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UNIVERSITY OF CALIFORNIA,
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Creative Routes to Unnatural Amino Acids, Chiral Phosphines, and Nitrogen-Heterocycles
DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Xintong Hou

Dissertation Committee:
Professor Vy M. Dong, Chair
Professor Christopher D. Vanderwal
Professor Scott D. Rychnovsky

2024

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In addition, thank you to my cohort Hannah Slocumb and Erin Kuker for being great friends and coworkers. I was lucky to join the lab with both of you at the same time. You both supported me so much for both chemistry and life. I will miss all the fun talks that we had together. By talking with you when I am facing challenges, I can always feel better and find solutions. The time goes so fast, and it is crazy that we all are graduating. I believe all of us will have a bright future!

To my family, thank you for supporting me so much during all these years. Thank you to my mom for taking care of me, listening to all my sadness and happiness, and supporting me for every decision that I made. Thank you for raising me and sometimes even sacrificing your own time to support my different interests. Without your life guidance, I will not become who I am right now. Thank you to my dad for the supports all these years. You provided the life that I am

living in and made it possible for me to come to United States for education. I also would like to thank my grandparents for all the love. Sorry that I haven't went back home for so many years. I miss you very much and I love you. To my partner, Ryan Davison. Thank you for supporting me throughout graduate school. You helped me so much to get through different challenges. Thank you for your willingness to listen to me and brainstorm. I appreciate all the compromises that you made over the last few years. I love you and I am looking forward to spending our life together.

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Vita

Xintong Hou

EDUCATION

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PROFESSIONAL EXPERIENCE

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| 2019 – 2024 | University of California, Irvine (Irvine, CA)
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| 2015 – 2018 | Gettysburg College (Gettysburg, PA)
Undergraduate Research Student
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2. West Regional ACS Conference, Las Vegas, NV, Oct 2022. (Oral)
3. Organic Symposium, Virtual, Irvine, CA, Oct 2021. (Oral)
4. SoCal Merck Virtual Symposium, Virtual, Jul 2021. (Poster)
5. 2021 #RSCTwitter Poster Conference, Virtual, Mar 2021. (Poster).
6. 6th Annual Cross-Disciplinary Science Institute Presentation, Gettysburg, PA, Oct 2018. (Poster)
7. Chemistry Department seminar series, Gettysburg, PA, Oct 2018. (Oral)
8. Celebration 2018, Gettysburg, PA, May 2018. (Poster)
9. 82nd Annual Intercollegiate Student Chemist Convention, Elizabethtown, PA, Apr 2018. (Oral)
10. Chemistry Department seminar, Gettysburg, PA, Mar 2018. (Oral)

PUBLICATIONS

1. Daniels, B. S.;* Hou, X.;* Corio, S. A.; Weissman, L. M.; Dong, V. M.; Hirschi, J. S.; Nie, S. Copper-Phosphido Catalysis: Enantioselective Addition of Phosphine to Cyclopropenes. *Angew. Chem. Int. Ed.* **2023**, 62, e202306511 (*equal contribution as co-first authors).
2. Werley, B. K.; Hou, X.; Bertonazzi, E. P.; Chianese, A.; Funk, T. W. Substituent Effects and Mechanistic Insights on the Catalytic Activities of (Tetraarylcyclopentadienone)iron Carbonyl Compounds in Transfer Hydrogenations and Dehydrogenations. *Organometallics*, **2023**, 42, 3053.
3. Parker, P. D.; Hou, X. Reducing Challenges in Organic Synthesis with Stereoselective Hydrogenation and Tandem Catalysis. *J. Am. Chem. Soc.* **2021**, 143, 6724.
4. Davison, R. T.; Parker, P. D.; Hou, X.; Chung, C. P.; Augustine, S. A.; Dong, V. M. Enantioselective Addition of α -Nitroesters to Alkynes. *Angew. Chem. Int. Ed.* **2021**, 60, 4599.

Abstract of the Dissertation

Creative Routes to Unnatural Amino Acids, Chiral Phosphines, and Nitrogen-Heterocycles

by

Xintong Hou

Doctor of Philosophy in Chemistry

University of California, Irvine, 2024

Professor Vy M. Dong, Chair

Hydrofunctionalization is a powerful tool to add fragments across unsaturated building blocks to furnish more complex structures and introduce new stereocenters. My PhD studies have focused on Rh and Cu-catalyzed hydrofunctionalization to build both carbon-carbon and carbon-heteroatom bonds in a stereoselective and regioselective manner. With careful pairing of transition-metals and ligands, we successfully accessed chiral α,α -disubstituted- α -amino acid (α,α -disubstituted- α -AA) precursors, chiral cyclopropyl phosphines and *N*-arylated pyrazole motifs.

In chapter 1, the study is focused on Rh-H catalyzed hydrofunctionalization of alkynes with α -nitroesters to synthesize α,α -disubstituted- α -AA building blocks. The method generates biologically important precursors bearing two contiguous stereocenters with high enantioselectivity, diastereoselectivity and regioselectivity. The transformation involves the Rh-H catalyzed isomerization of alkynes into Rh- π -allyl electrophiles through an allene intermediate. By trapping with nucleophiles, different allylic compounds can be formed stereoselectively. Mechanistic studies supported the presence of Rh-H and allene intermediates in the catalytic cycle. The allylic α,α -disubstituted- α -nitroester can be readily reduced to the corresponding amino ester

with indium powder. Building on this report, I also developed a Rh–H catalyzed nitroalkane addition to alkynes to afford allylic nitro compounds as chiral amine precursors. Although high diastereoselectivity was achieved with the transformation, optimization of enantioselectivity still remains challenging. The initial results of this study are included at the end of chapter 1.

In chapter 2, we developed a Cu-catalyzed hydrophosphination of cyclopropenes to build chiral cyclopropyl phosphines, which are biologically and chemically unique. A range of different cyclopropyl phosphines bearing different stereoelectronics can now be accessed. Supported by both experimental results and computational studies, we propose the transformation generates a Cu-phosphido species, which facilitates migratory insertion followed by protodemetalation to afford the desired products. Density function theory (DFT) calculations suggested migratory insertion is the rate- and stereo-determining step. With NMR studies, we identified a dimeric resting state structure, which can be brought back to the active monomer with addition of DBU. Transition state analysis indicates the stereoselectivity comes from a combination of dispersion and steric interactions. Insights of this study helps future phosphine ligand design and chiral phosphine synthesis.

In chapter 3, a Cu-catalyzed regiodivergent *N*-arylation of unsymmetric pyrazoles with aryne intermediates is investigated. The method provides a new vector for late-stage functionalization of pyrazole compounds to selectively access both *N*-arylated regioisomers. We propose pyrazole binds with Cu to form a Cu-pyrazolate which undergoes a 5-centered aminocupration with an aryne intermediate to afford the desired arylated pyrazoles. By enforcing steric or non-covalent interactions between ligands and the Cu catalyst, we can control the Cu-pyrazolate formation with either more hindered nitrogen atom (N^{α}) or less hindered nitrogen atom (N^{β}). The corresponding 5-centered transition structure undergoes bond formation with the aryne fragment

with high N^α - or N^β - selectivity. The methodology is compatible with a wide scope of pyrazoles bearing different stereoelectronics; we exemplify more than 60 different N^α - and N^β -arylated pyrazoles with moderate to high regioselectivity. We also performed the transformation with different aryne precursors which demonstrates the generality of this reaction.

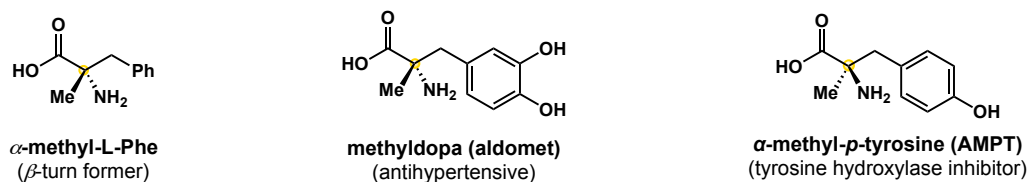
Chapter 1 – Enantioselective Addition of α -Nitroesters to Alkynes¹

1.1 Introduction

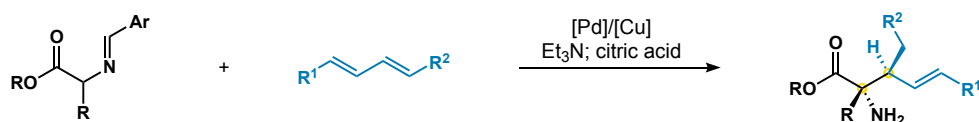
By designing and synthesizing α -amino acids (α -AAs), chemists have expanded the genetic code, shed light on protein function, and enabled innovative medical applications.^{1–8} The α,α -disubstituted α -AAs and related analogs attract interest due to their metabolic stability, unique conformations, and potent bioactivity (Figure 1.1).^{9–11} Enantioenriched α,α -disubstituted α -AAs are targeted by various strategies, including phase-transfer catalysis, organocatalysis, and transition-metal catalysis.^{12–16} Despite an interest in these motifs, methods for the enantio- and diastereoselective preparation of α,α -disubstituted α -AAs bearing contiguous stereocenters remain sought after;^{17–24} emerging reports feature pre-functionalized allylic partners. The direct addition of an amino acid surrogate to a π -system represents an attractive approach to α,α -disubstituted α -AAs. Towards this end, Zi and coworkers exploited synergistic Pd/Cu catalysis for the stereodivergent coupling of aldimine esters and 1,3-dienes.^{25–27} In a complementary approach, we propose using a Rh-hydride (Rh-H) catalyst to couple α -nitrocarbonyls and alkynes to generate the corresponding α -AA precursors. This atom-economical²⁸ coupling exploits two simple functional groups and provides rapid access to synthons for the building blocks of life.²⁹

¹Adapted with permission from Davison, R. T.; Parker, P. D.; Hou, X.; Chung, C. P.; Augustine, S. A.; Dong, V. M. *Angew. Chem. Int. Ed.* **2021**, *60*, 4599–4603. © 2021 John Wiley & Sons, Inc.

A. Inspiration: biologically active α,α -disubstituted α -AAs and analogs.



B. Hydrofunctionalization: synthesis of α -AAs with contiguous stereocenters.



C. Proposal: asymmetric coupling of α -nitrocarbonyls with alkynes.



Figure 1.1. Enantioselective addition of α -nitroesters to alkynes. **(A).** α,α -disubstituted α -AAs with biological activities. **(B).** Previous methods to access α -AA analogs. **(C).** Our proposed Rh-H catalysis to synthesize α -AA precursors.

Based on literature precedent,^{30–39} we envisioned a tandem catalytic cycle for the asymmetric coupling of α -nitrocarbonyls **1** and alkynes **2** to yield α -AA synthons **3** (Figure 1.2). Wolf and Werner discovered that Rh-H complexes isomerize alkynes (**2**) via an allene intermediate (**4**) to form Rh- π -allyl species **IV**.⁴⁰ By using this isomerization, the Breit laboratory achieved asymmetric and catalytic couplings of alkynes with a wide-range of heteroatom nucleophiles to afford branched allylic products.^{41–45} In comparison, the analogous coupling of alkynes with carbon nucleophiles remains more limited, with only three asymmetric variants.^{46–49} We previously reported that aldehydes couple to alkynes with high enantio- and diastereoselectivity when using a chiral Rh-H catalyst in synergy with a chiral amine co-catalyst.⁴⁶ Xing and coworkers expanded this approach for the coupling of ketones with alkynes, however, an achiral amine co-catalyst furnishes the branched products with little to no diastereocontrol.⁴⁸

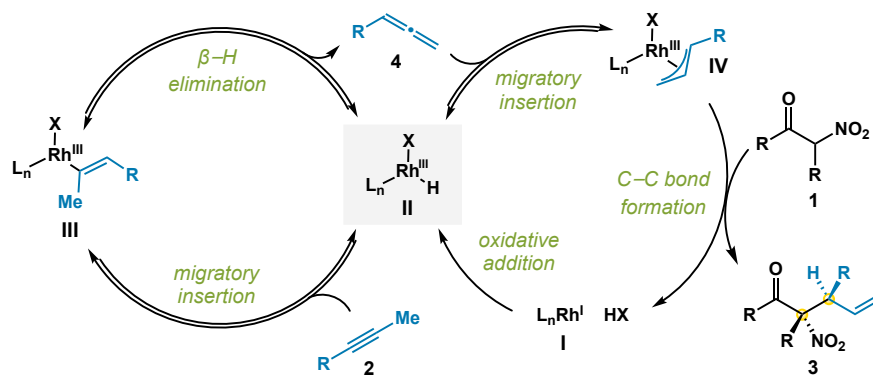


Figure 1.2. Proposed mechanism for Rh-catalyzed allylation.

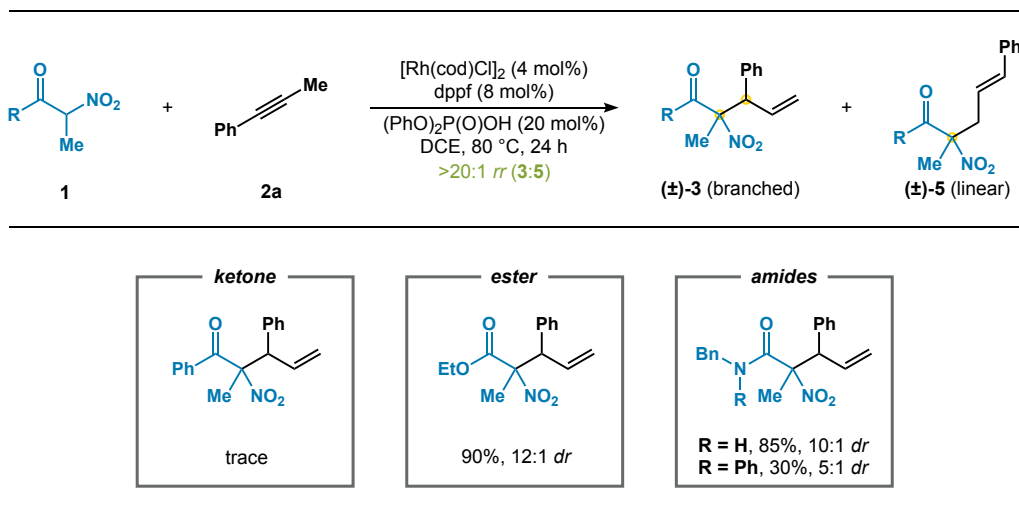
In related studies, we and Breit independently reported that 1,3-dicarbonyls can couple to alkynes to generate branched allylic carbonyl motifs.^{50–54} Promising reactivity and regioselectivity has been achieved. However, obtaining high levels of enantio- and diastereoselectivity has been challenging. It occurred to us that α -nitrocarbonyls display comparable chelation aptitude^{55,56} and acidity ($pK_a = \text{ca. } 8$)⁵⁷ to 1,3-dicarbonyls. Thus, we imagined α -nitrocarbonyls would be suitable nucleophiles for trapping Rh- π -allyl species **IV**. With this design in mind, we set out to couple α -nitrocarbonyls and alkynes with enantio- and diastereocontrol.

1.2 Results and Discussion

In initial studies, we discovered that various α -nitrocarbonyls add to the commercially available alkyne **2a** (Table 1.1). Using a combination of $[\text{Rh}(\text{cod})\text{Cl}]_2$, dppf, and diphenyl phosphate, we observe allylic α -nitroketone, α -nitroester, and α -nitroamide products as single regioisomers ($>20:1$ *rr*) with moderate to high diastereoselectivity (5:1–12:1 *dr*).⁵⁸ In accordance with previous reports, there is a preference for the branched regioisomer, which bears two

contiguous stereocenters.^{30–33,41–45,46–49,50–54} Our findings complement an enantioselective Pd-catalyzed α -nitroester allylation reported by Ooi and coworkers.^{59–63} In Ooi's study, the use of allylic carbonates affords linear regioisomers with one stereocenter.

Table 1.1. Rh-catalyzed allylation with various α -nitrocarbonyls.^[a]

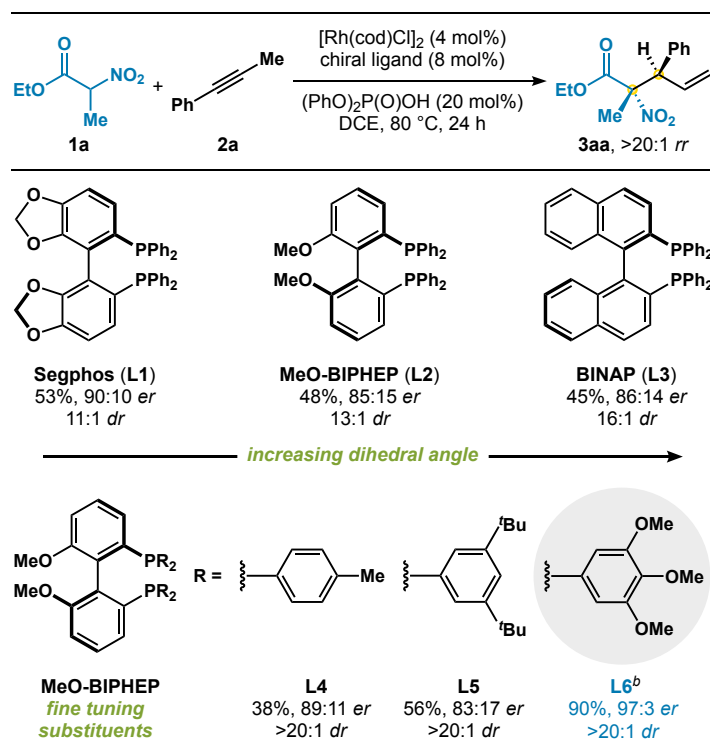


^[a] **1** (0.10 mmol), **2a** (0.15 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.0 mol%), dppf (8.0 mol%), $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ (20 mol%), DCE (0.20 mL), 80 °C, 24 h. Yields determined by ^1H NMR referenced to an internal standard. Cod = 1,5-cyclooctadiene, dppf = 1,1'-bis(diphenylphosphino)ferrocene, DCE = 1,2-dichloroethane.

Next, we focused on an enantioselective variant for the coupling of α -nitroesters with alkynes because the resulting motifs are readily converted to α -AAs.^{64–73} To identify the appropriate chiral catalyst, we selected α -nitroester **1a** and alkyne **2a** as the model substrates (Table 1.2). Using atropisomeric bisphosphine ligands **L1–L3** with a range of dihedral angles,⁷⁴ we observe the allylic α -AA precursor **3aa** with moderate yields (45–53%) and enantioselectivities (85:15–90:10 *er*). Ultimately, we found that commercial MeO-BIPHEP ligand **L6** affords **3aa** in 90% yield with 97:3 *er*, $>20:1$ *dr*, and $>20:1$ *rr* on preparative scale (1 mmol).^{75,76} This coupling relies on the use of alkynes as the unsaturated partner instead of activated olefins, imines,

propargylic carbonates, and allylic leaving groups.^{59–63,64–73} Next, we explored the scope of this transformation to access unique β -aryl α -nitroester motifs.

Table 1.2. Investigation of chiral ligands.^[a]

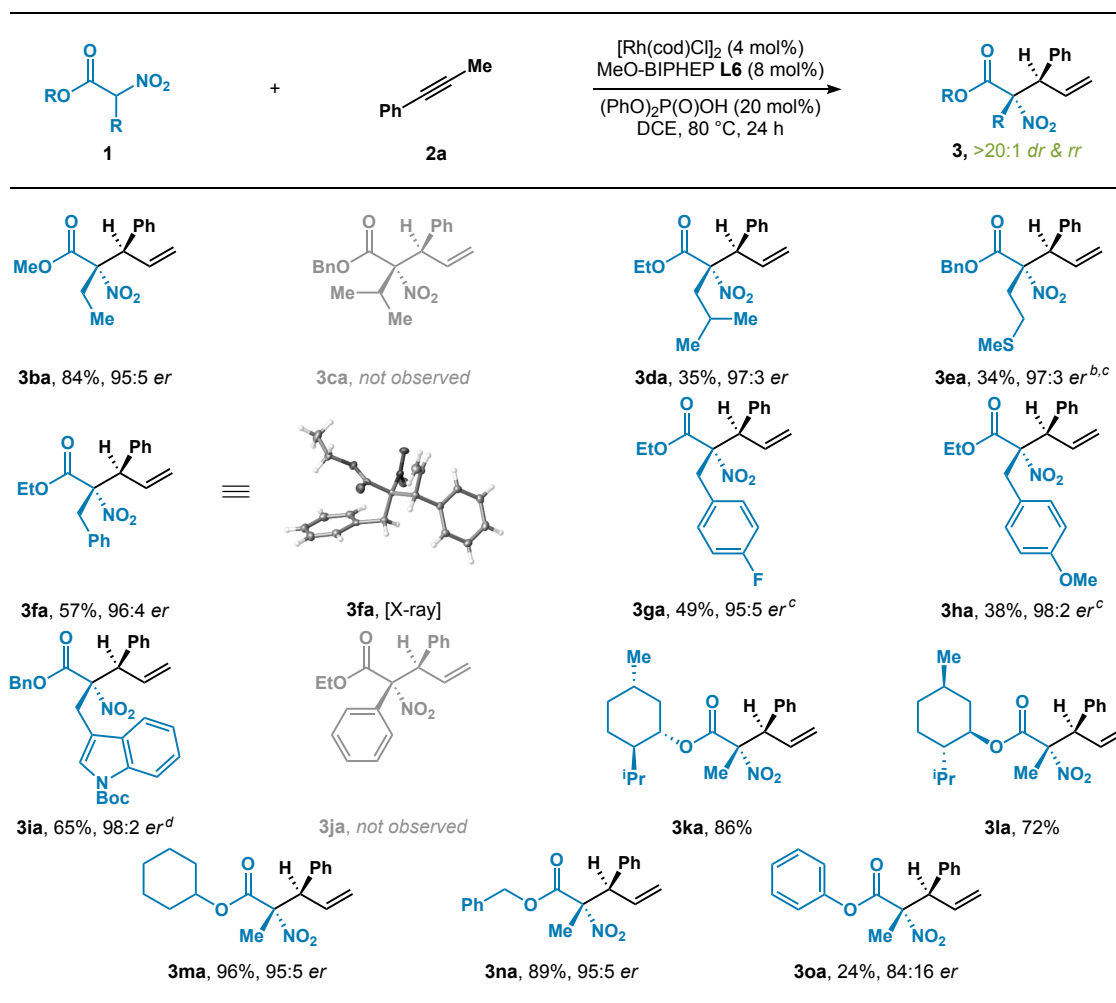


^[a]**1a** (0.10 mmol), **2a** (0.15 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.0 mol%), chiral ligand (8.0 mol%), $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ (20 mol%), DCE (0.20 mL), 80 °C, 24 h. Yields determined by ^1H NMR referenced to an internal standard. ^[b]Isolated yield for a 1 mmol reaction.

With this protocol, we explored the asymmetric coupling of various α -nitroesters with **2a** (Table 1.3). Analogs of ethylalanine (**3ba**), leucine (**3da**), methionine (**3ea**), phenylalanine (**3fa**), 4-fluoro-phenylalanine (**3ga**), tyrosine (**3ha**), and tryptophan (**3ia**) are generated with moderate to high yields (34–84%) and excellent levels of enantioselectivity ($\geq 95:5$ *er*). The absolute configuration of **3fa** was confirmed by X-ray crystallographic analysis.^{75,76} In the case of lower yielding substrates, we often recover α -nitroester **1**.⁷⁵ The bulkier β -branched α -nitroesters **1c** and **1j** do not couple to **2a** to form analogs of valine (**3ca**) and phenylglycine (**3ja**), respectively. Alkyl-

substituted esters **3ka-3na** provide higher reactivity than aryl ester **3oa**. We see high levels of diastereocontrol (>20:1 *dr*) for forming **3ka** and **3la**, which suggests the C–C bond is forged by catalyst control.

Table 1.3. α -Nitrocarbonyl scope for Rh-catalyzed alkyne allylation.^[a]

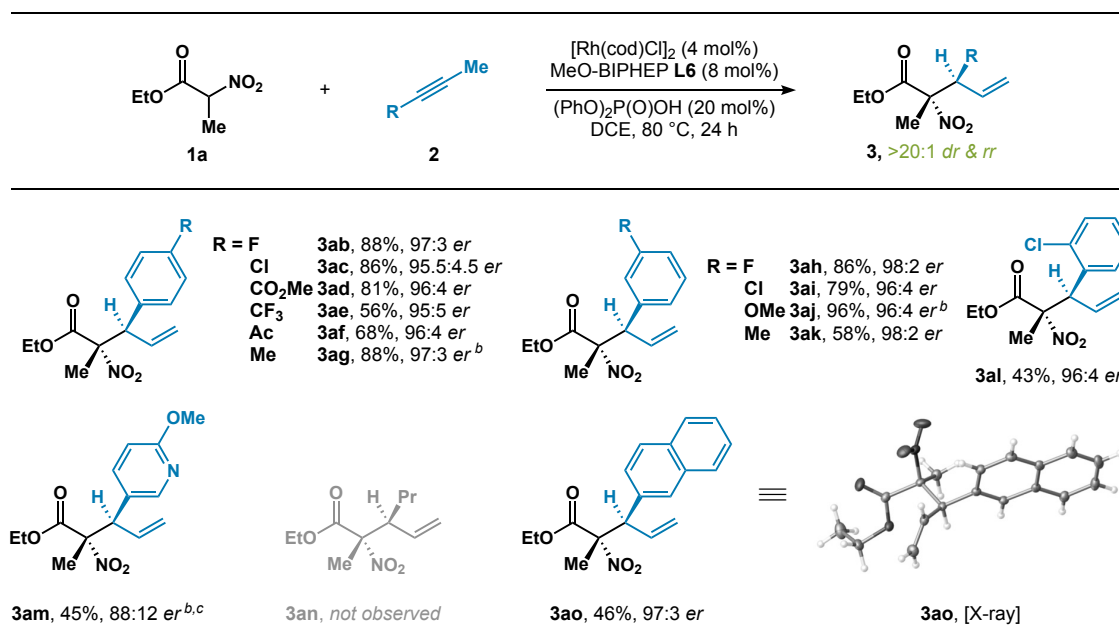


^[a] **1** (0.10 mmol), **2a** (0.15 mmol), [Rh(cod)Cl]₂ (4.0 mol%), MeO-BIPHEP **L6** (8.0 mol%), (PhO)₂P(O)OH (20 mol%), DCE (0.20 mL), 80 °C, 24 h. Isolated yields. ^[b] 6:1 *dr*. ^[c] Yields based on recovered starting material (brsm): **3ea** (76%), **3ga** (96%), and **3ha** (65%). ^[d] [Rh(cod)Cl]₂ (8 mol%) and **L6** (16 mol%) instead of standard conditions.

Table 1.4 captures results from our study on the addition of **1a** to various alkynes **2**. Aryl alkynes possessing a variety of electronics and substitution patterns participate in the asymmetric

coupling (**3ab–3al** and **3ao**). Alkynes bearing halides (**2b**, **2c**, **2h**, **2i** and **2l**), carbonyls (**2d** and **2f**), and extended π -systems (**2o**) transform to the corresponding allylic α -nitroesters **3**. Aryl alkynes with electron-donating substituents (**1g** and **1j**) display lower conversion under standard conditions. Increasing the catalyst loading results in improved yields of **3ag** and **3aj** (88% and 96%, respectively), while maintaining high stereoselectivity ($\geq 96:4$ *er* and $>20:1$ *dr*). The presence of an ortho-substituent on alkyne **2l** imparts lower reactivity (46%), presumably due to steric hindrance. Pyridyl alkyne **2m** converts to allylic α -nitroester **3am** with a higher catalyst loading. It appears that an aromatic or heteroaromatic substituent on the alkyne is critical for reactivity (see **3an**). The absolute configuration of **3ao** was confirmed by X-ray crystallographic analysis.^{75,76}

Table 1.4. Alkyne scope for Rh-catalyzed allylation.^[a]



^[a] **1a** (0.10 mmol), **2** (0.15 mmol), [Rh(cod)Cl]₂ (4.0 mol%), MeO-BIPHEP **L6** (8.0 mol%), (PhO)₂P(O)OH (20 mol%), DCE (0.20 mL), 80 °C, 24 h. Isolated yields. ^[b] [Rh(cod)Cl]₂ (7.5 mol%) and **L6** (15 mol%) instead of standard conditions. ^[c] 15:1 *dr*.

Further experiments provide support for the mechanism depicted in Figure 1.3. First, we monitored a mixture of [Rh(cod)Cl]₂, MeO-BIPHEP **L6**, and diphenyl phosphate by ¹H NMR

spectroscopy (See appendix 1, page 98 for more details). We observe a resonance in the spectrum at -16.2 ppm. The observed resonance is consistent with reported values for Rh(III)-H complexes.^{77–79} This resonance disappears in the ^1H NMR spectrum upon the addition of alkyne **2a**. Second, we subjected deuterated alkyne **d-2a** to the standard reaction conditions (Figure 1.3A). We observe deuterium scrambling into the β -, γ -, and δ -positions of allylic α -nitroester **d-3aa**. The incorporation of hydrogen atoms at the δ -position of **d-3aa** supports reversible β -H elimination in the isomerization pathway. Third, to examine the plausibility of an allene intermediate in the catalytic cycle, we subjected 1-phenylallene (**4a**) to the standard conditions (Figure 1.3B). We observe **3aa** (14% yield) when using an excess of allene **4a**. Moreover, the remaining amount of allene **4a** is consumed. These results, which are in agreement with previous reports that suggest maintaining a low concentration of allene intermediate **4** slows competitive polymerization.^{38,41,80–}

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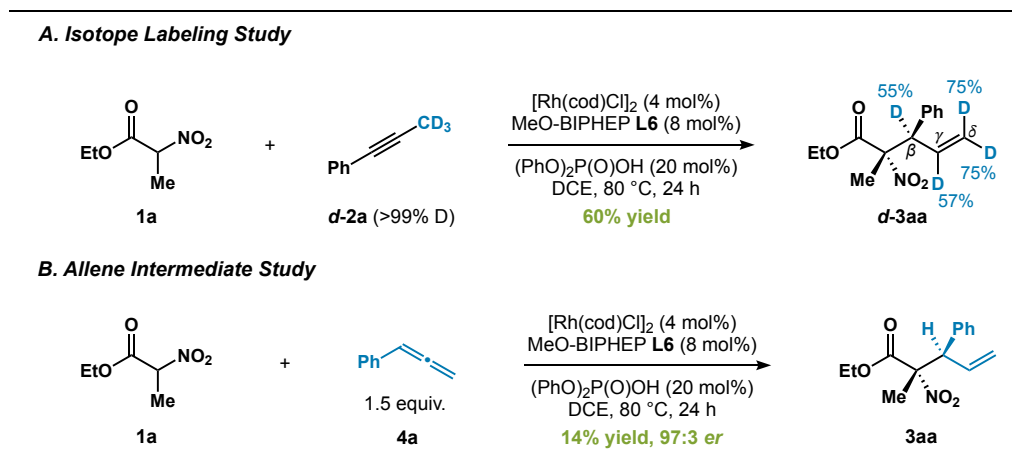
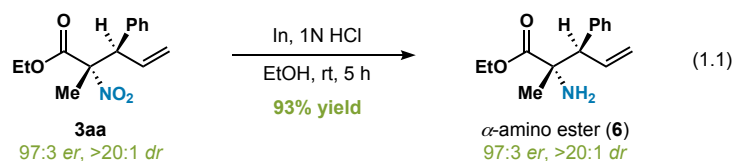


Figure 1.3. Mechanistic studies.

Treating allylic α -nitroester **3aa** with In powder readily yields the corresponding α -amino ester **6** in 93% yield (eq 1.1). This simple reduction allows for rapid access to α,α -disubstituted α -amino esters that contain two contiguous stereocenters, without stereoablation.



1.3 Conclusion and Future Work

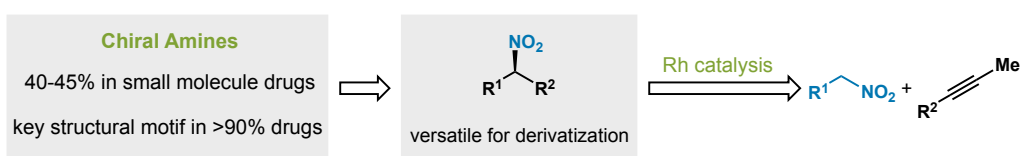
The use of Rh-H catalysis offers an approach to novel α -AAs. The allylic α -AA precursors prepared contain an olefin handle that is attractive due to its potential use for protein modifications,^{83,84} glycopeptide synthesis,⁸⁵ and cyclizations.⁸⁶ Our strategy offers a solution to the challenging preparation of contiguous stereocenters in an acyclic framework, with diastereo- and enantiocontrol. Insights from this study will guide development of related α -nitrocarbonyl coupling reactions with alkynes. In particular, our laboratory has found initial success in the enantioselective addition of α -nitroamides to alkynes, which could provide a way to couple peptides containing α -nitroamide residues with alkynes. Future studies will focus on widening scope and understanding the origins of stereocontrol. The high diastereocontrol achieved occurs without the need for a chiral amine (co-catalyst) as previously observed.⁴⁶ where a chiral amine co-catalyst was required for diastereocontrol.

1.4 Initial Results Based on Nitroester Studies

Enantiopure amine motifs are frequently observed in pharmaceutical drugs and critical as an intermediate to access related structures.^{87–90} Transition-metal catalyzed transformations are attractive as an atom-economical way to afford the amine synthons.²⁸ Nitro group is common in

natural products and versatile to be transferred into different functionalities including amines (Figure 1.4 A).^{91,92} Transition metal-catalyzed allylations of alkenes to trap with nitroalkanes have been previously studied and provided a direct access to allylic nitroalkane compounds.^{63,93–95} Thus, based off nitroester studies in chapter 1, I was interested in expanding the idea and developing asymmetric couplings between nitroalkanes and alkynes as an complementary method to furnish allylic chiral amines (after reduction) (Figure 1.4 B). Under Rh–H catalysis, I imagine nitroalkane as nucleophile can add to Rh- π -allyl to yield α,β -chiral allylic nitroalkanes which provide access to corresponding amines with an alkene handle.

A. Chiral amines are common in drug molecules



B. Proposal: asymmetric addition of nitroalkanes to alkynes

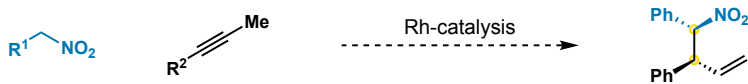
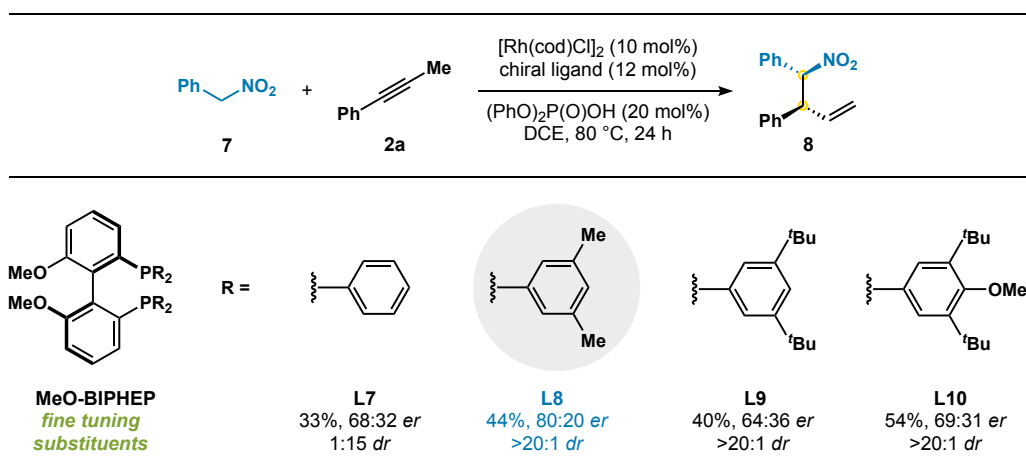


Figure 1.4. Asymmetric addition of nitroalkanes to alkynes. **(A).** Inspiration to construct nitro-containing compounds. **(B).** proposed enantioselective coupling between nitroalkane and alkyne under Rh catalysis.

The initial investigation of achiral and racemic ligands with increasing bite angles reveals DPEPhos as the optimal ligand with moderate yield and diastereoselectivity (63%, 1:13 *dr*). Diastereoselectivity outcome is consistent with what we observed with Rh-catalyzed nitroester coupling with alkynes. After exploration of chiral bisphosphine ligands, OMe-BIPHEP family gives promising enantioselectivity. 3,5-Me substituents on aryl group (**L8**) performs the best and give moderate reactivity and enantioselectivity (44%, 80:20 *er*, >20:1 *dr*) (Table 1.5). Different

attempts were made to improve the enantioselectivity including exploration of Rh sources, ligands, and acid additives. However, no obvious improvement of enantioselectivity was observed (see Appendix 1, page 122 for more details).

Table 1.5. Investigation of chiral ligands for nitroalkane and alkyne coupling.^[a]



^[a] **7** (0.10 mmol), **2a** (0.15 mmol), [Rh(cod)Cl]₂ (10 mol%), chiral ligand (12 mol%), (PhO)₂P(O)OH (20 mol%), DCE (0.40 mL), 80 °C, 24 h. Yields determined by ¹H NMR referenced to an internal standard. Diastereoselectivity determined by analyzing ¹H NMR of the crude mixture.

In conclusion, a highly diastereoselective addition of nitroalkane addition to alkyne was achieved. The current efforts will focus on improving the enantioselectivity of the transformation. In the future, incorporation of machine learning to guide ligand design and selection can potentially help to optimize this reaction and future transformations.

1.5 Author Contributions

Ryan T. Davison (R.T.D.) and Prof. Vy M. Dong (V.M.D) conceived of the project idea discussed in Chapter 1. R.T.D. identified the optimal conditions for the transformation (Table 1.2) with the help of Sara A. Augustine (S.A.A.). Dr. Patrick D. Parker (P.D.P), Xintong Hou (X.H.) and Crystal P. Chung (C.P.C.) explored the α -nitroster scope (Table 1.3). R.T.D. explored the alkyne scope (Table 1.4). X.H. explored the mechanistic insights for the transformation (Figure 1.3). R.T.D. demonstrated the reduction of nitro group to amino group (eq 1.1). All authors analyzed the experimental results, contributed to supporting information and edited the manuscript. X.H. independently studied the nitroalkane and alkyne coupling (Table 1.5).

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Chapter 2 – Copper-Phosphido Catalysis: Enantioselective Addition of Phosphines to Cyclopropenes²

2.1 Introduction

By inventing strategies to forge C–P bonds, chemists provide entrance to organophosphorus architectures for versatile applications in medicine and catalysis.^{1–4} Among these architectures, the cyclopropyl phosphine motif garners attention because of its distinctive steric and electronic attributes. For example, a cyclic analogue of fosmidomycin shows enhanced antibiotic activity against *E. coli*, presumably due to restricted rotation.⁵ In the realm of catalysis, Takasago's cyclopropyl phosphine ligand, 2,2-diphenylcyclopropylphosphines (cBRIDP) outperforms its 2,2-diphenylvinylphosphines (vBRIDP) in Suzuki-Miyaura cross coupling (Figure 2.1A).⁶ Considering ways to construct cyclopropyl phosphines, we focused on hydrophosphination: the direct addition of a P–H bond across a C–C multiple bond.^{7–12} Hydrophosphination represents an attractive and atom-economical platform¹³ for controlled synthesis of molecules with stereogenic carbon and/or phosphorous atoms. While progress has been made,^{14–16} stereoselective methods remain rare beyond use of alkynes,^{17,18} oxa-bicycles,^{19,20} and Michael acceptors.^{21–31} Driven by strain release,^{32,33} cyclopropenes show high reactivity,^{34–44} and the hydrofunctionalization of cyclopropenes has enabled a direct access to a diverse range of enantiomerically enriched rings.^{45–62} In this report, we disclose enantioselective Cu-catalyzed

²Adapted with permission from Daniels, B. S.; Hou, X.; Corio, S. A.; Weissman, L. M.; Dong, V. M.; Hirschi, J. S.; Nie, S. *Angew. Chem. Int. Ed.* **2023**, 62, e202306511. © 2023 John Wiley & Sons, Inc.

hydrophosphination to access a range of cyclopropyl-phosphines at ambient temperature. A unique Cu–phosphido mechanism is supported by both experimental and theoretical studies. We provide insights into ligand trends for selectivity using buried volume analysis.

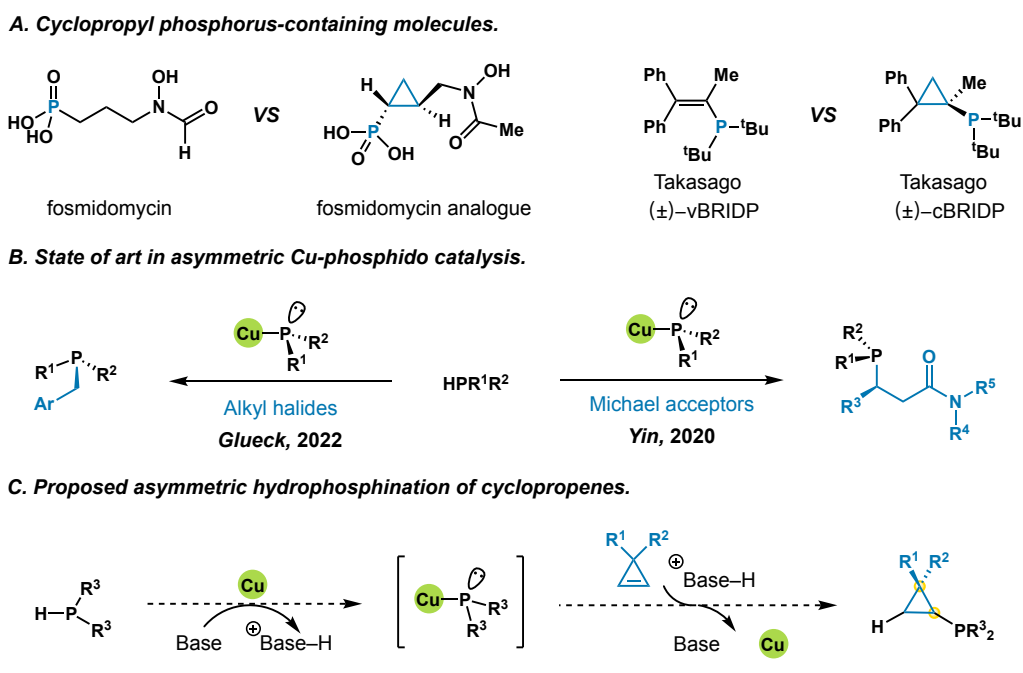


Figure 2.1. Inspiration of asymmetric hydrophosphination of cyclopropenes. (A). Importance of cyclopropyl phosphorus-containing molecules. (B). Highlights of previous studies about Cu–phosphido chemistry. (C). Our proposed Cu-catalyzed asymmetric hydrophosphination of cyclopropenes.

Organophosphorous partners bearing P–H bonds with a wide range of acidities (pK_a 9.0 to 22.4)⁶³ can be activated with transition metal catalyst.^{64–75} For secondary phosphines, coordination followed by deprotonation results in a metal-phosphido complex^{21,23,25–31,76–88} with high nucleophilicity, and recent studies have revealed impressive versatility of catalytically generated Cu–phosphido complexes.^{25,27,28,76–80,86–88} Glueck elucidated mechanistic and structural details,^{79,80} while both Glueck and Yin demonstrated catalytic transformations using Cu–phosphidos (Figure 2.1B).^{27,28} Although Cu catalyzed hydrophosphination has been studied, both phosphine oxides

and phosphites ring-opened to afford allylic phosphine oxides and allylic phosphonates, respectively.⁸⁹ At the start of our studies, there was only one transformation, using phosphine oxides and cyclopropenes, that provided the ring-retained cyclopropyl phosphine product, albeit as a racemic mixture.⁷⁵ Coinciding with our efforts, the Wang group was independently pursuing the enantioselective addition of phosphines to cyclopropenes by Pd-catalysis; their asymmetric version occurs by Pd–H insertion into the cyclopropene.¹² While promising, the scope is limited strictly to ester-bearing cyclopropenes and requires precious metal.⁹⁰ Although precious metals can be practical on industrial scales,⁹¹ earth abundant metals are more sustainable and economical. They also provide an opportunity to uncover novel and complementary reactivity.^{92–94} As an alternative to Pd–H mechanisms, we imagined a strategy involving Cu–phosphido catalysis. Insertion of a Cu–phosphido into cyclopropenes, followed by protodemetalation, would generate chiral cyclopropyl phosphines (Figure 2.1C).^{76–88}

2.2 Results and Discussion

We choose diphenyl phosphine (**2a**) and cyclopropene **1a** as model substrates. For the convenience of handling and analysis, the cyclopropyl phosphine products were oxidized with sulfur to generate the corresponding phosphine sulfides.⁹⁵ In previous studies using copper catalysis, Yin’s group demonstrated the superiority of Taniaphos ligands for the Cu-catalyzed alkylation of secondary phosphines.²⁷ However, Taniaphos ligands showed low enantioselectivity in this transformation (Table 2.1, entry 7). Instead, we found that the DuPhos ligand family is most promising (Table 2.1, entry 8,9). Higher selectivity was correlated with larger R-substituents on the ligand (92% yield, 98:2 *er*). The addition of base is necessary to promote the formation of Cu–

phosphido (Table 2.1, entry 3). With further tuning of the reaction stoichiometry, we developed a convenient and practical protocol for the asymmetric coupling of phosphines and cyclopropenes under Cu catalysis.

Table 2.1. Ligand effects on asymmetric hydrophosphination.^[a]

entry	variations	yield (%)	<i>er</i>
1	—	92	98:2
2	without Cu(CH ₃ CN)PF ₆	—	—
3	without DBU	—	—
4	no (R,R)- <i>i</i> Pr-DuPhos	77	—
5	6 mol% ((R,R)- <i>i</i> Pr-DuPhos	91	79:21
6	L1 instead of L5	90	85:15
7	L2 instead of L5	82	64:36
8	L3 instead of L5	70	90:10
9	L4 instead of L5	73	92:8

R-SEGPHOS (**L1**)

Taniaphos (**L2**)

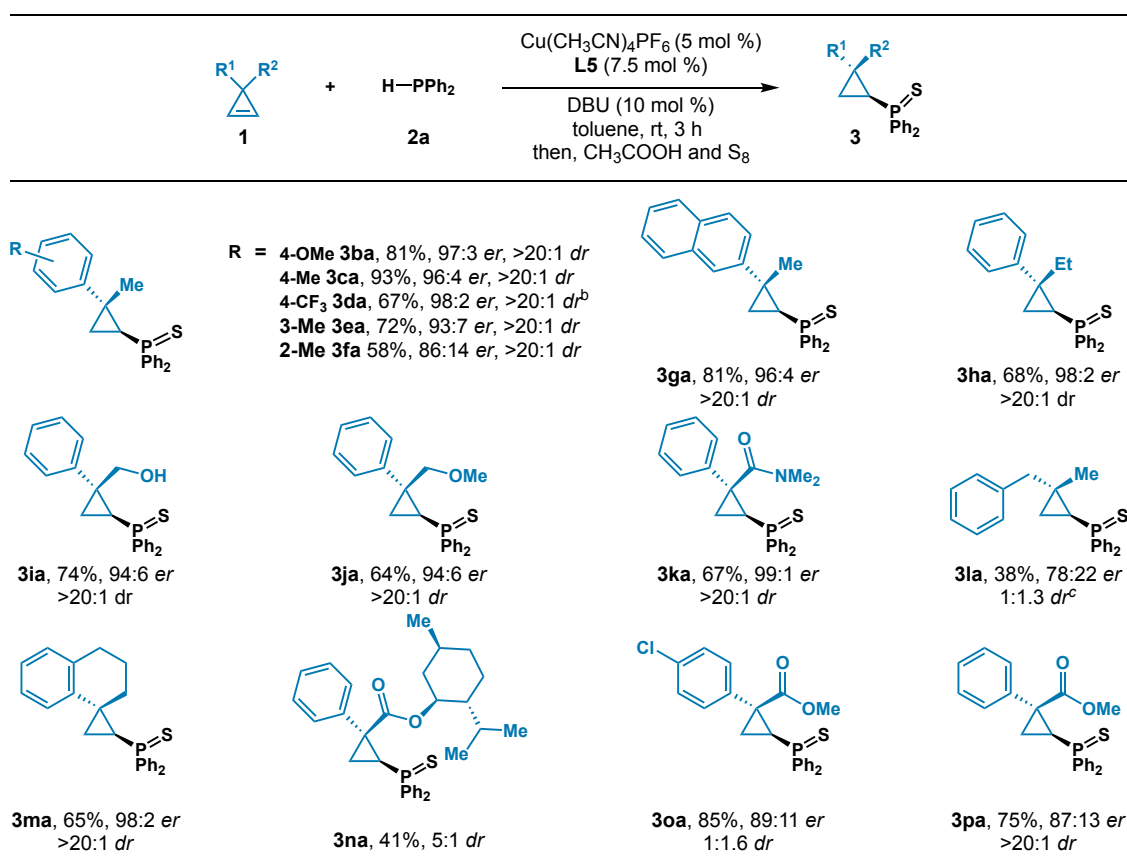
DuPhos
R = Me(**L3**), Et(**L4**), *i*Pr(**L5**)

^[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), Cu(CH₃CN)₄PF₆ (5.0 mol%), ligand (7.5 mol%), DBU (10 mol%), toluene (0.40 mL), 3 h. Yield determined by GC-FID analysis of the reaction mixture, which was referenced to 1,3,5-trimethoxybenzene as internal standard. Enantioselectivity determined by chiral SFC.

We demonstrated the utility of this Cu catalyzed transformation with fifteen unique cyclopropenes bearing different functionalities with a range of electronic and steric properties as summarized in Table 2.2. High yields (81-93%) and stereoselectivities (96:4-97:3 *er*) are observed

for cyclopropenes with electron-rich aromatic rings (**3ba**, **3ca**). An electron-poor aromatic ring (**3da**) gives good stereoselectivity (>20:1 *dr*, 98:2 *er*) and moderate yield (67%). Diphenyl phosphine (**2a**) successfully adds to cyclopropenes bearing more sterically hindered meta- (**3ea**) and ortho-substituted (**3fa**) aryl rings with slightly lower stereoselectivities (86:14-93:7 *er*, >20:1 *dr*). Substituents on the cyclopropene can be replaced with bulkier naphthyl (**3ga**) and ethyl groups (**3ha**). Cyclopropenes with alcohol (**3ia**) and methyl ether (**3ja**) substituents undergo the transformation with moderate yields (64-74%) and high stereoselectivities (>20:1 *dr*, 94:6 *er*). In addition, amide substituted cyclopropene (**3ka**) undergoes hydrophosphination (67% yield, >20:1 *dr*, 99:1 *er*). However, when the aryl group on cyclopropene is replaced with a benzyl group (**3la**), the reactivity (38%) and stereoselectivity (78:22 *er*, 1:1.3 *dr*) are both lowered. With this transformation, we also successfully prepared spirocyclic phosphine **3ma**.^{96,97} Menthol ester cyclopropene (**3na**) gives moderate diastereoselectivity (5:1 *dr*). Ester bearing cyclopropenes (**3oa**, **3pa**) give excellent reactivity (75-85%) but lower stereoselectivities (87:13-89:11 *er*, >20:1-1:1.6 *dr*).

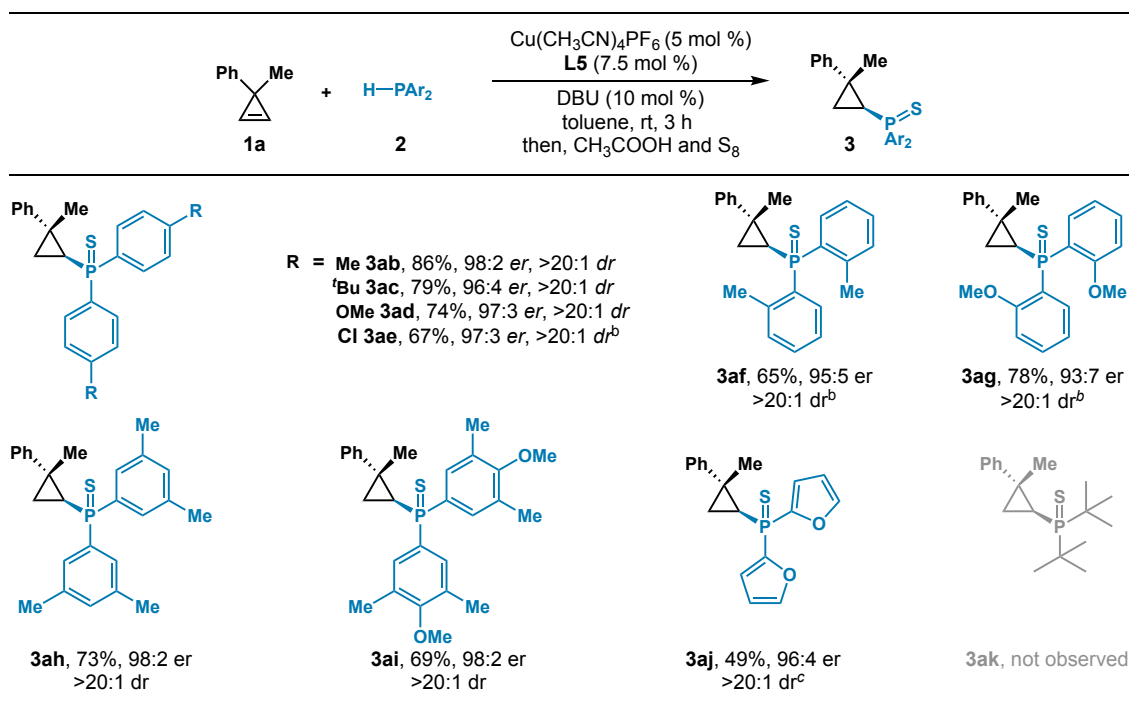
Table 2.2. Hydrophosphination of various cyclopropenes.^[a]



^[a]Reaction conditions: **1** (0.12 mmol), **2a** (0.10 mmol), Cu(CH₃CN)₄PF₆ (5.0 mol%), ligand (7.5 mol%), DBU (10 mol%), toluene (0.40 mL), 3 h. Isolated yield of **3**. Diastereomeric ratios (*dr*) were determined from ¹H NMR analysis of the unpurified reaction mixture. Enantioselectivity determined by chiral SFC. ^bReaction time is 24 hours. ^c inseparable diastereomers.

Our method encompasses a range of phosphine nucleophiles as shown in Table 2.3. Phosphines bearing electron donating Me, ^tBu, and OMe groups at the para position (**3ab**, **3ac**, **3ad**) add to cyclopropenes (74–86%) with high enantioselectivities (96:4–98:2 *er*). Electron poor phosphines are well-tolerated (**3ae**). Even phosphines with ortho- substituted (**3af**, **3ag**), 3,5- substituted (**3ah**) and 3,4,5- substituted aromatic rings (**3ai**) transform in 65–78% yield and high enantioselectivities (93:7–98:2 *er*). This method tolerates heterocyclic phosphines, such as 2-furyl **2j**, which gives **3aj** (49% yield, 96:4 *er*) at elevated temperature (80 °C, 12 hours). However, alkyl substituted phosphine (**3ak**) failed to give any reactivity.

Table 2.3. Hydrophosphination of cyclopropene with various phosphines.^[a]



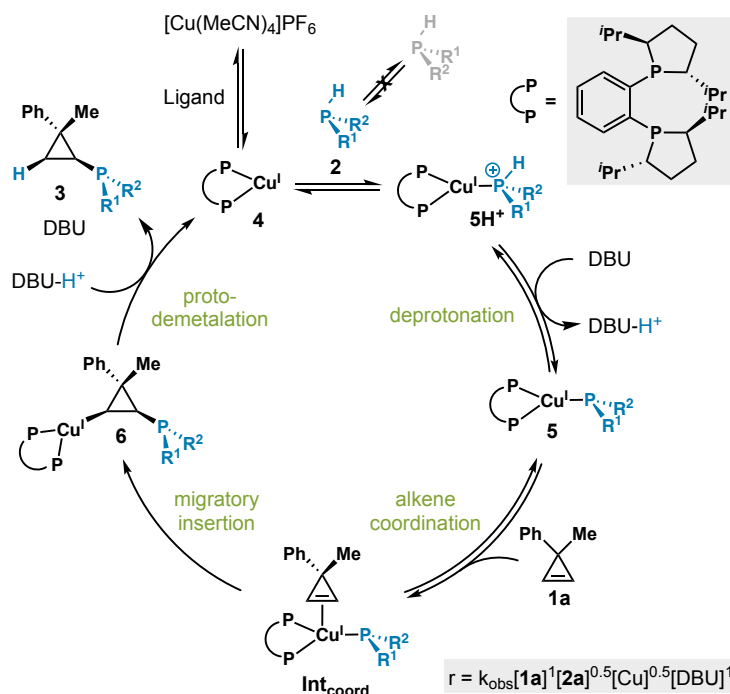
^[a]Reaction conditions: **1** (0.12 mmol), **2a** (0.10 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (5.0 mol%), ligand (7.5 mol%), DBU (10 mol%), toluene (0.40 mL), 3 h. Isolated yield of **3**. Diastereomeric ratios (*dr*) were determined from ^1H NMR analysis of the unpurified reaction mixture. Enantioselectivity determined by chiral SFC. ^[b]Reaction performed for 12 hours.

^[c]Reaction performed at 80 °C for 12 hours.

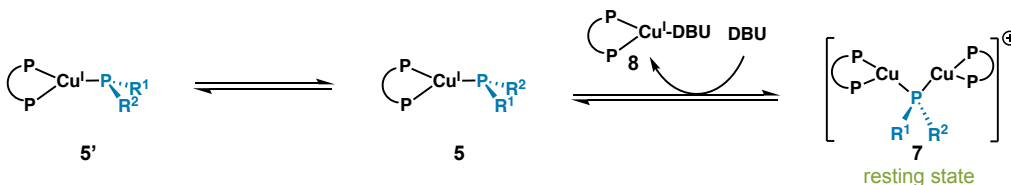
2.3 Mechanistic Studies

Based on literature precedent^{27,79,80} and our own observations, we propose the general catalytic cycle in Figure 2.2A. Initially, $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ binds to (*R,R*)-*i*-Pr-DuPhos to generate a mono(chelate) species **4** followed by the coordination of phosphine (**2**) and deprotonation to generate Cu–phosphido complex **5**. The novel step in the cycle involves addition of Cu–phosphido intermediate (**5**) to the cyclopropene (**1a**). We imagined that **5** could undergo either direct nucleophilic attack^{75,98} or insertion into the cyclopropene π -bond.^{99,100} Lastly, elimination of the copper catalyst regenerates **4** and releases cyclopropyl phosphine **3** to complete the catalytic cycle.

A. Proposed catalytic cycle



B. NMR studies



C. Isotope labeling study

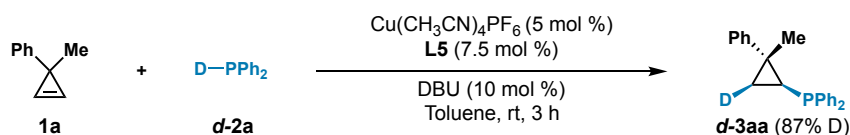


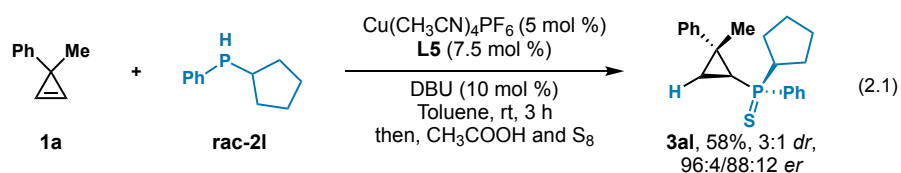
Figure 2.2. Proposed mechanism and experimental studies. **(A)** Proposed catalytic cycle for Cu-catalyzed hydrophosphination. **(B)** Observation of resting state by NMR studies. **(C)** Deuterium labeling study revealed *syn*-addition of P–D to cyclopropene double bond.

To investigate our proposed mechanism, we performed a series of experiments. These experiments were performed in THF which provided a completely homogeneous solution as compared to toluene. First, we obtained the rate law by variable time normalization analysis.¹⁰¹ The fractional order was observed for diphenyl phosphine (**2a**), possible because it involves in

other competitive pathways, and it is a strong coordinating compound that can act as a ligand to copper. We observed a first order dependence on the DBU concentration and a fractional order dependence on the copper catalyst concentration. In Yin's related study, the addition of a base (e.g., Barton's base) to a mixture of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$, bidentate phosphine ligand,²⁷ and secondary phosphine results in a complicated mixture. In stark contrast, we found that addition of various bases (e.g., DBU, $t\text{BuOK}$, and Et_3N) to a mixture of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$, (*R,R*)-*i*Pr-DuPhos, and diphenyl phosphine results in immediate and selective formation of a new species on the basis of ^{31}P NMR. This species was isolated and further characterized by ^{31}P NMR and mass spec analysis and determined to be a Cu-phosphido dimer **7** (Figure 2.2B). In this dimer, the lone pair of the X-type phosphido ligand of **5** acts as an L-type ligand to form a η^2 -bridge to another unit of Cu-DuPhos mono-chelate **4**. We propose this species to be the catalyst resting state. In line with this observation, our kinetics studies, and similar observations made by Appel and coworkers while studying copper hydride catalysis,¹⁰² we propose the DBU acts as not only a base but also an L-type ligand. The DBU undergoes ligand substitution with the dimeric resting state **7** to liberate the catalytically active monomeric Cu-phosphido **5**. This hypothesis is further supported by ^{31}P NMR studies which reveal decomposition of the dimer **7** in the presence of a large excess of DBU. Performing the transformation with isotopically labelled *d*-**2a** revealed that the hydrophosphination proceeds via a syn-addition of the P–D bond across the cyclopropene double bond (Figure 2.2C).¹⁰³

With this mechanism in mind, we examined the possibility of setting a phosphorus stereocenter via a dynamic kinetic asymmetric transformation (DyKAT). As outlined in the proposed mechanism, pyramidal inversion of the secondary phosphine is impractically slow at room temperature while epimerization of Cu-phosphido **5** with **5'** occurs rapidly.^{78–80,104} We

subjected unsymmetrically substituted phosphine **2l** to the reaction conditions to test this hypothesis and observed a 3:1 *dr* for the cyclopropyl phosphine products and an *er* of 96:4 and 88:12 for the major and minor diastereomers respectively (eq 2.1). Based on our prior results, we assume effective desymmetrization of the cyclopropene occurs with relatively low control over the configuration of the phosphorus stereocenter; these results are in line with a recent report from Glueck using a similar catalyst for asymmetric alkylation of secondary phosphines.⁸⁰ On the basis of ³¹P NMR studies, Glueck and coworkers were able to observe both Cu-phosphido diastereomers and measure the ratio of these phosphorus epimers (4:1 *dr*).⁷⁹ In our case, the dimeric nature of the resting state renders the bridging phosphorus atom non-stereogenic, thwarting our attempts at a similar analysis.



To support the proposed mechanism and analyze the details for the enantioselective hydrophosphination of cyclopropenes, we performed a density functional theory (DFT) analysis on the title reaction of 3-methyl-3-phenylcyclopropene (**1a**) and diphenyl phosphine (**2a**) catalyzed by Cu-*i*Pr-Duphos complex (**4**). DFT computations were performed utilizing ω B97XD/def2-TZVP PCM(toluene)// B97D/def2-SVP level of theory as implemented in Gaussian 16.^{105–111} Thermal corrections were computed using Grimme's quasi-rigid rotor harmonic oscillator approximation.¹¹² IRC calculations were performed to confirm that transition structures (TSs) connected minima along the potential energy surface. A thorough exploration of the catalyst

conformational space was performed using CREST. In addition, a detailed exploration of TS conformations was performed for the selectivity-determining step (see Appendix 2, page 236 for more details).

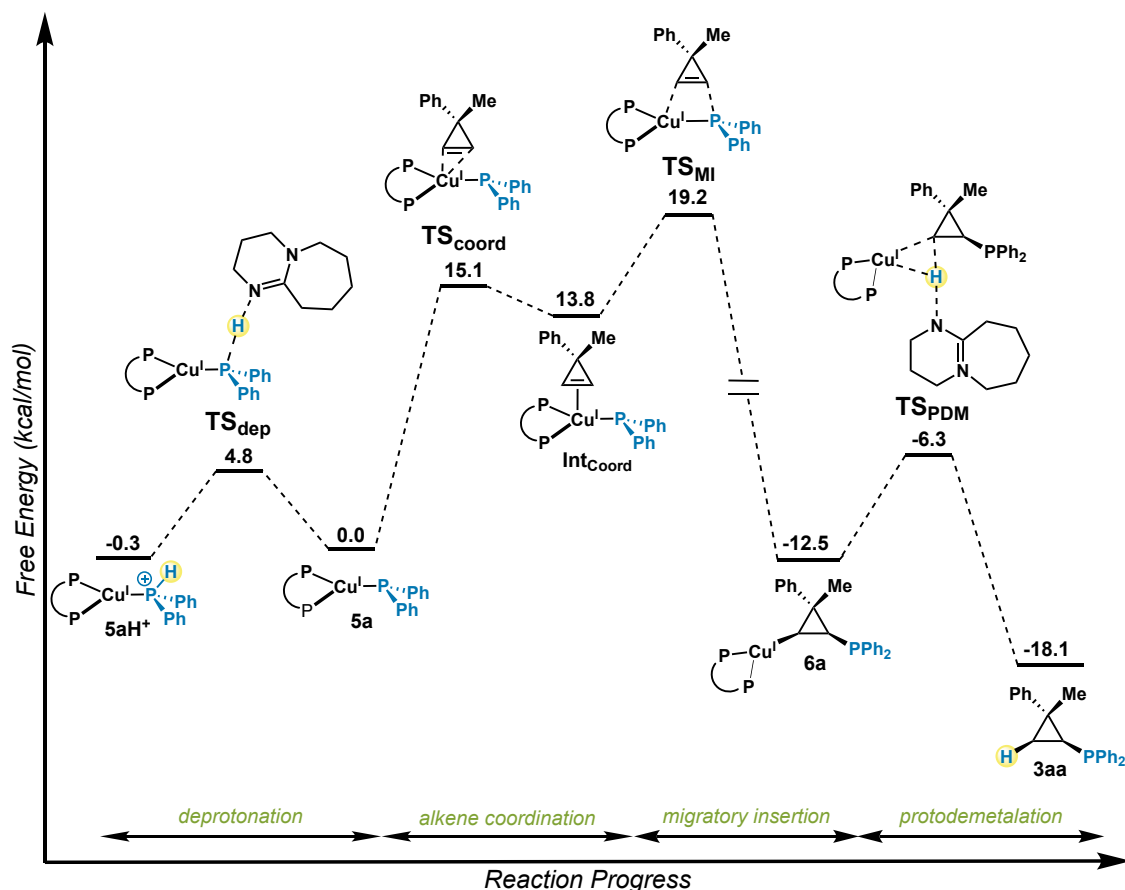


Figure 2.3. Reaction coordinate diagram for hydrophosphination of cyclopropene.

Our computational study sought to identify both the turnover-limiting and stereoselectivity-determining steps of the catalytic cycle and to explain the origins of experimentally observed stereoselectivity. The potential energy surface for the lowest energy pathway resulting from our investigation is shown in Figure 2.3. The reaction is initiated via the coordination of diphenyl phosphine **2a** to Cu-Duphos to give the Cu-HPPh₂⁺ complex **5aH⁺**.

Deprotonation of this cationic complex **5aH⁺** by DBU is a low barrier step (**TS_{Dep}**, $\Delta G^\ddagger = 4.8$ kcal/mol) that leads to the reversible formation of Cu-phosphido intermediate **5a** (chosen as the reference structure in the reaction coordinate). Following deprotonation, **5a** binds cyclopropene **1a** via π -coordination transition structure **TS_{Coord}** ($\Delta G^\ddagger = 15.1$ kcal/mol) to generate Cu-alkene complex **Int_{Coord}**. The subsequent 1,2-migratory insertion into the cyclopropene π -bond (**TS_{MI}**) has a free energy barrier of 19.2 kcal/mol relative to **5a** and represents a highly exothermic step in the pathway, which results in a stable, significantly lower energy copper coordinated cyclopropyl phosphine intermediate **6a** – residing 12.5 kcal/mol below the monomeric resting state **5a**. The reaction pathway then proceeds through a facile stereo- retentive protodemetalation with a barrier of 6.2 kcal/mol (**TS_{PDM}**, $\Delta G^\ddagger = -6.3$ kcal/mol relative to **5a**) – a copper mediated protonation from DBU occurs *syn* to the diphenyl phosphine substituent – to concomitantly regenerate **4** and afford the *syn*-hydrophosphinated cyclopropene product **3aa** (transferred proton shown in blue and highlighted in yellow).^{113–115} This protodemetalation step (**TS_{PDM}**) proceeds through a unique three-center, two-electron bond transition structure (C–Cu bond-breaking is 2.11 Å and C–H bond forming distance is 1.42 Å), consistent with the exclusive *syn* addition observed when the reaction is performed with *d*-**2a** (Figure 2.4 and Figure 2.2C). Incidentally, several alternative pathways for protodemetalation were also explored computationally (See Appendix 2 page 242 for more details). A *syn*-protodemetalation TS analogous to **TS_{PDM}**, whereby copper mediates the proton transfer from a protonated PPh₂ on the adjacent carbon, was found to be 25 kcal/mol higher in energy than **TS_{PDM}**.

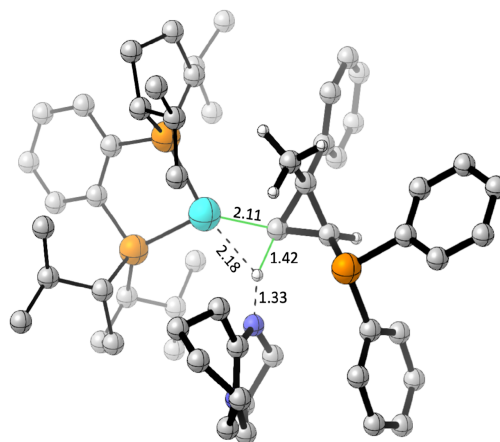


Figure 2.4. Three-center, two-electron bond transition structure for *syn*-protodemetalation.

Analysis of the potential energy surface indicates that **TS_{MI}** is the enantio- and diastereoselectivity-determining step in the hydrophosphination reaction. To investigate catalyst-substrate interactions that dictate the enantioselectivity in this reaction, a conformational search was conducted on **TS_{MI}** for transition structures that lead to the formation of both the major and minor enantiomers of **3aa**. The lowest energy transition structure which leads to the major enantiomer (Figure 2.5A, **TS_{MI-Major}**) is favored by 2.1 kcal/mol with respect to the lowest energy structure leading to the minor enantiomer (Figure 5A, **TS_{MI-Minor}**). At 298 K, a $\Delta\Delta G^\ddagger$ of 2.1 kcal/mol corresponds to a predicted *er* of 97.5:2.5, which is in excellent agreement with the experimental *er* of 98:2 ($\Delta\Delta G^\ddagger$ of 2.3 kcal/mol) for the title reaction.

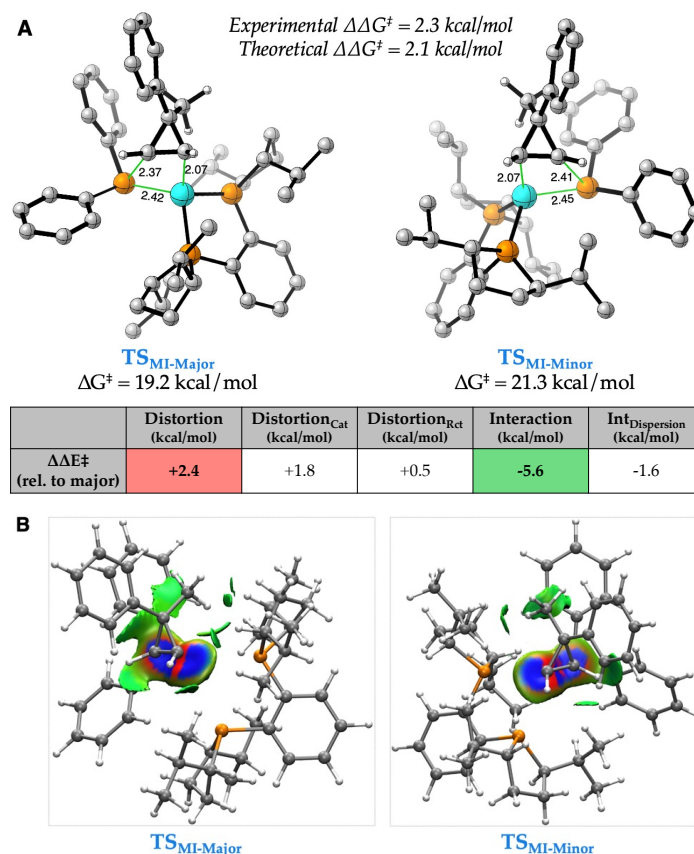


Figure 2.5. Analysis of potential surface energy for TS_{ML} step. **(A)** Lowest energy TSs of the enantioselectivity-determining step with experimental and theoretical free energy barriers after Boltzmann weighting. Also shown are components of the energy decomposition analysis relative to the major enantiomer. $\Delta\text{Distortion}$ of the catalyst (Cat) and reactants (Rct) versus overall $\Delta\text{Interaction}$ (including $\Delta\text{Dispersion}$) are highlighted. **(B)** Non-covalent interaction (NCI) plots depict dispersive interactions (shown in green) between Cu-DuPhos and PPh_2 with cyclopropene reactant for each TS leading to the major and minor enantiomers of the product (isosurface 0.009). Red and blue coloring in the NCI plot indicate areas of strongly attractive or repulsive interactions, while the green indicates areas of weakly attractive dispersion interactions.

To further evaluate the origin of enantioselectivity, a distortion-interaction analysis was performed on $\text{TS}_{\text{ML-Major}}$ and $\text{TS}_{\text{ML-Minor}}$.^{116–118} Distortion energy describes the energy required to distort reactants and catalysts from their respective ground states into the necessary transition state conformations. Energy decomposition reveals that the major enantiomer suffers a greater degree of distortion energy, 2.4 kcal/mol ($\Delta\Delta E^\ddagger$) more than the minor enantiomer (Figure 2.5A). The majority (1.8 kcal/mol) of this 2.4 kcal/mol difference in distortion energy arises from the

distortion of the diphenyl phosphine and Cu-DuPhos catalyst, while the remaining 0.6 kcal/mol arises from distortion of the cyclopropene substrate. Despite distortion energy favoring the minor enantiomer, advantageous interaction energy favors the major enantiomer by 5.6 kcal/mol. Interaction energy describes how the distorted catalyst and reactant fragments interact with one another within the TS, a portion of this can be accounted for as dispersion energy. The major enantiomer exhibits favorable dispersions in the form of significant CH- π interactions between the diphenyl phosphine and the cyclopropene methyl group as well as moderate dispersions amongst the Cu-DuPhos isopropyl groups and the cyclopropene substrate (Figure 2.5B).^{119,120} A visual comparison of the dispersion interactions in the enantioselectivity-determining transition structures shows that **TS_{MI-major}** enjoys more stabilizing dispersion interactions than **TS_{MI-minor}** (as evidenced by the green areas in the non-covalent interaction (NCI) plots of the two TSs shown in Figure 5B).^{121,122} In addition to the favorable dispersions imparted by the isopropyl groups in **TS_{MI-Major}**, the Cu-DuPhos catalyst also serves to add steric bulk to the catalytic pocket, blocking more than three-fourths of the pocket when coordinated to PPh₂, forcing the cyclopropene substrate to bind in the same pocket for both enantiomers (see Appendix 2, page 242 for more details).

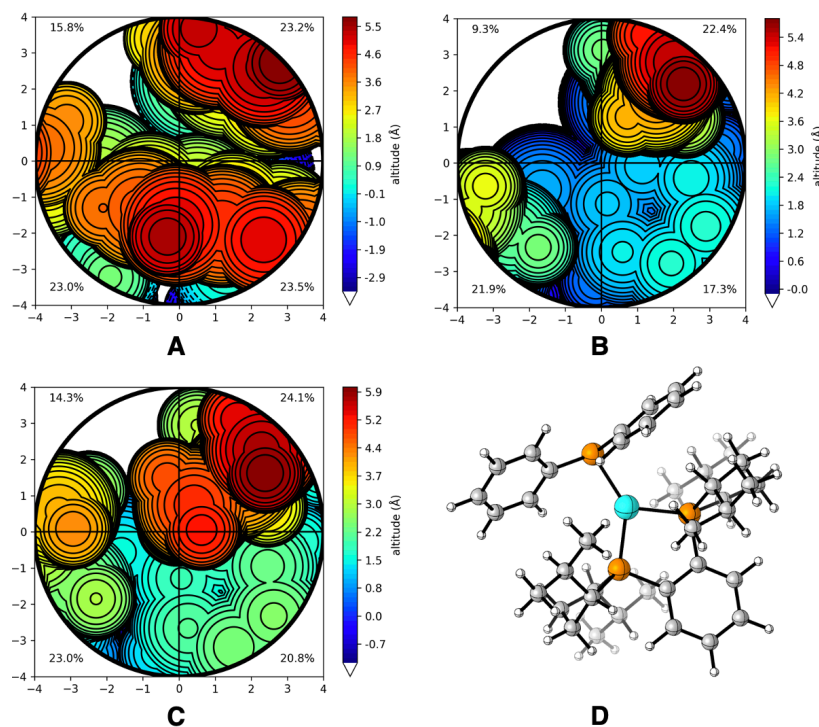


Figure 2.6. Steric maps depicting the catalytic pocket of Cu-phosphido with different ligands. (A) with R-SEGPPOS (**L1**), (B) with (R,R)-Me-DuPhos (**L3**), or (C) with (R,R)-*i*Pr-DuPhos (**L5**). The orientation of the copper-phosphido complexes in these steric maps is depicted in D.

From this analysis, steric interactions have been identified to play a key role in controlling stereoselectivity. Using this information, investigated the buried volume and steric maps for intermediate **5a** with **L1**, **L3**, **L4** and **L5** as ligands.^{123,124} The buried volume analysis reveals that ligand **L1** (Figure 2.6A) has a slightly smaller available free volume compared to the best ligand **L5** (Figure 2.6C). However, **L5** is more fluctional compared to the rigid biphenyl backbone of **L1**, thereby accommodating the incoming cyclopropene more readily. Plausibly leading to an overall reduction in the background reaction of **L5**, compared to **L1**, thus enabling better enantioselectivity in **L5**. Similarly, despite having the same backbone as **L5** (R=*i*Pr), ligands **L3** (R=Me, Figure 2.6B) and **L4** (R=Et) have more available free volume, leading to reduced steric control and slightly lower enantioselectivity.¹²⁵

2.4 Conclusion and Future Work

In conclusion, we report asymmetric hydrophosphination of cyclopropenes in high enantio- and diastereoselectivity. Mechanistic studies reveal an unusual dimeric resting state and a surprising rate enhancement effect from DBU, which plays an important role in forming the catalytically active monomer. Proof of concept for enrichment of phosphorus stereocenters is demonstrated through a DyKAT of an unsymmetrically substituted secondary phosphine. Both the enantio- and diastereoselectivity of the product is determined during the migratory insertion step. An analysis of the relevant TSs indicate that selectivity is controlled by a combination of dispersion and steric interactions. These insights will guide future studies on developing methods to set phosphorus stereocenters and design both mono- and bidentate phosphine ligands. These studies help advance our understanding of copper catalysis, hydrofunctionalization, and phosphine synthesis.

2.5 Author Contributions

Shaozhen Nie (S.N.) and Prof. Vy M. Dong (V.M.D.) conceived of the project idea discussed in Chapter 2. All authors co-wrote the text for the manuscript. X.H. and S.N. started the project and contributed to the exploration at the beginning stage of the project and optimization for the reaction with Pd catalysis and phosphine oxide/diphenyl phosphine. Brain S. Daniel (B.S.D.) contributed to the optimization for Cu-catalyzed hydrophosphination of cyclopropenes (Table 2.1). X.H. explored majority of the cyclopropene scope (Table 2.2). S.N. explored the phosphine scope (Table 2.3). B.S.D. explored the mechanistic insights and DyKAT with unsymmetric phosphine (Figure 2.2 and eq 2.1). S.A.C. conducted DFT calculations, constructed energy surface of the transformation and elucidated factors determining the enantioselectivity for the transformation (Figure 2.3-2.6).

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- (125) There is little difference between the buried volumes of L3 and L4, corresponding with the little difference in the observed ee for L3 and L4 (see Supplementary Information Table S2 for buried volumes and all steric maps).

Chapter 3 – Late Stage Regiodivergent *N*-Arylation of Unsymmetric Pyrazoles

3.1 Introduction

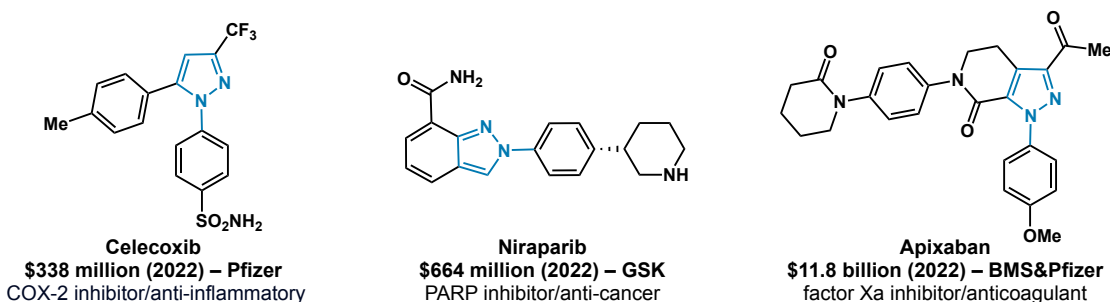
Catalytic transformations have revolutionized the discovery of medicines by enabling the tuning of a lead molecular structure at late stage within a synthetic route.^{1,2} Late-stage functionalization (LSF) to generate a diverse molecular library of complex structures is a powerful platform to establish structure-activity relationships (SAR) for drug discovery and allow chemists to efficiently identify the important pharmacological profile.^{3,4} In addition, pyrazoles, a class of five-membered heterocycles with two adjacent nitrogen atoms, have distinct therapeutic profiles and are prevalent in various fields of drug development, such as anti-inflammatory, antidepressant, anticancer, etc.^{5–7} Among the two hundred top-selling small molecule drugs in 2022, over twenty of them are pyrazole derivatives.⁸ Out of the 164 recent FDA-approved small molecule pharmaceuticals, 88% of them contain *N*-heterocycles and pyrazoles rank fourth.⁹ Specifically, *N*-aryl pyrazoles represent one of the most prominent bioactive motifs (Figure 3.1A).⁷ Despite their appealing properties, significant challenges arise for regioselective arylation of complex unsymmetric pyrazoles. Due to the inherent chemical similarity between the two nitrogen atoms caused by fast tautomerization, a mixture of either more hindered (N^α) or less hindered (N^β) nitrogen atom bond formation is observed.¹⁰ Therefore, a LSF strategy to selectively arylate the more hindered (N^α) or the less hindered (N^β) nitrogen atom is highly desired. Towards this end, transition-metal catalyzed cross-couplings present a reliable protocol for the regioselective synthesis of pyrazole derivatives using aryl halides or aryl boronic acids, such as Buchwald-

Hartwig, Ullmann and Chan-Lam couplings (Figure 3.1B, bottom right).^{11–20} However, these processes typically favor the formation of pyrazole **4**. Due to stereoelectronics, reductive elimination from the metal center usually favors C–N bond formation with the less hindered nitrogen atom (N^β). To furnish the N^α -aryl motif, different synthetic strategies involving ring synthesis with activated synthons are usually required, such as condensation of arylhydrazines with 1,3-dicarbonyls or α,β -unsaturated aldehydes (Figure 3.1B, left).^{21–28} Therefore, a catalytic process that enables the direct N^α -arylation of pyrazoles will be useful to expand the tool box for LSF of an established pyrazole core without introducing new synthetic routes (Figure 3.1B, top right).

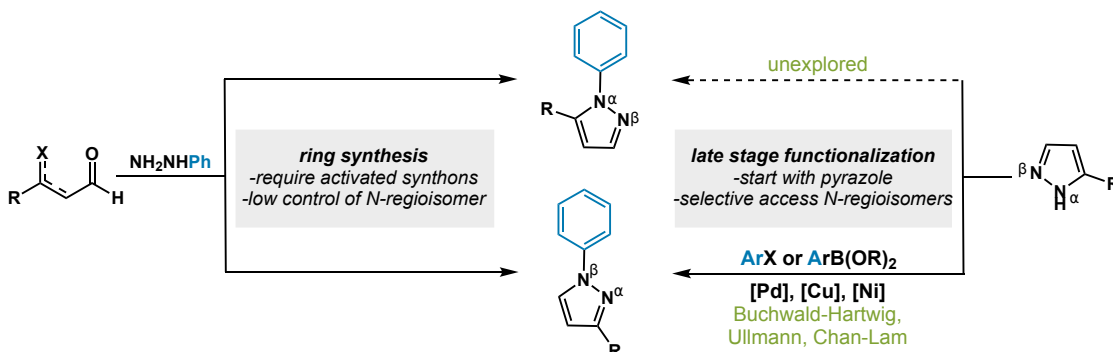
In the realm of pyrazole functionalization, numerous efforts have been made to target the more exposed nitrogen N^β ,^{13,29–34} while only a few studies have shed light on the regioselective activation of more hindered nitrogen N^α .^{35–39} In particular, our group recently developed an enantioselective hydroamination of cyclopropenes with different pyrazoles. We observed exclusive (>20:1 *r.r.*) bond formation at the more hindered nitrogen atom (N^α) on unsymmetrical substrates. With experimental and DFT calculations, we proposed the transformation undergoes a 5-centered aminocupration which involves a preformed Cu-pyrazolate with Cu ligated to N^β on pyrazole preferentially due to sterics. Subsequent C–N bond formation occurs at the neighboring N^α with the cyclopropenyl fragment.^{37,39} Inspired by our previous work, we are interested in addressing the challenges for LSF of pyrazoles and developing a regioselective method to access N^α -arylated pyrazoles with other strained systems via Cu-catalyzed hydroamination.⁴⁰ Arynes, with similar strain energy to cyclopropenes (54.1 and 50.0 kcal/mol, respectively),⁴¹ have shown great versatility as a transient intermediate to achieve novel catalysis and natural product synthesis.^{42–49} Among the various aryne activation strategies, the Kobayashi precursor stands out

as a mild protocol to slowly generate arynes with CsF in MeCN.⁵⁰ We believe that an arynes intermediate can go through similar 5-centered aminocupration to form a C–N bond with pyrazoles.

A. Inspiration: *N*-aryl pyrazoles in FDA-approved drug molecules.



B. Late stage functionalization: regio-selective arylation of unsymmetric pyrazoles.



C. Proposal: ligand-controlled regiodivergent *N*-arylation of unsymmetric pyrazoles.

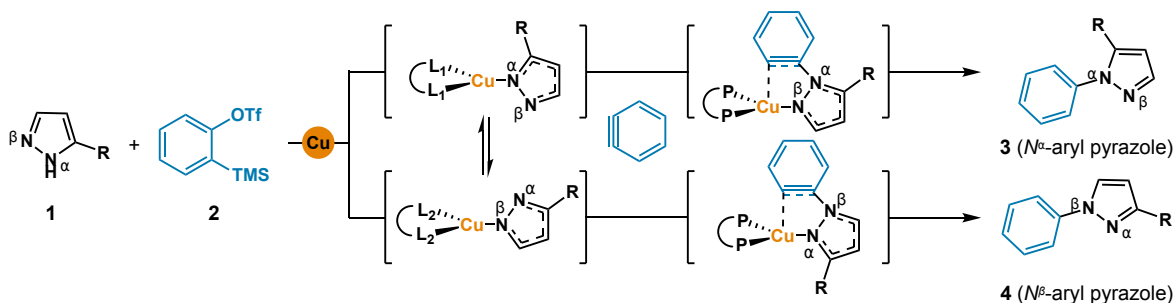


Figure 3.1. Reaction design for regiodivergent arylation of unsymmetric pyrazoles. **(A).** Importance of *N*-aryl pyrazoles in bioactive molecules. **(B).** Regioselective access to more hindered nitrogen atom (*N*^α) is limited. **(C).** Proposed ligand-controlled regiodivergent hydroamination of unsymmetric pyrazoles with arynes.

Recently, regiodivergent catalysis has shown promises in accessing structurally varied moieties using the same set of starting materials but distinct catalysts.^{51–57} Thus, by matching

ligands with Cu and pyrazole, we propose Cu-pyrazolates can be formed via either N^α - or N^β -atom of unsymmetric pyrazole (**1**), which undergoes the corresponding 5-centered aminocupration with Kobayashi aryne intermediate (**2**) to selectively yield either N^α -arylated pyrazoles (**3**) or N^β -arylated pyrazoles (**4**) (Figure 3.1C). The catalyst controlled regioselective N -arylation would resolve a long-standing synthetic challenge for pyrazole functionalization. The orthogonal arylation conditions can be classified as a LSF method and directly affords both regioisomeric analogs of pyrazole-containing structures for pharmaceutical studies.⁵⁸

3.2 Results and Discussion

To begin our study, we chose 3-phenylpyrazole **1a** and Kobayashi benzyne precursor **2a** as our model substrates to explore the regioselective formation of N -phenyl pyrazole **3a** and **4a** (Table 3.1).

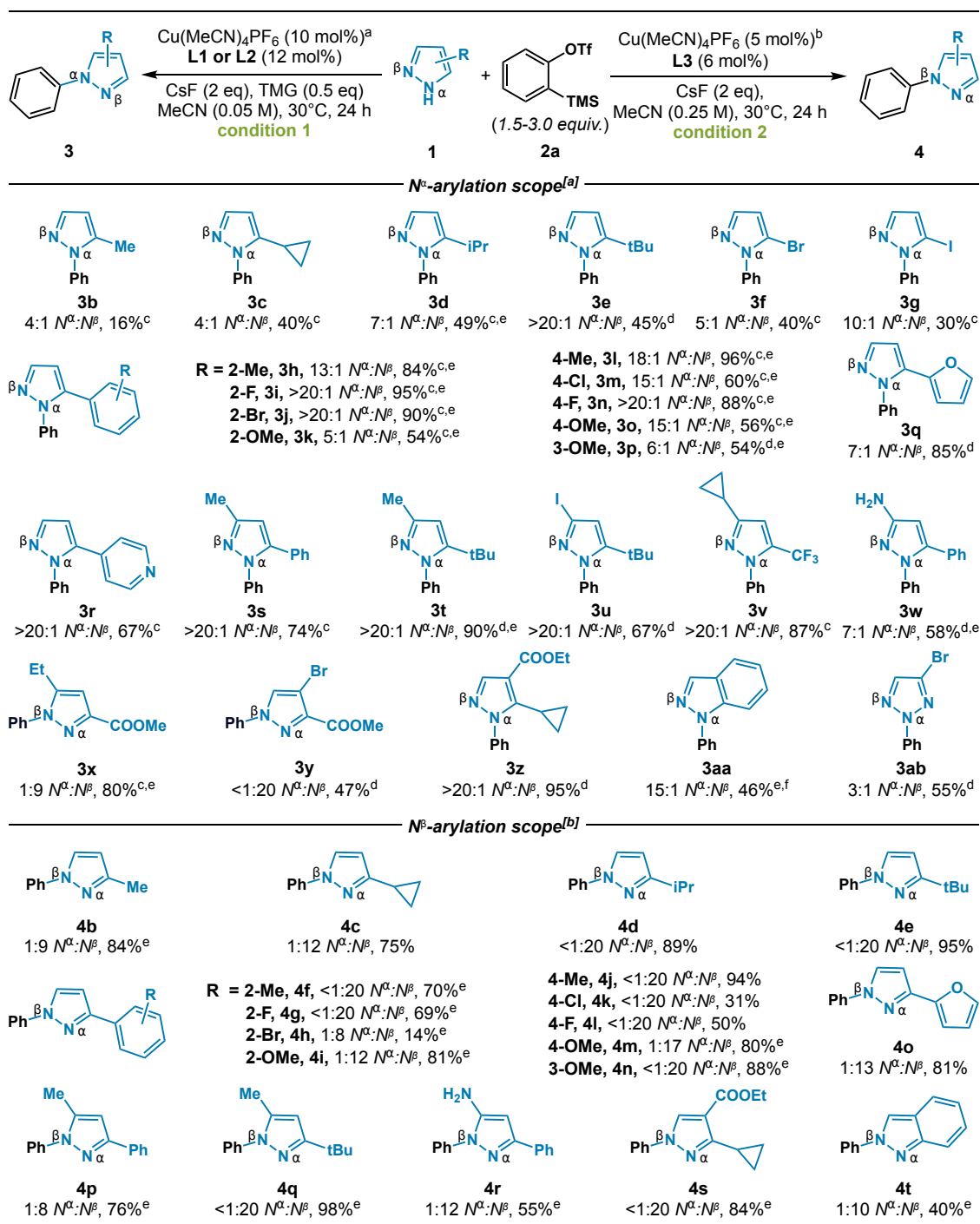
Table 3.1. Reaction optimization.^[a]

entry	variation	$N^\alpha:N^\beta$ (3a:4a)	yield	
1	none	1:1	75%	L1: R = Cy, L2: R = NEt₂ L3: 1,10-phen
2	with Cu(CH ₃ CN) ₄ (10 mol%)	1:12	38%	
3	with Cu(CH ₃ CN) ₄ (10 mol%) + L1 (12 mol%)	10:1	89%	
4	with Cu(CH ₃ CN) ₄ (10 mol%) + L1 (12 mol%) + TMG (0.5 eq)	>20:1	92%	
5	with Cu(CH ₃ CN) ₄ (10 mol%) + L2 (12 mol%) + TMG (0.5 eq)	>20:1	47%	
6	with Cu(CH ₃ CN) ₄ (5 mol%) + BINAP (6 mol%)	1:15	55%	
7	with Cu(CH ₃ CN) ₄ (5 mol%) + L3 (6 mol%)	<1:20	90%	

[a] Reactions were performed on a 0.050 mmol scale. Yield and N -Regioselectivity ($N^\alpha:N^\beta$) were determined by ¹H NMR analysis of the unpurified reaction mixture.

Knowing aryne is prone to free nucleophilic addition, we first examined the background reactivity with only activating reagent CsF added (entry 1), and found high reactivity but no regiocontrol over nitrogen arylation (75%, 1:1 $N^\alpha:N^\beta$). The addition of various Cu(I) precatalysts leads to a surprising increase in N^β -selectivity, albeit with a decrease in yields (entry 2, 38%, 1:12 $N^\alpha:N^\beta$). We attribute this phenomenon to the complexation of Cu catalyst with benzyne, which differs the energy barrier between N^α and N^β in forming the C–N bond. Inspired by the influence of the Cu catalyst over regiocontrol, we sought to obtain N^α -selectivity via a series of ligand investigation. We found Xantphos family offers promising results. In particular, dCyXantphos (**L1**) gives both high regioselectivity (10:1 $N^\alpha:N^\beta$) and reactivity (89%, entry 3). We envisioned that the use of base additives could facilitate Cu-pyrazolate formation and further improve N^α -selectivity. Indeed, both organic and inorganic bases are found to contribute, with TMG (1,1,3,3-tetramethylguanidine) providing the most pleasant results (>20:1 $N^\alpha:N^\beta$, 92%, entry 4). Similarly, NEt₂Xantphos (**L2**) furnishes an excellent ratio of **3a** over **4a** (>20:1), although with lower yield (47%, entry 5). With the optimized N^α -arylation conditions in hand, we wondered if a different ligand could also enhance the N^β -selectivity with Cu catalyst. To our delight, 1,10-phenanthroline (**L3**) affords excellent regioselectivity (<1:20 $N^\alpha:N^\beta$) and reactivity towards **4a** (90%, entry 7). With Cu catalysis, we have developed an orthogonal protocol to construct either N^α -phenyl pyrazole **3a** or N^β -phenyl pyrazole **4a** with excellent regiocontrol and reactivity under mild conditions.

Table 3.2. Regiodivergent N^α - and N^β -arylation with unsymmetric pyrazoles.



[a]. Reaction conditions: **1** (0.050 mmol), **2a** (0.075 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (10 mol%), ligand (12 mol%), TMG (50 mol%), CsF (2.0 equiv.), MeCN (1.0 mL), 12-24 h, 30 °C. [b] **1** (0.10 mmol), **2a** (0.15 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (5.0 mol%), **L3** (7.5 mol%), CsF (2.0 equiv.) MeCN (0.40 mL), 12-24 h, 30 °C. [c]. With ligand **L2**. [d]. With ligand **L1**. [e]. With CsF (4.0 equiv.) and **2a** (3.0 equiv.). [f]. With bis(dicyclohexylphosphino)methane (dcypm) ligand. Isolated yield of **3** and **4**. N -Regioselectivity ($N^\alpha:N^\beta$) were determined from ^1H NMR analysis of the unpurified reaction mixture.

We demonstrated the utility of this Cu-catalyzed regiodivergent transformation to 29 different unsymmetric pyrazoles to give N^α -arylated heterocycles shown in Table 3.2 (top). Under condition 1, alkyl substituted pyrazoles are compatible with the transformation, but we found the regioselectivity increases with the increase of substituent size on the pyrazole (**3b-3e**, 4:1 to >20:1 $N^\alpha:N^\beta$), presumably due to elevated steric congestion to form copper-pyrazolate with nitrogen atom N^α which will lead to the undesired formation of bond with less hindered nitrogen atom N^β . Halogen-containing pyrazoles also give moderate regioselectivity (**3f-3g**, 5:1 to 10:1 $N^\alpha:N^\beta$) with a lower reactivity (30-40%), which might be due to potential Cu-catalyzed oxidative addition side pathways. Excellent regioselectivity is observed for aryl substituted pyrazoles with different sterics, and electronics (**3h-3o**, 13:1 to >20:1 $N^\alpha:N^\beta$) with the exception of o- and m-methoxy substituted aryl pyrazoles to afford a lower regioselectivity (**3i**, **3p**, 5:1 to 6:1 $N^\alpha:N^\beta$). Heteroaryl substituted pyrazoles also afford the desired regioisomer successfully (**3q-3r**, 67%-85%, 7:1 to >20:1 $N^\alpha:N^\beta$). 3,5-Disubstituted pyrazoles undergo the transformation with excellent regioselectivity and reactivity (**3s-3v**, 67-90%, >20:1 $N^\alpha:N^\beta$). In addition, amino-pyrazole showed the hydroamination preferred with pyrazole nitrogen atom N^α over an amino substituent (**3w**, 58%, 7:1 $N^\alpha:N^\beta$). Interestingly, we observe the aryl group adds to the nitrogen atom N^β for 3-ester pyrazoles (**3x-3y**, 7:1 to >20:1 $N^\alpha:N^\beta$). We postulate the ester can chelate with the Cu catalyst and thus direct the Cu-pyrazolate formation with nitrogen atom N^α to enable the formation of N^β -arylated pyrazoles. Moving this ester group further away from the pyrazole nitrogen to avoid chelation, we observe 4-ester pyrazole restores the regioselectivity to arylate more hindered nitrogen and gives the N^α -arylated product (**3z**, >20:1 $N^\alpha:N^\beta$). We demonstrated the transformation with other N -heterocycles. Indazole showed high regioselectivity (**3aa**, 15:1 $N^\alpha:N^\beta$), but triazoles only showed moderate regioselectivity (**3ab**, 3:1 $N^\alpha:N^\beta$).

Table 3.3. Regiodivergent N^α -arylation with various aryne precursors.^[a]

1a	2	5	
Kobayashi aryne precursors			
 5a 16:1 $N^\alpha:N^\beta$, 76% ^b	 5b 12:1 $N^\alpha:N^\beta$, 81% ^c	 5c 11:1 $N^\alpha:N^\beta$, 50% ^c	 5d >20:1 $N^\alpha:N^\beta$, 84% ^c 5:1 $C^1:C^2$
 5e >20:1 $N^\alpha:N^\beta$, 84% ^d >20:1 $C^1:C^2$	 5c' 15:1 $N^\alpha:N^\beta$, 31%^d 1:8 $C^1:C^2$		
 5f 6:1 $N^\alpha:N^\beta$, 46% ^d >20:1 $C^1:C^2$	 5g 13:1 $N^\alpha:N^\beta$, 67% ^c 1:1 $C^1:C^2$	 5h >20:1 $N^\alpha:N^\beta$, 98% ^b 1.2:1 $C^1:C^2$	 5i 14:1 $N^\alpha:N^\beta$, 47% ^e 6:1 $C^1:C^2$
Smith aryne precursors			
 5m 12:1 $N^\alpha:N^\beta$, 50% ^{b,f} 2:1 $C^1:C^2$	 5j 2:1 $N^\alpha:N^\beta$, 47% ^{d,f} >20:1 $C^1:C^2$	 5k 4:1 $N^\alpha:N^\beta$, 55% ^{d,f} 3:1 $C^1:C^2$	 5l 7:1 $N^\alpha:N^\beta$, 34% ^{d,f} 2:1 $C^1:C^2$
	 5n >20:1 $N^\alpha:N^\beta$, 84% ^{b,f} 1:2 $C^1:C^2$	 5o >20:1 $N^\alpha:N^\beta$, 48% ^{b,f} 1:2 $C^1:C^2$	

[a]. Reaction conditions: **1a** (0.050 mmol), **2** (0.15 mmol), Cu(CH₃CN)₄PF₆ (10 mol%), ligand (12 mol%), TMG (50 mol%), CsF (4.0 equiv.), MeCN (1.0 mL), 12–24 h, 30 °C. [b]. with ligand **L2**. [c]. with ligand **L4**. [d]. with ligand **L1**. [e]. with ligand **L5**. [f]. Aryne generated using Smith precursor: **1a** (0.050 mmol), Smith aryne precursor (0.075 mmol), Cu(CH₃CN)₄PF₆ (10 mol%), ligand (12 mol%), TMG (50 mol%), K₃PO₄ (2.0 equiv.), MeCN (1.0 mL), 24 h, 30 °C. Isolated yield of **5**. N -Regioselectivity ($N^\alpha:N^\beta$) were determined from ¹H NMR analysis of the unpurified reaction mixture.

We can switch the regioselectivity to less hindered nitrogen atom N^β and successfully afford 19 different N^β -arylated N -heterocycles under condition 2 (Table 3.2, bottom). For alkyl substituted pyrazoles, we observed a similar trend as condition 1. The regioselectivity increases from 3-Me (**4b**, 1:9 $N^\alpha:N^\beta$), 3-cyclopropyl (**4c**, 1:12 $N^\alpha:N^\beta$), 3-iPr (**4d**, <1:20 $N^\alpha:N^\beta$) to 3-tBu (**4e**, <1:20 $N^\alpha:N^\beta$) substituted pyrazoles. Aryl (**4f-4n**, 14-94%, 1:8 to <1:20 $N^\alpha:N^\beta$) and furan (**4o**, 81%, 1:13 $N^\alpha:N^\beta$) substituted pyrazoles afforded corresponding arylated pyrazole product with moderate to excellent regioselectivity and reactivity. The regioselectivities of disubstituted pyrazoles are switched and favor the C–N bond formation with less hindered nitrogen N^β (**4p-4s**, 55-98%, 1:8 to <1:20 $N^\alpha:N^\beta$). With indazole, arylation also occurs at the less hindered nitrogen N^β (**4t**, 40%, 1:10 $N^\alpha:N^\beta$).

With Xantphos (**L1-L2**) and Josiphos ligands (**L4-L5**), Cu-catalyzed N^α -arylation of pyrazole **1a** encompasses a variety of Kobayashi precursors **2** with different stereoelectronic profiles (Table 3.3). All symmetric arynes showed high regioselectivity to form C–N bond between more hindered nitrogen atom N^α and aryne (**5a-5c**, 11:1 to 16:1 $N^\alpha:N^\beta$). In the case of unsymmetric arynes, regioselectivity on carbon electrophiles further complicate the regiocontrol, with up to four anticipated regioisomers.⁵⁹ 3-Substituted arynes (**5d-5f**) exhibit moderate to excellent regioselectivities for both aryne carbons (5:1 to >20:1) and pyrazole nitrogen atoms (6:1 to >20:1 $N^\alpha:N^\beta$). Weaker substituent effect is observed with distal substitutions, such as 4-phenyl and 4-methyl benzyne (**5g, 5h**), which afford the corresponding N^α -aryl product with high nitrogen regioselectivity but no carbon selectivity (67-98%, 13:1 to >20:1 $N^\alpha:N^\beta$, 1:1 $C^1:C^2$). Interestingly, we also showcase one of the rare examples of catalyst diverging aryne regioselectivity.⁶⁰ Using either Xantphos (**L1**) or Josiphos (**L5**) ligand, we observe the switch of carbon regioselectivity (1:8 $C^1:C^2$ and 6:1 $C^1:C^2$) while maintaining a desirable nitrogen regiocontrol (15:1 and 14:1

$N^\alpha:N^\beta$) with unsymmetric naphthyl aryne (**5c'**, **5i**). To expand the functionality of the scope and demonstrate the compatibility of the catalysis with other aryne precursors, we explored pyrazole arylation with Smith's oxonium aryne precursor, which releases aryne upon the addition of bases, such as K_3PO_4 .⁶¹ With this protocol, we found o-nitro group on aryne intermediate prefers to form C–N bond with C^I carbon and give moderate nitrogen selectivity (**5j**, 2:1 $N^\alpha:N^\beta$, >20:1 $C^I:C^2$). 4-substituted arynes furnish moderate to high regioselectivities on both carbon (2:1 to 3:1 $C^I:C^2$) and nitrogen (4:1 to >20:1 $N^\alpha:N^\beta$) with a variety of functional group tolerance (**5k–5o**).

3.3 Conclusion

In summary, we have developed a Cu-catalyzed hydroamination of pyrazoles with aryne intermediates that provides regiodivergent access to the arylation of both less and more hindered nitrogen atoms on unsymmetric pyrazoles. Our mild conditions omit the synthesis of N^α -aryl pyrazoles through functionalized starting materials and enables late-stage modifications with high functional group tolerance. Preliminary computational and experimental studies indicate a ligand-controlled mechanism, wherein ligands dictate the formation of Cu-pyrazolate with either N^α or N^β , followed by a 5-centered aminocupration with aryne to afford either of the pyrazole N -regioisomers. Base additives, such as TMG, were found to improve the regioselectivity towards the more hindered nitrogen N^α , presumably through facilitating proton transfer during Cu-pyrazolate formation and aminocupration. This work advances the understanding of Cu-amido catalyzed hydroamination, regiodivergent catalysis, and N -heterocycle functionalization. We imagine the insights obtained from this work to guide the regioselective transformation of heterocycles, and in particular to the late-stage modifications of bioactive pyrazoles.

3.4 Author Contributions

Minghao Wang (M.W.) and Vy M. Dong (V.M.D.) conceived of the project idea discussed in Chapter 3. M.W. and Lori D. Digal (L.D.D.) optimized the condition to access more hindered nitrogen atom (N^{α}) on unsymmetric pyrazoles (Table 3.1). X.H. and M.W. optimized the condition to access less hindered nitrogen atom (N^{β}) on unsymmetric pyrazoles (Table 3.1). M.W., X.H. and L.D.D. explored the pyrazole scope to access both N^{α} - and N^{β} -arylated products (Table 3.2). M.W. and X.H. contributed to the scope for aryne intermediates (Table 3.3). All authors analyzed the experimental results and contributed to the supporting information.

3.5 References

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Conclusion

Transition metal catalysis is a powerful platform for constructing complex small molecules from simple building blocks. With transition metal-catalyzed hydrofunctionalization of different unsaturated systems, we provide direct access to biologically and chemically important motifs. In particular, alkynes generate Rh- π -allyl intermediates which can be trapped by nitroesters and nitroalkane pronucleophiles to afford α,α -disubstituted- α -AA and chiral secondary amine precursors. In addition, a Cu catalyst can desymmetrize cyclopropenes with high stereo-control. Cu-phosphido intermediates formed under basic conditions can react with cyclopropenes to afford cyclopropyl phosphine compounds with high enantioselectivity and diastereoselectivity. Building on this study, we found several Cu catalysts that can also form Cu-pyrazolates from pyrazoles under basic conditions. Therefore, with strained aryne intermediates, these Cu-pyrazolate can react to achieve *N*-arylation of different pyrazoles. By using the appropriate ligands, we can form C–N bonds selectively with either the more hindered (N^α) or less hindered nitrogen atom (N^β) on unsymmetric pyrazoles. In all these studies, careful pairing of the transition metal (Rh and Cu) and ligand is crucial to generate desired small molecules with high stereo-control. We hope these studies guide the future efforts of related hydrofunctionalization to build other important small molecules stereo- and chemoselectively.

Appendices

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Appendix 1 – Supporting Information for Chapter 1

Enantioselective Coupling of Nitroesters and Alkynes¹

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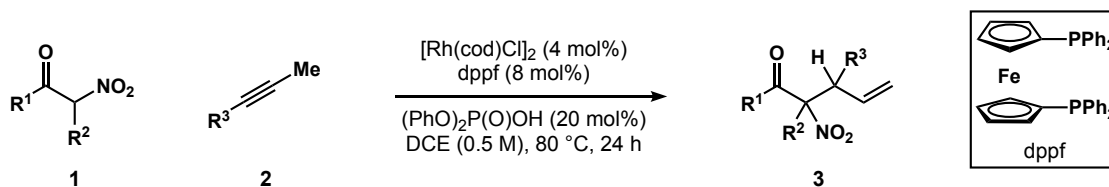
For additional details, see Davison, R. T.; Parker, P. D.; Hou, X.; Chung, C. P.; Augustine, S. A.; Dong, V. M. *Angew. Chem. Int. Ed.* **2021**, 60, 4599–4603.

1. Materials and Methods

Commercial reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar, Acros Organics or TCI and used without further purification. 1,2-Dichloroethane (DCE), toluene (PhMe), and tetrahydrofuran (THF) were purified using an Innovative Technologies Pure Solv system, degassed by three freeze-pump-thaw cycles, and stored over 3 Å MS within a N₂ filled glove box. Dimethylsulfoxide (DMSO), bromoform (CHBr₃) and dimethylformamide (DMF) were used without further purification (anhydrous >99.9% from Sigma Aldrich). All experiments were performed in oven-dried or flame-dried glassware under an atmosphere of N₂ or in a glove box with a N₂ atmosphere. Reactions were monitored using either thin-layer chromatography (TLC; EMD Silica Gel 60 F₂₅₄ plates) or gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD. Visualization of the developed plates was performed under UV light (254 nm) or with a KMnO₄ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products was performed via silica gel chromatography (flash column chromatography or preparative thin-layer chromatography). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. ¹H, ²H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker CRYO-500 or DRX-400 spectrometer. ¹H NMR spectra were internally referenced to the residual solvent signal or TMS. ¹³C NMR spectra were internally referenced to the residual solvent signal. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ¹³C and ¹⁹F NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory, and are reported in terms of frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were obtained by the University of California, Irvine Mass Spectrometry Center on a Micromass 70S-250 Spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Enantiomeric ratio (*er*) for enantioselective reactions was determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. Starting materials **1a**, **2a**, **2n** and all other reagents used for the synthesis of non-commercial starting materials **1**, **2**, and **5** were used without further purification from commercial sources (Sigma Aldrich, Combi-Blocks, Solvias and Alfa Aesar).

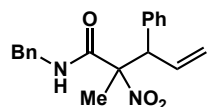
2. Nitrocarbonyl and Alkyne Coupling

A. General Procedure for Racemic Allylic Nitrocarbonyls



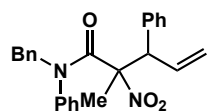
In a N₂-filled glovebox, to a 1 dram vial equipped with a magnetic stir bar was added [Rh(cod)Cl]₂ (2.0 mg, 0.004 mmol, 4 mol%), dppf (4.4 mg, 0.008 mmol, 8 mol%), diphenyl phosphate (5.0 mg, 0.02 mmol, 20 mol%), nitrocarbonyl **1** (0.1 mmol, 1 equiv.), alkyne **2** (0.15 mmol, 1.5 equiv.) and DCE (200 μ L, 0.5 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 °C for 24 hours. The resulting mixture was then cooled to room temperature, filtered through a pad of silica gel, and concentrated *in vacuo*. Diastereo- and regioselectivity ratios (*dr* and *rr*, respectively) were determined by ¹H NMR analysis of the crude reaction mixture. Allylic nitrocarbonyl **3** was isolated by flash column chromatography or preparatory TLC.

N-benzyl-2-methyl-2-nitro-3-phenylpent-4-enamide (Table 1, entry 3)



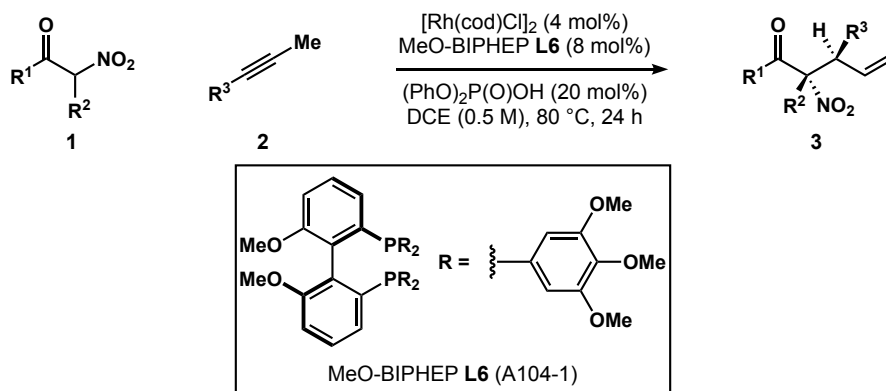
The title compound was synthesized according to general procedure A on 0.05 mmol scale and isolated by preparatory TLC (90:10 hexanes:EtOAc) as a yellow solid [85% yield (¹H NMR yield internally referenced to triphenylmethane), 10:1 *dr*, >20:1 *rr*]. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.31 (m, 3H), 7.28 – 7.26 (m, 3H), 7.21 – 7.19 (m, 2H), 7.14 – 7.12 (m, 2H), 6.93 (s, 1H), 6.23 (ddd, *J* = 16.8, 10.1, and 8.9 Hz, 1H), 5.22 – 5.17 (m, 2H), 4.42 (dd, *J* = 14.7 and 6.0 Hz, 1H), 4.35 – 4.31 (m, 2H), 1.78 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.0, 136.9, 136.3, 133.8, 129.1, 128.9, 128.8, 128.2, 128.1, 128.0, 120.2, 98.4, 57.3, 44.5, 18.9. IR (ATR): 3341, 2931, 1659, 1550, 1537, 1362, 934, 868 cm⁻¹. HRMS calculated for C₁₉H₂₀N₂O₃Na [M+Na]⁺ 347.1372, found 347.1364.

N-benzyl-2-methyl-2-nitro-*N*,3-diphenylpent-4-enamide (Table 1, entry 4)



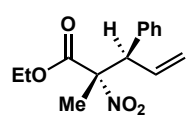
The title compound was synthesized according to general procedure A on 0.05 mmol scale and isolated by preparatory TLC (90:10 hexanes:EtOAc) as a yellow solid [30% yield (^1H NMR yield internally referenced to triphenylmethane), 5:1 *dr*, >20:1 *rr*]. ^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.23 (m, 11H), 7.17 – 7.15 (m, 2H), 7.12 – 7.10 (m, 2H), 6.31 (ddd, J = 17.1, 10.4, and 7.5 Hz, 1H), 5.18 (dt, J = 10.5 and 1.3 Hz, 1H), 5.05 (dt, J = 16.9 and 1.4 Hz, 1H), 4.93 (d, J = 14.1 Hz, 1H), 4.75 (d, J = 14.2 Hz, 1H), 4.59 (d, J = 7.5 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.8, 137.1, 136.3, 135.8, 130.2, 128.97, 128.95, 128.45, 128.44, 127.7, 127.7, 119.0, 96.5, 56.8, 56.6, 22.0. IR (ATR): 2962, 1653, 1542, 1494, 1394, 1260, 1078, 1023, 799 cm^{-1} . HRMS calculated for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 423.1685, found 423.1689.

B. General Procedure for Enantioenriched Allylic Nitrocarbonyls



In a N_2 -filled glovebox, to a 1 dram vial equipped with a magnetic stir bar was added $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.0 mg, 0.004 mmol, 4 mol%), (*R*)-MeO-BIPHEP (Solvias Catalog #: A104-1, 7.5 mg, 0.008 mmol, 8 mol%), diphenyl phosphate (5.0 mg, 0.02 mmol, 20 mol%), nitrocarbonyl **1** (0.1 mmol, 1 equiv.), alkyne **2** (0.15 mmol, 1.5 equiv.) and DCE (200 μL , 0.5 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 $^\circ\text{C}$ for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. Diastereo- and regioselectivity ratios (*dr* and *rr*, respectively) were determined by ^1H NMR analysis of the crude reaction mixture. Allylic nitrocarbonyl **3** was isolated by flash column chromatography or preparatory TLC.

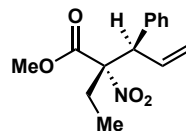
Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3aa)



The title compound was synthesized according to general procedure B on 1 mmol scale and isolated by FCC (20:1 hexanes:EtOAc) as a yellow oil [237 mg, 90% yield, 97:3 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -52.1^\circ$ (*c* 1.0, CHCl₃)]. **¹H NMR** (400

MHz, CDCl₃) δ 7.34 – 7.28 (m, 3H), 7.25-7.22 (m, 2H), 6.31 (ddd, *J* = 16.9, 10.3, 8.4 Hz, 1H), 5.24 (d, *J* = 8 Hz, 1H), 5.18 (d, *J* = 16 Hz, 1H), 4.41 (d, *J* = 8.4 Hz, 1H), 4.21 – 4.09 (m, 2H), 1.78 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.7, 136.7, 134.6, 129.8, 128.9, 128.2, 120.0, 96.4, 63.1, 55.3, 20.2, 13.9. **IR** (ATR): 2985, 1746, 1637, 1549, 1454, 1243, 1144, 855, 702 cm⁻¹. **HRMS** calculated for C₁₄H₁₇NO₄Na [M+Na]⁺ 286.1055, found 286.1057. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.4 min, *t*_{R2} (major) = 1.6 min.

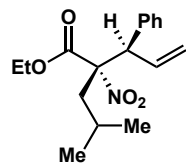
Methyl (2*S*,3*R*)-2-ethyl-2-nitro-3-phenylpent-4-enoate (3ba)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [22.0 mg, 84% yield, 95:5 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -66.6^\circ$ (*c* 0.7, CHCl₃)]. **¹H NMR** (400

MHz, CDCl₃) δ 7.33 – 7.28 (m, 3H), 7.12 (dd, *J* = 7.6 and 2.0 Hz, 2H), 6.35 (ddd, *J* = 17.0, 10.2, and 8.1 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 4.23 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H), 2.14 (dq, *J* = 14.7 and 7.4 Hz, 1H), 1.99 (dq, *J* = 14.8 and 7.4 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.9, 136.5, 135.6, 129.2, 128.8, 128.2, 118.9, 99.8, 55.0, 53.2, 28.9, 8.8. **IR** (ATR): 2955, 1749, 1546, 1456, 1436, 1232, 1127, 992, 927 cm⁻¹. **HRMS** calculated for C₁₄H₁₇NO₄Na [M+Na]⁺ 281.1501, found 281.1514. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.7 min, *t*_{R2} (major) = 2.0 min.

Ethyl (2*S*,3*R*)-2-isobutyl-2-nitro-3-phenylpent-4-enoate (3da)

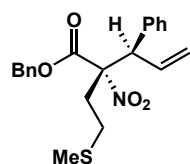


The title compound was synthesized according to general procedure B and isolated by preparatory TLC (98:2 hexanes:EtOAc) as a yellow oil [10.7 mg, 35% yield, 97:3 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -13.7^\circ$ (*c* 0.6, CHCl₃)]. **¹H NMR** (400 MHz,

CDCl₃) δ 7.33 – 7.28 (m, 3H), 7.10 – 7.09 (m, 2H), 6.34 (ddd, *J* = 17.5, 10.2, and 8.1 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 5.07 (d, *J* = 16.9 Hz, 1H), 4.31 – 4.21 (m, 3H), 2.01 (dd, *J* = 14.9 and

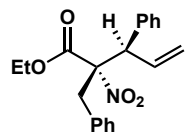
5.4 Hz, 1H), 1.83 (dd, $J = 14.9$ and 5.7 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 0.86 (d, $J = 6.7$ Hz, 3H), 0.83 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.7, 136.6, 135.7, 129.3, 128.8, 128.2, 119.0, 98.7, 62.7, 56.1, 43.9, 24.5, 23.8, 23.8, 14.0. IR (ATR): 2961, 2928, 2854, 1747, 1668, 1548, 1454, 1369, 1224, 1133, 1032, 925 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 328.1525, found 328.1531. Chiral SFC (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 4% i PrOH, 2 mL/min, 210 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , $t_{\text{R}1}$ (major) = 4.2 min, $t_{\text{R}2}$ (minor) = 7.2 min.

Benzyl (2*S*,3*R*)-2-(2-(methylthio)ethyl)-2-nitro-3-phenylpent-4-enoate (3ea)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a white solid [13.2 mg, 34% yield (76% brsm), 97:3 *er*, 6:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -14.5^\circ$ (c 0.7, CHCl_3)]. ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.36 (m, 3H), 7.34 – 7.28 (m, 5H), 7.13 – 7.10 (m, 2H), 6.34 (ddd, $J = 16.9$, 10.2, and 8.2 Hz, 1H), 5.23 (d, $J = 12.0$ Hz, 1H), 5.20 (d, $J = 12.0$ Hz, 1H), 5.19 (d, $J = 10.3$ Hz, 1H), 5.06 (dt, $J = 16.9$ and 1.1 Hz, 1H), 4.20 (d, $J = 8.2$ Hz, 1H), 2.46 – 2.32 (m, 2H), 2.24 – 2.17 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.8, 136.0, 135.0, 134.3, 129.2, 129.1, 129.0, 129.0, 128.9, 128.4, 119.5, 98.6, 68.7, 55.9, 35.7, 28.4, 15.4. IR (ATR): 2913, 1738, 1545, 1453, 1263, 1227, 1166, 933 cm^{-1} . HRMS calculated for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$ 408.1245, found 408.1229. Chiral SFC: 150 mm CHIRALCEL AD-H, 1% i PrOH, 2 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , $t_{\text{R}1}$ (minor) = 9.8 min, $t_{\text{R}2}$ (major) = 11.7 min.

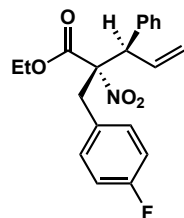
Ethyl (2*S*,3*R*)-2-benzyl-2-nitro-3-phenylpent-4-enoate (3fa)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a pale yellow solid [19.2 mg, 57% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -4.8^\circ$ (c 0.5, CHCl_3)]. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.30 (m, 3H), 7.24 – 7.23 (m, 3H), 7.19 – 7.13 (m, 4H), 6.35 (ddd, $J = 17.5$, 10.0, and 7.8 Hz, 1H), 5.23 (d, $J = 10.3$ Hz, 1H), 5.10 (d, $J = 16.9$ Hz, 1H), 4.34 (d, $J = 7.8$ Hz, 1H), 4.07 – 3.97 (m, 2H), 3.48 (d, $J = 14.8$ Hz, 1H), 3.18 (d, $J = 14.8$ Hz, 1H), 1.01 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.9, 136.4, 135.6, 134.0, 130.5, 129.5, 128.9, 128.4, 128.3, 127.8, 119.3, 100.2, 62.7, 56.3, 41.7, 13.6. IR (ATR): 2984, 1739, 1548, 1496, 1455, 1265, 1199, 1092, 928 cm^{-1} . HRMS calculated for $\text{C}_{20}\text{H}_{21}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 362.1368, found 362.1371. Chiral

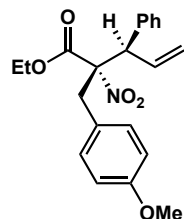
SFC: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.7 min, *t*_{R2} (major) = 2.4 min.

Ethyl (2*S*,3*R*)-2-(4-fluorobenzyl)-2-nitro-3-phenylpent-4-enoate (**3ga**)



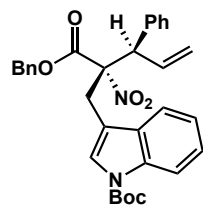
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a white solid [17.4 mg, 49% yield (96% brsm), 95:5 *er*, >20:1 *dr*, >20:1 *rr*, [α]²⁴_D = -2.1° (*c* 0.4, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.31 (m, 3H), 7.18 – 7.12 (m, 4H), 6.94 – 6.90 (m, 2H), 6.34 (ddd, *J* = 16.9, 10.3, and 7.9 Hz, 1H), 5.24 (dd, *J* = 10.4 and 1.2 Hz, 1H), 5.10 (dt, *J* = 16.9 and 1.3 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 4.09 – 3.95 (m, 2H), 3.44 (d, *J* = 14.8 Hz, 1H), 3.16 (d, *J* = 14.8 Hz, 1H), 1.05 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 165.8, 162.5 (d, *J* = 246.7 Hz), 136.2, 135.5, 132.2 (d, *J* = 8.0 Hz), 129.8 (d, *J* = 3.4 Hz), 129.4, 129.0, 128.4, 119.4, 115.3 (d, *J* = 21.3 Hz), 100.2, 62.8, 56.5, 40.9, 13.7. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.9. **IR** (ATR): 2987, 1745, 1605, 1545, 1507, 1267, 1245, 1227, 1210, 1099, 1026, 995, 858 cm⁻¹. **HRMS** calculated for C₂₀H₂₀FN₂O₄Na [*M*+Na]⁺ 380.1274, found 380.1280. **Chiral SFC:** 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 2.2 min, *t*_{R2} (major) = 5.2 min.

Ethyl (2*S*,3*R*)-2-(4-methoxybenzyl)-2-nitro-3-phenylpent-4-enoate (**3ha**)



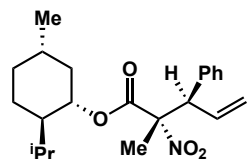
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a pale yellow solid [14.2 mg, 38% yield (65% brsm), 98:2 *er*, >20:1 *dr*, >20:1 *rr*, [α]²⁴_D = +9.5° (*c* 0.7, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.36 – 7.30 (m, 3H), 7.17 – 7.16 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.34 (ddd, *J* = 17.0, 10.3, and 7.9 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 5.09 (d, *J* = 16.9 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 4.09 – 4.01 (m, 2H), 3.76 (s, 3H), 3.42 (d, *J* = 14.8 Hz, 1H), 3.14 (d, *J* = 14.8 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.0, 159.2, 136.5, 135.7, 131.6, 129.5, 128.9, 128.3, 125.8, 119.2, 113.8, 100.3, 62.7, 56.2, 55.3, 40.9, 13.7. **IR** (ATR): 2962, 1738, 1612, 1548, 1513, 1455, 1250, 1180, 1114, 1032, 929 cm⁻¹. **HRMS** calculated for C₂₁H₂₃NO₅Na [*M*+Na]⁺ 392.1474, found 392.1457. **Chiral SFC:** 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 3.0 min, *t*_{R2} (major) = 7.3 min.

***Tert*-butyl-3-((2*S*,3*R*)-2-((benzyloxy)carbonyl)-2-nitro-3-phenylpent-4-en-1-yl)-1*H*-indole-1-carboxylate (3ia)**



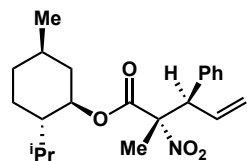
The title compound was synthesized according to general procedure B (modifications: 8.0 mol% Rh-precatalyst and 16 mol% **L6**) and isolated by preparatory TLC (9:1 hexanes:EtOAc) as a yellow solid [35.0 mg, 65% yield, 98:2 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -11.6^{\circ}$ (*c* 0.4, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.50-7.39 (m, 5H), 7.38-7.33 (m, 2H), 7.32-7.24 (m, 5H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.44 (ddd, *J* = 17.0, 10.2, and 7.8 Hz, 1H), 5.27 (d, *J* = 10.3 Hz, 1H), 5.14 (d, *J* = 16.9 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 3.58 (d, *J* = 15.5 Hz, 1H), 3.41 (d, *J* = 15.5 Hz, 1H), 1.69 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.2, 149.6, 136.2, 135.4, 135.2, 134.0, 130.6, 129.5, 129.2, 128.8, 128.64, 128.59, 128.5, 126.3, 124.7, 122.7, 119.6, 118.9, 115.5, 112.3, 99.3, 84.0, 68.8, 56.6, 31.4, 28.4. **IR** (ATR): 2978, 1732, 1548, 1452, 1367, 1256, 1211, 1152, 769, 747, 700 cm⁻¹. **HRMS** calculated for C₃₂H₃₂N₂O₆Na [M+Na]⁺ 563.2158, found 563.2151. **Chiral SFC**: 150 mm CHIRALCEL AD-H, 4% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (major) = 3.9 min, *t*_{R2} (minor) = 4.8 min.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3ka)



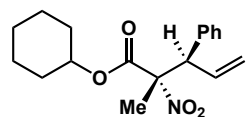
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [32.0 mg, 86% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = +3.5^{\circ}$ (*c* 1.4, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 3H), 7.24 – 7.23 (m, 2H), 6.29 (ddd, *J* = 17.0, 9.9, and 8.1 Hz, 1H), 5.23 (d, *J* = 9.9 Hz, 1H), 5.15 (d, *J* = 16.9 Hz, 1H), 4.68 (td, *J* = 10.9 and 4.4 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 1.87 (d, *J* = 11.9 Hz, 1H), 1.77 (s, 3H), 1.67 – 1.59 (m, 3H), 1.46 – 1.36 (m, 2H), 1.04 – 0.92 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.87 – 0.80 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.66 (d, *J* = 7.0 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.2, 136.7, 134.8, 129.9, 128.7, 128.1, 119.7, 96.2, 77.8, 55.0, 46.8, 40.1, 34.1, 31.5, 26.0, 23.2, 22.0, 20.9, 20.4, 15.9. **IR** (ATR): 2956, 2928, 2870, 1741, 1551, 1454, 1386, 1343, 1245, 1143, 1037, 981 cm⁻¹. **HRMS** calculated for C₂₂H₃₁NO₄Na [M+Na]⁺ 396.2151, found 396.2148.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3la)



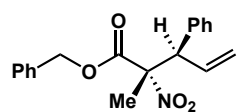
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [26.8 mg, 72% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D = -45.6^\circ$ (*c* 1.3, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 3H), 7.23 – 7.22 (m, 2H), 6.32 (ddd, *J* = 17.0, 10.2, and 8.3 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 16.9 Hz, 1H), 4.71 (td, *J* = 11.0 and 4.4 Hz, 1H), 4.34 (d, *J* = 8.3 Hz, 1H), 1.82 (d, *J* = 11.5 Hz, 1H), 1.79 – 1.75 (m, 1H), 1.73 (s, 3H), 1.69 – 1.65 (m, 2H), 1.49 – 1.41 (m, 1H), 1.39 – 1.33 (m, 1H), 1.05 – 1.00 (m, 1H), 0.88 (d, *J* = 1.7 Hz, 3H), 0.87 (d, *J* = 2.2 Hz, 3H), 0.84 – 0.81 (m, 2H), 0.72 (d, *J* = 6.9 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.6, 136.7, 134.9, 129.8, 128.8, 128.1, 119.6, 96.3, 77.6, 55.4, 46.9, 40.1, 34.1, 31.5, 25.9, 23.1, 22.0, 21.0, 20.8, 15.9. **IR** (ATR): 2956, 2870, 1738, 1551, 1454, 1387, 1245, 1143, 1037, 981 cm⁻¹. **¹H HRMS** calculated for C₂₂H₃₅N₂O₄ [M+NH₄]⁺ 391.2597, found 391.2585.

Cyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3ma)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [30.4 mg, 96% yield, 95:5 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D = -35.8^\circ$ (*c* 1.3, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 3H), 7.25 – 7.22 (m, 2H), 6.31 (ddd, *J* = 16.9, 10.3, and 8.3 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 16.9 Hz, 1H), 4.81 – 4.75 (m, 1H), 4.39 (d, *J* = 8.3 Hz, 1H), 1.80 – 1.74 (m, 1H), 1.77 (s, 3H), 1.74 – 1.59 (m, 3H), 1.51 – 1.42 (m, 2H), 1.41 – 1.26 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.1, 136.7, 134.7, 129.8, 128.7, 128.1, 119.8, 96.3, 75.7, 55.1, 31.1, 31.0, 25.3, 23.4, 23.4, 20.2. **IR** (ATR): 2939, 2861, 1742, 1551, 1453, 1387, 1345, 1265, 1146, 1117, 1008, 928 cm⁻¹. **HRMS** calculated for C₁₈H₂₇N₂O₄ [M+NH₄]⁺ 335.1971, found 335.1975. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.5 min, *t*_{R2} (major) = 1.8 min.

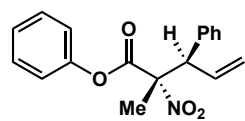
Benzyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3na)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [29.0 mg, 89% yield, 95:5 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D = -34.4^\circ$ (*c* 1.3, CHCl₃)]. **¹H**

NMR (500 MHz, CDCl₃) δ 7.36 (dd, J = 5.0 and 1.8 Hz, 3H), 7.28 (dd, J = 5.1 and 1.8 Hz, 3H), 7.24 (dd, J = 6.6 and 2.5 Hz, 2H), 7.20 (dd, J = 7.0 and 2.3 Hz, 2H), 6.30 (ddd, J = 16.9, 10.2, and 8.5 Hz, 1H), 5.22 (d, J = 10.3 Hz, 1H), 5.16 (d, J = 16.9 Hz, 1H), 5.13 (d, J = 12.5 Hz, 1H), 5.09 (d, J = 12.2 Hz, 1H), 4.42 (d, J = 8.4 Hz, 1H), 1.79 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.5, 136.5, 134.4, 134.3, 129.7, 128.8, 128.8, 128.8, 128.5, 128.1, 120.0, 96.3, 68.5, 55.2, 20.0. **IR** (ATR): 1748, 1550, 1497, 1454, 1387, 1343, 1263, 1235, 1142, 1121, 1030, 992, 931 cm⁻¹. **HRMS** calculated for C₁₉H₂₃N₂O₄ [M+NH₄]⁺ 343.1658, found 343.1671. **Chiral SFC**: 150 mm CHIRALCEL AD-H, 3% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (major) = 3.0 min, t_{R2} (minor) = 3.4 min.

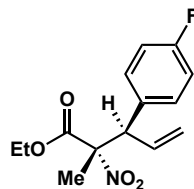
Phenyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3oa)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a yellow oil [7.4 mg, 24% yield, 84:16 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D = -20.3^\circ$ (*c* 0.4, CHCl₃)]. **¹H NMR**

(500 MHz, CDCl₃) δ 7.37 – 7.31 (m, 6H), 7.24 – 7.23 (m, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.38 (ddd, J = 16.9, 10.1, and 8.5 Hz, 1H), 5.31 (d, J = 10.2 Hz, 1H), 5.26 (d, J = 16.9 Hz, 1H), 4.54 (d, J = 8.5 Hz, 1H), 1.97 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.2, 150.1, 136.4, 134.3, 129.9, 129.7, 128.9, 128.4, 126.8, 121.0, 120.4, 96.3, 55.2, 20.2. **IR** (ATR): 1767, 1555, 1492, 1454, 1387, 1265, 1231, 1188, 1161, 1106, 932 cm⁻¹. **HRMS** calculated for C₁₈H₂₁N₂O₄ [M+NH₄]⁺ 329.1501, found 329.1503. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 210 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 4.0 min, t_{R2} (major) = 5.4 min.

Ethyl (2*S*,3*R*)-3-(4-fluorophenyl)-2-methyl-2-nitropent-4-enoate (3ab)

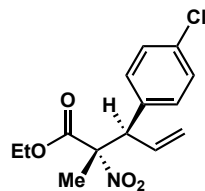


The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [25.5 mg, 88% yield, 97:3 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D = -45.2^\circ$ (*c* 1.3, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.26 – 7.19 (m, 2H), 7.05 – 6.98 (m, 2H), 6.26 (ddd, J = 16.9,

10.2, 8.3 Hz, 1H), 5.28 – 5.21 (m, 1H), 5.16 (dt, J = 16.9, 1.2 Hz, 1H), 4.39 (d, J = 8.3 Hz, 1H), 4.22 – 4.11 (m, 2H), 1.76 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) 166.4, 162.4 (d, J = 247.4 Hz), 134.3, 132.3 (d, J = 3.4 Hz), 131.3 (d, J = 8.0 Hz), 120.0, 115.6 (d, J =

21.4 Hz), 96.0, 63.0, 54.4, 20.0, 13.8. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.3. **IR** (ATR): 2985, 1746, 1550, 1509, 1241, 1227, 1163, 1015, 836, 733 cm⁻¹. **HRMS** calculated for C₁₄H₁₆FNO₄Na [M+Na]⁺ 304.0961, found 304.0970. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 6% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 4.6 min, t_{R2} (major) = 5.1 min.

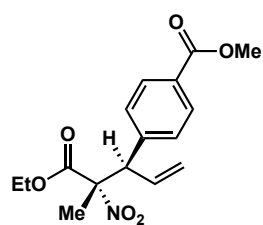
Ethyl (2*S*,3*R*)-3-(4-chlorophenyl)-2-methyl-2-nitropent-4-enoate (3ac)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [25.5 mg, 86% yield, 95.5:4.5 *er*, >20:1 *dr*, >20:1 *rr*, [α]_D²⁴ = -61.1° (*c* 1.1, CHCl₃)]. **¹H**

NMR (400 MHz, CDCl₃) δ 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 2H), 6.25 (ddd, *J* = 16.9, 10.2, 8.4 Hz, 1H), 5.27 – 5.20 (m, 1H), 5.16 (dt, *J* = 16.9, 1.2 Hz, 1H), 4.37 (d, *J* = 8.4 Hz, 1H), 4.25 – 4.08 (m, 2H), 1.76 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.4, 135.1, 134.04, 134.00, 131.0, 128.9, 120.2, 95.9, 63.0, 54.5, 20.1, 13.8. **IR** (ATR): 2984, 1746, 1550, 1492, 1242, 1124, 1093, 1014, 930, 830 cm⁻¹. **HRMS** calculated for C₁₄H₁₆ClNO₄Na [M+Na]⁺ 320.0666, found 320.0664. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 6% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 6.6 min, t_{R2} (major) = 8.1 min.

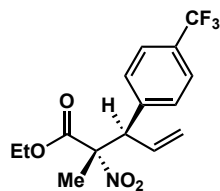
Methyl 4-((3*R*,4*S*)-5-ethoxy-4-methyl-4-nitro-5-oxopent-1-en-3-yl)benzoate (3ad)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (5:1 hexanes:EtOAc) as a yellow oil [26.0 mg, 81% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, [α]_D²⁴ = -48.8° (*c* 1.1, CHCl₃)]. **¹H**

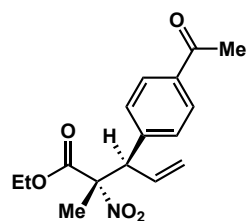
NMR (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H), 7.37 – 7.30 (m, 2H), 6.28 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.29 – 5.23 (m, 1H), 5.18 (dt, *J* = 16.9, 1.1 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), 4.22 – 4.09 (m, 2H), 3.90 (s, 3H), 1.77 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.6, 166.3, 141.8, 133.7, 129.88, 129.86, 129.71, 120.5, 95.8, 63.1, 55.0, 52.2, 20.1, 13.8. **IR** (ATR): 2984, 1748, 1721, 1611, 1552, 1436, 1280, 1111, 858, 761 cm⁻¹. **HRMS** calculated for C₁₆H₁₉NO₆Na [M+Na]⁺ 344.1110, found 344.1110. **Chiral SFC**: 150 mm CHIRALCEL AD-H, 2% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (major) = 3.5 min, t_{R2} (minor) = 4.5 min.

Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(4-(trifluoromethyl)phenyl)pent-4-enoate (**3ae**)



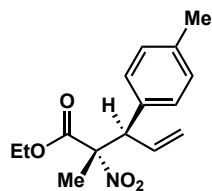
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a colorless oil [18.5 mg, 56% yield, 95:5 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]_D^{24} = -47.7^\circ$ (*c* 0.6, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.28 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.28 (dt, *J* = 10.2, 1.0 Hz, 1H), 5.19 (dt, *J* = 16.9, 1.1 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 1H), 4.22 – 4.13 (m, 2H), 1.78 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.4, 140.99, 140.98, 133.8, 130.3, 125.7 (q, *J* = 3.7 Hz), 123.4, 120.8, 95.9, 63.3, 55.1, 20.3, 13.9. **¹⁹F NMR** (376 MHz, CDCl₃) δ -63.0. **IR** (ATR): 2987, 1747, 1619, 1552, 1447, 1324, 1245, 1122, 1069, 1017, 846, 736 cm⁻¹. **HRMS** calculated for C₁₅H₁₆F₃NO₄Na [M+Na]⁺ 354.0929, found 354.0937. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL OD-H, 3% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (major) = 3.5 min, *t*_{R2} (minor) = 4.0 min.

Ethyl (2*S*,3*R*)-3-(4-acetylphenyl)-2-methyl-2-nitropent-4-enoate (**3af**)



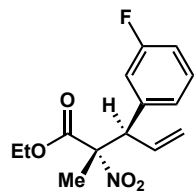
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (5:1 hexanes:EtOAc) as a colorless oil [20.9 mg, 68% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]_D^{24} = -82.5^\circ$ (*c* 0.8, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.39 – 7.32 (m, 2H), 6.29 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.33 – 5.22 (m, 1H), 5.19 (dt, *J* = 16.9, 1.1 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 1H), 4.23 – 4.10 (m, 2H), 2.58 (s, 3H), 1.78 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 197.5, 166.3, 142.0, 136.7, 133.7, 129.9, 128.6, 120.5, 95.8, 63.1, 55.0, 26.6, 20.2, 13.8. **IR** (ATR): 2984, 1746, 1683, 1550, 1359, 1267, 1244, 1146, 1016, 854 cm⁻¹. **HRMS** calculated for C₁₆H₁₉NO₅Na [M+Na]⁺ 328.1161, found 328.1174. **Chiral SFC**: 150 mm CHIRALCEL AD-H, 3% *i*PrOH, 2 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (major) = 2.9 min, *t*_{R2} (minor) = 4.0 min.

Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(*p*-tolyl)pent-4-enoate (**3ag**)



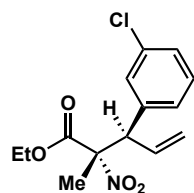
The title compound was synthesized according to general procedure B (modifications: 7.5 mol% Rh-precatalyst and 15 mol% **L6**) and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [24.5 mg, 88% yield, 97:3 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -57.4^{\circ}$ (*c* 1.2, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.12 (s, 4H), 6.29 (ddd, *J* = 16.9, 10.3, 8.4 Hz, 1H), 5.21 (ddd, *J* = 10.3, 1.4, 0.9 Hz, 1H), 5.19 – 5.13 (m, 1H), 4.36 (d, *J* = 8.4 Hz, 1H), 4.20 – 4.12 (m, 2H), 2.32 (s, 3H), 1.76 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.6, 137.8, 134.6, 133.4, 129.43, 129.38, 119.5, 96.2, 62.8, 54.8, 21.1, 20.0, 13.8. **IR** (ATR): 2984, 1746, 1550, 1384, 1242, 1144, 1017, 927, 856, 820 cm⁻¹. **HRMS** calculated for C₁₅H₁₉NO₄Na [M+Na]⁺ 300.1212, found 300.1215. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 2% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.3 min, *t*_{R2} (major) = 1.5 min.

Ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-methyl-2-nitropent-4-enoate (**3ah**)



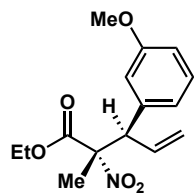
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [24.2 mg, 86% yield, 98:2 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -52.7^{\circ}$ (*c* 1.0, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 1H), 7.05 – 6.95 (m, 3H), 6.25 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.28 – 5.23 (m, 1H), 5.19 (dt, *J* = 16.9, 1.2 Hz, 1H), 4.40 (d, *J* = 8.5 Hz, 1H), 4.23 – 4.12 (m, 2H), 1.78 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.3, 162.7 (d, *J* = 246.6 Hz), 139.0 (d, *J* = 7.1 Hz), 133.8, 130.1 (d, *J* = 8.3 Hz), 125.3 (d, *J* = 3.0 Hz), 120.3, 116.7 (d, *J* = 22.2 Hz), 115.0 (d, *J* = 21.0 Hz), 95.9, 63.0, 54.7, 20.0, 13.8. **¹⁹F NMR** (376 MHz, CDCl₃) δ -112.49. **IR** (ATR): 2986, 1746, 1551, 1244, 1154, 1135, 1014, 932, 876, 788 cm⁻¹. **HRMS** calculated for C₁₄H₁₆FNO₄Na [M+Na]⁺ 304.0961, found 304.0966. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 7% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 3.9 min, *t*_{R2} (major) = 4.2 min.

Ethyl (2*S*,3*R*)-3-(3-chlorophenyl)-2-methyl-2-nitropent-4-enoate (**3ai**)



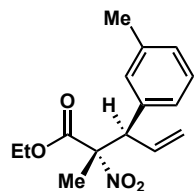
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [23.5 mg, 79% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -47.9^\circ$ (*c* 1.0, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.22 (m, 3H), 7.17 – 7.10 (m, 1H), 6.24 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.28 – 5.23 (m, 1H), 5.19 (dt, *J* = 16.9, 1.2 Hz, 1H), 4.38 (d, *J* = 8.5 Hz, 1H), 4.23 – 4.11 (m, 2H), 1.78 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.3, 138.7, 134.7, 133.7, 129.90, 129.89, 128.2, 127.7, 120.4, 95.9, 63.1, 54.7, 20.0, 13.8. **IR** (ATR): 2984, 1746, 1550, 1243, 1145, 1094, 932, 858, 774, 698 cm⁻¹. **HRMS** calculated for C₁₄H₁₆ClNO₄Na [M+Na]⁺ 320.0666, found 320.0665. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL OD-H, 2% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 2.0 min, *t*_{R2} (major) = 2.2 min.

Ethyl (2*S*,3*R*)-3-(3-methoxyphenyl)-2-methyl-2-nitropent-4-enoate (**3aj**)



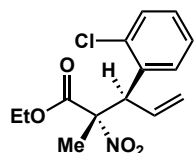
The title compound was synthesized according to general procedure B (modifications: 7.5 mol% Rh-precatalyst and 15 mol% **L6**) and isolated by preparatory TLC (10:1 hexanes:EtOAc) as a colorless oil [28.1 mg, 96% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -48.4^\circ$ (*c* 1.2, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.24 (t, *J* = 7.9 Hz, 1H), 6.85 – 6.77 (m, 3H), 6.29 (ddd, *J* = 16.9, 10.3, 8.4 Hz, 1H), 5.22 (ddd, *J* = 19.3, 14.1, 0.9 Hz, 2H), 4.38 (d, *J* = 8.4 Hz, 1H), 4.22 – 4.12 (m, 2H), 3.80 (s, 3H), 1.78 (s, 3H), 1.22 (d, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.6, 159.7, 138.0, 134.3, 129.6, 121.8, 119.8, 115.7, 113.1, 96.1, 62.9, 55.3, 55.1, 20.1, 13.8. **IR** (ATR): 2983, 1746, 1550, 1243, 1161, 1141, 1047, 1016, 858, 772 cm⁻¹. **HRMS** calculated for C₁₅H₁₉NO₅Na [M+Na]⁺ 316.1161, found 316.1148. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 6% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 6.2 min, *t*_{R2} (major) = 9.3 min.

Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(*m*-tolyl)pent-4-enoate (**3ak**)



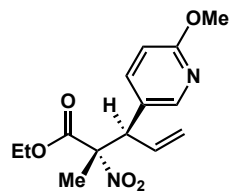
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow oil [16.0 mg, 58% yield, 98:2 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -49.9^\circ$ (*c* 0.7, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.05 – 7.00 (m, 2H), 6.30 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1H), 5.23 (ddd, *J* = 10.2, 1.4, 0.9 Hz, 1H), 5.21 – 5.15 (m, 1H), 4.37 (d, *J* = 8.5 Hz, 1H), 4.21 – 4.10 (m, 2H), 2.33 (s, 3H), 1.77 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.6, 138.3, 136.5, 134.6, 130.3, 128.8, 128.6, 126.5, 120.0, 96.2, 62.9, 55.1, 21.5, 20.0, 13.8. **IR** (ATR): 2983, 1746, 1550, 1246, 1141, 1016, 929, 858, 768, 706 cm⁻¹. **HRMS** calculated for C₁₅H₁₉NO₄Na [M+Na]⁺ 300.1212, found 300.1206. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 0.5% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.3 min, *t*_{R2} (major) = 1.4 min.

Ethyl (2*S*,3*R*)-3-(2-chlorophenyl)-2-methyl-2-nitropent-4-enoate (**3al**)



The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a colorless oil [12.7 mg, 43% yield, 96:4 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -41.9^\circ$ (*c* 0.7, CHCl₃)]. **¹H NMR** (500 MHz, CDCl₃) δ 7.47 – 7.39 (m, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.12 (m, 1H), 6.28 (ddd, *J* = 17.0, 10.2, 7.5 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 5.17 – 5.07 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.74 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.9, 135.2, 134.5, 134.4, 130.0, 129.4, 129.1, 127.4, 119.6, 96.0, 63.1, 49.7, 20.9, 13.8. **IR** (ATR): 2984, 1747, 1549, 1242, 1132, 1107, 1036, 1015, 929, 755 cm⁻¹. **HRMS** calculated for C₁₄H₁₆ClNO₄Na [M+Na]⁺ 320.0666, found 320.0657. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 1% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 1.3 min, *t*_{R2} (major) = 1.6 min.

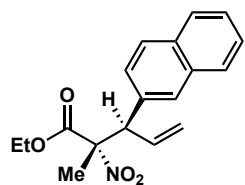
Ethyl (2*S*,3*R*)-3-(6-methoxypyridin-3-yl)-2-methyl-2-nitropent-4-enoate (**3am**)



The title compound was synthesized according to general procedure B (modifications: 7.5 mol% Rh-precatalyst and 15 mol% **L6**) and isolated by preparatory TLC (5:1 hexanes:EtOAc) as a yellow oil [13.1 mg, 45% yield, 88:12 *er*, 15:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -58.9^\circ$ (*c* 0.7, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.49 – 7.44 (m, 1H), 6.73 – 6.66 (m, 1H), 6.24 (ddd,

$J = 16.9, 10.2, 8.2$ Hz, 1H), 5.27 – 5.23 (m, 1H), 5.16 (dt, $J = 16.9, 1.2$ Hz, 1H), 4.34 (d, $J = 8.2$ Hz, 1H), 4.19 (qd, $J = 7.1, 0.7$ Hz, 2H), 3.92 (s, 3H), 1.78 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 166.3, 163.8, 148.0, 139.4, 133.9, 125.0, 120.2, 110.9, 95.8, 63.1, 53.6, 52.0, 20.0, 13.8. **IR** (ATR): 2983, 1747, 1550, 1493, 1393, 1295, 1244, 1132, 1015, 832 cm^{-1} . **HRMS** calculated for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 317.1113, found 317.1115. **Chiral SFC**: 150 mm CHIRALCEL AD-H, 1% i PrOH, 2 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , $t_{\text{R}1}$ (major) = 2.4 min, $t_{\text{R}2}$ (minor) = 2.9 min.

Ethyl (2*S*,3*R*)-2-methyl-3-(naphthalen-2-yl)-2-nitropent-4-enoate (3ao)



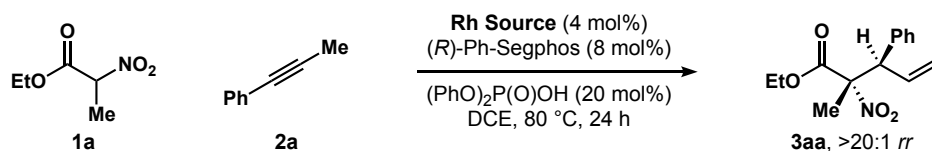
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (20:1 hexanes:EtOAc) as a yellow solid [14.4 mg, 46% yield, 97:3 *er*, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_{\text{D}} = -64.5^\circ$ (c 0.4, CHCl_3)].

^1H NMR (500 MHz, CDCl_3) δ 7.81 (td, $J = 7.8, 3.6$ Hz, 3H), 7.72 (d, $J = 1.5$ Hz, 1H), 7.52 – 7.45 (m, 2H), 7.35 (dd, $J = 8.6, 1.9$ Hz, 1H), 6.41 (ddd, $J = 16.9, 10.3, 8.3$ Hz, 1H), 5.31 – 5.25 (m, 1H), 5.22 (dt, $J = 16.9, 1.2$ Hz, 1H), 4.60 (d, $J = 8.3$ Hz, 1H), 4.21 – 4.10 (m, 2H), 1.83 (s, 3H), 1.18 (t, $J = 7.2$ Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 166.6, 134.48, 134.45, 134.0, 133.3, 132.9, 129.1, 128.3, 128.0, 127.6, 127.0, 126.4, 120.0, 96.2, 62.9, 55.2, 20.2, 13.8. **IR** (ATR): 2987, 1741, 1548, 1246, 1122, 994, 862, 814, 745 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{Na}]^+$ 336.1212, found 336.1213. **Chiral SFC**: 150 mm CHIRALCEL OJ-H, 1% i PrOH, 2 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , $t_{\text{R}1}$ (minor) = 5.6 min, $t_{\text{R}2}$ (major) = 6.2 min.

3. Nitroester and Alkyne Coupling Optimization

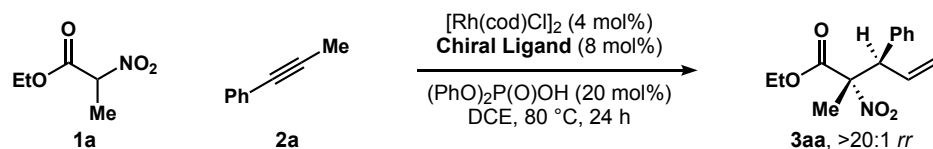
General Procedure for Figures S1-S3: To a 1 dram vial equipped with a magnetic stir bar was added Rh-precatalyst (0.004 mmol, 8 mol% Rh), chiral ligand (0.004 mmol, 8 mol%), acid co-catalyst (0.01 mmol, 20 mol%), nitrocarbonyl **1** (0.05 mmol, 1 equiv.), alkyne **2** (0.075 mmol, 1.5 equiv.) and DCE (100 μ L, 0.5 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 $^{\circ}$ C for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. Diastereo- and regioselectivity ratios (*dr* and *rr*, respectively) were determined by ^1H NMR analysis of the crude reaction mixture. ^1H NMR yields, which were referenced to an internal standard (triphenylmethane), are reported. Chiral SFC analysis for enantioselectivity ratios (*er*).

A. Rh Sources (Figure S1)



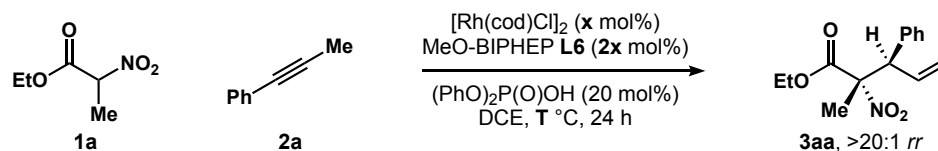
Entry	Rh Source	Result
1	[Rh(cod)Cl] ₂	53%, 90:10 <i>er</i> , 11:1 <i>dr</i>
2	[Rh(coe)Cl] ₂	45%, 88:12 <i>er</i> , 11:1 <i>dr</i>
3	[Rh(C ₂ H ₄) ₂ Cl] ₂	51%, 89:11 <i>er</i> , 8:1 <i>dr</i>
4	[Rh(cod)OMe] ₂	trace
5	[Rh(cod) ₂]SbF ₆	trace
6	[Rh(cod) ₂]BF ₄	trace

B. Chiral Ligands (Figure S2)



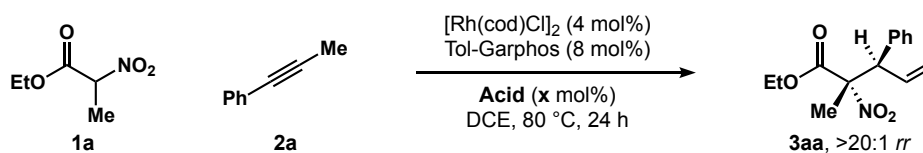
Entry	Chiral Ligand	Result
1	(<i>R</i>)-Ph-Segphos	53%, 90:10 <i>er</i> , 11:1 <i>dr</i>
2	(<i>R</i>)-DM-Segphos	55%, 65:35 <i>er</i> , 10:1 <i>dr</i>
3	(<i>R</i>)-DTBM-Segphos	24%, 77:23 <i>er</i> , n/a <i>dr</i>
4	(<i>R</i>)-Ph-BINAP	45%, 86:14 <i>er</i> , 16:1 <i>dr</i>
5	(<i>R</i>)-Tol-BINAP	39%, 85:15 <i>er</i> , 14:1 <i>dr</i>
6	(<i>R</i>)-Xyl-BINAP	24%, 92:8 <i>er</i> , 7:1 <i>dr</i>
7	(<i>R</i>)-DTBM-BINAP	25%, 68:32 <i>er</i> , 4:1 <i>dr</i>
8	(<i>R</i>)-MeO-BIPHEP (A101)	48%, 85:15 <i>er</i> , 13:1 <i>dr</i>
9	(<i>R</i>)-MeO-BIPHEP (A102)	38%, 89:11 <i>er</i> , >20:1 <i>dr</i>
10	(<i>R</i>)-MeO-BIPHEP (A104)	75%, 97:3 <i>er</i> , >20:1 <i>dr</i>
11	(<i>R</i>)-MeO-BIPHEP (A107)	43%, 68:32 <i>er</i> , 10:1 <i>dr</i>
12	(<i>R</i>)-MeO-BIPHEP (A108)	no reaction
13	(<i>R</i>)-MeO-BIPHEP (A109)	42%, 66:34 <i>er</i> , 16:1 <i>dr</i>
14	(<i>R</i>)-MeO-BIPHEP (A116)	trace
15	(<i>R</i>)-MeO-BIPHEP (A120)	21%, 88:12 <i>er</i> , 7:1 <i>dr</i>
16	(<i>R</i>)-MeO-BIPHEP (A121)	56%, 83:17 <i>er</i> , >20:1 <i>dr</i>
17	(<i>R</i>)-Ph-Garphos	66%, 85:15 <i>er</i> , 18:1 <i>dr</i>
18	(<i>R</i>)-Tol-Garphos	41%, 89:11 <i>er</i> , >20:1 <i>dr</i>
19	(<i>R</i>)-DMM-Garphos	45%, 90:10 <i>er</i> , 15:1 <i>dr</i>
20	(<i>R</i>)-BTfM-Garphos	no reaction
21	(<i>R</i>)-DTBM-Garphos	23%, 64:36 <i>er</i> , n/a <i>dr</i>
22	(<i>R</i>)-Ph-Synphos	63%, 82:18 <i>er</i> , 13:1 <i>dr</i>
23	(<i>R</i>)-Difluorophos	35%, 93:7 <i>er</i> , >20:1 <i>dr</i>

C. Catalyst Loadings and Temperature (Figure S3)



Entry	Catalyst Loading/Temperature	Result
1	$x = 2$, $T = 80$	47%, 98:2 <i>er</i> , $>20:1$ <i>dr</i>
2	$x = 1$, $T = 80$	23%, 98:2 <i>er</i> , $>20:1$ <i>dr</i>
3	$x = 4$, $T = 60$	47%, 98:2 <i>er</i> , $>20:1$ <i>dr</i>

D. Acid Co-Catalysts (Figure S4)

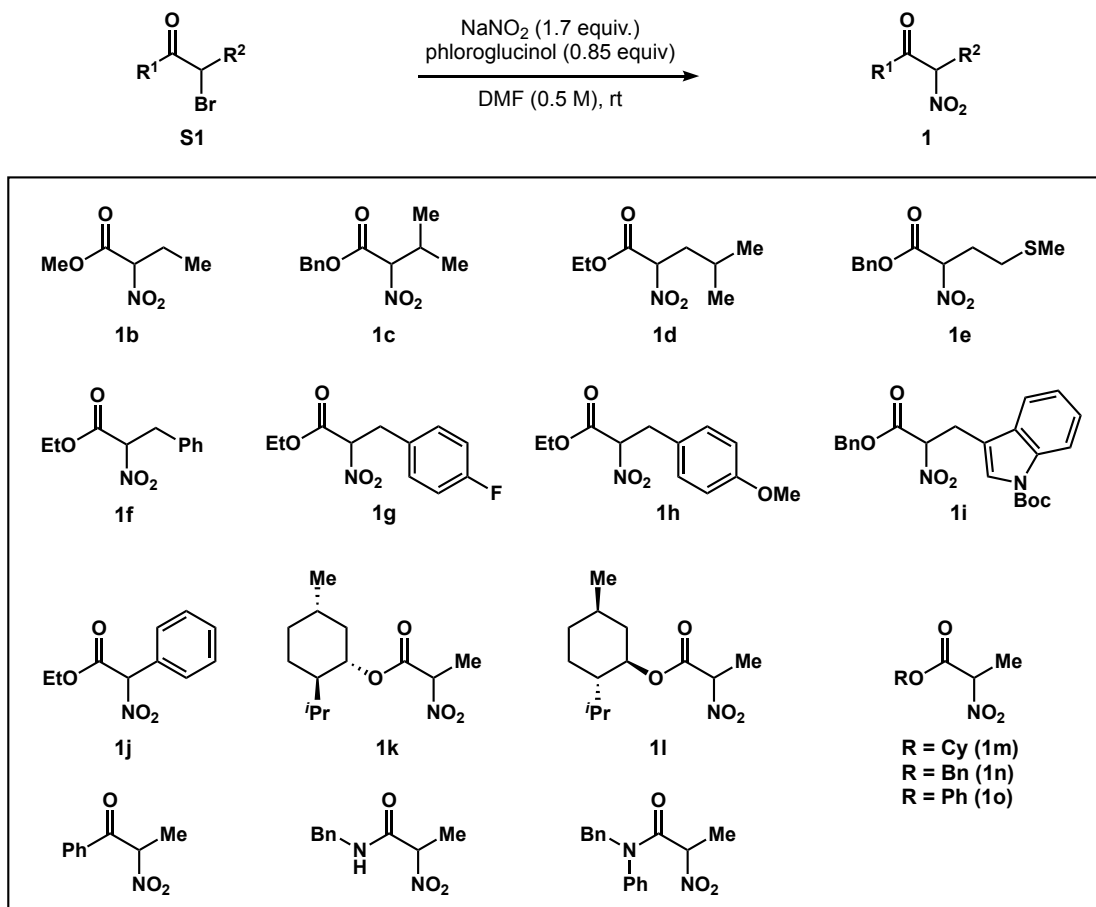


Entry	Catalyst Loading/Temperature	Result
1	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$, $x = 0$	10%, 62:38 <i>er</i> , 15:1 <i>dr</i>
2	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$, $x = 5$	58%, 85:15 <i>er</i> , 15:1 <i>dr</i>
3	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$, $x = 10$	62%, 87:13 <i>er</i> , 15:1 <i>dr</i>
4	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$, $x = 20$	41%, 89:11 <i>er</i> , $>20:1$ <i>dr</i>
5	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$, $x = 50$	28%, 91:9 <i>er</i> , 15:1 <i>dr</i>
6	TsOH, $x = 20$	71%, 85:15 <i>er</i> , $>20:1$ <i>dr</i>
7	PPTS, $x = 20$	45%, 84:16 <i>er</i> , $>20:1$ <i>dr</i>
8	TFA, $x = 20$	41%, 90:10 <i>er</i> , 15:1 <i>dr</i>
9	BzOH, $x = 20$	13%, n/a <i>er</i> , 2:1 <i>dr</i>
10	PhOH, $x = 20$	10%, n/a <i>er</i> , 2:1 <i>dr</i>

4. Preparation of Starting Materials

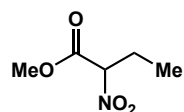
A. General Procedure for Nitration (α -Nitrocarbonyls)

The synthesis of α -bromo carbonyls were performed using standard literature-reported procedures.



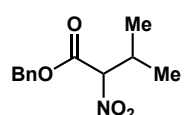
To a round bottom flask equipped with a stir bar was added sodium nitrite (1.7 equiv), phloroglucinol (0.85 equiv), and DMF (0.5 M). The heterogeneous solution was stirred at room temperature for 10 minutes to allow for maximum dissolution of the sodium nitrite. The α -bromocarbonyl **S1** (1.0 equiv) was added, and the reaction became yellow in color. Upon completion (as indicated by TLC and a homogeneous amber-brown color), the reaction was extracted with Et_2O ($\times 3$). The organic phase was washed with a saturated solution of NaHCO_3 , H_2O ($\times 3$), and brine, dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography to afford the desired α -nitrocarbonyl product (**1**).

Methyl 2-nitrobutanoate (1b)



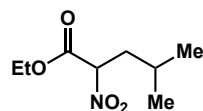
Prepared according to the general procedure for nitration using NaNO_2 (1.8 g, 26 mmol), phloroglucinol (1.6 g, 13 mmol), and DMF (30 mL). To the resulting solution was added methyl 2-bromobutanoate (1.7 mL, 15 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 94:6 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (1.2 g, 8.4 mmol, 56%). ^1H NMR (500 MHz, CDCl_3) δ 5.04 (dd, $J = 5.5$ and 9.3 Hz, 1H), 3.82 (s, 3H), 2.29 (ddq, $J = 14.7$, 9.2, and 7.4 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.04 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.1, 89.4, 53.6, 24.0, 10.2. IR (ATR): 2961, 1750, 1557, 1507, 1438, 1373, 1289, 1209, 1093, 999 cm^{-1} . HRMS calculated for $\text{C}_5\text{H}_{13}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 165.0875, found 165.0879.

Benzyl 3-methyl-2-nitrobutanoate (1c)



Prepared according to the general procedure for nitration using NaNO_2 (0.33 g, 4.8 mmol), phloroglucinol (0.30 g, 2.4 mmol), and DMF (5.6 mL). To the resulting solution was added benzyl 3-methyl-2-bromobutanoate (0.76 g, 2.8 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 99:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.48 g, 2.0 mmol, 72%). ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.33 (m, 5H), 5.26 (d, $J = 12.2$ Hz, 1H), 5.23 (d, $J = 12.2$ Hz, 1H), 4.92 (d, $J = 8.1$ Hz, 1H), 2.67 (dhept, $J = 8.0$ and 6.8 Hz, 1H), 1.07 (d, $J = 6.7$ Hz, 3H), 1.04 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.9, 134.5, 129.0, 128.9, 128.6, 93.7, 68.4, 30.4, 18.9, 18.5. IR (ATR): 2972, 1749, 1557, 1456, 1297, 1186, 1003, 907 cm^{-1} . HRMS calculated for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 255.1345, found 255.1333.

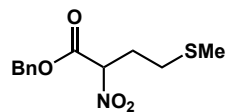
Ethyl 4-methyl-2-nitropentanoate (1d)



Prepared according to the general procedure for nitration using NaNO_2 (0.28 g, 4.0 mmol), phloroglucinol (0.25 g, 2.0 mmol), and DMF (4.8 mL). To the resulting solution was added ethyl 4-methyl-2-bromopentanoate (0.53 g, 2.4 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 96:4 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.25 g, 1.3 mmol, 56%). ^1H NMR (400 MHz, CDCl_3) δ 5.18 (dd, $J = 9.9$ and 5.2 Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.27 (ddd, $J = 15$, 9.9 and 5.7 Hz, 1H), 1.93 (ddd, $J = 14.1$, 8.5 and 5.2 Hz, 1H), 1.64 – 1.61 (m,

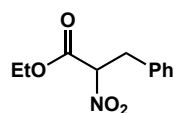
1H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.97 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.0, 86.9, 63.1, 38.9, 25.2, 22.6, 21.5, 14.0. IR (ATR): 2964, 1749, 1559, 1372, 1268, 1193, 1018, 853 cm^{-1} . HRMS calculated for $\text{C}_8\text{H}_{19}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 207.1345, found 207.1337.

Benzyl 4-(methylthio)-2-nitrobutanoate (1e)



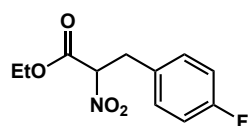
Prepared according to the general procedure for nitration using NaNO_2 (0.19 g, 2.8 mmol), phloroglucinol (0.18 g, 1.4 mmol), and DMF (3.3 mL). To the resulting solution was added benzyl 4-(methylthio)-2-bromobutanoate (0.50 g, 1.6 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 99:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.21 g, 0.78 mmol, 47%). ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.32 (m, 5H), 5.45 (dd, $J = 8.5$ and 5.2 Hz, 1H), 5.27 (d, $J = 12.1$ Hz, 1H), 5.24 (d, $J = 12.2$ Hz, 1H), 2.64 – 2.56 (m, 2H), 2.53 – 2.48 (m, 1H), 2.44 – 2.37 (m, 1H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.4, 134.3, 129.0, 128.9, 128.5, 86.4, 68.8, 30.0, 29.6, 15.4. IR (ATR): 2919, 1748, 1557, 1456, 1435, 1291, 1267, 1192, 964 cm^{-1} . HRMS calculated for $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$ 292.0620, found 292.0610.

Ethyl 2-nitro-3-phenylpropanoate (1f)



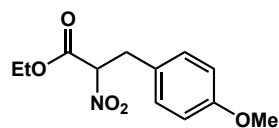
Prepared according to the general procedure for nitration using NaNO_2 (0.29 g, 4.2 mmol), phloroglucinol (0.27 g, 2.1 mmol), and DMF (5.0 mL). To the resulting solution was added ethyl 2-bromo-3-phenylpropanoate (0.64 g, 2.5 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 99:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.32 g, 1.4 mmol, 58%). ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.28 (m, 3H), 7.21 (d, $J = 7.2$ Hz, 2H), 5.34 (dd, $J = 9.5$ and 5.8 Hz, 1H), 4.28 (q, $J = 6.6$ Hz, 2H), 3.56 (dd, $J = 14.6$ and 9.5 Hz, 1H), 3.48 (dd, $J = 14.6$ and 5.8 Hz, 1H), 1.28 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.2, 134.2, 129.1, 129.0, 127.9, 89.3, 63.3, 36.4, 14.0. IR (ATR): 2985, 1747, 1558, 1456, 1373, 1268, 1209, 1019, 859 cm^{-1} . HRMS calculated for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 241.1188, found 241.1184.

Ethyl 2-nitro-3-(4-fluorophenyl)propanoate (1g)



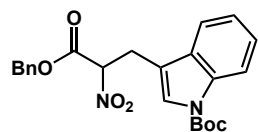
Prepared according to the general procedure for nitration using NaNO_2 (0.39 g, 5.6 mmol), phloroglucinol (0.36 g, 2.8 mmol), and DMF (6.6 mL). To the resulting solution was added ethyl 2-bromo-3-(4-fluorophenyl)propanoate (0.91 g, 3.3 mmol). The reaction was complete after 3 hours at room temperature. Purification by flash column chromatography using 99:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.41 g, 1.7 mmol, 51%). **^1H NMR** (500 MHz, CDCl_3) δ 7.20 – 7.17 (m, 2H), 7.03 – 6.98 (m, 2H) 5.29 (dd, J = 9.5 and 5.8 Hz, 1H), 4.28 (qd, J = 7.2 and 2.1 Hz, 2H), 3.53 (dd, J = 14.7 and 9.6 Hz, 1H), 3.45 (dd, J = 14.7 and 5.8 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 164.0, 162.5 (d, J = 246.5 Hz), 130.7 (d, J = 8.2 Hz), 129.9 (d, J = 3.3 Hz), 116.1 (d, J = 21.6 Hz), 89.3, 63.4, 35.6, 14.0. **^{19}F NMR** (376 MHz, CDCl_3) δ -114.6. **IR** (ATR): 2986, 1747, 1559, 1510, 1373, 1269, 1222, 1160, 1100, 1016, 861 cm^{-1} . **HRMS** calculated for $\text{C}_{11}\text{H}_{12}\text{FNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 264.0648, found 264.0649.

Ethyl 3-(4-methoxyphenyl)-2-nitropropanoate (1h)



Prepared according to the general procedure for nitration using NaNO_2 (0.21 g, 3.1 mmol), phloroglucinol (0.20 g, 1.5 mmol), and DMF (3.6 mL). To the resulting solution was added ethyl 3-(4-methoxyphenyl)-2-bromopropanoate (0.52 g, 1.8 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 99:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.35 g, 1.4 mmol, 76%). **^1H NMR** (500 MHz, CDCl_3) δ 7.12 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.28 (dd, J = 9.5 and 5.6 Hz, 1H), 4.28 (qd, J = 7.1 and 2.2 Hz, 2H), 3.78 (s, 3H), 3.50 (dd, J = 14.6 and 9.5 Hz, 1H), 3.42 (dd, J = 14.7 and 5.8 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 164.2, 159.3, 130.1, 126.1, 114.5, 89.6, 63.3, 55.4, 35.7, 14.0. **IR** (ATR): 2938, 1747, 1559, 1514, 1465, 1373, 1302, 1179, 1029, 910, 861 cm^{-1} . **HRMS** calculated for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{O}_5$ $[\text{M}+\text{NH}_4]^+$ 271.1294, found 271.1289.

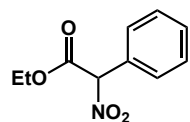
Tert-butyl 3-(3-(benzyloxy)-2-nitro-3-oxopropyl)-1*H*-indole-1-carboxylate (1i)



Prepared according to the general procedure for nitration using NaNO_2 (0.13 g, 1.9 mmol), phloroglucinol (0.12 g, 0.93 mmol), and DMF (2.2 mL). To the resulting solution was added *tert*-butyl 3-(3-(benzyloxy)-2-bromo-3-

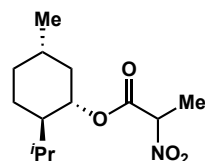
oxopropyl)-1*H*-indole-1-carboxylate (0.50 g, 1.1 mmol). The reaction was complete after 3 hours at room temperature. Purification by flash column chromatography using 90:10 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a light yellow solid (0.15 g, 0.36 mmol, 33%). **¹H NMR** (500 MHz, CDCl₃) δ 8.21 (bs, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52 (s, 1H), 7.44-7.40 (m, 4H), 7.35-7.32 (m, 3H), 5.56 (dd, *J* = 9.3 and 5.7 Hz, 1H), 5.31 (s, 2H), 3.77 (dd, *J* = 15.4 and 9.3 Hz, 1H), 3.67 (dd, *J* = 15.3 and 5.7 Hz, 1H), 1.73 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 164.0, 149.4, 135.5, 134.1, 129.2, 129.0, 128.8, 128.4, 125.0, 124.8, 122.9, 118.3, 115.6, 112.8, 87.5, 84.1, 68.8, 28.2, 26.3. **IR** (ATR): 2979, 1722, 1562, 1450, 1390, 1360, 1332, 1255, 1153, 1092, 743, 697 cm⁻¹. **¹H RMSS** calculated for C₂₃H₂₄N₂O₆Na [M+Na]⁺ 447.1515, found 447.1532.

Ethyl 2-nitro-2-phenylacetate (1j)



In a glove-box, to an oven-dried vial was added Pd₂(dba)₃ (0.29 g, 32 μ mol), ^tBuXPhos (0.53 g, 0.13 mmol), and CsHCO₃ (0.29 g, 1.5 mmol). Next, toluene (6.3 mL), ethyl nitroacetate (0.28 mL, 2.5 mmol), and bromobenzene (0.13 mL, 1.3 mmol) were added to give a heterogeneous reaction mixture. The solution was then heated to 80 °C and stirred vigorously for 6 h. After cooling, the reaction mixture was diluted with EtOAc and acidified with HCl (1 M). The aqueous layer was extracted with additional EtOAc ($\times$ 3) and washed with brine. The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The crude residue was purified by flash chromatography 97:3 hexanes:EtOAc to afford the desired α -nitrocarbonyl as a colorless oil (0.25 g, 1.2 mmol, 97%). The ¹H and ¹³C NMRs are in accordance with the literature.¹ **¹H NMR** (500 MHz, CDCl₃) δ 7.51 – 7.41 (m, 5H), 6.16 (s, 1H), 4.39 – 4.28 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 164.1, 130.9, 130.0, 129.2, 91.0, 63.5, 14.0.

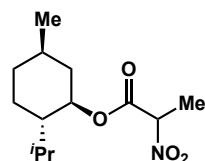
(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-nitropropanoate (1k)



Prepared according to the general procedure for nitration using NaNO₂ (0.40 g, 5.8 mmol), phloroglucinol (0.37 g, 2.9 mmol), and DMF (6.9 mL). To the resulting solution was added (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2-bromopropanoate (1.0 g, 3.4 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 97:3 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.44 g, 1.7 mmol, 49%). **¹H NMR** (500 MHz, CDCl₃) δ 5.17 (q, *J*

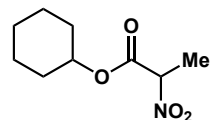
= 7.1 Hz, 1H), 4.78 (td, J = 10.9 and 4.5 Hz, 1H), 2.02 – 2.01 (m, 1H), 1.82 – 1.78 (m, 1H), 1.78 (d, J = 7.1 Hz, 3H), 1.69 (d, J = 12.5 Hz, 2H), 1.54 – 1.46 (m, 1H), 1.42 (t, J = 11 Hz, 1H), 1.10 – 0.99 (m, 2H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 0.89 – 0.83 (m, 1H), 0.76 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.9, 164.8, 83.6, 83.5, 77.7, 47.0, 46.9, 40.4, 40.3, 34.2, 34.1, 31.5, 26.3, 26.3, 23.4, 22.0, 22.0, 20.8, 20.8, 16.2, 16.2, 15.9, 15.9. IR (ATR): 2956, 2871, 1745, 1560, 1452, 1389, 1203, 1024, 953 cm^{-1} . HRMS calculated for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 275.1971, found 275.1958.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-nitropropanoate (1l)



Prepared according to the general procedure for nitration using NaNO_2 (0.34 g, 4.9 mmol), phloroglucinol (0.31 g, 2.4 mmol), and DMF (5.7 mL). To the resulting solution was added (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2-bromopropanoate (0.83 g, 2.9 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 97:3 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.34 g, 1.3 mmol, 46%). ^1H NMR (500 MHz, CDCl_3) δ 5.17 (q, J = 7.1 Hz, 1H), 4.78 (td, J = 10.9 and 4.5 Hz, 1H), 2.02 – 2.01 (m, 1H), 1.82 – 1.78 (m, 1H), 1.78 (d, J = 7.1 Hz, 3H), 1.69 (d, J = 12.5 Hz, 2H), 1.54 – 1.46 (m, 1H), 1.42 (t, J = 11 Hz, 1H), 1.10 – 0.99 (m, 2H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 0.89 – 0.83 (m, 1H), 0.76 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.9, 164.8, 83.6, 83.5, 77.7, 47.0, 46.9, 40.4, 40.3, 34.2, 34.1, 31.5, 26.3, 26.3, 23.4, 22.0, 22.0, 20.8, 20.8, 16.2, 16.2, 15.9, 15.9. IR (ATR): 2956, 2871, 1745, 1560, 1452, 1389, 1203, 1024, 953 cm^{-1} . HRMS calculated for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 275.1971, found 275.1980.

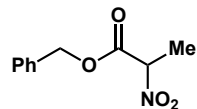
Cyclohexyl 2-nitropropanoate (1m)



Prepared according to the general procedure for nitration using NaNO_2 (0.50 g, 7.3 mmol), phloroglucinol (0.46 g, 3.7 mmol), and DMF (8.6 mL). To the resulting solution was added cyclohexyl 2-bromopropanoate (1.0 g, 4.3 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 97:3 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.52 g, 2.6 mmol, 60%). ^1H NMR (400 MHz, CDCl_3) δ 5.17 (q, J = 7.1 Hz, 1H), 4.92 – 4.87 (m, 1H), 1.85 – 1.82 (m, 2H), 1.78 (d, J = 7.2 Hz, 3H), 1.72 – 1.68 (m, 2H), 1.53 – 1.46 (m, 3H), 1.42

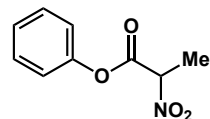
– 1.35 (m, 2H), 1.32 – 1.32 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 164.7, 83.6, 75.9, 31.2, 31.1, 25.3, 23.4, 23.4, 15.9. **IR** (ATR): 2939, 2861, 1743, 1558, 1450, 1390, 1205, 1120, 1008, 901 cm⁻¹. **HRMS** calculated for C₉H₁₉N₂O₄ [M+NH₄]⁺ 219.1336, found 219.1345.

Benzyl 2-nitropropanoate (1n)



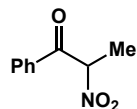
Prepared according to the general procedure for nitration using NaNO₂ (0.37 g, 5.4 mmol), phloroglucinol (0.34 g, 2.7 mmol), and DMF (6.4 mL). To the resulting solution was added benzyl 2-bromopropanoate (1.0 g, 3.2 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 96:4 hexanes:EtOAc afforded the desired α-nitrocarbonyl as a colorless oil (0.42 g, 2.0 mmol, 63%). **¹H NMR** (400 MHz, CDCl₃) δ 7.41 – 7.32 (m, 5H), 5.25 (s, 2H), 5.23 (q, *J* = 7.1 Hz, 1H), 1.80 (d, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.1, 134.4, 129.0, 128.9, 128.5, 83.3, 68.6, 15.8. **IR** (ATR): 1749, 1558, 1455, 1392, 1360, 1312, 1191, 1084, 1026, 873 cm⁻¹. **HRMS** calculated for C₁₀H₁₅N₂O₄ [M+NH₄]⁺ 227.1032, found 227.1026.

Phenyl 2-nitropropanoate (1o)



Prepared according to the general procedure for nitration using NaNO₂ (0.44 g, 6.3 mmol), phloroglucinol (0.40 g, 3.2 mmol), and DMF (3.7 mL). To the resulting solution was added phenyl 2-bromopropanoate (0.85 g, 3.7 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 97:3 hexanes:EtOAc afforded the desired α-nitrocarbonyl as a colorless oil (0.33 g, 4.8 mmol, 77%). **¹H NMR** (500 MHz, CDCl₃) δ 7.47 (dd, *J* = 7.9 and 7.9 Hz, 2H), 7.34 (dd, *J* = 7.6 and 7.6 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 5.48 (q, *J* = 7.1 Hz, 1H), 1.99 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 163.7, 150.0, 129.8, 126.9, 121.0, 83.3, 15.9. **IR** (ATR): 1768, 1558, 1492, 1456, 1389, 1359, 1185, 1083, 1024, 923 cm⁻¹. **HRMS** calculated for C₉H₁₃N₂O₄ [M+NH₄]⁺ 213.0875, found 213.0874.

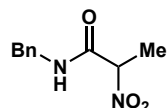
2-Nitro-1-phenylpropan-1-one



Prepared according to the general procedure for nitration using NaNO₂ (0.55 g, 8.0 mmol), phloroglucinol (0.53 g, 4.2 mmol), and DMF (9.4 mL). To the resulting solution was added 2-bromopropiophenone (1.0 g, 4.7 mmol). The reaction was complete after 4

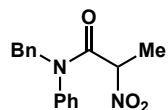
hours at room temperature. Purification by flash column chromatography using 90:10 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a colorless oil (0.13 g, 0.72 mmol, 15%). The ^1H and ^{13}C NMRs are in accordance with the literature.² **^1H NMR** (500 MHz, CDCl_3) δ 7.90–7.87 (m, 2H), 7.55 (tt, J = 6.8 and 1.3 Hz, 1H), 7.47–7.42 (m, 2H), 5.12 (q, J = 7.0 Hz, 1H), 1.40 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 202.4, 134.0, 133.4, 128.9, 128.7, 69.4, 22.2.

N-benzyl-2-nitropropanamide



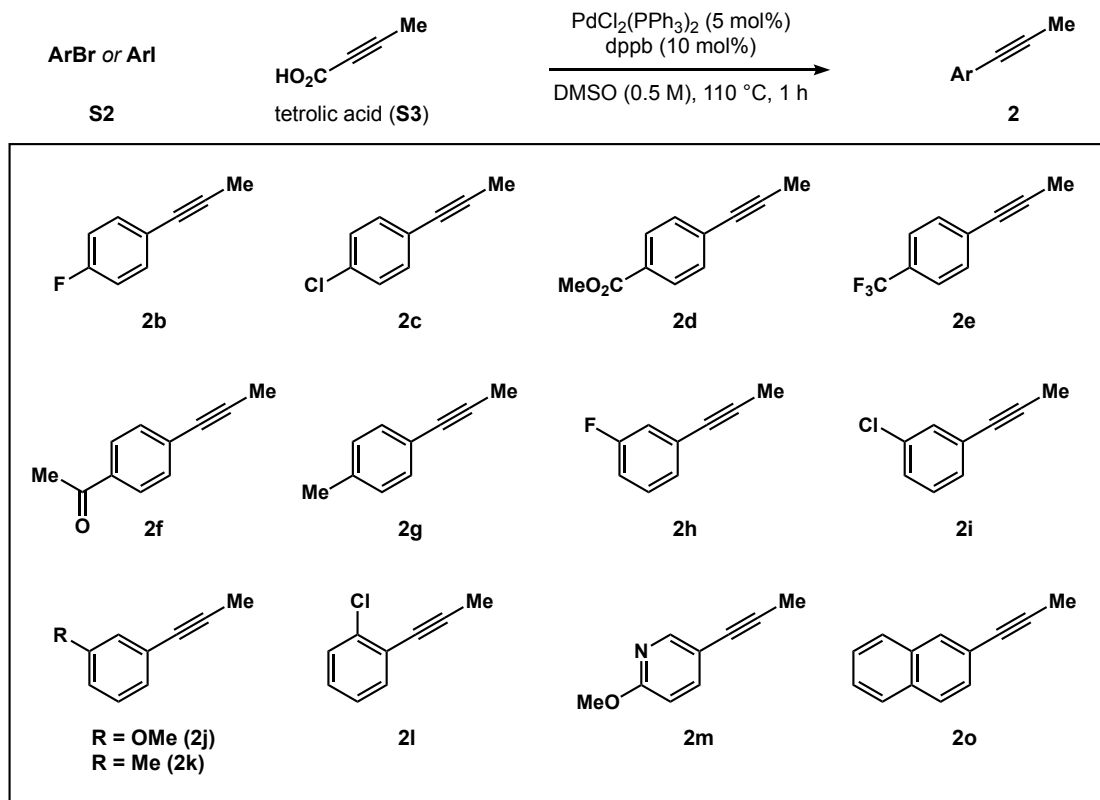
Prepared according to the general procedure for nitration using NaNO_2 (0.48 g, 7.0 mmol), phloroglucinol (0.44 g, 3.5 mmol), and DMF (8.3 mL). To the resulting solution was added *N*-benzyl-2-bromopropanamide (1.0 g, 4.1 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 97:3 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a white solid (0.12 g, 0.58 mmol, 14%). **^1H NMR** (500 MHz, CDCl_3) δ 7.36 – 7.28 (m, 3H), 7.26 – 7.23 (m, 2H), 6.71 (s, 1H), 5.12 (q, J = 6.96 Hz, 1H), 4.44 (dd, J = 5.7 and 1.5 Hz, 2H), 1.76 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 164.0, 136.9, 129.0, 128.0, 127.8, 84.6, 44.2, 16.2. **IR** (ATR): 3254, 3092, 2936, 1659, 1553, 1453, 1225, 1078 753 cm^{-1} . **HRMS** calculated for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 209.0926, found 209.0920.

N-benzyl-2-nitro-*N*-phenylpropanamide



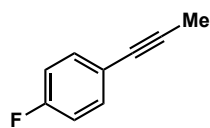
Prepared according to the general procedure for nitration using NaNO_2 (0.55 g, 8.0 mmol), phloroglucinol (0.51 g, 4.0 mmol), and DMF (9.5 mL). To the resulting solution was added *N*-benzyl-2-bromo-phenylpropanamide (1.5 g, 4.7 mmol). The reaction was complete after 4 hours at room temperature. Purification by flash column chromatography using 4:1 hexanes:EtOAc afforded the desired α -nitrocarbonyl as a white solid (1.0 g, 3.5 mmol, 74%). **^1H NMR** (500 MHz, CDCl_3) δ 7.38 – 7.36 (m, 3H), 7.30 – 7.26 (m, 3H), 7.20 – 7.18 (m, 2H), 7.06 (s, 2H), 5.05 (d, J = 6.8 Hz, 1H), 5.02 (d, J = 14.2 Hz, 1H), 4.84 (d, J = 14.2 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 165.1, 140.4, 136.2, 130.2, 129.2, 129.0, 128.7, 128.5, 127.9, 80.5, 53.8, 15.9. **IR** (ATR): 3058, 2936, 1659, 1553, 1497, 1453, 1417, 1245, 1202, 701 cm^{-1} . **HRMS** calculated for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_3$ $[\text{M}+\text{NH}_4]^+$ 302.1505, found 302.1515.

B. General Procedure for Decarboxylative Cross-Coupling (Alkynes)



To a flame-dried Schlenk tube was added $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), 1,4-bis(diphenylphosphino)butane (10 mol%), and DMSO (0.5 M). To the resulting solution was added aryl halide **S2** (1 equiv.), tetrolic acid (**S3**, 1.2 equiv.), and DBU (3 equiv.). The reaction mixture was then heated to 110 $^\circ\text{C}$. Upon reaction completion, the reaction mixture was cooled to room temperature, quenched with H_2O , and extracted with DCM (x3). The combined organic layers were washed with H_2O and brine, dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography to afford the desired alkyne product (**2**).

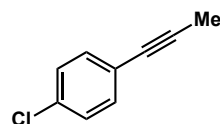
1-Fluoro-4-(prop-1-yn-1-yl)benzene (**2b**)



Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10

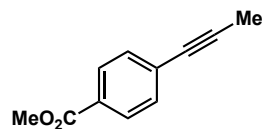
mL, 0.5 M). To the resulting solution was added 4-fluoriodobenzene (1.11 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a colorless oil (209 mg, 1.56 mmol, 31%). The ^1H NMR was in accordance with the literature.³ ^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.32 (m, 2H), 7.00 – 6.93 (m, 2H), 2.03 (s, 3H).

1-Chloro-4-(prop-1-yn-1-yl)benzene (2c)



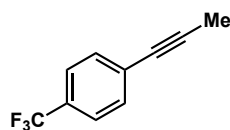
Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 1-chloro-4-iodobenzene (1.19 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a clear oil (590 mg, 3.92 mmol, 78%). The ^1H NMR was in accordance with the literature.³ ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 2.04 (s, 3H).

Methyl 4-(prop-1-yn-1-yl)benzoate (2d)



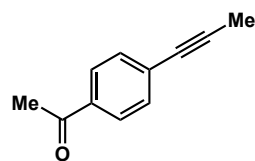
Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added methyl-4-bromobenzoate (1.08 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 20:1 hexanes:EtOAc afforded the desired alkyne as a white solid (298 mg, 1.71 mmol, 34%). The ^1H NMR was in accordance with the literature.³ ^1H NMR (400 MHz, CDCl_3): δ 7.98 – 7.91 (m, 2H), 7.48 – 7.40 (m, 2H), 3.91 (s, 3H), 2.08 (s, 3H).

1-(Prop-1-yn-1-yl)-4-(trifluoromethyl)benzene (2e)



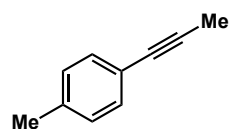
Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 1-bromo-4-(trifluoromethyl)-benzene (1.13 g, 5 mmol, 1 equiv.), 2-butynoic acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 40:1 hexanes:EtOAc afforded the desired alkyne as a colorless oil (408 mg, 2.21 mmol, 44%). The ^1H NMR was in accordance with the literature.³ ^1H NMR (400 MHz, CDCl_3): δ 7.56 – 7.50 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 2.07 (s, 3H).

1-(4-(Prop-1-yn-1-yl)phenyl)ethan-1-one (2f)



Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 4'-bromoacetophenone (995 mg, 5 mmol, 1 equiv.), 2-butynoic acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 10:1 hexanes:EtOAc afforded the desired alkyne as a white solid (201 mg, 1.27 mmol, 25%). The ^1H NMR was in accordance with the literature.³ ^1H NMR (400 MHz, CDCl_3): δ 7.90 – 7.84 (m, 2H), 7.49 – 7.42 (m, 2H), 2.58 (s, 3H), 2.08 (s, 3H).

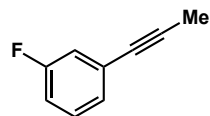
1-Methyl-4-(prop-1-yn-1-yl)benzene (2g)



Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 4-bromotoluene (855 mg, 5 mmol, 1 equiv.), 2-butynoic acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a colorless oil (533 mg, 4.09 mmol, 82%). The ^1H NMR was in

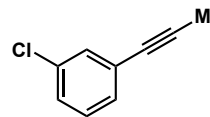
accordance with the literature.³ **¹H NMR** (400 MHz, CDCl₃): δ 7.31 – 7.26 (m, 2H), 7.13 – 7.05 (m, 2H), 2.33 (s, 3H), 2.04 (s, 3H).

1-Fluoro-3-(prop-1-yn-1-yl)benzene (2h)



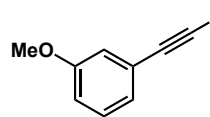
Prepared according to the general procedure for decarboxylative cross-coupling using PdCl₂(PPh₃)₂ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 1-bromo-3-fluorobenzene (875 mg, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a colorless oil (342 mg, 2.55 mmol, 51%). The ¹H NMR was in accordance with the literature.⁴ **¹H NMR** (400 MHz, CDCl₃): δ 7.25 – 7.19 (m, 1H), 7.16 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.08 (ddd, *J* = 9.6, 2.6, 1.4 Hz, 1H), 6.97 (tdd, *J* = 8.4, 2.6, 1.1 Hz, 1H), 2.05 (s, 3H).

1-Chloro-3-(prop-1-yn-1-yl)benzene (2i)



Prepared according to the general procedure for decarboxylative cross-coupling using PdCl₂(PPh₃)₂ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 3-chloriodobenzene (1.19 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a yellow oil (250 mg, 1.66 mmol, 33%). The ¹H NMR was in accordance with the literature.⁵ **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (t, *J* = 1.8 Hz, 1H), 7.28 – 7.17 (m, 3H), 2.04 (s, 3H).

