aue/ark/pj/nam> gtg namphos-g5dbe.log
Processing: namphos-g5dbe.log
126

C	-5.766524	-1.854708	-1.841419
C	-6.004270	-2.917661	-0.961847
C	-6.719553	-4.028529	-1.425353
C	-7.191327	-4.079245	-2.738503
C	-6.947121	-3.016188	-3.609152
C	-6.232761	-1.904701	-3.155451
C	-5.568887	-2.853432	0.494584
N	-4.284499	-2.202210	0.744478
C	-4.265302	-1.370285	1.952945
C	-4.872577	0.010395	1.767057
C	-4.454685	0.842850	0.718419
C	-4.992718	2.120434	0.567870
C	-5.957865	2.587793	1.465533
C	-6.379995	1.768218	2.512158
C	-5.840451	0.487127	2.657778
C	-3.092584	-2.781875	0.277156
C	-1.872225	-2.119178	0.397162
C	-0.649581	-2.687155	-0.047548
C	-0.684187	-3.972095	-0.680938
C	-1.936509	-4.621125	-0.821005
C	-3.102314	-4.061002	-0.358223
C	0.610472	-2.001633	0.084982
C	1.782023	-2.626476	-0.337745
C	1.719547	-3.897092	-0.978298
C	0.521002	-4.543316	-1.155206
C	0.628524	-0.621490	0.666696
C	0.643242	0.531776	-0.149487
C	0.549640	1.839641	0.375429
C	0.564513	1.973880	1.785013
C	0.555043	0.847559	2.613597

C	0.563002	-0.426693	2.047841
P	0.211160	3.181695	-0.881707
C	-0.882349	4.448308	0.038444
C	-0.232476	5.735090	0.582499
C	-1.262556	6.630544	1.295689
C	-2.436980	6.986901	0.373603
C	-3.086723	5.722322	-0.206048
C	-2.055373	4.817205	-0.901247
O	0.822287	0.401479	-1.510382
C	-0.324323	0.059923	-2.297960
O	0.580676	3.247564	2.283774
C	0.567183	3.433368	3.689858
N	3.049207	-2.001279	-0.087453
C	4.026173	-2.115010	-1.174126
C	5.188973	-1.144625	-1.041582
C	5.010673	0.151023	-0.539087
C	6.095523	1.021779	-0.424641
C	7.370322	0.622590	-0.835228
C	7.554578	-0.659988	-1.352798
C	6.471779	-1.537598	-1.444317
C	1.858574	4.059745	-1.213969
C	2.441273	3.568806	-2.558651
C	3.669952	4.397291	-2.969264
C	4.749129	4.393075	-1.877145
C	4.178498	4.834686	-0.520347
C	2.938663	4.013670	-0.118085
C	3.589068	-2.264077	1.269895
C	4.064506	-3.683195	1.546445
C	5.404084	-4.043739	1.339434
C	5.842601	-5.347495	1.581506
C	4.945824	-6.313650	2.041101
C	3.610364	-5.966821	2.259070
C	3.176303	-4.663424	2.013748
H	0.543461	0.947723	3.692294
H	0.529082	-1.295039	2.701001
H	1.564664	5.110234	-1.358141
H	2.717583	2.508969	-2.469370
H	1.673052	3.621846	-3.339552
H	4.083644	4.014655	-3.911596
H	3.354123	5.433579	-3.165029

H	5.157826	3.377585	-1.786131
H	5.586312	5.042663	-2.165407
H	4.948428	4.755777	0.259828
H	3.901372	5.898521	-0.573022
H	3.230330	2.966710	0.045910
H	2.539863	4.374382	0.835087
H	-1.301625	3.899326	0.890014
H	-1.661975	5.329684	-1.792668
H	-2.541322	3.904694	-1.268683
H	-3.884499	5.992991	-0.910863
H	-3.565530	5.157100	0.607884
H	-2.068840	7.614841	-0.451582
H	-3.181373	7.586328	0.914001
H	-0.774217	7.544538	1.659953
H	-1.645157	6.104598	2.183463
H	0.203414	6.309494	-0.247660
H	0.584939	5.489081	1.264824
H	0.035324	-0.019418	-3.326375
H	-0.755423	-0.895262	-1.986644
H	-1.077412	0.853843	-2.240315
H	0.578527	4.513619	3.846759
H	-0.337827	3.010945	4.145528
H	1.451512	2.988764	4.164539
H	0.487814	-5.516260	-1.640751
H	2.638448	-4.369740	-1.306704
H	-1.839092	-1.126804	0.828930
H	-1.966059	-5.595435	-1.303866
H	-4.031901	-4.599388	-0.488888
H	3.481249	-1.903122	-2.102528
H	4.444150	-3.131191	-1.277434
H	4.417871	-1.567427	1.426338
H	2.804310	-1.991287	1.980067
H	6.110601	-3.292270	0.994428
H	6.885989	-5.605823	1.418331
H	5.285882	-7.327744	2.234709
H	2.906975	-6.710514	2.625112
H	2.136090	-4.400651	2.188979
H	6.624413	-2.543375	-1.830764
H	8.541576	-0.984045	-1.672979
H	8.212261	1.304088	-0.746537

H 5.946172 2.014527 -0.009054
H 4.018030 0.457365 -0.221882
H -5.600717 -3.866591 0.931406
H -6.314215 -2.264948 1.041919
H -6.908808 -4.862982 -0.752342
H -7.742690 -4.951048 -3.081199
H -7.307547 -3.054161 -4.633689
H -6.037773 -1.072699 -3.827276
H -5.213667 -0.989340 -1.489651
H -4.799325 -1.889532 2.764598
H -3.230214 -1.279286 2.289925
H -6.176303 -0.149943 3.473723
H -7.133941 2.119802 3.211707
H -6.379073 3.582223 1.344756
H -4.660272 2.753017 -0.250805
H -3.705556 0.483474 0.017619

More stable conformer **APdPh$_2$** [bis(N,N-dibenzyl)-2,7-diamino]: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=2.453 Å, C-Pd-C angle=82.17°. ($E_{e,rel}$=0 kcal/mol)

(Near identical conformation to **A**)

Processing: pddiphnamphos-h6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3440.5886484

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
792.73259	836.782	397.610	334.334	837.047	46.894	41.486

Processing: pddiphnamphos-h6dsdbe.log
149
C 3.718805 1.426683 -1.909930
C 3.597143 0.005695 -2.502343
C 4.991953 -0.602385 -2.757850

C	5.849327	0.323223	-3.640949
C	5.966786	1.734799	-3.050176
C	4.579123	2.340683	-2.798625
P	2.500685	-1.046998	-1.378060
C	2.443701	-2.772489	-2.147989
C	1.103408	-3.483913	-1.863273
C	1.065335	-4.883674	-2.500898
C	2.245285	-5.755106	-2.049504
C	3.581760	-5.042042	-2.296298
C	3.607454	-3.651582	-1.638969
C	0.833872	-0.299254	-1.726571
C	0.104667	0.323888	-0.683500
C	-1.111288	1.006521	-0.943564
C	-1.635053	0.896820	-2.239536
C	-0.978074	0.249968	-3.277119
C	0.275774	-0.309178	-3.025647
C	-1.885841	1.896457	-0.012625
C	-3.161223	1.431701	0.467883
C	-3.970642	2.296750	1.271572
C	-3.504539	3.598239	1.561562
C	-2.295253	4.036570	1.084254
C	-1.459125	3.202928	0.284856
C	-3.631062	0.112673	0.217265
C	-4.859423	-0.345559	0.694228
C	-5.664605	0.551758	1.464742
C	-5.218873	1.818366	1.745289
N	-5.320831	-1.634885	0.426199
C	-6.362925	-2.268305	1.220781
C	-7.762654	-2.252207	0.612432
C	-8.722697	-3.160165	1.080734
C	-10.021171	-3.152120	0.572674
C	-10.378323	-2.237221	-0.421624
C	-9.427567	-1.334958	-0.899321
C	-8.128068	-1.342136	-0.385029
N	-0.202886	3.706009	-0.171405
C	-0.022078	3.883059	-1.630954
C	-0.676228	5.121707	-2.229966
C	-2.067848	5.192108	-2.400356
C	-2.664258	6.328617	-2.947044
C	-1.878571	7.415610	-3.339368

C	-0.493556	7.357326	-3.180086
C	0.098458	6.218869	-2.628169
O	0.652593	0.234931	0.581923
C	-0.240772	0.178635	1.722956
O	1.015116	-0.914001	-4.002814
C	0.488724	-0.985488	-5.320436
C	-4.731323	-2.470570	-0.607329
C	-3.703204	-3.493060	-0.129186
C	-3.000045	-3.331514	1.070319
C	-2.050701	-4.275416	1.471741
C	-1.792909	-5.394874	0.678769
C	-2.494891	-5.567705	-0.517416
C	-3.443426	-4.624614	-0.914100
C	0.399605	4.829020	0.565869
H	1.375383	4.992817	0.088861
H	3.078177	0.072926	-3.465665
H	4.896243	-1.575980	-3.251381
H	5.506035	-0.777519	-1.804090
H	6.844538	-0.119218	-3.776542
H	5.396845	0.388473	-4.642142
H	6.550951	2.380375	-3.718593
H	6.518142	1.685814	-2.099729
H	4.070732	2.495633	-3.762287
H	4.671960	3.329616	-2.331107
H	2.722975	1.866640	-1.775618
H	4.167180	1.363403	-0.908909
H	2.540518	-2.643208	-3.232527
H	0.965497	-3.576640	-0.776127
H	0.260916	-2.893105	-2.234610
H	0.112028	-5.368156	-2.254562
H	1.091343	-4.778852	-3.596324
H	2.224362	-6.723884	-2.565656
H	2.145806	-5.969390	-0.975049
H	3.745687	-4.939721	-3.379995
H	4.413756	-5.644587	-1.910241
H	4.575933	-3.175529	-1.817969
H	3.525602	-3.761539	-0.552247
H	-2.586665	1.380596	-2.441600
H	-1.427347	0.217433	-4.261860
H	-0.549833	1.180658	2.015463

H	0.338971	-0.279343	2.521370
H	-1.112261	-0.434528	1.481929
H	-0.449086	-1.554155	-5.347948
H	1.243991	-1.505304	-5.912247
H	0.321021	0.013747	-5.741320
H	-1.978235	5.046723	1.305159
H	-4.124250	4.260149	2.162350
H	-5.841721	2.488011	2.334180
H	-6.647617	0.246347	1.804776
H	-2.990168	-0.559370	-0.337942
H	-0.396225	2.992956	-2.133462
H	1.058235	3.923337	-1.816975
H	-2.687759	4.351337	-2.101176
H	-3.743514	6.364108	-3.072126
H	-2.343333	8.299273	-3.768674
H	0.127122	8.196040	-3.484909
H	1.179499	6.178564	-2.509924
C	0.621458	4.602895	2.048541
H	-0.156661	5.769596	0.422106
H	-6.382763	-1.802004	2.212069
H	-6.066131	-3.310943	1.397536
H	-8.449082	-3.880889	1.849310
H	-10.752410	-3.863877	0.947030
H	-11.388465	-2.232001	-0.822195
H	-9.694858	-0.621839	-1.674966
H	-7.390041	-0.639743	-0.761001
H	-4.286968	-1.818220	-1.367436
H	-5.547365	-3.003552	-1.114147
H	-3.994664	-4.772063	-1.841133
H	-2.313373	-6.444161	-1.134245
H	-1.059371	-6.131815	0.994063
H	-1.517604	-4.137399	2.408860
H	-3.203672	-2.467088	1.695333
Pd	2.808917	-0.857089	1.000516
C	0.283521	5.609686	2.961373
C	0.535836	5.455513	4.325745
C	1.127847	4.282476	4.794798
C	1.472995	3.272258	3.893144
C	1.226957	3.434416	2.528585
H	-0.182214	6.524704	2.599731

H	0.264488	6.248110	5.018622
H	1.322052	4.154053	5.856503
H	1.941123	2.359007	4.247609
H	1.501887	2.647473	1.831396
C	4.622163	-1.673651	1.260385
C	5.772413	-0.920318	0.972439
C	7.050832	-1.480301	1.085208
C	7.208126	-2.803596	1.499964
C	6.073811	-3.555703	1.813354
C	4.797448	-2.994244	1.704623
H	5.680482	0.117011	0.659312
H	7.924150	-0.873777	0.852726
H	8.200352	-3.238491	1.590612
H	6.179437	-4.582473	2.158271
H	3.933070	-3.591538	1.982577
C	2.887298	-0.718277	3.043285
C	2.114874	-1.598452	3.827178
C	2.076561	-1.503507	5.223477
C	2.829768	-0.529040	5.880418
C	3.621432	0.341814	5.127412
C	3.650523	0.242614	3.731476
H	1.532715	-2.383774	3.344999
H	1.466457	-2.199116	5.797068
H	2.810665	-0.456935	6.965235
H	4.226540	1.096196	5.627200
H	4.293732	0.920028	3.173631

Less stable conformer **JPdPh$_2$** [bis(N,N-dibenzyl)-2,7-diamino]: B3LYP/6-31G(d)/SDD for pre-reductive elimination step, O-Pd distance=2.417 Å, C-Pd-C angle=82.45°. ($E_{e,rel}$=2.95 kcal/mol)

(Near identical conformation to **J**)

Processing: pddiphnamphos6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3440.5839465

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
792.58859	836.711	396.606	335.474	836.972	46.894	41.497

Processing: pddiphnamphos6dsdbe.log
149

C	-1.287605	-4.414736	1.658780
C	-1.491689	-3.418215	0.498391
C	-2.300181	-4.064959	-0.648180
C	-1.649240	-5.374032	-1.125352
C	-1.448405	-6.364984	0.029797
C	-0.642034	-5.723407	1.167389
P	-2.183944	-1.709033	0.953986
Pd	-2.900405	-0.431280	-0.967609
C	-4.825162	-0.963815	-1.126052
C	-5.801372	-0.200238	-0.462089
C	-7.147458	-0.583010	-0.468386
C	-7.551660	-1.731154	-1.152770
C	-6.596440	-2.482702	-1.840001
C	-5.250650	-2.099488	-1.832824
C	-0.665516	-0.812113	1.567350
C	-0.053488	0.119577	0.692547
C	1.080212	0.874995	1.069881
C	1.633348	0.597154	2.327697
C	1.081419	-0.321159	3.208993
C	-0.074425	-1.011681	2.837875
C	1.757540	1.968151	0.292492
C	3.083239	1.697972	-0.208012
C	3.844780	2.752810	-0.805075
C	3.278855	4.044476	-0.883508
C	2.016197	4.289634	-0.410859
C	1.220024	3.264448	0.184657
C	5.148608	2.470088	-1.283283
C	5.694279	1.213749	-1.205826
C	4.937788	0.129947	-0.659247
C	3.655768	0.395275	-0.176921
N	-0.092370	3.589029	0.621708
C	-0.746363	4.774745	0.046725
O	-0.630129	0.292653	-0.562898
C	0.227969	0.027088	-1.698398
O	-0.670821	-1.915970	3.668457

C	-0.142766	-2.113231	4.972703
C	-3.333876	-1.926223	2.424837
C	-3.730973	-0.546584	2.993143
C	-4.703437	-0.684675	4.177312
C	-5.945046	-1.504089	3.797898
C	-5.546638	-2.875176	3.234807
C	-4.590830	-2.737619	2.036265
C	-3.299976	0.525609	-2.737448
C	-2.750880	0.002680	-3.925391
C	-2.976365	0.603721	-5.170857
C	-3.773162	1.746366	-5.262422
C	-4.332312	2.281251	-4.099020
C	-4.101527	1.674804	-2.860957
H	1.544471	-0.479108	4.175111
H	2.518407	1.150271	2.628411
H	-2.795389	-2.475389	3.200807
H	-5.114314	-2.245593	1.210710
H	-4.308830	-3.735766	1.681962
H	-6.438811	-3.434693	2.926684
H	-5.061493	-3.466691	4.026508
H	-6.521398	-0.958921	3.036971
H	-6.602976	-1.623974	4.668424
H	-4.995104	0.312154	4.532941
H	-4.186102	-1.176616	5.015033
H	-4.206278	0.045799	2.199853
H	-2.837595	0.005313	3.309237
H	-0.498862	-3.169349	0.094022
H	-3.325627	-4.270425	-0.313822
H	-2.386404	-3.358011	-1.480563
H	-2.264075	-5.824827	-1.915103
H	-0.672515	-5.145637	-1.576960
H	-2.430469	-6.680612	0.412585
H	-0.946549	-7.273348	-0.328324
H	-0.544408	-6.422470	2.008763
H	0.377728	-5.512175	0.814118
H	-2.259129	-4.649105	2.115136
H	-0.673310	-3.965518	2.443335
H	-4.572097	2.100515	-1.977456
H	-4.955486	3.171480	-4.155633
H	-3.961162	2.210833	-6.227583

H	-2.540888	0.168007	-6.068558
H	-2.151478	-0.907109	-3.893300
H	-5.515836	0.704530	0.069753
H	-7.880712	0.024773	0.058508
H	-8.597405	-2.028152	-1.161509
H	-6.897567	-3.369009	-2.395234
H	-4.532356	-2.693196	-2.391144
H	-0.390470	0.205098	-2.577131
H	1.084085	0.701081	-1.699563
H	0.563434	-1.015927	-1.673725
H	-0.799102	-2.843935	5.448282
H	0.878805	-2.512191	4.938323
H	-0.151564	-1.182858	5.553701
H	3.862928	4.852772	-1.317776
H	1.620756	5.294164	-0.470595
H	3.051401	-0.416706	0.204823
N	5.498445	-1.148060	-0.608736
H	5.732968	3.283521	-1.707579
H	6.714739	1.055934	-1.535487
H	-1.779090	4.741659	0.420143
C	-0.778504	4.836098	-1.468379
H	-0.322581	5.713869	0.439377
C	-0.441770	3.425924	2.047044
H	-1.530607	3.304645	2.103010
H	-0.002463	2.497861	2.407893
C	-0.021763	4.574671	2.956739
C	-0.981490	5.409035	3.543107
C	-0.606138	6.459059	4.384726
C	0.743736	6.692972	4.648684
C	1.712631	5.869408	4.068704
C	1.332706	4.819023	3.233141
H	-2.036025	5.231632	3.341289
H	-1.367913	7.093176	4.831066
H	1.040289	7.509291	5.302038
H	2.766410	6.043255	4.271519
H	2.094030	4.184337	2.787616
C	-0.583155	6.063315	-2.114870
C	-0.650412	6.157017	-3.505883
C	-0.908212	5.016638	-4.268464
C	-1.108712	3.789400	-3.632150

C	-1.048753	3.701007	-2.240527
H	-0.372500	6.952960	-1.523697
H	-0.494984	7.117461	-3.991186
H	-0.958481	5.083705	-5.352249
H	-1.331771	2.901266	-4.214918
H	-1.217494	2.748416	-1.748729
C	6.633861	-1.530974	-1.435100
C	4.930162	-2.216887	0.195946
H	6.445434	-2.541961	-1.820714
H	6.660241	-0.885526	-2.320016
C	7.993461	-1.515685	-0.741713
C	9.057417	-2.233217	-1.306130
C	10.322024	-2.215484	-0.719058
C	10.540469	-1.483117	0.451060
C	9.485843	-0.772071	1.024118
C	8.220425	-0.787852	0.431029
H	8.892312	-2.812193	-2.213100
H	11.135248	-2.778244	-1.170089
H	11.524134	-1.471162	0.912716
H	9.645214	-0.201927	1.935787
H	7.401333	-0.234508	0.880714
C	4.056136	-3.214530	-0.560444
H	5.759243	-2.764129	0.665212
H	4.366671	-1.768680	1.021533
C	3.912770	-4.518702	-0.068552
C	3.116105	-5.451342	-0.734048
C	2.454167	-5.093053	-1.911641
C	2.593031	-3.796757	-2.411856
C	3.388279	-2.864170	-1.740465
H	4.438742	-4.809875	0.838829
H	3.025227	-6.461500	-0.343312
H	1.845719	-5.821551	-2.440396
H	2.090751	-3.512265	-3.332975
H	3.502620	-1.860643	-2.139438

Less stable conformer **JPdPh$_2$** [bis(N,N-dibenzyl)-2,7-diamino]: B3LYP/6-31G(d)/SDD for pre-reductive elimination step, O-Pd distance=3.065 Å, C-Pd-C angle=160.0°. ($E_{e,rel}$=17.67 kcal/mol)

(Near identical conformation to **J**)

Processing: pddiphnamphos-ha6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3440.5604886

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
792.70890	836.795	395.928	335.284	837.053	46.894	41.369

Processing: pddiphnamphos-ha6dsdbe.log
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C	4.966465	4.539036	-1.570957
C	3.885389	3.653844	-1.485680
C	4.144483	2.281960	-1.364097
C	5.456972	1.807924	-1.343089
C	6.530431	2.699734	-1.433504
C	6.281962	4.067824	-1.545070
C	2.461829	4.171652	-1.606032
N	1.545729	3.597307	-0.613279
C	1.885631	3.967010	0.781082
C	1.772813	5.449379	1.109006
C	2.919487	6.250159	1.200998
C	2.824088	7.612130	1.497129
C	1.573801	8.195740	1.705866
C	0.422274	7.408866	1.619992
C	0.522267	6.048612	1.326311
C	0.161056	3.594406	-0.959911
C	-0.341512	4.571039	-1.869754
C	-1.664735	4.593102	-2.237606
C	-2.581478	3.660002	-1.703034
C	-2.108658	2.664542	-0.787660
C	-0.709593	2.625920	-0.443277
C	-3.046248	1.738692	-0.256174
C	-4.402389	1.781040	-0.577658
C	-4.847696	2.773257	-1.507597
C	-3.959454	3.673197	-2.040898
C	-0.258056	1.567303	0.518690

C	0.507880	0.419752	0.195559
C	0.833524	-0.558655	1.175744
C	0.478984	-0.292891	2.520994
C	-0.294463	0.821508	2.851538
C	-0.663108	1.709142	1.850927
O	1.047097	0.194036	-1.034051
C	0.354413	0.507186	-2.250859
P	1.748414	-2.106797	0.672370
C	3.554670	-1.612898	0.982774
C	3.814835	-0.762073	2.244936
C	5.273153	-0.266263	2.280916
C	6.279814	-1.420566	2.185386
C	5.999476	-2.295469	0.956471
C	4.544238	-2.794813	0.938092
O	0.936098	-1.157952	3.471937
C	0.525612	-0.979726	4.820845
C	1.306034	-3.498779	1.875719
C	1.826582	-4.860418	1.354421
C	1.551775	-5.984409	2.370201
C	0.060342	-6.090000	2.713882
C	-0.491473	-4.735416	3.177910
C	-0.208652	-3.623407	2.151993
Pd	1.314258	-2.832954	-1.435736
C	3.202583	-2.630682	-2.234987
C	3.755101	-1.418339	-2.694788
C	4.865763	-1.387465	-3.545639
C	5.469013	-2.579283	-3.956362
C	4.952959	-3.796909	-3.508514
C	3.844679	-3.817114	-2.652700
C	-0.695701	-3.302268	-1.290909
C	-0.970341	-4.649717	-1.621396
C	-2.246723	-5.079398	-2.004541
C	-3.303360	-4.169166	-2.050314
C	-3.070687	-2.834860	-1.705378
C	-1.792416	-2.417151	-1.319361
H	-0.606765	1.006649	3.870937
H	-1.271607	2.570171	2.112654
H	1.819311	-3.259837	2.814028
H	1.320591	-5.088655	0.407671
H	2.895806	-4.824453	1.134127

H	1.919937	-6.936948	1.967592
H	2.126248	-5.791987	3.289073
H	-0.493216	-6.415438	1.821413
H	-0.102266	-6.856199	3.483100
H	-1.573354	-4.805338	3.351506
H	-0.036057	-4.467977	4.144073
H	-0.719376	-3.858479	1.212021
H	-0.625488	-2.680481	2.510586
H	3.753300	-0.984194	0.104641
H	4.384682	-3.435896	1.816299
H	4.375881	-3.401798	0.044570
H	6.681401	-3.155277	0.934620
H	6.191361	-1.722385	0.038340
H	6.208911	-2.039835	3.092473
H	7.305174	-1.029993	2.153663
H	5.438402	0.309994	3.200868
H	5.434486	0.429474	1.445214
H	3.608715	-1.358199	3.143402
H	3.142447	0.100074	2.274520
H	-0.169409	-5.389795	-1.589328
H	-2.414046	-6.123735	-2.261741
H	-4.297762	-4.494379	-2.346694
H	-3.888798	-2.117809	-1.746771
H	-1.648948	-1.373412	-1.045429
H	3.475819	-4.783643	-2.307556
H	5.416695	-4.731902	-3.817657
H	6.334074	-2.558519	-4.614961
H	5.259006	-0.431657	-3.887045
H	3.303858	-0.475722	-2.392600
H	0.699332	-0.232766	-2.976243
H	-0.726780	0.419886	-2.127710
H	0.607672	1.512671	-2.592199
H	0.974110	-1.805023	5.376692
H	0.889965	-0.028227	5.227758
H	-0.566239	-1.023774	4.916182
H	-2.025892	5.352716	-2.927538
H	0.328007	5.330845	-2.255041
H	-2.695165	1.010070	0.459667
N	-5.307449	0.878784	-0.019952
H	-4.312405	4.415985	-2.752869

H	-5.883583	2.798272	-1.826142
H	2.076101	3.897362	-2.594569
H	2.484508	5.273529	-1.570588
H	2.912483	3.632362	0.959090
H	1.242149	3.387781	1.444309
H	3.896584	5.798857	1.043777
H	3.726208	8.214690	1.567529
H	1.496005	9.254596	1.938499
H	-0.555038	7.854229	1.788168
H	-0.378886	5.444130	1.266659
H	3.308166	1.593357	-1.282259
H	5.640166	0.739097	-1.274364
H	7.551693	2.328291	-1.418440
H	7.108950	4.770110	-1.612377
H	4.776510	5.606312	-1.663628
C	-4.856633	-0.305028	0.693388
C	-6.746683	1.088640	-0.066045
H	-7.163476	0.782938	0.902738
H	-6.944715	2.164340	-0.137832
C	-7.490462	0.350196	-1.176016
H	-5.621923	-1.079736	0.557363
H	-3.957722	-0.697725	0.205101
C	-4.585355	-0.138556	2.187901
C	-4.210915	-1.265651	2.934098
C	-3.955633	-1.163848	4.301229
C	-4.071063	0.071831	4.946407
C	-4.441802	1.197971	4.211071
C	-4.697427	1.092553	2.840377
H	-4.120278	-2.230295	2.438239
H	-3.676256	-2.050425	4.865176
H	-3.881464	0.152149	6.013687
H	-4.536578	2.162896	4.702838
H	-4.978279	1.973179	2.270516
C	-8.876673	0.171251	-1.068994
C	-9.593371	-0.472680	-2.076992
C	-8.930240	-0.955263	-3.208593
C	-7.549909	-0.787184	-3.320980
C	-6.834516	-0.137798	-2.311071
H	-9.398516	0.537147	-0.186347
H	-10.667605	-0.604672	-1.976529

H -9.485887 -1.461912 -3.993051
H -7.024231 -1.162334 -4.195142
H -5.760032 -0.010364 -2.403373

Low-energy conformer of **EvanPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step.

C-Pd-C angle=87.68^o

Processing: pddiphevanphos-b6dsdbe.log

PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy -2363.0072496

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
516.71651	545.940	274.116	245.954	546.082	45.725	38.880

Processing: pddiphevanphos-b6dsdbe.log

97

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C -4.925624 -0.874117 0.116343
C -6.087187 -0.030327 0.081619
C -7.209141 -0.347925 0.893726
C -7.199743 -1.448608 1.718851
C -6.053600 -2.279261 1.765017
C -6.079373 1.104155 -0.765763
C -4.991167 1.401420 -1.552572
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C -3.795209 -0.555290 -0.699139
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C -1.331498 -1.045059 -0.249424
C -0.161177 -1.806413 -0.431601
C -0.301983 -3.061280 -1.073190
C -1.547517 -3.494267 -1.536742
C -2.664152 -2.677531 -1.382722
P 1.438725 -1.026895 0.129368
C 2.757770 -1.545721 -1.102171
C 2.377658 -1.055172 -2.516634
C 3.460751 -1.416044 -3.547607
C 4.837214 -0.877851 -3.132656

C	5.215784	-1.367382	-1.728179
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O	0.828278	-3.816105	-1.206042
C	0.753096	-5.058192	-1.892217
O	-2.752674	0.790614	-2.312015
C	-2.766995	1.870147	-3.237990
Pd	0.800436	1.312715	0.314632
C	-0.041631	3.159750	0.588950
C	0.471549	4.197463	1.388932
C	-0.257186	5.367242	1.629408
C	-1.521476	5.542639	1.063082
C	-2.050278	4.532238	0.258316
C	-1.319327	3.360843	0.027435
C	2.555818	2.237807	0.079240
C	2.929813	2.731063	-1.184058
C	4.190081	3.301458	-1.395315
C	5.104289	3.407469	-0.344512
C	4.739209	2.944563	0.920964
C	3.479536	2.370862	1.130157
C	1.785755	-1.911793	1.770297
C	2.582769	-1.013297	2.741541
C	2.717310	-1.668488	4.126625
C	3.335539	-3.071096	4.036544
C	2.543030	-3.962514	3.070053
C	2.409755	-3.319214	1.677488
H	-1.654476	-4.450428	-2.034095
H	-3.620489	-3.003259	-1.781632
H	2.806431	-2.638096	-1.115907
H	4.094952	0.096359	-0.593683
H	4.435492	-1.385703	0.290441
H	6.180379	-0.942617	-1.423032
H	5.344400	-2.460584	-1.746057
H	4.812570	0.221085	-3.134059
H	5.600604	-1.179663	-3.861489
H	3.176112	-1.023266	-4.532414
H	3.514297	-2.510623	-3.650705
H	2.246901	0.034786	-2.494632
H	1.416104	-1.483949	-2.822508

H	0.774765	-2.024691	2.191647
H	3.583860	-0.819764	2.333702
H	2.091385	-0.037572	2.827949
H	3.318653	-1.026199	4.782515
H	1.721402	-1.741597	4.589364
H	4.373843	-2.987057	3.682562
H	3.380848	-3.533139	5.031014
H	3.020948	-4.946645	2.977716
H	1.538676	-4.141347	3.482646
H	3.407764	-3.247292	1.223621
H	1.812340	-3.958350	1.021039
H	-1.759347	2.582648	-0.590898
H	-3.036546	4.651519	-0.188238
H	-2.085918	6.454192	1.245931
H	0.168953	6.146665	2.258651
H	1.459998	4.099949	1.829459
H	2.228931	2.680420	-2.013410
H	4.450913	3.675163	-2.383776
H	6.082034	3.854171	-0.507245
H	5.434600	3.030352	1.753975
H	3.222340	2.021681	2.127115
H	-1.773892	1.259613	2.045244
H	-2.841556	-0.139008	1.715653
H	-1.213413	-0.400502	2.424146
H	1.769160	-5.456185	-1.893608
H	0.088106	-5.762814	-1.377183
H	0.412267	-4.925093	-2.926383
H	-6.954789	1.748525	-0.790142
H	-5.015035	2.274623	-2.193618
H	-4.079986	-2.648830	1.036327
H	-6.044759	-3.145240	2.421846
H	-8.079673	0.302735	0.851168
H	-8.063036	-1.680792	2.336024
H	-1.815343	1.812435	-3.768086
H	-3.591739	1.771397	-3.955551
H	-2.831898	2.838939	-2.728833

Figure S4 (repeat). B3LYP/6-31G(d)(SDD) [5d] optimized structure for more stable conformer $QPdPh_2$ of *N*,*N*-dibenzyl-2-aminoNPhosPdPh_2. O-Pd distance=2.338 Å, C-Pd-C angle=86.28°. Atom colors: nitrogen, blue; oxygen, red; palladium, teal. Cartesian coordinates below are for enantiomer.

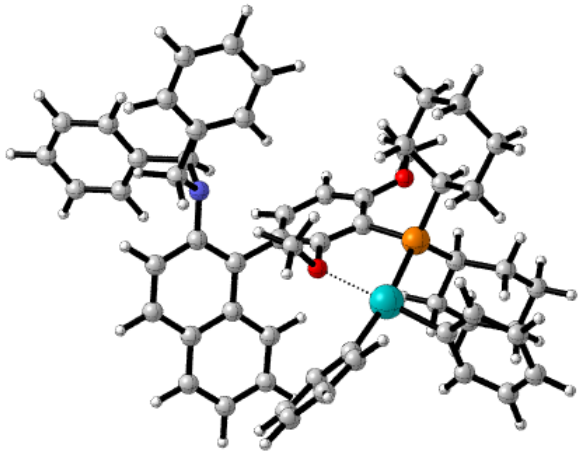

Table S4. Thermodynamic parameters and Cartesian coordinates from additional optimized NPhos and N_2Phos structures at various levels of theory.

$QPdPh_2$, more stable conformer of ***N*,*N*-dibenzyl-2-aminoNPhosPdPh_2**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=2.338 Å, C-Pd-C angle=86.28°. ($E_{e,rel}$=0.00 kcal/mol)

(Not identical conformation as **A**, cyclohexyls slightly reversed and 2-aminobenzyls rotated.)

Processing: pdnamphos-c6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2844.5345751

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.10760	680.039	332.339	285.788	680.246	46.318	40.217

ccl00:/aue/chem126/aue/ark/pj/nam> gtg pdnamphos-c6dsdbe.log

Processing: pdnamphos-c6dsdbe.log
121

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C	3.344923	-0.983177	-2.222129
C	3.190669	0.424155	-2.838112
C	4.101211	0.610161	-4.063944
C	5.569528	0.319190	-3.724412
C	5.723105	-1.084366	-3.123387
P	2.248899	-1.149098	-0.696962
Pd	2.347453	0.711019	0.855862
C	2.121059	2.332242	2.075679
C	1.397021	3.431843	1.574201
C	1.064167	4.520479	2.388703
C	1.448491	4.537799	3.730910
C	2.173379	3.461255	4.246687
C	2.512192	2.379920	3.425890
C	0.528612	-0.987879	-1.388438
C	-0.348140	-0.061995	-0.794180
C	-1.592263	0.289410	-1.366603
C	-1.934911	-0.345454	-2.562071
C	-1.137981	-1.330817	-3.142562
C	0.079983	-1.664490	-2.548471
C	-2.451128	1.395976	-0.826957
C	-2.068494	2.752675	-1.111528
C	-2.846397	3.836167	-0.586004
C	-3.995499	3.539501	0.188581
C	-4.367584	2.239409	0.421121
C	-3.605529	1.145968	-0.081162
C	-0.926481	3.076521	-1.898587
C	-0.573201	4.386127	-2.140309
C	-1.341140	5.450650	-1.610915
C	-2.454884	5.175894	-0.851521
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O	0.065169	0.590029	0.365033
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C	0.506888	-3.353086	-4.199587
C	2.418174	-2.964907	-0.188281
C	1.090943	-3.591185	0.286685
C	1.279389	-5.063668	0.693387

C	2.368082	-5.232384	1.762202
C	3.686460	-4.588363	1.311614
C	3.486510	-3.115502	0.917649
C	4.308934	0.867059	1.229922
C	5.110624	1.778156	0.518751
C	6.494188	1.836866	0.719293
C	7.110737	0.997141	1.649498
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C	4.942265	0.045239	2.177720
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H	4.935418	-2.303931	-1.522427
H	5.163387	-0.610516	-1.085431
H	6.768408	-1.269374	-2.845482
H	5.462501	-1.835394	-3.884883
H	6.196209	0.422214	-4.619684
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H	3.773765	-0.066609	-4.867889
H	3.991781	1.631318	-4.451588
H	2.145864	0.599883	-3.123448
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H	2.747251	-3.508981	-1.084757
H	0.710190	-3.025082	1.150030
H	0.331470	-3.522059	-0.497868
H	0.324988	-5.472053	1.052157
H	1.552041	-5.647889	-0.198209
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H	2.035152	-4.755872	2.696124
H	4.090101	-5.144839	0.452347
H	4.437574	-4.658069	2.108592
H	4.440159	-2.674705	0.611133
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H	-1.466490	-1.810379	-4.056633
H	-1.701423	0.206200	1.410232
H	-0.345626	0.946058	2.324369
H	-0.295357	-0.792525	1.891695
H	-0.443152	-3.879965	-4.046734
H	1.299143	-4.080210	-4.384369
H	0.417709	-2.684556	-5.064949

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H	-4.589503	4.359060	0.586161
H	-3.056980	5.982793	-0.440401
H	-1.050031	6.478715	-1.807417
H	-0.326944	2.275212	-2.315859
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H	7.088042	2.552994	0.154317
H	8.185041	1.045878	1.809421
H	6.787469	-0.545921	3.122324
H	4.355777	-0.653907	2.768770
H	3.100163	1.567273	3.845959
H	2.485750	3.465360	5.289510
H	1.191167	5.382376	4.366172
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C	-4.461068	-0.419463	1.602613
C	-4.861271	-0.868562	-0.788039
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C	-6.293516	-0.367079	-0.894837
H	-4.362731	-0.767627	-1.752921
H	-5.506944	-0.107936	1.759540
C	-4.315746	-1.862587	2.065056
H	-3.852178	0.224397	2.249188
C	-3.260252	-2.674242	1.628396
C	-3.116445	-3.975149	2.113367
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C	-5.079593	-3.685143	3.484946
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H	-3.909148	-5.497204	3.423926
H	-5.794851	-4.072821	4.205713
H	-6.054368	-1.770203	3.334700
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C	-7.927618	1.199579	-1.789933
C	-6.614420	0.736226	-1.699851
H	-7.098536	-1.868890	0.424596
H	-9.430319	-1.045642	0.276572

H -9.969407 0.921971 -1.147583
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H -5.829195 1.234256 -2.263232

QPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=3.055 Å, C-Pd-C angle=161.23°. ($E_{e,rel}$=19.38 kcal/mol)

Processing: pdnamphos6dsdbe.log
PG=C01
Method BasisSet Imaginary Freqs
RB3LYP GenECP 0

HF Energy
-2844.5036936

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.35717	680.161	327.340	285.918	680.355	46.318	40.078

Processing: pdnamphos6dsdbe.log
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C	-4.706981	1.800078	3.376141
C	-3.602023	1.550375	2.334116
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C	4.123460	-1.266888	-1.414586
Pd	-2.824361	0.169836	-1.313181
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C	-4.341557	2.600718	-1.624734
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C	-3.702567	4.935058	-1.596361
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C	-2.204205	3.232054	-0.738902
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C	-2.858901	-3.161459	0.949210
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H	-1.035680	-2.382645	0.128490
H	-3.495426	-3.009569	1.832016
H	-3.462997	-2.958756	0.061017
H	-3.266179	-5.288863	0.896352
H	-1.823324	-4.810838	0.009984
H	-2.138006	-4.890482	3.063215
H	-1.154748	-5.988205	2.098207
H	0.229733	-4.176567	3.183303
H	0.345219	-4.136482	1.427564
H	-1.394399	-2.308900	3.172302
H	0.071136	-1.856316	2.308153
H	-5.099440	1.850736	-1.862051
H	-5.588589	4.207898	-2.352785
H	-3.924337	5.979046	-1.804430
H	-1.754918	5.341893	-0.762175
H	-1.253097	2.987762	-0.270149
H	-4.927806	-1.880113	-2.196791
H	-5.007419	-3.784486	-3.751127
H	-2.902076	-4.776910	-4.635777
H	-0.708910	-3.813065	-3.951125
H	-0.620982	-1.895305	-2.411118
H	-0.239900	0.667749	-2.868567
H	0.289839	2.116327	-1.977688
H	1.491791	0.885293	-2.473889
H	-1.714377	0.200467	5.497357
H	0.056176	0.323297	5.302292
H	-0.973747	1.774840	5.098670
H	5.546942	3.138150	-2.718348
H	5.410178	0.808001	-1.995281
H	1.018791	4.048425	0.375987
H	1.193756	6.377563	-0.349013
H	4.691332	5.440100	-2.668892
H	3.034881	7.103732	-1.869953
C	3.520903	-2.659337	-1.334372
H	3.915076	-0.859196	-2.410103
H	5.219482	-1.351881	-1.330042
C	3.854561	-0.687558	0.966922
H	3.466279	-1.698853	1.124496

C	5.326307	-0.643796	1.353835
H	3.279603	-0.020939	1.610620
C	6.070647	-1.825825	1.469318
C	7.423224	-1.792996	1.817433
C	8.053920	-0.571155	2.055666
C	7.323330	0.615032	1.947594
C	5.972120	0.577404	1.602059
H	5.582157	-2.780921	1.289728
H	7.981646	-2.721546	1.905275
H	9.105514	-0.542159	2.328670
H	7.805074	1.570463	2.139262
H	5.411410	1.505396	1.526665
C	2.131175	-2.840375	-1.321389
C	1.584259	-4.124093	-1.346281
C	2.419133	-5.245995	-1.372353
C	3.803492	-5.075184	-1.373955
C	4.348278	-3.788209	-1.356319
H	1.485528	-1.967090	-1.288795
H	0.504737	-4.246801	-1.364358
H	1.990901	-6.244641	-1.393629
H	4.461315	-5.940372	-1.390909
H	5.428454	-3.658502	-1.366885

QPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=3.052 Å, C-Pd-C angle=161.02°. ($E_{e,rel}$=21.20 kcal/mol)

Processing: pdnamphos-b6dsdbe.log

PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy

-2844.5007986

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.10816	679.979	330.188	286.258	680.173	46.318	40.150

Processing: pdnamphos-b6dsdbe.log
121

C	7.067464	-1.572945	-1.226996
C	5.806712	-1.019275	-1.484133
C	4.911245	-1.737089	-2.288013
C	5.271412	-2.974289	-2.823962
C	6.535200	-3.512591	-2.570218
C	7.433847	-2.806760	-1.768864
C	5.469182	0.361889	-0.940347
N	4.064097	0.515661	-0.553105
C	3.647071	-0.353578	0.571033
C	4.388172	-0.130417	1.882024
C	5.420261	-0.997027	2.268496
C	6.116652	-0.798903	3.462900
C	5.789369	0.274058	4.293038
C	4.761685	1.144551	3.921971
C	4.068490	0.942628	2.727929
C	3.561961	1.855356	-0.547899
C	4.426998	2.928326	-0.186850
C	4.001429	4.232368	-0.200079
C	2.678744	4.558406	-0.588648
C	1.786620	3.498147	-0.961055
C	2.237256	2.131612	-0.913384
C	0.484111	3.863602	-1.409154
C	0.084265	5.181139	-1.453103
C	0.959860	6.217845	-1.052132
C	2.232877	5.906633	-0.634881
C	1.325803	1.038351	-1.382148
C	0.078504	0.707078	-0.799188
C	-0.795765	-0.249403	-1.382853
C	-0.421511	-0.807509	-2.628524
C	0.826540	-0.525403	-3.192901
C	1.674047	0.377051	-2.564573
O	-0.424516	1.383287	0.277143
C	0.339443	1.535239	1.483045
P	-2.433824	-0.599834	-0.555697
C	-3.540763	0.708156	-1.369836
C	-3.323524	0.923741	-2.883715
C	-4.123030	2.143566	-3.380818
C	-5.618282	2.029618	-3.055783

C	-5.837614	1.766627	-1.560052
C	-5.046175	0.536856	-1.081714
O	-1.341657	-1.589138	-3.262936
C	-1.003446	-2.192751	-4.503791
C	-3.068345	-2.303874	-1.072542
C	-4.293739	-2.704881	-0.214617
C	-4.889684	-4.041833	-0.692039
C	-3.848249	-5.168346	-0.678172
C	-2.595059	-4.767059	-1.467605
C	-2.015808	-3.429554	-0.973179
Pd	-2.351071	-0.508235	1.701043
C	-3.681046	1.040187	2.022212
C	-3.394003	2.406628	1.822822
C	-4.190243	3.416659	2.373443
C	-5.312293	3.089049	3.139436
C	-5.631216	1.745507	3.345113
C	-4.832580	0.741529	2.783697
C	-0.978888	-2.014546	2.059019
C	-1.350827	-2.693185	3.240169
C	-0.469329	-3.543822	3.919357
C	0.812158	-3.764298	3.412485
C	1.198035	-3.130757	2.228149
C	0.312591	-2.275676	1.563620
H	1.121583	-0.962559	-4.138617
H	2.618883	0.629002	-3.033989
H	-3.382509	-2.202491	-2.118228
H	-3.969845	-2.797024	0.830799
H	-5.068397	-1.935336	-0.232337
H	-5.746294	-4.305015	-0.058220
H	-5.283323	-3.919609	-1.712581
H	-3.563003	-5.382407	0.361896
H	-4.279032	-6.093164	-1.083409
H	-1.828268	-5.548256	-1.386621
H	-2.847373	-4.685189	-2.536311
H	-1.706474	-3.532336	0.072135
H	-1.119206	-3.184436	-1.545092
H	-3.209145	1.615841	-0.848047
H	-5.421012	-0.348393	-1.614151
H	-5.215926	0.383004	-0.012934
H	-6.904647	1.619180	-1.350155

H	-5.521827	2.642355	-0.975923
H	-6.052539	1.201483	-3.636102
H	-6.145668	2.940040	-3.368410
H	-3.972911	2.262989	-4.461906
H	-3.718145	3.050476	-2.907787
H	-3.640581	0.028817	-3.435874
H	-2.263653	1.075172	-3.107782
H	-2.354065	-2.559363	3.653582
H	-0.788972	-4.040504	4.833445
H	1.500444	-4.428540	3.929368
H	2.193746	-3.301542	1.822794
H	0.640170	-1.808645	0.636578
H	-5.120214	-0.297922	2.946318
H	-6.506526	1.477193	3.933936
H	-5.933964	3.872602	3.566178
H	-3.933549	4.461466	2.206426
H	-2.526404	2.691878	1.229478
H	-0.366311	1.925824	2.217564
H	0.714617	0.567493	1.825973
H	1.158713	2.244932	1.348625
H	-1.880210	-2.771869	-4.798171
H	-0.790629	-1.438773	-5.271707
H	-0.142186	-2.864567	-4.402741
H	4.677940	5.032053	0.092504
H	5.438681	2.700333	0.129916
H	-0.200801	3.090221	-1.733571
H	-0.914979	5.426816	-1.802786
H	2.925901	6.690840	-0.338823
H	0.628507	7.252054	-1.084824
H	5.666855	1.105457	-1.722325
H	6.165031	0.584095	-0.114186
H	3.789365	-1.390559	0.250408
H	2.574483	-0.211327	0.711941
H	5.676565	-1.837880	1.627948
H	6.910306	-1.485683	3.746036
H	6.325970	0.428323	5.225475
H	4.493671	1.977354	4.567031
H	3.267829	1.623246	2.452948
H	3.924052	-1.326278	-2.474685
H	4.562339	-3.520843	-3.440813

H 6.814245 -4.476158 -2.988190
H 8.417401 -3.218516 -1.557807
H 7.769094 -1.031628 -0.595789

QPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=3.012 Å, C-Pd-C angle=160.59^o. ($E_{e,rel}$=25.26 kcal/mol)

Processing: pdnamphos-a6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2844.4943221

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.44112	680.239	327.915	285.618	680.434	46.318	40.143

Processing: pdnamphos-a6dsdbe.log
121
C -5.099034 0.716016 -0.566916
C -3.638278 0.972942 -0.991537
C -3.596334 1.407495 -2.471898
C -4.463519 2.662186 -2.693281
C -5.911562 2.455259 -2.229847
C -5.959016 1.974978 -0.773257
P -2.446427 -0.405813 -0.459315
Pd -2.235053 -0.566076 1.796175
C -3.319171 1.102174 2.346634
C -2.894229 2.442141 2.239616
C -3.521877 3.472269 2.948302
C -4.606527 3.193337 3.784412
C -5.058774 1.877821 3.902346
C -4.429892 0.854107 3.183068
C -0.884642 0.070765 -1.376532
C 0.100594 0.862204 -0.727528
C 1.273505 1.303025 -1.395451

C	1.397616	0.976102	-2.746571
C	0.446287	0.225555	-3.428192
C	-0.695833	-0.211259	-2.753852
C	2.242220	2.264673	-0.769420
C	1.875007	3.655989	-0.777092
C	2.677591	4.616154	-0.078151
C	3.830436	4.157750	0.604898
C	4.198007	2.837151	0.559723
C	3.433089	1.860108	-0.147643
C	0.704843	4.134359	-1.436247
C	0.363046	5.468959	-1.410821
C	1.166047	6.409799	-0.723646
C	2.300474	5.985152	-0.071206
N	3.851038	0.499431	-0.125376
C	4.514752	-0.015871	1.075669
O	-0.222862	1.280272	0.525070
C	0.727930	1.292703	1.600656
O	-1.691424	-0.889666	-3.391957
C	-1.544557	-1.209288	-4.768511
C	-3.088846	-2.037484	-1.166292
C	-4.213156	-2.620126	-0.276696
C	-4.804336	-3.898057	-0.899730
C	-3.726426	-4.960818	-1.150588
C	-2.574163	-4.386108	-1.985400
C	-1.992991	-3.110174	-1.350749
C	-1.108373	-2.294596	1.938368
C	-1.703938	-3.279155	2.759613
C	-0.972728	-4.350910	3.286525
C	0.382121	-4.488248	2.980198
C	0.994622	-3.545959	2.149312
C	0.256250	-2.473656	1.637558
H	0.584292	0.020921	-4.482109
H	2.244828	1.369474	-3.301344
H	-3.508082	-1.789630	-2.148301
H	-3.792781	-2.852126	0.709381
H	-5.012153	-1.892758	-0.113354
H	-5.586984	-4.295559	-0.240698
H	-5.296973	-3.644987	-1.850933
H	-3.331267	-5.308033	-0.185249
H	-4.161563	-5.837446	-1.647890

H	-1.777610	-5.132803	-2.099611
H	-2.936701	-4.157909	-2.999741
H	-1.567900	-3.353279	-0.371167
H	-1.175815	-2.733988	-1.969759
H	-3.266321	1.809528	-0.385677
H	-5.517672	-0.098499	-1.174439
H	-5.142946	0.409192	0.481604
H	-6.993696	1.765091	-0.473399
H	-5.593863	2.768501	-0.106579
H	-6.394090	1.705045	-2.874530
H	-6.484913	3.383717	-2.347968
H	-4.436745	2.941967	-3.754807
H	-4.022295	3.502542	-2.137457
H	-3.961911	0.593624	-3.111697
H	-2.570590	1.622932	-2.785097
H	-2.765268	-3.212669	3.004633
H	-1.464575	-5.081455	3.926225
H	0.953169	-5.324242	3.377190
H	2.046967	-3.648744	1.892153
H	0.762647	-1.762619	0.988300
H	-4.820005	-0.160073	3.280936
H	-5.907275	1.648255	4.544387
H	-5.096832	3.993721	4.333586
H	-3.162009	4.495062	2.849510
H	-2.050155	2.686744	1.597192
H	0.150056	1.068776	2.499961
H	1.490545	0.525010	1.454078
H	1.193084	2.276441	1.693017
H	-2.444517	-1.763863	-5.039270
H	-1.475550	-0.304672	-5.385373
H	-0.663550	-1.838912	-4.942543
H	4.438536	4.872337	1.154839
H	5.098333	2.525591	1.075781
H	0.079136	3.433256	-1.976658
H	-0.532637	5.803307	-1.927706
H	2.929327	6.693018	0.464010
H	0.885003	7.459198	-0.713105
H	4.131077	-1.028997	1.251319
C	6.042410	-0.102268	1.112017
H	4.165402	0.586611	1.921997

C	4.258406	-0.149686	-1.383360
C	4.058179	-1.655233	-1.396165
H	3.675511	0.299817	-2.185680
H	5.314920	0.059386	-1.608303
C	6.621860	-1.075604	1.940250
C	8.005636	-1.186826	2.067584
C	8.845819	-0.332425	1.349299
C	8.285832	0.629751	0.509471
C	6.897344	0.745523	0.394019
H	5.976168	-1.755427	2.492517
H	8.428143	-1.946151	2.720530
H	9.925090	-0.420815	1.439603
H	8.927912	1.295787	-0.061264
H	6.484512	1.501100	-0.266572
C	2.788801	-2.219402	-1.207417
C	2.610586	-3.602275	-1.252617
C	3.700540	-4.443454	-1.496064
C	4.967745	-3.892368	-1.688003
C	5.143316	-2.507256	-1.632637
H	1.939615	-1.569492	-1.021947
H	1.621563	-4.021294	-1.089247
H	3.561393	-5.520852	-1.530918
H	5.822566	-4.538027	-1.872230
H	6.135070	-2.082458	-1.769047

RPdPh$_2$, more stable conformer of ***N*,*N*-dibenzyl-7-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=2.346 Å, C-Pd-C angle=87.36°. ($E_{e,rel}$=0 kcal/mol)

(Near identical conformation to **A**, but naphthyl rotated near 180°)

Processing: pddiph7namphos-hb6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2844.5483268

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.61547	680.386	328.015	284.598	680.587	46.318	39.997

Processing: pddiph7namphos-hb6dsdbe.log

121

C	-5.046358	1.780074	0.355600
C	-5.760572	1.091404	-0.628881
C	-7.018229	1.576972	-1.016056
C	-7.550183	2.724016	-0.429101
C	-6.828616	3.407249	0.554907
C	-5.576687	2.932212	0.944225
C	-5.215701	-0.167883	-1.299888
N	-3.867331	-0.562795	-0.919056
C	-2.798944	0.042053	-1.706216
C	-2.617121	-0.555865	-3.096563
C	-2.696854	-1.938640	-3.314627
C	-2.509851	-2.468281	-4.592225
C	-2.244423	-1.624499	-5.673567
C	-2.171465	-0.245651	-5.468957
C	-2.360178	0.282072	-4.189199
C	-3.627911	-1.453338	0.120790
C	-4.681703	-1.765514	1.040786
C	-4.492430	-2.674377	2.049602
C	-3.247509	-3.327149	2.248763
C	-2.162921	-2.985604	1.373836
C	-2.389830	-2.070459	0.315665
C	-3.067686	-4.295081	3.267166
C	-1.857952	-4.933346	3.423051
C	-0.778783	-4.594953	2.576032
C	-0.895224	-3.630386	1.586306
C	0.296733	-3.336886	0.733122
C	0.987080	-2.104225	0.733725
C	2.077470	-1.843708	-0.116792
C	2.557399	-2.912063	-0.912499
C	1.914313	-4.151519	-0.910040
C	0.792871	-4.339166	-0.105684
P	2.759598	-0.114402	-0.169715
C	4.549394	-0.266186	0.439118
C	4.772699	-1.422802	1.434346
C	6.243066	-1.500090	1.883015
C	6.732951	-0.174332	2.481763

C	6.489926	0.990655	1.512608
C	5.017277	1.061562	1.075450
O	0.564144	-1.092433	1.597029
C	0.825390	-1.335291	3.004206
O	3.684647	-2.663458	-1.642158
C	4.210516	-3.694526	-2.467168
Pd	1.085970	1.132433	1.068512
C	1.472881	2.998030	0.460050
C	0.723582	3.576748	-0.580106
C	1.030732	4.849654	-1.073571
C	2.086525	5.584077	-0.528978
C	2.824188	5.033907	0.520765
C	2.518022	3.758890	1.011095
C	-0.396635	1.924974	2.245038
C	-1.590615	1.183446	2.361908
C	-2.610608	1.560752	3.245202
C	-2.466460	2.700521	4.038995
C	-1.294989	3.453990	3.937513
C	-0.282097	3.073985	3.050371
C	2.943778	0.258120	-2.007228
C	1.569440	0.248530	-2.707596
C	1.702092	0.565464	-4.206991
C	2.420572	1.902067	-4.437432
C	3.789288	1.913764	-3.743841
C	3.668349	1.602807	-2.240959
H	0.181164	-5.086262	2.716788
H	3.557075	-0.541331	-2.435163
H	4.671971	1.577546	-1.800372
H	3.120199	2.412540	-1.745295
H	4.278014	2.887439	-3.875781
H	4.442898	1.166584	-4.219568
H	2.535846	2.094205	-5.512158
H	1.806398	2.719531	-4.033039
H	2.267827	-0.240168	-4.699489
H	0.706987	0.573843	-4.667510
H	1.080223	-0.724389	-2.577251
H	0.919792	0.996517	-2.234215
H	5.157165	-0.469094	-0.454126
H	4.135652	-1.270364	2.318324
H	4.474337	-2.376932	0.990140

H	6.364160	-2.315680	2.607811
H	6.867596	-1.758924	1.014894
H	7.797224	-0.243687	2.740657
H	6.193934	0.019713	3.420959
H	7.128155	0.866369	0.624844
H	6.783099	1.941170	1.976229
H	4.868227	1.902155	0.390770
H	4.386438	1.269055	1.950825
H	0.278303	-5.295448	-0.126849
H	2.267843	-4.966966	-1.529269
H	0.400062	-2.292713	3.306839
H	0.338028	-0.518841	3.534567
H	1.905113	-1.318440	3.186392
H	4.507413	-4.569052	-1.874857
H	5.091700	-3.267428	-2.948578
H	3.489343	-4.001804	-3.234630
H	-1.721804	-5.684279	4.195968
H	-3.907072	-4.531017	3.917449
H	-5.312629	-2.898799	2.727714
H	-5.635901	-1.258796	0.959956
H	-1.573391	-1.879162	-0.369232
H	-5.897938	-1.008236	-1.126267
H	-5.213982	-0.019468	-2.387739
H	-7.584423	1.052543	-1.784378
H	-8.526712	3.086714	-0.740179
H	-7.241638	4.302837	1.011520
H	-5.001782	3.448408	1.708347
H	-4.071803	1.421016	0.670658
H	-1.866964	-0.012447	-1.135448
H	-3.017215	1.113270	-1.808237
H	-2.314727	1.358701	-4.037867
H	-1.980932	0.421640	-6.305577
H	-2.104298	-2.037903	-6.668826
H	-2.576346	-3.542661	-4.744181
H	-2.914942	-2.600084	-2.481004
H	-0.118176	3.036920	-1.005853
H	0.432102	5.271662	-1.878695
H	2.322920	6.574788	-0.909176
H	3.641615	5.597810	0.966397
H	3.105279	3.358911	1.833457

H 0.609414 3.691512 2.984977
H -1.166985 4.345054 4.549605
H -3.253931 2.994929 4.729192
H -3.514371 0.957758 3.310415
H -1.731163 0.282992 1.768565

RPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-7-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=2.334 Å, C-Pd-C angle=85.60°. ($E_{e,rel}$=0.46 kcal/mol)

(Near identical conformation to **A**)

Processing: pddiph7namphos-h6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2844.5475982

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
644.04613	680.055	337.916	285.684	680.266	46.318	40.569

Processing: pddiph7namphos-h6dsdbe.log
121
C -2.863728 3.952424 -0.383195
C -3.137216 2.882015 -1.256395
C -3.326059 3.193168 -2.614908
C -3.216779 4.505959 -3.086999
C -2.935558 5.550525 -2.203961
C -2.763433 5.268858 -0.847136
Pd -3.037412 0.978772 -0.525405
C -4.980115 0.858534 -1.002117
C -5.976573 1.311913 -0.119514
C -7.334912 1.162421 -0.420782
C -7.732352 0.569273 -1.620867
C -6.755271 0.136647 -2.519252
C -5.397374 0.284734 -2.214942
P -2.600677 -1.163280 0.509833

C	-0.926568	-0.894646	1.274678
C	-0.239514	0.300077	0.992029
C	0.954969	0.667139	1.650303
C	1.482507	-0.250387	2.564024
C	0.874618	-1.475766	2.824412
C	-0.323589	-1.797563	2.182457
O	-0.782923	1.167699	0.046545
C	0.002105	1.330710	-1.161994
C	1.609372	1.998662	1.478654
C	2.966687	2.113163	1.015300
C	3.558829	3.418551	0.960972
C	2.805388	4.556839	1.341281
C	1.498957	4.425267	1.754825
C	0.909240	3.143557	1.822768
C	4.901155	3.524210	0.509755
C	5.623582	2.427209	0.113284
C	5.034696	1.122991	0.116983
C	3.721167	0.997143	0.566809
O	-0.967401	-2.988142	2.367542
C	-0.405872	-3.941503	3.259259
H	-0.117210	3.049267	2.164663
N	5.777063	0.020519	-0.307036
C	5.372782	-1.341778	-0.001843
C	4.577698	-2.065402	-1.086541
C	3.914924	-1.375959	-2.107892
C	3.182277	-2.069635	-3.075052
C	3.101943	-3.462305	-3.032545
C	3.761961	-4.159365	-2.016488
C	4.496223	-3.464576	-1.055872
C	-3.679541	-1.585942	1.997389
C	-3.768648	-0.372553	2.948394
C	-4.663850	-0.669194	4.163647
C	-6.063024	-1.131040	3.733725
C	-5.974634	-2.342137	2.795455
C	-5.088647	-2.051758	1.570426
C	-2.447413	-2.779852	-0.461074
C	-1.049904	-2.971161	-1.086114
C	-0.961261	-4.288658	-1.875974
C	-2.050758	-4.389541	-2.952367
C	-3.444586	-4.173492	-2.346768

C	-3.521297	-2.848338	-1.569997
C	6.954001	0.152857	-1.153273
C	8.298895	0.061141	-0.437586
C	9.450918	-0.231123	-1.181034
C	10.701513	-0.288524	-0.567094
C	10.817992	-0.061573	0.807002
C	9.676036	0.222260	1.556385
C	8.424356	0.283688	0.937705
H	-3.189998	-2.410246	2.527252
H	-5.019996	-2.957709	0.957103
H	-5.564078	-1.279991	0.952424
H	-6.975914	-2.639601	2.458958
H	-5.561643	-3.199425	3.348879
H	-6.672634	-1.373371	4.613811
H	-6.572696	-0.307880	3.212716
H	-4.195934	-1.453125	4.778426
H	-4.732121	0.224783	4.796886
H	-2.766617	-0.082919	3.288272
H	-4.174139	0.486516	2.397272
H	-2.615074	-3.595225	0.256173
H	-0.838406	-2.130376	-1.763899
H	-0.274735	-2.955712	-0.314725
H	0.036361	-4.376249	-2.325341
H	-1.064346	-5.131688	-1.176210
H	-1.998121	-5.362004	-3.458836
H	-1.870909	-3.624719	-3.722566
H	-3.681789	-5.008142	-1.669897
H	-4.209352	-4.183551	-3.133763
H	-4.526751	-2.710994	-1.160559
H	-3.362401	-2.011398	-2.262385
H	2.393294	0.012077	3.094351
H	1.329244	-2.155557	3.534833
H	1.023243	1.624477	-0.915381
H	-0.494349	2.117935	-1.727282
H	-0.000502	0.393286	-1.728376
H	0.593193	-4.255602	2.932173
H	-1.080085	-4.799219	3.238093
H	-0.347699	-3.549920	4.282546
H	0.917734	5.297907	2.037691
H	3.275883	5.536199	1.292202

H	5.367491	4.506612	0.491318
H	6.660136	2.552920	-0.179238
H	3.233526	0.030962	0.540318
H	6.887981	1.099500	-1.701206
H	6.907967	-0.630318	-1.922109
H	9.366381	-0.416805	-2.250326
H	11.584090	-0.517138	-1.158857
H	11.791004	-0.110039	1.288358
H	9.756045	0.396837	2.626263
H	7.537432	0.502336	1.525062
H	4.801413	-1.330469	0.933662
H	6.281509	-1.920267	0.212894
H	5.017857	-4.014835	-0.274657
H	3.713586	-5.244610	-1.979607
H	2.539160	-4.001876	-3.789536
H	2.678491	-1.519056	-3.865363
H	3.975827	-0.292503	-2.146496
H	-5.695606	1.799006	0.810927
H	-8.083044	1.523486	0.282508
H	-8.787541	0.457066	-1.857639
H	-7.047029	-0.314490	-3.465947
H	-4.659225	-0.052262	-2.938997
H	-3.575456	2.402603	-3.319596
H	-3.362992	4.713004	-4.145669
H	-2.858781	6.572666	-2.567421
H	-2.552580	6.074783	-0.146216
H	-2.722727	3.761659	0.679664

RPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-7-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=3.207 Å, C-Pd-C angle=85.48°. ($E_{e,rel}$=10.04 kcal/mol)

(Near identical conformation to **A**)

Processing: pddiph7namphos-ha6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy

-2844.5323326

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
643.49948	679.830	341.889	288.258	680.048	46.318	40.640

Processing: pddiph7namphos-ha6dsdbe.log
121

C	8.474275	-0.693548	-0.631899
C	8.293623	-0.113786	0.628242
C	9.416161	0.370019	1.314669
C	10.691478	0.266885	0.760454
C	10.863002	-0.316795	-0.497777
C	9.750878	-0.794007	-1.191788
C	6.919355	-0.016396	1.285215
N	5.779796	-0.121807	0.386238
C	5.399722	1.108567	-0.288628
C	4.601915	2.107782	0.545679
C	3.847294	1.711127	1.655890
C	3.112920	2.647718	2.387896
C	3.122841	3.994112	2.018933
C	3.874567	4.399464	0.912619
C	4.610300	3.462603	0.186878
C	5.050691	-1.302936	0.241361
C	5.634324	-2.553488	0.620673
C	4.926565	-3.722889	0.502781
C	3.606235	-3.754127	-0.018961
C	3.020937	-2.516147	-0.446771
C	3.758464	-1.314004	-0.281271
C	2.868702	-4.960047	-0.116786
C	1.584225	-4.955569	-0.612214
C	1.002892	-3.743817	-1.047033
C	1.688363	-2.541438	-0.987829
C	1.046291	-1.309569	-1.537021
C	-0.165373	-0.793130	-1.020031
C	-0.827900	0.306673	-1.603593
C	-0.215584	0.913532	-2.729663
C	0.989859	0.431126	-3.243830
C	1.598605	-0.671392	-2.648881
P	-2.467031	0.890563	-0.931488
C	-2.211584	2.748971	-0.632409

C	-0.809609	3.067501	-0.070102
C	-0.629488	4.572892	0.190431
C	-1.714337	5.129047	1.122346
C	-3.115644	4.801690	0.589631
C	-3.286049	3.293605	0.337907
O	-0.745407	-1.419701	0.056752
C	-0.116136	-1.183272	1.321259
O	-0.858689	1.995796	-3.264282
C	-0.288810	2.649409	-4.389000
Pd	-3.435715	-0.056863	1.146102
C	-4.545036	-1.627736	0.582544
C	-3.894700	-2.805499	0.184881
C	-4.630802	-3.878875	-0.331748
C	-6.019750	-3.795820	-0.449580
C	-6.671743	-2.632068	-0.036420
C	-5.942972	-1.558942	0.489876
C	-4.114561	-0.444235	2.998930
C	-3.663122	-1.520401	3.785214
C	-3.958213	-1.594178	5.149907
C	-4.734198	-0.603762	5.757383
C	-5.216752	0.457444	4.989149
C	-4.918701	0.529429	3.623523
C	-3.576439	0.781733	-2.459355
C	-3.601724	-0.665384	-3.000975
C	-4.515802	-0.792263	-4.231464
C	-5.939194	-0.306990	-3.926573
C	-5.919415	1.134063	-3.399969
C	-5.007606	1.280071	-2.167755
H	-0.004401	-3.753163	-1.452709
H	-3.129749	1.430400	-3.221262
H	-4.991252	2.331964	-1.859789
H	-5.429288	0.707372	-1.331980
H	-6.934548	1.463626	-3.143110
H	-5.564443	1.806028	-4.196248
H	-6.568529	-0.376072	-4.823429
H	-6.389955	-0.964426	-3.169594
H	-4.099426	-0.199659	-5.060580
H	-4.531035	-1.836357	-4.569229
H	-2.586816	-0.987803	-3.261272
H	-3.958002	-1.344112	-2.216519

H	-2.315810	3.254363	-1.600610
H	-0.663124	2.520839	0.874323
H	-0.029911	2.720477	-0.753210
H	0.369010	4.751679	0.609015
H	-0.667515	5.108548	-0.770153
H	-1.594793	6.213190	1.245478
H	-1.596631	4.684948	2.122078
H	-3.285534	5.346766	-0.351057
H	-3.883861	5.146395	1.293542
H	-4.294909	3.091443	-0.035032
H	-3.206901	2.759776	1.298319
H	2.521441	-1.059525	-3.070708
H	1.451964	0.891642	-4.108510
H	0.926418	-1.518385	1.316045
H	-0.686878	-1.754014	2.054604
H	-0.161206	-0.117290	1.578380
H	0.703889	3.055476	-4.157217
H	-0.967539	3.469295	-4.630230
H	-0.213351	1.974854	-5.251091
H	1.015900	-5.878639	-0.682532
H	3.334035	-5.886540	0.212157
H	5.388938	-4.660205	0.804019
H	6.656799	-2.587402	0.980131
H	3.271903	-0.381564	-0.537954
H	6.824638	-0.781062	2.064308
H	6.846667	0.944488	1.812505
H	9.288827	0.833132	2.291575
H	11.550535	0.647995	1.306549
H	11.855423	-0.394307	-0.933600
H	9.873690	-1.246413	-2.172503
H	7.610652	-1.063892	-1.176353
H	4.841068	0.846242	-1.194233
H	6.318874	1.598271	-0.638236
H	5.204241	3.787416	-0.665626
H	3.897766	5.446942	0.623223
H	2.559173	4.723566	2.594317
H	2.537495	2.324148	3.251457
H	3.839321	0.665758	1.949615
H	-2.812939	-2.878568	0.248947
H	-4.110451	-4.782340	-0.643831

H -6.588247 -4.631379 -0.850158
H -7.755155 -2.559186 -0.106805
H -6.470733 -0.673018 0.830157
H -5.321185 1.357422 3.041810
H -5.833819 1.227053 5.448928
H -4.970068 -0.665092 6.817091
H -3.589605 -2.432652 5.737667
H -3.077928 -2.315019 3.327672

RPdPh$_2$, less stable conformer of ***N*,*N*-dibenzyl-7-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. O-Pd distance=3.054 Å, C-Pd-C angle=161.67°. ($E_{e,rel}$=22.78 kcal/mol)

(Near identical conformation to **J**, but naphthyl rotated near 180°)

Processing: pddiph7namphos-hc6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2844.5120183

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
643.93767	680.002	339.104	286.745	680.206	46.318	40.408

Processing: pddiph7namphos-hc6dsdbe.log
121
C 0.606912 0.924996 -2.009107
C -0.563094 0.794117 -1.224428
C -1.390643 -0.356046 -1.295905
C -1.057307 -1.343434 -2.255154
C 0.130204 -1.259737 -2.987260
C 0.942292 -0.141145 -2.849005
O -1.955312 -2.353251 -2.446668
H 0.410873 -2.036318 -3.687172
H 1.843323 -0.066397 -3.450404
O -1.006564 1.802734 -0.419686
P -2.904864 -0.442832 -0.211031
C -0.108573 2.463715 0.490426

H	-0.689193	2.650515	1.396390
H	0.239887	3.406938	0.064994
H	0.744851	1.825733	0.731846
C	-1.638511	-3.396183	-3.357637
H	-2.483795	-4.085574	-3.322179
H	-0.724457	-3.925101	-3.060743
H	-1.523131	-3.014156	-4.379586
C	1.417608	2.178797	-2.079889
C	0.834980	3.332856	-2.577243
C	1.564867	4.534603	-2.720523
C	2.897369	4.571929	-2.374843
C	3.541953	3.416477	-1.867034
C	2.804593	2.197370	-1.701348
C	4.913124	3.421512	-1.497439
C	5.534931	2.306500	-0.993677
C	4.814413	1.082101	-0.823956
C	3.465489	1.058985	-1.174534
H	1.071052	5.419086	-3.112938
H	3.474305	5.487190	-2.487000
H	5.477277	4.345338	-1.603784
H	6.571911	2.373859	-0.684454
H	2.900469	0.141833	-1.079648
H	-0.212923	3.309783	-2.864086
N	5.449901	-0.045336	-0.305011
C	4.682609	-1.187287	0.161872
C	6.898533	-0.162035	-0.241061
C	4.297380	-2.224434	-0.892916
C	4.721819	-2.132413	-2.221667
C	4.363140	-3.111336	-3.153131
C	3.574364	-4.194879	-2.765964
C	3.141867	-4.292334	-1.440001
C	3.500882	-3.314391	-0.513335
H	5.273722	-1.679437	0.944861
H	3.776152	-0.823755	0.662325
H	5.326097	-1.284503	-2.530100
H	4.703311	-3.024513	-4.182017
H	3.300214	-4.959058	-3.488655
H	2.526324	-5.131609	-1.126398
H	3.155163	-3.395937	0.515576
H	7.162338	-1.201977	-0.474429

H	7.336767	0.433994	-1.050381
C	7.544190	0.221711	1.088524
C	6.846982	0.916433	2.081379
C	7.476911	1.265629	3.279497
C	8.811607	0.924939	3.497868
C	9.515595	0.228728	2.511035
C	8.884183	-0.121347	1.318600
H	5.807492	1.183181	1.916126
H	6.919949	1.804229	4.041708
H	9.300598	1.195425	4.429808
H	10.554610	-0.046114	2.673483
H	9.436637	-0.669449	0.557139
C	-3.427734	-2.243420	0.024857
C	-2.274854	-3.189238	0.426964
C	-2.770435	-4.642554	0.530990
C	-3.917491	-4.778295	1.541487
C	-5.051877	-3.796437	1.220172
C	-4.540517	-2.349382	1.096591
H	-3.831785	-2.567136	-0.941673
H	-1.879335	-2.870670	1.396979
H	-1.449089	-3.131929	-0.284019
H	-1.934057	-5.293850	0.816109
H	-3.112252	-4.985983	-0.457786
H	-4.296358	-5.808510	1.558582
H	-3.532897	-4.566832	2.549637
H	-5.535041	-4.091576	0.276359
H	-5.828615	-3.843206	1.994361
H	-5.379183	-1.685778	0.875794
H	-4.127651	-2.019775	2.059408
C	-4.192869	0.403758	-1.316184
C	-5.646562	0.286531	-0.815415
C	-6.578736	1.204486	-1.625430
C	-6.515038	0.887599	-3.125583
C	-5.069419	0.935885	-3.637778
C	-4.128309	0.035211	-2.814844
H	-3.894596	1.455904	-1.214365
H	-5.708594	0.542166	0.245563
H	-5.990014	-0.750681	-0.933297
H	-6.288253	2.250016	-1.451145
H	-7.606827	1.100085	-1.255854

H	-7.143198	1.585786	-3.693700
H	-6.927490	-0.117681	-3.300292
H	-5.026548	0.640412	-4.694401
H	-4.702318	1.971626	-3.588555
H	-3.108863	0.138584	-3.196947
H	-4.415123	-1.016267	-2.951977
Pd	-2.612062	0.497090	1.826171
C	-4.047629	1.975001	1.709235
C	-5.100418	1.914248	2.648785
C	-5.939982	3.008176	2.892176
C	-5.764398	4.195892	2.179702
C	-4.743325	4.279659	1.229110
C	-3.904739	3.184108	0.997636
H	-5.275609	0.994194	3.207649
H	-6.735965	2.928091	3.630333
H	-6.419124	5.045489	2.358759
H	-4.598881	5.201553	0.668162
H	-3.117349	3.276799	0.251150
C	-1.086327	-0.711205	2.537371
C	0.222686	-0.915026	2.058895
C	1.227323	-1.456493	2.867159
C	0.951795	-1.827570	4.186091
C	-0.340394	-1.658735	4.685384
C	-1.340863	-1.122321	3.865250
H	0.469407	-0.649231	1.032460
H	2.232561	-1.587890	2.468793
H	1.732973	-2.250072	4.813593
H	-0.574245	-1.952827	5.706871
H	-2.345342	-1.021876	4.282072

SPdPh$_2$, more stable stable form of *o,o,o,o*-**tetramethyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=82.23º, ($E_{e,rel}$=0.00 kcal/mol).

Processing: pdnamtmphos-b6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3001.7740609

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
714.77811	754.513	352.390	309.351	754.713	46.495	40.395

ccl00:/aue/chem126/aue/ark/pj/nam> gtg pdnamtmphos-b6dsdbe.log
Processing: pdnamtmphos-b6dsdbe.log
133

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C	2.808310	1.915022	2.429140
C	3.357228	3.201707	2.275363
C	3.345166	4.133295	3.319309
C	2.797972	3.793139	4.558410
C	2.269831	2.513660	4.742923
Pd	2.580729	0.628970	0.857312
C	4.471565	0.153811	1.324912
C	4.784428	-0.907184	2.189133
C	6.112914	-1.282781	2.418064
C	7.160066	-0.596544	1.800340
C	6.864364	0.479426	0.960721
C	5.535967	0.855720	0.733416
P	2.045887	-0.840638	-0.985632
C	3.363464	-1.158265	-2.287802
C	4.589821	-1.873835	-1.677485
C	5.681722	-2.091133	-2.740327
C	6.102177	-0.767414	-3.394062
C	4.889797	-0.040689	-3.993141
C	3.782602	0.173507	-2.946838
C	0.580796	-0.057191	-1.846166
C	-0.168298	0.929446	-1.145479
C	-1.387876	1.439924	-1.662342
C	-1.725782	1.066952	-2.970452
C	-0.987437	0.162509	-3.716529
C	0.137565	-0.429670	-3.136792
C	-2.356676	2.357757	-0.964214
C	-3.275449	1.925760	0.019137
C	-4.111812	2.923722	0.625767
C	-4.077277	4.242667	0.262924
C	-3.213541	4.695885	-0.761918
C	-2.351497	3.737362	-1.385793

C	-1.466733	4.228374	-2.392829
C	-1.458235	5.557214	-2.762074
C	-2.328681	6.487723	-2.149989
C	-3.186862	6.056047	-1.164474
N	-3.423106	0.597375	0.469123
C	-3.394342	-0.552924	-0.455252
C	-4.686836	-1.348293	-0.665348
C	-4.670874	-2.753636	-0.489048
C	-5.837452	-3.490582	-0.731230
C	-7.007954	-2.871297	-1.158715
C	-7.009899	-1.496829	-1.374028
C	-5.862892	-0.724913	-1.143945
C	-3.425627	-3.514467	-0.078680
C	-5.932027	0.754594	-1.449133
O	0.347880	1.333158	0.072678
C	0.109874	2.689741	0.533119
O	0.862447	-1.381817	-3.792925
C	0.497476	-1.743018	-5.118028
C	-4.036705	0.389323	1.799030
C	-3.696644	-0.911951	2.515074
C	-4.726918	-1.800662	2.903114
C	-4.392392	-2.965771	3.606803
C	-3.073077	-3.253148	3.944160
C	-2.067702	-2.352440	3.602186
C	-2.362817	-1.174164	2.904223
C	-6.192777	-1.530712	2.627805
C	-1.253045	-0.187500	2.634624
C	1.331677	-2.518517	-0.447159
C	1.317737	-3.644590	-1.502038
C	0.638280	-4.915042	-0.958325
C	1.283471	-5.395641	0.348576
C	1.298160	-4.275207	1.397761
C	1.983965	-3.005445	0.865939
H	-1.308840	-0.096138	-4.717401
H	-2.628577	1.491530	-3.401084
H	2.935452	-1.803455	-3.058325
H	4.999303	-1.279408	-0.854901
H	4.298441	-2.841676	-1.252851
H	6.548323	-2.579887	-2.277686
H	5.309435	-2.777878	-3.516068

H	6.570659	-0.126145	-2.633910
H	6.859757	-0.946258	-4.168086
H	5.191696	0.927252	-4.414005
H	4.487998	-0.633603	-4.828864
H	4.144128	0.861326	-2.170299
H	2.915613	0.653575	-3.416443
H	0.286880	-2.263931	-0.213428
H	3.049911	-3.210564	0.699319
H	1.939363	-2.207408	1.615134
H	1.805789	-4.613185	2.310536
H	0.263850	-4.033522	1.685437
H	2.316320	-5.716414	0.146494
H	0.752502	-6.275114	0.734849
H	0.677207	-5.706358	-1.718585
H	-0.427113	-4.706546	-0.779834
H	2.349593	-3.890913	-1.787563
H	0.812545	-3.309712	-2.411392
H	3.807140	3.487965	1.326084
H	3.772329	5.122601	3.165899
H	2.792818	4.512921	5.373465
H	1.852598	2.230835	5.707717
H	1.876318	0.594095	3.870402
H	5.334336	1.706400	0.086974
H	7.668712	1.037189	0.484871
H	8.191872	-0.887409	1.980796
H	6.326460	-2.111681	3.090211
H	3.990765	-1.451726	2.693203
H	0.895705	2.890409	1.256332
H	0.180728	3.386148	-0.304303
H	-0.867257	2.765902	1.006886
H	1.226999	-2.492437	-5.429542
H	-0.508767	-2.178555	-5.154451
H	0.547756	-0.882621	-5.796529
H	-4.741851	4.953563	0.748615
H	-4.830731	2.623294	1.376430
H	-0.784660	3.542566	-2.881585
H	-0.771065	5.891646	-3.535003
H	-3.860404	6.753727	-0.671755
H	-2.313356	7.530939	-2.452385
H	-3.687853	1.211894	2.432942

H	-5.127580	0.482763	1.736278
H	-2.608919	-1.238394	-0.129117
H	-3.077964	-0.172972	-1.423508
H	-5.818613	-4.567914	-0.585525
H	-7.905224	-3.457315	-1.340054
H	-7.909305	-1.006370	-1.739250
H	-1.039024	-2.547918	3.895570
H	-2.832352	-4.163162	4.487675
H	-5.185305	-3.650836	3.896633
H	-0.301086	-0.551012	3.031987
H	-1.117642	0.017419	1.570637
H	-1.455248	0.780159	3.114519
H	-6.802313	-2.373350	2.968114
H	-6.547961	-0.639476	3.161491
H	-6.400754	-1.382114	1.564119
H	-6.818078	0.976758	-2.052455
H	-5.991431	1.367714	-0.543430
H	-5.054735	1.106355	-2.002765
H	-3.654049	-4.578793	0.033951
H	-2.631717	-3.432047	-0.832442
H	-3.013506	-3.163899	0.872422

SPdPh$_2$, less stable stable conformer of *o,o,o,o*-**tetramethyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=160.86º, ($E_{e,rel}$=16.37 kcal/mol).

Processing: pdnamtmphos6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3001.7479707

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
714.69369	754.432	351.050	310.067	754.626	46.495	40.376

Processing: pdnamtmphos6dsdbe.log
133

C	5.701479	-2.058706	-1.374496
C	4.460215	-1.416474	-1.593495
C	3.320994	-2.188231	-1.918268
C	3.417903	-3.585480	-1.939786
C	4.627462	-4.223214	-1.676152
C	5.759822	-3.458849	-1.411383
C	4.374274	0.104376	-1.614393
N	3.469970	0.732823	-0.626794
C	3.471509	0.179841	0.740125
C	4.818048	-0.020337	1.444712
C	5.113789	-1.280575	2.020367
C	6.319997	-1.455844	2.710949
C	7.227192	-0.411050	2.858080
C	6.915619	0.837939	2.330676
C	5.718424	1.054069	1.634313
C	2.971378	2.018689	-0.920695
C	3.686454	2.790486	-1.899225
C	3.320819	4.059100	-2.258915
C	2.213380	4.699030	-1.655623
C	1.464919	3.964430	-0.679931
C	1.822008	2.607120	-0.343714
C	0.343262	4.628673	-0.098769
C	0.004889	5.918359	-0.450385
C	0.759235	6.633537	-1.408265
C	1.843600	6.025274	-1.997927
C	0.919588	1.911245	0.639179
C	-0.089123	0.982187	0.286896
C	-0.897016	0.342337	1.265625
C	-0.586084	0.570962	2.627236
C	0.341295	1.552630	2.990520
C	1.051185	2.218095	1.998961
O	-0.299497	0.570997	-0.996294
C	-0.400437	1.517764	-2.076655
P	-2.271688	-0.791075	0.701169
C	-1.354367	-2.444328	0.549750
C	-0.328519	-2.731302	1.668477
C	0.495498	-3.993251	1.347517
C	-0.391980	-5.218217	1.090596
C	-1.440792	-4.921021	0.010894
C	-2.268297	-3.671815	0.359887

O	-1.209676	-0.214574	3.550786
C	-0.965741	0.012679	4.932266
C	-3.560791	-0.958236	2.074718
C	-4.812505	-1.709733	1.557211
C	-5.823361	-1.946352	2.694340
C	-6.244032	-0.633727	3.368102
C	-5.017101	0.166383	3.825534
C	-4.022450	0.389252	2.672620
Pd	-3.338191	-0.088631	-1.167295
C	-3.037665	-1.740746	-2.370318
C	-1.853491	-1.985879	-3.095519
C	-1.808353	-2.900506	-4.153272
C	-2.954649	-3.613408	-4.514489
C	-4.141051	-3.403118	-3.808924
C	-4.174425	-2.489075	-2.748593
C	-3.982224	1.767588	-0.523323
C	-5.288014	1.992334	-1.012602
C	-5.874699	3.264023	-1.011116
C	-5.174427	4.351078	-0.485863
C	-3.891419	4.152997	0.031173
C	-3.311397	2.880544	0.015236
H	0.539145	1.777045	4.031143
H	1.784717	2.965883	2.289039
H	-3.087550	-1.555036	2.863205
H	-5.279099	-1.104199	0.768473
H	-4.551214	-2.665984	1.099687
H	-6.701867	-2.470591	2.296587
H	-5.374624	-2.615492	3.444149
H	-6.818761	-0.029198	2.651718
H	-6.910998	-0.835261	4.216369
H	-5.326820	1.137605	4.232435
H	-4.515244	-0.371207	4.645008
H	-4.505203	0.976304	1.884410
H	-3.176106	0.979353	3.027829
H	-0.802729	-2.294123	-0.388088
H	-2.813968	-3.866741	1.293522
H	-3.004028	-3.485289	-0.426241
H	-2.111807	-5.779808	-0.118049
H	-0.946515	-4.762369	-0.958012
H	-0.904421	-5.497362	2.023671

H	0.224240	-6.079896	0.803236
H	1.192677	-4.192337	2.172014
H	1.113936	-3.799865	0.459118
H	-0.852190	-2.869144	2.624158
H	0.349912	-1.883031	1.799470
H	-5.872259	1.159144	-1.411782
H	-6.879208	3.400061	-1.407157
H	-5.625886	5.340182	-0.472089
H	-3.339782	4.994362	0.447255
H	-2.314169	2.758773	0.432505
H	-5.112173	-2.360723	-2.207043
H	-5.039661	-3.955287	-4.078075
H	-2.922243	-4.327329	-5.334091
H	-0.878550	-3.055729	-4.698247
H	-0.946002	-1.445025	-2.834775
H	-1.033192	1.033559	-2.822684
H	-0.876195	2.441701	-1.742327
H	0.583461	1.730888	-2.499159
H	-1.571968	-0.722920	5.463332
H	0.091731	-0.138326	5.181748
H	-1.272429	1.021607	5.234560
H	3.906525	4.599433	-2.999271
H	4.578006	2.375782	-2.350089
H	-0.257490	4.111176	0.638972
H	-0.856301	6.389479	0.016165
H	2.438575	6.551791	-2.740966
H	0.481208	7.649141	-1.675224
H	4.004892	0.395709	-2.603578
H	5.386628	0.516938	-1.524167
H	2.938042	-0.773093	0.725409
H	2.872899	0.848078	1.353063
C	4.160286	-2.457078	1.952648
H	6.542188	-2.428853	3.142461
H	8.159899	-0.564116	3.394792
H	7.601761	1.670671	2.467224
C	5.433787	2.453198	1.135851
C	2.012595	-1.541180	-2.303233
H	2.536223	-4.171725	-2.187603
H	4.691323	-5.308097	-1.697015
H	6.713454	-3.950001	-1.234272

C 6.991283 -1.297654 -1.141476
H 1.260958 -2.300423 -2.538366
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H 7.276510 -0.705504 -2.020856
H 6.928172 -0.613570 -0.290297
H 6.112115 3.169872 1.609896
H 5.563911 2.547697 0.052397
H 4.408297 2.771619 1.351655
H 4.605357 -3.331312 2.437837
H 3.214237 -2.247237 2.467992
H 3.916571 -2.740673 0.924248

$SPdPh_2$, less stable conformer of *o,o,o,o*-**tetramethyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh_2**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=160.82°, ($E_{e,rel}$=18.23 kcal/mol).

Processing: pdnamtmphos-a6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3001.7450045

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
714.30133	754.257	354.800	312.127	754.454	46.495	40.502

Processing: pdnamtiprphos6dsdbe.log
133
C -3.787278 -3.681867 0.432918
C -3.456952 -2.603983 -0.420580
C -3.581596 -2.756289 -1.820276
C -4.055800 -3.965755 -2.340923
C -4.391417 -5.025453 -1.502148
C -4.251041 -4.880927 -0.124876
C -2.928537 -1.298014 0.164534

N	-3.867885	-0.144831	0.125772
C	-5.295885	-0.528606	0.091614
C	-6.360757	0.465560	0.550164
C	-7.484330	0.699124	-0.283364
C	-8.503876	1.550974	0.157197
C	-8.446330	2.159382	1.407629
C	-7.364799	1.896736	2.240052
C	-6.323904	1.051850	1.833209
C	-3.429685	1.113504	-0.329596
C	-2.190783	1.699584	0.016511
C	-1.901936	3.048714	-0.409085
C	-2.814374	3.757759	-1.256300
C	-4.006467	3.103616	-1.649193
C	-4.300880	1.846599	-1.196921
C	-2.524278	5.082914	-1.673417
C	-1.380172	5.723113	-1.256328
C	-0.489553	5.048784	-0.389561
C	-0.739577	3.756067	0.017994
C	-1.167993	1.020068	0.881503
C	0.164843	0.753396	0.467110
C	1.144660	0.238178	1.355615
C	0.775957	0.062447	2.712420
C	-0.542228	0.268741	3.124131
C	-1.481431	0.737432	2.212674
P	2.887188	-0.026204	0.731130
C	3.770001	-1.306928	1.805715
C	5.118181	-1.714175	1.161808
C	5.898311	-2.678244	2.074319
C	5.079561	-3.929927	2.416270
C	3.710943	-3.548831	2.996373
C	2.948059	-2.587659	2.067605
O	0.622183	1.110635	-0.770218
C	-0.036593	0.659765	-1.964277
O	1.765251	-0.273612	3.589825
C	1.441469	-0.466992	4.959125
C	3.659989	1.668885	1.088752
C	5.190399	1.720573	0.903983
C	5.698099	3.171977	0.959826
C	5.307493	3.854081	2.277689
C	3.794792	3.762156	2.517794

C	3.279408	2.312070	2.440282
Pd	3.002119	-0.689418	-1.427649
C	2.007185	-2.501260	-1.303676
C	2.647578	-3.435185	-2.147894
C	2.036178	-4.636098	-2.530136
C	0.765429	-4.952966	-2.048054
C	0.117366	-4.063722	-1.186034
C	0.735030	-2.862644	-0.819974
C	4.016585	0.928218	-2.212467
C	3.445553	2.189281	-2.481891
C	4.069918	3.116541	-3.323159
C	5.297647	2.812724	-3.917805
C	5.895267	1.577533	-3.660520
C	5.266938	0.658330	-2.811206
H	-0.833336	0.117815	4.156236
H	-2.488207	0.936010	2.557338
H	3.967987	-0.810180	2.762884
H	4.909509	-2.202012	0.200272
H	5.738620	-0.843169	0.939500
H	6.840248	-2.959128	1.585775
H	6.173139	-2.155708	3.003215
H	4.928785	-4.522636	1.502561
H	5.631390	-4.568273	3.118496
H	3.105964	-4.448886	3.166082
H	3.850574	-3.074810	3.980394
H	2.754180	-3.084525	1.111390
H	1.976225	-2.350580	2.504117
H	3.212661	2.274005	0.288923
H	5.674230	1.149711	1.708836
H	5.476620	1.266889	-0.048380
H	6.787997	3.183601	0.831748
H	5.277155	3.728989	0.111122
H	5.836160	3.363779	3.109150
H	5.629433	4.903415	2.278587
H	3.534114	4.190949	3.494391
H	3.271056	4.366176	1.762184
H	3.708638	1.726825	3.264647
H	2.194810	2.310266	2.581401
H	3.651967	-3.228780	-2.526632
H	2.558166	-5.325349	-3.191271

H	0.286821	-5.886784	-2.333075
H	-0.871276	-4.304885	-0.801418
H	0.210707	-2.197496	-0.135391
H	5.769357	-0.289551	-2.614163
H	6.854886	1.331725	-4.111738
H	5.785447	3.533468	-4.569836
H	3.596102	4.077405	-3.516862
H	2.489871	2.453703	-2.031804
H	0.621100	0.962856	-2.780218
H	-0.124132	-0.430016	-1.960539
H	-1.015178	1.127211	-2.085267
H	2.380046	-0.730179	5.449675
H	1.039465	0.449132	5.409363
H	0.721896	-1.284553	5.091239
H	-4.694770	3.612751	-2.319813
H	-5.217270	1.379554	-1.526141
H	-0.046195	3.277345	0.698007
H	0.403499	5.556841	-0.034594
H	-3.235132	5.586039	-2.325216
H	-1.166185	6.738826	-1.577078
H	-5.371234	-1.405078	0.745458
H	-5.564604	-0.898037	-0.903758
H	-2.036374	-1.007208	-0.391367
H	-2.599477	-1.472179	1.192864
C	-7.657452	0.038127	-1.638574
H	-9.357979	1.729720	-0.491378
H	-9.246425	2.817635	1.735678
H	-7.321196	2.344559	3.230291
C	-5.194904	0.810848	2.807524
C	-3.177208	-1.656300	-2.776432
H	-4.151355	-4.075892	-3.418394
H	-4.755834	-5.960282	-1.919850
H	-4.505136	-5.707425	0.534319
C	-3.650824	-3.595489	1.940900
H	-5.547023	0.929189	3.837990
H	-4.756130	-0.185963	2.708714
H	-4.390080	1.538475	2.651464
H	-8.578525	0.389401	-2.113536
H	-6.834361	0.254059	-2.331437
H	-7.727082	-1.053780	-1.560824

H -3.470297 -1.906482 -3.800573
H -3.623489 -0.689281 -2.523637
H -2.088326 -1.518374 -2.774807
H -4.018399 -4.513468 2.409533
H -2.607699 -3.463488 2.253895
H -4.219707 -2.760001 2.367481

$TPdPh_2$, more stable form of *o,o,o,o*-**tetraiospropyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh_2**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=83.63°, ($E_{e,rel}$=0.00 kcal/mol).

Processing: pdnamtiprphos-b6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3316.2563336

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
858.45138	904.944	401.699	349.929	905.182	46.821	41.058

Processing: pdnamtiprphos-b6dsdbe.log
157
C 3.686298 2.341737 3.261270
C 3.727715 2.335934 1.854909
C 3.806607 3.582972 1.207053
C 3.806039 4.782420 1.927698
C 3.739150 4.764613 3.322728
C 3.682255 3.538015 3.987913
Pd 3.448568 0.632260 0.771398
C 5.404922 0.367462 1.101307
C 5.857134 -0.479035 2.126998
C 7.220347 -0.749906 2.291141
C 8.164350 -0.170999 1.440743
C 7.730816 0.693163 0.432865
C 6.368006 0.966929 0.271715
P 2.795231 -1.267454 -0.574849
C 4.019097 -1.889902 -1.858313

C	5.265716	-2.498720	-1.174795
C	6.298356	-2.957148	-2.220121
C	6.704592	-1.809300	-3.154159
C	5.472537	-1.195301	-3.833398
C	4.426818	-0.737557	-2.802233
C	1.290519	-0.623882	-1.482548
C	0.581573	0.469981	-0.902810
C	-0.539837	1.051691	-1.545240
C	-0.854934	0.559184	-2.821650
C	-0.210008	-0.514735	-3.410897
C	0.838344	-1.130297	-2.719522
C	-1.359578	2.236098	-1.093764
C	-2.564220	2.149564	-0.357112
C	-3.226807	3.383025	-0.037471
C	-2.750758	4.608187	-0.420582
C	-1.567944	4.725052	-1.185903
C	-0.877493	3.520522	-1.537325
C	0.319115	3.662191	-2.303653
C	0.783192	4.900952	-2.692127
C	0.085811	6.081096	-2.344382
C	-1.069479	5.986429	-1.603205
N	-3.146350	0.955415	0.141131
C	-3.226493	-0.280182	-0.667424
C	-4.595418	-0.799028	-1.147207
C	-4.973299	-2.141389	-0.847518
C	-6.187095	-2.633313	-1.344708
C	-7.028096	-1.846902	-2.126337
C	-6.639501	-0.555518	-2.452421
C	-5.425198	-0.022037	-1.994874
C	-4.062868	-3.106328	-0.076638
C	-5.036298	1.359468	-2.523905
O	1.094918	0.887345	0.309828
C	0.529786	1.966615	1.085994
O	1.472048	-2.233631	-3.211302
C	1.088419	-2.747216	-4.479739
C	-4.063807	1.098167	1.296527
C	-4.359909	-0.131759	2.160777
C	-5.705343	-0.559120	2.341195
C	-5.966511	-1.608636	3.232940
C	-4.946395	-2.233220	3.943025

C	-3.636677	-1.798824	3.782560
C	-3.326224	-0.747458	2.910117
C	-6.895766	0.132666	1.665674
C	-1.888776	-0.234833	2.870567
C	2.106548	-2.767291	0.354474
C	1.921427	-4.057189	-0.470621
C	1.267837	-5.169337	0.369653
C	2.056551	-5.448533	1.656743
C	2.241507	-4.165361	2.479391
C	2.896423	-3.045009	1.653118
H	-0.526252	-0.862313	-4.386125
H	-1.663157	1.044383	-3.362032
H	3.536888	-2.669657	-2.452133
H	5.726164	-1.761852	-0.508590
H	4.980952	-3.354877	-0.552203
H	7.179828	-3.361901	-1.707090
H	5.875865	-3.780016	-2.817173
H	7.219080	-1.035469	-2.567147
H	7.418970	-2.164247	-3.908328
H	5.765071	-0.344753	-4.462864
H	5.019000	-1.940324	-4.504973
H	4.842449	0.084595	-2.204982
H	3.545695	-0.340214	-3.319658
H	1.108802	-2.414822	0.653833
H	3.928192	-3.331574	1.410781
H	2.963744	-2.125919	2.246221
H	2.846992	-4.367348	3.372344
H	1.259923	-3.822056	2.838372
H	3.043920	-5.856802	1.394164
H	1.550169	-6.216416	2.255582
H	1.180303	-6.083603	-0.231952
H	0.241800	-4.868571	0.630769
H	2.900135	-4.410387	-0.823805
H	1.321017	-3.855998	-1.362623
H	3.866230	3.626848	0.120586
H	3.862346	5.731477	1.397594
H	3.742301	5.695378	3.885075
H	3.645510	3.509810	5.075479
H	3.665477	1.398944	3.805350
H	6.058407	1.659925	-0.506439

H	8.454849	1.168943	-0.225885
H	9.223360	-0.380424	1.569258
H	7.542373	-1.413616	3.091378
H	5.144574	-0.940745	2.806023
H	1.073599	1.940898	2.028020
H	0.703796	2.924495	0.595530
H	-0.531771	1.802966	1.249654
H	1.734547	-3.608948	-4.655155
H	0.040670	-3.072216	-4.481382
H	1.243353	-2.009164	-5.276280
H	-3.300938	5.507547	-0.153353
H	-4.162291	3.353578	0.503555
H	0.876039	2.777749	-2.589414
H	1.697511	4.968986	-3.275736
H	-1.622005	6.879755	-1.320767
H	0.462828	7.050052	-2.658998
H	-3.613942	1.852677	1.951211
H	-5.016210	1.517734	0.964374
H	-2.729021	-1.072461	-0.109159
H	-2.612080	-0.117575	-1.546145
H	-6.483468	-3.652044	-1.120826
H	-7.969454	-2.248404	-2.493037
H	-7.276810	0.046624	-3.094262
H	-2.844649	-2.269629	4.356886
H	-5.175442	-3.045879	4.627821
H	-6.987536	-1.943113	3.380100
C	-0.831335	-1.352937	2.844161
H	-1.767808	0.331467	1.945594
C	-1.630801	0.719469	4.056639
C	-8.122747	-0.773133	1.457430
C	-7.313969	1.388731	2.462437
H	-6.587251	0.446521	0.663628
C	-6.065320	2.447901	-2.162323
H	-4.090561	1.658898	-2.075965
C	-4.809232	1.316880	-4.050207
C	-4.800025	-4.267186	0.614242
C	-2.969211	-3.675152	-1.008661
H	-3.572297	-2.549908	0.727601
H	-4.100154	-4.806159	1.262789
H	-5.623070	-3.906620	1.238437

H	-5.198366	-4.994546	-0.103107
H	-2.293203	-4.337499	-0.453147
H	-3.424469	-4.259951	-1.817422
H	-2.365555	-2.886586	-1.470757
H	-5.713362	3.430653	-2.496597
H	-7.036221	2.262618	-2.636515
H	-6.229831	2.500316	-1.080456
H	-4.461363	2.291836	-4.412791
H	-4.058934	0.564153	-4.319391
H	-5.730791	1.069069	-4.589556
H	0.161678	-0.923638	2.669654
H	-0.784861	-1.903820	3.790822
H	-1.033766	-2.075697	2.045385
H	-0.616590	1.133978	4.010910
H	-2.338913	1.555993	4.065559
H	-1.735358	0.188896	5.010632
H	-8.856153	-0.252517	0.831333
H	-7.852964	-1.704807	0.951839
H	-8.623661	-1.019419	2.401118
H	-8.140814	1.907557	1.961985
H	-7.650171	1.108359	3.467919
H	-6.489364	2.100405	2.580131

TPdPh$_2$, less stable conformer of *o,o,o,o*-**tetraiospropyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=160.72º, ($E_{e,rel}$=15.73 kcal/mol).

Processing: pdnamtiprphos-a6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3316.2312720

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
858.36920	904.782	396.946	351.202	905.004	46.821	40.982

Processing: pdnamtiprphos-a6dsdbe.log
157

C	3.830725	-2.441081	0.242663
C	3.363815	-1.293726	0.946971
C	3.425799	-1.270462	2.363580
C	3.992368	-2.357680	3.044836
C	4.457789	-3.472519	2.360834
C	4.363187	-3.512265	0.972542
C	2.671512	-0.167128	0.170381
N	3.247846	1.193285	0.225420
C	4.716357	1.374259	0.259344
C	5.566219	0.686297	-0.817629
C	6.606802	-0.209452	-0.443111
C	7.406693	-0.773399	-1.447203
C	7.216971	-0.464168	-2.789542
C	6.244042	0.461218	-3.146243
C	5.428462	1.062731	-2.178641
C	2.448921	2.299564	0.602638
C	1.126513	2.535333	0.162543
C	0.476782	3.779924	0.502393
C	1.116374	4.728231	1.365214
C	2.401667	4.412453	1.865766
C	3.036568	3.258894	1.493737
C	0.471699	5.948898	1.694994
C	-0.763614	6.260171	1.175886
C	-1.389483	5.351052	0.292099
C	-0.792439	4.151747	-0.031789
C	0.372079	1.594945	-0.732349
C	-0.878637	1.010166	-0.396852
C	-1.624017	0.236566	-1.325345
C	-1.115257	0.119358	-2.642940
C	0.130463	0.655017	-2.976892
C	0.844107	1.376058	-2.027375
P	-3.293092	-0.440139	-0.821063
C	-3.702883	-1.961293	-1.866494
C	-4.948052	-2.687749	-1.301423
C	-5.353929	-3.870314	-2.200161
C	-4.202562	-4.866831	-2.387023
C	-2.938388	-4.156573	-2.889114
C	-2.547751	-2.980283	-1.976725

O	-1.506543	1.270141	0.786970
C	-0.841339	1.077178	2.044111
O	-1.908170	-0.497061	-3.565562
C	-1.432614	-0.654781	-4.894813
C	-4.441058	0.969747	-1.363282
C	-5.940811	0.615361	-1.299774
C	-6.807902	1.871511	-1.492733
C	-6.491595	2.574823	-2.819439
C	-4.992998	2.883841	-2.934671
C	-4.121197	1.631161	-2.721423
Pd	-3.460661	-0.979314	1.371192
C	-2.110541	-2.544313	1.464776
C	-2.652588	-3.606330	2.222775
C	-1.854834	-4.634225	2.741505
C	-0.482507	-4.644694	2.488504
C	0.080676	-3.625221	1.715293
C	-0.726583	-2.599764	1.209821
C	-4.863881	0.421727	1.948327
C	-4.611807	1.793651	2.156058
C	-5.497671	2.605217	2.873132
C	-6.675268	2.068408	3.400629
C	-6.959726	0.716212	3.201356
C	-6.071285	-0.087068	2.475876
H	0.527484	0.561077	-3.979912
H	1.781955	1.831715	-2.315495
H	-3.937017	-1.581132	-2.867807
H	-4.708984	-3.053820	-0.294353
H	-5.795995	-2.007714	-1.192141
H	-6.228295	-4.372864	-1.766839
H	-5.669830	-3.487696	-3.182646
H	-3.983591	-5.349254	-1.423641
H	-4.496500	-5.665697	-3.080250
H	-2.102076	-4.864953	-2.948493
H	-3.109313	-3.786734	-3.912117
H	-2.314617	-3.359922	-0.976635
H	-1.639690	-2.508313	-2.356411
H	-4.246800	1.708716	-0.574632
H	-6.180119	-0.101680	-2.097488
H	-6.182049	0.145819	-0.342503
H	-7.868919	1.594179	-1.450553

H	-6.629998	2.558651	-0.653757
H	-6.792020	1.924107	-3.654623
H	-7.078404	3.497379	-2.915825
H	-4.766054	3.324493	-3.914442
H	-4.720445	3.638930	-2.182559
H	-4.301916	0.916988	-3.535836
H	-3.066569	1.916291	-2.777471
H	-3.726026	-3.640008	2.422797
H	-2.308397	-5.429215	3.330557
H	0.142421	-5.443126	2.881389
H	1.148538	-3.627652	1.508060
H	-0.261101	-1.829439	0.596537
H	-6.332218	-1.134742	2.320339
H	-7.877072	0.287424	3.600738
H	-7.365799	2.698733	3.956012
H	-5.266965	3.658651	3.022857
H	-3.701926	2.239408	1.757101
H	-1.639091	1.080153	2.788624
H	-0.336658	0.109083	2.066298
H	-0.136875	1.884192	2.253478
H	-2.223645	-1.182754	-5.429882
H	-1.253525	0.315523	-5.374417
H	-0.513115	-1.252207	-4.924484
H	2.883872	5.096731	2.560152
H	4.004786	3.042678	1.927199
H	-1.291260	3.489269	-0.727667
H	-2.353706	5.601380	-0.142709
H	0.982938	6.638892	2.362636
H	-1.250370	7.197560	1.430068
H	5.104606	1.101091	1.243037
H	4.887531	2.448252	0.154563
H	1.652665	-0.083408	0.550014
H	2.565892	-0.467198	-0.871803
C	6.961883	-0.501301	1.020111
H	8.197935	-1.463369	-1.176054
H	7.844201	-0.922173	-3.550260
H	6.134824	0.739438	-4.189695
C	4.515268	2.210601	-2.611061
C	2.842631	-0.141097	3.216147
H	4.044399	-2.338262	4.129820

H	4.882303	-4.313020	2.904064
H	4.714662	-4.394794	0.449278
C	3.717990	-2.583013	-1.281889
H	3.724568	2.314415	-1.865650
C	5.310174	3.535450	-2.630163
C	3.836326	1.987914	-3.975283
C	7.713718	-1.824943	1.245630
C	7.795960	0.659699	1.608482
H	6.033659	-0.582369	1.592831
C	3.914644	0.569679	4.066773
H	2.407645	0.611844	2.556727
C	1.709693	-0.663714	4.126145
C	4.775173	-3.509398	-1.910080
C	2.309069	-3.069144	-1.688544
H	3.883785	-1.597365	-1.728933
H	7.784515	-2.022515	2.321013
H	7.192874	-2.670016	0.786379
H	8.738202	-1.792200	0.855929
H	8.023864	0.474450	2.665362
H	8.746305	0.758352	1.070010
H	7.278243	1.622404	1.538232
H	4.654748	4.377105	-2.885115
H	5.768007	3.747122	-1.657570
H	6.116081	3.493387	-3.372669
H	3.094036	2.773772	-4.159263
H	4.552688	2.028242	-4.803403
H	3.328675	1.017596	-4.020479
H	2.231094	-3.149430	-2.780153
H	2.106869	-4.058860	-1.262232
H	1.518153	-2.396210	-1.342196
H	4.727029	-3.426740	-3.001879
H	5.787931	-3.236329	-1.599490
H	4.605431	-4.563461	-1.660718
H	1.218706	0.171567	4.640520
H	0.953877	-1.213562	3.556132
H	2.095780	-1.342211	4.895658
H	3.468127	1.401961	4.623587
H	4.364618	-0.114143	4.796060
H	4.724570	0.973621	3.449810

$TPdPh_2$, less stable conformer of *o,o,o,o*-**tetraiospropyl-*N*,*N*-dibenzyl-2-aminoNPhosPdPh_2**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=160.25°, ($E_{e,rel}$=25.19 kcal/mol).

