Title

The Stereoselective Formation and Cleavage of C—F Bonds via Group 11 Catalysis

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The Stereoselective Formation and Cleavage of C-F Bonds via Group 11 Catalysis

By

Thomas Joseph O'Connor

A dissertation submitted in partial satisfaction of the

requirements for the degree of

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Chemistry

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University of California, Berkeley

Committee in charge:

Professor F. Dean Toste, Chair
Professor T. Don Tilley
Professor Joseph L. Napoli

Summer 2021

Abstract

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Doctor of Philosophy in Chemistry

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Professor F. Dean Toste, Chair

Chapter 1 – The gold(I)-catalyzed, stereoselective hydrofluorination of electron-deficient alkynes with triethylamine trihydrogen fluoride (Et3N·3HF) is described. Fluorinated *α,β*-unsaturated aldehydes, amides, esters, ketones, and nitriles were isolated in moderate to good yields as single diastereomers. In all but four cases, the (*Z*)-vinyl fluorides were initially formed in ≥97% diastereoselectivity. This work constitutes the first catalytic example of the diastereoselective preparation of a variety of *β*-alkyl, *β*-fluoro Michael acceptors from alkynes. Additionally, the described work expands access to *β*-aryl, *β*-fluoro Michael acceptors to the synthesis of *β*-fluoro-*α,β*-unsaturated amides and nitriles. The monofluoroalkenes formed through this strategy were readily transformed into other fluorine-containing compounds, and the developed method was applied to the synthesis of a fluorinated analogue of Exoderil, a topical antimycotic.

Chapter 2 – The copper-catalyzed silylation of propargylic difluorides to generate axially chiral, tetrasubstituted, monofluoroallenes in both good yields (24 examples >80%) and enantioselectivities (82–98% *ee*). Compared to previously reported synthetic routes to axially chiral allenes (ACAs) from prochiral substrates, a mechanistically distinct reaction has been developed: the enantiodiscrimination between enantiotopic fluorides to set an axial stereocenter. DFT calculations and vibrational circular dichroism (VCD) suggest that *β*-fluoride elimination from an alkenyl copper intermediate likely proceeds through a *syn*-*β*-fluoride elimination pathway rather than an anti-elimination pathway. The effects of the C1-symmetric Josiphos-derived ligand on reactivity and enantioselectivity were investigated. Not only does this report showcase that alkenyl copper species—like their alkyl counterparts—can undergo *β*-fluoride elimination, but that this elimination can be achieved in an enantioselective fashion. The resulting monofluoroallenes were shown to undergo a copper-catalyzed desilylative acylation. A kinetic resolution was developed, generating propargyl fluorine-containing quaternary stereocenters. Current efforts are underway to better understand the system that aim to achieve dynamic kinetic resolution.

Acknowledgements

As I reflect back on my time at Berkeley, it makes me realize just how lucky I was to take part in this educational experience, which undoubtedly shaped the person who I am today. I am fortunate that I have been surrounded by supportive friends, family, and colleagues who have not only encouraged me but who have also have inspired me to be the best version of myself. The opportunities that they have provided me could never be paid back, only forward which I intend to do. The enjoyment and satisfaction I have gained from higher education is an opportunity every individual should have access to.

I would first like to thank my family for their love and support. My parents and my brother John have always kept me grounded, especially when I would get lost in the details of research, and reminded me that there is a world beyond the fume hood. As for my grandparents, who mean the world to me, your love and support was always uplifting. Nothing was more exciting than receiving a letter or box in the mail from my grandmother, who knew exactly what I needed before I did.

My time at Berkeley was made possible only because of my experiences and the people I met during my undergraduate career during my career at Vassar College. I could not have made it to Berkeley without the support and advice from everyone in the chemistry department, who I consider to be my extended family. Professor Stuart Belli, Professor Christopher Smart, and Professor Joseph Tanski enabled me to pursue my interests in research and taught me the responsibilities of a scientist. My two summer internships, at the University of Kansas with Professor Michael Clift and at the University of Berkeley in the lab of John Hartwig, were instrumental in shaping my research interests and allowed me to discover a field that I am truly passionate about. I could not imagine doing anything else for a living.

Dean has been the best Ph.D. advisor that I could have ever asked for and I am fortunate to have had the pleasure of working in his research group (family) the past five years. His ability to guide students to success in a plethora of research topics has always been inspiring. The intellectual freedom Dean grants his students is only one of the benefits working in his research groups entails. He has cultivated a group culture that is creative, collaborative, and supportive. Dean has allowed me to become an independent, creative scientist whose only limitation is my imagination. I never once felt like I could not pursue my own ideas, no matter how far-fetched or improbable that they seemed. My favorite saying from Dean, which I lived by, was "It is your Ph.D., make of it what you will."

The members of the Toste group made the past five years in California feel like home to me. Not only are they great scientists who you can chat with about research for hours, but they are also great people. There are too many to mention everyone, but I would like to give a shout-out to a few here. In particular I would to thank Cindy Hong, Edward Miller, Mari Morimoto, Stephen Bierschenk, Banruo Huang, Katie Chung, Mark Levin, Alec Christian, Spencer Scholz, Patti Zhang, Lillian Hale, Patrick Moon, René Rahimoff, Kacper Skakuj, Trandon Bender, Anna Wuttig, Alex Zhukhovitskiy, Steve Jacob, Ilia Kobylianskii, and Junqi Li for their support, friendship, and advice. Not only have I learned a great deal from all of you, but your friendship over the years has made my career at Berkeley truly special. You are all great people as well as brilliant scientists and I hope that we stay in touch. It was a pleasure having Edward and Mari as classmates. You two were with me from the beginning of this journey and I could not have asked for two better friends.

I will never forget the years that I have spent in Latimer Hall. This experience has made me grow as an individual and as a scientist. The saying "It takes a village to raise a child" holds true for graduate school: "It takes a research group to raise a scientist."

Also, I would like to give a shout-out to Hasan Celik for being the best NMR Facility director. I wish you all the best!

The Stereoselective Formation and Cleavage of C-F Bonds via Group 11 Catalysis

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Chapter 1

Gold-Catalyzed Hydrofluorination of Electron-Deficient Alkynes: Stereoselective Synthesis of β-Fluoro Michael Acceptors

Portions of this chapter have previously appeared in:

O'Connor, T.J.; Toste, F.D. *ACS Catal.* **2018**, 8, 5947–5951

1.1 Introduction

New routes towards the selective fluorination of small molecules have been targeted in recent years due to the differences in the physical and biological properties between fluorinated compounds and those of their non-fluorinated analogs.[1] For example, fluorinated small molecules serve as precursors to fluorinated polymers, such Teflon, and can be useful positron emission tomography (PET) markers. Incorporation of fluorine into pharmaceutical products is also an important application of fluorination chemistry.[2] In 2014, about 25% of all commercial drugs contained at least one C–F bond.[2b,3] A fluorinated motif of particular interest is the monofluoroalkene. Monofluoroalkenes are isosteric with peptide bonds, and several bioactive compounds containing this motif have been reported (Figure 1.1).[4]

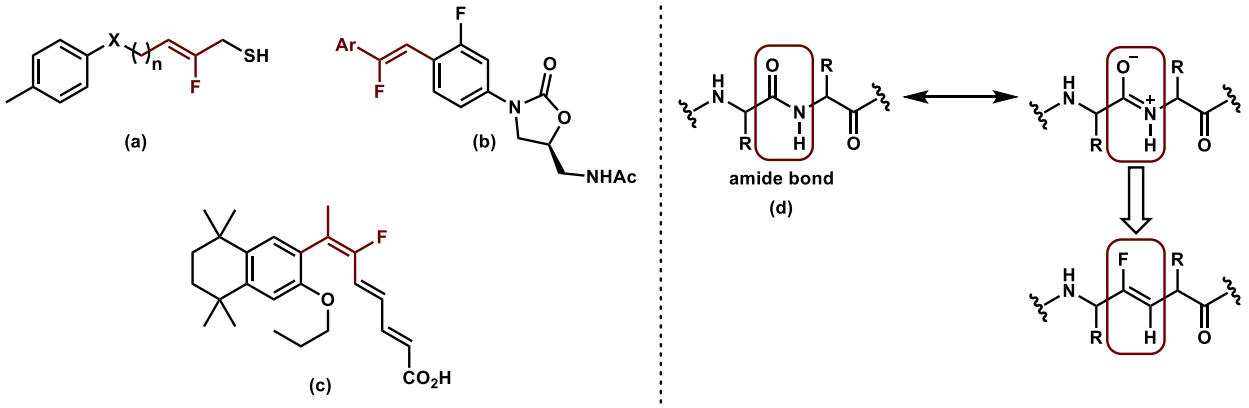


Figure 1.1. Selected examples of bioactive monofluoroalkenes. Monofluoroalkenes have found to be effective against both cancer (a) and type 2 diabetes (b). These molecules can also function as antimicrobial agents (c). The monofluoroalkene motif is seen as a peptide bond isostere (d).

A specific class of monofluoroalkenes of interest is *β*-fluoro Michael acceptors. Although several synthetic protocols exist to access *α*-fluoro, *α,β*-unsaturated carbonyl compounds—the Horner–Wadsworth–Emmons reaction[5], the Julia Olefination[6], the Peterson Olefination[7], and the Reformatsky reaction[8]—the stereoselective synthesis of *β*-fluoro, α,β-unsaturated carbonyl compounds has proven to be a challenge, especially if *β*-alkyl substituents are desired (Figure 1.2).[4b,9] Previous methods to access (*Z*)-*β*-fluoro-*α,β*-unsaturated carbonyl compounds are limited by the formation of products with low diastereoselectivities or yields,[10] the requirement for prefunctionalized starting materials,[11] and narrow functional group tolerance.[11b,11c,12] Because of these limitations, a stereoselective and functional group tolerant method to access (*Z*)-*β*-alkyl, *β*-fluoro-*α,β*-unsaturated carbonyl compounds would be highly desirable.

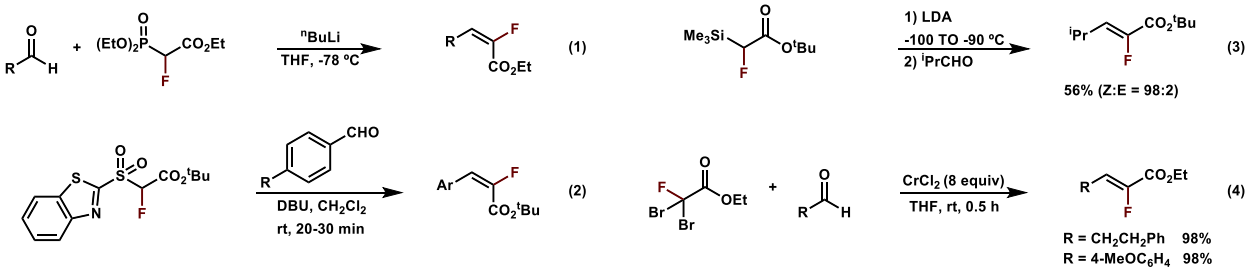


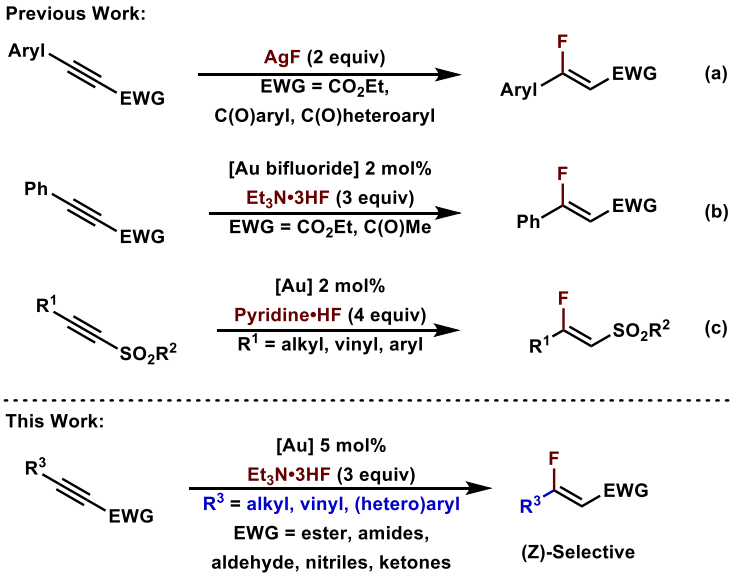
Figure 1.2 Stoichiometric routes to *α*-fluoro, *α,β*-unsaturated carbonyl compounds. Fluorinated precursors have

been utilized in the Horner–Wadsworth–Emmons reaction (1), Julia Olefination (2), Peterson Olefination (3), and Reformatsky reaction (4) to generate stereodefined monofluoroalkenes.

The hydrofluorination of electron-deficient alkynes is perhaps the most direct method to generate (*Z*)-*β*-fluoro *α,β*-unsaturated carbonyl compounds from commercially available starting materials. Although some electron-deficient alkynes can undergo hydrofluorination in the absence of a catalyst, the diastereoselectivities of these reactions are generally moderate, especially for *β*-alkyl substrates.[10a,10b,12] Traditional chromatographic techniques often fail to separate (*E*) and (*Z*) isomers of monofluoroalkenes; therefore, it is essential that the desired monofluoroalkenes are synthesized with high diastereomeric ratios.[13]

Since Sadighi's seminal report of the gold-catalyzed hydrofluorination of internal alkynes in 2007, other research groups have expanded the use of coinage metals for alkyne hydrofluorination.[14] Both Jiang, with excess AgF, (Scheme 1a) and Nolan, with a catalytic amount of gold, (Scheme 1b) prepared *β*-aryl, *β*-fluoro-*α,β*-unsaturated esters or ketones from electron deficient, unsymmetrical alkynes.[14c,14e] However, neither procedure reported the synthesis of *β*-alkyl, *β*-fluoro Michael acceptors or utilized alternative electron withdrawing groups such as nitriles or amides. Alternative conditions were described by Hammond and Xu for the gold-catalyzed hydrofluorination of alkynes with a new DMPU/HF fluorinating reagent, but this procedure did not expand access to (*Z*)-*β*-fluoro-*α,β*-unsaturated carbonyl compounds.[14d] The first gold-catalyzed synthesis of a *β*-alkyl-*β*-fluoro Michael acceptor was demonstrated by Hammond and Xu in 2017 (Scheme 1c).[14f]

Scheme 1.1. Generation of *β*-fluoro Michael acceptors from alkynes with coinage metals.



Although *β*-alkyl-*β*-fluorovinylsulfones could be accessed in a (*Z*)-selective manner, alkynes that did not bear a sulfonyl group—such as aroyl and phosphonyl—failed to undergo hydrofluorination. Despite these advances in alkyne hydrofluorination by coinage metals, a general procedure to synthesize

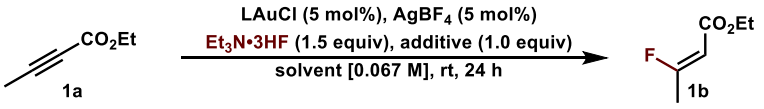
a variety of (*Z*)-*β*-alkyl, *β*-fluoro Michael acceptors from electron-deficient alkynes is still an unsolved challenge.

This chapter describes the development of a method to prepare a diverse array of *β*-alkyl, *β*-fluoro Michael acceptors from the gold-catalyzed hydrofluorination of electron-deficient alkynes. In addition to forming *β*-fluoro-*α*,*β*-unsaturated esters and ketones, this method is the first gold-catalyzed procedure to generate *β*-fluoro-*α*,*β*-unsaturated amides, nitriles, and aldehydes. A variety of *β*-alkyl as well as *β*-aryl substituents were tolerated; notably, 3° alkyl, alkenyl, and *o*-tolyl. Furthermore, this work demonstrates that the monofluoroalkene products are synthetically versatile fluorinated building blocks.

1.2 Results and Discussion

The hydrofluorination of ethyl 2-butynoate (**1a**) with $Et_3N{\bullet}3HF$ to form ethyl (*Z*)-3-fluorobut-2-enoate (**1b**) was selected as a model reaction. Monofluoroalkene **1b** formed in moderate yields and low stereoselectivities under conditions similar to those reported by Sadighi (see Table 1.1, entry 1).[14a] Reactions employing $AgBF_4$ as the silver salt afforded alkene **1b** in greater chemical yield compared to reactions conducted in the presence of other silver salts (entry 1 and 2, see the supporting information for further details). Upon switching from gold catalysts bearing NHC-ligands to gold catalysts bearing phosphine ligands, modest improvements in both yield and stereoselectivity were observed (entries 3 and 4). Unfortunately, reactions conducted with several triaryl or trialkyl phosphine gold(I) complexes as catalysts generated a purple hue after several hours in the presence of $Et_3N{\bullet}3HF$, which has been reported by others as a visual indication of catalyst decomposition.[15]

Table 1.1 Effect of the reaction conditions on the hydrofluorination of 1a.



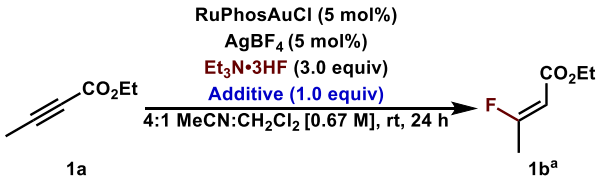
Entry	L	Solvent	Additive	Yield [%] (Z:E)[b]
1	IPr	CH_2Cl_2	$KHSO_4$	50 (66:34)
2[c]	IPr	CH_2Cl_2	$KHSO_4$	43 (70:30)
3	PPh_3	CH_2Cl_2	$KHSO_4$	55 (60:40)
4	PCy_3	CH_2Cl_2	$KHSO_4$	64 (75:25)
5	CyJohnPhos	CH_2Cl_2	$KHSO_4$	84 (55:45)
6	RuPhos	CH_2Cl_2	$KHSO_4$	57 (56:44)
7[d]	RuPhos	CH_2Cl_2	$KHSO_4$	62 (97:3)
8[d]	RuPhos	CH_2Cl_2	p-Cl BA[e]	66 (97:3)
9	RuPhos	CH_3CN	p-Cl BA	70 (97:3)
10	RuPhos	1:4 CH_2Cl_2:CH_3CN	p-Cl BA	76 (96:4)
11[f]	RuPhos	1:4 CH_2Cl_2:CH_3CN	p-Cl BA	71 (96:4)
12	RuPhos	1:4 CH_2Cl_2:CH_3CN	none	65 (96:4)
13[g]	RuPhos	1:4 CH_2Cl_2:CH_3CN	p-Cl BA	80 (96:4)

[a]General reaction conditions: 0.2 mmol **1a**, plastic vial. [b]Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard. [c]5 mol% $AgSBF_6$ [d]4 h. [e]*p*-chlorobenzoic acid. [f]10 mol% *p*-Cl BA. [g]3.0 equiv $Et_3N{\bullet}3HF$.

Cationic-gold(I) complexes with dialkylbiarylphosphine ligands are known to be more stable towards decomposition pathways than cationic gold(I) complexes triaryl or trialkyl phosphines.[16] Upon switching the gold catalyst to CyJohnPhosAuCl, monofluoroalkene **1b** was generated in 84% yield. However, the stereoselectivity of the reaction conducted with CyJohnPhosAuCl decreased relative to the stereoselectivity of the reaction conducted with Cy_3PAuCl as the catalyst (entry 3 and 4). Examination of a variety of dialkylbiaryl phosphinegold(I) complexes revealed that only reactions with RuPhos as the ligand afforded the greatest *Z:E* selectivity of **1b** (entries 6 and 7). For instance, in the presence of CyJohnPhos the yield of **1b** after 4 hours was 85% but with a *Z:E* of 77:23.

In addition to the ligand effect on the reaction, both the solvent and additive were found to influence the yield and stereoselectivity of the hydrofluorination of alkynoate **1a**. Switching from potassium bisulfate to *p*-chlorobenzoic acid (*p*-Cl BA), a more soluble acid co-additive, resulted in a modest improvement in the yield of monofluoroalkene **1b** (entry 8). Reactions conducted with RuPhosAuCl and CH_3CN as the solvent afforded the hydrofluorination product in a further improved yield while maintaining the *Z*-selectivity observed at shorter reaction times (entry 8 and 9). The change in solvent also ensured that the *Z*:*E* ratio did not decrease over time, permitting easier reaction monitoring as alkene isomerization was largely suppressed. Ultimately, reactions conducted in a solvent mixture of CH_3CN:CH_2Cl_2 maintained the high stereoselectivity of the hydrofluorination of alkyne **1a** while affording alkene **1b** in an improved yield (entry 9 and 10). The beneficial improvement in the yield of **1b** was observed with as little as 10 mol% *p*-Cl BA (entry 11 and 12). Other acid additives were examined, but benzoic acid derivatives appeared to provide an optimal pKa range (Table 1.2). Increasing the equivalents of $Et_3N{\bullet}3HF$ did not have a significant influence on the reaction (Table 1.1, entry 13); however, reactions with $Et_3N{\bullet}2HF$, $Et_3N{\bullet}HF$, and pyridine•HF (70% HF) failed to generate alkene **1b** (Table 1.3).

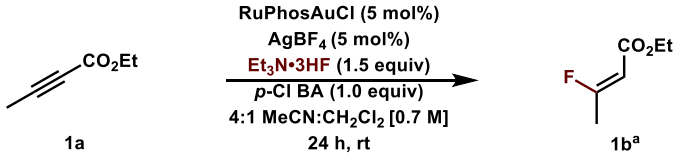
Table 1.2 Effect of acid additive on the hydrofluorination of 1a.



Entry	Additive	Yield [%] (Z:E)[b]
1	p-CN benzoic acid	48 (>98:2)
2	p-Cl benzoic acid	80 (96:4)
3	benzoic acid	62 (97:3)
4	p-Et benzoic acid	71 (97:3)
5	p-OMe benzoic acid	73 (97:3)
6	TsOH	65 (97:3)
7	Cl_3CCO_2H	31 (>98:2)
8	$HNTf_2$	34 (>98:2)

[a]General reaction conditions: 0.2 mmol **1a**, plastic vial. [b]Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard.

Table 1.3 Effect of reaction vessel, HF source and temperature on the hydrofluorination of 1a.



1a 1b[a]

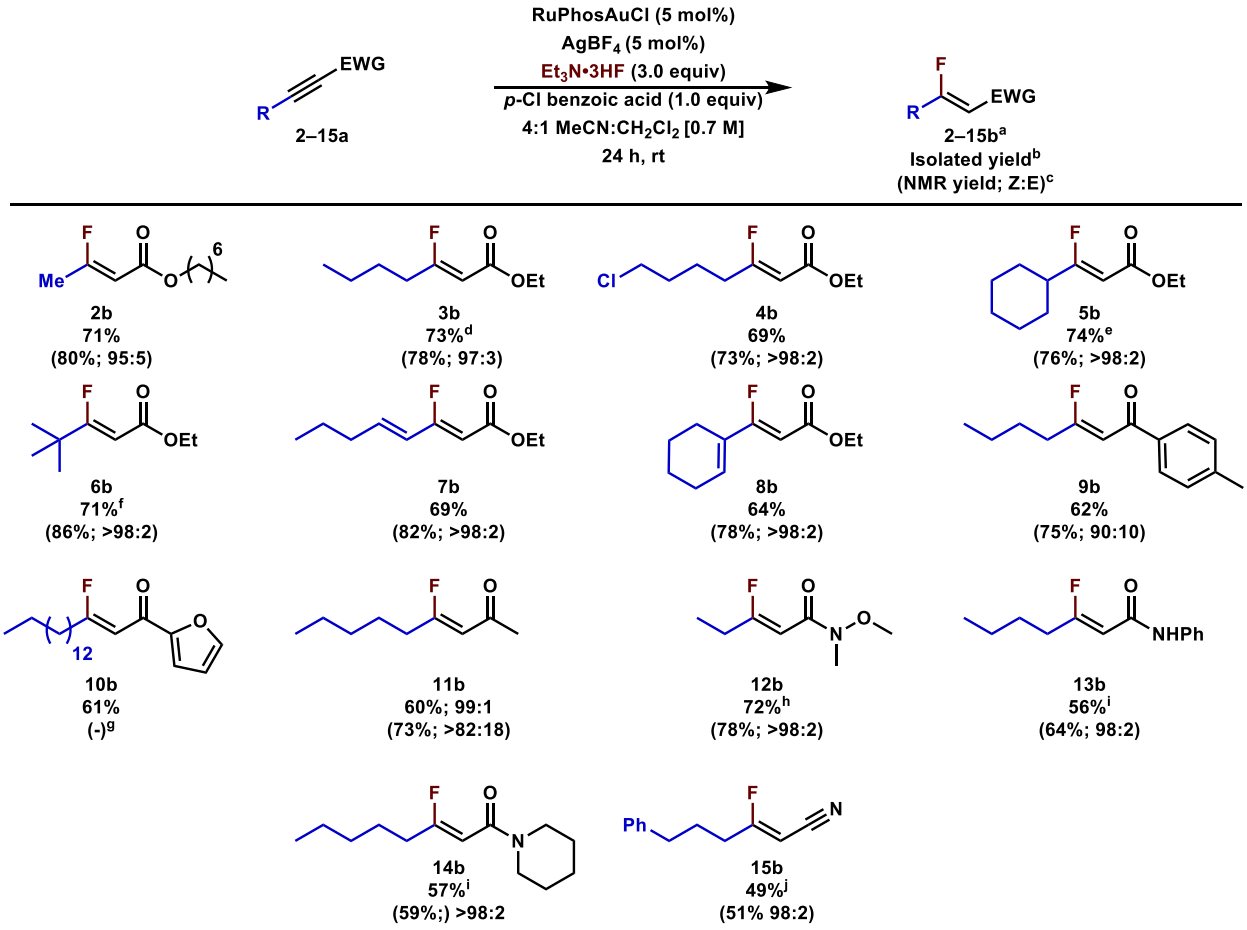
Entry	Deviation from Standard Conditions	Yield [%] (Z:E)[b]
1	None	76 (96:4)
2	$Et_3N•2HF$	5 (>98:2)
3	$Et_3N•1HF$	<2
4	pyridine•HF(30:70)	NR
5	Glass Vial	74 (97:3)
6	50 °C, Glass vial	78 (62:38)

[a]General reaction conditions: 0.2 mmol **1a**, 1.5 equiv HF source. [b]Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

1.2.1 Scope of Gold-Catalyzed Hydrofluorination

Having identified suitable reactions conditions for the hydrofluorination of alkyne **1a**, the hydrofluorination of *β*-alkyl alkynoates, alkynones, alkynamides, and alkynenitriles was investigated (Table 1.4). Methyl, 1° alkyl, 2° alkyl, and vinyl *β*-substituted alkynoates underwent hydrofluorination in the presence of $Et_3N•3HF$ in a *Z*-selective manner in good yields. Notably, the final products were all isolated as a single diastereomer after standard silica gel column chromatography. Importantly, these results highlight this operationally simple, one-step route to *β*-alkyl, *β*-fluoro Michael acceptors from alkynes. The hydrofluorination reaction was also shown to be scalable, as fluoroalkenes **3b** and **5b** were both prepared on a gram scale in good yield and with excellent *Z*-selectivity. For substrate **6a** with a bulky *β*-substituents, a higher reaction temperature was required to obtain the product in moderate yield (**6b**). The hydrofluorination of alkynoates bearing *β*-vinyl substituents provided straightforward access to fluorinated dienes **7b** and **8b**. Hydrofluorination of the *γ,δ*-alkene of either **7a** or **8a** was not detected by ^{19}F NMR spectroscopy. The reaction conditions for the hydrofluorination of *β*-alkyl alkynoates were also suitable for the hydrofluorination of *β*-alkyl (hetero)aryl alkynones **9b** and **10b**. Although methyl ketone **11a** proved to be a challenging substrate, **11b** was isolated with only a trace amount of the *E*-isomer. Both 2° and 3° *β*-alkyl alkynamides (**12**–**14a**) as well as alkynonitrile derivative **15a** underwent hydrofluorination to provide **12-15b** in moderate yields. Dec-2-ynal was the only substrate that did not undergo hydrofluorination in a regioselective manner given standard conditions in Table 2 (72%, *Z:E* = 51:49). Although conducting the reaction at 5 °C did afford a *Z:E* ratio of >98:2 the yield after 24 hours was only 22%. Unfortunately, after 96 hours at 5 °C the yield increased to 51% but the *Z:E* ratio decreased to 70:30.

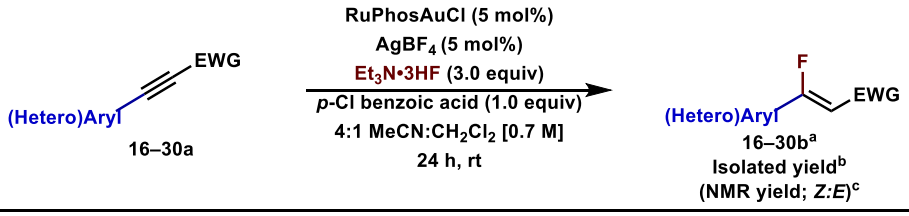
Table 1.4. Scope of *β*-alkyl, *β*-fluoro Michael acceptors.

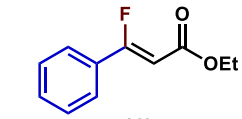


[a]Standard reaction conditions: 0.5 mmol **2–15a**, 3.0 equiv $Et_3N•3HF$, 1.0 equiv *p*-Cl BA, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 $MeCN:CH_2Cl_2$ [0.7 M], rt, 24 h. [b]**2–15b** isolated as a single isomer, expect 11b. [c]Dteremined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d]6.0 mmol scale. [e]5.0 mmol scale. [f]55°C. [g] Insoluble product. [h] 1.25 M, 4.0 equiv $Et_3N•3HF$. [I] 1.25 M, 4.0 equiv $Et_3N•3HF$, 48 h. [j]1.43 M, 4.5 equiv $Et_3N•3HF$, 50°C.

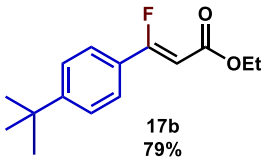
To showcase the generality of this method, the hydrofluorination reactions of a variety of electron deficient alkynes bearing *β*-aryl substituents were also explored (Table 1.5). Generally, the yields of *β*-aryl-monofluoroalkenes **16–30b** were comparable to those of their *β*-alkyl-analogs **2–15b**. In contrast to previous procedures, even a monofluoroalkene bearing an *ortho*-substituted aryl group (**19b**) were generated in modest yield.[14e] Compared to the esters and ketones, even the more electrophilic 2-phenylpropiolaldehyde afforded **27b** in a *Z*-selective manner. Moreover, both *β*-aryl alkynonitriles and alkynamides were suitable substrates, generating otherwise difficult to access fluorinated motifs (**28–30b**). Furthermore, to determine the feasibility of this methodology it was compared to that of Hammond and Xu and the two methods were found to be complimentary (Table 1.6).[14f]

Table 1.5 Scope of *β*-aryl, *β*-fluoro Michael acceptors.

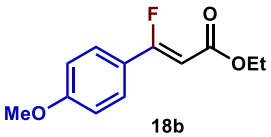




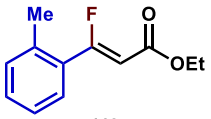
16b
65%
(79%; >98:2)



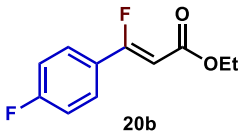
17b
79%
(88%; >98:2)



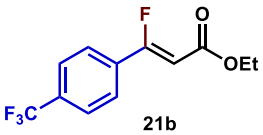
18b
79%
(86%; >98:2)



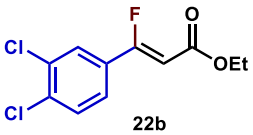
19b
53%[d]
(63%; >98:2)



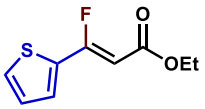
20b
77%
(87%; >98:2)



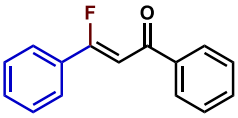
21b
73%[e]
(84%; >98:2)



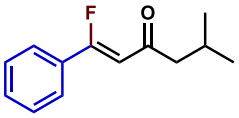
22b
71%[e]
(86%; >98:2)



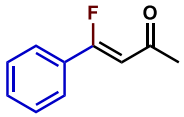
23b
80%
(88%; >98:2)



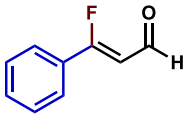
24b
66%[e]
(85%; 96:4)



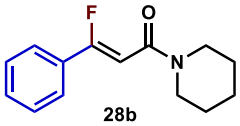
25b
54%[e]
(60%; >98:2)



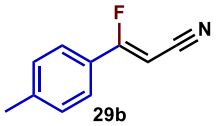
26b
60%
(65%; >98:2)



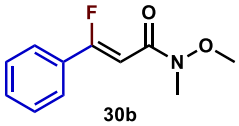
27b
63%[f]
(70%; >98:2)



28b
64%[g]
(74%; >98:2)



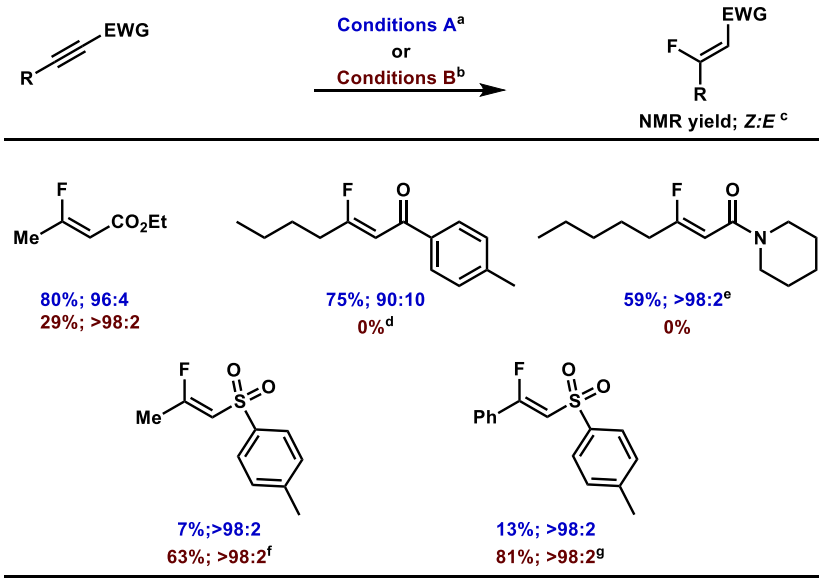
29b
68%[h]
(75%; >98:2)



30b
71%[e]
(73%; >98:2)

[a]Standard reaction conditions: 0.5 mmol **16–30a**, 3.0 equiv $Et_3N•3HF$, 1.0 equiv *p*-Cl BA, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 MeCN:CH_2Cl_2 [0.7 M], rt, 24 h. [b]**16–30b** isolated as a single isomer. [c]Dteremined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d] 1.43 M, 45°C. [e] 45°. [f]4.5 mmol scale. [g] 1.25 M, 55°C, 4.0 equiv $Et_3N•3HF$. [h]45°C, 48 h, 4.0 equiv $Et_3N•3HF$.

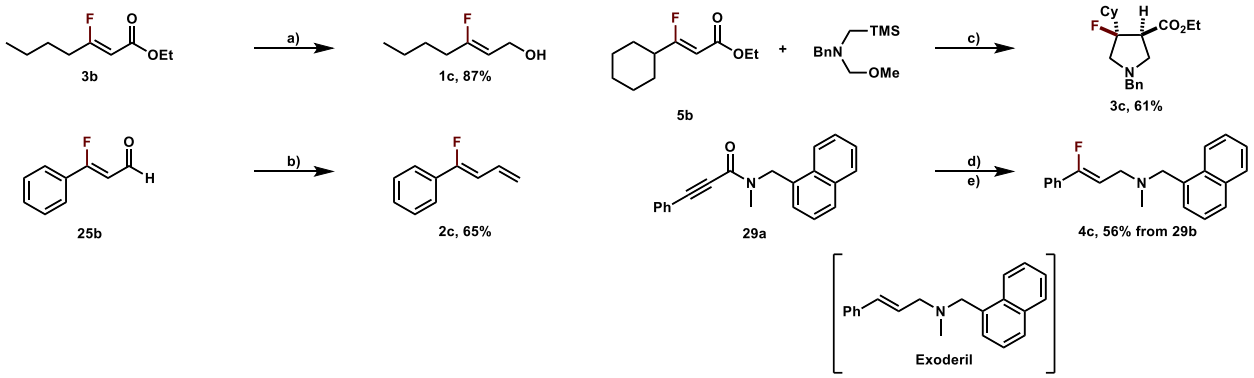
Table 1.6 Comparison of gold-catalyzed, hydrofluorination conditions.



[a]Conditions A: 0.5 mmol alkyne, 3.0 equiv $Et_3N{\bullet}3HF$, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 MeCN:CH_2Cl_2 [0.7 M], rt, 24 h, plastic vial. [b]Conditions B: 0.2 mmol alkyne, 4.0 equiv pyridine•HF (70% HF), 2.5 mol% JohnPhosAuNTf$_2$, $PhCF_3$ [0.4 M], rt, 8 h, plastic vial. [c]Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d]Only 19% of the difluoro β-ketone was detected by ^{19}F NMR spectroscopy and GC-MS analysis. [m]odified conditions A: 4.0 equiv $Et_3N{\bullet}3HF$, 4:1 MeCN:CH_2Cl_2 [1.25 M], 48 h. [f]Literature value: 64% *Z*. [g]Literature value: 90% *Z*.

The monofluoroalkenes generated from our catalytic process underwent a series of transformations demonstrating that β-fluoro Michael acceptors are valuable fluorinated building blocks (Scheme 2). For example, ester **3b** was reduced in the presence of DIBAL–H to yield the fluorinated allylic alcohol **1c** in high yield.[17] Aldehyde **27b** underwent Wittig olefination in modest yield to afford a 1-fluoro-2,4-diene **2c**.[18] In the presence of a suitable 1,3-ylide, ester **5b** underwent a regioselective [3+2] cycloaddition to generate a pyrrolidine with a quaternary fluorine center (**3c**).[19] Finally, amide **31b** was reduced in the presence of Meerwein's salt to furnish a fluorine-containing analog of Exoderil **4c**.[20]

Scheme 1.2 Diversification of fluorinated Michael Acceptors.



[a]Yield given is for isolated product at specified scale. a) **3b** (2.32 mmol), DIBAL–H, CH_2Cl_2, 0°C. b) ^{n}BuLi, Ph_3PMeBr, **27b** (0.3 mmol), THF 0°C. c) **5b** (0.3 mmol), ylide TFA, 0°C to rt. D) **31a** (1.96 mmol), 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 1.0 equiv *p*-Cl BA, 4.0 equiv $Et_3N{\bullet}3HF$, 45°C, 48 h, MeCN:CH_2Cl_2 [1.25 M]. e) Me_3OBF_4, 2,6-di-^{t}Bu-pyridine, **31b** (0.54 mmol), CH_2Cl_2, rt; $NaBH_4$, MeOH, -10°C.

1.3 Conclusion

In conclusion, a stereoselective hydrofluorination of electron-deficient alkynes catalyzed by a RuPhos-ligated gold(I) complex was developed. For the first time, direct access to a variety of (*Z*)-*β*-alkyl, *β*-fluoro Michael acceptors was achieved. In addition, (*Z*)-*β*-aryl, *β*-fluoro *α,β*-unsaturated amides and nitriles were conveniently accessed with the disclosed method. The synthetic potential of the resulting monofluoroalkene was demonstrated with various transformations of the products without the loss of the newly installed fluorine atom, and with the synthesis of a fluorinated analog of Exoderil.

1.4 Supporting Information

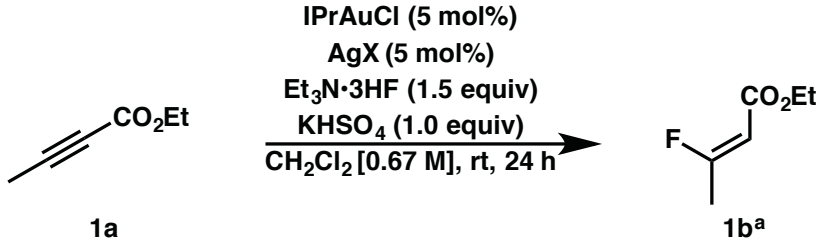
1.4.1 General Experimental Details

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Vessels used in air-free reactions were oven-dried prior to use. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed using ICN SiliTech 32-63D 60Å silica gel. Commercial grade solvents were used without further purification except as indicated below. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), toluene (PhMe), diethyl ether (Et_2O), dimethyl formamide (DMF), triethylamine (Et_3N) and tetrahydrofuran (THF) were dried by passing commerically available pre-dried, oxygen-free formulations through activated alumina columns under argon. Thin layer chromatography analysis was performed using Merck 60 pre-coated silica gel plates with F254 indicator. Visualization was accomplished by iodine, p-anisaldehyde, potassium permanganate, Dragendorff-Munier, and/or UV light (254 nm). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AVQ-400, DRX-500 and AV-600 instruments with 400, 500 and 600 MHz frequencies. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker DRX-500 and AV-600 instruments with a ^{13}C operating frequency of 126 and 150 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded on Bruker AVQ-400, DRX-500 and AV-600 instruments with 376, 471, and 565 MHz frequencies. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$, δ 5.32 for CH_2Cl_2) was used as an internal reference for ^{1}H spectra. For ^{13}C spectra, chemical shifts are reported relative to the δ 77.16 resonance of $CDCl_3$ and relative to the δ 53.84 for CD_2Cl_2. For ^{19}F spectra, chemical shifts are reported in relative to the δ -113.15 resonance of PhF. Coupling constants are reported in Hz. Mass spectral data were obtained from either the UC-Berkeley Catalysis Center operated by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI (or APCI) mode or the QB3/Chemistry Mass Spectrometry Facility at UC-Berkeley. FTIR measurements were recorded on a Bruker Vertex 80 FTIR spectrometer in the Catalysis Center at UC-Berkeley and are reported in frequency of absorption (cm^{-1}). Alkynes (11a),[21] (13a),[22] (18a, 20a, 23a),[23] (17a),[24] (19a, 21a),[25] (22a),[26] (24a),[27] (25a),[28] (26a),[21a] (29a),[29] 5-phenylpent-2-yn-1-ol,[30] 1-methyl-4-(prop-1-ynylsulfonyl)benzene,[31] and 1-methyl-4-(phenylethynylsulfonyl)benzene[31] could be prepared according to previously reported procedures; the spectral data were in agreement. Gold complexes were synthesized according to the procedure outlined in Mauleon et al[32] and their spectra match those reported in the literature.[32-33] JohnPhosAuNTf$_2$ was prepared as described by Gagosz and coworkers.[34]

1.4.2 Investigation of Reaction Conditions

In a nitrogen-filled glove-box, solvent was added to a 4 mL glass vial charged with LAuCl (0.01 mmol, 5 mol%) and AgX (0.01 mmol, 5 mol%). After 4–5 minutes of mixing with a syringe in the absence of light, the resulting mixture was filtered through a glass fiber pad (packed into the neck of 9" pipette) into a 2 mL screw-lid plastic centrifuge tube containing specified additive. Alkyne **1a** (23 μL, 0.20 mmol, 1 equiv) was added and the centrifuge tube sealed and brought outside the glove-box. In the absence of light, the plastic centrifuge tube was opened (exposed to air) and the fluorination reagent added. The reaction was sealed and placed on a IKA KS 130 basic shaker table (560 revolutions/min) under protection from light. After the designated time, the reaction was diluted with an appropriate solvent (500 μL total), charged with 2,4-dinitrofluorobenzene (25 μL, 0.20 mmol, 1 equiv), filtered into an NMR tube, and analyzed by ^{1}H and ^{19}F NMR spectroscopy.

Table S1. Effect of the silver salt on the hydrofluorination of **1a**.

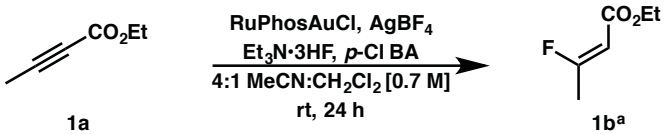


1a **1b**[a]

Entry	AgX	Yield [%] (*Z:E*)[b]
1	BF_4	50 (66:34)
2	SbF_6	43 (70:30)
3	OTf	26 (69:31)
4	OMs	NR
5	CF_3CO_2	31 (70:30)

[a] General reaction conditions: 0.2 mmol **1a**, plastic vial. [b] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

Table S2. Control studies for the hydrofluorination of **1a**.



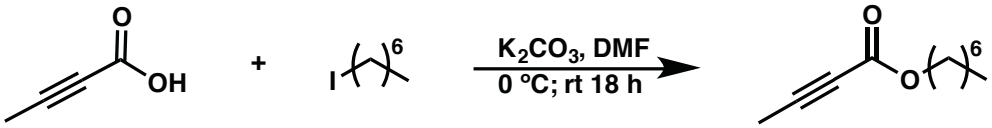
1a **1b**[a]

Entry	Au [mol%]	Ag [mol%]	RuPhos [mol%]	HF [equiv]	*p*-Cl BA [equiv]	Yield [%] (*Z:E*)[b]
1	5	5	0	1.5	1.0	76 (96:4)
2	0	5	0	1.5	1.0	NR
3	0	5	5	1.5	1.0	NR
4	0	0	5	1.5	1.0	NR
5	5	5	0	1.5	0	65 (96:4)

[a] General reaction conditions: 0.2 mmol **1a**, plastic vial. [b] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

1.4.3 Synthesis of Alkynes

heptyl but-2-ynoate (**2a**)



Prepared according to a published procedure.[35] To a stirring solution of but-2-ynoic acid (1.26 g, 15.0 mmol, 1 equiv) in dimethyl formamide (12.6 mL) at 0 °C was added potassium carbonate 5.18 g, 37.5 mmol, 2.5 equiv) under a flow of nitrogen. After heptyl iodide (3.7 mL, 22.5 mmol, 1.5 equiv) was added dropwise and the resultant reaction mixture was stirred at RT. After completion of the reaction (by TLC), the reaction mixture was diluted with water (50 mL) and ethyl acetate (100 mL). The separated organic phase was washed with ice cold, deionized water (dH_2O) (3 x 80 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude reside was purified by silica gel column chromatography (10:1 hexanes:ethyl acetate).

Colorless oil (24%, 656 mg):

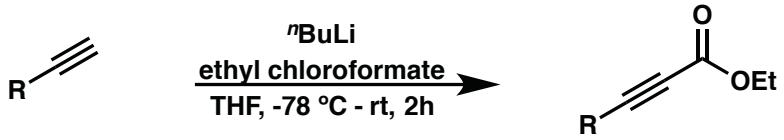
^{1}H NMR (600 MHz, CD_2Cl_2) δ 4.10 (t, *J* = 6.8 Hz, 2H), 1.97 (s, 3H), 1.66 – 1.60 (m, 2H), 1.37 – 1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ = 154.1, 85.4, 72.8, 66.2, 32.1, 29.3, 28.9, 26.2, 23.0, 14.2, 3.9.

HRMS (ESI+) calc'd for $C_{11}H_{19}O_2^+$ $[M+H]^+$: 183.1380, found: 183.1380.

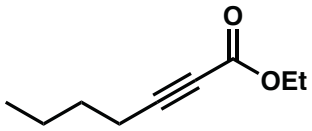
IR (neat) 2927, 2243, 1707 cm^{-1}.

Synthesis of alkynes **3a, 4a, 5a, 6a** and **8a.**



Prepared according to a published procedure.[36] To a solution of terminal alkyne (18.0 mmol, 1 equiv) at -78 °C was added ^{n}BuLi (7.2 mL, 2.5 M in hexanes, 18.0 mmol, 1 equiv), and the reaction was stirred for 30 minutes at -78 °C. Ethyl chloroformate (1.71 mL, 18.0 mmol, 1 equiv) was added dropwise, and then the reaction warmed to room temperature and stirred for 2 h. The reaction was quenched with ice cold, deionized water (125 mL) and extracted with Et_2O (3 x 150 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexanes:ethyl acetate).

ethyl hept-2-ynoate (**3a**)

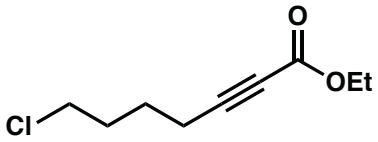


Light yellow oil (48%, 1.33 g):

In accordance with previously reported spectra.[22]

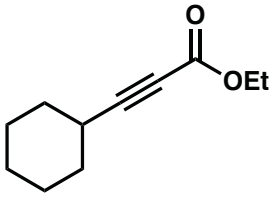
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 7.1 Hz, 2H), 1.53 (p, *J* = 7.2 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

ethyl 7-chlorohept-2-ynoate (**4a**)



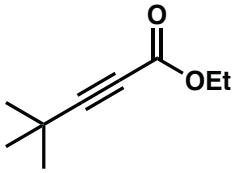
Colorless oil (70%, 2.38 g):
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.1, 2H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.36 (t, *J* = 6.9 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.77 – 1.69 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 88.2, 73.8, 61.9, 44.2, 31.4, 24.8, 18.1, 14.1.
HRMS (ESI+) calc'd for $C_9H_{14}ClO_2^+$ $[M+H]^+$: 189.0677, found: 189.0677.
IR (neat) 2984, 2236, 1704, 1246, 1072, 730 cm^{-1}.

ethyl 3-cyclohexylpropiolate (**5a**)



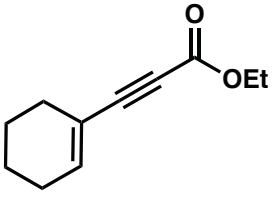
Colorless oil (81%, 2.64g):
In accordance with previously reported spectra.[37]
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.2 Hz, 2H), 2.51 – 2.45 (m, 1H), 1.87 – 1.76 (m, 2H), 1.73 – 1.64 (m, 2H), 1.54 – 1.45 (m, 3H), 1.34 – 1.23 (m, 6H)

ethyl 4,4-dimethylpent-2-ynaote (**6a**)



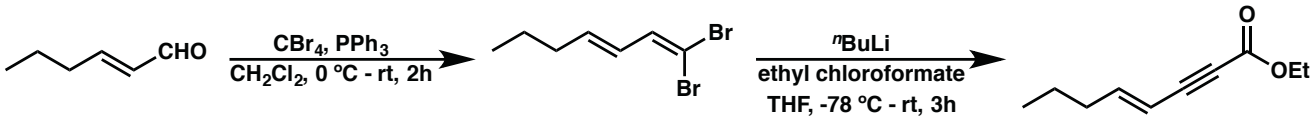
Colorless oil (81%, 2.25 g):
In accordance with previously reported spectra.[37]
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.23 (s, 9H).

ethyl 3-(cyclohex-1-en-1-yl)propiolate (**8a**)



light yellow oil (67%, 2.15 g):
In accordance with previously reported spectra.[37]
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 – 6.36 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.15 – 2.06 (m, 4H), 1.64 – 1.58 (m, 2H), 1.58 – 1.54 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

ethyl-(*E*)-oct-4-en-2-ynoate (**7a**)

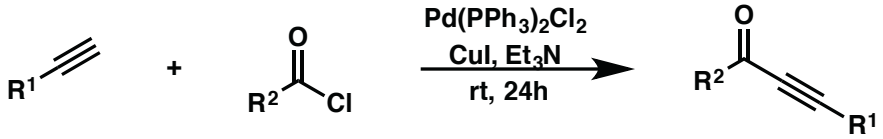


Prepared according to a modified literature procedure.[38] To a CH_2Cl_2 (59 mL) solution of carbon tetrabromide (5.8 g, 17.5 mmol, 2 equiv) was added a CH_2Cl_2 solution of triphenylphosphine (9.2 g, 35.0 mmol, 4 equiv) at 0 °C dropwise. The reaction mixture was warmed to rt and stirred for 30 minutes before a CH_2Cl_2 (4 mL) solution of (*E*)-hex-2-enal (8.75 mmol, 1.04 mL, 1.0 equiv) was slowly added. The resulting mixture was stirred at rt for 2 h before the addition of dH_2O (50 mL) to partition the organic layer. The mixture was extracted with CH_2Cl_2 (3 x 20 mL), dried over Na_2SO_4, filtered, and concentrated. To this residue was added Et_2O (40 mL) and the resulting suspension filtered. The ethereal filtrate is concentrated and chromatographed through a silica gel column (hexanes) to afford (*E*)-1,1-dibromo-hepta-1,3-diene as a light yellow oil whose ^1H and ^{13}C spectra matched reported values.[39]

To a THF solution (28 mL) of (*E*)-1,1-dibromo-hepta-1,3-diene (1.08 g, 4.25 mmol, 1.0 equiv) at -78 °C was added ^nBuLi (3.57 mL, 2.5 M in hexanes, 8.93 mmol, 2.1 equiv) dropwise. The resulting solution was stirred at -78 °C for 30 min before ethyl chloroformate (0.41 mL, 4.72 mmol, 1.0 equiv) was added dropwise. After the dropwise addition, the reaction mixture was stirred at -78 °C for 30 min and then stirred at rt for 2 h. To this solution was added saturated NH_4Cl (50 mL). The aqueous layer was separated, extracted with Et_2O (3 x 25 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel column chromatography (Et_2O:hexanes 1:9) to afford ethyl-(*E*)-oct-4-en-2-ynoate (7a) as a yellow oil (25% from (*E*)-hex-2-enal, 304 mg).

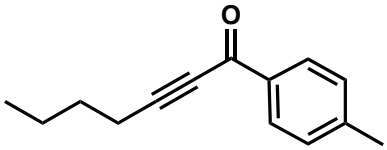
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (dt, *J* = 14.6, 7.1 Hz, 1H), 5.53 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.41 (p, *J* = 7.3 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 152.4, 107.2, 85.6, 79.5, 61.9, 35.5, 21.5, 14.1,
HRMS (ESI+) calc'd for $C_{10}H_{15}O_2^+$ $[M+H]^+$: 167.1067, found: 167.1065.
IR (neat) 2962, 2933, 2874, 2212, 1704, 1626, 1245, 1096 cm^{-1}.

Synthesis of alkynes **9a** and **10a**



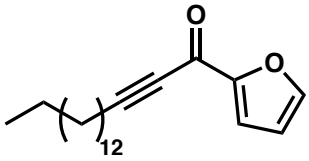
Prepared from a modified procedure.[40] To a solution of Et_3N (20 mL) was added terminal alkyne (12.5 mmol, 1.25 equiv), acyl chloride (10.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.5 mol%), and CuI (2.5 mol%). After 24 h of stirring at rt, MeOH (10 mL) was added, the solvent evaporated and Et_2O (150 mL) was added. The mixture was filtered, washed with 3 M HCl (75 mL), dH_2O (75 mL), brine (75 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (EtOAc:hexanes) to afford **9a** or **10a**.

1-(4-methylphenyl)hept-2-yn-1-one (**9a**)



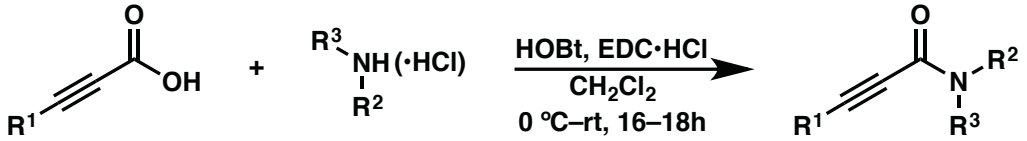
tan/yellow oil (50%, 1.00 g):
In accordance with previously reported spectra.[41]
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.73 – 1.59 (m, 2H), 1.56 – 1.44 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

1-(furan-2-yl)heptadec-2-yn-1-one (**10a**)



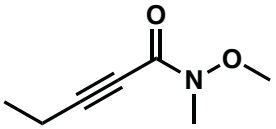
orange solid (48%, 1.51 g):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.30 (d, *J* = 3.5 Hz, 1H), 6.56 – 6.54 (m, 1H), 2.44 (t, *J* = 7.1 Hz, 1H), 1.63 (p, *J* = 7.2 Hz, 2H), 1.44 (p, *J* = 7.1 Hz, 2H), 1.33 – 1.21 (m, 20H), 0.86 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 153.4, 147.8, 120.7, 112.6, 112.6, 95.7, 79.1, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.0, 27.8, 22.8, 19.3, 14.2, 14.2.
HRMS (ESI+) calc'd for $C_{21}H_{33}O_2^+$ $[M+H]^+$: 317.2475, found: 317.2471.
IR (neat) 2919, 2849, 2210, 1626, 1458, 794 cm^{-1}.

Synthesis of alkynes **12a, 14a, 28a, 30a** and **31a.**



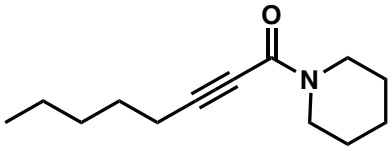
Prepared according to a modified literature procedure.[42] To an ice-cold solution of acid (10.7 mmol, 1.0 equiv) in CH_2Cl_2 (71 mL), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC•HCl) (11.8 mmol, 1.1 equiv) and 1-hydroxybenzotriazole (HOBt) (13.91 mmol, 1.3 equiv; concentrated twice with distilled benzene) were added and the mixture stirred for 5 min. The amine (13.91 mmol 1.3 equiv; if HCl salt of amine added 1.3 equiv Et_3N) was then added and the reaction was allowed to reach rt overnight. After 16–19 h the solvent was evaporated and the residue dissolved in EtOAc (150 mL). The organic phase was washed with 1 M HCl (100 mL), saturated $NaHCO_3$ (100 mL), brine (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (EtOAc:hexanes) to afford pure **12a, 14a, 28a, 30a** and **31a**.

N-methoxy-*N*-methylpent-2-ynamide (**12a**)



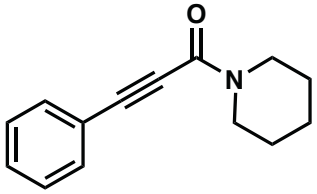
colorless oil (68%, 1.55 g, 16.2 mmol scale, employed HCl salt of amine):
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.33 – 3.01 (m, 3H), 2.28 (q, *J* = 7.5 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 94.4, 72.4, 61.9, 32.2, 12.7, 12.5.
HRMS (ESI+) calc'd for $C_7H_{12}NO_2^+$ $[M+H]^+$: 142.0863, found: 142.0860.
IR (neat) 2980, 2939, 2235, 1636, 1412, 1378, 988, 722 cm^{-1}.

1-(piperidin-1-yl)oct-2-yn-1-one (**14a**)



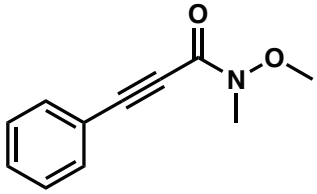
orange oil (88%, 1.95 g, 10.7 mmol scale):
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.55 (t, *J* = 5.6 Hz, 2H), 3.42 (t, *J* = 5.5 Hz, 2H), 2.21 (t, *J* = 7.2 Hz, 2H), 1.54 – 1.49 (m, 2H), 1.48 – 1.43 (m, 4H), 1.42 – 1.37 (m, 2H), 1.28 – 1.15 (m, 4H), 0.76 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 92.8, 73.7, 47.8, 41.9, 30.8, 27.3, 26.2, 25.2, 24.3, 21.9, 18.7, 13.7.
HRMS (APCI+) calc'd for $C_{13}H_{22}NO^+$ $[M+H]^+$: 208.1696, found: 208.1691.
IR (neat) 2933, 2857, 2244, 2222, 1622, 1428, 1266, 1234, 731 cm^{-1}.

3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-one (**28a**)



white solid (75%, 963 mg, 6.0 mmol scale)
In accordance with previously reported spectra.[43]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.33 (m, 2H), 3.77 (t, *J* = 5.7, 5.1 Hz, 2H), 3.62 (t, *J* = 5.6 Hz, 2H), 1.70 – 1.62 (m, 4H), 1.58 (p, *J* = 5.7 Hz, 2H).

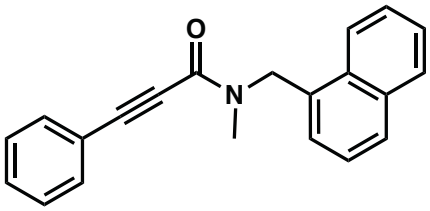
N-methoxy-*N*-methyl-3-phenylpropiolamide (**30a**)



colorless oil (62%, 2.13 g, 18 mmol scale, employed HCl salt of amine)
In accordance with previously reported spectra.[44]

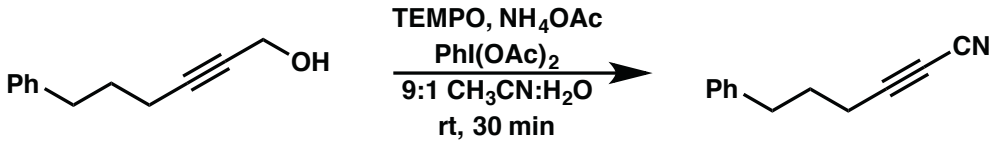
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 2H), 3.82 (s, 3H), 3.26 (bs, 3H).

N-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylpropiolamide (**31a**)



opaque, colorless oil (98%, 1.85 g, 6.3 mmol scale):
^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers ca. 59:41) δ 8.15 (d, *J* = 8.4 Hz, 1H, major rotamer), 8.09 (d, *J* = 8.3 Hz, 0.7H, minor rotamer), 7.92 – 7.81 (m, 3.4H), 7.60 – 7.38 (m, 11.4H), 7.36 – 7.25 (m, 5.2H), 5.34 (s, 1.4H, minor rotamer), 5.14 (s, 2H, major rotamer), 3.11 (s, 3H, major rotamer), 2.98 (s, 2.2H minor rotamer).
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 154.5, 133.8, 133.8, 132.4, 132.3, 131.6, 131.5, 131.4, 131.2, 130.0, 129.0, 128.8, 128.6, 128.6, 128.5, 128.4, 127.3, 126.7, 126.6, 126.1, 126.0, 125.4, 125.3, 125.1, 123.8, 122.5, 120.4, 120.2, 90.7, 90.5, 81.7, 52.5, 47.7, 35.5, 32.2.
HRMS (APCI+) calc'd for $C_{21}H_{18}NO^+$ $[M+H]^+$: 300.1383, found: 300.1381.
IR (neat) 3060, 2926, 2855, 2213, 1740, 1665, 1619, 1398, 1244, 1109, 908, 760, 728, 689 cm^{-1}.

6-phenylhex-2-ynenitrile (**15a**)



Prepared according to a modified literature report.[45] To a solution of 9:1 CH_3CN:dH_2O was added (under a positive flow of N_2) 5-phenylpent-2-yn-1-ol (1.22 g, 7.0 mmol, 1.0 equiv) followed by TEMPO (55 mg, 5 mol%), NH_4OAc (2.09 g, 27.2 mmol, 3.88 equiv) and $PhI(OAc)_2$ (4.94 g, 15.33, 2.19 equiv). The suspension was stirred at rt for 30 min, concentrated and diluted with dH_2O (40 mL) and Et_2O (80 mL). The layers were separated and the aqueous layer extracted with Et_2O (2 x 80 mL). The organics were collected and washed with brine (200 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (1:15 Et_2O:hexanes) to afford **15a** as a colorless oil (1.04 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.94 (p, *J* = 7.3 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 128.7, 128.6, 126.5, 105.4, 87.1, 55.8, 34.6, 28.7, 18.2.
HRMS (ESI+) calc'd for $C_{11}H_{11}NNa^+$ $[M+Na]^+$: 192.0784, found: 192.0780.
IR (neat) 3028, 2939, 2314, 2259, 1496, 1454, 743, 608, 500 cm^{-1}.

1.4.4 General Procedures for Gold-Catalyzed Alkyne Hydrofluorination

Attention: Hydrogen fluoride amine complexes are hazardous and should be handled with care. In case of skin contact, calcium gluconate gel should be applied to the affected area and medical attention sought. Although some hydrogen fluoride amine complexes are known to etch normal laboratory glassware, the catalytic hydrofluorination reactions disclosed in this communication can be contacted in glass vials without a significant decrease in yield. However, plastic, screw-lid centrifuge tubes are recommended.

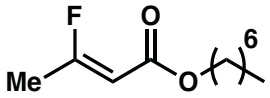
Notes:

- Before each experiment (1–24 h), RuPhosAuCl (white solid) was dissolved in dry dichloromethane, filtered through a plug of basic alumina (1-inch of basic alumina layered on a glass fiber pad in a Kimble 5-3/4" Monster Pipette) into a 20-mL vial that had been rinsed with dry dichloromethane (1 mL), and concentrated.
- Glass vials, stir bars, and heating blocks were utilized for reactions conducted at elevated temperatures. Only a slight decrease in the NMR yield (1–3%) of **1b** was observed upon switching from plastic to glass reaction vessels. Reactions at room temperature were conducted in plastic, screw-lid centrifuge tubes that were heated at 70 °C for 5–7 days before being pumped in a nitrogen-filled glovebox.
- Presence of water results in competitive hydration of the alkyne.
- See substrate tables for variations on the standard procedures below.

Standard Procedure for 0.5 mmol scale

In a nitrogen-filled glove-box (in the absence of light) solvent (700 μL) was added to a 4-mL glass vial charged with RuPhosAuCl (17.5 mg, 0.025 mmol, 5 mol%) and $AgBF_4$ (5 mg, 0.025 mmol, 5 mol%). After 8–10 minutes of mixing with a syringe, the white slurry was filtered through a glass fiber pad (packed into the neck of 9" pipette) into a 2-mL screw-lid plastic centrifuge tube containing *p*-chlorobenzoic acid (87 mg, 0.5 mmol, 1 equiv). Alkyne (**2-30a**) was quickly added to the reaction mixture. Outside the glove-box, in the absence of light, the plastic centrifuge tube was opened (briefly exposed to air) and $Et_3N{\bullet}3HF$ (250 μL, 1.50 mmol, 3 equiv) added. The reaction was sealed and placed on an IKA KS 130 basic shaker table (560 revolutions/min) under the protection from light. After 24 hours, the reaction mixture was transferred to a round bottom flask (50 mL) with dichloromethane (15 mL) and treated with a 10% Na_2CO_3 solution (15 mL). After stirring for 20–30 minutes, the biphasic solution was transferred to a separatory funnel with dichloromethane (20 mL) and additional 10% Na_2CO_3 (10 mL) added. The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 30 mL). Dichloromethane was added to the organic fractions until the total volume reached 200 mL. Then the organics were washed with brine (1 x 150 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed (hexanes:Et_2O) to afford **2–30b**.

heptyl (*Z*)-3-fluorobut-2-enoate (**2b**)

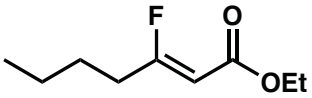


Column chromatography (SiO_2, eluting with 1:30→1:20 Et_2O:hexanes) afforded the desired product as a colorless oil (71.8 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.16 (d, *J* = 32.6 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.00 (d, *J* = 16.6 Hz, 3H), 1.61 (p, *J* = 6.7 Hz, 2H), 1.37 – 1.20 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H).

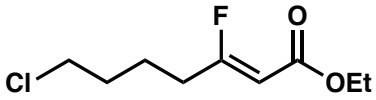
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8 (d, *J* = 283.8 Hz), 163.9 (d, *J* = 2.1 Hz), 131.7, 129.0, 99.7 (d, *J* = 5.0 Hz), 64.4, 31.8, 29.0, 28.7, 26.0, 22.7, 19.2 (d, *J* = 26.5 Hz), 14.1.
^{19}F NMR (565 MHz, $CDCl_3$) δ -73.6 (dq, *J* = 32.7, 16.4 Hz).
HRMS (APCI+) calc'd for $C_{11}H_{20}FO_2^+$ $[M+H]^+$: 203.1442, found: 203.1443.
IR (neat) 2956, 2928, 2858, 1716, 1687, 1219, 1136, 1037 cm^{-1}.

ethyl (*Z*)-3-fluorohept-2-enoate (**3b**)



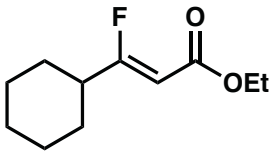
Column chromatography (SiO_2, eluting with 1:30→1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (763.4 mg, 73%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.15 (d, *J* = 33.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.25 (dt, *J* = 17.0, 7.5 Hz, 2H), 1.53 (p, *J* = 7.5 Hz, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3 (d, *J* = 286.4 Hz), 163.9 (d, *J* = 1.6 Hz), 131.7, 129.0, 98.9 (d, *J* = 5.3 Hz), 60.2, 32.8 (d, *J* = 23.8 Hz), 27.7 (d, *J* = 1.9 Hz), 22.0, 14.3, 13.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ -80.0 (dt, *J* = 33.8, 17.2 Hz).
HRMS (APCI+) calc'd for $C_9H_{16}FO_2^+$ $[M+H]^+$: 175.1129, found: 175.1121.
IR (neat) 2961, 2936, 2875, 1727, 1715, 1681, 1215, 1133, 1037, 907, 836 cm^{-1}.

ethyl (*Z*)-7-chloro-3-fluorohept-2-enoate (**4b**)



Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a colorless oil (72.0 mg, 69%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (d, *J* = 33.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.29 (dt, *J* = 16.9, 7.4 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.66 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2 (d, *J* = 286.1 Hz), 163.7 (d, *J* = 1.8 Hz), 99.4 (d, *J* = 5.0 Hz), 60.3, 44.3, 32.3 (d, *J* = 24.2 Hz), 31.5, 23.0 (d, *J* = 1.9 Hz), 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -80.6 (dt, *J* = 33.7, 17.0 Hz).
HRMS (APCI+) calc'd for $C_9H_{15}ClFO_2^+$ $[M+H]^+$: 209.0739, found: 209.0736.
IR (neat) 2960, 2874, 1722, 1681, 1271, 1214, 1133, 1037, 839 cm^{-1}.

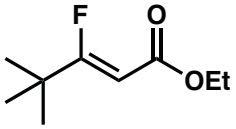
ethyl (*Z*)-3-cyclohexyl-3-fluoroacrylate (**5b**)



Column chromatography (SiO_2, eluting with 1:24 Et_2O:hexanes) afforded the desired product as a colorless oil (740.0 mg, 74%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (d, *J* = 34.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.21 – 2.12 (m, 1H), 1.91 – 1.87 (m, 2H), 1.81 – 1.78 (m, 2H), 1.71 – 1.67 (m, 1H), 1.29 – 1.25 (m, 7H), 1.21 – 1.16 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8 (d, *J* = 287.7 Hz), 164.3, 97.0 (d, *J* = 5.4 Hz), 60.2, 41.7 (d, *J* = 22.2 Hz), 29.4 (d, *J* = 2.2 Hz), 25.8, 25.7, 14.4.

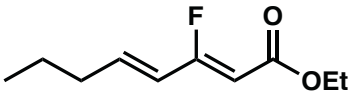
^{19}F NMR (565 MHz, $CDCl_3$) δ -85.3 (dd, *J* = 34.3, 14.9 Hz).
HRMS (APCI+) calc'd for $C_{11}H_{18}FO_2^+$ $[M+H]^+$: 201.1285, found: 201.1288.
IR (neat) 2981, 2932, 2858, 1728, 1712, 1675, 1199, 1140, 1041, 910 cm^{-1}.

ethyl (*Z*)-3-fluoro-4,4-dimethylpent-2-enoate (**6b**)



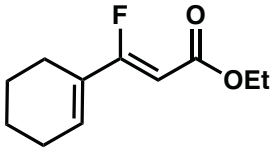
Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (62.0 mg, 71%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.20 (d, *J* = 34.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 178.7 (d, *J* = 289.4 Hz), 164.4, 95.8 (d, *J* = 6.1 Hz), 60.2, 36.0 (d, *J* = 21.5 Hz), 26.9 (d, *J* = 2.8 Hz), 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -89.8 (d, *J* = 34.2 Hz).
HRMS (APCI+) calc'd for $C_9H_{16}FO_2^+$ $[M+H]^+$: 175.1129, found: 175.1124.
IR (neat) 2974, 2876, 1730, 1711, 1672, 1278, 1175, 1099, 1038 cm^{-1}.

ethyl (2*Z*, 4*E*)-3-fluoroocta-2,4-dienoate (**7b**)



Column chromatography (SiO_2, eluting with 1:24 Et_2O:hexanes) afforded the desired product as a light yellow oil (64.0 mg, 69%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.82 (dd, *J* = 24.1, 15.6 Hz, 1H), 5.14 (d, *J* = 32.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.17 – 2.13 (m, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1 (d, *J* = 277.7 Hz), 164.4 (d, *J* = 2.2 Hz), 141.1 (d, *J* = 5.0 Hz), 121.6 (d, *J* = 20.9 Hz), 98.8 (d, *J* = 6.4 Hz), 60.2, 34.7, 21.8, 14.3, 13.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ -101.1 (dd, *J* = 32.6, 24.1 Hz).
HRMS (APCI+) calc'd for $C_{10}H_{16}FO_2^+$ $[M+H]^+$: 187.1129, found: 187.1121.
IR (neat) 2962, 2934, 2875, 1721, 1704, 1658, 1627, 1229, 1136, 1037, 966 cm^{-1}.

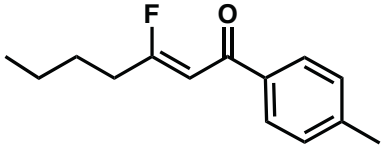
ethyl (*Z*)-3-(cyclohex-1-en-1-yl)-3-fluoroacrylate (**8b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a light yellow oil (63.0 mg, 64%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 – 6.58 (m, 1H), 5.23 (d, *J* = 34.2 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 6H), 2.23 – 2.18 (m, 8H), 2.06 (q, *J* = 4.7, 3.0 Hz, 9H), 1.72 – 1.65 (m, 9H), 1.63 – 1.56 (m, 10H), 1.27 (t, *J* = 7.1 Hz, 8H).

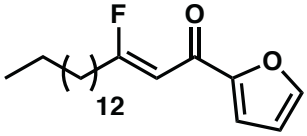
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8 (d, *J* = 277.8 Hz), 164.7, 133.8 (d, *J* = 8.8 Hz), 128.5 (d, *J* = 17.5 Hz), 95.3 (d, *J* = 6.9 Hz), 60.2, 25.8, 23.8 (d, *J* = 2.8 Hz), 22.0, 21.5, 14.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ -101.2 (d, *J* = 34.7 Hz).
HRMS (APCI+) calc'd for $C_{11}H_{16}FO_2^+$ $[M+H]^+$: 199.1129, found: 199.1126.
IR (neat) 2981, 2935, 2864, 1723, 1700, 1642, 1320, 1249,1150, 1044, 731 cm^{-1}.

(*Z*)-3-fluoro-1-(4-methylphenyl)hept-2-en-1-one (**9b**)



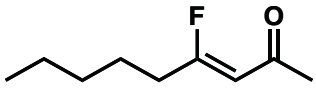
Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a light yellow oil (68.0 mg, 62%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.04 (d, *J* = 34.3 Hz, 1H), 2.40 (s, 3H), 2.36 (dt, *J* = 17.0, 7.7 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.47 – 1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 188.5, 170.8 (d, *J* = 286.9 Hz), 143.6, 135.9, 129.3, 128.6, 103.7 (d, *J* = 5.4 Hz), 33.1 (d, *J* = 24.0 Hz), 27.9, 22.2, 21.7, 13.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -81.4 (dt, *J* = 34.3, 17.4 Hz).
HRMS (APCI+) calc'd for $C_{14}H_{18}FO^+$ $[M+H]^+$: 221.1336, found: 221.1333.
IR (neat) 2959, 2932, 2872, 1679, 1629, 1605, 1572, 1237, 1181, 895, 732 cm^{-1}.

(*Z*)-3-fluoro-1-(furan-2-yl)heptadec-2-en-1-one (**10b**)



Column chromatography (SiO_2, eluting with 1:1 CH_2Cl_2:hexanes) afforded the desired product as a white solid (102.0 mg, 61%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.11 (d, *J* = 33.7 Hz, 1H), 2.34 (dt, *J* = 17.3, 7.6 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.42 – 1.21 (m, 23H), 0.87 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 172.4 (d, *J* = 291.2 Hz), 153.5, 146.2, 116.9, 112.6, 102.4 (d, *J* = 3.2 Hz), 33.6 (d, *J* = 23.2 Hz), 32.0, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.0, 25.9 (d, *J* = 1.5 Hz), 22.8, 14.2.
^{19}F NMR (565 MHz, $CDCl_3$) δ -79.1 (dt, *J* = 34.3, 17.4 Hz).
HRMS (APCI+) calc'd for $C_{21}H_{34}FO_2^+$ $[M+H]^+$: 337.2537, found: 337.2537.
IR (neat) 3123, 3094, 2953, 2914, 2849, 1690, 1628, 1469, 1399, 1276, 1018, 890, 750 cm^{-1}.

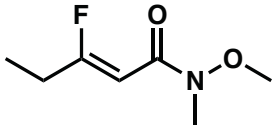
(*Z*)-4-fluorononon-3-en-2-one (**11b**)



Column chromatography (SiO_2, eluting with 1:10 Et_2O:hexanes) afforded the desired product as a colorless liquid (47.5 mg, 60%; *Z*:*E* = 99:1).

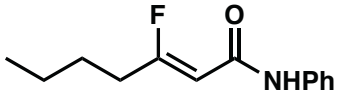
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, *J* = 38.4 Hz, 1H), 2.33 (d, *J* = 3.9 Hz, 3H), 2.31 – 2.22 (m, 2H), 1.58 – 1.50 (m, 2H), 1.33 – 1.29 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C (126 MHz, $CDCl_3$) δ 196.7, 171.9 (d, *J* = 283.3 Hz), 109.3 (d, *J* = 8.1 Hz), 32.9 (d, *J* = 25.2 Hz), 31.2 (d, *J* = 6.3 Hz), 31.1, 25.4 (d, *J* = 1.8 Hz), 22.4, 13.9.
^{19}F NMR (470 MHz, $CDCl_3$) δ -80.1 (dtd, *J* = 38.8, 17.5, 4.1 Hz).
HRMS (ESI+) calc'd for $C_9H_{16}FO^+$ $[M+H]^+$: 159.1180, found: 159.1184.
IR (neat) 2959, 2932, 2864, 1667, 1364, 1250, 910, 732 cm^{-1}.

(*Z*)-3-fluoro-*N*-methoxy-*N*-methylpent-2-enamide (**12b**)



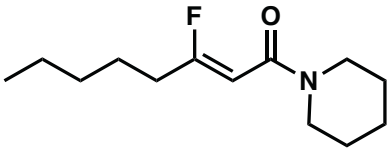
Column chromatography (SiO_2, eluting with 1:4→1:2 Et_2O:hexanes) afforded the desired product as a colorless oil (58.0 mg, 72%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 (d, *J* = 33.8 Hz, 1H), 3.65 (s, 3H), 3.17 (s, 3H), 2.29 (dq, *J* = 14.9, 7.5 Hz, 2H), 1.16 – 1.10 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5 (d, *J* = 284.8 Hz), 164.6, 96.0, 61.5, 32.1, 26.5 (d, *J* = 25.3 Hz), 10.3 (d, *J* = 3.9 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -85.5 (bs).
HRMS (ESI+) calc'd for $C_7H_{13}FNO_2^+$ $[M+H]^+$: 162.0925, found: 162.0928.
IR (neat) 2977, 2941, 2246, 1686, 1647, 1378, 1181, 1104, 1060, 978, 878, 811, 730 cm^{-1}.

(*Z*)-3-fluoro-*N*-phenylhept-2-enamide (**13b**)



Column chromatography (SiO_2, eluting with 3:7→2:1 Et_2O:hexanes) afforded the desired product as a white solid (61.4 mg, 56%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 11.7 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 38.3 Hz, 1H), 2.30 (dt, *J* = 18.3, 7.5 Hz, 2H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1 (d, *J* = 273.0 Hz), 161.7, 137.9, 129.0, 124.4, 120.2, 103.7 (d, *J* = 7.1 Hz), 32.3 (d, *J* = 25.9 Hz), 27.7 (d, *J* = 1.9 Hz), 22.0, 13.7 (d, *J* = 2.2 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -88.6 (dtd, *J* = 37.5, 18.3, 11.8 Hz).
HRMS (ESI+) calc'd for $C_{13}H_{17}FNO_2^+$ $[M+H]^+$: 222.1289, found: 222.1281.
IR (neat) 3274, 3138, 2956, 1689, 1646, 1599, 1550, 1441, 1375, 1310, 1253, 1151, 900, 752, 688 cm^{-1}.

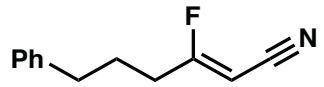
(*Z*)-3-fluoro-1-(piperidin-1-yl)oct-2-en-1one (**14b**)



Column chromatography (SiO_2, eluting with 1:3→4:1 Et_2O:hexanes) afforded the desired product as a colorless oil (65.4 mg, 57%).

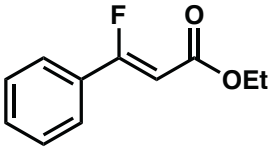
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.18 (d, *J* = 38.5 Hz, 1H), 3.55 (t, *J* = 5.6 Hz, 2H), 3.39 (t, *J* = 5.5 Hz, 2H), 2.20 (dt, *J* = 15.8, 7.6 Hz, 2H), 1.63 – 1.59 (m, 2H), 1.56 – 1.49 (m, 6H), 1.32 – 1.27 (m, 4H), 0.86 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1 (d, *J* = 269.0 Hz), 163.2, 100.4 (d, *J* = 13.9 Hz), 47.9, 42.4, 32.2 (d, *J* = 25.7 Hz), 31.1, 26.5, 25.5, 25.4 (d, *J* = 1.9 Hz), 24.6, 22.4, 14.0.
^{19}F NMR (565 MHz, $CDCl_3$) δ -92.4 (dt, *J* = 38.4, 16.4 Hz).
HRMS (APCI+) calc'd for $C_{13}H_{23}FNO^+$ $[M+H]^+$: 228.1758, found: 228.1761.
IR (neat) 3067, 2932, 2857, 1690, 1623, 1439, 1254, 1227, 1025, 729 cm^{-1}.

(*Z*)-3-fluoro-6-phenylhex-2-enenitrile (**15b**)



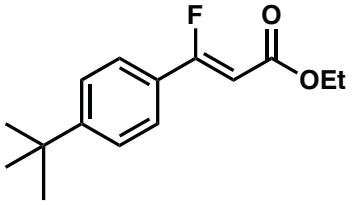
Column chromatography (SiO_2, eluting with 1:3→4:1 Et_2O:hexanes) afforded the desired product as a colorless oil (46.5 mg, 49%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.17 (d, *J* = 6.9 Hz, 2H), 4.77 (d, *J* = 32.6 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.35 (dt, *J* = 15.9, 7.6 Hz, 2H), 1.91 (p, *J* = 7.6 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6 (d, *J* = 285.1 Hz), 140.4, 128.7, 128.5, 126.5, 112.9 (d, *J* = 3.2 Hz), 79.1 (d, *J* = 13.8 Hz), 34.7, 31.6 (d, *J* = 22.0 Hz), 26.8 (d, *J* = 1.4 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -85.9 (dt, *J* = 33.1, 16.7 Hz).
HRMS (APCI+) calc'd for $C_{21}H_{34}FO_2^+$ $[M+H]^+$: 337.2537, found: 337.2537.
IR (neat) 3085, 2939, 2231, 1669, 1496, 1454, 1333, 1176, 910, 886, 732, 699 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-phenylacrylate (**16b**)



Column chromatography (SiO_2, eluting with 1:30 Et_2O:hexanes) afforded the desired product as a colorless oil (63.0 mg, 65%).
In accordance with previously reported spectra.[14c]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.90 (d, *J* = 33.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -97.1 (d, *J* = 33.3 Hz).

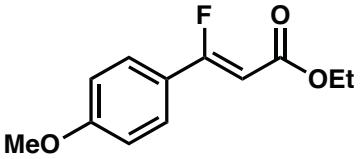
ethyl (*Z*)-3-(4-(*tert*-butyl)phenyl)-3-fluoroacrylate (**17b**)



Column chromatography (SiO_2, eluting with 1:15→1:12 Et_2O:hexanes) afforded the desired product as a light yellow oil (98.5 mg, 79%).

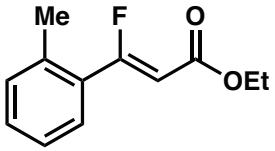
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 33.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.34 – 1.31 (m, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6 (d, *J* = 277.2 Hz), 164.3 (d, *J* = 2.1 Hz), 155.3, 127.9 (d, *J* = 26.0 Hz), 125.9 (d, *J* = 1.8 Hz), 125.6 (d, *J* = 8.0 Hz), 96.4 (d, *J* = 6.9 Hz), 60.4, 35.1, 31.2, 14.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ -97.0 (d, *J* = 33.2 Hz).
HRMS (APCI+) calc'd for $C_{15}H_{20}FO_2^+$ $[M+H]^+$: 251.1442, found: 251.1443.
IR (neat) 3083, 2964, 1721, 1702, 1653, 1331, 1283, 1269, 1158, 1110, 828, 731 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-methoxyphenyl)acrylate (**18b**)



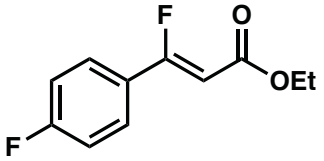
Column chromatography (SiO_2, eluting with 1:15→1:12 Et_2O:hexanes) afforded the desired product as a colorless oil (89.0 mg, 79%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 33.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.31 (t, *J* = 7.1, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6 (d, *J* = 276.2 Hz), 164.4 (d, *J* = 2.2 Hz), 162.3, 127.5 (d, *J* = 8.2 Hz), 123.0 (d, *J* = 26.3 Hz), 114.4 (d, *J* = 2.0 Hz), 95.2 (d, *J* = 7.0 Hz), 60.3, 55.5, 14.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ -96.7 (d, *J* = 32.9 Hz).
HRMS (APCI+) calc'd for $C_{12}H_{14}FO_3^+$ $[M+H]^+$: 225.0921, found: 225.0920.
IR (neat) 2980, 2936, 1717, 1648, 1605, 1513, 1287, 1255, 1151, 1023, 826, 729 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(2-methylphenyl)acrylate (**19b**)



Column chromatography (SiO_2, eluting with 1:1:24 CH_2Cl_2:Et_2O:hexanes) afforded the desired product as a colorless oil (55.0 mg, 53%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 5.57 (d, *J* = 32.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.45 (d, *J* = 3.5 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6 (d, *J* = 283.4 Hz), 164.0 (d, *J* = 2.9 Hz), 137.3, 131.3, 131.0, 129.1 (d, *J* = 5.7 Hz), 126.1, 101.7 (d, *J* = 7.4 Hz), 60.5, 20.7 (d, *J* = 3.9 Hz), 14.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ -78.5 (dd, *J* = 31.8, 4.0 Hz).
HRMS (APCI+) calc'd for $C_{12}H_{14}FO_2^+$ $[M+H]^+$: 209.0972, found: 209.0970.
IR (neat) 3087, 2981, 2934, 1724, 1707, 1658, 1324, 1264, 1154, 1045, 1024, 835, 766, 725 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-fluorophenyl)acrylate (**20b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (80.5 mg, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 33.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

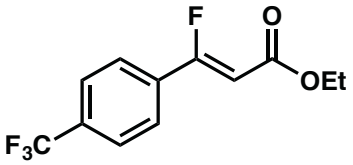
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 165.4 (d, *J* = 277.0 Hz), 164.1 – 163.3 (m), 128.0 (t, *J* = 8.4 Hz), 127.0 (dd, *J* = 26.9, 3.3 Hz), 116.2 (dd, *J* = 22.3, 1.7 Hz), 97.2 (dd, *J* = 6.8, 1.5 Hz), 60.5, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.6 (d, *J* = 33.6 Hz, 1F), -108.3 – -108.4 (m, 1F).

HRMS (APCI+) calc'd for $C_{11}H_{11}F_2O_2^+$ $[M+H]^+$: 213.0722, found: 213.0721.

IR (neat) 3093, 2984, 1720, 1655, 1604, 1510, 1281, 1237, 1157, 1105, 1056, 894, 830 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-(trifluoromethyl)phenyl)acrylate (**21b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (96.0 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 5.97 (d, *J* = 32.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

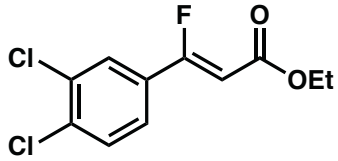
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5 (d, *J* = 277.4 Hz), 163.6 (d, *J* = 2.2 Hz), 134.2 (d, *J* = 26.9 Hz), 133.2 (q, *J* = 33.0 Hz), 126.1 (d, *J* = 7.7 Hz), 126.0 – 126.0 (m), 122.8 (q, *J* = 272.7 Hz), 99.4 (d, *J* = 6.9 Hz), 60.8, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -64.2 (s, 3F), -98.2 (d, *J* = 32.4 Hz, 1F).

HRMS (APCI+) calc'd for $C_{12}H_{11}F_4O_2^+$ $[M+H]^+$: 263.0690, found: 263.0697.

IR (neat) 3089, 2986, 1723, 1659, 1414, 1320, 1279, 1165, 1127, 1114, 1068, 1013, 833 cm^{-1}.

ethyl (*Z*)-3-(3,4-dichlorophenyl)-3-fluoroacrylate (**22b**)

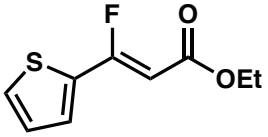


Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (93.0 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.88 (d, *J* = 32.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

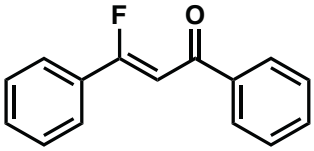
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, *J* = 277.2 Hz), 163.5 (d, *J* = 2.4 Hz), 136.0, 133.6 (d, *J* = 2.1 Hz), 131.1 (d, *J* = 1.9 Hz), 130.7 (d, *J* = 27.6 Hz), 127.5 (d, *J* = 8.2 Hz), 124.7 (d, *J* = 7.6 Hz), 98.8 (d, *J* = 6.6 Hz), 60.8, 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -98.3 (d, *J* = 33.0 Hz).
HRMS (APCI+) calc'd for $C_{11}H_{10}Cl_2FO_2^+$ [M+H]$^+$: 263.0036, found: 263.0038.
IR (neat) 3100, 2990, 2911, 1700, 1656, 1468, 1395, 1330, 1274, 1253, 1024, 847, 816, 764 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(thiophen-2-yl)acrylate (**23b**)



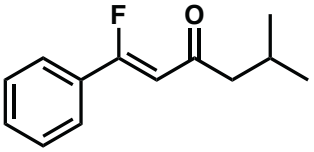
Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (80.0 mg, 80%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H), 7.09 – 7.06 (m, 1H), 5.71 (d, *J* = 32.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, *J* = 2.7 Hz), 161.7 (d, *J* = 274.0 Hz), 133.9 (d, *J* = 31.7 Hz), 129.6, 128.7 (d, *J* = 4.9 Hz), 128.3, 96.1 (d, *J* = 6.5 Hz), 60.5, 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -92.0 (d, *J* = 32.7 Hz).
HRMS (APCI+) calc'd for $C_9H_{10}FO_2S^+$ [M+H]$^+$: 201.0380, found: 201.0377.
IR (neat) 3094, 2981, 1715, 1699, 1642, 1368, 1264, 1226, 1150, 1038, 824, 707 cm^{-1}.

(*Z*)-3-fluoro-1,3-diphenylprop-2-en-1-one (**24b**)



Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a yellow oil (74.0 mg, 66%).
In accordance with previously reported spectra.[11a]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.45 (m, 5H), 6.80 (d, *J* = 34.2 Hz, 1H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -98.3 (d, *J* = 34.2 Hz).