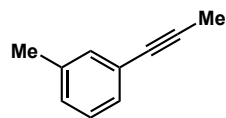
1-Methoxy-3-(prop-1-yn-1-yl)benzene (2j)



Prepared according to the general procedure for decarboxylative cross-coupling using PdCl₂(PPh₃)₂ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 3-bromoanisole (935 mg, 5 mmol, 1 equiv.),

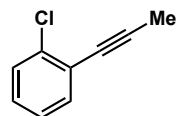
2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 20:1 hexanes:EtOAc afforded the desired alkyne as a colorless oil (582 mg, 3.98 mmol, 80%). The ¹H NMR was in accordance with the literature.³ ¹H NMR (400 MHz, CDCl₃): δ 7.21 – 7.16 (m, 1H), 6.98 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.93 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.83 (ddd, *J* = 8.4, 2.7, 1.0 Hz, 1H), 3.79 (s, 3H), 2.05 (s, 3H).

1-Methyl-3-(prop-1-yn-1-yl)benzene (2k)



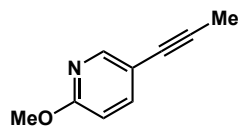
Prepared according to the general procedure for decarboxylative cross-coupling using PdCl₂(PPh₃)₂ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 3-bromotoluene (855 mg, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a yellow oil (591 mg, 4.54 mmol, 91%). The ¹H NMR was in accordance with the literature.³ ¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.12 (m, 3H), 7.10 – 7.05 (m, 1H), 2.31 (s, 3H), 2.05 (s, 3H).

1-Chloro-2-(prop-1-yn-1-yl)benzene (2l)



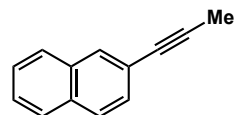
Prepared according to the general procedure for decarboxylative cross-coupling using PdCl₂(PPh₃)₂ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 1-chloro-2-iodobenzene (1.19 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using hexanes afforded the desired alkyne as a colorless oil (541 mg, 3.59 mmol, 72%). The ¹H NMR was in accordance with the literature.⁶ ¹H NMR (400 MHz, CDCl₃): δ 7.42 (dt, *J* = 7.6, 3.4 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.22 – 7.14 (m, 2H), 2.12 (s, 3H).

2-Methoxy-5-(prop-1-yn-1-yl)pyridine (2m)



Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 5-bromo-2-methoxypyridine (940 mg, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 20:1 hexanes:EtOAc afforded the desired alkyne as a yellow oil (632 mg, 4.30 mmol, 86%). The ^1H NMR was in accordance with the literature.⁵ ^1H NMR (400 MHz, CDCl_3): δ 8.21 (d, J = 2.2 Hz, 1H), 7.55 (dd, J = 8.6, 2.3 Hz, 1H), 6.66 (dd, J = 8.6, 0.7 Hz, 1H), 3.93 (s, 3H), 2.05 (s, 3H).

2-(Prop-1-yn-1-yl)naphthalene (2o)



Prepared according to the general procedure for decarboxylative cross-coupling using $\text{PdCl}_2(\text{PPh}_3)_2$ (176 mg, 0.25 mmol, 5 mol%), 1,4-bis(diphenylphosphino)butane (213 mg, 0.50 mmol, 10 mol%), and DMSO (10 mL, 0.5 M). To the resulting solution was added 2-bromonaphthalene (1.04 g, 5 mmol, 1 equiv.), 2-butyric acid (505 mg, 6 mmol, 1.2 equiv.), and DBU (2.2 mL, 15 mmol, 3 equiv.). The reaction was complete after 1 hour at 110 °C. Purification by flash column chromatography using 40:1 hexanes:EtOAc afforded the desired alkyne as a colorless oil (584 mg, 3.51 mmol, 70%). The ^1H NMR was in accordance with the literature.⁶ ^1H NMR (400 MHz, CDCl_3): δ 7.93 – 7.89 (m, 1H), 7.83 – 7.72 (m, 3H), 7.51 – 7.42 (m, 3H), 2.11 (s, 3H).

5. Mechanistic Experiments

A. NMR Spectroscopy Experiments:

In a N₂-filled glovebox, (*R*)-MeO-BIPHEP **L6** (A104-1, 19.6 mg, 0.02 mmol, 8 mol%) and [Rh(cod)Cl]₂ (5.4 mg, 0.01 mmol, 4 mol%) were dissolved with DCE-*d*₄ (0.8 mL) in a 1-dram vial. The resulting solution was heated at 80 °C for 15 min and then diphenyl phosphate (13.8 mg, 0.06 mmol, 20 mol%) was added. The reaction mixture was then heated at 80 °C for an additional 30 min and transferred to a J. Young NMR tube to perform ¹H NMR spectroscopy. A resonance at -16.2 ppm was *observed* in less than ten minutes at rt in the ¹H NMR spectrum (Figure S5). Alkyne **2a** (48 mg, 0.41 mmol) was then added and the dark brown solution was heated at 80 °C for 30 min. The Rh-H resonance (at -16.2 ppm) was *not observed* in the ¹H NMR spectrum (Figure S6).

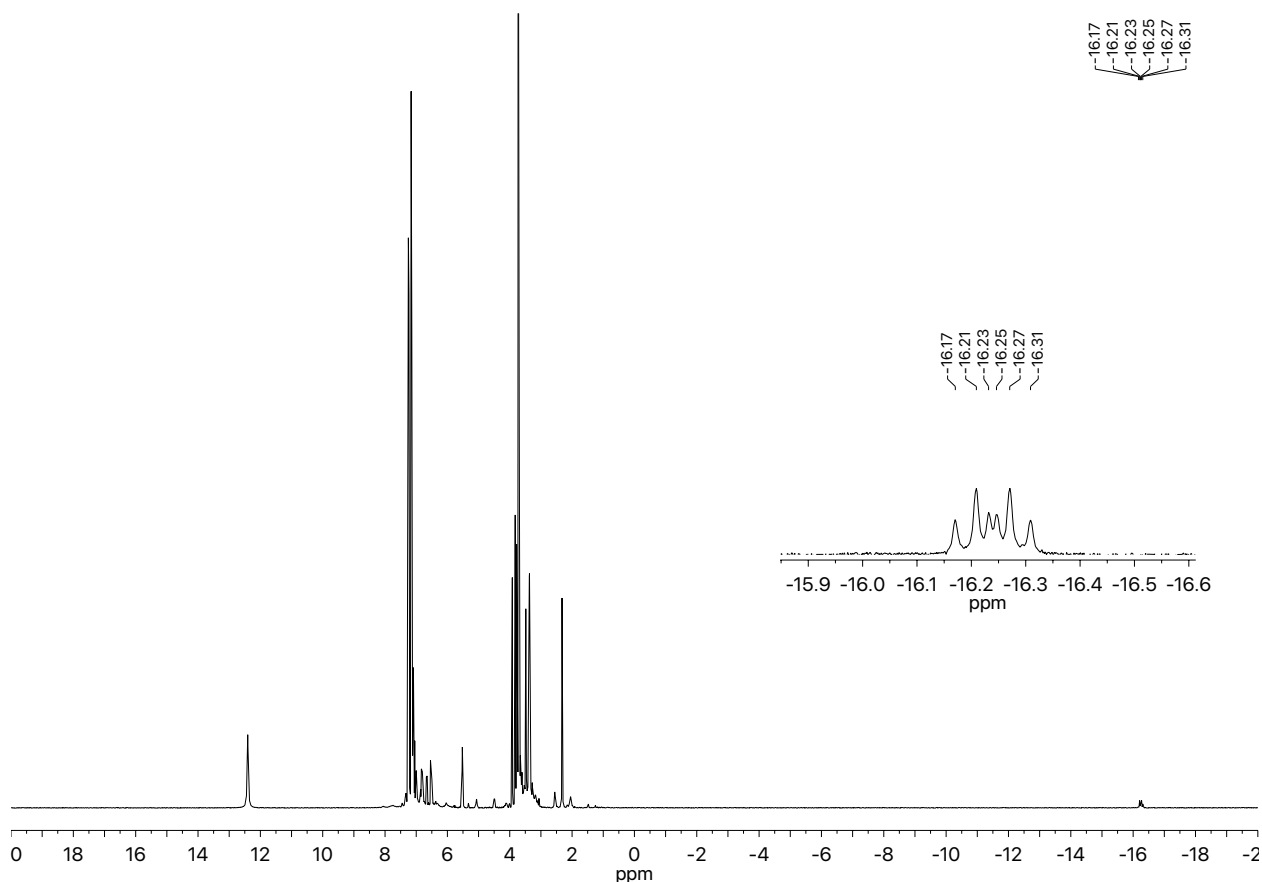


Figure S5. ¹H NMR (400 MHz) for a mixture of [Rh(cod)Cl]₂, (*R*)-MeO-BIPHEP **L6**, and diphenyl phosphate in DCE-*d*₄ (δ 3.79 ppm). Rh-H resonance is *observed* at -16.2 ppm.

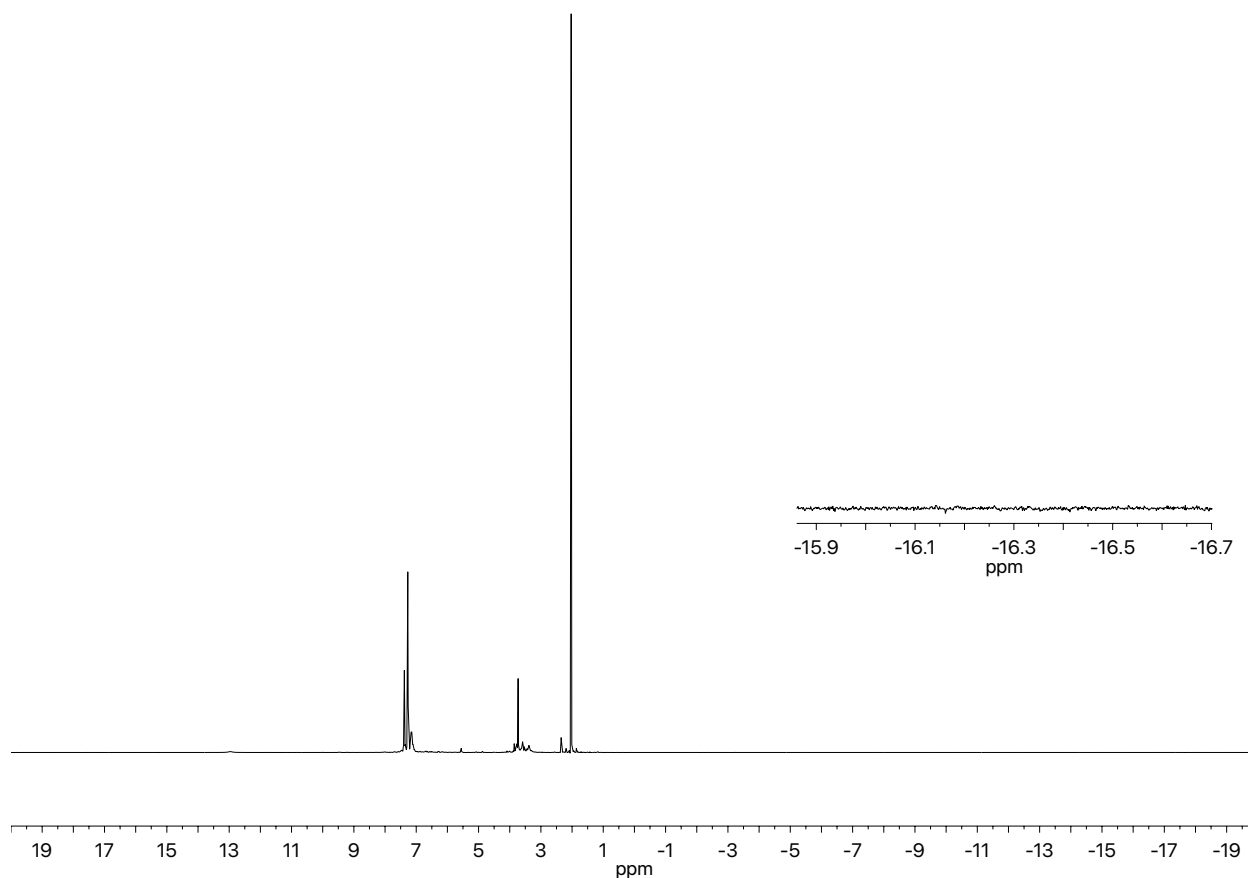
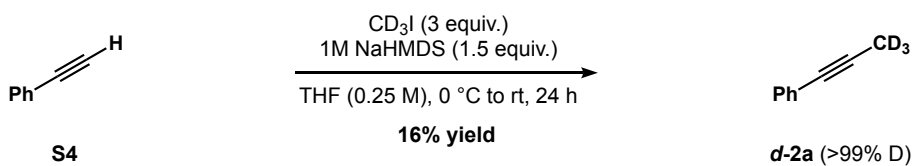


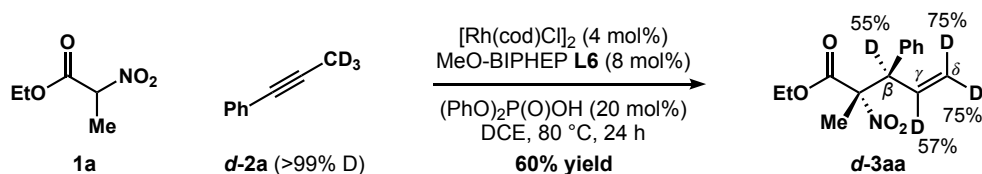
Figure S6. ^1H NMR (400 MHz) for a mixture of $[\text{Rh}(\text{cod})\text{Cl}]_2$, (*R*)-MeO-BIPHEP **L6**, diphenyl phosphate, and alkyne **2a** in $\text{DCE-}d_4$ (δ 3.79 ppm). Rh-H resonance is *not observed* at -16.2 ppm.

B. Deuterated Alkyne Synthesis and Experiment:



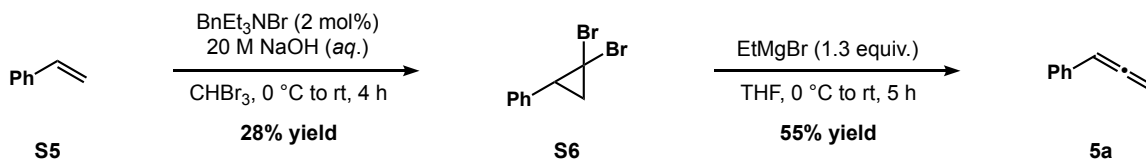
Preparation of (Prop-1-yn-1-yl- d_3)benzene-ethynylbenzene (*d*-2a): To a round bottom flask containing ethynylbenzene (**S4**, 204 mg, 2 mmol) in THF (8 mL) was slowly added 1M NaHMDS in THF (3 mL, 3 mmol, 1.5 equiv.) at 0 $^\circ\text{C}$. To the resulting mixture was added iodomethane- d_3 (0.37 mL, 6 mmol, 3 equiv.). The reaction mixture was then stirred at rt for 24 h. Upon completion, the reaction mixture was quenched with H_2O and extracted with EtOAc (x3). The combined

organic layers were washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (hexanes) to afford alkyne **d-2a** as a clear, colorless oil [39 mg, 16% yield]. The ^1H NMR was in accordance with the literature.⁷ ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.37 (m, 2H), 7.31 – 7.23 (m, 3H). ^2H NMR (61 MHz, CDCl_3) δ 2.03.

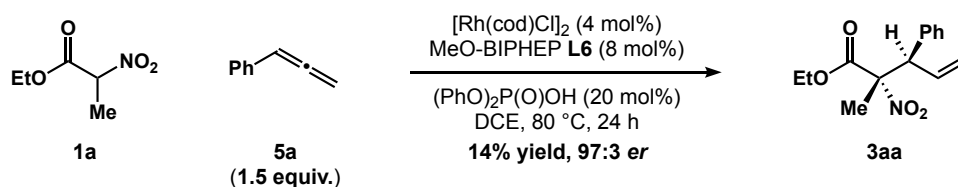


Deuterated Alkyne Mechanistic Experiment: According to *General Procedure for Enantioenriched Allylic Nitrocarbonyls* to a 1 dram vial equipped with a magnetic stir bar was added $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.0 mg, 0.004 mmol, 4 mol%), (*R*)-MeO-BIPHEP **L6** (A104-1, 7.5 mg, 0.008 mmol, 8 mol%), diphenyl phosphate (5.0 mg, 0.02 mmol, 20 mol%), ethyl-2-nitropropionate (14.7 mg, 0.1 mmol, 1 equiv.), alkyne **d-2a** (17.9 mg, 0.15 mmol, 1.5 equiv.) and DCE (200 μL , 0.5 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 °C for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. The crude residue was purified by preparatory TLC (20:1 hexanes:EtOAc) to afford allylic nitroester **d-3aa** as a clear, yellow oil [16.0 mg, 60% yield]. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 6.35 – 6.28 (m, 0.43H), 5.25 – 5.15 (m, 0.50 H), 4.42 – 4.40 (m, 0.45H), 4.18 – 4.12 (m, 2H), 1.78 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H). ^2H NMR (61 MHz, CDCl_3) δ 6.33, 5.21, 4.40.

C. 1-Phenylallene Synthesis and Experiment:



Preparation of 1-Phenylallene (5a): To a round bottom flask containing styrene (**S5**, 1.35 g, 13 mmol) in CHBr_3 (5 mL, 2.6 M) was added benzyltriethylammonium chloride (71 mg, 0.26 mmol, 0.02 equiv) in one portion. To the resulting mixture was added 20 M NaOH (aq, 5 mL) at 0 °C. The reaction mixture was then stirred at 0 °C for 3 h and then at rt for 1 h. Upon completion, the reaction mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (hexanes) to afford **S6** as a clear, yellow oil [1 g, 28% yield]. The ^1H NMR was in accordance with the literature.⁸ ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.29 (m, 3H), 7.26 (dd, J = 5.4, 2.7 Hz, 2H), 2.96 (dd, J = 10.4, 8.4 Hz, 1H), 2.14 (dd, J = 10.5, 7.7 Hz, 1H), 2.02 (t, J = 8.0 Hz, 1H). To a round bottom flask containing **S6** (994 mg, 3.6 mmol) in THF (7.2 mL, 0.5 M) was added 1M EtMgBr (4.68 mL, 4.68 mmol, 1.3 equiv) dropwise at 0 °C. The reaction mixture was then gently warmed to rt and stirred for 3 h. Upon completion, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed 1M HCl (10 mL), saturated NaHCO_3 (10 mL), and then brine. The combined organic layers were then dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (hexanes) to afford allene **5a** as a clear, colorless oil [232 mg, 55% yield]. The ^1H NMR was in accordance with the literature.⁸ ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.30 (m, 4H), 7.24 – 7.18 (m, 1H), 6.18 (t, J = 6.8 Hz, 1H), 5.16 (d, J = 6.8 Hz, 2H).

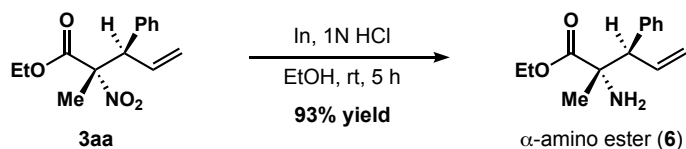


Allene Mechanistic Experiments: According to *General Procedure for Enantioenriched Allylic Nitrocarbonyls* to a 1 dram vial equipped with a magnetic stir bar was added $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.0 mg, 0.004 mmol, 4 mol%), (*R*)-MeO-BIPHEP (A104-1, 7.5 mg, 0.008 mmol, 8 mol%), diphenyl phosphate (5.0 mg, 0.02 mmol, 20 mol%), ethyl-2-nitropropionate (14.7 mg, 0.1 mmol, 1 equiv.), 1-phenylallene (17.4 mg, 0.15 mmol, 1.5 equiv.) and DCE (200 μL , 0.5 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 °C for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. Diastereo- and regioselectivity ratios

(*dr* and *rr*, respectively) were determined by ^1H NMR analysis of the crude reaction mixture. ^1H NMR yield, which was referenced to an internal standard (triphenylmethane), is reported. Chiral SFC analysis for enantioselectivity ratios (*er*). Observed **3aa** (14% yield, 0.014 mmol, 97:3 *er*) in the crude ^1H NMR spectrum.

***Note:** In the absence of nucleophile **1a**, 1-phenylallene (0.15 mmol) is completely consumed in the standard reaction conditions above. The 1-phenylallene mass appears to convert to a gel-like substance that is not soluble in the reaction medium.

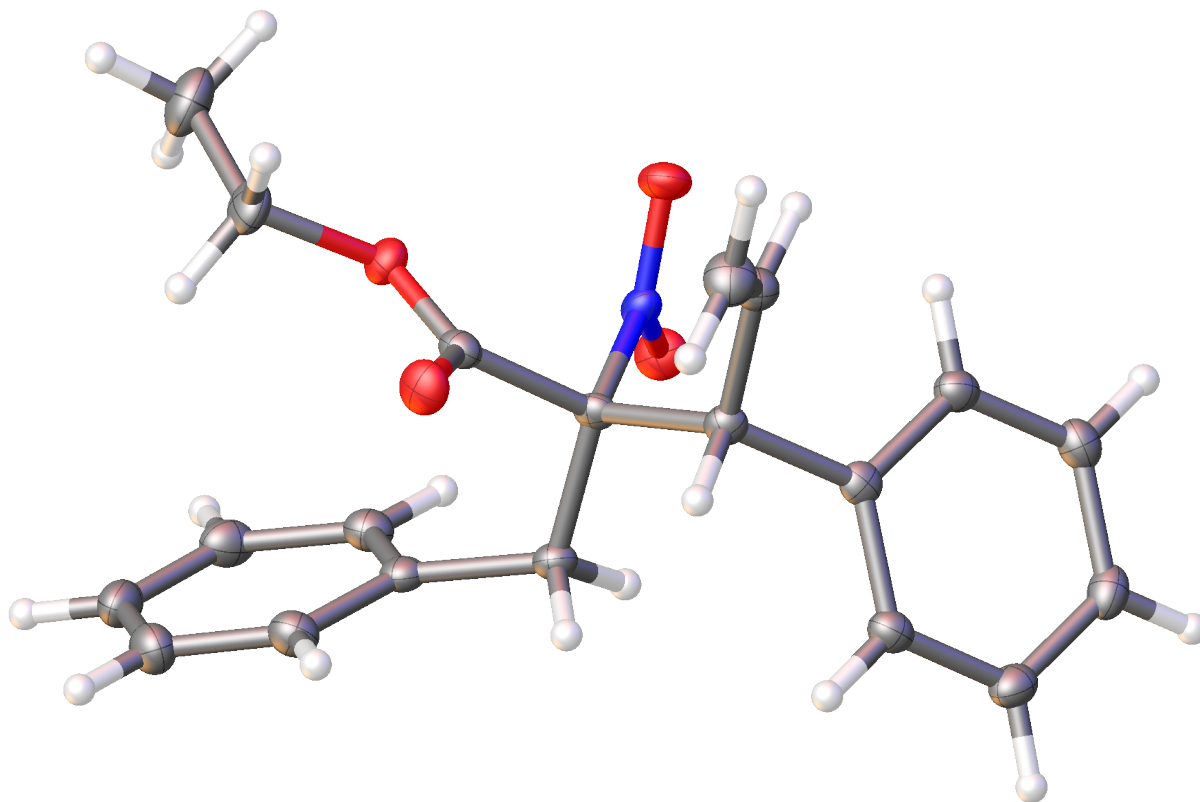
6. Reduction of Allylic Nitroester 3aa to Amino Ester 6



Preparation of Ethyl (2S,3R)-2-amino-2-methyl-3-phenylpent-4-enoate (6): To a round bottom flask containing nitroester (26 mg, 0.1 mmol) in EtOH (2 mL, 0.05 M) was added indium powder (115 mg, 1 mmol, 10 equiv, 325 mesh) in one portion. To the resulting suspension was added 1N HCl (*aq*, 1 mL, 1 mmol, 10 equiv.). The clear reaction mixture was then stirred at rt for 5 h. Upon completion (visible grey precipitate), the reaction mixture was cooled to 0 °C, quenched with saturated NaHCO₃ (*aq*) slowly, and extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried with anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by preparatory TLC (2:1 hexanes:EtOAc) to afford the title compound as a clear, yellow oil [22 mg, 93% yield, >20:1 *dr*, 97:3 *er*, [α]²⁴_D = -29.9° (*c* 1.0, CHCl₃)]. **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.20 (m, 5H), 6.25 (ddd, *J* = 17.0, 10.1, 9.3 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.62 (d, *J* = 9.2 Hz, 1H), 1.76 (br, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 176.7, 139.6, 137.2, 129.7, 128.4, 127.2, 117.9, 61.5, 61.4, 58.8, 25.6, 14.4. **IR** (ATR): 3384, 3319, 2978, 2930, 1726, 1454, 1219, 1104, 1021, 916 cm⁻¹. **HRMS** calculated for C₁₄H₂₀NO₂ [M+H]⁺ 234.1494, found 234.1494. **Chiral SFC** (of the corresponding benzamide): 150 mm CHIRALCEL AD-H, 6% *i*PrOH, 2 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 6.9 min, *t*_{R2} (major) = 9.9 min.

7. X-Ray Crystallographic Data

X-ray Crystallographic Data for 3fa (CCDC 2014416)



The single crystal X-ray diffraction studies were carried out on a Bruker SMART Platinum 135 CCD diffractometer equipped with Cu K α radiation (λ = 1.5478). Crystals of the subject compound were used as received. (grown from acetonitrile/pentane by vapor diffusion.)

A 0.225 x 0.200 x 0.180 mm colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(1) K using ω and ϕ scans. Crystal-to-detector distance was 45 mm using variable exposure time (1, 3 and 5s) depending on the detector ϕ position, with a scan width of 1.4°. Data collection was 100.0% complete to 67.679° in ϕ . A total of 14039 reflections were collected covering the indices, $-7 \leq h \leq 7$, $-17 \leq k \leq 16$, $-25 \leq l \leq 24$. 3399 reflections were found to be symmetry independent, with a R_{int} of 0.0368. Indexing and unit cell refinement indicated a **Primitive, Orthorhombic** lattice. The space group was found to be ***P*2₁2₁2₁**. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S1.

Table S1. Crystal data and structure refinement for **3fa**.

Report date	2020-07-05	
Identification code	pp01083	
Empirical formula	C ₂₀ H ₂₁ N O ₄	
Molecular formula	C ₂₀ H ₂₁ N O ₄	
Formula weight	339.38	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 6.0404(3) Å	∠ = 90°.
	b = 14.3407(7) Å	∠ = 90°.
	c = 20.6337(10) Å	∠ = 90°.
Volume	1787.36(15) Å ³	
Z	4	
Density (calculated)	1.261 Mg/m ³	
Absorption coefficient	0.716 mm ⁻¹	
F(000)	720	
Crystal size	0.225 x 0.2 x 0.18 mm ³	
Crystal color, habit	colorless block	
Theta range for data collection	3.753 to 70.261°.	
Index ranges	-7<=h<=7, -17<=k<=16, -25<=l<=24	
Reflections collected	14039	
Independent reflections	3399 [R(int) = 0.0368]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7533 and 0.6729
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3399 / 0 / 227
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0268$, $wR_2 = 0.0680$
R indices (all data)	$R_1 = 0.0270$, $wR_2 = 0.0681$
Absolute structure parameter	-0.04(4)
Largest diff. peak and hole	0.245 and -0.140 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3fa**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	6640(2)	3553(1)	6535(1)	19(1)
O(2)	3256(2)	3277(1)	6112(1)	24(1)
O(3)	8826(2)	4308(1)	5486(1)	22(1)
O(4)	8318(2)	5657(1)	5926(1)	22(1)
N(1)	7644(2)	4894(1)	5746(1)	16(1)
C(1)	8607(4)	2601(1)	7286(1)	34(1)
C(2)	6443(3)	2716(1)	6935(1)	25(1)
C(3)	4919(2)	3733(1)	6152(1)	17(1)
C(4)	5180(2)	4668(1)	5798(1)	15(1)
C(5)	4240(2)	4617(1)	5089(1)	16(1)
C(6)	5050(3)	3791(1)	4700(1)	20(1)
C(7)	3769(3)	3081(1)	4543(1)	26(1)
C(8)	3971(2)	5428(1)	6198(1)	17(1)
C(9)	4117(3)	5328(1)	6931(1)	18(1)
C(10)	2376(3)	4900(1)	7260(1)	22(1)
C(11)	2435(3)	4801(1)	7934(1)	27(1)
C(12)	4237(3)	5127(1)	8278(1)	26(1)
C(13)	5986(3)	5549(1)	7957(1)	25(1)
C(14)	5916(3)	5660(1)	7286(1)	21(1)
C(15)	4555(3)	5543(1)	4735(1)	16(1)
C(16)	6520(3)	5745(1)	4405(1)	19(1)
C(17)	6794(3)	6585(1)	4082(1)	21(1)
C(18)	5114(3)	7245(1)	4085(1)	22(1)
C(19)	3159(3)	7060(1)	4415(1)	22(1)
C(20)	2878(3)	6211(1)	4734(1)	19(1)

Table S3. Bond lengths [Å] and angles [°] for **3fa**.

O(1)-C(2)	1.4613(18)	O(4)-N(1)-O(3)	123.48(13)
O(1)-C(3)	1.3312(19)	O(4)-N(1)-C(4)	119.46(12)
O(2)-C(3)	1.2013(19)	O(1)-C(2)-C(1)	106.97(14)
O(3)-N(1)	1.2261(17)	O(1)-C(3)-C(4)	111.79(12)
O(4)-N(1)	1.2259(17)	O(2)-C(3)-O(1)	126.10(14)
N(1)-C(4)	1.5271(19)	O(2)-C(3)-C(4)	121.87(14)
C(1)-C(2)	1.504(3)	N(1)-C(4)-C(3)	108.63(12)
C(3)-C(4)	1.535(2)	N(1)-C(4)-C(5)	107.26(11)
C(4)-C(5)	1.571(2)	N(1)-C(4)-C(8)	110.34(12)
C(4)-C(8)	1.550(2)	C(3)-C(4)-C(5)	111.46(12)
C(5)-C(6)	1.513(2)	C(3)-C(4)-C(8)	108.18(12)
C(5)-C(15)	1.528(2)	C(8)-C(4)-C(5)	110.96(12)
C(6)-C(7)	1.320(2)	C(6)-C(5)-C(4)	114.42(12)
C(8)-C(9)	1.522(2)	C(6)-C(5)-C(15)	112.76(12)
C(9)-C(10)	1.394(2)	C(15)-C(5)-C(4)	111.08(12)
C(9)-C(14)	1.394(2)	C(7)-C(6)-C(5)	123.01(15)
C(10)-C(11)	1.397(2)	C(9)-C(8)-C(4)	115.86(12)
C(11)-C(12)	1.382(3)	C(10)-C(9)-C(8)	118.80(14)
C(12)-C(13)	1.386(3)	C(14)-C(9)-C(8)	122.37(14)
C(13)-C(14)	1.394(2)	C(14)-C(9)-C(10)	118.82(14)
C(15)-C(16)	1.399(2)	C(9)-C(10)-C(11)	120.71(16)
C(15)-C(20)	1.394(2)	C(12)-C(11)-C(10)	119.81(17)
C(16)-C(17)	1.386(2)	C(11)-C(12)-C(13)	120.12(15)
C(17)-C(18)	1.387(2)	C(12)-C(13)-C(14)	120.11(16)
C(18)-C(19)	1.389(2)	C(9)-C(14)-C(13)	120.40(16)
C(19)-C(20)	1.394(2)	C(16)-C(15)-C(5)	121.20(14)
		C(20)-C(15)-C(5)	120.49(13)
C(3)-O(1)-C(2)	115.50(13)	C(20)-C(15)-C(16)	118.30(14)
O(3)-N(1)-C(4)	116.92(12)	C(17)-C(16)-C(15)	120.96(15)

C(16)-C(17)-C(18)	120.25(15)
C(17)-C(18)-C(19)	119.56(14)
C(18)-C(19)-C(20)	120.11(15)
C(15)-C(20)-C(19)	120.81(15)

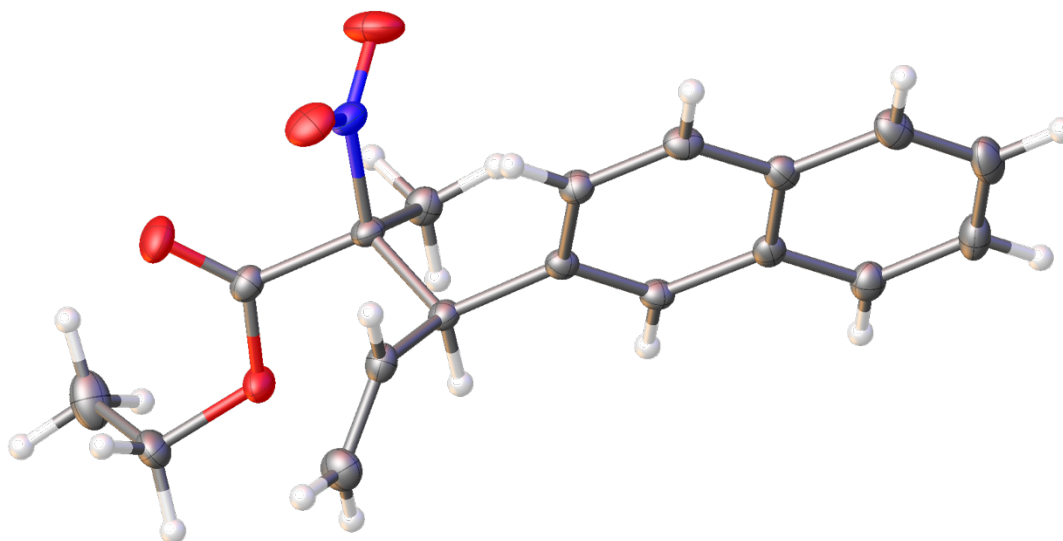
Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3fa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	21(1)	15(1)	21(1)	4(1)	-1(1)	-1(1)
O(2)	21(1)	22(1)	28(1)	3(1)	1(1)	-7(1)
O(3)	16(1)	22(1)	29(1)	0(1)	4(1)	4(1)
O(4)	19(1)	19(1)	29(1)	0(1)	-1(1)	-6(1)
N(1)	13(1)	16(1)	19(1)	4(1)	0(1)	0(1)
C(1)	44(1)	28(1)	30(1)	11(1)	-8(1)	-2(1)
C(2)	32(1)	18(1)	26(1)	8(1)	1(1)	-1(1)
C(3)	17(1)	16(1)	18(1)	-1(1)	4(1)	0(1)
C(4)	11(1)	15(1)	19(1)	0(1)	2(1)	-1(1)
C(5)	13(1)	18(1)	18(1)	0(1)	-1(1)	-1(1)
C(6)	20(1)	19(1)	20(1)	0(1)	1(1)	1(1)
C(7)	33(1)	21(1)	25(1)	-3(1)	0(1)	-2(1)
C(8)	15(1)	16(1)	19(1)	0(1)	0(1)	2(1)
C(9)	18(1)	15(1)	20(1)	-1(1)	1(1)	4(1)
C(10)	20(1)	24(1)	24(1)	-1(1)	1(1)	1(1)
C(11)	27(1)	28(1)	25(1)	5(1)	6(1)	2(1)
C(12)	31(1)	29(1)	19(1)	3(1)	0(1)	9(1)
C(13)	24(1)	28(1)	24(1)	-4(1)	-4(1)	4(1)
C(14)	20(1)	21(1)	23(1)	-2(1)	2(1)	2(1)
C(15)	16(1)	18(1)	14(1)	-3(1)	-2(1)	-2(1)
C(16)	17(1)	21(1)	18(1)	-1(1)	0(1)	2(1)
C(17)	21(1)	24(1)	18(1)	0(1)	2(1)	-3(1)
C(18)	32(1)	17(1)	18(1)	2(1)	-2(1)	-2(1)
C(19)	26(1)	19(1)	21(1)	-1(1)	-2(1)	5(1)
C(20)	17(1)	22(1)	18(1)	-2(1)	1(1)	1(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **3fa**.

	x	y	z	U(eq)
H(1A)	9819	2577	6971	51
H(1B)	8580	2021	7537	51
H(1C)	8833	3130	7580	51
H(2A)	6143	2165	6660	30
H(2B)	5215	2787	7249	30
H(5)	2604	4532	5135	20
H(6)	6551	3783	4562	23
H(7A)	2263	3073	4676	31
H(7B)	4353	2577	4298	31
H(8A)	4586	6043	6076	20
H(8B)	2388	5425	6073	20
H(10)	1137	4674	7024	27
H(11)	1239	4510	8154	32
H(12)	4277	5062	8736	31
H(13)	7234	5763	8194	30
H(14)	7103	5963	7069	25
H(16)	7685	5300	4402	23
H(17)	8137	6709	3859	26
H(18)	5299	7819	3862	27
H(19)	2011	7512	4424	26
H(20)	1528	6086	4954	23

X-ray Crystallographic Data for 3ao (CCDC 2014415)



The single crystal X-ray diffraction studies were carried out on a Bruker SMART APEX II CCD diffractometer equipped with Cu K α radiation (λ = 1.5478). Crystals of the subject compound were used as received. (Grown from ethyl acetate/hexane by vapor diffusion.)

A 0.225 x 0.200 x 0.180 mm colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(1) K using ω and ϕ scans. Crystal-to-detector distance was 40 mm using variable exposure time (2, 4 and 8s) depending on the detector ϕ position, with a scan width of 1.4°. Data collection was 100.0% complete to 67.679° in ϕ . A total of 15586 reflections were collected covering the indices, $-7 \leq h \leq 7$, $-10 \leq k \leq 10$, $-37 \leq l \leq 31$. 3053 reflections were found to be symmetry independent, with a R_{int} of 0.0284. Indexing and unit cell refinement indicated a **Primitive, Orthorhombic** lattice. The space group was found to be ***P*2₁2₁2₁**. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S1.

Table S6. Crystal data and structure refinement for **3ao**.

Report date	2020-07-05
Identification code	rd3100
Empirical formula	C ₁₈ H ₁₉ N O ₄
Molecular formula	C ₁₈ H ₁₉ N O ₄
Formula weight	313.34
Temperature	100.0 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 6.14300(10) Å $\alpha = 90^\circ$. b = 8.2993(2) Å $\beta = 90^\circ$. c = 31.1195(7) Å $\gamma = 90^\circ$.
Volume	1586.55(6) Å ³
Z	4
Density (calculated)	1.312 Mg/m ³
Absorption coefficient	0.761 mm ⁻¹
F(000)	664
Crystal size	0.34 x 0.04 x 0.03 mm ³
Crystal color, habit	colorless needle
Theta range for data collection	2.840 to 70.988°.
Index ranges	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -37 ≤ l ≤ 31
Reflections collected	15586
Independent reflections	3053 [R(int) = 0.0284]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7534 and 0.6222
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3053 / 0 / 211
Goodness-of-fit on F ²	1.075
Final R indices [I > 2sigma(I)]	R1 = 0.0252, wR2 = 0.0632

R indices (all data)	$R1 = 0.0267, wR2 = 0.0638$
Absolute structure parameter	0.02(6)
Extinction coefficient	0.0010(3)
Largest diff. peak and hole	0.161 and -0.123 e.Å ⁻³

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ao**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	7576(2)	6398(1)	7127(1)	21(1)
O(2)	4036(2)	6691(2)	7299(1)	28(1)
O(3)	1718(2)	6936(2)	6512(1)	29(1)
O(4)	1729(2)	4342(2)	6480(1)	38(1)
N(1)	2648(2)	5638(2)	6526(1)	21(1)
C(1)	5452(2)	6324(2)	7051(1)	18(1)
C(2)	5104(2)	5650(2)	6597(1)	17(1)
C(3)	6217(2)	6771(2)	6256(1)	15(1)
C(4)	5775(3)	8543(2)	6327(1)	18(1)
C(5)	7249(3)	9512(2)	6495(1)	25(1)
C(6)	5973(3)	3933(2)	6575(1)	20(1)
C(7)	8251(3)	7046(2)	7542(1)	24(1)
C(8)	7991(3)	5816(2)	7891(1)	33(1)
C(9)	5783(3)	6233(2)	5796(1)	16(1)
C(10)	7313(3)	5334(2)	5582(1)	16(1)
C(11)	6999(3)	4826(2)	5150(1)	16(1)
C(12)	8567(3)	3897(2)	4926(1)	21(1)
C(13)	8190(3)	3435(2)	4509(1)	25(1)
C(14)	6251(3)	3872(2)	4299(1)	27(1)
C(15)	4709(3)	4766(2)	4507(1)	23(1)
C(16)	5031(3)	5265(2)	4939(1)	18(1)
C(17)	3476(3)	6199(2)	5162(1)	19(1)
C(18)	3831(3)	6674(2)	5578(1)	18(1)

Table S8. Bond lengths [Å] and angles [°] for **3ao**.

O(1)-C(1)	1.3269(19)	C(11)-C(12)	1.417(2)
O(1)-C(7)	1.4601(19)	C(11)-C(16)	1.423(2)
O(2)-C(1)	1.2020(19)	C(12)-H(12)	0.9500
O(3)-N(1)	1.2201(18)	C(12)-C(13)	1.373(2)
O(4)-N(1)	1.2228(19)	C(13)-H(13)	0.9500
N(1)-C(2)	1.5253(19)	C(13)-C(14)	1.406(3)
C(1)-C(2)	1.535(2)	C(14)-H(14)	0.9500
C(2)-C(3)	1.568(2)	C(14)-C(15)	1.366(3)
C(2)-C(6)	1.523(2)	C(15)-H(15)	0.9500
C(3)-H(3)	1.0000	C(15)-C(16)	1.421(2)
C(3)-C(4)	1.512(2)	C(16)-C(17)	1.413(2)
C(3)-C(9)	1.524(2)	C(17)-H(17)	0.9500
C(4)-H(4)	0.9500	C(17)-C(18)	1.369(2)
C(4)-C(5)	1.318(2)	C(18)-H(18)	0.9500
C(5)-H(5A)	0.9500		
C(5)-H(5B)	0.9500	C(1)-O(1)-C(7)	116.92(12)
C(6)-H(6A)	0.9800	O(3)-N(1)-O(4)	123.81(14)
C(6)-H(6B)	0.9800	O(3)-N(1)-C(2)	117.53(13)
C(6)-H(6C)	0.9800	O(4)-N(1)-C(2)	118.65(14)
C(7)-H(7A)	0.9900	O(1)-C(1)-C(2)	108.45(12)
C(7)-H(7B)	0.9900	O(2)-C(1)-O(1)	125.89(15)
C(7)-C(8)	1.499(3)	O(2)-C(1)-C(2)	125.65(14)
C(8)-H(8A)	0.9800	N(1)-C(2)-C(1)	105.90(12)
C(8)-H(8B)	0.9800	N(1)-C(2)-C(3)	109.71(12)
C(8)-H(8C)	0.9800	C(1)-C(2)-C(3)	110.29(12)
C(9)-C(10)	1.372(2)	C(6)-C(2)-N(1)	109.48(13)
C(9)-C(18)	1.426(2)	C(6)-C(2)-C(1)	109.49(12)
C(10)-H(10)	0.9500	C(6)-C(2)-C(3)	111.80(13)
C(10)-C(11)	1.422(2)	C(2)-C(3)-H(3)	105.5

C(4)-C(3)-C(2)	113.56(12)	C(10)-C(9)-C(18)	119.03(14)
C(4)-C(3)-H(3)	105.5	C(18)-C(9)-C(3)	121.28(14)
C(4)-C(3)-C(9)	113.00(12)	C(9)-C(10)-H(10)	119.1
C(9)-C(3)-C(2)	112.74(12)	C(9)-C(10)-C(11)	121.77(15)
C(9)-C(3)-H(3)	105.5	C(11)-C(10)-H(10)	119.1
C(3)-C(4)-H(4)	119.1	C(10)-C(11)-C(16)	118.36(14)
C(5)-C(4)-C(3)	121.85(15)	C(12)-C(11)-C(10)	122.34(14)
C(5)-C(4)-H(4)	119.1	C(12)-C(11)-C(16)	119.30(14)
C(4)-C(5)-H(5A)	120.0	C(11)-C(12)-H(12)	119.9
C(4)-C(5)-H(5B)	120.0	C(13)-C(12)-C(11)	120.19(16)
H(5A)-C(5)-H(5B)	120.0	C(13)-C(12)-H(12)	119.9
C(2)-C(6)-H(6A)	109.5	C(12)-C(13)-H(13)	119.7
C(2)-C(6)-H(6B)	109.5	C(12)-C(13)-C(14)	120.64(16)
C(2)-C(6)-H(6C)	109.5	C(14)-C(13)-H(13)	119.7
H(6A)-C(6)-H(6B)	109.5	C(13)-C(14)-H(14)	119.7
H(6A)-C(6)-H(6C)	109.5	C(15)-C(14)-C(13)	120.51(15)
H(6B)-C(6)-H(6C)	109.5	C(15)-C(14)-H(14)	119.7
O(1)-C(7)-H(7A)	109.4	C(14)-C(15)-H(15)	119.7
O(1)-C(7)-H(7B)	109.4	C(14)-C(15)-C(16)	120.68(16)
O(1)-C(7)-C(8)	111.11(14)	C(16)-C(15)-H(15)	119.7
H(7A)-C(7)-H(7B)	108.0	C(15)-C(16)-C(11)	118.67(15)
C(8)-C(7)-H(7A)	109.4	C(17)-C(16)-C(11)	119.25(14)
C(8)-C(7)-H(7B)	109.4	C(17)-C(16)-C(15)	122.07(15)
C(7)-C(8)-H(8A)	109.5	C(16)-C(17)-H(17)	119.5
C(7)-C(8)-H(8B)	109.5	C(18)-C(17)-C(16)	120.97(15)
C(7)-C(8)-H(8C)	109.5	C(18)-C(17)-H(17)	119.5
H(8A)-C(8)-H(8B)	109.5	C(9)-C(18)-H(18)	119.7
H(8A)-C(8)-H(8C)	109.5	C(17)-C(18)-C(9)	120.61(14)
H(8B)-C(8)-H(8C)	109.5	C(17)-C(18)-H(18)	119.1
C(10)-C(9)-C(3)	119.67(14)		

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ao**. The anisotropic displacement

factor exponent takes the form: $-2 \square^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	17(1)	33(1)	14(1)	-2(1)	0(1)	-1(1)
O(2)	21(1)	41(1)	21(1)	-3(1)	5(1)	6(1)
O(3)	16(1)	34(1)	35(1)	5(1)	1(1)	7(1)
O(4)	22(1)	34(1)	57(1)	-2(1)	-2(1)	-11(1)
N(1)	14(1)	29(1)	19(1)	1(1)	2(1)	-2(1)
C(1)	17(1)	19(1)	17(1)	3(1)	2(1)	2(1)
C(2)	12(1)	21(1)	16(1)	1(1)	0(1)	-2(1)
C(3)	12(1)	18(1)	15(1)	0(1)	1(1)	0(1)
C(4)	20(1)	20(1)	16(1)	1(1)	2(1)	3(1)
C(5)	28(1)	20(1)	26(1)	-2(1)	0(1)	1(1)
C(6)	22(1)	18(1)	20(1)	2(1)	1(1)	1(1)
C(7)	23(1)	32(1)	18(1)	-6(1)	-3(1)	-3(1)
C(8)	45(1)	34(1)	21(1)	0(1)	-6(1)	12(1)
C(9)	16(1)	15(1)	16(1)	2(1)	-1(1)	-2(1)
C(10)	14(1)	17(1)	16(1)	2(1)	-2(1)	-1(1)
C(11)	19(1)	14(1)	16(1)	2(1)	2(1)	-3(1)
C(12)	23(1)	21(1)	18(1)	2(1)	2(1)	0(1)
C(13)	33(1)	23(1)	18(1)	-2(1)	7(1)	2(1)
C(14)	40(1)	26(1)	14(1)	0(1)	1(1)	-4(1)
C(15)	27(1)	23(1)	17(1)	3(1)	-5(1)	-2(1)
C(16)	21(1)	16(1)	16(1)	3(1)	-1(1)	-2(1)
C(17)	16(1)	20(1)	20(1)	4(1)	-4(1)	-1(1)
C(18)	15(1)	19(1)	19(1)	0(1)	0(1)	1(1)

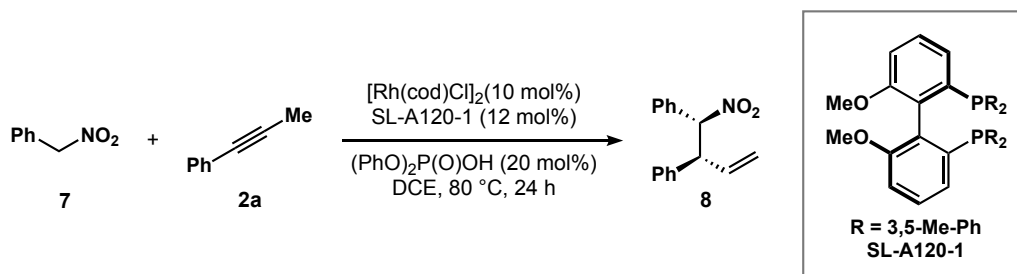
Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ao**.

	x	y	z	U(eq)
H(3)	7819	6633	6300	18
H(4)	4397	8971	6248	22
H(5A)	8635	9101	6575	30
H(5B)	6926	10621	6535	30
H(6A)	5298	3285	6802	31
H(6B)	7555	3944	6615	31
H(6C)	5623	3467	6294	31
H(7A)	7362	8007	7611	29
H(7B)	9793	7386	7526	29
H(8A)	8853	4858	7821	50
H(8B)	6453	5517	7916	50
H(8C)	8497	6269	8164	50
H(10)	8617	5042	5727	19
H(12)	9883	3594	5064	25
H(13)	9249	2813	4361	30
H(14)	6011	3544	4011	32
H(15)	3409	5057	4361	27
H(17)	2165	6502	5022	22
H(18)	2766	7304	5722	21

8. References

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9. General Procedure for Nitroalkane and Alkyne Coupling



To a 1 dram vial equipped with a magnetic stir bar was added $[\text{Rh(cod)Cl}]_2$ (2.5 mg, 0.005 mmol, 10 mol% Rh), chiral ligand (7.0 mg, 0.005 mmol, 10 mol%), $(\text{PhO})_2\text{P(O)OH}$ (5.0 mg, 0.02 mmol, 20 mol%), nitroalkane **7** (14 mg, 0.1 mmol, 1 equiv.), alkyne **2** (17 mg, 0.15 mmol, 1.5 equiv.) and DCE (400 μL , 0.25 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 $^\circ\text{C}$ for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. Diastereo- and regioselectivity ratios (*dr* and *rr*, respectively) were determined by ^1H NMR analysis of the crude reaction mixture. ^1H NMR yields, which were referenced to an internal standard (triphenylmethane), are reported. Chiral SFC analysis for enantioselectivity ratios (*er*).

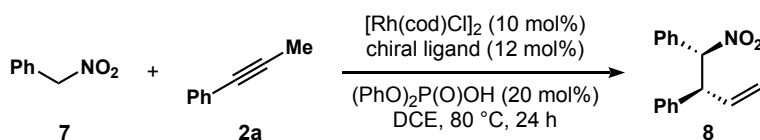
(1-nitrobut-3-ene-1,2-diyl)dibenzene (**8**)

The title compound was synthesized according to general procedure for nitroalkane and alkyne coupling and isolated by preparatory TLC (80:20 hexanes:EtOAc) as a yellow solid [11 mg, 44% yield, 79:21 *er*, >20:1 *dr*, >20:1 *rr*, ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.36 (m, 2H), 7.24 (dd, J = 6.9, 1.3 Hz, 3H), 7.16 (ddd, J = 7.5, 6.4, 1.4 Hz, 2H), 7.12 – 7.08 (m, 1H), 7.06 – 7.01 (m, 2H), 6.11 (ddd, J = 16.4, 10.3, 8.3 Hz, 1H), 5.77 (d, J = 11.6 Hz, 1H), 5.31 (dd, J = 17.0, 1.2 Hz, 1H), 5.22 (d, J = 10.2 Hz, 1H), 4.40 (dd, J = 11.6, 8.3 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.43, 136.32, 132.57, 129.81, 128.89, 128.79, 128.51, 128.37, 127.39, 118.57, 95.36, 54.13. **IR** (ATR): 3032, 2921, 2850, 1547, 1361, 934, 762, 719, 696, 663 cm^{-1} . **HRMS** calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 276.1000, found 276.0995. **Chiral SFC**: 250 mm CHIRALCEL OB-H, 0.5% $i\text{PrOH}$, 3.0 mL/min, 210 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 7.3 min, t_{R2} (major) = 9.3 min.

10. Nitroalkane and Alkyne Coupling Optimization

General Procedure for Figures S5-S7: To a 1 dram vial equipped with a magnetic stir bar was added Rh-precatalyst (0.0025 mmol, 10 mol% Rh), chiral ligand (0.005 mmol, 10 mol%), acid co-catalyst (0.01 mmol, 20 mol%), nitroalkane **7** (0.05 mmol, 1 equiv.), alkyne **2** (0.075 mmol, 1.5 equiv.) and DCE (200 μ L, 0.25 M). The vial was then sealed with a Teflon-lined screw cap and heated to 80 $^{\circ}$ C for 24 hours. The resulting mixture was then cooled to room temperature and concentrated *in vacuo*. Diastereo- and regioselectivity ratios (*dr* and *rr*, respectively) were determined by ^1H NMR analysis of the crude reaction mixture. ^1H NMR yields, which were referenced to an internal standard (triphenylmethane), are reported. Chiral SFC analysis for enantioselectivity ratios (*er*).

A. Chiral lignds (Figure S5):



Entry	Ligand	yield, d.r., e.r.
1	Segphos	20%, 1:5 <i>dr</i> , 35:65 <i>er</i>
2	(R)-DTBM-Segphos	30%, >20:1 <i>dr</i> , 66:34 <i>er</i>
3	(R)-DM-Segphos	—
4	SL-A001-1	33%, 1:15 <i>dr</i> , 32:68 <i>er</i>
5	SL-A104-1	20%, 1:19 <i>dr</i> , 51:49 <i>er</i>
6	SL-A107-1	36%, >20:1 <i>dr</i> , 66:34 <i>er</i>
7	SL-A108-1	—
8	SL-A-109-1	54%, >20:1 <i>dr</i> , 69:31 <i>er</i>
9	SL-A116-1	36%, >20:1 <i>dr</i> , 69:31 <i>er</i>
10	SL-A120-1	44%, 1:15 <i>dr</i> , 79:21 <i>er</i>
11	SL-J009-1	—
12	(R)-Binap	30%, 1:15 <i>dr</i> , 55:45 <i>er</i>
13	DACH-Trost	35%, 1:15 <i>dr</i> , 55:45 <i>er</i>
14	(R)-DMM-Garphos	35%, >20:1 <i>dr</i> , 81:19 <i>er</i>
15	(R)-DTBM-Garphos	56%, >20:1 <i>dr</i> , 69:31 <i>er</i>
16	Me-BPE	—
17	Me-Duphos	—

B. Chiral lignds (Figure 6):

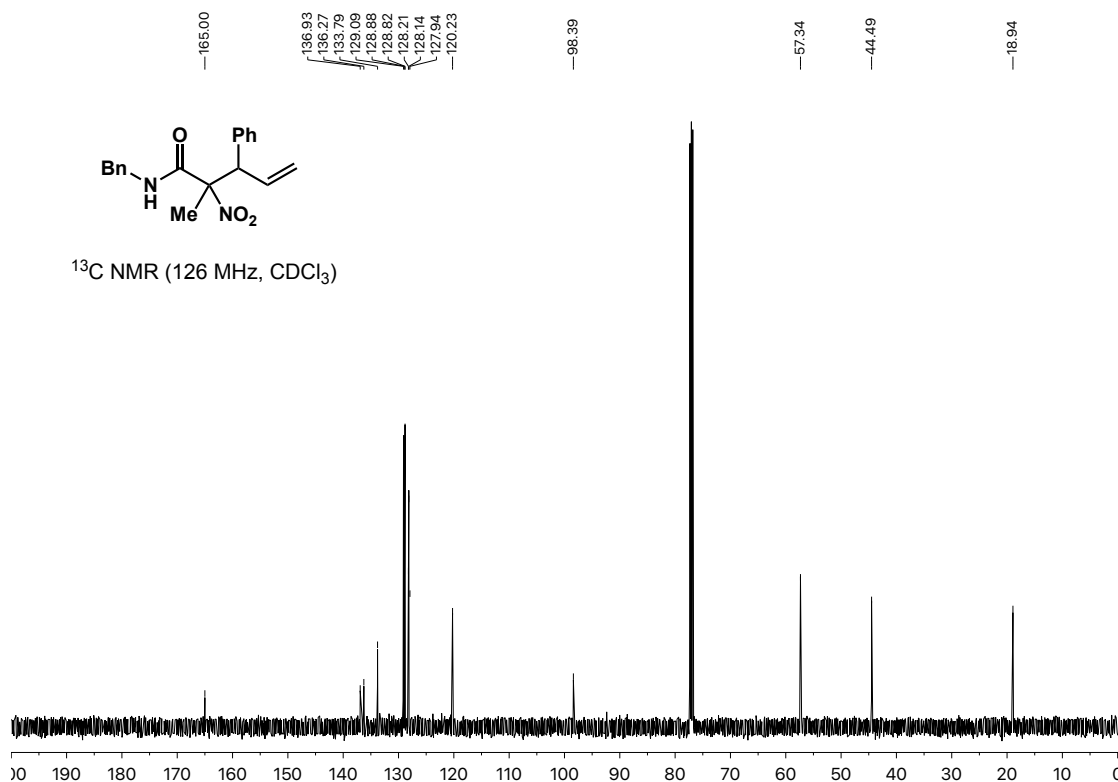
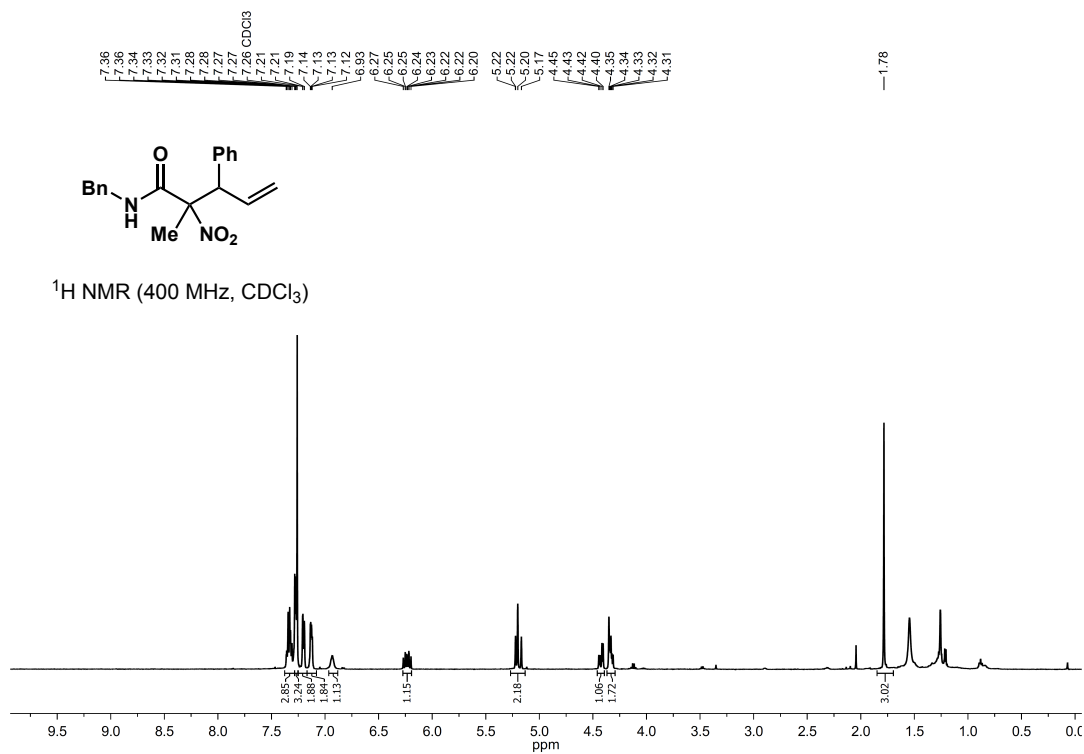
Entry	[Rh] catalyst	yield, d.r., e.r.
1	[Rh(coe)Cl] ₂	26%, >20:1 dr, —
2	[Rh(C ₂ H ₄)Cl] ₂	20%, >20:1 dr, —
3	[Rh(cod)OMe] ₂	—
4	Rh(cod) ₂ SbF ₆	—
5	Rh(cod) ₂ BF ₄	trace

C. Different acids (Figure S7):

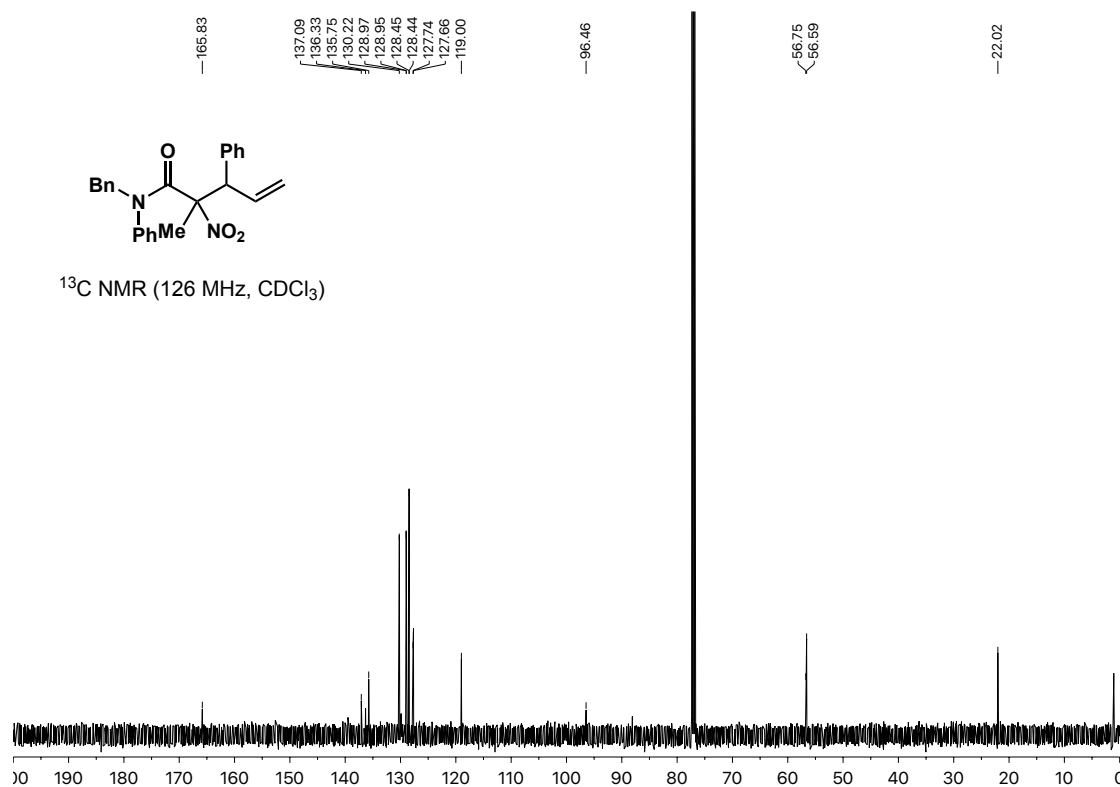
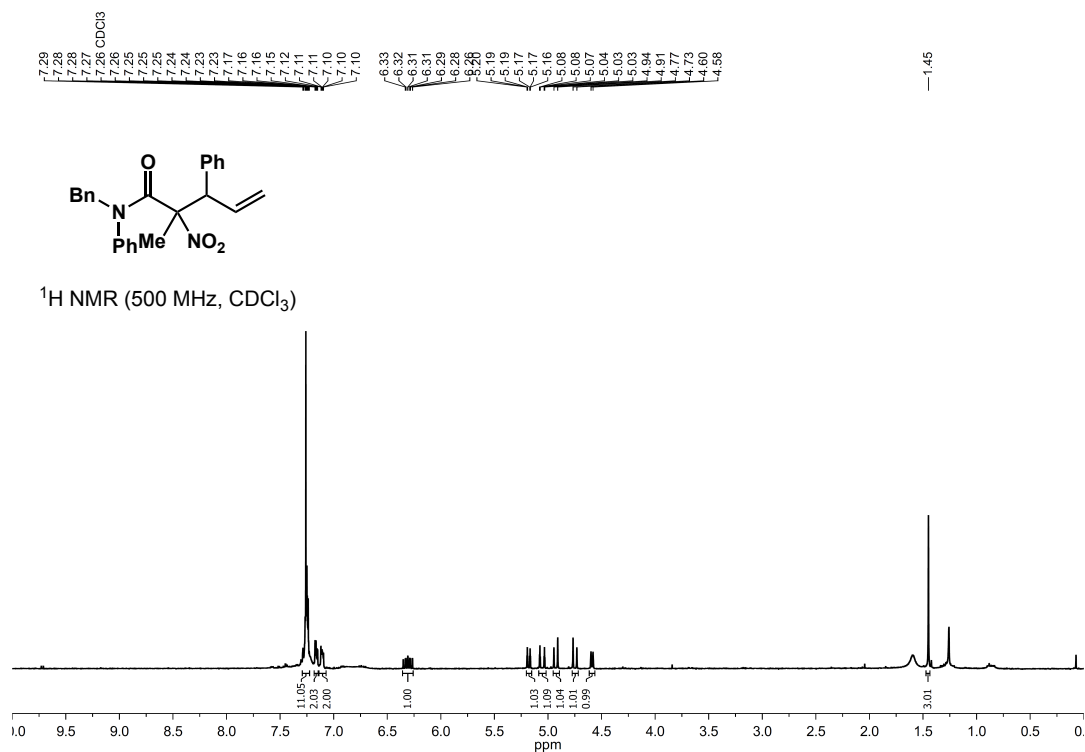
Entry	acid	yield, d.r., e.r.
1	PPTS	22%, >20:1 dr, 73:27 er
2	TFA	64%, >20:1 dr, 70:30 er
3	MsOH	22%, >20:1 dr, 67:33 er
4	BzOH	—
5	Ph ₂ PO(OH)	—
6	(PhO) ₂ P(O)OH (50 mol%)	20%, 8:1 dr, 70:30 er
7	(PhO) ₂ P(O)OH (10 mol%)	34%, >20:1 dr, 71:29 er
8	no acid	—

11. NMR Spectra

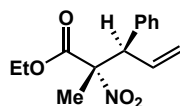
N-benzyl-2-methyl-2-nitro-3-phenylpent-4-enamide (Table 1, entry 3)



***N*-benzyl-2-methyl-2-nitro-*N*,3-diphenylpent-4-enamide (Table 1, entry 4)**

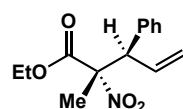
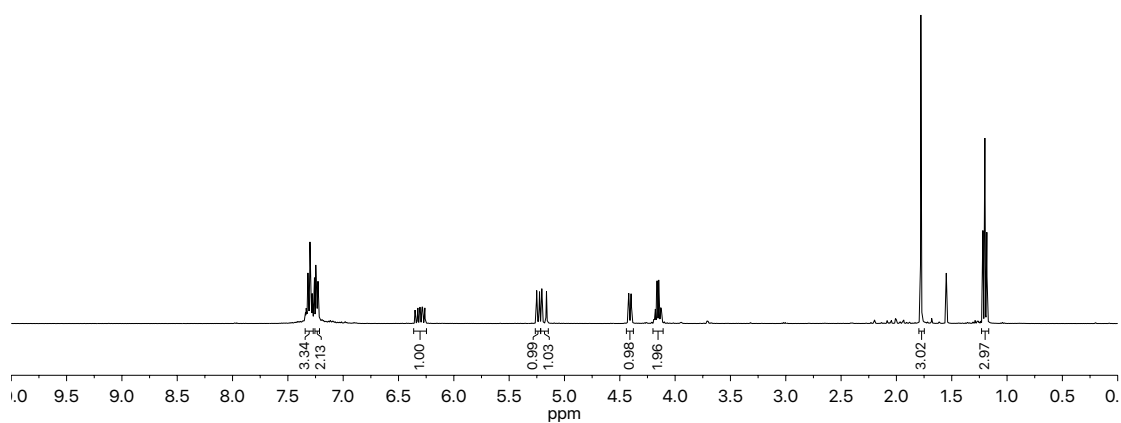


Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3aa)



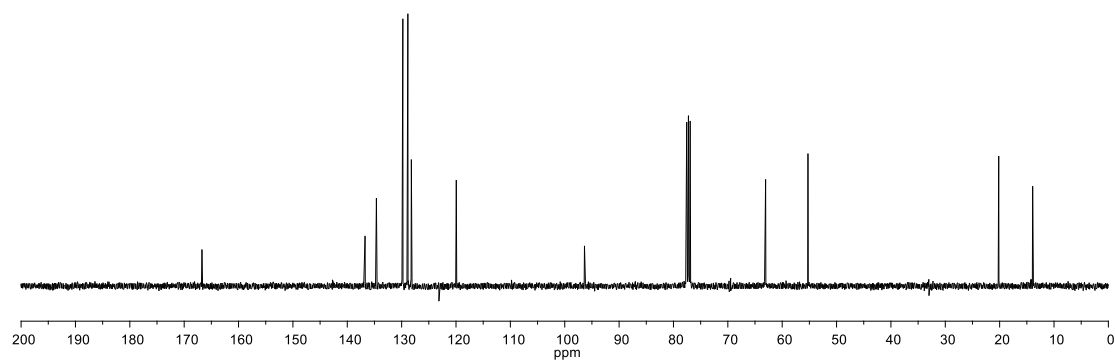
3aa

¹H NMR (400 MHz, CDCl₃)

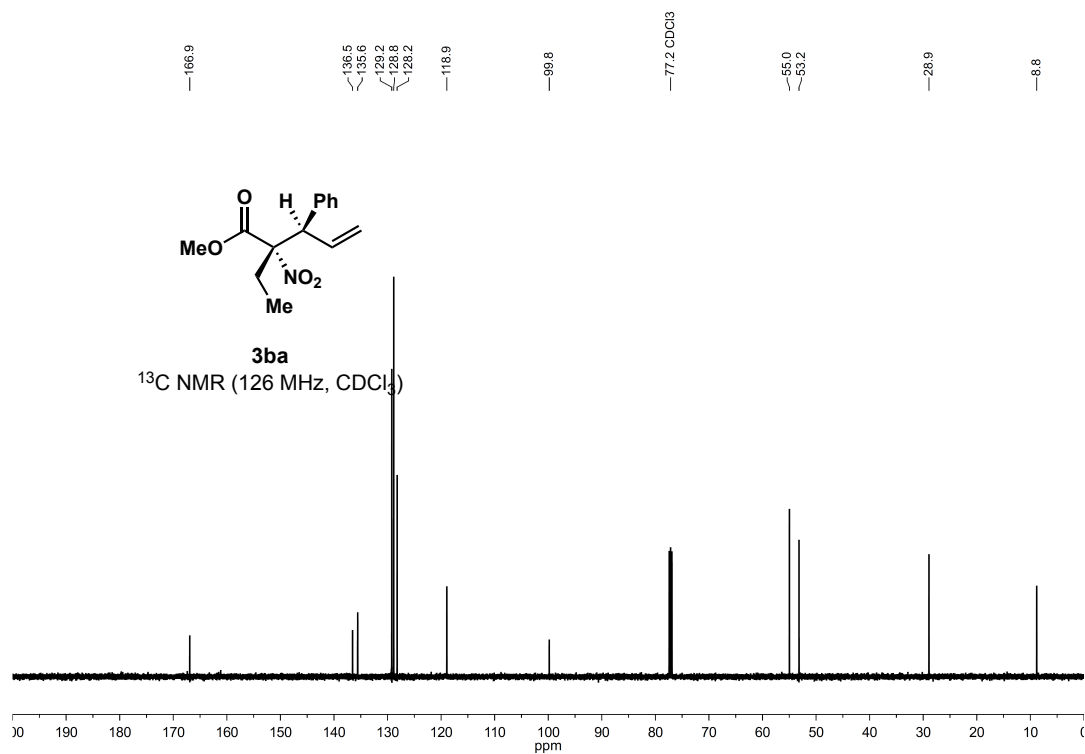
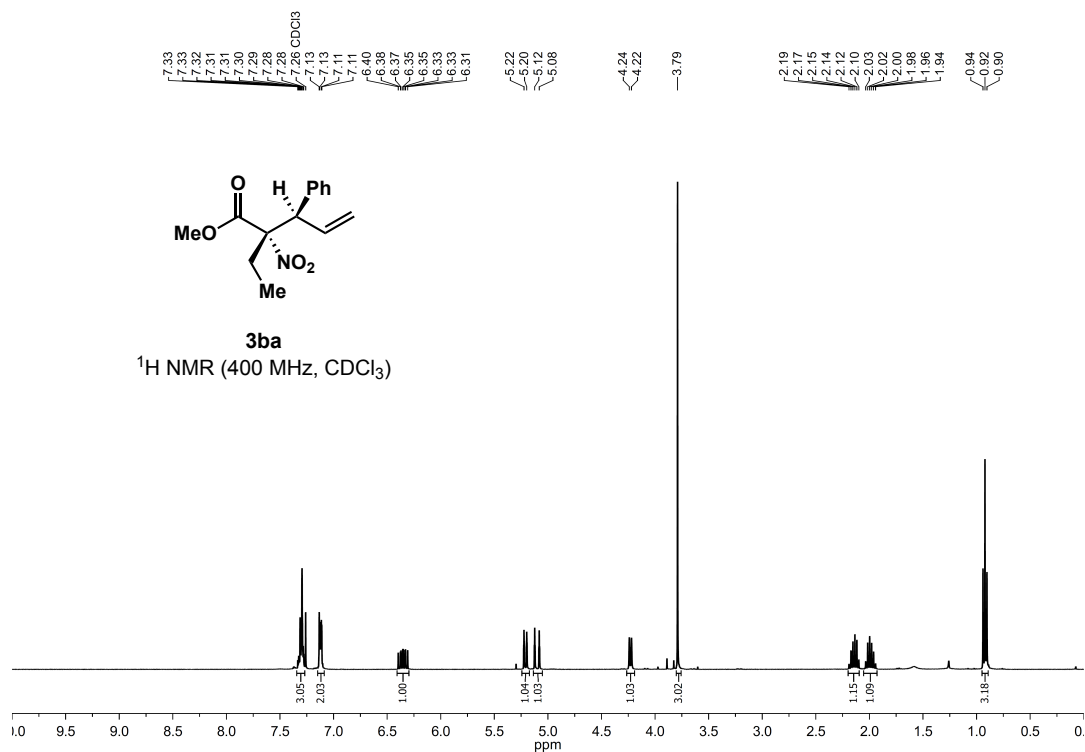


3aa

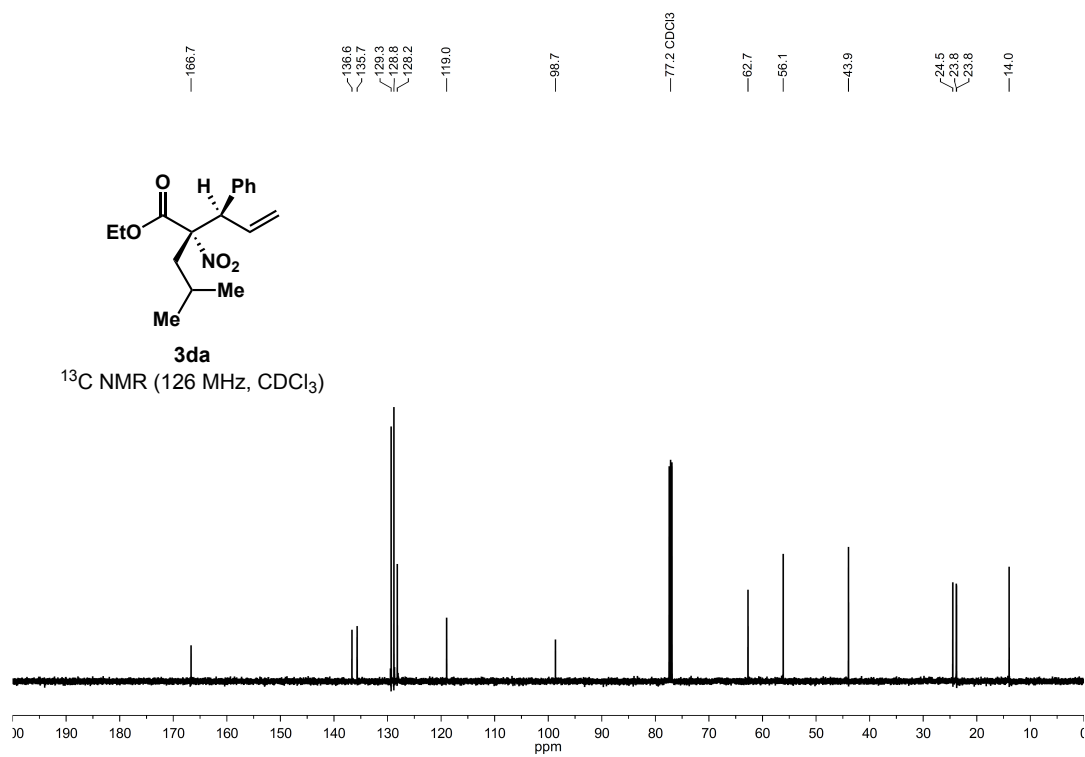
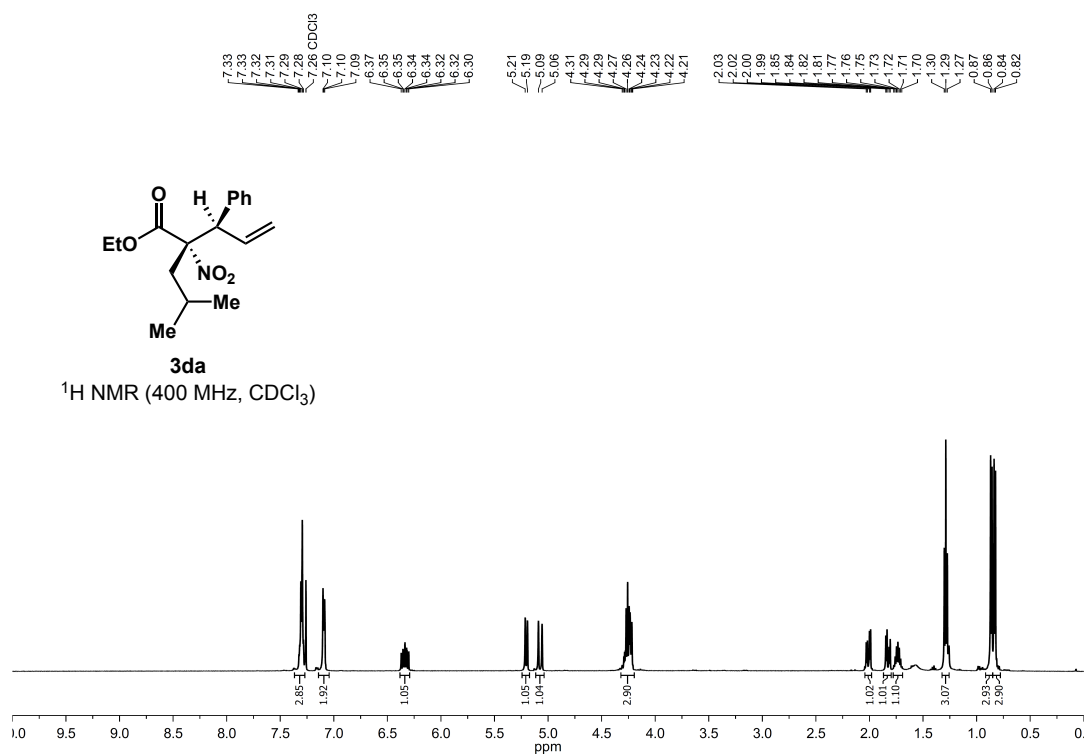
¹³C NMR (126 MHz, CDCl₃)



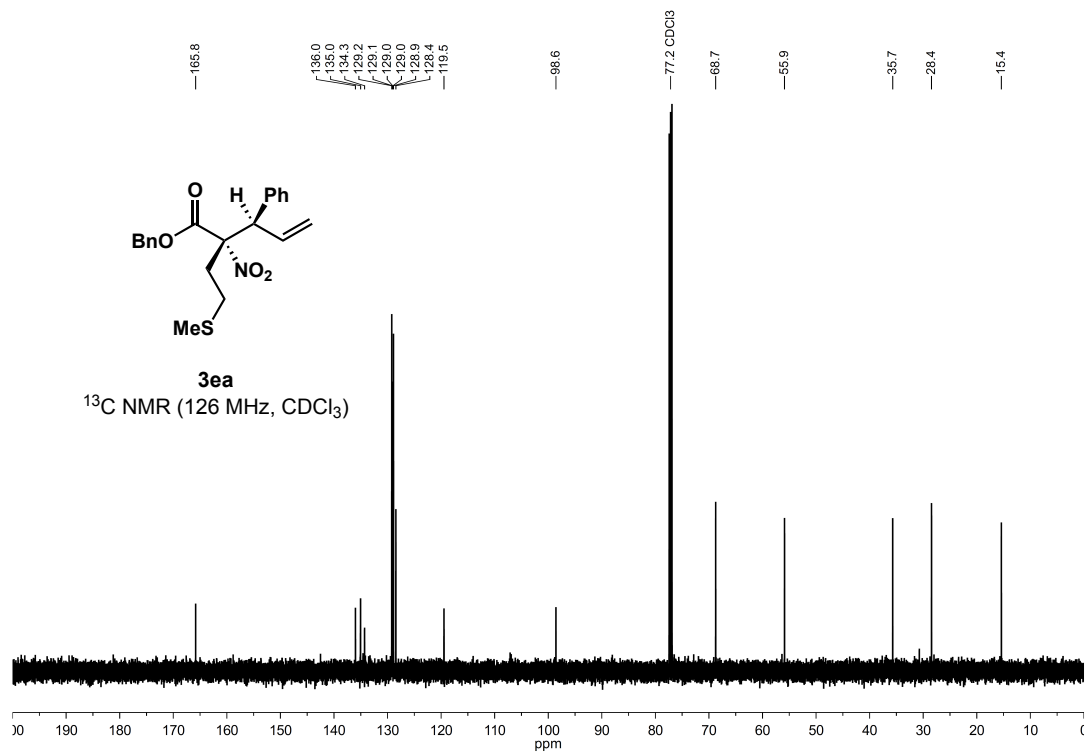
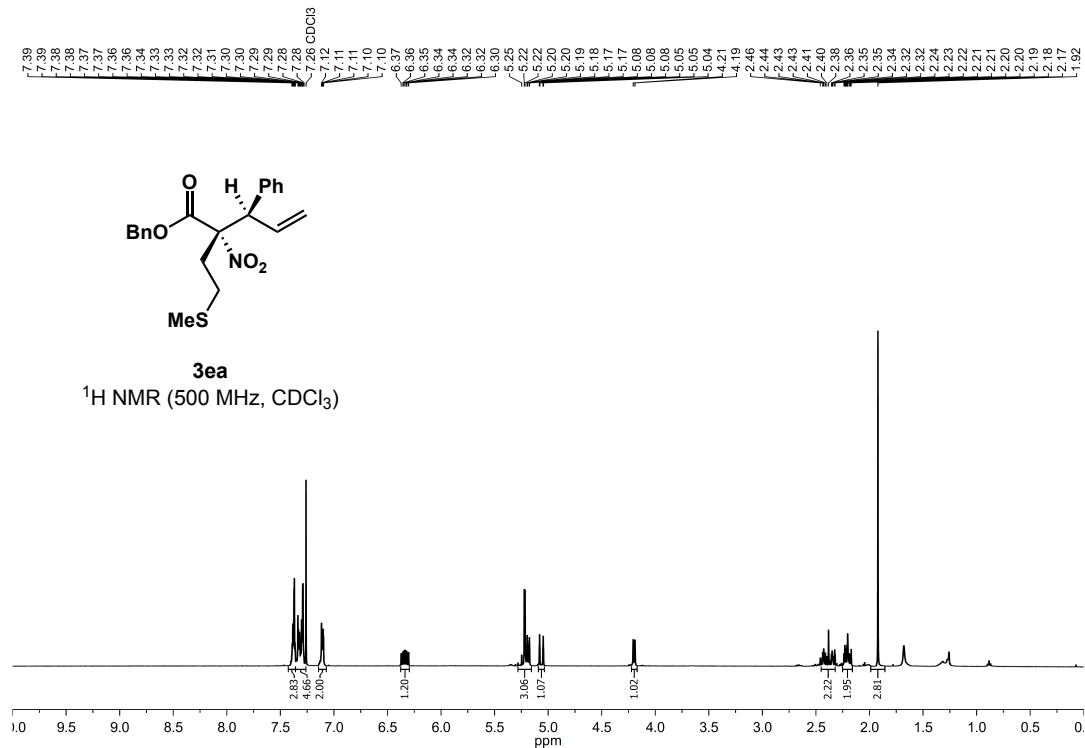
Methyl (2*S*,3*R*)-2-ethyl-2-nitro-3-phenylpent-4-enoate (**3ba**)



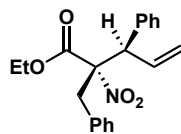
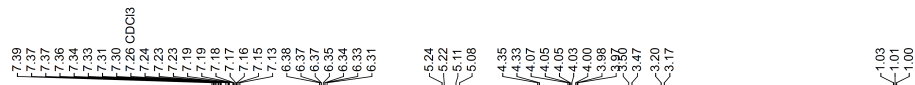
Ethyl (2*S*,3*R*)-2-isobutyl-2-nitro-3-phenylpent-4-enoate (**3da**)



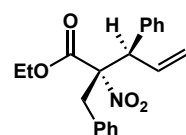
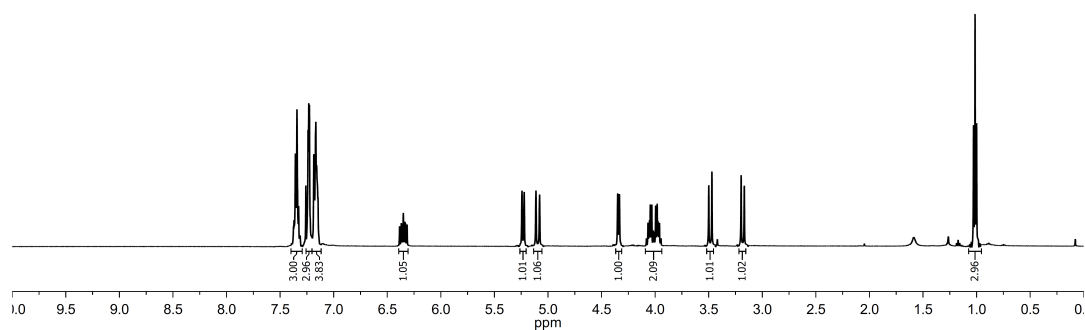
Benzyl (2*S*,3*R*)-2-(2-(methylthio)ethyl)-2-nitro-3-phenylpent-4-enoate (3ea)



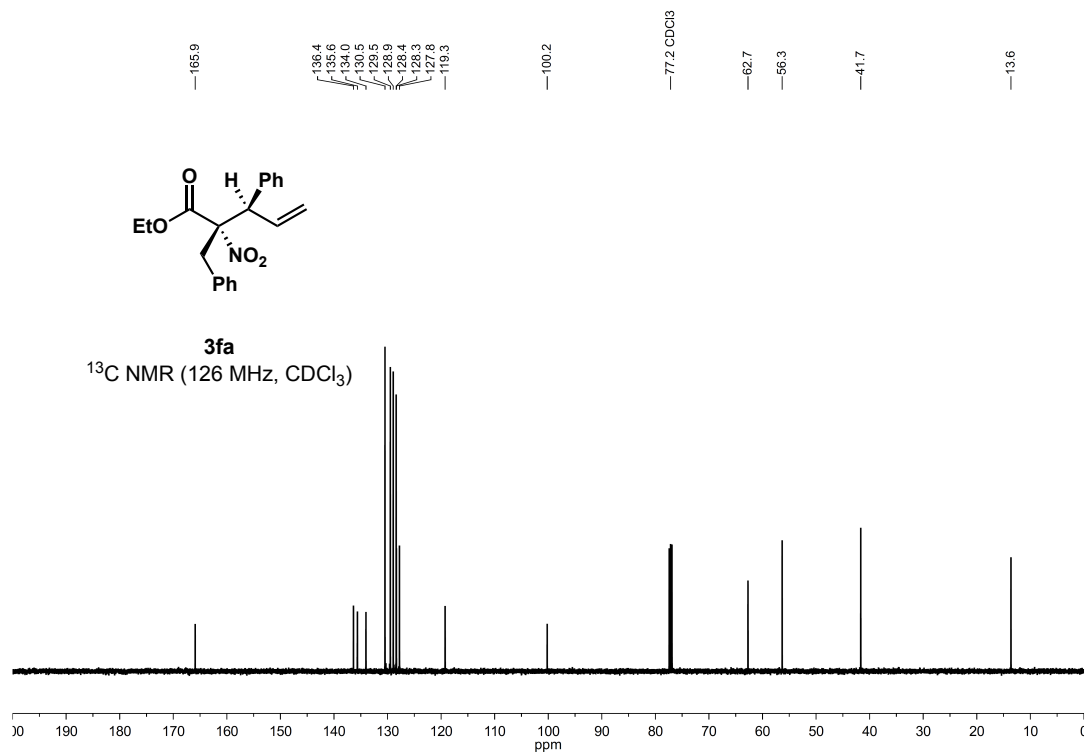
Ethyl (2*S*,3*R*)-2-benzyl-2-nitro-3-phenylpent-4-enoate (3fa)



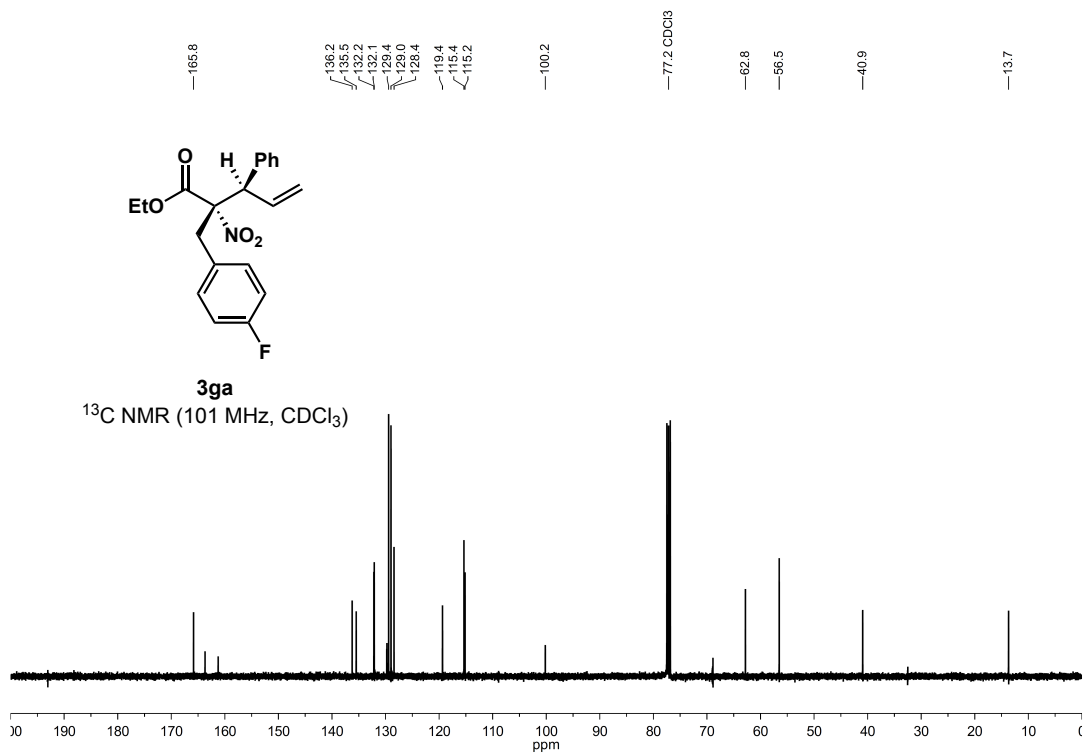
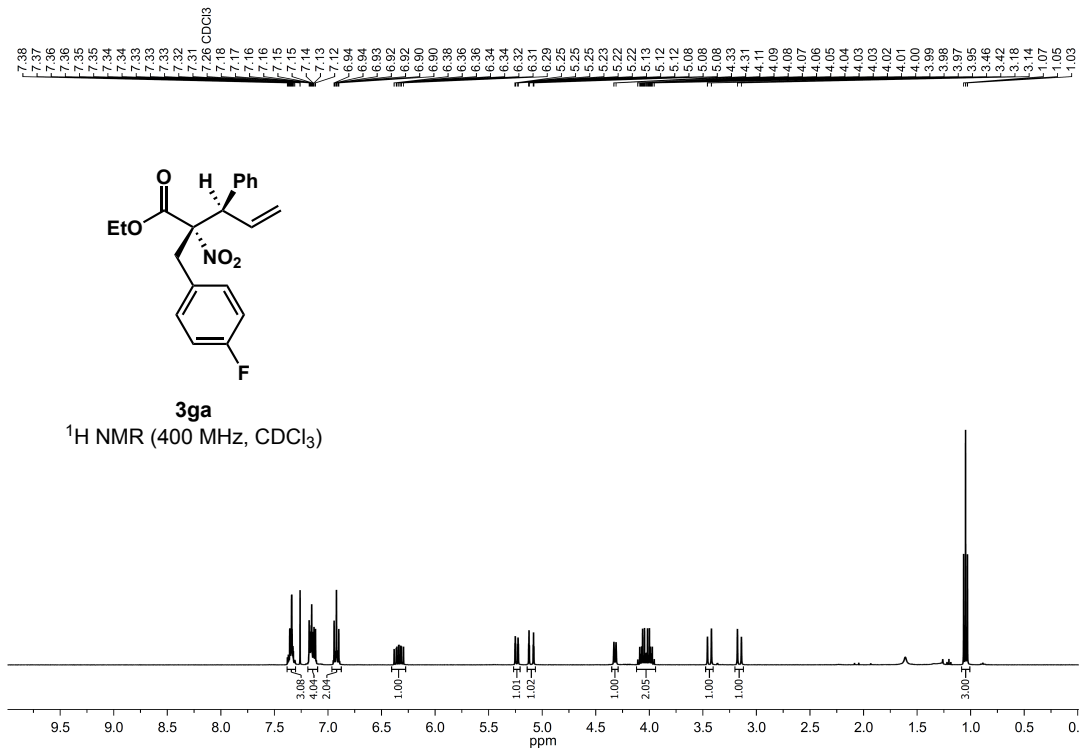
3fa
¹H NMR (500 MHz, CDCl₃)

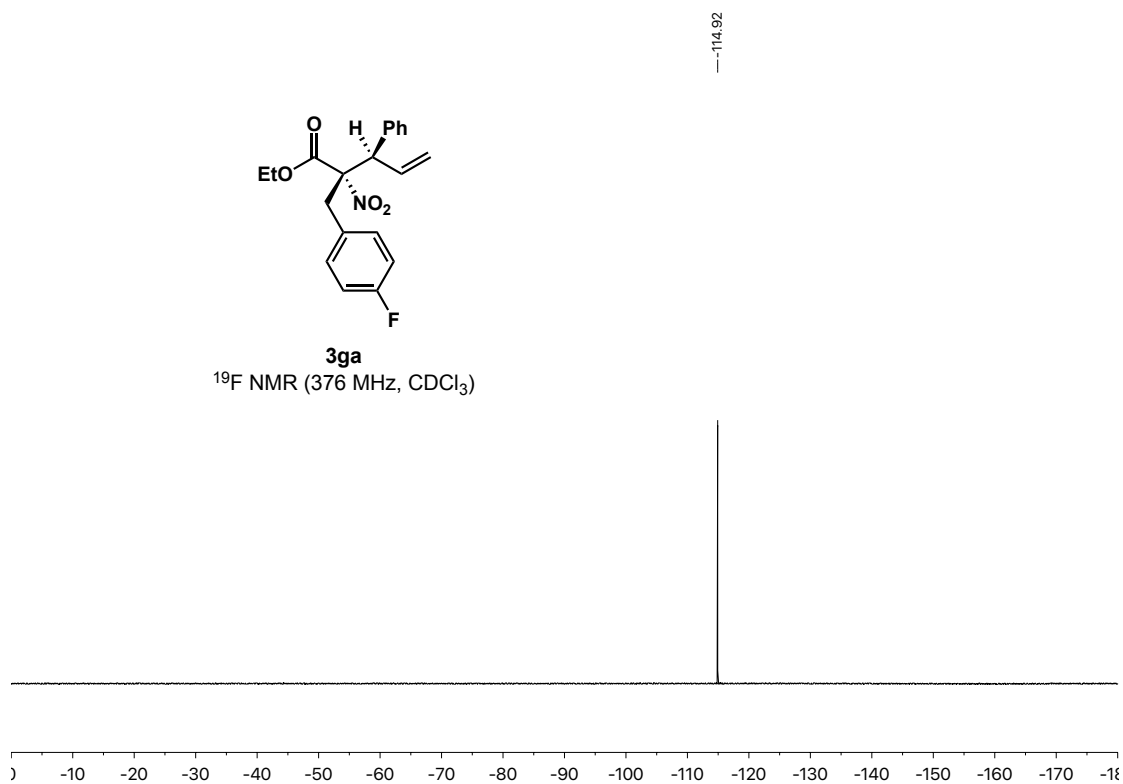


3fa
¹³C NMR (126 MHz, CDCl₃)

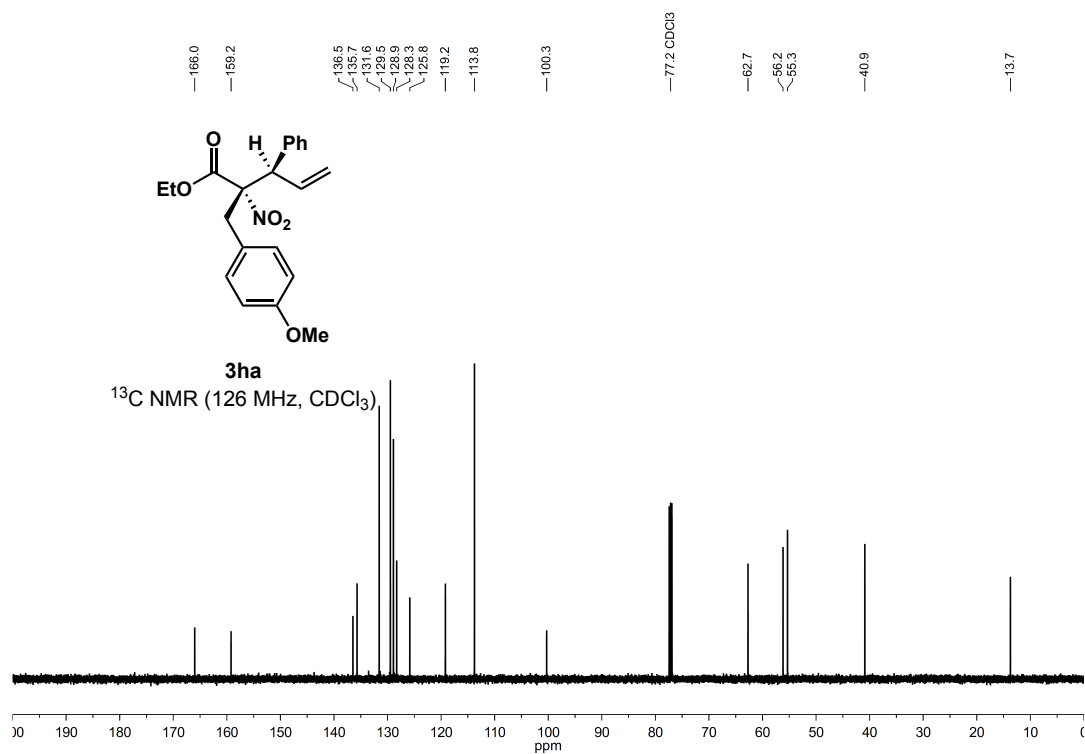
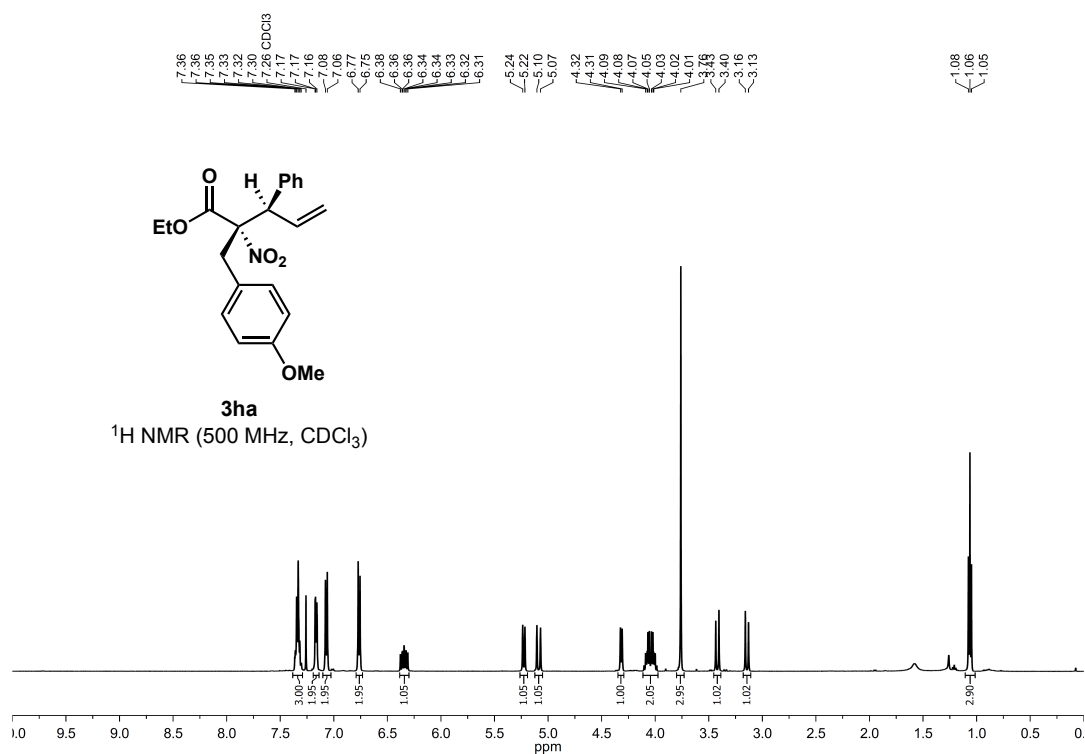


Ethyl (2*S*,3*R*)-2-(4-fluorobenzyl)-2-nitro-3-phenylpent-4-enoate (3ga)

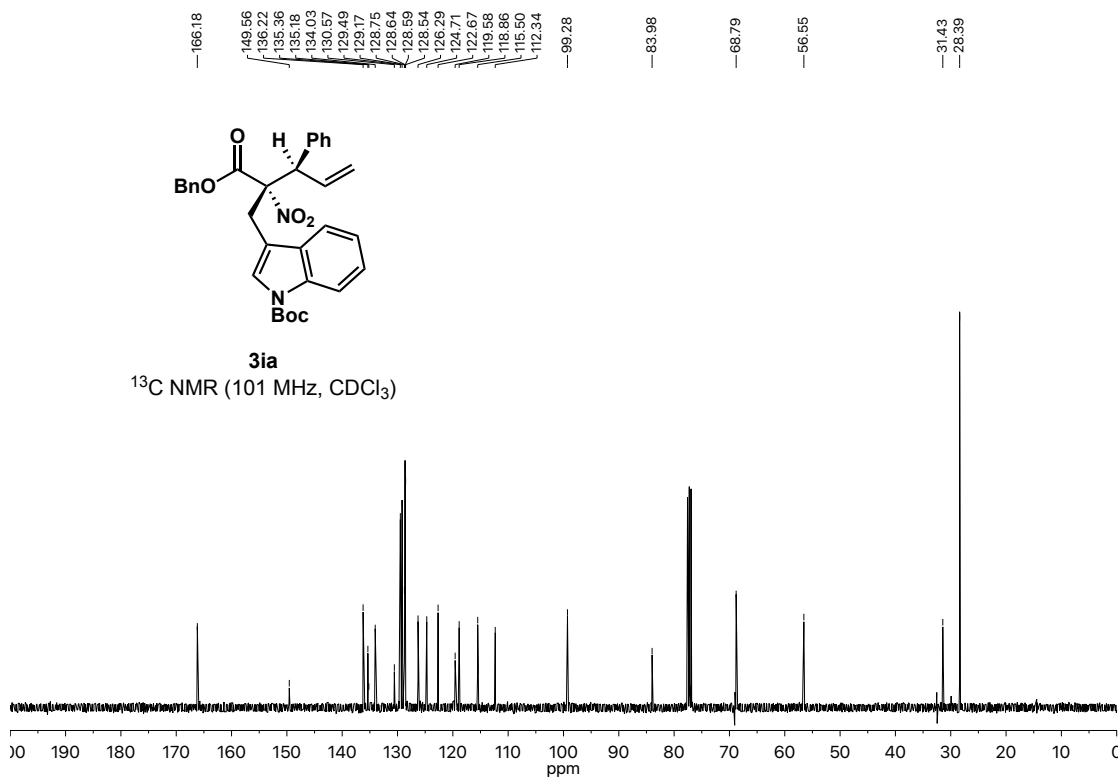
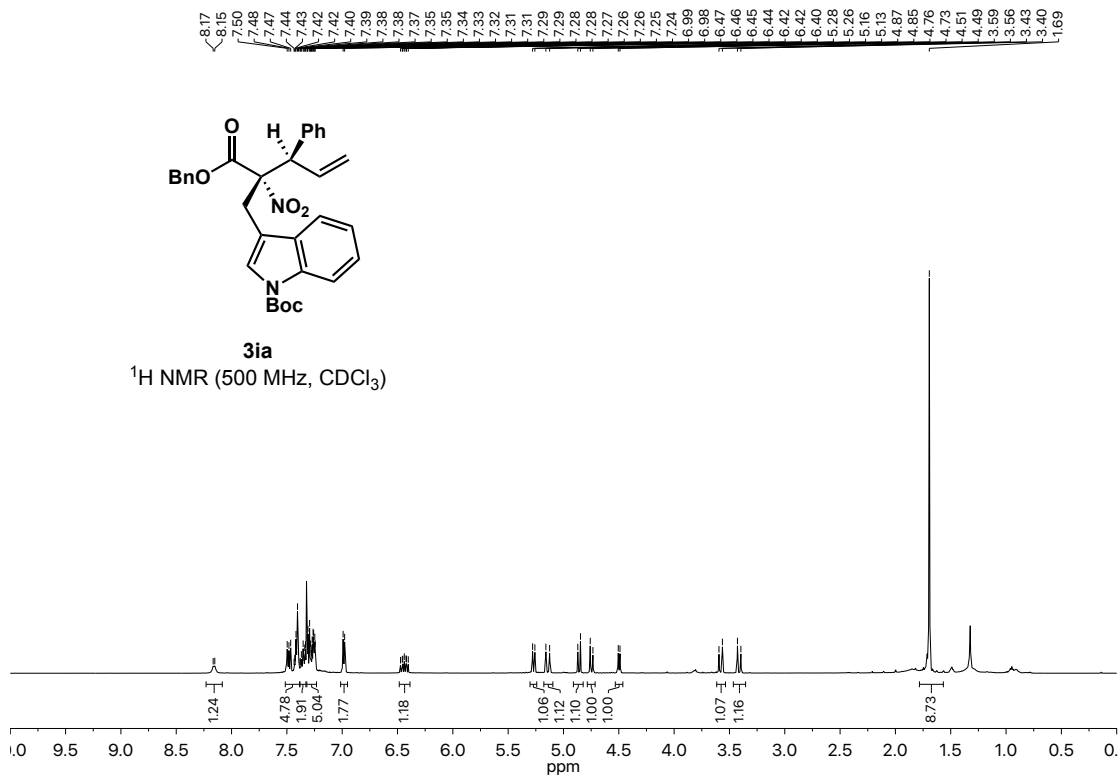




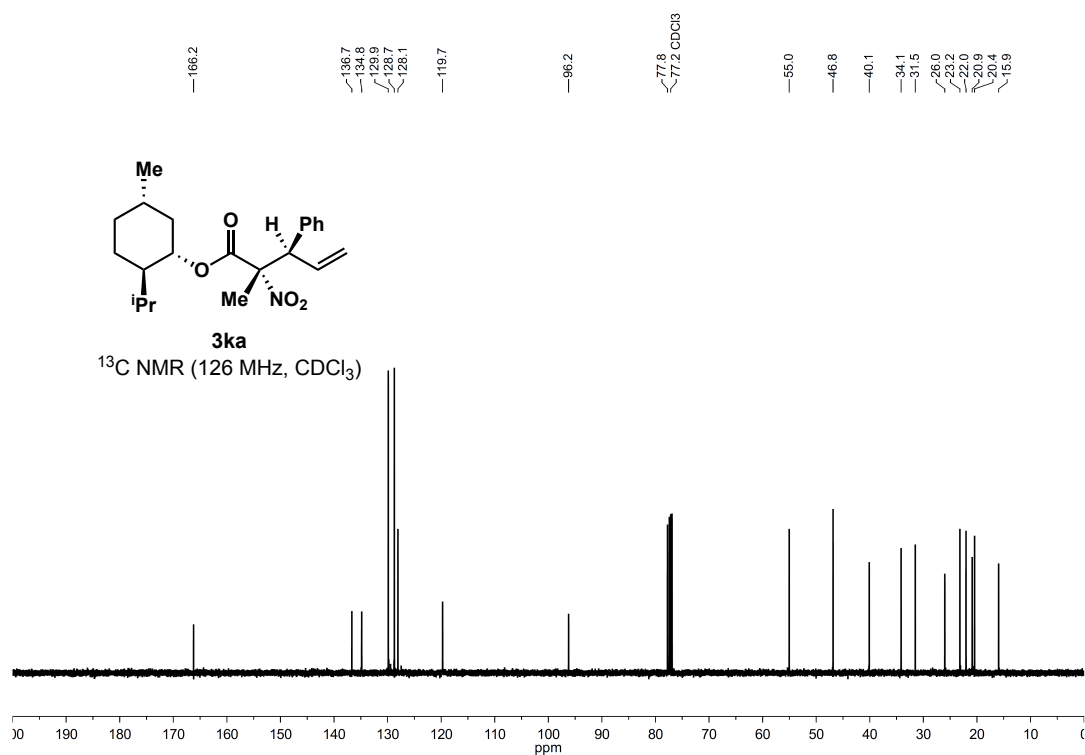
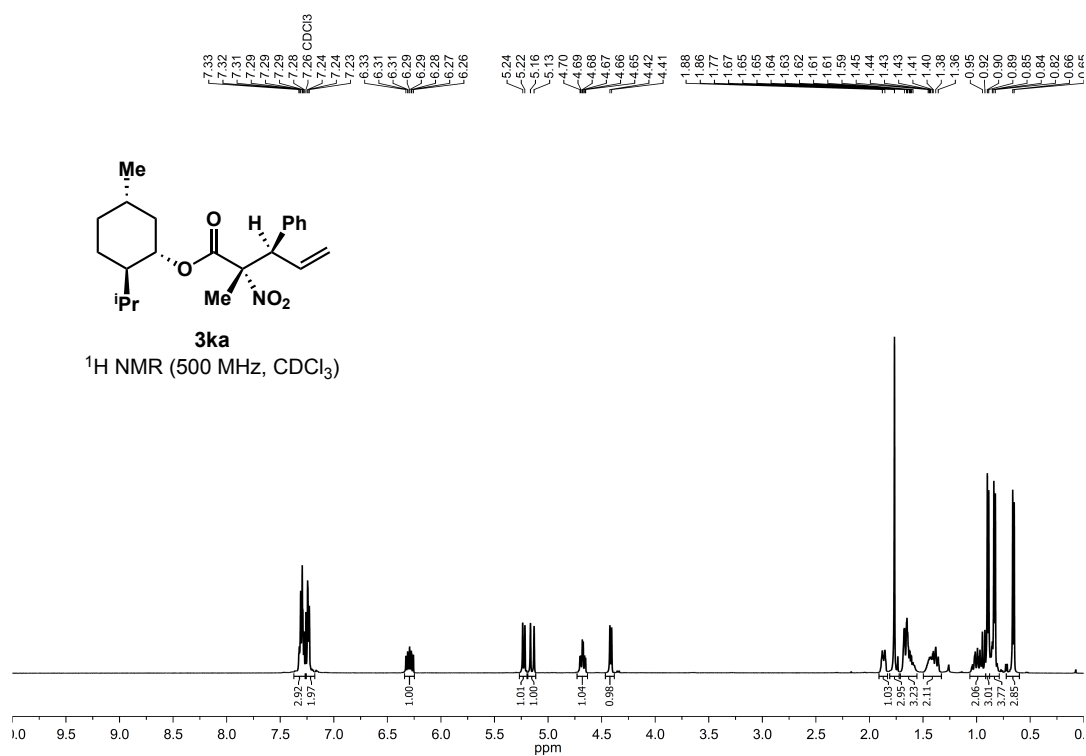
Ethyl (2*S*,3*R*)-2-(4-methoxybenzyl)-2-nitro-3-phenylpent-4-enoate (3ha)



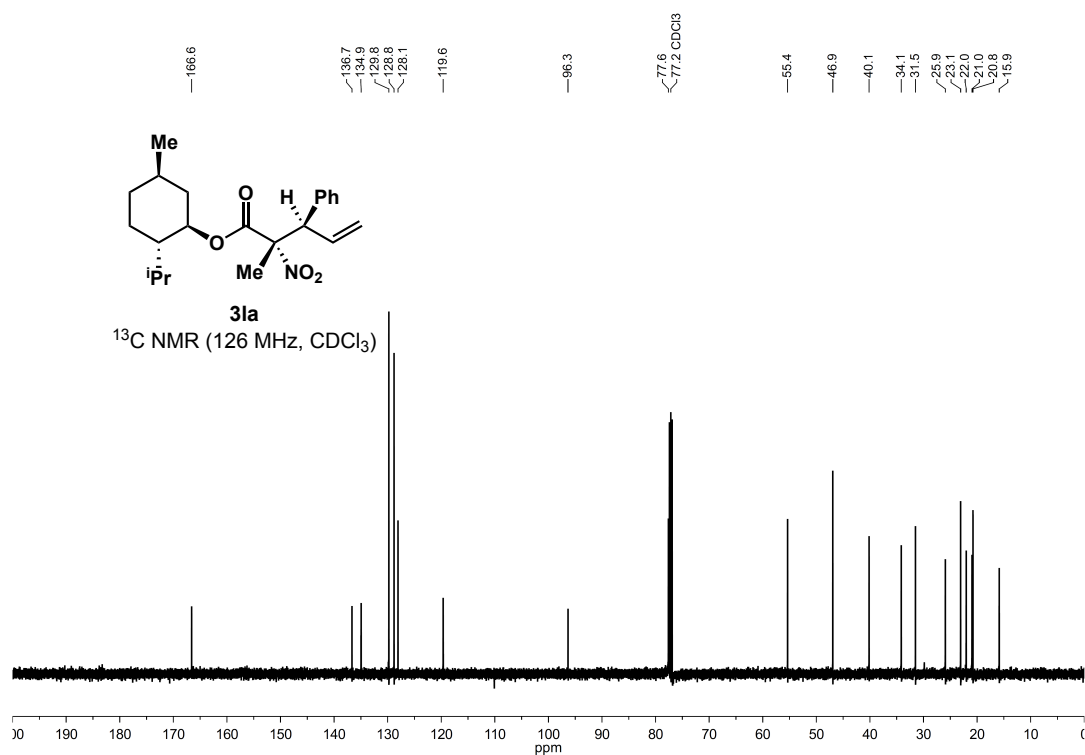
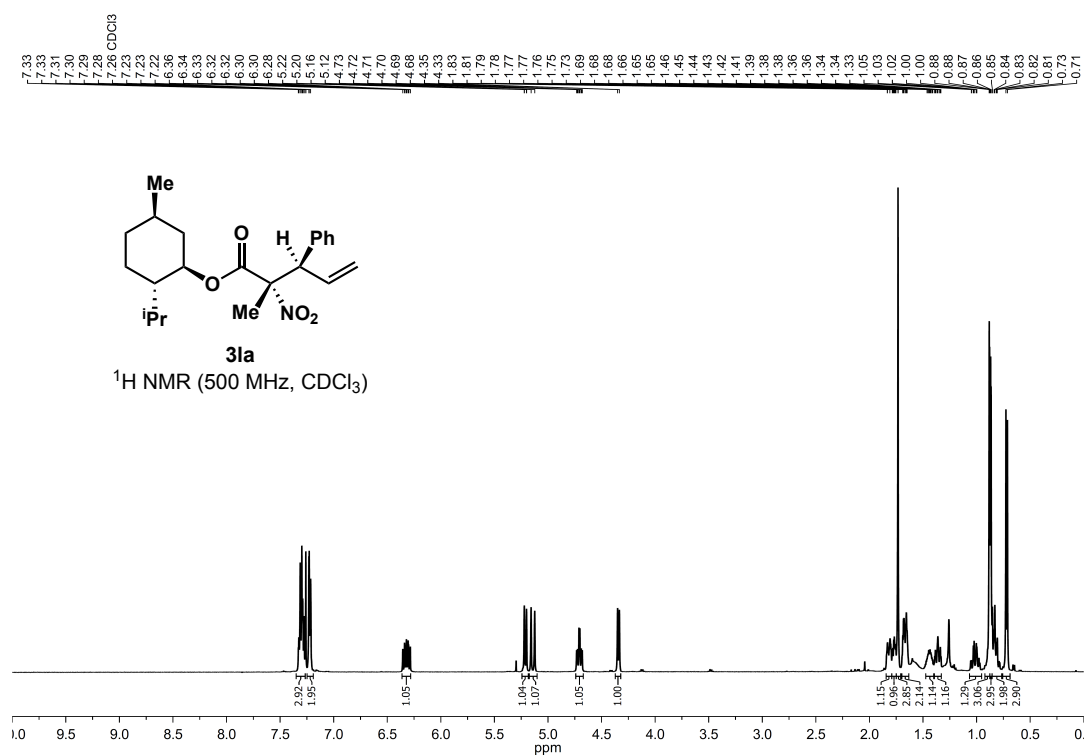
***Tert*-butyl-3-((2*S*,3*R*)-2-((benzyloxy)carbonyl)-2-nitro-3-phenylpent-4-en-1-yl)-1*H*-indole-1-carboxylate (3ia)**



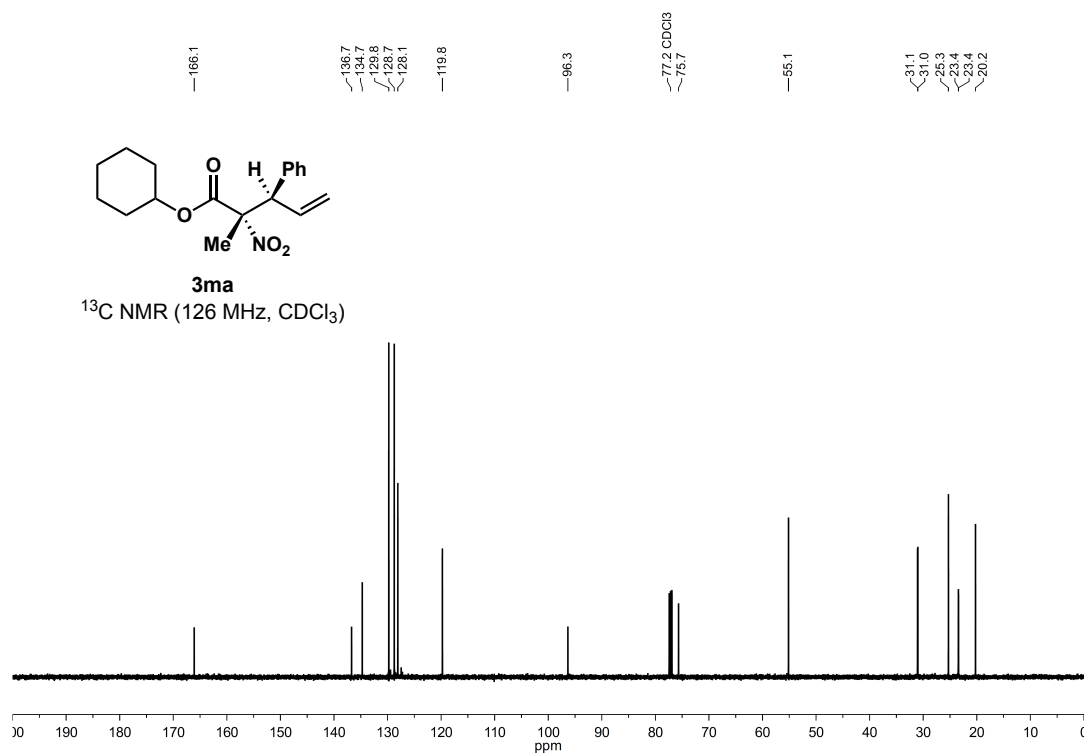
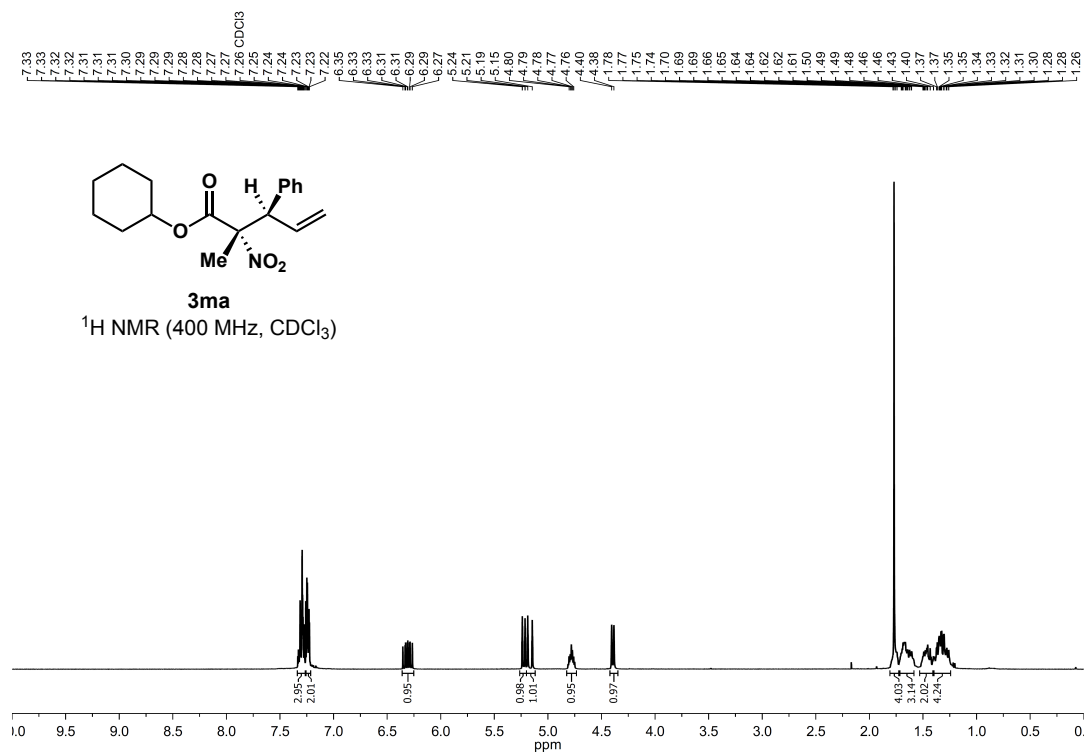
**(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate
(3ka)**



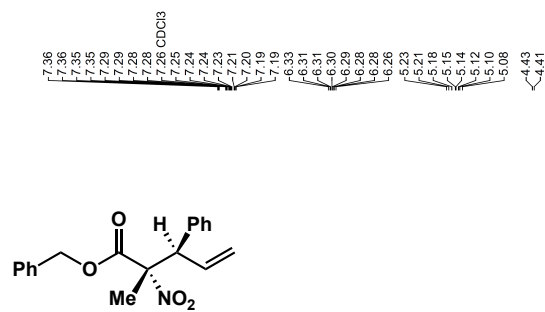
**(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate
(3la)**



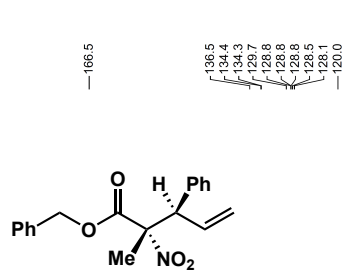
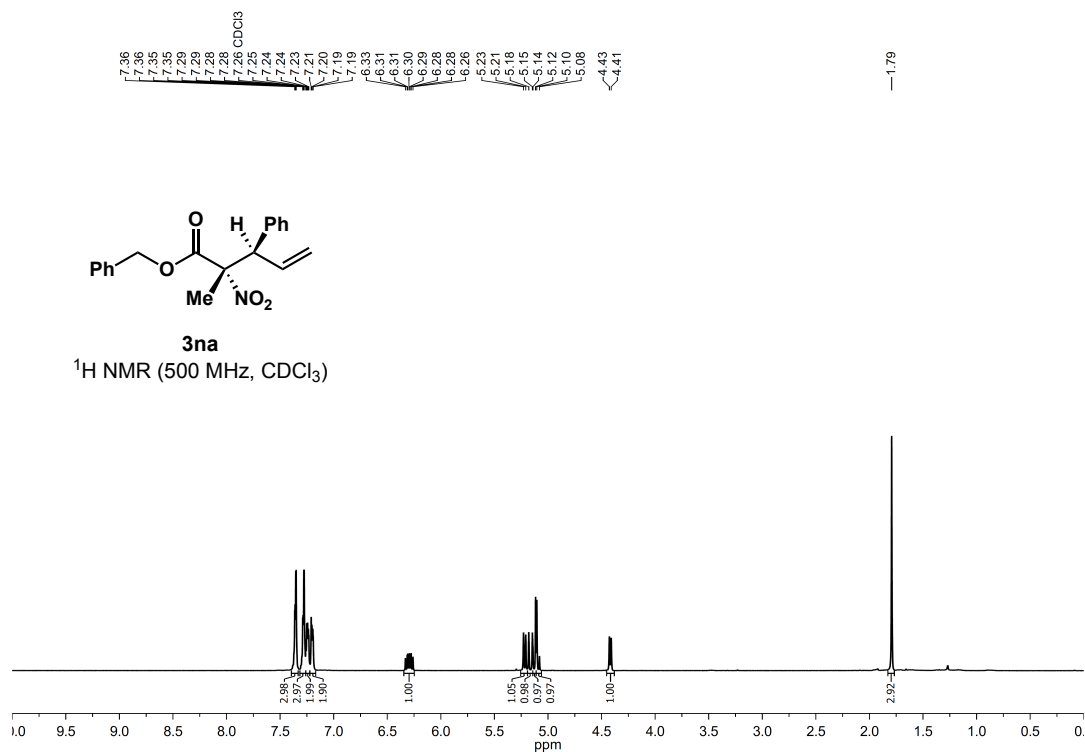
Cyclohexyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (**3ma**)



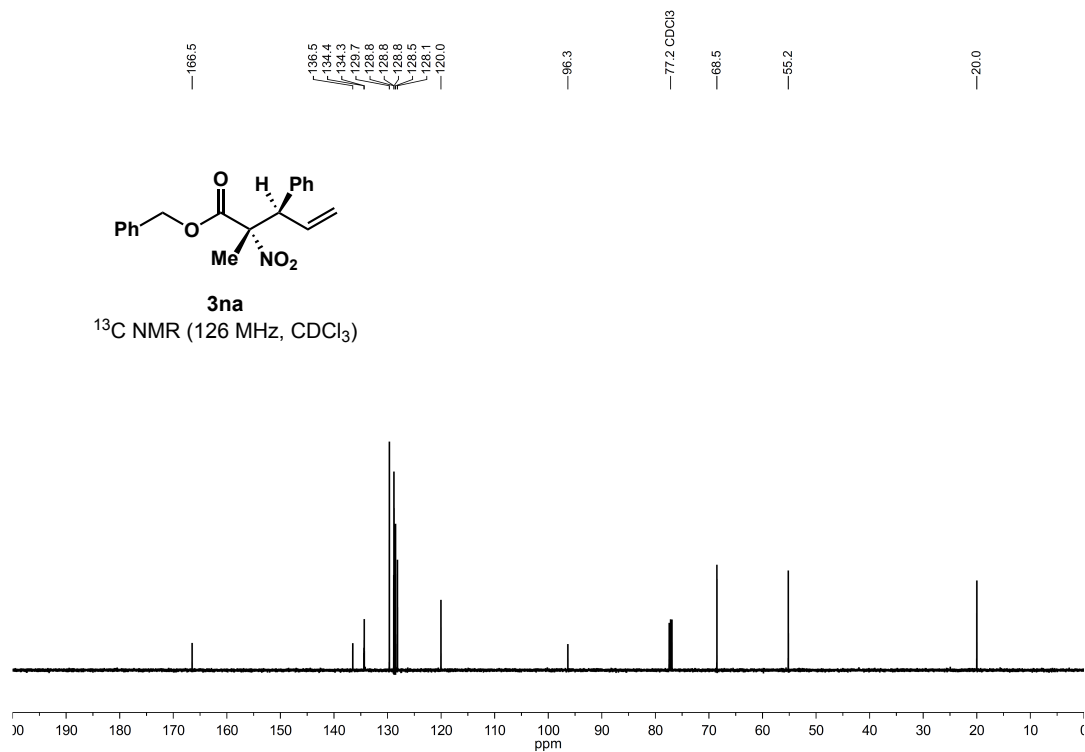
Benzyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (3na)



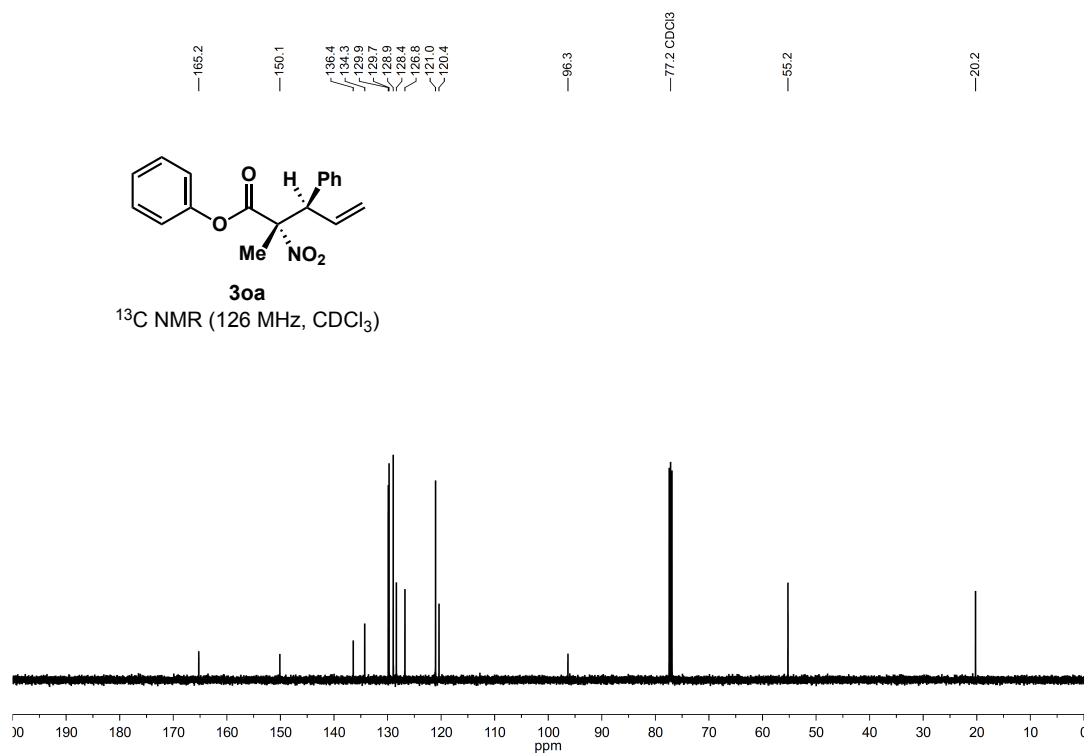
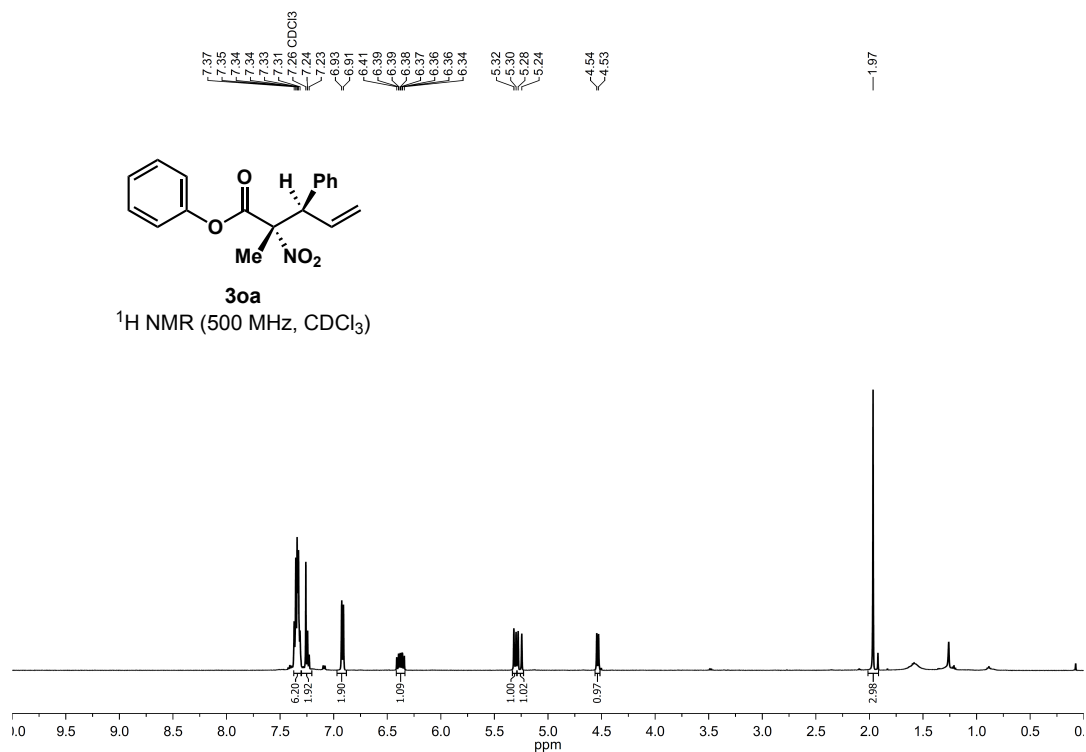
3na
¹H NMR (500 MHz, CDCl₃)



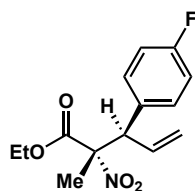
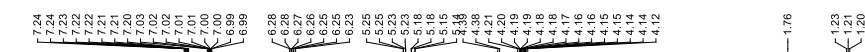
3na
¹³C NMR (126 MHz, CDCl₃)



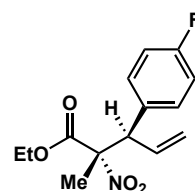
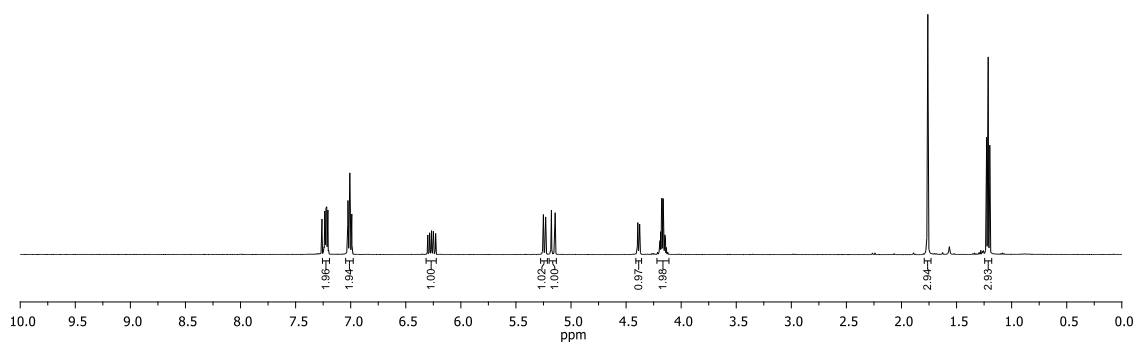
Phenyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate (**3a**)



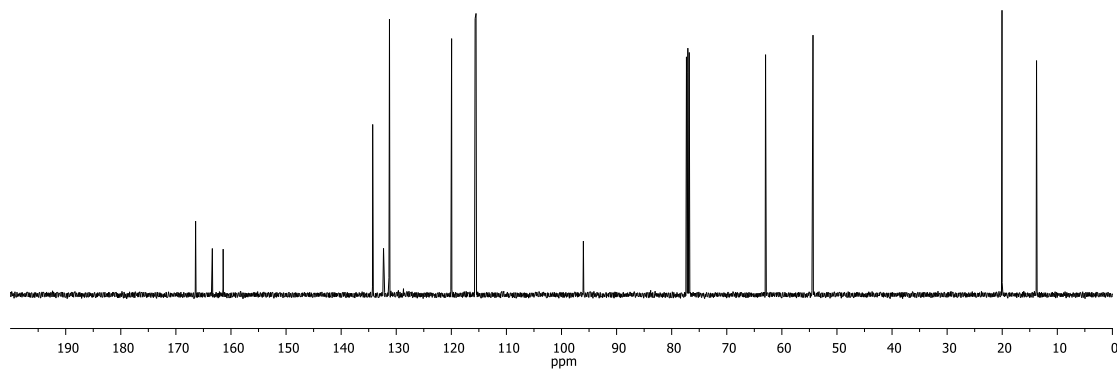
Ethyl (2*S*,3*R*)-3-(4-fluorophenyl)-2-methyl-2-nitropent-4-enoate (**3ab**)

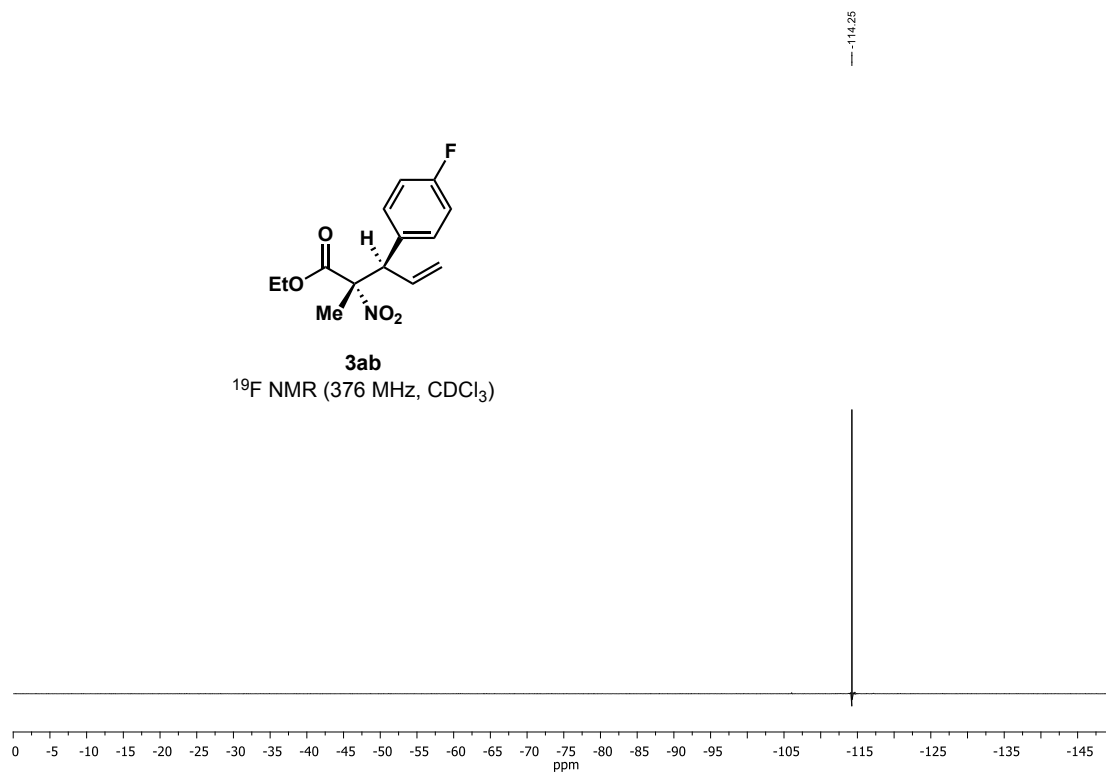


3ab
¹H NMR (500 MHz, CDCl₃)

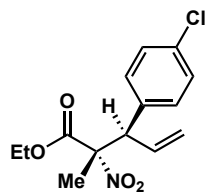


3ab
¹³C NMR (126 MHz, CDCl₃)



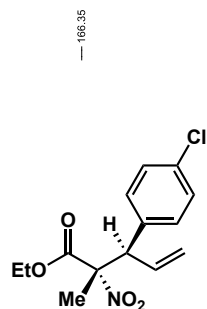
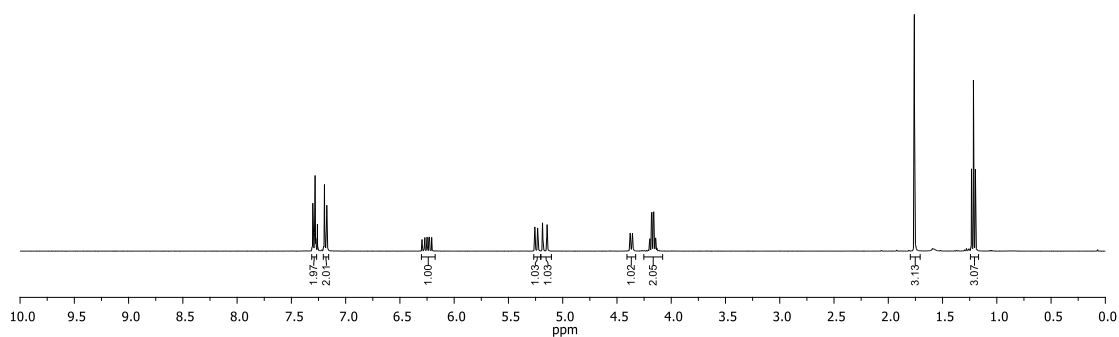


Ethyl (2*S*,3*R*)-3-(4-chlorophenyl)-2-methyl-2-nitropent-4-enoate (**3ac**)



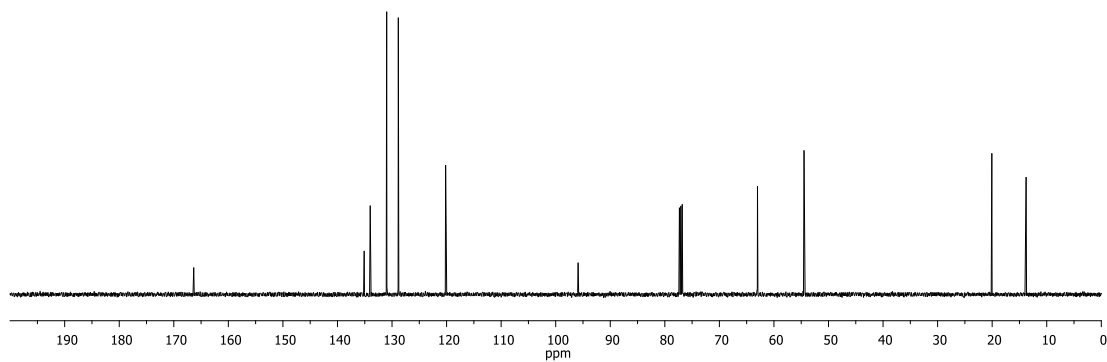
3ac

¹H NMR (400 MHz, CDCl₃)

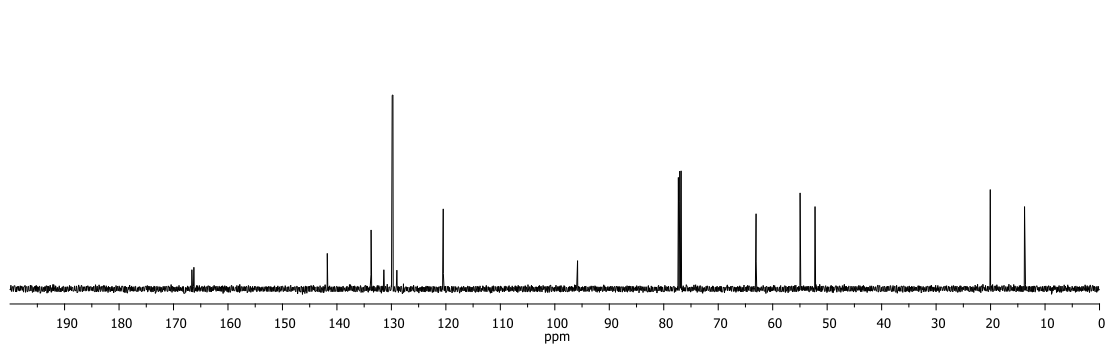
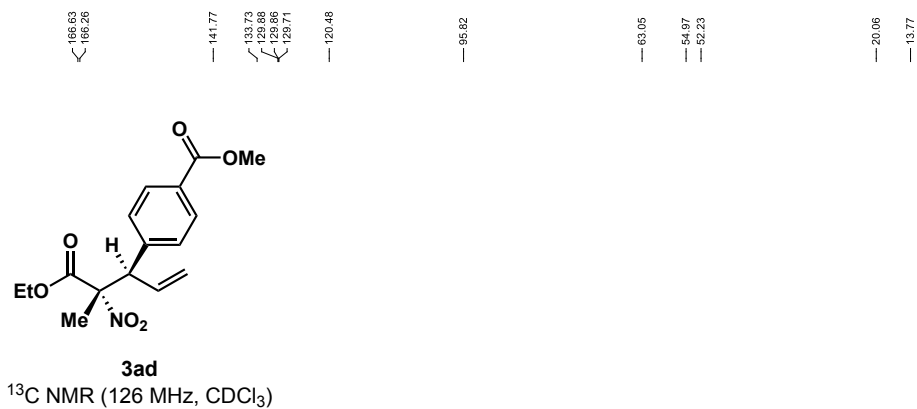
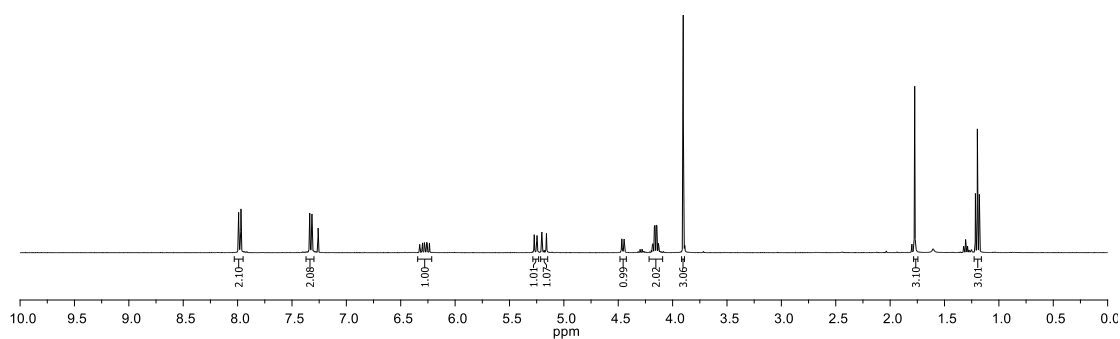
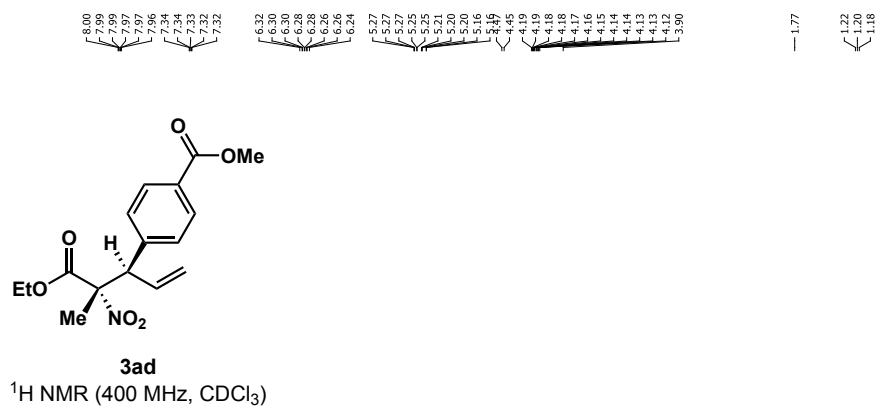


3ac

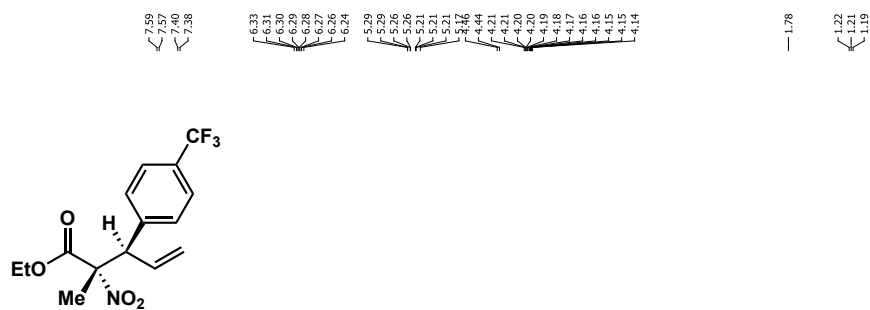
¹³C NMR (126 MHz, CDCl₃)



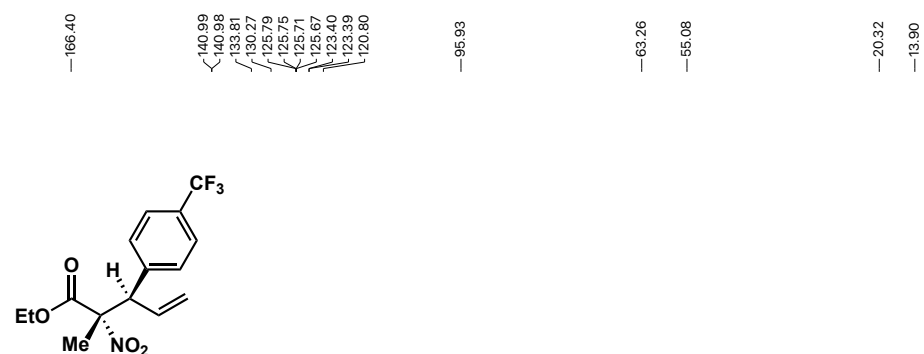
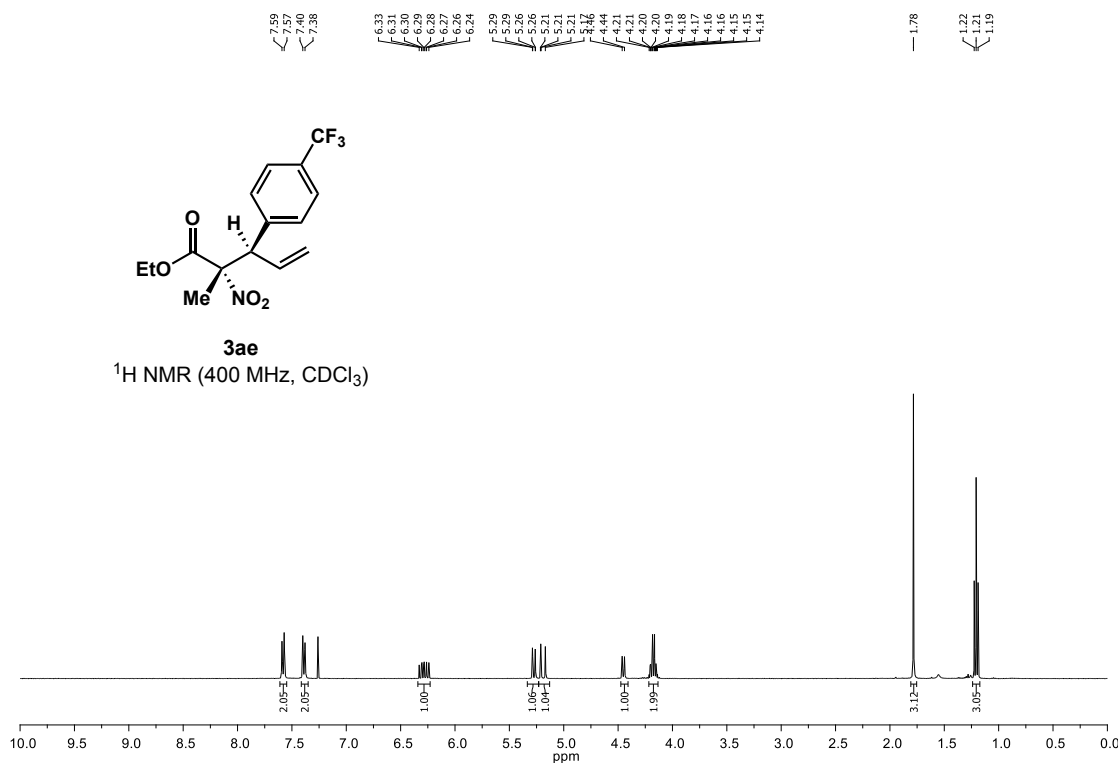
Methyl 4-((3*R*,4*S*)-5-ethoxy-4-methyl-4-nitro-5-oxopent-1-en-3-yl)benzoate (**3ad**)



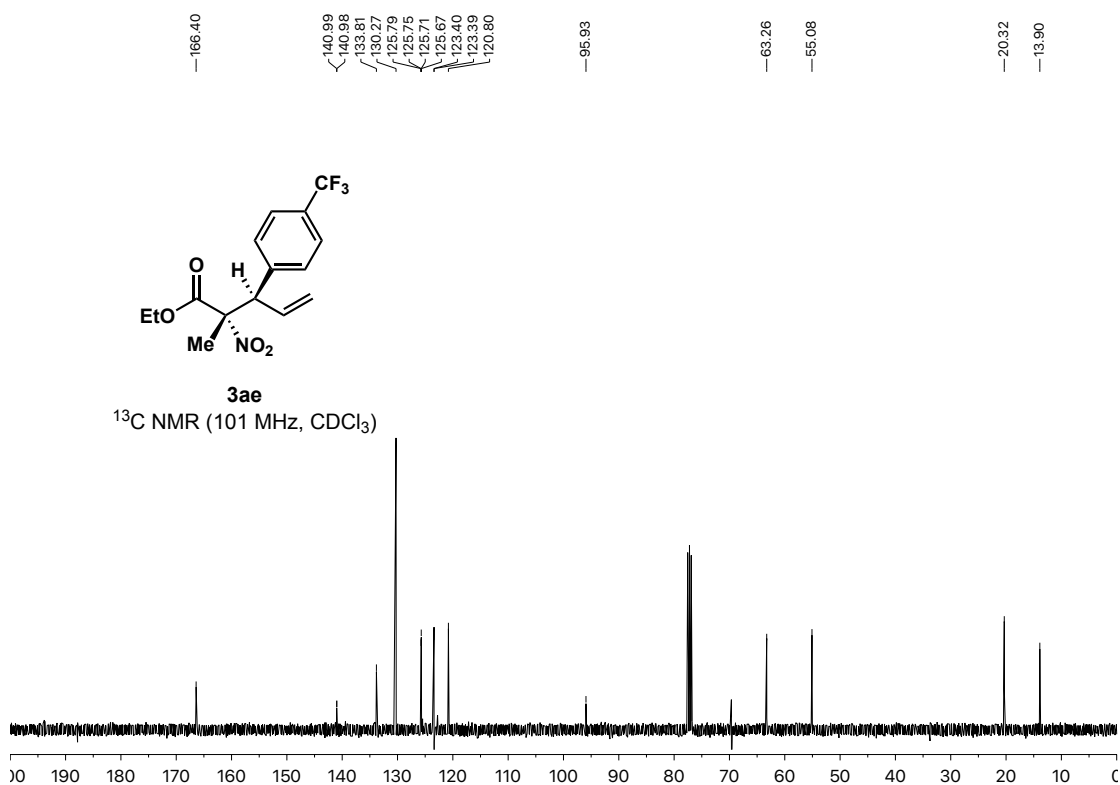
Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(4-(trifluoromethyl)phenyl)pent-4-enoate (3ae)

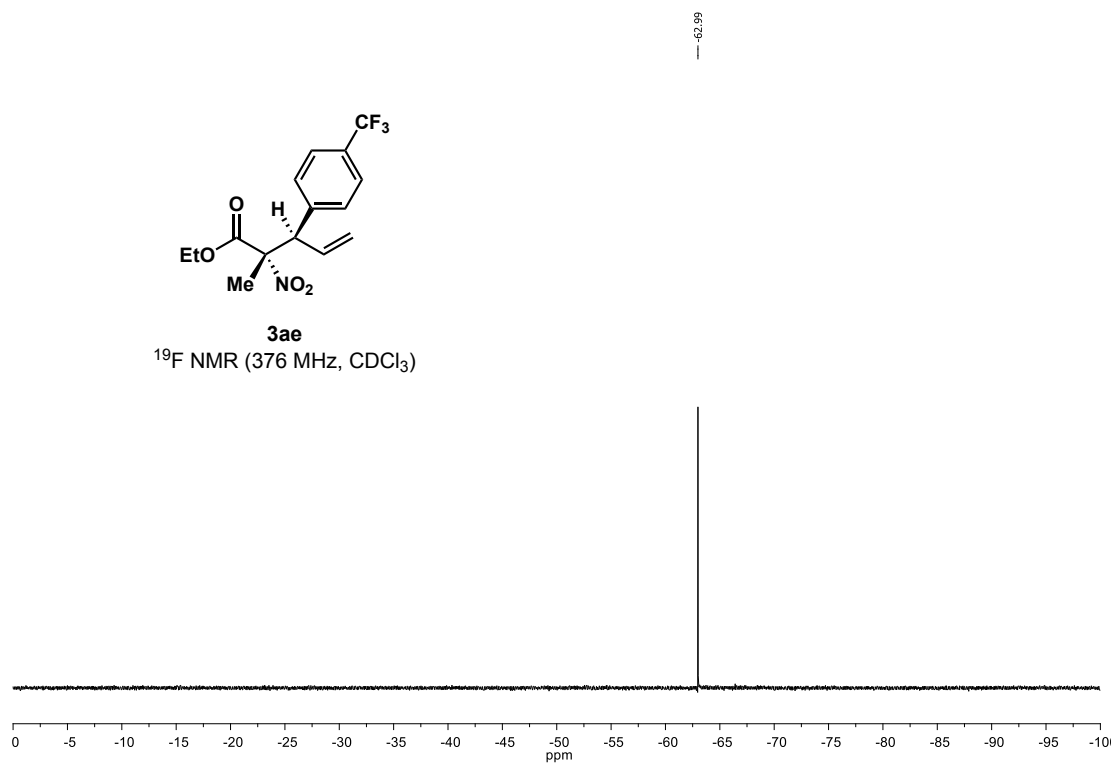


3ae
¹H NMR (400 MHz, CDCl₃)

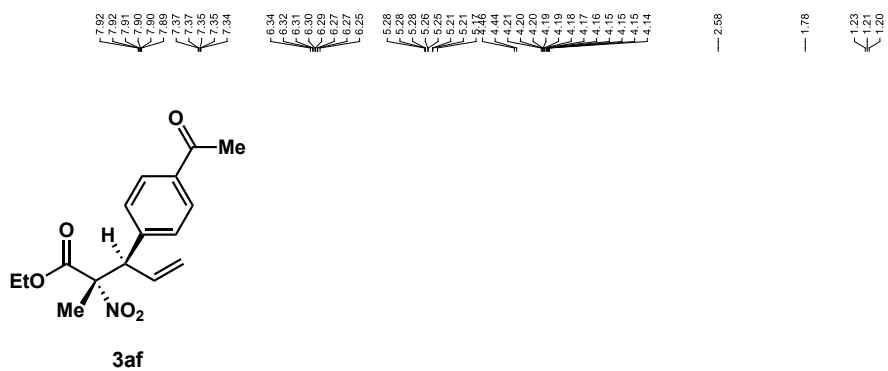


3ae
¹³C NMR (101 MHz, CDCl₃)

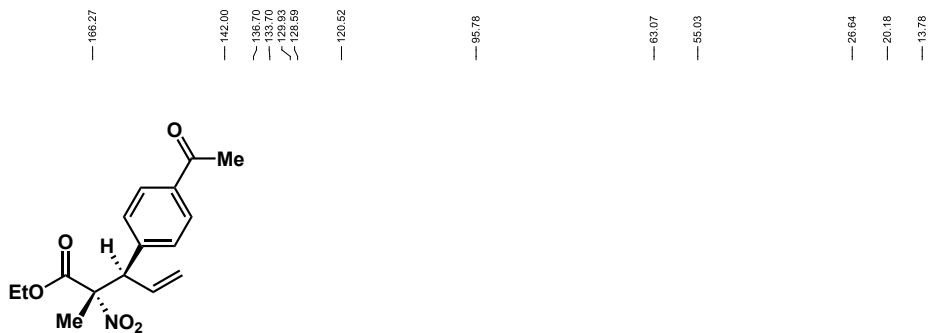
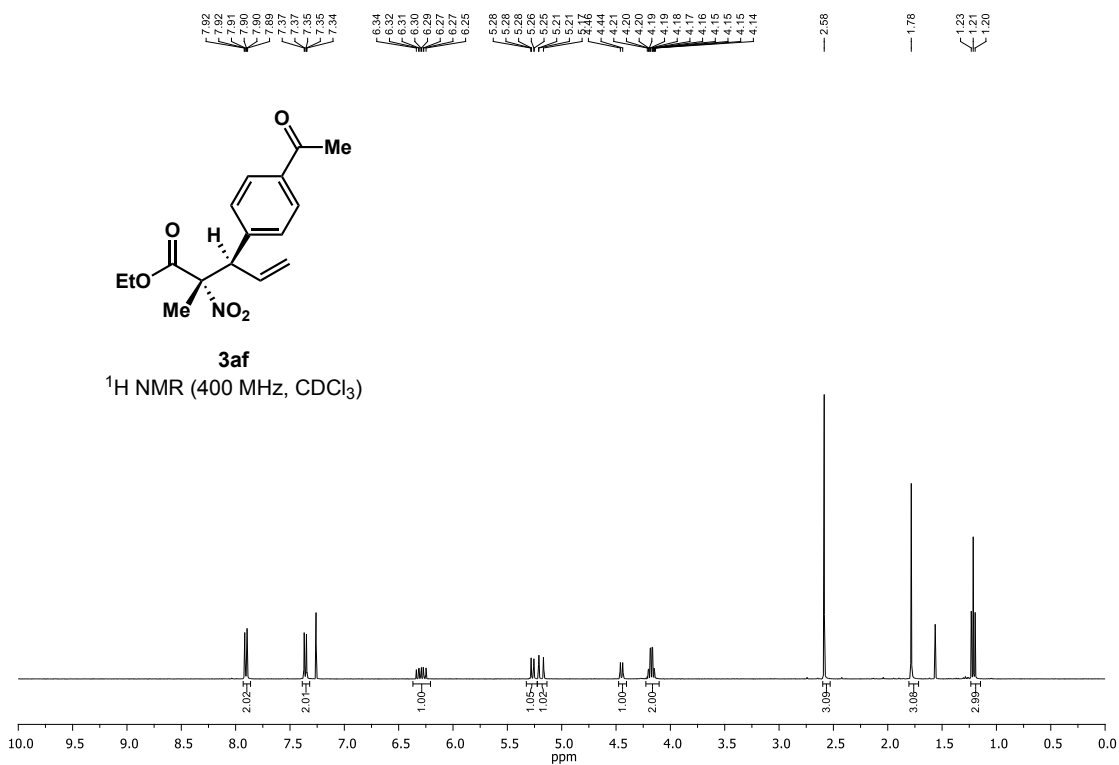




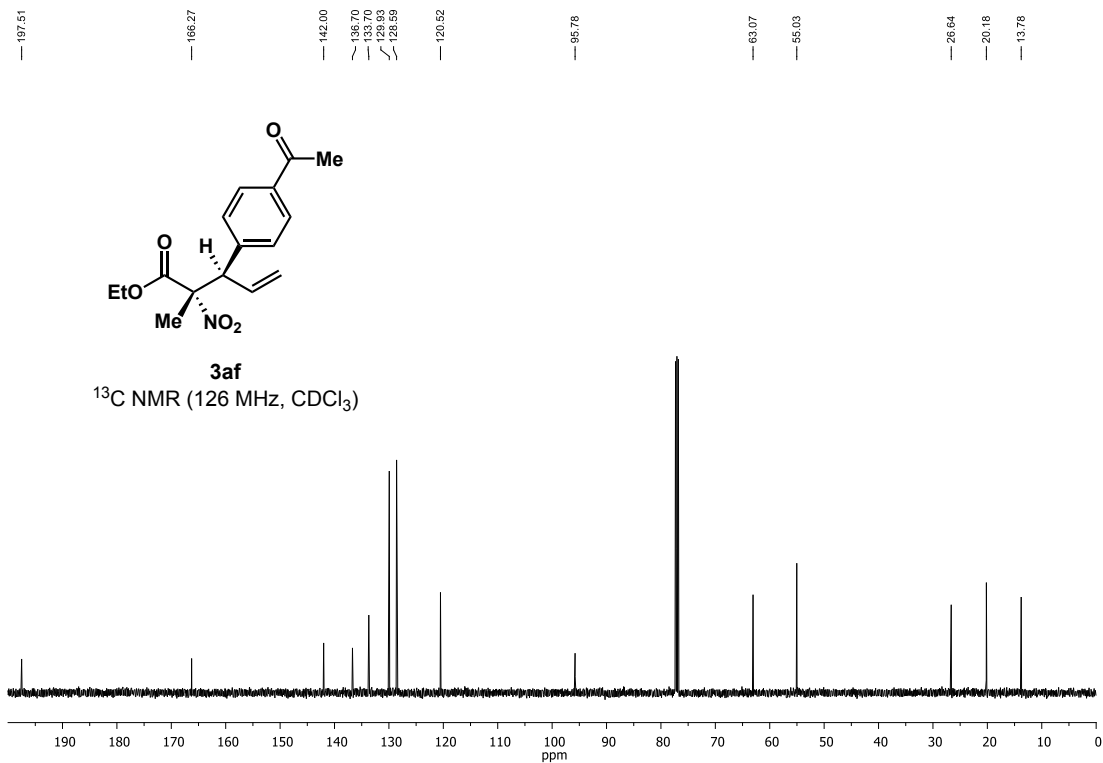
Ethyl (2*S*,3*R*)-3-(4-acetylphenyl)-2-methyl-2-nitropent-4-enoate (3af)



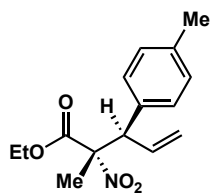
¹H NMR (400 MHz, CDCl₃)



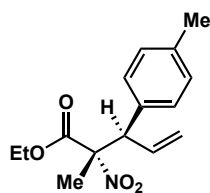
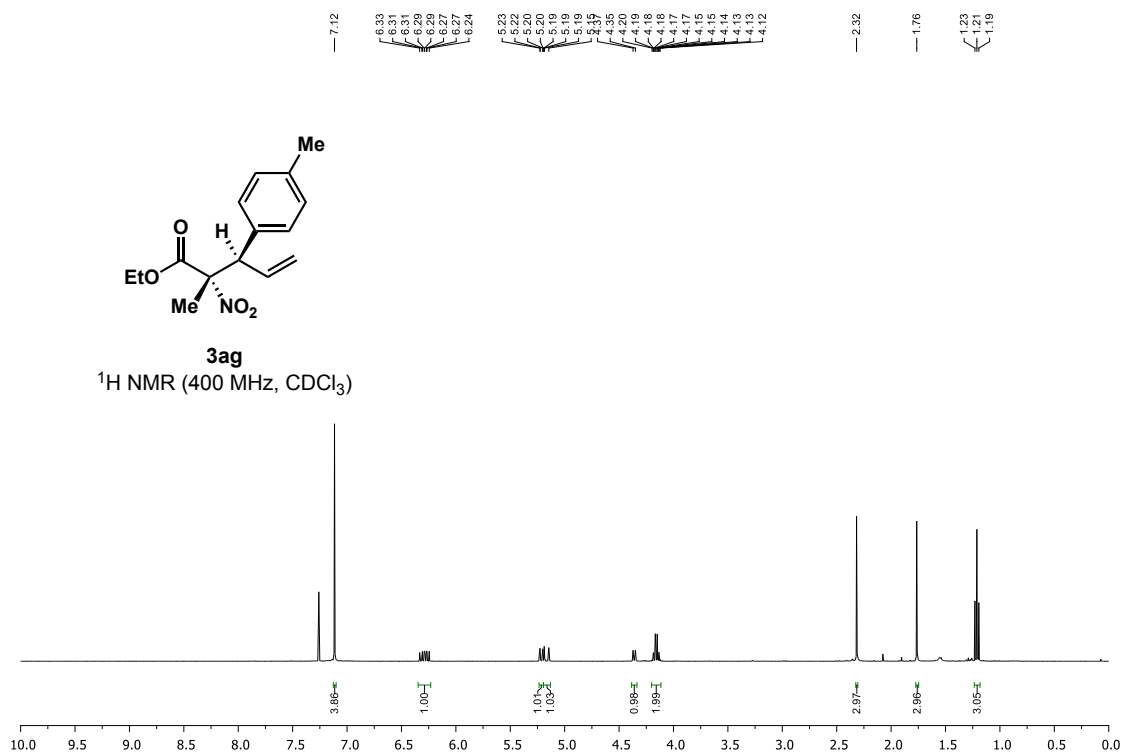
¹³C NMR (126 MHz, CDCl₃)



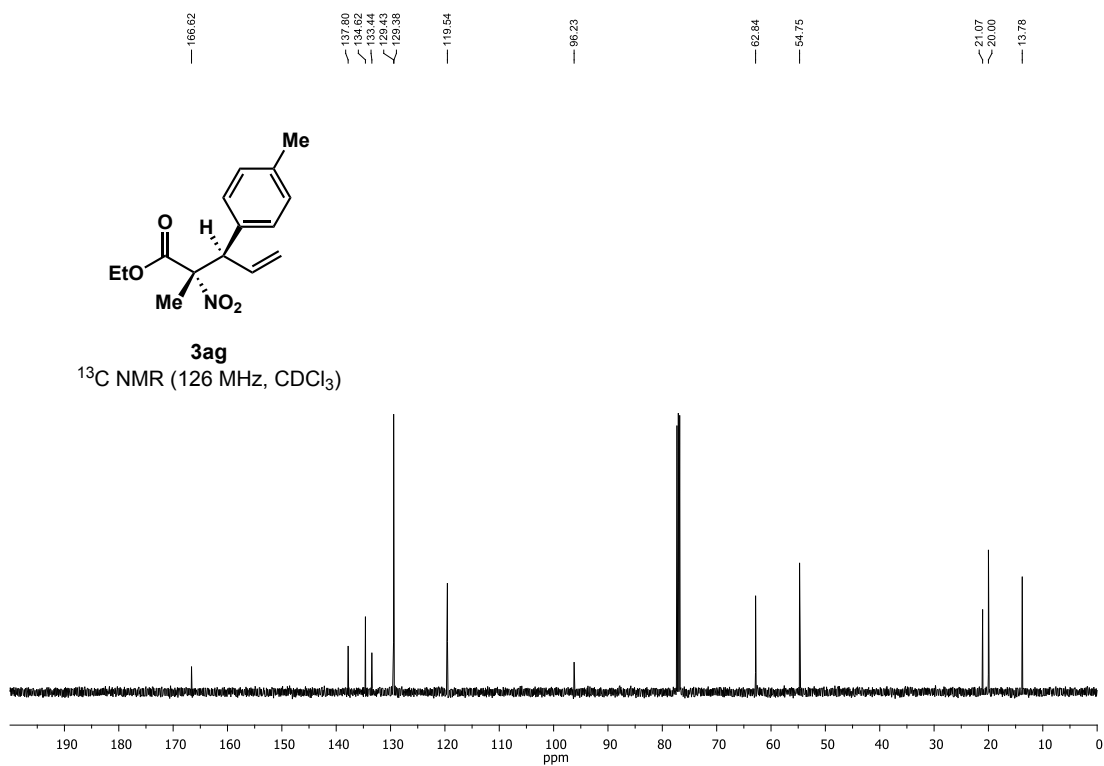
Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(*p*-tolyl)pent-4-enoate (**3ag**)



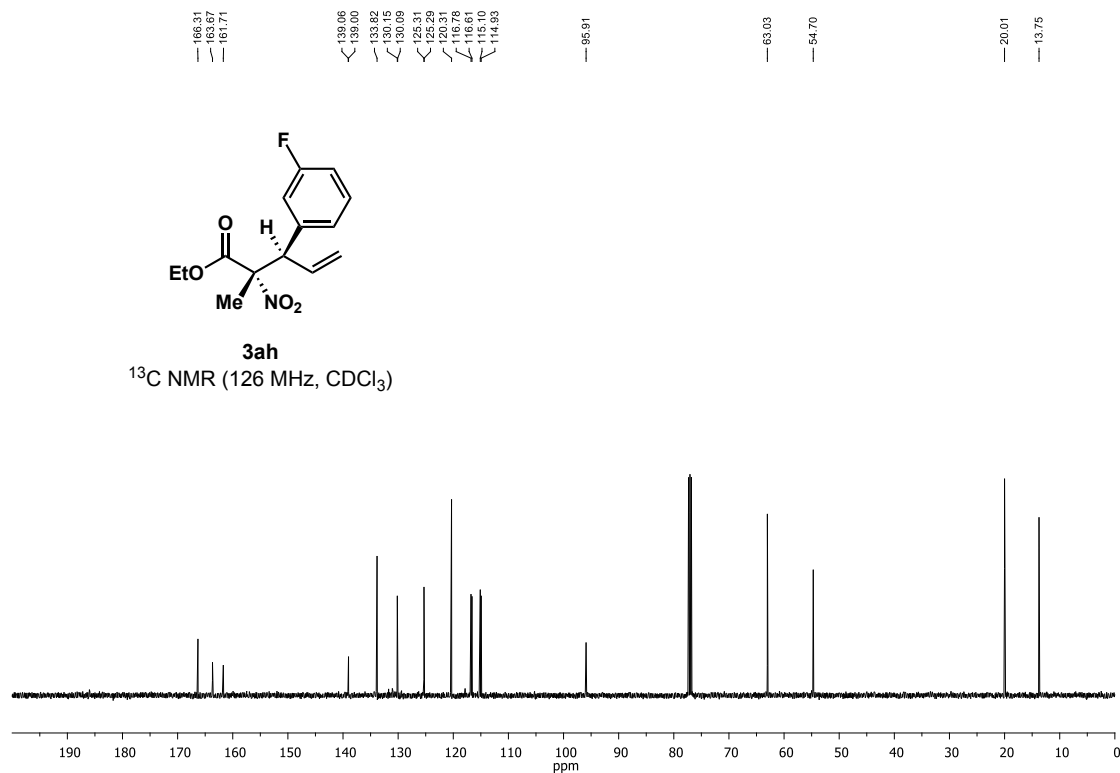
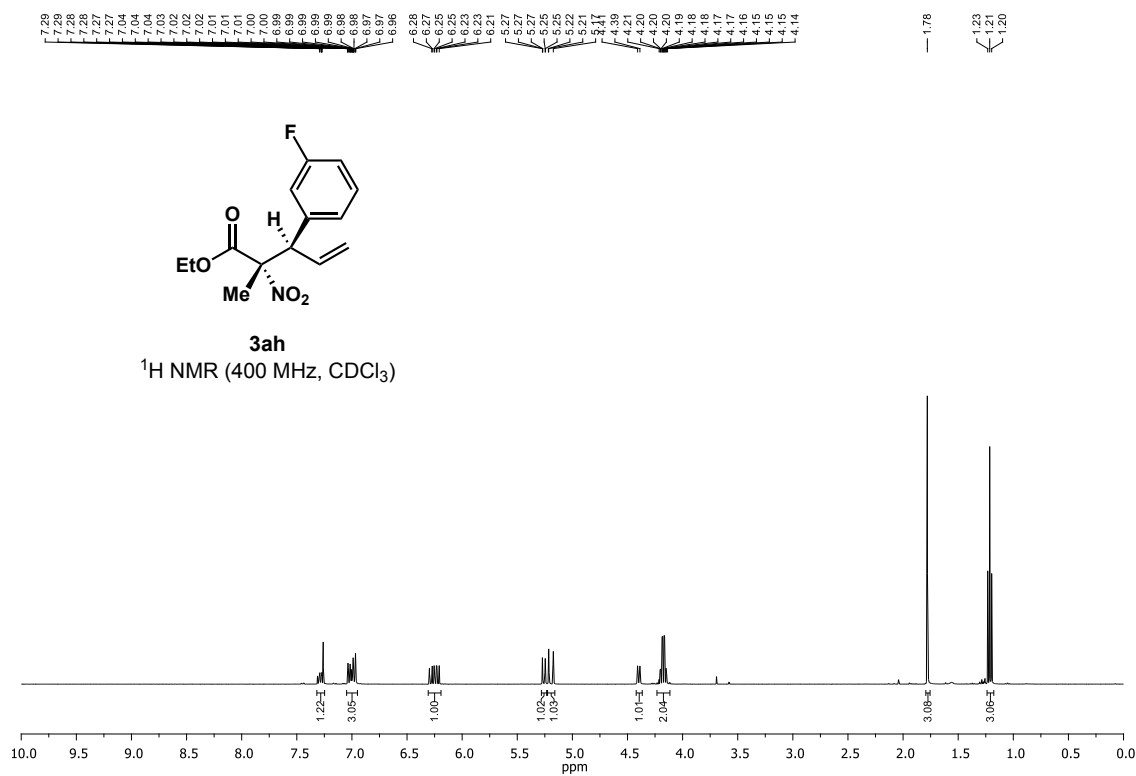
3ag
¹H NMR (400 MHz, CDCl₃)

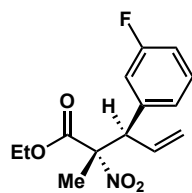


3ag
¹³C NMR (126 MHz, CDCl₃)



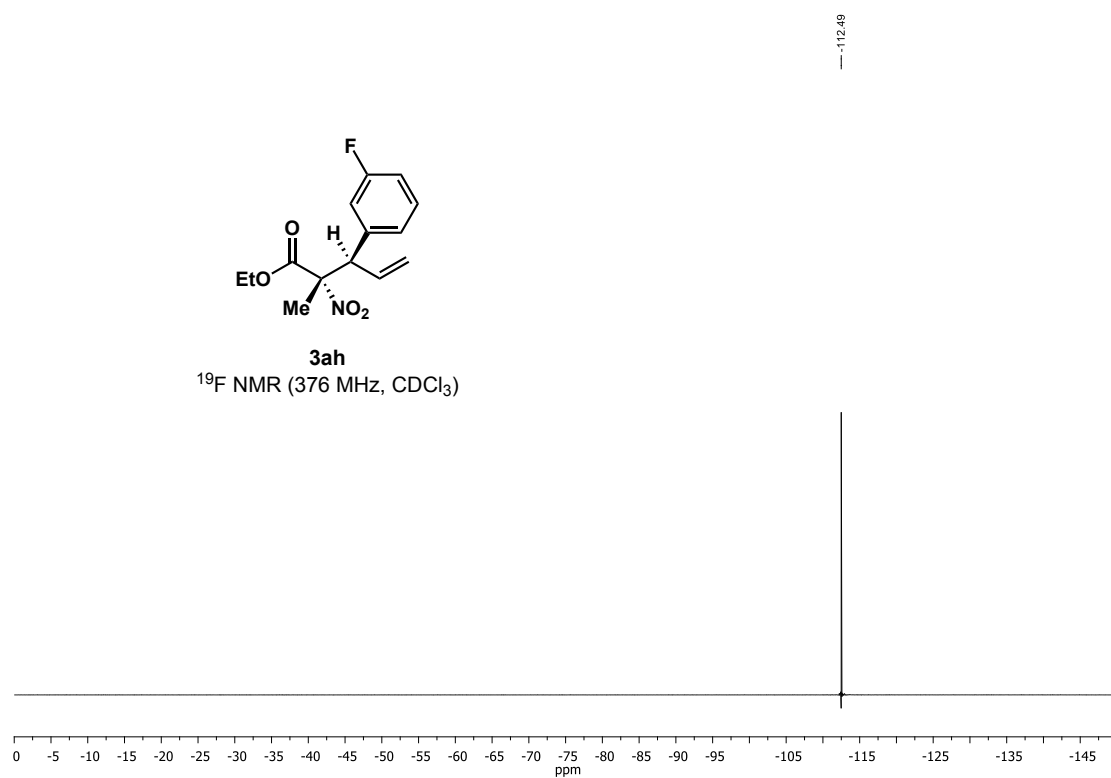
Ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-methyl-2-nitropent-4-enoate (**3ah**)



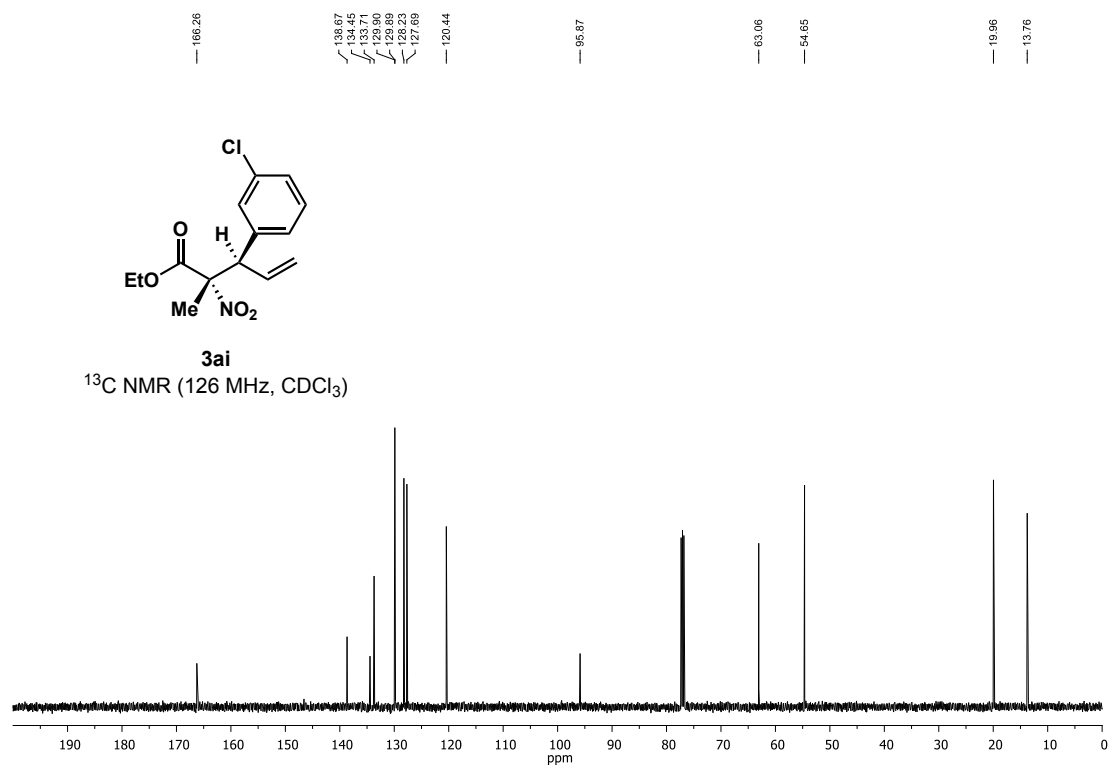
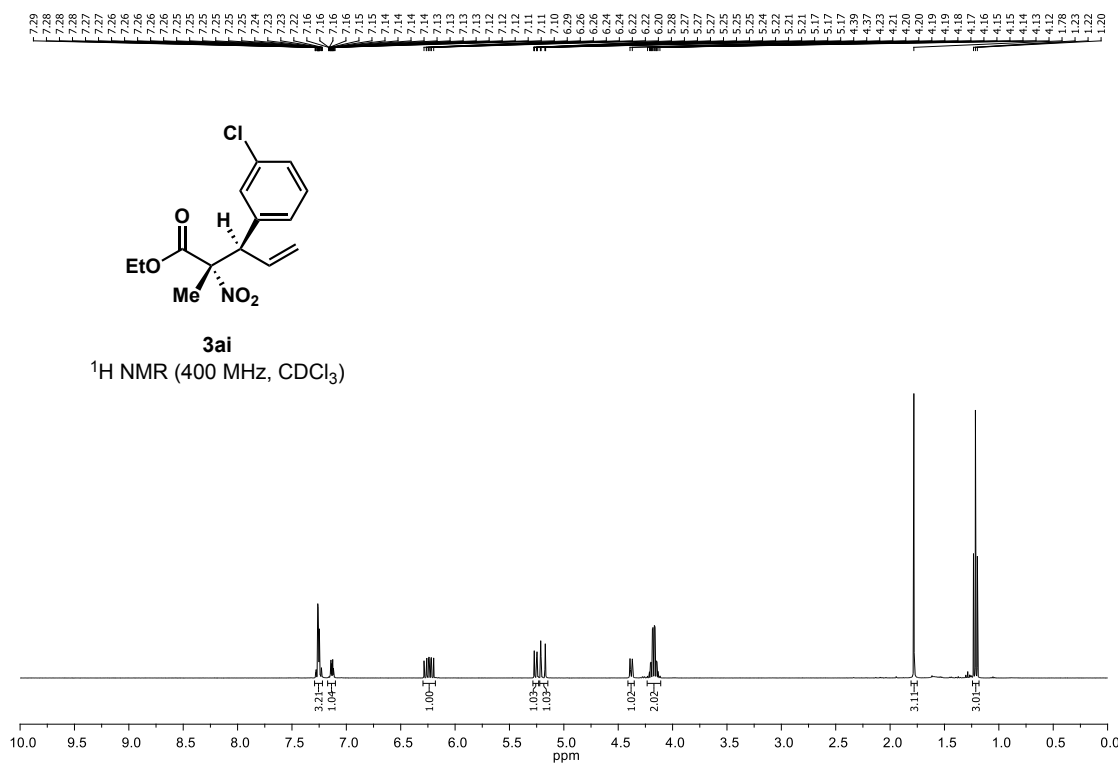


3ah

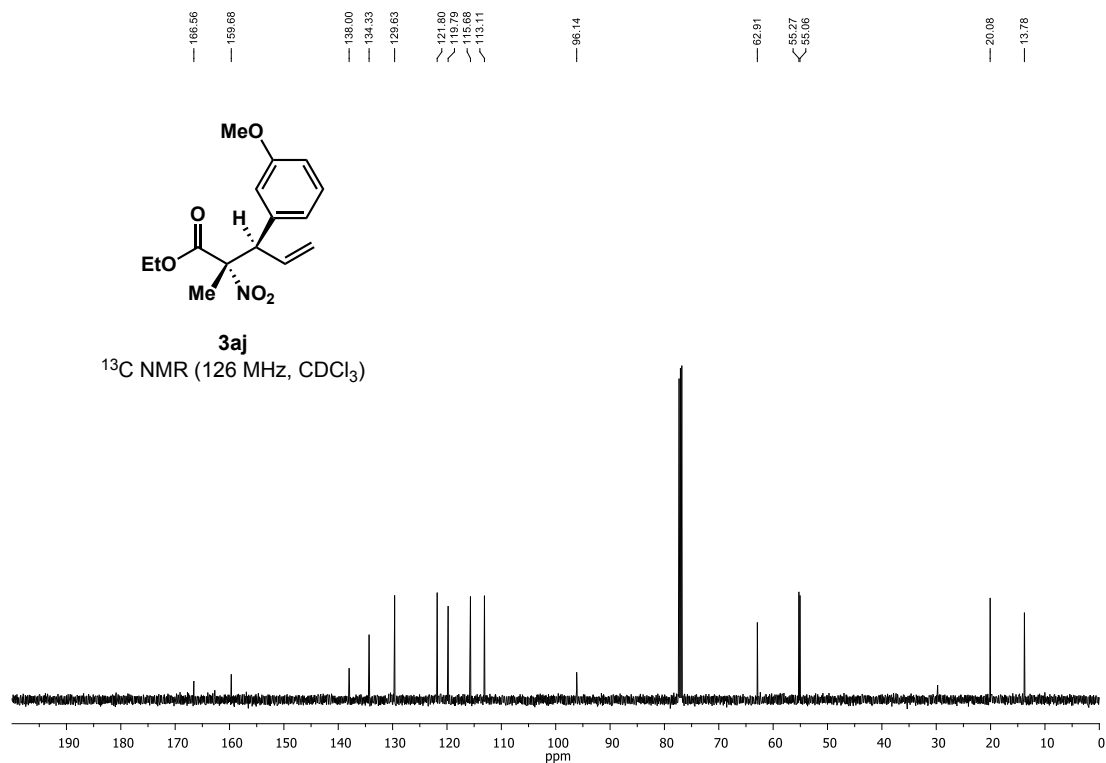
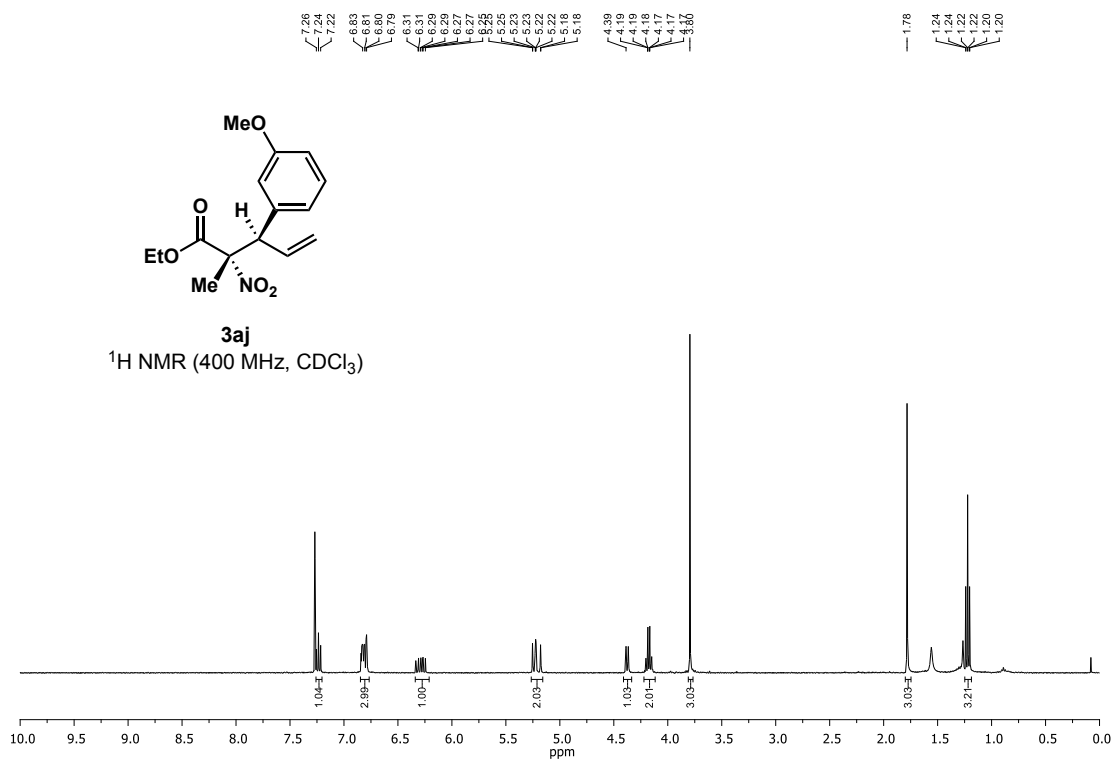
^{19}F NMR (376 MHz, CDCl_3)



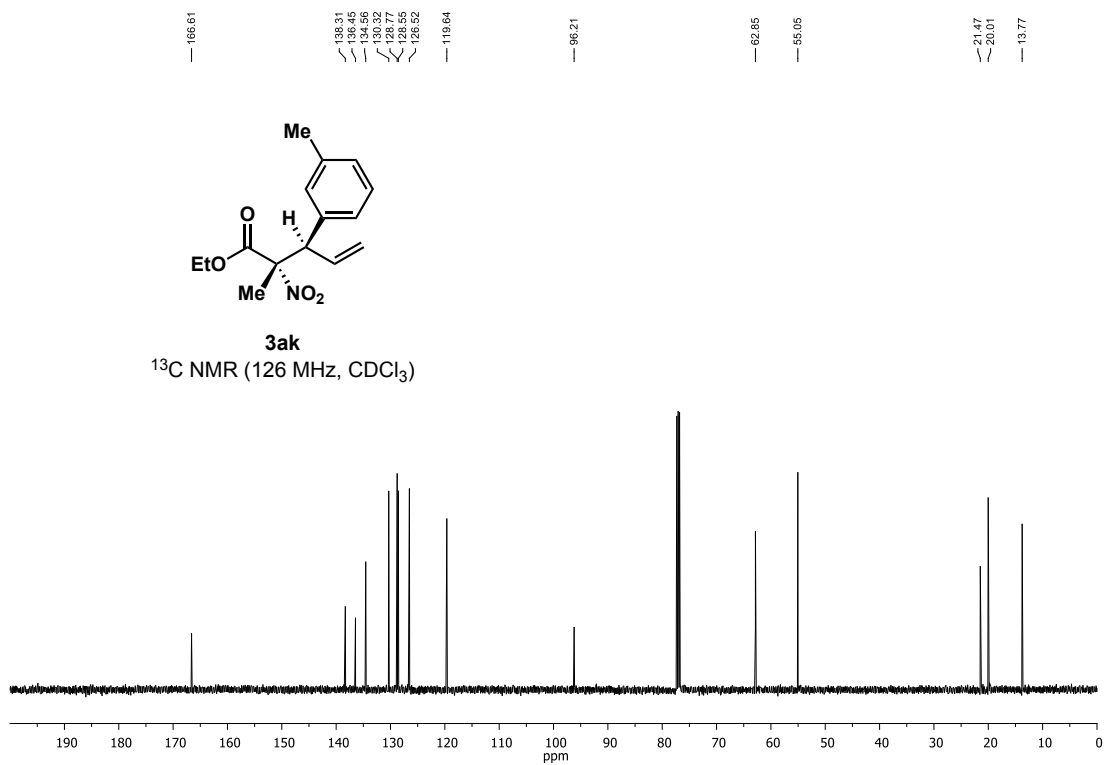
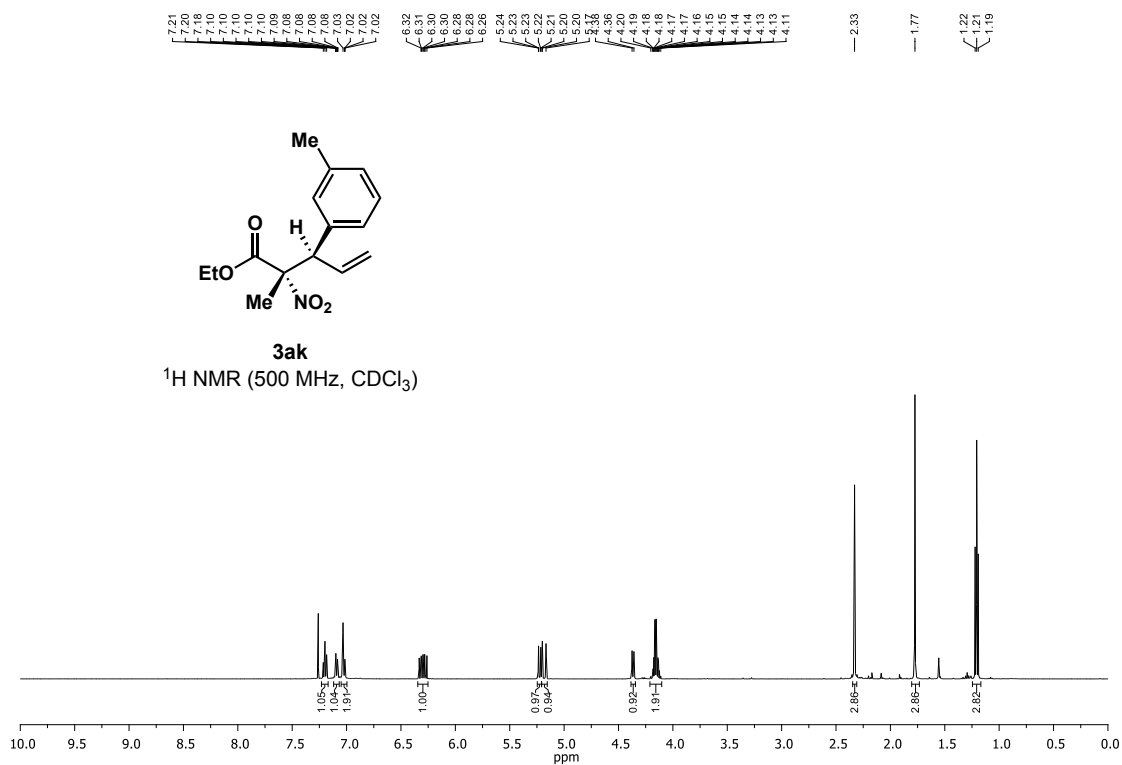
Ethyl (2*S*,3*R*)-3-(3-chlorophenyl)-2-methyl-2-nitropent-4-enoate (3ai**)**