Processing: pdnamtiprphos6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3316.2161920

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
858.94903	905.199	395.057	349.387	905.422	46.821	41.017

Processing: pdnamtiprphos6dsdbe.log
157

C	5.853757	-1.640901	-1.354037
C	4.477957	-1.336735	-1.589642
C	3.586475	-2.388987	-1.933603
C	4.065797	-3.710191	-1.926638
C	5.388647	-4.012470	-1.641433
C	6.276326	-2.975739	-1.379798
C	4.056974	0.133945	-1.644009
N	3.037559	0.643021	-0.693723
C	3.138969	0.217417	0.724009
C	4.490320	0.231376	1.465774
C	4.952275	-0.973557	2.075214
C	6.133281	-0.946790	2.828027
C	6.865318	0.224632	2.996332
C	6.396497	1.403074	2.434328
C	5.207791	1.434073	1.689410
C	2.431419	1.880531	-1.034109
C	3.065114	2.670996	-2.054778
C	2.609561	3.902594	-2.440305
C	1.493037	4.497663	-1.812066
C	0.818560	3.743707	-0.798592
C	1.246308	2.405194	-0.459976
C	-0.295097	4.377057	-0.167493
C	-0.695598	5.650330	-0.513809

C	-0.023223	6.377260	-1.522646
C	1.052682	5.801673	-2.157669
C	0.369182	1.695431	0.541024
C	-0.709674	0.833813	0.208810
C	-1.550501	0.269397	1.210577
C	-1.202955	0.489741	2.565925
C	-0.185095	1.384307	2.907029
C	0.550817	1.989819	1.897200
O	-0.970353	0.420466	-1.062441
C	-1.008080	1.335887	-2.171440
P	-3.055833	-0.734526	0.726882
C	-2.403694	-2.515847	0.772305
C	-1.443347	-2.854430	1.932904
C	-0.852256	-4.267617	1.765744
C	-1.940064	-5.340527	1.626488
C	-2.912600	-4.987513	0.493653
C	-3.513143	-3.584088	0.685330
O	-1.896996	-0.206823	3.509827
C	-1.609222	0.009224	4.884383
C	-4.360566	-0.576552	2.091936
C	-5.724118	-1.127971	1.606925
C	-6.762234	-1.114568	2.744073
C	-6.946435	0.290994	3.330635
C	-5.598762	0.886723	3.758709
C	-4.575006	0.862892	2.609418
Pd	-4.008239	-0.135126	-1.242396
C	-3.694993	-1.866742	-2.322437
C	-2.491701	-2.186249	-2.983803
C	-2.432094	-3.165136	-3.981665
C	-3.583422	-3.867900	-4.346054
C	-4.789790	-3.583373	-3.703011
C	-4.837429	-2.606440	-2.701160
C	-4.664322	1.764194	-0.759205
C	-6.006232	1.934786	-1.168154
C	-6.591887	3.201024	-1.289473
C	-5.852921	4.342105	-0.973680
C	-4.532008	4.202864	-0.539540
C	-3.954982	2.933899	-0.428513
H	0.046575	1.601672	3.942021
H	1.331242	2.695537	2.169595

H	-4.001340	-1.199953	2.919046
H	-6.077386	-0.500578	0.778746
H	-5.631919	-2.142101	1.212152
H	-7.718578	-1.500157	2.367737
H	-6.439648	-1.804068	3.539043
H	-7.400431	0.942065	2.569951
H	-7.642317	0.264033	4.179235
H	-5.732544	1.919398	4.105961
H	-5.203236	0.317124	4.614050
H	-4.941037	1.483794	1.785294
H	-3.637892	1.308735	2.947440
H	-1.833878	-2.557417	-0.164748
H	-4.096958	-3.580183	1.616190
H	-4.194575	-3.360422	-0.139577
H	-3.721858	-5.726856	0.438863
H	-2.388770	-5.023969	-0.471855
H	-2.498293	-5.417873	2.571789
H	-1.484601	-6.323701	1.451194
H	-0.199036	-4.491372	2.619851
H	-0.213851	-4.284027	0.871311
H	-1.981155	-2.796623	2.887851
H	-0.627557	-2.127335	1.984037
H	-6.618310	1.061994	-1.405827
H	-7.625113	3.292703	-1.618981
H	-6.302603	5.328546	-1.057942
H	-3.947214	5.086498	-0.290951
H	-2.927483	2.861528	-0.078874
H	-5.791488	-2.420506	-2.206639
H	-5.692928	-4.126907	-3.974592
H	-3.539825	-4.631338	-5.119200
H	-1.486268	-3.379711	-4.476817
H	-1.581320	-1.651636	-2.720746
H	-1.621542	0.838652	-2.924904
H	-1.478212	2.278761	-1.886465
H	-0.007359	1.518490	-2.567027
H	-2.280893	-0.652731	5.433362
H	-0.569751	-0.249391	5.120589
H	-1.803973	1.048071	5.178124
H	3.137979	4.452236	-3.216038
H	3.967618	2.309784	-2.524653

H	-0.833030	3.854658	0.613551
H	-1.539571	6.101325	0.001459
H	1.591099	6.339054	-2.935177
H	-0.353302	7.377541	-1.787992
H	3.661768	0.312064	-2.644443
H	4.957058	0.746045	-1.562745
H	2.725854	-0.786028	0.789073
H	2.454134	0.845846	1.282635
C	4.161797	-2.288054	2.020579
H	6.490627	-1.857814	3.295127
H	7.784283	0.218138	3.577154
H	6.947845	2.325677	2.594014
C	4.721471	2.808880	1.229400
C	2.110778	-2.273068	-2.347896
H	3.378255	-4.514912	-2.176103
H	5.733332	-5.043363	-1.652582
H	7.319323	-3.210655	-1.200362
C	6.928314	-0.559113	-1.169951
H	1.910096	-3.218939	-2.867335
C	1.160708	-2.250004	-1.137517
C	1.747871	-1.177709	-3.366373
C	8.177269	-1.021199	-0.397434
C	7.362473	0.004702	-2.542089
H	6.504139	0.257117	-0.578420
C	5.727365	3.514917	0.299752
H	3.799279	2.689136	0.664182
C	4.382917	3.706144	2.439032
C	5.013890	-3.555214	2.213671
C	3.022020	-2.275207	3.064353
H	3.715675	-2.381892	1.026033
H	2.430731	-3.197347	3.002499
H	3.435541	-2.205918	4.078087
H	2.341906	-1.427692	2.926755
H	4.401609	-4.439037	2.001790
H	5.870529	-3.572161	1.533444
H	5.381751	-3.658272	3.241502
H	3.959903	4.659657	2.100612
H	3.653077	3.223926	3.100082
H	5.271969	3.929244	3.040232
H	5.313930	4.465468	-0.056260

H 6.671031 3.732343 0.813810
H 5.960599 2.901781 -0.577571
H 8.804527 -0.151423 -0.171990
H 7.912014 -1.495506 0.551602
H 8.792347 -1.718708 -0.978305
H 8.103081 0.803987 -2.415326
H 7.818721 -0.785134 -3.150933
H 6.520230 0.411095 -3.112564
H 0.768396 -1.404978 -3.803314
H 1.669995 -0.189002 -2.908797
H 2.472693 -1.132697 -4.187737
H 0.128270 -2.401171 -1.467709
H 1.412391 -3.048523 -0.430154
H 1.205098 -1.290547 -0.619156

UPdPh$_2$, conformer of **2,7-bis-(*N*,*N*-dimesitylamino)N$_2$PhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=82.64^o

Processing: pdph2namphosme126dsdbe.log
PG=C01

Method BasisSet Imaginary Freqs
RB3LYP GenECP 0

HF Energy
-3912.3513396

ZPE E298 S298 Squasihar Equasihar Strans Srot
1002.11972 1059.055 486.017 414.344 1059.372 47.314 42.322
ccl00:/aue/chem126/aue/ark/pj/nam> gtg pdph2namphosme126dsdbe.log
Processing: pdph2namphosme126dsdbe.log
185
C 3.386548 -4.340834 -2.566033
C 2.740591 -2.958152 -2.810577
C 3.819091 -1.895031 -3.112035
C 4.712955 -2.318091 -4.290292
C 5.345161 -3.696921 -4.053763
C 4.268743 -4.750679 -3.759123
P 1.705872 -2.413766 -1.339296

C	0.219720	-3.587247	-1.194384
C	-0.384730	-4.102715	-2.516425
C	-1.650945	-4.941129	-2.261283
C	-1.383449	-6.101230	-1.292560
C	-0.776638	-5.589919	0.021744
C	0.492461	-4.754785	-0.220682
C	0.849014	-0.814216	-1.790098
C	0.564126	0.100879	-0.734968
C	-0.171724	1.293267	-0.961980
C	-0.650622	1.493175	-2.265137
C	-0.377034	0.643991	-3.324119
C	0.380255	-0.505135	-3.086509
C	-0.616037	2.315784	0.054224
C	0.136764	3.448921	0.436460
C	-0.420148	4.316476	1.429934
C	-1.653932	4.106531	1.984411
C	-2.458810	3.020073	1.576213
C	-1.945392	2.123632	0.587783
C	-2.776258	1.039942	0.184698
C	-4.042736	0.812463	0.731805
C	-4.524762	1.728868	1.716701
C	-3.750861	2.791344	2.110976
N	1.406571	3.781548	-0.069562
C	1.725672	3.661303	-1.508984
C	2.190968	4.944573	-2.193665
C	3.510719	5.061849	-2.683921
C	3.902353	6.240235	-3.331909
C	3.027500	7.311745	-3.517738
C	1.718724	7.169624	-3.049232
C	1.285490	6.011280	-2.396574
C	4.529749	3.945456	-2.557782
C	3.481960	8.587085	-4.188799
C	-0.154919	5.932599	-1.941170
N	-4.823231	-0.274807	0.341785
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C	-4.704309	-2.793096	0.304849
C	-4.413275	-3.142746	1.644797
C	-4.848505	-4.373555	2.143635
C	-5.567538	-5.280233	1.358154
C	-5.834394	-4.924900	0.035574

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O	1.064315	-0.269187	0.501119
C	0.425921	0.144466	1.732903
O	0.669167	-1.389833	-4.086467
C	0.248849	-1.100478	-5.411830
C	-3.630737	-2.221294	2.554389
C	-6.049892	-6.592416	1.931434
C	-5.742214	-3.415846	-1.960351
C	2.320432	4.670409	0.681889
C	2.644472	4.266197	2.112680
C	3.211962	2.999649	2.370837
C	3.481395	2.618243	3.690065
C	3.243742	3.474019	4.767665
C	2.762305	4.754815	4.487567
C	2.472378	5.173369	3.183647
C	3.606779	2.064870	1.249728
C	2.046352	6.616328	2.982829
C	3.549566	3.044768	6.184427
C	-6.270386	-0.308429	0.577465
C	-7.081968	0.902406	0.118013
C	-8.073181	1.434401	0.974572
C	-8.847110	2.519095	0.546279
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C	-7.720490	2.539306	-1.557639
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C	-8.358502	0.860288	2.349832
C	-9.498888	4.294350	-1.139898
C	-5.935742	0.907861	-2.178573
H	-0.761181	0.873626	-4.309937
H	-1.265153	2.371378	-2.443746
H	2.084803	-3.037097	-3.679789
H	3.995100	-4.318423	-1.656953
H	2.612880	-5.101879	-2.410978
H	4.733497	-5.722680	-3.551171
H	3.639418	-4.886943	-4.652136
H	6.032662	-3.639330	-3.197978
H	5.945139	-3.995497	-4.923264
H	5.491587	-1.561398	-4.452904
H	4.109266	-2.348481	-5.210142
H	4.441570	-1.749502	-2.219165

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H	1.281454	-5.402978	-0.624469
H	0.874571	-4.360061	0.727174
H	-0.542301	-6.430879	0.687124
H	-1.522748	-4.974732	0.546264
H	-0.688182	-6.813243	-1.762036
H	-2.312142	-6.651014	-1.094416
H	-2.040215	-5.320710	-3.215472
H	-2.434153	-4.295277	-1.837098
H	0.354710	-4.726640	-3.037557
H	-0.615195	-3.268315	-3.184879
H	0.837304	-0.512661	2.496658
H	0.672564	1.178484	1.969091
H	-0.655586	0.018634	1.656771
H	0.623737	-1.921826	-6.025062
H	-0.844988	-1.060484	-5.489726
H	0.674063	-0.155104	-5.770593
H	-2.034739	4.796502	2.734369
H	0.146825	5.179259	1.741228
H	-2.418248	0.388897	-0.600032
H	-4.127977	3.478988	2.864985
H	-5.501097	1.587422	2.160874
H	3.251870	4.672465	0.106684
H	1.966307	5.708706	0.651888
H	2.476767	2.876899	-1.651395
H	0.827835	3.316355	-2.013997
H	4.921950	6.318244	-3.704623
H	1.009119	7.981111	-3.201351
H	2.610791	5.455704	5.306911
H	3.896878	1.630681	3.874221
H	-6.640313	-1.197871	0.055807
H	-6.474142	-0.498117	1.638183
H	-9.604849	2.918259	1.217913
H	-7.587407	2.953704	-2.555449
H	-4.300189	-1.453393	-1.343514
H	-3.128826	-1.400421	-0.042967
H	-6.382626	-5.618516	-0.598899
H	-4.614309	-4.632818	3.174535
H	-9.159704	1.424418	2.836887

H	-8.678295	-0.188057	2.305380
H	-7.485826	0.898662	3.014850
H	-6.117190	1.346465	-3.165303
H	-4.900479	1.128737	-1.896510
H	-6.016725	-0.180414	-2.283620
H	-9.675374	4.293814	-2.221217
H	-10.472192	4.315096	-0.637730
H	-8.987143	5.235228	-0.895938
H	-6.340056	-4.228834	-2.383442
H	-6.315952	-2.489744	-2.086665
H	-4.839730	-3.320921	-2.576657
H	-3.412627	-2.713112	3.507157
H	-2.673357	-1.921537	2.109429
H	-4.173387	-1.293993	2.768604
H	-5.285337	-7.059369	2.562797
H	-6.940950	-6.450043	2.557436
H	-6.315268	-7.301852	1.140831
H	-0.726121	6.785391	-2.321083
H	-0.648686	5.019094	-2.295351
H	-0.248446	5.927584	-0.849864
H	5.497389	4.266478	-2.955380
H	4.689283	3.635663	-1.518299
H	4.230121	3.047799	-3.113096
H	2.674057	9.044370	-4.770895
H	3.809086	9.331465	-3.450165
H	4.325777	8.406931	-4.863417
H	2.008425	7.135342	3.945619
H	2.751952	7.164003	2.345778
H	1.056854	6.725463	2.521919
H	4.050566	1.149440	1.646837
H	2.760463	1.782873	0.619663
H	4.349682	2.539503	0.592059
H	3.578490	1.953736	6.268786
H	4.524733	3.426732	6.516542
H	2.799504	3.422448	6.889015
Pd	2.749918	-2.039443	0.806098
C	4.186214	-3.432021	0.842090
C	5.461986	-3.110375	0.347084
C	6.470276	-4.077625	0.265860
C	6.230487	-5.385086	0.693597

C	4.975956	-5.709629	1.213841
C	3.967735	-4.742698	1.294352
H	5.677936	-2.097493	0.014914
H	7.447179	-3.802474	-0.127264
H	7.013623	-6.136708	0.634041
H	4.778684	-6.719036	1.569600
H	3.006622	-5.018811	1.718613
C	3.362710	-1.734973	2.740060
C	4.596631	-1.172333	3.114422
C	4.921317	-0.932018	4.453993
C	4.018864	-1.262752	5.468839
C	2.795464	-1.841817	5.127450
C	2.481178	-2.080684	3.784002
H	5.332838	-0.931785	2.350428
H	5.886535	-0.496111	4.705544
H	4.274271	-1.088782	6.511527
H	2.088304	-2.121586	5.906239
H	1.528724	-2.558752	3.555109

VPdPh$_2$, conformer of **2,7-bis-(*N*,*N*-di-t-butylamino)N$_2$PhosPdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=83.28^o

‘

Processing: pdph2namphostbu46dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-2988.1028231

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
801.13812	843.530	363.356	322.749	843.721	46.505	40.402

Processing: pdph2namphostbu46dsdbe.log
145

C	-5.729460	1.717118	1.554884
C	-4.577732	2.218699	0.893956
C	-3.680317	1.305232	0.254090

C	-3.998703	-0.084698	0.319107
C	-5.134389	-0.564255	0.954415
C	-6.003113	0.370836	1.582497
C	-4.288502	3.604054	0.848920
C	-3.185375	4.057907	0.174930
C	-2.277962	3.183924	-0.501587
C	-2.502209	1.803004	-0.425919
C	-1.652072	0.785241	-1.143816
C	-0.448678	0.207368	-0.680454
C	0.280268	-0.748119	-1.428321
C	-0.262720	-1.165431	-2.666425
C	-1.483777	-0.659521	-3.115477
C	-2.153359	0.287834	-2.352099
P	1.871806	-1.387921	-0.687139
C	1.333986	-3.068922	0.014059
C	2.183835	-3.471873	1.239213
C	1.637293	-4.745758	1.905936
C	1.521553	-5.907336	0.908763
C	0.677640	-5.505460	-0.308755
C	1.222726	-4.235826	-0.988633
O	0.078055	0.584484	0.556877
C	-0.670964	0.160174	1.718531
O	0.441103	-2.095053	-3.376433
C	-0.044846	-2.509518	-4.645897
N	-1.179534	3.757324	-1.243492
C	-0.051045	4.344957	-0.399476
C	1.304152	3.790284	-0.901096
N	-5.477543	-1.962700	1.019763
C	-6.086103	-2.500633	-0.247353
C	-7.216773	-1.539580	-0.688596
C	3.063107	-1.708728	-2.103005
C	3.333779	-0.396668	-2.871064
C	4.343130	-0.610870	-4.011954
C	5.651476	-1.230678	-3.501211
C	5.379771	-2.535670	-2.740405
C	4.385292	-2.320603	-1.585564
C	-4.715409	-2.797316	2.017706
C	-3.593205	-3.662041	1.393924
C	-1.581903	4.382914	-2.563437
C	-2.399827	5.702729	-2.464228

C	-5.673835	-3.704672	2.833879
C	-4.047984	-1.874171	3.065147
C	-5.088853	-2.622859	-1.430257
C	-6.755961	-3.874840	-0.046474
C	-2.467888	3.393523	-3.350196
C	-0.354307	4.628396	-3.467740
C	-0.183757	3.896738	1.073081
C	0.019179	5.892088	-0.357079
H	-1.920070	-0.994171	-4.048459
H	-3.106522	0.664085	-2.707186
H	0.695699	-3.213584	-5.028965
H	-0.133871	-1.662206	-5.336779
H	-1.015205	-3.014535	-4.560866
H	-1.684822	0.558348	1.689777
H	-0.134424	0.564466	2.576112
H	-0.695094	-0.934325	1.769861
H	2.598005	-2.420018	-2.789826
H	2.397608	0.006859	-3.274650
H	3.728428	0.354262	-2.173680
H	4.541107	0.345843	-4.512483
H	3.898498	-1.274276	-4.769371
H	6.150576	-0.520639	-2.826569
H	6.339688	-1.411217	-4.337127
H	6.315818	-2.947484	-2.342693
H	4.976532	-3.286146	-3.437664
H	3.224497	-3.640655	0.932644
H	2.208225	-2.646044	1.958714
H	0.319258	-2.852405	0.382395
H	0.643734	-4.533615	2.329495
H	2.281604	-5.026941	2.748679
H	-0.359572	-5.325877	0.012252
H	1.089357	-6.789600	1.398010
H	2.527980	-6.197292	0.572065
H	0.640314	-6.326434	-1.036820
H	2.215222	-4.455658	-1.405448
H	0.584633	-3.956020	-1.831336
H	4.835824	-1.660536	-0.837215
H	4.195877	-3.279461	-1.088978
H	-2.975125	5.120473	0.151363
H	-4.955404	4.301386	1.350774

H	-6.397555	2.424137	2.041405
H	-6.886341	-0.009824	2.085889
H	-3.321301	-0.794216	-0.137988
H	-2.763167	3.855099	-4.299054
H	-1.920097	2.476437	-3.573802
H	-3.384365	3.136650	-2.811478
H	-0.705378	4.951441	-4.454452
H	0.314774	5.406832	-3.097401
H	0.220660	3.707313	-3.599024
H	-2.595865	6.081451	-3.474736
H	-3.372126	5.533654	-1.992320
H	-1.883109	6.490611	-1.915556
H	0.849963	6.183786	0.295658
H	0.201656	6.352398	-1.330338
H	-0.892321	6.328017	0.065643
H	2.107453	4.115208	-0.230756
H	1.287690	2.697093	-0.896256
H	1.557793	4.127317	-1.906765
H	0.706705	4.221520	1.618089
H	-1.055701	4.332780	1.568407
H	-0.233012	2.812531	1.158644
H	-5.607375	-3.010371	-2.316068
H	-4.666503	-1.650867	-1.698775
H	-4.263820	-3.303856	-1.204964
H	-7.715571	-1.945240	-1.575989
H	-7.963615	-1.429983	0.104801
H	-6.841597	-0.545550	-0.944903
H	-7.266484	-4.150422	-0.975803
H	-6.042341	-4.672732	0.172602
H	-7.505001	-3.841918	0.749333
H	-5.140614	-4.122555	3.695934
H	-6.517860	-3.115666	3.207136
H	-6.068177	-4.546361	2.265329
H	-3.573199	-2.499694	3.828086
H	-3.277847	-1.232758	2.631712
H	-4.781100	-1.233086	3.564237
H	-3.051380	-4.198009	2.183109
H	-3.979838	-4.413197	0.699861
H	-2.869955	-3.039897	0.854656
Pd	2.431627	0.245292	1.012105

C	4.397134	-0.031816	1.279272
C	5.311257	0.713347	0.514230
C	6.688040	0.477413	0.600279
C	7.184425	-0.498373	1.467132
C	6.289238	-1.225931	2.253861
C	4.912700	-0.990432	2.166162
H	4.952540	1.487098	-0.160761
H	7.372347	1.065920	-0.007996
H	8.253918	-0.680130	1.537872
H	6.660882	-1.976662	2.948686
H	4.240653	-1.560836	2.801612
C	2.654797	1.578985	2.546718
C	3.206629	2.862795	2.389139
C	3.216861	3.791377	3.435022
C	2.688522	3.453025	4.683585
C	2.163137	2.174684	4.875549
C	2.156875	1.251307	3.822403
H	3.645863	3.146793	1.435367
H	3.647346	4.778660	3.276687
H	2.700613	4.171623	5.499598
H	1.767621	1.887896	5.848349
H	1.765455	0.252431	4.014001

Conformer of **N_2PhosPd-naphthyl, *o*-tolyl**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. C-Pd-C angle=82.87°

Processing: pdnaptolnamphos6dsdbe.log
Method Basis Set Imaginary Freqs
RB3LYP GenECP

HF
-3633.53741200

Processing: pdnaptolnamphos6dsdbe.log
Frequency job incomplete: pdnaptolnamphos6dsdbe.log
158

C	3.763466	-2.804710	-1.647180
C	4.408500	-3.128637	-0.447141
C	4.254560	-4.421351	0.071273

C	3.469259	-5.368056	-0.587776
C	2.828985	-5.035697	-1.784879
C	2.979061	-3.751418	-2.311807
C	5.267983	-2.114810	0.304549
N	5.836963	-1.051678	-0.507076
C	6.991621	-1.431954	-1.307633
C	8.338581	-1.385850	-0.591313
C	9.422550	-2.096252	-1.125860
C	10.676288	-2.050618	-0.517360
C	10.863557	-1.296906	0.644580
C	9.788849	-0.592692	1.187989
C	8.534375	-0.636505	0.573459
C	5.258664	0.216538	-0.588956
C	6.008095	1.303101	-1.139798
C	5.444704	2.549341	-1.247645
C	4.127768	2.818812	-0.798130
C	3.372345	1.761590	-0.197913
C	3.964328	0.469456	-0.133710
C	3.542363	4.099412	-0.908526
C	2.265228	4.329478	-0.467863
C	1.473005	3.299908	0.125154
C	2.032137	2.016662	0.271255
C	1.365584	0.928291	1.066943
C	0.251546	0.131399	0.711164
C	-0.346715	-0.774219	1.625467
C	0.241200	-0.907360	2.905826
C	1.381457	-0.180376	3.254216
C	1.916977	0.711376	2.338128
P	-1.847894	-1.731559	1.057876
C	-2.984336	-1.920313	2.545776
C	-3.360073	-0.544039	3.134485
C	-4.307414	-0.691565	4.338062
C	-5.565570	-1.491968	3.972532
C	-5.193254	-2.858492	3.380896
C	-4.254511	-2.716212	2.169424
O	-0.328778	0.226057	-0.549045
C	0.554107	0.123970	-1.692295
O	-0.341583	-1.786001	3.772242
C	0.179044	-1.912589	5.088166
N	0.140825	3.604892	0.517456

C	-0.242421	3.468837	1.937678
C	0.134111	4.645352	2.830540
C	-0.854562	5.477206	3.370665
C	-0.519257	6.552894	4.196604
C	0.818983	6.815507	4.491064
C	1.816445	5.994746	3.957428
C	1.476409	4.918701	3.137475
C	-1.117487	-3.448473	0.687035
C	-0.880806	-4.375332	1.897766
C	-0.198399	-5.688958	1.474119
C	-0.991562	-6.416472	0.380115
C	-1.231496	-5.495788	-0.824467
C	-1.916995	-4.182004	-0.412583
Pd	-2.557810	-0.610061	-0.972322
C	-2.906382	0.199273	-2.835247
C	-2.420449	-0.440392	-4.003944
C	-2.615432	0.158536	-5.259627
C	-3.312779	1.359003	-5.396198
C	-3.816933	1.983797	-4.256210
C	-3.611786	1.404500	-3.000652
C	-4.483458	-1.169057	-1.131210
C	-5.505239	-0.363954	-0.520609
C	-6.874893	-0.807383	-0.547168
C	-7.200938	-2.026936	-1.196655
C	-6.212685	-2.769612	-1.799164
C	-4.862877	-2.337121	-1.770722
C	-0.518681	4.765951	-0.101235
C	-0.506079	4.796813	-1.617858
C	-0.285423	6.009338	-2.283716
C	-0.307502	6.074334	-3.677756
C	-0.544519	4.919253	-4.424716
C	-0.772157	3.706631	-3.769805
C	-0.758883	3.647718	-2.375249
H	1.842814	-0.289235	4.227771
H	2.788169	1.295639	2.619503
H	-2.442075	-2.481282	3.310692
H	-4.784914	-2.211082	1.356031
H	-3.987764	-3.712808	1.798791
H	-6.096887	-3.402978	3.079076
H	-4.702138	-3.468441	4.154761

H	-6.153221	-0.926638	3.235776
H	-6.204568	-1.620758	4.855944
H	-4.582130	0.302809	4.713300
H	-3.777217	-1.200476	5.157692
H	-3.855051	0.059161	2.363262
H	-2.457354	-0.000920	3.437634
H	-0.134710	-3.197521	0.260097
H	-2.932045	-4.400054	-0.055051
H	-2.032568	-3.527746	-1.282246
H	-1.839521	-6.006473	-1.582492
H	-0.266089	-5.263794	-1.297920
H	-1.960458	-6.741071	0.788132
H	-0.463960	-7.326934	0.067121
H	-0.074090	-6.337114	2.351960
H	0.812279	-5.466272	1.101984
H	-1.844811	-4.613395	2.368711
H	-0.278367	-3.868332	2.655316
H	-4.028357	1.904668	-2.130808
H	-4.364279	2.920169	-4.338116
H	-3.461901	1.796099	-6.380813
H	-2.228161	-0.340018	-6.147667
C	-1.742626	-1.797006	-3.963734
C	-5.224104	0.870392	0.132669
C	-7.873844	-0.012064	0.080218
H	-8.237989	-2.354295	-1.216318
H	-6.460987	-3.697693	-2.310016
H	-4.118267	-2.950024	-2.268702
H	-0.096521	0.182771	-2.563143
H	1.267600	0.946146	-1.705213
H	1.079106	-0.837172	-1.668144
H	-0.467765	-2.632795	5.591950
H	1.208065	-2.293400	5.080171
H	0.147849	-0.956722	5.625230
H	4.121887	4.910960	-1.342791
H	1.854322	5.326029	-0.551548
H	3.365812	-0.345423	0.250845
H	6.024073	3.364964	-1.674550
H	7.036646	1.155825	-1.448646
H	-1.561228	4.720037	0.242269
H	-0.125077	5.721058	0.283826

H	-1.330126	3.329846	1.968762
H	0.203213	2.556887	2.330636
H	-1.900282	5.277346	3.145331
H	-1.303042	7.184388	4.607083
H	1.084414	7.651795	5.132424
H	2.861345	6.190783	4.184464
H	2.259707	4.286243	2.728459
H	-0.090148	6.910424	-1.704831
H	-0.132725	7.023928	-4.177487
H	-0.557893	4.963676	-5.510702
H	-0.981263	2.807728	-4.341141
H	-0.950580	2.706667	-1.869674
H	6.823883	-2.451632	-1.679705
H	7.024344	-0.800595	-2.202480
H	9.281810	-2.691712	-2.026239
H	11.505370	-2.608264	-0.945269
H	11.838706	-1.263204	1.122921
H	9.923920	-0.006112	2.093130
H	7.699523	-0.088533	1.000138
H	6.096346	-2.649416	0.789196
H	4.692565	-1.660573	1.118687
H	4.762980	-4.692382	0.994765
H	3.370049	-6.369101	-0.176172
H	2.228887	-5.775211	-2.307841
H	2.493605	-3.487068	-3.247764
H	3.886845	-1.810816	-2.067038
C	-6.215267	1.621273	0.727681
H	-4.191130	1.209761	0.149273
H	-5.968103	2.561857	1.213836
C	-7.558429	1.173723	0.704323
H	-8.904021	-0.361773	0.054164
H	-8.336881	1.769157	1.174719
H	-2.485929	-2.605389	-3.933165
H	-1.124030	-1.961633	-4.854742
H	-1.108929	-1.919152	-3.079438

X_2PdPh_2, conformer of associated **bis(Phos)$PdPh_2$**, N-Phos structure without 2,7-amino substituents: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. P-Pd distances=2.557, 2.621 Å, C-Pd-C angle=79.94°.

Processing: pddiphdi0namphos6dsdbe.log

PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3905.7121378

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
879.27856	927.234	411.638	360.324	927.465	47.076	41.499

Processing: pddiphdi0namphos6dsdbe.log
Frequency job incomplete: pddiphdi0namphos6dsdbe.log
163

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C	-1.757075	-0.255455	2.040855
C	-1.217458	-1.684388	1.838666
C	-0.964218	-2.398800	3.177834
C	-2.205458	-2.381308	4.080108
C	-2.684346	-0.942492	4.311771
P	-1.758463	0.764393	0.434678
Pd	0.308110	0.277158	-0.990765
C	-0.863779	-0.962751	-2.148489
C	-0.918340	-2.334171	-1.840666
C	-1.673278	-3.235882	-2.601159
C	-2.408664	-2.788242	-3.700136
C	-2.370905	-1.430474	-4.025387
C	-1.605040	-0.542072	-3.265184
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C	-4.294548	-0.483105	-0.454695
C	-5.491468	-0.472230	-1.217303
C	-5.639989	0.515485	-2.192625
C	-4.665626	1.480915	-2.410246
C	-3.529668	1.489857	-1.601597
C	-6.619571	-1.433884	-1.028729
C	-7.000014	-2.242840	-2.086751
C	-8.083611	-3.144925	-1.980719
C	-8.792682	-3.238609	-0.806230
C	-8.458902	-2.418373	0.304845
C	-7.366339	-1.492366	0.197979

C	-9.193491	-2.486536	1.520060
C	-8.879545	-1.674460	2.585672
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C	-2.042001	2.484221	1.252955
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C	-3.612302	4.170398	2.321153
C	-2.738576	5.329393	1.819108
C	-1.286168	4.879819	1.599486
C	-1.212820	3.649044	0.678332
C	1.547104	0.032594	-2.625468
C	2.625139	-0.861113	-2.720154
C	3.432680	-0.930050	-3.862295
C	3.181502	-0.102217	-4.956904
C	2.106395	0.787569	-4.895222
C	1.303642	0.843301	-3.751995
P	2.254438	1.514123	0.254881
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C	2.518161	4.476640	-0.199116
C	2.237869	5.581713	-1.235997
C	3.150796	5.460597	-2.464464
C	3.065381	4.058198	-3.083326
C	3.351137	2.959253	-2.045428
C	1.997587	2.052812	2.069276
C	1.776147	0.802141	2.951164
C	1.324391	1.183038	4.371071
C	2.335232	2.116197	5.051325
C	2.631856	3.337830	4.171807
C	3.068277	2.934861	2.749826
C	3.927433	0.678669	0.422962
C	3.962005	-0.723763	0.648561
C	5.180996	-1.428695	0.800154
C	6.368592	-0.702727	0.667280
C	6.378756	0.673267	0.490371
C	5.163826	1.364711	0.426211

O	2.741926	-1.313501	0.796053
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C	5.842913	-3.865965	0.385824
C	6.010585	-5.197765	0.896123
C	5.623421	-5.487623	2.231653
C	5.092200	-4.504593	3.033862
C	4.935845	-3.189174	2.538279
C	6.553186	-6.200606	0.047405
C	6.906141	-5.916177	-1.252112
C	6.725823	-4.608775	-1.763400
C	6.208592	-3.611075	-0.965917
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H	7.312352	-1.231268	0.769221
H	1.371841	3.043000	-1.275907
H	4.379585	3.063732	-1.692326
H	3.263922	1.980068	-2.516740
H	3.771584	3.965150	-3.918433
H	2.063177	3.902968	-3.508228
H	4.189941	5.658628	-2.160058
H	2.893200	6.227740	-3.206718
H	2.355969	6.567396	-0.766004
H	1.187387	5.514463	-1.557591
H	3.530224	4.604200	0.198732
H	1.824802	4.594053	0.641365
H	1.054878	2.616256	2.046587
H	4.007330	2.370467	2.809029
H	3.280226	3.832146	2.168992
H	3.411365	3.958549	4.633392
H	1.731602	3.967997	4.108396
H	3.270388	1.564349	5.228004
H	1.966671	2.431325	6.036173
H	1.180274	0.274500	4.970895
H	0.344426	1.682137	4.322404
H	2.720510	0.246784	3.017735

H	1.059950	0.120967	2.487311
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H	-2.989388	-3.485692	-4.299370
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H	-0.360308	-2.724476	-0.993612
H	2.852064	-1.522149	-1.892395
H	4.257676	-1.640042	-3.893788
H	3.805380	-0.155411	-5.845971
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H	6.051798	4.511609	0.372481
H	6.921927	3.260188	1.302437
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H	5.754087	-6.499734	2.607258
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H	-1.651910	3.866907	-2.833870
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H	-3.912262	3.194316	0.414871
H	-4.140278	2.132008	1.790981
H	-4.659881	4.490124	2.397431
H	-3.297292	3.891092	3.337878
H	-3.146339	5.699888	0.866777
H	-2.777831	6.170259	2.523595
H	-0.695352	5.701117	1.172566
H	-0.829010	4.639526	2.571787
H	-1.596983	3.915721	-0.309287

H -0.174031 3.345216 0.532228
H -0.956063 0.295106 2.556800
H -1.925903 -2.262681 1.242864
H -0.287415 -1.636615 1.261006
H -0.641265 -3.431218 2.988059
H -0.133237 -1.905435 3.704170
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H -6.276082 0.063541 1.237631
H -10.016576 -3.194145 1.589527
H -9.450655 -1.736579 3.508155

Q--QPdPh$_2$, more stable dissociated form of **bis(*N*,*N*-dibenzyl-2-aminoNPhos)PdPh$_2$**, one phosphine ligand dissociated to loose complex: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. P-Pd distance=6.396 Å, C-Pd-C angle=86.17°. ($E_{e,rel}$=0.00 kcal/mol, $G_{298,rel}$=0.00 kcal/mol)

Processing: pddiphdi2namphos6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-5097.8106317

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
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Processing: pddiphdi2namphos6dsdbe.log
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C 9.680852 -0.681380 -2.660372

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C	12.217518	-0.578967	-3.882421
C	11.777693	0.480250	-3.084313
C	8.313656	-0.745262	-1.994603
N	8.323455	-1.117485	-0.559826
C	8.799417	-2.482734	-0.308844
C	7.886797	-3.547011	-0.894712
C	8.420940	-4.636039	-1.592617
C	7.590976	-5.648815	-2.081650
C	6.212339	-5.578906	-1.880559
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C	10.016526	-0.269792	1.021152
C	7.708832	3.172139	1.880000
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C	9.440255	3.923440	3.408144
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C	6.641316	1.218578	-0.014884
C	5.461026	0.525374	0.346938
C	4.230921	0.761453	-0.309496
C	4.220817	1.709686	-1.362792
C	5.365463	2.426877	-1.712309
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C	1.820255	-0.889698	-1.196955
C	2.851260	-1.450813	-2.195168
C	2.186353	-2.410571	-3.198237
C	1.010899	-1.744038	-3.928069
C	-0.011391	-1.176713	-2.931621
C	0.644568	-0.210761	-1.930190
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C	2.865456	2.947332	-2.911177

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C	-6.516200	-0.500498	-3.130902
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H	0.528040	-2.460904	-4.604803
H	-0.820021	-0.661120	-3.465782
H	-0.481102	-2.007855	-2.383915
H	1.009799	0.674915	-2.458715
H	-0.096742	0.143005	-1.203714
H	3.310663	-0.586768	2.352826
H	2.525792	-2.973275	0.597070
H	4.172309	-2.433483	0.934477
H	3.516897	-4.359501	2.380235
H	3.875819	-2.932204	3.344534
H	1.077666	-3.932947	2.582558
H	1.797088	-3.997262	4.188919
H	0.212097	-2.049919	3.953129
H	1.852656	-1.521027	4.314514
H	0.499932	-1.517474	1.564525
H	0.890970	-0.112946	2.563255
H	10.633991	-1.129830	0.788207
H	11.440222	0.522339	2.402743

H 6.745103 3.329710 1.408934
H 11.153495 2.648601 3.601989
H 9.805060 4.665758 4.112617
H 9.822897 -2.651145 -0.683572
H 8.836229 -2.613337 0.778877
H 7.689792 -1.481261 -2.511232
H 7.808246 0.217399 -2.082434
H 9.495545 -4.693290 -1.752815
H 8.022482 -6.487377 -2.622166
H 5.563518 -6.363067 -2.261777
H 4.597077 -4.433691 -1.023056
H 6.089286 -2.635693 -0.159807
H 9.489428 -2.596673 -3.626000
H 11.721027 -2.512289 -4.699727
H 13.195036 -0.537192 -4.355695
H 12.411784 1.350841 -2.937158
H 10.184790 1.261229 -1.868197

Q--QPdPh$_2$, less stable conformer of dissociated form of **bis(*N*,*N*-dibenzyl-2-aminoNPhos)PdPh$_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. P-Pd distance=6.009 Å, C-Pd-C angle=83.95°. ($E_{e,rel}$=3.81 kcal/mol, $G_{298,rel}$=3.96 kcal/mol)

Processing: pddiphdi2namphos-a6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-5097.8045579

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
1173.74174	1239.129	568.602	463.680	1239.534	47.927	43.784

Processing: pddiphdi2namphos-a6dsdbe.log
219
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C -2.281982 0.525571 1.541025
C -2.366382 -0.483309 2.704686

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C	-2.580272	1.447909	4.351768
C	-2.458337	2.447081	3.192198
P	-2.505842	-0.302378	-0.145519
Pd	-1.137244	-2.321897	0.335750
C	-0.771050	-3.411967	-1.301530
C	-1.541047	-4.543817	-1.609862
C	-1.337765	-5.238498	-2.808478
C	-0.352373	-4.826014	-3.708437
C	0.431927	-3.712269	-3.397955
C	0.230026	-3.014404	-2.200519
C	-4.257158	-0.720228	-0.648977
C	-5.444126	-0.653875	0.117857
C	-6.669727	-1.173947	-0.369478
C	-6.655120	-1.816307	-1.613476
C	-5.512109	-1.905970	-2.396612
C	-4.327951	-1.342266	-1.920643
C	-7.992387	-1.092271	0.334784
C	-8.727578	0.098841	0.382699
C	-9.987859	0.111290	1.050644
C	-10.502819	-1.014426	1.642903
C	-9.801381	-2.244034	1.596523
C	-8.533159	-2.285836	0.927332
C	-10.320932	-3.420529	2.200057
C	-9.620311	-4.604037	2.165178
C	-8.360020	-4.650892	1.523032
C	-7.832314	-3.528164	0.923037
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C	-8.638453	2.552122	0.444324
C	-7.673095	3.699749	0.198102
C	-8.156783	4.967796	-0.144130
C	-7.283808	6.046077	-0.312644
C	-5.911106	5.864339	-0.144334
C	-5.419049	4.600382	0.194824
C	-6.292348	3.525979	0.366007
O	-5.330965	-0.032901	1.333007
C	-6.055205	-0.501596	2.474267
O	-3.169142	-1.353396	-2.630845
C	-3.094274	-2.113944	-3.833745
C	-8.210315	1.368540	-1.679942

C	-9.570059	1.568222	-2.333710
C	-10.459690	0.494381	-2.492750
C	-11.710093	0.681958	-3.082687
C	-12.092920	1.949463	-3.528978
C	-11.215999	3.025278	-3.383183
C	-9.965746	2.833178	-2.790292
C	-1.932438	1.136382	-1.254547
C	-3.041950	1.856870	-2.044265
C	-2.479672	3.075951	-2.797725
C	-1.310969	2.686315	-3.714401
C	-0.208566	1.961684	-2.928344
C	-0.756464	0.740290	-2.170052
C	-0.065506	-3.751262	1.267704
C	-0.729087	-4.694655	2.074091
C	-0.017596	-5.542872	2.930153
C	1.376431	-5.480117	2.982373
C	2.052851	-4.567115	2.169693
C	1.339634	-3.719798	1.314930
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C	2.517981	2.994706	1.569248
C	2.229977	3.901796	2.781390
C	1.280716	5.052420	2.394857
C	1.829145	5.869665	1.215895
C	2.125776	4.970642	0.006560
C	3.064835	3.810396	0.379098
C	3.083944	0.755432	3.494096
C	3.161342	-0.786468	3.559249
C	2.717032	-1.326963	4.928118
C	3.524669	-0.700894	6.073566
C	3.462255	0.832117	6.016460
C	3.902575	1.374515	4.643681
C	5.287548	1.600717	1.663811
C	6.020466	0.575357	1.010659
C	7.415327	0.657962	0.793243
C	8.083555	1.756388	1.345619
C	7.414240	2.765041	2.029218
C	6.022875	2.696770	2.168025
O	5.289321	-0.493355	0.571187
C	5.719271	-1.822529	0.880570
C	8.196392	-0.334958	-0.012790

C	9.124379	-1.197068	0.667978
C	9.889293	-2.159197	-0.071009
C	9.708352	-2.230213	-1.473435
C	8.835931	-1.389414	-2.115595
C	8.068550	-0.415576	-1.409823
C	10.792626	-3.019288	0.608200
C	10.941233	-2.956611	1.974625
C	10.176127	-2.025209	2.715855
C	9.295980	-1.173576	2.084179
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C	6.019442	4.765031	3.383925
N	7.183492	0.436321	-2.129953
C	7.461944	1.889374	-2.106192
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C	8.234554	3.052968	-4.231388
C	9.231661	3.481090	-5.111070
C	10.571996	3.214848	-4.828933
C	10.906837	2.523060	-3.661746
C	9.907670	2.101267	-2.784363
C	6.714061	-0.001707	-3.450689
C	5.948719	-1.312352	-3.471643
C	6.192052	-2.246920	-4.485457
C	5.441873	-3.421735	-4.573267
C	4.436890	-3.677779	-3.639553
C	4.188558	-2.751412	-2.622373
C	4.935065	-1.574635	-2.539994
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H	1.536113	2.606237	1.246468
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H	1.179783	4.560935	-0.379475
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H	3.826307	2.464819	4.629610
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H	3.159820	-1.062700	7.043891
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H	2.551895	-1.232566	2.765645
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H	6.728385	4.429100	4.151380
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H	8.740380	-1.457189	-3.191617
H	8.717688	-0.470822	2.673274
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H	11.634559	-3.619758	2.484640
H	6.039932	0.794061	-3.794548
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H	7.716152	2.170205	-1.085150
H	7.191463	3.268115	-4.455017
H	8.960641	4.022363	-6.014022
H	11.351094	3.546844	-5.510141

H	11.949040	2.317047	-3.431321
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H	6.975306	-2.052332	-5.216009
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H	3.851261	-4.591401	-3.697802
H	3.406124	-2.947840	-1.894037
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H	-7.584662	-2.240533	-1.983713
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H	-3.363025	-3.159022	-3.653605
H	-3.739246	-1.683609	-4.610452
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H	-3.483161	1.161673	-2.767462
H	-3.851766	2.172874	-1.376000
H	-3.280973	3.552034	-3.377507
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H	-1.682282	2.024643	-4.511160
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H	0.598423	1.646179	-3.602067
H	0.243151	2.663274	-2.210322
H	-1.091184	-0.019636	-2.883552
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H	-3.396924	-0.832650	2.821064
H	-1.763688	-1.381386	2.480438
H	-1.996092	-0.593712	4.840436
H	-0.784063	0.315295	3.944472
H	-3.644833	1.248599	4.547338
H	-2.171247	1.880560	5.273682
H	-3.003762	3.370727	3.425006
H	-1.401930	2.730427	3.069936
H	-4.064194	1.681455	1.954720
H	-2.840779	2.575209	1.062445
H	-10.564801	1.028956	1.067082
H	-11.469799	-0.976276	2.139286
H	-6.865588	-3.586517	0.435433

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H -10.026503 -5.497953 2.630293
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H -9.282588 3.673175 -2.686281
H -11.501738 4.013543 -3.734616
H -13.065158 2.094897 -3.992509
H -12.383414 -0.163208 -3.200913
H -10.168363 -0.497004 -2.155761

Q_2PdPh_2, conformer of associated form of **bis(*N*,*N*-dibenzyl-2-aminoNPhos)$PdPh_2$**: B3LYP/6-31G(d)/SDD for pre-reductive elimination step. P-Pd distances=2.547, 2.625 Å, C-Pd-C angle=79.01°. ($E_{e,rel}$=5.98 kcal/mol, $G_{298,rel}$=8.99 kcal/mol; remarkably $G_{298,rel}$=17.45 kcal/mol using distorted non-quasiharmonic frequencies!)

Processing: pddiphdi2namphos-b6dsdbe.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-5097.8010984

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
1176.24745	1240.480	536.098	458.547	1240.820	47.927	43.332

Processing: pddiphdi2namphos-b6dsdbe.log
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C -5.766362 -3.129855 -4.077802
C -5.653671 -4.429709 -4.639207

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C	-6.222408	-2.031110	-4.842216
C	-6.345101	-0.787082	-4.279126
C	-6.007346	-0.531064	-2.915207
C	-5.535267	-1.591884	-2.126325
C	-5.261307	-1.474024	-0.647887
C	-4.080040	-1.027378	0.001009
C	-3.945496	-1.072435	1.421335
C	-5.074258	-1.455969	2.177028
C	-6.239374	-1.918706	1.557330
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C	-2.702783	1.201573	2.743098
C	-2.889946	2.074387	1.480361
C	-2.947950	3.570065	1.835461
C	-4.066555	3.871324	2.841575
C	-3.947106	2.973315	4.078713
C	-3.882293	1.481203	3.700902
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C	-2.801698	-0.516011	-2.032048
O	-4.986470	-1.344864	3.534844
C	-6.104562	-1.707941	4.330092
Pd	-0.045258	-1.003574	0.939910
C	-0.544966	-2.995534	0.746397
C	-1.428530	-3.546133	-0.194693
C	-1.681275	-4.922497	-0.250998
C	-1.055907	-5.795427	0.640455
C	-0.165006	-5.274164	1.581100
C	0.089067	-3.899823	1.621198
P	1.349934	1.080956	1.381384
C	1.286608	1.968180	3.086834
C	2.565606	2.722713	3.512524
C	2.293565	3.618555	4.735648
C	1.724552	2.816529	5.915314
C	0.491760	2.002032	5.494736
C	0.796465	1.115905	4.273999
C	0.741517	2.540267	0.322430
C	1.440950	3.914825	0.391081
C	0.652981	4.985346	-0.388873

C	0.396884	4.562885	-1.840849
C	-0.342019	3.219228	-1.888543
C	0.411862	2.119054	-1.122574
C	3.195577	0.750471	1.209940
C	4.100372	1.293941	0.272089
C	5.506216	1.116751	0.385161
C	5.971929	0.277383	1.399643
C	5.106712	-0.379693	2.264547
C	3.734392	-0.145541	2.165220
O	3.580103	2.088522	-0.720625
C	3.865532	1.736396	-2.078404
C	6.522014	1.861393	-0.428344
C	7.519887	1.184804	-1.151632
C	8.507582	1.938241	-1.851450
C	8.522108	3.309333	-1.832492
C	7.556589	4.031303	-1.090865
C	6.554531	3.301174	-0.368494
C	5.653905	4.058263	0.436375
C	5.713466	5.433339	0.486660
C	6.677016	6.145691	-0.265972
C	7.583033	5.450888	-1.032080
O	2.830915	-0.749011	2.991774
C	3.278254	-1.751908	3.891349
C	1.418148	-1.651418	-0.358094
C	1.262346	-1.376818	-1.729187
C	2.186464	-1.820227	-2.683274
C	3.298836	-2.568001	-2.291693
C	3.470740	-2.857687	-0.936020
C	2.544026	-2.406240	0.008392
C	-2.000820	-1.674951	3.760867
C	-2.290186	-1.116593	5.168770
C	-1.654758	-2.013693	6.248287
C	-2.132376	-3.468278	6.134316
C	-1.893119	-4.020249	4.722023
C	-2.525971	-3.125105	3.642310
N	7.586745	-0.240761	-1.184739
N	-6.113171	0.806661	-2.416200
H	5.013547	5.976930	1.115969
H	-4.524974	-6.120446	-1.925844
H	-7.092471	-2.251773	2.134158

H	-7.195219	-2.319973	-0.306275
H	-0.906720	-1.749716	3.680465
H	-3.611233	-3.129838	3.770888
H	-2.309461	-3.535977	2.654947
H	-2.296315	-5.037556	4.635699
H	-0.812875	-4.100409	4.536201
H	-3.208147	-3.511529	6.363576
H	-1.629719	-4.093997	6.883722
H	-1.883550	-1.611240	7.244350
H	-0.559420	-1.982788	6.144295
H	-3.370934	-1.068167	5.334094
H	-1.902601	-0.097460	5.278397
H	-1.779730	1.529746	3.239708
H	-4.818676	1.196319	3.206502
H	-3.812924	0.881151	4.607647
H	-4.793727	3.144233	4.757044
H	-3.040409	3.244860	4.640791
H	-5.038943	3.694230	2.358975
H	-4.048403	4.930397	3.130041
H	-3.093890	4.162444	0.924368
H	-1.981971	3.881790	2.261413
H	-3.828011	1.786962	0.987039
H	-2.095292	1.881968	0.754352
H	2.694567	-2.674222	1.050160
H	4.325050	-3.448574	-0.609842
H	4.012847	-2.923176	-3.030376
H	2.024530	-1.594440	-3.736187
H	0.395841	-0.819759	-2.075958
H	-1.926423	-2.899494	-0.909814
H	-2.359688	-5.308822	-1.008190
H	-1.248812	-6.864739	0.594756
H	0.341637	-5.938264	2.279581
H	0.804638	-3.528521	2.352854
H	-1.781222	-0.158042	-2.175463
H	-2.888804	-1.526704	-2.438681
H	-3.503925	0.152073	-2.534772
H	-5.807978	-1.516982	5.363018
H	-6.984825	-1.099757	4.087238
H	-6.353707	-2.770623	4.217156
H	-6.499566	-2.187284	-5.882257

H	-6.740999	0.017688	-4.885668
H	-4.680887	-3.901799	-0.917752
H	-5.921042	-4.566205	-5.684666
H	-5.140820	-6.484518	-4.317417
H	7.042287	0.152434	1.517858
H	5.505683	-1.039103	3.025485
H	3.299859	2.442229	-2.690677
H	4.928032	1.845601	-2.307392
H	3.531357	0.715009	-2.291461
H	2.379288	-2.135589	4.376535
H	3.780668	-2.567715	3.357745
H	3.955460	-1.341014	4.651594
H	0.507627	2.724259	2.904512
H	3.345983	1.995148	3.767119
H	2.965806	3.326725	2.692674
H	3.218845	4.128414	5.034409
H	1.580095	4.407754	4.454264
H	2.497937	2.128185	6.287426
H	1.476341	3.486833	6.748358
H	0.145403	1.379892	6.330684
H	-0.333940	2.689471	5.254619
H	1.568713	0.390522	4.542022
H	-0.084531	0.534574	3.992425
H	-0.230443	2.669799	0.822508
H	1.330662	1.868346	-1.655816
H	-0.191503	1.205102	-1.095164
H	-0.499132	2.903189	-2.928415
H	-1.342799	3.347394	-1.449919
H	1.358320	4.471919	-2.367749
H	-0.178330	5.334285	-2.369497
H	1.201842	5.935683	-0.356501
H	-0.312620	5.166105	0.108154
H	2.450685	3.839106	-0.018813
H	1.533236	4.242619	1.432063
H	9.248251	1.408824	-2.440069
H	9.278627	3.856466	-2.390464
H	4.919541	3.538118	1.037818
H	8.346927	5.976854	-1.600471
H	6.706962	7.231105	-0.224725
C	6.538459	-0.960524	-1.937303

C	8.923519	-0.826743	-1.312747
H	6.462160	-1.968016	-1.519359
H	5.585210	-0.474492	-1.729142
C	6.771250	-1.067479	-3.440071
C	7.067164	-2.309834	-4.018363
C	7.277543	-2.434234	-5.393916
C	7.201479	-1.310112	-6.216834
C	6.912476	-0.064091	-5.654532
C	6.698091	0.054448	-4.280857
H	7.133139	-3.188979	-3.381736
H	7.500418	-3.409119	-5.820128
H	7.363335	-1.402688	-7.287602
H	6.847144	0.816922	-6.288165
H	6.474624	1.030024	-3.859077
C	9.020925	-2.252604	-0.789316
H	9.291424	-0.819405	-2.352535
H	9.607301	-0.193725	-0.734141
C	9.814153	-3.186359	-1.467460
C	9.979400	-4.482113	-0.972973
C	9.341031	-4.866555	0.206861
C	8.538560	-3.946079	0.885657
C	8.382452	-2.650000	0.393165
H	10.305533	-2.895812	-2.393473
H	10.599763	-5.191618	-1.514547
H	9.461794	-5.875859	0.591301
H	8.031613	-4.239120	1.801651
H	7.746004	-1.941274	0.913134
C	-6.081097	1.865244	-3.437527
C	-7.117458	1.063585	-1.355718
H	-6.858887	2.023304	-0.898073
C	-8.569103	1.104845	-1.816860
H	-6.991392	0.301837	-0.587153
C	-9.240177	-0.061891	-2.216619
C	-10.571769	-0.015239	-2.630516
C	-11.261397	1.199912	-2.646817
C	-10.609027	2.366430	-2.246186
C	-9.274118	2.315980	-1.837068
H	-8.717075	-1.013810	-2.203927
H	-11.073959	-0.930198	-2.934390
H	-12.299957	1.234876	-2.965312

H	-11.137610	3.316405	-2.250120
H	-8.771257	3.228358	-1.525175
C	-5.722850	3.242401	-2.906189
H	-5.324506	1.575093	-4.175242
H	-7.037529	1.947996	-3.979040
C	-4.558437	3.458873	-2.156785
C	-4.195629	4.749429	-1.769828
C	-4.994093	5.843267	-2.115484
C	-6.159774	5.637321	-2.852771
C	-6.517410	4.344948	-3.244612
H	-3.938091	2.610939	-1.879335
H	-3.279709	4.905517	-1.207118
H	-4.706707	6.846623	-1.812746
H	-6.790582	6.479206	-3.126131
H	-7.423692	4.188536	-3.825074

II. The Reservoir Effect: Enhanced Biocatalytic Processes facilitated by Micellar Catalysis and its Applications towards 1-Pot Sequences

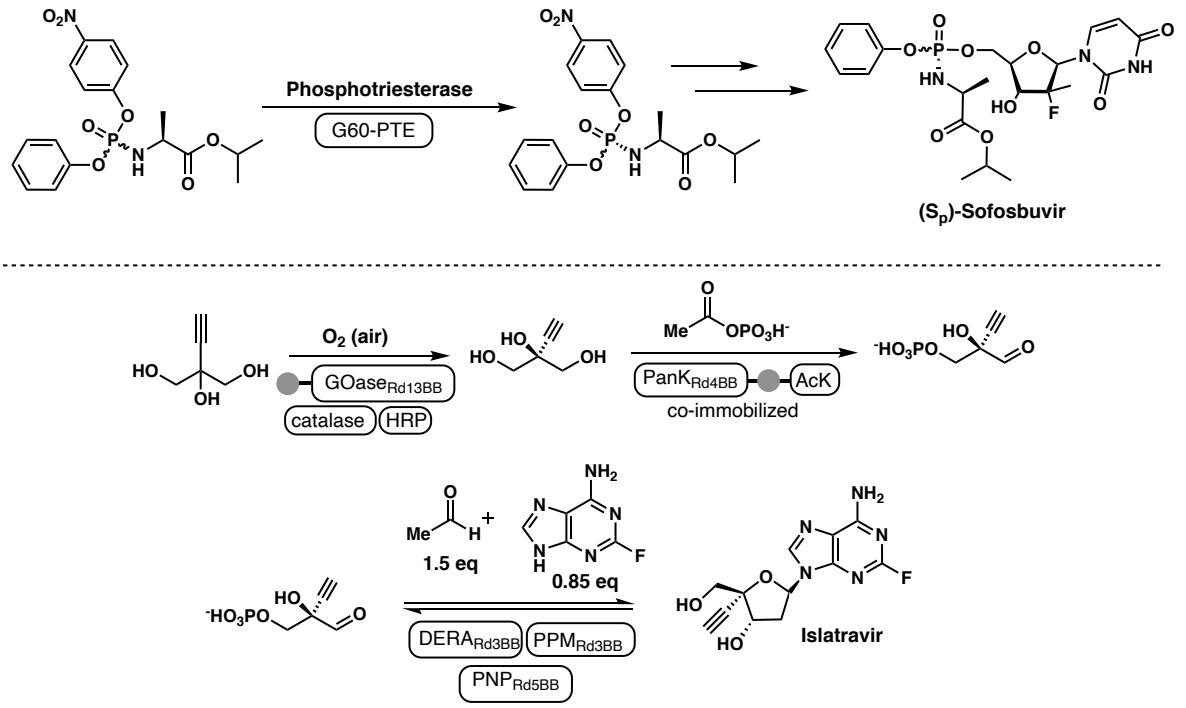
2.1 Introduction and Background

Biocatalysis in the realm of organic synthesis and methodology refers to the use of enzymes isolated from a cell culture to achieve a desired transformation catalytically.[1] Its recognition as a powerful tool for the production of agrochemicals, natural products and API's has increased over the years due to markedly high stereoselectivity, ease of use, and mild aqueous conditions when compared to traditional chemo-catalytic processes.[2-7] The use of the methodology in academia and the industrial setting has recently been supercharged by the recent Nobel prize awarded for directed evolution, which continue to increase the scope of transformations that can occur bio-catalytically.[8]

Generally, there are two approaches to the development and use of biocatalysis in asymmetric organic methodology, the first being enzymatic kinetic resolution, which is a means of discriminating between two enantiomers in a mixture. With this method, one enantiomer reacts at a rate orders of magnitude faster than its counterpart due to its compatibility towards the active site of the enzyme employed. Upon reaction completion, the unreacted starting material and product can easily be separated. An application of this process was recently showcased for the synthesis of a diastereometrically pure nucleotide phosphoamidate intermediate towards the anti-viral Sofosbuvir.[9] The chemistry utilized an evolved phosphotriesterase for the transformation. The second approach, recently applied in the cascade synthesis of the HIV medication Islatravir[10] (Figure 1), is nominally known as

biocatalyzed asymmetric synthesis, in which an achiral substrate becomes chiral through its interaction in the active site of the enzyme. For this method, the chirality of the afforded product, and in-turn the enantiomeric excess, is promoted due to the enzymes' morphology at the active site and the orientation of the substrate in the catalytic pocket during the chemical transformation, with one spatial positioning of the substrate greatly favored over the other. This approach leads to a higher conversion and overall greater yield when compared to the aforementioned biocatalytic kinetic resolution.

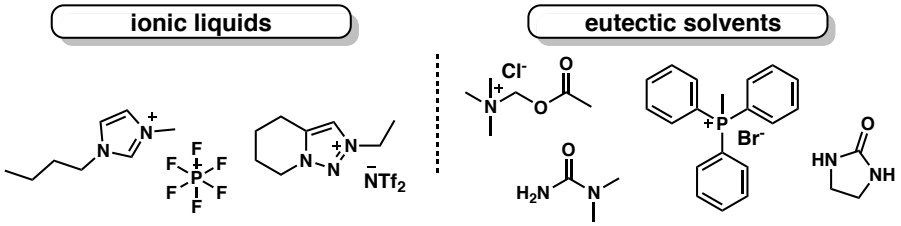
Figure 1. Representative Examples of Enzymatic Kinetic Resolution (top) and Asymmetric Biocatalysis (bottom)



As much as these powerful emerging methodologies have established themselves in process development, the vast majority of biocatalytic transformations occur in an aqueous media due to ability of organic solvents to denature the enzyme, lowering its activity. This parameter establishes limitations in substrate complexity and lipophilicity due to the innate

incompatibility of the organic substrates and the aqueous media in which the biocatalytic transformations occur. Strategies have arisen to mitigate this issue and in turn make biocatalytic transformations more attractive in academia and commercial settings; including bioengineering of chimeric enzymes to increase their tolerability towards organic solvents or increase their thermostability. Another strategy involves the development and use of ionic liquids which are water-like in character but exhibit poor biodegradability or deep eutectic solvents (Figure 2).[11-15] Nonetheless, larger and highly lipophilic substrates still express poor compatibility and overall lower conversions to the desired product.

Figure 2. Commonly Utilized Ionic Liquids (left) and Deep Eutectic Solvents

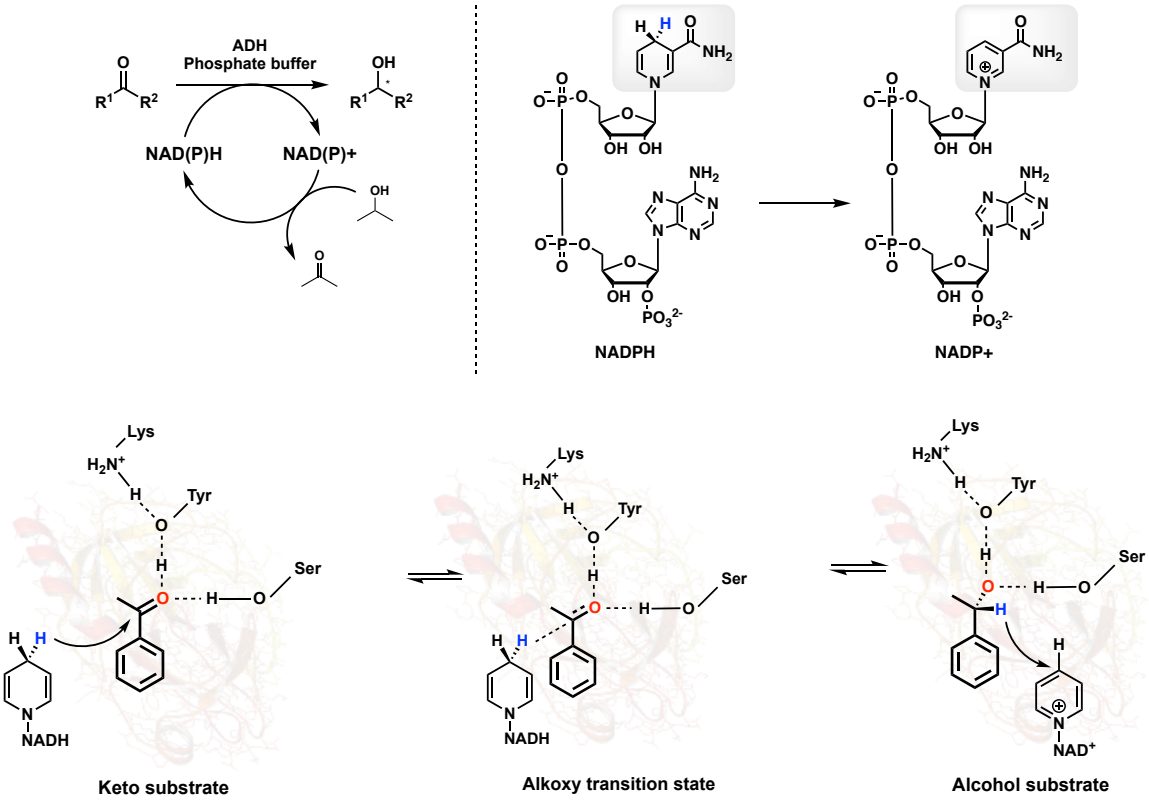


While the use of surfactants to mimic in vivo conditions in biochemistry is far from new, most of the systems described rely on emulsions[16] or reverse microemulsions[17] using an organic or greasy solvent (e.g., hexane, octane) composing the hydrophobic phase of the system. Those methods are adapted most notably when enzymes and substrates have different solubilities, allowing for a larger contact surface, but by definition, do not avoid the use of organic solvents. To begin to address the challenges associated with biocatalysis and its use in organic methodology, designer surfactants including TPGS-750-M were explored as a viable medium due to its ability to enable numerous organic transformations of highly functionalized substrates.[18] The use of TPGS-750-M in synthetic biology had precedent in the literature as it has been observed to accelerate the production of styrene by *Escherichia coli*

through interaction with the membrane of the whole cell, in addition to 1-pot fermentation then, cyclopropanation, confirming aqueous media-containing TPGS-750-M is bio-compatible.[19,20] With this knowledge, we explored its compatibility towards other enzyme classes in the hopes of expanding chemo-enzymatic tandem processes that could be performed to access more complex, enantioenriched products. The preliminary focus was on the oxidoreductase class of enzymes: the first being the well characterized and widely used alcohol dehydrogenase (ADH) and later the subset of enzymes commonly referred to as the Old Yellow Enzyme (OYE) or ENE-reductases, which catalyze the reduction of α,β-unsaturated compounds.

The alcohol dehydrogenase acquired from the commercial supplier Johnson Matthey was investigated. This subset of enzymes reduces a ketone into a chiral alcohol or can generate a ketone depending on the pH of the aqueous buffer that is present (Figure 3). In the mechanism of action, the reducing agent, NADPH, nominally referred to as the co-factor, functions as the hydride donor.

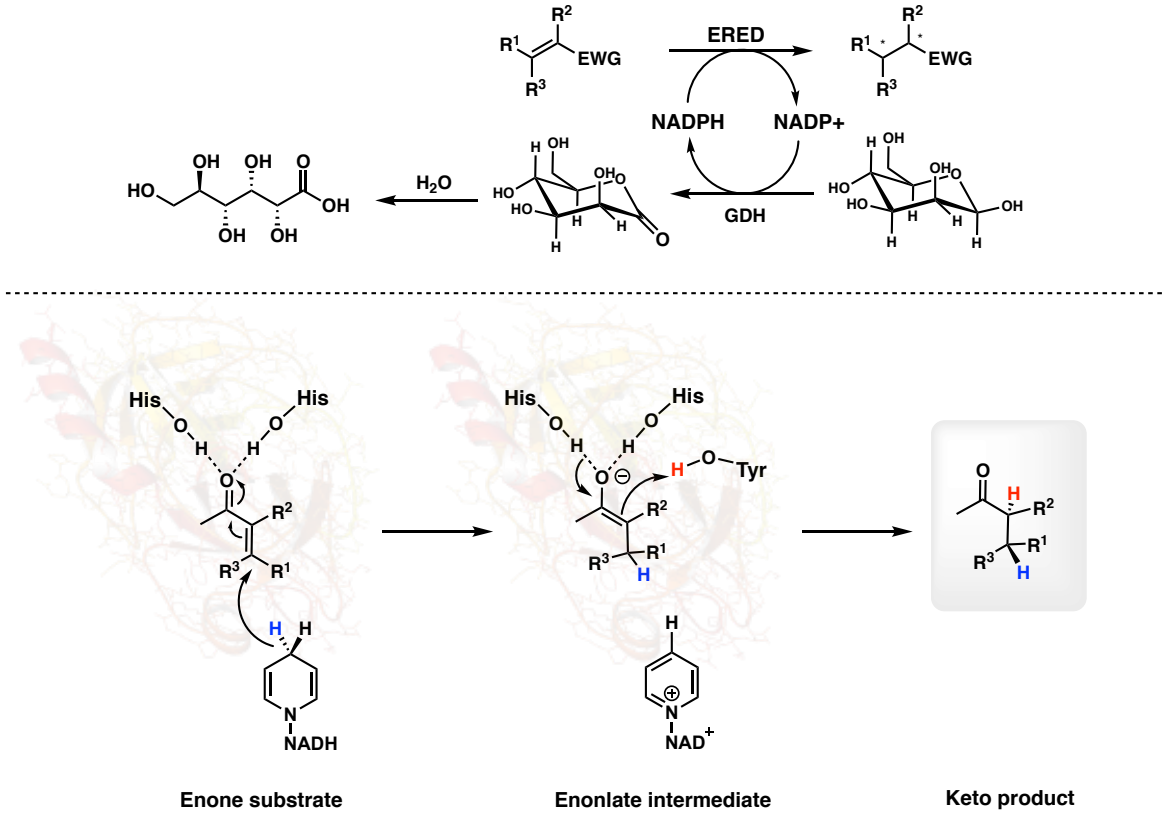
Figure 3. General Mechanism for Ketone Reduction by the Oxidoreductase ADH



The co-factor is typically used stoichiometrically as a hydride donor, however, this can prove to be a costly process due to the expense of the co-factor and some of its other derivates. Nonetheless, the co-factor can be regenerated *in situ* by the reduction of $NAD(P)^+$. This can be achieved by a second enzyme or a sacrificial reductant like isopropanol which is applied in excess. The sacrificial reductant also functions as a driver of the equilibrium towards the desired chiral product alcohol. In the active site of the ADH family of enzymes, three amino acid residues are conserved: serine, tyrosine, and lysine. They are primarily responsible for the bioactivity of the enzyme and impart the desired chirality to the substrate in which they activate due to the orientation imposed by the intermolecular forces between the substrate and the active site. Hydride donation by the co-factor yields the chiral alcohol.[21]

The subset of enzymes referred to as the Old Yellow Enzyme (OYE) family of oxidoreductases is used extensively to catalyze the reduction of activated Csp^2-Csp^2 bonds including α,β-unsaturated aldehydes, ketones, carboxylic acid derivatives, nitriles and nitro group-containing compounds due to its excellent stereoselectivity, and its broad functional group tolerance via an *anti*-reduction after activation by two conserved histidine residues in the catalytic pocket. Hydride conjugate addition from a nucleotide co-factor, followed by subsequent protonation from a tyrosine residue in the active site affords the desired enantio-rich alkane (Figure 4). For our purposes, we acquired the family of enzymes, ERED, from the commercial supplier Codexis. Like the ADH class of enzymes, these enzymes employ NADP as the co-factor. To recycle the nicotinamide co-factor, glucose dehydrogenase (GDH) is used in tandem with an excess of glucose as the sacrificial reductant. In the mechanism of action, GDH converts glucose to gluconolactone which hydrolyses to gluconic acid under buffered aqueous conditions. This method in turn makes the reduction irreversible.[22,23]

Figure 4. General Mechanism for activated Csp^2-Csp^2 Reduction by Ene-Reductase



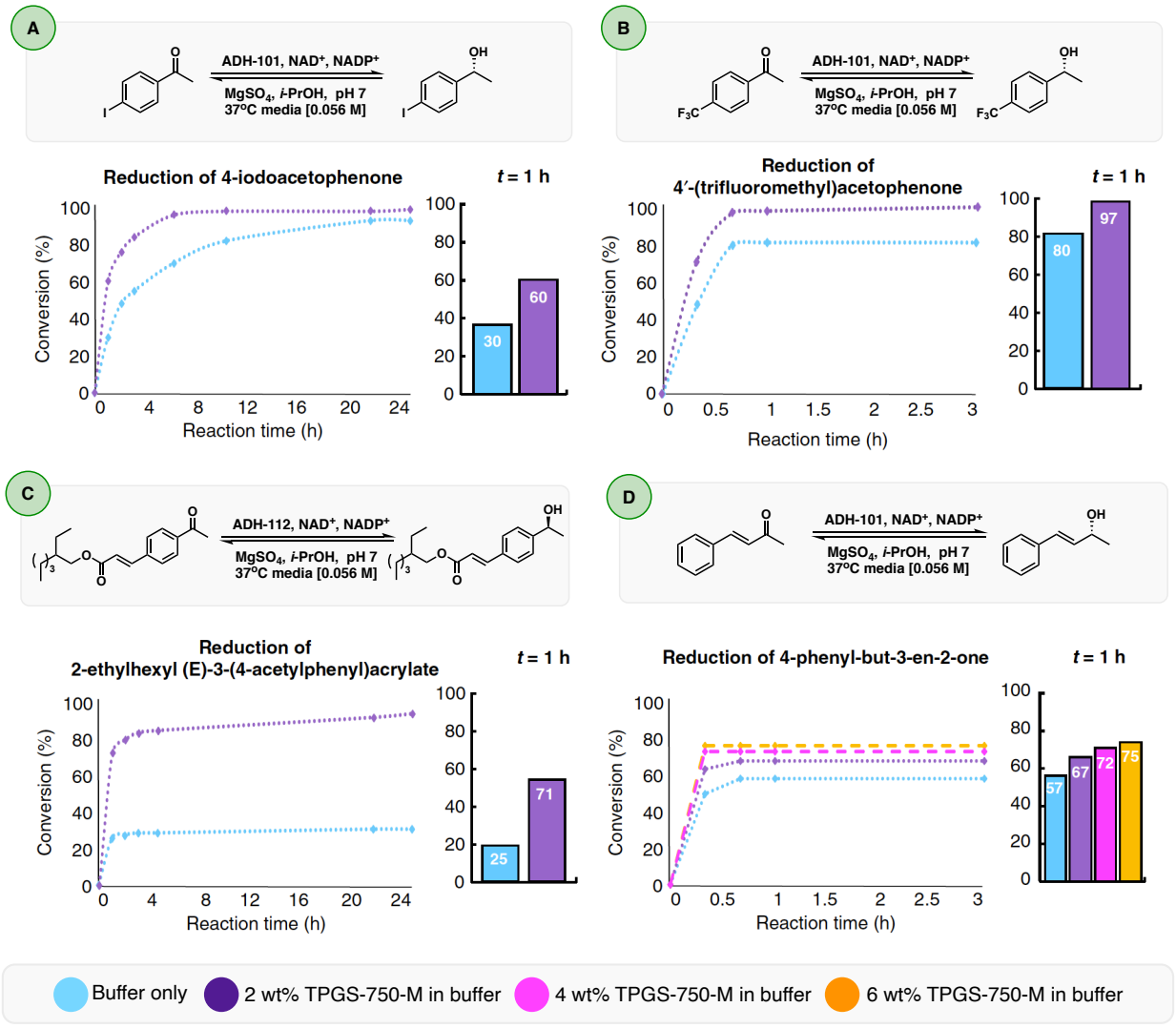
2.2 Results and Discussion

We first explored the effect of surfactant-containing media on the ADH class of enzymes. To establish the compatibility of alcohol dehydrogenases and micelles derived from TPGS-750-M in water, asymmetric reductions of four different ketones were evaluated. These educts included 4-iodoacetophenone (Figure 5a), 4′-(trifluoromethyl)acetophenone (Figure 5b), the product from a Heck coupling, 2-ethylhexyl (E)-3-(4-acetylphenyl)acrylate (Figure 5c), and 4-phenyl-but-3-en-2-one (Figure 5d); all reactions were performed in a phosphate buffer (0.2 M) at pH 7 with and without 2 wt% of TPGS-750-M. Remarkably, enzymatic superactivity[24] is observed as the lipophilicity of the substrate increased.

Indeed, the presence of the surfactant positively impacted the outcome of the reaction, leading to faster reaction rates. In the case of Figure 5a, the reduction went to completion far more rapidly in the presence of micelles. Enantiomeric excesses were excellent (>99.8% ee) in both cases. By slightly increasing the lipophilicity of the substrate (Figure 5b), the reaction plateaued at 80% conversion in buffer alone, while reaching completion in the corresponding aqueous surfactant solution. The same observation was made in Figure 5c, with an even greater gap between both media (plateauing at 30 *vs.* 92%). The slope discontinuity after one hour in buffer may indicate enzyme saturation. The phenomenon was reduced, or suppressed, at a given substrate concentration (20 mg of enzyme for 0.4 mmol of ketone [0.056 M]), in the presence of TPGS-750-M.

Our rationale for these observations is that under typical conditions, entrance to the enzymatic pocket is eventually hindered by the buildup of water-insoluble substrates and potentially as well due to the more lipophilic products, all looking to gain (re)entry. This leads to incomplete conversions in solely buffered aqueous media, as these data show. In the presence of micelle-forming TPGS-750-M, however, the micelles function both as a desirable solvent (*vs*. the surrounding water) and as a reservoir, housing and releasing substrates and products as a normal matter of dynamic exchange between micelles.[25] Educts undergoing such a phenomenon find their way to the far less encumbered enzymatic cavity, enabling eventual reduction. Thus, micelles in the buffer help to control both substrate and product concentrations in an aqueous medium, providing a measured supply that does not overwhelm the enzyme leading to enzymatic inhibition, thereby allowing for higher rates of conversion.

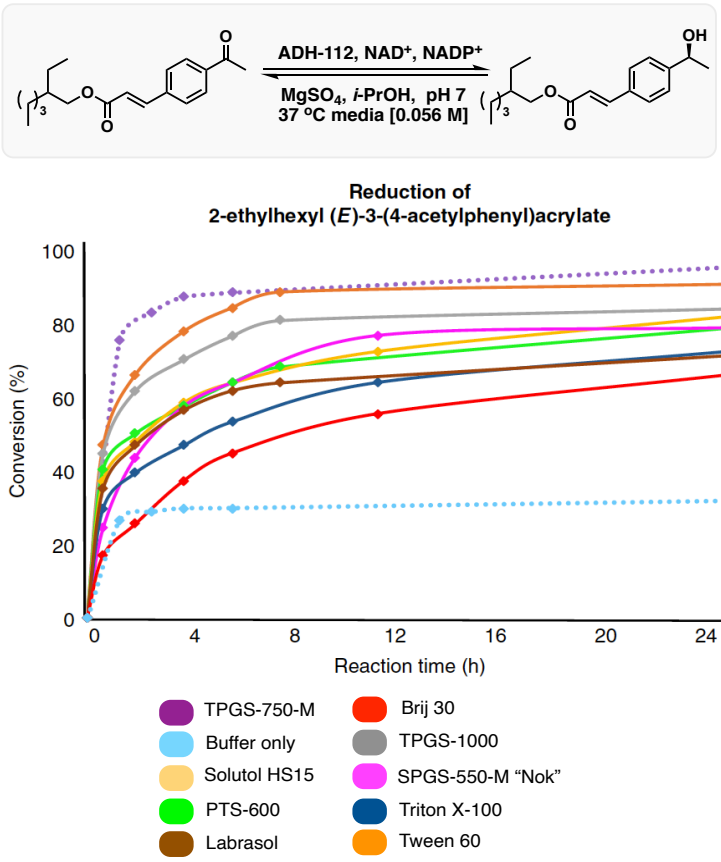
Figure 5. Ketone Reductions with/without TPGS-750-M



To further investigate this hypothesis, the impact of the concentration of TPGS-750-M on reaction rates associated with reduction of both an aryl ketone (Figure 5c) and an enone (Fig. 5d) were assessed. The former, a keto ester, shows a dramatic difference between the extent of conversion in buffer *vs.* that in 2 wt% TPGS-750-M, raising the overall conversion from ca. 30 to over 90%. For the enone, also a challenging substrate for this particular enzyme, its reduction stops at 49% conversion under purely buffered conditions.

While in-depth structural investigations would be needed to understand why such a dramatic stop to this reaction occurred, it is worth mentioning that, by increasing the amount of TPGS-750-M to 6 wt%, the conversion jumps to 75%. These results confirm that increasing the available volume of solvent in this aqueous medium helps to moderate enzyme saturation, supporting a reservoir effect. Based on these early observations, several other commercially available nonionic surfactants were evaluated under identical conditions (Figure 6). Reduction by ADH-112 of 2-ethylhexyl (E)-3- (4-acetylphenyl)acrylate was monitored over time (cf. Figure 5c). Comparisons between Tween 60 (orange line), TPGS-1000 (light gray line), solutol HS15 (yellow line), SPGS-550-M (aka "Nok"; pink line), PTS-600 (green line), Triton X-100 (dark blue line), labrasol (brown line), and Brij 30 (red line) were compared to the initial results obtained in buffer vs. those from 2 wt% TPGS-750-M/buffer. In line with expectations, given that each surfactant is capable of serving in a similar capacity, all led to superior results compared to that in buffer alone, again lending further credence to the proposed "reservoir" effect. None, however, outperformed use of 2 wt% TPGS-750-M.

Figure 6. Comparisons of Commercially Available Surfactants

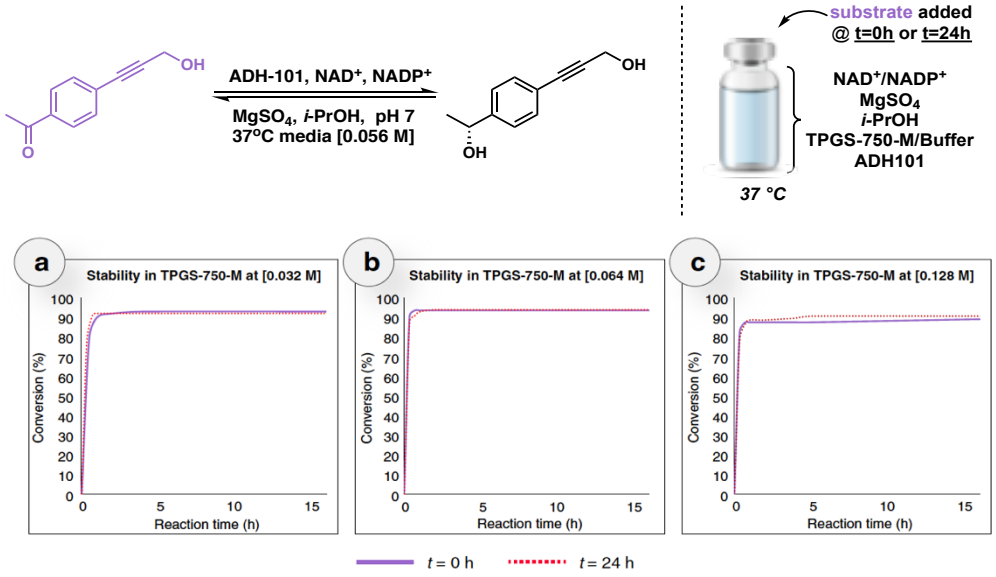


The stability of the enzyme ADH 101 in the presence of TPGS-750-M over time was further evaluated, as surfactants, on occasion, have been reported to denature enzymes.[24] Reduction of 1-(4-(3-hydroxyprop-1-yn-1-yl)phenyl) ethan-1-one at 0.032 M was carried out, and after 24 h of incubation (Figure 7a), there was no apparent impact on enzymatic activity. Even at higher substrate concentrations (Figure 7b, c—[0.064 M] and [0.128 M], respectively), where only incomplete conversion is achieved (plateaued at 90%), no loss of activity was observed after 24 h of incubation. Circular dichroism (CD) analyses further confirmed that the enzyme structure is not compromised in the presence of surfactant. ^{1}H NMR spectra, taken with and without surfactant present, overlap perfectly, especially in the amide and CH_3 regions

where no strong interaction is detected. The absence of signal modification in the CH_3 region tends to exclude the hypothesis that the enzyme is inside the micelle. The micelles also remain undisturbed by the presence of the protein as the same average diameter was detected by dynamic light scattering analyses of a solution of TPGS-750-M/buffer in the presence of, or in the absence of, ADH-101.

Following optimization of experimental conditions, sequential two-step, one-pot processes were investigated. Cross-coupling reactions, as well as hydration of alkynes, were directly followed by reduction of each ketone-containing product by ADH in the same pot. While some early experimental challenges had to be overcome (*vide infra*), second-stage enzymatic reductions were found to be compatible with the presence of metals, such as palladium, copper, rhodium, iron and gold, along with various salts that may have been generated from a prior reaction. While most metal-mediated reactions performed in TPGS-750-M/H_2O involve substrate concentrations of 0.5 M, such conditions are not compatible with the reductases being used, leading to incomplete conversions. Therefore, dilution of the medium was required prior to addition of the alcohol dehydrogenase, from [0.500 M] to [0.056 M] (dilution by ≈10 of the ketone), while the temperature was adjusted to 37 °C. Despite a claimed optimal pH of 7, we observed that the enzyme can tolerate a broader pH range (from 4 to 7). Cross-coupling reactions in water that involve basic conditions, however, are performed at elevated pH and hence, an adjustment to neutral-to-acidic conditions is required prior to the biocatalytic step. Tests where addition of an enzyme at a higher pH followed by pH lowering to 7 led to no reduction.

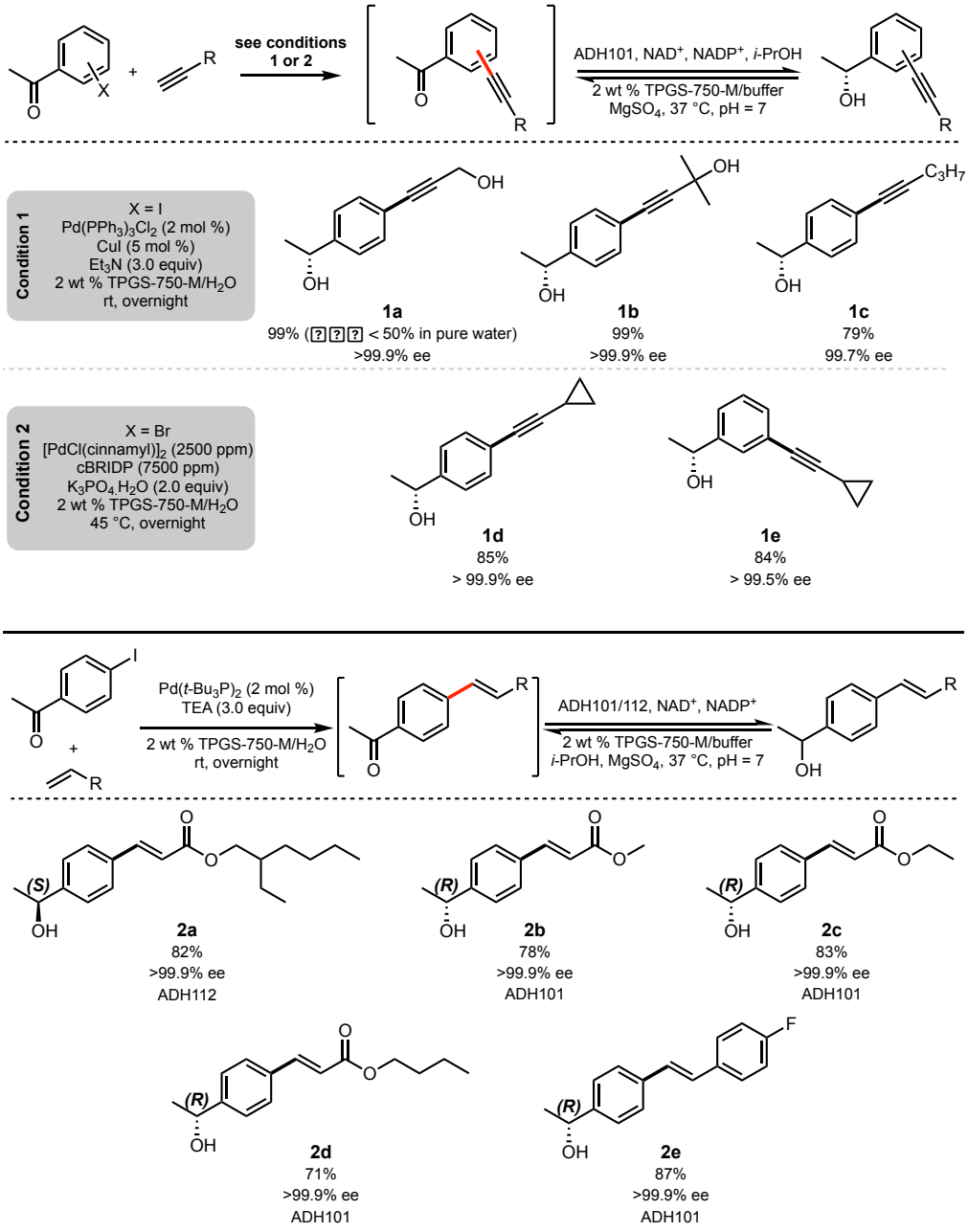
Figure 7. Stability of ADH-101 in aq. TPGS-750-M



The 1-pot Pd-catalyzed Sonogashira cross-coupling of an acetoaryl iodide or bromide followed by a biocatalytic ketone reduction was initially studied. Variations in experimental conditions mainly focused on the tolerance of the enzyme to the presence of copper and palladium, although only ppm levels of Pd are required for these reactions (Figure 8). Upon generation of an arylated product alkyne, the pH was decreased to seven, followed by addition of ADH and the cofactor. Asymmetric reduction of the ketone present in each afforded the corresponding nonracemic alcohols with excellent enantioselectivities (>99.5% ee). The overall yields of the two-step processes are identical to the yield characteristic of the first step alone, attesting to the impressive efficiency of the enzymatic process independent of its modified environment. The background sequence run in the absence of TPGS-750-M leading to product **1a** led to a significantly decreased overall yield (less than 50%), demonstrating of the importance of the surfactant in the tandem process. The enzyme also performed quite well in combination with Heck reactions (Figure 8).[26] Both ADH-101 and ADH-112, being (*R*)-

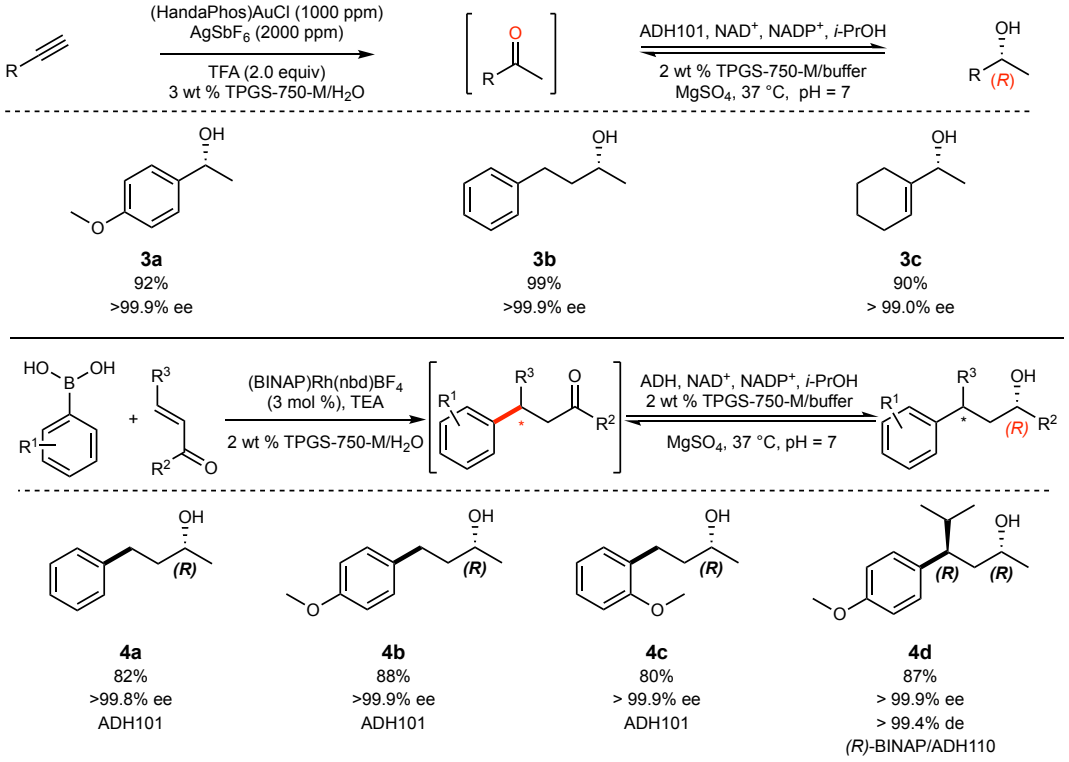
and (*S*)-selective, respectively, towards an acetophenone led to enantiomeric products (**2b**−**e** *vs*. **2a**) with essentially perfect fidelity (>99.9% ee). Notably, even 2 mol % of Pd (*i.e.,* 20,000 ppm) is well tolerated by the enzyme.

Figure 8. Sequential Sonogashira coupling/ADH-ketone Reduction (top) and Heck cross-coupling/ADH-ketone Reduction (bottom) enabled by TPGS-750-M



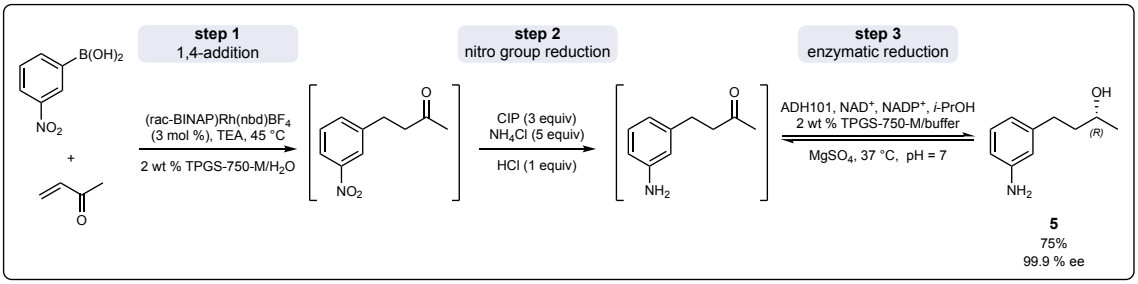
Switching to ppm-level gold catalysis, generation of ketones *in situ* via hydration of terminal alkynes[27] followed by their reduction to the corresponding nonracemic alcohols led to excellent results as well (Figure 9a). Lastly, exposure of the same enzymatic system to rhodium, used catalytically to affect an initial 1,4-addition[28] of a boronic acid to an enone, was of no consequence, as ketone reduction took place uneventfully (Figure 9b). Interestingly, a match/mismatch effect was observed with compound **4d**. Indeed, when the first step is conducted with *rac*-BINAP, ADH-110 transformed only the 4(*R*)-enantiomer, leaving the 4(*S*)-product intact. ADH-105, (*S*)-selective toward acetophenone, performed the reaction only on the 4(*S*)-enantiomer. When the reaction was conducted with (*R*)-BINAP a adduct of 97.5% ee (*R*) was obtained for this first step, while the final product (in a 1-pot process) was obtained (yield = 87%) with >99.9% ee and>99.4% de, with 2.5% of the opposite enantiomer remaining.

Figure 9. Au-catalyzed Hydration of Alkynes/ADH-Ketone Reduction (top) and Rhodium-catalyzed 1,4-additions/ADH-ketone Reduction (bottom) enabled by TPGS-750-M



To further illustrate the potential for these tandem events in synthesis, the 1-pot process could be smoothly extended to three-steps, the product (overall 75%, 99.9% ee) resulting from a sequential 1,4-addition, followed by a nitro group reduction and ultimately, reduction by ADH-101 (Figure 10). The enzyme fully reduced the ketone in less than 2 h, notwithstanding the presence of Rh, Fe, and other metal salts. The significant robustness having been added to the biocatalytic step by the presence of TPGS-750-M in the medium opens the door to additional, potentially even longer sequences, all in water under very mild conditions, as these enzymes appear to tolerate a mixture of residual catalysts in the pot from previous steps.

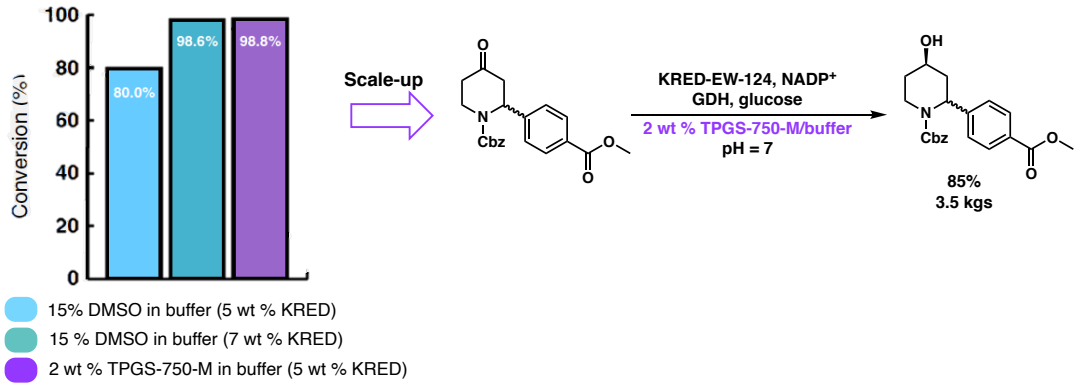
Figure 10. Sequential Reactions combining Chemo-catalysis and Bio-catalysis



The beneficial impact of TPGS-750-M on enzymatic activity was applied to an industrial scale process with the multi-kilogram synthesis of the functionalized chiral 4-piperidinol (Figure 11). The reaction, performed in TPGS-750-M/H_2O, was compared to that run using 15% DMSO/H_2O, both in a phosphate buffer at 40 °C using 5% KRED-EW-124. In aqueous TPGS-750-M the reaction reached 98% conversion after 25 h, while in DMSO/H_2O it stopped at 80%; an additional 2 wt% of enzyme was necessary to access the same 98% level of conversion. Extensive optimization also led to an increase of more than 50% in the concentration of the product in the reaction mixture, thus resulting in a substantial increase in productivity.

Indeed, compared to an optimized process in DMSO, the approach using TPGS-750-M/H_2O leads to a reduction of the Process Mass Intensity (PMI) of more than 32%, and a productivity increase of greater than 40%. Importantly, evaluation of ADH-101 on 4-phenylbut-3-en-2- one (Figure 5d), with 10 v/v % of THF in the reaction mixture, commonly used as cosolvent in industrial applications[29,30] showed no decrease in activity. Likewise, the presence of high concentrations of salts (e.g., 2 M NaCl)[31] did not alter the outcome. Additionally, the water-soluble surfactant is not extracted with the product and any residual traces can be easily separated by a filtration through a small pad of silica.

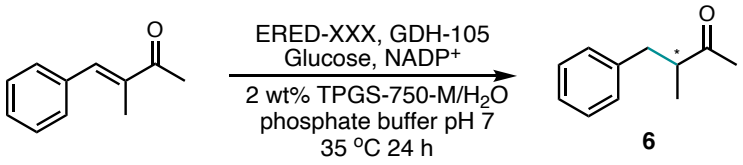
Figure 11. Industrial Scale Multi-kilogram Synthesis



After seeing the net positive effect surfactant-containing media imparted to the ADH family of enzymes, we explored another class, the OYE ENE-Reductases, to see if a similar phenomenon would occur. To determine the compatibility of the OYE class of enzymes and micelles derived from the designer surfactant TPGS-750-M in water, we selected 3-methyl-4-phenylbut-3-en-2-one (**6**) as the model substrate which can easily be prepared from the aldol condensation of methyl ethyl ketone and benzaldehyde. Activity was assessed without the presence of the co-solvent DMSO, which is typically employed with the buffered media (Table

1). We selected the class of commercially available EREDs from Codexis[32] for the selective reduction. From the seven ene-reductases screened, the ERED-103 showcased the greatest activity in the buffered surfactant medium, giving the highest conversion in addition to good enantiomeric excess. We were also encouraged when we observed that the presence of the surfactant did not affect the stereoselectivity of the enzyme (**entry 1**).

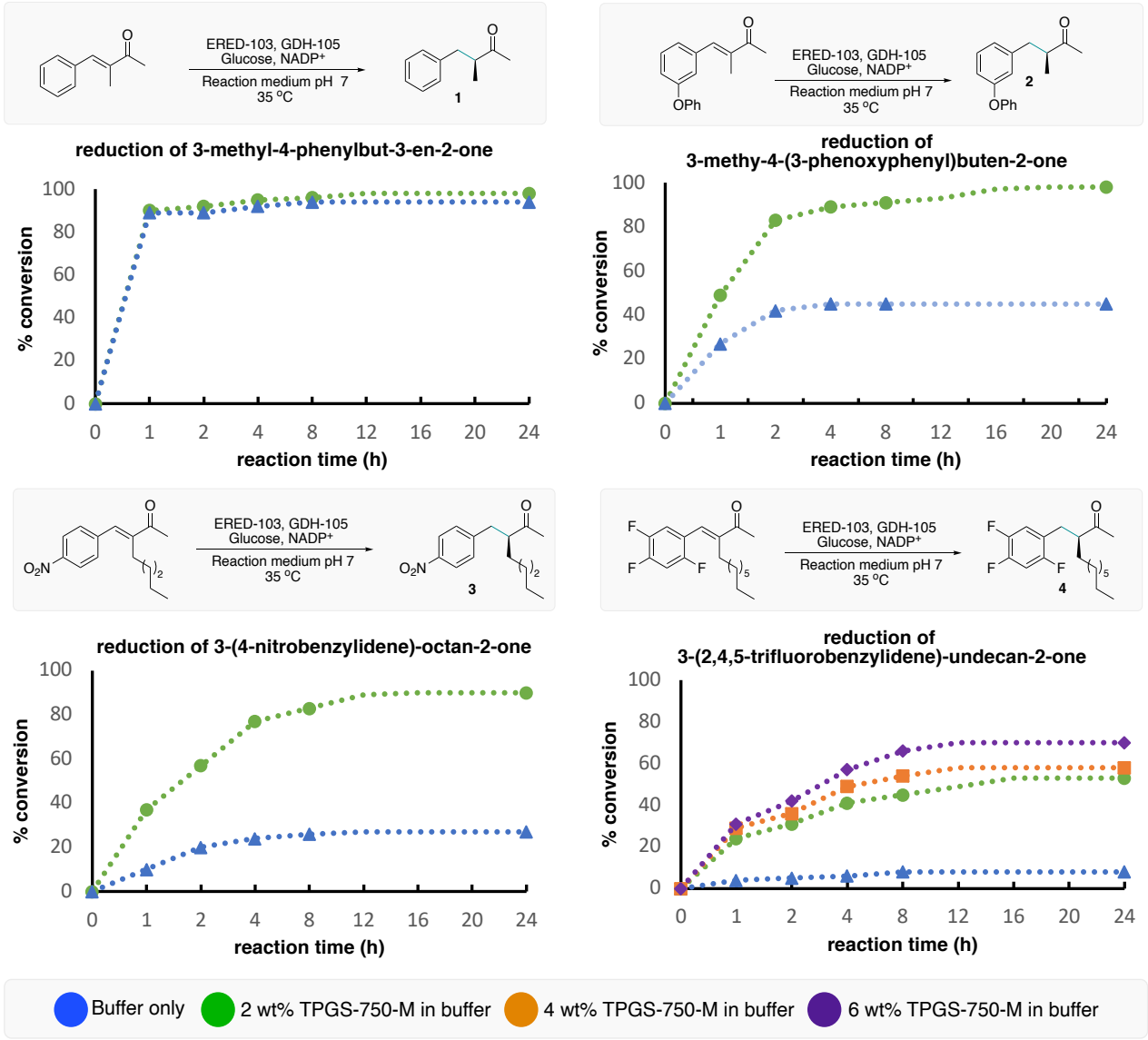
Table 1. ENE-Reductase Enzyme Screen in Aqueous Surfactant Media



Entry	Enzyme	% Conversion	% ee
1	ERED-103	99	93 (93)[a]
2	ERED-110	97	83
3	ERED-112	99	77
4	ERED-207	92	20
5	ERED-P1-A04	93	92
6	ERED-P1-E01	91	95
7	ERED-P1-H09	65	34

With this result available, we wanted to see if the presence of the surfactant in the buffered medium assisted the enzyme when dealing with more highly lipophilic substrates. Stereoselective reduction of four different enones varying in functionality and lipophilicity were assessed (Figure 12). These educts included 3-methyl-4-phenylbut-3-en-2-one (**6**), 3-methyl-4-(3-phenoxy-phenyl)but-3-en-2-one (**7**), 3-(4-nitrobenzylidene)octan-2-one (**8**) and 3-(2,4,5-trifluoro-benzyl)undecan-2-one (**9**), all products of an aldol condensation with their respective aryl aldehydes.

Figure 12. Enone Reduction with/without Surfactan

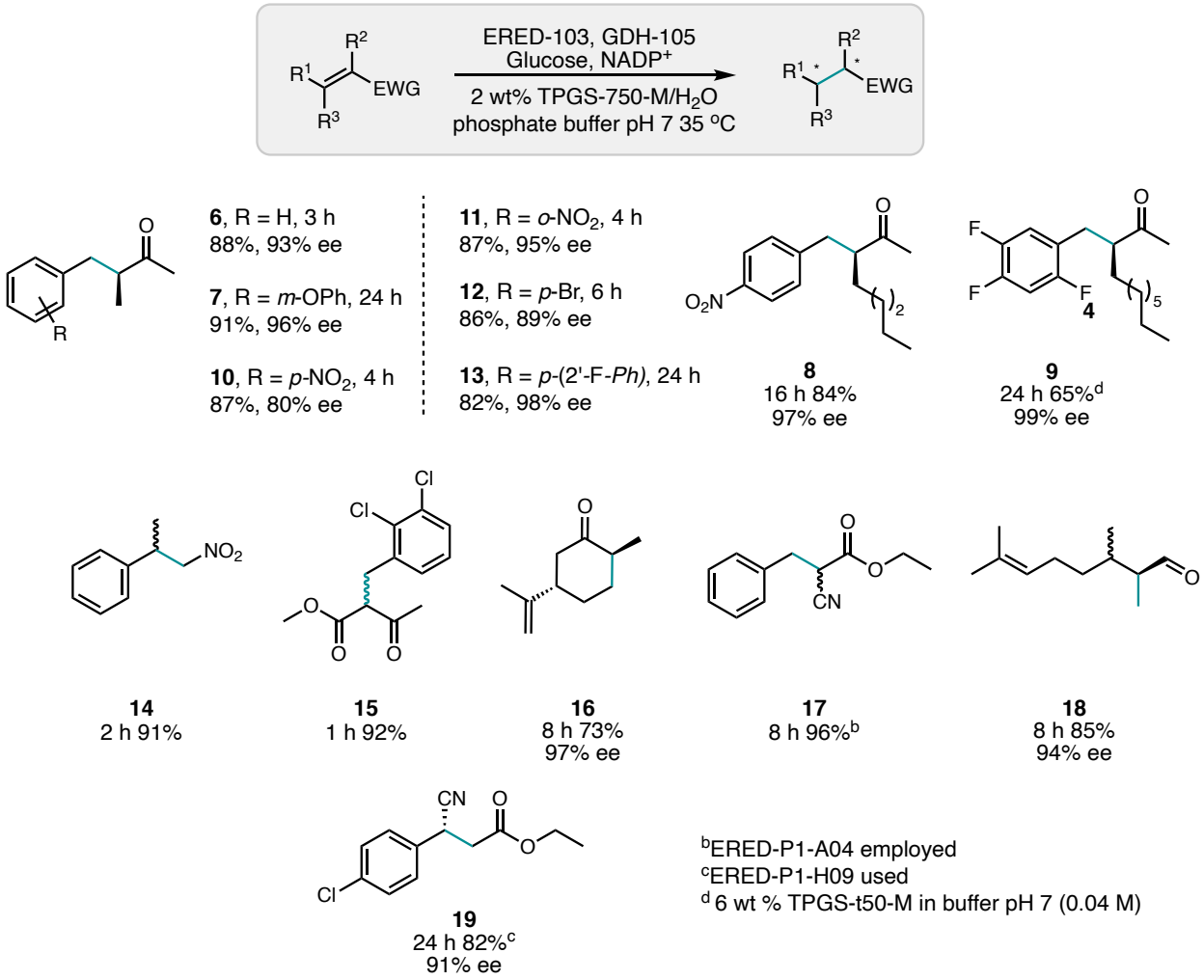


The reactions were performed in a phosphate buffer (0.1 M) at pH = 7 with and without TPGS-750-M present. For these substrates, we were pleased to discover that not only did the presence of the surfactant not interfere with the bio-catalytic activity of the enzyme, but the enzyme also seemed to exhibit increased activity directly correlated to increasing lipophilicity of the substrate. In the case of compounds **8** and **9**, not only were faster reaction rates observed, but the enzymatic transformation was also able to achieve a far greater degree of conversion

in the presence of micelles, while we observed slope discontinuity in media that contained just the buffer. This may indicate an unfavorable interaction between the substrate and the enzyme that is suppressed when micelles are in solution, lending credence to the reservoir effect that was observed with the alcohol-dehydrogenase class of enzymes (*vide supra*). This effect is more apparent in the case leading to product **9**; by increasing the amount of surfactant in solution to 6 wt %, the conversion reaches 70%, while enzymatic activity is essentially halted below 10% in just the buffered media.

We next investigated the scope of the ERED class of enzymes by exploring a variety of activated olefins (**Figure 13**). *ortho*-, *meta*-, and *para*-Substituted products **6-13** were all formed under optimized conditions, providing suitable enantiomeric excesses (80-98%). For the trifluoro-substituted enone precursor leading to product **9**, a maximum yield of 65% was obtained in the presence of a 6 wt % aqueous surfactant, in stark contrast to the same substrate in just a buffered medium which exhibited minimal conversion after 24 h. For educts, **14**, **15**, and **17**, reduction to the saturated alkane was achieved, however, with limited enantioselectivity observed. However, this could be attributed to the low pKa of the α-proton on the product, which can easily undergo epimerization or enolization in aqueous solutions. Nonetheless, the functional group tolerance of the methodology should be noted, especially when compared to traditional chemo-catalytic reductions. The terpenoid (*S*)-carvone **16**, and fragrance compound bergamal **18**, were also amenable to the reduction conditions, affording modest yields. For the precursor to the muscle relaxer baclofen **19**, conversion to the desired β-cyano-ester, was achieved. However, as robust as the enzymes were to substrates that were assessed, we did observe low to reactivity to unsaturated carboxylic acids, nitriles, and esters. Nonetheless, another class of enzymes or directed evolution could mitigate the limitation.

Figure 13. Substrate Scope of Bio-catalyzed Reduction of Activated Olefins



Following experimental compatibility and reaction scope, we investigated sequential, 1-pot processes with the goal of expanding the variety, as well as the number of transformations that could be performed under micellar conditions (**Figure 14**). A 1-pot enzymatic (ERED) enone reduction followed by ketone reduction with the aforementioned ADH-101 gave the alkyl alcohol **20** with two new stereocenters in good yield and high enantiomeric excess and diastereoselectivity (Figure 14A). We were pleased to see that the presence of the micellar medium did not negatively impact the efficacy of tandem biocatalytic processes. The biaryl adduct **13** could be formed in modest yields *via* a 1-pot ppm level Pd-catalyzed Suzuki-

Miyaura coupling followed by dilution of the reaction mixture with a 2 wt % TPGS-750-M phosphate buffer to facilitate enzymatic reduction. This sequence showcases the compatibility of the enzyme in the presence of aqueous micelles being used in especially valued Suzuki-Miyaura couplings (Figure 14B). The transaminase class of enzyme (ATA) provided by Codexis can also easily be employed in a telescoped sequence involving enone reduction to ultimately afford an alkyl amine with high enantiopurity and diastereoselectivity (Figure 14C). Extraction of the amine intermediate, solvent evaporation, and reintroduction of the intermediate into aqueous media for its conversion to the corresponding *N*-carboxybenzyl protected adduct **21** in modest overall yield. Palladium-catalyzed cyanation utilizing a Xantphos derived palladacycle,[33] can easily be telescoped to include a bio-catalytic sequence utilizing both an enone reductase and ADH to afford the enantiopure product **22** in 54% overall yield over three steps with high enantiomeric excess and diastereoselectivity (Figure 14D). The enzymes were able to perform their respective transformations in the presence of the required reagents associated with the Pd-catalyzed cyanation, as well as any by-products formed in any of these transformations, showcasing the compatibility of multi-step functionalization of a substrate mediated by aqueous micelles.

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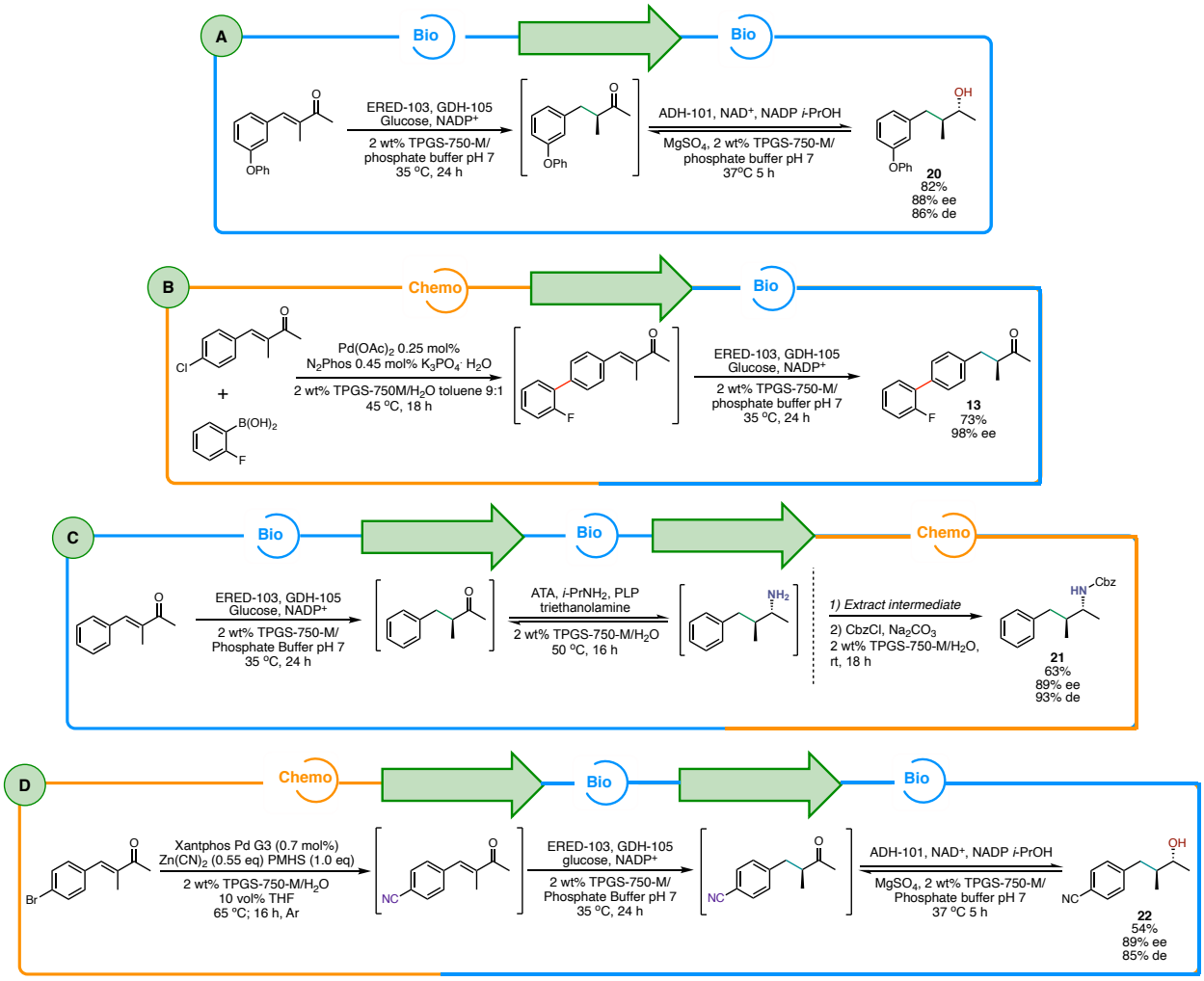
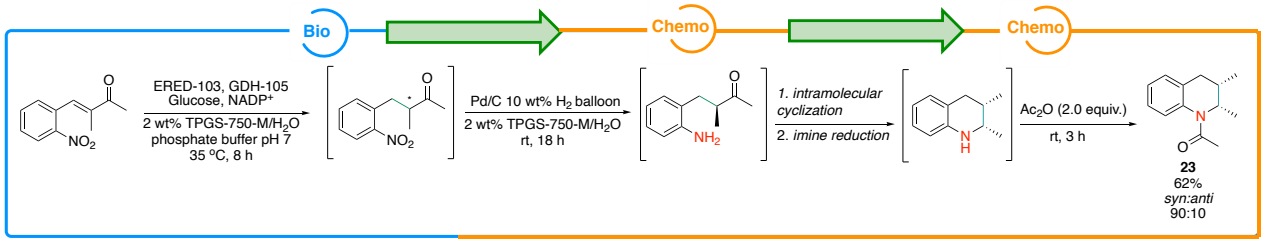
Figure 14. Tandem 1-pot Bio/Bio and Bio/Chemo Processes in Aqueous Micelles



To further illustrate the versatility of the micellar system, an even longer multi-step process utilizing the combination of both chemo- and bio-catalytic methods was assessed (**Figure 15**). After initial enzymatic (ERED) reduction of enone **23**, pH adjustment allowed for a Pd/C nitro group reduction, followed by intramolecular cyclization. The imine intermediate formed can be reduced by the presence of the Pd/C reducing agent, allowing for two chemical transformations using the same reagent in the pot. The intermediate amine could easily be acylated in situ via introduction of Ac_2O to afford the acylated tetrahydroquinoline **23** in 62% overall yield and in high stereoselectivity (*syn* : *anti* = 90:10).

Figure 15. Tandem Multi-step Bio/Chemo Processes in Aqueous Micelles



2.3 Conclusion

Aqueous solutions containing micelles derived from the tailor-made surfactant TPGS-750-M have been shown to be not only fully compatible with alcohol dehydrogenase and ene-reductases, but also responsible for enhancing enzymatic activity, especially towards highly lipophilic substrates. While no direct interactions are detected between both of these nanoreactors in the aqueous medium (i.e., between micelles and enzymes), the former appear to serve as reservoirs for substrates and mainly, products (and presumably catalysts), thereby moderating the degree of enzyme saturation. Chemo- and bio-catalysis can now be combined in a 1-pot sequential fashion involving four steps, both run under mild conditions, leading to virtually stereopure products of far greater complexities. Use of the surfactant also clearly increases the productivity associated with large-scale applications. These results suggest that similar outcomes might be anticipated using other types of enzymatic processes based on readily available kits. The future of organic synthesis, therefore, looks to involve such a "marriage" between both types of catalysis, used in tandem, and enabled by the presence of a designer surfactant, all in Nature's chosen "solvent": water.

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2.5 Experimental Data

1. General Information

Silica gel TLC plates (UV 254 indicator, thickness 200 mm standard grade, glass backed and 230-400 mesh from Merck) or Aluminum Oxide 60 F254 polyester basked plates (Sigma-Aldrich, 0.2 mm thick) were used. The developed TLC plate was analyzed by a UV lamp (254 nm). The plates were further analyzed with the use of an aqueous potassium permanganate stain or butanolic vanillin and developed with a heat gun. All commercially available reagents were used without further purification. A 2 wt % TPGS-750-M/H_2O solution was prepared by dissolving TPGS-750-M in degassed HPLC grade water. TPGS-750-M is also commercially available. Reagents were purchased from Sigma-Aldrich, Combi-Blocks, Alfa Aesar, or Acros Organics. Flash chromatography was performed using Silicycle Silicaflash® P60 unbonded grade silica. Codex® Ene Reductase Screening kit is commercially available from Codexis. ADH-101, ADH-105, ADH-110, and ADH-112 are commercially available from the enzyme kit EZK-001 from Johnson Matthey. The ^{1}H and ^{13}C NMR were recorded at 25 ºC on either a Varian Unity Inova 500 MHz or a Varian Unity Inova 600 MHz spectrometers in $CDCl_3$ with residual $CHCl_3$ (^{1}H = 7.26 ppm, ^{13}C = 77.16 ppm) as the internal standard. Chemical shifts are reported in parts per million (ppm). The data presented will be reported as follows; chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (if applicable) and integration. HRMS data were recorded on a Waters Micromass LCT TOF ES+ Premier mass spectrometer using ESI ionization. Chiral HPLC data were collected using an Agilent 1220 HPLC. HRMS data were recorded on a Waters Micromass. LCT α-values were measured on a

Perkin Elmer Polarimeter 341 in a cuvette (l=10cm) at 589 nm (Na lamp). Concentration *c* is given in g/100mL.

2. Preparation of Buffer Solution

Aqueous 1 M stock solutions of potassium phosphate monobasic (**A**) and potassium phosphate dibasic (**B**) were prepared. A pH 7 phosphate buffer solution was then prepared by mixing 38.5 mL of solution **A** with 61.5 mL of solution **B**. The pH was controlled and adjusted, if needed, with a 1 M solution of NaOH or HCl. The buffer solution was diluted with HPLC grade water to 0.1 M. TPGS-750-M, as a wax, was dissolved in water (2 wt %) and used as medium for the reaction. 4 and 6 wt % of TPGS-750-M in the buffer solution were also prepared. TPGS-750-M is available from Sigma-Aldrich (catalog #733857 (solution) or #763896 (wax)). Potassium phosphate monobasic and dibasic were purchased from Sigma Aldrich.

3. **Conversion Monitoring in Buffer and TPGS-750-M/Buffer**

To evaluate the impact of TGPS-750-M on the conversion of four different substrates by alcohol dehydrogenases, comparative monitoring was performed. To a 1 dr vial were added the ketone (0.2 mmol, 1 equiv), $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg) and $NADP^+$ (2.4 mg). *i*-PrOH (0.4 mL) and a [0.2 M] phosphate buffer solution at pH = 7 (3.2 mL) (with or without 2 wt % TPGS-750-M) were then added, followed by ADH-101 or ADH-112 (20 mg). The reaction was stirred at 37 °C for 24 h and monitored by HPLC (4-iodoacetophenone – calibration curve shown below) or by ^1H NMR.

4. Screening of Surfactants

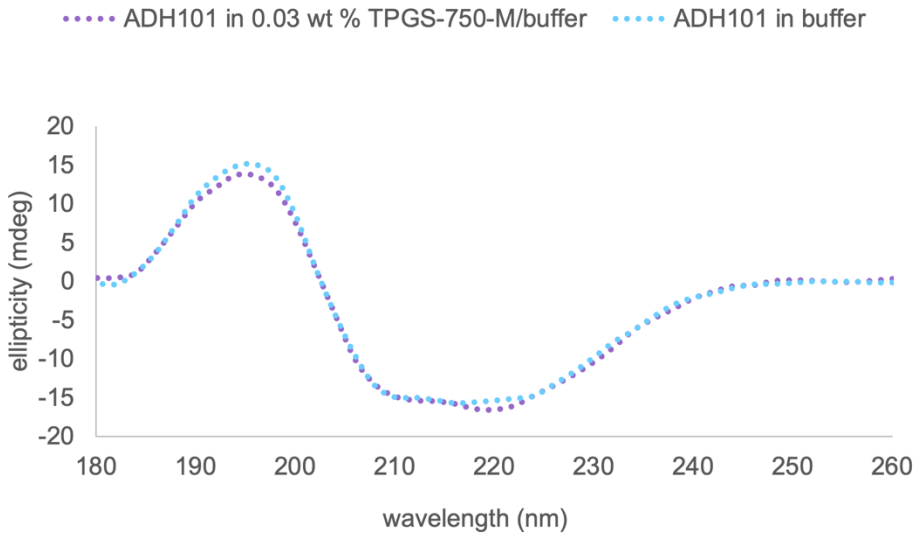
To a 1 dr vial was added 2-ethylbutyl (*E*)-3-(4-acetylphenyl)acrylate (54.9 mg, 0.2 mmol, 1 equiv), $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg) and $NADP^+$ (2.4 mg). *i*-PrOH (0.4 mL) and a

solution of 2 wt % of surfactant in a [0.2 M] phosphate buffer at pH = 7 (3.2 mL) were then added, followed by ADH112 (20 mg). The reaction was shaken at 37 °C (shaker) for 24 h. Samples were taken at different times up to 24 h, dissolved in EtOAc and washed with distilled water. The organic layers were filtered through a pipette filled with cotton and silica gel, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The samples were analyzed by ^1H NMR to determine the conversion (2.62 ppm (s) → 1.51 ppm (d))

5. Incubation Study

The stability of ADH-101 in the aqueous surfactant solution has been evaluated as follows: To a 1 dr vial was added 1-(4-(3-hydroxyprop-1-yn-1-yl)phenyl)ethan-1-one (case A: 20 mg, case B: 40 mg, case C: 80 mg, 1 equiv), $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg) and $NADP^+$ (2.4 mg). *i*-PrOH (0.4 mL) and a solution of 2 wt % TPGS-750-M in a [0.2 M] phosphate buffer at pH = 7 (3.2 mL) were then added, followed by ADH-101 (20 mg). The reaction was stirred at 37 °C for 24 h. Samples were taken at different times up to 24 h, dissolved in EtOAc and washed with distilled water. The organic layers were filtered through a pipette filled with cotton and silica gel, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The samples were analyzed by ^1H NMR to determine the conversion (2.59 ppm (s) → 1.49 ppm (d))

6. Circular Dichroism Spectrum



This spectrum shows the secondary structure of ADH101 in aqueous buffer solution (blue line) and 0.03 wt % TPGS-750-M/buffer (purple line). All spectra are characteristic of proteins with both α-helical and β-sheet components, indicating the secondary structure has been conserved in presence of the surfactant. The secondary structure of ADH101 has been evaluated by circular dichroism, with and without the surfactant in the buffer solution.

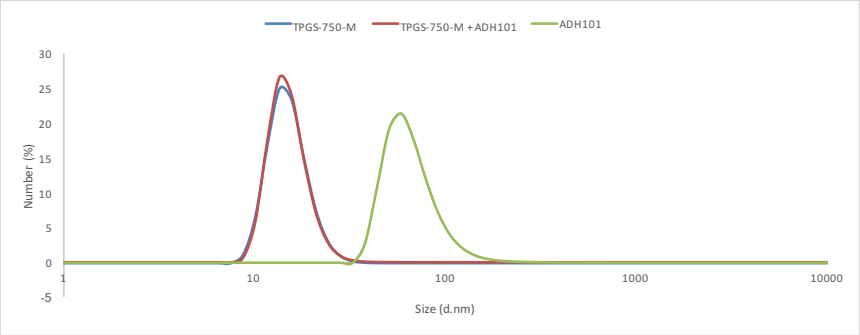
The circular dichroism spectra were obtained using a JASCO J-1500 spectropolarimeter (JASCO corporation, Tokyo, Japan) with a 0.1 mm pathlength, U-shaped quartz cuvette. The following conditions were employed: scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample. CD protein spectra were corrected for the corresponding buffer or TPGS-750/buffer signal.

The amount of TPGS-750-M had to be lowered (0.03 wt % TPGS-750-M in a [0.05M] phosphate buffer at pH7) as a strong absorbance was observed in the far UV, affecting the signal of the helix portion of the protein. Four samples were prepared at 37 °C:

- sample 1: .2.6 mg of ADH-101 in 1 mL of the 0.03 wt % TPGS-750-M/buffer solution
- sample 2: 2.6 mg of ADH-101 in 1 mL of the buffer solution
- sample 3: 0.03 wt % TPGS-750-M/buffer solution (for blank)
- sample 4: buffer solution (for blank)

The analysis required a lower concentration of enzymes [0.024M] than the reaction [0.056M].

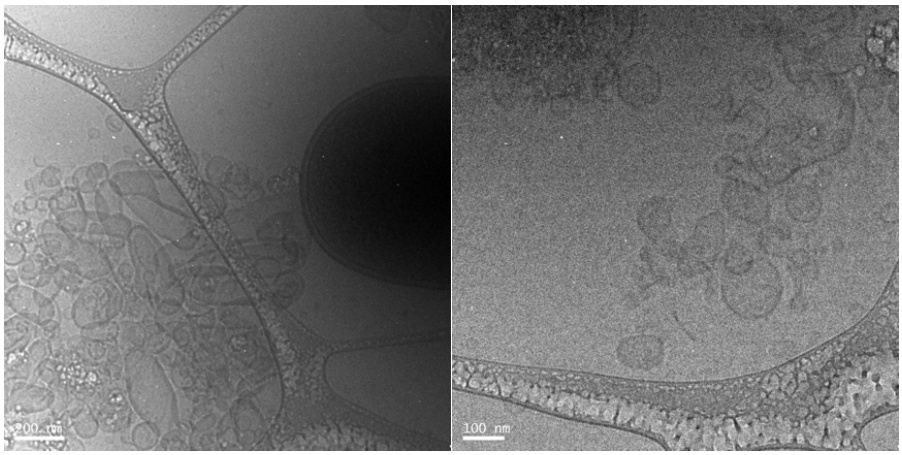
7. Dynamic Light Scattering



DLS measurements have been taken for TPGS-750-M/buffer (blue), ADH101 (green) and ADH101 in TPGS-750-M (red).

DLS analysis of a solution of 2 wt % TPGS-750-M/buffer, of ADH101 in buffer and a solution of ADH101 in 2 wt % TPGS-750-M/buffer, all in presence of 11% *i*-PrOH, have been performed to evaluated the impact of ADH101 on micelle size. Dynamic light scattering (DLS) was measured on a Malvern Zetasizer Nano ZS.

8. Cryo-TEM Imaging



The cryoTEM image has been taken with a magnification at 11.5kX (a) and 19 kX (b). The scale bar corresponds to 100 nm.