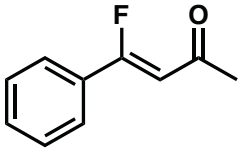
(*Z*)-3-fluoro-1,3-diphenylprop-2-en-1-one (**25b**)



Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a yellow oil (74.0 mg, 54%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.06 (d, *J* = 38.9 Hz, 1H), 2.65 (dd, *J* = 6.9, 2.1 Hz, 2H), 2.26 – 2.18 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

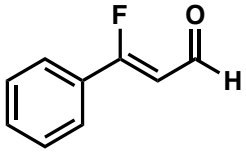
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7 (d, *J* = 2.7 Hz), 164.7 (d, *J* = 274.1 Hz), 131.6, 130.7 (d, *J* = 27.5 Hz), 129.0 (d, *J* = 2.1 Hz), 125.8 (d, *J* = 8.0 Hz), 106.7 (d, *J* = 9.5 Hz), 52.8 (d, *J* = 5.0 Hz), 24.9 (d, *J* = 1.4 Hz), 22.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -128.2 (d, *J* = 38.6 Hz).
HRMS (APCI+) calc'd for $C_{13}H_{16}FO^+$ $[M+H]^+$: 207.1180, found: 207.1185.
IR (neat) 3066, 2957, 2871, 1639, 1619, 1578, 1325, 1286, 1191, 1003, 766, 687 cm^{-1}.

(*Z*)-4-fluoro-4-phenylbut-3-en-2-one (**26b**)



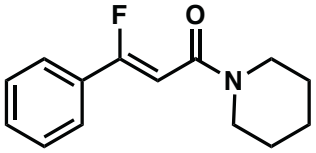
Column chromatography (SiO_2, eluting with 1:10 Et_2O:hexanes) afforded the desired product as a white solid (49.0 mg, 60%).
In accordance with previously reported spectra.[14e]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.53 – 7.40 (m, 3H), 6.06 (d, *J* = 38.6 Hz, 1H), 2.48 (d, *J* = 4.2 Hz, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -97.6 (dd, *J* = 38.6, 3.5 Hz).

(*Z*)-3-fluoro-3-phenylacrylaldehyde (**27b**)



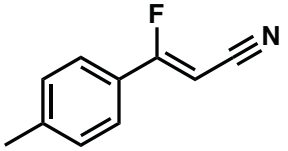
Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a yellow solid (423.0 mg, 63%).
In accordance with previously reported spectra.[11a]
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.18 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.09 (dd, *J* = 33.8, 7.6 Hz, 1H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -106.0 (d, *J* = 33.7 Hz).

(*Z*)-3-fluoro-3-phenyl-1-(piperidin-1-yl)prop-2-en-1-one (**28b**)



Column chromatography (SiO_2, eluting with 3:1→ 9:1 Et_2O:hexanes) afforded the desired product as a white solid (75.0 mg, 64%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.40 – 7.38 (m, 3H), 5.97 (d, *J* = 38.4 Hz, 1H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.49 (t, *J* = 5.5 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.60 (h, *J* = 5.5 Hz, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 159.5 (d, *J* = 260.2 Hz), 131.0 (d, *J* = 28.0 Hz), 130.4, 128.8 (d, *J* = 2.1 Hz), 125.0 (d, *J* = 7.2 Hz), 99.6 (d, *J* = 16.1 Hz), 48.0 (d, *J* = 1.9 Hz), 42.7, 26.7, 25.6, 24.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ -107.4 (d, *J* = 39.3 Hz).
HRMS (APCI+) calc'd for $C_{14}H_{17}FNO^+$ $[M+H]^+$: 234.1289, found: 234.1288.
IR (neat) 3062, 2935, 2856, 1663, 1611, 1436, 1246, 1164, 1006, 871, 765 cm^{-1}.

(*Z*)-3-fluoro-3-(4-methylphenyl)acrylonitrile (**29b**)



Column chromatography (SiO_2, eluting with 1:24→1:15 Et_2O:hexanes) afforded the desired product as a white solid (54.6 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 5.36 (d, *J* = 32.9 Hz, 1H), 2.41 (s, 3H).

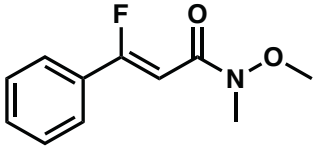
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9 (d, *J* = 274.3 Hz), 143.7, 129.9 (d, *J* = 2.1 Hz), 125.7 (d, *J* = 24.4 Hz), 125.5 (d, *J* = 7.9 Hz), 113.9, 75.5 (d, *J* = 16.0 Hz), 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.0 (d, *J* = 33.0 Hz).

HRMS (APCI+) calc'd for $C_{10}H_9FN^+$ $[M+H]^+$: 162.0714, found: 162.0709.

IR (neat) 3077, 2922, 2218, 1642, 1605, 1514, 1330, 1075, 822, 774 cm^{-1}.

(*Z*)-3-fluoro-*N*-methoxy-*N*-methyl-3-phenylacrylamide (**30b**)



Column chromatography (SiO_2, eluting with 1:1→3:1 Et_2O:hexanes) afforded the desired product as a yellow oil (74.2 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.44 – 7.38 (m, 3H), 6.37 (d, *J* = 33.5 Hz, 1H), 3.71 (s, 3H), 3.24 (s, 3H).

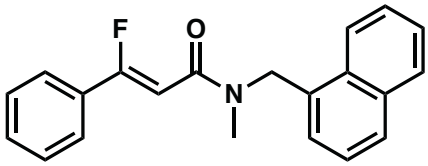
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9 (d, *J* = 275.1 Hz), 164.4, 131.3 (d, *J* = 26.6 Hz), 131.0, 128.8 (d, *J* = 2.0 Hz), 125.5 (d, *J* = 7.7 Hz), 95.5, 61.7, 32.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.7 (d, *J* = 34.0 Hz).

HRMS (ESI+) calc'd for $C_{11}H_{13}FNO_2^+$ $[M+H]^+$: 210.0925, found: 210.0926.

IR (neat) 3065, 2937, 1667, 1632, 1495, 1376, 1177, 995, 766 cm^{-1}.

(*Z*)-3-fluoro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylacrylamide (**31b**)



Column chromatography (SiO_2, eluting with 0:1→1:13 EtOAc:CH_2Cl_2) afforded the desired product as a yellow oil (344.3 mg, 55%).

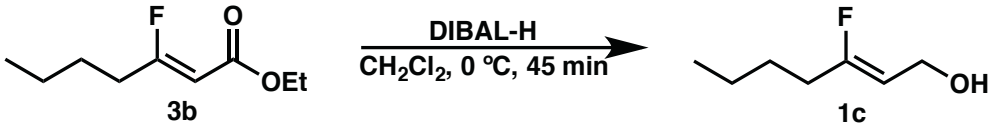
^{1}H NMR (mixture of rotamers, 600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1.5H), 7.61 – 7.24 (m, 14H), 6.09 (d, *J* = 37.4 Hz, 1H), 6.08 (d, *J* = 35.9 Hz, 0.5H), 5.17 (s, 2H), 5.08 (s, 1H), 3.07 (s, 1.4H), 2.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 164.4, 161.8 (d, *J* = 265.5 Hz), 160.6 (d, *J* = 263.1 Hz), 133.8, 133.7, 132.1, 131.6, 131.4, 130.8 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 7.4 Hz), 130.4, 130.4, 128.9, 128.6 (d, *J* = 1.9 Hz), 128.5, 128.4, 128.2, 126.9, 126.5, 125.9, 125.9, 125.5, 125.1, 125.0 (d, *J* = 7.3 Hz), 124.9 (d, *J* = 7.4 Hz), 123.8, 123.6, 122.1, 99.2 (d, *J* = 14.4 Hz), 98.6 (d, *J* = 13.1 Hz), 51.7, 48.1, 34.9 (d, *J* = 2.4 Hz), 33.4.

^{19}F NMR (mixture of rotamers, 565 MHz, $CDCl_3$) δ -104.1 (d, *J* = 35.9 Hz, 0.5F), -105.3 (d, *J* = 37.4 Hz, 1F).
HRMS (APCI+) calc'd for $C_{21}H_{19}FNO^+$ $[M+H]^+$: 320.1445, found: 320.1449.
IR (neat) 3059, 924, 1664, 1610, 1579, 1398, 1115, 1044, 791, 763, 731, 688, 596 cm^{-1}.

1.4.5 Procedures for Derivatizations of Fluorinated Michael Acceptors

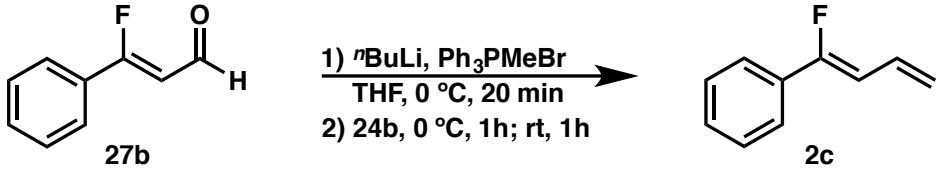
Reduction of ester (**3b**):



Prepared according to a modified literature procedure.[17] Ester (**3b**) (405 mg, 2.32 mmol, 1.0 equiv) was added to 25-mL Schlenk flask containing CH_2Cl_2 (4.6 mL, 0.5 M). The reaction vessel was placed in an ice water bath and the reaction mixture was allowed to reach 0 °C before the dropwise addition (9 minutes) of DIBAL-H (1.0 M in hexanes, 6.17 mL, 6.17 mmol, 2.5 equiv). After stirring for 45 min at 0 °C, 3.5 M HCl (4 mL) was added dropwise. The reaction was transferred to a separatory funnel and diluted with CH_2Cl_2 (40 mL) and 3.5 M HCl (40 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 40 mL). The organics were dried over Na_2SO_4, filtered, concentrated, and the crude residue purified by silica gel column chromatography (1:1 Et_2O:hexanes) to afford **1c**, (*Z*)-3-fluorohept-2-en-1-ol, as a colorless oil (267.0 mg, 87%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.81 (dt, *J* = 37.2, 7.1 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 2H), 2.39 (bs, 1H), 2.17 (dt, *J* = 17.5, 7.5 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 162.2 (d, *J* = 257.9 Hz), 105.1 (d, *J* = 13.4 Hz), 55.6 (d, *J* = 7.8 Hz), 31.9 (d, *J* = 27.0 Hz), 28.5 (d, *J* = 1.6 Hz), 22.4, 13.9.
^{19}F NMR (470 MHz, CD_2Cl_2) δ -106.1 (dt, *J* = 36.2, 17.6 Hz).
HRMS (ESI+) calc'd for $C_7H_{14}FO^+$ $[M+H]^+$: 133.1023, found: 133.1022.
IR (neat) 3316, 2959, 2933, 2874, 1706, 1159, 1073, 1006, 972 cm^{-1}.

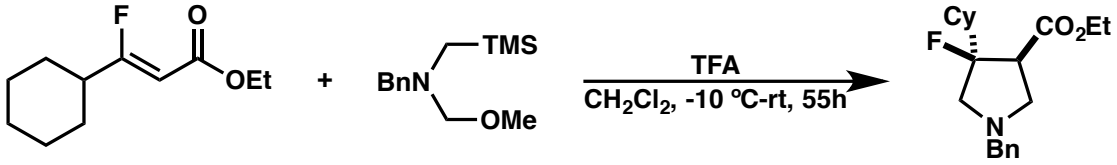
Witting olefination of aldehyde (**27b**):



Prepared according to a modified literature procedure.[18] To a suspension of methyltriphenylphosphonium bromide (137 mg, 0.375 mmol, 1.25 equiv) in THF (1.9 mL, 0.2 M wrt Ph_3PMeBr) at 0 °C was added ^{n}BuLi (2.5 M in hexanes, 150 μL, 0.375 mmol, 1.25 equiv) dropwise. The reaction was stirred for 20 min before **27b** (45 mg, 0.3 mmol, 1.0 equiv) in a solution of THF (300 μL, 1.0 M wrt **27b**) was added dropwise (4 min). After stirring at 0 °C for 1 h, the reaction was warmed to rt and stirred for another hour before the addition of saturated NH_4Cl (1 mL). The reaction mixture was transferred to a separatory funnel and diluted with Et_2O (40 mL) and NH_4Cl (40 mL). The phases were separated and the aqueous layer extracted with Et_2O (3 x 40 mL). The organics were washed with brine (120 mL), dried over Na_2SO_4, filtered, concentrated, and the crude residue purified by silica gel column chromatography (hexanes) to afford **2c**, (*Z*)-(1-fluorobuta-1,3-dien-1-yl)benzene, as a colorless oil (29.0 mg, 65%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (dt, *J* = 17.2, 10.6 Hz, 1H), 6.12 (dd, *J* = 35.1, 10.8 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9 (d, *J* = 255.4 Hz), 132.1 (d, *J* = 27.7 Hz), 129.2, 129.0 (d, *J* = 6.6 Hz), 128.7 (d, *J* = 2.2 Hz), 124.3 (d, *J* = 7.5 Hz), 117.5 (d, *J* = 3.4 Hz), 107.1 (d, *J* = 13.8 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -118.5 (d, *J* = 35.0 Hz).
HRMS (EI+) calc'd for $C_{10}H_9F$: 148.0688, found: 148.0686.
IR (neat) 3089, 3061, 2925, 1649, 1494, 1449, 1320, 1281, 1009, 992, 901, 760, 603 cm^{-1}.

Cycloaddition of ester (**5b**):

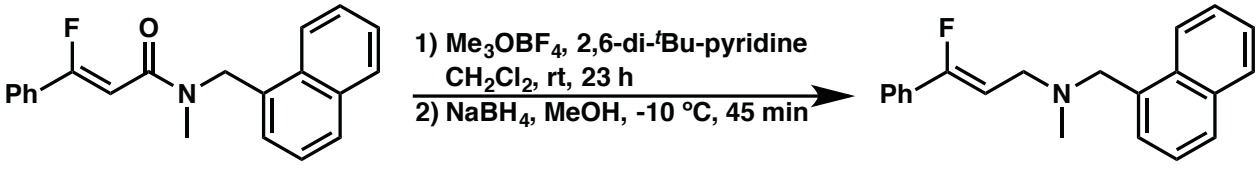


5b **3c**

Prepared according to a modified literature procedure.[19a] To a solution of **5b** (60 mg, 0.3 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL, 0.3 M) at -10 °C (ice-acetone slurry) was added trifluoroacetic acid (6 μL, 22 mol%) followed by dropwise addition of ylide[46] (214 mg, 0.9 mmol, 3.0 equiv). The reaction was warmed to rt. Addition ylide and TFA were added after 7 h (0.3 mmol ylide and 11 mol% TFA), 23 h (1.5 mmol ylide and 22 mol% TFA), 32 h (0.6 mmol ylide and 11 mol% TFA), 44 h (500 μL CH_2Cl_2, 2.0 mmol ylide, and 33 mol% TFA), and 53 h (1.5 mmol ylide and 11 mol% TFA). After 55 h, the reaction mixture was transferred to a separatory funnel with CH_2Cl_2 (100 mL), washed with saturated $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (1:7 EtOAc:hexanes) to afford **3c**, ethyl 1-benzyl-4-cyclohexyl-4-fluoropyrrolidine-3-carboxylate, as a colorless oil (61 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 4.26 – 4.11 (m, 2H), 3.73 (d, *J* = 13.1 Hz, 1H), 3.62 (d, *J* = 13.1 Hz, 1H), 3.19 – 3.10 (m, 2H), 2.98 (dd, *J* = 25.8, 11.2 Hz, 1H), 2.84 (tt, *J* = 6.7, 3.2 Hz, 1H), 2.68 (dd, *J* = 28.9, 11.2 Hz, 1H), 1.99 (d, *J* = 12.7 Hz, 1H), 1.92 (dt, *J* = 15.3, 12.3 Hz, 1H), 1.84 – 1.76 (m, 3H), 1.69 (d, *J* = 12.3 Hz, 1H), 1.31 – 0.94 (m, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7 (d, *J* = 7.1 Hz), 138.7, 128.7, 128.4, 127.2, 105.9 (d, *J* = 183.8 Hz), 61.4 (d, *J* = 25.8 Hz), 60.8, 60.1, 54.8, 49.2 (d, *J* = 22.1 Hz), 43.9 (d, *J* = 23.4 Hz), 27.7 (d, *J* = 7.1 Hz), 27.1 (d, *J* = 4.5 Hz), 26.3 (d, *J* = 10.7 Hz), 26.2, 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -153.3 (tq, *J* = 25.6, 13.7 Hz).
HRMS (ESI+) calc'd for $C_{20}H_{29}FNO_2^+$: 334.2177, found: 334.2173.
IR (neat) 3063, 3029, 2928, 2854, 2799, 1451, 1371, 1231, 1179, 1027, 911, 732, 699 cm^{-1}.

Reduction of amide (**31b**), generation of fluorine containing analog of Exoderil:



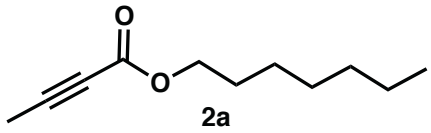
31b **4c**

Prepared according to a modified literature procedure.[20] In a nitrogen-filled glovebox, to a solution of **31b** (173.0 mg, 0.54 mmol, 1 equiv) in CH_2Cl_2 (17.2 mL, 0.031 M) was added 2,6-di-*tert*-butylpryidine (362 μL, 1.61 mmol, 2.92 equiv) followed by the portionwise addition (3 min) of trimethyloxonium tetrafluoroborate (216 mg, 1.46 mmol, 2.65 equiv). The reaction mixture was stirred for 23 h at rt, removed from the glovebox, placed under nitrogen from a Schlenk line, and submerged into an ice-acetone slurry (-10 °C). Anhydrous methanol (5.8 mL) was added dropwise (4 min) and the reaction was stirred for 10 min. Sodium borohydride (219 mg, 5.67 mmol, 10.3 equiv) was added in equal portions over 5 min and the reaction mixture stirred for 45 min at -10 °C. Saturated $NaHCO_3$ (15 mL) was added dropwise to the chilled reaction mixture. The biphasic mixture was diluted with CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ (50 mL) and the layers separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 70 mL), the organics combined, dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (1:15 EtOAc:hexanes) to afford **4c**, as a yellow oil (93.2 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.53 – 7.47 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 5.66 (dt, *J* = 37.1, 7.3 Hz, 1H), 4.00 (s, 2H), 3.45 (d, *J* = 7.3 Hz, 2H), 2.34 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 249.3 Hz), 134.9, 134.0, 132.6, 132.4 (d, *J* = 29.1 Hz), 129.0, 128.6, 128.6, 128.1, 127.6, 126.0, 125.7, 125.3, 124.7, 124.3 (d, *J* = 6.9 Hz), 103.1 (d, *J* = 15.3 Hz), 60.2, 51.5 (d, *J* = 4.4 Hz), 42.5.
^{19}F NMR (565 MHz, $CDCl_3$) δ -118.8 (d, *J* = 37.1 Hz).
HRMS (ESI+) calc'd for $C_{21}H_{21}FN^+$: 306.1653, found: 306.1651.
IR (neat) 3058, 3043, 2928, 2837, 2790, 1679, 1447, 1364, 1279, 1016, 980, 791, 774, 760, 689 cm^{-1}.

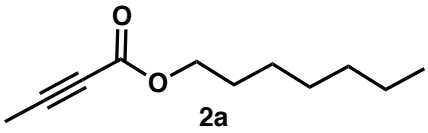
1.4.6 Spectra Data

^{1}H NMR (600 MHz, CD_2Cl_2)



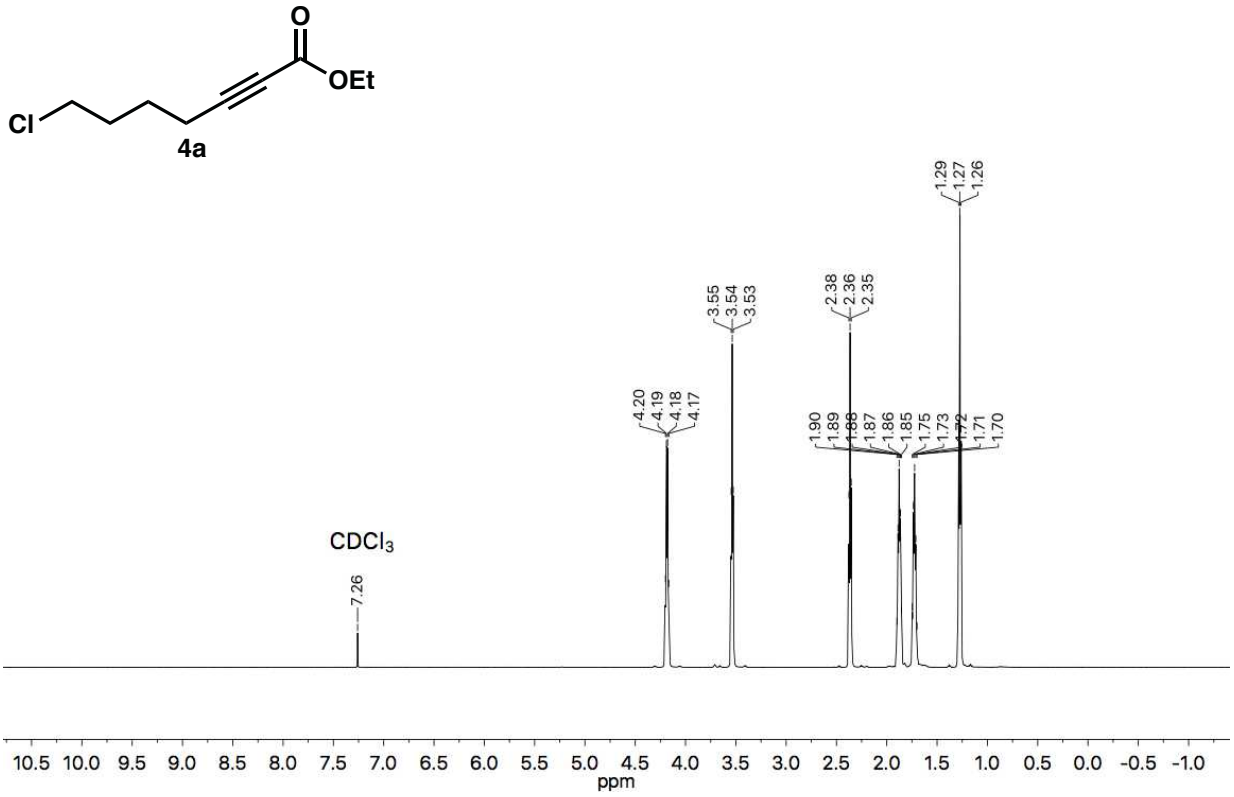
2a

^{13}C NMR (151 MHz, CD_2Cl_2)

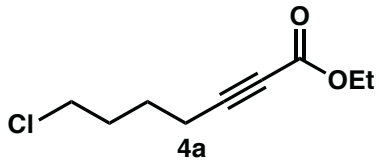


2a

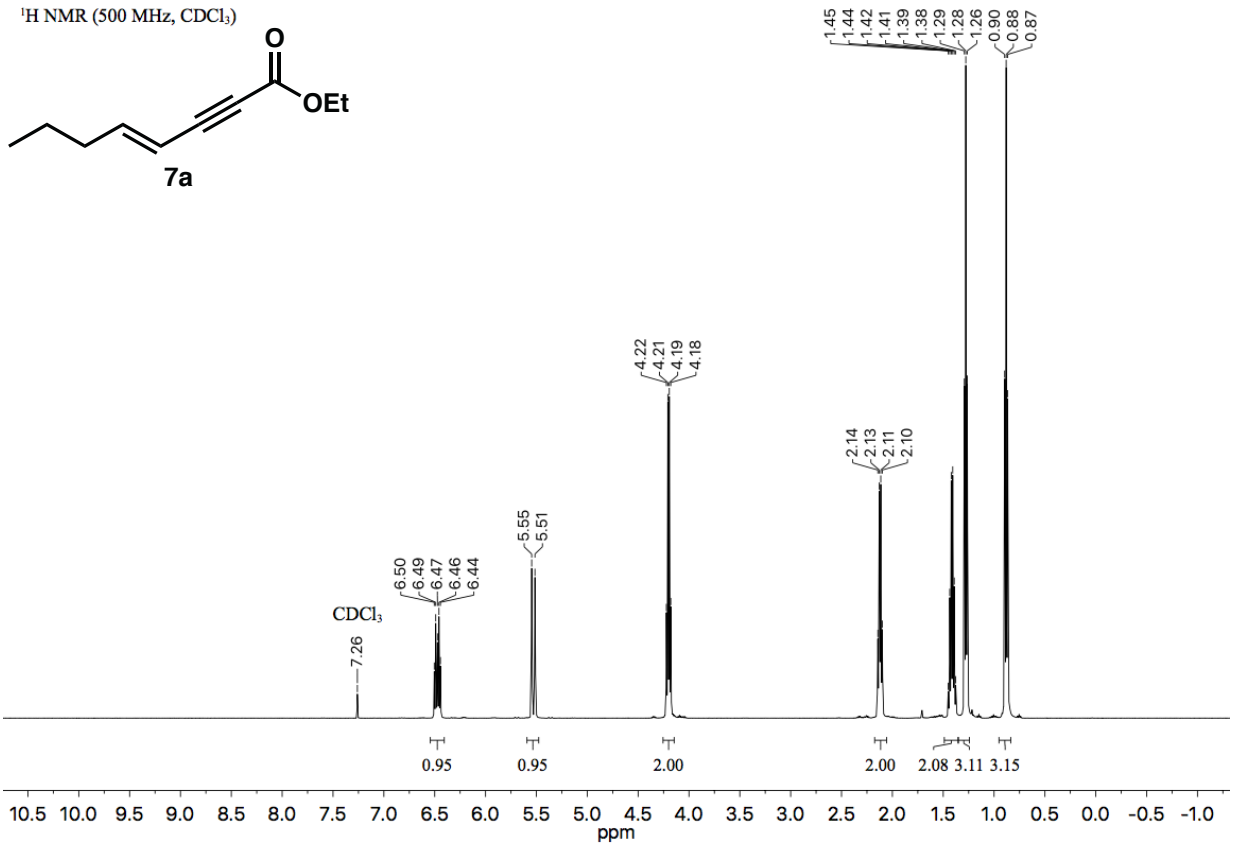
^{1}H NMR (600 MHz, $CDCl_3$)



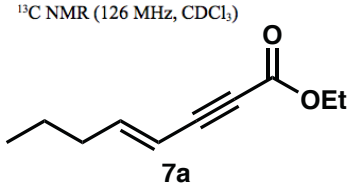
^{13}C NMR (151 MHz, $CDCl_3$)



4a

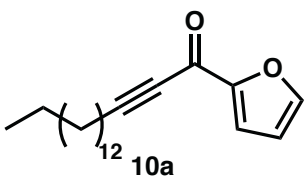

^{1}H NMR (500 MHz, CDCl$_3$)
O
OEt
7a
1.45
1.44
1.42
1.41
1.39
1.38
1.29
1.28
1.26
0.90
0.88
0.87
4.22
4.21
4.19
4.18
2.14
2.13
2.11
2.10
5.55
5.51
6.50
6.49
6.47
6.46
6.44
CDCl$_3$
7.26
0.95
0.95
2.00
2.00
2.08
3.11
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

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



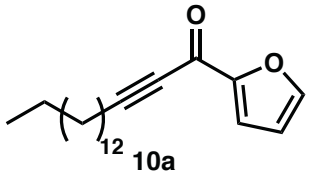
7a

^{1}H NMR (600 MHz, $CDCl_3$)



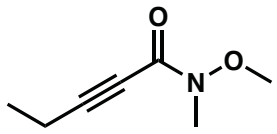
10a

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



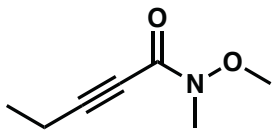
10a

^{1}H NMR (600 MHz, $CDCl_3$)



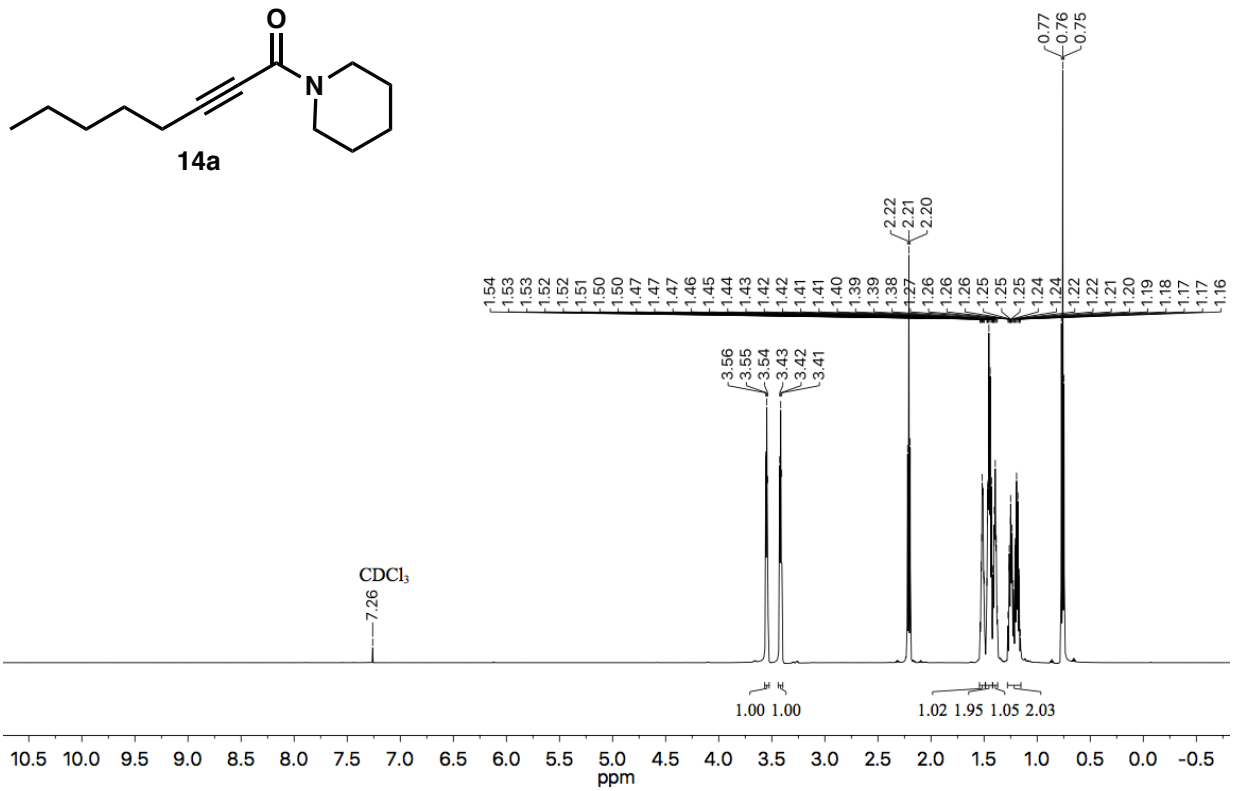
12a

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

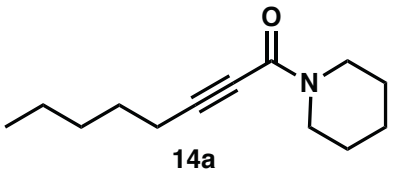


12a

^{1}H NMR (600 MHz, $CDCl_3$)

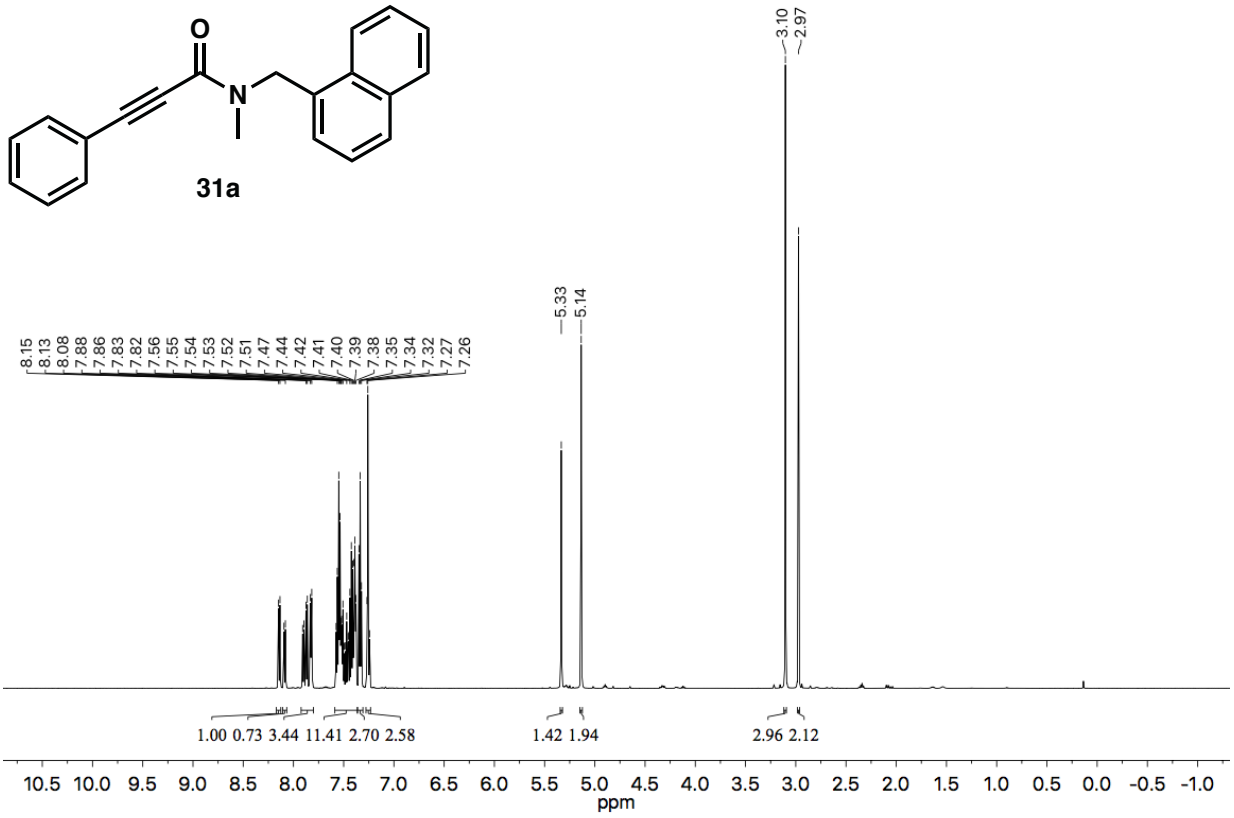


^{13}C NMR (151 MHz, $CDCl_3$)

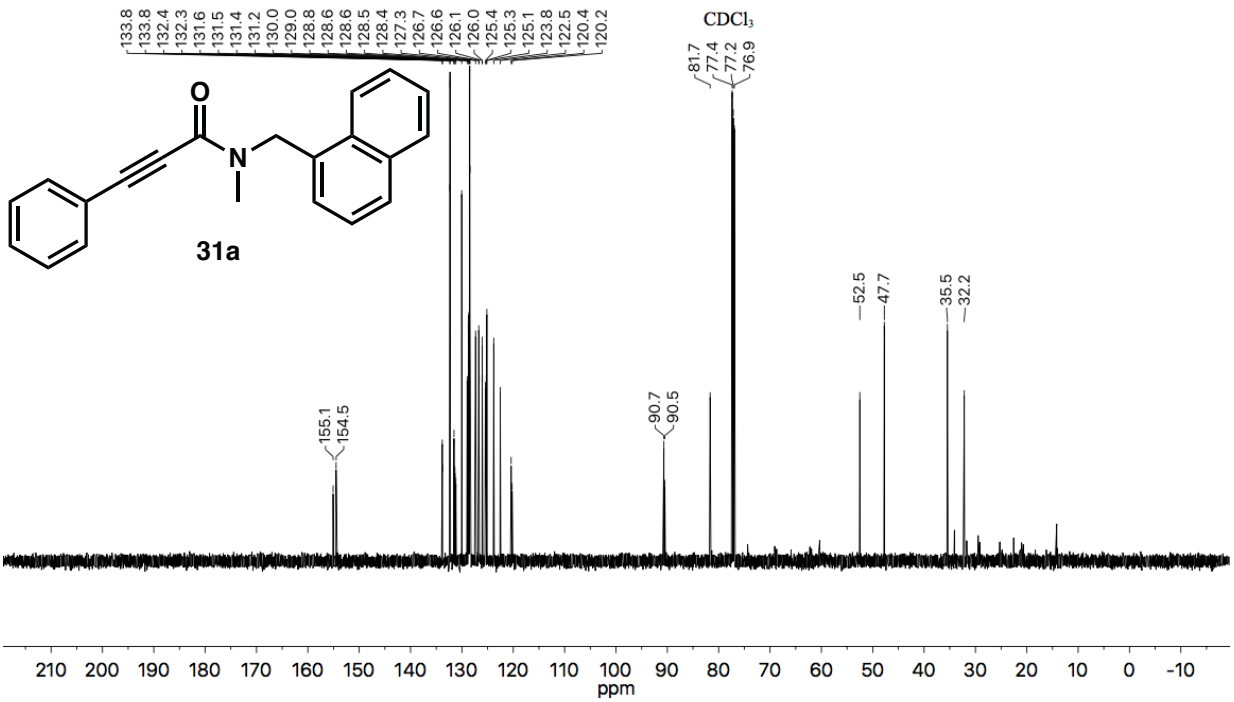


14a

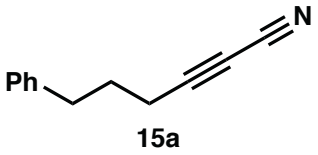
^{1}H NMR (600 MHz, $CDCl_3$)



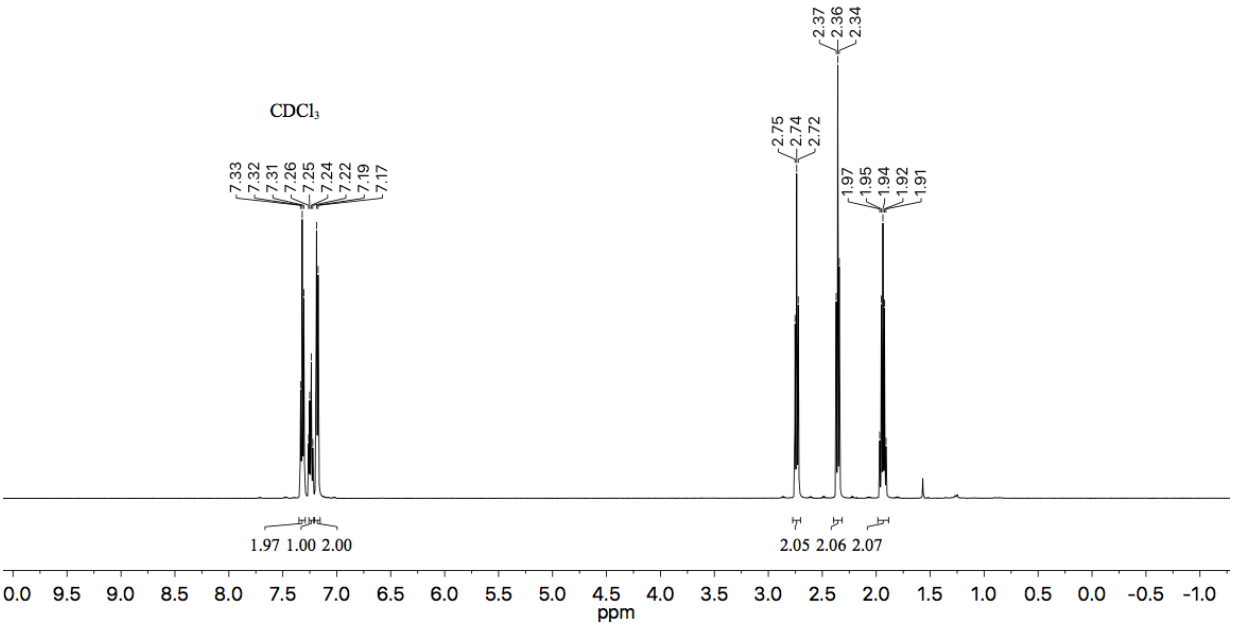
^{13}C NMR (151 MHz, $CDCl_3$)



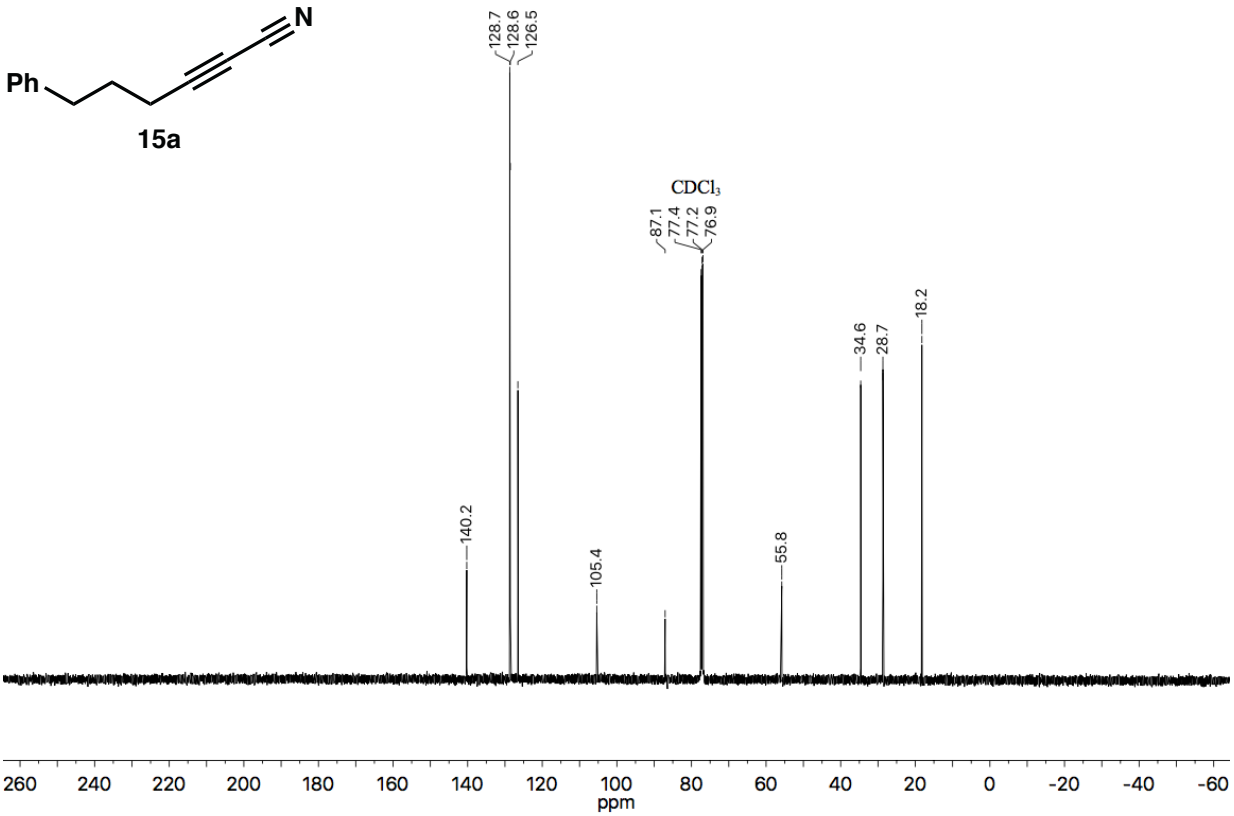
^{1}H NMR (500 MHz, $CDCl_3$)



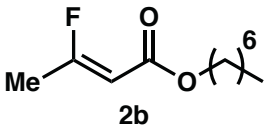
15a



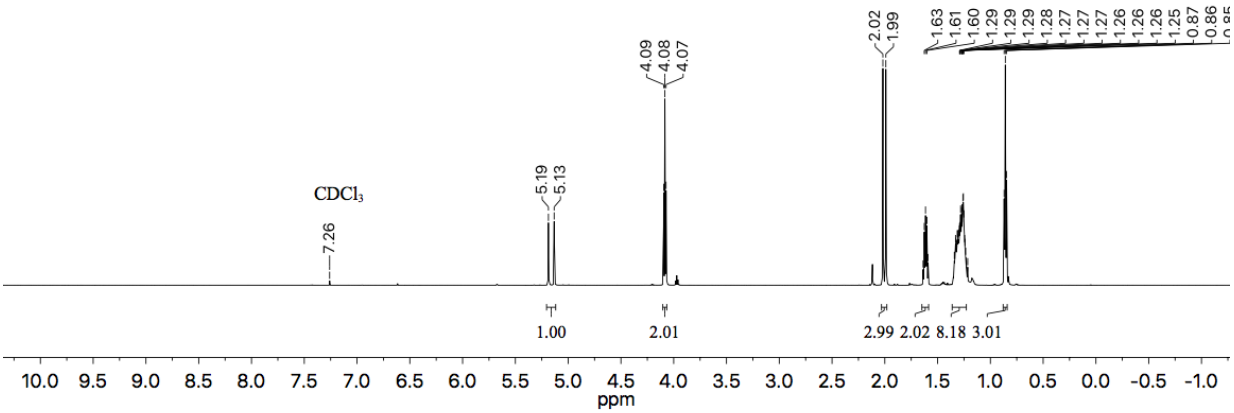
^{13}C NMR (126 MHz, $CDCl_3$)



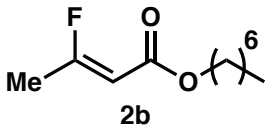
^{1}H NMR (600 MHz, $CDCl_3$)



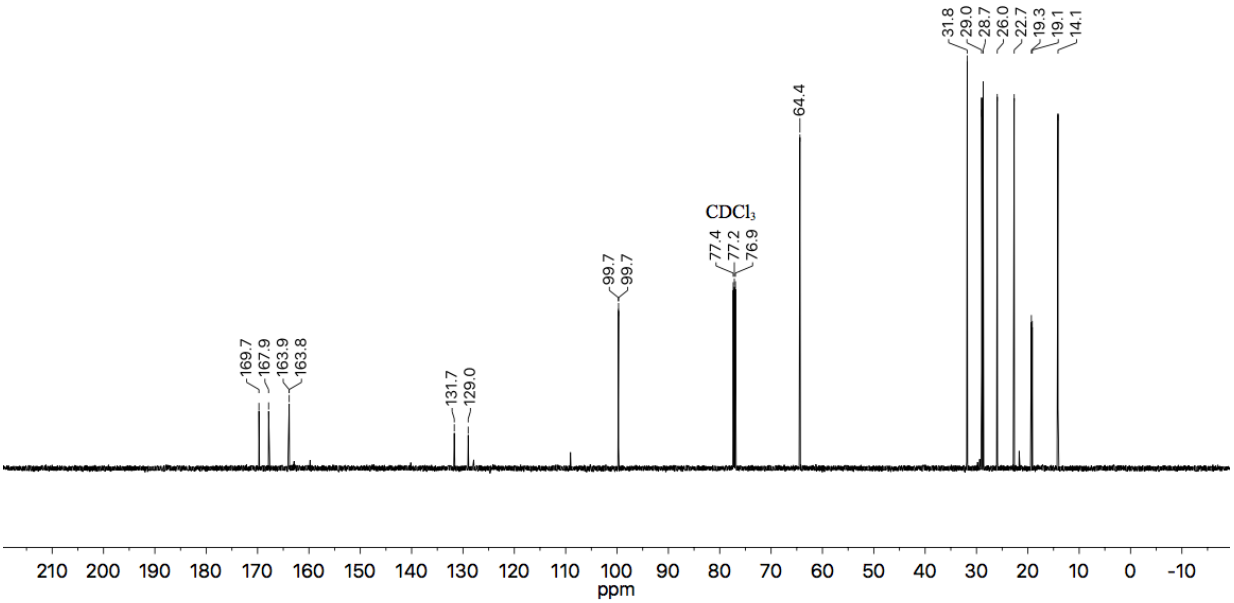
2b



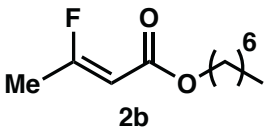
^{13}C NMR (151 MHz, $CDCl_3$)



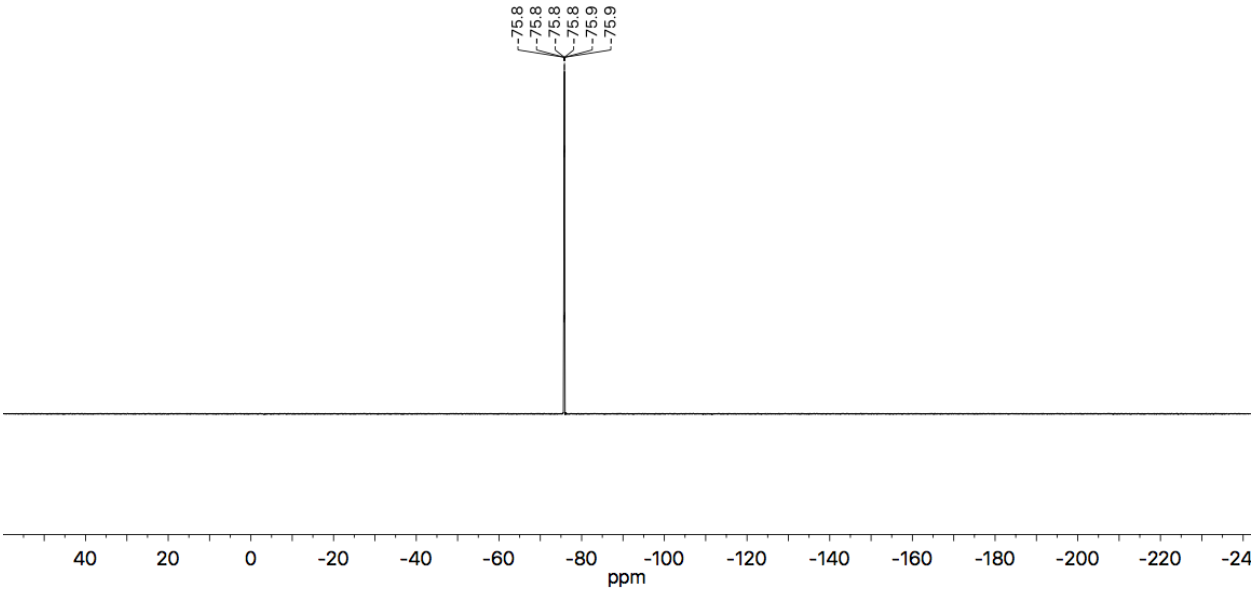
2b



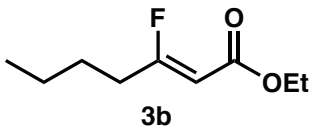
^{19}F NMR (565 MHz, $CDCl_3$)



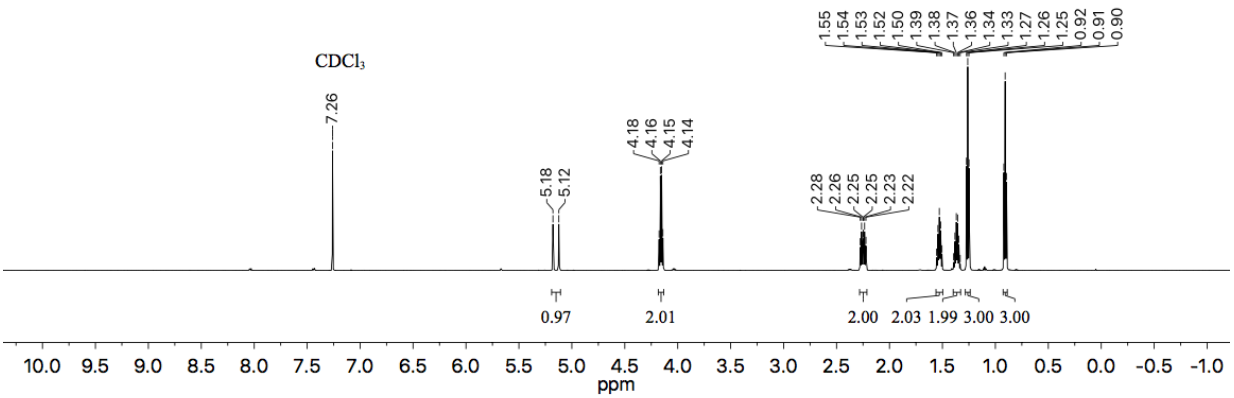
2b



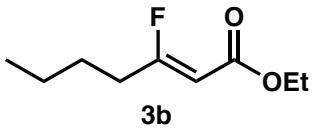
^{1}H NMR (600 MHz, $CDCl_3$)



3b

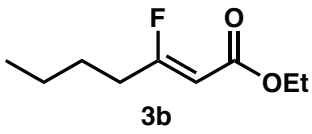


^{13}C NMR (151 MHz, $CDCl_3$)



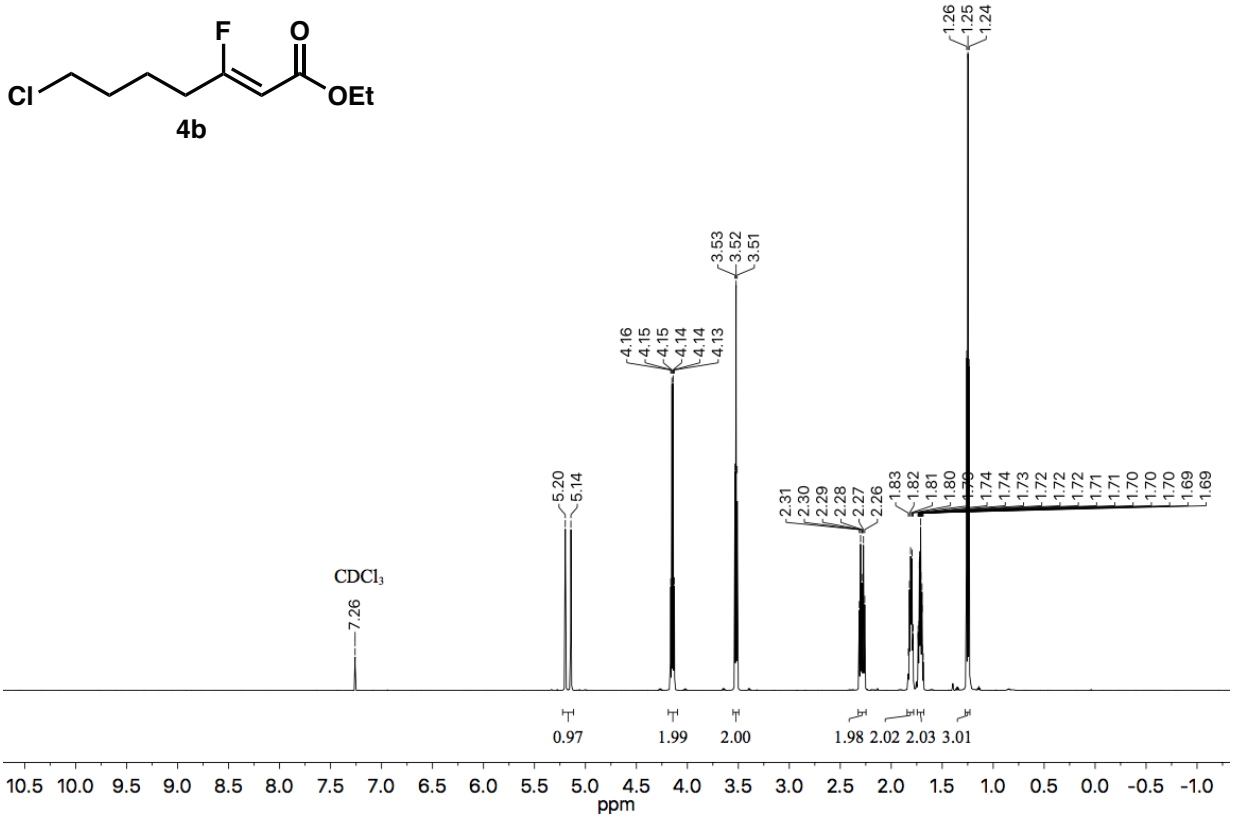
3b

^{19}F NMR (565 MHz, $CDCl_3$)

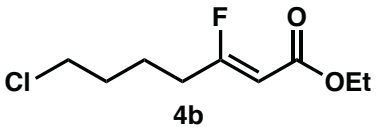


3b

^{1}H NMR (600 MHz, $CDCl_3$)

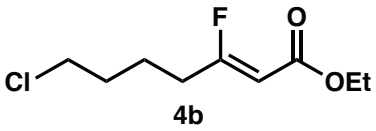


^{13}C NMR (151 MHz, $CDCl_3$)



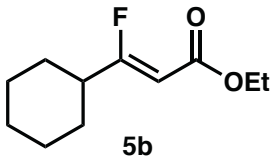
4b

^{19}F NMR (565 MHz, $CDCl_3$)



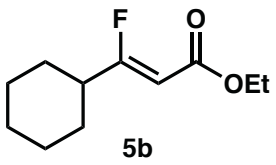
4b

^{1}H NMR (600 MHz, $CDCl_3$)



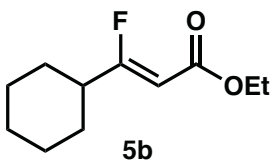
5b

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



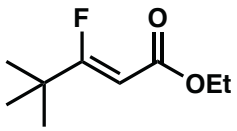
5b

^{19}F NMR (565 MHz, $CDCl_3$)



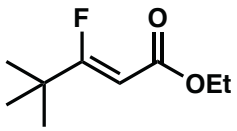
5b

^{1}H NMR (600 MHz, $CDCl_3$)



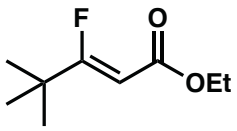
6b

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

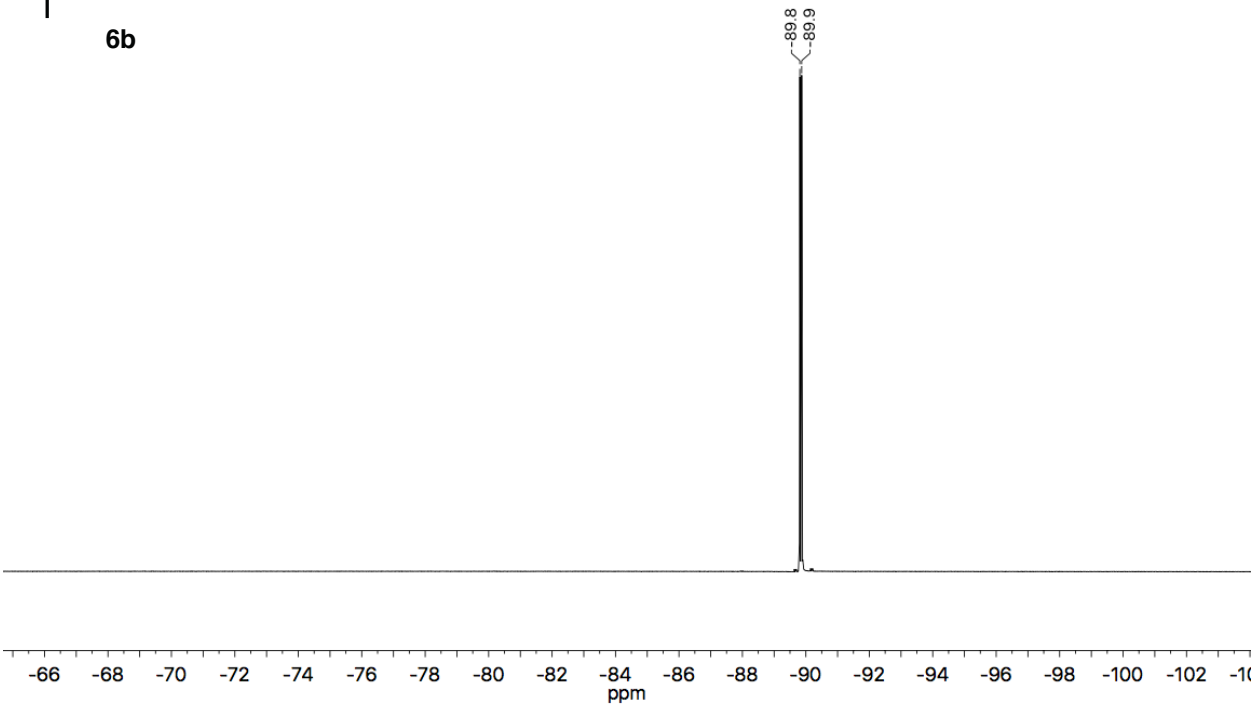


6b

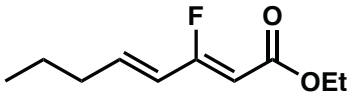
^{19}F NMR (565 MHz, $CDCl_3$)



6b

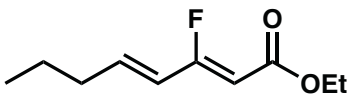


^{1}H NMR (600 MHz, $CDCl_3$)



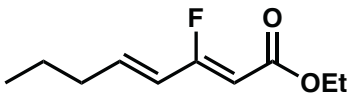
7b

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



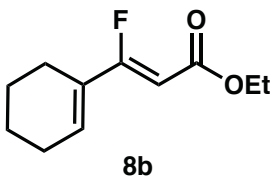
7b

^{19}F NMR (565 MHz, $CDCl_3$)



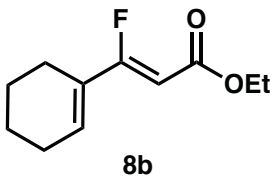
7b

^{1}H NMR (600 MHz, $CDCl_3$)



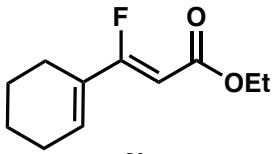
8b

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



8b

^{19}F NMR (565 MHz, $CDCl_3$)



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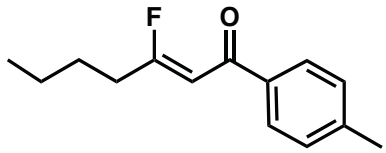
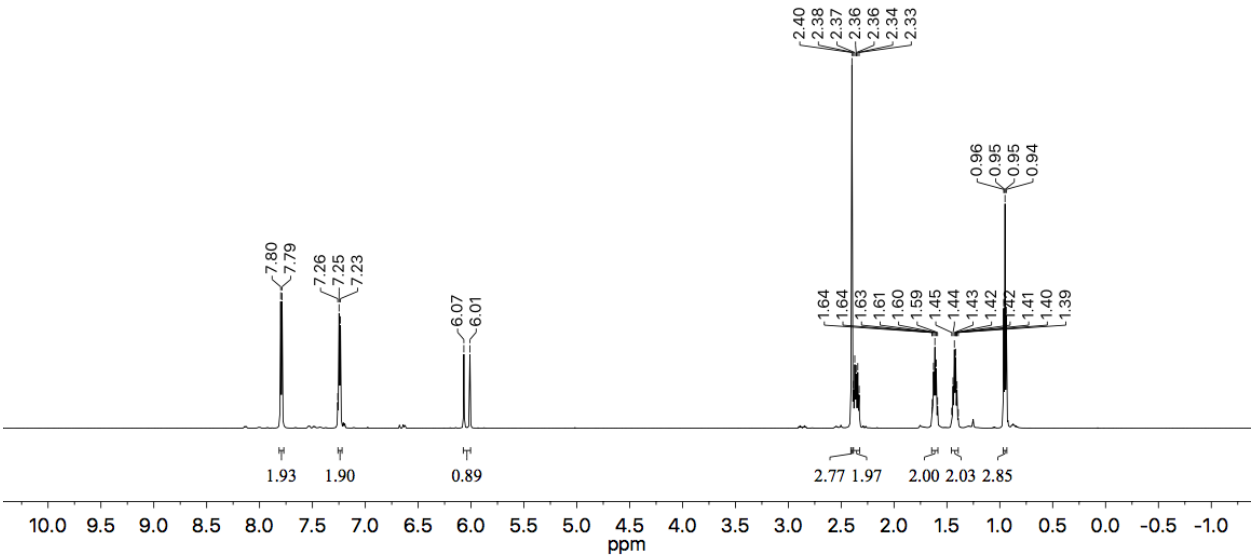

F
O

9b


7.80
7.79
7.26
7.25
7.23
6.07
6.01
2.40
2.38
2.37
2.36
2.36
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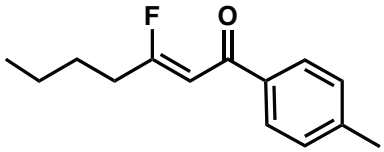
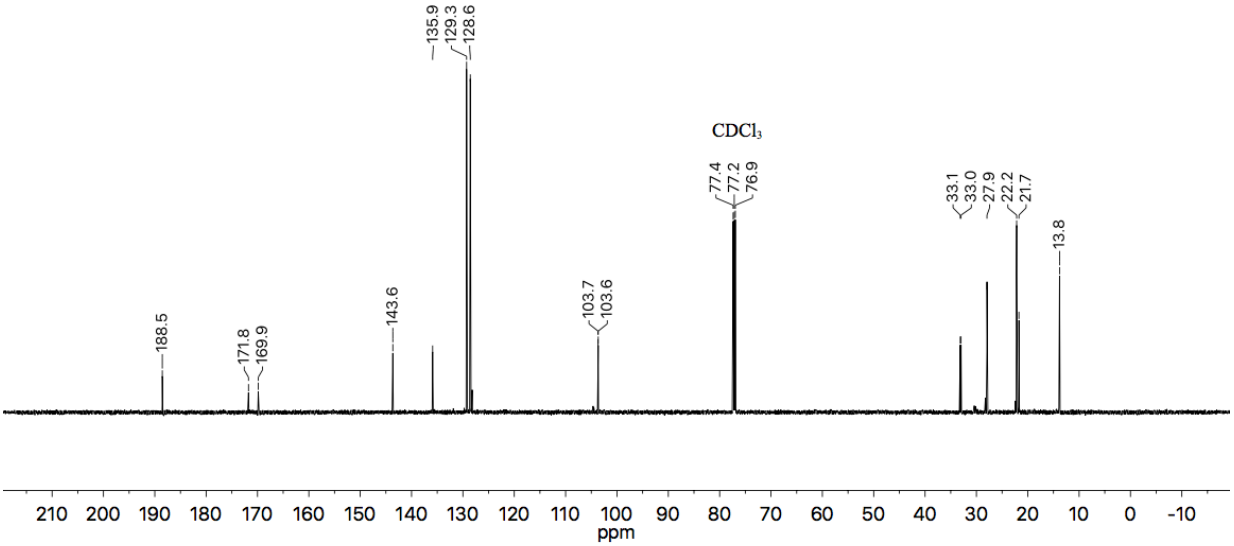
2.33
1.64
1.64
1.63
1.61
1.60
1.59
1.45
1.44
1.43
1.42
1.42
1.41
1.40
1.39
0.96
0.95
0.95
0.94
1.93
1.90
0.89
2.77
1.97
2.00
2.03
2.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

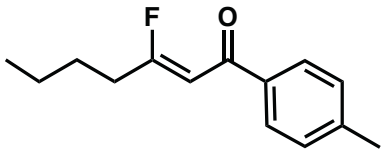
^{13}C NMR (151 MHz, $CDCl_3$)



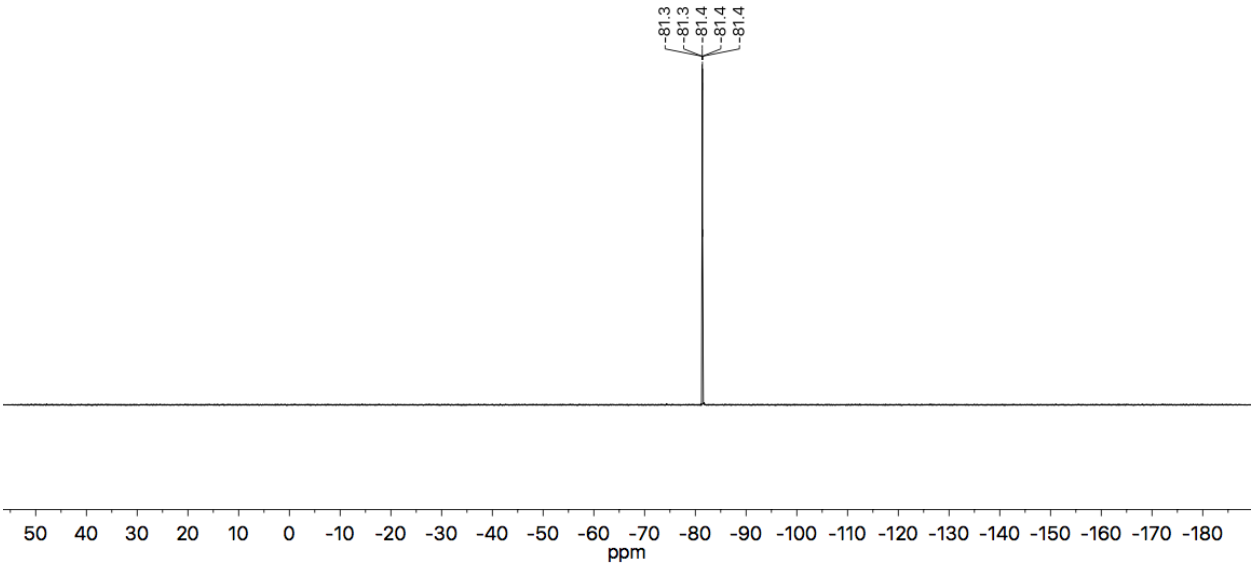
9b



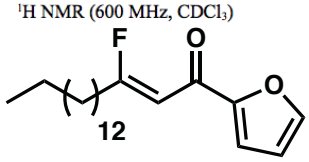
^{19}F NMR (565 MHz, $CDCl_3$)



9b

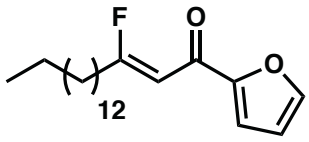


^{1}H NMR (600 MHz, $CDCl_3$)

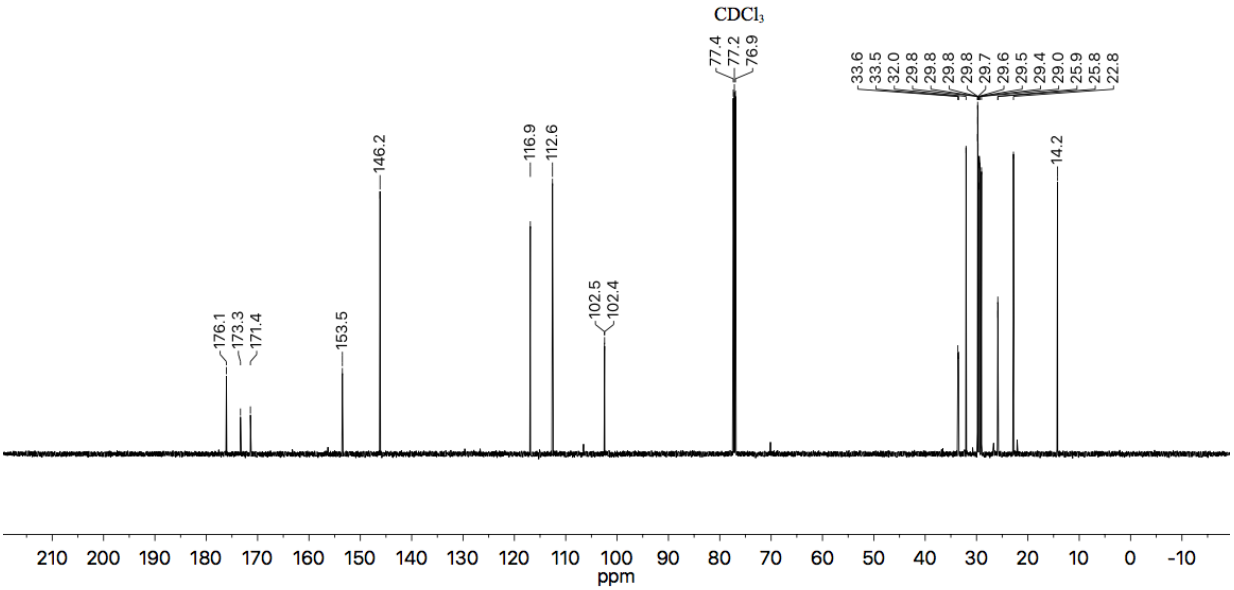


10b

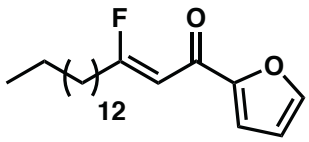
^{13}C NMR (151 MHz, $CDCl_3$)



10b

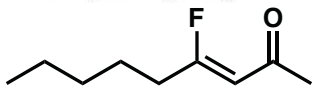


^{19}F NMR (565 MHz, $CDCl_3$)

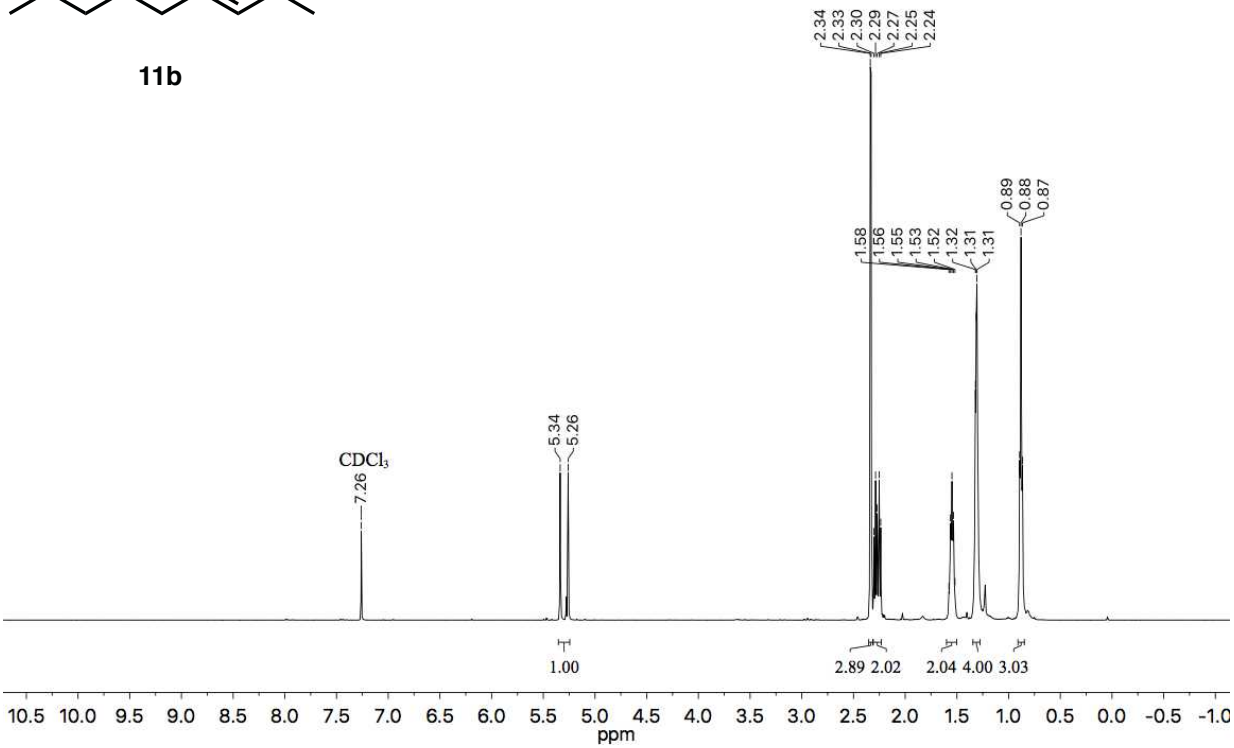


10b

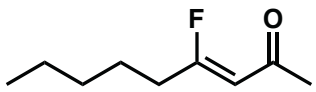
^{1}H NMR (500 MHz, $CDCl_3$)



11b

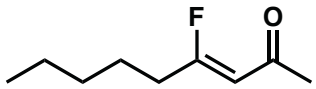


^{13}C NMR (126 MHz, $CDCl_3$)

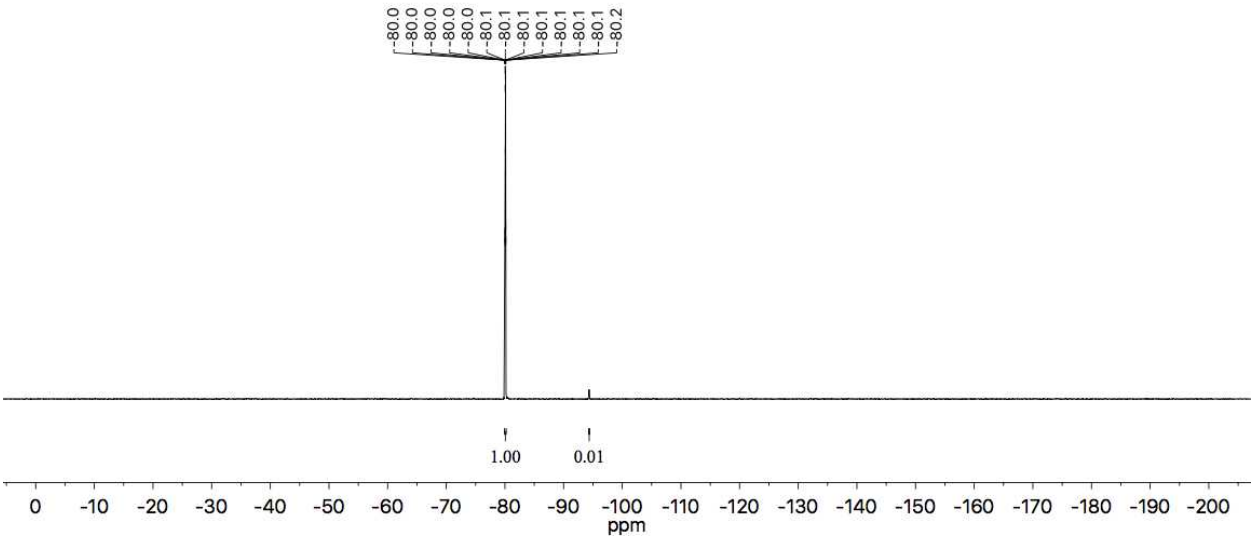


11b

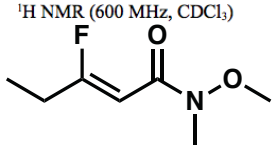
^{19}F NMR (470 MHz, $CDCl_3$)



11b

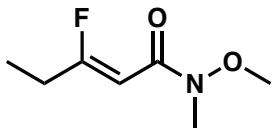


^{1}H NMR (600 MHz, $CDCl_3$)



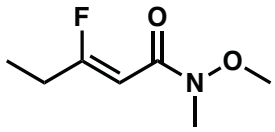
12b

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



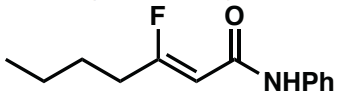
12b

^{19}F NMR (565 MHz, $CDCl_3$)

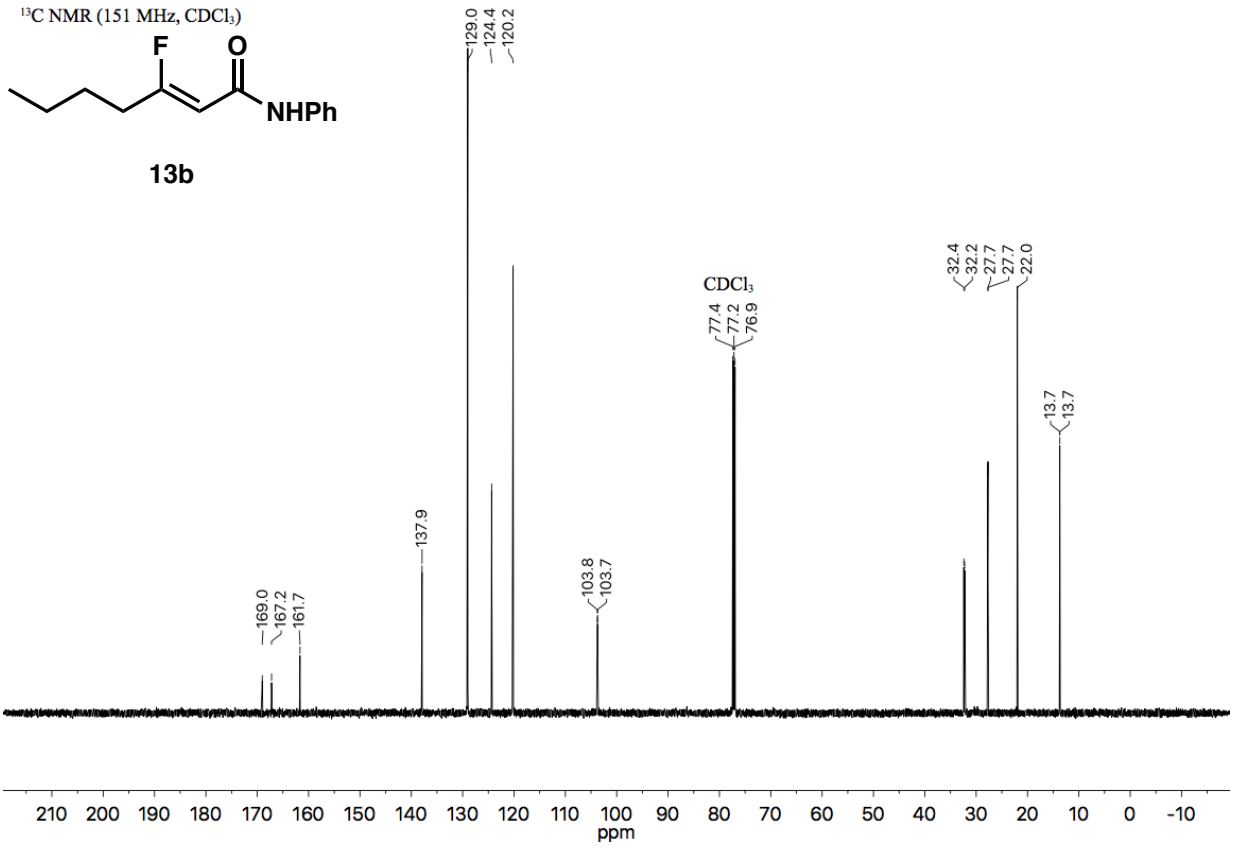


12b

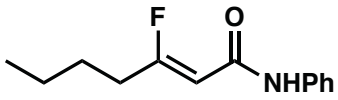
^{1}H NMR (600 MHz, $CDCl_3$)



13b

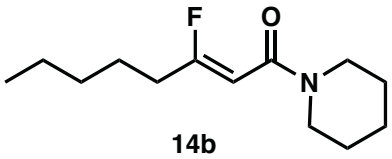

13C NMR (151 MHz, CDCl3)
F
O
NHPh
13b
129.0
124.4
120.2
CDCl3
77.4
77.2
76.9
32.4
32.2
27.7
27.7
22.0
13.7
13.7
137.9
103.8
103.7
169.0
167.2
161.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (565 MHz, $CDCl_3$)

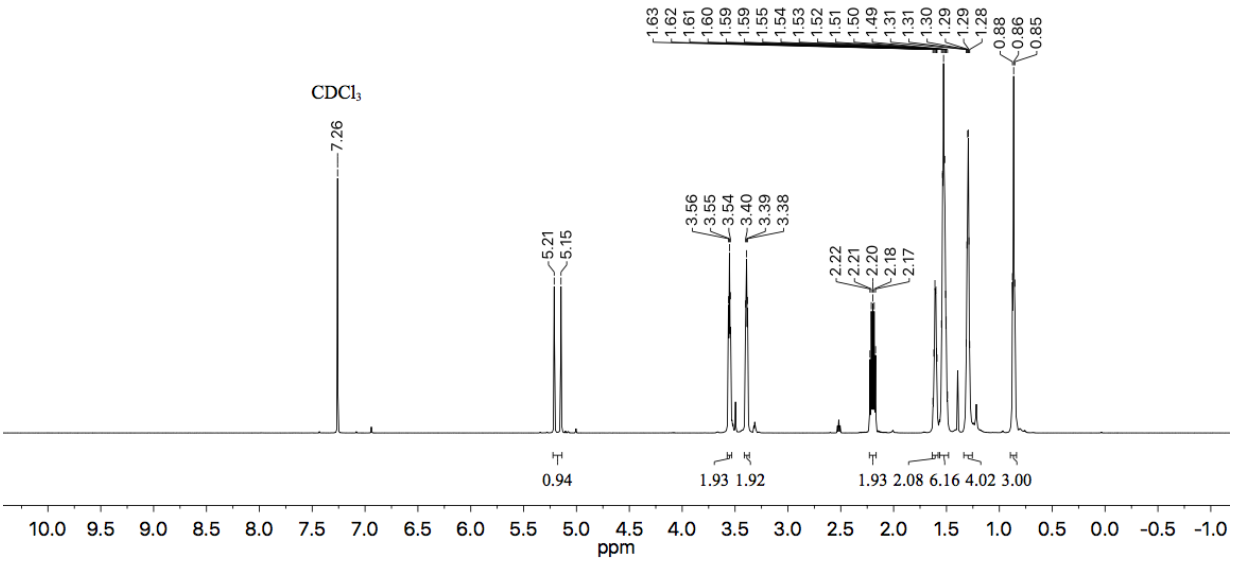


13b

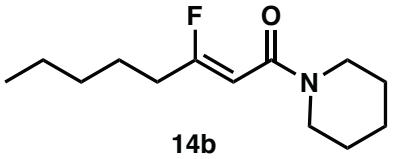
^{1}H NMR (600 MHz, $CDCl_3$)



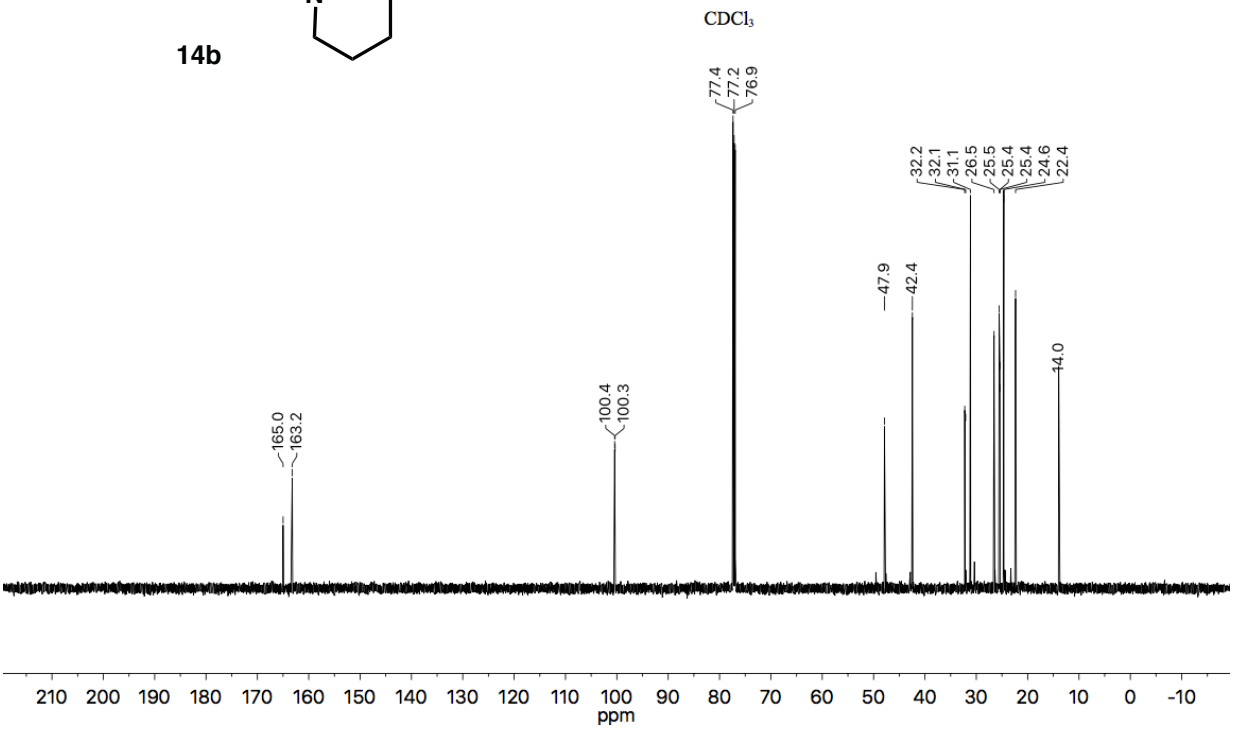
14b



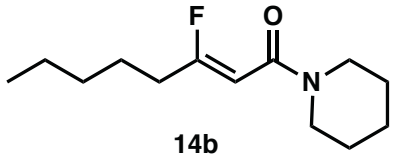
^{13}C NMR (151 MHz, $CDCl_3$)



14b

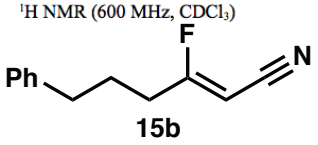


^{19}F NMR (565 MHz, $CDCl_3$)

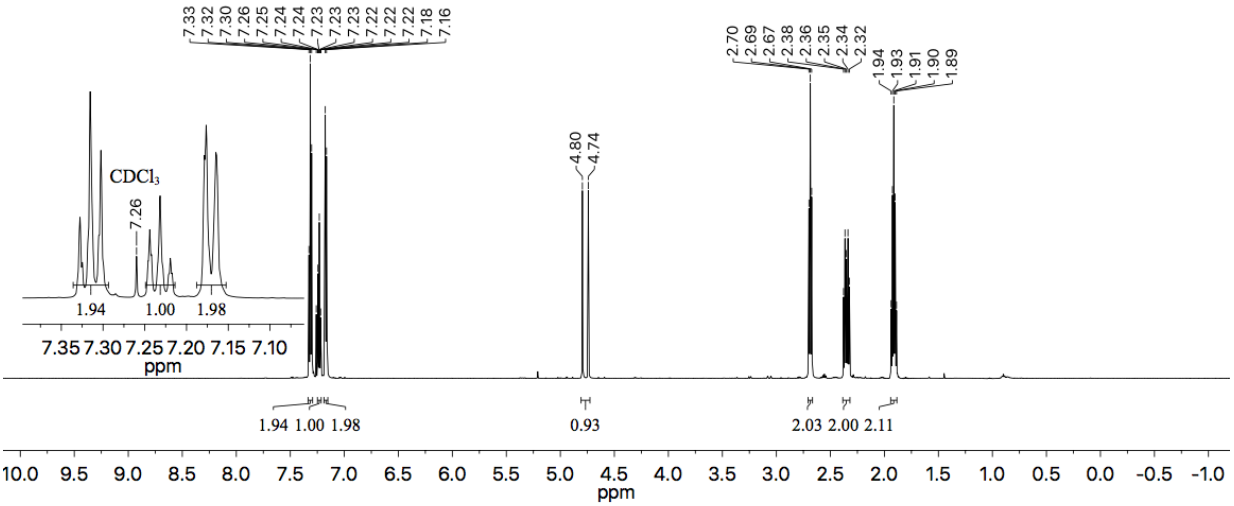


14b

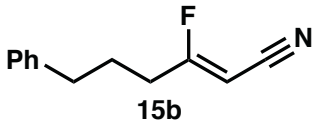
^{1}H NMR (600 MHz, $CDCl_3$)



15b

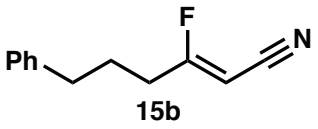


^{13}C NMR (151 MHz, $CDCl_3$)