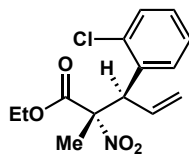
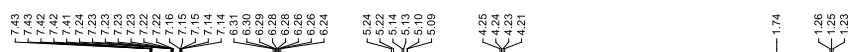
Ethyl (2*S*,3*R*)-3-(3-methoxyphenyl)-2-methyl-2-nitropent-4-enoate (**3aj**)



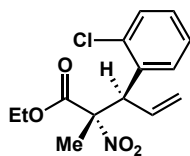
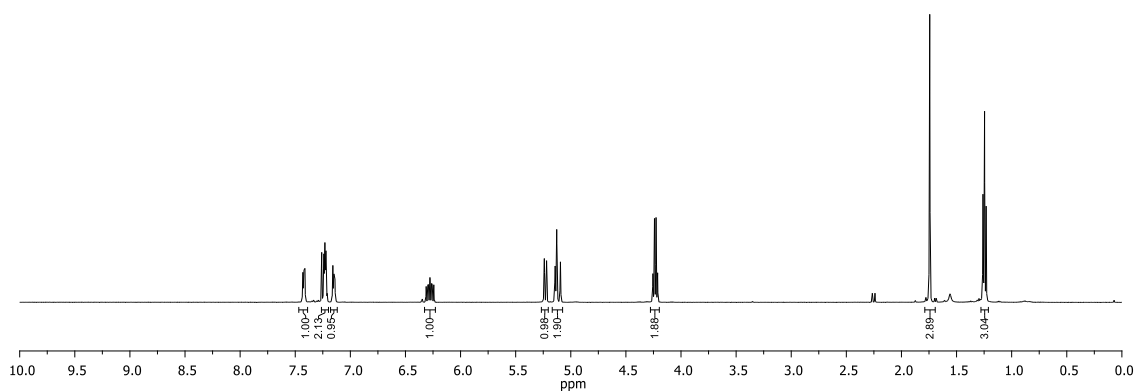
Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-(*m*-tolyl)pent-4-enoate (3ak)



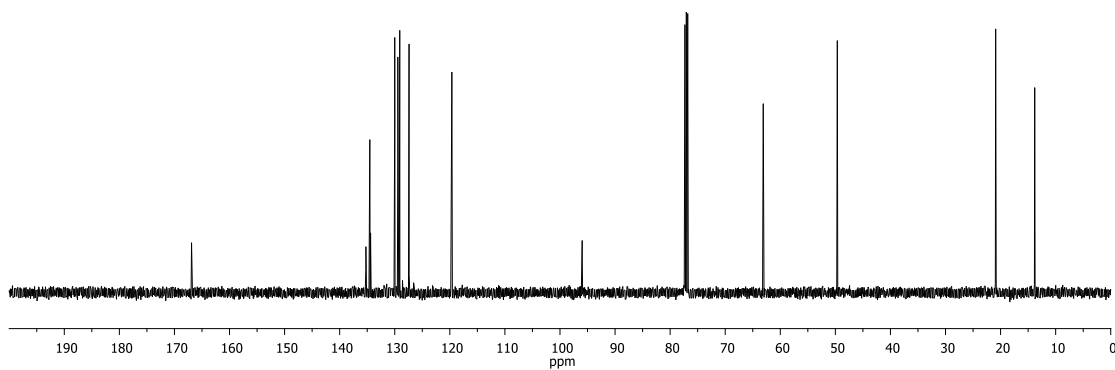
Ethyl (2*S*,3*R*)-3-(2-chlorophenyl)-2-methyl-2-nitropent-4-enoate (**3al**)



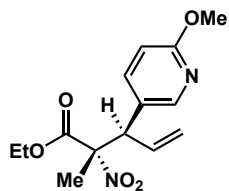
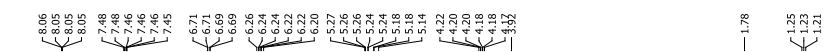
3al
¹H NMR (500 MHz, CDCl₃)



3al
¹³C NMR (126 MHz, CDCl₃)

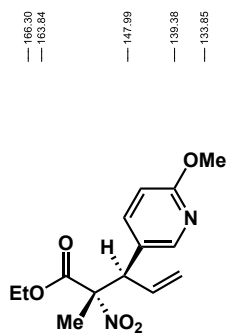
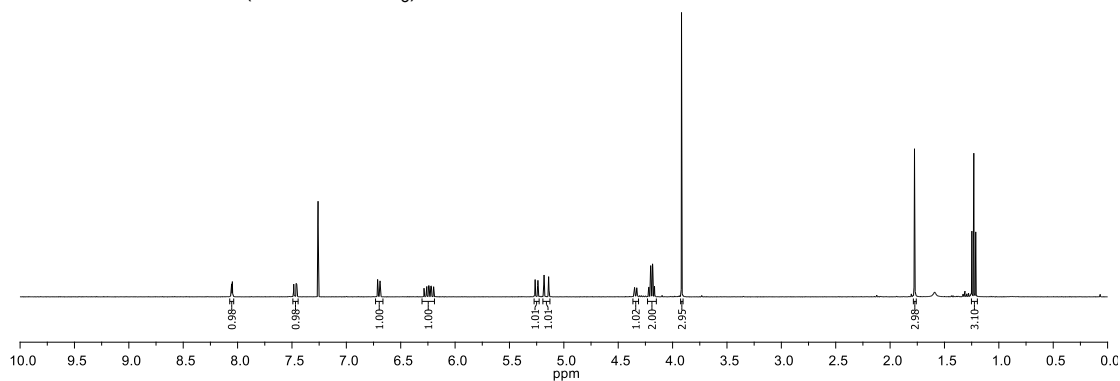


Ethyl (2*S*,3*R*)-3-(6-methoxypyridin-3-yl)-2-methyl-2-nitropent-4-enoate (3am)



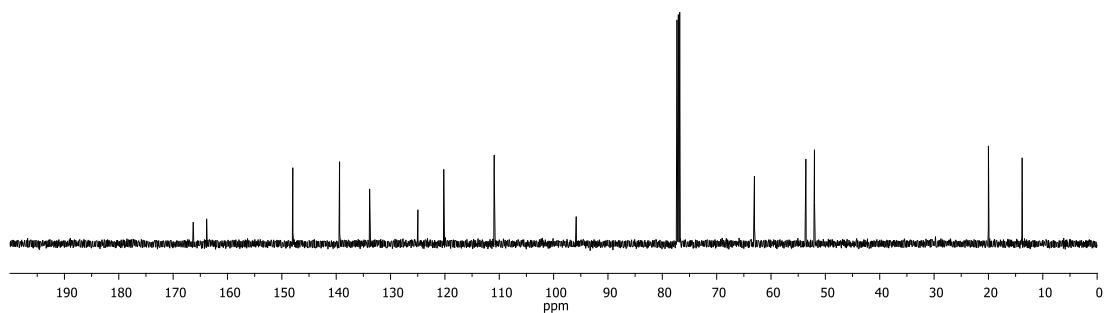
3am

¹H NMR (400 MHz, CDCl₃)

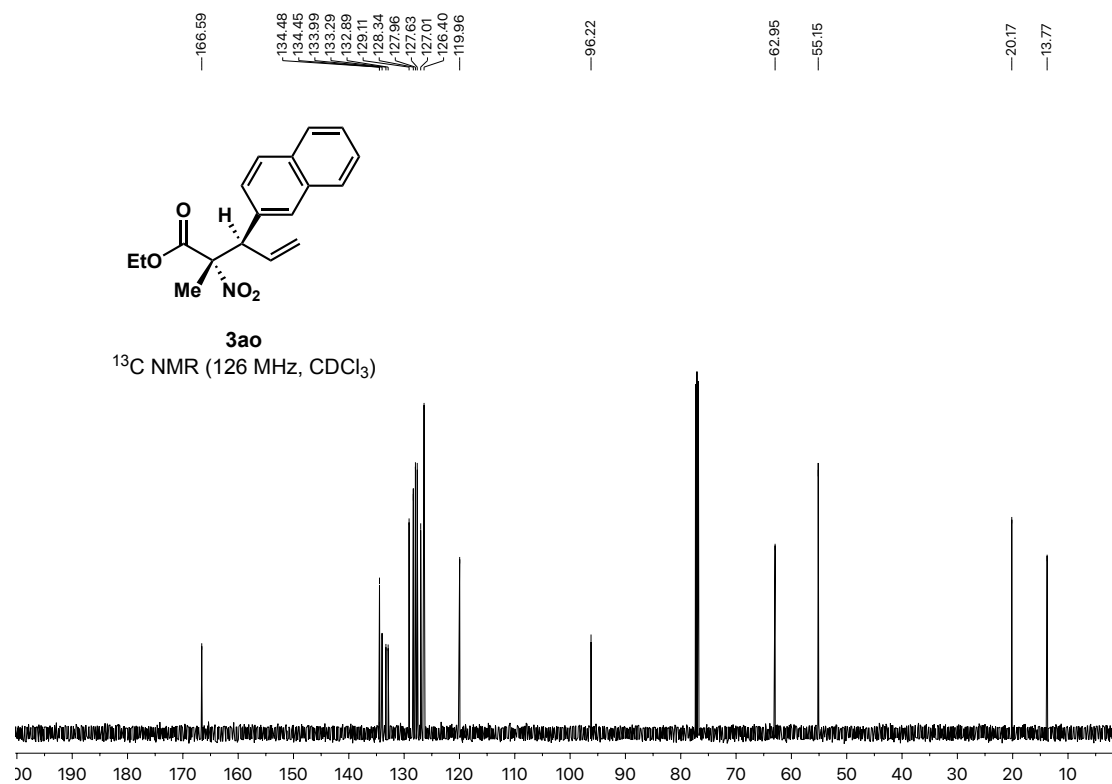
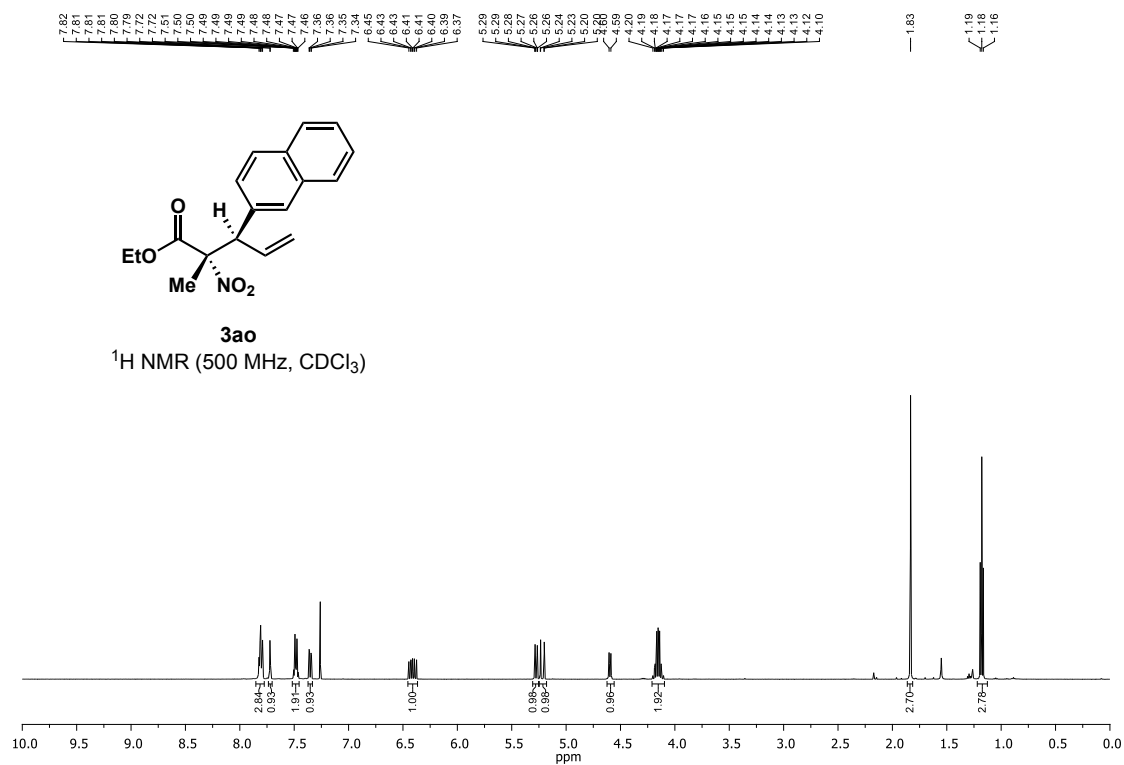


3am

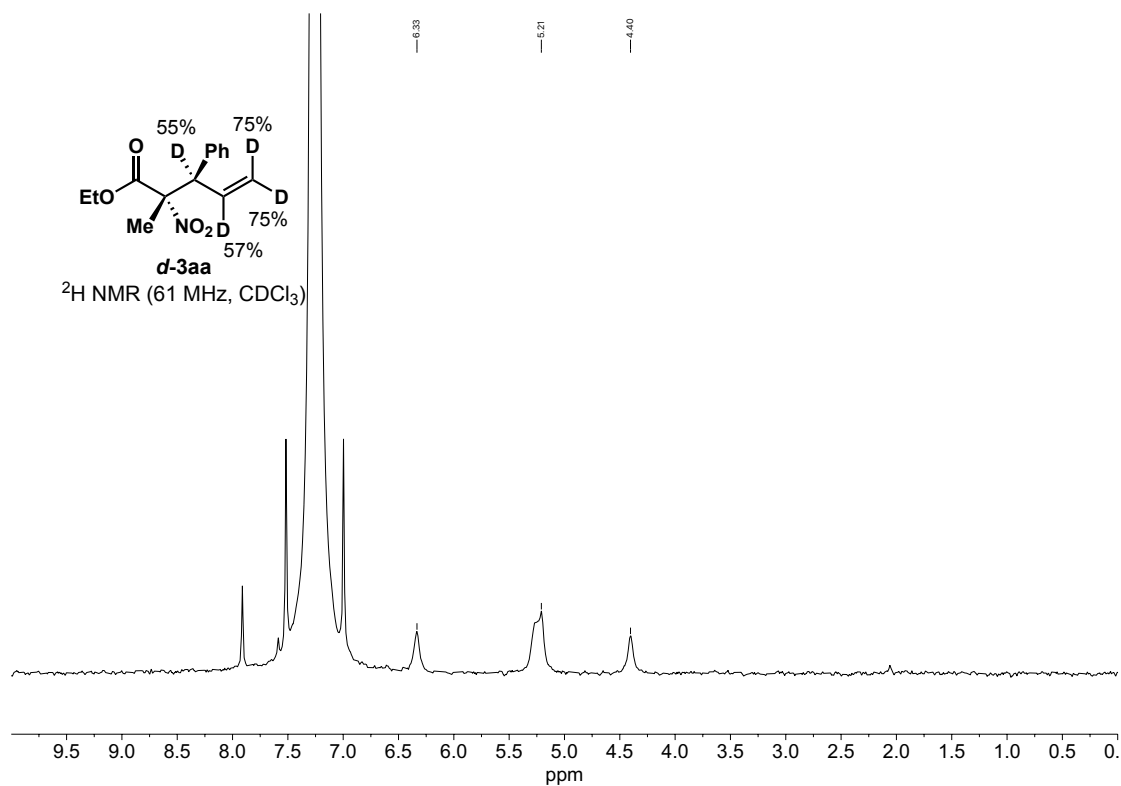
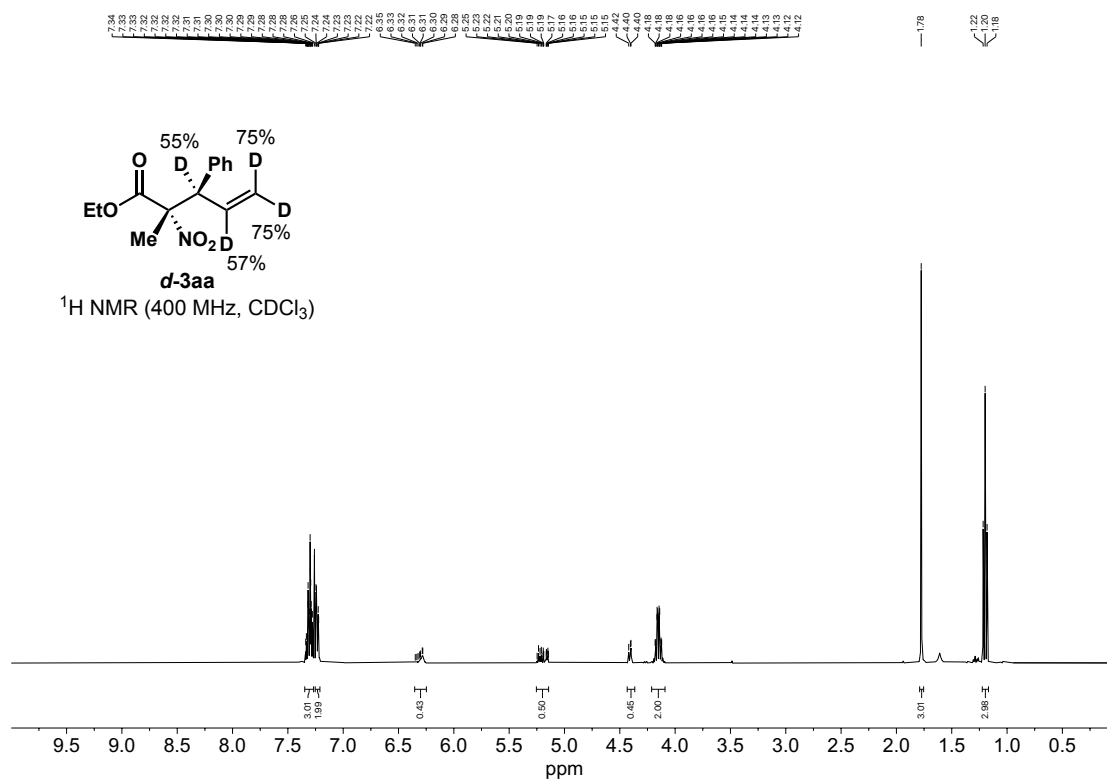
¹³C NMR (126 MHz, CDCl₃)



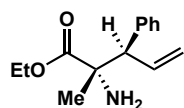
Ethyl (2*S*,3*R*)-2-methyl-3-(naphthalen-2-yl)-2-nitropent-4-enoate (3ao**)**



Ethyl (2*S*,3*R*)-2-methyl-2-nitro-3-phenylpent-4-enoate-3,4,5,5-*d*₄ (*d*-3aa)

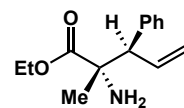
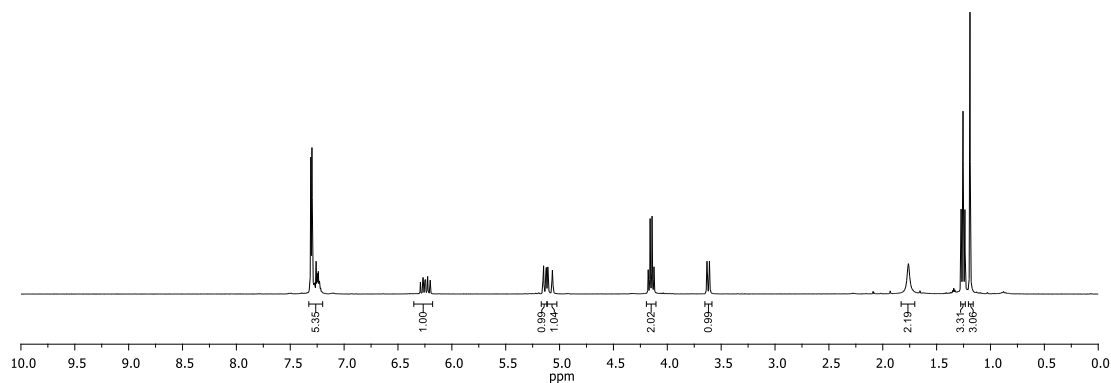


Ethyl (2*S*,3*R*)-2-amino-2-methyl-3-phenylpent-4-enoate (6**)**



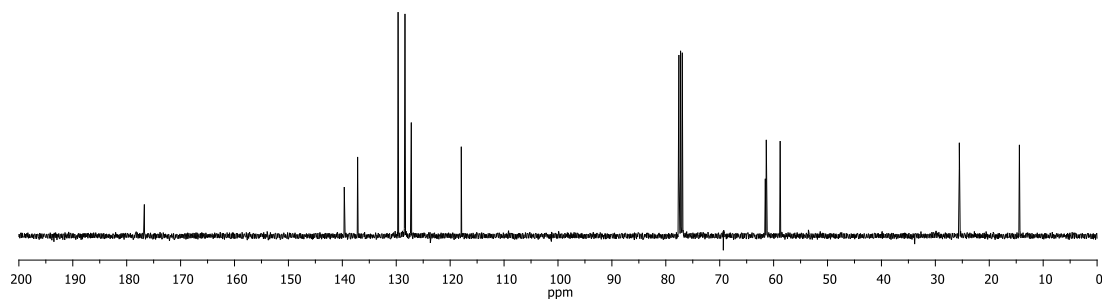
6

¹H NMR (400 MHz, CDCl₃)

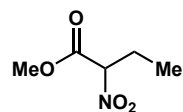


6

¹³C NMR (101 MHz, CDCl₃)

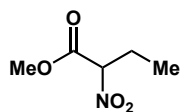
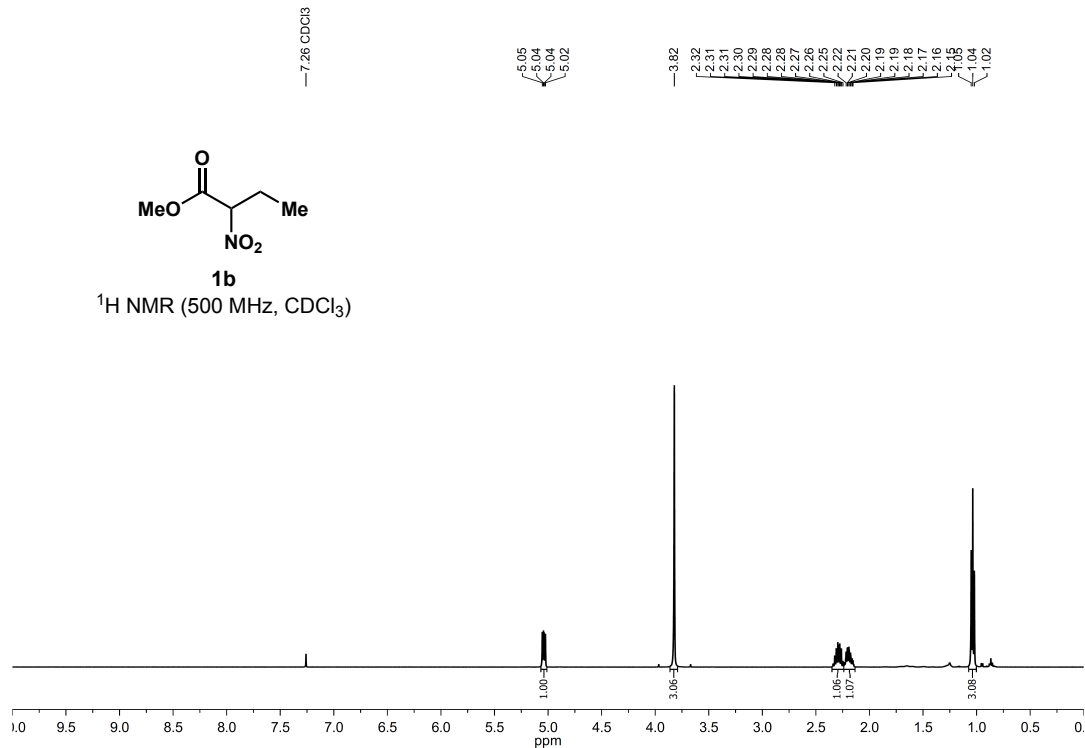


Methyl 2-nitrobutanoate (1b)



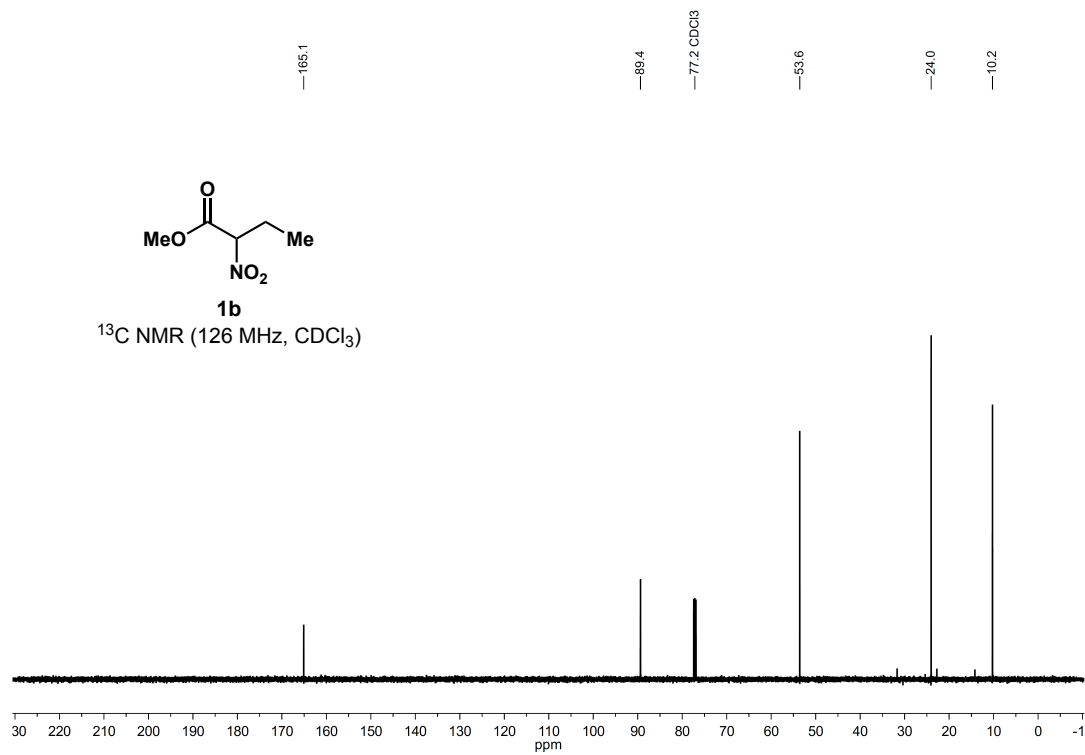
1b

¹H NMR (500 MHz, CDCl₃)

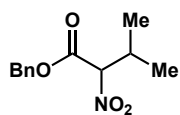
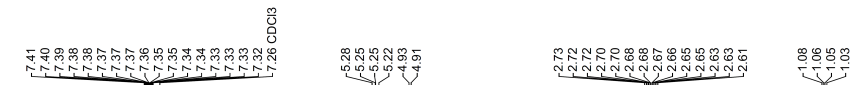


1b

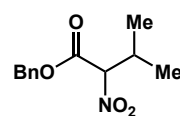
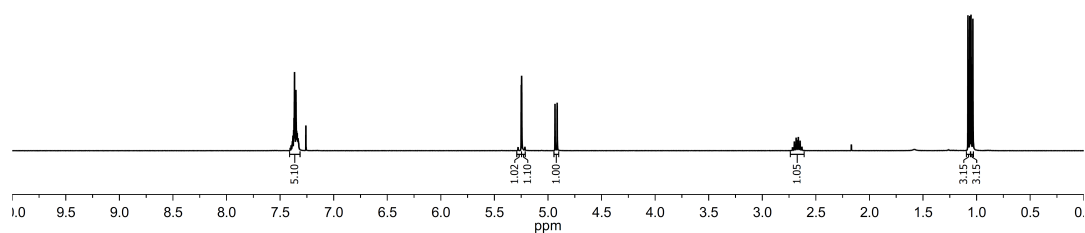
¹³C NMR (126 MHz, CDCl₃)



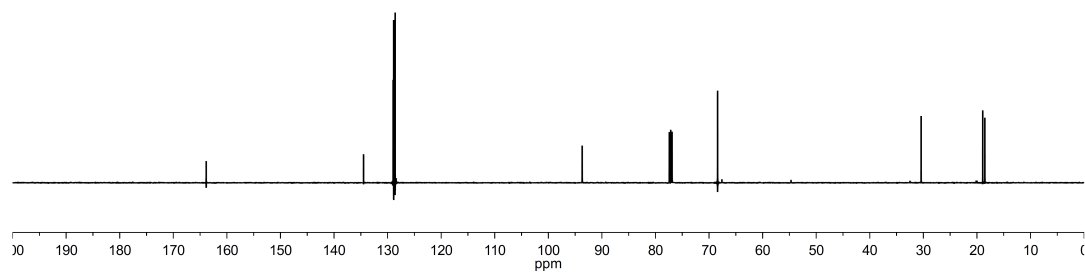
Benzyl 3-methyl-2-nitrobutanoate (1c)



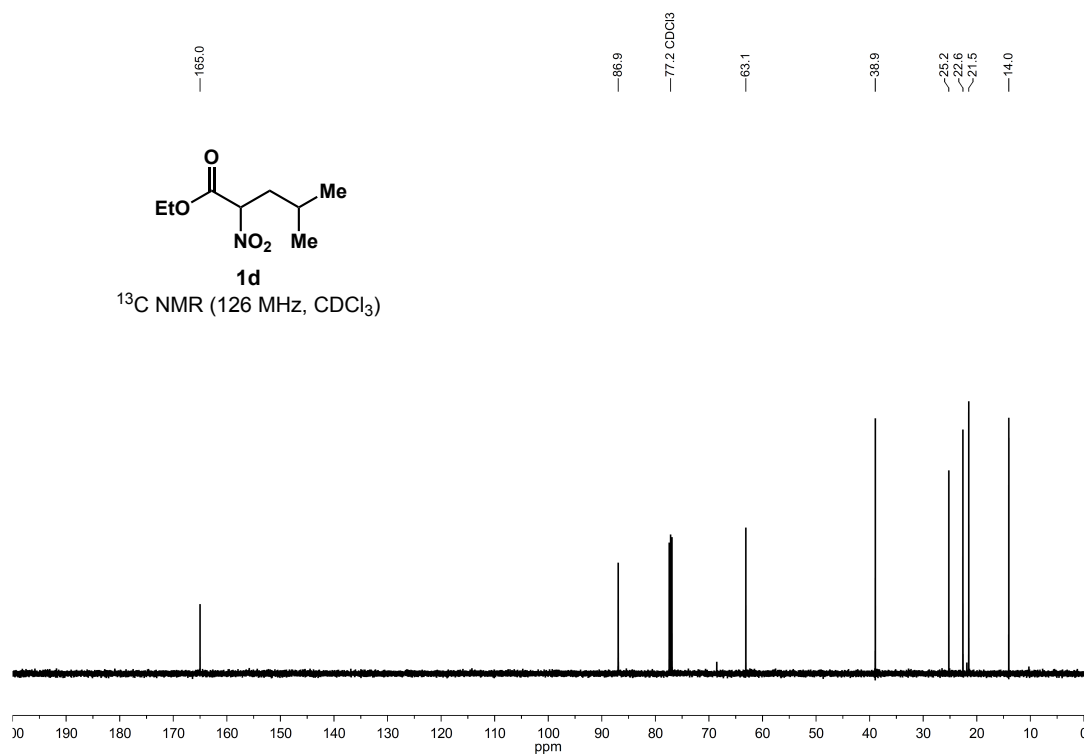
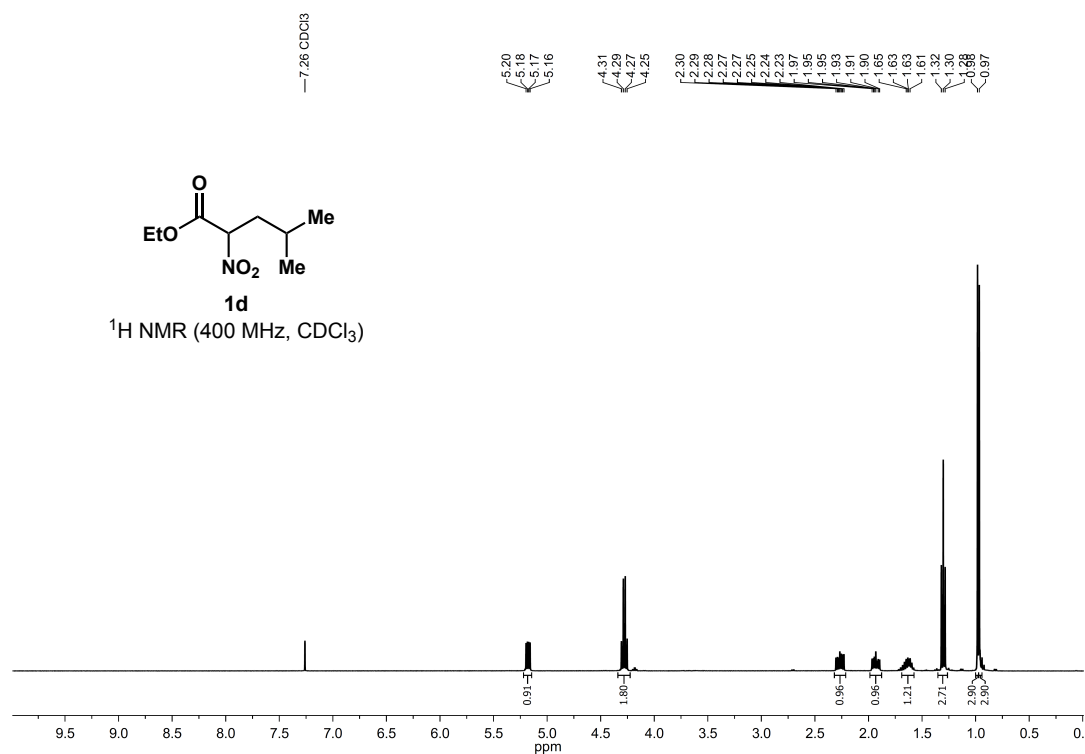
1c
¹H NMR (400 MHz, CDCl₃)



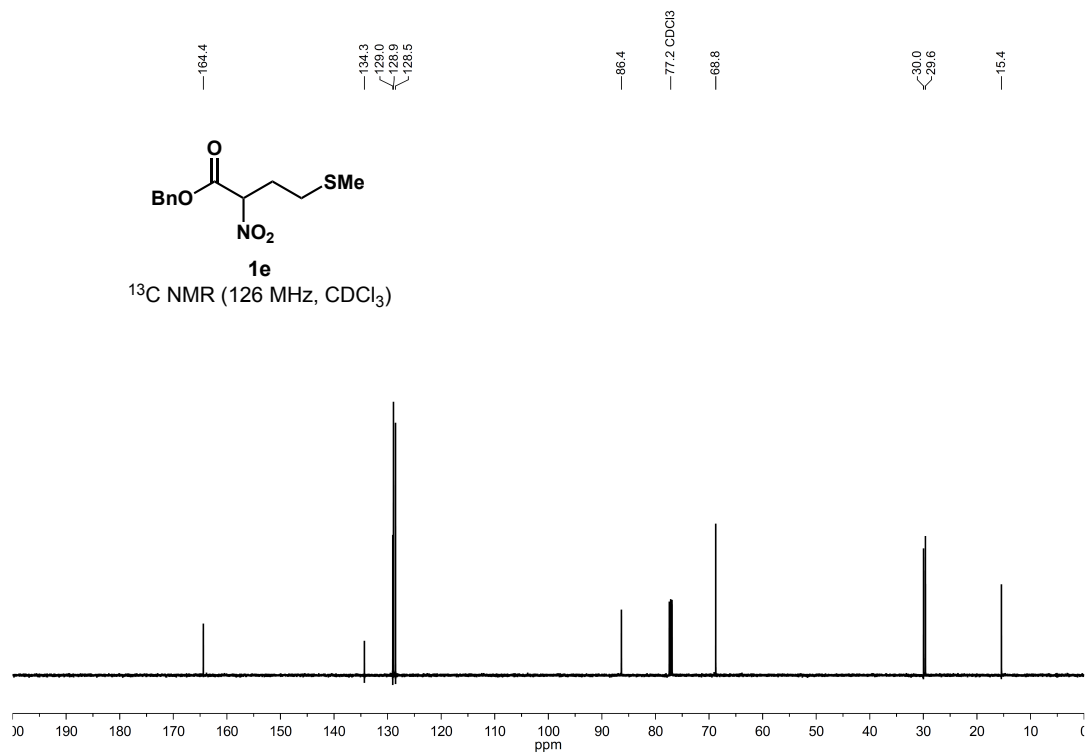
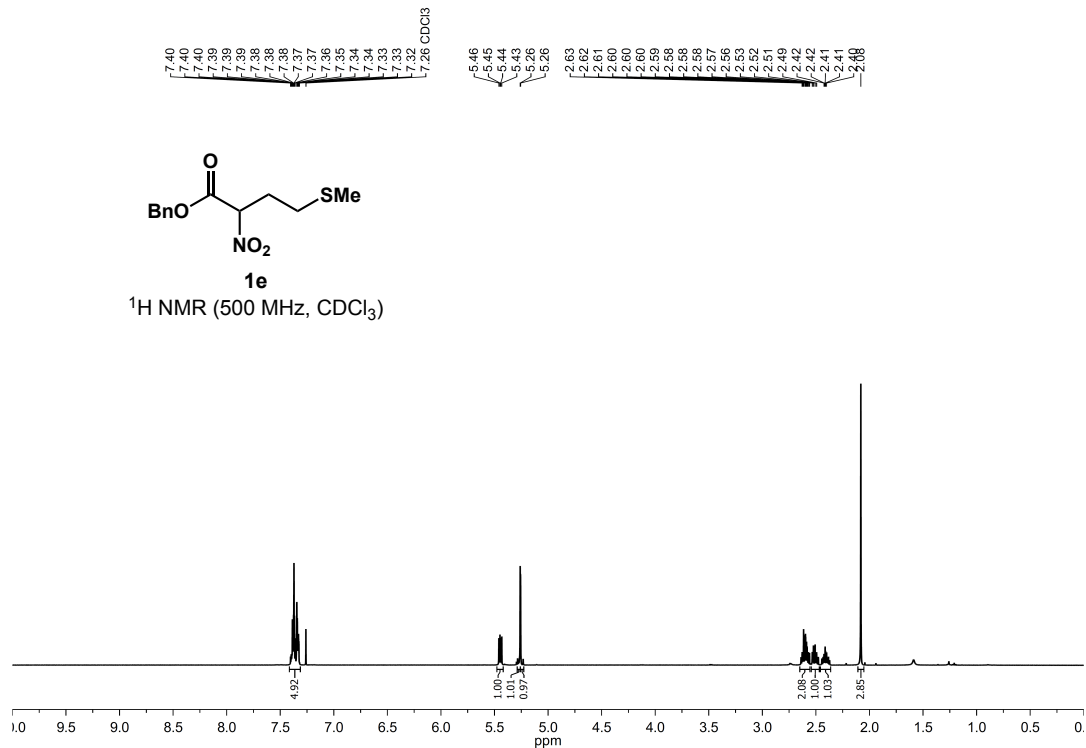
1c
¹³C NMR (126 MHz, CDCl₃)



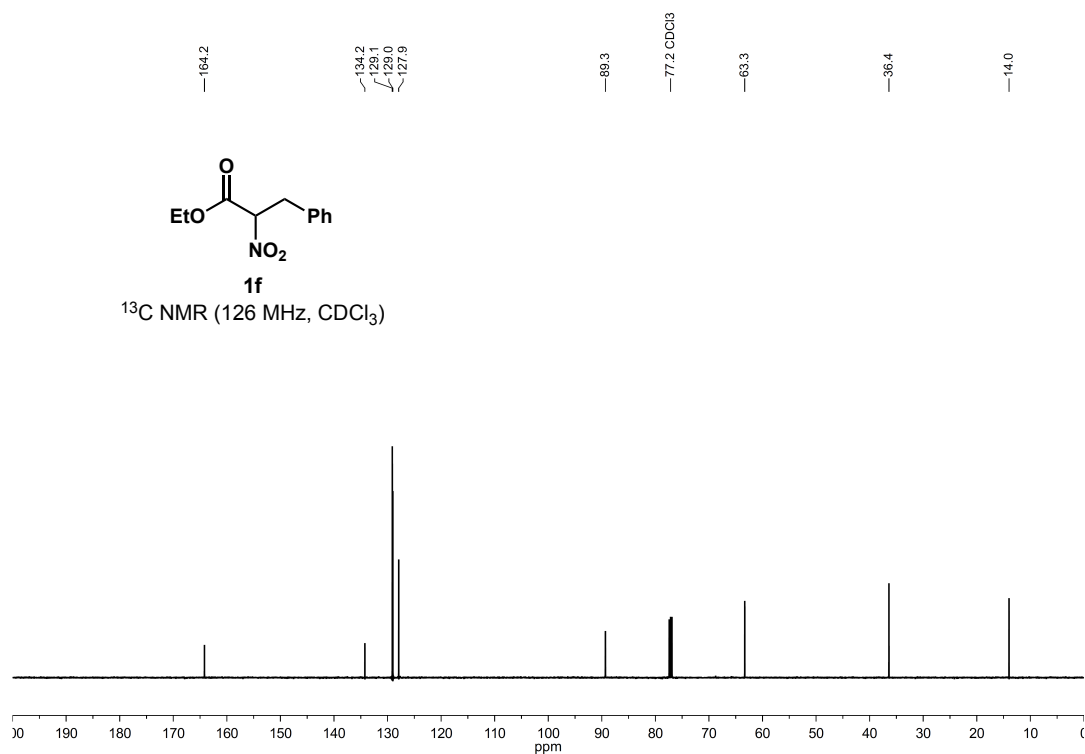
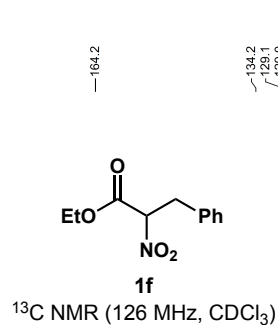
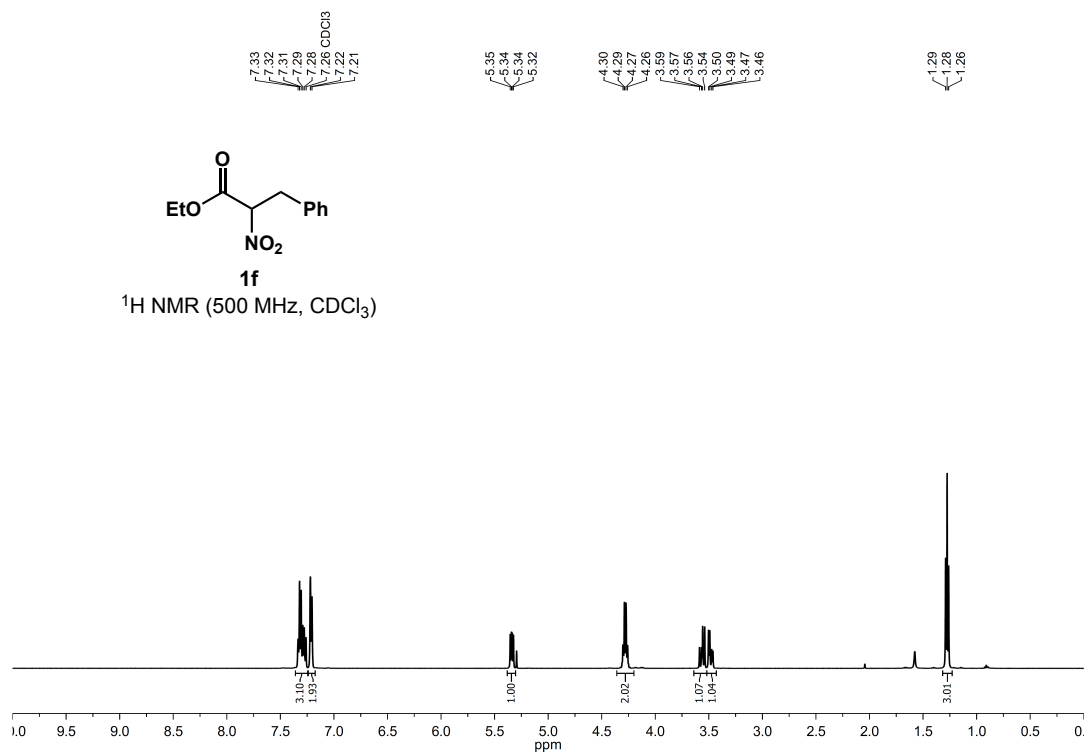
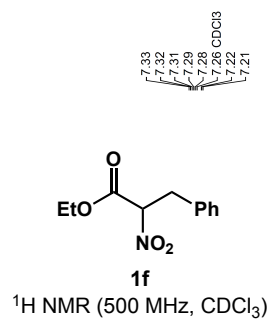
Ethyl 4-methyl-2-nitropentanoate (1d)



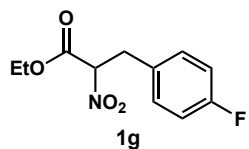
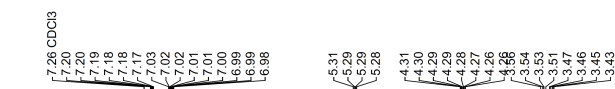
Benzyl 4-(methylthio)-2-nitrobutanoate (1e)



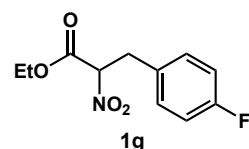
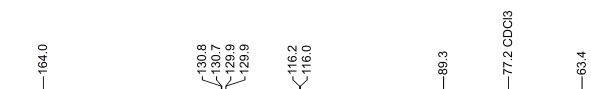
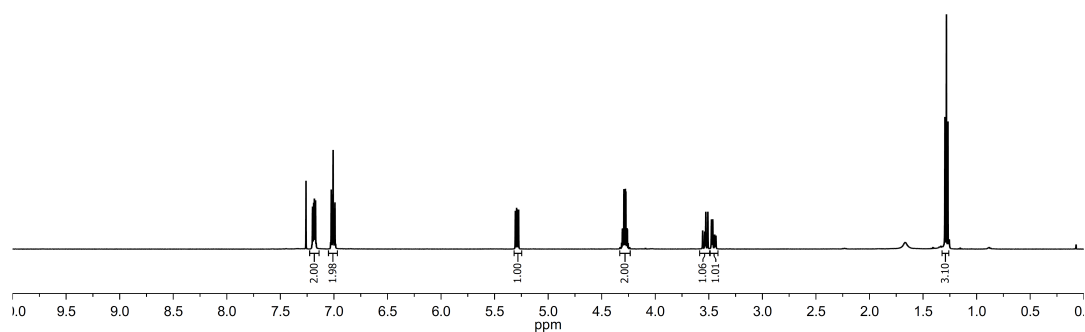
Ethyl 2-nitro-3-phenylpropanoate (1f)



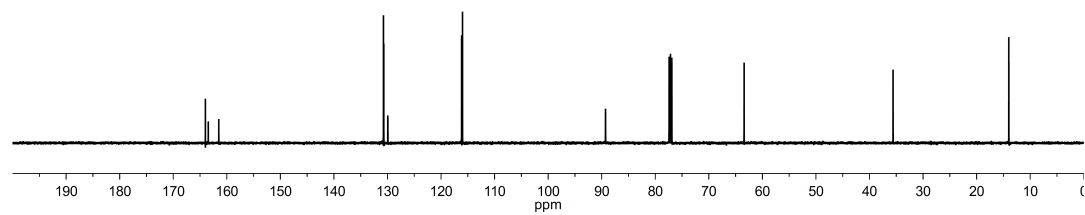
Ethyl 2-nitro-3-(4-fluorophenyl)propanoate (1g)

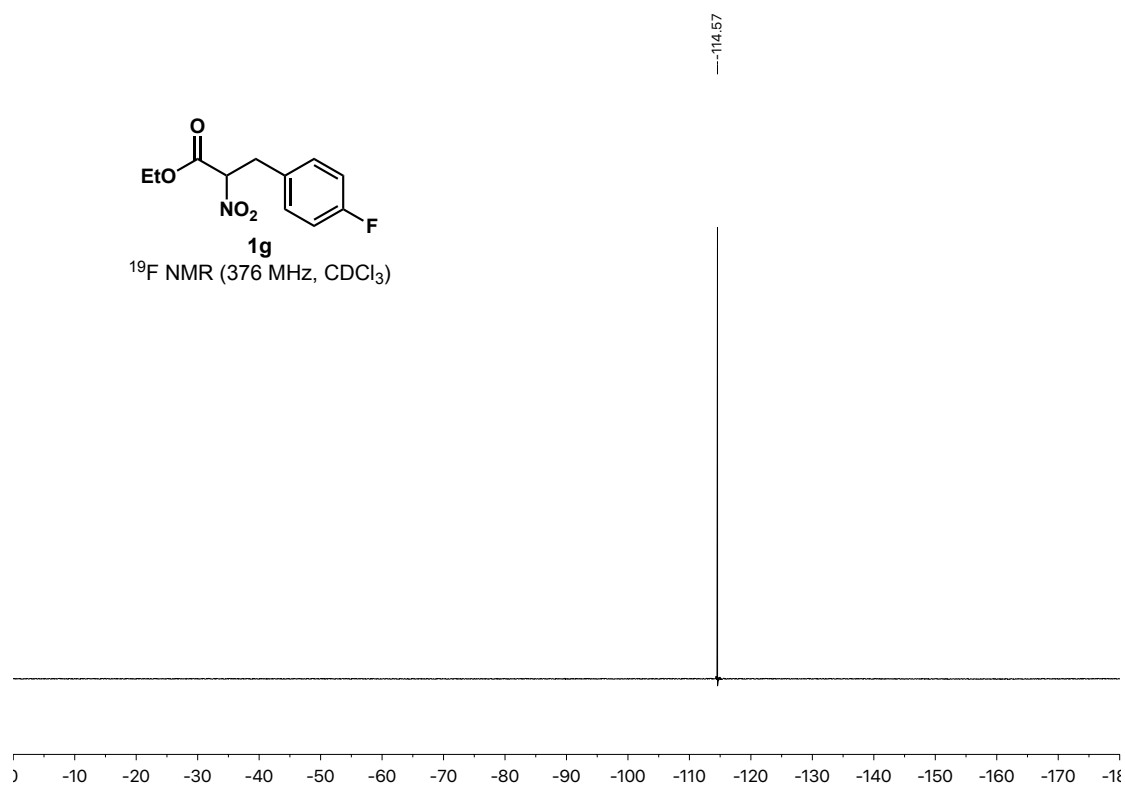


¹H NMR (500 MHz, CDCl₃)

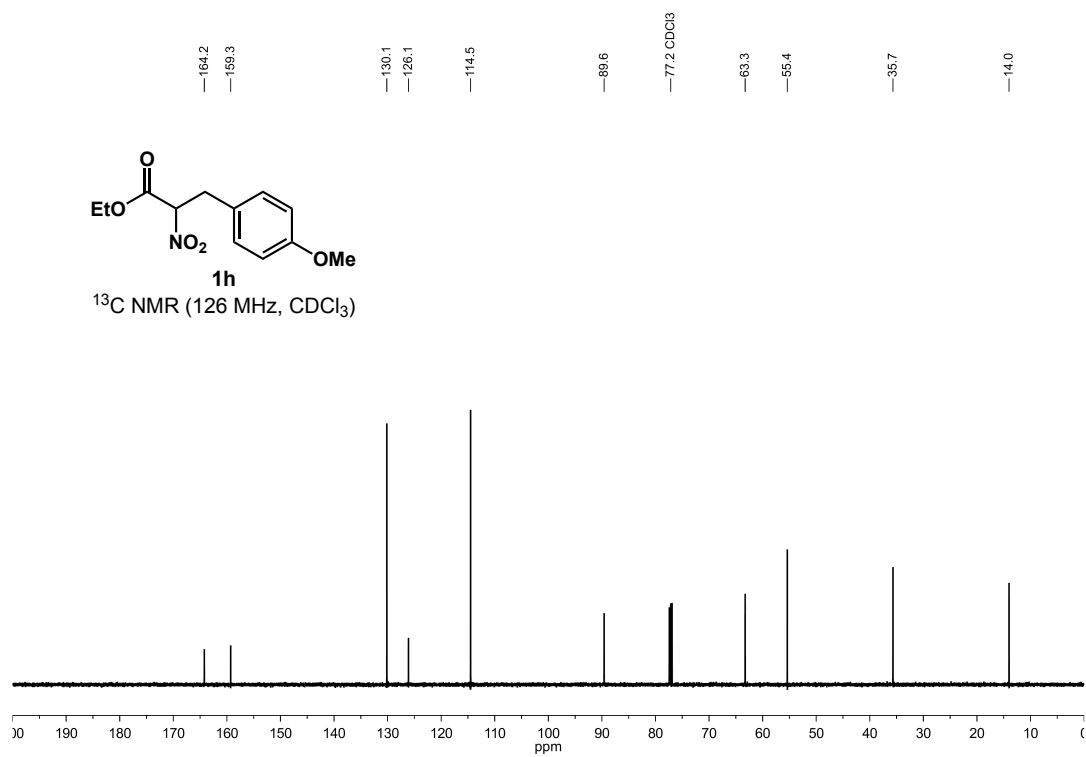
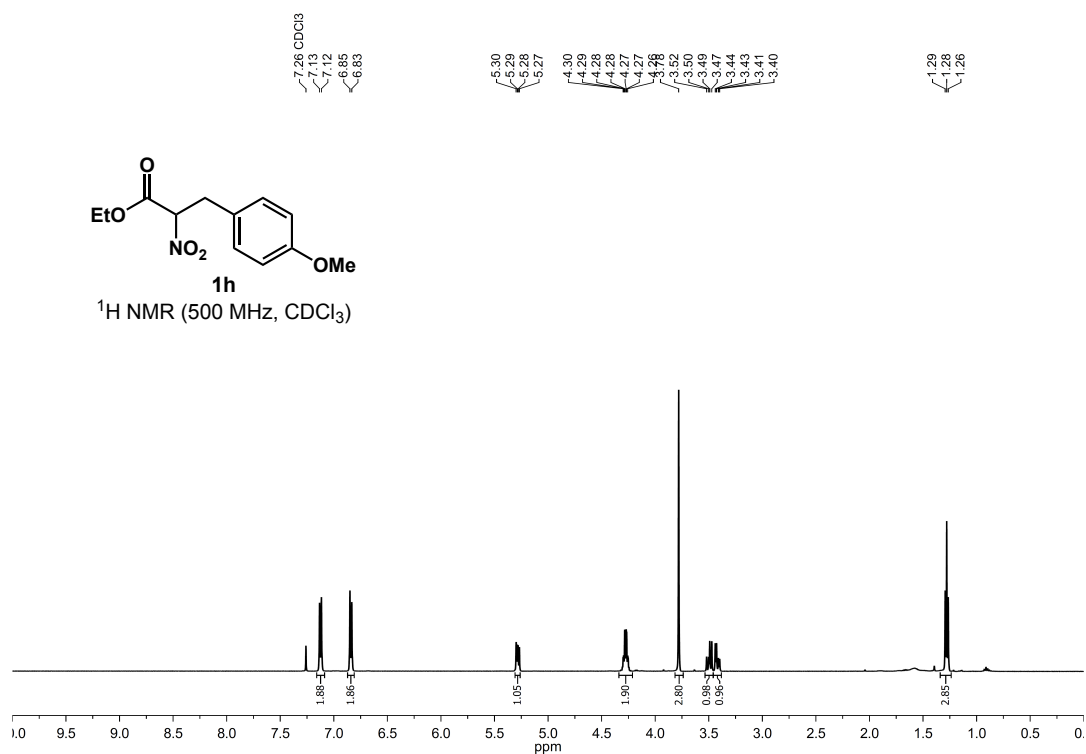


¹³C NMR (126 MHz, CDCl₃)

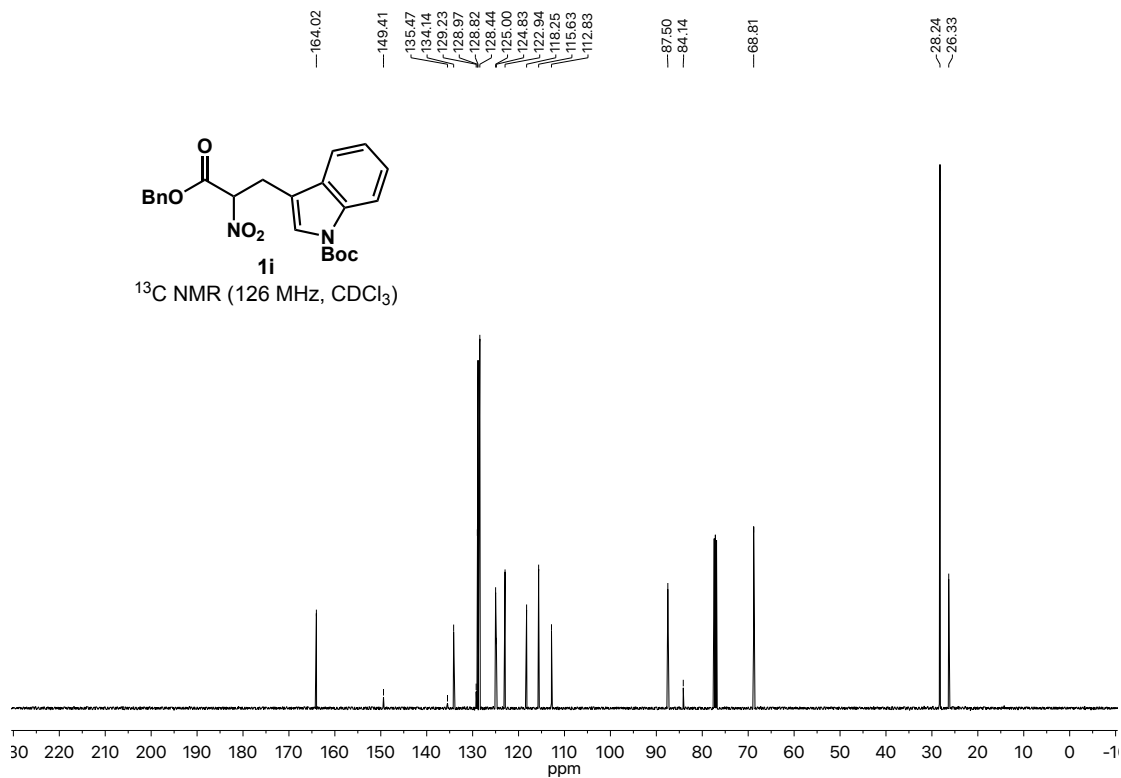
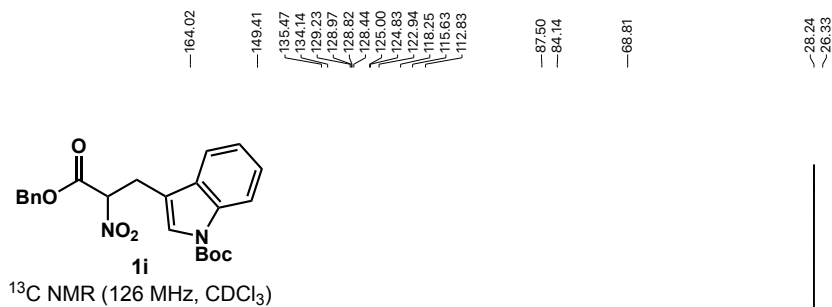
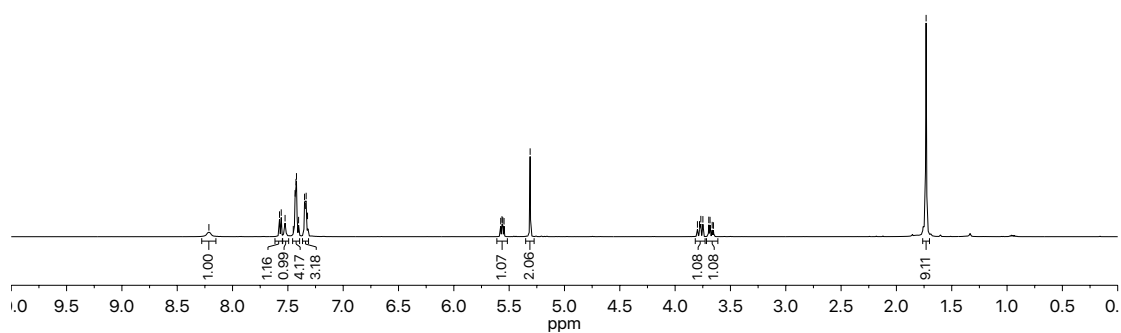
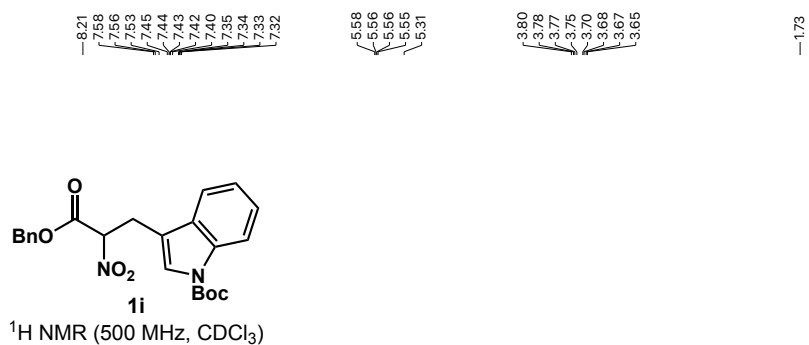




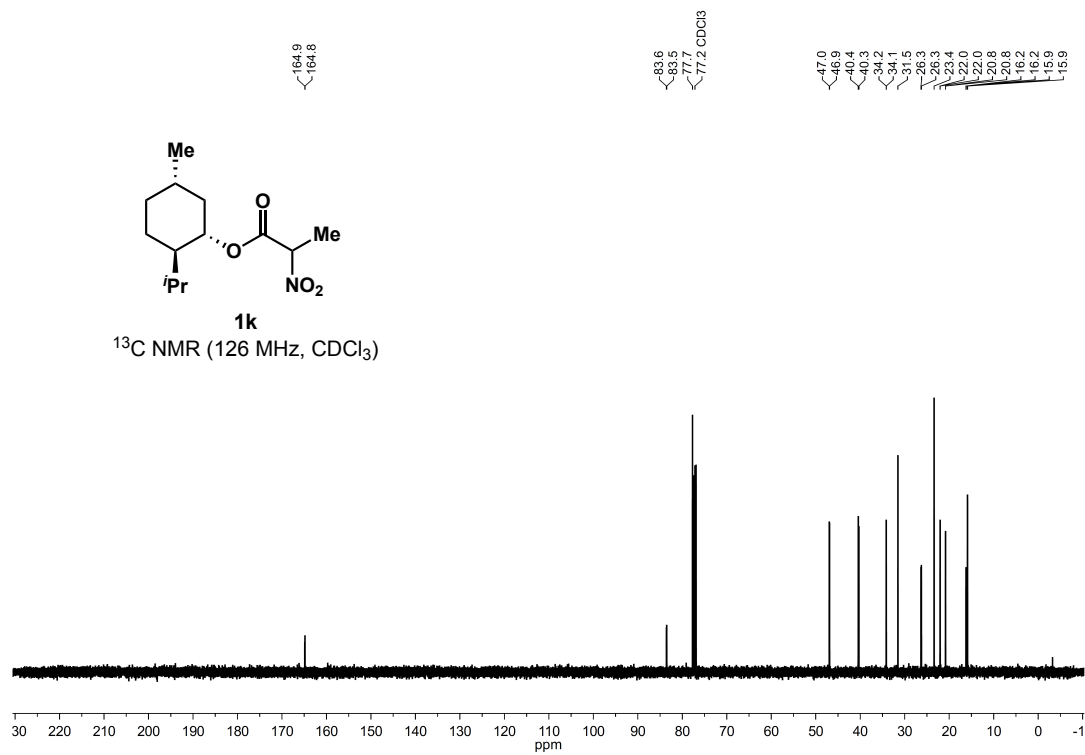
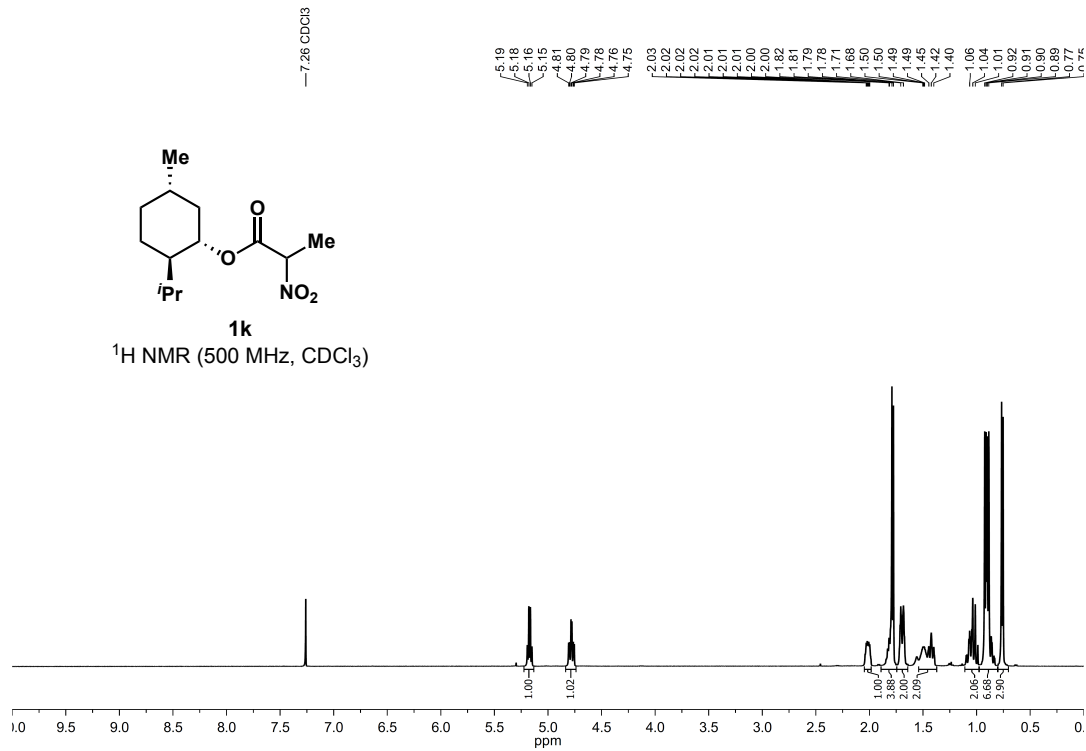
Ethyl 3-(4-methoxyphenyl)-2-nitropropanoate (1h)



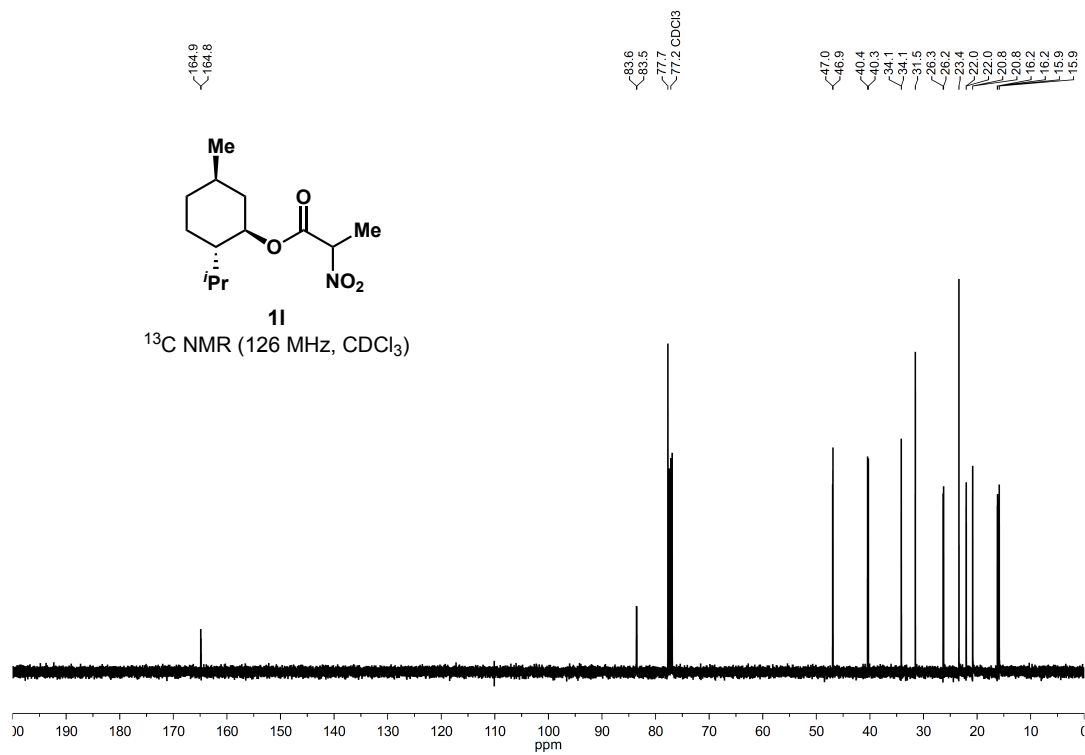
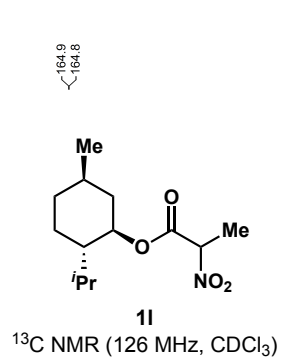
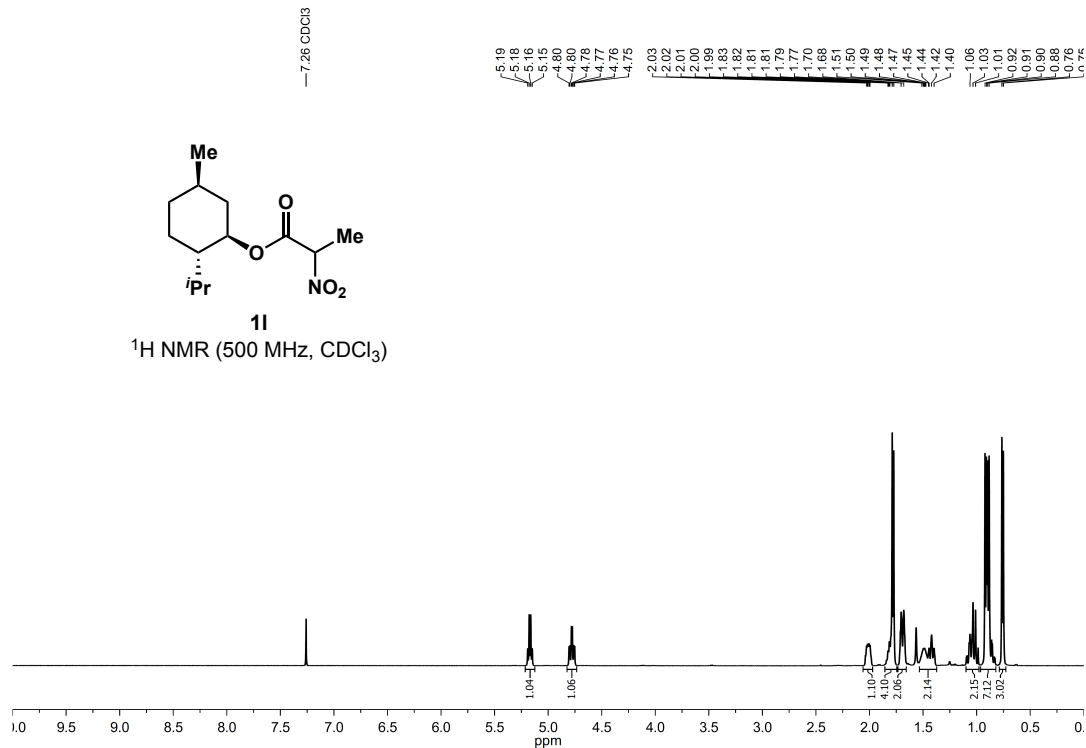
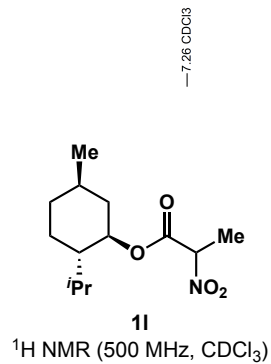
***Tert*-butyl 3-(3-(benzyloxy)-2-nitro-3-oxopropyl)-1*H*-indole-1-carboxylate (**1i**)**



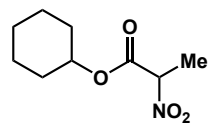
(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-nitropropanoate (1k)



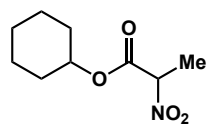
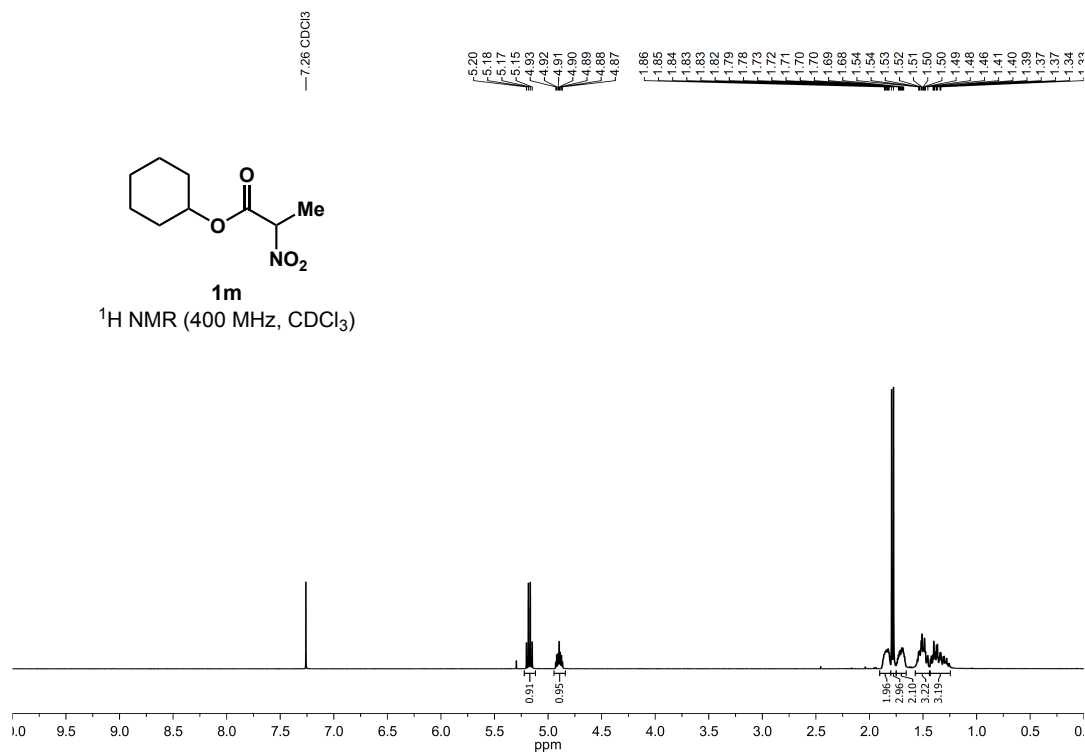
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-nitropropanoate (1I)



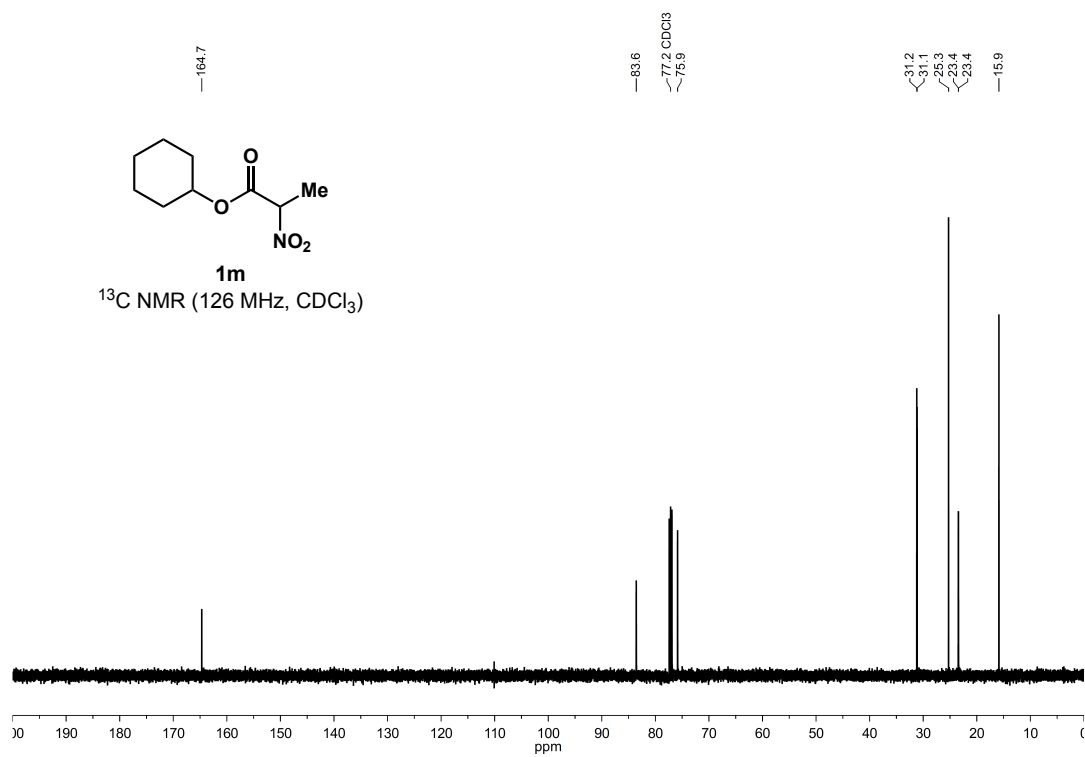
Cyclohexyl 2-nitropropanoate (1m)



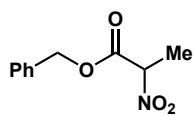
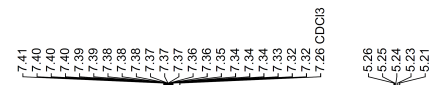
1m
 ^1H NMR (400 MHz, CDCl_3)



1m
 ^{13}C NMR (126 MHz, CDCl_3)

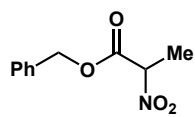
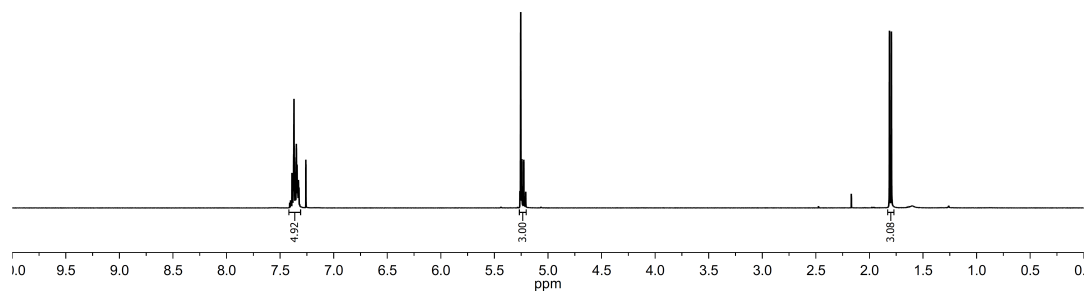


Benzyl 2-nitropropanoate (1n)



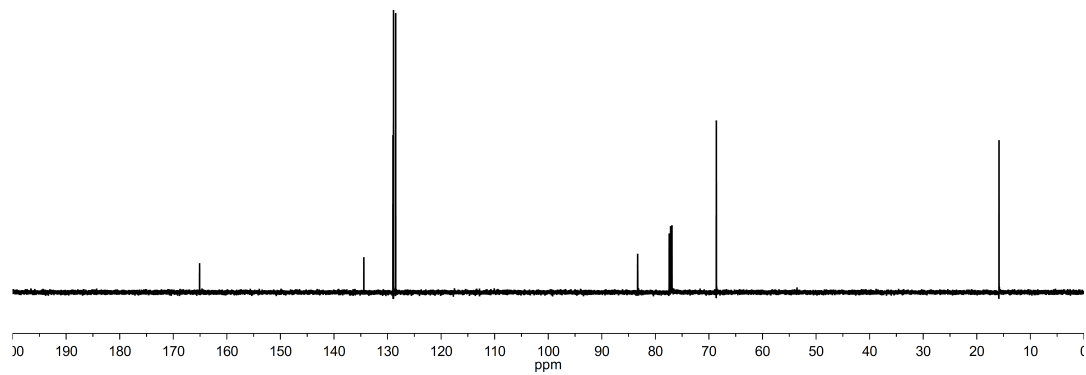
1n

¹H NMR (400 MHz, CDCl₃)

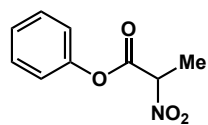


1n

¹³C NMR (126 MHz, CDCl₃)

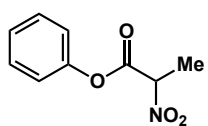
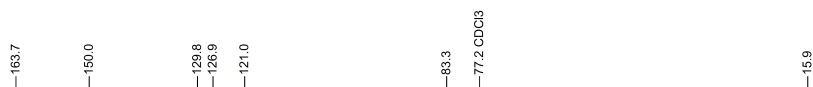
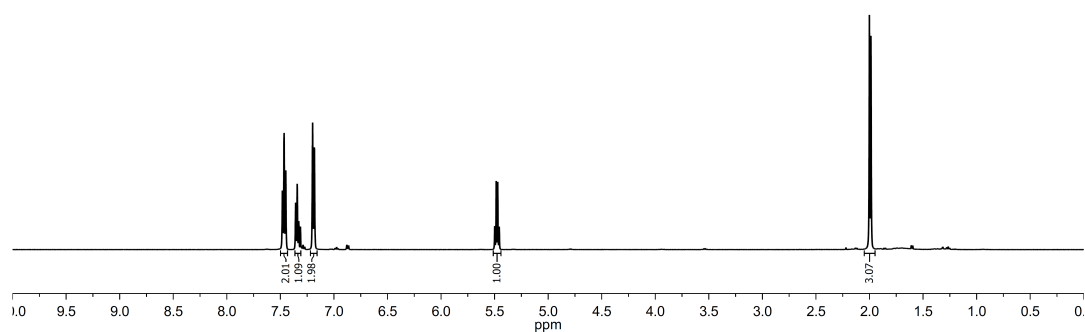


Phenyl 2-nitropropanoate (1o)



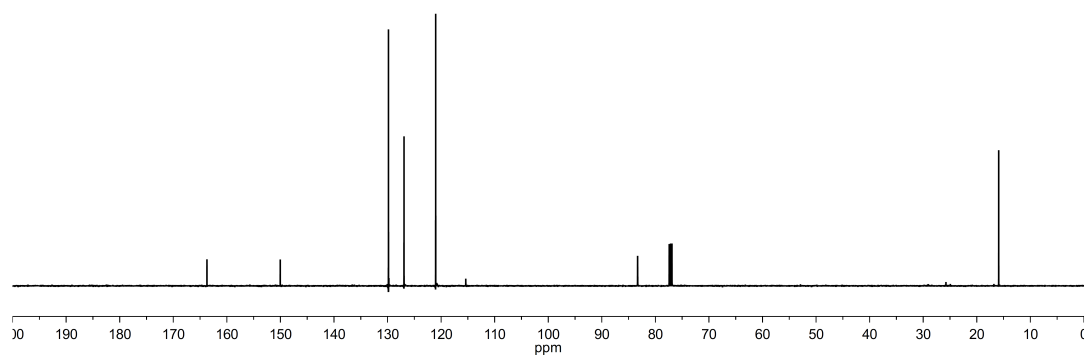
1o

¹H NMR (500 MHz, CDCl₃)

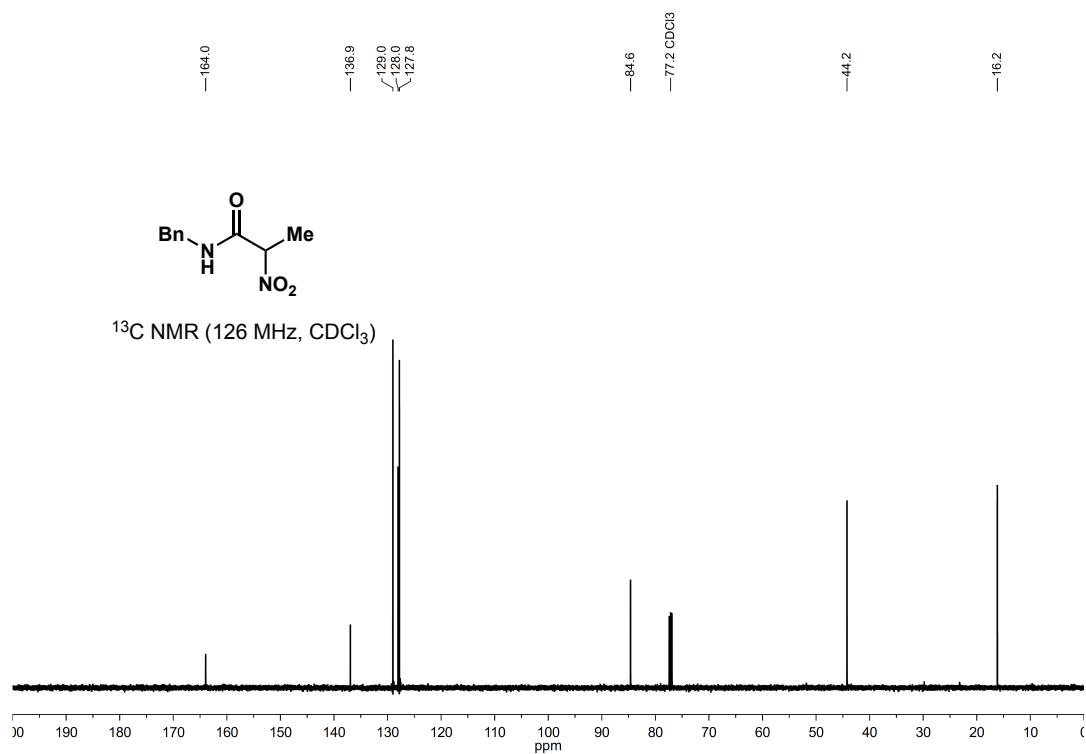
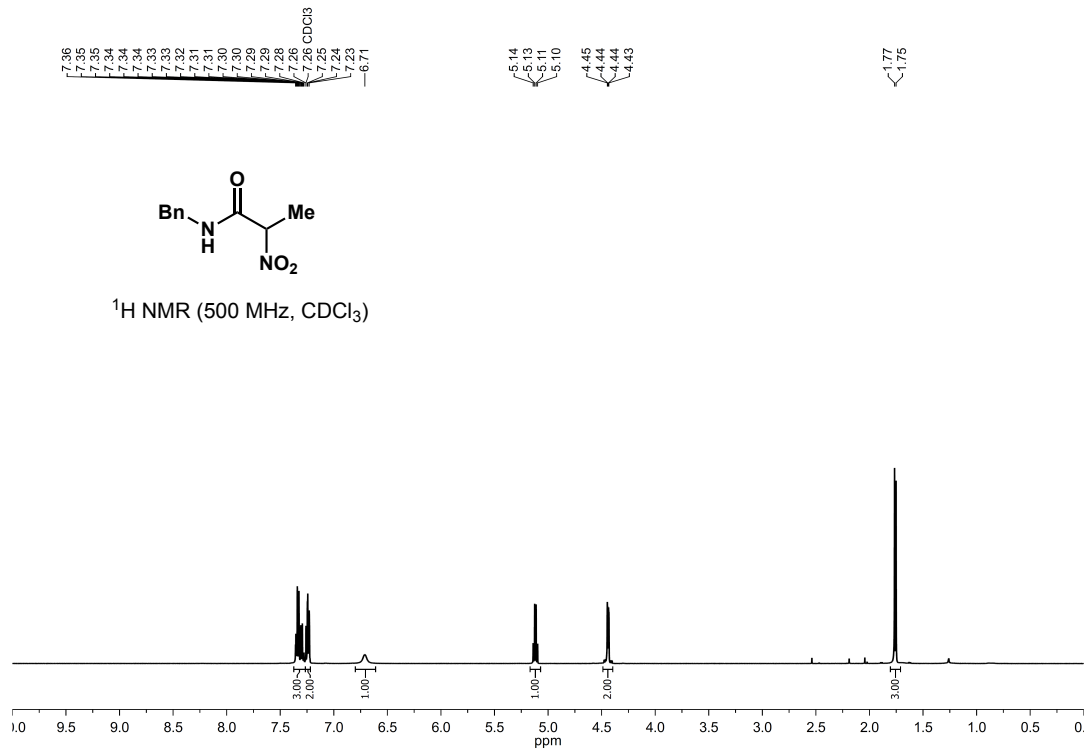


1o

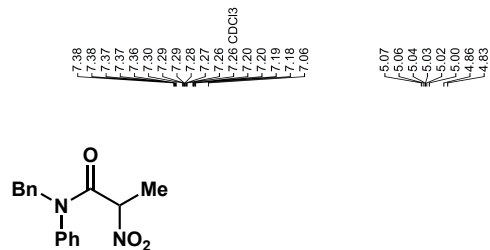
¹³C NMR (126 MHz, CDCl₃)



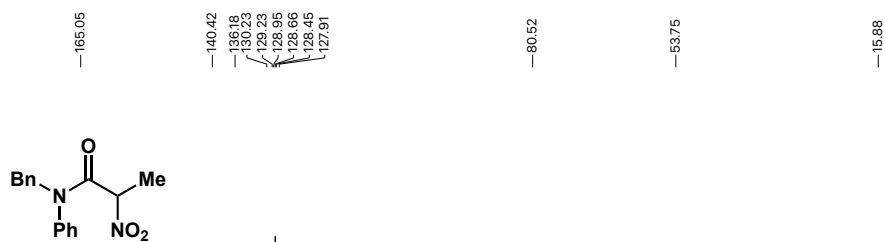
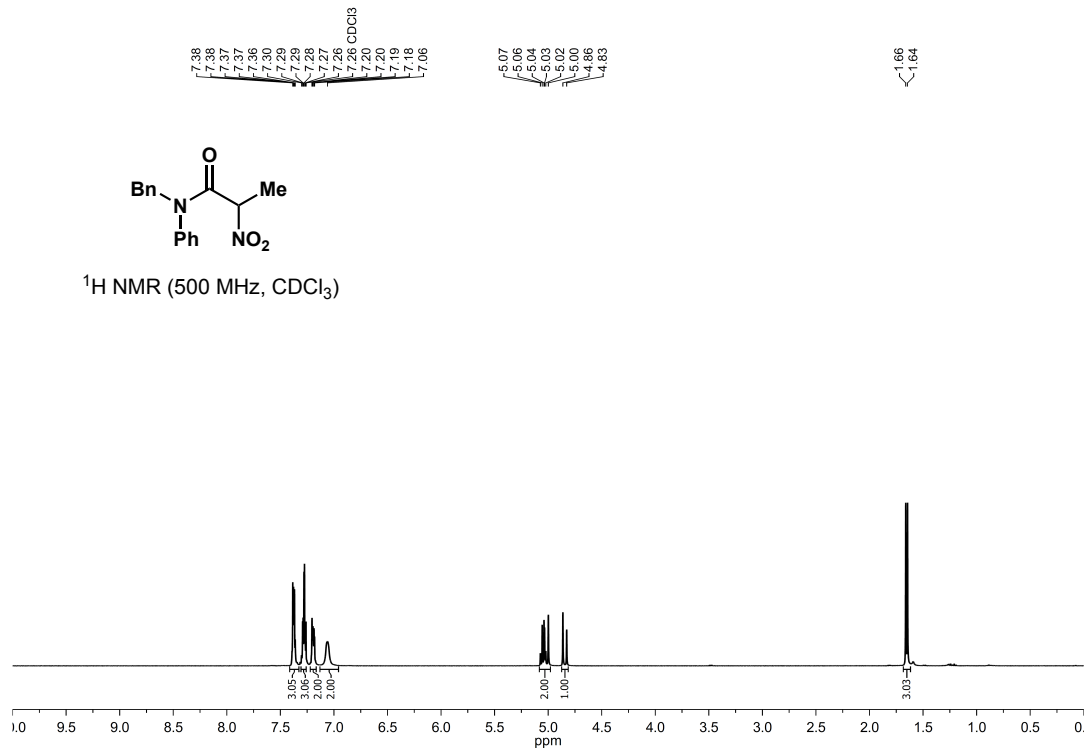
N-benzyl-2-nitropropanamide



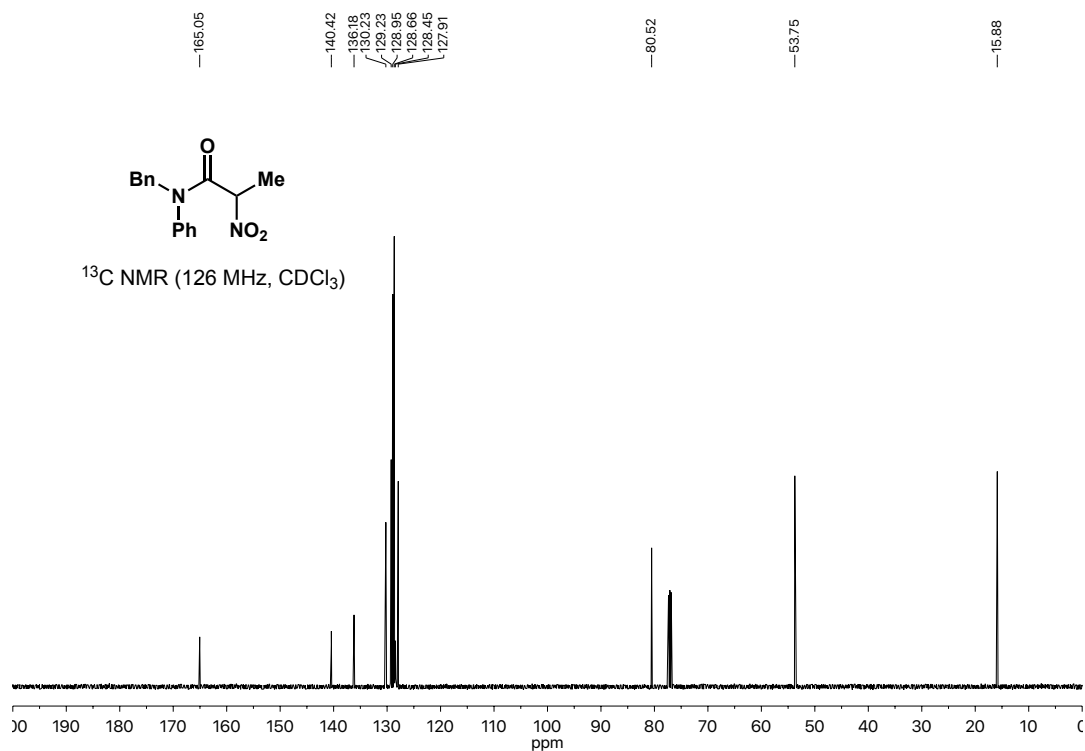
N-benzyl-2-nitro-*N*-phenylpropanamide



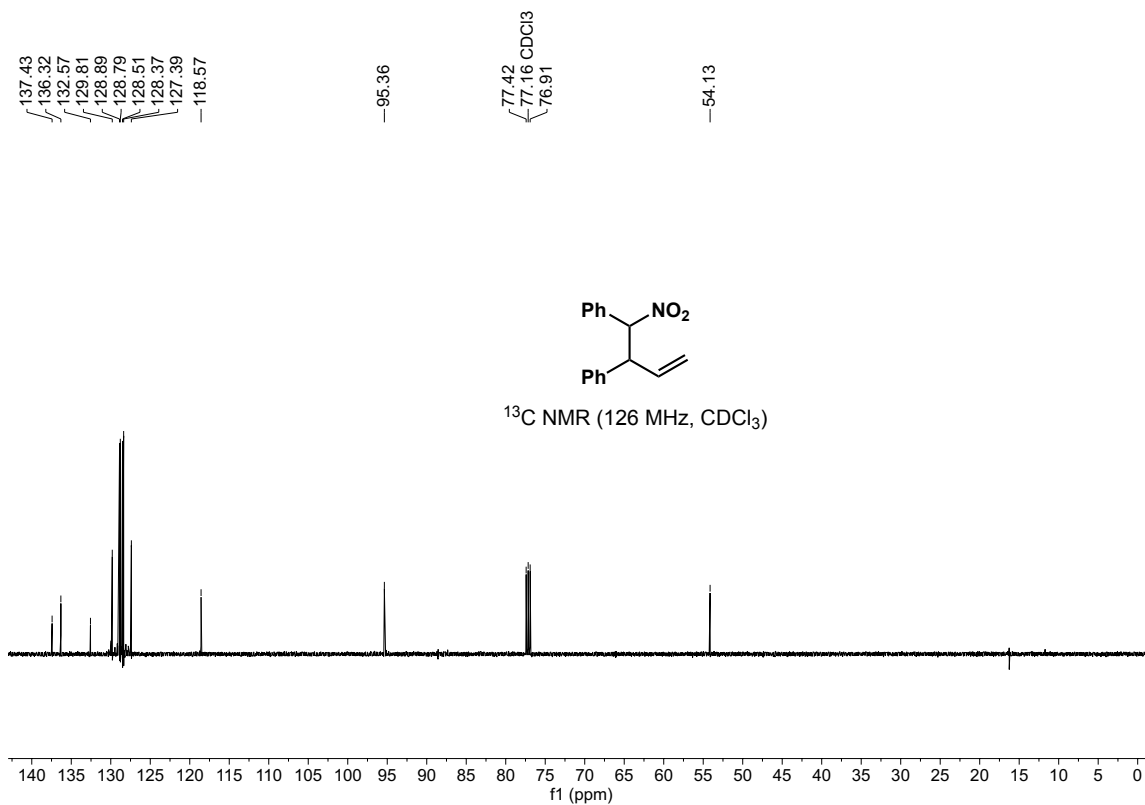
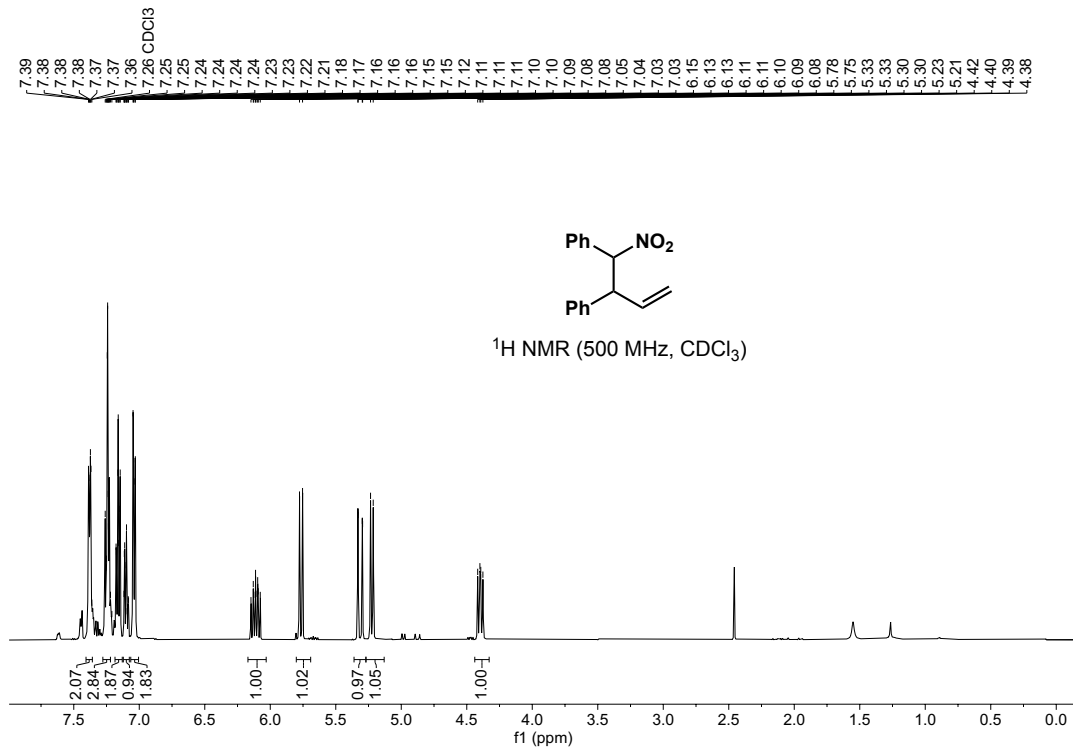
¹H NMR (500 MHz, CDCl₃)



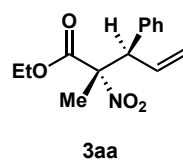
¹³C NMR (126 MHz, CDCl₃)



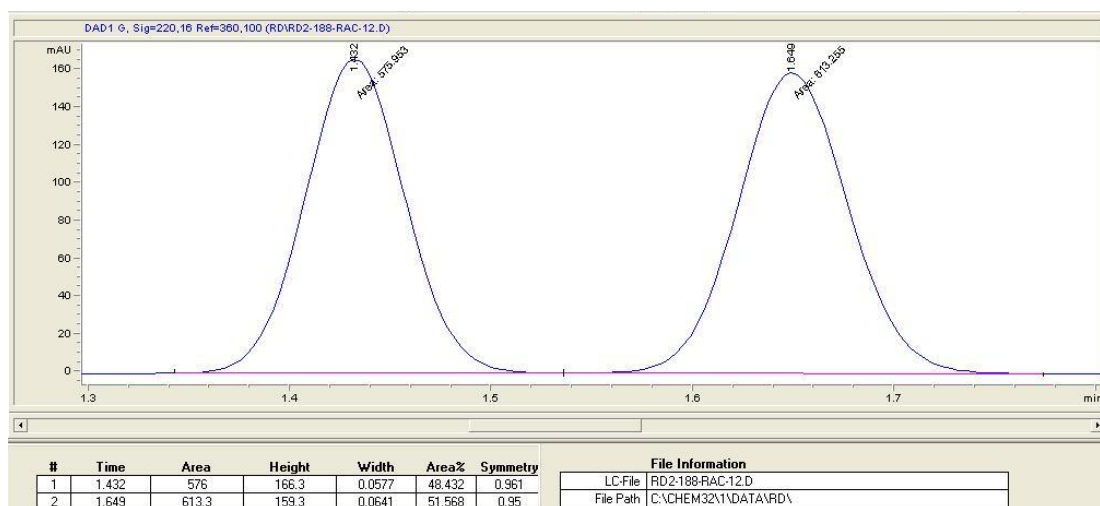
(1-nitrobut-3-ene-1,2-diyl)dibenzene (8)



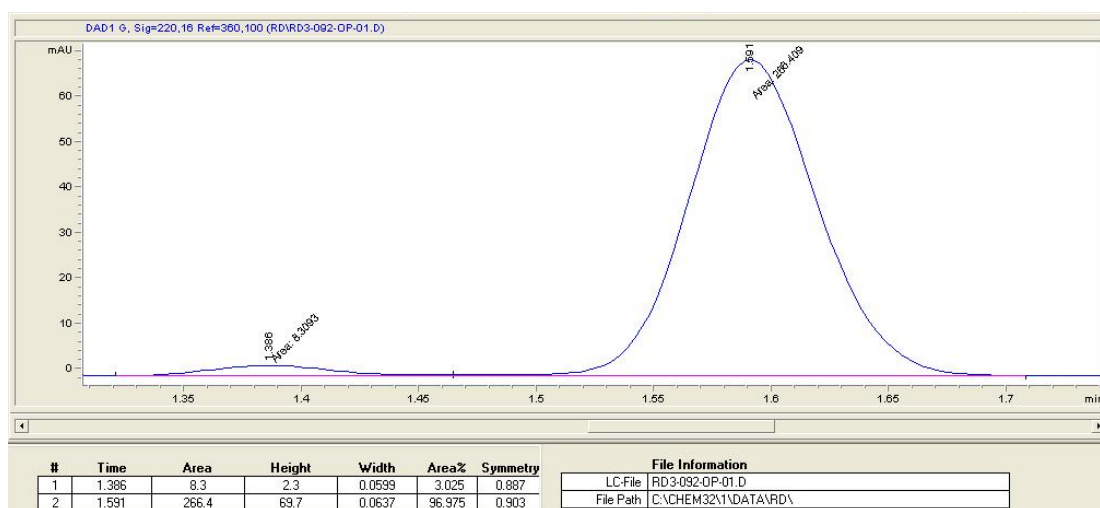
12. SFC Traces

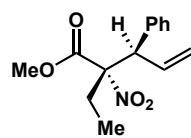


Racemic



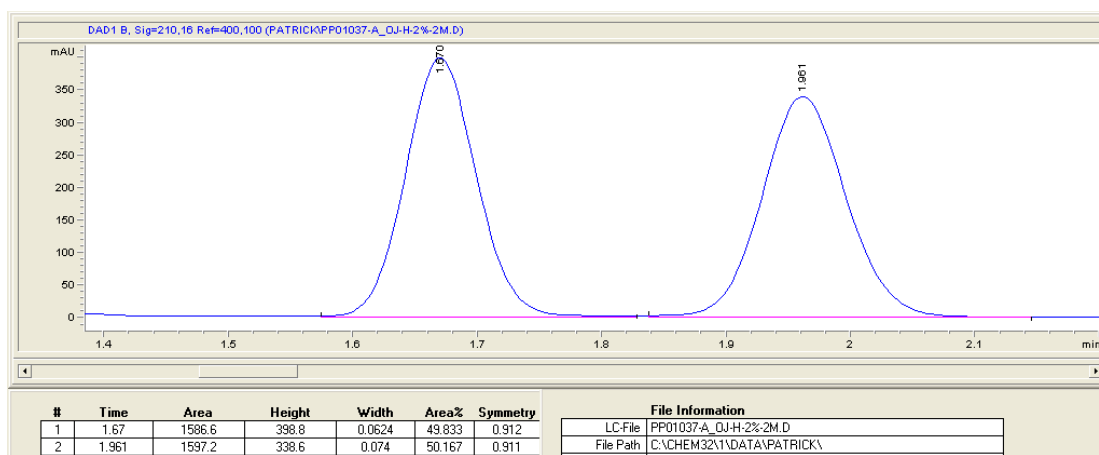
Enantiomerically Enriched



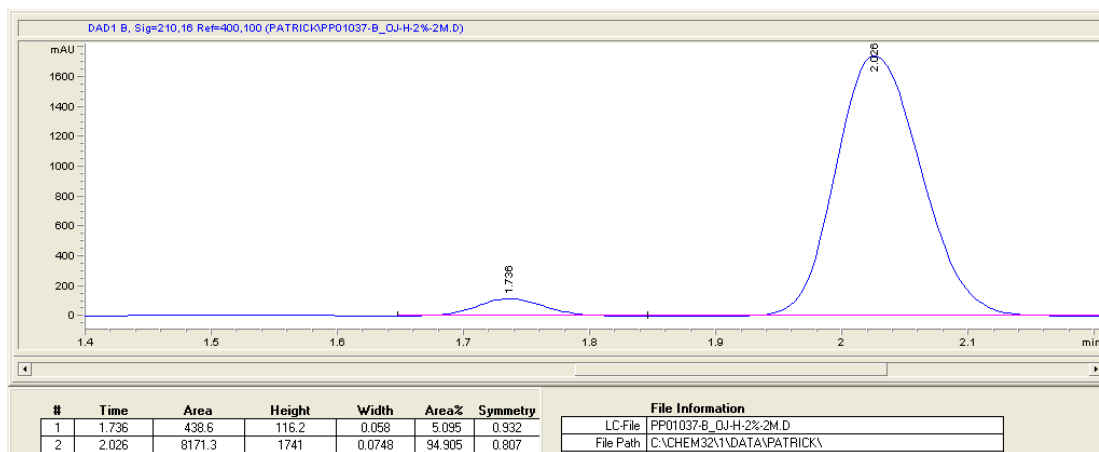


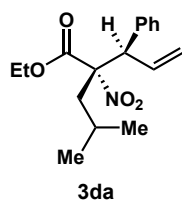
3ba

Racemic

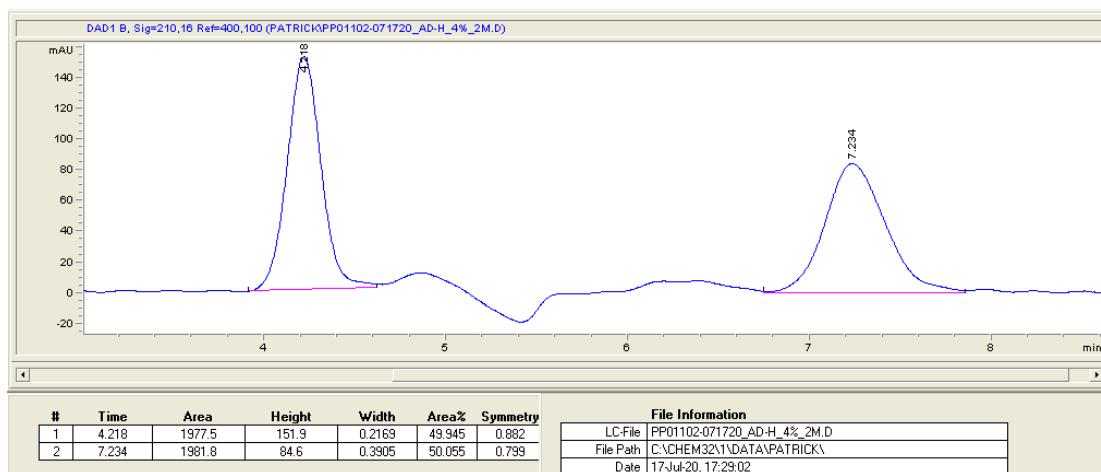


Enantiomerically Enriched

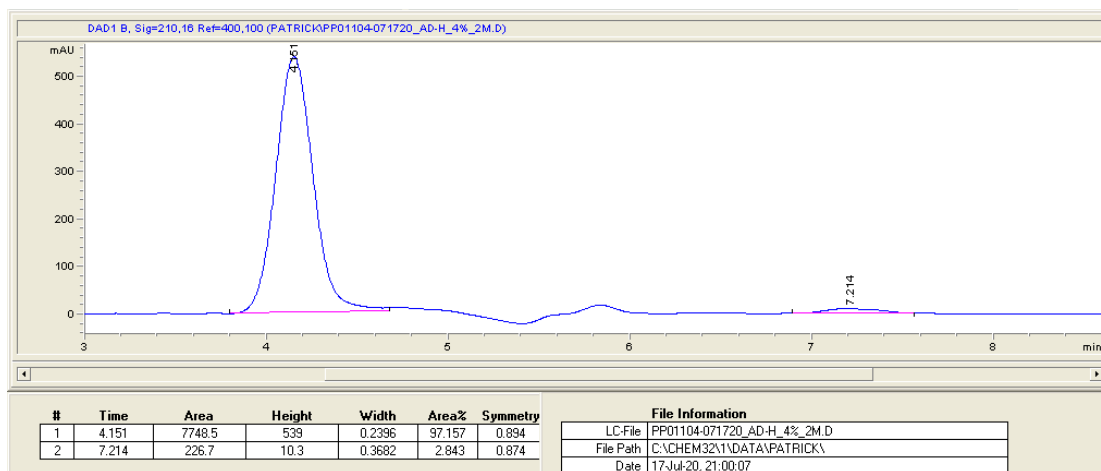


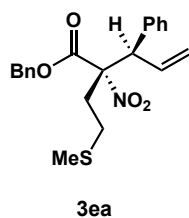


Racemic

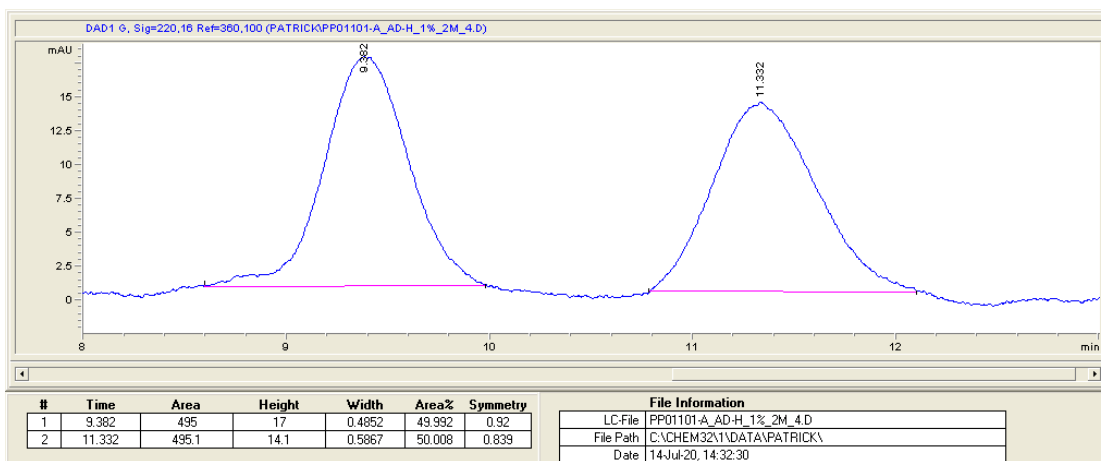


Enantiomerically Enriched

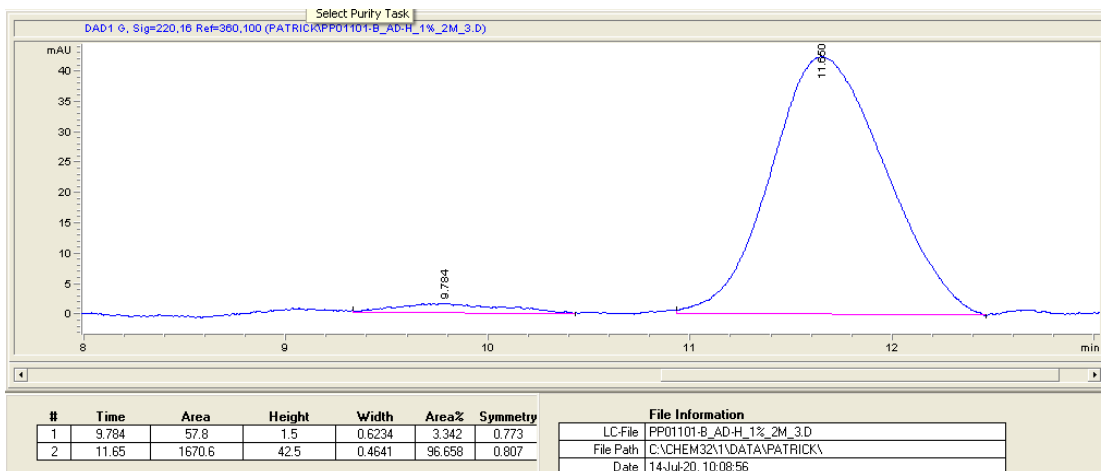


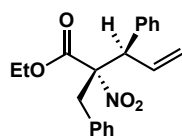


Racemic



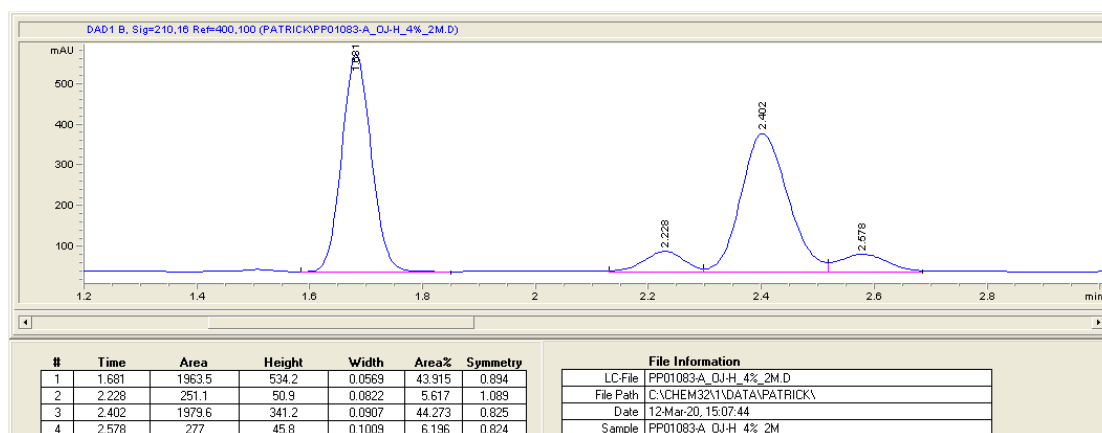
Enantiomerically Enriched



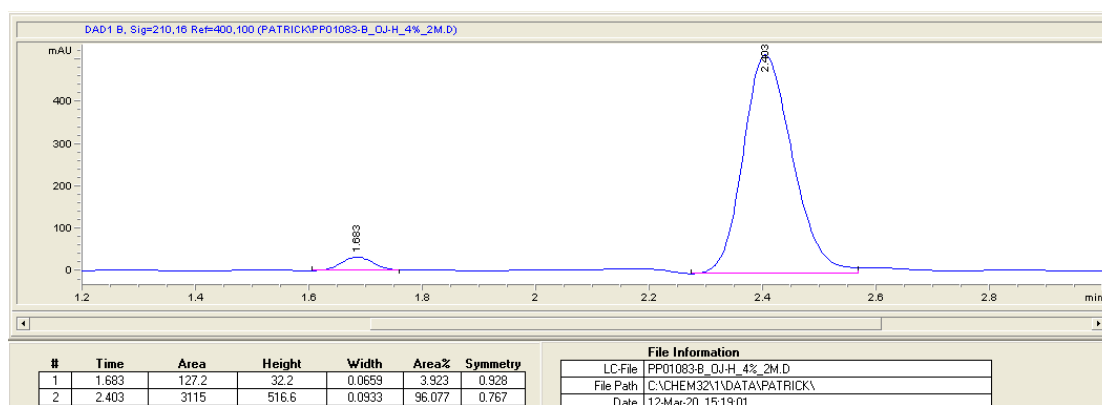


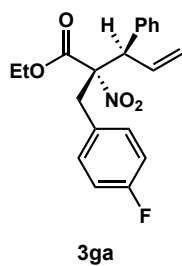
3fa

Racemic

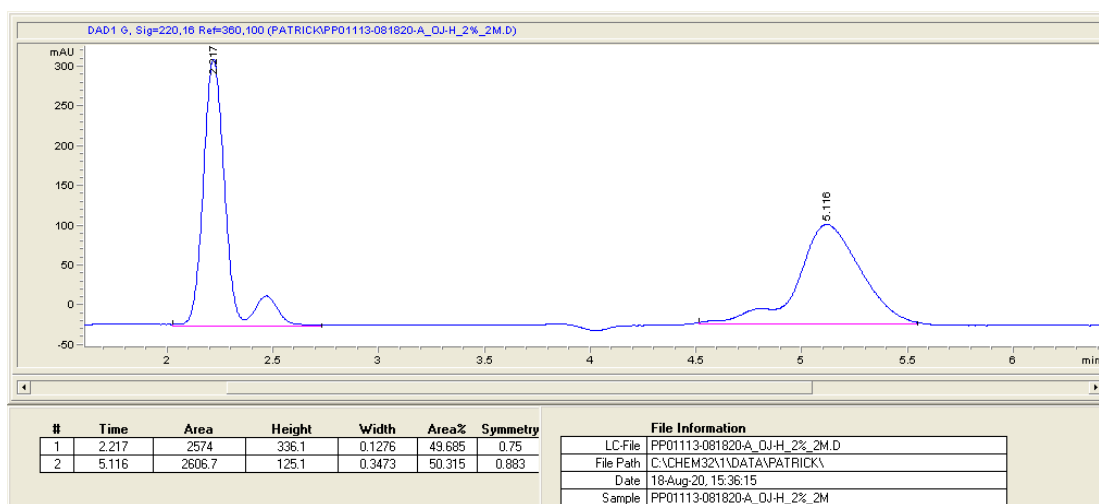


Enantiomerically Enriched

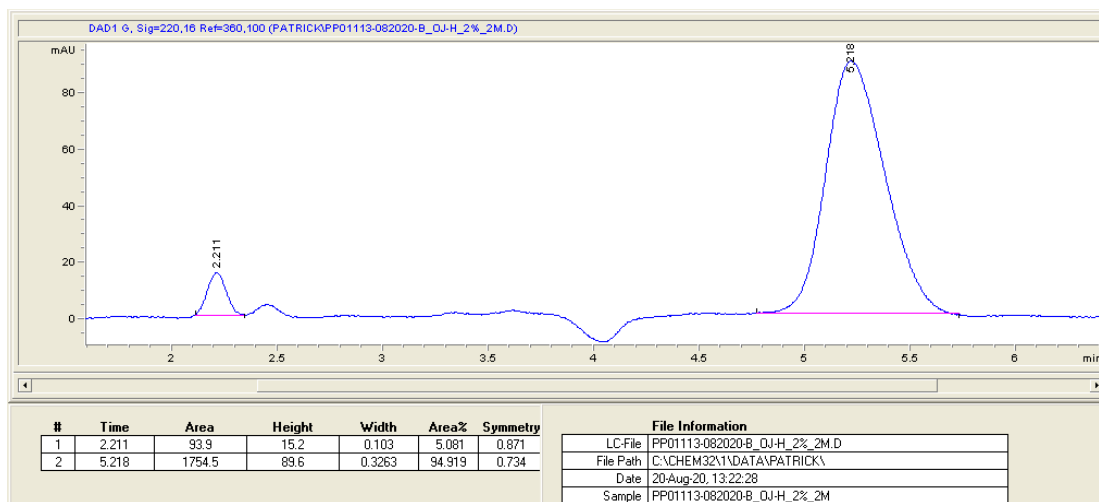


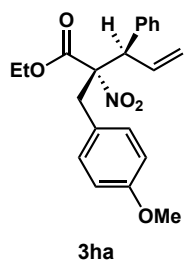


Racemic

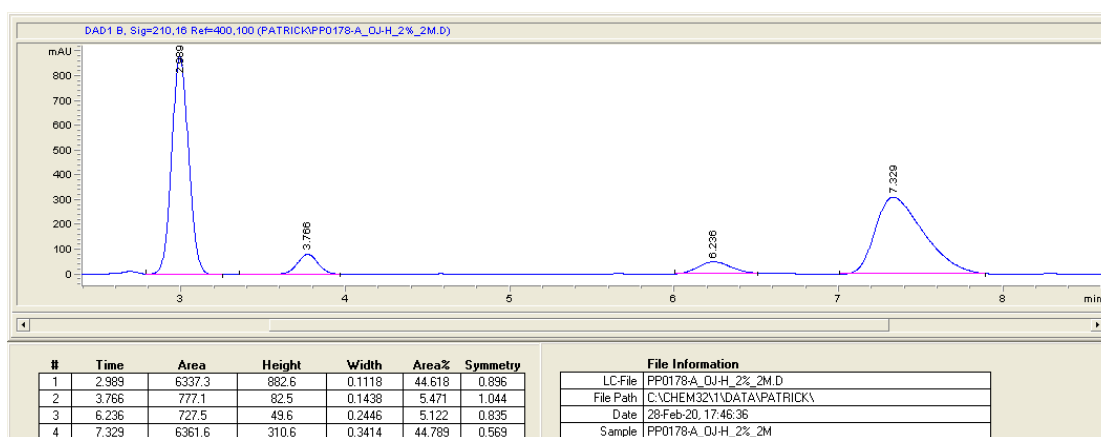


Enantiomerically Enriched

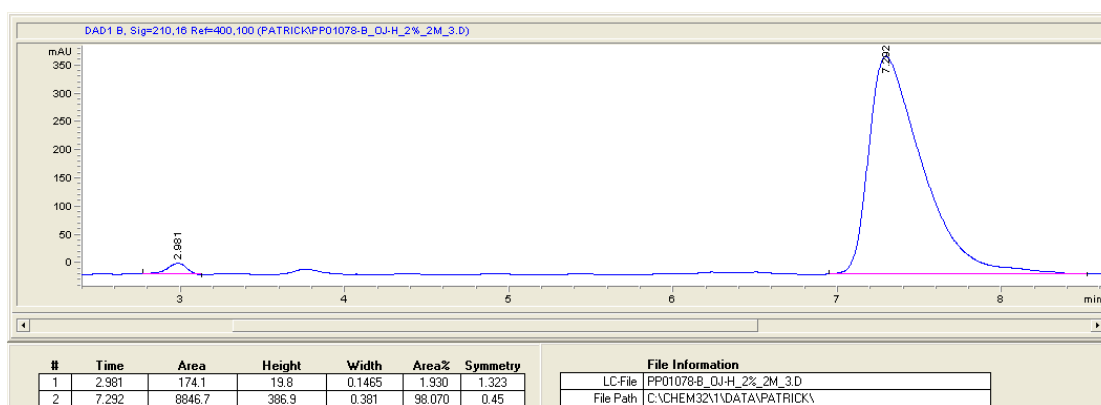


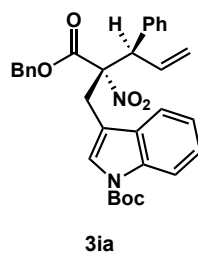


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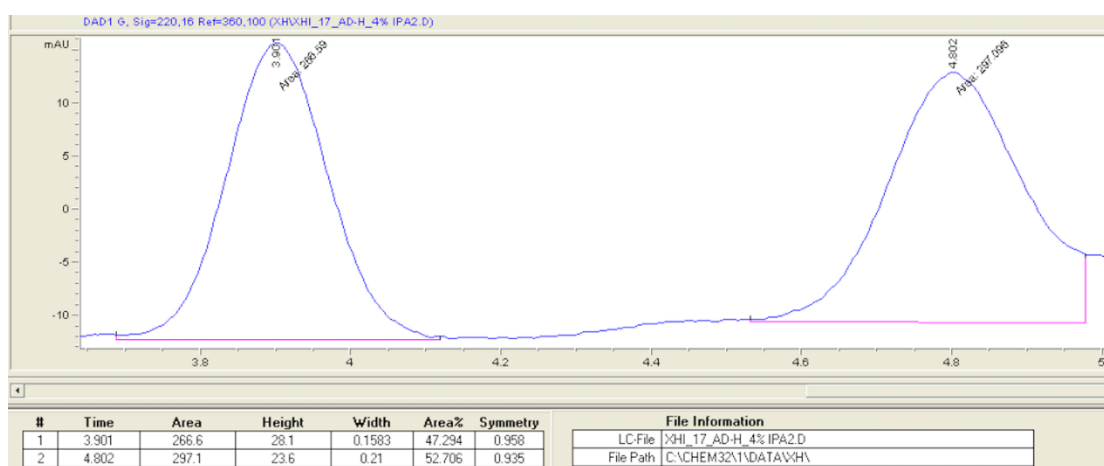


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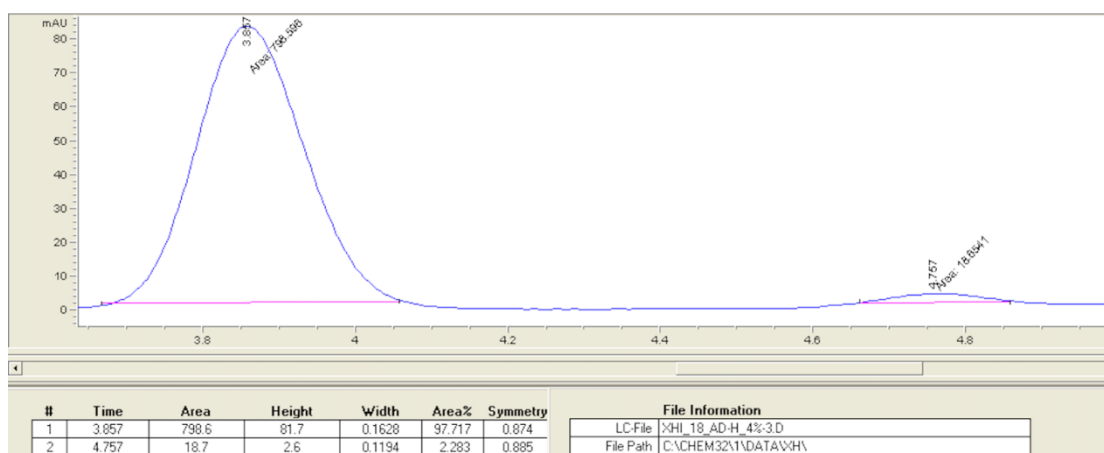


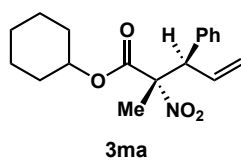


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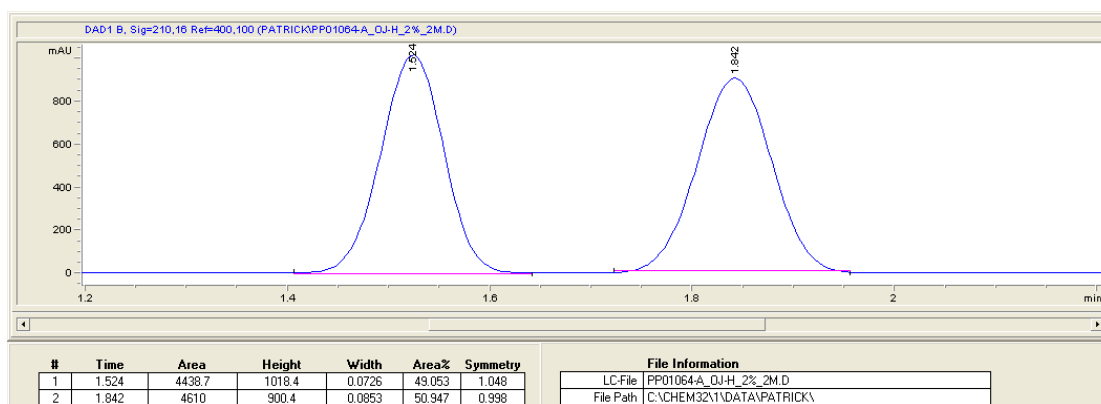


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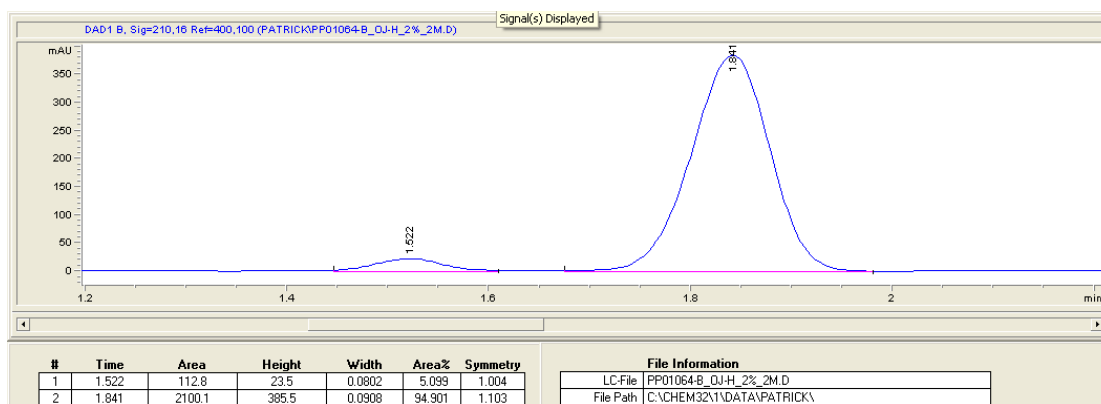


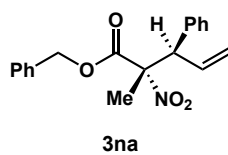


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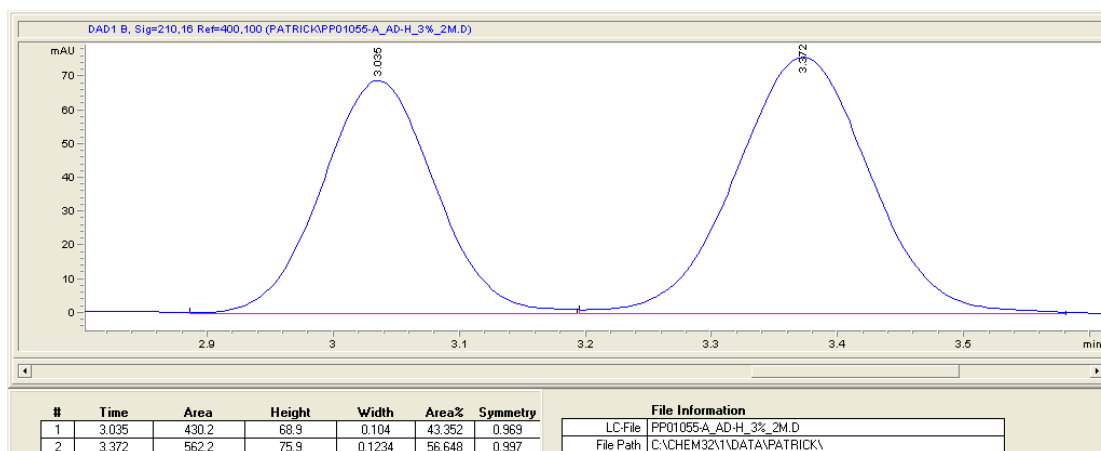


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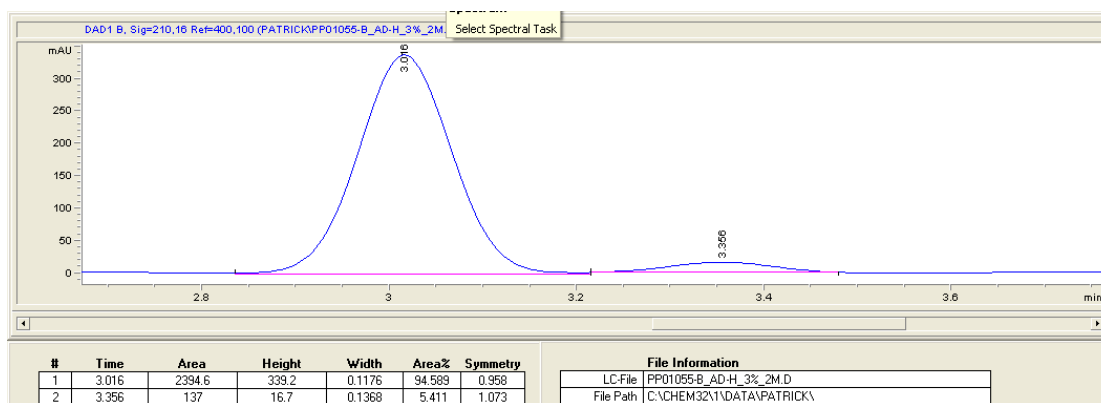


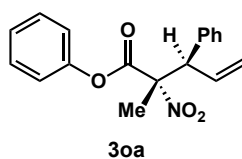


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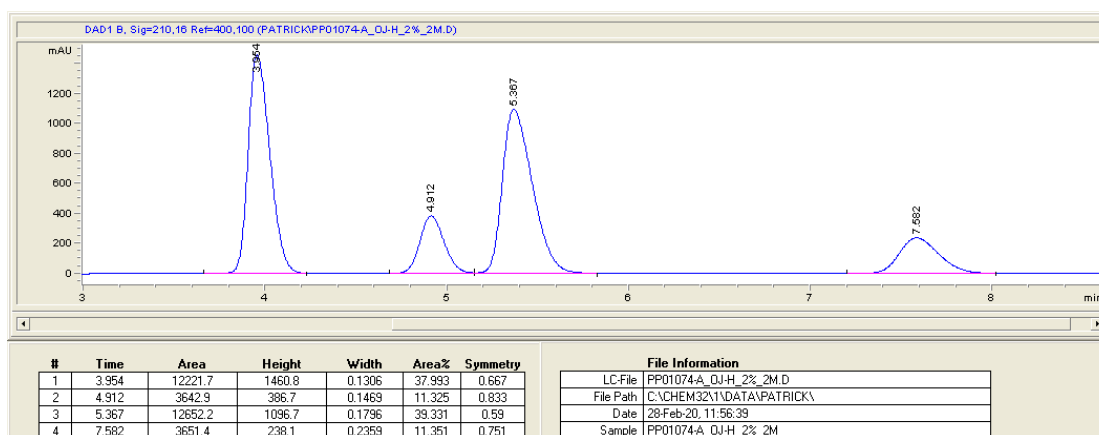


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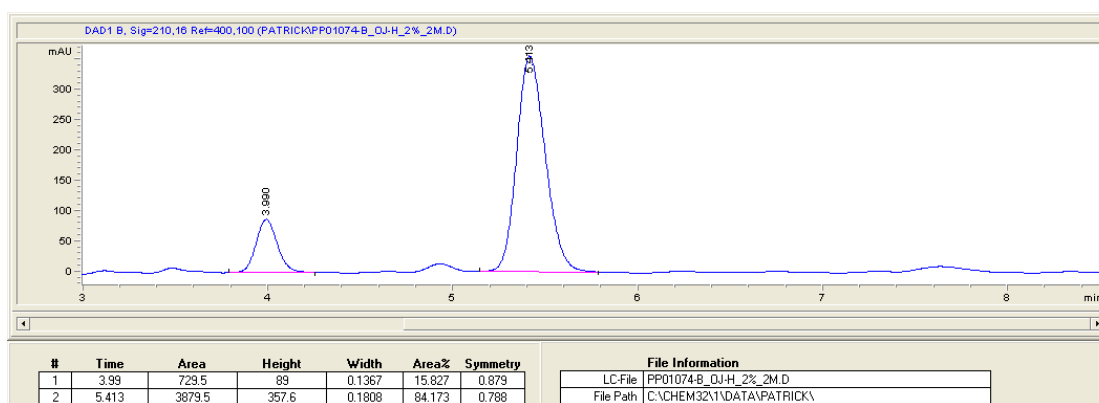


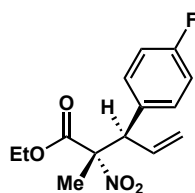


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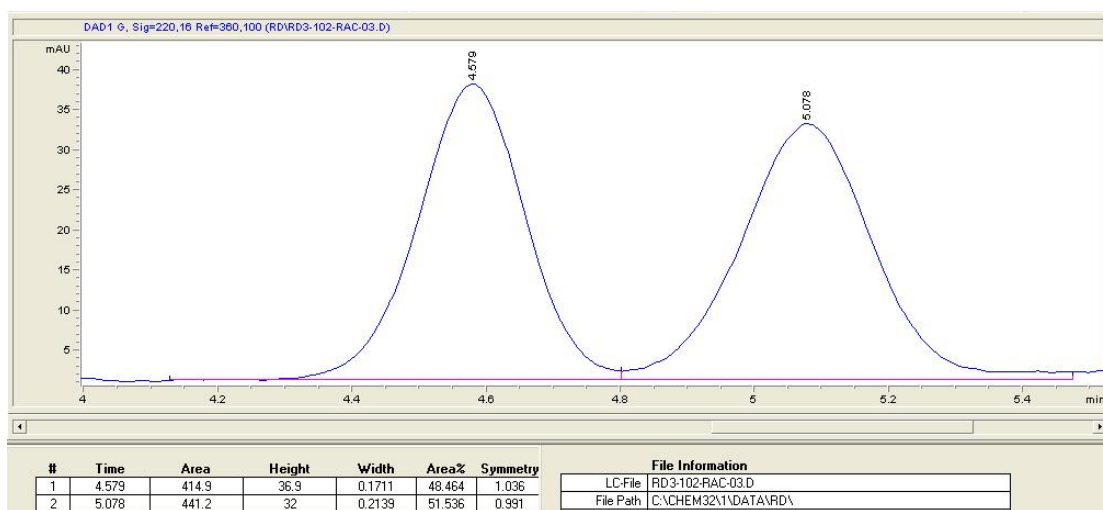
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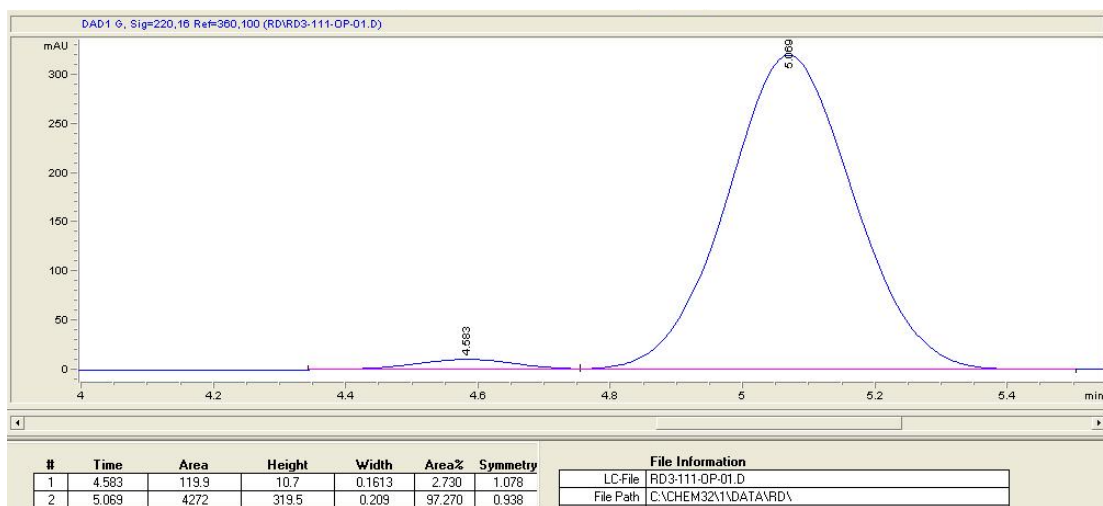


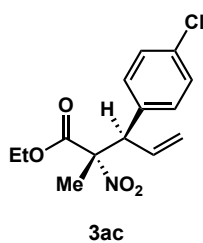
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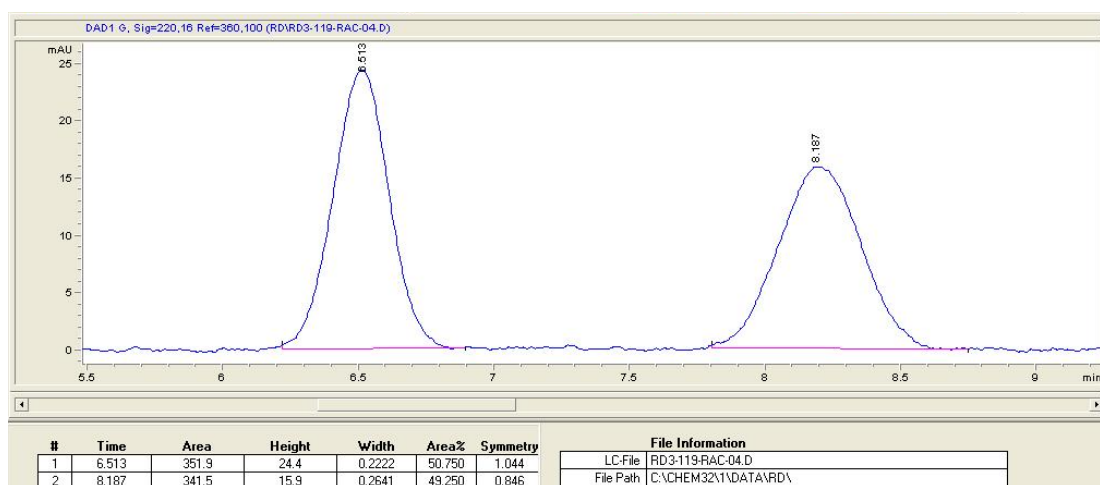


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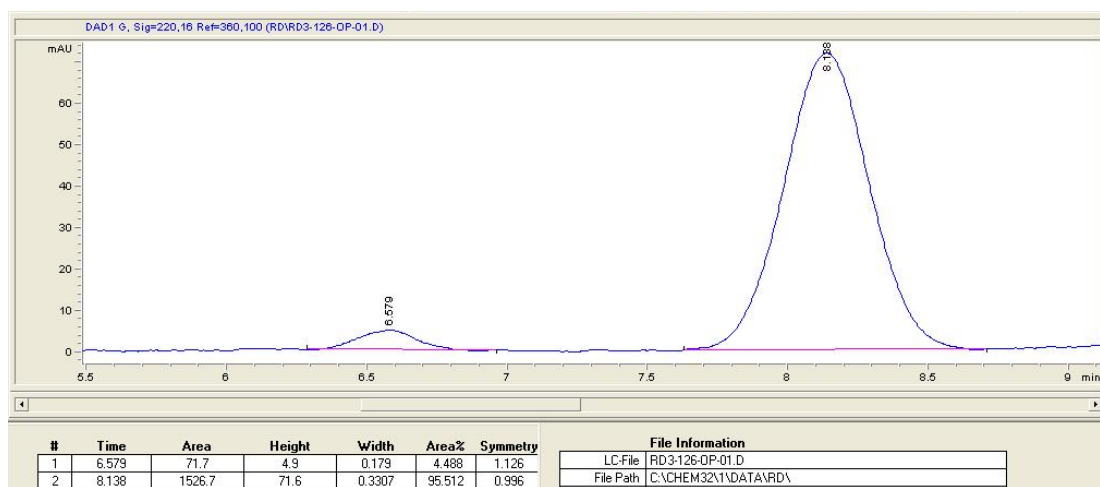


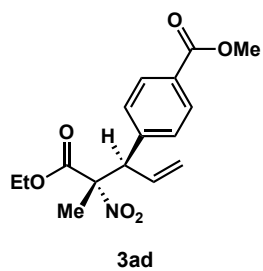


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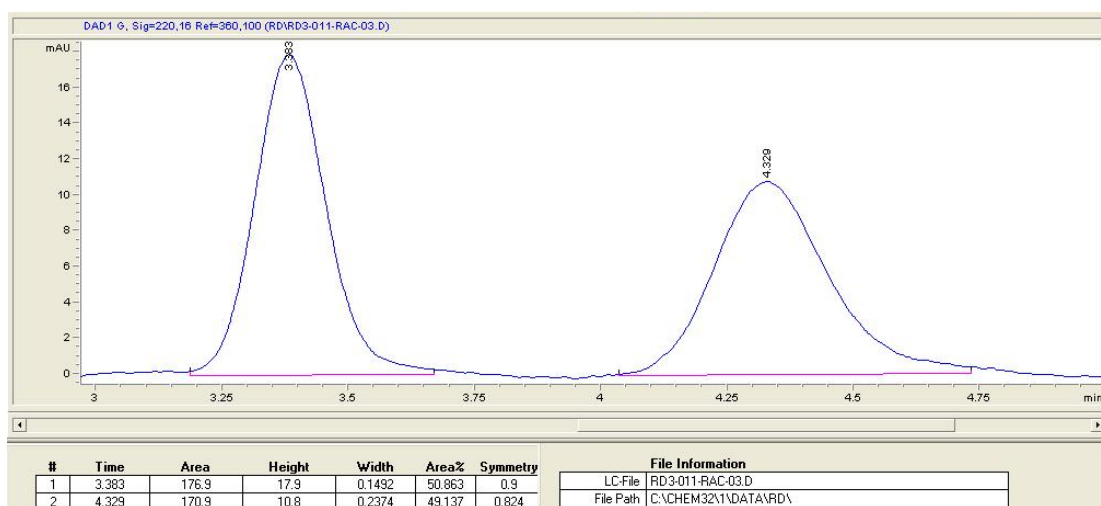


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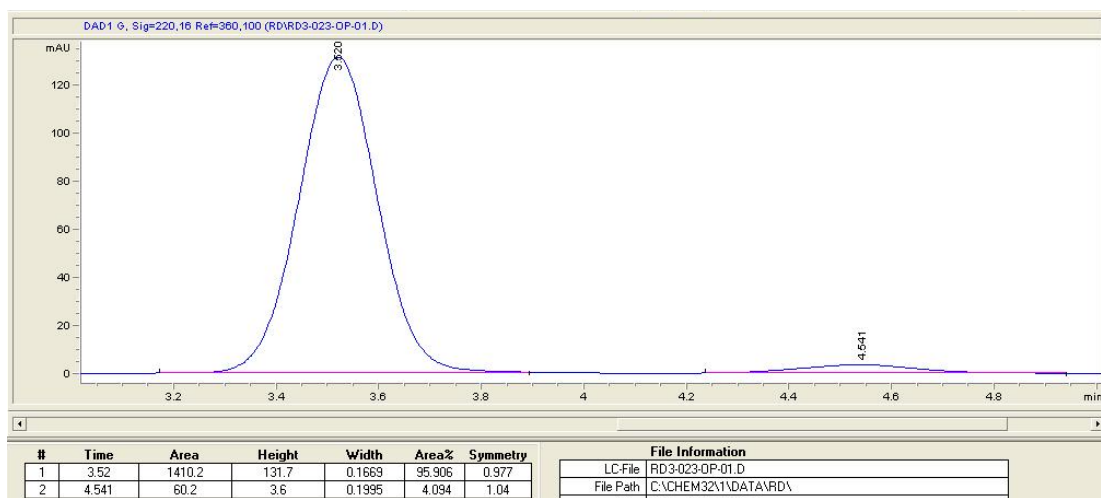


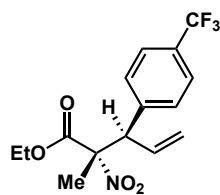


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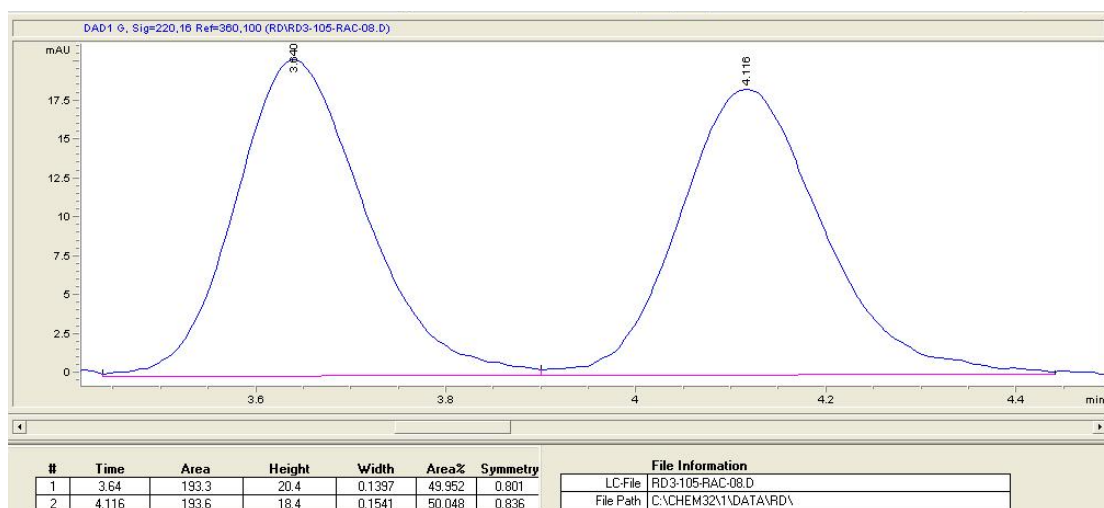
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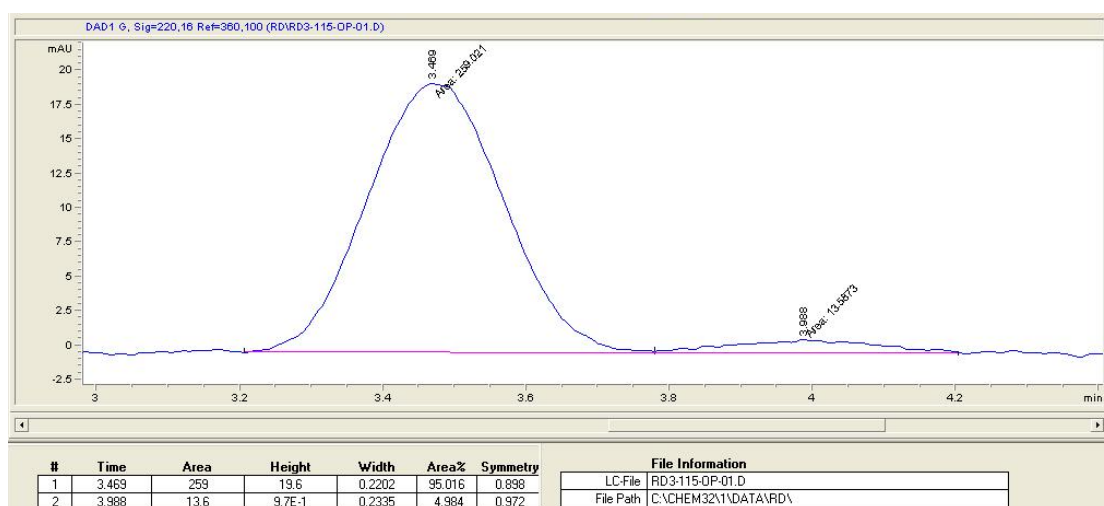


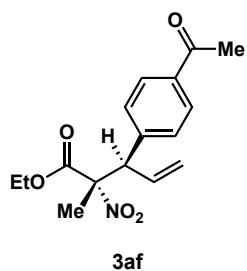
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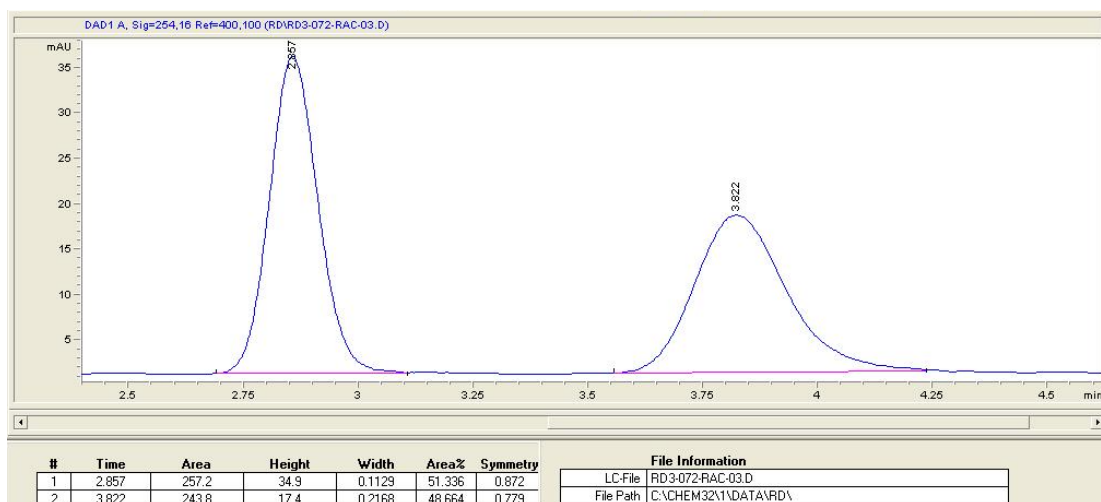


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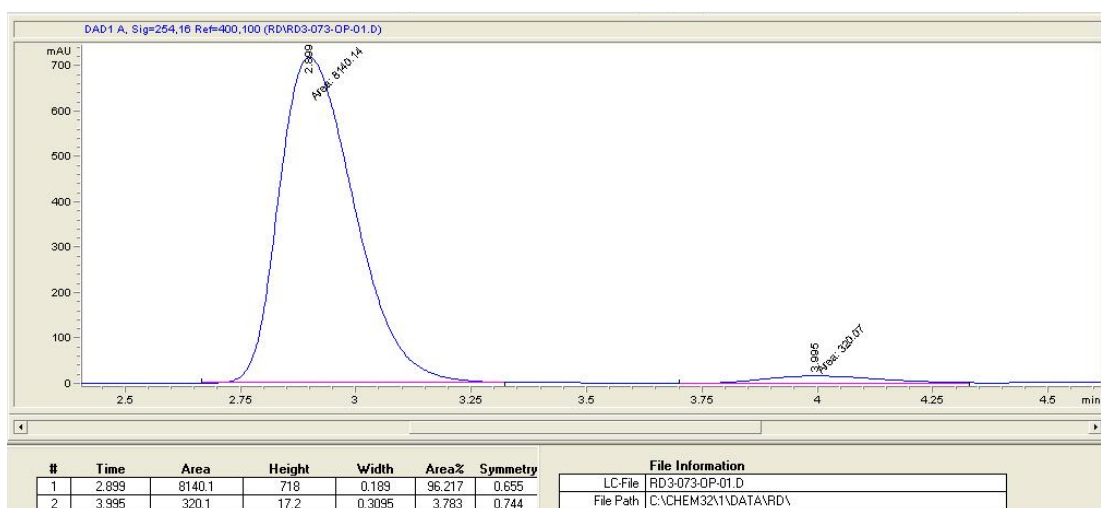


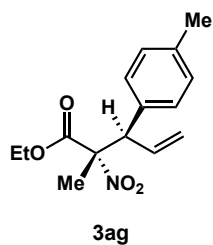


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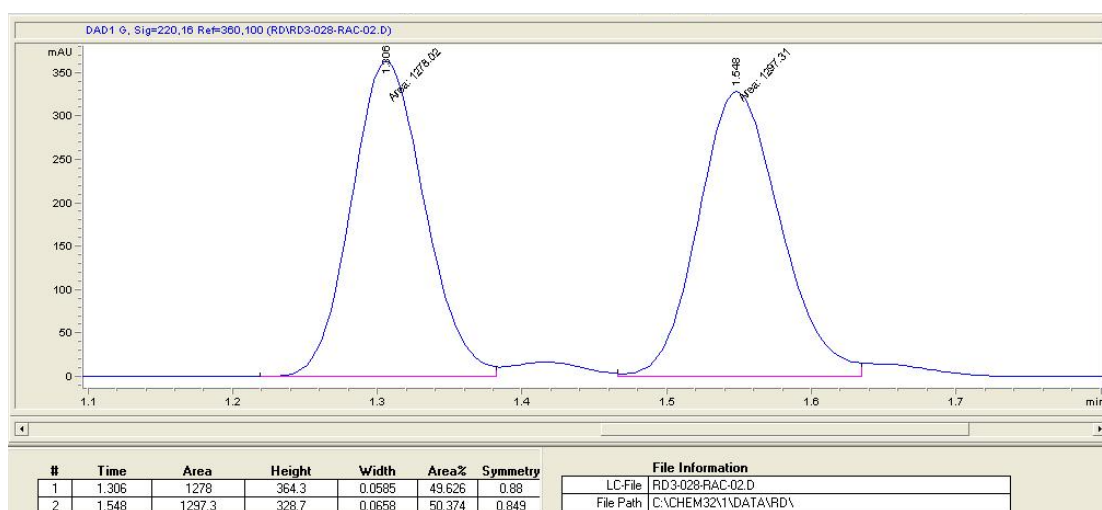


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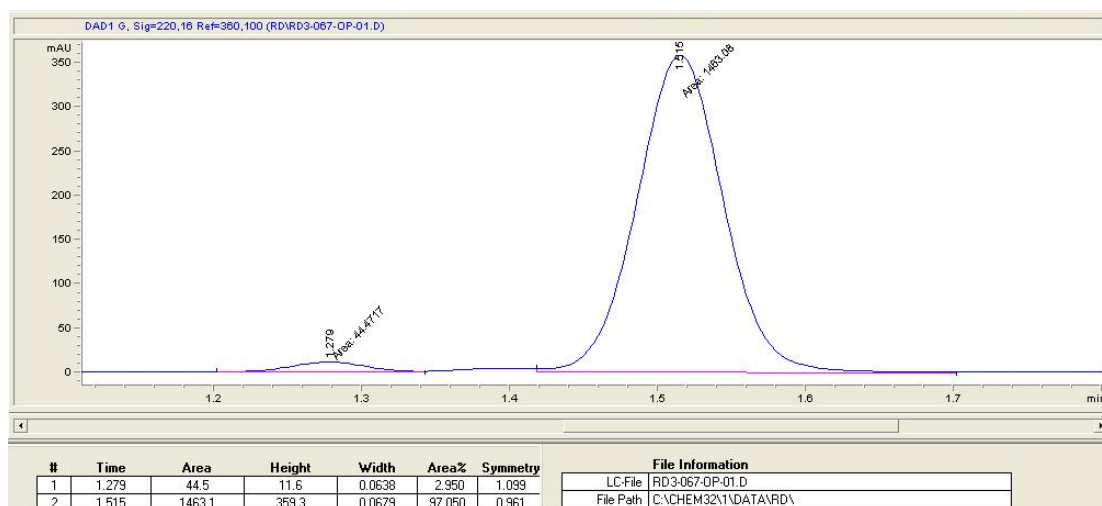


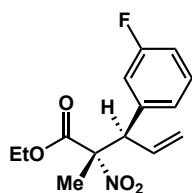


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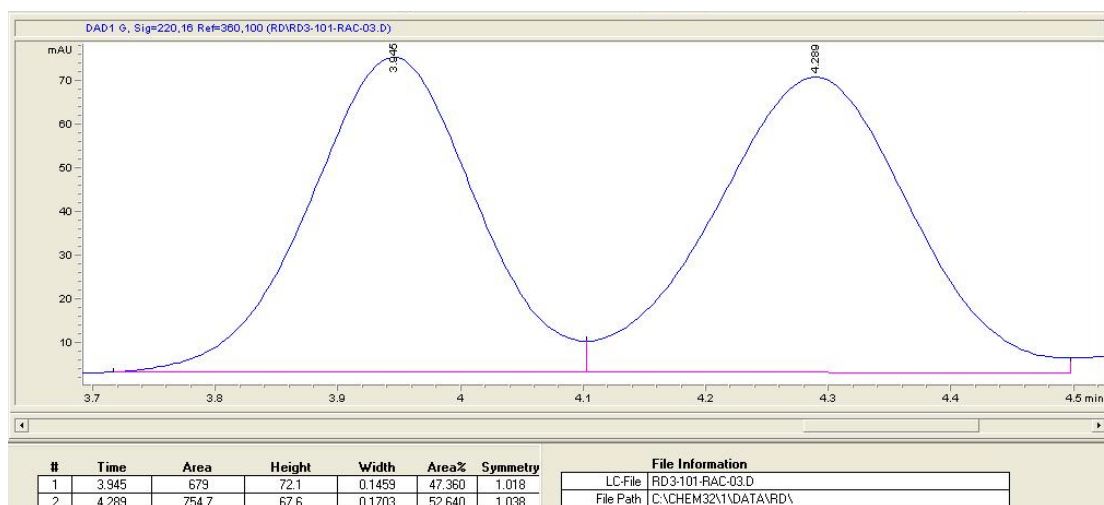
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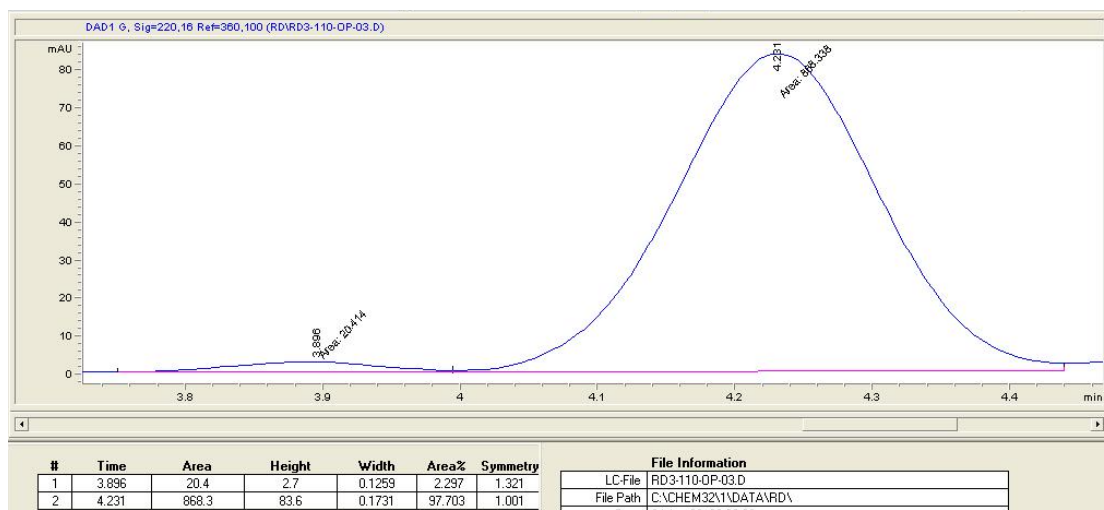


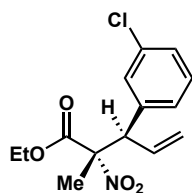
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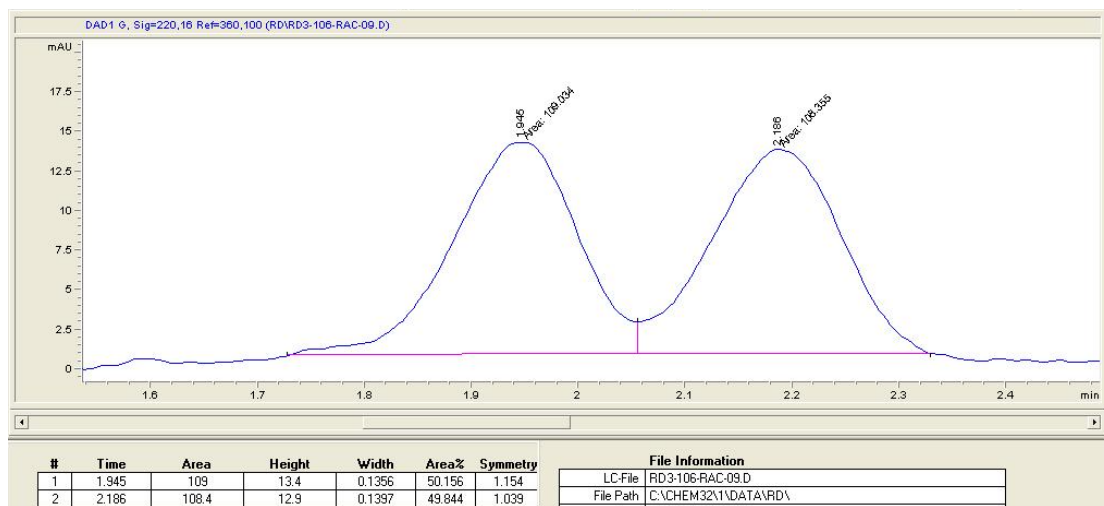
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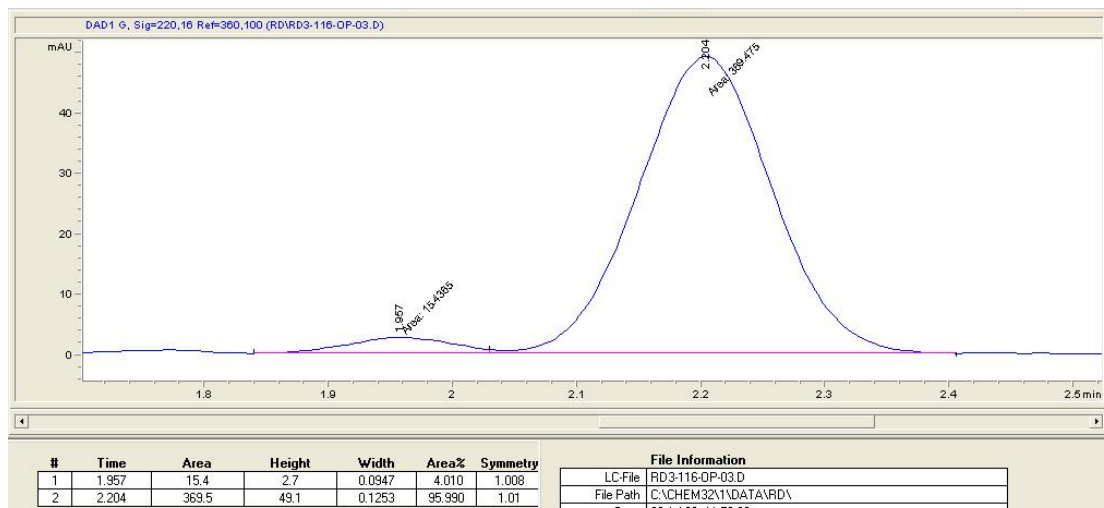


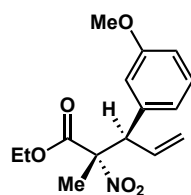
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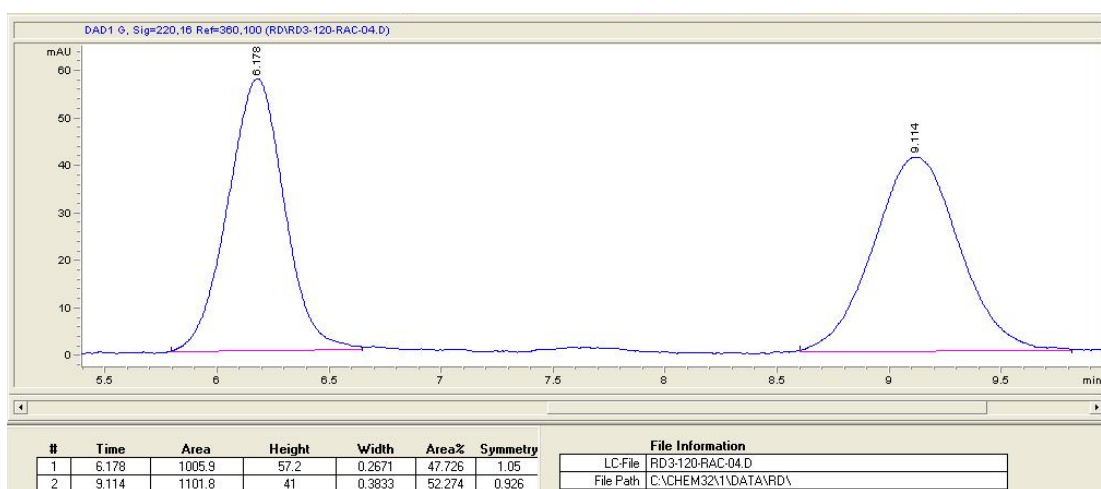
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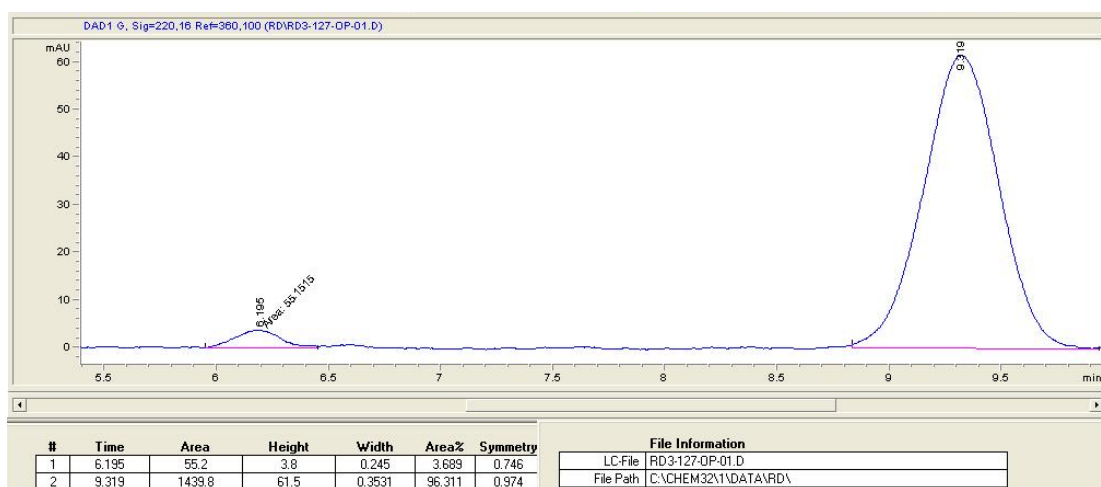


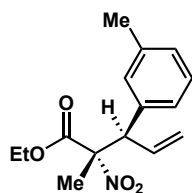
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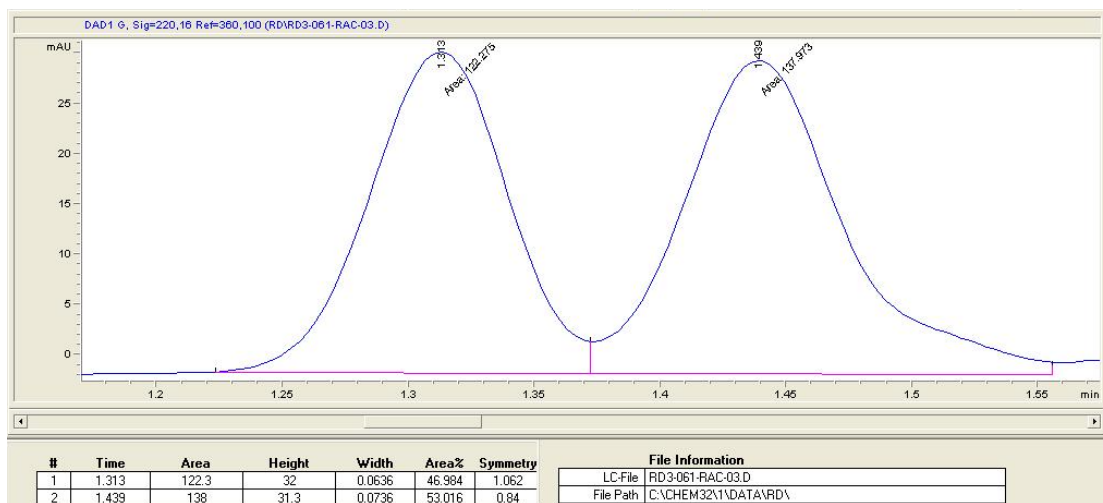
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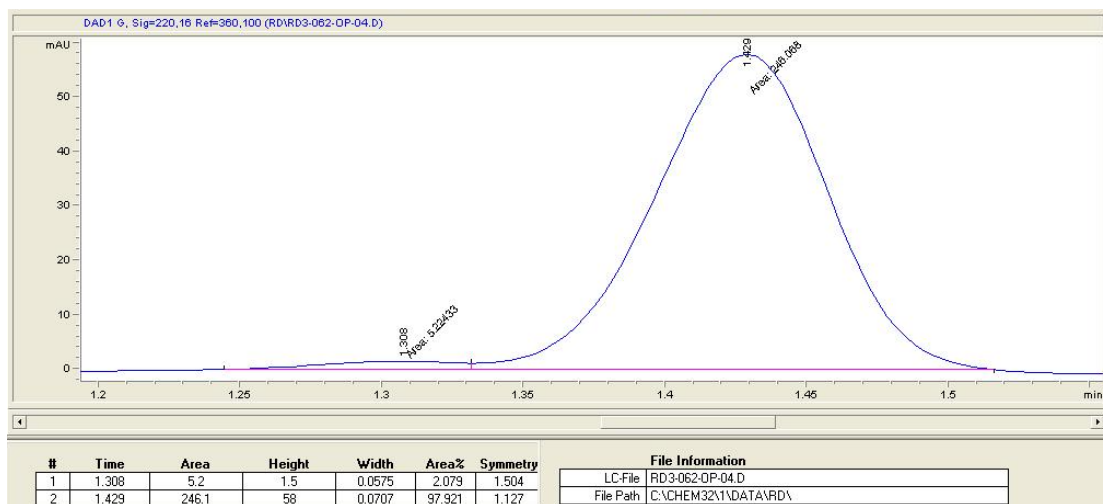


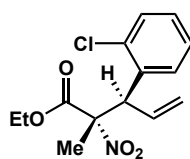
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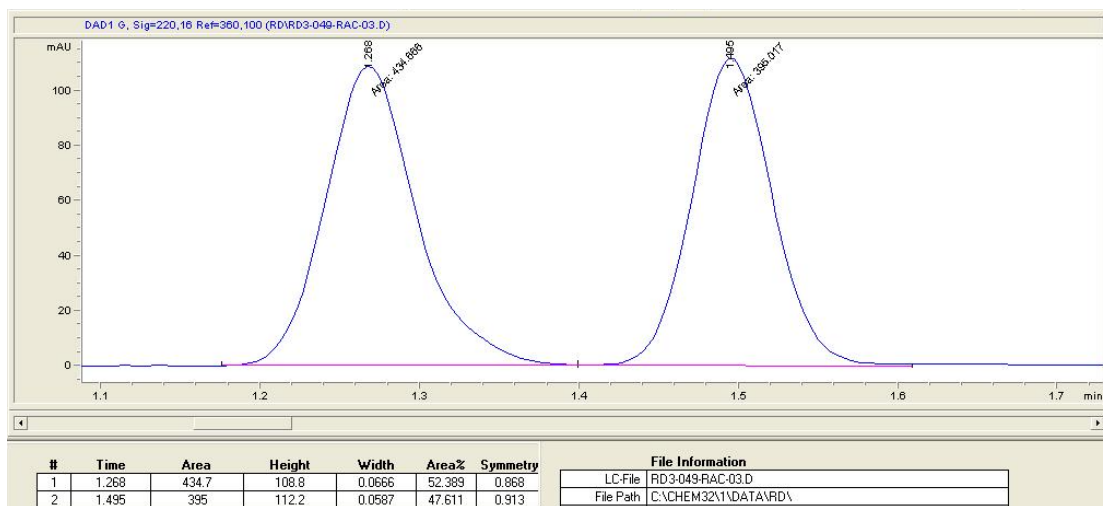
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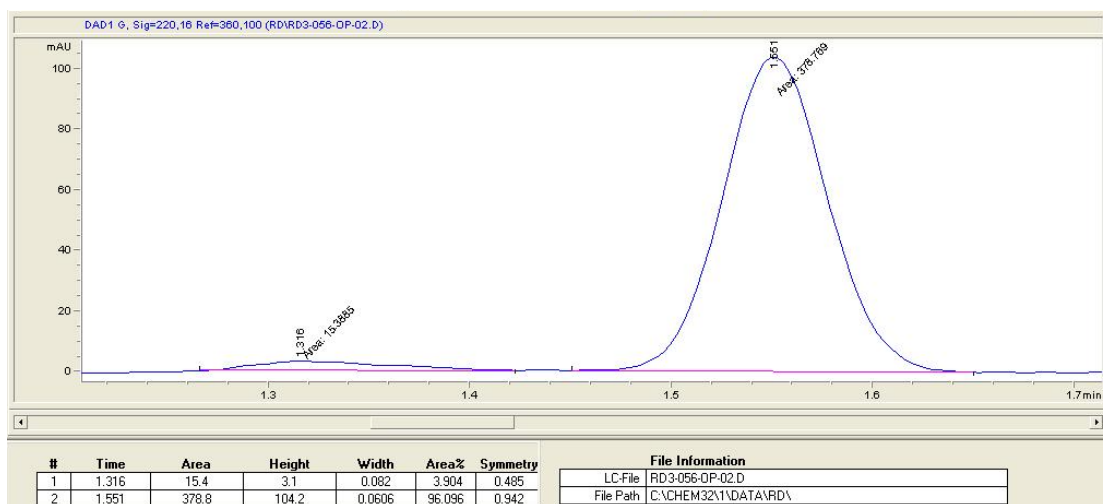


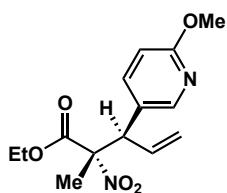
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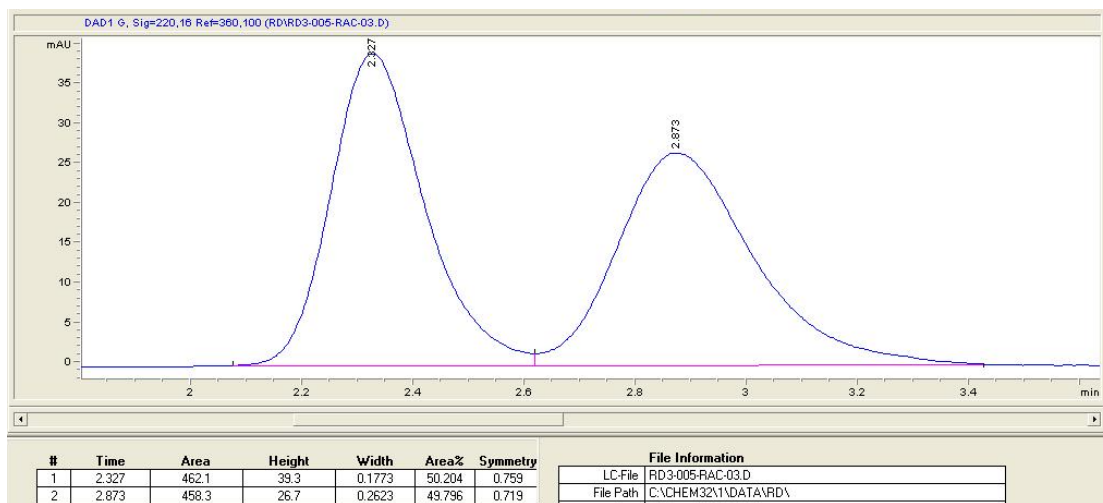
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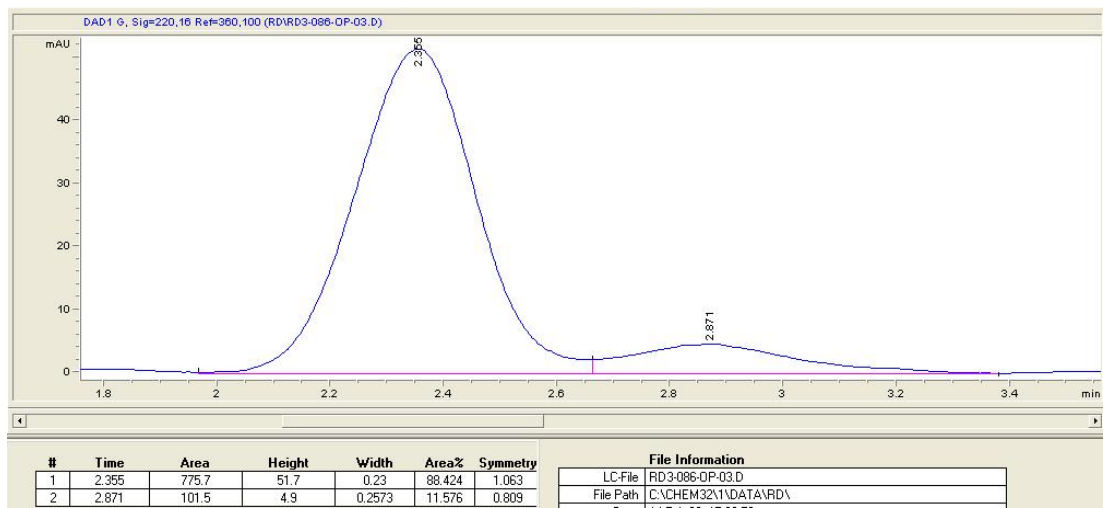


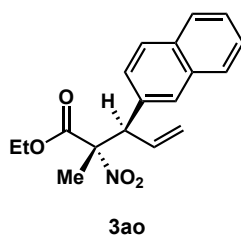
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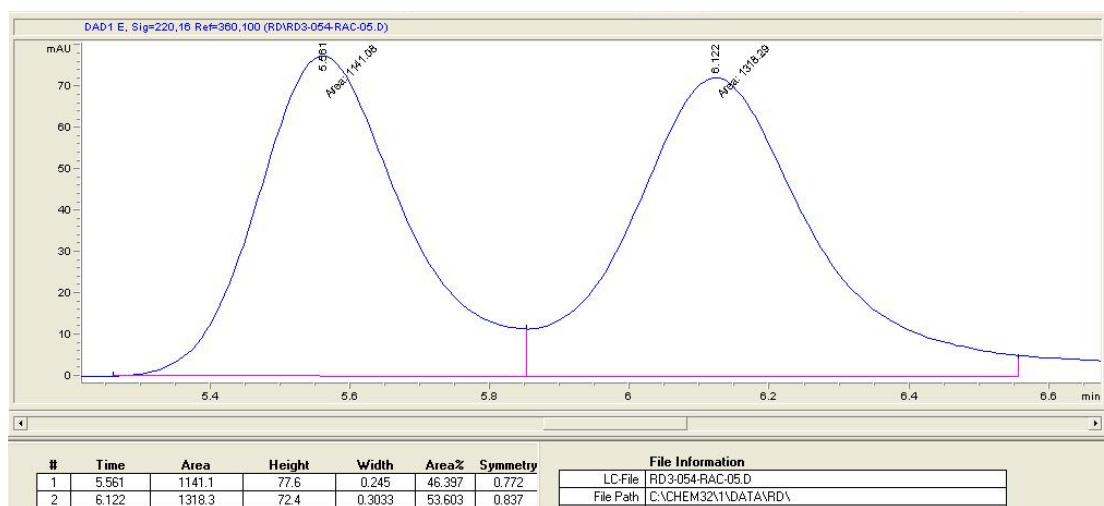


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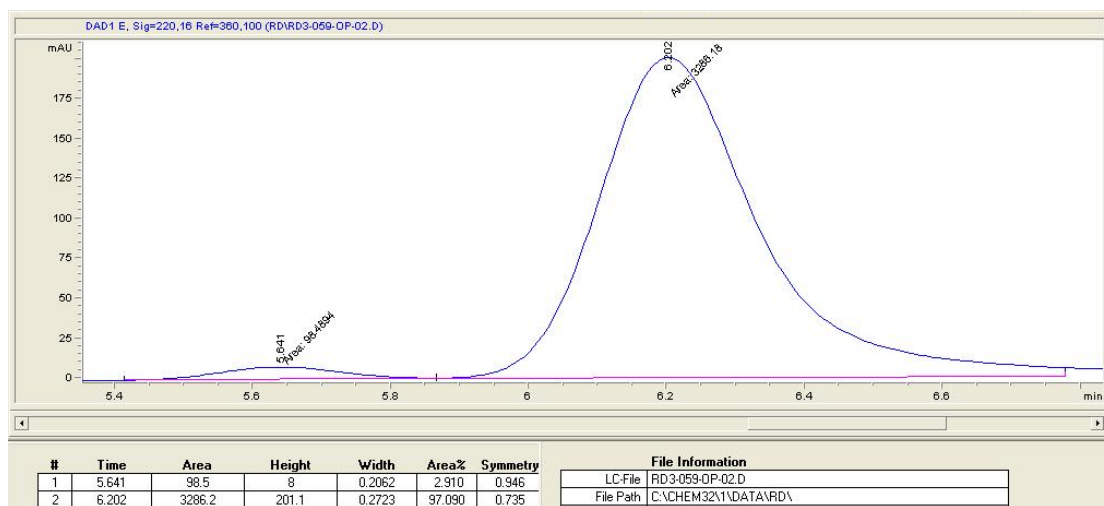


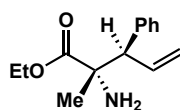


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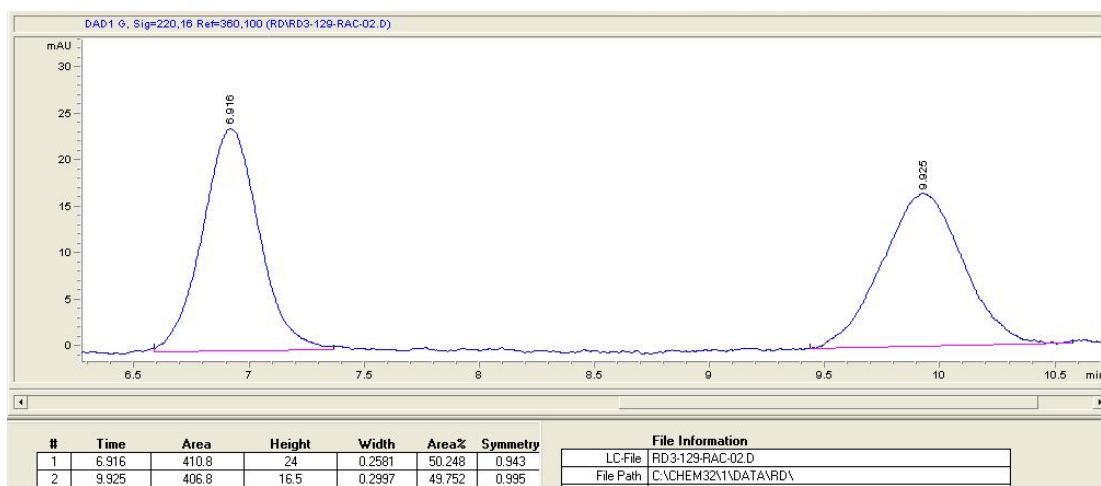
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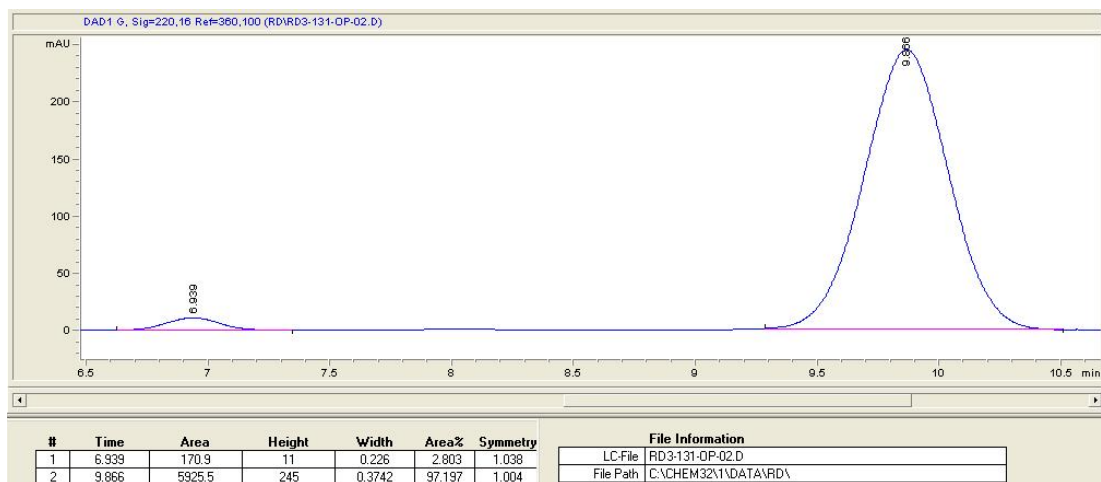


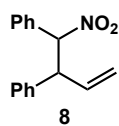
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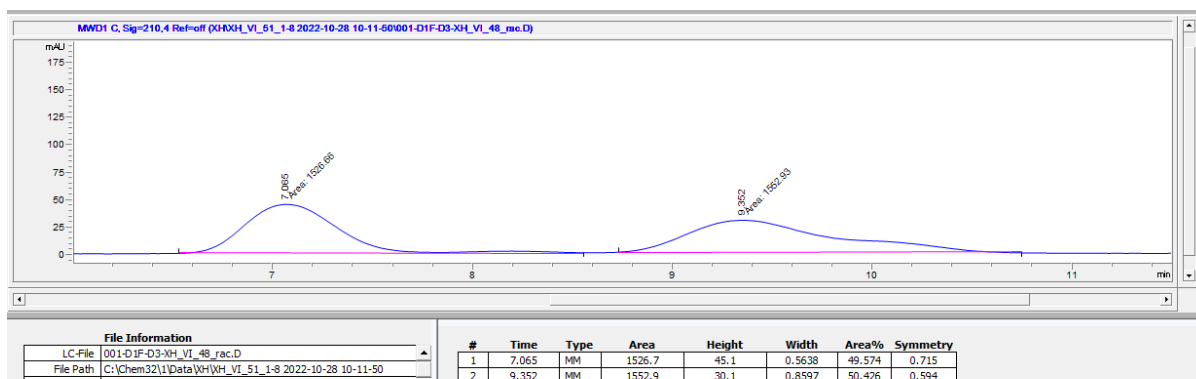


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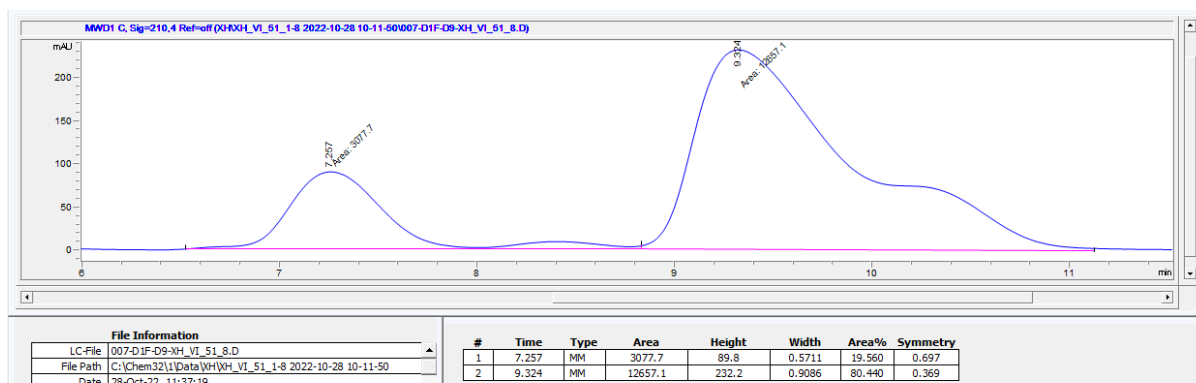




Racemic



Enantiomerically Enriched



Appendix 2 – Supporting Information for Chapter 2

Copper-Phosphido Catalysis: Enantioselective Addition of Phosphines to Cyclopropenes

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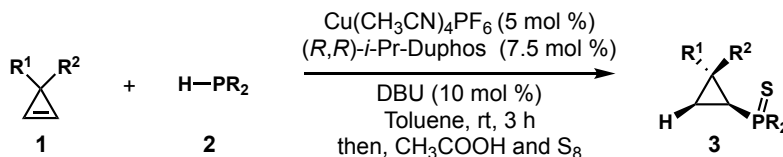
For additional details, see Daniels, B. S.; Hou, X.; Corio, S. A.; Weissman, L. M.; Dong, V. M.; Hirschi, J. S.; Nie, S. Copper-Phosphido Catalysis: Enantioselective Addition of Phosphine to Cyclopropenes. *Angew. Chem. Int. Ed.* **2023**, 62, e202306511.