For cryo-TEM images, samples were prepared by plunge-freezing in liquid ethane (FEI Vitrobot Mk IV). They were then kept under LN2 before being transferred into a cryo transfer TEM holder (Gatan Single Tilt Cryo-Transfer Holder 626) and loaded into the microscope (FEI Tecnai G2 Sphera). The samples were imaged under low-dose conditions in order to minimize beam damage and images were acquired with a CCD camera (Gatan Ultrscan 1000 2k x 2k).

9. 1-Pot Sonogashira then ADH reduction

The general procedure (condition 1) for the 1-pot Sonogashira followed by ADH reduction is as follows: To a dried 1 dr vial were added, under an argon atmosphere, $Pd(PPh_3)_3Cl_2$ (2.8 mg, 2 mol%), CuI (1.9 mg, 5 mol %), aryl iodide (1 equiv, 0.2 mmol), alkyne (1.5 equiv, 0.3 mmol) and Et_3N (3 equiv, 84 µL). A 2 wt % TPGS-750-M/H_2O (0.4 mL) was added. The reaction was stirred at rt under argon until complete. The pH was adjusted to 7 with a solution of HCl 1 M. The concentration was adjusted to [0.056 M] by adding 2.6 mL of a 2 wt % TPGS-750-M/buffer solution (phosphate, pH = 7). $MgSO_4$ (0.8 mg), NAD+ (2.6 mg), NADP+ (2.4 mg), *i*-PrOH (0.6 mL) and ADH-101 (20 mg) were added in succession. The reaction was stirred at 37 °C until complete. The reaction was then dissolved in EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The product was purified by flash chromatography.

The general procedure (condition 2) for the 1-pot Sonogashira followed by ADH reduction is as follows: In an over-dried, argon-flushed vial, equipped with a stir bar, was added [PdCl(cinnamyl)]2 (2.6 mg) and cBRIDP (10.6 mg) under inert atmosphere (glovebox). Dry THF (2 mL; previously degassed for 1 h) was added. The solution was stirred for 0.5 h under argon.

To a dried 1 dr vial, under argon, was added 60 μL of the stock solution (1500 ppm). THF was flushed with argon. $K_3PO_4 \cdot H_2O$ (2 equiv), the ketone (1 equiv) and the alkyne (1.2 equiv) were then added to the vial, which was capped with a rubber septum. TPGS-750-M/H_2O (0.4 mL) was added and the reaction was stirred at 45 °C under argon atmosphere for 24 h. The concentration was adjusted to [0.056 M] by adding 2.6 mL of a 2 wt % TPGS-750-M/buffer solution (phosphate, pH = 7). The pH was adjusted to 7 with a solution of HCl 1 M. *i*-PrOH (0.6 mL), $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg) and ADH101 (20 mg) were added in succession. The reaction was stirred at 37 °C until complete, and then it was dissolved in EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and then concentrated under vacuum. The product was purified by flash chromatography.

10. 1-Pot Heck then ADH reduction

The general procedure for the 1-pot Heck followed by ADH reduction is as follows: To a dried 1 dr vial were added, under an argon atmosphere, $Pd(P(t\text{-}Bu_3))_2$ (Fu catalyst) (2.0 mg, 2 mol %), aryl iodide (1 equiv, 0.2 mmol), alkene (2 equiv, 0.4 mmol) and Et_3N (3 equiv, 84 μL). A 2 wt % TPGS-750-M/H_2O (0.4 mL) was then added. The reaction was stirred at 45 °C under argon until completion. The pH was adjusted to 7 with a solution of HCl 1 M. The concentration was adjusted to [0.056 M] by adding 2.6 mL of a 2 wt % TPGS-750-M/buffer solution (phosphate, pH = 7). $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg), *i*-PrOH (0.6 mL) and ADH101 or ADH112 (20 mg) were then added in succession. The reaction was stirred at 37 °C until complete. The reaction was then dissolved in EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The product was purified by flash chromatography.

11. 1-Pot alkyne hydration then ADH reduction

The first step involves the preparation of the gold pre-catalyst. (Tetrahydrothiophene)-gold(I) chloride was generated from tetrahydrothiophene and auric acid according to a known procedure.[2] A 10 mL round- bottom flask equipped with a Teflon-coated magnetic stir bar and septum was charged with HandaPhos (27.3 mg, 0.05 mmol) and (tetrahydrothiophene)gold(I) chloride (16.0 mg, 0.05 mmol). A rubber septum was added to the flask, which was degassed and filled with argon. The flask was covered with aluminum foil to protect it from light. Anhydrous DCM (2 mL) was added via syringe and the reaction was stirred for 2 h. After the solvent was removed under vacuum, the product was put under high vacuum overnight to remove trace amounts of solvent and tetrahydrothiophene. A white solid was obtained (35.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 11.8, 4.3 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.01 (s, 2H), 6.91 (ddd, *J* = 7.4, 4.8, 2.6 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 4.95 (dd, *J* = 10.3, 3.7 Hz, 1H), 3.88 (s, 3H), 3.70 (d, *J* = 7.6 Hz, 3H), 3.30 – 3.20 (m, 2H), 2.92 (ddt, *J* = 37.3, 13.8, 6.8 Hz, 3H), 1.53 (s, 2H), 1.25 (dd, *J* = 9.0, 3.5 Hz, 12H), 1.18 (d, *J* = 6.8 Hz, 6H), 0.96 (d, *J* = 17.2 Hz, 9H); 13C NMR (101 MHz, CDCl3) δ 163.23, 157.36, 157.08, 147.55, 147.12, 139.96, 134.26, 130.49, 128.32, 128.23, 125.65, 125.57, 121.24, 113.10, 111.68, 104.79, 103.21, 77.19, 55.84, 55.26, 34.72, 34.43, 34.09, 34.07, 33.94, 29.56, 25.95, 25.88, 24.77, 24.02, 23.93; 31P NMR (162 MHz, CDCl3) δ 59.97.

HandaPhos-gold(I) chloride (0.8 mg, 0.001 mmol) and silver(I) hexafluoroantimonate (0.7 mg, 0.002 mmol) were charged under an argon atmosphere into a 5 mL microwave vial containing a Teflon-coated magnetic stir bar and a rubber septum. The vial was covered with

aluminum foil to protect the compounds from light. Anhydrous DCM (1 mL) was added via syringe and the reaction was stirred for 15-20 min prior to use.

The gold pre-catalyst is used to catalyze the alkyne hydration step of the following 1-pot, 2-steps sequence: To a dried 1 dr vial was added, under an argon atmosphere, 0.2 mL of the gold pre-catalyst solution (1000 ppm or 0.1 mol %). Dichloromethane was evaporated under Argon. Alkyne (0.2 mmol, 1.0 equiv) was added to the vial, followed by toluene (20 µL), a 3 wt % TPGS-750-M/H_2O solution (0.2 mL, 1.0 M), and trifluoroacetic acid (46 mg, 0.4 mmol, 2.0 equiv). The resulting mixture was stirred at rt for 24 h. The pH was adjusted to 7 with a solution of NaOH (1 M). The concentration was adjusted to [0.056 M] by adding 2.6 mL of a 2 wt v/v % TPGS-750-M/buffer solution (phosphate, pH = 7) and *i*-PrOH (0.6 mL). Anhydrous??? $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg) and ADH101 (20 mg) were added in succession. The reaction was stirred at 37 °C until complete, after which it was dissolved in EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The product was purified by flash chromatography.

12. 1-Pot 1,4-addition then ADH reduction

To an oven-dried 1 dr vial was added, under inert atmosphere (glovebox) $Rh(nbd)_2BF_4$ (11.2 mg) and BINAP (18.7 mg). Dry DCM (1 mL) was added under Argon and the solution was stirred for 1 min. To a dried 1 dr vial was added, under an argon atmosphere, 0.2 mL of the stock solution (3 mol %). Dichloromethane was evaporated under argon. Boronic acid (0.2 mmol, 1.0 equiv), followed by a 2 wt % TPGS-750-M/H_2O solution (0.4 mL, [0.5 M]) and TEA (84 µL, 0.6 mmol, 3.0 equiv) were added in succession. The reaction was stirred for 15 min until homogeneous. Vinyl ketone was then added (0.2 mmol, 1.0 equiv). The reaction was

stirred 12 h at room temperature. The concentration was adjusted to [0.056M] by adding 2.6 mL of a 2 wt % TPGS-750-M/Buffer solution (phosphate, pH = 7) and *i*-PrOH (0.6 mL).

Note: at this stage, the pH of the solution is 7. There is no need to adjust the pH for this reaction.

Anhydrous $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg) and ADH101 (20 mg) were added in succession. The reaction was stirred at 37 °C until completion. The reaction was dissolved in EtOAc. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The product was purified by flash chromatography.

13. 1-Pot, 3-step reaction utilizing ADH

To a 15 mL round-bottom flask was added, under argon, $Rh(nbd)_2BF_4$ (4.9 mg, 3 mol%) and *rac*-BINAP (8.2 mg, 3 mol%) in DCM (1 mL). The solution was stirred for 5 min and the solvent was removed under argon. 3-Nitrophenylboronic acid (91.8 mg, 0.44 mmol, 1.0 equiv) was added, followed by a 2 wt % solution of TPGS-750-M/H_2O and TEA (184 µL, 1.32 mmol, 3.0 equiv). After 15 min, methyl vinyl ketone (37 µL, 0.44 mmol, 1.0 equiv) was added and the reaction was stirred at 45 °C for 12 h. After completion of the first step, Carbonyl Iron Powder (CIP – 73.7 mg, 1.3 mmol, 3.0 equiv) and NH_4Cl (117.7 mg, 2.2 mmol, 5.0 equiv) were added. HCl (12 M; 37 µL, 0.44 mmol, 1.0 equiv) was added and the reaction was stirred under argon overnight. After completion of the second step, the reaction was diluted with a 2 wt % TPGS-750-M/buffer solution (6.2 mL) and *i*-PrOH (1.3 mL). The pH was adjusted to 7 with a 1M HCl solution. Anhydrous $MgSO_4$ (1.8 mg), NAD^+ (5.7 mg), $NADP^+$ (5.3 mg), and ADH101 (44 mg) were added as solids. The reaction was stirred at 37 °C for 2 h. After completion, the pH of the aqueous solution was adjusted to 10 and the product was extracted

with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by flash chromatography (100:0 to 50:50 hexanes/EtOAc).

14. Industrial Scale-up

To a 2 wt % solution of TPGS-750-M in phosphate buffer (pH = 7.05, 10 v) was added glucose (2.0 equiv) in a mechanically stirred reactor equipped with pH controller at 25 °C. The suspension was further stirred for 20 min, and to the resulting mixture was sequentially added $NADP^+$ (1.2 wt %), GDH (1.0 wt %) and KRED-EW-124 (5 wt %). The ketone (3.0 kg, 8.2 mol, 1.0 equiv) was added and the pH of the reaction mixture was adjusted to 6.8-7.2 by addition of 1 M aqueous NaOH at 25 °C. The resulting reaction mixture was heated to 40 °C and stirred for 24 h until completion of the reaction as determined by HPLC. As the reaction proceeded, the product precipitated out from the reaction mixture and formed a suspension. The resulting suspension was filtered at 40 °C, and the resulting wet cake was washed with water and dried to give product **6** as an off-white solid (3.5 kg, purity 97%, yield 85%).

15. ERED Enzyme Screen

To evaluate the impact of TGPS-750-M on the conversion of the model substrate by ENE-reductase, comparative monitoring was performed. In a 5 dr vial, GHD-105 (20mg), glucose (2 equiv, 123 mg) and $NADP^+$ (5 mg) were added followed by addition of 10 mL of phosphate buffer at pH 7 (with or without 2 wt % of TPGS-750-M) to make a stock solution. The vial was lightly swirled to allow the components to fully dissolve. Enone (5 mg) and ENE-reductases (10 mg) were added into seven labeled 1 dr equipped with magnetic stir bars. The stock solution (containing GDH-105, glucose, and $NADP^+$ in phosphate buffer, 1 mL) was added to each 1-dr vial. The reactions were stirred at 35 ºC for 24 h. After 24 h, the reactions were extracted with MTBE (5x) and concentrated *in vacuo.* The samples were analyzed by ^1H

NMR to determine the conversion. (2.47 ppm (s) → 1.11 ppm (d)). The enantioselectivity was determined by HPLC analysis (Chiracel OJ-H column, hexanes/*i*-propanol 99.5:0.5, flow rate 0.5 mL/min) t_1 15.2 min (minor) t_2 16.42 min (major).

16. Conversion Monitoring in Phosphate Buffer and TPGS-750-M/Phosphate Buffer utilizing ERED

To evaluate the impact of TGPS-750-M on the conversion of four different substrates by ENE-reductase, comparative monitoring with and without surfactant in buffer was performed. In a 5 dr vial, GHD-105 (20mg), glucose (2 equiv relative to substrate) and $NADP^+$ (5 mg) were added followed by addition of 10 mL of phosphate buffer at pH = 7 (with or without 2 wt % of TPGS-750-M) to make a stock solution (4 and 6 wt % of TPGS-750-M in the buffer solution were also prepared). The vial was lightly swirled to allow the components to fully dissolve. In 1 dr vials, each equipped with a magnetic stir bar, enone (5 mg) and ERED-103 (10 mg) were added. The stock solution (containing GDH-105, glucose, and $NADP^+$ in phosphate buffer, 1mL) was added to each 1 dr vial. The reactions were stirred at 35 ºC. At each time interval noted, the reactions were extracted with MTBE (5x) and concentrated *in vacuo* and monitored by ^{1}H NMR.

17. Concentration Effect Studies

To evaluate the impact of increased concentration on the activity of the enzyme in 2 wt % of TPGS-750-M in phosphate buffer, reaction monitoring was performed. In a 1 dr vial equipped with a magnetic stir bar, GHD-105 (2mg), glucose (12.3 mg) and $NADP^+$ (0.5 mg), enone (5 mg) and ERED (10 mg) were added followed by addition of 2 wt % of TPGS-750-M in phosphate buffer at pH = 7 to reach desired concentration (poor stirring of components was observed at 0.5 M). The reactions were stirred at 35 ºC for 24 h. After 24 h the organic layers

were extracted with MTBE (5x) and concentrated *in vacuo.* The samples were analyzed by ^{1}H NMR to determine the conversion. (2.47 ppm (s) → 1.11 ppm (d)).

18. General Procedure for Enantioselective Reduction of Activated Olefins

To a 5 dr vial equipped with a magnetic stir bar was added olefin (50 mg), ERED-103 (70 mg), GDH-105 (20 mg), glucose (2 equiv. to olefin), and $NADP^+$ (5 mg). 5-7 mL (substrate dependent) of 2 wt % of TPGS-750-M in phosphate buffer at pH = 7 was added to the vial. The reaction was set to stir at 35 ºC. The reaction was monitored via TLC or ^{1}H NMR. Upon completion, the organic layers were extracted with MTBE (5x), dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude material was purified via flash chromatography to afford the unsaturated alkane.

19. 1-pot ERED Reduction, then ADH Reduction

ADH-101 is commercially available within the enzyme kit EZK-001 from Johnson Matthey. NAD^+ was purchased from Bioworld. Isopropanol was purchased from VWR. All other commercially available reagents were used without further purification. To a 5 dr vial equipped with a magnetic stir bar was added olefin (50 mg), ERED-103 (70 mg), GDH-105 (20 mg), $NADP^+$ (5mg) and glucose (2 equiv relative to olefin). TPGS-750-M (5 mL, 2 wt %) in phosphate buffer at pH 7 was added to the vial. The reaction was set to stir at 35 ºC for 24 h. The reaction was monitored via TLC. Upon completion, anhydrous $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg) and ADH-101 (20 mg) were added in succession. *i*-PrOH (0.6 mL) was added to the reaction mixture. The reaction was stirred at 35 °C for 5 h. The reaction was extracted with EtOAc (5x). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude material was purified via flash chromatography.

20. 1-Pot Pd-Catalyzed Suzuki-Miyaura coupling, then ERED Reduction

To an oven dried 1 dr vile equipped with a stir bar was added $Pd(OAc)_2$ (2.25 mg, 0.01 mmol) and N_2Phos^5 (14.8 mg, 0.018 mmol). The vial was capped with a 14/20 rubber septum sealed with Teflon tape. The vial was evacuated and backfilled with argon three times and left under a continuous flow of argon. Anhydrous toluene (1 mL) was added to the vial to achieve the desired Pd concentration (50 μL of stock solution equates to 1000 ppm loading for a 0.5 mmol reaction). The mixture was set to stir for 15 min. At this point the catalyst is ready and may be added to the reaction mixture.

To an oven dried, 10 mL flask equipped with a magnetic stir bar was charged aryl chloride (0.25 mmol), organoboron (0.38 mmol), and potassium phosphate (0.38 mmol). The vial was fitted with a rubber septum and sealed with Teflon tape. The reaction flask was purged with argon with the use of a vent needle. At this point, a solution of 2 wt % TPGS-750-M in (0.9 mL) followed by the catalyst solution (125 μL) via syringe. The reaction was monitored by GC-MS. Upon completion of the reaction, the pH was adjusted to 7 with a HCl (1 M) and, ERED-103 (70mg), GDH-105 (20mg), $NADP^+$ (5mg) and glucose (2 equiv. to olefin) were added to the flask. 5 mL of 2 wt% TPGS-750-M in phosphate buffer at pH 7 was added to the vial. The reaction was set to stir at 35 ºC for 24 h. Upon completion the reaction was filtered over a pad of celite and the organics were extracted with MTBE (5x). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo.* The crude material was purified via flash chromatography.

21. 1-Pot ERED Reduction, then Amine Formation utilizing Transaminase (ATA)

To a 5 dr vial equipped with a magnetic stir bar was added olefin (20 mg, $1.272.10^{-4}$ mol), ERED-103 (40 mg), GDH-105 (8 mg), glucose (46 mg), and $NADP^+$ (2 mg). TPGS-750-M (4

mL, 2 wt %) in phosphate buffer at pH = 7 was added to the vial. The reaction was set to stir at 35 ºC overnight. The reaction was monitored via TLC or ^{1}H NMR. The concentration was adjusted to [0.01 M] by adding 8.72 mL of a fresh solution* (triethanolamine, [118 mM], pH = 8.5) previously made (see the protocol below). The ATA-256 (100 mg) was then added and the reaction was stirred at 50 °C. Upon completion, the reaction was quenched by adding 5 N NaOH (1.5 mL) to increase reaction pH > 11 and extracted into EtOAc (5 x 10 mL). The organic layers, separated by centrifugation, were combined and evaporated. To a 2 dr vial containing the product from the second step were added 2 wt % of TPGS-750-M in water (0.9 mL) and sodium carbonate (40 mg, 3 equiv). The reaction was cooled to 0 °C and benzyl chloroformate (18 µL, 1 equiv) was added. The reaction was stirred for 20 min at 0 °C and allowed to warm to rt and stirred overnight. The solution is acidified to pH = 2 (0 °C) and extracted with EtOAc (3 x 1 mL). The organic layers were combined and dried over anhydrous $MgSO_4$ and concentrated *in vacuo.* The crude material was purified via flash chromatography to afford the desired compound.

*Fresh solution for step 2:

In a 20 mL flask were added triethanolamine (0.21 g), isopropylamine (1.06 mL), PLP (3.4 mg) and 2 wt % of TPGS-750-M in water (4 mL). The pH was adjusted to 8.5 with HCl 12 M. The volume was brought to 8.72 mL by adding 2 wt % of TPGS-750-M in water.

22. 1-Pot Pd-catalyzed Cyanation, ERED Reduction, then ADH Reduction

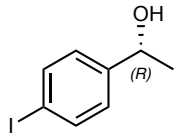
Aryl bromide (1 equiv, 0.2 mmol), $Zn(CN)_2$ (12.9 mg, 0.55 equiv), Xantphos palladacycle (1.7 mg, 0.7 mol %) were added to an oven-dried 10 mL flask equipped with a magnetic stir bar. The reaction vial was evacuated and backfilled with argon (3x). PMHS (13µL, 1 equiv) was added under argon followed by dry THF (40 µL, 10 vol %) and 2 wt %

TPGS-750-M/H_2O (360 µL). The reaction mixture was stirred at 65°C, overnight. The reaction was monitored via TLC. Upon completion, ERED-103 (70 mg), GDH-105 (20 mg), $NADP^+$ (5mg) and glucose (2 equiv relative to olefin). TPGS-750-M (5.6 mL; 2 wt %) in phosphate buffer at pH 7 was added to the vial. The reaction was set to stir at 35 ºC for 24 h. The reaction was monitored via TLC. Upon completion, anhydrous $MgSO_4$ (0.8 mg), NAD^+ (2.6 mg), $NADP^+$ (2.4 mg) and ADH-101 (20 mg) were added in succession, followed by *i*-PrOH (0.6 mL). The reaction was stirred at 35 °C for 5 h. The reaction was extracted with EtOAc three times. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude material was purified via flash chromatography

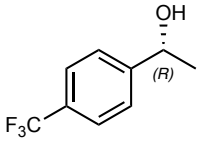
23. 1-Pot ERED Reduction, Pd/C Nitro-reduction, then Acylation

To a 5 dr vial equipped with a magnetic stir bar was added olefin (1.0 equiv, 50 mg), ERED-103 (70 mg), GDH-105 (20 mg), $NADP^+$ (5 mg) and glucose (2 equiv relative to olefin). TPGS-750-M (4 mL; 2 wt %) in phosphate buffer at pH 7 was added to the vial. The reaction was set to stir at 35 ºC for 24 h. The reaction was monitored via TLC. Upon completion, HCl (100 µL, 1 M) was added to the reaction and the mixture was filtered through a cotton plug-Celite pipette to remove any enzymatic reduction by-products. The pH was adjusted to pH 7 and 10 wt % Pd/C (20 mg) was then added to the reaction mixture. The reaction vessel was purged with H_2 via balloon and fitted with another balloon of H_2. The reaction was set to stir at rt overnight. The reaction was monitored via TLC. Upon completion, the H_2 balloon was removed and acetic anhydride (2.0 equiv) was added to the mixture. The reaction was set to stir for an additional 4 h. The reaction was monitored via TLC. Upon completion, the reaction was extracted with EtOAc (5x) and the organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* The crude material was purified via flash chromatography.

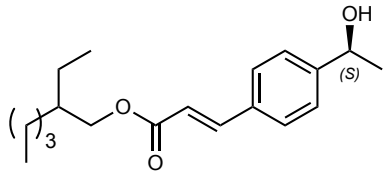
24. **Analytical data for products**



(*R*)-1-(4-iodophenyl)ethan-1-ol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.17 – 7.11 (m, 2H), 4.87 (qd, *J* = 6.4, 3.5 Hz, 1H), 1.80 (d, *J* = 3.7 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 137.7, 127.5, 92.8, 70.0, 25.4**; R enantiomer:** $\boldsymbol{a_D^{20.0}}$= + 19.96 (*c*0.867 in $CHCl_3$) (ADH101); **S enantiomer:** $\boldsymbol{a_D^{20.0}}$= - 30.64 (*c*0.780 in $CHCl_3$) (ADH112); $\mathbf{R_f}$ = 0.71 (hexanes/EtOAc, 1:1 v/v)

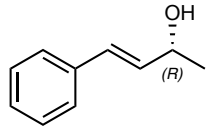


(*R*)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 4.97 (q, *J* = 6.5 Hz, 1H), 2.00 (t, *J* = 9.9 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 149.8, 129.7, 125.8, 125.6, 125.6, 125.6, 125.5, 125.4, 123.2, 70.0, 25.5; $\mathbf{R_f}$ = 0.68 (hexanes:EtOAc, 1:1 v/v).

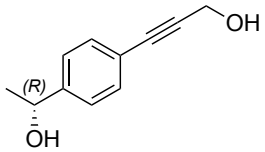


2-ethylbutyl (*S,E*)-3-(4-(1-hydroxyethyl)phenyl)acrylate: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.66 (d, J=16.0, 1H), 7.52 (d, *J*=8.1, 2H), 7.40 (d, *J*=8.1, 2H), 6.43 (d, *J*=16.0, 1H), 4.93 (qd, *J*=6.4, 3.2, 1H), 4.17 – 4.08 (m, 2H), 1.98 (d, *J*=3.5, 1H), 1.71 – 1.61 (m, 1H), 1.51 (d, *J*=6.5, 3H), 1.49 – 1.38 (m, 2H), 1.38 – 1.28 (m, 6H), 0.92 (dt, *J*=10.8, 7.1, 6H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.4, 148.4, 144.3, 133.6, 128.3, 126.0, 118.1, 70.0, 67.1, 38.9, 30.6, 29.0, 25.3,

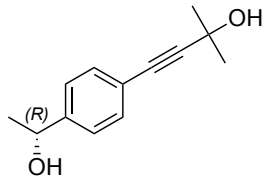
23.9, 23.1, 14.1, 11.1; $\boldsymbol{a_D^{20.0}}$= - 16.83 (*c*0.873 in $CHCl_3$) (ADH112); TLC (1:1 hexanes:EtOAc, 1:1 v/v): $\mathbf{R_f}$ = 0.59.



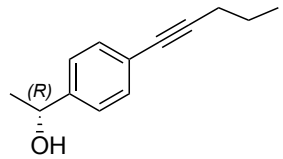
(*R*,*E*)-4-phenylbut-3-en-2-ol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.58 (dd, *J* = 15.9, 1.2 Hz, 1H), 6.28 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.50 (pd, *J* = 6.4, 1.2 Hz, 1H), 1.83 – 1.59 (m, 1H), 1.39 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 136.8, 133.7, 129.5, 128.7, 127.8, 126.6, 69.1, 69.1, 23.6; TLC (hexanes:EtOAc, 1:1 v/v): $\mathbf{R_f}$ = 0.68.



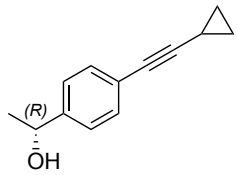
(*R*)-3-(4-(1-hydroxyethyl)phenyl)prop-2-yn-1-ol (1a): . **Yield** 99% - ee > 99% *pale yellow powder* **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 2H), 4.91 (qd, *J*=6.5, 2.6, 1H), 4.50 (d, *J*=5.9, 2H), 1.89 (d, *J*=3.3, 1H), 1.80 (t, *J*=6.1, 1H), 1.49 (d, *J*=6.5, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** = 146.3, 132.0, 125.5, 121.7, 87.2, 85.7, 70.2, 51.8, 25.3; $\boldsymbol{a_D^{20.0}}$= + 54.05 (*c*0.740 in $CHCl_3$); TLC (hexanes:EtOAc, 1:1, v/v): $\mathbf{R_f}$ = 0.45; **HRMS (m/z):** **[M]$^+$** calcd. for $C_{11}H_{12}O_2$, 176.0837; found, 176.0840.



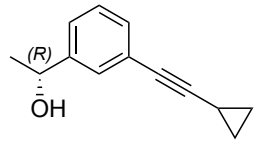
(*R*)-4-(4-(1-hydroxyethyl)phenyl)-2-methylbut-3-yn-2-ol (1b): Yield: 99% - ee > 99% *yellow powder* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 8.3, 2.2 Hz, 2H), 7.30 (dd, *J* = 8.3, 2.5 Hz, 2H), 4.94 – 4.81 (m, 1H), 2.25 (bs, 1H), 2.04 (bs, 1H), 1.71 (bs, 0.5H), 1.62 (s, 6H), 1.47 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0, 131.9, 125.4, 121.9, 93.8, 82.1, 70.2, 65.7, 31.6, 25.3; $a_D^{20.0}$= + 54.29 (*c*1.387 in $CHCl_3$); TLC (hexanes:EtOAc, 1:1 v/v): **R_f** = 0.28; **HRMS (m/z): [M-H_2O]$^+$** calcd. for $C_{13}H_{14}O$, 186.1045; found, 186.1042.



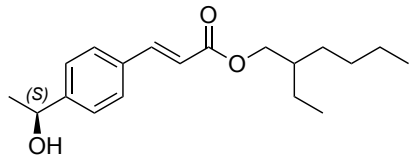
(*R*)-1-(4-(pent-1-yn-1-yl)phenyl)ethan-1-ol (1c): Yield: 79% - ee > 99% *brown powder* **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.42 – 7.36 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.88 (qt, *J* = 9.1, 4.8 Hz, 1H), 2.39 (td, *J* = 7.1, 1.1 Hz, 2H), 1.84 (d, *J* = 3.3 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.48 (dd, *J* = 6.4, 1.3 Hz, 3H), 1.06 (td, *J* = 7.4, 1.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 145.2, 137.6, 131.7, 127.5, 125.3, 123.2, 90.3, 80.6, 70.2, 25.3, 25.2, 22.3, 21.5, 13.7; $a_D^{20.0}$= + 20.07 (*c*0.847 in $CHCl_3$); TLC (hexanes:EtOAc 1:1 v/v): **R_f**= 0.55.



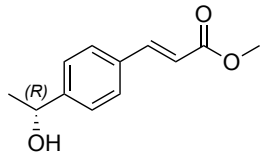
(*R*)-1-(4-(cyclopropylethynyl)phenyl)ethan-1-ol (1d): Yield: 77% - > 99.9% ee *Off-white powder* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.36 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.93 – 0.84 (m, 2H), 0.84 – 0.77 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 145.2, 131.8, 125.3, 123.1, 93.5, 75.7, 70.2, 25.2, 8.7, 0.3; $a_D^{20.0}$= + 56.27 (*c*0.773 in $CHCl_3$); TLC (hexanes:EtOAc, 8:1 v/v): **R_f** = 0.31; **HRMS (m/z): [M]$^+$** calcd. for $C_{13}H_{14}O$, 186.1045; found, 186.1045.



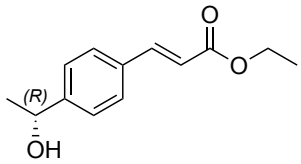
(*R*)-1-(3-(cyclopropylethynyl)phenyl)ethan-1-ol (1e): Yield: 68% - > 99.5% ee *Pale yellow oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.40 (d, *J* = 1.9 Hz, 1H), 7.31 – 7.20 (m, 3H), 4.85 (q, *J* = 6.4 Hz, 1H), 1.92 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.92 – 0.84 (m, 2H), 0.84 – 0.78 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 146.0, 130.8, 128.8, 128.5, 124.7, 93.6, 75.8, 70.2, 25.2, 8.7, 0.3; $a_D^{20.0}$= + 38.98 (*c*0.947 in $CHCl_3$); TLC (hexanes:EtOAc, 8:1 v/v): **R_f** = 0.38; **HRMS (m/z): [M]$^+$** calcd. for $C_{13}H_{14}O$, 186.1045; found, 186.1043.



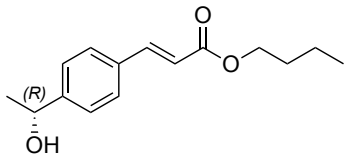
2-ethylhexyl (*E*)-3-(4-((*S*)-1-hydroxyethyl)phenyl)acrylate (2a): Yield: 82% - ee > 99% - *yellow oil* **^{1}H NMR (600 MHz, $CDCl_3$) δ** = 7.66 (d, *J*=16.0, 1H), 7.52 (d, *J*=8.1, 2H), 7.40 (d, *J*=8.1, 2H), 6.43 (d, *J*=16.0, 1H), 4.93 (qd, *J*=6.4, 3.2, 1H), 4.17 – 4.08 (m, 2H), 1.98 (d, *J*=3.5, 1H), 1.71 – 1.61 (m, 1H), 1.51 (d, *J*=6.5, 3H), 1.49 – 1.38 (m, 2H), 1.38 – 1.28 (m, 6H), 0.92 (dt, *J*=10.8, 7.1, 6H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.4, 148.4, 144.3, 133.6, 128.3, 126.0, 118.1, 70.0, 67.1, 38.9, 30.6, 29.0, 25.3, 23.9, 23.1, 14.1, 11.1; $\boldsymbol{a_D^{20.0}}$= - 16.83 (*c*0.873 in $CHCl_3$) (ADH112); TLC (hexanes:EtOAc, 1:1 v/v): **R_f** = 0.59; **HRMS (m/z): $[M\text{-}H_2O]^+$** calcd. for $C_{19}H_{26}O_2$, 286.1933; found, 286.1934.



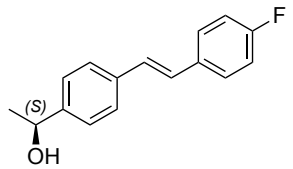
methyl (*R*,*E*)-3-(4-(1-hydroxyethyl)phenyl)acrylate (2b): Yield: 78% – >99.9% ee *pale yellow oil* **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.68 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.42 – 7.37 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.92 (q, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 2.04 (bs, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.6, 148.4, 144.6, 133.7, 128.4, 126.0, 117.7, 70.1, 51.8, 25.3; $a_D^{20.0}$= +23.3 (*c*0.593 in $CHCl_3$); TLC (hexanes:EtOAc, 7:3 v/v): **R_f** = 0.30.



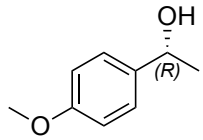
ethyl (*R,E*)-3-(4-(1-hydroxyethyl)phenyl)acrylate (2c): Yield: 83% – >99.9% ee *pale yellow oil* **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.68 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.37 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.93 (q, *J* = 6.5 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.89 (bs, 1H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.2, 148.2, 144.3, 133.8, 128.4, 126.0, 118.3, 70.2, 60.7, 25.3, 14.5; $\boldsymbol{a_D^{20.0}}$= +40.2 (*c*1.264 in $CHCl_3$); TLC (hexanes:EtOAc, 7:3 v/v): **R_f** = 0.30; **HRMS (m/z): [M]$^+$** calcd. for $C_{13}H_{16}O_3$, 220.1099; found, 220.1101.



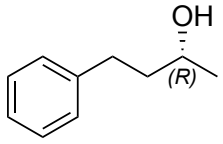
butyl (*R,E*)-3-(4-(1-hydroxyethyl)phenyl)acrylate (2d): Yield: 71% – >99.9% ee *pale yellow oil* **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.93 (q, *J* = 6.5 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.99 (bs, 1H), 1.73 – 1.66 (m, 2H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.3, 148.2, 144.3, 133.8, 128.4, 126.0, 118.2, 70.2, 64.6, 30.9, 25.3, 19.3, 13.9; $a_D^{20.0}$= +34.3 (*c*2.136 in $CHCl_3$); TLC (hexanes:EtOAc, 7:3 v/v): **R_f** = 0.32.



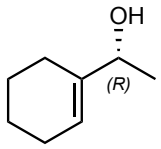
(*S,E*)-1-(4-(4-fluorostyryl)phenyl)ethan-1-ol (2e): Yield: 87% – >99.9% ee *white powder* **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.52 – 7.46 (m, 4H), 7.41 – 7.36 (m, 2H), 7.10 – 6.99 (m, 4H), 4.93 (qd, *J* = 6.4, 3.0 Hz, 1H), 1.81 (d, *J* = 3.5 Hz, 1H), 1.53 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 163.5, 161.5, 145.4, 136.6, 133.7, 128.1, 128.1, 127.6, 126.7, 125.9, 115.9, 115.7, 70.3, 25.3; $a_D^{20.0}$= +18+8 (*c*0.529 in $CHCl_3$); TLC (hexanes:EtOAc, 7.5:2.5 v/v): **R_f** = 0.28; **HRMS (m/z): [M-H_2O]$^+$** calcd. for $C_{16}H_{13}F$, 224.1001; found, 224.1005.



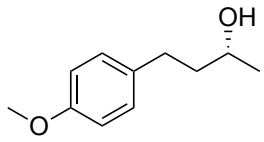
(*R*)-1-(4-methoxyphenyl)ethan-1-ol (3a): Yield: 92% – >99.9% ee *yellow oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.34 – 7.29 (m, 2H), 6.92 – 6.87 (m, 2H), 4.87 (qd, J = 6.5, 1.7 Hz, 1H), 3.81 (d, J = 0.8 Hz, 3H), 1.83 (d, J = 26.1 Hz, 1H), 1.49 (dd, J = 6.4, 1.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 159.1, 138.1, 126.8, 114.0, 70.1, 55.4, 25.2; $\boldsymbol{a_D^{20.0}}$= +18.0 (*c*0.421 in $CHCl_3$); TLC (hexanes:EtOAc, 1:1 v/v): **R_f** = 0.57.



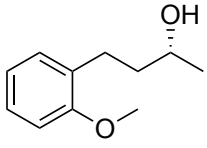
(*R*)-4-phenylbutan-2-ol (3b): Yield: 99% – >99.9% ee *colorless oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.30 (td, *J* = 7.4, 1.4 Hz, 2H), 7.24 – 7.17 (m, 3H), 3.89 – 3.79 (m, 1H), 2.77 (ddd, *J* = 13.7, 9.3, 6.3 Hz, 1H), 2.69 (ddd, *J* = 13.7, 9.2, 7.0 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.45 (s, 1H), 1.25 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 142.2, 128.5, 126.0, 67.7, 41.0, 32.3, 23.8; $a_D^{20.0}$= -16.3 (*c*1.100 in $CHCl_3$); TLC (hexanes:EtOAc, 8:2 v/v): **R_f** = 0.33.



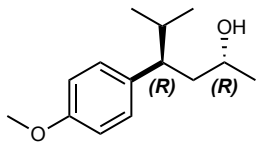
(*R*)-1-(cyclohex-1-en-1-yl)ethan-1-ol (3c): Yield: 90% – >99.0% ee *pale yellow oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 5.68 (tdd, *J* = 3.4, 2.6, 1.5 Hz, 1H), 4.17 (q, *J* = 6.5 Hz, 1H), 2.11 – 1.93 (m, 4H), 1.72 – 1.50 (m, 5H), 1.41 – 1.35 (m, 1H), 1.27 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 141.4, 121.7, 72.3, 25.0, 23.8, 22.8, 22.8, 21.7; $\mathbf{a_D^{20.0}}$= +1.9 (c0.667 in CHCl3); TLC (hexanes:EtOAc, 8:2 v/v): **R_f** = 0.38.



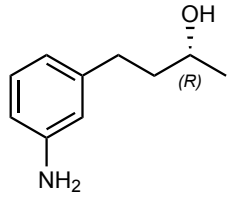
(***R***)**-4-(4-methoxyphenyl)butan-2-ol (4b): Yield:** 88% – >99.9%ee *yellow oil* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 2H), 6.86 – 6.82 (m, 2H), 3.87 – 3.81 (m, 1H), 3.80 (s, 3H), 2.75 – 2.58 (m, 2H), 1.82 – 1.68 (m, 2H), 1.26 (s, 1H), 1.23 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 134.2, 129.4, 114.0, 67.7, 55.4, 41.2, 31.4, 23.8; $a_D^{20.0}$= -5.3 (*c*0.414 in $CHCl_3$); TLC (hexanes:EtOAc, 8:2 v/v): **R_f** = 0.28.



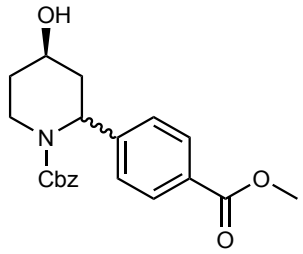
(*R*)-4-(2-methoxyphenyl)butan-2-ol (4c): Yield: 80% – >99.9% ee *colorless oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.22 – 7.14 (m, 2H), 6.95 – 6.85 (m, 2H), 3.85 (s, 3H), 3.73 (dqd, *J* = 8.1, 6.2, 4.5 Hz, 1H), 2.79 (dt, *J* = 13.6, 8.1 Hz, 1H), 2.69 (ddd, *J* = 13.6, 8.1, 5.4 Hz, 1H), 1.80 – 1.66 (m, 2H), 1.27 (s, 1H), 1.20 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 130.2, 127.3, 120.9, 110.5, 67.2, 55.5, 39.9, 26.2, 23.3; $a_D^{20.0}$= -9.8 (*c*0.579 in $CHCl_3$); TLC (hexanes:EtOAc, 8:2 v/v): **R_f** = 0.28.



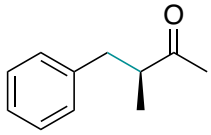
(2*R*,4*R*)-4-(4-methoxyphenyl)-5-methylhexan-2-ol (4d): Yield: 87% – >99.9% ee - > 99.4% de (0.6% of (2*R*)-(4*S*)) – *white solid* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.10 – 7.02 (m, 2H), 6.88 – 6.80 (m, 2H), 3.80 (s, 3H), 3.56 (i-PrOH, J = 6.2 Hz, 1H), 2.26 (ddd, J = 11.4, 7.4, 4.7 Hz, 1H), 1.94 – 1.71 (m, 3H), 1.33 – 1.22 (bs, 1H), 1.13 (d, J = 6.1 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 0.71 (d, J = 6.7 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 158.1, 135.6, 129.4, 113.7, 67.5, 55.3, 49.7, 42.9, 34.0, 31.7, 23.0, 22.8, 21.1, 20.4, 14.3; $\boldsymbol{a_D^{20.0}}$= -1.2 (*c*0.310 in $CHCl_3$); TLC (hexanes:EtOAc, 8:2 v/v): $\mathbf{R_f}$ = 0.17; **HRMS (m/z): [M]$^+$** calcd. for $C_{14}H_{22}O_2$, 222.1620; found, 222.1627. The 1-4 addition of 4-methoxyphenylboronic acid to 5-methylhex-3-en-2-one, catalyzed by (*R*-BINAP)Rh(nbd)BF_4 in presence of TEA led to **(*R*)**-4-(4-methoxyphenyl)-5-methylhexan-2-one. The configuration of the stereogenic center has been determined by comparing the specific rotation of the compound with literature ($a_D^{20.0}$= +29.0 (*c*1.200 in $CHCl_3$)).[10] The reduction of the resulting ketone was performed in the same pot with ADH110, (*R*)-selective toward acetophenone. By structural extrapolation, the second stereogenic center has been determined as (*R*).



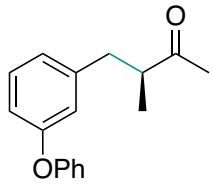
(*R*)-4-(3-aminophenyl)butan-2-ol: Yield: 75% - > 99.9% ee *yellow oil* **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.08 (t, J = 7.6 Hz, 1H), 6.64 – 6.60 (m, 1H), 6.58 – 6.51 (m, 2H), 3.90 – 3.79 (m, 1H), 2.73 – 2.54 (m, 2H), 1.83 – 1.69 (m, 2H), 1.27 (bs, 1H), 1.23 (d, J = 6.2 Hz, 3H).; **^{13}C NMR (126 MHz, $CDCl_3$) δ** 146.6, 143.4, 129.5, 118.9, 115.4, 112.9, 105.1, 67.7, 40.8, 32.3, 29.8, 23.8.; $\boldsymbol{a_D^{20.0}}$= -4.7 (c0.792 in $CHCl_3$); TLC (hexanes:EtOAc, 1:1 v/v): $\mathbf{R_f}$ = 0.31. HPLC was performed on *N*-(3-(3-hydroxybutyl)phenyl)acetamide to facilitate the analysis. The acetylation was performed at 0 °C in THF (0.0038 M) in presence of acetic anhydride (1.1 equiv).



Benzyl-(*R*)-4-hydroxy-2-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate: off-white solid (8.2 mol scale (3.5 kg) - purity 97% - **Yield** 85% **^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ** 7.95 (m, 2H), 7.34 (m, 7H), 5.52 (d, J = 4.6 Hz, 1H), 5.13 (d, J = 3.0 Hz, 2H), 4.83 (d, J = 4.5 Hz, 1H), 4.09 (m, 1H), 3.85 (s, 3H), 3.41 (m, 1H), 2.81 (td, J = 13.6, 2.8 Hz, 1H), 2.50 (m, 2H), 1.78 (m, 1H), 1.67 (m, 1H), 1.30 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 155.0, 145.7, 129.5, 128.4, 127.8, 127.4, 126.3, 66.5, 63.0, 53.6, 37.4, 34.3; **HRMS (m/z): [M]$^+$** calcd. for $C_{21}H_{23}NO_5$, 369.1576; found, 369.1601.

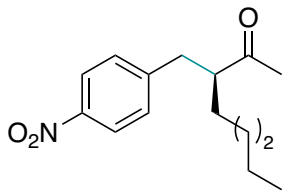


(*S*)-3-methyl-4-phenylbutan-2-one (6): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 3.02 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.85 (h, *J* = 7.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.10 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 212.24, 139.80, 129.05, 128.55, 126.37, 48.94, 39.05, 28.98, 16.36. **Yield:** 88% (3 h) as a colorless oil, 93% ee. **S enantiomer** $\alpha_D^{20.0}$ = +29.8 (c0.981 in $CHCl_3$) (ERED-103) **R$_f$** = 0.28 (10% EtOAc/hex). The enantioselectivity was determined by HPLC analysis (Chiracel OJ-H column, hexanes/*i*-propanol 99.5:0.5, flow rate 0.5 mL/min) t_1 15.2 min (minor) t_2 16.42 min (major).

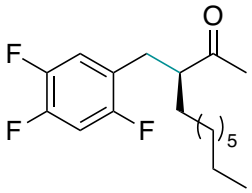


(*S*)-3-methyl-4-(3-phenoxyphenyl)butan-2-one (7): ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.37 – 7.30 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 9.5 Hz, 2H), 2.98 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.81 (h, *J* = 7.1 Hz, 1H), 2.54 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.10 (s, 3H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, cdcl$_3$) δ** 212.01, 157.38, 157.34, 141.90, 129.87, 129.81, 124.05, 123.34, 119.51, 118.92, 116.87, 48.73, 38.78, 28.98, 16.39. **Yield**: 91% (24 h) as a pale yellow oil, 96% ee (ERED-103). **R$_f$**: 0.25 (10% Et_2O/hexanes) The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 98:2, flow rate 1 mL/min) t_1 17.4 min

(minor) t_2 18.1 min (major). Molecular formula: $C_{17}H_{18}O_2$ EI-MS $[M^{\cdot}]^+$ calcd: 254.1307 found: 277.1207 $[M + Na]^+$

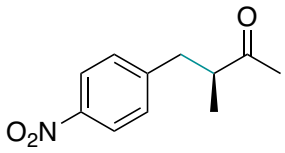


(*S*)-3-(4-nitrobenzyl)octan-2-one (8): ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 3.02 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.87 – 2.80 (m, 1H), 2.76 (dd, *J* = 13.4, 5.8 Hz, 1H), 2.03 (s, 3H), 1.69 – 1.61 (m, 1H), 1.50 – 1.42 (m, 1H), 1.32 – 1.23 (m, 6H), 0.90 – 0.85 (t, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 211.17, 147.95, 129.87, 123.84, 54.38, 37.17, 31.94, 31.89, 30.22, 26.86, 22.56, 14.10. **Yield**: 84% as a pale yellow oil, 97% ee (ERED-103). **R$_f$**: 0.20 (15% EtOAc/hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OJ-H column, hexanes/*i*-propanol 90:10, flow rate 1 mL/min) t_1 7.29 min (major) t_2 8.13 min (minor). Molecular formula: $C_{15}H_{21}NO_3$ EI-MS $[M^{\cdot}]^+$ calcd: 263.1521 found: 263.1523

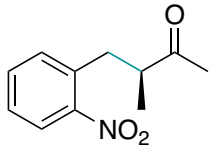


(*S*)-3-(2,4,5-trifluorobenzyl)undecan-2-one (9): ^{1}H NMR (600 MHz, cdcl$_3$) δ 6.95 (ddd, *J* = 10.5, 8.8, 6.9 Hz, 1H), 6.86 (td, *J* = 9.7, 6.6 Hz, 1H), 2.83 – 2.75 (m, 2H), 2.69 – 2.64 (m, 1H), 2.05 (s, 3H), 1.64 – 1.57 (m, 1H), 1.45 – 1.37 (m, 1H), 1.30 – 1.20 (m, 13H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 211.32, 119.05, 118.95, 105.69, 105.46, 105.29, 53.01, 31.96, 31.77, 30.14, 29.92, 29.77, 29.48, 29.33, 27.13, 22.78, 14.22. **Yield:** 65% as a

yellow oil, 99% ee (ERED-103). **R_f**: 0.30 (5% Et_2O/hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 98:2, flow rate 1 mL/min) t_1 3.55 min (minor) t_2 3.81 min (major). Molecular formula: $C_{18}H_{25}F_3O$ EI-MS $[M^{\cdot}]^+$ calcd: 314.1858 found: 326.1232 $[M + Na]^+$

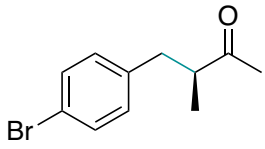


(*S*)-3-methyl-4-(4-nitrophenyl)-3-butan-2-one (10): ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 6.7 Hz, 2H), 3.12 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.85 (p, *J* = 7.1 Hz, 1H), 2.66 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.12 (s, 3H), 1.14 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, cdcl$_3$) δ** 210.96, 147.87, 146.75, 129.97, 123.81, 48.50, 38.39, 28.97, 16.72. **Yield**: 87% as a pale-yellow oil, 80% ee. **S enantiomer $\alpha_D^{20.0}$** = +10.1 (c1.05 in $CHCl_3$) (ERED-103). **R_f**: 0.25 (20% EtOAc/hexanes). The enantioselectivity was determined by HPLC analysis (Lux 5u Cellulose-2 column, hexanes/*i*-propanol 95:5, flow rate 0.5 mL/min) t_1 19.08 min (minor) t_2 20.20 min (major).

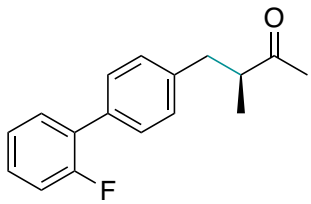


(*S*)-3-methyl-4-(2-nitrophenyl)butan-2-one (11): ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.95 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.30 (m, 2H), 3.34 (dd, *J* = 13.3, 6.9 Hz, 1H), 2.97 (h, *J* = 7.0 Hz, 1H), 2.81 (dd, *J* = 13.3, 7.0 Hz, 1H), 2.12 (s, 3H), 1.13 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, cdcl$_3$) δ** 211.49, 135.15, 133.40, 133.11, 127.74, 125.17, 47.46, 35.83, 29.13, 16.80. Yield: 87% as a pale yellow oil 96% ee (ERED-103). **R_f**: 0.30 (25%

EtOAc/hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OJ-H column, hexanes/*i*-propanol 90:10, flow rate 0.7 mL/min) t_1 12.79 min (major) t_2 13.85 min (minor).

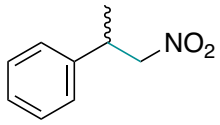


(*S*)-4-(4-bromophenyl)-3-methyl-3-butan-2-one (12): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 2.95 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.80 (p, *J* = 7.1 Hz, 1H), 2.51 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.09 (s, 3H), 1.09 (dd, *J* = 7.0, 1.3 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 211.74, 138.86, 131.64, 130.8 120.24, 48.78, 38.29, 29.03, 16.47. **Yield:** 86% as a colorless oil, 88% ee (ERED-103). **R_f:** 0.30 (10% EtOAc/hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OJ-H column, hexanes/*i*-propanol 95:5, flow rate 0.5 mL/min) t_1 29.94 min (minor) t_2 31.51 min (major).

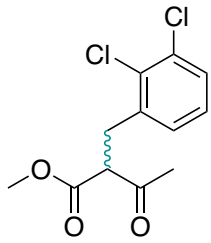


(*S*)-4-(2'-fluoro-[1,1'-biphenyl]-4-yl)-3-methyl-3-butan-2-one (13): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.49 (m2H), 7.44 (m, 1H), 7.31 (m1H), 7.27 – 7.18 (m, 3H), 7.16 (m, 1H), 3.07 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.89 (h, *J* = 7.0 Hz, 1H), 2.62 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.15 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 212.15, 139.37, 130.79, 130.77, 129.17, 128.99, 128.92, 124.48, 124.45, 116.31, 116.12, 48.89, 38.66, 28.98, 16.48. **Yield**: 82% as a white solid 99% ee (ERED-103). **R_f:** 0.30 (10% EtOAc/hexanes). The enantioselectivity was

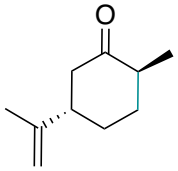
determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 98:2, flow rate 1.0 mL/min) t_1 7.23 min (minor) t_2 7.82 min (major). Molecular formula: $C_{17}H_{17}FO$ EI-MS $[M^{\cdot}]^+$ calcd: 256.1263 found: 279.1162 $[M + Na]^+$



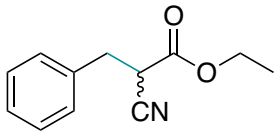
(1-nitropropan-2-yl)benzene (14): ^{1}H NMR (600 MHz, cdcl$_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 2H), 4.77 (h, *J* = 6.8 Hz, 1H), 3.32 (dd, *J* = 14.0, 7.4 Hz, 1H), 3.00 (dd, *J* = 14.0, 6.9 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 135.64, 129.10, 128.94, 127.54, 84.55, 41.29, 18.92. **Yield:** 91% as a colorless oil (ERED-103) **R_f**: 0.27 (5% EtOAc/hexanes).



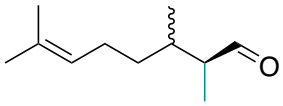
methyl-2-(2,3-dichlorobenzyl)-3-oxobutanoate (15): As a 1:1 mixture with the enol ether. **^{1}H NMR (500 MHz, cdcl$_3$) δ** 7.35 (m, 1H), 7.19 – 7.16 (m, 1H), 7.12 (m, 1H), 3.97 (dd, *J* = 8.2, 6.5 Hz, 1H), 3.71 (s, 3H), 3.35 (dd, *J* = 14.0, 6.6 Hz, 1H), 3.28 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 201.90, 169.30, 129.94, 129.35, 128.92, 128.68, 127.42, 58.45, 42.99, 32.83, 28.77. **Yield:** 92% as a colorless oil (ERED-103). **R_f:** 0.25 (15% EtOAc/Hex)



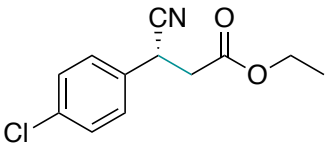
(2*S*,5*S*)-Carvone (16): ^{1}H NMR (500 MHz, cdcl$_3$) δ 4.77 – 4.72 (m, 2H), 2.47 – 2.42 (m, 1H), 2.40 – 2.32 (m, 2H), 2.32 – 2.27 (m, 1H), 2.13 (ddt, *J* = 12.9, 6.2, 3.4 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.74 (d, *J* = 2.2 Hz, 3H), 1.68 – 1.62 (m, 1H), 1.38 (dd, *J* = 13.1, 3.5 Hz, 1H), 1.04 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 212.80, 147.77, 109.74, 47.01, 44.88, 35.05, 30.91, 30.76, 20.61, 14.47. **Yield**: 73% as a pale yellow oil (ERED-103) **R$_f$:** 0.60 (5% EtOAc/Hexanes) . The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 99:1, flow rate 0.7 mL/min) t_1 6.26 min (major) t_2 6.74 min (minor).



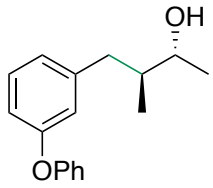
ethyl 2-cyano-3-phenyl-2-propanoate (17): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.36 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.73 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.30 (dd, *J* = 13.8, 5.8 Hz, 1H), 3.21 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 165.64, 135.41, 129.15, 128.99, 127.91, 116.27, 63.05, 39.80, 35.89, 14.05. **Yield**: 96% as a pale-yellow oil (ERED-P1-A04). **R$_f$:** 0.30 (10% EtOAc/hexanes)



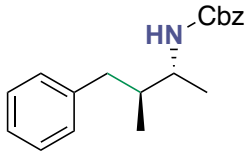
(2*S*)-2,3,7-trimethyloct-6-enal (18): Data for major diastereomer **^{1}H NMR (500 MHz, cdcl$_3$) δ** 9.68 (d, *J* = 1.9 Hz, 1H), 5.09 (m, 1H), 2.38 – 2.26 (m, 1H), 2.08 – 1.88 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.43 – 1.16 (m, 2H), 1.05 (s, 3H), 0.99 (s, 3H), 0.84 (d, *J* = 6.9 Hz, 3H); for the minor diastereomer, the following diagnostic signals were observed: **δ** 9.65 (d, J = 1.5 Hz, 1H), 1.00 (d, J = 7.0 Hz, 3H), 0.84(d, J = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 205.96, 205.89, 131.98, 124.23, 124.15, 51.69, 50.68, 34.91, 33.57, 33.41, 32.31, 25.88, 25.84, 25.79, 17.81, 17.45, 15.52, 10.03, 8.26. **Yield**: 85% as a colorless oil 92% ee (ERED-103). **R$_f$:** 0.70 (5% EtOAc/hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 99:1, flow rate 0.7 mL/min) t_1 4.16 min (minor) t_2 5.81 min (major).



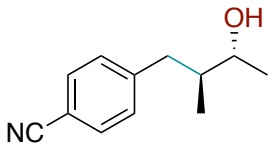
ethyl (*R*)-3-(4-chlorophenyl)-3-cyanopropanoate (19): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.29 (t, *J* = 7.4 Hz, 1H), 4.19 (qq, *J* = 7.1, 3.7 Hz, 2H), 3.01 (dd, *J* = 16.6, 7.8 Hz, 1H), 2.83 (dd, *J* = 16.6, 7.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 169.03, 134.84, 133.11, 129.62, 128.94, 119.64, 61.74, 40.00, 32.76, 14.22. Yield: 82% as a colorless oil, **R enantiomer $\alpha_D^{20.0}$** = -8.1 (c0.991 in $CHCl_3$) 96% ee (ERED-P1-H09). The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 98:2, flow rate 1.0 mL/min) t_1 17.75 min (major) t_2 19.92 min (minor).



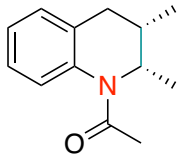
(2*R*,3*S*)-3-methyl-4-(3-phenoxyphenyl)butan-2-ol (20): ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.34 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.94 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.88 – 6.83 (m, 2H), 3.70 (p, *J* = 6.2 Hz, 1H), 2.91 – 2.84 (m, 1H), 2.34 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.49 (s, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, cdcl$_3$) δ** 157.23, 143.32, 129.84, 129.59, 124.35, 123.19, 119.91, 118.84, 116.52, 71.51, 42.27, 39.07, 20.00, 14.78. **Yield**: 82% as a colorless oil, 88% ee, 86% de (ERED-103, ADH-101). The enantioselectivity was determined by HPLC analysis (Lux 5u Cellulose-2 column, hexanes/*i*-propanol 99:1, flow rate 0.5 mL/min) t_1 16.94 min (minor) t_2 19.93 min (major). Molecular formula: $C_{17}H_{18}O_2$ EI-MS $[M^{\cdot}]^+$ calcd: 254.1307 found: 236.1210 $[M - H_2O]^+$



benzyl ((2*R*,3*S*)-3-methyl-4-phenylbutan-2-yl)carbamate (16): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 – 7.29 (m, 5H), 7.29 – 7.24, 7.23 (m, 2H) – 7.04 (m, 3H), 5.11 (s, 2H), 4.61 (s, 1H), 3.83 (s, 1H), 2.76 (dd, *J* = 13.4, 5.4 Hz, 1H), 2.32 (dd, *J* = 13.4, 9.1 Hz, 1H), 1.89 (s, 1H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 155.9, 140.8, 136.7, 129.1 (2C), 128.6, (2C) 128.3 (3C), 128.2 (2C), 125.9, 66.6, 50.5, 40.3, 39.6, 18.4, 14.5. **Yield**: 62% as a yellow oil (ERED-103, ATA-256). **HRMS (m/z):** $[M+Na]^+$ calcd. for $C_{19}H_{23}NO_2$, 320.1627; found, 320.1629

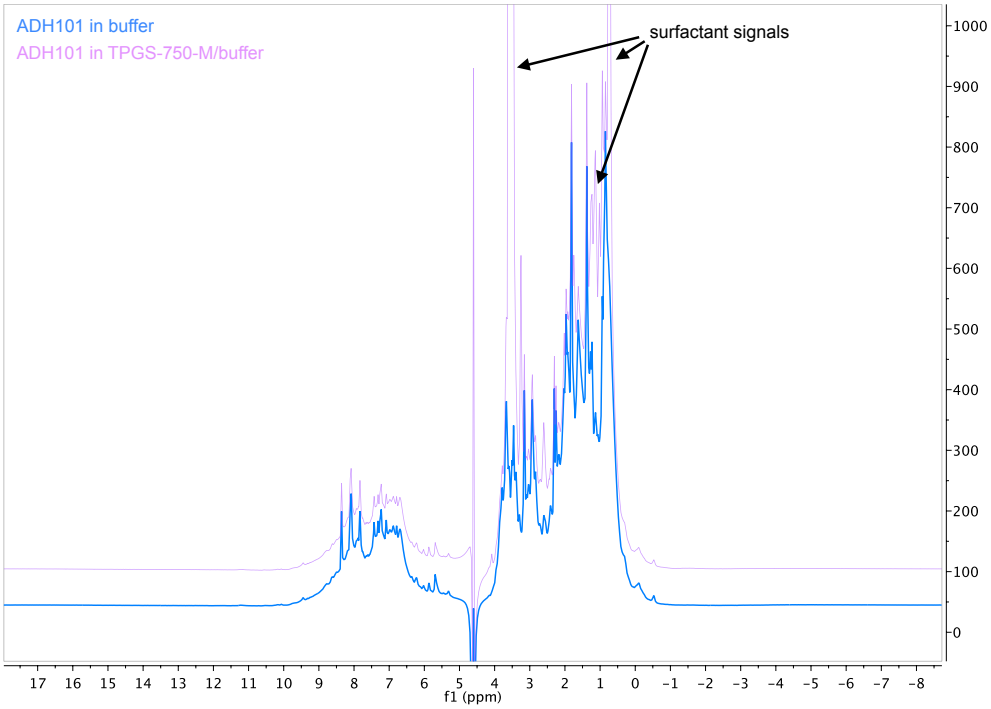


4-((2*S*,3*R*)-3-hydroxy-2-methylbutyl)benzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.65 (p, *J* = 6.2 Hz, 1H), 2.98 (dd, *J* = 13.4, 4.5 Hz, 1H), 2.39 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.78 (dtd, *J* = 12.4, 6.5, 3.3 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 147.15, 132.19, 132.15, 130.10, 130.05, 119.24, 109.75, 71.33, 42.17, 39.17, 20.45, 14.89. **Yield:** 54% as a light yellow oil 89% ee, 85% de (ERED-103, ADH-101). **R_f** 0.31 (35% EtOAc/Hexanes). The enantioselectivity was determined by HPLC analysis (Chiracel OD-H column, hexanes/*i*-propanol 98:2, flow rate 0.7 mL/min) t_1 52.31 min (minor) t_2 54.02 min (major). Molecular formula: $C_{12}H_{15}NO$ EI-MS $[M^{\cdot}]^+$ calcd: 189.1154 found: 171.1053 $[M - H_2O]^+$

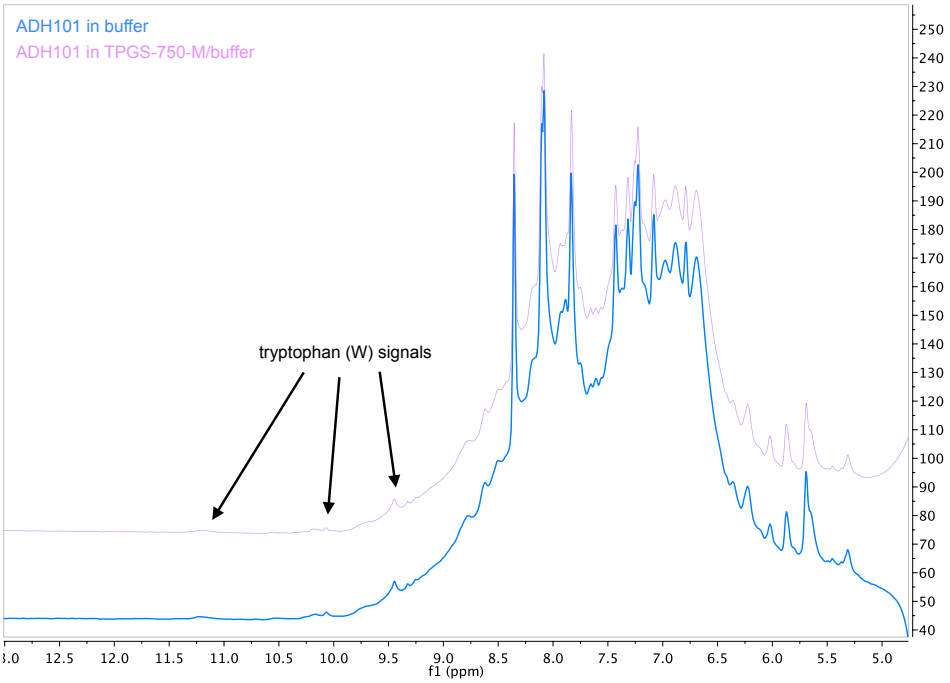


1-((2*S*,3*S*)-2,3-dimethyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one: *syn : anti* = 90:10; For *syn* isomer: **^{1}H NMR (500 MHz, $cdcl_3$) δ** 7.13 (m, 4H), 2.92 (dd, *J* = 17.5, 6.7 Hz, 1H), 2.44 (dd, *J* = 17.5, 11.6 Hz, 1H), 2.24 (s, 3H), 2.21 – 2.15 (m, 1H), 1.14 (t, *J* = 6.9 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $cdcl_3$) δ** 170.08, 129.19, 125.86, 125.61, 124.88, 32.37, 32.07, 29.85, 23.75, 19.75, 18.76. **Yield:** 55% as a yellow oil. (ERED-103). **R_f:** 0.30 (25% EtOAc/Hexanes)

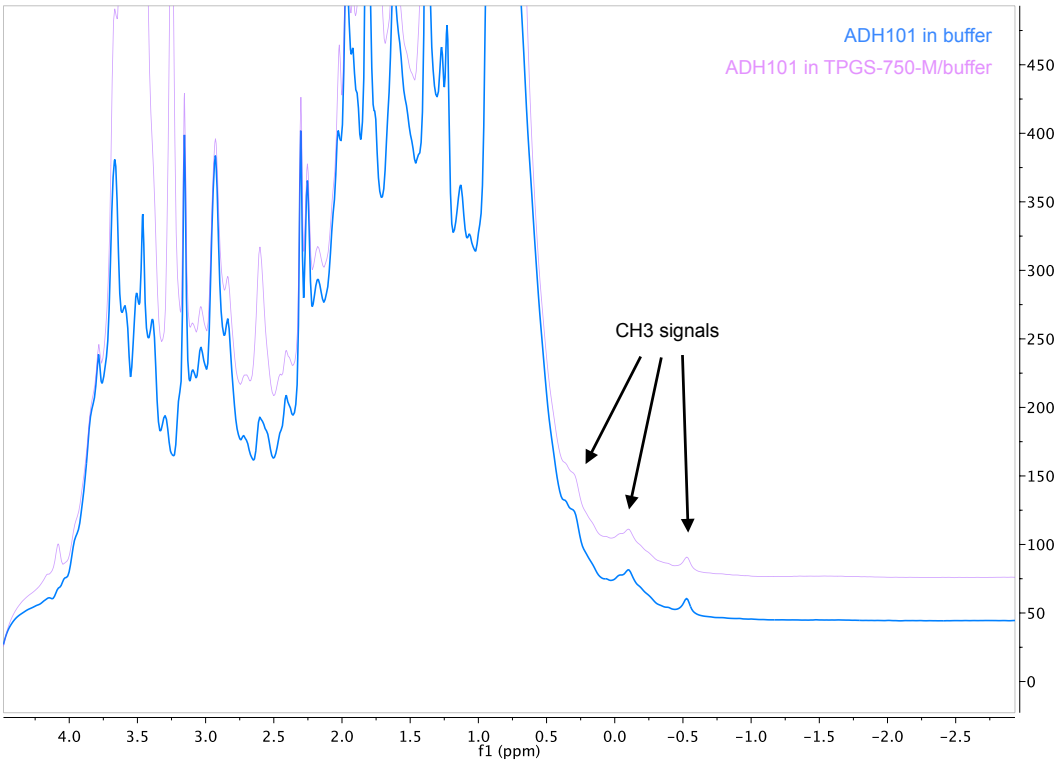
25. ^{1}H, ^{13}C Spectra of Compounds



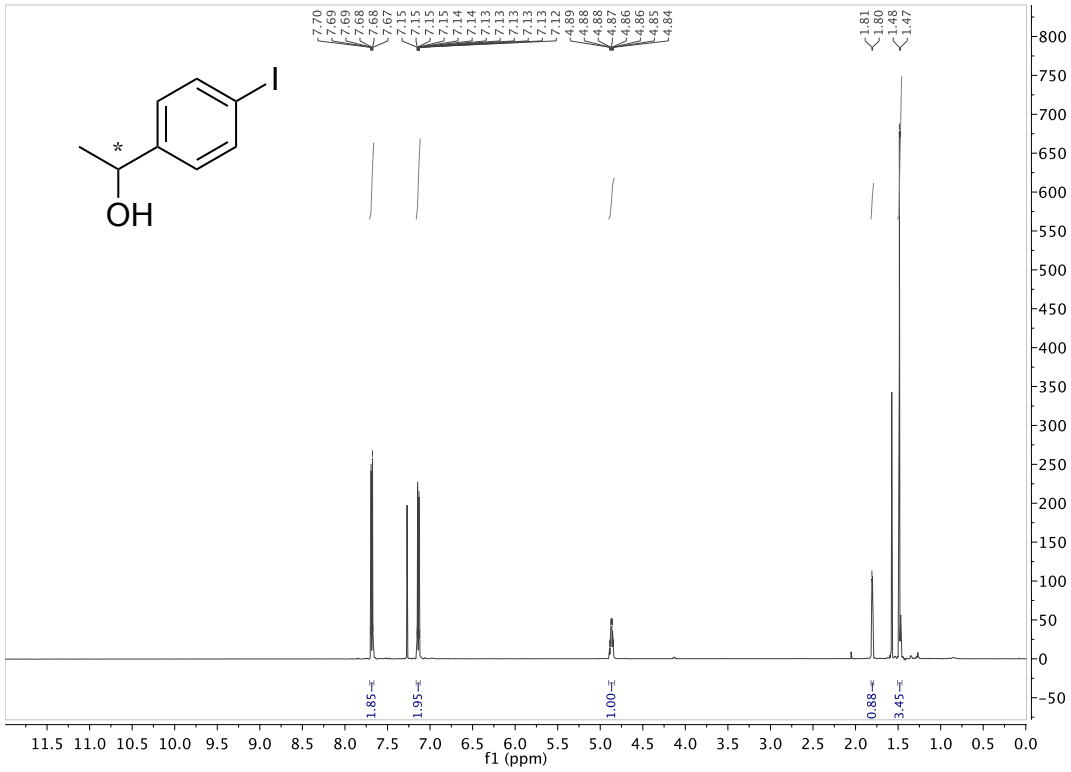
Supplementary figure 9: ^{1}H NMR spectra of ADH101. *The ^{1}H NMR spectra of ADH101 has been taken in D_2O (blue line) and TPGS-750-M/D_2O (purple line). This figure shows the full spectra.*

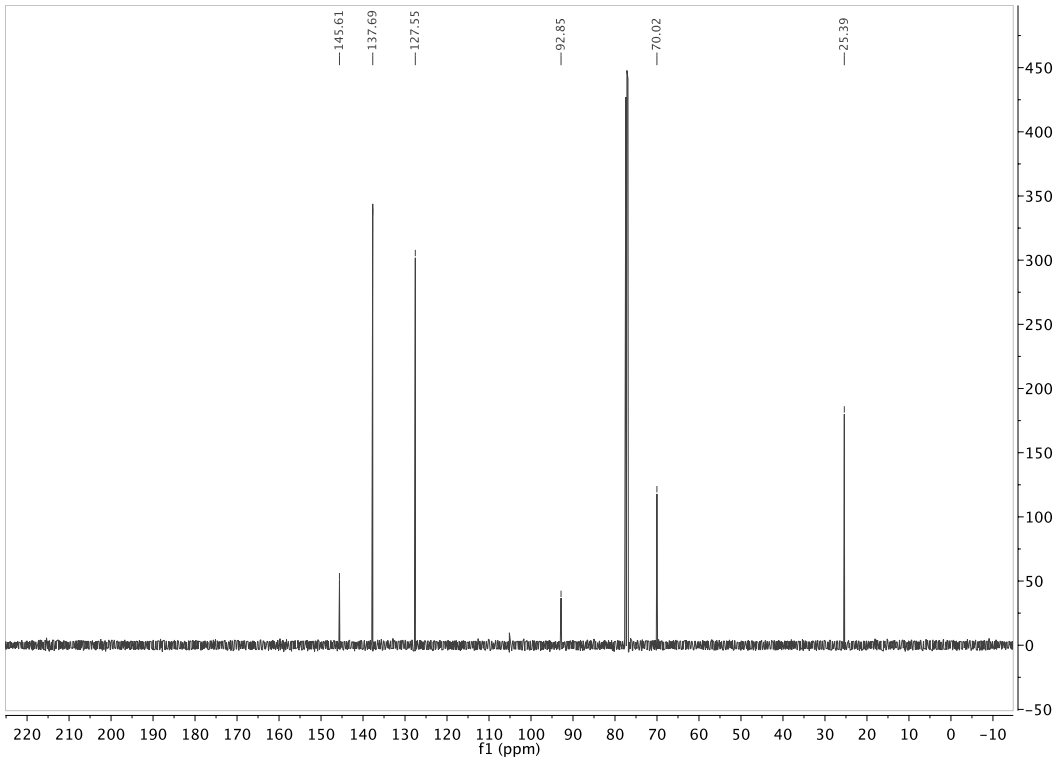


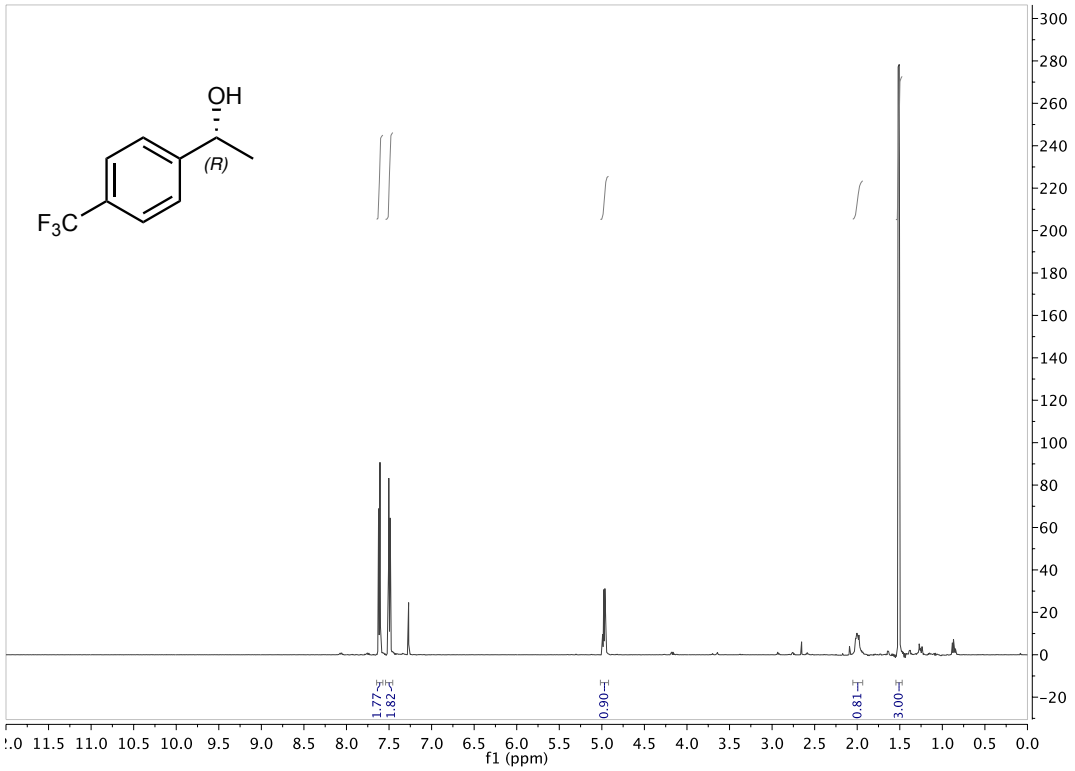
Supplementary figure 10: ^{1}H NMR spectra of ADH101. *The ^{1}H NMR spectra of ADH101 has been taken in D_2O (blue line) and TPGS-750-M/D_2O (purple line). This figure shows a zoom on the amide signal section.*

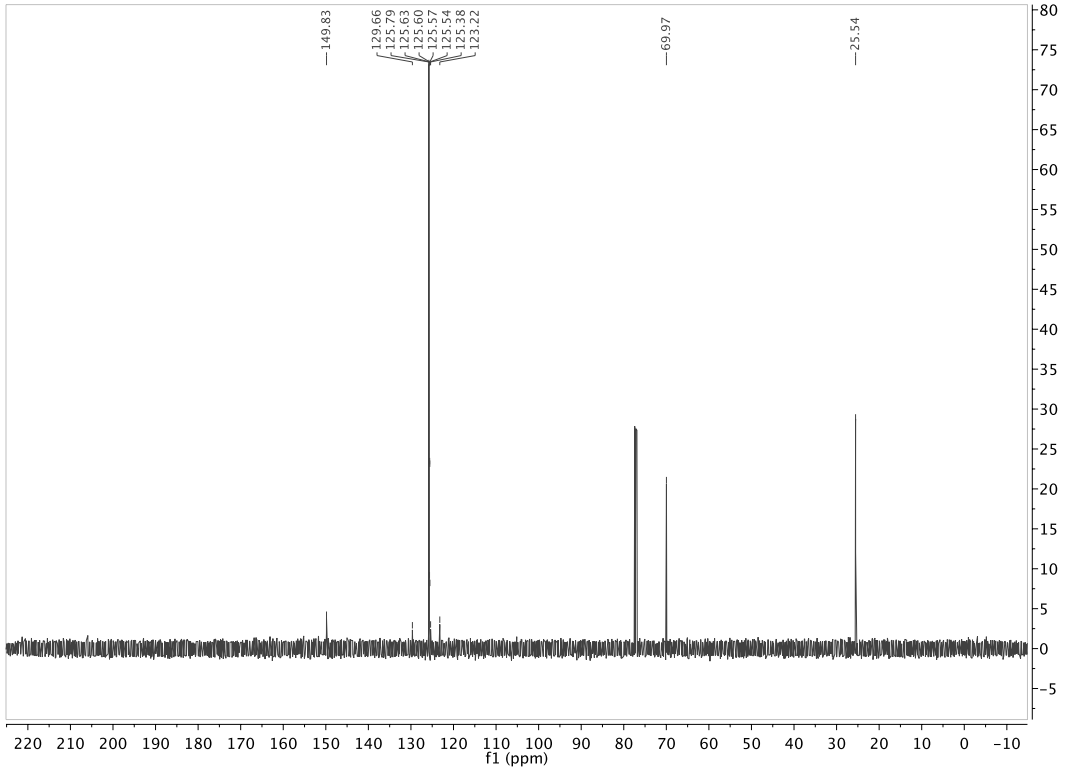


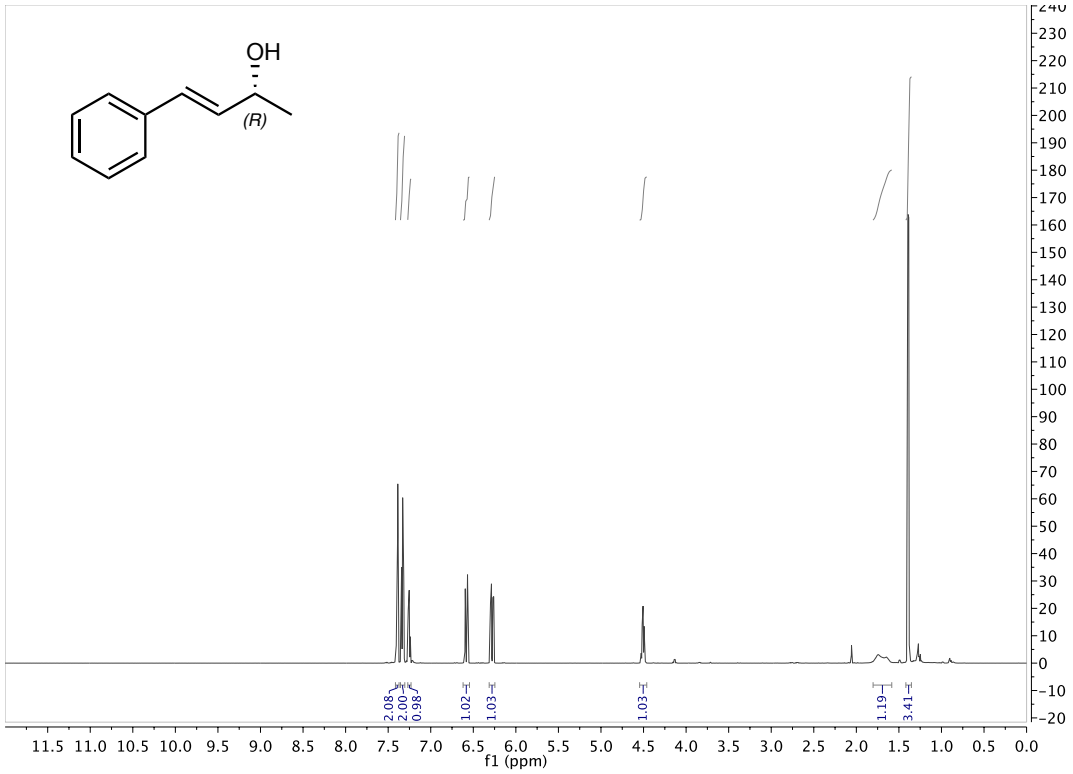
Supplementary figure 11: ^{1}H NMR spectra of ADH101. *The ^{1}H NMR spectra of ADH101 has been taken in D_2O (blue line) and TPGS-750-M/D_2O (purple line). This figure shows a zoom on the hydrophobic signal section.*

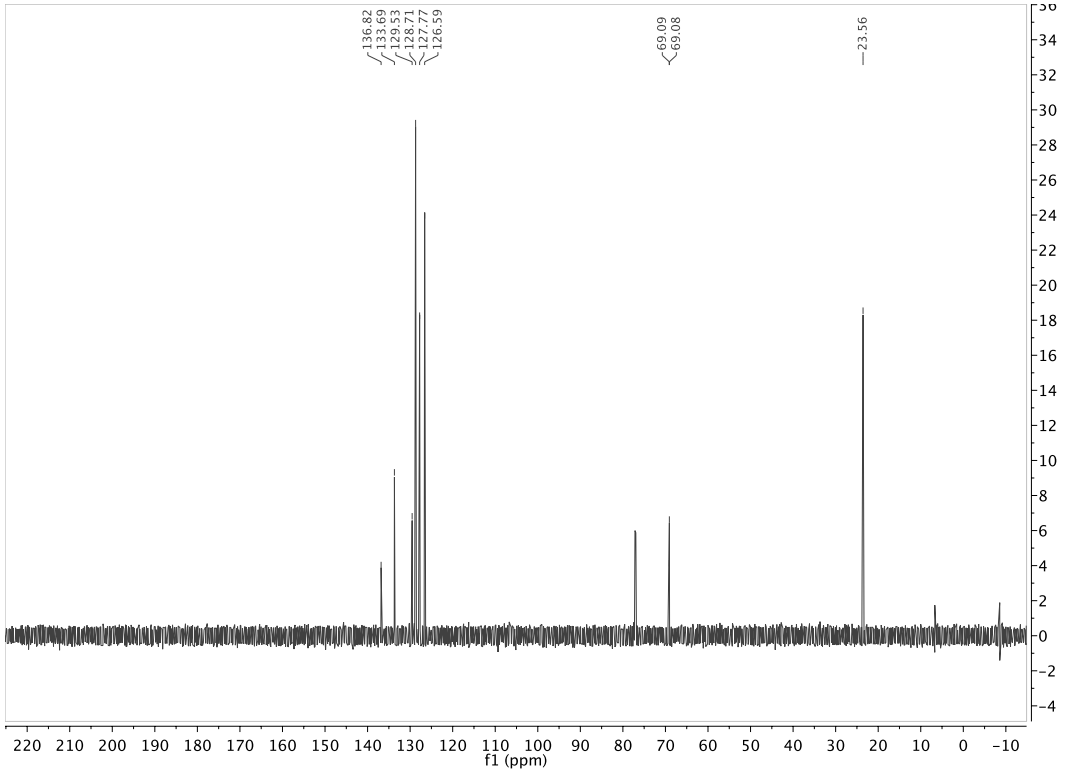

7.70
7.69
7.69
7.68
7.68
7.67
7.15
7.15
7.15
7.15
7.14
7.14
7.13
7.13
7.13
7.13
7.12
4.89
4.88
4.88
4.87
4.86
4.86
4.85
4.84
1.81
1.80
1.48
1.48
1.47
I
*
OH
1.85
1.95
1.00
0.88
3.45
f1 (ppm)


145.61
137.69
127.55
92.85
70.02
25.39
f1 (ppm)


OH
(R)
F3C
1.77
1.82
0.90
0.81
3.00
f1 (ppm)


149.83
129.66
125.79
125.63
125.60
125.57
125.54
125.38
123.22
69.97
25.54
f1 (ppm)


OH
(R)
2.08
2.00
0.98
1.02
1.03
1.03
1.19
3.41
f1 (ppm)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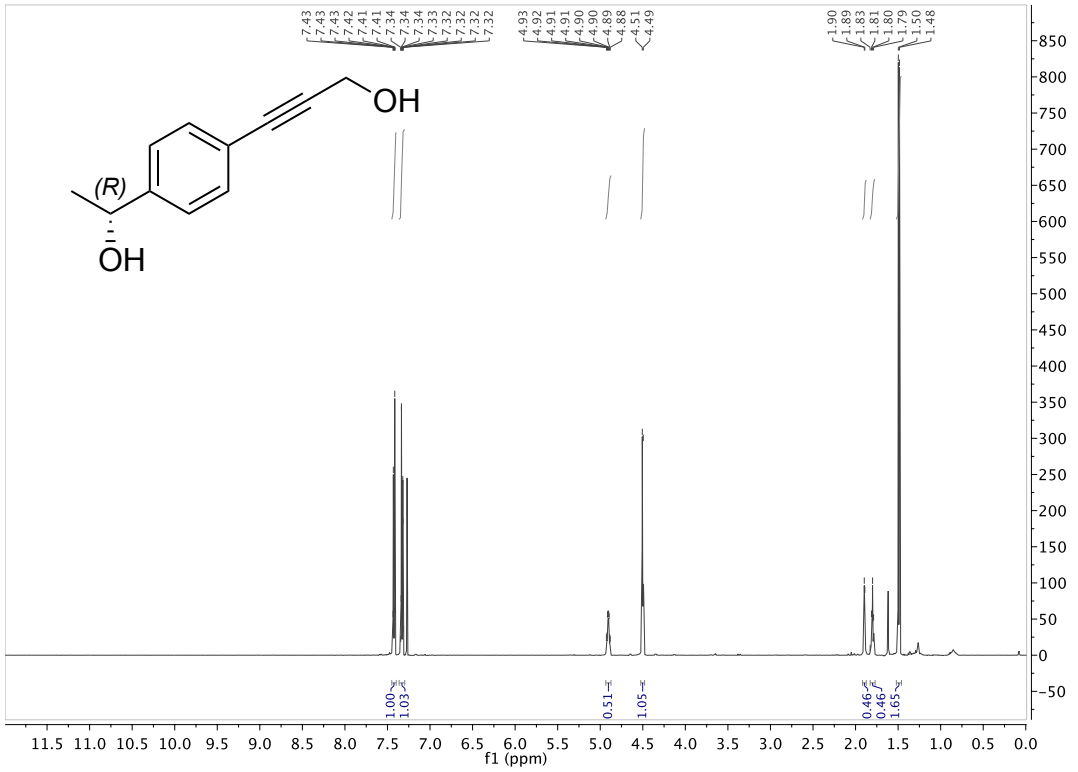
133.69
129.53
128.71
127.77
126.59
69.09
69.08
23.56
f1 (ppm)


7.43
7.43
7.43
7.42
7.41
7.41
7.34
7.34
7.34
7.33
7.32
7.32
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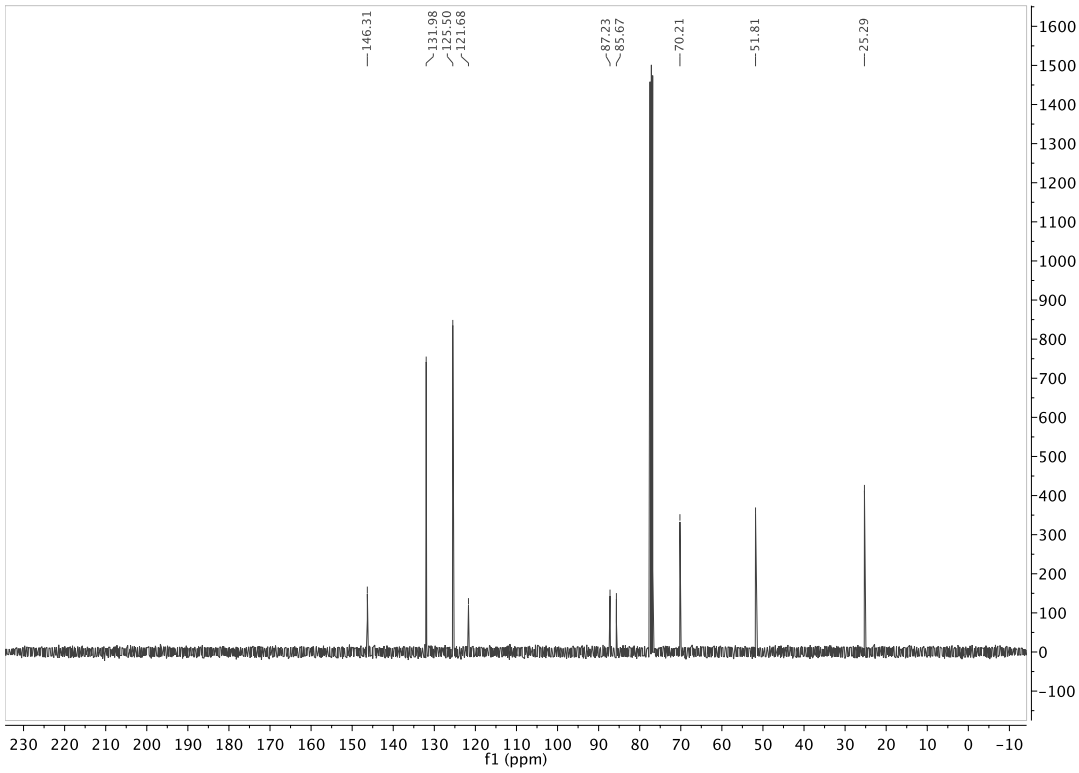
7.32
4.93
4.92
4.91
4.91
4.90
4.90
4.89
4.88
4.51
4.49
1.90
1.89
1.83
1.81
1.80
1.79
1.50
1.48
OH
(R)
OH
1.00
1.03
0.51
1.05
0.46
0.46
1.65
f1 (ppm)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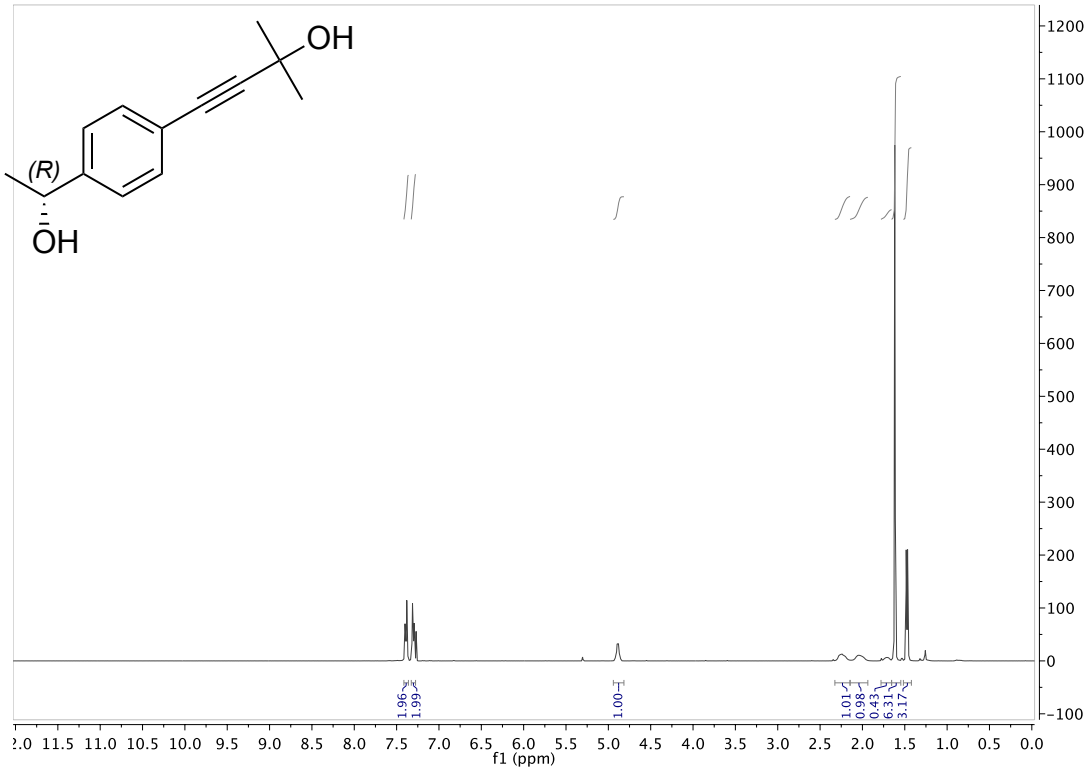
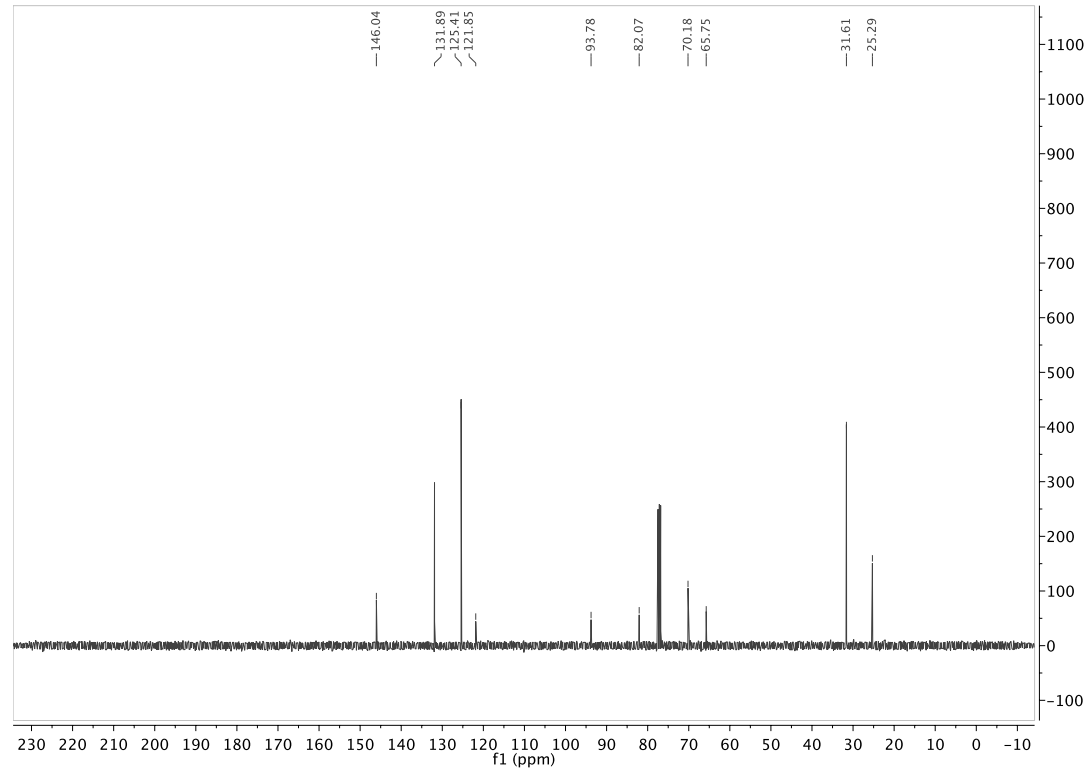
131.98
125.50
121.68
87.23
85.67
70.21
51.81
25.29
f1 (ppm)


OH
(R)
OH
1.96
1.99
1.00
1.01
0.98
0.43
6.31
3.17
f1 (ppm)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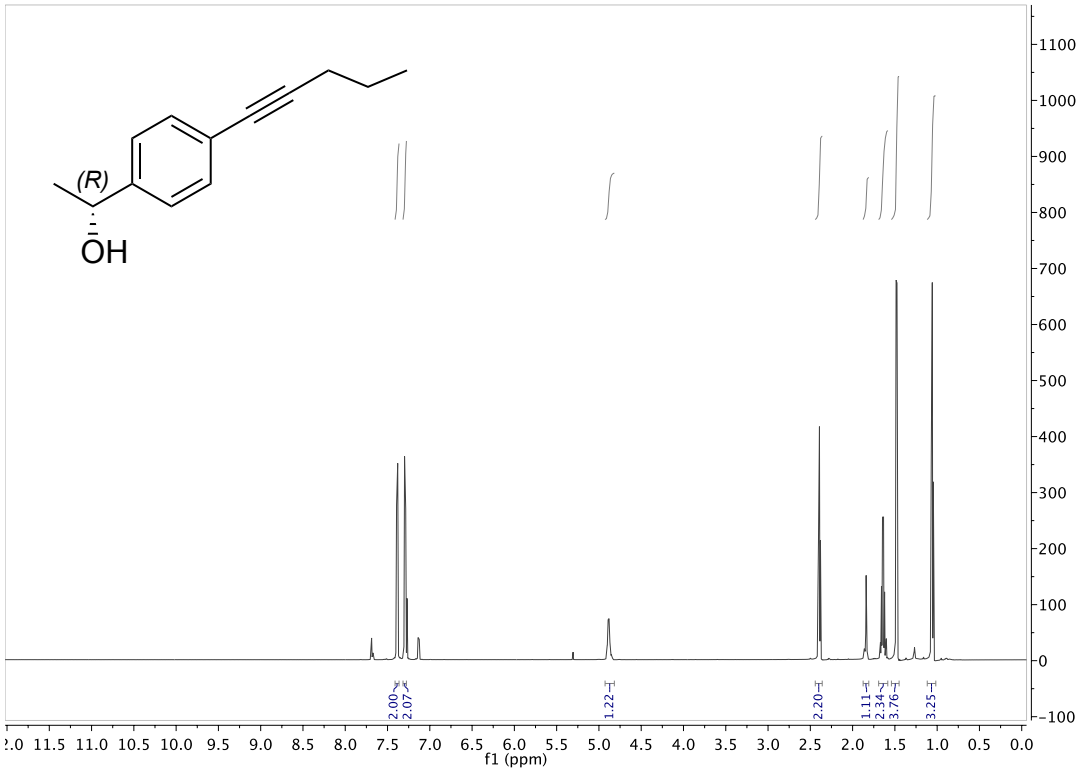
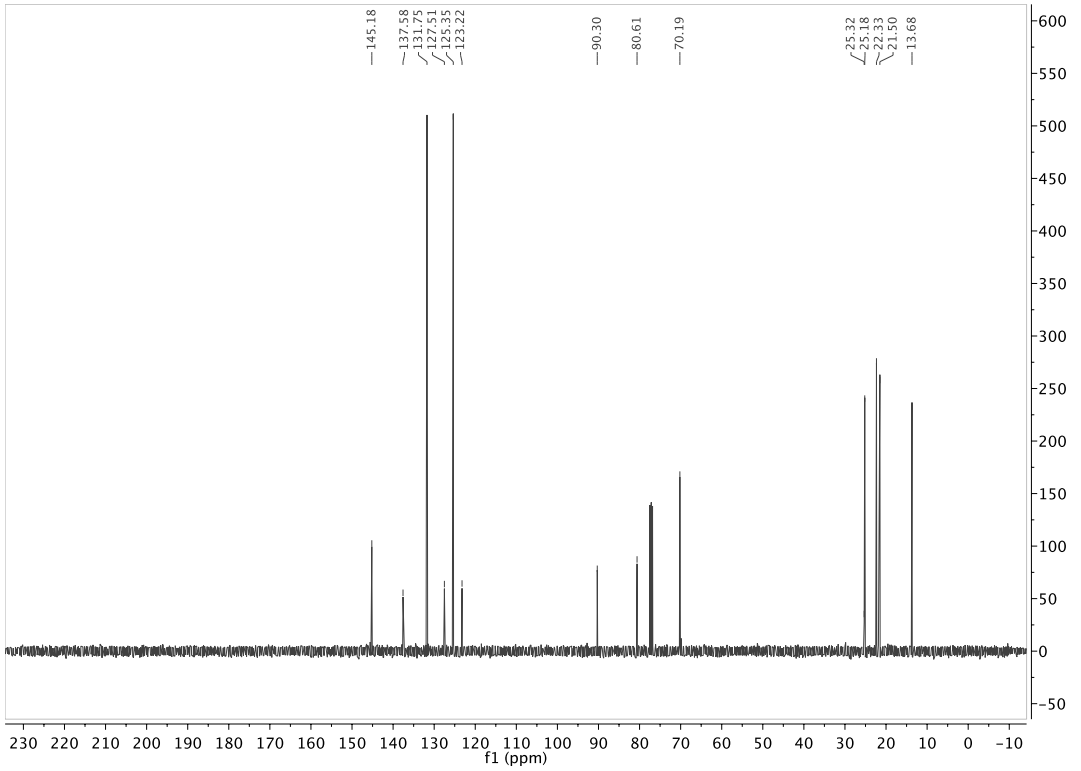
82.07
70.18
65.75
31.61
25.29
f1 (ppm)


(R)
OH
2.00
2.07
1.22
2.20
1.11
2.34
3.76
3.25
f1 (ppm)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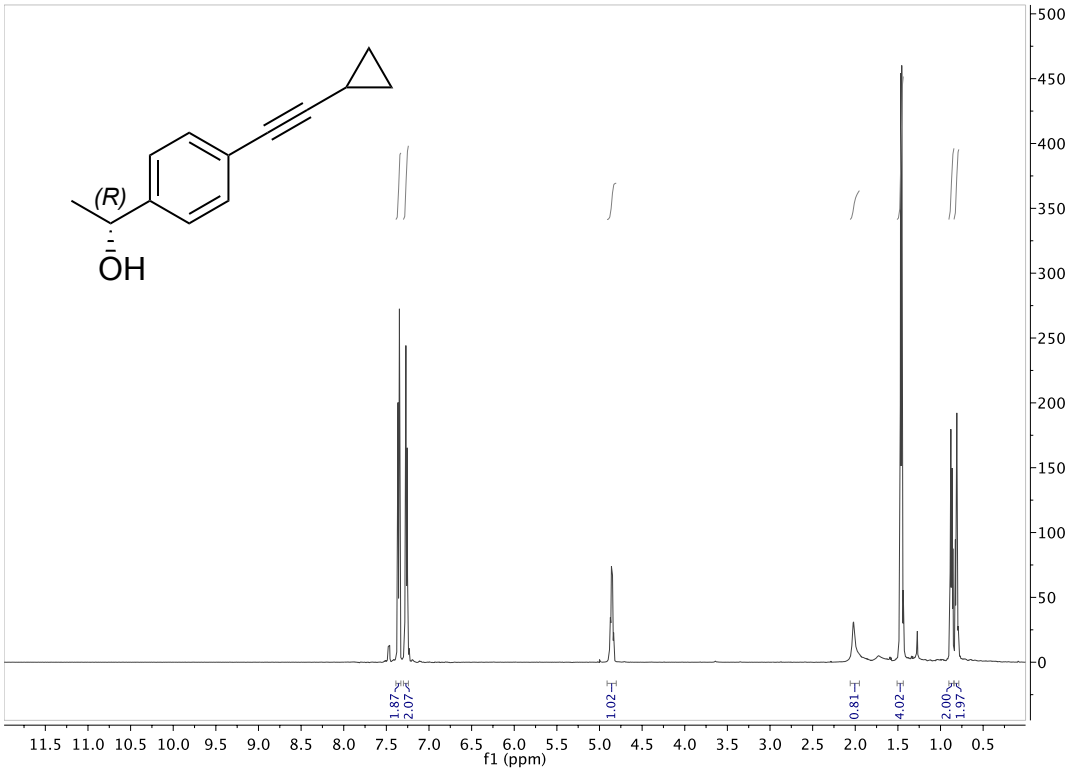
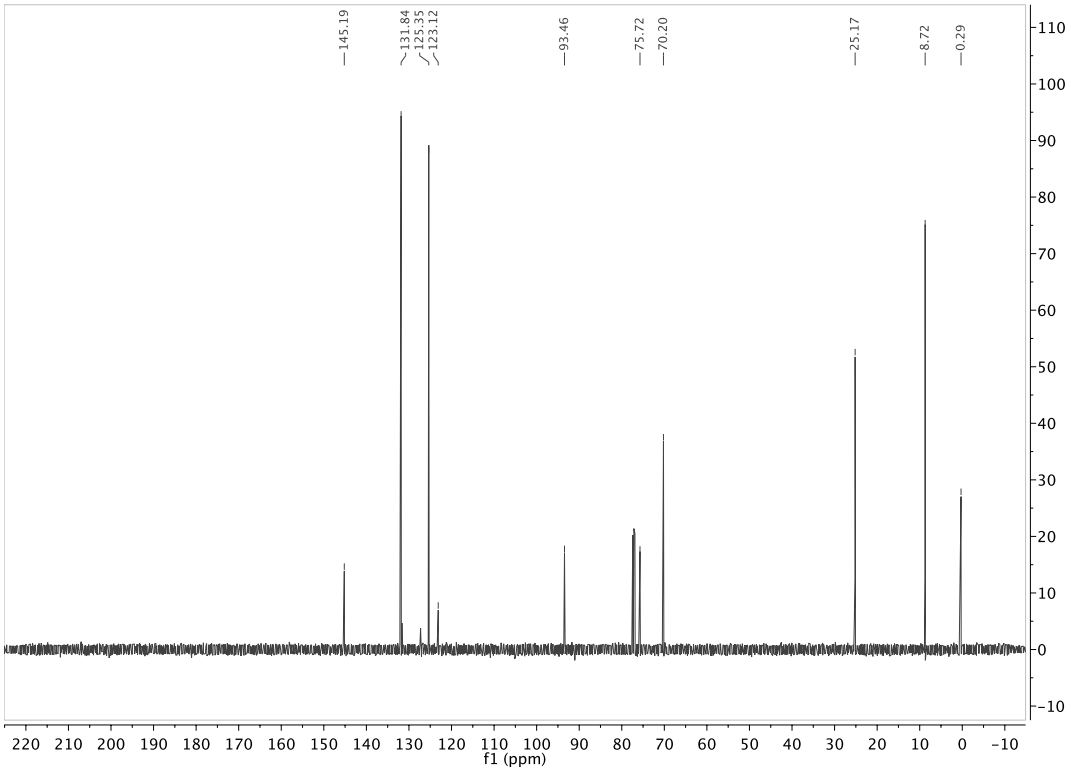
127.51
125.35
123.22
90.30
80.61
70.19
25.32
25.18
22.33
21.50
13.68
f1 (ppm)


(R)
OH
1.87
2.07
1.02
0.81
4.02
2.00
1.97
f1 (ppm)


145.19
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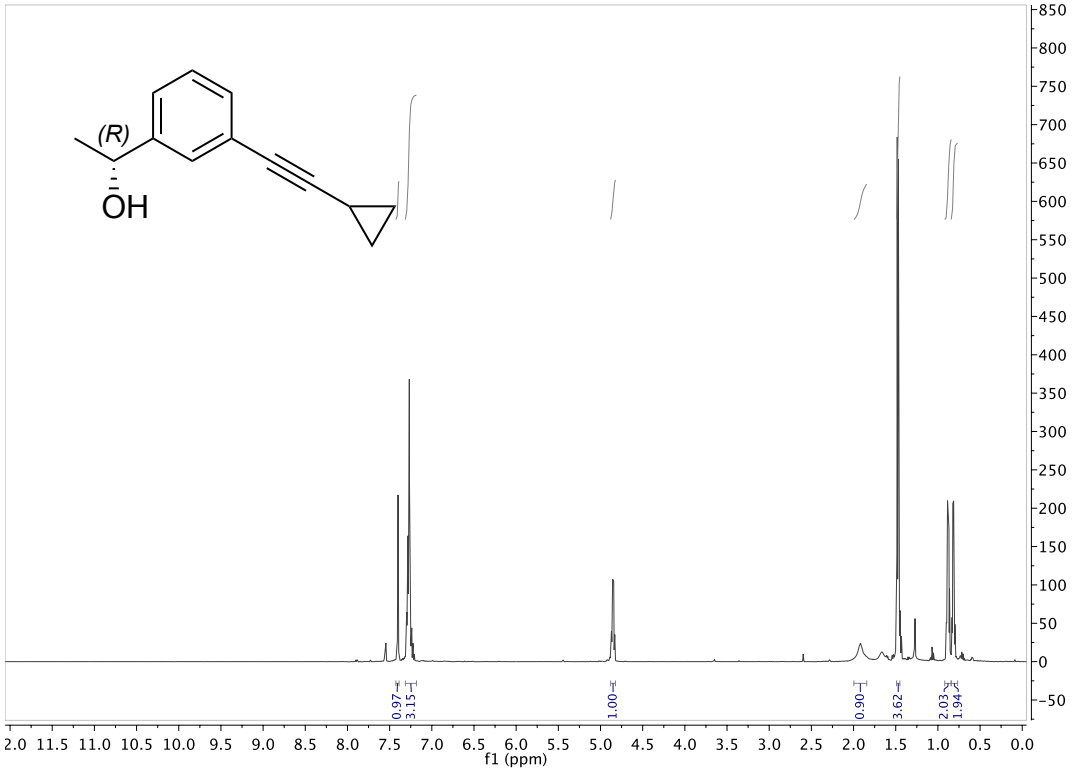
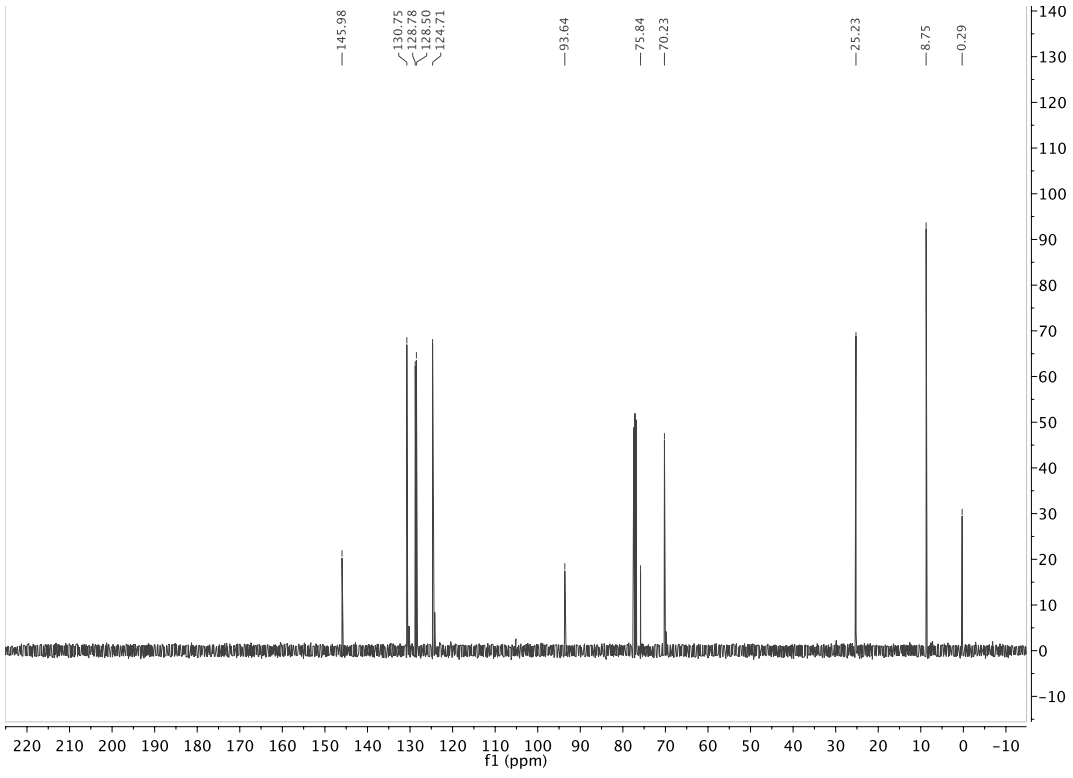
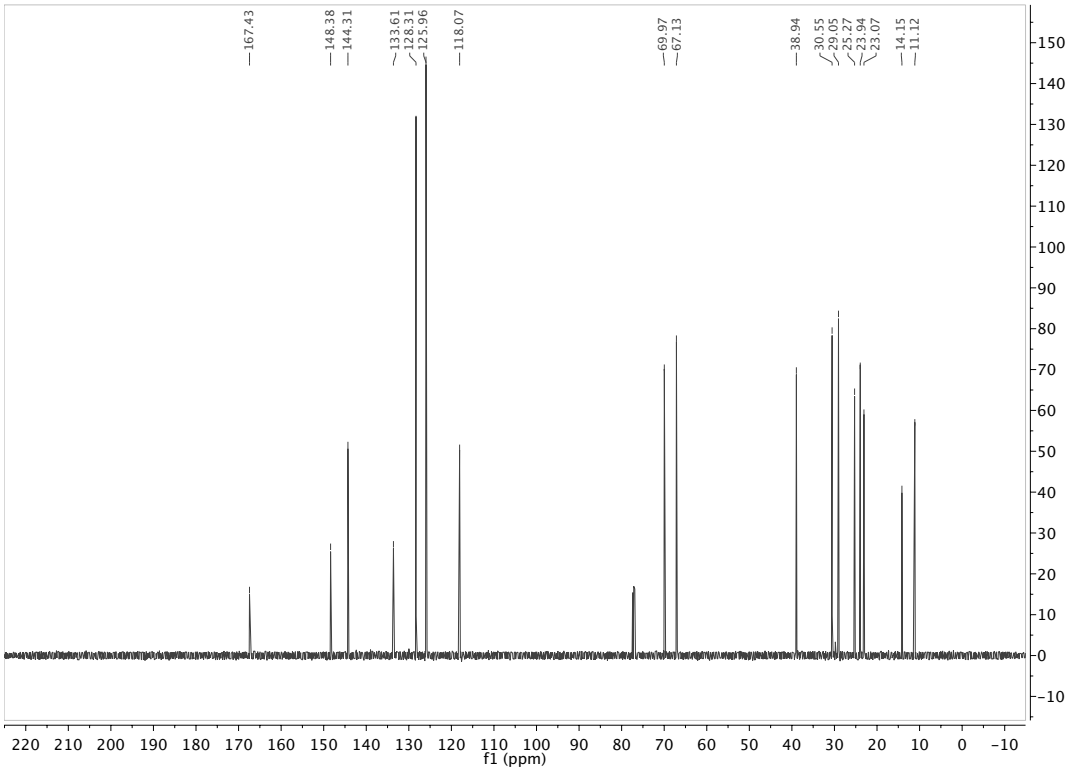
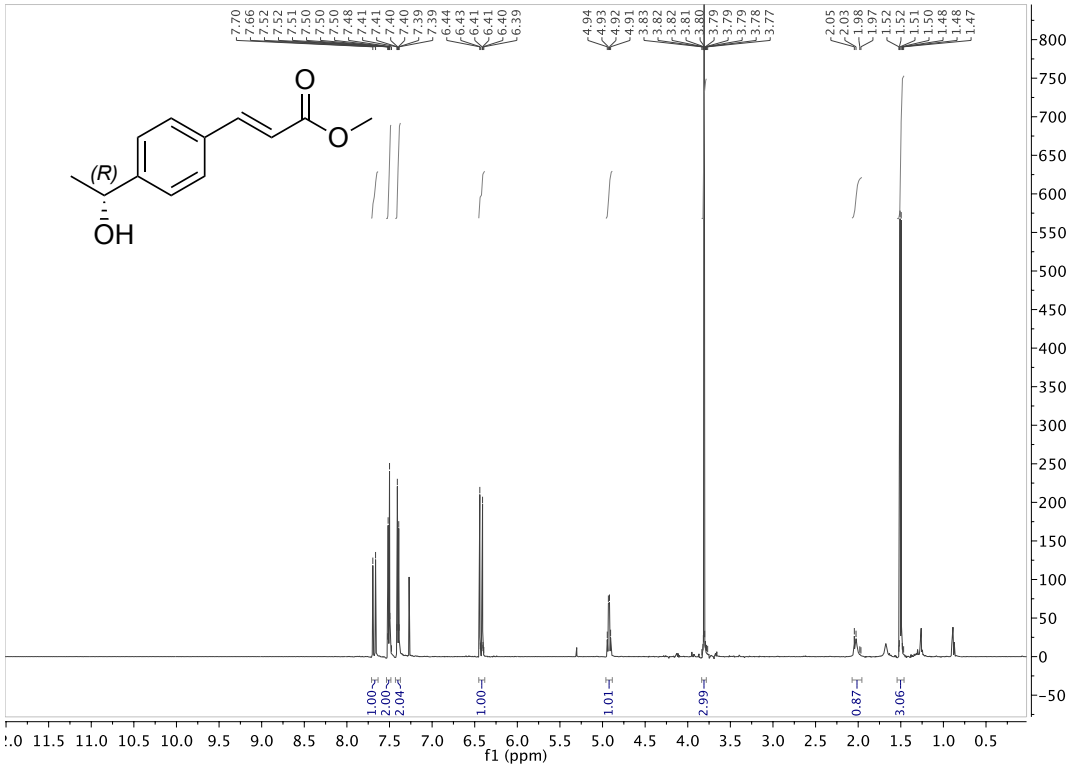
125.35
123.12
93.46
75.72
70.20
25.17
8.72
0.29
f1 (ppm)

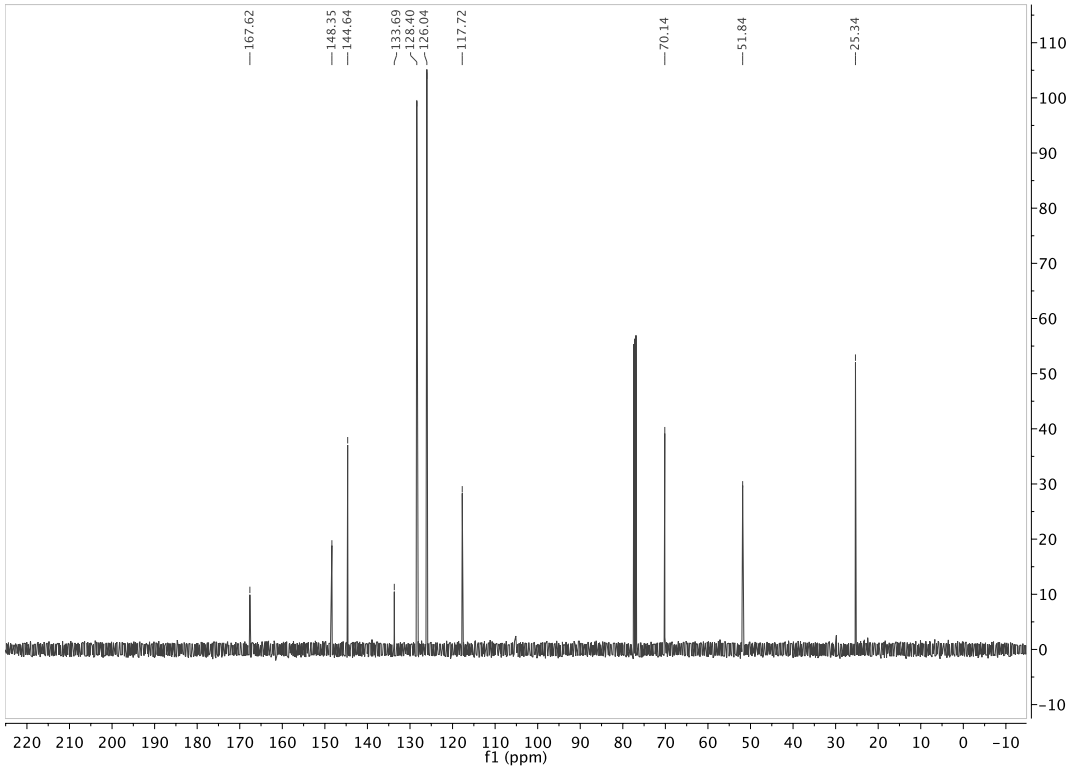

(R)
OH
0.97
3.15
1.00
0.90
3.62
2.03
1.94
f1 (ppm)