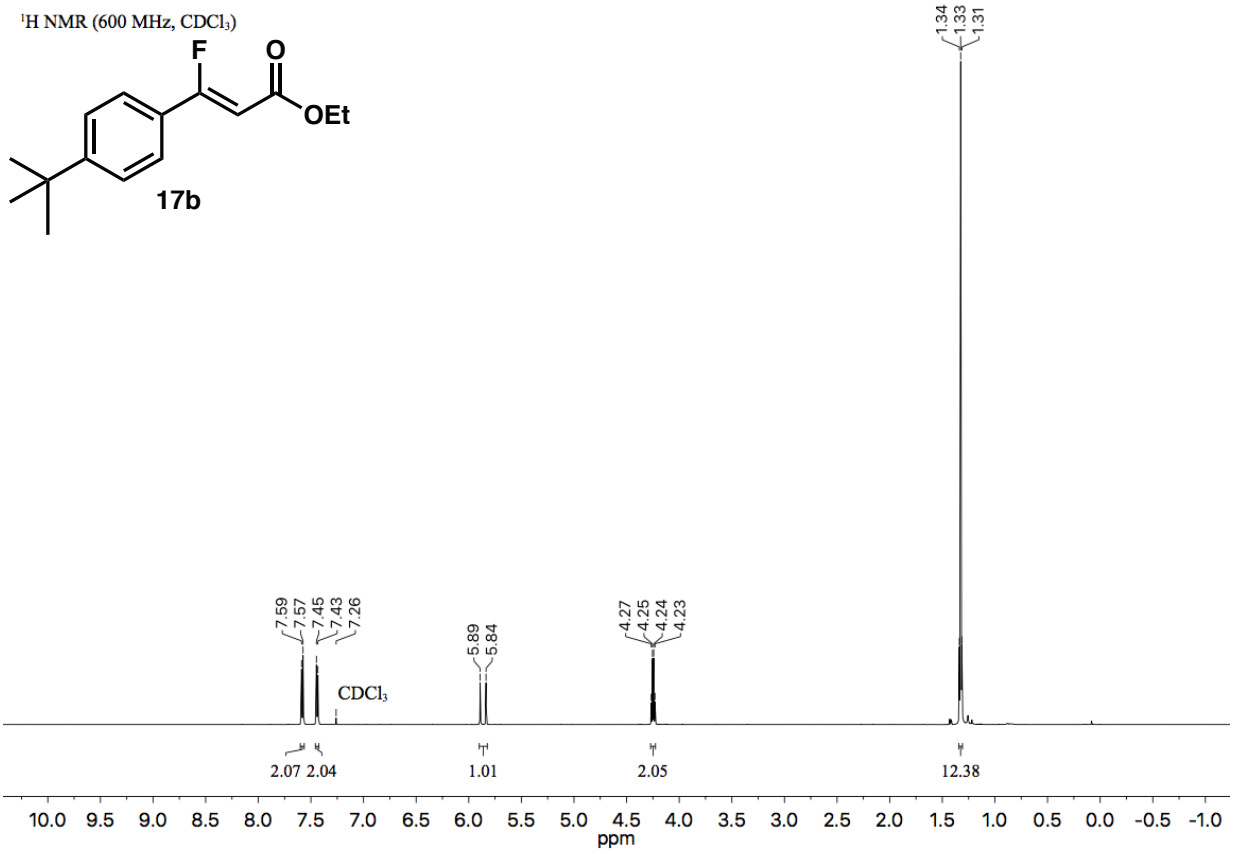


15b

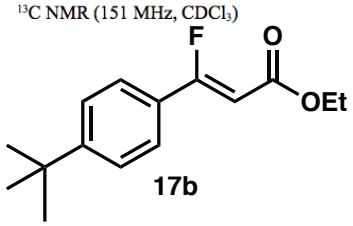
^{19}F NMR (565 MHz, $CDCl_3$)



15b

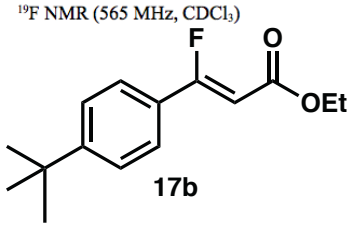

1H NMR (600 MHz, CDCl3)
F
O
OEt
17b
1.34
1.33
1.31
7.59
7.57
7.45
7.43
7.26
CDCl3
5.89
5.84
4.27
4.25
4.24
4.23
2.07 2.04
1.01
2.05
12.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

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

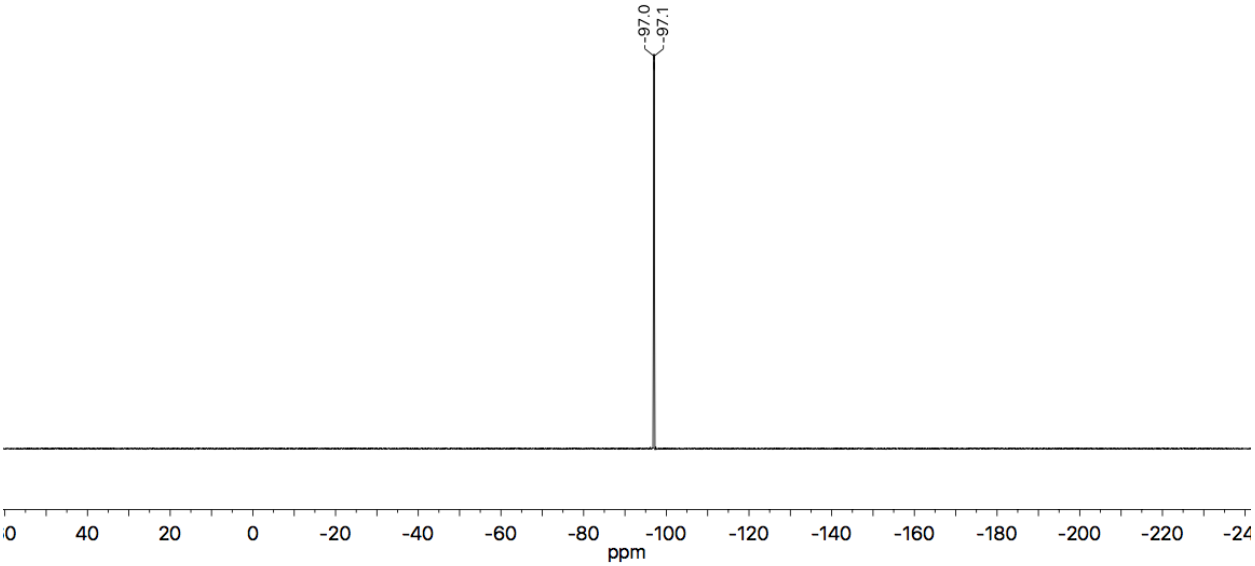


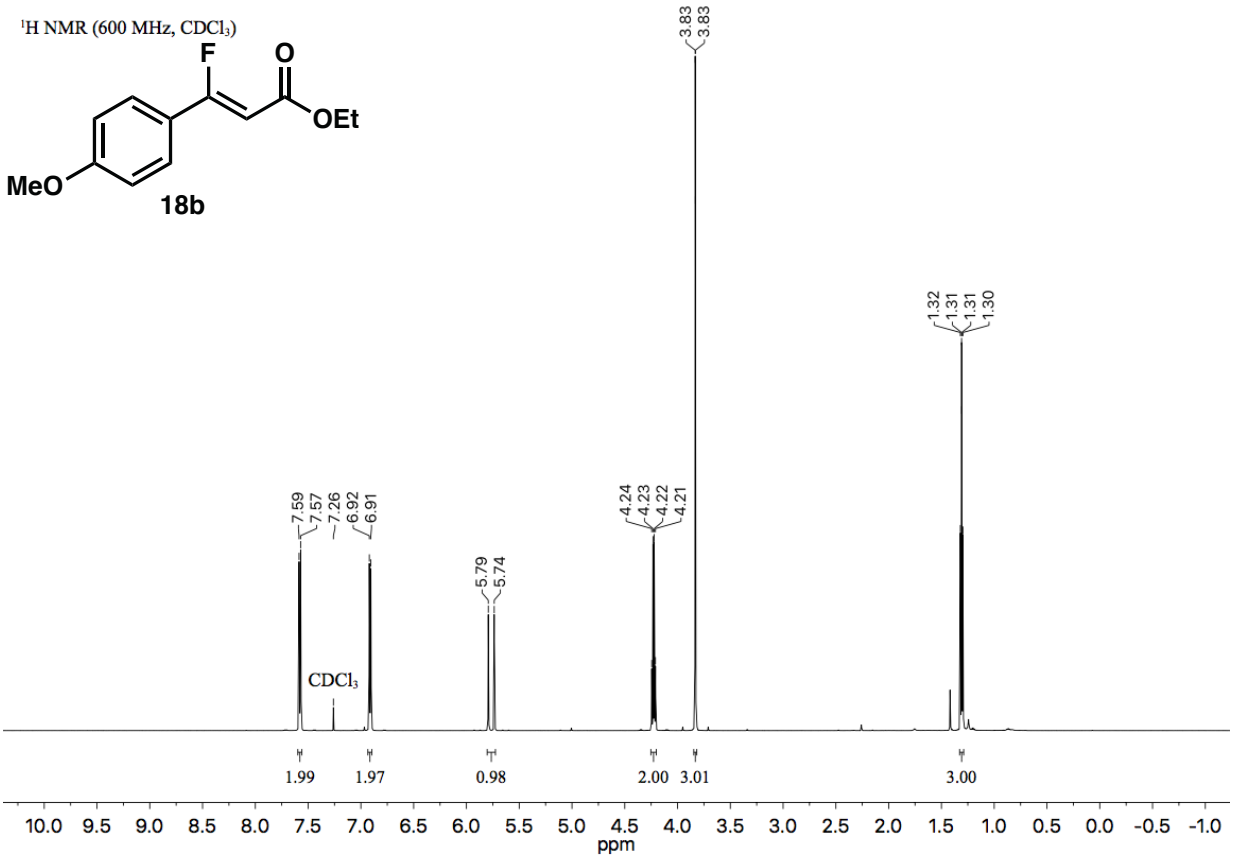
17b

^{19}F NMR (565 MHz, $CDCl_3$)

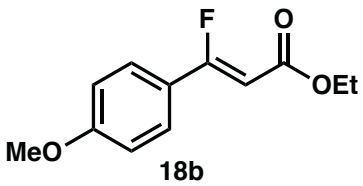


17b

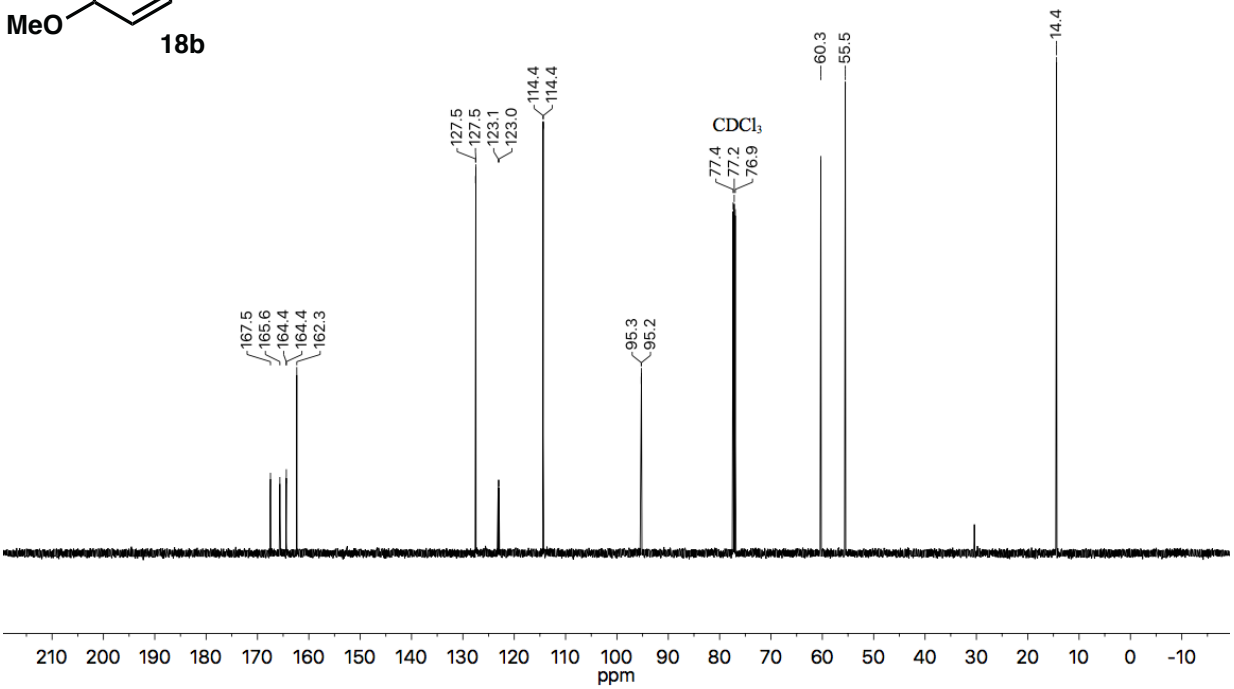



1H NMR (600 MHz, CDCl3)
F
O
OEt
MeO
18b
3.83
3.83
1.32
1.31
1.31
1.30
7.59
7.57
7.26
6.92
6.91
5.79
5.74
4.24
4.23
4.22
4.21
CDCl3
1.99
1.97
0.98
2.00
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

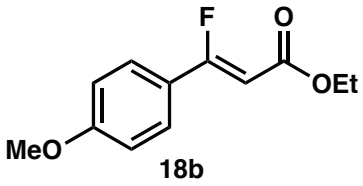
^{13}C NMR (151 MHz, $CDCl_3$)



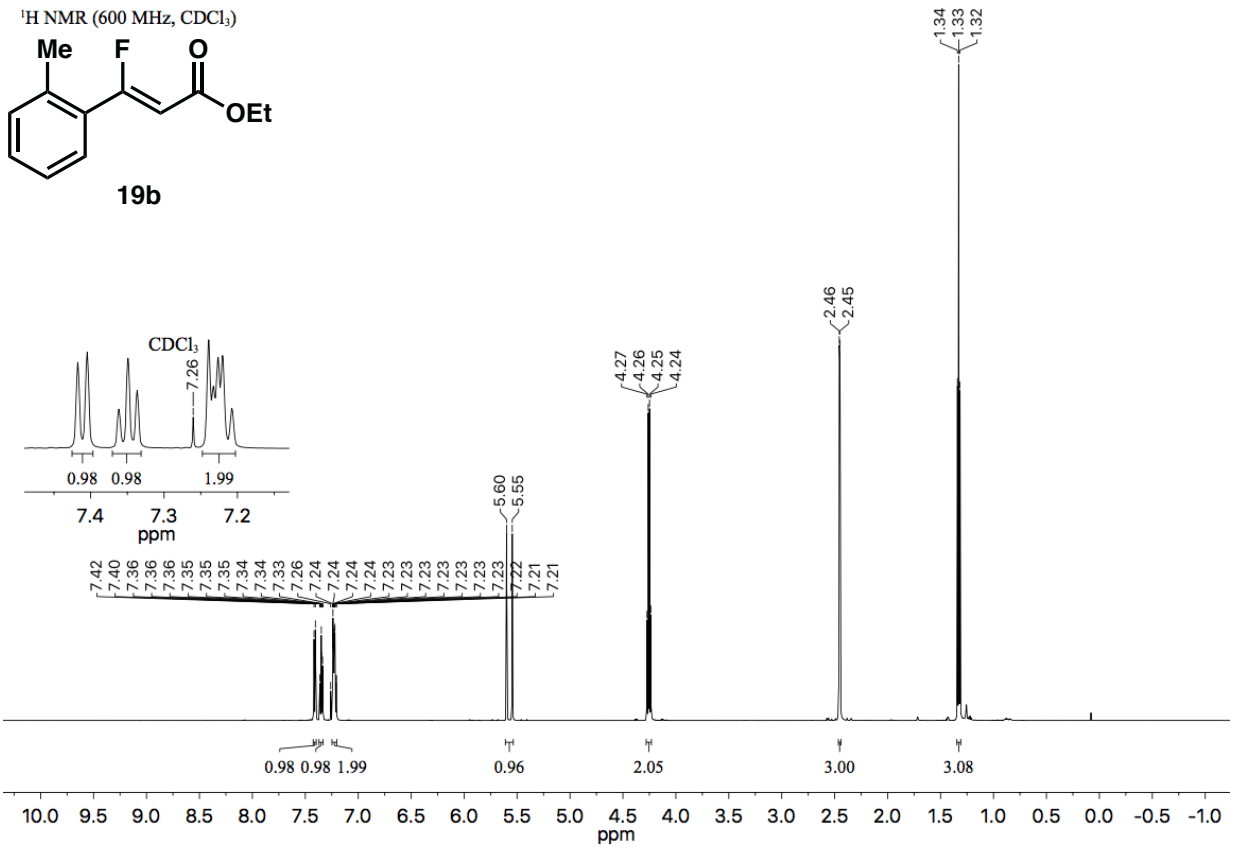
18b



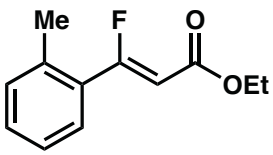
^{19}F NMR (565 MHz, $CDCl_3$)



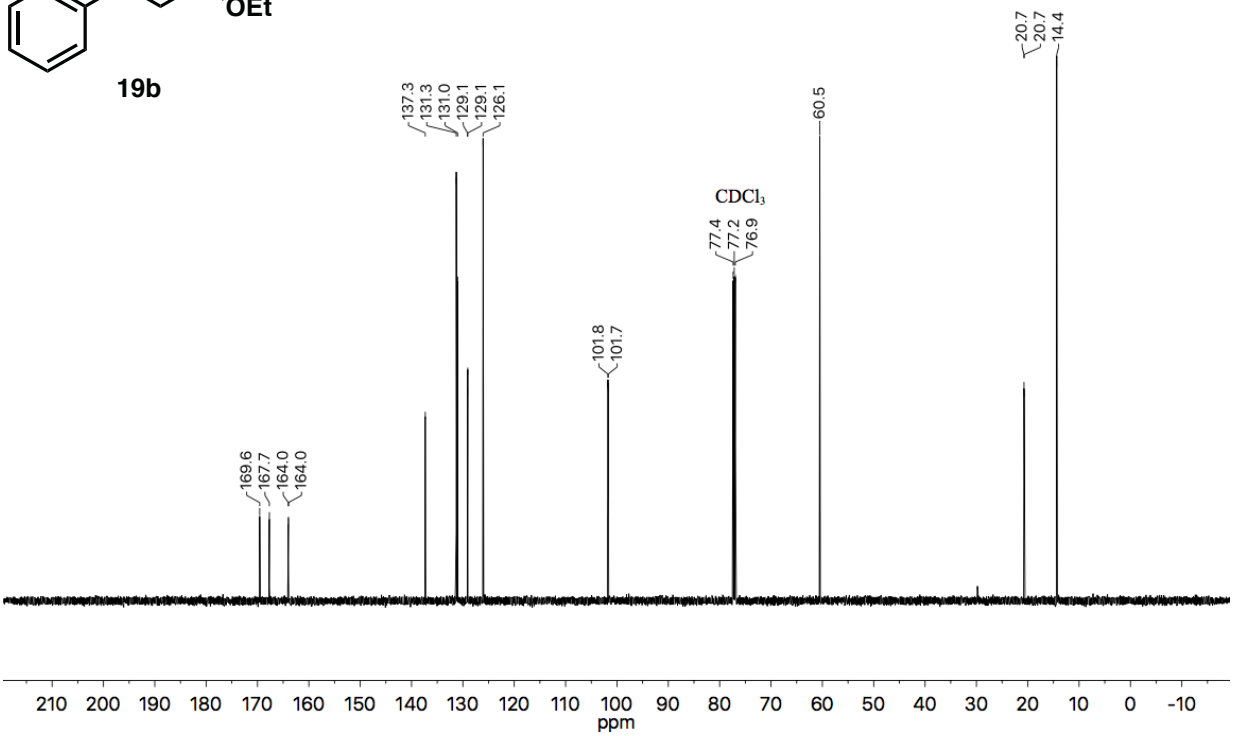
18b


¹H NMR (600 MHz, CDCl₃)
Me
F
O
OEt
19b
CDCl₃
7.26
0.98 0.98 1.99
7.4 7.3 7.2
ppm
7.42 7.40 7.36 7.36 7.35 7.35 7.34 7.33 7.26 7.24 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.23 7.22 7.21 7.21
5.60 5.55
4.27 4.26 4.25 4.24
2.46 2.45
1.34 1.33 1.32
0.98 0.98 1.99
0.96
2.05
3.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

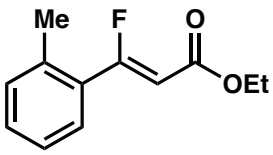
^{13}C NMR (151 MHz, $CDCl_3$)



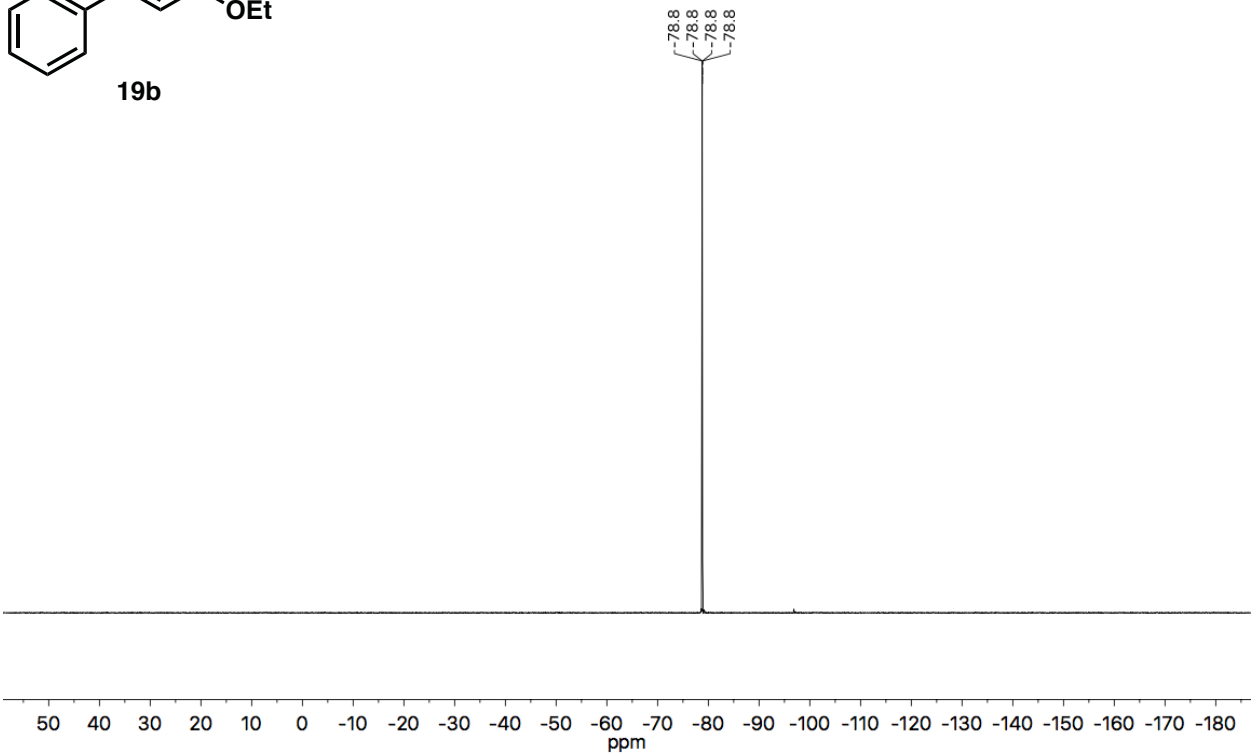
19b



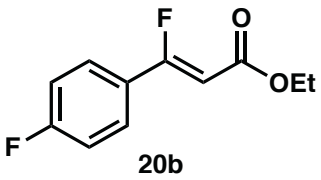
^{19}F NMR (565 MHz, $CDCl_3$)



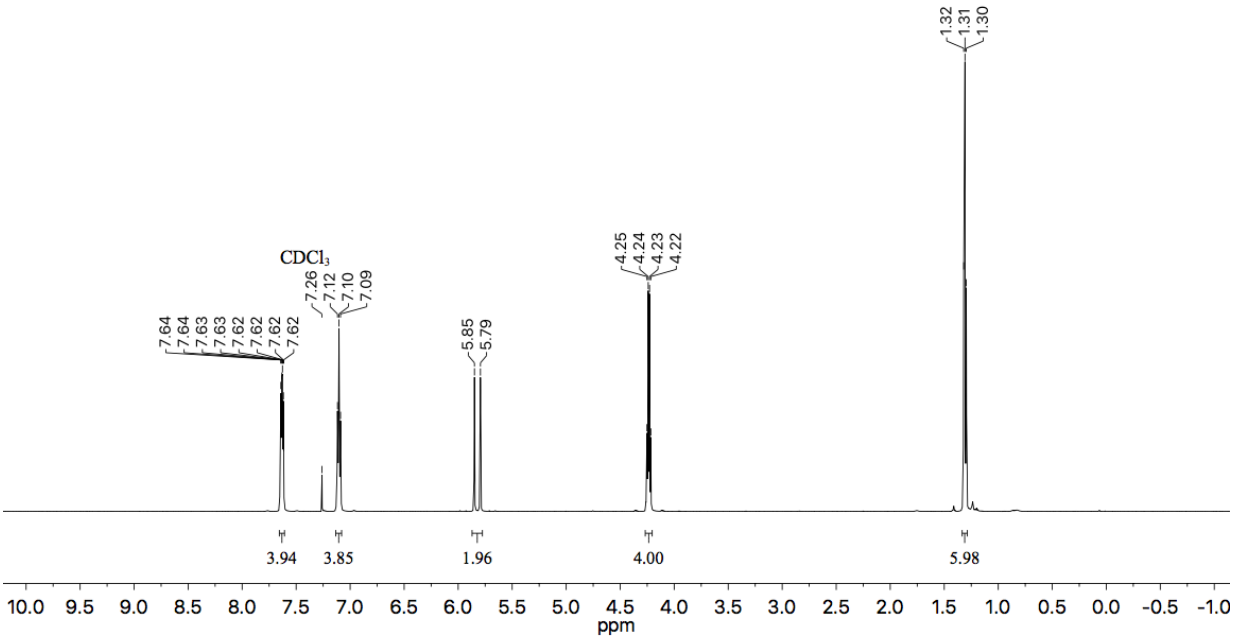
19b



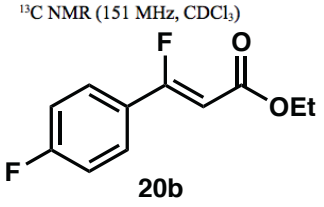
^{1}H NMR (600 MHz, $CDCl_3$)



20b

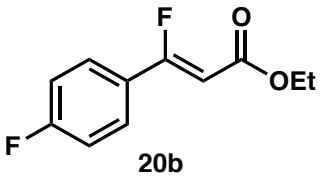


^{13}C NMR (151 MHz, $CDCl_3$)

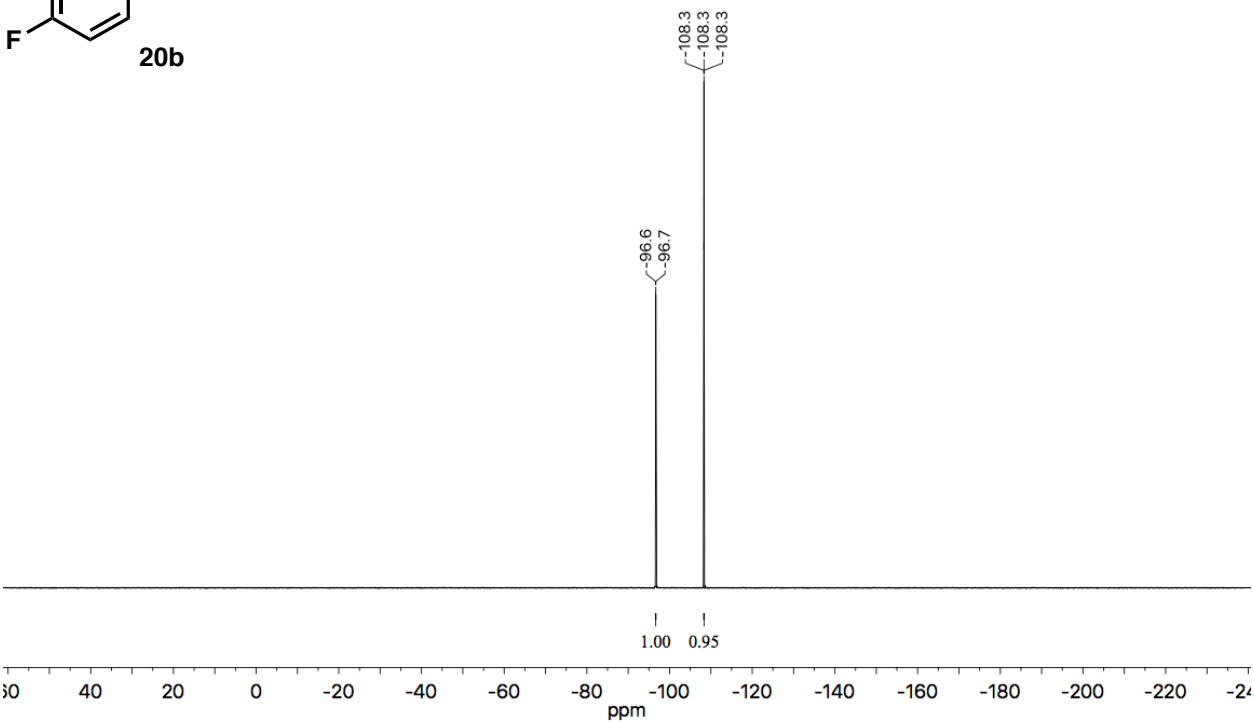


20b

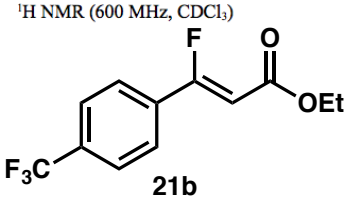
^{19}F NMR (565 MHz, $CDCl_3$)



20b

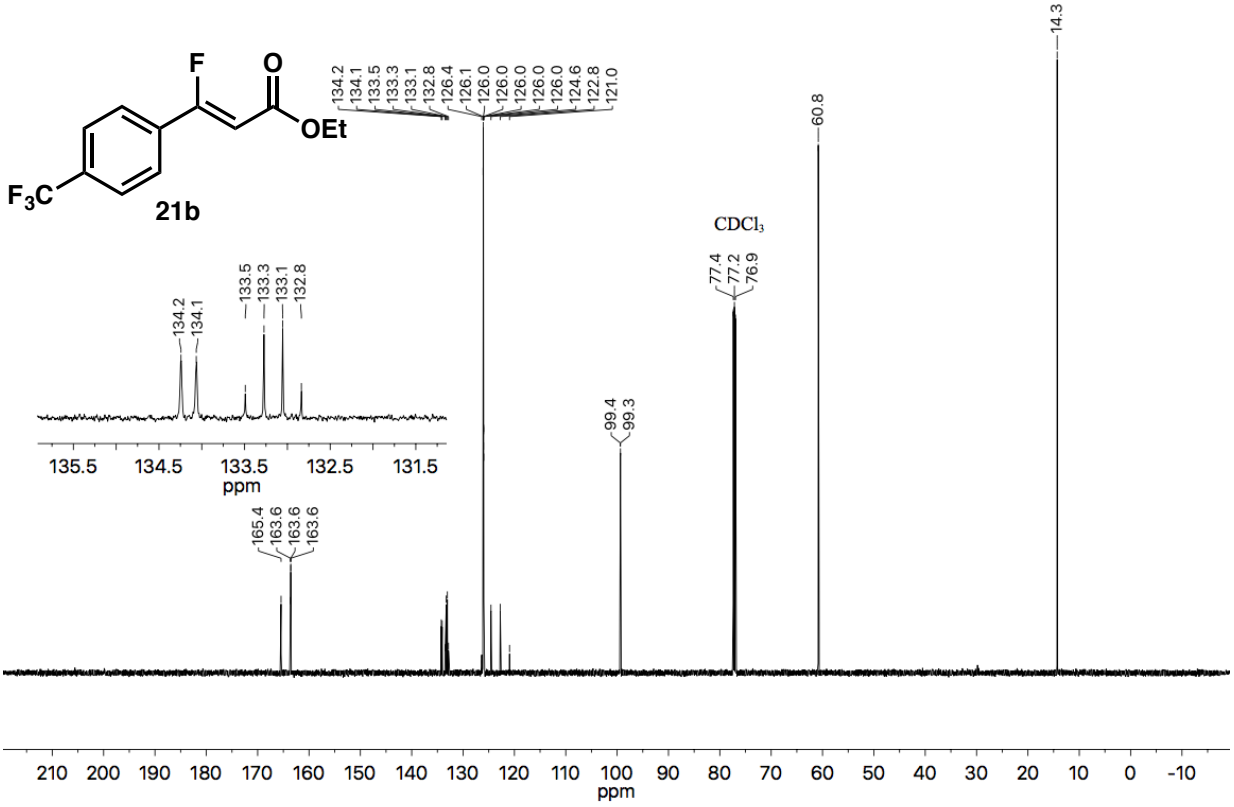


^{1}H NMR (600 MHz, $CDCl_3$)

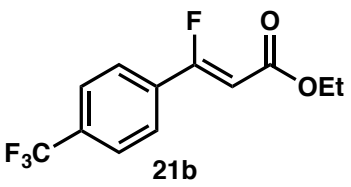


21b

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

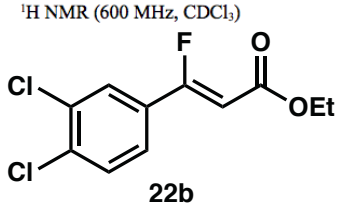


^{19}F NMR (565 MHz, $CDCl_3$)



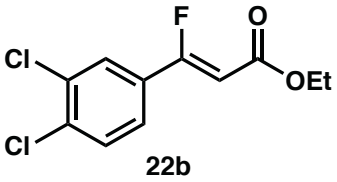
21b

^{1}H NMR (600 MHz, $CDCl_3$)



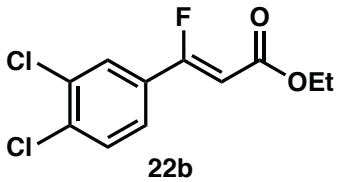
22b

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

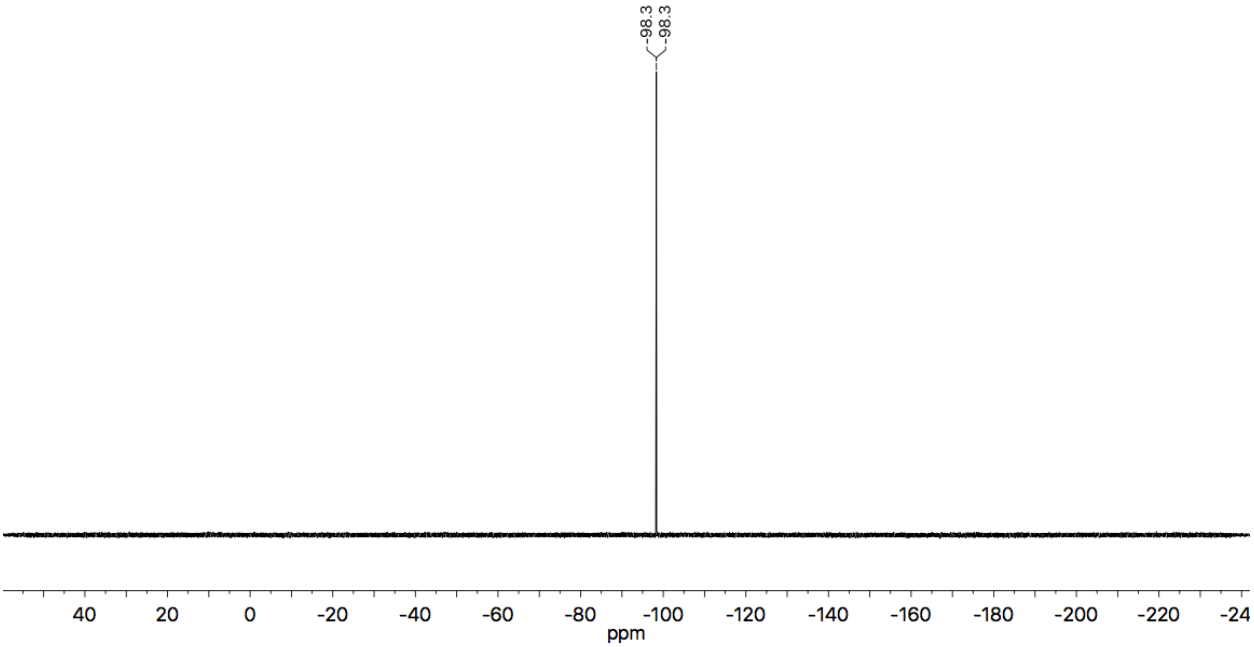


22b

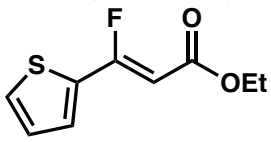
^{19}F NMR (565 MHz, $CDCl_3$)



22b

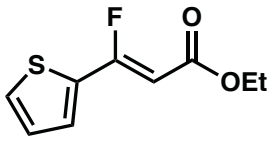


^{1}H NMR (600 MHz, $CDCl_3$)



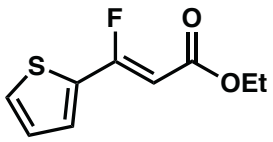
23b

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

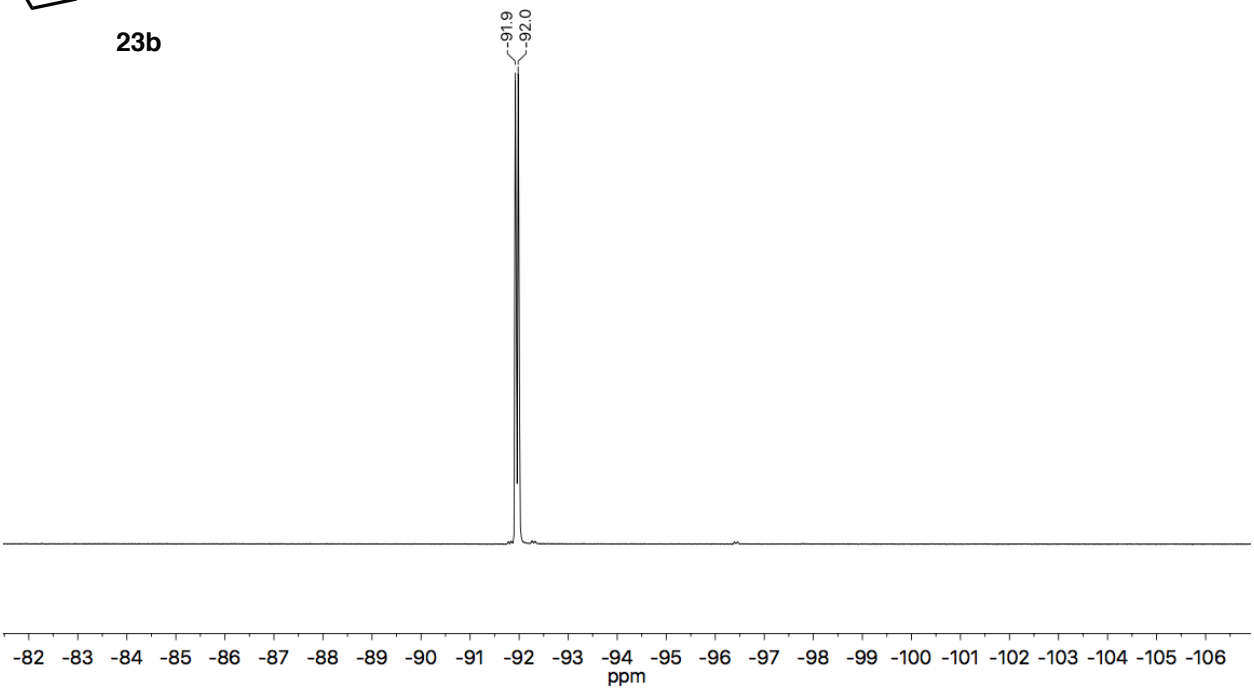


23b

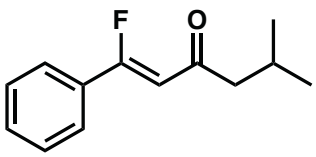
^{19}F NMR (565 MHz, $CDCl_3$)



23b

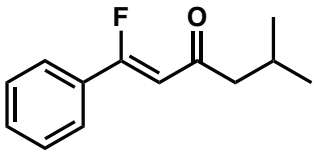


^{1}H NMR (600 MHz, $CDCl_3$)



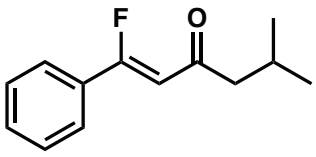
25b

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

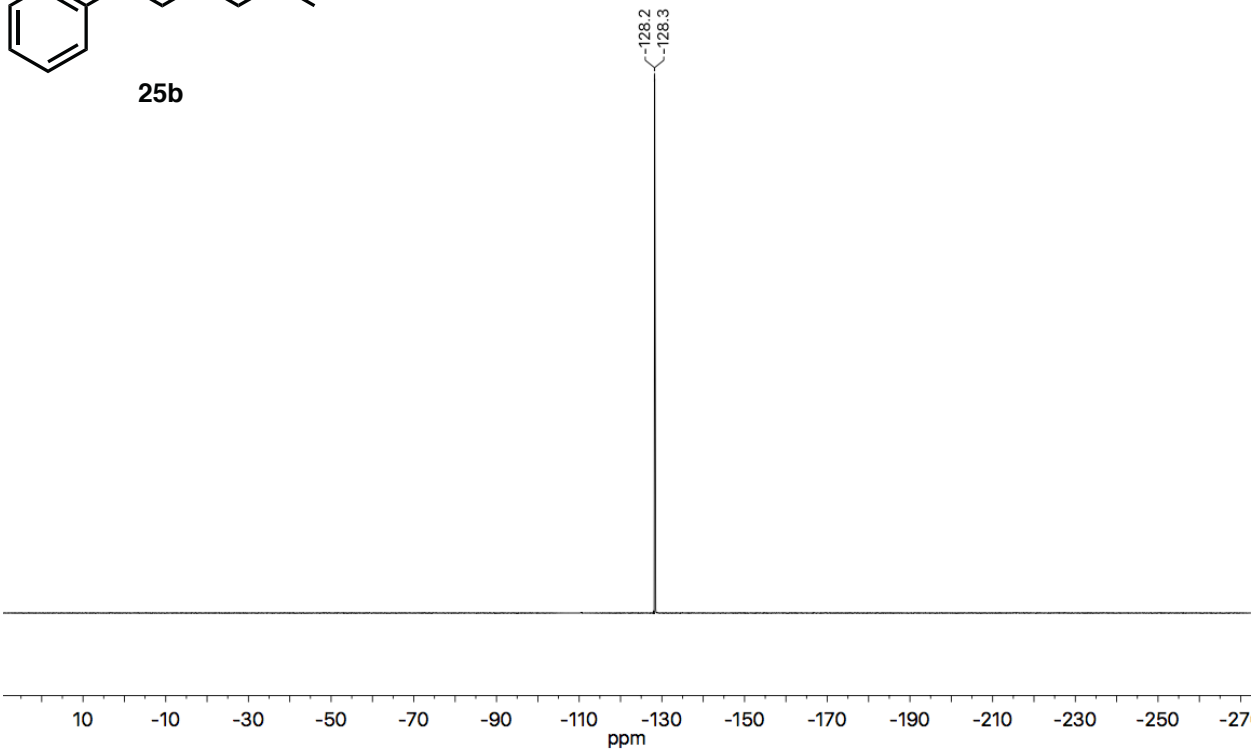


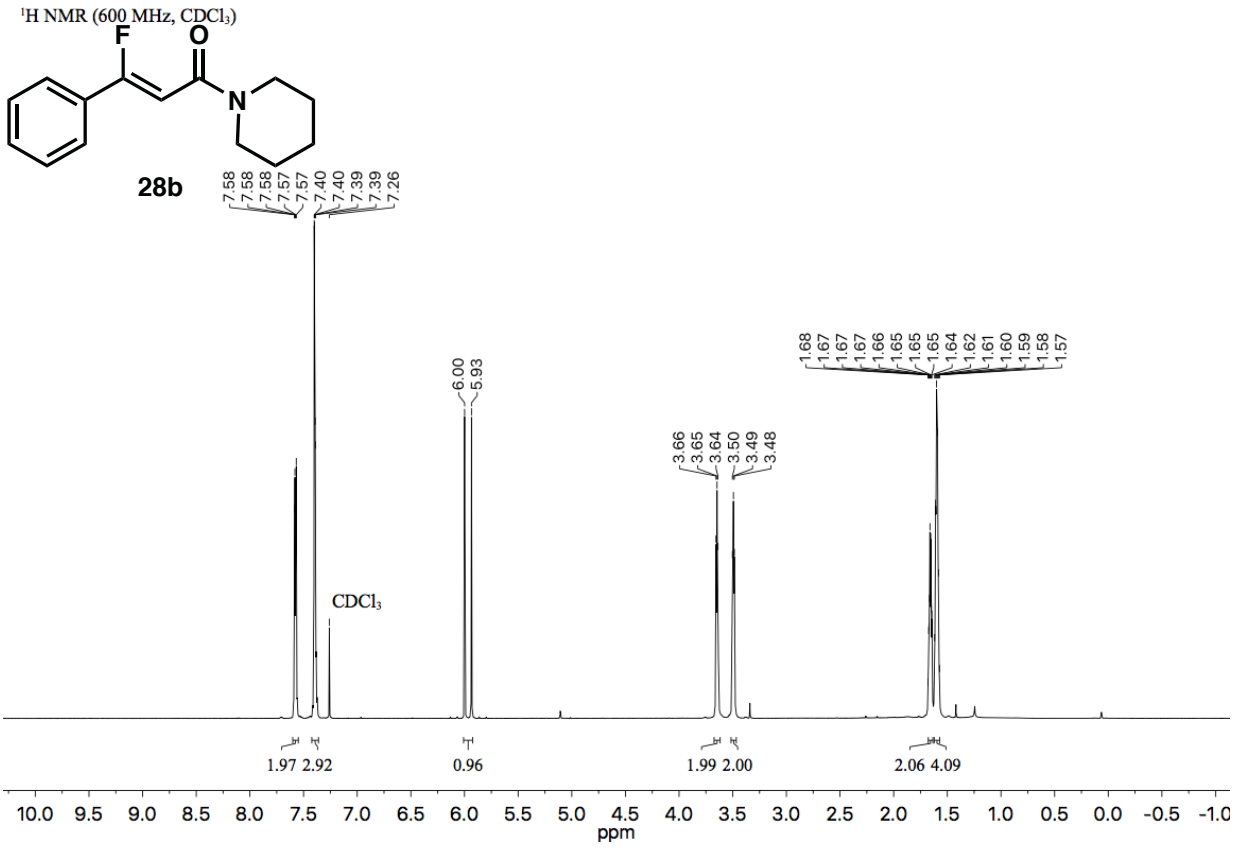
25b

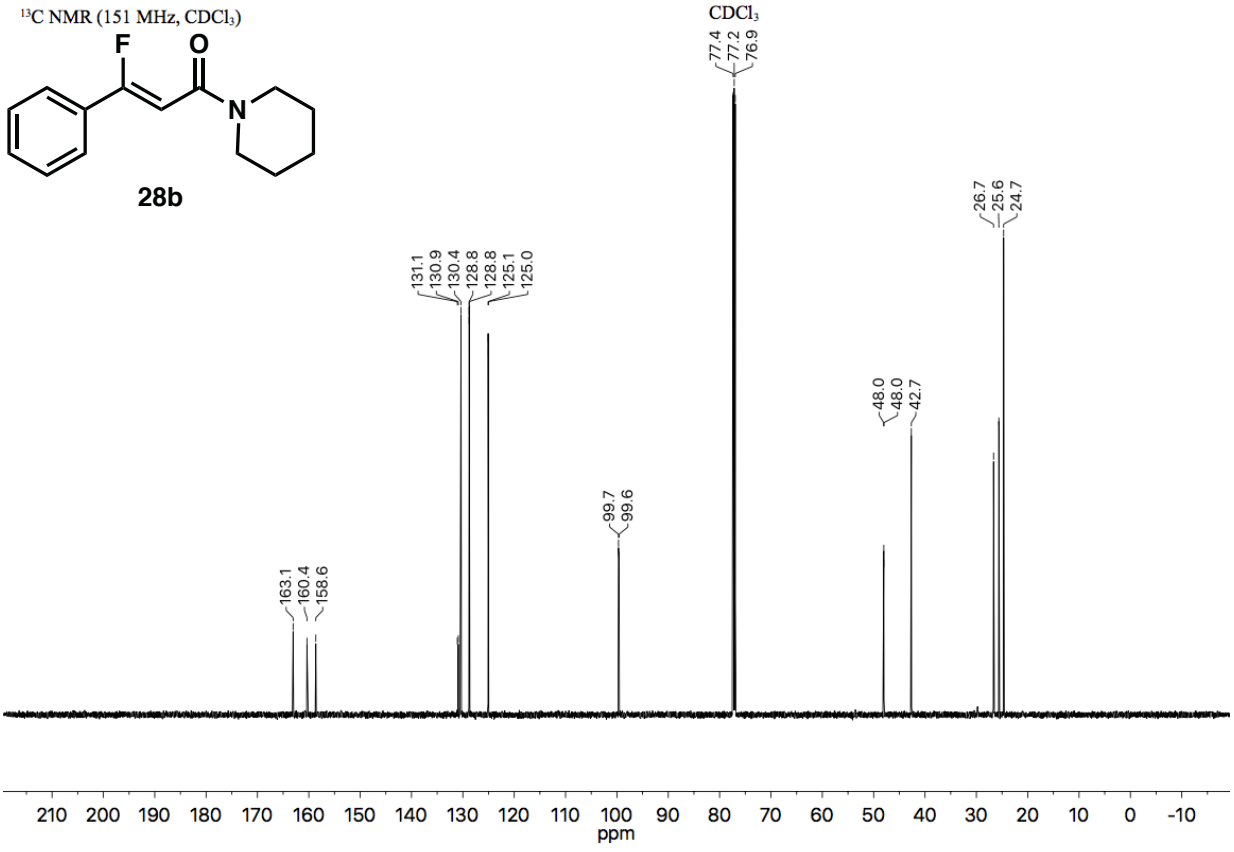
^{19}F NMR (565 MHz, $CDCl_3$)



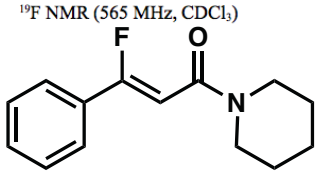
25b




^{1}H NMR (600 MHz, $CDCl_3$)
F
O
N
28b
7.58
7.58
7.58
7.57
7.57
7.40
7.40
7.39
7.39
7.26
6.00
5.93
3.66
3.65
3.64
3.50
3.49
3.48
1.68
1.67
1.67
1.67
1.66
1.65
1.65
1.65
1.64
1.62
1.61
1.60
1.59
1.58
1.57
$CDCl_3$
1.97 2.92
0.96
1.99 2.00
2.06 4.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

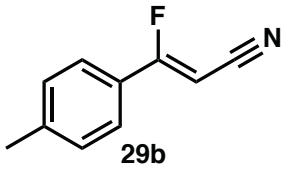

^{13}C NMR (151 MHz, $CDCl_3$)
F
O
N
28b
$CDCl_3$
77.4
77.2
76.9
131.1
130.9
130.4
128.8
128.8
125.1
125.0
99.7
99.6
48.0
48.0
42.7
26.7
25.6
24.7
163.1
160.4
158.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (565 MHz, $CDCl_3$)

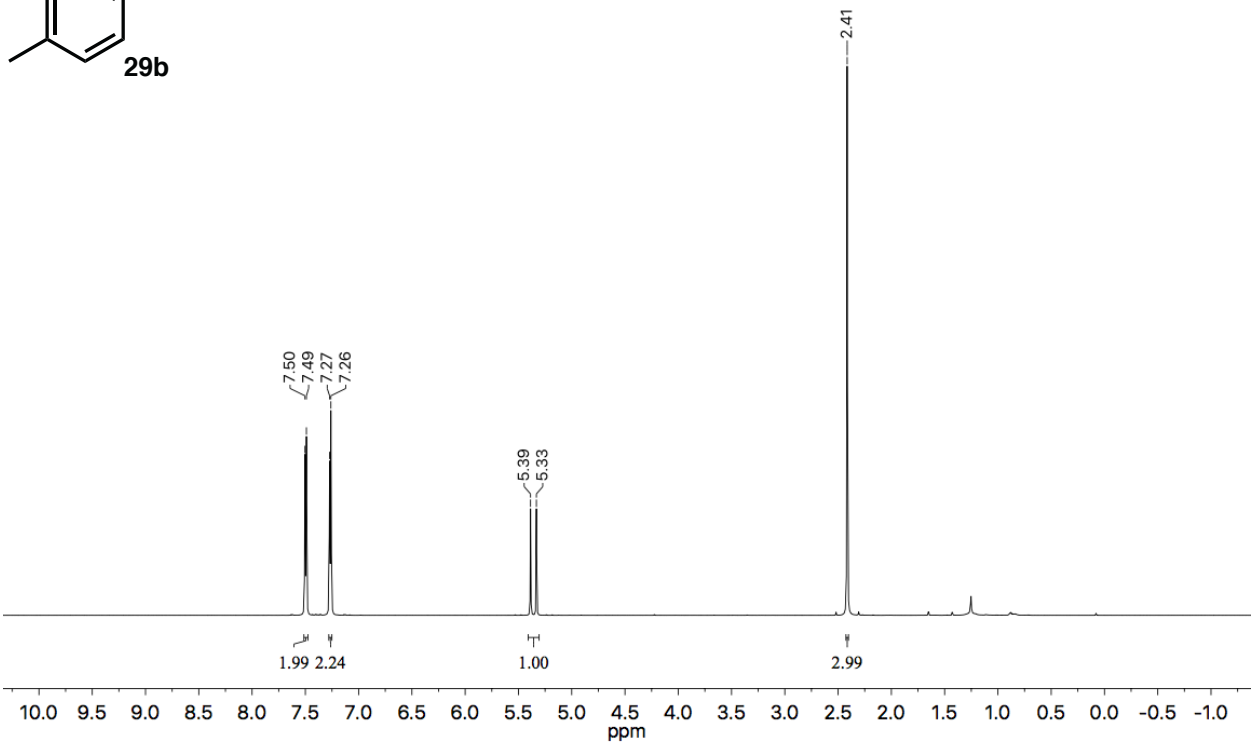


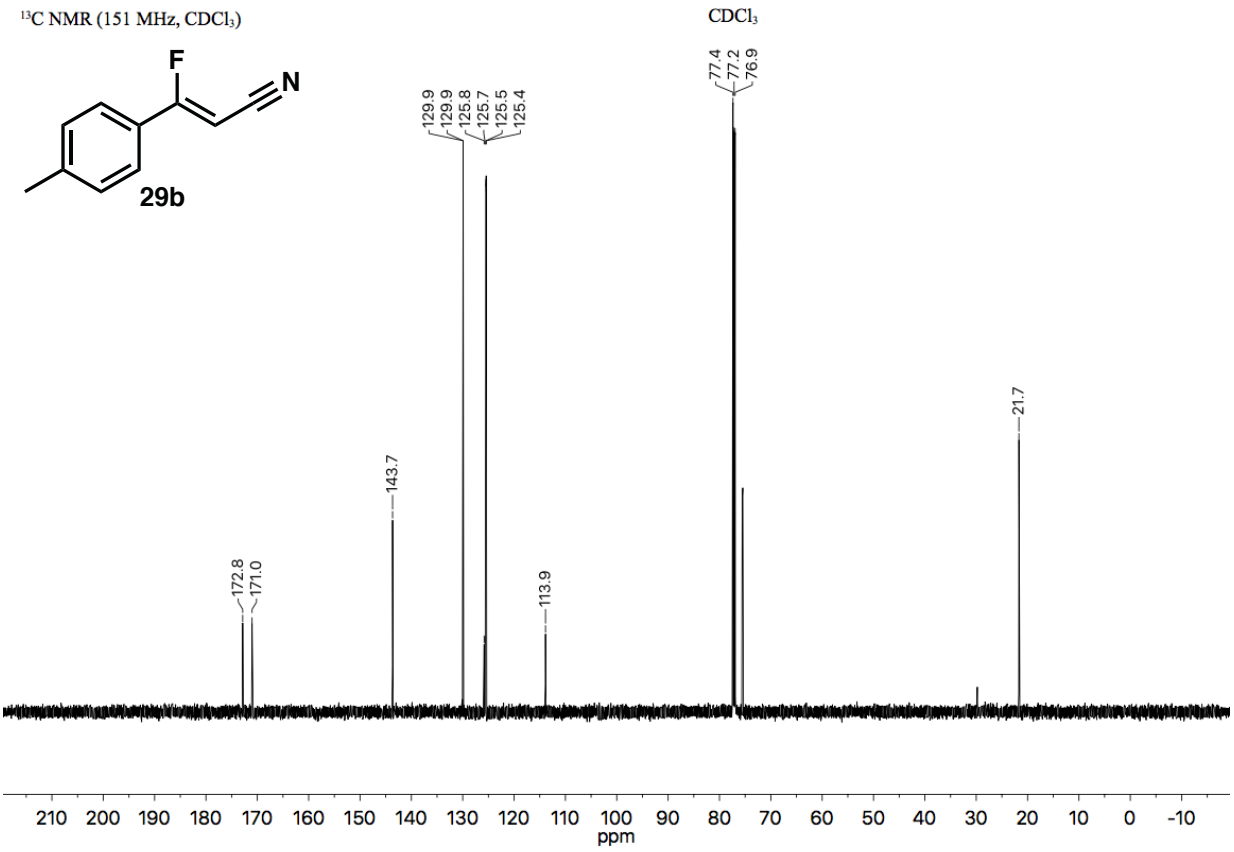
28b

^{1}H NMR (600 MHz, $CDCl_3$)

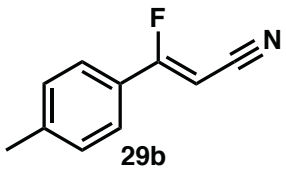


29b



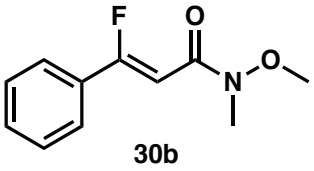

^{13}C NMR (151 MHz, $CDCl_3$)
F
N
29b
$CDCl_3$
77.4
77.2
76.9
129.9
129.9
125.8
125.7
125.5
125.4
143.7
172.8
171.0
113.9
21.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (565 MHz, $CDCl_3$)



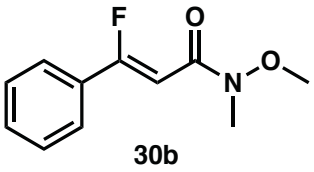
29b

^{1}H NMR (600 MHz, $CDCl_3$)



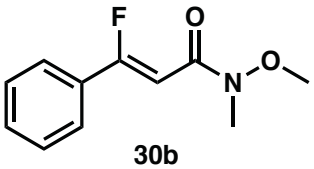
30b

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

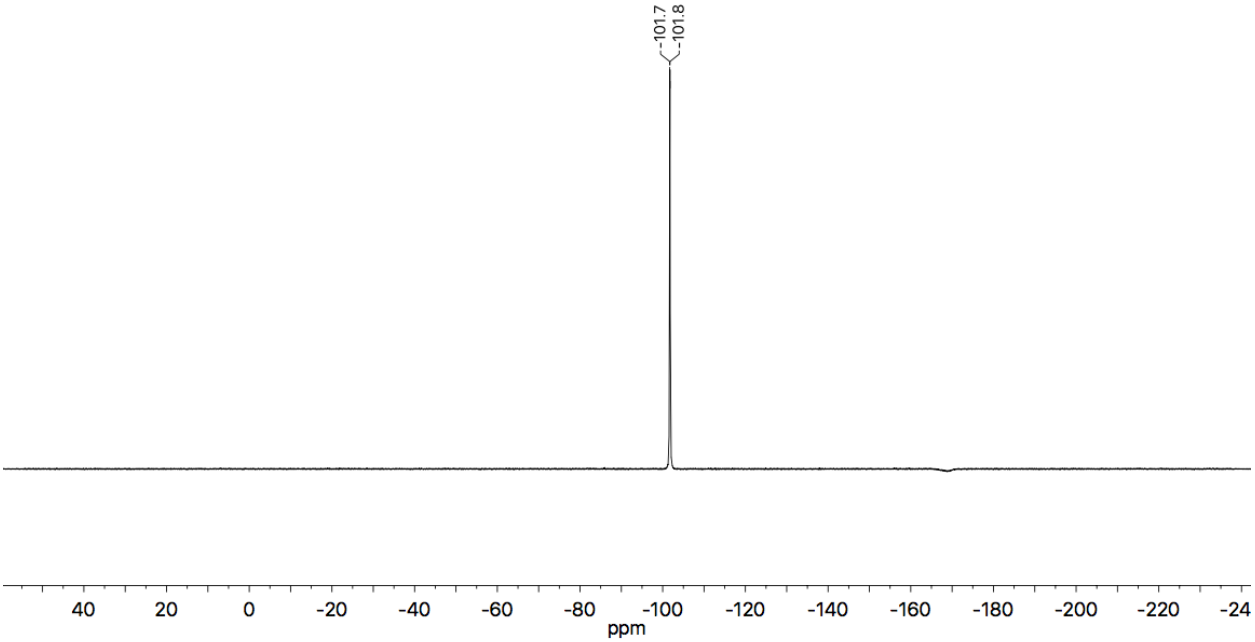


30b

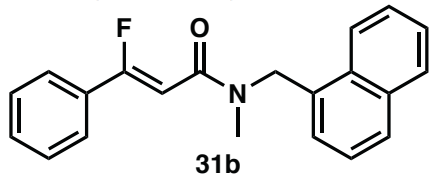
^{19}F NMR (565 MHz, $CDCl_3$)



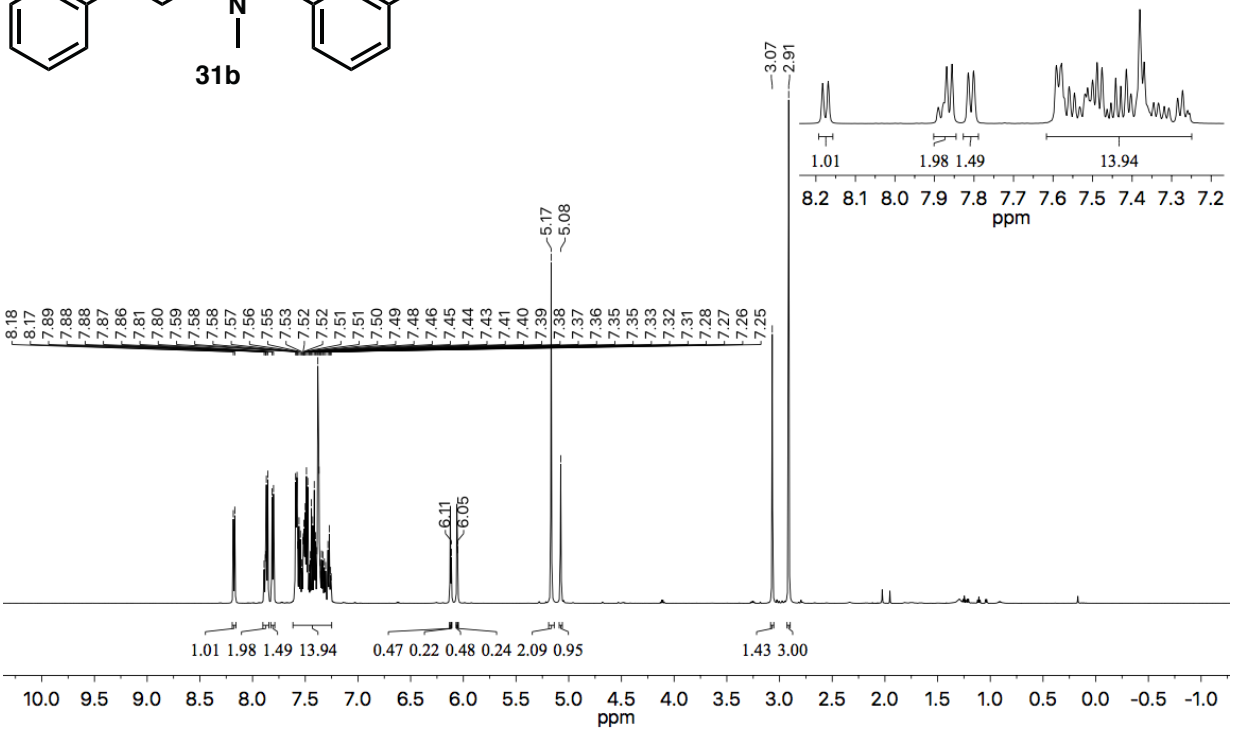
30b



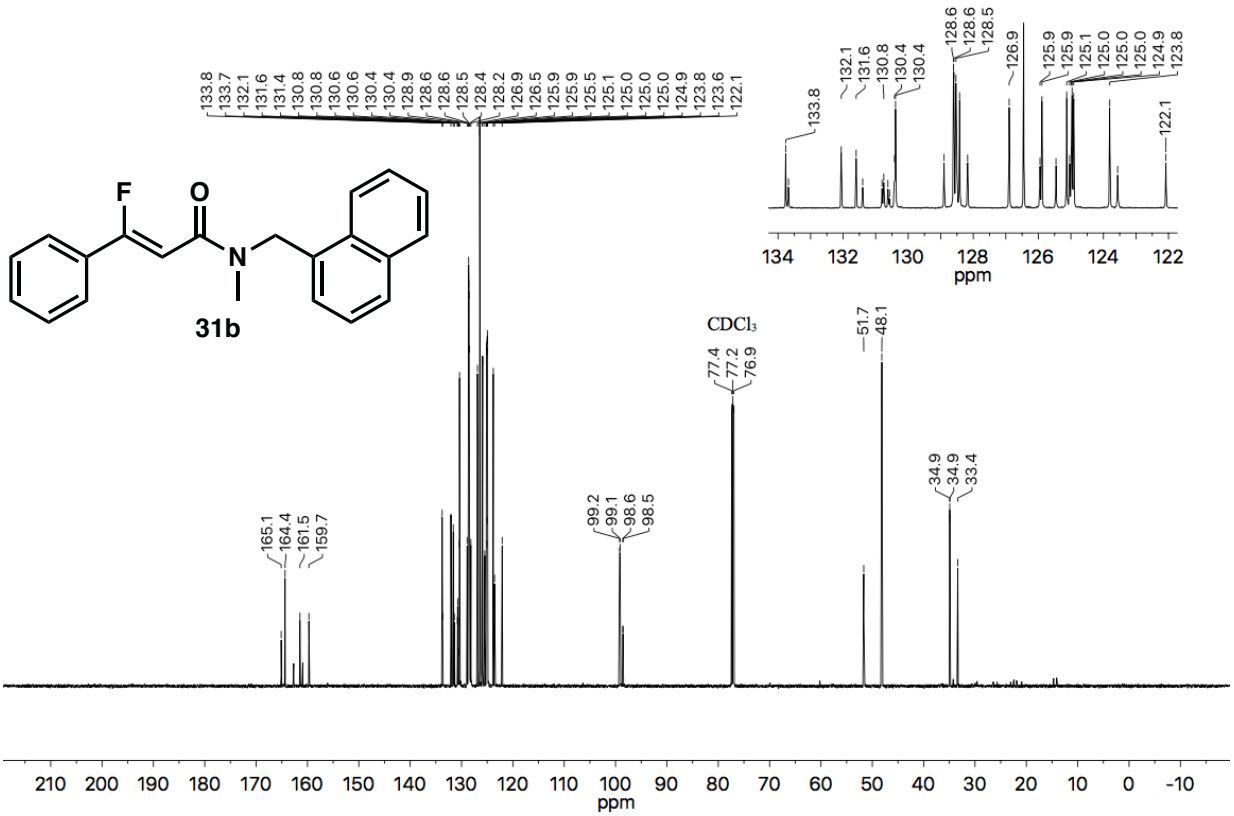
^{1}H NMR (600 MHz, $CDCl_3$)



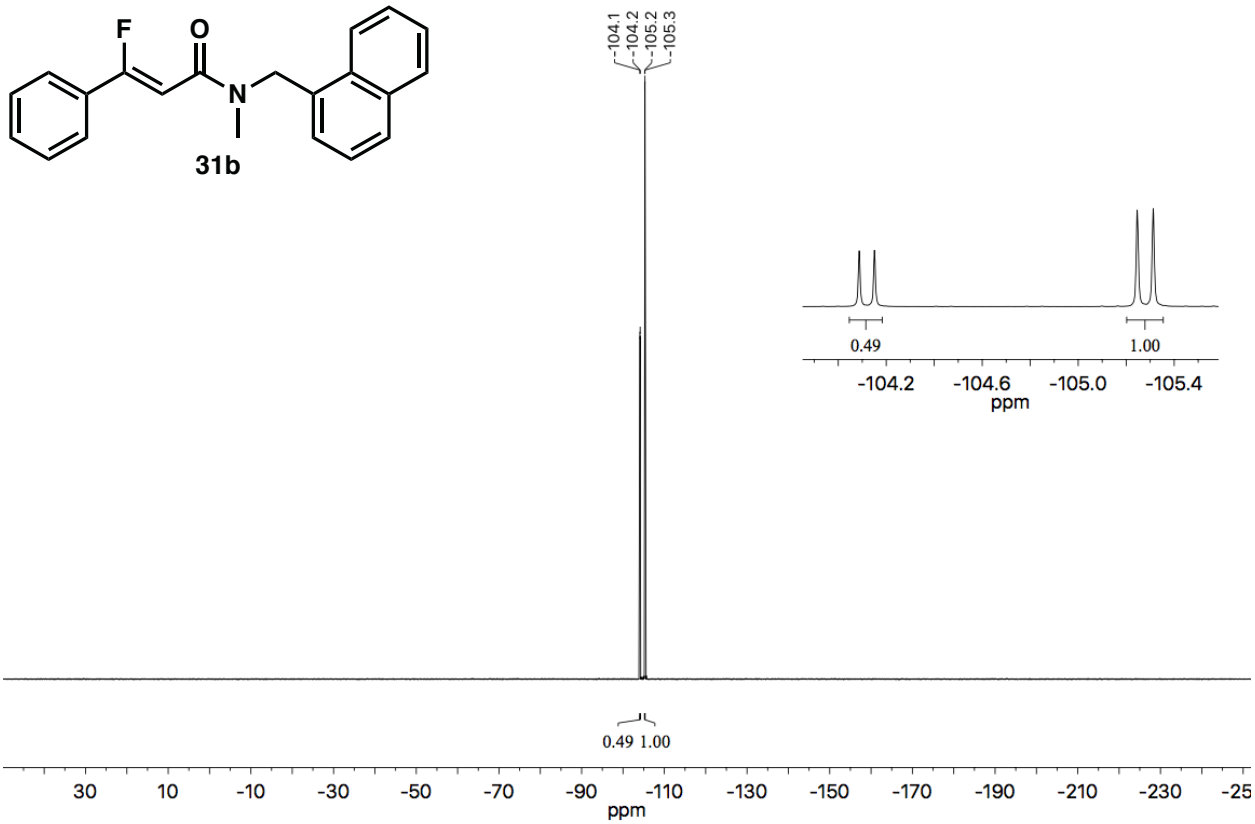
31b



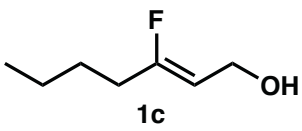
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

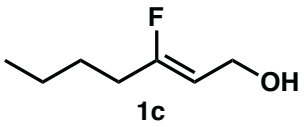


^{1}H NMR (500 MHz, CD_2Cl_2)



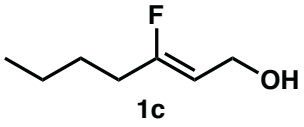
1c

^{13}C NMR (126 MHz, CD_2Cl_2)



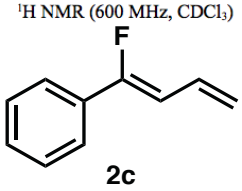
1c

^{19}F NMR (470 MHz, CD_2Cl_2)

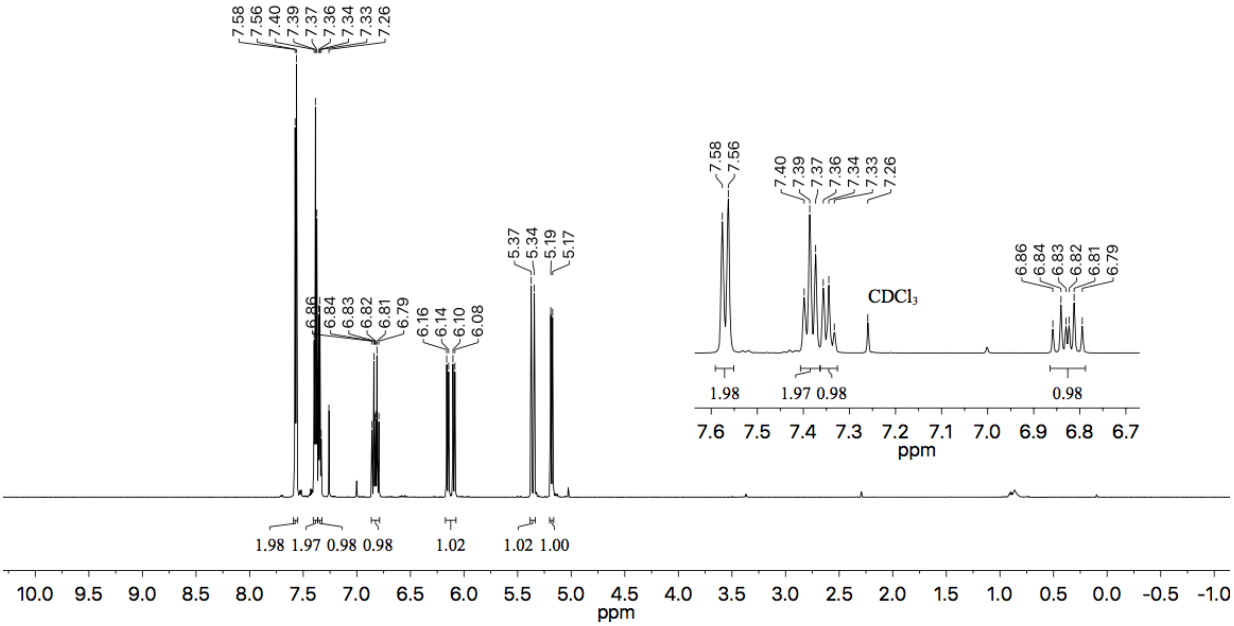


1c

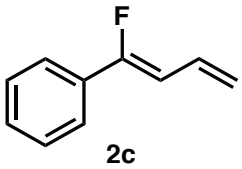
^{1}H NMR (600 MHz, $CDCl_3$)



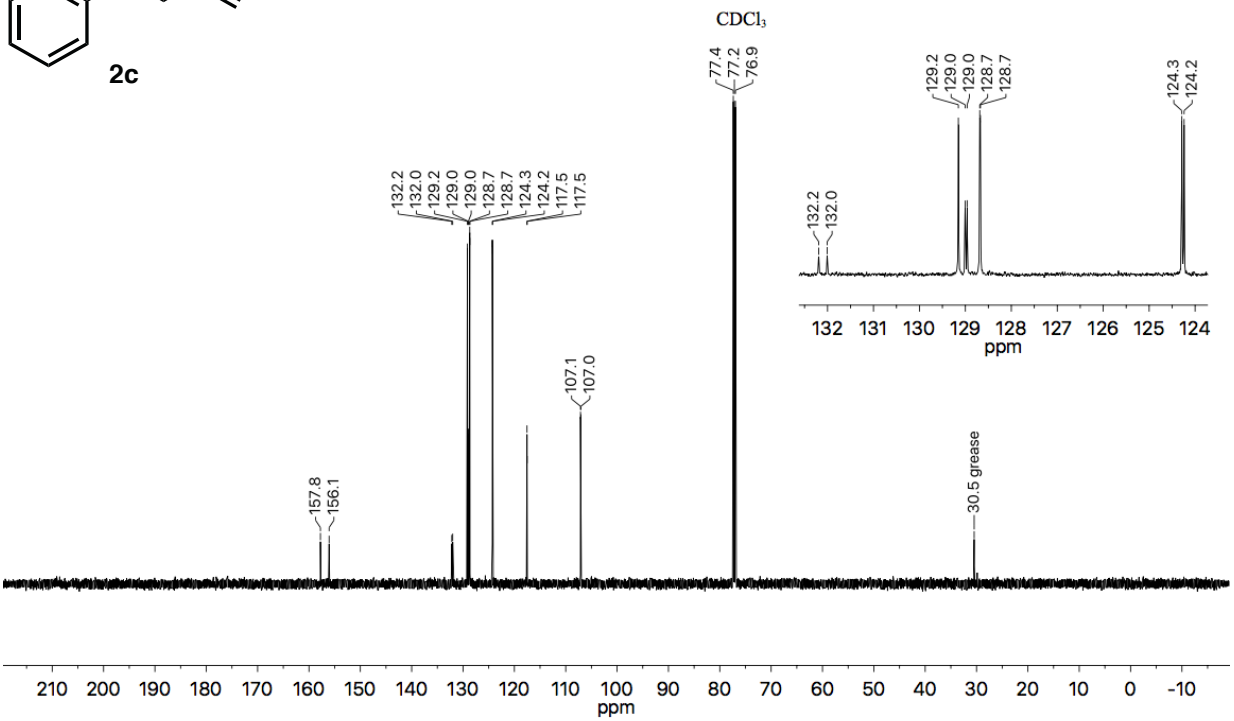
2c



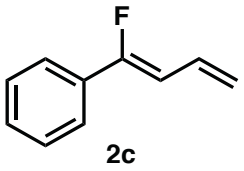
^{13}C NMR (151 MHz, $CDCl_3$)



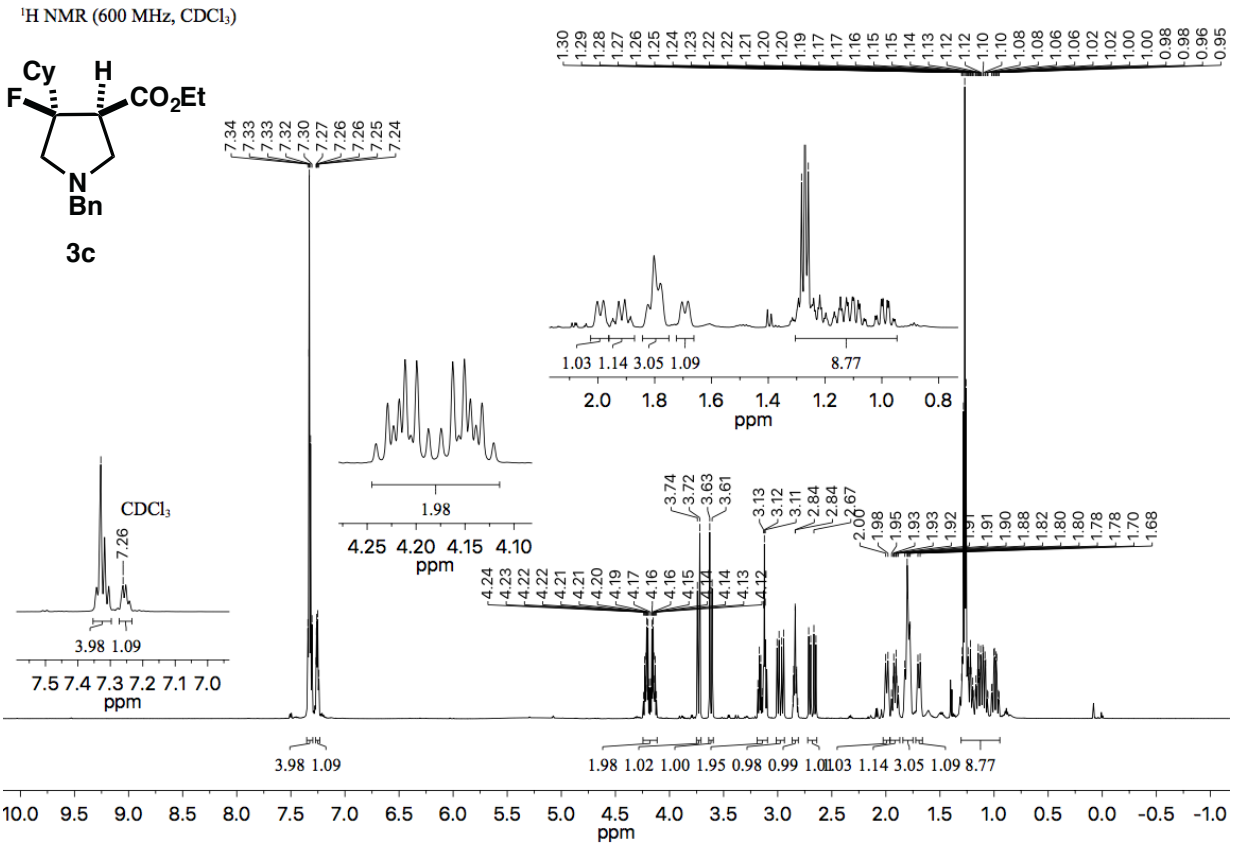
2c



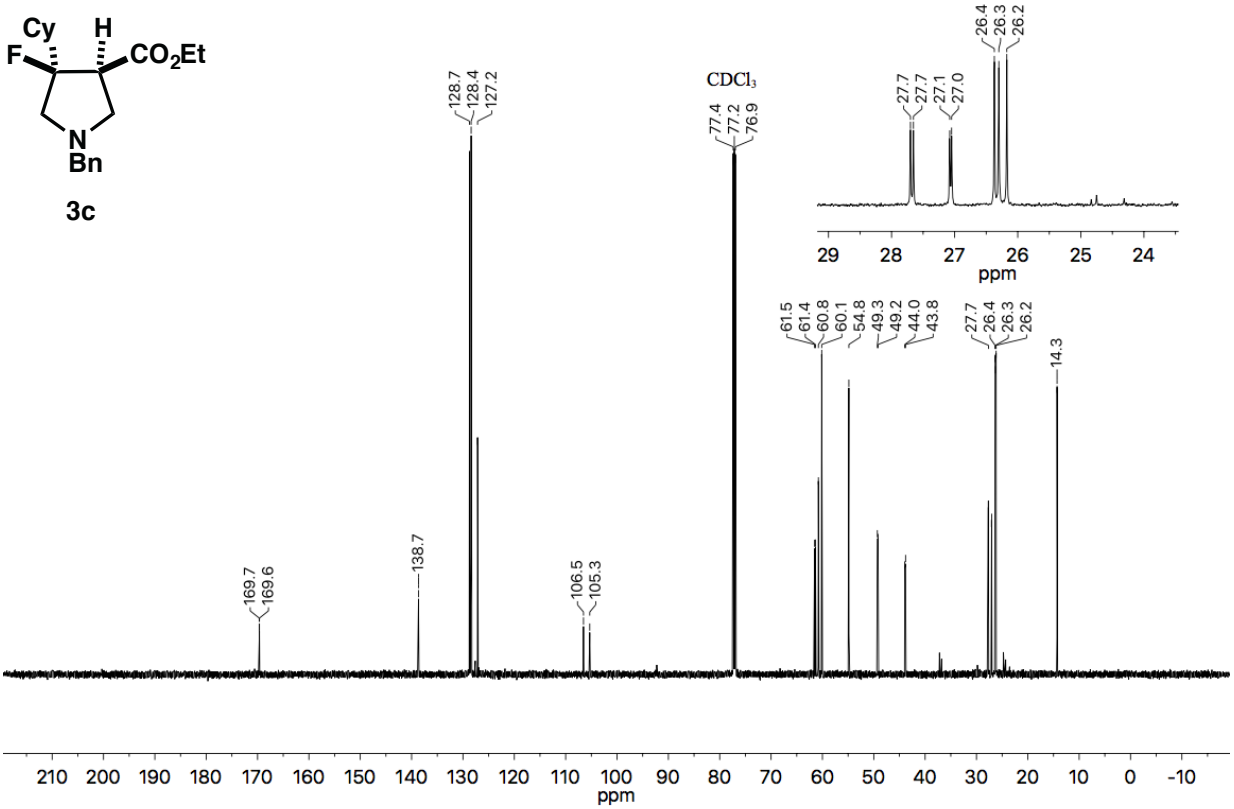
^{19}F NMR (565 MHz, $CDCl_3$)



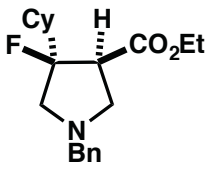
2c


^{1}H NMR (600 MHz, CDCl$_3$)
Cy
H
F
CO$_2$Et
N
Bn
3c
CDCl$_3$
7.26
3.98 1.09
7.5 7.4 7.3 7.2 7.1 7.0
ppm
1.98
4.25 4.20 4.15 4.10
ppm
1.03 1.14 3.05 1.09
8.77
2.0 1.8 1.6 1.4 1.2 1.0 0.8
ppm
3.98 1.09
1.98 1.02 1.00 1.95 0.98 0.99 1.01 1.03 1.14 3.05 1.09 8.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

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

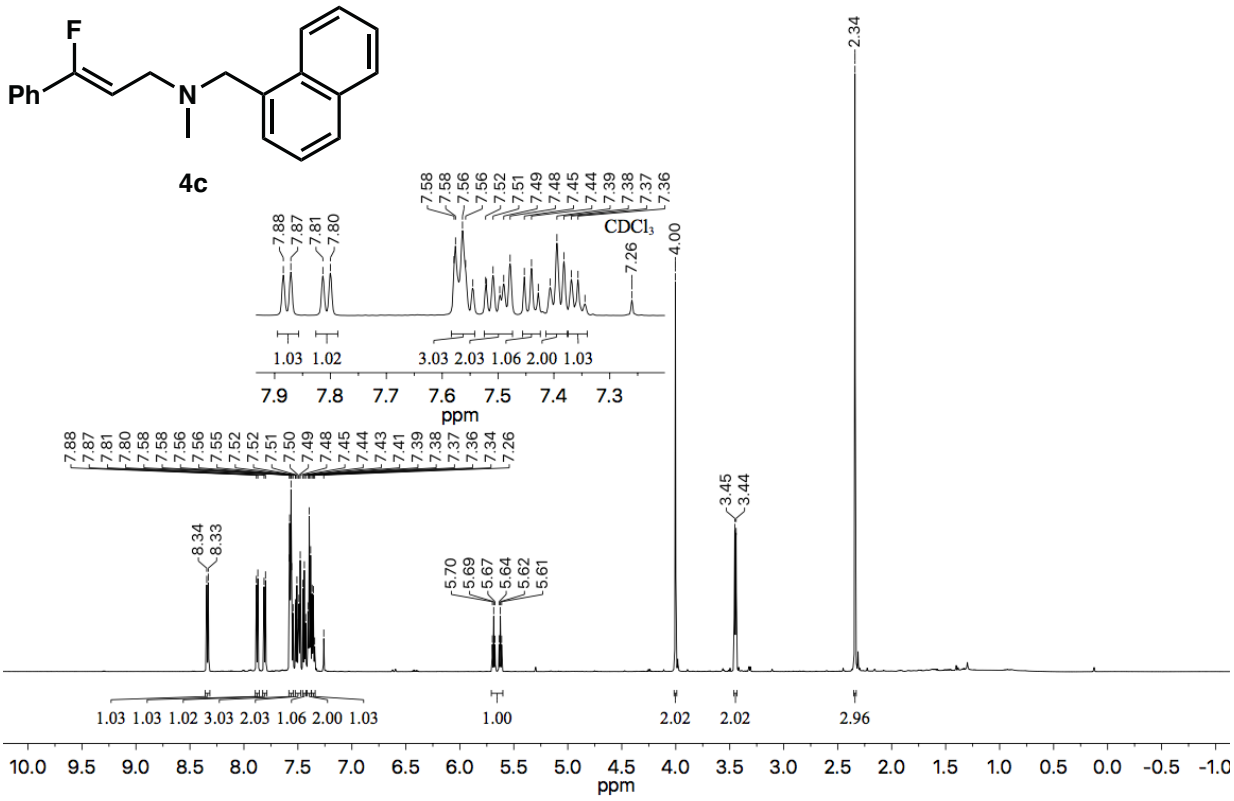


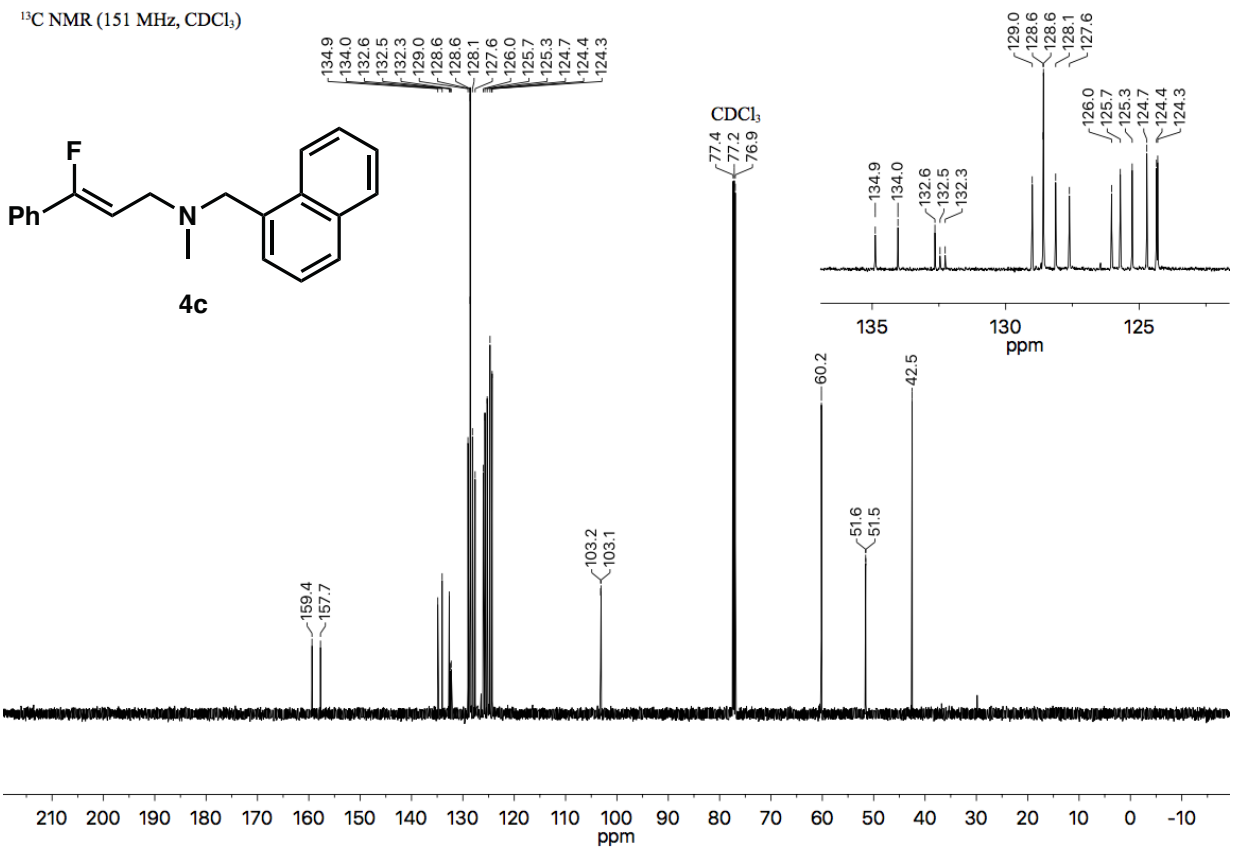
^{19}F NMR (565 MHz, $CDCl_3$)



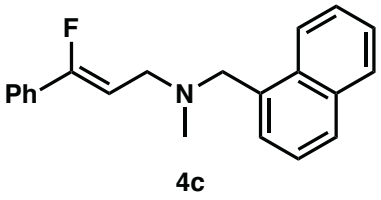
3c

^{1}H NMR (600 MHz, $CDCl_3$)




^{13}C NMR (151 MHz, $CDCl_3$)
F
Ph
N
4c
134.9
134.0
132.6
132.5
132.3
129.0
128.6
128.6
128.1
127.6
126.0
125.7
125.3
124.7
124.4
124.3
$CDCl_3$
77.4
77.2
76.9
159.4
157.7
103.2
103.1
60.2
51.6
51.5
42.5
ppm

^{19}F NMR (565 MHz, $CDCl_3$)



4c

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Chapter 2

Generation of Axially Chiral Allenes through a Copper-Catalyzed, Enantioselective β-Fluoride Elimination

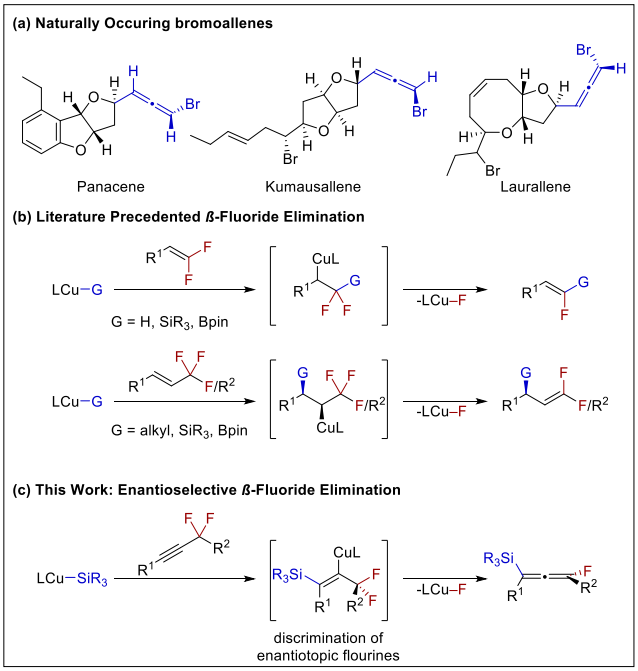
Portions of this chapter have previously appeared in:

O'Connor, T.J.; Mai, B. K.; Nafie, J.; Liu, P.; Toste, F.D. *JACS*. 2021, x, xxxx–xxxx

2.1 Introduction

The pursuit of synthetic methods to access structurally diverse allenes stems from their applications in both medicinal and materials chemistry as well as their ability to serve as a reactive functional group for further synthetic manipulations.[1-2] These cumulenes can exhibit axial chirality, and most of the naturally occurring allenic compounds that have been isolated are nonracemic.[1a,1c] Although enantiopure bromoallenes have been discovered in nature (Scheme 2.1a) and axially chiral bromo-, chloro-, and iodoallenes have been synthesized, the corresponding axially chiral fluoroallenes are largely unknown.[3-4] Specifically, to the best of our knowledge, there is a single report where an enantioenriched tetrasubstituted, axially chiral monofluoroallene has been prepared, albeit in modest enantioselectivity.[4c] Due to a lack of general synthetic routes toward this chiral, fluorinated motif, their potential applications have remained unexplored.