1. General

Commercial reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar, or TCI and used without further purification. Toluene was purified using an Innovative Technologies Pure Solv system, degassed by three freeze-pump-thaw cycles, and stored over 3 Å MS within a N₂ filled glove box. All experiments were performed in oven-dried or flame-dried glassware. Reactions were monitored using either thin-layer chromatography (TLC) or gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD. Visualization of the developed plates was performed under UV light (254 nm) or KMnO₄ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products were performed via silica gel chromatography (both column and preparative thin-layer chromatography). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. Solvent was purchased from Fisher. ¹H, ²H, ¹³C, ³¹P and ¹⁹F NMR spectra were recorded on Bruker AVANCE 600, CRYO500 or DRX400 spectrometer. ¹H NMR spectra were internally referenced to the residual solvent signal or TMS. ¹³C NMR spectra were internally referenced to the residual solvent signal. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for ²H, ¹³C, ³¹P, and ¹⁹F NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR and are reported in terms of frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Enantiomeric ratio for enantioselective reactions was determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. Cyclopropene **1a-1m** used here were known compounds and synthesized according to reported methods.^{1,2} Phosphine **2a-2b**, **2d**, **2f-2j** used here were known compounds and donated by Solvias. **2c** and **2e** used here were synthesized according to reported methods.³

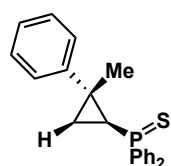
2. General procedure for the hydrophosphination of cyclopropene

A. General Procedure for Hydrophosphination with Cu



In a N₂-filled glovebox, (*R,R*)-*i*-Pr-Duphos (**L3**) (0.0075 mmol), and toluene (0.30 mL) were added to a 1-dram vial containing Cu(CH₃CN)₄PF₆ (0.005 mol). The resulting mixture was stirred for 30 min and then DBU (0.01 mmol), phosphine (0.10 mmol) and Cyclopropene (0.12 mmol, 1 M in toluene) were added. The mixture was held at room temperature until no starting material was observed by TLC. The reaction was quenched by acetic acid (20 μL) and S₈ and the reaction was stirred for another 30 mins. The diastereoselectivity ratio was determined by ¹H NMR analysis of the unpurified reaction mixture. Isolated yields (obtained by column chromatography on silica gel or preparative thin-layer chromatography) of the title compound are reported.

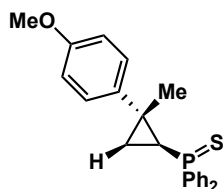
((1*S*,2*R*)-2-methyl-2-phenylcyclopropyl)diphenylphosphine sulfide (**3aa**)^a



White solid, 92% yield, 98:2 *er*, >20:1 *dr*, [α]_D²⁴ = +76.9 (*c* 0.2, CHCl₃). ³¹P NMR (162 MHz, CDCl₃) δ 45.09 ppm. ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.74 – 7.71 (m, 2H), 7.69 – 7.54 (m, 3H), 7.41 – 7.40 (m, 3H), 7.32 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 1.97 – 1.84 (m, 2H), 1.77 (td, *J* = 13.8, 6.6 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.3, 136.5 (d, *J* = 84.4 Hz), 133.7 (d, *J* = 85.7 Hz), 131.8 (d, *J* = 10.1 Hz), 131.7 (d, *J* = 2.5 Hz), 131.0 (d, *J* = 2.5 Hz), 130.7 (d, *J* = 10.1 Hz), 128.7 – 128.6 (m), 128.5, 126.5, 29.0 (d, *J* = 3.8 Hz), 25.4 (d, *J* = 78.1 Hz), 19.4 (d, *J* = 6.3 Hz), 19.2 (d, *J* = 5.0 Hz). IR (ATR): 2970, 1739, 1601, 1496, 1435, 1103, 854, 769, 693, 608 cm⁻¹. HRMS calculated for C₂₂H₂₂PS [M]⁺ 348.1102, found 348.1053. Chiral SFC: 100 mm CHIRALCEL OJ-H, 3% *i*PrOH, 2.5 mL/min, 240 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 8.6 min, *t*_{R2} (major) = 15.3 min.

a. Reaction was scaled with 1.2 mmol diphenyl phosphine and it gives 82% yield and >20:1 *dr* without sulfide oxidation.

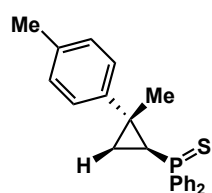
((1*S*,2*R*)-2-(4-methoxyphenyl)-2-methylcyclopropyl)diphenylphosphine sulfide (**3ba**)



White solid, 81% yield, 97:3 *er*, >20:1 *dr*, [α]_D²⁴ = +101.8 (*c* 0.6, CHCl₃). ³¹P NMR (162 MHz, CDCl₃) δ 45.09 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.11 – 8.07 (m, 2H), 7.77 – 7.74 (m, 2H), 7.63 – 7.54 (m, 3H), 7.53 – 7.42 (m, 3H), 7.32 – 7.18 (m, 2H), 6.89 – 6.87 (m, 2H), 3.84 (s, 3H), 1.94 (ddd, *J* = 19.2, 6.0, 4.2 Hz, 1H), 1.86 (td, *J* = 9.0, 6.0 Hz, 1H), 1.78 (td, *J* = 9.0, 4.8 Hz, 1H), 1.57 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 158.1, 138.6 (d, *J* = 2 Hz),

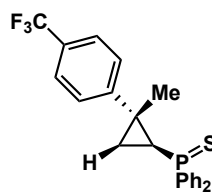
136.6 (d, $J = 84.6$ Hz), 133.8 (d, $J = 84.6$ Hz), 131.8 (d, $J = 10.6$ Hz), 131.6 (d, $J = 3.0$ Hz), 131.0 (d, $J = 3.0$ Hz), 130.7 (d, $J = 10.6$ Hz), 128.6 (d, $J = 2.0$ Hz), 128.5 (d, $J = 2.0$ Hz), 127.6, 113.9, 55.4, 28.4 (d, $J = 4.5$ Hz), 25.4 (d, $J = 77.0$ Hz), 19.7 (d, $J = 6.0$ Hz), 19.2 (d, $J = 4.5$ Hz). **IR** (ATR): 2927, 1609, 1513, 1435, 1244, 1103, 1030, 831, 733, 692, 606. **HRMS** calculated for $C_{23}H_{23}OPS [M]^+$ 378.1207, found 378.1193. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 8% i PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 9.5 min, t_{R2} (major) = 11.8 min.

((1*S*,2*R*)-2-methyl-2-(*p*-tolyl)cyclopropyl)diphenylphosphine sulfide (3ca)



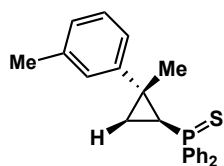
White solid, 93% yield, 96:4 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +101.0$ (c 0.6, $CHCl_3$). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 43.97 ppm. **1H NMR** (600 MHz, $CDCl_3$) δ 8.04 (dd, $J = 12.6, 7.8$ Hz, 2H), 7.70 (dd, $J = 12.0, 7.2$ Hz, 2H), 7.60 – 7.48 (m, 3H), 7.45 – 7.35 (m, 3H), 7.11 (s, 4H), 2.33 (s, 3H), 1.95 – 1.84 (m, 1H), 1.83 – 1.79 (m, 1H), 1.77 – 1.74 (m, 1H), 1.54 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.3 (d, $J = 2.0$ Hz), 136.6 (d, $J = 84.6$ Hz), 136.1, 134.2 (d, $J = 84.6$ Hz), 131.8 (d, $J = 10.6$ Hz), 131.6 (d, $J = 3.0$ Hz), 131.0 (d, $J = 2.0$ Hz), 130.7 (d, $J = 10.6$ Hz), 129.3, 128.6 (d, $J = 3.0$ Hz), 128.5 (d, $J = 2.0$ Hz), 126.3 (d, $J = 2.0$ Hz), 28.6 (d, $J = 4.5$ Hz), 25.5 (d, $J = 77.0$ Hz), 21.0, 19.4 (d, $J = 6.0$ Hz), 19.2 (d, $J = 6.0$ Hz). **IR** (ATR): 2922, 1515, 1435, 1103, 912, 817, 729, 692, 606. **HRMS** calculated for $C_{23}H_{23}PS [M]^+$ 362.1258, found 362.1260. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5 % i PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 7.1 min, t_{R2} (major) = 10.7 min.

((1*S*,2*R*)-2-methyl-2-(4-(trifluoromethyl)phenyl)cyclopropyl)diphenylphosphine sulfide (3da)



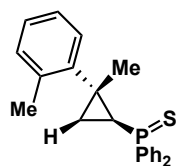
White solid, 67% yield, 98:2 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +69.4$ (c 0.3, $CHCl_3$). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 44.57 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.69 ppm. **1H NMR** (600 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.74 – 7.67 (m, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.48 (m, 4H), 7.45 – 7.36 (m, 3H), 7.30 (d, $J = 6.0$ Hz, 2H), 1.98 (ddd, $J = 18.0, 6.0, 4.8$ Hz, 1H), 1.86 (td, $J = 9.0, 6.0$ Hz, 1H), 1.79 (td, $J = 9.0, 4.8$ Hz, 1H), 1.55 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.1 (q, $J = 2.0$ Hz), 136.2 (d, $J = 84.6$ Hz), 133.4 (d, $J = 84.6$ Hz), 131.8 (d, $J = 3.0$ Hz), 131.7 (d, $J = 10.6$ Hz), 131.2 (d, $J = 3.0$ Hz), 130.7 (d, $J = 10.6$ Hz), 128.8 (q, $J = 31.7$ Hz), 128.7 (d, $J = 2.0$ Hz), 128.6 (d, $J = 2.0$ Hz), 126.8, 125.6 (q, $J = 4.5$ Hz), 124.2 (q, $J = 271.8$ Hz), 28.5 (d, $J = 3.0$ Hz), 25.9 (d, $J = 77.0$ Hz), 19.4 (d, $J = 4.5$ Hz), 18.9 (d, $J = 4.5$ Hz). **IR** (ATR): 2926, 1617, 1436, 1322, 1164, 1115, 1066, 842, 724, 692. **HRMS** calculated for $C_{23}H_{20}F_3PS [M]^+$ 416.0975, found 416.0956. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5 % i PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (major) = 3.2 min, t_{R2} (minor) = 4.2 min.

((1S,2R)-2-methyl-2-(m-tolyl)cyclopropyl)diphenylphosphine sulfide (3ea)



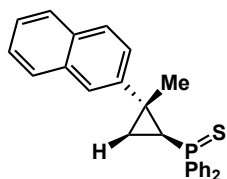
White solid, 72% yield, 93:7 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +102.2$ (*c* 0.5, CHCl₃). ³¹P NMR (162 MHz, CDCl₃) δ 45.12 ppm. ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.73 – 7.68 (m, 2H), 7.58 – 7.50 (m, 3H), 7.43 – 7.36 (m, 3H), 7.20 – 7.16 (m, 1H), 7.03 (dd, *J* = 7.1, 2.3 Hz, 3H), 2.32 (s, 3H), 1.94 – 1.81 (m, 2H), 1.76 (td, *J* = 8.8, 4.0 Hz, 1H), 1.53 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 146.37 (s), 138.28 (s), 131.99 (d, *J* = 10.3 Hz), 131.38 (d, *J* = 81.25 Hz), 130.82 (d, *J* = 10.3 Hz), 128.69 (d, *J* = 2.0 Hz), 128.60 (d, *J* = 1.3 Hz), 127.35 (d, *J* = 1.2 Hz), 127.31 (s), 123.62 (d, *J* = 1.1 Hz), 29.00 (d, *J* = 3.75), 25.52 (d, *J* = 77.7 Hz), 21.61 (s), 19.55 (d, *J* = 5.3 Hz), 19.24 (d, *J* = 4.2 Hz). IR (ATR): 3051.93, 2922.56, 1435.35, 101.70, 901.9, 726.38, 691.48, 608.87. HRMS calculated for C₂₃H₂₃PS [M]⁺ 362.1258, found 362.1268. Chiral SFC: 100 mm CHIRALCEL OJ-H, 10 % *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 2.9 min, *t*_{R2} (major) = 3.6 min.

((1S,2R)-2-methyl-2-(o-tolyl)cyclopropyl)diphenylphosphine sulfide (3fa)



White solid, 58% yield, 86:14 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +20.9$ (*c* 0.4, CHCl₃). ³¹P NMR (242 MHz, CDCl₃) δ 43.7 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.09 (ddd, *J* = 13.2, 7.5, 1.2 Hz, 2H), 7.78 (m, 2H), 7.55 (m, 3H), 7.44 (m, 3H), 7.15 (m, 1H), 7.09 (m, 3H), 2.27 (s, 3H), 2.02, (dt, *J* = 8.7, 6.4 Hz, 1H), 1.92 (ddd, *J* = 19.0, 6.3, 4.5, 1H), 1.54 (td, *J* = 9.2, 4.5 Hz, 1H), 1.50 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 144.9 (d, *J* = 2.2 Hz), 136.6 (d, *J* = 1.5 Hz), 136.4, 135.8, 134.1, 133.5, 131.9, 131.8, 131.6 (d, *J* = 3 Hz), 131.1 (d, *J* = 3 Hz), 131.0, 130.9, 130.8, 129.0 (d, *J* = 1 Hz), 128.7, 128.6 (d, *J* = 3 Hz), 128.5, 126.9, 126.0, 29.8 (d, *J* = 4 Hz), 23.3 (d, *J* = 80.0 Hz), 20.0 (d, *J* = 5 Hz), 19.4 (d, *J* = 5 Hz), 19.1 IR (ATR) 2925, 1771, 1737, 1435, 1100 cm⁻¹. HRMS calculated for C₂₃H₂₃PS [M]⁺ 362.1258, found 362.1257. Chiral SFC: 100 mm CHIRALCEL AD-H, 15% *i*PrOH, 2.5 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (Major) = 3.67 min, *t*_{R2} (Minor) = 5.39 min

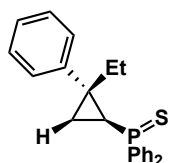
((1S,2R)-2-methyl-2-(naphthalen-2-yl)cyclopropyl)diphenylphosphine sulfide (3ga)



White solid, 81% yield, 96:4 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +125.0$ (*c* 0.5, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 43.77 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.13 – 8.01 (m, 2H), 7.84 – 7.68 (m, 5H), 7.66 (s, 1H), 7.62 – 7.53 (m, 3H), 7.52 – 7.36 (m, 5H), 7.31 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.97 – 1.88 (m, 2H), 1.66 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 143.5 (d, *J* = 3.0 Hz), 136.5 (d, *J* = 84.6 Hz), 133.9, 133.4, 132.1, 131.9 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 10.6 Hz), 128.7 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 3.0 Hz), 128.4, 127.8, 127.6, 126.4, 125.8, 124.9, 124.8 (d, *J* = 1.5 Hz), 29.0 (d, *J* = 3.0 Hz), 25.7 (d, *J* = 77.0 Hz), 19.4 (d, *J* = 4.5 Hz), 19.2 (d, *J* = 4.5 Hz). IR (ATR): 3053, 1599, 1436, 1083, 857, 818, 748, 603.

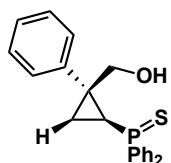
HRMS calculated for $C_{26}H_{23}PS$ $[M]^+$ 398.1258, found 398.1268. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 15% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 10.1 min, t_{R2} (major) = 13.0 min.

((1S,2R)-2-ethyl-2-phenylcyclopropyl)diphenylphosphine sulfide (3ha)



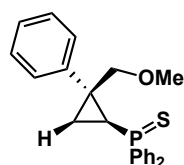
White solid, 68% yield, 98:2 *er*, >20:1 *dr*, $[\alpha]^{24}_D = +52.9$ (*c* 0.3, CHCl₃). **³¹P NMR** (243 MHz, CDCl₃) δ 43.43 ppm. **¹H NMR** (600 MHz, CDCl₃) δ 8.23 – 8.12 (m, 2H), 7.78 – 7.71 (m, 2H), 7.69 – 7.58 (m, 3H), 7.49 – 7.40 (m, 3H), 7.36 – 7.31 (m, 2H), 7.30 – 7.22 (m, 3H), 2.28 – 2.20 (m, 1H), 1.95 – 1.82 (m, 3H), 1.80 – 1.70 (m, 1H), 0.70 (t, *J* = 7.2, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 144.1 (d, *J* = 1.5 Hz), 136.9 (d, *J* = 84.6 Hz), 133.6 (d, *J* = 84.6 Hz), 132.0 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 4.5 Hz), 128.5 (d, *J* = 3.0 Hz), 128.4, 128.1 (d, *J* = 1.0 Hz), 126.6, 35.8 (d, *J* = 4.5 Hz), 25.8 (d, *J* = 78.5 Hz), 25.4 (d, *J* = 4.5 Hz), 17.0 (d, *J* = 3.0 Hz), 11.7. **IR (ATR)**: 2964, 2926, 1600, 1436, 1103, 1026, 915, 727, 692, 609. **HRMS** calculated for $C_{23}H_{24}PS$ $[M+H]^+$ 363.1336, found 363.1326. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 3% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 6.0 min, t_{R2} (major) = 13.3 min.

((1S,2R)-2-(hydroxymethyl)-2-phenylcyclopropyl)diphenylphosphine sulfide (3ia)



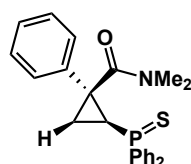
Yellow oil, 74% yield, 94:6 *er*, >20:1 *dr*, $[\alpha]^{24}_D = +109.4$ (*c* 0.4, CHCl₃). **³¹P NMR** (243 MHz, CDCl₃) δ 41.63 ppm. **¹H NMR** (600 MHz, CDCl₃) δ 8.02 – 7.93 (m, 2H), 7.81 – 7.73 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.36 (m, 3H), 7.31 – 7.23 (m, 4H), 7.21 – 7.17 (m, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.80 (d, *J* = 12.0 Hz, 1H), 2.70 (s, 1H), 2.03 (dt, *J* = 9.0, 7.2 Hz, 1H), 1.72 – 1.61 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 143.1 (d, *J* = 2.0 Hz), 134.2 (d, *J* = 81.5 Hz), 133.6 (d, *J* = 78.5 Hz), 131.9 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 2.0 Hz), 128.8 (d, *J* = 13.6 Hz), 128.7 (d, *J* = 12.1 Hz), 128.6, 128.5 (d, *J* = 2.0 Hz), 127.2, 65.0 (d, *J* = 6.0 Hz), 37.4 (d, *J* = 4.5 Hz), 26.0 (d, *J* = 78.5 Hz), 17.8 (d, *J* = 4.5 Hz). **IR (ATR)**: 3391, 3055, 1436, 1102, 1055, 750, 721, 611. **HRMS** calculated for $C_{22}H_{21}OPS$ $[M]^+$ 364.1051, found 364.1045. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 10% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, t_{R1} (minor) = 5.2 min, t_{R2} (major) = 7.6 min.

((1S,2R)-2-(methoxymethyl)-2-phenylcyclopropyl)diphenylphosphine sulfide (3ja)



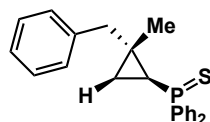
Yellow oil, 64% yield, 94:6 *er*, >20:1 *dr*, $[\alpha]_D^{24} = 65.5$ (*c* 0.1, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 43.45 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.05 – 7.97 (m, 2H), 7.70 – 7.63 (m, 2H), 7.57 – 7.46 (m, 3H), 7.41 – 7.32 (m, 3H), 7.28 – 7.20 (m, 4H) 7.18 – 7.14 (m, 1H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 3.03 (s, 3H), 2.00 (ddd, *J* = 19.2, 6.6, 4.8 Hz, 1H), 1.87 (td, *J* = 9.0, 6.6 Hz, 1H), 1.77 – 1.71 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 143.2 (d, *J* = 1.5 Hz), 136.3 (d, *J* = 86.1 Hz), 133.6 (d, *J* = 86.1 Hz), 131.8 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 12.1 Hz), 128.5, 128.5 (d, *J* = 7.6 Hz), 128.0 (d, *J* = 1.5 Hz), 127.0, 73.0 (d, *J* = 6.0 Hz), 58.3, 34.4 (d, *J* = 4.5 Hz), 24.7 (d, *J* = 77.0 Hz), 17.3 (d, *J* = 4.5 Hz). IR (ATR): 3055, 2921, 1436, 1100, 724, 606. HRMS calculated for C₂₃H₂₃OPS [M]⁺ 378.1207, found 378.1208. Chiral SFC: 100 mm CHIRALCEL OJ-H, 5% ⁱPrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 6.7 min, *t*_{R2} (major) = 7.7 min.

(1R,2S)-2-(diphenylphosphorothioyl)-N,N-dimethyl-1-phenylcyclopropane-1-carboxamide (3ka)



Yellow oil, 67% yield, 99:1 *er*, >20:1 *dr*, $[\alpha]_D^{24} = -26.0$ (*c* 0.5, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 45.96 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.07 – 8.01f (m, 2H), 7.72 – 7.67 (m, 2H), 7.53 – 7.46 (m, 3H), 7.44 – 7.31 (m, 7H), 7.29 – 7.24 (m, 1H), 2.89 (s, 3H), 2.84 (s, 3H), 2.45 (ddd, *J* = 20.0, 8.0, 4.0 Hz, 1H), 2.14 (td, *J* = 12.0, 8.0 Hz, 1H), 1.86 (dt, *J* = 12.0, 4.0 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.2 (d, *J* = 4.5 Hz), 139.2 (d, *J* = 1.5 Hz), 135.7 (d, *J* = 82.5 Hz), 133.6 (d, *J* = 88.5 Hz), 131.9 (d, *J* = 10.5 Hz), 131.4 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 3.0 Hz), 128.9, 128.4 (d, *J* = 1.5 Hz), 128.4 (d, *J* = 1.5 Hz), 127.4, 126.6, 37.9, 36.7 (d, *J* = 4.5 Hz), 35.9, 26.5 (d, *J* = 76.5 Hz), 17.7 (d, *J* = 3.0 Hz). IR (ATR): 3055, 2924, 2230, 1639, 1435, 1394, 1100, 909, 724, 625. HRMS calculated for C₂₄H₂₄NOPS [M]⁺ 405.1316, found 405.1315. Chiral SFC: 100 mm CHIRALCEL OJ-H, 5% ⁱPrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 5.0 min, *t*_{R2} (major) = 9.2 min.

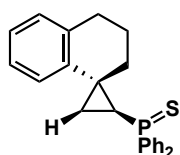
((1S,2S)-2-benzyl-2-methylcyclopropyl)diphenylphosphine sulfide (3la)



white solid, 38% yield, 77:23 *er* for both diastereomers, 1.1:3 *dr* (inseparable diastereomer), ³¹P NMR (162 MHz, CDCl₃) δ 46.17, 46.10. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (ddd, *J* = 13.1, 7.9, 1.6 Hz, 1H), 7.76 – 7.63 (m, 5H), 7.58 – 7.52 (m, 2H), 7.45 – 7.27 (m, 11H), 7.22 – 7.14 (m, 7H), 3.46 (d, *J* = 13.9 Hz, 0.71H), 2.81 (dd, *J* = 13.8, 2.8 Hz, 1H), 2.58 (d, *J* = 13.7 Hz, 1H), 2.40 (d, *J* = 14.0 Hz, 0.74H), 1.98 – 1.91 (m, 0.78H), 1.68 – 1.61 (m, 1H), 1.53 (dtd, *J* = 14.8, 8.8, 6.0 Hz, 2H), 1.27 – 1.24 (m, 1.5H), 1.22 (s, 3H), 1.15 (d, *J* = 2.3 Hz, 2.5H). ¹³C NMR (151 MHz, CDCl₃) δ 140.36, 138.69, 136.91 (d, *J* = 84.56 Hz), 136.83 (d, *J* = 84.56 Hz), 134.15 (d, *J* = 84.56 Hz), 133.76 (d, *J* = 84.56 Hz), 131.77 (d, *J* = 7.6 Hz), 131.69, 131.65 (d, *J* = 7.6 Hz), 131.33 (d, *J* = 3.02 Hz), 131.02 (d, *J* = 3.02), 130.95

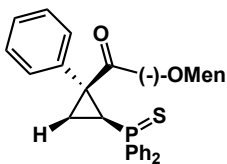
(d, $J = 3.02$), 130.74 (d, $J = 1.5$ Hz), 130.67 (d, $J = 1.5$ Hz), 129.70, 129.47, 128.74 (d, $J = 12.8$ Hz), 128.65, 128.64 (d, $J = 12.8$ Hz), 128.56, 128.52 (d, $J = 15.1$ Hz), 128.16 (s), 126.74 (s), 126.08 (s), 47.80 (s), 37.79 (d, $J = 5.7$ Hz), 26.65 (d, $J = 4.3$ Hz), 26.25 (d, $J = 4.4$ Hz), 25.52 (s), 23.45 (d, $J = 80.4$ Hz), 21.64 (d, $J = 80.6$ Hz), 19.34 (d, $J = 4.1$ Hz), 19.10 (d, $J = 4.1$ Hz), 17.14 (d, $J = 5.7$ Hz). **IR** (ATR): 3056, 2922, 1435, 1102, 726, 691, 609. **HRMS** calculated for $C_{24}H_{24}NOPS$ $[M]^+ 362.1258$, found 362.1246. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 15% i PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (minor diastereomer, major) = 3.1 min, t_{R2} (minor diastereomer, minor) = 3.4, t_{R1}^2 (major diastereomer, minor) = 3.8 min, t_{R2}^2 (major diastereomer, major) = 5.0 min.

((1*R*,2*S*)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2-yl)diphenylphosphine sulfide (3ma)



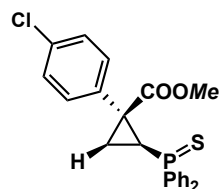
White solid, 65% yield, 98:2 *er*, >20:1 *dr*. $[\alpha]_D^{24} = +72.3$ (c 0.2, $CHCl_3$). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 43.83 ppm. **1H NMR** (600 MHz, $CDCl_3$) δ 7.95 (dd, $J = 13.2$ Hz, 2H), 7.70 (dd, $J = 13.2$, 7.8 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.48 – 7.37 (m, 5H), 7.17 – 7.01 (m, 3H), 6.80 (d, $J = 7.8$ Hz, 1H), 2.81 – 2.66 (m, 2H), 2.21 – 1.99 (m, 4H), 1.68 – 1.60 (m, 2H), 1.42 – 1.33 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.9 (d, $J = 1.5$ Hz), 138.4, 136.9 (d, $J = 84.6$ Hz), 133.2 (d, $J = 84.6$ Hz), 131.9 (d, $J = 10.6$ Hz), 131.7 (d, $J = 3.0$ Hz), 131.0 (d, $J = 1.5$ Hz), 130.6 (d, $J = 10.6$ Hz), 129.3, 128.7 (d, $J = 3.0$ Hz), 128.6 (d, $J = 3.0$ Hz), 126.4, 125.8, 121.5, 30.2, 27.9 (d, $J = 75.5$ Hz), 27.88 (d, $J = 4.5$ Hz), 27.7 (d, $J = 4.5$ Hz), 23.5 (d, $J = 4.5$ Hz), 22.0. **HRMS** calculated for $C_{24}H_{23}PS$ $[M]^+ 374.1258$, found 374.1262. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 3.0% i PrOH, 3.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 12.3 min, t_{R2} (major) = 15.4 min.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl(1*R*,2*S*)-2-(diphenylphosphorothioyl)-1-phenylcyclopropane-1-carboxylate (3na)



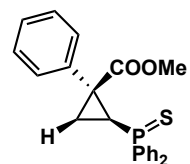
Yellow oil, 41% yield, 5:1 *dr*. **^{31}P NMR** (243 MHz, $CDCl_3$) δ 44.22 ppm. **1H NMR** (600 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.74 – 7.65 (m, 2H), 7.52 – 7.45 (m, 3H), 7.42 – 7.28 (m, 5H), 7.26 – 7.19 (m, 3H), 4.53 (dt, $J = 12.0$, 6.0 Hz, 1H), 2.28 (ddd, $J = 18.0$, 12.0, 6.0 Hz, 1H), 2.26 – 1.97 (m, 2H), 1.67 (td, $J = 9.6$, 4.8 Hz, 1H), 1.57 – 1.46 (m, 3H), 1.34 – 1.25 (m, 1H), 1.22 – 1.15 (m, 1H), 0.95 – 0.81 (m, 2H), 0.79 (d, $J = 6.0$ Hz, 3H), 0.77 – 0.65 (m, 2H), 0.62 (d, $J = 6.0$ Hz, 3H), 0.43 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.6 (d, $J = 5.1$ Hz), 139.4 (d, $J = 4.5$ Hz), 135.1 (d, $J = 84.6$ Hz), 133.8 (d, $J = 87.6$ Hz), 131.7 (d, $J = 10.6$ Hz), 131.5 (d, $J = 3.0$ Hz), 131.2 (d, $J = 3.0$ Hz), 131.1 (d, $J = 10.2$ Hz), 128.7, 128.6 (d, $J = 12.6$ Hz), 128.5, 128.5 (d, $J = 12.2$ Hz), 127.8, 75.5, 47.1, 40.1, 38.0 (d, $J = 4.8$ Hz), 34.3, 31.4, 25.7 (d, $J = 77.6$ Hz), 25.5, 23.01, 22.1, 20.8, 15.9, 15.8 (d, $J = 3.3$ Hz). **IR** (ATR): 3056, 2954, 2867, 1721, 1436, 1298, 1176, 1099, 732, 691. **HRMS** calculated for $C_{32}H_{38}O_2PS$ $[M+H]^+ 517.2330$, found 517.2349.

Methyl (1R,2S)-1-(4-chlorophenyl)-2-(diphenylphosphorothioyl)cyclopropane-1-carboxylate (30a)



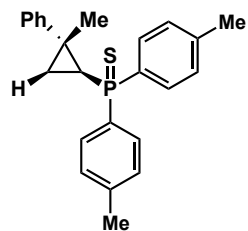
yellow solid, 85% yield, 89:11 *er*, 1:1.6 *dr*, $[\alpha]_D^{24} = +20.4$ (*c* 0.3, CHCl₃). ³¹P NMR (162 MHz, CDCl₃) δ 44.30 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.06 – 7.96 (m, 2H), 7.80 – 7.72 (m, 2H), 7.64 – 7.52 (m, 3H), 7.50 – 7.42 (m, 3H), 7.33 – 7.25 (m, 4H), 3.50 (s, 3H), 4.42 (ddd, *J* = 18.0, 7.2, 4.8 Hz, 1H), 2.16 (dt, *J* = 9.0, 7.8 Hz, 1H), 1.74 (td, *J* = 9.6, 4.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 169.0 (d, *J* = 4.5 Hz), 137.3 (d, *J* = 1.5 Hz), 134.7 (d, *J* = 86.1 Hz), 134.0, 133.0 (d, *J* = 86.1 Hz), 131.7 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.6 Hz), 130.3 (d, *J* = 1.5 Hz), 128.9, 128.61, 128.6 (d, *J* = 25.7 Hz), 52.3, 36.4 (d, *J* = 4.5 Hz), 25.5 (d, *J* = 77.0 Hz), 16.4 (d, *J* = 3.0 Hz). IR (ATR): 2918, 2849.38, 1733.15, 1435.09, 1426.60, 1304.21, 1099.24, 715.89, 730.24, 690.15. HRMS calculated for C₂₃H₂₁ClO₂PS [M+H]⁺ 427.0688, found 427.0702. Chiral SFC: 100 mm CHIRALCEL OD-H, 10% ⁱPrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 6.6 min, *t*_{R2} (major) = 8.0 min.

methyl 2-(diphenylphosphorothioyl)-1-phenylcyclopropane-1-carboxylate (3pa)



Yellow solid, 75% yield, 87:13 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +34.5$ (*c* 0.5, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 43.50 ppm. ¹H NMR (600 MHz, CDCl₃) δ 7.99 – 7.93 (m, 2H), 7.74 – 7.65 (m, 2H), 7.55 – 7.45 (m, 3H), 7.43 – 7.27 (m, 5H), 7.27 – 7.21 (m, 3H), 3.44 (s, 3H), 2.37 (ddd, *J* = 18.6, 9.6, 4.8 Hz, 1H), 2.15 (dt, *J* = 9.6, 7.8 Hz, 1H), 1.68 (td, *J* = 9.6, 4.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 169.3 (d, *J* = 6.0 Hz), 138.8 (d, *J* = 1.5 Hz), 135.0 (d, *J* = 86.1 Hz), 133.1 (d, *J* = 86.1 Hz), 131.7 (d, *J* = 10.6 Hz), 131.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.6 Hz), 128.9 (d, *J* = 1.5 Hz), 128.7, 128.6 (d, *J* = 15.1 Hz), 128.5 (d, *J* = 16.6 Hz), 128.0, 52.2, 37.1 (d, *J* = 4.5 Hz), 25.0 (d, *J* = 77.0 Hz), 16.3 (d, *J* = 3.0 Hz). IR (ATR): 2919, 2849, 1733, 1435, 1304, 1109, 755, 737, 713, 620. HRMS calculated for C₂₃H₂₂O₂PS [M+H]⁺ 393.1078, found 393.1076. Chiral SFC: 100 mm CHIRALCEL OJ-H, 3% ⁱPrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 10.5 min, *t*_{R2} (major) = 16.5 min.

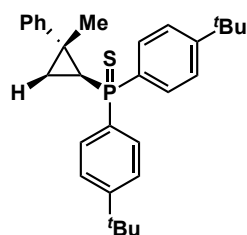
((1S,2R)-2-methyl-2-phenylcyclopropyl)di-p-tolylphosphine sulfide (3ab)



White solid, 86% yield, 98:2 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +59.4$ (*c* 0.2, CHCl₃). ³¹P NMR (162 MHz, CDCl₃) δ 43.22 ppm. ¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.24 – 7.16 (m, 5H), 2.44 (s, 3H), 2.34 (s, 3H), 1.90 (ddd, *J* = 19.0, 6.4, 4.7 Hz, 1H), 1.83 (td, *J* = 8.9, 6.4 Hz, 1H), 1.74 (td, *J* = 8.9, 4.7 Hz, 1H), 1.54 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 146.5 (d, *J* = 1.5 Hz), 142.1 (d, *J* = 3.0 Hz), 141.4 (d, *J* = 3.0 Hz), 133.5 (d, *J* = 85.5 Hz), 131.8

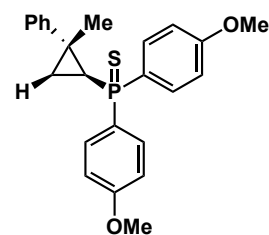
(d, $J = 10.5$ Hz), 130.8 (d, $J = 10.5$ Hz), 130.6 (d, $J = 87.0$ Hz), 129.4 (d, $J = 6.0$ Hz), 129.3 (d, $J = 7.5$ Hz), 128.7, 126.6 (d, $J = 1.5$ Hz), 126.5, 28.9 (d, $J = 3.0$ Hz), 25.7 (d, $J = 78.0$ Hz), 21.7 (d, $J = 1.5$ Hz), 21.5 (d, $J = 1.5$ Hz), 19.4 (d, $J = 6.0$ Hz), 19.3 (d, $J = 4.5$ Hz). **IR** (ATR): 3021, 2954, 2921, 2870, 1599, 1496, 1445, 1101, 909, 806, 725, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{24}\text{H}_{25}\text{PS}$ $[\text{M}]^+$ 376.1414, found 376.1401. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 3.0% *i*PrOH, 3.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (Major) = 11.9 min, t_{R2} (Minor) = 24.9 min.

((1S,2R)-2-methyl-2-phenylcyclopropyl)bis(4-(tert-butyl)phenyl)phosphine sulfide (3ac)



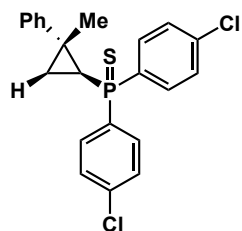
White solid, 79% yield, 96:4 *er*, >20:1 *dr*, $[\alpha]_{\text{D}}^{24} = +62.6$ (*c* 0.5, CHCl_3). ^{31}P NMR (243 MHz, CDCl_3) δ 42.96 ppm. ^1H NMR (499 MHz, CDCl_3) δ 8.05 – 7.93 (m, 2H), 7.74 – 7.65 (m, 2H), 7.62 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.25 (m, 3H), 2.03 – 1.86 (m, 2H), 1.82 – 1.74 (m, 1H), 1.63 (s, 3H), 1.43 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.0 (d, $J = 3.8$ Hz), 154.3 (d, $J = 2.5$ Hz), 146.5, 133.3 (d, $J = 88.2$ Hz), 131.6 (d, $J = 10.1$ Hz), 130.5 (d, $J = 88.2$ Hz), 130.6 (d, $J = 10.1$ Hz), 129.5 (d, $J = 3.8$ Hz), 128.6, 126.5, 126.4, 125.6 (d, $J = 12.6$ Hz), 35.0 (d, $J = 20.2$ Hz), 31.2 (d, $J = 12.6$ Hz), 28.9 (d, $J = 3.8$ Hz), 25.7 (d, $J = 78.1$ Hz), 19.4 (d, $J = 5.0$ Hz), 19.3 (d, $J = 4.4$ Hz). **IR** (ATR): 2960, 1598, 1495, 1392, 1088, 837, 766, 750, 717, 698, 565 cm^{-1} . **HRMS** calculated for $\text{C}_{30}\text{H}_{37}\text{PS}$ $[\text{M}]^+$ 460.2354, found 460.2351. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 3% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 5.8 min, t_{R2} (major) = 7.7 min.

Bis(4-methoxyphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ad)



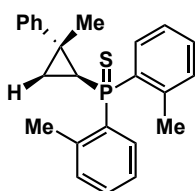
White solid, 74% yield, 97:3 *er*, >20:1 *dr*. $[\alpha]_{\text{D}}^{24} = +70.9$ (*c* 0.4, CHCl_3). ^{31}P NMR (243 MHz, CDCl_3) δ 42.26 ppm. ^1H NMR (600 MHz, CDCl_3) δ 8.01 – 7.85 (m, 2H), 7.68 – 7.52 (m, 2H), 7.35 – 7.12 (m, 5H), 7.08 – 6.95 (m, 2H), 6.95 – 6.86 (m, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 1.94 – 1.68 (m, 3H), 1.54 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.2 (d, $J = 3.0$ Hz), 161.7 (d, $J = 3.0$ Hz), 146.4 (d, $J = 1.4$ Hz), 133.5 (d, $J = 12.1$ Hz), 132.5 (d, $J = 12.1$ Hz), 128.6, 128.0 (d, $J = 90.6$ Hz), 126.5, 126.4, 125.0 (d, $J = 90.6$ Hz), 114.1 (d, $J = 13.6$ Hz), 114.06 (d, $J = 13.6$ Hz), 55.4 (d, $J = 7.6$ Hz), 28.8 (d, $J = 4.5$ Hz), 26.0 (d, $J = 78.5$ Hz), 19.33 (d, $J = 4.5$ Hz), 19.31 (d, $J = 4.5$ Hz). **IR** (ATR): 2926, 1592, 1497, 1251, 1177, 1102, 1025, 799, 727, 699. **HRMS** calculated for $\text{C}_{24}\text{H}_{25}\text{O}_2\text{PS}$ $[\text{M}]^+$ 408.1313, found 408.1306. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 15% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2 , t_{R1} (major) = 5.3 min, t_{R2} (minor) = 9.1 min.

Bis(4-chlorophenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide(3ae)



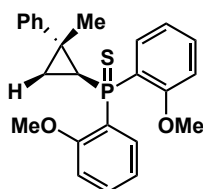
White solid, 67% yield, 97:3 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +56.9$ (*c* 0.5, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 44.10 ppm. ¹H NMR (600 MHz, CDCl₃) δ 7.94 (dd, *J* = 12.6, 8.4 Hz, 2H), 7.61 (dd, *J* = 12.0, 8.4 Hz, 2H), 7.52 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.37 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 1.89 (dt, *J* = 19.2, 3.0 Hz, 1H), 1.82 – 1.74 (m, 2H), 1.54 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 145.8 (d, *J* = 1.5 Hz), 138.5 (d, *J* = 4.5 Hz), 137.9 (d, *J* = 4.5 Hz), 134.6 (d, *J* = 86.1 Hz), 133.1 (d, *J* = 10.6 Hz), 132.1 (d, *J* = 86.1 Hz), 132.0 (d, *J* = 12.1 Hz), 129.01 (d, *J* = 27.2 Hz), 129.0 (d, *J* = 1.5 Hz), 128.8, 126.7, 126.3, 29.1 (d, *J* = 4.5 Hz), 25.3 (d, *J* = 78.5 Hz), 19.33, 19.3. IR (ATR): 2924, 1578, 1387, 1086, 1013, 817, 748, 725, 698, 623. HRMS calculated for C₂₂H₁₉Cl₂PS [M]⁺ 416.0322, found 416.0324. Chiral SFC: 100 mm CHIRALCEL OJ-H, 15% *i*PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 3.7 min, *t*_{R2} (major) = 9.6 min.

((1S,2R)-2-methyl-2-phenylcyclopropyl)di-*o*-tolylphosphine sulfide (3af)



White solid, 65% yield, 95:5 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +71.2$ (*c* 0.4, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 44.79 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.61 (dd, *J* = 16.2, 7.8 Hz, 1H), 7.70 (dd, *J* = 14.4, 7.8 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.27 – 7.19 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 2.17 (s, 3H), 2.12 – 2.05 (m, 1H), 2.02 – 1.96 (m, 1H), 1.85 (td, *J* = 9.0, 4.8 Hz, 1H), 1.52 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 146.2 (d, *J* = 4.5 Hz), 140.4 (d, *J* = 9.1 Hz), 140.1 (d, *J* = 9.1 Hz), 138.4 (d, *J* = 13.6 Hz), 134.4 (d, *J* = 15.1 Hz), 134.3 (d, *J* = 83.1 Hz), 132.4 (d, *J* = 10.6 Hz), 131.8 (d, *J* = 6.0 Hz), 131.7 (d, *J* = 34.7 Hz), 131.3 (d, *J* = 80.0 Hz), 131.2 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 1.5 Hz), 126.3 (d, *J* = 7.6 Hz), 126.2 (d, *J* = 48.3 Hz), 126.1 (d, *J* = 19.6 Hz), 29.4 (d, *J* = 4.5 Hz), 25.3 (d, *J* = 74.0 Hz), 22.1 (d, *J* = 3.0 Hz), 21.8 (d, *J* = 4.5 Hz), 19.7 (d, *J* = 4.5 Hz), 18.8 (d, *J* = 6.0 Hz). IR (ATR): 2924, 1736, 1447, 1240, 1068, 755, 720, 681, 608. HRMS calculated for C₂₄H₂₅PS [M]⁺ 376.1414, found 376.1420. Chiral SFC: 100 mm CHIRALCEL OJ-H, 10% *i*PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 4.2 min, *t*_{R2} (major) = 5.2 min.

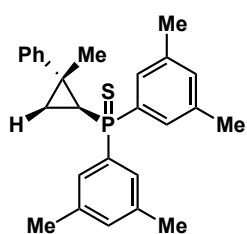
Bis(2-methoxyphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ag)



White solid, 78% yield, 93:7 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +56.9$ (*c* 0.5, CHCl₃). ³¹P NMR (243 MHz, CDCl₃) δ 40.68 ppm. ¹H NMR (600 MHz, CDCl₃) δ 8.43 (ddd, *J* = 16.5, 7.6, 1.6 Hz, 1H), 7.57 (tt, *J* = 7.9, 1.3 Hz, 1H), 7.36 (tt, *J* = 7.9, 1.3 Hz, 1H), 7.30 – 7.16 (m, 4H), 7.15 – 7.05 (m, 3H), 6.91 – 6.86 (m, 3H), 3.74 (s, 3H), 3.40 (s, 3H), 2.27 (dt, *J* = 9.4, 7.1 Hz), 1.93 (ddd, *J* = 21.3, 6.8, 4.8 Hz, 1H), 1.64

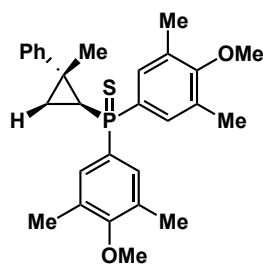
(td, $J = 9.5, 4.8$ Hz, 1H), 1.36 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 160.2 (d, $J = 1.5$ Hz), 159.9 (d, $J = 3.0$ Hz), 147.5 (d, $J = 1.5$ Hz), 136.4 (d, $J = 10.6$ Hz), 133.6 (d, $J = 3.0$ Hz), 132.4 (d, $J = 3.0$ Hz), 131.1 (d, $J = 6.0$ Hz), 128.3, 126.7 (d, $J = 1.2$ Hz), 126.1, 125.4 (d, $J = 89.1$ Hz), 121.0 (d, $J = 13.6$ Hz), 120.97 (d, $J = 84.6$ Hz), 120.7 (d, $J = 13.6$ Hz), 112.1 (d, $J = 6.0$ Hz), 110.7 (d, $J = 6.0$ Hz), 55.9, 55.2, 28.8 (d, $J = 4.2$ Hz), 25.6 (d, $J = 81.5$ Hz), 19.3 (d, $J = 6.0$ Hz), 19.2 (d, $J = 4.9$ Hz). **IR (ATR)**: 3062, 2935, 2871, 2836, 1587, 1575, 1474, 1430, 1212, 1245, 1021, 909, 755, 730, 712, 699, 606 cm^{-1} . **HRMS** calculated for $\text{C}_{24}\text{H}_{25}\text{O}_2\text{PS}$ $[\text{M}]^+$ 408.1313, found 408.1328. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 2.0 % $i\text{PrOH}$, 1.9 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 22.8 min, t_{R2} (major) = 24.7 min.

Bis(3,5-dimethylphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide(3ah)



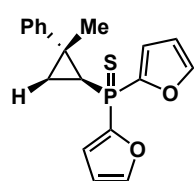
White solid, 73% yield, 98:2 *er*, >20:1 *dr*, $[\alpha]_{\text{D}}^{24} = +56.9$ (c 0.5, CHCl_3). **^{31}P NMR** (243 MHz, CDCl_3) δ 43.84 ppm. **^1H NMR** (600 MHz, CDCl_3) δ 7.62 (d, $J = 13.5$ Hz, 2H), 7.34 – 7.18 (m, 8H), 7.04 (s, 1H), 2.39 (s, 6H), 2.29 (s, 6H), 1.89 (ddd, $J = 18.9, 4.3, 2.4$ Hz, 1H), 1.80 – 1.78 (m, 2H), 1.54 (s, 3H). **^{13}C NMR** (150 MHz, CDCl_3) δ 146.5 (d, $J = 1.5$ Hz), 138.3 (d, $J = 12.0$ Hz), 138.2 (d, $J = 10.5$ Hz), 136.4 (d, $J = 83.1$ Hz), 133.6 (d, $J = 84.0$ Hz), 133.4 (d, $J = 3.0$ Hz), 132.8 (d, $J = 3.0$ Hz), 129.6 (d, $J = 10.5$ Hz), 128.6, 128.3 (d, $J = 10.5$ Hz), 126.6 (d, $J = 1.5$ Hz), 126.5, 28.7 (d, $J = 4.5$ Hz), 25.9 (d, $J = 77.4$ Hz), 21.5 (d, $J = 1.5$ Hz), 19.5 (d, $J = 6.0$ Hz), 18.7 (d, $J = 4.5$ Hz). **IR (ATR)** 3025, 2915, 2866, 1600, 1449, 1124, 850, 766, 720, 691, 627 cm^{-1} . **HRMS** calculated for $\text{C}_{26}\text{H}_{29}\text{PS}$ $[\text{M}]^+$ 404.1728, found 404.1747. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 2.0% $i\text{PrOH}$, 1.9 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 3.98 min, t_{R2} (major) = 5.56 min.

Bis(4-methoxy-3,5-dimethylphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ai)



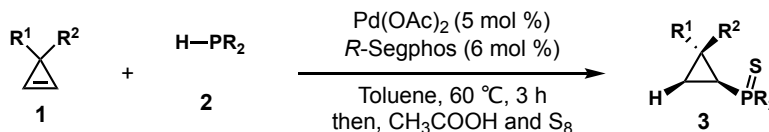
White solid, 69% yield, 98:2 *er*, >20:1 *dr*. $[\alpha]_{\text{D}}^{24} = +44.0$ (c 0.7, CHCl_3). **^{31}P NMR** (243 MHz, CDCl_3) δ 42.63 ppm. **^1H NMR** (600 MHz, CDCl_3) δ 7.70 (d, $J = 13.2$ Hz, 2H), 7.42 – 7.33 (m, 4H), 7.32 – 7.27 (m, 3H), 3.85 (s, 3H), 3.75 (s, 3H), 2.40 (s, 6H), 2.31 (s, 6H), 1.92 (ddd, $J = 19.2, 10.8, 4.8$ Hz, 1H), 1.87 – 1.76 (m, 2H), 1.61 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 159.9 (d, $J = 4.5$ Hz), 159.4 (d, $J = 3.0$ Hz), 146.4 (d, $J = 1.5$ Hz), 132.4 (d, $J = 10.6$ Hz), 131.2 (d, $J = 86.1$ Hz), 131.34 (d, $J = 24.2$ Hz), 131.3, 128.6, 128.5 (d, $J = 86.1$ Hz), 126.5 (d, $J = 0.6$ Hz), 126.4, 59.7 (d, $J = 27.2$ Hz), 28.7 (d, $J = 4.5$ Hz), 26.1 (d, $J = 78.5$ Hz), 19.3 (d, $J = 4.5$ Hz), 18.8 (d, $J = 4.5$ Hz), 16.3 (d, $J = 4.5$ Hz). **IR (ATR)**: 2954, 1472, 1276, 1215, 1110, 1004, 769, 724, 628, 598. **HRMS** calculated for $\text{C}_{28}\text{H}_{33}\text{O}_2\text{PS}$ $[\text{M}]^+$ 464.1939, found 464.1939. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 10% $i\text{PrOH}$, 2.5 mL/min, 220 nm, 44 $^\circ\text{C}$, nozzle pressure = 200 bar CO_2 , t_{R1} (minor) = 1.8 min, t_{R2} (major) = 3.8 min.

Di(furan-2-yl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3aj)



White solid, 49% yield, 96:4 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +42.9$ (*c* 0.2, CHCl₃). **³¹P NMR** (243 MHz, CDCl₃) δ 16.36 ppm, **¹H NMR** (600 MHz, CDCl₃) δ 7.84 (s, 1H), 7.71 (s, 1H), 7.42 – 7.32 (m, 4H), 7.30 – 7.27 (m 1H), 7.25 (t, *J* = 6.0 Hz, 1H), 7.21 (t, *J* = 6.0 Hz, 1H), 6.60 (t, *J* = 4.5 Hz, 1H), 6.54 (t, *J* = 4.5 Hz, 1H), 2.14 (td, *J* = 9.0, 6.6 1H), 1.84 (dt, *J* = 21.0, 5.4 Hz, 1H), 1.65 (td, *J* = 9.6, 4.8 Hz, 1H), 1.61 (m, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.0 (d, *J* = 4.5 Hz), 148.3 (d, *J* = 6.0 Hz), 148.2 (d, *J* = 7.6 Hz), 146.4 (d, *J* = 4.5 Hz), 128.6, 127.3 (d, *J* = 1.5 Hz), 126.7, 121.8 (d, *J* = 3.0 Hz), 121.6 (d, *J* = 1.5 Hz), 111.3 (d, *J* = 9.1 Hz), 111.2 (d, *J* = 9.1 Hz), 30.0 (d, *J* = 7.6 Hz), 22.7 (d, *J* = 89.1 Hz), 20.4 (d, *J* = 7.6 Hz), 18.3 (d, *J* = 4.5 Hz). **IR** (ATR): 2955, 1602, 1495, 1366, 1208, 1126, 1003, 908, 741, 700, 654. **HRMS** calculated for C₁₈H₁₇O₂PS [M]⁺ 328.0687, found 328.0675. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5% *i*PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 3.7 min, *t*_{R2} (major) = 4.2 min.

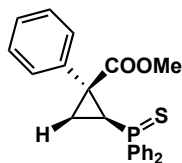
B. General Procedure for Hydrophosphination with Pd



In a N₂-filled glovebox, *R*-Segphos (0.006 mmol), and toluene (0.30 mL) were added to a 1-dram vial containing Pd(OAc)₂ (0.005 mol). The resulting mixture was stirred for 30 min and then phosphine (0.10 mmol) and Cyclopropene (0.12 mmol, 1M in toluene) were added. The mixture was held at 60 °C until no starting material was observed by TLC. The reaction was quenched by acetic acid (20 μ L) and S₈ and the reaction was stirred for another 30 mins. The diastereoselectivity ratio was determined by ¹H NMR analysis of the unpurified reaction mixture. Isolated yields (obtained by column chromatography on silica gel or preparative thin-layer chromatography) of the title compound are reported.

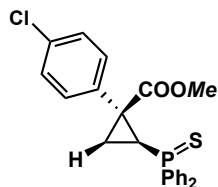
The difference of reactivity observed for Cu and Pd stems from their different mechanisms (Pd-hydride versus Cu-phosphido insertions), with the latter pathway occurring at lower temperatures (room temperature versus 60° C).

methyl 2-(diphenylphosphorothioyl)-1-phenylcyclopropane-1-carboxylate (3pa)



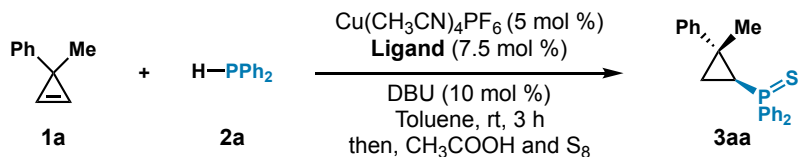
(R)-DM-SEGPPOS was used as ligand instead of standard procedure of Pd catalyzed hydrophosphination. White solid, 84% yield, 96:4 *er*, >20:1 *dr*, $[\alpha]_D^{24} = +56.3$ (*c* 0.5, CHCl₃). **³¹P NMR** (243 MHz, CDCl₃) δ 43.50 ppm. **¹H NMR** (600 MHz, CDCl₃) δ 7.99 – 7.93 (m, 2H), 7.74 – 7.65 (m, 2H), 7.55 – 7.45 (m, 3H), 7.43 – 7.27 (m, 5H), 7.27 – 7.21 (m, 3H), 3.44 (s, 3H), 2.37 (ddd, *J* = 18.6, 9.6, 4.8 Hz, 1H) 2.15 (dt, *J* = 9.6, 7.8 Hz, 1H), 1.68 (td, *J* = 9.6, 4.8 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 169.3 (d, *J* = 6.0 Hz), 138.8 (d, *J* = 1.5 Hz), 135.0 (d, *J* = 86.1 Hz), 133.1 (d, *J* = 86.1 Hz), 131.7 (d, *J* = 10.6 Hz), 131.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.6 Hz), 128.9 (d, *J* = 1.5 Hz), 128.7, 128.6 (d, *J* = 15.1 Hz), 128.5 (d, *J* = 16.6 Hz), 128.0, 52.2, 37.1 (d, *J* = 4.5 Hz), 25.0 (d, *J* = 77.0 Hz), 16.3 (d, *J* = 3.0 Hz). **IR** (ATR): 2919, 2849, 1733, 1435, 1304, 1109, 755, 737, 713, 620. **HRMS** calculated for C₂₃H₂₂O₂PS [M+H]⁺ 393.1078, found 393.1076. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 3% ⁱPrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 10.5 min, *t*_{R2} (major) = 16.5 min.

Methyl(1R,2S)-1-(4-chlorophenyl)-2-(diphenylphosphorothioyl)cyclopropane-1-carboxylate (3oa)



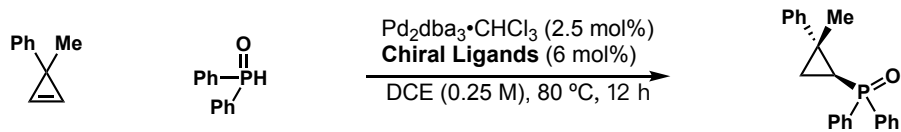
(R)-DM-SEGPPOS was used as ligand instead of standard procedure of Pd catalyzed hydrophosphination. White solid, 68% yield, 94:6 *er*, 9:1 *dr*, $[\alpha]_D^{24} = +70.9$ (*c* 0.2, CHCl₃). **³¹P NMR** (162 MHz, CDCl₃) δ 44.30 ppm. **¹H NMR** (600 MHz, CDCl₃) δ 8.06 – 7.96 (m, 2H), 7.80 – 7.72 (m, 2H), 7.64 – 7.52 (m, 3H), 7.50 – 7.42 (m, 3H), 7.33 – 7.25 (m, 4H), 3.50 (s, 3H), 4.42 (ddd, *J* = 18.0, 7.2, 4.8 Hz, 1H), 2.16 (dt, *J* = 9.0, 7.8 Hz, 1H), 1.74 (td, *J* = 9.6, 4.8 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 169.0 (d, *J* = 4.5 Hz), 137.3 (d, *J* = 1.5 Hz), 134.7 (d, *J* = 86.1 Hz), 134.0, 133.0 (d, *J* = 86.1 Hz), 131.7 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.6 Hz), 130.3 (d, *J* = 1.5 Hz), 128.9, 128.61, 128.6 (d, *J* = 25.7 Hz), 52.3, 36.4 (d, *J* = 4.5 Hz), 25.5 (d, *J* = 77.0 Hz), 16.4 (d, *J* = 3.0 Hz). **IR** (ATR): 2918, 2849.38, 1733.15, 1435.09, 1426.60, 1304.21, 1099.24, 715.89, 730.24, 690.15. **HRMS** calculated for C₂₃H₂₁ClO₂PS [M+H]⁺ 427.0688, found 427.0702. **Chiral SFC**: 100 mm CHIRALCEL OD-H, 10% ⁱPrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO₂, *t*_{R1} (minor) = 6.6 min, *t*_{R2} (major) = 8.5 min.

3. Cu-catalyzed hydrophosphination of cyclopropene optimization by ligand screen (Table S1)



Entry	Chiral Ligands	<i>er</i>
1	(<i>R</i>)-BINAP	51:49 <i>er</i>
2	(<i>R</i>)-Tol-BINAP	56:44 <i>er</i>
3	(<i>R</i>)-Xyl-BINAP	59:41 <i>er</i>
4	(<i>R</i>)-DTBM-BINAP	52:48 <i>er</i>
5	(<i>R</i>)-SegPhos	70:30 <i>er</i>
6	(<i>R</i>)-DM-SegPhos	85:15 <i>er</i>
7	(<i>R</i>)-DTBM-SegPhos	81:19 <i>er</i>
8	(<i>R</i>)-iPr-Pybox	51:49 <i>er</i>
9	(<i>R</i>)-Ph-Pybox	51:49 <i>er</i>
10	Indenyl-Pybox	84:46 <i>er</i>
11	(<i>R</i>)-Ph-GarPhos	56:44 <i>er</i>
12	(<i>R</i>)-Tol-GarPhos	71:29 <i>er</i>
13	(<i>R</i>)-Xyl-GarPhos	80:20 <i>er</i>
14	(<i>R</i>)-DMM-GarPhos	85:15 <i>er</i>
15	(<i>R</i>)-DTBM-GarPhos	73:27 <i>er</i>
16	(<i>R</i>)-MeO-BIPHEP (A101)	—
17	(<i>R</i>)-MeO-BIPHEP (A104)	90:10 <i>er</i>
18	(<i>R</i>)-MeO-BIPHEP (A107)	57:43 <i>er</i>
19	SL-JOSIPHOS (J004-1)	80:20 <i>er</i>
20	SL-JOSIPHOS (J005-1)	86:14 <i>er</i>
21	SL-JOSIPHOS (J007-1)	73:27 <i>er</i>
22	SL-JOSIPHOS (J009-1)	—
23	SL-JOSIPHOS (J011-1)	55:45 <i>er</i>
24	SL-JOSIPHOS (J015-1)	—
25	SL-JOSIPHOS (J212-1)	53:47 <i>er</i>
26	SL-Taniaphos (T001)	64:36 <i>er</i>
27	SL-Taniaphos (T002)	53:47 <i>er</i>
28	(<i>R</i>)-Me-BPE	65:35 <i>er</i>
29	(<i>R</i>)-Et-BPE	17:83 <i>er</i>
30	(<i>R</i>)-iPr-BPE	—
31	(<i>R</i>)-Ph-BPE	—
32	(<i>R</i>)-Me-DuPhos	90:10 <i>er</i>
33	(<i>R</i>)-Et-DuPhos	92:8 <i>er</i>
34	(<i>R</i>)-iPr-DuPhos	98:2 <i>er</i>

4. Initial Study with Diphenyl Phosphine Oxide and Cyclopropene with Pd (Table S2).



Entry	Chiral Ligands	Yield, <i>er</i>
1	(S)-Josiphos (J015-2)	72%, 49:50 <i>er</i>
2	(S)-Josiphos (J015-2)	50%, 63:37 <i>er</i>
3	(S,S)-BDPP	35%, 29:71 <i>er</i>
4	(R,R)-DIOP	46%, 56:44 <i>er</i>
5	(R,R)-Me-DuPhos	no reaction
6	(R,R)-iPr-DuPhos	no reaction
7	(S,S)-Et-BPE	no reaction
8	(R,R)-Ph-BPE	no reaction

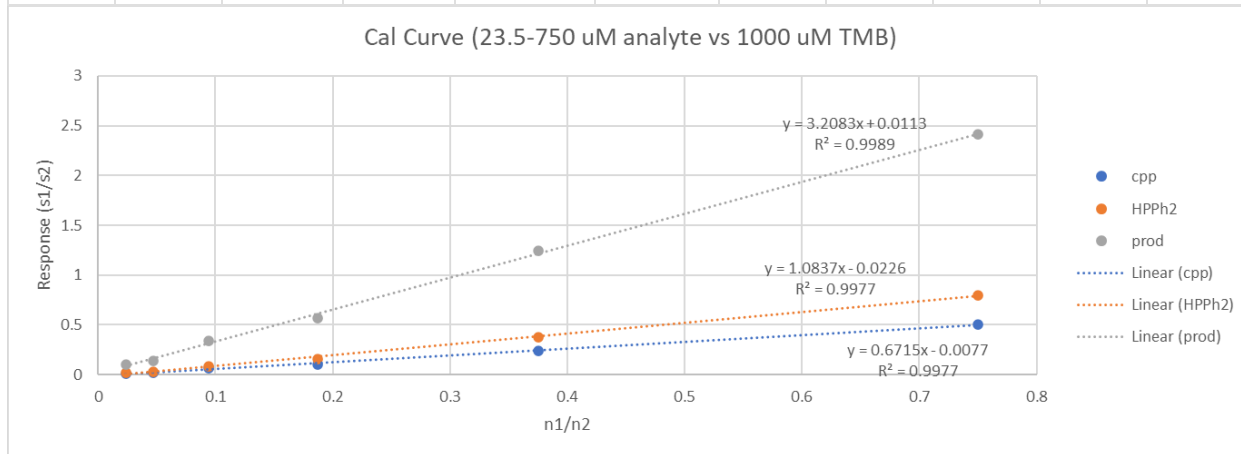
5. Mechanistic Studies.

A. Variable time normalization analysis

The order of each component of the reaction was determined using variable time normalization analysis, as described by Burés.⁴ 5 uL aliquots were taken from the reactions at the designated time points and diluted to 1 mL with dichloromethane, then analyzed by GC/FID. THF is used as solvent to have a homogeneous solution. Reaction in THF gives the same yield and stereoselectivity for this transformation as it is in toluene.

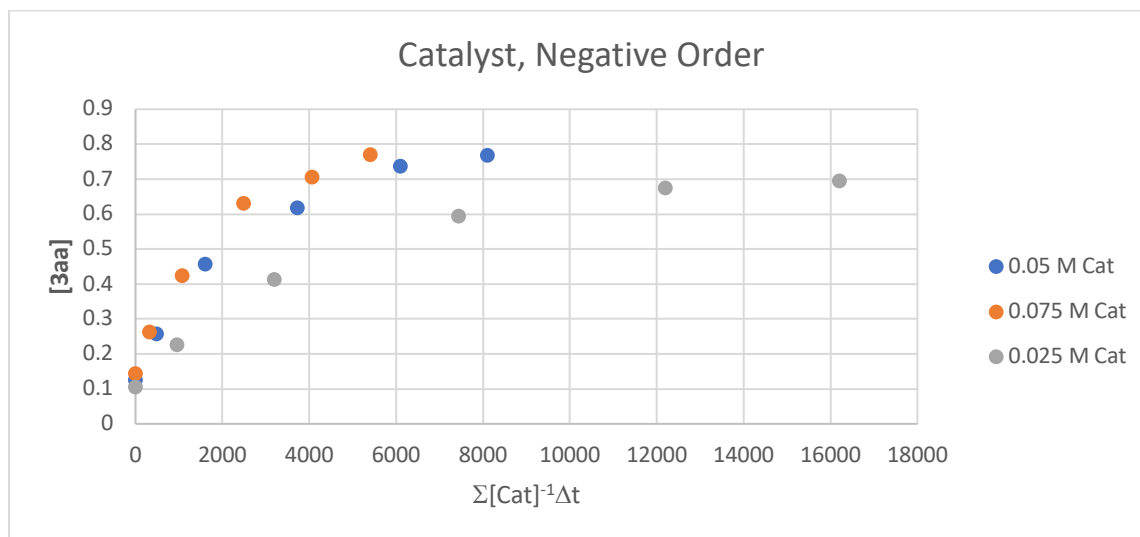
Calibration Curve:

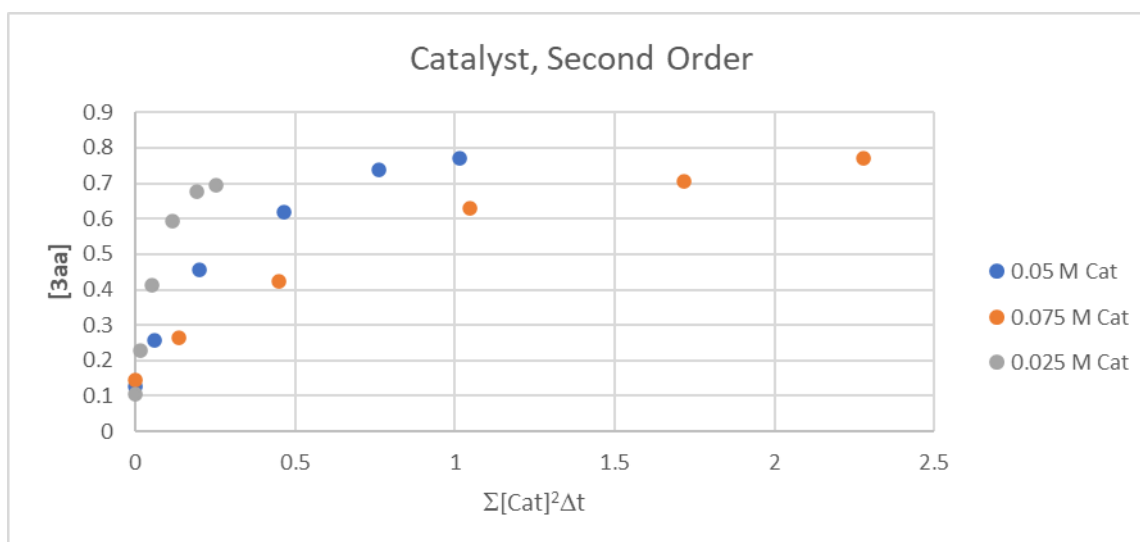
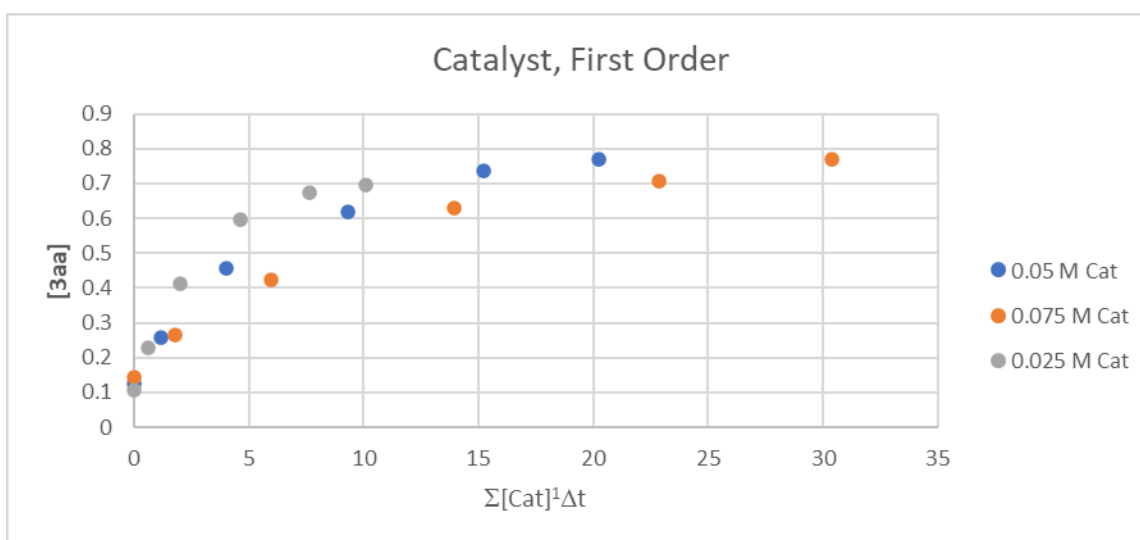
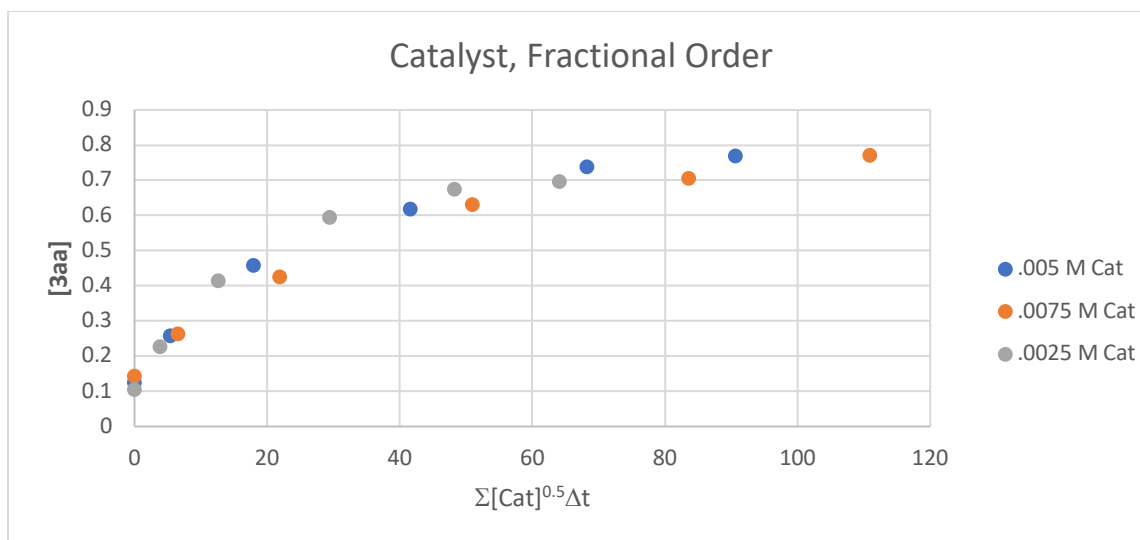
vial	[uM] n1	4.14 (TMB)	2.31 (cpp)	4.95 (HPPH2)	8.42 (prod)		n1/n2	cpp/s2	HPPH2/s2	prod/s2
10	5.85	67.4			5.4		0.00585			
11	11.7	71.8			4		0.0117			
12	23.5	72.4	1.1	1.4	7.6		0.0235	0.015193	0.019337	0.104972
13	46.9	75.9	1.8	2.2	10.7		0.0469	0.023715	0.028986	0.140975
14	94	70.7	4.5	6	24		0.094	0.063649	0.084866	0.339463
15	187.5	73.2	7.5	11.3	41.4		0.1875	0.102459	0.154372	0.565574
16	375	69.2	16.6	26.3	86		0.375	0.239884	0.380058	1.242775
17	750	68.1	34.1	54.3	164.3		0.75	0.500734	0.797357	2.412628



Order of catalyst

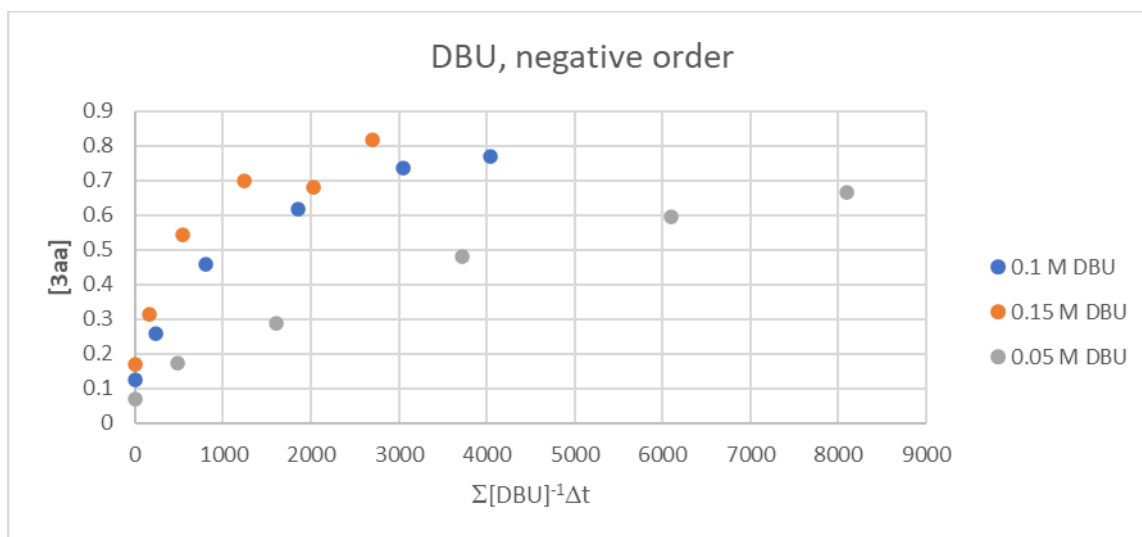
5% Cu										Cat			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[Cat]	Negative order	Fractional order	First order	Second order
20	47.3	65.4	88	27.1		1.088683	1.262495	0.125607	0.05	0	0	0	0
44	38.7	64.7	73	54.3		0.902361	1.061995	0.258044		480	5.366563146	1.2	0.06
100	23.9	62.9	50.6	93		0.577403	0.763174	0.457309		1600	17.88854382	4	0.2
206	10.8	58	28.1	115.7		0.28881	0.467918	0.618237		3720	41.59086438	9.3	0.465
325	6.5	62	25.9	147.4		0.167618	0.406332	0.737491		6100	68.20007331	15.25	0.7625
425	4.2	65.2	23.8	161.7		0.107413	0.357692	0.769485		8100	90.56075309	20.25	1.0125
7.5% Cu										Cat			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[Cat]	Negative order	Fractional order	First order	Second order
20	44.4	64.6	83.9	30.6		1.03516	1.219306	0.144095	0.075	0	0	0	0
44	32.2	59.9	63.5	51.4		0.812128	0.999077	0.263916		320	6.57267069	1.8	0.135
100	23.4	63.7	36	87.5		0.558604	0.542354	0.424608		1066.666667	21.9089023	6	0.45
206	15.6	80.8	40.9	164.4		0.299031	0.487947	0.630651		2480	50.93819785	13.95	1.04625
325	6.7	67.5	26	153.6		0.159308	0.37629	0.70574		4066.666667	83.52769002	22.875	1.715625
425	3.8	65.6	21.1	163		0.097746	0.317658	0.770948		5400	110.9138179	30.375	2.278125
2.5% Cu										Cat			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[Cat]	Negative order	Fractional order	First order	Second order
20	39.6	58.7	65.4	20.6		1.01626	1.048943	0.105834	0.025	0	0	0	0
44	44.5	72.4	77.8	53.6		0.92693	1.012444	0.227209		960	3.794733192	0.6	0.015
100	25.4	62.6	51.3	83.9		0.615804	0.77705	0.414206		3200	12.64911064	2	0.05
206	13.5	62.2	34.3	119.4		0.334736	0.52971	0.594793		7440	29.40918224	4.65	0.11625
325	5.8	57	21.1	124.1		0.163024	0.362439	0.67508		12200	48.22473432	7.625	0.190625
425	6.1	68.8	24.5	154.3		0.143525	0.349455	0.695509		16200	64.03612262	10.125	0.253125

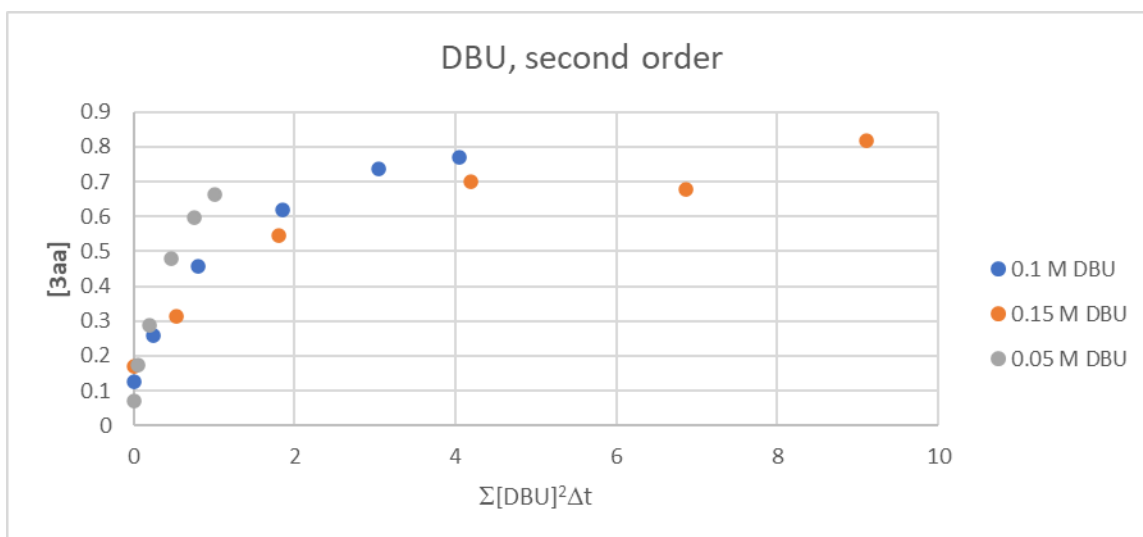
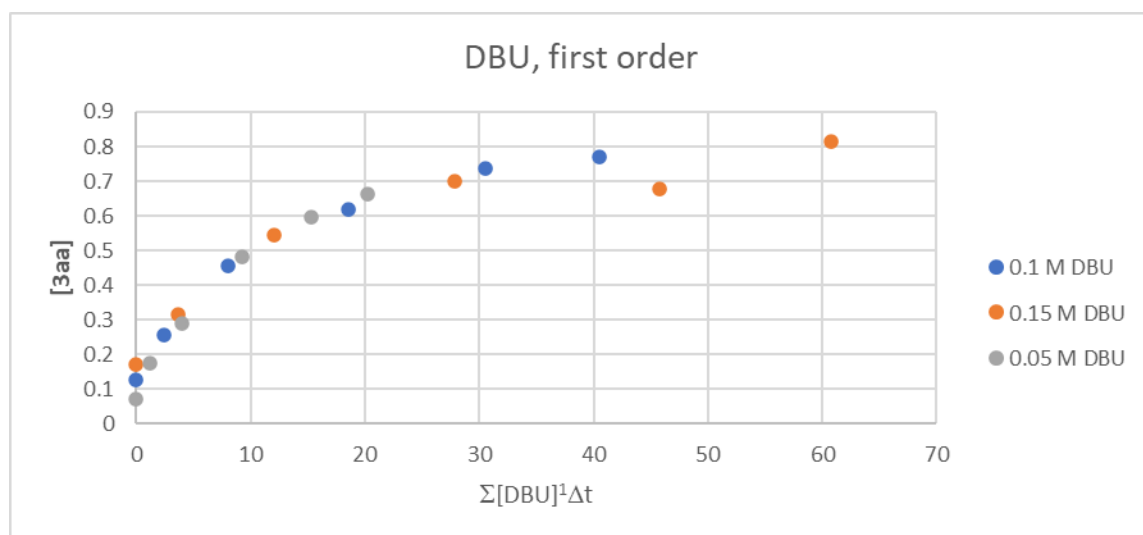
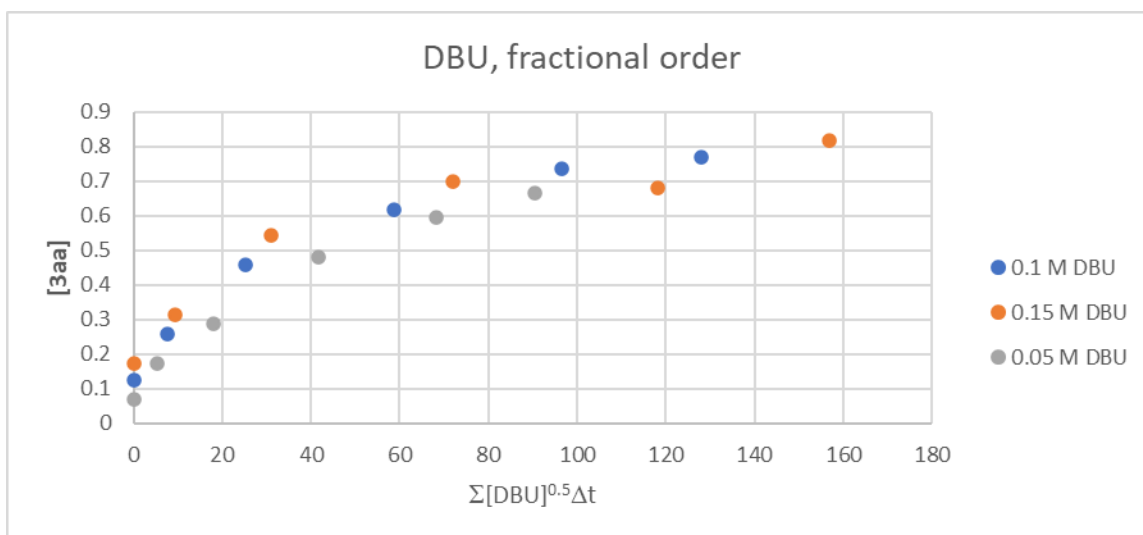




Order of DBU

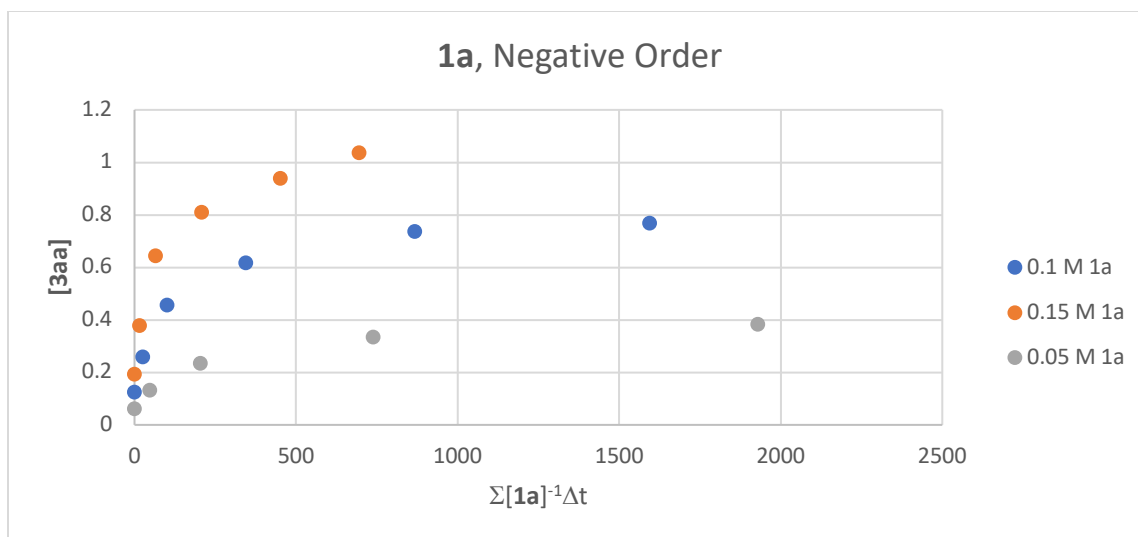
10% DBU										DBU			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[DBU]	Negative order	Fractional order	First order	Second order
20	47.3	65.4	88	27.1		1.088683	1.262495	0.125607	0.1	0	0	0	0
44	38.7	64.7	73	54.3		0.902361	1.061995	0.258044		240	7.589466384	2.4	0.24
100	23.9	62.9	50.6	93		0.577403	0.763174	0.457309		800	25.29822128	8	0.8
206	10.8	58	28.1	115.7		0.28881	0.467918	0.618237		1860	58.81836448	18.6	1.86
325	6.5	62	25.9	147.4		0.167618	0.406332	0.737491		3050	96.44946864	30.5	3.05
425	4.2	65.2	23.8	161.7		0.107413	0.357692	0.769485		4050	128.0722452	40.5	4.05
15% DBU										DBU			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[DBU]	Negative order	Fractional order	First order	Second order
20	38.3	61.8	74.7	34.7		0.934527	1.136235	0.171463	0.15	0	0	0	0
44	31.4	61.1	54.3	62.2		0.776901	0.840922	0.31376		160	9.295160031	3.6	0.54
100	17.4	62.9	38.3	110.5		0.423488	0.582729	0.54403		533.3333333	30.98386677	12	1.8
206	7.6	67.2	25.7	151.7		0.179915	0.373757	0.700094		1240	72.03749024	27.9	4.185
325	3.2	66.6	6.4	145.9		0.083033	0.109529	0.679288		2033.333333	118.1259921	45.75	6.8625
425	2	71.4	19.7	187.7		0.053189	0.275455	0.815863		2700	156.8558255	60.75	9.1125
5% DBU										DBU			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	[DBU]	Negative order	Fractional order	First order	Second order
20	46.3	59.7	78.8	14.1		1.166584	1.238842	0.070064	0.05	0	0	0	0
44	40.7	58.5	65.3	33.3		1.047701	1.050881	0.173877		480	5.366563146	1.2	0.06
100	33.1	64.6	57.7	60.6		0.774626	0.845058	0.288847		1600	17.88854382	4	0.2
206	20	59.6	44.9	92.6		0.511276	0.716024	0.480734		3720	41.59086438	9.3	0.465
325	15.9	69.7	19.4	134.3		0.351237	0.277693	0.597042		6100	68.20007331	15.25	0.7625
425	11.4	65.5	33.6	140.3		0.270697	0.494212	0.664106		8100	90.56075309	20.25	1.0125

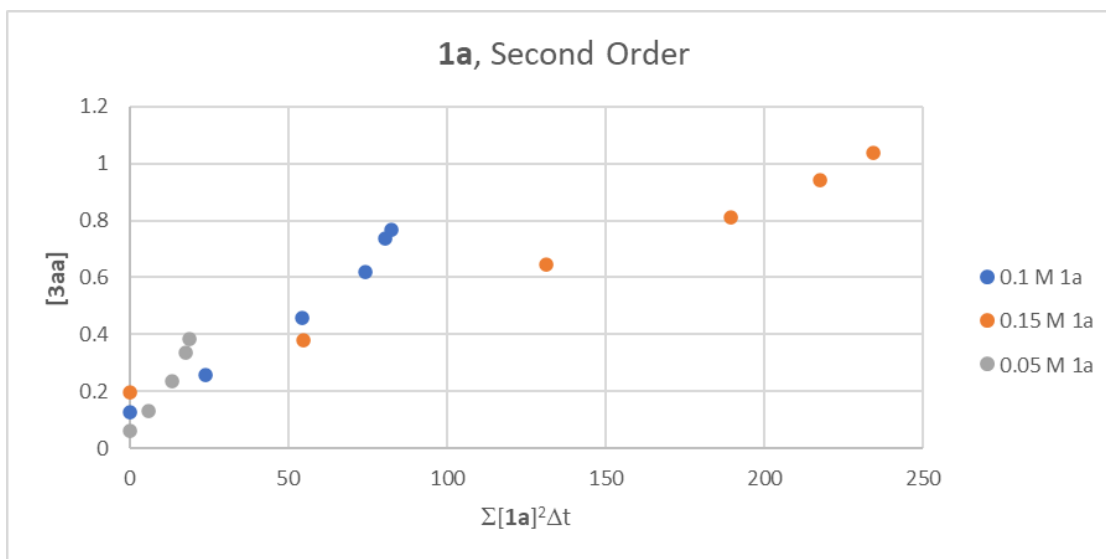
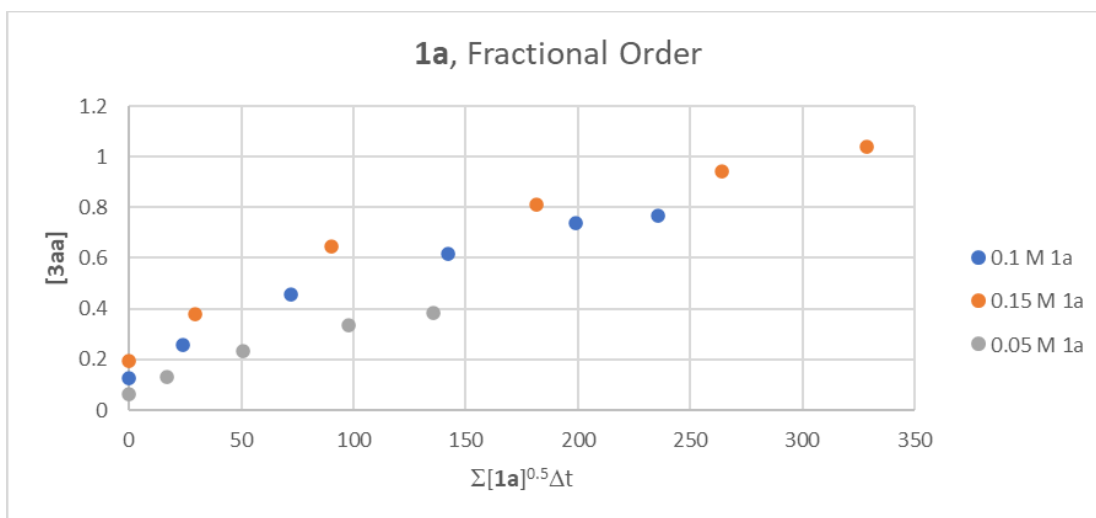




Order of cyclopropene (1a)

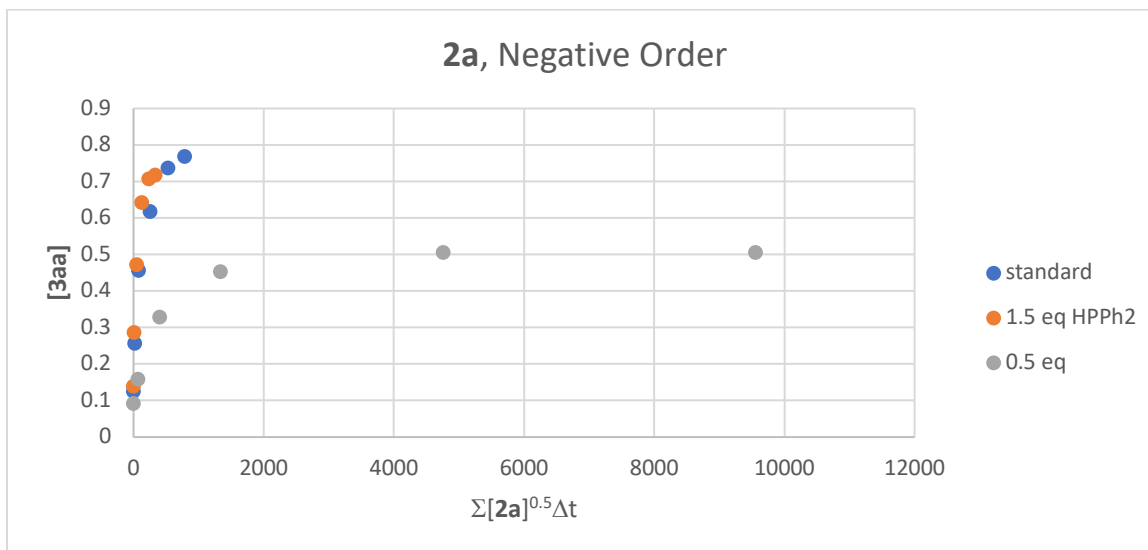
1 eq CPP									CPP			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	Negative order	Fractional order	First order	Second order
20	47.3	65.4	88	27.1		1.088683	1.262495	0.125607	0	0	0	0
44	38.7	64.7	73	54.3		0.902361	1.061995	0.258044	24.1079566	23.94620312	23.89252683	23.78553493
100	23.9	62.9	50.6	93		0.577403	0.763174	0.457309	99.79570599	72.11538218	65.32591632	54.44135216
206	10.8	58	28.1	115.7		0.28881	0.467918	0.618237	344.5393341	141.8748407	111.235181	74.32494256
325	6.5	62	25.9	147.4		0.167618	0.406332	0.737491	865.9799968	198.7232078	138.3926334	80.52265032
425	4.2	65.2	23.8	161.7		0.107413	0.357692	0.769485	1593.170458	235.8062977	152.144189	82.41370311
1.5 eq CPP									CPP			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	Negative order	Fractional order	First order	Second order
20	63.1	58.2	66	36.9		1.626292	1.067289	0.194072	0	0	0	0
44	56.9	61.4	55.3	75.2		1.391734	0.851944	0.378205	15.90443648	29.4820528	36.21630988	54.65087921
100	39.4	62.9	30.3	130.8		0.944431	0.465366	0.644627	63.84625524	90.00565771	101.6289304	131.0582172
206	21.5	60.9	3.5	159.1		0.537292	0.073887	0.81076	206.9229242	181.2433701	180.1602527	189.2390529
325	19.4	67.8	3.8	205.3		0.437646	0.072573	0.940285	451.0409793	264.3279621	238.1690714	217.5165575
425	16.1	64.2	1.4	214.4		0.384985	0.040977	1.037393	694.1633266	328.4618487	279.3006256	234.434605
0.5 eq CPP									CPP			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	Negative order	Fractional order	First order	Second order
20	21.5	58.2	83.3	12.1		0.561686	1.341581	0.06125	0	0	0	0
44	20.5	69.8	90.8	30.5		0.448907	1.221242	0.132648	47.49686973	17.06020983	12.12711497	6.12778823
100	10.3	59.6	64.8	45.5		0.268869	1.024129	0.234406	203.5343235	50.60828543	32.22485384	13.34062944
206	5.7	73.4	69.9	79.6		0.127132	0.899618	0.334477	738.885709	97.77540251	53.21293812	17.49628681
325	2.6	63	58.6	78		0.072937	0.879172	0.382362	1928.473614	135.4130242	65.1170605	18.68711143





Order of diphenylphosphine (2a)

1 eq HPPH2						HPPH2			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	
20	47.3	65.4	88	27.1		1.088683	1.262495	0.125607	
44	38.7	64.7	73	54.3		0.902361	1.061995	0.258044	
100	23.9	62.9	50.6	93		0.577403	0.763174	0.457309	
206	10.8	58	28.1	115.7		0.28881	0.467918	0.618237	
325	6.5	62	25.9	147.4		0.167618	0.406332	0.737491	
425	4.2	65.2	23.8	161.7		0.107413	0.357692	0.769485	
1.5 eq HPPH2						HPPH2			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	
20	43.7	60.3	128.9	27.8		1.09087	1.993398	0.14015	
44	33.1	59.8	110.6	55.7		0.835883	1.727506	0.286777	
100	28.1	77.3	120.5	118.1		0.552903	1.459317	0.472668	
206	11.9	66.2	84.5	137.5		0.279205	1.198704	0.643862	
325	8.1	69.1	78.5	157.7		0.186061	1.069147	0.707811	
425	6.7	84.1	82.5	194.7		0.130127	0.926064	0.718067	
0.5 eq HPPH2						HPPH2			
t (min)	cpp	TMB	HPPH2	prod		[cpp]	[HPPH2]	[prod]	
20	45.8	62.5	33.4	19.4		1.102919	0.51398	0.093199	
44	45.1	78.4	12	40.9		0.868268	0.162094	0.159056	
100	39.7	82	14	87.8		0.732568	0.1784	0.330195	
206	28.1	76.3	2.3	111.9		0.559999	0.04867	0.453581	
325	22.3	67.8	0	111.1		0.501353	0.020854	0.507214	
425	22.3	71	0	116.2		0.479274	0.020854	0.506583	



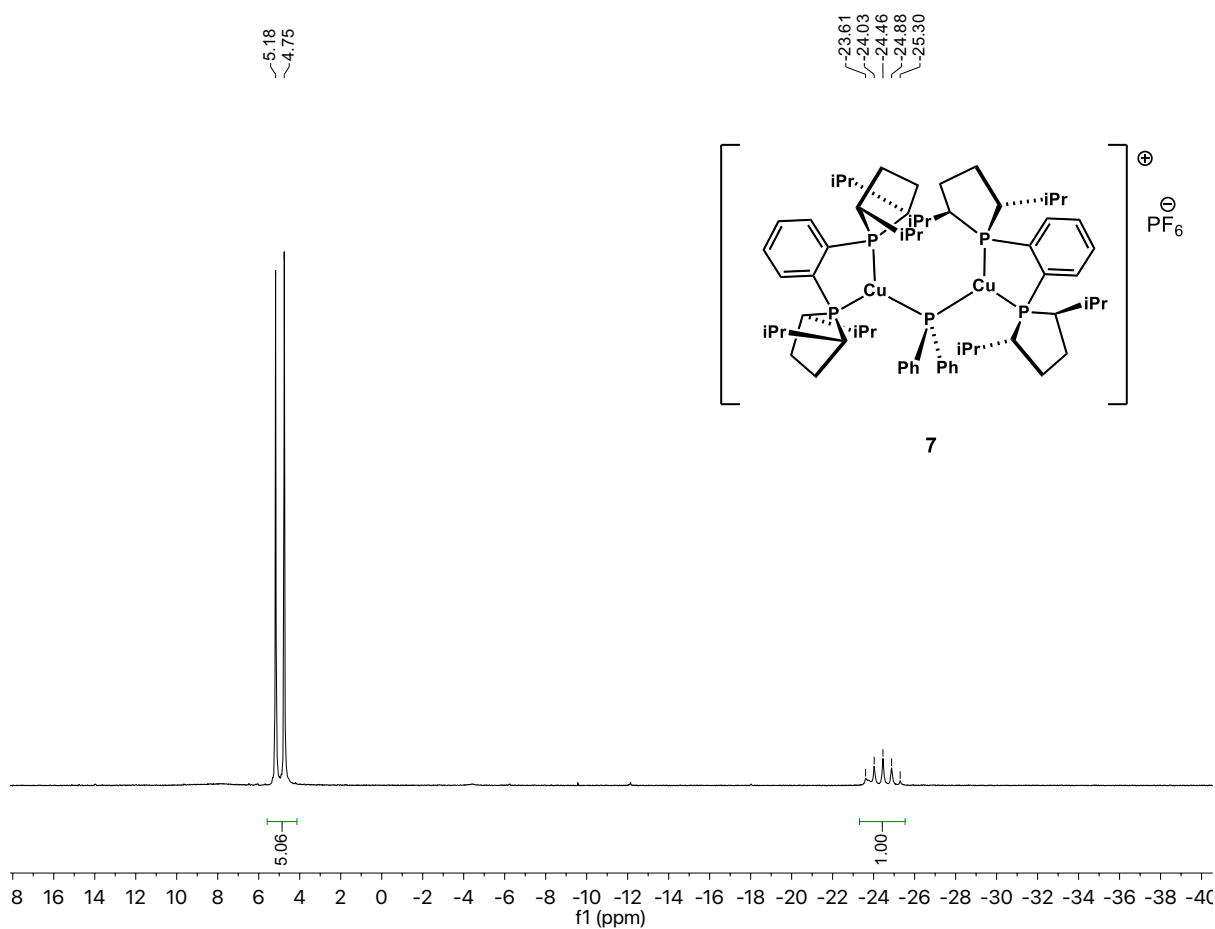


B. NMR Study of the Cu-Dimer 7 with 2a.

Procedure for synthesis of Cu dimer 7

In a N₂-filled glovebox, (*R,R*)-*i*-Pr-Duphos (**L3**) (0.05 mmol) and THF (1 mL) were added to a 1-dram vial containing Cu(CH₃CN)₄PF₆ (0.05 mol). The resulting mixture was stirred for 30 min and then diphenylphosphine **2a** (0.025 mmol) was added. Stirring was continued for 5 minutes. DBU (0.025 mmol) was then added, and the solution was stirred for another 30 minutes. THF was removed under reduced pressure, and the resulting solid was washed with n-pentane (1 mL).

³¹P NMR of Cu dimer 7:



Time-of-flight mass spectrum of Cu dimer 7:

Note that the expected m/z for the cationic Cu dimer is 1149.5, and incorporation of 2 oxygen atoms (through incidental exposure to atmospheric O_2 during sample preparation) corresponds to the observed m/z of $1149.5 + 32 = 1179.5$; presumably this oxygen incorporation occurs through oxidation of the phosphine ligands.

Openlynx Report - bsdaniel

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Vial:1:152
Date:11-Jul-2022

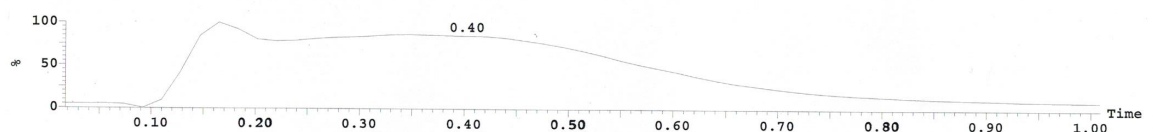
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Page 1

Sample Report:

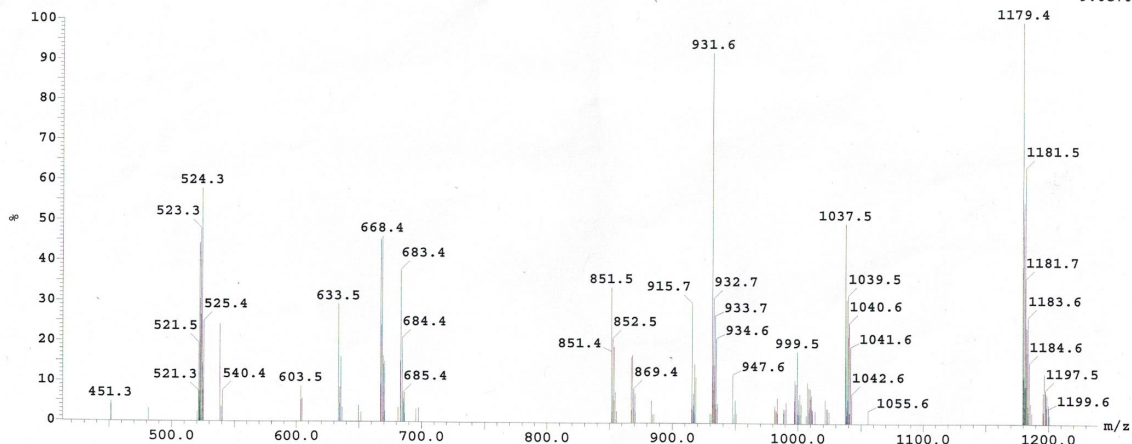
1: TOF MS ES+ :TIC Smooth (SG, 2x2)

5.6e+005



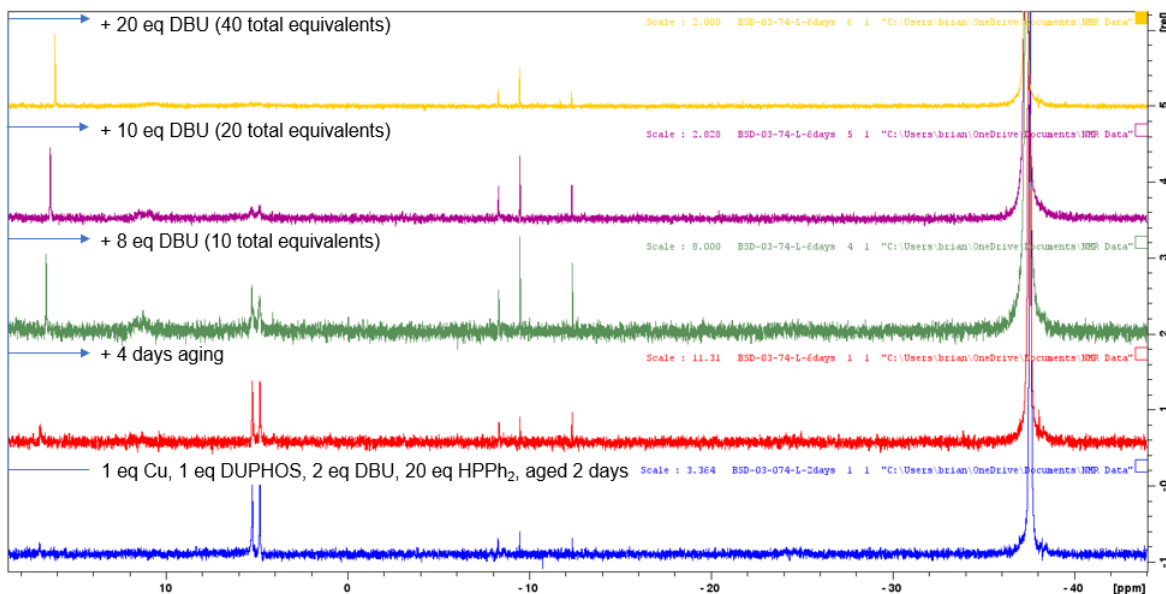
Center (Cen,4, 80.00, Ar); Combine (16:27-(1:11+44:65))

1:TOF MS ES+
9.6e+004



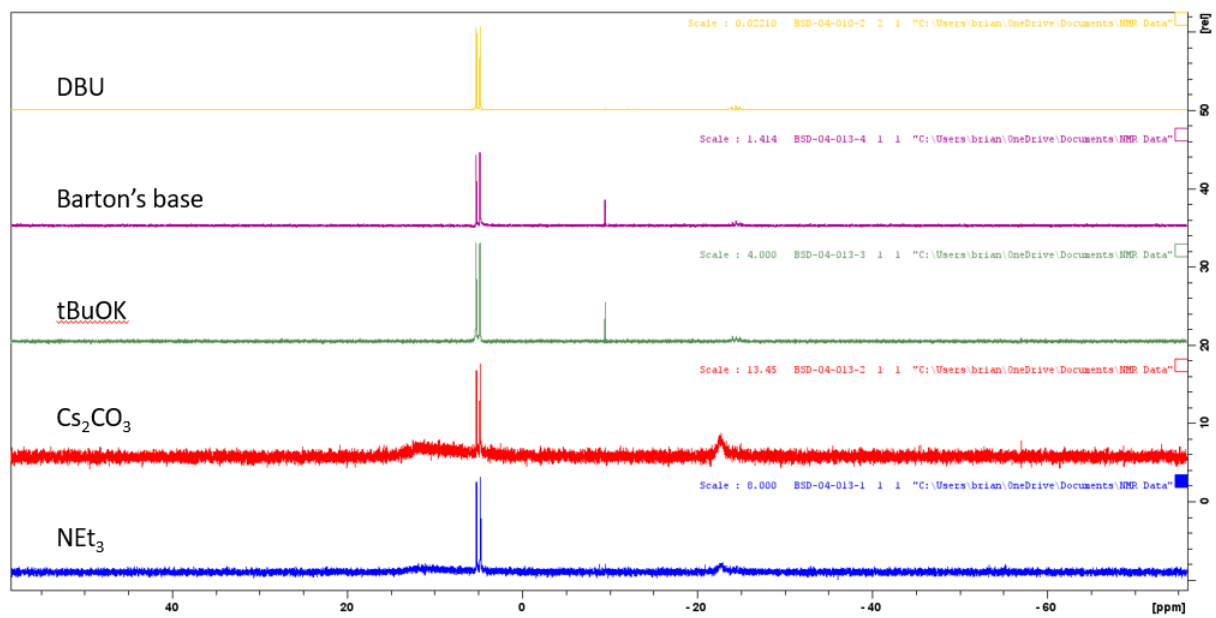
Catalyst aging and base-induced decomposition experiments.

The dimeric catalyst resting state remained stable in solution under the model reaction conditions (excluding cyclopropene) for up to 6 days. Addition of excess DBU to this solution resulted in gradual decomposition of the dimeric resting state, evidenced by the disappearance of the 5.0 ppm doublet and concomitant formation of a new species at 16.4 ppm tentatively assigned to a Cu-DuPhos-DBU adduct.



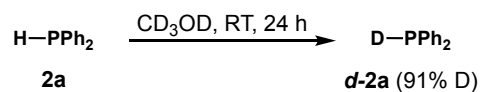
Effect of base on dimer formation

A variety of bases were tested for their ability to form the dimeric Cu resting state. These samples were prepared according to a modified version of **Procedure for synthesis of Cu dimer 7** where DBU was replaced with various bases and ^{31}P NMR analysis was conducted prior to concentration under reduced pressure or trituration.



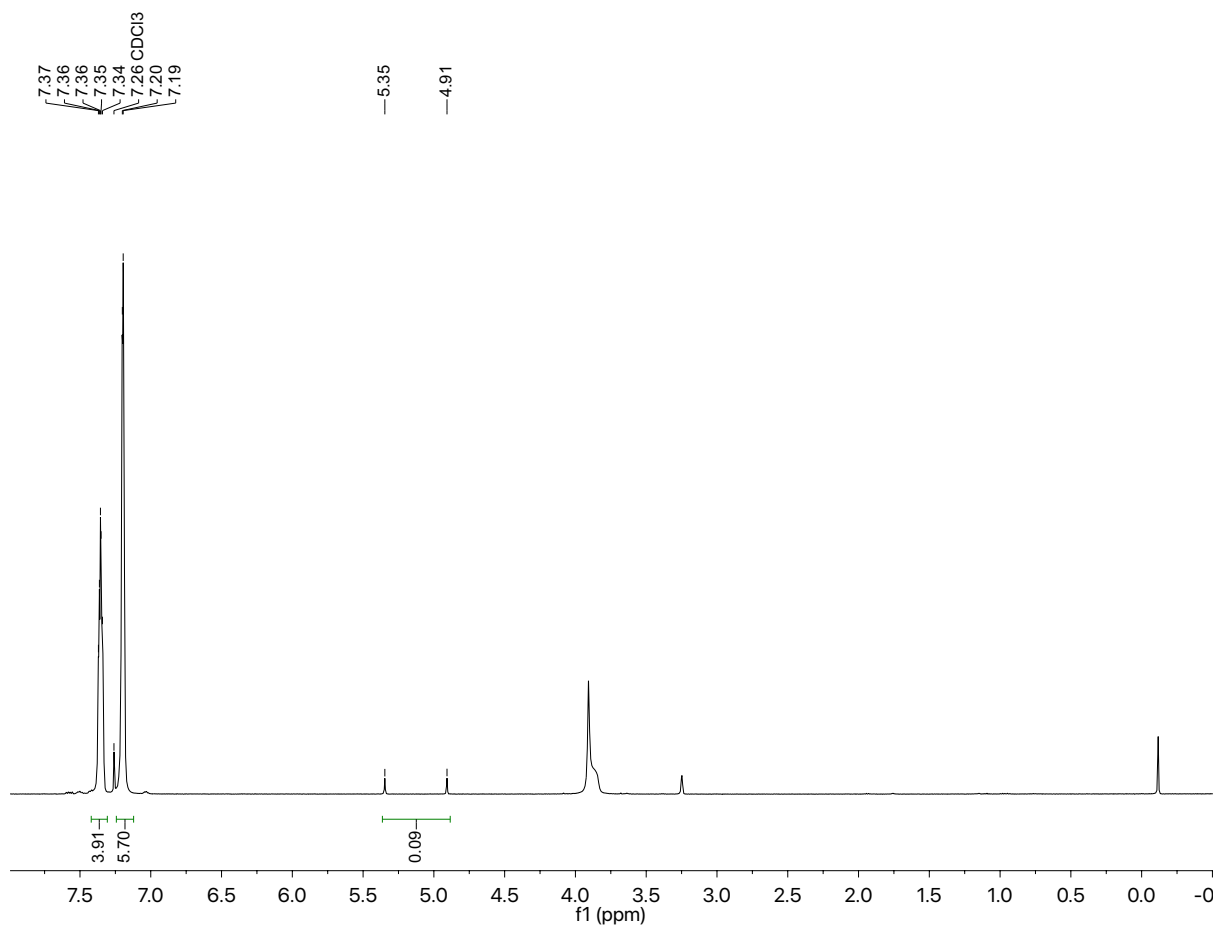
C. Deuterium Labeling Study

Synthesis of *d*-2a:

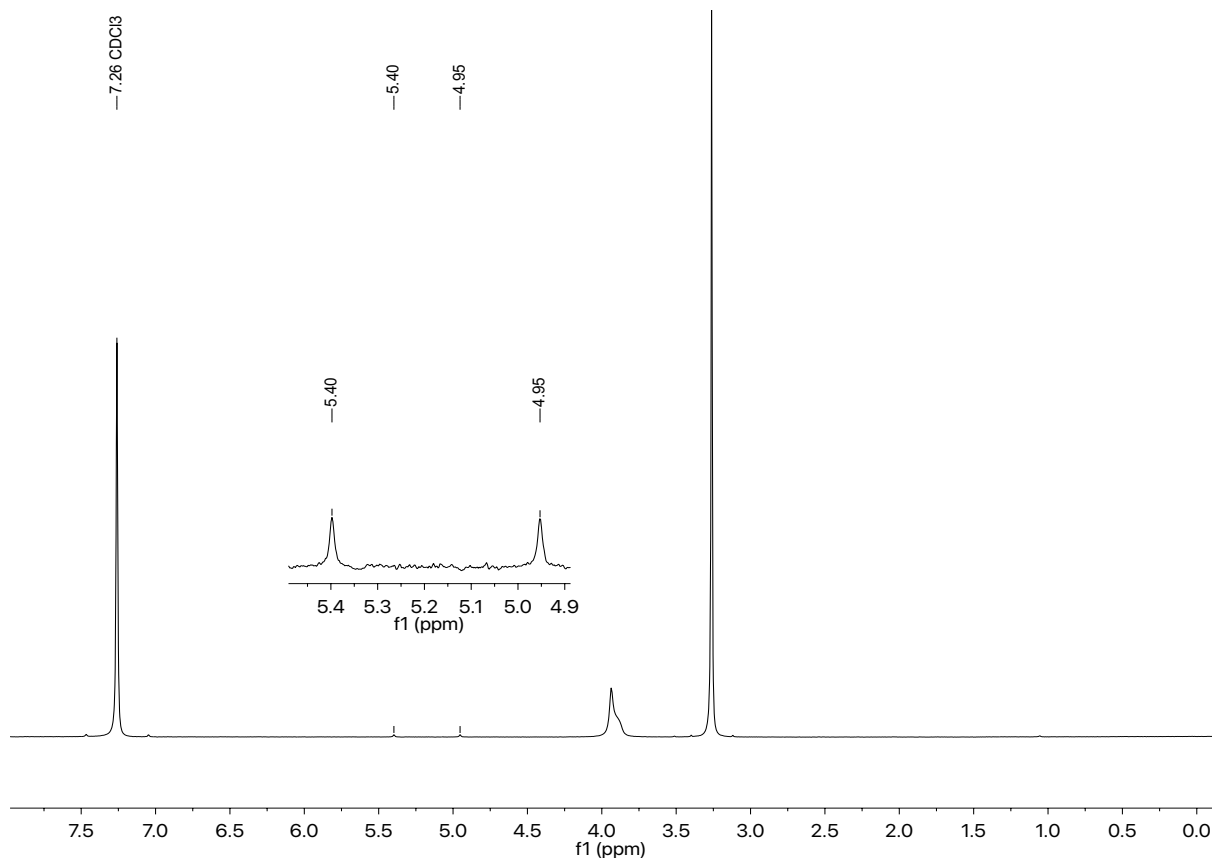


In an N₂ filled glovebox, diphenyl phosphine **2a** (0.5 mmol) was dissolved in methanol-d₄ (1 mL) in a 1-dram vial and stirred overnight. The solution was concentrated under vacuo and result in **d-2a** with 91% D incorporation which was determined by ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.34 (m, 4H), 7.20–7.19 (m, 6H), 5.13 (d, *J* = 176 Hz, 1H). The deuterium incorporation was further confirmed by ²H NMR (61 MHz, CDCl₃) δ 5.18 (d, *J* = 27 Hz).

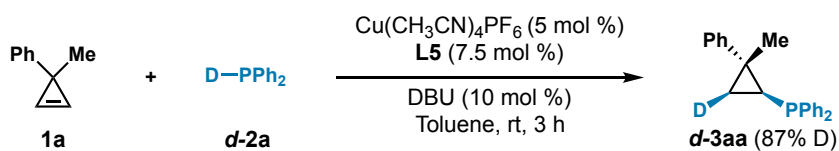
¹H NMR of *d*-2a



^2H NMR of *d*-2a

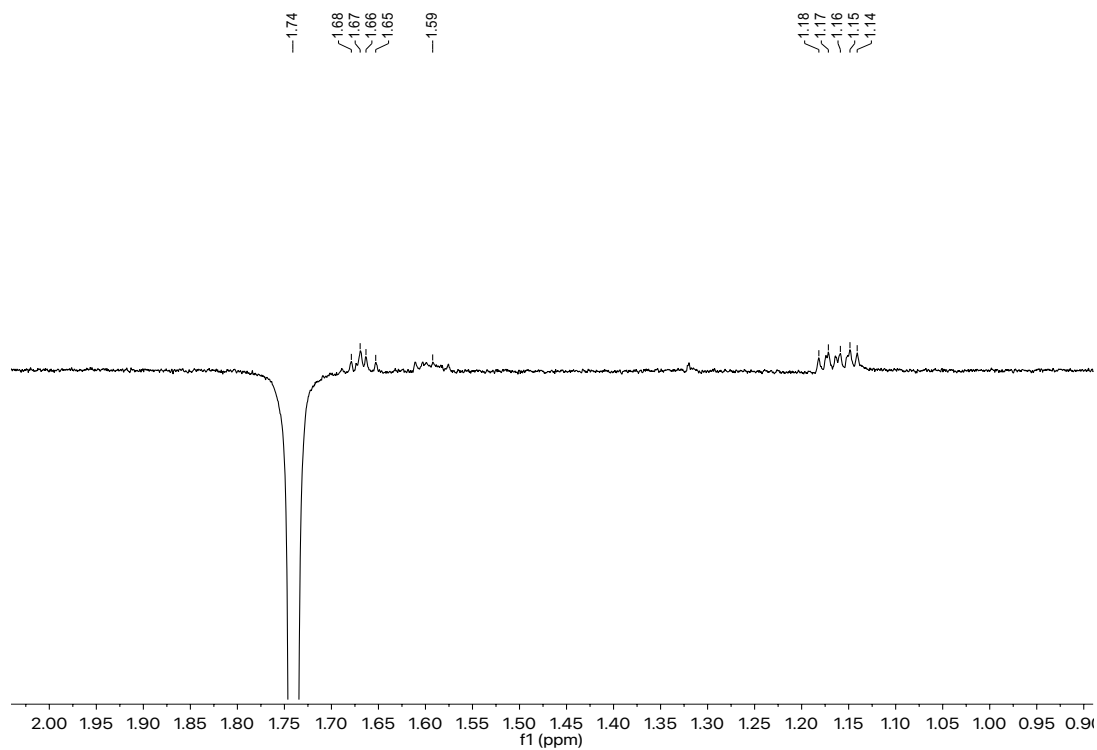


Synthesis of *d*-3aa:

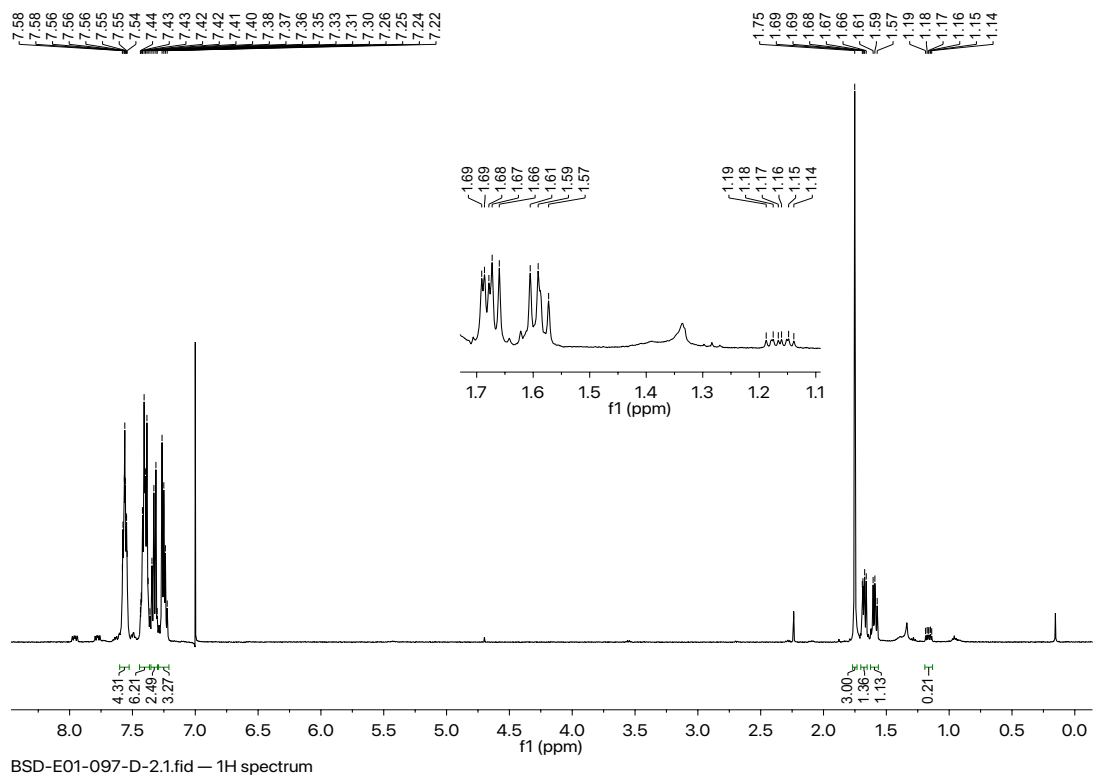


Following the **General Procedure for Hydrophosphination with Cu**, *d*-2a was used as a coupling partner. The assignment of the proton *syn* to the methyl of the cyclopropyl ring was made according to 1-D gNOE experiments shown below. The 91% deuterium incorporation into *d*-2a and 79% deuterium incorporation into the *syn*-methyl proton corresponds to a 87% deuterium incorporation into this position. Exclusive *syn* deuterium incorporation was confirmed by ^2H NMR of *d*-3aa. No oxidation with elemental sulfur was performed to achieve adequate separation of alkyl proton peaks.

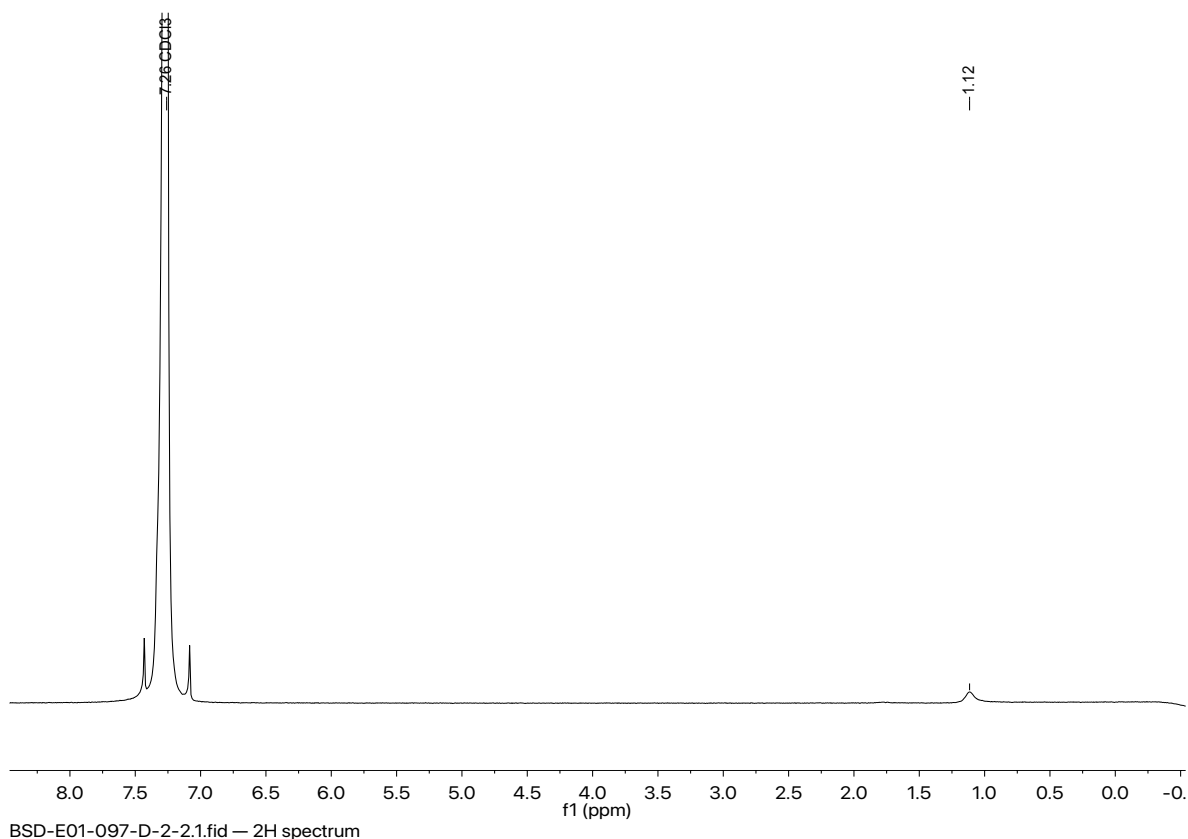
gNOE experiments to assign *syn*-methyl proton



^1H NMR of *d*-3aa

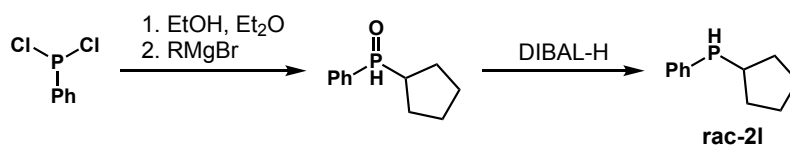


²H NMR of *d*-3aa



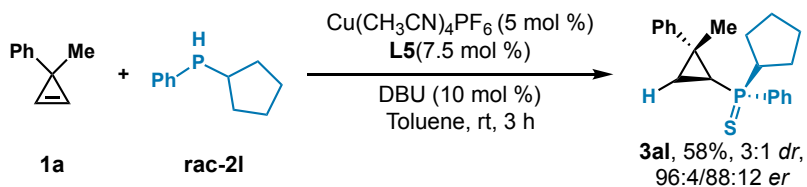
D. Dynamic Kinetic Asymmetric Transformation

Synthesis of *rac*-2l:



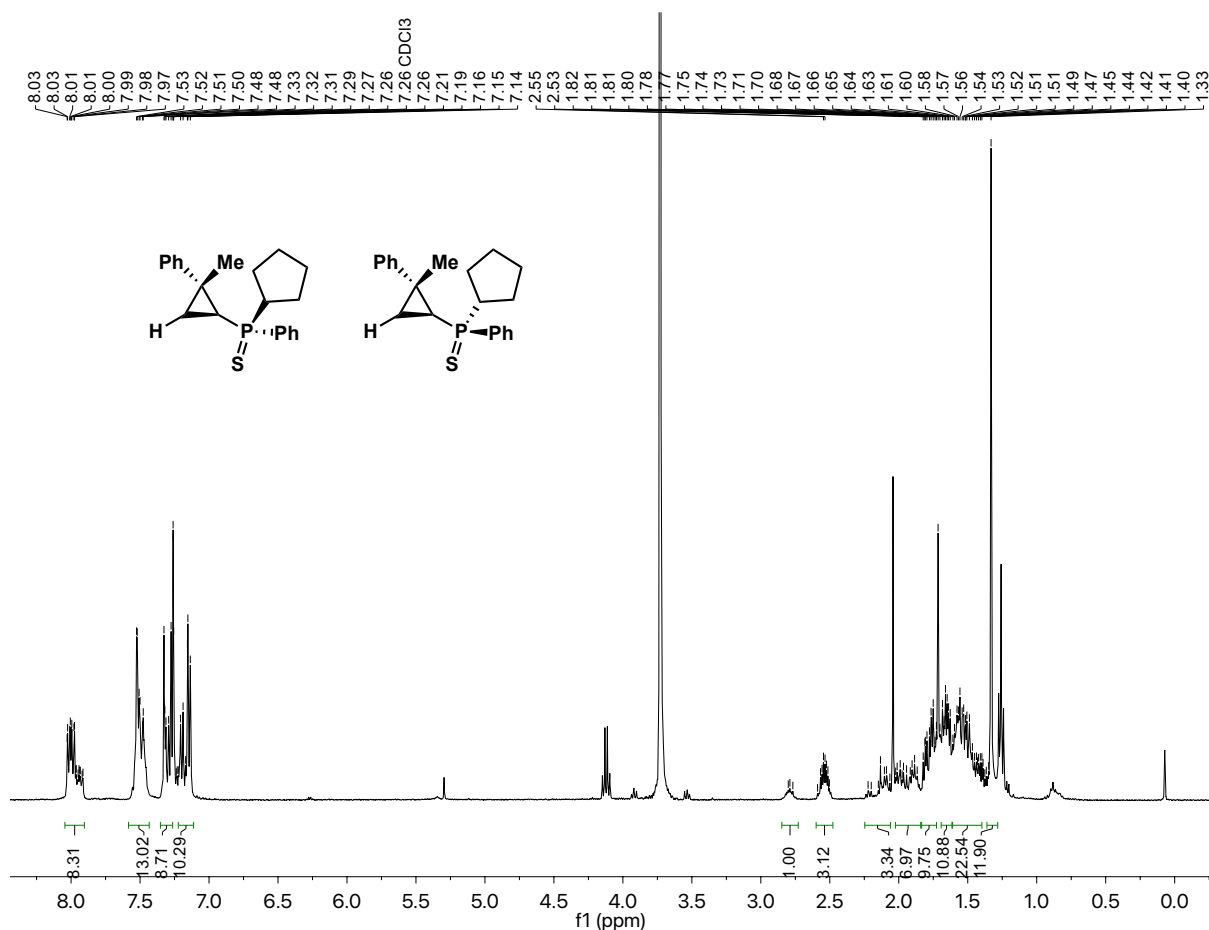
Reduction of the secondary phosphine oxide, prepared according to a known procedure,⁵ was performed according to a reported procedure⁶ to give secondary phosphine *rac*-2l. A small amount of residual secondary phosphine remained.

Synthesis of 3al:

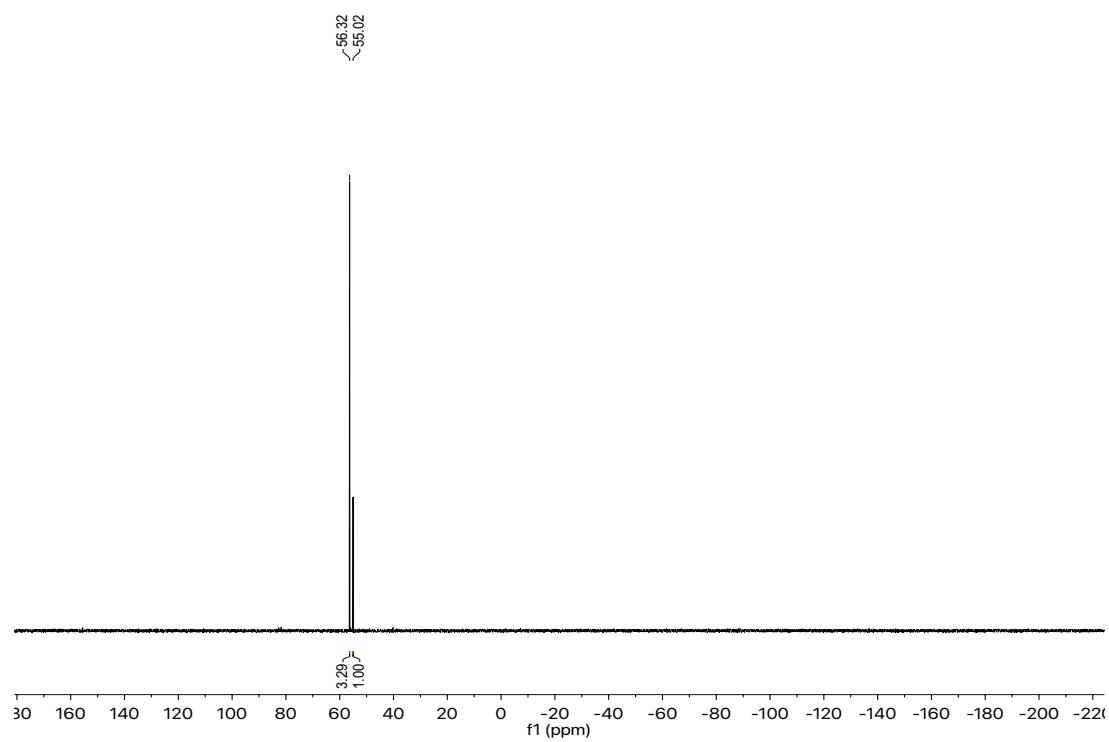


Following the **General Procedure for Hydrophosphination with Cu**, **rac-2l** was used as a coupling partner. The racemic standard was prepared according to this general procedure using *rac*-BINAP as ligand. The diastereomers proved inseparable by column chromatography and preparatory thin layer chromatography and were thus isolated as a mixture.

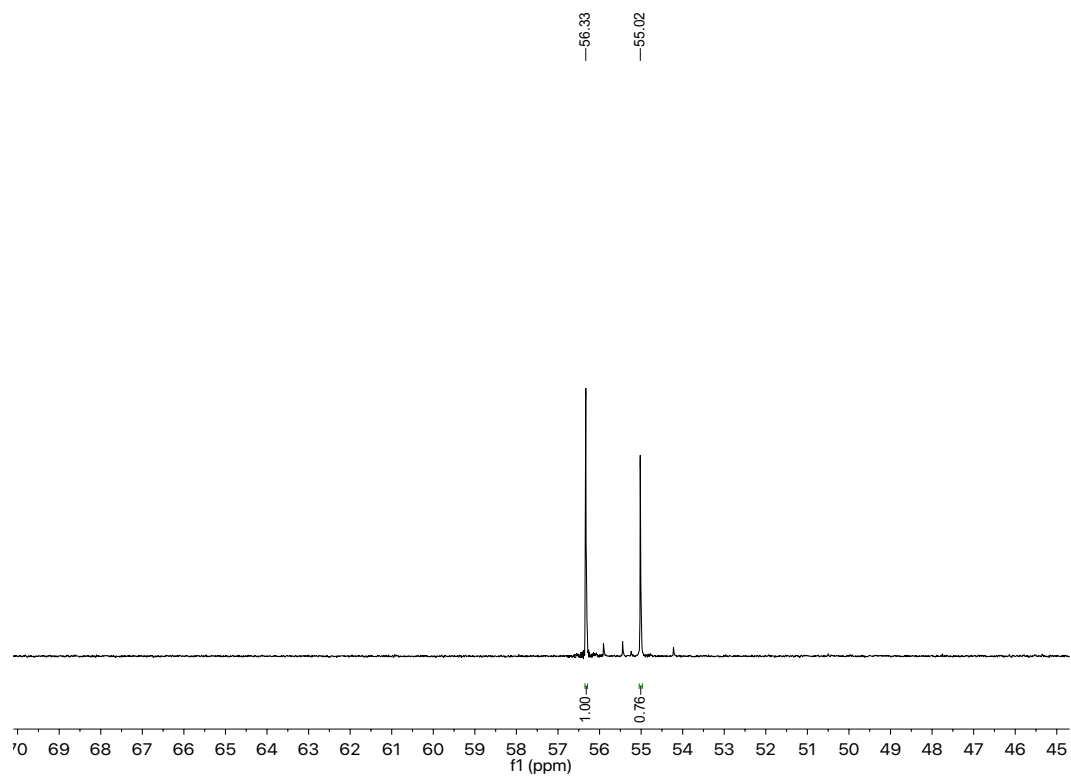
¹H NMR of 3al (DCE added as internal standard after isolation to verify yield)



^{31}P NMR of 3al



^{31}P NMR of crude *rac*-3al



6. Computational Studies.

A. General Information

Density functional theory (DFT) was employed to study the mechanism of the enantioselective hydrophosphination of cyclopropenes via Cu-phosphido catalyst. The coupling of 3-methyl-3-phenylcyclopropene and diphenylphosphine (**1a** and **2a**, respectively) was chosen as the model substrate system for our theoretical study using Cu-(R,R)-*i*-Pr-DuPhos (**L5**) as the catalytic species. All ground state and transition state optimizations as well as the calculation of vibrational frequencies were performed at the B97D/def2SVP level of theory in gas phase, as implemented in Gaussian 16.⁷⁻⁹ Single point energies were computed at the ω B97XD/def2TZVP level of theory utilizing a polarized continuum solvation model (PCM) for toluene.¹⁰⁻¹² Thermal corrections to free energies were implemented using Grimme's quasi-rigid rotor harmonic oscillator (QRRHO) approximation.¹³ Transition structures (TSs) were verified as exhibiting one sole imaginary frequency, and intrinsic reaction coordinate calculations were performed to confirm the TSs connect the minima along the potential energy surface. Conformational analysis for all TSs and ground state structures was carried out. To aid in discerning the origins of enantioselectivity, distortion-interaction analysis was conducted on the lowest-energy TSs that lead to the formation of each product enantiomer. Molecular graphics were generated using CYLView and VMD.¹⁴ Steric maps were generated using the SEQCROW package of ChimeraX.^{15,16}

B. Analysis of Mechanistic Pathway

Deprotonation of Acidified Cu-phosphido Complex

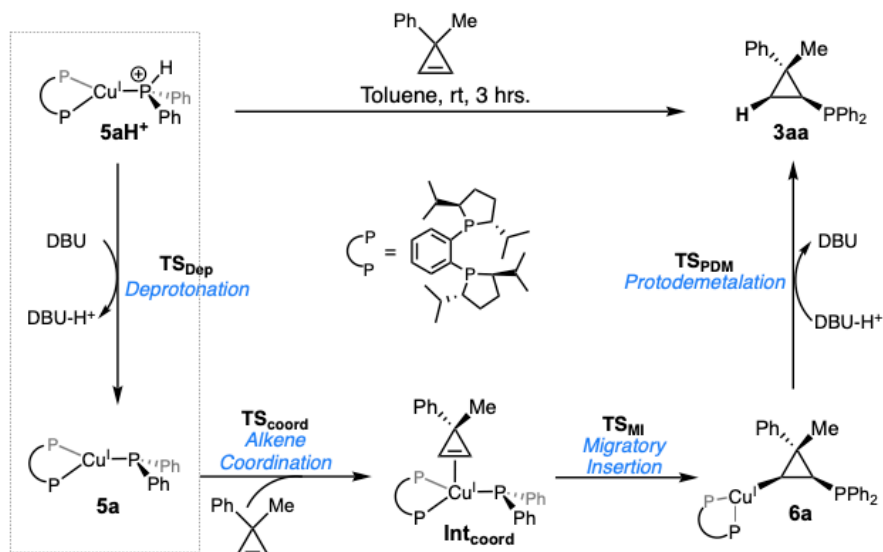


Figure S1. A general mechanistic scheme for copper-catalyzed hydrophosphination of cyclopropenes

For the deprotonation of acidified phosphine following addition into copper, TS_{Dep} was modeled in the presence of the base additive, an external molecule of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Transfer of the proton from protonated phosphine to DBU was found to occur at a P-H bond distance of 1.65 Å and an N-H bond distance of 1.38 Å. TS_{Dep} produces protonated DBU for subsequent catalytic steps and the copper-phosphido monomer (**5a**) used as the comparative baseline for analysis of pathway energetics. The $\Delta G^\ddagger$ for TS_{Dep} is 4.8 kcal/mol relative to **5a** and is facile.

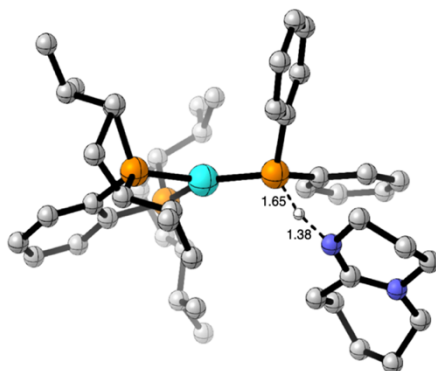


Figure S2. Transition state for the deprotonation of protonated phosphine by DBU.

In lieu of the aforementioned addition-deprotonation sequence, oxidative addition of protonated phosphine into the Cu-DuPhos catalyst was explored as an alternative pathway to form reactive complex **6a**. However, transfer of the proton from P to Cu with concomitant oxidization of Cu(I) to Cu(III) could not be located on the energy surface.

Coordination of Cu-phosphido with 3-methyl-3-phenylcyclopropene

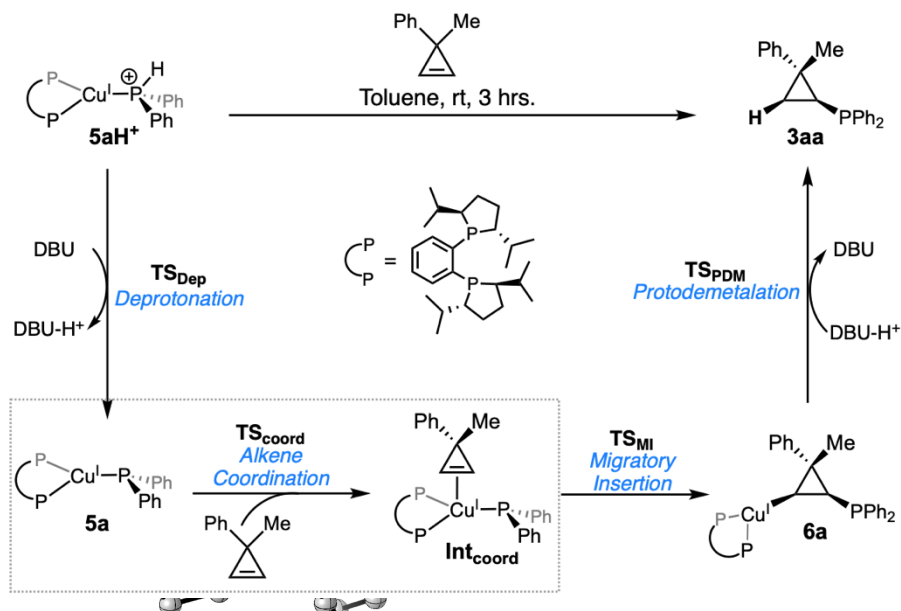


Figure S3. A general mechanistic scheme for copper-catalyzed hydrophosphination of cyclopropenes.

Figure S4. Transition structure for the coordination of copper to the π -bond of cyclopropene.

Alkene coordination (TS_{coord}) of Cu catalyst to cyclopropene exhibits a $\Delta G^\ddagger$ of 15.1 kcal/mol with the resulting copper-alkene complex lying 13.8 kcal/mol in energy, as found via reverse reaction coordinate analysis from TS_{mi} .

Migratory Insertion of Cu-phosphido into 3-methyl-3-phenylcyclopropene

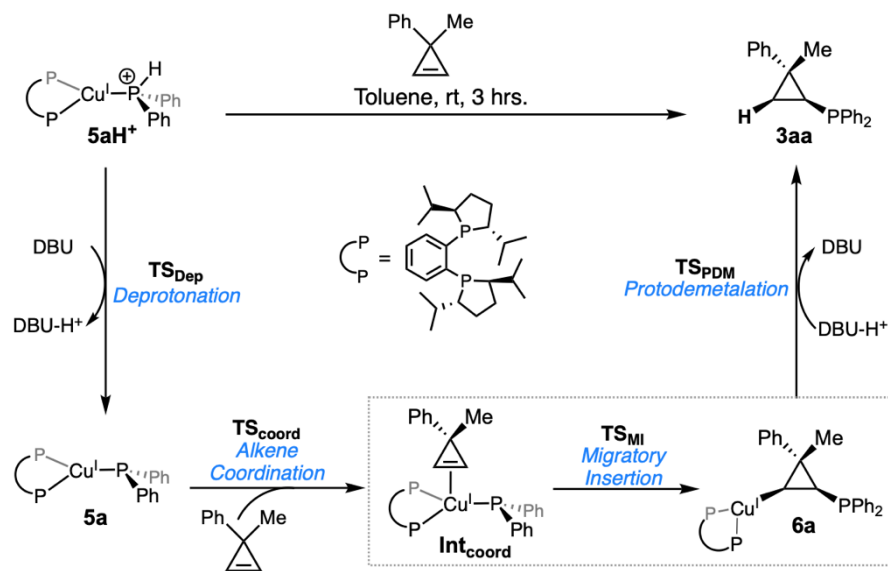


Figure S5. A general mechanistic scheme for copper-catalyzed hydrophosphination of cyclopropenes.

Following coordination, Cu-phosphido performs a 1,2-migratory insertion into the coordinated π -bond of cyclopropene with Cu-DuPhos and *syn* addition of PPh₂. Migratory insertion serves as the enantio- and diastereoselectivity step in the hydrophosphination reaction. Four possible stereoisomeric products can be formed from the migratory insertion TSs: two in which cyclopropene approaches the catalytic pocket with its methyl group oriented forward (**TS_{MI-Major}** and **TS_{MI-Minor}**), and two in which the cyclopropene approaches phenyl-forward (**TS_{MI-Dia1}** and **TS_{MI-Dia2}**). The latter are transition structures that lead to the diastereomeric products of **TS_{MI-Major}** and **TS_{MI-Minor}**, exhibiting larger free energies ($\Delta\Delta G^\ddagger = 3.6$ kcal/mol and 2.5 kcal/mol with respect to **TS_{MI-Major}**). A conformational search was conducted for each transition structure that leads to the product stereoisomers as shown in Figure S6 with their relative free energies determined via a Boltzmann weighting of all TS conformation within 3.0 kcal/mol of the lowest

energy TS that leads to each stereoisomer.

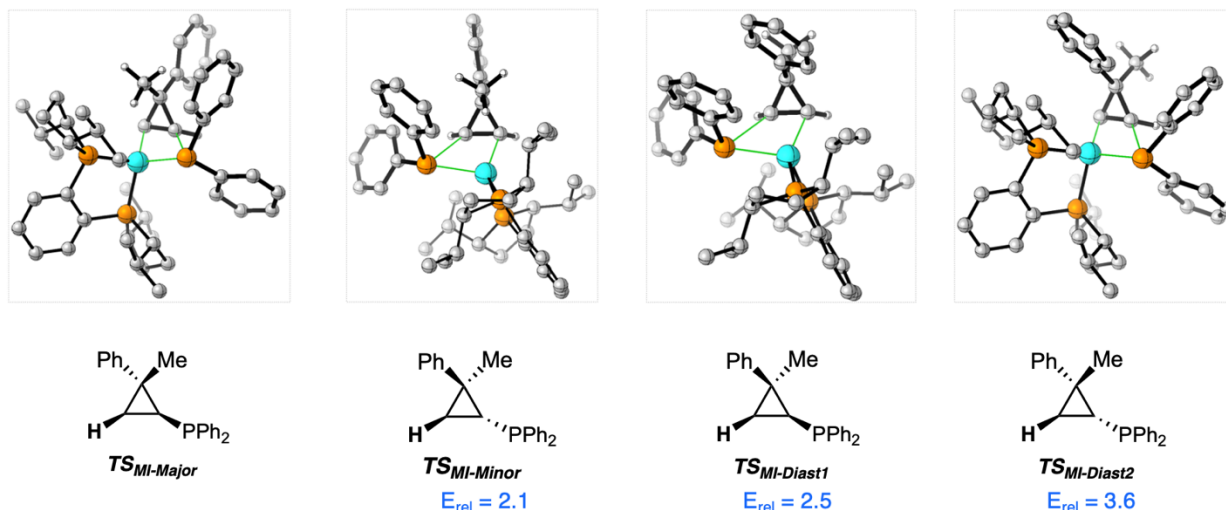


Figure S6. Migratory insertion transition state structures leading to the four possible stereoisomeric products formed from the hydrophosphination of cyclopropenes. Free energies provided are relative to the $TS_{MI-Major}$.

$TS_{MI-Major}$ was also used to probe this system's functional//basis set dependence. Table S1 outlines the free energy and geometric differences amongst various functionals, basis sets and solvation models. The cyclophosphinated intermediate resulting from migratory insertion (**6a**) as well as TS_{PDM} were also optimized correspondingly and used to calculate the relative energy difference across the different levels of theory. Though the barrier height for $TS_{MI-Major}$ varied somewhat, the relative energy between $TS_{MI-Major}$ and TS_{PDM} was consistently large and indicative of $TS_{MI-Major}$ being the turnover-limiting step for cyclopropene across all levels of theory.

Table S1: Energetics and bond lengths for $TS_{MI-Major}$ across various functional//basis set pairings. Chosen functional//basis set is shown in blue. Relative free energy is with respect to the corresponding **6a** or TS_{PDM}

Level of Theory	Single Point Energy (Hartree)	Free Energy Correction (Hartree)	Free Energy (Hartree)	Rel. Free Energy to 6a (kcal/mol)	Rel. Free Energy to TS_{PDM} (kcal/mol)	rC-P (Å)	rC-Cu (Å)	rCu-P (Å)
PCM- ω B97XD/def2TZVP//B97D/def2SVP	-4532.39315179	0.899144	-4531.49400779	31.7	25.5	2.37	2.07	2.42
SMD- ω B97XD/def2TZVP//B97D/def2SVP	-4532.42652559	0.899145	-4531.52738059	33.0	34.1	2.37	2.07	2.42
PCM- ω B97XD/def2TZVP//B97D/def2SVP, def2TZVP (Cu)	-4532.39337853	0.899593	-4531.49378553	32.3	30.4	2.37	2.05	2.41
PCM-M06L/6-311+G**//B97D/def2SVP	-4532.23144555	0.899144	-4531.33230155	23.0	22.0	2.37	2.07	2.42
PCM-M06L/6-311+G**//M06L/6-31G*	-4532.36468435	0.931461	-4531.43322335	23.2	19.5	2.30	2.00	2.31
PCM-PBE/def2TZVPP//B3LYP-GD3/def2SVP	-4529.81928327	0.924733	-4528.89455027	25.1	25.5	2.40	2.08	2.42

Protodemetalation of Cu-DuPhos for Product Release

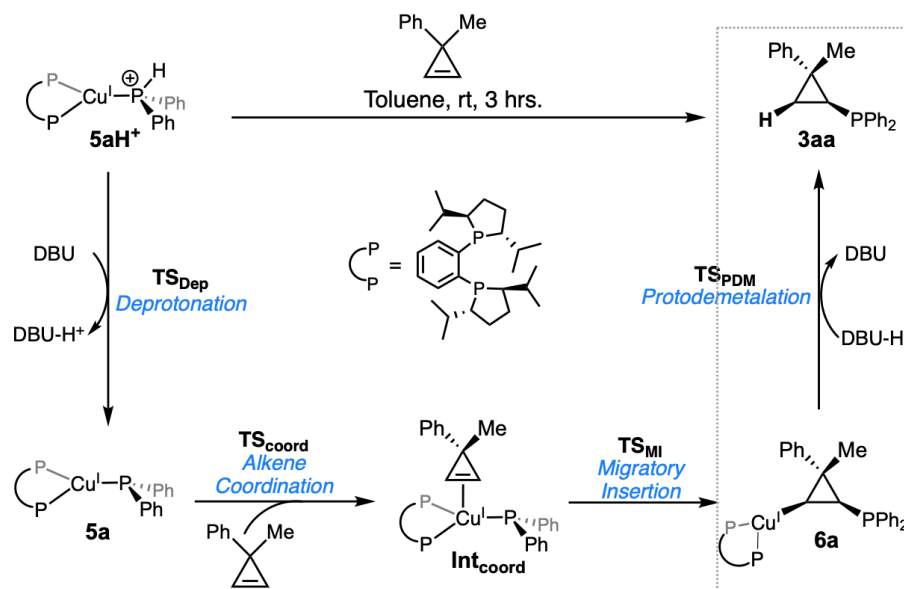


Figure S10. A general mechanistic scheme for copper-catalyzed hydrophosphination of cyclopropenes.

Several potential mechanisms were explored for the release of Cu-DuPhos catalyst and formation of the final hydrophosphinated product. A pathway involving the elimination of Cu-DuPhos to give a carbanion on cyclopropane, coupled with subsequent protonation via DBU-H⁺ could not be located. Additionally, direct displacement of Cu-DuPhos by a coordinated, protonated DBU could not be located. However, two protodemetalation pathways were found: (1) intermolecular protodemetalation of Cu-DuPhos by an external molecule of DBU-H⁺, exhibiting a $\Delta\Delta G^\ddagger = -6.3$ kcal/mol relative to **5** (**TS_{PDM}**); and (2) intramolecular protodemetalation of Cu-DuPhos by an adjacent protonated diphenylphosphine, exhibiting a $\Delta\Delta G^\ddagger = 19.3$ kcal/mol relative to **5** (**TS_{PDM-Alt.}**). Both strategies exhibit mediation via copper to accomplish the proton transfer, and both involve proton transfer on the same face as Cu-DuPhos and PPh₂.

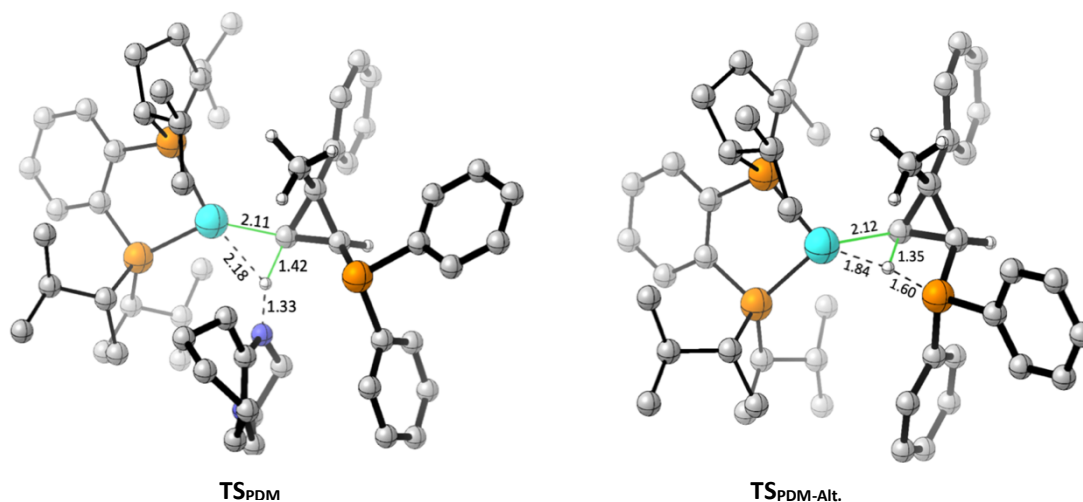


Figure S7. Transition state structures for the protodemetalation of Cu-DuPhos intermolecularly by DBU (TS_{PDM}) (on left) (chosen pathway), and the protodemetalation of Cu-DuPhos intramolecularly by a protonated phosphine ($TS_{PDM-Alt.}$) (on right).

Further exploration into the protodemetalation via external $DBU-H^+$ was conducted. Attempts to first coordinate $DBU-H^+$ to Cu-DuPhos so as to perform an intramolecular version of this protodemetalation resulted in dissociation of $DBU-H^+$ followed by an intermolecular protodemetalation. Attempts to locate an *anti*-protodemetalation, whereby $DBU-H^+$ approaches from the opposite face as Cu-DuPhos and PPh_2 , were unsuccessful and illustrated the importance of the copper mediation in this protodemetalation mechanism.

C. Origin of Enantioselectivity

The lowest-lying structures for $TS_{MI-Major}$ and $TS_{MI-Minor}$ were each located and computed to exhibit a $\Delta\Delta G^\ddagger$ of 2.1 kcal/mol, correlating to an enantiomeric ratio of 97.5:2.5. A distortion-interaction analysis was performed on the lowest-lying TSs leading to each product enantiomer using Cu-DuPhos and PPh_2 as the catalyst (“Cat”) fragment and the cyclopropene substrate as the reactant (“Rct”) fragment. The net distortion energy between enantiomers was found to 2.4 kcal/mol, favoring the minor enantiomer.

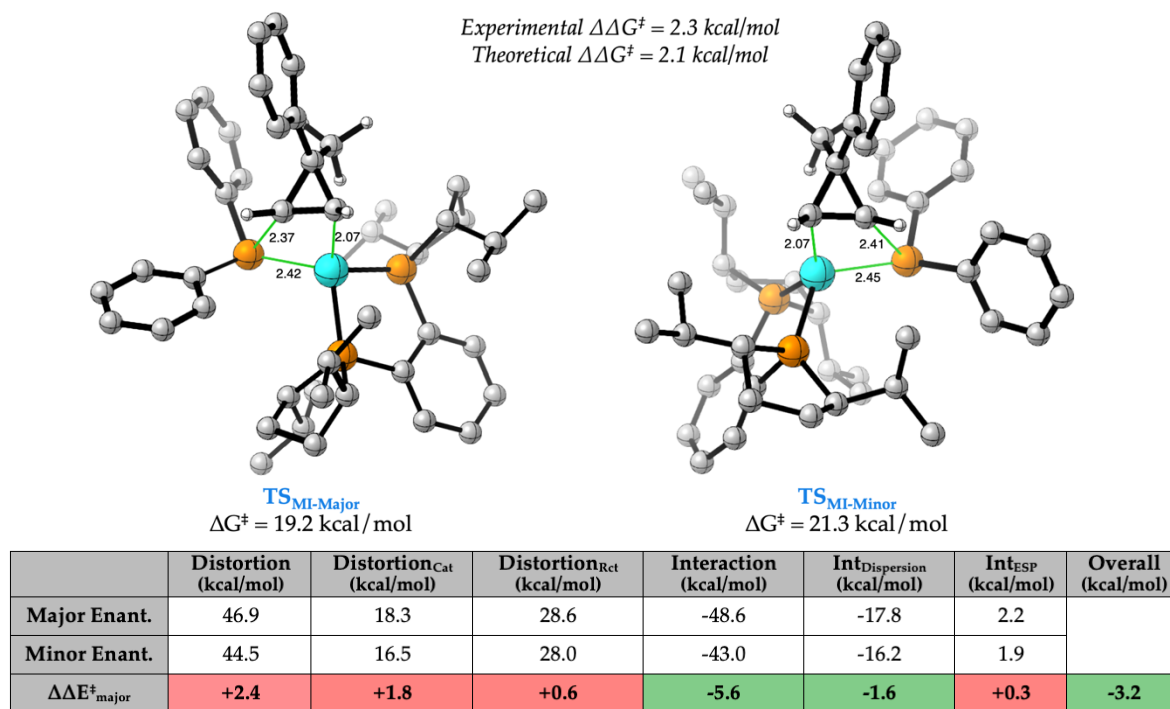


Figure S8. Experimental and theoretical free energy barriers of the lowest-energy transition state structures leading to the major and minor enantiomers. Also shown is the distortion (ΔD)-interaction (ΔI) analysis, defining the magnitude at which each contributes to the enantioselectivity.

Interaction energy favors the TS leading to the major enantiomer by 5.6 kcal/mol. Electrostatics (Int_{ESP}) unsurprisingly contributes to only a small portion of this, specifically 0.3 kcal/mol. However, dispersions contribute more significantly to this net interaction energy with a difference of 1.6 kcal/mol between the TS leading to the product enantiomers, favoring **TS_{ML-Major}**. A non-covalent interaction (NCI) plot was generated to illustrate the differing magnitude of dispersive energy between major and minor enantiomers (isosurface set to 0.009). The blue and red indicate significant, covalent interactions from the insertion of copper-phosphido into the cyclopropene, whereas the green indicates dispersions between the catalyst and reactant fragments.

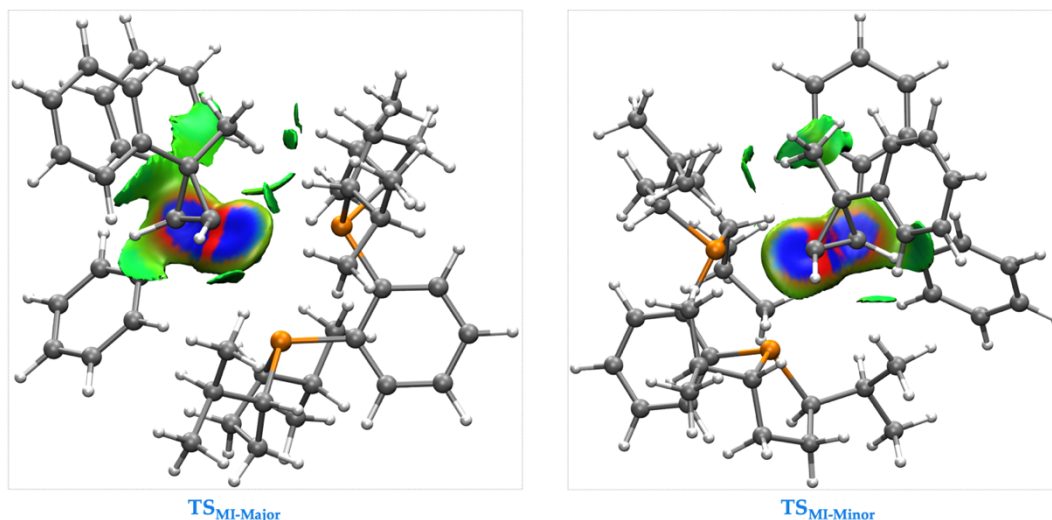
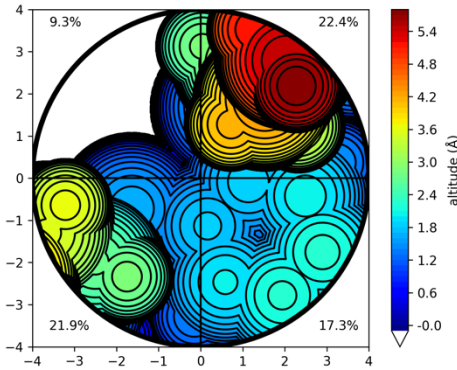
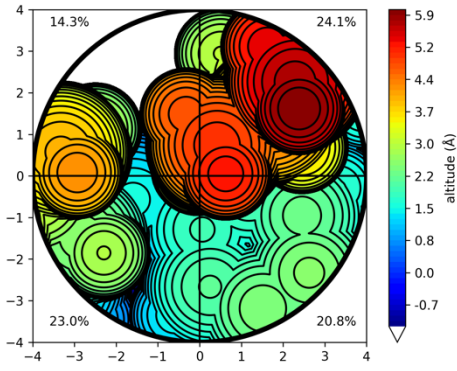


Figure S9. Non-covalent interaction plot depicting the dispersive interactions (shown in green) of Cu-DuPhos and PPh_2 with cyclopropene at the TS leading to each enantiomer (isosurface of 0.009).

A steric map was generated to depict the steric atmosphere an incoming cyclopropene substrate experiences as it approaches the catalytic pocket. When bound to diphenyl phosphine, the Cu-iPr-DuPhos catalyst occupies a significant portion of the catalytic pocket realty, namely 82.2% buried volume (Table S2, L5). As a result, cyclopropene is forced to bind in the same quadrant across all stereoisomers. Topographic steric maps were also generated for the other ligands screened experimentally (R-SEGPPOS, (R,R)-Et-DuPhos, and (R,R)-Me-DuPhos) as copper-phosphido intermediates. Buried volumes were calculated for each as insight into the catalytic pocket prior to cyclopropene coordination and to offer computational support for experimentally observed enantioselectivities (Table S2).

Table S2. Steric maps depicting the catalytic pocket of Cu-L and Cu(L)-PPh₂ prior to coordination of cyclopropene (4 Å radii around center)

Ligand	Steric Map Representation as “Cu(L#)-PPh ₂ ”	Buried Volume “Cu(L#)-PPh ₂ ”	Experimental <i>ee</i>
L1 R-SEGPHOS		85.5%	85:15
L3 (R,R)-Me-DuPhos		71.6%	90:10

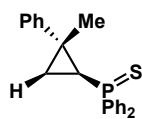
L4 (R,R)-Et-DuPhos		70.9%	92:8
L5 (R,R)-<i>i</i>Pr-DuPhos		82.2%	98:2

7. References

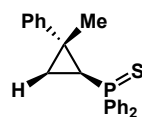
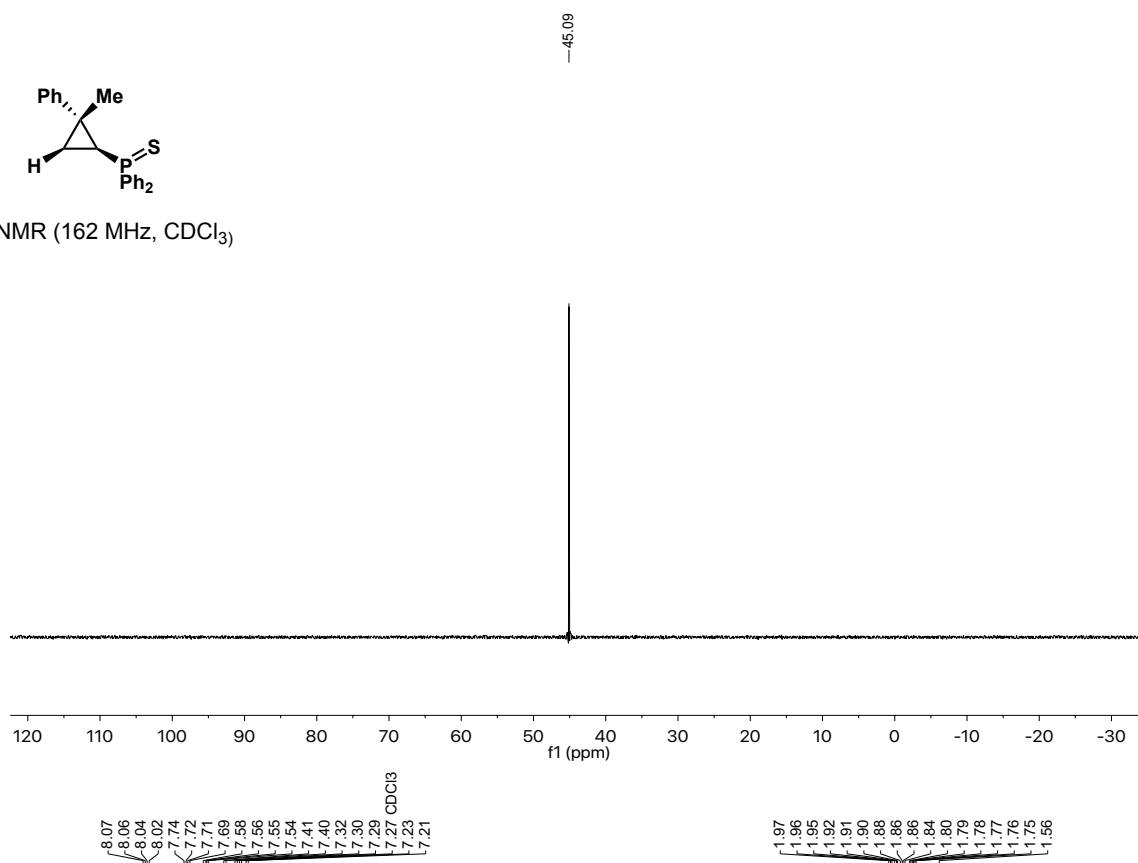
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8. NMR Spectra of Unknown Compounds

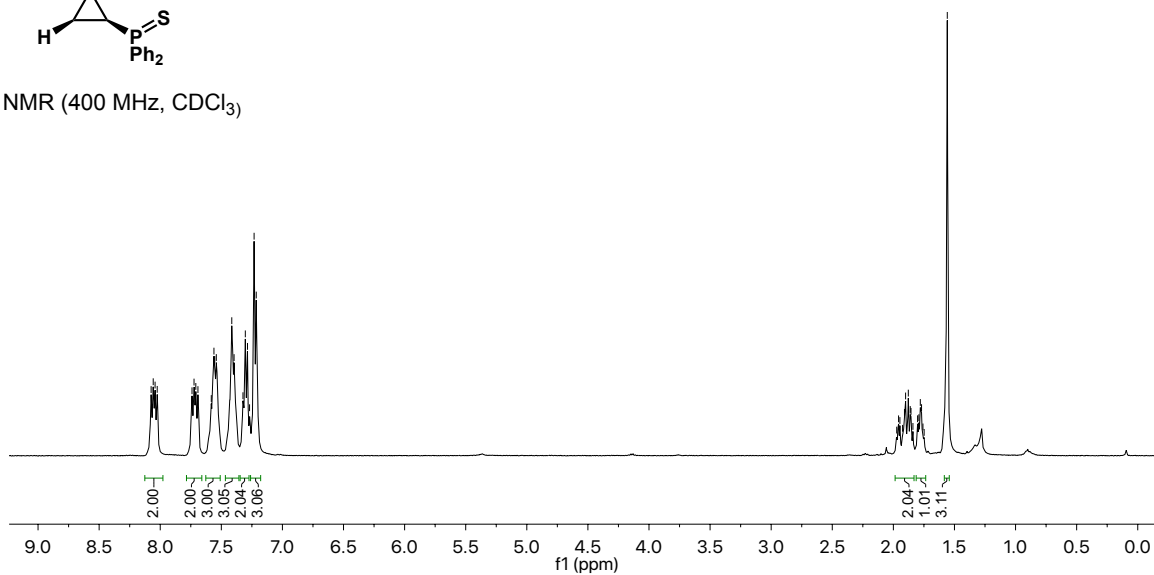
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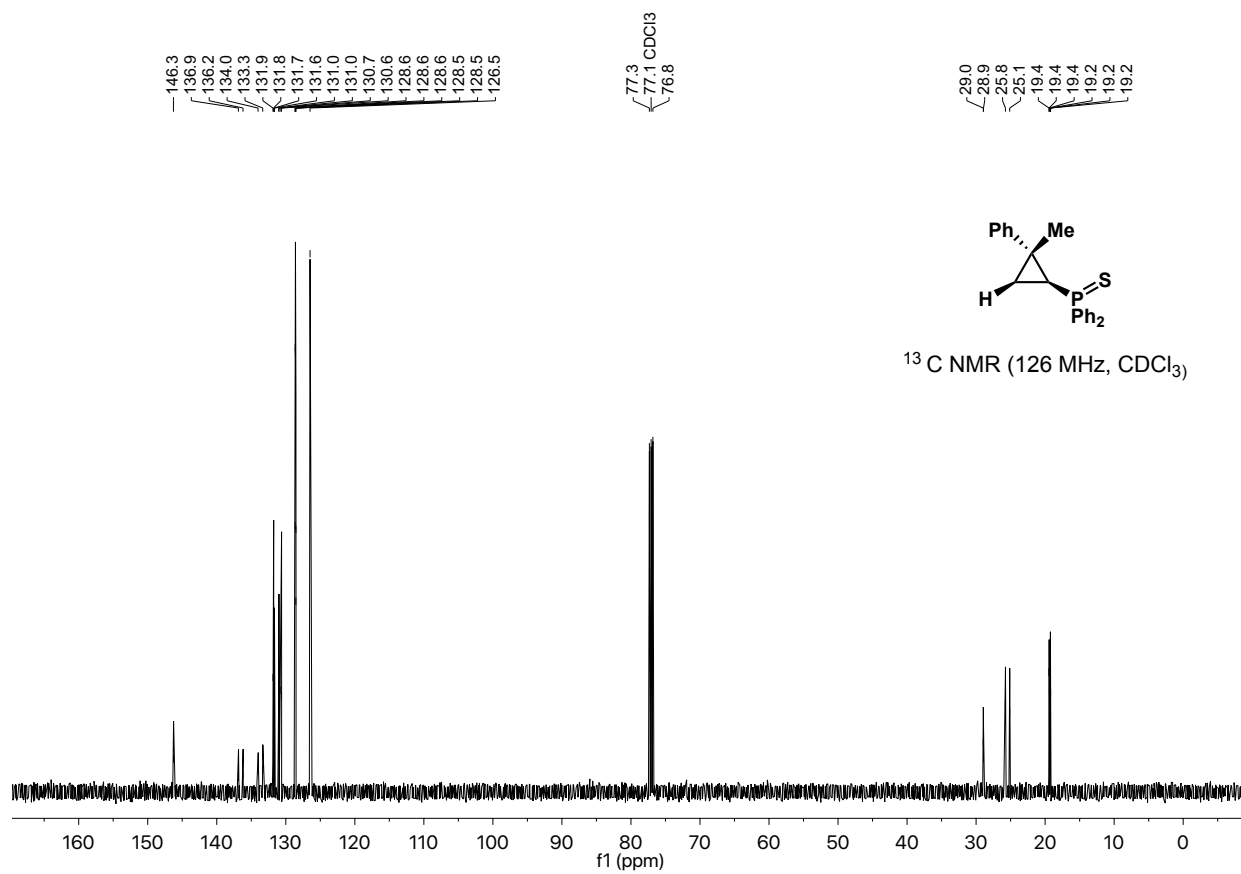


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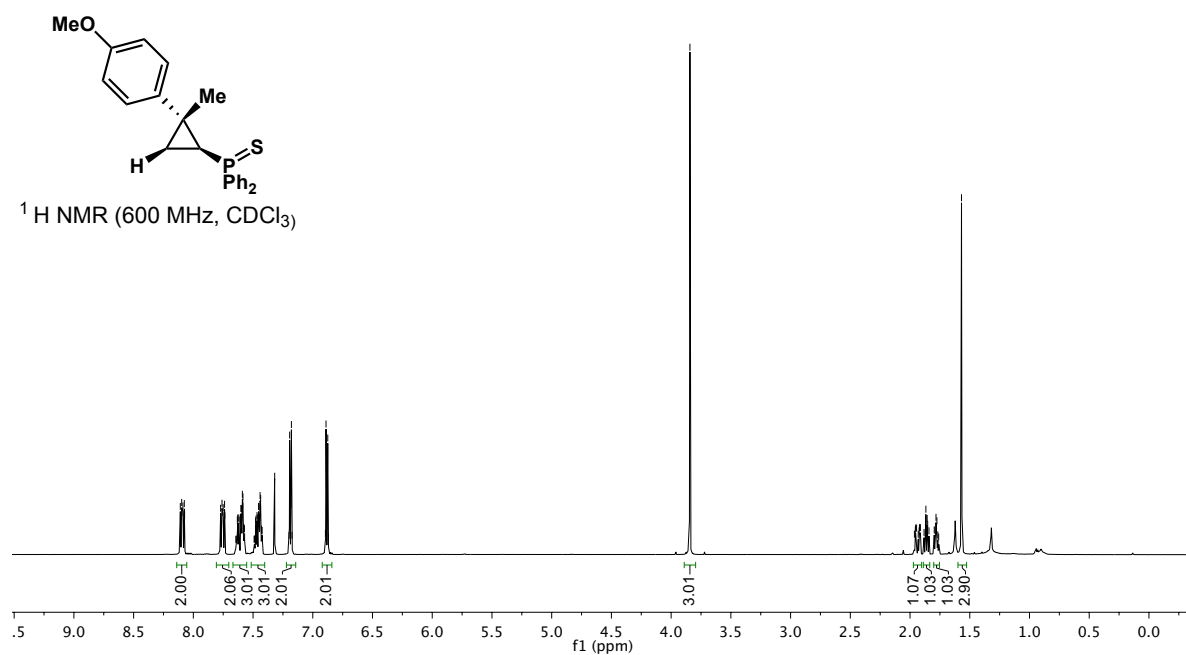
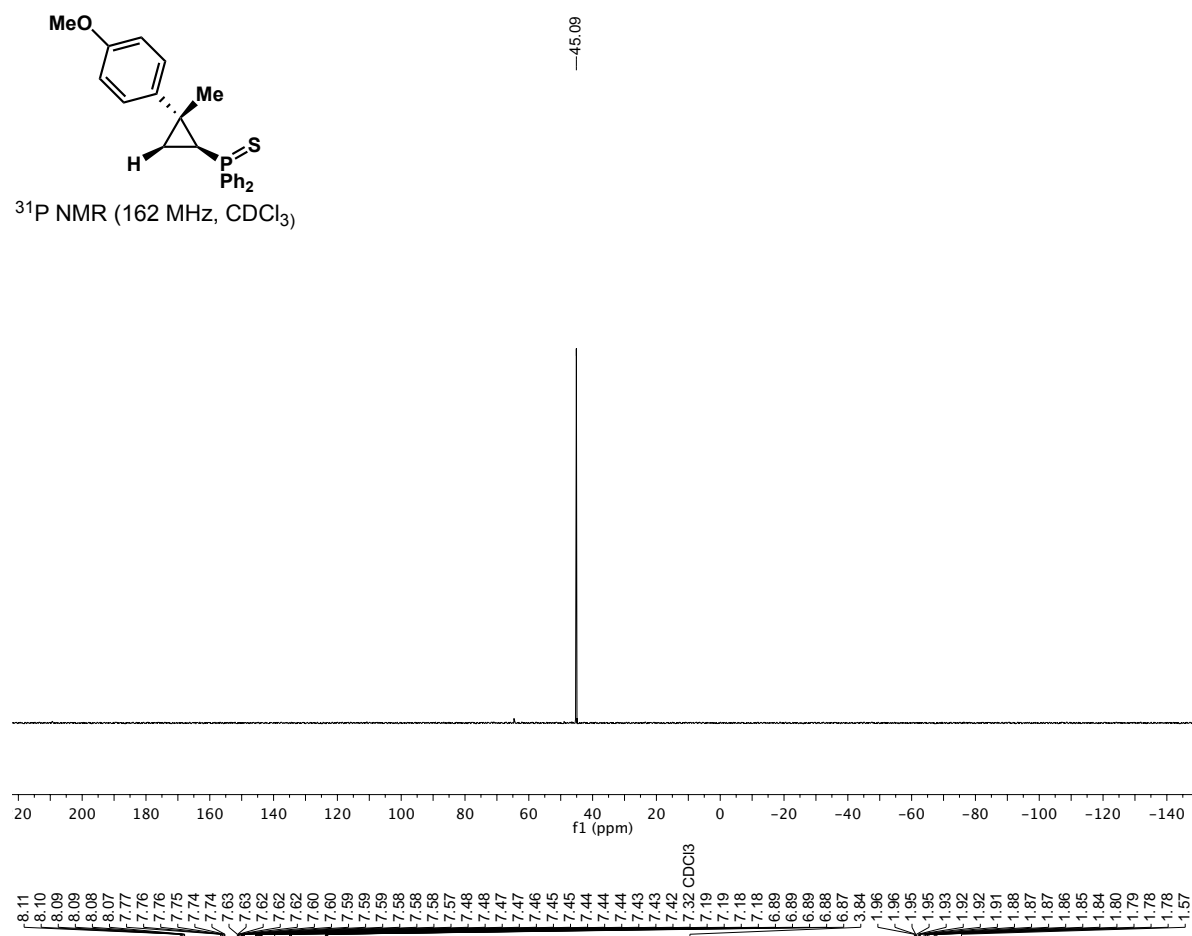


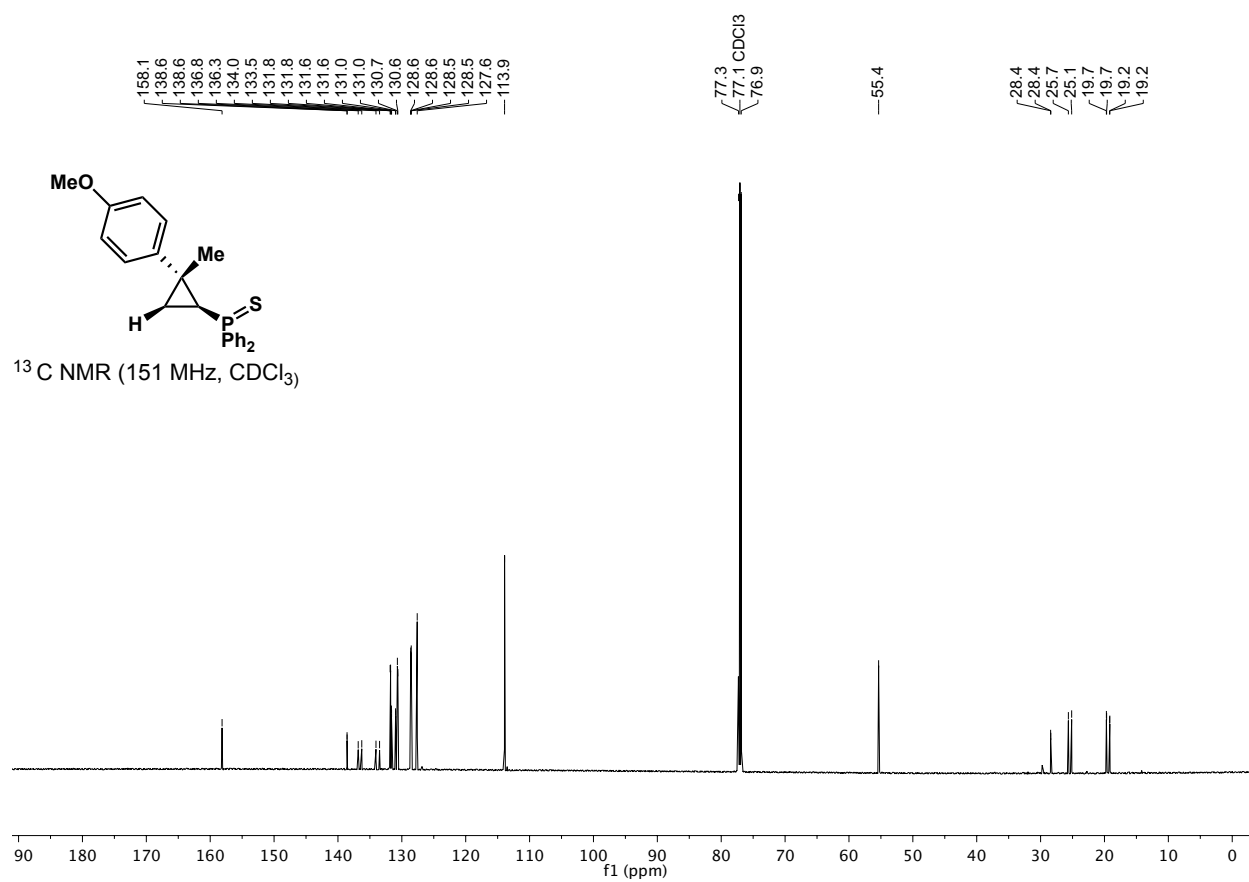
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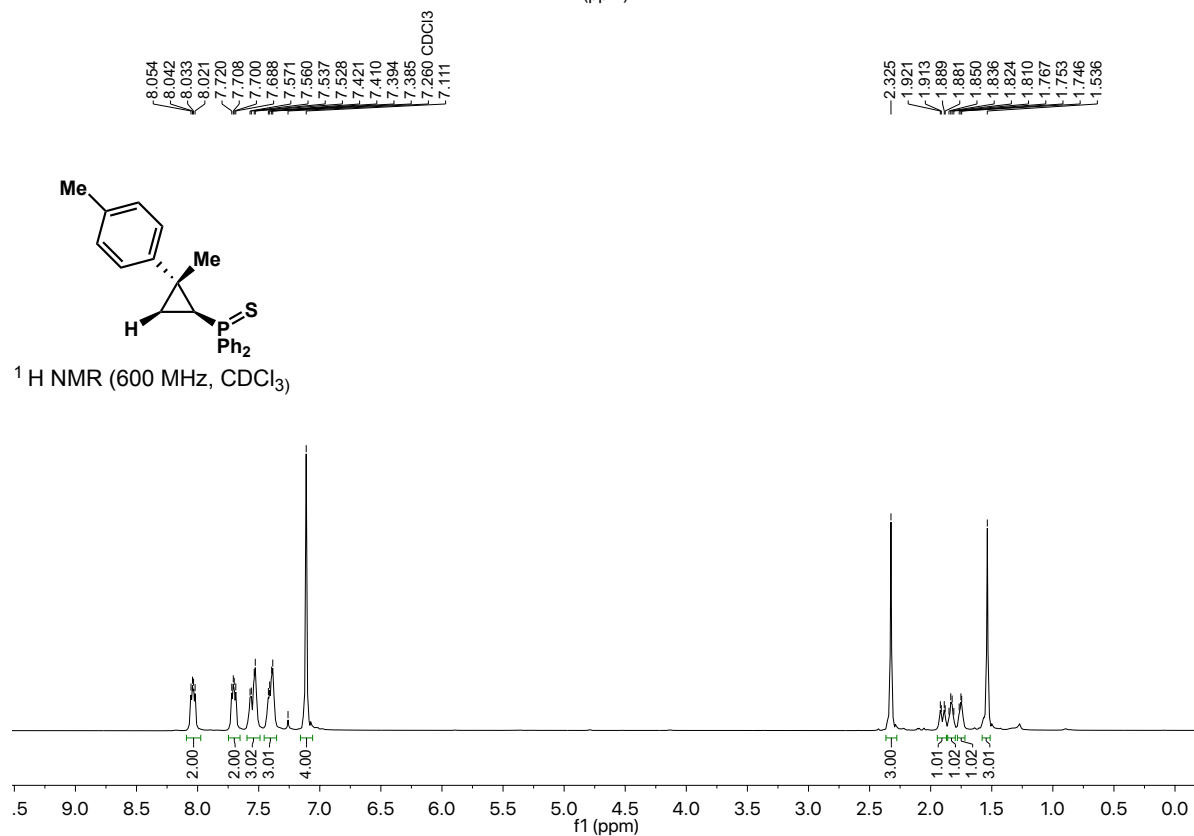
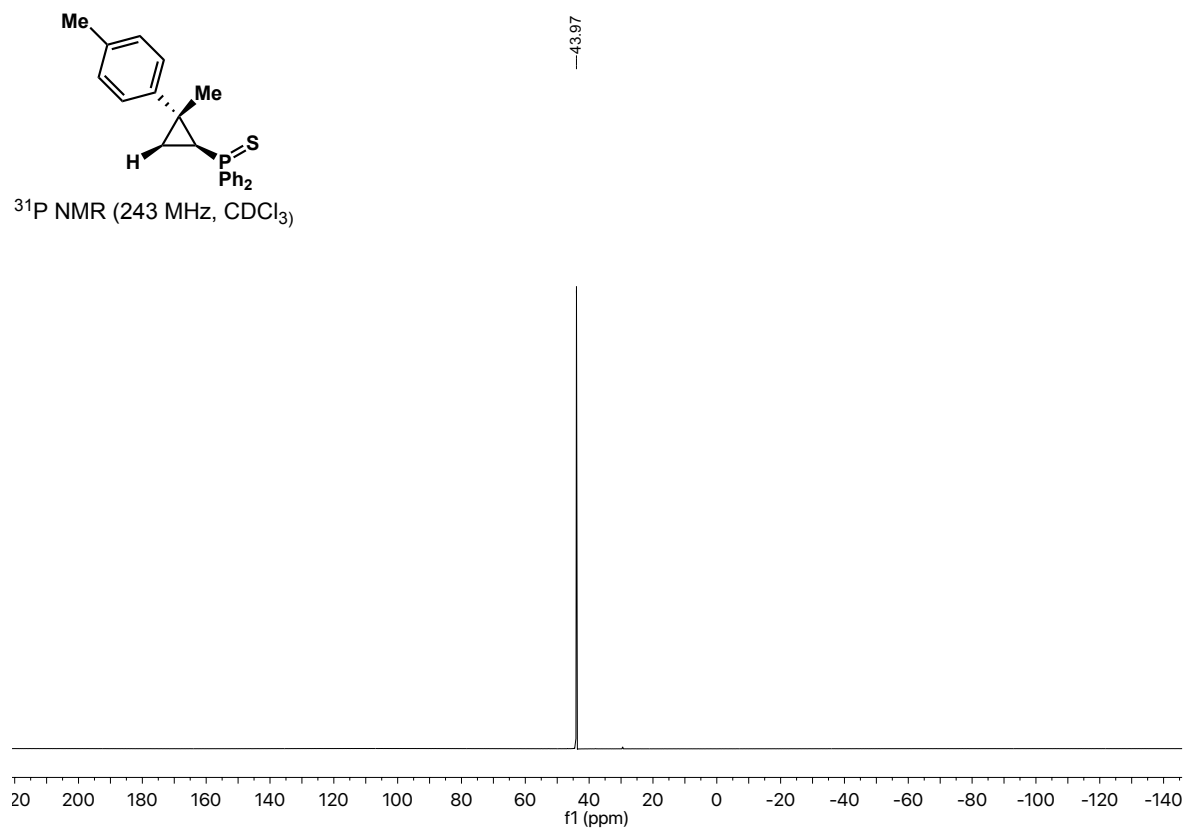