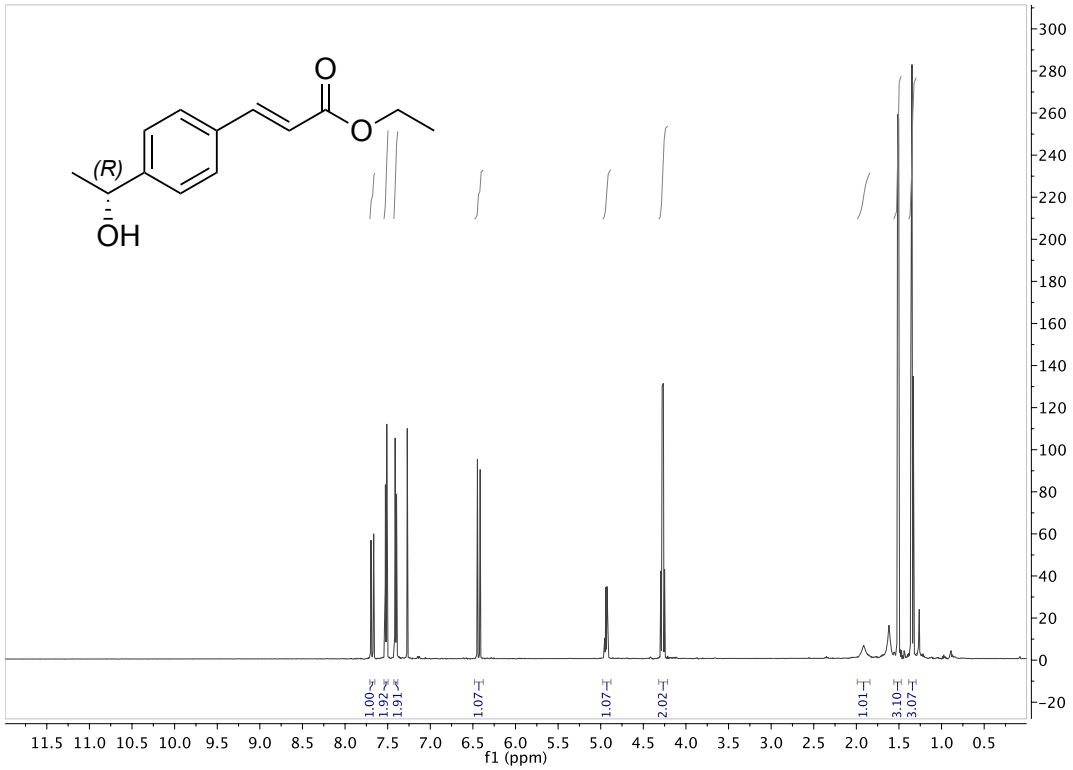

145.98
130.75
128.78
128.50
124.71
93.64
75.84
70.23
25.23
8.75
0.29
f1 (ppm)

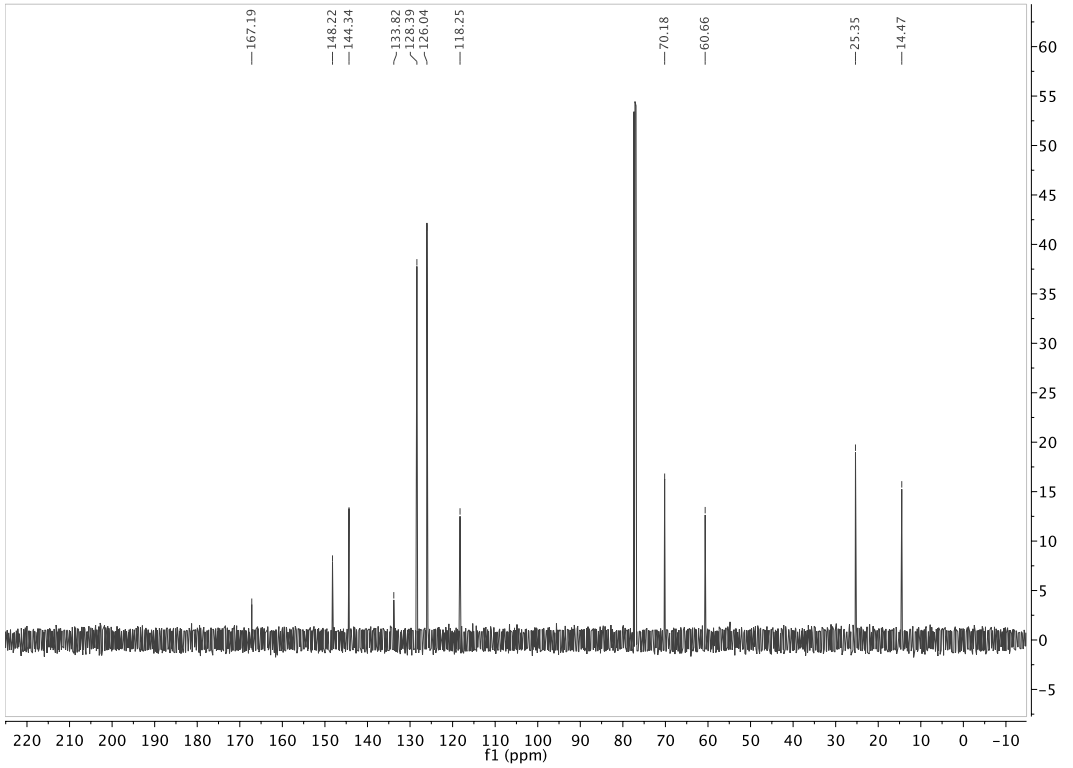

O
O
*
OH
f1 (ppm)

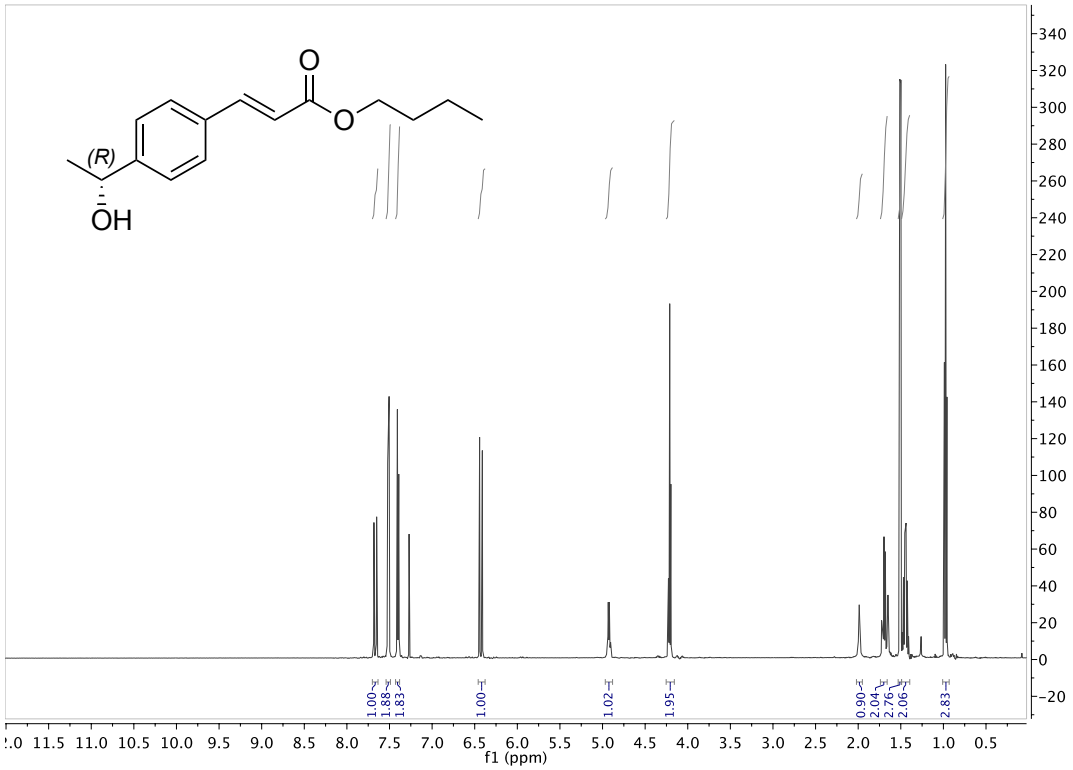

167.43
148.38
144.31
133.61
128.31
125.96
118.07
69.97
67.13
38.94
30.55
29.05
25.27
23.94
23.07
14.15
11.12
f1 (ppm)

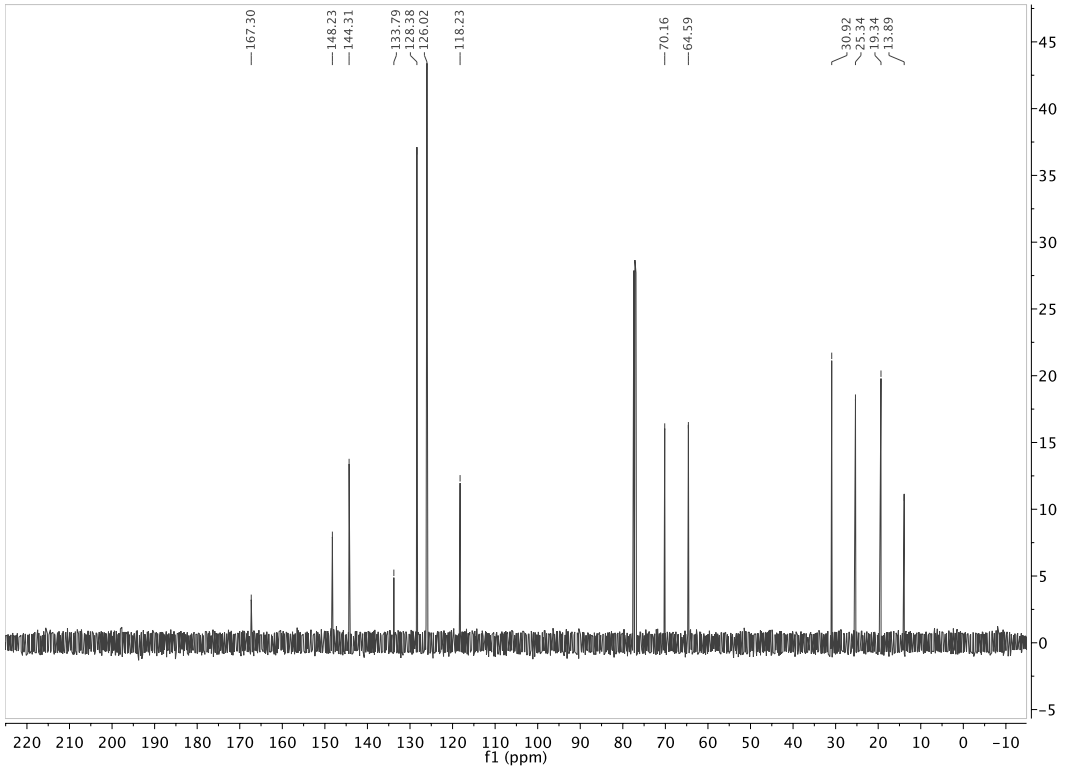

7.70
7.66
7.52
7.52
7.51
7.50
7.50
7.50
7.48
7.41
7.41
7.40
7.40
7.39
7.39
6.44
6.43
6.41
6.41
6.40
6.39
4.94
4.93
4.92
4.91
3.83
3.82
3.82
3.81
3.80
3.79
3.79
3.79
3.78
3.77
2.05
2.03
1.98
1.97
1.52
1.52
1.51
1.50
1.48
1.47
O
O
(R)
OH
1.00
2.00
2.04
1.00
1.01
2.99
0.87
3.06
f1 (ppm)

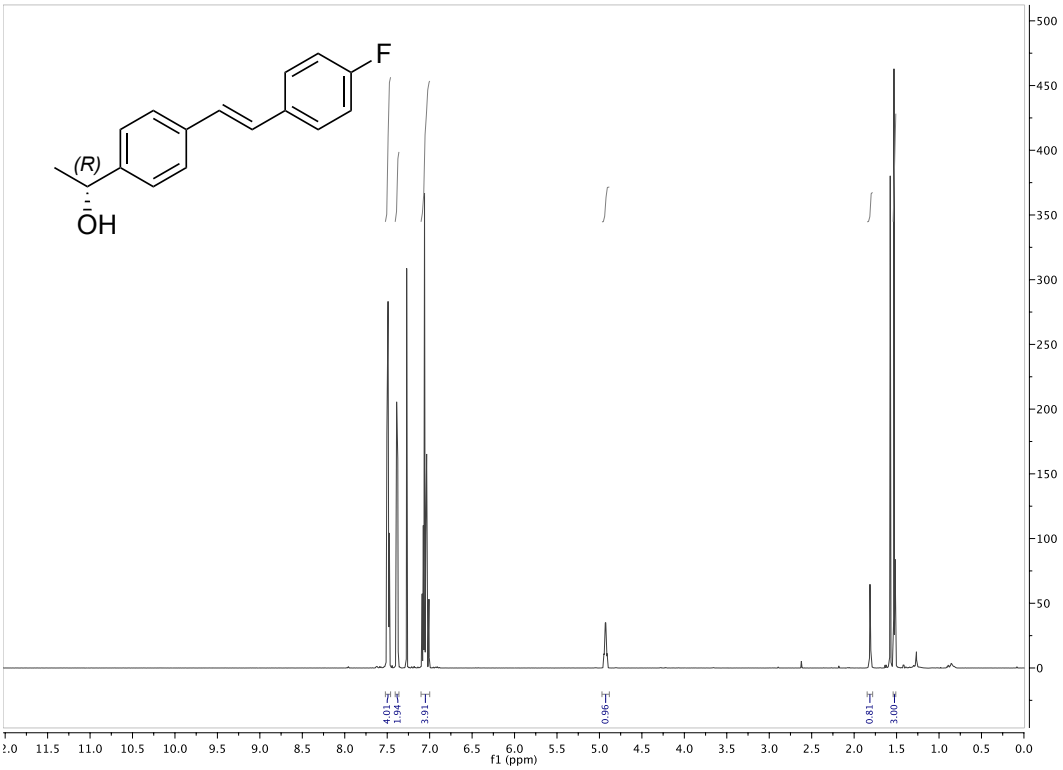

167.62
148.35
144.64
133.69
128.40
126.04
117.72
70.14
51.84
25.34
f1 (ppm)

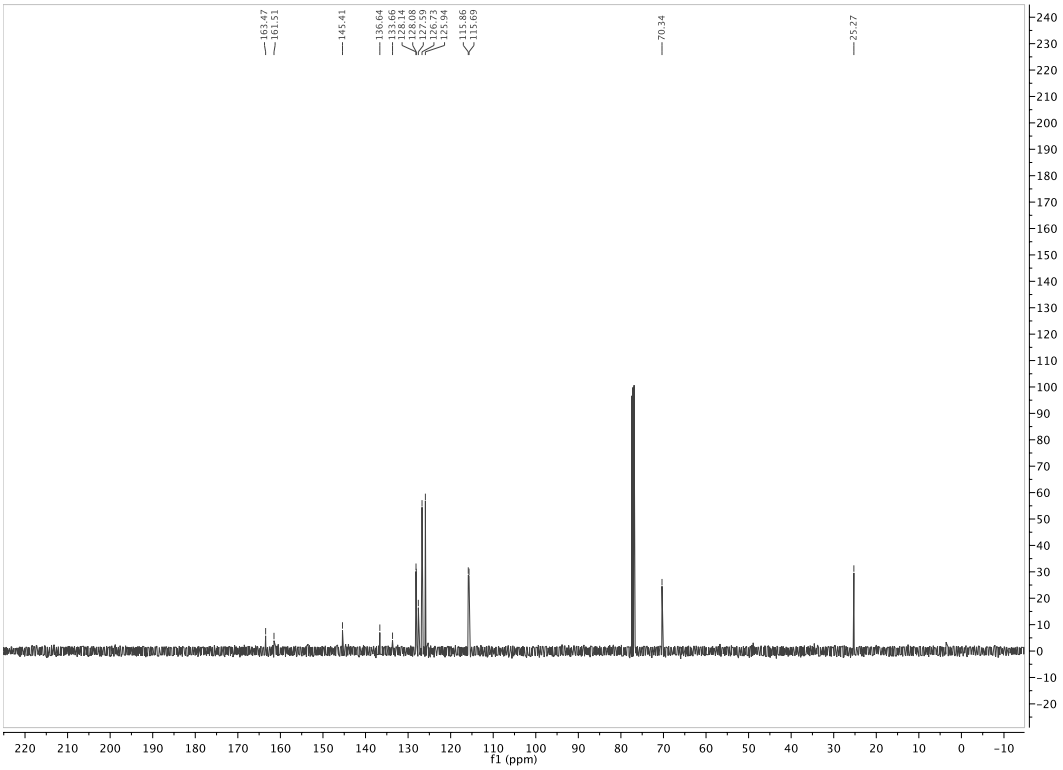

O
O
(R)
OH
1.00
1.92
1.91
1.07
1.07
2.02
1.01
3.10
3.07
f1 (ppm)

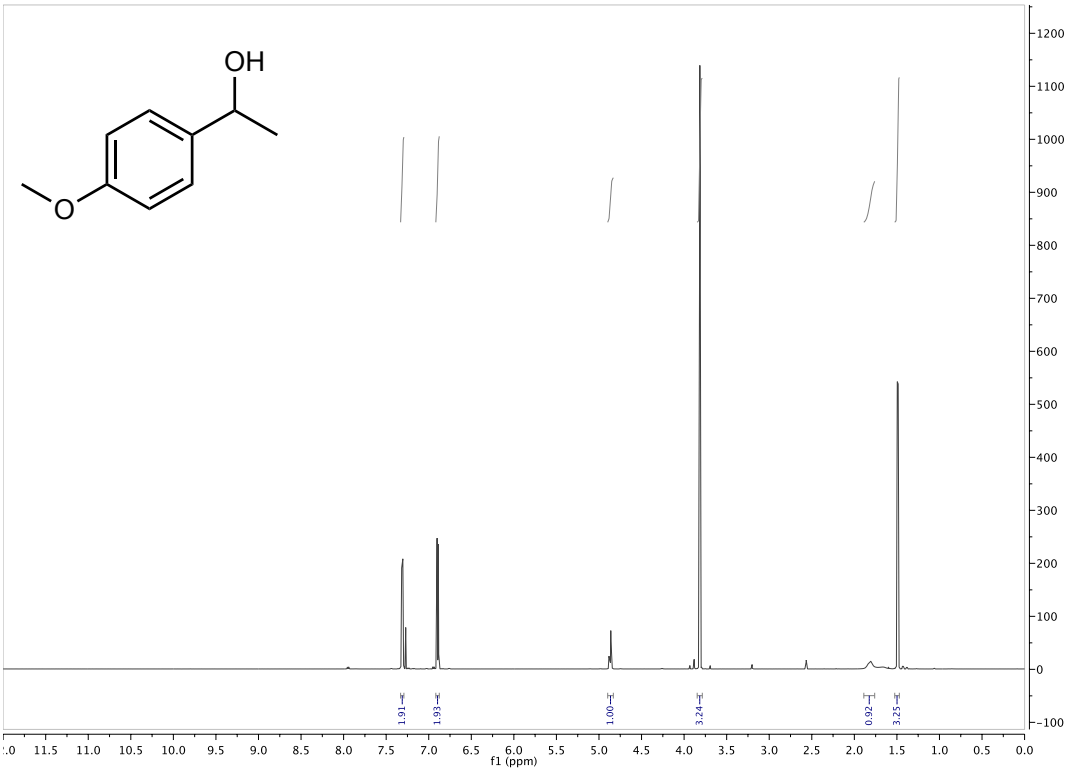

167.19
148.22
144.34
133.82
128.39
126.04
118.25
70.18
60.66
25.35
14.47
f1 (ppm)

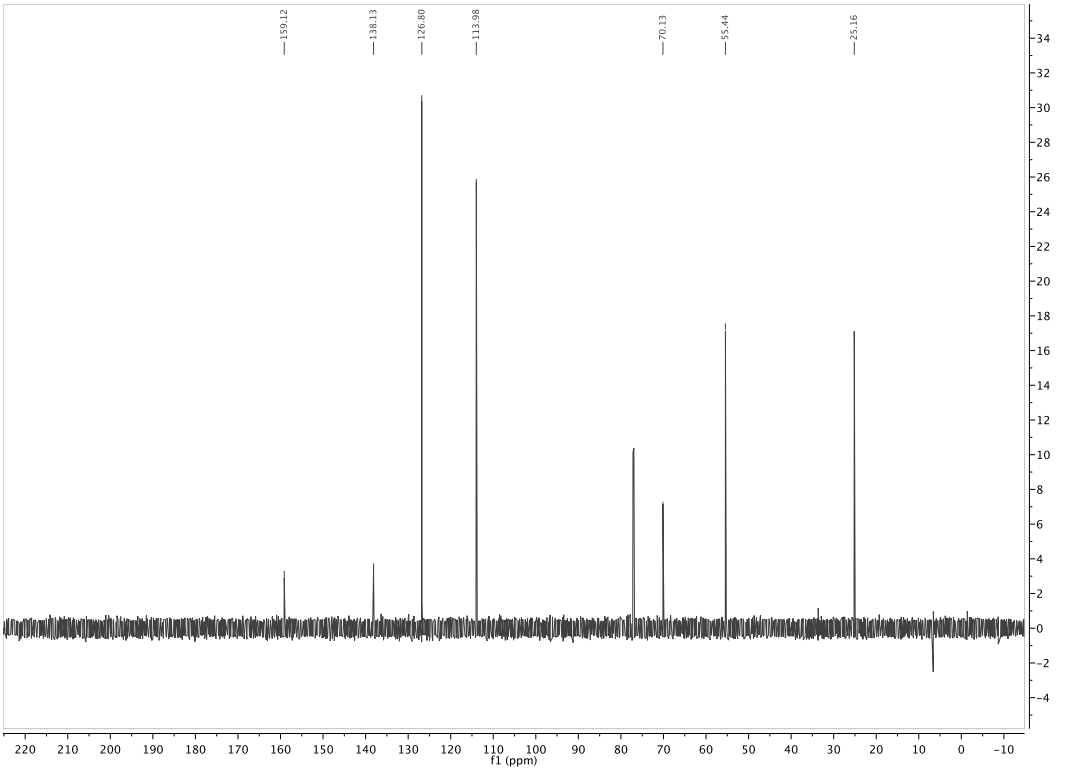

O
O
(R)
OH
1.00
1.88
1.83
1.00
1.02
1.95
0.90
2.04
2.76
2.06
2.83
f1 (ppm)

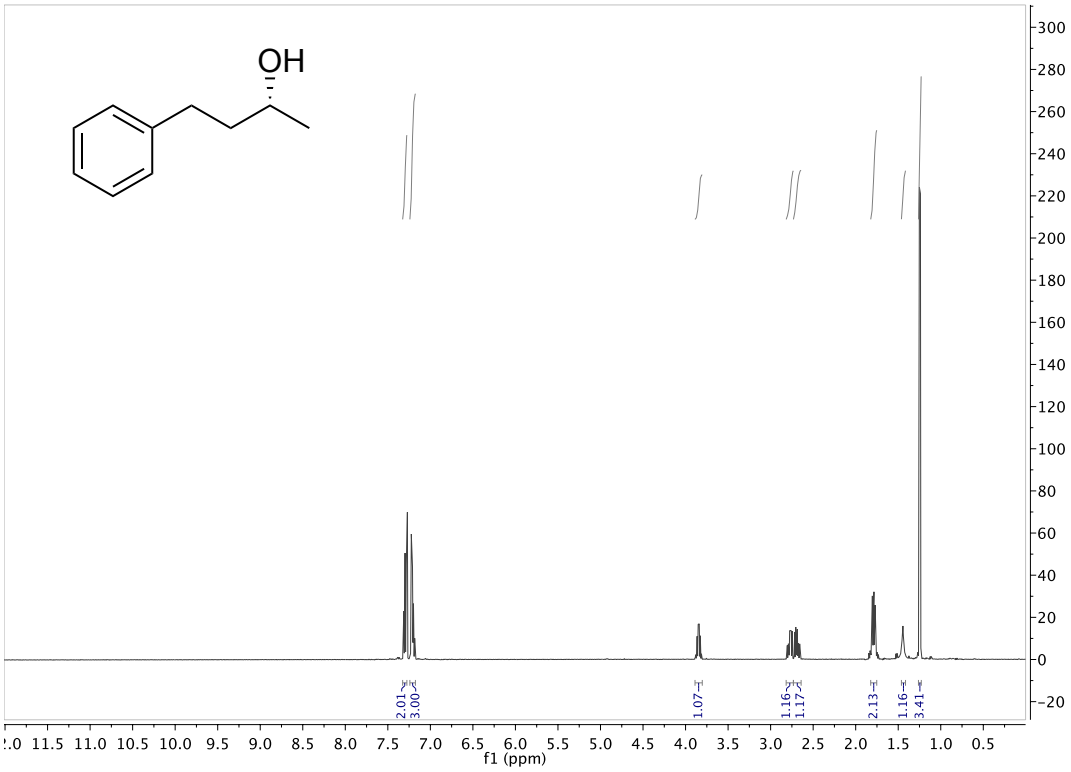

167.30
148.23
144.31
133.79
128.38
126.02
118.23
70.16
64.59
30.92
25.34
19.34
13.89
f1 (ppm)

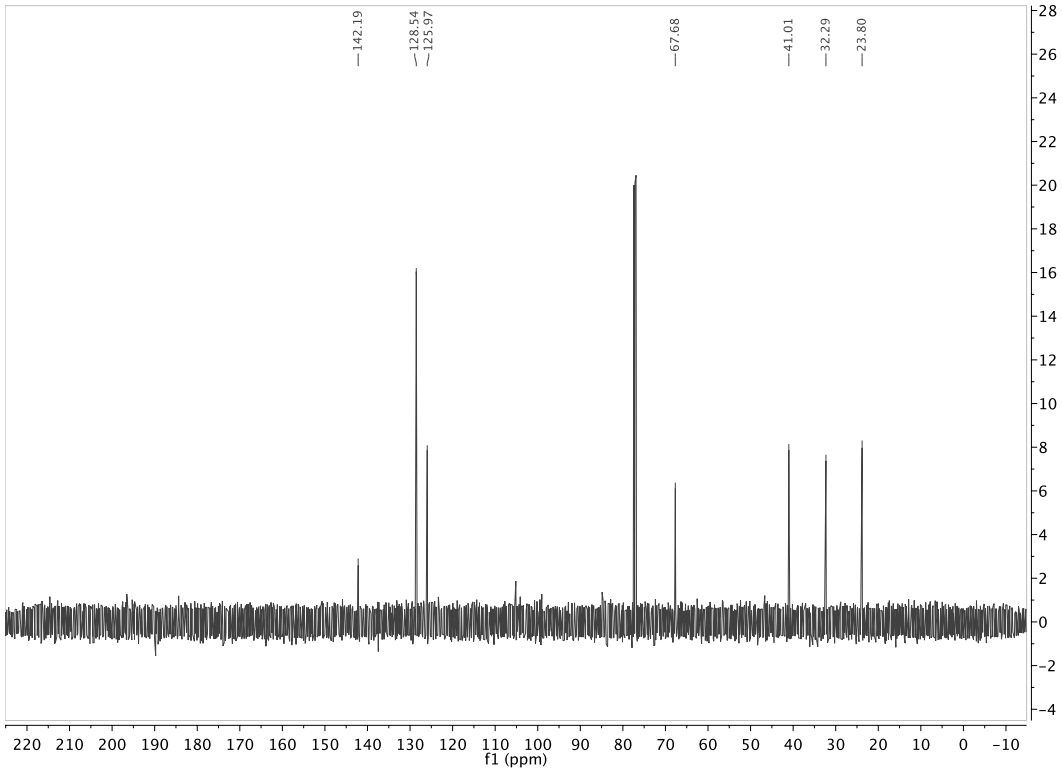

F
(R)
OH
4.01
1.94
3.91
0.96
0.81
3.00
f1 (ppm)

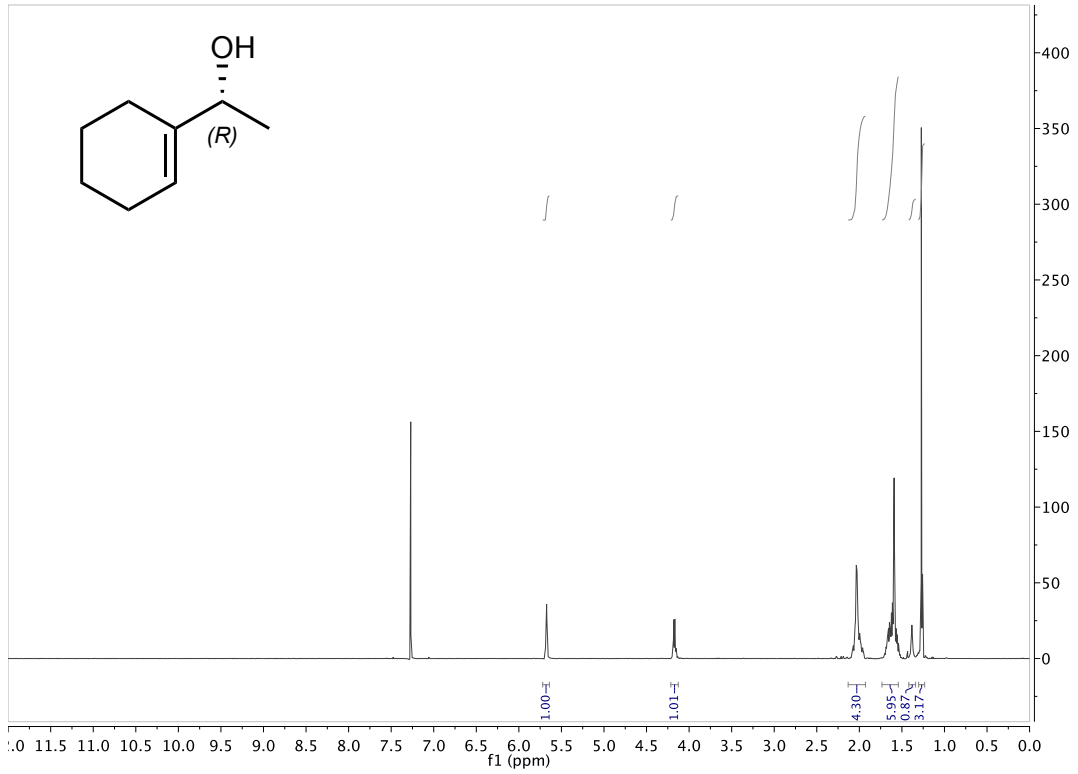

163.47
161.51
145.41
136.64
133.66
128.14
128.08
127.59
126.73
125.94
115.86
115.69
70.34
25.27
f1 (ppm)

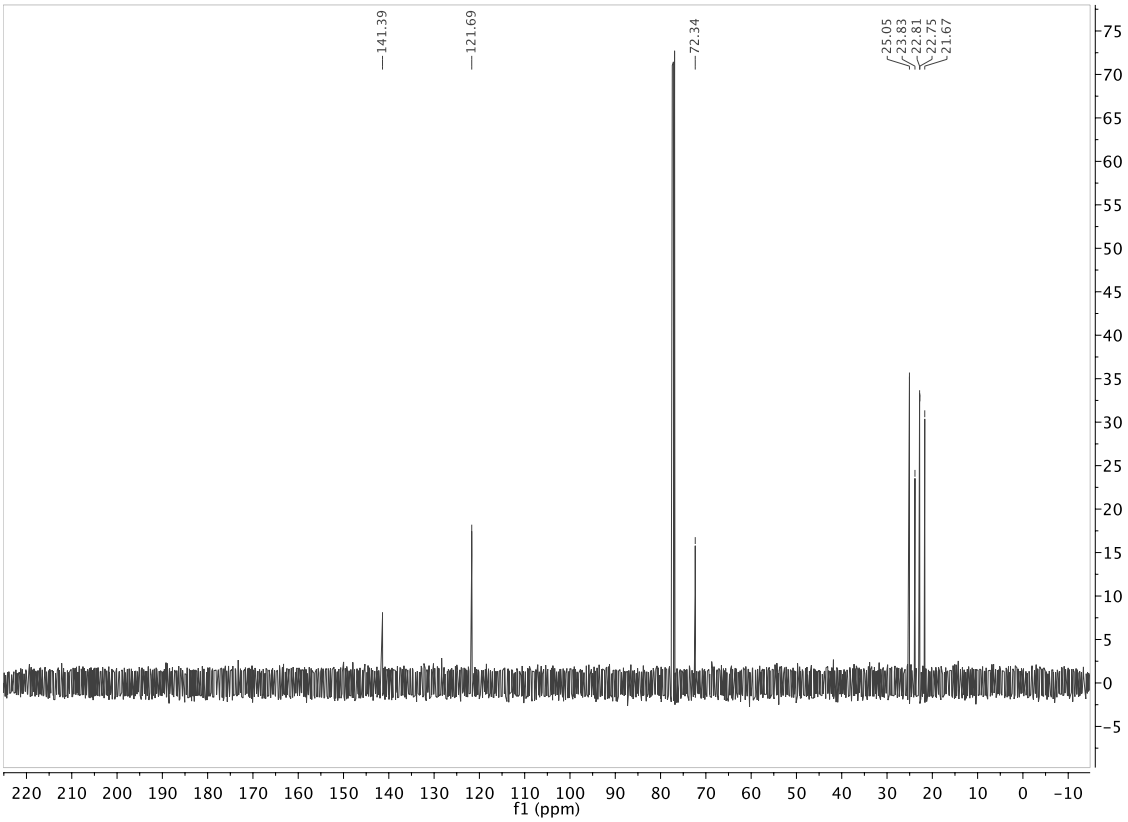

OH
O
1.91
1.93
1.00
3.24
0.92
3.25
f1 (ppm)

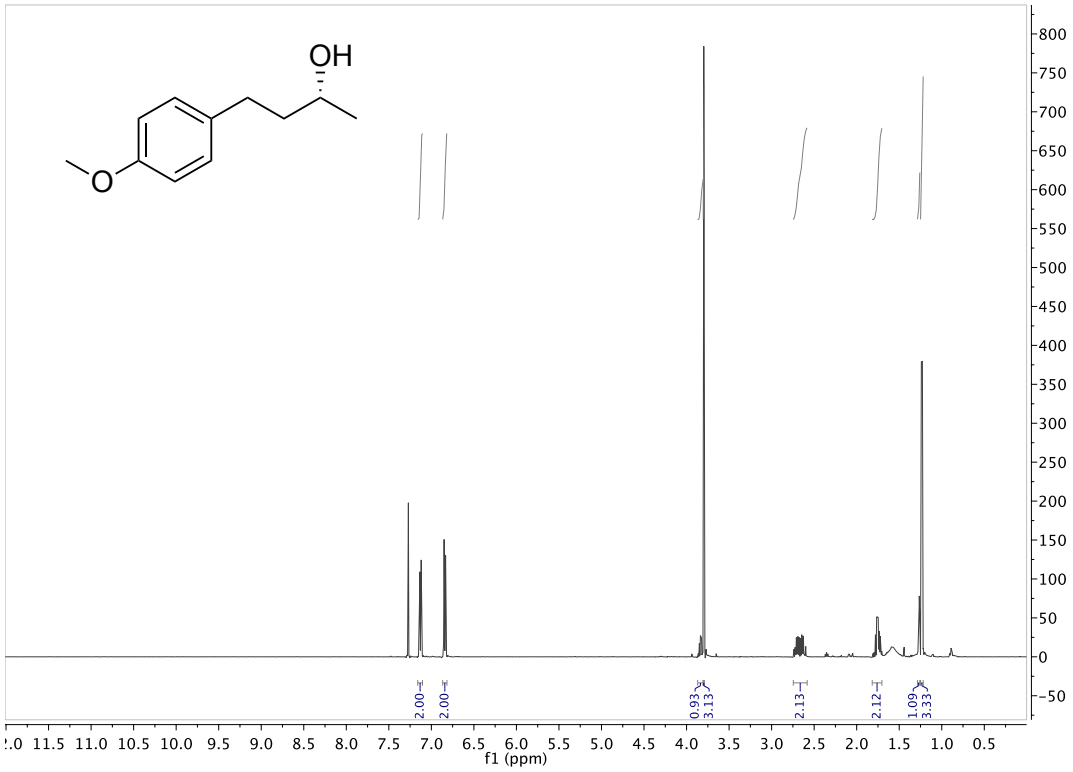

159.12
138.13
126.80
113.98
70.13
55.44
25.16
f1 (ppm)

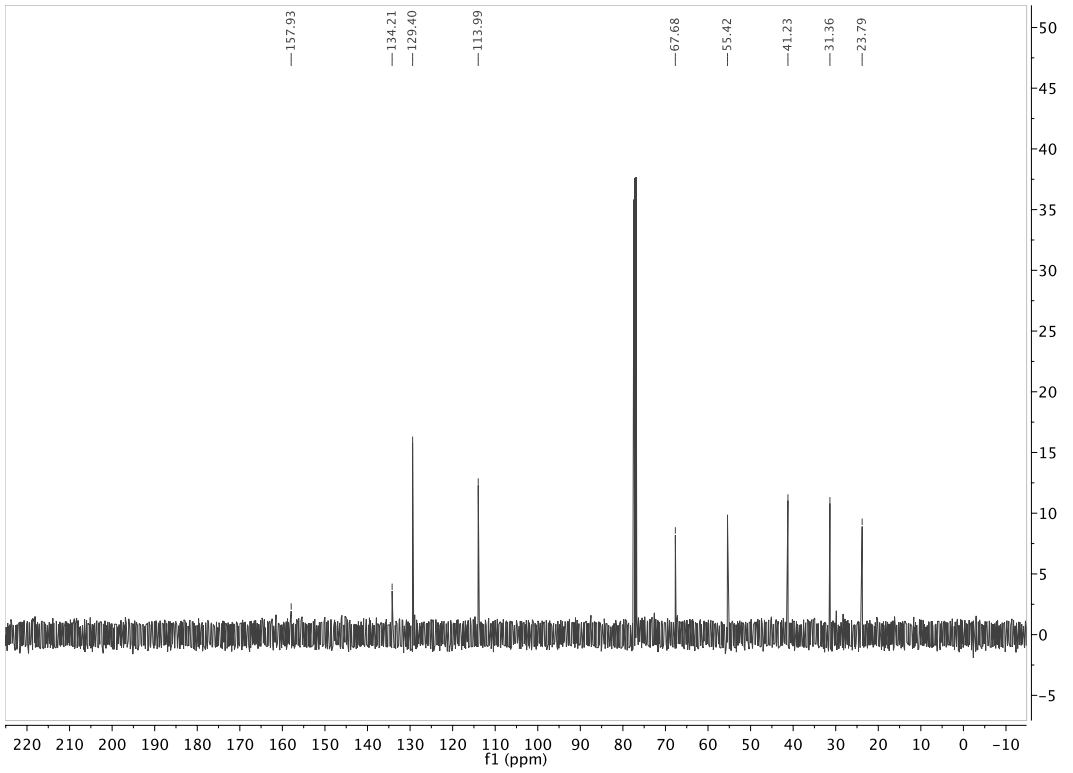

OH
2.01
3.00
1.07
1.16
1.17
2.13
1.16
3.41
f1 (ppm)

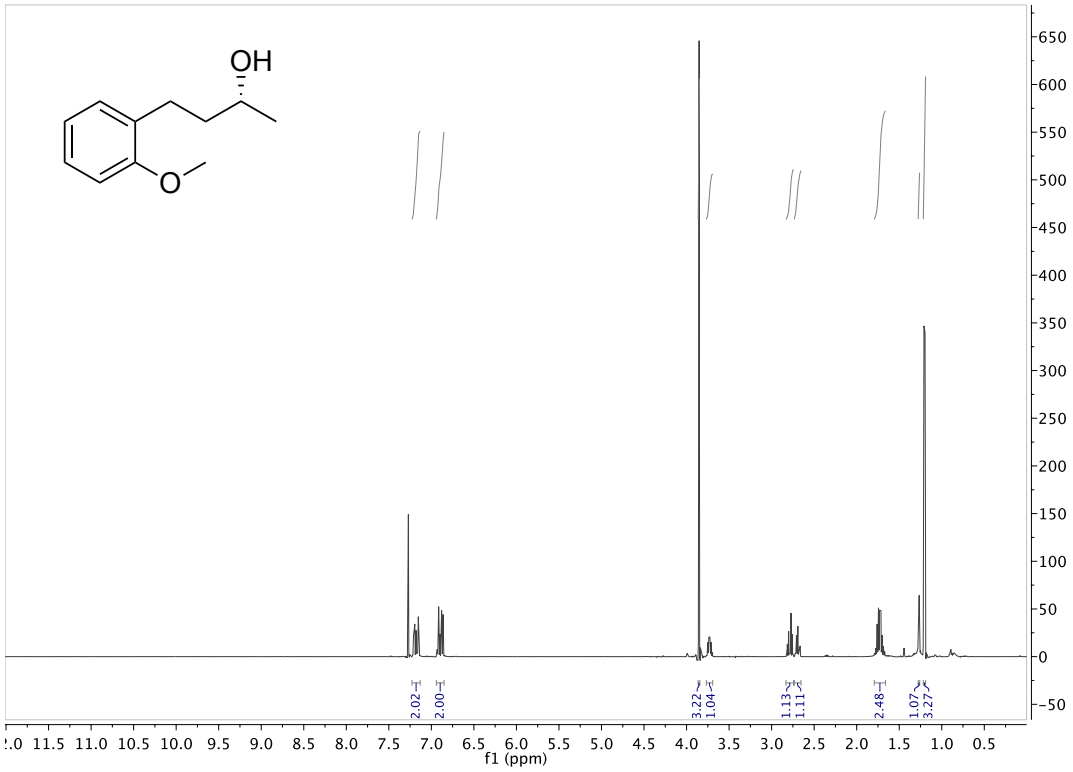

142.19
128.54
125.97
67.68
41.01
32.29
23.80
f1 (ppm)

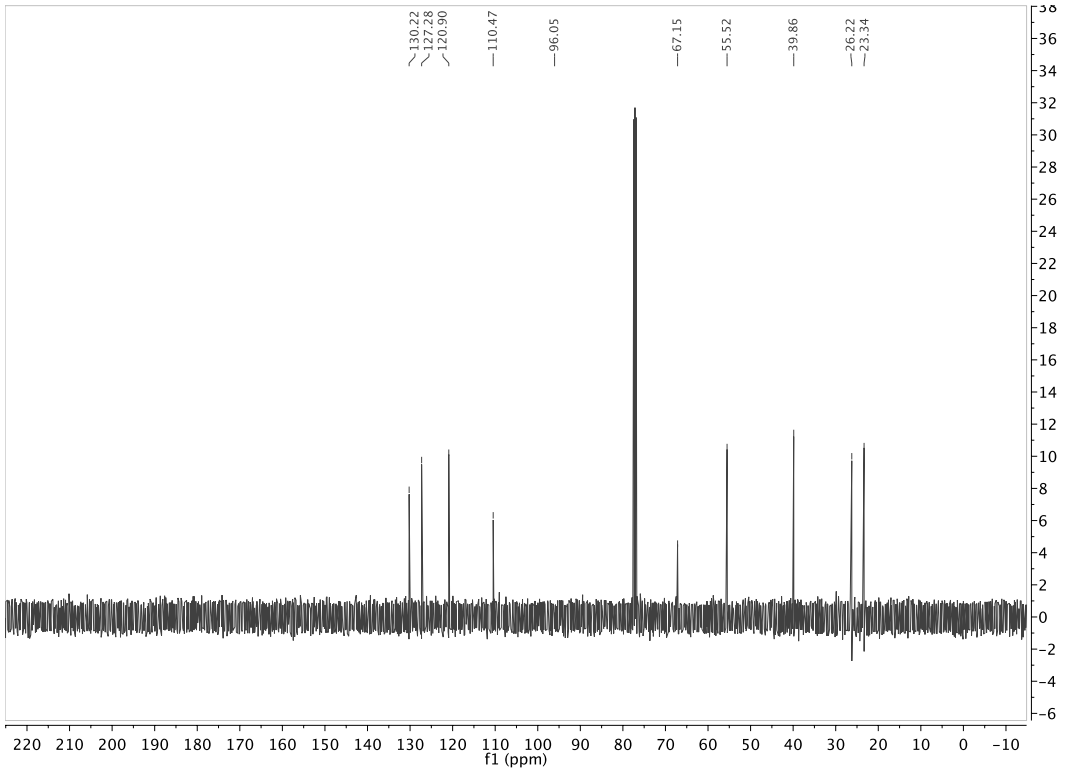

OH
(R)
1.00
1.01
4.30
5.95
0.87
3.17
f1 (ppm)

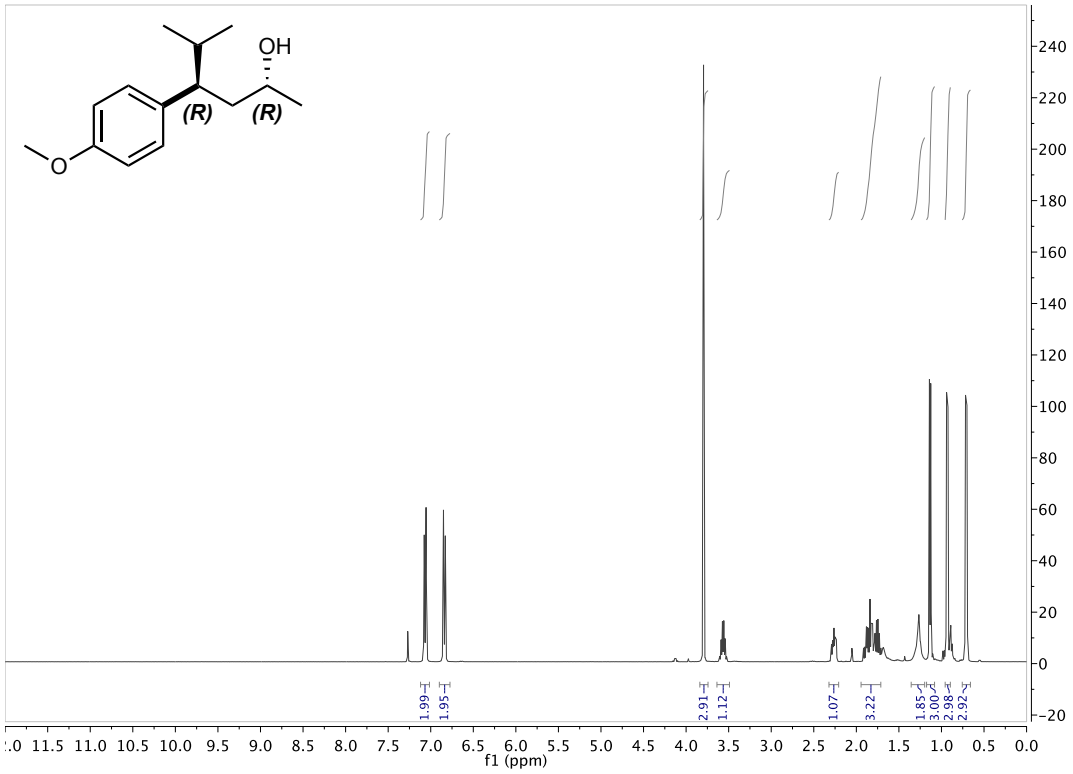

141.39
121.69
72.34
25.05
23.83
22.81
22.75
21.67
f1 (ppm)

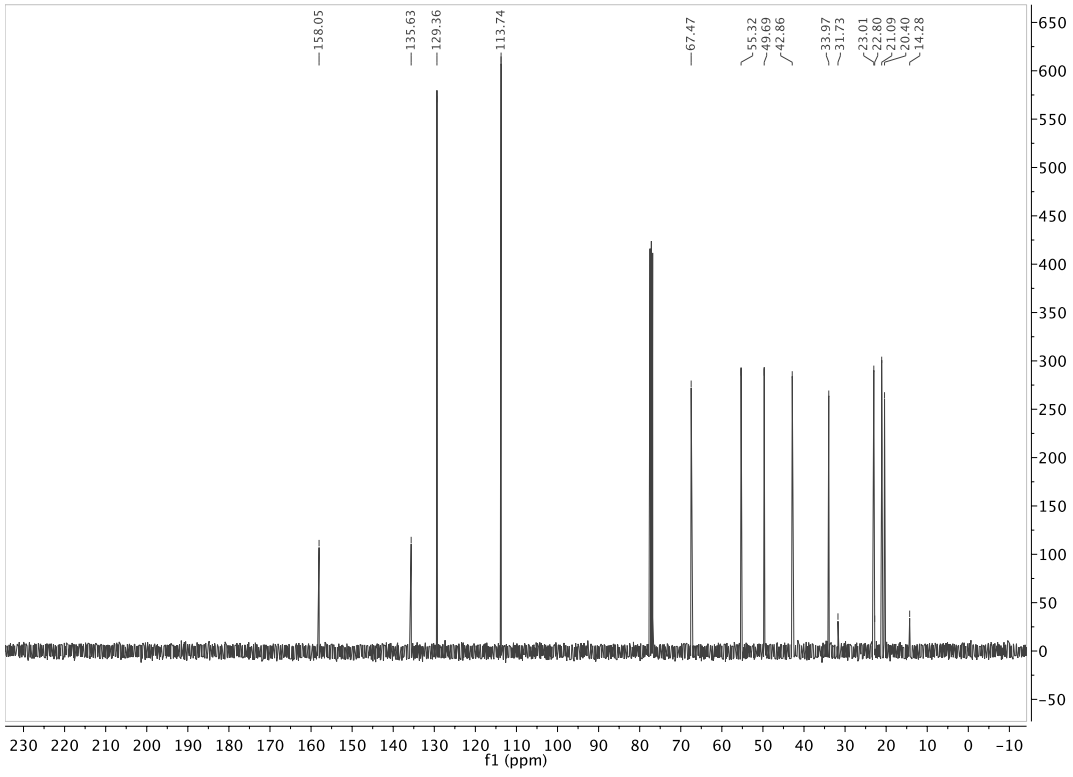

OH
O
2.00
2.00
0.93
3.13
2.13
2.12
1.09
3.33
f1 (ppm)

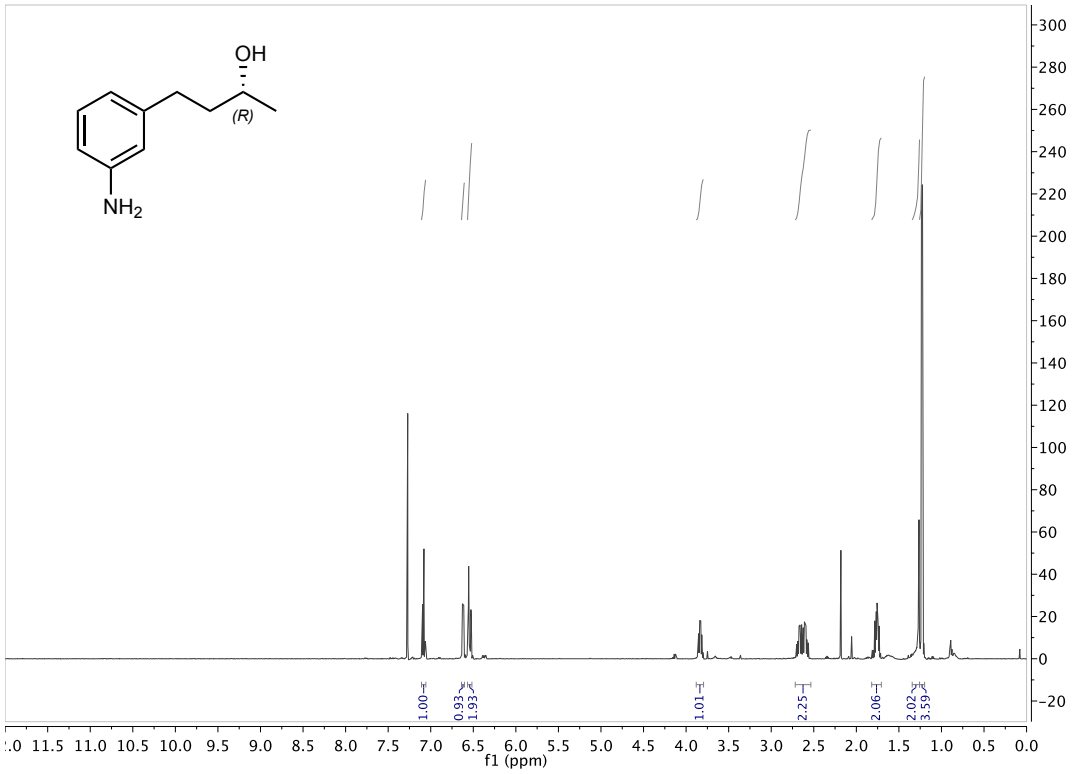

157.93
134.21
129.40
113.99
67.68
55.42
41.23
31.36
23.79
f1 (ppm)

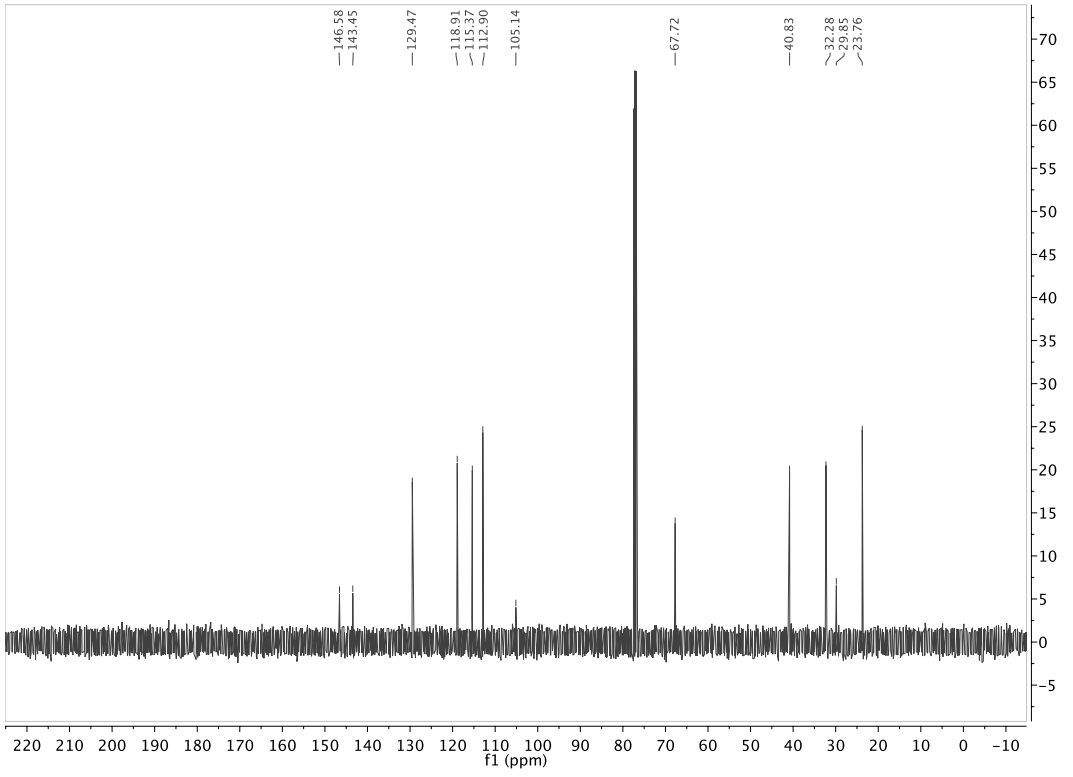

OH
O
2.02
2.00
3.22
1.04
1.13
1.11
2.48
1.07
3.27
f1 (ppm)

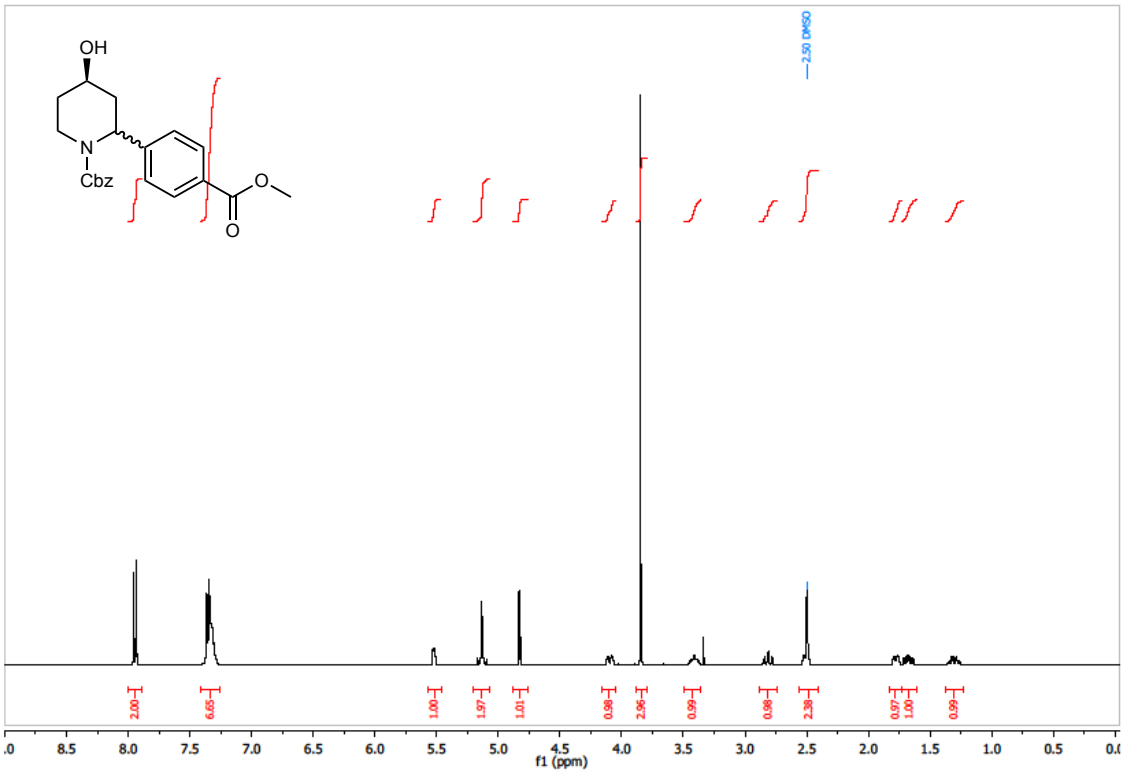

130.22
127.28
120.90
110.47
96.05
67.15
55.52
39.86
26.22
23.34
f1 (ppm)

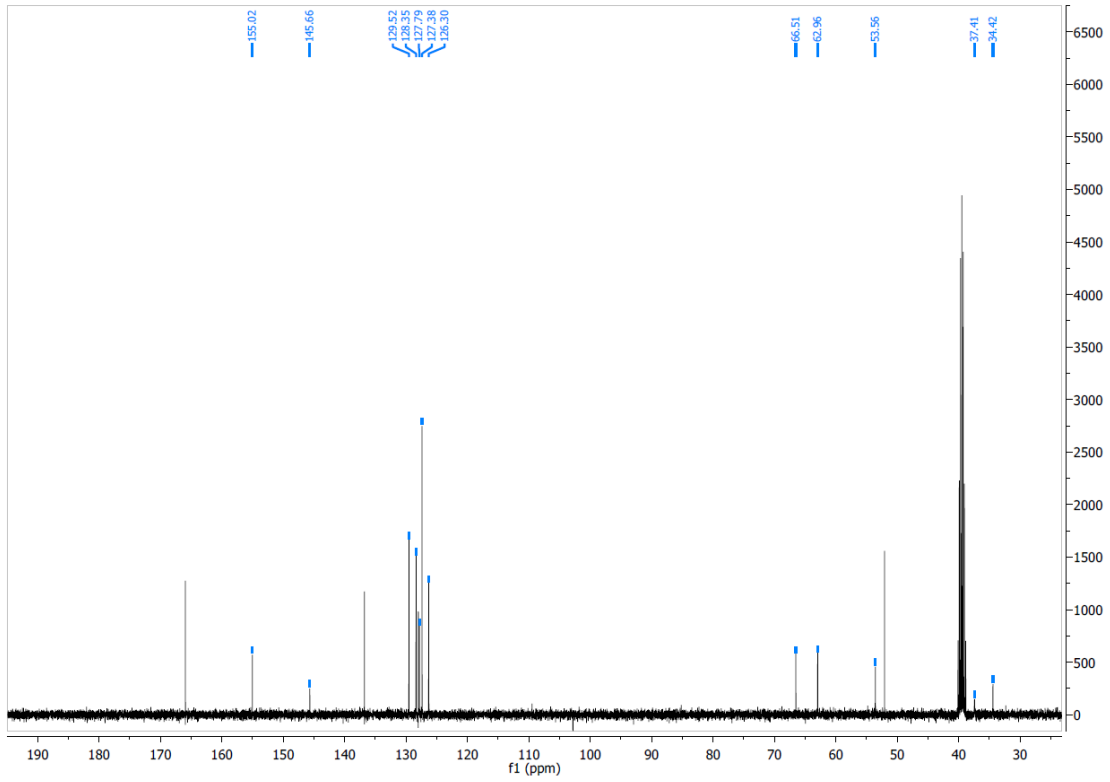

OH
(R)
(R)
O
1.99
1.95
2.91
1.12
1.07
3.22
1.85
3.00
2.98
2.92
f1 (ppm)

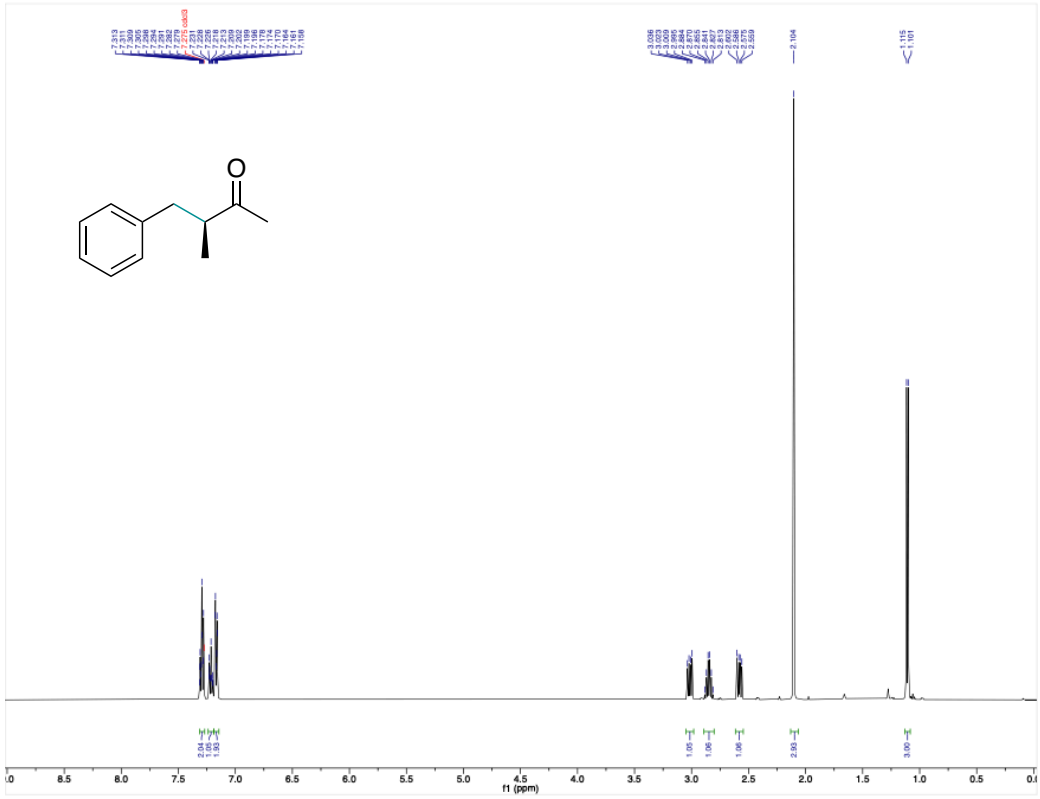

158.05
135.63
129.36
113.74
67.47
55.32
49.69
42.86
33.97
31.73
23.01
22.80
21.09
20.40
14.28
f1 (ppm)

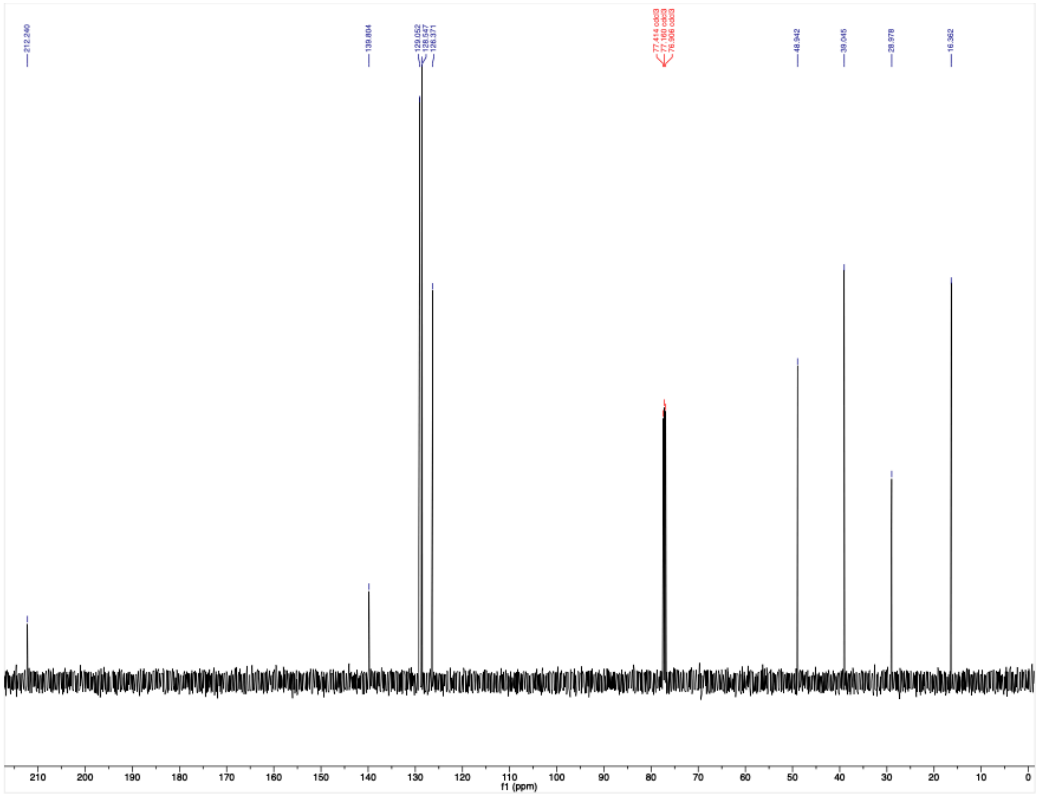

OH
(R)
NH2
1.00
0.93
1.93
1.01
2.25
2.06
2.02
3.59
f1 (ppm)

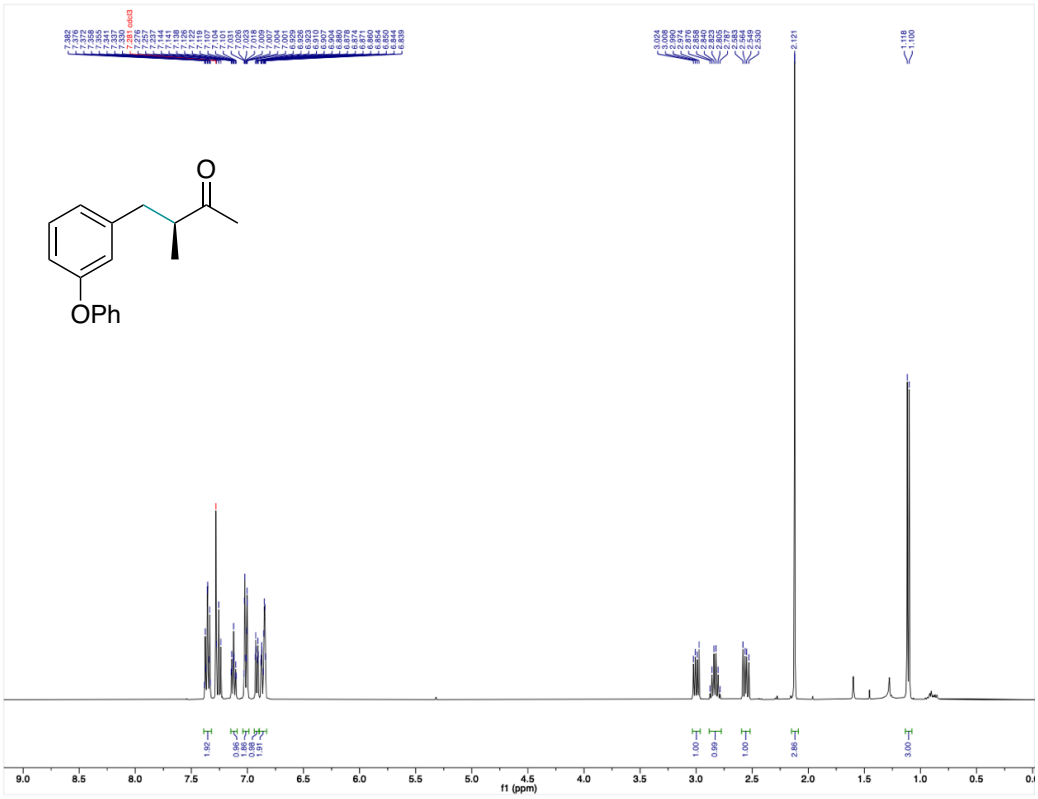

146.58
143.45
129.47
118.91
115.37
112.90
105.14
67.72
40.83
32.28
29.85
23.76
f1 (ppm)

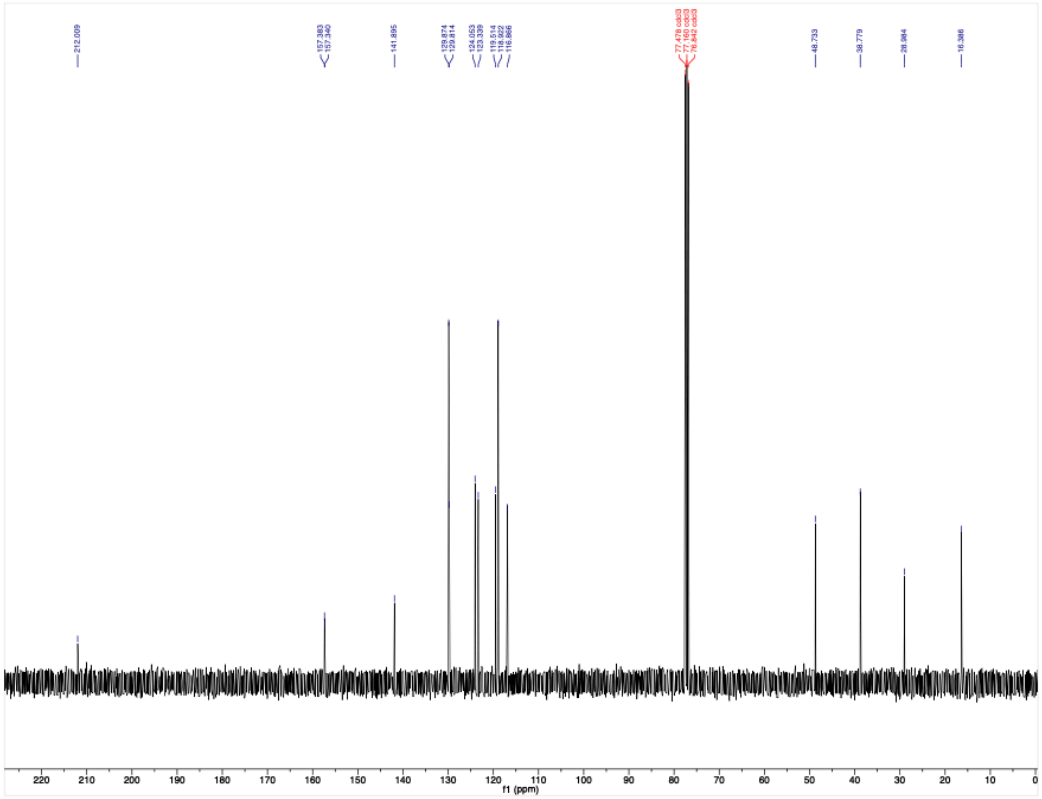

OH
N
Cbz
O
O
2.50 DMSO
2.00
6.65
1.00
1.97
1.01
0.98
2.96
0.99
0.98
2.38
0.97
1.00
0.99
f1 (ppm)

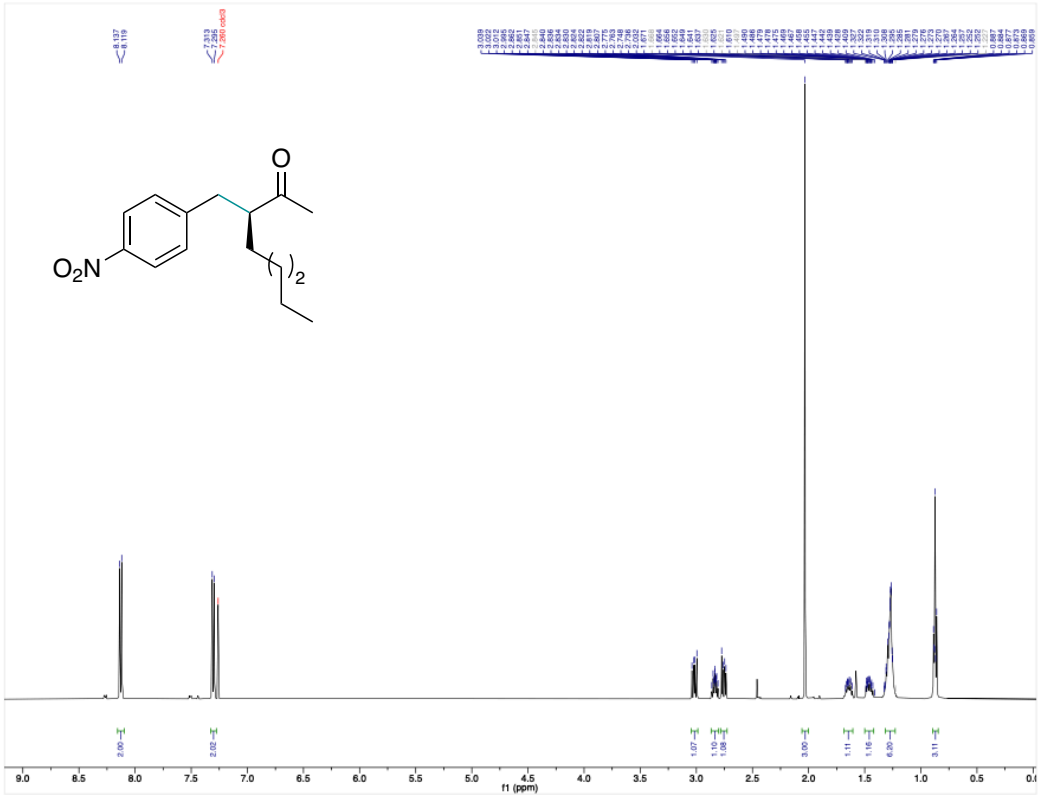

155.02
145.66
129.52
128.35
127.79
127.38
126.30
65.51
62.96
53.56
37.41
34.42
f1 (ppm)

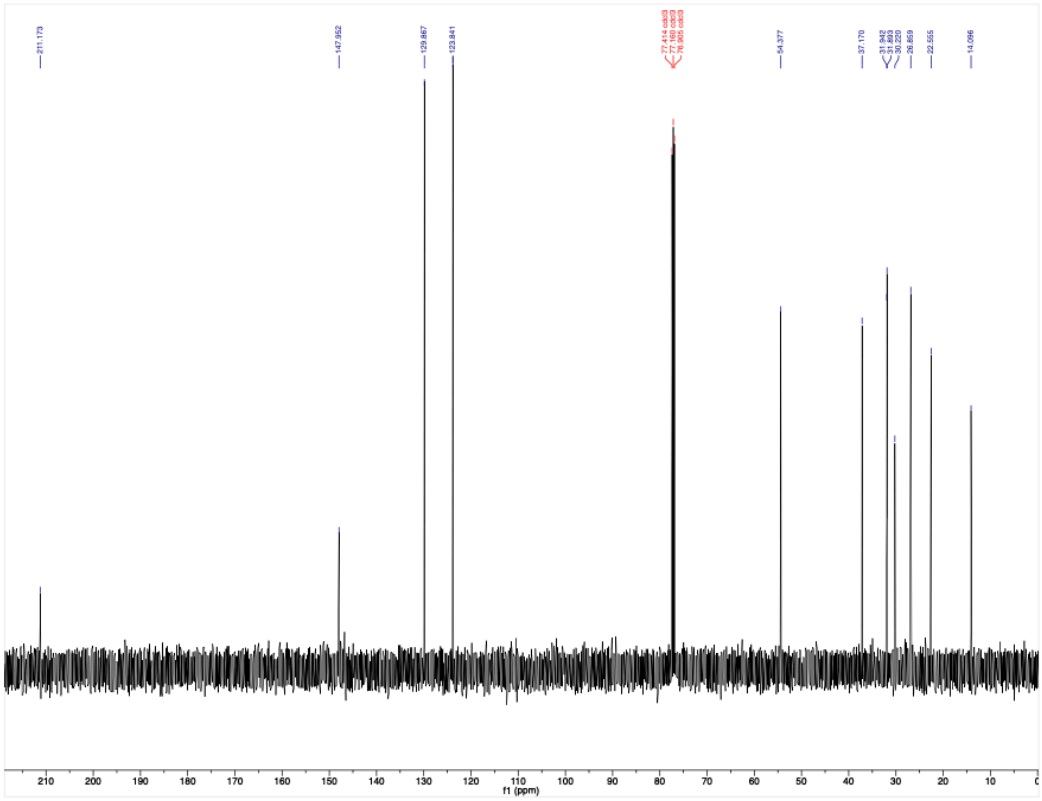

O
f1 (ppm)

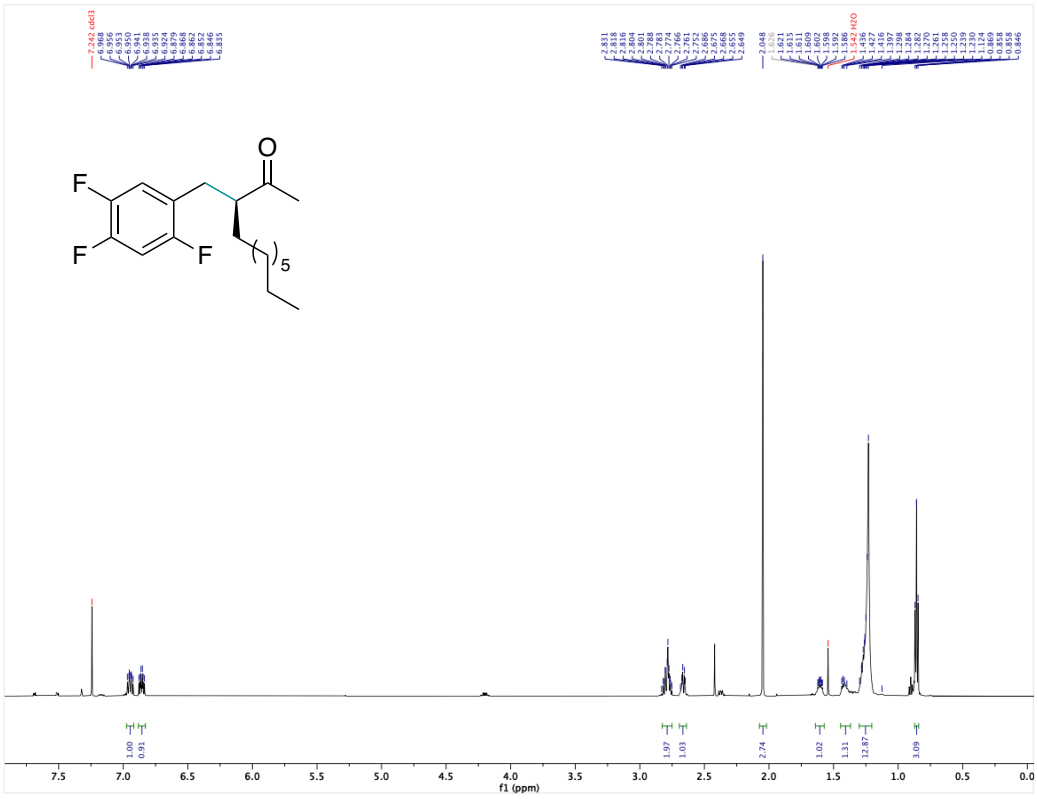

f1 (ppm)

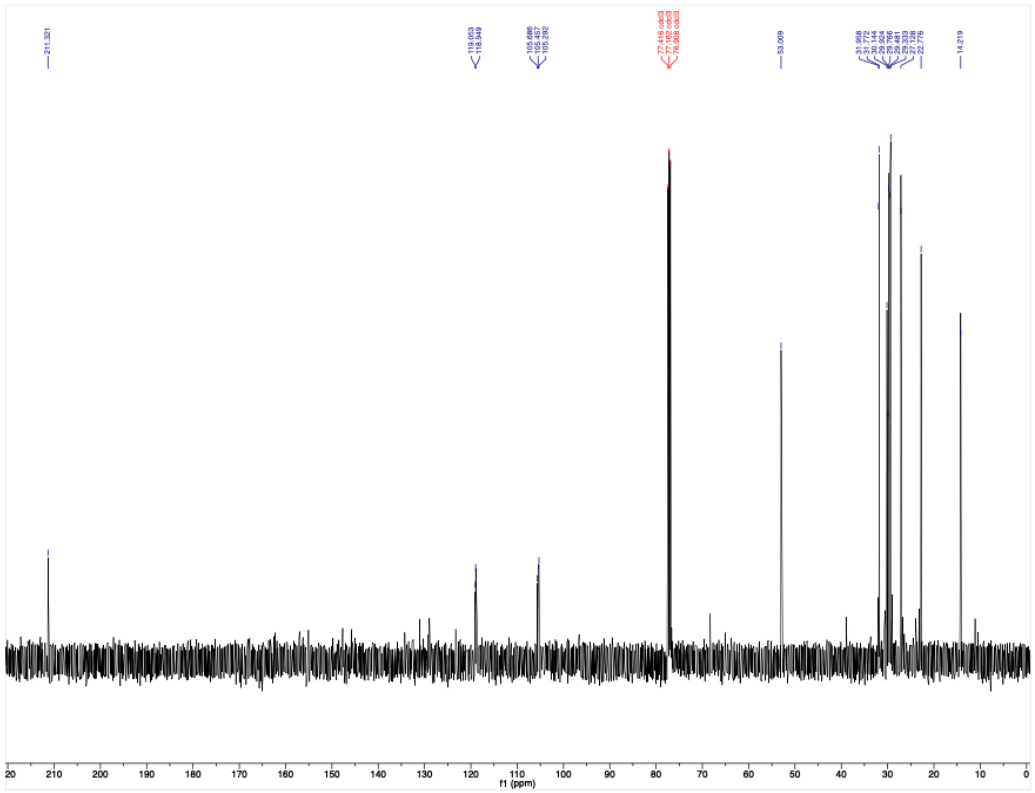

O
OPh
f1 (ppm)


f1 (ppm)

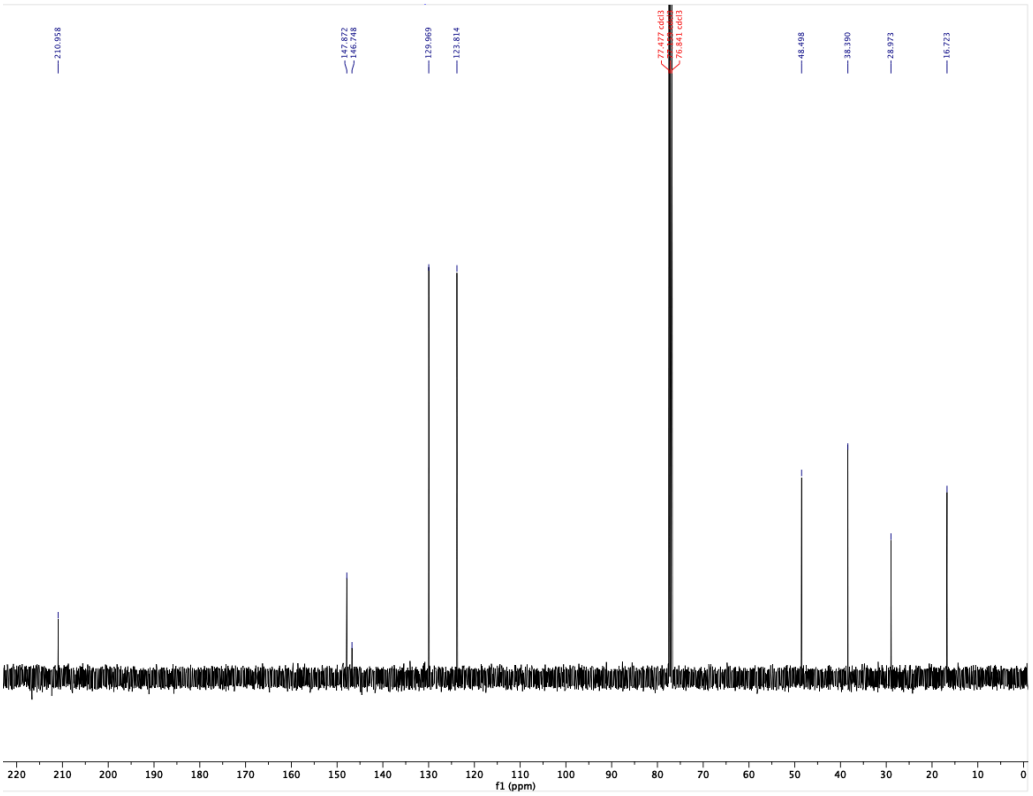

O
O2N
2
f1 (ppm)

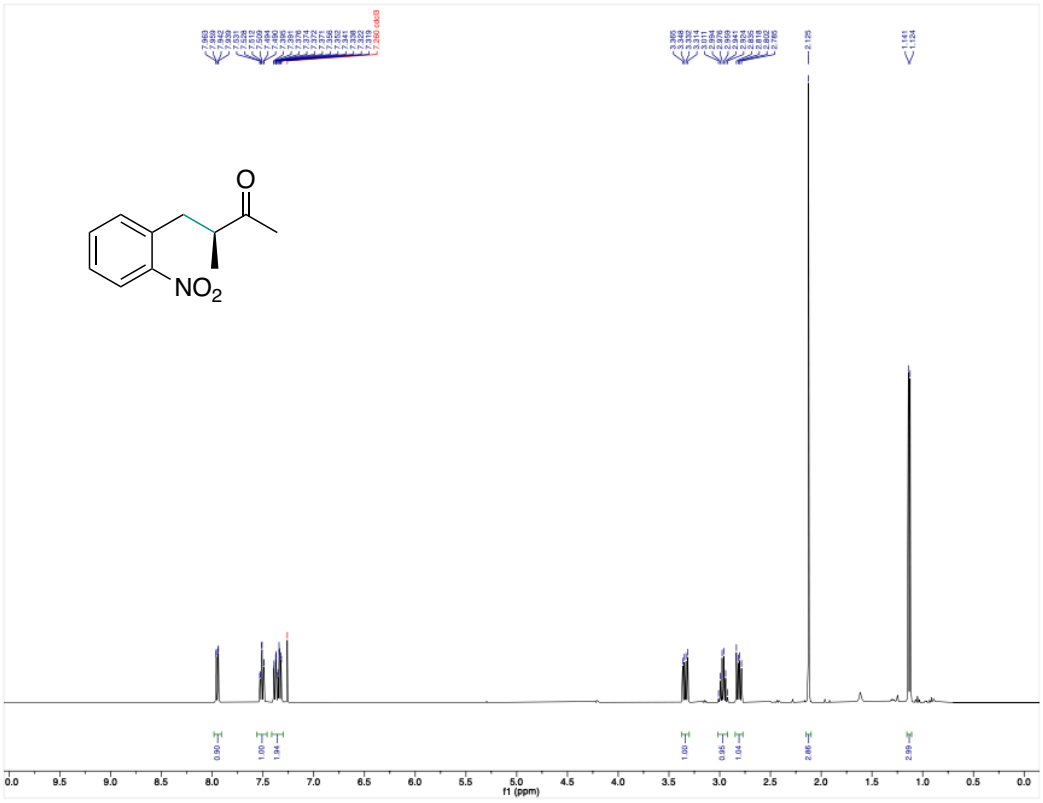

211.173
147.852
139.867
123.841
77.416
77.160
76.903
54.377
37.170
31.942
31.893
30.353
28.859
22.555
14.096
f1 (ppm)

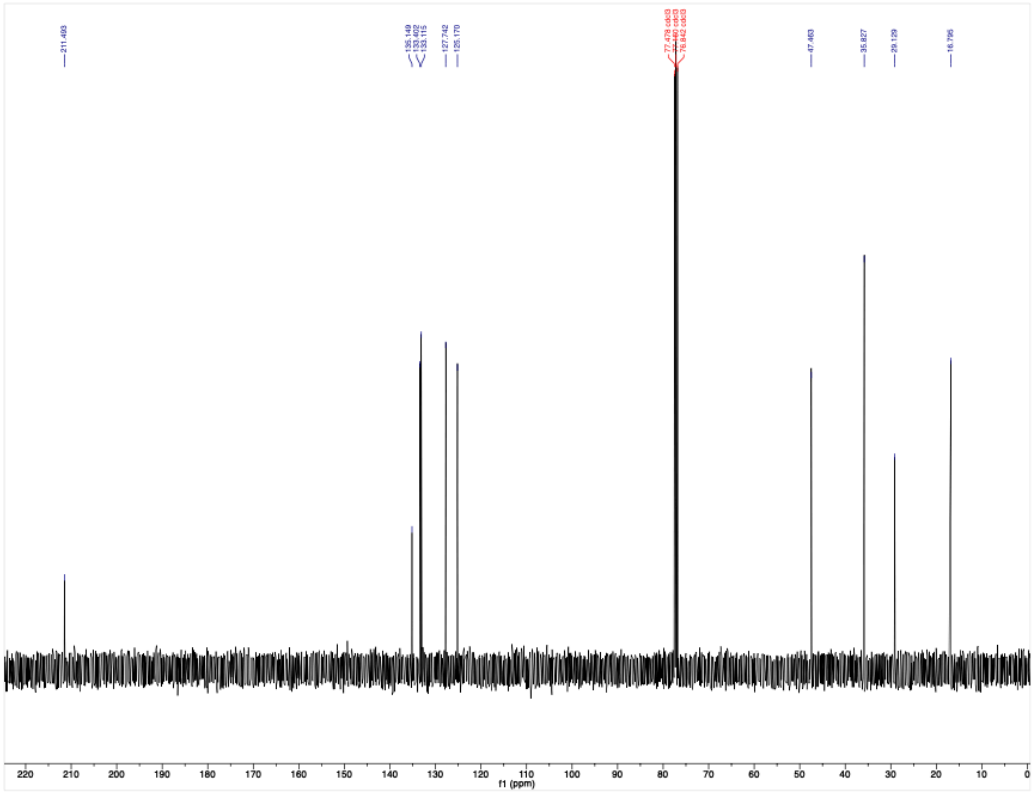

O
F
F
F
5
f1 (ppm)


f1 (ppm)

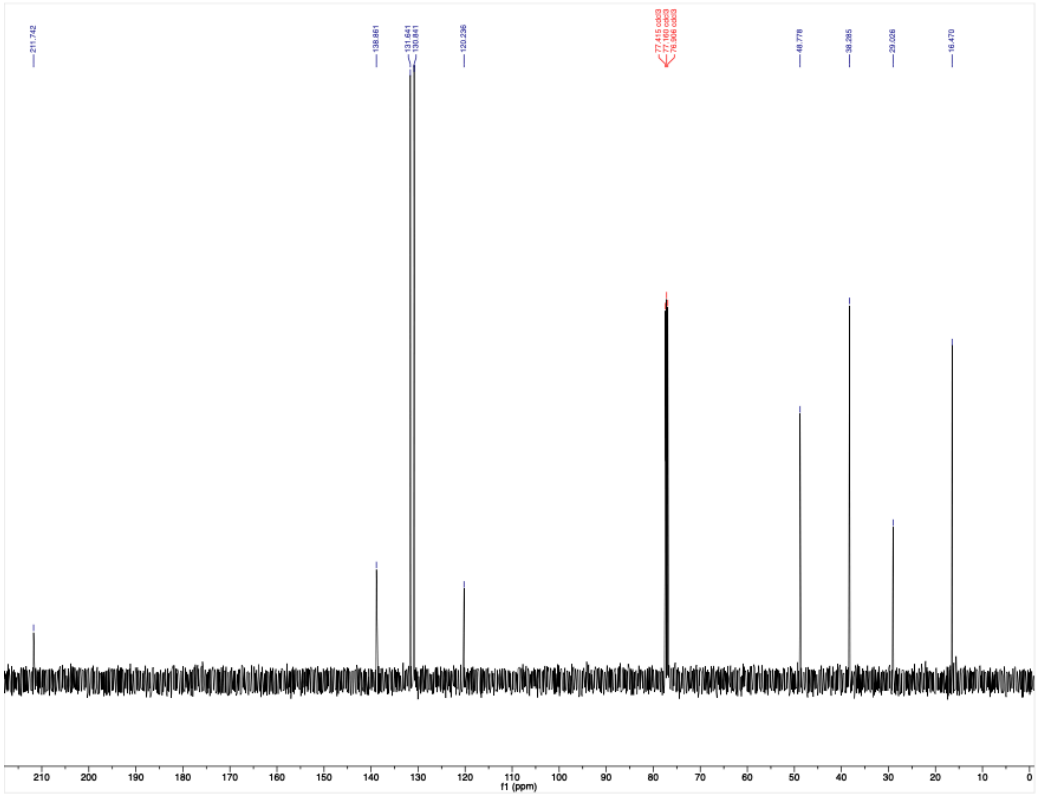

O
O_2N
f1 (ppm)

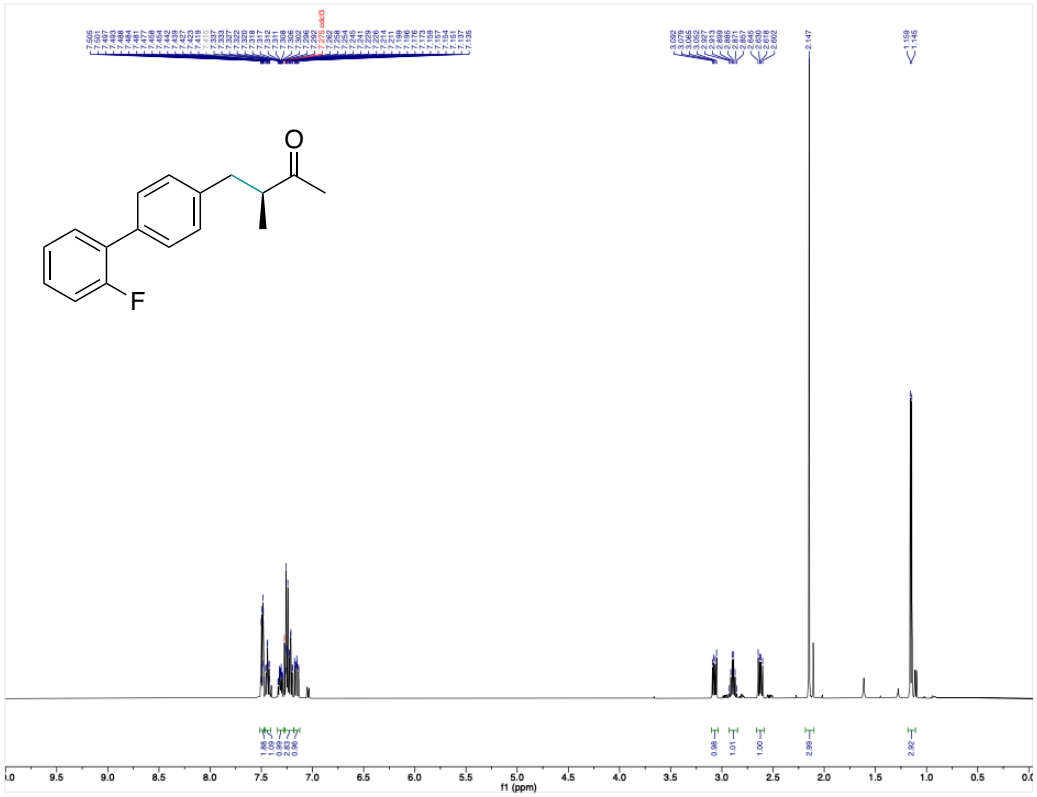

f1 (ppm)

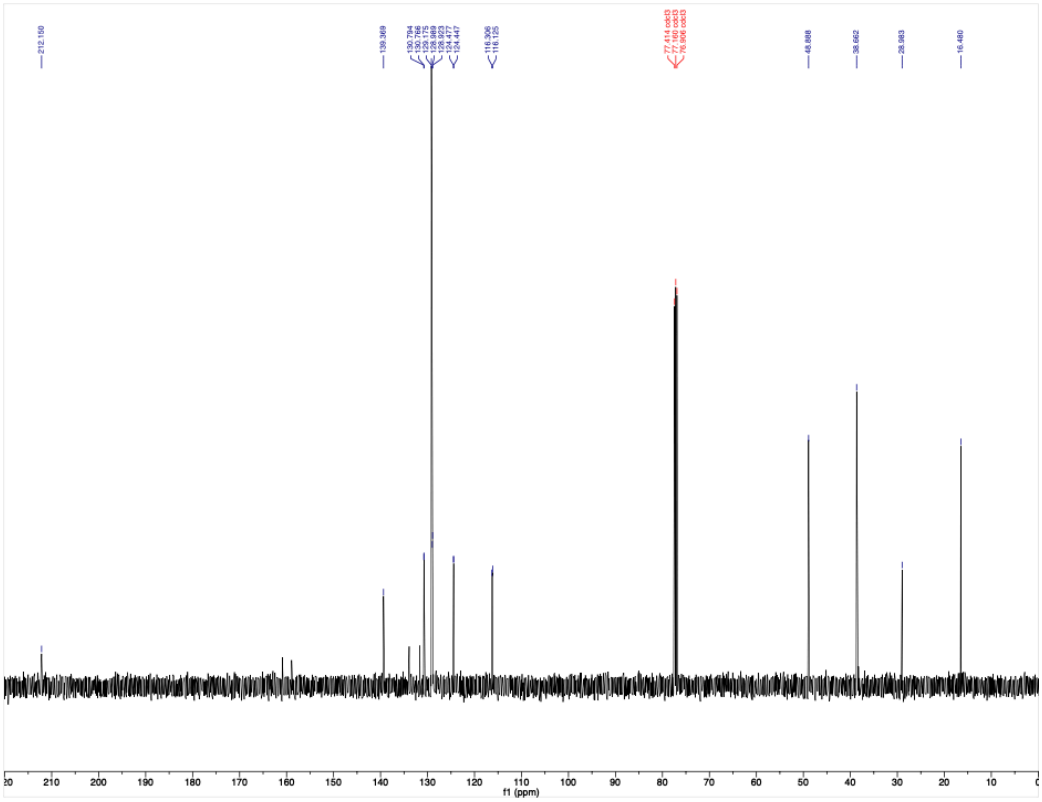

O
NO2
f1 (ppm)

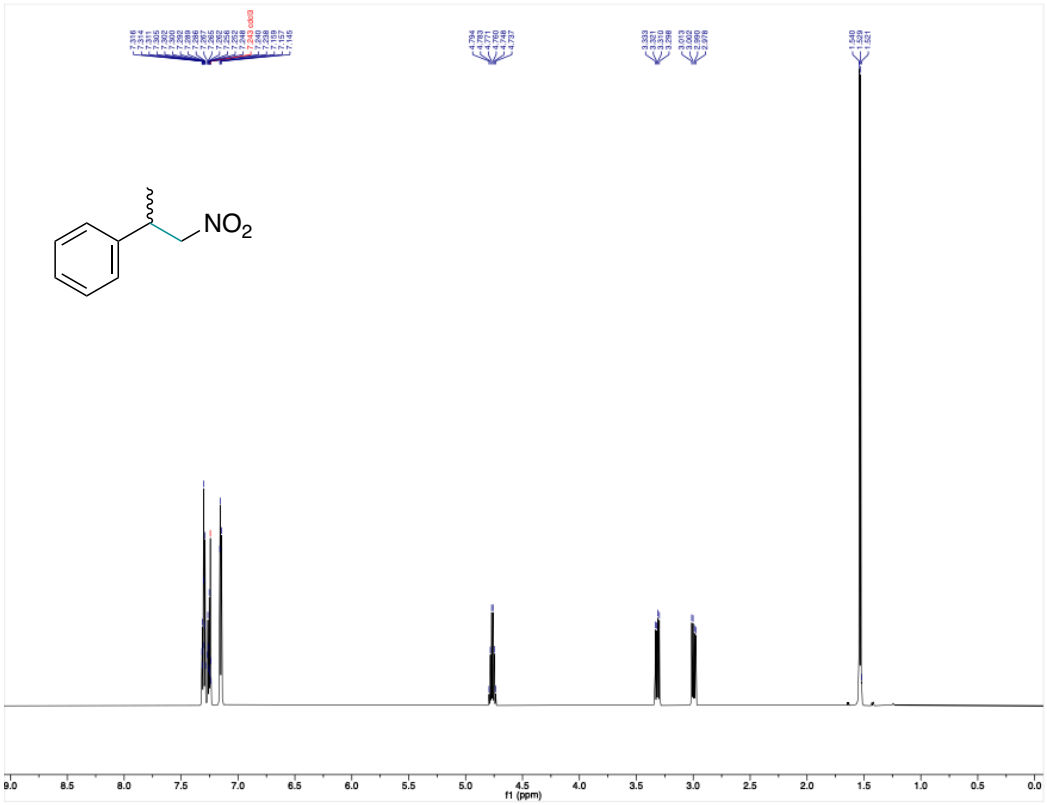

f1 (ppm)

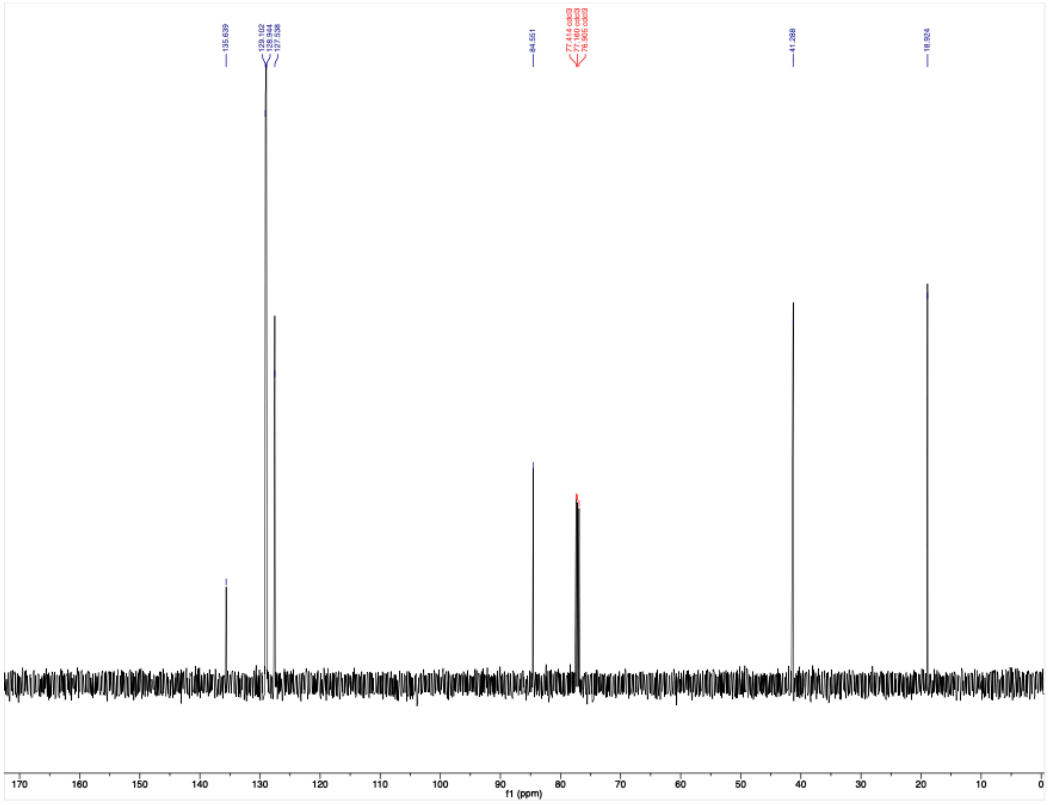

O
Br
f1 (ppm)

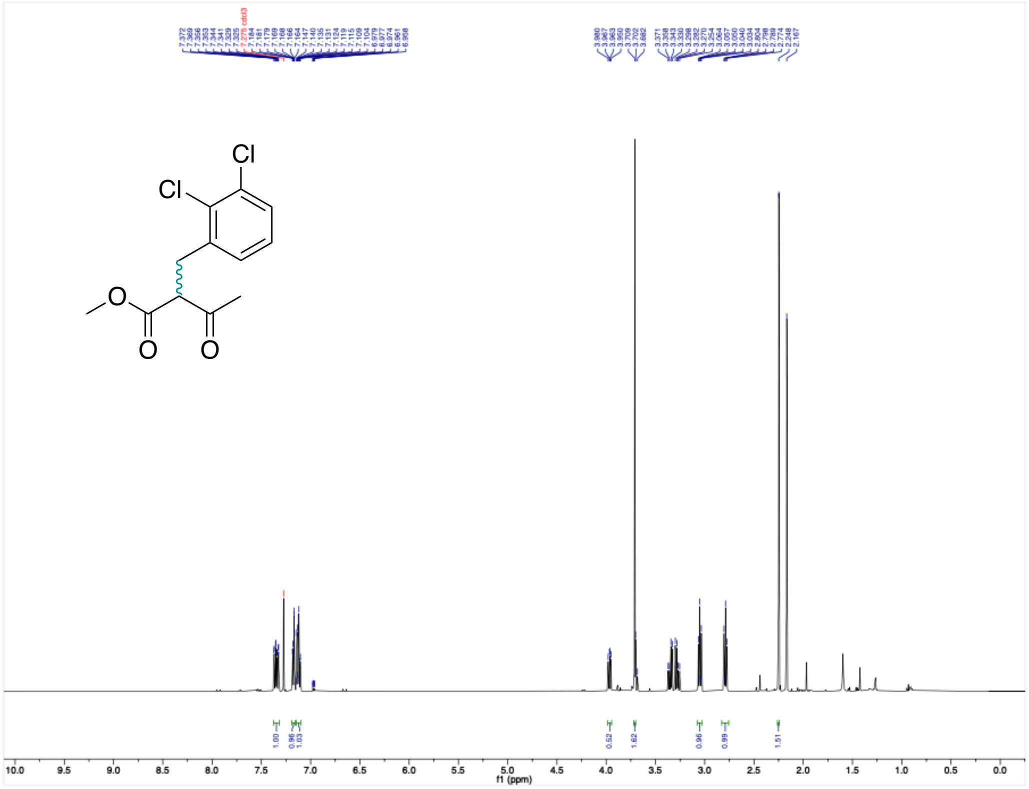

f1 (ppm)

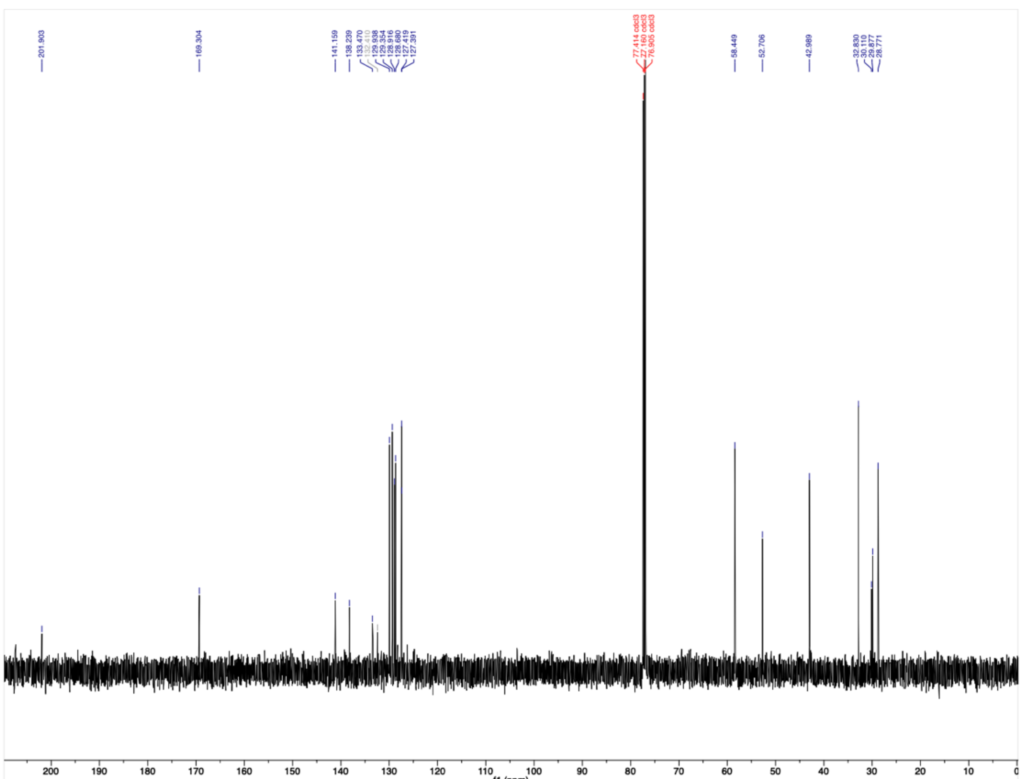

O
F
f1 (ppm)

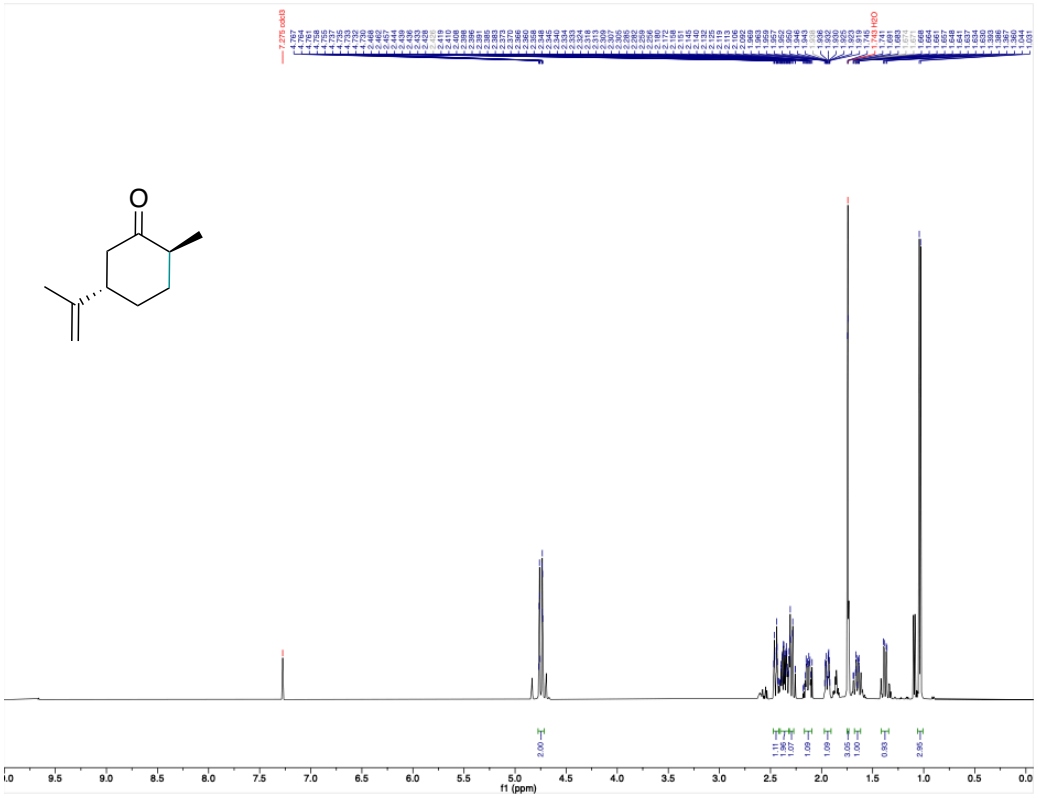

f1 (ppm)

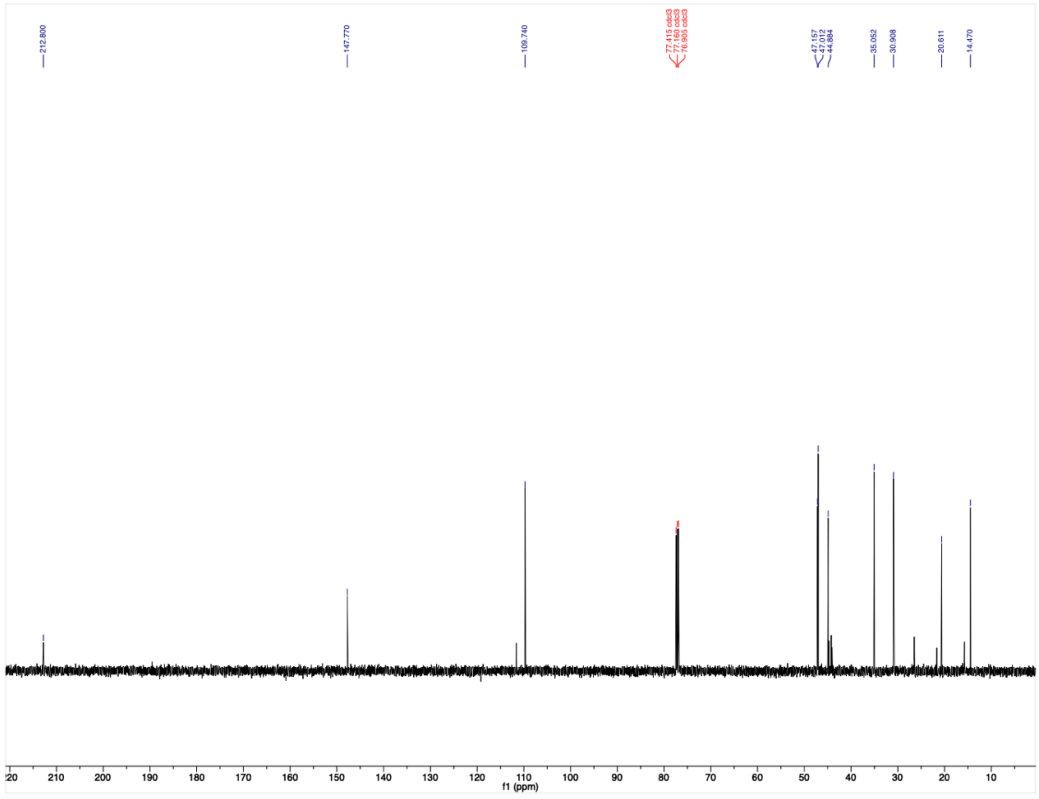

NO2
f1 (ppm)

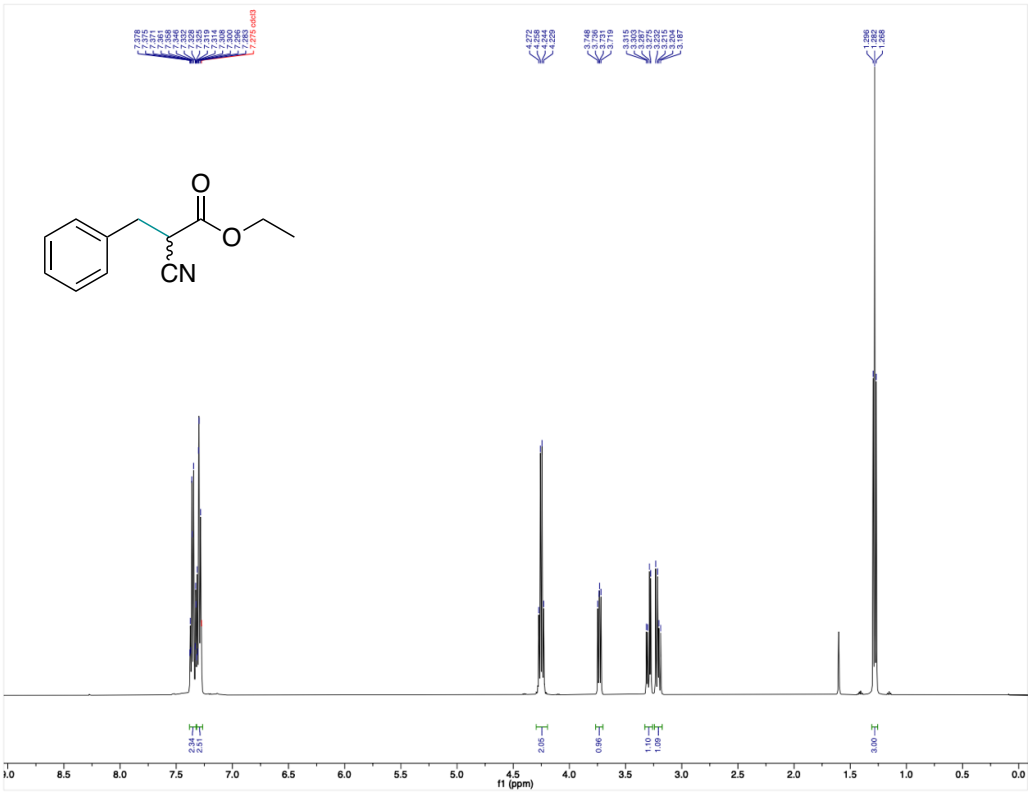

f1 (ppm)