An emerging route toward the catalytic synthesis of ACAs has been from prochiral substrates.[5] This strategy overcomes the requirement for a stoichiometric amount of a chiral auxiliary and or enantioenriched substrates. Prochiral substrates that have been transformed into ACAs include propargylic electrophiles, 1,3-enynes, terminal alkynes, 1,3-dienes, racemic allenes, and vinyl triflates.[6] In the case of vinyl triflates, it was demonstrated that *β*-hydride elimination occurred in an enantioselective fashion, revealing a new mechanistic route for the synthesis of ACAs.[6f] Of the classes of ACAs (1,3-di-, tri-, and tetrasubstituted), tetrasubstituted ACAs remain difficult to synthesize in high enantiopurity.[7] Moreover, the incorporation of a functional group directly attached to ACAs that permits further transformations has gained popularity as evidenced by recent reports of boryl and silyl substituted ACAs.[8-9] Access to tetrasubstituted, boryl or silyl monofluoro ACAs would permit an array of further transformations that could generate quaternary, fluorine-containing stereocenters by way of axial-to-point chirality transfer.[3a,10]



Scheme 2.1 Allenyl Halide Natural Products and Synthesis of Monofluoro ACAs *via* Enantioselective *β*-Fluoride Elimination

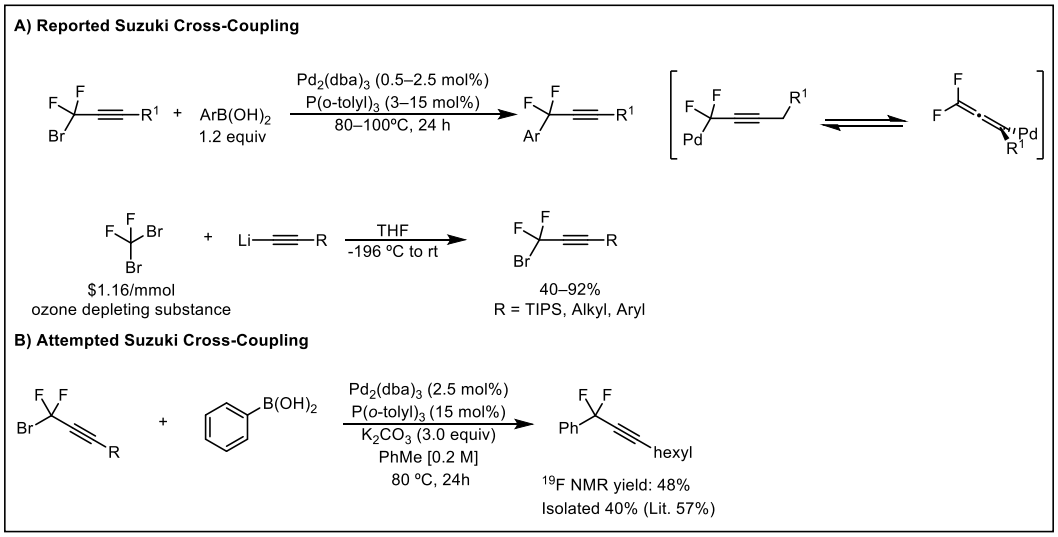
The development of defluorination methods of (poly)fluorinated compounds has emerged as a complimentary strategy to access complex, fluorine-functionalized motifs that have typically been accessed from nonfluorinated substrates.[11] Of the metals that catalyze such defluorination reactions, copper has been shown to be exceptionally competent, as evidenced by the numerous reports of catalytic hydrodefluorinations, defluoroborylations, and defluorosilylations of fluoroarenes and fluoroolefins.[12] An emerging trend in this field is the enantioselective defluorination of allylic CF_3 or CF_2R groups, forging stereocenters adjacent to mono and difluoroolefins (Scheme 2.1b).[13] Recently, a rare example of enantioselective defluorination via oxidative addition to a *gem*-difluoride has been reported as a method to generate products with a fluorine-containing stereogenic unit.[14] A mechanistically different approach was envisioned to achieve the desymmetrization of difluoromethylene groups, proceeding through an enantioselective *β*-fluoride elimination reaction, might be employed in the enantioselective synthesis of monofluoro ACAs (Scheme 2.1c).

To this end, it was hypothesized that reaction of propargylic difluorides with a suitable chiral copper nucleophile would form an alkenyl copper species that could undergo an enantioselective, *β*-fluoride elimination to generate tetrasubstituted monofluoro ACAs (Scheme 2.1c). Potential obstacles toward achieving this transformation included controlling both the regioselectivity[15] and enantioselectivity of the process, avoiding undesired reactivity of the alkenyl copper intermediate[16], and preventing further silylation of the product.[17] This worked described in this chapter demonstrates that *β*-fluoride elimination from an alkenyl copper species is possible and the discrimination of enantiotopic fluorides is a viable elementary process to achieve asymmetric synthesis of ACAs. DFT studies predict that this elimination proceeds through a *syn*-elimination pathway, which is in contrast to some studies of alkyl copper species that undergo *β*-fluoride elimination.[12b,12g-i,13b,13c,13f,13g]

2.2 Results and Discussion

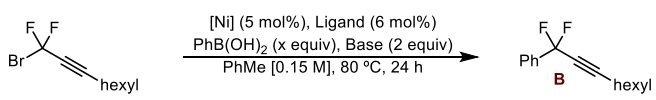
2.2.1 Propargyl Difluorides

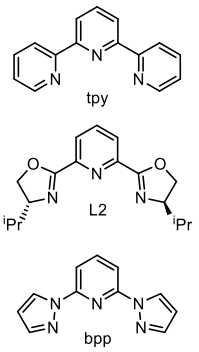
To assess if our transformation was feasible, the synthesis of internal propargylic difluorides had to be achieved. In our hands, existing routes to access this fluorinated motif utilizing deoxyfluorination reagents, such as DAST, were unsuccessful.[18] This result was not too surprising given the fact that the deoxyfluorination of ketones is a particularly challenging transformation, especially for ketones in conjugation with either alkenes or alkynes.[18] Recently, a palladium-catalyzed Suzuki cross-coupling procedure was reported (Zhang 2014) that employed difluoro propargyl bromides as the electrophile and boronic acids as the nucleophile.[19] However, this method proved to be ineffective for the synthesis of internal propargylic difluorides that possessed primary alkyl groups attached to the other terminus of the alkyne (Scheme 2.2B). Although the desired product was detected after the reaction, these difluoroalkynes were challenging to purify because of the allenyl and defluorinated byproducts that were produced by the palladium catalyst.[20] Therefore, other metals to achieve this transformation were examined, revealing that nickel complexes gave the desired product without significant allenyl byproducts (Table 2.1).



Scheme 2.2 Synthesis of Propargylic Difluorides: Palladium-Catalyzed Suzuki Cross-Coupling

Table 2.1 Optimization of Nickel-Catalyzed Suzuki Cross-Coupling[a]





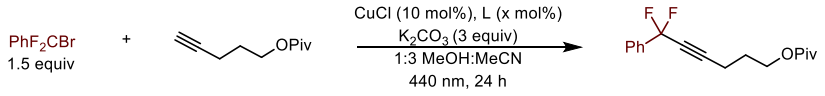
[Ni]	L	$PhB(OH)_2$ (equiv)	Base	B ^{19}F NMR yield (%)	SM (%)
$NiCl_2$dppe	tpy	1.5	K_2CO_3	44	19
$NiCl_2$dppe	tpy	1.5	Cs_2CO_3	34	19
$NiCl_2$dppe	tpy	1.2	K_2CO_3	37	26
$NiCl_2$dppe	L2	1.5	K_2CO_3	5	22
$NiCl_2$dppe	4'-Cl tpy	1.5	K_2CO_3	31	31
$NiCl_2$dppe	bpp	1.5	K_2CO_3	49	0
$NiBr_2$dppe	bpp	1.5	K_2CO_3	50	0
(dppe)NiBrMes	bpp	1.5	K_2CO_3	44	0
(dppe)NiBrMes	bpp	2.2	K_2CO_3	63	0

[a]Standard conditions: alkyne (0.10 mmol), [Ni] (5 mol%), L (6 mol%), PhMe (0.8 mL), 80 °C, 24 h. Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard.

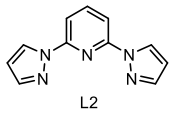
Although a reliable route was developed to generate internal propargylic difluorides, it still required the use of dibromodifluoromethane–which is an expensive ($1.16/mmol), ozone depleting substance–cryogenic temperatures, and alkyl lithium reagents (Scheme 2.2A). The latter hampered the functional group tolerance of the synthetic route. It was envisioned that an alternative route that utilizing a cheaper, more environmentally friendly fluorinated building block and avoided the use alkyl lithium reagents. Recently, there have been reports of both photoinduced and thermal conditions that couple alkynyl copper species with activated alkyl halide electrophiles, such as alkyl iodides and benzyl bromides.[21] This work inspired the development of the Sonogashira cross-coupling of terminal alkynes with difluoro benzyl bromides in the presence of copper catalyst. A method to generate the required difluoro benzyl bromides was optimized that utilized silver-catalyzed decarboxylation of readily available aryl difluorocarboxylic acids, which can be made in two steps from ethyl bromodifluoroacetate ($0.06/mmol) (See SI). With access to large quantities of the necessary electrophile, suitable conditions for the photoinduced Sonogashira cross-coupling were developed (Table 2.2 and 2.3). Importantly, tridentate ligands, specifically terpyridine were very effective for this transformation whereas bidentate

pyridines largely returned unreacted alkyne. The deprotection of the pivalate group was problematic, but removing methanol as a cosolvent overcame this unproductive, side reaction. Although several Cu(I) salts could be employed cationic Cu(I) precursors were the most effective for this transformation.

Table 2.2 Initial Results of Copper-Catalyzed, Photoinduced Sonogashira Cross-Coupling[a]



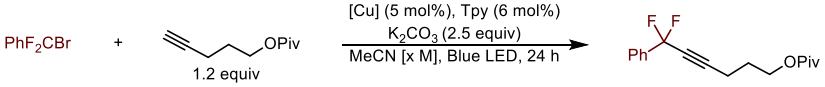
L (%)	^{19}F yield (SM %)
Tpy (12)	73% (60)
Tpy (20)	52% (98)
L2 (12)	trace (143)
dtbpy (12)	5% (126)
1,10-Phen (12)	nd (150)
3,4,7,8-Me-Phen (12)	10% (25)



L2

[a]Standard conditions: alkyne (0.10 mmol), MeOH:MeCN 3:1 (1.0 mL), 24 °C, 24 h, Blue LED (440 nm Kessil). Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard.

Table 2.3 Optimization of Copper-Catalyzed, Photoinduced Sonogashira Cross-Coupling[a]

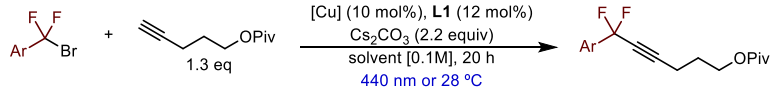


[Cu]	MeCN [X M]	^{19}F yield (SM %)
$Cu(MeCN)_4BF_4$	0.2	75% (17)
$Cu(MeCN)_4BF_4$	0.1	92% (<2%)
$Cu(MeCN)_4OTf$	0.2	90% (nd)
$Cu(MeCN)_4BF_4$	0.1 (DCM)	13% (70)
$Cu(MeCN)_4BF_4$	0.1 (THF)	4% (38)

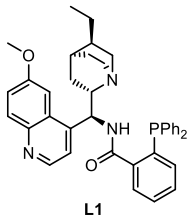
[a]Standard conditions: $PhCF_2Br$ (0.10 mmol), solvent (1.0 mL), 24 °C, 24 h, Blue LED (440 nm Kessil). Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard.

Although the reaction was scalable, it required rigorously degassed solvents for reproducible results. An alternative system was developed that utilized a tridentate P, N, N ligand and a copper salt. This catalytic system did not require rigorously degassed solvents nor blue LED (440 nm) irradiation (Table 2.4). With the optimal conditions in hand, a variety of alkynes were tested in the reaction, affording access to internal propargylic difluorides with functional groups that would have not been tolerated by existing technologies (Table 2.5). Having developed an affordable, functional group tolerant, and environmentally friendly route to this underrepresented motif, the focus turned to the generation of axially chiral monofluoroallenes.

Table 2.4 Optimization of Copper-Catalyzed, Thermal Sonogashira Cross-Coupling[a]

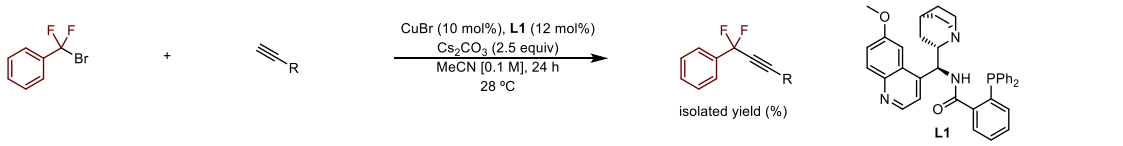


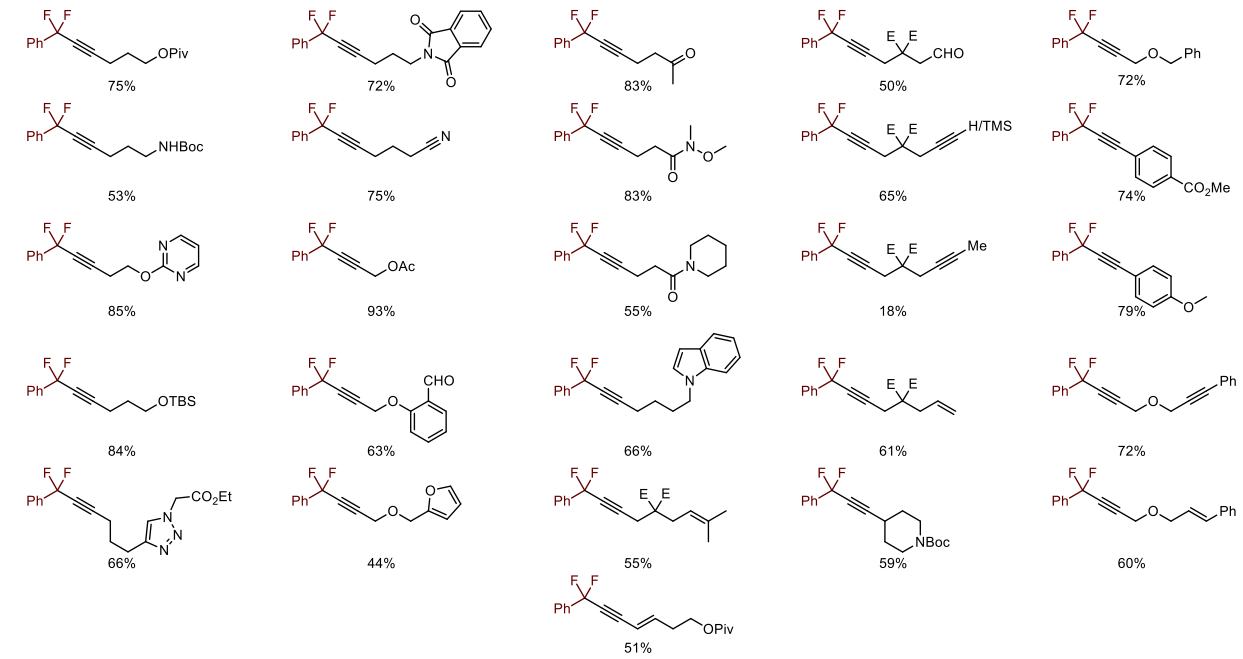
Ar	Cu	solvent	hv or Δ	^{19}F yield (SM %)
Ph	CuCl	dioxane	hv	36% (17)
Ph	CuCl	THF	hv	55% (10)
Ph	CuCl	MeCN	hv	65% (3)
Ph	$Cu(MeCN)_4BF_4$	MeCN	hv	50% (12%)
Ph	CuCl	MeCN	28 °C	96% (1%)
p-CN	CuCl	MeCN	28 °C	35% (17%)
p-NO_2	CuCl	MeCN	28 °C	8% (3%)
p-CN	CuCl	THF	34 °C	52% (7%)
p-CN	CuBr	THF	34 °C	60% (0%)
p-Ac	CuBr	MeCN	28 °C	50% (1%)
p-Br	CuBr	MeCN	28 °C	96% (0%)



[a]Standard conditions: $PhCF_2Br$ (0.10 mmol), solvent (1.0 mL), 24 h, hv = Blue LED (440 nm Kessil). Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard.

Table 2.5 Scope of Copper-Catalyzed, Thermal Sonogashira Cross-Coupling[a]





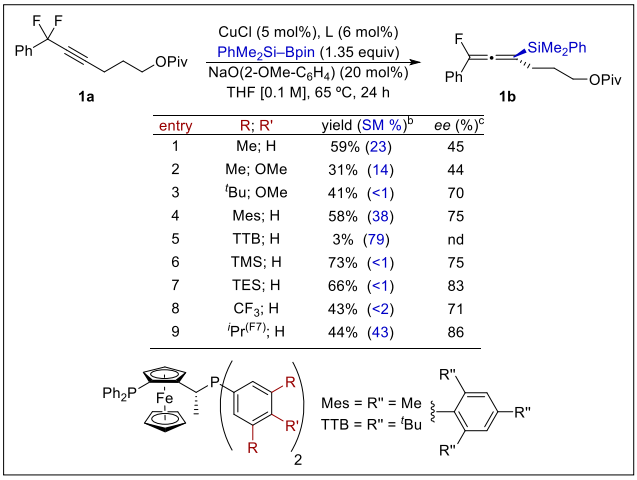
[a]Standard conditions: $PhCF_2Br$ (3.0 mmol), alkyne (1.2 equiv), MeCN (30 mL), 24 h, 28 °C. Reported percentages are of isolated yields.

2.2.2 Copper-Catalyzed, Enantioselective *β*-fluoride Elimination

The investigation began by determining if *β*-fluoride elimination was feasible from a vinyl copper intermediate. In the presence of a suitable base, the borylation of **1a** with B_2pin_2 generated the desired boryl, monofluoroallene in approximately 40% NMR yield. Attempts at isolating this product, however, were unsuccessful.[8b] It was hypothesized that the corresponding silyl, monofluoroallene of **1a** would be isolable, and gratifyingly discovered that the silylation of **1a** with $PhMe_2SiBpin$ (**2**) led to **1b**. After a brief optimization of conditions, over 40 chiral ligands were examined for this transformation. Of the chiral ligands employed, only four gave the desired allene in greater than 20% *ee*.

Fortunately (*R*, *S*)-Josiphos afforded **1b** in a modest yield (71%) and promising enantioselectivity (20% *ee*). A series of Josiphos ligands was generated to evaluate their steric and electronic effects (See SI Tables S1 and S2) on the reaction. Josiphos ligands containing aryl groups on both phosphorus atoms demonstrated good reactivity and enantioselectivity, specifically when the alkyldiarylphosphorus moiety possessed bulky 3,5-substituted arenes (Table 2.6 compare entries 2, 3; SI Tables S2 and S3). However, once the 3,5-substituents became sterically too demanding, for example with the TTB derivative, the reactivity dropped significantly (entry 5). Moreover, it appeared that steric rather than electronic factors played a decisive role in determining the enantioselectivity of the transformation (compare entries 3, 8).

Table 2.6 Structural Effect of Josiphos on Transformation[a]



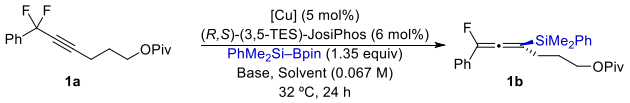
entry	R; R'	yield (SM %)[b]	*ee* (%)[c]
1	Me; H	59% (23)	45
2	Me; OMe	31% (14)	44
3	^{t}Bu; OMe	41% (<1)	70
4	Mes; H	58% (38)	75
5	TTB; H	3% (79)	nd
6	TMS; H	73% (<1)	75
7	TES; H	66% (<1)	83
8	CF_3; H	43% (<2)	71
9	^{i}Pr$^{(F7)}$; H	44% (43)	86

[a]Standard conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.135 mmol, 1.35 equiv), CuCl (5 mol%), L (6 mol%), THF (1.0 mL), 65 °C, 24 h. [b]Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard. [c]Determined by HPLC with a chiral stationary phase.

Further optimization led to simplified reaction conditions (Table 2.7). By lowering the temperature and changing the solvent, the enantiomeric excess of **1b** improved to 90%; but the overall conversion of **1a** dropped (entry 1). Increasing the amount of phenoxide base resulted in decoordination of the ligand, determined by ^{31}P NMR spectroscopy, and erosion of the *ee* of **1b**.[22] By using an insoluble source of fluoride (CsF), an increase in the chemical yield of **1b** was achieved (83%, entry 2). Possible roles of CsF could be either trapping FBpin[23] and/or releasing CsOAr from ArOBpin.[24] Fortunately, the transformation proceeded with CsF as the sole base, removing the chance of phosphine decoordination due to excess phenoxide.[25] The reaction proceeded well in nonpolar, low coordinating solvents (entries

4-7), and the removal of MeCN led to in an increase in catalytic activity (entries 8, 9). Switching to $[Cu(OTf)]_2 \bullet C_6H_6$ as the copper source afforded the desired allene in almost quantitative yield (entry 10).

Table 2.7 Reaction Optimization[a]



entry	[Cu]	Base (mol%)	Solvent	yield (SM %)[b]	*ee* (%)[c]
1	$Cu(MeCN)_4BF_4$	A (20)	PhMe	50% (49)	90
2	"	A (20), CsF (100)	"	83% (13)	90
3	"	CsF (150)	"	75% (11)	91
4	$Cu(MeCN)_4BF_4$	"	THF	39% (48)	74
5	"	"	Dioxane	65% (20)	91
6	"	"	Cyclohexane	50% (31)	87
7	"	"	MTBE	75% (10)	92
8	"[d]	"	"	74% (<1)	91
9	$Cu(MeCN)_4OTf$[d]	"	"	82% (4)	90
10	$[CuOTf]_2 \bullet C_6H_6$ (2.5%)	CsF (160)	"	98% (-)	90

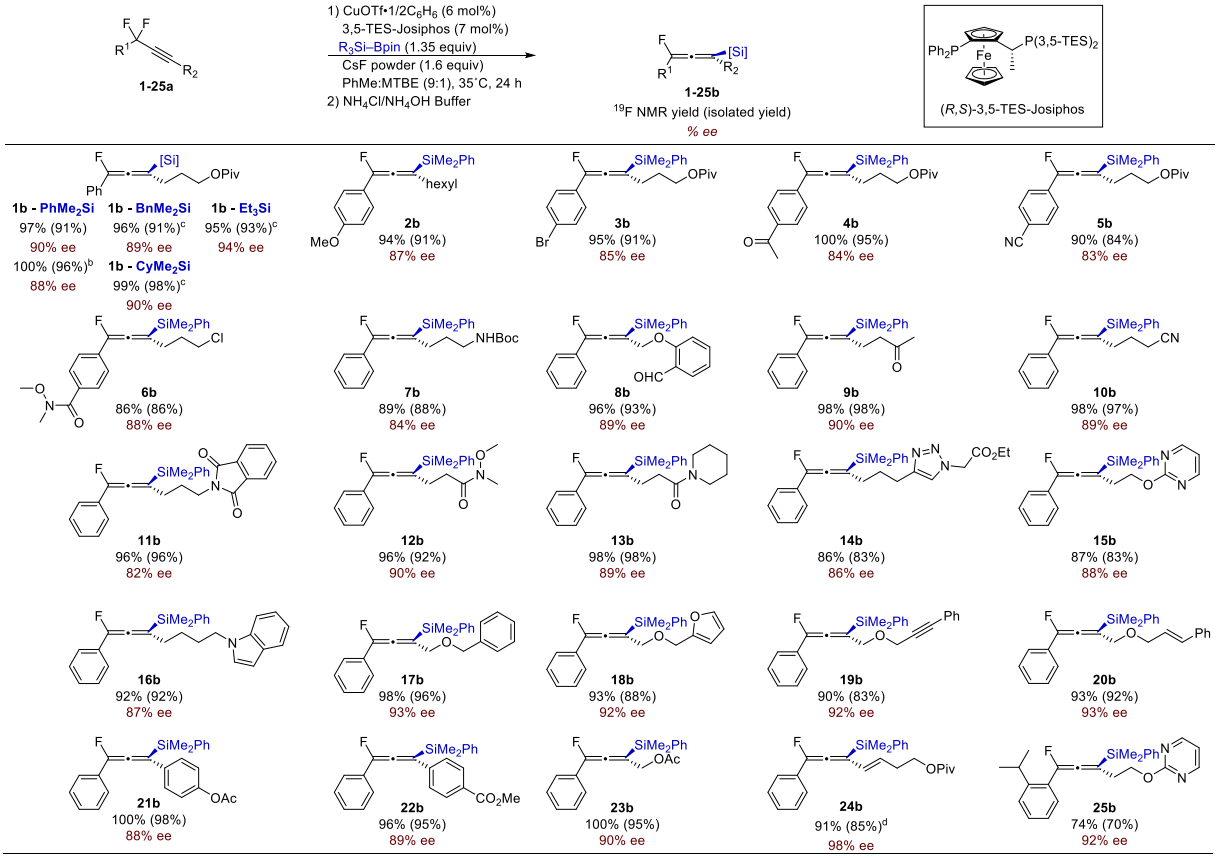
[a]Standard conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.135 mmol, 1.35 equiv), [Cu] (5 mol%), L (6 mol%), solvent (1.5 mL), 32 °C, 24 h. A = $NaO(2\text{-}OMeC_6H_4)$. [b]Yield was determined by ^{19}F NMR of crude reaction, using PhF as an internal standard. [c]Determined by HPLC with a chiral stationary phase. [d]MeCN removed before reaction.

With the optimal conditions were established, a series of difluoroalkynes were subjected to defluorosilylation. A range of functional groups were tolerated under the optimal reaction conditions, affording the desired allenes **1–24b** in high yields (83–98%) and in good enantioselectivities (82–98%) after isolation (Table 2.8). Notably, alkynes (**19b**), alkenes (**20b**), enynes (**24b**), aldehydes (**8b**), ketones (**9b**) propargylic acetates (**23b**) as well as alkyl and aryl halides (**3b** and **6b**) were tolerated. Coordinating heterocycles (**14-16b**, **18b**, and **25b**), amides (**7b**, **11-13b**), and nitriles (**5b** and **10b**) also did not hamper catalysis. Although changing the electronics of the aryl ring slightly decreased the enantiomeric excess of the reaction (**1-6b**), increasing the steric bulk of the aryl group was well tolerated (**25b**). To explore the scalability of this method, **1b** was synthesized on a 6 mmol scale without a significant loss in enantioselectivity or chemical yield. It was discovered that other silylboranes could be utilized for this transformation when (*R,S*)-3,5-Trip-Josiphos was employed as the ligand (**1b-BnMe$_2$Si**, **1b-CyMe$_2$Si**, and **1b-Et$_3$Si**). These allenyl silanes were synthesized on gram scales with comparable yields and enantioselectivities to **1b-PhMe$_2$Si**. When the aryl group of alkyne **1a** was exchanged for either, alkynyl, alkenyl, or alkyl substituents or when the alkyl chain of alkyne **1a** was changed from 1° to 2° the reaction either produced the desired monofluoroallene in lower yield and enantiomeric excess or the reaction failed to occur (See SI for current limitations).

Determination of the absolute configuration of allene **10b** was achieved using vibrational circular dichroism (VCD).[26] After a careful conformational search (see SI for details) at four levels of theory, B3LYP/6-31G(d), B3PW91/6-31G(d), B3LYP/cc-pVTZ, and B3PW91/cc-pVTZ,[27] the resulting conformers were Boltzmann averaged and plotted with a line width of 5 cm^{-1} to produce the final theoretical spectra. The IR and VCD spectra were then frequency scaled[27] for comparison to the experimental data. Calculations at all four levels of theory matched well, proving the absolute

configuration of **10b** to be *S*. Of the four methods employed, the best agreement with experimental data was from the B3PW91/cc-pVTZ level. The comparison of experimental and theoretical spectra was quantified[28] using BioTools (Jupiter, FL) CompareVOA software, with high neighborhood similarity for IR (90.4) and VCD (69.6), ESI (Enantiomeric Similarity Index) for VCD (62.9) and a confidence level of 99%. Of particular note was the asymmetric allene C-C-C stretch observed at 1933 cm^{-1}, which was one of many closely correlated bands between experiment and theory. The absolute configuration of **12b** and **1b-SiEt$_3$** were also determined to be *S* by VCD (See SI for details).

Table 2.8 Scope of Asymmetric β-Fluoride Elimination[a]



[a]Standard conditions: **1**–**25a** (0.20 mmol, 1.0 equiv), **2** (0.27 mmol, 1.35 equiv), CuOTf·1/2C_6H_6 (6 mol%), L (7 mol%), CsF (1.6-1.8 equiv) 9:1 PhMe:MTBE or MTBE (3.0 mL), 35-45˚C, 24 h. Reported yields are of isolated allene. Enantiomeric excess was determined by HPLC with a chiral stationary phase.[b] **1a** (6.0 mmol), CsF(25%)–CaF_2 (1.6 equiv), 30 h;[c] **1a** (2.5-3.0 mmol), $R_3SiBpin$ (1.35-1.45 equiv), Cu (8-9 mol%), 3,5-TripJosiphos (9-10 mol%), CsF(25%)–CaF_2 (1.8-2.5 equiv), MTBE, 28-45˚C, 30-48h;[d] NaO(2-$OMeC_6H_4$) (30 mol%), CsF (1.0 equiv), PhMe, 27˚C.

On the basis of previous reports regarding CuF[12c,12e,16a,25,29] and copper silyl species[15b,15f,17d,30], the following mechanism for the copper-catalyzed reaction is proposed (Figure 2.1). First, a complex between Josiphos and [CuOTf] undergoes salt metathesis with CsF to generate JosiphosCuF (**Cu1**).[16a,25,29d] σ-Bond metathesis with $PhMe_2SiBpin$ (**2**) generates $JosiphosCuSiMe_2Ph$ (**Cu2**), and releases FBpin.[12c,12e] Subsequent coordination and silylation of the triple bond generates an alkenyl Cu species (**Cu3**).[15a,15e,31] A β-fluoride elimination[12g] regenerates **Cu1**, which is trapped by either FBpin,[23,32] **2**,[15c] or decomposes the formed allenylsilane (**c**). As FBpin is more Lewis acidic than B_2pin_2,[32] the same is likely true with **2**. By using a judicious amount of CsF and a nonpolar solvent it is proposed that the precipitation of Cs[F_2Bpin][23-24] drives this reaction forward. ^1H, ^{19}F, and ^{11}B NMR studies have identified **Cu1**, **Cu2**, $LCuF_2Bpin$, as well as LCuOH and confirmed the generation of **Cu2** from both **Cu1** and $LCuF_2Bpin$ (See SI Section 7). **Cu2** was also shown to react with alkyne **1a**, generating both allene **1b** and FBpin. It appears that $LCuF_2Bpin$ acts as a reservoir of Cu^IF and, under catalytic conditions, a monomeric or dimeric CuF was not observed. Over the course of the reaction only **Cu2**, $LCuF_2Bpin$, and LCuOH were observed, which converged to **Cu2** after the alkyne has been consumed (See SI Section 7). Based on our experiments, it appears that the silylation of the alkyne and the β-fluoride elimination reactions are the

rate- and selectivity-determining steps, respectively. Using (*R*,*S*)-3,5-TES-JosiphosCuF$_2$Bpin as a catalyst, the desired allene **1b** was obtained in a similar yield and enantiomeric excess, demonstrating its catalytically competence (See SI Section 7).

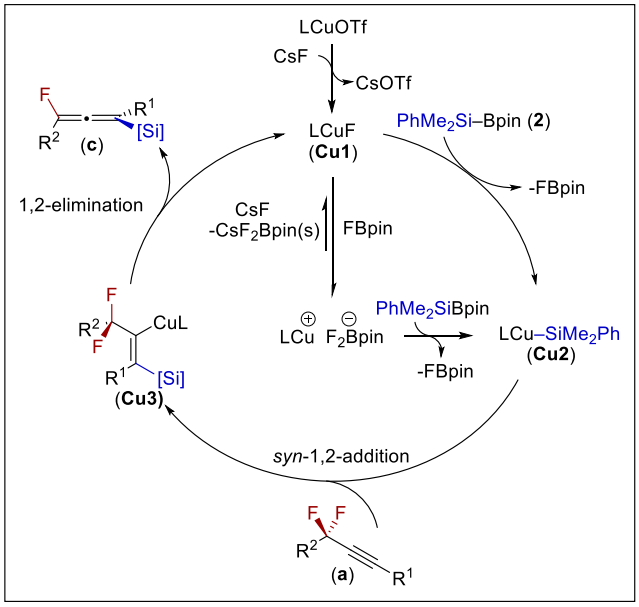


Figure 2.1 Proposed catalytic cycle

Density functional theory (DFT) calculations were performed to investigate the reaction mechanism and origin of enantioselectivity of this Cu-catalyzed asymmetric silylation of propargylic difluorides. The DFT calculations were performed at the M06/SDD(Cu,Fe)–6-311+G(d,p)/SMD(toluene)//B3LYP-D3/SDD(Cu,Fe)–6-31G(d) level of theory using difluoroalkyne 27a and PhMe$_2$SiBpin (**2**) as model substrates. The (*R*,*S*)-3,5-TMS-Josiphos ligand was used in the DFT calculations for simplicity, because the use of this ligand in the ligand screening provided only slightly lower *ee* than using (*R*,*S*)-3,5-TES-Josiphos (Table 1, entries 6 and 7). Based on the proposed catalytic cycle, the computed reaction energy profile is shown in Figure 2.2. The association of FBpin to monomeric LCuF (**26**) to form a heterodimer (**29**) is exergonic by 4.0 kcal/mol, suggesting that the more stable complex **29** can be an off-cycle reservoir of Cu$^{\text{I}}$F. Although the dimerization of LCuF is exergonic by 7.3 kcal/mol, its formation is expected to be less favorable than forming **29** due to the low concentrations of LCuF under catalytic conditions (see Figure S1 for detailed discussions about the equilibrium of **26**, **29**, and the dimer of LCuF).

The σ-bond metathesis between monomeric LCuF (**26**) and PhMe$_2$SiBpin (**2**) takes place *via* a four-membered cyclic transition state (**TS-1**) to form silyl copper intermediate **30** and FBpin. This step requires a low activation barrier of 6.7 kcal/mol with respect to **26** and is exergonic by 24.7 kcal/mol. Migratory insertion of alkyne **27a** into the silyl copper (TS-2) gives alkenyl copper species **31**. This migratory insertion is highly regioselective for the formation of Cu–C bond at the alkyne terminus adjacent to the difluoromethylene. The transition state leading to the other regioisomer, **TS-2'**, is 10.9 kcal/mol higher in energy than **TS-2**. The high level of regioselectivity is due to steric repulsions between

the silyl and the more hindered alkyne terminus(C1) in **TS-2'** as well as inductive effects of the difluoro substituents that stabilize the building negative charge at C1 in **TS-2**.

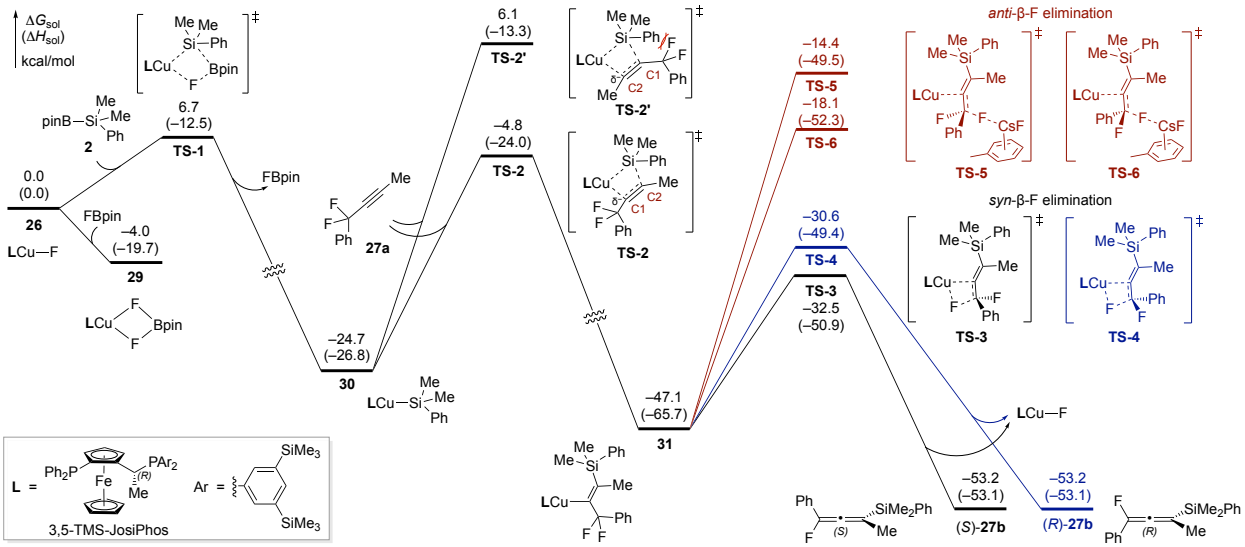


Figure 2.2 Computed reaction energy profiles of the Cu-catalyzed silylation and asymmetric *β*-fluoride elimination. Gibb free energies and enthalpies (in kcal/mol) are with respect to the CuF **26a.**

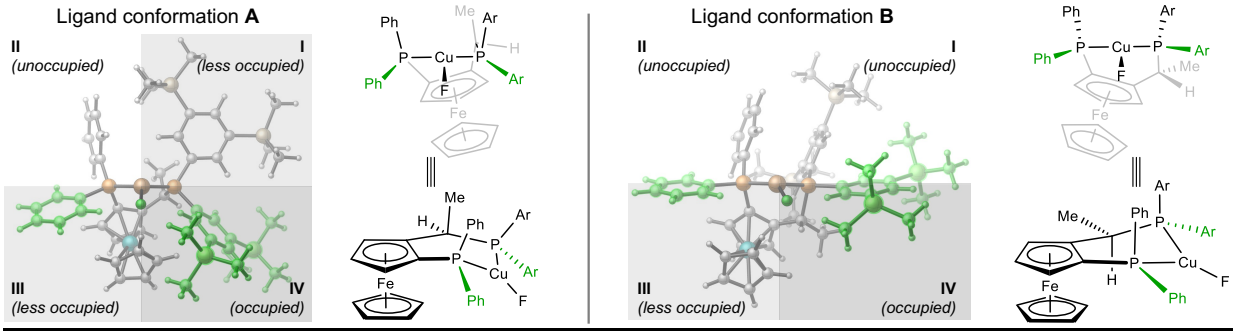
From **31**, both *syn*[12g-i]- and *anti*[13b]-*β*-fluoride elimination pathways were calculated. The *syn*-elimination of either of the two diastereotopic *β*-F in **31** (via **TS-3** and **TS-4**) involves a four-membered cyclic transition state, while the *anti*-*β*-fluoride elimination is facilitated by CsF as a Lewis acid (via **TS-5** and **TS-6**). The FBPin-facilitated *anti*-elimination was also computed and is also less favorable than the *syn*-elimination (see Figure S3). The *syn*-elimination pathways require much lower barriers than the *anti*-elimination, which is in contrast to a computational study by Hoveyda and Torker that suggested the *β*-fluoride elimination from alkyl copper species favors the *anti*-pathway due to Lewis acid (*i.e.* Na^+) coordination to the F^- leaving group and the Bpin group on the substrate.[13b] In the present study, the lack of such chelating Lewis-acid coordination in the *anti*-pathway, the weaker Lewis acidity of CsF, and the strain release effect that alleviates steric repulsions between the $SiMe_2Ph$ group and the Cu in the *syn*-elimination transition state changed the reaction mechanism to favor the *syn*-elimination.[33]

Among the three key elementary steps in the catalytic cycle, the alkyne migratory insertion (**TS-2**) has the highest activation free energy ($\Delta G^{\ddagger}$ = 19.9 kcal/mol with respect to **30**). This finding is consistent with our experimental results that suggest this step being the rate-determining step (*vide supra*). The enantioselectivity-determining step is the *syn*-*β*-fluoride elimination. **TS-3**, which leads to the (*S*)-enantiomer of the monofluoroallene product, is 1.9 kcal/mol more stable than **TS-4** that leads to the (*R*)-enantiomer. The predicted enantioselectivity is consistent with the absolute configuration of the product identified by the VCD analysis.

Next, detailed analysis was performed to investigate the effects of the Josiphos ligand on the reactivity and enantioselectivity of the *β*-fluoride elimination. Because of the conformational flexibility of the (*R,S*)-3,5-TMS-Josiphos ligand,[34] a careful conformational search was performed for all intermediates and transition states in the catalytic cycle. These calculations revealed at least four different conformers of the 3,5-TMS-

Josiphos-supported copper complexes. The two most stable and catalytically active ligand conformations **A** and **B** are shown in Table 2.9 (see Figures S4-S6 for all possible ligand conformations). Ligand conformation **A** involves a twist-boat-type six-membered ring and is more favorable in the copper fluoride (**26**), the σ-bond metathesis transition state (**TS-1**), and the silyl copper intermediate (**30**). In more sterically encumbered structures, including the migratory insertion transition state (**TS-2**), alkenyl copper (**31**), and the *β*-fluoride elimination transition states (**TS-3** and **TS-4**), ligand conformation B becomes more favorable. This ligand conformation involves a half-chair type six-membered ring, which points the Ar and Ph groups in quadrants **I** and **II** away from the Cu center. As such, the bulky $SiMe_2Ph$ group is placed between these unoccupied quadrants to minimize steric repulsions between the ligand and the $SiMe_2Ph$ group on the substrate.

Table 2.9 Relative free energies of conformers of (*R,S*)-3,5-TMS-Josiphos-supported copper complexes and transition states.[a]



Ligand conformation	LCuF (**26**)	*σ*-Bond metathesis (**TS-1**)	Silyl copper (**30**)	Migratory insertion (**TS-2**)	Alkenyl copper (**31**)	*Syn*-*β*-fluoride elimination	
						TS-3	**TS-4**
A	**0.0**	**6.7**	**−24.7**	2.9	−42.8	−26.7	−28.4
B	4.8	10.8	−23.5	**−4.8**	**−47.1**	**−32.5**	**−30.6**

[a] All Gibbs free energies are in kcal/mol with respect to the monomeric copper fluoride **26**. Bold numbers indicate the favorable ligand conformation.

Ligand conformation **B** not only stabilizes the silylalkenyl copper species, but also plays a significant role in controlling the enantioselectivity of the *β*-fluoride elimination. The *P*-phenyl group in quadrant **III** and the *P*-3,5-TMS-phenyl group in quadrant **IV** point towards the Cu center and thus occupy these quadrants. The larger size of the 3,5-TMS-phenyl compared to phenyl indicates that the ligand-substrate repulsions in quadrant **IV** would be more pronounced than those in quadrant **III**. Indeed, quadrant diagrams of the *β*-fluoride elimination transition states (Figure 2.3) support this hypothesis. In the less favorable transition state **TS-4**, the phenyl group on the substrate is located in the more occupied quadrant **IV**, leading to steric repulsion with a TMS group on the ligand. By contrast, in the more favorable *β*-fluoride elimination transition state **TS-3**, the much smaller fluoro group is located in quadrant **IV**, and thus the ligand-substrate steric repulsions are diminished. Next, energy decomposition analysis (EDA)[35] calculations were performed to quantitatively analyze the ligand-substrate non-covalent interactions in **TS-3** and **TS-4** (see SI for computational details). The EDA calculations revealed that the dominant factor controlling the enantioselectivity is the Pauli repulsion (*i.e.* steric repulsion) between the (*R,S*)-3,5-TMS-Josiphos ligand and the substrate. The Pauli repulsion energy (ΔE_{Pauli}) in **TS-4** is 1.7 kcal/mol higher than that in **TS-3**, and thus destabilizes the former transition state.

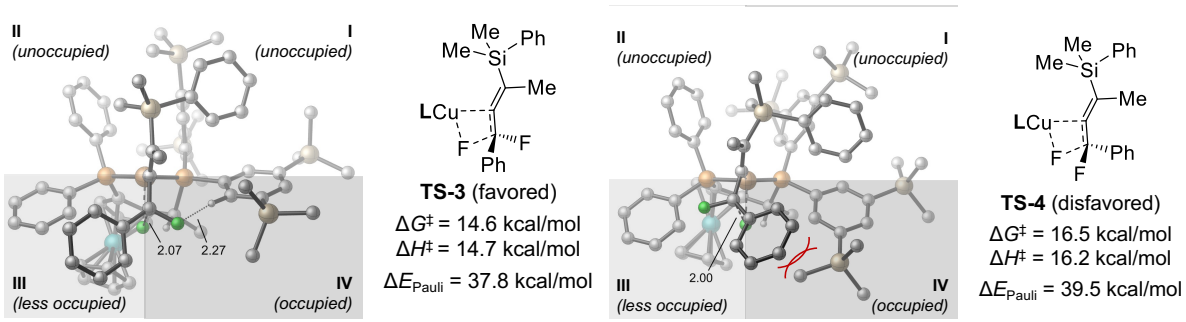


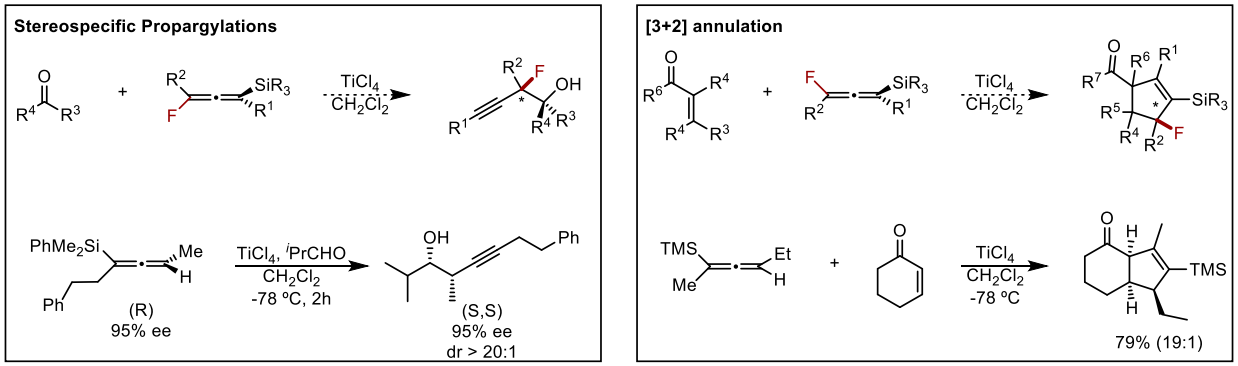
Figure 2.3 Origin of enantioselectivity in *syn*-*β*-fluoride elimination. Most hydrogen atoms are omitted for clarity. Gibbs free energies and enthalpies are with respect to **31**. ΔE_{Pauli} is the Pauli repulsion energy between the substrate and the Josiphos ligand from EDA calculations.

Finally, the enantioselectivity-determining *syn*-*β*-F elimination transition states of the reaction of the same substrate (**27a**) catalyzed by a SegPhos-supported Cu complex were calculated. The computed enantioselectivity is diminished ($\Delta\Delta G^{\ddagger}$ = 0.2 kcal/mol, Figure S7), indicating the C2-symmetric SegPhos ligand is not effective for asymmetric induction. This prediction is consistent with the low *ee* of 12% obtained experimentally at 65 °C with 5 mol% CuCl, 40 mol% sodium phenoxide, and 6 mol% SegPhos ligand. Taken together, these ligand effect analyses revealed the unique roles of the conformationally flexible C1-symmetric Josiphos ligand, where it lowers the activation barrier for the rate-determining alkyne migratory insertion step and improves the enantioselectivity of the *β*-F elimination.

2.3 Product Diversification: Chirality Transfer

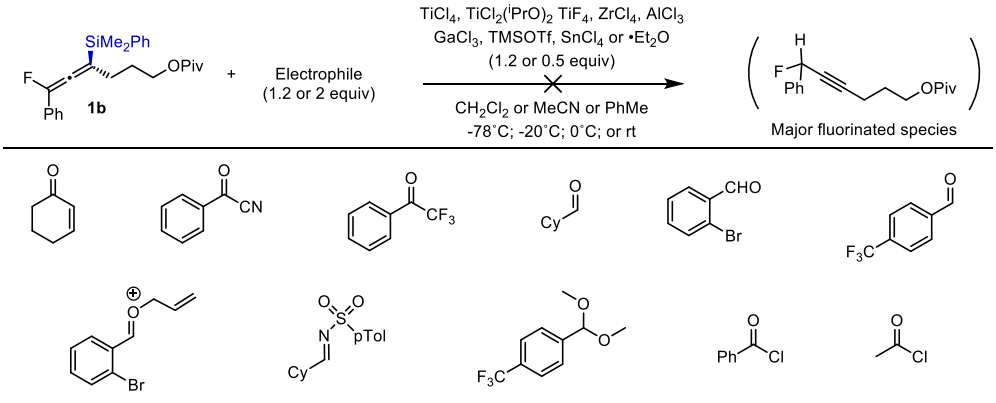
2.3.1 Chirality Transfer

Now with access to tetrasubstituted silyl monofluoro ACAs, further transformations that could generate fluorine-containing quaternary stereocenters *via* axial-to-point chirality transfer were investigated (Scheme 2.3).[3a,10] Allenylsilanes are known to undergo stereospecific propargylation with aldehydes, ketones, and activated imines in the presence of stoichiometric amount of Lewis acids such as $TiCl_4$, $SnCl_4$, $ScOTf_2$, $ZrCl_4$, $BF_3{\bullet}Et_2O$, and TMSOTf (Scheme 2.3A).[3a,10] In addition to propargylations of carbonyl compounds, allenylsilanes can undergo formal [3+2] annulations with *α,β*-unsaturated carbonyl compounds, creating both complex cyclic and bicyclic ring systems (Scheme 2.3B).[10] If the monofluoro allenes described in this chapter could be leveraged for similar reactivity, then the generation of fluorine-containing quaternary stereocenters, which would otherwise be challenging to synthesize or are currently inaccessible, could easily be obtained from readily available fluorinated building blocks.[36]



Scheme 2.3 Proposed Synthesis of Fluorine-Containing Stereocenters from Monofluoroallenyl Silanes (Top) along with Literature Precedent (Bottom)

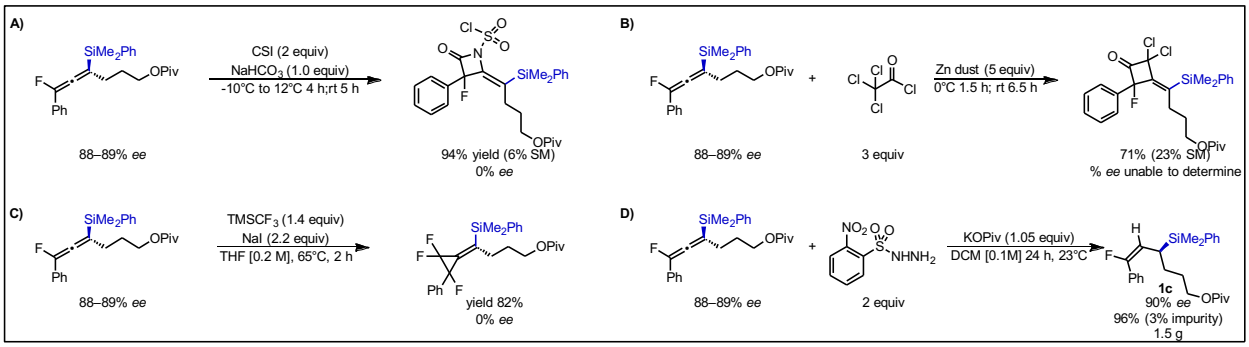
Attempts at utilizing allene **1b** for the propargylations and [3+2] annulations with a variety of electrophiles failed to afford the desired products possessing fluorine-containing quaternary stereocenters (Scheme 2.4). Allenylsilane **1b** was found to be unreactive at low temperatures (-78˚C), which is in contrast to its non-fluorinated counterparts.[3a,10] Increasing the temperature often lead to consumption of **1b**, but in most cases resulted in the formation of the protodesilylated alkyne. Unfortunately, chiral transfer did not occur under the reaction conditions that afforded this secondary propargylic fluoride. The remaining mass balance of the reactions was accounted for by undesirable defluorination byproducts. Although **1b** was stable to certain Lewis acids at room temperature (such as $TiCl_4$), the presence of both a Lewis acid and electrophile resulted in the consumption of **1b**. Based upon this observation, it is believed that the desired product may initially be formed but that the resulting fluorine-containing quaternary stereocenter was labile in the presence of such Lewis acidic metals. This is supported by literature reports whereby unactivated tertiary fluorides are known to undergo defluorination in the presence of Lewis acids. The tertiary fluorides that would be generated from the propargylations and [3+2] annulations should be even more prone to Lewis acid abstraction as they would be benzylic and either propargylic or allylic.



Scheme 2.4 Attempts at Lewis Acid Mediated Propargylations

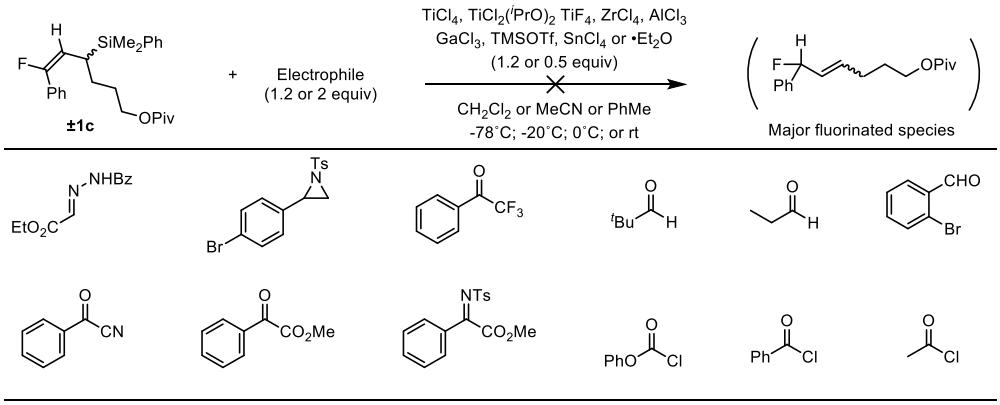
Other reactions were sought that would generate less labile fluorine atoms in the absence of strong Lewis acids (Scheme 2.5). Although the cycloaddition between racemic **1b** and chlorosulfonyl isocyanate (CSI) gave the expected lactam, chirality did not transfer from enantioenriched **1b** (Scheme 2.5A). Dichloroketene, which was generated *in situ* with zinc dust, was also effectively trapped by racemic **1b**, but

the enantiomers could not be resolved by chiral HPLC (Scheme 2.5B). Allene **1b** was also reactive with difluorocarbene generated from trimethylsilyltrifluoromethane ($TMSCF_3$) and sodium iodide, but chirality did not transfer when enantioenriched **1b** was employed (Scheme 2.5C). Finally, while the hydrogenation of allene **1b** with Pd/C, Pt/C and Rh/C gave complex mixtures, the diimide reduction was not only regioselective, but proceeded with chirality transfer to afford chiral allylic silane **1c** (Scheme 2.5D).



Scheme 2.5 Reactivity of monofluoroallenyl silanes

Compared to allenylsilanes, allylic silanes are more reactive toward the addition of electrophiles such as carbonyl compounds (aldehydes, ketones, imines, etc.). It was envisioned that by employing **1c** rather than **1b** that chiral tertiary, allylic fluorides could be accessed (Scheme 2.6). However, similar to **1b**, **1c** was rather unreactive at low temperatures (-78˚C) and as the temperature was increased protodesilylation became the dominant pathway, furnishing the secondary, allylic fluoride (Scheme 2.6). Unfortunately, chirality transfer for the protodesilylation product did not occur under Lewis acid catalyzed conditions.



Scheme 2.6 Attempts at Lewis Acid Mediated Allylations

2.4 Conclusion

In conclusion, the first copper-catalyzed, enantioselective *β*-fluoride elimination has been achieved. The resulting monofluoro ACAs represent the first examples of fluorine-containing, chiral tetrasubstituted allenes. It is expected that such a motif will find value in pharmaceutical and agrochemical chemistry in

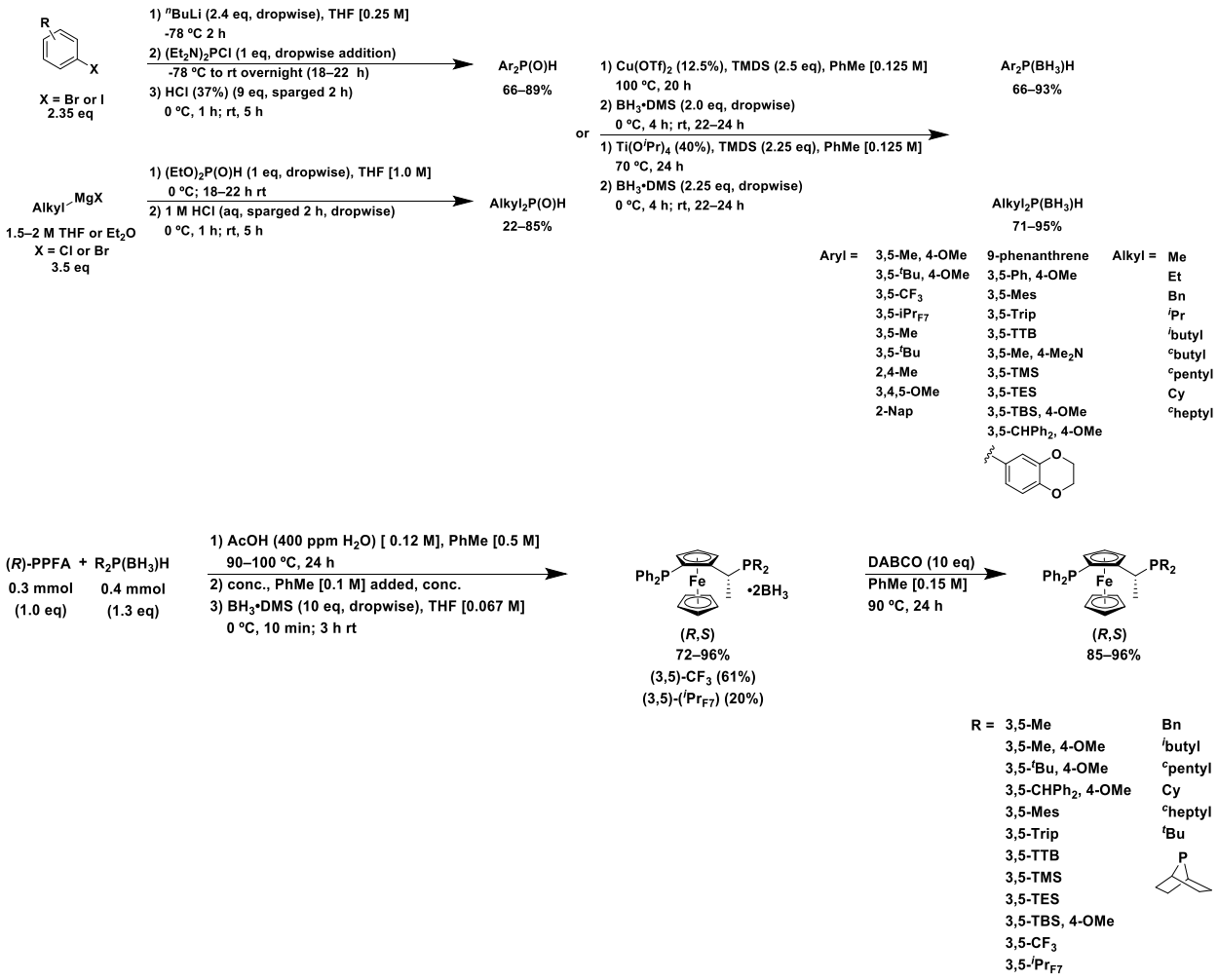
addition to being a valuable building block for the generation of more elaborate fluorine-containing stereocenters. DFT calculations of the reaction mechanisms predicted that this elimination occurs in a *syn*-fashion, which is promoted by strain release of the *Z*-*β*-silylalkenyl copper intermediate. The unique roles of the C1-symmetric Josiphos-derived ligand in promoting the reactivity and enantioselectivity were investigated. It is believed that lessons learned from this desymmetrization could be leveraged for the creation of other fluorine-containing stereocenters *via* defluorination pathways.

2.5 Supporting Information

2.5.1 General Information

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Vessels used in air-free reactions were oven-dried and cooled under dynamic vacuum (once at ambient temperature, vessels were refilled with nitrogen and evacuated two more times) prior to use. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed using ICN SiliTech 32-63D 60Å silica gel. Commercial grade solvents were used for reactions without further purification except as indicated below. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), toluene (PhMe), benzene (C_6H_6), diethyl ether (Et_2O), dimethyl formamide (DMF), triethylamine (Et_3N) and tetrahydrofuran (THF) were dried by passing commerically available pre-dried, oxygen-free formulations through activated alumina columns under argon. Trifluorotoluene ($PhCF_3$), cyclohexane (C_6H_{12}), methyl tert-butyl ether (MBTE), acetic acid (AcOH), trifluoroacetic acid (TFA), pyridine, diethylamine (Et_2NH) and 1,2-dichloroethane (DCE) were distilled under a nitrogen atmosphere from either CaH_2 or P_2O_5 as described in literature. All solvents employed in alkyne silylation reactions were degassed by freeze-pump-thaw cycles (three cycles) using liquid nitrogen and stored over activated 3 Å molecular sieves. Thin layer chromatography analysis was performed using Merck 60 pre-coated silica gel plates with F254 indicator. Visualization was accomplished by iodine, p-anisaldehyde, potassium permanganate, Dragendorff-Munier, cerium ammonium molybdate, and/or UV light (254 nm). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AVQ-400, DRX-500, Neo-500 and AV-600 instruments with 400, 500 and 600 MHz frequencies. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker DRX-500, Neo-500, and AV-600 instruments with a ^{13}C operating frequency of 126 and 150 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded on Bruker AVQ-400, DRX-500, Neo-500, and AV-600 instruments with 376, 471, and 565 MHz frequencies. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$, δ 5.32 for CH_2Cl_2) was used as an internal reference for ^{1}H spectra. For ^{13}C spectra, chemical shifts are reported relative to the δ 77.16 resonance of $CDCl_3$ and relative to the δ 53.84 for CD_2Cl_2. For ^{19}F spectra, chemical shifts are reported in relative to the δ -113.15 resonance of PhF. Coupling constants are reported in Hz. Mass spectral data were obtained from either the UC-Berkeley Catalysis Center operated by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI (or APCI) mode or the QB3/Chemistry Mass Spectrometry Facility at UC-Berkeley.

2.5.2 General Ligand Synthesis



General notes for Josiphos synthesis

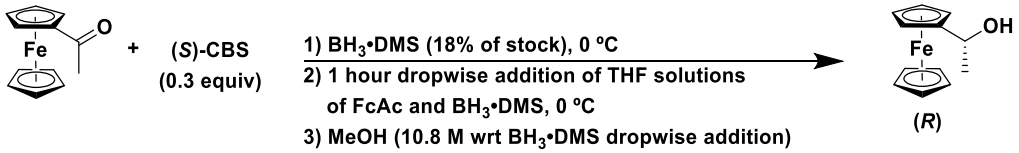
Aryl bromides or iodides were purchased or prepared following reported procedures.[37] For 1-Br, 3,5-TMS-C_6H_3 and 1-Br, 3,5-TES-C_6H_3, the bromoarenes were isolated in approximately 70–90% purity with the remainder being the trisilyl arene.[38] The trisilyl arene did not inhibit the subsequent halogen lithium exchange nor isolation of the desired secondary phosphine oxide (SPO). Alkyl and aryl SPOs were prepared according literature procedures.[39] Although aryl SOPs can be synthesized by the route outlined for alkyl SPOs, it was found that the route with $(Et_2N)PCl_2$ was more general with respect to the electronics of the aryl lithiate or Grignard reagent. Typically, electron rich, less sterically hindered aryl nucleophiles led to a mixture of the desired aryl SPO contaminated with the corresponding aryl phosphonic acid (phosphonic acids are presumed to form upon aqueous workup; neither basic nor acidic quenches (with or without nitrogen sparging) solved this dilemma. An alternative procedure with (EtO)-2P(O)H with KH or NaH can be employed if the alkyl halide is valuable.[40] The reduction of SPOs proceeded well with either $Cu(OTf)_2$[41] or $Ti(O^iPr)_4$[42], but for substrates with functional groups that may have been effected in the presence of $Cu(OTf)_2$ (i.e. TMS, TES, CF_3, $^iPr_{F7}$), $Ti(O^iPr)_4$ was employed. For

reactions conducted with $Cu(OTf)_2$, 1,1,3,3-tetramethyldisiloxane (TMDS) was added in two portions (1–1.25 eq, then 1 eq 12 hours into the reaction).

The water content of the AcOH employed for the synthesis of the bis-BH_3 protected Josiphos derivatives was pivotal for reproducible results. The water content of glacial AcOH (400 mL) distilled from P_2O_5 under nitrogen and sparged with argon for 5 hours had a water content of less than 5 ppm, as determined by Karl Fischer titration (same for distilled TFA). The water content of a new, unopened bottle of glacial AcOH purchased from Sigma-Alrich contained about 400 ppm of water after being sparged with argon for 5 hours (about 1100 ppm for a new bottle of TFA). Reactions conducted with the AcOH containing <5 ppm H_2O primarily generated the monooxide, monoborane Josiphos adduct where the diphenylphosphinoferrocenyl moiety had been oxidized to the phosphine oxide and the phosphine moiety alpha to (*R*)-methyl stereocenter was protected by BH_3. There were some exceptions to this chemical transformation depending on the secondary phosphine borane employed, but this could have been due to residual water contaminating the secondary phosphine borane substrate (secondary phosphine boranes are hydroscopic and were stored in a nitrogen glovebox immediately after isolation by column chromatography). The monooxide, monoborane Josiphos was also observed if all the reagents were added to the AcOH (<5 ppm H_2O) and degassed (three freeze-pump-thaw cycles with liquid nitrogen) prior to heating under nitrogen gas flow. It is also important to run the substitution reactions under a dynamic flow of nitrogen gas and not in a sealed vessel (gas evolution occurs upon heating a mixture of AcOH and protected phosphine borane). It does not appear that BH_3 is responsible for the mono-oxidation, as heating Cy_2PH (purchased from Strem) and (*R*)-PPFA in AcOH(<5 ppm H_2O) and PhMe also produced the undesired monooxide, monoborane Josiphos (termed Josi(O)Phos). Several Josi(O)Phos ligands were screened for the catalytic, β-fluoride elimination transformation, but most gave the desired allene in less than 20% enantiomeric excess (Cu:L was 1:1).

Specific Examples:

Synthesis of (*R*, *S*)-3,5-TES-Josiphos



(*R*)-(1-Hydroxyethyl)ferrocene

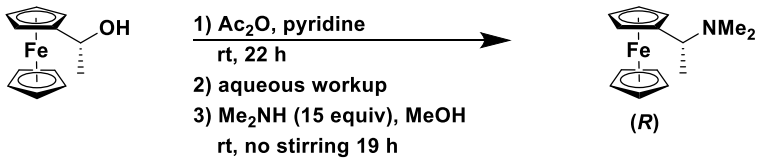
Prepared from a modified literature procedure.[43]

(*S*)-CBS 95% (17.5 g, 60 mmol, 0.3 equiv) was charged to a cycled, 1000 mL, 3-neck round bottom flask fitted with two 250 mL addition funnels. Acetylferrocene (46.6 g, 200 mmol, 1.0 equiv) was added to the first addition funnel and the system was evacuated and placed under a nitrogen atmosphere. Acetylferrocene was dissolved in 230 mL THF [0.87 M], BH_3•DMS (19.4 mL, 200 mL, 1 equiv) was added to the second addition

funnel followed by 200 mL THF [1.0 M], and the reaction vessel was placed in an ice bath (0 °C). Once the vessel was cold, 40 mL (18%) of the BH_3•DMS THF solution was added over the course of five minutes. After stirring for 2 minutes at 0 °C, the THF solutions of acetylferrocene and BH_3•DMS were added are the same time with similar rates over the course of 1 hour (the rate of the BH_3•DMS had to be decreased over the course of the addition so that both solutions would empty the addition funnels at the same time). The reaction was monitored by TLC and after 80 minutes at 0 °C, MeOH (18.5 mL, 10.8 M wrt BH_3•DMS) was added over the course of four minutes (gas evolution). Saturated ammonium chloride (300 mL) was **slowly** added followed by 250 mL Et_2O. The layers were separated and the aqueous phase was extracted with Et_2O (2 *x* 450 mL). The organic phases were washed with water (2 *x* 350 mL), brine (350 mL), dried over $MgSO_4$, filtered, and concentrated. The crude residue was concentrated onto silica gel and purified by silica gel column chromatography (1:2 to 2:1 Et_2O:Hexanes) to afford an orange solid which was analyzed by chiral HPLC (42.48 g, 92%, >98% *ee*).

The spectra data were in agreement.[43]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.58–4.51 (m, 1H), 4.24 – 4.21 (m, 9H), 4.17 (s, 1H), 1.85 (d, *J* = 4.0 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H).



(*R*)-Ugi's Amine

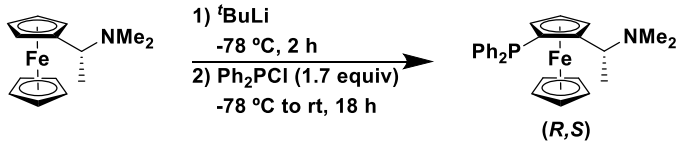
Prepared according to a modified literature procedure.[43]

(*R*)-(1-Hydroxyethyl)ferrocene (42.32 g, 183.9 mmol, 1.0 equiv) was added to a 1000 mL 3-neck round bottom flask and the system was cycled twice and placed under nitrogen. Pyridine (130 mL, [1.41 M]), Et_3N (54 mL, [3.47 M]), and DMAP (5 mol%) were added to the vessel followed by Ac_2O 99% (sparged with nitrogen gas, 74 mL, 783 mmol, 4.25 equiv). The solution was allowed to stir at room temperature for 22 hours (monitored by GC-MS) before 120 mL of solvent was removed at 200 mtorr at 24 °C. The reaction was diluted with Et_2O (1000–1200 mL), washed with ice water (700 mL), water (2 *x* 500 mL), brine (500 mL), dried over Na_2SO_4, filtered, and concentrated to an orange solid (do not heat the rotovap bath above 30 °C when removing bulk solvent, residue solvent was removed at 200 mtorr on a Schlenck line). The crude acetate was dissolved, with stirring, in MeOH (1050 mL, [0.175 M], sparged with nitrogen gas for 1 hour) and then Me_2NH (40% aqueous solution, 350 mL, 2760 mmol, 15 equiv) was added. The vessel was wrapped with aluminum foil and after 1 minute, **stirring was stopped**. After 24 hours, a 1000 mL beaker was filled with ice and slowly dispensed into the reaction vessel. Et_2O (500 mL) was added but phase separation was not

achieved. The solution was concentrated, **protected from light**, to about $\frac{1}{4}^{th}$ of the original volume (temperature of rotovap bath 35 °C<) and extracted with Et_2O (3 x 600 mL). The organic phases were concentrated to about 1100 mL and the amine product was extracted with an 8.5% aqueous solution of H_3PO_4 (800 mL). The aqueous layer was washed with ether (700 mL), and the pH adjusted to 8–9 by slowing adding NaOH (solid) to a stirring solution of the acidic aqueous layer. The slightly basic aqueous layer was extracted with Et_2O (2 x 1000 mL, 1 x 500 mL), dried over Na_2SO_4, filtered and concentrated to afford (*R*)-Ugi's amine as a dark red oil (43.1 g, 91% from (*R*)-alcohol). The amine was left under vacuum (200 mtorr) for 48 hours before being transferred into a nitrogen filled glovebox for storage.

The spectra data were in agreement.[43]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.14–4.12 (m, 1H), 4.11 (t, *J* = 1.9 Hz, 2H), 4.10 (s, 5H), 4.09 – 4.08 (m, 1H), 3.58 (q, *J* = 6.9 Hz, 1H), 2.07 (s, 6H), 1.43 (d, *J* = 6.9 Hz, 3H).



(*R*)-N,N-Dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-PPFA)

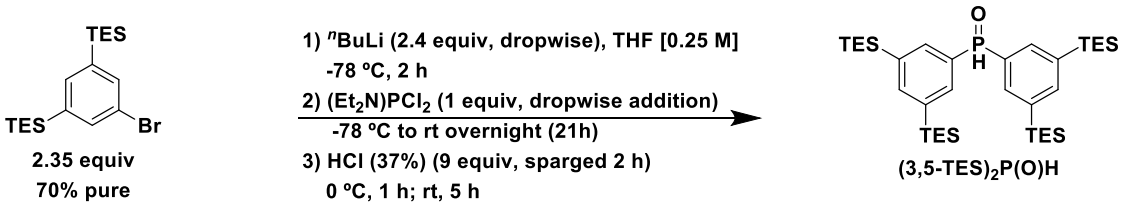
Prepared according to a literature procedure.[44]

(*R*)-Ugi's amine (10.0 g, 40 mmol, 1.0 equiv) was transferred into a 250 mL rbf in a glovebox, diluted in Et_2O (44 mL, [0.91 M]), sealed with a septa, and removed from the glovebox. The solution was placed in a -78 °C bath. After 20 minutes, ^{t}BuLi [1.7 M in pentane] (31 mL, 52.0 mmol, 1.3 equiv) was added dropwise over 21 minutes. After 40 minutes the mixture was removed to room temperature and allowed to stir for 2.5 hours. The mixture was placed in a -78 °C bath for 30 minutes before Ph_2PCl (13 mL, 68 mmol, 1.7 equiv) was added dropwise over the course of six minutes. The reaction was allowed to reach 0 °C over the course of 5.5 hours and removed to rt. After 13 hours at rt, the reaction was cooled to 0 °C, diluted with 40 mL Et_2O, and saturated $NaHCO_3$ (20 mL) was slowly added. A subsequent portion of saturated $NaHCO_3$ (120 mL) was added followed by benzene (400 mL). The phases were separated and the aqueous layer was extracted with benzene (250 mL). The combined organic fractions were combined, washed with water (3 x 300 mL), dried over Na_2SO_4, filtered, and concentrated to an orange solid. The crude solid was purified by silica gel chromatography (2:3 EtOAc:Hexanes 5% Et_3N) to afford an orange foam. The foam was dissolved in EtOAc and concentrated (to remove residual Et_3N) before being recrystallized from hot EtOH to yield orange crystals (13.63 g, 77%, 2 batches).

The spectra data matched the literature, indicating the isolation of a single diastereomer.[44]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (ddt, *J* = 7.5, 5.1, 2.7 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.23 – 7.15 (m, 5H), 4.37 (s, 1H), 4.24 (t, *J* = 2.5 Hz, 1H), 4.15 (qd, *J* = 6.7, 2.6 Hz, 1H), 3.94 (s, 5H), 3.85 (s, 1H), 1.77 (s, 6H), 1.26 (d, *J* = 6.7 Hz, 3H).

^{31}P NMR (243 MHz, $CDCl_3$) δ -22.92 (s).



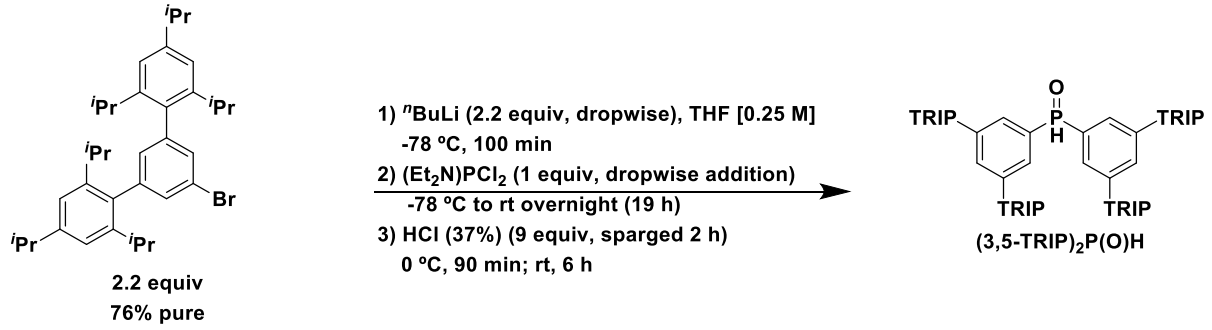
bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide

A vigorously stirred solution of 1-Br 3,5-TES-C_6H_3 (27.5 g, 50.47 mmol, 2.35 equiv) in 200 mL THF [0.25 M] was placed in a -78 °C acetone bath. After 30 min, ^{n}BuLi [2.5 M in hexanes] (20.6 mL, 51.5 mmol, 2.4 equiv) was added dropwise (over the course of 15 minutes). The bath was maintained at -78 °C for 2 hours, then $(Et_2N)PCl_2$ (3.74 g, 21.5 mmol, 1.0 equiv) was weighed out into a syringe in a nitrogen-filled glovebox and dispensed dropwise (3-minute addition) into the -78 °C solution of the aryl lithiate. The reaction was left in the -78 °C bath, but dry ice was no longer added to the cooling bath(allowing ambient temperature to be reached within 18 h). The reaction was checked by ^{31}P NMR after 18 h and two peaks were present (61.97:61.84 in a ratio of about 0.18: 1.0). After 3 more hours at room temperature, the reaction was cooled to 0 °C. Once at 0 °C, concentrated HCl (37%) (16.3 mL, 198 mmol, 9.0 equiv), which was sparged with nitrogen gas for 2 hours prior to use, was added over the course of 3 minutes. After 1 hour at 0 °C, the ice bath was removed and the reaction was stirred at room temperature for 5 hours. The solution was poured onto 1 M HCl (300 mL), diluted with EtOAc (500 mL), and separated. The aqueous phase was extracted with EtOAc (500 mL) and the organic phases were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:10 to 1:6 EtOAc:Hexanes; $R_f \approx 0.25$ in 1:6 EtOAc:Hexanes) to afford the desired SOP as a colorless oil (11.54 g, 81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 474.3 Hz, 1H), 7.79–7.76 (m, 2H), 7.71 (d, *J* = 13.6 Hz, 4H), 0.90 (t, *J* = 8.0 Hz, 36H), 0.76 (q, *J* = 8.1, 7.7 Hz, 24H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 24.6 (s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1 (d, *J* = 2.6 Hz), 137.2 (d, *J* = 8.9 Hz), 136.7 (d, *J* = 11.1 Hz), 130.1 (d, *J* = 98.0 Hz), 7.4, 3.3.



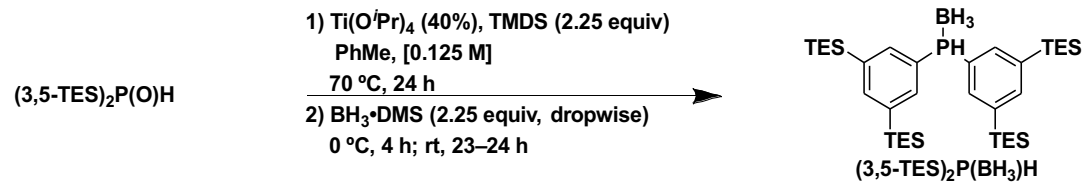
bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide

A vigorously stirred solution of 1-Br 3,5-TRIP-C_6H_3 (15.39 g (76% purity), 22.0 mmol, 2.2 equiv)[45] in 200 mL THF [0.25 M] was placed in a -78 °C acetone bath. After 30 min, *n*BuLi [2.5 M in hexanes] (8.8 mL, 22.0 mmol, 2.2 equiv) was added dropwise (over the course of 15 minutes). The bath was maintained at -78 °C for 100 minutes, then $(Et_2N)PCl_2$ (1.57 g, 9.0 mmol, 1.0 equiv) was weighed out into a syringe in a nitrogen-filled glovebox and dispensed dropwise (3-minute addition) into the -78 °C solution of the aryl lithiate. The reaction was left in the -78 °C bath, but dry ice was no longer added to the cooling bath(allowing ambient temperature to be reached within 19 h). The reaction was checked by ^{31}P NMR after 19 h and only one peak detected. The reaction was cooled to 0 °C. Once at 0 °C, concentrated HCl (37%) (7.0 mL, 81 mmol, 9.0 equiv), which was sparged with nitrogen gas for 2 hours prior to use, was added over the course of 3 minutes. After 90 minutes at 0 °C, the ice bath was removed and the reaction was stirred at room temperature for 6 hours. The solution was poured onto 1 M HCl (300 mL), diluted with EtOAc (500 mL), and separated. The aqueous phase was extracted with EtOAc (500 mL) and the organic phases were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:10 to 1:3 to 1:2 EtOAc:Hexanes; $R_f \approx 0.5$ in 1:3 EtOAc:Hexanes) to afford the desired SOP as a colorless solid (7.01 g, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 479.2 Hz, 1H), 7.61 (d, *J* = 13.9 Hz, 4H), 7.29 (s, 2H), 7.04 (s, 8H), 2.94 (p, *J* = 6.9 Hz, 4H), 2.58 (h, *J* = 6.7 Hz, 8H), 1.31 (d, *J* = 6.9 Hz, 24H), 1.04 (dd, *J* = 7.0, 4.0 Hz, 35H), 1.00 (d, *J* = 6.8 Hz, 12H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 22.25 (dp, *J* = 479.3, 14.1 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 146.4, 141.8 (d, *J* = 13.2 Hz), 135.6 (d, *J* = 3.0 Hz), 135.5, 131.8, 131.0, 129.7 (d, *J* = 11.0 Hz), 120.7, 34.5, 30.6, 24.3, 24.3, 24.2, 24.2, 24.1, 24.0.



bis(3,5-bis(triethylsilyl)phenyl)phosphine borane

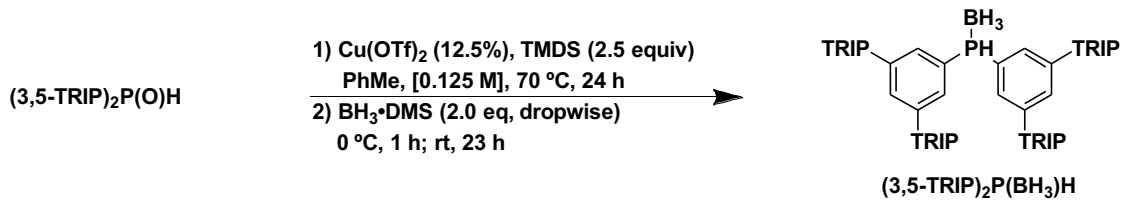
To a PhMe (50 mL, [0.3 M]) solution of the corresponding 3,5-TES SPO (11.2 g, 16.9 mmol, 1.0 eq), $Ti(O^iPr)_4$ 97% (2.0 mL, 40 mol%) and TMDS 97% (3.9 mL, 21.3 mmol, 1.25 equiv) were sequentially added under a positive flow of nitrogen at room temperature. After the addition, the reaction was placed in a 70 °C oil bath. After 11 hours, another portion of TMDS (3.0 mL, 17 mmol, 1.0 equiv) was added. After a total of 24 hours at 70 °C, the reaction was cooled to 0 °C and BH_3•DMS (4 mL, 43 mmol, 2.5 eq) was added dropwise (over a period of 2 minutes). After 90 minutes at 0 °C, the ice bath was removed. After 24 hours at room temperature, 5–10 grams of silica gel was added and the slurry was allowed to stir for about 5 minutes under nitrogen. The slurry was filtered over a pad of silica gel with $CH_2Cl_2$and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:8 to 1:3 CH_2Cl_2:Hexanes; $R_f \approx 0.20$ in 1:7 CH_2Cl_2:Hexanes) to afford the desired secondary phosphine borane as a white solid (9.99 g, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.70 (m, 2H), 7.68 (d, *J* = 11.7 Hz, 4H), 6.29 (dq, *J* = 375.5, 6.9 Hz, 1H), 0.92 (t, *J* = 7.8 Hz, 36H), 0.76 (q, *J* = 8.5, 8.1 Hz, 24H). The signal for $B\underline{H}_3$ is broad and baseline 1.8–0.66 (3H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 1.2 (s).

^{11}B NMR (160 MHz, $CDCl_3$) δ -40.9 (bs).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1 (d, *J* = 2.3 Hz), 138.9 (d, *J* = 8.8 Hz), 137.6 (d, *J* = 7.3 Hz), 124.9 (d, *J* = 54.0 Hz), 7.4, 3.4.



bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane

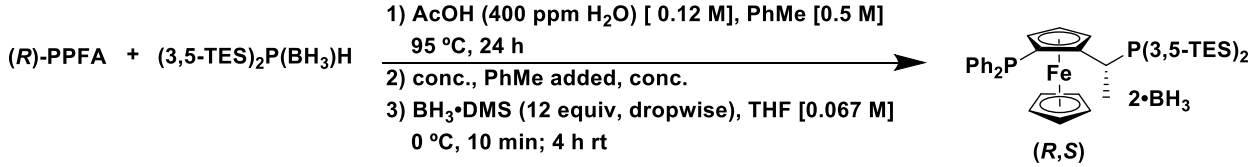
A cycled 500 mL Schlenk round bottom was charged with (3,5-TRIP)$_2$P(O)H (6.42 g, 6.35 mmol, 1.0 equiv) and placed under vacuum. The flask was refilled with nitrogen and PhMe (51 mL, 0.125 M) and Cu(OTf)$_2$ (300 mg, 12.5 mol%), which was weighed in a glovebox, were added. The flask was briefly cycled before the addition of TMDS (2.4 mL, 13 mmol, 2.0 equiv) at room temperature. The vessel was placed in a oil bath set at 100 °C and after 9 hours additional TMDS (600 µl, 3.2 mmol, 0.5 equiv) was added by syringe. After 14 addition hours, the reaction was removed to room temperature, cooled 0 °C, and BH$_3$•DMS (1.3 mL, 13 mmol, 2.0 eq) was added dropwise (over a period of 2 minutes). After 45 minutes at 0 °C, the ice bath was removed. After 23 hours at room temperature, 10–20 grams of silica gel was added and the slurry was allowed to stir for about 5 minutes under nitrogen. The slurry was filtered over a pad of silica gel with $CH_2Cl_2$and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:7 to 1:3 CH_2Cl_2:Hexanes; $R_f \approx 0.50$ in 1:3 CH_2Cl_2:Hexanes) to afford the desired secondary phosphine borane as a white solid (5.31 g, 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.57 (m, 4H), 7.26–7.21 (m, 2H), 7.10–7.02 (m, 8H), 6.38 (dp, *J* = 378.1, 6.7 Hz, 1H), 3.00–2.92 (m, 4H), 2.58 (tq, *J* = 13.9, 6.9 Hz, 8H), 1.33 (t, *J* = 5.5 Hz, 24H), 1.12–1.03 (m, 35H), 1.00–0.95 (m, 12H). The signal for B$\underline{H}_3$ is broad and baseline 1.2–0.8 (3H).

^{31}P NMR (243 MHz, $CDCl_3$) δ -0.2 (s).

^{11}B NMR (193 MHz, $CDCl_3$) δ -40.2 (s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 146.5 (d, *J* = 15.4 Hz), 141.8 (d, *J* = 10.5 Hz), 135.6, 134.8 (d, *J* = 2.5 Hz), 132.5 (d, *J* = 9.0 Hz), 125.7 (d, *J* = 54.8 Hz), 120.8, 34.5 (d, *J* = 2.3 Hz), 30.7, 24.3, 24.2, 24.2–24.1 (m).



(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(3,5-bis(triethylsilyl)phenyl)phosphine•2BH$_3$

(*R,S*)-(3,5-TES)Josiphos•2BH$_3$

In a nitrogen-filled glovebox, (*R*)-PPFA (3.2 g, 7.2 mmol, 1.0 equiv), (3,5-TES)$_2$P(BH$_3$)H (5.6 g, 8.5 mmol, 1.2 equiv), and PhMe (19 mL, [0.375 M]) were added to a 500 mL Schlenk round bottom reaction flask. The flask was sealed with a septum, removed from the glovebox and AcOH (59 mL, [0.12 M]) was added at room

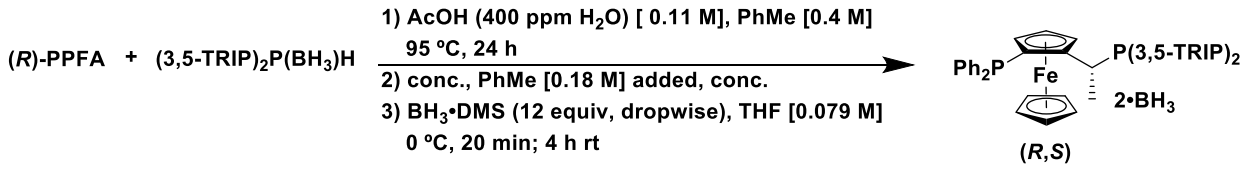
temperature. The reaction was briefly cycled three times (vacuum was applied until light bubbling occurred and then the vessel was refilled with nitrogen) and placed in a 95 °C oil bath. After 24 hours, the reaction was removed to room temperature. Once room temperature was reached (cooling can be applied to expediate the process), the reaction was concentrated to a thick orange oil on a Schlenk line (200 mtorr at 35 °C). The flask was refilled with nitrogen and PhMe (20 mL) was added to dissolve the orange sludge. Once dissolved, the solution was concentrated again to an orange, thick oil (at 200 mtorr). The sludge was then placed in a 35 °C bath under dynamic vacuum (200 mtorr) for 20 minutes. The flask was refilled with nitrogen, THF (72 mL, [0.1 M]) was added, and the reaction was cooled to 0 °C. BH_3•DMS (7.4 mL, 86.4 mmol, 12 equiv) was added over the course of 5 minutes, and the reaction was left to stir at 0 °C for 15 minutes before being removed to room temperature. After being stirred at room temperature for 4 hours, the solution was slowly poured onto a saturated aqueous solution of $NaHCO_3$ (500 mL) and diluted with EtOAc (400 mL). The phases were separated and the organic layer was washed with brine (300 mL), dried over Na_2SO_4, filtered, and concentrated to an orange solid. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:17 EtOAc:Hexanes; $R_f \approx 0.5$ in 1:14 EtOAc:Hexanes) to afford (*R,S*)-(3,5-TES)Josiphos•2BH_3 as an orange solid (7.16 g, 98%). The product is easily visualized by TLC (the product is an orange spot by TLC and can easily be monitored during column chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.8 Hz, 2H), 7.75 (s, 1H), 7.72 (t, *J* = 9.0 Hz, 2H), 7.55 (s, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.5, 7.1 Hz, 2H), 7.26 (d, *J* = 10.3 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 2H), 6.82 – 6.71 (m, 2H), 5.44 (s, 1H), 4.58–4.50 (m, 2H), 3.96 (s, 6H), 1.78 (dd, *J* = 15.8, 7.1 Hz, 3H), 0.95 (t, *J* = 7.9 Hz, 19H), 0.81 (t, *J* = 7.8 Hz, 30H), 0.58 (q, *J* = 7.9 Hz, 11H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 28.9 (s, 1P), 15.0 (s, 1P).