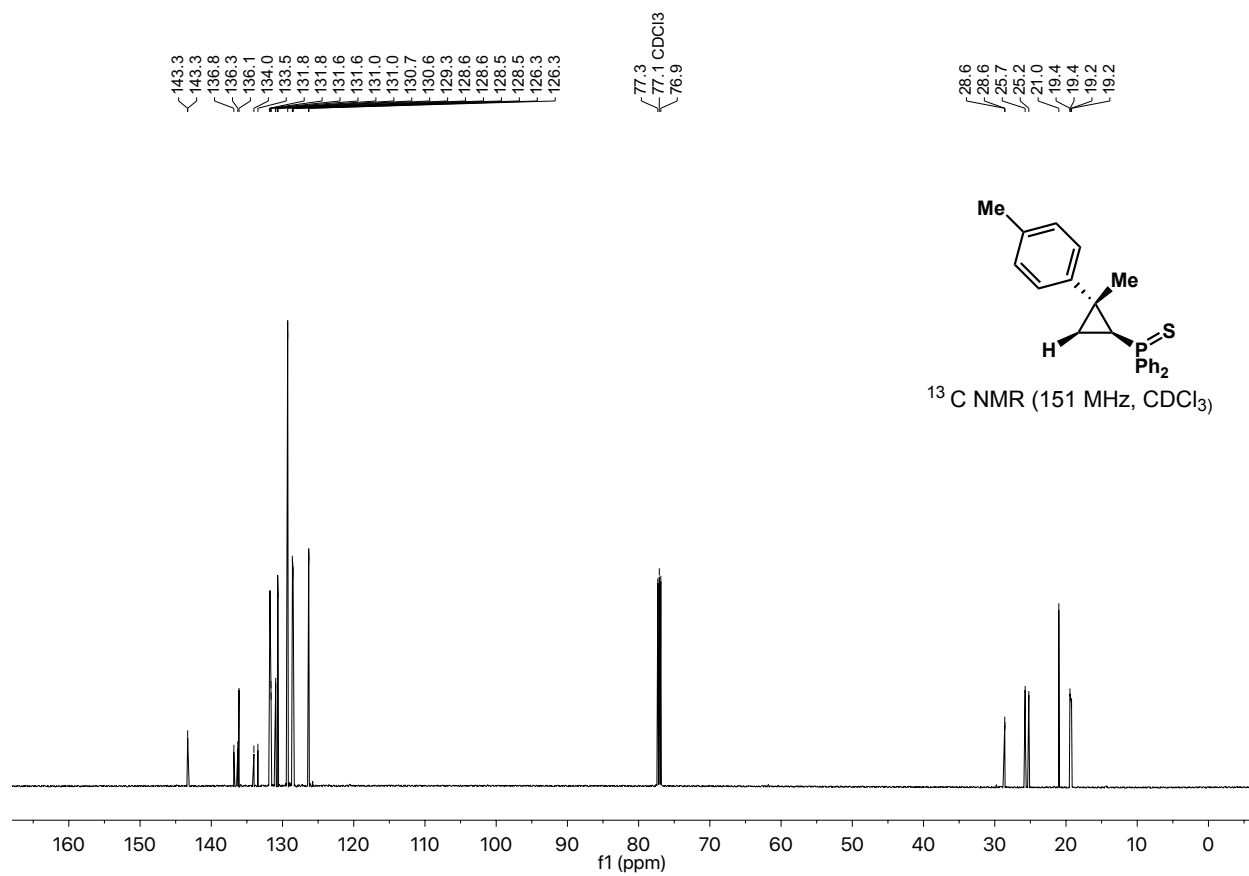
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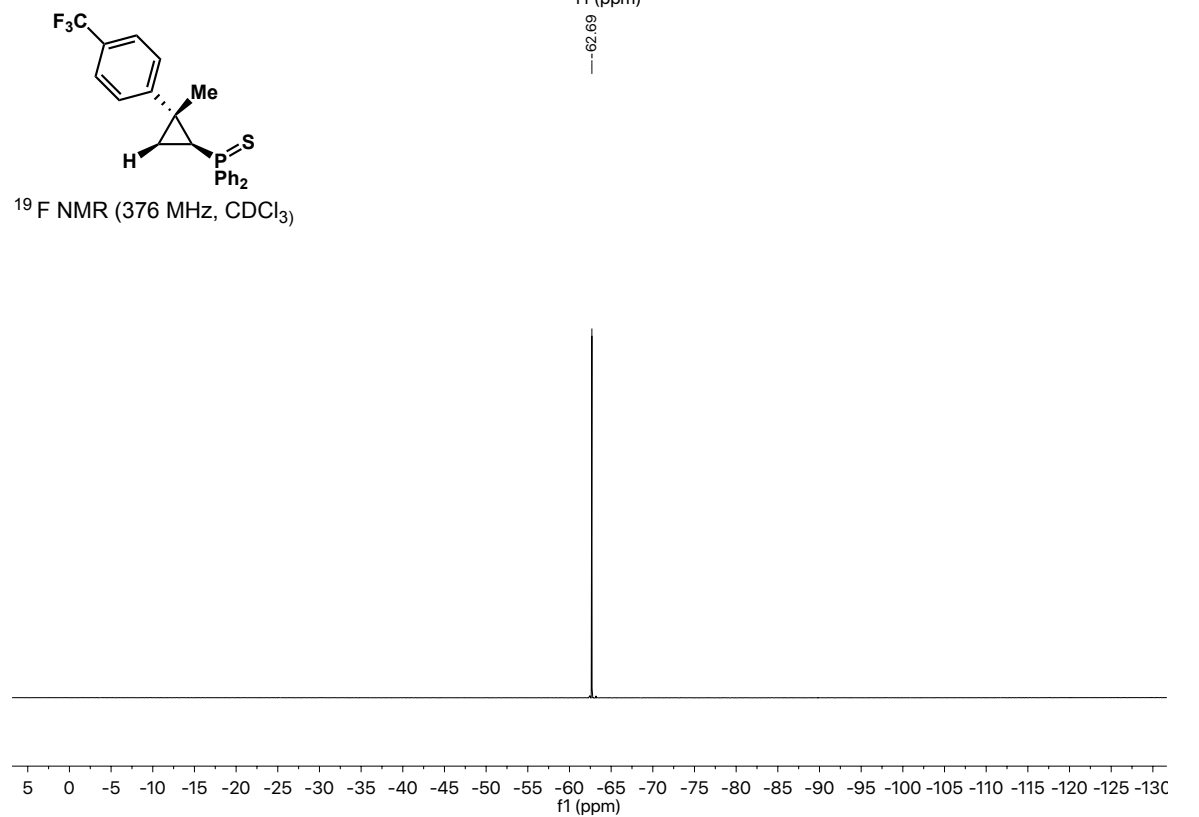
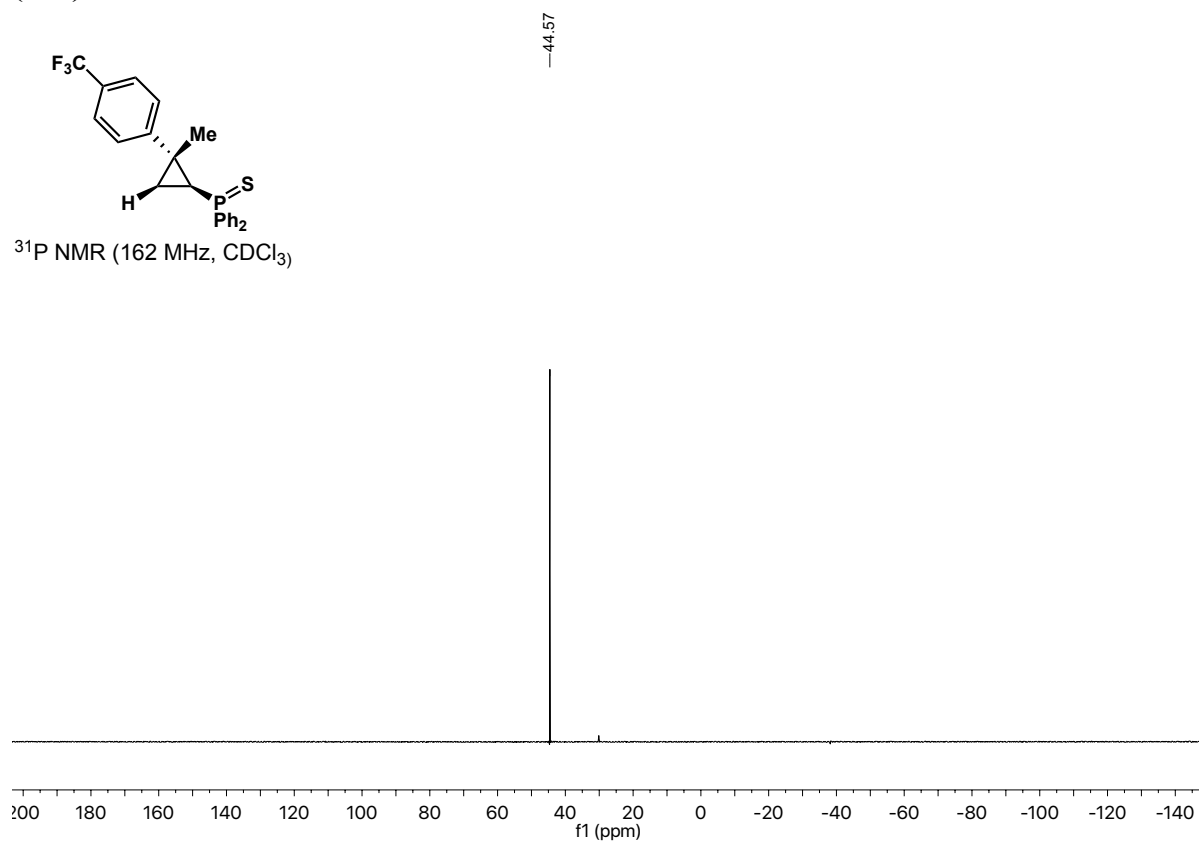


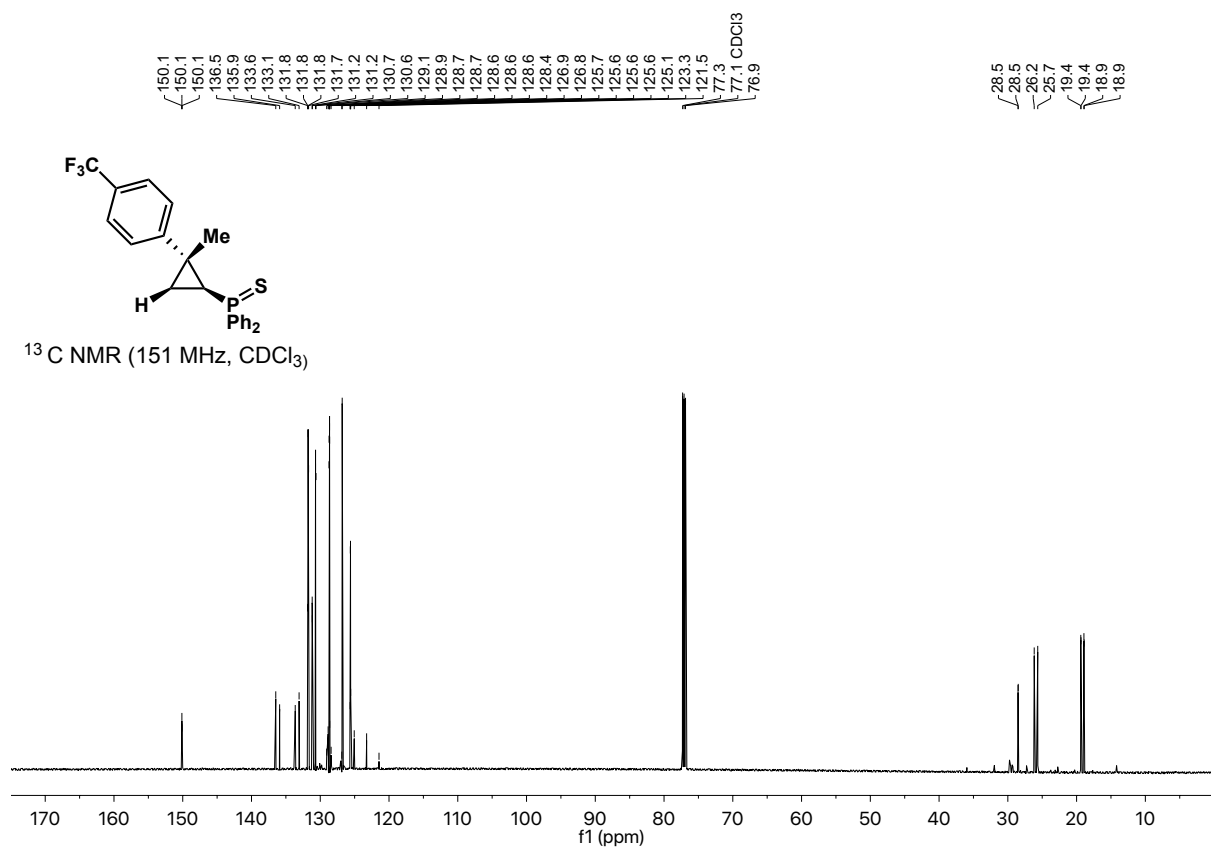
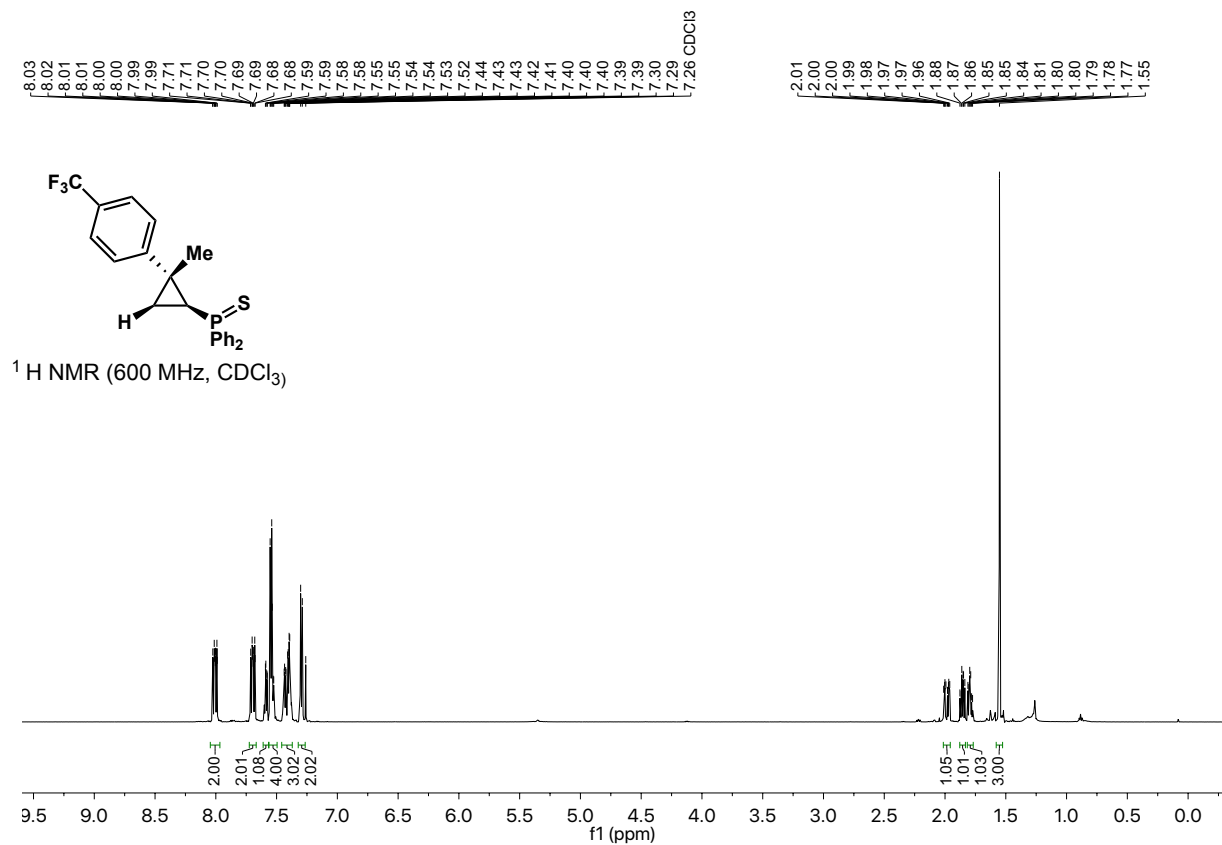
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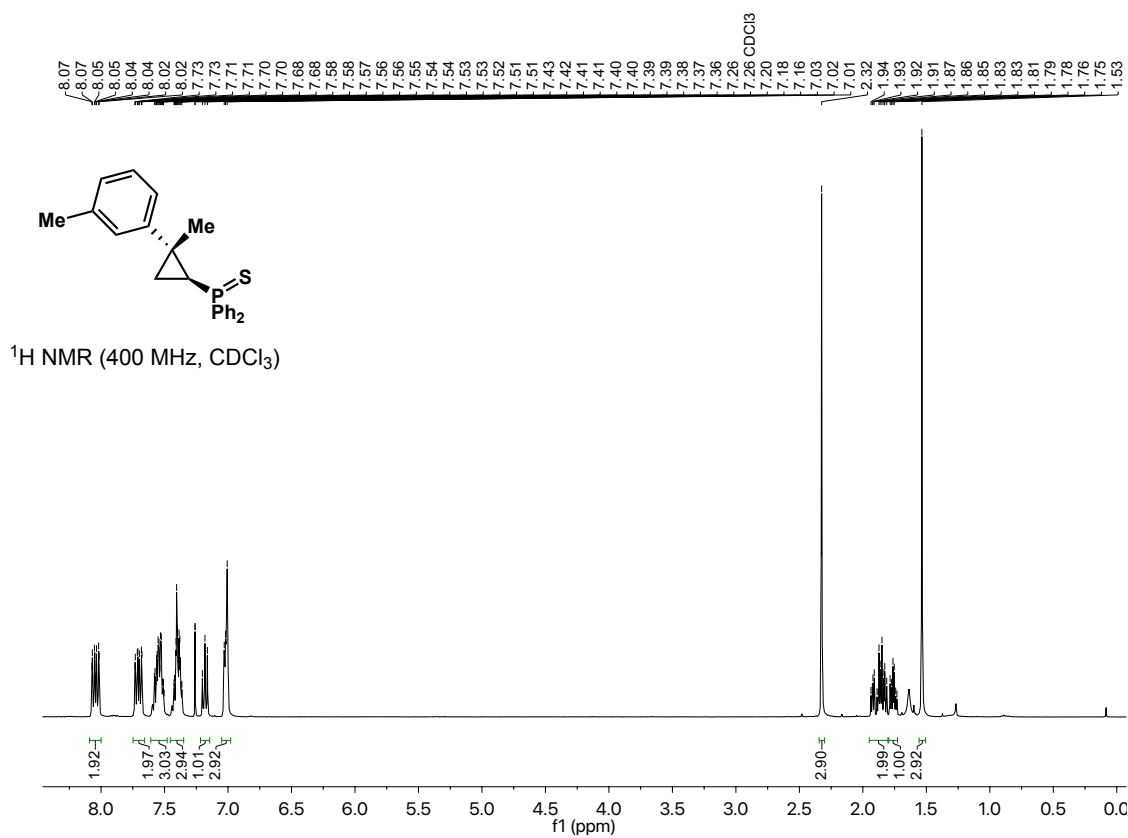
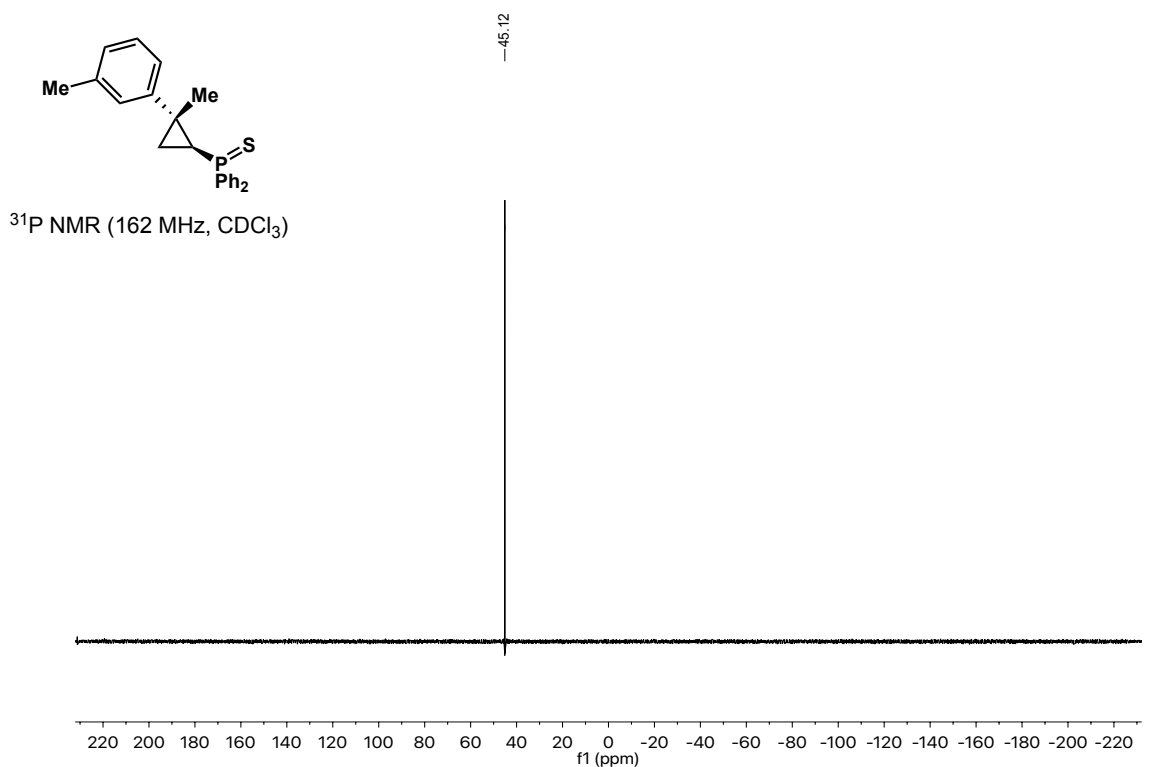


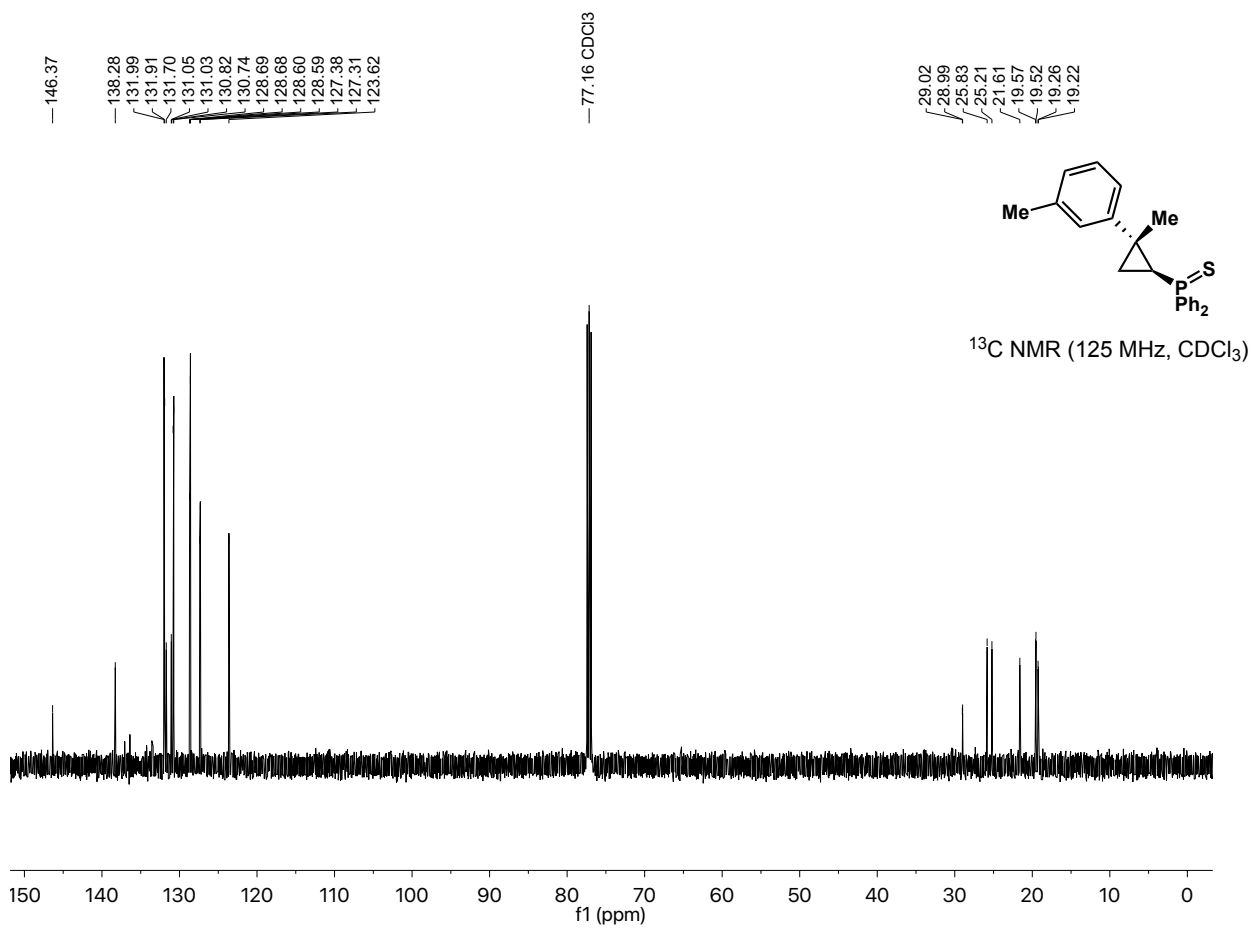
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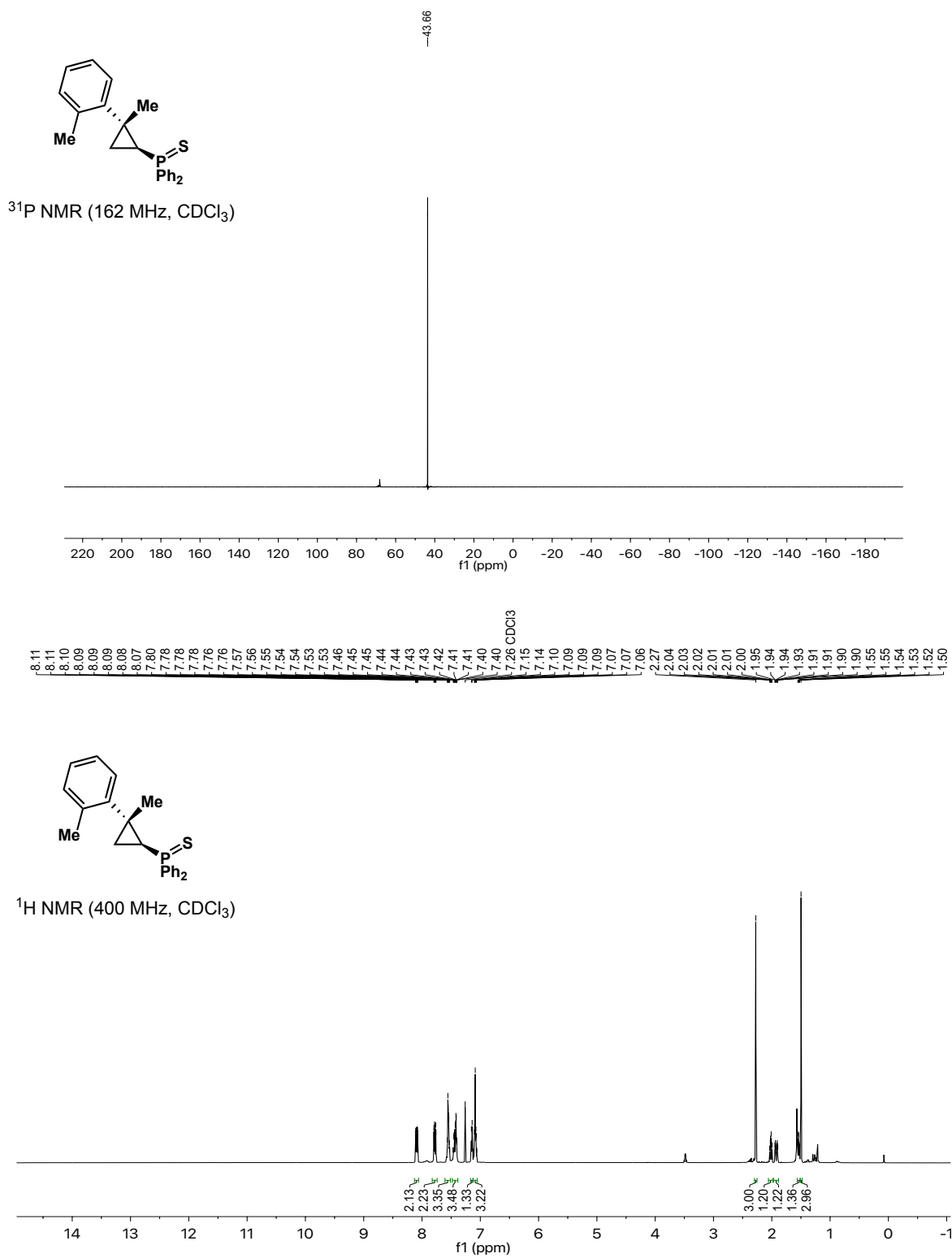


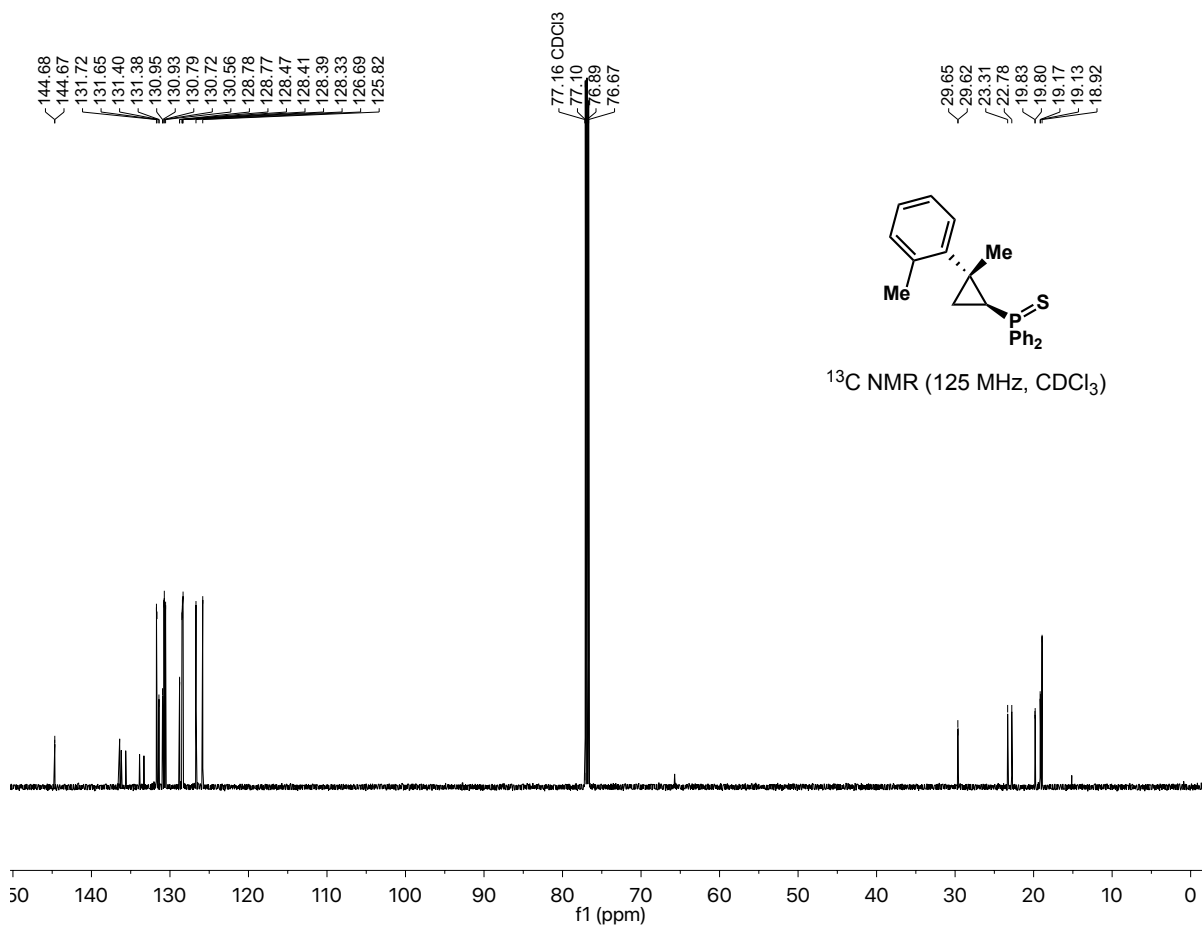
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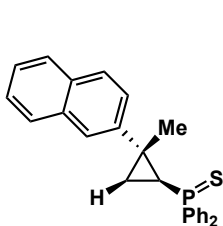


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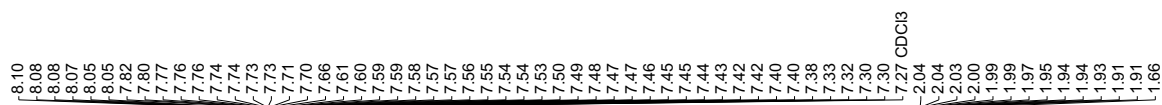
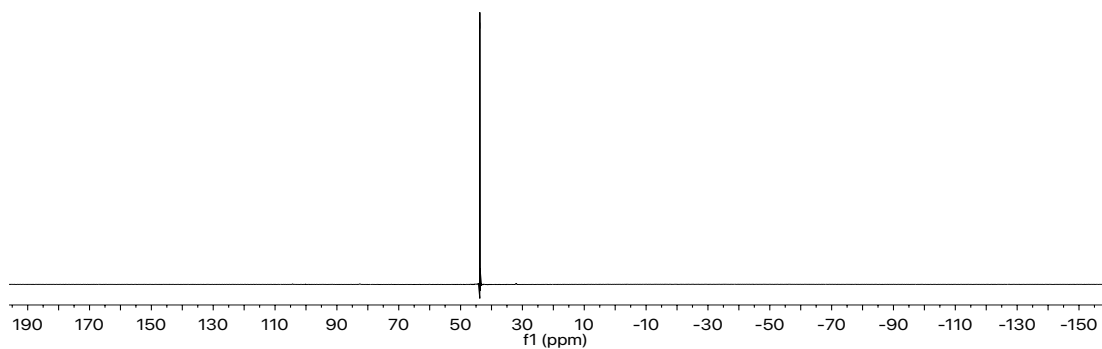




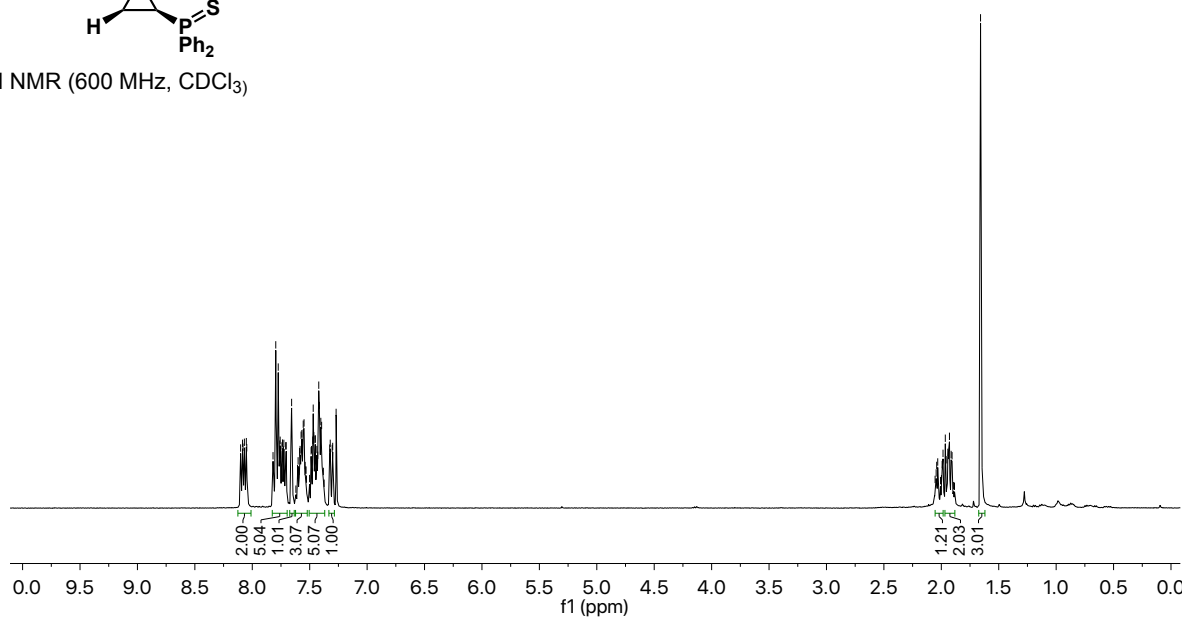
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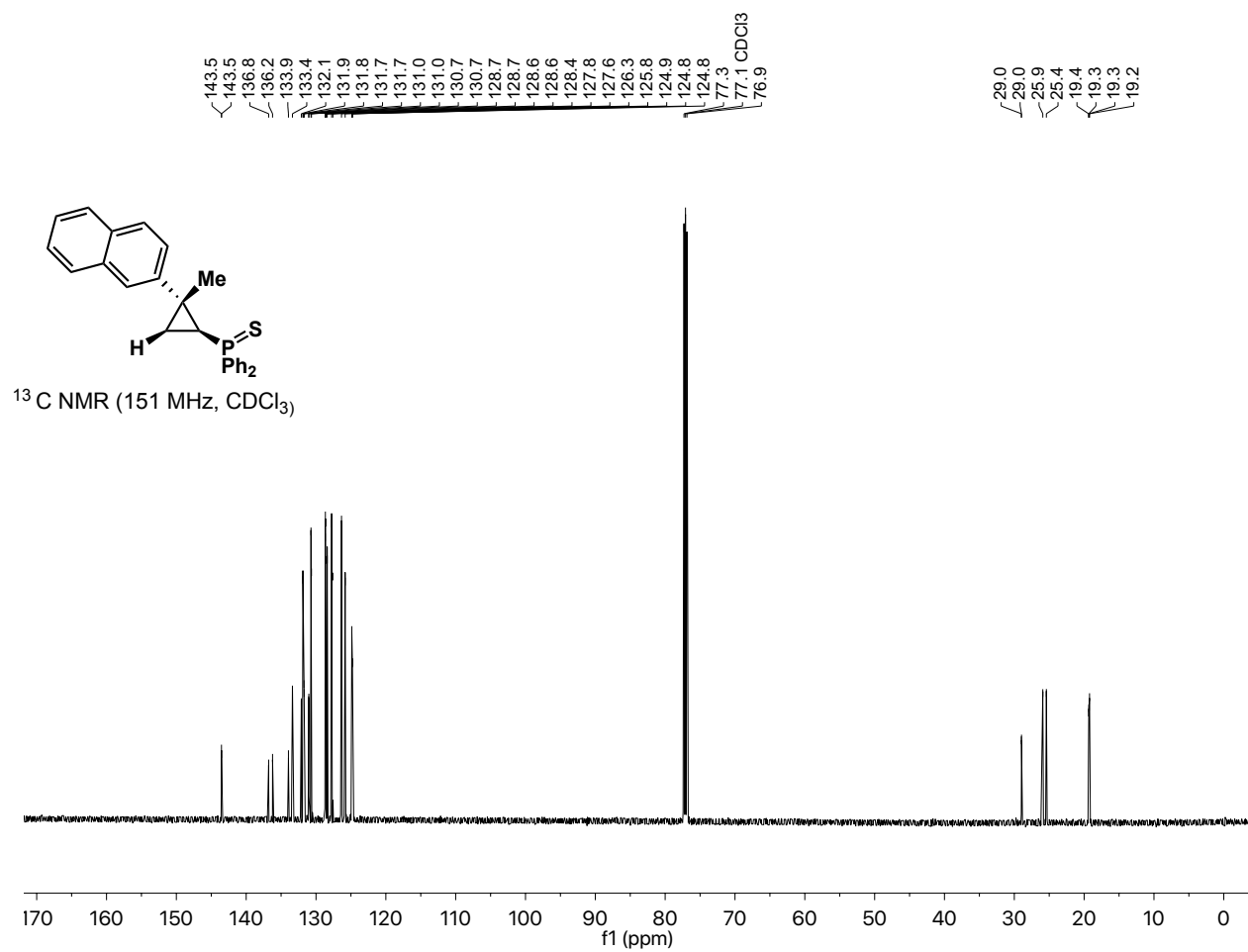


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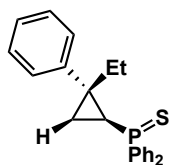


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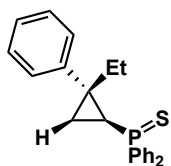
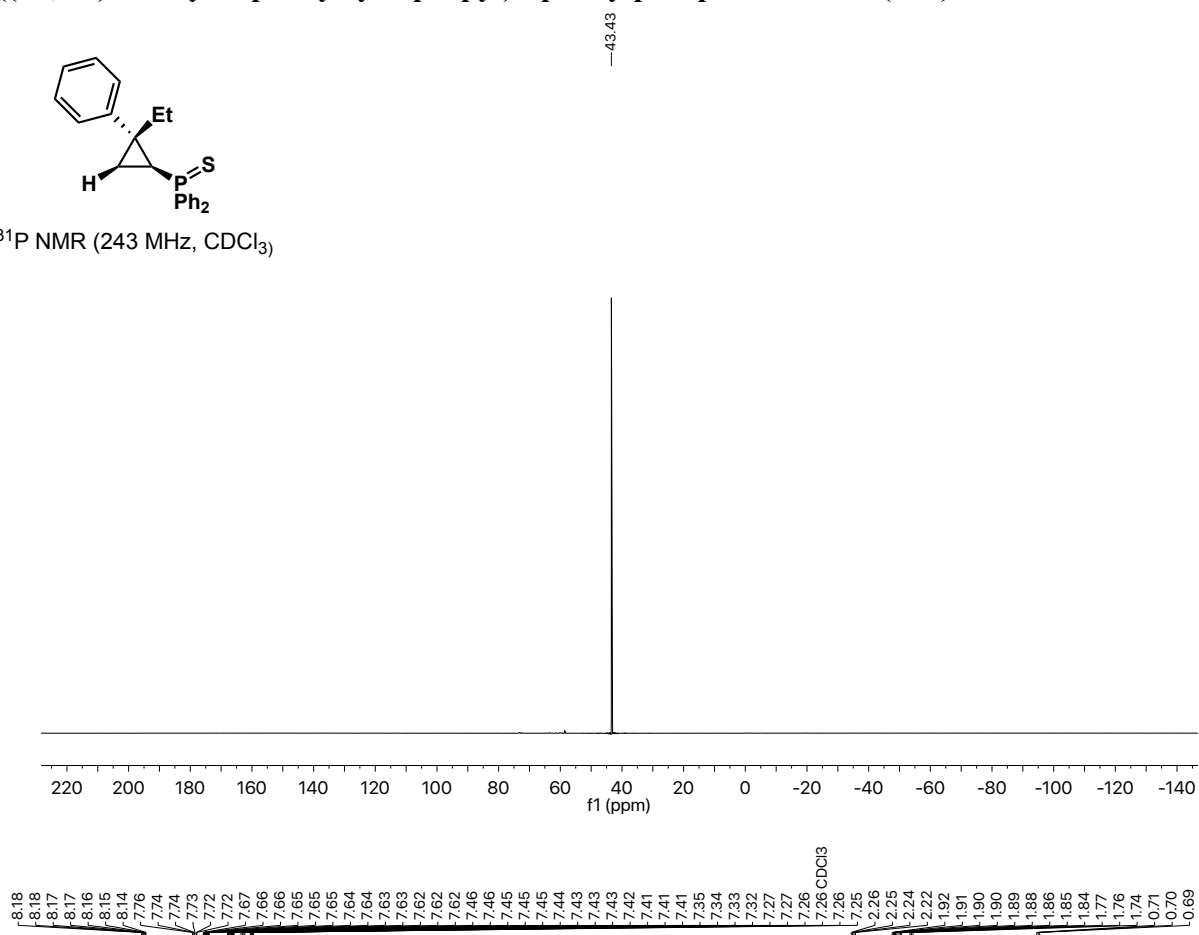




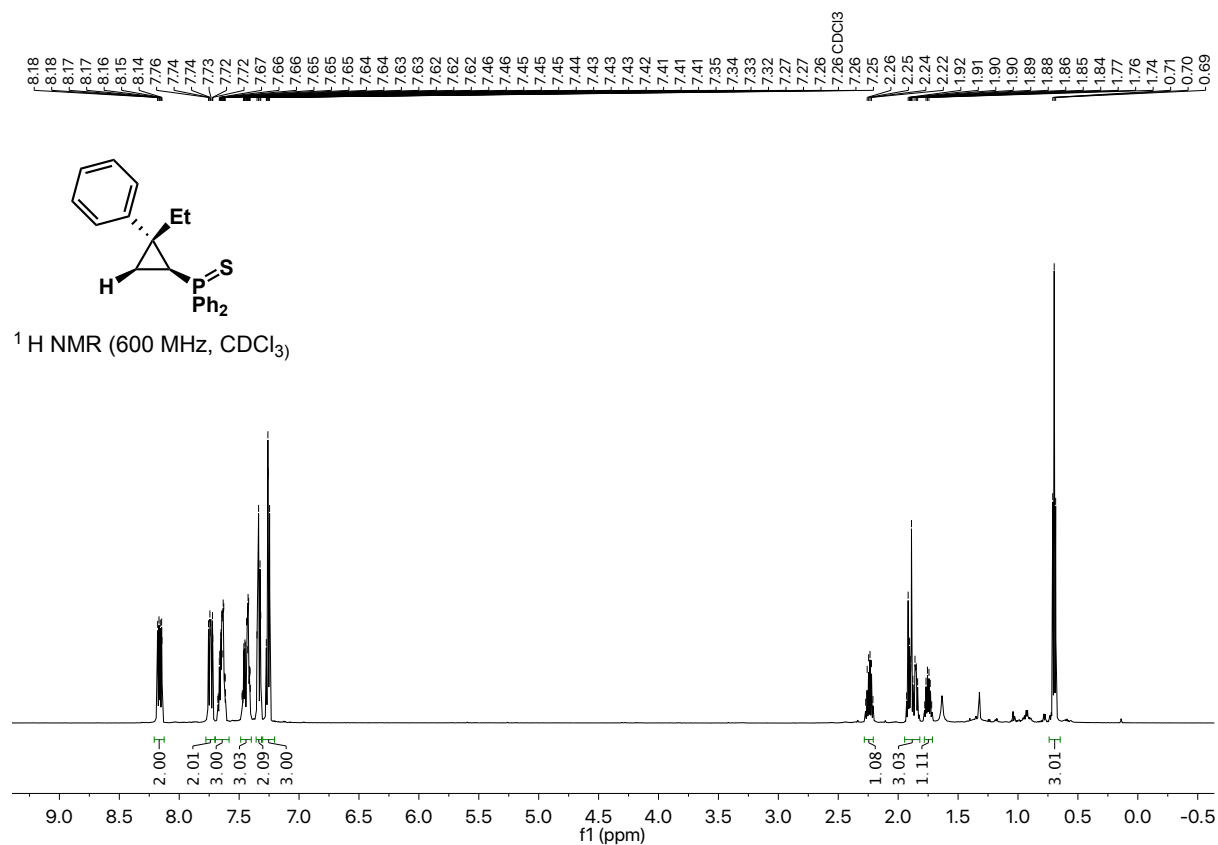
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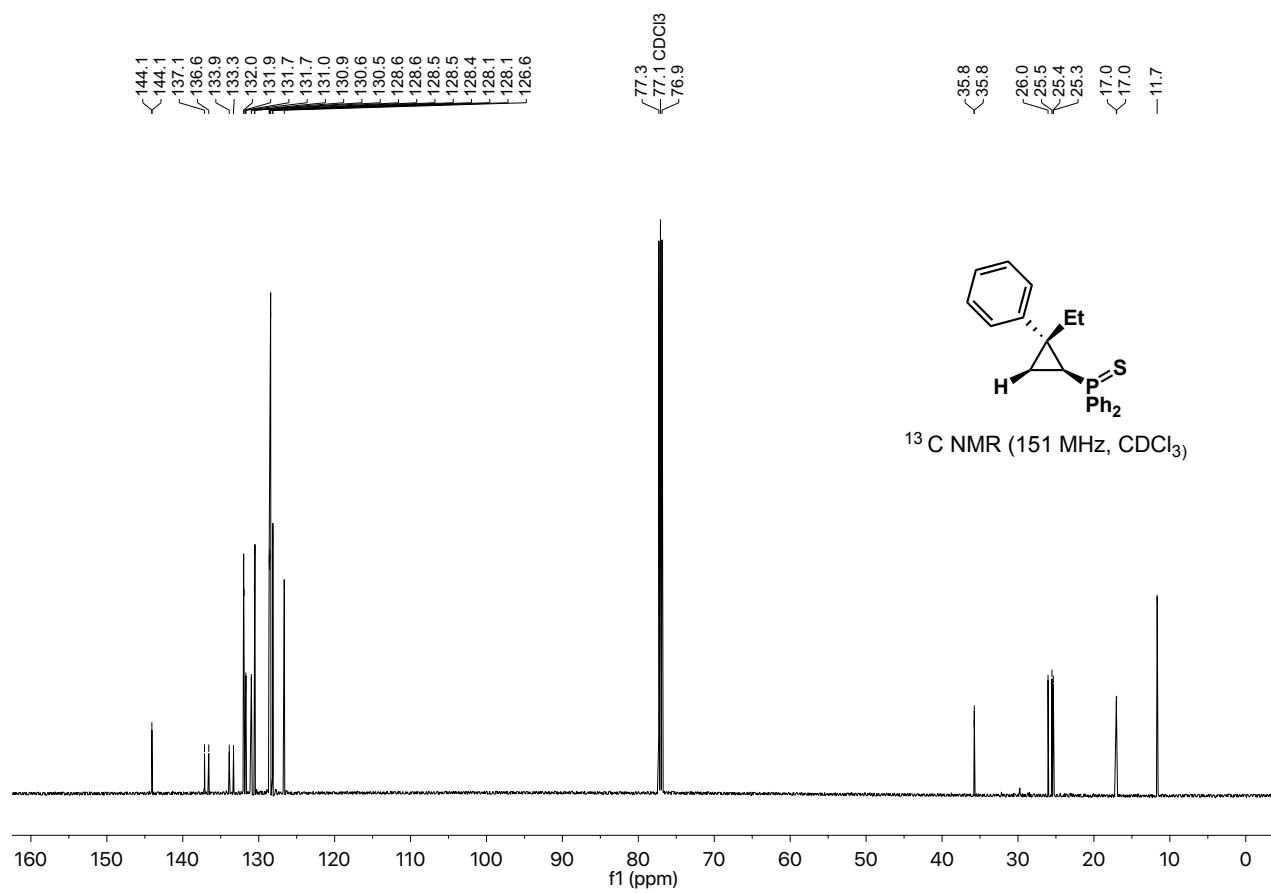


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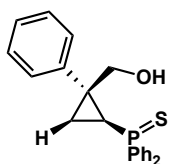


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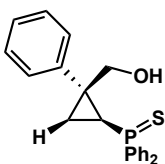
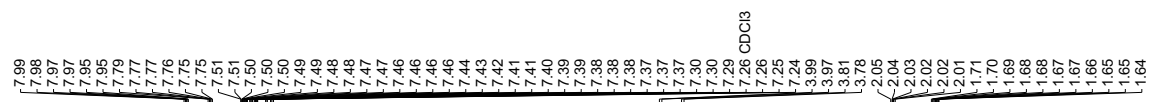
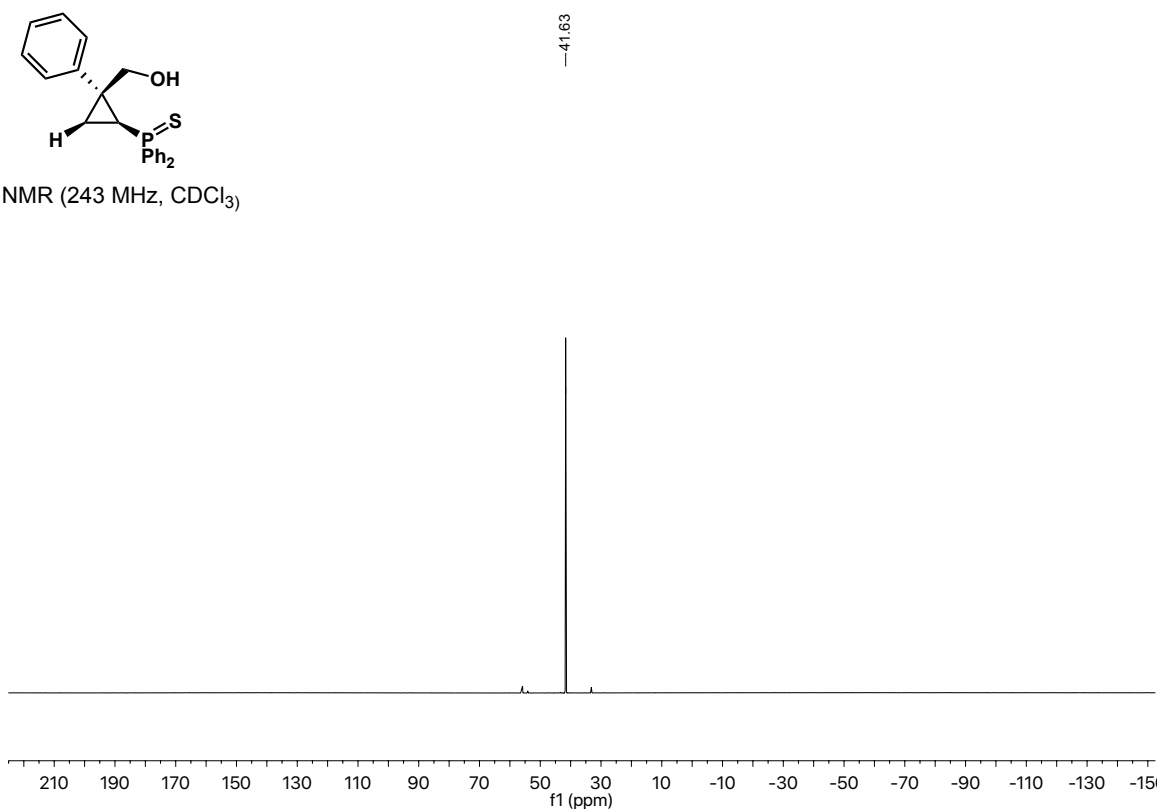




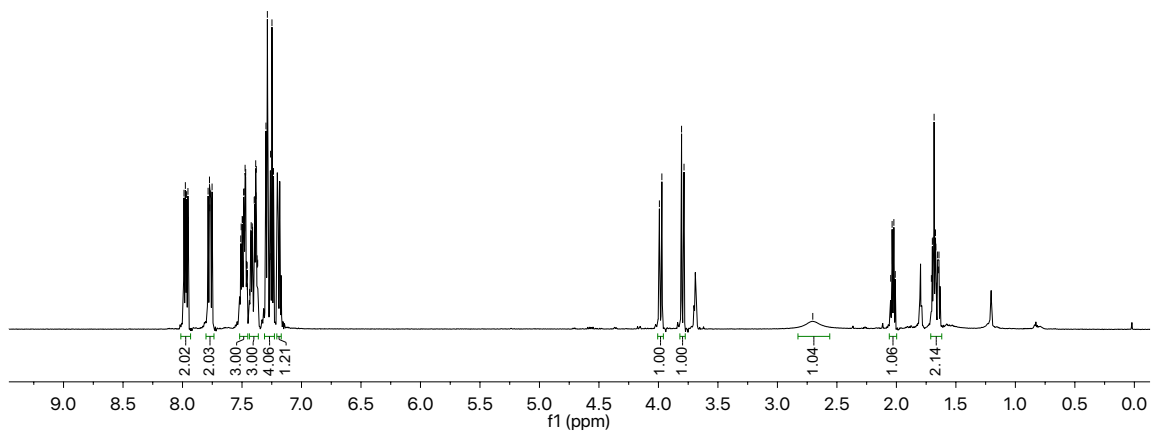
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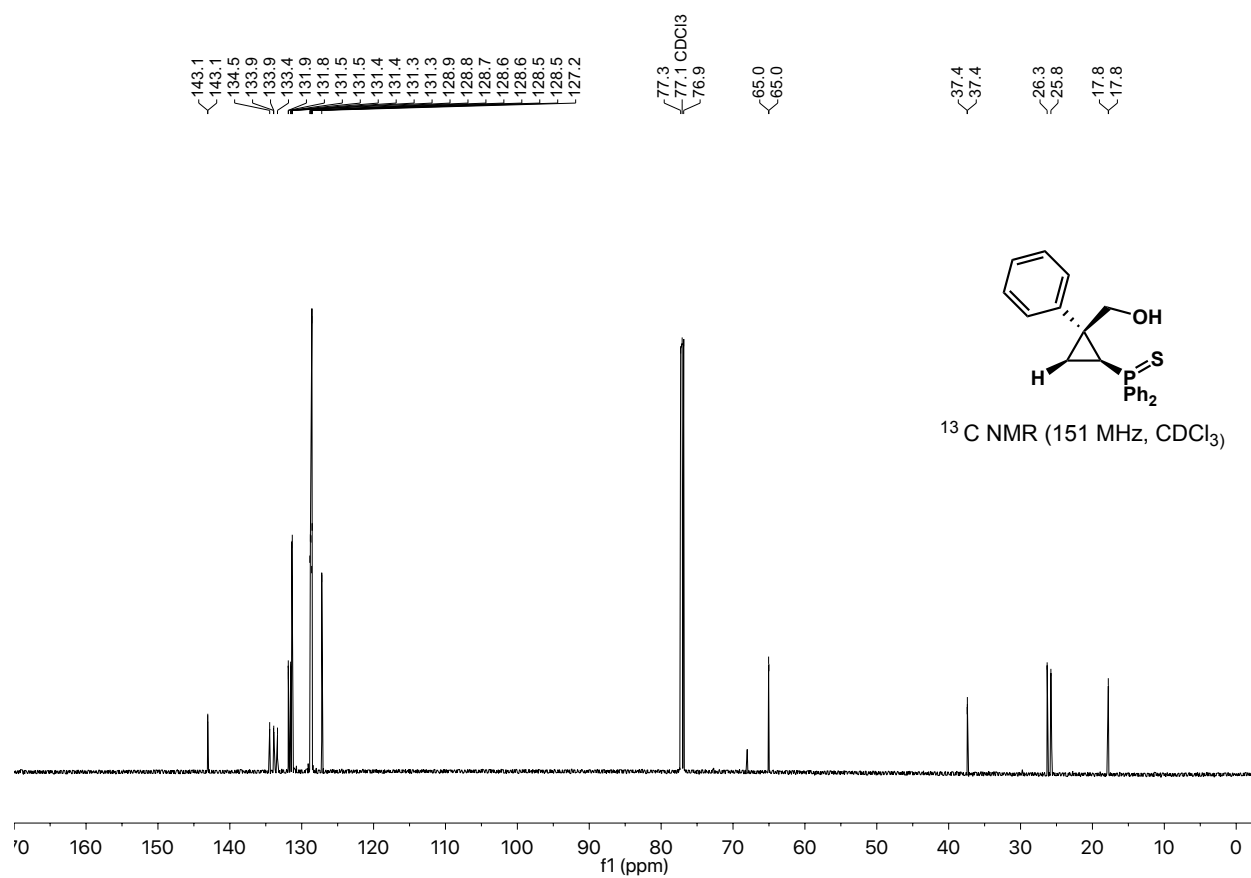


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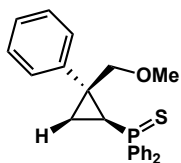


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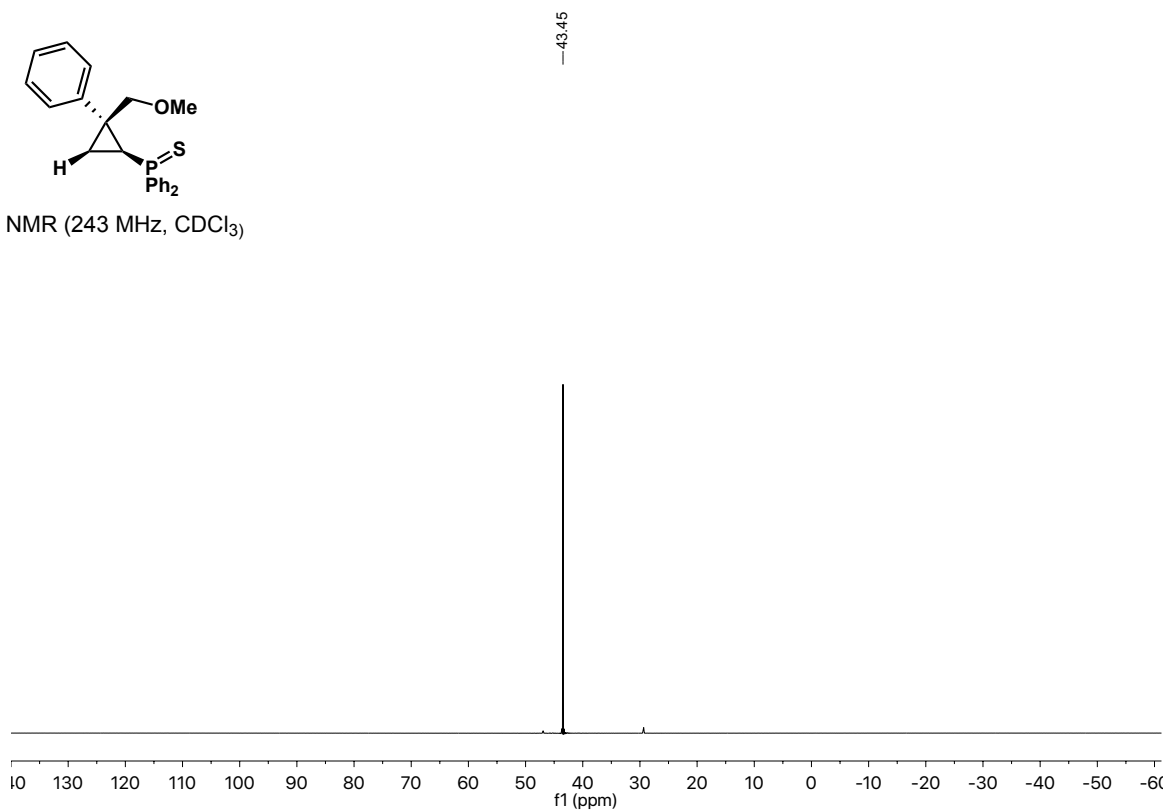




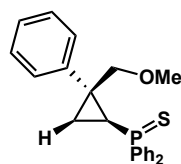
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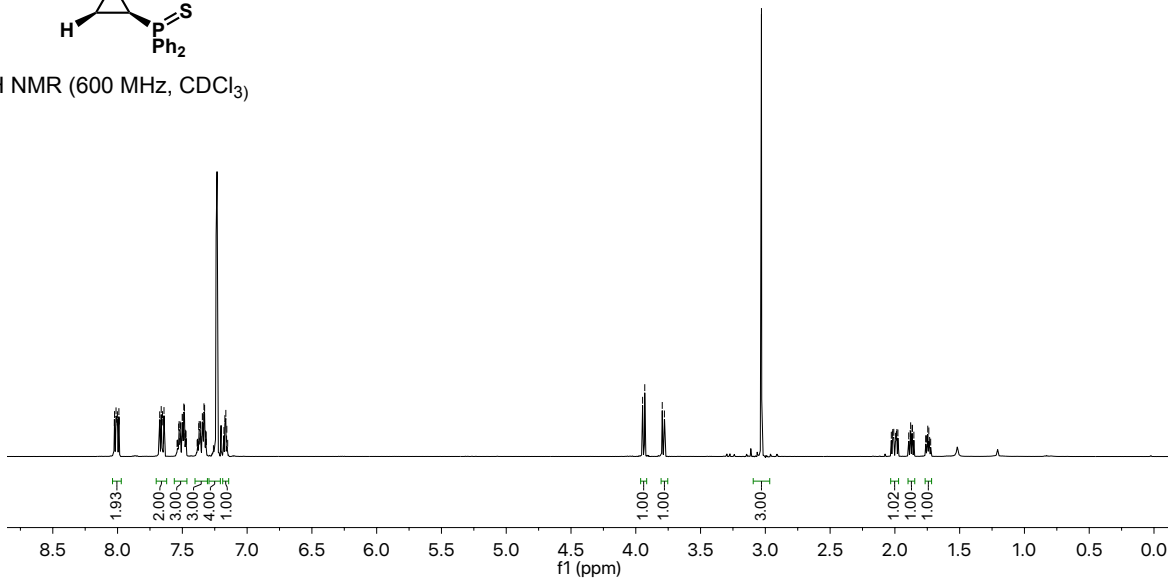
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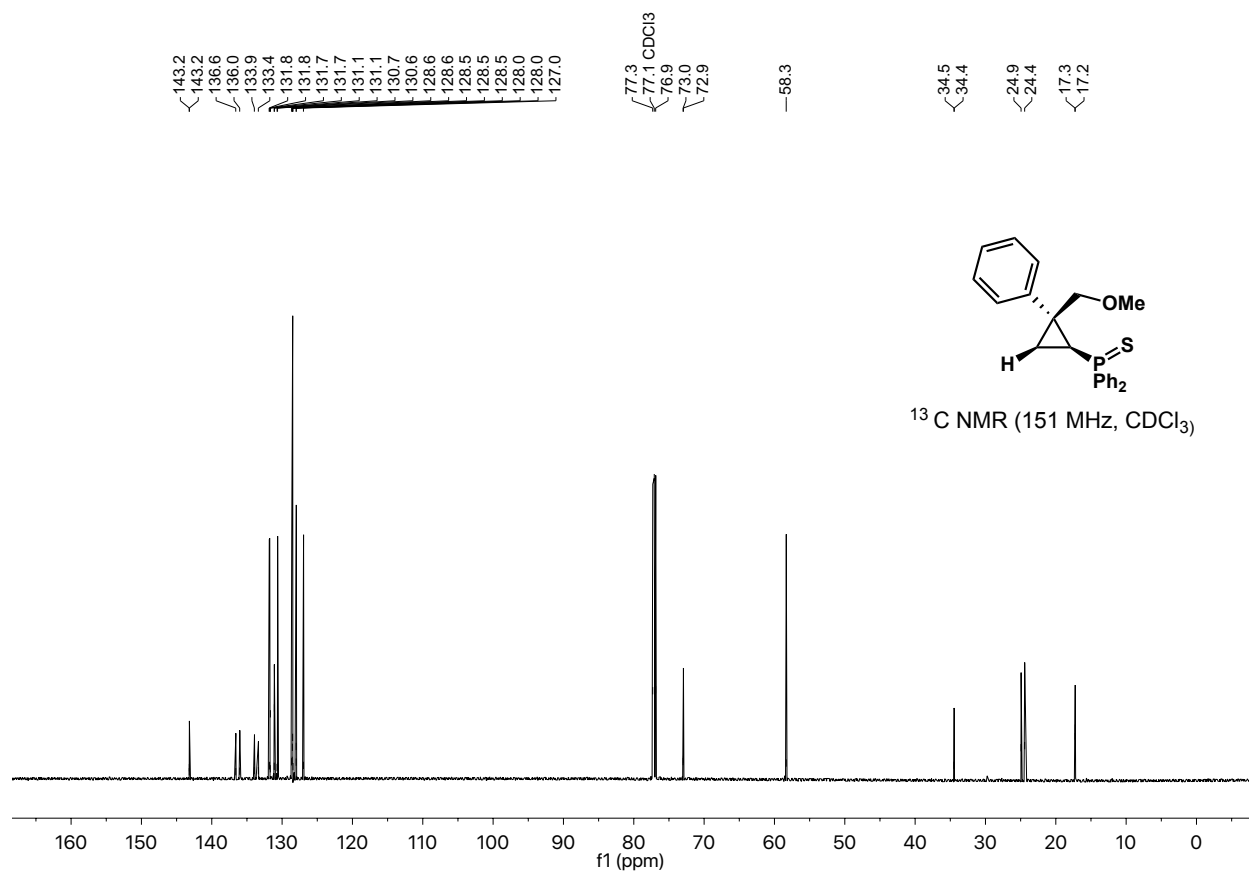


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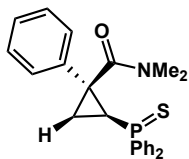


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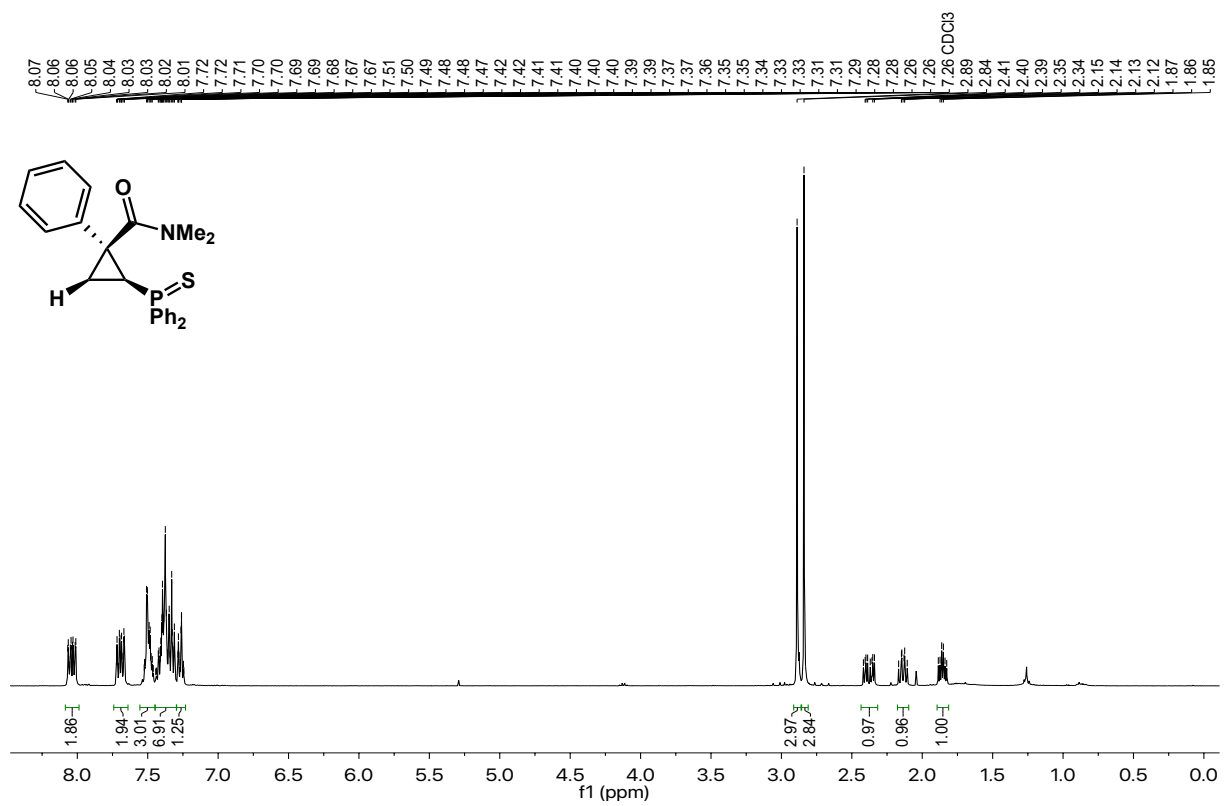
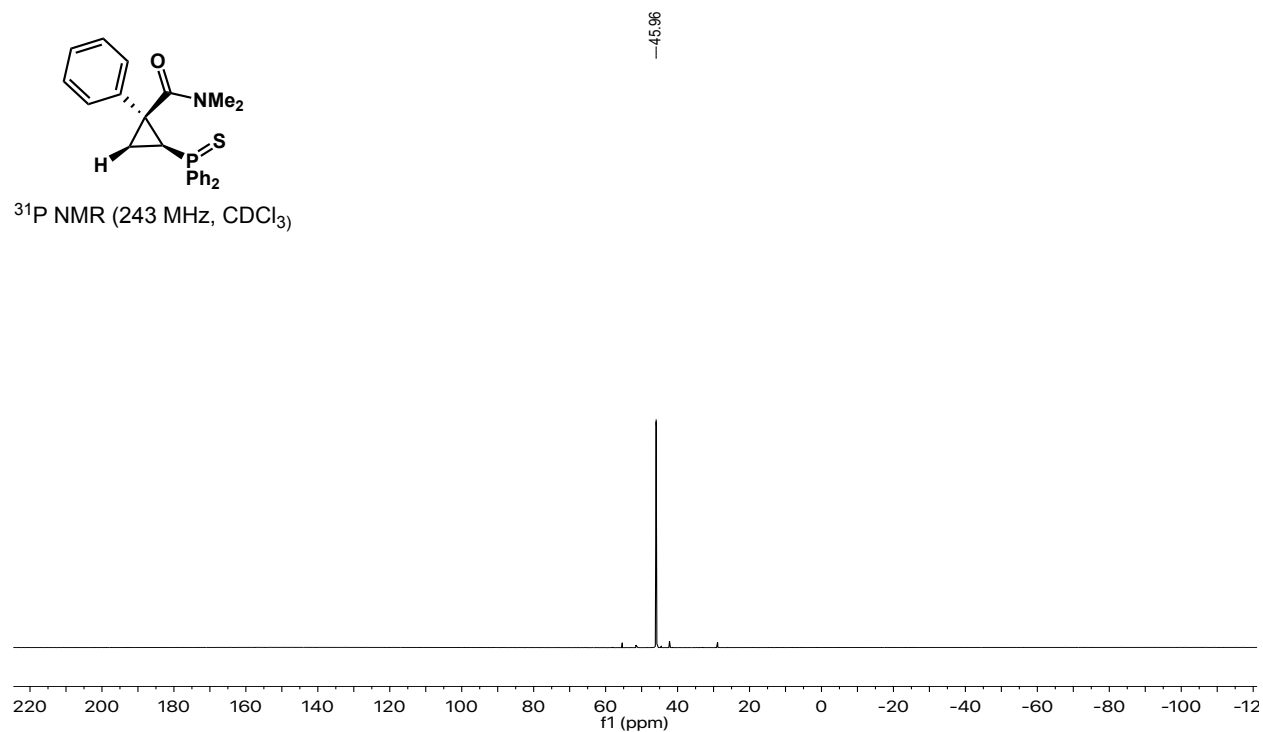




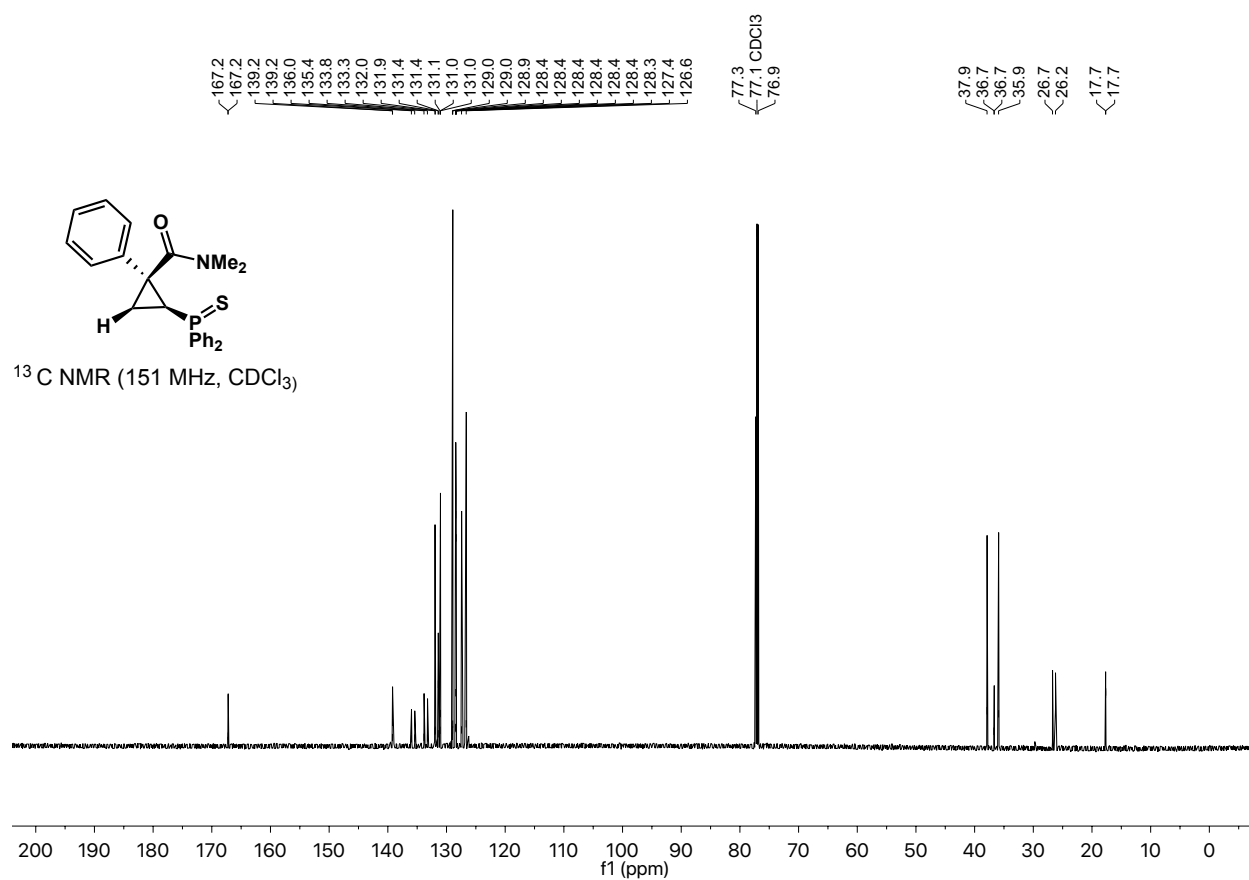
(1*R*,2*S*)-2-(diphenylphosphorothioyl)-*N,N*-dimethyl-1-phenylcyclopropane-1-carboxamide (3ka)



^{31}P NMR (243 MHz, CDCl_3)

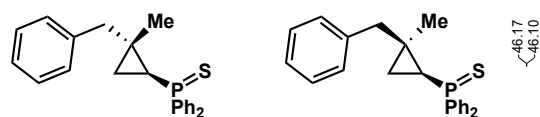


XHIV_112_400 MHz_purified.1.fid — ^1H spectrum

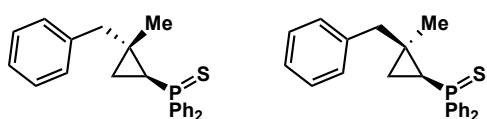
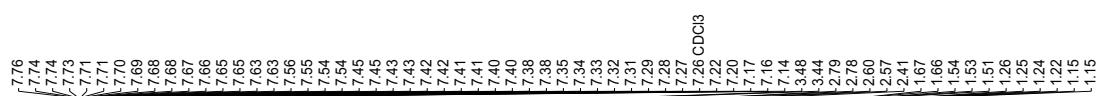
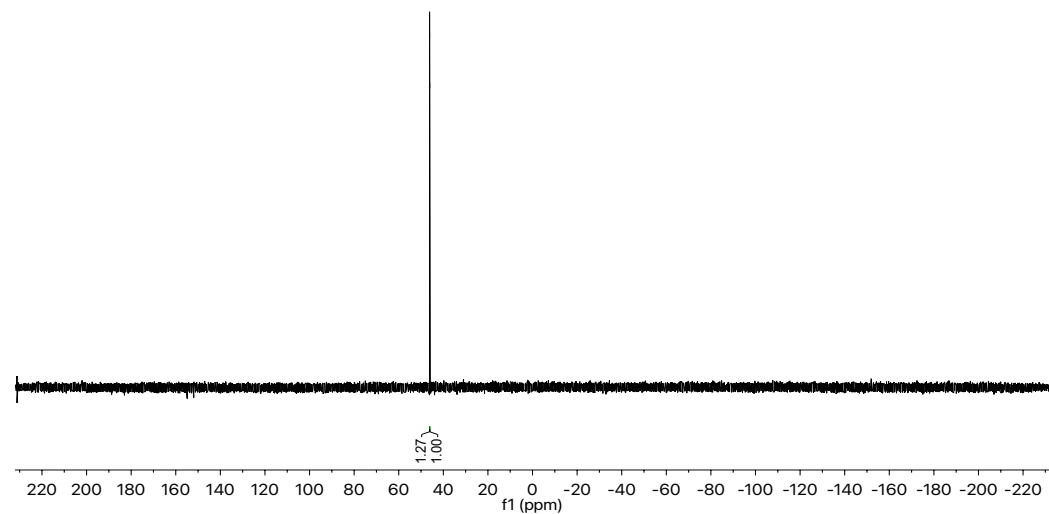


((1S,2R) or (1S, 2S)-2-benzyl-2-methylcyclopropyl)diphenylphosphine sulfide (3la)

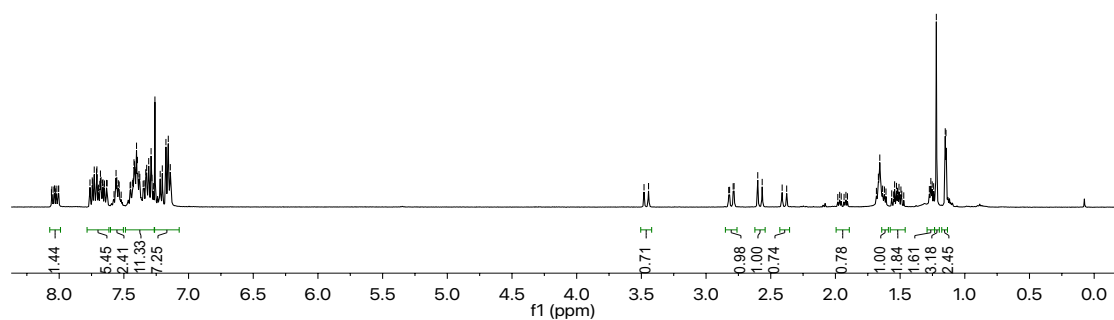
*Inseparable diastereomers.

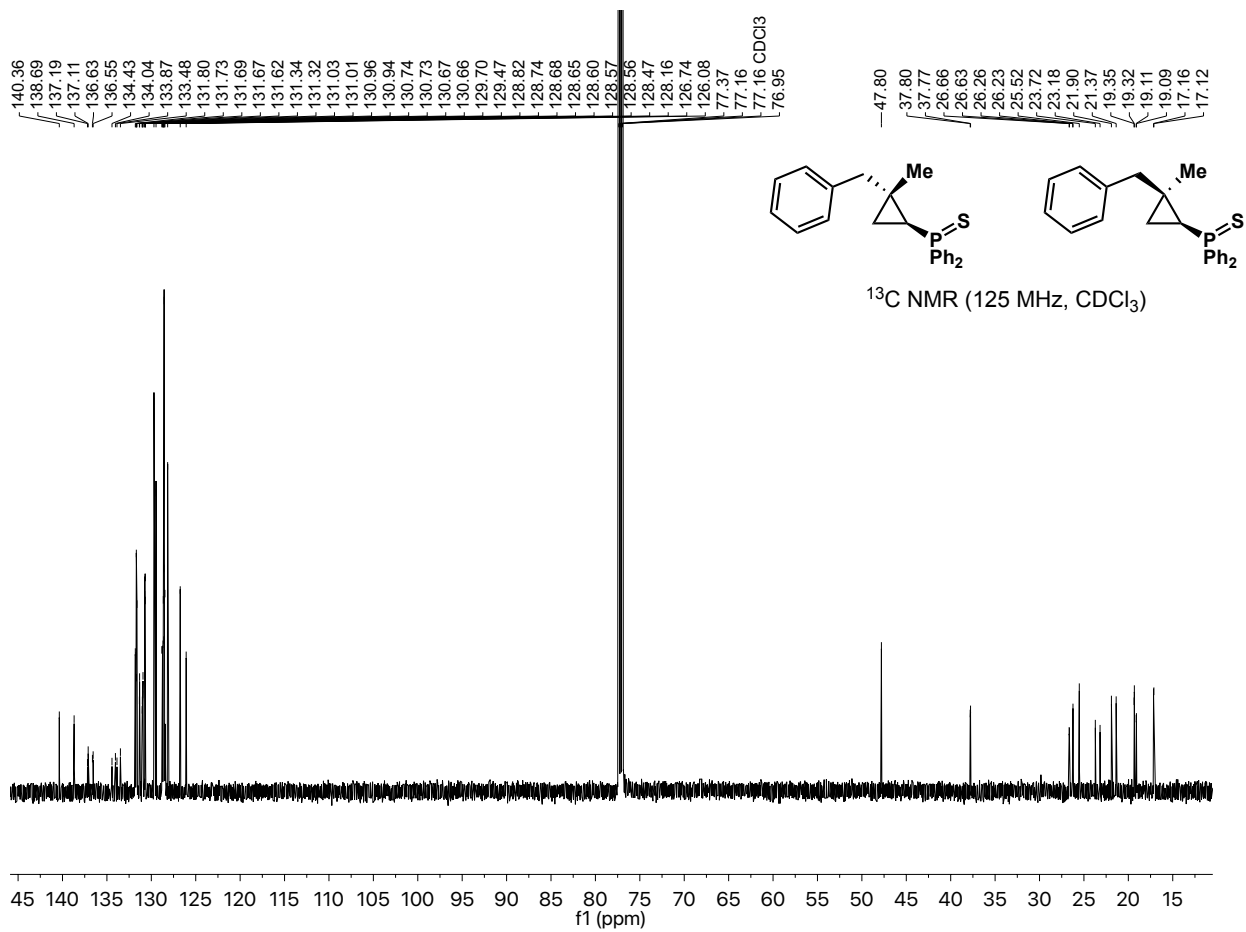


^{31}P NMR (162 MHz, CDCl_3)

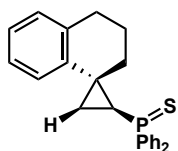


^1H NMR (400 MHz, CDCl_3)

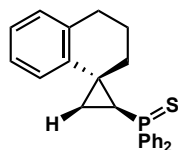
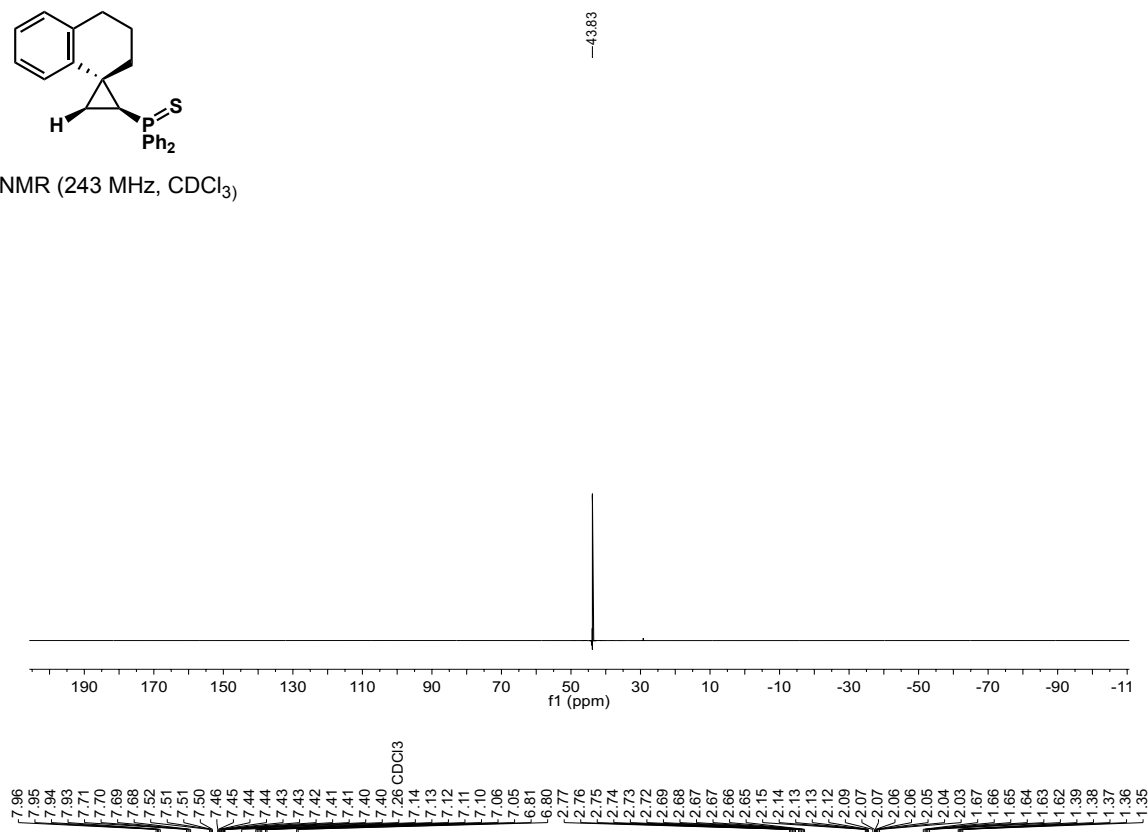




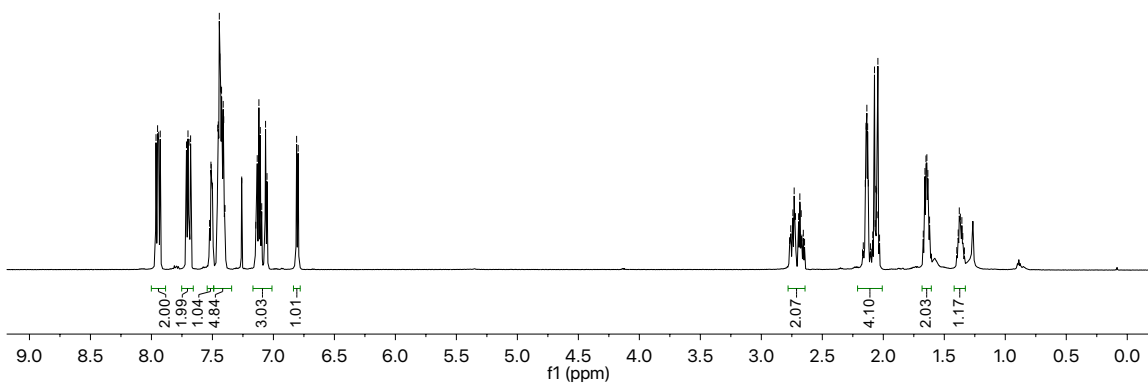
((1*R*,2*S*)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2-yl)diphenylphosphine sulfide (3ma)

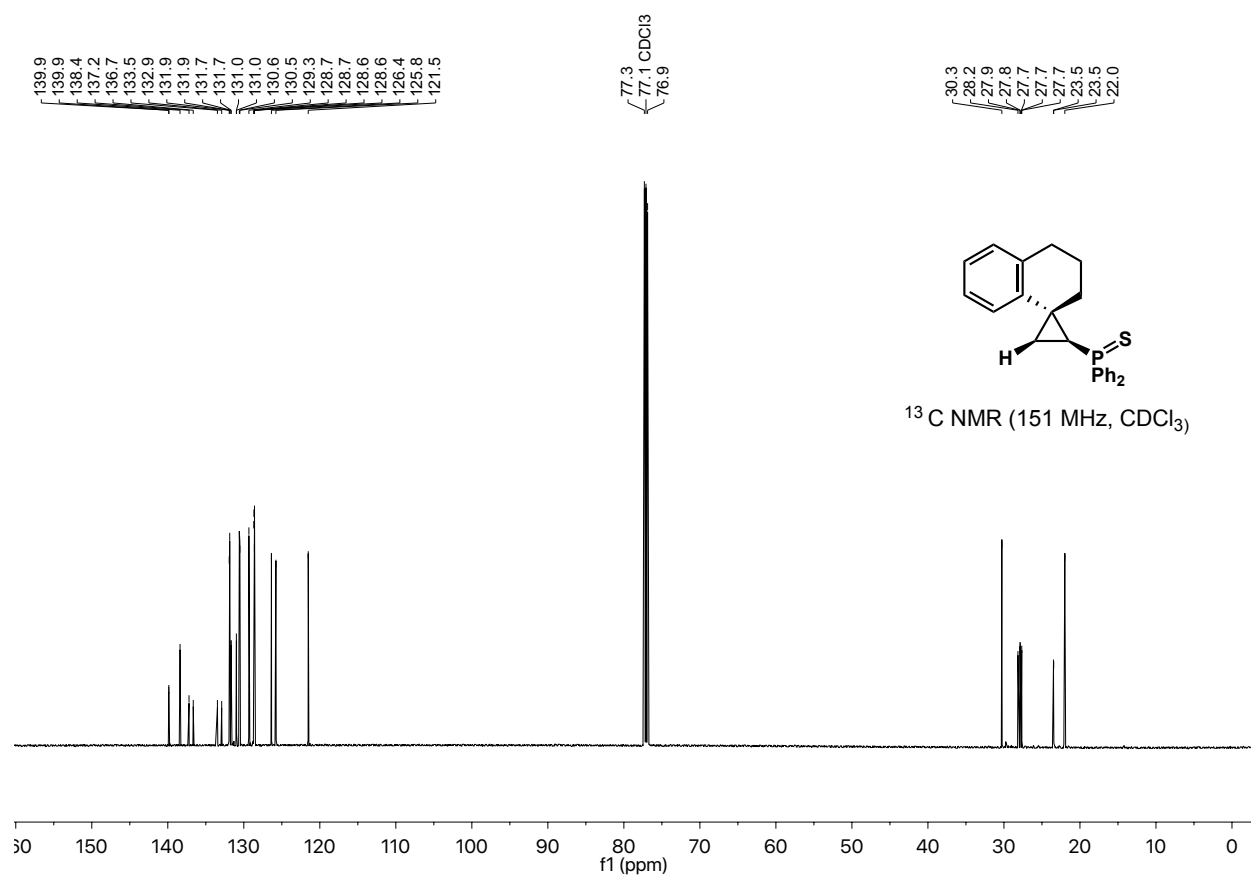


^{31}P NMR (243 MHz, CDCl_3)

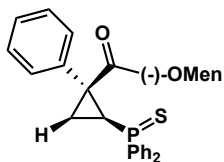


^1H NMR (600 MHz, CDCl_3)

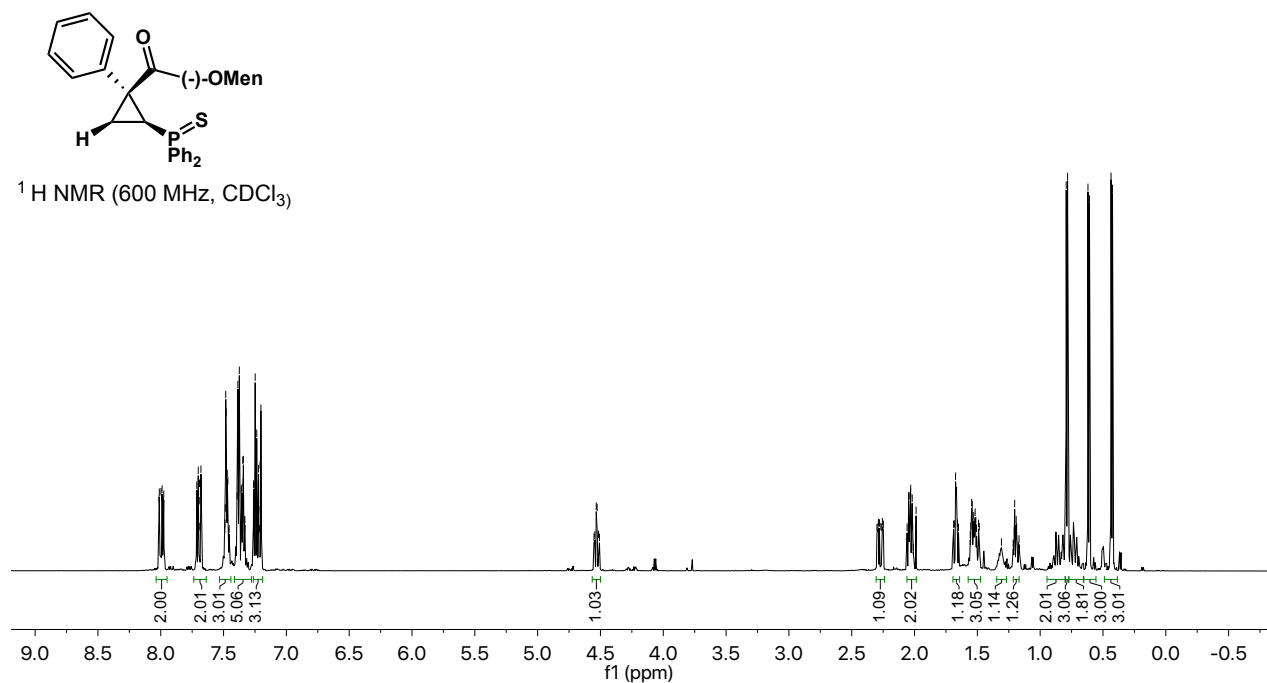
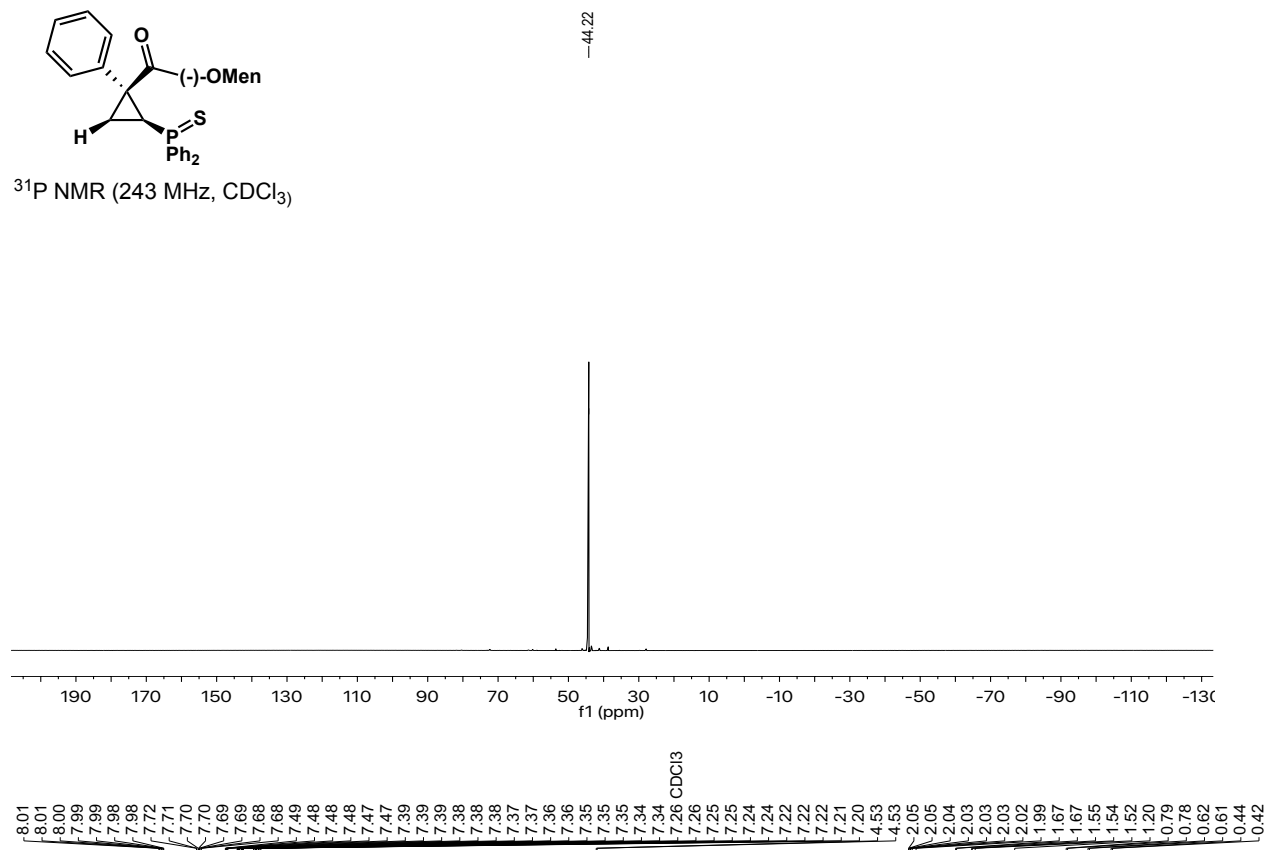


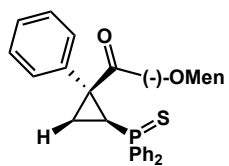


(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl(1*R*,2*S*)-2-(diphenylphosphorothioyl)-1-phenylcyclopropane-1-carboxylate (3na)

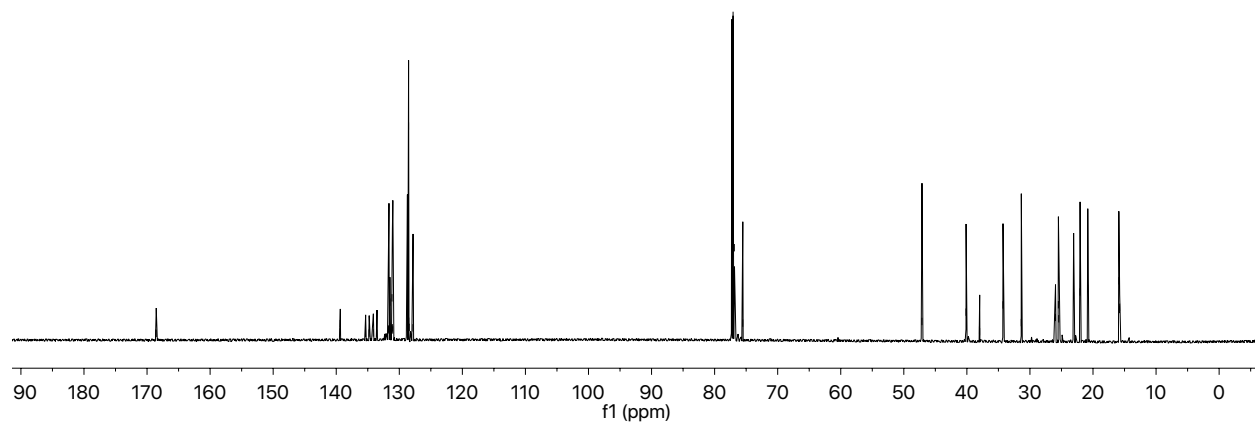


^{31}P NMR (243 MHz, CDCl_3)

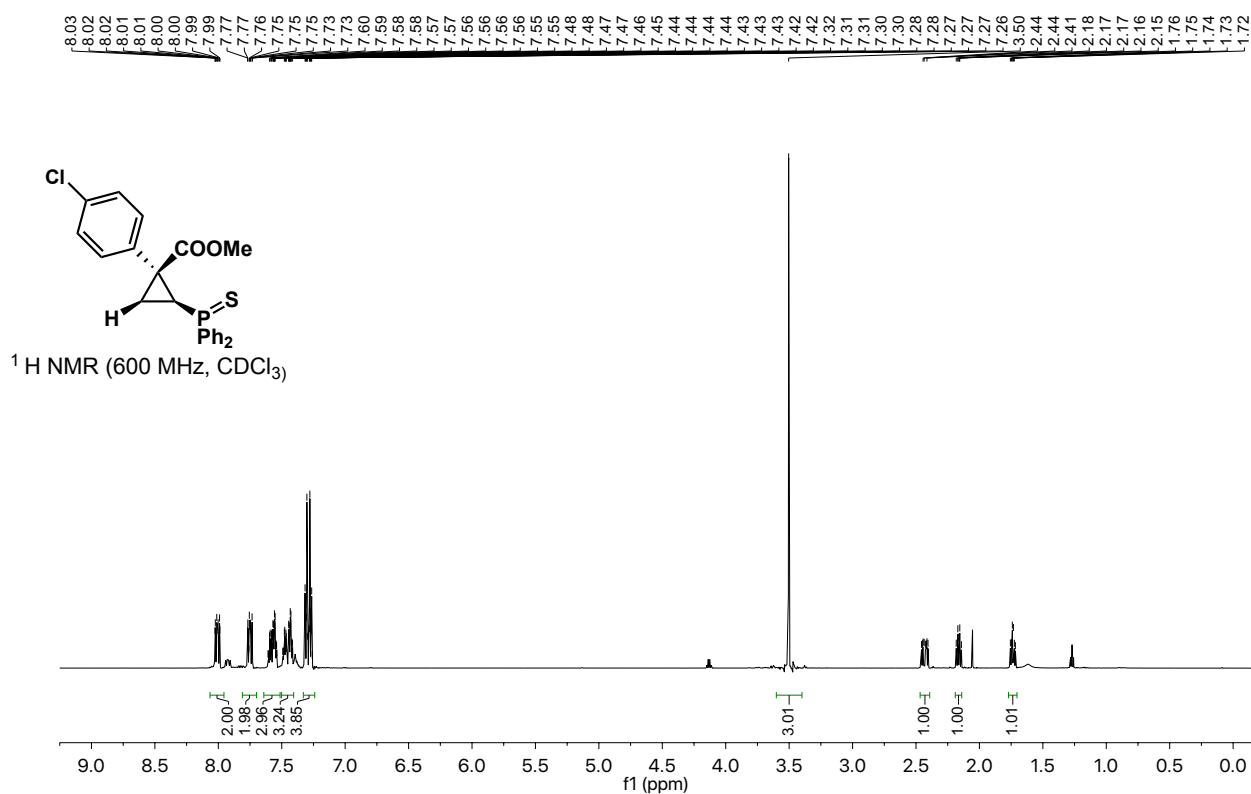
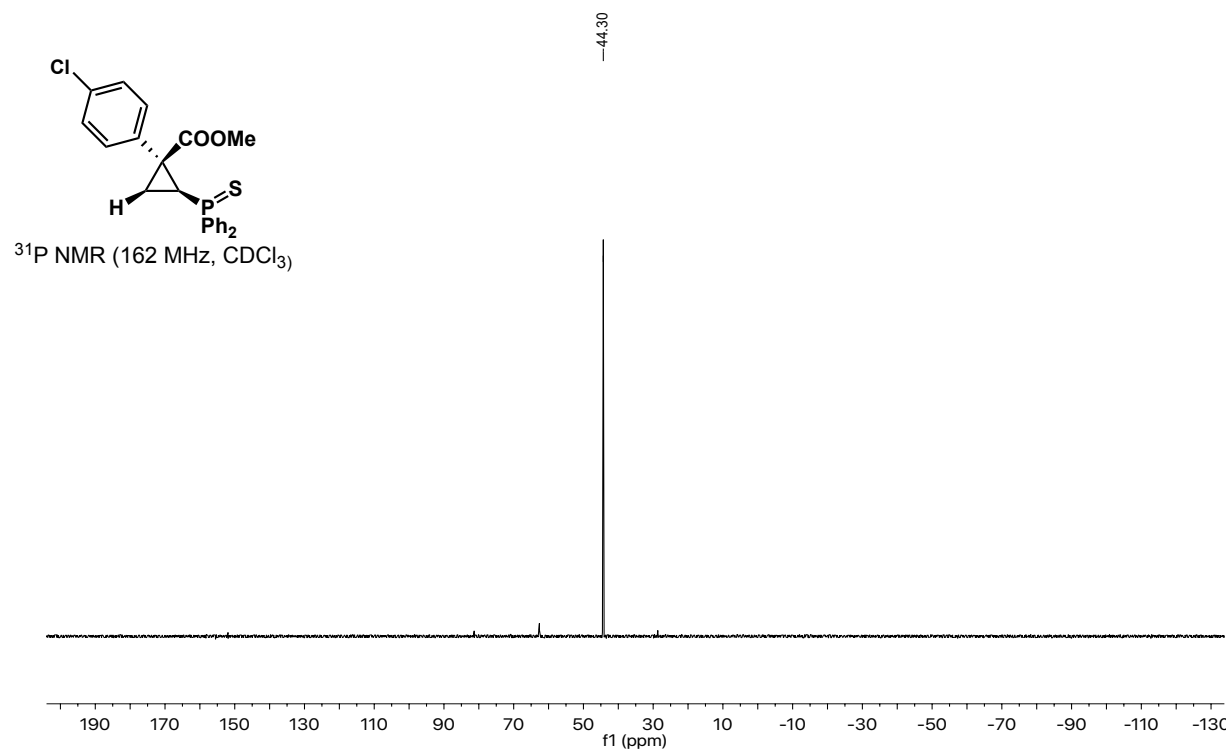


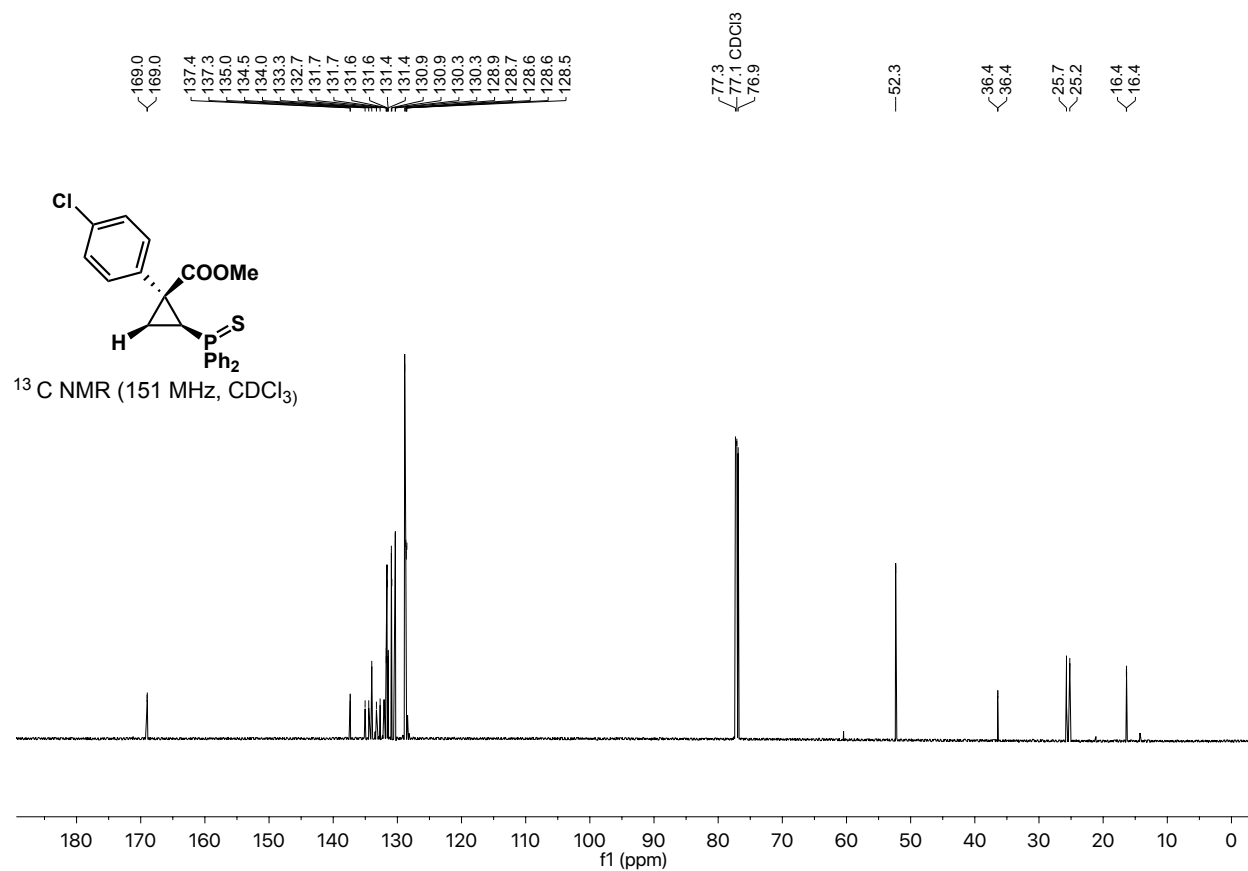


^{13}C NMR (151 MHz, CDCl_3)

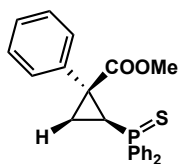


Methyl(1R,2S)-1-(4-chlorophenyl)-2-(diphenylphosphorothioyl)cyclopropane-1-carboxylate (30a)

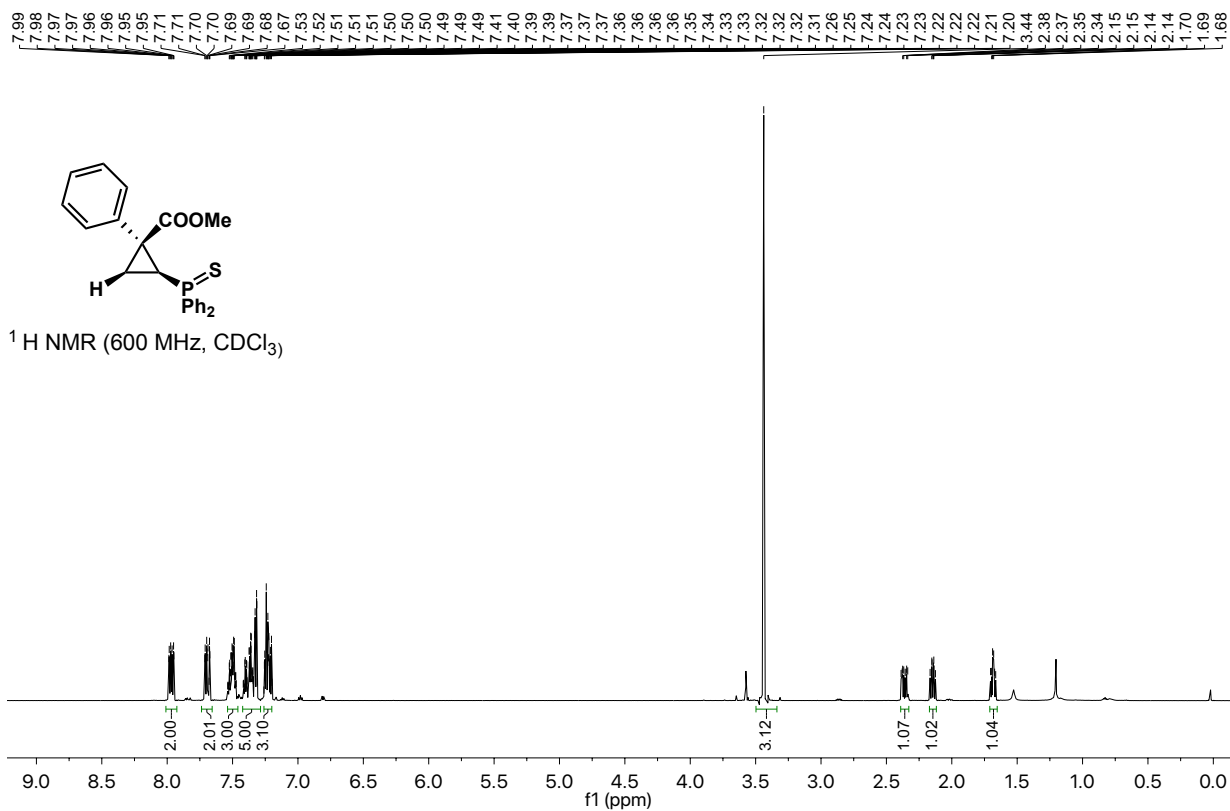
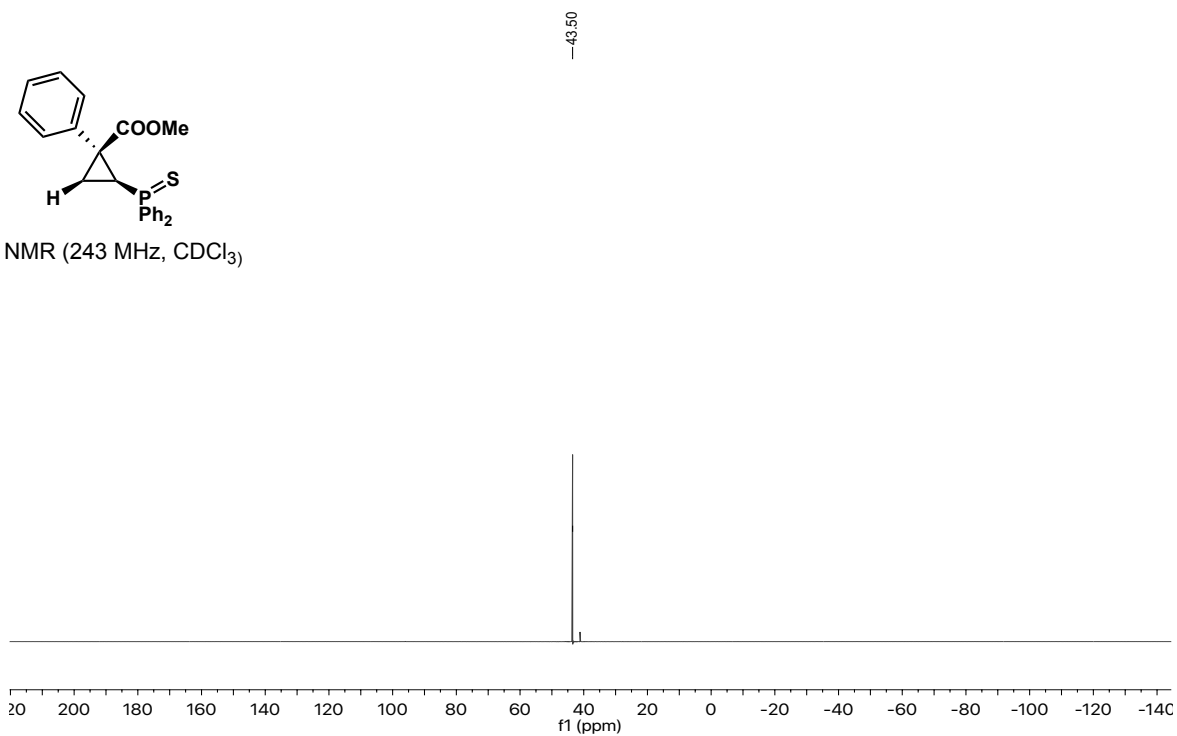


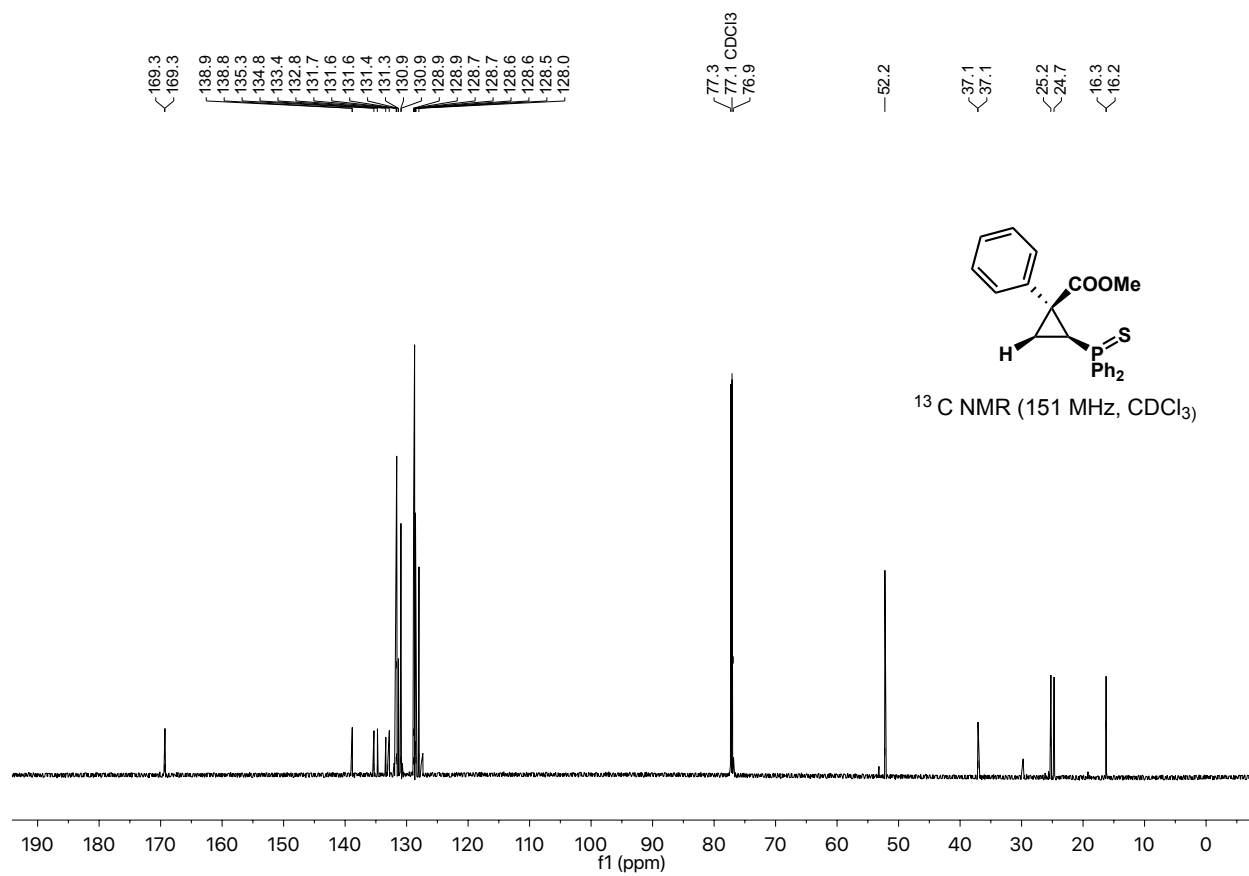


Methyl (1*R*,2*S*)-2-(diphenylphosphorothioyl)-1-phenylcyclopropane-1-carboxylate (3pa)

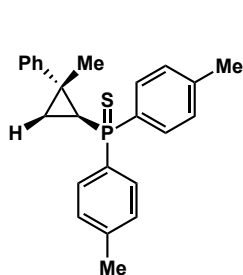


^{31}P NMR (243 MHz, CDCl_3)

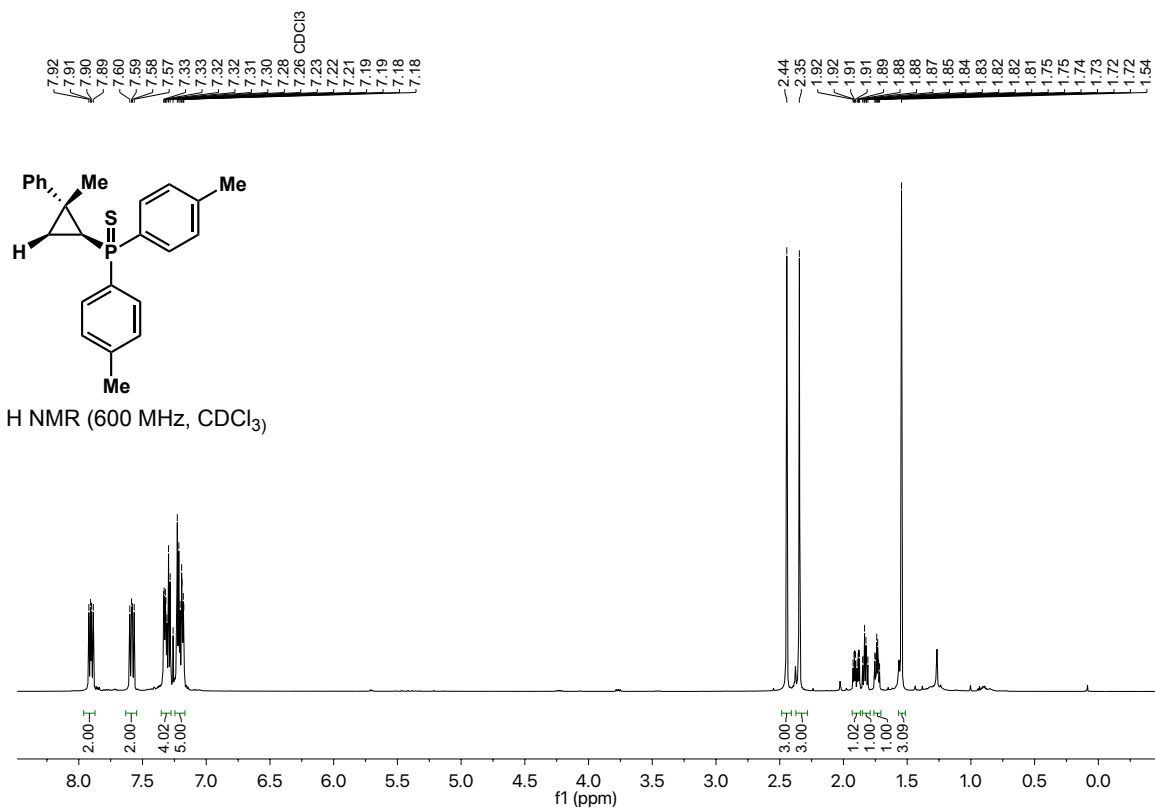
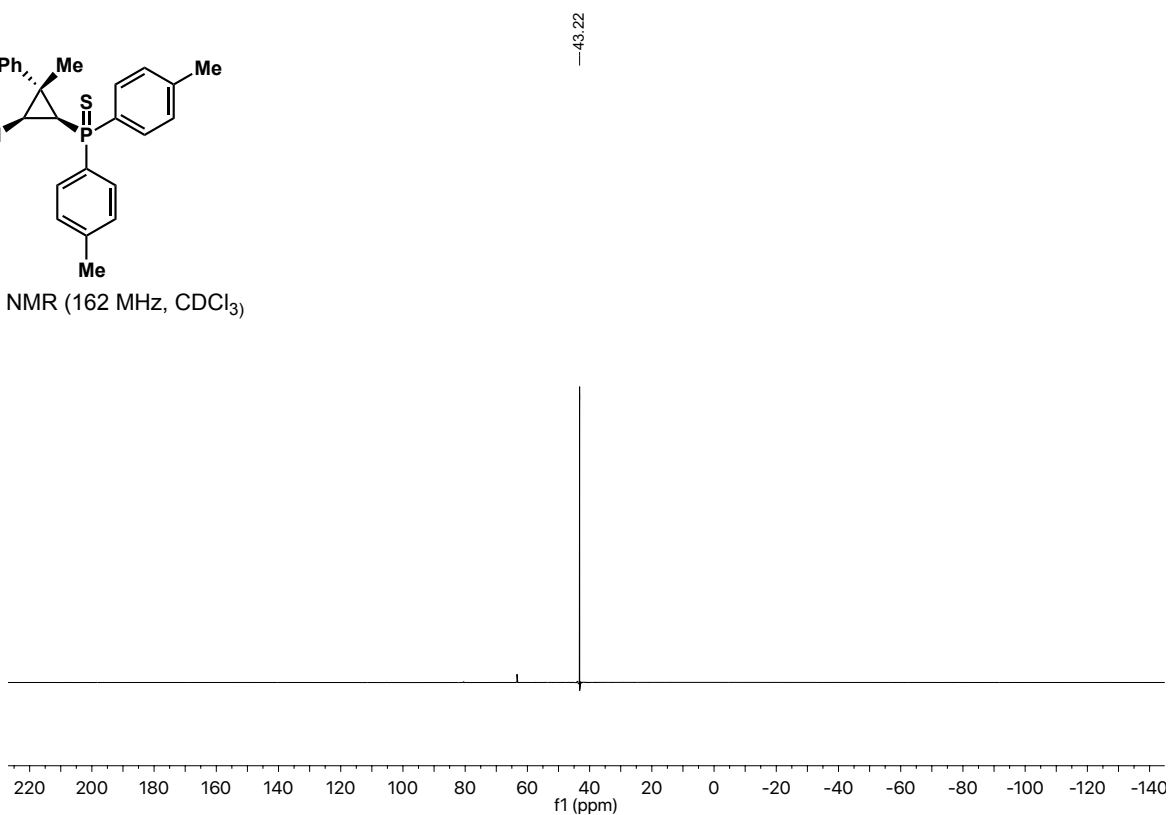


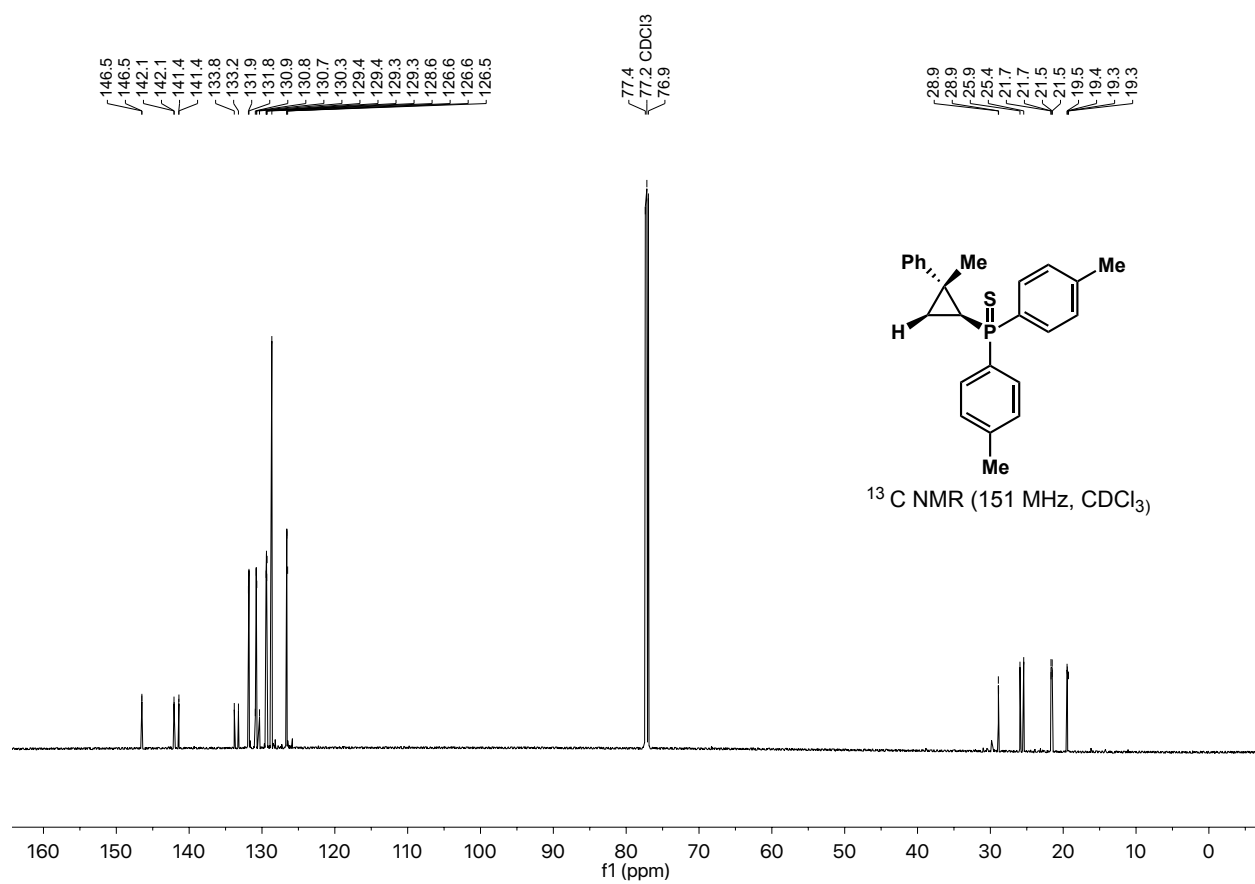


((1S,2R)-2-methyl-2-phenylcyclopropyl)di-p-tolylphosphine sulfide (3ab)

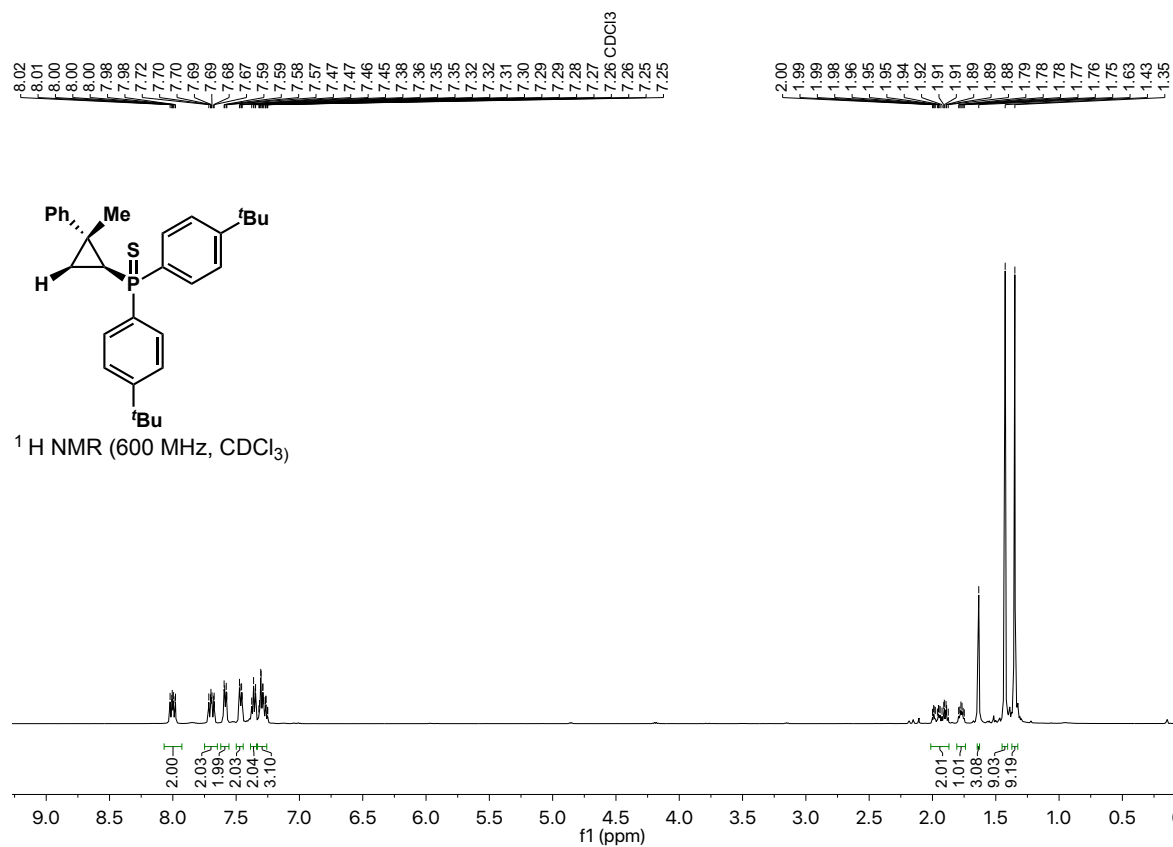
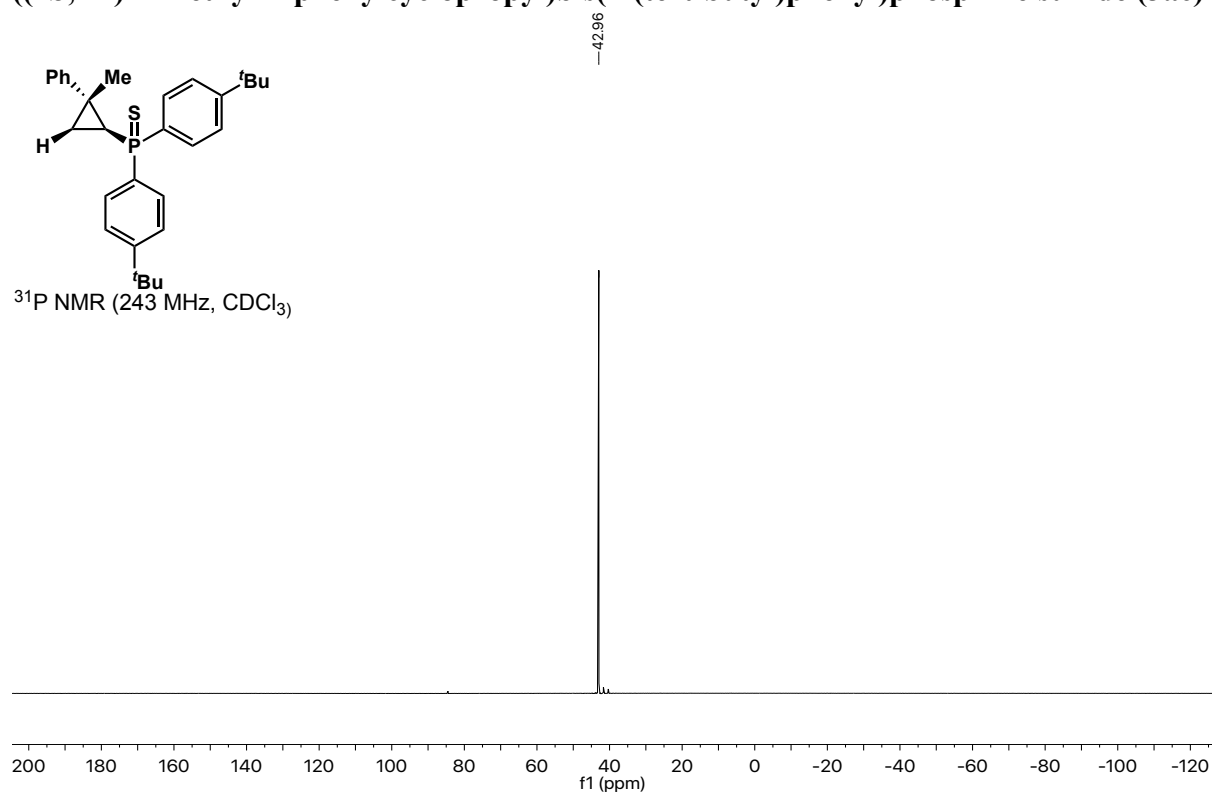


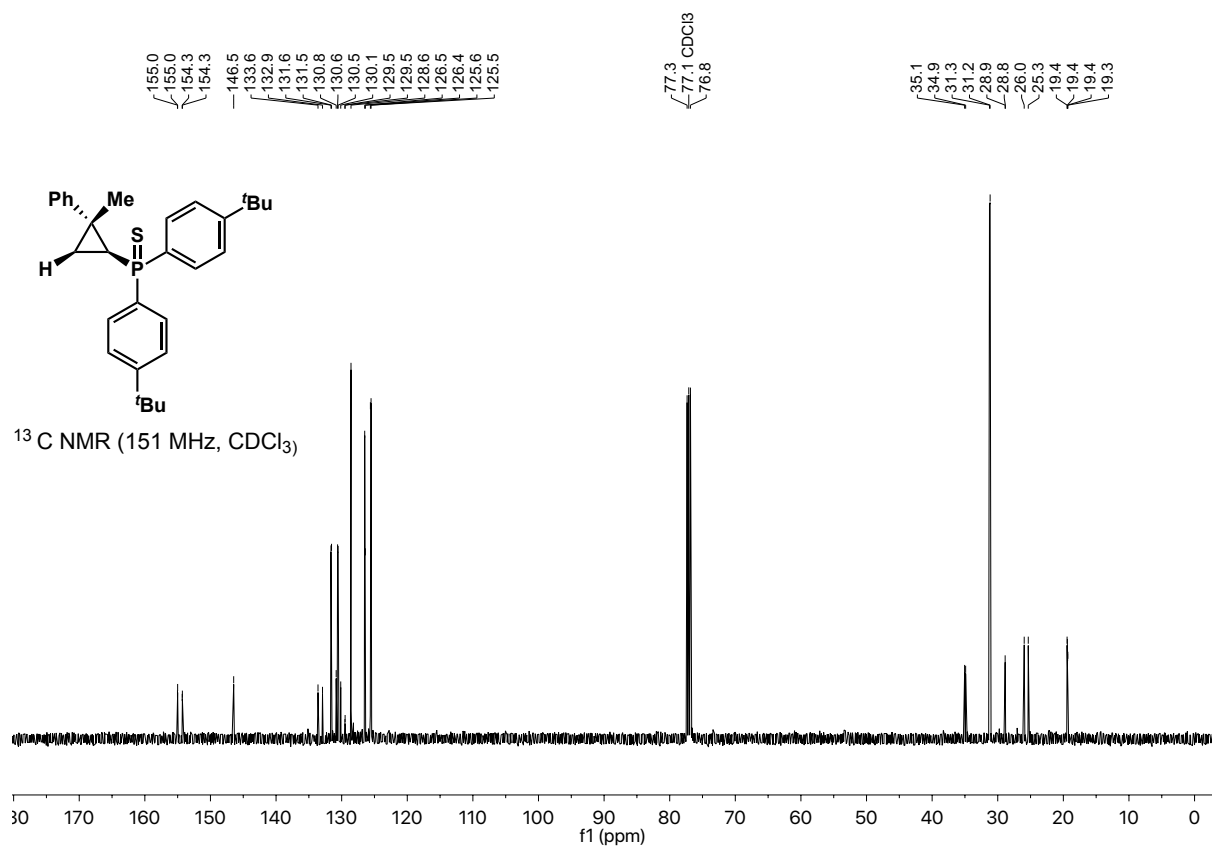
^{31}P NMR (162 MHz, CDCl_3)



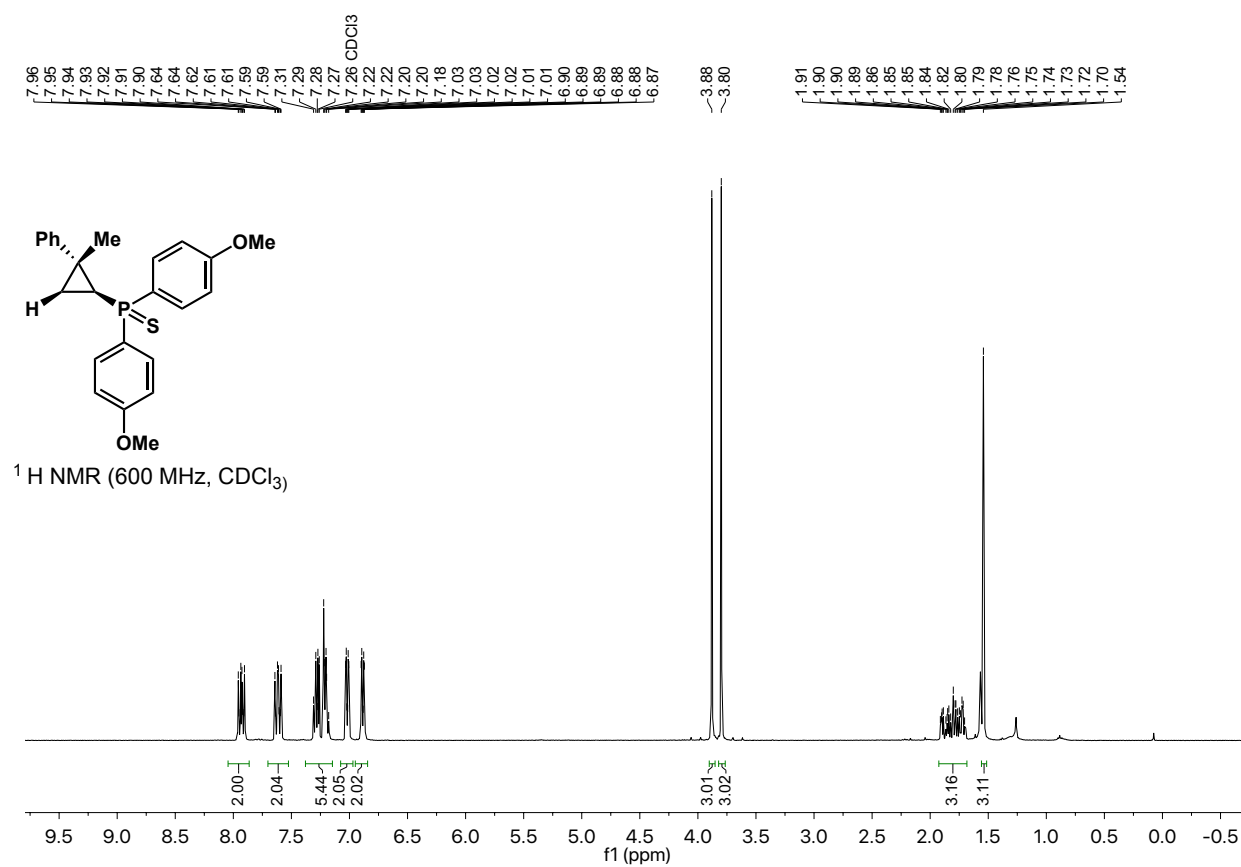
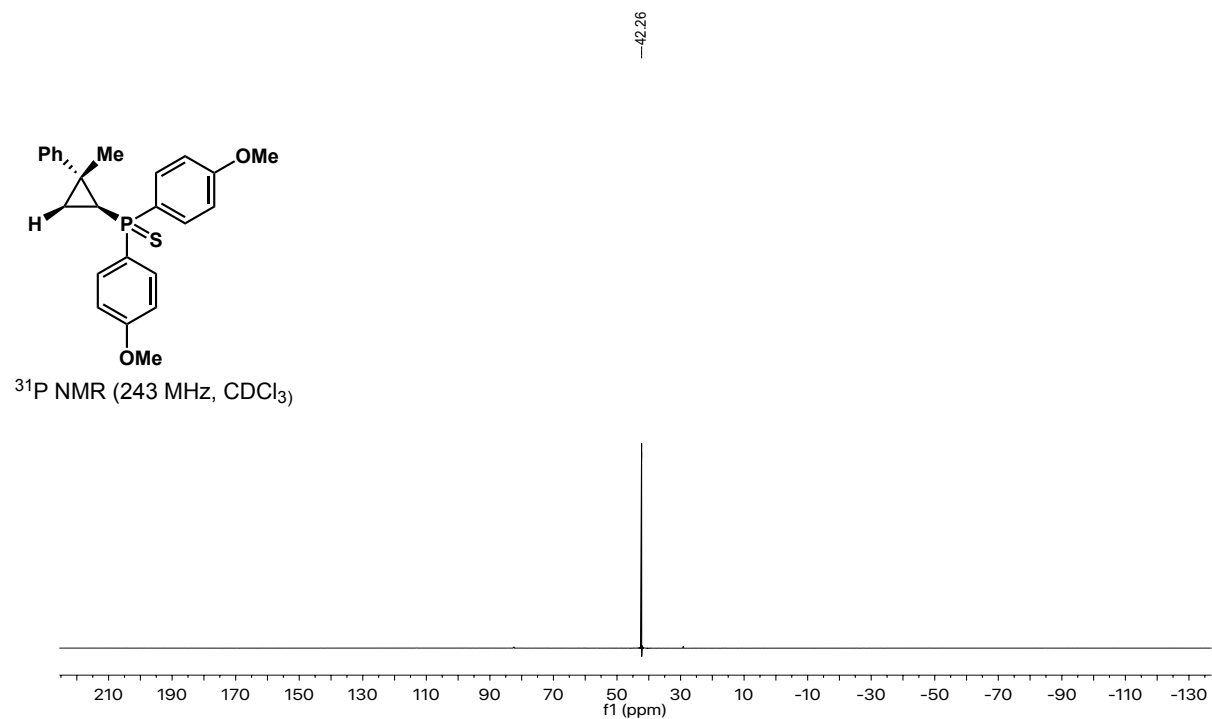


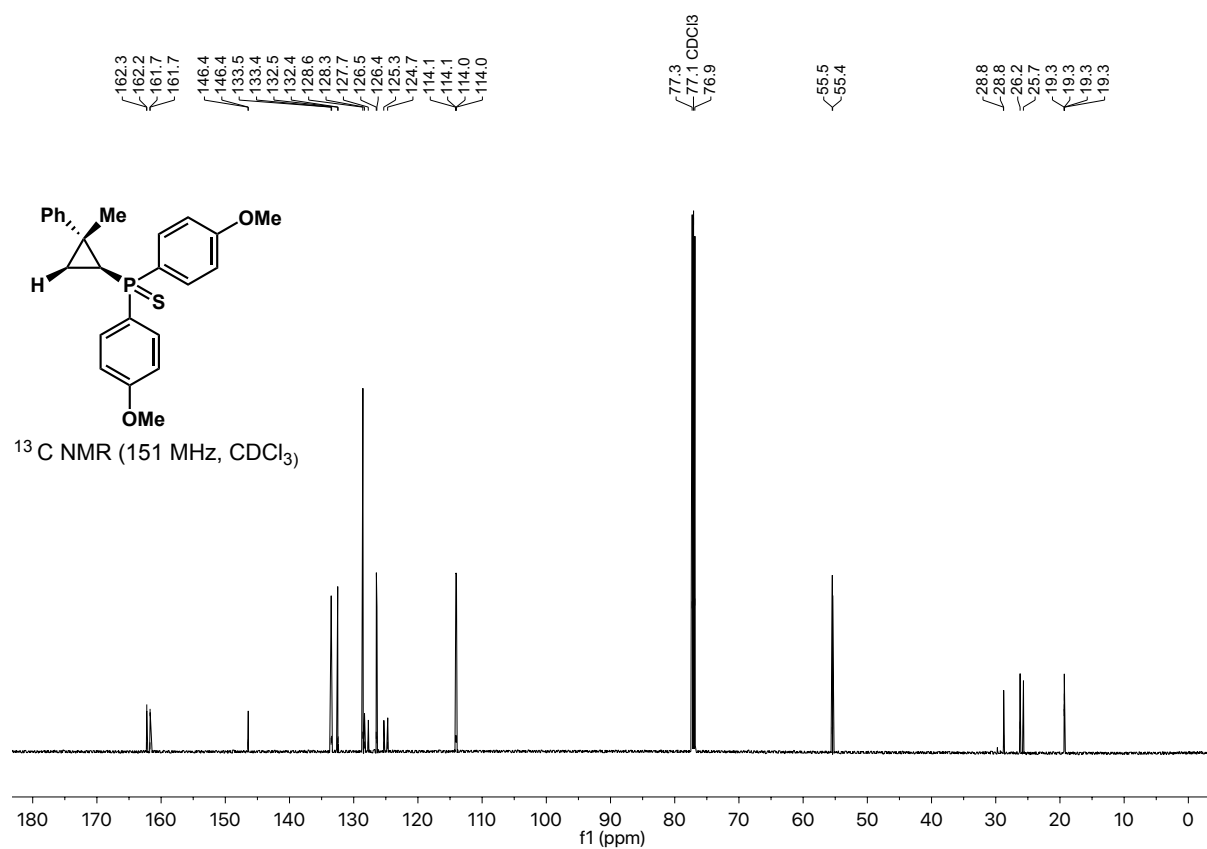
((1S,2R)-2-methyl-2-phenylcyclopropyl)bis(4-(tert-butyl)phenyl)phosphine sulfide (3ac)



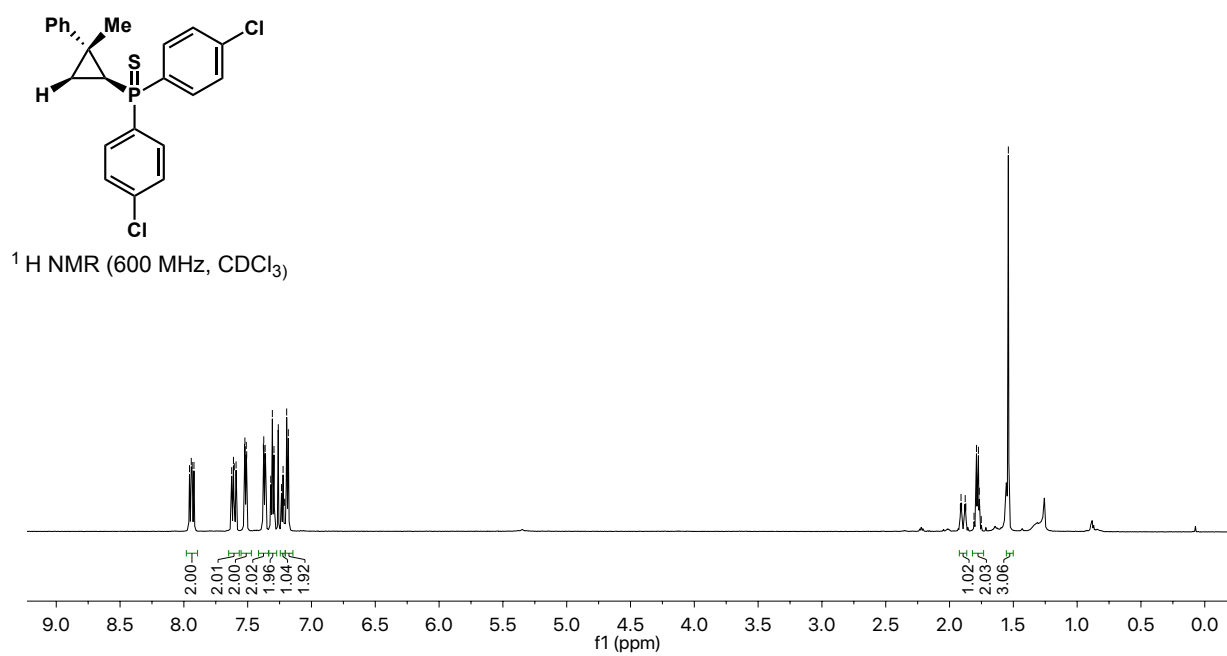
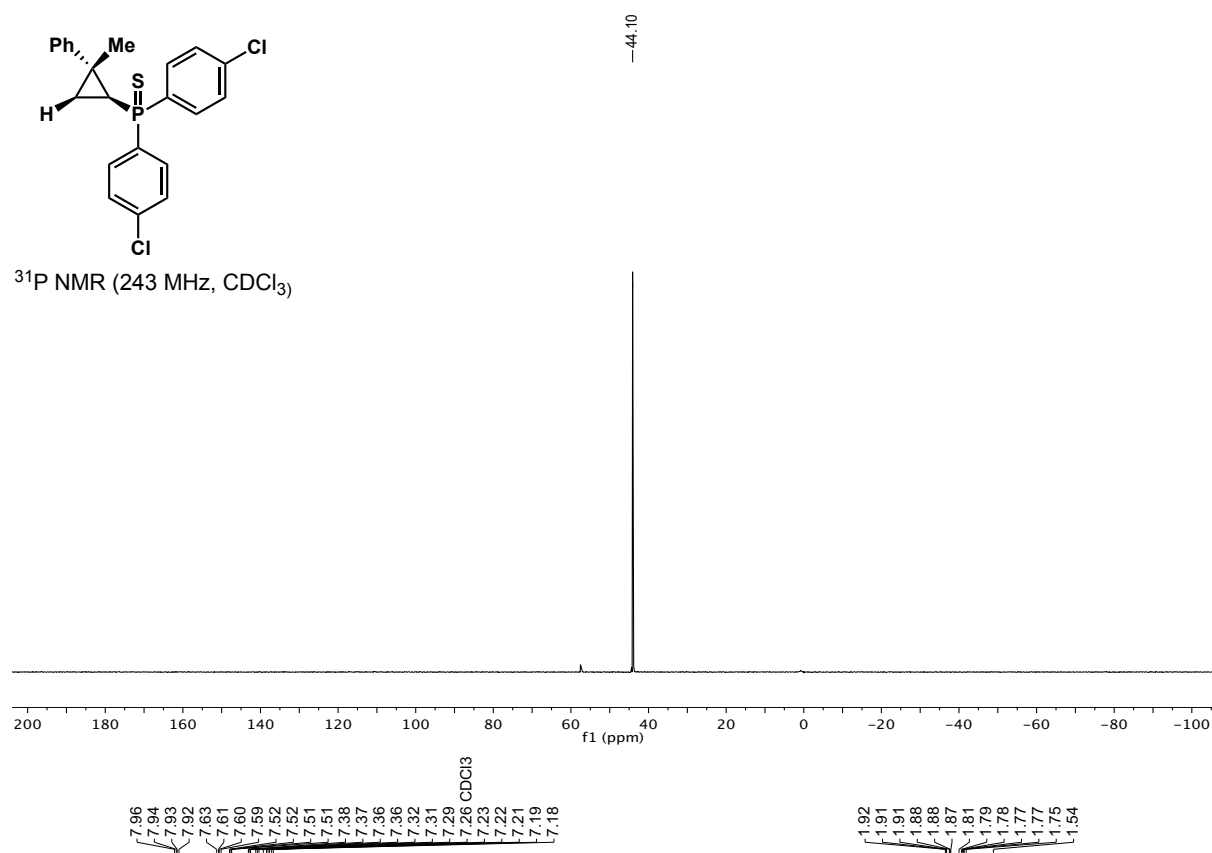


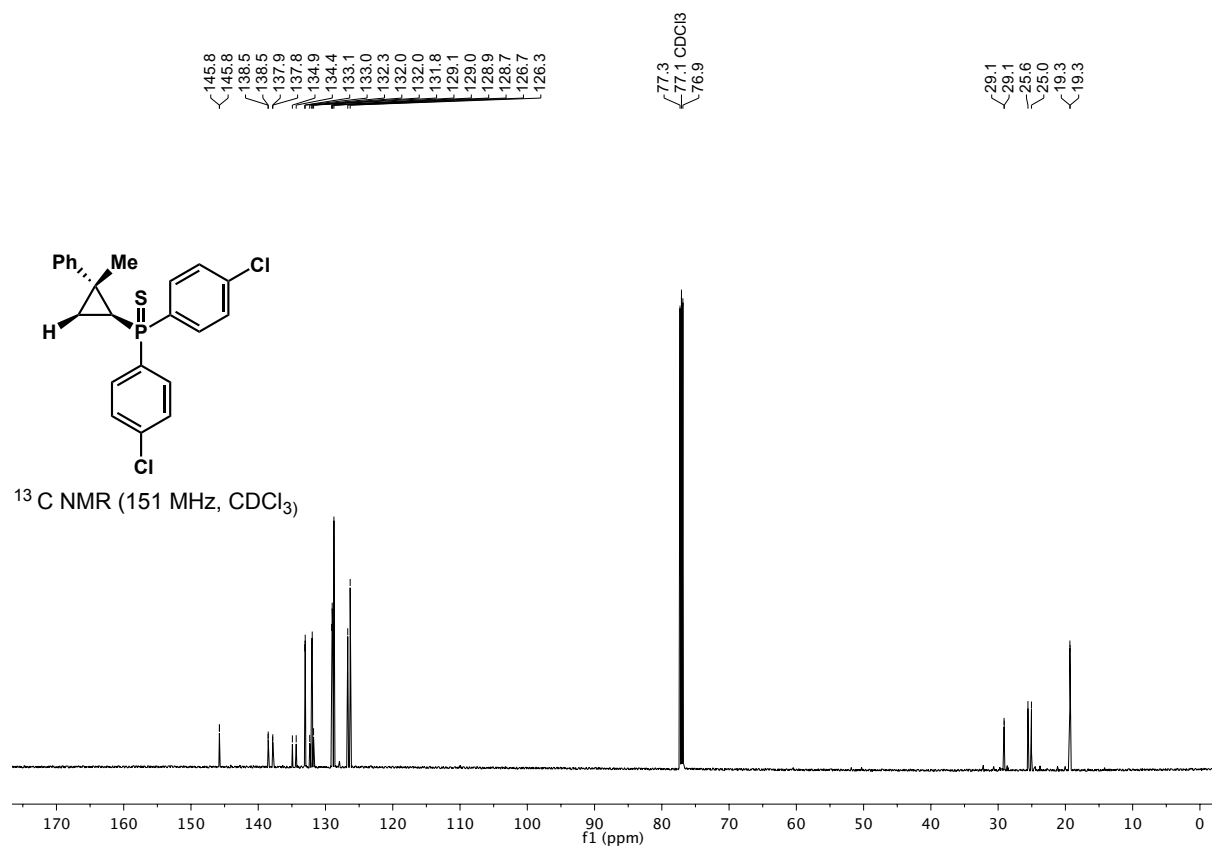
Bis(4-methoxyphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ad)



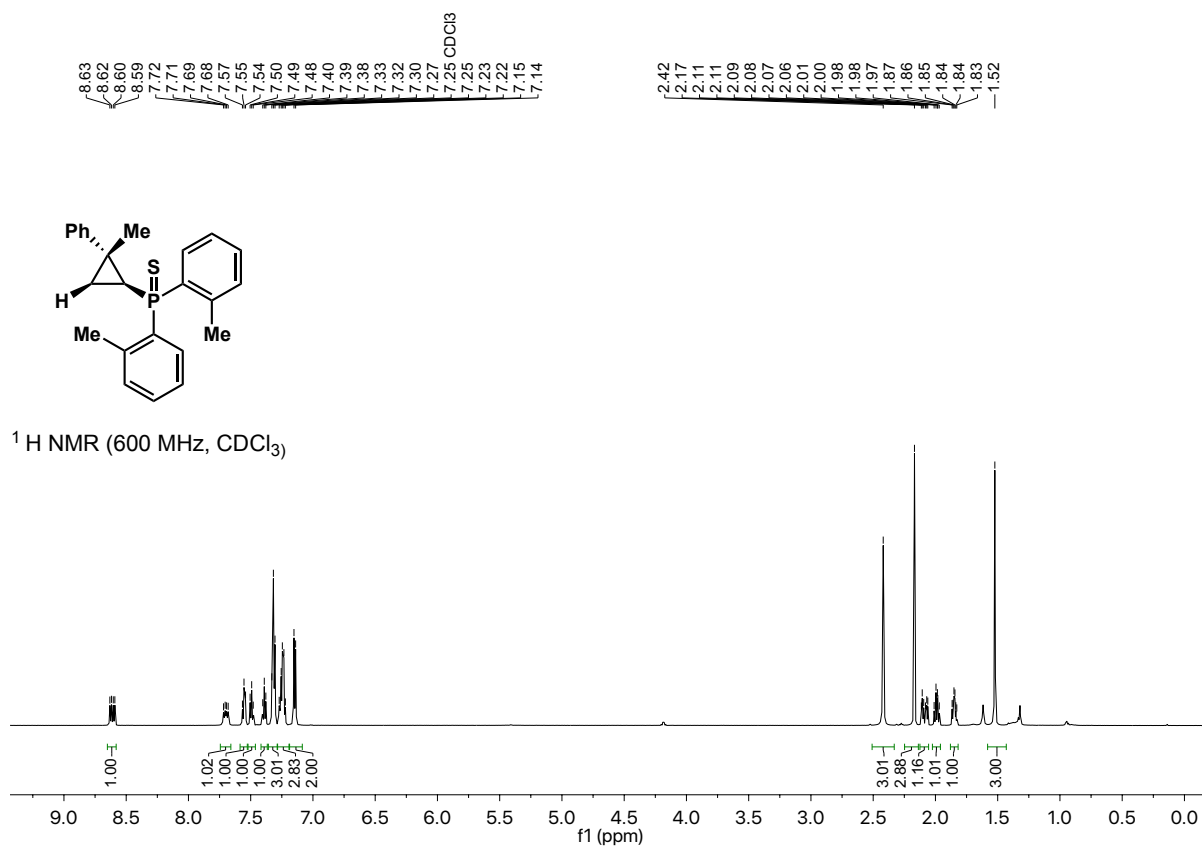
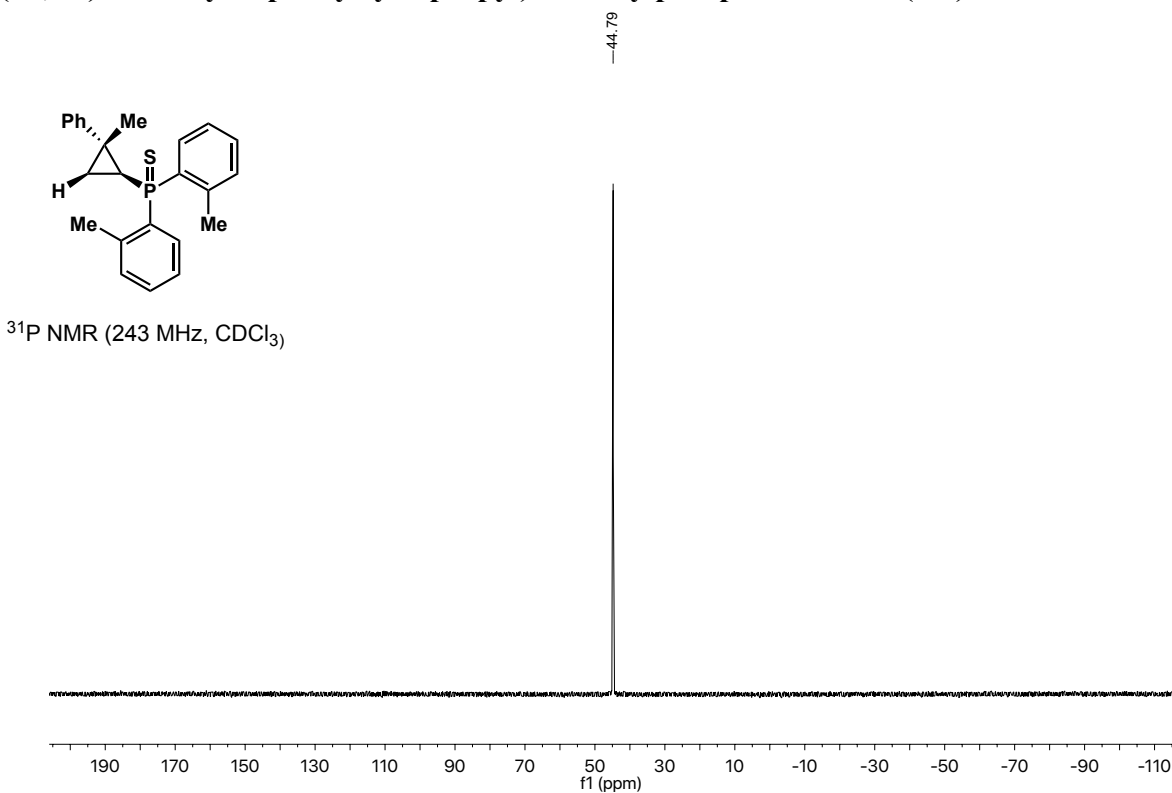


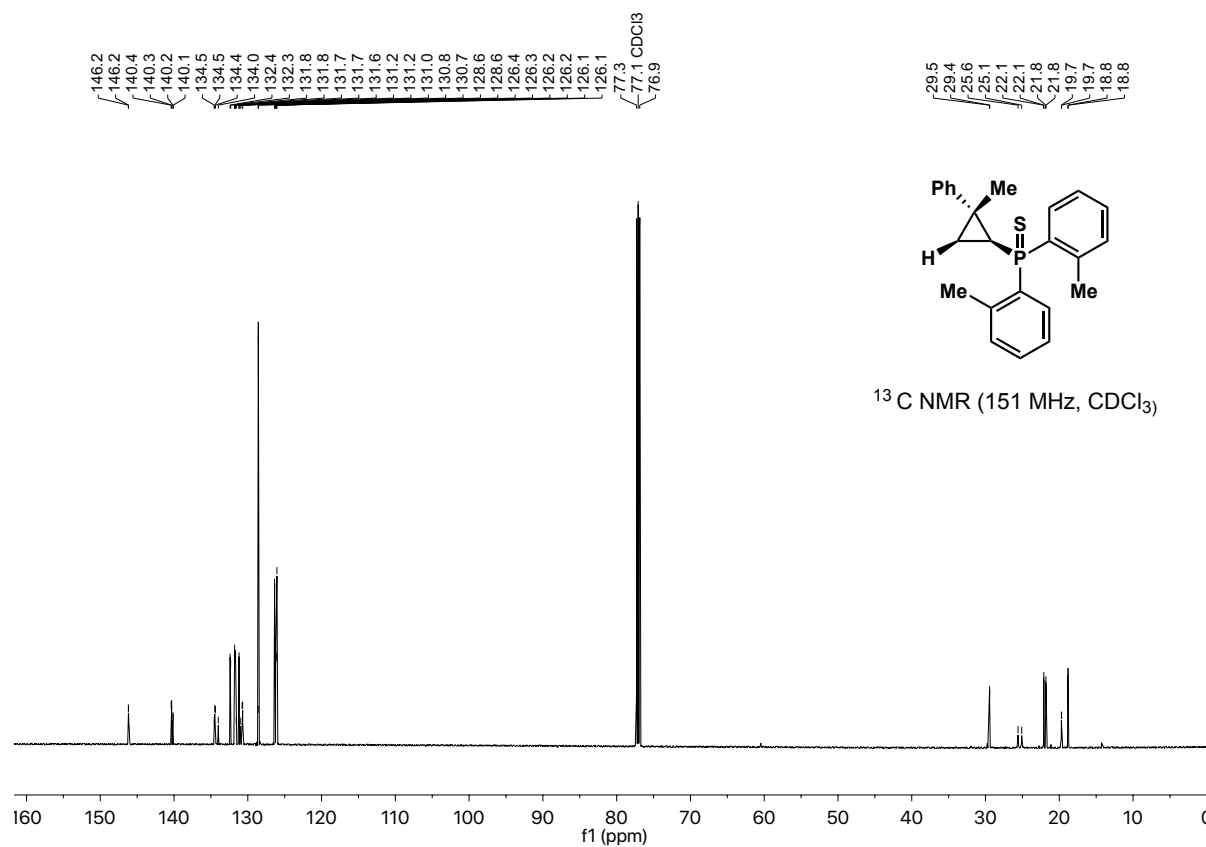
Bis(4-chlorophenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ae)



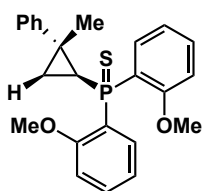


((1*S*,2*R*)-2-methyl-2-phenylcyclopropyl)di-*o*-tolylphosphine sulfide (3af)

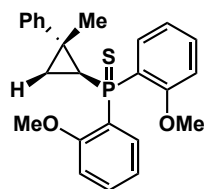
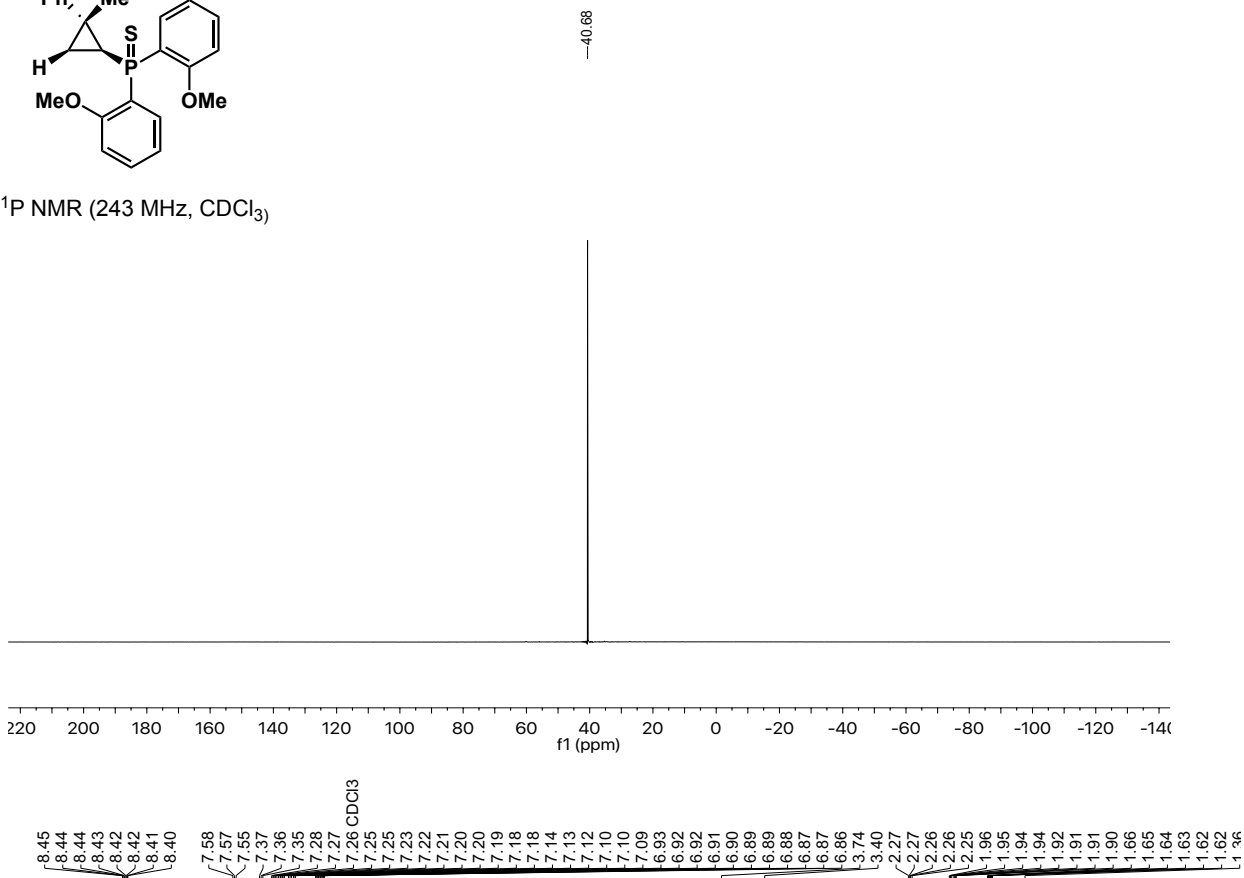




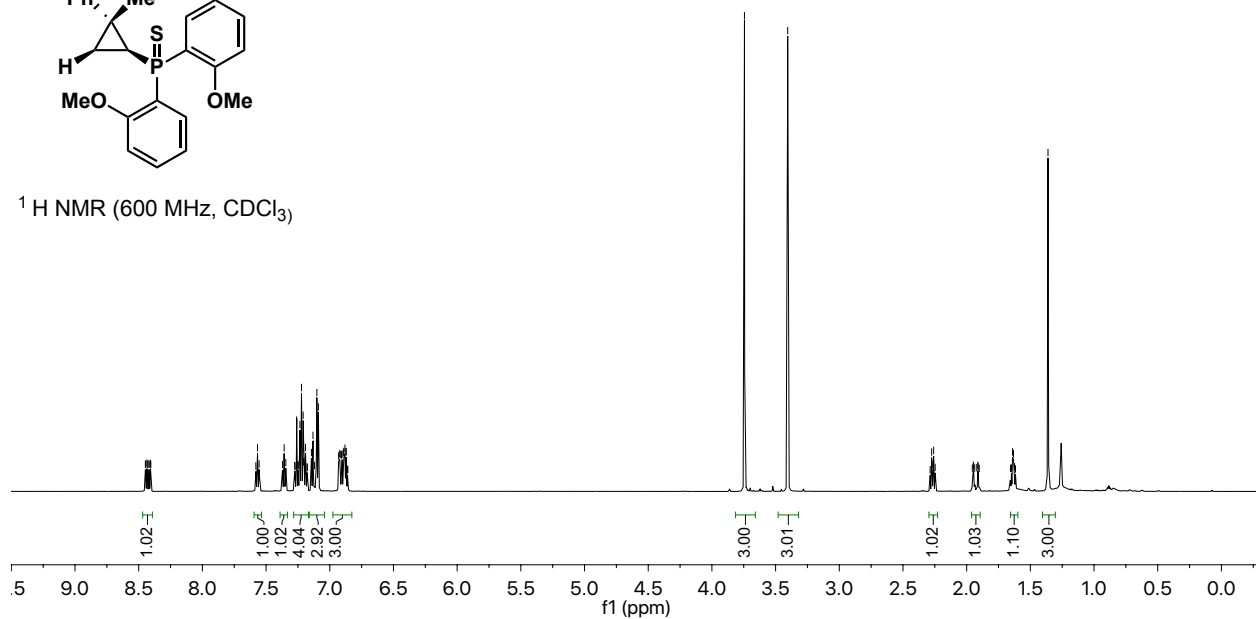
Bis(2-methoxyphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ag)

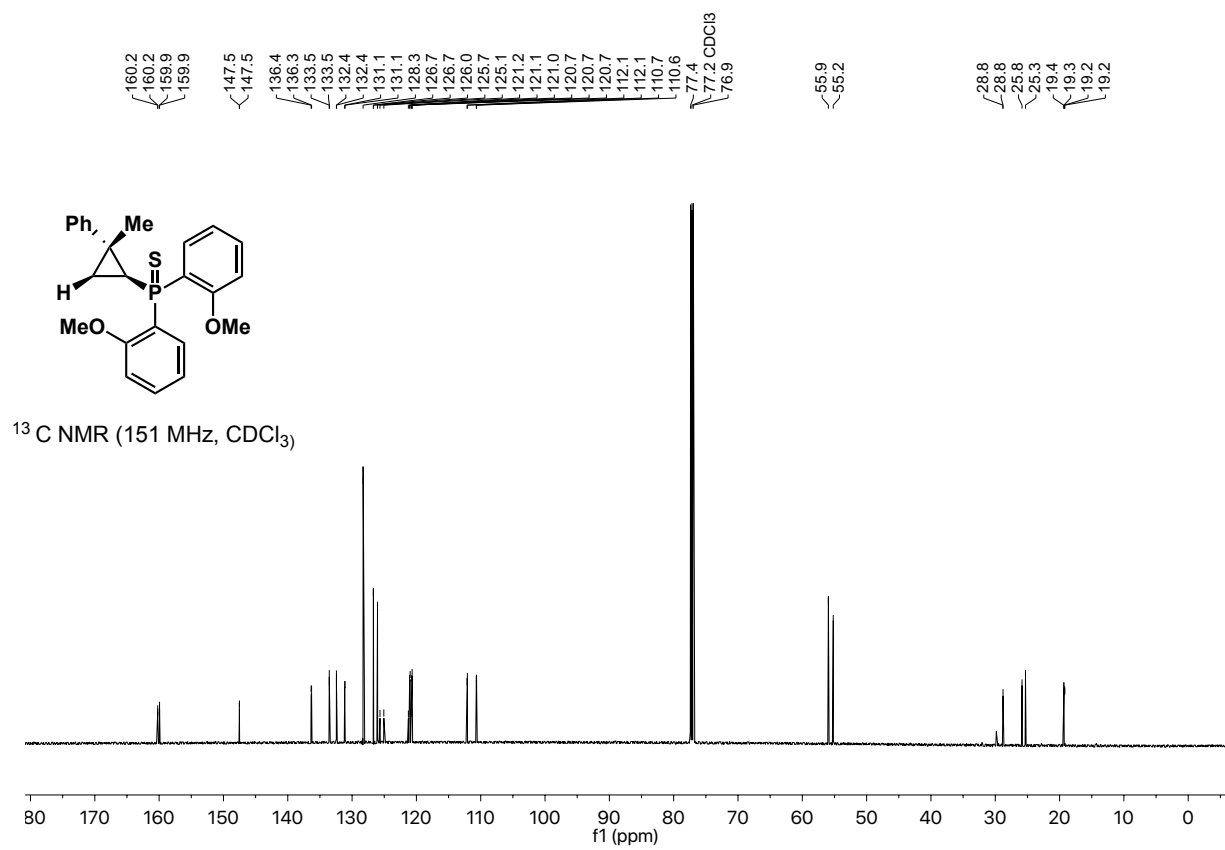


^{31}P NMR (243 MHz, CDCl_3)

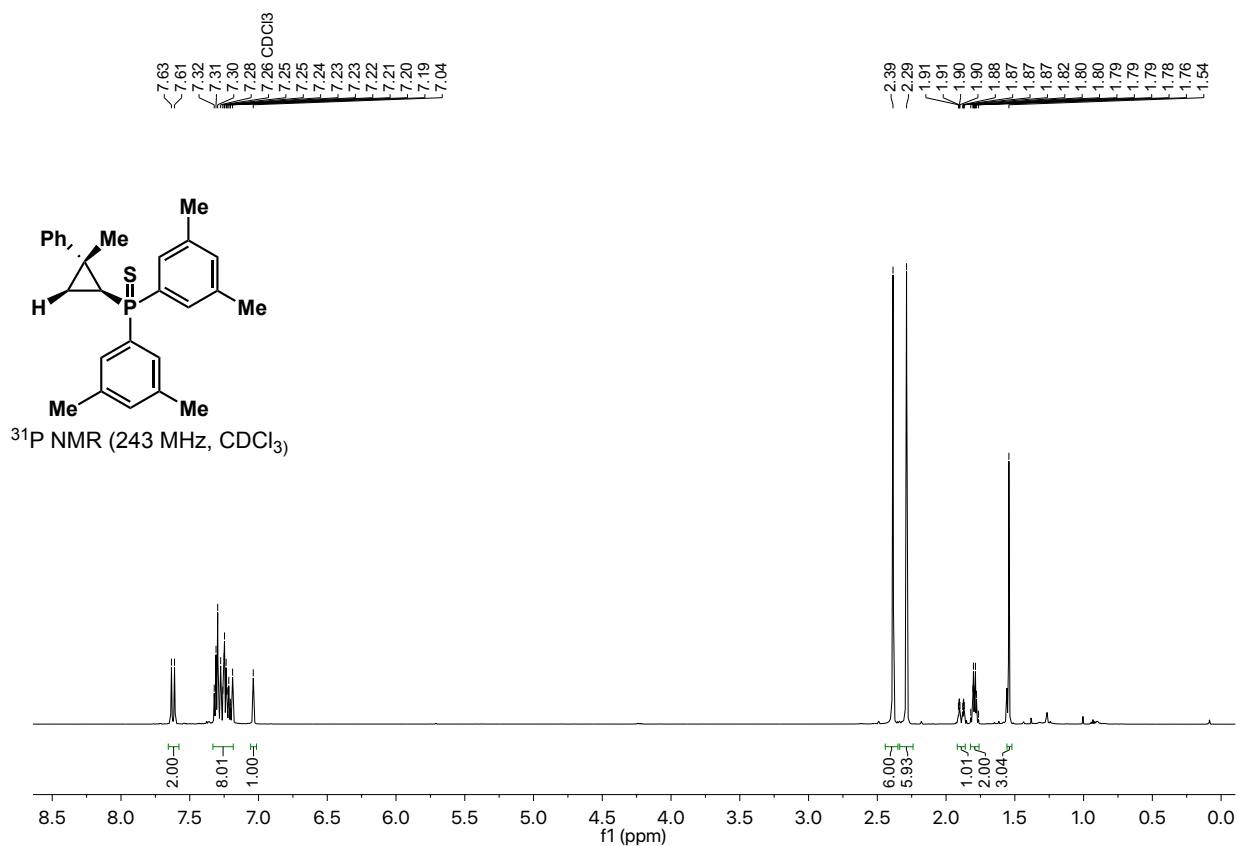
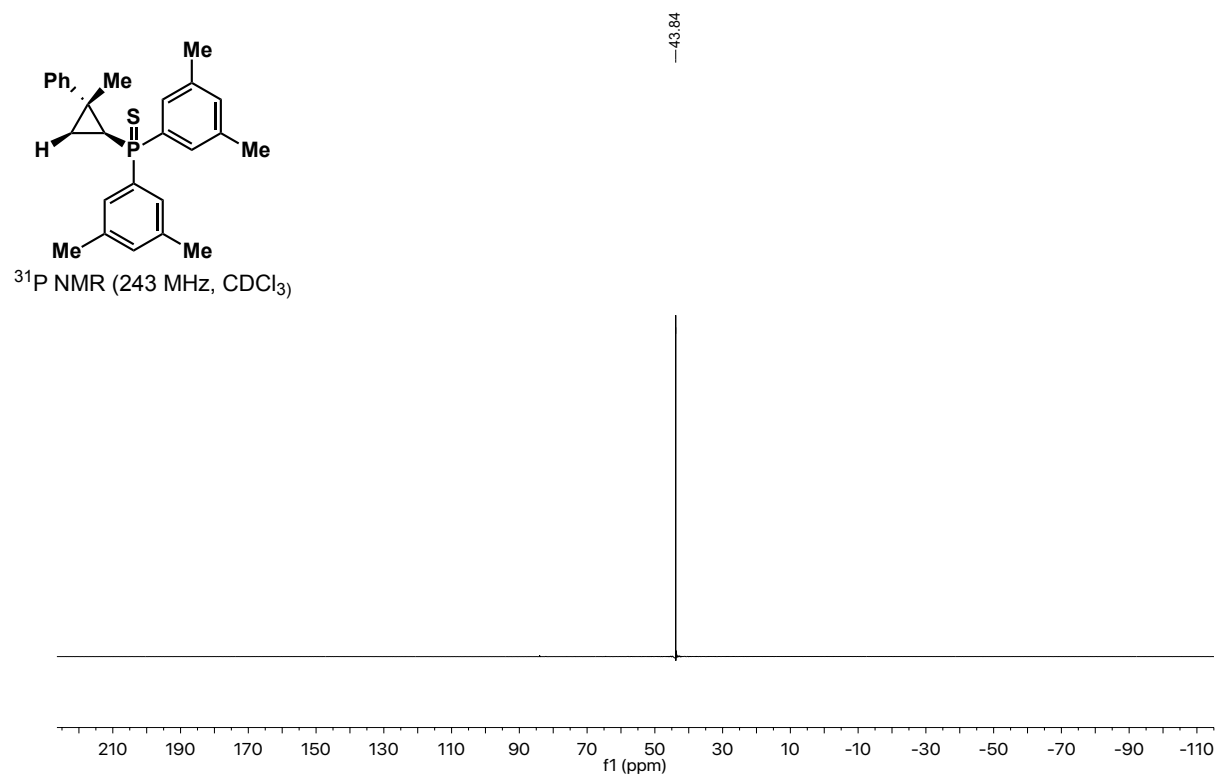


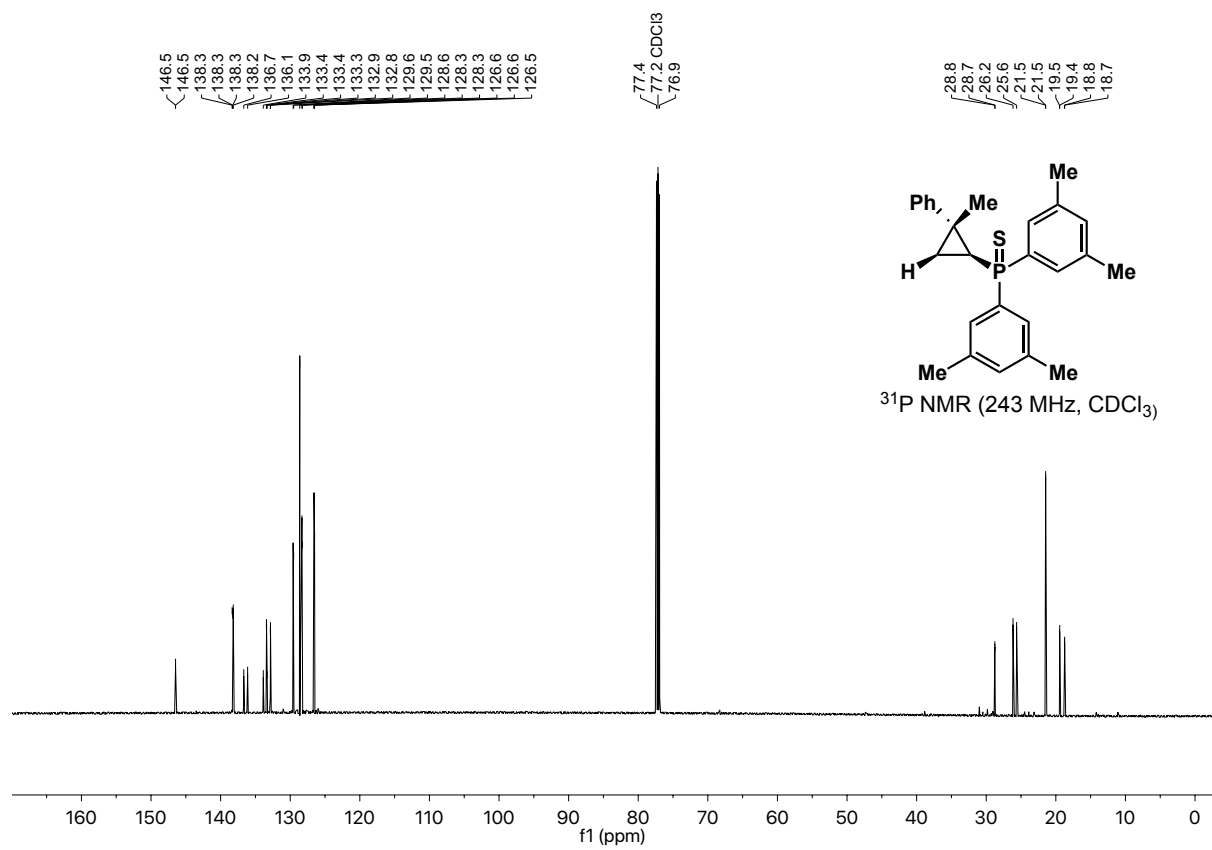
^1H NMR (600 MHz, CDCl_3)



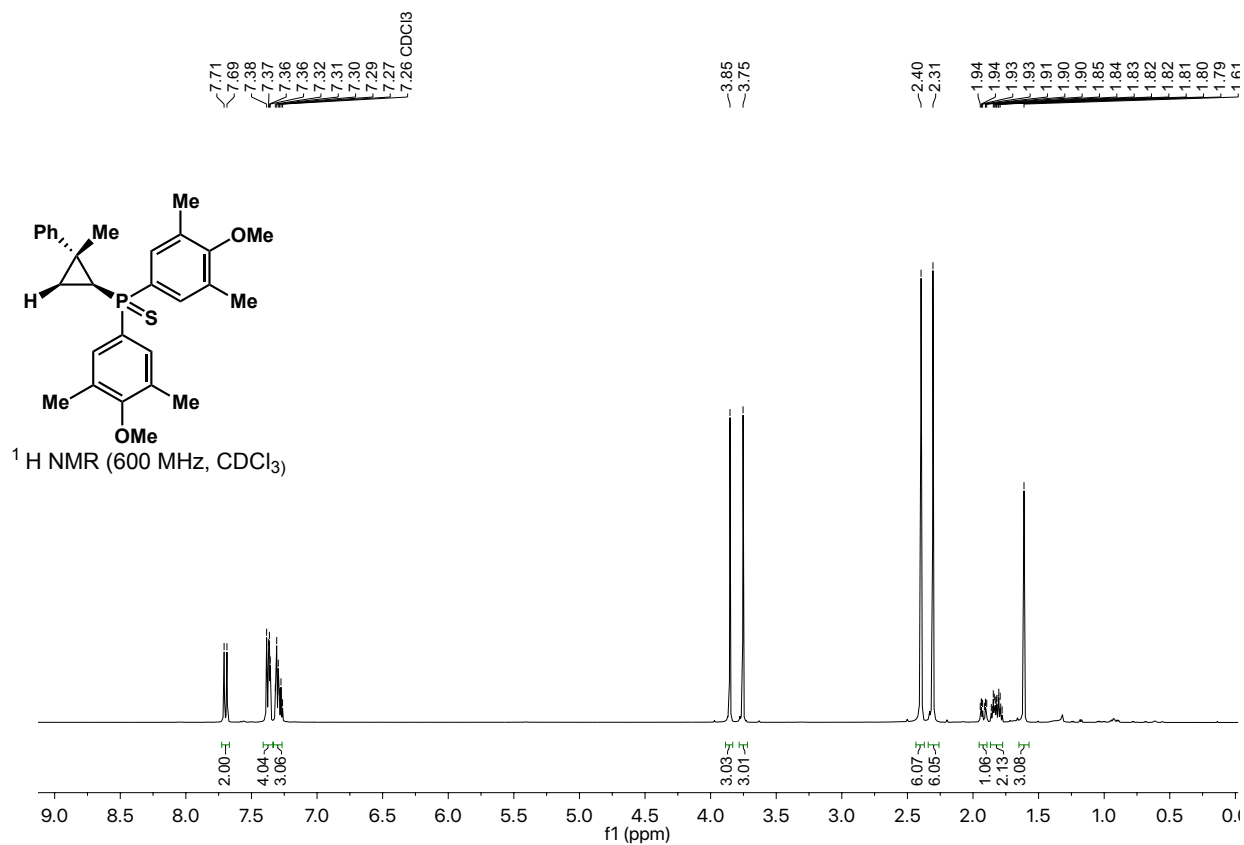
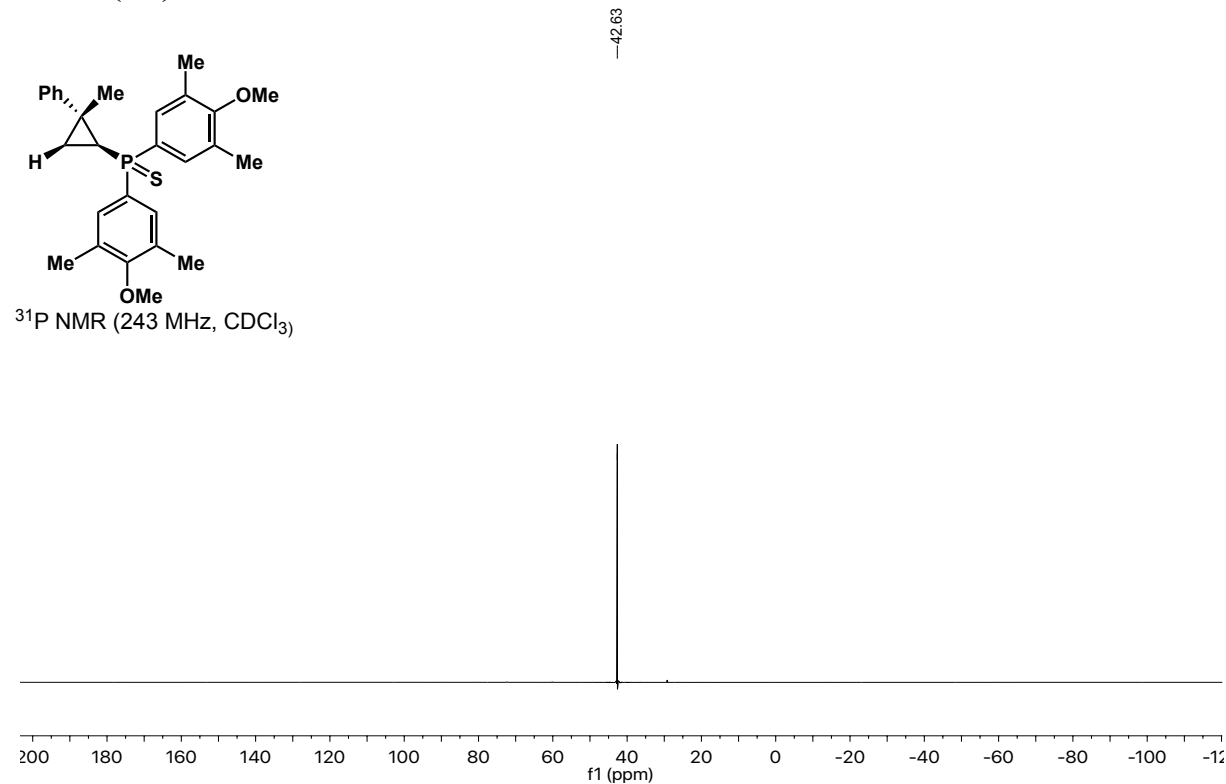


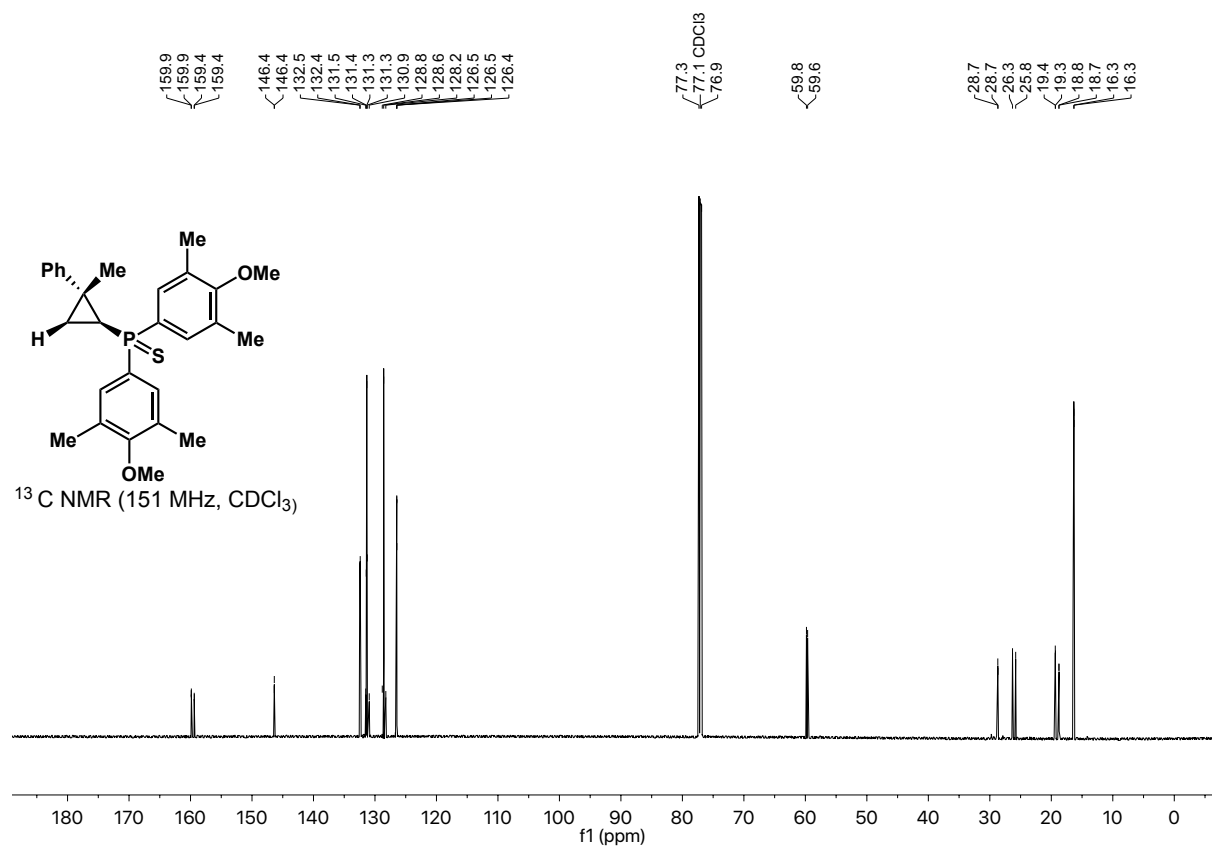
Bis(3,5-dimethylphenyl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ah)



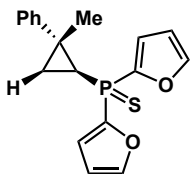


Bis(4-methoxy-3,5-dimethylphenyl)((1*S*,2*R*)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3ai)

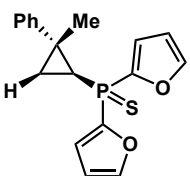
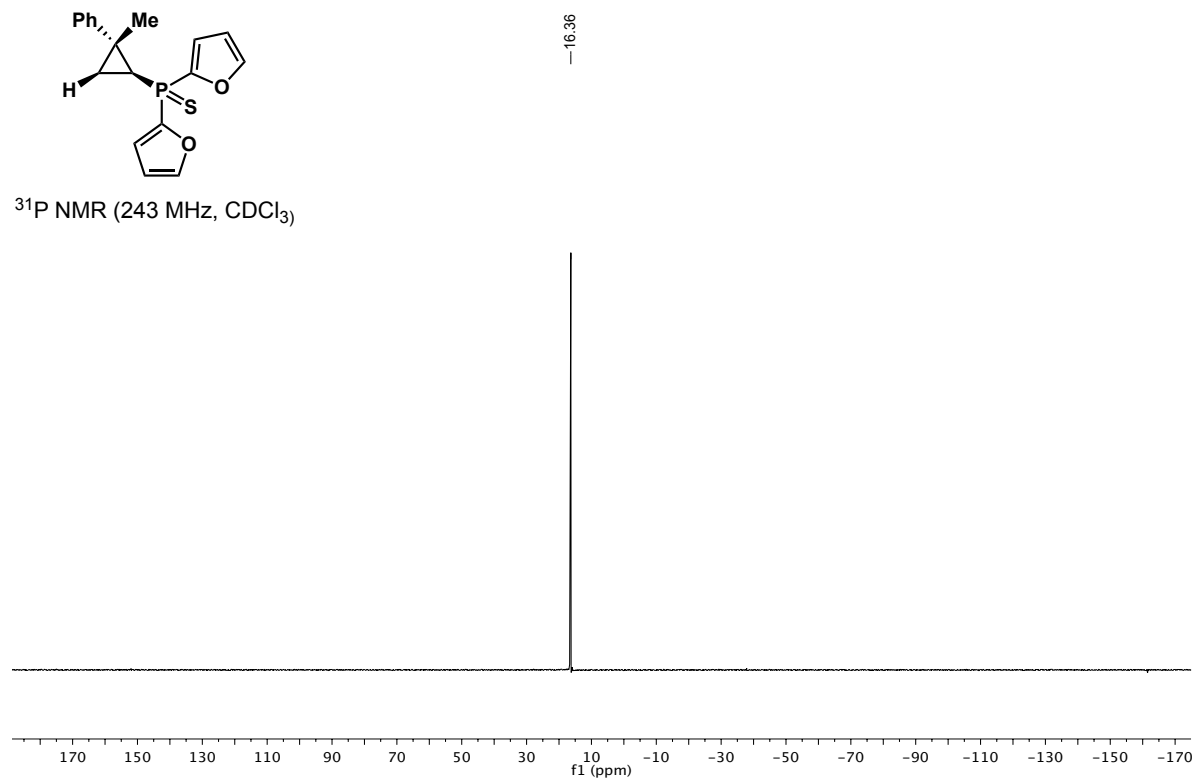




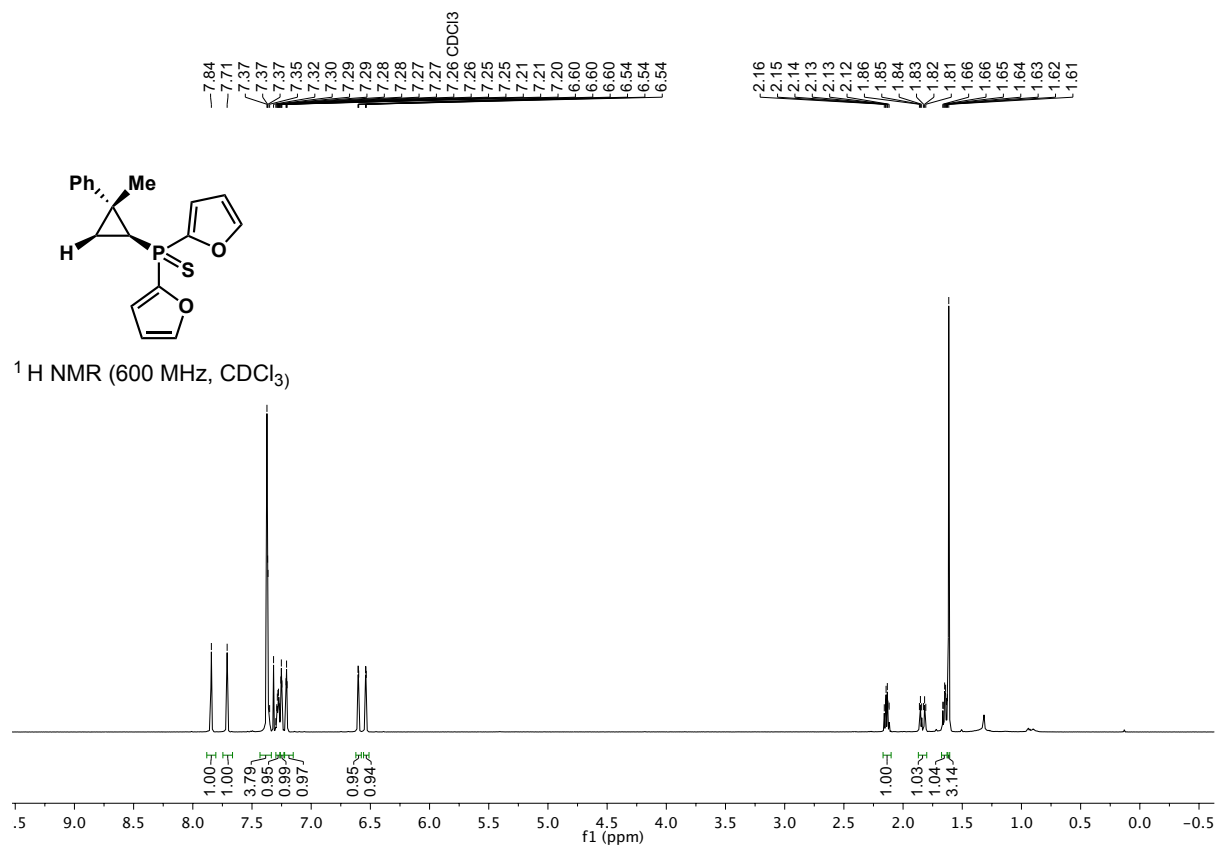
di(furan-2-yl)((1S,2R)-2-methyl-2-phenylcyclopropyl)phosphine sulfide (3aj)

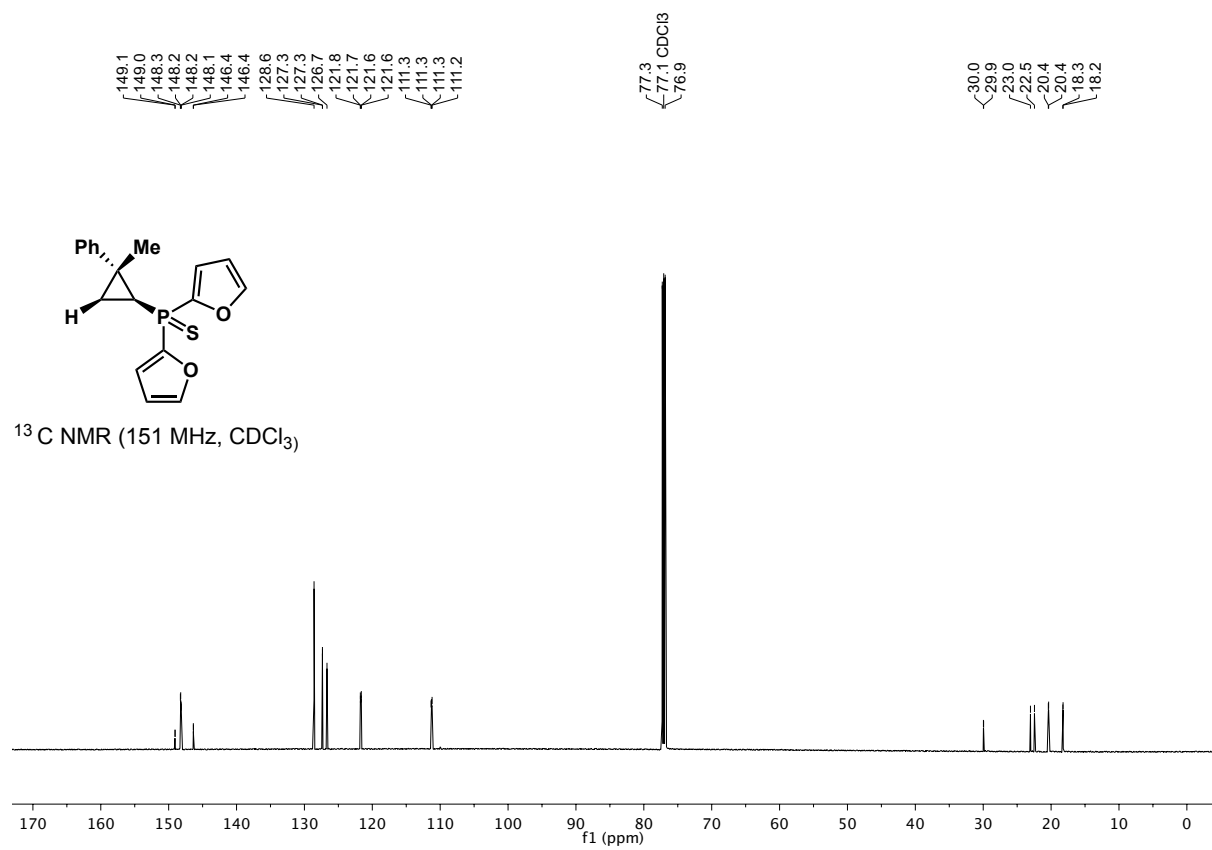


^{31}P NMR (243 MHz, CDCl_3)



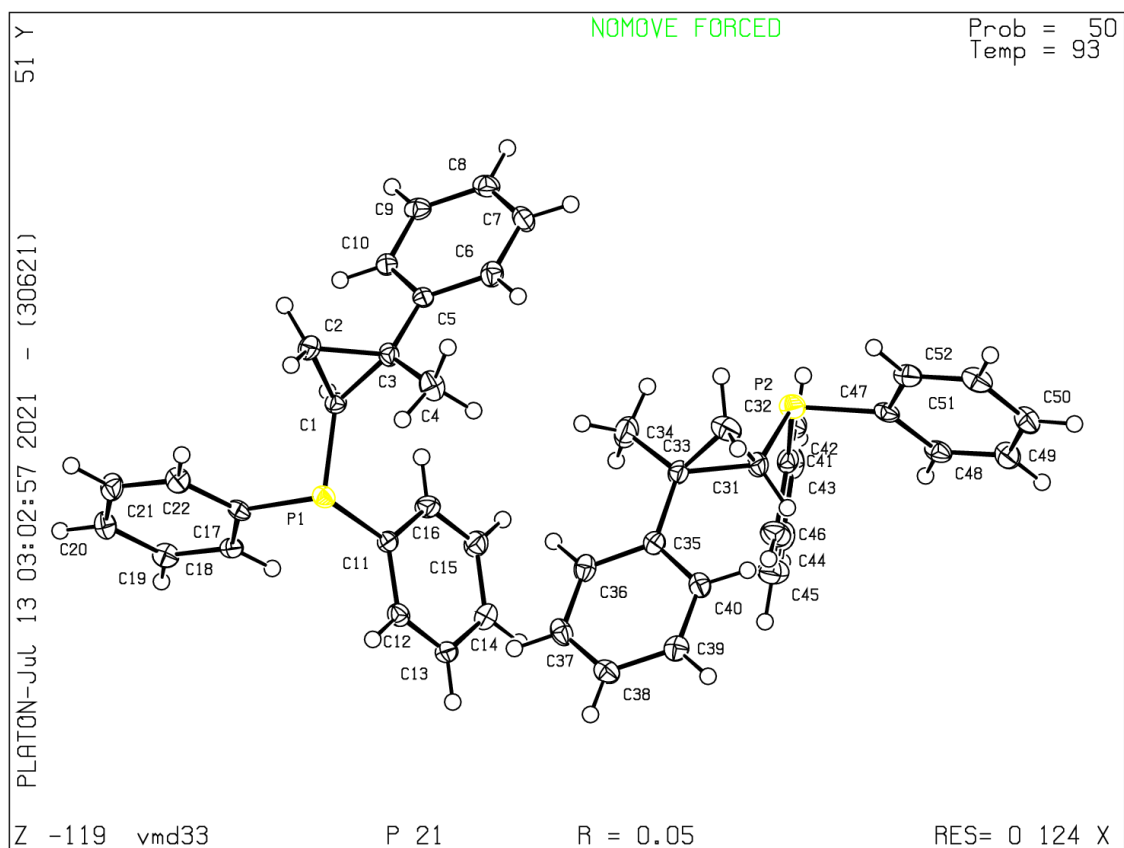
^1H NMR (600 MHz, CDCl_3)

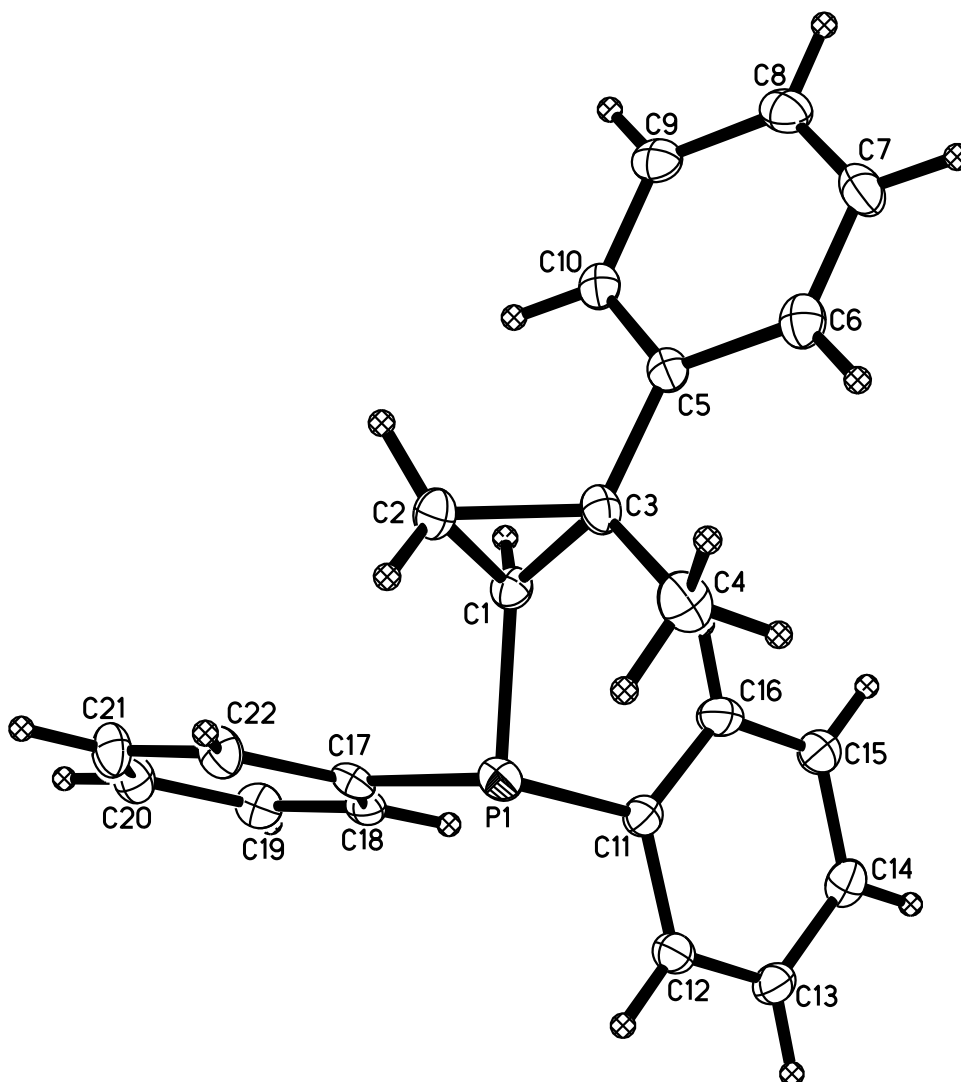




9. X-ray Crystallography Data

X-ray Data Collection, Structure Solution and Refinement for 3aa





Experimental Summary

X-ray Data Collection, Structure Solution and Refinement for 3aa.