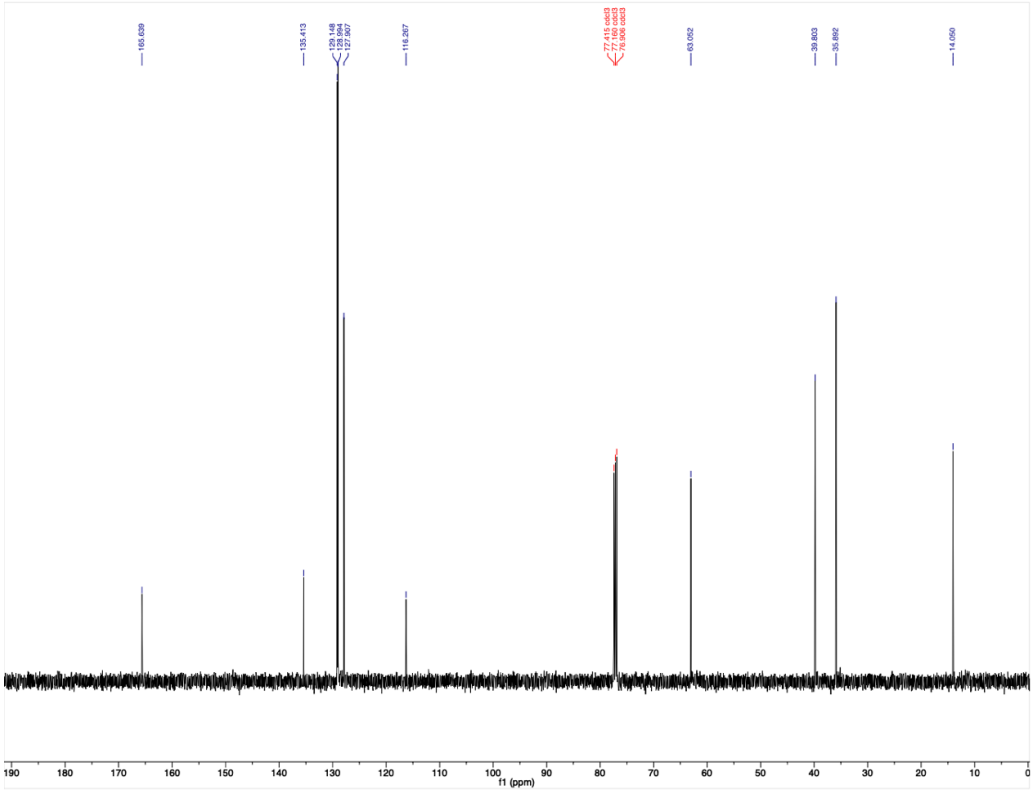

Cl
Cl
O
O
O
f1 (ppm)

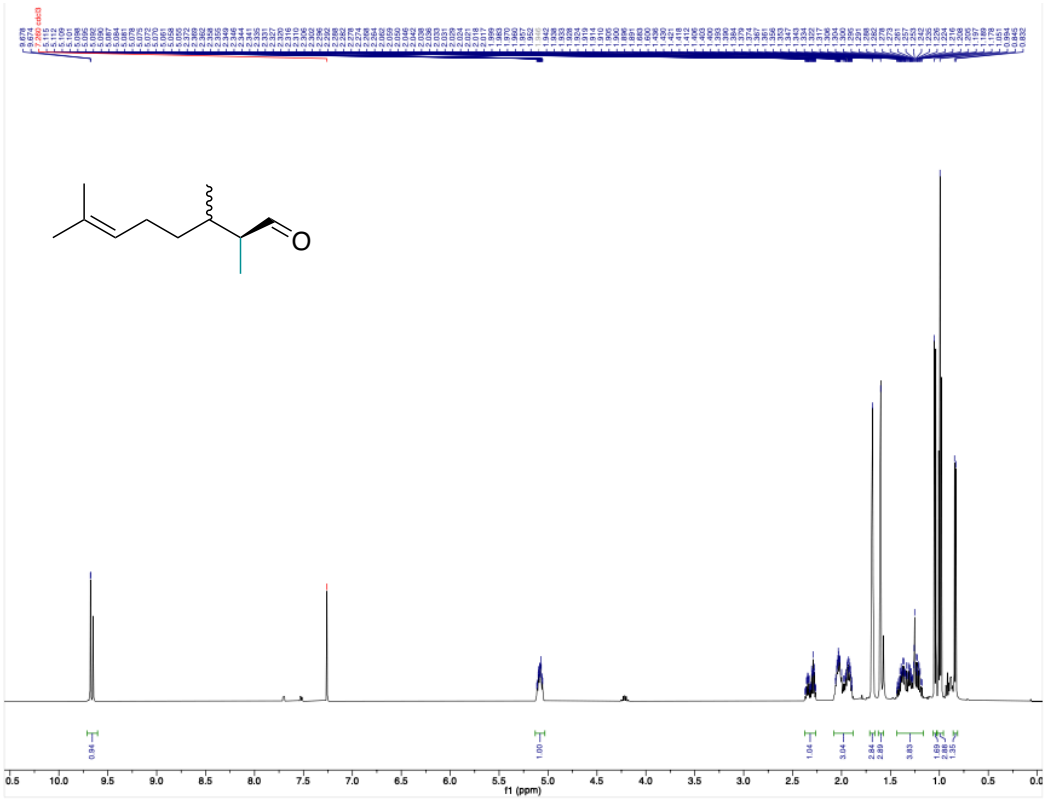

f1 (ppm)

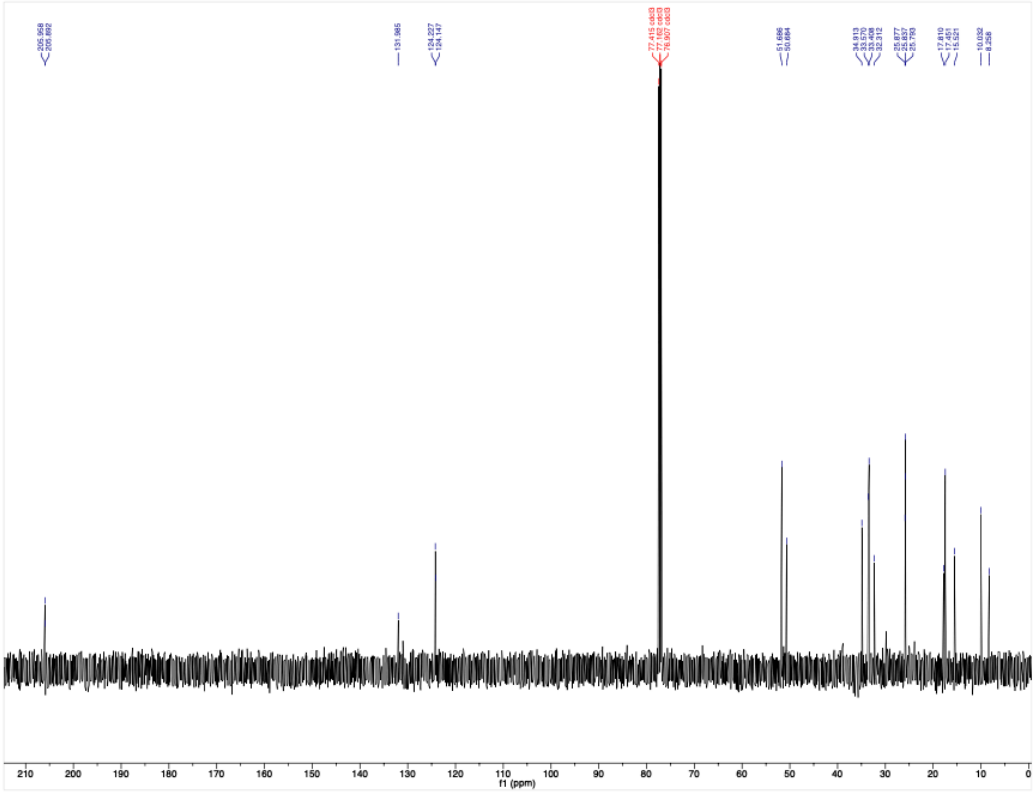

O
f1 (ppm)

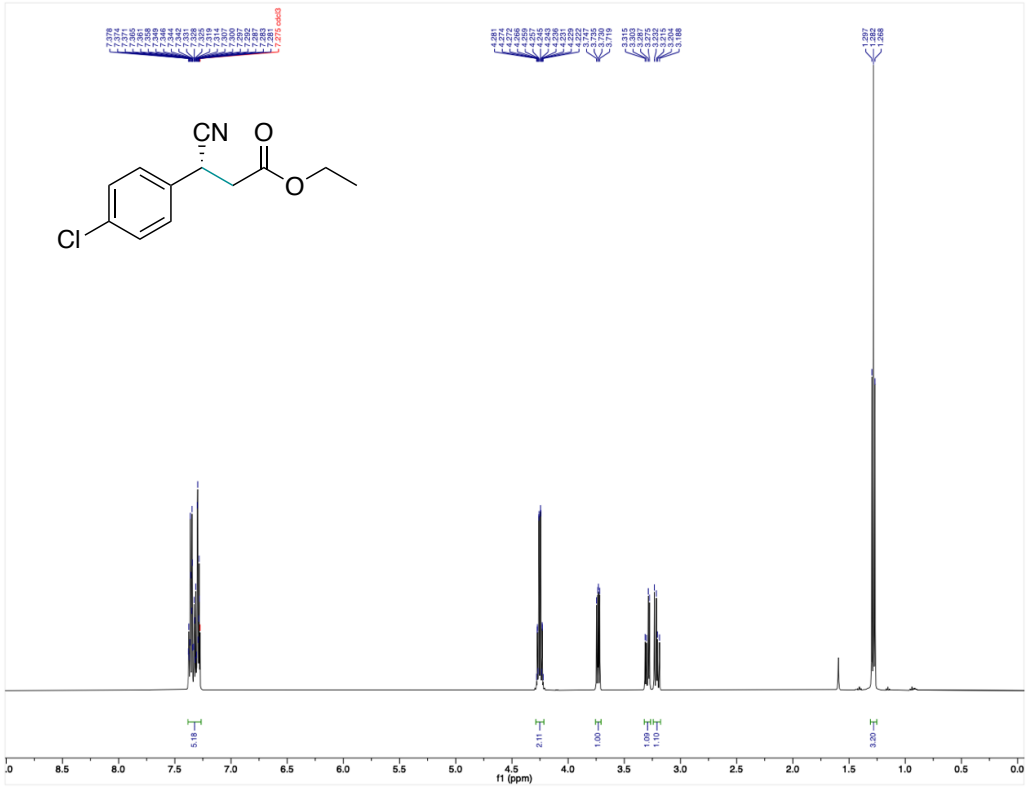

212.800
147.770
109.740
77.419
77.000
76.580
47.157
47.012
44.864
35.052
30.908
20.611
14.470
f1 (ppm)

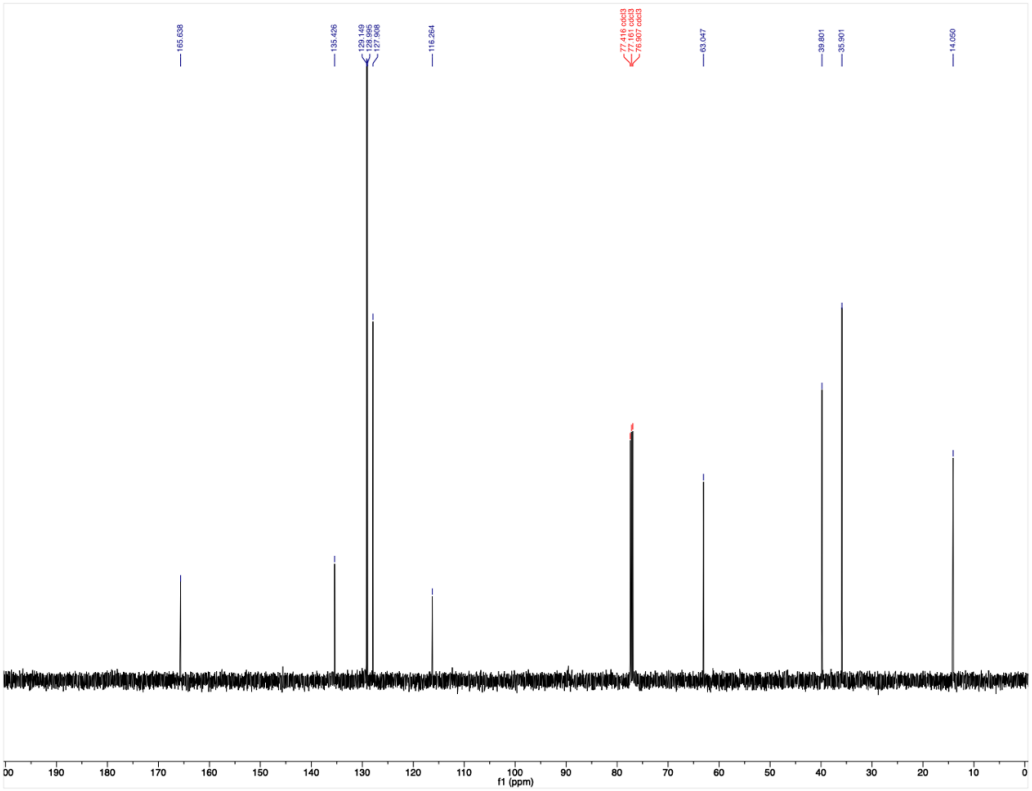

O
O
CN
f1 (ppm)

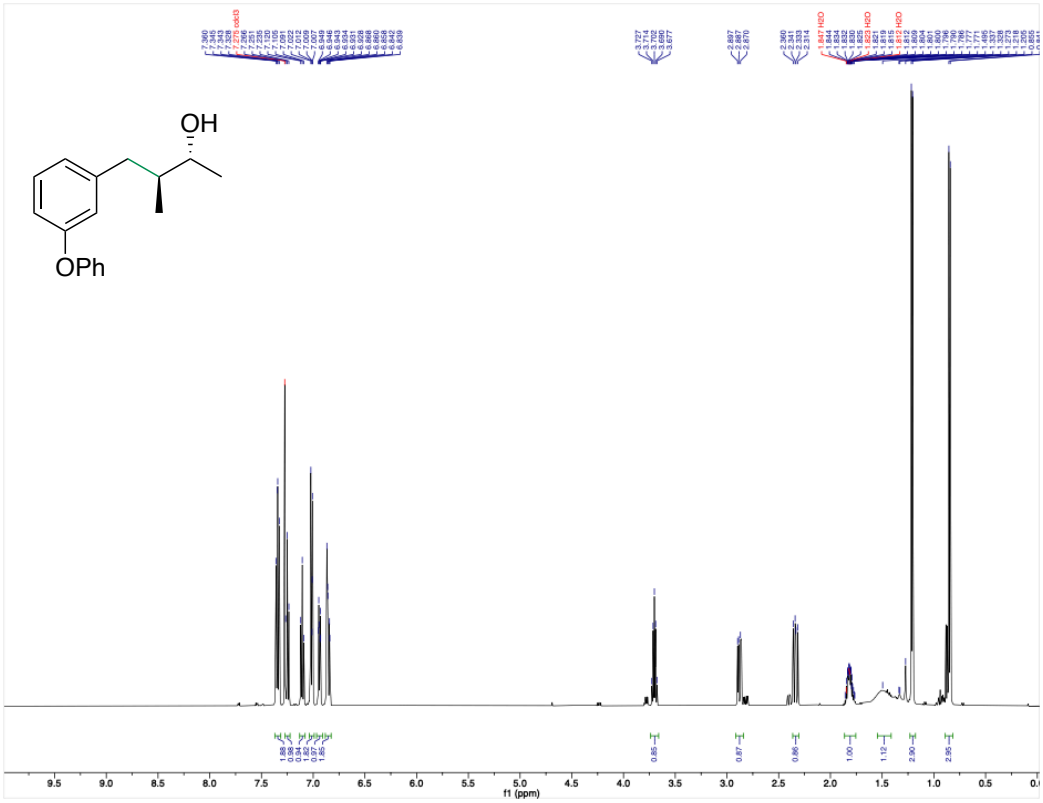

f1 (ppm)

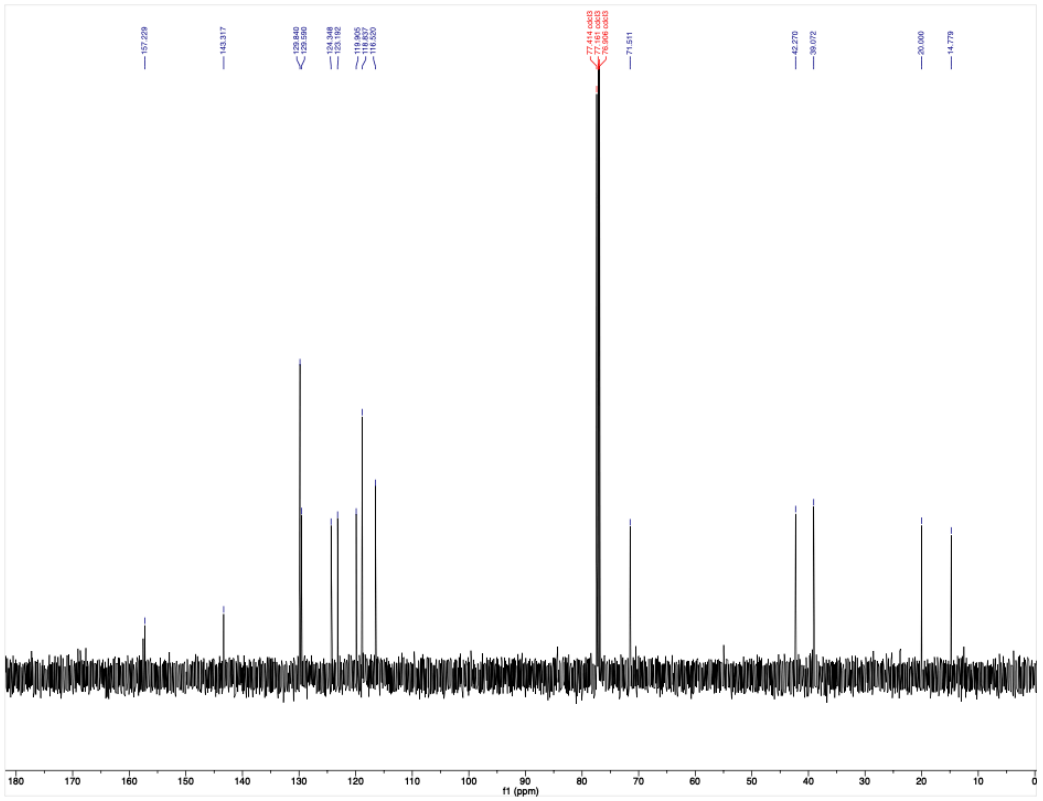

O
0.94
1.00
1.04
3.04
2.84
2.89
3.83
1.69
1.45
1.35
f1 (ppm)

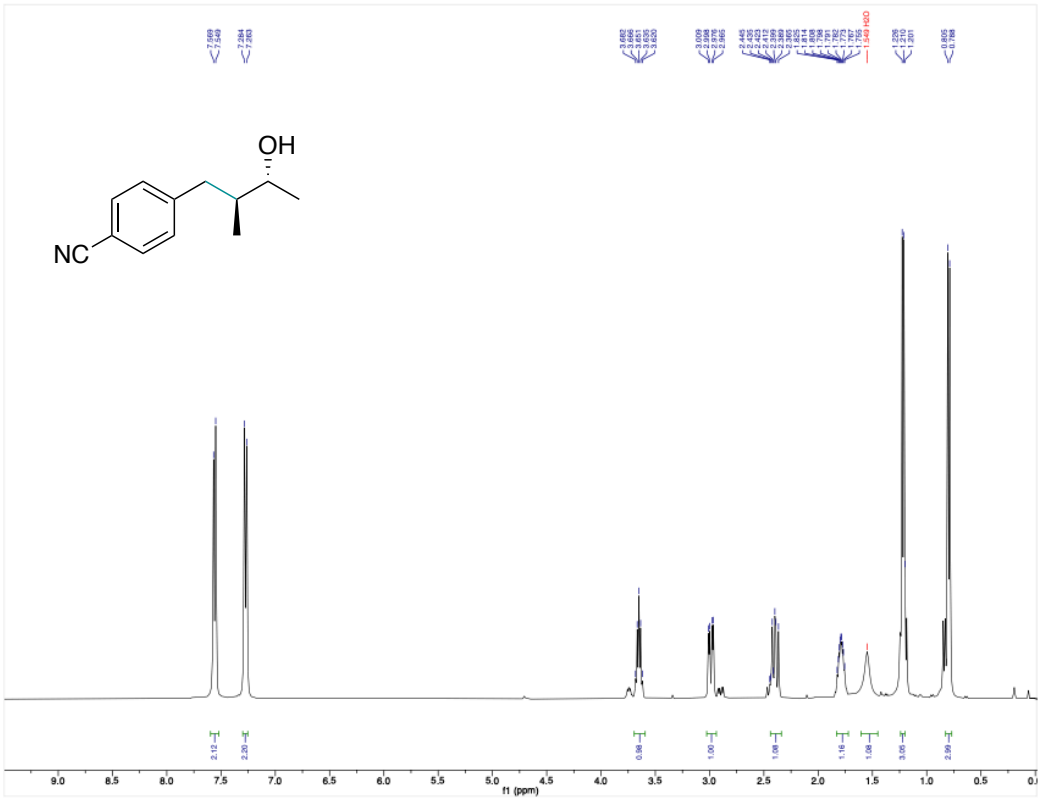

205.958
205.892
131.985
124.227
124.147
77.415
77.163
76.907
51.686
50.684
34.813
33.570
33.408
32.316
25.877
25.793
17.810
17.601
15.521
10.052
9.858
f1 (ppm)

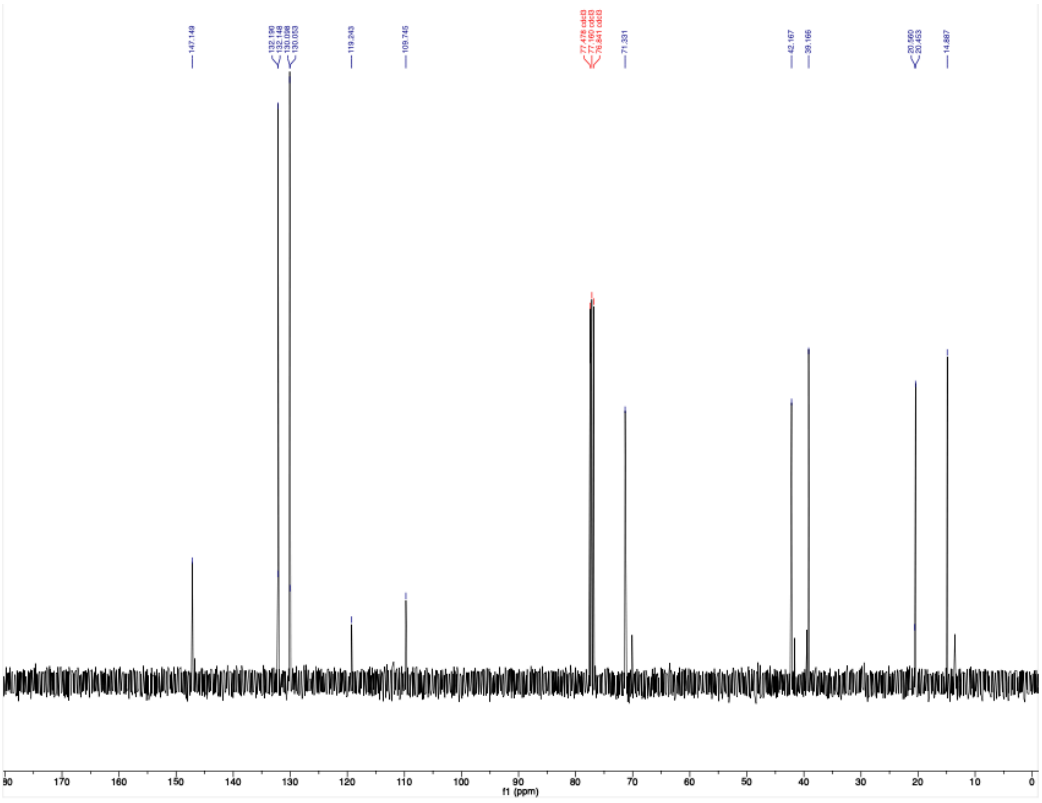

CN
O
O
Cl
f1 (ppm)

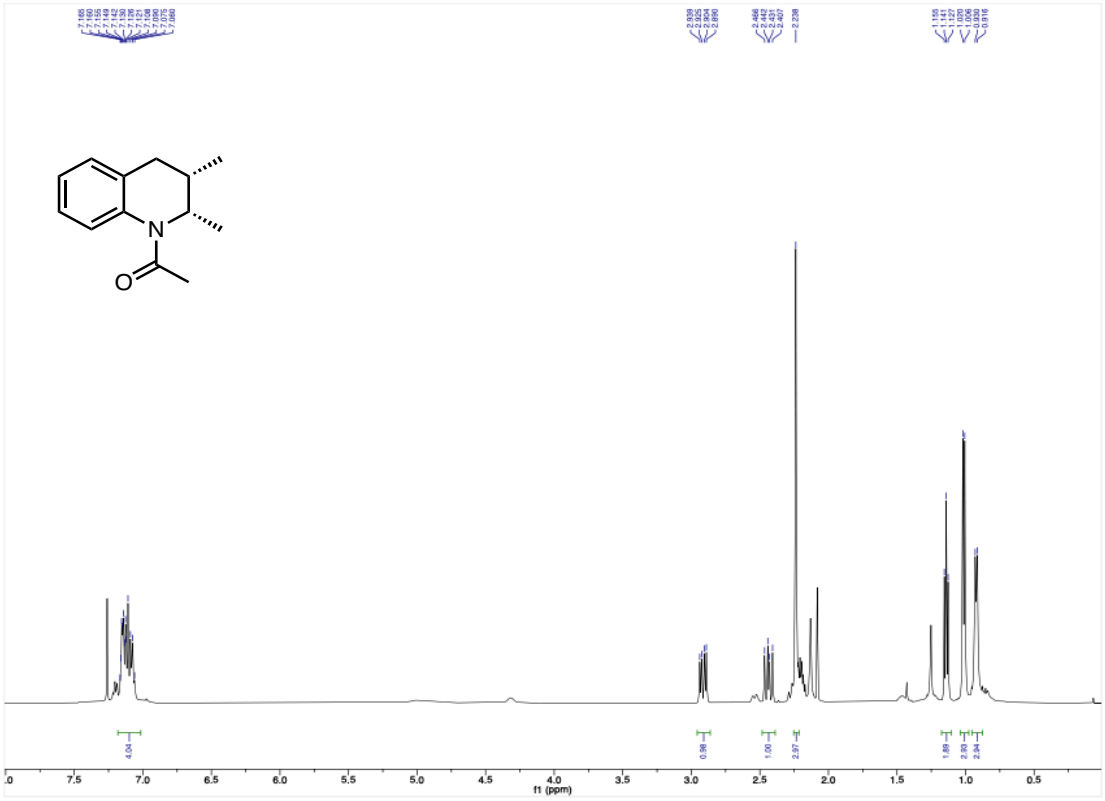

f1 (ppm)

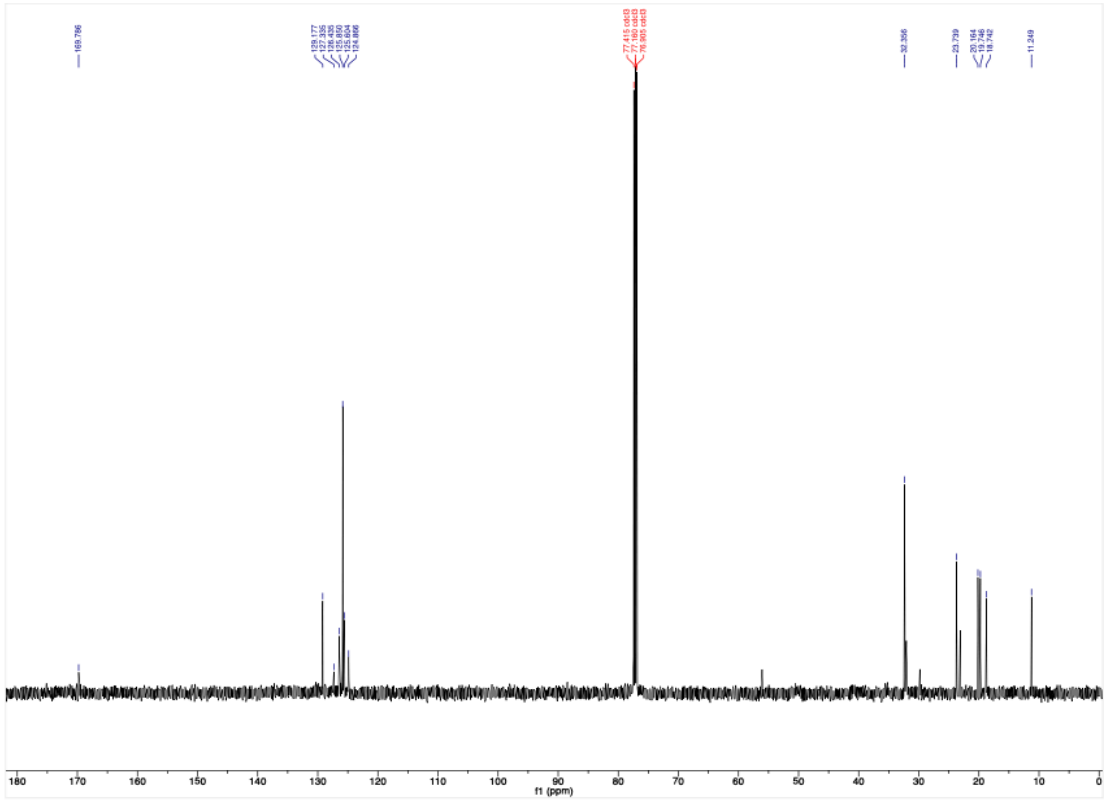

OH
OPh
f1 (ppm)


f1 (ppm)

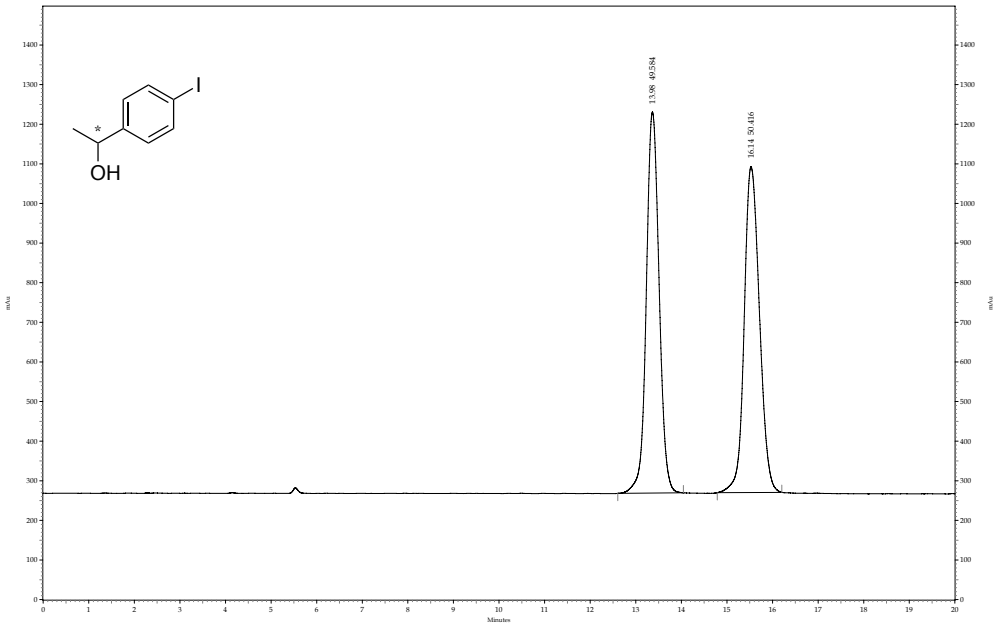

OH
NC
f1 (ppm)

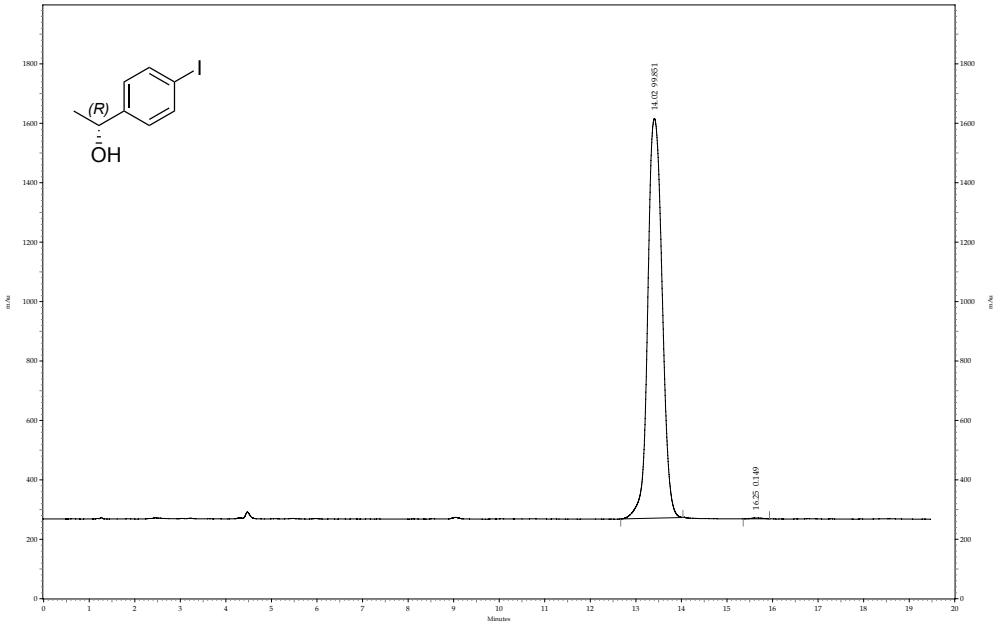

f1 (ppm)

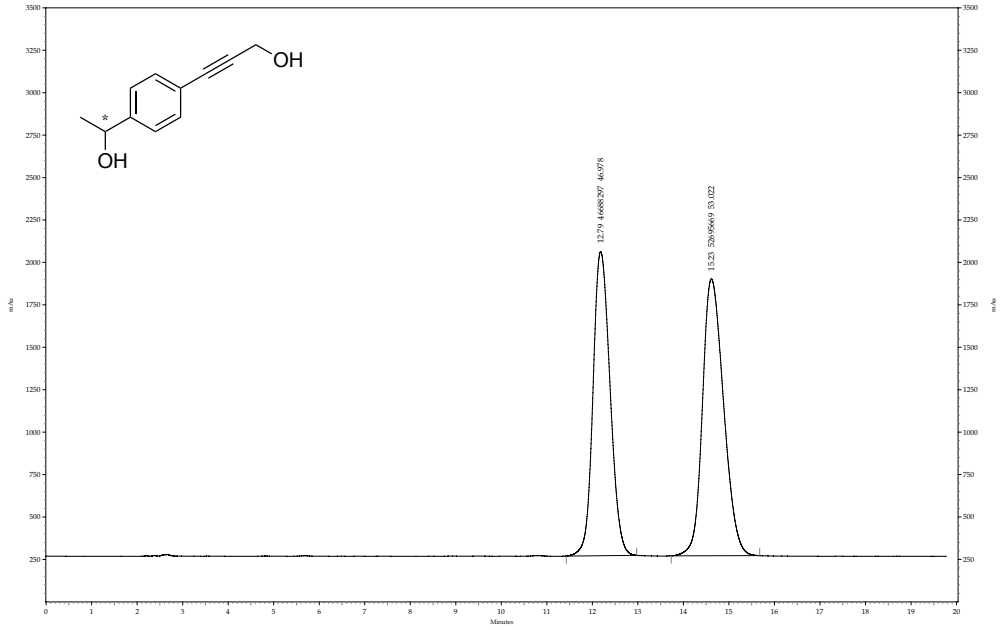

N
O
f1 (ppm)

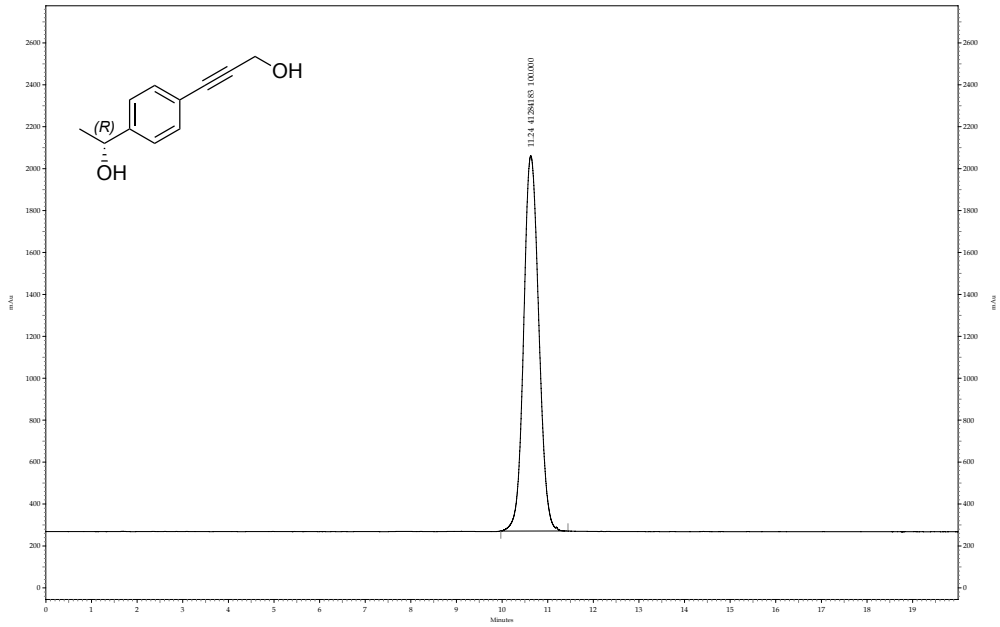

f1 (ppm)

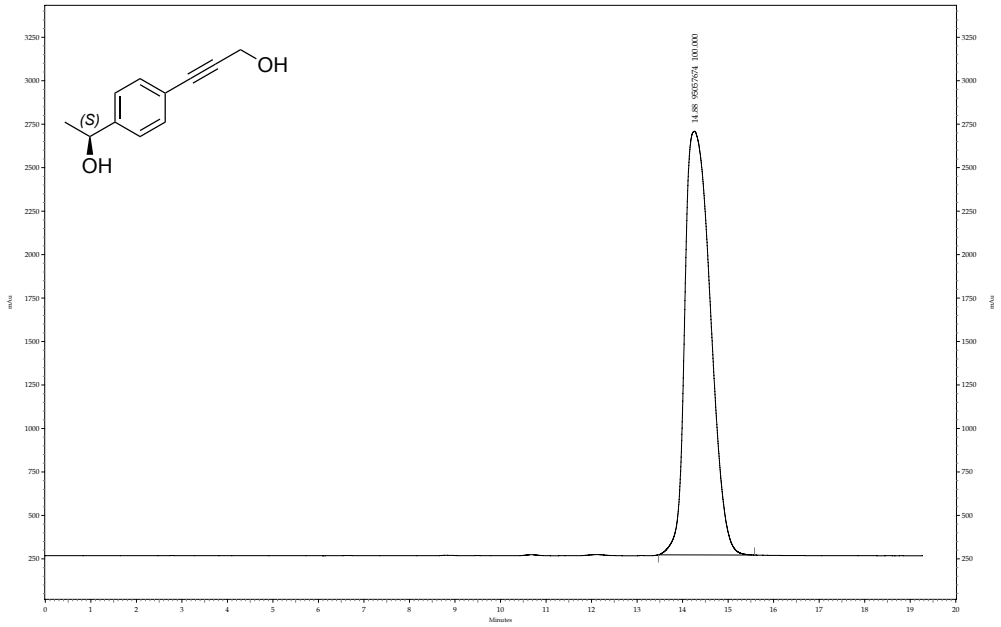
26.Chrial HPLC Data for Compounds

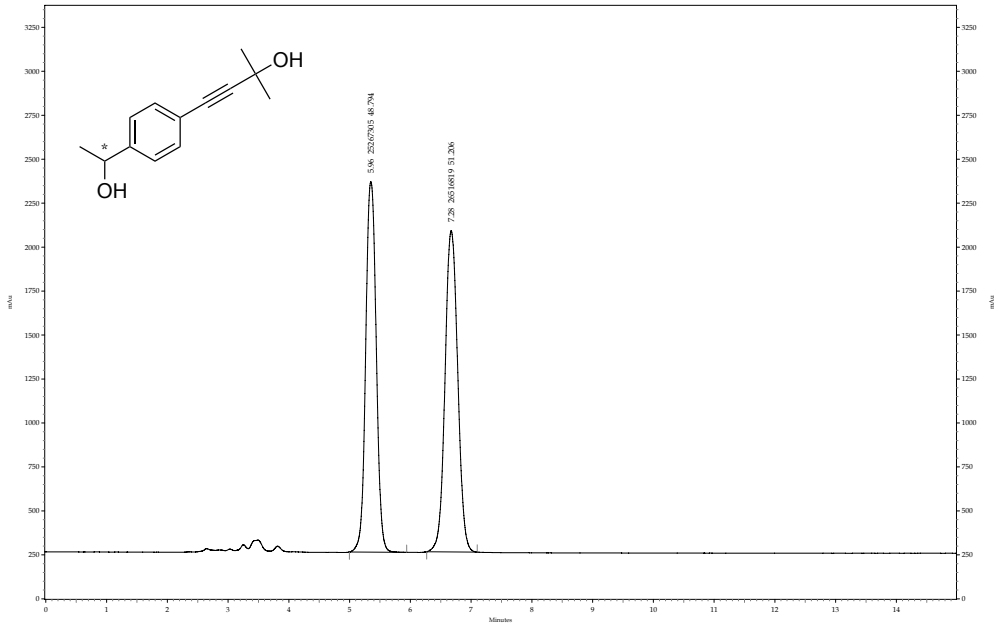


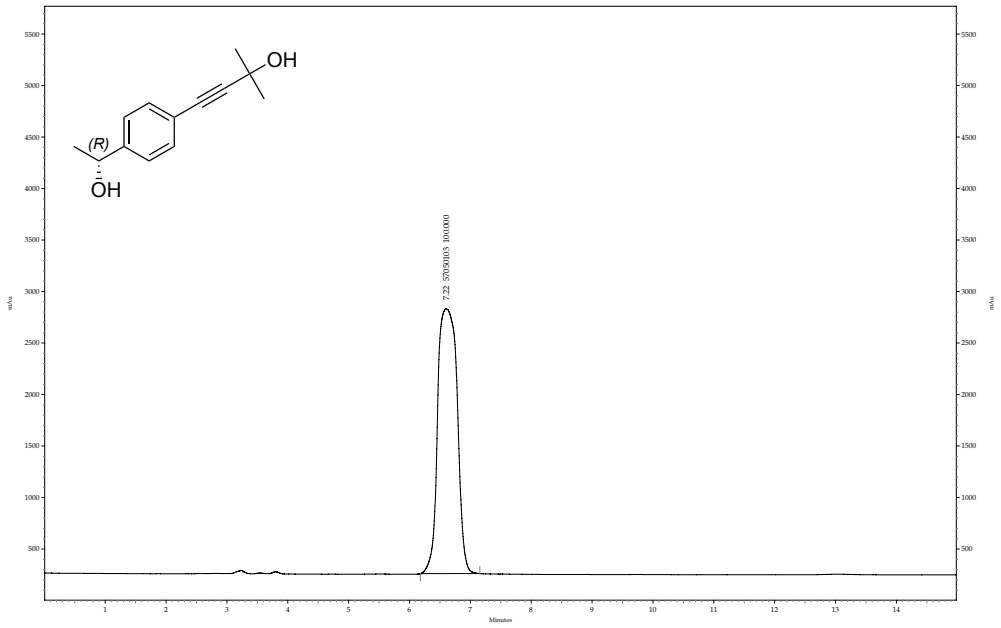


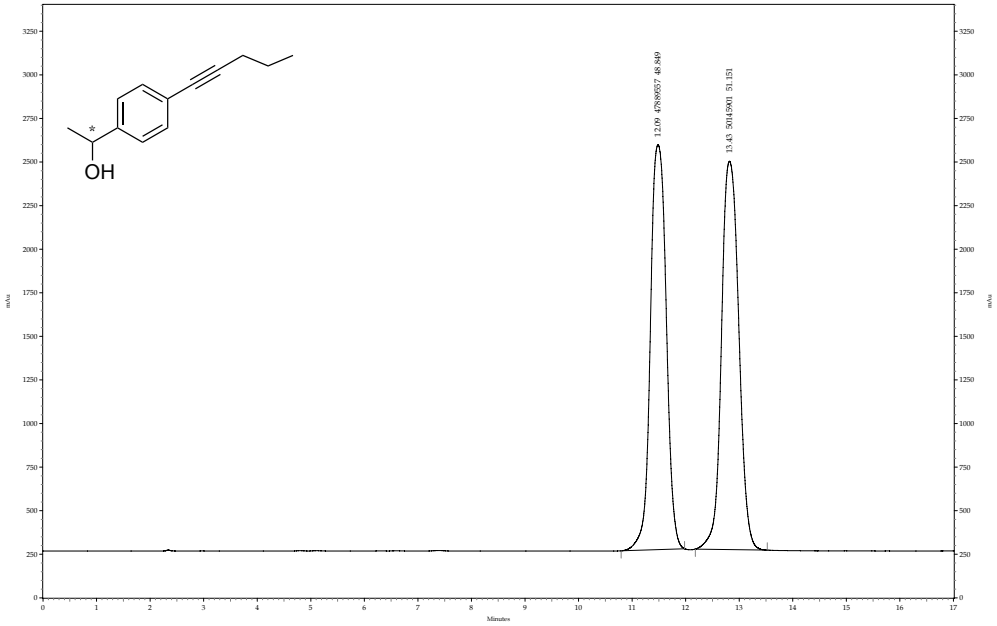

OH
OH
12.79 44688297 46.978
15.23 520.9669 53.022
m/Au
Minutes

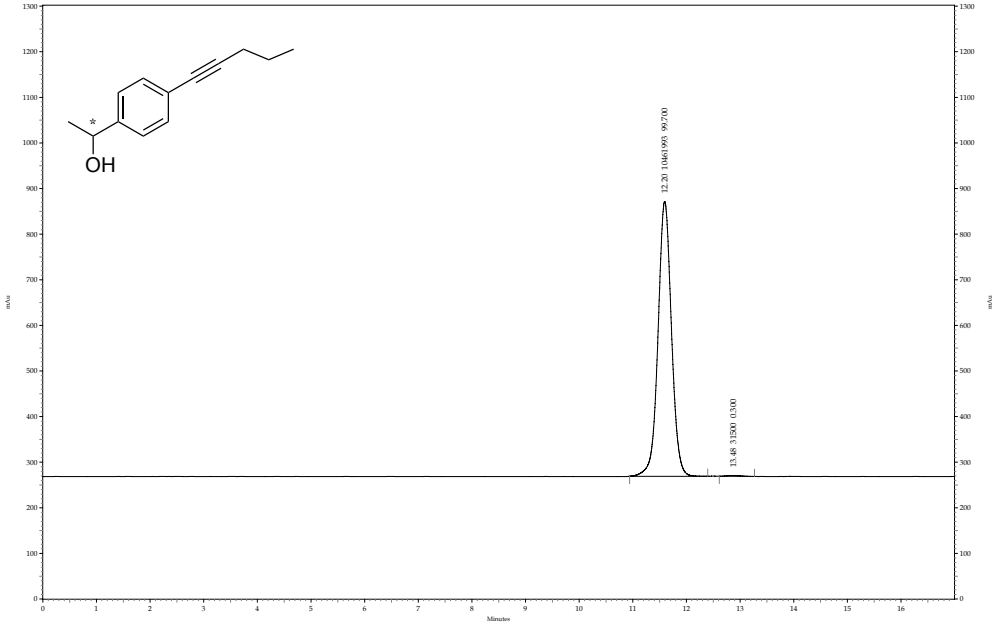

OH
(R)
OH
11.24 41284183 100.000
m/Au
Minutes

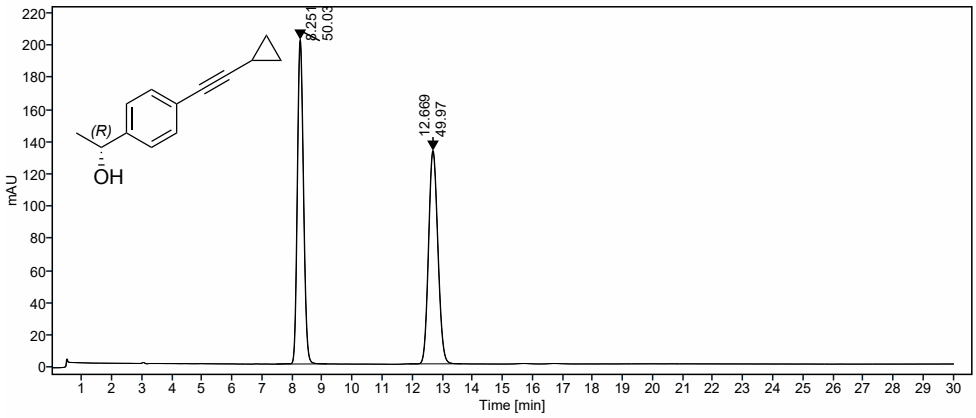

OH
(S)
OH
14.88 9567674 100.000
mAu
Minutes


OH
OH
*
5.96 2252670 15 48.794
7.28 2651681 9 51.206
mAu
Minutes


OH
(R)
OH
7.22 5703003 100.000
mAu
Minutes

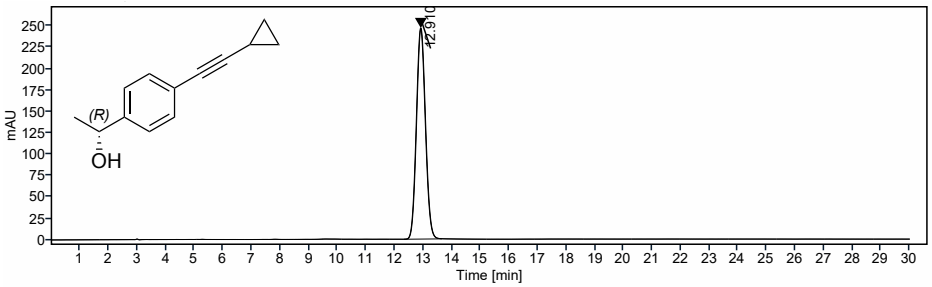

OH
12.09 47889057 48.849
13.43 50149901 51.151
mAu
Minutes


OH
12.20 10461998 99.700
13.48 31500 0.300
mAu
Minutes



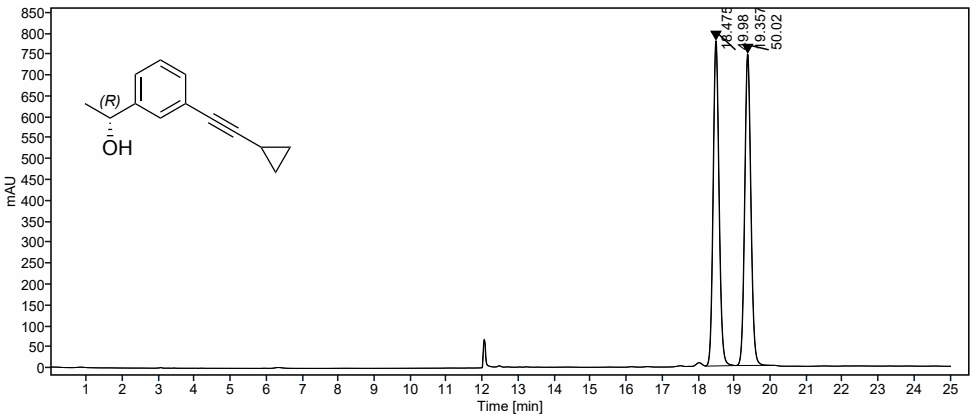
Signal: DAD1A,Sig=245,4 Ref=off

RT [min]	Area	Area%
8.251	2850.2932	50.0332
12.669	2846.5050	49.9668



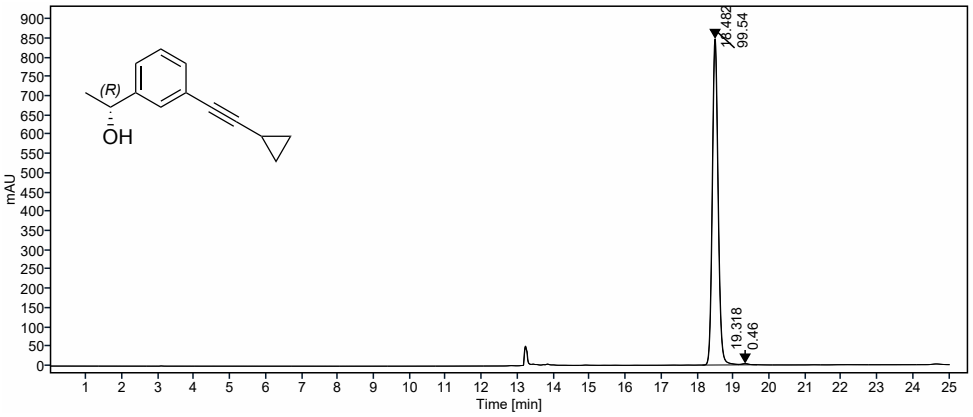
Signal: DAD1A,Sig=245,4 Ref=off

RT [min]	Area	Area%
12.910	5404.8865	100.0000



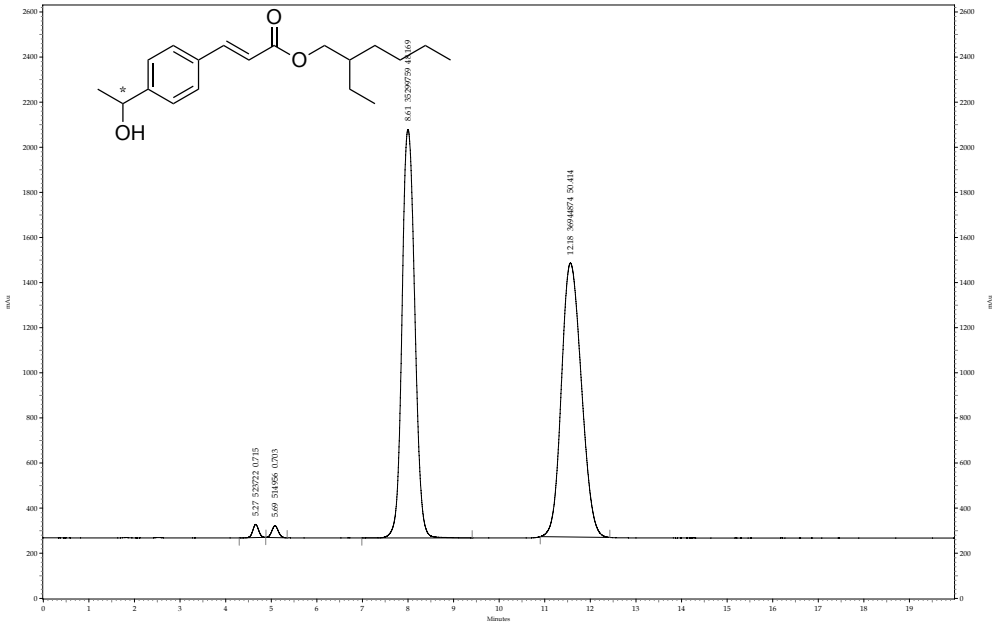
Signal: DAD1A,Sig=245,4 Ref=off

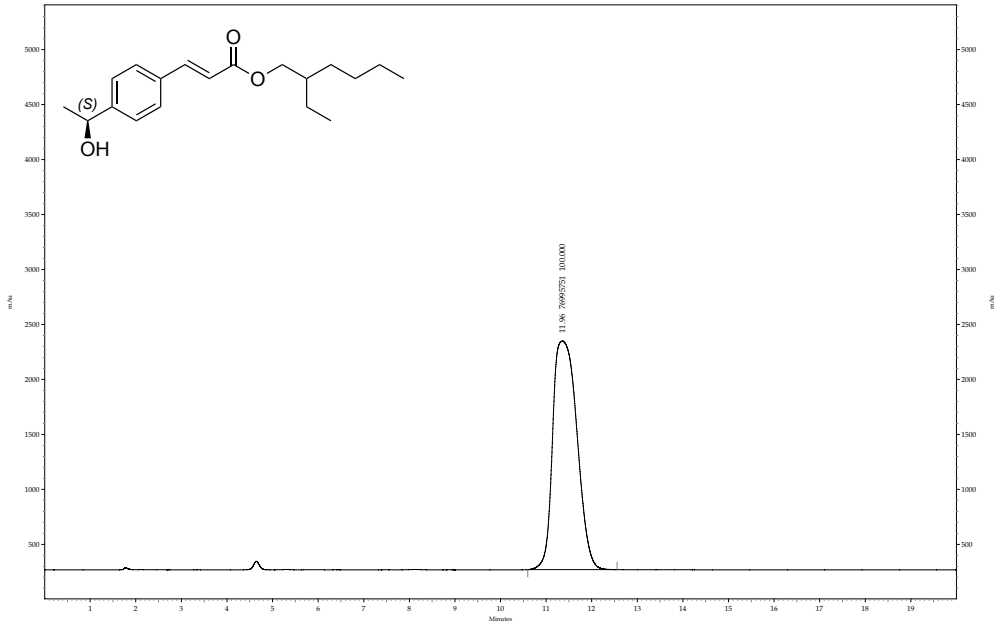
RT [min]	Area	Area%
18.475	8876.5342	49.9824
19.357	8882.7724	50.0176

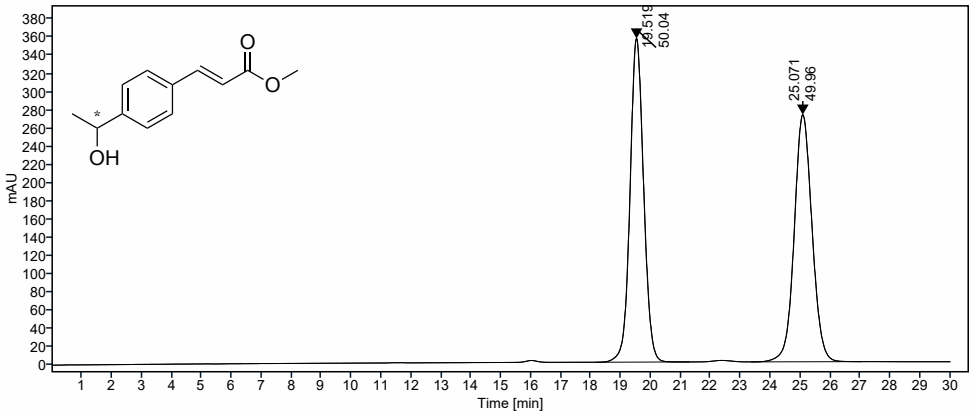


Signal: DAD1A,Sig=245,4 Ref=off

RT [min]	Area	Area%
18.482	9518.1775	99.5355
19.318	44.4151	0.4645

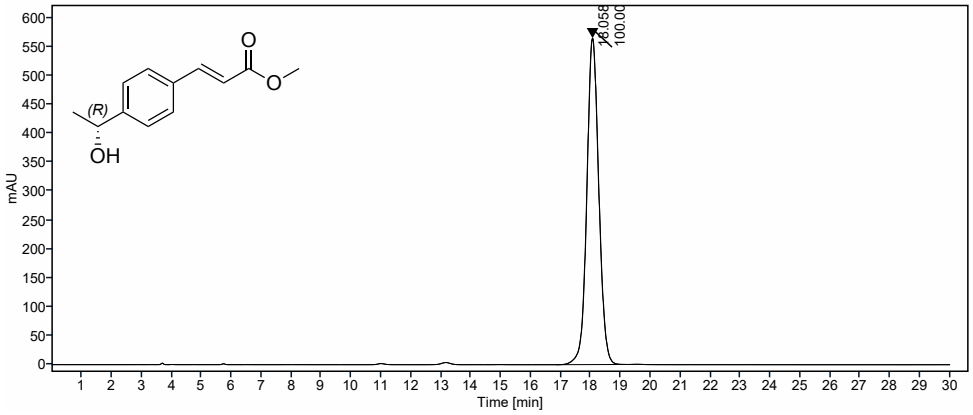

O
O
OH
*
8.61 35290759 44.069
12.18 36944874 50.414
5.27 523722 0.715
5.69 514956 0.703
m/Au
Minutes


O
O
(S)
OH
11.96 76995751 100.000
m/Au
Minutes



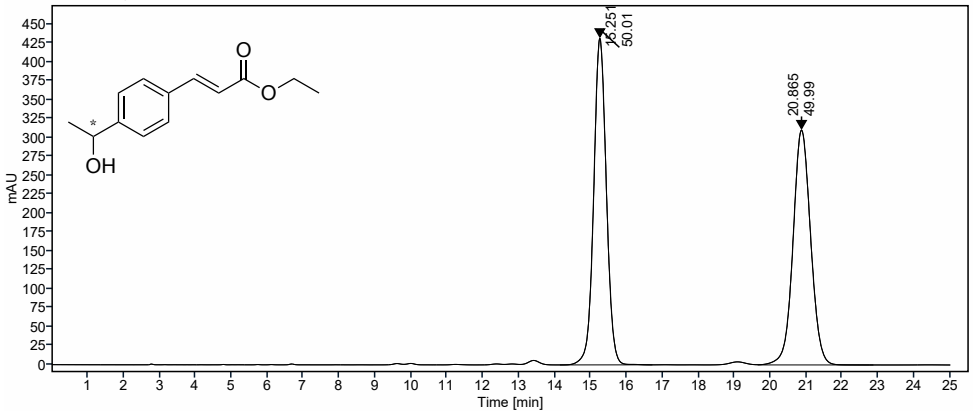
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
19.519	11271.3008	50.0371
25.071	11254.5693	49.9629



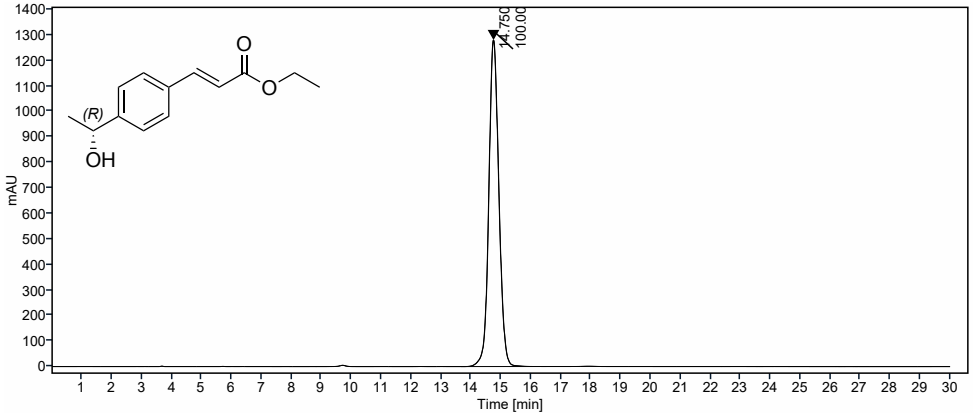
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
18.058	15722.4491	100.0000



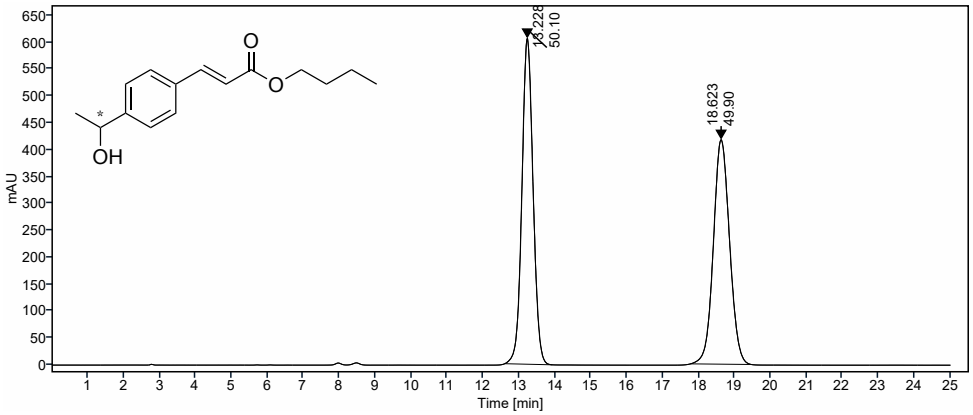
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
15.251	10614.7483	50.0125
20.865	10609.4553	49.9875



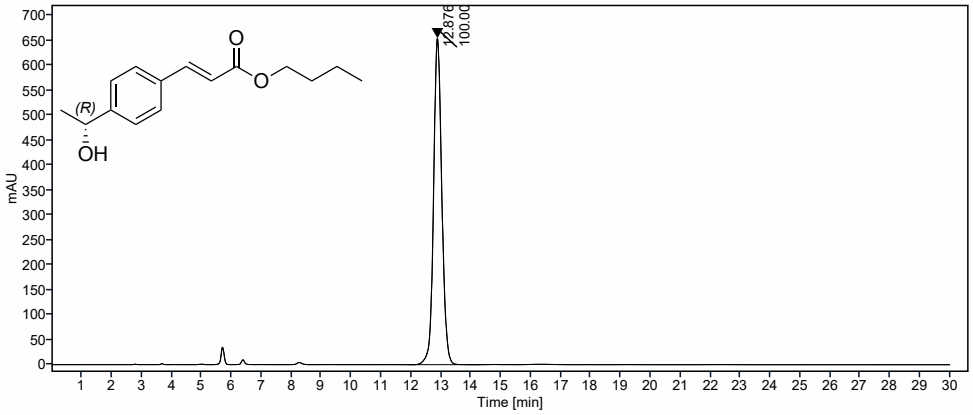
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
14.750	29878.4082	100.0000



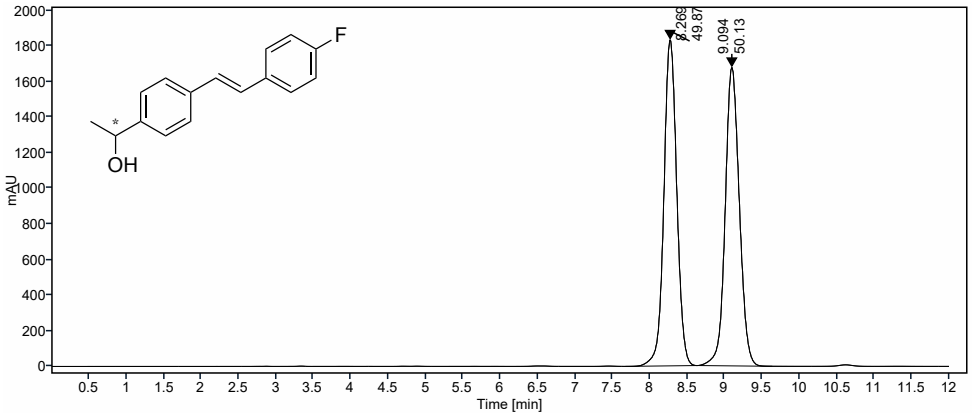
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
13.228	13106.5645	50.0983
18.623	13055.1367	49.9017



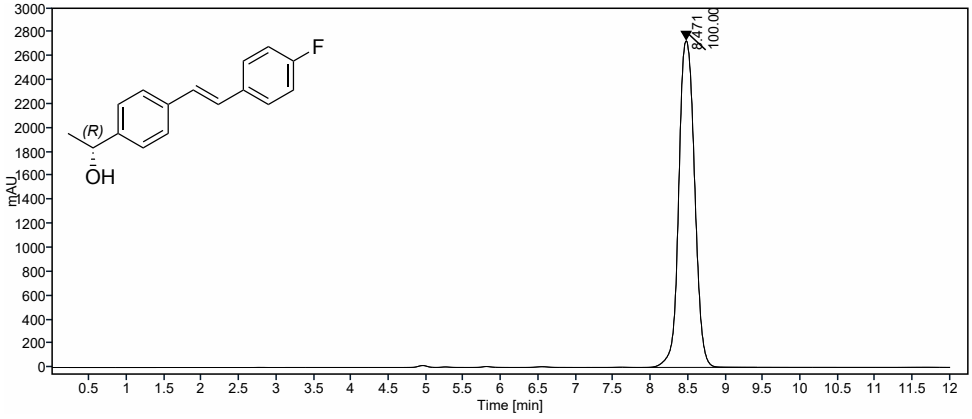
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
12.876	12548.9631	100.0000



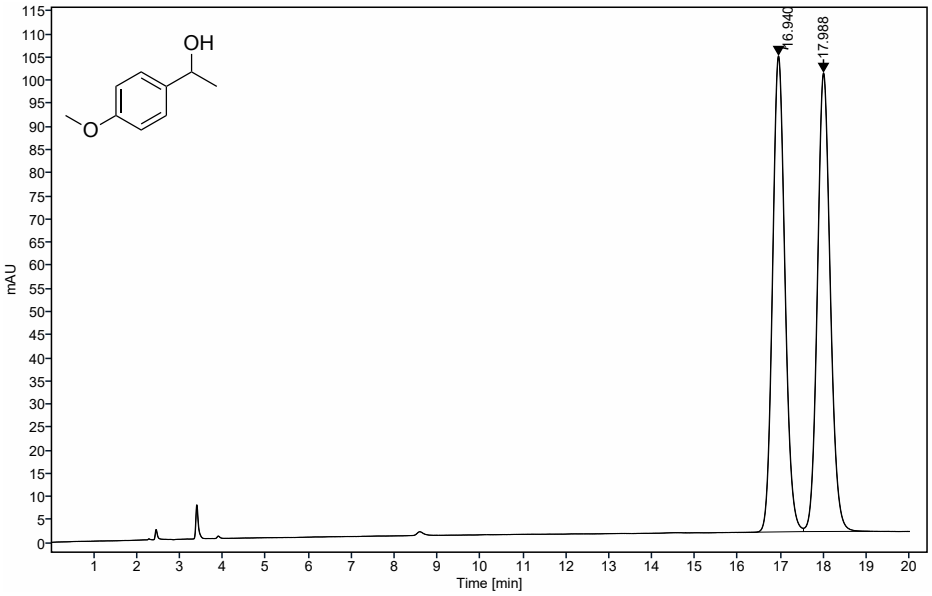
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
8.269	21952.6575	49.8702
9.094	22066.8901	50.1298



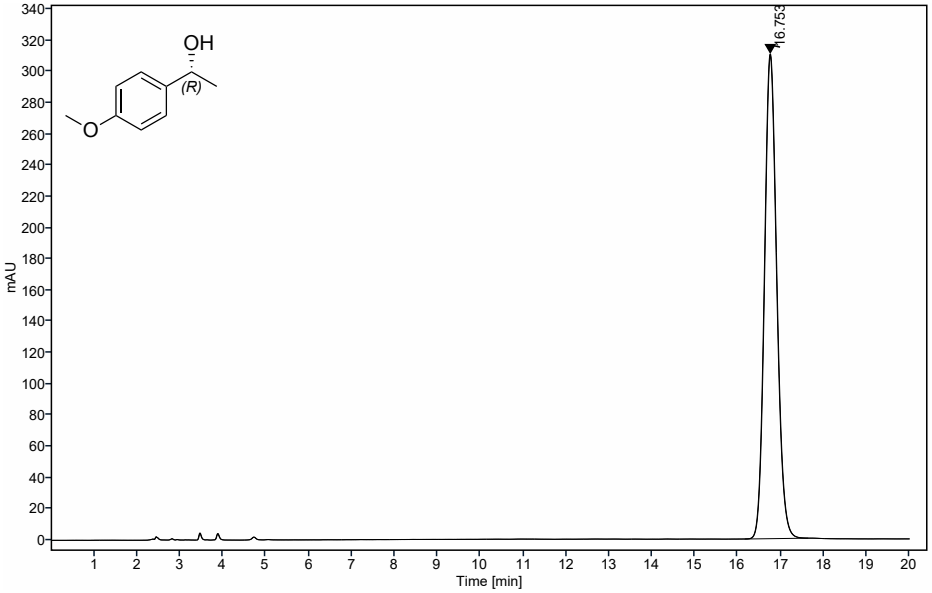
Signal: DAD1A,Sig=275,4 Ref=off

RT [min]	Area	Area%
8.471	40015.7533	100.0000



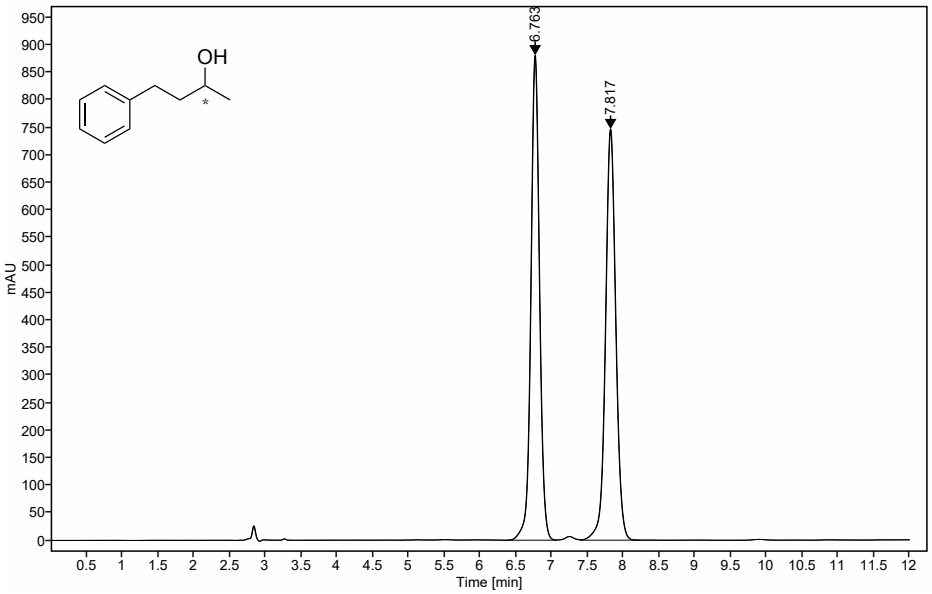
Signal: DAD1A,Sig=230,4 Ref=off

RT [min]	Area	Area%
16.940	2062.6187	49.9028
17.988	2070.6502	50.0972



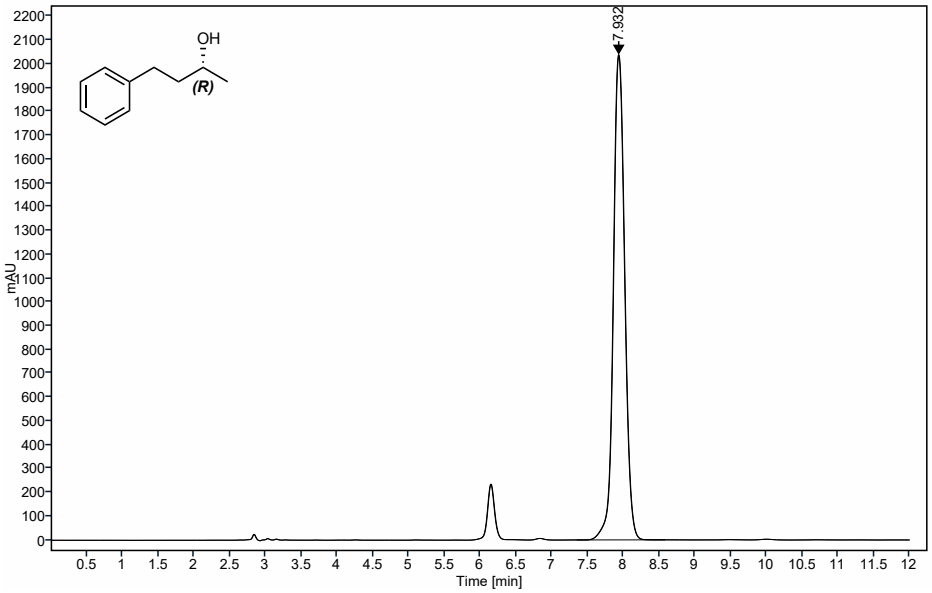
Signal: DAD1A,Sig=230,4 Ref=off

RT [min]	Area	Area%
16.753	6168.0357	100.0000



Signal: DAD1A,Sig=210,4 Ref=off

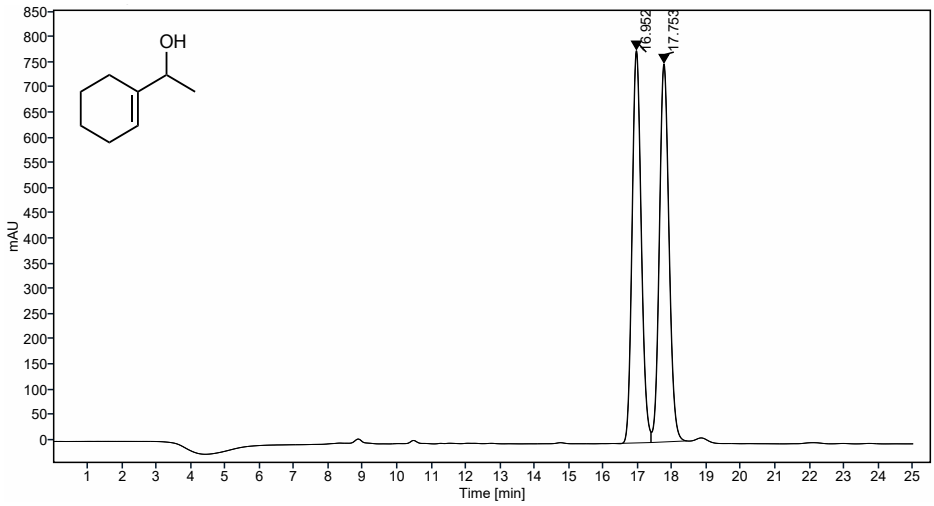
RT [min]	Area	Area%
6.763	7394.2139	49.7560
7.817	7466.7338	50.2440



Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
7.932	22472.4771	100.0000

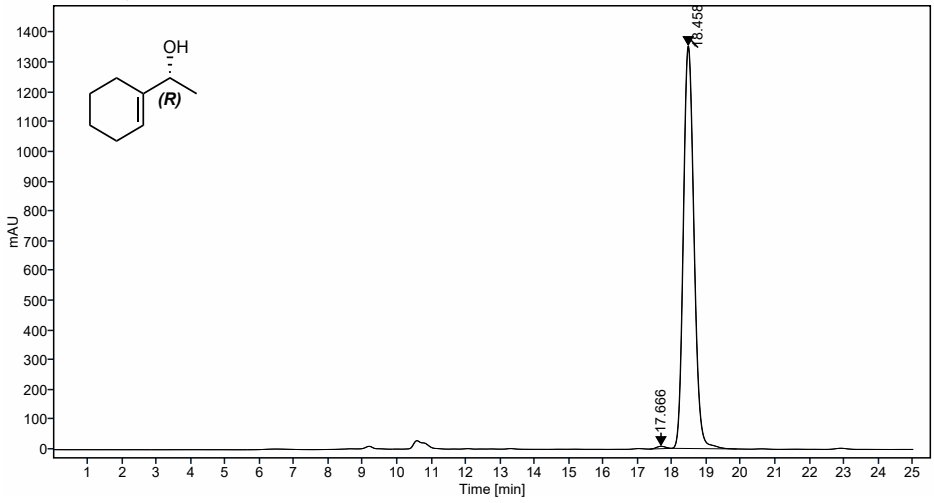
Supplementary figure 12: Chiral HPLC chromatogram of the reaction catalyzed by ADH101 for 3b



Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
16.952	14396.9785	49.5798
17.753	14640.9917	50.4202

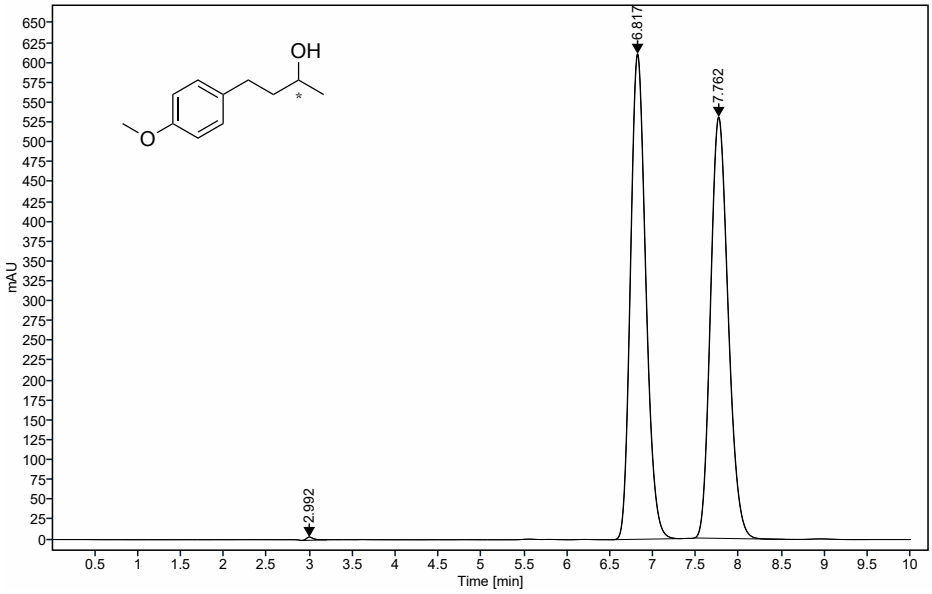
Supplementary figure 13: Chiral HPLC chromatogram of the racemate 3c



Signal: DAD1A,Sig=210,4 Ref=off

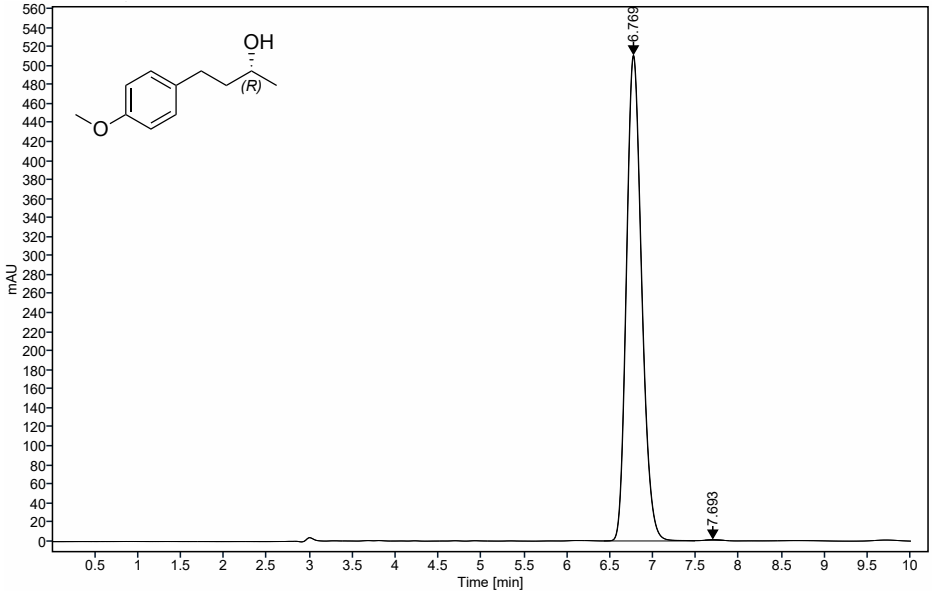
RT [min]	Area	Area%
17.666	143.8802	0.4935
18.458	29013.3826	99.5065

Supplementary figure 14: Chiral HPLC chromatogram of the reaction catalyzed by ADH101 for 3c



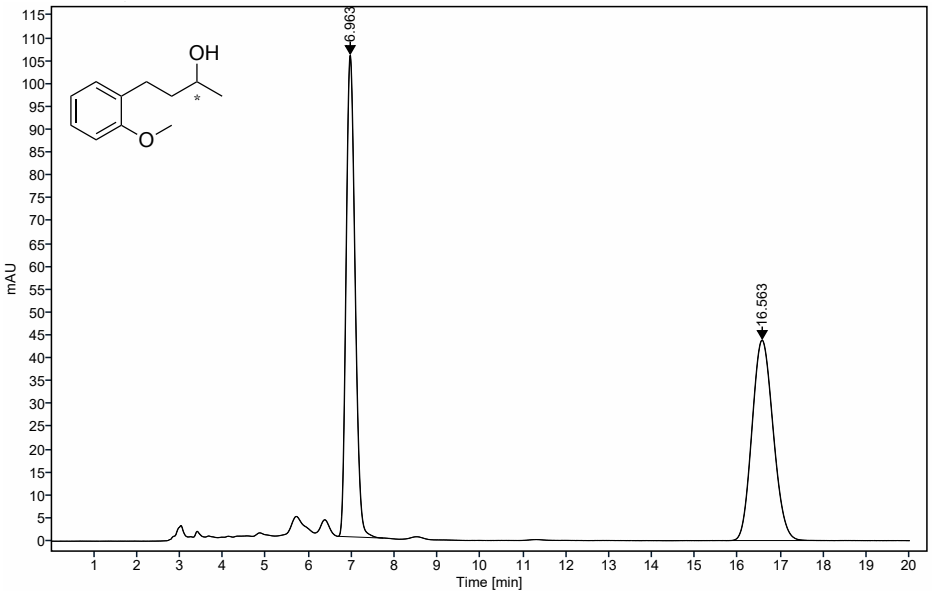
Signal: DAD1A,Sig=225,4 Ref=off

RT [min]	Area	Area%
2.992	24.7018	0.1626
6.817	7600.0252	50.0314
7.762	7565.7943	49.8060



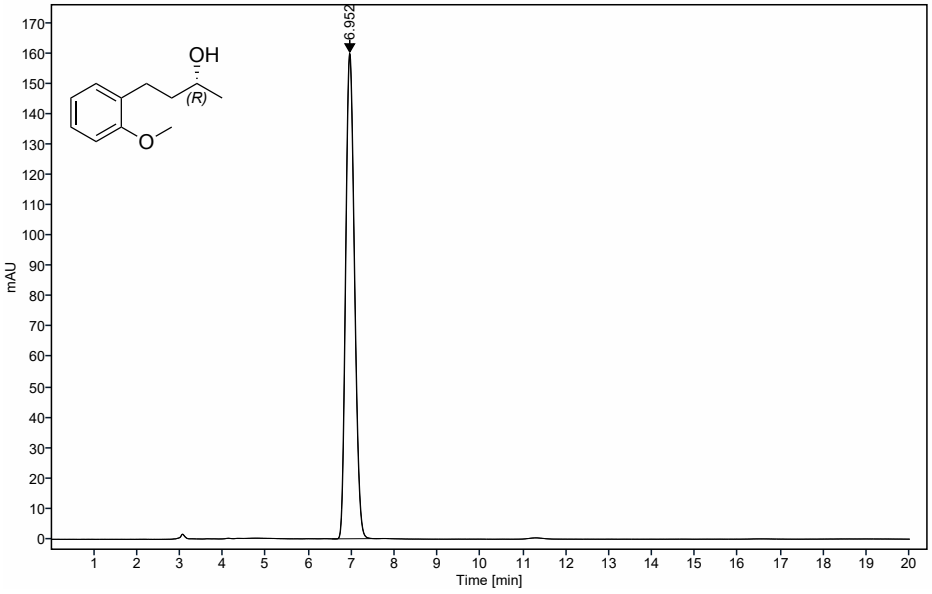
Signal: DAD1A,Sig=225,4 Ref=off

RT [min]	Area	Area%
6.769	6302.6683	99.9065
7.693	5.9000	0.0935



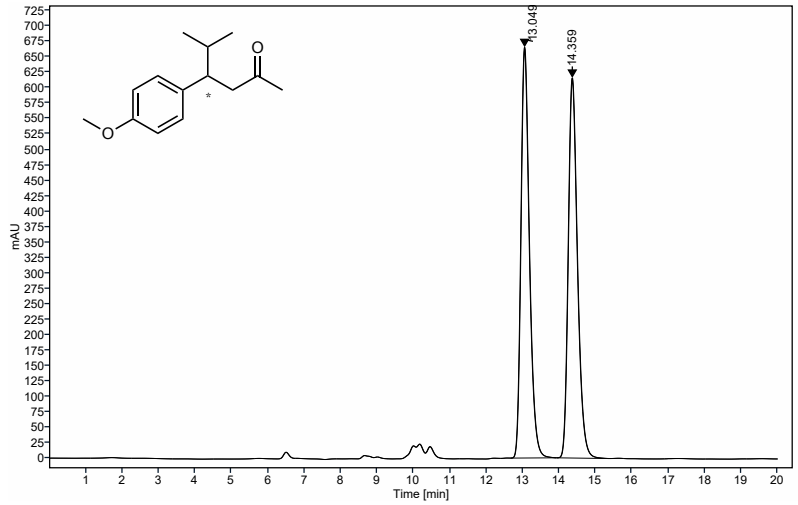
Signal: DAD1A,Sig=270,4 Ref=off

RT [min]	Area	Area%
6.963	1526.7877	50.4661
16.563	1498.5838	49.5339



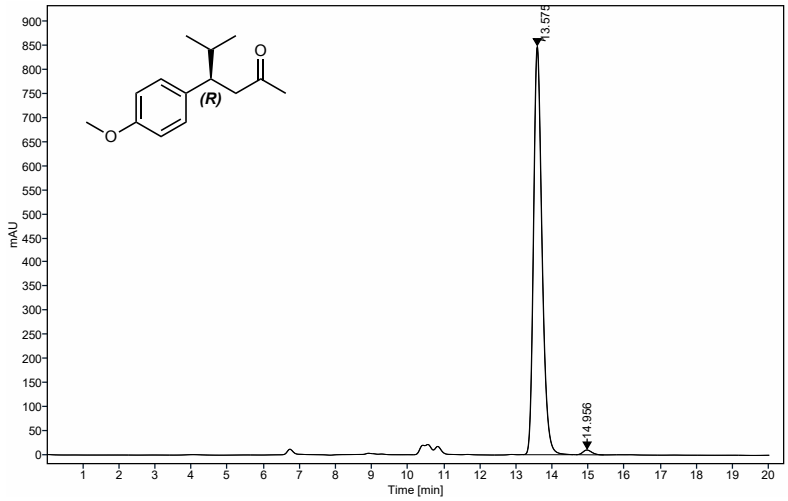
Signal: DAD1A,Sig=270,4 Ref=off

RT [min]	Area	Area%
6.952	2278.7716	100.0000



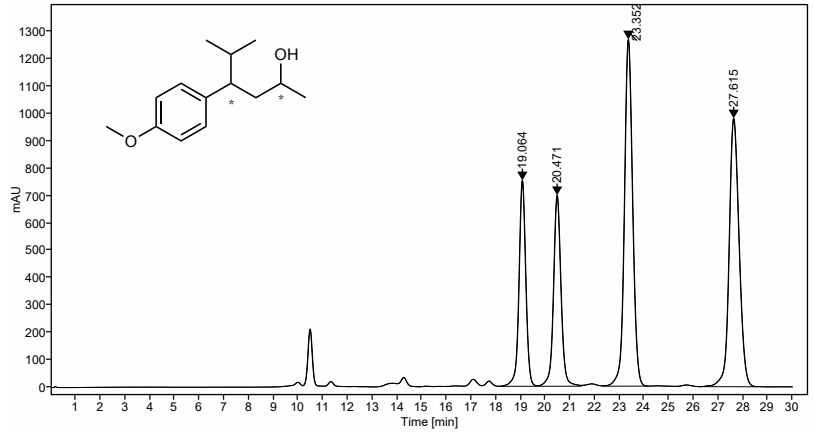
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
13.049	10795.8985	49.9176
14.359	10831.5571	50.0824



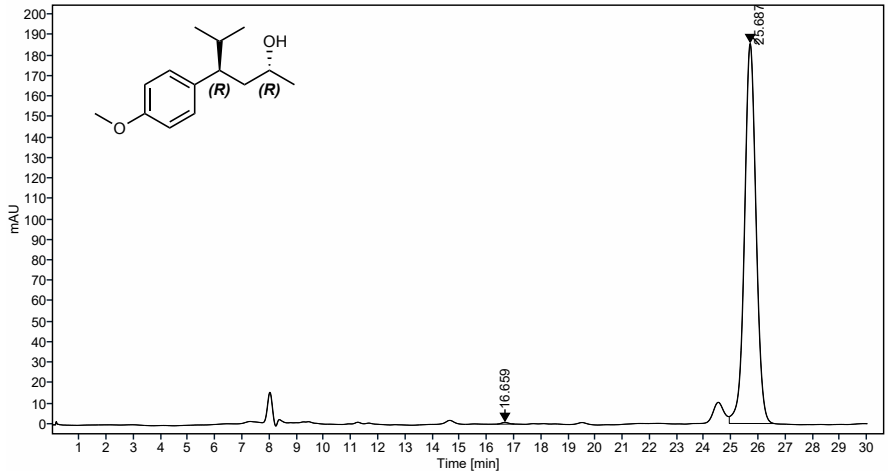
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
13.575	13876.7652	98.7906
14.956	169.8743	1.2094



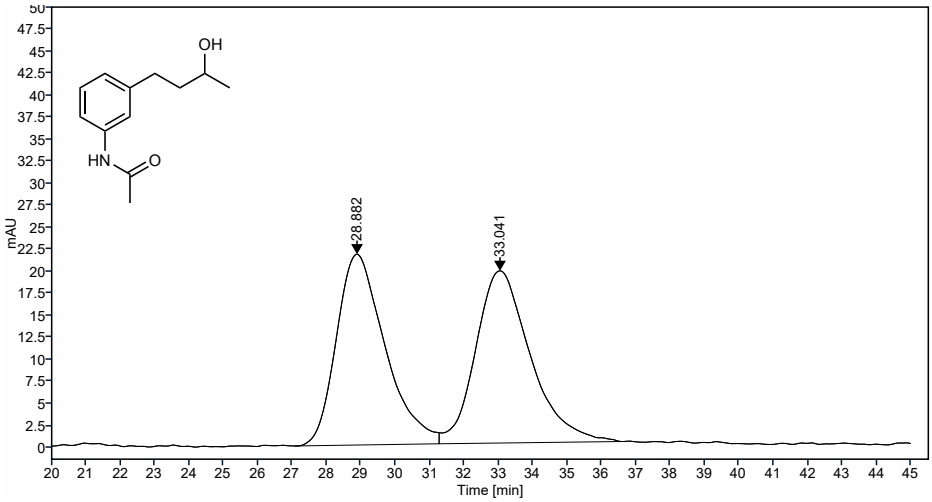
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
19.064	14395.4719	16.7441
20.471	14732.2702	17.1358
23.352	29353.2039	34.1422
27.615	27492.5511	31.9779



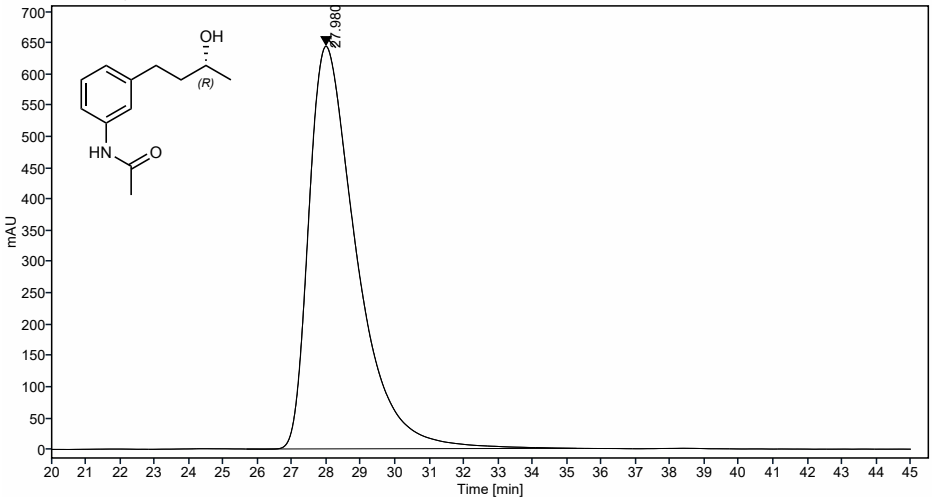
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
16.659	15.3483	0.2796
25.687	5474.2155	99.7204



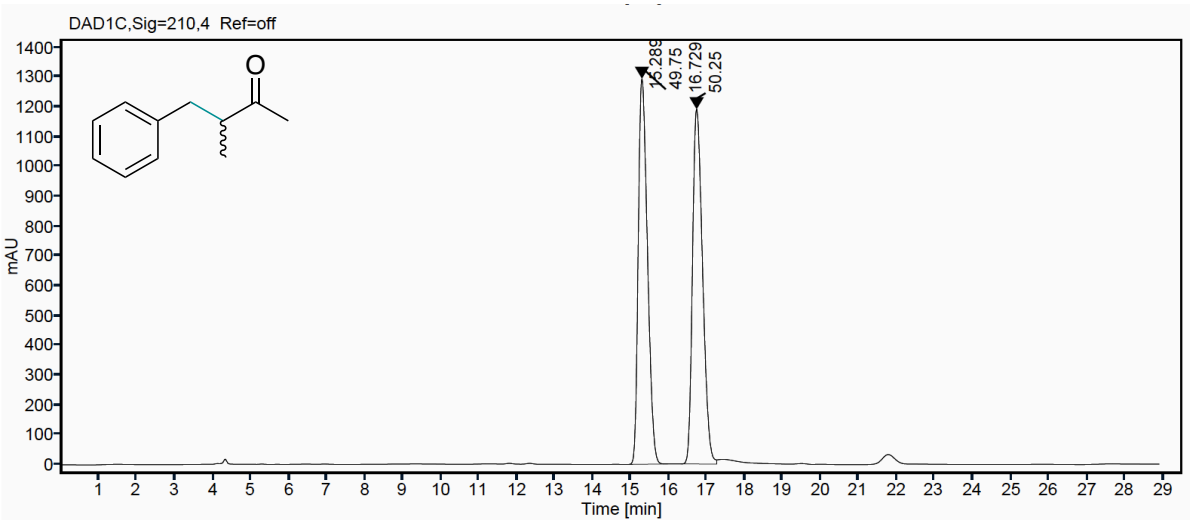
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
28.882	2129.0792	49.6123
33.041	2162.3568	50.3877



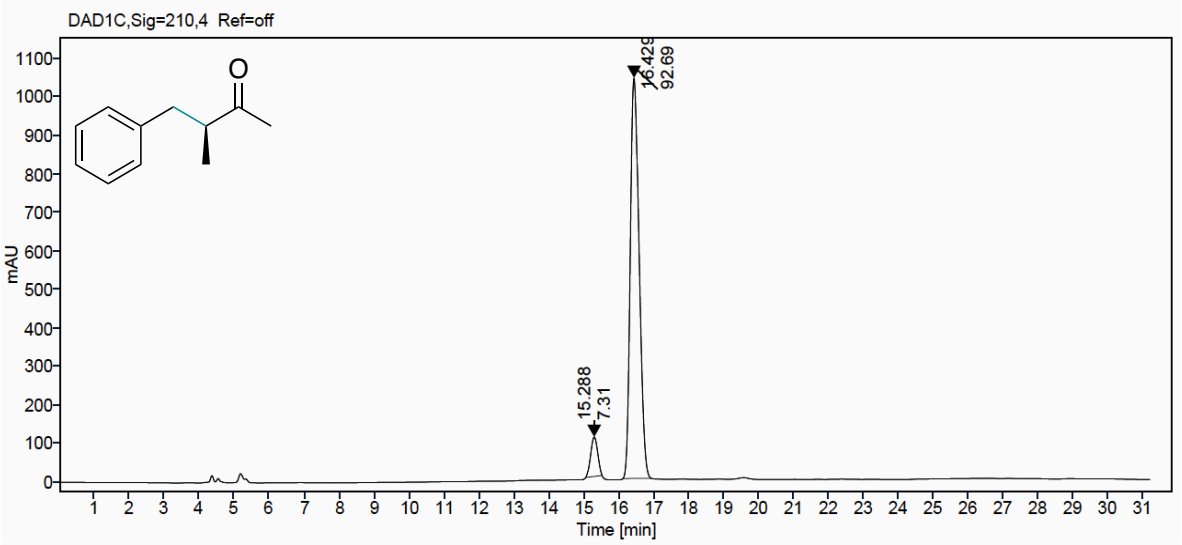
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
27.980	62010.1851	100.0000



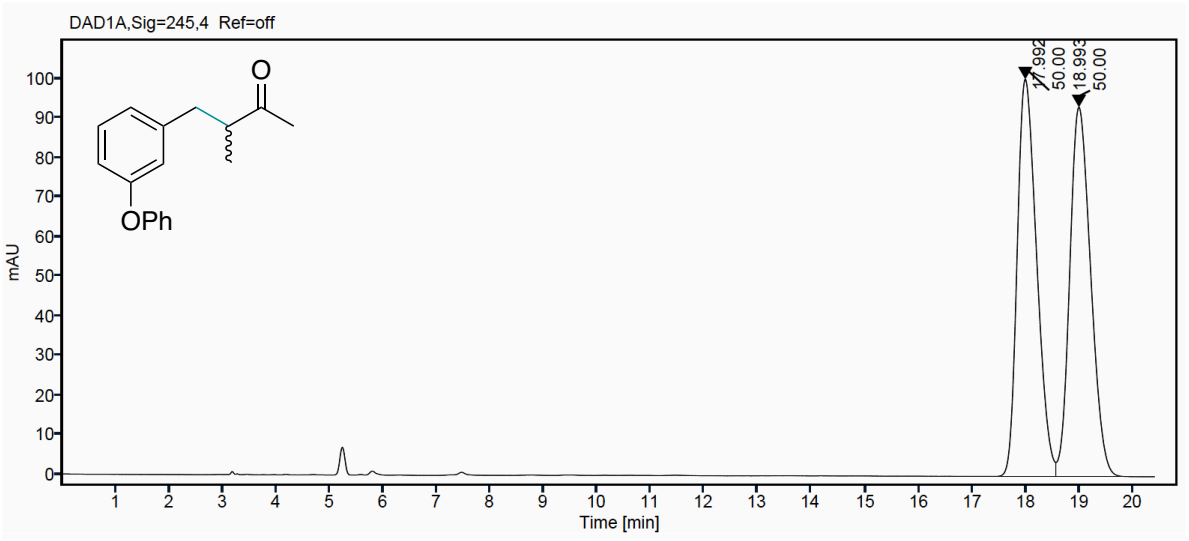
Signal: DAD1C,Sig=210,4 Ref=off

RT [min]	Area	Area%
15.289	21702.8687	49.7475
16.729	21923.1576	50.2525
Sum	43626.0263	



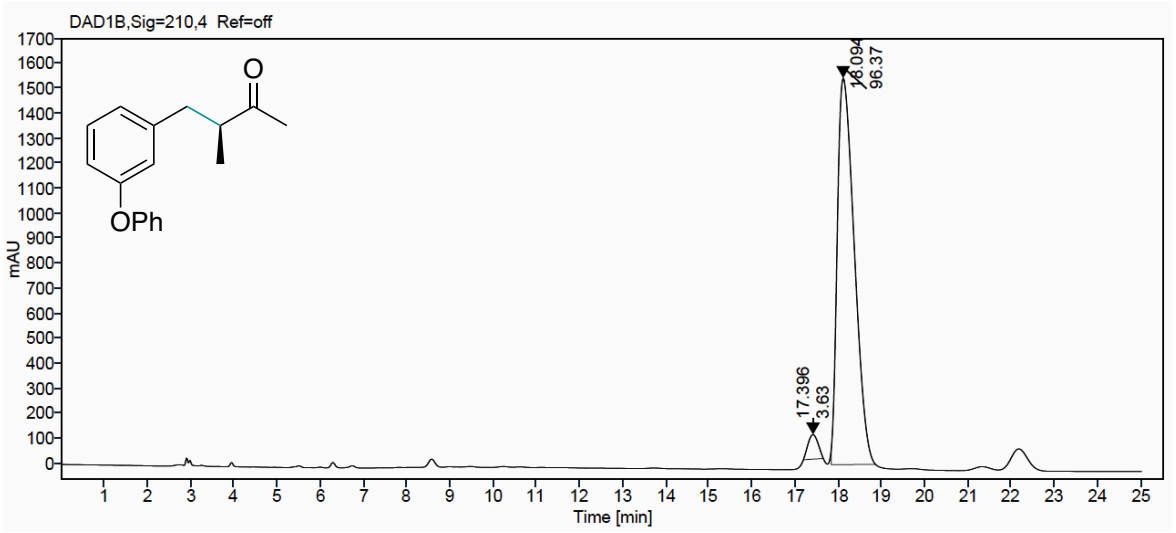
Signal: DAD1C,Sig=210,4 Ref=off

RT [min]	Area	Area%
15.288	1438.2339	7.3052
16.429	18249.6836	92.6948
Sum	19687.9176	



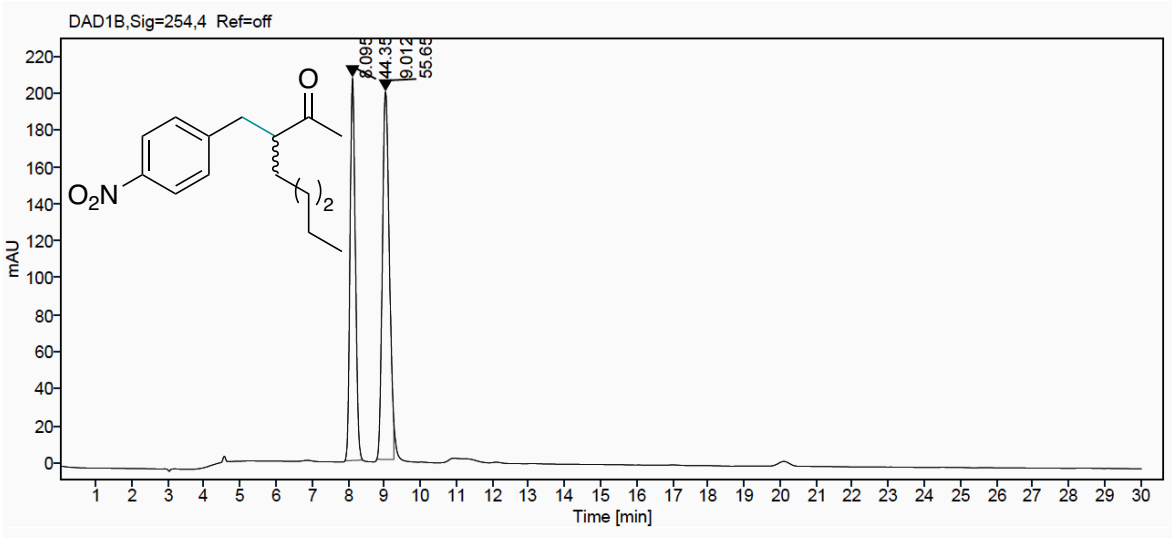
Signal: DAD1A,Sig=245,4 Ref=off

RT [min]	Area	Area%
17.992	2532.8344	50.0046
18.993	2532.3725	49.9954
Sum	5065.2069	



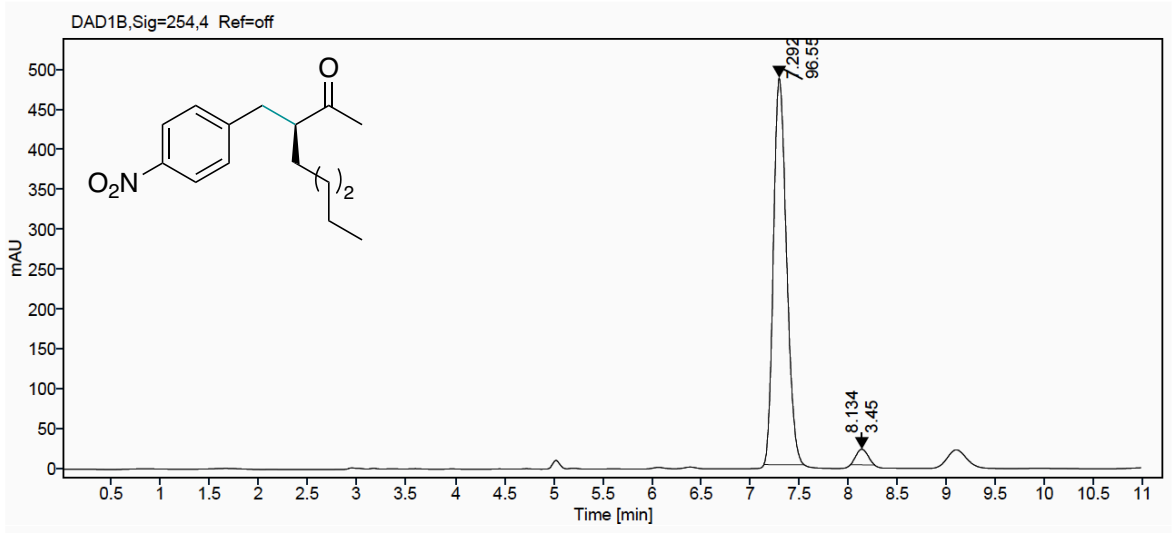
Signal: DAD1B,Sig=210,4 Ref=off

RT [min]	Area	Area%
17.396	1587.6900	3.6271
18.094	42185.2490	96.3729
Sum	43772.9390	



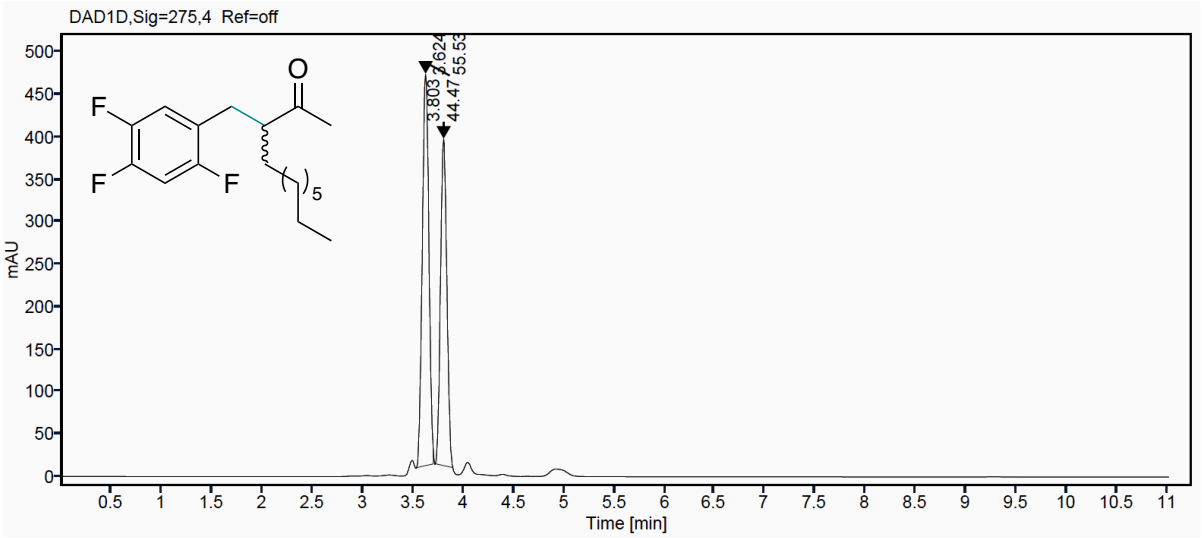
Signal: DAD1B,Sig=254,4 Ref=off

RT [min]	Area	Area%
8.095	2129.4370	44.3478
9.012	2672.2338	55.6522
Sum	4801.6709	



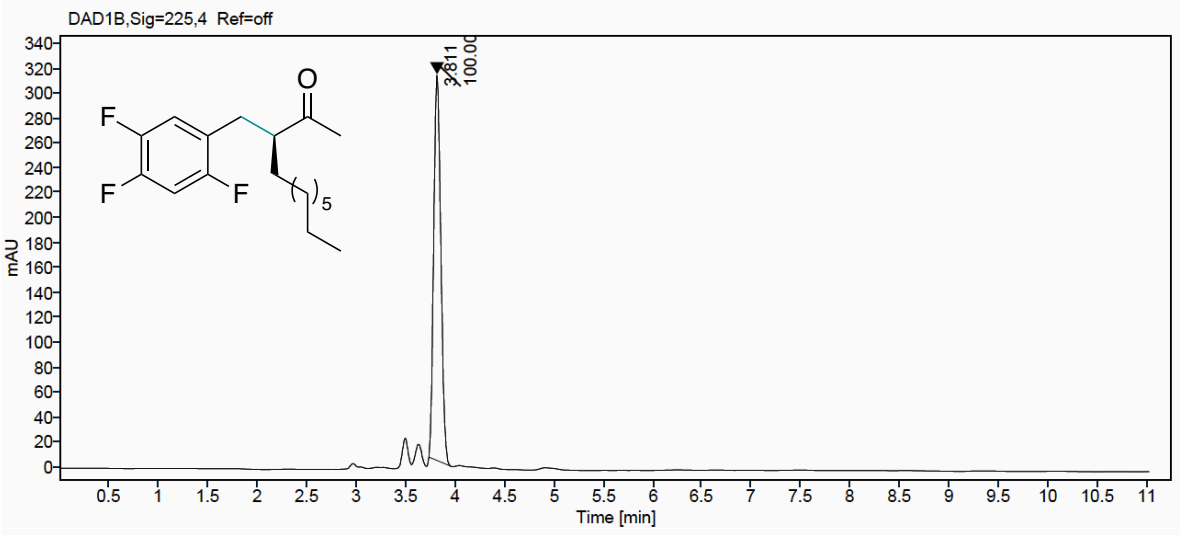
Signal: DAD1B,Sig=254,4 Ref=off

RT [min]	Area	Area%
7.292	4464.8899	96.5469
8.134	159.6927	3.4531
Sum	4624.5827	



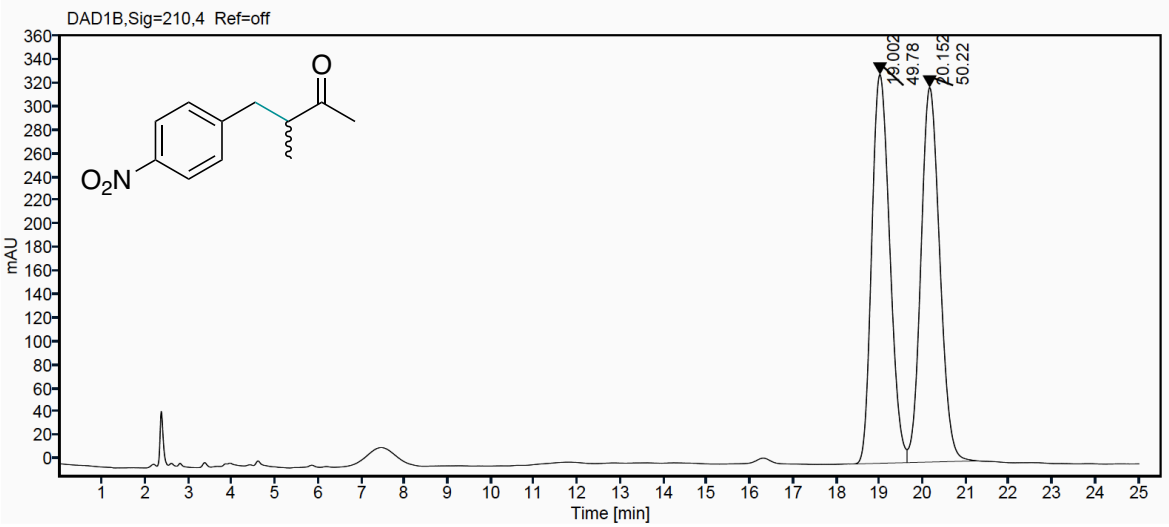
Signal: DAD1D,Sig=275,4 Ref=off

RT [min]	Area	Area%
3.624	2101.3499	55.5288
3.803	1682.9017	44.4712
Sum	3784.2516	



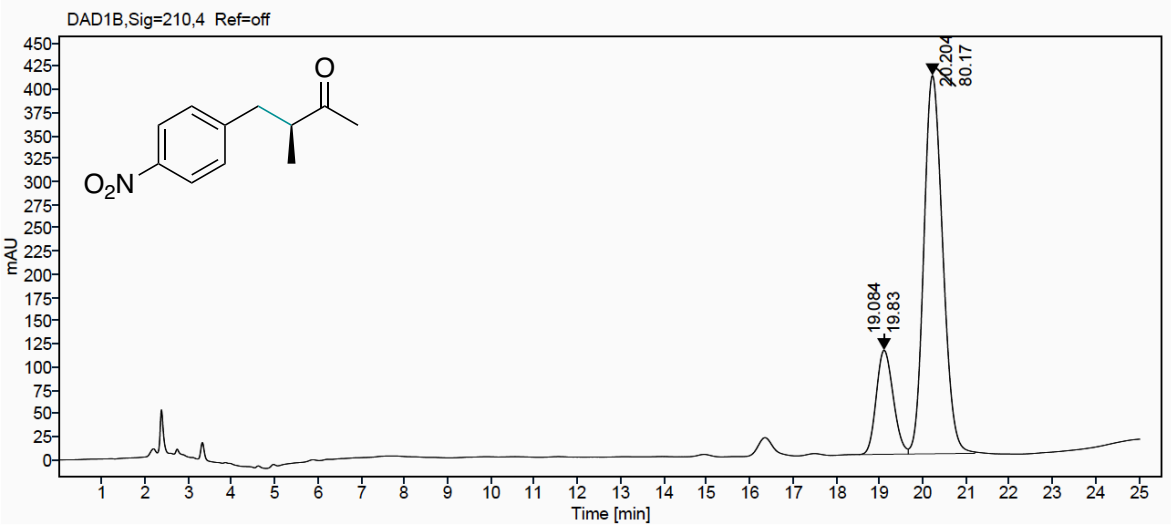
Signal: DAD1B,Sig=225,4 Ref=off

RT [min]	Area	Area%
3.811	1550.5153	100.0000
Sum	1550.5153	



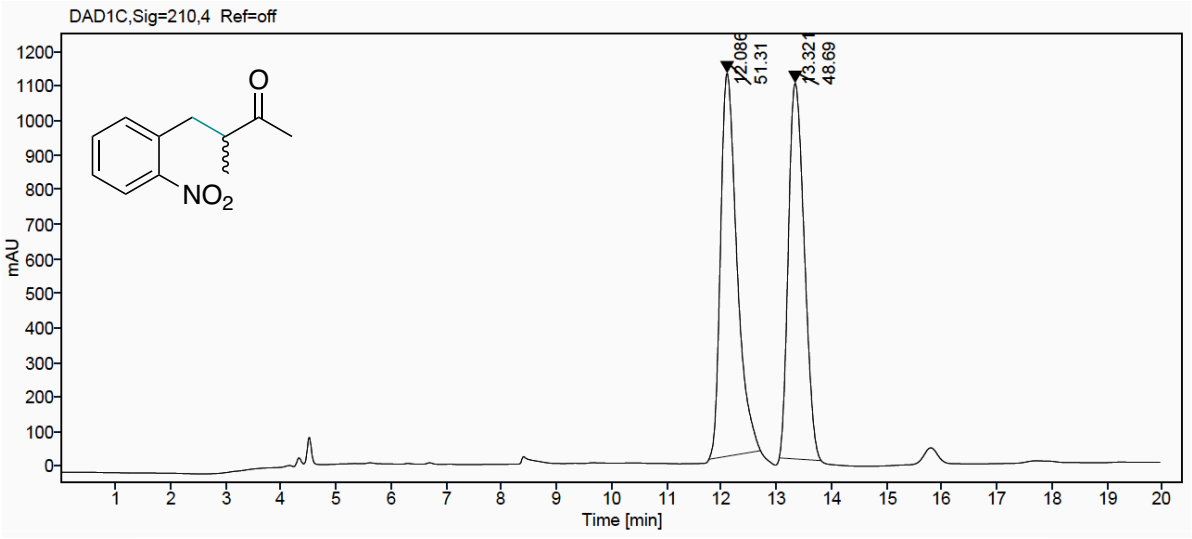
Signal: DAD1B,Sig=210,4 Ref=off

RT [min]	Area	Area%
19.002	9574.4207	49.7827
20.152	9658.0165	50.2173
Sum	19232.4372	