^{11}B NMR (193 MHz, $CDCl_3$) δ -35.4 (bs), -38.5 (bs).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 143.56 (d, J = 2.3 Hz), 142.34 (d, J = 2.4 Hz), 140.28 (d, J = 7.8 Hz), 139.80 (d, J = 8.7 Hz), 137.29 (d, J = 6.5 Hz), 136.94 (d, J = 6.7 Hz), 134.05 (d, J = 9.6 Hz), 133.60, 133.19, 132.71, 132.37, 132.31, 131.59 (d, J = 2.4 Hz), 130.28 (d, J = 2.5 Hz), 129.23 (d, J = 48.3 Hz), 128.72 (d, J = 10.3 Hz), 128.50 (d, J = 10.1 Hz), 126.15 (d, J = 50.4 Hz), 98.30 (dd, J = 17.2, 6.1 Hz), 72.32 (d, J = 3.2 Hz), 72.15 (dd, J = 7.9, 3.8 Hz), 71.39 (d, J = 6.3 Hz), 70.98, 67.75 (dd, J = 62.0, 3.9 Hz), 27.48 (d, J = 31.0 Hz), 23.55 (d, J = 3.9 Hz), 7.72 (d, J = 8.7 Hz), 3.75.



(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine•2BH$_3$

(*R,S*)-(3,5-TRIP)Josiphos•2BH$_3$

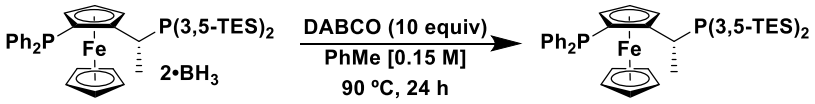
In a nitrogen-filled glovebox, (*R*)-PPFA (1.6 g, 3.63 mmol, 1.0 equiv), (3,5-TRIP)$_2$P(BH$_3$)H (4.05 g, 4.0 mmol, 1.1 equiv), and PhMe (9 mL, [0.4 M]) were added to a 250 mL Schlenk round bottom reaction flask. The flask was sealed with a septum, removed from the glovebox and AcOH (5932 mL, [0.11 M]) was added at room temperature. The reaction was briefly cycled three times (vacuum was applied until light bubbling occurred and then the vessel was refilled with nitrogen) and placed in a 95 °C oil bath. After 24 hours, the reaction was removed to room temperature. Once room temperature was reached (cooling can be applied to expediate the process), the reaction was concentrated to a thick orange oil on a Schlenk line (200 mtorr at 35 °C). The flask was refilled with nitrogen and PhMe (20 mL) was added to dissolve the orange sludge. Once dissolved, the solution was concentrated again to an orange foam (at 200 mtorr). The foam was then placed in a 35 °C bath under vacuum (200 mtorr) for 20 minutes. The flask was refilled with nitrogen, THF (46 mL, [0.079 M]) was added, and the reaction was cooled to 0 °C. BH$_3$•DMS (3.8 mL, 44.0 mmol, 12 equiv) was added over the course of 5 minutes, and the reaction was left to stir at 0 °C for 20 minutes before being removed to room temperature. After being stirred at room temperature for 4 hours, the solution was slowly poured onto a saturated aqueous solution of $NaHCO_3$ (500 mL) and diluted with EtOAc (400 mL). The phases were separated and the organic layer was washed with brine (300 mL), dried over Na_2SO_4, filtered, and concentrated to an orange solid. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:20 to 1:9 Et_2O:Hexanes) to afford (*R,S*)-(3,5-TRIP)Josiphos•2BH$_3$ as an orange solid (4.96 g, 96%). The product is easily visualized by TLC (the product is an orange spot by TLC and can easily be monitored during column chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60–7.52 (m, 4H), 7.47–7.40 (m, 5H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.17 (s, 1H), 7.09 (s, 2H), 7.04 (s, 2H), 7.02 (s, 4H), 7.00 (s, 2H), 6.59 (s, 2H), 4.70 (s, 1H), 4.30 (s, 5H), 4.22 (s, 1H), 3.79 (s, 1H), 3.34 (s, 1H), 3.01–2.89 (m, 4H), 2.63–2.54 (m, 4H), 2.46 (dt, *J* = 20.9, 6.8 Hz, 4H), 1.81 (dd, *J* = 15.9, 6.8 Hz, 3H), 1.35–1.28 (m, 26H), 1.06 (d, *J* = 6.8 Hz, 7H), 1.04–0.98 (m, 20H), 0.97–0.91 (m, 18H), 0.77 (s, 6H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 24.7 (bs, 1P), 14.9 (s, 1P).

^{11}B NMR (193 MHz, $CDCl_3$) δ -35.5 (bs), -38.7 (bs).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 148.5, 148.4, 146.8, 146.5, 146.4, 146.2, 141.2 (d, *J* = 10.1 Hz), 141.0 (d, *J* = 10.2 Hz), 135.9 (d, *J* = 16.5 Hz), 134.5, 134.2, 133.1 (d, *J* = 9.4 Hz), 132.8, 131.9, 131.5, 131.0 (dd, *J* = 28.4, 2.4 Hz), 129.7 (d, *J* = 56.9 Hz), 128.6 (d, *J* = 9.9 Hz), 128.4 (d, *J* = 10.0 Hz), 120.8, 120.7, 120.7, 120.5, 94.7, 73.7, 70.7, 69.1, 68.6, 68.2, 34.5 (d, *J* = 3.8 Hz), 30.7, 30.6, 30.5, 24.6, 24.3, 24.3, 24.3, 24.2, 24.1, 24.1, 24.0, 24.0, 23.7.



(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(3,5-bis(triethylsilyl)phenyl)phosphine

(*R,S*)-(3,5-TES)Josiphos

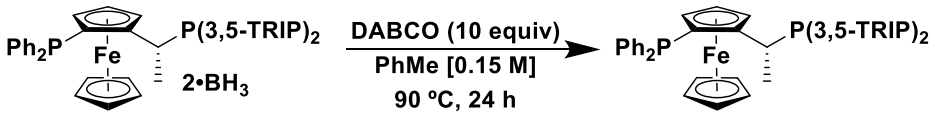
In a nitrogen filled glovebox, (*R,S*)-(3,5-TES)Josiphos•2BH_3 (6.89 g, 6.45 mmol, 1 equiv), 1,4-diazabicyclo[2.2.2]octane (DABCO) (7.2 g, 64.5 mmol, 10 equiv) were added to a 250 ml Schlenk round bottom flask followed by PhMe (43 mL [0.15 M]). The flask was sealed with a septum, removed from the glovebox, placed in a 90 °C oil bath under a flow of N_2 gas. After 24 hours, the reaction was removed to room temperature and concentrated to an orange sludge. The round bottom was moved into the glovebox and a silica gel column was prepared (column volume = 75 mL) with 1:19 Et_2O:pentane. The concentrated reaction was loaded onto the column and eluted with Et_2O:pentane (1:19 to 1:10). Only the orange fractions were collected and analyzed by TLC ($KMnO_4$ and Dragendorff-Munier stains were used to ensure DABCO did not bleed through the column). The desired fractions were concentrated to afford pure product as a thick orange oil which was concentrated at 35 °C for five hours (6.61 g, 98%). The oil solidified upon storage in a freezer (-30 °C). All other JosiPhos derivatives were typically solids (except one). An NMR sample of the ligand in $CDCl_3$ was exposed to air for 17 hours and less than 1% of the ligand had oxidized. The sample was concentrated and passed through a plug of silica gel in air with 1:19 Et_2O:hexanes as the eluent. Analysis by ^{31}P NMR revealed about 2% oxidation. For ease of screening, stocks solutions were prepared in stored at -30 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.74 (m, 2H), 7.62 (s, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 6.0 Hz, 2H), 7.47–7.43 (m, 3H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.32–7.27 (m, 2H), 7.23–7.17 (m, 3H), 4.30 (t, *J* = 2.5 Hz, 1H), 4.13 (s, 1H), 3.97 (s, 1H), 3.90 (s, 5H), 3.88–3.86 (m, 1H), 1.45 (t, *J* = 6.6 Hz, 3H), 1.01 (dt, *J* = 10.8, 7.9 Hz, 36H), 0.90–0.68 (m, 18H). Residual PhMe present.

^{31}P NMR (243 MHz, $CDCl_3$) δ 8.2 (d, *J* = 31.1 Hz, 1P), -24.5 (d, *J* = 30.9 Hz, 1P).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 141.4, 141.3, 141.3, 140.6, 139.9 (dd, *J* = 9.6, 2.1 Hz), 139.4, 138.4 (d, *J* = 15.5 Hz), 136.3 (d, *J* = 21.9 Hz), 135.8 (d, *J* = 22.6 Hz), 135.6 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 5.3 Hz), 133.6 (d, *J* = 23.0 Hz), 132.7 (dd, *J* = 16.7, 2.6 Hz), 129.1, 128.1 (d, *J* = 8.3 Hz), 127.6 (d, *J* = 5.6 Hz), 127.2, 99.6

(dd, *J* = 26.5, 20.3 Hz), 75.1 (dd, *J* = 11.0, 3.3 Hz), 71.4 (d, *J* = 4.1 Hz), 69.5, 69.3 (t, *J* = 4.5 Hz), 68.9, 30.6 (dd, *J* = 20.0, 9.9 Hz), 16.9, 7.6, 3.6 (d, *J* = 7.1 Hz).



(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine

(*R,S*)-(3,5-TRIP)Josiphos

In a nitrogen filled glovebox, (*R,S*)-(3,5-TRIP)Josiphos•2BH_3 (4.90 g, 3.45 mmol, 1 equiv), 1,4-diazabicyclo[2.2.2]octane (DABCO) (3.90 g, 34.5 mmol, 10 equiv) were added to a 200 ml Schlenk bomb followed by PhMe (24 mL [0.144 M]). The bomb was sealed, removed from the glovebox, placed in a 90 °C oil bath under a flow of N_2 gas. After 24 hours, the reaction was removed to room temperature and concentrated to an orange sludge (about 2-3 mL of PhMe was present). The round bottom was moved into the glovebox and a silica gel column was prepared (column volume = 100 mL) with 1:19 Et_2O:pentane. The crude reaction micture was loaded onto the column and eluted with Et_2O:pentane (1:19 to 1:12). Only the orange fractions were collected and analyzed by TLC ($KMnO_4$ and Dragendorff-Munier stains were used to ensure DABCO did not bleed through the column). The desired fractions were concentrated to afford pure product as an orange foam which was concentrated at 35 °C for three hours (4.77 g, 99%). The solid was stored in a freezer (-30 °C).

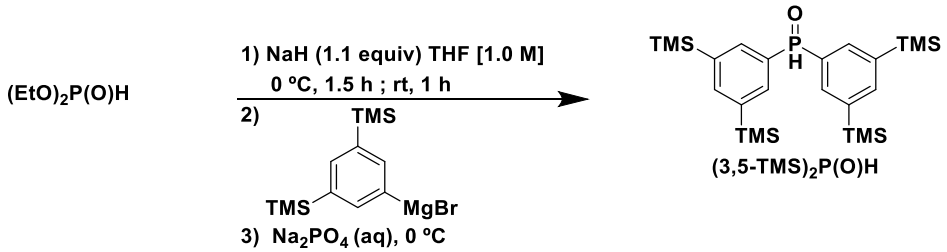
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.24–7.22 (m, 3H), 7.19 (dd, *J* = 6.2, 1.6 Hz, 2H), 7.15–7.12 (m, 4H), 7.08–7.03 (m, 6H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 2H), 6.90 (d, *J* = 1.8 Hz, 4H), 6.88 (d, *J* = 1.8 Hz, 2H), 6.86–6.82 (m, 1H), 6.80 (t, *J* = 1.5 Hz, 1H), 6.50 (td, *J* = 7.8, 1.6 Hz, 2H), 4.02 (t, *J* = 2.5 Hz, 1H), 3.91 (s, 1H), 3.82 (s, 5H), 3.74 (s, 1H), 3.49 (q, *J* = 7.1 Hz, 1H), 2.83 (pd, *J* = 7.0, 4.2 Hz, 4H), 2.56 (dp, *J* = 10.6, 6.8 Hz, 6H), 2.45 (p, *J* = 6.9 Hz, 2H), 2.25 (s, 4H), 1.43 (t, *J* = 7.3 Hz, 3H), 1.24–1.20 (m, 24H), 0.94–0.88 (m, 30H), 0.84 (d, *J* = 6.9 Hz, 6H), 0.78 (d, *J* = 6.9 Hz, 6H), 0.70 (d, *J* = 6.9 Hz, 6H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 2.2 (s, 1P), -25.9 (d, *J* = 33.3 Hz, 1P).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0 (d, *J* = 7.5 Hz), 146.6 (d, *J* = 6.2 Hz), 146.4 (d, *J* = 19.2 Hz), 140.5 (d, *J* = 5.2 Hz), 140.2, 140.1, 139.0 (dd, *J* = 10.4, 2.0 Hz), 138.0, 137.7, 137.6, 137.0, 136.7, 135.6, 135.5, 135.4, 135.3, 132.7, 132.7, 132.6, 130.9 (d, *J* = 15.6 Hz), 130.6, 129.2, 129.0, 128.4, 128.1 (d, *J* = 7.9 Hz), 127.8 (d, *J* = 6.1 Hz), 127.6, 125.5, 120.6 (d, *J* = 5.6 Hz), 120.5, 120.3, 97.3 (dd, *J* = 24.8, 16.0 Hz), 74.9 (dd, *J* = 10.9, 3.5

Hz), 71.4 (d, *J* = 4.0 Hz), 70.1, 69.6, 68.7, 34.5 (d, *J* = 4.1 Hz), 30.6, 30.5, 30.4, 24.7, 24.6, 24.4, 24.3, 24.1, 23.8, 23.7, 21.6.

Selected Examples for Secondary Phosphine Borane Synthesis



bis(3,5-bis(trimethylsilyl)phenyl)phosphine oxide

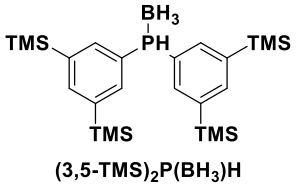
Prepared according to a modified literature report.[40,46]

To a 250 mL Schlecnk round bottom flask was added NaH 60% in mineral oil (1.32 g, 33 mmol, 1.1 equiv), THF (30 mL, [1.0 M]), and the slurry cooled to 0 °C. Then, $(EtO)_2P(O)H$ (3.8 mL, 29.5 mmol, 1.0 equiv, distilled under nitrogen) was added dropwise. After 90 minutes at 0 °C, the slurry was removed to room temperature and stirred for another 60 minutes. The slurry of the deprotonated SPO was transferred to the addition funnel (situated above the prepared Grignard mixture)with an additional THF (15 mL). The THF solution of 1-MgBr 3,5-TMS-C_6H_3 (80 mL, [0.8 M], 2.16 equiv) (prepared from 1-Br 3,5-TMS-C_6H_3 (26.46 g, 76 mmol, 2.3 equiv), Mg (2.2 g, 90 mmol, 3 equiv), THF for aryl–Br 60 mL, THF for Mg 20 mL) was cooled to -12 °C and the deprotonated SPO was added dropwise over the course of 30 minutes. After 90 minutes the reaction had reached 2 °C and was allowed to continue to reach room temperature. After 24 hours, the reaction was cooled to 0 °C and a saturated, aqueous solution of Na_2PO_4 (70 mL) was added slowly. The resulting gel was filtered over a pad of celite on a medium sized pore frit. The vessel was rinsed with Et_2O (2 x 350 mL) and subsequently poured onto the frit. The resulting biphasic solution was washed with saturated NH_4Cl (300 mL), brine (300 mL), dried over Na_2SO_4, filtered, and concentrated to afford a vicious yellow oil with milky, white chunks. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:4 to 1:3 to 3: 7 EtOAc:Hexanes; $R_f \approx 0.25$ in 1:4 EtOAc:Hexanes) to afford the desired SPO as a white solid (6.11 g, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 475.7 Hz, 1H), 7.84–7.82 (m, 4H), 7.81 (d, *J* = 1.3 Hz, 2H), 0.26 (s, 36H).

^{31}P NMR (203 MHz, $CDCl_3$) δ 23.2 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1 (d, *J* = 2.7 Hz), 140.4 (d, *J* = 9.1 Hz), 135.8 (d, *J* = 11.0 Hz), 129.8 (d, *J* = 97.5 Hz), -1.2.



$(3,5\text{-TMS})_2P(BH_3)H$

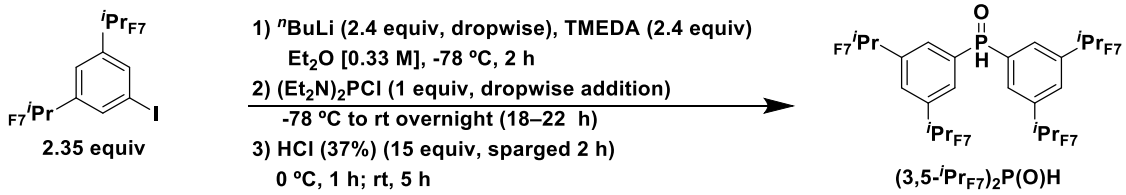
bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane

To a PhMe (50 mL, [0.4 M]) solution of the corresponding 3,5-TMS SPO (4.9 g, 10 mmol, 1.0 eq), $Ti(O^iPr)_4$ 97% (1.2 mL, 40 mol%) and TMDS 97% (2.3 mL, 12.5 mmol, 1.25 equiv) were sequentially added under a positive flow of nitrogen at room temperature. After the addition, the reaction was placed in a 70 °C oil bath. After 10 hours, another portion of TMDS (1.8 mL, 10 mmol, 1.0 equiv) was added. After a total of 22.5 hours at 70 °C, the reaction was cooled to 0 °C and BH_3•DMS (1.9 mL, 20 mmol, 2.0 eq) was added dropwise. After 2 hours at 0 °C, the ice bath was removed. After 22 hours at room temperature, 5–10 grams of silica gel was added and the slurry was allowed to stir for about 5 minutes under nitrogen. The slurry was filtered over a pad of silica gel with DCM and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:7 to 1:3 DCM:Hexanes; $R_f \approx 0.4$ in 1:3 DCM:Hexanes) to afford the desired secondary phosphine borane as a white solid (4.39 g, 90%). About 2% of the phosphine oxide is present.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.83–7.82 (m, 4H), 6.36 (dq, *J* = 376.4, 6.9 Hz, 1H), 0.32 (s, 36H). The signals for the $B\underline{H}_3$ protons are baseline.

^{31}P NMR (202 MHz, $CDCl_3$) δ 0.94 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2 (d, *J* = 2.4 Hz), 140.8 (d, *J* = 7.1 Hz), 138.1 (d, *J* = 8.9 Hz), 124.8 (d, *J* = 53.7 Hz), -1.1.



$(3,5\text{-}^i\text{Pr}_{F7})_2P(O)H$

bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine oxide

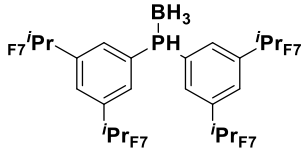
Prepared according to a modified literature procedure.[47]

1,3-Bis(perfluoropropan-2-yl)-iodo-benzene (12.42g, 23 mmol, 2.3 equiv) was added to Et_2O (70 mL, [0.33 M]) and cooled to -78 °C. TMEDA (3.5 mL, 23 mmol, 2.3 equiv) was added (solution became slightly yellow upon addition) and ^{n}BuLi [2.5 M in hexanes] (9.2 mL, 23 mmol, 2.3 equiv) was added dropwise over the course of 10 minutes (the reaction became brown, not completely homogenous). After 2 hours of stirring at -78 °C, $(Et_2N)PCl_2$ (1.74 g, 10 mmol, 1.0 equiv) was added dropwise to the aryl lithiate. After 6 hours the cooling bath had reached -32 °C, after 8 hours the bath had reached 0 °C. Seventeen hours after the addition of $(Et_2N)PCl_2$, ^{31}P nmr analysis indicated one major species at 59.6 ppm. The reaction was stirred for an additional two hours before it was cooled to 0 °C. Concentrated HCl (37%) (12.4 mL, 150 mmol, 15 equiv), which was sparged with nitrogen gas for 2 hours prior to use, was added over the course of 3 minutes. After 90 minutes at 0 °C, the ice bath was removed and the reaction was stirred at room temperature for 5 hours. The solution was poured onto 1.25 M HCl (300 mL), diluted with EtOAc (500 mL), and separated. The aqueous phase was extracted with EtOAc (300 mL) and the organic phases were combined, washed with H_2O (300 mL), brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:6 to 1:3 EtOAc:Hexanes; $R_f \approx 0.7$ in 1:3 EtOAc:Hexanes) to afford the desired SOP as a colorless solid (5.06 g, 58%).

The ^{1}H spectra data matched the literature.[47]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 507.1 Hz, 1H), 8.12–8.10 (m, 4H), 8.10 – 8.08 (m, 2H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 14.56 (s).



$(3,5\text{-}^i Pr_{F7})_2P(BH_3)H$

bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane

Notes: This secondary phosphine appears to be moderately air stable and may be suitable for isolation without borane protection. Before the addition of BH_3•DMS, the crude reaction was analyzed by ^{31}P NMR and indicated a one major and one minor species. Suggesting the addition of BH_3•DMS may not be suitable for the protection of this secondary phosphine (due to the low chemical yield). Suggestion: isolate the free phosphine or attempt an alternative reduction prodcedure ($CeCl_3$ (with or without $NaBH_4$) and LAH,[48] or DIBAL–H[39,49] may prove fruitful).

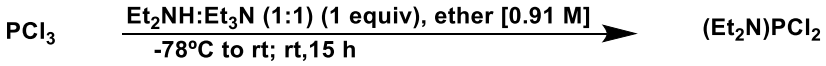
To a PhMe (24mL, [0.4 M]) solution of the corresponding 3,5-$^{i}Pr_{F7}$ SPO (4.85 g, 5.54 mmol, 1.0 eq), $Ti(O^{i}Pr)_4$ 97% (700 μL, 40 mol%) and TMDS 97% (1.3 mL, 7 mmol, 1.25 equiv) were sequentially added under a positive flow of nitrogen at room temperature. After the addition, the reaction was placed in a 70 °C oil bath. After 12 hours, another portion of TMDS (500 mL, 2.8 mmol, 0.5 equiv) was added. After a total of 24 hours at 70 °C, the reaction was cooled to 0 °C and BH_3•DMS (1.6 mL, 16.6 mmol, 3.0 eq) was added dropwise. After 1 hours at 0 °C, the ice bath was removed. After 2 hours at room temperature the brown solution became a brown sludge, and the stir bar stopped stirring. After 22 hours at room temperature, 5–10 grams of silica gel was added under nitrogen. The sludge was filtered over a pad of silica gel with DCM and concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:7 to 1:3 DCM:Hexanes; $R_f \approx 0.4$ in 1:3 DCM:Hexanes) to a mixture of the desired secondary phosphine borane, secondary phosphine, and phosphine oxide as a white solid (360 mg, 7%). This mixture can be used in the subsequent step to afford the bisborane adduct in 20% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.8 Hz, 4H), 8.03 (s, 2H), 6.65 (dq, *J* = 388.8, 7.4 Hz, 1H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 14.8 (s, $R_2P(O)H$), 4.3 (s, $R_2P(BH_3)H$), -40.2 (s, R_2PH).

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.62–-75.74 (m), -182.37 (p, *J* = 7.7 Hz).

2.5.3 Synthesis of Reagents



Dichloro(diethylamino)phosphine

Prepared according to a modified literature procedure.[50]

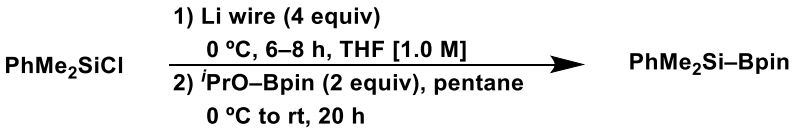
To a 1000 mL, 3-neck round bottom flask with Et_2O (555 mL, [0.91 M]) at -78 C, PCl_3 (45 mL, 505 mmol, 1.01 equiv) was added. Et_3N (70 mL, 500 mmol, 1.0 eqiuv) and Et_2NH (52 mL, 500 mmol, 1.0 equiv) were added to a 250 mL addition and thoroughly mixed. The amine mixture was added dropwise over the course 120 minutes to the vigorously stirred, -78 °C solution of PCl_3. Amine mixture had been added, dry ice was no longer added to the cooling bath. After 5 hours, the cooling bath was removed (the reaction becomes very thick and stirring may halt if a small stir bar was utilized; if this occurs attempt to swirl the flask and rinse down the slurry from the reaction vessel walls with minimum Et_2O; if stirring cannot be achieved the chemical yield should not drop too much). After being at room temperature for 15 hours, the slurry was rapidly filtered over a medium frit under a nitrogen blanket, rinsed with pentane (2 x 300 mL) (pentane was sparged for 90 minutes while being dried over $MgSO_4$), and concentrated to a yellow oil on a rotovap. The yellow oil was transferred to a cycled distillation apparatus and the crude residue distilled (40–44 °C, 150 mtorr) to afford

Et_2NPCl_2 as a colorless oil (65.5 g, 75%). The product does not appear to be extremely sensitive to air (an NMR could be obtained in reagent grade $CDCl_3$ within 15 minutes without hydrolysis or oxidation).

The spectra data matched an authentic sample purchased from Sigma-Aldrich.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.34 (dq, *J* = 13.0, 7.2 Hz, 4H), 1.19 (t, *J* = 7.2 Hz, 6H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 162.5 (s).



Dimethylphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane

Prepared according to a literature procedure.[51]

In air, lithium wire 99% (2.78 g, 400 mmol, 4.0 equiv) was cut into small pieces (tweezers and scissors were cleaned with acetone, hexanes, then dried) into a tarred 20 mL vial containing 10 mL of hexanes. The lithium pieces were transferred to a 250 mL Schlenk round bottom reaction vessel and pentane (20 mL) was added. The lithium pieces were stirred under nitrogen for two minutes and the pentane was removed by pipette under a nitrogen flow. This rinse was repeated once more. Anhydrous THF (30 mL) was added and after two minutes of stirring, removed by pipette. The cleaned lithium pieces were briefly cycled under vacuum three times before THF (100 mL, [1.0 M]) was added and the reaction vessel was placed in a 0 °C bath with vigorous stirring. After 30 minutes, $PhMe_2SiCl$ (16.8 mL, 100 mmol, 1.0 equiv, distilled under nitrogen) was added dropwise over the course of eight minutes. By the end of the addition, the THF became slightly yellow, whereas the lithium wire transformed from a gray/silver color to a copper hue. After one hour, the THF achieved a deep red/purple color. After 7 hours, the solution of $PhMe_2SiLi$ was canula transferred dropwise to a 0 °C solution of ^{i}PrOBpin (42 mL, 206 mmol, 2.06 equiv, distilled prior to use) in pentane [103 mL, 2.0 M wrt to ^{i}PrOBpin] over the course of 40 minutes (do not increase the rate of addition; a faster rate of addition led to a decrease in yield). The reaction was allowed to warm to room temperature overnight (19–20 hours). The next morning, a 200 mL Schlenk round bottom reaction vessel was modified with a short distillation head equipped with a receiving 100 mL Schlenk bomb. The white slurry was quickly filtered under a nitrogen blanket (nitrogen tube taped to an inverted, large plastic funnel) over oven-dried celite (dried under vacuum, 200 mtorr) on an oven-dried, medium sized frit (which was cooled under a nitrogen flow prior to filtration). The celite was rinsed with pentane (2 x 150 mL), and the solvent removed on a rotovap. The residue was

quickly transferred to the cooled 200 mL Schlenk reaction vessel (a minimum amount of pentane was used to rinse the crude from the first flask to the 200 mL Schlenk vessel) and the pentane removed. The residue was distilled at 200 mtorr. Everything below 100 °C was discarded (appears to be mostly pinB–O–Bpin), the desired silylborane was collected between 110 –116 °C (65%, 17.04 g) as a colorless oil (the oil remaining in the distillation flask was mostly the disilane with unidentified byproducts). The product was transferred into a glovebox and stored at -25 °C. At this temperature it solidified to a white solid. After removing the silylborane from the freezer it remained a solid. Samples that had been left outside of the glovebox freezer but in the glovebox (greater than 4–6 weeks) began to liquefy (perhaps from the introduction of trace water from microsyringes). For catalytic reactions, small quantities were removed from the 20 mL vial in the freezer and gently warmed to 26 °C prior to use (so that a microsyringe could be used to transfer the reagent). The major impurity in the Sigma Aldrich supplied $PhMe_2SiBpin$ was identified by GC-MS and NMR as $PhMe_2Si–O–Bpin$. Reactions were more reproducible when $PhMe_2Si–O–Bpin$ was absent (using an excess of the silylborane was not an appropriate solution). Careful distillation can be used to purify $PhMe_2SiBpin$ (the yield may decrease because the boiling point of $PhMe_2Si–O–Bpin$ tails into the beginning of the boiling point of $PhMe_2SiBpin$; however, the synthesis of $PhMe_2SiBpin$ can be done on scale with relative ease). Both $PhMe_2SiCl$ and $^{i}PrOBpin$ should be distilled and sparged prior to use. It was found that cleaning the surface of the lithium metal by stirring it with 5 mol % TMSCl (wrt to the mmol of Li) in THF for 30 minutes to an hour with a subsequent THF wash (2 x 30 mL) lead to a decrease in the amount of $PhMe_2Si–O–Bpin$.

The spectra data matched the literature.[51]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2H), 7.38–7.35 (m, 3H), 1.29 (s, 12H), 0.37 (s, 6H).

^{11}B NMR (160 MHz, $CDCl_3$) δ 34.8 (bs).

Quenching the excess lithium:

Note: After the addition of every portion of ROH species, monitor the vessel to ensure that the reaction does not run away (often it takes 2–3 minutes after each ROH portion to know if an appropriate amount of alcohol has been added). If too much ROH is added and the gas evolution is too vigorous, stop stirring and place the vessel in a -78 °C bath. Once at -78 °C begin stirring. If gas evolution seems under control place the vessel back in the 0 °C bath. Quenching the excess lithium wire should be done under an atmosphere of nitrogen with a large vent needle in the septa that is fitted on the top of the reaction vessel.

The 250 mL round bottom flask containing the excess lithium was placed in a 0 °C bath and isopropanol (50-75 mL) was slowly added. MeOH (1–3 mL) was slowly added. The vessel was monitored to gauge gas evolution. When gas evolution ceased more MeOH (3–4 mL) was added and gass evolution was monitored again. This process was repeated until all the lithium wire pieces had dissolved. Once the lithium was

dissolved, the vessel was removed to rt and water was slowly added. The solution was slowly neutralized and discarded.

Sodium Phenolates

Prepared according to a modified, literature procedure.[52]

Note: Metal phenolates are hydroscopic and should be thoroughly purified before use in the catalytic reaction. The purity of the phenolate is crucial to obtain reproducible results. Potassium phenolates were prepared with KH powder, and were more soluble than their sodium analogs.

In a nitrogen filled glovebox, NaH powder 95% (1.26 g, 50 mmol, 1.0 equiv) was added to a 200 mL round bottom flask. The vessel was sealed and transferred to a Schleck line where THF (25 mL, [2.0 M])was added. The phenol (50 mmol, 1.0 equiv), which was azetroped with anhydrous benzene ($3x$) and, when necessary, distilled under nitrogen), was dissolved in THF (25 mL [2.0]) and added to the vigorously stirred slurry of NaH. After 60–70 minutes, the solution was concentrated, concentrated at an evaluated temperature (40–90 ^{o}C at 200 mtorr, depending on the molecular weight of the phenol) to yield a powder. The flask and solid was transferred back inside the glovebox and dissolved in a minimum amount of THF (about 6 g of sodium phenolate required 40–50 mL THF, dependent on substituents). The solution was filtered over a fine frit and concentrated until a white solid began to precipitate out of solution (about 10 mL THF remaining). Hexane was added to facilitate further precipitation and slurry was filter over a medium sized frit. Off white solid was washed with benzene (enough to cover the solid), followed by hexane (washes should remove any colored impurities) to yield a white solid, that was dried at 30–40 ^{o}C at 200 mtorr for 8–10 hours. For 2-methoxyphenol (8.41 mL, 75 mmol, 1.0 equiv) and NaH (1.89 g, 75 mmol, 1.0 equiv), 10.4 g (95%) of a white solid was obtained, which was stored in a -25 ^{o}C freezer in the glovebox. Most phenolates were stored in the glovebox, protected from light, but shelf lives were prolonged by freezer storage (>6 months).

2.5.4 Synthesis of Substrates

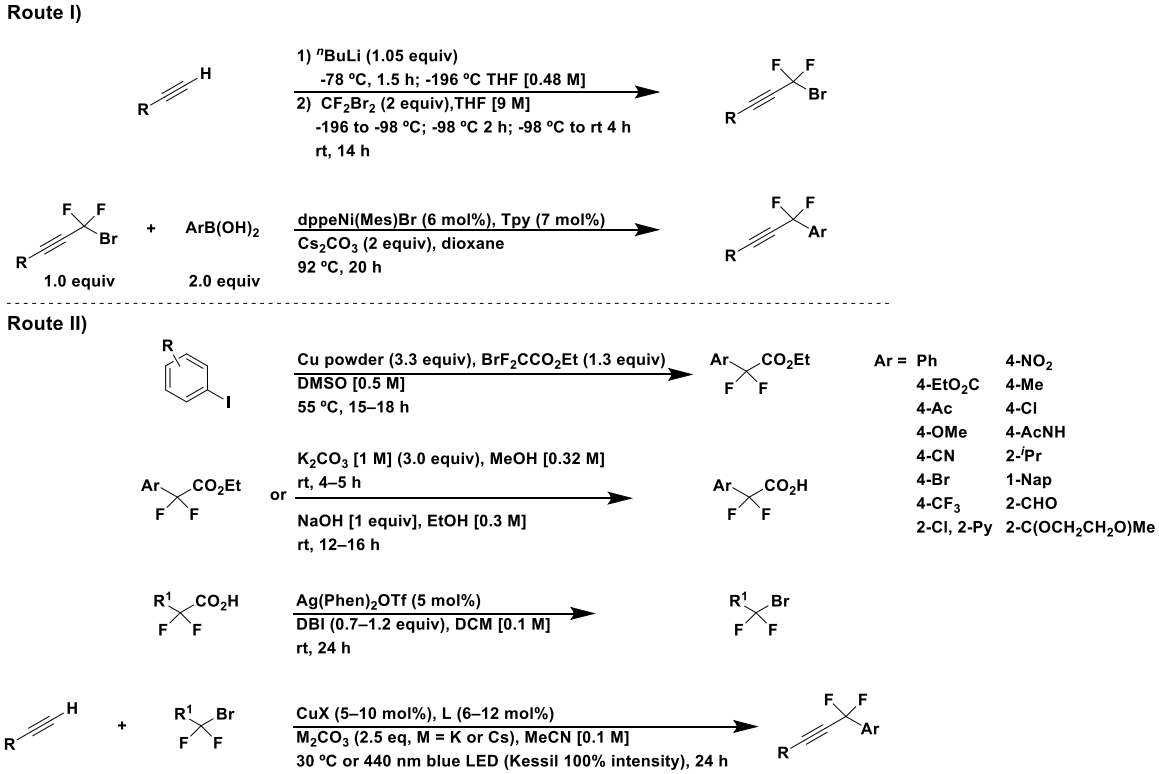
General Routes:

Two general routes were taken for the synthesis of the internal, difluoroalkynes.

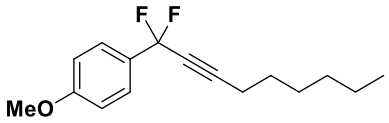
Route (I) utilizes CF_2Br_2 as the fluorinated building block following literature reports.[53] Freezing the THF solution of the lithium acetylide with liquid nitrogen gave improved yields for alkynes bearing a 1^{o} alkyl group relative to reaction conditions that utilize a -110 ^{o}C cooling bath (which works well for R = TIPS).[20a] The

palladium Suzuki coupling of the bromodifluoropropargyl electrophiles when R was a 1° aliphatic group gave reaction mixtures that were difficult to purify by column chromatography (due to isomerization of the propargyl palladium intermediate, which resulted in of allene formation), thus reported conditions were modified to ease purification.[19]

Route (II) employed ethyl bromodifluoroacetate as the fluorinated building block. After the copper promoted coupling with aryl iodidesthe resulting esters were transformed into either their respective carboxylic acids literature reported conditions.[54] From the carboxylic acid intermediates, either decarboxylative bromination or decarboxylative alkynylation conditions were applied.[55] A photochemical procedure was developed to couple the bromodifluoroarenes with terminal alkynes. The difluoroalkynyl TIPS substrates were subsequently deprotected and arylated.



Route I



1-(1,1-difluorononon-2-yn-1-yl)-4-methoxybenzene (**2a**)

Prepared according to a modified literature procedure.[19]

In a nitrogen filled glovebox, dppeNi(Mes)Br (157 mg, 6 mol%), terpyridine (66 mg, 7 mol%), Cs_2CO_3 (2.9 g, 8.8 mmol, 2.2 equiv), 4-methoxyphenylboronic acid (1.22 g, 8.0 mmol, 2.0 equiv), and 1,4-dioxane (28 mL, [0.143 M]) were added to a 50 mL Schlenk reaction flask. The flask was sealed with a septum, removed from the glovebox, and fitted to a Schlenk line. The alkyne, 1-bromo-1,1-difluorononon-2-yne, (956mg, 4.0 mmol, 1 equiv) was added under a flow of N_2 and the reaction mixture was briefly cycled three times before being placed into a 92 °C oil bath. After 20 hours, the reaction was filtered over a plug of silica gel with Et_2O and the filtrate concentrated. The crude residue was concentrated onto celite and purified by silica gel column chromatography (1:16 EtOAc:Hexanes; $R_f \approx 0.5$) to afford alkyne **1a** as a light yellow oil (298 mg, 28%). Note: dppeNiBr_2 can be used in place of dppeNi(Mes)Br.

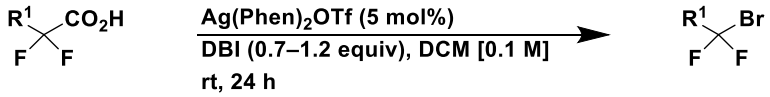
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.35 (tt, *J* = 7.2, 4.9 Hz, 2H), 1.60 (p, *J* = 7.3 Hz, 2H), 1.49–1.38 (m, 2H), 1.38–1.26 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.24 (s, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4 (t, *J* = 1.7 Hz), 129.1 (t, *J* = 28.7 Hz), 127.2 (t, *J* = 4.2 Hz), 113.8, 112.6 (t, J = 228.7 Hz), 90.9 (t, *J* = 5.9 Hz), 74.4 (t, *J* = 41.3 Hz), 55.5, 31.3, 28.6, 27.9, 22.6, 18.7 (t, *J* = 2.3 Hz), 14.1.

HRMS (ESI+) calc'd for $C_{16}H_{21}FNa_2NO^{3+}$ $[M+2Na-F]^{3+}$: 293.1277, found 293.1267.

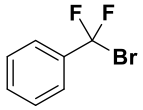
Route II



General Procedure A: Decarboxylative Bromination of Difluorocarboxylic Acids

To an oven-dried round bottom flask containing a large magnetic stir bar Ag(Phen)$_2$OTf (5 mol%) was added and the flask evacuated. After being refilled with nitrogen gas, CH_2Cl_2 (0.1 M), the desired difluorocarboxylic acid (1.0 equiv), and dibromoisocyanuric acid (DBI) (0.7–1.2 equiv) were sequentially added. The mixture was degassed, the allowed to stir at room temperature in the dark for 24 h. The mixture was diluted with pentane, filtered over a plug of SiO_2, and rinsed with Et_2O. The organics were washed with a 50% saturated solution of $Na_2S_2O_3$, Brine, dried over $MgSO_4$, filtered, and carefully concentrated (some of the products are volatile). The crude reaction mixture was purified by silica gel column chromatography to afford the desired

bromodifluoromethylarenes. (Notable limitations: electron rich aryl rings are brominated whereas allylic and vinylic carboxylic acids lead to complex reaction mixtures.)

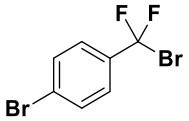


(bromodifluoromethyl)benzene **(1Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (3.9 g, 5 mol%), 2,2-difluoro-2-phenylacetic acid (12.0 g, 70 mmol , 1.0 equiv), and DBI (18.1 g, 63 mmol, 0.9 equiv), and CH_2Cl_2 (700 mL) were used. After anhydrous CH_2Cl_2 was poured into the vessel, the reaction was sparged with nitrogen gas for 30 minutes before the addition of DBI. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 200 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (400 mL), Brine (300 mL), dried over $MgSO_4$, filtered, and carefully concentrated (rotovap bath was cooled to 6 °C, vacuum was set at about 200–400 mtorr).The crude residue was purified by column chromatography on SiO_2 (pentane) to afford the title compound as a colorless liquid (11.51 g, 79 % yield). (Notes: The yield for the desired compound is less when compared to its NMR yield due to its volatility. The reactions below still work if there is a trace amount of pentane remaining after column chromatography).

In accordance with previously reported spectra.[56]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.53–7.43 (m, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -43.49 (s, 2F).

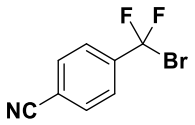


1-bromo-4-(bromodifluoromethyl)benzene **(2Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-bromophenyl)-2,2-difluoroacetic acid (1.51 g, 6.0 mmol , 1.0 equiv), and DBI (1.55 g, 5.4 mmol, 0.9 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (hexanes) to afford the title compound as a colorless liquid (1.31 g, 76% yield).

In accordance with previously reported spectra.[57]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -44.01 (s, 2F).

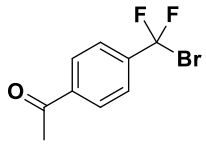


4-(bromodifluoromethyl)benzonitrile **(3Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-cyanophenyl)-2,2-difluoroacetic acid (1.2 g, 6.0 mmol , 1.0 equiv), and DBI (2.0 g, 7.0 mmol, 1.17 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:9) to afford the title compound as a colorless liquid (1.25 g, 90% yield).

In accordance with previously reported spectra.[57]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -46.31 (s, 2F).



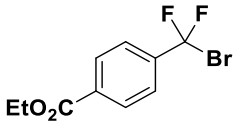
1-(4-(bromodifluoromethyl)phenyl)ethan-1-one **(4Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-acetylphenyl)-2,2-difluoroacetic acid (1.3 g, 6.0 mmol , 1.0 equiv), and DBI (1.43 g, 5.0 mmol, 0.83 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:9) to afford the title compound as a colorless liquid (1.42 g, 95% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 2.62 (s, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -45.26 (s, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 141.9 (t, *J* = 24.0 Hz), 139.2 (t, *J* = 1.4 Hz), 128.7, 124.8 (t, *J* = 5.0 Hz), 117.6 (t, *J* = 304.1 Hz), 26.8.

HRMS (ESI+) calc'd for $C_9H_7BrF_2NaO^+$ $[M+Na]^+$: 270.9541, found 270.9541.

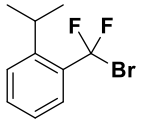


ethyl 4-(bromodifluoromethyl)benzoate **(5Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-(ethoxycarbonyl)phenyl)-2,2-difluoroacetic acid (1.47 g, 6.0 mmol , 1.0 equiv), and DBI (1.54 g, 5.4 mmol, 0.9 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a colorless liquid (1.38 g, 83% yield).

In accordance with previously reported spectra.[58]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -45.14 (s, 2F).



1-(bromodifluoromethyl)-2-isopropylbenzene **(6Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2,2-difluoro-2-(2-isopropylphenyl)acetic acid (1.3 g, 6.0 mmol , 1.0 equiv), and DBI (2.0 g, 7.0 mmol, 1.17 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude

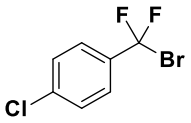
residue was purified by column chromatography on SiO_2 (hexanes) to afford the title compound as a colorless liquid (1.14 g, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.50–7.46 (m, 2H), 7.29–7.23 (m, 1H), 3.65 (dtt, *J* = 13.7, 6.8, 1.6 Hz, 1H), 1.33 (d, *J* = 6.9 Hz, 6H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -40.78 (s, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2 (t, *J* = 2.5 Hz), 134.9 (t, *J* = 20.9 Hz), 131.7, 127.9, 125.7, 123.8 (t, *J* = 8.5 Hz), 117.9 (t, *J* = 305.0 Hz), 29.3 (t, *J* = 2.4 Hz), 24.1.

HRMS (ESI+) calc'd for $C_{10}H_{12}BrF_2Na^+$ $[M+H]^+$: 270.9904 , found 270.9901.

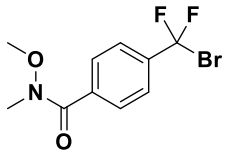


1-(bromodifluoromethyl)-4-chlorobenzene **(7Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-chlorophenyl)-2,2-difluoroacetic acid (1.24 g, 6.0 mmol , 1.0 equiv), and DBI (1.65 g, 6.3 mmol, 0.96 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (hexanes) to afford the title compound as a light yellow liquid (1.08 g, 74% yield).

In accordance with previously reported spectra.[59]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -43.76 (s, 2F).



4-(bromodifluoromethyl)-N-methoxy-N-methylbenzamide **(8Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (1.85 g, 5 mol%), 2,2-difluoro-2-(4-(methoxy(methyl)carbamoyl)phenyl)acetic acid (15.55 g, 60.0 mmol , 1.0 equiv), and DBI (15.55 g, 54.0 mmol, 0.90 equiv), and CH_2Cl_2 (600 mL) were used. After CH_2Cl_2 was added, the difluoroacetic acid and DBI were added and the reaction briefly cycled three times

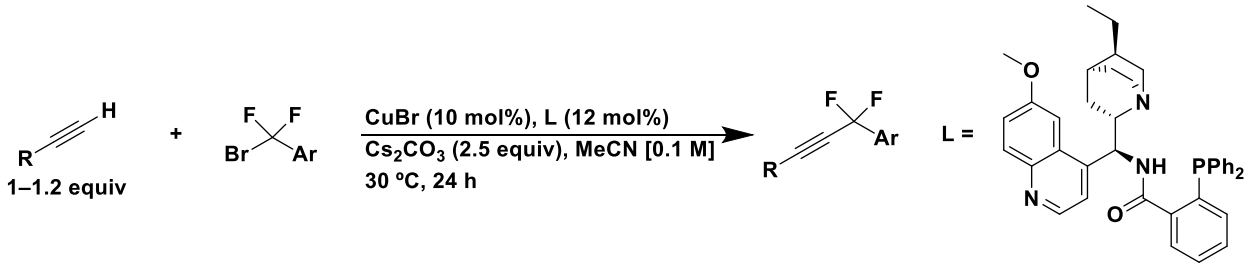
before being left under a dynamic nitrogen atmosphere. After 24 h of vigorous stirring at room temperature (in the absence of light), the reaction was filtered over a pad of silica and rinsed with Et_2O (3 x 100 mL). The organics were washed with a 50% saturated solution of $Na_2S_2O_3$ (200 mL), Brine (150 mL), dried over $MgSO_4$, filtered, and carefully concentrated. The crude residue was purified by column chromatography on SiO_2 (hexanes) to afford the title compound as a light yellow oil (13.1 g, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 3.50 (s, 3H), 3.33 (s, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -44.46 (s, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 139.7 (t, *J* = 23.9 Hz), 137.0, 128.53, 124.1 (t, *J* = 5.1 Hz), 117.8 (t, J = 303.8 Hz), 61.3, 33.4.

HRMS (ESI+) calc'd for $C_{10}H_{10}BrF_2NNaO_2^+$ $[M+Na]^+$: 315.9755 , found 315.9754.

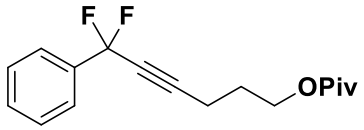


General Procedure B: Aryldifluoromethylation of Terminal Alkynes (Thermal Conditions)

In a nitrogen filled glovebox, an oven-dried 50 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with Cs_2CO_3 (2.5–3.0 eq), L (12 mol%), and CuBr (10 mol%). The flask was sealed with a rubber septum, removed from the glovebox, and placed under a nitrogen flow from a Schleck line. After the addition of anhydrous MeCN (0.2 M) (passed over an activated alumina column under Argon and stored over stored over 3A molecular sieves), the mixture was stirred for 10–15 minutes before the sequential addition of the bromodifluoromethylarene (1.0 equiv), terminal alkyne (1.0–1.3 equiv), and MeCN (total concentration = 0.1 M). The flask was briefly cycled three times (to remove introduced oxygen) and placed in an oil bath set at 30 °C. After 24 hours of vigorous stirring, the reaction was filtered over a plug of silica, rinsed with either EtOAc or Et_2O, and concentrated. The crude reaction mixture was purified by silica gel column chromatography to afford the desired propargyl gem difluorides. Note: Upon scaling up to 10 mmol from 3–4 mmol, the reaction time had to be increased to 48 hours to ensure comparable yields.

General Procedure C: Aryldifluoromethylation of Terminal Alkynes (Blue LED Conditions)

In a nitrogen filled glovebox, an oven-dried 50 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with K_2CO_3 (2.5–3.0 eq), terpyridine (Tpy) (12 mol%), and $Cu(MeCN)_4BF_4$ (10 mol%). MeCN (0.1 M) (passed over an activated alumina column, degassed (3 freeze, pump, thaw cycles), and stored over 3A molecular sieves) was added and the mixture was allowed to stir for 10–15 minutes before the sequential addition of the bromodifluoromethylarene (1.0 equiv) and terminal alkyne (1.0–1.3 equiv). The flask was sealed with a rubber septum, removed from the glovebox, placed under a nitrogen flow, and placed between two, Kessil 440 nm blue photoredox lamps that were set at 100% intensity that were located about 3 cm from the sides of the vessel. A fan was located above the flask so that the temperature did not go above 30–35 °C. After 24 hours of vigorous stirring, the reaction was filtered over a plug of silica, rinsed with either EtOAc or Et_2O, and concentrated. The crude reaction mixture was purified by silica gel column chromatography to afford the desired propargyl gem difluorides.



6,6-difluoro-6-phenylhex-4-yn-1-yl pivalate **(1a):**

Following general procedure **B**, Cs_2CO_3 (3.9 g, 12.0 mmol, 3.0 eq), L (300 mg, 12 mol%), CuBr (58 mg, 10 mol%), $PhCF_2Br$ (828 mg, 4.0 mmol, 1.0 equiv), the corresponding terminal alkyne (740 mg, 4.4 mmol, 1.1 equiv), and MeCN (40 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 120 mL), and concentrated. After being loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:16) to afford the title compound as a colorless oil (881 mg, 74 % yield).

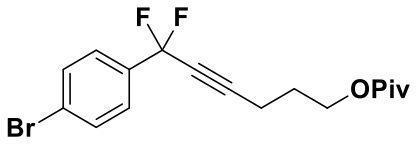
Scale up following general procedure **B**, In a glovebox Cs_2CO_3 (10.6 g, 12.0 mmol, 2.5 eq), L (957 mg, 12 mol%), and CuBr (187 mg, 10 mol%) were charged to a 250 mL Schleck round bottom reaction flask. Under a flow of nitrogen from a Schlenk line, 70 mL MeCN was added and the mixture was stirred for about 10 minutes. Then $PhCF_2Br$ (3.5 g, 16.0 mmol, 1.2 equiv), the corresponding terminal alkyne (2.2 g, 13.0 mmol, 1.0 equiv), and MecN (50 mL) were added. The flask was briefly cycled 3 times before being placed in a 24 °C oil bath with vigorous stirring. After 48 h, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 120 mL), and concentrated. After being loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:16) to afford the title compound as a colorless oil (3.29 g, 86 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.51–7.41 (m, 3H), 4.15 (t, *J* = 6.2 Hz, 2H), 2.45 (tt, *J* = 7.1, 4.8 Hz, 2H), 1.94 (p, *J* = 6.7 Hz, 2H), 1.20 (s, 9H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.15 (t, *J* = 4.6 Hz, 2F)

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 136.6 (t, *J* = 28.1 Hz), 130.7 (d, *J* = 2.0 Hz), 128.6, 125.4 (t, *J* = 4.6 Hz), 112.3 (t, *J* = 230.6 Hz), 89.5 (t, *J* = 5.8 Hz), 74.9 (t, *J* = 41.5 Hz), 62.8, 38.9, 27.3, 27.2, 15.6 (t, *J* = 4.1, 2.5 Hz).

HRMS (ESI+) calc'd for $C_{17}H_{20}FO_2^+$ $[M-F]^+$: 275.1442, found 275.1442.



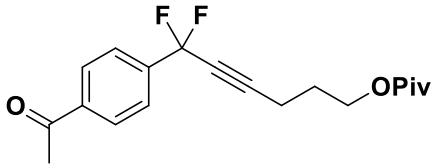
6-(4-bromophenyl)-6,6-difluorohex-4-yn-1-yl pivalate **(3a):** Following general procedure **B**, Cs_2CO_3 (2.0 g, 6.25 mmol, 2.5 eq), L (96 mg, 6.25 mol%), CuBr (18 mg, 5 mol%), 1-bromo-4-(bromodifluoro)benzene (714 mg, 2.5 mmol, 1.0 equiv), the corresponding terminal alkyne (546 mg, 3.25 mmol, 1.3 equiv), and MeCN (25 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:Et_2O 1:9) to afford the title compound as a light yellow oil (590 mg, 63% yield). (Note: do not half the catalyst loading).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.13 (t, *J* = 6.2 Hz, 2H), 2.43 (tt, *J* = 7.2, 4.9 Hz, 2H), 1.92 (p, *J* = 6.7 Hz, 2H), 1.19 (s, 9H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -74.43 (d, *J* = 4.4 Hz, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 135.6 (t, *J* = 28.8 Hz), 131.9, 127.2 (t, *J* = 4.5 Hz), 125.2 (t, *J* = 1.9 Hz), 111.8 (t, *J* = 231.0 Hz), 90.0 (t, *J* = 5.8 Hz), 74.4 (t, *J* = 41.2 Hz), 62.7, 38.9, 27.3, 27.2, 15.5 (t, *J* = 2.3 Hz).

HRMS (ESI+) calc'd for $C_{17}H_{20}BrFO_2^{+2}$ $[M+H-F]^{+2}$: 354.0620, found 354.0613.



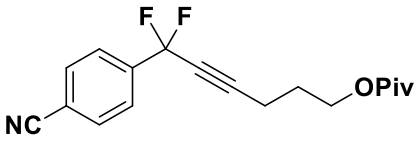
6-(4-acetylphenyl)-6,6-difluorohex-4-yn-1-yl pivalate **(4a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), 1-(4-(bromodifluoromethyl)phenyl)ethan-1-one (750 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (605 mg, 3.6 mmol, 1.2 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:5) to afford the title compound as a light yellow oil (420 mg, 41% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 2.57 (s, 3H), 2.41 (tt, *J* = 7.1, 4.8 Hz, 2H), 1.94–1.83 (m, 2H), 1.14 (s, 9H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.51 (d, *J* = 6.1 Hz, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 178.3, 140.5 (t, *J* = 28.5 Hz), 138.7, 128.5, 125.6 (t, *J* = 4.4 Hz), 111.5 (t, *J* = 231.5 Hz), 90.4 (t, *J* = 5.8 Hz), 74.3 (t, *J* = 41.1 Hz), 62.6, 38.8, 27.1, 26.9, 26.7, 15.4 (t, *J* = 2.1 Hz).

HRMS (ESI+) calc'd for $C_{19}H_{22}F_2NaO_3^+$ $[M+Na]^+$: 359.1429, found 359.1432.



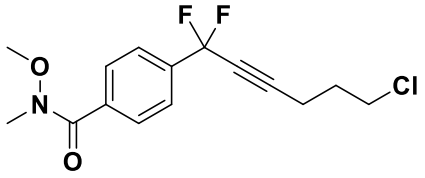
6-(4-cyanophenyl)-6,6-difluorohex-4-yn-1-yl pivalate **(5a):** Following general procedure **C**, K_2CO_3 (1.05 g, 7.5 mmol, 2.5 eq), Tpy (84 mg, 13 mol%), $Cu(MeCN)_4BF_4$ (113 mg, 12 mol%), 4-(bromodifluoromethyl)benzonitrile (700 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (656 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 48 h of vigorous stirring and irradiation by two 440 nm Blue LED lamps (two Kessil photoredox lamps at 100% intensity), the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:16 to 1:9) to a afford the title compound as a light yellow oil (375 mg, 39% yield, purity ≥ 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.70 (m, 4H), 4.11 (t, *J* = 6.2 Hz, 2H), 2.42 (tt, *J* = 7.2, 5.0 Hz, 2H), 1.90 (p, *J* = 6.7 Hz, 2H), 1.16 (s, 9H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.02 (t, *J* = 5.1 Hz, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 140.7 (t, *J* = 29.1 Hz), 132.5, 126.2 (t, *J* = 4.5 Hz), 117.9, 114.6, 111.0 (t, *J* = 232.3 Hz), 91.0 (t, *J* = 5.8 Hz), 73.8 (t, *J* = 40.9 Hz), 62.5, 38.8, 27.2, 26.9 (t, *J* = 2.0 Hz), 15.4 (t, *J* = 2.3 Hz).

HRMS (ESI+) calc'd for $C_{18}H_{19}F_2NNaO^+$ $[M+H]^+$: 342.1276, found 342.1271.



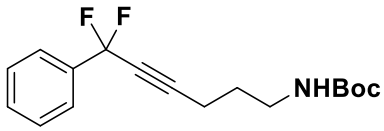
4-(6-chloro-1,1-difluorohex-2-yn-1-yl)-N-methoxy-N-methylbenzamide **(6a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuI (57 mg, 10 mol%), **8Br** (930 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (605 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 2:3 to 1:1) to afford the title compound as a colorless oil (513 mg, 54% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 3.59 (t, *J* = 6.3 Hz, 2H), 3.50 (s, 3H), 3.32 (s, 3H), 2.51 (tt, *J* = 6.9, 4.8 Hz, 2H), 1.99 (p, *J* = 6.6 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -74.90 (d, *J* = 5.0 Hz, 2F)

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 138.1 (t, J = 28.4 Hz), 136.4 (d, J = 2.1 Hz), 128.4, 125.04 (t, J = 4.3 Hz), 111.7 (t, J = 231.2 Hz), 89.6 (t, J = 5.8 Hz), 74.6 (t, J = 41.3 Hz), 61.9, 43.3, 33.4, 30.3 (d, J = 2.0 Hz), 16.0 (t, J = 2.2 Hz).

HRMS (ESI+) calc'd for $C_{15}H_{16}ClF_2NNaO_2^+$ $[M+Na]^+$: 338.0730, found 338.0738.



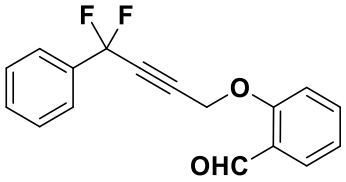
tert-butyl (6,6-difluoro-6-phenylhex-4-yn-1-yl)carbamate **(7a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (605 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:5) to afford the title compound as a colorless oil (475 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.62 (m, 2H), 7.46–7.40 (m, 3H), 4.74 (s, 1H), 3.20 (q, *J* = 6.6 Hz, 2H), 2.37 (tt, *J* = 6.9, 4.8 Hz, 2H), 1.76 (t, *J* = 7.0 Hz, 1H), 1.43 (s, 9H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.87 (m, 2F)

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 136.5 (t, *J* = 28.2 Hz), 130.7, 128.6, 125.4 (t, *J* = 4.6 Hz), 112.3 (t, *J* = 230.4 Hz), 90.0, 79.4, 74.7 (t, *J* = 41.4 Hz), 39.7, 28.5, 28.2, 16.1.

HRMS (ESI+) calc'd for $C_{17}H_{21}F_2NNaO_2^+$ $[M+Na]^+$: 332.1433, found 332.1439.



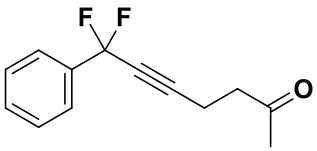
2-((4,4-difluoro-4-phenylbut-2-yn-1-yl)oxy)benzaldehyde **(8a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), bromodifluoromethylbenzene (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (598 mg, 3.6 mmol, 1.2 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:13 to 1:5) to afford the title compound as a tan solid (549 mg, 64% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.90–7.84 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.59–7.52 (m, 1H), 7.50–7.43 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.15–7.05 (m, 2H), 4.99–4.92 (m, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -76.64 (d, *J* = 108.0 Hz).

^{13}C NMR (151 MHz, $CDCl_3$) δ 189.3, 159.5, 135.9, 135.5 (t, *J* = 27.5 Hz), 131.1 (d, *J* = 3.9 Hz), 128.9, 128.9, 128.7, 1257, 125.7, 125.3 (t, *J* = 4.7 Hz), 113.2, 112.0 (t, *J* = 232.4 Hz), 81.2 (t, *J* = 42.7 Hz), 56.2.

HRMS (ESI+) calc'd for $C_{17}H_{12}F_2NaO_2^+$ $[M+H]^+$: 309.0698, found 309.0699.



7,7-difluoro-7-phenylhept-5-yn-2-one **(9a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the

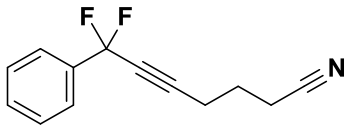
corresponding terminal alkyne (400 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:3) to afford the title compound as an orange oil (554 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.60 (m, 2H), 7.49–7.38 (m, 3H), 2.72 (dd, *J* = 8.2, 6.3 Hz, 2H), 2.63–2.52 (m, 2H), 2.15 (s, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -74.01 (t, *J* = 5.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.5, 136.4 (t, *J* = 28.2 Hz), 130.7 (d, *J* = 2.0 Hz), 128.6, 125.4 (t, *J* = 4.5 Hz), 112.3 (t, *J* = 230.3 Hz), 89.6 (t, *J* = 5.9 Hz), 74.4 (t, *J* = 41.4 Hz), 41.3 (t, *J* = 2.0 Hz), 29.8, 13.0 (t, *J* = 2.3 Hz).

HRMS (ESI+) calc'd for $C_{13}H_{13}F_2O^+$ $[M+H]^+$: 223.0929, found 223.0924.



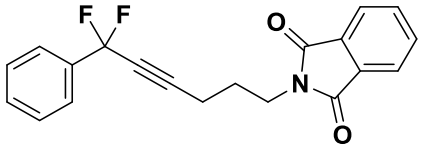
7,7-difluoro-7-phenylhept-5-ynenitrile **(10a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (370 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:4) to afford the title compound as an orange oil (494 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.50–7.42 (m, 3H), 2.53 (tt, *J* = 7.0, 4.8 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.93 (p, *J* = 7.0 Hz, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -74.57 (d, *J* = 5.2 Hz, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.15 (t, *J* = 28.1 Hz), 130.8 (t, *J* = 1.6 Hz), 128.6, 125.3 (t, *J* = 4.7 Hz), 118.7, 112.1 (t, *J* = 231.1 Hz), 87.8 (t, *J* = 5.8 Hz), 75.9 (t, *J* = 41.7 Hz), 23.8 (t, *J* = 2.1 Hz), 17.6 (t, *J* = 2.2 Hz), 16.2.

HRMS (ESI+) calc'd for $C_{13}H_{11}FN^+$ $[M-F]^+$: 200.0870, found 200.867.



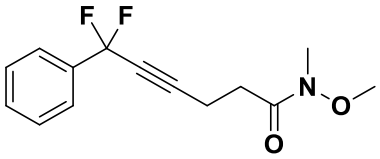
2-(6,6-difluoro-6-phenylhex-4-yn-1-yl)isoindoline-1,3-dione (**11a**)**:** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (850 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:4) to afford the title compound as a light yellow oil (724 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.68–7.60 (m, 4H), 7.46–7.37 (m, 3H), 3.77 (t, *J* = 6.9 Hz, 2H), 2.42 (td, *J* = 7.4, 3.6 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -73.94 (t, *J* = 5.1 Hz, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 136.3 (t, *J* = 28.1 Hz), 134.0, 132.0, 130.6, 128.5, 125.4 (t, *J* = 4.5 Hz), 123.3, 112.2 (t, *J* = 230.5 Hz), 89.5 (t, *J* = 5.9 Hz), 74.6 (t, *J* = 41.3 Hz), 37.1, 26.8, 16.5.

HRMS (ESI+) calc'd for $C_{20}H_{15}FNO_2^+$ $[M-F]^+$: 320.1081, found 320.1078.



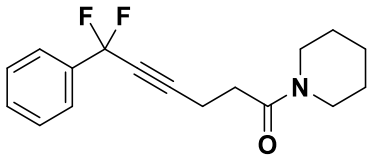
6,6-difluoro-N-methoxy-N-methyl-6-phenylhex-4-ynamide (**12a**)**:** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (487 mg, 3.45 mmol, 1.15 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:2) to afford the title compound as a yellow oil (670 mg, 83% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67–7.63 (m, 2H), 7.45–7.38 (m, 3H), 3.64 (s, 3H), 3.15 (s, 3H), 2.74 – 2.62 (m, 4H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.96 (s, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 136.4 (t, *J* = 28.2 Hz), 130.6 (t, *J* = 2.0 Hz), 128.5, 125.4 (t, J = 4.4 Hz), 112.3 (t, *J* = 230.3 Hz), 89.9 (t, *J* = 6.1 Hz), 74.4 (t, *J* = 41.4 Hz), 61.3, 32.2, 30.3, 14.0 (t, *J* = 2.5 Hz).

HRMS (ESI+) calc'd for $C_{14}H_{15}FNO_2^+$ $[M\text{-}F]^+$: 248.1081, found 248.1079.



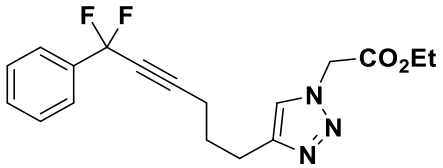
6,6-difluoro-6-phenyl-1-(piperidin-1-yl)hex-4-yn-1-one **(13a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (500 mg, 3.0 mmol, 1.0 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:CH_2Cl_2 1:9) to afford the title compound as a yellow oil (479 mg, 54% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.62 (m, 2H), 7.45–7.37 (m, 3H), 3.52 (d, *J* = 5.4 Hz, 2H), 3.34 (d, *J* = 5.4 Hz, 2H), 2.72–2.64 (m, 2H), 2.61–2.53 (m, 2H), 1.64–1.56 (m, 2H), 1.56–1.46 (m, 4H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -73.85 (t, *J* = 5.5 Hz, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 136.4 (t, *J* = 28.1 Hz), 130.6 (t, *J* = 1.9 Hz), 128.5, 125.4 (t, *J* = 4.6 Hz), 112.3 (t, *J* = 230.3 Hz), 90.1 (t, *J* = 5.9 Hz), 74.3 (t, *J* = 41.3 Hz), 46.4, 42.9, 31.4 (d, *J* = 1.7 Hz), 26.4, 25.5, 24.5, 14.7 (t, *J* = 2.2 Hz).

HRMS (ESI+) calc'd for $C_{17}H_{19}FNO^+$ $[M\text{-}F]^+$: 272.1445, found 272.1442.



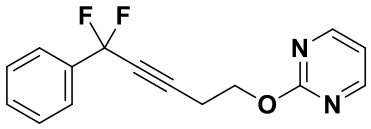
ethyl 2-(4-(6,6-difluoro-6-phenylhex-4-yn-1-yl)-1H-1,2,3-triazol-1-yl)acetate **(14a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (724 mg, 3.5 mmol, 1.16 equiv), the corresponding terminal alkyne (669 g, 3.0 mmol, 1.0 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 100 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:CH_2Cl_2 1:9) to afford the title compound as an orange oil (684 mg, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.45–7.37 (m, 4H), 5.08 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.38 (tt, *J* = 7.0, 4.9 Hz, 2H), 2.00–1.94 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.68–-73.74 (m, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 147.0, 136.4 (t, *J* = 28.1 Hz), 130.6, 128.5, 125.3 (t, *J* = 4.5 Hz), 122.5, 112.3 (t, *J* = 230.2 Hz), 90.3 (t, *J* = 5.8 Hz), 74.7 (t, *J* = 41.2 Hz), 62.3, 50.8, 27.2 (t, *J* = 2.1 Hz), 24.5, 17.9 (t, *J* = 2.2 Hz), 14.0.

HRMS (ESI+) calc'd for $C_{18}H_{20}F_2N_3O_2^+$ $[M+H]^+$: 348.1518, found 348.1511.



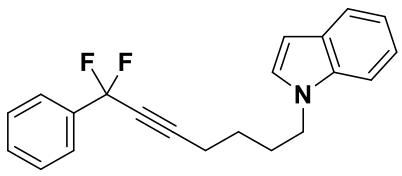
2-((5,5-difluoro-5-phenylpent-3-yn-1-yl)oxy)pyrimidine **(15a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (600 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:$CH_2Cl_2$1:30) to afford the title compound as a yellow oil (704 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 7.71–7.62 (m, 2H), 7.45–7.37 (m, 3H), 6.91 (t, *J* = 4.8 Hz, 1H), 4.52 (t, *J* = 7.0 Hz, 2H), 2.87 (tt, *J* = 7.0, 4.8 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -74.39 (t, *J* = 4.5 Hz, 2F)

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 159.4, 136.2 (t, *J* = 28.1 Hz), 130.6, 128.5, 125.4 (t, *J* = 4.5 Hz), 115.4, 112.2 (t, *J* = 230.7 Hz), 86.7 (t, *J* = 5.9 Hz), 75.5 (t, *J* = 41.5 Hz), 64.2 (t, *J* = 2.3 Hz), 19.3 (d, *J* = 2.2 Hz).

HRMS (ESI+) calc'd for $C_{15}H_{12}F_2N_2NaO^+$ $[M+H]^+$: 297.0810, found 297.0808.



1-(7,7-difluoro-7-phenylhept-5-yn-1-yl)-1H-indole **(16a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (650 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After

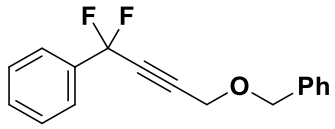
being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:10) to afford the title compound as a yellow oil (646 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77–7.73 (m, 3H), 7.57–7.48 (m, 3H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 4.18 (t, *J* = 7.0 Hz, 2H), 2.42–2.34 (m, 2H), 2.06–1.98 (m, 2H), 1.67–1.60 (m, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.73 (d, *J* = 5.3 Hz, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5 (t, *J* = 28.2 Hz), 136.0, 130.7, 128.7, 128.6, 127.7, 125.4 (t, *J* = 4.6 Hz), 121.6, 121.1, 119.4, 112.4 (t, *J* = 230.3 Hz), 109.4, 101.3, 90.2 (t, *J* = 6.0 Hz), 74.9 (t, *J* = 41.3 Hz), 45.8, 29.3, 25.1, 18.3.

HRMS (ESI+) calc'd for $C_{21}H_{19}F_2N^+$ $[M+Na]^+$: 346.1378, found 346.1378.



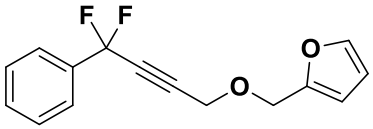
(4-(benzyloxy)-1,1-difluorobut-2-yn-1-yl)benzene **(17a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (587 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a light yellow oil (592 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.55–7.48 (m, 3H), 7.44–7.35 (m, 5H), 4.67 (s, 2H), 4.35 (t, *J* = 4.2 Hz, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.69 (s, 2F)

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 136.0 (t, *J* = 27.7 Hz), 130.9, 128.7, 128.6, 128.6, 128.2, 128.2, 112.16 (t, *J* = 231.8 Hz), 85.6 (t, *J* = 5.9 Hz), 79.8 (t, *J* = 42.0 Hz), 72.2, 56.9 (t, *J* = 2.2 Hz).

HRMS (ESI+) calc'd for $C_{17}H_{14}F_2NaO^+$ $[M+H]^+$: 295.0905, found 295.0902.



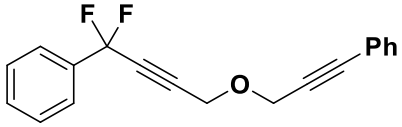
2-(((4,4-difluoro-4-phenylbut-2-yn-1-yl)oxy)methyl)furan **(18a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (531 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 24 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:18) to afford the title compound as a light yellow oil (350 mg, 44% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.50–7.45 (m, 3H), 7.44 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.39 (d, *J* = 3.3 Hz, 1H), 6.37 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.58 (s, 2H), 4.30 (t, *J* = 4.2 Hz, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.78 (s, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 143.4, 135.9 (t, *J* = 27.7 Hz), 130.9 (t, *J* = 1.7 Hz), 128.7, 125.4 (t, *J* = 4.7 Hz), 112.1 (t, *J* = 231.9 Hz), 110.6, 110.5, 85.2 (t, *J* = 5.9 Hz), 79.9 (t, *J* = 42.2 Hz), 63.6, 56.5.

HRMS (ESI+) calc'd for $C_{15}H_{12}F_2NaO_2^+$ $[M+H]^+$: 285.0698, found 285.0693.



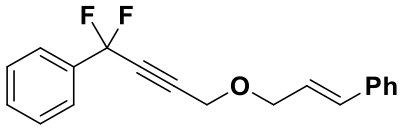
(1,1-difluoro-4-((3-phenylprop-2-yn-1-yl)oxy)but-2-yn-1-yl)benzene **(19a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (700 mg, 3.3 mmol, 1.1 equiv), the corresponding terminal alkyne (510 mg, 3.0 mmol, 1.0 equiv), and MeCN (30 mL) were used. After 24 h at 24 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a light yellow oil (639 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.51–7.44 (m, 5H), 7.37–7.32 (m, 3H), 4.52 (s, 2H), 4.49 (t, *J* = 4.2 Hz, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.78–-75.92 (m, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.8 (t, *J* = 27.6 Hz), 131.9, 130.9, 128.8, 128.7, 128.5, 125.4 (t, *J* = 4.7 Hz), 122.3, 112.1 (t, *J* = 231.9 Hz), 87.5, 84.9 (t, *J* = 5.9 Hz), 83.7, 80.0 (t, *J* = 42.1 Hz), 58.0, 56.3.

HRMS (ESI+) calc'd for $C_{19}H_{14}F_2NaO^+$ $[M+H]^+$: 319.0905, found 319.0899.



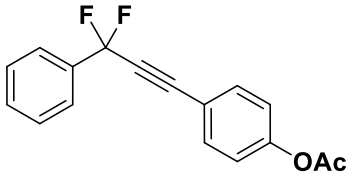
(4-(cinnamyloxy)-1,1-difluorobut-2-yn-1-yl)benzene **(20a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (700 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (570 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) were used. After 24 h at 24 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (CH_2Cl_2:hexanes 2:1) to afford the title compound as a light yellow oil (533 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.6 Hz, 2H), 7.53–7.46 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.39–7.34 (m, 2H), 7.33–7.29 (m, 1H), 6.68 (dd, *J* = 16.0, 6.2 Hz, 1H), 6.37–6.25 (m, 1H), 4.36 (q, *J* = 3.9 Hz, 2H), 4.31–4.26 (m, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.71 (d, *J* = 39.8 Hz, 2F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 136.3–135.4 (m), 133.9, 130.9 (d, *J* = 2.0 Hz), 128.7, 128.7, 128.0, 126.7, 125.4 (t, *J* = 4.7 Hz), 124.6, 112.1 (t, *J* = 231.7 Hz), 85.7–85.5 (m), 79.6 (t, *J* = 42.0 Hz), 70.8 (d, *J* = 2.2 Hz), 56.8 (d, *J* = 2.1 Hz).

HRMS (ESI+) calc'd for $C_{19}H_{16}F_2NaO^+$ $[M+H]^+$: 321.1061, found 321.1066.



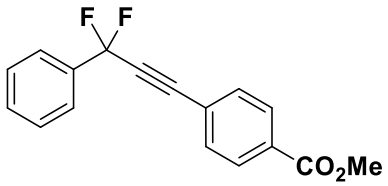
4-(3,3-difluoro-3-phenylprop-1-yn-1-yl)phenyl acetate **(21a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (724 mg, 3.5 mmol, 1.09 equiv), the corresponding terminal alkyne (570 mg, 3.2 mmol, 1.0 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15 to 1:9) to afford the title compound as a light yellow oil (400 mg, 46% yield).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.55–7.49 (m, 3H), 7.17–7.13 (m, 2H), 2.29 (s, 3H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -74.87 (s, 2F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 169.4, 152.7, 136.6 (t, *J* = 28.0 Hz), 134.0, 131.5, 129.3, 125.9, 122.8, 118.0 (t, *J* = 2.7 Hz), 113.5 (t, *J* = 230.8 Hz), 88.7 (t, *J* = 6.0 Hz), 82.3 (t, *J* = 41.8 Hz), 21.4.

HRMS (ESI+) calc'd for $C_{17}H_{12}F_2NaO_2^+$ $[M+H]^+$: 309.0698, found 309.0694.



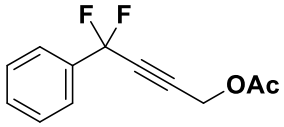
methyl 4-(3,3-difluoro-3-phenylprop-1-yn-1-yl)benzoate **(22a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (653 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (561 mg, 3.5 mmol, 1.17 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with Et_2O (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a light yellow oil (450 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.78–7.74 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.50–7.46 (m, 3H), 3.92 (s, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -75.58 (s, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 136.0 (t, *J* = 27.9 Hz), 132.2, 131.3, 130.9, 129.6, 128.7, 125.4 (t, *J* = 4.6 Hz), 124.6 (t, *J* = 2.4 Hz), 112.6 (t, *J* = 231.9 Hz), 87.6 (t, *J* = 6.0 Hz), 84.3 (t, *J* = 42.3 Hz), 52.4.

HRMS (ESI+) calc'd for $C_{17}H_{12}F_2NaO_2^+$ $[M+H]^+$: 309.0698, found 309.0692.



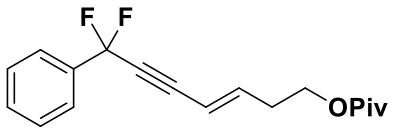
4,4-difluoro-4-phenylbut-2-yn-1-yl acetate **(23a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (390 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:6) to afford the title compound as a light yellow oil (604 mg, 90% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2H), 7.50–7.42 (m, 3H), 4.80 (t, *J* = 4.2 Hz, 2H), 2.10 (s, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -76.35 (d, *J* = 4.6 Hz).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 135.6 (t, *J* = 27.6 Hz), 131.0 (t, *J* = 1.9 Hz), 128.7, 125.39 (t, *J* = 4.7 Hz), 112.0 (t, *J* = 232.2 Hz), 83.4 (t, *J* = 5.8 Hz), 79.4 (t, *J* = 42.3 Hz), 51.4 (t, *J* = 2.1 Hz), 20.5.

HRMS (ESI+) calc'd for $C_{12}H_{10}F_2NaO_2^+$ $[M+Na]^+$: 247.0541, found 247.0543.



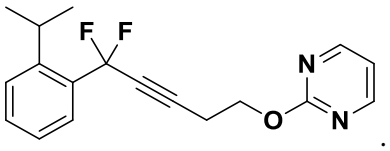
(*E*)-7,7-difluoro-7-phenylhept-3-en-5-yn-1-yl pivalate **(24a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (700 mg, 3.2 mmol, 1.1 equiv), the corresponding terminal alkyne (541 mg, 3.0 mmol, 1.0 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:25 to1:16) to afford the title compound as a light yellow oil (400 mg, 43% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 7.4 Hz, 2H), 7.52–7.45 (m, 3H), 6.40 (dt, *J* = 16.0, 7.0 Hz, 1H), 5.74–5.67 (m, 1H), 4.13 (t, *J* = 6.3 Hz, 2H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.20 (s, 9H).

^{19}F NMR (470 MHz, CD_2Cl_2)

^{13}C NMR (126 MHz, CD_2Cl_2) δ 178.6, 145.7 (t, *J* = 3.4 Hz), 136.7 (t, *J* = 28.2 Hz), 131.5–131.3 (m), 129.2, 125.9 (t, *J* = 4.5 Hz), 113.4 (t, *J* = 230.3 Hz), 109.9 (t, *J* = 3.3 Hz), 88.0 (t, *J* = 6.3 Hz), 81.2 (t, *J* = 41.5 Hz), 62.8, 39.2, 33.2, 27.5.

HRMS (ESI+) calc'd for $C_{18}H_{20}F_2NaO_2^+$ $[M+Na]^+$: 329.1324, found 329.1326



2-((5,5-difluoro-5-(2-isopropylphenyl)pent-3-yn-1-yl)oxy)pyrimidine **(25a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), **6Br** (750 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (540 mg, 3.6 mmol, 1.2 equiv), and MeCN (30 mL) were used. After 24 h at 30 °C, the reaction was filtered over a pad of silica, rinsed with EtOAc (3 x 80 mL), and concentrated. After being dry loaded onto celite, the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:4 to 1:3) to afford the title compound as a light yellow oil (425 mg, 45% yield).

^{1}H NMR (600 MHz, $CDCl_3$)δ 8.48 (d, J = 4.8, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.42–7.38 (m, 2H), 7.21–7.18 (m, 1H), 6.92 (t, *J* = 4.8 Hz, 1H), 4.50 (t, *J* = 7.1 Hz, 2H), 3.60 (p, *J* = 6.8 Hz, 1H), 2.85 (tt, *J* = 7.1, 4.7 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 6H).

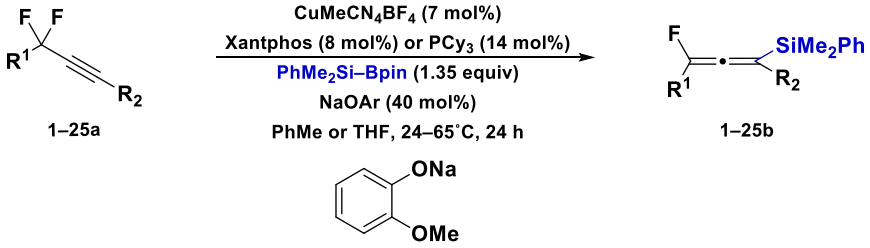
^{19}F NMR (565 MHz, $CDCl_3$) δ -74.85 (t, *J* = 5.2 Hz, 2F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.7, 159.4, 147.9, 133.0 (t, *J* = 26.1 Hz), 130.8, 127.3, 125.5, 125.0 (t, *J* = 7.9 Hz), 115.4, 112.1 (t, *J* = 232.7 Hz), 86.1 (t, *J* = 6.0 Hz), 76.4 (t, *J* = 41.5 Hz), 64.3, 29.2 (d, *J* = 2.1 Hz), 24.2, 19.3.

HRMS (ESI+) calc'd for $C_{18}H_{18}F_2N_2NaO^+$ $[M+Na]^+$: 339.1279, found 339.1274.

2.5.5 General Procedure for Alkyne Silylation

Notes: All reactions were setup and conducted in the absence of light. For the racemic transformation, two initial experiments were performed for each substrate at 35 °C (with either Xantphos or PCy_3 as the ligand with PhMe as the solvent). Depending on the yield and selectivity the, most substrates gave the desired, racemic allene in greater than 85% yield (some adjustments to the temperature (21–65 °C) had to be made depending on the functional groups present). The conditions with Xantphos at 35 °C were the most general. In cases where reactions with Xantphos as the ligand failed, switching to PCy_3 and using THF as the solvent was often a solution.



For HPLC traces:

In a nitrogen filled glovebox, a stir bar, $Cu(MeCN)_4BF_4$ (2.2 mg, 7 mol%), ligand (Xantphos 4.8 mg, 8 mol% or PCy_3 2.2 mg, 14 mol%) were charged to a 1-dram vial. Solvent (1.5 mL [0.067 M] of either PhMe or THF) was added by a plastic syringe (stored in an 80 °C oven and cooled under vacuum) and the mixture was stirred at ambient temperature for 35–45 minutes before the addition of the sodium phenoxide (6 mg, 40 mol%). The mixture was stirred for an additional 5 minutes before the sequential addition of $PhMe_2SiBpin$ (37 μL, 0.135 mmol, 1.35 equiv) and difluoroalkyne (0.1 mmol, 1.0 equiv). The vial was sealed with a ptfe-lined, thermal-rated cap, secured with electrical tape, removed from the glovebox, and placed in a preheated, heating block set at 700 rpm. After 24 h, the reaction was removed to ambient temperature, diluted with EtOAc (500 μL) and PhF (9.5 μL, 0.1 mmol, 1.0 equiv) was added. The contents were thoroughly mixed and an ^{19}F NMR was acquired. The reaction was then filtered over a glass pipette packed with silica, the plug was rinsed with EtOAc, the solution concentrated, and subsequently purified by preparative TLC.

Large Scale:

Note: Upon scaling up the reaction with sodium phenoxides bases there was no drop in yield due to the heterogenous nature of the reaction. The NH_4OH buffer (pH ca 10) used throughout this publication was prepared from 90g NH_4Cl, 500 mL dH_2O, and 375 mL concentrated (28–30%) NH_4OH. This quench

ensures that most of the residual $PhMe_2SiBpin$ is consumed, permitting easier product separation. For the enantioselective variant, this quench was found to be critical to prevent product racemization that could occur after the reaction. Other methods of quenching were not as efficient in consuming unreacted $PhMe_2SiBpin$ or removing copper species and preventing degradation of the enantiopurity of the allene products.

For $PhMe_2SiBpin$:

In a nitrogen filled glovebox, an oven-dried 250 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with $Cu(MeCN)_4BF_4$ (136 mg, 7 mol%) and Xantphos (286 mg, 8 mol%). PhMe (60 mL, [0.1 M]) was added and the mixture was stirred at ambient temperature for 45–60 minutes before the addition of the sodium phenoxide (350 mg, 40 mol%). The mixture was stirred for an additional 3–5 minutes before the sequential addition of $PhMe_2SiBpin$ (2.1 g, 8.1 mmol, 1.35 equiv) and difluoroalkyne **1a** (1.77 g, 6.0 mmol, 1.0 equiv). The round bottom was sealed with a rubber septum, removed from the glovebox, placed under a flow of N_2 gas, and placed in an oil bath set at 35 °C (the stir rate was set at the maximum speed allowed that did not invoke splattering of reaction mixture onto the upper walls of the flask). After 24 h, the reaction was allowed to cool to ambient temperature and quenched with an NH_4OH buffer (100 mL). The biphasic mixture was vigorously stirred for 10–15 minutes before being diluted with EtOAc (50 mL). The contents were transferred to a separatory funnel with EtOAc and an additional 75 mL of NH_4OH buffer and 200 mL of EtOAc were added. After the contents were vigorously shaken, the aqueous layer was disposed. The organic layer was washed with dH_2O (200 mL), brine (200 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue loaded on celite and purified by column chromatography on SiO_2 (hexanes with 6% EtOAc) to afford racemic **1b** as a colorless oil (2.36 g, 96% yield).

For $BnMe_2SiBpin$:

In a nitrogen filled glovebox, an oven-dried 250 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with $Cu(MeCN)_4BF_4$ (68 mg, 7 mol%) and Xantphos (143 mg, 8 mol%). PhMe (45 mL, [0.067 M]) was added and the mixture was stirred at ambient temperature for 45–60 minutes before the addition of the sodium phenoxide (175 mg, 40 mol%). The mixture was stirred for an additional 3–5 minutes before the sequential addition of $BnMe_2SiBpin$ (1.11 g, 4.05 mmol, 1.35 equiv) and difluoroalkyne **1a** (883 mg, 3.0 mmol, 1.0 equiv). The round bottom was sealed with a rubber septum, removed from the glovebox, placed under a flow of N_2 gas, and placed in an oil bath set at 45 °C (the stir rate was set at the maximum speed allowed that did not invoke splattering of reaction mixture onto the upper walls of the flask). After 24 h, the reaction was allowed to cool to ambient temperature and quenched with an NH_4OH buffer (100 mL). The biphasic mixture was vigorously stirred for 10–15 minutes before being diluted with EtOAc (50 mL). The contents were transferred to a separatory funnel with EtOAc and an additional 75 mL of NH_4OH buffer and 200 mL of EtOAc were added. After the contents were vigorously shaken, the aqueous layer was disposed. The organic layer was washed with dH_2O (200 mL), brine (200 mL), dried over Na_2SO_4,

filtered, and concentrated. The crude residue loaded on celite and purified by column chromatography on SiO_2 (EtOAc:hexanes 1:25 to1:17) to afford racemic **1b-$SiMe_2Cy$** as a colorless oil (1.23 g, 97% yield).

For $Et_3SiBpin$:

In a nitrogen filled glovebox, an oven-dried 250 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with $Cu(MeCN)_4BF_4$ (79 mg, 7 mol%) and PhMe (52 mL, [0.067 M]). PPh_2Me (100 mg, 14 mol%) was added dropwise and the mixture was stirred at ambient temperature for 45–60 minutes before the addition of the sodium phenoxide (201 mg, 40 mol%). The mixture was stirred for an additional 3–5 minutes before the sequential addition of $Et_3SiBpin$ (1.15 g, 4.05 mmol, 1.35 equiv) and difluoroalkyne **1a** (1.03 g, 3.5 mmol, 1.0 equiv). The round bottom was sealed with a rubber septum, removed from the glovebox, placed under a flow of N_2 gas, and placed in an oil bath set at 45 °C (the stir rate was set at the maximum speed allowed that did not invoke splattering of reaction mixture onto the upper walls of the flask). After 25 h, the reaction was allowed to cool to ambient temperature and quenched with an NH_4OH buffer (100 mL). The biphasic mixture was vigorously stirred for 10–15 minutes before being diluted with EtOAc (50 mL). The contents were transferred to a separatory funnel with EtOAc and an additional 75 mL of NH_4OH buffer and 200 mL of EtOAc were added. After the contents were vigorously shaken, the aqueous layer was disposed. The organic layer was washed with dH_2O (200 mL), brine (200 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue loaded on celite and purified by column chromatography on SiO_2 (Et_2O:hexanes 1:25 to1:17) to afford racemic **1b-$SiEt_3$** as a colorless oil (1.36 g, 99% yield). Note: For other bulky silylboranes ($CyMe_2SiBpin$), PPh_2Me was also the preferred ligand. These conditions minimized the formation of the undesired difluoroallylic vinylsilane.

2.5.6 Enantioselective Silylation Procedure

Notes: CsF (99%) was dried under high vacuum with P_2O_5 at 180 °C for 5 days before being brought into a glovebox (<0.1 ppm of H_2O and O_2) and grounded into a fine powder with a mortar and pestle. If the CsF is not properly dried, then the reaction becomes irreproducible. Upon scaling up the reaction, CsF-CaF_2 (25% CsF) was prepared in an effort to increase the surface area of the fluoride source, which provided effective. **After isolation** the enantioenriched allenes were **stored neat in a freezer at -20 °C**, where they were stable toward racemization for at least 2 months (was not monitored for long periods of time). Depending on the electronics of the allene (neutral allenes appeared less prone toward racemizing), racemization at room temperature was observed over the course of several weeks to 1-2 months if stored neat in air (enantiomeric purity could drop by up to 5% within this period). Racemization was significantly slower when stored in solution (even at room temperature).