A colorless crystal of approximate dimensions 0.220 x 0.257 x 0.308 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the

monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that space group $P2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present ($Z = 4$).

Least-squares analysis yielded $wR2 = 0.1278$ and $Goof = 1.077$ for 417 variables refined against 8588 data ($0.74 \text{ \AA}$), $R1 = 0.0472$ for those 7374 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack⁶ parameter.

Table 1. Crystal data and structure refinement for vmd33.

Identification code	vmd33
Empirical formula	C ₂₂ H ₂₁ P
Formula weight	316.36
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 9.8115(9) \text{ \AA}$ $\angle = 90^\circ$. $b = 9.7532(9) \text{ \AA}$ $\angle = 104.1492(18)^\circ$. $c = 18.8582(18) \text{ \AA}$ $\angle = 90^\circ$.
Volume	1749.9(3) Å ³
Z	4
Density (calculated)	1.201 Mg/m ³
Absorption coefficient	0.155 mm ⁻¹
F(000)	672
Crystal color	colorless
Crystal size	0.308 x 0.257 x 0.220 mm ³
Theta range for data collection	2.141 to 28.700°
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 12$, $-25 \leq l \leq 24$
Reflections collected	26276
Independent reflections	8588 [$R(\text{int}) = 0.0406$]

Completeness to theta = 25.242° 99.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.8017 and 0.7527

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 8588 / 1 / 417

Goodness-of-fit on F2 1.077

Final R indices [I>2sigma(I) = 7374 data] R1 = 0.0472, wR2 = 0.1232

R indices (all data, 0.74 Å) R1 = 0.0557, wR2 = 0.1278

Absolute structure parameter 0.08(5)

Largest diff. peak and hole 1.221 and -0.284 e.Å⁻³

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å² x 103)

for vmd33. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	12138(1)	5570(1)	9661(1)	18(1)
C(1)	12692(3)	7340(3)	9611(2)	16(1)
C(2)	14235(3)	7616(3)	9669(2)	22(1)
C(3)	13165(3)	7919(3)	8955(2)	18(1)
C(4)	13202(4)	6967(3)	8328(2)	25(1)
C(5)	12819(3)	9400(3)	8775(2)	16(1)
C(6)	12554(3)	9862(3)	8055(2)	21(1)
C(7)	12288(3)	11244(3)	7882(2)	24(1)
C(8)	12291(3)	12188(3)	8429(2)	23(1)
C(9)	12541(3)	11742(3)	9149(2)	21(1)
C(10)	12796(3)	10357(3)	9318(2)	17(1)

C(11)	10241(3)	5651(3)	9262(2)	16(1)
C(12)	9502(3)	4408(3)	9132(2)	19(1)
C(13)	8068(3)	4391(4)	8825(2)	21(1)
C(14)	7341(3)	5615(4)	8629(2)	23(1)
C(15)	8065(3)	6851(3)	8747(2)	24(1)
C(16)	9499(3)	6868(3)	9059(2)	22(1)
C(17)	12247(3)	5525(3)	10645(2)	16(1)
C(18)	11077(3)	5533(3)	10952(2)	17(1)
C(19)	11257(3)	5497(3)	11700(2)	20(1)
C(20)	12596(3)	5469(4)	12166(2)	23(1)
C(21)	13765(3)	5479(4)	11871(2)	23(1)
C(22)	13592(3)	5492(4)	11119(2)	22(1)
P(2)	7340(1)	9337(1)	5390(1)	23(1)
C(31)	8023(3)	7587(3)	5480(2)	20(1)
C(32)	9572(3)	7417(4)	5549(2)	27(1)
C(33)	8965(3)	7032(3)	6190(2)	20(1)
C(34)	9288(4)	7968(4)	6853(2)	35(1)
C(35)	8864(3)	5521(3)	6327(2)	18(1)
C(36)	9156(3)	4997(3)	7042(2)	21(1)
C(37)	9136(3)	3581(3)	7167(2)	22(1)
C(38)	8825(3)	2680(3)	6587(2)	21(1)
C(39)	8496(3)	3186(3)	5875(2)	21(1)
C(40)	8514(3)	4584(3)	5747(2)	19(1)
C(41)	5759(3)	9245(3)	5728(2)	20(1)
C(42)	5161(3)	10496(3)	5880(2)	22(1)
C(43)	3966(4)	10521(4)	6133(2)	26(1)
C(44)	3315(4)	9295(4)	6247(2)	26(1)
C(45)	3895(4)	8055(4)	6117(2)	30(1)

C(46)	5114(4)	8029(4)	5860(2)	28(1)
C(47)	6639(3)	9324(3)	4394(2)	19(1)
C(48)	5221(3)	9234(3)	4036(2)	22(1)
C(49)	4801(3)	9163(4)	3280(2)	26(1)
C(50)	5795(3)	9176(3)	2863(2)	25(1)
C(51)	7202(3)	9295(4)	3211(2)	25(1)
C(52)	7626(3)	9373(3)	3966(2)	23(1)

Table 3. Bond lengths [Å] and angles [°] for vmd33.

P(1)-C(1)	1.819(3)
P(1)-C(11)	1.831(3)
P(1)-C(17)	1.832(3)
C(1)-C(2)	1.515(4)
C(1)-C(3)	1.533(4)
C(2)-C(3)	1.521(4)
C(3)-C(5)	1.503(4)
C(3)-C(4)	1.510(4)
C(5)-C(10)	1.390(4)
C(5)-C(6)	1.394(4)
C(6)-C(7)	1.396(4)
C(7)-C(8)	1.383(5)
C(8)-C(9)	1.389(5)
C(9)-C(10)	1.396(4)
C(11)-C(16)	1.396(4)
C(11)-C(12)	1.403(4)
C(12)-C(13)	1.384(4)
C(13)-C(14)	1.394(5)

C(14)-C(15)	1.389(5)
C(15)-C(16)	1.386(4)
C(17)-C(22)	1.402(4)
C(17)-C(18)	1.407(4)
C(18)-C(19)	1.377(4)
C(19)-C(20)	1.392(4)
C(20)-C(21)	1.393(4)
C(21)-C(22)	1.386(4)
P(2)-C(41)	1.818(3)
P(2)-C(31)	1.826(3)
P(2)-C(47)	1.834(3)
C(31)-C(32)	1.503(5)
C(31)-C(33)	1.528(4)
C(32)-C(33)	1.519(5)
C(33)-C(35)	1.503(4)
C(33)-C(34)	1.518(5)
C(35)-C(40)	1.402(4)
C(35)-C(36)	1.404(4)
C(36)-C(37)	1.402(4)
C(37)-C(38)	1.378(5)
C(38)-C(39)	1.393(5)
C(39)-C(40)	1.385(4)
C(41)-C(46)	1.396(5)
C(41)-C(42)	1.414(4)
C(42)-C(43)	1.370(5)
C(43)-C(44)	1.396(5)
C(44)-C(45)	1.385(5)
C(45)-C(46)	1.396(5)

C(47)-C(48) 1.392(4)
 C(47)-C(52) 1.406(4)
 C(48)-C(49) 1.386(5)
 C(49)-C(50) 1.394(4)
 C(50)-C(51) 1.381(4)
 C(51)-C(52) 1.385(5)

C(1)-P(1)-C(11) 102.96(14)
 C(1)-P(1)-C(17) 97.55(14)
 C(11)-P(1)-C(17) 102.70(13)
 C(2)-C(1)-C(3) 59.86(19)
 C(2)-C(1)-P(1) 118.1(2)
 C(3)-C(1)-P(1) 123.1(2)
 C(1)-C(2)-C(3) 60.64(19)
 C(5)-C(3)-C(4) 117.5(3)
 C(5)-C(3)-C(2) 117.1(3)
 C(4)-C(3)-C(2) 115.5(3)
 C(5)-C(3)-C(1) 116.1(3)
 C(4)-C(3)-C(1) 118.3(3)
 C(2)-C(3)-C(1) 59.5(2)
 C(10)-C(5)-C(6) 117.9(3)
 C(10)-C(5)-C(3) 121.5(3)
 C(6)-C(5)-C(3) 120.6(3)
 C(5)-C(6)-C(7) 121.3(3)
 C(8)-C(7)-C(6) 120.1(3)
 C(7)-C(8)-C(9) 119.3(3)
 C(8)-C(9)-C(10) 120.3(3)
 C(5)-C(10)-C(9) 121.1(3)

C(16)-C(11)-C(12)	118.3(3)
C(16)-C(11)-P(1)	124.0(2)
C(12)-C(11)-P(1)	117.7(2)
C(13)-C(12)-C(11)	120.8(3)
C(12)-C(13)-C(14)	120.2(3)
C(15)-C(14)-C(13)	119.5(3)
C(16)-C(15)-C(14)	120.3(3)
C(15)-C(16)-C(11)	120.9(3)
C(22)-C(17)-C(18)	118.2(3)
C(22)-C(17)-P(1)	117.4(2)
C(18)-C(17)-P(1)	124.4(2)
C(19)-C(18)-C(17)	120.6(3)
C(18)-C(19)-C(20)	120.8(3)
C(19)-C(20)-C(21)	119.3(3)
C(22)-C(21)-C(20)	120.2(3)
C(21)-C(22)-C(17)	120.9(3)
C(41)-P(2)-C(31)	104.25(15)
C(41)-P(2)-C(47)	102.69(13)
C(31)-P(2)-C(47)	97.29(14)
C(32)-C(31)-C(33)	60.2(2)
C(32)-C(31)-P(2)	116.8(2)
C(33)-C(31)-P(2)	122.9(2)
C(31)-C(32)-C(33)	60.7(2)
C(35)-C(33)-C(34)	117.2(3)
C(35)-C(33)-C(32)	115.7(3)
C(34)-C(33)-C(32)	117.6(3)
C(35)-C(33)-C(31)	116.6(3)
C(34)-C(33)-C(31)	117.9(3)

C(32)-C(33)-C(31)	59.1(2)
C(40)-C(35)-C(36)	117.7(3)
C(40)-C(35)-C(33)	121.2(3)
C(36)-C(35)-C(33)	121.0(3)
C(37)-C(36)-C(35)	120.8(3)
C(38)-C(37)-C(36)	120.2(3)
C(37)-C(38)-C(39)	119.6(3)
C(40)-C(39)-C(38)	120.4(3)
C(39)-C(40)-C(35)	121.2(3)
C(46)-C(41)-C(42)	117.9(3)
C(46)-C(41)-P(2)	124.6(2)
C(42)-C(41)-P(2)	117.5(2)
C(43)-C(42)-C(41)	121.3(3)
C(42)-C(43)-C(44)	120.1(3)
C(45)-C(44)-C(43)	119.8(3)
C(44)-C(45)-C(46)	120.1(3)
C(41)-C(46)-C(45)	120.8(3)
C(48)-C(47)-C(52)	118.1(3)
C(48)-C(47)-P(2)	125.3(2)
C(52)-C(47)-P(2)	116.7(2)
C(49)-C(48)-C(47)	120.9(3)
C(48)-C(49)-C(50)	120.4(3)
C(51)-C(50)-C(49)	119.3(3)
C(50)-C(51)-C(52)	120.5(3)
C(51)-C(52)-C(47)	120.9(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vmd33. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
P(1)	17(1)	17(1)	20(1)	3(1)	5(1)	1(1)
C(1)	16(2)	18(1)	16(2)	0(1)	4(1)	-1(1)
C(2)	15(2)	24(2)	24(2)	3(1)	-2(1)	-1(1)
C(3)	14(1)	22(2)	16(2)	3(1)	3(1)	1(1)
C(4)	31(2)	26(2)	20(2)	0(1)	11(2)	7(1)
C(5)	9(1)	21(1)	18(1)	4(1)	4(1)	-2(1)
C(6)	17(2)	27(2)	19(2)	1(1)	4(1)	0(1)
C(7)	21(2)	27(2)	22(2)	10(1)	4(1)	0(1)
C(8)	18(2)	20(2)	30(2)	4(1)	6(1)	-2(1)
C(9)	15(2)	20(2)	28(2)	0(1)	6(1)	-2(1)
C(10)	11(1)	23(2)	17(2)	2(1)	5(1)	-2(1)
C(11)	17(1)	18(1)	15(1)	0(1)	4(1)	-2(1)
C(12)	23(2)	16(1)	18(2)	1(1)	5(1)	1(1)
C(13)	26(2)	21(2)	17(2)	-1(1)	4(1)	-7(1)
C(14)	21(2)	26(2)	20(2)	-2(2)	1(1)	-1(1)
C(15)	25(2)	20(2)	25(2)	0(1)	-1(1)	2(1)
C(16)	23(2)	15(2)	26(2)	0(1)	3(1)	0(1)
C(17)	19(1)	11(1)	20(2)	4(1)	6(1)	3(1)
C(18)	13(1)	14(1)	24(2)	2(1)	3(1)	1(1)
C(19)	16(1)	22(1)	25(2)	0(2)	10(1)	2(1)
C(20)	26(2)	25(2)	17(2)	2(1)	5(1)	3(1)
C(21)	14(1)	31(2)	23(2)	4(2)	1(1)	3(1)
C(22)	15(1)	26(2)	25(2)	4(2)	6(1)	3(1)
P(2)	20(1)	18(1)	30(1)	4(1)	3(1)	2(1)
C(31)	18(2)	18(2)	20(2)	3(1)	-1(1)	4(1)

C(32)	24(2)	23(2)	37(2)	8(2)	10(2)	2(1)
C(33)	18(2)	20(2)	19(2)	0(1)	-1(1)	0(1)
C(34)	45(2)	26(2)	26(2)	-3(2)	-8(2)	0(2)
C(35)	11(1)	20(1)	21(2)	2(1)	3(1)	3(1)
C(36)	17(2)	28(2)	18(2)	-1(1)	3(1)	2(1)
C(37)	17(2)	30(2)	21(2)	8(1)	7(1)	4(1)
C(38)	18(2)	22(2)	26(2)	5(1)	8(1)	2(1)
C(39)	15(2)	25(2)	23(2)	0(1)	6(1)	2(1)
C(40)	15(1)	25(2)	19(2)	4(1)	5(1)	2(1)
C(41)	24(2)	17(1)	17(2)	-2(1)	1(1)	1(1)
C(42)	29(2)	14(1)	19(2)	0(1)	-2(1)	2(1)
C(43)	33(2)	26(2)	17(2)	-1(2)	0(1)	8(2)
C(44)	29(2)	35(2)	16(2)	-3(2)	6(1)	-3(2)
C(45)	38(2)	26(2)	29(2)	-4(2)	15(2)	-8(2)
C(46)	38(2)	20(2)	29(2)	-2(1)	13(2)	-2(1)
C(47)	17(1)	13(1)	28(2)	6(1)	6(1)	1(1)
C(48)	16(1)	20(1)	32(2)	8(2)	8(1)	1(1)
C(49)	15(2)	31(2)	32(2)	11(2)	3(1)	2(1)
C(50)	25(2)	25(2)	26(2)	7(2)	7(1)	4(1)
C(51)	20(2)	23(2)	35(2)	6(2)	15(1)	4(1)
C(52)	16(2)	18(1)	35(2)	5(2)	6(1)	2(1)

Table 5. Hydrogen coordinates (x 104) and isotropic displacement parameters ($\text{\AA}^2$ x 103) for vmd33.

x	y	z	U(eq)
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H(1A)	12221	8016	9871	20
H(2A)	14861	6815	9682	27
H(2B)	14672	8405	9970	27
H(4A)	13859	7325	8057	38
H(4B)	12261	6902	8001	38
H(4C)	13512	6055	8521	38
H(6A)	12554	9225	7674	25
H(7A)	12104	11536	7387	28
H(8A)	12125	13131	8314	27
H(9A)	12538	12382	9528	25
H(10A)		12956	10064	9812 20
H(12A)		9992	3567	9255 23
H(13A)		7578	3542	8749 26
H(14A)		6358	5604	8415 27
H(15A)		7574	7688	8614 29
H(16A)		9983	7719	9135 26
H(18A)		10156	5562	10642 21
H(19A)		10456	5492	11899 24
H(20A)		12711	5443	12681 27
H(21A)		14683	5476	12185 28
H(22A)		14396	5479	10923 26
H(31A)		7410	6891	5166 24
H(32A)		10153	8257	5595 33
H(32B)		9876	6663	5271 33
H(34A)		10180	7693	7184 53
H(34B)		8533	7901	7108 53
H(34C)		9361	8917	6694 53

H(36A)	9369	5609	7445	25
H(37A)	9337	3242	7654	26
H(38A)	8836	1720	6673	26
H(39A)	8257	2569	5474	25
H(40A)	8284	4913	5258	23
H(42A)	5596	11336	5806	27
H(43A)	3579	11373	6231	31
H(44A)	2476	9313	6414	32
H(45A)	3463	7220	6203	36
H(46A)	5508	7173	5774	34
H(48A)	4533	9222	4314	27
H(49A)	3829	9105	3044	32
H(50A)	5507	9104	2346	30
H(51A)	7884	9324	2930	30
H(52A)	8597	9460	4198	27

Table 6. Torsion angles [°] for vmd33.

C(11)-P(1)-C(1)-C(2) -161.2(2)
 C(17)-P(1)-C(1)-C(2) 93.9(2)
 C(11)-P(1)-C(1)-C(3) -90.5(2)
 C(17)-P(1)-C(1)-C(3) 164.5(2)
 P(1)-C(1)-C(2)-C(3) 113.9(3)
 C(1)-C(2)-C(3)-C(5) 105.8(3)
 C(1)-C(2)-C(3)-C(4) -109.3(3)
 C(2)-C(1)-C(3)-C(5) -107.5(3)
 P(1)-C(1)-C(3)-C(5) 146.7(2)
 C(2)-C(1)-C(3)-C(4) 104.4(3)

P(1)-C(1)-C(3)-C(4) -1.3(4)
 P(1)-C(1)-C(3)-C(2) -105.8(3)
 C(4)-C(3)-C(5)-C(10) -178.4(3)
 C(2)-C(3)-C(5)-C(10) -34.1(4)
 C(1)-C(3)-C(5)-C(10) 33.3(4)
 C(4)-C(3)-C(5)-C(6) -0.4(4)
 C(2)-C(3)-C(5)-C(6) 143.8(3)
 C(1)-C(3)-C(5)-C(6) -148.8(3)
 C(10)-C(5)-C(6)-C(7) 0.7(4)
 C(3)-C(5)-C(6)-C(7) -177.3(3)
 C(5)-C(6)-C(7)-C(8) 0.4(5)
 C(6)-C(7)-C(8)-C(9) -1.0(5)
 C(7)-C(8)-C(9)-C(10) 0.5(5)
 C(6)-C(5)-C(10)-C(9) -1.2(4)
 C(3)-C(5)-C(10)-C(9) 176.8(3)
 C(8)-C(9)-C(10)-C(5) 0.6(5)
 C(1)-P(1)-C(11)-C(16) -5.8(3)
 C(17)-P(1)-C(11)-C(16) 95.2(3)
 C(1)-P(1)-C(11)-C(12) 172.1(2)
 C(17)-P(1)-C(11)-C(12) -87.0(2)
 C(16)-C(11)-C(12)-C(13) -1.5(4)
 P(1)-C(11)-C(12)-C(13) -179.5(2)
 C(11)-C(12)-C(13)-C(14) 1.2(4)
 C(12)-C(13)-C(14)-C(15) -0.5(4)
 C(13)-C(14)-C(15)-C(16) 0.0(5)
 C(14)-C(15)-C(16)-C(11) -0.3(5)
 C(12)-C(11)-C(16)-C(15) 1.0(5)
 P(1)-C(11)-C(16)-C(15) 178.9(2)

C(1)-P(1)-C(17)-C(22)	-73.4(3)
C(11)-P(1)-C(17)-C(22)	-178.5(3)
C(1)-P(1)-C(17)-C(18)	106.1(3)
C(11)-P(1)-C(17)-C(18)	0.9(3)
C(22)-C(17)-C(18)-C(19)	-0.5(5)
P(1)-C(17)-C(18)-C(19)	-180.0(3)
C(17)-C(18)-C(19)-C(20)	0.7(5)
C(18)-C(19)-C(20)-C(21)	0.1(5)
C(19)-C(20)-C(21)-C(22)	-1.1(5)
C(20)-C(21)-C(22)-C(17)	1.3(5)
C(18)-C(17)-C(22)-C(21)	-0.5(5)
P(1)-C(17)-C(22)-C(21)	179.0(3)
C(41)-P(2)-C(31)-C(32)	-155.2(3)
C(47)-P(2)-C(31)-C(32)	99.7(3)
C(41)-P(2)-C(31)-C(33)	-84.9(3)
C(47)-P(2)-C(31)-C(33)	170.0(3)
P(2)-C(31)-C(32)-C(33)	114.3(3)
C(31)-C(32)-C(33)-C(35)	106.8(3)
C(31)-C(32)-C(33)-C(34)	-107.6(3)
C(32)-C(31)-C(33)-C(35)	-105.5(3)
P(2)-C(31)-C(33)-C(35)	150.1(2)
C(32)-C(31)-C(33)-C(34)	107.1(3)
P(2)-C(31)-C(33)-C(34)	2.6(4)
P(2)-C(31)-C(33)-C(32)	-104.4(3)
C(34)-C(33)-C(35)-C(40)	177.4(3)
C(32)-C(33)-C(35)-C(40)	-37.0(4)
C(31)-C(33)-C(35)-C(40)	29.7(4)
C(34)-C(33)-C(35)-C(36)	-4.4(4)

C(32)-C(33)-C(35)-C(36)	141.3(3)
C(31)-C(33)-C(35)-C(36)	-152.1(3)
C(40)-C(35)-C(36)-C(37)	1.9(5)
C(33)-C(35)-C(36)-C(37)	-176.5(3)
C(35)-C(36)-C(37)-C(38)	-0.1(5)
C(36)-C(37)-C(38)-C(39)	-1.6(5)
C(37)-C(38)-C(39)-C(40)	1.6(5)
C(38)-C(39)-C(40)-C(35)	0.2(5)
C(36)-C(35)-C(40)-C(39)	-1.9(4)
C(33)-C(35)-C(40)-C(39)	176.4(3)
C(31)-P(2)-C(41)-C(46)	-12.5(3)
C(47)-P(2)-C(41)-C(46)	88.5(3)
C(31)-P(2)-C(41)-C(42)	166.2(2)
C(47)-P(2)-C(41)-C(42)	-92.8(2)
C(46)-C(41)-C(42)-C(43)	-1.6(4)
P(2)-C(41)-C(42)-C(43)	179.6(2)
C(41)-C(42)-C(43)-C(44)	0.2(5)
C(42)-C(43)-C(44)-C(45)	1.2(5)
C(43)-C(44)-C(45)-C(46)	-1.2(5)
C(42)-C(41)-C(46)-C(45)	1.6(5)
P(2)-C(41)-C(46)-C(45)	-179.7(3)
C(44)-C(45)-C(46)-C(41)	-0.3(5)
C(41)-P(2)-C(47)-C(48)	-1.2(3)
C(31)-P(2)-C(47)-C(48)	105.3(3)
C(41)-P(2)-C(47)-C(52)	-179.4(2)
C(31)-P(2)-C(47)-C(52)	-72.9(3)
C(52)-C(47)-C(48)-C(49)	1.5(5)
P(2)-C(47)-C(48)-C(49)	-176.7(3)

C(47)-C(48)-C(49)-C(50)	0.2(5)
C(48)-C(49)-C(50)-C(51)	-1.6(5)
C(49)-C(50)-C(51)-C(52)	1.3(5)
C(50)-C(51)-C(52)-C(47)	0.4(5)
C(48)-C(47)-C(52)-C(51)	-1.8(5)
P(2)-C(47)-C(52)-C(51)	176.6(3)

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-

Definitions:

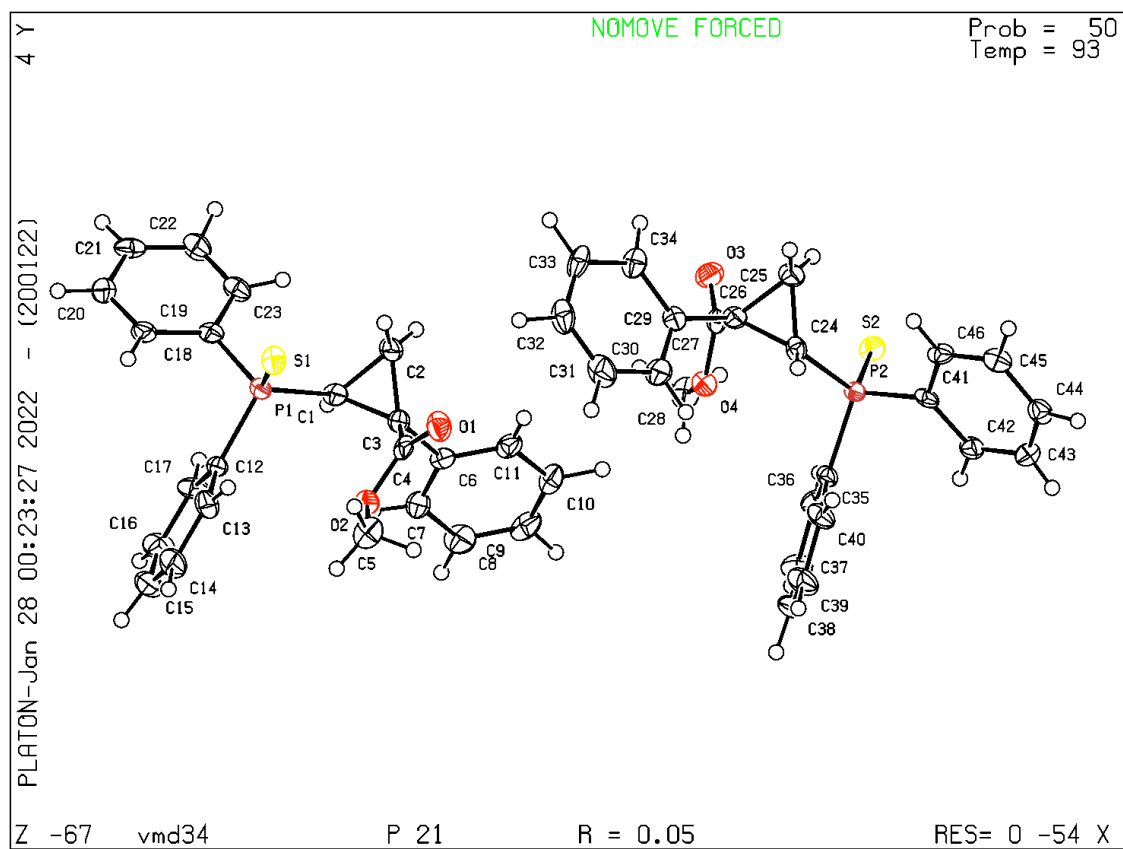
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

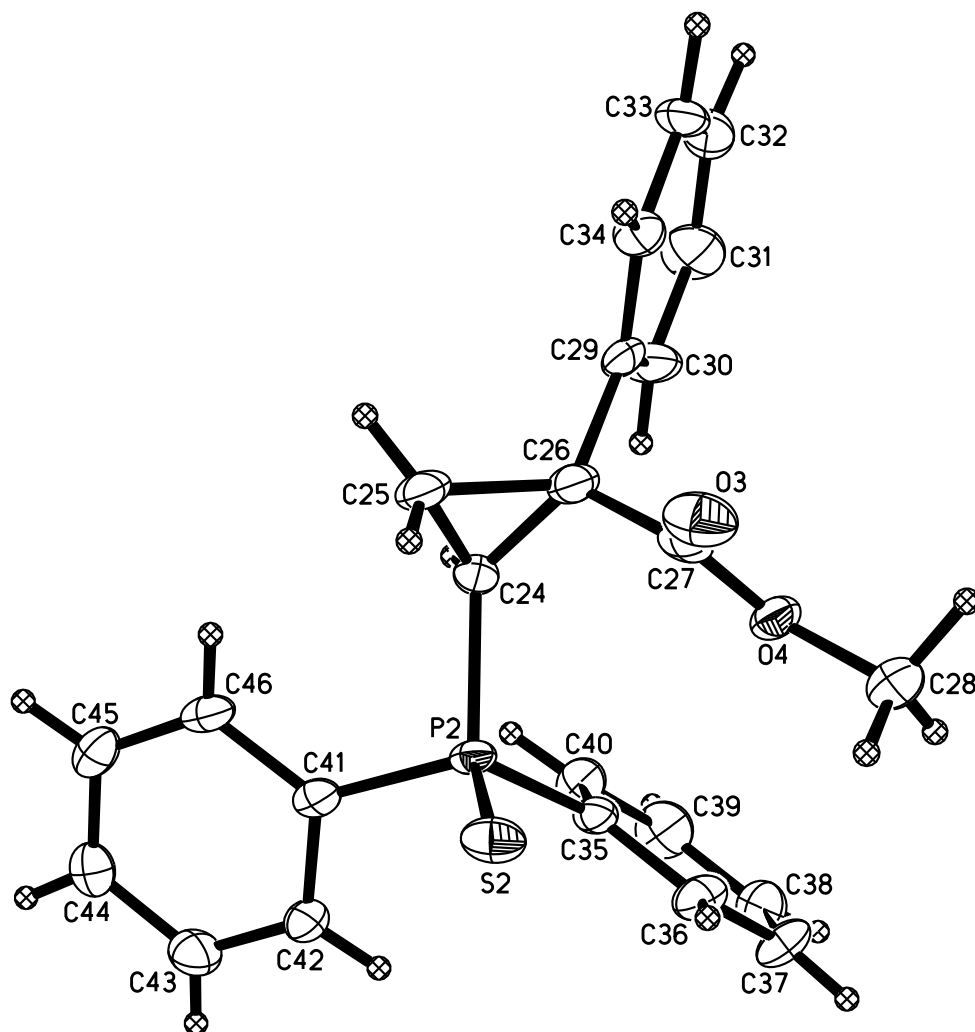
$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

X-ray Data Collection, Structure Solution and Refinement for 3la





A colorless crystal of approximate dimensions 0.268 x 0.295 x 0.426 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹ program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that space group $P2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis.

Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). There were two molecules of the formula-unit present ($Z = 4$).

Least-squares analysis yielded $wR2 = 0.1098$ and $Goof = 1.061$ for 655 variables refined against 8883 data ($0.77 \text{ \AA}$), $R1 = 0.0526$ for those 7627 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack⁶ parameter.

Table 1. Crystal data and structure refinement for vmd34.

Identification code	vmd34 (Xintong Hou)	
Empirical formula	$C_{23} H_{21} O_2 P S$	
Formula weight	392.43	
Temperature	93(2) K	
Wavelength	0.71073 $\text{\AA}$	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 9.2260(11) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 10.2235(12) \text{ \AA}$	$\beta = 91.032(2)^\circ$.
	$c = 21.602(3) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2037.2(4) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	824	
Crystal color	colorless	
Crystal size	$0.426 \times 0.295 \times 0.268 \text{ mm}^3$	
Theta range for data collection	0.943 to 27.483°	
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 13, -27 \leq l \leq 27$	
Reflections collected	25569	

Independent reflections	8883 [R(int) = 0.0452]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6010
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8883 / 1 / 655
Goodness-of-fit on F ²	1.061
Final R indices [I > 2sigma(I) = 7627 data]	R1 = 0.0526, wR2 = 0.1052
R indices (all data, 0.77 Å)	R1 = 0.0646, wR2 = 0.1098
Absolute structure parameter	0.06(3)
Largest diff. peak and hole	0.826 and -0.402 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³)

for vmd34. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	3082(1)	10363(1)	1172(1)	27(1)
P(1)	2231(1)	8961(1)	667(1)	18(1)
O(1)	3204(4)	8246(3)	2526(2)	34(1)
O(2)	971(3)	8218(3)	2081(1)	23(1)
C(1)	2684(5)	7338(4)	937(2)	22(1)
C(2)	4128(5)	7136(5)	1268(3)	32(1)
C(3)	2756(5)	6946(4)	1612(2)	23(1)
C(4)	2387(5)	7899(4)	2119(2)	23(1)
C(5)	474(7)	9128(5)	2549(3)	34(1)
C(6)	2302(5)	5550(4)	1768(2)	23(1)
C(7)	1072(5)	5000(5)	1518(3)	33(1)
C(8)	672(6)	3712(5)	1680(3)	38(1)
C(9)	1520(6)	3014(5)	2092(3)	36(1)
C(10)	2768(6)	3566(5)	2347(2)	32(1)
C(11)	3143(5)	4840(5)	2186(2)	28(1)
C(12)	262(4)	9068(4)	586(2)	20(1)
C(13)	-498(5)	9944(5)	954(2)	29(1)
C(14)	-1998(6)	10050(5)	889(3)	37(1)

C(15)	-2746(6)	9291(5)	453(3)	39(1)
C(16)	-1986(5)	8412(5)	82(3)	36(1)
C(17)	-496(5)	8303(5)	153(2)	27(1)
C(18)	2840(4)	8954(4)	-127(2)	20(1)
C(19)	2285(5)	9910(5)	-527(2)	27(1)
C(20)	2708(5)	9955(5)	-1136(2)	31(1)
C(21)	3720(5)	9074(5)	-1354(2)	29(1)
C(22)	4315(5)	8152(5)	-951(2)	31(1)
C(23)	3875(5)	8085(5)	-347(2)	27(1)
S(2)	8162(1)	-362(1)	3869(1)	26(1)
P(2)	7286(1)	1027(1)	4363(1)	18(1)
O(3)	8218(4)	1775(3)	2513(2)	35(1)
O(4)	6001(3)	1753(3)	2943(1)	24(1)
C(24)	7721(5)	2662(4)	4105(2)	22(1)
C(25)	9168(5)	2874(5)	3791(3)	30(1)
C(26)	7771(5)	3063(4)	3432(2)	24(1)
C(27)	7406(5)	2115(4)	2917(2)	24(1)
C(28)	5526(7)	837(5)	2462(3)	34(1)
C(29)	7295(5)	4442(4)	3263(2)	23(1)
C(30)	6139(5)	5032(5)	3543(3)	34(1)
C(31)	5732(6)	6312(5)	3370(3)	40(1)
C(32)	6493(6)	6978(5)	2934(3)	35(1)
C(33)	7670(6)	6403(5)	2652(2)	32(1)
C(34)	8066(6)	5116(5)	2813(2)	29(1)
C(35)	5314(4)	910(4)	4405(2)	21(1)

C(36)	4580(5)	-34(5)	4057(2)	28(1)
C(37)	3083(5)	-165(5)	4110(3)	36(1)
C(38)	2331(5)	637(5)	4509(3)	36(1)
C(39)	3051(6)	1573(5)	4851(3)	37(1)
C(40)	4553(5)	1718(5)	4803(2)	28(1)
C(41)	7882(4)	1017(4)	5169(2)	20(1)
C(42)	7245(5)	113(5)	5568(2)	26(1)
C(43)	7675(5)	64(5)	6186(2)	31(1)
C(44)	8743(5)	885(5)	6417(2)	26(1)
C(45)	9425(5)	1736(5)	6018(2)	26(1)
C(46)	8991(5)	1818(4)	5401(2)	24(1)

Table 3. Bond lengths [Å] and angles [°] for vmd34.

S(1)-P(1)	1.9575(15)
P(1)-C(1)	1.805(4)
P(1)-C(18)	1.814(5)
P(1)-C(12)	1.825(4)
O(1)-C(4)	1.203(5)
O(2)-C(4)	1.348(5)
O(2)-C(5)	1.454(6)
C(1)-C(3)	1.513(6)
C(1)-C(2)	1.514(7)
C(1)-H(1)	0.90(6)
C(2)-C(3)	1.492(7)
C(2)-H(2A)	0.93(5)
C(2)-H(2B)	1.02(7)
C(3)-C(4)	1.508(6)
C(3)-C(6)	1.527(6)
C(5)-H(5A)	1.00(5)
C(5)-H(5B)	0.98(6)
C(5)-H(5C)	0.90(8)
C(6)-C(7)	1.369(7)
C(6)-C(11)	1.385(7)
C(7)-C(8)	1.413(7)
C(7)-H(7)	0.93(5)
C(8)-C(9)	1.375(8)

C(8)-H(8)	0.98(5)
C(9)-C(10)	1.387(8)
C(9)-H(9)	1.01(6)
C(10)-C(11)	1.394(7)
C(10)-H(10)	1.06(5)
C(11)-H(11)	0.86(5)
C(12)-C(13)	1.395(6)
C(12)-C(17)	1.398(6)
C(13)-C(14)	1.392(7)
C(13)-H(13)	0.99(5)
C(14)-C(15)	1.393(8)
C(14)-H(14)	0.99(6)
C(15)-C(16)	1.401(8)
C(15)-H(15)	0.93(5)
C(16)-C(17)	1.385(7)
C(16)-H(16)	1.02(5)
C(17)-H(17)	0.94(5)
C(18)-C(23)	1.395(6)
C(18)-C(19)	1.396(6)
C(19)-C(20)	1.380(7)
C(19)-H(19)	0.94(5)
C(20)-C(21)	1.386(7)
C(20)-H(20)	0.93(5)
C(21)-C(22)	1.389(7)
C(21)-H(21)	0.94(4)

C(22)-C(23)	1.375(7)
C(22)-H(22)	1.00(6)
C(23)-H(23)	0.95(6)
S(2)-P(2)	1.9591(16)
P(2)-C(24)	1.810(5)
P(2)-C(41)	1.816(5)
P(2)-C(35)	1.827(4)
O(3)-C(27)	1.210(5)
O(4)-C(27)	1.351(5)
O(4)-C(28)	1.459(6)
C(24)-C(26)	1.513(7)
C(24)-C(25)	1.524(7)
C(24)-H(24)	0.87(4)
C(25)-C(26)	1.505(7)
C(25)-H(25A)	0.93(6)
C(25)-H(25B)	0.96(5)
C(26)-C(27)	1.509(6)
C(26)-C(29)	1.519(6)
C(28)-H(28A)	1.10(5)
C(28)-H(28B)	0.87(6)
C(28)-H(28C)	1.04(7)
C(29)-C(30)	1.375(7)
C(29)-C(34)	1.395(7)
C(30)-C(31)	1.410(7)
C(30)-H(30)	0.98(5)

C(31)-C(32)	1.367(8)
C(31)-H(31)	1.01(5)
C(32)-C(33)	1.386(8)
C(32)-H(32)	1.10(6)
C(33)-C(34)	1.408(7)
C(33)-H(33)	1.04(6)
C(34)-H(34)	0.98(5)
C(35)-C(40)	1.392(6)
C(35)-C(36)	1.392(6)
C(36)-C(37)	1.395(7)
C(36)-H(36)	0.91(5)
C(37)-C(38)	1.385(8)
C(37)-H(37)	0.87(5)
C(38)-C(39)	1.373(8)
C(38)-H(38)	0.98(5)
C(39)-C(40)	1.399(7)
C(39)-H(39)	0.98(6)
C(40)-H(40)	0.97(6)
C(41)-C(46)	1.397(6)
C(41)-C(42)	1.401(6)
C(42)-C(43)	1.386(7)
C(42)-H(42)	0.89(4)
C(43)-C(44)	1.380(7)
C(43)-H(43)	0.87(6)
C(44)-C(45)	1.383(7)

C(44)-H(44)	0.94(5)
C(45)-C(46)	1.388(7)
C(45)-H(45)	0.91(7)
C(46)-H(46)	0.89(5)

C(1)-P(1)-C(18)	103.2(2)
C(1)-P(1)-C(12)	108.1(2)
C(18)-P(1)-C(12)	103.56(19)
C(1)-P(1)-S(1)	113.83(17)
C(18)-P(1)-S(1)	113.70(15)
C(12)-P(1)-S(1)	113.44(15)
C(4)-O(2)-C(5)	115.5(4)
C(3)-C(1)-C(2)	59.1(3)
C(3)-C(1)-P(1)	124.1(3)
C(2)-C(1)-P(1)	118.4(3)
C(3)-C(1)-H(1)	115(4)
C(2)-C(1)-H(1)	120(3)
P(1)-C(1)-H(1)	111(4)
C(3)-C(2)-C(1)	60.4(3)
C(3)-C(2)-H(2A)	117(3)
C(1)-C(2)-H(2A)	121(3)
C(3)-C(2)-H(2B)	115(3)
C(1)-C(2)-H(2B)	115(3)
H(2A)-C(2)-H(2B)	116(5)
C(2)-C(3)-C(4)	118.8(4)

C(2)-C(3)-C(1)	60.5(3)
C(4)-C(3)-C(1)	121.5(4)
C(2)-C(3)-C(6)	118.0(4)
C(4)-C(3)-C(6)	112.1(4)
C(1)-C(3)-C(6)	117.0(4)
O(1)-C(4)-O(2)	124.6(4)
O(1)-C(4)-C(3)	125.1(4)
O(2)-C(4)-C(3)	110.1(4)
O(2)-C(5)-H(5A)	107(3)
O(2)-C(5)-H(5B)	108(3)
H(5A)-C(5)-H(5B)	111(4)
O(2)-C(5)-H(5C)	114(5)
H(5A)-C(5)-H(5C)	113(5)
H(5B)-C(5)-H(5C)	104(6)
C(7)-C(6)-C(11)	119.6(4)
C(7)-C(6)-C(3)	121.7(4)
C(11)-C(6)-C(3)	118.8(4)
C(6)-C(7)-C(8)	120.2(5)
C(6)-C(7)-H(7)	121(3)
C(8)-C(7)-H(7)	118(4)
C(9)-C(8)-C(7)	119.7(5)
C(9)-C(8)-H(8)	122(3)
C(7)-C(8)-H(8)	118(3)
C(8)-C(9)-C(10)	120.3(5)
C(8)-C(9)-H(9)	119(3)

C(10)-C(9)-H(9)	120(3)
C(9)-C(10)-C(11)	119.3(5)
C(9)-C(10)-H(10)	120(3)
C(11)-C(10)-H(10)	120(3)
C(6)-C(11)-C(10)	120.9(5)
C(6)-C(11)-H(11)	118(4)
C(10)-C(11)-H(11)	121(4)
C(13)-C(12)-C(17)	119.4(4)
C(13)-C(12)-P(1)	119.6(3)
C(17)-C(12)-P(1)	121.0(3)
C(14)-C(13)-C(12)	120.0(5)
C(14)-C(13)-H(13)	125(3)
C(12)-C(13)-H(13)	115(3)
C(13)-C(14)-C(15)	120.3(5)
C(13)-C(14)-H(14)	117(3)
C(15)-C(14)-H(14)	123(3)
C(14)-C(15)-C(16)	119.8(5)
C(14)-C(15)-H(15)	125(3)
C(16)-C(15)-H(15)	114(3)
C(17)-C(16)-C(15)	119.6(5)
C(17)-C(16)-H(16)	120(3)
C(15)-C(16)-H(16)	120(3)
C(16)-C(17)-C(12)	120.8(5)
C(16)-C(17)-H(17)	122(3)
C(12)-C(17)-H(17)	117(3)

C(23)-C(18)-C(19)	118.7(4)
C(23)-C(18)-P(1)	123.4(4)
C(19)-C(18)-P(1)	117.8(3)
C(20)-C(19)-C(18)	120.5(5)
C(20)-C(19)-H(19)	123(3)
C(18)-C(19)-H(19)	117(3)
C(19)-C(20)-C(21)	120.4(5)
C(19)-C(20)-H(20)	124(3)
C(21)-C(20)-H(20)	115(3)
C(20)-C(21)-C(22)	119.3(5)
C(20)-C(21)-H(21)	121(3)
C(22)-C(21)-H(21)	120(3)
C(23)-C(22)-C(21)	120.5(5)
C(23)-C(22)-H(22)	122(3)
C(21)-C(22)-H(22)	117(3)
C(22)-C(23)-C(18)	120.5(5)
C(22)-C(23)-H(23)	114(3)
C(18)-C(23)-H(23)	124(3)
C(24)-P(2)-C(41)	103.6(2)
C(24)-P(2)-C(35)	107.6(2)
C(41)-P(2)-C(35)	103.68(19)
C(24)-P(2)-S(2)	113.92(18)
C(41)-P(2)-S(2)	113.38(14)
C(35)-P(2)-S(2)	113.62(15)
C(27)-O(4)-C(28)	115.0(4)

C(26)-C(24)-C(25)	59.4(3)
C(26)-C(24)-P(2)	123.9(3)
C(25)-C(24)-P(2)	118.0(3)
C(26)-C(24)-H(24)	122(3)
C(25)-C(24)-H(24)	121(3)
P(2)-C(24)-H(24)	106(3)
C(26)-C(25)-C(24)	59.9(3)
C(26)-C(25)-H(25A)	120(3)
C(24)-C(25)-H(25A)	119(3)
C(26)-C(25)-H(25B)	111(3)
C(24)-C(25)-H(25B)	115(3)
H(25A)-C(25)-H(25B)	118(4)
C(25)-C(26)-C(27)	118.3(4)
C(25)-C(26)-C(24)	60.7(3)
C(27)-C(26)-C(24)	121.6(4)
C(25)-C(26)-C(29)	119.0(4)
C(27)-C(26)-C(29)	111.1(4)
C(24)-C(26)-C(29)	118.0(4)
O(3)-C(27)-O(4)	123.9(4)
O(3)-C(27)-C(26)	125.6(4)
O(4)-C(27)-C(26)	110.3(4)
O(4)-C(28)-H(28A)	110(3)
O(4)-C(28)-H(28B)	104(4)
H(28A)-C(28)-H(28B)	114(5)
O(4)-C(28)-H(28C)	114(3)

H(28A)-C(28)-H(28C)	106(4)
H(28B)-C(28)-H(28C)	110(5)
C(30)-C(29)-C(34)	119.9(4)
C(30)-C(29)-C(26)	121.6(4)
C(34)-C(29)-C(26)	118.4(4)
C(29)-C(30)-C(31)	119.7(5)
C(29)-C(30)-H(30)	122(3)
C(31)-C(30)-H(30)	119(3)
C(32)-C(31)-C(30)	120.5(5)
C(32)-C(31)-H(31)	120(3)
C(30)-C(31)-H(31)	119(3)
C(31)-C(32)-C(33)	120.5(5)
C(31)-C(32)-H(32)	116(3)
C(33)-C(32)-H(32)	124(3)
C(32)-C(33)-C(34)	119.3(5)
C(32)-C(33)-H(33)	124(3)
C(34)-C(33)-H(33)	116(3)
C(29)-C(34)-C(33)	120.0(5)
C(29)-C(34)-H(34)	128(3)
C(33)-C(34)-H(34)	112(3)
C(40)-C(35)-C(36)	120.0(4)
C(40)-C(35)-P(2)	120.4(3)
C(36)-C(35)-P(2)	119.6(3)
C(35)-C(36)-C(37)	119.7(5)
C(35)-C(36)-H(36)	116(3)

C(37)-C(36)-H(36)	125(3)
C(38)-C(37)-C(36)	120.1(5)
C(38)-C(37)-H(37)	117(3)
C(36)-C(37)-H(37)	123(3)
C(39)-C(38)-C(37)	120.3(5)
C(39)-C(38)-H(38)	118(3)
C(37)-C(38)-H(38)	122(3)
C(38)-C(39)-C(40)	120.3(5)
C(38)-C(39)-H(39)	122(3)
C(40)-C(39)-H(39)	118(3)
C(35)-C(40)-C(39)	119.6(5)
C(35)-C(40)-H(40)	121(4)
C(39)-C(40)-H(40)	119(4)
C(46)-C(41)-C(42)	118.6(4)
C(46)-C(41)-P(2)	123.2(3)
C(42)-C(41)-P(2)	118.1(3)
C(43)-C(42)-C(41)	120.1(5)
C(43)-C(42)-H(42)	122(3)
C(41)-C(42)-H(42)	117(3)
C(44)-C(43)-C(42)	121.0(5)
C(44)-C(43)-H(43)	122(4)
C(42)-C(43)-H(43)	117(4)
C(43)-C(44)-C(45)	119.2(5)
C(43)-C(44)-H(44)	115(3)
C(45)-C(44)-H(44)	126(3)

C(44)-C(45)-C(46)	120.6(4)
C(44)-C(45)-H(45)	120(4)
C(46)-C(45)-H(45)	119(4)
C(45)-C(46)-C(41)	120.4(4)
C(45)-C(46)-H(46)	120(3)
C(41)-C(46)-H(46)	119(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vmd34. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	32(1)	15(1)	32(1)	0(1)	-8(1)	-5(1)
P(1)	17(1)	11(1)	27(1)	0(1)	-1(1)	0(1)
O(1)	33(2)	30(2)	38(2)	6(2)	-11(2)	-4(2)
O(2)	24(2)	14(2)	30(2)	-1(1)	3(1)	4(1)
C(1)	22(2)	12(2)	34(3)	0(2)	3(2)	-2(2)
C(2)	22(2)	24(3)	50(3)	15(2)	3(2)	5(2)
C(3)	22(2)	17(2)	32(3)	6(2)	2(2)	2(2)
C(4)	28(3)	13(2)	27(3)	8(2)	-2(2)	-6(2)
C(5)	49(4)	19(2)	34(3)	-5(2)	8(3)	3(2)
C(6)	24(2)	13(2)	34(3)	2(2)	11(2)	5(2)
C(7)	32(3)	22(2)	45(3)	12(2)	3(2)	2(2)
C(8)	38(3)	21(3)	55(4)	1(2)	1(3)	-8(2)
C(9)	51(3)	14(2)	43(3)	3(2)	19(3)	2(2)
C(10)	46(3)	20(2)	29(3)	4(2)	13(2)	15(2)
C(11)	32(3)	22(3)	31(3)	4(2)	11(2)	4(2)
C(12)	16(2)	14(2)	29(2)	4(2)	2(2)	1(2)
C(13)	29(3)	24(2)	35(3)	1(2)	-1(2)	10(2)
C(14)	35(3)	34(3)	43(3)	3(3)	6(2)	18(2)
C(15)	22(3)	37(3)	60(4)	12(3)	-2(3)	2(2)
C(16)	26(3)	33(3)	49(3)	-3(3)	-4(2)	-10(2)

C(17)	20(2)	22(2)	41(3)	-7(2)	5(2)	-6(2)
C(18)	17(2)	14(2)	31(2)	-3(2)	0(2)	-5(2)
C(19)	20(2)	26(3)	36(3)	5(2)	8(2)	6(2)
C(20)	28(3)	30(3)	36(3)	9(2)	4(2)	4(2)
C(21)	19(2)	39(3)	29(3)	-9(2)	4(2)	-9(2)
C(22)	28(3)	26(3)	39(3)	-5(2)	1(2)	7(2)
C(23)	21(2)	21(2)	38(3)	-6(2)	-1(2)	3(2)
S(2)	29(1)	16(1)	33(1)	1(1)	9(1)	5(1)
P(2)	15(1)	11(1)	28(1)	2(1)	2(1)	0(1)
O(3)	33(2)	30(2)	41(2)	9(2)	11(2)	3(2)
O(4)	24(2)	16(2)	33(2)	-2(1)	-3(1)	-3(1)
C(24)	24(2)	15(2)	28(3)	2(2)	-5(2)	0(2)
C(25)	20(2)	20(3)	50(3)	9(2)	-3(2)	-6(2)
C(26)	20(2)	17(2)	34(3)	3(2)	0(2)	-4(2)
C(27)	24(2)	14(2)	32(3)	8(2)	0(2)	4(2)
C(28)	44(3)	23(3)	35(3)	-3(2)	-6(3)	-7(2)
C(29)	22(2)	15(2)	32(3)	0(2)	-7(2)	-6(2)
C(30)	33(3)	20(2)	50(3)	11(2)	4(2)	-1(2)
C(31)	39(3)	22(3)	60(4)	3(3)	-3(3)	9(2)
C(32)	44(3)	18(3)	43(3)	4(2)	-14(3)	0(2)
C(33)	51(3)	18(2)	26(3)	7(2)	-7(2)	-11(2)
C(34)	39(3)	19(2)	28(3)	0(2)	-5(2)	-6(2)
C(35)	16(2)	15(2)	31(2)	4(2)	-2(2)	0(2)
C(36)	29(3)	25(2)	31(3)	0(2)	4(2)	-8(2)
C(37)	28(3)	33(3)	47(3)	2(3)	-4(2)	-19(2)

C(38)	17(2)	41(3)	49(3)	11(3)	-4(2)	-4(2)
C(39)	27(3)	32(3)	52(3)	-3(3)	2(2)	11(2)
C(40)	21(2)	23(2)	42(3)	-4(2)	-2(2)	6(2)
C(41)	13(2)	12(2)	35(3)	-2(2)	2(2)	3(2)
C(42)	19(2)	24(3)	37(3)	6(2)	-3(2)	-5(2)
C(43)	27(3)	32(3)	35(3)	11(2)	4(2)	-3(2)
C(44)	24(2)	30(3)	25(3)	-3(2)	1(2)	7(2)
C(45)	23(2)	24(2)	32(3)	-8(2)	-1(2)	-3(2)
C(46)	21(2)	16(2)	36(3)	2(2)	6(2)	-3(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vmd34.

	x	y	z	U(eq)
H(1)	2340(50)	6720(60)	680(20)	39(16)
H(2A)	4690(50)	6400(60)	1190(20)	36(15)
H(2B)	4680(70)	7980(70)	1370(30)	61(19)
H(5A)	540(50)	8670(50)	2960(20)	35(14)
H(5B)	-530(70)	9360(60)	2450(30)	58(18)
H(5C)	940(70)	9900(80)	2550(30)	70(20)
H(7)	550(60)	5410(60)	1200(20)	41(15)
H(8)	-220(50)	3350(50)	1500(20)	32(14)
H(9)	1200(60)	2110(60)	2220(30)	51(16)
H(10)	3420(60)	3030(60)	2670(20)	42(15)
H(11)	3890(60)	5220(60)	2350(20)	39(16)
H(13)	100(50)	10420(50)	1270(20)	28(13)
H(14)	-2490(60)	10660(70)	1170(30)	58(18)
H(15)	-3720(50)	9380(50)	350(20)	27(13)
H(16)	-2530(50)	7870(50)	-250(20)	29(13)
H(17)	60(50)	7760(50)	-100(20)	28(13)
H(19)	1660(50)	10530(50)	-360(20)	22(12)

H(20)	2300(50)	10510(60)	-1440(20)	38(15)
H(21)	3950(40)	9060(40)	-1775(19)	8(10)
H(22)	5190(60)	7660(60)	-1100(30)	53(17)
H(23)	4460(60)	7530(60)	-90(30)	48(17)
H(24)	7420(40)	3190(40)	4391(19)	8(11)
H(25A)	9730(60)	3600(60)	3910(20)	42(16)
H(25B)	9660(50)	2090(50)	3660(20)	26(13)
H(28A)	5620(50)	1280(50)	2000(20)	40(15)
H(28B)	4640(70)	650(60)	2560(30)	60(20)
H(28C)	6140(60)	-20(70)	2450(30)	62(18)
H(30)	5570(50)	4580(60)	3860(20)	39(14)
H(31)	4900(50)	6740(50)	3580(20)	29(13)
H(32)	6090(60)	7970(60)	2820(20)	43(15)
H(33)	8260(60)	6840(60)	2300(20)	45(16)
H(34)	8890(50)	4800(50)	2580(20)	34(14)
H(36)	5140(50)	-520(50)	3800(20)	29(14)
H(37)	2590(50)	-770(50)	3920(20)	26(13)
H(38)	1270(50)	600(50)	4540(20)	36(14)
H(39)	2540(60)	2170(60)	5130(30)	52(17)
H(40)	5050(60)	2350(60)	5070(30)	51(17)
H(42)	6470(40)	-320(40)	5427(18)	13(11)
H(43)	7200(60)	-460(70)	6420(30)	60(20)
H(44)	8930(50)	810(50)	6840(20)	39(15)
H(45)	10220(70)	2190(70)	6150(30)	70(20)
H(46)	9430(50)	2370(50)	5150(20)	24(13)

Table 6. Torsion angles [°] for vmd34.

C(18)-P(1)-C(1)-C(3)	163.7(4)
C(12)-P(1)-C(1)-C(3)	-87.1(4)
S(1)-P(1)-C(1)-C(3)	40.0(4)
C(18)-P(1)-C(1)-C(2)	93.5(4)
C(12)-P(1)-C(1)-C(2)	-157.2(4)
S(1)-P(1)-C(1)-C(2)	-30.2(4)
P(1)-C(1)-C(2)-C(3)	114.8(4)
C(1)-C(2)-C(3)-C(4)	-111.9(4)
C(1)-C(2)-C(3)-C(6)	106.8(5)
P(1)-C(1)-C(3)-C(2)	-105.3(4)
C(2)-C(1)-C(3)-C(4)	107.7(5)
P(1)-C(1)-C(3)-C(4)	2.4(6)
C(2)-C(1)-C(3)-C(6)	-108.5(4)
P(1)-C(1)-C(3)-C(6)	146.2(3)
C(5)-O(2)-C(4)-O(1)	4.9(6)
C(5)-O(2)-C(4)-C(3)	179.6(4)
C(2)-C(3)-C(4)-O(1)	-48.2(6)
C(1)-C(3)-C(4)-O(1)	-119.4(5)
C(6)-C(3)-C(4)-O(1)	95.2(5)
C(2)-C(3)-C(4)-O(2)	137.1(4)
C(1)-C(3)-C(4)-O(2)	65.9(5)
C(6)-C(3)-C(4)-O(2)	-79.5(4)
C(2)-C(3)-C(6)-C(7)	-114.7(5)

C(4)-C(3)-C(6)-C(7)	101.6(5)
C(1)-C(3)-C(6)-C(7)	-45.5(6)
C(2)-C(3)-C(6)-C(11)	66.9(6)
C(4)-C(3)-C(6)-C(11)	-76.9(5)
C(1)-C(3)-C(6)-C(11)	136.1(4)
C(11)-C(6)-C(7)-C(8)	-0.6(8)
C(3)-C(6)-C(7)-C(8)	-179.0(5)
C(6)-C(7)-C(8)-C(9)	0.2(8)
C(7)-C(8)-C(9)-C(10)	-0.3(8)
C(8)-C(9)-C(10)-C(11)	0.7(8)
C(7)-C(6)-C(11)-C(10)	1.1(7)
C(3)-C(6)-C(11)-C(10)	179.5(4)
C(9)-C(10)-C(11)-C(6)	-1.1(7)
C(1)-P(1)-C(12)-C(13)	116.4(4)
C(18)-P(1)-C(12)-C(13)	-134.5(4)
S(1)-P(1)-C(12)-C(13)	-10.8(4)
C(1)-P(1)-C(12)-C(17)	-64.7(4)
C(18)-P(1)-C(12)-C(17)	44.3(4)
S(1)-P(1)-C(12)-C(17)	168.0(3)
C(17)-C(12)-C(13)-C(14)	0.0(7)
P(1)-C(12)-C(13)-C(14)	178.9(4)
C(12)-C(13)-C(14)-C(15)	-0.4(8)
C(13)-C(14)-C(15)-C(16)	0.3(8)
C(14)-C(15)-C(16)-C(17)	0.2(8)
C(15)-C(16)-C(17)-C(12)	-0.6(8)

C(13)-C(12)-C(17)-C(16)	0.5(7)
P(1)-C(12)-C(17)-C(16)	-178.3(4)
C(1)-P(1)-C(18)-C(23)	-21.3(4)
C(12)-P(1)-C(18)-C(23)	-134.0(4)
S(1)-P(1)-C(18)-C(23)	102.5(4)
C(1)-P(1)-C(18)-C(19)	161.7(3)
C(12)-P(1)-C(18)-C(19)	49.0(4)
S(1)-P(1)-C(18)-C(19)	-74.5(4)
C(23)-C(18)-C(19)-C(20)	2.8(7)
P(1)-C(18)-C(19)-C(20)	180.0(4)
C(18)-C(19)-C(20)-C(21)	-1.8(7)
C(19)-C(20)-C(21)-C(22)	-0.6(7)
C(20)-C(21)-C(22)-C(23)	2.0(7)
C(21)-C(22)-C(23)-C(18)	-0.9(7)
C(19)-C(18)-C(23)-C(22)	-1.5(7)
P(1)-C(18)-C(23)-C(22)	-178.5(4)
C(41)-P(2)-C(24)-C(26)	164.6(4)
C(35)-P(2)-C(24)-C(26)	-86.0(4)
S(2)-P(2)-C(24)-C(26)	40.9(4)
C(41)-P(2)-C(24)-C(25)	94.3(4)
C(35)-P(2)-C(24)-C(25)	-156.3(4)
S(2)-P(2)-C(24)-C(25)	-29.4(4)
P(2)-C(24)-C(25)-C(26)	114.8(4)
C(24)-C(25)-C(26)-C(27)	-112.3(5)
C(24)-C(25)-C(26)-C(29)	107.7(5)

P(2)-C(24)-C(26)-C(25)	-105.1(4)
C(25)-C(24)-C(26)-C(27)	107.1(5)
P(2)-C(24)-C(26)-C(27)	2.0(6)
C(25)-C(24)-C(26)-C(29)	-109.3(5)
P(2)-C(24)-C(26)-C(29)	145.6(4)
C(28)-O(4)-C(27)-O(3)	3.6(6)
C(28)-O(4)-C(27)-C(26)	179.7(4)
C(25)-C(26)-C(27)-O(3)	-48.1(6)
C(24)-C(26)-C(27)-O(3)	-119.3(5)
C(29)-C(26)-C(27)-O(3)	94.9(5)
C(25)-C(26)-C(27)-O(4)	135.9(4)
C(24)-C(26)-C(27)-O(4)	64.6(5)
C(29)-C(26)-C(27)-O(4)	-81.2(4)
C(25)-C(26)-C(29)-C(30)	-108.8(5)
C(27)-C(26)-C(29)-C(30)	108.6(5)
C(24)-C(26)-C(29)-C(30)	-38.6(6)
C(25)-C(26)-C(29)-C(34)	70.9(6)
C(27)-C(26)-C(29)-C(34)	-71.7(5)
C(24)-C(26)-C(29)-C(34)	141.1(4)
C(34)-C(29)-C(30)-C(31)	0.6(7)
C(26)-C(29)-C(30)-C(31)	-179.8(4)
C(29)-C(30)-C(31)-C(32)	-1.2(8)
C(30)-C(31)-C(32)-C(33)	0.5(8)
C(31)-C(32)-C(33)-C(34)	0.7(8)
C(30)-C(29)-C(34)-C(33)	0.7(7)

C(26)-C(29)-C(34)-C(33)	-179.0(4)
C(32)-C(33)-C(34)-C(29)	-1.3(7)
C(24)-P(2)-C(35)-C(40)	-61.4(4)
C(41)-P(2)-C(35)-C(40)	48.0(4)
S(2)-P(2)-C(35)-C(40)	171.5(3)
C(24)-P(2)-C(35)-C(36)	121.4(4)
C(41)-P(2)-C(35)-C(36)	-129.2(4)
S(2)-P(2)-C(35)-C(36)	-5.7(4)
C(40)-C(35)-C(36)-C(37)	-0.1(7)
P(2)-C(35)-C(36)-C(37)	177.0(4)
C(35)-C(36)-C(37)-C(38)	-0.2(8)
C(36)-C(37)-C(38)-C(39)	0.5(8)
C(37)-C(38)-C(39)-C(40)	-0.5(8)
C(36)-C(35)-C(40)-C(39)	0.1(7)
P(2)-C(35)-C(40)-C(39)	-177.0(4)
C(38)-C(39)-C(40)-C(35)	0.2(8)
C(24)-P(2)-C(41)-C(46)	-26.8(4)
C(35)-P(2)-C(41)-C(46)	-139.1(4)
S(2)-P(2)-C(41)-C(46)	97.2(4)
C(24)-P(2)-C(41)-C(42)	156.5(3)
C(35)-P(2)-C(41)-C(42)	44.2(4)
S(2)-P(2)-C(41)-C(42)	-79.5(3)
C(46)-C(41)-C(42)-C(43)	2.6(7)
P(2)-C(41)-C(42)-C(43)	179.5(4)
C(41)-C(42)-C(43)-C(44)	-0.8(7)

C(42)-C(43)-C(44)-C(45)	-2.2(7)
C(43)-C(44)-C(45)-C(46)	3.5(7)
C(44)-C(45)-C(46)-C(41)	-1.7(7)
C(42)-C(41)-C(46)-C(45)	-1.4(6)
P(2)-C(41)-C(46)-C(45)	-178.1(4)

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Definitions:

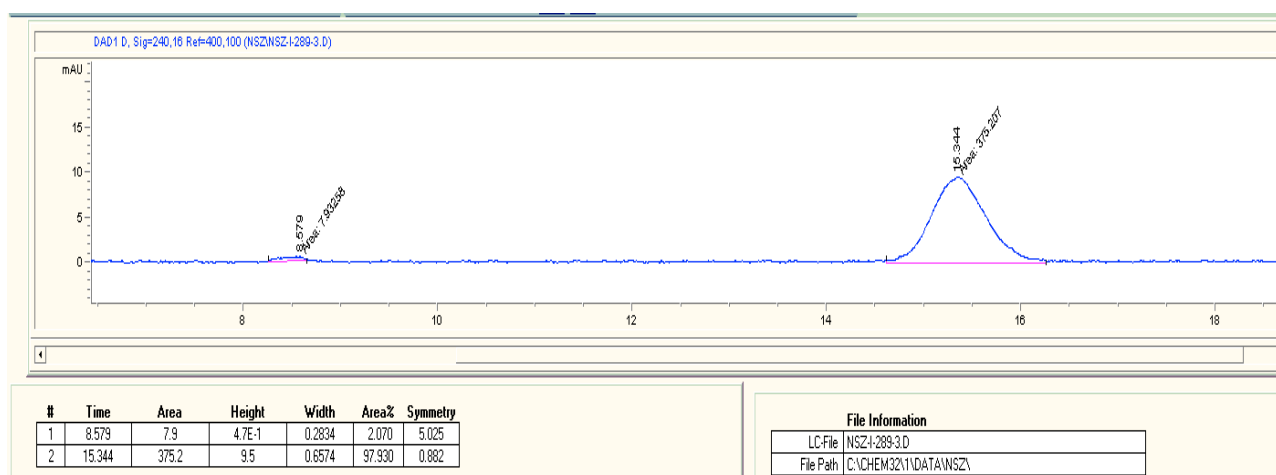
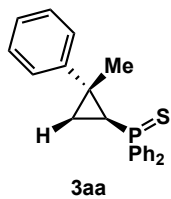
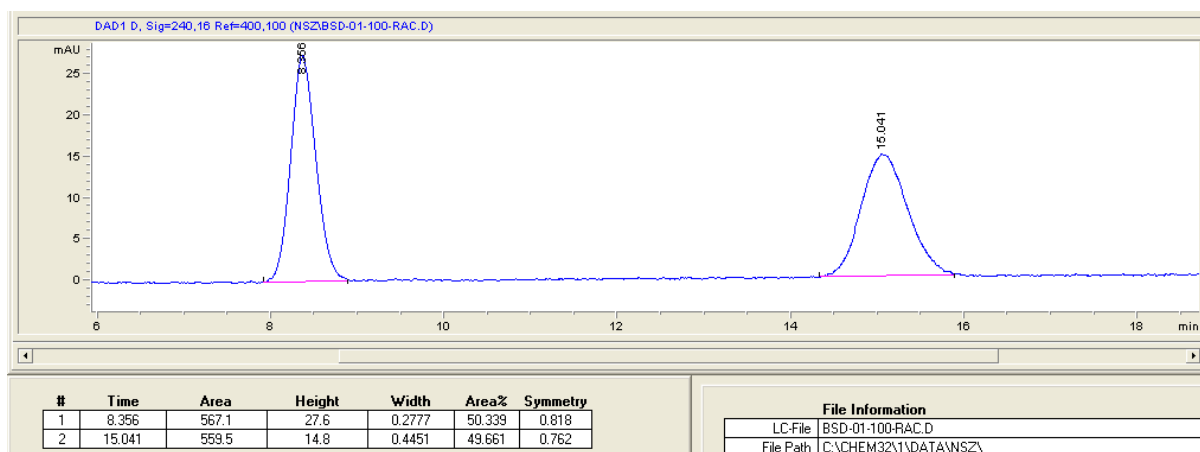
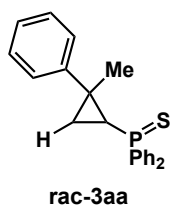
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

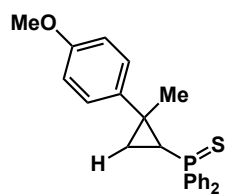
$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

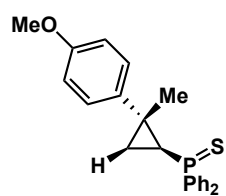
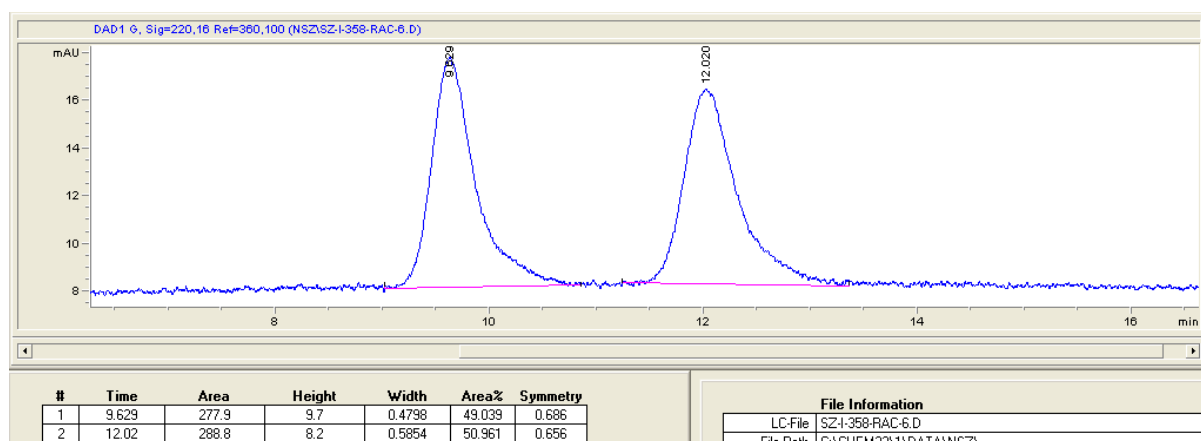
The thermal ellipsoid plot is shown at the 50% probability level.

10. SFC Spectra

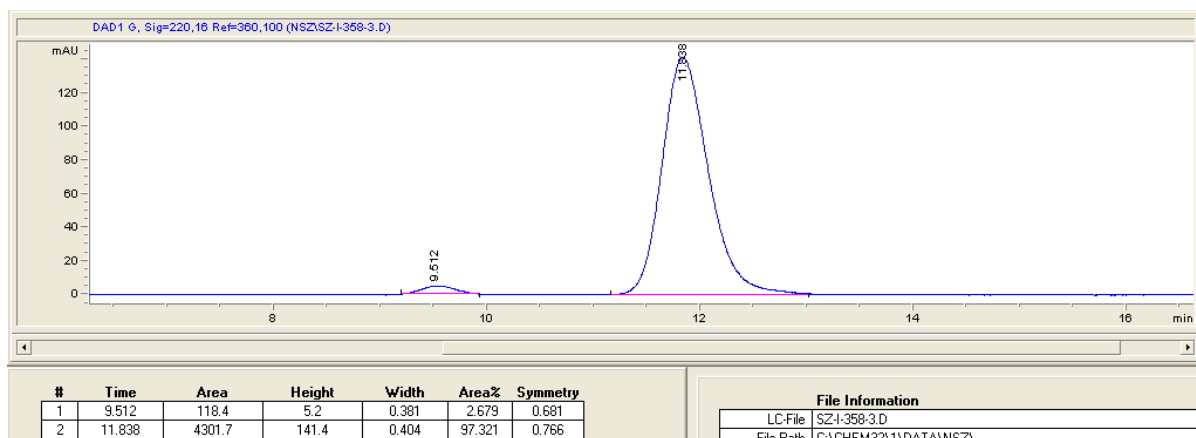


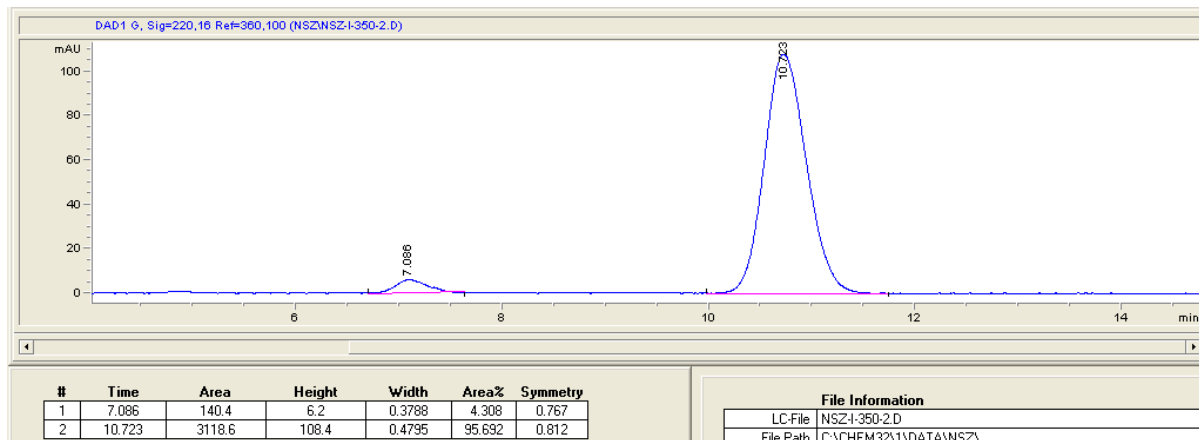
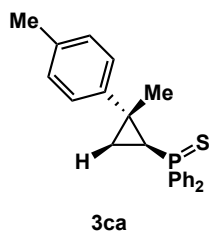
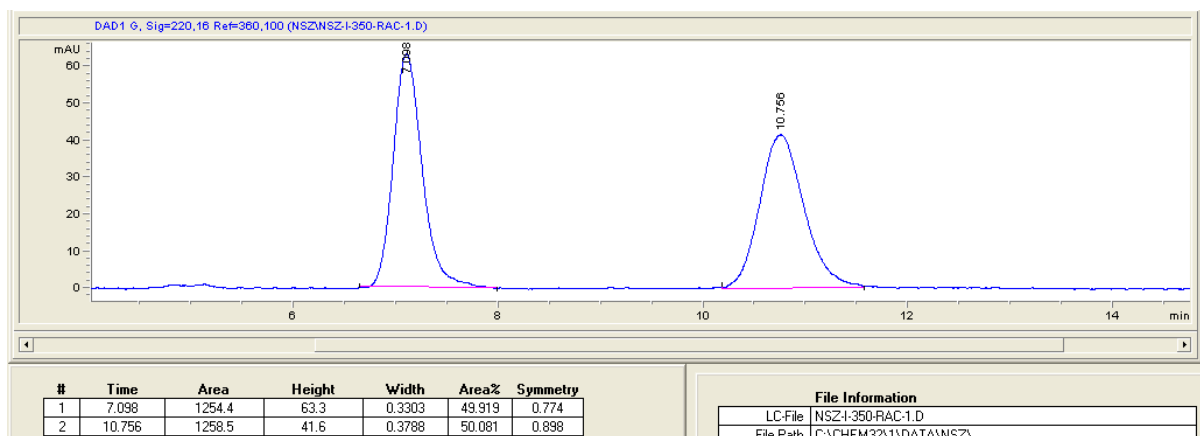
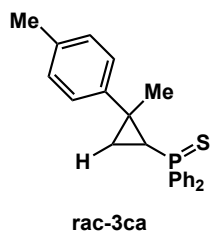


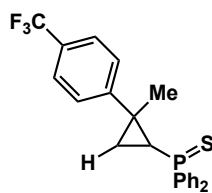
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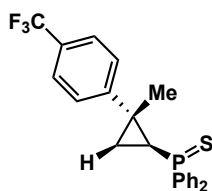
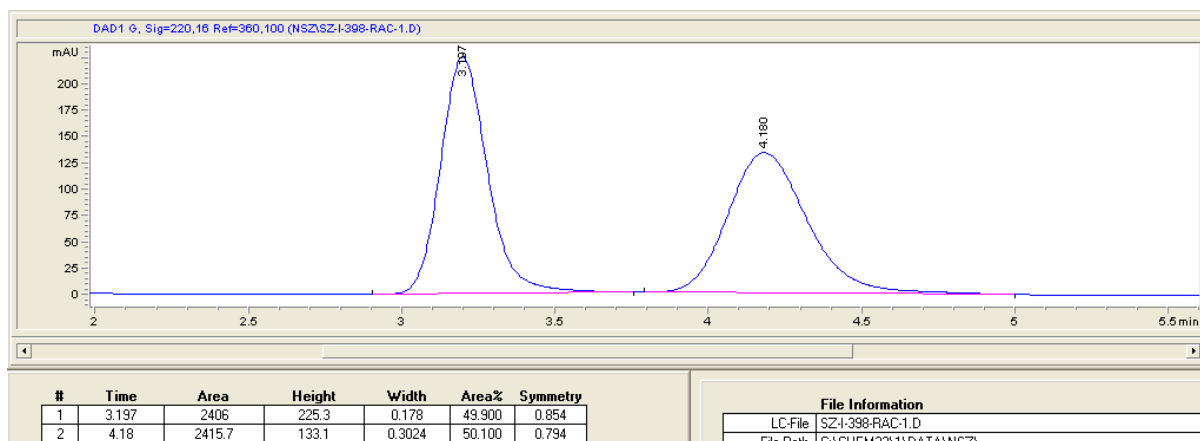
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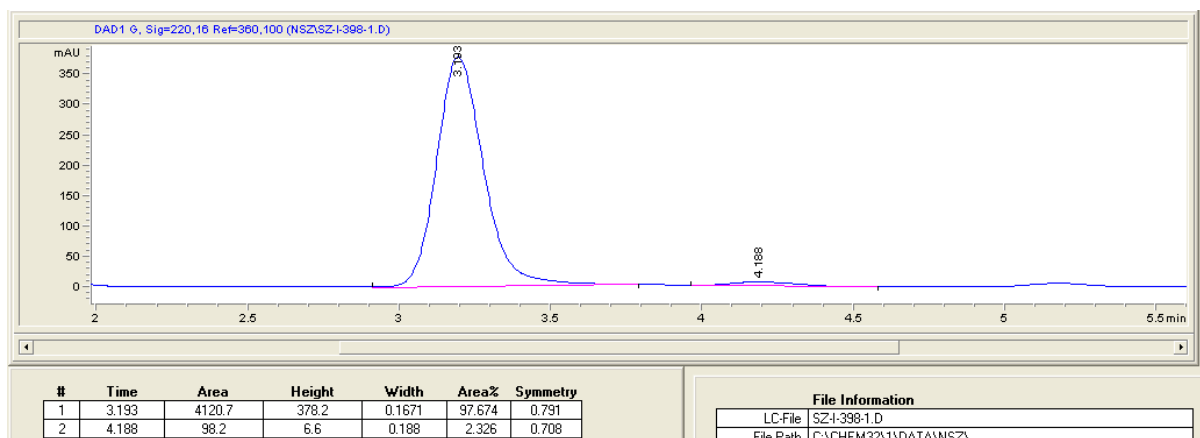


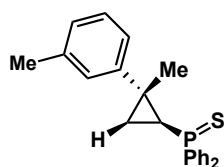


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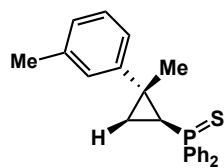
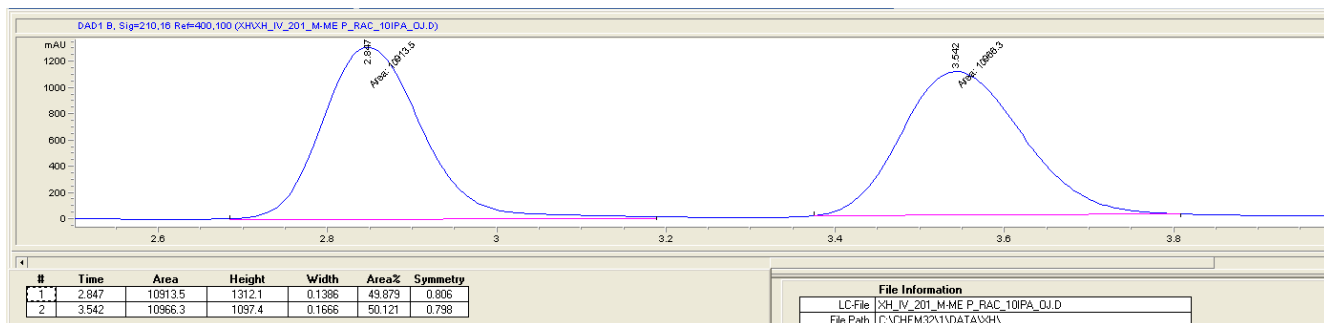


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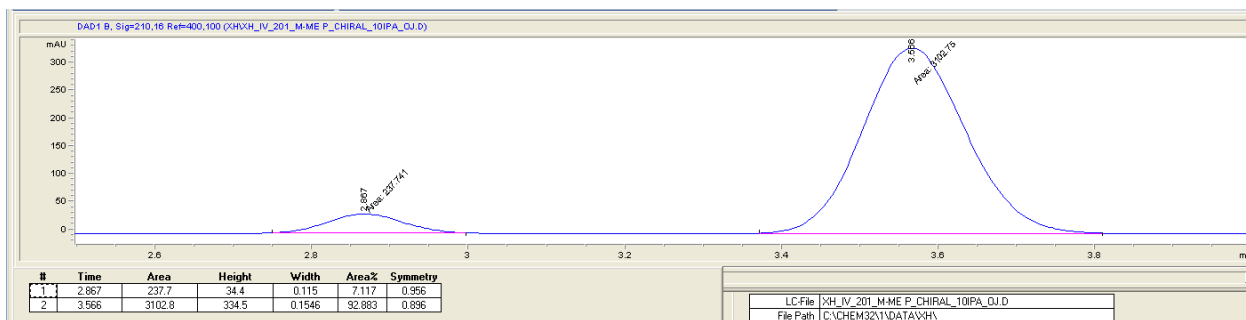


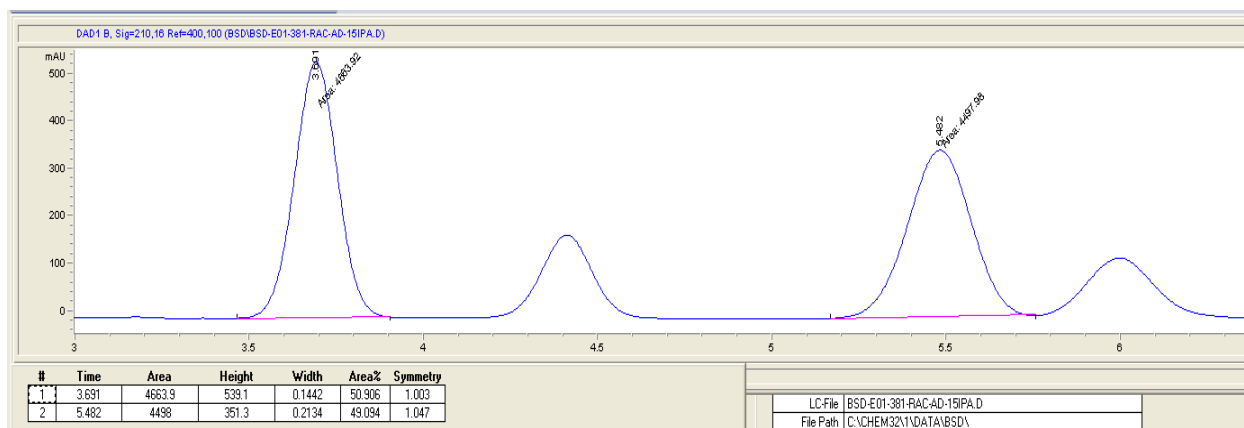
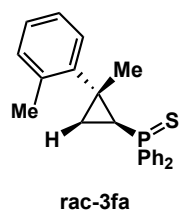


rac-3ea

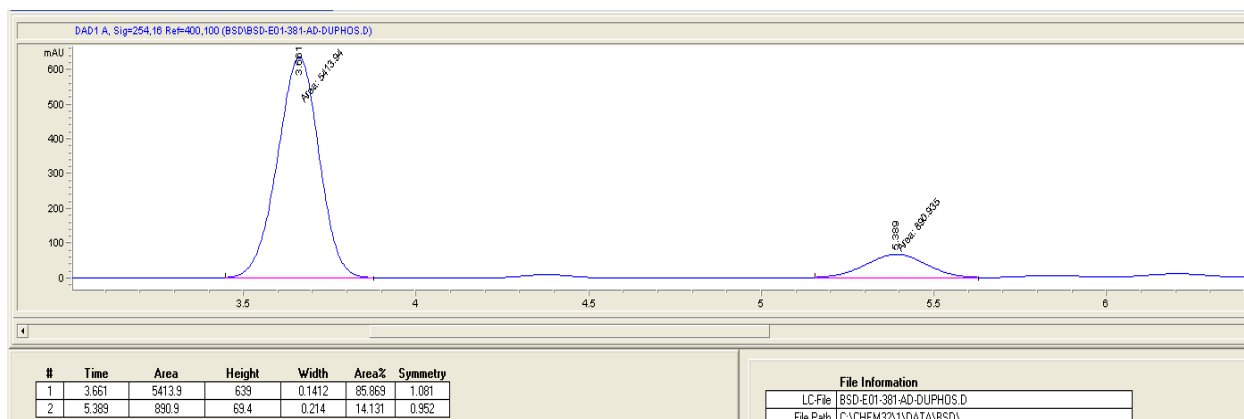
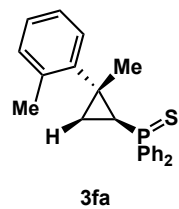


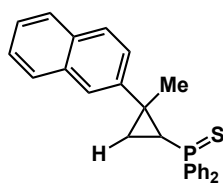
3ea



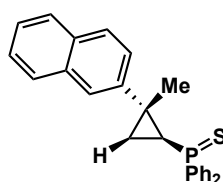
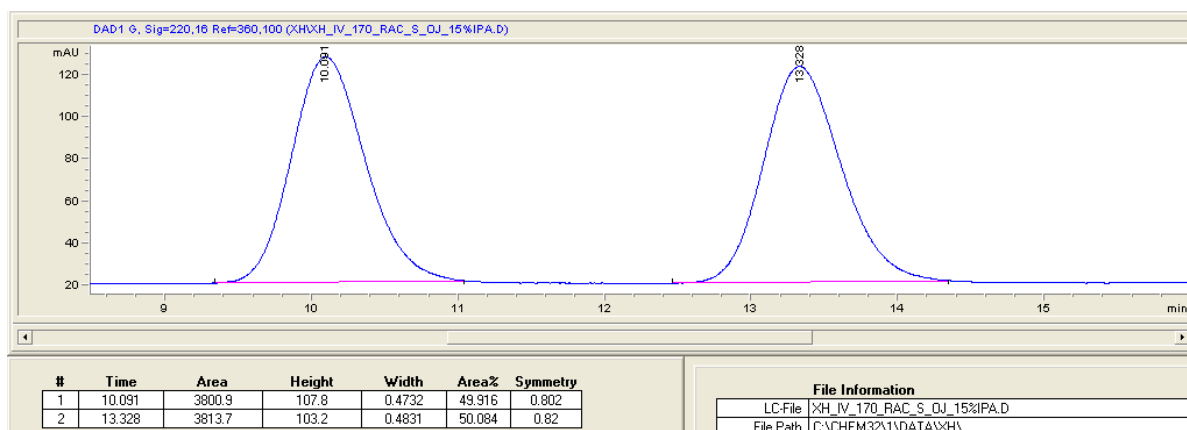


*Inseparable diastereomers for racemic condition.

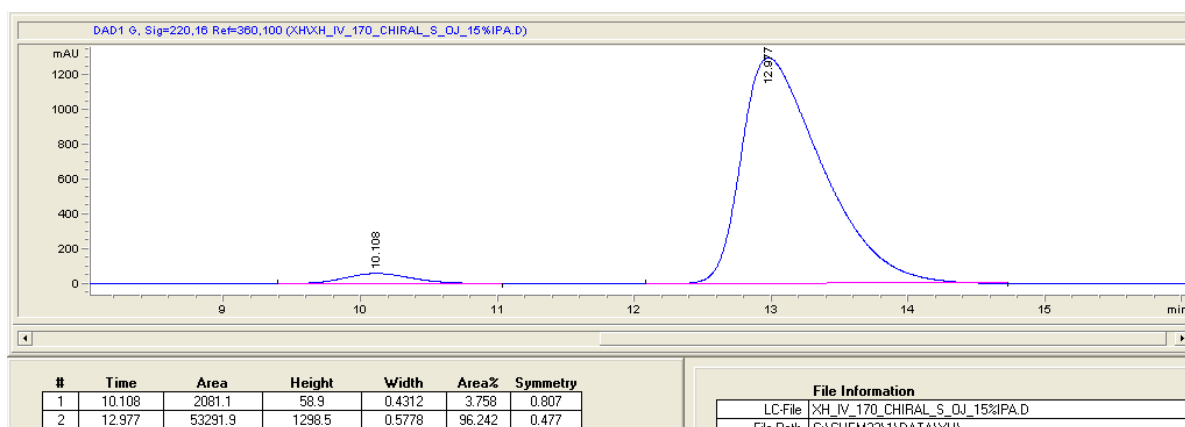


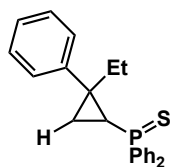


rac-3ga

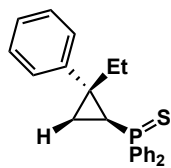
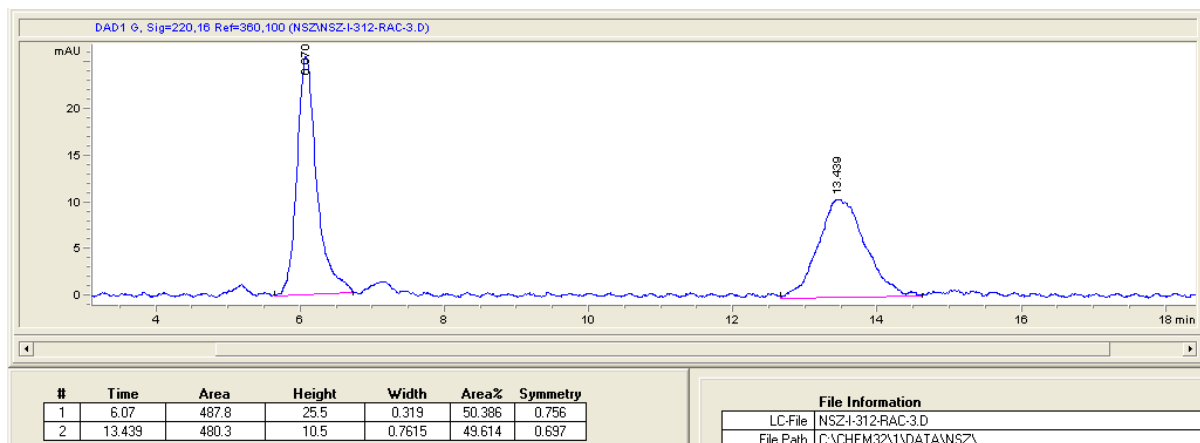


3ga

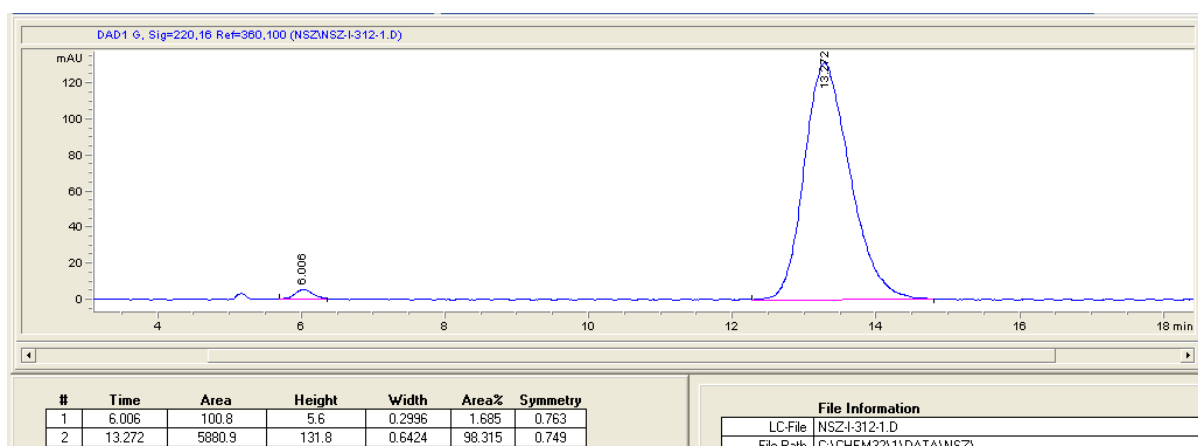


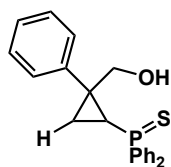


rac-3ha

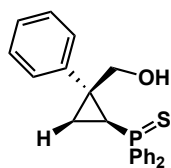
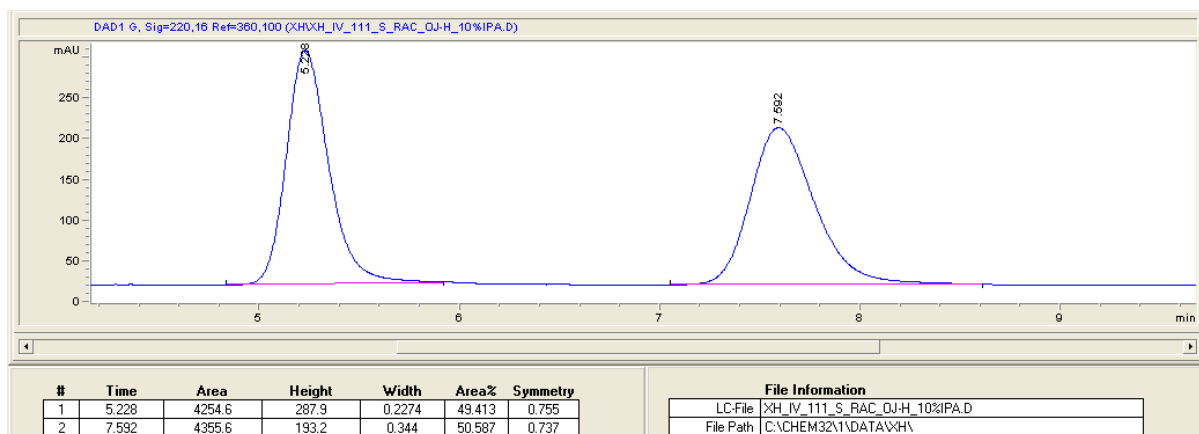


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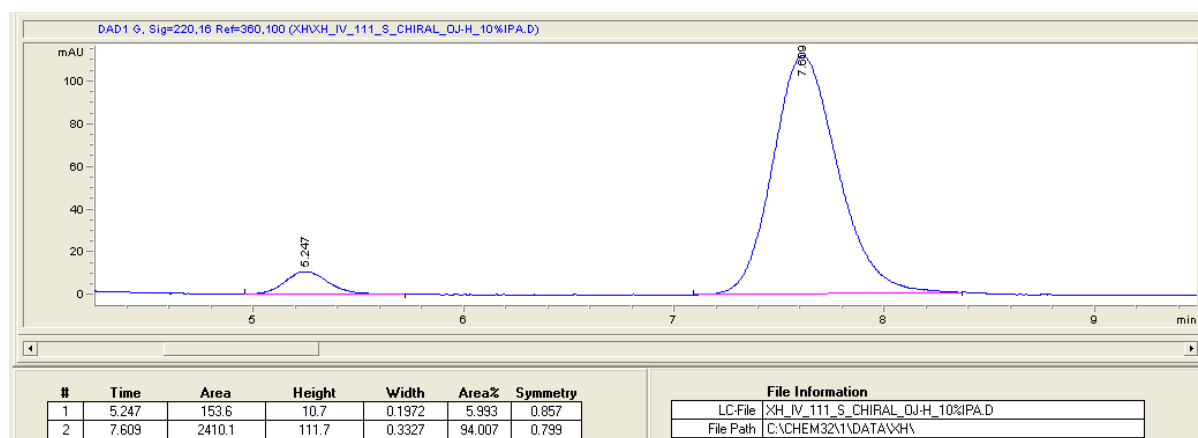


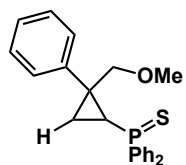


rac-3ia

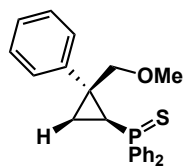
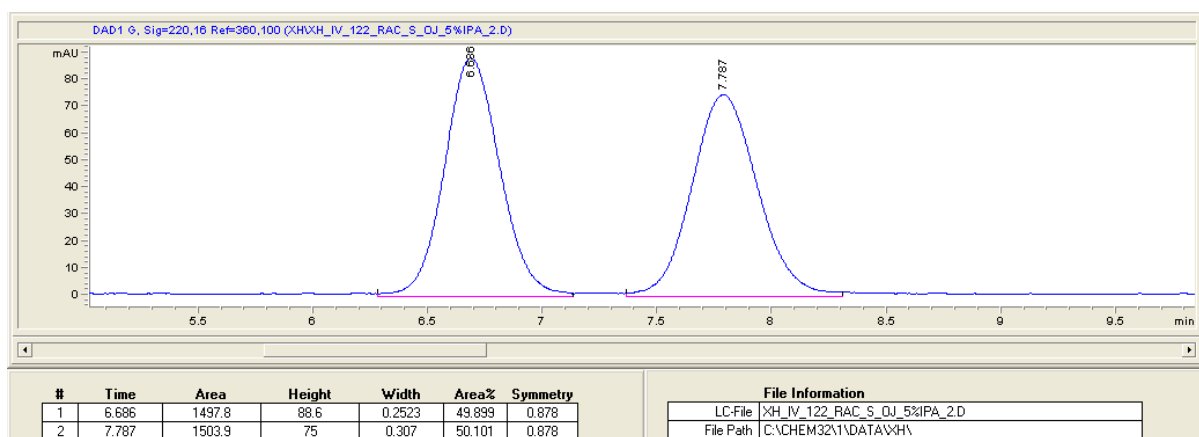


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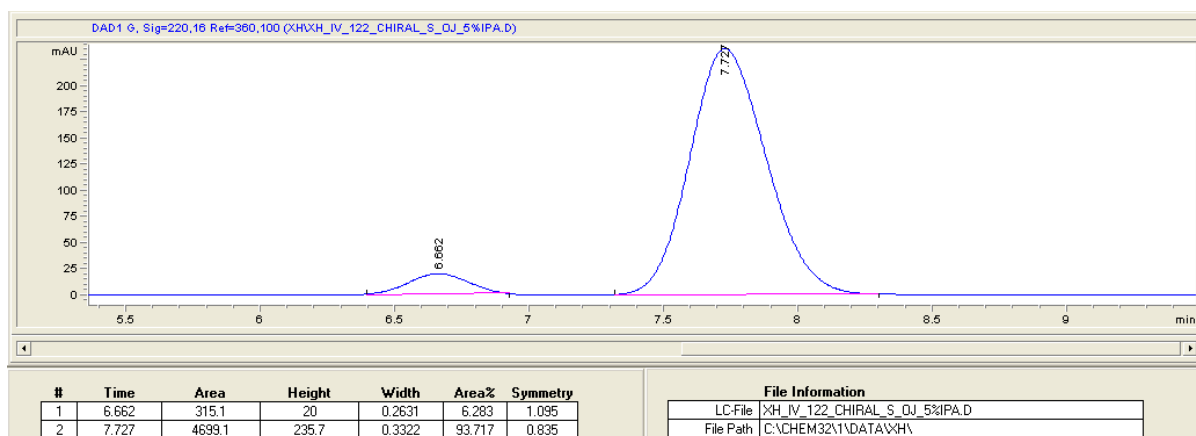


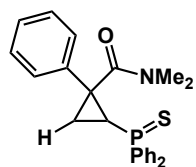


rac-3ja

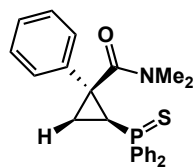
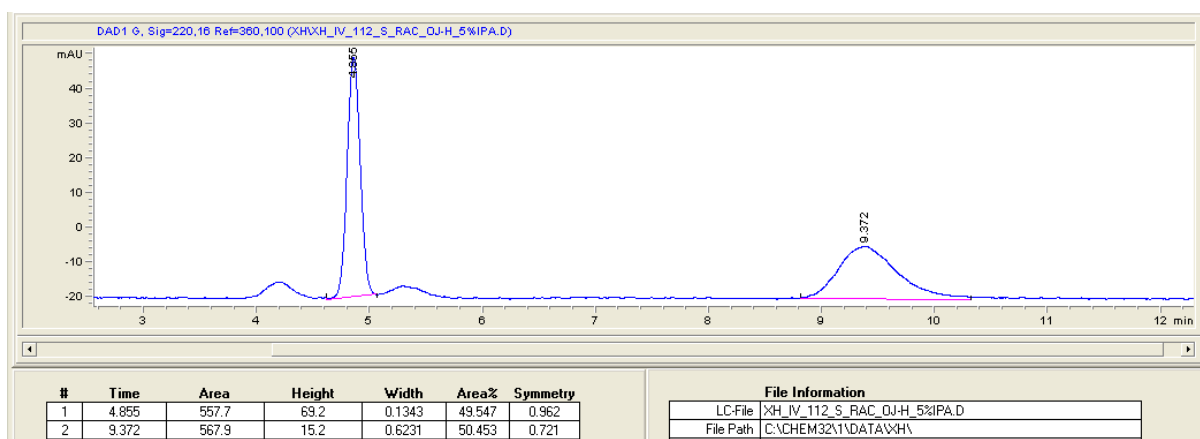


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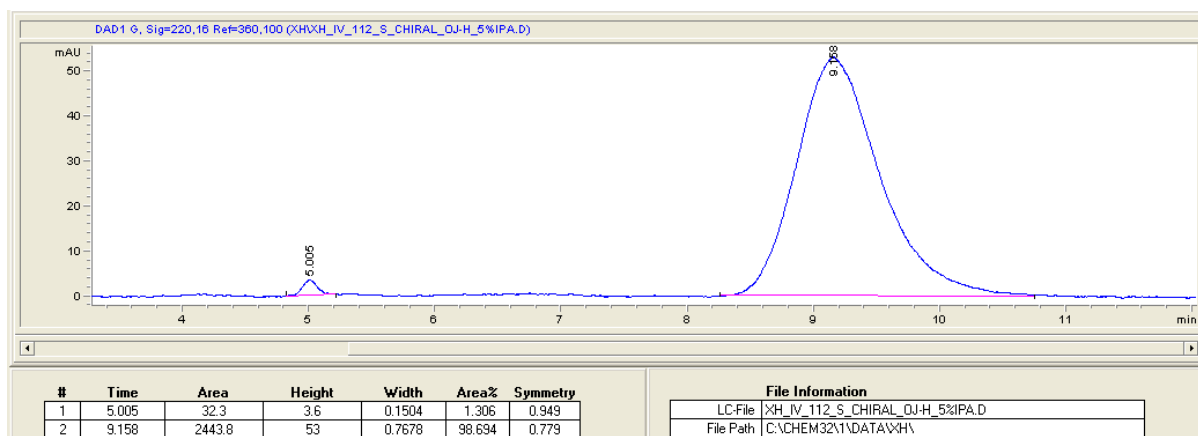




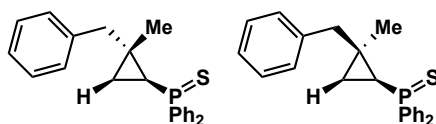
rac-3ka



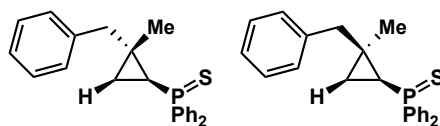
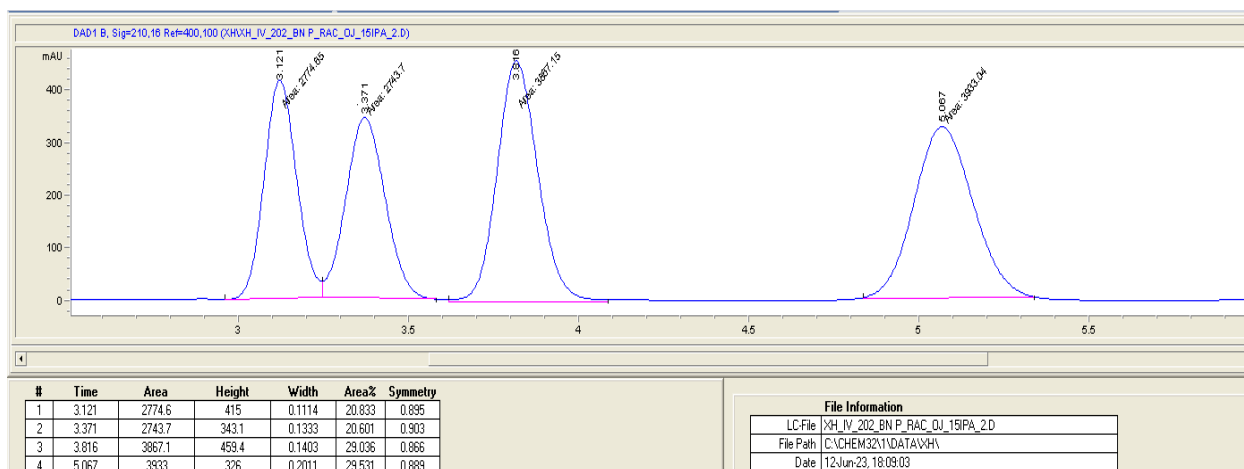
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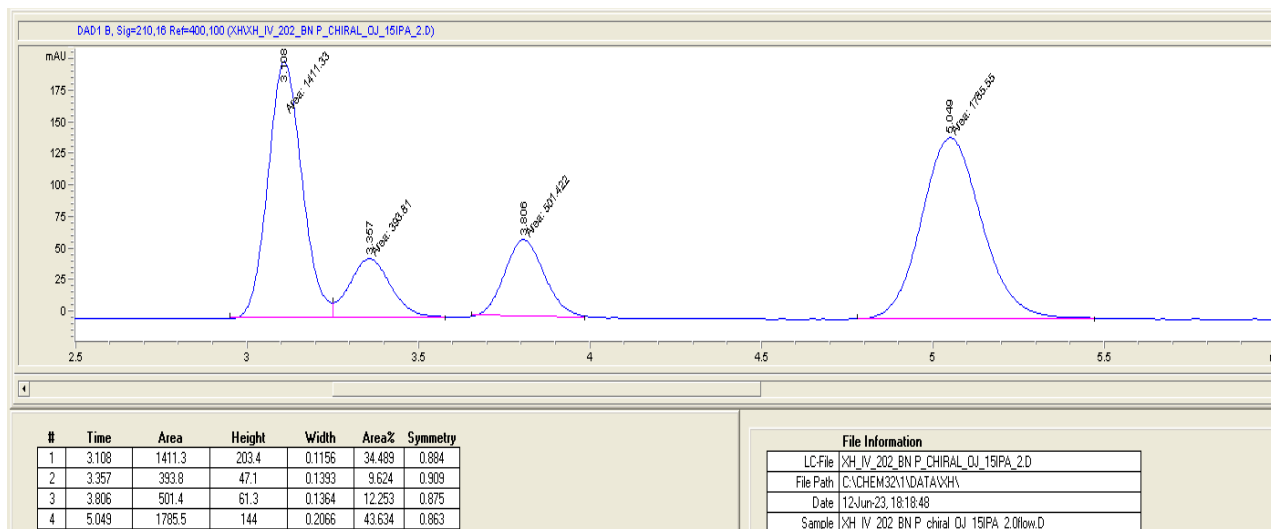
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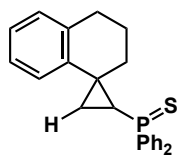


rac-3la

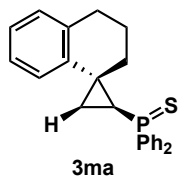
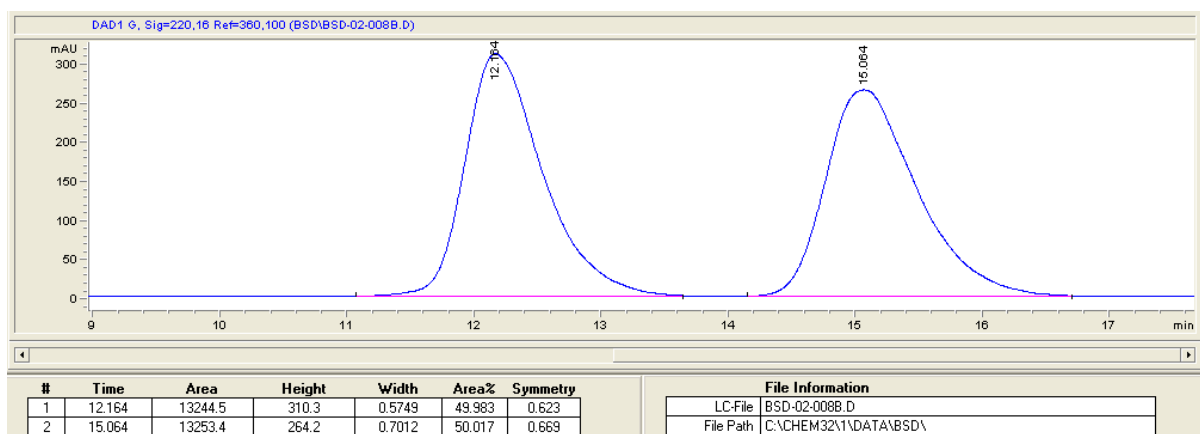


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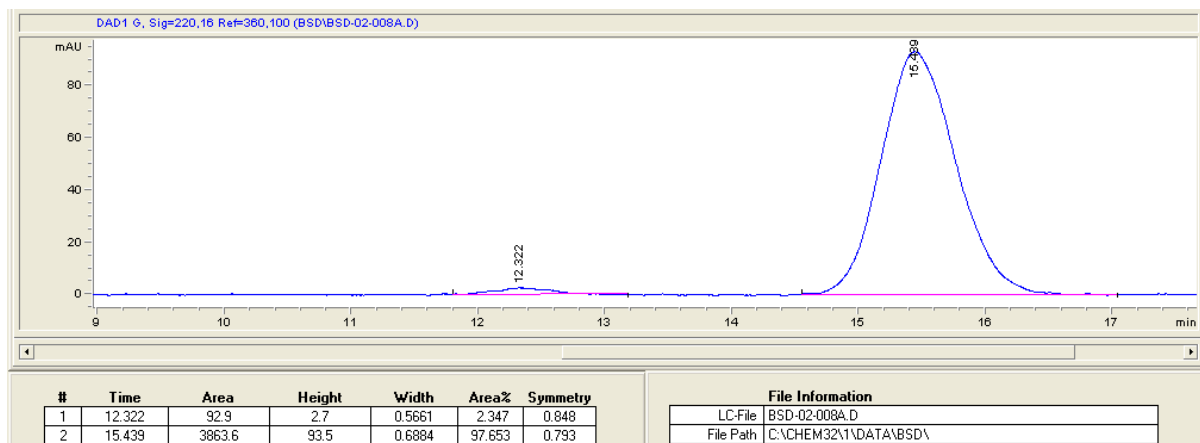


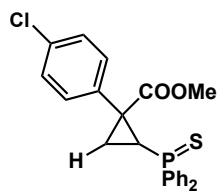


rac-3ma

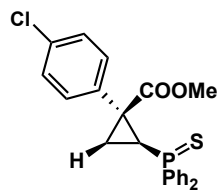
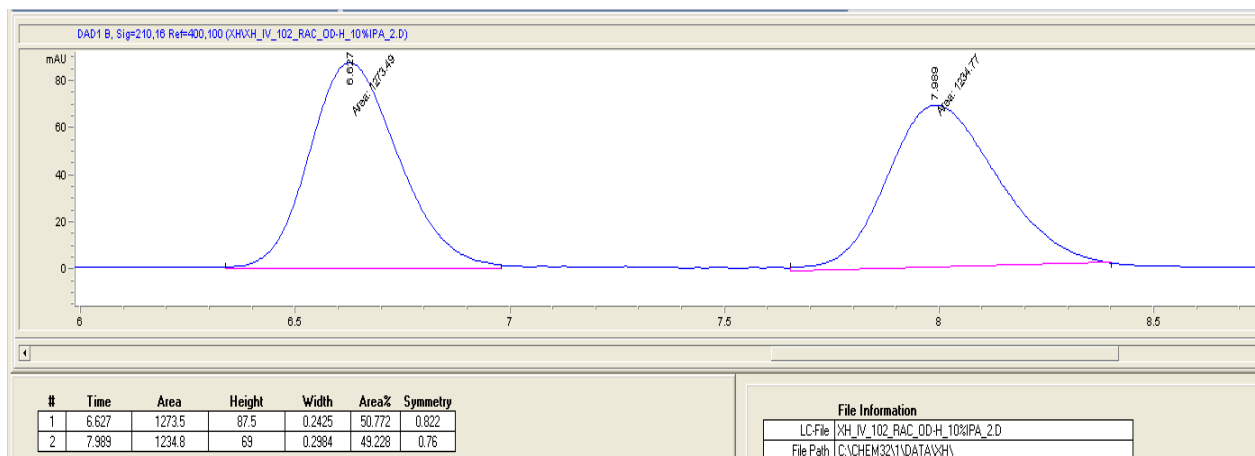


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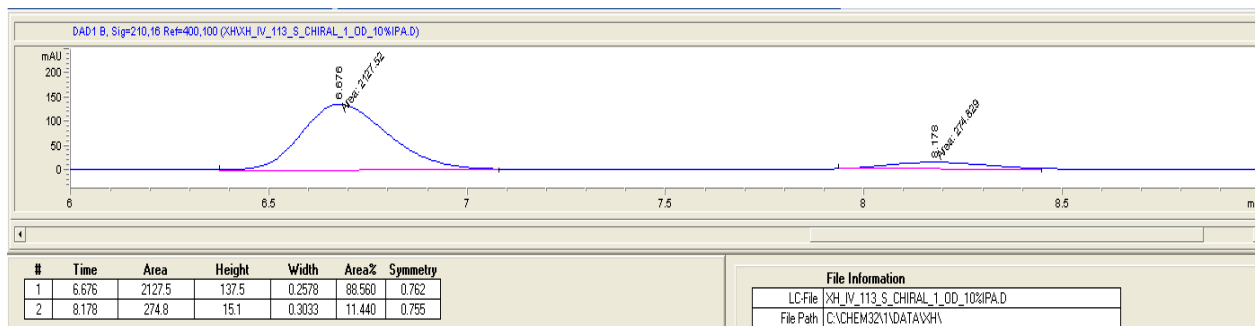


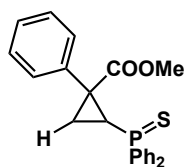


rac-3oa

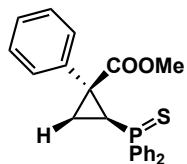
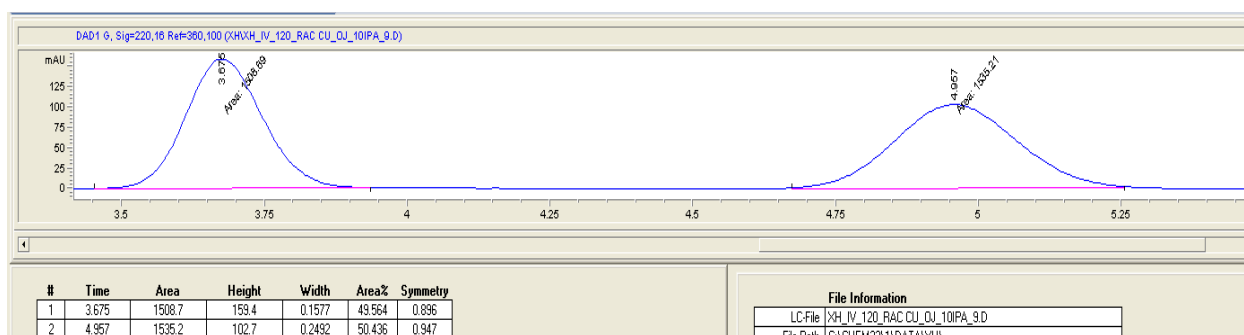


3oa

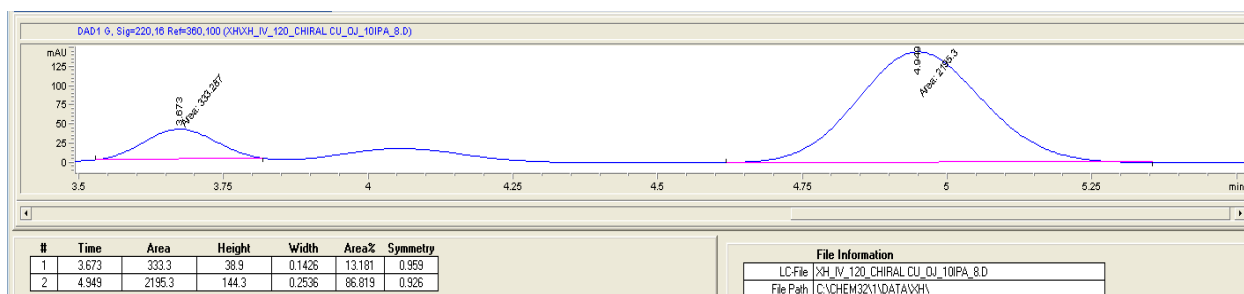


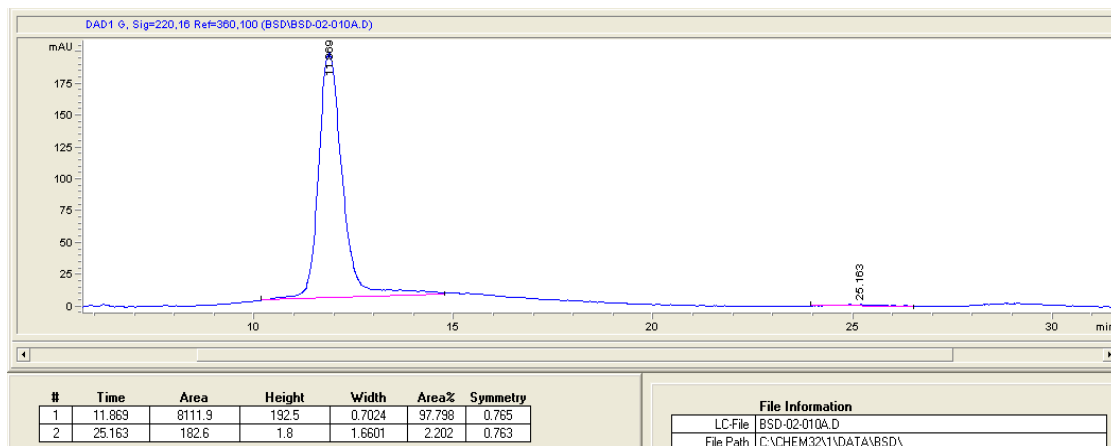
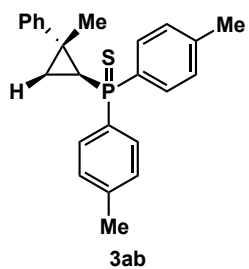
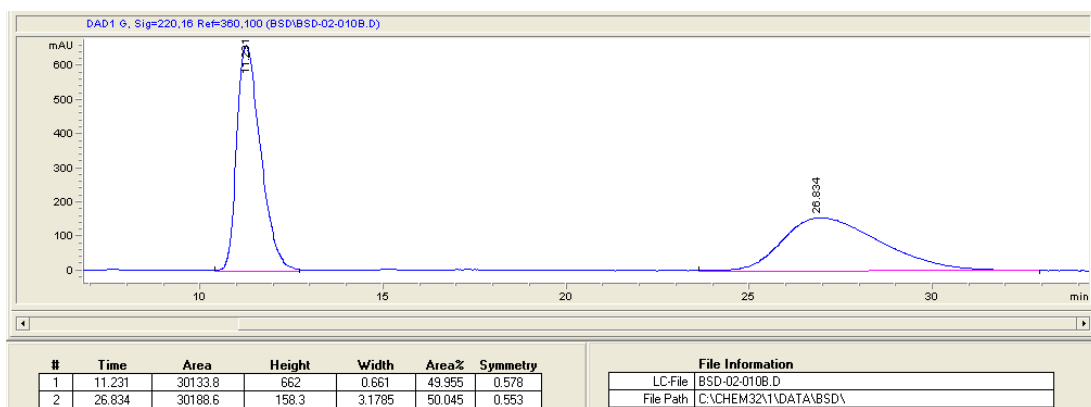
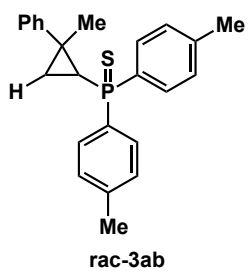


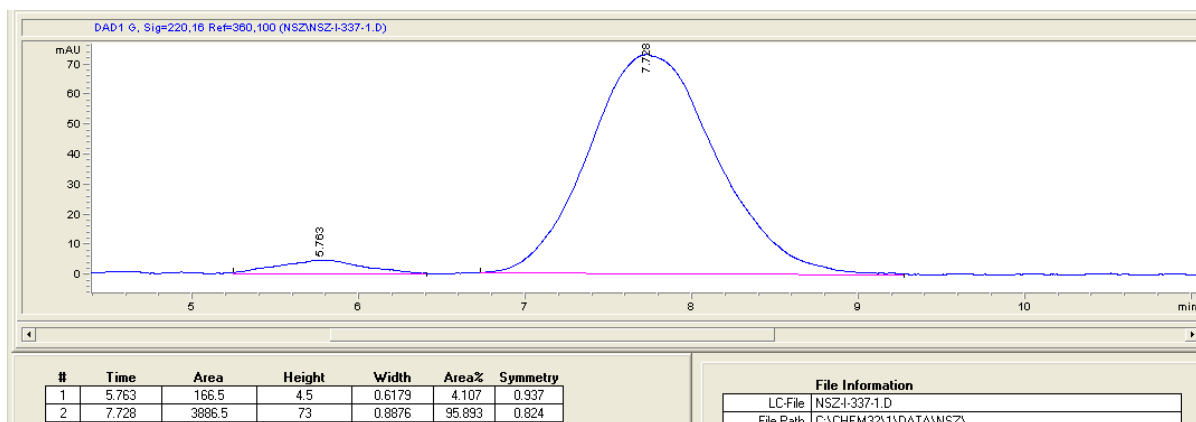
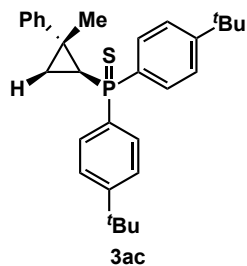
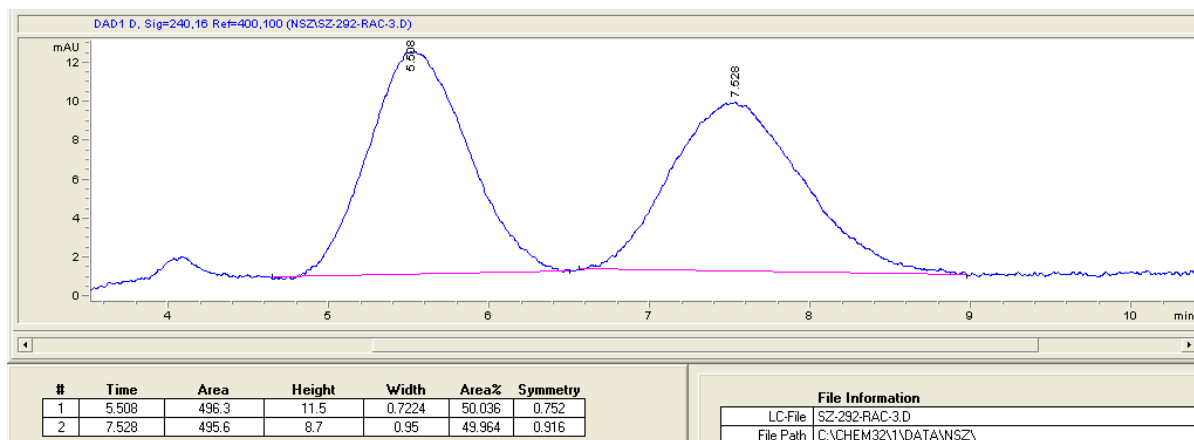
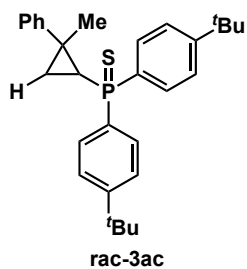
rac-3pa

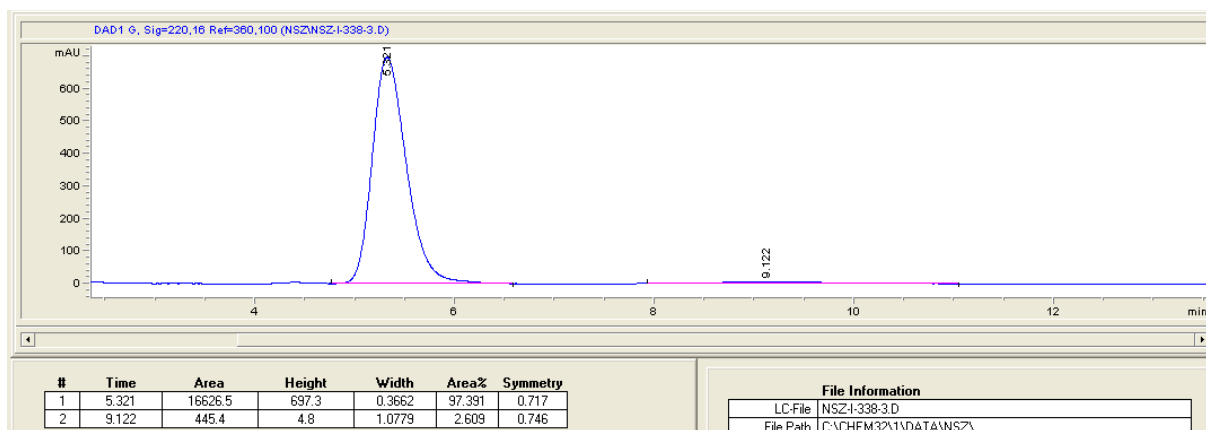
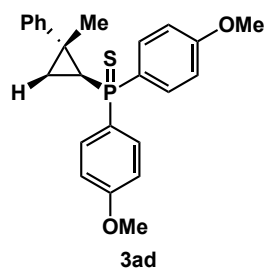
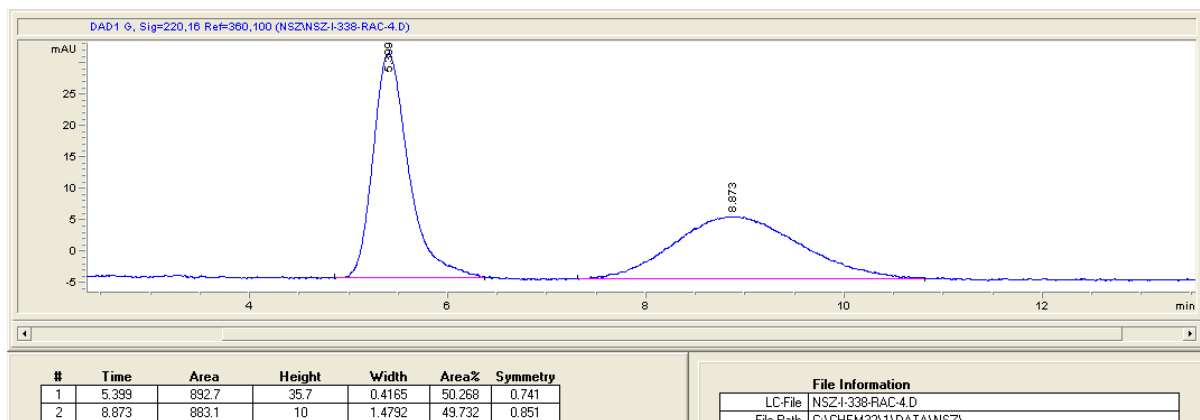
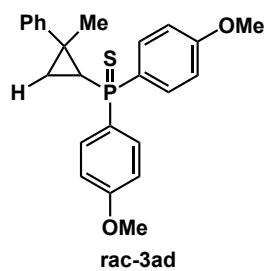


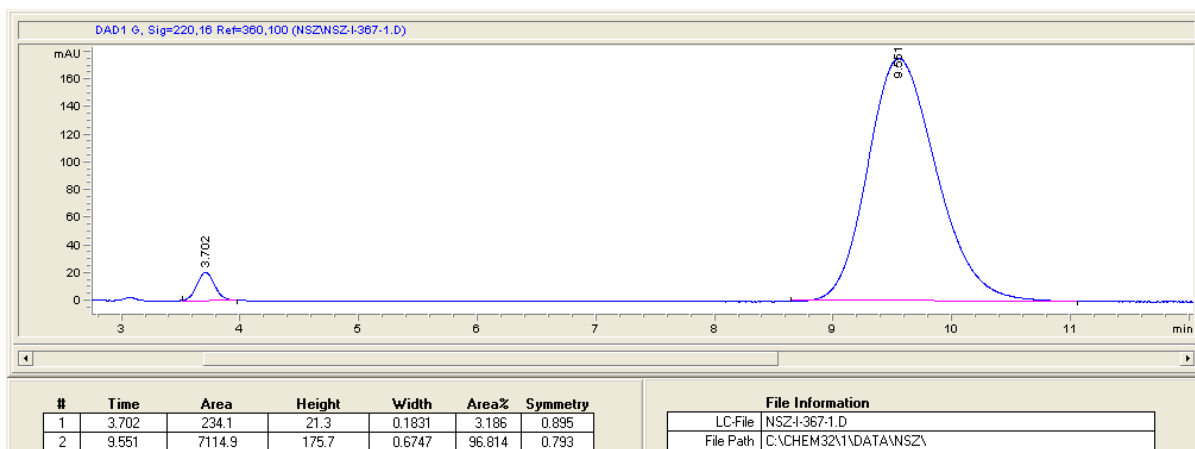
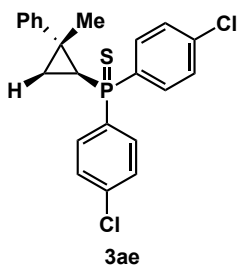
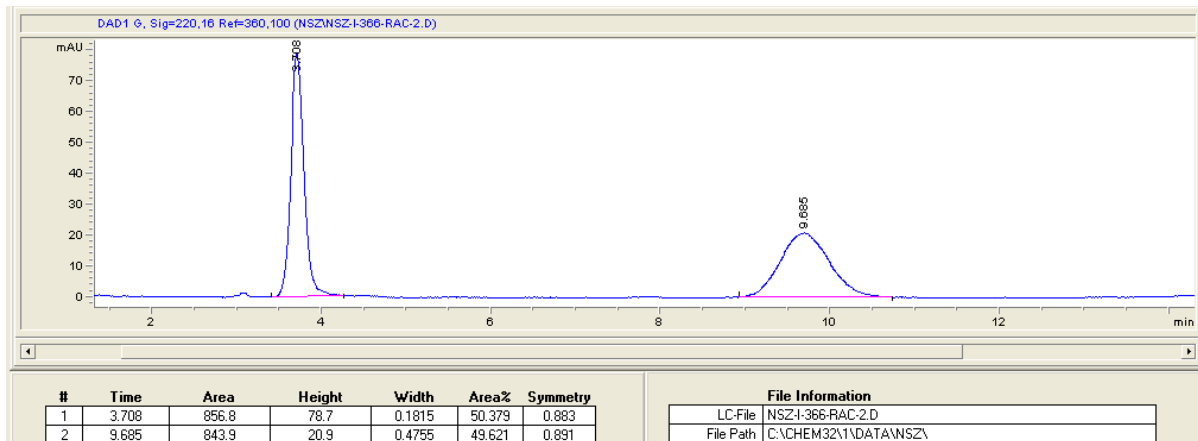
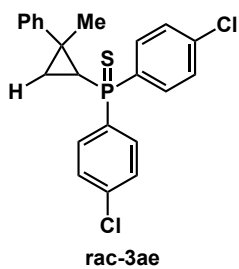
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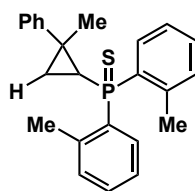




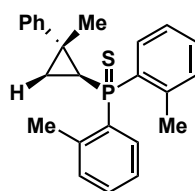
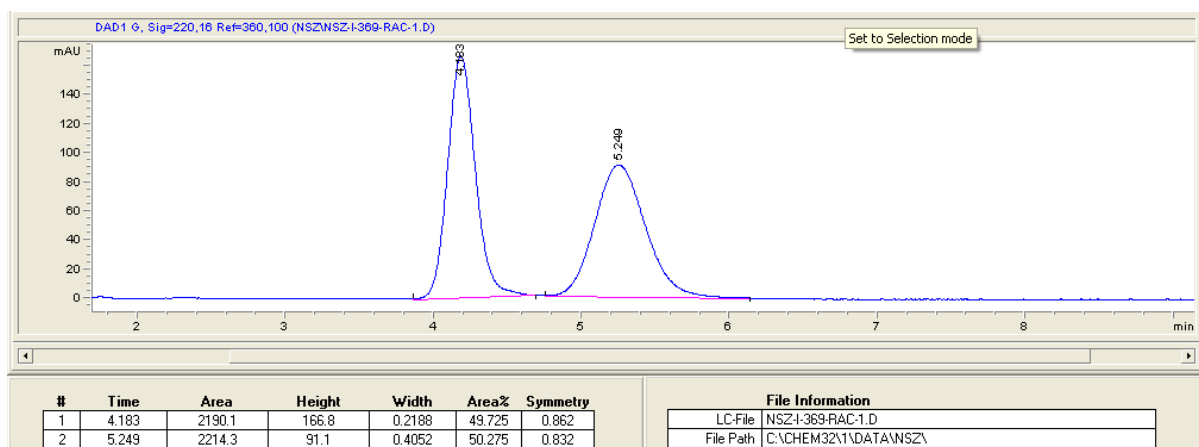




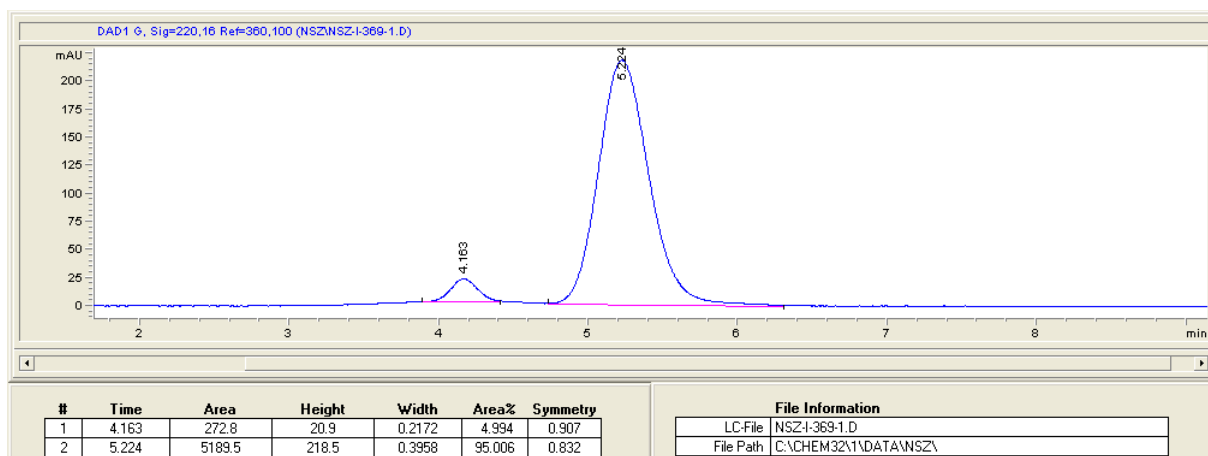


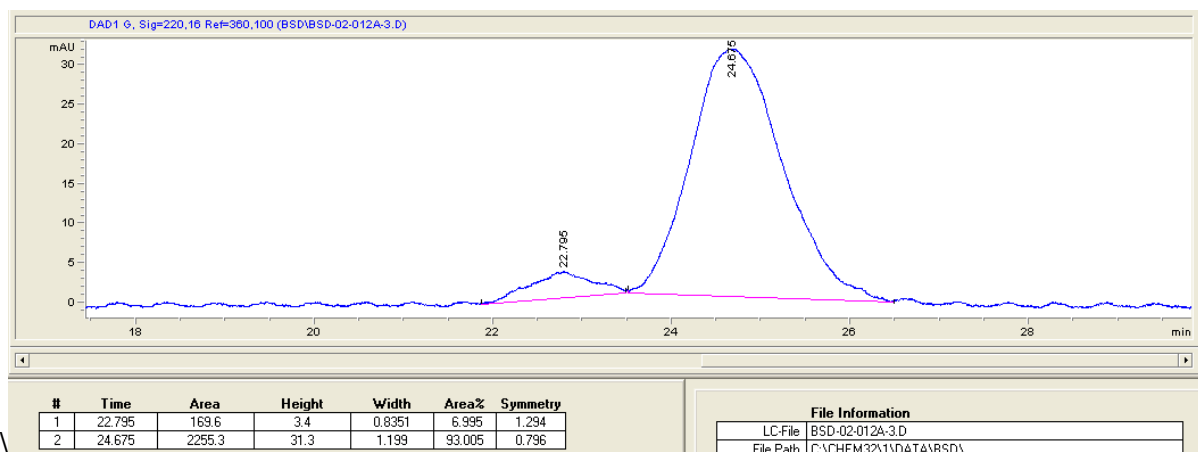
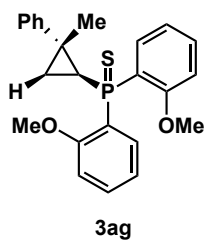
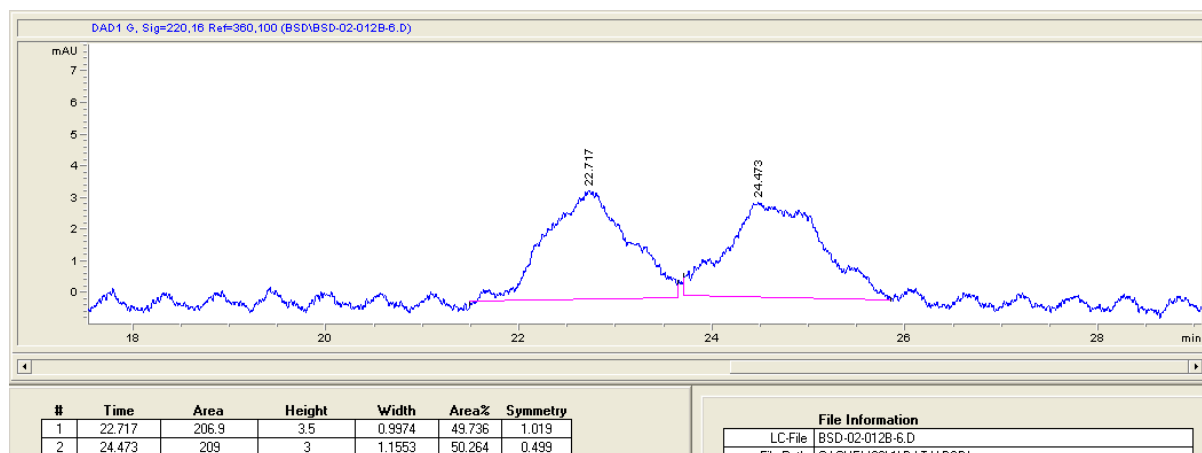
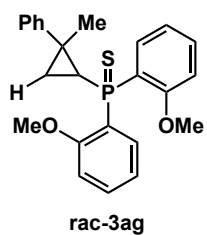


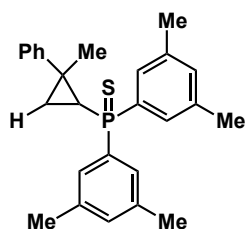
rac-3af



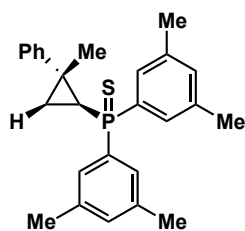
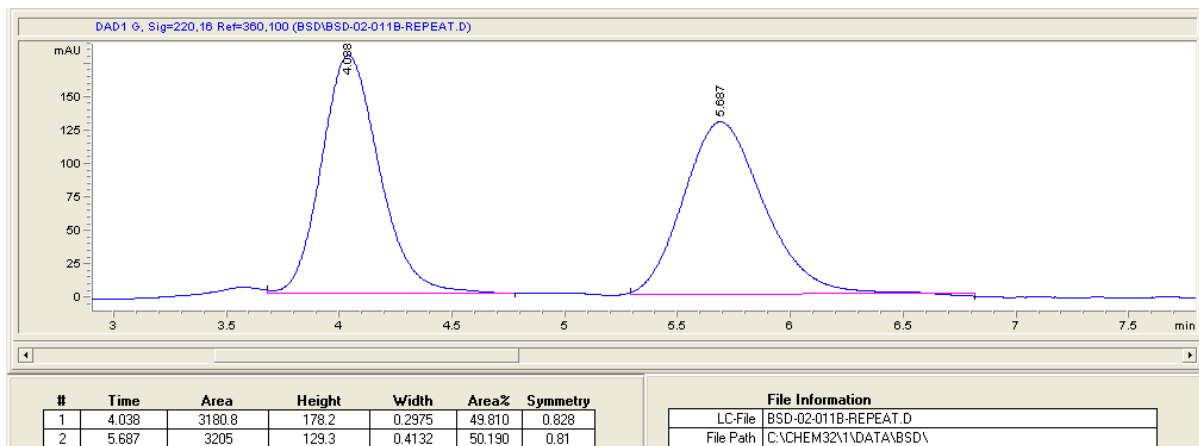
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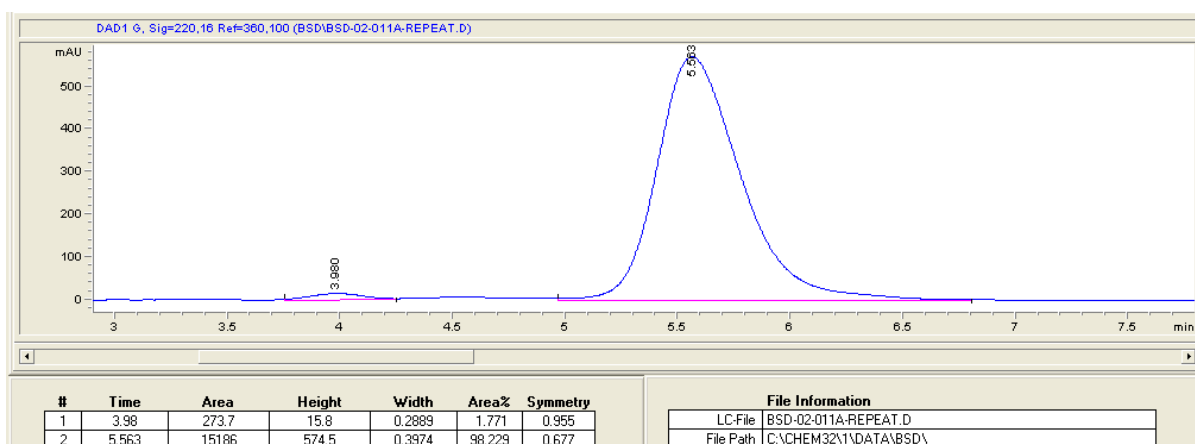


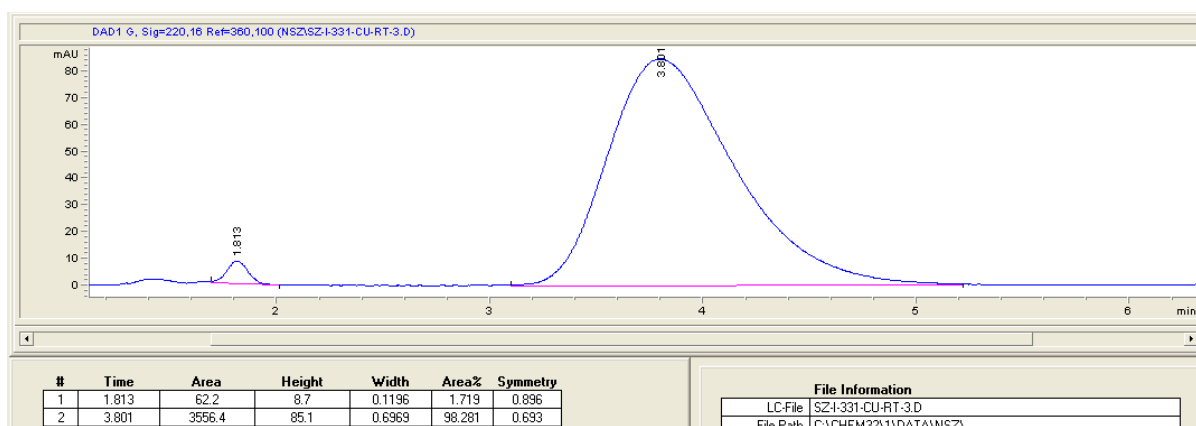
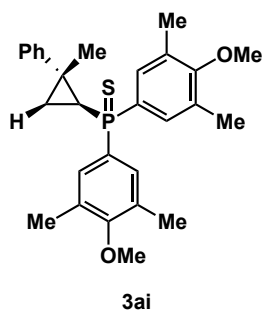
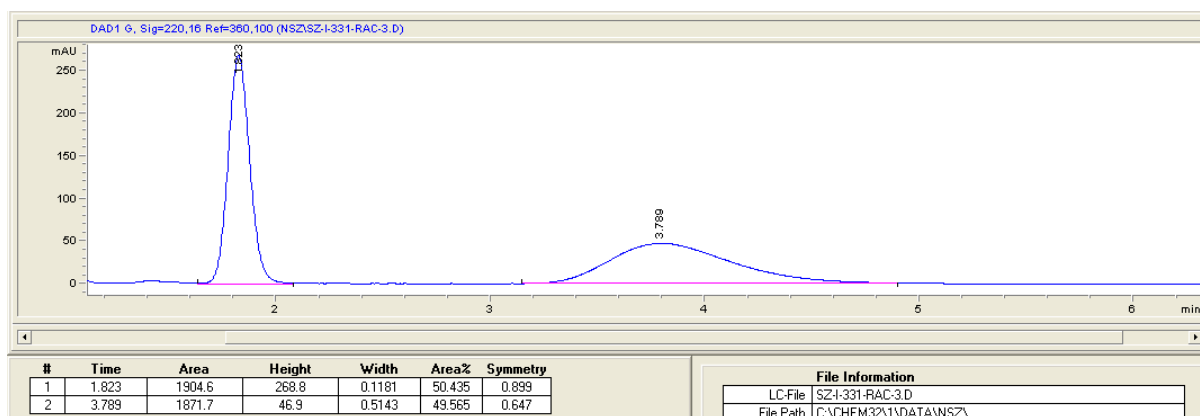
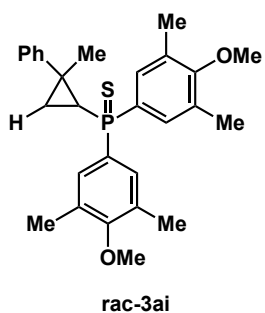


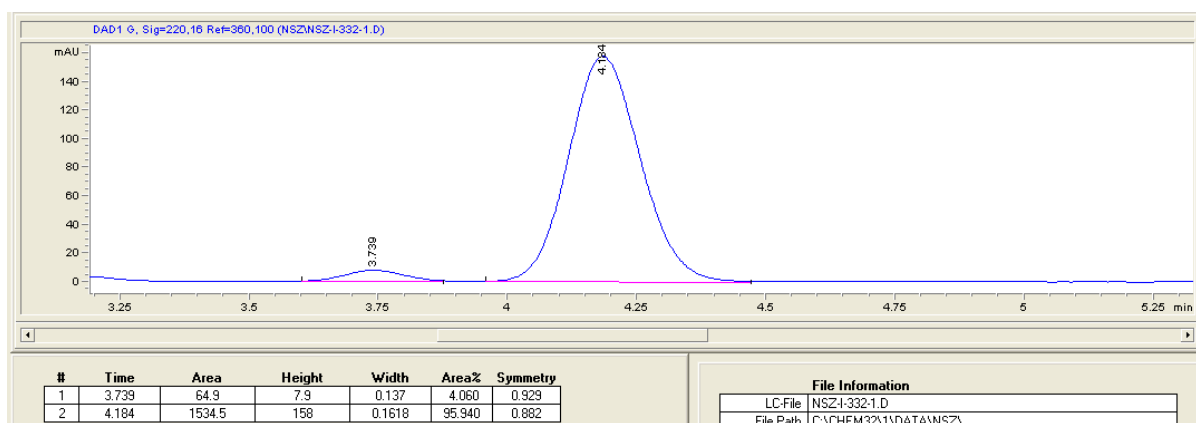
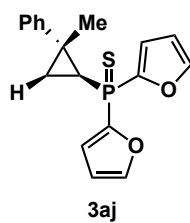
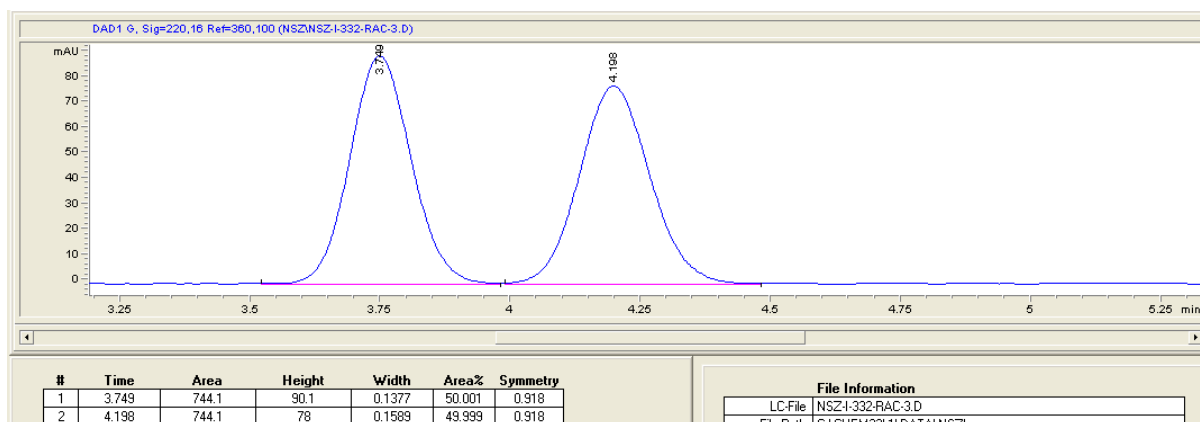
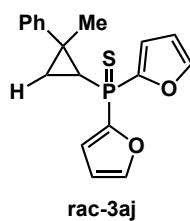
rac-3ah

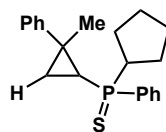


3ah

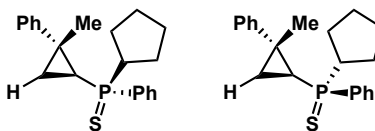
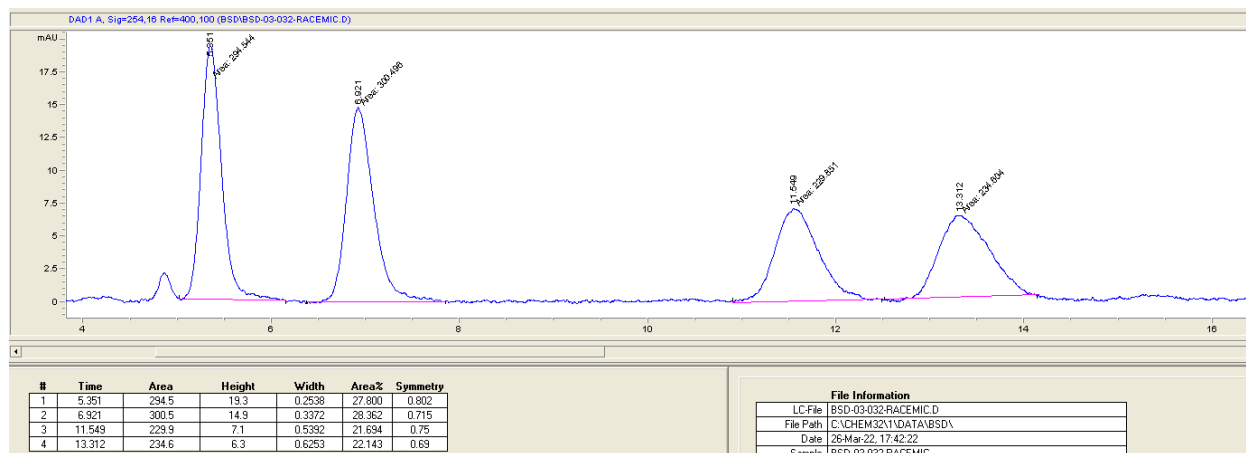




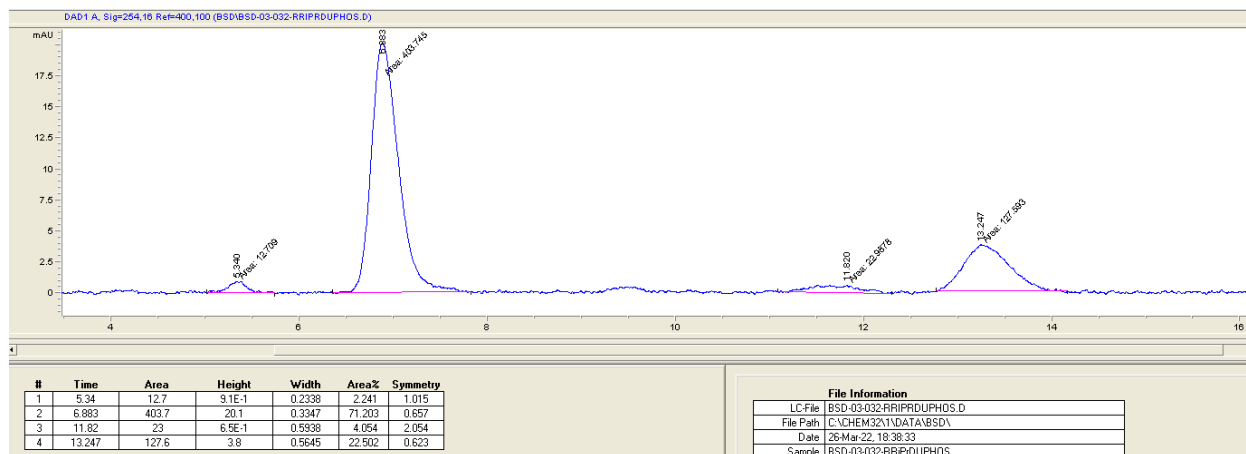




rac-3al



3al



11. XYZ File for Computational Models

124				C	3.1927880	2.2725850	
Intermediate "5aH+"					0.3304110		
<i>Thermal Free Energy Correction = 0.979136</i>				C	2.0393480	2.2199410	-
<i>Electronic Energy = -4608.00884797</i>					2.2459290		
<i>Corrected Free Energy = -4607.02971197</i>				C	2.7624160	3.6159610	-
C	4.9724030	-2.4379750	-		0.3138090		
2.3165650				C	2.8709280	3.4616680	-
C	3.9165650	-2.7009620	-		1.8396010		
1.4292950				H	1.7125020	3.8276830	-
C	3.1020290	-1.6586630	-		0.0342680		
0.9355030				H	3.3672280	4.4555300	
C	3.3667040	-0.3201160	-		0.0704640		
1.3585980				H	2.5383070	4.3697410	-
C	4.4256290	-0.0733690	-		2.3726820		
2.2577500				H	3.9311430	3.2975740	-
C	5.2286050	-1.1211400	-		2.1153540		
2.7330830				P	2.2625130	1.0427800	-
H	5.5897180	-3.2650410	-		0.7791680		
2.6883530				P	1.6933120	-1.9693620	
H	3.7204360	-3.7351970	-		0.2377950		
1.1317220				Cu	0.5113920	-0.0393040	
H	4.6200780	0.9518460	-		0.2068180		
2.5955930				P	-1.2939810	1.1578670	
H	6.0481080	-0.9110640	-		0.7081290		
3.4313970				C	-2.5373660	0.4889520	
C	0.9929970	-3.6842870	-		1.8802640		
0.1062550				C	-3.8695700	0.9547020	
C	2.5126900	-2.5008960			1.8739940		
1.8516760				C	-2.1777500	-0.5830400	
C	1.7881880	-4.6897360			2.7225230		
0.7897080				C	-4.8296820	0.3490650	
C	2.9174540	-3.9642670			2.7002100		
1.5625030				H	-4.1570990	1.7795340	
H	1.0914250	-5.1702820			1.2113410		
1.5008160				C	-3.1366680	-1.1799150	
H	2.2118510	-5.5010390			3.5572600		
0.1685480				H	-1.1497520	-0.9641460	
H	3.1806770	-4.5013940			2.6930530		
2.4911270				C	-4.4645550	-0.7175230	
H	3.8370070	-3.9450910			3.5428920		
0.9516140				H	-5.8664040	0.7088080	
					2.6875530		

H	-2.8515210	-2.0138730		N	-5.3404730	-0.3609050	-
4.2111050				1.2797930			
H	-5.2169630	-1.1888150		C	-2.9315830	-1.0765730	-
4.1876020				1.4972230			
C	-0.8007710	2.8311180		H	-2.9519690	-1.5747100	-
1.2848630				2.4875290			
C	-1.1816790	3.9806390		H	-1.9737710	-0.5348750	-
0.5593510				1.4630290			
C	0.0616160	2.9645820		H	-4.1532510	3.0769350	-
2.3953680				2.4396950			
C	-0.6972500	5.2455690		H	-6.6694010	2.7435400	-
0.9360160				1.8697960			
H	-1.8501360	3.8850120	-	C	-5.8332070	-1.6758700	-
0.3055950				0.8255850			
C	0.5335620	4.2304330		H	-5.7808320	-1.7385300	
2.7755440				0.2845450			
H	0.3662360	2.0745320		H	-6.9063910	-1.6985700	-
2.9614000				1.0883920			
C	0.1599140	5.3721970		H	-6.4138150	1.0333280	-
2.0425440				0.0877530			
H	-0.9941470	6.1342850		C	-2.9923630	-2.1335050	-
0.3650330				0.3758820			
H	1.1998590	4.3272640		H	-3.3808280	-1.6630090	
3.6420280				0.5438250			
H	0.5360560	6.3601420		H	-1.9645260	-2.4630550	-
2.3357890				0.1313160			
H	-2.1281560	1.4554510	-	C	-5.1646780	-2.9096780	-
0.4334190				1.4543310			
C	-4.0178960	-0.0037230	-	H	-5.8920820	-3.7422840	-
1.4721160				1.4271030			
C	-4.5195070	2.3342790	-	H	-4.9804880	-2.6930760	-
1.7021180				2.5237130			
C	-5.9560770	1.9142920	-	C	-3.8626380	-3.3414000	-
2.0313240				0.7530320			
H	-4.4984150	2.8530540	-	H	-4.1012940	-3.9226310	
0.7156370				0.1594760			
C	-6.3312830	0.7205640	-	H	-3.3000430	-4.0201810	-
1.1526350				1.4248440			
H	-6.0202330	1.6138080	-	C	0.8266760	-4.0841030	-
3.0948360				1.5928110			
H	-7.3184020	0.3196100	-	H	1.8307460	-4.3072400	-
1.4493720				2.0032580			
N	-3.5922770	1.2143760	-	C	-0.0243380	-5.3645800	-
1.6736520				1.6908750			

H	-1.0470940	-5.1742130	-	H	0.0670510	0.2972400	-
1.3082260				2.3335530			
H	-0.1086220	-5.6966660	-	H	-1.2665870	1.2846290	-
2.7426960				2.9817510			
H	0.4116570	-6.1935330	-	H	0.1820730	0.9305940	-
1.1032380				3.9992000			
C	0.2014710	-2.9599790	-	C	0.2255150	3.6148540	-
2.4376860				3.4328650			
H	0.8473850	-2.0627180	-	H	-0.8619410	3.6805250	-
2.4784010				3.6267920			
H	0.0385180	-3.3024640	-	H	0.5533440	4.5900020	-
3.4767210				3.0288900			
H	-0.7766460	-2.6588390	-	H	0.7333530	3.4532580	-
2.0209570				4.4044800			
H	-0.0321660	-3.5804290		H	2.4501700	1.7437780	-
0.3032330				3.1567030			
C	1.5322920	-2.2580070		C	4.7150850	2.0172360	
3.0390440				0.4831870			
H	0.5071690	-2.5426390		H	5.1511190	1.8224250	-
2.7160080				0.5161870			
C	1.8805740	-3.1057060		C	5.4463060	3.2309980	
4.2760450				1.0877860			
H	1.2175920	-2.8374210		H	5.4358500	4.1051560	
5.1200360				0.4119320			
H	1.7621450	-4.1876120		H	4.9798000	3.5301400	
4.0848230				2.0476030			
H	2.9260760	-2.9231840		H	6.5036080	2.9752430	
4.5937830				1.2890790			
C	1.5225230	-0.7651570		C	4.9524520	0.7760520	
3.4147870				1.3634070			
H	1.2839540	-0.1262410		H	4.4396450	-0.1172700	
2.5413580				0.9655670			
H	0.7738810	-0.5554570		H	6.0314520	0.5449740	
4.2009640				1.4363750			
H	2.5182450	-0.4603750		H	4.5715940	0.9620470	
3.7918970				2.3877270			
H	3.4169220	-1.8836550		H	2.7349590	2.1893780	
2.0147650				1.3349280			
C	0.5148200	2.4536630	-				
2.4650560				124			
H	0.0704660	2.7161130	-	TS-dep			
1.4844610				<i>Thermal Free Energy Correction = 0.975953</i>			
C	-0.1668880	1.1708000	-	<i>Electronic Energy = -4607.99744170</i>			
2.9750250				<i>Corrected Free Energy = -4607.02148870</i>			

C	5.0831270	-2.3071760	-	H	2.0882970	4.0799010	-
2.4275890				0.1470030			
C	4.0576980	-2.5640420	-	H	3.7904280	4.5797550	-
1.5037740				0.0933620			
C	3.2843390	-1.5142910	-	H	2.9208680	4.4431450	-
0.9604680				2.5177980			
C	3.5486660	-0.1760490	-	H	4.2209170	3.2700220	-
1.3838590				2.2234820			
C	4.5801460	0.0651310	-	P	2.4593920	1.1965080	-
2.3159480				0.7824650			
C	5.3493110	-0.9886840	-	P	1.9093990	-1.8090840	
2.8321550				0.2556730			
H	5.6693350	-3.1396360	-	Cu	0.7151870	0.1217970	
2.8360200				0.2007160			
H	3.8507740	-3.5989190	-	P	-1.3232010	0.9034920	
1.2163800				0.6318210			
H	4.7779140	1.0907750	-	C	-2.3701310	-0.2567200	
2.6500730				1.6047320			
H	6.1475020	-0.7819100	-	C	-3.6959630	0.0792750	
3.5557430				1.9631210			
C	1.2064490	-3.5146450	-	C	-1.8938620	-1.5505470	
0.0989960				1.9025700			
C	2.7438350	-2.3944500		C	-4.5218890	-0.8599860	
1.8442620				2.6014670			
C	2.1149040	-4.5479820		H	-4.0778160	1.0848990	
0.6406070				1.7462240			
C	3.2075440	-3.8234670		C	-2.7182080	-2.4924210	
1.4745890				2.5405480			
H	1.4884910	-5.1822470		H	-0.8642800	-1.8043860	
1.2942080				1.6205890			
H	2.5872030	-5.2288220	-	C	-4.0361060	-2.1501240	
0.0930320				2.8893730			
H	3.4795840	-4.4046820		H	-5.5481160	-0.5860830	
2.3731080				2.8791960			
H	4.1331360	-3.7346180		H	-2.3314160	-3.4943380	
0.8795880				2.7681680			
C	3.4479800	2.4313610		H	-4.6826240	-2.8822980	
0.2805620				3.3891900			
C	2.2454960	2.3510510	-	C	-1.2626060	2.4487730	
2.2718780				1.6288470			
C	3.1153370	3.7723020	-	C	-1.1721690	3.6960080	
0.4258910				0.9678350			
C	3.1830300	3.5372800	-	C	-1.2260430	2.4208810	
1.9429300				3.0413670			

C	-1.0385380	4.8863510		H	-6.3132110	3.4633880	-
1.7020210				0.8859700			
H	-1.2135960	3.7368020	-	C	-6.4010830	-1.1361950	-
0.1288420				1.2745700			
C	-1.1028470	3.6136340		H	-6.4562600	-1.5436130	-
3.7730190				0.2416010			
H	-1.2964960	1.4601020		H	-7.4293250	-0.8463160	-
3.5670040				1.5556470			
C	-1.0036940	4.8489000		H	-6.4114250	1.2904280	
3.1074590				0.3258410			
H	-0.9723810	5.8471110		C	-3.7169530	-2.2662950	-
1.1750720				0.9675550			
H	-1.0797510	3.5778860		H	-4.0462330	-2.0269410	
4.8698630				0.0590390			
H	-0.9047100	5.7785120		H	-2.7914830	-2.8593660	-
3.6816620				0.8545180			
H	-2.4267850	1.2423120	-	C	-5.9229000	-2.2219460	-
0.5444370				2.2489410			
C	-4.2670850	0.2398800	-	H	-6.7932400	-2.8573790	-
1.3741420				2.4970150			
C	-4.2929030	2.6330740	-	H	-5.6203120	-1.7308660	-
0.9112620				3.1935750			
C	-5.7699580	2.5960550	-	C	-4.7843120	-3.0978140	-
1.3026430				1.6966670			
H	-4.1831550	2.8354370		H	-5.1971170	-3.8545060	-
0.1756080				1.0012810			
C	-6.3850960	1.2951490	-	H	-4.3237160	-3.6557280	-
0.7852270				2.5356240			
H	-5.8696710	2.6304740	-	C	0.8768600	-3.8226050	-
2.4043950				1.5776160			
H	-7.4266320	1.1937470	-	H	1.8327950	-3.9649670	-
1.1388720				2.1192890			
N	-3.6177480	1.3783190	-	C	0.0705080	-5.1313320	-
1.2290600				1.6718860			
N	-5.6242960	0.1232310	-	H	-0.9033320	-5.0197200	-
1.2611540				1.1533240			
C	-3.3814110	-0.9553420	-	H	-0.1319390	-5.3914310	-
1.7020390				2.7280260			
H	-3.4013000	-1.1103580	-	H	0.6089970	-5.9778280	-
2.7996730				1.2070720			
H	-2.3489710	-0.6443760	-	C	0.1126270	-2.6676730	-
1.4721310				2.2506280			
H	-3.7647880	3.4545980	-	H	0.7290890	-1.7516680	-
1.4335110				2.3236830			

H	-0.1959980	-2.9487130	-
3.2753040			
H	-0.7984360	-2.4173980	-
1.6737450			
H	0.2338380	-3.4595290	
0.4315660			
C	1.7546590	-2.2850140	
3.0433850			
H	0.7912510	-2.7528890	
2.7501650			
C	2.2792450	-3.0380990	
4.2816780			
H	1.6046560	-2.8688750	
5.1417000			
H	2.3431090	-4.1286340	
4.1162160			
H	3.2864710	-2.6710030	
4.5618730			
C	1.4827030	-0.8154240	
3.4132220			
H	1.0341220	-0.2502920	
2.5730270			
H	0.7798560	-0.7516370	
4.2643390			
H	2.4251320	-0.3105390	
3.7036120			
H	3.6168080	-1.7477790	
2.0566040			
C	0.7330150	2.6885730	-
2.4342660			
H	0.3328800	2.9461660	-
1.4323060			
C	-0.0390290	1.4587450	-
2.9463040			
H	0.1304190	0.5737860	-
2.3030110			
H	-1.1278110	1.6520410	-
2.9579350			
H	0.2859630	1.2009410	-
3.9740470			
C	0.4868710	3.8873140	-
3.3679000			
H	-0.5995100	4.0274470	-
3.5264850			

H	0.8892000	4.8305040	-
2.9555710			
H	0.9533130	3.7164470	-
4.3584910			
H	2.5807320	1.8219620	-
3.1842220			
C	4.9504930	2.0898730	
0.4660390			
H	5.3895620	1.8463290	-
0.5211080			
C	5.7444810	3.2706330	
1.0575480			
H	5.8019530	4.1284700	
0.3633420			
H	5.2821220	3.6195010	
2.0022910			
H	6.7801740	2.9539220	
1.2831580			
C	5.0999240	0.8577890	
1.3775050			
H	4.5480780	-0.0143760	
0.9862390			
H	6.1629170	0.5699510	
1.4788260			
H	4.7077920	1.0856690	
2.3889560			
H	2.9774420	2.4172950	
1.2829200			

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Intermediate "5a"

Thermal Free Energy Correction = 0.983949

Electronic Energy = -4608.01314663

Corrected Free Energy = -4607.02919763

C	6.4070030	1.2858600	
0.1500090			
C	5.1321080	1.8586950	
0.0261170			
C	3.9641550	1.0632670	
0.0292540			
C	4.0928680	-0.3489470	
0.2097630			
C	5.3845390	-0.9072760	
0.3247630			

C	6.5347250	-0.1049930		P	2.2665950	1.8051760	-
	0.2863990				0.1614780		
H	7.2966630	1.9277670		Cu	0.8637430	0.1459090	
	0.1458120				0.5033050		
H	5.0508160	2.9458500	-	P	-1.3409340	-0.3797710	
	0.0512170				0.6749020		
H	5.4994140	-1.9868540		C	-2.2287720	0.8965580	-
	0.4630740				0.3255220		
H	7.5261460	-0.5654210		C	-3.2345960	0.6219250	-
	0.3798020				1.2858440		
C	2.3069000	3.4655830		C	-1.9541060	2.2601890	-
	0.7212670				0.0490480		
C	2.2324590	2.6224370	-	C	-3.9028750	1.6566490	-
	1.8645800				1.9633590		
C	2.8935910	4.5113880	-	H	-3.4717530	-0.4171560	-
	0.2787190				1.5364980		
C	3.1152670	3.8794540	-	C	-2.6288160	3.2948990	-
	1.6814460				0.7110850		
H	2.2045030	5.3729480	-	H	-1.1703980	2.5028350	
	0.3476290				0.6815970		
H	3.8494260	4.9102220		C	-3.6036490	3.0019610	-
	0.1114140				1.6844780		
H	2.9333860	4.6146230	-	H	-4.6549380	1.4090360	-
	2.4850250				2.7251760		
H	4.1688800	3.5708080	-	H	-2.3816140	4.3394410	-
	1.7923510				0.4805590		
C	2.3985110	-2.6651210	-	H	-4.1175940	3.8101950	-
	0.9502600				2.2192310		
C	3.0637870	-2.6485840		C	-1.2769580	-1.8729080	-
	1.7794530				0.4290370		
C	2.5268730	-4.0278550	-	C	-1.1928290	-3.1439240	
	0.2157080				0.1945210		
C	3.5060750	-3.8816850		C	-1.2404890	-1.8338510	-
	0.9568690				1.8452080		
H	1.5316670	-4.3045400		C	-1.0770530	-4.3224530	-
	0.1760780				0.5594910		
H	2.8294020	-4.8326870	-	H	-1.2199030	-3.2065530	
	0.9077980				1.2918110		
H	3.5460770	-4.7958620		C	-1.1372840	-3.0137040	-
	1.5760000				2.6009070		
H	4.5290780	-3.7276160		H	-1.2782170	-0.8678900	-
	0.5651260				2.3594030		
P	2.5638200	-1.3845750		C	-1.0541010	-4.2664110	-
	0.4567390				1.9648560		

H	-1.0102930	-5.2913000	-	C	-5.0288010	2.0182600	
	0.0472580				1.6432430		
H	-1.1063520	-2.9523220	-	H	-4.7963400	2.1988560	
	3.6968630				0.5799490		
H	-0.9681100	-5.1859770	-	H	-4.3150620	2.6367900	
	2.5567530				2.2152770		
H	-3.4008360	-1.4063800		C	-7.4986520	1.3954630	
	1.2217910				1.5044090		
C	-5.1531480	-0.4728720		H	-8.5025440	1.8551130	
	0.9135070				1.4470090		
C	-4.5214330	-2.6649450	-	H	-7.5807860	0.5704290	
	0.0953690				2.2382770		
C	-5.9742940	-2.7357770	-	C	-6.4693310	2.4426410	
	0.5539200				1.9653000		
H	-3.8308110	-2.5275740	-	H	-6.6782010	3.4134770	
	0.9496020				1.4758460		
C	-6.4388820	-1.3375580	-	H	-6.5872060	2.6050640	
	0.9642540				3.0542460		
H	-6.6196130	-3.1097230		C	2.9273640	3.4429340	
	0.2632670				2.1361100		
H	-7.5107000	-1.3473250	-	H	4.0142520	3.2554790	
	1.2238580				2.0263230		
N	-4.3572470	-1.5442760		C	2.7418330	4.8093220	
	0.8331160				2.8217570		
N	-6.2469640	-0.3659010		H	1.6634680	5.0317320	
	0.1379600				2.9511870		
C	-4.7468900	0.5419240		H	3.2128860	4.8107260	
	1.9649510				3.8228770		
H	-5.2317190	0.2447030		H	3.1912140	5.6284170	
	2.9175970				2.2304150		
H	-3.6605810	0.3971120		C	2.3319000	2.3185990	
	2.1152670				3.0036110		
H	-4.2074800	-3.5885310		H	2.5365330	1.3161740	
	0.4215800				2.5803470		
H	-6.0712090	-3.4290030	-	H	2.7565670	2.3460240	
	1.4074090				4.0248280		
C	-7.1862400	0.7853860		H	1.2322320	2.4316250	
	0.1310680				3.0872950		
H	-6.7959430	1.5545940	-	H	1.2253580	3.6749050	
	0.5661950				0.8510510		
H	-8.1212710	0.3954330	-	C	0.7469750	2.8693850	-
	0.3056960				2.2684750		
H	-5.8790370	-0.9789520	-	H	0.1958040	3.2470610	-
	1.8517890				1.3838250		

C	0.5988630	3.9203870	-
	3.3837340		
H	-0.4613100	3.9881420	-
	3.6926560		
H	0.9185840	4.9276690	-
	3.0593820		
H	1.1961320	3.6377420	-
	4.2734530		
C	0.0849930	1.5525130	-
	2.7036930		
H	0.1802850	0.7792930	-
	1.9206510		
H	-0.9924360	1.7033270	-
	2.8946410		
H	0.5624110	1.1711760	-
	3.6280420		
H	2.6895110	1.9442270	-
	2.6100000		
C	1.8647270	-2.8894100	
	2.7446930		
H	0.9647260	-3.0909900	
	2.1271320		
C	1.5845540	-1.6355770	
	3.5926270		
H	1.3547080	-0.7597330	
	2.9575040		
H	0.7189240	-1.8009190	
	4.2612100		
H	2.4637530	-1.3884960	
	4.2206500		
C	2.0948390	-4.1022760	
	3.6659130		
H	1.2704850	-4.1849380	
	4.3994200		
H	2.1412660	-5.0546880	
	3.1072490		
H	3.0408200	-3.9882280	
	4.2319790		
H	3.9051460	-2.2325150	
	2.3666450		
C	3.3304720	-2.4182710	-
	2.1644270		
H	4.3756280	-2.3198210	-
	1.8081720		

C	3.2721860	-3.5788150	-
	3.1770960		
H	3.6962990	-4.5154800	-
	2.7723610		
H	2.2240580	-3.7755820	-
	3.4784490		
H	3.8468960	-3.3189840	-
	4.0862990		
C	2.9284690	-1.1096830	-
	2.8687550		
H	2.9549910	-0.2469240	-
	2.1821500		
H	3.6053460	-0.8906130	-
	3.7159150		
H	1.8961000	-1.1938080	-
	3.2607820		
H	1.3601320	-2.5549010	-
	1.3136490		

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TS-coord

Thermal Free Energy Correction = 0.897574

Electronic Energy = -4532.39817411

Corrected Free Energy = -4531.50060011

C	-5.3548880	-2.2657170	
	0.4811520		
C	-4.0081630	-2.5622810	
	0.2245540		
C	-3.0189790	-1.5548790	
	0.2242760		
C	-3.4069690	-0.2050340	
	0.4558290		
C	-4.7647730	0.0746950	
	0.7243210		
C	-5.7330620	-0.9401680	
	0.7447280		
H	-6.1026800	-3.0689260	
	0.4799110		
H	-3.7243720	-3.6004690	
	0.0237420		
H	-5.0784370	1.1051270	
	0.9173410		
H	-6.7810960	-0.6917700	
	0.9554190		

C	-0.6197380	-3.1219170		C	2.6715510	-0.7642940	-
	1.2902840				3.1161440		
C	-1.3651080	-3.3567240	-	C	4.9620610	0.0569140	-
	1.4117900				1.7313130		
C	-0.1741180	-4.3852370		H	3.7137120	1.5872420	-
	0.5147870				0.8576080		
C	-1.2021530	-4.6575300	-	C	3.8809660	-1.4548010	-
	0.5892840				3.2903880		
H	0.8102250	-4.1839890		H	1.7833480	-1.0840430	-
	0.0517450				3.6733000		
H	-0.0400000	-5.2516820		C	5.0372860	-1.0485250	-
	1.1866280				2.5986740		
H	-0.9117380	-5.5123790	-	H	5.8497220	0.3787520	-
	1.2260380				1.1717920		
H	-2.1697600	-4.9290730	-	H	3.9225290	-2.3108070	-
	0.1241280				3.9779700		
C	-2.5667090	2.3169500	-	H	5.9853210	-1.5850000	-
	1.0412880				2.7348240		
C	-2.7829020	2.3487930		C	1.4038630	2.8129660	-
	1.7697050				1.3771390		
C	-2.8100330	3.6728710	-	C	0.7799040	3.3911880	-
	0.3369860				0.2449250		
C	-3.5695300	3.4171440		C	2.3383690	3.6168460	-
	0.9708800				2.0823020		
H	-1.8304650	4.1315920	-	C	1.0471510	4.7122450	
	0.1074640				0.1550030		
H	-3.3430400	4.3834570	-	H	0.0794150	2.7798340	
	0.9929150				0.3340320		
H	-3.6981700	4.3479390		C	2.6234610	4.9278850	-
	1.5531030				1.6756150		
H	-4.5879290	3.0517460		H	2.8439040	3.1994540	-
	0.7368640				2.9626930		
P	-2.1213390	1.1494800		C	1.9736280	5.4897240	-
	0.4170720				0.5575610		
P	-1.2313320	-1.9618430	-	H	0.5392390	5.1256720	
	0.1094300				1.0377800		
Cu	-0.1033040	0.0566010	-	H	3.3535560	5.5235130	-
	0.2268690				2.2402630		
P	0.9228490	1.1405640	-	H	2.1955430	6.5184160	-
	2.0000540				0.2452990		
C	2.5737900	0.3428700	-	C	1.7708920	0.3905040	
	2.2352660				1.0818580		
C	3.7503490	0.7405800	-	C	1.4877550	-0.4879580	
	1.5516330				2.0431630		