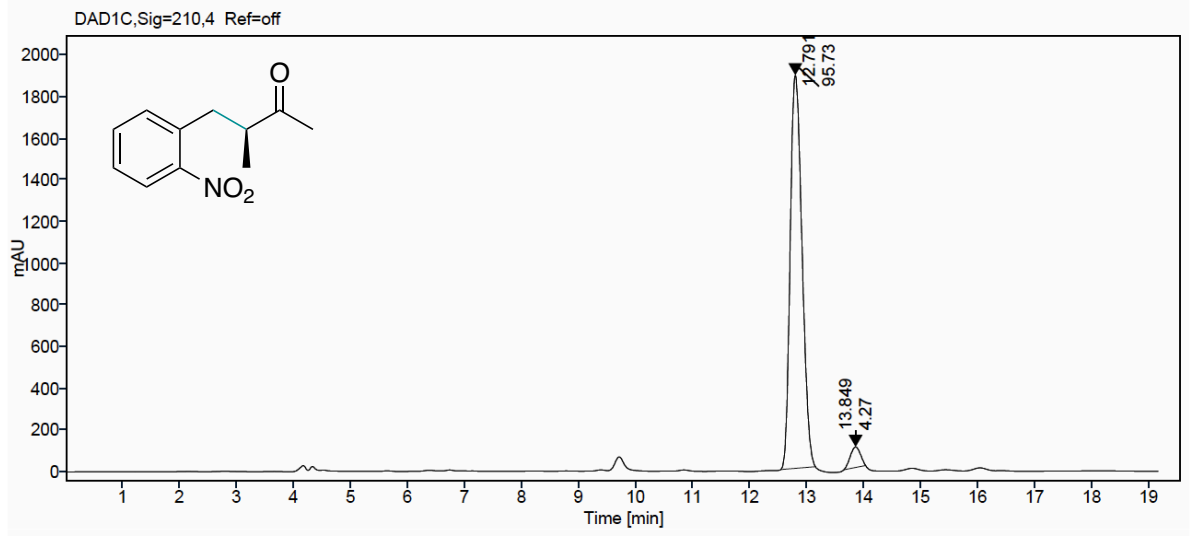
Signal: DAD1B,Sig=210,4 Ref=off

RT [min]	Area	Area%
19.084	3065.7096	19.8309
20.204	12393.5593	80.1691
Sum	15459.2689	



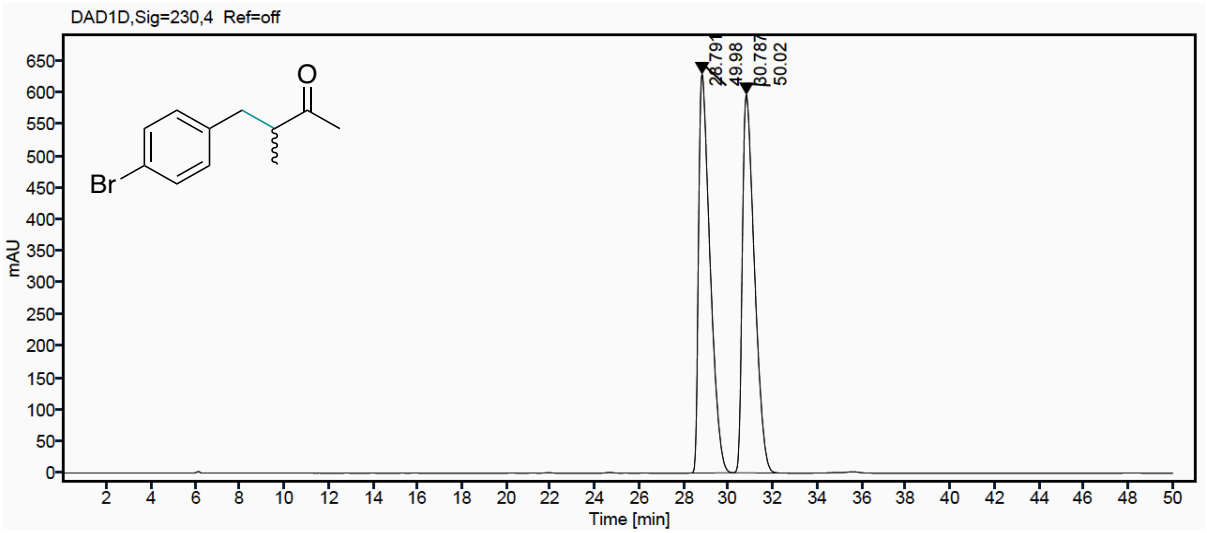
Signal: DAD1C,Sig=210,4 Ref=off

RT [min]	Area	Area%
12.086	22872.5599	51.3058
13.321	21708.2743	48.6942
Sum	44580.8343	



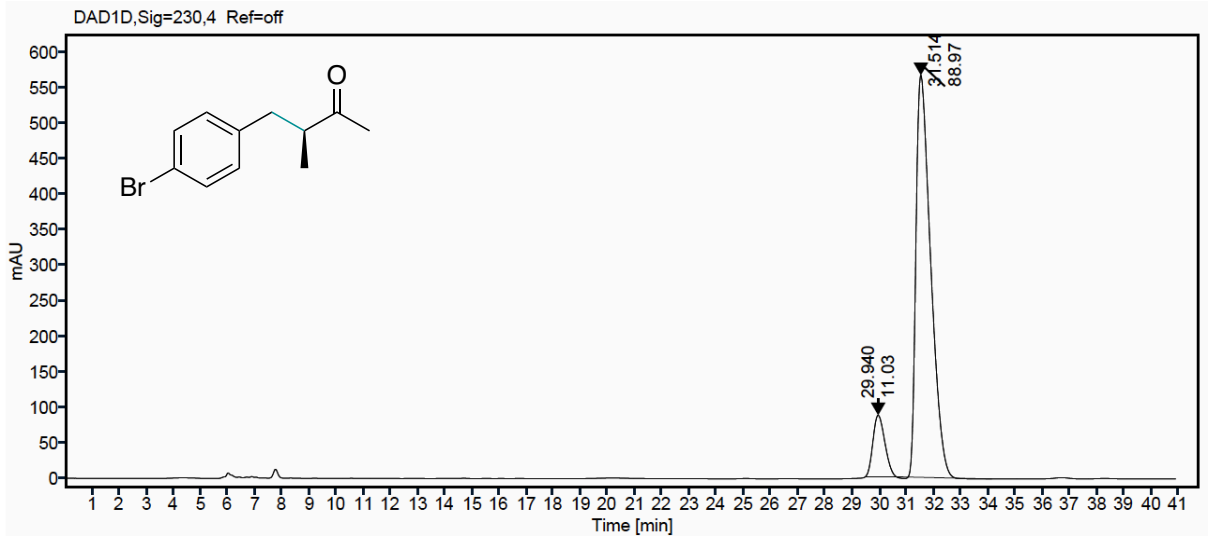
Signal: DAD1C,Sig=210,4 Ref=off

RT [min]	Area	Area%
12.791	27124.3557	95.7291
13.849	1210.1524	4.2709
Sum	28334.5082	



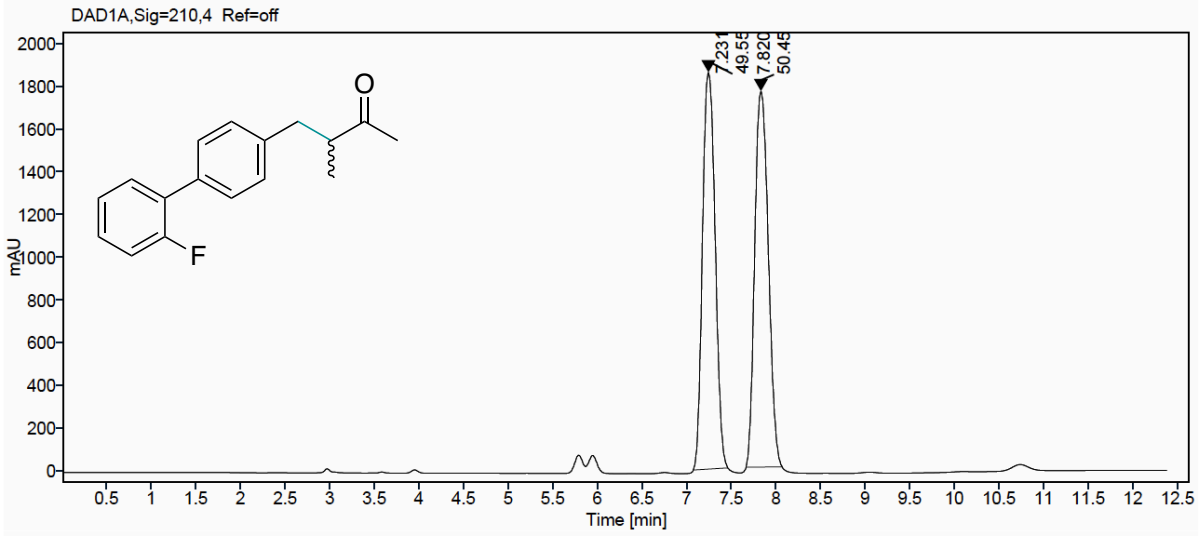
Signal: DAD1D,Sig=230,4 Ref=off

RT [min]	Area	Area%
28.791	22751.7105	49.9755
30.787	22774.0037	50.0245
Sum	45525.7142	



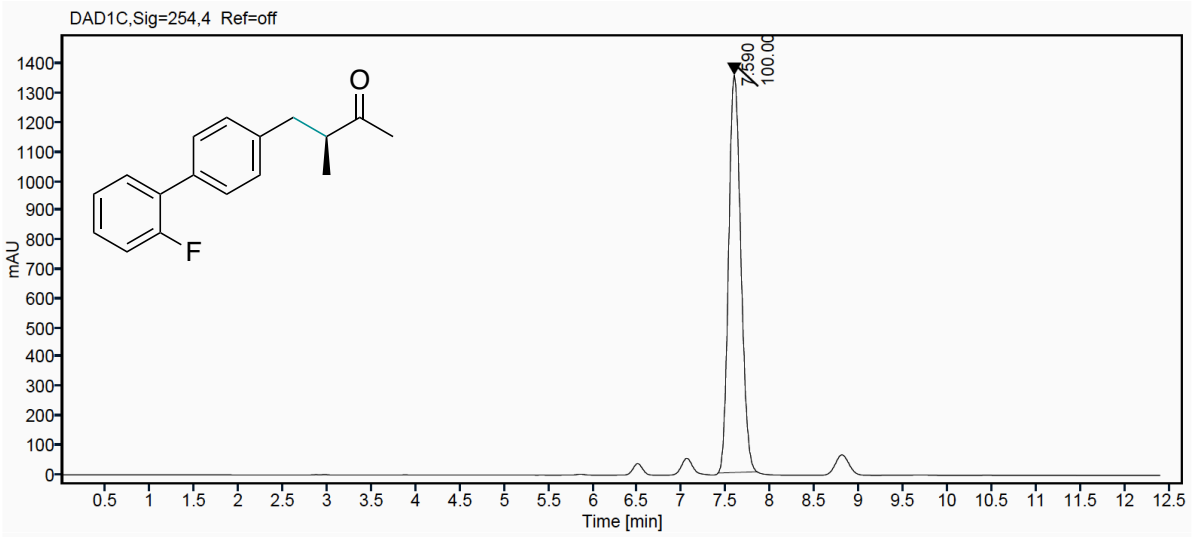
Signal: DAD1D,Sig=230,4 Ref=off

RT [min]	Area	Area%
29.940	2639.6488	11.0313
31.514	21289.1329	88.9687
Sum	23928.7818	



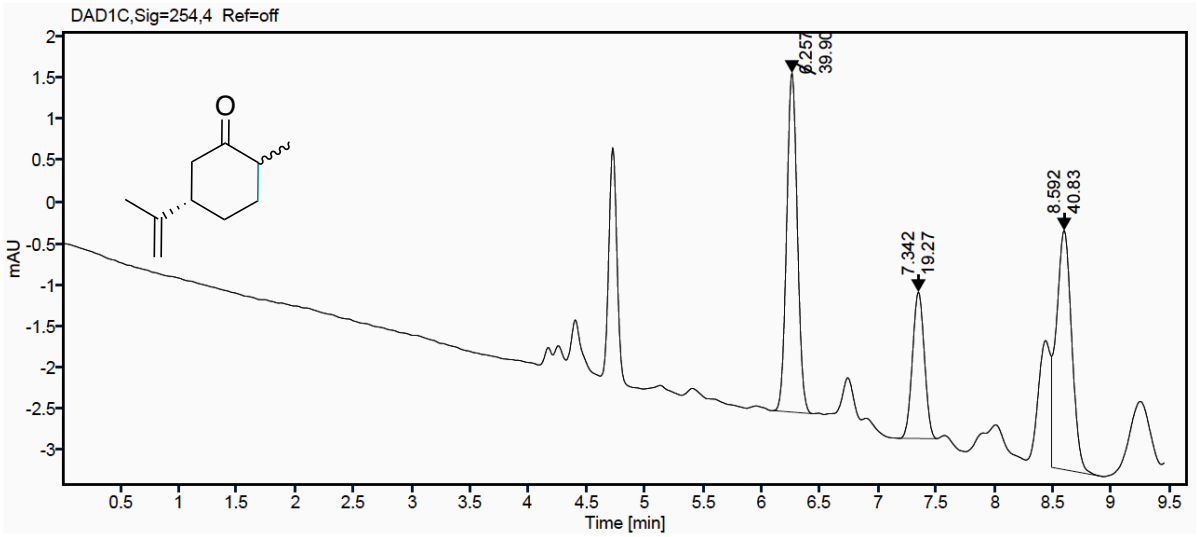
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
7.231	18289.8210	49.5458
7.820	18625.1391	50.4542
Sum	36914.9601	



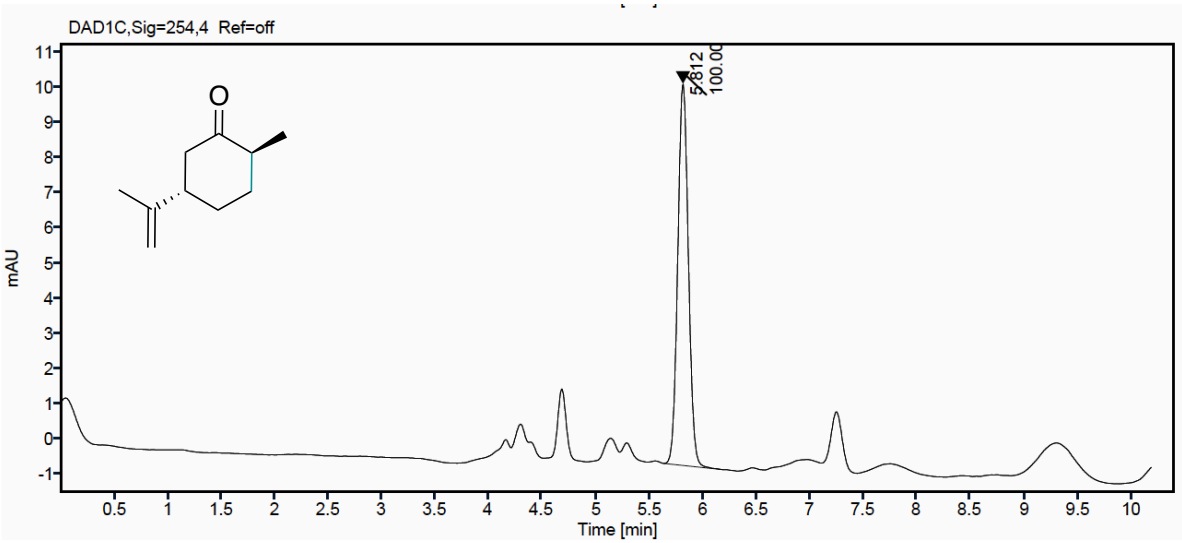
Signal: DAD1C,Sig=254,4 Ref=off

RT [min]	Area	Area%
7.590	12974.6033	100.0000
Sum	12974.6033	



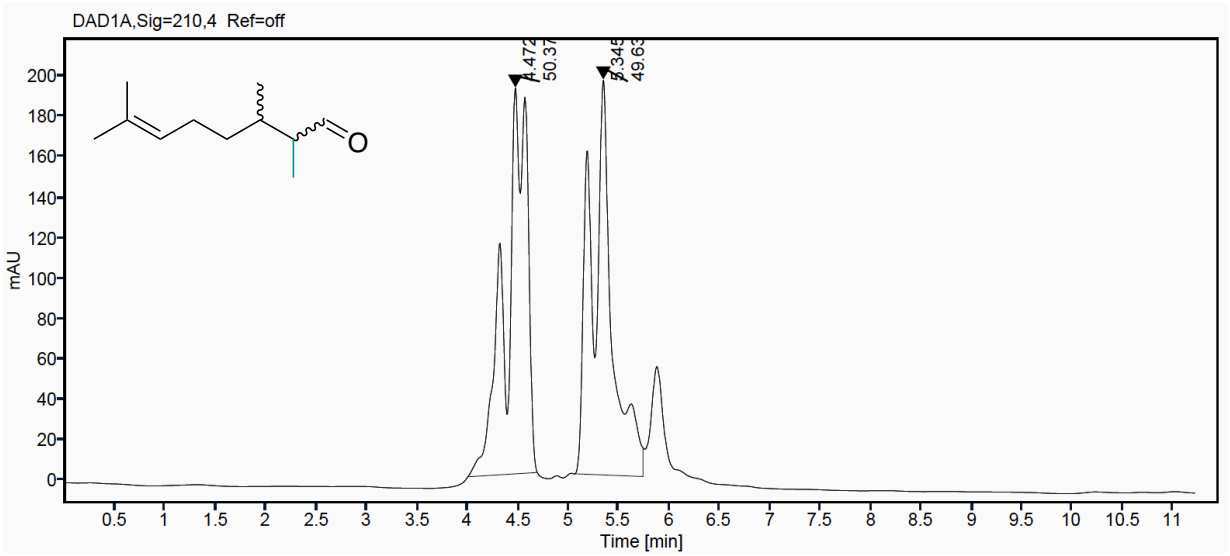
Signal: DAD1C,Sig=254,4 Ref=off

RT [min]	Area	Area%
6.257	26.2212	39.8977
7.342	12.6628	19.2675
8.592	26.8370	40.8347



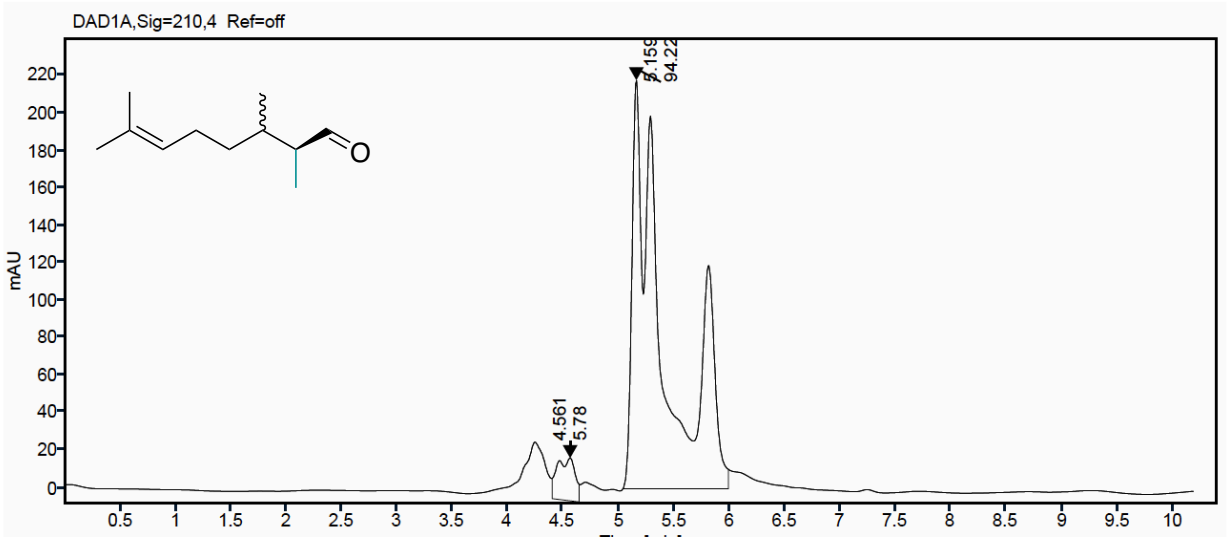
Signal: DAD1C,Sig=254,4 Ref=off

RT [min]	Area	Area%
5.812	74.7292	100.0000
Sum	74.7292	



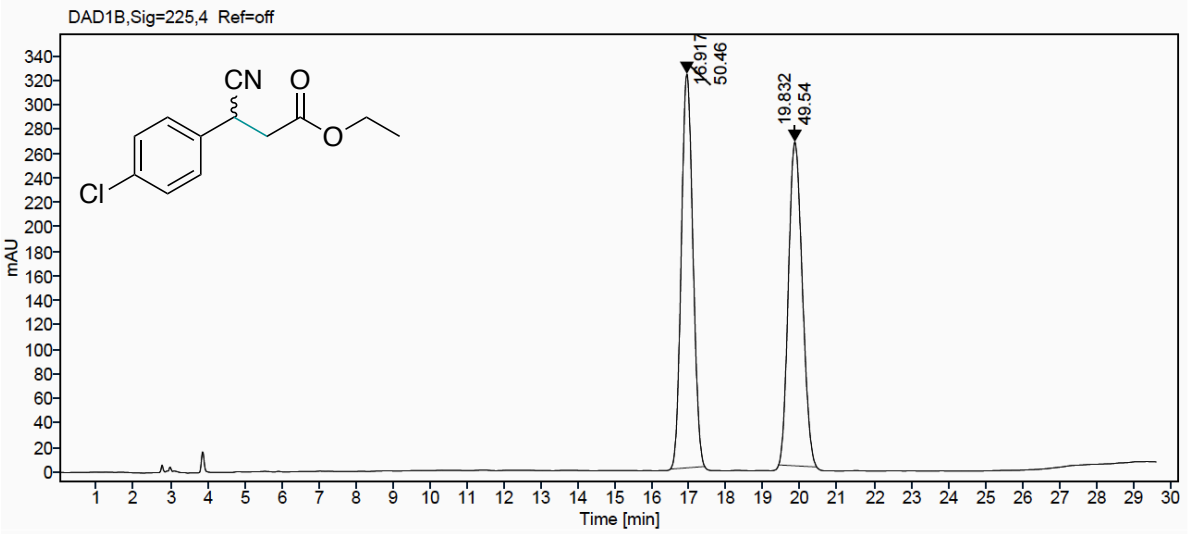
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
4.472	2839.6297	50.3694
5.345	2797.9750	49.6306
Sum	5637.6046	



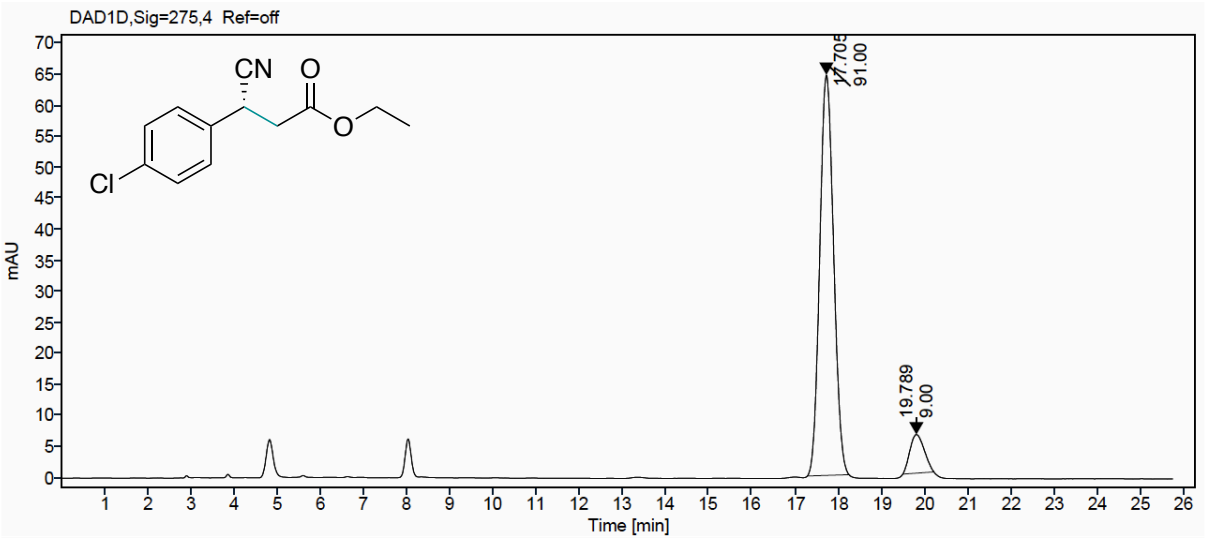
Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Area	Area%
4.561	255.3051	5.7777
5.159	4163.5316	94.2223
Sum	4418.8368	



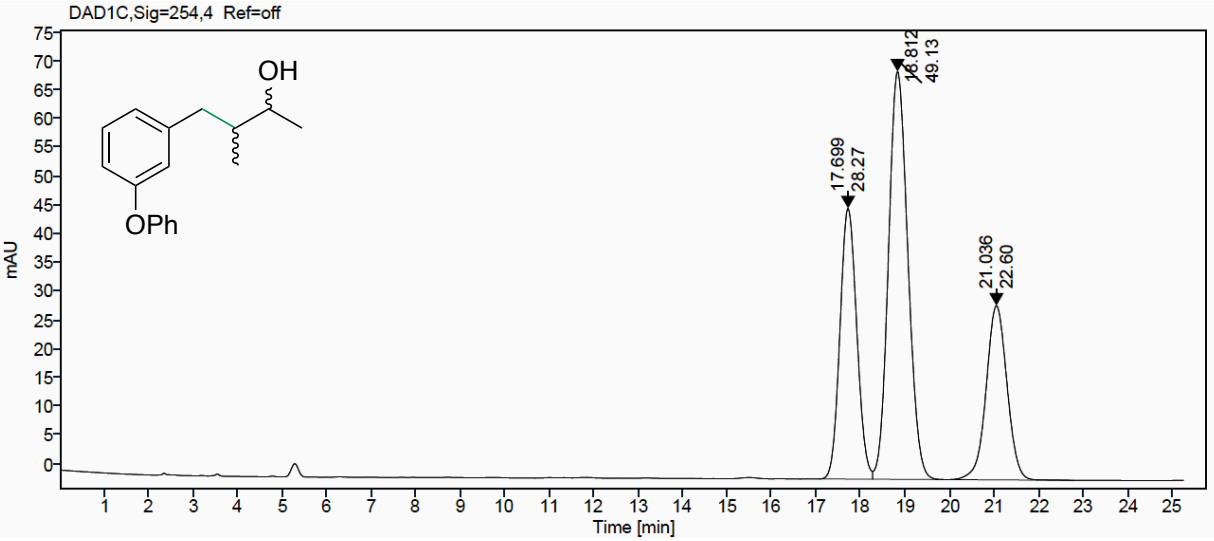
Signal: DAD1B,Sig=225,4 Ref=off

RT [min]	Area	Area%
16.917	6995.6657	50.4560
19.832	6869.2293	49.5440
Sum	13864.8950	



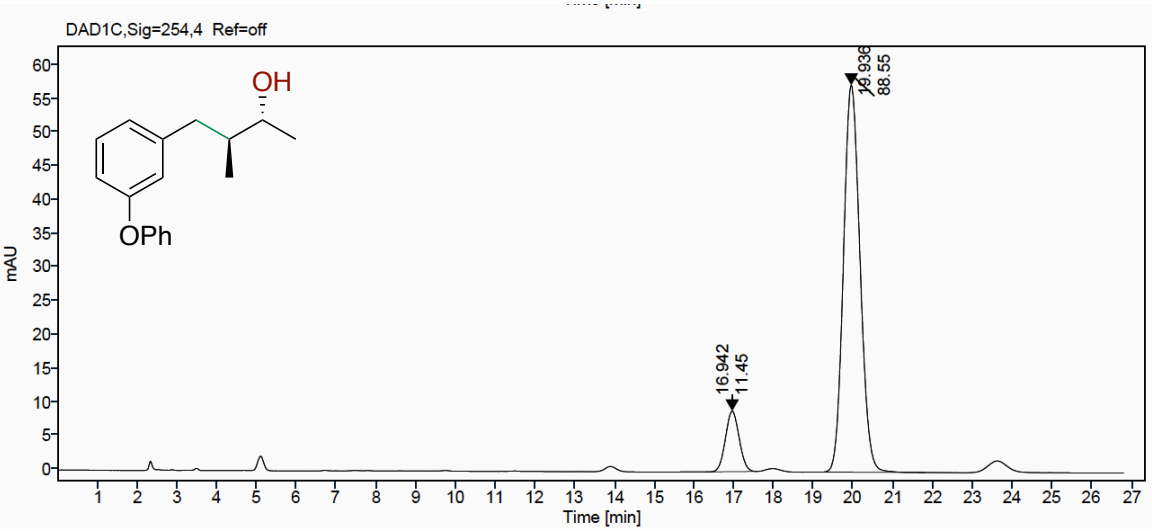
Signal: DAD1D,Sig=275,4 Ref=off

RT [min]	Area	Area%
17.705	1441.0306	91.0005
19.789	142.5111	8.9995
Sum	1583.5417	



Signal: DAD1C,Sig=254,4 Ref=off

RT [min]	Area	Area%
17.699	1235.8353	28.2703
18.812	2147.5742	49.1267
21.036	988.0926	22.6030
Sum	4371.5021	



Signal: DAD1C,Sig=254,4 Ref=off

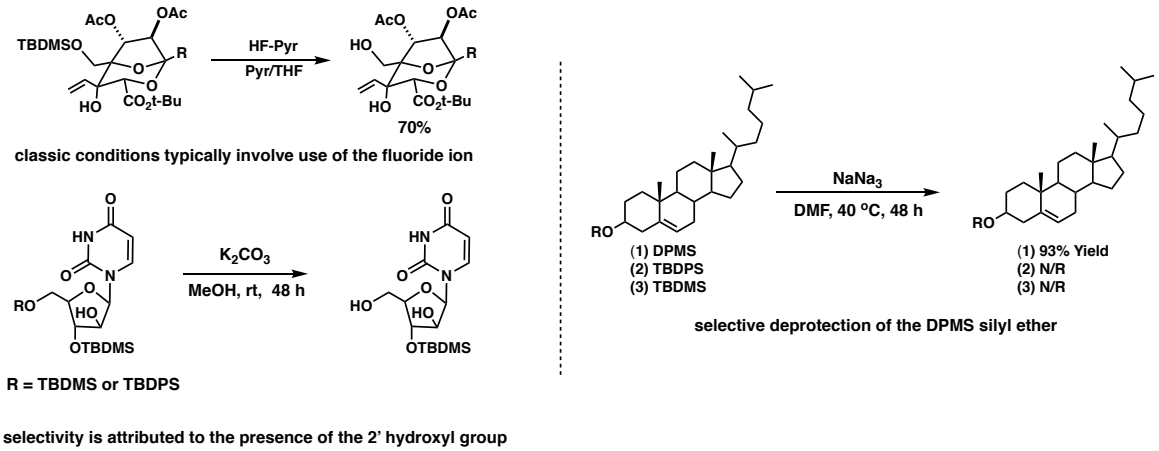
RT [min]	Area	Area%
16.942	214.6432	11.4496
19.936	1660.0353	88.5504
Sum	1874.6786	

III. Selective Deprotection of the Diphenylmethylsilyl (DPMS) Hydroxyl Protecting Group under Aqueous Conditions

3.1 Introduction and Background

Protecting group chemistry as used in organic synthesis has been developed to address myriad needs associated with synthetic transformations.[1] A silyl ether moiety is often employed for the protection of the alcohol functional group, among others. Its versatility is often attributed to its reactivity, chemoselectivity in its removal, as well as ease of use in synthesis. The group is typically characterized by a central silicon atom covalently bound to an alkoxy group and accompanied by alkyl or aryl groups on silicon. The aryl and alkyl groups proximal to the silicon contribute substantially to the nature of the silyl ether: by effecting both the steric and electronic nature of the Si-O-R bond, the desired ease of cleavage can be achieved as well as needed selectivity within a highly functionalized substrate. As with most other reactions within organic synthesis, deprotection protocols depend on organic solvents as the reaction medium[1] (Figure 1). Even hydrolysis reactions almost invariably involve organic co-solvents required for solubilization purposes, which, by definition, creates an immediate wastewater stream upon workup, aside from organic waste that is predominantly from the solvent.

Figure 1. Selected Examples of Traditional Silyl Ether Deprotection Conditions



As organic synthesis begins to expand into new technologies enabling some commonly utilized reactions to be run using nanoparticle technology in water,[2] this raises the question as to whether protecting groups are even required under such circumstances. However, until new technologies arise under which chemistry in water is operating,[3] protecting groups still have a useful place in synthetic chemistry. Thus, we sought to create new, environmentally friendly methodologies which employ the infrequently used diphenylmethylsilyl (DPMS) hydroxyl protecting group for selective deprotection.

Since the DPMS hydroxyl protecting group was introduced,[4] its use has been rather limited relative to other silyl ether derivatives. Unmasking by fluoride ion, similar to other silicon-based analogs, affords the corresponding free alcohol quickly in THF at room temperature in the presence of TBAF. Hence, while the protection step is high yielding, the selectivity of DPMS ether deprotection is usually a key factor that lies behind use of other more common silyl ethers (TMS, TBS, TIPS, TBDPS).[5-6] There is one report illustrating preferential removal of the DPMS residue achievable in the presence of TBS and TBDPS groups using $NaNa_3$ in warm DMF[7] (vide supra), a solvent to be avoided due to its hazardous nature. Under more

modern, greener, conditions and with newly discovered elements of selectivity to its credit, the DPMS protecting group could be valued addition to organic synthesis.

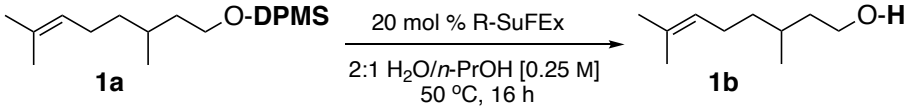
3.2 Results and Discussion

An initial observation revealed that cleavage of a DPMS-protected alcohol takes place upon exposure to catalytic amounts of benzylsulfonyl fluoride within a mixture of water and IPA (2:1) at 50 °C. Several additional sulfonyl fluorides were also screened in an alcohol/water mixture to evaluate each as alternatives for deprotection (Table 1). While the original Sharpless conditions employing SuFEx (sulfur(VI) fluoride exchange) reagents in click chemistry called for a 1:1 mixture of acetonitrile/water as reaction medium,[8] *n*-propanol was selected due to its relatively benign nature and lower cost relative to acetonitrile. Benzylsulfonyl fluoride (entry 2), as well as sulfonyl fluorides bearing electron-withdrawing groups, such as 4-nitrobenzenesulfonyl fluoride (entry 6), led to very efficient desilylation of model substrate **1a**. Another especially effective SuFEx reagent is perfluorobutanesulfonyl fluoride (entry 5). By contrast, the typical alkyl or aryl analogs (entries 1, 3, and 4) were either sluggish or gave little-to-no conversion after sixteen hours under otherwise identical conditions. From this study, perfluorobutanesulfonyl fluoride was chosen for its high reactivity as well as its substantially lower cost compared to its 4-nitrophenyl- or benzyl- analogs.

Notwithstanding the effectiveness of a SuFEx reagent to desilylate a DPMS ether, the main question surrounding selectivity remained. As illustrated in Tables 2a and 2b, the chemoselectivity associated with these deprotections, while unexpected, is noteworthy. Complete removal of the DPMS residue in **2a** could be achieved within four hours at a concentration of 0.25 M with virtually no deprotection of the TBS, TIPS, or TBDPS ethers (entries 2, 4 and 5) under identical reaction conditions (entry 3). As expected, the TMS ether

is especially labile and is hydrolyzed. Deprotections of other silyl ethers did eventually take place, requiring 72 hours to reach completion. Similar results were obtained in the case of allylic educt **4a**. On the other hand, phenolic DPMS ethers do not participate in this deprotection chemistry, perhaps adding to the selectivity of this method.[9] However, all types of silyl protected propargylic alcohols underwent facile deprotection upon treatment with SuFEx reagents.

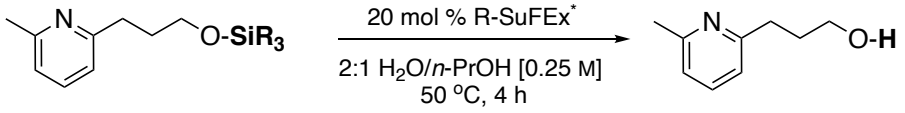
Table 1. Deprotection of citronellyldiphenylmethylsilyl ether 1a using sulfonyl fluorides



1a **1b**

Entry	R	Yield (%)[a]
1	*n*-C_4H_9-	0
2	$PhCH_2$-	86
3	Ph-	17
4	4-propylphenyl-	0
5	**perfluorobutyl-**	**94**
6	*4*-nitrophenyl-	90

Table 2a. Chemoselectivity of perfluorobutanesulfonyl fluoride towards alkyl silyl ethers

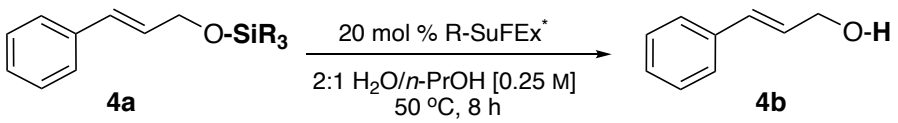


2a **2b**

Entry	silyl ether (SiR_3)	Yield (%)[a]
1	TMS	95
2	TIPS	0 (86)[b]
3	DPMS	91
4	TBS	0 (89)[b]
5	TBDPS	0 (84)[b]

[*R-SuFEx = *n*-$C_4F_9SO_2F$; [a] Isolated yields. [b] Isolated yields after 72 h. 0.5 mmol scale

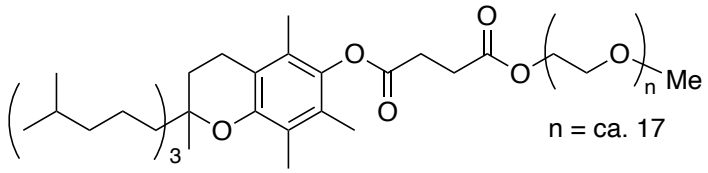
Table 2b. Chemoselectivity of perfluorobutanesulfonyl fluoride towards allylic silyl ethers



Entry	silyl ether (SiR_3)	Yield (%)[a]
1	TIPS	0
2	DPMS	83
3	TBS	trace

As part of our ongoing efforts to assist with the "switch" of organic synthesis from an organic solvent to a water-based discipline using nanoreactors derived from newly engineered and benign surfactants,[10] it has been found that fluoride ion is reluctant towards entering the hydrophobic micellar inner core, thereby all but eliminating the option to cleave silyl ethers in this manner "in water." This was attributed to the highly favorable status of hydrated fluoride ion, and hence, silyl ether cleavage appeared to require a "dry" source of this ion to be available in an aqueous micellar medium. This led us to examine a lipophilic SuFEx reagent in the presence of nanomicelles, where a water-stable sulfonyl fluoride might release fluoride in return for the oxygen in an alcohol, all taking place within the inner hydrophobic core of a micellar environment.[11] Hence, as an alternative set of reaction conditions, we investigated the effectiveness of a SuFEx reagent within micelles derived from TPGS-750-M (Figure 2).[12] Use of this surfactant medium may broaden the scope of substrates, in particular those with solubility and/or reactivity issues in water/alcohol mixtures.

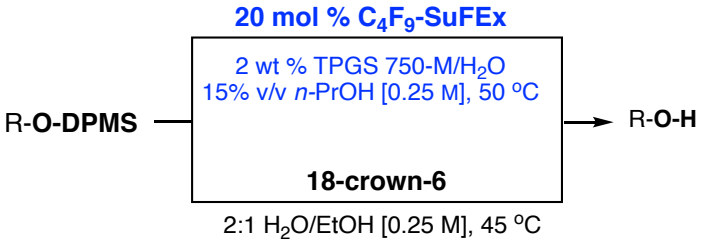
Figure 2. Structure of Designer Surfactant TPGS-750-M

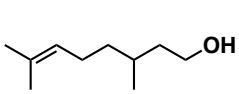


TPGS-750-M

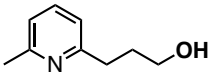
As shown in Scheme 1 (results in blue), various primary alcohols derived from DPMS ethers containing a wide variety of functional groups are amenable, leading to good-to-excellent yields of deprotected alcohols. These include nitro (**16b**), benzylic (**6b, 9b,10b**) propargylic (**5b**), allylic (**4b, 7b, 11b, 13b, 15b**) heteroaromatic (**2b, 9b, 16b**), and alkyl (**1-3b, 12b, 17-19b**). Notable cases include the tolerance exhibited by several basic nitrogen-containing educts affording product alcohols **2, 9, 14** and **16**, as well as an allylic cyclopropane leading to product **3**. Secondary alcohols were also deprotected, although there was a noticeable increase in reaction times, likely due to steric effects. Diol-containing substrates also exhibited selectivity towards the DPMS ether, as both TBS and TIPS ethers remained intact (**17-19b**). The case of product **20b** is especially noteworthy in that a DPMS derivative of a *secondary* alcohol is deprotected in the presence of a *primary* TBS ether. Aryl and silyl enol ethers were nonresponsive to these conditions (**21-23b**). Tertiary alcohols showed no reactivity whatsoever towards conversion to the corresponding free alcohols (**24b**). The Z-olefin-containing product **11** derived from the corresponding Z-silyl ether indicated, along with the examples cited above, that an explanation for the observed selectivity may not be based simply on the presence of adventitious acid.

Scheme 1. Scope of DPMS ether deprotection

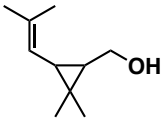




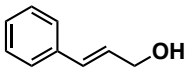
1b
12 h 88%
2.5 h 91%



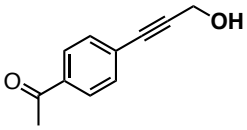
2b
6 h 94%
3 h 90%[a]



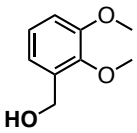
3b
16 h 94%
3 h 94%



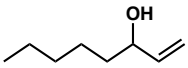
4b
8 h 93 %
2 h 85%[a]



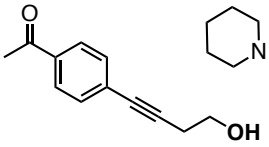
5b
12 h 79%
6 h 88%



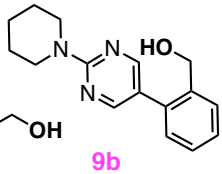
6b
12 h 83%
2.5 h 93%



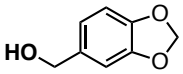
7b
36 h 68%
22 h 75%



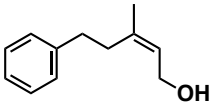
8b
12 h 79%
4 h 93%



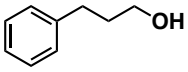
9b
14 h 89%
8 h 86%



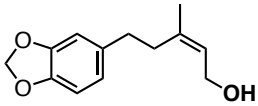
10b
12 h 92 %
1 h 83%[a]



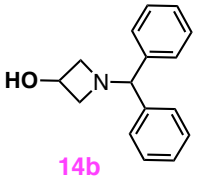
11b
16 h 86%
3 h 92%[a]



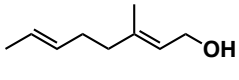
12b
14 h 89%
2.5 h 94%



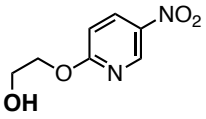
13b
16 h 90%
4 h 92%



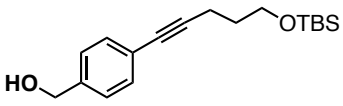
14b
24 h 80%
20 h 78%



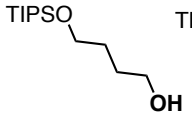
15b
6 h 85%
3 h 91%



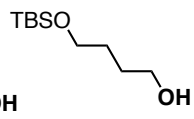
16b
5 h 86%
6 h 79%



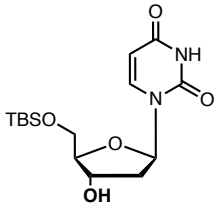
17b
16 h 71%
8 h 80%



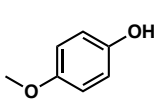
18b
12 h 82%
3 h 89%



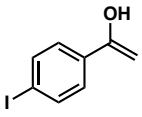
19b
12 h 90 %
3 h 86%



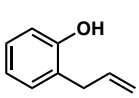
20b
10 h 86%
8 h 81%



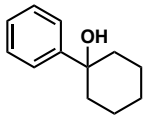
21b
24 h N/R
24 h trace



22b
24 h N/R
24 h N/R



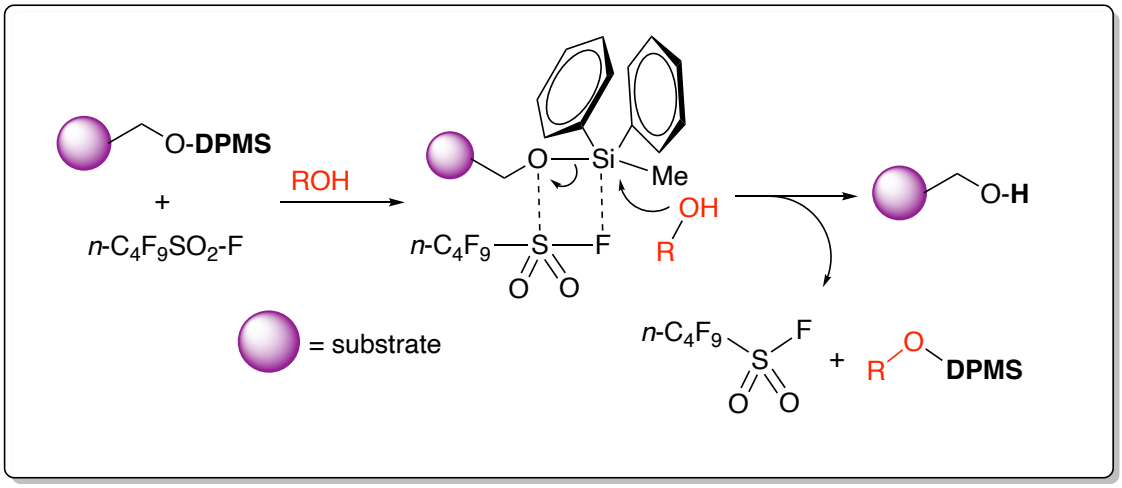
23b
24 h N/R
24 h trace



24b
24 h N/R
24 h N/R

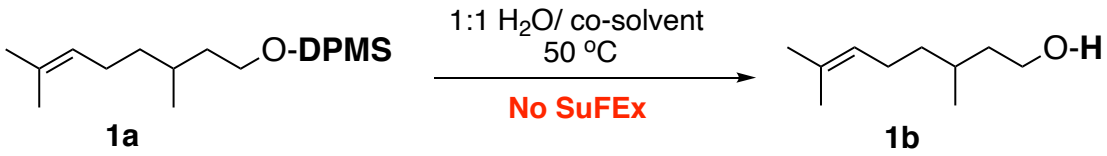
A number of mechanisms have been proposed in the literature to account for cleavage of silyl ethers.[13] Both steric and electronic effects at silicon have been studied, and it has been determined that the substitution around this atom plays a crucial role in determining the reactivity and mechanistic pathways followed.[14-15] While fluoride ion is typically crucial in chemoselective deprotections of silyl ethers,[16-17] in this case it is unlikely to be acting as the active species as the sulfonyl fluoride can be reclaimed intact upon completion of the reaction. Krutak described decades ago the remarkable stability of alkyl sulfonyl fluorides under aqueous conditions in their generation and subsequent use of SuFEx derivatives.[18] They showed that the weak reactivity of the -SO_2F moiety tolerates a wide array of reaction conditions. Sulfonyl fluorides have also been known to possess high reactivity towards silicon under basic conditions, as Gembus has described in the interconversion of silyl ethers to tosylates.[19] With respect to selective deprotection of DPMS ethers, a similar mechanism as described by Gembus may be operating here (Scheme 2). Thus, the sulfonyl fluoride is acting as both a strong Lewis acid and weak Lewis base, coordinating to the silicon-oxygen bond in a Negishi-like 2+2 fashion. This, in turn, leads to a more electrophilic silicon, susceptible to nucleophilic attack by alcohol at a far greater rate than that of other trisubstituted silyl groups.

Scheme 2. Proposed Mechanism for SuFEx-catalyzed deprotection



The electron-poor nature of the DPMS ether, which may account for its susceptibility, in general, leads to the free alcohol along with the intact sulfonyl fluoride for further use. While evaluating the effectiveness of a variety of water/solvent mixtures for deprotections of DPMS ethers, we serendipitously came across the ability of crown ethers to affect the same cleavage of the Si-O bond in the total absence of a SuFEx reagent. In again testing model substrate **1a**, complete deprotection occurred after only 1.5 hours at 50 °C when using a 1:1 mixture of water and 18-crown-6 (Table 3). Crown ether-like solvents (e.g., PEG 200 or 400; entries 2, 3) were notably ineffective. Smaller crown ethers (entries 4, 5) afforded the desired free alcohol **2**, albeit at a slower rate. Several solvents alone (entries 7-9) led to recovery of starting material. Further evaluation of **1a** (Table 4) indicated that the amount of 18-crown-6 was pivotal.

Table 3. Screening Various Co-solvents and Crown Ethers

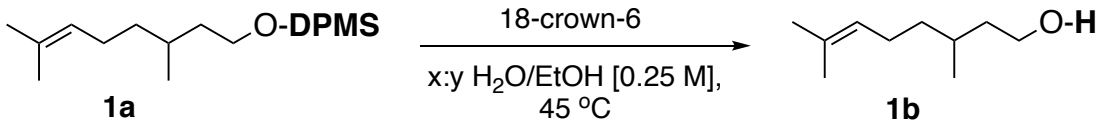


1a **1b**

entry	co-solvent	time (h)	yield (%)
1	none	24	0
2	PEG 200	24	0
3	PEG 400	24	0
4	12-crown-4	24	71
5	15-crown-5	24	56
6	**18-crown-6**	**1.5**	**97**
7	*t*-butanol	24	0
8	*n*-propanol	24	0
9	ethanol	24	0

Upon introduction of a co-solvent, in this case ethanol in a 2:1 ratio to water (with 5 equiv of crown ether present), rates of reactions increased significantly (e.g., entry 2 vs. entry 4). When a stoichiometric amount of crown was present in combination with a 2:1 ratio of water/ethanol, complete deprotection was observed in only four hours (entry 7). Further reducing the quantity of crown ether, however, increased reaction times, presumably due to a drop in the solubilizing properties of the reaction medium. The reaction appears to essentially stop when run at room temperature (entry 8).

Table 4. Preliminary Screening of 18-crown-6



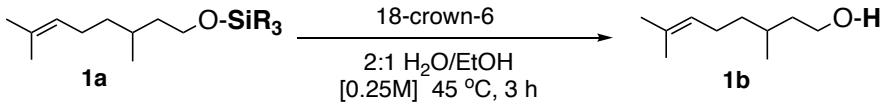
1a **1b**

entry	crown (equiv)	H_2O/EtOH (x:y)	T (°C)	time	yield (%)[a]
1	10	100:0	45	75 min	91
2	5	100:0	45	45 h	90
3	2	100:0	45	45 h	20
4	5	2:1	45	90 min	98
5	2	2:1	45	2 h	90
6	1	100:0	45	45 h	18
7	**1**	**2:1**	**45**	**4 h**	**94**
8	1	2:1	25	16 h	5
9	0.5	2:1	45	26 h	90
10	0.2	2:1	45	16 h	6

[a] Isolated yields; 0.5 mmol scale.

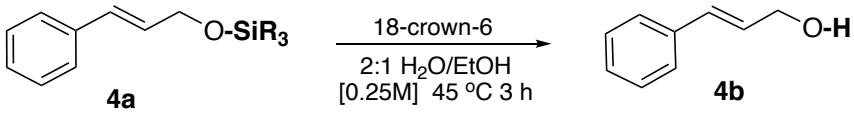
The observed selectivity under these crown ether conditions was similar to that observed using the SuFEx reagent (Table 5a, 5b). Alkyl and allylic DPMS ethers are cleaved preferentially over their TBS, TIPS, and TBDPS ether counterparts. After 24 h, the TIPS and TBDPS ethers remained untouched (Table 5a, entries 2 and 5; Table 5b, entries 1 and 3) while only minimal conversion was observed with the TBS ether (entry 4). These conditions, as noted previously, do not discriminate between the TMS and DPMS groups (entries 1 and 3). As with SuFEx conditions (vide supra), both aryl and enol silyl ethers are unreactive.

Table 5a. Selectivity for deprotection of an alkyl silyl ethers mediated by 18-crown-6



entry	silyl ether (SiR_3)	yield (%)[a]
1	TMS	92
2	TIPS	0 (0)[b]
3	DPMS	89
4	TBS	0 (5)[b]
5	TBDPS	0 (0)[b]

Table 5b. Selectivity for deprotection an allylic silyl ether mediated by 18-crown-6



entry	silyl ether (SiR_3)	yield (%)[a]
1	TIPS	0
2	DPMS	90
3	TBS	trace

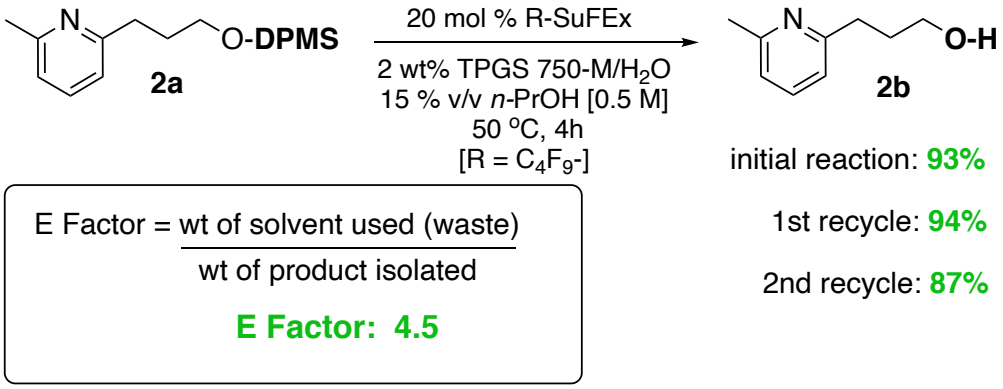
As shown by the examples in Scheme 1 (results in black), 18-crown-6 ether is equally as effective as the SuFEx reagent for DPMS ether deprotections. These comparisons also revealed that the former leads to faster rates of Si-O bond cleavage, at even somewhat lower temperatures.

Use of a primary alcohol as co-solvent proved crucial for this selective chemistry. When co-solvents such as THF or EtOAc were examined, minimal conversion was observed after 24 hours suggesting that the alcohol may play a role in these reactions. Our surfactant technology

was incompatible with 18-crown-6, as its presence in the medium led to significantly slower reactions. This may be due to the hydrophilic nature of 18-crown-6, in which case it prefers to remain in the aqueous phase while the substrate would prefer the inner micellar lipophilic core. 18-Crown-6 is known to accelerate various substitution reactions.[20] Silyl migration from one hydroxyl function to another is a phenomenon described by Friesen, where migration was observed upon treatment of a *tris*-silylated aryl glucal with base.[21] In our case, the crown ether may be acting as a mediator for the silyl migration of the DPMS ether to the more readily available alkanol in solution. The possibility for trace acid being responsible for this selective deprotection was ruled out based on data from Davies, comparing rates of acid-catalyzed hydrolysis of varying silyl ethers. It was noted that all silyl ethers tested (TMS, TBS, DPMS, TIPS, and TBSPS) hydrolyzed in a 1% HCl/MeOH media.[22] However, pH measurements indicated that the reaction medium involved (pH ~5) in these selective deprotections is *not* acidic enough to facilitate a standard acid-catalyzed deprotection.

Recycling of the aqueous TPGS-750-M-containing reaction mixture is readily achieved by an in-flask extraction with minimal amounts of MTBE as the extraction solvent (Scheme 4). However, due to the lipophilic nature of the SuFEx catalyst, re-addition of the sulfonyl fluoride (20 mol %) is required with each recycle. The yields and reaction times of the two recycles did not vary significantly, while the E Factor[23-24] (based on organic solvent used), as a measure of waste produced relative to the amount of product obtained, remained relatively low, especially when compared to other deprotection protocols in the literature.

Scheme 4. E Factor determination and recycling studies



3.3 Conclusion

In summary, two new methods for deprotection of primary and secondary alkyl DPMS ethers have been uncovered, where chemistry in water appears to be responsible for the unexpected chemoselectivities observed. Either catalytic amounts of perfluorobutanesulfonyl fluoride (*n*-$C_4F_9SO_2F$), or a stoichiometric amount of 18-crown-6 ether, can be used for these purposes. Both methods are technically straightforward, offer a recyclable and safe aqueous medium, and rely on reagents that are items of commerce. The precise role of 18-crown-6, in particular, awaits further elucidation. Nonetheless, an eventual understanding of exactly how both a SuFEx reagent and crown ether facilitate the highly selective deprotection of DPMS ethers may lead to related additional, environmentally responsible chemistry in water waiting to be discovered.

3.4 References

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9. It is appreciated that other, alternative mechanisms exist, e.g., involving displacement of the DPMS-O group by water. However, this was shown to be unlikely, as studies with $^{18}OH_2$ led to no incorporation of ^{18}O into the product alcohol.

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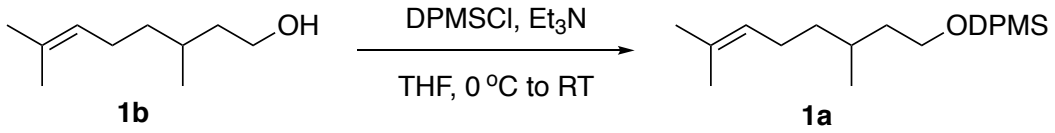
3.5 Experimental Data

1. General Information

A solution of 2 wt % TPGS-750-M/H_2O was prepared by dissolving TPGS-750-M in degassed HPLC grade water from Fisher Chemical. The resulting solution is stored under argon. The synthesis of TPGS-750-M has been described previously in detail and is available from Sigma-Aldrich (catalog #763896 (wax)). 18-Crown-6 is commercially available from Sigma-Aldrich (catalog #186651). Perfluoro-1-butanesulfonyl fluoride is also commercially available from Sigma-Aldrich (catalog #319732). Certified Grade 1-propanol was purchased from Fisher Chemical. All commercially available starting alcohols were purchased from Sigma-Aldrich or Fisher Chemical. They were used without further purification.

Silica Gel 60 F254 plates (Merck, 0.25nm) were used for thin layer chromatography (TLC). Flash chromatography was done with either an Isolera™ One 3.0 Biotage or a standard glass column using Silica Gel 60 (EMD, 40-63 μm). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on either a Varian Unity Inova 500 MHz or a Varian Unity Inova 600 MHz spectrometer in $CDCl_3$ with residual $CHCl_3$ (^{1}H = 7.26 ppm, ^{13}C = 77.16 ppm) as internal standard. Chemical shifts are reported in parts per million (ppm). The data presented will be reported as follows; chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (if applicable) and integration. HRMS data were recorded on a Waters Micromass LCT TOF ES+ Premier mass spectrometer using ESI ionization.

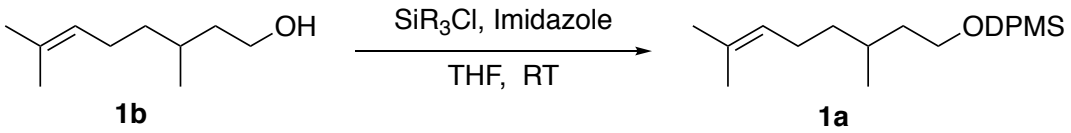
2. General Procedure for the protection of DPMS ethers



1b **1a**

All of the alcohols were protected using a modified literature procedure[2]. A round bottom flask under argon was charged with diphenylmethylchlorosilane to which THF was added. The resulting mixture was cooled to 0 °C. Triethylamine was added to the flask followed by a slow addition of a solution of the alcohol in THF over a period of 3 min, resulting in a heterogeneous mixture. The reaction was allowed to warm to rt. The reaction progress was monitored by TLC, and upon completion (3-12 h) the reaction solvent was evaporated under reduced pressure. The resulting crude mixture was diluted with ethyl ether and water. The aqueous layer was extracted with ethyl ether and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography.

3. General Procedure for the protection of various SiR_3 Ethers



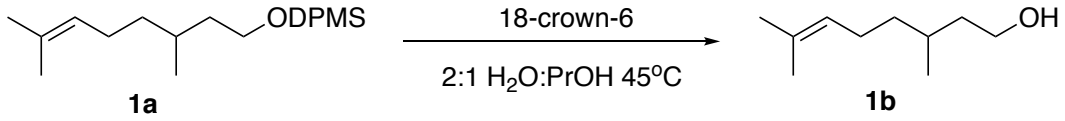
1b **1a**

All other silyl ethers screened for selectivity were synthesized using a modified literature procedure. A round bottom flask under argon was charged with silyl chloride to which was added THF. To the resulting mixture was added imidazole followed by a solution of the alcohol in THF over a period of 3 min, resulting in a heterogeneous mixture. The reaction progress

[2] *J. Org. Chem.* ***2013,*** *9, 2620.*

was monitored by TLC, and upon completion (1-6 h) the reaction solvent was evaporated under reduced pressure. The resulting crude mixture was diluted with ethyl ether and water. The aqueous layer was extracted with ethyl ether and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (10% Et_2O in hexanes).

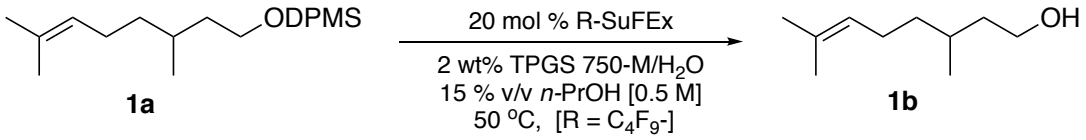
4. Utilization of 18-crown-6 for DPMS Ether Deprotections



1a **1b**

To a reaction vial equipped with a magnetic stir bar was added 18-crown-6 (53 mg, 0.20 mmol, 1.00 equiv). To this was added ethanol (0.27 mL) and HPLC water (0.53 mL) for a final concentration of 0.25 M. The mixture was stirred at 45 °C giving a clear, homogeneous solution. To this was added **1a** (70.5 mg, 0.20 mmol, 1.00 equiv) dropwise *via* microliter syringe, resulting in a heterogeneous mixture. The reaction progress was monitored by TLC, and upon complete consumption of starting material the vial was brought to rt, then diluted with ethyl ether (2.00 mL). This was shaken and allowed to separate, and the organic layer removed via pipet and filtered over a pad of anhydrous Na_2SO_4 into a round bottom flask. This extraction was repeated an additional two times, and the combined organics were concentrated *in vacuo* to give a crude oil. This was purified by column chromatography (25% diethyl ether in hexanes) to give the pure product.

5. Utilization of Perfluoro-1-butanesulfonylfluoride for DPMS Ether Deprotections



To a reaction vial equipped with a magnetic stir bar was added the DPMS ether (0.20 mmol 1 equiv). To this was added a solution of 2 wt % TPGS 750-M/ H_2O (0.85 mL) and propanol (0.15 mL). Perfluoro-1-butanesulfonylfluoride (12.1mg, 0.04 mmol, 0.20 equiv) was added via microliter syringe resulting in a heterogeneous mixture. The reaction progress was monitored by TLC. Upon complete consumption of starting material (6-24 h), the reaction was allowed to cool to rt, then diluted with ethyl ether (2.0 mL). The vile was shaken and the solution was allowed to separate. This extraction was repeated an additional two times and the combined organics were concentrated *in vacuo* to give a crude oil. This was purified by column chromatography to give the pure product.

6. Recycle Study

The initial reaction was set up according to the general procedure (5) stated above. Upon completion of the reaction, the reaction mixture was extracted three times with MTBE in flask (0.6 mL total). The organic extractions were placed in a flask and reduced under pressure. The crude product was purified via a plug of silica with a mixture of EtOAc/hexanes to provide the desired product.

The surfactant solution was then charged with additional DPMS alcohol (0.25 mmol) and 10 mol % perfluoro-1-butanesufonylfluoride. The reaction was sealed and allowed to stir at 50 °C, according to the general procedure.

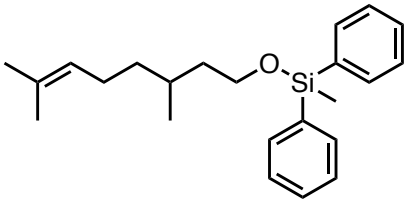
E Factor calculation:

Density of MTBE: 0.74/g/mL

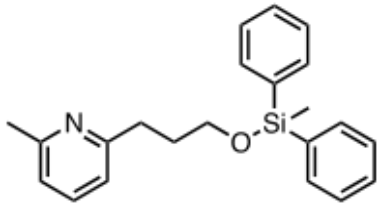
$$E\ Factor = \frac{Waste\ (mg)}{Product\ (mg)}$$

$$E\ Factor = \frac{(0.6mL\ of\ MTBE)\left(\frac{0.74g}{mL}\right)}{0.098g} = 4.5$$

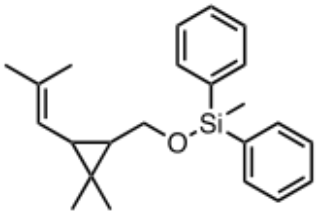
7. Analytical Data for Silyl Ether-protected Products



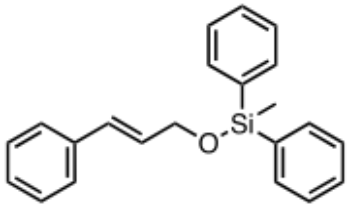
((3,7-Dimethyloct-6-en-1-yl)oxydiphenylmethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.59 (dd, 4H), 7.44-7.36 (m, 6H), 5.11-5.06 (m, 1H), 3.79-3.69 (m, 2H), 2.04-1.87 (m, 2H), 1.7 (s, 3H) 1.65-1.55 (m, 2H), 1.60 (s, 3H) 1.44-1.36 (m, 1H) 1.34-1.26 (m, 1H) 1.18-1.10 (m, 1H) 0.85 (d, *J* = 6.6 Hz 3H) 0.65 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 136.45, 134.47, 131.20, 129.86, 127.95, 125.00, 61.92, 39.79, 37.30, 29.25, 25.86, 25.59, 19.68, 17.78, -2.88. **Yield**: 89%, 4 h; colorless liquid. **R_f**: 0.80 (25% Et_2O in hexanes). **Chemical Formula**: $C_{23}H_{32}OSi$ EI-MS $[M^+]$ Calcd: 352.2222; found: 337.1988 $[M\text{-}CH_3]^+$



2-Methyl-6-(3-((diphenylmethylsilyl)oxy)propyl)pyridine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 4H), 7.47 – 7.36 (m, 7H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.87 – 2.82 (m, 2H), 2.52 (s, 3H), 2.05 – 1.98 (m, 2H), 0.65 (s, 3H).**^{13}C NMR (126 MHz, $CDCl_3$) δ** 161.32, 157.86, 136.57, 136.34, 134.49, 129.89, 127.96, 120.54, 119.70, 63.07, 34.90, 32.88, 24.69, -2.91. **Yield**: 91%, 4 h; brown oil. **R_f**: 0.34 (15% EtOAc/hexanes). **Chemical Formula:** $C_{22}H_{25}ONSi$ EI-MS $[M^+]$ Calcd: 347.1705; found: 347.1711

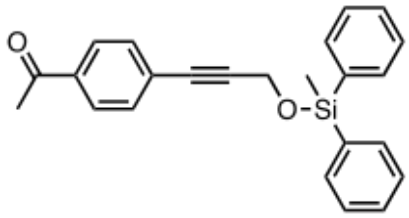


((2,2-Dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropyl)methoxy)diphenylmethylsilane: **^{1}H NMR** (**500 MHz, $CDCl_3$**) major isomer: **δ** 7.61 – 7.59 (m, 4H), 7.40 – 7.36 (m, 6H), 4.85 (ddq, *J* = 9.7, 7.1, 1.4 Hz, 2H), 3.89 (ddd, *J* = 11.2, 6.2, 1.4 Hz, 1H), 3.72 (ddd, *J* = 7.5, 4.0, 1.4 Hz, 1H), 3.63 (ddd, *J* = 11.2, 8.3, 1.3 Hz, 1H), 1.69 (d, *J* = 1.7 Hz, 3H), 1.64 (d, *J* = 1.3 Hz, 3H), 1.07 (d, *J* = 1.4 Hz, 3H), 1.01 (d, *J* = 1.3 Hz, 3H), 0.81 (ddd, *J* = 8.3, 4.2, 1.3 Hz, 1H), 0.64 (d, *J* = 1.4 Hz, 3H).**^{13}C NMR** **(126 MHz, $CDCl_3$**) mixture of isomers: 136.58, 134.66, 134.55, 134.53, 134.14, 132.84, 129.82, 129.80, 127.92, 127.87, 123.89, 119.58, 77.41, 77.16, 76.91, 64.38, 61.30, 34.99, 30.81, 28.95, 28.68, 26.31, 25.86, 25.78, 22.78, 22.45, 21.57, 18.61, 18.39, 15.62, -2.65, -2.71.**Yield**: 85%, 4 h; colorless oil. **R_f:** 0.65 (10% EtOAc/hexanes). **Chemical Formula**: $C_{23}H_{30}OSi$ EI-MS [M^+] Calcd: 350.2065; found: 350.2076.

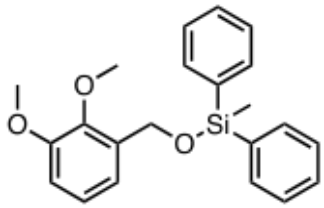


(Cinnamyloxy)diphenylmethylsilane: **^{1}H NMR** (**600 MHz, $CDCl_3$**) **δ** 7.64 – 7.62 (m, 4H), 7.43 – 7.41 (m, 2H), 7.40 – 7.38 (m, 4H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.22 (td, *J* = 7.0, 1.5 Hz, 1H), 6.58 (dd, *J* = 15.9, 1.8 Hz, 1H), 6.31 – 6.27 (m, 1H), 4.42 (dd, *J* = 5.5, 1.8 Hz, 2H), 0.69 (s, *J* = 1.5 Hz, 3H).**^{13}C NMR** **(151 MHz, $CDCl_3$**) **δ** 139.76, 138.65, 137.20, 133.09, 132.70, 131.29, 131.19, 130.71, 130.21, 129.23, 67.06, -0.00. **Yield**: 85%, 6

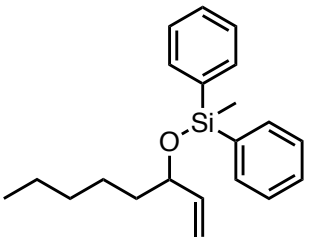
h; colorless oil. **R_f**: 0.33 (15%Et_2O/hexanes). **Chemical Formula**: $C_{22}H_{22}OSi$ EI-MS [M^+] Calcd: 330.1440; found: 330.1425.



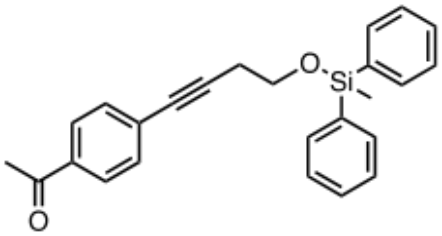
1-(4-(3-((Diphenylmethylsilyl)oxy)prop-1-yn-1-yl)phenyl)ethan-1-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.69 – 7.66 (m, 4H), 7.41 – 7.39 (m, 8H), 4.63 (s, 2H), 2.59 (s, 3H), 0.77 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 171.11, 137.19, 134.63, 134.13, , 131.84, 130.22, 130.04, 129.70, 128.38, 128.07, 127.86, 51.77, 26.77, -1.08. **Yield**: 69% 3 h; yellow oil. **R_f**: 0.65 (15 % EtOAc/hexanes). **Chemical Formula:** $C_{24}H_{22}O_2Si$ EI-MS [M^+] Calcd: 370.1389; found: 370.1384.



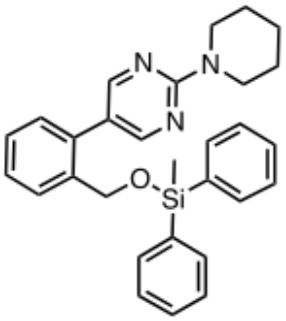
((2,3-Dimethoxybenzyl)oxy)diphenylmethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.61 (dd, 4H), 7.45-7.37 (m, 6H), 7.14-7.13 (d, 1H), 7.09-7.05 (t, 1H) 6.86-6.85 (d, 1H) 4.87 (s, 2H), 3.86 (s, 3H), 3.75 (s, 3H), 0.70 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 152.43, 136.11, 134.74, 134.54, 129.97, 129.16, 128.00, 124.07, 120.14, 111.53, 60.75, 60.65, 55.92, -2.86. **Yield**: 96% 4 h; colorless oil. **R_f**: 0.33 (15% Et_2O in hexanes). **Chemical Formula:** $C_{22}H_{24}O_3Si$ EI-MS [M^+] Calcd: 364.1494; found: 364.149



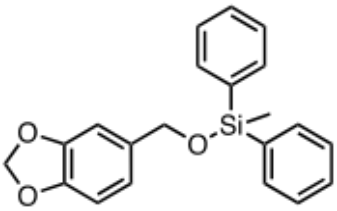
(Oct-1-en-3-yloxy)diphenylmethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (m, *J* = 6.7, 5.2, 1.5 Hz, 4H), 7.41 – 7.34 (m, 6H), 5.83 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.08 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.01 (ddd, *J* = 10.4, 1.7, 1.1 Hz, 1H), 4.20 – 4.15 (m, 1H), 1.51 – 1.45 (m, 1H), 1.34 – 1.15 (m, 7H), 0.84 (t, *J* = 7.1 Hz, 3H), 0.65 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 141.41, 136.94, 136.86, 134.69, 134.63, 129.86, 129.83, 127.91, 127.89, 114.42, 74.84, 37.98, 31.93, 24.93, 22.79, 14.23, -1.97. **Yield**: 89%, 8 h; colorless liquid. **R_f**: 0.42 (hexanes). **Chemical Formula:** $C_{21}H_{28}OSi$ EI-MS [M^+] Calcd: 324.1909; found: 324.1909.



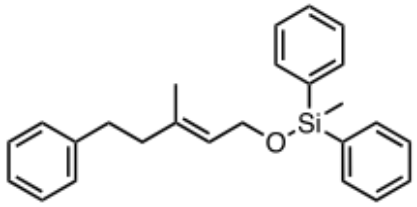
1-(4-(4-((Diphenylmethylsilyl)oxy)but-1-yn-1-yl)phenyl)ethan-1-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.62 – 7.59 (m, 4H), 7.43 – 7.34 (m, 8H), 3.91 – 3.88 (t, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.57 (s, 3H), 0.67 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 197.50, 136.01, 135.84, 134.51, 131.86, 130.10, 130.03, 128.85, 128.29, 128.07, 81.35, 62.01, 26.73, 23.87, -2.84. **Yield**: 76%, 4 h; yellow oil. **R_f**: 0.27 (15% EtOAc/hexanes). **Chemical Formula**: $C_{25}H_{24}O_2Si$ EI-MS [M^+] Calcd: 384.1545; found: 384.1546



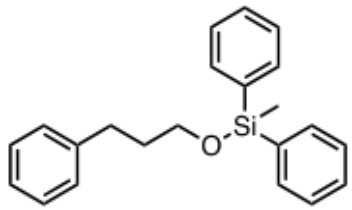
5-(2-(((Diphenylmethylsilyl)oxy)methyl)phenyl)-2-(piperidin-1-yl)pyrimidine: **^{1}H NMR** (**600 MHz, $CDCl_3$**) **δ** 8.26 (s, 2H), 7.54 (ddd, *J* = 6.8, 4.0, 1.6 Hz, 5H), 7.40 – 7.36 (m, 2H), 7.33 (qd, *J* = 7.1, 1.3 Hz, 6H), 7.15 (dd, *J* = 7.2, 1.7 Hz, 1H), 4.68 (s, 2H), 3.82 – 3.79 (m, 4H), 1.71 – 1.67 (m, 2H), 1.65 – 1.61 (m, 4H), 0.60 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 160.83, 157.40, 138.38, 135.72, 135.10, 134.39, 129.91, 129.89, 128.72, 127.92, 127.82, 127.70, 121.75, 63.34, 44.94, 25.83, 24.93, -2.94. **Yield**: 85%, 4 h; colorless oil. **R_f**: 0.30 (7.5% EtOAc/hexanes). **Chemical Formula:** $C_{29}H_{31}ON_3Si$ EI-MS $[M^+]$ Calcd: 465.2236; found: 466.2315 $[M+H]^+$.



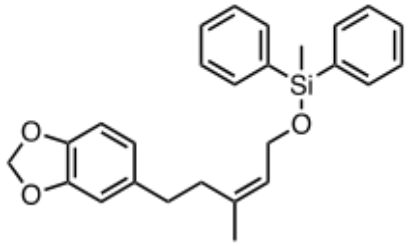
(Benzo[d][1,3]dioxol-5-ylmethoxy)diphenylmethylsilane: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 7.63-7.61 (dd, *J* = 6.4 Hz, 4H), 7.45-7.37 (m, 6H), 6.84 (s, *J* = 0.9 Hz, 1H), 6.75 (d, *J* = 1.0 Hz, 2H), 5.94 (s, 2H), 4.69 (s, *J* = 0.7 Hz, 2H) 0.69 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 147.75, 146.81, 135.93, 134.76, 134.54, 130.05, 128.05, 120.03, 108.12, 107.69, 101.02, 65.39, -2.74. **Yield**: 83%, 4 h; colorless liquid. **R_f**: 0.30 (10% Et_2O/hexanes). **Chemical Formula:** $C_{21}H_{20}O_3Si$ EI-MS $[M^+]$ Calcd: 348.1181; found: 348.1182.



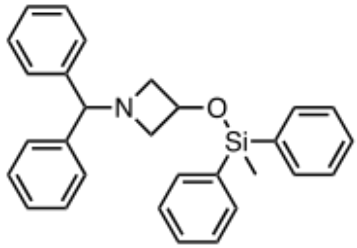
(*E*)-(3-Methyl-5-phenylpent-2-en-1-yl)oxy)diphenylmethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 6.4, 1.6 Hz, 3H), 7.55 – 7.53 (m, 1H), 7.43 – 7.38 (m, 6H), 7.35 – 7.29 (m, 3H), 7.20 (m, 3H), 5.42 (m, 1H), 4.30 – 4.27 (d, 2H), 2.70 (t, *J* = 9.6, 6.9 Hz, 2H), 2.30 – 2.27 (d, 2H), 1.59 (s, 3H), 0.66 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** 142.32, 137.55, 136.33, 134.57, 134.15, 129.90, 128.44, 127.97, 125.90, 124.16, 60.62, 41.51, 34.45, 16.61, -2.57. **Yield**: 78%, 5 h; colorless oil. **R_f**: 0.40 (10% Et_2O/hexanes). **Chemical Formula:** $C_{25}H_{28}O_3Si$ EI-MS [M^+] Calcd: 404.1807; found: 357.1917 [M-CH_3]$^+$



Diphenylmethyl(3-phenylpropoxy)silane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.52 (dd, 4H), 7.47-7.39 (m, 6H), 7.30-7.27 (t, 2H), 7.21-7.17 (m, 3H), 3.78-3.75 (t, 2H), 2.75-2.71 (t, *J* = 7.7Hz, 2H), 1.96-1.89 (m, 2H) 0.69 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 142.19, 136.34, 134.48, 129.91, 128.58, 128.00, 127.98, 125.81, 62.86, 34.26, 32.22, -2.90. **Yield**: 87%, 3 h; colorless liquid. **R_f**: 0.80 (25% Et_2O in hexanes). **Chemical Formula:** $C_{22}H_{24}OSi$ EI-MS [M^+] Calcd: 332.1596; found: 317.1361 [M-CH_3]$^+$

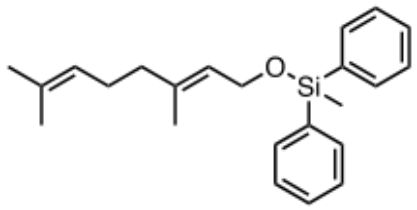


±(*Z*)-((5-(Benzo[1,3]dioxol-5-yl)-3-methylpent-2-en-1-yl)oxy)diphenylmethylsilane: **^{1}H NMR** **(500 MHz, $CDCl_3$) δ** 7.61 – 7.58 (m, 4H), 7.39 (m, 6H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.91 (s, 2H), 5.38 (td, *J* = 6.5, 1.5 Hz, 1H), 4.26 (d, *J* = 6.5 Hz, 2H), 2.62 – 2.58 (m, 2H), 2.22 (dd, *J* = 9.7, 6.5 Hz, 2H), 1.55 (s, 3H), 0.64 (s, 3H). **^{13}C NMR** **(126 MHz, $CDCl_3$) δ** 147.62, 145.68, 137.39, 136.28, 136.15, 134.56, 129.91, 127.96, 124.22, 121.14, 108.95, 108.23, 100.86, 60.59, 41.77, 34.15, 16.58, -2.59. **Yield**: 82%, 4 h; colorless oil. **R_f**: 0.32 (5% EtOAc/hexanes). **Chemical Formula**: $C_{26}H_{28}O_3Si$ EI-MS [M^+] Calcd: 416.1807; found: 439.1700 [M+Na]$^+$

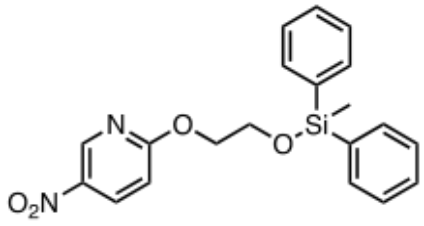


Benzhydryl-3-((diphenylmethylsilyl)oxy)azetidine: **^{1}H NMR** **(500 MHz, $CDCl_3$) δ** 7.54 (d, *J* = 7.4 Hz, 4H), 7.39 (m, 11H), 7.27 (s, 2H), 7.24 (s, 1H), 7.18 (t, *J* = 7.3 Hz, 2H), 4.53 (p, *J* = 6.2 Hz, 1H), 4.35 (s, 1H), 3.47 (td, *J* = 6.2, 2.3 Hz, 2H), 2.95 (td, *J* = 6.3, 2.3 Hz, 2H), 0.60 (s, 3H). **^{13}C NMR** **(126 MHz, $CDCl_3$) δ** 142.40, 135.74, 134.39, 130.09, 128.52, 128.48, 128.05, 127.58, 127.19, 78.62, 63.55, 62.39, -2.48. **Yield**: 77%, 12 h; colorless oil. **R_f**: 0.32

(15% Et_2O/hexanes). **Chemical Formula**: $C_{29}H_{29}ONSi$ EI-MS [M^+] Calcd: 435.2018; found: 435.2018.

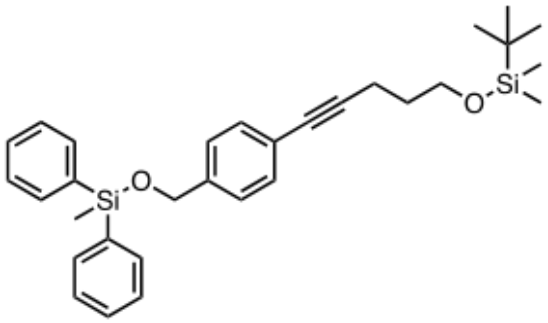


(*E*)-((3,7-Dimethylocta-2,6-dien-1-yl)oxy)diphenylmethylsilyl: <u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.3, 1.3 Hz, 4H), 7.45 – 7.36 (m, 6H), 5.42 – 5.37 (m, 1H), 5.06 – 5.01 (m, 1H), 4.24 (dt, *J* = 6.7, 1.1 Hz, 2H), 1.97 (tq, *J* = 9.7, 5.0, 3.6 Hz, 4H), 1.71 (s, *J* = 1.2 Hz, 3H), 1.65 (s, *J* = 1.5 Hz, 3H), 1.55 (s, *J* = 3.0 Hz, 3H), 0.66 (s, *J* = 0.9 Hz, 3H). **<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ** 138.46, 136.29, 134.57, 131.97, 129.88, 127.96, 124.61, 124.04, 60.27, 32.31, 26.78, 25.80, 23.57, 17.76, -2.59. **Yield**: 81%, 4 h; colorless oil. **R_f**: 0.35 (10% Et_2O/hexanes). **Chemical Formula**: $C_{23}H_{30}OSi$ EI-MS [M^+] Calcd: 350.2065; found: 350.2066



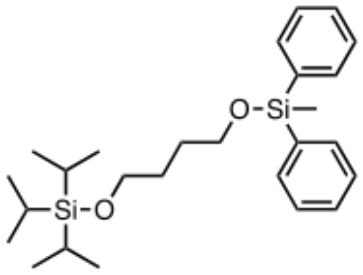
2-(2-((Diphenylmethylsilyl)oxy)ethoxy)-5-nitropyridine: <u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.8 Hz, 1H), 8.31 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.60 – 7.57 (m, 4H), 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 4H), 6.73 (d, *J* = 9.1 Hz, 1H), 4.57 – 4.54 (m, 2H), 4.08 – 4.06 (m, 2H), 0.67 (s, 3H). **<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ** 167.06, 144.81, 135.74, 134.48, 133.97, 130.10, 128.04, 111.54, 76.91, 68.68, 61.87, -2.82. **Yield**: 79%, 4 h; yellow oil. **R_f**: 0.35 (25%

EtOAc/hexanes). **Chemical Formula**: $C_{20}H_{20}O_4N_2Si$ EI-MS [M^+] Calcd: 380.1192; found: 365.0958 [$M-CH_3$]$^+$

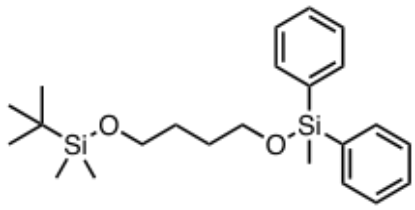


***t*-Butyldimethyl((5-(4-(((diphenylmethylsilyl)oxy)methyl)phenyl)pent-4-yn-1-yl)oxy)silane:**

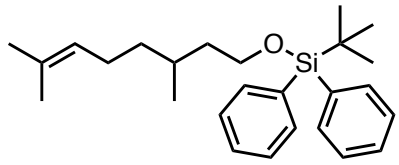
<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 4H), 7.44 – 7.41 (m, 2H), 7.40 – 7.36 (m, 4H), 7.35 – 7.33 (d, 2H), 7.23 (d, *J* = 7.5, 0.8 Hz, 2H), 4.77 (s, 2H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.78 (m, 2H), 0.91 (s, 9H), 0.65 (s, 3H), 0.08 (s, 6H). **<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ** 140.21, 135.84, 134.53, 131.58, 130.08, 128.07, 126.39, 105.16, 89.72, 80.81, 77.41, 77.16, 76.90, 65.15, 61.80, 31.93, 26.12, 15.99, -2.78, -5.14. **Yield**: 94%, 4 h; colorless oil. **R_f**: 0.32 (4% EtOAc/hexanes). **Chemical Formula**: $C_{31}H_{40}O_2Si_2$ EI-MS [M^+] Calcd: 500.2566; found: 523.2465 [M+Na]$^+$



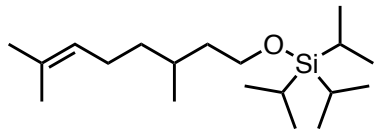
9,9-Diisopropyl-10-methyl-2,2-diphenyl-3,8-dioxa-2,9-disilaundecane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.39 – 7.32 (m, 6H), 3.69 (dd, *J* = 6.9, 4.4 Hz, 2H), 3.65 (dt, *J* = 6.3, 3.2 Hz, 2H), 1.60 (tt, *J* = 5.2, 2.9 Hz, 4H), 1.04 (s, *J* = 2.4 Hz, 21H), 0.62 (s, *J* = 2.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 134.32, 129.71, 127.80, 63.47, 63.38, 63.18, 29.54, 29.10, 18.03, 12.00, -3.05. **Yield:** 81%, 3 h; light yellow oil. **R_f**: 0.45 (100% hexanes). **Chemical Formula**: $C_{26}H_{42}O_2Si_2$ EI-MS [M^+] Calcd: 442.2723; found: 442.2720.



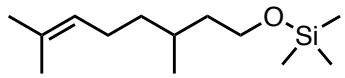
9,9,10,10-Tetramethyl-2,2-diphenyl-3,8-dioxa-2,9-disilaundecane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 4H), 7.38 – 7.33 (m, 6H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 1.61 – 1.53 (m, 4H), 0.85 (s, 9H), 0.61 (s, 3H), 0.00 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 136.40, 134.48, 129.88, 127.96, 63.56, 63.14, 29.41, 29.22, 26.12, 18.49, -2.88, -5.13. **Yield:** 77%, 4 h; light yellow oil. **R_f:** 0.42 (100% hexanes). **Chemical Formula**: $C_{23}H_{36}O_2Si_2$ EI-MS [M^+] Calcd: 400.2254; found: 400.2254.



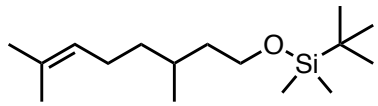
(*t*-Butyl-((3,7-dimethyloct-6-en-1-yl)oxy)diphenylsilane: <u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.43 – 7.36 (m, 6H), 5.09 (dddd, *J* = 7.1, 5.7, 2.9, 1.4 Hz, 1H), 3.73 – 3.67 (m, 2H), 1.99 – 1.92 (m, 2H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.64 – 1.59 (m, 5H), 1.38 – 1.29 (m, 2H), 1.16 – 1.11 (m, 1H), 1.05 (s, 9H), 0.84 (d, *J* = 6.5 Hz, 3H). **<u>^{13}C NMR</u> (151 MHz, $CDCl_3$) δ** 135.57, 134.17, 131.03, 129.47, 127.56, 124.91, 62.20, 39.63, 37.17, 29.05, 26.87, 25.72, 25.49, 19.61, 19.21, 17.65. **Yield**: 68%, 8 h; colorless oil. **R_f**: 0.75 (10% EtOAc/hexanes). Chemical Formula: $C_{26}H_{38}OSi$ EI-MS [M^+] Calcd: 394.2692 found: 394.2692.



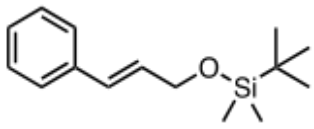
***t*-Butyl-((3,7-dimethyloct-6-en-1-yl)oxy)triisopropylsilane: <u>^{1}H NMR</u> (600 MHz, $CDCl_3$) δ** 5.10 (m, 1H), 3.74 – 3.68 (m, 2H), 2.02 – 1.93 (m, 2H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.61 – 1.57 (m, 6H), 1.37 – 1.31 (m, 2H), 1.16 (dtd, *J* = 9.5, 5.9, 5.1, 2.1 Hz, 1H), 1.07 – 1.05 (m, 20H), 0.89 (d, *J* = 6.5 Hz, 3H). **<u>^{13}C NMR</u> (151 MHz, $CDCl_3$) δ** 131.19, 125.08, 105.18, 61.84, 40.24, 37.41, 29.30, 25.67, 19.85, 18.20, 17.78, 12.19. **Yield**: 94%, 4 h; colorless oil. **R_f**: 0.75 (10% EtOAc/hexanes). **Chemical Formula**: $C_{19}H_{40}OSi$ EI-MS [M^+] Calcd: 312.6130; found: 269.2297 $[M-C_3H_7]^+$.



((3,7-Dimethyloct-6-en-1-yl)oxy)trimethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (ddq, *J* = 8.4, 5.5, 1.4 Hz, 1H), 3.64 – 3.57 (m, 2H), 1.97 (tq, *J* = 14.8, 7.6 Hz, 2H), 1.68 (s, *J* = 1.5 Hz, 3H), 1.60 (s, *J* = 1.3 Hz, 3H), 1.58 – 1.50 (m, 2H), 1.37 – 1.30 (m, 2H), 1.19 – 1.12 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.11 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** 131.25, 125.01, 61.07, 39.96, 37.38, 29.35, 25.87, 25.62, 19.74, 17.78, -0.30. **Yield:** 79%, 4 h **R_f:** 0.75 (10% EtOAc/hexanes).

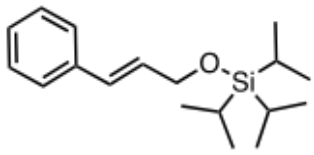


***t*-Butyl-((3,7-dimethyloct-6-en-1-yl)oxy)dimethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ** 5.10 (tp, *J* = 7.0, 1.4 Hz, 1H), 3.67 – 3.60 (m, 2H), 2.02 – 1.93 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.57 – 1.54 (m, 3H), 1.33 (m, 2H), 1.19 – 1.12 (m, 1H), 0.89 (s, 9H), 0.05 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 131.22, 125.05, 61.62, 40.10, 37.37, 29.28, 26.13, 25.87, 25.65, 19.79, 18.50, 17.79, -5.11. **Yield:** 84%, 4 h; colorless oil. **R_f**: 0.75 (10% EtOAc/hexanes). **Chemical Formula**: $C_{16}H_{34}OSi$ EI-MS [M^+] Calcd: 270.2379; found: 270.2376.

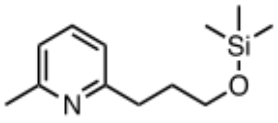


***t*-Butyl(cinnamyloxy)dimethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.57 (dd, *J* = 15.7, 2.0 Hz, 1H), 6.27 (dtd, *J* = 15.9,

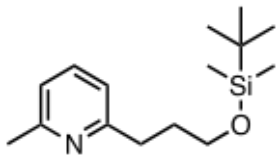
5.1, 0.9 Hz, 1H), 4.34 (dt, *J* = 5.1, 1.2 Hz, 2H), 0.93 (d, *J* = 0.9 Hz, 9H), 0.10 (d, *J* = 0.9 Hz, 6H). **δ ^{13}C NMR (126 MHz, $CDCl_3$) δ** 133.36129.46, 129.18, 128.49, 127.29, 126.37, 63.89, 25.98, 18.47, -5.13. **Yield**: 75%, 3 h; colorless liquid. **R_f**: 0.30 (15% Et_2O/hexanes).



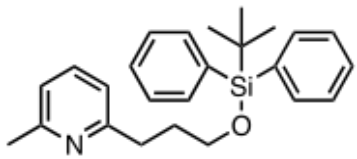
(Cinnamyloxy)triisopropylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 6.65 (dd, *J* = 15.7, 2.1 Hz, 1H), 6.33 – 6.27 (m, 1H), 4.44 (dd, *J* = 4.8, 1.9, 0.8 Hz, 2H), 1.20 – 1.14 (m, 3H), 1.12 – 1.09 (d, 18H). **δ ^{13}C NMR (126 MHz, $CDCl_3$) δ** 137.41, 129.52, 129.19, 128.63, 127.35, 126.52, 64.07, 18.20, 12.24. **Yield**: 89%, 3 h; colorless liquid **R_f**: 0.75 (5% EtOAc/hexanes). **Chemical Formula:** $C_{13}H_{30}OSi$ EI-MS [M^+] Calcd. 290.2066 found: 290.2065.



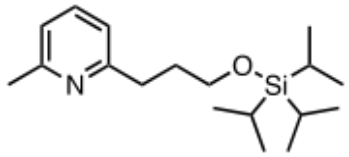
2-Methyl-6-(3-((trimethylsilyl)oxy)propyl)pyridine:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.7 Hz, 1H), 6.85 (dd, *J* = 7.7, 2.7 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.71 – 2.67 (m, 2H), 2.41 (s, 3H), 1.86 – 1.82 (m, 2H), -0.01 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 161.70, 158.17, 136.92, 120.88, 62.53, 35.24, 33.31, 26.44, 24.98, -0.00. **Yield**: 86% 4 h; light yellow oil. **R_f**: 0.34 (10% EtOAc/hexanes). **Chemical Formiula**: $C_{12}H_{21}NOSi$ EI-MS [M^+] Calcd: 223.1392 found: 223.1391.



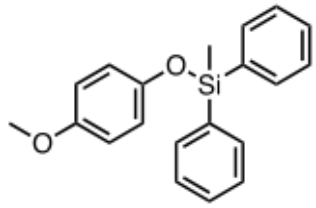
2-Methyl-6-(3-((*t*-butyldimethylsilyl)oxy)propyl)pyridine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.6 Hz, 1H), 6.95 (dd, *J* = 7.6, 2.2 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.83 – 2.79 (m, 2H), 2.52 (s, 3H), 1.96 – 1.90 (m, 2H), 0.90 (s, 9H), 0.04 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 161.72, 158.19, 136.90, 120.86, 119.98, 62.55, 35.25, 33.31, 25.00, 16.98, -0.00, -2.31. **Yield**: 89% 4 h; light yellow oil. **Rf**: 0.36 (10% EtOAc/hexanes). **Chemical Formula:** $C_{15}H_{27}NOSi$ EI-MS [M^+] Calcd: 265.1862; found: 265.1867.



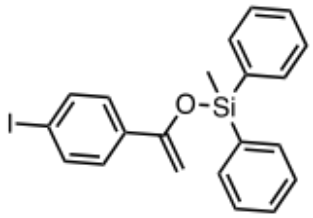
2-Methyl-6-(3-((*t*-butyldiphenylsilyl)oxy)propyl)pyridine: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.65 – 7.63 (m, 4H), 7.38 – 7.33 (m, 5H), 7.24 (s, 1H), 6.91 (dd, *J* = 14.2, 7.6 Hz, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.85 – 2.82 (m, 2H), 2.49 (s, 3H), 1.99 – 1.94 (m, 2H), 1.04 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 161.27, 157.68, 136.42, 134.77, 133.95, 129.59, 127.67, 120.38, 119.57, 63.30, 34.70, 32.75, 26.85, 24.49, 19.21. **Yield**: 83%, 12 h; light yellow oil. **R_f**: 0.32 (10% EtOAc/hexanes). **Chemical Formula**: $C_{25}H_{31}NOSi$ EI-MS [M^+] Calcd: 389.2175; found: 389.2171.



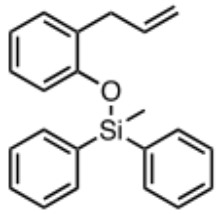
2-Methyl-6-(3-((triisopropylsilyl)oxy)propyl)pyridine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 9.7, 7.7 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.84 – 2.79 (m, 2H), 2.50 (s, 3H), 1.96 – 1.91 (m, 2H), 1.03 (d, *J* = 3.9 Hz, 18H).**^{13}C NMR (126 MHz, $CDCl_3$) δ** 161.45, 157.68, 136.42, 120.36, 119.62, 62.78, 34.75, 33.23, 24.49, 18.03, 12.01. **Yield**: 90%, 4 h; light yellow oil. **R_f**: 0.28 (10% EtOAc/hexanes). **Chemical Formula**: $C_{18}H_{33}ONSi$ EI-MS [M^+] Calcd: 307.2332; found: 307.2344.



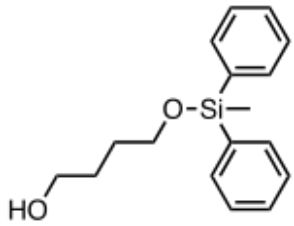
4-((Diphenylmethylsilyl)oxy)anisole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 4H), 7.46 – 7.39 (m, 6H), 6.79 – 6.71 (m, 4H), 3.73 (s, 3H), 0.75 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 155.89, 150.41, 137.22, 136.04, 131.73, 129.62, 122.19, 116.12, 57.21, -1.01. **Yield**: 83% 6 h; colorless oil. **R_f**: 0.31 (5% EtOAc/hexanes). **Chemical Formula:** $C_{20}H_{20}O_2Si$ EI-MS [M^+] Calcd: 320.1232; found: 320.1235



((1-(4-Iodophenyl)vinyl)oxy)diphenylmethylsilane: ^{1}H NMR (600 MHz, C_6D_6) δ 7.65 – 7.63 (m, 4H), 7.40 – 7.37 (m, 2H), 7.21 – 7.19 (m, 2H), 7.19 – 7.17 (m, 6H), 4.71 (d, *J* = 2.2 Hz, 1H), 4.41 (d, *J* = 2.2 Hz, 1H), 0.65 (s, 3H). **^{13}C NMR (151 MHz, C_6D_6) δ** 154.70, 137.22, 136.92, 135.25, 134.26, 130.03, 127.95, 127.00, 94.03, 92.35, -3.24. **Yield**: 78%, 6 h; colorless oil. **R_f**: 0.30 (5% Et_2O/hexanes). **Chemical Formula:** $C_{21}H_{19}OISi$ EI-MS [M^+] Calcd: 442.0249; found: 442.0233.

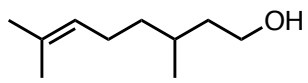


(2-Allylphenoxy)diphenylmethylsilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 6.6, 1.5 Hz, 4H), 7.47 – 7.37 (m, 6H), 7.14 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.97 (td, *J* = 7.7, 1.8 Hz, 1H), 6.89 (td, *J* = 7.4, 1.3 Hz, 1H), 6.69 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.97 (ddtd, *J* = 16.8, 10.2, 6.6, 1.4 Hz, 1H), 5.05 – 4.99 (m, 2H), 3.42 (dt, *J* = 6.7, 1.5 Hz, 2H), 0.76 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 155.89, 150.41, 137.22, 136.04, 131.73, 130.33, 129.62, 122.19, 116.12, 57.21, -1.01. **Yield**: 76%, 6 h; colorless oil. **R_f**: 0.30 (5% Et_2O/hexanes). **Chemical Formula**: $C_{22}H_{22}OSi$ EI-MS [M^+] Calcd: 330.1439; found: 330.1431.

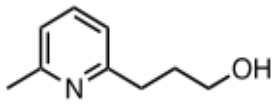


4-((Methyldiphenylsilyl)oxy)butan-1-ol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.44 – 7.36 (m, 6H), 3.76 – 3.73 (m, 2H), 3.65 – 3.61 (m, 2H), 1.68 – 1.64 (m, 4H), 0.65 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 135.81, 134.33, 129.89, 127.90, 63.45, 62.78, 29.75, 29.26, -3.12. **Yield:** 85%, 2 h; light yellow oil. **R_f**: 0.26 (25% EtOAc/hexanes). **Chemical Formula:** $C_{17}H_{22}O_2Si$ EI-MS [M^+] Calcd: 286.1389; found: 286.1390.

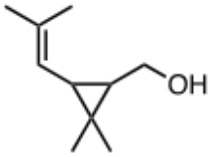
8. Analytical Data for Free Alcohols



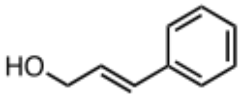
3,7-Dimethyloct-6-en-1-ol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 5.14 – 5.08 (m, 1H), 3.70 (m, 2H), 2.00 (tq, *J* = 14.8, 7.5 Hz, 2H), 1.70 (d, *J* = 3.0 Hz, 3H), 1.62 (d, *J* = 2.8 Hz, 3H), 1.37 (dtdd, *J* = 21.2, 8.4, 5.1, 2.6 Hz, 3H), 1.21 (tdd, *J* = 13.6, 6.7, 3.4 Hz, 2H), 0.92 (dd, *J* = 6.5, 2.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 131.25, 124.69, 61.20, 37.21, 29.17, 25.70, 25.45, 19.52, 17.63. **Yield**: 88% 12 h (SFx), 91% 2.5 h (18-crown-6), colorless oil. **R_f:** 0.35 (50% Et_2O/hexanes).



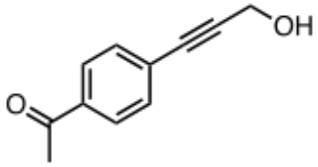
3-(6-Methyl-2-pyridinyl)-1-propanol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.52 – 7.48 (m, 1H), 6.98 (d, *J* = 7.7 Hz, 2H), 3.72 (td, *J* = 5.6, 2.8 Hz, 2H), 2.94 (td, *J* = 6.9, 2.9 Hz, 2H), 2.51 (d, *J* = 2.8 Hz, 3H), 1.97 (dtq, *J* = 8.7, 5.9, 3.3, 2.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 160.69, 157.30, 137.06, 120.02, 62.35, 61.91, 35.63, 31.55, 24.07. **Yield:** 94% 6 h (SFx), 90% 3 h (18-crown-6), reddish brown oil. **R_f:** 0.25 (65% EtOAc/hexanes).



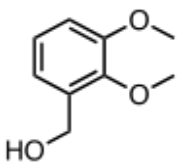
[2,2-Dimethyl-3-(2-methyl-1-propen-1-yl)cyclopropyl]methanol: ^{1}H NMR (500 MHz, $CDCl_3$) δ major isomer 4.87 (1H, d, *J* = 8.1), 3.77 (1H, dd, *J* = 6.6, 11.4), 3.55 (1H, dd, *J* = 8.5, 11.4), 1.70 (3H, s,), 1.67 (3H, s,), 1.15 (3H, s), 1.11 (1H, dd, *J* = 5.3, 8.1), 1.06 (3H, s), 0.83 (1H, ddd, *J* = 8.5, 6.6, 5.3); minor isomer: 4.96 (1H, d, *J* = 8.2), 3.67 (1H, dd, *J* = 7.6, 11.6), 3.61 (1H, dd, *J* = 8.0, 11.6), 1.73 (3H, s), 1.70 (3H, s), 1.38 (1H, dd, *J* = 8.2), 1.12 (3H, s), 1.07–1.04 (1H, m) 1.04 (3H, s) **^{13}C NMR (126 MHz, $CDCl_3$) δ** major isomer: 133.0, 123.5, 63.5, 35.1, 28.6, 25.6, 22.7, 21.3, 18.3, 15.5; minor isomer 135.0, 119.1, 60.4, 31.0, 28.8, 26.2, 25.8, 22.3, 20.8, 18.4. **Yield**: 94% 16 h (SFx), 94% 3 h (18-crown-6).



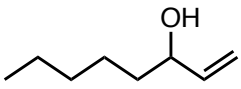
(2*E*)-3-Phenyl-2-propen-1-ol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.60 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.35 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.31 (dd, *J* = 5.7, 1.6 Hz, 2H), 1.77 – 1.66 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 136.71, 131.07, 128.55, 127.69, 126.49, 126.48, 63.63. **Yield**: 93%, 8 h (SFx), 85%, 2 h (18-crown-6), white solid. **R_f**: 0.40 (25% EtOAc/hexanes).



1-(4-(3-Hydroxyprop-1-yn-1-yl)phenyl)ethan-1-one: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 7.92 – 7.89 (m, 2H), 7.53 – 7.49 (m, 2H), 4.53 (d, *J* = 6.2 Hz, 2H), 2.60 (s, 3H), 1.75 (t, *J* = 6.2 Hz, 1H). **^{13}C NMR** **(126 MHz, $CDCl_3$) δ** 197.46, 136.63, 131.94, 128.38, 127.55, 90.62, 85.06, 51.78, 26.78. **Yield**: 79%, 12 h (SFx), 88%, 6 h (18-crown-6), ; red oil. **R_f**: 0.37 (50% EtOAc/hexanes).

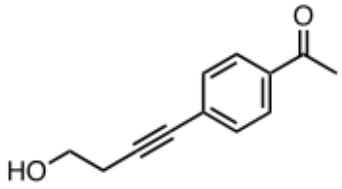


(2,3-Dimethoxyphenyl)metanol: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 7.03 (td, *J* = 7.9, 1.5 Hz, 1H), 6.92 – 6.86 (m, 2H), 4.68 (dd, *J* = 6.4, 1.5 Hz, 2H), 3.87 (d, *J* = 1.4 Hz, 3H), 3.86 (d, *J* = 1.5 Hz, 3H), 2.18 (tdd, *J* = 6.3, 4.1, 2.3 Hz, 1H). **^{13}C NMR** **(126 MHz, $CDCl_3$) δ** 152.50, 134.58, 124.18, 120.64, 112.23, 61.56, 60.87, 55.81. **Yield**: 83% 12 h (SFx), 93% 2.5 h (18-crown-6), white solid. **R_f**: 0.32 (25% EtOAc/hexanes).

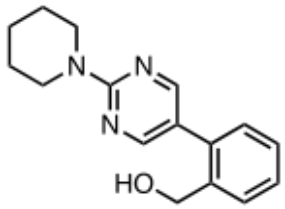


1-Octen-3-ol: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 5.85 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.20 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.08 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.07 (tdd, *J* = 7.4, 5.5, 1.3 Hz, 1H), 1.70 – 1.54 (m, 1H), 1.54 – 1.44 (m, 2H), 1.38 (dddd, *J* = 13.6, 8.5, 6.6, 3.0 Hz, 1H), 1.34 – 1.23

(m, 5H), 0.89 – 0.84 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 141.32, 114.46, 73.24, 36.97, 31.74, 24.99, 22.58, 14.00. **Yield:** 68% 36 h (SFx), 75% 22 h (18-crown-6); colorless liquid. **R_f**: 0.35 (25% EtOAc/hexanes).

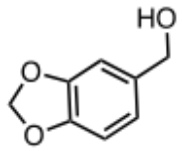


1-(4-(4-Hydroxybut-1-yn-1-yl)phenyl)ethan-1-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.86 (d, 2H), 7.49 – 7.45 (d, 2H), 3.82 (q, *J* = 6.2 Hz, 2H), 2.71 (t, *J* = 6.2 Hz, 2H), 2.57 (s, 3H), 1.75 (t, *J* = 6.3 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 196.55, 131.80, 128.31, 128.19, 104.99, 90.16, 81.82, 61.03, 26.61, 23.93. **Yield:** 79% 12 h (SFx), 93% 4 h (18-Crown-6) tan solid. **R_f**: 0.35 (80% Et_2O/hexanes). **Chemical Formula**: $C_{12}H_{12}O_2$ EI-MS $[M^+]$ Calcd: 188.0837; found: 189.0913 $[M+H]^+$.

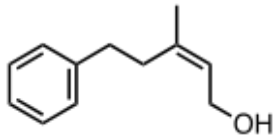


(2-(2-(Piperidin-1-yl)pyrimidin-5-yl)phenyl)metanol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.55 – 7.52 (m, 1H), 7.39 – 7.32 (m, 2H), 7.21 – 7.19 (m, 1H), 4.61 (d, *J* = 4.3 Hz, 2H), 3.82 – 3.79 (m, 4H), 1.99 (d, *J* = 5.0 Hz, 1H), 1.68 (dddd, *J* = 8.3, 6.9, 3.9, 2.2 Hz, 2H), 1.64 – 1.59 (m, 4H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 160.83, 148.91, 137.72, 137.10, 129.91, 129.89, 128.72, 127.92, 127.82, 63.34, 44.94, 25.83, 24.93. **Yield**: 89% 14 h (SFx), 86% 8 h

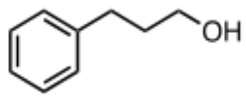
(18-crown-6). colorless oil. **R_f:** 0.27 (60 EtOAc in hexanes). **Chemical Formula**: $C_{16}H_{19}ON_3$ EI-MS $[M^+]$ Calcd: 269.1528; found: 270.1608 $[M+H]^+$.



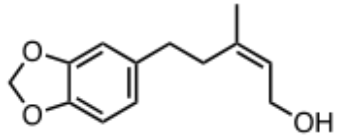
Benzo[*d*][1,3]dioxol-5-ylmethanol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.86 (s, *J* = 1.5 Hz, 1H), 6.79 (m, *J* = 7.9, 6.1 Hz, 2H), 5.95 (s, *J* = 1.9 Hz, 2H), 4.57 (s, *J* = 3.4 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 147.90, 135.00, 120.59, 108.30, 107.98, 101.10, 100.97, 65.29, **Yield:** 92% 12 h(SFx), 83% 1 h (18-crown-6), 85%; white solid. **R_f**: 0.33 (40% Et_2O/hexanes).



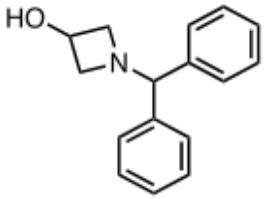
(2*E*)-3-Methyl-5-phenyl-2-penten-1-ol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.43 (tp, *J* = 6.9, 1.3 Hz, 1H), 4.16 (d, *J* = 6.9 Hz, 2H), 2.79 – 2.74 (m, 2H), 2.35 (dd, *J* = 9.5, 6.7 Hz, 2H), 1.75 (s, 3H), 1.28 – 1.16 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 141.98, 132.21, 128.37, 128.32, 125.85, 123.90, 59.28, 41.38, 34.34, 16.40. **Yield:** 87% 16 h (SFx), 92% 3 h (18-crown-6), yellow oil. **R_f:** 0.26 (25% EtOAc/hexanes).



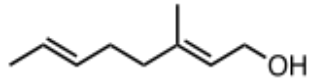
3-Phenyl-1-propanol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.31 – 7.27 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 3H), 3.68 (td, *J* = 6.5, 1.2 Hz, 2H), 2.74 – 2.69 (m, 2H), 1.90 (dtd, *J* = 9.0, 7.6, 7.0, 5.8 Hz, 2H), 1.55 (d, *J* = 7.1 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 141.85, 128.44, 128.41, 125.87, 62.04, 34.16, 32.09. **Yield:** 89% 14 h (SFx), 94% 2.5 h (18-crown-6), colorless oil. **R_f:** 0.31 (25% EtOAc/hexanes).



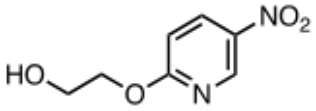
(*Z*)-5-(Benzo[1,3]dioxol-5-yl)-3-methylpent-2-en-1-ol: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.91 (s, 2H), 5.41 (m, 1H), 4.14 (d, *J* = 6.9 Hz, 2H), 2.68 – 2.63 (m, 2H), 2.28 (dd, *J* = 8.9, 7.2 Hz, 2H), 1.71 (s, 3H), 1.25 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 147.65, 145.73, 139.17, 135.95, 124.08, 121.31, 108.94, 108.23, 100.89, 59.48, 41.78, 34.21, 16.53. Yield: 90% 16 h (SFx), 92% 4 h (18-crown-6); yellow oil. **R_f**: 0.40 (25% EtOAc/hexanes).



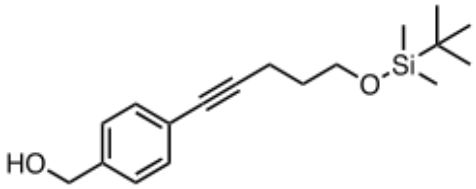
1-(Diphenylmethyl)-3-azetidinol: **^{1}H NMR** (**600 MHz, $CDCl_3$**) **δ** 7.39 – 7.36 (m, 4H), 7.26 (t, *J* = 7.7 Hz, 4H), 7.19 – 7.16 (m, 2H), 4.44 (p, *J* = 5.8 Hz, 1H), 4.33 (s, 1H), 3.54 – 3.51 (m, 2H), 2.90 – 2.87 (m, 2H). **^{13}C NMR** (**151 MHz, $CDCl_3$**) **δ** 141.87, 128.44, 127.41, 127.16, 78.45, 63.36, 62.08, **Yield:** 80% 24 h (SFx), 78% 20 h (18-crown-6), white solid. **R_f:** 0.29 (25% EtOAc/hexanes).



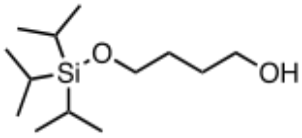
(Z)-3,7-Dimethylocta-2,6-dien-1-ol: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 5.42 (td, *J* = 7.2, 1.5 Hz, 1H), 5.08 (m, 1H), 4.07 (d, *J* = 7.2 Hz, 2H), 2.11 – 2.03 (m, 4H), 1.73 (d, *J* = 1.3 Hz, 3H, 1.58 (s, 3H), 1.17 (d, *J* = 6.1 Hz, 1H). **^{13}C NMR** (**126 MHz, $CDCl_3$**) **δ** 132.31, 124.47, 123.81, 58.86, 31.95, 26.53, 25.61, 23.37, 17.60. **Yield:** 85% 6 h (SFx), 91% 3 h (18-crown-6), tan oil. **R_f:** 0.36 (25% EtOAc/hexanes).



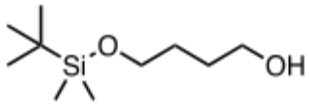
2-((5-Nitropyridin-2-yl)oxy)ethan-1-ol: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 9.06 (d, *J* = 2.8 Hz, 1H), 8.38 (dd, *J* = 9.1, 2.9 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 4.59 – 4.57 (m, 2H), 4.02 – 3.99 (m, 2H). **^{13}C NMR** (**126 MHz, $CDCl_3$**) **δ** 167.06, 144.73, 139.81, 134.30, 111.64, 69.46, , 61.52. **Yield:** 86% 5 h (SFx), 79% 6 h (18-crown-6), white solid. **R_f**: 0.35 (80% EtOAc/hexanes).