CsF(25%)-CaF_2 preparation:

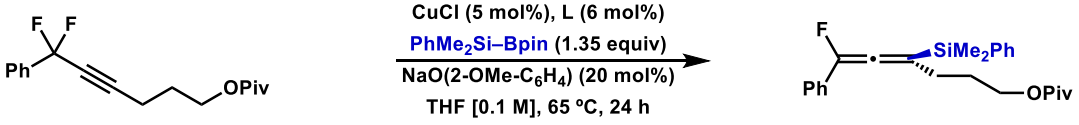
In air, CsF (99% from ChemImpex, dried at 180 °C for 5 days) (18.23 g, 120 mmol, 1 equiv), CaF_2 (99%) (28.1 g, 360 mmol, 4 equiv), and MeOH (new bottle from Sigma-Aldrich of optima filtered <0.07% H_2O) (400 mL) were added to a 1000 mL round bottom flask. The flask was sonicated for 5 minutes before

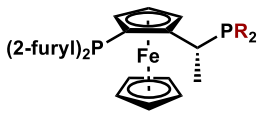
the MeOH was slowly removed on a rotovap (ca 60-100 torr) at 35 °C. After 45 minutes the temperature was increased to 80 °C, which was maintained for 75 minutes. The clumpy powder was ground into a fine powder with a mortar and pestle and dried under high vacuum with P_2O_5 at 110 °C for 48 h. Afterwards, CsF-CaF_2 was transferred into a nitrogen filled glovebox and grounded into a fine powder with a mortar and pestle. Molecular weight used for stoichiometry: 386.11.

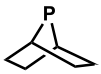
For Screening:

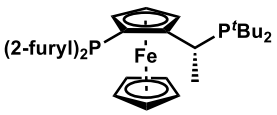
In a nitrogen filled glovebox, a stir bar, CuX (x mol%), ligand (x +1 mol%) were charged to a 1-dram vial. Solvent (500 μL) was added and the mixture was stirred at ambient temperature for 45–60 minutes. (If the ligand was an oil, then a 0.06 M solution was prepared and x + 1 mol% was added dropwise to a stirring solution (400 μL) of the copper salt.) Additional solvent (1 mL) was added and the solution was stirred for 60 seconds before the sequential addition of CsF , $PhMe_2SiBpin$, and difluoroalkyne (0.1 mmol, 1.0 equiv). The vial was sealed with a ptfe-lined, thermal-rated cap, secured with electrical tape, removed from the glovebox, and placed in a preheated, heating block set at 1000 rpm (or 10/10 stir setting on an ika stir plate). After 24 h, the reaction was removed to ambient temperature, diluted with EtOAc (500 μL) and PhF (9.5 μL, 0.1 mmol, 1.0 equiv) and the NH_4OH (1 mL) were added. The contents were vigorously stirred for 4 minutes and the layers were allowed to separate. An ^{19}F NMR was acquired. The organics were combined, washed with brine (2 mL), concentrated, purified by preparative TLC, and the enantiomeric excess was determined by a chiral HPLC.

Table S1 Alkyl, Aryl Josiphos Ligands Examined



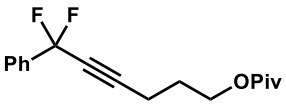


R	^{19}F NMR yield (SM %)	*ee* %
^{t}Bu	31% (63)	42
L0	27% (23)	-4
^{c}heptyl	9% (61)	5.5
Cy	68% (61)	33
^{c}pentyl	42% (<2)	44
^{i}butyl	41% (<1)	57
Bn	42% (<1)	60
	42% (<1)	70

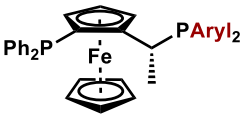


L0

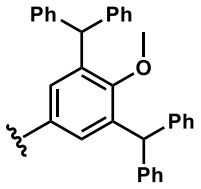
Table S2 Aryl, Aryl Josiphos Ligands Examined



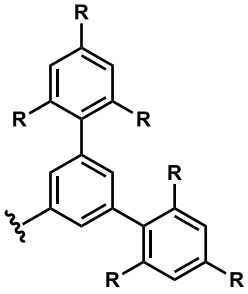
CuCl (5 mol%), L (6 mol%)
$PhMe_2Si–Bpin$ (1.35 equiv)
$NaO(2\text{-}OMe\text{-}C_6H_4)$ (20 mol%)
THF [0.1 M], 65 °C, 24 h



Aryl	^{19}F NMR yield (SM %)	*ee* %
3,5-Me	59% (23)	45
3,5-Me 4-OMe	31% (14)	44
3,5-^{t}Bu 4-OMe	41% (<1)	70
3,5-diBn 4-OMe	45% (33)	72
3,5-Ph 4-OMe	34% (3)	52
3,5-Mes	58% (38)	75
3,5-Trip	50% (32)	76
3,5-TTB	3% (79)	nd
3,5-TMS	73% (<1)	75
3,5-TES	66% (<1)	83
3,5-TBS 4-OMe	53% (43)	55
3,5-CF_3	43% (<2)	71
3,5-^{i}Pr$^{(F7)}$	44% (43)	86

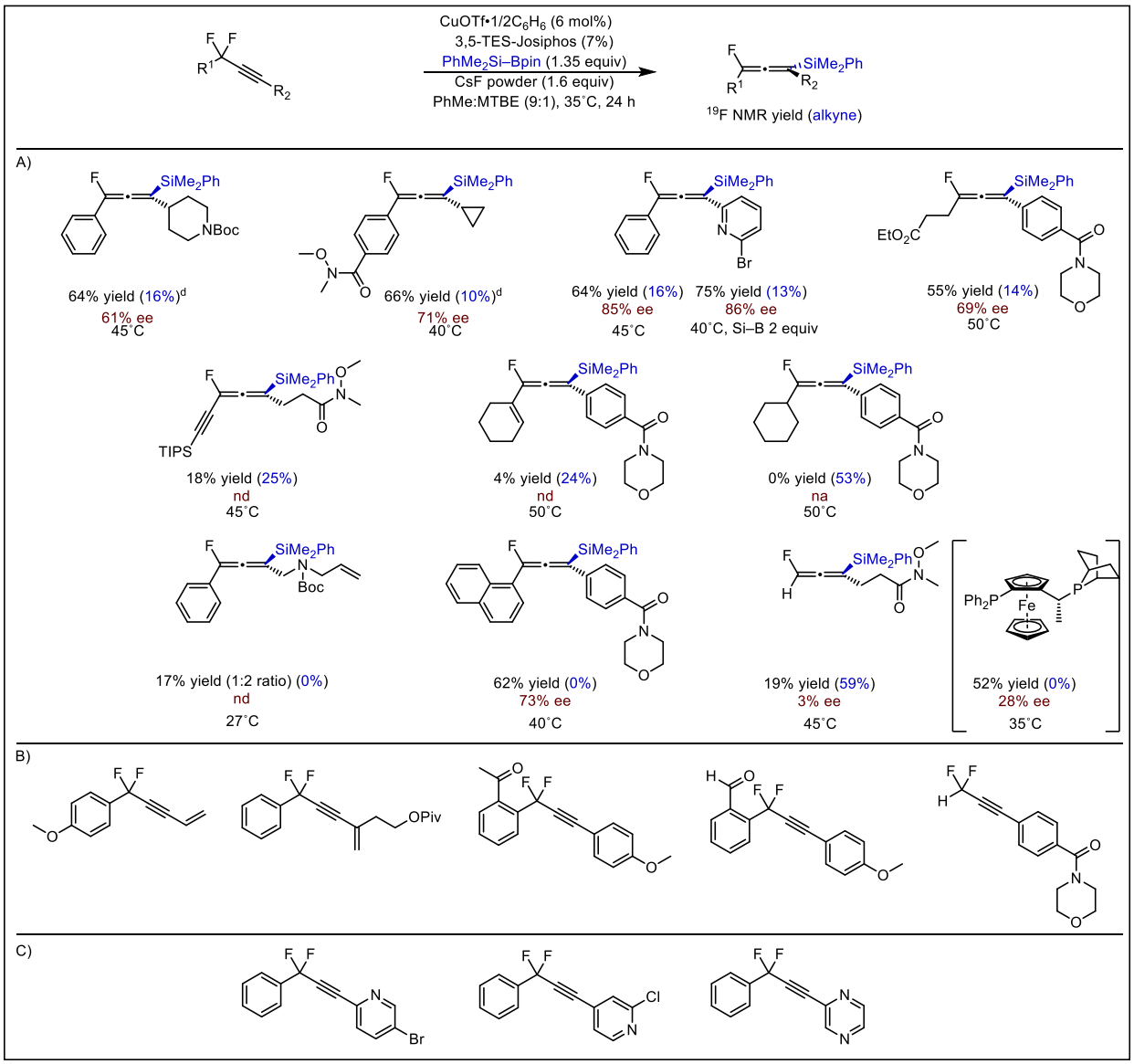


3,5-diBn 4-OMe



Mes = R = Me
Trip = R = ^{i}Pr
TTB = R = ^{t}Bu

Table SL Limitations of Defluorosilylation



[A]Limitations for copper-catalyzed defluorosilylation

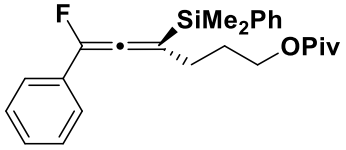
[B]Silyl allene product either not detected or <5% yield that could not be separated from byproducts under racemic conditions.

[C]Could not resolve the enantiomers by chiral HPLC analysis

For isolation–General Procedure D:

In a nitrogen filled glovebox, a stir bar, CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), and PhMe (800 μL) were charged to a 2-dram vial. (*R,S*)-3,5- TES-JosiPhos (240 μL, 0.06 M in PhMe, 7 mol%) was added dropwise to the stirring solution of copper. After 60 minutes, PhMe (1.7 mL) and MTBE (300 μL) were added. After an additional 60 seconds of stirring, CsF (49 mg, 0.32 mmol, 1.6 equiv), $PhMe_2SiBpin$ (71 mg, 0.27 mmol, 1.35 equiv), and difluoroalkyne (0.2 mmol, 1.0 equiv) were added in sequence. The vial was sealed with a ptfe-lined, thermal-rated cap, secured with electrical tape, removed from the glovebox, and placed in a preheated,

ika heating block set at 10/10 stir setting. After 24 h, the reaction was removed to ambient temperature. PhF (19 μL, 0.2 mmol, 1.0 equiv), EtOAc (1 mL), and NH_4OH buffer (2 mL) were added and vigorously stirred for 4–5 minutes. After an ^{19}F NMR was acquired, the reaction was transferred to a 60 mL separatory funnel with EtOAc (25–30 mL total) and NH_4OH buffer (20 mL) was added. The layers were shaken and the aqueous phase disposed. The organic layer was washed with dH_2O (20 mL), Brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on SiO_2 to afford **1–25b**.



4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl pivalate **(1b):** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **1a** (54 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20 to1:17) to afford the title compound as a light yellow oil (75 mg, 91% yield, 90% *ee*).

Large scale synthesis of **1b** (repeated twice, 2 months apart):

In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (91.0 mg, 6 mol%), and PhMe (29 mL) were charged to a 250 mL Schlenk round bottom flask. (*R,S*)-3,5- TES-Josiphos (1.47 mL, 0.285 M in PhMe, 7 mol%) was added dropwise to the stirring solution of copper. After 60 minutes, PhMe (50 mL) and MTBE (9.0 mL) were added. After an additional 2 minutes of stirring, CsF(25%)-CaF_2 (3.71 g, 9.6 mmol, 1.6 equiv of CsF), $PhMe_2SiBpin$ (2.12g, 8.1 mmol, 1.35 equiv), and **1a** (1.77g, 6.0 mmol, 1.0 equiv) were added in sequence. While being stirred, the round bottom was sealed with a septum, secured with electrical tape, removed from the glovebox, placed under a flow of N_2, and placed in a preheated oil bath set at 33 °C. After 30 h, the reaction was removed to ambient temperature. PhF (560 μL, 6.0 mmol, 1.0 equiv), NH_4OH buffer (100 mL), and EtOAc (50 mL) were added and vigorously stirred for 8–10 minutes under N_2. After an ^{19}F NMR was acquired, the reaction was filtered over a pad of celite, rinsed with EtOAc (3 x 125 mL), and the filtrate was transferred to a separatory funnel with EtOAc and NH_4OH buffer (100 mL) was added. The layers were shaken and the aqueous phase disposed. The organic layer was washed with dH_2O (300 mL), Brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was loaded on celite and purified by column chromatography on SiO_2 (Et_2O:hexanes 1:20 to1:15) to afford the title compound as a light yellow oil (1st run: 2.38 g, 96% yield, 89% *ee*; 2nd run: 2.43 g, 98% yield, 88% *ee*).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.65–7.62 (m, 2H), 7.47–7.41 (m, 5H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 4.06 (td, *J* = 6.3, 2.2 Hz, 2H), 2.40 (ddd, *J* = 15.3, 9.0, 6.5 Hz, 2H), 1.95–1.81 (m, 2H), 1.19 (s, 9H), 0.53 (d, *J* = 5.0 Hz, 6H).

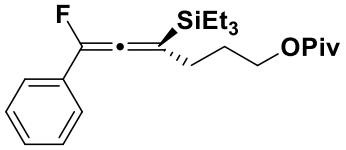
^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.26 (t, *J* = 9.3 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.2 (d, *J* = 27.5 Hz), 178.7, 143.3 (d, *J* = 224.6 Hz), 136.9, 134.4, 132.7 (d, *J* = 32.5 Hz), 130.2, 129.1, 128.6, 128.0, 124.2 (d, *J* = 13.0 Hz), 123.8 (d, *J* = 3.8 Hz), 63.9, 39.2, 29.1, 28.3, 27.5, -2.9 (d, *J* = 6.8 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{31}FNaO_2Si^+$ $[M+Na]^+$: 433.1970, found 433.1971.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: 99.9:00.1 hexanes:iPrOH; 7.09 min (major) and 7.93 min (minor)

Note: For the trialkylsilylboranes the order of addition of the reagents (silylborane, alkyne, and then CsF(25%)-CaF_2) is important.



Large scale synthesis of **1b-SiEt$_3$**:

In a nitrogen filled glovebox, $(PPh_3)_3CuF{\cdot}2MeOH$ (224 mg, 8 mol%), (*R,S*)-3,5- Trip-Josiphos (376 mg, 9 mol%) and MTBE (45 mL) were charged to a 100 mL Schlenk round bottom flask. After 60 minutes, $Et_3SiBpin$ (981 mg, 4.05 mmol, 1.35 equiv), and **1a** (900 mg, 3.0 mmol, 1.0 equiv), and CsF(25%)-CaF_2 (2.9 g, 7.5 mmol, 2.5 equiv of CsF) were added in sequence. While being stirred, the round bottom was sealed with a septum, secured with electrical tape, removed from the glovebox, placed under a flow of N_2, and placed in a preheated oil bath set at 45 °C. After 30 h, the reaction was removed to ambient temperature. PhF (280 μL, 3.0 mmol, 1.0 equiv), NH_4OH buffer (100 mL), and EtOAc (50 mL) were added and vigorously stirred for 8–10 minutes under N_2. After an ^{19}F NMR was acquired, the reaction was filtered over a pad of celite, rinsed with EtOAc (3 x 125 mL), and the filtrate was transferred to a separatory funnel with EtOAc and NH_4OH buffer (100 mL) was added. The layers were shaken and the aqueous phase disposed. The organic layer was washed with dH_2O (300 mL), Brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:20 to1:17) to afford the title compound as a colorless oil (1.08 g, 93% yield, 94% *ee*).

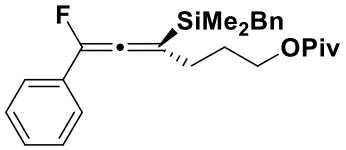
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38–7.32 (m, 4H), 7.26–7.22 (m, 1H), 4.08 (td, *J* = 6.2, 1.9 Hz, 2H), 2.43–2.34 (m, 2H), 1.98–1.80 (m, 2H), 1.18 (s, 9H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.71 (qd, *J* = 7.9, 3.3 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -159.81 (t, *J* = 9.4 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 195.5 (d, *J* = 27.0 Hz), 178.7, 142.8 (d, *J* = 223.6 Hz), 132.9 (d, *J* = 32.7 Hz), 129.0 (d, *J* = 1.8 Hz), 127.8, 123.7 (d, *J* = 3.7 Hz), 122.9 (d, *J* = 13.3 Hz), 64.0, 39.2, 29.2, 28.3, 27.5, 7.6, 3.6.

HRMS (ESI+) calc'd for $C_{23}H_{35}FNaO_2Si^+$ $[M+Na]^+$: 413.2283, found 413.2280.

Determination of enantiomeric ratio by HPLC analysis: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 6.91 min (major) and 6.30 min (minor)



Large scale synthesis of **1b-SiMe$_2$Bn**:

In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (61 mg, 8 mol%) and MTBE (40 mL) were charged to a 100 mL Schlenk round bottom flask. (*R,S*)-3,5-Trip-Josiphos (1.35 mL, 0.2 M in MTBE, 9 mol%) was added dropwise to the stirring solution of copper. After 60 minutes, **1a** (900 mg, 3.0 mmol, 1.0 equiv) and $BnMe_2SiBpin$ (1.2 g, 4.35 mmol, 1.45 eq) were added to the stirring solution. Once $BnMe_2SiBpin$ had dissolved, CsF(25%)-CaF_2 (2.08 g, 5.4 mmol, 1.8 equiv of CsF) was added. While being stirred, the round bottom was sealed with a septum, secured with electrical tape, removed from the glovebox, placed under a flow of N_2, and placed in a preheated oil bath set at 28 °C. After 48 h, the reaction was removed to ambient temperature. PhF (280 μL, 3.0 mmol, 1.0 equiv), NH_4OH buffer (100 mL), and EtOAc (50 mL) were added and vigorously stirred for 8–10 minutes under N_2. After an ^{19}F NMR was acquired, the reaction was filtered over a pad of celite, rinsed with EtOAc (3 x 125 mL), and the filtrate was transferred to a separatory funnel with EtOAc and NH_4OH buffer (100 mL) was added. The layers were shaken and the aqueous phase disposed. The organic layer was washed with dH_2O (300 mL), Brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:20 to1:17) to afford the title compound as a colorless oil (1.16 g, 91% yield, 89% *ee*).

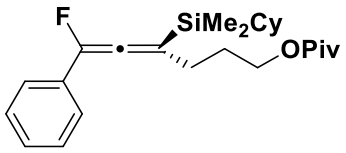
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.6, 6.7 Hz, 3H), 7.23–7.18 (m, 2H), 7.16–7.12 (m, 1H), 7.07 (d, *J* = 6.8 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 2.42–2.36 (m, 2H), 2.31 (q, *J* = 13.8 Hz, 2H), 1.97–1.79 (m, 2H), 1.21 (s, 9H), 0.19 (d, *J* = 18.4 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -159.52 (t, *J* = 9.5 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 195.8 (d, *J* = 27.3 Hz), 178.7, 143.2 (d, *J* = 224.5 Hz), 139.5, 132.6 (d, *J* = 32.6 Hz), 129.1, 129.1, 129.0, 128.8, 127.9, 125.0, 123.9 (d, *J* = 13.0 Hz), 123.7 (d, *J* = 3.6 Hz), 64.0, 39.2, 29.0, 28.3, 27.6, 25.6, -3.1, -3.6.

HRMS (ESI+) calc'd for $C_{26}H_{33}FNaO_2Si^+$ $[M+Na]^+$: 447.2126, found 447.2119.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 19.77 min (major) and 22.96 min (minor)



Large scale synthesis of **1b-SiMe$_2$Cy**:

In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (57 mg, 9 mol%) and MTBE (37 mL) were charged to a 100 mL Schlenk round bottom flask. (*R,S*)-3,5-Trip-Josiphos (1.25 mL, 0.2 M in MTBE, 10 mol%) was added dropwise to the stirring solution of copper. After 60 minutes, **1a** (750 mg, 2.5 mmol, 1.0 equiv) and $CyMe_2SiBpin$ (1.2 g, 4.35 mmol, 1.45 eq) were added to the stirring solution. After three minutes of stirring, CsF(25%)-CaF_2 (2.41 g, 6.25 mmol, 2.5 equiv of CsF) was added. While being stirred, the round bottom was sealed with a septum, secured with electrical tape, removed from the glovebox, placed under a flow of N_2, and placed in a preheated oil bath set at 39 °C. After 30 h, the reaction was removed to ambient temperature. PhF (235 μL, 2.5 mmol, 1.0 equiv), NH_4OH buffer (100 mL), and EtOAc (50 mL) were added and vigorously stirred for 8–10 minutes under N_2. After an ^{19}F NMR was acquired, the reaction was filtered over a pad of celite, rinsed with EtOAc (3 x 125 mL), and the filtrate was transferred to a separatory funnel with EtOAc and NH_4OH buffer (100 mL) was added. The layers were shaken and the aqueous phase disposed. The organic layer was washed with dH_2O (300 mL), Brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:17 to1:14) to afford the title compound as a colorless oil (1.02 g, 98% yield, 90% *ee*).

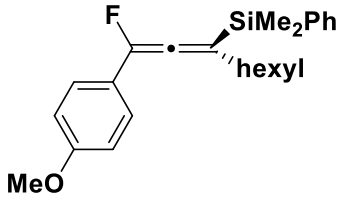
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40–7.32 (m, 4H), 7.27–7.22 (m, 1H), 4.09 (td, *J* = 6.3, 1.9 Hz, 2H), 2.43–2.35 (m, 2H), 1.97–1.82 (m, 2H), 1.77–1.69 (m, 5H), 1.26–1.21 (m, 5H), 1.20 (s, 9H), 0.82 (tt, *J* = 12.2, 2.8 Hz, 1H), 0.14 (d, *J* = 9.2 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -159.66 (t, *J* = 9.5 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 195.2 (d, *J* = 27.0 Hz), 178.7, 142.9 (d, *J* = 223.8 Hz), 132.9 (d, *J* = 32.7 Hz), 129.0 (d, *J* = 1.8 Hz), 127.8, 124.0 (d, *J* = 13.3 Hz), 123.7 (d, *J* = 3.6 Hz), 64.0, 39.2, 29.3, 28.6 (d, *J* = 2.3 Hz), 28.4, 28.0, 27.6, 27.4, 25.9, -5.0 (d, *J* = 2.7 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{37}FNaO_2Si^+$ $[M+Na]^+$: 439.2439, found 439.2440.

Determination of enantiomeric ratio by HPLC analysis: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 33.49 min (major) and 30.66 min (minor)



(1-fluoro-1-(4-methoxyphenyl)nona-1,2-dien-3-yl)dimethyl(phenyl)silane **(2b):** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **2a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 45 °C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:23) to afford the title compound as a light yellow oil (70 mg, 91% yield; 2% **2a** by ^{19}F NMR).

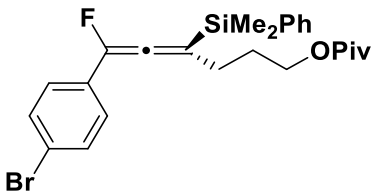
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.60–7.58 (m, 2H), 7.41–7.37 (m, 3H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.27 (qd, *J* = 8.9, 6.5 Hz, 2H), 1.57–1.43 (m, 2H), 1.33–1.19 (m, 7H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.47 (d, *J* = 6.0 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.77 (t, *J* = 9.2 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.4 (d, *J* = 27.6 Hz), 159.8, 143.2 (d, *J* = 223.0 Hz), 137.5, 134.5, 130.0, 128.5, 125.1 (d, *J* = 3.2 Hz), 114.6, 55.9, 33.0, 32.2, 29.5, 29.3, 29.3, 23.2, 14.4, -2.8 (d, *J* = 7.0 Hz).

HRMS (ESI+) calc'd for $C_{24}H_{31}FNaOSi^+$ $[M+Na]^+$: 405.2020, found 405.2017.

Determination of enantiomeric ratio by HPLC analysis: OJ column, 1.0 mL/min: hexanes; 7.97 min (major) and 7.30 min (minor)



6-(4-bromophenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate (**3b**)**:** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **3a** (75 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:23) to afford the title compound as a colorless oil (89 mg, 91% yield).

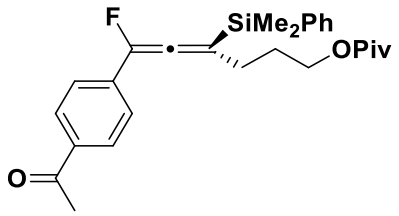
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.57 (d, *J* = 5.7 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42–7.37 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.01 (td, *J* = 6.2, 3.1 Hz, 1H), 2.40–2.31 (m, 2H), 1.90–1.74 (m, 2H), 1.14 (s, 9H), 0.48 (d, *J* = 4.4 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.06 (t, *J* = 9.2 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 195.0 (d, *J* = 27.0 Hz), 178.1, 141.9 (d, *J* = 224.8 Hz), 136.1, 133.8, 131.6, 131.3 (d, *J* = 33.3 Hz), 129.7, 128.0, 124.8 (d, *J* = 3.3 Hz), 124.3 (d, *J* = 12.8 Hz), 121.0, 63.2, 38.6, 28.4, 27.7, 26.9, -3.6 (d, *J* = 4.9 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{30}BrFNaO_2Si^+$ $[M+Na]^+$: 511.1075, found 511.1077.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 0.5 mL/min: hexanes:iPrOH 99.9:00.1; 11.80 min (major) and 11.14 min (minor)



6-(4-acetylphenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate (**4b**)**:** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **4a** (70 mg, 0.2 mmol, 1.0 equiv) were used at 34 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:7) to afford the title compound as a colorless oil (86 mg, 95% yield).

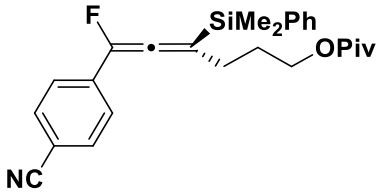
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 5.7 Hz, 2H), 7.43–7.35 (m, 5H), 4.01 (td, *J* = 6.3, 3.0 Hz, 2H), 2.58 (s, 3H), 2.41–2.33 (m, 2H), 1.91–1.76 (m, 2H), 1.13 (s, 9H), 0.49 (d, *J* = 4.8 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.06 (t, *J* = 9.1 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.6, 195.9 (d, *J* = 26.8 Hz), 178.7, 142.3 (d, *J* = 225.1 Hz), 137.4 (d, *J* = 32.2 Hz), 136.5, 136.5, 134.4, 130.3, 129.1, 128.6, 124.6 (d, *J* = 12.7 Hz), 123.7 (d, *J* = 3.3 Hz), 63.8, 39.1, 29.0, 28.3, 27.5, 27.0, -3.0 (d, *J* = 5.1 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{30}BrFNaO_2Si^+$ $[M+Na]^+$: 475.2075, found 475.2071.

Determination of enantiomeric ratio by HPLC analysis: IA column, 1.0 mL/min: hexanes:iPrOH 99:1; 9.84 min (major) and 9.14 min (minor)



6-(4-cyanophenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate **(5b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **5a** (68 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a colorless oil (74 mg, 84% yield).

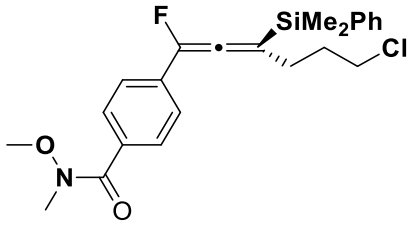
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.56–7.54 (m, 2H), 7.41–7.36 (m, 5H), 4.06–3.94 (m, 2H), 2.42–2.33 (m, 2H), 1.89–1.74 (m, 2H), 1.13 (s, 9H), 0.49 (d, *J* = 5.4 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.35 (t, *J* = 9.3 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 195.3 (d, *J* = 26.3 Hz), 178.6, 141.6 (d, *J* = 225.4 Hz), 137.5 (d, *J* = 32.7 Hz), 136.3, 134.3, 132.9, 130.4, 128.7, 125.3 (d, *J* = 12.5 Hz), 124.1 (d, *J* = 3.6 Hz), 119.4, 111.1, 63.7, 39.1, 29.0, 28.3, 27.5, -3.0 (d, *J* = 2.5 Hz).

HRMS (ESI+) calc'd for $C_{26}H_{30}FNNaO_2Si^+$ $[M+Na]^+$: 458.1922, found 458.1927.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 8.53 min (major) and 9.25 min (minor)



(R)-4-(6-chloro-3-(dimethyl(phenyl)silyl)-1-fluorohexa-1,2-dien-1-yl)-N-methoxy-N-methylbenzamide **(6b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240

μL, 0.06 M in PhMe, 6 mol%), and **6a** (63 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:3 to 1:2) to afford the title compound as a colorless oil (75 mg, 86% yield).

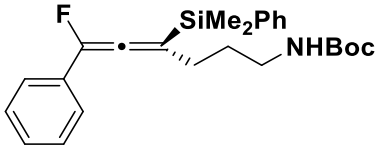
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.58 (s, 3H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.37 (s, 3H), 2.42 (q, *J* = 8.0 Hz, 2H), 2.03–1.88 (m, 2H), 0.48 (d, *J* = 4.8 Hz, 6H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -158.64 (t, *J* = 9.1 Hz, 1F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.6 (d, *J* = 27.1 Hz), 169.4, 142.1 (d, *J* = 226.1 Hz), 136.0, 134.5 (d, *J* = 32.5 Hz), 133.8, 132.9, 129.9, 128.8, 128.2, 123.4 (d, *J* = 12.5 Hz), 122.8 (d, *J* = 3.4 Hz), 61.2, 44.3, 33.8, 31.4, 29.2, -3.2 (d, *J* = 2.7 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{30}BrFNaO_2Si^+$ $[M+Na]^+$: 454.1376, found 454.1372.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 27.75 min (major) and 26.25 min (minor)



tert-butyl(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)carbamate (**7b**)**:** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **7a** (62 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:23) to afford the title compound as a yellow oil (77 mg, 88% yield).

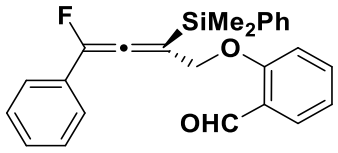
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.48–7.45 (m, 2H), 7.30–7.20 (m, H), 7.17–7.11 (m, 1H), 4.40 (s, 1H), 2.94 (q, *J* = 6.8 Hz, 2H), 2.20–2.13 (m, 2H), 1.60–1.47 (m, 2H), 1.28 (s, 9H), 0.36 (d, *J* = 6.2 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.37 (t, *J* = 9.3 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.1 (d, *J* = 27.2 Hz), 156.3, 143.2 (d, *J* = 224.4 Hz), 137.0, 134.4, 133.6, 132.7 (d, *J* = 32.4 Hz), 130.2, 129.1 (d, *J* = 1.7 Hz), 128.6, 127.9, 124.5 (d, *J* = 13.1 Hz), 123.7 (d, *J* = 3.6 Hz), 79.2, 40.5, 29.9, 29.8, 28.7, -2.9 (d, *J* = 8.7 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{32}FNNaO_2Si^+$ $[M+Na]^+$: 448.2079, found 448.2079.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 10.56 min (major) and 13.16 min (minor)



2-((2-(dimethyl(phenyl)silyl)-4-fluoro-4-phenylbuta-2,3-dien-1-yl)oxy)benzaldehyde **(8b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **8a** (58 mg, 0.2 mmol, 1.0 equiv) were used at 40 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20 to 1:15) to afford the title compound as a colorless oil (75 mg, 93% yield).

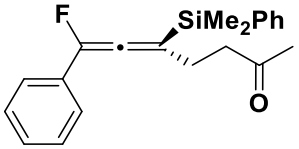
^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.24 (s, 1H), 7.71 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.48–7.34 (m, 6H), 7.30–7.27 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 4.92 (dd, *J* = 7.9, 4.4 Hz, 2H), 0.56 (d, *J* = 1.8 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -158.99 (t, *J* = 7.8 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 199.1 (d, *J* = 29.7 Hz), 189.6, 160.9, 143.8 (d, *J* = 228.0 Hz), 136.1, 136.1, 134.3, 131.5 (d, *J* = 31.6 Hz), 130.4, 129.1, 129.1, 128.7, 128.6, 128.5, 125.7, 124.0 (d, *J* = 3.7 Hz), 121.5, 120.5 (d, *J* = 12.4 Hz), 113.4, 68.5 (d, *J* = 2.1 Hz), -2.7 (d, *J* = 2.2 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{23}FNaO_2Si^+$ $[M+Na]^+$: 425.1344, found 425.1347.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.77 min (major) and 10.47 min (minor)



5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-5,6-dien-2-one **(9b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **9a** (44.5 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a colorless oil (66 mg, 98% yield).

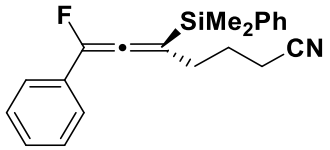
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.44–7.36 (m, 5H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 2.67–2.48 (m, 4H), 1.99 (s, 3H), 0.50 (d, *J* = 8.0 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -158.53 (t, *J* = 10.1 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 207.5, 195.4 (d, *J* = 27.5 Hz), 143.5 (d, *J* = 225.5 Hz), 136.8 (d, *J* = 1.7 Hz), 134.5, 132.4 (d, *J* = 32.5 Hz), 130.2, 129.0 (d, *J* = 1.8 Hz), 128.6, 128.1, 124.4 (d, *J* = 12.9 Hz), 123.8 (d, *J* = 3.7 Hz), 42.2, 30.4, 26.6, -3.0 (d, *J* = 5.9 Hz).

HRMS (ESI+) calc'd for $C_{21}H_{23}FNaOSi^+$ $[M+Na]^+$: 361.1394, found 361.1382.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 10.92 min (major) and 9.69 min (minor)



5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-5,6-dienenitrile **(10b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **10a** (44 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a yellow oil (65 mg, 97% yield).

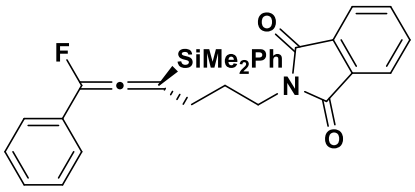
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.48–7.42 (m, 5H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 2.45 (q, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 6.8 Hz, 2H), 1.88 (ddt, *J* = 41.1, 14.0, 7.1 Hz, 2H), 0.55 (d, *J* = 7.8 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.89 (t, *J* = 9.2 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.4 (d, *J* = 27.7 Hz), 143.5 (d, *J* = 225.7 Hz), 136.6, 134.4, 132.3 (d, *J* = 32.5 Hz), 130.3, 129.1, 128.6, 128.2, 123.8 (d, *J* = 3.6 Hz), 123.4 (d, *J* = 13.0 Hz), 119.8, 31.3, 24.9, 16.7, -3.0 (d, *J* = 12.1 Hz).

HRMS (ESI+) calc'd for $C_{21}H_{24}FNSi^+$ $[M+H]^+$: 336.1578, found 336.1567.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 15.62 min (major) and 20.56 min (minor)



2-(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)isoindoline-1,3-dione **(11b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **11a** (68 mg, 0.2 mmol, 1.0 equiv) were used at 45 °C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:9 to 1:6) to afford the title compound as a colorless oil (87 mg, 96% yield).

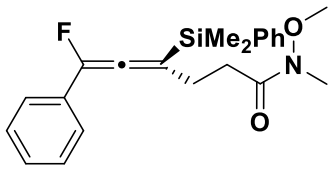
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.60–7.57 (m, 2H), 7.40–7.35 (m, 7H), 7.28–7.24 (m, 1H), 3.70–3.62 (m, 2H), 2.37–2.30 (m, 2H), 1.96–1.80 (m, 2H), 0.49 (d, *J* = 4.4 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.12 (t, J = 9.3 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.2 (d, *J* = 27.5 Hz), 168.7, 143.3 (d, *J* = 225.0 Hz), 136.8, 134.4 (d, *J* = 2.6 Hz), 133.6, 132.7. 132.7, 132.5, 130.1, 129.0, 128.5, 127.9, 124.1 (d, *J* = 12.9 Hz), 123.8 (d, *J* = 3.4 Hz), 123.5, 37.9, 30.1, 28.2, -2.9 (d, *J* = 12.3 Hz).

HRMS (ESI+) calc'd for $C_{28}H_{26}FNNaO_2Si^+$ $[M+Na]^+$: 478.1609, found 478.1602.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 17.68 min (major) and 16.52 min (minor)



4-(dimethyl(phenyl)silyl)-6-fluoro-N-methoxy-N-methyl-6-phenylhexa-4,5-dienamide **(12b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **12a** (54 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:6 to 1:5 to 1:4) to afford the title compound as a colorless oil (70.5 mg, 92% yield).

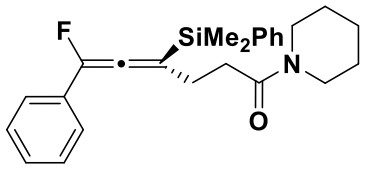
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.63 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.43–7.35 (m, 5H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 3.50 (s, 3H), 2.97 (s, 3H), 2.72–2.64 (m, 2H), 2.59–2.52 (m, 2H), 0.50 (d, *J* = 13.6 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.58 (t, *J* = 9.7 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 195.4 (d, *J* = 27.4 Hz), 173.4, 143.6 (d, *J* = 225.0 Hz), 137.0, 134.5, 132.6 (d, *J* = 32.6 Hz), 130.1, 128.9, 128.5, 127.9, 124.8 (d, *J* = 13.0 Hz), 123.8 (d, *J* = 3.5 Hz), 61.4, 32.3, 30.9, 27.3, -2.9 (d, *J* = 9.4 Hz).

HRMS (ESI+) calc'd for $C_{22}H_{26}FNNaO_2Si^+$ $[M+Na]^+$: 406.1609, found 406.1609.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 10.13 min (major) and 7.89 min (minor)



4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenyl-1-(piperidin-1-yl)hexa-4,5-dien-1-one **(13b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **13a** (58.5 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a colorless oil (80 mg, 98% yield).

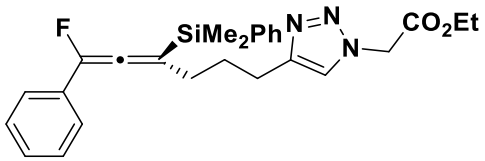
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.63–7.61 (m, 2H), 7.42–7.35 (m, 5H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.1 Hz, 1H), 3.37 (dddd, *J* = 52.2, 12.4, 7.4, 3.7 Hz, 2H), 3.23 (q, *J* = 5.7 Hz, 2H), 2.72–2.64 (m, 1H), 2.58–2.50 (m, 2H), 2.47–2.41 (m, 1H), 1.55–1.47 (m, 2H), 1.42–1.35 (m, 3H), 1.26 (t, *J* = 7.2 Hz, 1H), 0.50 (d, *J* = 14.5 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.76 (t, *J* = 10.1 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 195.2 (d, *J* = 27.3 Hz), 169.9, 143.5 (d, *J* = 224.7 Hz), 137.1, 134.5, 132.7 (d, *J* = 32.6 Hz), 130.1, 129.0, 128.5, 127.9, 125.0 (d, *J* = 12.9 Hz), 123.8 (d, *J* = 3.6 Hz), 46.8, 43.0, 31.9, 28.1, 26.9, 26.0, 25.1, -2.9 (d, *J* = 10.1 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{30}FNNaOSi^+$ $[M+Na]^+$: 430.1973, found 430.1967.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 16.79 min (major) and 13.73 min (minor)



ethyl 2-(4-(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)-1H-1,2,3-triazol-1-yl)acetate **(14b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **14a** (70 mg, 0.2 mmol, 1.0 equiv) were used at 40 °C. The crude residue

was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a colorless oil (78 mg, 83% yield, residual EtOAc).

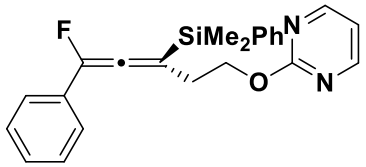
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.43–7.32 (m, 7H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.23 (s, 1H), 5.05 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.36 (qd, *J* = 8.6, 3.5 Hz, 2H), 1.96–1.80 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.48 (d, *J* = 8.2 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.53 (t, *J* = 9.0 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 195.6 (d, *J* = 27.2 Hz), 166.6, 147.8, 142.5 (d, *J* = 224.3 Hz), 136.5, 133.89, 132.2 (d, *J* = 32.6 Hz), 129.5, 128.5, 128.0, 127.3, 124.0 (d, *J* = 13.0 Hz), 123.2 (d, *J* = 3.8 Hz), 122.1, 62.2, 50.7, 31.5, 28.4, 24.9, 13.9, -3.5 (d, *J* = 13.8 Hz).

HRMS (ESI+) calc'd for $C_{26}H_{31}FN_3O_2Si^+$ $[M+H]^+$: 464.2164, found 464.2163.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 70:30; 6.82 min (major) and 8.37 min (minor)



2-((3-(dimethyl(phenyl)silyl)-5-fluoro-5-phenylpenta-3,4-dien-1-yl)oxy)pyrimidine **(15b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **15a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:3 to 1:2) to afford the title compound as a colorless oil (65 mg, 83% yield).

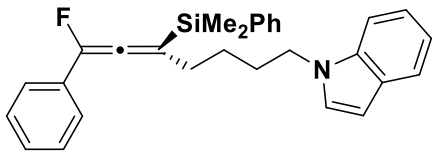
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.61 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.42–7.33 (m, 7H), 7.27–7.23 (m, 1H), 6.86 (t, *J* = 4.8 Hz, 1H), 4.49 (td, *J* = 6.9, 1.4 Hz, 2H), 2.79 (q, *J* = 7.9, 7.4 Hz, 2H), 0.51 (d, *J* = 3.9 Hz, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2) δ -159.52 (t, *J* = 8.6 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 197.0 (d, *J* = 28.0 Hz), 165.6, 159.6, 143.1 (d, *J* = 225.4 Hz), 136.7 (d, *J* = 1.7 Hz), 134.5, 132.4 (d, *J* = 32.3 Hz), 130.2, 129.0 (d, *J* = 1.8 Hz), 128.5, 128.0, 123.9 (d, *J* = 3.6 Hz), 121.0 (d, *J* = 12.9 Hz), 115.5, 66.3 (d, *J* = 2.3 Hz), 31.9, -3.0 (d, *J* = 2.1 Hz).

HRMS (ESI+) calc'd for $C_{23}H_{23}FN_2NaOSi^+$ $[M+Na]^+$: 413.1456, found 413.1451.

Determination of enantiomeric ratio by HPLC analysis: OD column, 1.0 mL/min: hexanes:iPrOH 99:01; 24.74 min (major) and 22.33 min (minor)



(16b): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **16a** (65 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:19) to afford the title compound as a colorless oil (81 mg, 92% yield).

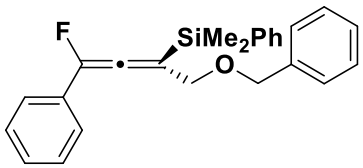
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.63–7.59 (m, 3H), 7.44–7.39 (m, 5H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 4.03 (t, *J* = 7.3 Hz, 2H), 2.37–2.27 (m, 2H), 1.88–1.78 (m, 2H), 1.63–1.49 (m, 2H), 0.49 (d, *J* = 6.0 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.38 (t, *J* = 9.0 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.2 (d, *J* = 27.4 Hz), 143.1 (d, *J* = 224.2 Hz), 137.0, 136.5, 134.4, 132.7 (d, *J* = 32.6 Hz), 130.2, 129.2, 129.1, 128.6, 128.3, 128.0, 124.5 (d, *J* = 12.9 Hz), 123.8 (d, *J* = 3.9 Hz), 121.8, 121.3, 119.6, 109.9, 101.3, 46.6, 32.3, 30.3, 26.5, -2.9 (d, *J* = 10.1 Hz).

HRMS (ESI+) calc'd for $C_{29}H_{30}FNNaSi^+$ $[M+Na]^+$: 462.2024, found 462.2017.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.25 min (major) and 15.84 min (minor)



(1-(benzyloxy)-4-fluoro-4-phenylbuta-2,3-dien-2-yl)dimethyl(phenyl)silane **(17b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **17a** (68 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column

chromatography on SiO_2 (EtOAc:hexanes 1:41) to afford the title compound as a colorless oil (75 mg, 96% yield).

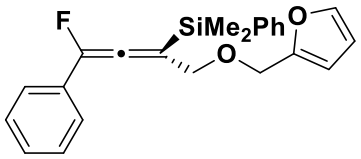
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 6.3 Hz, 2H), 7.45 (dt, *J* = 13.3, 6.3 Hz, 7H), 7.37–7.33 (m, 4H), 7.30 (d, *J* = 7.3 Hz, 2H), 4.57–4.48 (m, 2H), 4.35 (dd, *J* = 7.9, 4.2 Hz, 2H), 0.59 (d, *J* = 5.1 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.61 (t, *J* = 8.1 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.6 (d, *J* = 28.6 Hz), 142.9 (d, *J* = 225.7 Hz), 138.7, 136.9, 134.5, 132.3 (d, *J* = 32.0 Hz), 130.2, 129.1, 128.8, 128.5, 128.3, 128.2, 128.1, 124.0 (d, *J* = 3.7 Hz), 122.4 (d, *J* = 12.6 Hz), 72.9, 70.7, -2.5 (d, *J* = 7.8 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{25}FNaOSi^+$ $[M+Na]^+$: 411.1551, found 411.1551.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 6.90 min (major) and 6.49 min (minor)



(4-fluoro-1-(furan-2-ylmethoxy)-4-phenylbuta-2,3-dien-2-yl)dimethyl(phenyl)silane **(18b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **18a** (53 mg, 0.2 mmol, 1.0 equiv) were used at 27°C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a light yellow oil (67 mg, 88% yield).

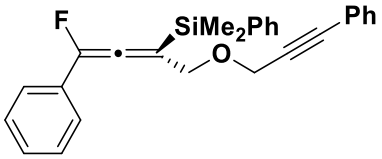
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.61 (d, *J* = 5.7 Hz, 2H), 7.43–7.36 (m, 5H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 4.40 (d, *J* = 2.5 Hz, 2H), 4.26 (dd, *J* = 7.8, 4.2 Hz, 2H), 0.52 (d, *J* = 4.4 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.64 (t, *J* = 8.0 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.6 (d, *J* = 28.7 Hz), 152.1, 143.4, 142.9 (d, *J* = 225.9 Hz), 136.8, 134.49, 132.2 (d, *J* = 31.9 Hz), 130.2, 129.1, 128.5, 128.2, 124.0 (d, *J* = 3.7 Hz), 122.1 (d, *J* = 12.5 Hz), 110.8, 110.1, 70.2, 64.5, -2.6 (d, *J* = 6.7 Hz).

HRMS (ESI+) calc'd for $C_{23}H_{23}FNaO_2Si^+$ $[M+Na]^+$: 401.1344, found 401.1344.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 8.26 min (major) and 7.43 min (minor)



(4-fluoro-4-phenyl-1-((3-phenylprop-2-yn-1-yl)oxy)buta-2,3-dien-2-yl)dimethyl(phenyl)silane **(19b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **19a** (60 mg, 0.2 mmol, 1.0 equiv) were used at 27 °C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:50 to 1:33) to afford the title compound as a colorless oil (69 mg, 83% yield).

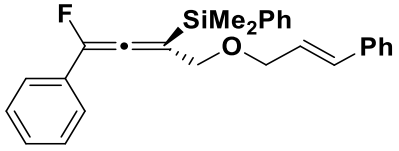
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 5.3 Hz, 2H), 7.43–7.33 (m, 12H), 7.29 (t, *J* = 7.0 Hz, 1H), 4.41 (dd, *J* = 8.1, 2.7 Hz, 2H), 4.35 (s, 2H), 0.56 (d, *J* = 4.3 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.48 (t, *J* = 8.2 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.7 (d, *J* = 28.9 Hz), 143.0 (d, *J* = 226.1 Hz), 136.8, 134.5, 132.3, 130.2, 129.1, 128.9, 128.5, 128.3, 124.0 (d, *J* = 3.7 Hz), 123.1, 122.0 (d, *J* = 12.6 Hz), 87.0, 85.3, 70.0, 58.7, -2.6 (d, *J* = 2.9 Hz).

HRMS (ESI+) calc'd for $C_{27}H_{25}FNaOSi^+$ $[M+Na]^+$: 435.1551, found 435.1547.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 9.14 min (major) and 8.34 min (minor)



(1-(cinnamyloxy)-4-fluoro-4-phenylbuta-2,3-dien-2-yl)dimethyl(phenyl)silane **(20b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **20a** (60 mg, 0.2 mmol, 1.0 equiv) were used at 26 °C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a colorless oil (77 mg, 92% yield).

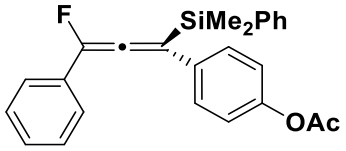
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.45–7.38 (m, 7H), 7.38–7.30 (m, 5H), 7.27 (t, *J* = 6.9 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.32 (dd, *J* = 8.0, 3.4 Hz, 2H), 4.12 (t, *J* = 4.3 Hz, 2H), 0.56 (d, *J* = 5.2 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.60 (t, *J* = 8.1 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.4 (d, *J* = 28.7 Hz), 142.9 (d, *J* = 225.6 Hz), 137.3, 136.9, 134.5, 132.87, 132.3 (d, *J* = 31.9 Hz), 130.2, 129.1, 129.1, 128.5, 128.2, 127.0, 126.4, 124.0 (d, *J* = 3.8 Hz), 122.5 (d, *J* = 12.6 Hz), 71.5, 70.6, -2.5 (d, *J* = 5.7 Hz).

HRMS (ESI+) calc'd for $C_{27}H_{27}FNaOSi^+$ $[M+Na]^+$: 437.1707, found 437.1703.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99.95:00.05; 16.15 min (major) and 12.31 min (minor)



4-(1-(dimethyl(phenyl)silyl)-3-fluoro-3-phenylpropa-1,2-dien-1-yl)phenyl acetate **(21b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **21a** 57 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a light yellow oil (79 mg, 98% yield).

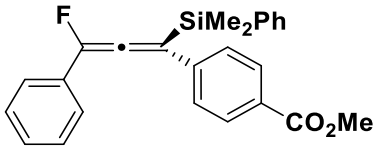
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.70–7.67 (m, 2H), 7.48–7.39 (m, 9H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 2.27 (s, 3H), 0.60 (d, *J* = 9.6 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -157.86 (s, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 202.0 (d, *J* = 28.4 Hz), 169.8, 151.2, 143.2 (d, *J* = 227.6 Hz), 137.3, 134.5, 134.0, 131.9 (d, *J* = 32.4 Hz), 130.3, 130.0 (d, *J* = 2.3 Hz), 129.2, 128.7, 128.5, 124.0 (d, *J* = 3.3 Hz), 122.5, 21.4, -1.6 (d, *J* = 4.0 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{23}FNaO_2Si^+$ $[M+Na]^+$: 425.1344, found 425.1348.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 0.2 mL/min: hexanes:iPrOH 99.85:00.15; 47.08 min (major) and 44.98 min (minor)



methyl 4-(1-(dimethyl(phenyl)silyl)-3-fluoro-3-phenylpropa-1,2-dien-1-yl)benzoate **(22b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in

PhMe, 7 mol%), and **22a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:33 to 1:20) to afford the title compound as a colorless oil (77 mg, 95% yield).

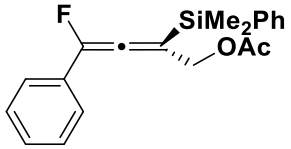
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.50–7.43 (m, 9H), 7.39–7.35 (m, 1H), 3.92 (s, 3H), 0.63 (d, *J* = 8.2 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.71 (s, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 203.6 (d, *J* = 28.9 Hz), 167.0, 143.5 (d, *J* = 228.1 Hz), 141.2, 137.0, 134.5, 131.6 (d, *J* = 32.0 Hz), 130.3, 130.3, 130.2, 129.3, 128.8 (d, *J* = 2.3 Hz), 128.7, 128.7, 124.6 (d, *J* = 12.8 Hz), 124.1 (d, *J* = 3.3 Hz), 52.5, -1.7 (d, *J* = 7.5 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{23}FNaO_2Si^+$ $[M+Na]^+$: 425.1344, found 425.1342.

Determination of enantiomeric ratio by HPLC analysis: OJ column, 1.0 mL/min: hexanes; 32.66 min (major) and 44.41 min (minor)



2-(dimethyl(phenyl)silyl)-4-fluoro-4-phenylbuta-2,3-dien-1-yl acetate **(23b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **23a** (45 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:33 to 1:20) to afford the title compound as a colorless oil (64 mg, 95% yield).

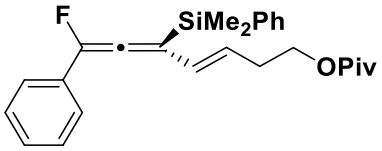
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.62–7.60 (m, 2H), 7.44–7.39 (m, 5H), 7.36 (d, *J* = 1.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 4.89–4.74 (m, 2H), 1.90 (s, 3H), 0.53 (d, *J* = 1.6 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -158.60 (t, *J* = 8.8 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.3 (d, *J* = 29.2 Hz), 170.6, 143.8 (d, *J* = 227.4 Hz), 136.3, 134.4, 131.9 (d, *J* = 31.7 Hz), 130.4, 129.1 (d, *J* = 1.7 Hz), 128.6, 128.5, 124.1 (d, *J* = 3.7 Hz), 120.8 (d, *J* = 12.3 Hz), 63.9 (d, *J* = 2.0 Hz), 20.9, -2.7 (d, *J* = 4.1 Hz).

HRMS (ESI+) calc'd for $C_{20}H_{21}FNaO_2Si^+$ $[M+Na]^+$: 363.1187, found 363.1183.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 21.14 min (major) and 13.25 min (minor)



(*E*)-5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-3,5,6-trien-1-yl pivalate **(24b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), **24a** (62 mg, 0.2 mmol, 1.0 equiv), CsF (30 mg, 0.2 mmol, 1.0 equiv), and sodium 2-methoxyphenolate (9.0 mg, 30 mol%) were used at 27 °C with PhMe as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:20) to afford the title compound as a colorless oil (72 mg, 85% yield).

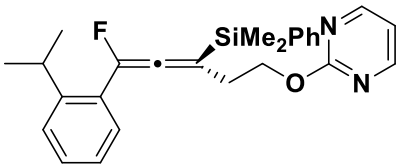
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 5.3 Hz, 2H), 7.39 (m, 5H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 6.13 (d, *J* = 14.8 Hz, 1H), 5.94–5.85 (m, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.40 (q, *J* = 6.9 Hz, 2H), 1.15 (s, 9H), 0.50 (d, *J* = 3.2 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -157.23 (s, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 201.2 (d, *J* = 27.2 Hz), 178.6, 141.5 (d, *J* = 226.0 Hz), 137.3, 134.4, 134.3 (d, *J* = 5.2 Hz), 132.2 (d, *J* = 32.7 Hz), 130.1, 129.1, 128.6, 128.4, 128.2, 124.0 (d, *J* = 3.2 Hz), 122.4 (d, *J* = 13.6 Hz), 63.5 (d, *J* = 2.1 Hz), 39.2, 33.1, 27.5, -1.9 (d, *J* = 3.8 Hz).

HRMS (ESI+) calc'd for $C_{26}H_{31}FNaO_2Si^+$ $[M+Na]^+$: 445.1970, found 445.1970.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 18.33 min (major) and 13.83 min (minor)



2-((3-(dimethyl(phenyl)silyl)-5-fluoro-5-(2-isopropylphenyl)penta-3,4-dien-1-yl)oxy)pyrimidine**(25b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **25a** (63.5, 0.2 mmol, 1.0 equiv) were used at 45 °C with MTBE as the solvent. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:5) to afford the title compound as a colorless oil (61 mg, 70% yield).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.47 (d, *J* = 4.7 Hz, 2H), 7.58 (d, *J* = 6.0 Hz, 2H), 7.40–7.33 (m, 5H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.17 (*t*, J = 7.4 Hz, 1H), 6.90 (*t*, J = 4.7 Hz, 1H), 4.53 (dt, *J* = 7.9, 5.9 Hz, 2H), 3.32 (p, *J* = 6.9 Hz, 1H), 2.81–2.67 (m, 2H), 1.20 (t, *J* = 6.6 Hz, 6H), 0.52 (d, *J* = 4.7 Hz, 9H).

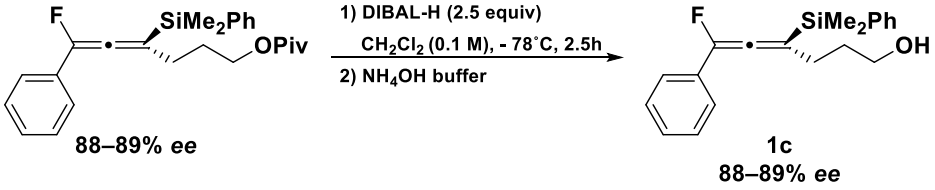
^{19}F NMR (565 MHz, CD_2Cl_2) δ -137.54 (t, *J* = 9.0 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 198.5 (d, *J* = 29.5 Hz), 165.7, 159.7, 147.7, 142.0 (d, *J* = 228.9 Hz), 136.7, 134.5, 130.5 (d, *J* = 30.9 Hz), 129.8, 128.8 (d, *J* = 3.4 Hz), 128.5, 126.4, 126.2, 117.1 (d, *J* = 13.7 Hz), 115.5, 66.5 (d, J = 2.2 Hz), 31.7, 30.8, 24.6, 24.3, -2.9 (d, *J* = 10.0 Hz).

HRMS (ESI+) calc'd for $C_{26}H_{29}FN_2NaO_2Si^+$ $[M+Na]^+$: 455.1925, found 455.1928.

Determination of enantiomeric ratio by HPLC analysis: ADH column, 1.0 mL/min: hexanes:iPrOH 99.7:00.3; 23.83 min (major) and 21.98 min (minor)

2.5.7 Procedures for Derivatizations of Fluoroallenes



4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-ol **(1c):** In a nitrogen filled glovebox, **1b** (616 mg, 1.5 mmol, 1.0 equiv) and CH_2Cl_2 (15 mL, 0.1 M) was added to a 50 mL Schlenk round bottom flask and sealed with a septum. The flask was removed from the glovebox and placed in a -78 °C bath (dry ice/acetone) under a flow of nitrogen. After reaching -78 °C, DIBAL-H (1 M in hexanes, 3.8 mL, 2.5 equiv) was added dropwise over the course of 4 minutes. After stirring at -78 °C for 150 minutes, the contents were quickly poured onto a vigorously stirring NH_4Cl/NH_4OH aqueous buffer (75 mL in a 250 mL Erlenmeyer flask). The reaction flask was quickly rinsed with CH_2Cl_2 (3 x 5 mL) and added to the Erlenmeyer flask. The organic layer was then diluted with Et_2O (100 mL), and the mixture was vigorously stirred for 10 minutes before being filtered over a pad of celite. The layers were separated and the aqueous layer was extracted with Et_2O (200 mL). The organics were combined and washed with dH_2O (150 ml), Brine (150 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:3 to 1:2) to afford the title compound as a colorless oil (488 mg, 99% yield).

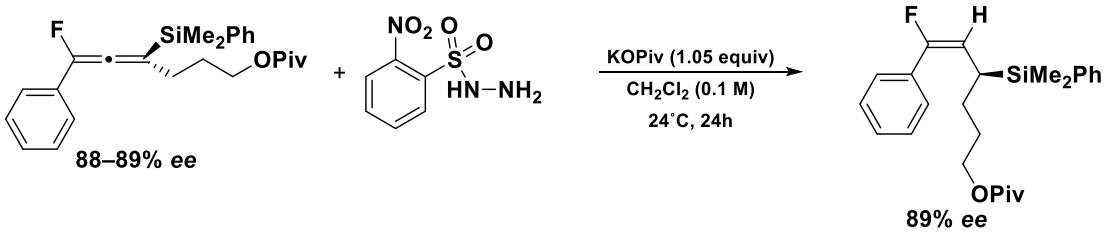
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.65–7.61 (m, 2H), 7.45–7.36 (m, 7H), 7.28 (t, *J* = 7.0 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.37 (q, *J* = 8.1, 7.6 Hz, 2H), 1.82–1.68 (m, 3H), 0.52 (d, *J* = 6.3 Hz, 6H).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.37 (t, *J* = 9.3 Hz, 1F).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.0 (d, *J* = 27.3 Hz), 143.1 (d, *J* = 224.2 Hz), 137.1 (d, *J* = 1.7 Hz), 134.4, 132.8 (d, *J* = 32.7 Hz), 130.2, 129.1 (d, *J* = 1.8 Hz), 128.6, 127.9, 124.7 (d, *J* = 13.0 Hz), 123.7 (d, *J* = 3.6 Hz), 62.4, 32.3 (d, *J* = 1.9 Hz), 29.0, -2.9 (d, *J* = 7.5 Hz).

HRMS (ESI+) calc'd for $C_{20}H_{23}FNaOSi^+$ $[M+Na]^+$: 349.1394, found 349.1393.

Determination of enantiomeric ratio by HPLC analysis: IB column, 1.0 mL/min: hexanes:iPrOH 95:05; 6.79 min (major) and 7.66 min (minor)



(*E*)-4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhex-5-en-1-yl pivalate **(2c):** In a nitrogen filled glovebox, a 20 mL vial was charged with a stir bar, **1b** (189 mg, 0.46 mmol, 1.0 equiv), and CH_2Cl_2 (4.6 mL, 0.1 M). KOPiv (67 mg, 0.48 mmol, 1.05 eq) and 2-nitrobenzenesulfonylhydrazide (200 mg, 0.92 mmol, 2.0 equiv) were added, the vial was sealed with a ptfe lined cap, removed from the glovebox and placed in a 24 °C heating block (8/10 stir setting). After 24 hours, the mixture was diluted with Et_2O (5 mL), filtered over a plug and SiO_2. The SiO_2 was rinsed with Et_2O (3 x 25 mL), concentrated, and the crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:15) to afford the title compound as a colorless oil (188 mg, 99% yield; 97% purity based on ^{19}F NMR).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.1 Hz, 2H), 7.38–7.31 (m, 8H), 5.20 (dd, *J* = 22.9, 12.7 Hz, 1H), 3.96 (t, *J* = 6.3 Hz, 2H), 2.04 (t, *J* = 12.2 Hz, 1H), 1.84–1.77 (m, 1H), 1.65–1.59 (m, 1H), 1.53–1.44 (m, 1H), 1.34–1.28 (m, 1H), 1.16 (s, 9H), 0.32 (d, *J* = 16.7 Hz, 6H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.39 (d, *J* = 22.9 Hz, 1F).

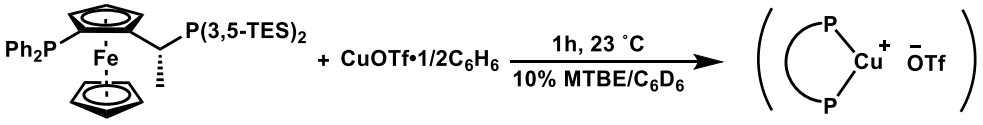
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 156.4 (d, *J* = 239.5 Hz), 136.9, 134.1, 132.4 (d, *J* = 30.1 Hz), 129.3, 128.8, 128.3, 127.9, 127.8 (d, *J* = 4.4 Hz), 109.8 (d, *J* = 24.6 Hz), 64.0, 38.8, 28.7, 27.3, 26.6 (d, *J* = 2.1 Hz), 25.2 (d, *J* = 4.9 Hz), -4.7 (d, *J* = 101.7 Hz).

HRMS (ESI+) calc'd for $C_{25}H_{33}FNaO_2Si^+$ $[M+Na]^+$: 435.2126, found 435.2121.

Determination of enantiomeric ratio by HPLC analysis: OJ column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 39.28 min (major) and 45.02 min (minor)

2.5.8 Preliminary NMR Studies

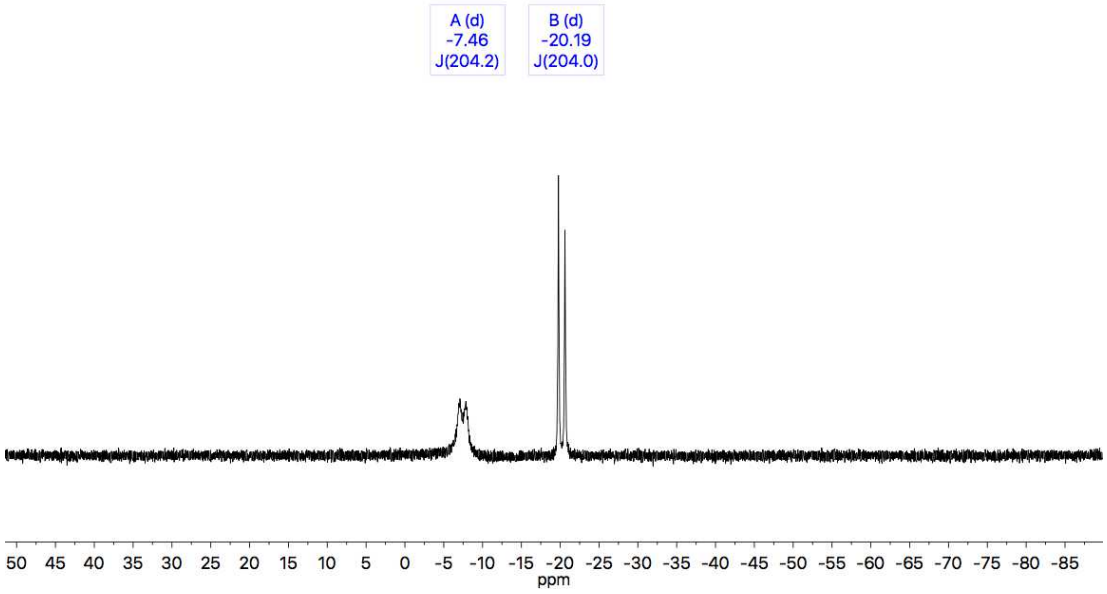
Formation of LCuOTf and LCu(^{t}BuCN)$_n$OTf:



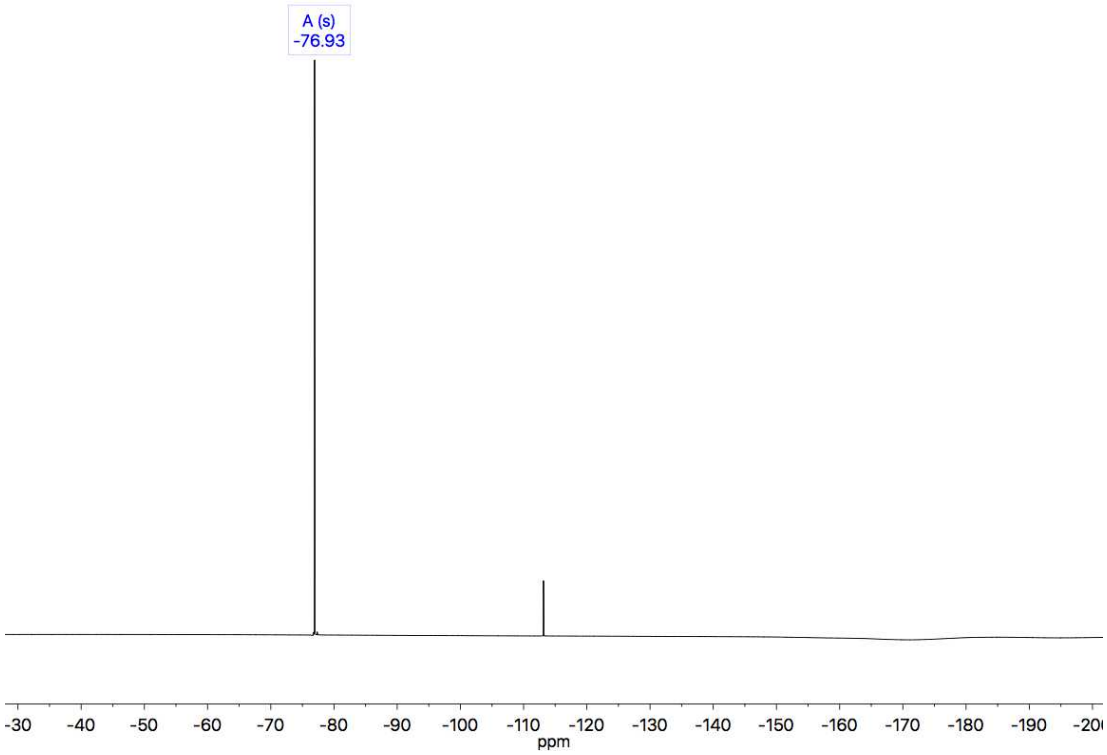
^{31}P 8.2 (*d*, 31.1 Hz),
-24.5 (*d*, 30.9 Hz)

^{31}P -7.46 (*d*, 204.2 Hz)
-20.19 (*d*, 204.0 Hz)
^{19}F -76.93 (s)

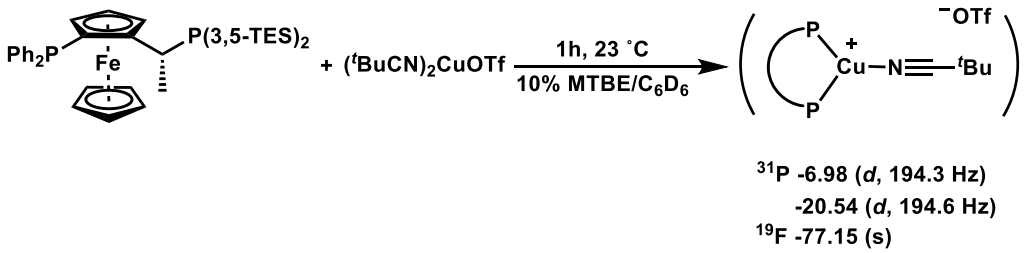
In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (7.0 mg, 0.028 mmol, 1 equiv) and a 20% MTBE/C_6D_6 solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (280 µL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, an aliquot was transferred to a J-Young NMR tube and the mixture analyzed by NMR. PhF was used as an internal standard.



^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

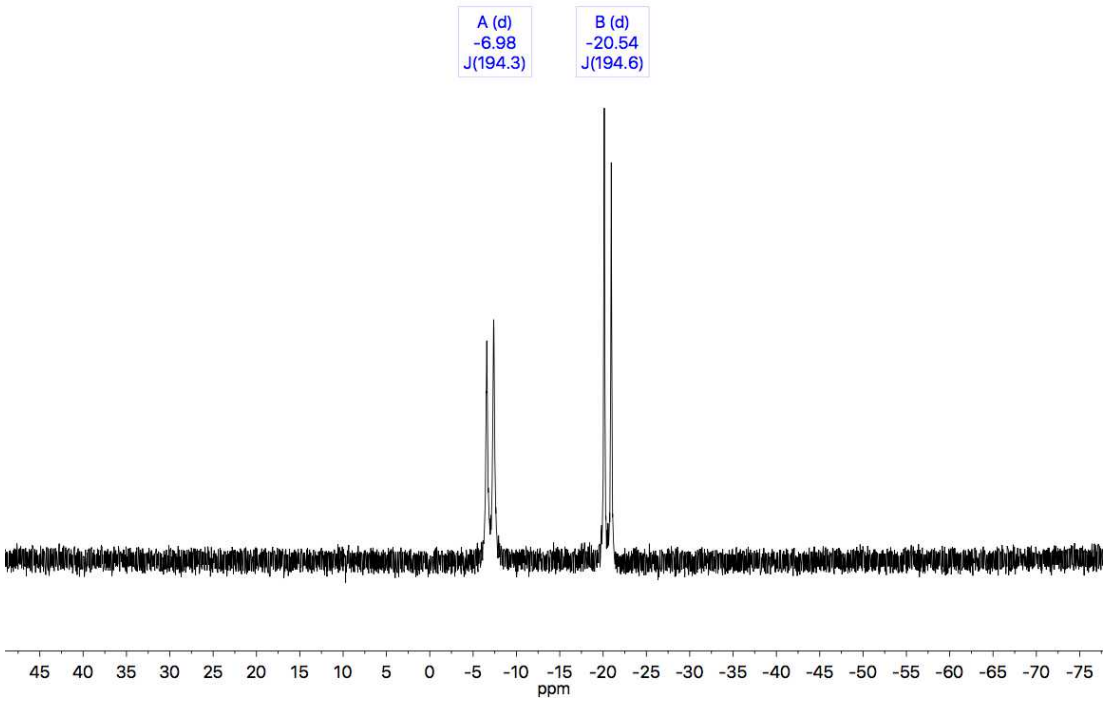


^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

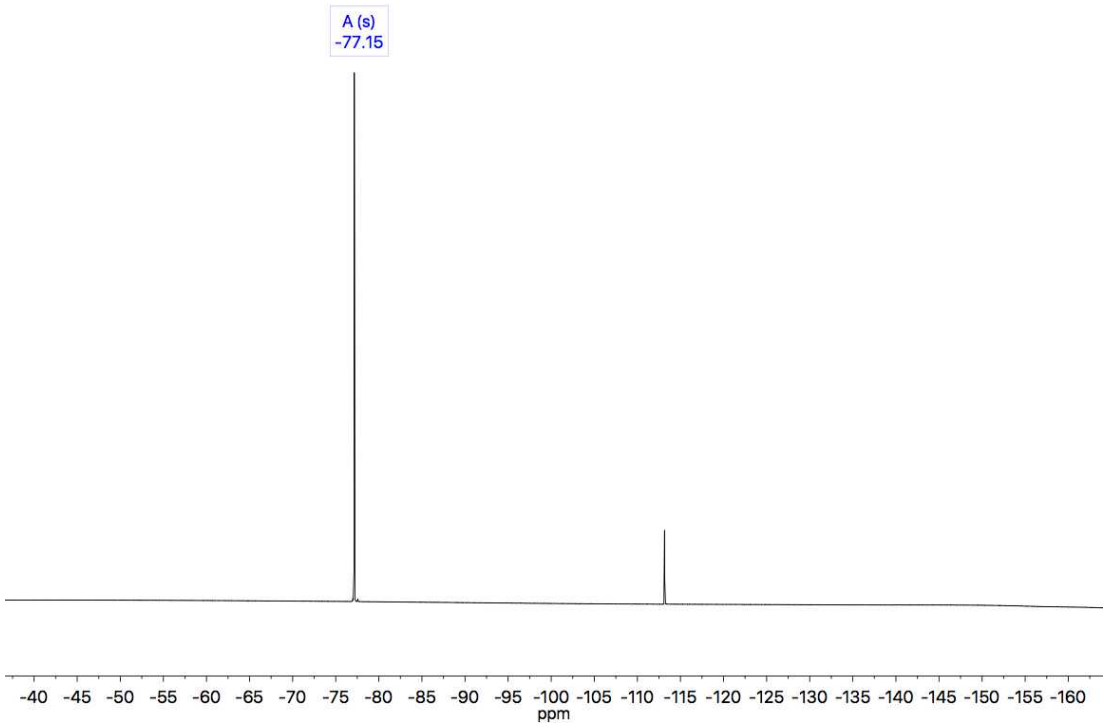


^{31}P -6.98 (*d*, 194.3 Hz)
-20.54 (*d*, 194.6 Hz)
^{19}F -77.15 (s)

In a nitrogen filled glovebox, Cu(^{t}BuCN)$_2$OTf (10.6 mg, 0.028 mmol, 1 equiv) and a 20% MTBE/C_6D_6 solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (280 µL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, an aliquot was transferred to a J-Young NMR tube and the mixture analyzed by NMR. PhF was used as an internal standard.



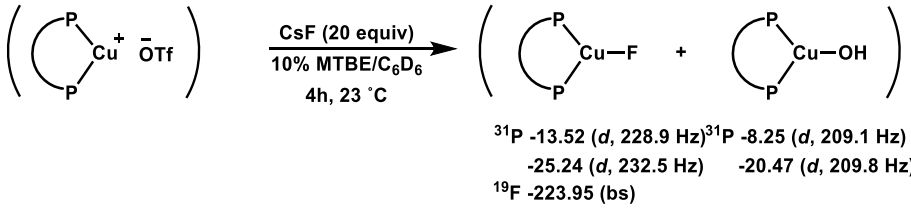
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

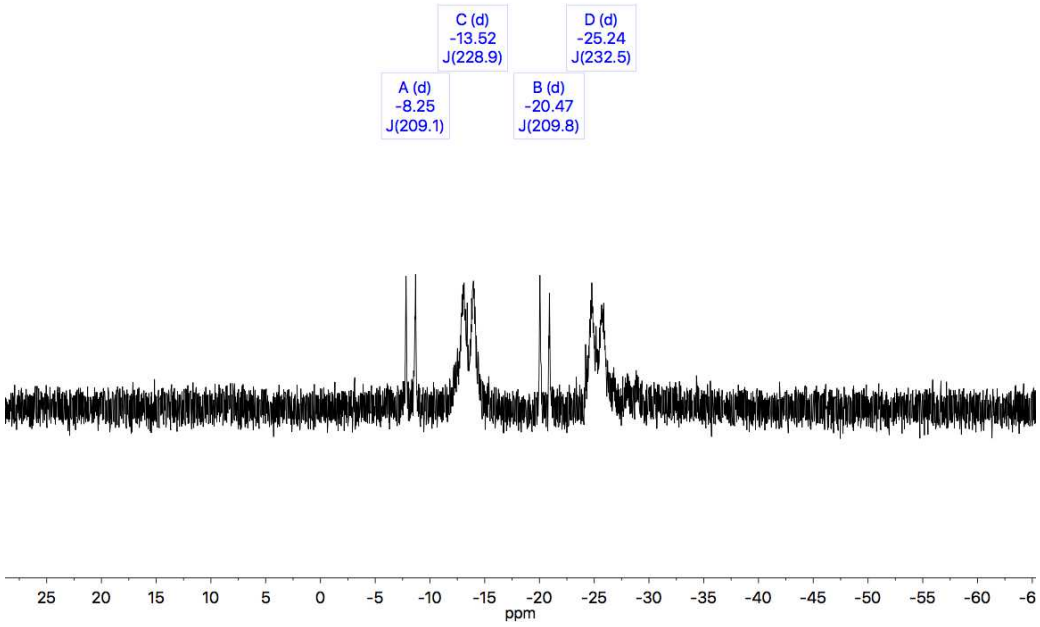


^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

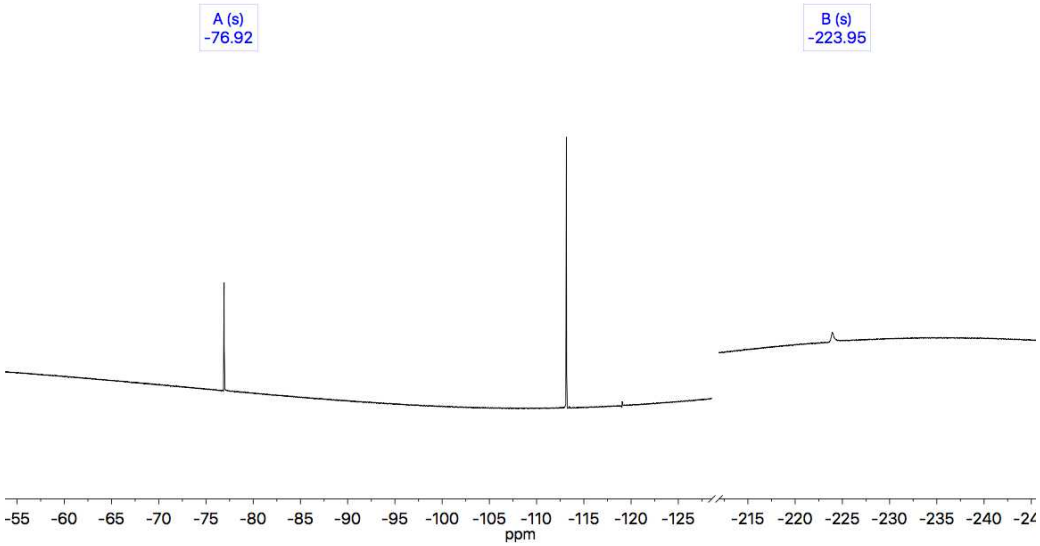
Formation of [LCuF] from LCuOTf and LCu(^{t}BuCN)$_n$OTf:

The contents of the J-Young NMR tubes were transferred back into the 1-dram vials located in the glovebox and CsF (85 mg, 0.56 mmol, 20 equiv) was added. The mixtures were vigorously stirred (10/10 stir setting on an ika stirring plate) 4 hours. The solid was allowed to settle, aliquots were transferred to J-Young NMR tubes, and the solutions were analyzed by NMR. After 24 hours of stirring with CsF, the presumed Cu-OH species converts to the Cu-F.

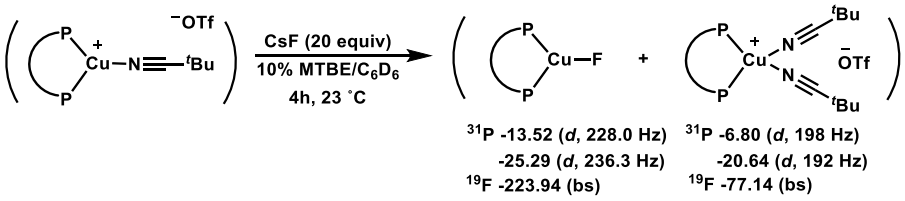


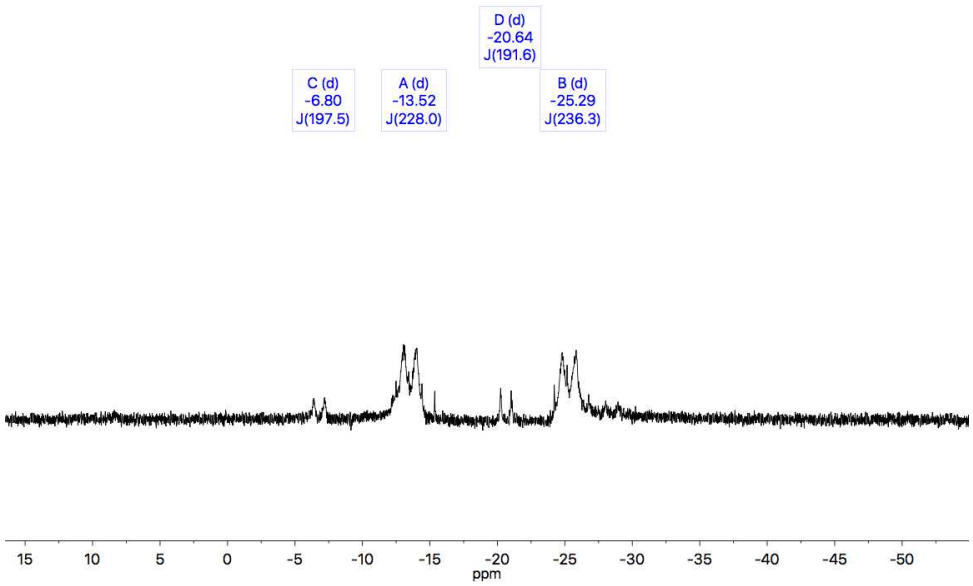


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

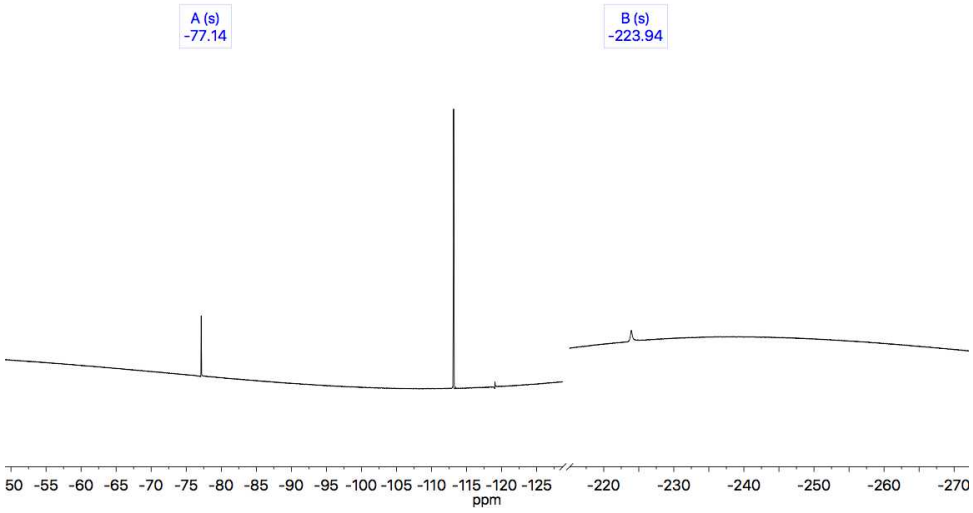


^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)





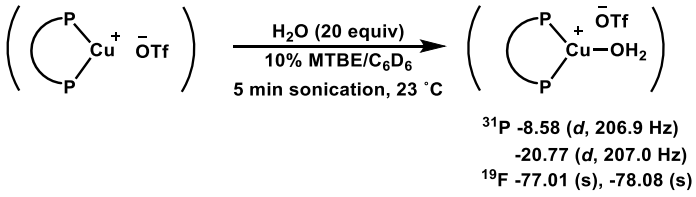
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

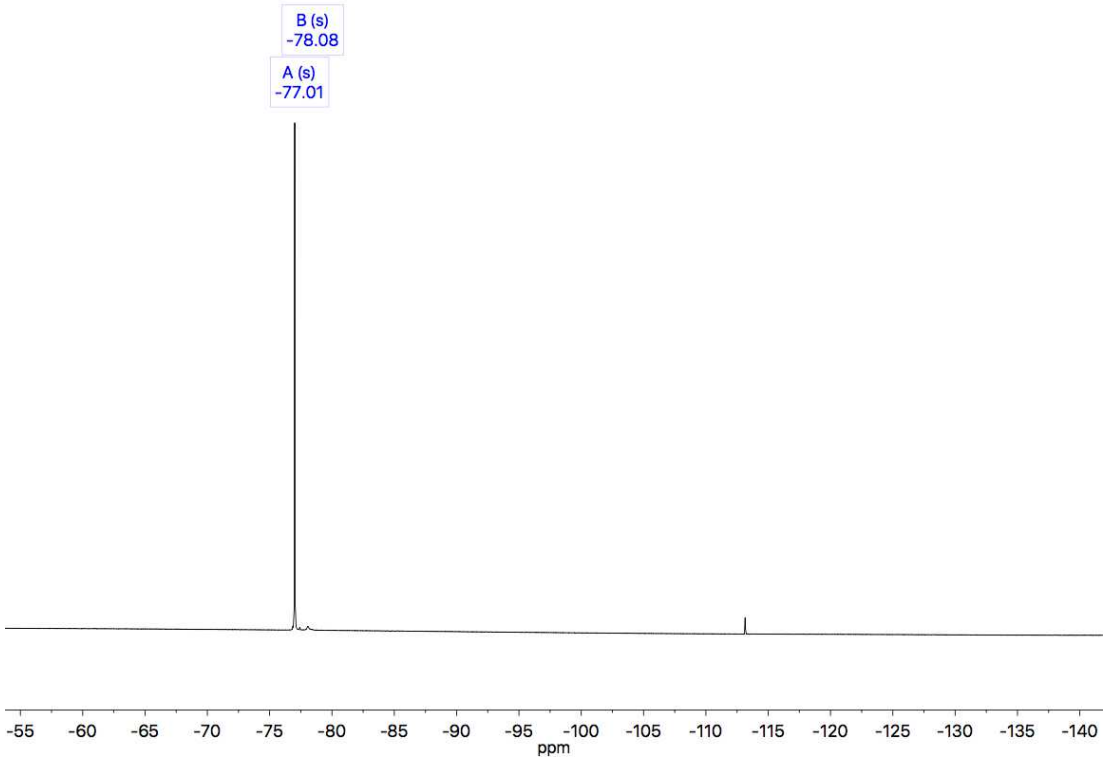


^{19} F NMR (565 MHz, 10% MTBE/C_6D_6)

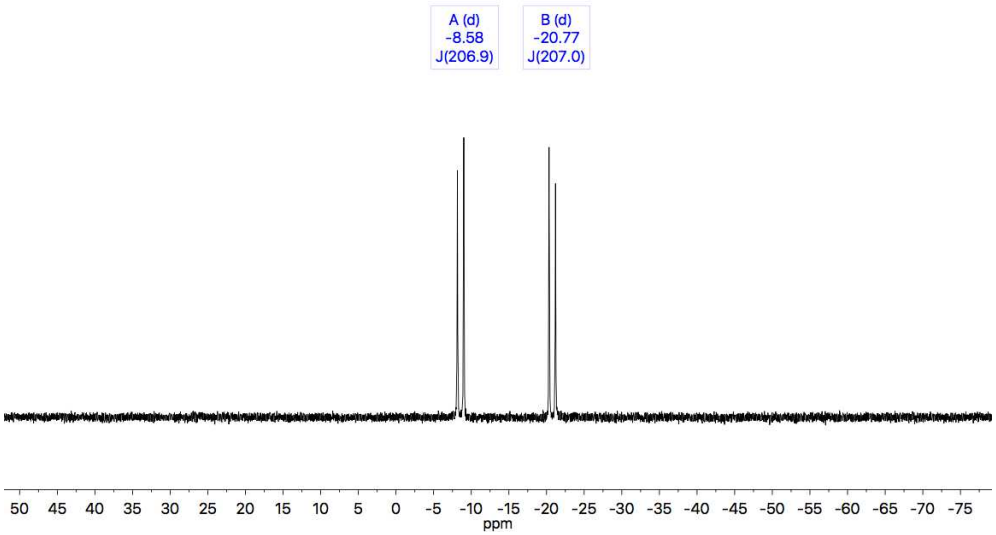
Formation of LCuOH and LCu(H$_2$O)OTf:

In a nitrogen filled glovebox, CuOTf·0.5C$_6$H$_6$ (7.0 mg, 0.028 mmol, 1 equiv) and a 20% MTBE/C$_6$D$_6$ solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R*,*S*)-3,5-TES-Josiphos (280 µL (0.1 M in C$_6$D$_6$), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, half of the solution was transferred to an NMR tube, sealed with a rubber septum, and removed from the glovebox. Under a flow of N_2, N_2 sparged water (5 µL, 0.28 mmol, 20 equiv) was added and the NMR tube sonicated for 5 minutes before being analyzed. Under nitrogen, the other half of the solution was transferred to an NMR tube containing CsOH·H$_2$O (19 mg, 0.11 mmol, 8 equiv) and sonicated for 5 minutes before being analyzed. PhF was used as an internal standard.