H	1.8833810	1.4599160		H	-0.0085470	2.2630380	
	0.8764610				3.9385300		
H	1.0074340	-0.6889380		H	-1.4617360	1.2127520	
	3.0025490				3.9914440		
C	2.6695790	-0.8443260		C	-2.2328200	3.8595400	
	1.1762830				3.7571040		
C	4.0421680	-0.6308620		H	-1.4176460	4.2419430	
	1.7866140				4.4008170		
C	5.1463550	-1.4439010		H	-2.7699380	4.7326020	
	1.4395950				3.3439970		
C	4.2639740	0.4102160		H	-2.9374050	3.2960710	
	2.7216570				4.4018090		
C	6.4158350	-1.2244290		H	-3.4529440	1.7591300	
	1.9994680				2.4251430		
H	5.0210240	-2.2509950		H	-1.6365910	2.3768920	-
	0.7112930				1.6351090		
C	5.5315570	0.6334010		C	-3.6785040	1.8144530	-
	3.2797920				1.9981110		
H	3.4274260	1.0578560		H	-4.5728100	1.5341890	-
	3.0108860				1.4071910		
C	6.6180120	-0.1842320		C	-4.1010710	2.9009870	-
	2.9218130				3.0075690		
H	7.2542290	-1.8708610		H	-4.8002820	2.4734940	-
	1.7074110				3.7518150		
H	5.6720010	1.4524570		H	-4.6098560	3.7551140	-
	3.9976920				2.5240490		
H	7.6110460	-0.0115140		H	-3.2173750	3.2874440	-
	3.3566360				3.5531190		
C	2.5738340	-1.9697830		C	-3.1867980	0.5754890	-
	0.1506620				2.7656940		
H	1.5839400	-1.9482690	-	H	-2.8724940	-0.2337960	-
	0.3316130				2.0875920		
H	3.3306220	-1.8593310	-	H	-3.9808130	0.1789190	-
	0.6430370				3.4269780		
H	2.7166890	-2.9568110		H	-2.3094760	0.8404340	-
	0.6348880				3.3859240		
C	-1.6569250	2.9363800		H	-2.3776430	-3.3083540	-
	2.6650970				1.8559280		
H	-0.9858220	3.5406640		C	-0.3408420	-3.1330330	-
	2.0225560				2.5630610		
C	-0.8221160	1.8283960		H	0.6429840	-2.8702270	-
	3.3274590				2.1235440		
H	-0.3679810	1.1624920		C	-0.1480300	-4.3858550	-
	2.5765870				3.4374660		

H	0.5020120	-4.1443380	-	C	-3.7996170	-2.7305620	
	4.2998540				0.1614420		
H	0.3267360	-5.2187300	-	C	-2.8544950	-1.6816810	
	2.8865540				0.1933870		
H	-1.1201790	-4.7426750	-	C	-3.2932720	-0.3677850	
	3.8344080				0.5201180		
H	0.2726700	-2.6132030		C	-4.6532160	-0.1648020	
	1.6949530				0.8428220		
C	-1.6061380	-3.3296870		C	-5.5762630	-1.2206810	
	2.4683510				0.8268050		
H	-2.5953260	-3.6233070		H	-5.8611470	-3.3446560	
	2.0680710				0.4446460		
C	-1.7764680	-2.0190320		H	-3.4778070	-3.7405580	-
	3.2601860				0.1122670		
H	-2.5665180	-2.1242470		H	-5.0027260	0.8378390	
	4.0277650				1.1089970		
H	-0.8309170	-1.7653800		H	-6.6272390	-1.0325670	
	3.7783000				1.0807810		
H	-2.0394810	-1.1667100		C	-0.3507250	-3.2417710	
	2.6108020				1.0263240		
C	-1.1397900	-4.4449680		C	-1.2219580	-3.2831500	-
	3.4252270				1.6467160		
H	-1.7981080	-4.4818830		C	0.1280950	-4.3979640	
	4.3145450				0.1170500		
H	-1.1618230	-5.4435100		C	-0.9482860	-4.6356400	-
	2.9517210				0.9474370		
H	-0.1058380	-4.2517390		H	1.0684760	-4.0923950	-
	3.7749590				0.3793650		
C	-0.8037070	-1.9513820	-	H	0.3557190	-5.3097130	
	3.4305520				0.6974830		
H	-1.8163750	-2.1487130	-	H	-0.6572520	-5.4201020	-
	3.8360600				1.6689130		
H	-0.8348320	-1.0131500	-	H	-1.8725910	-4.9929500	-
	2.8504910				0.4527070		
H	-0.1211410	-1.7946670	-	C	-2.6051980	2.3059230	-
	4.2859490				0.7942680		
				C	-2.7418380	2.1049560	
					2.0087380		
				C	-2.8371950	3.5994740	
					0.0241240		
				C	-3.5604940	3.2219150	
					1.3214440		
				H	-1.8570050	4.0492590	
					0.2660150		

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Intermediate "Int-coord"

Thermal Free Energy Correction = 0.89939

Electronic Energy = -4532.40194821

Corrected Free Energy = -4531.50255821

C	-5.1489600	-2.5102050	
	0.4736370		

H	-3.3919510	4.3553030	-	H	0.1146240	2.8139200	
	0.5590720				0.4243360		
H	-3.7067610	4.0933370		C	2.1920910	5.1213940	-
	1.9854230				1.9176080		
H	-4.5718060	2.8436380		H	2.3692270	3.3944500	-
	1.0755350				3.2147230		
P	-2.0728220	1.0412500		C	1.6578390	5.6479680	-
	0.5513010				0.7242490		
P	-1.0685850	-1.9882970	-	H	0.4837810	5.2006740	
	0.2373180				1.0528610		
Cu	0.0476930	0.0697480	-	H	2.7926220	5.7617810	-
	0.0616930				2.5777890		
P	0.7671280	1.2124410	-	H	1.8406720	6.6947500	-
	1.9976450				0.4489190		
C	2.4519630	0.5341200	-	C	1.8416330	0.5616580	
	2.3668980				0.8622850		
C	3.6451230	1.0143310	-	C	1.3151660	-0.3607960	
	1.7712120				1.7150400		
C	2.5604490	-0.5654650	-	H	2.1102850	1.6231080	
	3.2538320				0.8168280		
C	4.8826450	0.4070580	-	H	0.9009670	-0.4230150	
	2.0314060				2.7242150		
H	3.6009340	1.8668370	-	C	2.6372560	-0.7229610	
	1.0848550				1.0496300		
C	3.7963110	-1.1804900	-	C	3.8809350	-0.5734670	
	3.5090850				1.8993350		
H	1.6601620	-0.9431480	-	C	5.0575790	-1.3140380	
	3.7503500				1.6338570		
C	4.9676020	-0.7003760	-	C	3.9107140	0.3321260	
	2.8960130				2.9898550		
H	5.7864080	0.7923860	-	C	6.2098590	-1.1568740	
	1.5408030				2.4215610		
H	3.8449040	-2.0355040	-	H	5.0803850	-2.0170990	
	4.1972870				0.7951340		
H	5.9359130	-1.1781840	-	C	5.0604990	0.4898960	
	3.0939180				3.7778190		
C	1.1891450	2.9271770	-	H	3.0165500	0.9234210	
	1.4465300				3.2206350		
C	0.6803750	3.4711370	-	C	6.2197060	-0.2551000	
	0.2442810				3.4987800		
C	1.9553020	3.7864560	-	H	7.1079660	-1.7442880	
	2.2764660				2.1883870		
C	0.8976610	4.8137110		H	5.0513030	1.2006110	
	0.1111600				4.6149740		

H	7.1207570	-0.1330330		H	-3.3965190	3.4589780	-
	4.1137470				3.1849930		
C	2.7066630	-1.7922150	-	C	-3.3054600	0.6922690	-
	0.0352190				2.6148750		
H	1.7757100	-1.7941290	-	H	-2.9631890	-0.1693190	-
	0.6234990				2.0197720		
H	3.5366010	-1.6014310	-	H	-4.1292870	0.3491380	-
	0.7368970				3.2696300		
H	2.8482760	-2.7959620		H	-2.4575620	1.0098110	-
	0.4126570				3.2510880		
C	-1.5711060	2.5678040		H	-2.2628070	-3.2517340	-
	2.9239250				2.0206690		
H	-0.7357330	2.9187190		C	-0.2877520	-2.9148270	-
	2.2862690				2.8353600		
C	-1.0720640	1.3683780		H	0.6969820	-2.6009750	-
	3.7467140				2.4330350		
H	-0.8913180	0.4951450		C	-0.0466810	-4.0911830	-
	3.0974730				3.7989110		
H	-0.1334880	1.6078780		H	0.5318280	-3.7439030	-
	4.2811490				4.6761840		
H	-1.8355010	1.0782380		H	0.5235480	-4.9135820	-
	4.4964170				3.3286130		
C	-1.9565190	3.7266270		H	-1.0080590	-4.5028930	-
	3.8614580				4.1678670		
H	-1.1314950	3.9299530		H	0.5249210	-2.7230030	
	4.5709320				1.4529960		
H	-2.1620000	4.6625390		C	-1.2787170	-3.6259000	
	3.3098570				2.2075020		
H	-2.8579920	3.4691010		H	-2.2604740	-3.9500330	
	4.4534550				1.8120020		
H	-3.4045910	1.4630950		C	-1.5053270	-2.4118190	
	2.6201540				3.1269720		
H	-1.7096870	2.4314330	-	H	-2.2245270	-2.6579310	
	1.4305110				3.9312350		
C	-3.7619770	1.8632670	-	H	-0.5495240	-2.1142080	
	1.7282570				3.6002880		
H	-4.6214580	1.5285760	-	H	-1.8934160	-1.5383320	
	1.1146940				2.5768700		
C	-4.2470090	3.0188600	-	C	-0.7018480	-4.7903390	
	2.6273730				3.0376240		
H	-4.9790280	2.6402360	-	H	-1.3225610	-4.9581040	
	3.3665090				3.9388390		
H	-4.7391080	3.8258840	-	H	-0.6723810	-5.7390440	
	2.0540780				2.4711070		

H	0.3284380	-4.5561100	
	3.3726620		
C	-0.8939860	-1.7254600	-
	3.5968860		
H	-1.9027400	-1.9899120	-
	3.9731010		
H	-0.9827610	-0.8359810	-
	2.9506680		
H	-0.2712610	-1.4455840	-
	4.4667170		

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TS-MI-Major

Thermal Free Energy Correction = 0.899145

Electronic Energy = -4532.39315182

Corrected Free Energy = -4531.49400682

C	-5.4800180	-2.0490610	
	0.0778630		
C	-4.1334540	-2.4107080	-
	0.0787090		
C	-3.0977970	-1.4558700	
	0.0178260		
C	-3.4380390	-0.0943940	
	0.2616770		
C	-4.7959600	0.2518790	
	0.4292050		
C	-5.8127960	-0.7113050	
	0.3410050		
H	-6.2646430	-2.8124750	-
	0.0002110		
H	-3.8849260	-3.4583480	-
	0.2792810		
H	-5.0700890	1.2921170	
	0.6318140		
H	-6.8609010	-0.4138920	
	0.4729120		
C	-0.8212050	-3.1763950	
	1.1456610		
C	-1.4522350	-3.2767850	-
	1.5961680		
C	-0.3714810	-4.4155870	
	0.3355210		
C	-1.3588280	-4.6131580	-
	0.8222660		

H	0.6372100	-4.2218530	-
	0.0764900		
H	-0.2876750	-5.3151260	
	0.9712130		
H	-1.0670450	-5.4527220	-
	1.4795880		
H	-2.3535520	-4.8698590	-
	0.4078570		
C	-2.3316760	2.4859900	-
	0.9832750		
C	-2.7603260	2.3183020	
	1.7969540		
C	-2.5363880	3.8016880	-
	0.1913440		
C	-3.4060490	3.5012510	
	1.0364420		
H	-1.5497000	4.1723550	
	0.1403590		
H	-2.9711450	4.5950640	-
	0.8244360		
H	-3.5271710	4.3888410	
	1.6835730		
H	-4.4227630	3.2197780	
	0.7005150		
P	-2.0913580	1.1879090	
	0.4041920		
P	-1.3147600	-1.9386480	-
	0.2240360		
Cu	-0.1503310	0.0110790	
	0.2471610		
P	1.2580330	0.9498870	-
	1.4833650		
C	2.8555540	0.2392660	-
	2.0587410		
C	4.0977630	0.6121910	-
	1.4931990		
C	2.8340540	-0.7971220	-
	3.0185810		
C	5.2786750	-0.0465160	-
	1.8646000		
H	4.1333290	1.4065200	-
	0.7396590		
C	4.0159020	-1.4598530	-
	3.3884180		

H	1.8790920	-1.0944770	-	C	4.9212370	-1.6089350	
	3.4650280				1.6935770		
C	5.2425350	-1.0898430	-	C	3.9726340	0.2785340	
	2.8090040				2.8729730		
H	6.2302310	0.2437150	-	C	6.1060200	-1.4756530	
	1.4006260				2.4373170		
H	3.9779790	-2.2683490	-	H	4.8548670	-2.4037840	
	4.1306700				0.9438260		
H	6.1670720	-1.6094290	-	C	5.1554820	0.4165340	
	3.0927250				3.6127650		
C	1.6382520	2.7244190	-	H	3.1394490	0.9664710	
	1.2294730				3.0590690		
C	2.4804580	3.4559420	-	C	6.2340060	-0.4614540	
	2.1022780				3.4002620		
C	1.0083370	3.4210080	-	H	6.9363900	-2.1721560	
	0.1706050				2.2587620		
C	2.6708490	4.8348890	-	H	5.2352410	1.2143930	
	1.9239510				4.3634010		
H	2.9893120	2.9353420	-	H	7.1600870	-0.3570430	
	2.9233110				3.9804120		
C	1.1923310	4.8017170		C	2.4855760	-2.0420970	
	0.0027860				0.1304630		
H	0.3737550	2.8565860		H	3.3271080	-2.0539200	-
	0.5233440				0.5848040		
C	2.0247290	5.5177960	-	H	2.4913440	-2.9940180	
	0.8749710				0.6974660		
H	3.3291850	5.3833690	-	H	1.5492080	-1.9901120	-
	2.6108990				0.4488880		
H	0.6929070	5.3165380		C	-1.6351120	2.6890600	
	0.8349780				2.8045180		
H	2.1772570	6.5962310	-	H	-0.7541600	3.0483130	
	0.7395640				2.2351460		
C	1.9162180	0.4753390		C	-1.2133060	1.4422130	
	0.7437600				3.5997370		
C	1.2596850	-0.3470550		H	-0.9123330	0.6201310	
	1.7174280				2.9273570		
H	2.4123200	1.4447010		H	-0.3611950	1.6711060	
	0.8961680				4.2674180		
H	1.1596310	-0.0628110		H	-2.0567580	1.0878120	
	2.7728300				4.2258760		
C	2.5518860	-0.8587880		C	-2.0573620	3.8112150	
	1.0895400				3.7716350		
C	3.8263940	-0.7332810		H	-1.2761190	3.9606510	
	1.8900400				4.5412400		

H	-2.2107740	4.7790380		C	-1.8730540	-3.4100120	
	3.2595850				2.2597930		
H	-2.9988180	3.5426700		H	-2.8483360	-3.6630920	
	4.2922650				1.7986690		
H	-3.5277950	1.7476430		C	-2.0483540	-2.1296630	
	2.3542260				3.0965520		
H	-1.3544340	2.5185570	-	H	-2.8323150	-2.2675780	
	1.5021350				3.8658410		
C	-3.4005630	2.1422460	-	H	-1.0974700	-1.8794270	
	2.0532040				3.6044810		
H	-4.3571150	1.9011330	-	H	-2.3234070	-1.2616990	
	1.5490270				2.4753660		
C	-3.6540440	3.3232090	-	C	-1.4782270	-4.5753440	
	3.0116680				3.1889730		
H	-4.3259860	3.0067430	-	H	-2.1838280	-4.6385230	
	3.8325940				4.0398410		
H	-4.1270180	4.1858450	-	H	-1.4909110	-5.5521310	
	2.5075010				2.6711860		
H	-2.7021570	3.6665030	-	H	-0.4616710	-4.4156430	
	3.4637230				3.6006750		
C	-2.9532420	0.9156120	-	C	-0.7138750	-1.7626710	-
	2.8668950				3.4807630		
H	-2.7661100	0.0382290	-	H	-1.7330820	-1.8279400	-
	2.2270440				3.9112070		
H	-3.7203450	0.6365060	-	H	-0.6639960	-0.8703440	-
	3.6143030				2.8323110		
H	-2.0104640	1.1411330	-	H	-0.0061360	-1.6144660	-
	3.4014910				4.3182040		
H	-2.4457740	-3.1736120	-				
	2.0729630						
C	-0.3843570	-3.0481570	-				
	2.7025190						
H	0.6059720	-2.9162130	-				
	2.2203010						
C	-0.2851650	-4.2376810	-				
	3.6761580						
H	0.4125110	-3.9948940	-				
	4.5005200						
H	0.0850790	-5.1572560	-				
	3.1869860						
H	-1.2753070	-4.4592560	-				
	4.1238900						
H	0.0537670	-2.6875560					
	1.6139930						

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TS-MI-Minor

Thermal Free Energy Correction = 0.897875

Electronic Energy = -4532.38770331

Corrected Free Energy = -4531.48982831

C	5.6744960	-1.6375310	-
	0.3180020		
C	4.3610070	-2.1176130	-
	0.2057580		
C	3.2615340	-1.2343600	-
	0.1506670		
C	3.4895620	0.1701790	-
	0.2212900		
C	4.8170890	0.6348270	-
	0.3441200		

C	5.9020630	-0.2541080	-	P	1.5156200	-1.8436160	-
0.3892920				0.0297200			
H	6.5150970	-2.3420210	-	Cu	0.1963410	0.0080500	-
0.3579630				0.3142400			
H	4.1885200	-3.1978550	-	P	-1.2697980	0.6834350	
0.1742690				1.5318600			
H	5.0146720	1.7090770	-	C	-2.5312100	-0.3176410	
0.4093660				2.4363770			
H	6.9233730	0.1365290	-	C	-3.8478570	-0.5504320	
0.4833110				1.9636080			
C	1.3620420	-3.2288780	-	C	-2.1455200	-0.9202910	
1.3064720				3.6567190			
C	1.5030960	-3.0041060		C	-4.7391700	-1.3617310	
1.4537080				2.6853290			
C	1.6173630	-4.5816110	-	H	-4.1744470	-0.0952930	
0.5669810				1.0218500			
C	1.9871580	-4.3780880		C	-3.0327880	-1.7391150	
0.9299570				4.3743880			
H	0.7120210	-5.2096120	-	H	-1.1343860	-0.7419200	
0.6483150				4.0451570			
H	2.4288110	-5.1371550	-	C	-4.3336680	-1.9643340	
1.0744030				3.8894300			
H	1.5704860	-5.1963560		H	-5.7541570	-1.5271240	
1.5482200				2.3004970			
H	3.0837260	-4.4358320		H	-2.7096440	-2.1957670	
1.0534360				5.3191410			
C	2.1624480	2.4026410		H	-5.0298520	-2.6016330	
1.3830090				4.4501260			
C	2.6288710	2.7444820	-	C	-2.0599130	2.3131520	
1.3752370				1.2572200			
C	2.3678110	3.8475810		C	-1.2624680	3.3053800	
0.8542760				0.6336980			
C	3.2250870	3.8066410	-	C	-3.3492180	2.6945040	
0.4191860				1.7020480			
H	1.3806440	4.2827820		C	-1.7305060	4.6083080	
0.6119370				0.4333640			
H	2.8126600	4.5029200		H	-0.2684000	3.0279950	
1.6236650				0.2708740			
H	3.2907400	4.8005590	-	C	-3.8198850	4.0039230	
0.8981790				1.5049640			
H	4.2607210	3.5261780	-	H	-3.9898940	1.9679970	
0.1477140				2.2127500			
P	2.0397910	1.3538270	-	C	-3.0206110	4.9689360	
0.2125400				0.8667430			

H	-1.0880450	5.3442860	-	H	-1.2356120	2.0957150	-
0.0692160				1.6195110			
H	-4.8259700	4.2708540		H	2.2207140	-2.6019860	
1.8556290				2.1935990			
H	-3.3958890	5.9886530		C	0.0991100	-2.9935440	
0.7123580				2.1155830			
C	-1.1920560	-0.5716480	-	H	-0.1247560	-1.9325450	
1.7336360				2.3316480			
C	-1.9346400	-0.3850550	-	C	-1.0245920	-3.5149220	
0.5213850				1.2042260			
H	-1.1091180	-1.5434470	-	H	-0.8779990	-4.5851000	
2.2413420				0.9597090			
H	-2.5320220	-1.1436510	-	H	-2.0000250	-3.4062280	
0.0008170				1.7129390			
C	-2.4224200	0.3161720	-	H	-1.0792090	-2.9423440	
1.7799400				0.2597570			
C	-3.7037180	-0.2708140	-	C	0.1145950	-3.7472240	
2.3241670				3.4548230			
C	-4.7213200	0.5456910	-	H	-0.8677740	-3.6542920	
2.8738660				3.9541370			
C	-3.9381810	-1.6695130	-	H	0.3185190	-4.8264480	
2.2928730				3.3072900			
C	-5.9149290	-0.0078840	-	H	0.8914760	-3.3419610	
3.3676060				4.1325400			
H	-4.5829440	1.6311810	-	C	2.1613180	-3.0441420	-
2.9145540				2.6213750			
C	-5.1295770	-2.2236790	-	H	3.2368700	-3.1692930	-
2.7816440				2.3810910			
H	-3.1679460	-2.3311180	-	C	1.7648930	-4.1386270	-
1.8792380				3.6321680			
C	-6.1287950	-1.3952380	-	H	0.6947090	-4.0367690	-
3.3245820				3.9026280			
H	-6.6838210	0.6540470	-	H	2.3604890	-4.0444520	-
3.7883070				4.5605280			
H	-5.2787370	-3.3111090	-	H	1.9196920	-5.1558470	-
2.7407120				3.2264020			
H	-7.0613530	-1.8273560	-	C	1.9648630	-1.6555030	-
3.7102470				3.2542710			
C	-2.2273630	1.8101020	-	H	2.3276130	-0.8454160	-
1.9960890				2.5984770			
H	-2.2630940	2.0416520	-	H	2.5166780	-1.5920490	-
3.0791290				4.2120210			
H	-2.9887810	2.4220440	-	H	0.8951560	-1.4583850	-
1.4776550				3.4501980			

H	0.2900980	-3.1684730	-
1.5775710			
H	3.4156970	2.3283670	-
2.0338440			
H	1.1575120	2.3199330	
1.8407820			
C	1.4601230	3.2190180	-
2.2883550			
H	0.5747310	3.4259220	-
1.6530200			
C	3.1664540	1.8773680	
2.4433180			
H	4.1546060	1.7208450	
1.9668730			
C	3.3505780	2.8718100	
3.6067570			
H	3.9736820	2.4156810	
4.4000790			
H	3.8469410	3.8075970	
3.2903670			
H	2.3701300	3.1338200	
4.0520710			
C	2.6715090	0.5301140	
3.0040860			
H	2.5122810	-0.2156710	
2.2079620			
H	3.3981100	0.1133930	
3.7275620			
H	1.7004270	0.6717300	
3.5170550			
C	1.0753050	2.1090050	-
3.2834250			
H	1.9452520	1.8534400	-
3.9222040			
H	0.7311800	1.1944320	-
2.7654470			
H	0.2518070	2.4466960	-
3.9394670			
C	1.8044390	4.5134480	-
3.0489060			
H	1.9366630	5.3810220	-
2.3760500			
H	2.7374390	4.3856120	-
3.6345370			

H	0.9913820	4.7614970	-
3.7573770			

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Intermediate "6a"

Thermal Free Energy Correction = 0.897791

Electronic Energy = -4532.44233832

Corrected Free Energy = -4531.54454732

C	5.8603110	-0.4525220	
1.2227960			
C	4.6753090	-1.2052060	
1.2042200			
C	3.4762430	-0.6736290	
0.6841600			
C	3.4738900	0.6633740	
0.1920410			
C	4.6741860	1.4041020	
0.2045360			
C	5.8625670	0.8548540	
0.7114080			
H	6.7805340	-0.8909150	
1.6299040			
H	4.6892100	-2.2265400	
1.5999800			
H	4.6842820	2.4276320	-
0.1854720			
H	6.7846190	1.4502090	
0.7124740			
C	2.1100670	-3.1259340	-
0.5255480			
C	2.0369110	-2.6995500	
2.2613770			
C	1.8787630	-4.3435280	
0.4015310			
C	2.5601960	-4.0638430	
1.7489890			
H	0.7898860	-4.4589550	
0.5675990			
H	2.2307740	-5.2838990	-
0.0592870			
H	2.3742590	-4.8753450	
2.4764730			
H	3.6565230	-4.0189520	
1.5992540			

C	1.3199740	2.7867610		H	-7.1563050	0.9485920	
	0.6613660				3.7893170		
C	2.4456920	2.4973540	-	C	-2.2619100	2.5127770	-
	1.9021170				0.1608990		
C	1.3081570	4.0066640	-	C	-1.9886140	2.6174430	-
	0.2939550				1.5445110		
C	2.5098230	3.8956240	-	C	-2.4456570	3.7037500	
	1.2426030				0.5785580		
H	0.3749580	3.9829540	-	C	-1.9237020	3.8758510	-
	0.8824160				2.1693380		
H	1.3035110	4.9597910		H	-1.8230480	1.7095800	-
	0.2626380				2.1332100		
H	2.5198910	4.7058930	-	C	-2.3777360	4.9589150	-
	1.9943100				0.0466540		
H	3.4476600	3.9946000	-	H	-2.6600190	3.6503630	
	0.6619570				1.6533910		
P	1.8837410	1.3602560	-	C	-2.1185160	5.0517690	-
	0.4839730				1.4263480		
P	1.8751970	-1.6415220		H	-1.7140570	3.9336330	-
	0.6685770				3.2455750		
Cu	0.3852240	-0.3234180	-	H	-2.5327100	5.8696220	
	0.5811540				0.5469600		
P	-2.2605460	0.8560940		H	-2.0665190	6.0328020	-
	0.7007720				1.9157700		
C	-3.8654200	0.9163170		C	-2.5993290	-0.2395890	-
	1.6398440				0.7421590		
C	-5.0314460	0.2643340		C	-1.3543610	-0.8312250	-
	1.1792970				1.4034280		
C	-3.8988420	1.5546230		H	-3.4494540	0.0896540	-
	2.9010930				1.3642980		
C	-6.2059330	0.2752950		H	-1.4295390	-0.8628940	-
	1.9513080				2.5046570		
H	-5.0194810	-0.2608310		C	-2.3638360	-1.7526810	-
	0.2169290				0.7106740		
C	-5.0777980	1.5797180		C	-3.3144050	-2.5611130	-
	3.6644450				1.5634660		
H	-2.9870820	2.0233840		C	-3.7741150	-3.8365920	-
	3.2970930				1.1556360		
C	-6.2364200	0.9393550		C	-3.7770370	-2.0823020	-
	3.1902110				2.8162140		
H	-7.1033380	-0.2371330		C	-4.6484120	-4.5937430	-
	1.5799300				1.9556330		
H	-5.0877820	2.0870510		H	-3.4494290	-4.2521940	-
	4.6383400				0.1960480		

C	-4.6531090	-2.8312470	-	C	2.1181870	2.9338060	
	3.6132410				1.9827410		
H	-3.4371810	-1.1033080	-	H	3.2027410	2.9528310	
	3.1749560				1.7565760		
C	-5.0965840	-4.0978010	-	C	1.7647340	4.2380590	
	3.1893600				2.7255970		
H	-4.9821670	-5.5796420	-	H	2.2443850	4.2486930	
	1.6045960				3.7233840		
H	-4.9903370	-2.4238430	-	H	2.1025330	5.1394820	
	4.5759190				2.1823610		
H	-5.7806260	-4.6872340	-	H	0.6687260	4.3152330	
	3.8136080				2.8721610		
C	-1.9448270	-2.4068670		C	1.8308670	1.7339390	
	0.6001990				2.9014880		
H	-2.8081790	-2.6150790		H	2.0512330	0.7728640	
	1.2636860				2.4091290		
H	-1.4237010	-3.3650040		H	2.4324320	1.7902710	
	0.4014720				3.8288570		
H	-1.2407080	-1.7501960		H	0.7595060	1.7212140	
	1.1326170				3.1804620		
C	1.4476970	2.3730130	-	H	2.7790010	-2.2040980	
	3.0909620				2.9169890		
H	0.4233730	2.4734590	-	C	0.6941200	-2.7786460	
	2.6831450				3.0400870		
C	1.5561230	0.9884610	-	H	-0.0592450	-3.2438990	
	3.7521390				2.3751680		
H	1.3343800	0.1826110	-	C	0.8281360	-3.6517170	
	3.0286720				4.3034840		
H	0.8359880	0.8984870	-	H	-0.1229900	-3.6507250	
	4.5876040				4.8694620		
H	2.5763570	0.8272160	-	H	1.0778960	-4.7037580	
	4.1555140				4.0738600		
C	1.6460330	3.4793410	-	H	1.6183750	-3.2479680	
	4.1436010				4.9686230		
H	0.9872580	3.2954600	-	H	1.2633090	-3.0437020	-
	5.0140270				1.2347810		
H	1.4033670	4.4832720	-	C	3.4127230	-3.1066270	-
	3.7496670				1.3642390		
H	2.6930560	3.4940600	-	H	4.2755590	-2.9280740	-
	4.5089470				0.6935120		
H	3.4453180	2.1694270	-	C	3.3472470	-1.9594800	-
	2.2484870				2.3886210		
H	0.2796780	2.5309820		H	4.3044150	-1.8559540	-
	0.9349470				2.9343610		

H	2.5461890	-2.1589160	-
	3.1271920		
H	3.1171720	-0.9927150	-
	1.9102330		
C	3.6555670	-4.4397840	-
	2.0983850		
H	4.5263250	-4.3473710	-
	2.7759040		
H	3.8611470	-5.2728620	-
	1.4010630		
H	2.7742250	-4.7129790	-
	2.7125770		
C	0.1821070	-1.3833840	
	3.4390920		
H	0.9010730	-0.8932220	
	4.1253460		
H	0.0402890	-0.7235590	
	2.5644900		
H	-0.7906140	-1.4637890	
	3.9599010		

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TS-MI-Diast1

Thermal Free Energy Correction = 0.897708

Electronic Energy = -4532.38771939

Corrected Free Energy = -4531.49001139

C	-5.4942460	-1.6388440	
	0.9792550		
C	-4.7727110	-0.5649830	
	0.4373960		
C	-3.3632230	-0.5958800	
	0.3556400		
C	-2.6647940	-1.7504390	
	0.8097900		
C	-3.4078400	-2.8246990	
	1.3475270		
C	-4.8065920	-2.7730490	
	1.4397530		
H	-6.5893030	-1.5915630	
	1.0355160		
H	-5.3172600	0.3059700	
	0.0611710		

H	-2.8894730	-3.7224760	
	1.6987800		
H	-5.3570410	-3.6217910	
	1.8653790		
C	-3.3100990	1.3280850	-
	1.9103790		
C	-2.9462920	2.3161500	
	0.6441990		
C	-4.3379070	2.4349310	-
	1.5118330		
C	-4.2754460	2.7876960	
	0.0035980		
H	-4.1468340	3.3382120	-
	2.1189690		
H	-5.3601940	2.0979660	-
	1.7703280		
H	-4.4086420	3.8761220	
	0.1549020		
H	-5.1152530	2.3047430	
	0.5342750		
C	-0.0490490	-1.9723590	
	2.3778850		
C	-0.5733050	-3.7236200	
	0.2322030		
C	0.6784960	-3.3400870	
	2.3593040		
C	-0.1824870	-4.3512520	
	1.5923160		
H	1.6454190	-3.2136840	
	1.8400200		
H	0.9148540	-3.6883510	
	3.3802900		
H	0.3354850	-5.3191230	
	1.4642170		
H	-1.0987300	-4.5642290	
	2.1769050		
P	-0.8066500	-1.8653460	
	0.6255850		
P	-2.3843820	0.8127570	-
	0.3455800		
Cu	-0.1917850	0.0505680	-
	0.4953840		
P	1.3651480	1.1582770	
	1.0442170		

C	1.9432860	2.9078540		C	0.4328260	0.7229430	-
	1.1372650				2.3618290		
C	2.9502590	3.4270240		C	1.0787230	1.5450320	-
	0.2858260				1.3737260		
C	1.3368590	3.7825550		H	-0.3259500	1.1058680	-
	2.0675040				3.0610050		
C	3.3378460	4.7734230		H	0.9615560	2.6223450	-
	0.3680030				1.2019260		
H	3.4253920	2.7607280	-	C	1.9136450	0.9737240	-
	0.4428210				2.4940330		
C	1.7135380	5.1346900		C	2.9180680	-0.1455150	-
	2.1411300				2.3439610		
H	0.5640190	3.3943660		C	2.5565630	-1.4620090	-
	2.7432190				2.6788050		
C	2.7165220	5.6345350		C	4.2527840	0.1113520	-
	1.2918780				1.9660890		
H	4.1235710	5.1558320	-	C	3.4975260	-2.5040690	-
	0.2972330				2.6368990		
H	1.2294650	5.7961940		H	1.5184830	-1.6423740	-
	2.8718030				2.9718670		
H	3.0162830	6.6889430		C	5.1970280	-0.9236570	-
	1.3518130				1.9195310		
C	2.9164390	0.1876030		H	4.5507500	1.1311470	-
	1.0826760				1.6923830		
C	4.1143880	0.6624810		C	4.8238380	-2.2369150	-
	1.6726510				2.2592530		
C	2.8724380	-1.1671400		H	3.1951950	-3.5259550	-
	0.6736990				2.9038580		
C	5.2122200	-0.1935330		H	6.2250030	-0.7101410	-
	1.8559090				1.6009300		
H	4.1811120	1.7059610		H	5.5633740	-3.0474360	-
	2.0028120				2.2191640		
C	3.9627450	-2.0221380		C	2.3687680	2.0118790	-
	0.8683990				3.5313790		
H	1.9745910	-1.5373390		H	3.3590880	2.4392570	-
	0.1688970				3.2788410		
C	5.1417640	-1.5429340		H	2.4576490	1.5357080	-
	1.4668190				4.5286500		
H	6.1296900	0.1979730		H	1.6374220	2.8399100	-
	2.3161570				3.6025980		
H	3.8999140	-3.0620430		H	-3.1184060	1.9754320	
	0.5250360				1.6826770		
H	6.0013770	-2.2094150		C	-1.8210100	3.3842650	
	1.6134440				0.6859930		

H	-0.9135540	2.8618760		C	0.4210310	-3.9197360	-
1.0392860				0.9474920			
C	-1.4930620	3.9927400	-	H	1.3245360	-3.3028780	-
0.6873170				0.7724370			
H	-2.3590810	4.5490420	-	C	-1.0292040	-1.7020860	
1.0961270				3.5501820			
H	-0.6465700	4.6981370	-	H	-1.9189570	-2.3542870	
0.5930730				3.4459080			
H	-1.1994800	3.2162850	-	C	-0.3798650	-2.0017310	
1.4170010				4.9161860			
C	-2.1484590	4.4843720		H	-1.0550110	-1.6856880	
1.7084150				5.7347360			
H	-1.3072070	5.1984420		H	-0.1659080	-3.0772340	
1.7837180				5.0562140			
H	-3.0515290	5.0539440		H	0.5713300	-1.4433350	
1.4113410				5.0234210			
H	-2.3307180	4.0535610		C	-1.4906640	-0.2323040	
2.7123640				3.5225210			
C	-3.8984140	0.1796120	-	H	-1.9755170	0.0318190	
2.7666710				2.5680710			
H	-4.7615110	-0.2424850	-	H	-2.2087230	-0.0313880	
2.2128250				4.3407190			
C	-4.4160980	0.7379510	-	H	-0.6169020	0.4374120	
4.1066320				3.6398660			
H	-3.5761700	1.1618320	-	C	-0.2359950	-3.4325720	-
4.6930380				2.2506570			
H	-4.8813820	-0.0651140	-	H	-1.1738020	-3.9935980	-
4.7100820				2.4387480			
H	-5.1671360	1.5365520	-	H	-0.4736210	-2.3542960	-
3.9592530				2.1979300			
C	-2.8887800	-0.9524680	-	H	0.4370380	-3.5914030	-
3.0182330				3.1132480			
H	-2.5913670	-1.4519940	-	C	0.8741920	-5.3832120	-
2.0801990				1.0988880			
H	-3.3269410	-1.7183440	-	H	1.4800450	-5.7289390	-
3.6869190				0.2410260			
H	-1.9650610	-0.5641410	-	H	-0.0001550	-6.0580750	-
3.4860370				1.1990160			
H	-2.5030450	1.7900800	-	H	1.4934500	-5.4932250	-
2.5123030				2.0095590			
H	-1.5512880	-4.1196380	-				
0.1018010				116			
H	0.7041690	-1.1634660		TS-MI-Diastr2			
2.4091380				<i>Thermal Free Energy Correction = 0.897782</i>			

Electronic Energy = -4532.38577416
 Corrected Free Energy = -4531.48799216

C	-2.1938470	-4.8512280	-
	1.6872170		
C	-1.0045580	-4.1837750	-
	1.3608620		
C	-1.0084270	-2.8701960	-
	0.8410250		
C	-2.2565570	-2.2101150	-
	0.6624280		
C	-3.4460830	-2.8999010	-
	0.9847220		
C	-3.4245350	-4.2074870	-
	1.4908160		
H	-2.1557340	-5.8721170	-
	2.0883290		
H	-0.0545160	-4.7019990	-
	1.5164710		
H	-4.4136540	-2.4102160	-
	0.8422320		
H	-4.3662790	-4.7155230	-
	1.7346690		
C	1.4805390	-2.9632650	
	0.9247330		
C	1.7302600	-2.6145570	-
	1.8534320		
C	2.7937850	-3.4111700	
	0.2402310		
C	2.4907870	-3.7981380	-
	1.2103970		
H	3.4926370	-2.5584870	
	0.2380140		
H	3.2927250	-4.2248740	
	0.7962120		
H	3.4108270	-4.0459940	-
	1.7705940		
H	1.8644070	-4.7102350	-
	1.2286420		
C	-3.0836940	0.6464880	-
	1.3334490		
C	-3.9138220	-0.5513030	
	1.0831930		
C	-4.3687480	1.1832430	-
	0.6570890		

C	-5.0051160	0.0572320	
	0.1673060		
H	-4.0896960	2.0143700	
	0.0144480		
H	-5.0745810	1.6006690	-
	1.3968220		
H	-5.8711740	0.4196970	
	0.7501690		
H	-5.3976160	-0.7178030	-
	0.5185360		
P	-2.3139360	-0.4718170	
	0.0181080		
P	0.5856530	-1.9813670	-
	0.4486820		
Cu	-0.0841680	0.0255990	
	0.4996720		
P	0.2537700	2.1438740	-
	0.6572920		
C	1.7350990	3.2155720	-
	0.8847590		
C	2.1033380	4.2128650	
	0.0502450		
C	2.5695300	3.0033850	-
	2.0071040		
C	3.2802260	4.9562000	-
	0.1226020		
H	1.4641390	4.3993230	
	0.9209180		
C	3.7520980	3.7427900	-
	2.1758970		
H	2.2900510	2.2412740	-
	2.7430280		
C	4.1142390	4.7195320	-
	1.2318280		
H	3.5539960	5.7208300	
	0.6166070		
H	4.3894320	3.5590690	-
	3.0511210		
H	5.0377000	5.2986090	-
	1.3614460		
C	-0.9852750	3.3680370	-
	0.0590870		
C	-1.8693690	3.0465990	
	0.9970750		

C	-1.1372730	4.6254940	-	H	5.4147050	0.5163120	-
0.6951300				0.9556850			
C	-2.8812390	3.9364070		H	5.4290370	-2.1852780	
1.3952160				2.4385110			
H	-1.7522370	2.0849050		H	6.4782560	-1.3803610	
1.5080900				0.3036300			
C	-2.1451440	5.5155320	-	C	2.5316920	1.8489390	
0.2958840				3.5339980			
H	-0.4563370	4.9025400	-	H	2.9929380	1.1764800	
1.5101230				4.2843810			
C	-3.0267460	5.1750140		H	3.2979650	2.5916090	
0.7494850				3.2348880			
H	-3.5535490	3.6588530		H	1.6880730	2.3793430	
2.2184590				4.0165100			
H	-2.2458070	6.4837100	-	C	2.6141880	-1.4521050	-
0.8043770				2.3871770			
H	-3.8138550	5.8743680		C	1.7489080	-0.4787700	-
1.0595370				3.2044410			
C	0.8486240	1.6528910		H	2.3728480	0.3247720	-
1.6352880				3.6384560			
C	0.6584790	0.4305300		H	1.2553260	-1.0114640	-
2.3828530				4.0422550			
H	0.4843480	2.6477490		C	3.8006270	-1.9448490	-
1.9252180				3.2357210			
H	0.0549120	0.3858800		H	4.3299340	-1.0798850	-
3.3008050				3.6797830			
C	2.0428570	1.0415980		H	4.5371470	-2.5109620	-
2.3182170				2.6365430			
C	3.2026810	0.3262430		H	3.4538880	-2.5938590	-
1.6662510				4.0657410			
C	3.8044430	0.7705560		H	0.9656690	-0.0090830	-
0.4750420				2.5828000			
C	3.8046290	-0.7488110		H	3.0296760	-0.9016490	-
2.3593110				1.5208890			
C	4.9685660	0.1539230	-	H	1.0887020	-2.9660720	-
0.0200880				2.6845150			
H	3.3683500	1.6170260	-	H	1.7022280	-2.1865460	
0.0566200				1.6792040			
C	4.9773870	-1.3526870		C	0.6389660	-4.0544510	
1.8829800				1.6329050			
H	3.3433380	-1.1015140		H	0.2147930	-4.7432650	
3.2912340				0.8753930			
C	5.5643600	-0.9051450		C	-0.5219280	-3.4056970	
0.6834340				2.4080060			

H	-1.1678460	-2.7972360	
	1.7547280		
H	-1.1499880	-4.1758990	
	2.8958510		
H	-0.1230210	-2.7287710	
	3.1875560		
C	1.4945340	-4.8906370	
	2.6056810		
H	0.8499300	-5.5814920	
	3.1829530		
H	2.2556830	-5.4996640	
	2.0843670		
H	2.0168070	-4.2296890	
	3.3262860		
C	-3.7444560	0.1282850	
	2.4691150		
H	-3.4014520	1.1684880	
	2.3113380		
C	-2.6895920	-0.6177080	
	3.3034060		
H	-1.7275440	-0.6941830	
	2.7681200		
H	-2.5116070	-0.1004500	
	4.2654470		
H	-3.0408430	-1.6451570	
	3.5265640		
C	-5.0722890	0.1864010	
	3.2499560		
H	-4.8935620	0.5734450	
	4.2715270		
H	-5.8223850	0.8427760	
	2.7718110		
H	-5.5109640	-0.8276260	
	3.3446260		
H	-4.1192790	-1.6219610	
	1.2745460		
C	-3.2389770	0.0041900	-
	2.7368440		
H	-3.7932970	-0.9505640	-
	2.6469880		
C	-1.8514550	-0.2860300	-
	3.3359350		
H	-1.2454890	-0.9367830	-
	2.6850310		

H	-1.9420580	-0.7774130	-
	4.3235460		
H	-1.2920000	0.6604960	-
	3.4635100		
C	-4.0244790	0.9188230	-
	3.6983340		
H	-3.5617400	1.9250890	-
	3.7402800		
H	-4.0103330	0.4946060	-
	4.7208590		
H	-5.0825570	1.0384070	-
	3.4011220		
H	-2.3642760	1.4781770	-
	1.4493680		

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TS-PDM

Thermal Free Energy Correction = 1.139611

Electronic Energy = -4995.04024280

Corrected Free Energy = -4993.90063180

C	6.5726740	-0.5185680	-
	0.7793770		
C	5.4657800	-1.1717180	-
	0.2162040		
C	4.2014330	-0.5458700	-
	0.1439160		
C	4.0603840	0.7691290	-
	0.6788960		
C	5.1830940	1.4143470	-
	1.2419760		
C	6.4339180	0.7827900	-
	1.2885560		
H	7.5423590	-1.0296810	-
	0.8228010		
H	5.5925470	-2.1900050	
	0.1598950		
H	5.0801350	2.4248100	-
	1.6545550		
H	7.2945330	1.3016420	-
	1.7284650		
C	2.8802150	-3.2129180	
	0.3488690		
C	3.2453220	-1.4575480	
	2.4698230		

C	3.6739260	-3.8008880		H	-3.3708360	-3.5388500	
	1.5602210				0.0925310		
C	4.1970860	-2.6781560		C	-6.6345030	-2.8008550	
	2.4915910				2.1057070		
H	3.0129980	-4.4822430		H	-6.0264980	-0.7227420	
	2.1274300				2.0755050		
H	4.5200480	-4.4160130		C	-6.3218470	-4.1189270	
	1.2014170				1.7244890		
H	4.3433110	-3.0541890		H	-4.8911670	-5.3937420	
	3.5195620				0.6979130		
H	5.1922360	-2.3423370		H	-7.5551550	-2.5932330	
	2.1541040				2.6660720		
C	2.3708010	3.0394140		H	-6.9961670	-4.9437860	
	0.5203060				1.9869880		
C	2.3561540	2.6384600	-	C	-4.6414090	0.4947940	-
	2.2631660				0.3218780		
C	1.6190210	4.0770240	-	C	-5.1725570	0.0462060	-
	0.3482870				1.5509430		
C	2.2935520	4.0952170	-	C	-5.0024800	1.7747010	
	1.7310290				0.1461000		
H	0.5636530	3.7608150	-	C	-6.0121190	0.8754330	-
	0.4570900				2.3117510		
H	1.6077930	5.0735230		H	-4.9333280	-0.9612240	-
	0.1277200				1.9139640		
H	1.7696800	4.7678360	-	C	-5.8559630	2.6022020	-
	2.4327260				0.6054080		
H	3.3222300	4.4881370	-	H	-4.6078210	2.1271320	
	1.6213760				1.1060720		
P	2.3981850	1.5762090	-	C	-6.3519580	2.1589300	-
	0.6861660				1.8432370		
P	2.7246820	-1.3580960		H	-6.4135850	0.5168290	-
	0.6458030				3.2682280		
Cu	0.9504330	-0.1275860	-	H	-6.1405910	3.5904000	-
	0.2110480				0.2208320		
P	-3.4750430	-0.5297570		H	-7.0150650	2.8027490	-
	0.7099490				2.4348080		
C	-4.5824350	-1.9898040		C	-2.3570160	-1.2657700	-
	1.0432400				0.5978960		
C	-4.2775770	-3.3150180		C	-0.9328930	-0.7773900	-
	0.6622830				0.8952740		
C	-5.7702110	-1.7474560		H	-2.9115980	-1.6383420	-
	1.7727260				1.4731560		
C	-5.1429140	-4.3703190		H	-0.7272990	-0.8950280	-
	1.0047980				1.9737400		

C	-1.1935070	-2.1421580	-	C	0.9164750	3.1124220	-
0.1919660				4.3445100			
C	-0.9910410	-3.4161280	-	H	0.0943910	2.7165320	-
0.9800660				4.9707060			
C	-0.6311350	-4.6229860	-	H	0.6345810	4.1354000	-
0.3370720				4.0363180			
C	-1.1838050	-3.4592080	-	H	1.8208760	3.1826900	-
2.3820600				4.9806120			
C	-0.4626740	-5.8154720	-	H	3.2854070	2.4727080	-
1.0627430				2.8389330			
H	-0.4878800	-4.6468910		H	1.7382810	2.7358950	
0.7475220				1.3719170			
C	-1.0083680	-4.6440400	-	C	3.7428830	3.4833100	
3.1097180				1.0937020			
H	-1.4762020	-2.5494820	-	H	4.4899120	3.4934360	
2.9200960				0.2767110			
C	-0.6431620	-5.8332860	-	C	3.6863430	4.9003830	
2.4537000				1.6960770			
H	-0.1875280	-6.7352420	-	H	4.6440460	5.1387870	
0.5312530				2.1956370			
H	-1.1611550	-4.6397030	-	H	3.5069180	5.6755020	
4.1964180				0.9288170			
H	-0.5073920	-6.7621730	-	H	2.8814910	4.9710830	
3.0210260				2.4550780			
C	-0.8710010	-2.2395180		C	4.2134650	2.4824380	
1.2953540				2.1641420			
H	-1.5636510	-2.9323270		H	4.2592970	1.4516380	
1.8094990				1.7732060			
H	0.1585350	-2.6085960		H	5.2185970	2.7508300	
1.4380240				2.5388600			
H	-0.9483680	-1.2516990		H	3.5137980	2.4925180	
1.7759620				3.0238770			
C	1.1660400	2.1781370	-	H	3.8085360	-0.5336620	
3.1476060				2.7054230			
H	0.2693460	2.1782130	-	C	2.0292030	-1.5224300	
2.5032310				3.4357470			
C	1.3849210	0.7402560	-	H	1.3641070	-2.3493010	
3.6528640				3.1168680			
H	1.5265960	0.0261120	-	C	2.4679590	-1.8046660	
2.8195740				4.8861840			
H	0.5148780	0.3951560	-	H	1.5970030	-1.7409460	
4.2427170				5.5653000			
H	2.2816120	0.6887330	-	H	2.9098420	-2.8099020	
4.3015310				5.0062810			

H	3.2149820	-1.0565460		C	-2.6912800	4.6981180	
	5.2186190				1.4434100		
H	1.8262090	-3.5461240		H	-1.9627490	5.5302510	
	0.4150990				1.5517510		
C	3.3590660	-3.6353010	-	H	-3.6501720	5.1599410	
	1.0640960				1.1395220		
H	4.4291500	-3.3716570	-	C	-1.0306750	2.1060660	
	1.1664780				1.6341870		
C	2.5747220	-2.9104530	-	H	-0.1933860	1.4794880	
	2.1729500				1.2809640		
H	2.8867500	-3.2771280	-	H	-1.7336380	1.4030110	
	3.1688890				2.1234680		
H	1.4895280	-3.0944360	-	C	-2.9023730	3.9922600	
	2.0658950				2.7882860		
H	2.7469870	-1.8171400	-	H	-3.4589750	3.0529880	
	2.1519230				2.6100330		
C	3.2285470	-5.1609980	-	H	-3.5626580	4.6318930	
	1.2304280				3.4025460		
H	3.6156850	-5.4737520	-	C	-0.5045960	3.1545720	
	2.2185840				2.6250400		
H	3.7930690	-5.7095390	-	H	-0.0387380	3.9836820	
	0.4536500				2.0597830		
H	2.1658860	-5.4610660	-	H	0.3021840	2.6973500	
	1.1687940				3.2265470		
C	1.2295010	-0.2091270		C	-1.6010290	3.7008670	
	3.3923990				3.5526740		
H	1.8572910	0.6300950		H	-1.8133660	2.9696400	
	3.7516570				4.3562850		
H	0.9002410	0.0281410		H	-1.2387080	4.6226390	
	2.3657060				4.0479110		
H	0.3300790	-0.2693720		N	-2.2936190	3.8429790	
	4.0328840				0.3042100		
C	-2.2166290	2.1773070	-	H	-2.4213560	5.4821620	-
	1.9484890				0.9975020		
C	-1.6921110	2.6223500		H	-0.9994450	3.9429460	-
	0.3652470				2.2570490		
C	-2.0712710	3.6836340	-	H	-2.5664250	3.9994690	-
	2.1783610				3.1136790		
C	-2.7073800	4.4120070	-	H	-3.2863160	1.8972840	-
	0.9965360				1.9525260		
H	-3.8122510	4.3585270	-	H	-1.7215900	1.5883810	-
	1.0620660				2.7416300		
N	-1.6081100	1.8198810	-	H	-1.0717670	0.6009240	-
	0.6727390				0.5977260		

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Product "3aa"

Thermal Free Energy Correction = 1.143486

Electronic Energy = -4995.06294180

Corrected Free Energy = -4993.91945580

C	-6.6283460	-0.8469590	-
	0.6373360		
C	-5.7009940	0.0318430	-
	0.0581920		
C	-4.3161260	-0.2504770	-
	0.0562200		
C	-3.8589400	-1.4425710	-
	0.7004320		
C	-4.8084340	-2.3158910	-
	1.2747790		
C	-6.1814050	-2.0331060	-
	1.2387820		
H	-7.6967870	-0.5990730	-
	0.6226780		
H	-6.0676080	0.9639610	
	0.3781650		
H	-4.4708380	-3.2309130	-
	1.7714750		
H	-6.8961360	-2.7304600	-
	1.6928070		
C	-3.7312390	2.6615920	
	0.4568860		
C	-3.5823580	0.9155070	
	2.5859580		
C	-4.6869500	3.0121020	
	1.6432260		
C	-4.8386580	1.8175380	
	2.6219460		
H	-4.2874310	3.8926540	
	2.1789680		
H	-5.6793960	3.3086030	
	1.2552970		
H	-5.0463060	2.1689350	
	3.6476450		
H	-5.7092910	1.2024220	
	2.3393280		
C	-1.5644690	-3.4092290	-
	0.0713820		

C	-1.8865810	-2.4162340	-
	2.6876140		
C	-1.0646860	-4.2827460	-
	1.2539200		
C	-1.8689770	-3.9538430	-
	2.5185810		
H	-0.0059800	-4.0261190	-
	1.4256510		
H	-1.1069050	-5.3579080	-
	1.0072300		
H	-1.4536570	-4.4558480	-
	3.4107020		
H	-2.9050320	-4.3266260	-
	2.4088370		
P	-2.0398170	-1.7710840	-
	0.9157500		
P	-3.1053560	0.9120820	
	0.7541210		
Cu	-1.1554040	0.1598300	-
	0.1310630		
P	3.5637770	1.0867930	
	0.5094250		
C	4.6300630	2.6093460	
	0.5133030		
C	4.0380720	3.8933000	
	0.5222070		
C	6.0357270	2.5031420	
	0.6002630		
C	4.8385350	5.0445970	
	0.6128310		
H	2.9493090	4.0024830	
	0.4446930		
C	6.8315160	3.6566820	
	0.6913630		
H	6.5128450	1.5149740	
	0.5819790		
C	6.2365380	4.9306950	
	0.6991010		
H	4.3652930	6.0349580	
	0.6097600		
H	7.9230890	3.5590070	
	0.7504970		
H	6.8604410	5.8305950	
	0.7674210		

C	4.5402090	-0.0471180	-	H	0.8389120	2.6539150	-
0.5885500				2.8582200			
C	4.5335910	0.0208440	-	C	-0.8598540	5.5615110	-
1.9981990				2.2736200			
C	5.3529810	-1.0128320		H	-1.4102000	6.3053760	-
0.0437870				0.3087320			
C	5.3232530	-0.8579230	-	H	-0.1587600	4.5570910	-
2.7577420				4.0703790			
H	3.9120470	0.7635390	-	H	-1.2993110	6.4089540	-
2.5113760				2.8135670			
C	6.1635270	-1.8748530	-	C	0.6668490	2.1894810	
0.7154280				1.3860020			
H	5.3572150	-1.0857310		H	1.1777940	3.0451450	
1.1388350				1.8661870			
C	6.1451030	-1.8038020	-	H	-0.4117060	2.2542010	
2.1186000				1.6076530			
H	5.3056200	-0.7977300	-	H	1.0575670	1.2663820	
3.8534320				1.8382080			
H	6.8093560	-2.6039430	-	C	-0.6258810	-1.7657110	-
0.2098440				3.3353620			
H	6.7708520	-2.4809040	-	H	0.1807790	-1.7541570	-
2.7134180				2.5760370			
C	2.2281770	1.6863370	-	C	-0.9406310	-0.3087230	-
0.6433460				3.7180110			
C	0.9862800	0.8418620	-	H	-1.3235660	0.2653190	-
0.8658100				2.8523120			
H	2.5969000	2.2208790	-	H	-0.0375460	0.2062380	-
1.5316070				4.0970120			
H	0.6396650	0.7908150	-	H	-1.7136520	-0.2721440	-
1.9053220				4.5107370			
C	0.8993140	2.2022550	-	C	-0.1117650	-2.5372710	-
0.1205490				4.5625260			
C	0.2789230	3.3603300	-	H	0.7260270	-1.9869600	-
0.8716850				5.0311020			
C	-0.3647800	4.4116560	-	H	0.2600750	-3.5428700	-
0.1814730				4.2941490			
C	0.3413740	3.4432330	-	H	-0.9095080	-2.6548620	-
2.2829010				5.3226380			
C	-0.9242210	5.5000690	-	H	-2.7800090	-2.0975410	-
0.8736260				3.2580430			
H	-0.4265710	4.3973810		H	-0.6871320	-3.1592470	
0.9111210				0.5492290			
C	-0.2211280	4.5244390	-	C	-2.6446540	-3.9949930	
2.9755460				0.8716260			

H	-3.6037240	-4.0853840		H	-3.1827140	1.3503470	-
	0.3245210				2.0304800		
C	-2.2500930	-5.3934280		C	-4.5560900	4.4460350	-
	1.3849450				1.1353720		
H	-2.9802690	-5.7416420		H	-4.9864910	4.6473620	-
	2.1396010				2.1344340		
H	-2.2201680	-6.1466700		H	-5.2680220	4.8175680	-
	0.5772290				0.3752530		
H	-1.2517800	-5.3621890		H	-3.6160600	5.0223440	-
	1.8657630				1.0451790		
C	-2.8526370	-3.0516890		C	-1.3022220	0.2871040	
	2.0718070				3.5101370		
H	-3.1417190	-2.0340380		H	-1.6968750	-0.6055690	
	1.7553000				4.0324130		
H	-3.6431160	-3.4346850		H	-0.9879860	-0.0277560	
	2.7439380				2.4995450		
H	-1.9138270	-2.9710750		H	-0.4038450	0.6355640	
	2.6538700				4.0516080		
H	-3.8453890	-0.1177830		C	2.4324520	-2.9741130	-
	2.8843890				1.4684950		
C	-2.3817880	1.3806890		C	2.0349760	-2.4598430	
	3.4608740				0.7991050		
H	-1.9458420	2.2935190		C	2.8510200	-4.3797070	-
	3.0034730				1.0179330		
C	-2.8089100	1.7449800		C	3.6667230	-4.2451890	
	4.8959800				0.2652680		
H	-1.9156810	1.9563060		H	4.7045110	-3.9361340	
	5.5132750				0.0266210		
H	-3.4562800	2.6395290		N	1.6451770	-2.3129350	-
	4.9291540				0.4365970		
H	-3.3554450	0.9032280		C	3.7712030	-3.2929150	
	5.3654430				2.5000520		
H	-2.8017500	3.2567180		H	3.5100070	-4.2387680	
	0.5540980				3.0261920		
C	-4.2732380	2.9415570	-	H	4.8552400	-3.3608060	
	0.9663760				2.2726060		
H	-5.2301700	2.3966270	-	C	1.2225500	-1.6994940	
	1.0834070				1.8438230		
C	-3.3019850	2.4509180	-	H	0.2484260	-1.4971720	
	2.0548330				1.3651290		
H	-3.6772800	2.7203600	-	H	1.6978190	-0.7117280	
	3.0598700				2.0007120		
H	-2.3053640	2.9126160	-	C	3.5530220	-2.1016190	
	1.9292970				3.4372270		

H	3.6730580	-1.1654160		C	-4.3466430	2.2502220	
	2.8584740				0.9254180		
H	4.3680350	-2.1141270		C	-5.4687260	1.8185510	
	4.1847740				1.6489250		
C	1.0294690	-2.4092380		H	-6.4890100	0.1162130	
	3.1940800				2.5370390		
H	0.9401930	-3.4993070		H	-4.7637910	-1.5240140	
	3.0183890				1.8247990		
H	0.0765080	-2.0870420		H	-4.2385550	3.3144710	
	3.6496090				0.6855550		
C	2.1943490	-2.1181740		H	-6.2259890	2.5453180	
	4.1591480				1.9673220		
H	2.0376880	-1.1339810		C	-1.9177940	-2.6742020	
	4.6432540				1.3700400		
H	2.2070740	-2.8730380		C	-3.0622200	-2.2103250	-
	4.9695390				1.1196940		
N	3.0900220	-3.2594900		C	-2.7154180	-3.8647040	
	1.1957280				0.7440060		
H	3.7287070	-5.2198280		C	-3.7231880	-3.3398410	-
	0.7929670				0.2982040		
H	1.9421800	-4.9854130	-	H	-2.0037730	-4.5580910	
	0.8340620				0.2596850		
H	3.4537790	-4.8981930	-	H	-3.2373330	-4.4382480	
	1.7861050				1.5309050		
H	3.3394570	-2.3762040	-	H	-4.0952490	-4.1489800	-
	1.6939840				0.9520190		
H	1.8407500	-3.0224120	-	H	-4.6096120	-2.9232080	
	2.4022560				0.2152550		
H	1.0006410	-0.1412090	-	C	-2.2101290	2.4409590	-
	0.3516330				2.1773190		
				C	-1.3365240	3.5655980	
117					0.2359220		
TS-PDM-Alt.				C	-1.0915280	3.5095030	-
<i>Thermal Free Energy Correction = 0.905566</i>					2.2862160		
<i>Electronic Energy = -4532.85651908</i>				C	-1.1825510	4.4307060	-
<i>Corrected Free Energy = -4531.95095308</i>					1.0531380		
C	-5.6158890	0.4579170		H	-0.1067880	3.0001970	-
	1.9678210				2.3001010		
C	-4.6411250	-0.4681030		H	-1.1726150	4.0735180	-
	1.5631430				3.2317980		
C	-3.5071750	-0.0498120		H	-0.2952940	5.0834040	-
	0.8361860				0.9863420		
C	-3.3610880	1.3315670		H	-2.0635160	5.0906140	-
	0.5082920				1.1569480		

P	-1.8610710	1.8784710	-	C	3.7594550	3.4596520	
	0.4196800				3.3340330		
P	-2.2052070	-1.2074170		H	4.6277070	4.8906330	
	0.2246670				1.9434310		
Cu	-0.4013290	0.1627980	-	H	2.8559860	1.8378330	
	0.1833690				4.4624020		
P	3.1475810	0.8165080	-	H	3.8989890	4.1025130	
	0.4748870				4.2120060		
C	4.8694890	0.5439940	-	C	2.6142660	-0.8198300	
	1.0990580				0.2121340		
C	5.0333010	0.2629180	-	C	1.1322480	-0.9480400	
	2.4740570				0.3866590		
C	6.0036030	0.5683000	-	H	3.2634230	-1.2147650	
	0.2567300				1.0090250		
C	6.3093940	-0.0061640	-	H	0.7786150	-1.3958950	
	2.9960910				1.3292740		
H	4.1593090	0.2571600	-	C	1.8390340	-1.8523640	-
	3.1391580				0.6109260		
C	7.2781030	0.3037460	-	C	1.9259580	-3.3060700	-
	0.7835900				0.1925270		
H	5.8883250	0.7969700		C	1.7323930	-4.3486980	-
	0.8098440				1.1274280		
C	7.4329690	0.0145250	-	C	2.1296430	-3.6711780	
	2.1514950				1.1612550		
H	6.4277770	-0.2238750	-	C	1.7280080	-5.6961250	-
	4.0650960				0.7244150		
H	8.1543480	0.3226500	-	H	1.5863910	-4.1188960	-
	0.1231030				2.1876450		
H	8.4307670	-0.1895030	-	C	2.1283150	-5.0139820	
	2.5597940				1.5650060		
C	3.4128740	1.7933130		H	2.2908450	-2.8943940	
	1.0722120				1.9186040		
C	3.9928980	3.0775480		C	1.9210330	-6.0376030	
	0.9400000				0.6230280		
C	2.9991850	1.3615630		H	1.5781930	-6.4823430	-
	2.3503650				1.4753630		
C	4.1684050	3.9011380		H	2.2932510	-5.2620410	
	2.0616710				2.6213060		
H	4.3210020	3.4304050	-	H	1.9193130	-7.0888310	
	0.0470630				0.9363810		
C	3.1751710	2.1903820		C	1.6455110	-1.5921840	-
	3.4732030				2.1022480		
H	2.5349820	0.3777750		H	2.5263410	-1.9337440	-
	2.4771510				2.6774740		

H	0.7605130	-2.1310860	-	H	-5.6492370	2.0309090	-
	2.4772590				2.7055790		
H	1.4963470	-0.5161680	-	H	-4.3217450	1.1421150	-
	2.2933210				3.5134320		
C	-0.0829740	3.4396760		H	-3.8360490	-1.5732900	-
	1.1439330				1.5902460		
H	0.7306310	2.9793550		C	-2.0423120	-2.6365890	-
	0.5470180				2.2135210		
C	-0.3728850	2.5252800		H	-1.1099060	-2.9804340	-
	2.3472990				1.7180000		
H	-0.6099130	1.4877760		C	-2.5661260	-3.7978220	-
	2.0388580				3.0767550		
H	0.5077230	2.4737610		H	-1.8543110	-4.0128790	-
	3.0098510				3.8956060		
H	-1.2340850	2.9083770		H	-2.6924390	-4.7254030	-
	2.9301820				2.4898110		
C	0.3953720	4.8129150		H	-3.5422930	-3.5396100	-
	1.6473540				3.5329010		
H	1.2890510	4.6834210		H	-0.8347970	-2.8608750	
	2.2844610				1.2265520		
H	0.6700210	5.4930750		C	-2.1202250	-2.4371100	
	0.8208790				2.8877190		
H	-0.3945110	5.3039980		H	-3.2053120	-2.3257440	
	2.2503390				3.0833630		
H	-2.1577460	3.9581660		C	-1.4057780	-1.1652800	
	0.8653050				3.3793290		
H	-1.9919360	1.5954350	-	H	-1.5533550	-1.0358300	
	2.8567290				4.4675320		
C	-3.6643920	2.9199630	-	H	-0.3157760	-1.2376790	
	2.4354870				3.1959720		
H	-4.0065030	3.5094560	-	H	-1.7784010	-0.2518510	
	1.5610120				2.8802450		
C	-3.7597590	3.8293080	-	C	-1.6105290	-3.6598270	
	3.6747810				3.6756280		
H	-4.8179690	4.0742560	-	H	-1.7610950	-3.5103660	
	3.8833440				4.7611490		
H	-3.2142950	4.7805220	-	H	-2.1316720	-4.5893590	
	3.5373080				3.3832120		
H	-3.3468350	3.3188360	-	H	-0.5276400	-3.8059460	
	4.5671940				3.4921950		
C	-4.5976420	1.7059510	-	C	-1.7072400	-1.4251650	-
	2.6001570				3.1019720		
H	-4.5388780	1.0156060	-	H	-2.6200400	-1.0680080	-
	1.7399030				3.6177560		

H	-1.3027610	-0.5827080	-
	2.5078140		
H	-0.9567580	-1.6858530	-
	3.8697190		
H	0.9363250	0.8355300	-
	0.3806860		

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DBU Starting Material

Thermal Free Energy Correction = 0.203839

Electronic Energy = -462.112730877

Corrected Free Energy = -461.908891877

C	0.3701820	-0.7280960	-
	0.1378020		
C	2.7306120	-0.8478450	
	0.1769200		
C	2.7986170	0.6146140	-
	0.2843630		
H	2.9723700	-0.9074790	
	1.2622950		
C	1.5924000	1.3581490	
	0.2880330		
H	2.7574380	0.6560090	-
	1.3907400		
H	1.5413460	2.3883950	-
	0.1180440		
N	1.4337540	-1.4618240	-
	0.0556050		
N	0.3384930	0.6728920	-
	0.0513820		
C	-0.9279720	-1.4861500	-
	0.4136090		
H	-1.2487460	-1.2998600	-
	1.4594790		
H	-0.6441820	-2.5488500	-
	0.3514060		
H	3.5063820	-1.4514890	-
	0.3380300		
H	3.7357450	1.1066500	
	0.0396690		
C	-0.8489060	1.4807010	
	0.2605200		
H	-1.0653860	1.4598360	
	1.3557190		

H	-0.5702150	2.5259330	
	0.0263510		
H	1.6952310	1.4537780	
	1.3946440		
C	-2.0966930	-1.1807240	
	0.5486380		
H	-1.6860190	-0.9783690	
	1.5579100		
H	-2.7318510	-2.0809400	
	0.6536220		
C	-2.1280240	1.1471950	-
	0.5243340		
H	-2.7469380	2.0633850	-
	0.5778250		
H	-1.8354050	0.9057140	-
	1.5639020		
C	-2.9629730	0.0053790	
	0.0843280		
H	-3.5530230	0.3902280	
	0.9403270		
H	-3.6959290	-0.3397640	-
	0.6721980		

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3-Me-3-Ph-Cyclopropene Starting Material

Thermal Free Energy Correction = 0.127810

Electronic Energy = -386.989214194

Corrected Free Energy = -386.861404194

C	-2.3209730	0.6549710	-
	0.9889260		
C	-2.3209740	-0.6538000	-
	0.9897110		
C	-1.5139680	-0.0000720	
	0.1094750		
C	-2.0194720	-0.0009350	
	1.5597840		
H	-1.6491030	-0.8937060	
	2.1030430		
H	-1.6490890	0.8911780	
	2.1041130		
H	-3.1261500	-0.0009460	
	1.5905810		
C	0.0026080	-0.0000190	
	0.0252260		

C	0.7211260	-1.2125680		H	1.0495610	-4.9037980	-
	0.0017950				0.5072830		
C	0.7210940	1.2125680		H	-2.9136870	-3.4111510	
	0.0026000				2.1053060		
C	2.1256020	-1.2156520	-	H	-2.4873120	-5.8321630	
	0.0494490				1.7899260		
H	0.1684740	-2.1620670		C	2.8211930	-2.0514690	
	0.0173080				0.2217630		
C	2.1255670	1.2157240	-	C	1.5531710	-2.7667030	-
	0.0486410				2.1907060		
H	0.1684090	2.1620370		C	3.7113560	-2.4762360	-
	0.0187400				0.9740580		
C	2.8320650	0.0000530	-	C	2.9164780	-3.4313490	-
	0.0743810				1.8749650		
H	2.6709480	-2.1685280	-	H	3.9773800	-1.5757190	-
	0.0724070				1.5578310		
H	2.6708940	2.1686280	-	H	4.6633530	-2.9236510	-
	0.0709650				0.6379880		
H	3.9290450	0.0000870	-	H	3.4744720	-3.6765790	-
	0.1163940				2.7968810		
H	-2.6497370	1.6001100	-	H	2.7624870	-4.3887300	-
	1.4293690				1.3420000		
H	-2.6497350	-1.5984120	-	C	-3.1103660	-0.4407530	
	1.4312850				0.4243060		
				C	-2.1989600	-0.9420950	
					3.0460230		
116				C	-3.9610200	0.0745410	
Conformer 1 of TS-MI-Major					1.6091580		
<i>Thermal Free Energy Correction = 0.896017</i>				C	-3.7286300	-0.8483240	
<i>Electronic Energy = -4532.37308412</i>					2.8151060		
<i>Corrected Free Energy = -4531.47706712</i>				H	-3.6212890	1.0969450	
C	-0.6819390	-5.5158240			1.8641640		
	0.6161370			H	-5.0307930	0.1498070	
C	0.1850710	-4.5588350			1.3438370		
	0.0675810			H	-4.2536300	-0.4778310	
C	-0.0371820	-3.1751770			3.7151070		
	0.2393040			H	-4.1471440	-1.8496200	
C	-1.1769080	-2.7494550			2.5948540		
	0.9807170			P	-1.4670300	-0.9269880	
C	-2.0373370	-3.7253310			1.2678770		
	1.5293650			P	1.0771680	-1.8983690	-
C	-1.7990580	-5.0965590			0.5518270		
	1.3543360			Cu	0.1667350	0.1319290	-
H	-0.4814030	-6.5844960			0.0121350		
	0.4671470						

P	-0.6375460	2.0919370	-	H	-3.1093590	5.3766210	
	1.0942580				2.9872440		
C	-1.8622390	2.1052180	-	C	1.5465770	2.7643350	
	2.4956080				0.0139310		
C	-3.2705520	2.0924400	-	C	1.7232290	1.5616180	
	2.3292180				0.6642490		
C	-1.3531560	1.9572510	-	H	1.3468170	3.8190340	
	3.8090290				0.2350450		
C	-4.1287340	1.9171800	-	H	1.8777780	1.3744600	
	3.4261680				1.7376580		
H	-3.6964340	2.2153350	-	C	2.7608950	1.9857680	-
	1.3263520				0.3968190		
C	-2.2096670	1.7809670	-	C	4.0836440	2.5308610	
	4.9077940				0.0933730		
H	-0.2660390	1.9754300	-	C	5.2751770	2.3991510	-
	3.9647960				0.6605000		
C	-3.6034800	1.7555500	-	C	4.1750430	3.1855480	
	4.7216910				1.3482790		
H	-5.2158150	1.9036690	-	C	6.4995280	2.8948220	-
	3.2683520				0.1821530		
H	-1.7872250	1.6664660	-	H	5.2502620	1.9024650	-
	5.9152190				1.6363440		
H	-4.2752500	1.6179500	-	C	5.3955420	3.6851640	
	5.5789010				1.8251740		
C	-1.5261080	3.0796870		H	3.2705780	3.3002280	
	0.1891880				1.9573440		
C	-1.3355380	2.8008830		C	6.5688710	3.5415100	
	1.5650040				1.0630700		
C	-2.2990820	4.2216980	-	H	7.4062140	2.7749550	-
	0.1459370				0.7903090		
C	-1.8869660	3.6245840		H	5.4313670	4.1891420	
	2.5599770				2.8003000		
H	-0.7479350	1.9224190		H	7.5256890	3.9293450	
	1.8484630				1.4359910		
C	-2.8711320	5.0305070		C	2.7955040	1.2749660	-
	0.8480050				1.7463120		
H	-2.4510990	4.4779400	-	H	3.1176910	1.9632770	-
	1.2015970				2.5530540		
C	-2.6670320	4.7400400		H	3.5033940	0.4246460	-
	2.2100590				1.7285430		
H	-1.7142990	3.3837190		H	1.7937590	0.8912550	-
	3.6177370				1.9928030		
H	-3.4725940	5.9021210		C	-1.6452590	0.1890000	
	0.5562190				3.9540830		

H	-2.0057760	1.1500060		C	1.5739990	-1.7878680	-
	3.5439650				3.3973590		
C	-0.1078000	0.2209730		H	2.3071790	-0.9870510	-
	3.9895280				3.1801080		
H	0.3241030	0.3302600		C	2.0088230	-2.5026520	-
	2.9790380				4.6923610		
H	0.2471090	1.0636970		H	1.9496790	-1.8040670	-
	4.6131040				5.5487170		
H	0.2880430	-0.7171970		H	3.0447640	-2.8857140	-
	4.4256990				4.6467170		
C	-2.1806510	0.0496430		H	1.3346480	-3.3568280	-
	5.3930610				4.9059250		
H	-1.7806380	0.8610730		H	3.0758630	-1.0155450	
	6.0311760				0.5172420		
H	-3.2837260	0.0956790		C	2.8982240	-2.9246630	
	5.4452600				1.5007830		
H	-1.8564750	-0.9161860		H	2.4430530	-3.9131690	
	5.8310480				1.2922640		
H	-1.9152010	-1.9094590		C	2.1079140	-2.2548290	
	3.5032930				2.6386910		
H	-2.8333370	0.4127310	-	H	2.1001260	-2.8915820	
	0.2200740				3.5438200		
C	-3.7346180	-1.5180900	-	H	2.5740530	-1.2852850	
	0.4981510				2.9017970		
H	-3.7989680	-2.4788390		H	1.0626530	-2.0505840	
	0.0502480				2.3544700		
C	-5.1571720	-1.1362350	-	C	4.3520280	-3.1557950	
	0.9525540				1.9587940		
H	-5.5286030	-1.8737540	-	H	4.3634180	-3.6774240	
	1.6900620				2.9352070		
H	-5.8762060	-1.1108380	-	H	4.9288210	-3.7724070	
	0.1128450				1.2452320		
H	-5.1518240	-0.1427880	-	H	4.8782420	-2.1882870	
	1.4410330				2.0833480		
C	-2.8397640	-1.7151240	-	C	0.1981190	-1.1362810	-
	1.7357830				3.6139750		
H	-1.8028420	-1.9664630	-	H	-0.1283410	-0.5545530	-
	1.4569220				2.7340170		
H	-3.2288820	-2.5263370	-	H	0.2234150	-0.4516770	-
	2.3804910				4.4808430		
H	-2.8065030	-0.7815020	-	H	-0.5682810	-1.9108180	-
	2.3283640				3.8153840		
H	0.7765140	-3.5287850	-				
	2.3951660						

Conformer 1 of TS-MI-Minor*Thermal Free Energy Correction = 0.897876**Electronic Energy = -4532.38770352**Corrected Free Energy = -4531.48982752*

C	5.6744750	-1.6375980	-
0.3180610			
C	4.3609810	-2.1176610	-
0.2058010			
C	3.2615210	-1.2343920	-
0.1506970			
C	3.4895700	0.1701440	-
0.2213200			
C	4.8171020	0.6347730	-
0.3441660			
C	5.9020630	-0.2541780	-
0.3893530			
H	6.5150650	-2.3421000	-
0.3580320			
H	4.1884810	-3.1979000	-
0.1743090			
H	5.0146990	1.7090200	-
0.4094120			
H	6.9233770	0.1364440	-
0.4833830			
C	1.3619740	-3.2289040	-
1.3064480			
C	1.5030750	-3.0040860	-
1.4537260			
C	1.6172440	-4.5816310	-
0.5669280			
C	1.9871080	-4.3780810	-
0.9299880			
H	0.7118590	-5.2095770	-
0.6482050			
H	2.4286370	-5.1372420	-
1.0743640			
H	1.5704570	-5.1963350	-
1.5482860			
H	3.0836810	-4.4358280	-
1.0534210			
C	2.1625130	2.4026270	-
1.3830000			
C	2.6288910	2.7444600	-
1.3752550			

C	2.3678850	3.8475650	-
0.8542640			
C	3.2251380	3.8066140	-
0.4192160			
H	1.3807210	4.2827800	-
0.6119430			
H	2.8127590	4.5028990	-
1.6236430			
H	3.2907910	4.8005320	-
0.8982100			
H	4.2607740	3.5261420	-
0.1477640			
P	2.0398200	1.3538150	-
0.2125460			
P	1.5155980	-1.8436210	-
0.0297210			
Cu	0.1963510	0.0080740	-
0.3142380			
P	-1.2697910	0.6834700	-
1.5318600			
C	-2.5312090	-0.3175980	-
2.4363790			
C	-2.1455270	-0.9202330	-
3.6567310			
C	-3.8478510	-0.5504020	-
1.9636000			
C	-3.0327990	-1.7390520	-
4.3744020			
H	-1.1343970	-0.7418550	-
4.0451750			
C	-4.7391660	-1.3616950	-
2.6853220			
H	-4.1744320	-0.0952790	-
1.0218310			
C	-4.3336730	-1.9642820	-
3.8894350			
H	-2.7096610	-2.1956910	-
5.3191620			
H	-5.7541490	-1.5270980	-
2.3004830			
H	-5.0298600	-2.6015770	-
4.4501320			
C	-2.0599050	2.3131860	-
1.2571990			

C	-1.2624370	3.3054170		C	-6.1287890	-1.3952660	-
0.6337110				3.3245320			
C	-3.3492330	2.6945310		H	-6.6838420	0.6540130	-
1.7019660				3.7882560			
C	-1.7304780	4.6083400		H	-5.2787060	-3.3111260	-
0.4333470				2.7406680			
H	-0.2683470	3.0280400		H	-7.0613470	-1.8273940	-
0.2709400				3.7101870			
C	-3.8199010	4.0039450		C	-2.2273750	1.8101180	-
1.5048540				1.9960780			
H	-3.9899270	1.9680220		H	-2.2631080	2.0416640	-
2.2126420				3.0791190			
C	-3.0206050	4.9689600		H	-2.9887990	2.4220530	-
0.8666640				1.4776450			
H	-1.0879980	5.3443210	-	H	-1.2356260	2.0957410	-
0.0692070				1.6195000			
H	-4.8260040	4.2708700		H	2.2207100	-2.6019650	
1.8554720				2.1936000			
H	-3.3958840	5.9886720		C	0.0990970	-2.9934890	
0.7122540				2.1156200			
C	-1.1920460	-0.5716230	-	H	-0.1247520	-1.9324810	
1.7336290				2.3316590			
C	-1.9346240	-0.3850340	-	C	-1.0246260	-3.5148760	
0.5213710				1.2042950			
H	-1.1091050	-1.5434230	-	H	-0.8780620	-4.5850680	
2.2413320				0.9598210			
H	-2.5319960	-1.1436380	-	H	-2.0000500	-3.4061350	
0.0008020				1.7130150			
C	-2.4224180	0.3161860	-	H	-1.0792400	-2.9423360	
1.7799260				0.2598020			
C	-3.7037140	-0.2708140	-	C	0.1145930	-3.7471340	
2.3241410				3.4548790			
C	-4.7213300	0.5456790	-	H	-0.8677700	-3.6541850	
2.8738320				3.9542010			
C	-3.9381640	-1.6695150	-	H	0.3185100	-4.8263630	
2.2928430				3.3073710			
C	-5.9149380	-0.0079090	-	H	0.8914840	-3.3418590	
3.3675600				4.1325770			
H	-4.5829660	1.6311710	-	C	2.1612540	-3.0442260	-
2.9145240				2.6213580			
C	-5.1295570	-2.2236950	-	H	3.2368020	-3.1694150	-
2.7816030				2.3810780			
H	-3.1679170	-2.3311110	-	C	1.7647820	-4.1387160	-
1.8792130				3.6321270			

H	0.6946010	-4.0368210	-
3.9025860			
H	2.3603800	-4.0445840	-
4.5604910			
H	1.9195420	-5.1559340	-
3.2263410			
C	1.9648520	-1.6555930	-
3.2542850			
H	2.3276180	-0.8455030	-
2.5985040			
H	2.5166830	-1.5921780	-
4.2120290			
H	0.8951530	-1.4584470	-
3.4502350			
H	0.2900320	-3.1684700	-
1.5775490			
H	3.4156990	2.3283380	-
2.0338780			
H	1.1575800	2.3199290	
1.8407850			
C	1.4601280	3.2190070	-
2.2883480			
H	0.5747450	3.4259040	-
1.6529950			
C	3.1665240	1.8773430	
2.4432990			
H	4.1546700	1.7208050	
1.9668430			
C	3.3506750	2.8717840	
3.6067340			
H	3.9737760	2.4156450	
4.4000530			
H	3.8470530	3.8075620	
3.2903390			
H	2.3702340	3.1338130	
4.0520540			
C	2.6715670	0.5300970	
3.0040760			
H	2.5123190	-0.2156890	
2.2079560			
H	3.3981720	0.1133680	
3.7275440			
H	1.7004940	0.6717290	
3.5170570			

C	1.0752900	2.1090050	-
3.2834220			
H	1.9452280	1.8534330	-
3.9222090			
H	0.7311530	1.1944350	-
2.7654480			
H	0.2517910	2.4467120	-
3.9394560			
C	1.8044290	4.5134460	-
3.0488900			
H	1.9366540	5.3810150	-
2.3760270			
H	2.7374230	4.3856210	-
3.6345320			
H	0.9913620	4.7614980	-
3.7573500			

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Conformer 2 of TS-MI-Minor

Thermal Free Energy Correction = 0.899652

Electronic Energy = -4532.38608455

Corrected Free Energy = -4531.48643255

C	5.8641400	0.5561040	-
0.5196180			
C	4.8288910	-0.3784450	-
0.6632180			
C	3.4842920	-0.0421160	-
0.3814540			
C	3.1816250	1.2917790	
0.0077420			
C	4.2375910	2.2203490	
0.1544820			
C	5.5690440	1.8605920	-
0.0928420			
H	6.8979090	0.2644040	-
0.7446990			
H	5.0768730	-1.3803170	-
1.0190600			
H	4.0150570	3.2483630	
0.4601690			
H	6.3696160	2.6005910	
0.0333630			
C	2.5778620	-2.3853310	-
1.9486800			

C	2.6833900	-2.5872030		C	-2.4021600	-4.4293160	
	0.7977370				1.6185830		
C	3.5810100	-3.4697740	-	H	-1.2543640	-3.1171900	
	1.4365220				0.3345810		
C	3.8071560	-3.3951880		C	-3.4567550	-3.3833830	
	0.1044200				3.5375510		
H	3.2041450	-4.4694170	-	H	-3.1230920	-1.2560570	
	1.7172440				3.7715630		
H	4.5493890	-3.3474110	-	C	-3.1999240	-4.5360130	
	1.9592520				2.7684840		
H	3.8656550	-4.4114620		H	-2.2043400	-5.3153070	
	0.5388580				1.0004350		
H	4.7779160	-2.9175150		H	-4.0829480	-3.4513470	
	0.3207850				4.4371820		
C	1.1574910	2.3651670		H	-3.6249680	-5.5045460	
	2.0219240				3.0618550		
C	1.5020370	3.6177880	-	C	-2.7754530	0.7269330	
	0.4816980				1.8039160		
C	0.6322380	3.8086200		C	-2.5968980	2.0203360	
	1.8465320				2.3444870		
C	1.4987250	4.5061540		C	-4.0683190	0.3600930	
	0.7881470				1.3578280		
H	-0.4129760	3.7644510		C	-3.6637180	2.9322790	
	1.4817040				2.4062800		
H	0.6102140	4.3591710		H	-1.6118750	2.3196990	
	2.8043760				2.7198750		
H	1.1330190	5.5263660		C	-5.1363650	1.2654020	
	0.5713590				1.4273660		
H	2.5306500	4.6128650		H	-4.2289640	-0.6352890	
	1.1775660				0.9298260		
P	1.4075360	1.8241550		C	-4.9379380	2.5603050	
	0.2114290				1.9431130		
P	2.1124450	-1.3027680	-	H	-3.4992020	3.9345960	
	0.4681120				2.8239770		
Cu	0.1659030	-0.0866840	-	H	-6.1256810	0.9648560	
	0.3342570				1.0584430		
P	-1.3274900	-0.4005290		H	-5.7728950	3.2715510	
	1.6071540				1.9889180		
C	-2.1034840	-2.0227830		C	-1.1820840	-0.2537710	-
	2.0066960				1.9020950		
C	-1.8651050	-3.1860280		C	-1.9131580	-0.6619240	-
	1.2395780				0.7549390		
C	-2.9151530	-2.1458610		H	-1.0040190	-0.8619880	-
	3.1638330				2.7994280		

H	-2.4658500	-1.5913770	-	H	0.1649260	-5.0576080	
	0.5637920				0.7191270		
C	-2.4665310	0.4963310	-	H	0.6261950	-3.9760730	-
	1.5664110				0.6243300		
C	-3.7100910	0.1449090	-	C	1.9126580	-4.1681770	
	2.3494060				2.6262540		
C	-4.7653710	1.0716330	-	H	1.0568360	-4.7415310	
	2.5292830				3.0305000		
C	-3.8651950	-1.1372760	-	H	2.7472550	-4.8768600	
	2.9350870				2.4519790		
C	-5.9203670	0.7318410	-	H	2.2353850	-3.4391740	
	3.2536410				3.3943200		
H	-4.6898980	2.0727820	-	C	3.0325810	-1.6332300	-
	2.0929950				3.2239930		
C	-5.0190120	-1.4803360	-	H	4.0236290	-1.1845030	-
	3.6541860				3.0137890		
H	-3.0618970	-1.8751260	-	C	3.1984090	-2.6256820	-
	2.8245310				4.3912450		
C	-6.0576300	-0.5462760	-	H	2.2251740	-3.0986930	-
	3.8196050				4.6325130		
H	-6.7200730	1.4750980	-	H	3.5559790	-2.1023220	-
	3.3742420				5.2988250		
H	-5.1070460	-2.4840910	-	H	3.9193780	-3.4296810	-
	4.0913710				4.1518020		
H	-6.9606860	-0.8116330	-	C	2.0696050	-0.5029200	-
	4.3845760				3.6204520		
C	-2.3853340	1.9318380	-	H	1.9577580	0.2519900	-
	1.0663860				2.8222290		
H	-2.3184030	2.6327280	-	H	2.4310210	0.0077100	-
	1.9197600				4.5336890		
H	-3.2552850	2.2117620	-	H	1.0592180	-0.9037250	-
	0.4475700				3.8263330		
H	-1.4788530	2.0468110	-	H	1.6149850	-2.8747110	-
	0.4527490				2.1958960		
H	3.0881870	-2.0171490		H	2.4673790	3.6980120	-
	1.6545930				1.0155080		
C	1.5094780	-3.4542600		H	0.3478200	1.7096040	
	1.3247570				2.3949590		
H	0.6797710	-2.7650640		C	0.4013710	3.9555290	-
	1.5696980				1.5204470		
C	0.9970860	-4.4718750		H	-0.5830660	3.9140070	-
	0.2920090				1.0165380		
H	1.7958080	-5.1801240		C	2.3562780	2.1590960	
	0.0010960				2.9827700		

H	3.2719780	2.5897840		C	3.2339010	-1.2629130	-
2.5331370				0.1242060			
C	2.1271760	2.8542560		C	3.4654300	0.1373530	-
4.3393150				0.2462490			
H	2.9404720	2.5926180		C	4.7928350	0.5929180	-
5.0433420				0.4006190			
H	2.1038350	3.9559060		C	5.8745240	-0.3007400	-
4.2485630				0.4271800			
H	1.1691740	2.5239840		H	6.4814370	-2.3884560	-
4.7885350				0.3306140			
C	2.5849120	0.6528710		H	4.1544400	-3.2292760	-
3.2097570				0.0913040			
H	2.7623170	0.1188490		H	4.9928560	1.6635550	-
2.2612960				0.5053780			
H	3.4562690	0.4806440		H	6.8958860	0.0829170	-
3.8701320				0.5461250			
H	1.6894900	0.2027670		C	1.3164170	-3.2873100	-
3.6813550				1.1887230			
C	0.4018310	2.9457120	-	C	1.4939700	-2.9757810	
2.6807610				1.5599260			
H	1.3933640	2.9419720	-	C	1.5868830	-4.6159000	-
3.1782260				0.4118960			
H	0.1730510	1.9198280	-	C	1.9697340	-4.3668520	
2.3389480				1.0752220			
H	-0.3563930	3.2241730	-	H	0.6847860	-5.2513860	-
3.4370400				0.4666140			
C	0.5957750	5.3799050	-	H	2.3970050	-5.1811790	-
2.0780400				0.9107140			
H	0.5283940	6.1613200	-	H	1.5553710	-5.1639720	
1.2985150				1.7220520			
H	1.5868320	5.4687190	-	H	3.0670410	-4.4245630	
2.5679840				1.1918630			
H	-0.1777180	5.5983260	-	C	2.1710800	2.4336800	
2.8389350				1.2923620			
				C	2.5961690	2.6679690	-
				1.4843490			
116				C	2.3756250	3.8563930	
Conformer 3 of TS-MI-Minor				0.7062800			
<i>Thermal Free Energy Correction = 0.897220</i>				C	3.2111430	3.7637120	-
<i>Electronic Energy = -4532.38309724</i>				0.5789890			
<i>Corrected Free Energy = -4531.48587724</i>				H	1.3867190	4.2875990	
C	5.6435310	-1.6800730	-	0.4646920			
0.3055240				H	2.8368420	4.5374640	
C	4.3299200	-2.1514100	-	1.4429910			
0.1619550							

H	3.2714490	4.7386360	-	C	-3.7117310	4.1318150	
	1.0962130				1.5993480		
H	4.2506610	3.4906690	-	H	-3.9035020	2.1169060	
	0.3149050				2.3571200		
P	2.0197450	1.3257110	-	C	-2.9224290	5.0591450	
	0.2598050				0.8962890		
P	1.4880430	-1.8624370		H	-1.0383000	5.3541950	-
	0.0409690				0.1594090		
Cu	0.1697980	-0.0168470	-	H	-4.6855020	4.4376290	
	0.2868360				2.0051350		
P	-1.2669710	0.7338910		H	-3.2736770	6.0878130	
	1.5549110				0.7450810		
C	-2.5257900	-0.2143220		C	-1.2328180	-0.6451120	-
	2.5150200				1.6584490		
C	-3.8642800	-0.3992320		C	-1.9863030	-0.4019650	-
	2.0856480				0.4564780		
C	-2.1267820	-0.8230940		H	-1.1723690	-1.6411050	-
	3.7276920				2.1193780		
C	-4.7646200	-1.1708270		H	-2.5514710	-1.1463970	
	2.8385200				0.1135310		
H	-4.1994430	0.0716920		C	-2.4487900	0.2583630	-
	1.1551090				1.7359100		
C	-3.0224760	-1.6043650		C	-3.6854520	-0.3237070	-
	4.4765590				2.3906760		
H	-1.0995720	-0.6787150		C	-3.8854960	-0.1363870	-
	4.0862930				3.7789620		
C	-4.3450640	-1.7834880		C	-4.6453880	-1.0846140	-
	4.0330240				1.6867690		
H	-5.7977390	-1.2965240		C	-4.9960800	-0.6861940	-
	2.4879400				4.4371120		
H	-2.6885300	-2.0668740		H	-3.1493350	0.4421420	-
	5.4146600				4.3509600		
H	-5.0471800	-2.3907840		C	-5.7617940	-1.6338540	-
	4.6189230				2.3411470		
C	-2.0246330	2.3786140		H	-4.5235630	-1.2478310	-
	1.2788330				0.6103850		
C	-1.2354220	3.3344740		C	-5.9446030	-1.4378580	-
	0.5906420				3.7199970		
C	-3.2722210	2.8111700		H	-5.1218510	-0.5283360	-
	1.7926160				5.5167720		
C	-1.6730840	4.6484660		H	-6.4947920	-2.2156100	-
	0.3937780				1.7660720		
H	-0.2719420	3.0201220		H	-6.8167220	-1.8654430	-
	0.1789640				4.2317070		

C	-2.2510020	1.7505030	-	H	2.2557760	-0.9451540	-
1.9847540				2.5705560			
H	-2.2512710	1.9682390	-	H	2.4254550	-1.7424920	-
3.0697730				4.1620060			
H	-3.0389600	2.3594650	-	H	0.8137490	-1.5875320	-
1.5027990				3.3827010			
H	-1.2730100	2.0529000	-	H	0.2402040	-3.2375950	-
1.5834930				1.4441970			
H	2.2205530	-2.5506730		H	3.3715480	2.2226670	-
2.2779360				2.1374560			
C	0.0976550	-2.9418300		H	1.1720790	2.3738700	
2.2368360				1.7662470			
H	-0.1245550	-1.8734590		C	1.4168120	3.1129120	-
2.4147660				2.3986390			
C	-1.0353450	-3.4978620		H	0.5420220	3.3504930	-
1.3582400				1.7595940			
H	-0.8895340	-4.5759970		C	3.1860810	1.9438020	
1.1512180				2.3591100			
H	-2.0048380	-3.3734270		H	4.1680950	1.7661910	
1.8749620				1.8773580			
H	-1.1034570	-2.9613600		C	3.3867290	2.9802940	
0.3937610				3.4825380			
C	0.1299500	-3.6452700		H	4.0183760	2.5522590	
3.6028280				4.2847060			
H	-0.8479000	-3.5396310		H	3.8812510	3.9023610	
4.1085220				3.1255850			
H	0.3381430	-4.7281400		H	2.4123190	3.2613650	
3.4928690				3.9294690			
H	0.9113360	-3.2117270		C	2.6935100	0.6202440	
4.2574670				2.9757300			
C	2.0948920	-3.1435440	-	H	2.5293180	-0.1568560	
2.5211990				2.2111050			
H	3.1742870	-3.2592950	-	H	3.4241950	0.2321920	
2.2936210				3.7109650			
C	1.6854150	-4.2707140	-	H	1.7255460	0.7832230	
3.4899840				3.4883220			
H	0.6108430	-4.1800850	-	C	1.0105490	1.9671740	-
3.7464940				3.3434850			
H	2.2662820	-4.2051910	-	H	1.8696280	1.6799810	-
4.4301060				3.9835150			
H	1.8493550	-5.2739660	-	H	0.6669180	1.0763220	-
3.0542110				2.7854650			
C	1.8864610	-1.7763590	-	H	0.1808920	2.2860520	-
3.1954400				4.0013570			

C	1.7573170	4.3739640	-
	3.2150230		
H	1.9029390	5.2669490	-
	2.5792830		
H	2.6815900	4.2176820	-
	3.8075440		
H	0.9358450	4.5982090	-
	3.9217410		

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Conformer 1 of TS-MI-Diast1

Thermal Free Energy Correction = 0.897844

Electronic Energy = -4532.37729365

Corrected Free Energy = -4531.47944965

C	-5.3196190	-1.8076370	
	1.2408050		
C	-4.6698420	-0.7609590	
	0.5707100		
C	-3.2723020	-0.7701530	
	0.3663160		
C	-2.5054250	-1.8492480	
	0.8907700		
C	-3.1789340	-2.9087720	
	1.5376670		
C	-4.5709600	-2.8980400	
	1.7100980		
H	-6.4070490	-1.7747860	
	1.3857290		
H	-5.2662510	0.0787820	
	0.1999160		
H	-2.6084060	-3.7574830	
	1.9264250		
H	-5.0646890	-3.7336580	
	2.2223610		
C	-3.2714350	0.3234320	-
	2.3512350		
C	-3.4109510	2.1345860	-
	0.2455020		
C	-4.5516330	1.1844930	-
	2.2947550		
C	-4.2536280	2.4674250	-
	1.5055130		
H	-4.9083360	1.4230710	-
	3.3149360		

H	-5.3570690	0.5975510	-
	1.8119580		
H	-3.6758260	3.1466960	-
	2.1579930		
H	-5.1820090	3.0022500	-
	1.2288050		
C	0.0284250	-1.6994300	
	2.5502780		
C	-0.2303030	-3.6981430	
	0.5752800		
C	0.8740510	-2.9870410	
	2.6870850		
C	0.1100890	-4.1407610	
	2.0226580		
H	1.8353460	-2.8372390	
	2.1568690		
H	1.1258990	-3.2051630	
	3.7401130		
H	0.6944090	-5.0783020	
	2.0357300		
H	-0.8137840	-4.3397030	
	2.5988200		
P	-0.6406510	-1.8319160	
	0.7659290		
P	-2.4347040	0.5498060	-
	0.6467370		
Cu	-0.1366030	0.0673150	-
	0.4642940		
P	1.3228700	1.3525410	
	1.0210860		
C	1.2136480	3.1916070	
	1.0867680		
C	1.9478200	4.0968670	
	0.2813940		
C	0.3193910	3.7357190	
	2.0427630		
C	1.7817230	5.4858550	
	0.4185990		
H	2.6578410	3.7200520	-
	0.4599000		
C	0.1462830	5.1212350	
	2.1755730		
H	-0.2413050	3.0543920	
	2.6961510		

C	0.8763310	6.0053760		C	2.9604400	-1.2366270	-
	1.3592760				1.0664430		
H	2.3636280	6.1660460	-	C	5.2636260	-1.4820290	-
	0.2176000				2.6270680		
H	-0.5521260	5.5132270		H	4.4307070	0.0791660	-
	2.9265210				3.8500320		
H	0.7468990	7.0904580		C	3.9566410	-2.1515090	-
	1.4630050				0.7087890		
C	3.1385580	0.9865910		H	2.0603580	-1.1530780	-
	1.0263810				0.4525260		
C	4.0884940	1.4415180		C	5.1191340	-2.2853610	-
	0.0844280				1.4875290		
C	3.5899070	0.1388180		H	6.1586740	-1.5717640	-
	2.0660010				3.2572300		
C	5.4364800	1.0671590		H	3.8344240	-2.7578700	
	0.1798440				0.1974970		
H	3.7641590	2.0405950	-	H	5.9010630	-3.0014560	-
	0.7703840				1.2035570		
C	4.9367150	-0.2493880		C	2.4673200	1.5885460	-
	2.1565220				3.6872890		
H	2.8709780	-0.2215710		H	3.4396860	2.0892290	-
	2.8143320				3.5056740		
C	5.8664020	0.2163980		H	2.5612060	1.0157810	-
	1.2124540				4.6315450		
H	6.1499890	1.4156240	-	H	1.6970720	2.3663170	-
	0.5776220				3.8384410		
H	5.2594660	-0.9149810		H	-4.0852990	1.8713030	
	2.9682720				0.5912750		
H	6.9188210	-0.0895180		C	-2.4843160	3.2788310	
	1.2733370				0.2378200		
C	0.5780770	0.4335310	-	H	-1.8603600	2.8558030	
	2.3774350				1.0471950		
C	1.1901910	1.3878300	-	C	-1.5290860	3.7917500	-
	1.5107040				0.8521700		
H	-0.1640710	0.6620240	-	H	-2.0711780	4.3700270	-
	3.1575460				1.6252330		
H	1.0829910	2.4811290	-	H	-0.7692020	4.4560360	-
	1.4884290				0.4082460		
C	2.0681010	0.6647120	-	H	-1.0012370	2.9561520	-
	2.5264420				1.3471060		
C	3.1006130	-0.3904660	-	C	-3.3042780	4.4356220	
	2.1861310				0.8330780		
C	4.2717920	-0.5438880	-	H	-2.6301260	5.2174990	
	2.9643470				1.2306830		

H	-3.9463270	4.9021400		H	0.4993320	-0.9082490	
0.0597120				5.1626470			
H	-3.9583580	4.0852640		C	-1.5815650	0.0121590	
1.6559910				3.4896480			
C	-3.5195540	-1.1331850	-	H	-2.0252450	0.1659950	
2.7993030				2.4916480			
H	-4.2140230	-1.5851980	-	H	-2.3587160	0.2197900	
2.0616990				4.2498760			
C	-4.2024130	-1.1741310	-	H	-0.7648310	0.7508890	
4.1808870				3.6033780			
H	-3.5670260	-0.6749600	-	C	0.6438790	-3.4155760	-
4.9400970				1.8356450			
H	-4.3535670	-2.2224850	-	H	-0.2400140	-3.9144100	-
4.5027330				2.2789990			
H	-5.1880920	-0.6735940	-	H	0.4676020	-2.3260140	-
4.1741110				1.8277260			
C	-2.2329700	-1.9652470	-	H	1.5142740	-3.6032240	-
2.8205180				2.4906280			
H	-1.7361470	-1.9719130	-	C	1.2119570	-5.4861120	-
1.8381380				0.5467150			
H	-2.4495660	-3.0119090	-	H	1.5420260	-5.9417670	
3.1072170				0.4048600			
H	-1.5008530	-1.5514180	-	H	0.3078770	-6.0277250	-
3.5391180				0.8922280			
H	-2.5498240	0.7902570	-	H	2.0126030	-5.6555220	-
3.0548440				1.2914630			
H	-1.1451230	-4.1972840					
0.2008840				116			
H	0.6945880	-0.8162170		Conformer 2 of TS-MI-Diast1			
2.5205390				<i>Thermal Free Energy Correction = 0.898843</i>			
C	0.9198600	-3.9758920	-	<i>Electronic Energy = -4532.37855680</i>			
0.4322570				<i>Corrected Free Energy = -4531.47971380</i>			
H	1.8285280	-3.4834580	-	C	-5.4596380	-0.4662830	
0.0424720				1.1898890			
C	-1.0161060	-1.4111380		C	-4.5419760	0.3981570	
3.6607940				0.5722210			
H	-1.8507450	-2.1353550		C	-3.2290370	-0.0230840	
3.5863540				0.2692010			
C	-0.4030870	-1.5451540		C	-2.8189120	-1.3341270	
5.0692900				0.6583840			
H	-1.1324490	-1.2139160		C	-3.7704730	-2.2086670	
5.8334530				1.2246950			
H	-0.1176950	-2.5859980		C	-5.0829010	-1.7863200	
5.3092720				1.4858530			

H	-6.4727320	-0.1137460		Cu	0.0054380	-0.1012780	-
	1.4221970				0.5469070		
H	-4.8545040	1.4162670		P	1.7572510	0.6617990	
	0.3208240				1.0129890		
H	-3.4733030	-3.2298080		C	1.1126870	2.1848650	
	1.4900560				1.8055430		
H	-5.8020420	-2.4806290		C	1.8753080	3.3180920	
	1.9388970				2.1877630		
C	-3.0303320	1.1142650	-	C	-0.2547600	2.1604860	
	2.3895520				2.1876200		
C	-2.4098860	2.8230400	-	C	1.2888700	4.3724340	
	0.3467660				2.9096370		
C	-4.1117480	2.2016690	-	H	2.9397720	3.3694010	
	2.1806930				1.9349260		
C	-3.6774720	3.2668560	-	C	-0.8327960	3.1997190	
	1.1376930				2.9229190		
H	-4.3588660	2.6775200	-	H	-0.8667930	1.3020760	
	3.1482340				1.8905690		
H	-5.0358540	1.6961170	-	C	-0.0640760	4.3230710	
	1.8413200				3.2870110		
H	-3.4731660	4.2291670	-	H	1.9032880	5.2396140	
	1.6413650				3.1874080		
H	-4.5091740	3.4670610	-	H	-1.8911600	3.1360310	
	0.4365770				3.2104160		
C	-0.4297370	-2.0117660		H	-0.5148720	5.1470350	
	2.3875490				3.8547000		
C	-1.0521010	-3.7108370		C	3.5569260	1.0108360	
	0.2127450				0.7599340		
C	0.2395480	-3.4023140		C	4.0636030	2.1169440	
	2.3034280				0.0385780		
C	-0.7617470	-4.3335300		C	4.4766430	0.0898560	
	1.6029670				1.3063130		
H	1.1639040	-3.3281610		C	5.4458530	2.2979560	-
	1.6966310				0.1232160		
H	0.5457080	-3.7751690		H	3.3712550	2.8408060	-
	3.2961500				0.4038790		
H	-0.3780490	-5.3655680		C	5.8597200	0.2648360	
	1.5199130				1.1394790		
H	-1.6908440	-4.3846740		H	4.0989040	-0.7837630	
	2.2036010				1.8519790		
P	-1.0223610	-1.8198510		C	6.3498240	1.3706800	
	0.5726800				0.4261190		
P	-2.0666120	1.0123650	-	H	5.8197490	3.1650820	-
	0.7480870				0.6843180		

H	6.5550090	-0.4727340		H	-2.5770430	2.8952220	
	1.5601750				0.7420960		
H	7.4309470	1.5092270		C	-1.1443930	3.6746130	-
	0.2939880				0.6748290		
C	0.9542490	0.2186760	-	H	-0.3070620	3.2208620	-
	2.3683390				0.1178360		
C	1.5168220	1.1137210	-	C	-0.7666980	3.6658700	-
	1.4105130				2.1668880		
H	0.3488440	0.5120300	-	H	-1.5889140	4.0564070	-
	3.2385770				2.7983720		
H	1.4811920	2.2084530	-	H	0.1176430	4.3095080	-
	1.3330980				2.3351720		
C	2.4657690	0.3244640	-	H	-0.5050400	2.6503140	-
	2.2943690				2.5158690		
C	3.3278540	-0.8050860	-	C	-1.3153230	5.1120890	-
	1.7636050				0.1558130		
C	4.7258370	-0.8211480	-	H	-0.3842630	5.6891330	-
	1.9674390				0.3138870		
C	2.7693980	-1.8778620	-	H	-2.1334370	5.6398150	-
	1.0357860				0.6857340		
C	5.5293660	-1.8504660	-	H	-1.5365280	5.1135720	
	1.4504460				0.9270410		
H	5.2097950	-0.0088940	-	C	-3.6136030	-0.2134110	-
	2.5176240				2.9180830		
C	3.5668950	-2.9027300	-	H	-4.3618060	-0.5557190	-
	0.5087520				2.1731610		
H	1.6875290	-1.8993980	-	C	-4.3412780	0.0025850	-
	0.8863880				4.2597010		
C	4.9578830	-2.8976820	-	H	-3.6368400	0.3961320	-
	0.7117590				5.0201490		
H	6.6139920	-1.8228870	-	H	-4.7460160	-0.9563090	-
	1.6185560				4.6370030		
H	3.0974160	-3.7179510		H	-5.1810470	0.7156810	-
	0.0590460				4.1676440		
H	5.5852920	-3.7004420	-	C	-2.5456090	-1.3006230	-
	0.3027590				3.0598820		
C	3.1395580	1.1940870	-	H	-2.0350070	-1.4907240	-
	3.3640660				2.1031880		
H	4.0188480	1.7340770	-	H	-2.9940330	-2.2500760	-
	2.9618600				3.4090200		
H	3.4849460	0.5738120	-	H	-1.7635680	-1.0008810	-
	4.2148400				3.7835980		
H	2.4235430	1.9439350	-	H	-2.2699110	1.4758130	-
	3.7479780				3.1098760		

H	-2.0669250	-3.9645960	-
0.1511300			
H	0.3396300	-1.2250050	
2.5188350			
C	-0.0202540	-4.1729060	-
0.8594990			
H	0.9894070	-3.9588740	-
0.4597750			
C	-1.4759070	-1.8723190	
3.5294430			
H	-2.3523240	-2.5067660	
3.2978130			
C	-0.9072060	-2.3545200	
4.8819640			
H	-1.6205320	-2.1183430	
5.6948070			
H	-0.7274600	-3.4447530	
4.9043690			
H	0.0480080	-1.8402930	
5.1081350			
C	-1.9626180	-0.4229320	
3.6925630			
H	-2.3951750	-0.0175210	
2.7640810			
H	-2.7384400	-0.3669190	
4.4799430			
H	-1.1220190	0.2313930	
3.9898890			
C	-0.1563580	-3.4524940	-
2.2083070			
H	-1.1381190	-3.6784340	-
2.6667090			
H	-0.0519100	-2.3578120	-
2.1148470			
H	0.6339410	-3.8018440	-
2.8988220			
C	-0.1250350	-5.6936440	-
1.1039510			
H	0.0837760	-6.3002690	-
0.2041580			
H	-1.1411150	-5.9528620	-
1.4647790			
H	0.5972470	-5.9980880	-
1.8850160			

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Conformer 3 of TS-MI-Diast1

Thermal Free Energy Correction = 0.900275

Electronic Energy = -4532.37973844

Corrected Free Energy = -4531.47946344

C	-4.9639850	0.0715910	
2.2174300			
C	-4.2087900	0.7310350	
1.2361100			
C	-3.0874500	0.1200220	
0.6317820			
C	-2.6955300	-1.1903300	
1.0549270			
C	-3.4803210	-1.8394360	
2.0361540			
C	-4.6048800	-1.2266750	
2.6084770			
H	-5.8264730	0.5731720	
2.6746970			
H	-4.4942740	1.7463100	
0.9432410			
H	-3.1896310	-2.8275400	
2.3986030			
H	-5.1828910	-1.7574330	
3.3756170			
C	-3.2543240	0.8329540	-
2.1891750			
C	-2.5245660	2.8253490	-
0.4797270			
C	-4.4137520	1.7960160	-
1.8753070			
C	-3.8427570	3.0984880	-
1.2729680			
H	-5.0015800	2.0098650	-
2.7880560			
H	-5.1026610	1.2987650	-
1.1661310			
H	-3.6275210	3.8069100	-
2.0937080			
H	-4.5918660	3.5948040	-
0.6275620			
C	-0.3966490	-2.8693250	
2.0138540			

C	-1.3687210	-3.5088920	-	C	3.4806300	1.1888080	
0.4443230				0.7733710			
C	-0.9114630	-4.3411150		C	3.9980390	2.2345090	-
1.8545060				0.0263000			
C	-1.8807750	-4.4522890		C	4.3947990	0.3066680	
0.6577880				1.3907300			
H	-0.0520790	-5.0168840		C	5.3821670	2.3974940	-
1.6895280				0.1922230			
H	-1.4016850	-4.6746140		H	3.3135500	2.9227170	-
2.7890870				0.5321980			
H	-1.9613350	-5.4951770		C	5.7792780	0.4607300	
0.3011900				1.2174520			
H	-2.9033510	-4.1533590		H	4.0106420	-0.5213770	
0.9454950				1.9995720			
P	-1.0464700	-1.8867840		C	6.2788730	1.5093350	
0.5104520				0.4280290			
P	-2.1004910	0.9928830	-	H	5.7627260	3.2187860	-
0.6790930				0.8144690			
Cu	0.0038550	-0.0927290	-	H	6.4683860	-0.2478210	
0.4845490				1.6944160			
P	1.6819210	0.8431600		H	7.3613090	1.6325840	
1.0431470				0.2916620			
C	0.9791510	2.4236510		C	0.9354970	0.1979520	-
1.6540870				2.3271480			
C	1.6851630	3.6402870		C	1.4683230	1.1415970	-
1.8374370				1.4065570			
C	-0.3761710	2.3868350		H	0.3294830	0.4253280	-
2.0810750				3.2158870			
C	1.0568600	4.7634670		H	1.4080250	2.2379230	-
2.4032700				1.3764540			
H	2.7395800	3.7078590		C	2.4455470	0.3274480	-
1.5507100				2.2374910			
C	-0.9945870	3.4994780		C	3.3118640	-0.7664250	-
2.6601810				1.6406960			
H	-0.9497740	1.4635560		C	4.7074260	-0.8040200	-
1.9456670				1.8574820			
C	-0.2837830	4.7051250		C	2.7607490	-1.7853870	-
2.8201040				0.8347600			
H	1.6284800	5.6935600		C	5.5111420	-1.8025140	-
2.5250040				1.2822640			
H	-2.0413910	3.4270730		H	5.1896370	-0.0336670	-
2.9853880				2.4663160			
H	-0.7681720	5.5837290		C	3.5550410	-2.7810790	-
3.2648820				0.2524720			

H	1.6814390	-1.7916020	-	C	-4.8106330	-0.6228540	-
0.6691980				3.5993480			
C	4.9435630	-2.7977220	-	H	-4.5150760	-0.0701660	-
0.4718670				4.5140070			
H	6.5939350	-1.7922190	-	H	-5.0415310	-1.6648270	-
1.4637710				3.8938510			
H	3.0839790	-3.5532960		H	-5.7366490	-0.1657130	-
0.3717590				3.2051440			
H	5.5723570	-3.5760390	-	C	-2.4586010	-1.3825080	-
0.0200030				3.0971280			
C	3.1235600	1.1516080	-	H	-1.6113090	-1.3338580	-
3.3391730				2.3950290			
H	4.0004070	1.7086880	-	H	-2.7105100	-2.4442000	-
2.9557350				3.2771570			
H	3.4735200	0.4961520	-	H	-2.1127190	-0.9477920	-
4.1613080				4.0560240			
H	2.4086180	1.8831030	-	H	-2.6526960	1.2582870	-
3.7587270				3.0196390			
H	-2.6735140	2.9976960		H	-2.1344000	-3.3418660	-
0.5994130				1.2228810			
C	-1.3275680	3.7195240	-	H	0.6927630	-2.8392860	
0.9160870				1.8125830			
H	-0.4711160	3.4246090	-	C	-0.0385320	-4.0034850	-
0.2851610				1.1134720			
C	-0.9141430	3.5227150	-	H	0.7989760	-3.7812190	-
2.3855580				0.4220320			
H	-1.7291050	3.8025710	-	C	-0.5895000	-2.3240640	
3.0818880				3.4557300			
H	-0.0433060	4.1635970	-	H	-1.6106850	-2.6023640	
2.6216550				3.7830790			
H	-0.6189200	2.4771430	-	C	0.4051990	-3.0416470	
2.5915500				4.3912430			
C	-1.6317480	5.1977320	-	H	0.2344560	-2.7442070	
0.6192420				5.4437020			
H	-0.7510660	5.8266000	-	H	0.3129450	-4.1424840	
0.8517070				4.3238150			
H	-2.4807350	5.5639830	-	H	1.4444370	-2.7662740	
1.2303990				4.1222240			
H	-1.8786470	5.3391950		C	-0.4466720	-0.8043170	
0.4492270				3.5907370			
C	-3.6677590	-0.6039280	-	H	-1.2539200	-0.2816940	
2.5659110				3.0511880			
H	-4.0364470	-1.1003960	-	H	-0.5073040	-0.5060480	
1.6435690				4.6550250			

H	0.5211370	-0.4553690		C	-0.6098960	-3.3413010	-
	3.1839400				1.1126700		
C	0.2525700	-3.2902430	-	C	-1.3359730	-3.0420460	
	2.4416500				1.5783890		
H	-0.5236210	-3.5440400	-	C	-1.7611810	-4.2306030	-
	3.1893620				0.5718420		
H	0.2911820	-2.1943870	-	C	-1.6051120	-4.4256060	
	2.3238260				0.9418080		
H	1.2342410	-3.6145120	-	H	-2.7147830	-3.7107150	-
	2.8334430				0.7551670		
C	-0.0253720	-5.5285000	-	H	-1.8158580	-5.1994820	-
	1.3471500				1.0989700		
H	-0.0426160	-6.1075440	-	H	-2.4980110	-4.9075590	
	0.4054850				1.3804920		
H	-0.8942330	-5.8397070	-	H	-0.7616720	-5.1115700	
	1.9612390				1.1413080		
H	0.8939230	-5.8073090	-	C	2.7713030	1.1892550	
	1.8957650				1.4738410		
				C	3.9766600	0.2291430	-
116					0.8936150		
Conformer 1 of TS-MI-Diast2				C	3.9871340	1.9632950	
<i>Thermal Free Energy Correction = 0.898681</i>					0.9088920		
<i>Electronic Energy = -4532.38580743</i>				C	4.8762210	1.0064220	
<i>Corrected Free Energy = -4531.48712643</i>					0.1030980		
C	3.0446290	-4.2967020		H	3.6094860	2.7554610	
	1.9375880				0.2377480		
C	1.7642190	-3.9124190		H	4.5557380	2.4712700	
	1.5146710				1.7078300		
C	1.5221040	-2.6546140		H	5.6766020	1.5579610	-
	0.9190880				0.4234320		
C	2.6099550	-1.7480800		H	5.3866350	0.3093450	
	0.7742840				0.7939210		
C	3.8974840	-2.1600610		P	2.3306540	-0.0377420	
	1.1826960				0.0696220		
C	4.1232860	-3.4197640		P	-0.1825470	-2.1644070	
	1.7556900				0.3378140		
H	3.1959020	-5.2816910		Cu	0.0300280	-0.0164040	-
	2.3974370				0.5039800		
H	0.9396240	-4.6156920		P	-0.6204880	2.0475940	
	1.6520920				0.6183240		
H	4.7482540	-1.4848080		C	-2.2398400	2.8937780	
	1.0625480				0.8200750		
H	5.1363120	-3.7059680		C	-2.7378230	3.8177390	-
	2.0660210				0.1310450		

C	-3.0426680	2.5837350		H	-0.8757910	2.4361530	-
	1.9423940				2.0150930		
C	-4.0099170	4.3885380		H	-0.2693020	0.1387900	-
	0.0233720				3.3241690		
H	-2.1249270	4.0788920	-	C	-2.2744970	0.6378200	-
	1.0013800				2.2635860		
C	-4.3188830	3.1503320		C	-3.3078120	-0.1473720	-
	2.0932180				1.4865200		
H	-2.6621980	1.8838460		C	-3.5807350	-1.4795350	-
	2.6950980				1.8577200		
C	-4.8107050	4.0504920		C	-4.1399570	0.4615910	-
	1.1310430				0.5259970		
H	-4.3838990	5.0958940	-	C	-4.6469770	-2.1889550	-
	0.7288380				1.2792960		
H	-4.9296670	2.8916340		H	-2.9485740	-1.9504530	-
	2.9684100				2.6212300		
H	-5.8082050	4.4937460		C	-5.1858860	-0.2538160	
	1.2467980				0.0807790		
C	0.4198780	3.4363750	-	H	-3.9779000	1.5084210	-
	0.0041860				0.2659470		
C	1.3420750	3.2583670	-	C	-5.4476720	-1.5818680	-
	1.0623710				0.2958880		
C	0.3759970	4.7031970		H	-4.8514060	-3.2213810	-
	0.6318630				1.5922600		
C	2.1948310	4.3014760	-	H	-5.8053500	0.2386400	
	1.4644750				0.8418220		
H	1.3874160	2.2919330	-	H	-6.2700120	-2.1400280	
	1.5753140				0.1697330		
C	1.2260690	5.7430540		C	-2.9319700	1.2967190	-
	0.2299140				3.4881070		
H	-0.3352230	4.8681050		H	-3.3483070	0.5199240	-
	1.4513180				4.1606020		
C	2.1442200	5.5481280	-	H	-3.7677390	1.9578570	-
	0.8212520				3.1843770		
H	2.8987720	4.1361010	-	H	-2.1927330	1.8921970	-
	2.2912370				4.0584450		
H	1.1738740	6.7140260		C	-2.5960460	-2.1588360	
	0.7403630				1.8107390		
H	2.8077250	6.3636770	-	C	-2.2275350	-0.9223900	
	1.1364280				2.6448900		
C	-1.1220010	1.4160320	-	H	-3.1137140	-0.2757170	
	1.6910750				2.7760810		
C	-0.8362750	0.1869650	-	H	-1.8633960	-1.2252730	
	2.3835540				3.6480330		

C	-3.7439630	-2.9248610		C	2.7752790	0.2648590	-
	2.4913470				3.1651300		
H	-4.5685940	-2.2265700		H	1.7913910	0.1847100	-
	2.7269890				2.6732080		
H	-4.1614820	-3.7172540		H	2.6508440	0.8308820	-
	1.8439100				4.1080410		
H	-3.4036310	-3.3898260		H	3.1055420	-0.7602720	-
	3.4394280				3.4232730		
H	-1.4381930	-0.3223830		C	5.1625370	1.0131310	-
	2.1566050				3.0095030		
H	-2.9665570	-1.8081430		H	5.0299020	1.5086960	-
	0.8288870				3.9904800		
H	-0.7990210	-3.1483370		H	5.9379100	1.5719760	-
	2.5415080				2.4544060		
H	-1.0059220	-2.6440270	-	H	5.5454930	-0.0103960	-
	1.8746560				3.1973370		
C	0.6042760	-4.0634230	-	H	4.3828190	-0.7803860	-
	1.7531220				1.0977100		
H	1.1697120	-4.5950360	-	C	2.9022220	0.5771260	
	0.9618980				2.8935630		
C	1.5376290	-3.0370520	-	H	3.6270680	-0.2598120	
	2.4196280				2.8734680		
H	1.8509360	-2.2445400	-	C	1.5369480	0.0383240	
	1.7220520				3.3620620		
H	2.4455300	-3.5284730	-	H	1.1155170	-0.6990610	
	2.8191730				2.6591520		
H	1.0115420	-2.5364700	-	H	1.6244780	-0.4431020	
	3.2549330				4.3549030		
C	0.1717160	-5.1034830	-	H	0.8099320	0.8700170	
	2.8065520				3.4337410		
H	1.0615820	-5.5083010	-	C	3.4095940	1.6172490	
	3.3264240				3.9128490		
H	-0.3724760	-5.9580130	-	H	2.7683780	2.5211020	
	2.3644890				3.8955860		
H	-0.4823830	-4.6344510	-	H	3.3742510	1.1941050	
	3.5688630				4.9353300		
C	3.8150070	0.9469570	-	H	4.4516940	1.9302380	
	2.2619500				3.7169920		
H	3.4848290	1.9829620	-	H	1.9084400	1.8768020	
	2.0610580				1.5219500		

Appendix 3 – Supporting Information for Chapter 3

Late Stage Regiodivergent *N*-Arylation of Unsymmetric Pyrazoles

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1. Material and Methods.

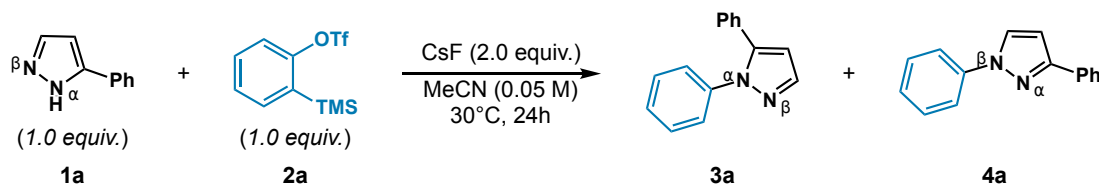
Commercial reagents were purchased from Combi-Block, Sigma Aldrich, Strem, Alfa Aesar, Ambeed, Synthonix, Synquest, Oakwood, or TCI and used without further purification. Acetonitrile (MeCN) (anhydrous >99.9% from Sigma Aldrich) were degassed and stored over 3 Å MS within a N₂ filled glove box. All experiments were performed in oven-dried or flame-dried glassware under an atmosphere of N₂ or in a glove box with a N₂ atmosphere. Reactions were monitored using thin-layer chromatography (TLC; EMD Silica Gel 60 F₂₅₄ plates). Visualization of the developed plates was performed under UV light (254 nm) or with a KMnO₄ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products was performed via silica gel chromatography (flash column chromatography or preparative thin-layer chromatography). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. ¹H, ¹³C, ¹⁹F NMR spectra and NOE experiments were recorded on a Bruker AVANCE-600, GN-500 or DRX-400 spectrometer. ¹H NMR spectra were internally referenced to the residual solvent signal. ¹³C NMR spectra were internally referenced to the residual solvent signal. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ¹³C and ¹⁹F NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory and are reported in terms of frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were obtained by the University of California, Irvine Mass Spectrometry Center on a Micromass 70S-250 Spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI).

2. Optimization of Copper-Catalyzed Hydroamination of Benzyne with Pyrazoles.

2.1. Optimization to Access More Hindered Nitrogen on Unsymmetric Pyrazoles.

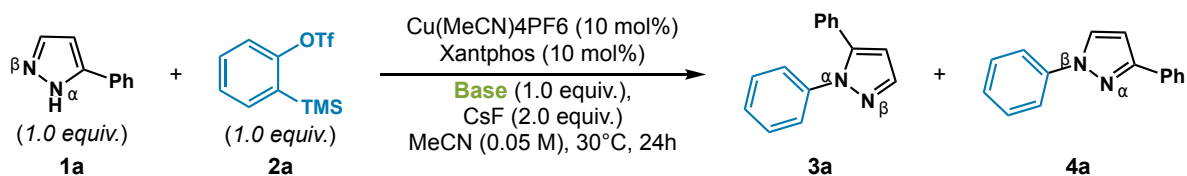
General Procedure for Table S1-8: In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added [Cu] catalyst (2.5-10 mol%), phosphine ligand and acetonitrile. After stirring for 30 min, pyrazole **1a** (0.05 mmol, 1.0 equiv.) and base (0.2-1.0 equiv.) were added. The resulting mixture was stirred for another 30 min followed by the addition of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (1.0-1.5 equiv.) and CsF (2.0-4.0 equiv.). The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. Reaction yield (%) was determined by ¹H NMR analysis of the crude mixture with internal standard trimethoxy benzene.

A. Optimization with Different Cu Sources (Figure S1).



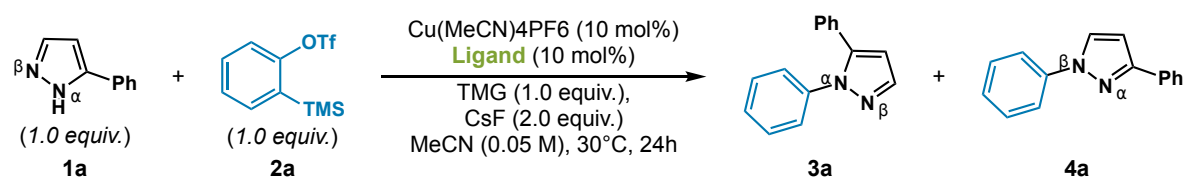
Entry	Derivation	N ^α :N ^β (3a : 4a)
1	none	1:1
2	DBU (0.5 equiv.)	trace
3	IPrCuCl (10 mol%)	1:5
4	CuCl (20 mol%)	1:12
5	Cu(MeCN) ₄ PF ₆ (10 mol%)	1:16
6	Cu-IPrDuphos (10 mol%)	1.3:1

B. Optimization with Base (Figure S2)



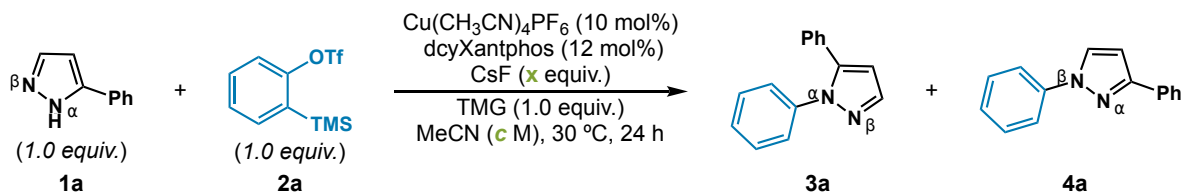
Entry	Base	$N^\alpha:N^\beta$ (3a:4a)
1	none	1:1
2	LiOiPr	1.8:1
3	LiOAc	1:1
4	Cs ₂ CO ₃	1.8:1
5	K ₃ PO ₄	3:1
6	Barton's base	1.3:1
7	TMG	10:1

C. Optimization with Ligands (Figure S3)



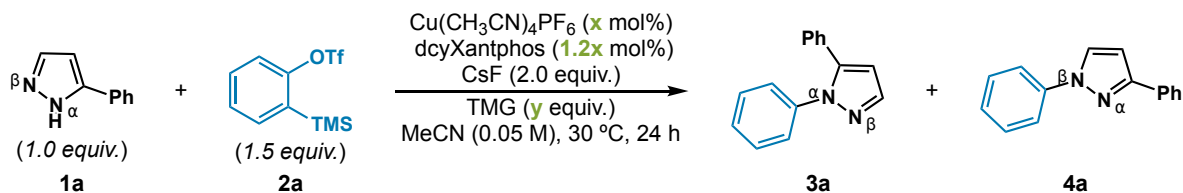
Entry	Ligand	$N^\alpha:N^\beta$ (3a:4a)
1	Xantphos	1:1
2	dppp	1.8:1
3	dppent	1:1
4	dcypm	1.8:1
5	dcype	3:1
6	tBuXantphos	1:9
7	dcyXantphos	16:1 (60%)

D. Optimization with Different Equivalence of CsF and Concentration (Figure S4)



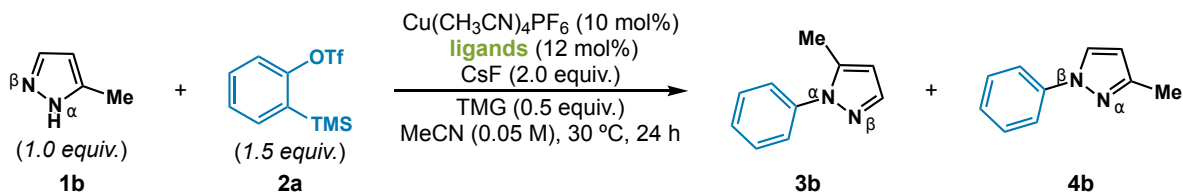
Entry	CsF/concentration	Yield, $N^\alpha:N^\beta$ (3a:4a)
1	$x = 2.0, c = 0.05$	60%, 16:1
2	$x = 2.0, c = 0.025$	38%, 10:1
3	$x = 2.0, c = 0.013$	51%, 15:1
4	$x = 1.0, c = 0.05$	35%, 10:1
5	$x = 3.0, c = 0.05$	46%, 12:1
6	$x = 4.0, c = 0.05$	10%, 4:1

E. Optimization with Different Equivalence of TMG and Catalyst Loading (Figure S5)



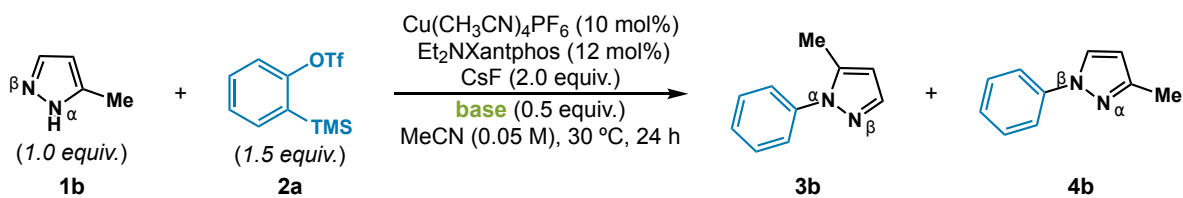
Entry	catalyst loading/TMG	Yield, $N^\alpha:N^\beta$ (3a:4a)
1	$x = 10, y = 1.0$	95%, >20:1
2	$x = 10, y = 0.5$	92%, >20:1
3	$x = 10, y = 0.2$	90%, 16:1
4	$x = 10, y = 0$	89%, 16:1
5	$x = 5, y = 0.5$	70%, 12:1
6	$x = 2.5, y = 0.5$	51%, 5:1
7	$x = 10, \text{K}_3\text{PO}_4$ instead of TMG ($y = 2.0$)	82%, 10:1

F. Optimization of Ligands for Smaller Substituents on Pyrazoles (Figure S6)



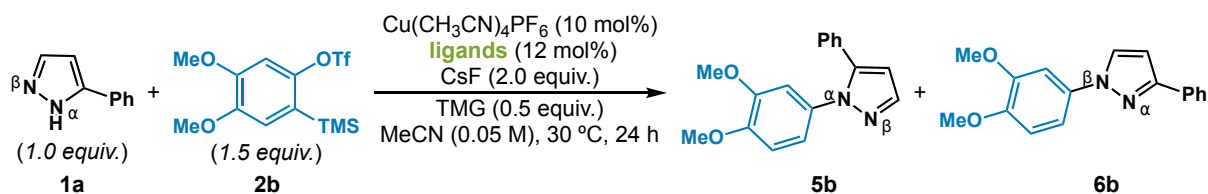
Entry	Ligand	$N^\alpha:N^\beta$ (3b:4b)
1	iPr-DuPhos	1.5:1
2	dCyPPF	1.6:1
3	JosiPhos (J009)	3.5:1
4	JosiPhos (J002)	1.7:1
5	TaniaPhos (T002)	1.2:1
6	WalPhos (W005)	1.7:1
7	WalPhos (W008)	1.5:1
8	Et₂N-XantPhos	4:1 (16%)
9	dCyXantPhos	1:1

G. Optimization of Base for Smaller Substituents on Pyrazoles (Figure S7)



Entry	Base	Yield, $N^\alpha:N^\beta$ (3b:4b)
1	LiOiPr	64%, 3:1
2	LiOAc	63%, 1:1
3	Cs ₂ CO ₃	57%, 3:1
4	K ₃ PO ₄	49%, 3:1
5	iPr ₂ EtN	32%, 1:1
6	Barton's Base	24%, 2:1
7	no base	59%, 4:1

H. Optimization of Ligands for Different Substituents on Aryne Precursors (Figure S8)

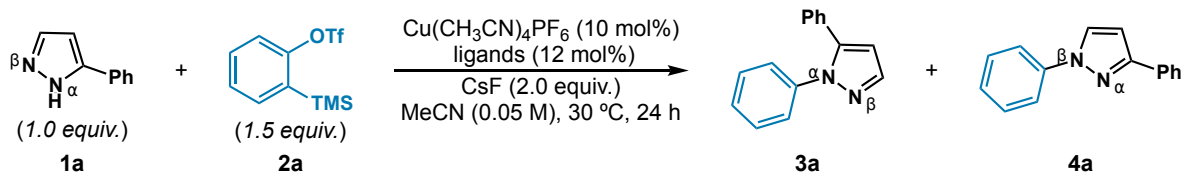


Entry	Ligand	Yield, $N^\alpha:N^\beta$ (5b:6b)
1	dCyXantPhos (L1)	21%, 2:1
2	Et2N-XantPhos (L2)	45%, 1:3
3	dppp	27%, 1:4
4	dppb	25%, 1:5
5	dpppent	12%, 1:3
6	XantPhos	13%, 1:1
7	NiXantPhos	9%, 1:1
8	dCype	15%, 2:1
9	dCypm	22%, 1:17
10	dCypb	14%, 1:1
11	tBuXantPhos	16%, 1:1
12	DPEPhos	trace
13	iPr-DuPhos	20%, 1:1
14	dCyPF	15%, 1:1
15	JosiPhos (J009)	48%, 8:1
16	JosiPhos (J002)	37%, 14:1

2.2. Optimization to Access Less Hindered Nitrogen on Asymmetric Pyrazoles.

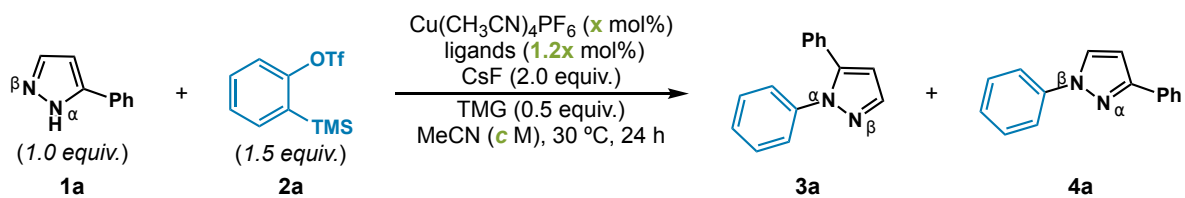
General Procedure for Table S9-10: In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added [Cu(CH₃CN)₄]PF₆ (2.5-10 mol%), ligand (3-12 mol%) and acetonitrile. After stirring for 30 min, pyrazole **1a** (0.1 mmol, 1.0 equiv.), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (0.15 mmol, 1.5 equiv.) and CsF (0.2 mmol, 2.0 equiv.) were added. The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. Reaction yield (%) was determined by ¹H NMR analysis of the crude mixture with internal standard trimethoxy benzene.

A. Optimization of Ligands (Figure S9)



Entry	Ligand	Yield, <i>N</i> ^α : <i>N</i> ^β (3a : 4a)
1	DavePhos	80%, 1:18
2	tBuDavePhos	38%, 1:17
3	CyJohnPhos	42%, <1:20
4	JohnPhos	73%, 1:16
5	BrettPhos	43%, 1:15
6	tBuBrettPhos	45%, <1:20
7	AdBrettPhos	30%, <1:20
8	AlPhos	52%, <1:20
9	RuPhos	67%, <1:20
10	BINAP	55%, 1:15
11	121954-50-5	40%, 1:1
12	P(4-F-Ph) ₃	40%, 1:4
13	P(2-furyl) ₃	81%, 1:10
14	PPh ₃	39%, 1:10
15	bpy	60%, 1:20
16	1,10-Phenanthroline	80%, 1:18

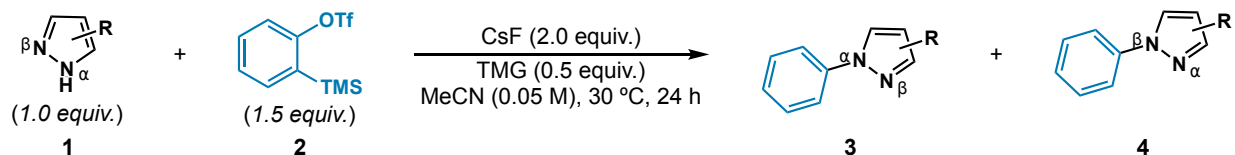
B. Optimization of Catalyst Loading and Concentration (Figure S10)



Entry	catalyst Loading/concentration	Yield, $N^{\alpha}:N^{\beta}$ (3a:4a)
1	$x = 5, c = 0.05$	84%, 1:19
2	$x = 5, c = 0.1$	87%, <1:20
3	$x = 5, c = 0.25$	90%, <1:20
4	$x = 2.5, c = 0.05$	71%, 1:18

2.3. Blank Reaction without Copper, Ligand or Base.

General Procedure for Table S11: In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added pyrazole **1** (0.1 mmol, 1.0 equiv.), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (0.15 mmol, 1.5 equiv.), CsF (0.2 mmol, 2.0 equiv.) and acetonitrile. The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. Reaction yield (%) was determined by ¹H NMR analysis of the crude mixture with internal standard trimethoxy benzene.

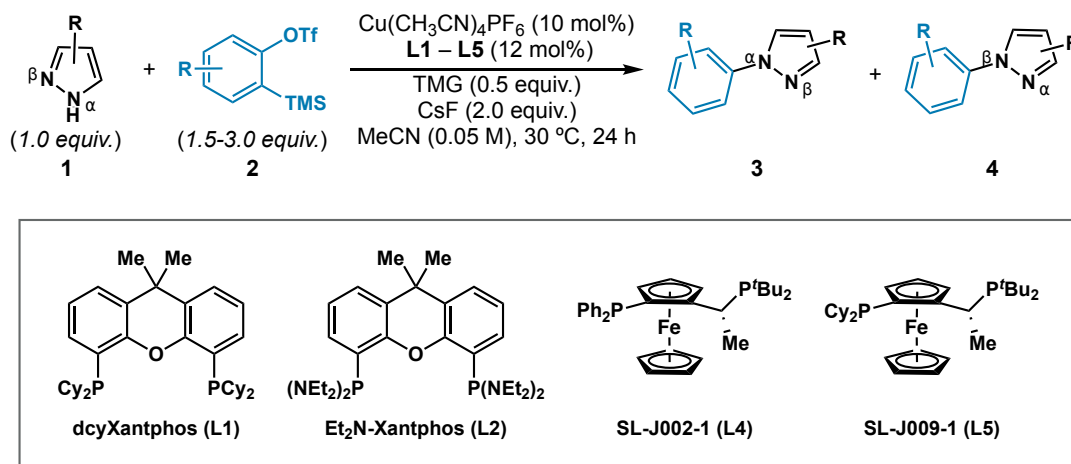


blank reaction for different pyrazoles

	R = Me: 1:1 N ^α :N ^β F: 1:1.7 N ^α :N ^β Br: 1:1.6 N ^α :N ^β		R = Me: 1:1.5 N ^α :N ^β F: 1:1.5 N ^α :N ^β Cl: 1:1.5 N ^α :N ^β		1:1 N ^α :N ^β		1:1 N ^α :N ^β
	1:1.7 N ^α :N ^β		1:13 N ^α :N ^β		1:8 N ^α :N ^β		1.5:1 N ^α :N ^β
	1:5 N ^α :N ^β		1:5 N ^α :N ^β		1:3 N ^α :N ^β		
	1:2.5 N ^α :N ^β		8:1 N ^α :N ^β		1:5 N ^α :N ^β		1:8 N ^α :N ^β
					1:13 N ^α :N ^β		1:4:1 N ^α :N ^β

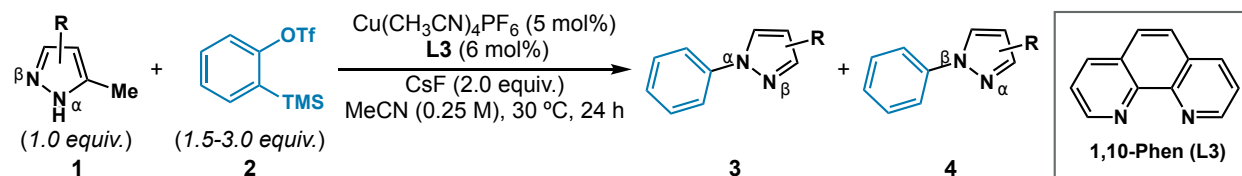
3. General Procedure for Selective Addition of Benzyne to asymmetric N-Heterocycles.

A. Addition of Aryne to More Hindered Nitrogen Atom (N^α) with Kobayashi Precursor.



In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added [Cu(CH₃CN)₄]PF₆ (1.9 mg, 0.005 mmol, 10 mol%), phosphine ligand (0.006 mmol, 12 mol%) and acetonitrile (1.0 mL, 0.05 M). After stirring for 30 min, pyrazole **1** (0.05 mmol, 1.0 equiv.) and 1,1,3,3-tetramethylguanidine (TMG, 2.9 mg, 0.025 mmol, 0.5 equiv.) were added. The resulting mixture was stirred for another 30 min followed by the addition of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) (0.075 mmol, 1.5 equiv.) and CsF (15.2 mg, 0.1 mmol, 2.0 equiv.). The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. If TLC shows majority of pyrazole **1** was left, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) (0.075 mmol, 1.5 equiv.) and CsF (15.2 mg, 0.1 mmol, 2.0 equiv.) were added again and the mixture was stirred another 24 hours at 30 °C. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. N^α- or N^β-arylated regioisomer was determined by ¹H NMR chemical shifts and NOE experiments. Pyrazole product **3** was isolated by preparatory TLC.

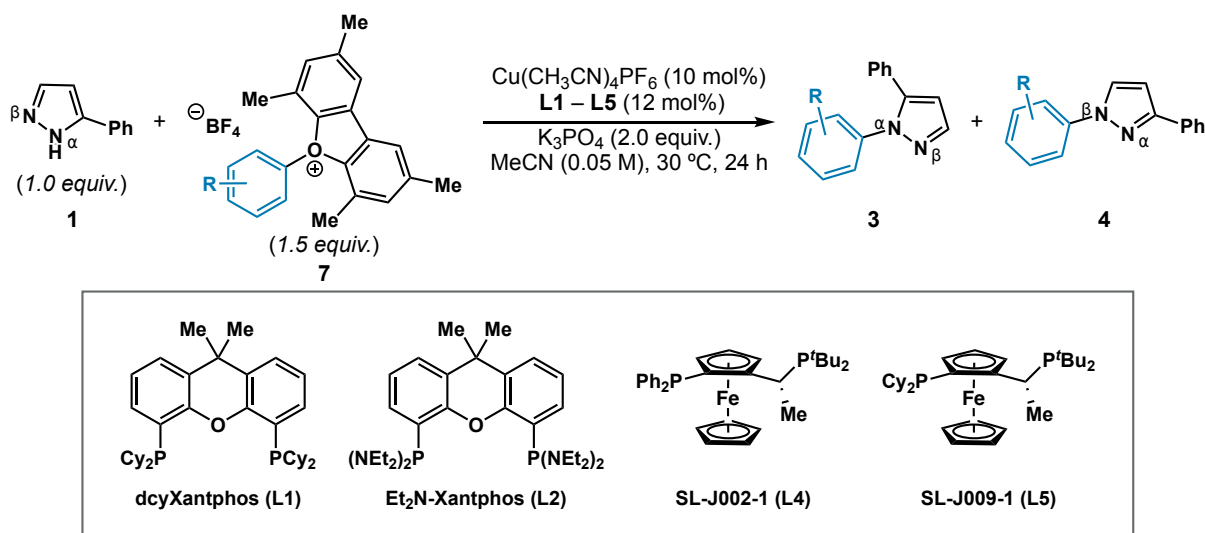
B. Addition of Benzyne to Less Hindered Nitrogen Atom (N^β) on Asymmetric Pyrazoles.



In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added [Cu(CH₃CN)₄]PF₆ (1.9 mg, 0.005 mmol, 5 mol%), 1,10-phenanthroline (**L3**) (1.1 mg, 0.006 mmol, 6 mol%) and acetonitrile (0.4 mL, 0.25 M). After stirring for 30 min, pyrazole **2** (0.1 mmol, 1.0 equiv.), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) (0.15 mmol, 1.5 equiv.) and CsF (30.4 mg, 0.2 mmol, 2.0 equiv.) were added. The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. If TLC shows majority of pyrazole **2** was left, 2-

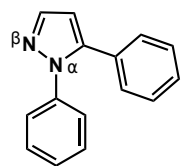
(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) (0.15 mmol, 1.5 equiv.) and CsF (30.4 mg, 0.2 mmol, 2.0 equiv.) were added again and the mixture was stirred another 24 hours at 30 °C. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. N^α- or N^β-arylated regioisomer was determined by ¹H NMR chemical shifts and NOE experiments. Pyrazole product **4** was isolated by preparatory TLC.

C. Addition of Aryne to More Hindered Nitrogen Atom (N^α) with Smith Precursor.



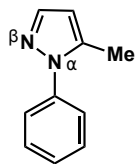
In a N₂ filled glovebox, to a 1-dram vial equipped with a magnetic stir bar was added $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (1.9 mg, 0.005 mmol, 10 mol%), phosphine ligand (0.006 mmol, 12 mol%) and acetonitrile (1.0 mL, 0.05 M). After stirring for 30 min, pyrazole **1** (0.05 mmol, 1.0 equiv.) was added. The resulting mixture was stirred for another 30 min followed by the addition of smith oxonium aryne precursor (**6**) (0.075 mmol, 1.5 equiv.) and K_3PO_4 (21.2 mg, 0.1 mmol, 2.0 equiv.). The vial was sealed with a Teflon-lined screw cap and stirred at 30 °C for 24 hours. The mixture was concentrated in vacuo. Regioselectivity (rr) was determined by ¹H NMR analysis of the crude mixture. N^α- or N^β-arylated regioisomer was determined by ¹H NMR chemical shifts and NOE experiments. Pyrazole product **3** was isolated by preparatory TLC.

1,5-diphenyl-1H-pyrazole (**3a**)



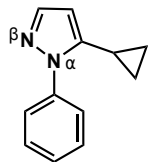
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [10 mg, 92% yield, >20:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 1.9 Hz, 1H), 7.44 – 7.27 (m, 8H), 7.26 – 7.17 (m, 2H), 6.52 (d, *J* = 1.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 143.10, 140.41, 140.23, 130.71, 128.99, 128.87, 128.55, 128.29, 127.51, 125.31, 107.95.¹

5-methyl-1-phenyl-1H-pyrazole (3b)



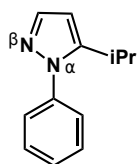
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [1.3 mg, 16% yield, 4:1 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.69 – 7.59 (m, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.25 (s, 1H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.51, 139.30, 138.20, 129.25, 128.21, 125.14, 107.14, 12.52.²

5-cyclopropyl-1-phenyl-1H-pyrazole (3c)



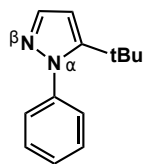
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [3.7 mg, 40% yield, 4:1 N^α:N^β]. ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.60 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 5.99 (d, J = 2.0 Hz, 1H), 1.82 (tt, J = 8.3, 5.1 Hz, 1H), 1.05 – 0.98 (m, 2H), 0.85 – 0.75 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 146.63, 139.46, 139.38, 129.24, 128.02, 125.07, 102.95, 29.84, 9.21, 7.85. IR (ATR): 3011, 2927, 2854, 1597, 1501, 1392, 1030, 926, 763, 695 cm⁻¹. HRMS calculated for C₁₂H₁₂N₂ [M+H]⁺ 185.1079, found 185.1088.

5-isopropyl-1-phenyl-1H-pyrazole (3d)



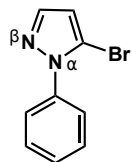
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [4.6 mg, 49% yield, 7:1 N²:N¹]. ¹H NMR (499 MHz, CDCl₃) δ 7.58 (d, J = 1.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.39 (m, 3H), 6.22 (d, J = 1.9 Hz, 1H), 3.06 (sept, J = 6.5 Hz, 1H), 1.19 (d, J = 6.8 Hz, 7H). ¹³C NMR (151 MHz, CDCl₃) δ 150.45, 140.30, 139.89, 129.26, 128.21, 126.06, 102.92, 25.58, 23.16. IR (ATR): 3065, 2966, 1598, 1502, 1395, 1007, 925, 764, 692 cm⁻¹. HRMS calculated for C₁₂H₁₄N₂ [M+Na]⁺ 209.1055, found 209.1046.

5-(tert-butyl)-1-phenyl-1H-pyrazole (3e)



The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [4.5 mg, 45% yield, >20:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, J = 1.9 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.41 – 7.37 (m, 2H), 6.19 (d, J = 2.0 Hz, 1H), 1.19 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 153.29, 142.31, 138.60, 129.26, 128.80, 128.76, 103.91, 32.05, 30.90.³

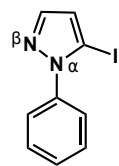
5-bromo-1-phenyl-1H-pyrazole (3f)



The title compound was synthesized according to general procedure A in 0.1 mmol scale of pyrazole **2** with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as brown solid [4.5 mg, 40% yield, 5:1 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 1.8 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.52 – 7.41 (m, 3H), 6.48 (d, J = 1.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 141.57, 139.09, 129.06, 128.65, 125.82, 112.94,

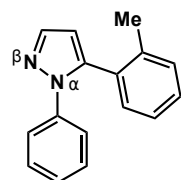
110.56. **IR** (ATR): 3132, 2924, 2853, 1598, 1502, 1416, 1394, 1092, 967, 918, 779, 755 cm^{-1} . **HRMS** calculated for $\text{C}_9\text{H}_7\text{BrN}_2$ $[\text{M}+\text{H}]^+$ 222.9871, found 222.9867.

5-iodo-1-phenyl-1H-pyrazole (3g)



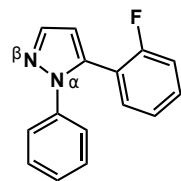
The title compound was synthesized according to general procedure A in 0.1 mmol scale of pyrazole **2** with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as brown oil [4.1 mg, 30% yield, 10:1 $\text{N}^\alpha:\text{N}^\beta$]. **^1H NMR** (400 MHz, CDCl_3) δ 7.69 (d, J = 1.8 Hz, 1H), 7.54 – 7.42 (m, 5H), 6.63 (d, J = 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl_3) δ 142.79, 140.24, 129.01, 128.81, 126.44, 117.58, 80.94.⁴

1-phenyl-5-(o-tolyl)-1H-pyrazole (3h)



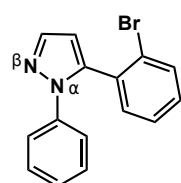
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [9.8 mg, 84% yield, 13:1 $\text{N}^\alpha:\text{N}^\beta$]. **^1H NMR** (600 MHz, CDCl_3) δ 7.75 (d, J = 1.8 Hz, 1H), 7.28 (td, J = 7.4, 1.8 Hz, 1H), 7.26 – 7.16 (m, 8H), 6.41 (d, J = 1.8 Hz, 1H), 1.98 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 142.31, 140.28, 140.20, 137.24, 130.95, 130.67, 130.48, 129.05, 128.88, 126.96, 125.95, 123.72, 108.90, 20.04. **IR** (ATR): 2923, 1599, 1497, 1451, 1380, 960, 924, 758, 690, 651 cm^{-1} . **HRMS** calculated for $\text{C}_{16}\text{H}_{14}\text{N}_2$ $[\text{M}+\text{H}]^+$ 235.1235, found 235.1242.

5-(2-fluorophenyl)-1-phenyl-1H-pyrazole (3i)



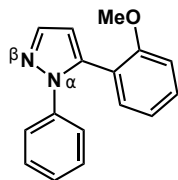
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11 mg, 95% yield, >20:1 $\text{N}^\alpha:\text{N}^\beta$]. **^1H NMR** (600 MHz, CDCl_3) δ 7.77 (d, J = 1.9 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.20 (td, J = 7.5, 1.8 Hz, 1H), 7.10 (td, J = 7.6, 1.2 Hz, 1H), 7.05 (ddd, J = 9.7, 8.3, 1.2 Hz, 1H), 6.57 (s, 1H). **^{13}C NMR** (151 MHz, CDCl_3) δ 159.50 (d, J = 249.9 Hz), 140.41, 140.27, 136.81, 131.47 (d, J = 2.4 Hz), 130.69 (d, J = 8.2 Hz), 129.01, 127.53, 124.42, 124.27 (d, J = 3.8 Hz), 118.97 (d, J = 14.9 Hz), 116.23 (d, J = 21.6 Hz), 109.51 (d, J = 2.0 Hz). **^{19}F NMR** (565 MHz, CDCl_3) δ -112.82. **IR** (ATR): 2925, 1598, 1499, 1385, 1229, 1217, 964, 925, 756, 692 cm^{-1} . **HRMS** calculated for $\text{C}_{15}\text{H}_{11}\text{FN}_2$ $[\text{M}+\text{H}]^+$ 239.0984, found 239.0983.

5-(2-bromophenyl)-1-phenyl-1H-pyrazole (3j)



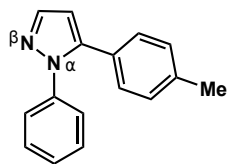
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [13 mg, 90% yield, >20:1 $\text{N}^\alpha:\text{N}^\beta$]. **^1H NMR** (600 MHz, CDCl_3) δ 7.77 (d, J = 1.9 Hz, 1H), 7.59 (dd, J = 7.9, 1.3 Hz, 1H), 7.34 – 7.18 (m, 8H), 6.52 (d, J = 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl_3) δ 141.37, 140.03, 133.26, 132.54, 132.35, 130.46, 130.42, 128.90, 127.42, 127.26, 124.23, 124.19, 109.48.⁵

5-(2-methoxyphenyl)-1-phenyl-1H-pyrazole (3k)



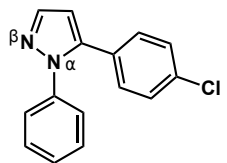
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [6.8 mg, 54% yield, 5:1 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.74 (d, J = 1.8 Hz, 1H), 7.34 (ddd, J = 8.3, 7.5, 1.8 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.26 (d, J = 3.2 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.97 (td, J = 7.5, 1.0 Hz, 1H), 6.79 (dd, J = 8.4, 1.0 Hz, 1H), 6.47 (d, J = 1.8 Hz, 1H), 3.36 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 156.59, 141.13, 140.05, 140.00, 131.37, 130.54, 128.64, 126.96, 123.73, 120.80, 120.23, 111.38, 108.84, 55.05. **IR** (ATR): 3200, 2928, 2365, 1499, 1385, 1261, 1248, 1024, 925, 790, 756, 691 cm⁻¹.⁶

1-phenyl-5-(p-tolyl)-1H-pyrazole (3l)



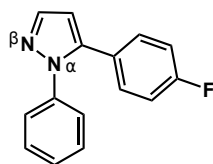
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11.2 mg, 96% yield, 18:1 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, J = 1.8 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.15 – 7.07 (m, 4H), 6.49 (d, J = 1.9 Hz, 1H), 2.34 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 143.44, 140.07, 139.99, 138.46, 129.34, 129.05, 128.76, 127.69, 127.55, 125.41, 107.71, 21.39. **IR** (ATR): 3125, 3063, 2921, 1597, 1498, 1384, 961, 925, 823, 785, 761, 701 cm⁻¹. **HRMS** calculated for C₁₆H₁₄N [M+H]⁺ 235.1235, found 235.1233.⁷

5-(4-chlorophenyl)-1-phenyl-1H-pyrazole (3m)



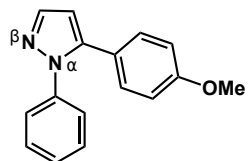
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [7.6 mg, 60% yield, 15:1 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (d, J = 1.9 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.31 – 7.26 (m, 4H), 7.19 – 7.13 (m, 2H), 6.51 (d, J = 1.9 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 142.11, 140.29, 139.72, 134.57, 130.11, 129.23, 129.05, 128.93, 127.97, 125.42, 108.08. **IR** (ATR): 3063, 2923, 2851, 1598, 1499, 1483, 1407, 1382, 1093, 1016, 960, 925, 690, 655, 759, 629 cm⁻¹. **HRMS** calculated for C₁₅H₁₁ClN₂ [M+H]⁺ 255.0689, found 255.0680.⁸

5-(4-fluorophenyl)-1-phenyl-1H-pyrazole (3n)



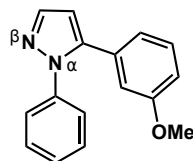
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [10.5 mg, 88% yield, >20:1 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, J = 1.9 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.24 – 7.17 (m, 2H), 7.03 – 6.96 (m, 2H), 6.49 (d, J = 1.9 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 162.76 (d, J = 248.8 Hz), 142.29, 140.24, 139.81, 130.72 (d, J = 8.2 Hz), 129.16, 127.85, 126.68 (d, J = 3.4 Hz), 125.40, 115.77 (d, J = 21.6 Hz), 107.93. **¹⁹F NMR** (376 MHz, CDCl₃) δ -113.18. **IR** (ATR): 3066, 2923, 1594, 1500, 1448, 1383, 1210, 835, 789, 768, 721, 607 cm⁻¹. **HRMS** calculated for C₁₅H₁₁FN₂ [M+H]⁺ 239.0984, found 239.0993.¹

5-(4-methoxyphenyl)-1-phenyl-1H-pyrazole (3o)



The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [7.0 mg, 56% yield, 15:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, J = 1.8 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.15 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 1.8 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.64, 142.96, 140.38, 130.17, 129.00, 127.44, 125.34, 123.16, 114.03, 107.45, 55.39.⁹

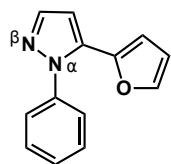
5-(3-methoxyphenyl)-1-phenyl-1H-pyrazole (3p)



The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [6.8 mg, 54% yield, 6:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.72 (d, J = 1.9 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.21 (t, J = 7.9 Hz, 1H), 6.85 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 6.82 (ddd, J = 7.6, 1.6, 0.9 Hz, 1H), 6.75 (dd, J = 2.6, 1.6 Hz, 1H), 6.52 (d, J = 1.9 Hz, 1H), 3.67 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.54, 143.03, 140.35, 140.21, 131.88, 129.65, 129.03, 127.64, 125.41, 121.35, 114.25, 114.21, 107.94, 55.29.⁵

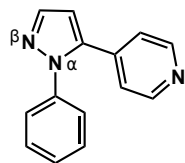
5-(furan-2-yl)-1-phenyl-1H-pyrazole

(3q)



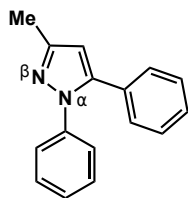
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (80:20 hexanes:EtOAc) as brown oil [8.9 mg, 85% yield, 7:1 N^α:N^β]. ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, J = 1.9 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.39 (dd, J = 1.8, 0.6 Hz, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.33 (dd, J = 3.4, 1.8 Hz, 1H), 5.97 (d, J = 3.4 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 144.69 (s), 142.63 (s), 140.41 (s), 140.38 (s), 134.50 (s), 129.17 (s), 128.58 (s), 125.96 (s), 111.34 (s), 108.89 (s), 106.36 (s). IR (ATR): 3128, 2923, 2852, 1501, 1393, 1218, 1071, 977, 926, 763, 694 cm⁻¹. HRMS calculated for C₁₃H₁₀N₂O [M+H]⁺ 211.0871, found 211.0865.

4-(1-phenyl-1H-pyrazol-5-yl)pyridine (3r)



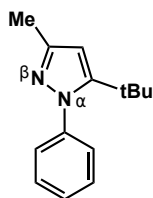
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (80:20 hexanes:EtOAc) as yellow oil [7.4 mg, 67% yield, >20:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (d, J = 5.3 Hz, 2H), 7.78 (d, J = 1.9 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 2H), 6.70 (d, J = 1.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 148.50, 140.90, 139.73, 139.68, 139.57, 129.54, 128.62, 125.56, 123.22, 109.42. IR (ATR): 3365, 2923, 1601, 1498, 1386, 924, 763, 693 cm⁻¹. HRMS calculated for C₁₄H₁₁N₃ [M+H]⁺ 222.1031, found 222.1020.

3-methyl-1,5-diphenyl-1H-pyrazole (3s)



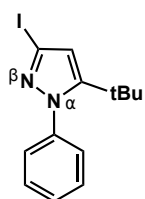
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [8.7 mg, 74% yield, >20:1 N α :N β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.17 (m, 11H), 6.32 (s, 1H), 2.40 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.35, 144.22, 139.54, 130.37, 129.10, 128.80, 128.62, 128.52, 127.67, 125.41, 107.90, 13.47.¹⁰

5-(tert-butyl)-3-methyl-1-phenyl-1H-pyrazole (3t)



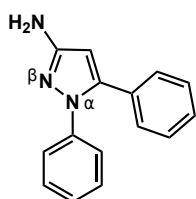
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [9.6 mg, 90% yield, >20:1 N α :N β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.49 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 5.98 (s, 1H), 2.28 (s, 3H), 1.17 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ 154.29, 147.47, 142.00, 129.23, 128.99, 128.79, 103.92, 32.09, 30.87, 13.40. **IR** (ATR): 2968, 2929, 1593, 1537, 1500, 1362, 1017, 1007, 774, 729, 696 cm⁻¹. **HRMS** calculated for C₁₄H₁₈N₂ [M+Na]⁺ 237.1368, found 237.1369.

5-(tert-butyl)-3-iodo-1-phenyl-1H-pyrazole (3u)



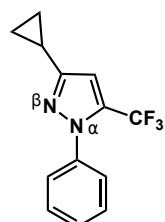
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11.0 mg, 67% yield, >20:1 N α :N β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 3H), 7.38 – 7.34 (m, 2H), 6.33 (s, 1H), 1.16 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ 155.59, 141.49, 129.63, 128.87, 128.86, 112.99, 95.29, 32.13, 30.70. **IR** (ATR): 3135, 2966, 2927, 1500, 1362, 1337, 1257, 1005, 949, 785, 774, 706, 695 cm⁻¹. **HRMS** calculated for C₁₃H₁₅IN₂ [M+Na]⁺ 349.0178, found 349.0175.

1,5-diphenyl-1H-pyrazol-3-amine (3v)



The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (80:20 hexanes:EtOAc) as white solid [6.8 mg, 58% yield, 7:1 N α :N β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.31 – 7.27 (m, 5H), 7.25 – 7.19 (m, 5H), 5.93 (s, 1H), 2.86 (s, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 154.37, 144.85, 139.48, 130.32, 129.08, 128.79, 128.71, 128.63, 127.13, 124.98, 96.14. **IR** (ATR): 3320 (br), 2923, 1594, 1557, 1500, 1383, 760, 693 cm⁻¹. **HRMS** calculated for C₁₅H₁₃N₃ [M+Na]⁺ 258.1007, found 258.1000.

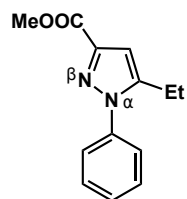
3-cyclopropyl-1-phenyl-5-(trifluoromethyl)-1H-pyrazole (3w)



The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11.0 mg, 87% yield, >20:1 N α :N β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.52 – 7.37 (m, 5H), 6.47 (s, 1H), 2.00 (dddd, J = 8.5, 6.6, 4.2, 2.5 Hz, 1H), 0.99 (tdd, J = 6.1, 4.3, 1.5 Hz, 2H), 0.87 – 0.78 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 155.60, 139.33, 133.06 (q, J =

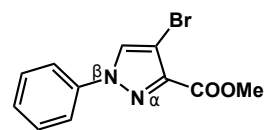
39.0 Hz), 129.16, 129.11, 125.76, 119.91 (q, $J = 269.0$ Hz), 105.65 (q, $J = 2.5$ Hz), 9.05, 8.35. **IR** (ATR): 2927, 1597, 1483, 1387, 1240, 1169, 1125, 1104, 973, 765, 686 cm^{-1} .¹¹

methyl 5-ethyl-1-phenyl-1H-pyrazole-3-carboxylate (3x)



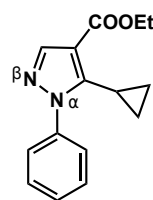
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (85:25 hexanes:EtOAc) as yellow oil [9.2 mg, 80% yield, 9:1 $N^\alpha:N^\beta$]. **¹H NMR** (400 MHz, CDCl_3) δ 7.49 – 7.37 (m, 5H), 6.84 (s, 1H), 3.78 (s, 3H), 2.74 (qd, $J = 7.6, 0.5$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H). **¹³C NMR** (151 MHz, CDCl_3) δ 159.86 (s), 155.05 (s), 140.37 (s), 133.47 (s), 128.70 (s), 128.59 (s), 126.09 (s), 110.88 (s), 52.07 (s), 21.41 (s), 13.81 (s). **IR** (ATR): 3065, 2969, 1731, 1503, 1444, 1283, 1227, 1105, 761, 692 cm^{-1} . **HRMS** calculated for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$ $[M+\text{Na}]^+$ 253.0953, found 253.0947.

methyl 4-bromo-1-phenyl-1H-pyrazole-3-carboxylate (3y)



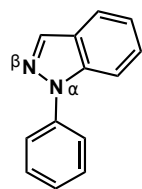
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow solid [5.5 mg, 39% yield, <1:20 $N^\alpha:N^\beta$]. **¹H NMR** (400 MHz, CDCl_3) δ 8.00 (s, 1H), 7.70 – 7.68 (m, 2H), 7.50 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 3.98 (s, 3H). **¹³C NMR** (151 MHz, CDCl_3) δ 161.59, 141.73, 139.18, 130.06, 129.80, 128.43, 120.11, 98.47, 52.43. **IR** (ATR): 3124, 2924, 1720, 1498, 1388, 1370, 1227, 1051, 957, 810, 746, 682, 649, 619 cm^{-1} . **HRMS** calculated for $\text{C}_{11}\text{H}_9\text{BrN}_2\text{O}_2$ $[M+\text{Na}]^+$ 302.9745, found 302.9738.

ethyl 5-cyclopropyl-1-phenyl-1H-pyrazole-4-carboxylate (3z)



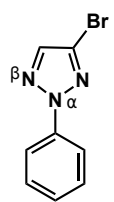
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (85:25 hexanes:EtOAc) as yellow oil [12.2 mg, 95% yield, >20:1 $N^\alpha:N^\beta$]. **¹H NMR** (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.53 – 7.46 (m, 4H), 7.44 – 7.40 (m, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 1.97 (tt, $J = 8.6, 5.5$ Hz, 1H), 1.38 (t, $J = 7.1$ Hz, 3H), 0.95 – 0.88 (m, 2H), 0.68 – 0.62 (m, 2H). **¹³C NMR** (151 MHz, CDCl_3) δ 163.35 (s), 147.48 (s), 142.34 (s), 139.62 (s), 129.07 (s), 128.49 (s), 125.58 (s, $J = 3.8$ Hz), 114.22 (s), 60.17 (s), 14.57 (s), 8.58 (s), 7.51 (s). **IR** (ATR): 3124, 2923, 1719, 1597, 1498, 1226, 1051, 958, 832, 746, 682, 650 cm^{-1} . **HRMS** calculated for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$ $[M+\text{H}]^+$ 257.1290, found 257.1281.

1-phenyl-1H-indazole (3aa)



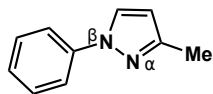
The title compound was synthesized according to general procedure A with dcypm ligand and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow solid [6.4 mg, 66% yield, 15:1 $N^\alpha:N^\beta$]. **¹H NMR** (600 MHz, CDCl_3) δ 8.21 (d, $J = 1.0$ Hz, 1H), 7.81 (dt, $J = 8.1, 1.0$ Hz, 1H), 7.77 (dt, $J = 8.6, 0.9$ Hz, 1H), 7.75 – 7.73 (m, 2H), 7.57 – 7.53 (m, 2H), 7.44 (ddd, $J = 8.3, 6.9, 1.1$ Hz, 1H), 7.39 – 7.35 (m, 1H), 7.24 (ddd, $J = 8.0, 6.9, 0.8$ Hz, 1H). **¹³C NMR** (151 MHz, CDCl_3) δ 140.35, 138.90, 135.54, 129.60, 127.29, 126.79, 125.47, 122.90, 121.66, 121.48, 110.57.¹²

4-bromo-2-phenyl-2H-1,2,3-triazole (3ab)



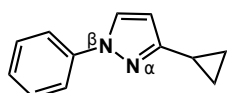
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless solid [6.2 mg, 55% yield, 3:1 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 8.05 – 8.01 (m, 2H), 7.76 (s, 1H), 7.49 (dd, J = 8.6, 7.4 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 139.58, 136.91, 129.52, 128.16, 124.12, 118.76. IR (ATR): 2924, 1597, 1496, 1445, 1371, 1130, 990, 959, 835, 753, 698, 688, 662 cm⁻¹. HRMS calculated for C₈H₆BrN₃ [M+H]⁺ 222.9745, found 218.9856.

3-methyl-1-phenyl-1H-pyrazole (4b)



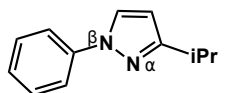
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [11.6 mg, 73% yield, 1:9 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.65 (d, J = 7.7 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.25 (s, 1H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 150.65, 140.17, 129.53, 127.68, 126.23, 119.08, 107.71, 13.80.¹³

3-cyclopropyl-1-phenyl-1H-pyrazole (4c)



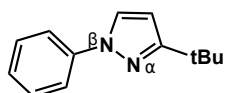
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [14 mg, 75% yield, 1:12 N^α:N^β]. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 8.7 Hz, 2H), 7.42 (dd, J = 8.6, 7.4 Hz, 2H), 7.24 (tt, J = 7.4, 1.1 Hz, 1H), 6.11 (d, J = 2.5 Hz, 1H), 2.07 (tt, J = 8.4, 5.0 Hz, 1H), 1.05 – 0.95 (m, 2H), 0.85 – 0.78 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 157.18, 140.12, 129.49, 127.55, 126.14, 119.04, 104.14, 9.38, 8.35.¹⁴

3-isopropyl-1-phenyl-1H-pyrazole (4d)



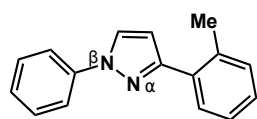
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [16.5 mg, 89% yield, <1:20 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 2.5, 0.5 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.49 – 7.38 (m, 2H), 7.26 – 7.21 (m, 1H), 6.29 (dd, J = 2.4, 0.5 Hz, 1H), 3.10 (hept, J = 6.9 Hz, 1H), 1.33 (d, J = 7.0 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 161.17, 140.37, 129.47, 127.37, 126.10, 119.19, 104.59, 28.12, 22.96. IR (ATR): 3049, 2962, 1601, 1529, 1502, 1302, 1042, 751, 689 cm⁻¹.¹⁵

3-(tert-butyl)-1-phenyl-1H-pyrazole (4e)



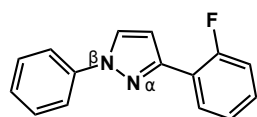
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [19 mg, 95% yield, <1:20 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, J = 2.4 Hz, 1H), 7.68 (d, J = 7.1 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 6.32 (d, J = 2.4 Hz, 1H), 1.38 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 163.82, 140.63, 129.43, 126.95, 125.87, 119.06, 104.31, 32.47, 30.65.¹⁶

1-phenyl-3-(o-tolyl)-1H-pyrazole (4f)



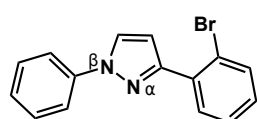
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [16 mg, 70% yield, <1:20 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.99 (d, J = 2.4 Hz, 1H), 7.78 (dd, J = 8.6, 1.4 Hz, 2H), 7.67 (dd, J = 5.3, 3.6 Hz, 1H), 7.47 (dd, J = 8.6, 7.4 Hz, 2H), 7.31 – 7.27 (m, 4H), 6.65 (d, J = 2.4 Hz, 1H), 2.58 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 153.48, 140.29, 136.36, 132.92, 131.05, 129.53, 129.40, 128.04, 127.07, 126.34, 125.97, 119.00, 108.11, 21.57.¹⁷

3-(2-fluorophenyl)-1-phenyl-1H-pyrazole (4g)



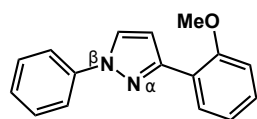
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [16 mg, 69% yield, <1:20 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 8.18 (td, J = 7.8, 1.9 Hz, 1H), 7.99 (d, J = 2.5 Hz, 1H), 7.78 (dd, J = 8.6, 1.2 Hz, 2H), 7.48 (dd, J = 8.6, 7.4 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.23 (td, J = 7.5, 1.2 Hz, 1H), 7.16 (ddd, J = 11.3, 8.2, 1.2 Hz, 1H), 6.94 (dd, J = 4.0, 2.5 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 160.44 (d, J = 249.5 Hz), 147.71, 140.20, 129.57, 129.46 (d, J = 8.4 Hz), 128.66 (d, J = 3.7 Hz), 127.87 (d, J = 2.5 Hz), 126.65, 124.42 (d, J = 3.3 Hz), 121.07 (d, J = 11.7 Hz), 119.28, 116.20 (d, J = 22.2 Hz), 108.64 (d, J = 10.5 Hz). **¹⁹F NMR** (565 MHz, CDCl₃) δ -115.88.¹⁷

3-(2-bromophenyl)-1-phenyl-1H-pyrazole (4h)



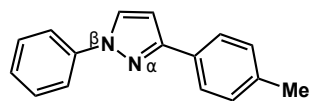
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [21 mg, 69% yield, <1:20 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.99 (d, J = 2.5 Hz, 1H), 7.82 (dd, J = 7.7, 1.8 Hz, 1H), 7.77 (d, J = 8.5 Hz, 2H), 7.68 (dd, J = 8.1, 1.3 Hz, 1H), 7.47 (dd, J = 8.5, 7.4 Hz, 2H), 7.39 (td, J = 7.5, 1.2 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.22 (td, J = 7.7, 1.8 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 152.23, 140.17, 134.32, 133.69, 131.42, 129.58, 129.49, 127.59, 127.13, 126.66, 122.26, 119.30, 109.07. **IR** (ATR): 2922, 1599, 1521, 1445, 1024, 956, 749, 686 cm⁻¹. **HRMS** calculated for C₁₅H₁₁BrN₂ [M+H]⁺ 299.0184, found 299.0171.

3-(2-methoxyphenyl)-1-phenyl-1H-pyrazole (4i)



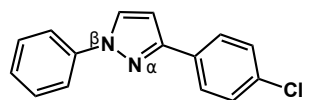
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [20 mg, 81% yield, 1:12 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 8.11 (dd, J = 7.7, 1.8 Hz, 1H), 7.96 (d, J = 2.5 Hz, 1H), 7.79 (d, J = 8.7 Hz, 2H), 7.46 (t, J = 7.9 Hz, 2H), 7.33 (ddd, J = 8.7, 7.4, 1.8 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.06 (dd, J = 8.0, 6.9 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 157.15, 150.12, 140.45, 129.50, 129.24, 129.03, 127.15, 126.29, 122.21, 121.03, 119.21, 111.46, 109.31, 55.65.¹⁴

1-phenyl-3-(p-tolyl)-1H-pyrazole (4j)



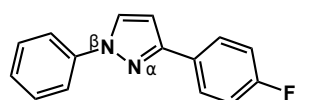
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [22.1 mg, 94% yield, <1:20 N^α:N^β]. **¹H NMR** (500 MHz, CDCl₃) δ 7.94 (d, J = 2.4 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.79 – 7.75 (m, 2H), 7.50 – 7.43 (m, 2H), 7.34 – 7.27 (m, 1H), 7.27 – 7.22 (m, 2H), 6.75 (d, J = 2.4 Hz, 1H), 2.40 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 153.08, 140.31, 137.97, 130.35, 129.52, 129.47, 128.06, 126.36, 125.84, 119.13, 104.98, 21.46. **IR** (ATR): 3058, 2918, 1597, 1509, 1446, 1263, 1119, 1043, 953, 938, 823, 755, 690 cm⁻¹. **HRMS** calculated for C₁₆H₁₄N₂ [M+H]⁺ 235.1235, found 235.1239.¹⁷

3-(4-chlorophenyl)-1-phenyl-1H-pyrazole (4k)



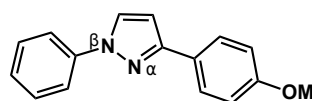
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [8.0 mg, 31% yield, <1:20 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (d, J = 2.6 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.79 – 7.73 (m, 2H), 7.53 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.31 (ddt, J = 8.6, 7.0, 1.2 Hz, 1H), 6.75 (d, J = 2.5 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 151.94, 140.21, 133.91, 131.74, 129.61, 128.97, 128.36, 127.23, 126.69, 119.26, 105.12. **IR** (ATR): 3058, 1598, 1505, 1441, 1087, 1044, 1012, 953, 939, 827, 754, 690 cm⁻¹. **HRMS** calculated for C₁₅H₁₁ClN₂ [M+H]⁺ 255.0689, found 255.0678.¹⁷

3-(4-fluorophenyl)-1-phenyl-1H-pyrazole (4l)



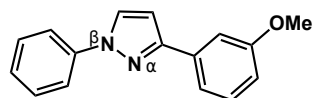
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11.9 mg, 50% yield, <1:20 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (d, J = 2.5 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.79 – 7.74 (m, 2H), 7.50 – 7.44 (m, 2H), 7.33 – 7.27 (m, 1H), 7.16 – 7.08 (m, 2H), 6.73 (d, J = 2.5 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 162.92 (d, J = 247.3 Hz), 152.16, 140.23, 129.59, 129.43 (d, J = 3.02 Hz), 128.30, 127.68 (d, J = 8.3 Hz), 126.60, 119.22, 115.71 (d, J = 21.6 Hz), 104.96. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.35. **IR** (ATR): 3059, 2923, 1597, 1506, 1446, 1221, 1155, 1043, 840, 751, 693, 605 cm⁻¹. **HRMS** calculated for C₁₅H₁₂FN₂ [M+H]⁺ 239.0984, found 239.0993.¹⁴

3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole (4m)



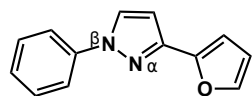
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [20 mg, 80% yield, 1:17 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 7.93 (d, J = 2.4 Hz, 1H), 7.87 – 7.85 (m, 2H), 7.77 (dq, J = 7.8, 1.1 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.28 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 6.71 (d, J = 2.5 Hz, 1H), 3.86 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 159.74, 152.90, 140.36, 129.52, 128.04, 127.24, 126.29, 126.03, 119.07, 114.18, 104.71, 55.44.¹⁴

3-(3-methoxyphenyl)-1-phenyl-1H-pyrazole (4n)



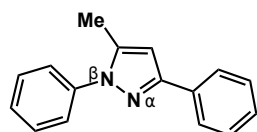
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [22 mg, 88% yield, <1:20 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, J = 2.5 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.53 – 7.45 (m, 4H), 7.35 (t, J = 7.9 Hz, 1H), 7.30 (tt, J = 7.4, 1.2 Hz, 1H), 6.91 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.77 (d, J = 2.5 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 160.06, 152.92, 140.33, 134.62, 129.80, 129.55, 128.12, 126.50, 118.97, 118.57, 114.12, 111.10, 105.33, 55.45.¹⁴

3-(furan-2-yl)-1-phenyl-1H-pyrazole (4o)



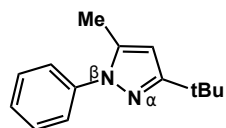
The title compound was synthesized according to general procedure B with [Cu(CH₃CN)₄]PF₆ (3.8 mg, 0.01 mmol, 10 mol%). It was isolated by preparatory TLC (80:20 hexanes:EtOAc) as yellow oil [17.1 mg, 81% yield, 1:13 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 2.5 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.50 (dd, J = 1.8, 0.8 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.33 – 7.27 (m, 1H), 6.78 (dd, J = 3.4, 0.8 Hz, 1H), 6.70 (d, J = 2.5 Hz, 1H), 6.50 (ddd, J = 3.3, 1.8, 0.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 148.62, 145.56, 142.31, 140.06, 129.56, 128.06, 126.73, 119.45, 111.54, 106.70, 105.10.¹⁴

5-methyl-1,3-diphenyl-1H-pyrazole (4p)



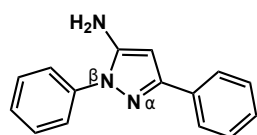
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [18 mg, 76% yield, 1:8 N^α:N^β]. ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.58 – 7.46 (m, 4H), 7.44 – 7.36 (m, 3H), 7.35 – 7.28 (m, 1H), 6.53 (s, 1H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 151.61, 140.36, 139.98, 133.38, 129.23, 128.70, 127.93, 127.80, 125.88, 125.16, 104.51, 12.70.¹⁸

3-(tert-butyl)-5-methyl-1-phenyl-1H-pyrazole (4q)



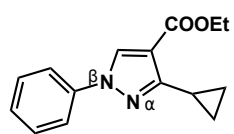
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [21 mg, 98% yield, <1:20 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, J = 4.3 Hz, 4H), 7.38 – 7.34 (m, 1H), 6.10 (d, J = 0.8 Hz, 1H), 2.31 (s, 3H), 1.37 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 162.17, 140.03, 139.17, 129.13, 127.37, 125.09, 103.82, 32.21, 30.65, 12.64.¹⁹

1,3-diphenyl-1H-pyrazol-5-amine (4r)



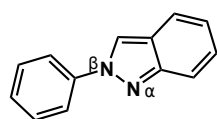
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (80:20 hexanes:EtOAc) as white solid [13 mg, 55% yield, 1:12 N^α:N^β]. ¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, J = 6.9 Hz, 0H), 7.64 (d, J = 7.3 Hz, 0H), 7.50 (t, J = 7.9 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.31 (t, J = 7.3 Hz, 0H), 5.97 (s, 1H), 3.86 (s, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 151.65, 145.91, 138.78, 133.59, 129.65, 128.61, 127.95, 127.60, 125.76, 124.29, 88.27.²⁰

ethyl 3-cyclopropyl-1-phenyl-1H-pyrazole-4-carboxylate (4s)



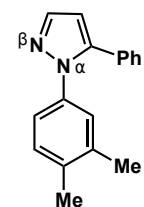
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (75:25 hexanes:EtOAc) as white solid [21.5 mg, 84% yield, <1:20 N^α:N^β]. **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (s, 1H), 7.69 – 7.60 (m, 2H), 7.50 – 7.39 (m, 2H), 7.29 (ddt, J = 8.0, 7.0, 1.2 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.59 (ddt, J = 8.4, 7.5, 5.1 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.08 – 0.97 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ 163.85, 157.63, 139.54, 131.08, 129.58, 127.11, 119.39, 114.58, 60.22, 14.59, 8.98, 8.26. **IR** (ATR): 3133, 2974, 1469, 1541, 1263, 1249, 1189, 1069, 772, 750, 684 cm⁻¹. **HRMS** calculated for C₁₅H₁₆N₂O₂ [M+H]⁺ 257.1290, found 257.1280.²¹

2-phenyl-2H-indazole (4t)



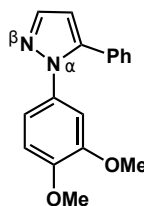
The title compound was synthesized according to general procedure B and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow solid [7.8 mg, 40% yield, 1:10 N^α:N^β]. **¹H NMR** (600 MHz, CDCl₃) δ 8.42 (d, J = 1.0 Hz, 1H), 7.91 (dd, J = 8.6, 1.2 Hz, 2H), 7.80 (dd, J = 8.8, 1.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.6, 7.3 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.33 (ddd, J = 8.8, 6.6, 1.1 Hz, 1H), 7.12 (ddd, J = 8.4, 6.6, 0.9 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.95, 140.70, 133.59, 129.73, 128.07, 126.99, 122.62, 121.18, 120.58, 120.53, 118.10.²²

1-(3,4-dimethylphenyl)-5-phenyl-1H-pyrazole (5a)



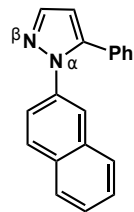
The title compound was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [9.4 mg, 76% yield, 16:1 N^α:N^β]. **¹H NMR** (500 MHz, CDCl₃) δ 7.75 (d, J = 1.9 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.20 (d, J = 2.3 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.92 (dd, J = 8.1, 2.3 Hz, 1H), 6.52 (d, J = 1.9 Hz, 1H), 2.26 (s, 3H), 2.23 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 143.44, 139.37, 137.79, 137.20, 136.65, 130.30, 130.03, 128.87, 128.59, 128.53, 126.43, 122.76, 107.61, 19.88, 19.59. **IR** (ATR): 3096, 3030, 2920, 2854, 1505, 1449, 1375, 971, 876, 786, 757, 699 cm⁻¹. **HRMS** calculated for C₁₇H₁₆N₂ [M+H]⁺ 249.1392, found 249.1390.

1-(3,4-dimethoxyphenyl)-5-phenyl-1H-pyrazole (5b)



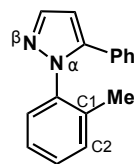
The title compound was synthesized according to general procedure A with **L4** and isolated by preparatory TLC (70:30 hexanes:EtOAc) as brown solid [11.4 mg, 81% yield, 12:1 N^α:N^β]. **¹H NMR** (499 MHz, CDCl₃) δ 7.70 (d, J = 1.8 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.26 – 7.21 (m, 2H), 6.87 (d, J = 2.1 Hz, 1H), 6.79 (d, J = 2.1 Hz, 1H), 6.78 (s, 1H), 6.50 (d, J = 1.8 Hz, 1H), 3.88 (s, 3H), 3.73 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.03, 148.40, 143.10, 140.10, 133.52, 130.83, 128.88, 128.55, 128.25, 117.59, 110.81, 109.22, 107.54, 56.14, 56.01. **IR** (ATR): 3184, 2924, 1599, 1518, 1247, 1224, 1176, 1125, 1022, 858, 791, 761, 702 cm⁻¹. **HRMS** calculated for C₁₇H₁₆N₂O₂ [M+H]⁺ 281.1290, found 281.1277.

1-(naphthalen-2-yl)-5-phenyl-1H-pyrazole (5c)



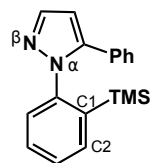
The title compound was synthesized according to general procedure A with **L4** and isolated by preparatory TLC (70:30 hexanes:EtOAc) as yellow solid [7.5mg, 50% yield, 11:1 N^α:N^β]. ¹H NMR (500 MHz, CDCl₃) δ 7.85 – 7.83 (m, 2H), 7.79 – 7.74 (m, 3H), 7.51 – 7.47 (m, 2H), 7.38 (dd, J = 8.7, 2.1 Hz, 1H), 7.30 – 7.27 (m, 5H), 6.56 (d, J = 1.7 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 143.31, 140.66, 137.77, 133.38, 132.34, 130.75, 128.94, 128.84, 128.65, 128.40, 128.29, 127.87, 126.81, 126.54, 123.70, 123.44, 108.15. IR (ATR): 3057, 2922, 1598, 1509, 1128, 926, 868, 830, 763, 753, 695 cm⁻¹. HRMS calculated for C₁₉H₁₄N₂ [M+Na]⁺ 293.1055, found 293.1050.

5-phenyl-1-(m-tolyl)-1H-pyrazole (5d)



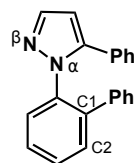
The title compound was synthesized according to general procedure A with **L4** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white oil [9.8 mg, 84% yield, >20:1 N^α:N^β, 1:5 C¹:C²]. ¹H NMR (499 MHz, CDCl₃) δ 7.73 (d, J = 1.9 Hz, 1H), 7.32– 7.26 (m, 1H), 7.26 – 7.21 (m, 6H), 7.18 – 7.15 (m, 2H), 6.56 (d, J = 1.9 Hz, 1H), 1.96 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 144.18, 140.20, 139.68, 135.75, 131.12, 130.42, 129.05, 128.54, 128.22, 128.13, 127.99, 126.71, 106.05, 17.67. IR (ATR): 3057, 2922, 1498, 1384, 1067, 960, 925, 757, 693 cm⁻¹. HRMS calculated for C₁₆H₁₄N₂ [M+H]⁺ 235.1235, found 235.1244.²³

5-phenyl-1-(2-(trimethylsilyl)phenyl)-1H-pyrazole (5e)



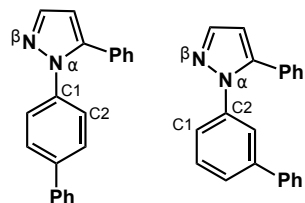
The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as colorless oil [7.2 mg, 49% yield, >20:1 N^α:N^β, >20:1 C¹:C²]. ¹H NMR (600 MHz, CD₃CN) δ 7.75 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 1.6 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.30 (tt, J = 7.7, 1.5 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.20 – 7.16 (m, 2H), 6.89 (d, J = 7.8 Hz, 1H), 6.63 (t, J = 1.6 Hz, 1H), 0.04 (s, 9H). ¹³C NMR (151 MHz, CD₃CN) δ 146.41, 144.42, 140.10, 139.12, 136.87, 131.23, 130.56, 129.40, 129.25, 129.01, 128.97, 128.66, 107.76, -0.62. IR (ATR): 3059, 2951, 1480, 1432, 1245, 1121, 925, 837, 757, 724, 694 cm⁻¹. HRMS calculated for C₁₈H₂₀N₂Si [M+H]⁺ 293.1474, found 293.1476.

1-([1,1'-biphenyl]-2-yl)-5-phenyl-1H-pyrazole (5f)



The title compound was synthesized according to general procedure A with **L1** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [6.8 mg, 46% yield, 6:1 N^α:N^β, >20:1 C¹:C²]. ¹H NMR (600 MHz, CD₃CN) δ 7.73 (d, J = 1.9 Hz, 1H), 7.60 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.45 – 7.43 (m, 3H), 7.40 (td, J = 6.6, 1.8 Hz, 2H), 7.38 – 7.29 (m, 7H), 6.60 (d, J = 1.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 143.23, 142.09, 140.58, 140.53, 140.17, 130.89, 129.39, 129.03, 128.89, 128.69, 128.41, 127.78, 127.22, 126.12, 124.04, 123.88, 108.08. IR (ATR): 3057, 2922, 1599, 1483, 1425, 1384, 965, 924, 888, 792, 756, 696 cm⁻¹. HRMS calculated for C₂₁H₁₆N₂ [M+H]⁺ 297.1392, found 297.1378.

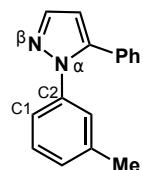
1-([1,1'-biphenyl]-4-yl)-5-phenyl-1H-pyrazole (5g) and 1-([1,1'-biphenyl]-3-yl)-5-phenyl-1H-pyrazole (5g')



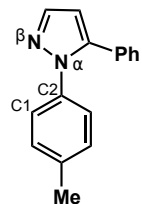
The title compounds were inseparable carbon regioisomers and synthesized according to general procedure A with **L4**. The mixture of regioisomers were isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [10 mg, 67% yield, 13:1 N^α:N^β, 1:1 C¹:C²]. **¹H NMR** (600 MHz, CDCl₃) δ 7.77 – 7.73 (m, 2H), 7.60 – 7.55 (m, 4H), 7.54 – 7.50 (m, 2H), 7.47 – 7.32 (m, 17H), 7.33 – 7.26 (m, 5H), 6.54 (d, J = 1.9 Hz, 1H), 6.53 (d, J = 1.9 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 143.23, 143.14, 142.09, 140.58, 140.56, 140.53, 140.25, 140.18, 140.17, 139.42, 130.89, 130.77, 129.38, 129.03, 128.99, 128.96, 128.89, 128.69, 128.66, 128.41, 128.40, 127.78, 127.72, 127.62, 127.22, 127.18, 126.11, 125.46, 124.04, 123.88, 108.14, 108.08. **IR** (ATR): 3032, 2923, 1486, 1384, 924, 842, 792, 757, 696 cm⁻¹. **HRMS** calculated for C₂₁H₁₆N₂ [M+H]⁺ 297.1392, found 297.1388.

5-phenyl-1-(p-tolyl)-1H-pyrazole (5h)

The title compounds was synthesized according to general procedure A with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [11 mg, 98% yield, >20:1 N^α:N^β, 1:1 C¹:C²].