(4-(5-(*t*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl)methanol: **^{1}H NMR** **(500 MHz, $CDCl_3$) δ** 7.40 – 7.37 (m, 2H), 7.29 – 7.26 (m, 2H), 4.68 (d, *J* = 5.9 Hz, 2H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.67 (t, *J* = 6.0 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 140.30, 131.85, 126.90, 123.49, 90.16, 80.63, 65.20, 61.79, 31.89, 26.12, 18.53, 15.99, -5.15. **Yield:** 71% 16 h (SFx), 80% 8 h (18-crown-6), 81%; brown oil. **R_f:** 0.35 (15% EtOAc/hexanes). **Chemical Formula**: $C_{18}H_{30}O_2$ EI-MS $[M^+]$ Calcd: 278.2245; found: 247.1154 $[M\text{-}C_4H_9]^+$

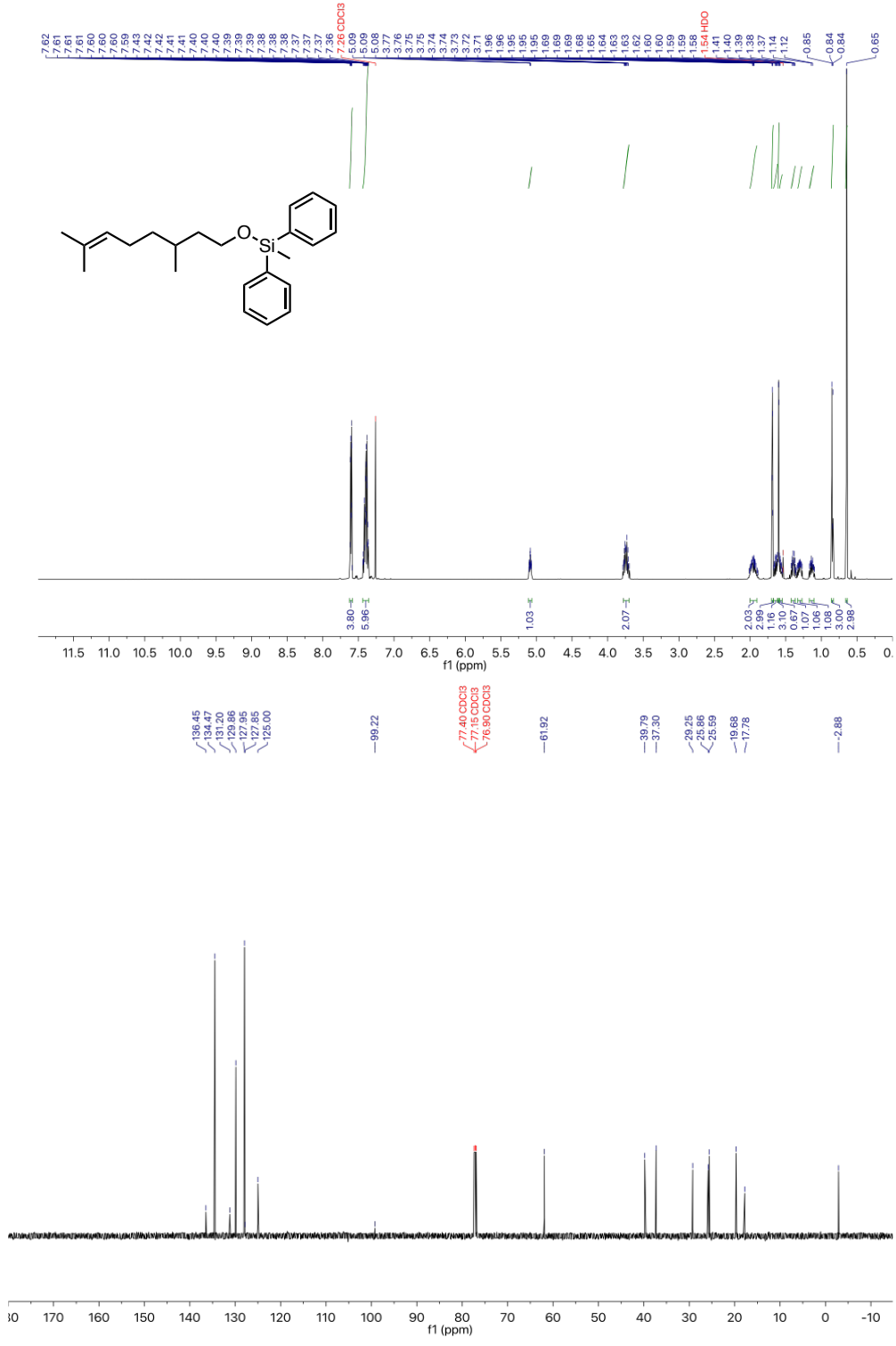


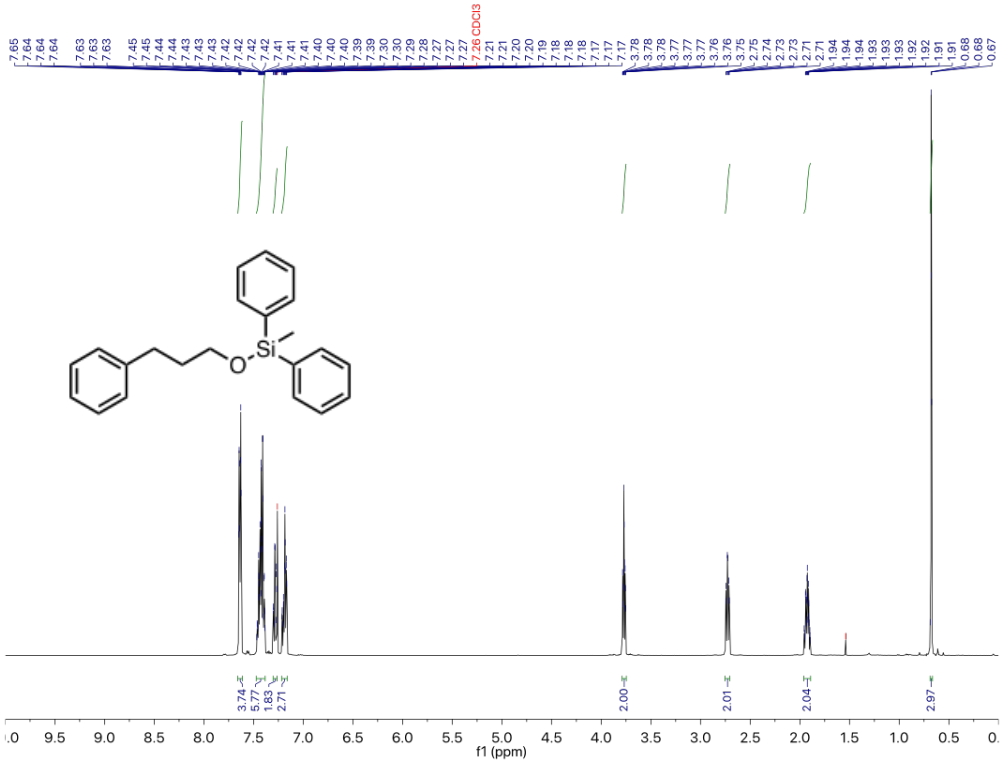
4-((Triisopropylsilyl)oxy)butan-1-ol: **^{1}H NMR** **(500 MHz, $CDCl_3$) δ** 3.73 (q, 2H), 3.64 (q, 2H), 2.54 (s, 1H), 1.69 – 1.59 (m, 5H), 1.05 (d, 18H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 63.59, 62.85, 30.35, 30.06, 17.96, 11.94. **Yield:** 82% 12 h (SFx) 89% 3 h (18-crown-6); colorless oil. **R_f**: 0.28 (25% EtOAc/hexanes).



4-((*t*-Butyldimethylsilyl)oxy)butan-1-ol: **^{1}H NMR** (**500 MHz, $CDCl_3$**) **δ** 3.63 (dt, *J* = 12.4, 5.7 Hz, 4H), 1.65 – 1.60 (m, 4H), 0.88 (s, 9H), 0.05 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 63.33, 62.77, 30.23, 29.86, 25.89, 18.29, -5.40. **Yield:** 90% 12 h (SFx), 86% 3 h (18-crown-6); colorless oil. **R_f:** 0.25 (25% EtOAc/hexanes).

9. ^{1}H NMR and ^{13}C NMR Spectra for Products




7.65 7.64 7.64 7.64 7.63 7.63 7.63 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.30 7.30 7.29 7.28 7.27 7.27 7.27 7.26 CDCl3 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.18 7.17 7.17 7.17 3.78 3.78 3.78 3.77 3.77 3.77 3.76 3.76 3.75 2.75 2.74 2.73 2.73 2.71 2.71 1.94 1.94 1.94 1.93 1.93 1.93 1.92 1.92 1.91 1.91 0.68 0.68 0.67
O
Si
3.74
5.77
1.83
2.71
2.00
2.01
2.04
2.97
f1 (ppm)
142.19
136.34
134.48
129.91
128.58
128.40
128.00
127.98
125.81
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77.15 CDCl3
76.90 CDCl3
62.86
34.26
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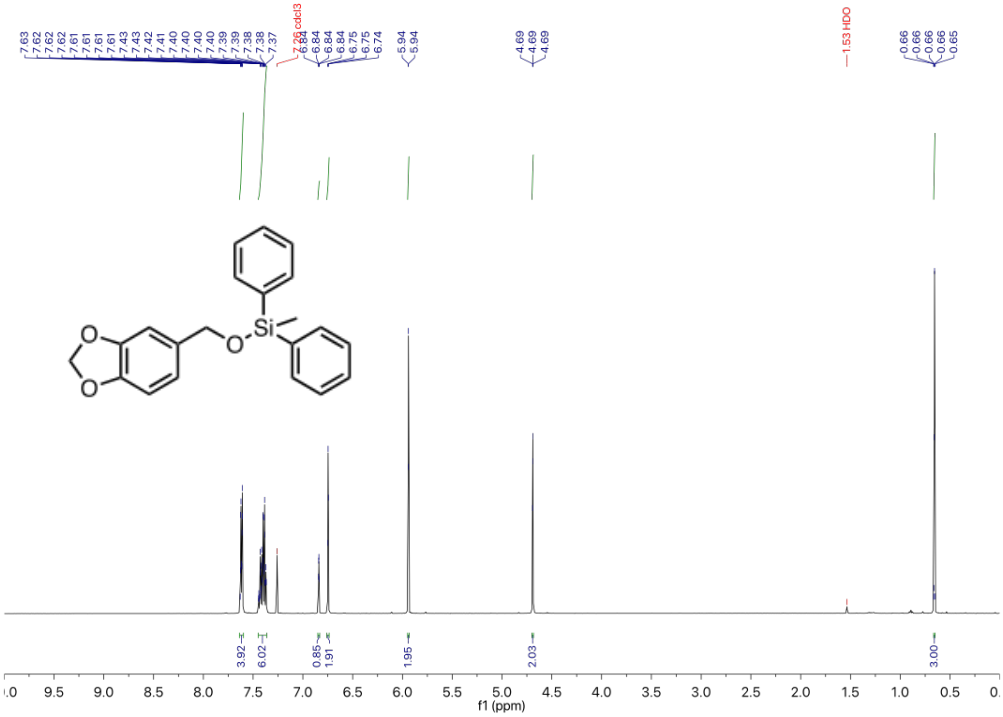
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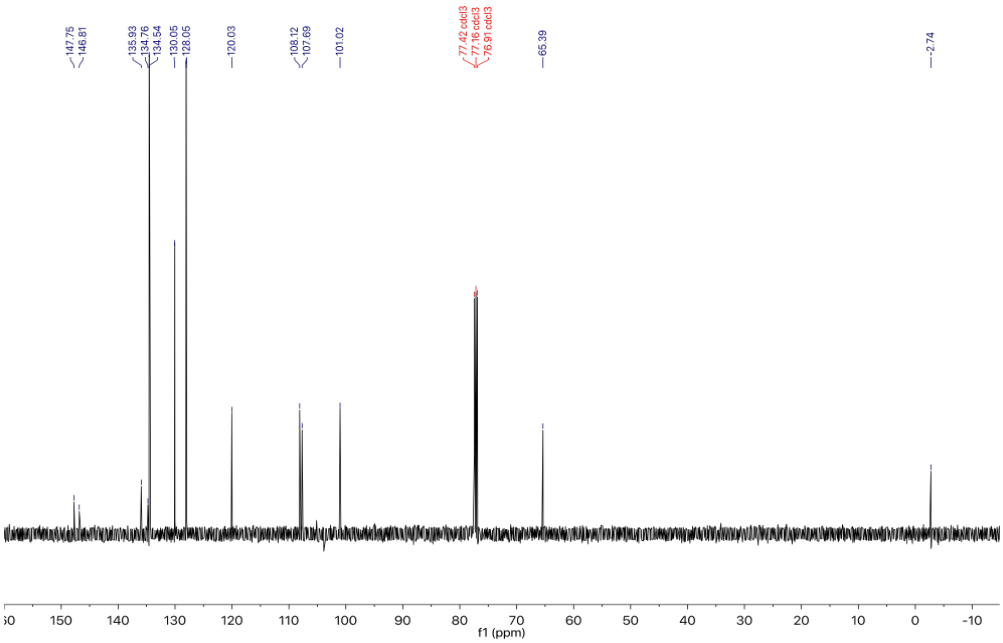
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.26 cdcl3
6.84
6.84
6.84
6.84
6.75
6.75
6.74
5.94
5.94
4.69
4.69
4.69
1.53 HDO
0.66
0.66
0.66
0.66
0.66
0.65
O
O
O
Si
3.92
6.02
0.85
1.91
1.95
2.03
3.00
f1 (ppm)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128.05
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101.02
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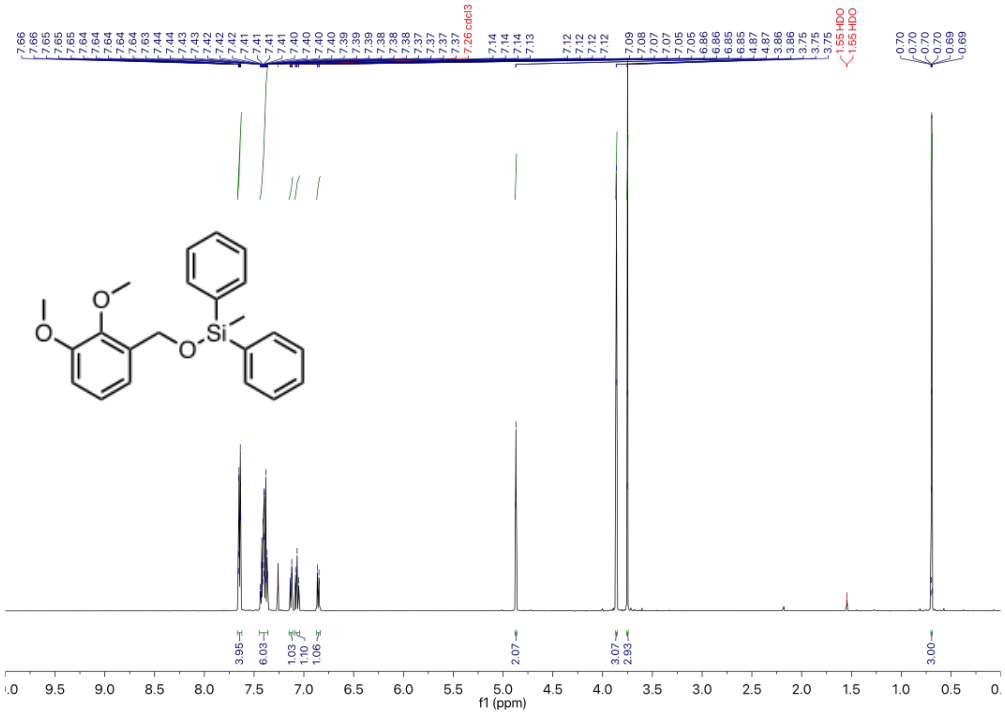
77.16 cdcl3
76.91 cdcl3
65.39
-2.74
f1 (ppm)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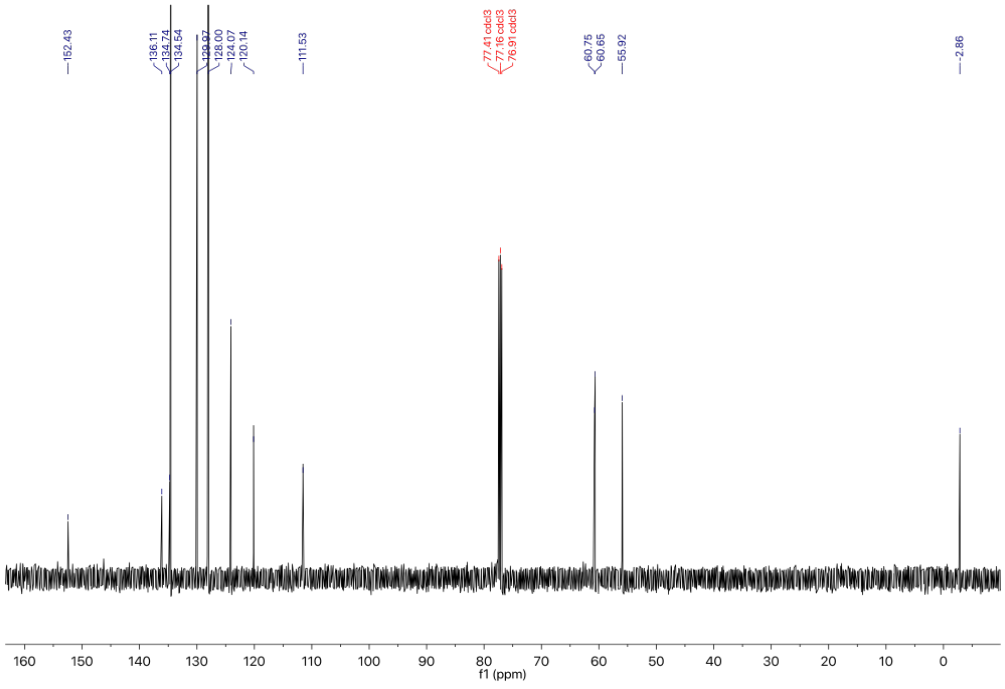
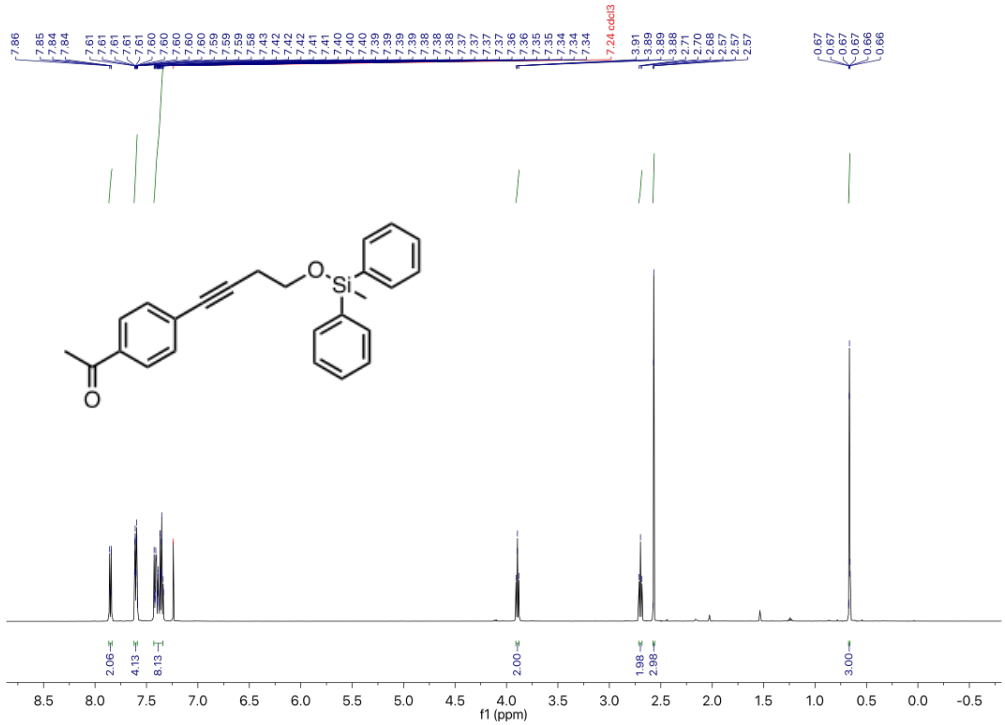
O
O
Si
O
3.95 6.03 1.03 1.10 1.06 2.07 3.07 2.93 3.00
f1 (ppm)


152.43 136.11 134.74 134.54 130.97 128.00 124.07 120.14 111.53 77.41 cdcl3 77.16 cdcl3 76.91 cdcl3 60.75 60.65 55.92 -2.86
f1 (ppm)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7.60
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3.91
3.89
3.89
3.88
2.71
2.70
2.68
2.57
2.57
2.57
0.67
0.67
0.67
0.67
0.66
0.66
0.66
O
Si
O
2.06
4.13
8.13
2.00
1.98
2.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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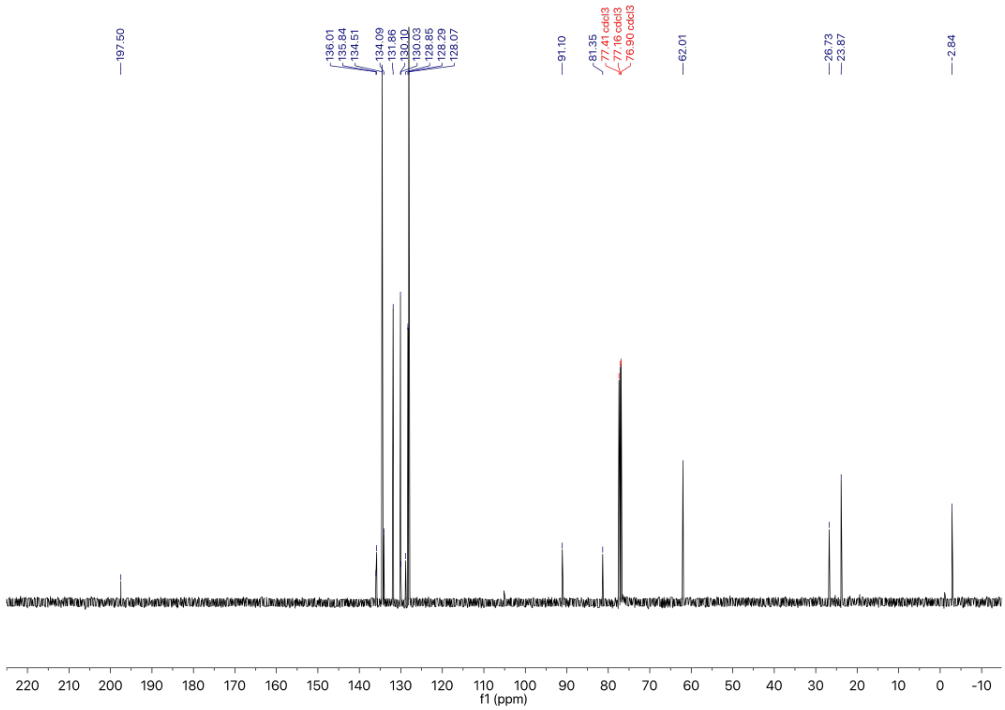
-0.5
f1 (ppm)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131.86
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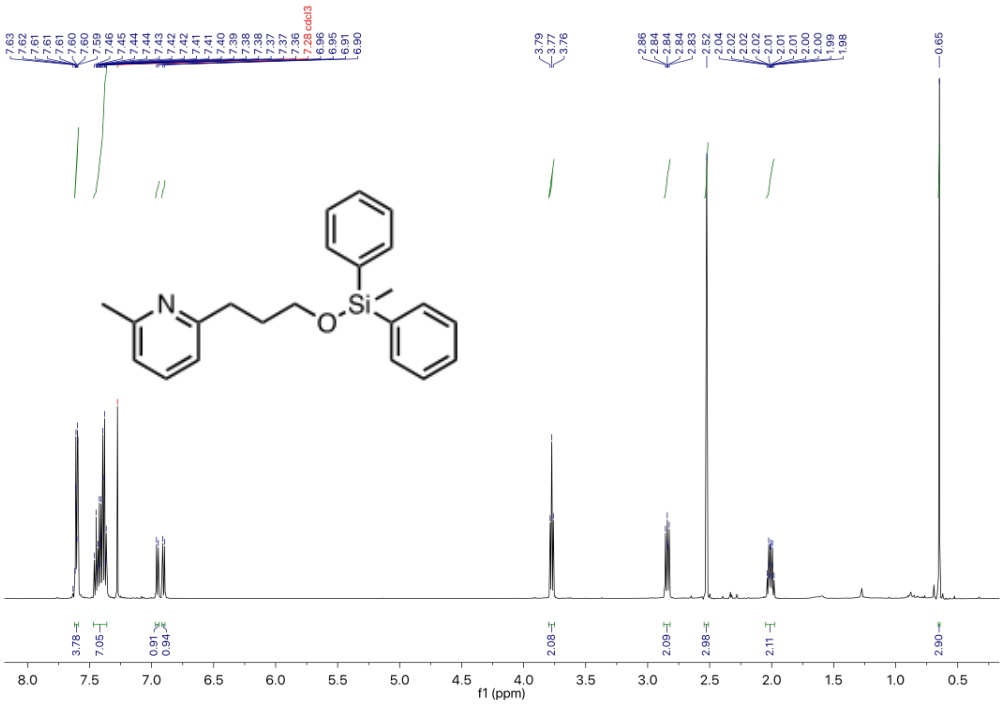
130.03
128.85
128.29
128.07
91.10
81.35
77.41 cdcl3
77.16 cdcl3
76.90 cdcl3
62.01
26.73
23.87
-2.84
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.28 cdcl3
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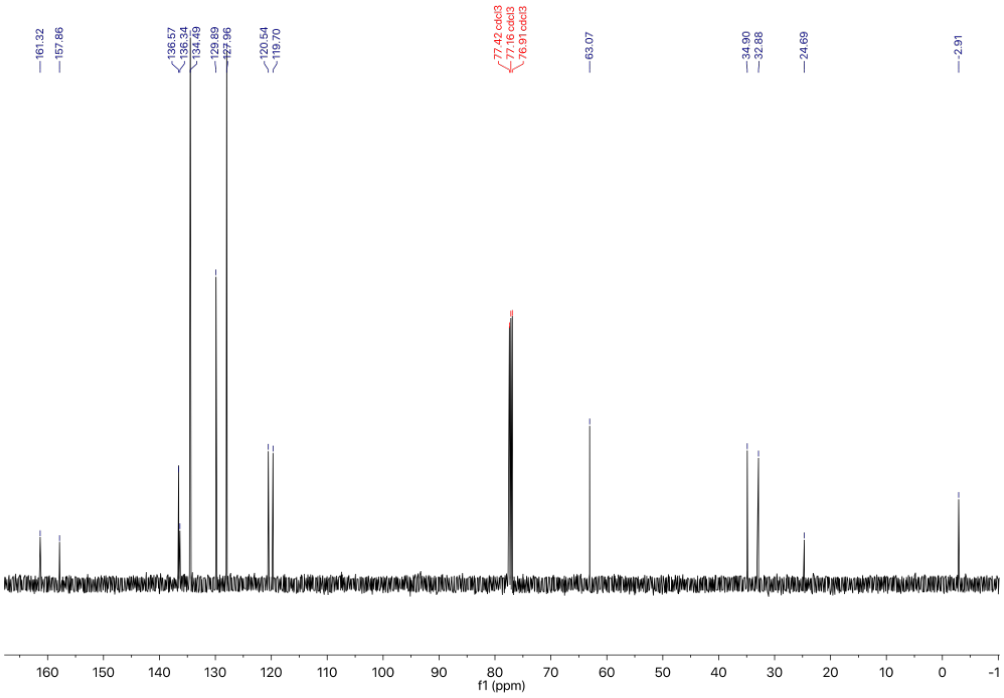
6.95
6.91
6.90
3.79
3.77
3.76
2.86
2.84
2.84
2.84
2.84
2.83
2.52
2.04
2.02
2.02
2.02
2.02
2.01
2.01
2.01
2.00
2.00
2.00
1.99
1.98
0.65
N
O
Si
3.78
7.05
0.91
0.94
2.08
2.09
2.98
2.11
2.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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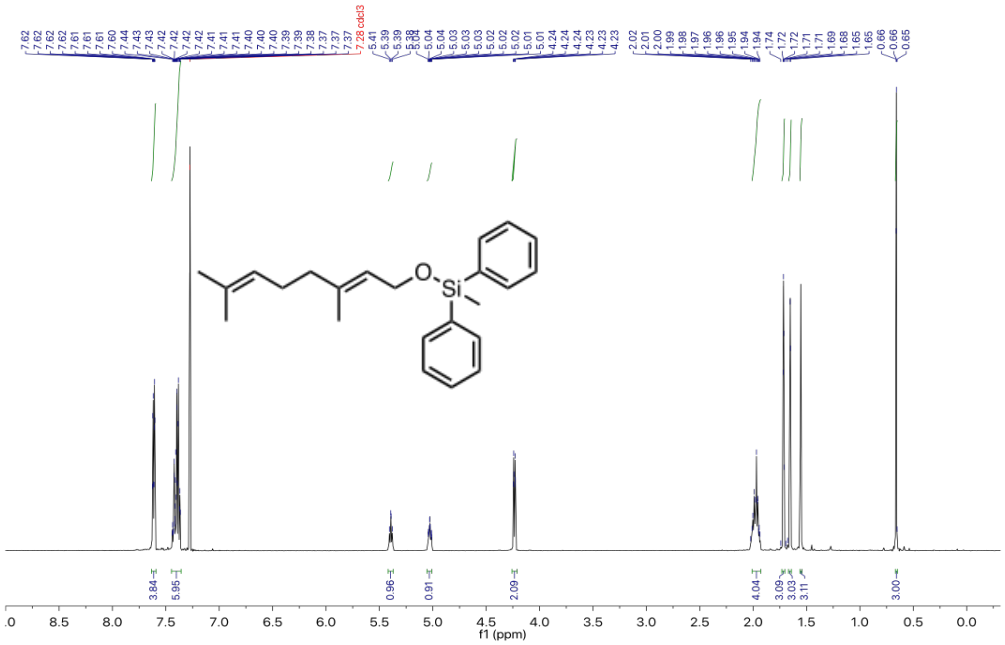
157.86
136.57
136.34
134.49
129.89
127.96
120.54
119.70
77.42 cdcl3
77.16 cdcl3
76.91 cdcl3
63.07
34.90
32.88
24.69
2.91
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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3.84
5.95
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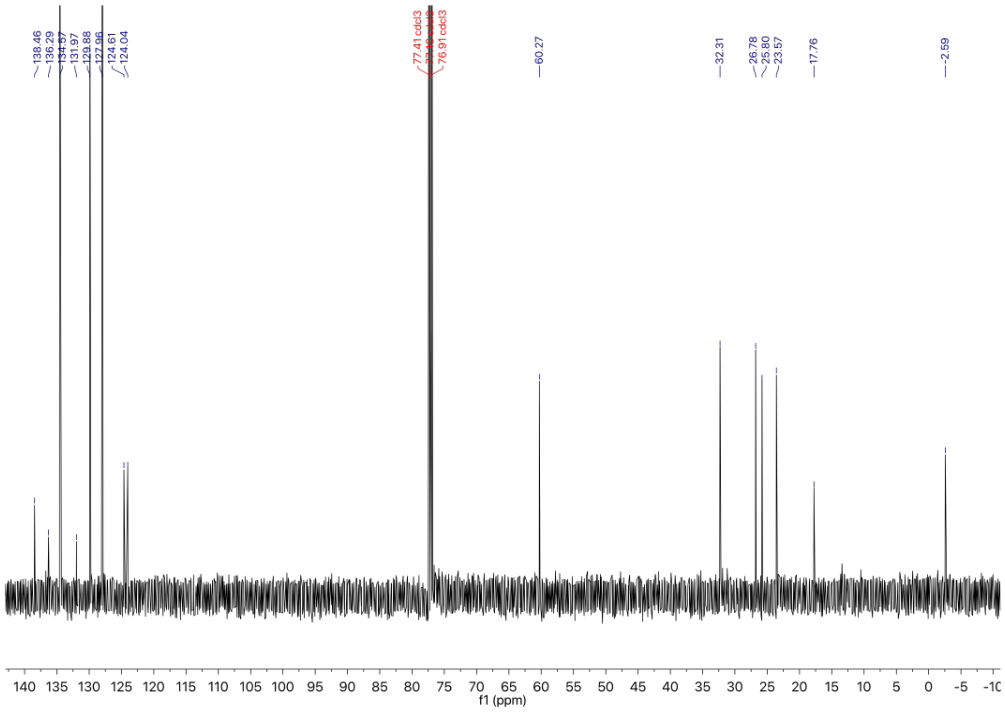
0.91
2.09
4.04
3.09
3.03
3.11
3.00
f1 (ppm)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136.29
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129.88
124.61
124.04
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76.91 cdcl3
60.27
32.31
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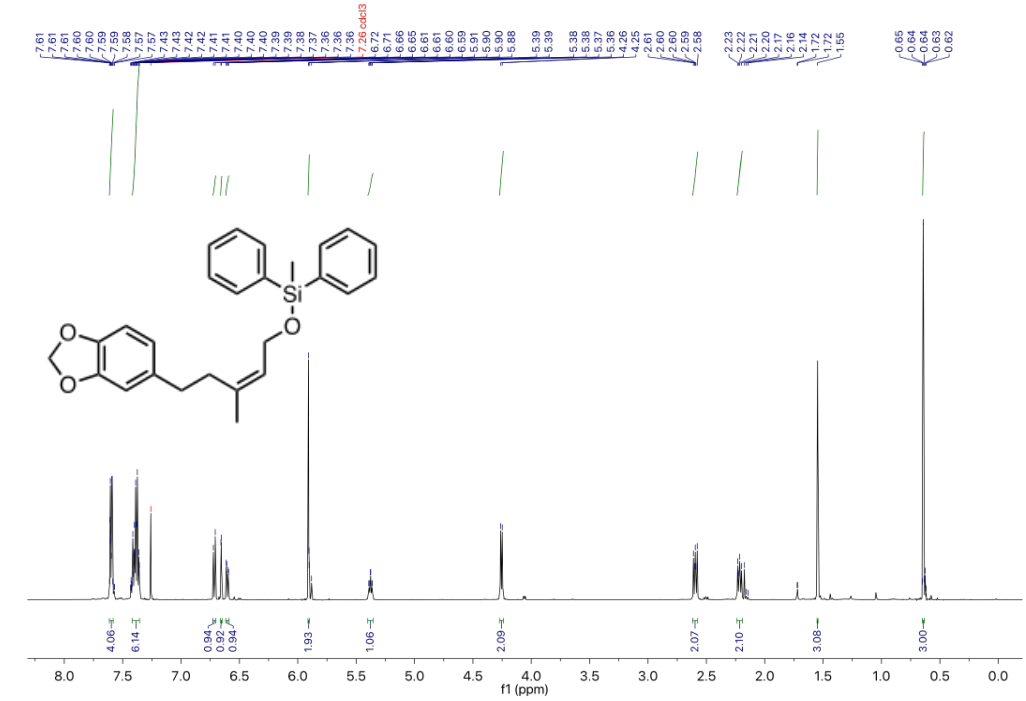
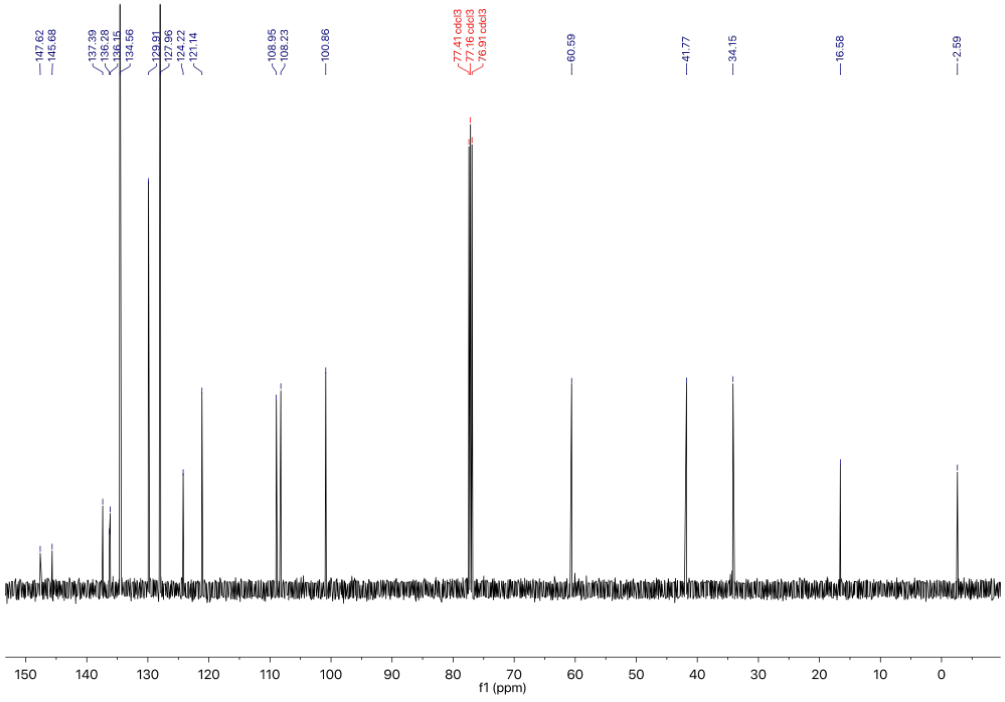
25.80
23.57
17.76
-2.59
f1 (ppm)


Si
O
O
O
f1 (ppm)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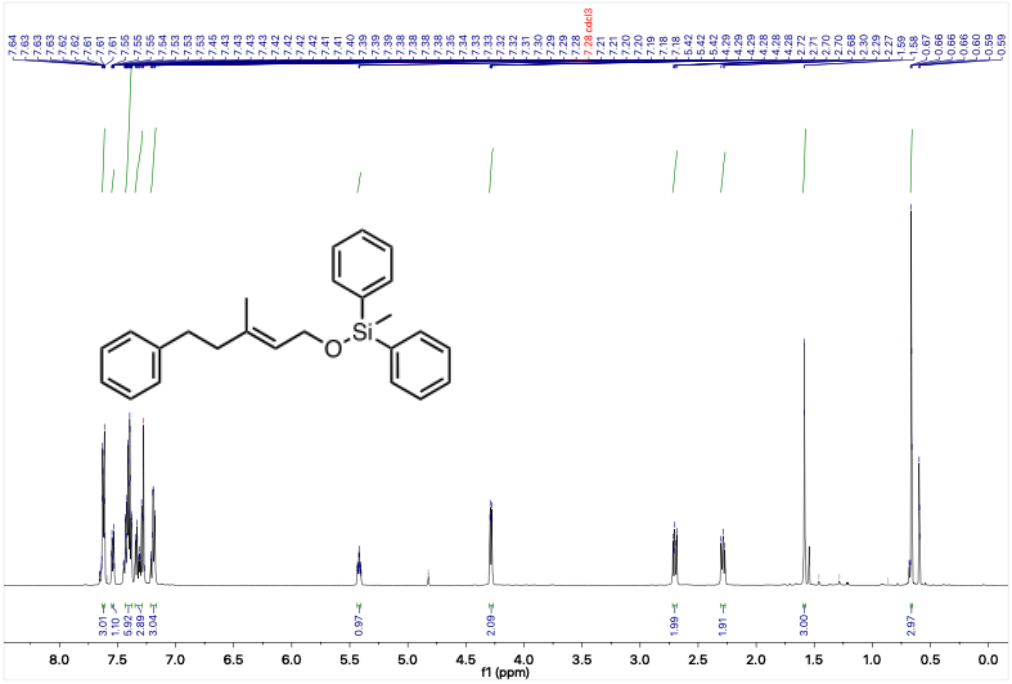
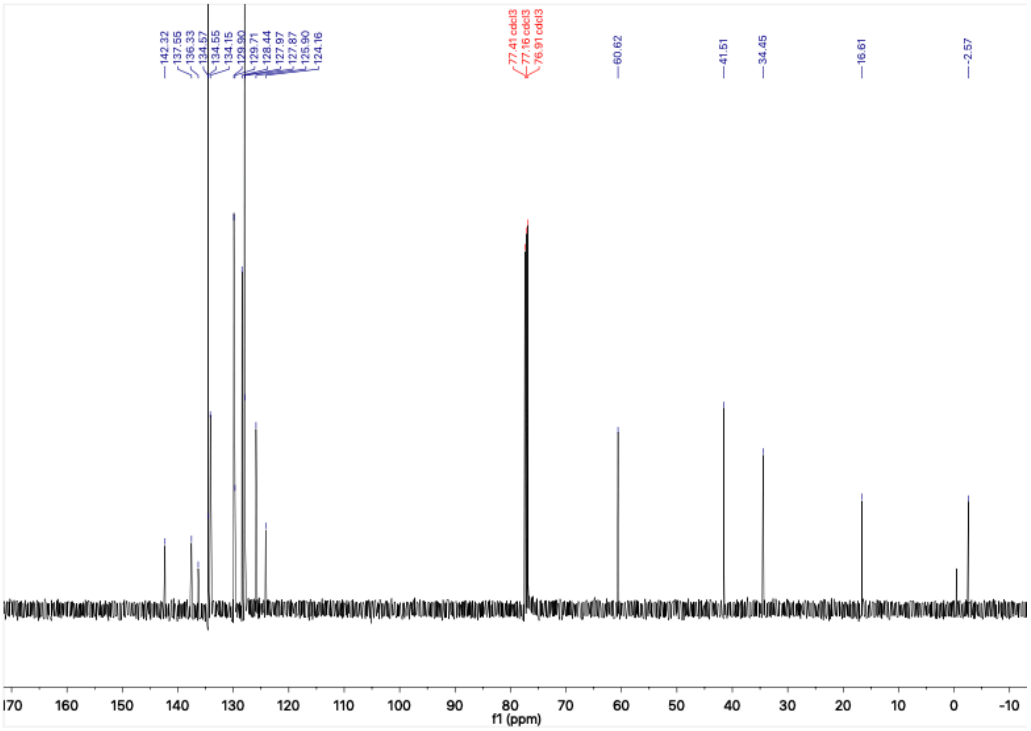
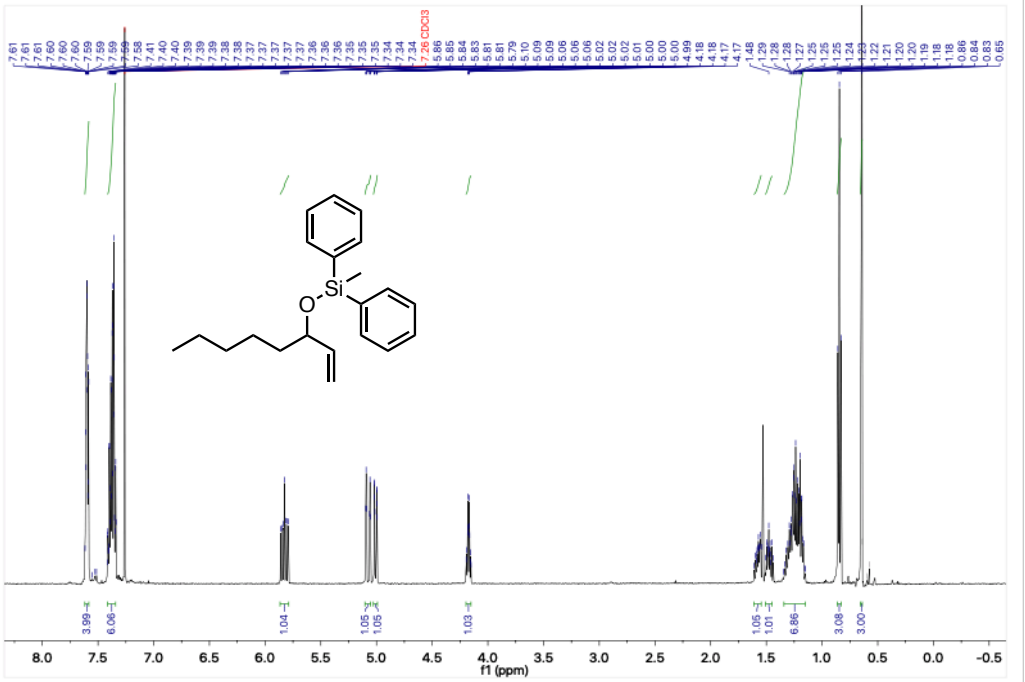
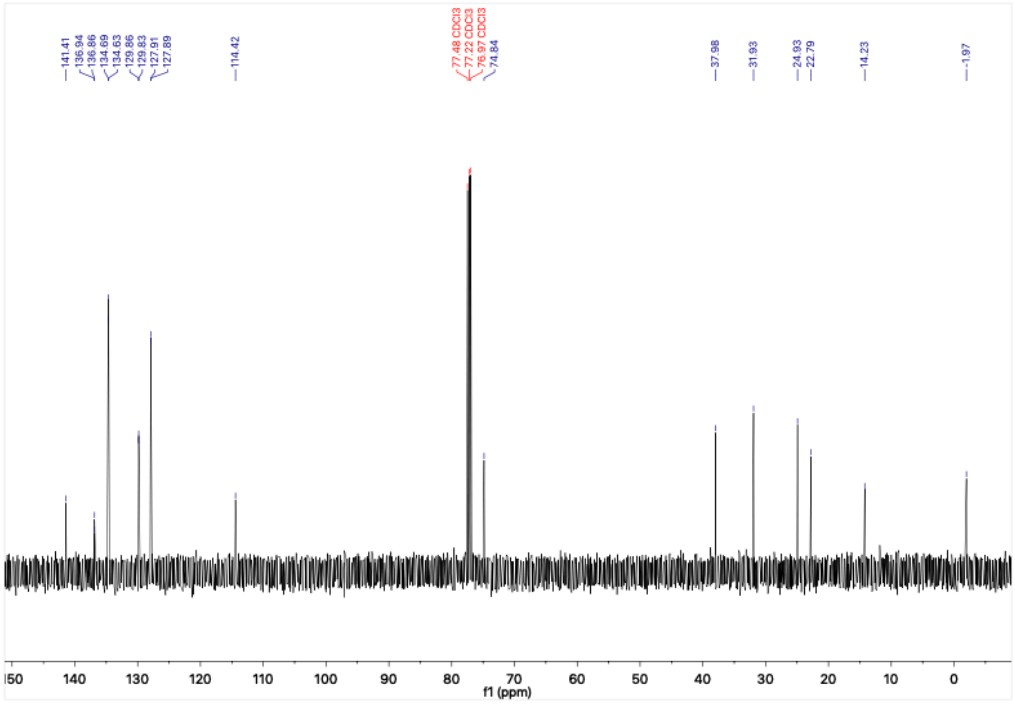
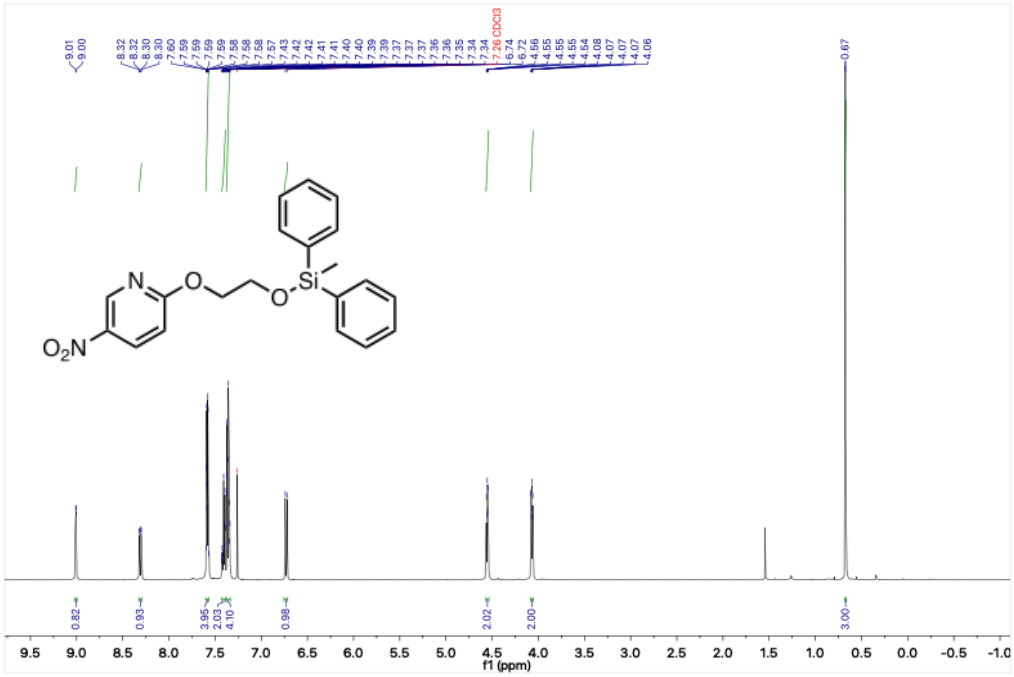

Si
O
f1 (ppm)


f1 (ppm)


O
Si
f1 (ppm)


f1 (ppm)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8.32
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8.30
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7.59
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7.59
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7.58
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7.57
7.43
7.42
7.42
7.41
7.41
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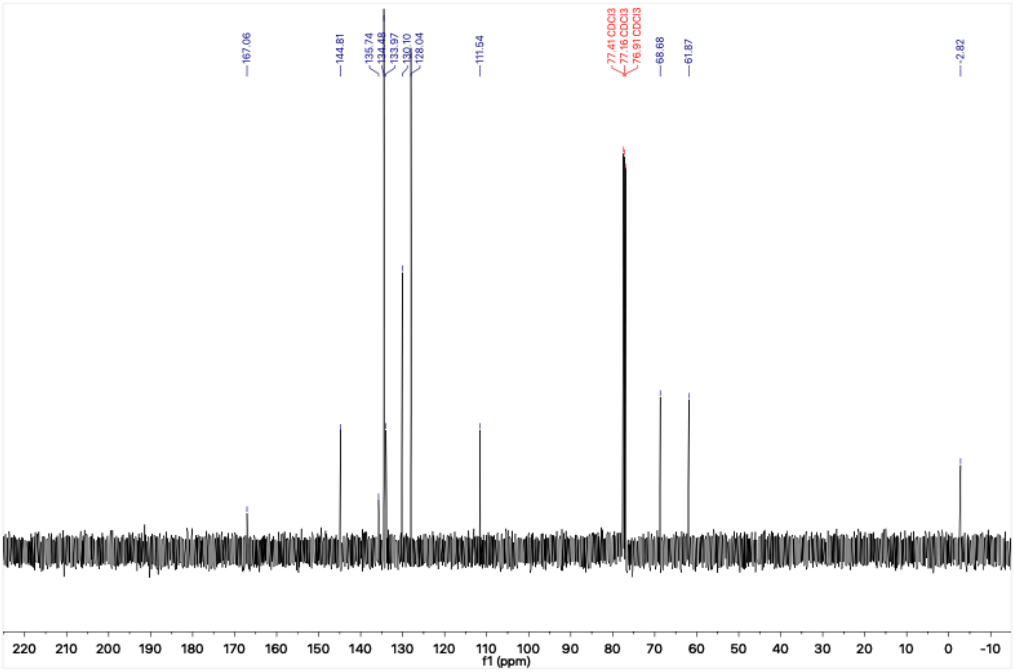
7.40
7.39
7.39
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
6.74
6.72
4.56
4.55
4.55
4.55
4.54
4.08
4.07
4.07
4.07
4.06
0.67
N
O
O
Si
O2N
0.82
0.93
3.95
2.03
4.10
0.98
2.02
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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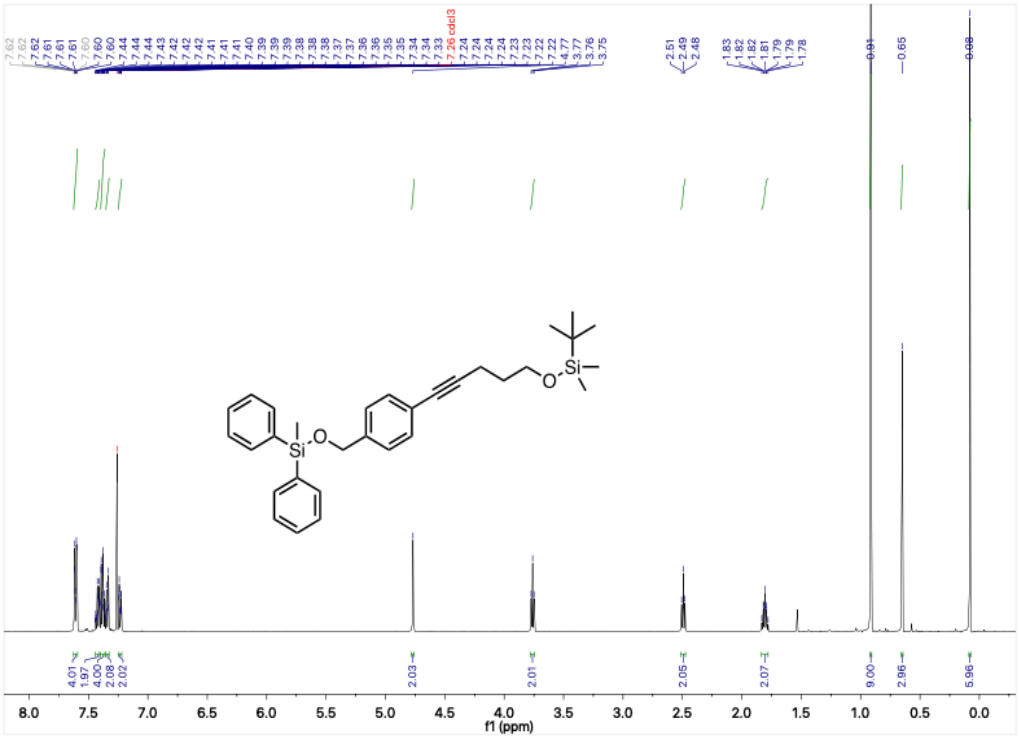
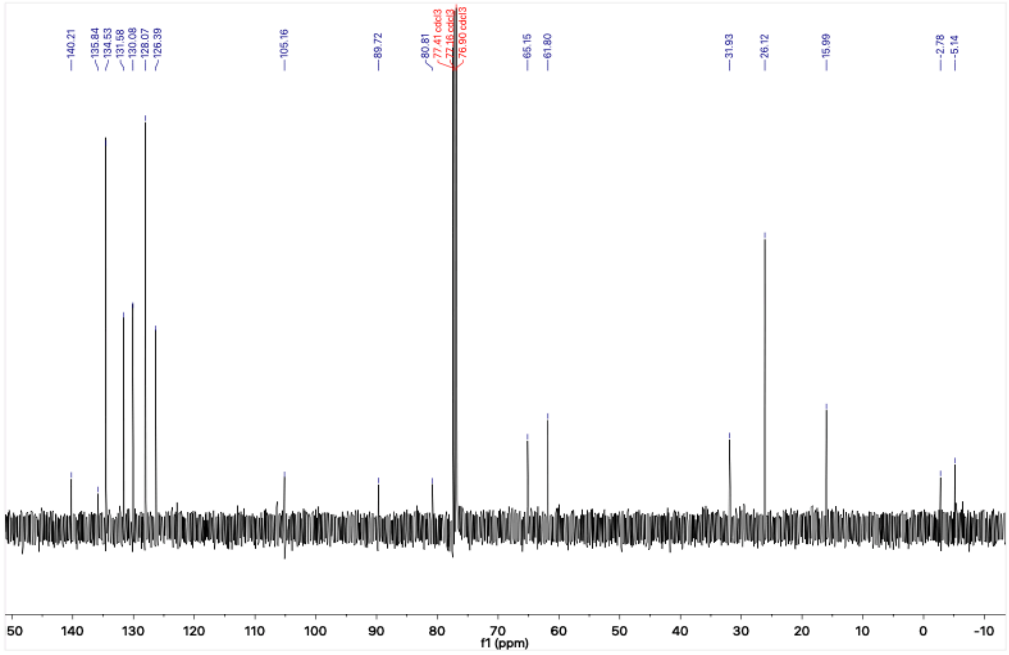
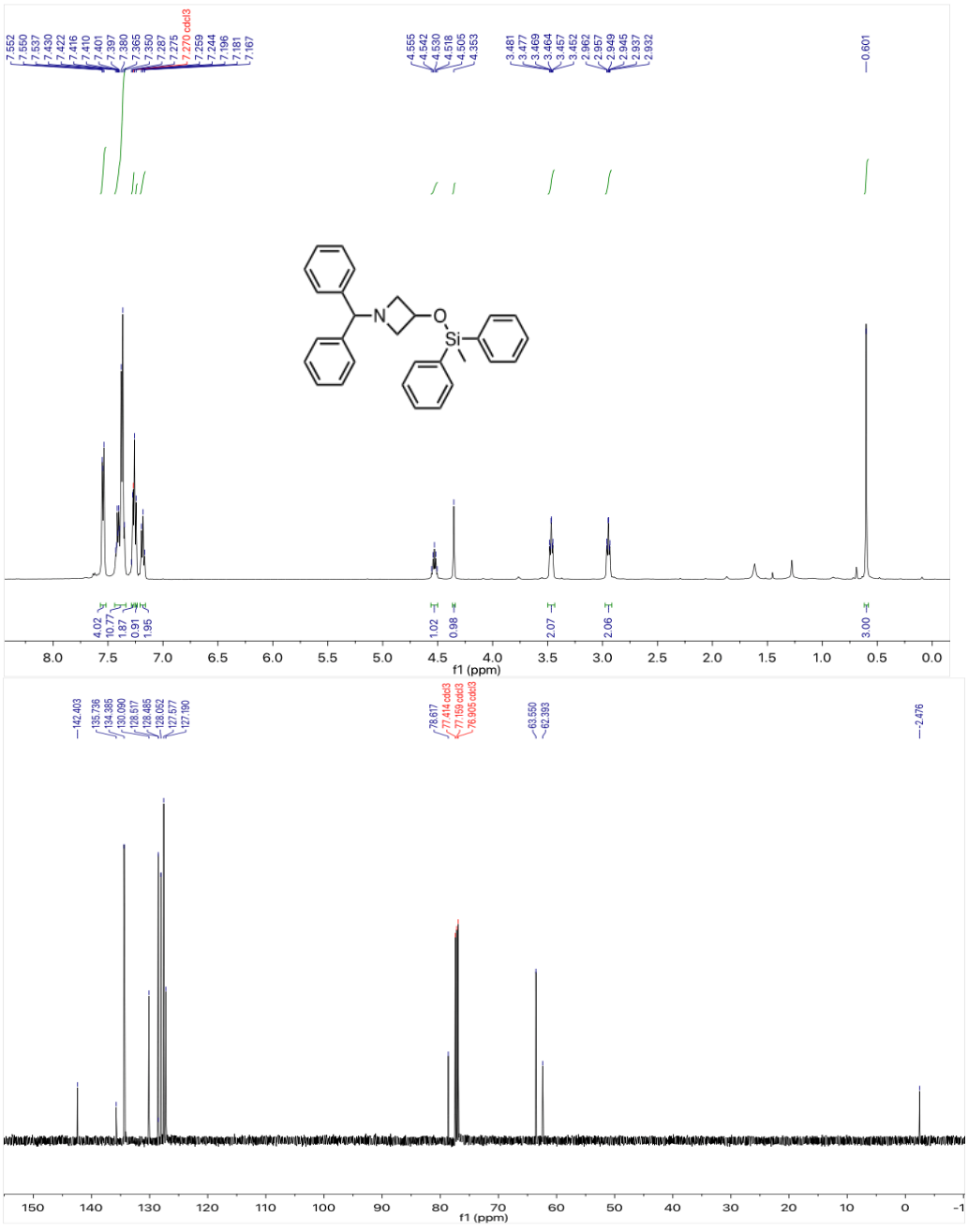
134.48
133.97
130.10
128.04
111.54
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.68
61.87
2.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


f1 (ppm)


f1 (ppm)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7.401
7.397
7.380
7.365
7.350
7.287
7.275
7.270 cdcl3
7.259
7.244
7.196
7.181
7.167
4.555
4.542
4.530
4.518
4.505
4.353
3.481
3.477
3.469
3.464
3.457
3.452
2.962
2.957
2.949
2.945
2.937
2.932
0.601
N
O
Si
4.02
10.77
1.87
0.91
1.95
1.02
0.98
2.07
2.06
3.00
f1 (ppm)
142.403
135.736
134.385
130.090
128.617
128.465
128.052
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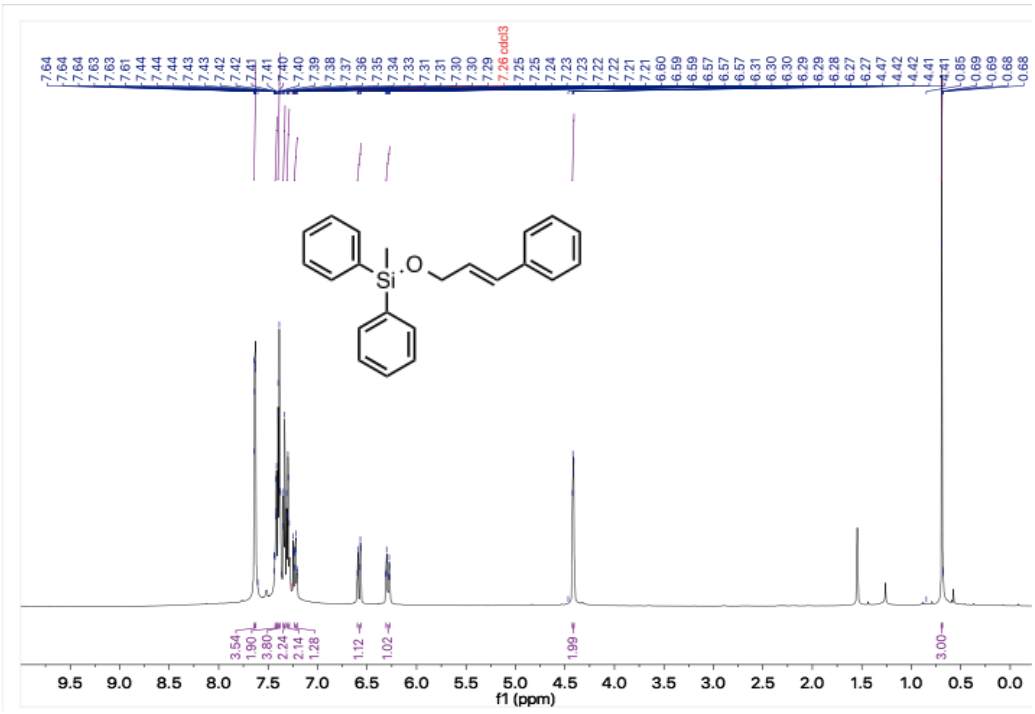
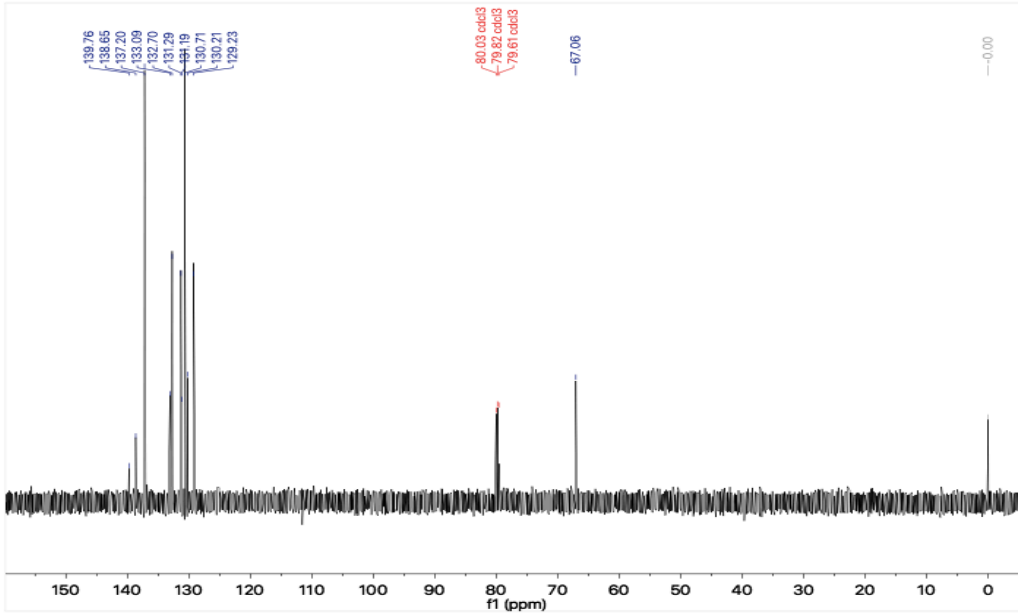
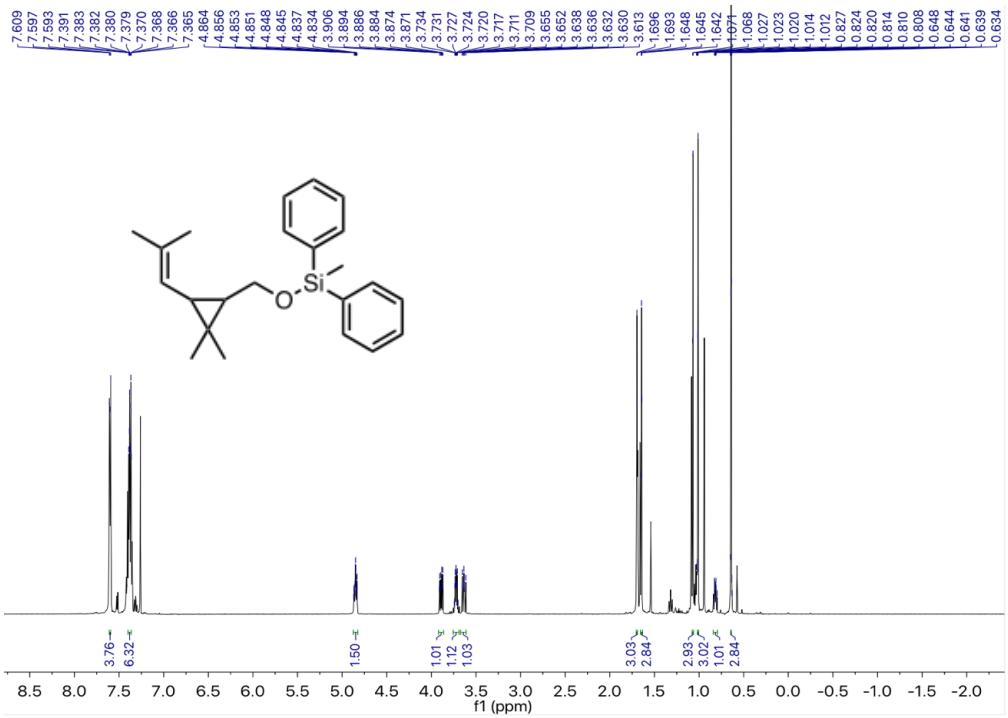
77.159 cdcl3
76.905 cdcl3
63.550
62.393
2.476
f1 (ppm)


7.64 7.64 7.64 7.63 7.63 7.61 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.31 7.31 7.30 7.30 7.29 7.26 cdcl3 7.25 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.21 6.60 6.59 6.59 6.57 6.57 6.31 6.30 6.30 6.29 6.29 6.28 6.27 6.27 4.47 4.42 4.42 4.41 4.41 0.85 0.69 0.69 0.68 0.68
Si
O
3.54 1.90 3.80 2.24 2.14 1.28 1.12 1.02 1.99 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


139.76 138.65 137.20 133.09 132.70 131.29 131.19 130.71 130.21 129.23
80.03 cdcl3 79.82 cdcl3 79.61 cdcl3
67.06
0.00
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.853
4.851
4.848
4.845
4.837
4.834
3.906
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3.886
3.884
3.874
3.871
3.734
3.731
3.727
3.724
3.720
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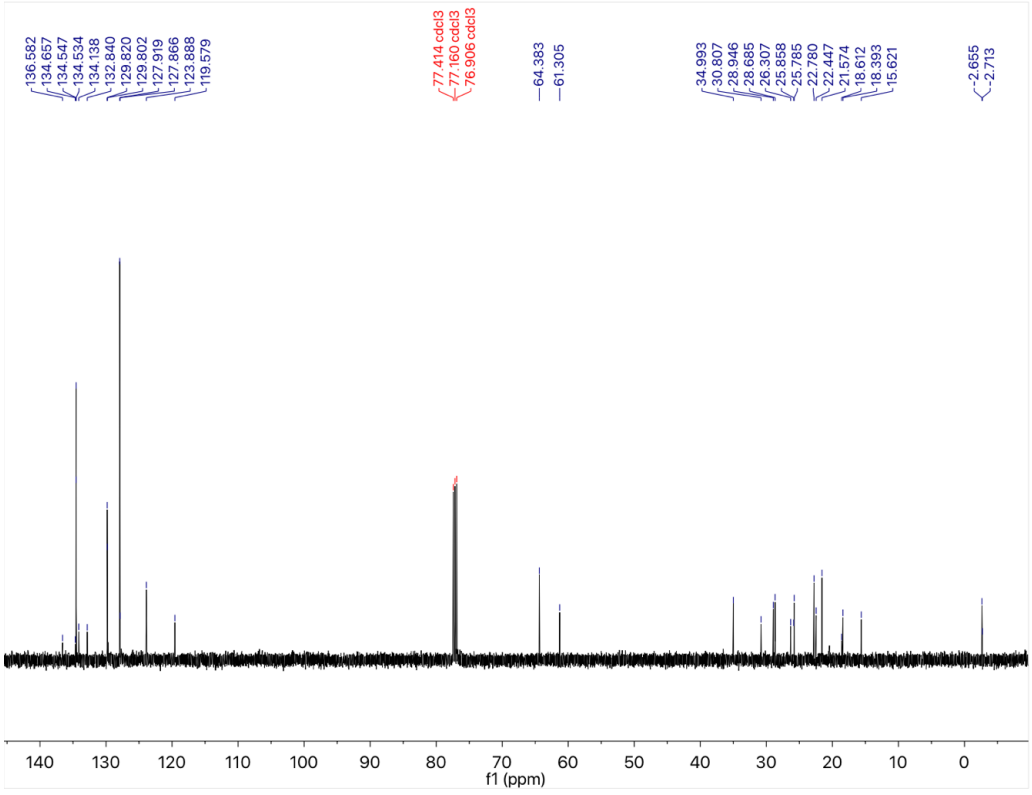
1.648
1.645
1.642
1.071
1.068
1.027
1.023
1.020
1.014
1.012
0.827
0.824
0.820
0.814
0.810
0.808
0.648
0.644
0.641
0.639
0.634
Si
O
3.76
6.32
1.50
1.01
1.12
1.03
3.03
2.84
2.93
3.02
1.01
2.84
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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132.840
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129.802
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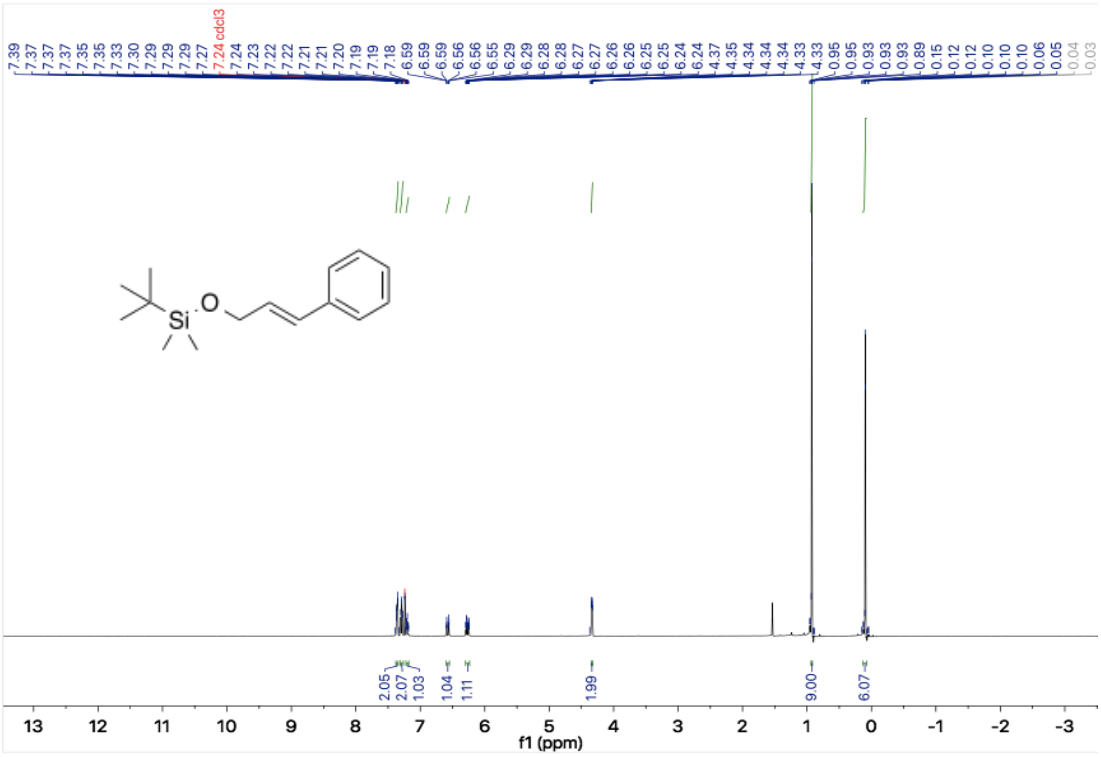
123.888
119.579
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
64.383
61.305
34.993
30.807
28.946
28.685
26.307
25.858
25.785
22.780
22.447
21.574
18.612
18.393
15.621
-2.655
-2.713
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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Si
O
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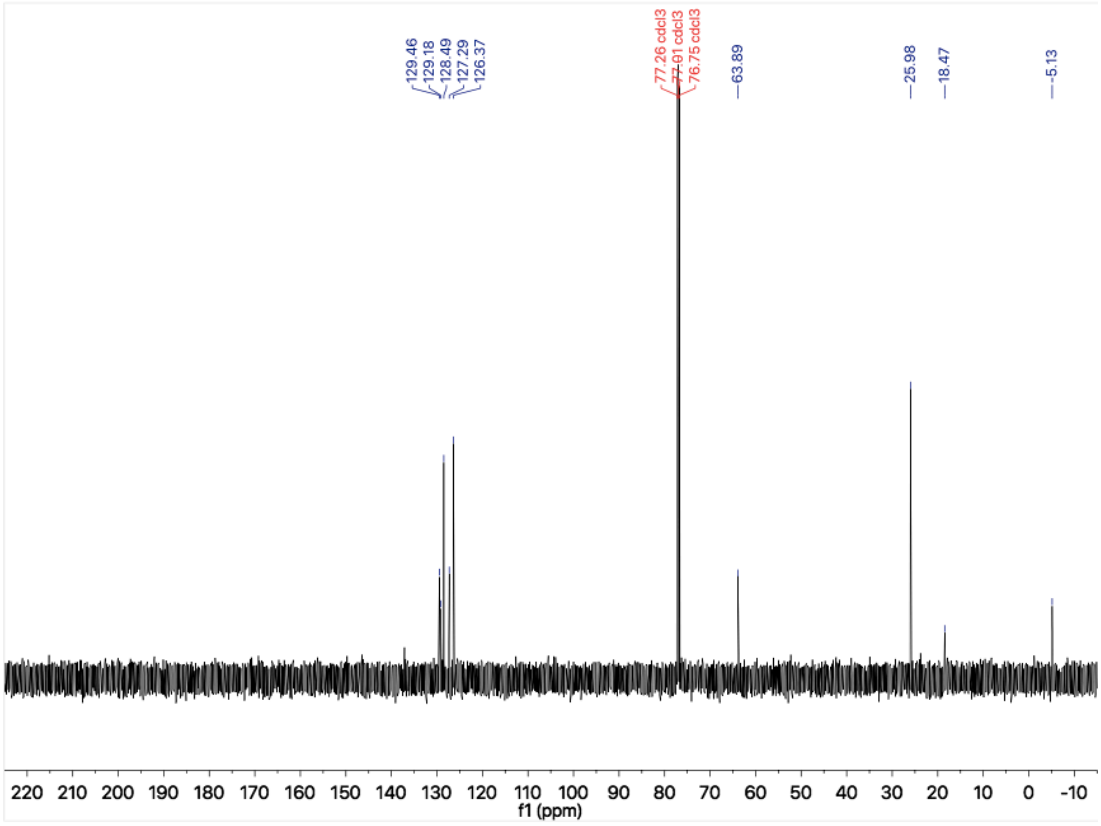
f1 (ppm)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77.26 cdcl3 77.01 cdcl3 76.75 cdcl3
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25.98
18.47
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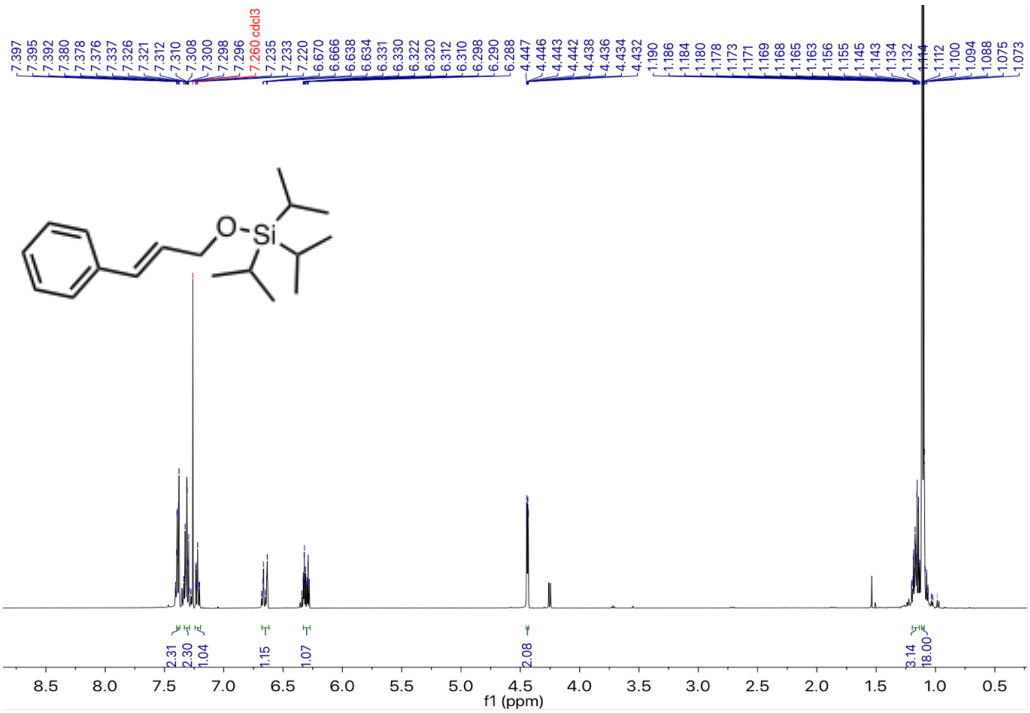
f1 (ppm)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7.300
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7.296
7.260 cdcl3
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7.233
7.220
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6.666
6.638
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6.331
6.330
6.322
6.320
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6.310
6.298
6.290
6.288
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4.446
4.443
4.442
4.438
4.436
4.434
4.432
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1.186
1.184
1.180
1.178
1.173
1.171
1.169
1.168
1.165
1.163
1.156
1.155
1.145
1.143
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1.132
1.114
1.112
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1.094
1.088
1.075
1.073
O
Si
2.31
2.30
1.04
1.15
1.07
2.08
3.14
18.00
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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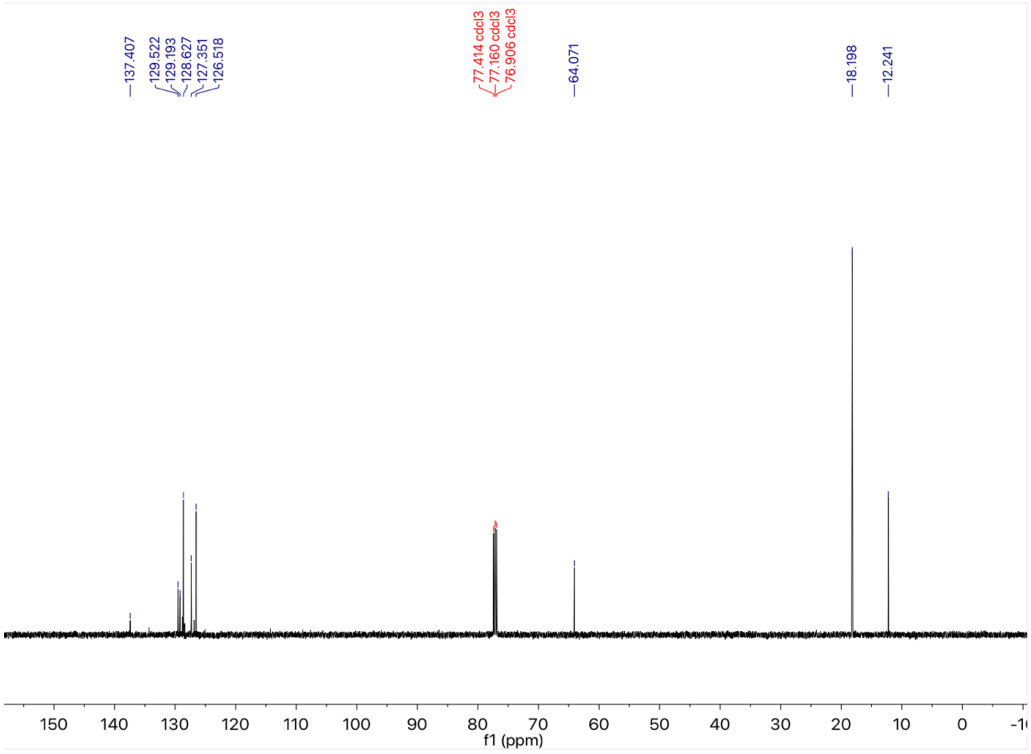
f1 (ppm)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50
40
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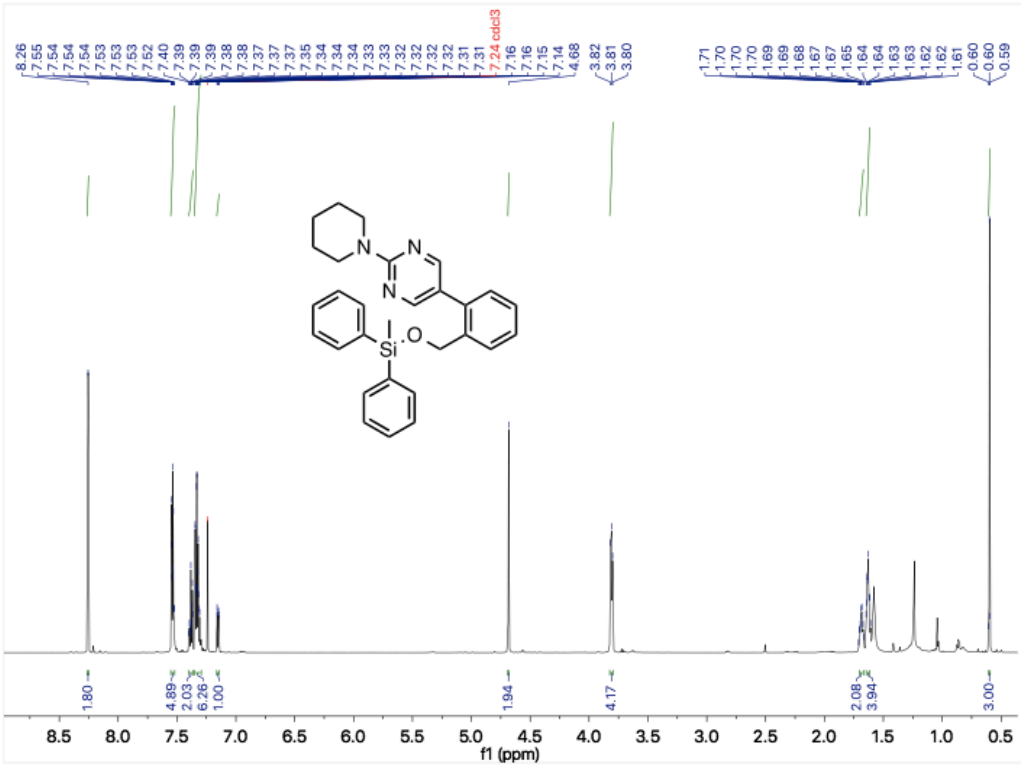
f1 (ppm)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7.38
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7.35
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7.33
7.33
7.32
7.32
7.32
7.32
7.31
7.31
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7.16
7.15
7.14
4.68
3.82
3.81
3.80
1.71
1.70
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
0.60
0.60
0.59
N
N
N
Si
O
1.80
4.89
2.03
6.26
1.00
1.94
4.17
2.08
3.94
3.00
8.5
8.0
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6.0
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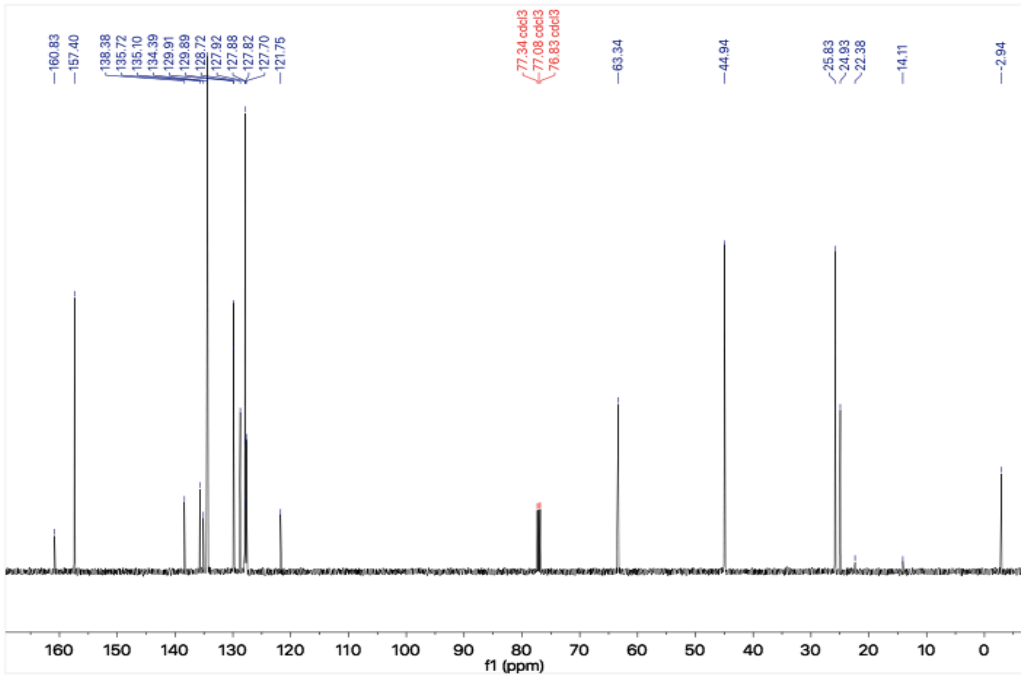
f1 (ppm)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127.92
127.88
127.82
127.70
121.75
77.34 cdcl3
77.08 cdcl3
76.83 cdcl3
63.34
44.94
25.83
24.93
22.38
14.11
2.94
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90
80
70
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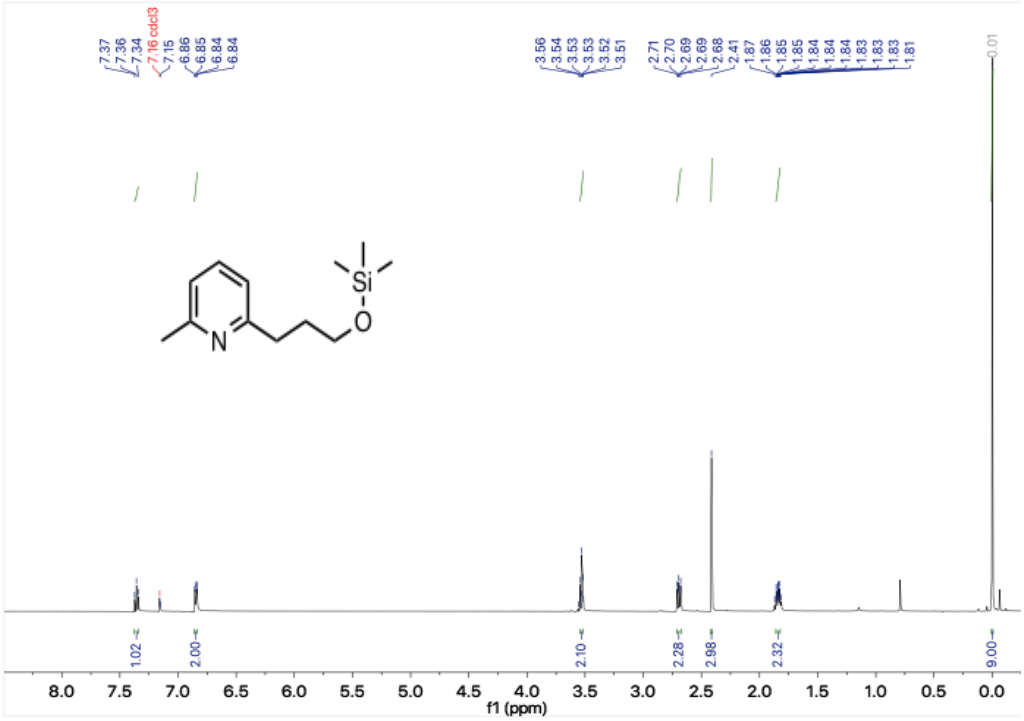
50
40
30
20
10
0
f1 (ppm)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6.84
3.56
3.54
3.53
3.53
3.52
3.51
2.71
2.70
2.69
2.69
2.68
2.41
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.83
1.81
0.01
Si
O
N
1.02
2.00
2.10
2.28
2.98
2.32
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
1.5
1.0
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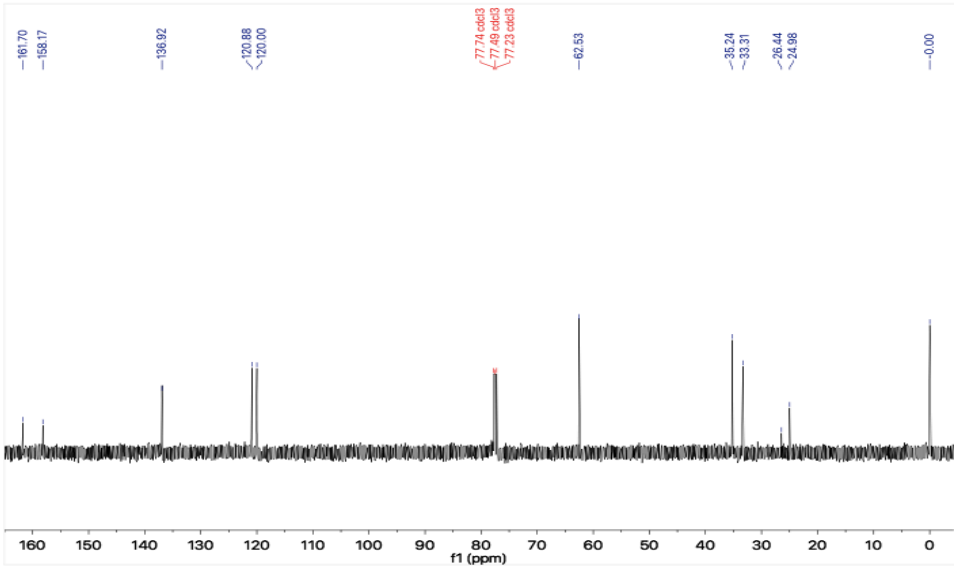
0.0
f1 (ppm)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158.17
136.92
120.88
120.00
77.74 cdcl3
77.49 cdcl3
77.23 cdcl3
62.53
35.24
33.31
26.44
24.98
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120
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90
80
70
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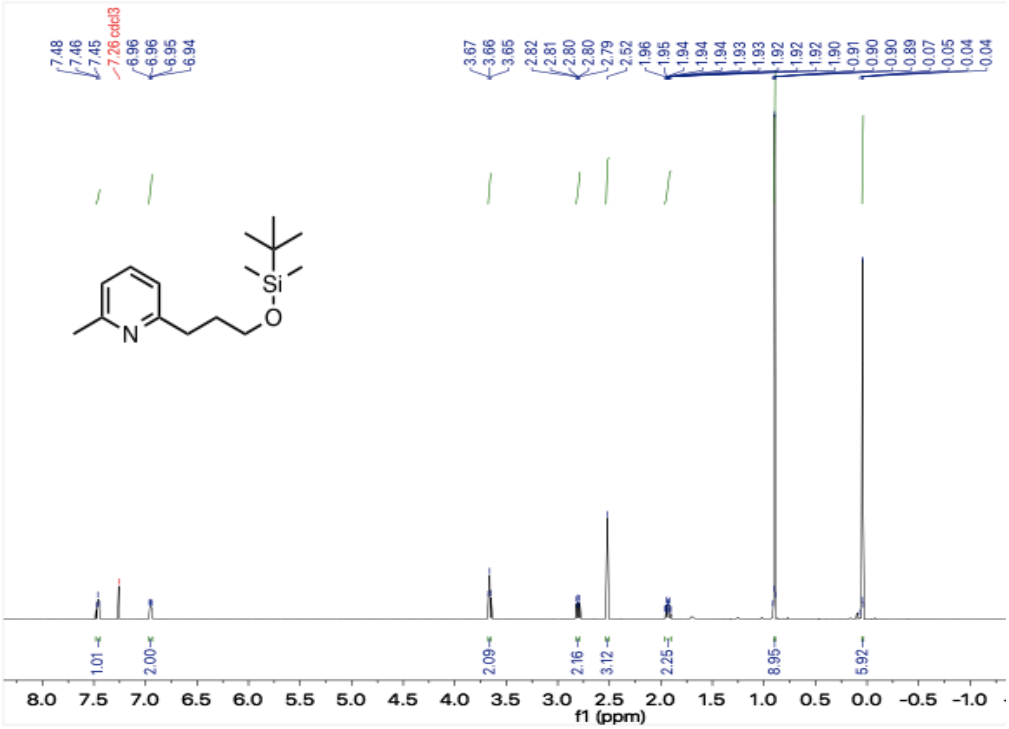
50
40
30
20
10
0
f1 (ppm)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6.96
6.95
6.94
3.67
3.66
3.65
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1.95
1.94
1.94
1.94
1.93
1.93
1.92
1.92
1.92
1.90
0.91
0.90
0.90
0.89
0.07
0.05
0.04
0.04
Si
O
N
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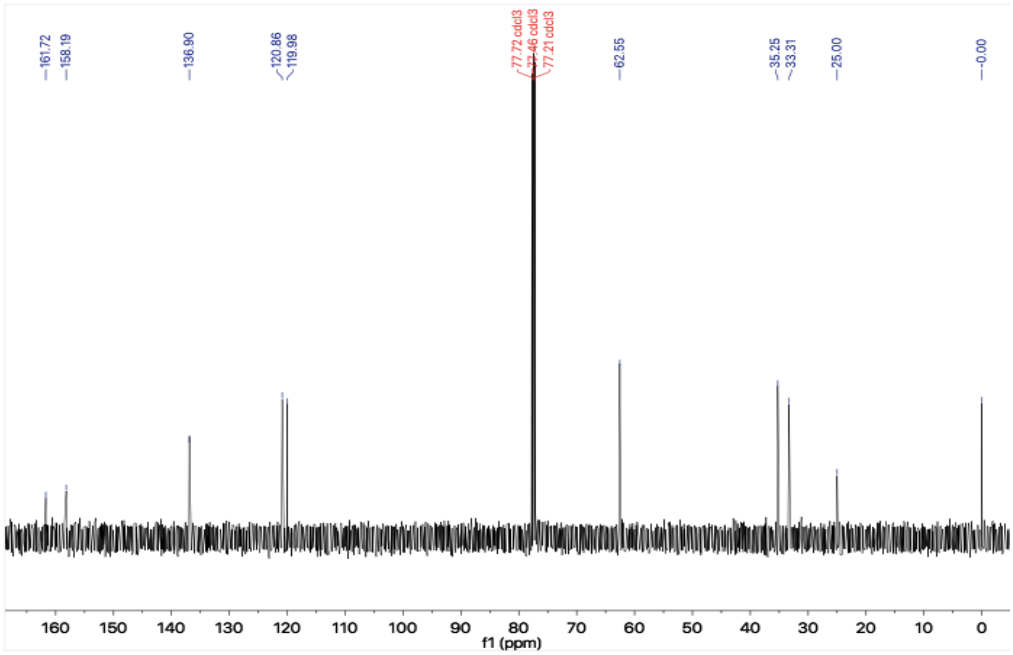
2.00
2.09
2.16
3.12
2.25
8.95
5.92
f1 (ppm)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120.86
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77.72 cdcl3
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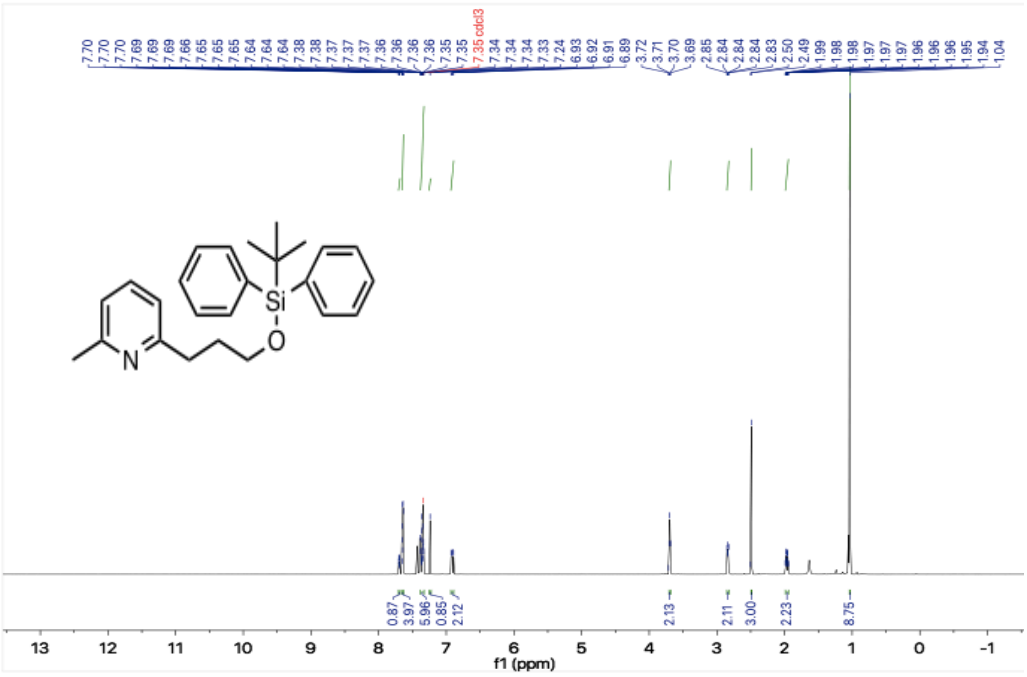
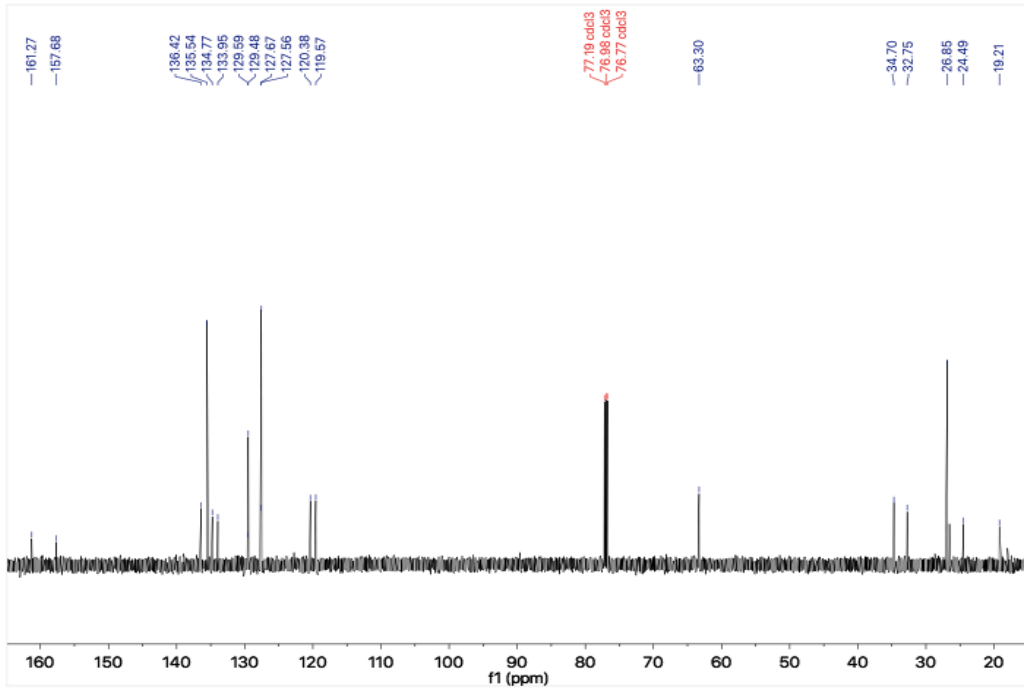
77.21 cdcl3
62.55
35.25
33.31
25.00
0.00
f1 (ppm)