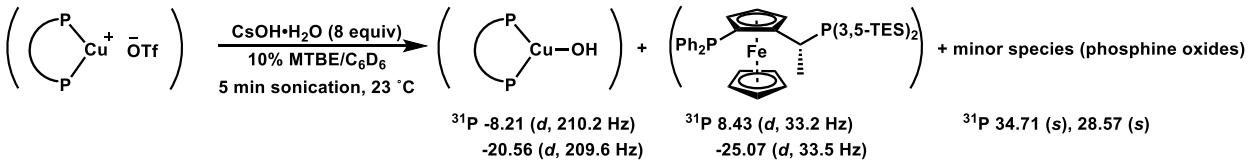




^{19}F NMR (565 MHz, 10% MTBE/C$_6$D$_6$)



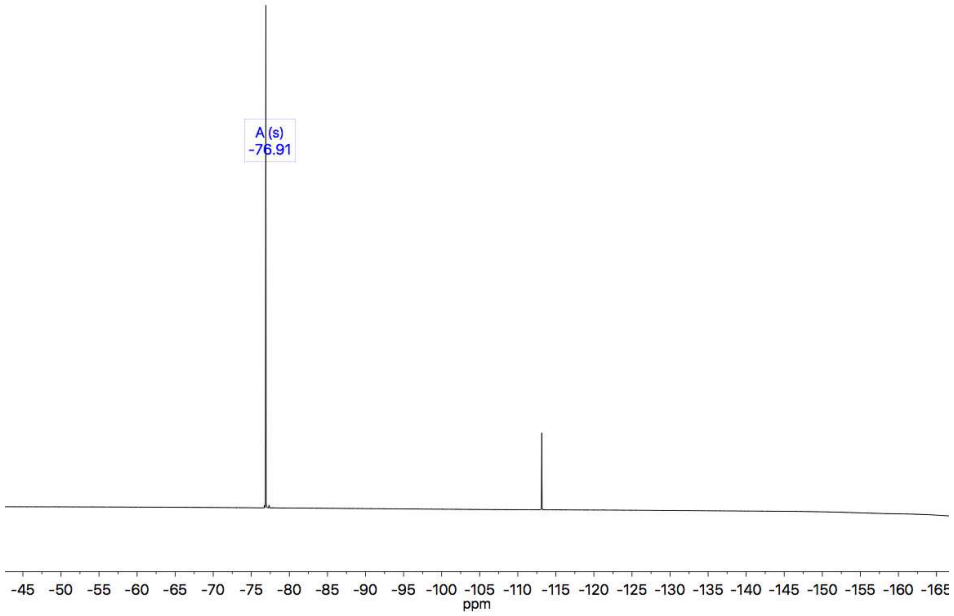
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)



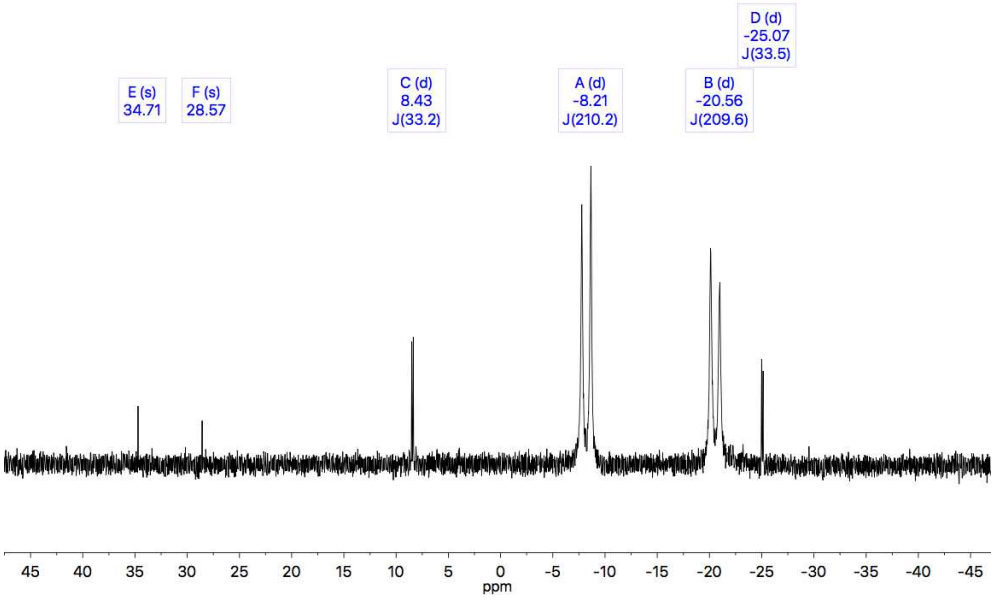
^{31}P -8.21 (*d*, 210.2 Hz)
-20.56 (*d*, 209.6 Hz)

^{31}P 8.43 (*d*, 33.2 Hz)
-25.07 (*d*, 33.5 Hz)

^{31}P 34.71 (*s*), 28.57 (*s*)



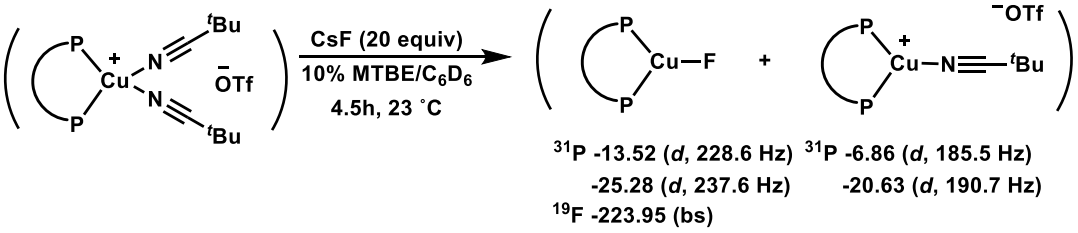
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

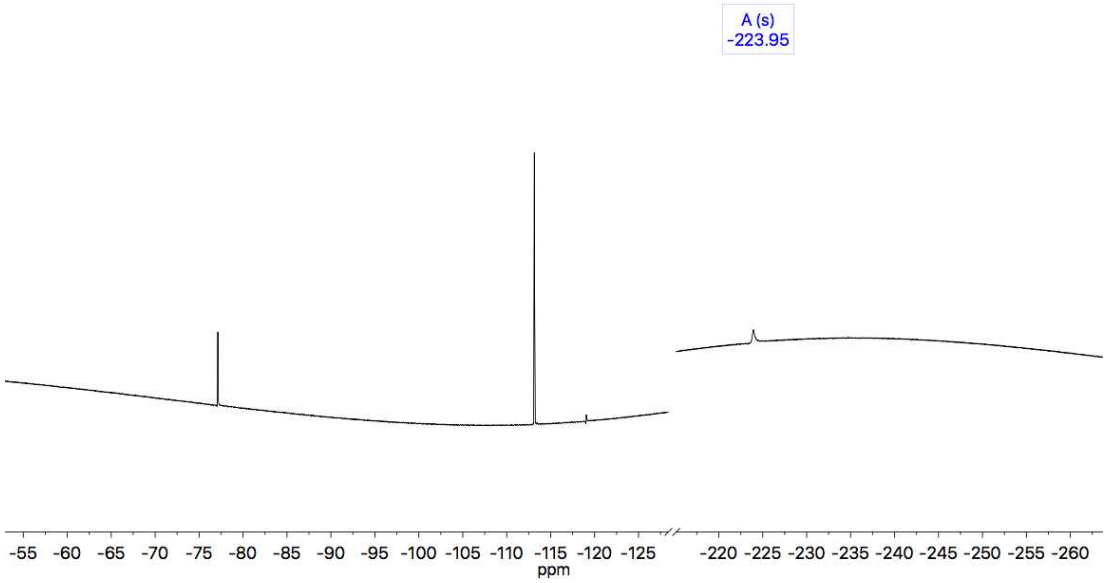


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

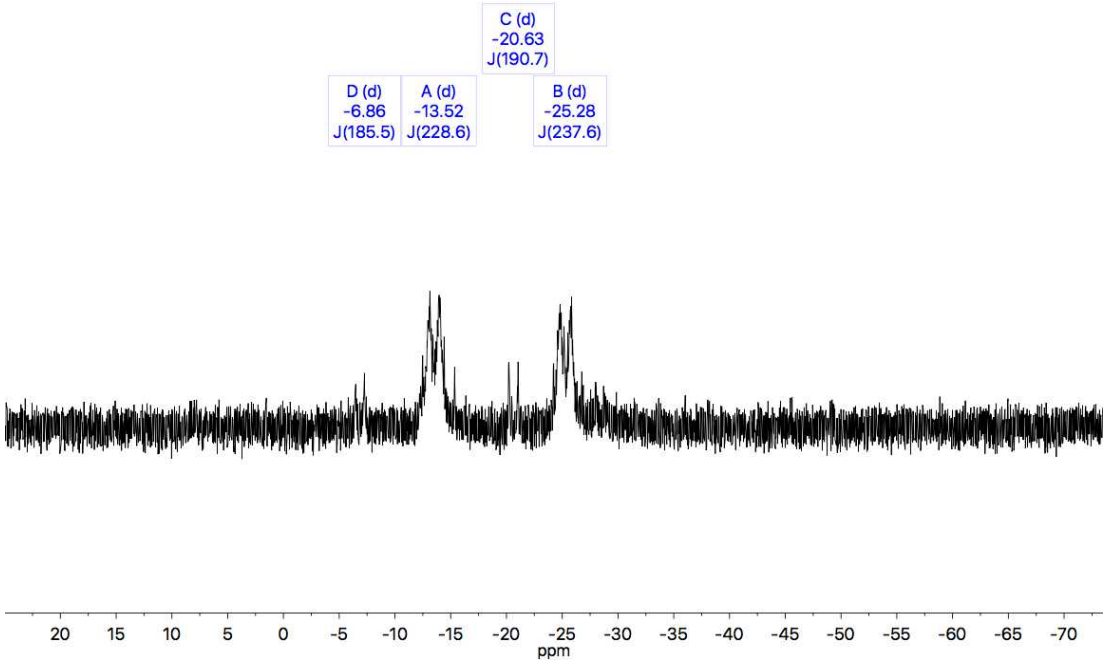
Reactivity of LCuF and LCuSiMe$_2$Ph: Generation of LCuF$_2$Bpin FBpin

In a nitrogen filled glovebox, Cu(^{t}BuCN)$_2$OTf (10.6 mg, 0.028 mmol, 1 equiv) and a 20% MTBE/C_6D_6 solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R*,*S*)-3,5-TES-Josiphos (280 µL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, CsF (85 mg 0.58 mmol, 20 equiv) was added and the mixture vigorously stirred for 5 hours. The solids were allowed to settle, and an aliquot was transferred to a J-Young NMR tube and analyzed.



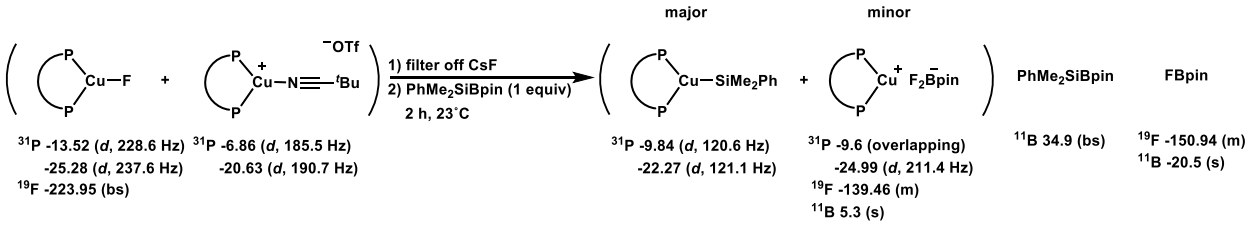


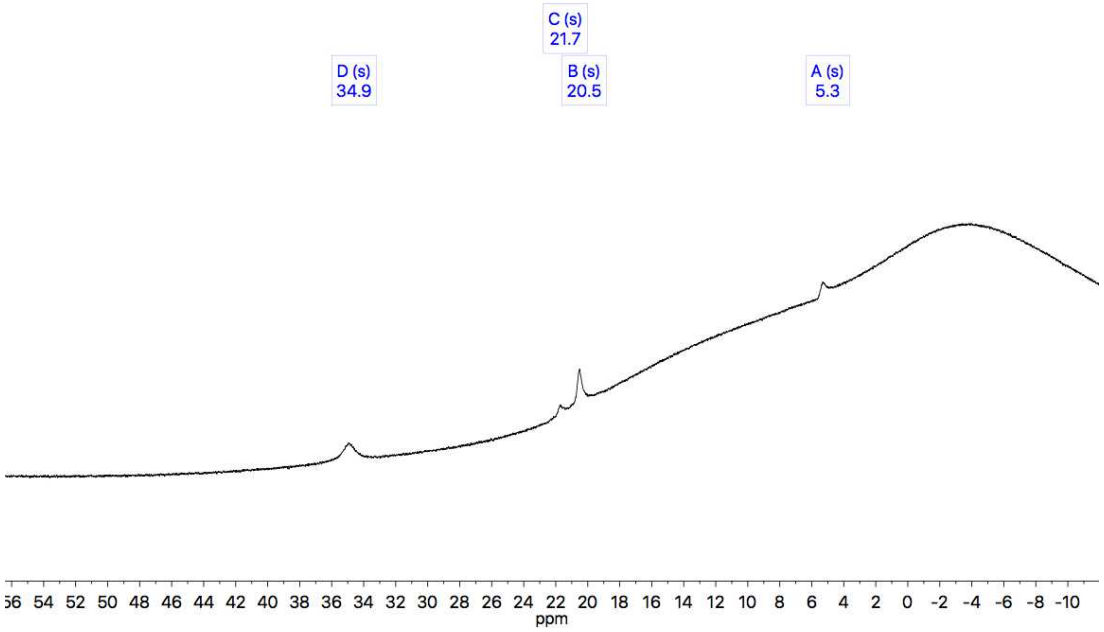
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



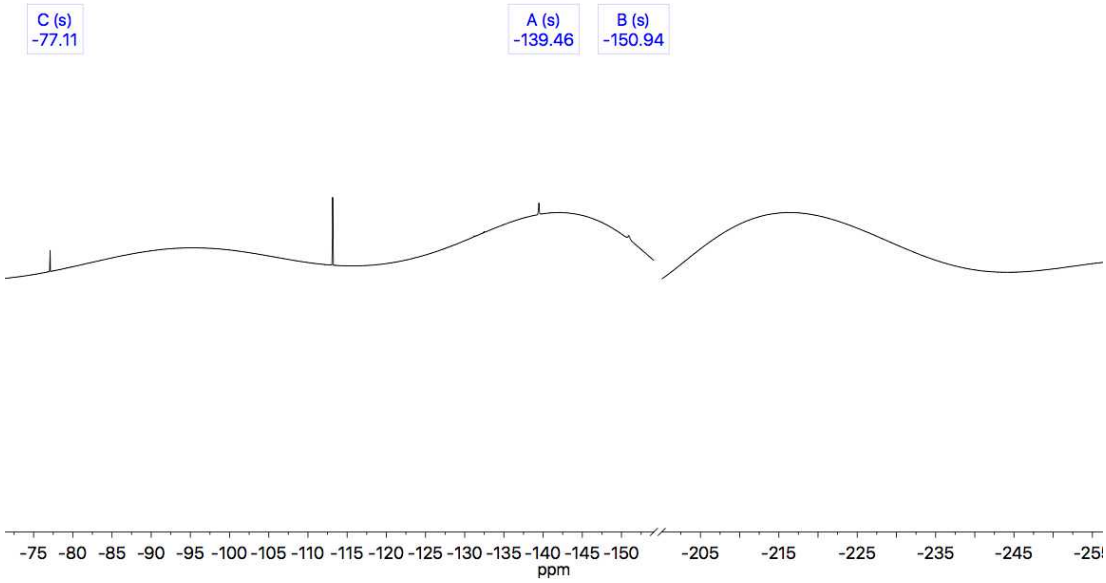
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

The contents of the J-Young NMR tube were transferred back into the 1-dram vial located in the glovebox. The solution was filtered through a pipette with glass fiber filter to remove excess CsF and CsOTf and rinsed with C_6D_6 (400 µL) into a new 1-dram vial. $PhMe_2SiBpin$ (7.3 mg, 0.028 mmol, 1 equiv) was added and the solution was stirred for 2 hours. An aliquot was transferred to a J-Young NMR tube and analyzed.

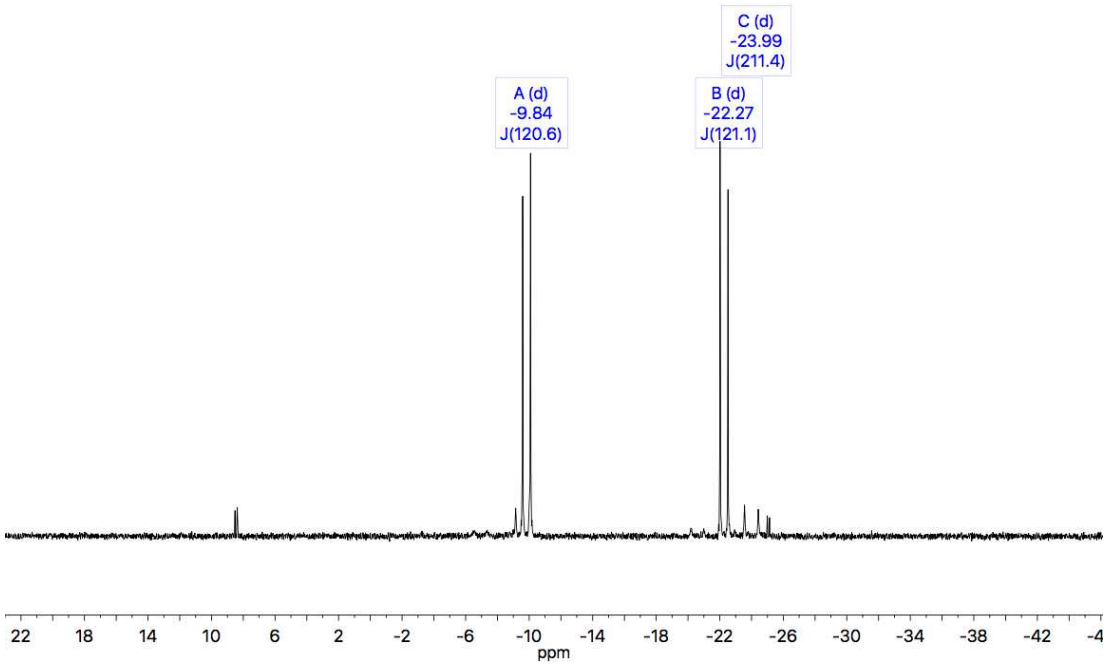




^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)

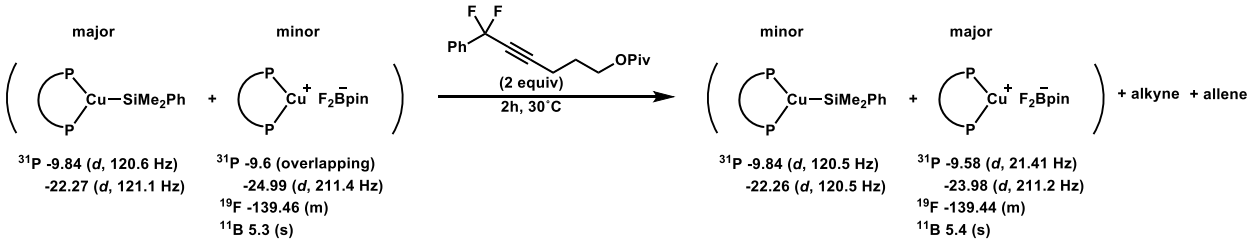


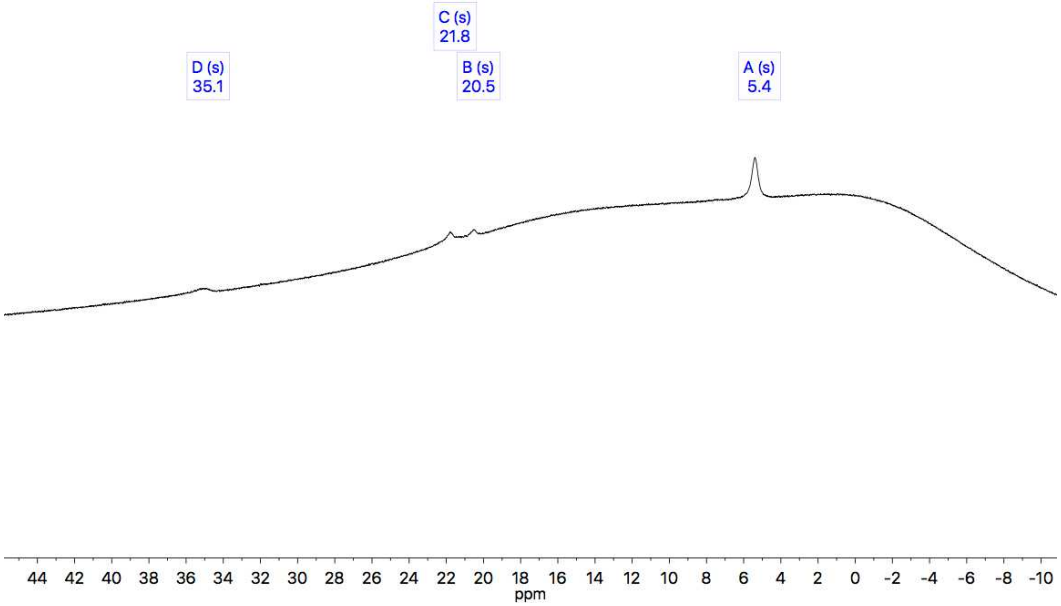
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



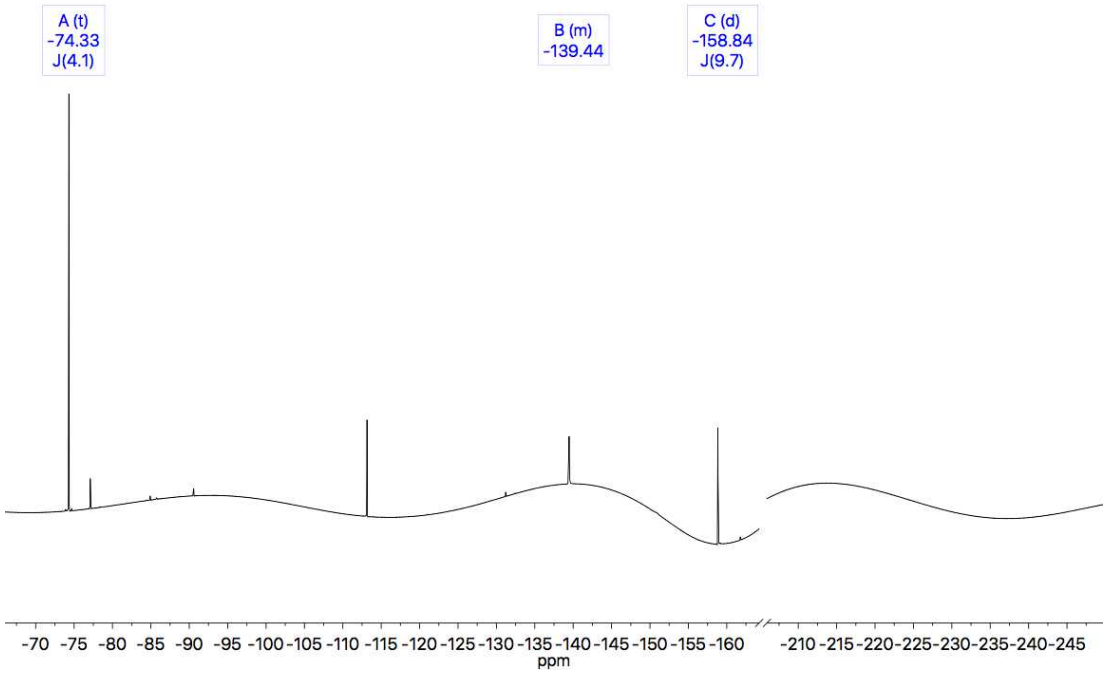
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

The contents of the J-Young NMR tube were transferred back into the 1-dram vial located in the glovebox. Difluoroalkyne **1a** (16.0 mg, 0.056 mmol, 2 equiv) was added and the solution was stirred for 2 hours at 33 °C. An aliquot was transferred to a J-Young NMR tube and analyzed.

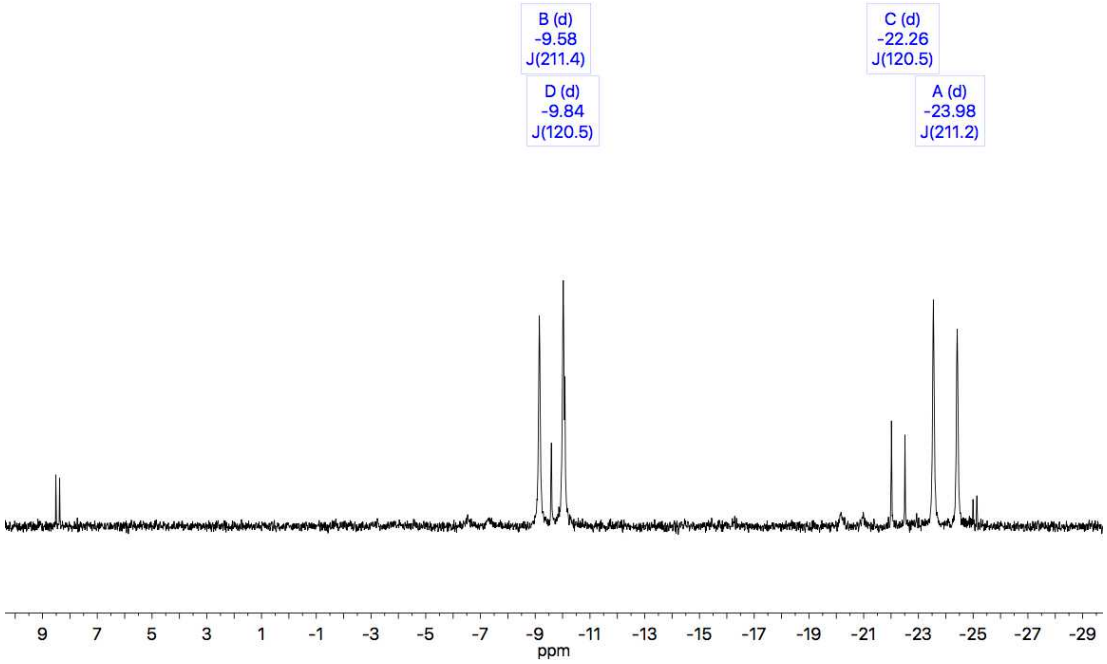




^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



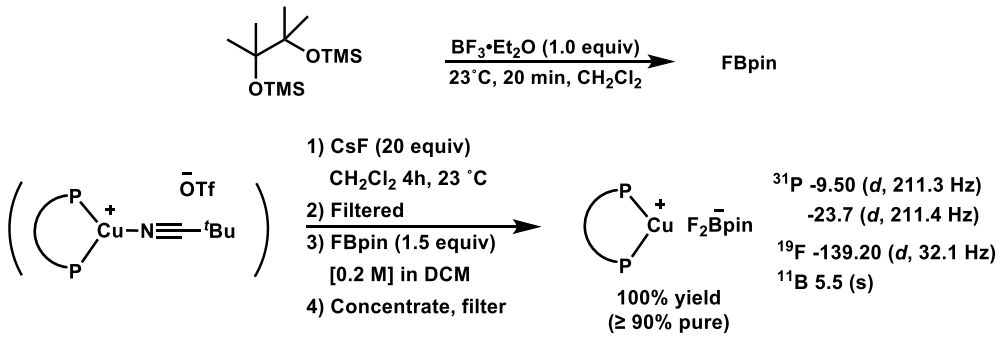
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

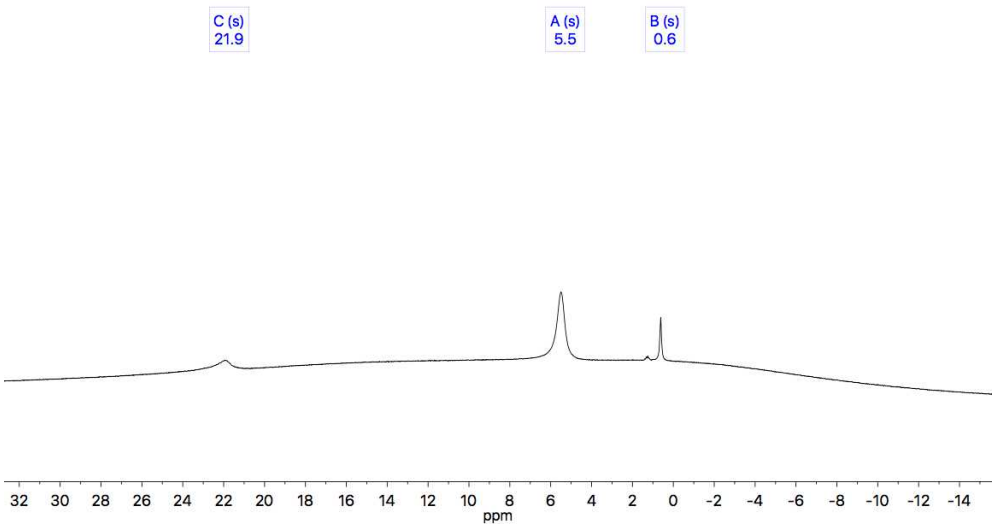


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

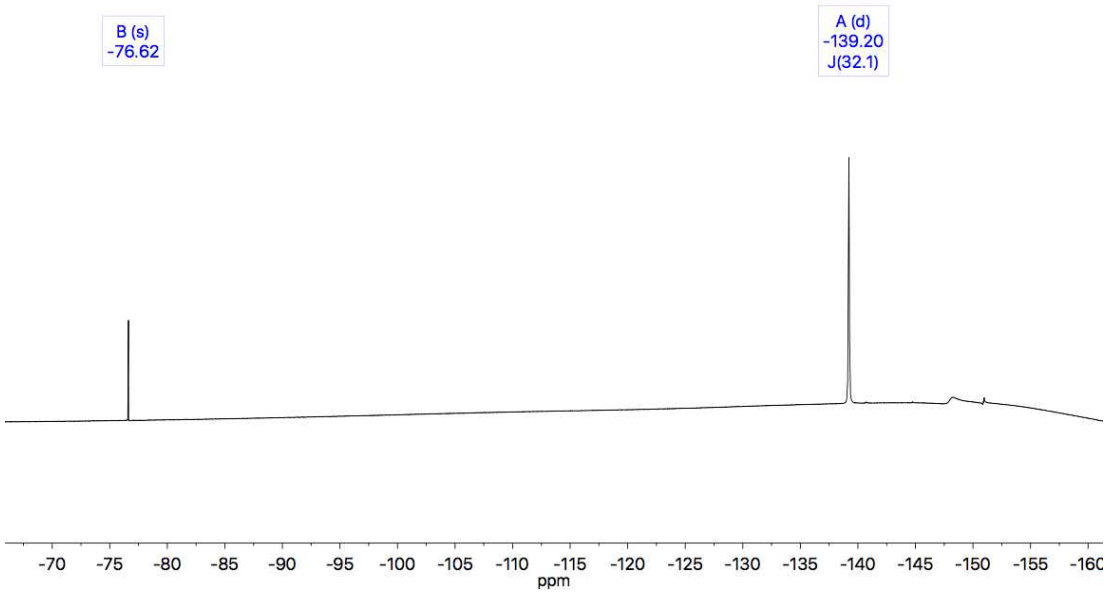
Preparation of (*R,S*)-3,5-TES-JosiphosCuF$_2$Bpin:

In a nitrogen filled glovebox, Cu(^{t}BuCN)$_2$OTf (10.6 mg, 0.028 mmol, 1 equiv) and CH_2Cl_2 (1.0 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (280 μL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, CsF (85 mg 0.58 mmol, 20 equiv) was added and the mixture vigorously stirred for 4 hours. The solution was filtered through a pipette with a glass fiber filter to remove excess CsF and CsOTf and rinsed with C_6D_6 (500 μL) into a new 1-dram vial. FBpin (210 μL (0.2 M in CH_2Cl_2, 0.042 mmol, 1.5 equiv) was added and the solution was stirred for 2 hours. The solution was concentrated to an orange foam, dissolved in 1 mL of pentane, filtered through a pipette with a glass fiber filter, and concentrated at 35 °C for 2 hours. The resulting orange foam was analyzed by NMR in C_6D_6. FBpin was prepared from adding BF_3·Et_2O (71 mg, 0.5 mmol, 1 equiv) to a stirring solution of the bis TMS ether of pinacol at 23 °C. The solution was allowed to stir for 3 hours before it was added to [Cu-F] (FBpin formation was monitored by NMR and the reaction was complete after 20 minutes. FBpin was stable in C_6D_6 and CH_2Cl_2 for at least48 hours (longer time points were not acquired). FBpin could not be isolated as it decomposed upon distillation.)

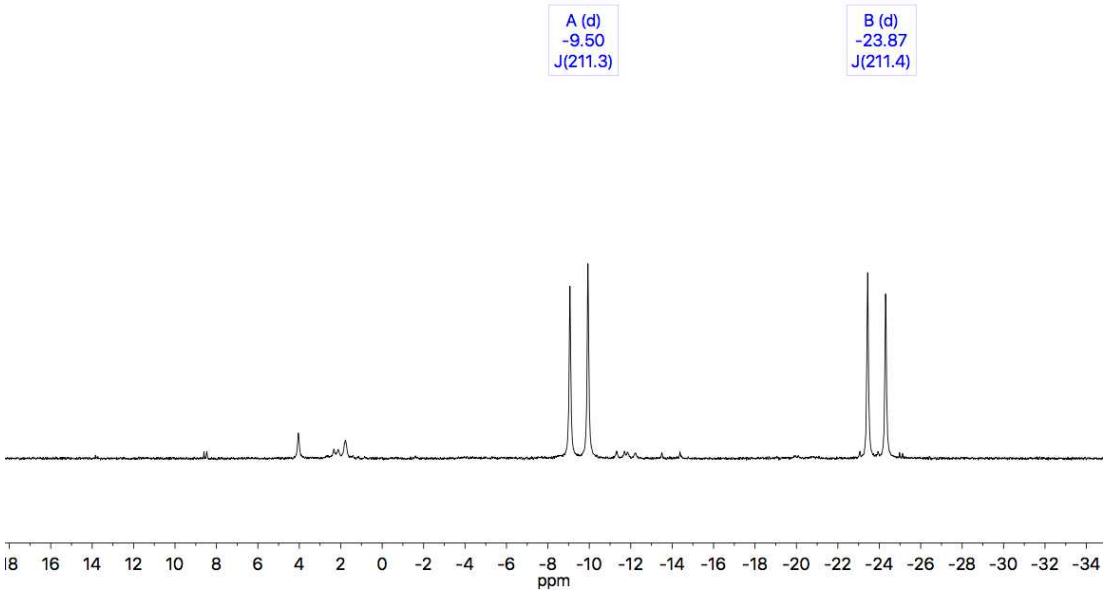




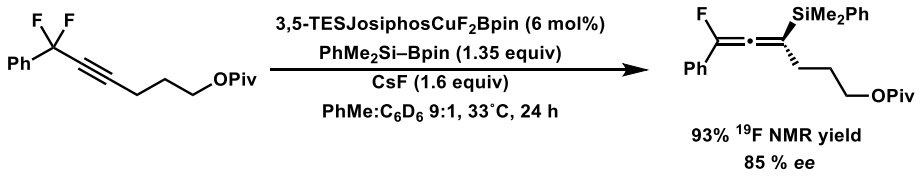
^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

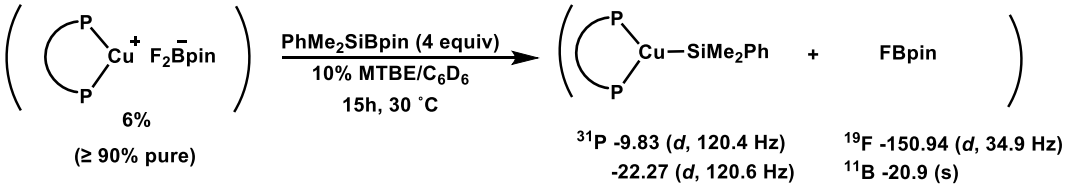


(*R,S*)-3,5-TES-JosiPhosCuF$_2$Bpin as a catalyst:

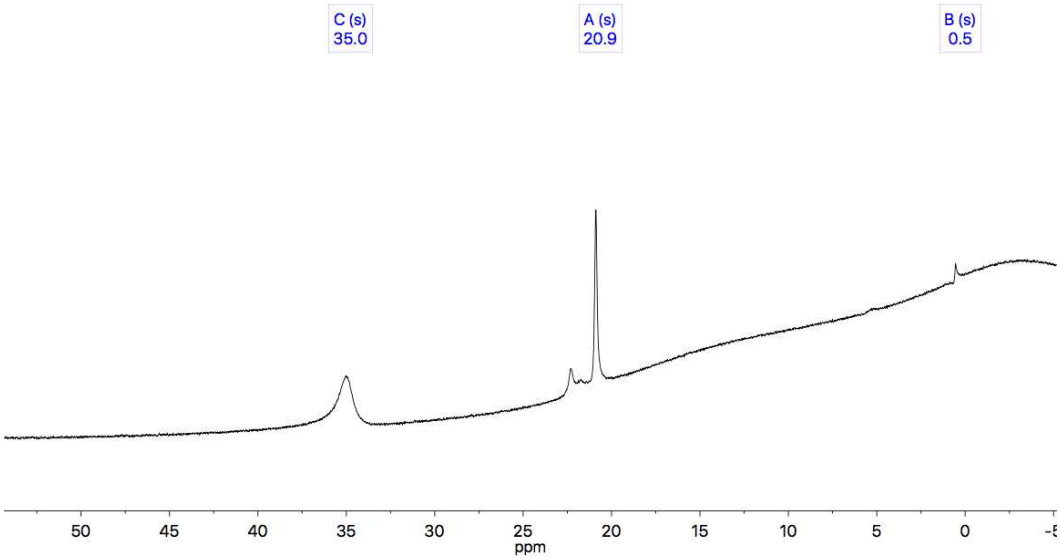
4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl pivalate **(1b):**

Crude (*R,S*)-3,5-TES-JosiphosCuF$_2$Bpin (170 µL, 0.035 M in C_6D_6, 6 mol%), was diluted with PhMe (1.3 mL) in a 1-dram vial. CsF (24 mg, 0.16 mmol, 1.6 equiv), PhMe$_2$SiBpin (37 µL, 0.135 mmol, 1.35 equiv), and **1a** (30 mg, 0.1 mmol, 1.0 equiv) were added. The vial was sealed with a ptfe-lined, thermal-rated cap, secured with electrical tape, removed from the glovebox, and placed in a 33 °C heating block set at 1000 rpm (or 10/10 stir setting on an ika stir plate). After 24 h, the reaction was removed to ambient temperature, diluted with EtOAc (500 µL) and PhF (9.5 µL, 0.1 mmol, 1.0 equiv) and the NH_4OH (1 mL) were added. The contents were vigorously stirred for 4 minutes and the layers were allowed to separate. An ^{19}F NMR was acquired. The organics were combined, washed with brine (2 mL), concentrated, purified by preparative TLC, and the enantiomeric excess was determined by a chiral HPLC.

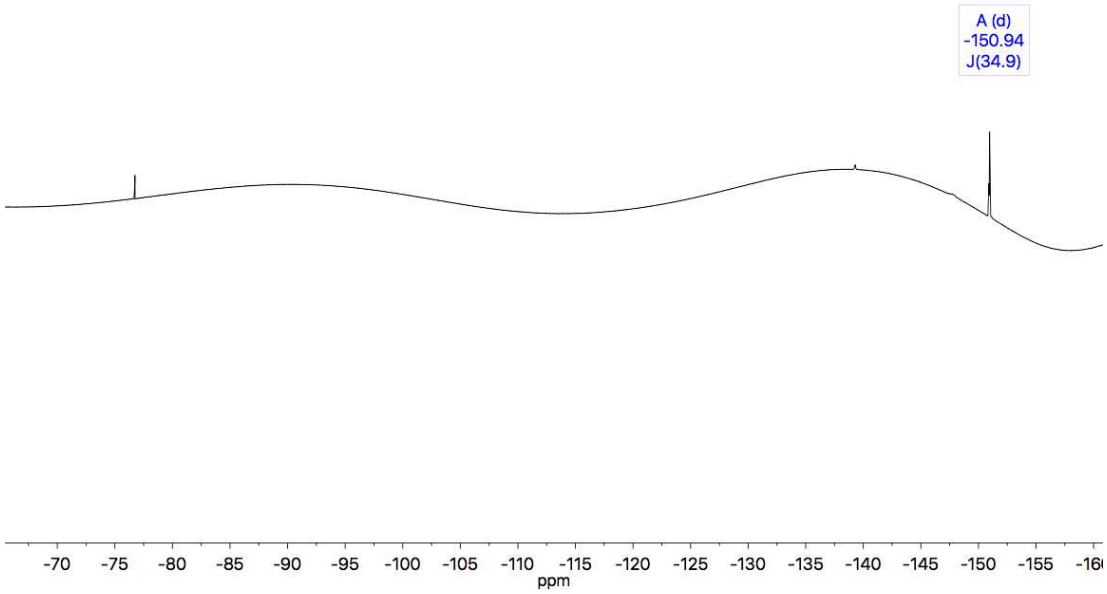
(*R,S*)-3,5-TES-JosiPhosCuF$_2$Bpin + PhMe$_2$SiBPin:



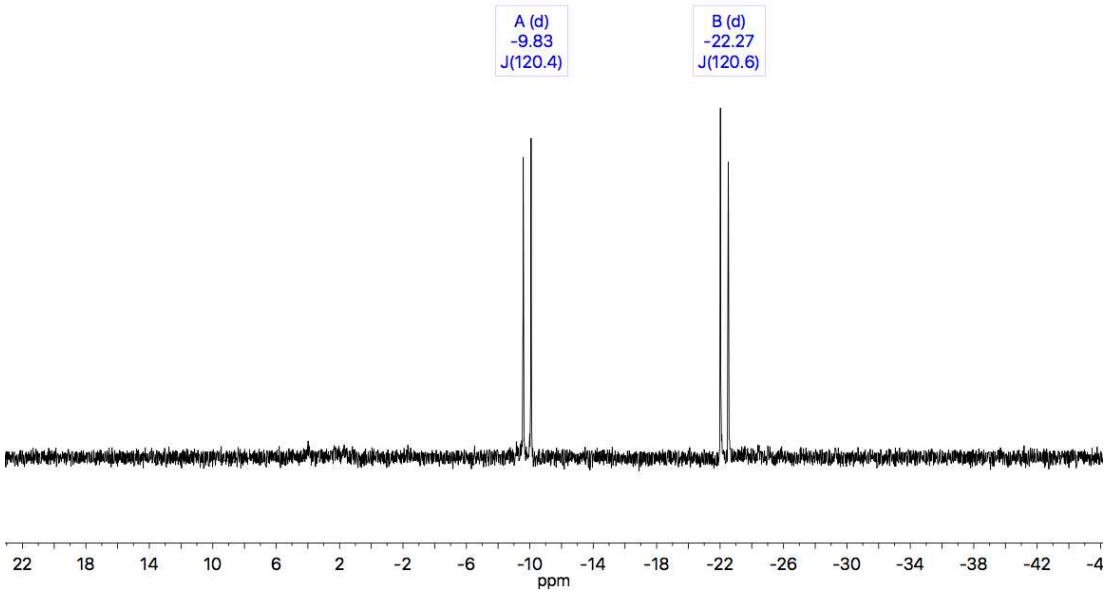
In a nitrogen filled glovebox, crude (*R,S*)-3,5-TES-JosiphosCuF$_2$Bpin (570 µL, 0.035 M in C_6D_6, 0.02 mmol), was diluted MTBE (150 µL) and C_6D_6 (750 µL) in a 1-dram vial with a stir bar. PhMe$_2$SiBpin (21 µL, 0.08 mmol, 4.0 equiv) was added, the vial sealed, and heated at 30 °C in the glovebox. After 4 hours, an aliquot was transferred to a J-Young NMR tube and analyzed.



^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



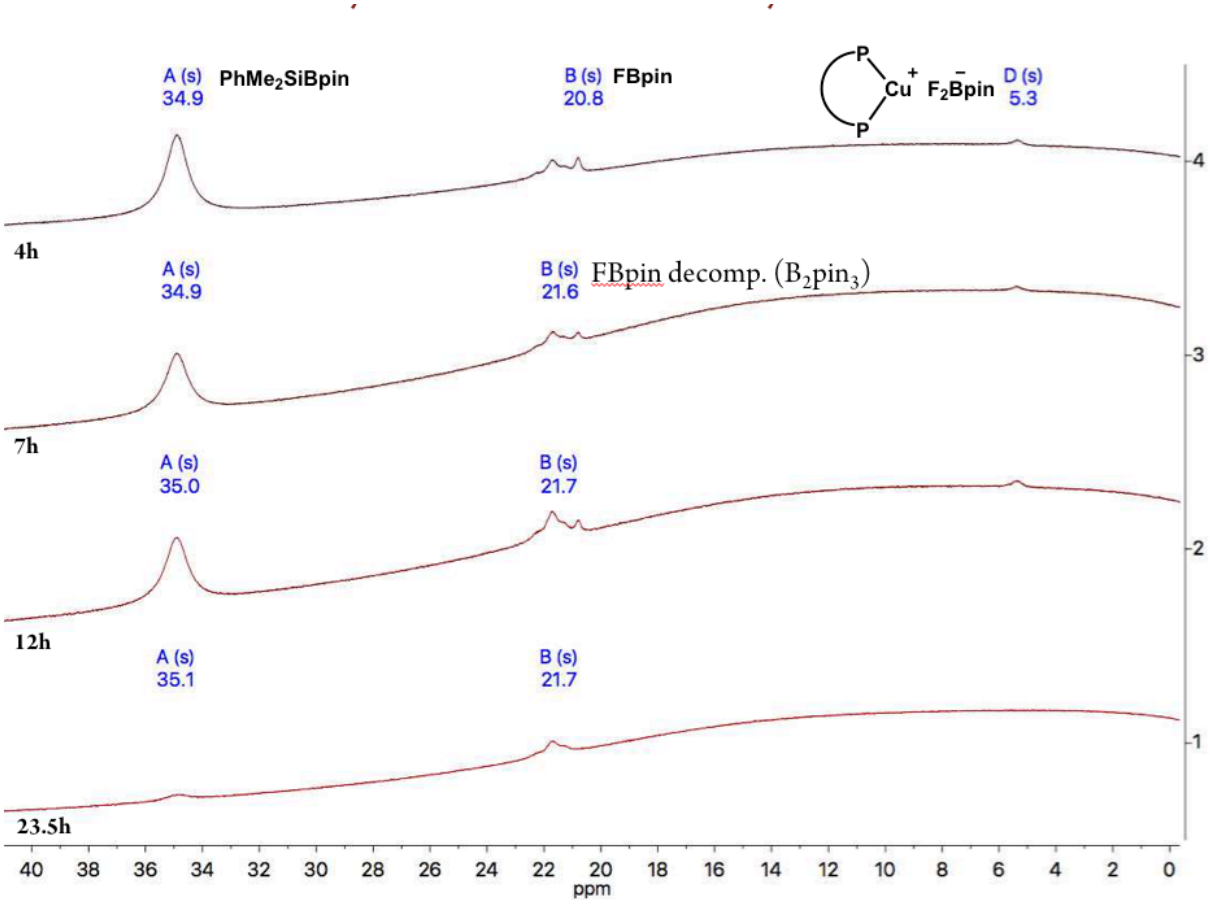
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



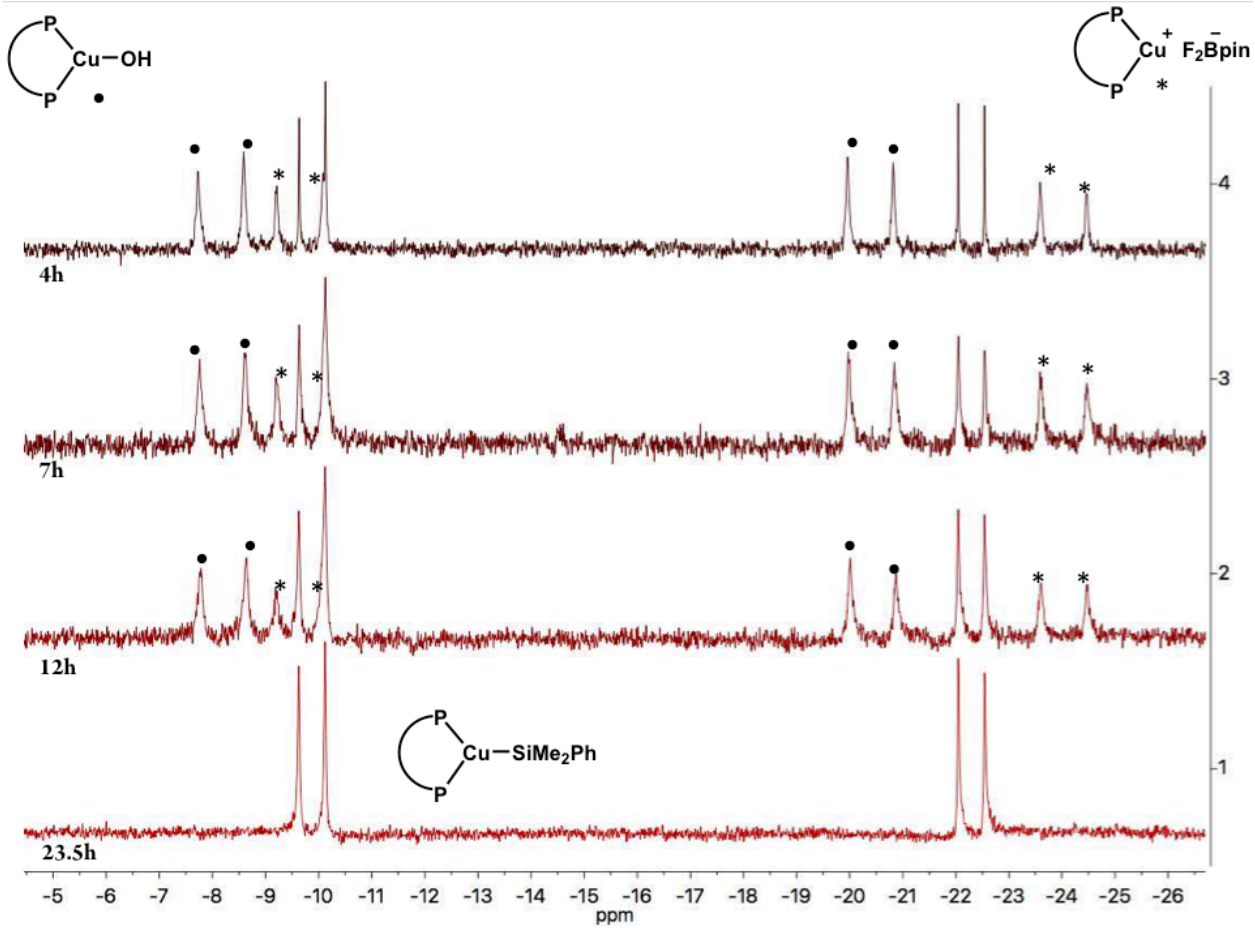
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

NMR Time Study under Catalytic Conditions:

In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (1.9 mg, 7.5 mol%) and a 20% MTBE/C_6D_6 solution (1.4 mL) were charged to a 1-dram vials containing a stir bar. (*R,S*)-3,5-TES-Josiphos (80 µL, 0.1 M in C_6D_6, 8 mol%) was added dropwise to a stirring solution of copper and after an addition 1 hour of stirring CsF (24 mg, 0.16 mmol, 1.6 equiv), $PhMe_2SiBpin$ (37 µL, 0.135 mmol, 1.35 equiv) and **1a** (30 mg, 0.1 mmol, 1.0 equiv) were added. The vials were sealed and heated at 35 °C in the glovebox. After 4, 7, 12, or 23.5 hours, a vial would be removed to 23 °C, an aliquot transferred to a J-Young NMR tube, and analyzed.



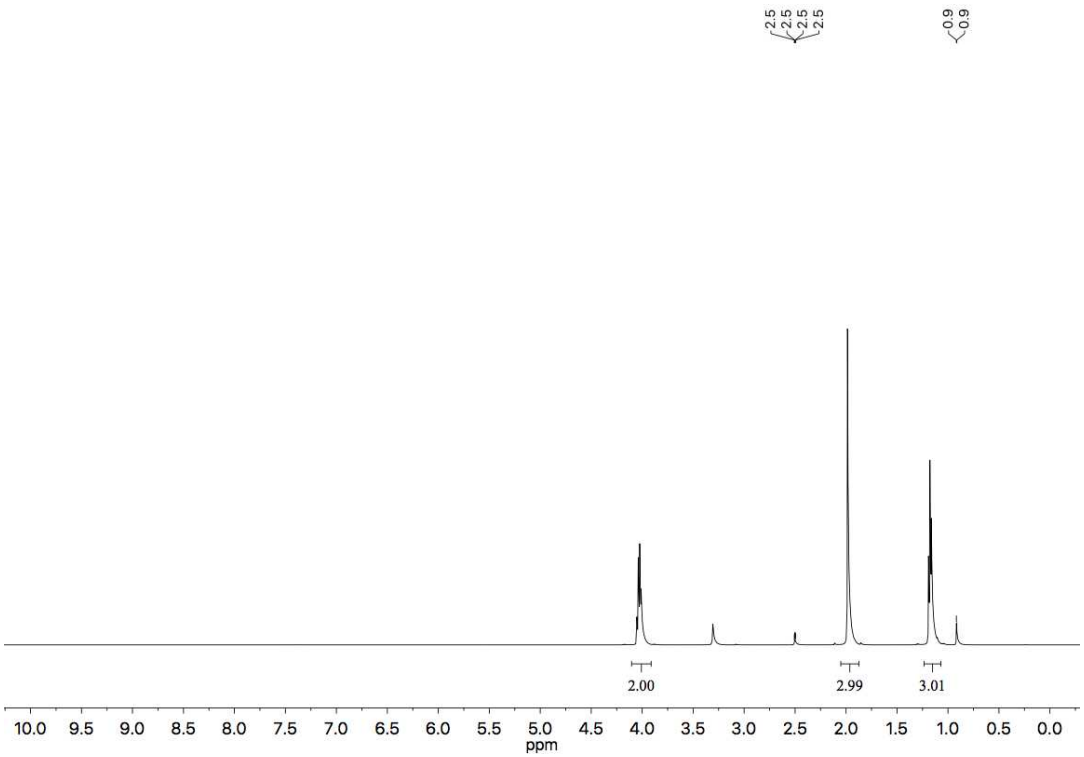
^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



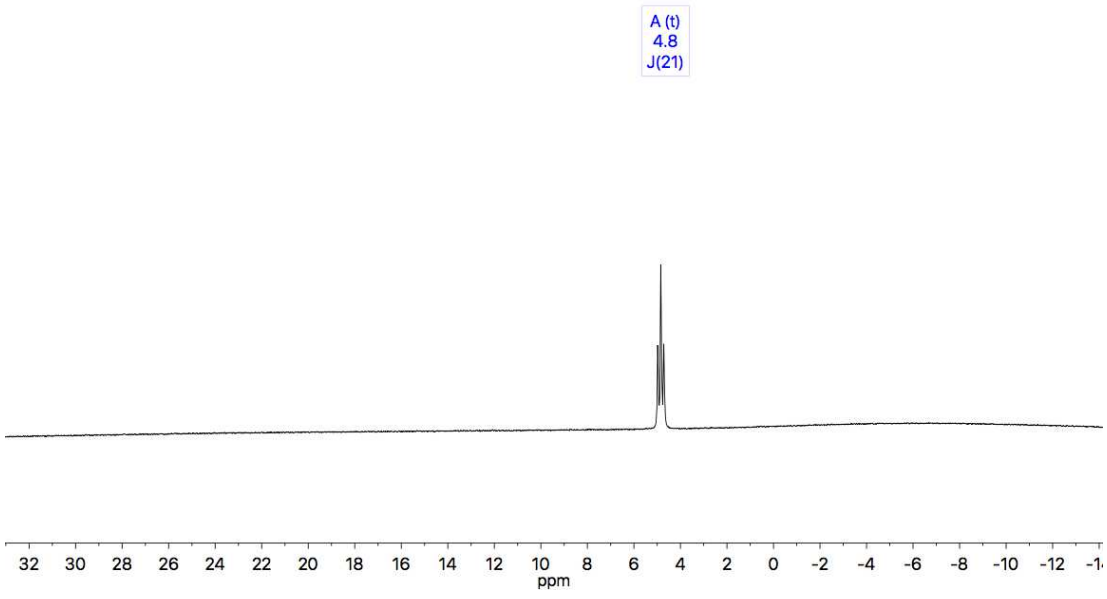
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

Identification of CsF_2Bpin:

Following general procedure D, but CuOTf·0.5C_6H_6 (1.9 mg, 7.5 mol%), (*R,S*)-3,5- TES-Josiphos (80 µL, 0.1 M in C_6D_6, 8 mol%), **1a** (30 mg, 0.2 mmol, 1.0 equiv), CsF (24 mg, 0.16 mmol, 1.6 equiv), and $PhMe_2SiBpin$ (37 µL , 0.135 mmol, 1.35 equiv) were used at 33 °C in 10% MTBE in C_6D_6 (1.4 mL). After 24 hours, the reaction was filtered over a pipette filled with a glass fiber pad and washed with EtOAc. The filter was washed with DMSO-d_6 and analyzed. EtOAc (integrated peaks) was the major species by ^{1}H NMR.



^{1}H NMR (500 MHz, DMSO-d_6)



^{11}B NMR (160 MHz, DMSO-d_6)

2.5.9 Computational Studies

I. Computational Methods

Density functional theory (DFT) calculations were carried out using the Gaussian 16 program[60] on Pitt CRC, XSEDE,[61] and the TACC Frontera supercomputers. Geometries of all stationary points were fully optimized using the dispersion-corrected[62] B3LYP-D3 functional.[62] The SDD basis set was used for copper and iron atoms, while the 6-31G(d) basis set was used for other atoms. Vibrational frequency calculations at the same level of theory of the optimization were performed to confirm if each structure is a local minimum or a transition state. Quasi-harmonic approximation with the Cramer and Truhlar approach[64] were performed using the GoodVibes package,[65] in which all vibrational frequencies below 100 cm^{-1} were shifted to 100 cm^{-1} before entropy calculations. Single-point energy calculations were carried out using the M06 functional[66] with the SDD basis set for copper and iron atoms and 6-311+G(d,p) basis set for other atoms. Solvation energy corrections were calculated using the SMD solvation model[67] and toluene as solvent in the single-point energy calculations. Non-covalent interactions between the substrate and the Josiphos ligand were dissected by using the second-generation energy decomposition analysis based on absolutely localized molecular orbitals (ALMO-EDA2)[68] algorithm, which is implemented in Q-Chem 5.3 package.[69] Following a similar procedure reported by our group,[70] the EDA calculations were performed using the optimized geometries of **TS-3** and **TS-4**, with the CuF moiety was removed to account for the non-covalent through-space interactions between the Josiphos and the allene fragments.

II. Additional Computational Results

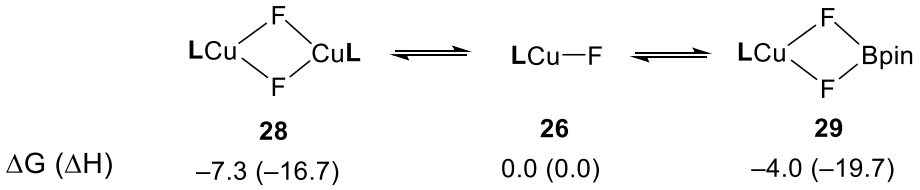
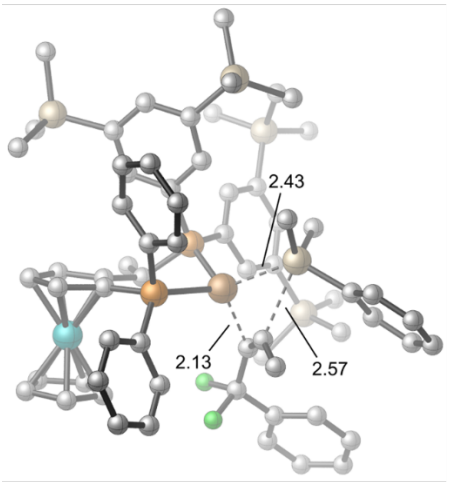
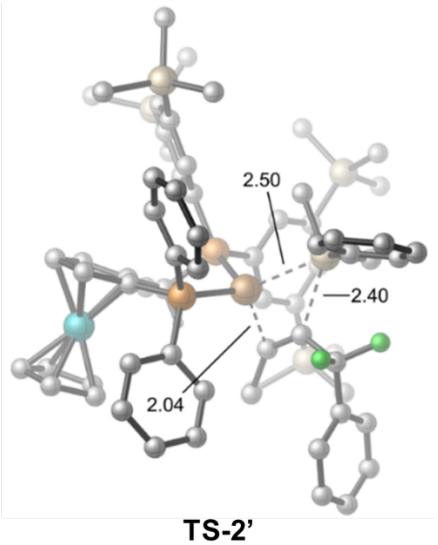


Figure S1. Relative Gibbs free energies and enthalpies of monomeric and dimer LCuF (**26** and **28**) and the heterodimer $LCuF_2Bpin$ (**29**). L = (*R*,*S*)-3,5-TMS-Josiphos. All energies (kcal/mol) are with respect to **26**.

From monomeric Cu^IF species **26**, the dimerization to form dimeric species **28** is exergonic by 7.3 kcal/mol, while the association with FBpin to form $LCuF_2Bpin$ species **29** is exergonic by 4.0 kcal/mol. Although the dimeric species **28** is 3.3 kcal/mol in energy than **29**, under catalytic conditions, the dimer dissociation is expected to be promoted by the low concentration of LCuF, and the conversion of monomeric LCuF to the more stable heterodimer **29**. Under catalytic conditions, neither **26** nor **28** was observed. This is likely due to the relatively low barrier to convert the LCuF species to silyl copper ($\Delta G‡$ = 6.7 kcal/mol with respect to the monomeric LCuF, **26**). Therefore, the catalyst resting state in the catalytic cycle is the silyl copper species **30** prior to the rate-determining transition state alkyne migratory insertion.

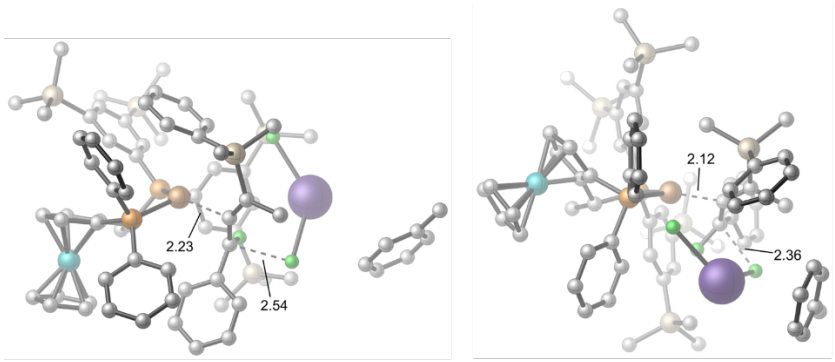


TS-2
$\Delta G‡ (\Delta H‡)$ = 19.9 (2.8)



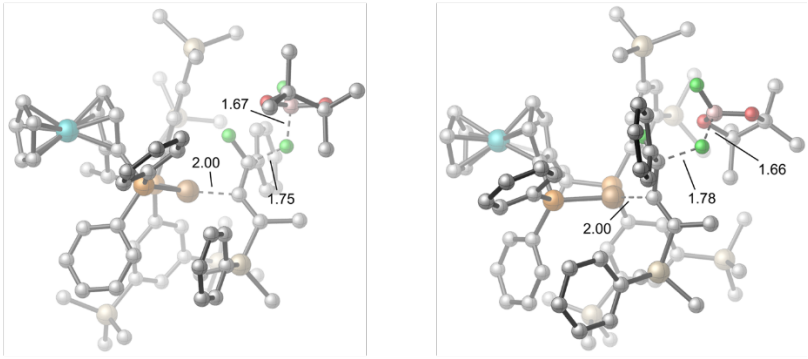
TS-2'
$\Delta G‡ (\Delta H‡)$ = 30.8 (13.5)

Figure S2. Optimized structures of the alkyne insertion transition states. Gibbs free energies and enthalpies (kcal/mol) are with respect to **30**.



TS-5
ΔG‡ (ΔH‡) = 32.7 (16.1)

TS-6
ΔG‡ (ΔH‡) = 29.0 (13.4)



TS-5-BpinF
ΔG‡ (ΔH‡) = 27.4 (11.3)

TS-6-BpinF
ΔG‡ (ΔH‡) = 24.9 (8.8)

Figure S3. Optimized structures of the *anti-β*-fluoride elimination transition states promoted by CsF(toluene) and BpinF giving the (*S*)-monofluoroallene product (**TS-5**) and the (*R*)-product (**TS-6**). Gibbs free energies and enthalpies (kcal/mol) are with respect to separated **31** and CsF(toluene) (or separated **31** and BpinF).

In all *anti*-elimination transition states, the Cu and the departing F are in an *anti*-periplanar geometry. All of the *anti-β*-fluoride elimination transition states investigated here are less stable than the *syn-β*-fluoride elimination transition state **TS-3** ($\Delta G^{\ddagger}$ = 14.6 kcal/mol with respect to **31**).

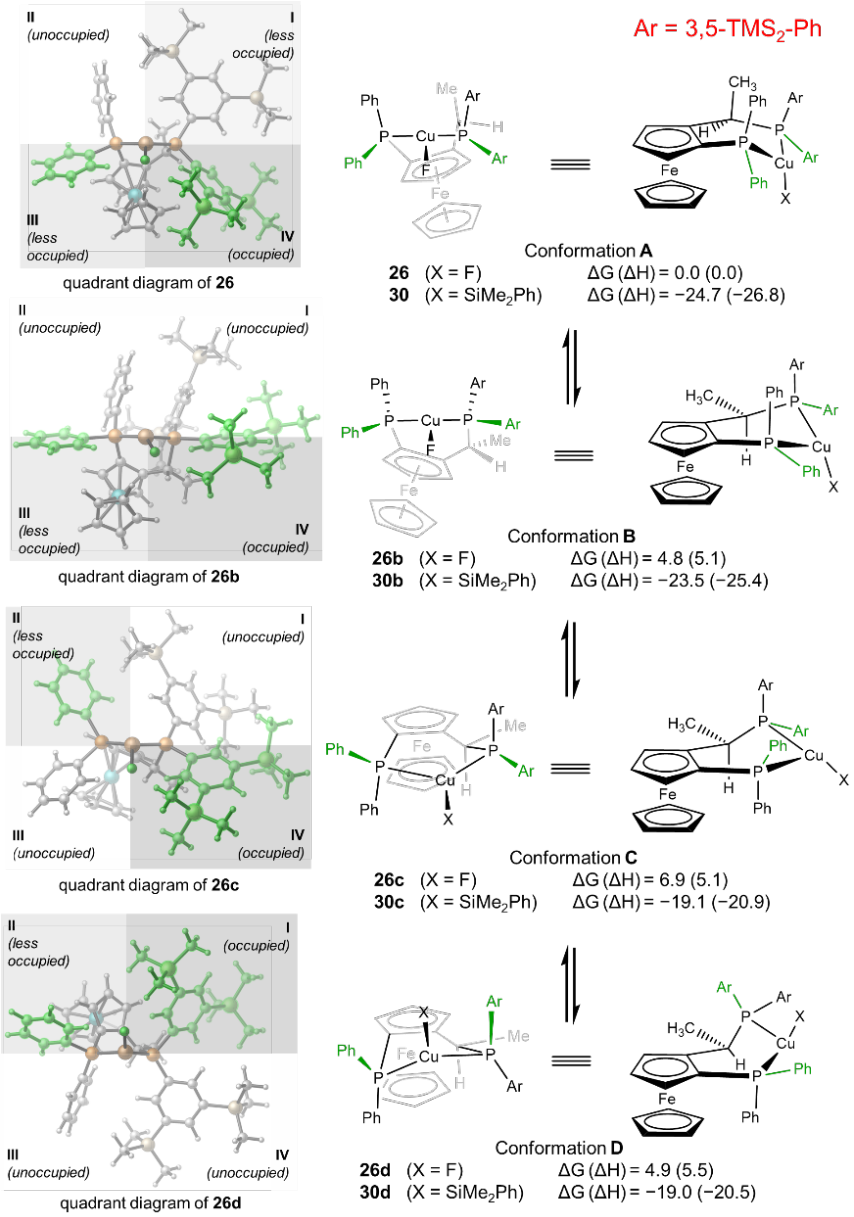


Figure S4. Conformers of LCu^{I}F and LCuSiMe$_2$Ph complexes supported by the (*R,S*)-3,5-TMS-Josiphos ligand. The *P*-phenyl and *P*-aryl groups "proximal" to the Cu center are highlighted in green. Gibbs free energies and enthalpies (in kcal/mol) are with respect to **26**.

In conformation **C**, the chiral carbon center is puckered out of plane, while two phosphorus atoms and Cu atom are nearly coplanar with the Cp ring. The steric environment of the ligand is pseudo-C_2-symmetric where the *P*-phenyl in quadrant **II** and the *P*-aryl in quadrant **IV** are in close proximity to the Cu center. In conformation **D**, the six-membered ring has a twist-boat-type geometry. The ligand in conformation **D** is pseudo-C_S-symmetric—quadrants **I** and **II** are occupied by the *P*-aryl and *P*-phenyl groups, respectively.

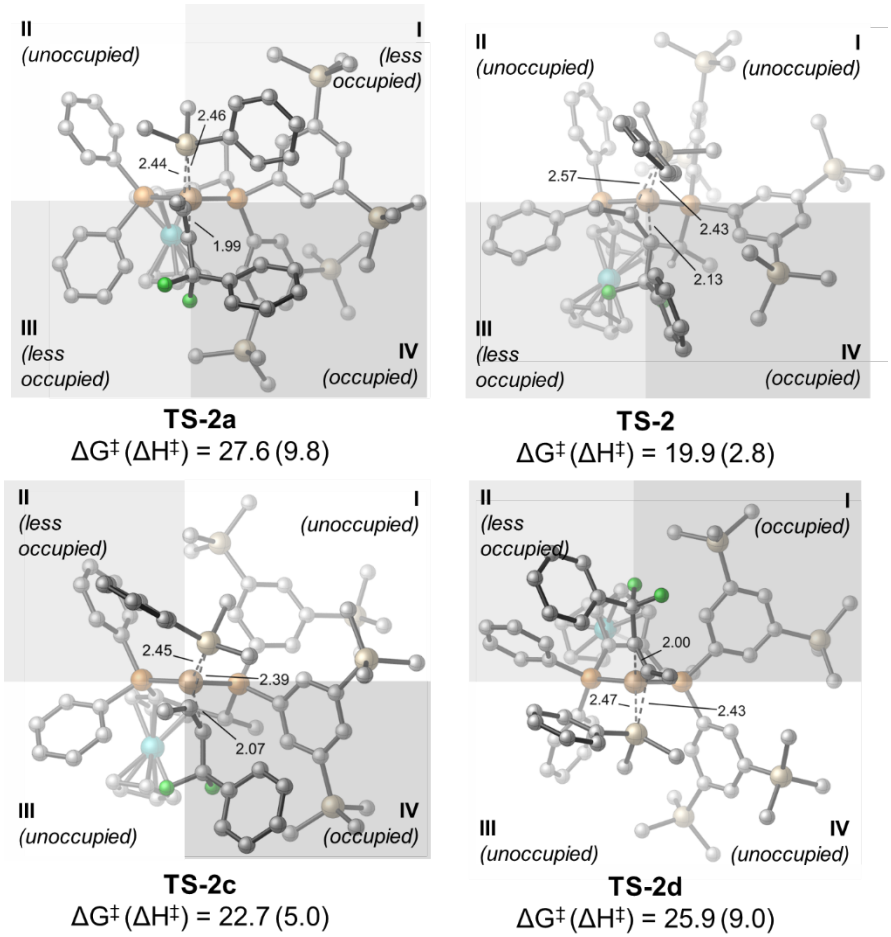


Figure S5. Conformers of the alkyne migratory insertion transition states with different conformations of the (*R,S*)-3,5-TMS-Josiphos ligand. Gibbs free energies and enthalpies (kcal/mol) are with respect to **30**.

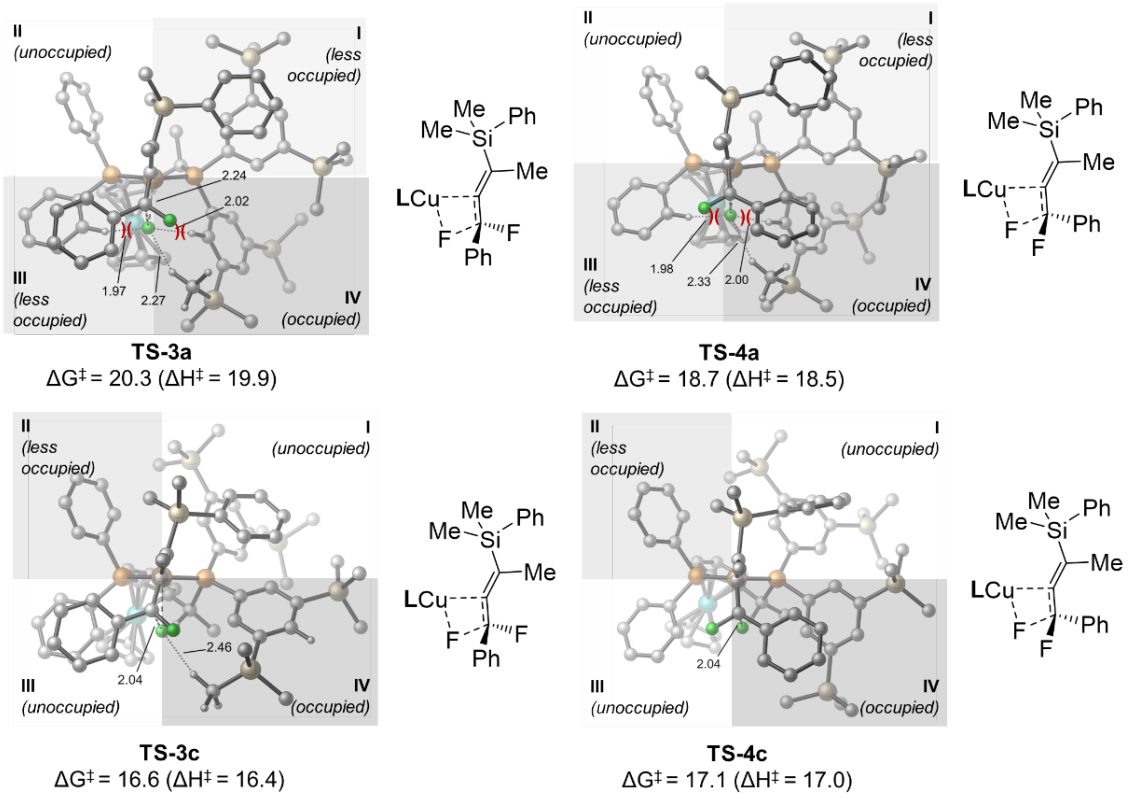


Figure S6. Optimized structures of *β*-fluoride elimination transition states with different conformations of the (*R,S*)-3,5-TMS-Josiphos ligand. Gibbs free energies and enthalpies (kcal/mol) are with respect to **31**. See Figure 3 in the manuscript for the optimized transition state structures with the most favorable ligand conformation (**B**).

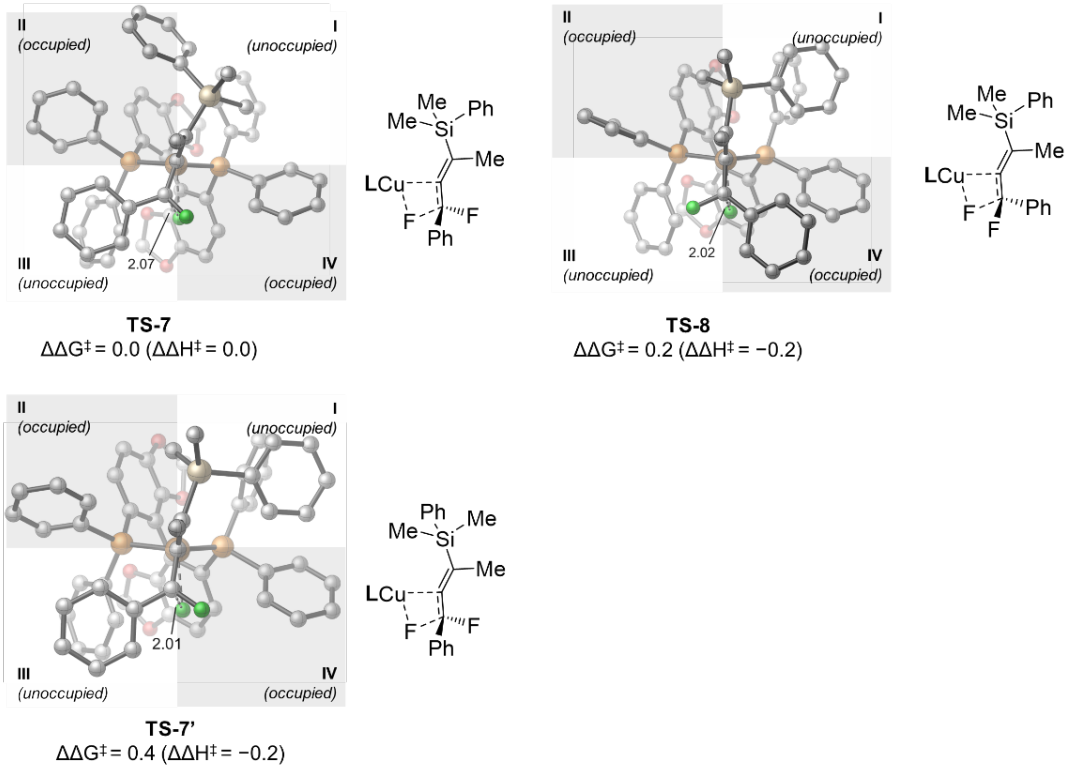


Figure S7. Optimized structures of the *syn*-*β*-fluoride elimination transition states with SegPhos ligand giving the (*S*)- and (*R*)-monofluoroallene products (**TS-7** and **TS-8**, respectively). Gibbs free energies and enthalpies (kcal/mol) are with respect to **TS-7**. A higher energy conformer of **TS-7** (**TS-7'**) is also shown.

III. Energy Values and Cartesian Coordinates

26
B3LYP-D3 SCF energy (au): -4129.85489483
B3LYP-D3 enthalpy (au): -4128.79705383
B3LYP-D3 free energy (au): -4128.97425883
M06 SCF energy (au): -4128.73334272
M06 enthalpy (au): -4127.67550172
M06 free energy (au): -4127.85270672
M06 free energy (quasi-harmonic) (au): -4127.83493489

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.259269	0.545569	1.231533
Fe	-2.527900	1.211320	4.348002
P	-1.285143	-1.415996	1.570151
P	-1.907557	2.035823	1.042103
C	-3.059249	1.525279	2.360831
C	-3.376103	0.163002	2.754927
C	-4.294775	0.251814	3.848415
H	-4.702795	-0.599325	4.379696
C	-4.544725	1.622897	4.142018
H	-5.155683	2.000850	4.951747
C	-3.784100	2.407926	3.232433
H	-3.709682	3.486728	3.224198
C	-1.097737	0.108158	5.386689
H	-0.928105	-0.950871	5.266907
C	-2.026537	0.703695	6.290734
C	-0.999005	2.393623	5.102169
H	-0.752928	3.368932	4.704578
C	-0.456843	1.151461	4.650564
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C	-4.355821	2.262599	-0.419847
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H	-6.178221	2.370082	-1.562472
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H	4.693105	-0.232268	4.081288
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H	3.442820	-0.064702	6.951595
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H	4.377342	-3.802682	4.941402
H	5.049683	-2.697090	6.151746

H 3.639754 -3.687751 6.548268
F 1.363436 1.014845 2.066376

26b

B3LYP-D3 SCF energy (au): -4129.84062031
B3LYP-D3 enthalpy (au): -4128.78308631
B3LYP-D3 free energy (au): -4128.96358431
M06 SCF energy (au): -4128.72498473
M06 enthalpy (au): -4127.66745073
M06 free energy (au): -4127.84794873
M06 free energy (quasi-harmonic) (au): -4127.82722942

Cartesian coordinates

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26c

B3LYP-D3 SCF energy (au):	-4129.83627738
B3LYP-D3 enthalpy (au):	-4128.78038938
B3LYP-D3 free energy (au):	-4128.95477238
M06 SCF energy (au):	-4128.72321485
M06 enthalpy (au):	-4127.66732685
M06 free energy (au):	-4127.84170985
M06 free energy (quasi-harmonic) (au):	-4127.82389647

Cartesian coordinates

ATOM	X	Y	Z
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Si	-4.187741	-6.800297	3.773827
Si	1.243100	-4.733105	4.232162
C	-6.176570	0.379013	-3.599706
H	-6.200167	0.715865	-4.643702
H	-7.181146	0.518882	-3.182021
H	-5.499678	1.037667	-3.043774
C	-4.007690	-1.747239	-4.337280
H	-3.701336	-2.794566	-4.228187
H	-4.097600	-1.536855	-5.410150
H	-3.200811	-1.117510	-3.948135
C	-6.997030	-2.526775	-4.223146
H	-7.968489	-2.379116	-3.736321
H	-7.125053	-2.294549	-5.287613
H	-6.740463	-3.589468	-4.141076
C	-9.599769	-2.142740	0.779068
H	-9.777904	-2.571626	-0.214424
H	-10.483599	-2.358385	1.391598
H	-9.527796	-1.054600	0.665592
C	-8.171951	-4.743314	1.691661
H	-7.375043	-5.151026	2.324726
H	-9.132273	-5.055067	2.120686
H	-8.078769	-5.207016	0.702594
C	-7.814517	-2.142479	3.319883
H	-6.938917	-2.573449	3.820877
H	-7.682948	-1.054087	3.290635
H	-8.686513	-2.358366	3.949130
C	-4.925144	-7.463252	2.160850
H	-5.315734	-6.648401	1.538628
H	-4.173892	-7.999872	1.569845
H	-5.755446	-8.152032	2.360747
C	-5.561016	-5.913269	4.753212
H	-5.466732	-4.824230	4.666823
H	-6.556914	-6.191679	4.388237
H	-5.516930	-6.163600	5.819799
C	-3.472322	-8.218812	4.798870
H	-3.056189	-7.858333	5.747329
H	-4.249220	-8.955360	5.037829
H	-2.672823	-8.740322	4.259529
C	2.395491	-4.532214	2.751106
H	2.325155	-5.394473	2.076667
H	2.132320	-3.634264	2.176270
H	3.441147	-4.441068	3.072011
C	1.497925	-3.286189	5.428576
H	1.292296	-2.336269	4.919920

H 0.831959 -3.355711 6.297093
H 2.531098 -3.250421 5.796017
C 1.532366 -6.375320 5.130116
H 0.867534 -6.486344 5.995690
H 1.360432 -7.229524 4.464094
H 2.564061 -6.442679 5.496217

26d

B3LYP-D3 SCF energy (au): -4129.83650979
B3LYP-D3 enthalpy (au): -4128.77888979
B3LYP-D3 free energy (au): -4128.95927879
M06 SCF energy (au): -4128.72442530
M06 enthalpy (au): -4127.66680530
M06 free energy (au): -4127.84719430
M06 free energy (quasi-harmonic) (au): -4127.82710251

Cartesian coordinates

ATOM X Y Z
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Fe -0.717410 -0.881134 2.661333
P 0.715960 -0.155224 -0.674159
P -2.705720 -0.402403 -1.704281
C -0.365793 -0.035284 0.794162
C -1.730068 -0.513198 0.868188
C -2.364040 0.165794 1.951786
H -3.379861 0.005594 2.285533
C -1.424981 1.059278 2.542536
H -1.601521 1.684805 3.407521
C -0.196560 0.938032 1.837213
H 0.717650 1.476528 2.043057
C -1.427868 -2.238809 4.052623
H -2.478071 -2.419038 4.241174
C -0.618036 -1.252522 4.692039
C 0.689298 -2.340687 3.130459
H 1.523120 -2.611410 2.497790
C -0.620489 -2.912220 3.086418
H -0.951529 -3.706422 2.429923
C 2.165967 0.855660 -0.209176
C 2.115149 2.216027 -0.560410
H 1.256412 2.597306 -1.115794
C 3.161281 3.060743 -0.182241
C 4.254569 2.557471 0.527618
C 4.306923 1.202266 0.868560

C	3.262650	0.351059	0.504966
H	3.300431	-0.702618	0.768665
C	1.340474	-1.867877	-0.872285
C	0.798411	-2.971260	-0.199232
H	0.057352	-2.809369	0.572327
C	1.220010	-4.268755	-0.503244
C	2.191738	-4.480524	-1.481891
C	2.743014	-3.385444	-2.155726
C	2.316637	-2.091534	-1.860680
H	2.743473	-1.248659	-2.399074
C	0.689345	-1.314535	4.120285
H	1.522285	-0.668649	4.364840
C	-2.395532	-1.425837	-0.124523
C	-3.610747	-2.173276	0.429421
H	-4.041296	-2.831017	-0.332376
H	-3.306196	-2.784693	1.287296
H	-4.391122	-1.485343	0.766391
H	-1.668747	-2.167247	-0.467713
H	-0.949871	-0.549230	5.444696
H	3.123746	4.113000	-0.450997
H	5.068758	3.218827	0.812724
H	5.158852	0.810131	1.418116
H	0.789024	-5.112380	0.029592
H	2.514661	-5.489274	-1.722983
H	3.499418	-3.541048	-2.920090
C	-4.095570	0.691455	-1.239172
C	-5.412840	0.281944	-0.984226
C	-3.746910	2.033132	-1.023906
C	-6.381922	1.188525	-0.522466
H	-5.686856	-0.757134	-1.151826
C	-4.672518	2.966311	-0.532236
H	-2.732197	2.353863	-1.252544
C	-5.983487	2.521017	-0.297020
H	-6.721404	3.231867	0.071401
C	-3.304437	-1.687022	-2.862871
C	-4.502277	-1.594504	-3.585387
C	-2.462012	-2.787012	-3.088145
C	-4.891373	-2.596096	-4.490742
H	-5.135909	-0.724398	-3.443619
C	-2.807070	-3.812252	-3.981430
H	-1.507550	-2.838567	-2.565072
C	-4.030571	-3.695536	-4.663814
H	-4.314877	-4.480163	-5.362864
Si	-4.017780	4.705211	-0.164364

Si	-8.134224	0.564158	-0.201825
Si	-1.615762	-5.262955	-4.212626
Si	-6.540848	-2.478076	-5.411573
C	-2.898388	5.241723	-1.584918
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H	-3.468536	5.351794	-2.515726
H	-2.428263	6.208942	-1.365153
C	-5.475044	5.891767	0.068466
H	-6.122761	5.580784	0.897553
H	-5.120192	6.905411	0.291130
H	-6.092255	5.947378	-0.836348
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H	-2.203881	3.849486	1.315326
H	-2.546897	5.549208	1.693925
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H	-7.381430	-1.522221	0.960380
H	-7.720409	-0.241963	2.134787
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H	-8.085158	-1.092106	-2.078836
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C	-9.262010	2.006536	0.266015
H	-8.922455	2.501578	1.183695
H	-9.295943	2.761974	-0.527961
H	-10.287497	1.658150	0.438301
C	-1.433522	-6.156946	-2.553331
H	-1.054072	-5.468677	-1.788874
H	-2.393504	-6.555518	-2.204709
H	-0.726331	-6.992613	-2.626698
C	0.069368	-4.583588	-4.737105
H	0.468268	-3.893558	-3.984290
H	0.800978	-5.391820	-4.861629
H	-0.000079	-4.041403	-5.687491
C	-2.298343	-6.440861	-5.524732
H	-2.425936	-5.935940	-6.489762
H	-1.615465	-7.284806	-5.680069
H	-3.271269	-6.852821	-5.230800
C	-7.091766	-0.670641	-5.474902
H	-7.282916	-0.268543	-4.473330
H	-6.334886	-0.036939	-5.951798
H	-8.021356	-0.572558	-6.048817
C	-6.321518	-3.155228	-7.164485

H -7.263190 -3.098562 -7.724161
H -5.567107 -2.583675 -7.717699
H -6.005573 -4.205360 -7.158720
C -7.841215 -3.505471 -4.494203
H -8.805741 -3.479352 -5.016476
H -7.532839 -4.554490 -4.410368
H -8.002159 -3.122936 -3.479201
F -0.672161 2.649745 -2.177729

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B3LYP-D3 SCF energy (au): -8259.78750969
B3LYP-D3 enthalpy (au): -8257.66983169
B3LYP-D3 free energy (au): -8257.99661469
M06 SCF energy (au): -8257.52201932
M06 enthalpy (au): -8255.40434132
M06 free energy (au): -8255.73112432
M06 free energy (quasi-harmonic) (au): -8255.69301763

Cartesian coordinates
ATOM X Y Z
Cu 0.476462 -2.845845 -1.265974
Fe -2.747827 0.793501 -0.578581
P -1.475440 -3.694152 -0.530989
P -0.330606 -1.089161 -2.382928
C -2.036270 -0.629717 -1.896895
C -2.860453 -1.242080 -0.873881
C -4.163789 -0.658645 -0.984428
H -5.006516 -0.871463 -0.342385
C -4.154936 0.308518 -2.031582
H -4.983423 0.945030 -2.314246
C -2.850008 0.332055 -2.588465
H -2.513113 0.965523 -3.396925
C -2.513026 1.143405 1.448120
H -2.708620 0.402299 2.212347
C -3.465651 2.055628 0.898591
C -1.455941 2.373940 -0.197561
H -0.708491 2.723395 -0.894844
C -1.273678 1.338494 0.769813
H -0.365600 0.771542 0.923343
C -0.539185 -1.410477 -4.183617
C -1.749301 -1.903651 -4.698331
H -2.603742 -2.046035 -4.045543
C -1.859699 -2.233059 -6.049177

H	-2.803751	-2.616446	-6.426882
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C	0.453740	-1.631478	-6.391974
H	1.324449	-1.547716	-7.036204
C	0.566442	-1.301502	-5.041446
H	1.524467	-0.968812	-4.657761
C	0.593042	0.495873	-2.286016
C	0.433585	1.562005	-3.184100
H	-0.230667	1.456945	-4.037076
C	1.143578	2.749444	-2.997247
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H	2.880633	1.908022	-0.189795
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C	-2.809190	2.816937	-0.115761
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H	-4.509845	2.128240	1.174335
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H	-3.993344	-1.656040	1.603381
H	-4.431815	-3.081821	0.647146
H	-3.260956	-3.227061	1.960549
H	-1.661660	-1.763800	0.792034
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C	-3.739178	-4.073957	-2.289552
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C	-4.303018	-4.517641	-3.498618
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C	-3.485532	-5.259365	-4.371879
H	-3.916805	-5.626635	-5.304242
C	-1.647776	-5.014680	0.727047
C	-2.845667	-5.710728	0.934885
C	-0.523214	-5.324188	1.507601
C	-2.962563	-6.690851	1.930824
H	-3.695563	-5.486936	0.293171
C	-0.592695	-6.298944	2.519146
H	0.406312	-4.793397	1.303526
C	-1.822593	-6.955688	2.710578
H	-1.893107	-7.713473	3.489981
H	-0.850714	-2.350051	-7.953409

H	2.565565	3.806192	-1.764503
F	1.986799	-2.771942	0.083630
Si	-1.043585	-6.556027	-5.259145
Si	-6.063609	-4.053682	-3.990193
Si	-4.623156	-7.554732	2.181458
Si	0.884127	-6.709627	3.627721
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H	0.420471	-7.607856	-3.502037
H	1.273130	-7.452259	-5.037303
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H	-0.042393	-4.730789	-6.630828
H	-0.094350	-6.249955	-7.548861
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H	-1.388434	-8.790946	-6.346655
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H	-7.161993	-6.221830	-3.388080
H	-8.091243	-5.383183	-4.644746
H	-6.605262	-6.250311	-5.066866
C	-6.849328	-3.021764	-2.612742
H	-6.910012	-3.581238	-1.671102
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Cu 3.112322 -4.072846 -0.926246
Fe 5.019297 -4.557741 -5.080600
P 3.730006 -6.239995 -0.947707
P 5.043666 -3.291063 -1.825245
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C 6.226104 0.261863 -3.608089
H 7.153967 0.772023 -3.854280