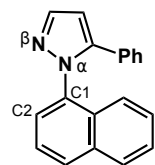


¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, J = 1.8 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.27 – 7.21 (m, 2H), 7.17 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 6.98 (dd, J = 8.1, 1.9 Hz, 1H), 6.50 (d, J = 1.9 Hz, 1H), 2.33 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 143.08, 140.30, 139.20, 130.82, 128.87, 128.65, 128.53, 128.32, 125.95, 122.45, 107.83, 21.43.²⁴



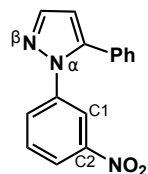
¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, J = 1.8 Hz, 1H), 7.31 – 7.30 (m, 3H), 7.25 – 7.23 (m, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 1.8 Hz, 1H), 2.36 (s, 3H).²⁴

1-(naphthalen-1-yl)-5-phenyl-1H-pyrazole (5i)



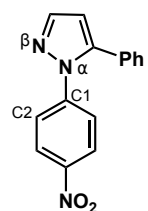
The title compounds was synthesized according to general procedure A with **L5** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as white solid [6.4 mg, 47% yield, 14:1 N^α:N^β, 6:1 C¹:C²]. **¹H NMR** (600 MHz, CDCl₃) δ 7.91 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 1.5 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.19 – 7.09 (m, 5H), 6.66 (d, J = 1.6 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 145.29, 140.60, 136.86, 134.42, 130.74, 130.26, 129.38, 128.45, 128.19, 128.17, 128.11, 127.43, 126.73, 125.77, 125.15, 123.52, 106.46. **IR** (ATR): 3054, 2924, 1510, 1408, 1129, 924, 801, 773, 757, 730, 695 cm⁻¹. **HRMS** calculated for C₁₉H₁₄N₂ [M+H]⁺ 271.1235, found 271.1234.

1-(3-nitrophenyl)-5-phenyl-1H-pyrazole (5j)



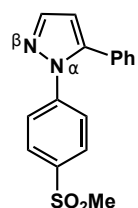
The title compound was synthesized according to general procedure C with **L1** and isolated by preparatory TLC (70:30 hexanes:EtOAc) as yellow solid [6.2 mg, 47% yield, 2:1 $N^\alpha:N^\beta$, >20:1 $C^1:C^2$]. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.24 (t, $J = 2.2$ Hz, 1H), 8.14 (ddd, $J = 8.2, 2.2, 1.0$ Hz, 1H), 7.78 (d, $J = 1.8$ Hz, 1H), 7.59 (ddd, $J = 8.1, 2.2, 1.0$ Hz, 1H), 7.48 (t, $J = 8.1$ Hz, 1H), 7.41 – 7.33 (m, 3H), 7.26 – 7.21 (m, 2H), 6.55 (d, $J = 1.8$ Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.55, 143.59, 141.51, 141.13, 130.43, 130.05, 129.77, 129.08, 129.03, 128.98, 121.90, 119.93, 109.15. **IR** (ATR): 3098, 2922, 1528, 1490, 1440, 1378, 1348, 923, 893, 801, 761, 737, 697, 674, 644 cm^{-1} . **HRMS** calculated for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 266.0930, found 266.0932. ²⁴

1-(4-nitrophenyl)-5-phenyl-1H-pyrazole (5k)



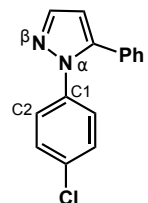
The title compound was synthesized according to general procedure C with **L1** and isolated by preparatory TLC (70:30 hexanes:EtOAc) as yellow solid [7.3 mg, 55% yield, 2:1 $N^\alpha:N^\beta$, 3:1 $C^1:C^2$]. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.20 (d, $J = 9.0$ Hz, 2H), 7.80 (d, $J = 1.8$ Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.38 (m, 3H), 7.29 – 7.23 (m, 2H), 6.57 (d, $J = 1.7$ Hz, 1H). **IR** (ATR): 2923, 2850, 1594, 1499, 1337, 751, 691, 651 cm^{-1} . ²⁴

1-(4-(methylsulfonyl)phenyl)-5-phenyl-1H-pyrazole (5l)



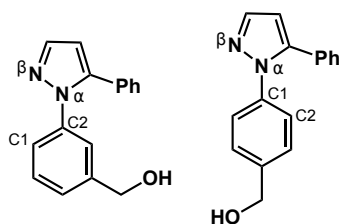
The title compound was synthesized according to general procedure C with **L1** and isolated by preparatory TLC (70:30 hexanes:EtOAc) as white solid [7.3 mg, 55% yield, 2:1 $N^\alpha:N^\beta$, 3:1 $C^1:C^2$]. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.90 – 7.88 (m, 2H), 7.77 (d, $J = 1.8$ Hz, 1H), 7.51 (d, $J = 8.6$ Hz, 2H), 7.39 – 7.34 (m, 3H), 7.25 – 7.22 (m, 2H), 6.54 (d, $J = 1.9$ Hz, 1H), 3.06 (s, 3H). **IR** (ATR): 2921, 1596, 1499, 1407, 1312, 1297, 1102, 958, 924, 771, 735, 703 cm^{-1} . ²⁴

1-(4-(methylsulfonyl)phenyl)-5-phenyl-1H-pyrazole (5m)



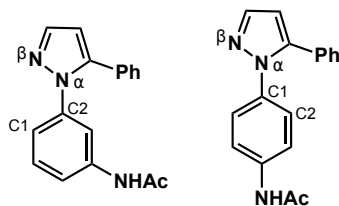
The title compound was synthesized according to general procedure C with **L2** and isolated by preparatory TLC (90:10 hexanes:EtOAc) as yellow oil [5.1 mg, 34% yield, 7:1 $N^\alpha:N^\beta$, 2:1 $C^1:C^2$]. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, $J = 1.7$ Hz, 1H), 7.36 – 7.28 (m, 5H), 7.28 – 7.20 (m, 4H), 6.51 (d, $J = 1.6$ Hz, 1H). **IR** (ATR): 2923, 1594, 1496, 1382, 1093, 959, 923, 830, 759, 696 cm^{-1} . ²⁴

(3-(5-phenyl-1H-pyrazol-1-yl)phenyl)methanol (5n) and (4-(3-phenyl-1H-pyrazol-1-yl)phenyl)methanol (5n')



The title compounds were inseparable carbon regioisomers and synthesized according to general procedure A with **L2**. The mixture of regioisomers were isolated by preparatory TLC (50:50 hexanes:EtOAc) as white solid [11 mg, 84% yield, >20:1 N^α:N^β, 1:2 C¹:C²]. ¹H NMR (600 MHz, CD₃CN) δ 7.68 (dd, J = 3.0, 1.8 Hz, 2.7H), 7.35 – 7.28 (m, 13H), 7.26 – 7.20 (m, 7H), 7.07 (dt, J = 5.3, 2.7 Hz, 2H), 6.56 (d, J = 1.9 Hz, 1.8H), 6.55 (d, J = 2.0 Hz, 1H), 4.58 (d, J = 3.1 Hz, 2H), 4.53 (d, J = 3.4 Hz, 3.6H), 3.27 (s, 1H), 3.23 (s, 1.8H). ¹³C NMR (151 MHz, CD₃CN) δ 144.49, 143.98, 142.70, 141.33, 141.05, 141.01, 140.11, 131.69, 131.63, 129.75, 129.69, 129.67, 129.44, 129.26, 129.25, 128.01, 126.61, 126.20, 124.84, 124.45, 108.64, 108.62, 64.02, 64.01. IR (ATR): 3304 (br), 2921, 2852, 2358, 1495, 1440, 1390, 1134, 1053, 932, 805, 763, 700 cm⁻¹. HRMS calculated for C₁₆H₁₄N₂O [M+Na]⁺ 273.1004, found 273.0999.

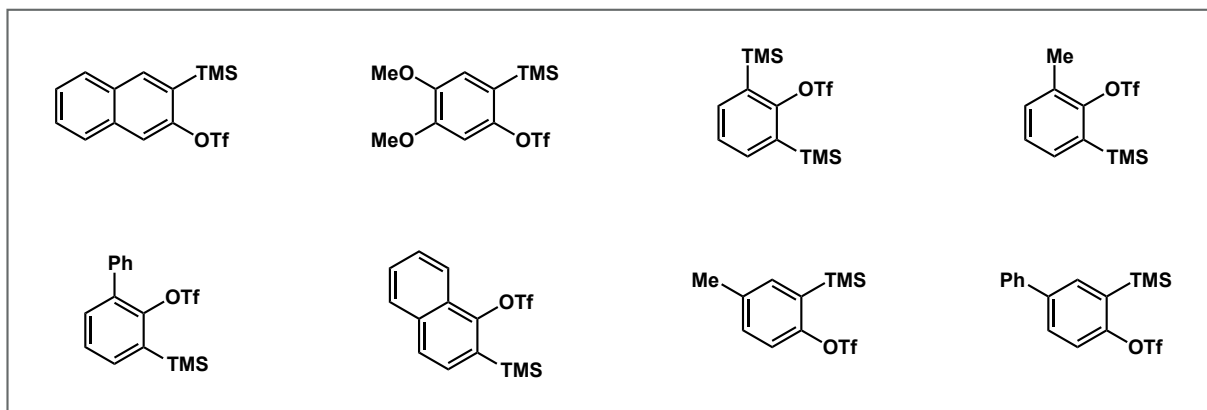
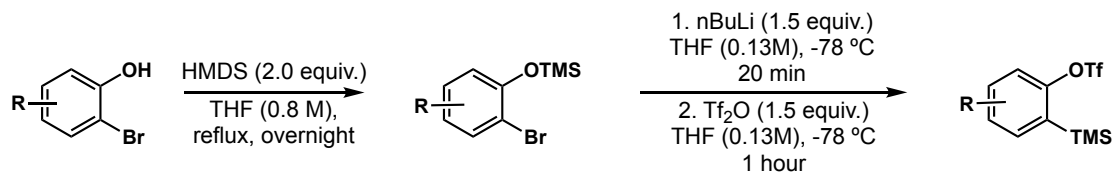
N-(3-(3-phenyl-1H-pyrazol-1-yl)phenyl)acetamide (5o) and N-(4-(3-phenyl-1H-pyrazol-1-yl)phenyl)acetamide (5o')



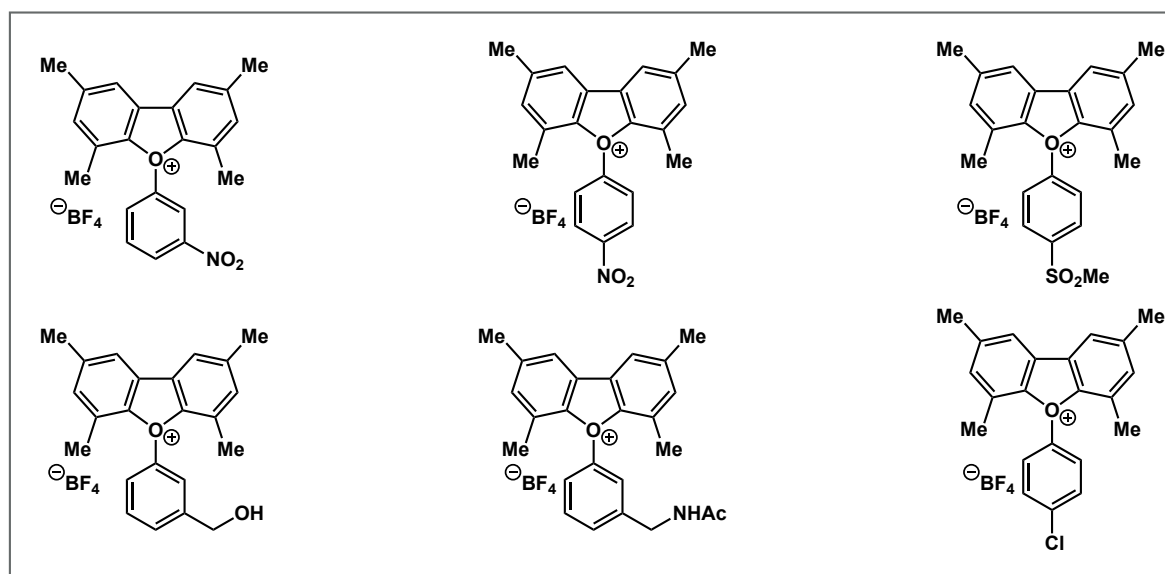
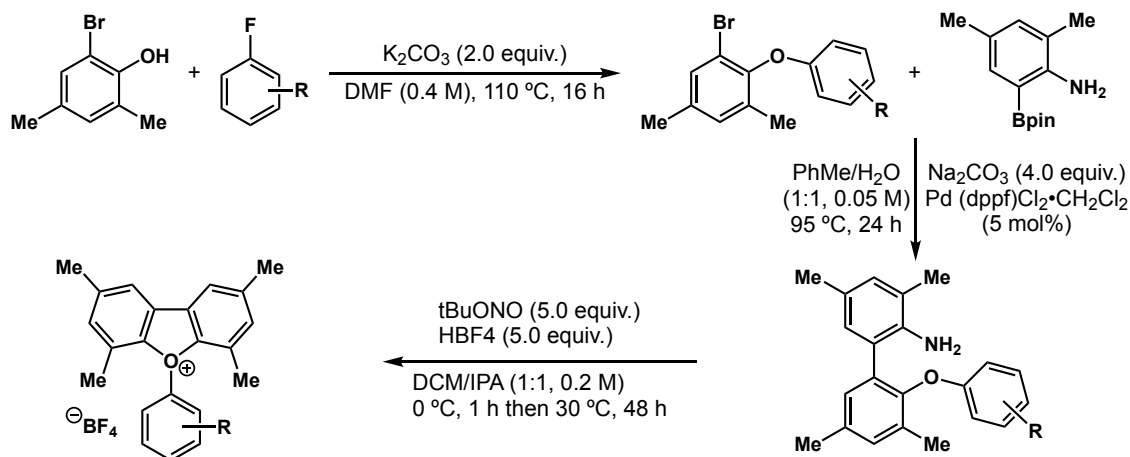
The title compounds were inseparable carbon regioisomers and synthesized according to general procedure A with **L2**. The mixture of regioisomers were isolated by preparatory TLC (70:30 hexanes:EtOAc) as orange solid [6.7 mg, 48% yield, >20:1 N^α:N^β, 1:2 C¹:C²]. ¹H NMR (600 MHz, CDCl₃) δ 8.21 (s, 2H), 8.07 (s, 1H), 7.70 (dd, J = 5.2, 1.9 Hz, 3H), 7.60 (d, J = 9.3 Hz, 2H), 7.51 (s, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.32 – 7.26 (m, 8H), 7.25 – 7.19 (m, 5H), 7.16 (t, J = 8.4 Hz, 4H), 6.84 (d, J = 8.0 Hz, 2H), 6.50 (dd, J = 5.4, 1.9 Hz, 3H), 2.11 (s, 3H), 2.04 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 168.83, 168.80, 143.41, 143.25, 140.41, 140.28, 139.14, 137.66, 135.90, 130.43, 130.30, 129.40, 128.81, 128.63, 128.47, 128.40, 125.91, 120.88, 120.09, 119.12, 116.77, 107.93, 107.75, 24.57, 24.49. IR (ATR): 3266, 3065, 2927, 1667, 1604, 1548, 1517, 1491, 1370, 1317, 909, 789, 759, 728, 695 cm⁻¹. HRMS calculated for C₁₇H₁₅N₃O [M+H]⁺ 278.1293, found 278.1290.

4. General Procedure to Prepare Starting Materials.

The synthesis of trifluoromethanesulfonate (Kobayashi precursors) were performed using standard literature-reported procedures.²⁵

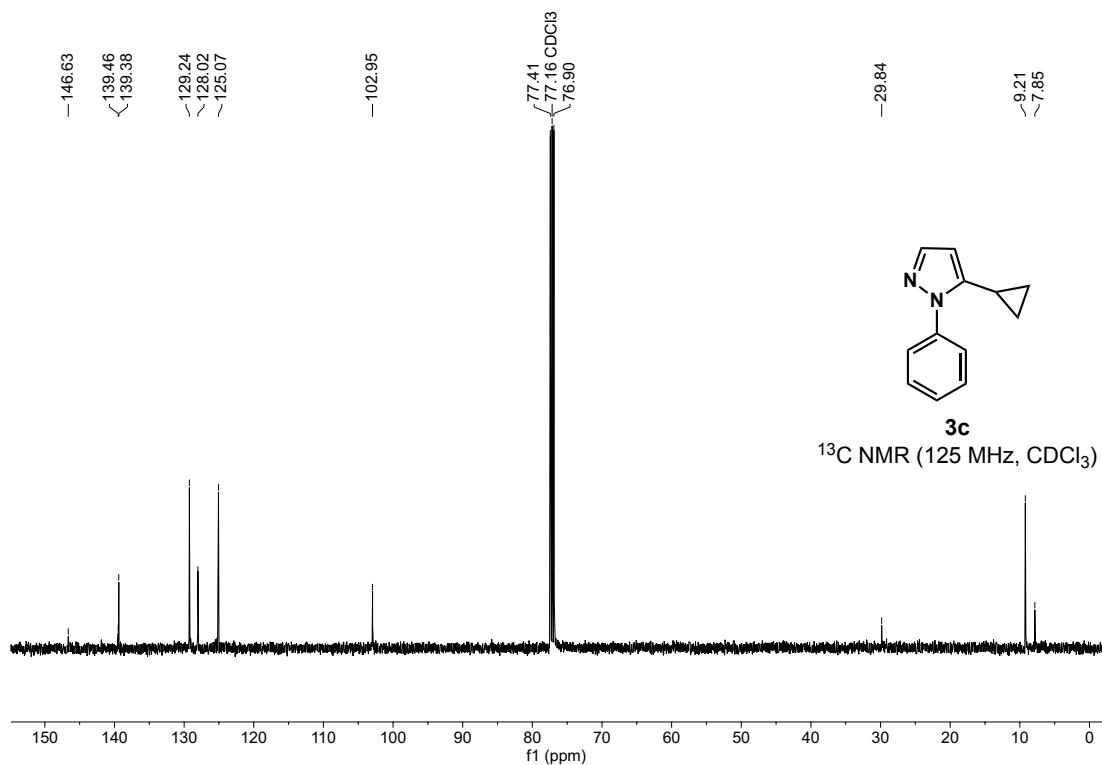
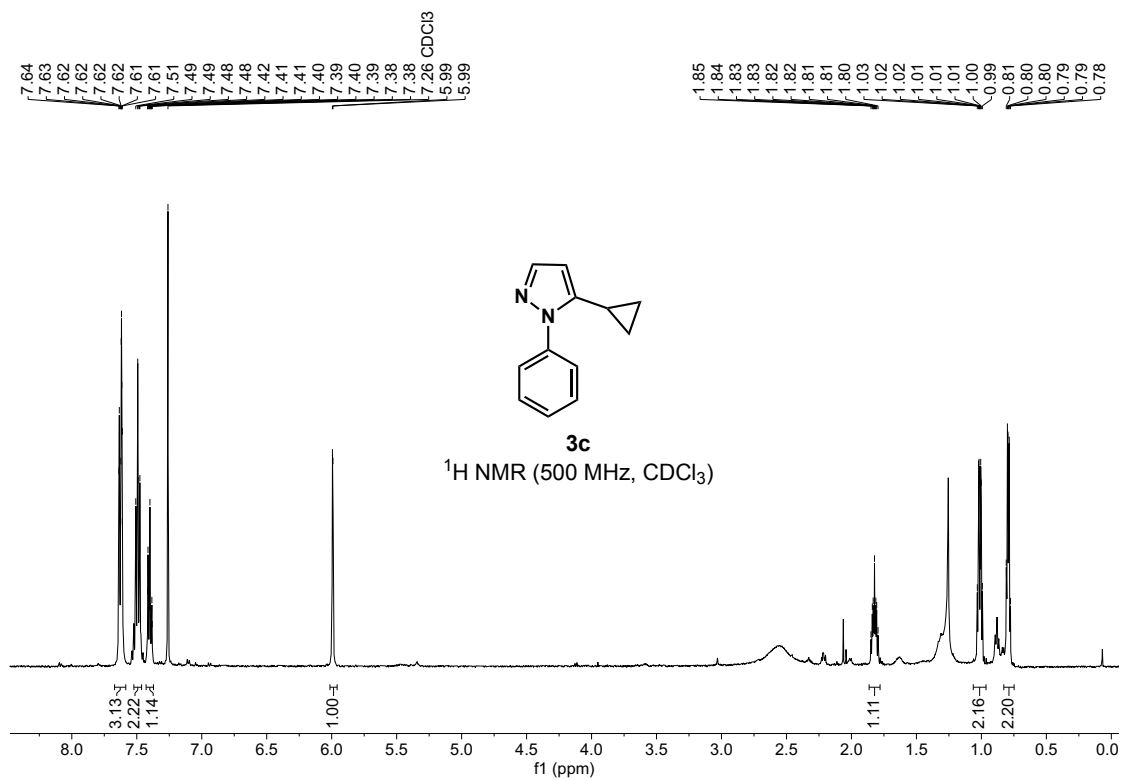


The synthesis of triaryloxonium ions (Smith precursors) were performed using standard literature-reported procedures.²⁶

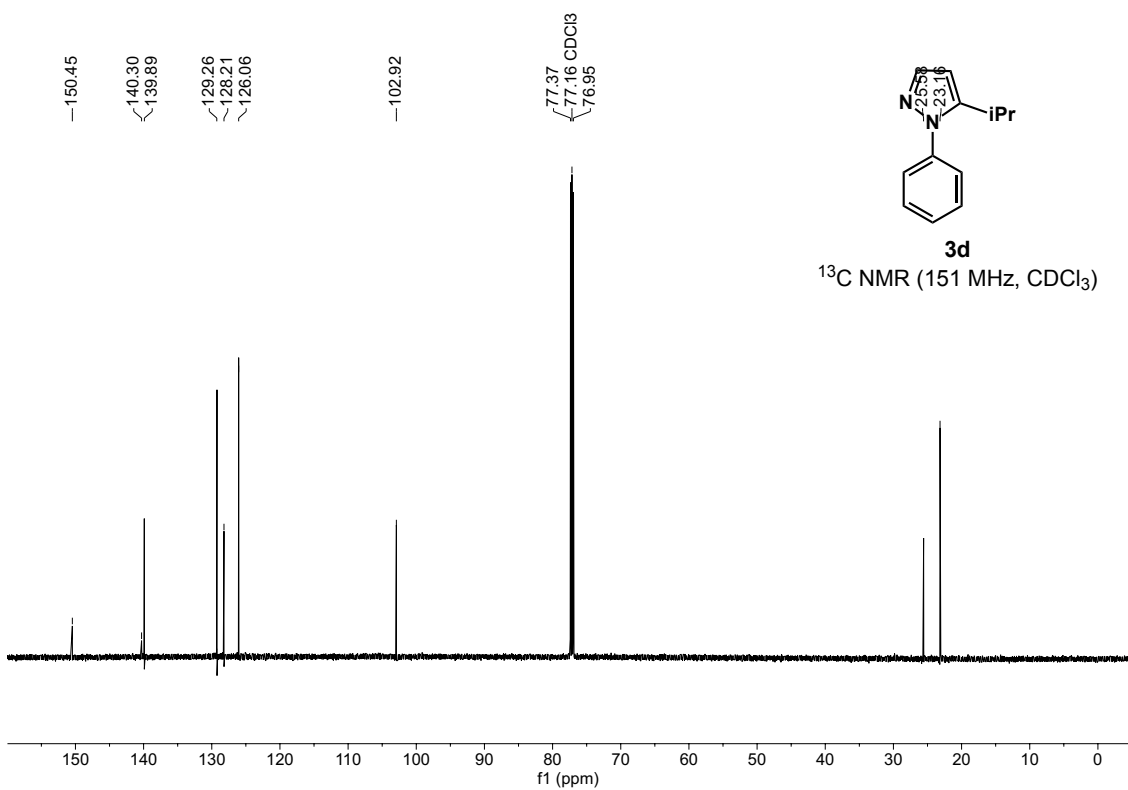
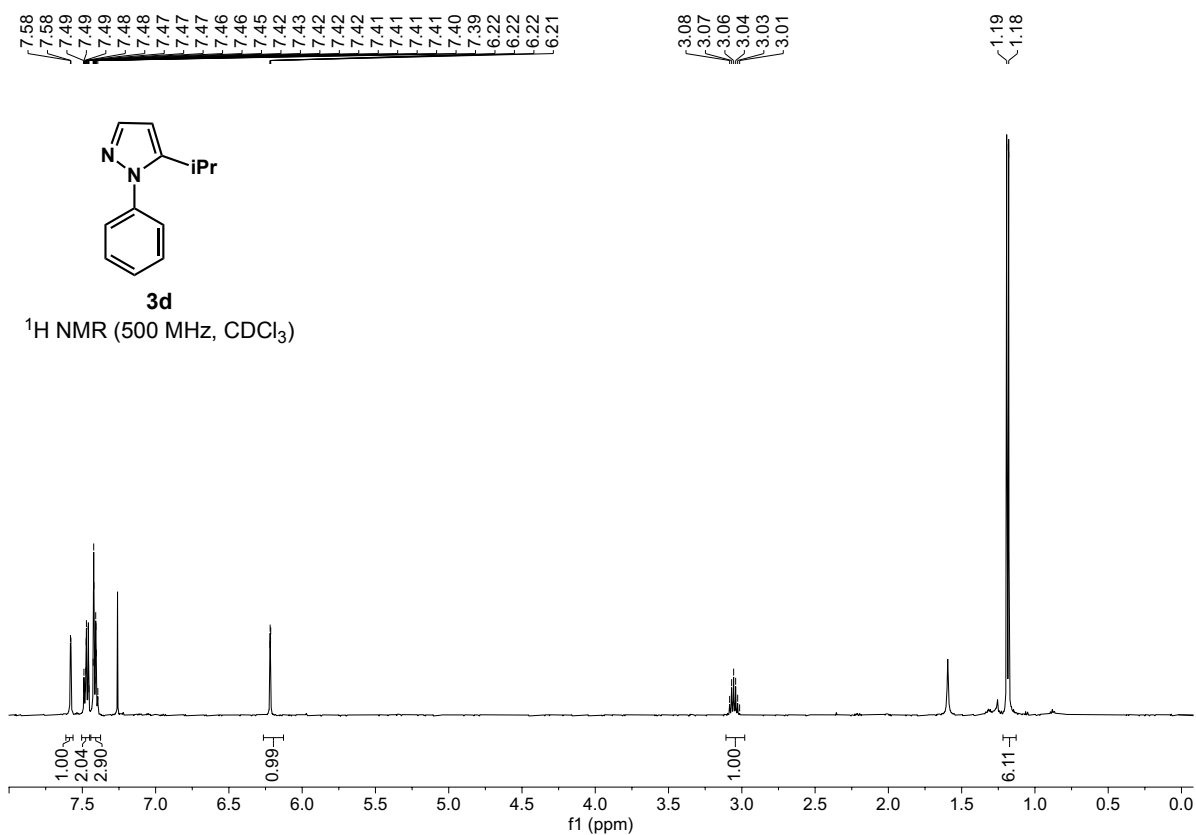


5. NMR Spectra

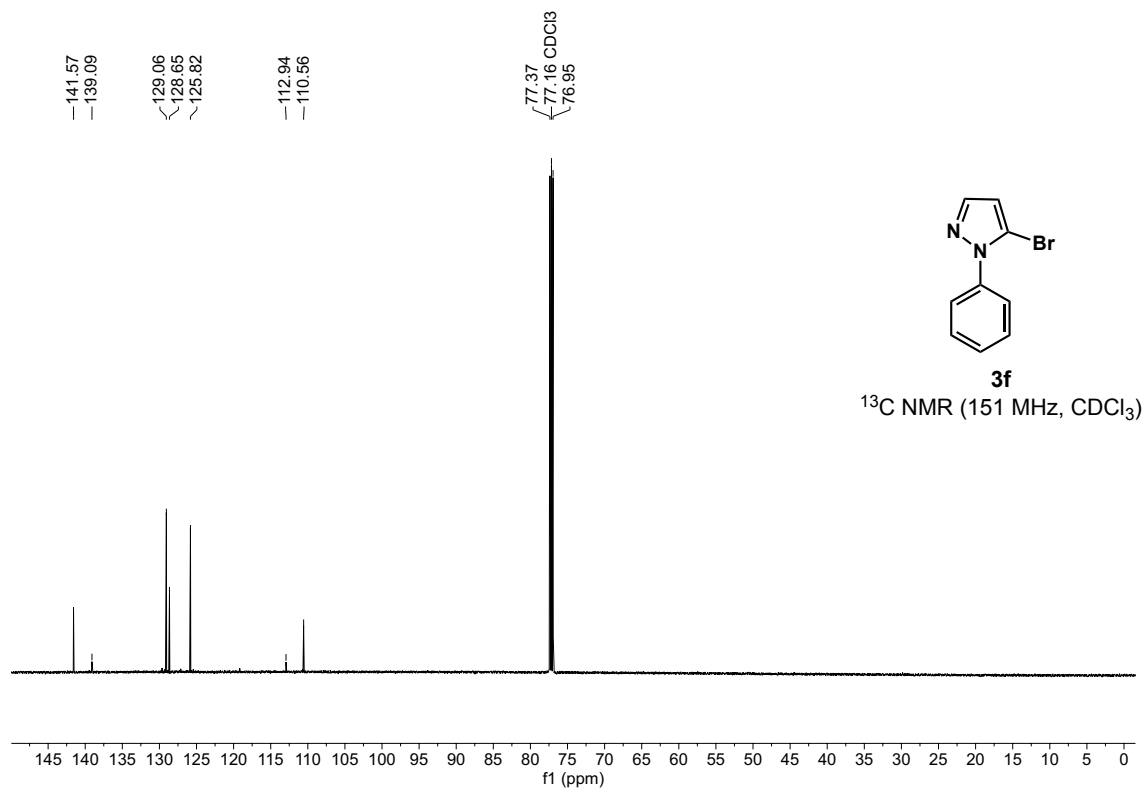
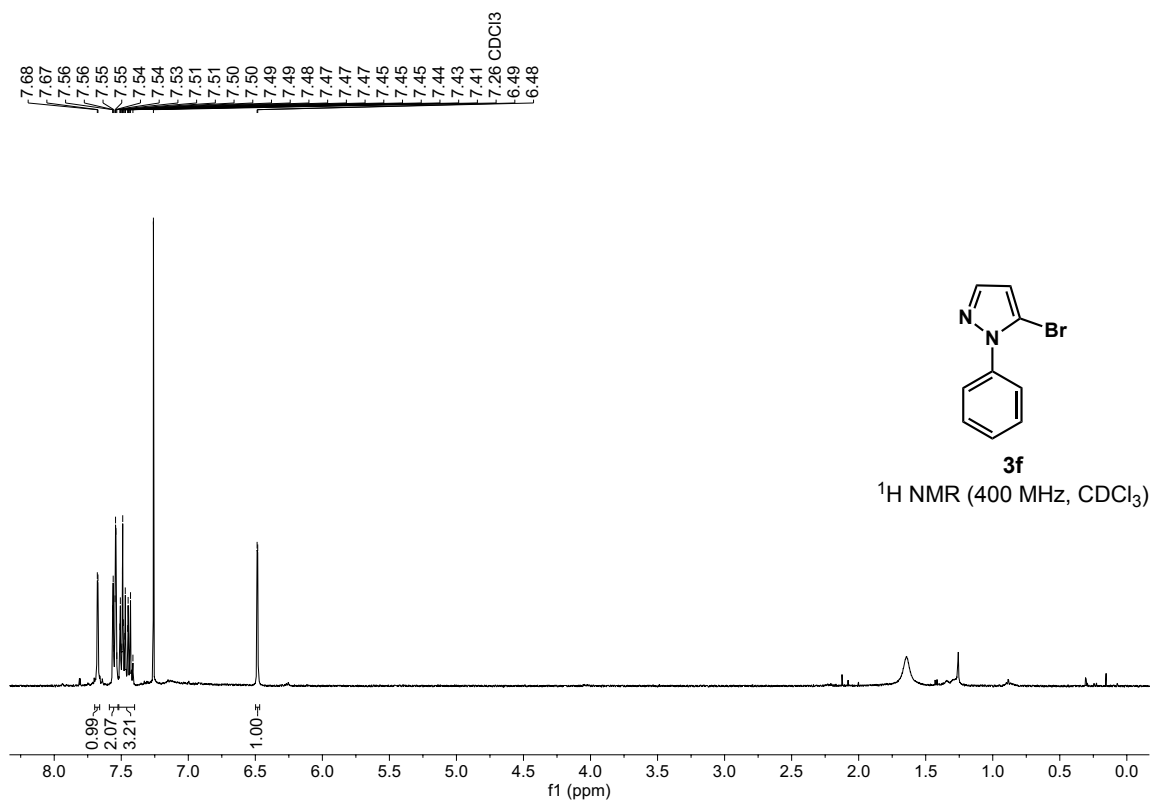
5-cyclopropyl-1-phenyl-1H-pyrazole (3c)



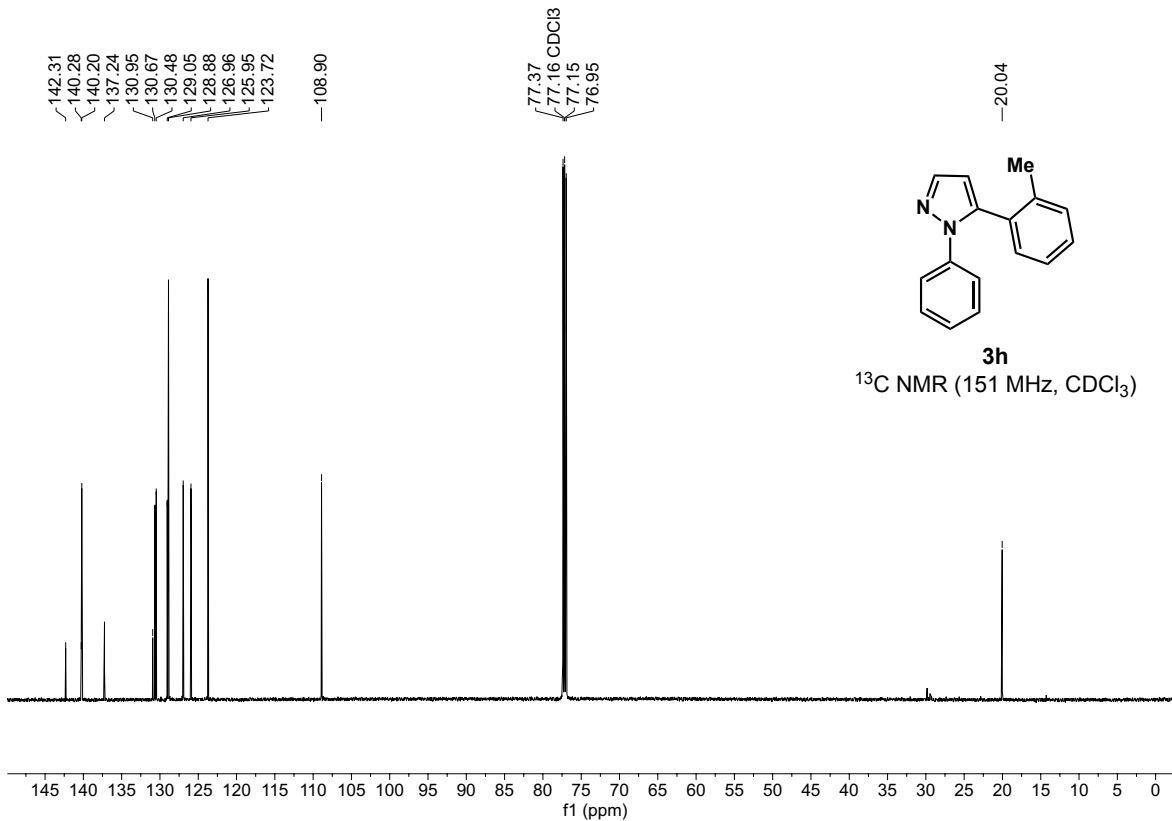
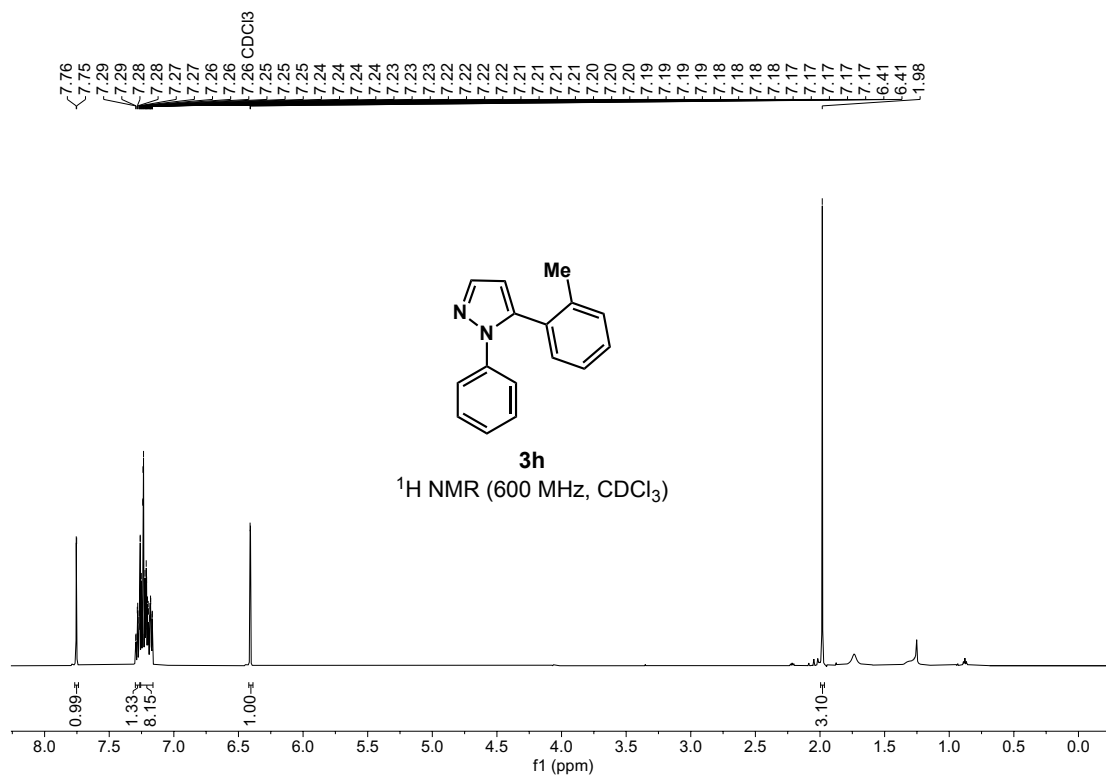
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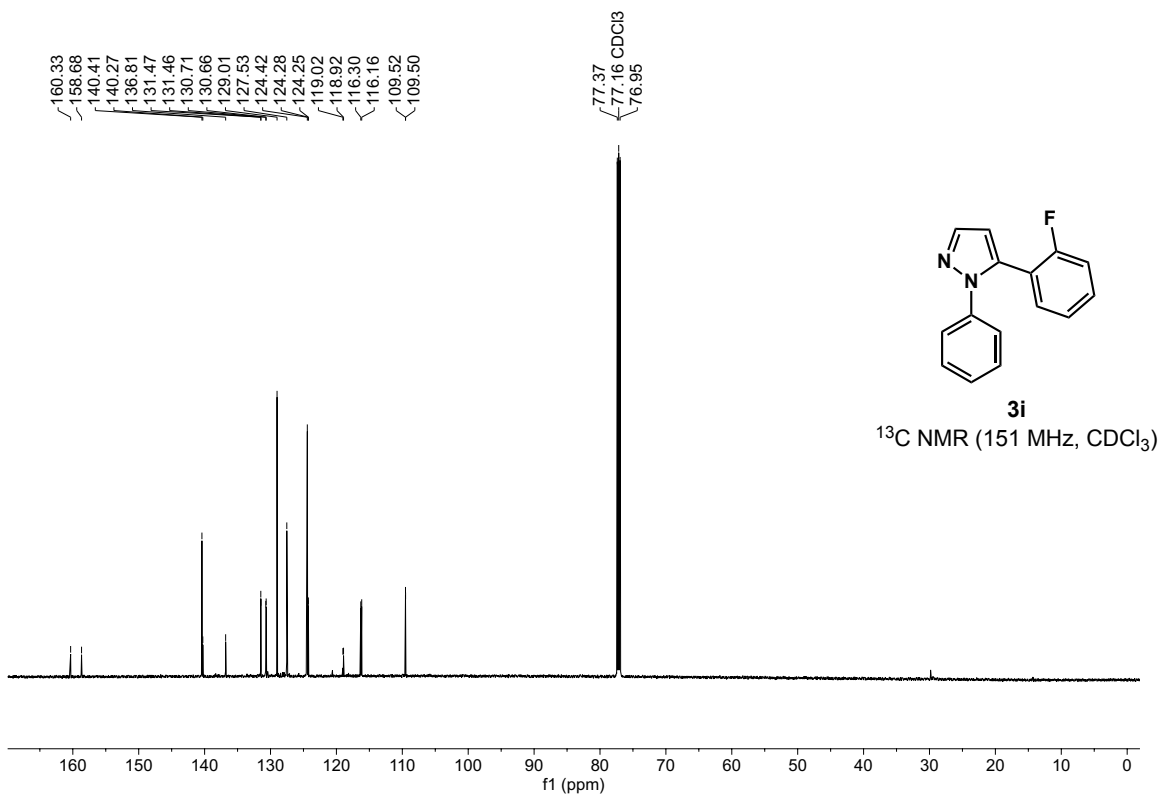
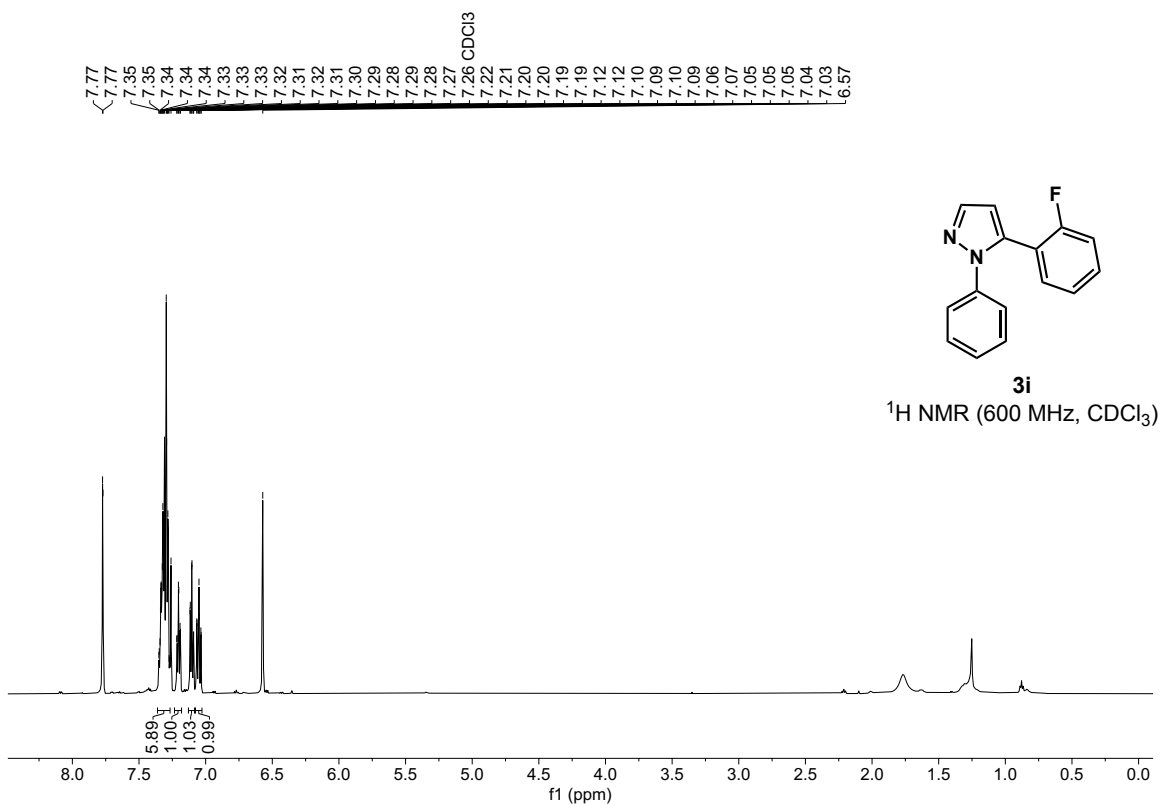
5-bromo-1-phenyl-1H-pyrazole (3f)

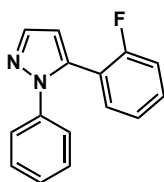


1-phenyl-5-(o-tolyl)-1H-pyrazole (3h)



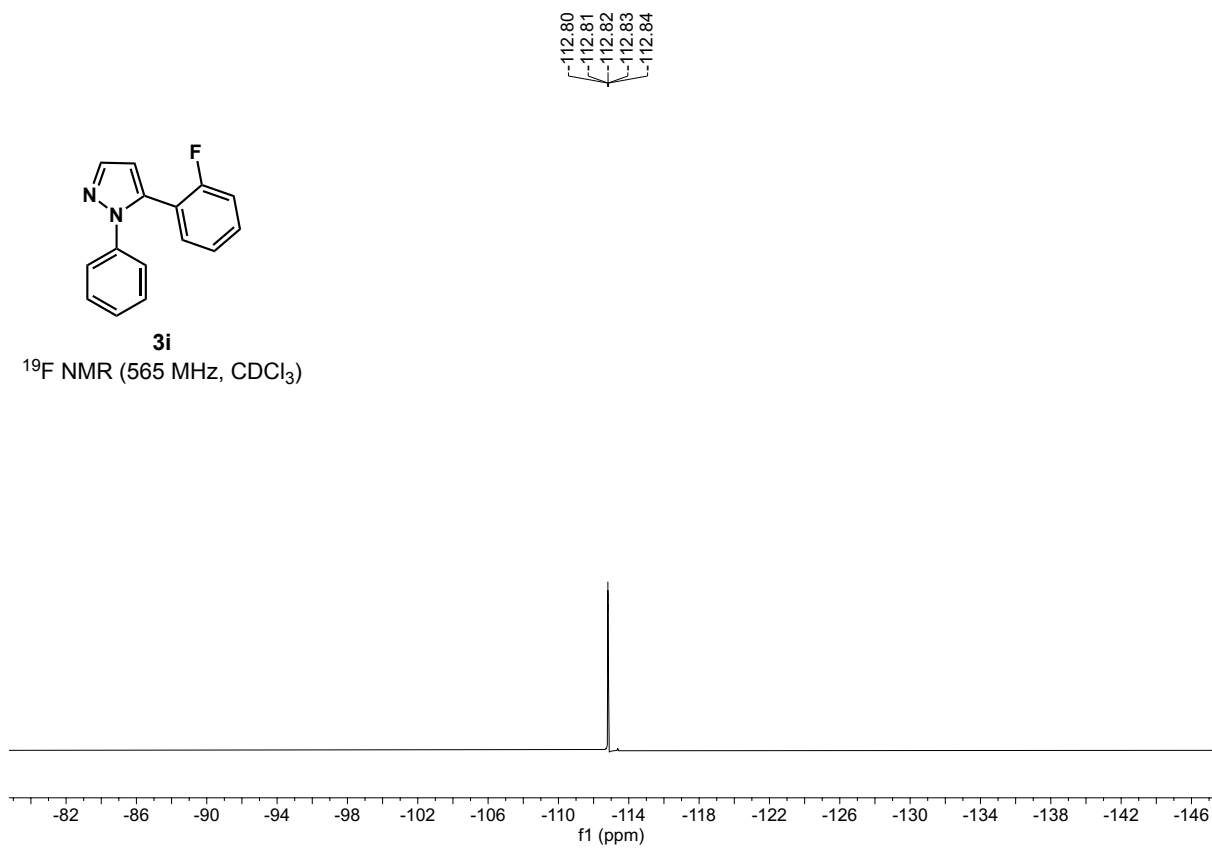
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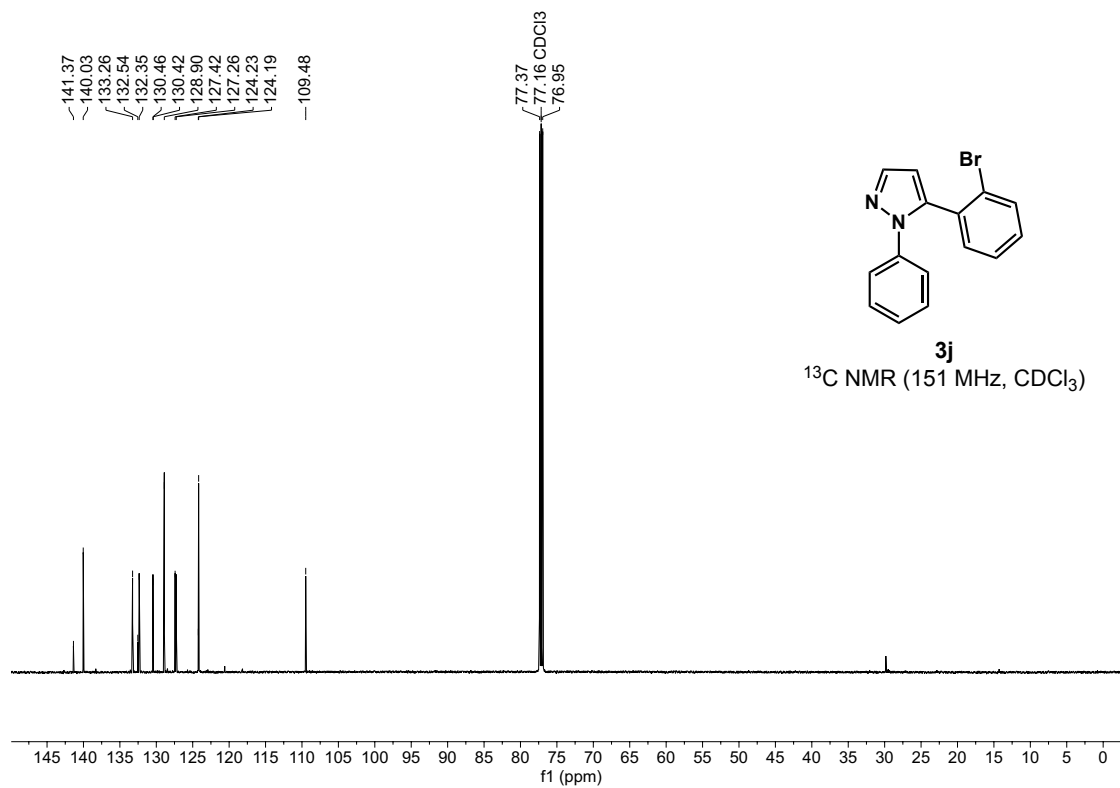
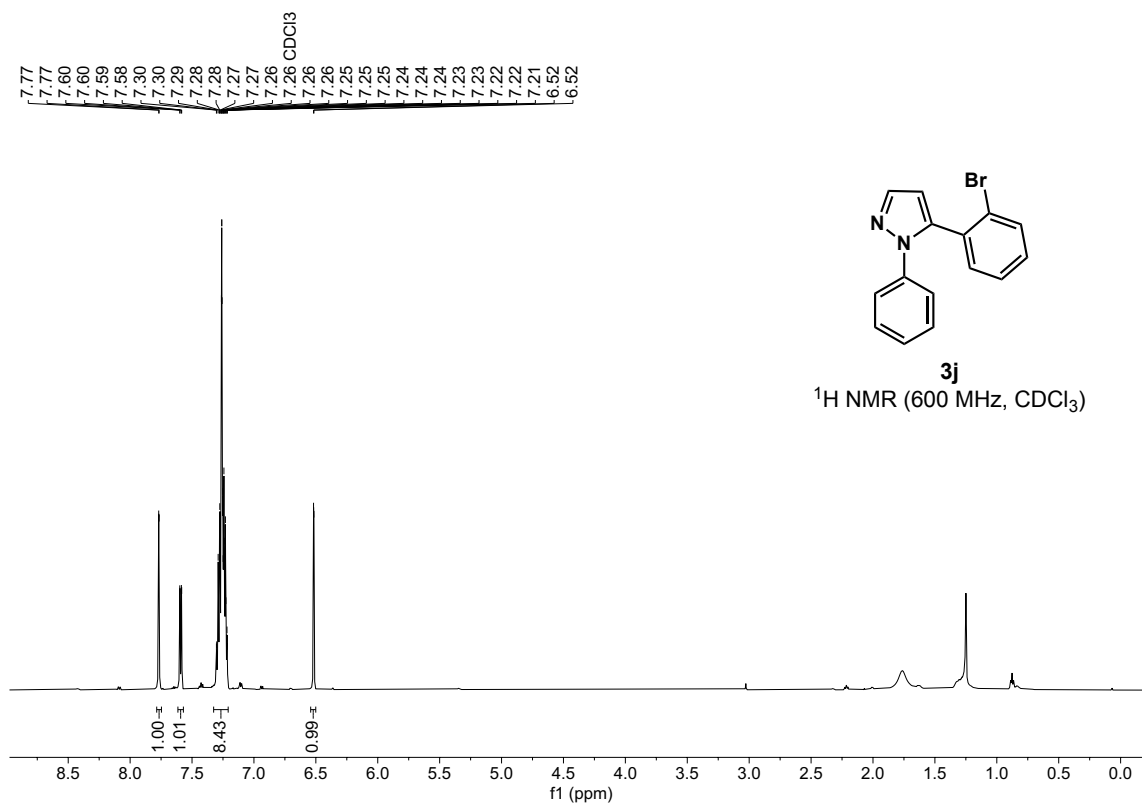


3i

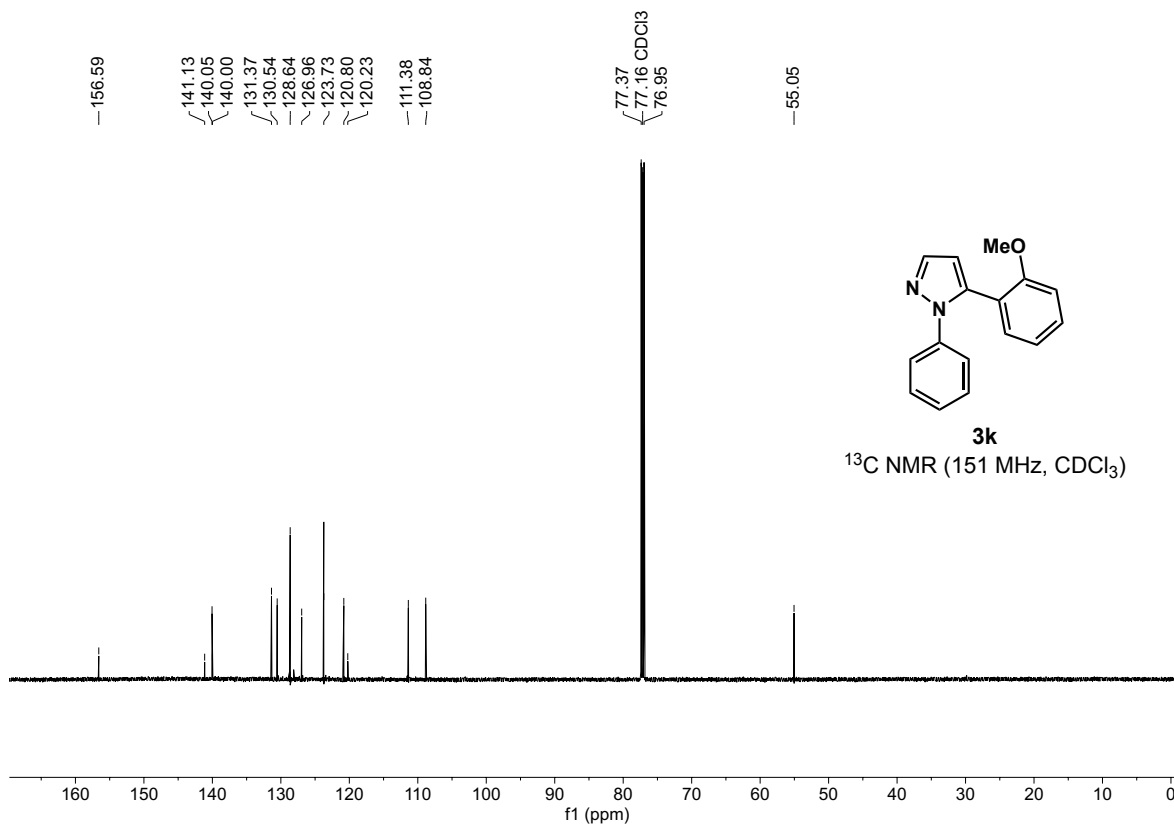
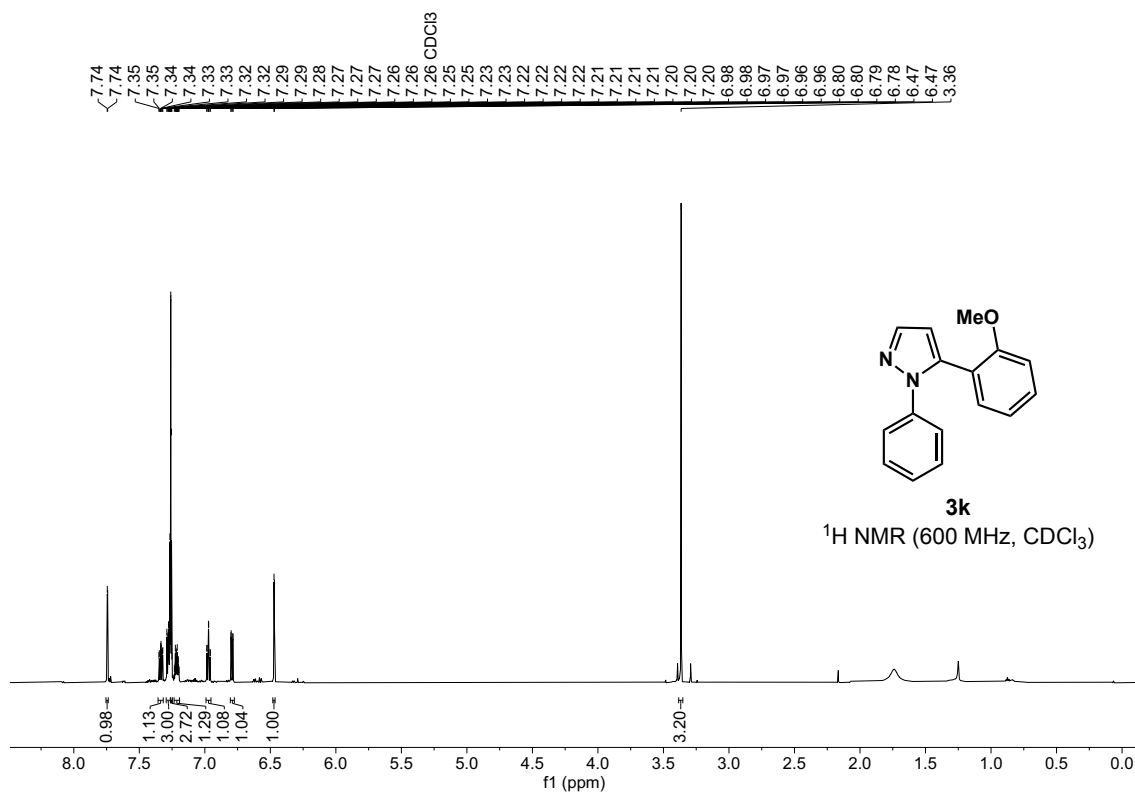
^{19}F NMR (565 MHz, CDCl_3)



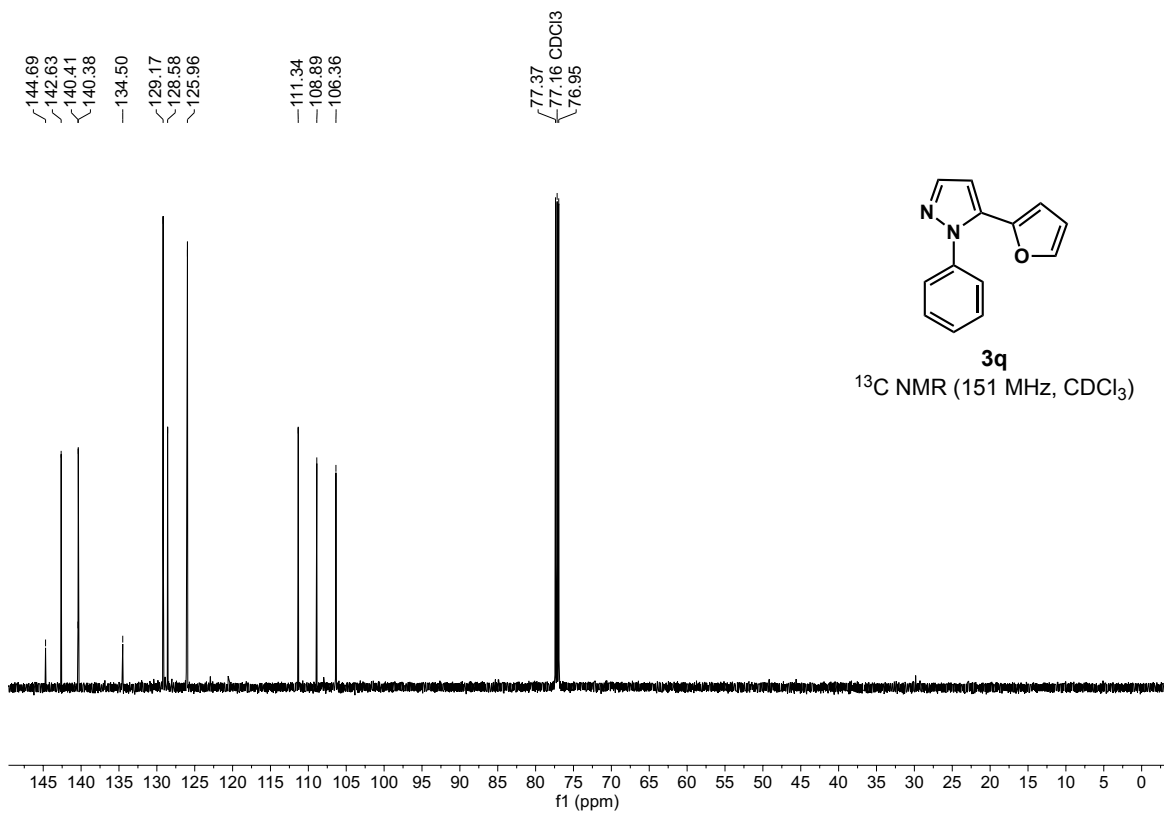
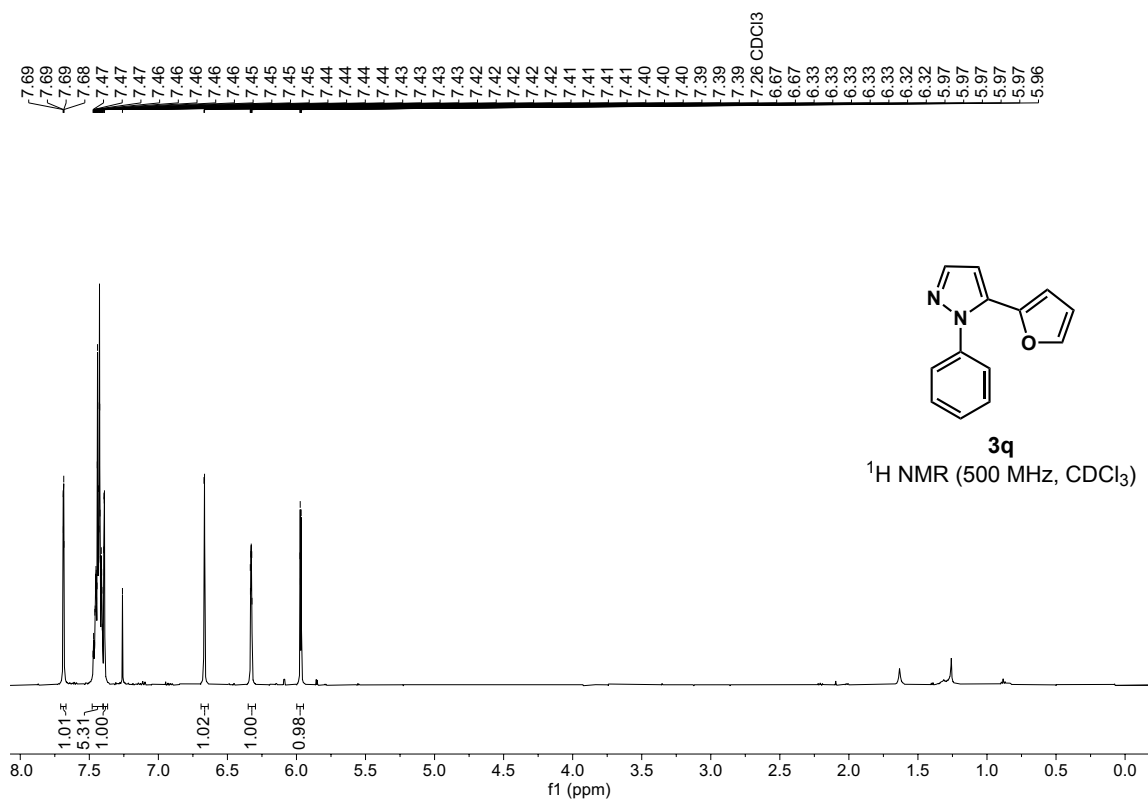
5-(2-bromophenyl)-1-phenyl-1H-pyrazole (3j)



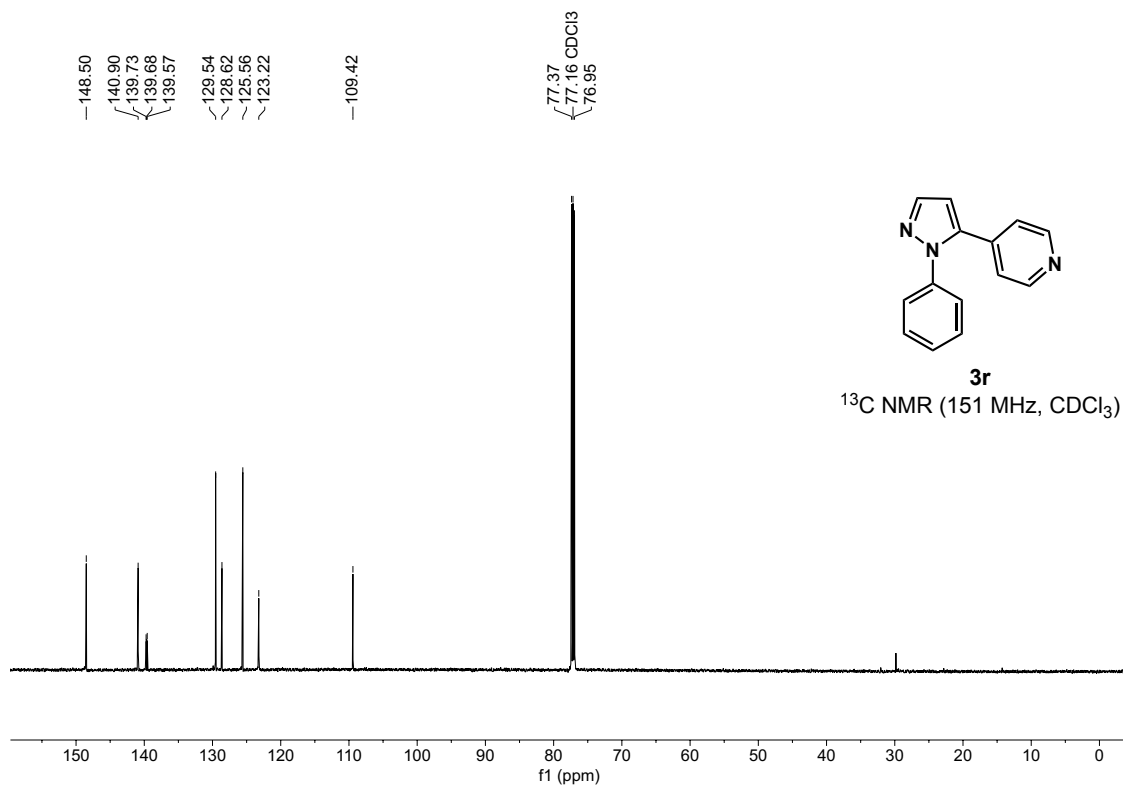
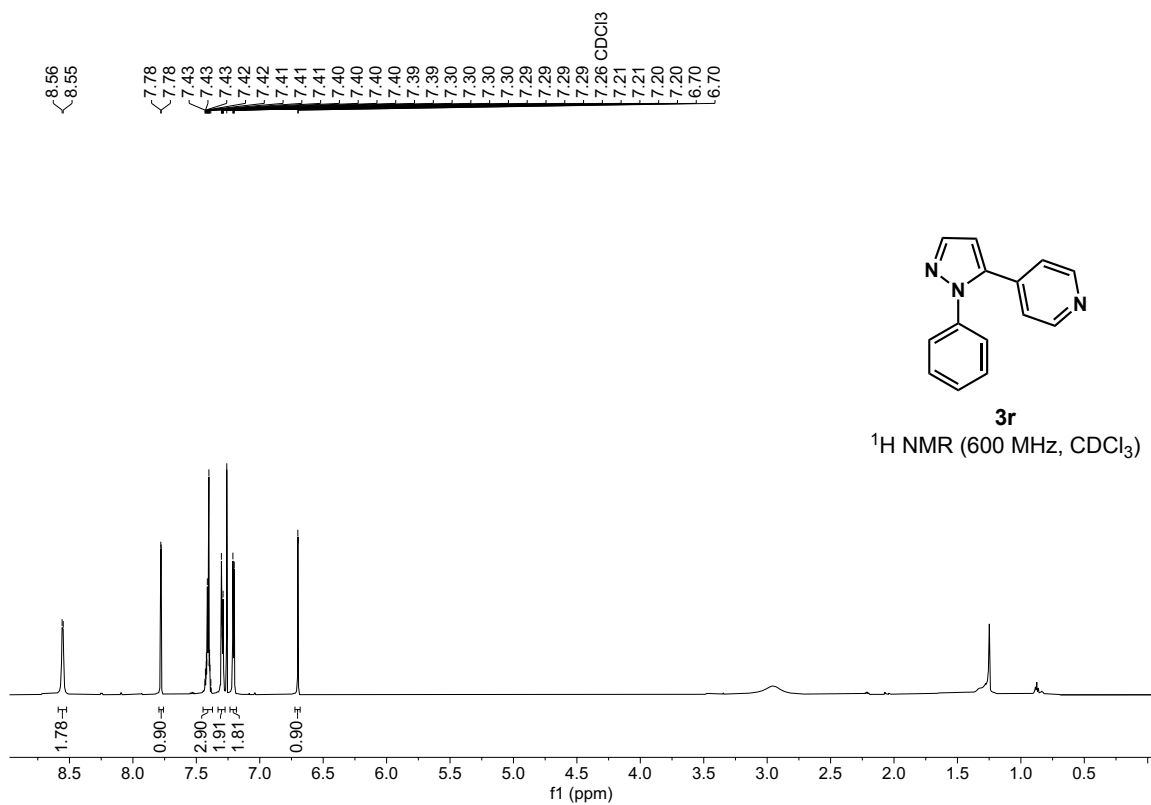
5-(2-methoxyphenyl)-1-phenyl-1H-pyrazole (3k)



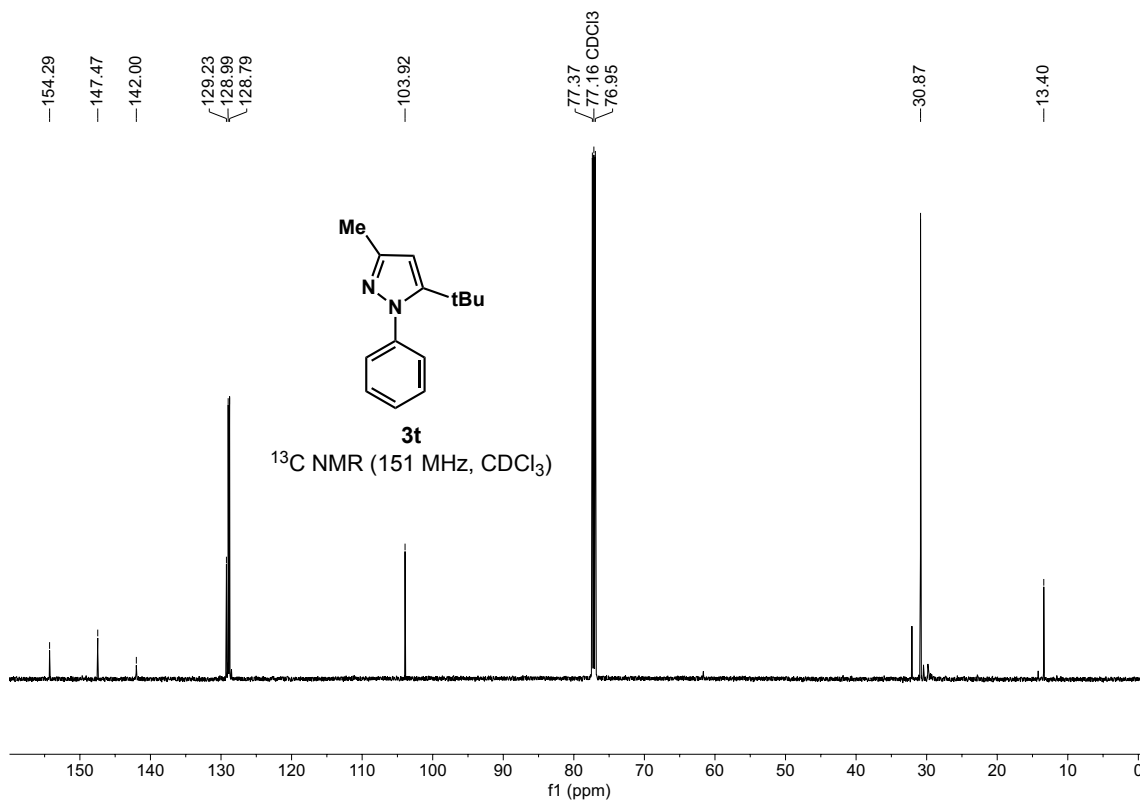
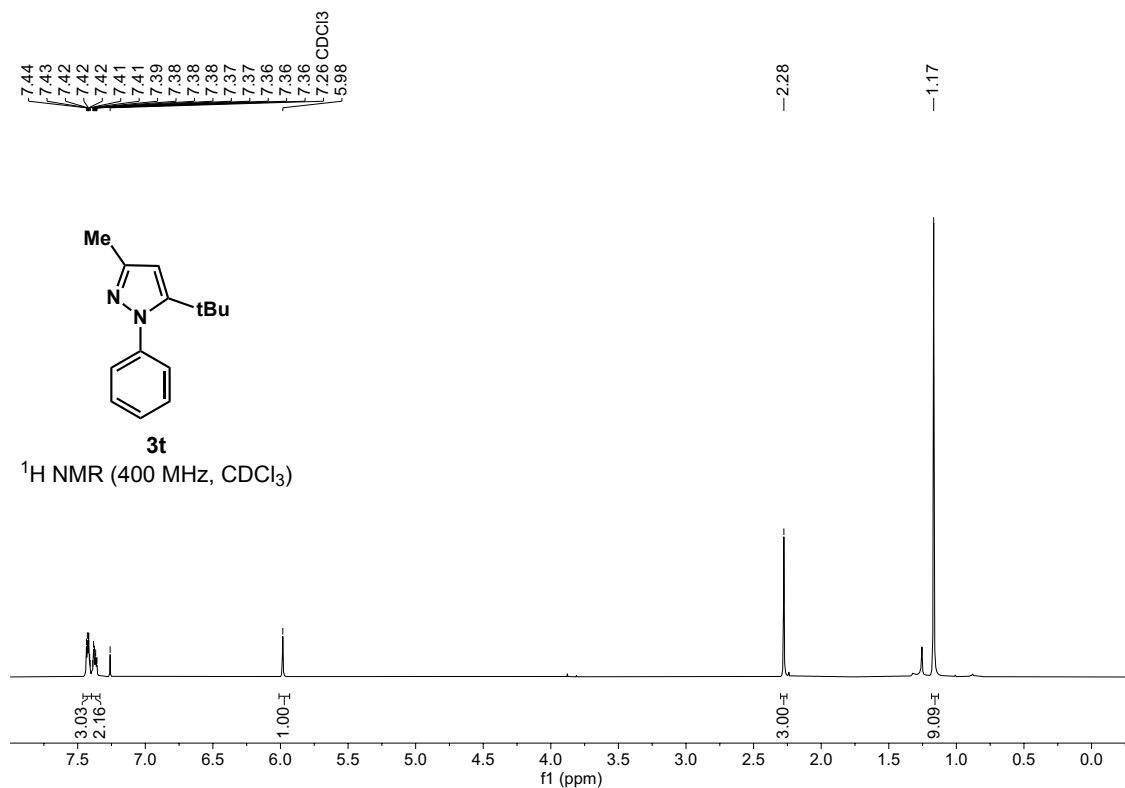
5-(furan-2-yl)-1-phenyl-1H-pyrazole (3q)



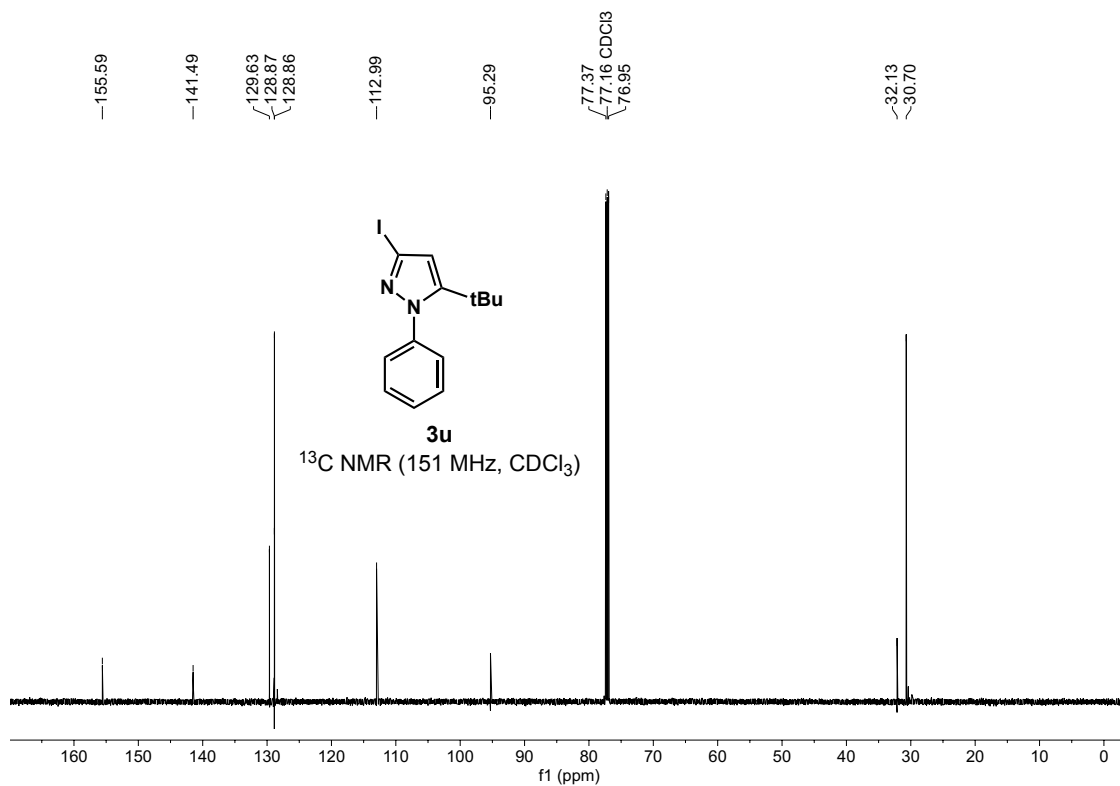
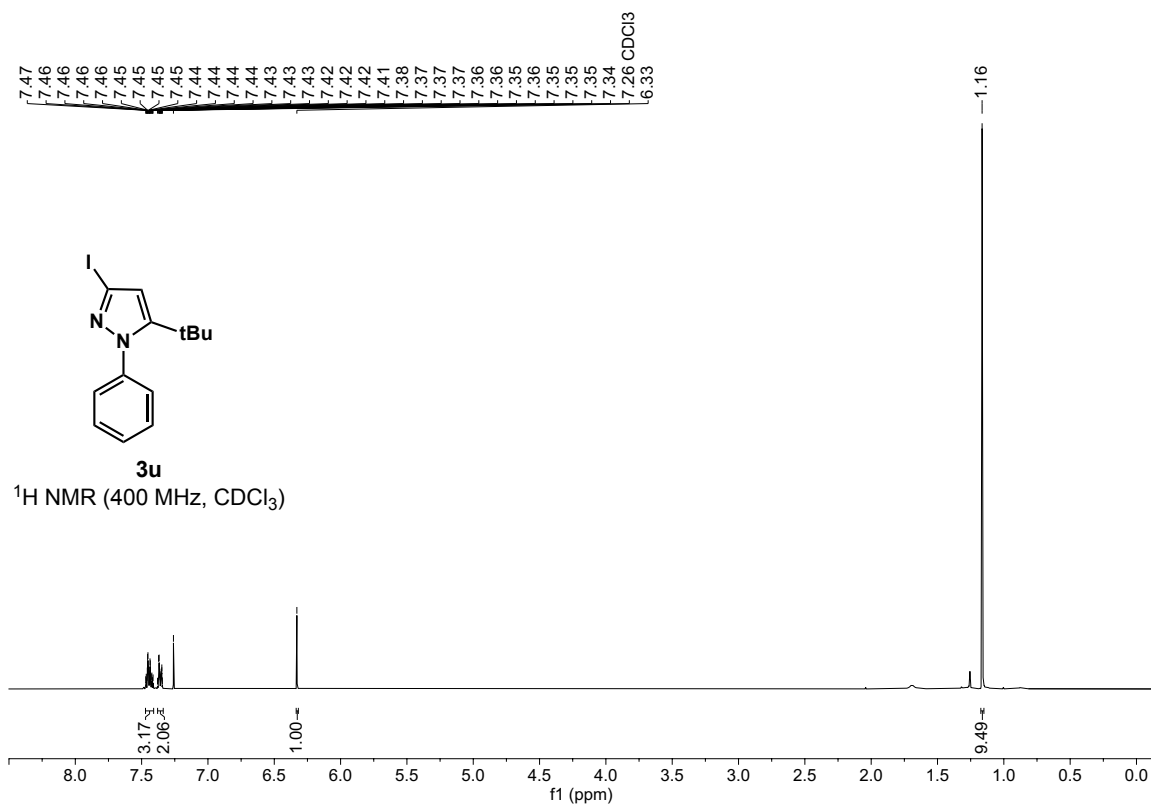
4-(1-phenyl-1H-pyrazol-5-yl)pyridine (3r)



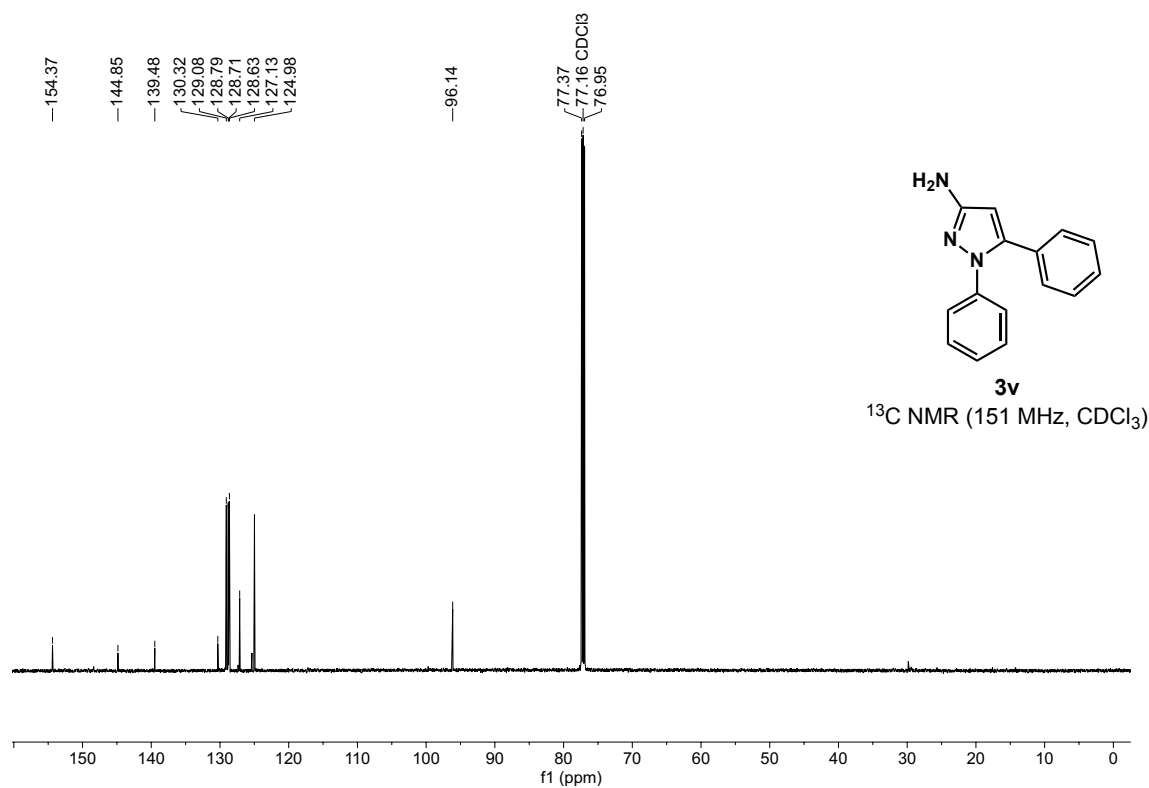
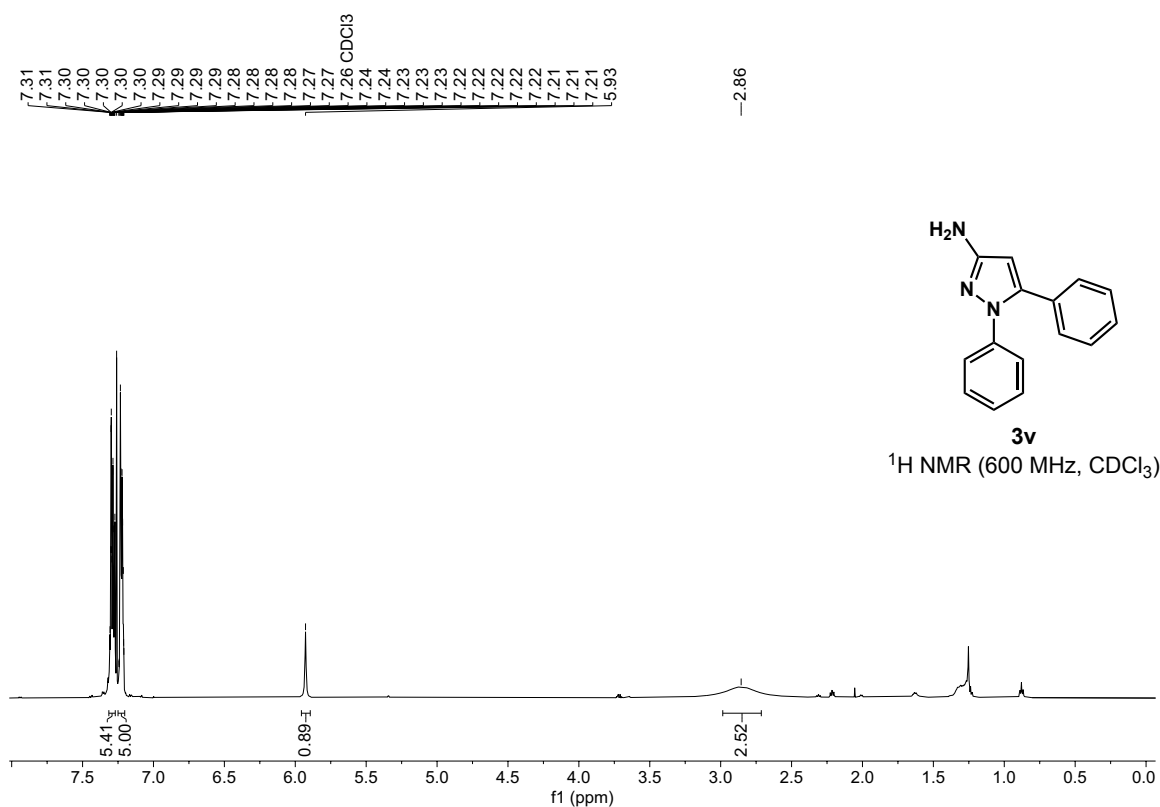
5-(tert-butyl)-3-methyl-1-phenyl-1H-pyrazole (3t)



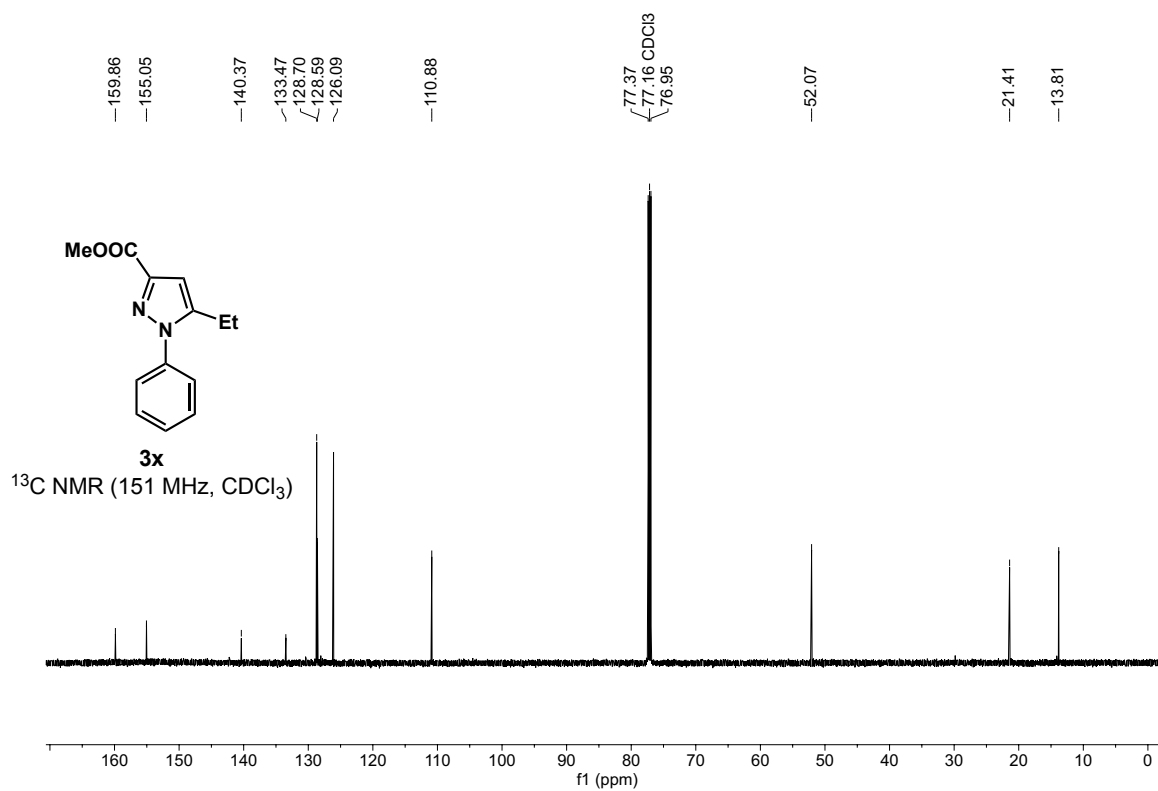
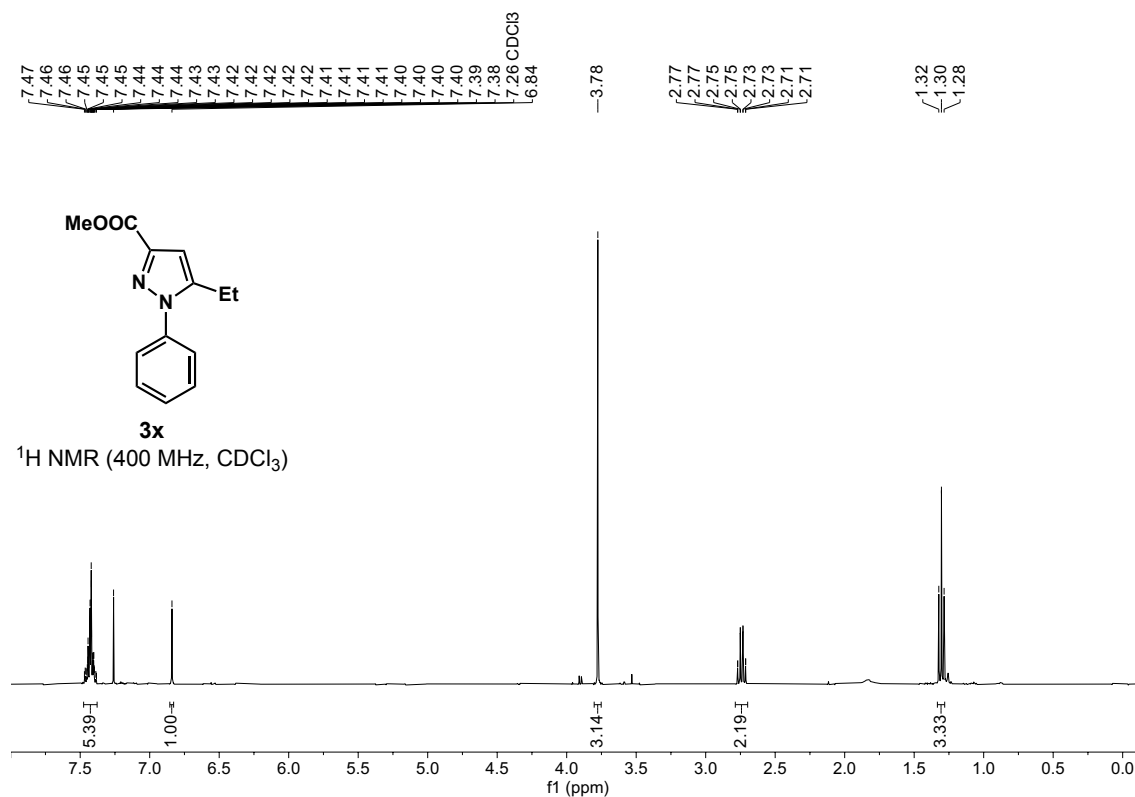
5-(tert-butyl)-3-iodo-1-phenyl-1H-pyrazole (3u)

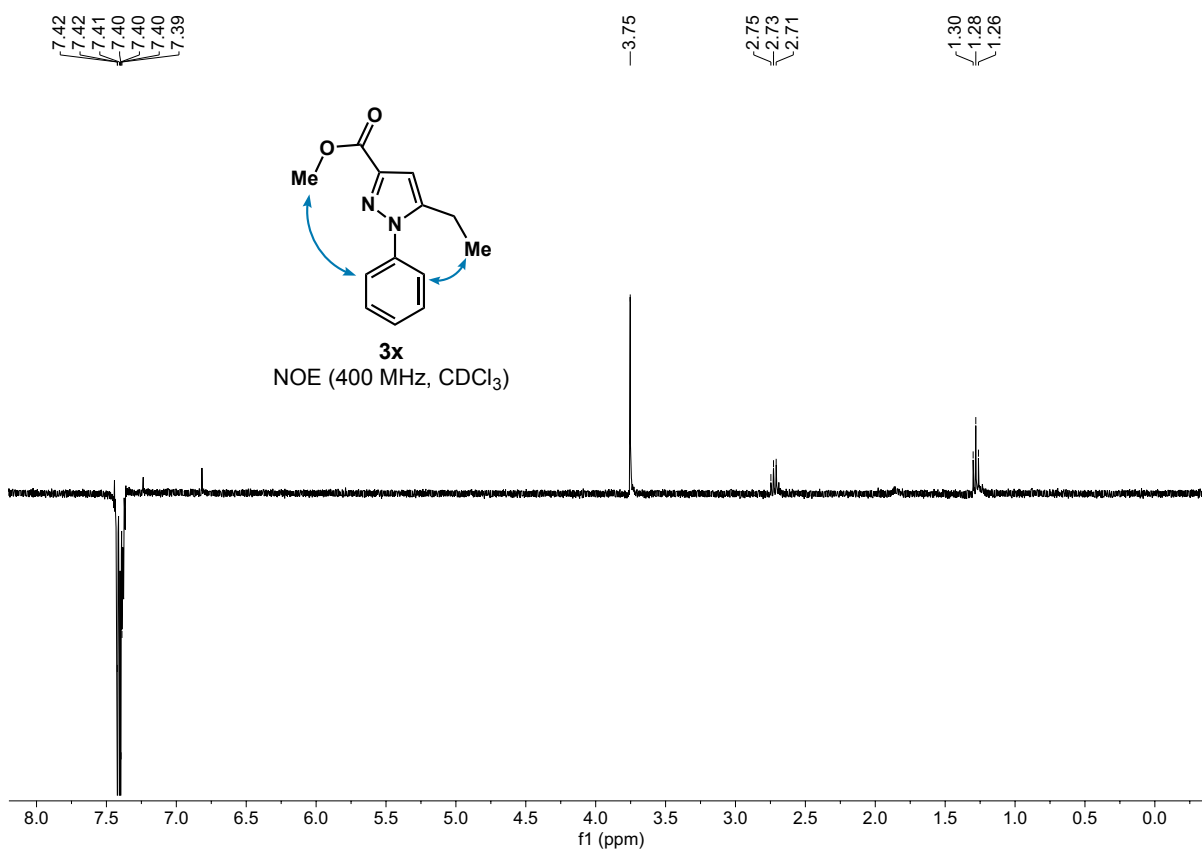


1,5-diphenyl-1H-pyrazol-3-amine (3v)

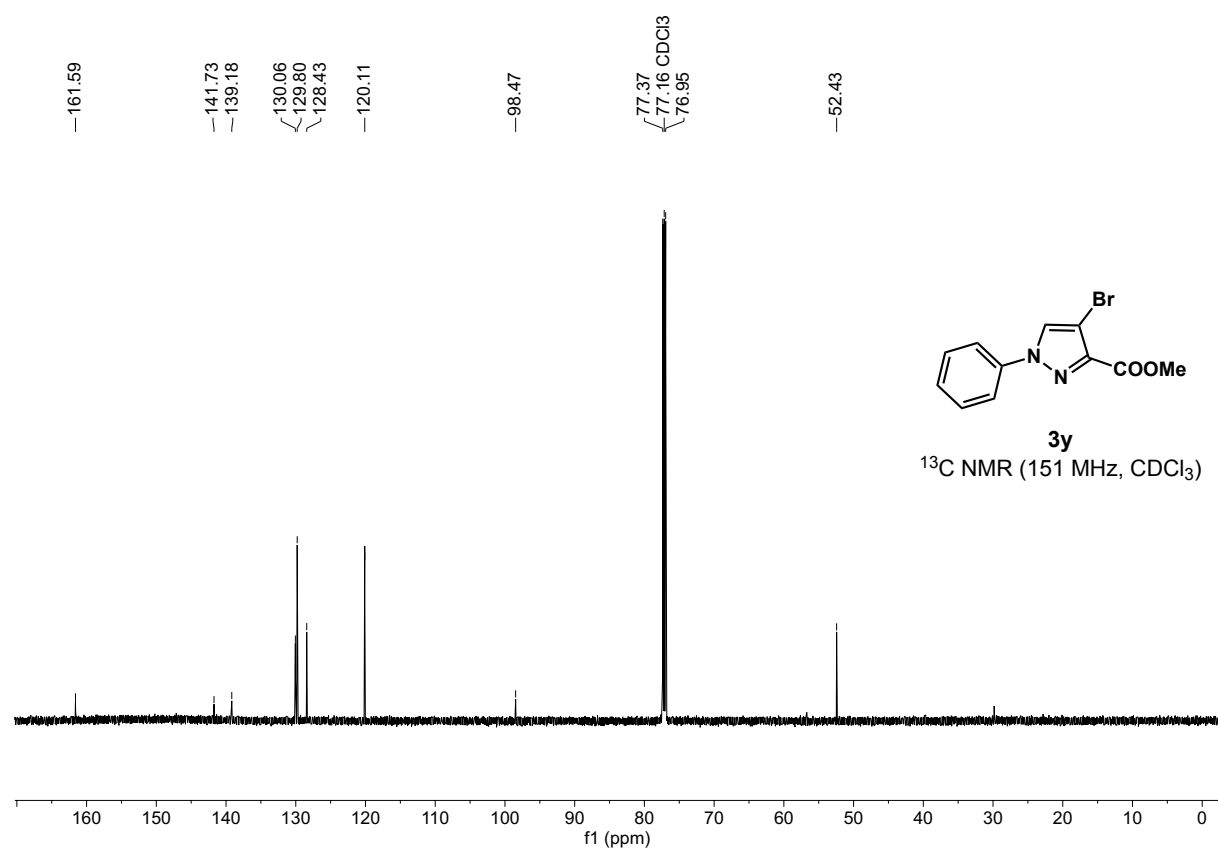
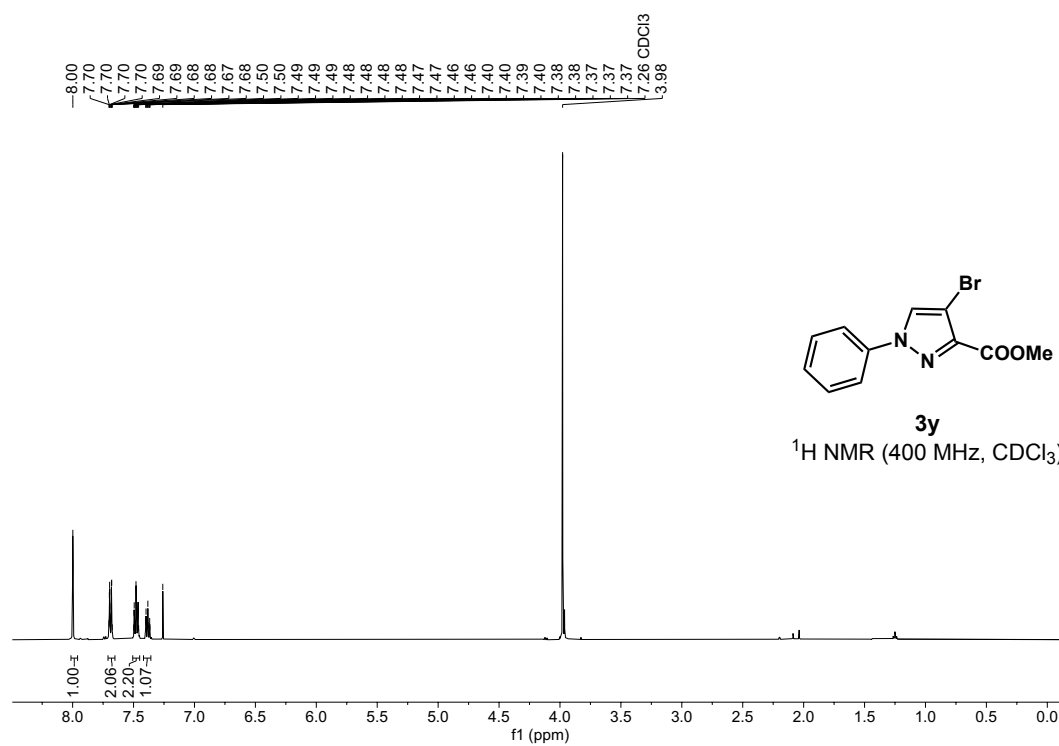


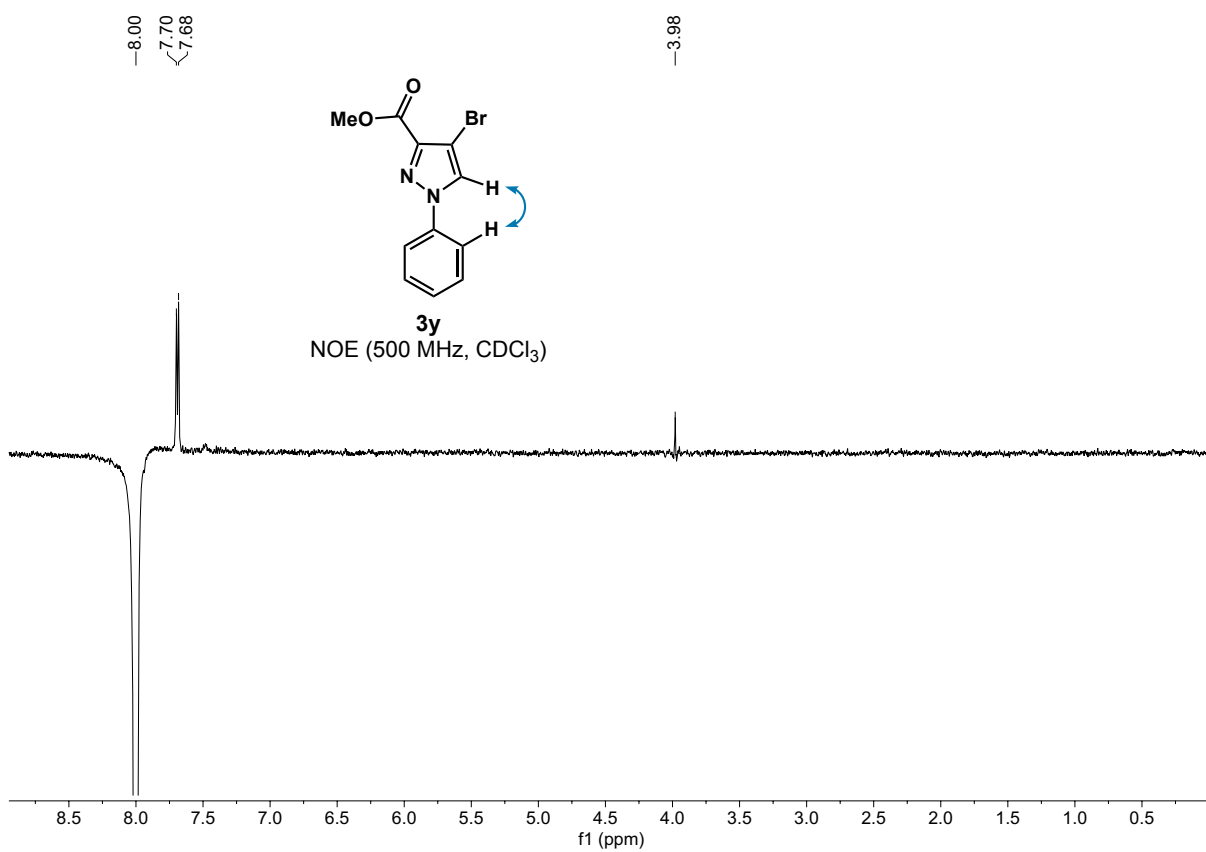
methyl 5-ethyl-1-phenyl-1H-pyrazole-3-carboxylate (3x)



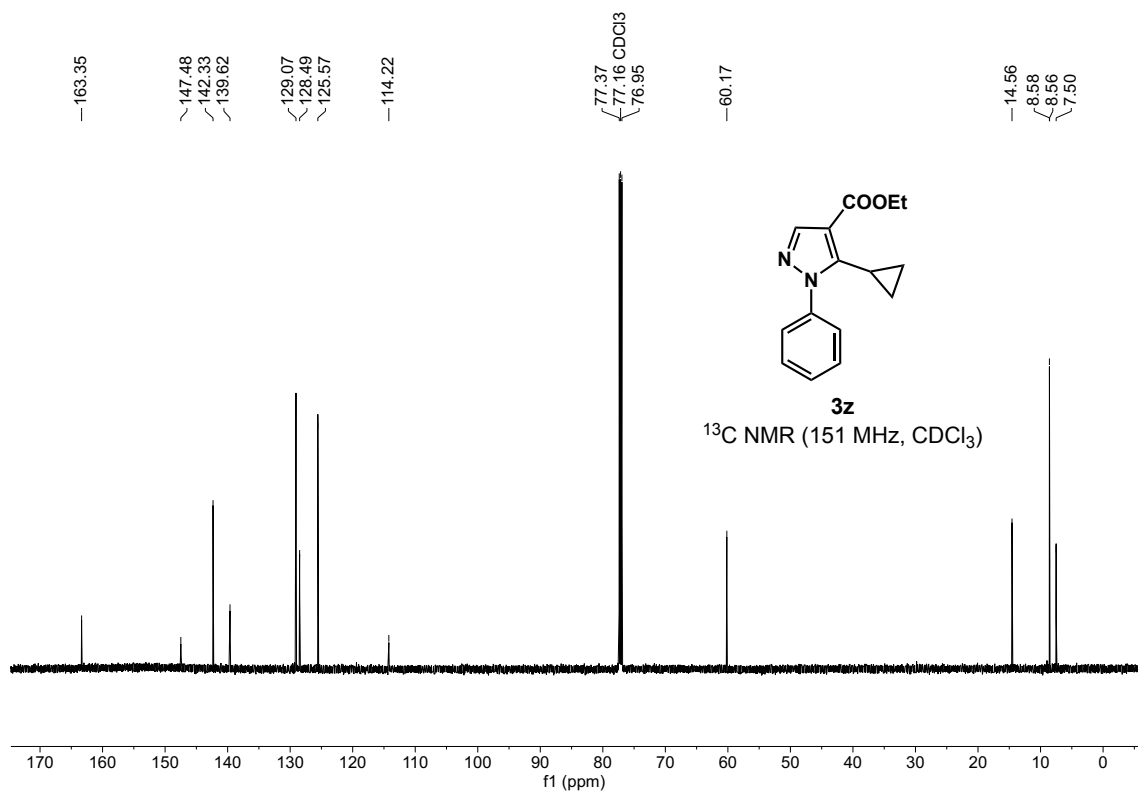
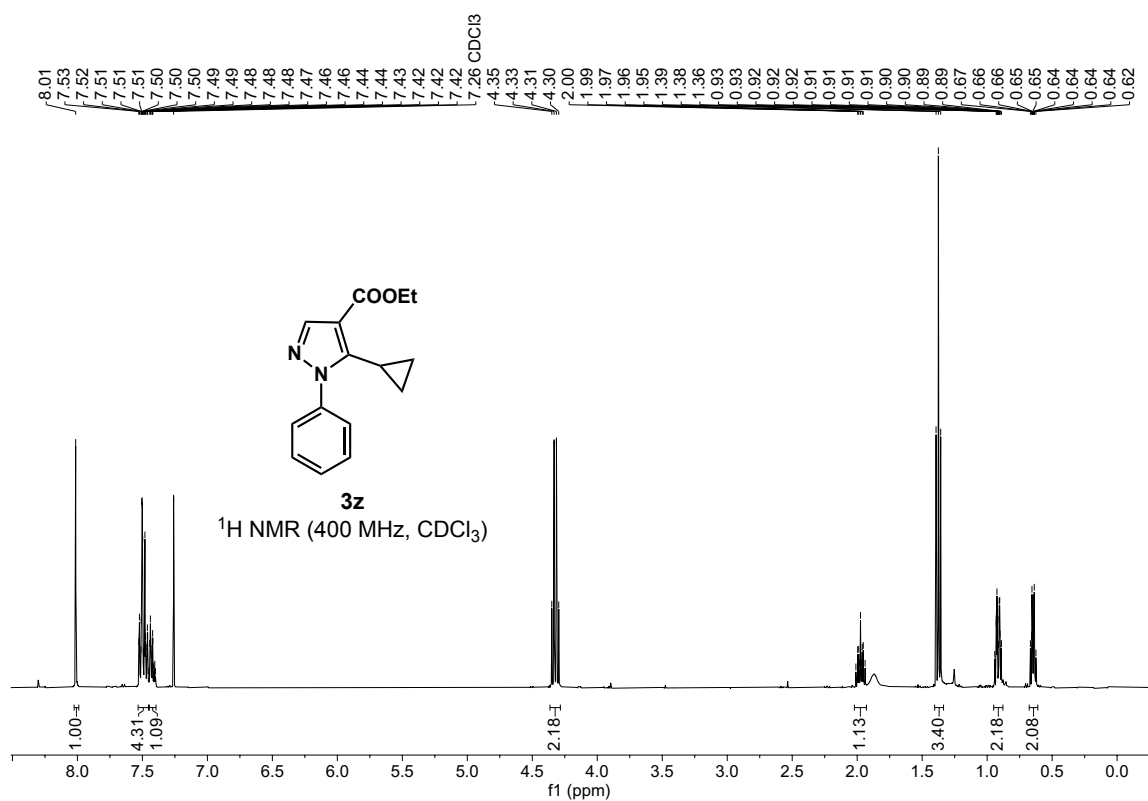


methyl 4-bromo-1-phenyl-1H-pyrazole-3-carboxylate (3y)

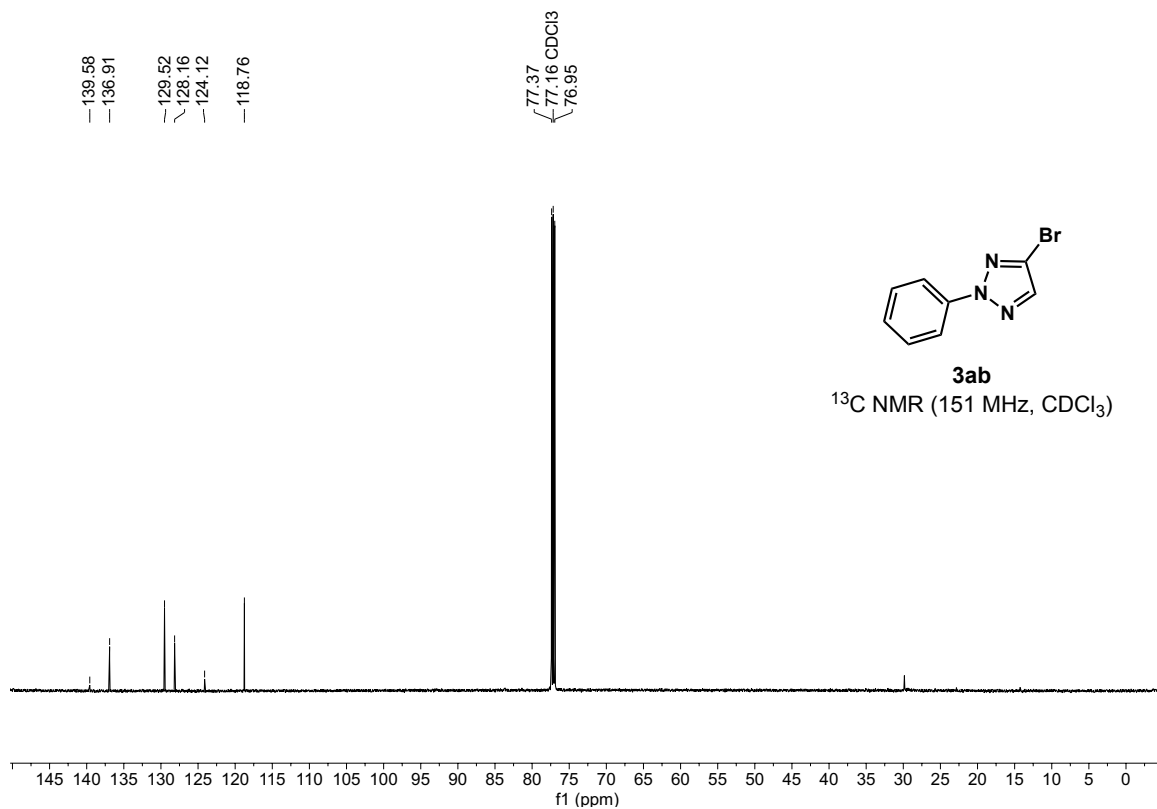
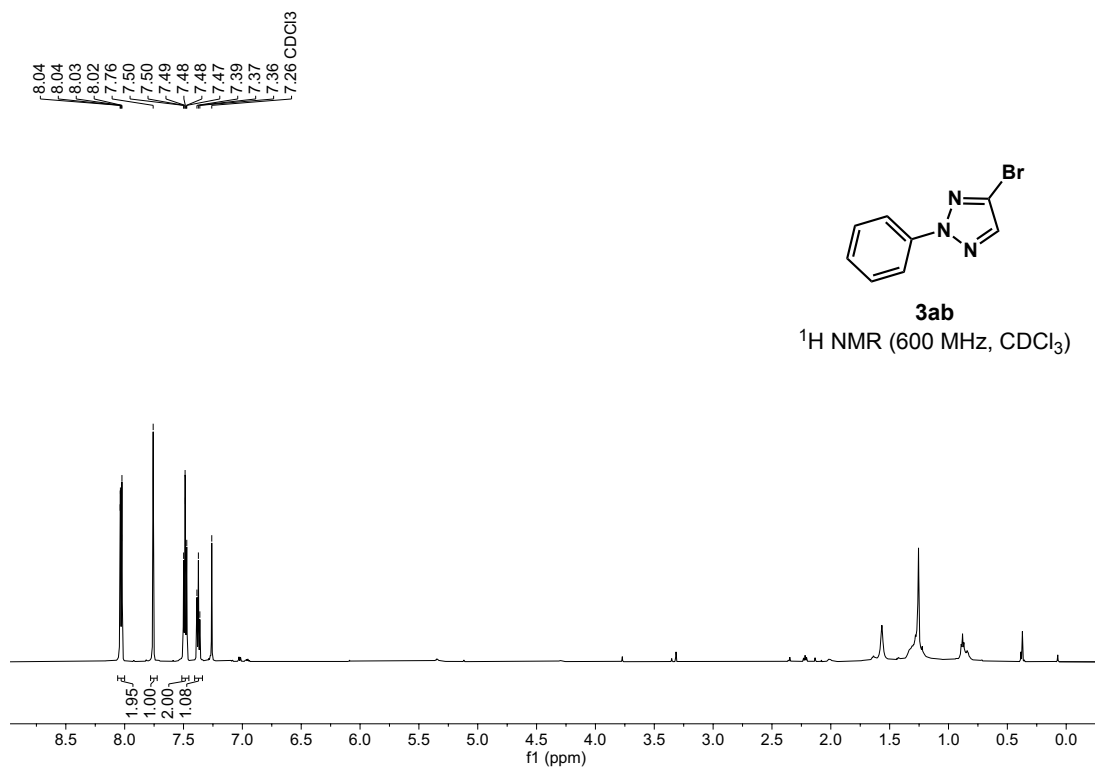




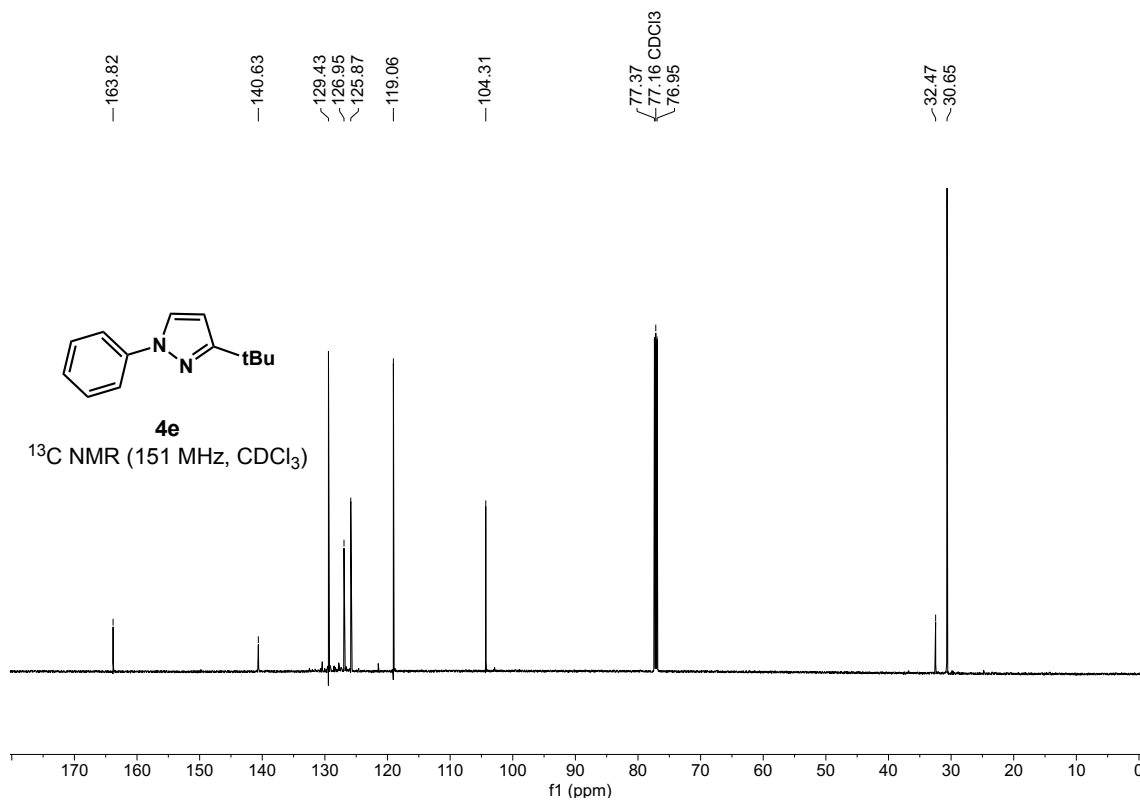
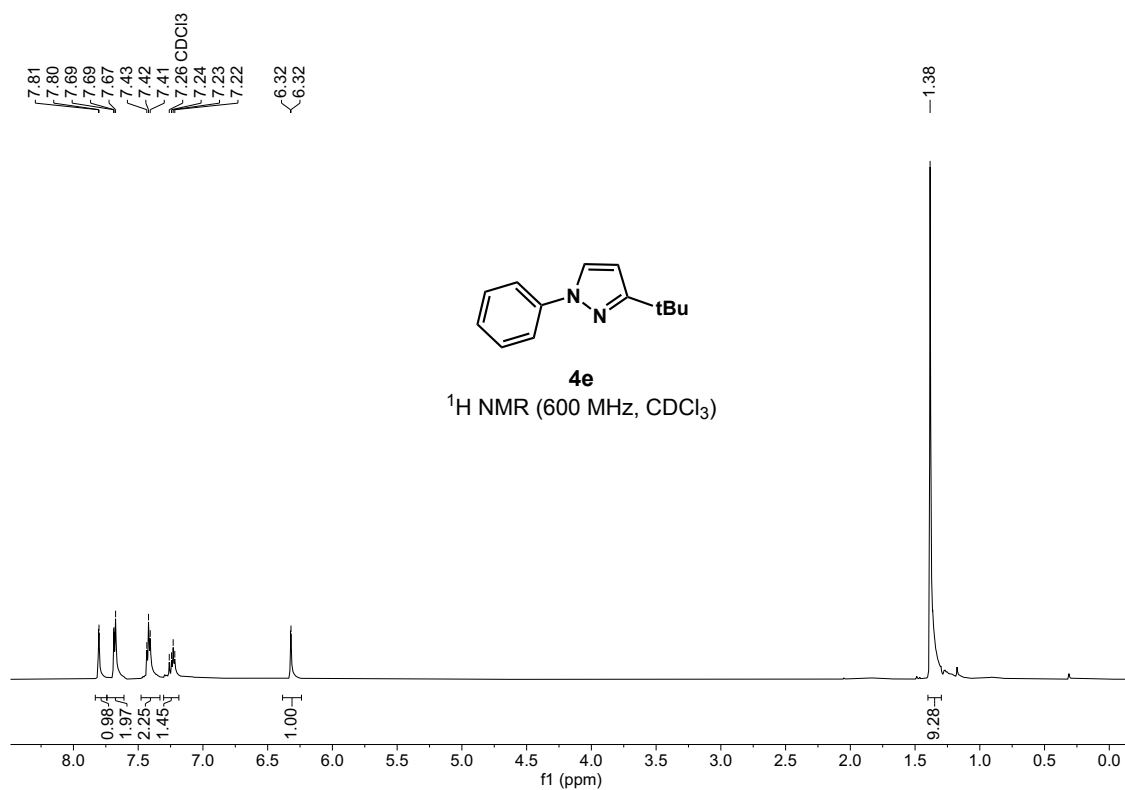
ethyl 5-cyclopropyl-1-phenyl-1H-pyrazole-4-carboxylate (3z)



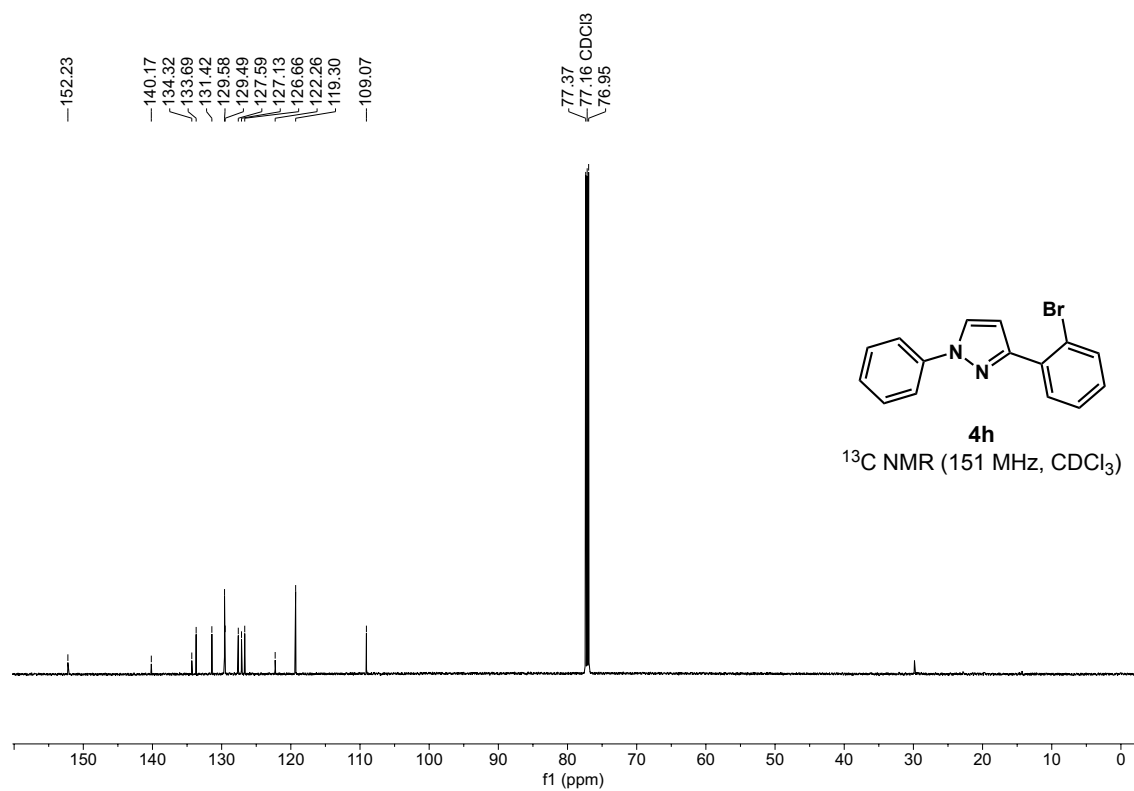
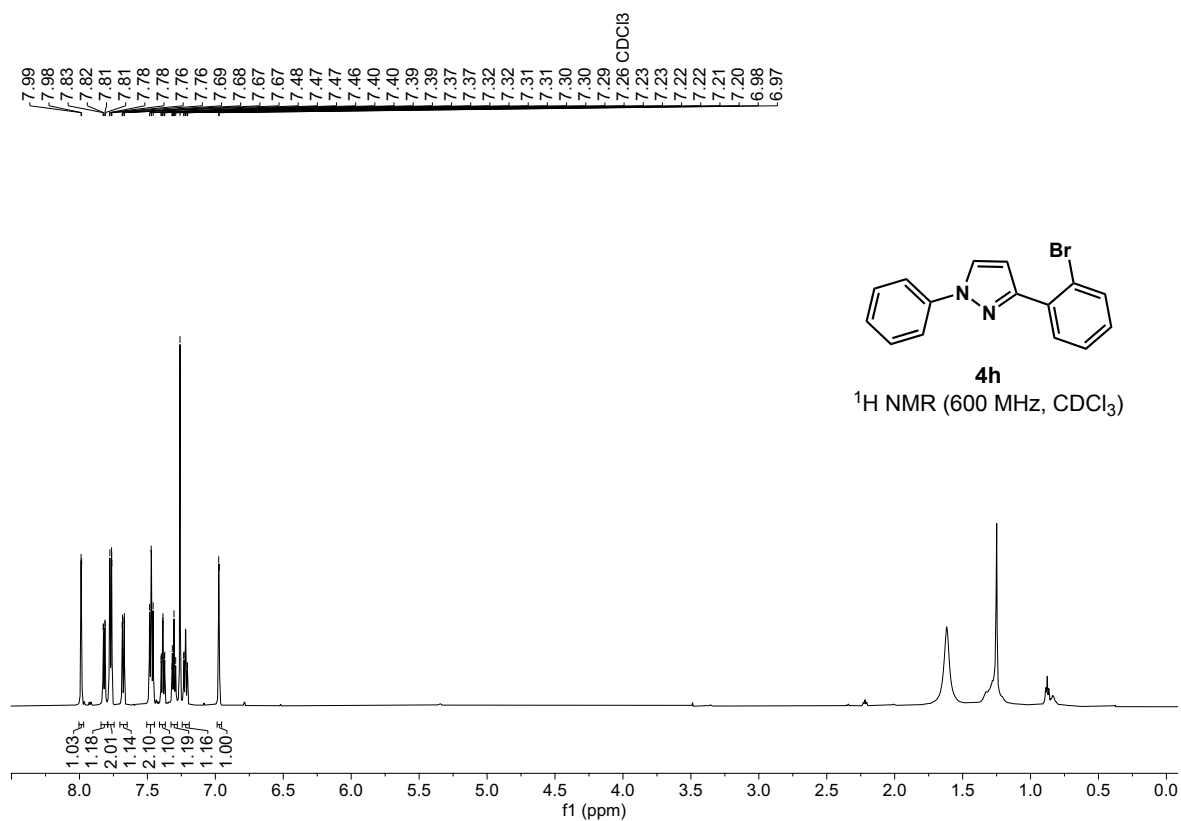
4-bromo-2-phenyl-2H-1,2,3-triazole (3ab)



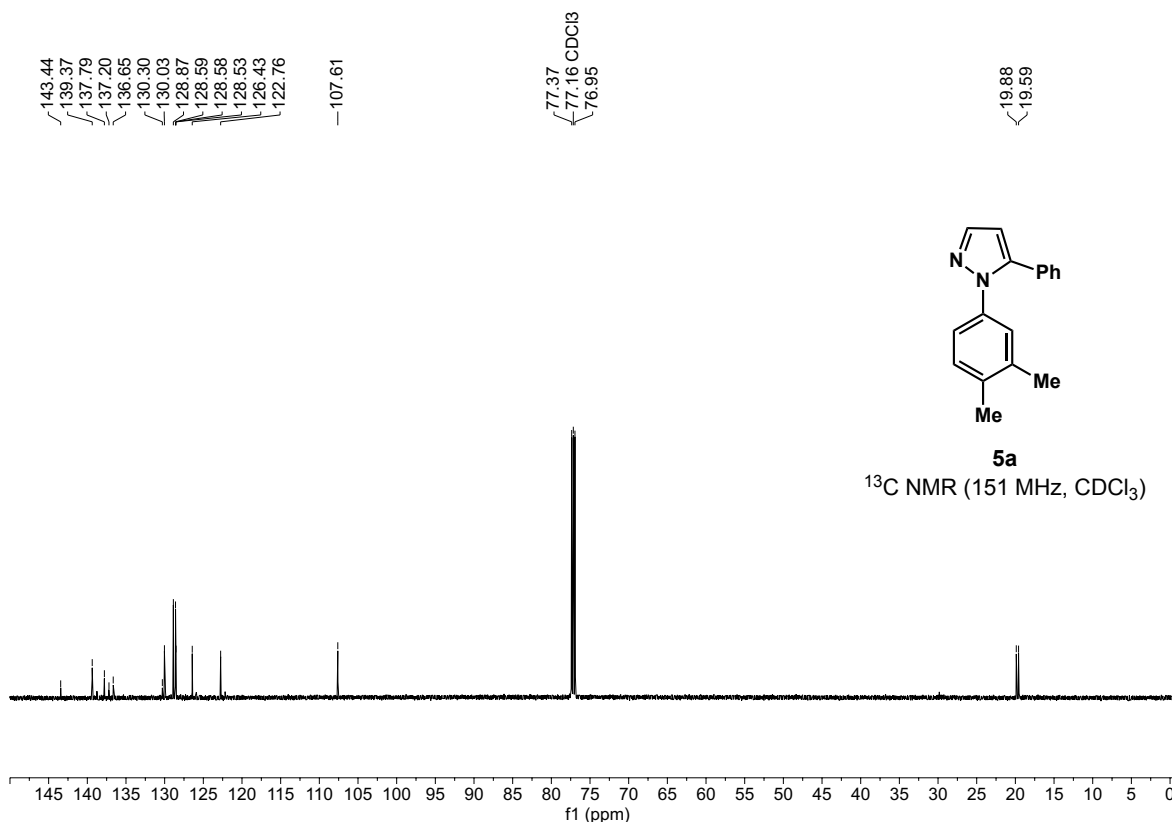
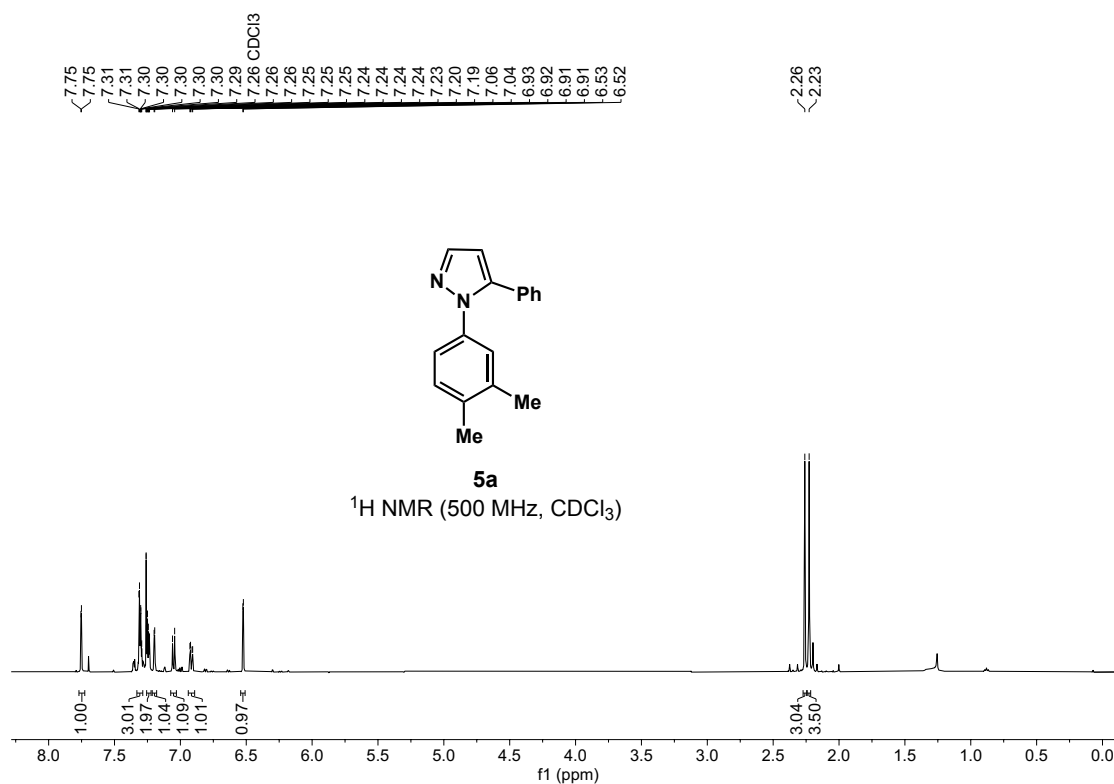
3-(tert-butyl)-1-phenyl-1H-pyrazole (4e)



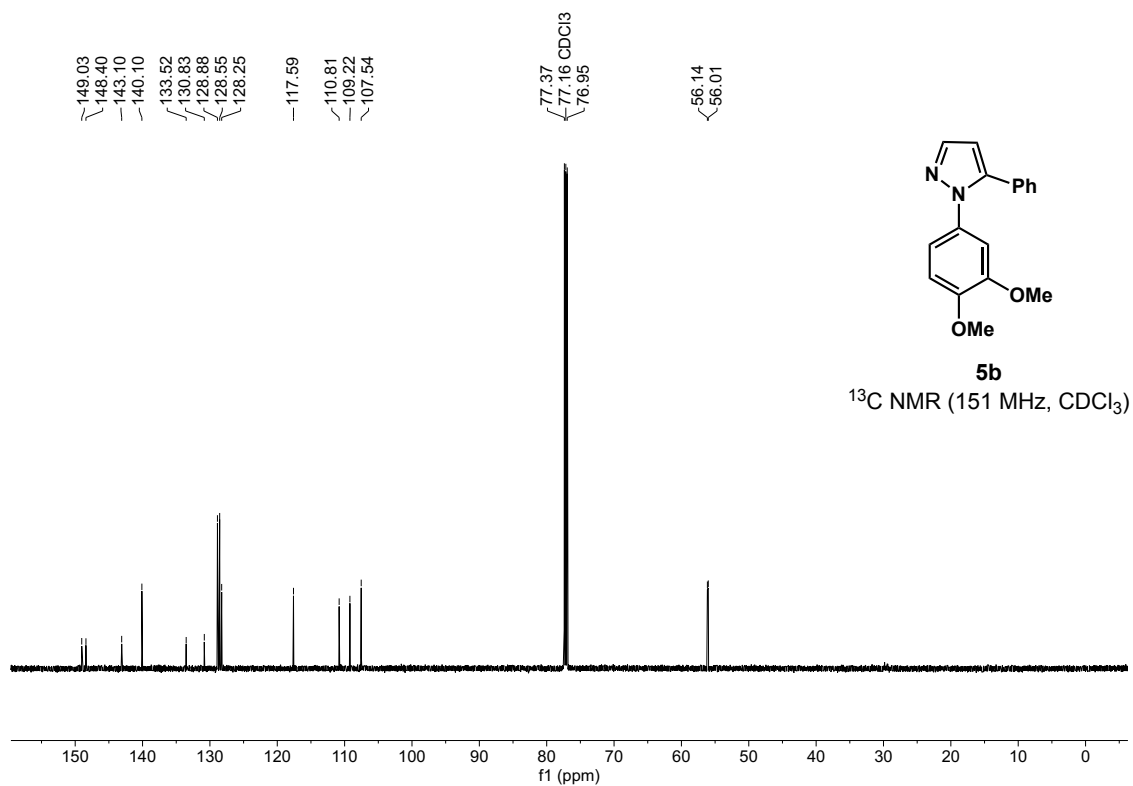
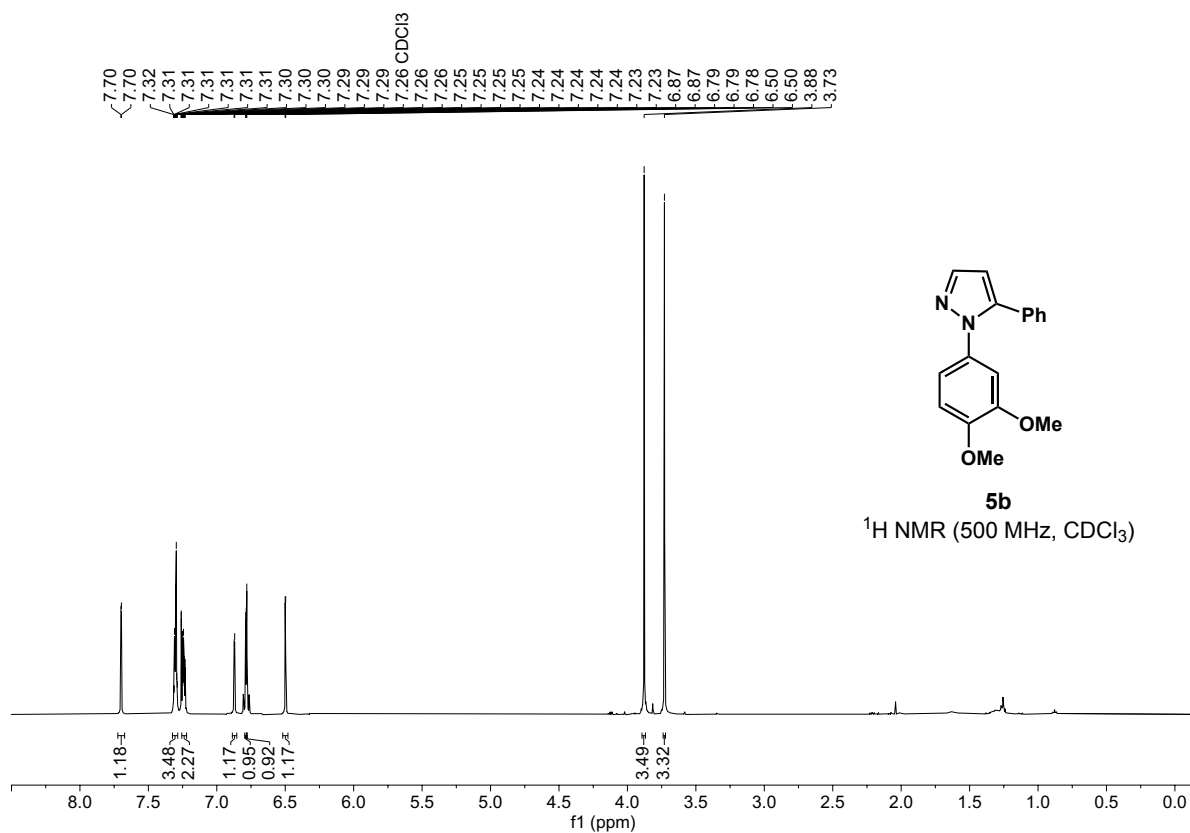
3-(2-bromophenyl)-1-phenyl-1H-pyrazole (4h)



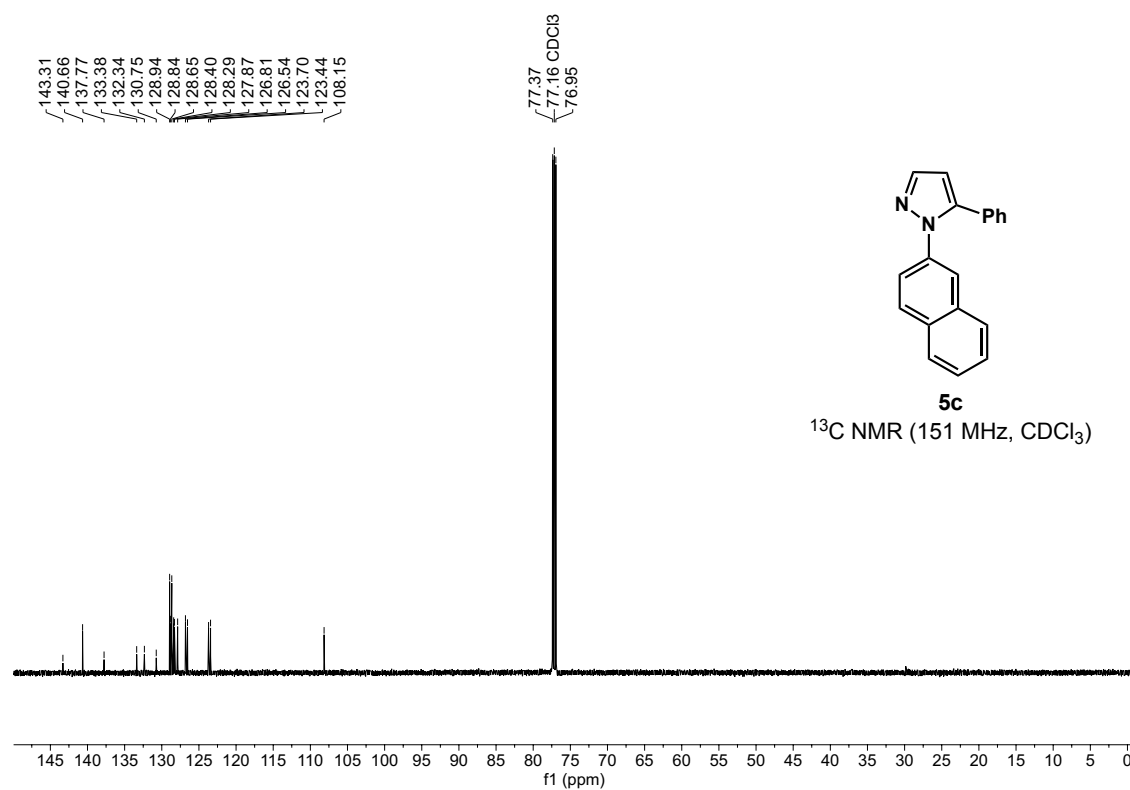
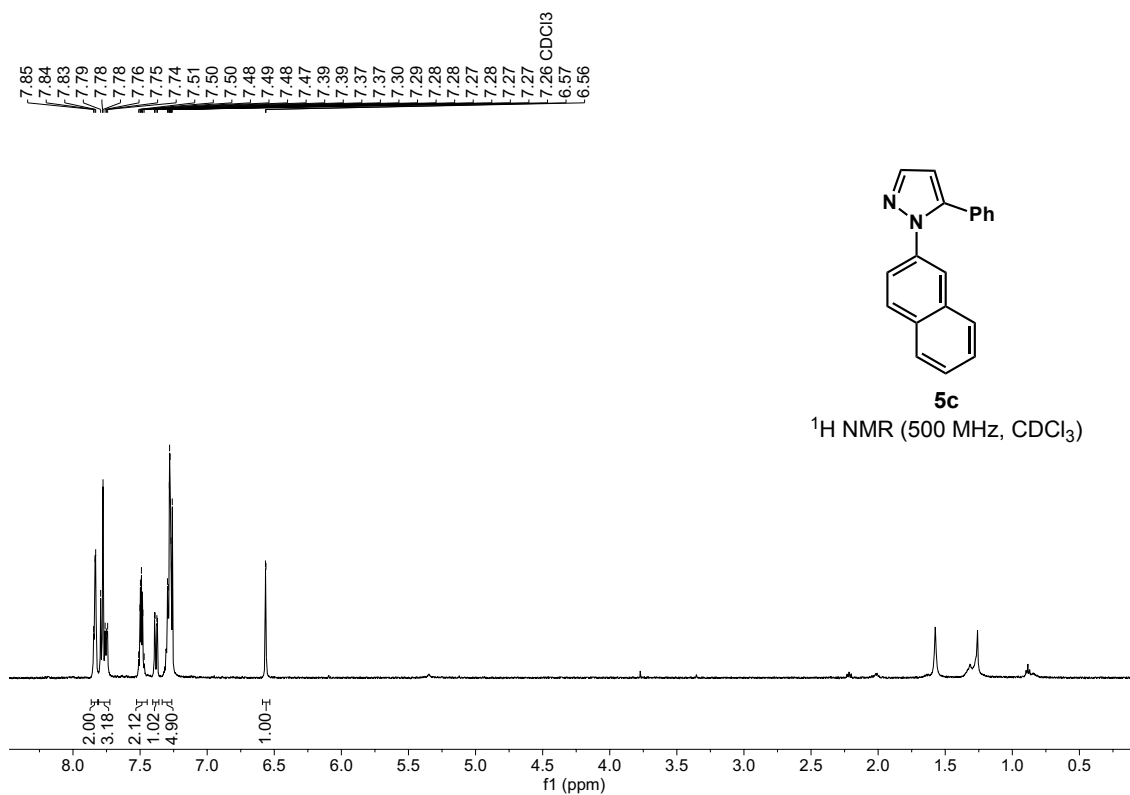
1-(3,4-dimethylphenyl)-5-phenyl-1H-pyrazole (5a)



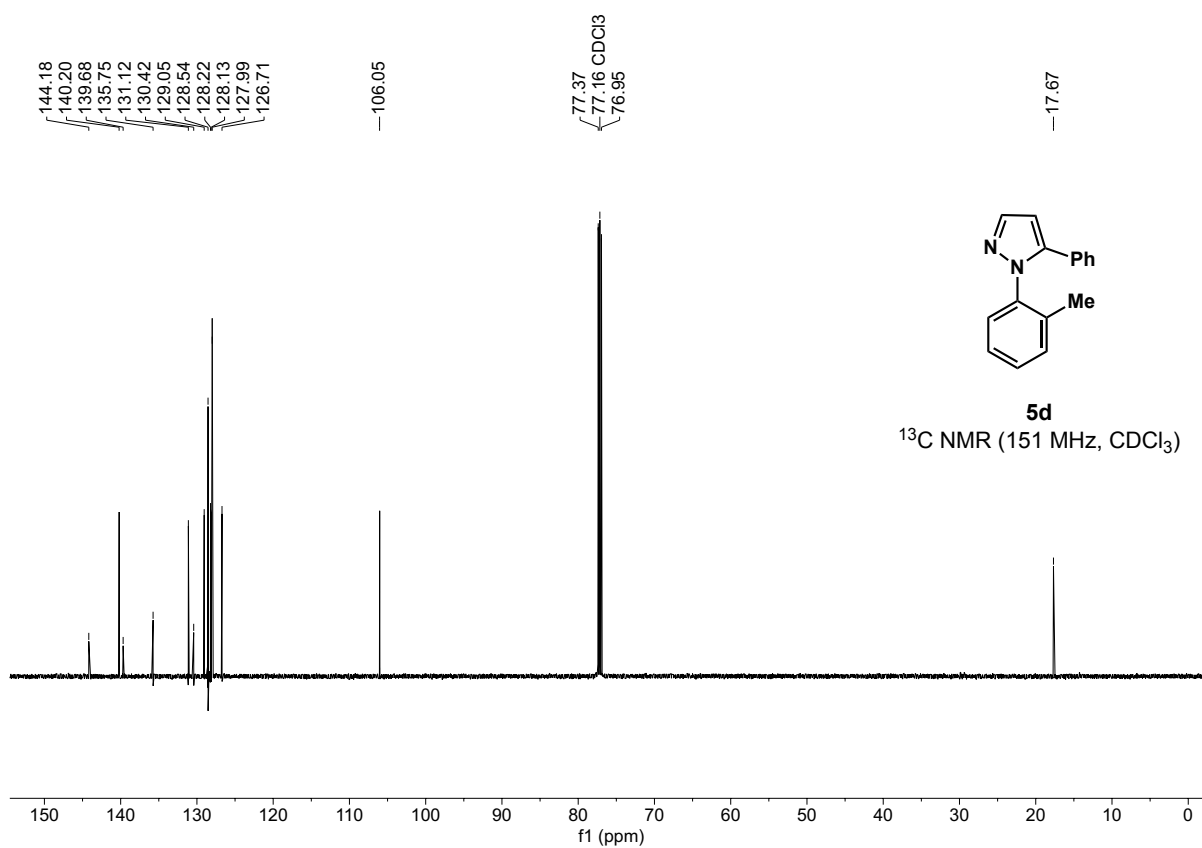
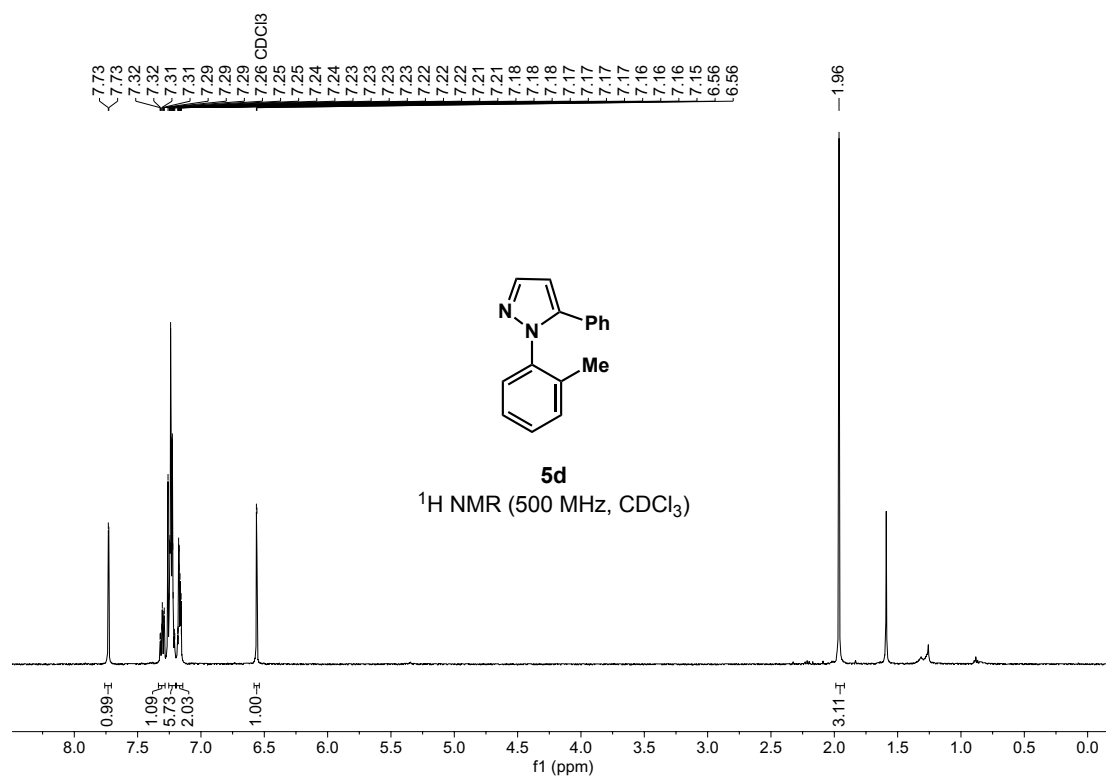
1-(3,4-dimethoxyphenyl)-5-phenyl-1H-pyrazole (5b)



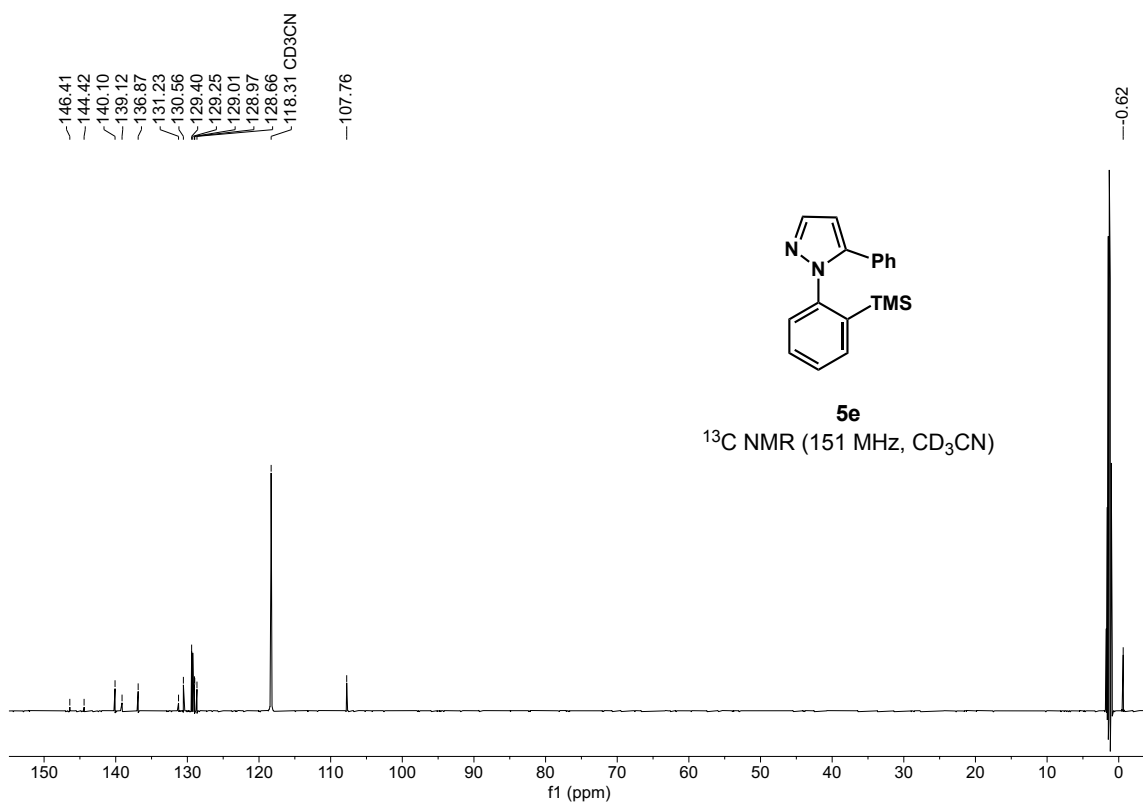
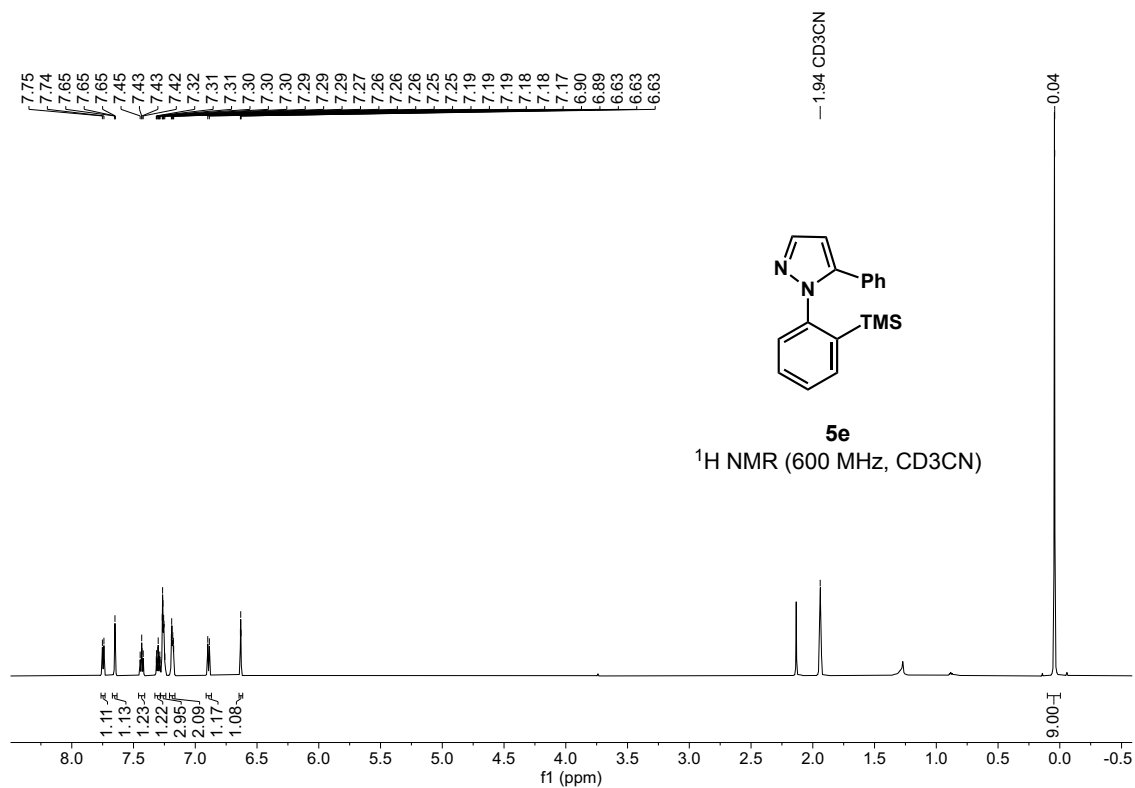
1-(naphthalen-2-yl)-5-phenyl-1H-pyrazole (5c)

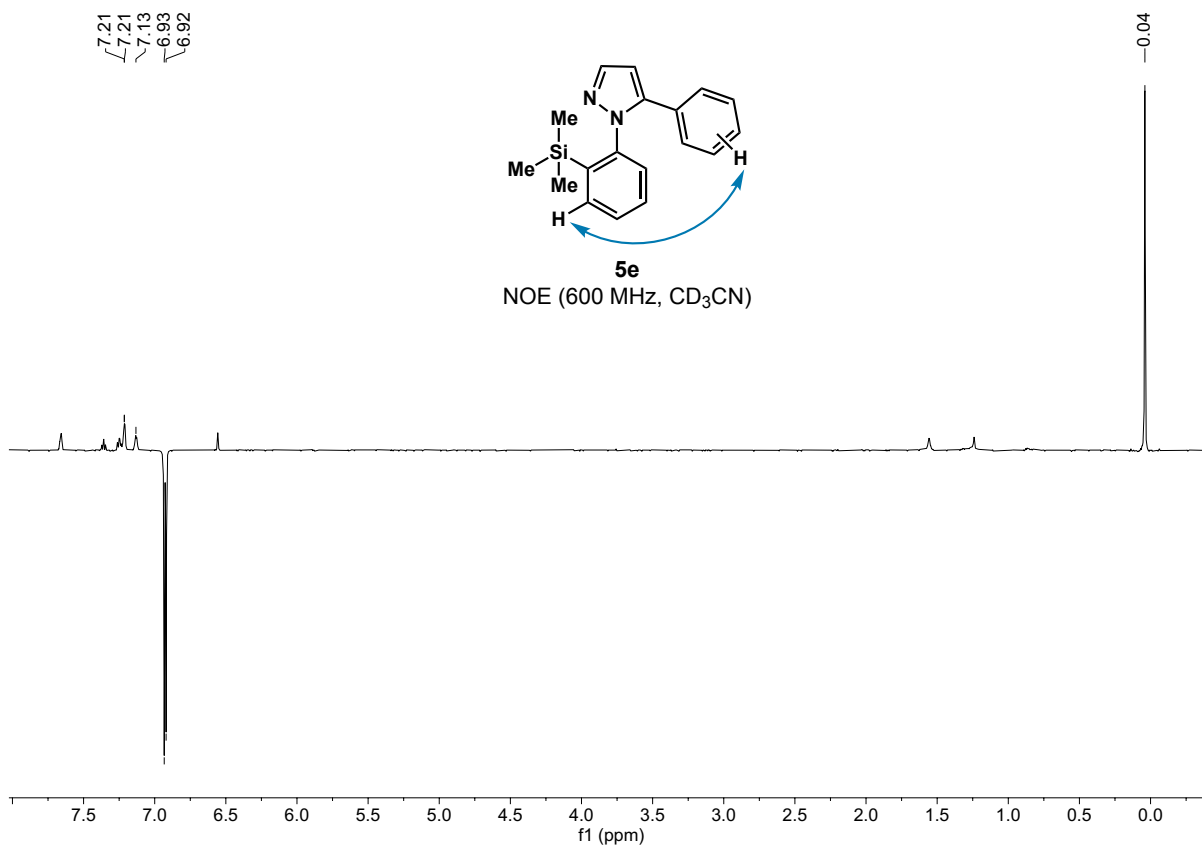


5-phenyl-1-(m-tolyl)-1H-pyrazole (5d)

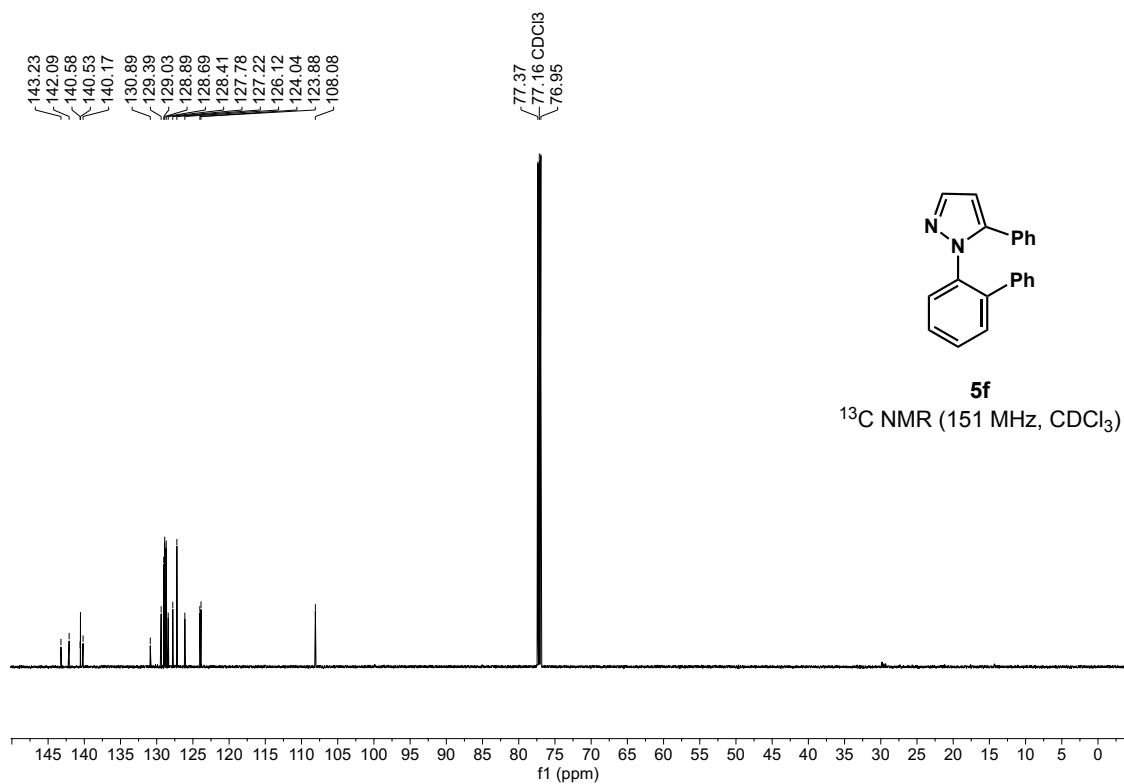
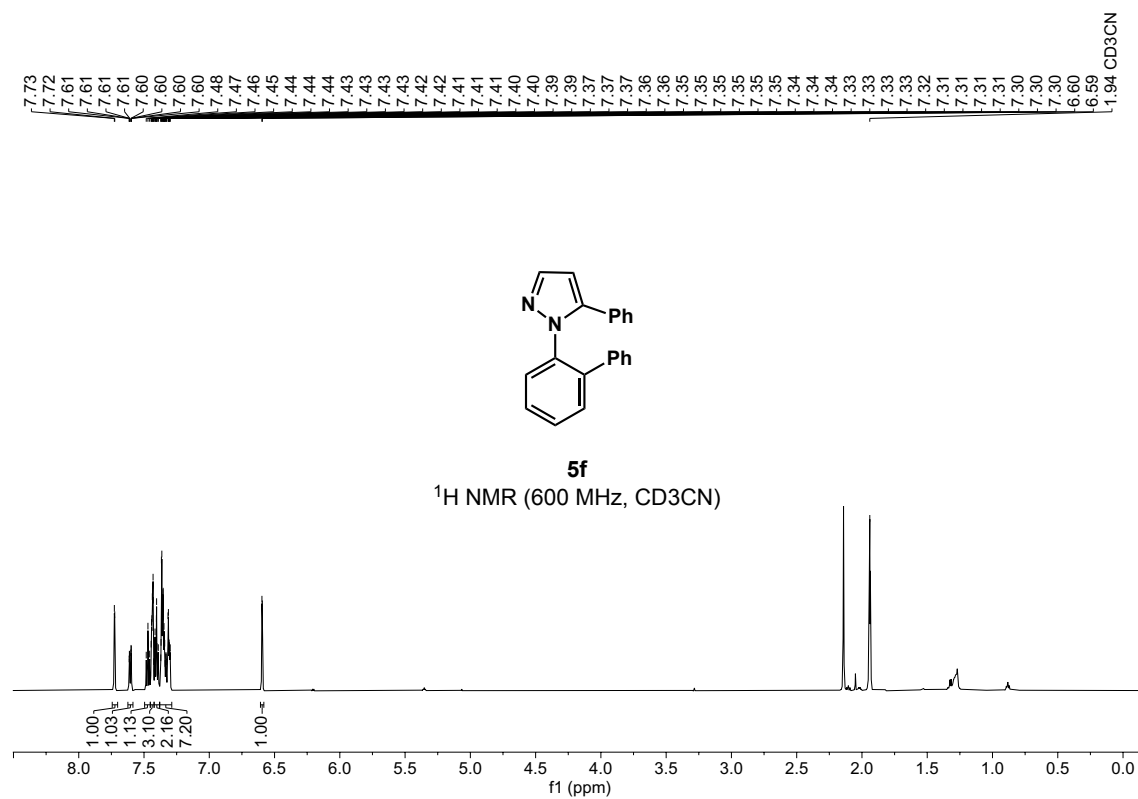


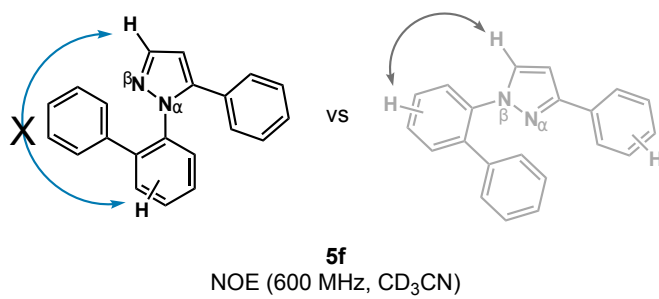
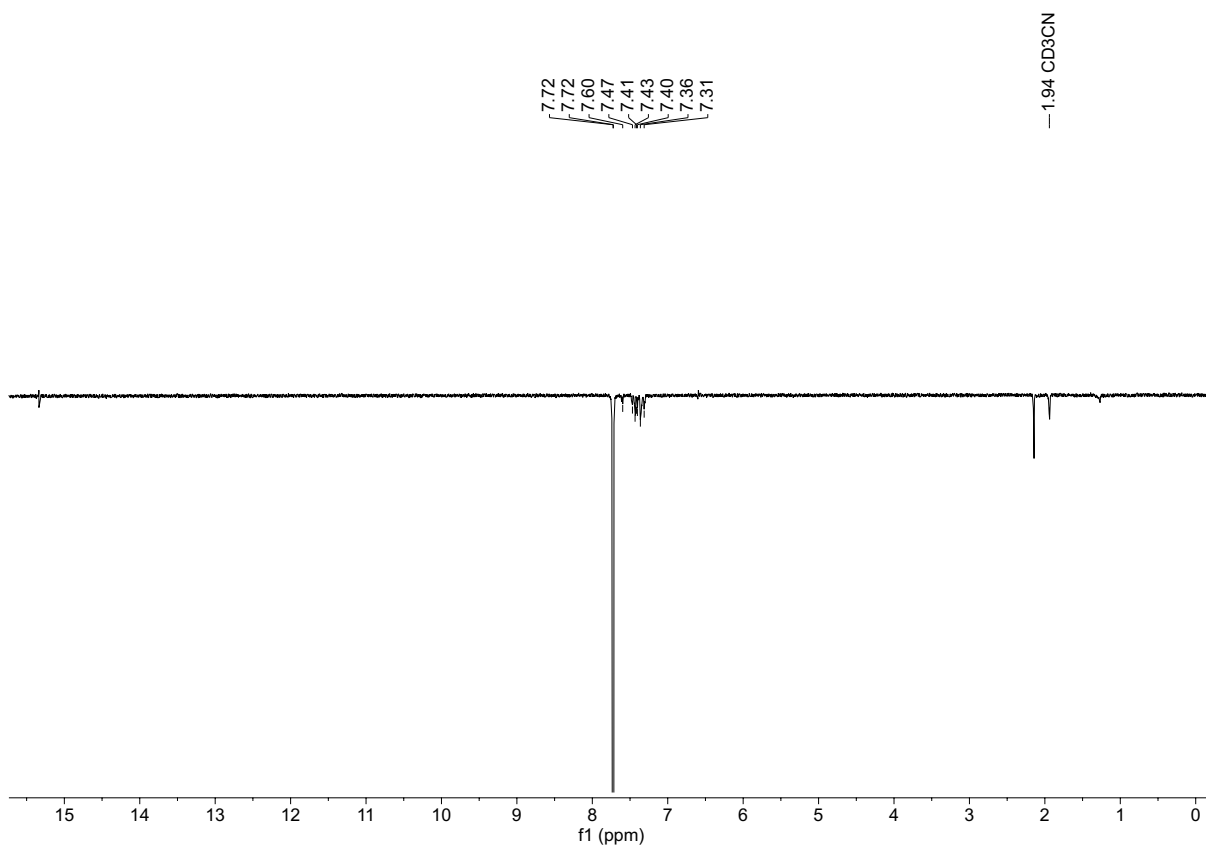
5-phenyl-1-(2-(trimethylsilyl)phenyl)-1H-pyrazole (5e)



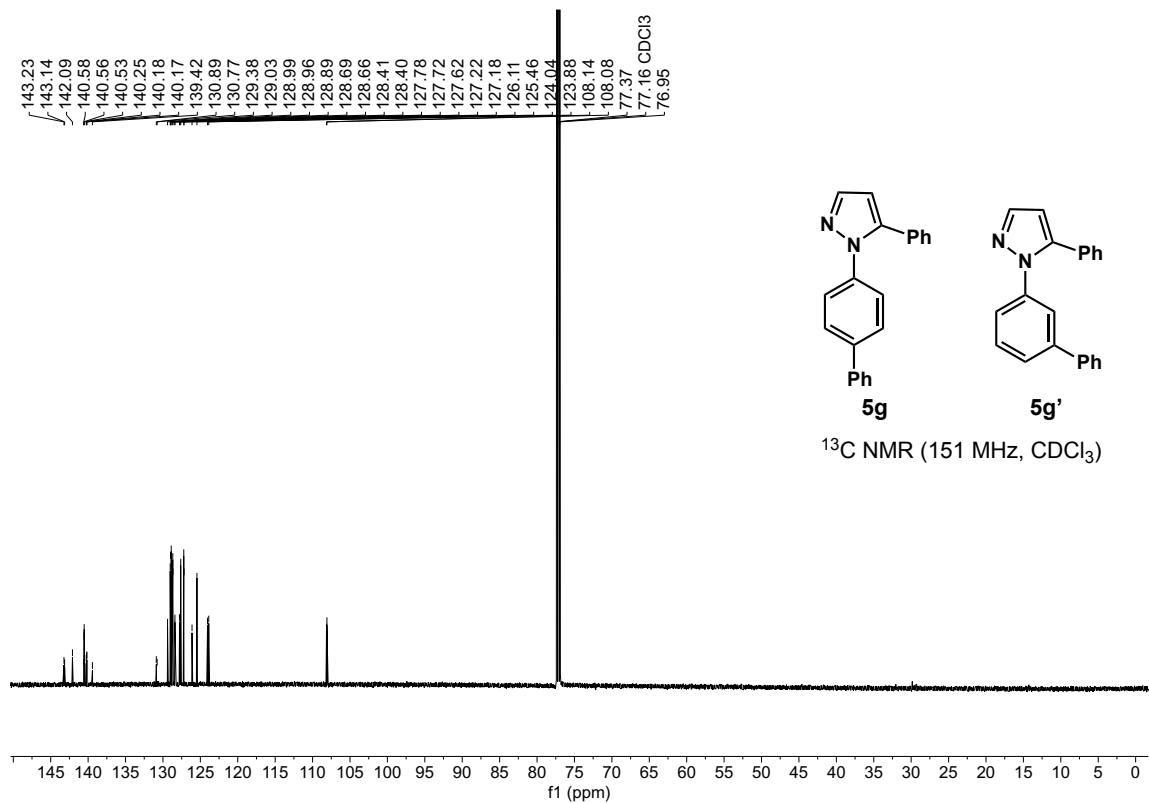
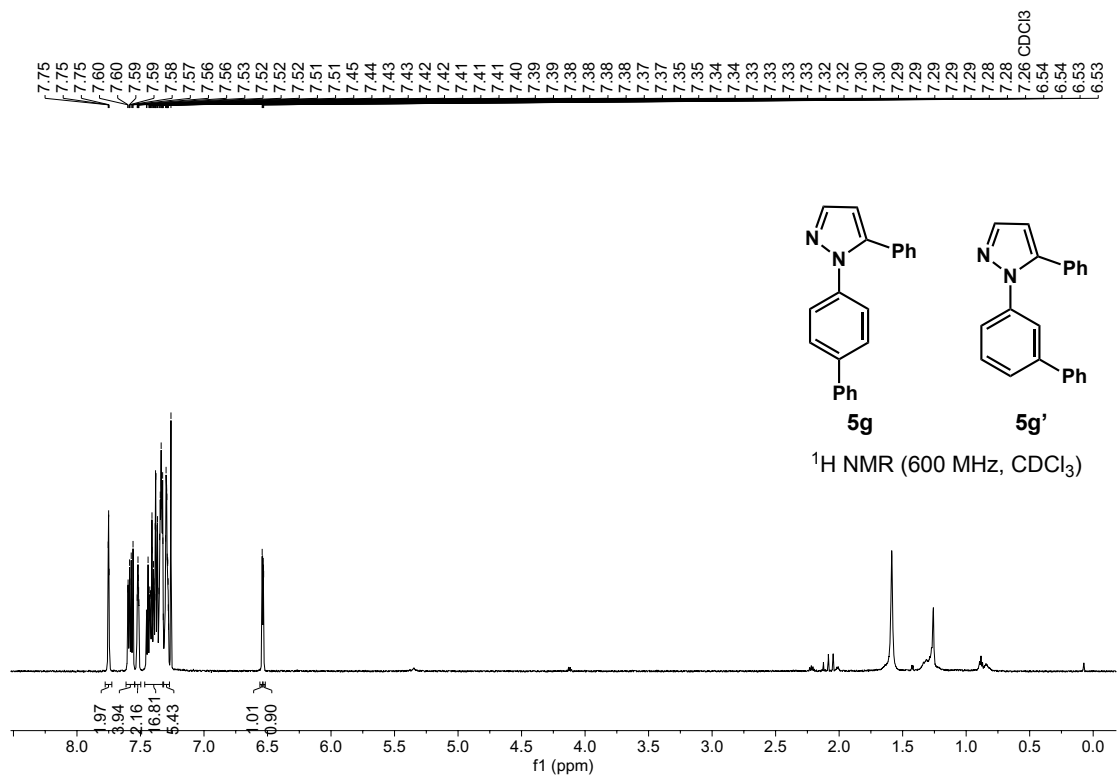


1-([1,1'-biphenyl]-2-yl)-5-phenyl-1H-pyrazole (5f)

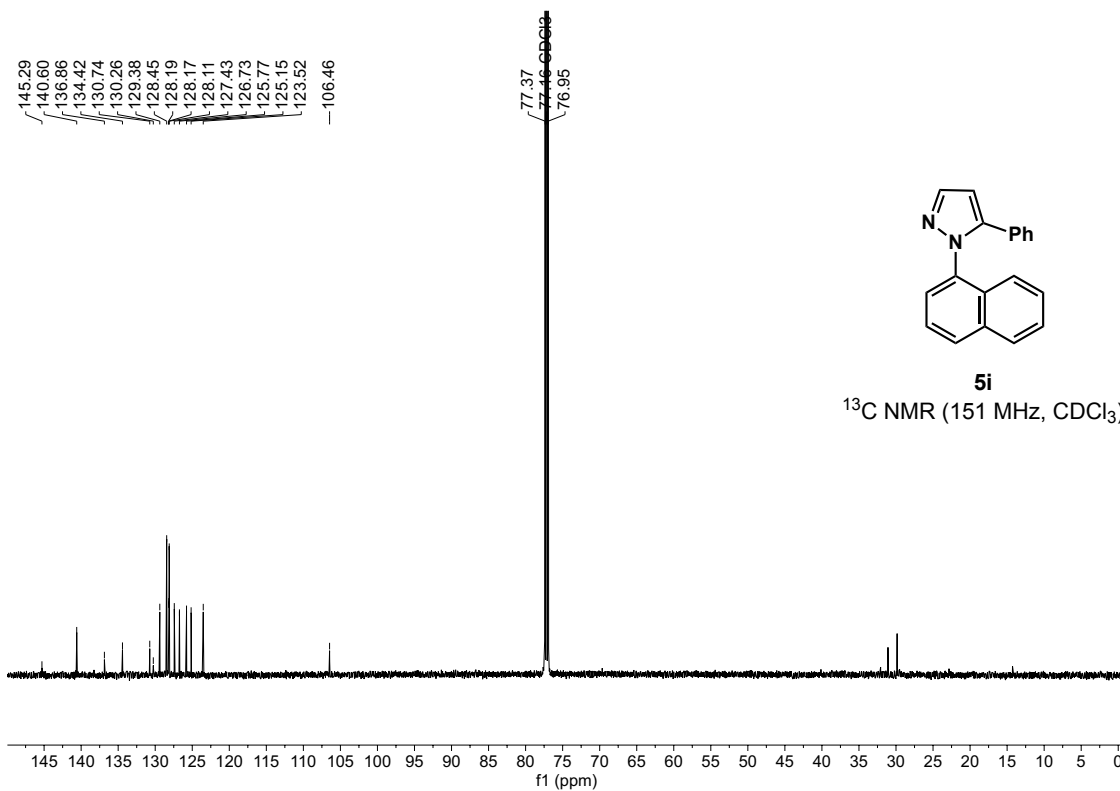
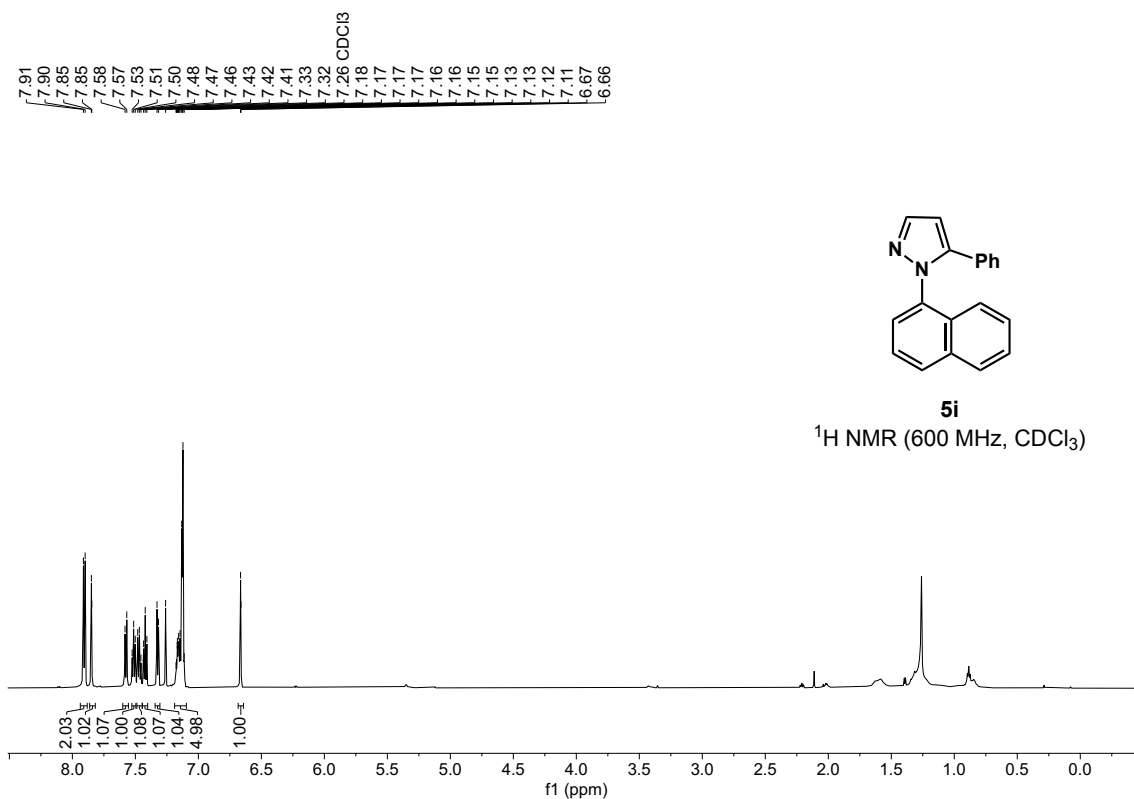




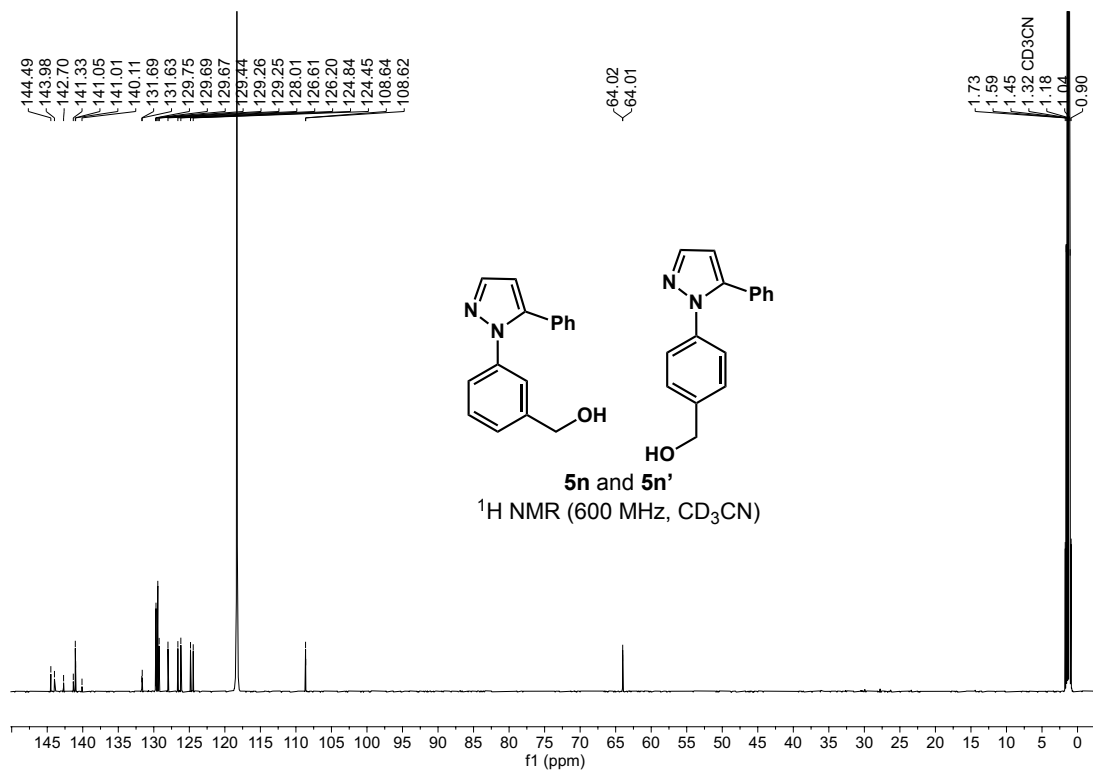
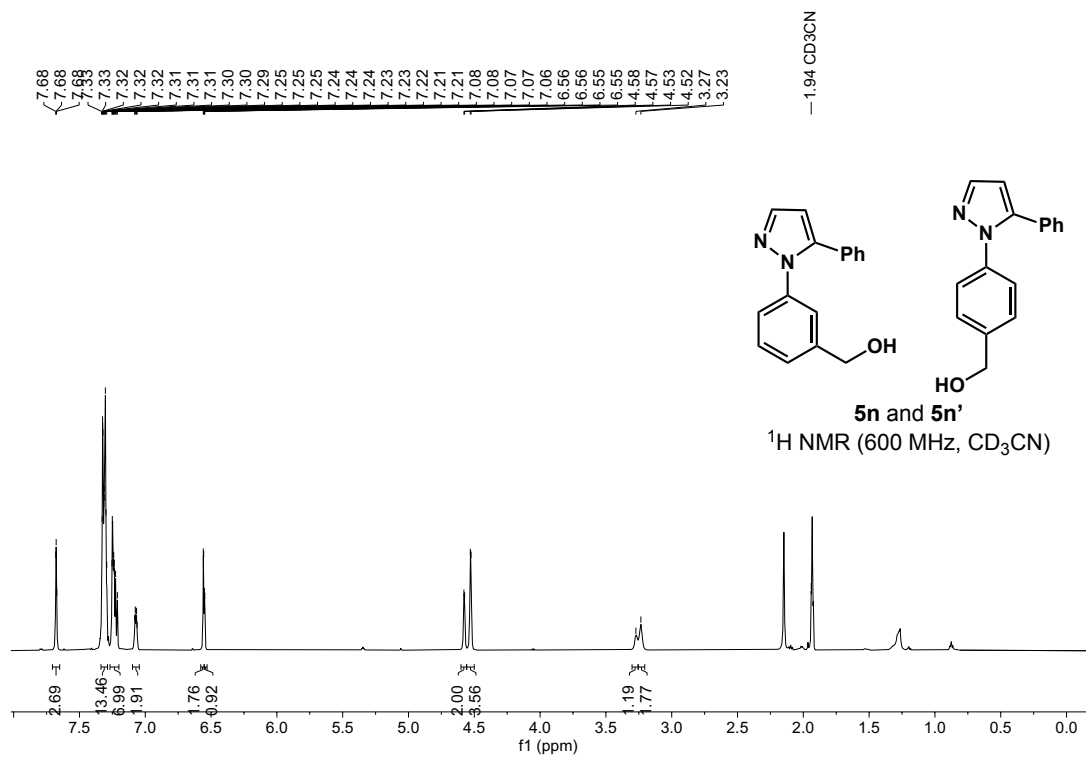
1-([1,1'-biphenyl]-4-yl)-5-phenyl-1H-pyrazole (5g) and 1-([1,1'-biphenyl]-3-yl)-5-phenyl-1H-pyrazole (5g')



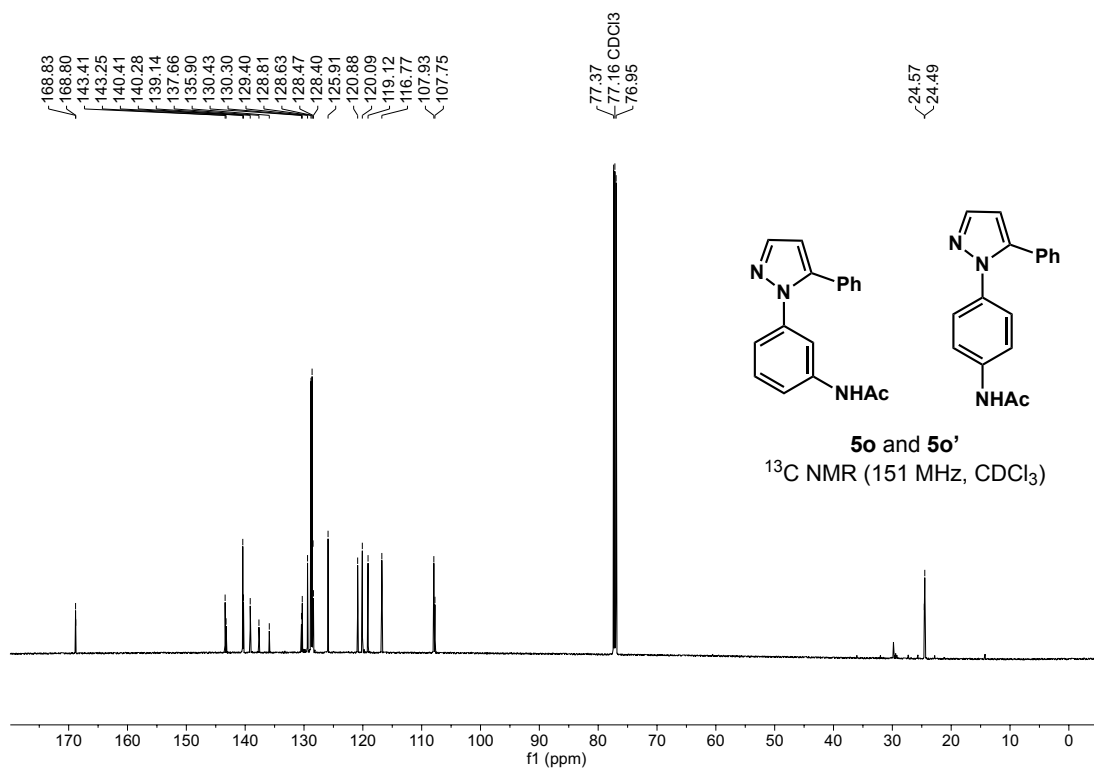
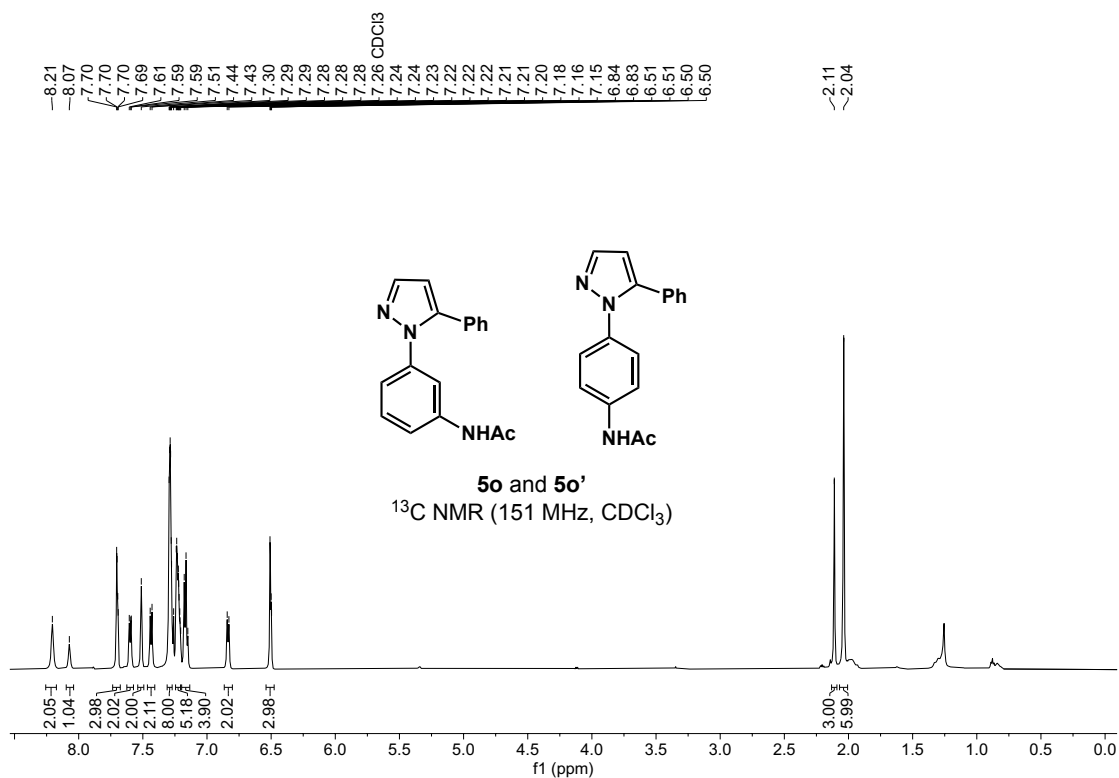
1-(naphthalen-1-yl)-5-phenyl-1H-pyrazole (5i)



(3-(5-phenyl-1H-pyrazol-1-yl)phenyl)methanol (5n) and (4-(3-phenyl-1H-pyrazol-1-yl)phenyl)methanol (5n')



N-(3-(3-phenyl-1H-pyrazol-1-yl)phenyl)acetamide (5o) and N-(4-(3-phenyl-1H-pyrazol-1-yl)phenyl)acetamide (5o')



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