Si
O
N
f1 (ppm)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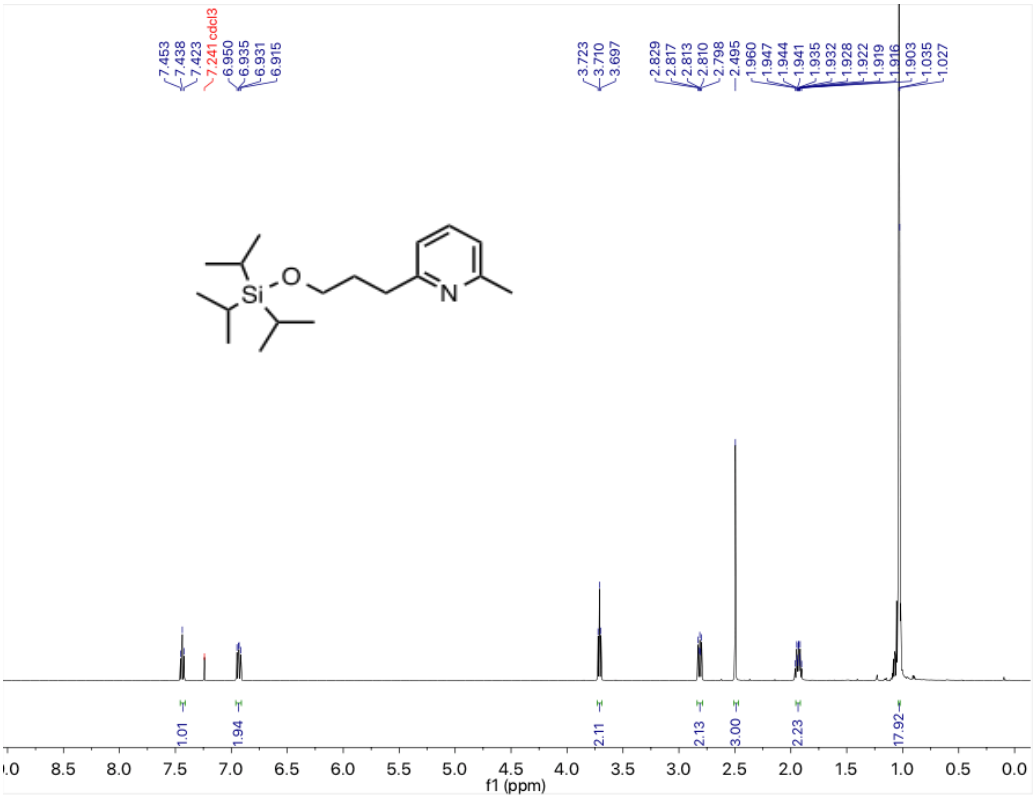
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3.697
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2.817
2.813
2.810
2.798
2.495
1.960
1.947
1.944
1.941
1.935
1.932
1.928
1.922
1.919
1.916
1.903
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O
N
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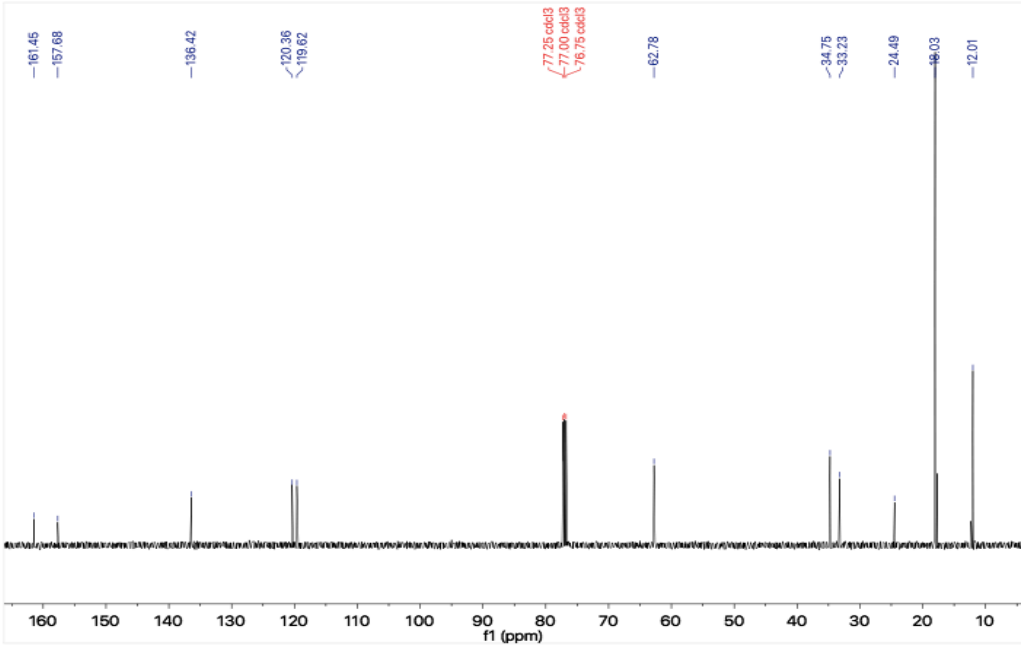
2.11
2.13
3.00
2.23
17.92
f1 (ppm)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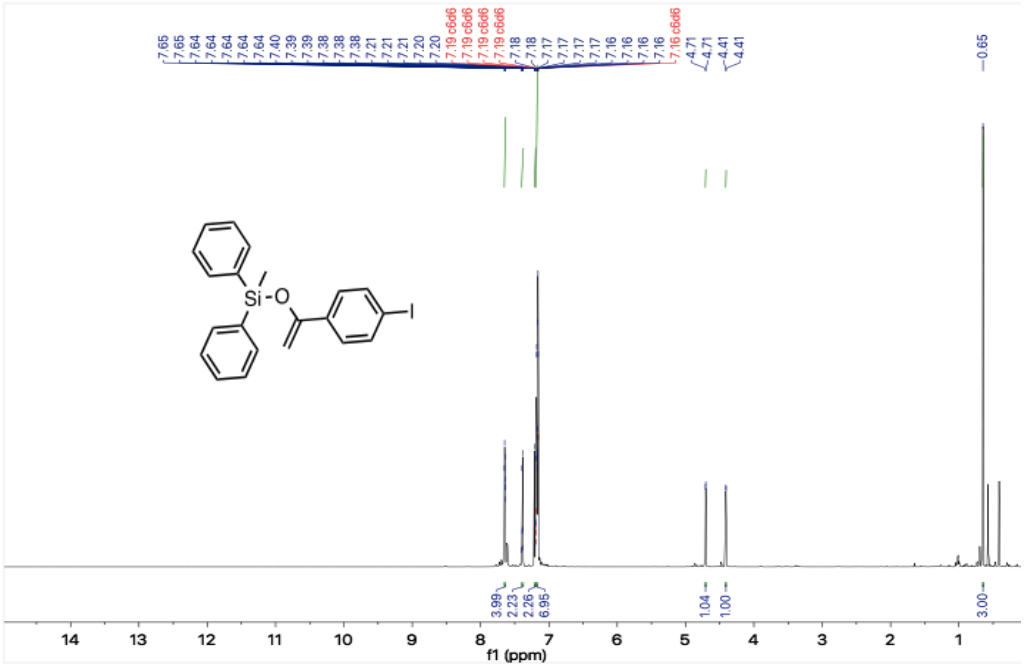
34.75
33.23
24.49
18.03
12.01
f1 (ppm)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7.20
7.19 c6d6
7.18
7.17
7.16
4.71
4.41
-0.65
Si
O
I
3.99
2.23
2.26
6.95
1.04
1.00
3.00
14
13
12
11
10
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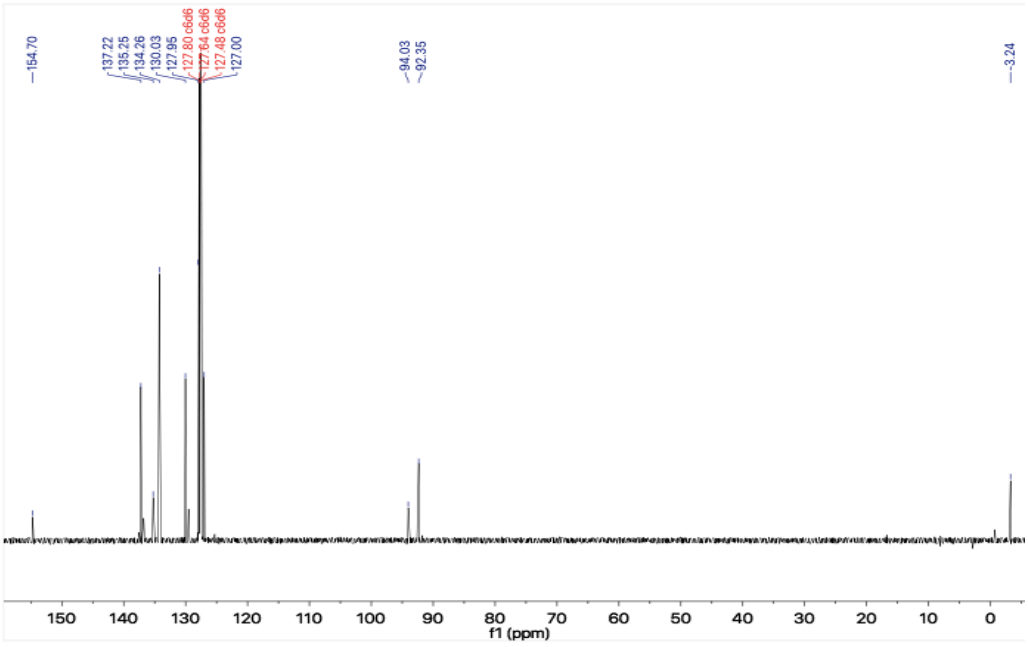
6
5
4
3
2
1
f1 (ppm)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135.25
134.26
130.03
127.95
127.80 c6d6
127.64 c6d6
127.48 c6d6
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94.03
92.35
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120
110
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90
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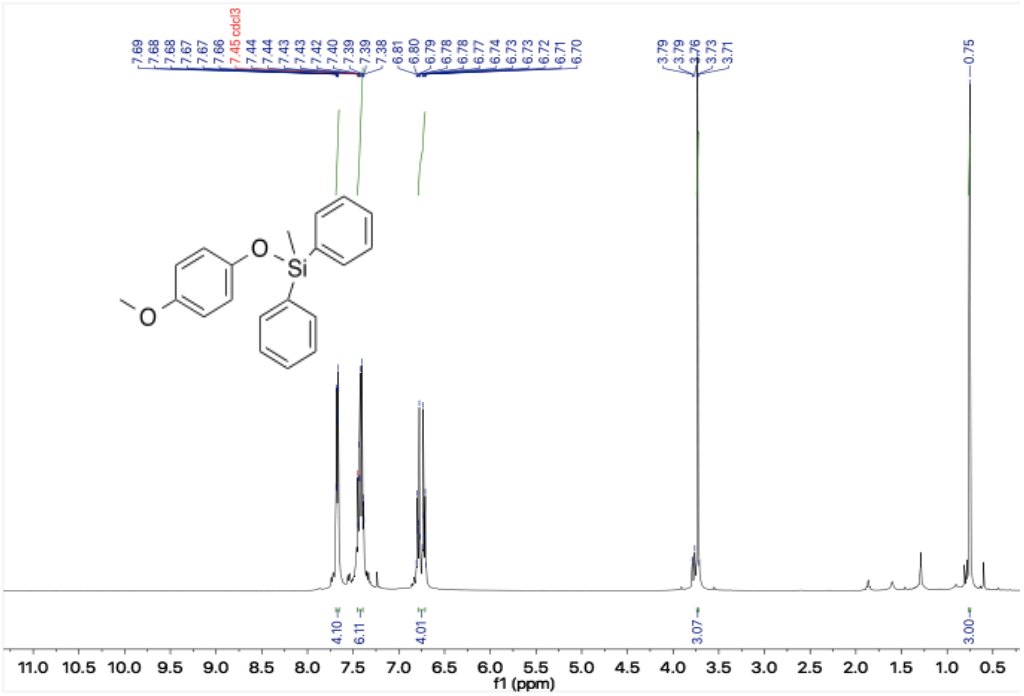
50
40
30
20
10
0
f1 (ppm)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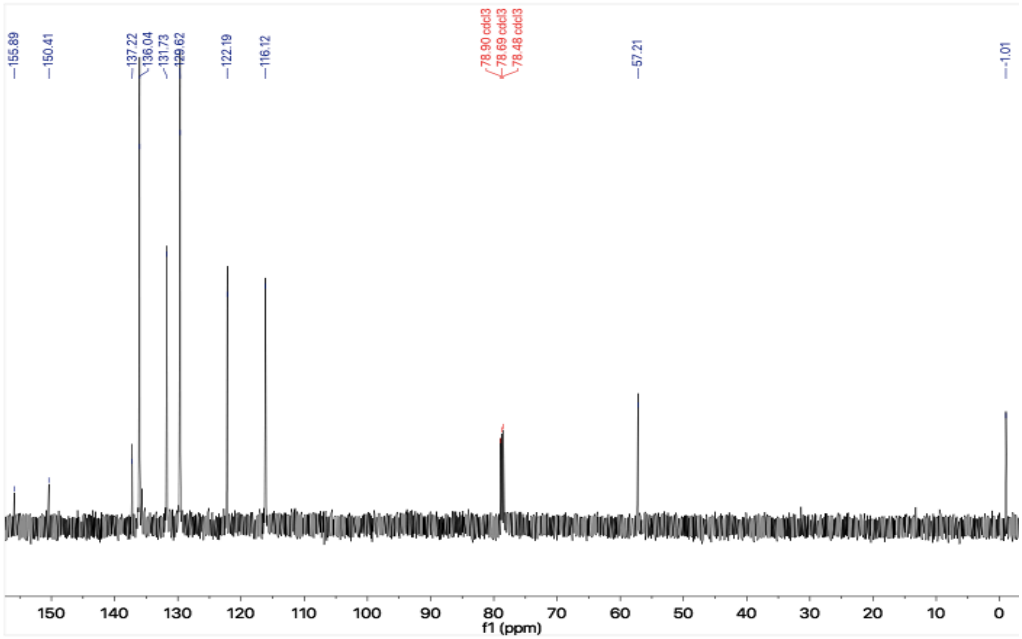
7.42
7.40
7.39
7.39
7.38
6.81
6.80
6.79
6.78
6.78
6.77
6.74
6.73
6.73
6.72
6.71
6.70
3.79
3.79
3.76
3.73
3.71
0.75
O
Si
O
4.10
6.11
4.01
3.07
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.62
122.19
116.12
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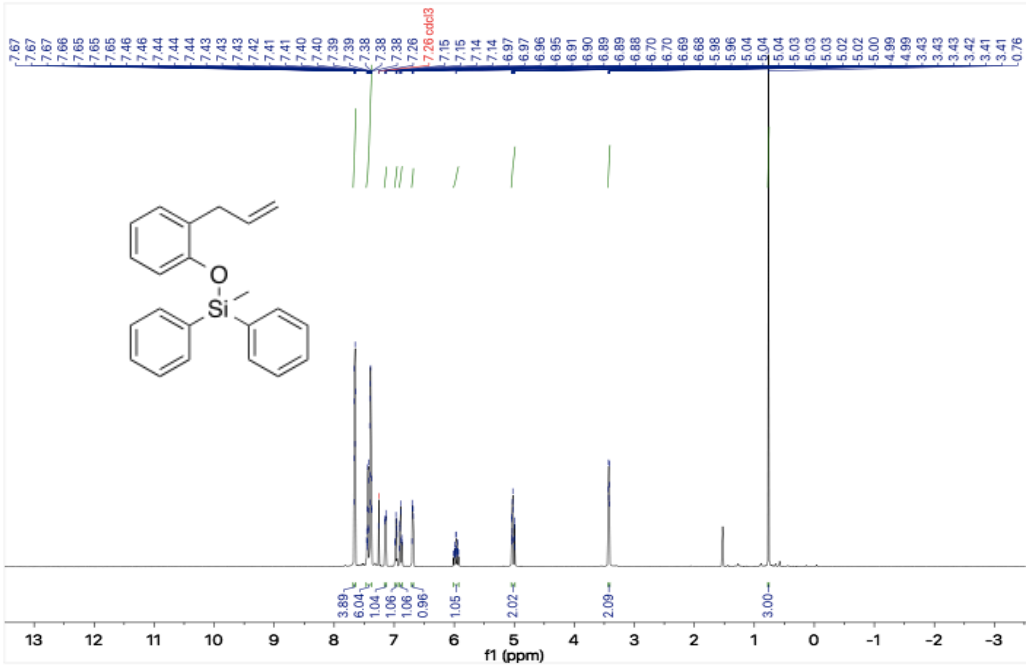
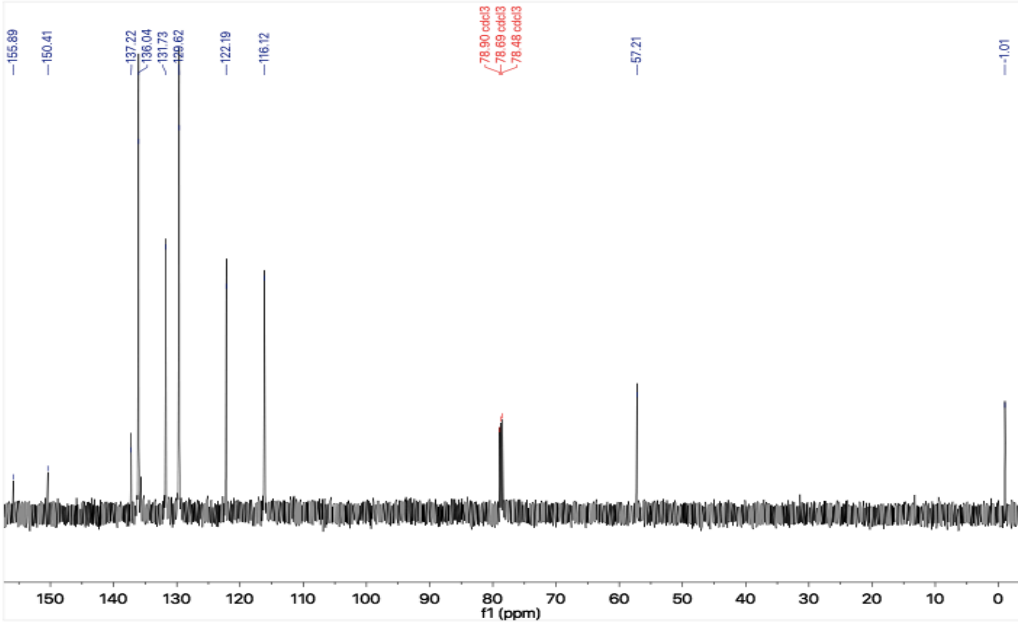
78.48 cdcl3
57.21
-1.01
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Si
f1 (ppm)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150.41
137.22
136.04
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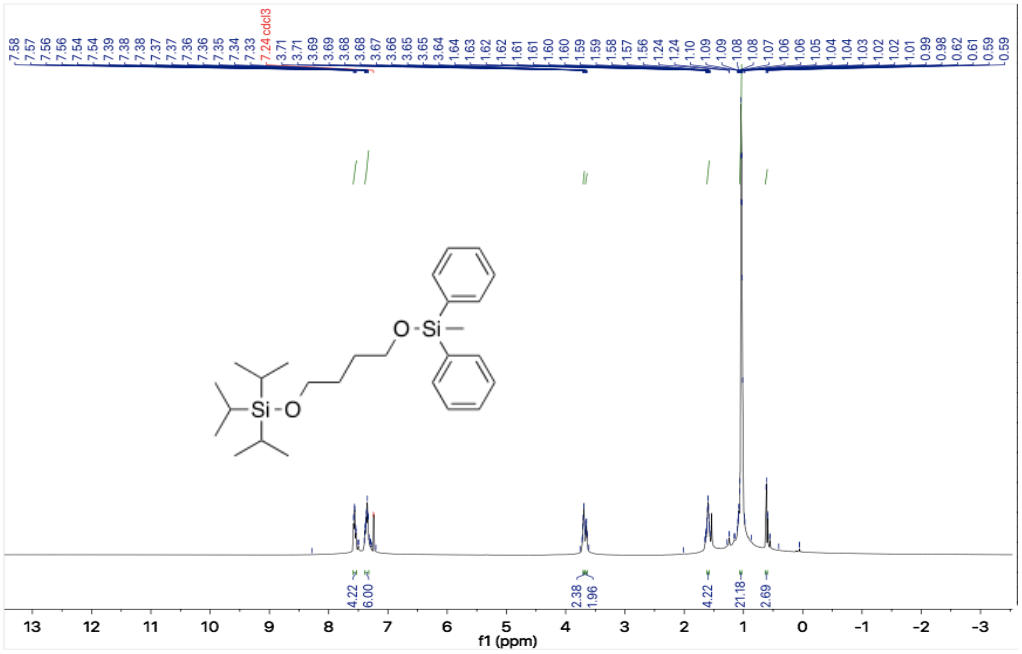
78.69 cdcl3
78.48 cdcl3
57.21
1.01
f1 (ppm)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O-Si
Si-O
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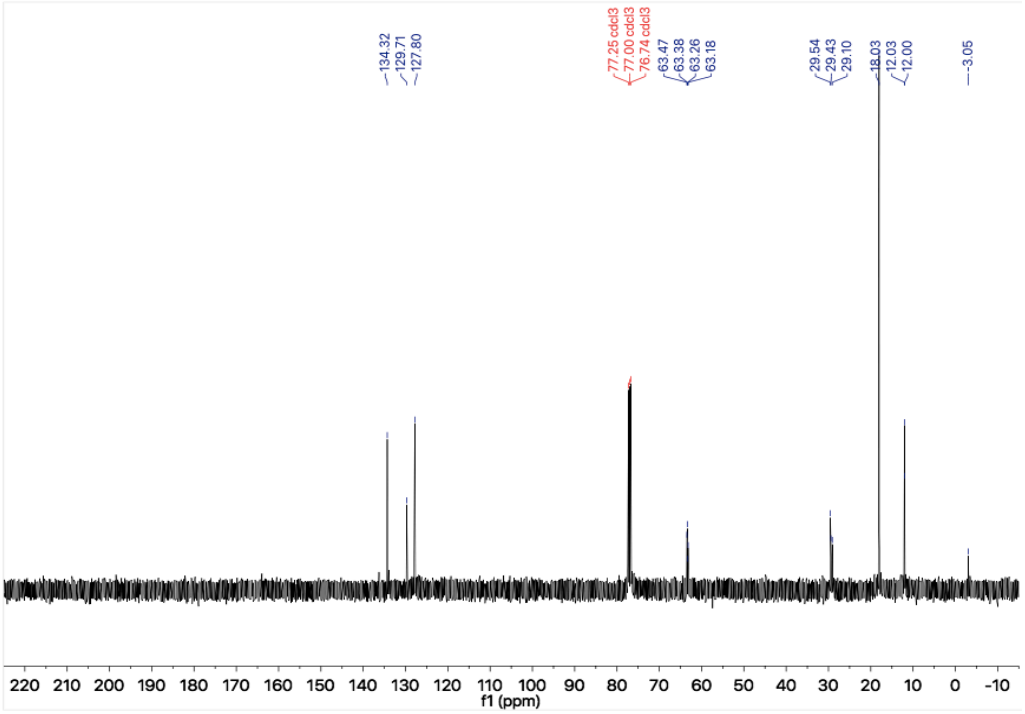
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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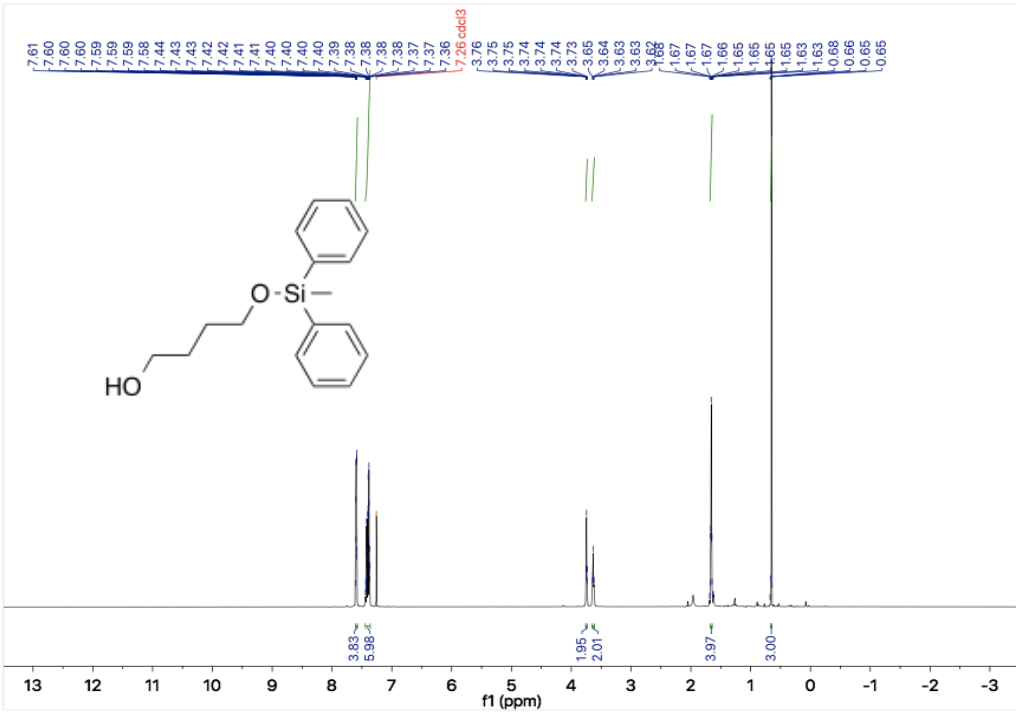
f1 (ppm)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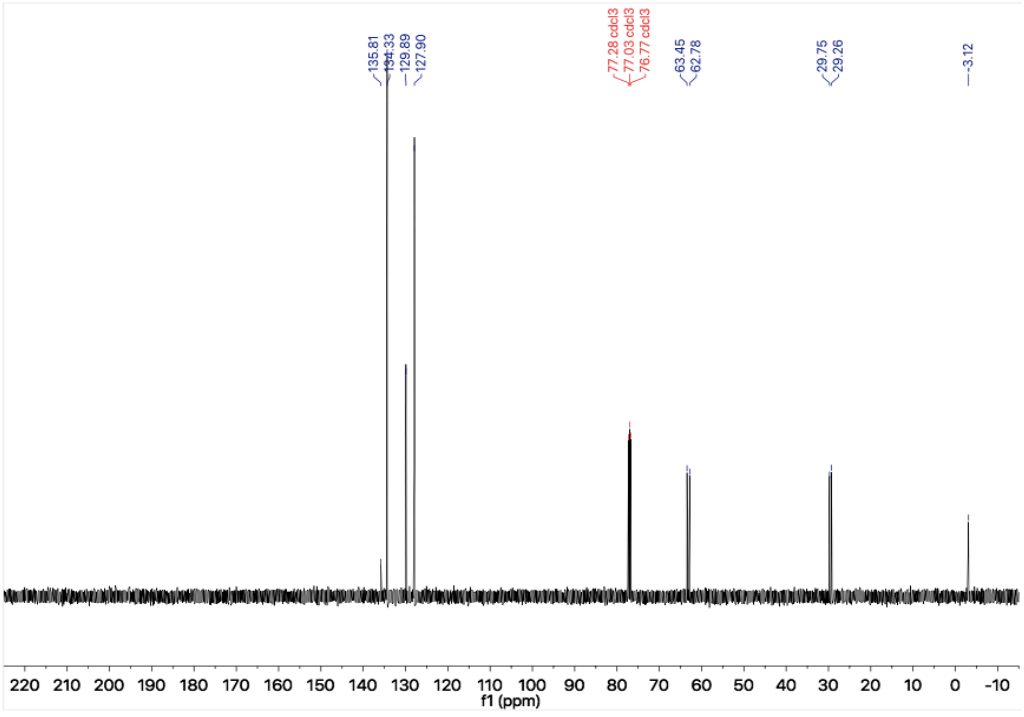
3.76 3.75 3.75 3.74 3.74 3.74 3.73 3.65 3.64 3.63 3.63 1.67 1.67 1.67 1.66 1.65 1.65 1.65 1.65 1.63 0.68 0.66 0.65 0.65
O-Si
HO
3.83 5.98 1.95 2.01 3.97 3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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77.28 cdcl3 77.03 cdcl3 76.77 cdcl3
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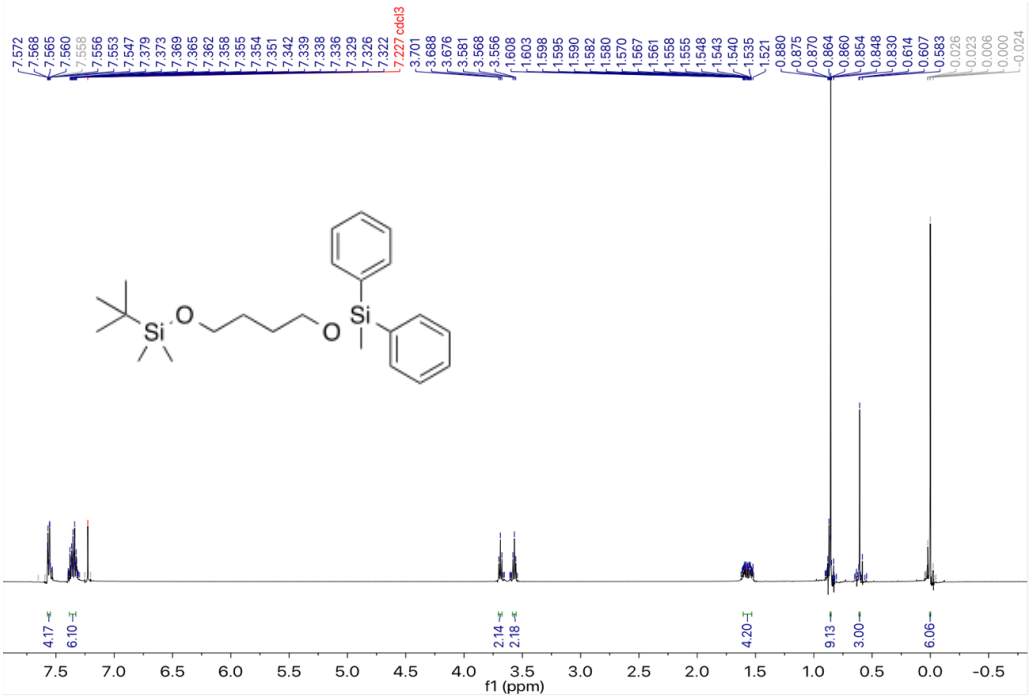
29.75 29.26
-3.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1.608
1.603
1.598
1.595
1.590
1.582
1.580
1.570
1.567
1.561
1.558
1.555
1.548
1.543
1.540
1.535
1.521
0.880
0.875
0.870
0.864
0.860
0.854
0.848
0.830
0.614
0.607
0.583
0.026
0.023
0.006
0.000
-0.024
Si
O
O
Si
4.17
6.10
2.14
2.18
4.20
9.13
3.00
6.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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1.0
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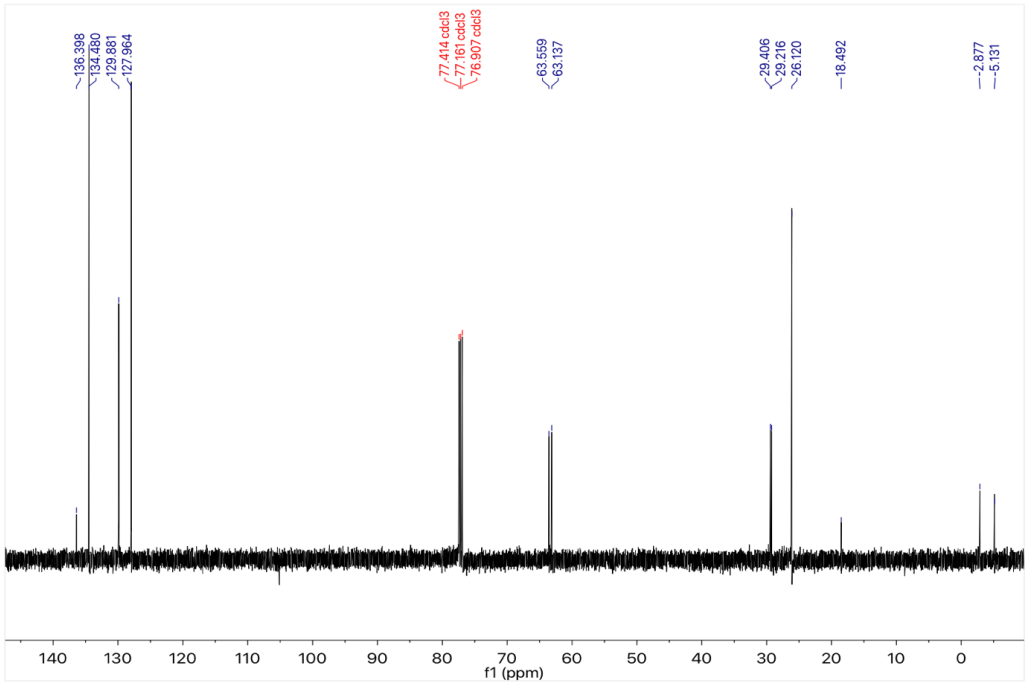
0.0
-0.5
f1 (ppm)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63.559
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29.406
29.216
26.120
18.492
-2.877
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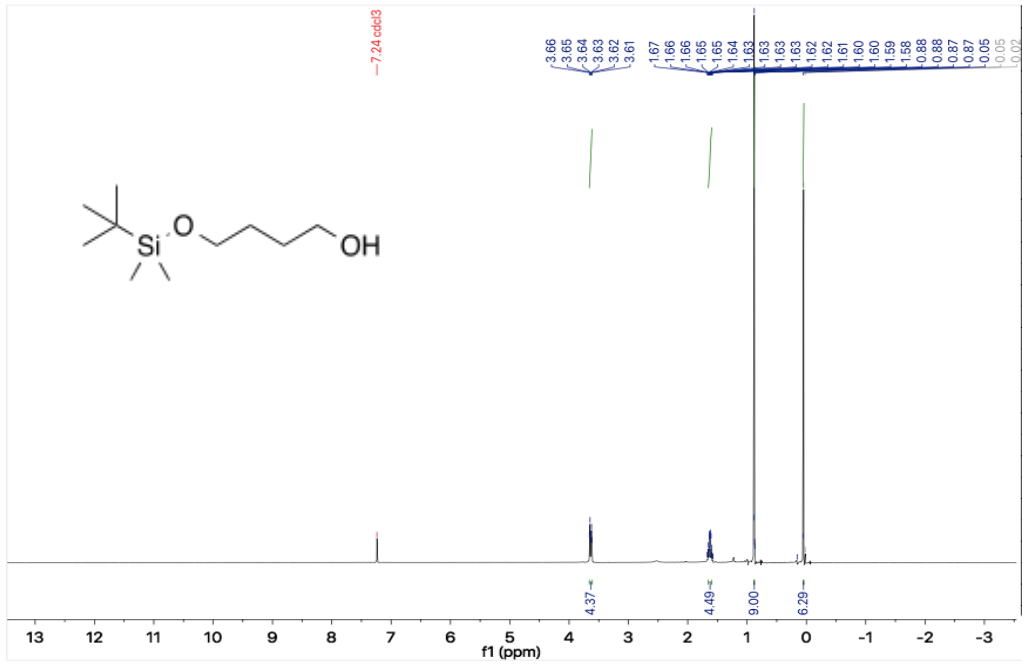
f1 (ppm)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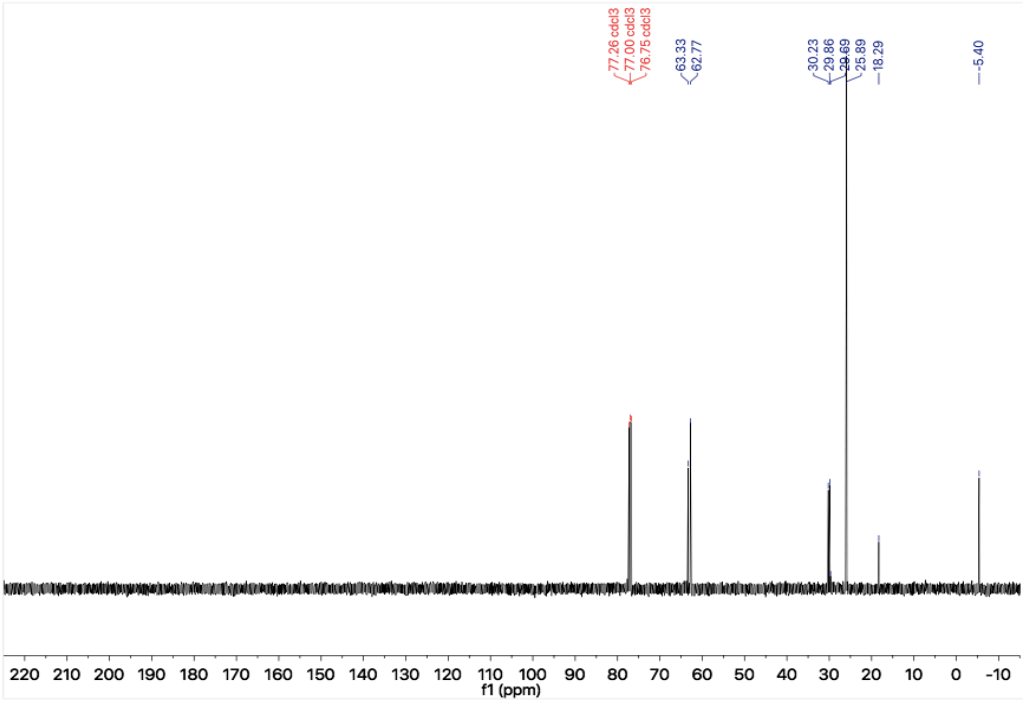
3.66
3.65
3.64
3.63
3.62
3.61
1.67
1.66
1.66
1.65
1.65
1.64
1.63
1.63
1.63
1.63
1.62
1.62
1.61
1.60
1.60
1.59
1.58
0.88
0.88
0.87
0.87
0.05
0.05
0.02
Si
O
OH
4.37
4.49
9.00
6.29
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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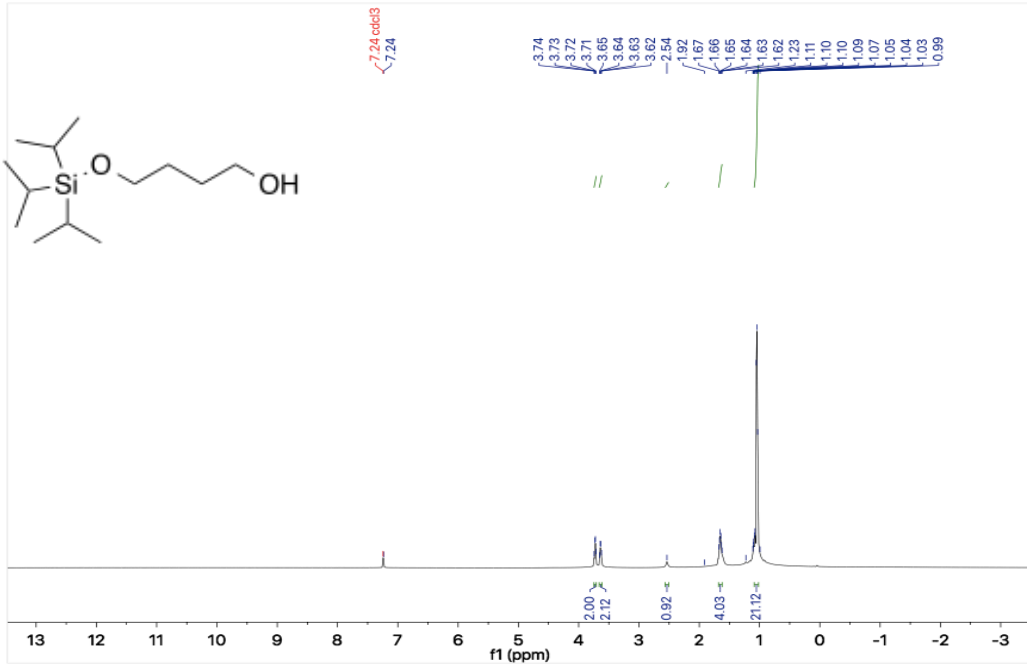
76.75 cdcl3
63.33
62.77
30.23
29.86
29.69
25.89
18.29
-5.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.24
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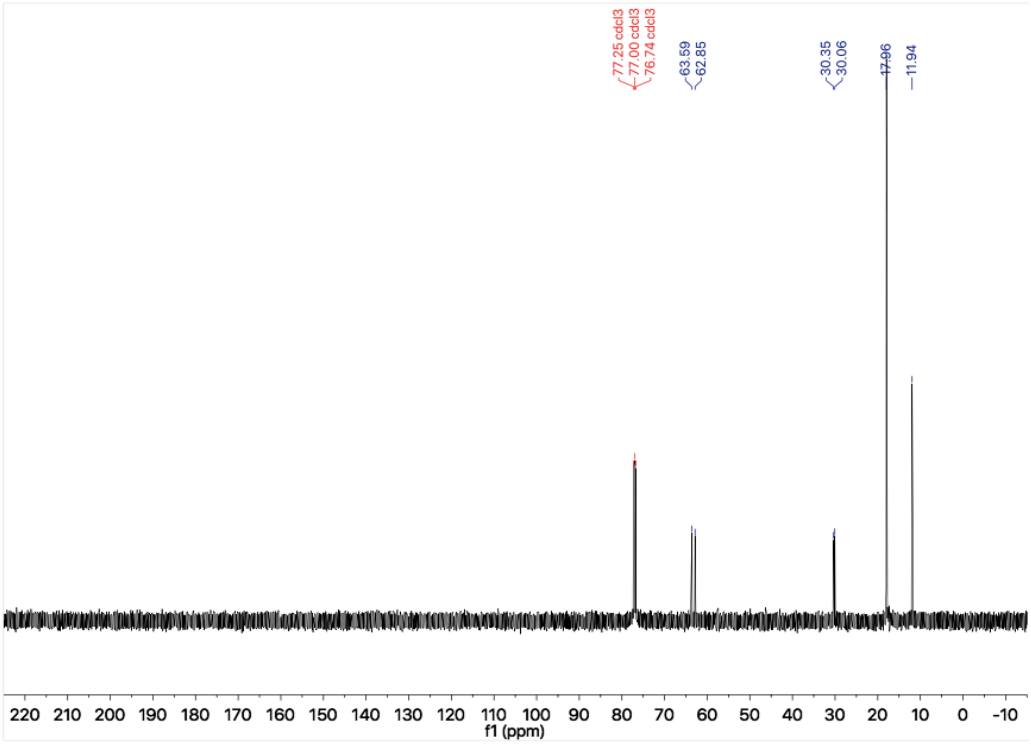
3.72
3.71
3.65
3.64
3.63
3.62
2.54
1.92
1.67
1.66
1.65
1.64
1.63
1.62
1.23
1.11
1.10
1.10
1.09
1.07
1.05
1.04
1.03
0.99
Si
O
OH
2.00
2.12
0.92
4.03
21.12
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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76.74 cdcl3
63.59
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30.06
17.96
11.94
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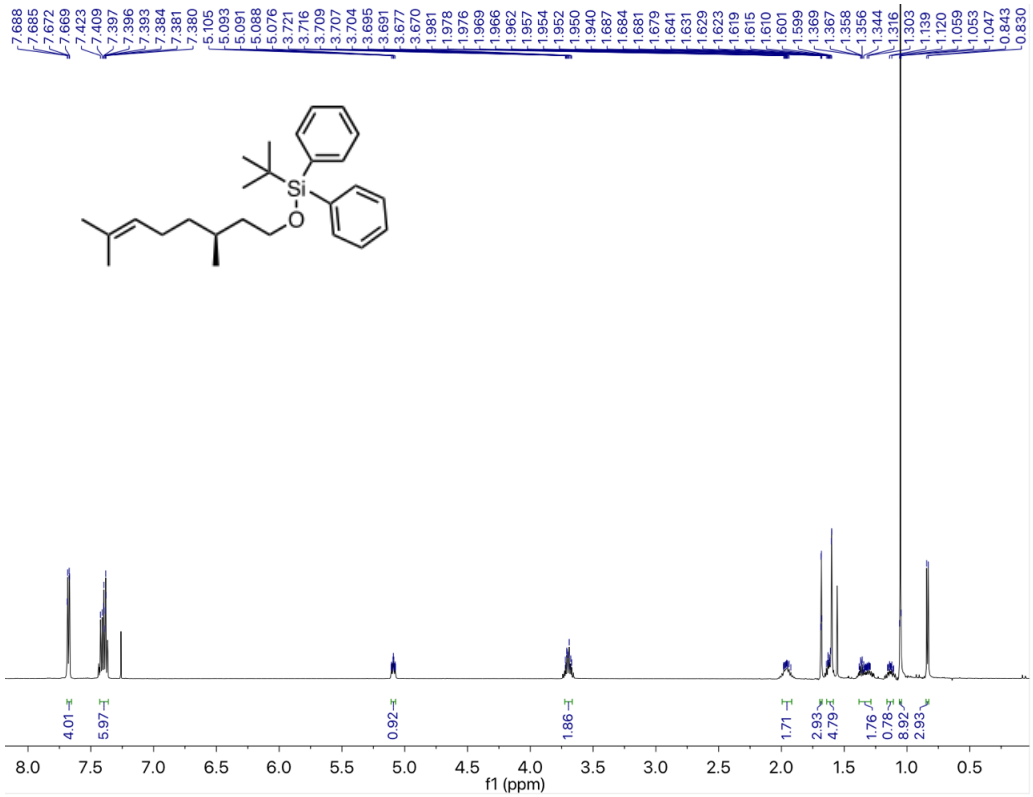
f1 (ppm)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7.380
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5.093
5.091
5.088
5.076
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3.716
3.709
3.707
3.704
3.695
3.691
3.677
3.670
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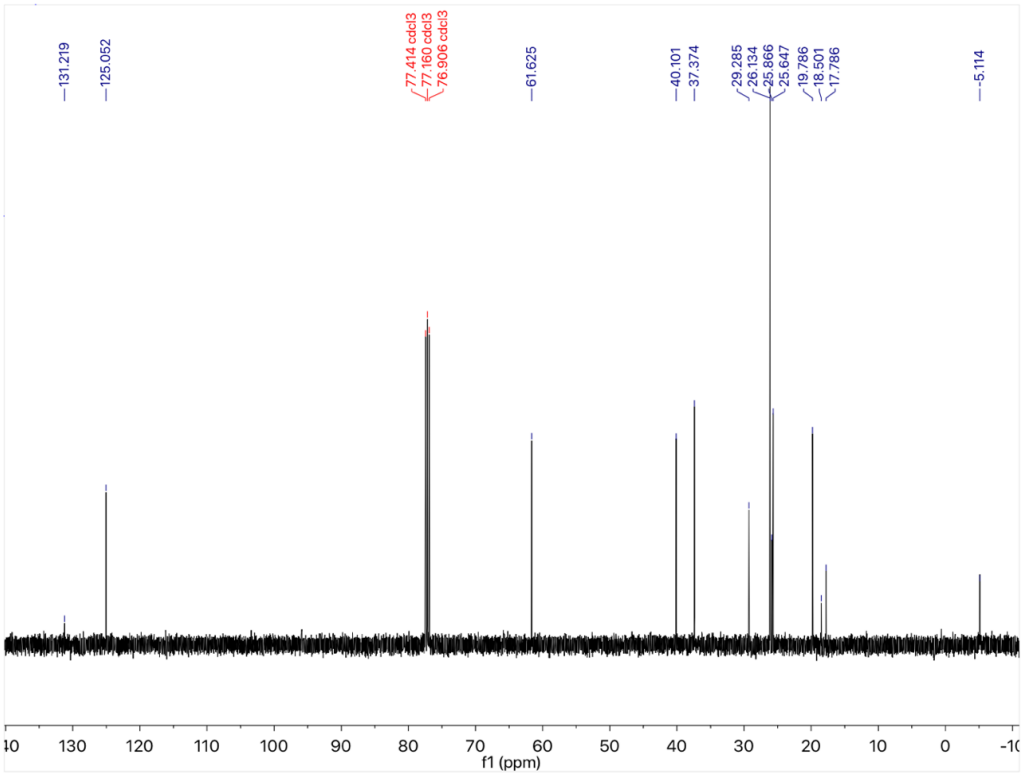
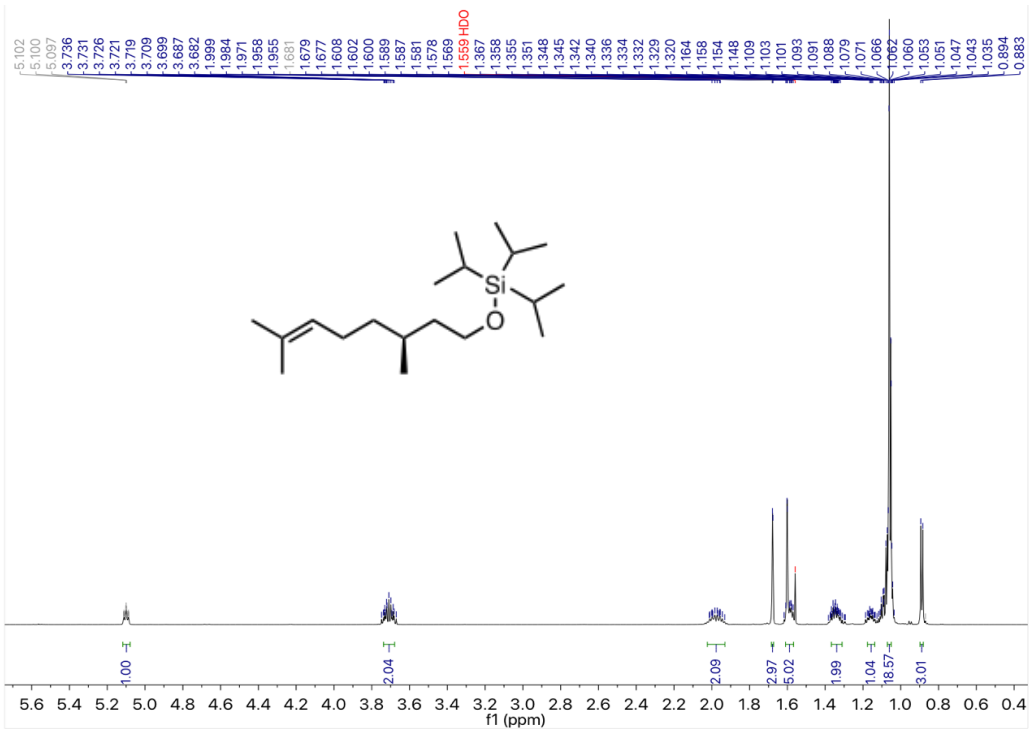
1.978
1.976
1.969
1.966
1.962
1.957
1.954
1.952
1.950
1.940
1.687
1.684
1.681
1.679
1.641
1.631
1.629
1.623
1.619
1.615
1.610
1.601
1.599
1.369
1.367
1.358
1.356
1.344
1.316
1.303
1.139
1.120
1.059
1.053
1.047
0.843
0.830
Si
O
4.01
5.97
0.92
1.86
1.71
2.93
4.79
1.76
0.78
8.92
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


131.219
125.052
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
61.625
40.101
37.374
29.285
26.134
25.866
25.647
19.786
18.501
17.786
-5.114
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.100
5.097
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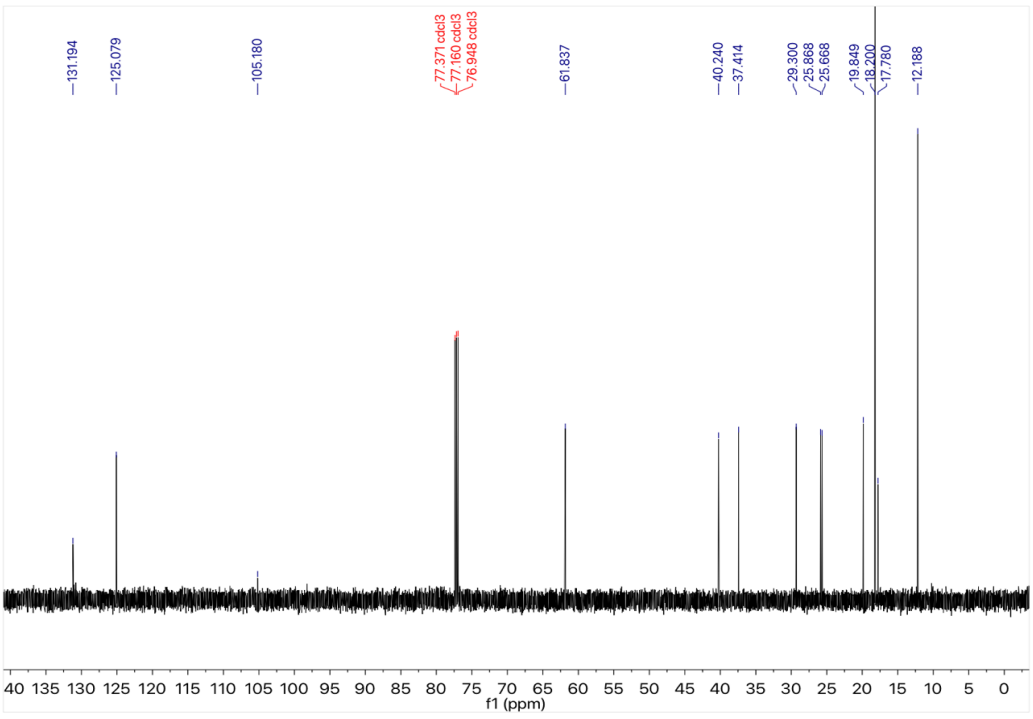
3.731
3.726
3.721
3.719
3.709
3.699
3.687
3.682
1.999
1.984
1.971
1.958
1.955
1.681
1.679
1.677
1.608
1.602
1.600
1.589
1.587
1.581
1.578
1.568
1.559 HDO
1.367
1.358
1.355
1.351
1.348
1.345
1.342
1.340
1.336
1.334
1.332
1.329
1.320
1.164
1.158
1.154
1.148
1.109
1.103
1.101
1.093
1.091
1.088
1.079
1.071
1.066
1.062
1.060
1.053
1.051
1.047
1.043
1.035
0.894
0.883
Si
O
1.00
2.04
2.09
2.97
5.02
1.99
1.04
18.57
3.01
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)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105.180
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77.160 cdcl3
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37.414
29.300
25.868
25.668
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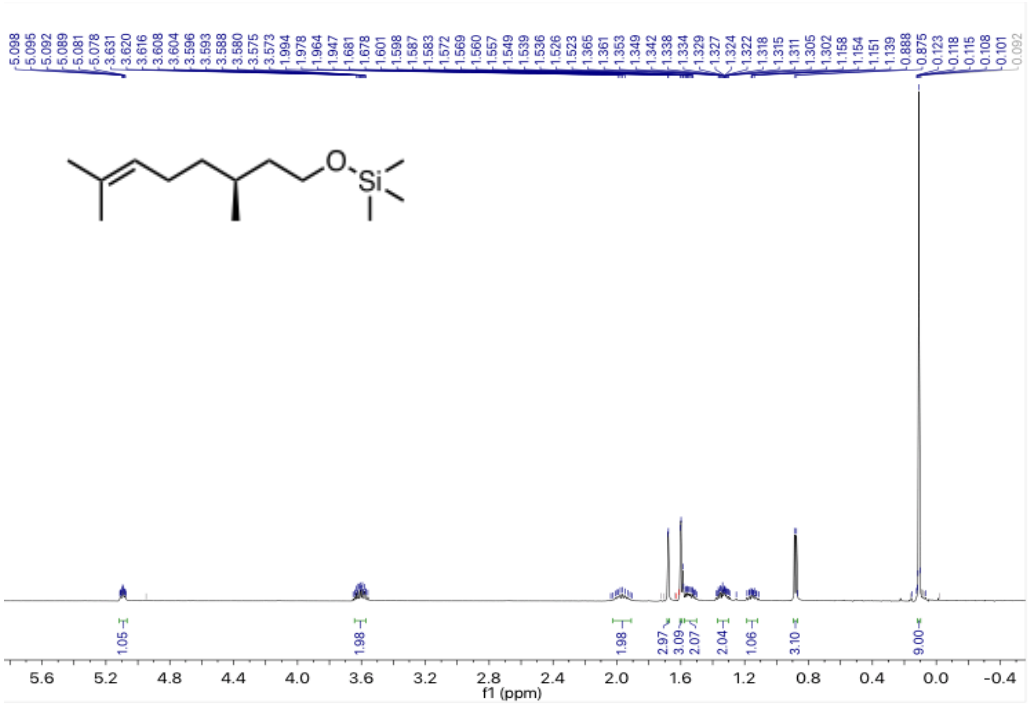
17.780
12.188
40 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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5.095
5.092
5.089
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5.078
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3.620
3.616
3.608
3.604
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3.588
3.580
3.575
3.573
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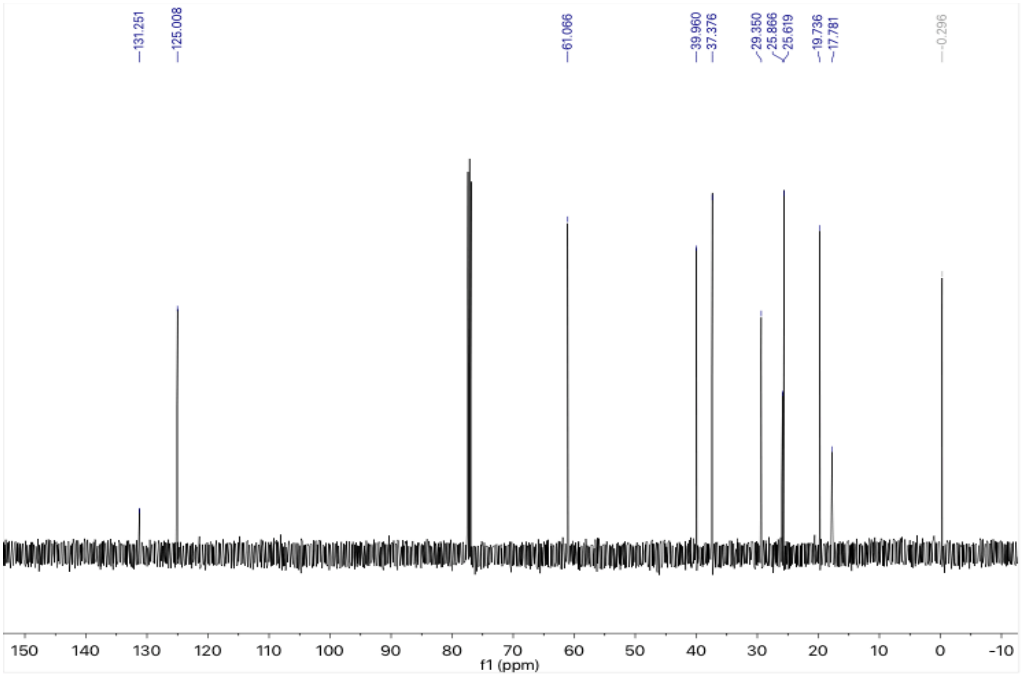
1.978
1.964
1.947
1.681
1.678
1.601
1.598
1.587
1.583
1.572
1.569
1.560
1.557
1.549
1.539
1.536
1.526
1.523
1.365
1.361
1.353
1.349
1.342
1.338
1.334
1.329
1.327
1.324
1.322
1.318
1.315
1.311
1.305
1.302
1.158
1.154
1.151
1.139
0.888
0.875
0.123
0.118
0.115
0.108
0.101
0.092
O
Si
1.05
1.98
1.98
2.97
3.09
2.07
2.04
1.06
3.10
9.00
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
f1 (ppm)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39.960
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25.866
25.619
19.736
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0.296
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100
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30
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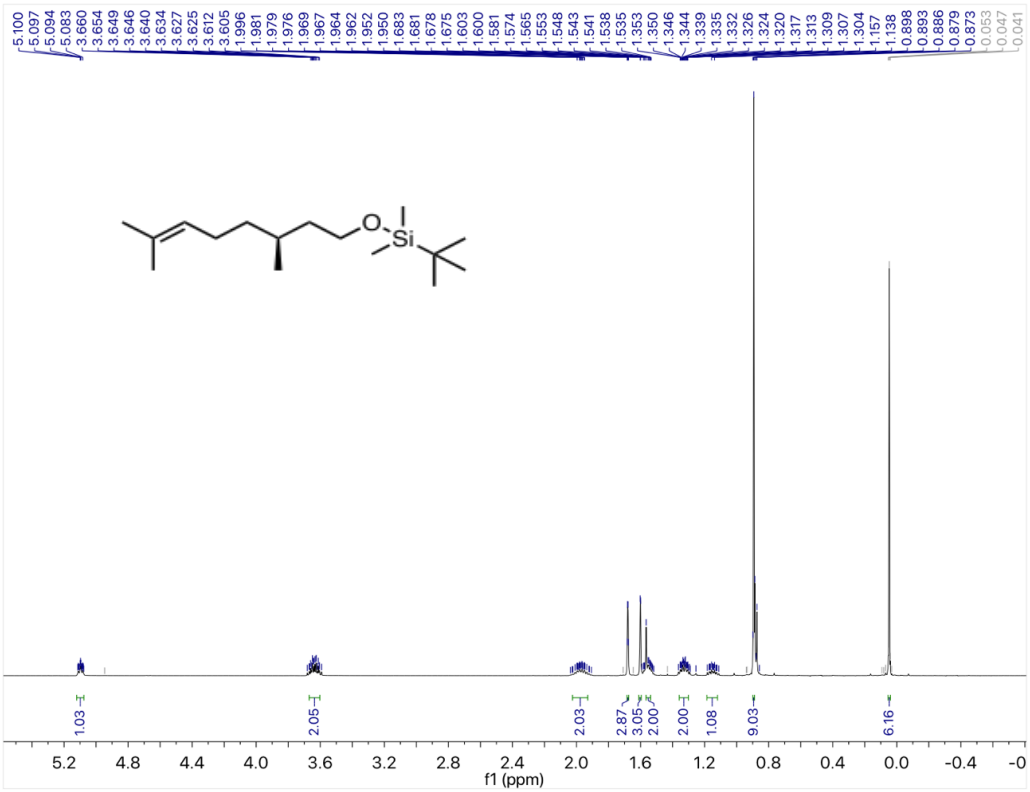
-10
f1 (ppm)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3.646
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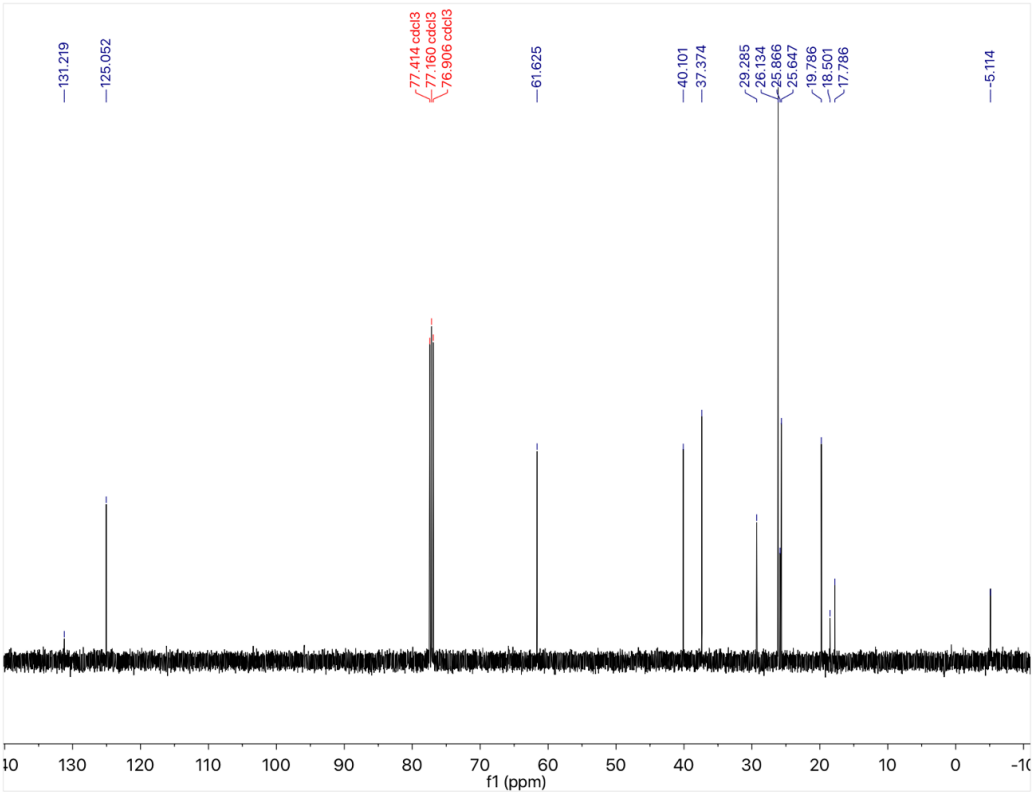
3.634
3.627
3.625
3.612
3.605
1.996
1.981
1.979
1.976
1.969
1.967
1.964
1.962
1.952
1.950
1.683
1.681
1.678
1.675
1.603
1.600
1.581
1.574
1.565
1.553
1.548
1.543
1.541
1.538
1.535
1.353
1.350
1.346
1.344
1.339
1.335
1.332
1.326
1.324
1.320
1.317
1.313
1.309
1.307
1.304
1.157
1.138
0.898
0.893
0.886
0.879
0.873
0.053
0.047
0.041
O
Si
1.03
2.05
2.03
2.87
3.05
2.00
2.00
1.08
9.03
6.16
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
f1 (ppm)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125.052
77.414 cdcl3
77.160 cdcl3
76.906 cdcl3
61.625
40.101
37.374
29.285
26.134
25.866
25.647
19.786
18.501
17.786
-5.114
130
120
110
100
90
80
70
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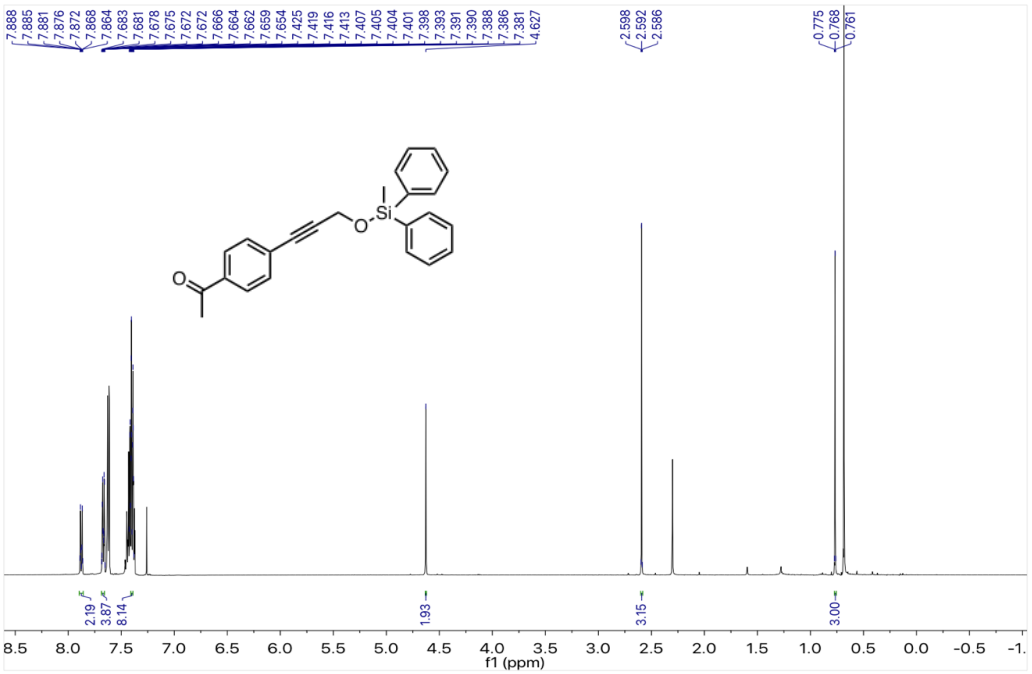
50
40
30
20
10
0
f1 (ppm)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7.872
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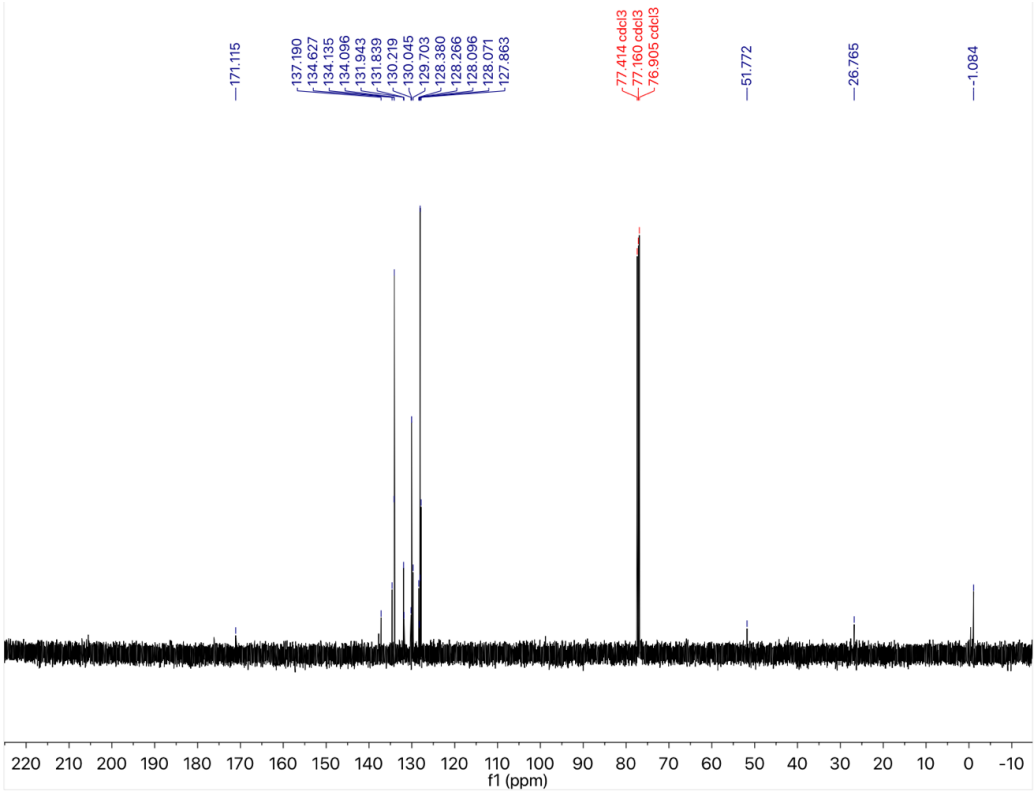
7.683
7.681
7.678
7.675
7.672
7.672
7.666
7.664
7.662
7.659
7.654
7.425
7.419
7.416
7.413
7.407
7.405
7.404
7.401
7.398
7.393
7.391
7.390
7.388
7.386
7.381
4.627
2.598
2.592
2.586
0.775
0.768
0.761
O
Si
O
2.19
3.87
8.14
1.93
3.15
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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134.096
131.943
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128.380
128.266
128.096
128.071
127.863
77.414 cdcl3
77.160 cdcl3
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51.772
26.765
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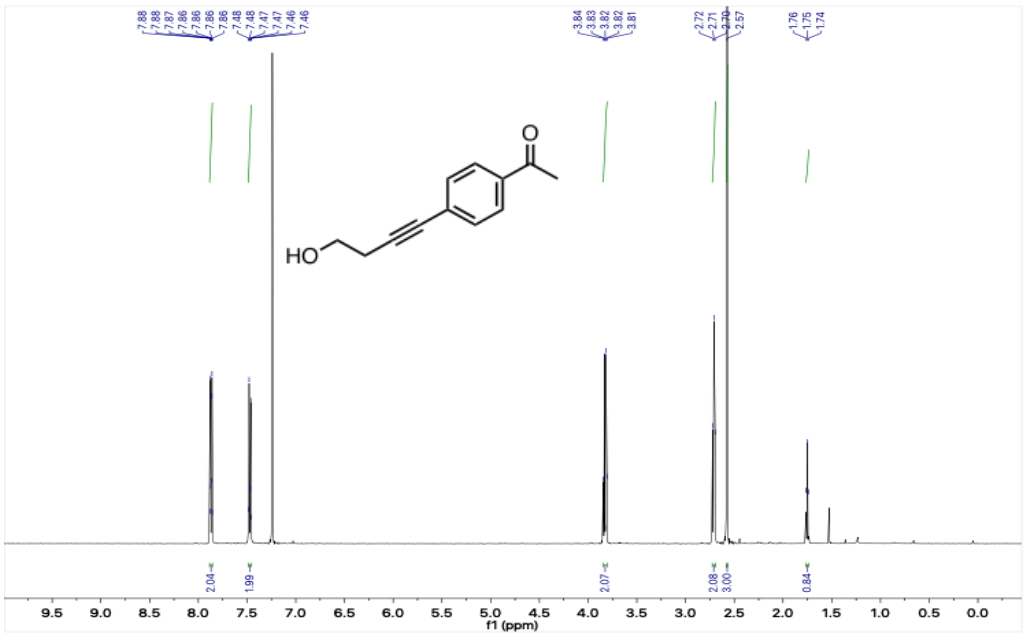
f1 (ppm)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7.86
7.86
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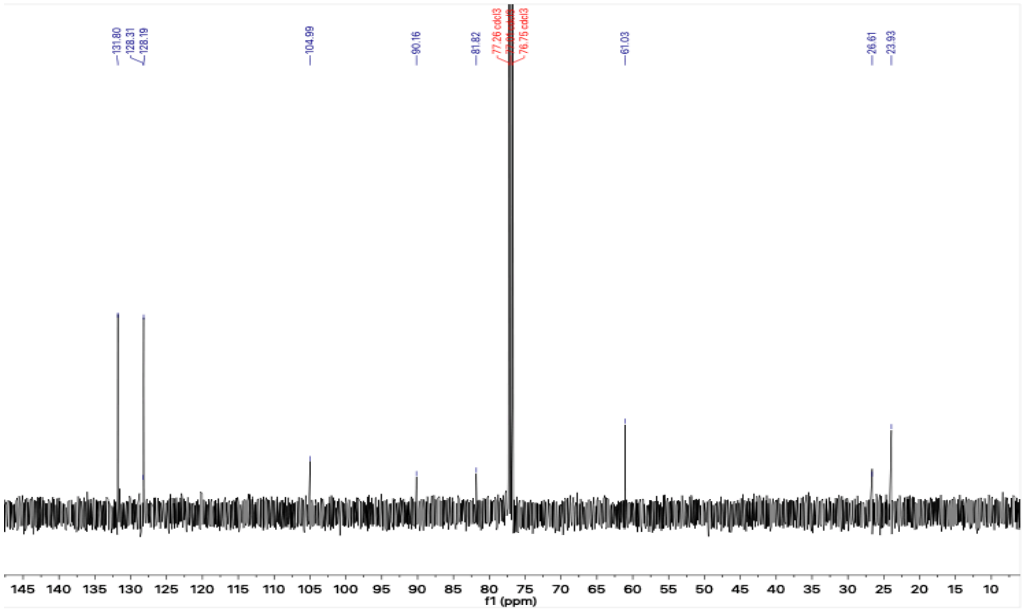
7.47
7.47
7.46
7.46
3.84
3.83
3.82
3.82
3.81
2.72
2.71
2.70
2.57
1.76
1.75
1.74
O
HO
2.04
1.99
2.07
2.08
3.00
0.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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81.82
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76.76 cdcl3
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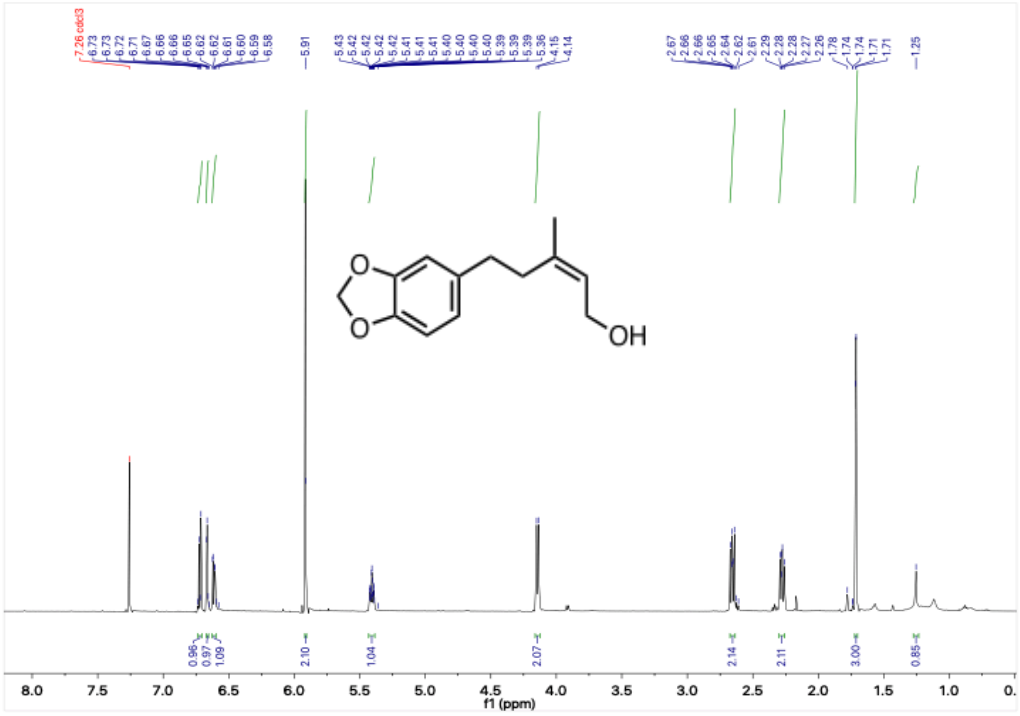
26.61
23.93
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)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6.71
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6.62
6.61
6.60
6.59
6.58
5.91
5.43
5.42
5.41
5.40
5.39
5.36
4.15
4.14
2.67
2.66
2.65
2.64
2.62
2.61
2.29
2.28
2.27
2.26
1.78
1.74
1.71
1.25
O
O
OH
0.98
0.97
1.09
2.10
1.04
2.07
2.14
2.11
3.00
0.85
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
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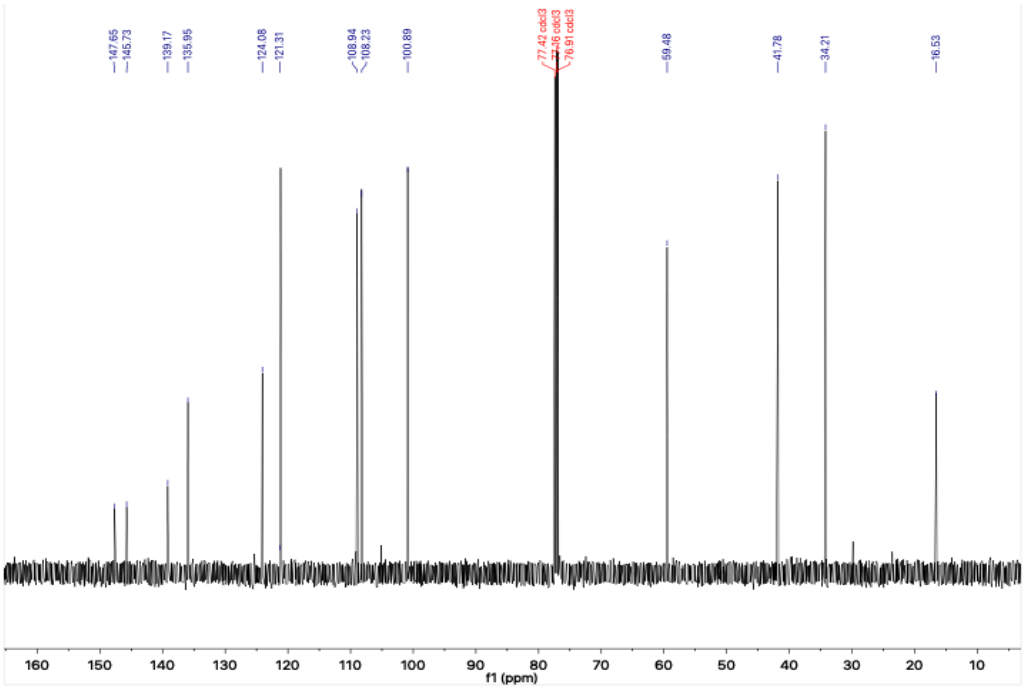
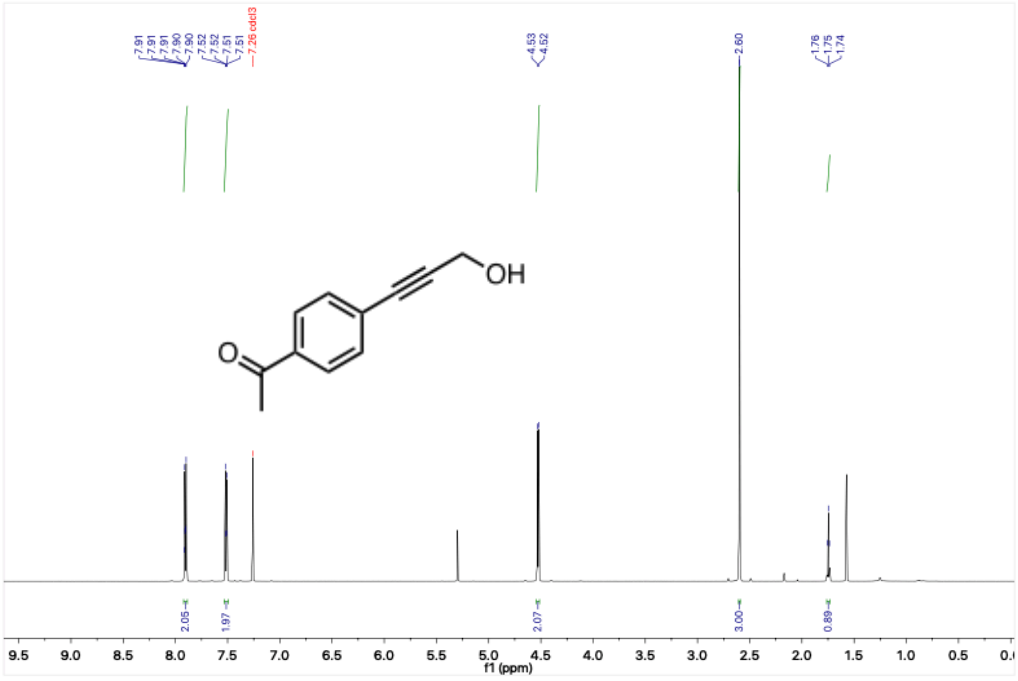
2.5
2.0
1.5
1.0
f1 (ppm)


147.65
145.73
139.17
135.95
124.08
121.31
108.94
108.23
100.89
77.42 cdcl3
77.16 cdcl3
76.91 cdcl3
59.48
41.78
34.21
16.53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.91
7.91
7.90
7.90
7.52
7.52
7.51
7.51
7.26 cdcl3
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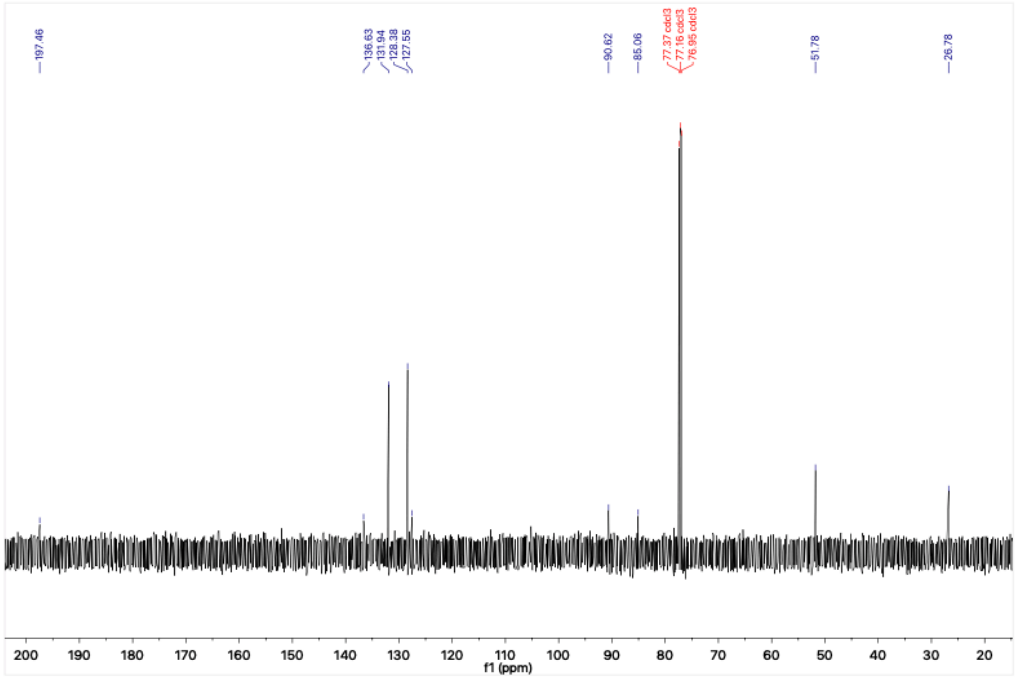
4.52
2.60
1.76
1.75
1.74
OH
O
2.05
1.97
2.07
3.00
0.89
f1 (ppm)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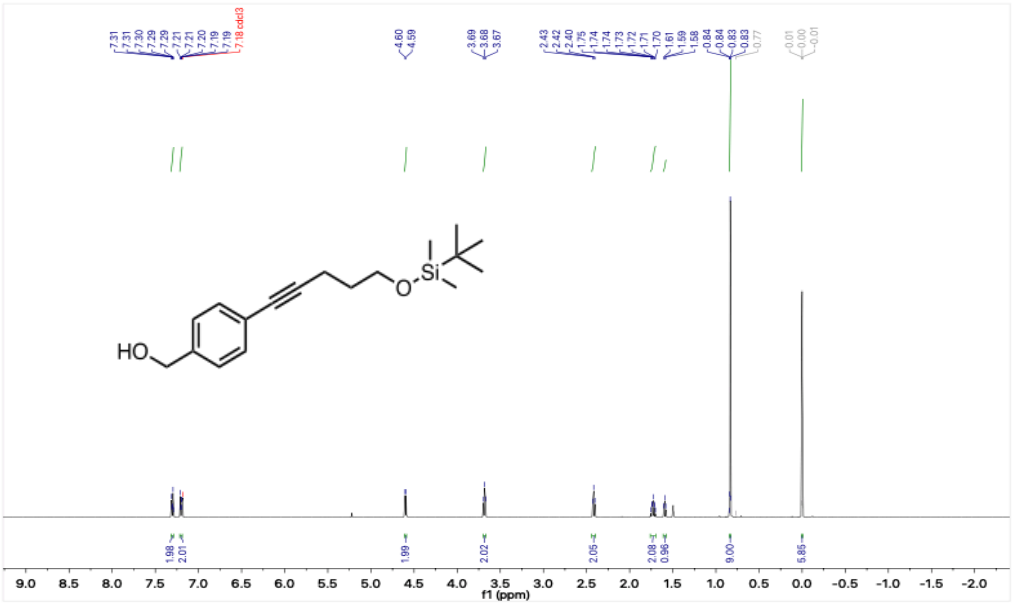
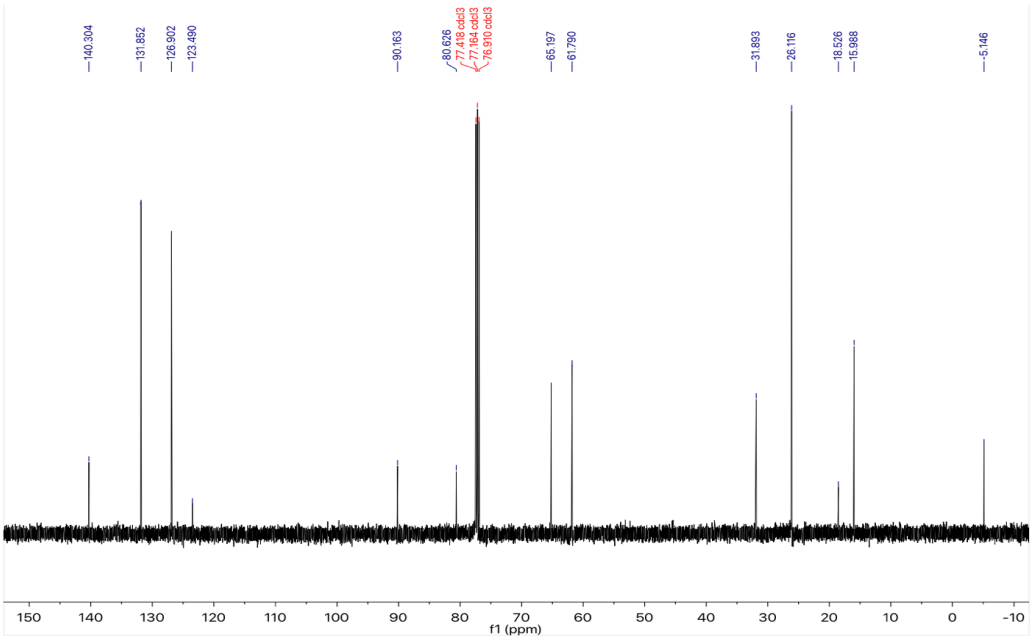
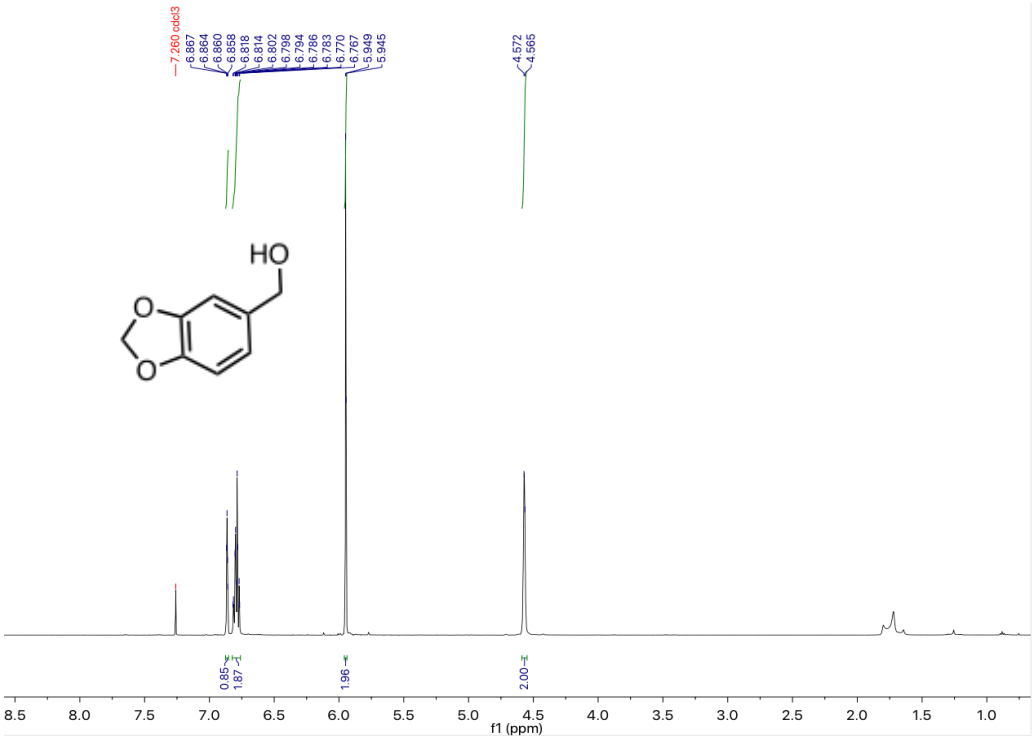
127.55
90.62
85.06
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
51.78
26.78
f1 (ppm)


HO
Si
O
f1 (ppm)


f1 (ppm)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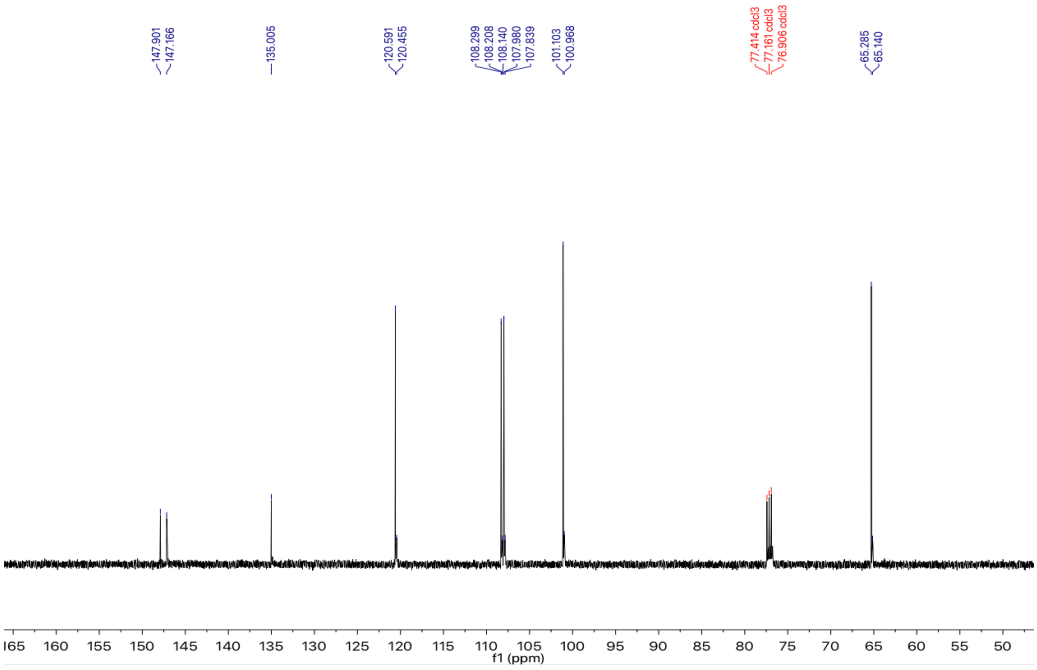
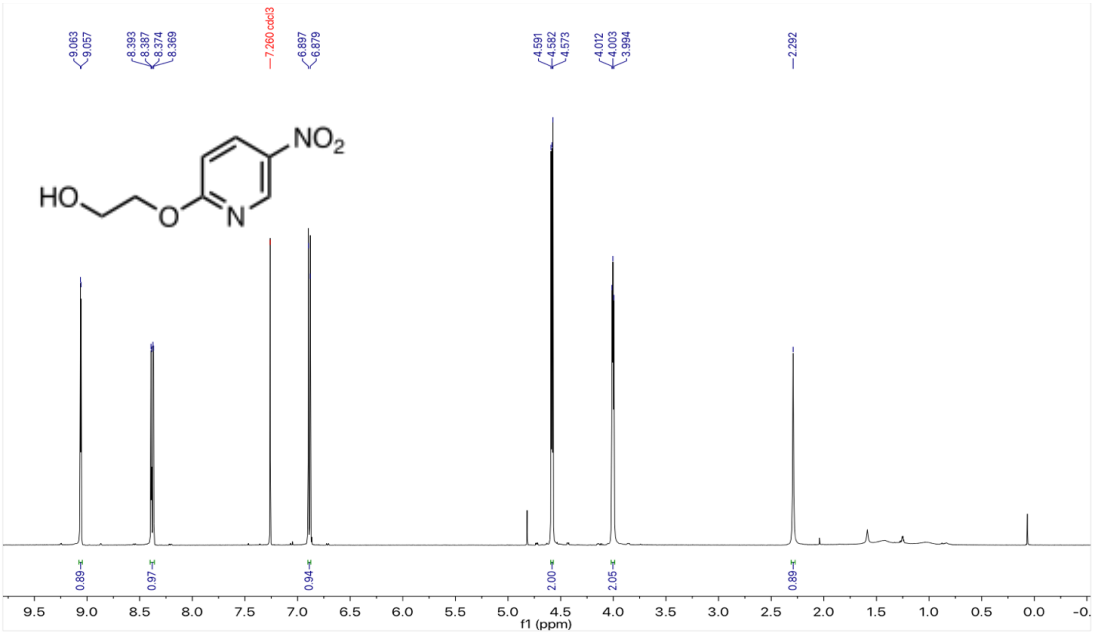
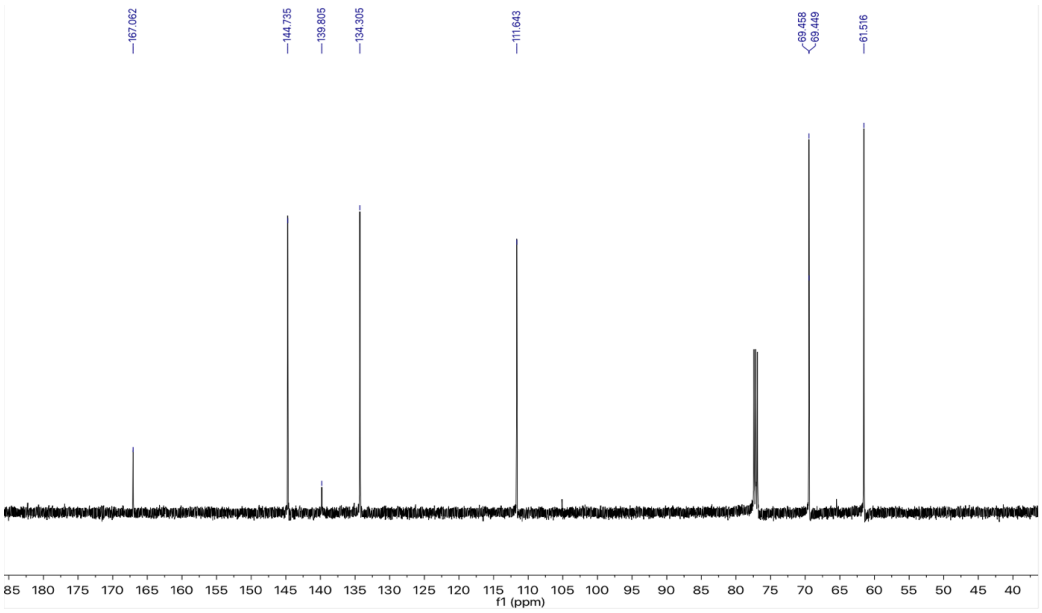
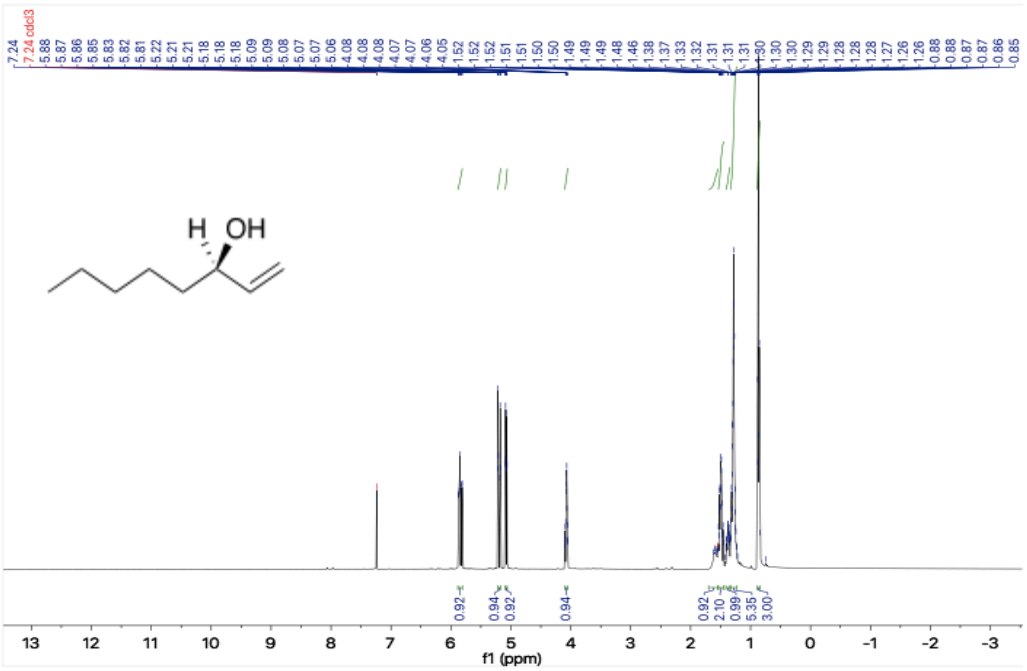
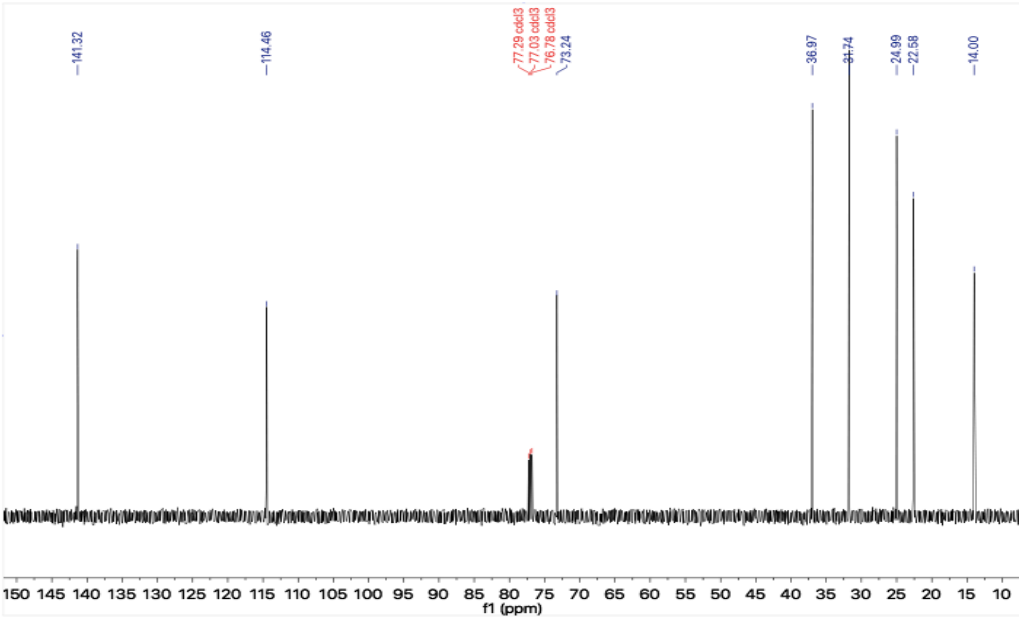
6.867
6.864
6.860
6.858
6.818
6.814
6.802
6.798
6.794
6.786
6.783
6.770
6.767
5.949
5.945
4.572
4.565
HO
O
O
0.85
1.87
1.96
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

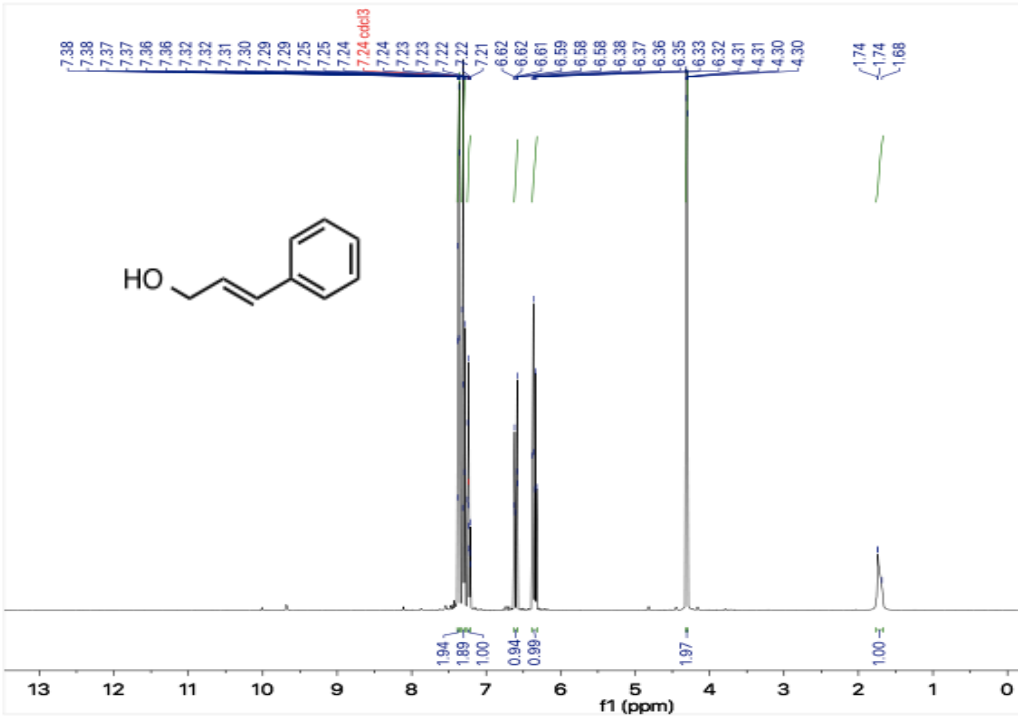

147.901
147.166
135.005
120.591
120.455
108.299
108.208
108.140
107.980
107.839
101.103
100.968
77.414 cdcl3
77.161 cdcl3
76.906 cdcl3
65.285
65.140
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

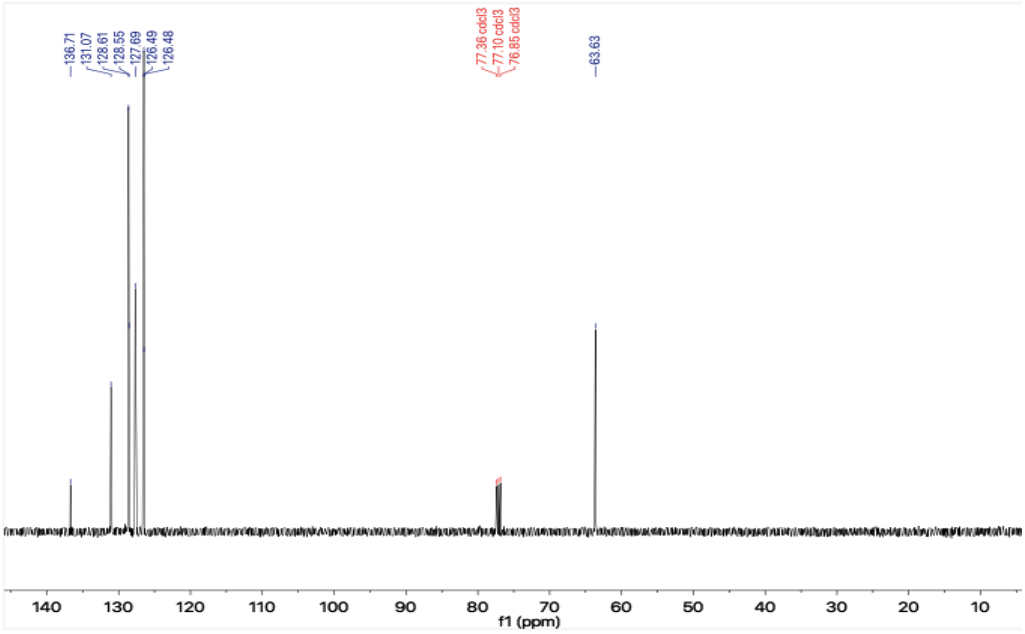

9.063
9.057
8.393
8.387
8.374
8.369
7.260 cdcl3
6.897
6.879
4.591
4.582
4.573
4.012
4.003
3.994
2.292
NO2
HO
O
N
0.89
0.97
0.94
2.00
2.05
0.89
f1 (ppm)

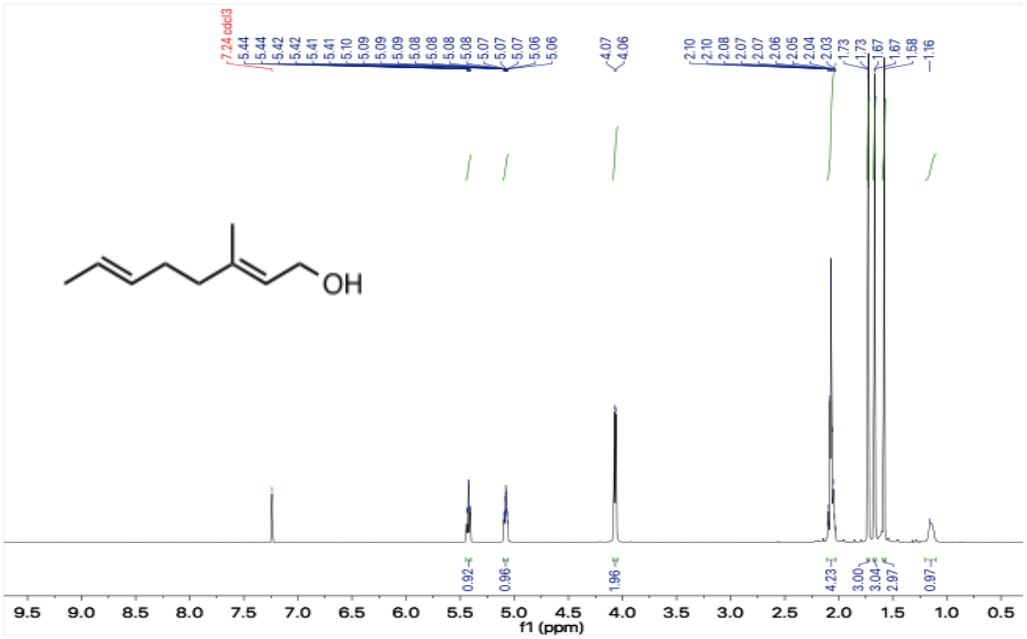

167.062
144.735
139.805
134.305
111.643
69.458
69.449
61.516
f1 (ppm)

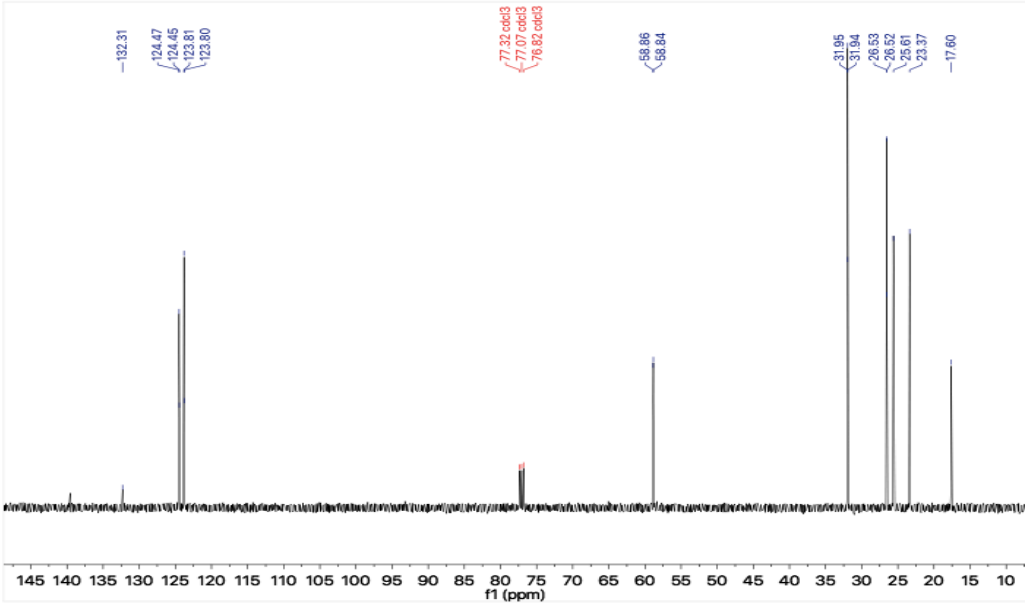

H OH
f1 (ppm)

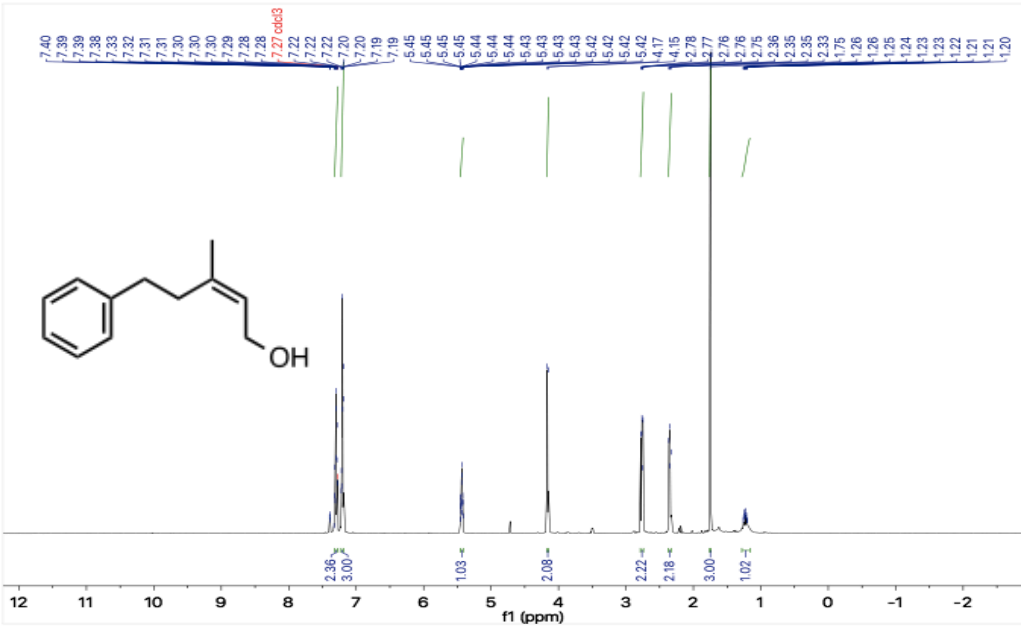

141.32
114.46
77.29 cdcl3
77.03 cdcl3
76.78 cdcl3
73.24
36.97
31.74
24.99
22.58
14.00
f1 (ppm)

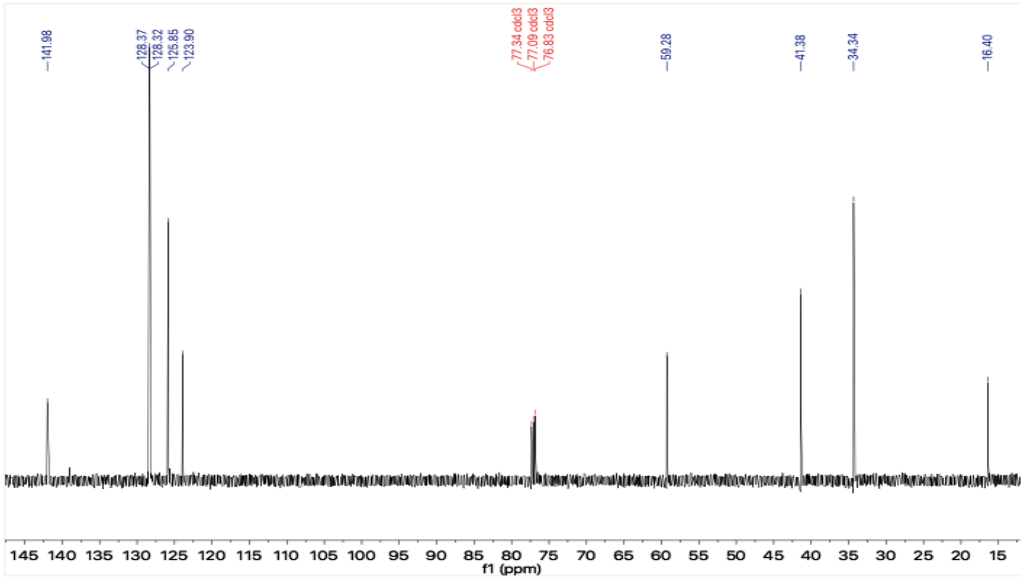

HO
f1 (ppm)

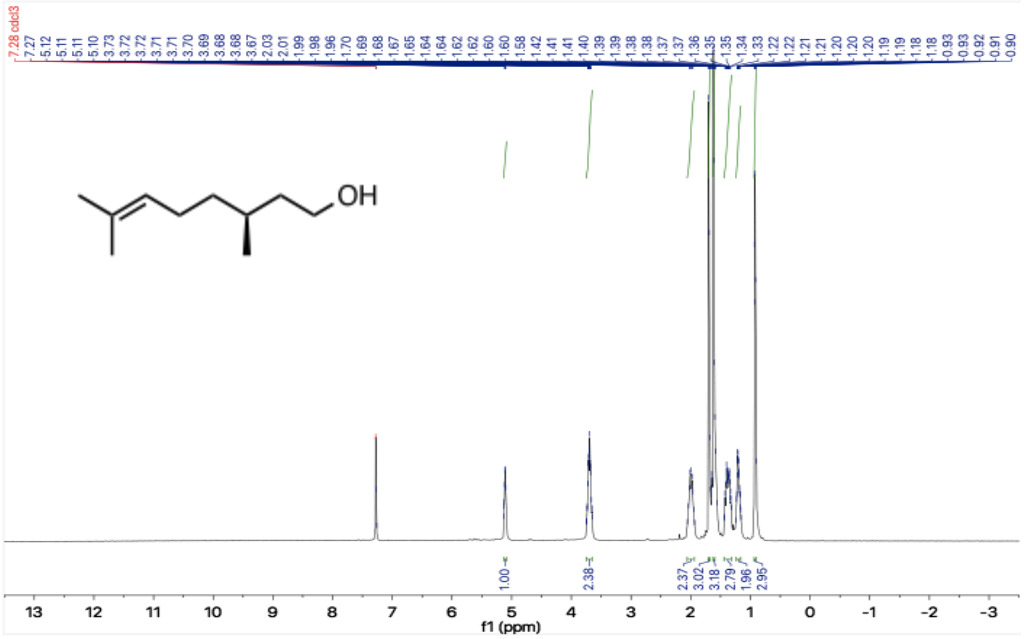

f1 (ppm)

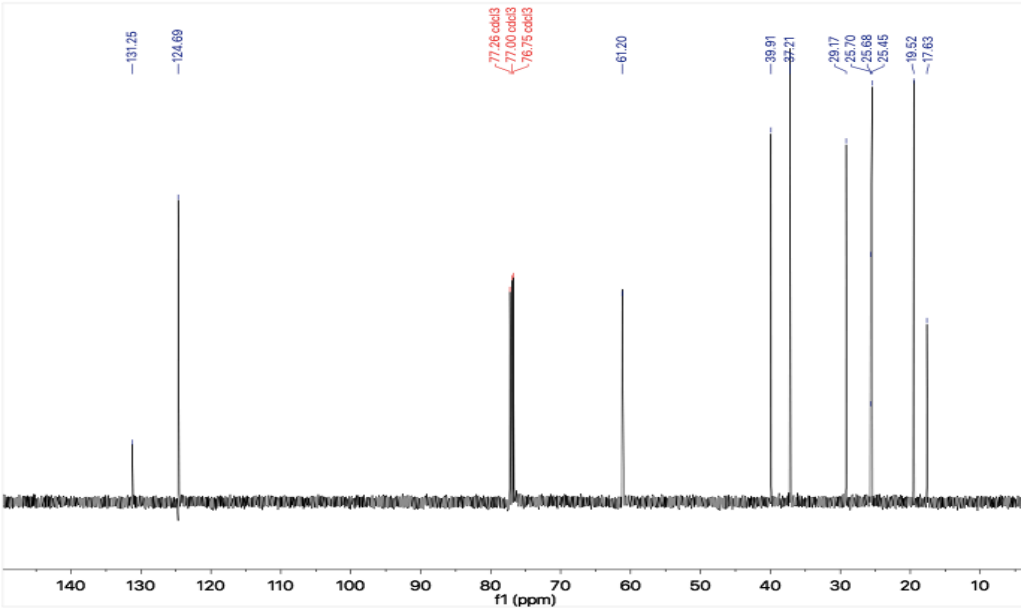

7.24 cdcl3
5.44
5.44
5.42
5.42
5.42
5.41
5.41
5.10
5.09
5.09
5.09
5.08
5.08
5.08
5.08
5.07
5.07
5.07
5.06
5.06
5.06
4.07
4.06
2.10
2.10
2.08
2.07
2.07
2.06
2.05
2.04
2.03
1.73
1.73
1.67
1.67
1.67
1.58
1.16
OH
0.92
0.96
1.96
4.23
3.00
3.04
2.97
0.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

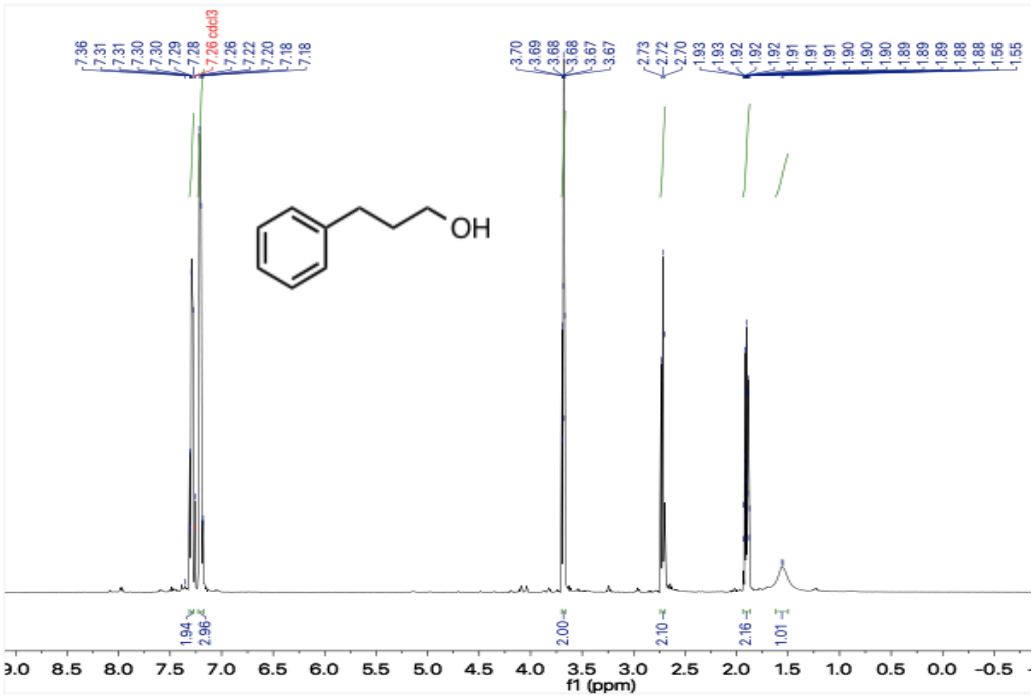

132.31
124.47
124.45
123.81
123.80
77.32 cdcl3
77.07 cdcl3
76.82 cdcl3
58.86
58.84
31.95
31.94
26.53
26.52
25.61
23.37
17.60
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

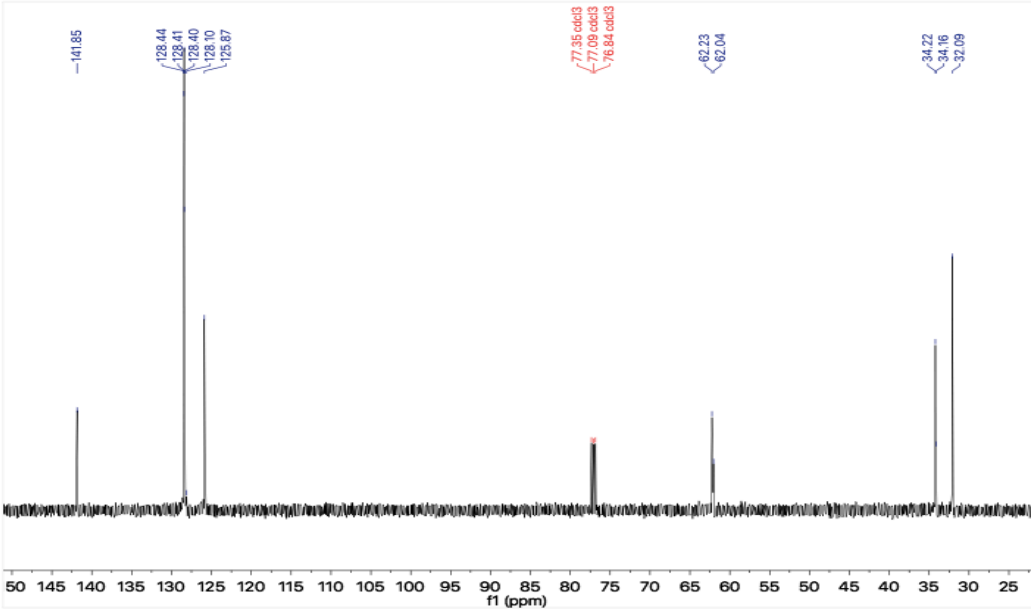

OH
f1 (ppm)

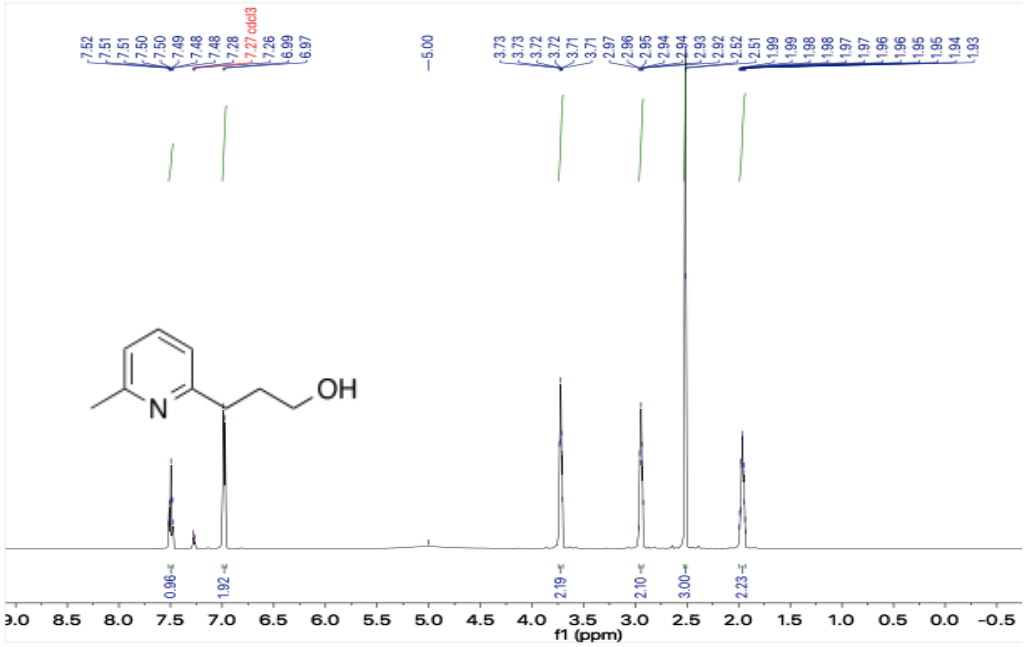

f1 (ppm)

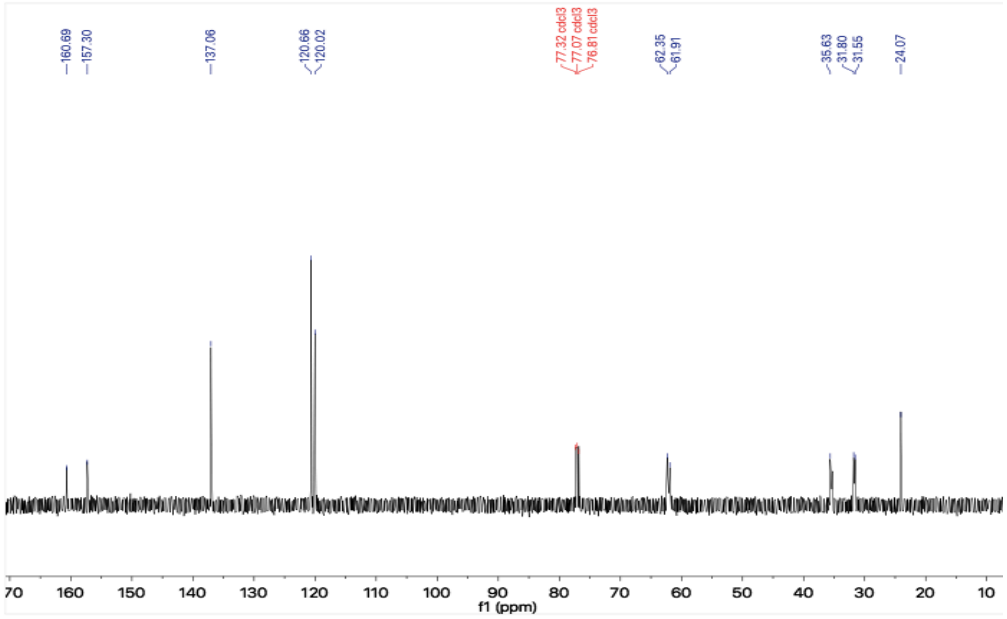

OH
f1 (ppm)

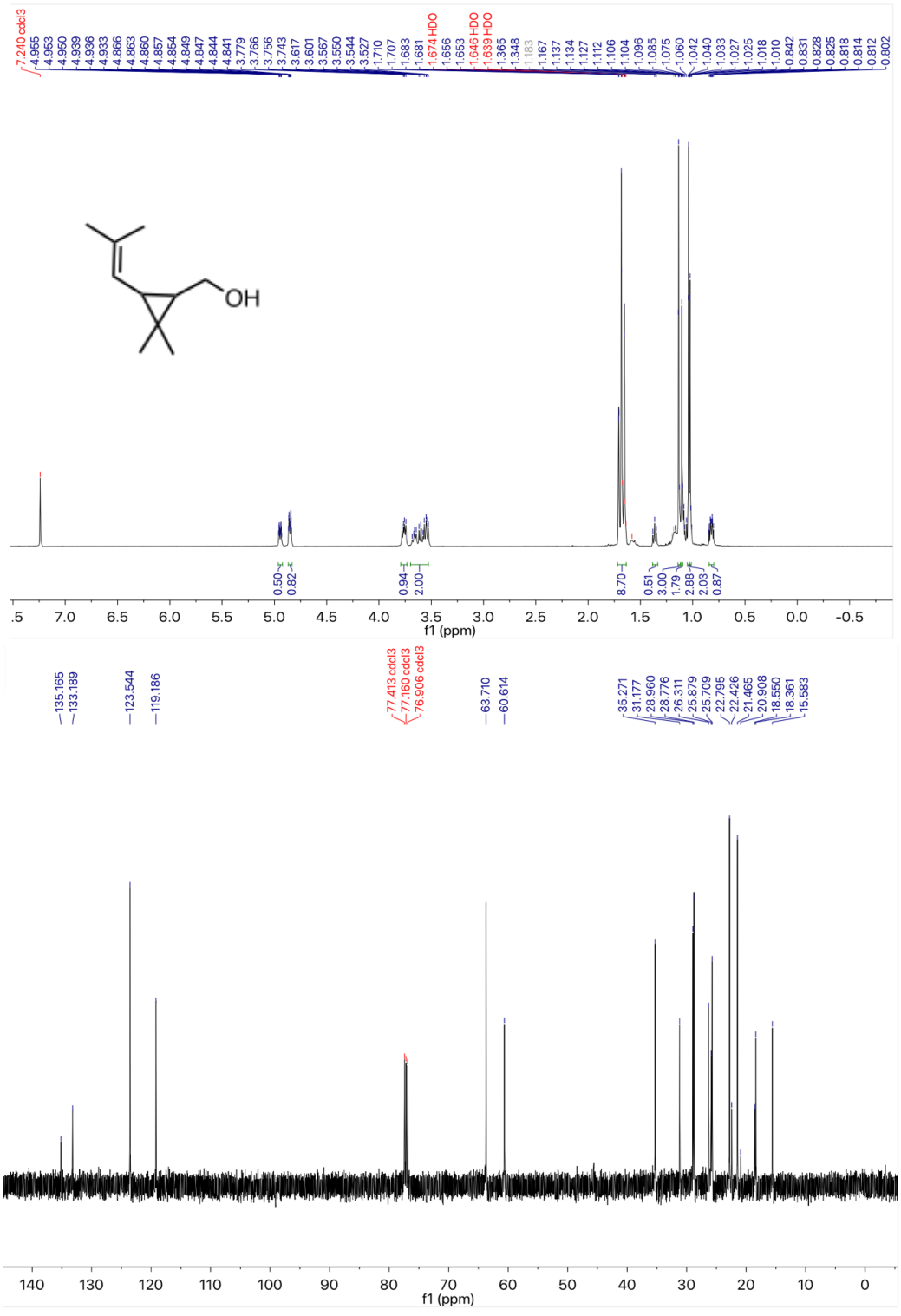

f1 (ppm)


7.36
7.31
7.31
7.30
7.30
7.29
7.28
7.26 cdcl3
7.26
7.22
7.20
7.18
7.18
3.70
3.69
3.68
3.68
3.67
3.67
2.73
2.72
2.70
1.93
1.93
1.92
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.89
1.88
1.88
1.56
1.55
OH
1.94
2.96
2.00
2.10
2.16
1.01
f1 (ppm)


141.85
128.44
128.41
128.40
128.10
125.87
77.35 cdcl3
77.09 cdcl3
76.84 cdcl3
62.23
62.04
34.22
34.16
32.09
f1 (ppm)


7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.28
7.27 cdcl3
7.26
6.99
6.97
5.00
3.73
3.73
3.72
3.72
3.71
3.71
2.97
2.96
2.95
2.94
2.94
2.93
2.92
2.52
2.51
1.99
1.99
1.98
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.93
OH
N
0.96
1.92
2.19
2.10
3.00
2.23
f1 (ppm)


160.69
157.30
137.06
120.66
120.02
77.32 cdcl3
77.07 cdcl3
76.81 cdcl3
62.35
61.91
35.63
31.80
31.55
24.07
f1 (ppm)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4.953
4.950
4.939
4.936
4.933
4.866
4.863
4.860
4.857
4.854
4.849
4.847
4.844
4.841
3.779
3.766
3.756
3.743
3.617
3.601
3.567
3.550
3.544
3.527
1.710
1.707
1.683
1.681
1.674 HDO
1.656
1.653
1.646 HDO
1.639 HDO
1.365
1.348
1.183
1.167
1.137
1.134
1.127
1.112
1.106
1.104
1.096
1.085
1.075
1.060
1.042
1.040
1.033
1.027
1.025
1.018
1.010
0.842
0.831
0.828
0.825
0.818
0.814
0.812
0.802
OH
0.50
0.82
0.94
2.00
8.70
0.51
3.00
1.79
2.88
2.03
0.87
f1 (ppm)
135.165
133.189
123.544
119.186
77.413 cdcl3
77.160 cdcl3
76.906 cdcl3
63.710
60.614
35.271
31.177
28.960
28.776
26.311
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25.709
22.795
22.426
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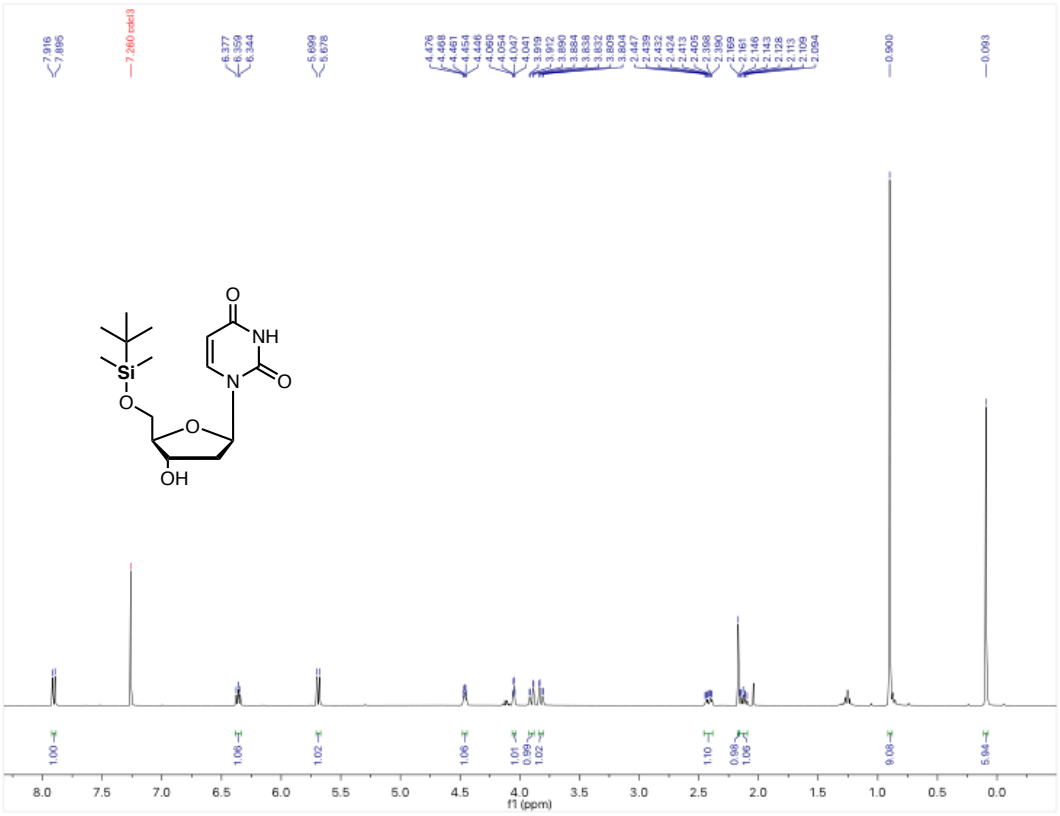
20.908
18.550
18.361
15.583
f1 (ppm)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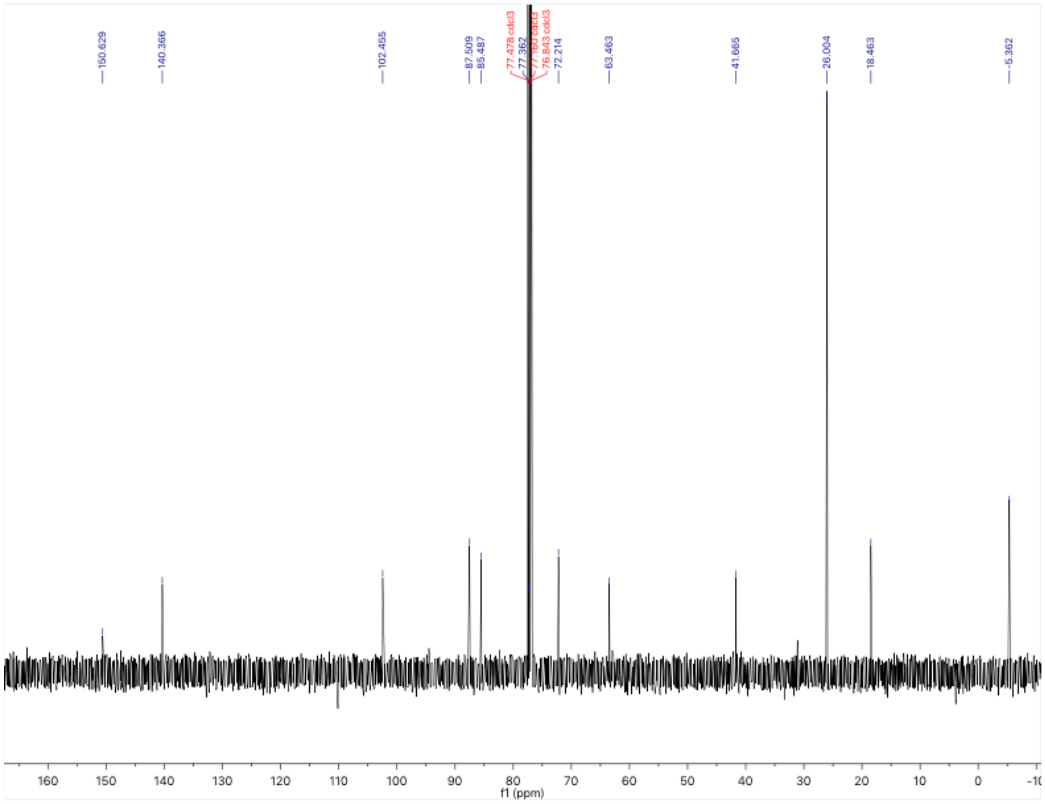
7.895
7.260 cdcl3
6.377
6.359
6.344
5.699
5.678
4.476
4.468
4.461
4.454
4.446
4.060
4.054
4.047
4.041
3.919
3.912
3.890
3.884
3.838
3.832
3.809
3.804
2.447
2.439
2.432
2.424
2.413
2.405
2.388
2.390
2.169
2.161
2.146
2.143
2.128
2.113
2.109
2.094
0.900
0.093
O
NH
N
O
Si
O
O
OH
1.00
1.06
1.02
1.06
1.01
0.99
1.02
1.10
0.98
1.06
9.08
5.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.629
140.366
102.455
87.509
85.487
77.478 cdcl3
77.362
77.161 cdcl3
76.843 cdcl3
72.214
63.463
41.665
26.004
18.463
-5.362
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)