C	4.996158	0.838288	-3.939562
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H	2.857706	0.660329	-3.821482
C	3.841596	-1.042794	-2.941547
H	2.922305	-1.556418	-2.667898
C	4.826516	-3.500370	-6.859647
H	5.665300	-3.126706	-7.433203
C	3.905280	-6.461962	-2.830445
H	4.536592	-5.569643	-7.675116
C	3.773864	-7.902457	-3.343420
H	3.721934	-7.903986	-4.438051
H	4.617176	-8.530968	-3.037238
H	2.859283	-8.367581	-2.973611
H	3.027393	-5.896558	-3.156024
C	5.400695	-6.481324	-0.227132
C	5.600546	-5.994321	1.071410
C	6.435266	-7.189048	-0.852004
C	6.781786	-6.252882	1.784245
H	4.807440	-5.408983	1.528225
C	7.657993	-7.422140	-0.204151
H	6.289071	-7.557403	-1.860693
C	7.795080	-6.963072	1.118795
H	8.730766	-7.154908	1.643831
C	2.895084	-7.799590	-0.400106
C	3.613952	-8.803935	0.258905
C	1.524975	-8.005273	-0.652678
C	3.023165	-10.015676	0.647725
H	4.663843	-8.642296	0.474723
C	0.899404	-9.218909	-0.317811
H	0.952333	-7.209118	-1.125877
C	1.672243	-10.205538	0.328747
H	1.198885	-11.148960	0.598455
H	9.418208	-2.590707	1.821337
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F	1.610131	-4.102520	-2.451468
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Si	9.084365	-8.283178	-1.088879
Si	4.095795	-11.264790	1.571721
Si	-0.901289	-9.638514	-0.722697
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H	6.015807	-3.845676	4.945828
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H	9.390608	-6.269706	3.844393
C	6.324478	-7.149193	4.677833
H	6.904249	-8.063857	4.504174
H	6.394629	-6.903500	5.744897
H	5.275342	-7.379185	4.455045
C	10.524828	-7.057257	-1.198132
H	10.821241	-6.711330	-0.200156
H	11.407061	-7.502325	-1.674197
H	10.235247	-6.175181	-1.782650
C	9.604969	-9.806195	-0.093270
H	8.779484	-10.524643	-0.021556
H	10.459502	-10.316887	-0.553942
H	9.892713	-9.530539	0.928722
C	8.530752	-8.783778	-2.826026
H	7.695037	-9.493449	-2.791537
H	8.204393	-7.911343	-3.405111
H	9.351022	-9.263464	-3.373588
C	4.482249	-10.572759	3.290123
H	4.960814	-9.589175	3.210435
H	3.566885	-10.448417	3.879592
H	5.159885	-11.230897	3.848007
C	3.182902	-12.914913	1.710231
H	2.934363	-13.319498	0.721771
H	3.796280	-13.659826	2.231286
H	2.247390	-12.806487	2.272420
C	5.720739	-11.470247	0.617887
H	6.398996	-12.162290	1.132340
H	5.545515	-11.856696	-0.393116
H	6.238797	-10.507742	0.522025
C	-1.724487	-10.255624	0.866695
H	-1.740551	-9.456185	1.613972
H	-2.758381	-10.573124	0.684618
H	-1.184908	-11.108029	1.296336
C	-1.804718	-8.144779	-1.419865
H	-2.884681	-8.323484	-1.473912
H	-1.652320	-7.255987	-0.803488
H	-1.464825	-7.908419	-2.430837
C	-0.901829	-11.029975	-2.009835
H	-0.433578	-10.695298	-2.943624
H	-0.348300	-11.907968	-1.655746
H	-1.924777	-11.350392	-2.244618

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B3LYP-D3 SCF energy (au):	-4641.09716281
B3LYP-D3 enthalpy (au):	-4639.84102981
B3LYP-D3 free energy (au):	-4640.04628481
M06 SCF energy (au):	-4639.79681005
M06 enthalpy (au):	-4638.54067705
M06 free energy (au):	-4638.74593205
M06 free energy (quasi-harmonic) (au):	-4638.72038624

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.431460	-0.761634	-0.003628
Fe	-1.484895	2.450943	2.879432
P	-2.142825	-1.753121	1.081692
P	-1.313143	1.235723	-0.377047
C	-2.237425	1.665011	1.137290
C	-2.585798	0.814244	2.270331
C	-3.367186	1.622638	3.158552
H	-3.756900	1.304386	4.114547
C	-3.490666	2.936600	2.622157
H	-3.983238	3.773490	3.099604
C	-2.800494	2.966892	1.383518
H	-2.676373	3.828754	0.743392
C	0.080805	1.761910	4.053060
H	0.201374	0.731438	4.359474
C	-0.647954	2.779679	4.741664
C	0.176624	3.684450	2.781218
H	0.371126	4.362931	1.961158
C	0.593014	2.319854	2.846268
H	1.171090	1.778512	2.111694
C	-2.611917	1.041424	-1.669276
C	-3.955350	1.390944	-1.482893
H	-4.277449	1.829089	-0.545129
C	-4.891426	1.150028	-2.490866
H	-5.933422	1.412329	-2.329686
C	-4.496206	0.566249	-3.694797
C	-3.157675	0.211841	-3.888391
H	-2.844442	-0.252270	-4.819881
C	-2.223808	0.440585	-2.878853
H	-1.186885	0.143068	-3.022000
C	-0.425967	2.772276	-0.841284
C	-1.068889	3.872482	-1.429643
H	-2.126023	3.815868	-1.676470

C	-0.350194	5.034756	-1.711280
H	-0.852915	5.884750	-2.165306
C	1.015165	5.102472	-1.415822
C	1.663294	3.998547	-0.856845
H	2.727894	4.039062	-0.641166
C	0.950984	2.830126	-0.576703
H	1.466845	1.970300	-0.155291
C	-0.586494	3.970940	3.954610
H	-1.074219	4.909667	4.184884
C	-2.198209	-0.628036	2.591811
H	-1.186472	2.661025	5.673263
C	-2.967462	-1.213491	3.786479
H	-2.765606	-0.626956	4.689956
H	-4.049441	-1.227270	3.620417
H	-2.642280	-2.238997	3.979800
H	-1.136533	-0.627481	2.850438
C	-3.821698	-1.816706	0.365040
C	-4.027274	-2.654722	-0.744956
C	-4.882786	-1.027077	0.817997
C	-5.268480	-2.734434	-1.387075
H	-3.195820	-3.258482	-1.101979
C	-6.141474	-1.054385	0.191049
H	-4.726979	-0.357441	1.656579
C	-6.309127	-1.917811	-0.900064
H	-7.278568	-1.953826	-1.395827
C	-1.813266	-3.422885	1.751667
C	-2.770905	-4.440367	1.815565
C	-0.492379	-3.692858	2.142572
C	-2.427105	-5.735540	2.238367
H	-3.791266	-4.224633	1.509170
C	-0.109682	-4.962556	2.599794
H	0.243045	-2.896073	2.078831
C	-1.094892	-5.967312	2.627289
H	-0.812362	-6.966687	2.952814
H	-5.228372	0.375782	-4.474294
H	1.573071	6.009039	-1.635351
Si	-5.545058	-3.890000	-2.857640
Si	-7.507436	0.070775	0.850289
Si	-3.752310	-7.080537	2.213815
Si	1.702596	-5.242614	3.090585
C	-3.958597	-4.859467	-3.195504
H	-3.665192	-5.457900	-2.324540
H	-4.097437	-5.547098	-4.038420
H	-3.122341	-4.194970	-3.444354

C	-6.013961	-2.849381	-4.367251
H	-6.222202	-3.478354	-5.241303
H	-6.907233	-2.244495	-4.168619
H	-5.200316	-2.162234	-4.625159
C	-6.952216	-5.081532	-2.431862
H	-7.865550	-4.539504	-2.158014
H	-7.192942	-5.733187	-3.280817
H	-6.676687	-5.721038	-1.584840
C	-9.033327	-0.065762	-0.257499
H	-9.434102	-1.086416	-0.269394
H	-9.831049	0.598553	0.095732
H	-8.802488	0.214488	-1.292496
C	-6.871106	1.854063	0.874573
H	-5.928790	1.931991	1.430399
H	-6.691216	2.229973	-0.139437
H	-7.596541	2.523684	1.353168
C	-7.919938	-0.453592	2.621437
H	-7.027362	-0.405187	3.257729
H	-8.681673	0.198516	3.066212
H	-8.294916	-1.483222	2.654980
C	-4.999123	-6.773472	3.605155
H	-4.515284	-6.825233	4.587721
H	-5.454182	-5.779890	3.511481
H	-5.807636	-7.514912	3.587973
C	-2.948226	-8.778340	2.424409
H	-3.700632	-9.574583	2.372519
H	-2.205702	-8.968409	1.640399
H	-2.441059	-8.866723	3.392702
C	-4.648410	-6.978407	0.545343
H	-3.955555	-7.161403	-0.284941
H	-5.458406	-7.715068	0.477552
H	-5.088600	-5.984785	0.394993
C	2.787493	-5.119207	1.549943
H	2.446844	-5.793261	0.754935
H	2.780274	-4.090172	1.173187
H	3.828586	-5.373966	1.787480
C	2.198757	-3.883233	4.305456
H	2.168364	-2.912371	3.798429
H	1.540254	-3.850820	5.181605
H	3.226957	-4.034574	4.658595
C	1.854110	-6.955746	3.885944
H	1.587677	-7.754567	3.182873
H	2.885480	-7.136815	4.212336
H	1.205710	-7.052797	4.765272

F 0.926863 -0.721418 2.119681
B 2.060351 -0.865803 1.244796
O 3.094251 -1.698267 1.759327
O 2.613905 0.420963 0.923597
C 4.223274 -0.856495 2.035923
C 4.043086 0.293614 0.975537
C 4.096235 -0.342110 3.479446
C 5.497113 -1.683946 1.880936
C 4.636720 1.642525 1.376652
C 4.538103 -0.113270 -0.420829
H 4.009108 -1.201550 4.151523
H 4.966878 0.250383 3.782444
H 3.196547 0.270457 3.592710
H 6.389956 -1.056250 1.986892
H 5.528256 -2.457692 2.655693
H 5.527102 -2.182093 0.909128
H 5.717828 1.563894 1.540604
H 4.468165 2.373513 0.576978
H 4.168072 2.025450 2.286367
H 4.184750 0.625599 -1.147959
H 5.631870 -0.156615 -0.471908
H 4.130413 -1.088497 -0.701571
F 1.451912 -1.505482 0.040336

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B3LYP-D3 SCF energy (au): -4631.00576963
B3LYP-D3 enthalpy (au): -4629.77392063
B3LYP-D3 free energy (au): -4629.97271463
M06 SCF energy (au): -4629.68589009
M06 enthalpy (au): -4628.45404109
M06 free energy (au): -4628.65283509
M06 free energy (quasi-harmonic) (au): -4628.63180246

Cartesian coordinates
ATOM X Y Z
Cu -0.399474 0.668091 0.878070
Fe -2.503153 1.443033 4.353867
P -1.599410 -1.174831 1.597992
P -2.107543 2.186422 1.060519
C -3.226055 1.779830 2.440103
C -3.567916 0.435651 2.872154
C -4.361182 0.567162 4.054899
H -4.750843 -0.263475 4.630458

C	-4.512068	1.948740	4.366018
H	-5.017679	2.356379	5.232038
C	-3.816587	2.696393	3.375803
H	-3.693014	3.770302	3.356690
C	-1.073496	0.256153	5.300050
H	-1.035370	-0.821510	5.246813
C	-1.797325	1.023501	6.259768
C	-0.772624	2.492567	4.802391
H	-0.480528	3.401954	4.295587
C	-0.439364	1.163732	4.398270
H	0.163171	0.894515	3.539985
C	-3.182968	2.244238	-0.426560
C	-4.576516	2.392678	-0.377962
H	-5.074399	2.498288	0.582340
C	-5.325576	2.381719	-1.556619
H	-6.405929	2.491239	-1.510705
C	-4.689888	2.226647	-2.791203
C	-3.300876	2.078664	-2.847496
H	-2.803825	1.944188	-3.803786
C	-2.550685	2.080145	-1.671126
H	-1.471112	1.946461	-1.706750
C	-1.654679	3.942818	1.352300
C	-2.556546	5.008897	1.218816
H	-3.579619	4.817306	0.905735
C	-2.140147	6.316265	1.473991
H	-2.843370	7.138192	1.368193
C	-0.819380	6.569454	1.857736
C	0.088931	5.514550	1.973460
H	1.121032	5.708364	2.252941
C	-0.325801	4.206404	1.714986
H	0.377823	3.379387	1.776621
C	-1.609671	2.405596	5.954339
H	-2.063874	3.239747	6.473661
C	-3.386085	-0.890190	2.162660
H	-2.414317	0.626075	7.055444
C	-4.393272	-1.011372	1.000099
H	-5.401055	-0.785816	1.367258
H	-4.171618	-0.305396	0.194935
H	-4.391458	-2.019924	0.577563
H	-3.628265	-1.669887	2.892043
C	-1.690688	-2.397803	0.226578
C	-1.320265	-3.737392	0.389452
C	-1.943580	-1.921671	-1.069479
C	-1.186327	-4.608116	-0.702666

H	-1.082000	-4.098895	1.383017
C	-1.848723	-2.759129	-2.192176
H	-2.176641	-0.865387	-1.201700
C	-1.461883	-4.096170	-1.981827
H	-1.344016	-4.747612	-2.845554
C	-0.835652	-2.149407	2.949008
C	-1.521692	-3.121568	3.687721
C	0.533305	-1.957237	3.185556
C	-0.874337	-3.900644	4.660524
H	-2.575659	-3.300832	3.484803
C	1.219010	-2.689345	4.167652
H	1.056768	-1.219047	2.582106
C	0.490051	-3.651110	4.889527
H	1.003069	-4.231946	5.654073
H	-5.275146	2.211317	-3.706499
H	-0.497156	7.588848	2.052715
Si	-0.551987	-6.361904	-0.385612
Si	-2.137769	-2.034724	-3.913712
Si	-1.833401	-5.277333	5.527221
Si	3.059836	-2.390035	4.501717
C	0.695994	-6.283367	1.036155
H	0.218822	-5.984151	1.977596
H	1.164639	-7.261597	1.200544
H	1.488309	-5.555038	0.827619
C	0.282638	-7.007007	-1.956099
H	0.688217	-8.013533	-1.797078
H	-0.419266	-7.064306	-2.796854
H	1.112277	-6.356666	-2.258521
C	-1.988989	-7.495553	0.101622
H	-2.753172	-7.535541	-0.683682
H	-1.640032	-8.519690	0.284374
H	-2.470548	-7.140020	1.020771
C	-1.825304	-3.362478	-5.223235
H	-2.505083	-4.215106	-5.106390
H	-1.976517	-2.954305	-6.229895
H	-0.797919	-3.742150	-5.171066
C	-0.935145	-0.592833	-4.139249
H	-1.065208	0.143894	-3.339275
H	0.104072	-0.938893	-4.095269
H	-1.082819	-0.080193	-5.097986
C	-3.920819	-1.410134	-4.028840
H	-4.127249	-0.663875	-3.253215
H	-4.114524	-0.939608	-5.001199
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C	-3.383526	-4.534707	6.320942
H	-3.116643	-3.806242	7.095977
H	-3.998005	-4.015160	5.575149
H	-4.008053	-5.307798	6.785000
C	-0.745339	-6.094845	6.837582
H	-1.292698	-6.892157	7.354545
H	0.150185	-6.544013	6.391939
H	-0.416553	-5.372579	7.594345
C	-2.337481	-6.536599	4.204579
H	-1.453590	-6.972523	3.723548
H	-2.933042	-7.356457	4.624203
H	-2.934880	-6.057415	3.418712
C	3.494660	-0.652917	3.909074
H	3.386492	-0.576196	2.822673
H	2.842718	0.098839	4.370647
H	4.532427	-0.398264	4.156362
C	3.353806	-2.538903	6.367138
H	2.753227	-1.807729	6.921361
H	3.098721	-3.536591	6.744703
H	4.408541	-2.357634	6.608087
C	4.072254	-3.693156	3.581523
H	3.892100	-3.627791	2.502878
H	5.147417	-3.555908	3.752982
H	3.805631	-4.704957	3.910884
Si	1.724793	0.818627	0.024989
C	1.703609	1.501841	-1.774314
C	2.986136	1.943611	0.936650
C	2.559183	-0.901506	-0.148720
H	1.251708	2.503018	-1.799994
H	2.714427	1.574091	-2.198690
H	1.111868	0.853655	-2.432088
H	2.622448	2.979853	0.928527
H	3.124619	1.652656	1.984846
H	3.973154	1.944282	0.453386
C	1.803820	-1.970559	-0.671764
C	3.888988	-1.183784	0.214337
C	2.341985	-3.248196	-0.832852
H	0.767427	-1.801331	-0.952384
C	4.435660	-2.464290	0.072503
H	4.517869	-0.391537	0.615311
C	3.663372	-3.503302	-0.452510
H	1.727529	-4.040616	-1.252677
H	5.465287	-2.650201	0.370993
H	4.086276	-4.498774	-0.566487

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B3LYP-D3 SCF energy (au): -5216.59938152
B3LYP-D3 enthalpy (au): -5215.20157352
B3LYP-D3 free energy (au): -5215.42340152
M06 SCF energy (au): -5215.05555271
M06 enthalpy (au): -5213.65774471
M06 free energy (au): -5213.87957271
M06 free energy (quasi-harmonic) (au): -5213.85593019

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.611020	-1.224608	0.056351
Fe	-1.780271	2.019888	3.161777
P	-2.341198	-2.152844	1.246363
P	-1.579682	0.837908	-0.126267
C	-2.496733	1.239926	1.402738
C	-2.803286	0.355112	2.514925
C	-3.622364	1.101472	3.421305
H	-3.992620	0.745442	4.371994
C	-3.809714	2.418626	2.909821
H	-4.344163	3.220547	3.402178
C	-3.121755	2.506523	1.672722
H	-3.053082	3.382907	1.044632
C	-0.313974	1.387609	4.477831
H	-0.288198	0.397613	4.915158
C	-0.994387	2.526017	5.009757
C	-0.041758	3.136313	2.993771
H	0.226349	3.700596	2.111414
C	0.274116	1.763212	3.234198
H	0.818628	1.102855	2.574744
C	-2.852873	1.091399	-1.434434
C	-2.434768	1.296763	-2.760873
H	-1.375494	1.361128	-2.990686
C	-3.370570	1.424645	-3.786581
H	-3.031511	1.586402	-4.806324
C	-4.737828	1.340953	-3.505287
C	-5.159538	1.127831	-2.192157
H	-6.218146	1.046990	-1.962176
C	-4.225384	1.004339	-1.162240
H	-4.571366	0.828327	-0.150781
C	-0.442647	2.262318	-0.377072
C	-0.870308	3.548993	-0.739545

H	-1.916701	3.729983	-0.967947
C	0.049114	4.594510	-0.828289
H	-0.289433	5.589099	-1.107010
C	1.403847	4.363870	-0.562956
C	1.840084	3.080170	-0.228903
H	2.889287	2.883447	-0.029652
C	0.919771	2.033457	-0.145926
H	1.252180	1.030147	0.100992
C	-0.822091	3.606785	4.092161
H	-1.251030	4.595899	4.189512
C	-2.303434	-1.054721	2.786043
H	-1.571947	2.553296	5.924839
C	-2.901023	-1.672544	4.058972
H	-2.668384	-1.042436	4.925595
H	-3.988740	-1.784732	4.000917
H	-2.474272	-2.661559	4.240421
H	-1.221093	-0.989633	2.936272
C	-4.014785	-2.063059	0.521374
C	-4.136867	-2.489335	-0.811680
C	-5.134797	-1.533116	1.170990
C	-5.353499	-2.401558	-1.502472
H	-3.251323	-2.875314	-1.314102
C	-6.369663	-1.402759	0.512499
H	-5.037417	-1.181505	2.192871
C	-6.452281	-1.852338	-0.815490
H	-7.398949	-1.748963	-1.342223
C	-2.224636	-3.851132	1.918257
C	-3.337994	-4.690970	2.033188
C	-0.955493	-4.341915	2.257615
C	-3.210574	-6.019277	2.469455
H	-4.314402	-4.307406	1.749092
C	-0.779727	-5.661523	2.705208
H	-0.093178	-3.689953	2.136068
C	-1.923336	-6.475956	2.805313
H	-1.803448	-7.505968	3.135493
H	-5.466513	1.436250	-4.305855
H	2.116107	5.182190	-0.628475
Si	0.812449	-2.910278	-2.655477
C	-0.146693	-1.355339	-3.169425
H	0.468454	-0.455443	-3.050902
H	-0.460557	-1.429007	-4.218462
H	-1.055280	-1.219597	-2.573635
C	1.977564	-3.365768	-4.082624
H	2.687493	-2.553991	-4.286274

H	2.556763	-4.268102	-3.856620
H	1.416014	-3.552387	-5.006170
C	-0.445268	-4.313317	-2.443351
C	-0.769676	-4.799411	-1.165289
C	-1.116559	-4.878773	-3.544136
C	-1.728431	-5.799831	-0.984630
H	-0.266087	-4.382868	-0.300438
C	-2.079171	-5.876713	-3.374253
H	-0.893284	-4.534244	-4.552511
C	-2.388996	-6.337817	-2.090881
H	-1.956543	-6.151168	0.016101
H	-2.590581	-6.291483	-4.239658
H	-3.140144	-7.112132	-1.954457
C	1.200908	-1.981432	-0.049151
C	1.788808	-2.678400	-1.057711
C	3.159172	-3.350550	-1.013193
H	3.719245	-3.140648	-0.099991
H	3.055701	-4.443057	-1.084594
H	3.777379	-3.043894	-1.867741
C	1.915645	-1.778277	1.254983
F	2.414511	-2.973796	1.803223
F	0.969291	-1.396864	2.250681
C	3.023114	-0.741330	1.325573
C	3.615149	-0.205981	0.178562
C	3.472670	-0.327594	2.587972
C	4.645365	0.731630	0.290919
H	3.256852	-0.515591	-0.796536
C	4.493917	0.613492	2.699535
H	3.009849	-0.741715	3.477444
C	5.084481	1.146302	1.549276
H	5.100066	1.138811	-0.608432
H	4.829776	0.931887	3.682657
H	5.881984	1.879592	1.635708
Si	-5.457040	-2.924677	-3.318948
Si	-7.785960	-0.519685	1.392894
Si	-4.728064	-7.140954	2.418843
Si	0.975623	-6.307340	3.005004
C	-6.904729	-2.010082	-4.128150
H	-6.963895	-2.250104	-5.196773
H	-7.868814	-2.276305	-3.678324
H	-6.775153	-0.925383	-4.034997
C	-3.840630	-2.448431	-4.168323
H	-3.653553	-1.373380	-4.071090
H	-2.989678	-2.982164	-3.733002

H	-3.871224	-2.695979	-5.237006
C	-5.731914	-4.794448	-3.412406
H	-6.667241	-5.084930	-2.918808
H	-5.777458	-5.140850	-4.452617
H	-4.908241	-5.322332	-2.919005
C	-9.390349	-0.742448	0.417717
H	-9.647556	-1.802436	0.305622
H	-10.226489	-0.248092	0.926797
H	-9.314738	-0.309018	-0.586886
C	-7.964429	-1.233158	3.136953
H	-7.034815	-1.118677	3.708135
H	-8.759539	-0.725110	3.696255
H	-8.204115	-2.302667	3.105948
C	-7.329236	1.315017	1.503021
H	-6.377049	1.444418	2.032142
H	-7.208385	1.749988	0.503070
H	-8.094108	1.896269	2.032888
C	-6.217034	-6.203264	3.117990
H	-6.056982	-5.931797	4.168179
H	-6.405595	-5.277717	2.560236
H	-7.127315	-6.812876	3.062895
C	-4.409244	-8.711621	3.422377
H	-5.288242	-9.367413	3.408513
H	-3.566014	-9.284077	3.017634
H	-4.182618	-8.478524	4.469577
C	-5.051099	-7.578059	0.603571
H	-4.211296	-8.148457	0.187955
H	-5.960649	-8.179033	0.481603
H	-5.161181	-6.668883	-0.000219
C	1.884579	-6.254829	1.349304
H	1.989762	-5.215923	1.021162
H	2.890261	-6.686747	1.425583
H	1.333964	-6.800161	0.573872
C	1.846401	-5.183952	4.251670
H	2.854993	-5.553889	4.475087
H	1.948296	-4.173692	3.841152
H	1.292392	-5.122796	5.195936
C	0.877585	-8.080203	3.662230
H	0.312798	-8.134622	4.600875
H	0.396265	-8.751919	2.941105
H	1.883013	-8.472798	3.856899

FBpin

B3LYP-D3 SCF energy (au): -511.191409182
B3LYP-D3 enthalpy (au): -510.994284182
B3LYP-D3 free energy (au): -511.039637182
M06 SCF energy (au): -511.030912753
M06 enthalpy (au): -510.833787753
M06 free energy (au): -510.879140753
M06 free energy (quasi-harmonic) (au): -510.879140571

Cartesian coordinates

ATOM	X	Y	Z
B	-0.662879	-1.643875	-0.008260
O	-1.963626	-2.002937	0.213435
O	0.262398	-2.594974	0.322772
C	-1.914412	-3.243668	0.975864
C	-0.491401	-3.811393	0.597374
C	-2.032235	-2.855184	2.454057
C	-3.090705	-4.119830	0.558606
C	0.212949	-4.581392	1.709298
C	-0.495865	-4.626875	-0.700658
H	-2.951590	-2.279688	2.596859
H	-2.068542	-3.737988	3.100358
H	-1.188442	-2.230269	2.763684
H	-3.035557	-5.097211	1.051102
H	-4.029639	-3.640772	0.853211
H	-3.114246	-4.271600	-0.522551
H	-0.374631	-5.459344	2.000465
H	1.190545	-4.925275	1.357251
H	0.372501	-3.956863	2.590770
H	0.538044	-4.802138	-1.012322
H	-0.989197	-5.594799	-0.566078
H	-1.005426	-4.083951	-1.503145
F	-0.324150	-0.461931	-0.506842

BpinSiMe2PhB3LYP-D3 SCF energy (au): -1012.30006325
B3LYP-D3 enthalpy (au): -1011.92918325
B3LYP-D3 free energy (au): -1012.00120725
M06 SCF energy (au): -1011.94056049
M06 enthalpy (au): -1011.56968049
M06 free energy (au): -1011.64170449
M06 free energy (quasi-harmonic) (au): -1011.63658724

Cartesian coordinates

ATOM	X	Y	Z

B	-3.830202	-1.191097	0.231675
O	-3.655825	-0.038866	-0.494372
O	-4.898893	-1.939492	-0.208459
C	-4.517327	-0.128382	-1.669947
C	-5.618526	-1.144777	-1.199441
C	-5.026114	1.268940	-2.009160
C	-3.638533	-0.669553	-2.804570
C	-6.784445	-0.479219	-0.459134
C	-6.141862	-2.082140	-2.283238
H	-4.185860	1.904396	-2.305928
H	-5.736374	1.228820	-2.843053
H	-5.516585	1.736992	-1.152967
H	-4.186968	-0.718927	-3.751029
H	-2.779120	-0.004951	-2.933488
H	-3.259156	-1.667854	-2.564311
H	-7.422582	0.090753	-1.142486
H	-7.390194	-1.255208	0.018347
H	-6.418274	0.193927	0.322191
H	-6.886062	-2.761059	-1.855064
H	-6.620700	-1.512785	-3.088175
H	-5.339781	-2.687288	-2.711193
Si	-2.576068	-1.846938	1.675731
C	-1.392056	-0.485187	2.252642
H	-1.949573	0.345386	2.701710
H	-0.684187	-0.852653	3.005666
H	-0.816047	-0.082652	1.411887
C	-3.541117	-2.529920	3.160597
H	-4.123634	-1.741825	3.653744
H	-4.237969	-3.313163	2.841157
H	-2.862352	-2.964523	3.904340
C	-1.588778	-3.251093	0.867906
C	-0.230374	-3.472833	1.157290
C	-2.211043	-4.119563	-0.050708
C	0.477666	-4.520829	0.564077
H	0.289008	-2.817616	1.853408
C	-1.509403	-5.170197	-0.645074
H	-3.257372	-3.967529	-0.308567
C	-0.161741	-5.373313	-0.338427
H	1.527673	-4.670676	0.803937
H	-2.011975	-5.827872	-1.350447
H	0.387677	-6.188640	-0.802465

Cs2F2-Toluene

B3LYP-D3 SCF energy (au): -783.262262129
B3LYP-D3 enthalpy (au): -782.977521129
B3LYP-D3 free energy (au): -783.060215129
M06 SCF energy (au): -782.968645408
M06 enthalpy (au): -782.683904408
M06 free energy (au): -782.766598408
M06 free energy (quasi-harmonic) (au): -782.756102279

Cartesian coordinates

ATOM	X	Y	Z
F	1.434038	2.878253	1.356130
Cs	0.883973	2.102713	4.013215
F	-1.677564	1.477324	3.040096
Cs	-1.077340	2.205682	0.353954
C	-5.676724	3.644701	0.325052
C	-5.120672	2.570964	1.027980
C	-4.142331	2.790782	2.001927
C	-3.707965	4.097793	2.290120
C	-4.268345	5.166399	1.577247
C	-5.244222	4.944648	0.601556
H	-6.440608	3.471879	-0.429348
H	-5.449535	1.555302	0.815626
H	-3.626937	1.971617	2.507397
H	-3.937890	6.182077	1.788295
H	-5.668668	5.786533	0.059454
C	2.235898	-1.784504	4.415589
C	1.158023	-1.850016	3.527722
C	1.240382	-1.233273	2.276565
C	2.391623	-0.532861	1.879603
C	3.471408	-0.489185	2.779299
C	3.397354	-1.104985	4.031402
H	2.178286	-2.269605	5.386594
H	0.249843	-2.377420	3.808148
H	0.388588	-1.283814	1.601652
H	4.375650	0.042908	2.491160
H	4.250633	-1.062324	4.704729
C	-2.641781	4.298096	3.345281
H	-1.959537	5.116945	3.078485
H	-3.094271	4.558114	4.312480
H	-2.095414	3.347303	3.453511
C	2.430383	0.242989	0.590690
H	1.775944	-0.214651	-0.164167
H	2.096049	1.292683	0.788409
H	3.443391	0.278083	0.173647

TS-1

B3LYP-D3 SCF energy (au):	-5142.19450934
B3LYP-D3 enthalpy (au):	-5140.76404534
B3LYP-D3 free energy (au):	-5140.98156134
M06 SCF energy (au):	-5140.69556503
M06 enthalpy (au):	-5139.26510103
M06 free energy (au):	-5139.48261703
M06 free energy (quasi-harmonic) (au):	-5139.46087069

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.328165	0.579360	0.923092
Fe	-3.038313	1.170101	4.509254
P	-1.644281	-1.282181	1.469502
P	-1.841736	2.258750	1.421525
C	-3.198869	1.714922	2.513355
C	-3.687693	0.362669	2.695941
C	-4.763816	0.432219	3.638519
H	-5.322754	-0.423288	3.997774
C	-4.953257	1.786779	4.034834
H	-5.658745	2.143026	4.774582
C	-3.991070	2.577042	3.348896
H	-3.833690	3.640036	3.468497
C	-1.834369	-0.131674	5.599239
H	-1.688760	-1.174629	5.372110
C	-2.861983	0.403160	6.429313
C	-1.607834	2.166098	5.621346
H	-1.272948	3.167640	5.390238
C	-1.062320	0.956153	5.092571
H	-0.240657	0.877709	4.397684
C	-2.701361	2.745760	-0.131651
C	-4.095209	2.752125	-0.280686
H	-4.730196	2.487267	0.559311
C	-4.669564	3.089624	-1.509093
H	-5.751088	3.084592	-1.617045
C	-3.858960	3.433315	-2.592682
C	-2.468564	3.439713	-2.447154
H	-1.832228	3.699312	-3.288850
C	-1.892983	3.092320	-1.226353
H	-0.811689	3.068027	-1.118730
C	-1.364388	3.878280	2.153283

C	-2.079308	5.057366	1.891179
H	-2.924891	5.038865	1.209414
C	-1.706682	6.257260	2.499381
H	-2.266501	7.164995	2.289743
C	-0.615239	6.290752	3.371546
C	0.107331	5.122704	3.625372
H	0.969857	5.145942	4.285861
C	-0.260361	3.922091	3.015869
H	0.320246	3.026124	3.190277
C	-2.720641	1.823909	6.446337
H	-3.374630	2.522750	6.952230
C	-3.458685	-0.885556	1.867741
H	-3.638050	-0.166283	6.924735
C	-4.336303	-0.776479	0.600021
H	-5.351919	-0.489590	0.894452
H	-3.963885	-0.006352	-0.083112
H	-4.388620	-1.724752	0.061032
H	-3.835768	-1.729798	2.455054
C	-1.771738	-2.646878	0.233124
C	-1.433332	-3.970843	0.535613
C	-2.161902	-2.343128	-1.080192
C	-1.524588	-4.995870	-0.419376
H	-1.070906	-4.210538	1.527017
C	-2.272480	-3.329740	-2.069485
H	-2.378794	-1.313081	-1.337091
C	-1.958453	-4.652602	-1.708749
H	-2.034640	-5.435066	-2.463762
C	-1.063871	-2.157018	2.976529
C	-1.832753	-3.126542	3.637018
C	0.218479	-1.872935	3.458912
C	-1.349575	-3.807356	4.764883
H	-2.823765	-3.367671	3.258176
C	0.743835	-2.514175	4.594167
H	0.801502	-1.114309	2.954075
C	-0.058019	-3.480890	5.222522
H	0.327167	-3.991931	6.102412
H	-4.307631	3.691764	-3.548080
H	-0.323218	7.225888	3.842241
Si	-1.075839	-6.765581	0.067308
Si	-2.777882	-2.883792	-3.834348
Si	-2.476908	-5.045383	5.638366
Si	2.432824	-1.974345	5.265630
C	-0.005284	-6.720463	1.626264
H	-0.560531	-6.324634	2.484773

H	0.342261	-7.726548	1.891256
H	0.871243	-6.080756	1.479567
C	-0.140729	-7.585617	-1.358646
H	0.126401	-8.620935	-1.114096
H	-0.743400	-7.608100	-2.274792
H	0.782678	-7.040005	-1.581385
C	-2.662160	-7.738602	0.426891
H	-3.336183	-7.739755	-0.438201
H	-2.439042	-8.782798	0.679922
H	-3.204329	-7.298837	1.272888
C	-4.061842	-4.139658	-4.434850
H	-4.963711	-4.112027	-3.811882
H	-4.361084	-3.933345	-5.469870
H	-3.668308	-5.162905	-4.402746
C	-1.258708	-2.958638	-4.962254
H	-0.527056	-2.189638	-4.688709
H	-0.759669	-3.932408	-4.887709
H	-1.533156	-2.800948	-6.012749
C	-3.514459	-1.141395	-3.857978
H	-2.768263	-0.383638	-3.593199
H	-3.893763	-0.897003	-4.857793
H	-4.349783	-1.049107	-3.153179
C	-3.952935	-4.077433	6.327037
H	-3.620009	-3.330230	7.057797
H	-4.473143	-3.541981	5.522826
H	-4.680965	-4.733352	6.819748
C	-1.535791	-5.900305	7.035696
H	-2.174354	-6.633181	7.543344
H	-0.654918	-6.432483	6.657251
H	-1.194082	-5.180959	7.789495
C	-3.089056	-6.317074	4.375924
H	-2.265410	-6.942596	4.013173
H	-3.847668	-6.979556	4.810333
H	-3.537074	-5.826028	3.503103
C	3.740515	-2.067981	3.904919
H	3.802521	-3.068049	3.461301
H	3.532350	-1.349463	3.104243
H	4.729256	-1.823356	4.314500
C	2.290345	-0.177244	5.835270
H	2.046915	0.458478	4.977563
H	1.500859	-0.046434	6.583931
H	3.235734	0.179721	6.262524
C	2.901534	-3.100316	6.712921
H	2.960244	-4.151341	6.404943

H	3.881372	-2.818180	7.116748
H	2.175379	-3.030303	7.531874
Si	1.115576	0.043684	-0.838319
C	-0.222951	0.306547	-2.209079
H	-0.028731	1.268713	-2.697841
H	-0.174217	-0.471351	-2.981137
H	-1.246496	0.345532	-1.829565
C	2.647423	0.716739	-1.751435
H	2.520260	1.768830	-2.028888
H	3.551882	0.607120	-1.151098
H	2.775236	0.140589	-2.677440
C	1.493012	-1.826021	-0.701241
C	2.090144	-2.338097	0.464522
C	1.259360	-2.730824	-1.751547
C	2.447831	-3.683395	0.576495
H	2.295227	-1.665851	1.290691
C	1.612378	-4.077756	-1.651275
H	0.788863	-2.388872	-2.668961
C	2.214613	-4.558569	-0.486696
H	2.911540	-4.046786	1.490396
H	1.411166	-4.752182	-2.480361
H	2.496384	-5.605846	-0.407404
F	1.197756	0.936876	2.651890
C	4.181519	1.823424	1.706838
C	3.394452	3.160862	1.347213
B	1.954267	1.361665	1.522894
O	2.009439	2.746063	1.353325
O	3.221811	0.774542	1.409228
C	3.537937	4.276900	2.388299
H	4.577479	4.616262	2.464630
H	2.917116	5.127148	2.089236
H	3.201437	3.952342	3.375332
C	3.719532	3.733027	-0.035254
H	3.618495	2.980469	-0.815078
H	3.015476	4.543242	-0.251713
H	4.736400	4.139575	-0.068938
C	5.444691	1.578294	0.884846
H	6.195776	2.349403	1.091627
H	5.867647	0.605306	1.154788
H	5.240544	1.571067	-0.186723
C	4.516635	1.700622	3.201711
H	4.924830	0.703388	3.389657
H	5.255992	2.444760	3.516813
H	3.621688	1.812561	3.819187

TS-2

B3LYP-D3 SCF energy (au):	-5216.51624183
B3LYP-D3 enthalpy (au):	-5215.12028083
B3LYP-D3 free energy (au):	-5215.34267783
M06 SCF energy (au):	-5214.98731903
M06 enthalpy (au):	-5213.59135803
M06 free energy (au):	-5213.81375503
M06 free energy (quasi-harmonic) (au):	-5213.78863520

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.879065	-1.767524	-0.126824
Fe	-1.016352	2.516691	2.202129
P	-2.793539	-1.627995	1.051234
P	-0.932796	0.541479	-0.724618
C	-1.774042	1.556326	0.538637
C	-2.428687	1.092750	1.748114
C	-3.057916	2.233639	2.343358
H	-3.601732	2.236822	3.277429
C	-2.785881	3.384803	1.546741
H	-3.085236	4.399309	1.775908
C	-1.994809	2.973354	0.442392
H	-1.598716	3.612407	-0.334424
C	0.060024	1.867584	3.851345
H	-0.228033	1.026146	4.468252
C	-0.347422	3.225986	4.025428
C	0.969743	3.108607	2.130003
H	1.485400	3.371941	1.216724
C	0.873643	1.794803	2.684009
H	1.318595	0.893709	2.290119
C	-1.980248	0.793296	-2.218697
C	-3.308074	1.236988	-2.150142
H	-3.738775	1.524666	-1.198952
C	-4.093829	1.296628	-3.302764
H	-5.125991	1.627175	-3.226810
C	-3.562052	0.926547	-4.538339
C	-2.238270	0.483335	-4.616622
H	-1.817663	0.185882	-5.573549
C	-1.457043	0.408825	-3.465070
H	-0.432303	0.051802	-3.532636
C	0.585152	1.504529	-1.112334
C	0.586426	2.651221	-1.921844

H	-0.330400	2.973752	-2.407120
C	1.765522	3.371206	-2.118500
H	1.757284	4.259611	-2.744755
C	2.955089	2.949674	-1.515348
C	2.962755	1.800237	-0.722045
H	3.882759	1.461453	-0.253610
C	1.784244	1.078147	-0.524972
H	1.794454	0.192974	0.099129
C	0.219692	3.992941	2.962156
H	0.063757	5.050257	2.789639
C	-2.434166	-0.302903	2.346059
H	-1.004300	3.601083	4.799882
C	-3.272284	-0.403666	3.628718
H	-2.897531	0.308848	4.372672
H	-4.331985	-0.190422	3.452666
H	-3.198959	-1.405747	4.057208
H	-1.400102	-0.564073	2.600021
C	-4.329680	-1.176912	0.165833
C	-4.650489	-1.951530	-0.960281
C	-5.168383	-0.113267	0.510983
C	-5.796114	-1.708665	-1.727910
H	-3.983240	-2.761422	-1.234844
C	-6.298892	0.209349	-0.261702
H	-4.924593	0.497887	1.372250
C	-6.598797	-0.611317	-1.360771
H	-7.484605	-0.388343	-1.953311
C	-3.232883	-3.111655	2.023124
C	-4.519483	-3.657693	2.052913
C	-2.192148	-3.762597	2.699214
C	-4.783585	-4.861981	2.727192
H	-5.319805	-3.151757	1.519167
C	-2.417059	-4.949225	3.412387
H	-1.189100	-3.346813	2.618831
C	-3.718522	-5.483060	3.403515
H	-3.903892	-6.419229	3.927220
H	-4.175096	0.971643	-5.433978
H	3.872114	3.511826	-1.670789
Si	-0.861935	-3.717142	-1.583003
C	-2.060605	-4.894907	-0.675764
H	-3.049092	-4.466489	-0.494737
H	-2.181333	-5.813755	-1.264180
H	-1.656285	-5.171213	0.303534
C	-1.638035	-3.129611	-3.226715
H	-2.493893	-2.473490	-3.040213

H	-0.921018	-2.545771	-3.814935
H	-1.969245	-3.978078	-3.841258
C	0.551864	-4.901480	-2.050618
C	1.119489	-5.730883	-1.062201
C	1.100737	-4.971421	-3.342410
C	2.195487	-6.572800	-1.343800
H	0.727289	-5.707369	-0.049075
C	2.176935	-5.815455	-3.634891
H	0.691583	-4.352182	-4.137681
C	2.732694	-6.614456	-2.634253
H	2.614015	-7.195796	-0.556272
H	2.582573	-5.846299	-4.643608
H	3.573366	-7.266595	-2.857605
C	0.730591	-2.469108	1.074377
C	0.937912	-2.504810	-0.212843
C	2.080862	-2.283735	-1.159907
H	2.934453	-1.887549	-0.597065
H	2.390150	-3.204470	-1.660557
H	1.805374	-1.558483	-1.933717
C	1.642550	-2.142877	2.163594
F	0.915590	-1.624161	3.252825
F	2.503257	-1.048137	1.845160
C	2.526512	-3.270944	2.656997
C	2.902336	-3.327834	4.003575
C	3.015657	-4.232045	1.765079
C	3.744392	-4.344468	4.455537
H	2.522226	-2.583669	4.693783
C	3.861850	-5.244168	2.217190
H	2.714334	-4.212639	0.724647
C	4.225604	-5.306752	3.564277
H	4.023263	-4.384951	5.505238
H	4.226309	-5.988618	1.514255
H	4.878804	-6.100128	3.918145
Si	-6.199791	-2.823358	-3.204868
Si	-7.274326	1.771887	0.156771
Si	-6.522926	-5.588507	2.623383
Si	-0.924757	-5.760314	4.243571
C	-5.501889	-2.063305	-4.789857
H	-4.417734	-1.925712	-4.711207
H	-5.704709	-2.703945	-5.657226
H	-5.942776	-1.078760	-4.984839
C	-5.421828	-4.521013	-2.910153
H	-4.327845	-4.468140	-2.876340
H	-5.764920	-4.958291	-1.965097

H	-5.691747	-5.212738	-3.717572
C	-8.080780	-2.986221	-3.338808
H	-8.564834	-2.014523	-3.495022
H	-8.356767	-3.629940	-4.182925
H	-8.504150	-3.427571	-2.428695
C	-6.220330	3.260969	-0.349810
H	-5.258553	3.248269	0.177469
H	-6.005885	3.249771	-1.425416
H	-6.721056	4.208973	-0.116731
C	-7.575101	1.829764	2.024322
H	-6.627546	1.823132	2.577140
H	-8.115433	2.740846	2.309194
H	-8.164148	0.969093	2.362110
C	-8.915712	1.774140	-0.781503
H	-9.520735	0.893721	-0.534304
H	-9.504491	2.664827	-0.531174
H	-8.759633	1.778560	-1.867055
C	-6.532755	-7.337555	3.340652
H	-5.828572	-7.989779	2.810596
H	-6.255785	-7.339157	4.401790
H	-7.529846	-7.786863	3.259013
C	-7.019851	-5.618189	0.794595
H	-8.040389	-5.995537	0.656066
H	-6.973781	-4.611435	0.360559
H	-6.340910	-6.256839	0.216882
C	-7.728047	-4.482530	3.577188
H	-7.704047	-3.455760	3.191944
H	-8.759115	-4.847625	3.491946
H	-7.471256	-4.443163	4.642423
C	-0.133225	-4.477666	5.385220
H	0.098489	-3.564023	4.826125
H	-0.803495	-4.211654	6.211526
H	0.807399	-4.847867	5.809713
C	0.285877	-6.225159	2.870432
H	0.481514	-5.343645	2.250117
H	1.251183	-6.565918	3.262003
H	-0.124995	-7.010076	2.223838
C	-1.479639	-7.285656	5.215552
H	-1.945950	-8.031085	4.559882
H	-0.623969	-7.766225	5.705197
H	-2.205030	-7.024463	5.995615

TS-2A

B3LYP-D3 SCF energy (au): -5216.50030602
B3LYP-D3 enthalpy (au): -5215.10416602
B3LYP-D3 free energy (au): -5215.32510102
M06 SCF energy (au): -5214.96877716
M06 enthalpy (au): -5213.57263716
M06 free energy (au): -5213.79357216
M06 free energy (quasi-harmonic) (au): -5213.76996714

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.397080	-1.955047	0.097647
Fe	-1.034147	2.212642	1.700344
P	-2.646676	-2.048944	0.913033
P	-0.927878	0.028728	-0.992351
C	-1.837656	1.124210	0.153650
C	-2.460776	0.752169	1.413295
C	-3.072714	1.938124	1.935436
H	-3.594335	2.011735	2.879065
C	-2.829987	3.023991	1.044039
H	-3.129448	4.052251	1.199889
C	-2.073833	2.527586	-0.050370
H	-1.695969	3.105835	-0.881824
C	0.176501	1.610209	3.263273
H	-0.045291	0.768594	3.905401
C	-0.248710	2.958871	3.465097
C	0.916522	2.867366	1.470968
H	1.348441	3.138083	0.517420
C	0.896604	1.553068	2.032476
H	1.304801	0.659491	1.581744
C	-2.114874	-0.204668	-2.387902
C	-3.369865	0.414513	-2.456625
H	-3.702066	1.067455	-1.658618
C	-4.213921	0.178673	-3.544363
H	-5.191006	0.652462	-3.575017
C	-3.810495	-0.666149	-4.579621
C	-2.558397	-1.284712	-4.519098
H	-2.226827	-1.945513	-5.315396
C	-1.719070	-1.060092	-3.429038
H	-0.752142	-1.545439	-3.393944
C	0.329687	1.135663	-1.757703
C	0.018830	2.061687	-2.765039
H	-1.000065	2.138880	-3.134134
C	1.017418	2.869222	-3.311513
H	0.766780	3.583397	-4.091598

C	2.337658	2.752221	-2.866453
C	2.657125	1.818458	-1.877527
H	3.683700	1.705919	-1.539319
C	1.657733	1.012266	-1.329558
H	1.913178	0.269038	-0.584198
C	0.210945	3.734993	2.358045
H	0.015585	4.787240	2.196037
C	-2.473499	-0.596511	2.120913
H	-0.849106	3.320050	4.290089
C	-3.404993	-0.632204	3.341192
H	-3.102169	0.131967	4.067012
H	-4.452817	-0.456372	3.077147
H	-3.344618	-1.603705	3.837714
H	-1.456208	-0.790545	2.472679
C	-4.228270	-1.767723	0.011994
C	-4.602302	-2.696093	-0.974380
C	-5.060227	-0.663572	0.230484
C	-5.768651	-2.543331	-1.736227
H	-3.959815	-3.551452	-1.152190
C	-6.233056	-0.457152	-0.516164
H	-4.782632	0.073822	0.972687
C	-6.567294	-1.410908	-1.488026
H	-7.466620	-1.261171	-2.082719
C	-3.056218	-3.473033	2.000979
C	-4.364621	-3.933406	2.197009
C	-2.002732	-4.120460	2.662778
C	-4.639339	-5.029644	3.031194
H	-5.181147	-3.433302	1.683063
C	-2.232128	-5.200235	3.530721
H	-0.993641	-3.755675	2.479444
C	-3.558451	-5.640854	3.690408
H	-3.755229	-6.489470	4.343086
H	-4.466935	-0.843309	-5.427604
H	3.114894	3.376895	-3.298691
Si	0.333581	-3.904872	-1.190590
C	1.148383	-5.551561	-0.695493
H	0.776880	-5.875400	0.283539
H	0.864999	-6.319504	-1.427500
H	2.237018	-5.499683	-0.658428
C	-1.462158	-4.471903	-1.549126
H	-1.969236	-4.747244	-0.618097
H	-2.026027	-3.673498	-2.037082
H	-1.461989	-5.352976	-2.207347
C	0.994714	-3.255933	-2.851186

C	0.547743	-3.816056	-4.063503
C	1.782171	-2.092710	-2.929800
C	0.856382	-3.231486	-5.294984
H	-0.073725	-4.708841	-4.052756
C	2.088311	-1.496940	-4.154300
H	2.139170	-1.628250	-2.019380
C	1.619968	-2.062215	-5.342652
H	0.492171	-3.682228	-6.215597
H	2.671956	-0.579896	-4.174073
H	1.844416	-1.594553	-6.298122
C	1.328869	-2.715281	0.800387
C	0.678423	-2.283748	1.850994
C	1.097990	-1.896324	3.234479
H	1.732179	-2.668728	3.689525
H	1.687677	-0.969508	3.236093
H	0.238509	-1.735577	3.900099
C	2.805218	-2.684594	0.535736
F	3.164571	-1.363078	0.230326
F	3.176554	-3.394491	-0.590196
C	3.641316	-3.158429	1.705874
C	3.609461	-4.513205	2.053745
C	4.400672	-2.264114	2.463685
C	4.327498	-4.967322	3.158795
H	3.013526	-5.204387	1.468505
C	5.120227	-2.721757	3.569464
H	4.419951	-1.214830	2.192382
C	5.083094	-4.072031	3.921475
H	4.294440	-6.020266	3.425220
H	5.706908	-2.020505	4.156757
H	5.639605	-4.426187	4.785101
Si	-6.202515	-3.794787	-3.086686
Si	-7.217906	1.127948	-0.237349
Si	-6.429483	-5.606125	3.203932
Si	-0.766894	-5.964065	4.449165
C	-4.604199	-4.535822	-3.770200
H	-4.814185	-5.206563	-4.612487
H	-3.930730	-3.745549	-4.120304
H	-4.063796	-5.114884	-3.012576
C	-7.139795	-2.894672	-4.463438
H	-6.548379	-2.058342	-4.853150
H	-7.354997	-3.573759	-5.297378
H	-8.097724	-2.493020	-4.111769
C	-7.295525	-5.164678	-2.369012
H	-8.224715	-4.755497	-1.954215

H	-7.566246	-5.899170	-3.137947
H	-6.781962	-5.697593	-1.560541
C	-6.207752	2.582085	-0.909849
H	-6.012608	2.469976	-1.983297
H	-6.728782	3.536277	-0.761647
H	-5.238216	2.646221	-0.400974
C	-8.880889	1.016512	-1.130377
H	-9.475111	1.922462	-0.960632
H	-8.749236	0.907886	-2.213770
H	-9.468871	0.160685	-0.778008
C	-7.474382	1.369055	1.622851
H	-8.041554	0.538625	2.059473
H	-6.511750	1.426849	2.146043
H	-8.019754	2.297471	1.832333
C	-7.120553	-5.890105	1.464813
H	-7.032005	-4.981772	0.856685
H	-6.571082	-6.686248	0.948218
H	-8.180117	-6.172689	1.488783
C	-7.432582	-4.244530	4.055677
H	-7.062557	-4.054749	5.070223
H	-7.364434	-3.303404	3.496192
H	-8.493532	-4.514144	4.128157
C	-6.496973	-7.200755	4.217702
H	-6.109946	-7.049594	5.232644
H	-7.529015	-7.560539	4.308077
H	-5.906596	-7.997806	3.750210
C	-0.207319	-4.767150	5.805422
H	0.085465	-3.804191	5.370556
H	-1.008659	-4.578605	6.529761
H	0.657385	-5.162655	6.352875
C	0.649791	-6.204349	3.223055
H	0.883032	-5.261880	2.715044
H	1.563952	-6.540493	3.727186
H	0.392290	-6.943411	2.455265
C	-1.284199	-7.615644	5.213618
H	-1.643762	-8.315215	4.449565
H	-0.436495	-8.087603	5.725081
H	-2.084067	-7.487540	5.953008

TS-3

B3LYP-D3 SCF energy (au): -5216.57289625

B3LYP-D3 enthalpy (au): -5215.17659625

B3LYP-D3 free energy (au): -5215.39710525

M06 SCF energy (au): -5215.03054474
M06 enthalpy (au): -5213.63424474
M06 free energy (au): -5213.85475374
M06 free energy (quasi-harmonic) (au): -5213.83270449

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.472402	-1.174869	0.242389
Fe	-2.093998	2.086035	3.258835
P	-2.258814	-2.149265	1.293655
P	-1.440218	0.902243	-0.008583
C	-2.521893	1.242707	1.427370
C	-2.877437	0.338213	2.504047
C	-3.858600	1.009861	3.302009
H	-4.302241	0.622156	4.208472
C	-4.100291	2.305321	2.755734
H	-4.755982	3.058076	3.173901
C	-3.277474	2.453160	1.608343
H	-3.210517	3.328573	0.977214
C	-0.821652	1.592802	4.811298
H	-0.829135	0.627730	5.301540
C	-1.616463	2.725175	5.170257
C	-0.392622	3.269370	3.287131
H	-0.019844	3.801582	2.423589
C	-0.067377	1.923999	3.647193
H	0.548851	1.226483	3.093499
C	-2.590557	1.180040	-1.421925
C	-2.072679	1.504931	-2.687660
H	-1.006727	1.674983	-2.807225
C	-2.914622	1.617756	-3.793459
H	-2.496336	1.872322	-4.763734
C	-4.289237	1.402365	-3.655124
C	-4.811298	1.072809	-2.403459
H	-5.875341	0.891507	-2.281581
C	-3.970471	0.959741	-1.295083
H	-4.394732	0.689358	-0.335253
C	-0.295062	2.337836	-0.076293
C	-0.656440	3.609997	-0.544644
H	-1.650999	3.780293	-0.946980
C	0.266214	4.656680	-0.510063
H	-0.019678	5.640542	-0.873353
C	1.555797	4.440101	-0.012513
C	1.921574	3.173312	0.448274
H	2.919938	2.992715	0.835593

C	1.000789	2.124373	0.415151
H	1.257504	1.146750	0.809456
C	-1.346496	3.762816	4.227058
H	-1.820119	4.736061	4.201323
C	-2.288901	-1.023706	2.817279
H	-2.326573	2.774776	5.985975
C	-2.860176	-1.654478	4.093858
H	-2.716966	-0.972528	4.940196
H	-3.929650	-1.879295	4.015667
H	-2.342292	-2.588919	4.323457
H	-1.209217	-0.881166	2.954194
C	-3.908916	-2.067070	0.504740
C	-4.013219	-2.463213	-0.838197
C	-5.044832	-1.568905	1.155508
C	-5.227820	-2.370741	-1.537174
H	-3.122315	-2.833437	-1.341945
C	-6.270156	-1.418571	0.487266
H	-4.966289	-1.257190	2.189411
C	-6.334010	-1.836179	-0.852779
H	-7.274924	-1.724208	-1.388801
C	-2.174378	-3.846953	1.972012
C	-3.298517	-4.664192	2.140810
C	-0.903989	-4.363981	2.251869
C	-3.175690	-5.994603	2.572630
H	-4.278814	-4.261515	1.900906
C	-0.729632	-5.687517	2.687856
H	-0.040316	-3.725579	2.085737
C	-1.881583	-6.478979	2.843997
H	-1.765189	-7.513221	3.163266
H	-4.945345	1.487058	-4.517389
H	2.271536	5.257816	0.012687
Si	0.537021	-2.998542	-2.834589
C	-0.429505	-1.408929	-3.150451
H	0.241783	-0.542546	-3.124472
H	-0.926648	-1.432635	-4.126455
H	-1.202899	-1.247858	-2.393641
C	1.577494	-3.390137	-4.369948
H	2.280511	-2.575616	-4.584971
H	2.157508	-4.311119	-4.243007
H	0.941619	-3.515830	-5.254638
C	-0.646695	-4.440191	-2.519791
C	-0.939567	-4.841256	-1.204417
C	-1.279805	-5.132125	-3.569506
C	-1.835165	-5.880253	-0.940234

H	-0.459241	-4.333527	-0.375492
C	-2.177906	-6.171166	-3.315060
H	-1.075887	-4.857947	-4.602795
C	-2.459469	-6.545322	-1.997522
H	-2.041228	-6.164307	0.085913
H	-2.659734	-6.686765	-4.142209
H	-3.160106	-7.351742	-1.795353
C	1.292138	-2.104024	-0.251955
C	1.674529	-2.809035	-1.337924
C	3.016498	-3.529470	-1.395364
H	3.635609	-3.326566	-0.514324
H	2.868103	-4.617124	-1.452187
H	3.589362	-3.245480	-2.287929
C	2.012213	-1.819108	0.910099
F	2.001163	-2.747592	1.894713
F	0.713396	-0.663203	2.036936
C	3.091907	-0.836257	1.041021
C	3.539195	-0.132955	-0.087626
C	3.709372	-0.622904	2.284582
C	4.598803	0.765361	0.024751
H	3.046433	-0.292864	-1.040599
C	4.764026	0.277332	2.391237
H	3.339988	-1.153140	3.154241
C	5.212793	0.973471	1.262450
H	4.939245	1.307909	-0.852660
H	5.235244	0.443866	3.355837
H	6.036450	1.677003	1.350086
Si	-5.353345	-2.886837	-3.353860
Si	-7.702783	-0.533282	1.340897
Si	-4.701019	-7.107445	2.587954
Si	1.033285	-6.346203	2.877099
C	-6.788966	-1.946474	-4.156537
H	-6.856381	-2.191208	-5.223685
H	-7.756276	-2.193244	-3.702798
H	-6.641513	-0.863366	-4.071361
C	-3.741564	-2.444091	-4.226639
H	-3.529578	-1.373484	-4.130493
H	-2.899507	-2.997373	-3.800235
H	-3.793180	-2.690881	-5.294627
C	-5.671814	-4.749434	-3.448466
H	-6.611693	-5.016232	-2.950071
H	-5.732661	-5.092145	-4.489168
H	-4.859764	-5.299866	-2.960705
C	-9.349196	-1.178206	0.668669

H	-9.460589	-2.253272	0.852946
H	-10.193177	-0.666482	1.147090
H	-9.436964	-1.014511	-0.412183
C	-7.591029	-0.827633	3.207155
H	-6.677641	-0.385025	3.622657
H	-8.442225	-0.370454	3.726199
H	-7.586147	-1.897541	3.447154
C	-7.525230	1.317662	0.984031
H	-6.558388	1.682301	1.352279
H	-7.565040	1.517871	-0.093834
H	-8.317199	1.905098	1.465143
C	-6.219388	-6.082738	3.065528
H	-6.100395	-5.634357	4.059040
H	-6.398960	-5.269641	2.351662
H	-7.120675	-6.707618	3.084756
C	-4.456993	-8.526622	3.814272
H	-5.336673	-9.181531	3.831915
H	-3.592129	-9.146567	3.549187
H	-4.298544	-8.150852	4.832027
C	-4.925524	-7.793835	0.835705
H	-4.061129	-8.403160	0.543881
H	-5.822945	-8.419062	0.751691
H	-5.011839	-6.975766	0.110126
C	1.883596	-6.143481	1.199067
H	1.955804	-5.080531	0.945222
H	2.899095	-6.558619	1.205010
H	1.314566	-6.636126	0.401977
C	1.948904	-5.318718	4.174495
H	2.987929	-5.653789	4.284383
H	1.967722	-4.263264	3.879844
H	1.466065	-5.388285	5.156376
C	0.972442	-8.167339	3.386357
H	0.453962	-8.302132	4.343431
H	0.454435	-8.776017	2.635388
H	1.985395	-8.572411	3.498529

TS-4

B3LYP-D3 SCF energy (au):	-5216.56705883
B3LYP-D3 enthalpy (au):	-5215.17087883
B3LYP-D3 free energy (au):	-5215.38944983
M06 SCF energy (au):	-5215.02805712
M06 enthalpy (au):	-5213.63187712
M06 free energy (au):	-5213.85044812

M06 free energy (quasi-harmonic) (au): -5213.82963629

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.668735	-1.472940	0.332642
Fe	-2.347709	2.226831	3.155837
P	-2.599836	-2.120139	1.334819
P	-1.040449	0.780504	0.203262
C	-2.400335	1.345727	1.285949
C	-3.130597	0.551747	2.255640
C	-4.185751	1.383254	2.760146
H	-4.897604	1.104440	3.523762
C	-4.108306	2.664411	2.139391
H	-4.744471	3.512771	2.355579
C	-3.009587	2.646043	1.240918
H	-2.669846	3.469719	0.628262
C	-1.613288	1.688228	5.013796
H	-1.871919	0.765606	5.517309
C	-2.324372	2.924038	5.105632
C	-0.579415	3.211604	3.617598
H	0.080872	3.640294	2.877656
C	-0.537912	1.864772	4.093751
H	0.156172	1.100060	3.772692
C	-1.657276	1.196898	-1.475559
C	-3.026032	1.155084	-1.779877
H	-3.754111	0.982310	-0.994573
C	-3.461857	1.313571	-3.095917
H	-4.525142	1.272739	-3.316023
C	-2.539838	1.514133	-4.124828
C	-1.173354	1.544078	-3.831567
H	-0.447353	1.690435	-4.627097
C	-0.733325	1.377672	-2.518388
H	0.331231	1.386732	-2.301286
C	0.320154	1.972072	0.512052
C	0.322975	3.288610	0.026946
H	-0.479630	3.630985	-0.620344
C	1.363324	4.156701	0.360500
H	1.361129	5.175314	-0.018963
C	2.407139	3.715272	1.180955
C	2.412071	2.402035	1.656789
H	3.226052	2.053676	2.287033
C	1.376617	1.526768	1.321053
H	1.382058	0.497189	1.668893
C	-1.681281	3.864493	4.244645

H	-2.004906	4.881154	4.061842
C	-2.850470	-0.863414	2.734802
H	-3.216733	3.103134	5.691582
C	-3.844639	-1.320918	3.811466
H	-3.848109	-0.613832	4.648936
H	-4.863342	-1.388566	3.414066
H	-3.569152	-2.303036	4.201089
H	-1.841445	-0.872503	3.166745
C	-4.185476	-2.238186	0.419969
C	-4.412434	-3.347103	-0.414967
C	-5.140521	-1.214124	0.445911
C	-5.576990	-3.458737	-1.190439
H	-3.664297	-4.135512	-0.451961
C	-6.312435	-1.272618	-0.326764
H	-4.973361	-0.349273	1.076055
C	-6.510307	-2.406082	-1.129579
H	-7.420115	-2.476267	-1.722162
C	-2.466708	-3.687283	2.279293
C	-3.527433	-4.578057	2.478922
C	-1.204158	-3.978130	2.819882
C	-3.351976	-5.770599	3.199017
H	-4.498126	-4.346591	2.052195
C	-0.994166	-5.139472	3.581742
H	-0.382676	-3.291411	2.618273
C	-2.082692	-6.015240	3.752461
H	-1.930182	-6.931442	4.323491
H	-2.881343	1.637571	-5.149011
H	3.216183	4.392780	1.441298
Si	-0.729124	-3.403640	-2.891525
C	-2.121464	-2.141395	-2.771842
H	-1.843314	-1.226818	-3.306302
H	-3.049119	-2.528527	-3.207323
H	-2.331950	-1.861140	-1.737583
C	-0.412560	-3.755360	-4.727328
H	-0.085269	-2.841799	-5.238774
H	0.358989	-4.518636	-4.878817
H	-1.327798	-4.097912	-5.225772
C	-1.179758	-5.045550	-2.042622
C	-1.528301	-6.200734	-2.766049
C	-1.134995	-5.152369	-0.638323
C	-1.827545	-7.404122	-2.119836
H	-1.564738	-6.168883	-3.852649
C	-1.439784	-6.347265	0.017223
H	-0.849802	-4.286690	-0.047736

C	-1.785709	-7.479648	-0.725969
H	-2.095115	-8.280793	-2.704950
H	-1.409250	-6.388811	1.101302
H	-2.024936	-8.411440	-0.220004
C	0.821932	-2.277626	-0.817581
C	0.862520	-2.833860	-2.048463
C	2.165702	-3.167194	-2.764160
H	3.049622	-2.910088	-2.170744
H	2.224058	-4.237623	-3.009168
H	2.234038	-2.629762	-3.719771
C	1.903642	-2.050676	0.052795
F	0.970782	-1.665986	1.777002
F	2.475752	-0.830056	0.007732
C	2.775132	-3.078236	0.638660
C	3.928642	-2.699521	1.344372
C	2.500120	-4.439964	0.437494
C	4.803105	-3.669015	1.825567
H	4.126256	-1.646568	1.508344
C	3.385132	-5.404622	0.914264
H	1.602597	-4.732430	-0.096568
C	4.536299	-5.024483	1.608757
H	5.693921	-3.368985	2.370652
H	3.173904	-6.455971	0.746274
H	5.221947	-5.781112	1.980867
Si	-5.866780	-4.984709	-2.273490
Si	-7.544110	0.153872	-0.207210
Si	-4.738868	-7.048465	3.305480
Si	0.723511	-5.592984	4.235839
C	-5.384365	-6.519137	-1.281918
H	-4.348325	-6.455411	-0.932845
H	-6.032079	-6.640667	-0.405637
H	-5.467394	-7.428356	-1.889852
C	-4.815877	-4.867726	-3.841305
H	-4.997121	-5.723507	-4.503690
H	-5.037733	-3.951813	-4.401868
H	-3.751865	-4.861944	-3.586278
C	-7.699095	-5.066112	-2.744037
H	-7.998913	-4.216229	-3.369001
H	-7.906954	-5.980304	-3.313401
H	-8.342652	-5.072672	-1.856223
C	-9.045113	-0.205500	-1.299176
H	-9.550614	-1.130096	-0.995780
H	-9.776495	0.609160	-1.235750
H	-8.758454	-0.312003	-2.352382

C	-8.063798	0.340084	1.604269
H	-8.551114	-0.568014	1.977950
H	-7.186304	0.532363	2.234220
H	-8.759463	1.177730	1.737975
C	-6.696333	1.755717	-0.752954
H	-5.826749	1.973024	-0.120936
H	-6.348420	1.694462	-1.790596
H	-7.381217	2.609871	-0.679612
C	-6.381229	-6.230993	2.842606
H	-6.624076	-5.405264	3.522082
H	-6.358419	-5.827133	1.823556
H	-7.202255	-6.956558	2.891525
C	-4.349266	-8.443578	2.085997
H	-3.388580	-8.915439	2.326980
H	-5.120561	-9.223592	2.102867
H	-4.281591	-8.054468	1.063750
C	-4.828721	-7.741156	5.064404
H	-5.600327	-8.516811	5.143669
H	-3.875985	-8.191801	5.367849
H	-5.068048	-6.953180	5.788224
C	1.870585	-4.098920	4.154591
H	1.749731	-3.509145	3.240339
H	1.676108	-3.427908	5.000937
H	2.919394	-4.412568	4.209142
C	1.328806	-7.043827	3.176453
H	1.218174	-6.815919	2.111562
H	2.382736	-7.279999	3.365553
H	0.736239	-7.942955	3.387255
C	0.560326	-6.183734	6.029669
H	-0.131125	-7.030645	6.117745
H	1.531576	-6.508746	6.423393
H	0.189077	-5.381129	6.678012

TS-5

B3LYP-D3 SCF energy (au):	-5608.20641495
B3LYP-D3 enthalpy (au):	-5606.66603395
B3LYP-D3 free energy (au):	-5606.91345095
M06 SCF energy (au):	-5606.49533544
M06 enthalpy (au):	-5604.95495444
M06 free energy (au):	-5605.20237144
M06 free energy (quasi-harmonic) (au):	-5605.17407049

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.716716	-2.069572	-0.819316
Fe	-1.432203	2.155932	1.990755
P	-2.197593	-2.412970	0.930934
P	-0.582410	0.238312	-1.011201
C	-1.653385	0.988889	0.279036
C	-2.226526	0.332515	1.450021
C	-3.256789	1.191147	1.946534
H	-3.855669	1.004856	2.825919
C	-3.314805	2.368302	1.148100
H	-3.962448	3.218930	1.315249
C	-2.326201	2.254827	0.135700
H	-2.126775	2.977930	-0.642801
C	-0.046493	1.793670	3.483553
H	0.228293	0.804530	3.826661
C	-1.121802	2.587321	3.987596
C	-0.126974	3.748905	2.256656
H	0.082525	4.505228	1.512071
C	0.569069	2.513876	2.416606
H	1.385937	2.168097	1.802193
C	-1.292037	0.886941	-2.587191
C	-2.668696	1.090571	-2.745343
H	-3.333488	0.953331	-1.903451
C	-3.197143	1.463668	-3.981415
H	-4.266843	1.628753	-4.076274
C	-2.359649	1.612921	-5.088001
C	-0.986240	1.400117	-4.944167
H	-0.323455	1.513273	-5.797693
C	-0.454315	1.045974	-3.703977
H	0.616168	0.893609	-3.609261
C	1.049190	1.081547	-1.017814
C	1.192731	2.454185	-0.769743
H	0.326321	3.047022	-0.496553
C	2.449844	3.052828	-0.843294
H	2.555206	4.114820	-0.636785
C	3.572037	2.288900	-1.180754
C	3.430818	0.929387	-1.460287
H	4.296543	0.326681	-1.716961
C	2.172260	0.328967	-1.385521
H	2.063675	-0.728438	-1.601249
C	-1.172696	3.794761	3.227802
H	-1.902001	4.586144	3.341926
C	-1.833641	-0.978466	2.107357
H	-1.808542	2.302971	4.774220

C	-2.445220	-1.150826	3.504643
H	-2.175367	-0.301867	4.142928
H	-3.536245	-1.215820	3.455538
H	-2.082452	-2.066986	3.976392
H	-0.746077	-0.988417	2.205881
C	-4.039460	-2.414500	0.984000
C	-4.758470	-1.454234	0.255896
C	-4.743266	-3.311080	1.798376
C	-6.158797	-1.380730	0.331750
H	-4.215165	-0.768012	-0.387105
C	-6.145120	-3.308954	1.869053
H	-4.188660	-4.034742	2.383542
C	-6.824863	-2.327591	1.131848
H	-7.913519	-2.296263	1.181615
C	-1.703138	-3.954049	1.791241
C	-2.234460	-5.159137	1.306098
C	-0.662245	-4.002993	2.725279
C	-1.812466	-6.404504	1.789250
H	-2.986186	-5.123386	0.527079
C	-0.129719	-5.227230	3.163737
H	-0.192358	-3.080187	3.052245
C	-0.751697	-6.408128	2.715331
H	-0.372432	-7.367113	3.073247
H	-2.771590	1.894064	-6.053153
H	4.552169	2.755689	-1.227915
Si	-0.073642	-3.655406	-3.770802
C	0.335510	-2.481853	-5.199336
H	1.314755	-2.729566	-5.626370
H	-0.409982	-2.554810	-6.000007
H	0.367423	-1.438490	-4.864503
C	-0.219598	-5.455047	-4.319285
H	0.714416	-5.848767	-4.738658
H	-0.526879	-6.061388	-3.450830
H	-0.997025	-5.546412	-5.088501
C	-1.751348	-3.201953	-3.021796
C	-2.503772	-2.116631	-3.523326
C	-2.423773	-4.175059	-2.234596
C	-3.872606	-2.005848	-3.270526
H	-2.025716	-1.363351	-4.142450
C	-3.795401	-4.055433	-1.993538
H	-1.894012	-5.070339	-1.870194
C	-4.522450	-2.984838	-2.516558
H	-4.429599	-1.169859	-3.684183
H	-4.303747	-4.822001	-1.415340

H	-5.590862	-2.911005	-2.331049
C	1.178870	-3.159806	-1.254926
C	1.333645	-3.595669	-2.505225
C	2.679465	-4.203814	-2.897345
H	3.236786	-4.504934	-1.997480
H	2.550519	-5.057844	-3.574524
H	3.261141	-3.453763	-3.452706
C	1.662761	-3.133608	0.002595
F	1.203428	-4.080738	0.857120
F	3.500993	-4.881149	-0.130190
C	2.526518	-2.133281	0.676928
C	3.917565	-2.262721	0.536080
C	1.999991	-1.128669	1.496166
C	4.758858	-1.359504	1.186224
H	4.275073	-3.137069	-0.003051
C	2.849884	-0.247282	2.164201
H	0.926322	-1.026530	1.589045
C	4.231916	-0.353268	1.999166
H	5.835536	-1.460891	1.076456
H	2.439232	0.515525	2.816369
H	4.893599	0.337950	2.514775
Si	-7.187739	-0.098526	-0.596804
Si	-7.046490	-4.637222	2.871739
Si	-2.669395	-7.976020	1.156770
Si	1.512956	-5.263969	4.108372
C	-8.208853	0.876890	0.663487
H	-8.870975	1.598197	0.168917
H	-8.834326	0.211451	1.270518
H	-7.556207	1.432292	1.347949
C	-6.061824	1.070726	-1.558895
H	-5.342304	1.571903	-0.900694
H	-5.500851	0.518353	-2.319935
H	-6.647139	1.844635	-2.069861
C	-8.339743	-1.000510	-1.797092
H	-8.974416	-1.724236	-1.271830
H	-8.998465	-0.299441	-2.324277
H	-7.764681	-1.552378	-2.550626
C	-8.571342	-3.869413	3.688838
H	-9.263196	-3.454554	2.945664
H	-9.123659	-4.619806	4.267520
H	-8.290848	-3.058743	4.371732
C	-7.572512	-6.031679	1.706681
H	-8.227963	-5.660619	0.909649
H	-6.699392	-6.493406	1.230395

H	-8.113159	-6.818261	2.247714
C	-5.869718	-5.321692	4.184443
H	-4.996336	-5.807203	3.732400
H	-5.503332	-4.532761	4.852052
H	-6.377254	-6.073062	4.801561
C	-3.557382	-8.757243	2.643717
H	-4.322878	-8.083881	3.049261
H	-4.054209	-9.692373	2.355972
H	-2.856597	-8.987686	3.456081
C	-3.866921	-7.519065	-0.219835
H	-3.230988	-7.129750	-1.027431
H	-4.407908	-8.401642	-0.582658
H	-4.610531	-6.767822	0.074007
C	-1.405598	-9.173100	0.426619
H	-0.539388	-9.347096	1.079019
H	-1.856078	-10.147259	0.201477
H	-1.100405	-8.691349	-0.510849
C	1.995159	-3.497993	4.585058
H	2.191606	-2.887039	3.696593
H	1.214334	-3.003740	5.176850
H	2.912229	-3.504499	5.186587
C	2.863188	-6.015797	3.014843
H	3.816549	-6.017013	3.560845
H	2.631965	-7.066494	2.789149
H	3.024231	-5.481821	2.067128
C	1.311509	-6.329621	5.662300
H	0.571073	-5.899741	6.347418
H	0.976589	-7.342805	5.406766
H	2.260403	-6.422283	6.205022
Cs	1.479439	-6.989988	-0.549831
F	-1.144688	-6.675924	-1.515139
C	5.124281	-9.642722	0.606293
C	5.238001	-10.173755	-0.681370
C	5.245891	-9.336099	-1.805933
C	5.124151	-7.953473	-1.604056
C	5.003424	-7.408078	-0.321230
C	5.006489	-8.262217	0.788160
H	5.125285	-10.310204	1.465312
H	5.325697	-11.250143	-0.816272
H	5.111894	-7.287735	-2.466309
H	4.809216	-6.340516	-0.197990
H	4.900051	-7.845812	1.786647
C	5.407819	-9.906713	-3.196854
H	4.887687	-9.297280	-3.944670

H 6.466320 -9.942278 -3.488358
H 5.018574 -10.928875 -3.262464

TS-5-FBpin
B3LYP-D3 SCF energy (au): -5727.78488610
B3LYP-D3 enthalpy (au): -5726.18993010
B3LYP-D3 free energy (au): -5726.43405910
M06 SCF energy (au): -5726.06848106
M06 enthalpy (au): -5724.47352506
M06 free energy (au): -5724.71765406
M06 free energy (quasi-harmonic) (au): -5724.69137596

Cartesian coordinates
ATOM X Y Z
Cu -0.476983 -2.298053 0.027635
Fe -2.744153 2.435872 -0.239980
P -2.371914 -2.070472 1.349278
P -0.041931 -0.069333 -0.240612
C -1.705068 0.645343 -0.490613
C -2.863860 0.421005 0.346762
C -4.015977 0.804167 -0.404732
H -5.034769 0.779737 -0.044600
C -3.596835 1.245222 -1.692417
H -4.239791 1.626404 -2.474641
C -2.178170 1.153756 -1.749455
H -1.552435 1.427064 -2.587309
C -3.821213 3.944281 0.682958
H -4.816721 3.817608 1.087725
C -3.501639 4.312358 -0.658614
C -1.519791 3.961877 0.472208
H -0.466415 3.851529 0.688608
C -2.596230 3.727519 1.383317
H -2.506106 3.427193 2.419182
C 0.930057 0.694134 -1.594078
C 0.968712 0.045067 -2.838083
H 0.458181 -0.906512 -2.976809
C 1.678801 0.616717 -3.896457
H 1.711315 0.112969 -4.855754
C 2.366011 1.820007 -3.716936
C 2.337560 2.461980 -2.476700
H 2.875467 3.394995 -2.330795
C 1.616509 1.904435 -1.420621
H 1.599616 2.402059 -0.455685

C	0.704729	0.620390	1.293110
C	0.047812	1.488345	2.174254
H	-0.938316	1.853652	1.923971
C	0.663585	1.894732	3.361487
H	0.140077	2.568629	4.034787
C	1.946314	1.442980	3.677769
C	2.613323	0.586735	2.796414
H	3.612803	0.227307	3.023600
C	1.997198	0.173997	1.616377
H	2.522719	-0.496299	0.948193
C	-2.079518	4.319980	-0.789077
H	-1.523681	4.519870	-1.695608
C	-2.863425	-0.266859	1.686296
H	-4.213626	4.504083	-1.450773
C	-4.160179	-0.102507	2.482089
H	-4.384445	0.962305	2.620098
H	-5.006834	-0.569062	1.969007
H	-4.065997	-0.568710	3.467806
H	-2.034335	0.121499	2.281028
C	-3.888912	-2.736187	0.577333
C	-4.018742	-2.486722	-0.798006
C	-4.910075	-3.418626	1.248332
C	-5.133658	-2.919898	-1.526323
H	-3.220048	-1.959238	-1.306878
C	-6.041664	-3.888248	0.559422
H	-4.819915	-3.589388	2.316978
C	-6.124781	-3.625797	-0.820710
H	-6.994012	-3.990319	-1.368641
C	-2.144616	-2.813428	3.002558
C	-2.342225	-4.187042	3.213721
C	-1.538709	-2.054793	4.016159
C	-1.997621	-4.795917	4.432561
H	-2.755608	-4.788922	2.408295
C	-1.150590	-2.625684	5.236748
H	-1.333292	-1.001889	3.843254
C	-1.410960	-3.993360	5.426819
H	-1.136472	-4.451563	6.374864
H	2.927577	2.251931	-4.540959
H	2.421321	1.753311	4.604245
Si	2.405353	-4.113560	0.978397
C	1.460143	-3.397220	2.457980
H	0.717781	-4.104317	2.845255
H	2.156458	-3.153987	3.270577
H	0.928797	-2.472420	2.208645

C	3.522210	-5.498213	1.633869
H	2.927679	-6.286162	2.113382
H	4.108025	-5.960359	0.831692
H	4.225250	-5.114546	2.383210
C	3.496545	-2.744942	0.257102
C	4.578986	-2.234897	1.000172
C	3.209883	-2.139700	-0.980208
C	5.333058	-1.153783	0.539367
H	4.833243	-2.679126	1.961187
C	3.963273	-1.059109	-1.449473
H	2.368896	-2.501002	-1.566627
C	5.020932	-0.560284	-0.687392
H	6.160680	-0.773904	1.134004
H	3.710178	-0.594967	-2.397602
H	5.598569	0.287540	-1.046791
C	0.128091	-4.084663	-0.645813
C	1.246335	-4.792176	-0.350008
C	1.657350	-6.104177	-1.005358
H	0.890010	-6.513841	-1.661054
H	2.561410	-5.957114	-1.613746
H	1.916492	-6.855591	-0.247748
C	-0.994697	-4.541899	-1.425280
F	-1.647164	-3.546332	-2.082268
F	-0.450972	-5.342047	-2.883513
C	-1.941803	-5.564120	-0.895297
C	-1.578998	-6.406436	0.165042
C	-3.200762	-5.713394	-1.493838
C	-2.455552	-7.399337	0.599687
H	-0.616862	-6.274817	0.645936
C	-4.082887	-6.688542	-1.038911
H	-3.467267	-5.082700	-2.325966
C	-3.711185	-7.540322	0.003047
H	-2.162091	-8.060162	1.408781
H	-5.058291	-6.785257	-1.505900
H	-4.395176	-8.309790	0.349921
B	-0.988865	-4.966386	-4.419288
O	-0.254060	-5.831794	-5.253635
O	-0.599743	-3.615215	-4.642749
C	0.849562	-5.070297	-5.765459
C	0.241496	-3.622553	-5.805485
C	2.027540	-5.181209	-4.781558
C	1.247467	-5.640553	-7.125481
C	1.258085	-2.491140	-5.687517
C	-0.653974	-3.395275	-7.034444

H	2.245627	-6.241190	-4.616539
H	2.929643	-4.695416	-5.171018
H	1.770426	-4.737038	-3.817013
H	2.011579	-5.015980	-7.603941
H	1.660122	-6.646944	-6.996877
H	0.384045	-5.714581	-7.790771
H	1.996675	-2.535553	-6.496747
H	0.732835	-1.532522	-5.757837
H	1.781865	-2.525615	-4.728667
H	-1.229237	-2.475968	-6.882238
H	-0.071397	-3.296140	-7.957603
H	-1.360123	-4.222759	-7.149745
Si	-5.274261	-2.590774	-3.392746
Si	-7.382518	-4.866887	1.463516
Si	-2.254886	-6.652520	4.684259
Si	-0.207078	-1.589915	6.506500
C	-3.688532	-1.810924	-4.050876
H	-3.386980	-0.933754	-3.466166
H	-2.855096	-2.521512	-4.062922
H	-3.847720	-1.477928	-5.084923
C	-5.606333	-4.229239	-4.277014
H	-5.968799	-4.052656	-5.297451
H	-4.681489	-4.811039	-4.353196
H	-6.359843	-4.834400	-3.757820
C	-6.738005	-1.408270	-3.636092
H	-6.555551	-0.453986	-3.126075
H	-6.905112	-1.195440	-4.699274
H	-7.665412	-1.829634	-3.229059
C	-9.080290	-4.311404	0.838921
H	-9.186161	-4.475583	-0.240216
H	-9.883427	-4.868323	1.336919
H	-9.242708	-3.243904	1.029165
C	-7.157537	-6.717434	1.137491
H	-7.184037	-6.939954	0.064210
H	-6.191504	-7.060583	1.523854
H	-7.946774	-7.304271	1.623626
C	-7.234960	-4.544672	3.322782
H	-6.278684	-4.907812	3.717924
H	-7.309318	-3.475866	3.555887
H	-8.032998	-5.062666	3.868414
C	-0.785723	-7.560089	3.904898
H	-0.595535	-7.203594	2.887066
H	0.123903	-7.376988	4.489970
H	-0.944450	-8.644719	3.863241

C	-3.894500	-7.155175	3.884788
H	-4.735154	-6.693305	4.416723
H	-3.949440	-6.847222	2.835707
H	-4.036636	-8.242498	3.918585
C	-2.315091	-7.039351	6.535271
H	-3.113070	-6.478660	7.036239
H	-2.505630	-8.107377	6.697292
H	-1.369743	-6.797051	7.035283
C	1.620758	-1.570991	6.017292
H	1.745657	-1.144970	5.015340
H	2.219113	-0.973874	6.717065
H	2.032493	-2.587171	6.001247
C	-0.882430	0.178277	6.486417
H	-1.955135	0.201951	6.711668
H	-0.368608	0.799021	7.230838
H	-0.729627	0.647808	5.507734
C	-0.415755	-2.350763	8.225538
H	0.000024	-3.364341	8.273851
H	0.103664	-1.748249	8.980643
H	-1.472275	-2.409000	8.512752
F	-2.338426	-5.216392	-4.300588

TS-6

B3LYP-D3 SCF energy (au):	-5608.21474450
B3LYP-D3 enthalpy (au):	-5606.67551250
B3LYP-D3 free energy (au):	-5606.92506450
M06 SCF energy (au):	-5606.49857692
M06 enthalpy (au):	-5604.95934492
M06 free energy (au):	-5605.20889692
M06 free energy (quasi-harmonic) (au):	-5605.17993942

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.905517	-2.618130	-1.106222
Fe	-1.465880	2.010774	1.349361
P	-1.906277	-2.751401	0.989666
P	-0.187946	-0.415872	-1.240071
C	-1.439019	0.526140	-0.161892
C	-1.972116	0.014655	1.089004
C	-3.126969	0.788418	1.433346
H	-3.729602	0.662117	2.322142
C	-3.305984	1.795199	0.445274
H	-4.058685	2.573494	0.456519

C	-2.263409	1.648972	-0.515195
H	-2.105397	2.297040	-1.364384
C	-0.706032	2.424491	3.244224
H	-0.835681	1.797712	4.115903
C	-1.590175	3.463606	2.825065
C	0.136306	3.332361	1.299881
H	0.750309	3.508101	0.429392
C	0.357966	2.335995	2.299368
H	1.168765	1.621672	2.313731
C	-0.227658	0.619608	-2.767452
C	-1.456522	0.910652	-3.379048
H	-2.383700	0.588491	-2.918808
C	-1.511266	1.601802	-4.591576
H	-2.476847	1.803803	-5.048142
C	-0.335560	2.022183	-5.212368
C	0.894780	1.723516	-4.621008
H	1.819265	2.022047	-5.108944
C	0.949741	1.015088	-3.422181
H	1.904838	0.712726	-3.013699
C	1.348187	-0.065431	-0.282306
C	2.019145	1.160827	-0.336693
H	1.634556	1.956596	-0.965048
C	3.182657	1.371890	0.408434
H	3.690636	2.331238	0.349976
C	3.678214	0.367969	1.243752
C	3.013214	-0.861203	1.308372
H	3.389436	-1.652652	1.952273
C	1.869873	-1.078161	0.537896
H	1.390587	-2.052390	0.542718
C	-1.065340	4.027950	1.623747
H	-1.523443	4.812969	1.035940
C	-1.454672	-1.150673	1.897596
H	-2.515782	3.746000	3.310125
C	-1.898919	-1.139906	3.364575
H	-1.590436	-0.204049	3.838113
H	-2.986056	-1.219706	3.458565
H	-1.449989	-1.974320	3.910944
H	-0.360669	-1.132850	1.867332
C	-3.732861	-2.715033	0.978679
C	-4.325960	-2.300142	-0.220953
C	-4.556479	-2.975688	2.084936
C	-5.714418	-2.124722	-0.341767
H	-3.675479	-2.084938	-1.067232
C	-5.952151	-2.864861	2.001685

H	-4.100710	-3.272533	3.023421
C	-6.502241	-2.426914	0.781082
H	-7.582810	-2.308321	0.707932
C	-1.340059	-4.069890	2.130733
C	-2.146438	-5.120047	2.590194
C	0.034739	-4.113361	2.407941
C	-1.617545	-6.173317	3.351783
H	-3.198856	-5.132539	2.332919
C	0.627527	-5.199932	3.065660
H	0.668493	-3.311478	2.042212
C	-0.226188	-6.205617	3.550291
H	0.208431	-7.054306	4.075280
H	-0.374700	2.560360	-6.155641
H	4.570342	0.540775	1.839691
Si	-1.308239	-3.651747	-4.861421
C	-2.339166	-4.839546	-5.915575
H	-3.127324	-5.300679	-5.307848
H	-2.823784	-4.316725	-6.749094
H	-1.726584	-5.646387	-6.333179
C	-2.436267	-2.369518	-4.072239
H	-3.139840	-2.863761	-3.390636
H	-1.848106	-1.653453	-3.494141
H	-3.010559	-1.810801	-4.819789
C	0.065847	-2.896970	-5.917114
C	0.254570	-3.252854	-7.264872
C	0.997630	-2.019469	-5.325354
C	1.334118	-2.756571	-8.002528
H	-0.443961	-3.930177	-7.751559
C	2.073449	-1.520622	-6.063759
H	0.918486	-1.746579	-4.272831
C	2.247323	-1.886686	-7.401550
H	1.459472	-3.045768	-9.043447
H	2.773524	-0.835992	-5.589343
H	3.086113	-1.496382	-7.973642
C	-0.345828	-4.316003	-2.242941
C	-0.423156	-4.655986	-3.537168
C	0.315167	-5.892880	-4.029914
H	1.039065	-6.234996	-3.279903
H	-0.413131	-6.695898	-4.217429
H	0.816067	-5.692432	-4.985232
C	0.005991	-4.968164	-1.092791
F	0.867487	-4.361009	-0.228122
F	2.019940	-6.131222	-1.509705
C	-0.752130	-6.099825	-0.537358

C	-0.076328	-7.163503	0.077568
C	-2.144883	-6.157048	-0.708430
C	-0.797663	-8.274827	0.509243
H	1.005538	-7.124962	0.098597
C	-2.855969	-7.273578	-0.275463
H	-2.657543	-5.316234	-1.165904
C	-2.182710	-8.336835	0.332857
H	-0.271343	-9.105873	0.971226
H	-3.934199	-7.310426	-0.406754
H	-2.737012	-9.209987	0.667247
Si	-6.431340	-1.466012	-1.964563
Si	-7.050148	-3.330235	3.469304
Si	-2.765489	-7.456034	4.128395
Si	2.514220	-5.339380	3.132918
C	-8.143382	-0.733566	-1.633046
H	-8.563573	-0.303877	-2.550453
H	-8.848952	-1.492633	-1.274049
H	-8.097139	0.063219	-0.881255
C	-5.250477	-0.142820	-2.621994
H	-4.995456	0.588602	-1.846221
H	-4.316763	-0.601536	-2.965505
H	-5.686204	0.393647	-3.473894
C	-6.561221	-2.874219	-3.223248
H	-7.224985	-3.670327	-2.865570
H	-6.953518	-2.513096	-4.182196
H	-5.576991	-3.318880	-3.413552
C	-8.271302	-1.924417	3.803072
H	-8.879368	-1.705802	2.916837
H	-8.956546	-2.179512	4.620665
H	-7.745628	-1.002710	4.079374
C	-7.993504	-4.914624	3.042845
H	-8.604531	-4.782446	2.141800
H	-7.300852	-5.743948	2.855441
H	-8.661906	-5.212763	3.860085
C	-5.962010	-3.629570	4.988646
H	-5.276697	-4.472585	4.837139
H	-5.357595	-2.748568	5.235848
H	-6.580154	-3.864402	5.863455
C	-3.041977	-6.985930	5.943747
H	-3.505839	-5.995017	6.024841
H	-3.699325	-7.706141	6.446927
H	-2.094464	-6.953686	6.494873
C	-4.435777	-7.434373	3.237263
H	-4.314891	-7.595306	2.161279

H	-5.095160	-8.217800	3.630027
H	-4.948965	-6.474792	3.375718
C	-1.978208	-9.173474	4.042122
H	-1.009822	-9.194685	4.556548
H	-2.620350	-9.924724	4.517881
H	-1.808968	-9.476340	3.003931
C	3.186872	-4.088211	4.389126
H	2.882722	-3.067937	4.121428
H	2.810119	-4.289703	5.398893
H	4.283314	-4.109675	4.427353
C	3.273396	-4.936239	1.444382
H	4.359443	-5.096251	1.498422
H	2.870189	-5.523711	0.609216
H	3.110683	-3.876498	1.209507
C	2.976275	-7.100697	3.642481
H	2.609488	-7.349774	4.645514
H	2.559414	-7.832215	2.939952
H	4.065514	-7.228007	3.647596
Cs	3.247374	-3.598703	-2.341317
F	1.355424	-1.488864	-2.362800
C	6.055700	-4.704064	-4.893228
C	5.777100	-5.796020	-4.061322
C	4.583771	-6.523907	-4.193697
C	3.693151	-6.140888	-5.212106
C	3.952530	-5.041207	-6.032268
C	5.136657	-4.312244	-5.871062
H	6.992140	-4.162648	-4.776617
H	6.494290	-6.087473	-3.296039
H	2.771482	-6.700843	-5.337146
H	3.227229	-4.738916	-6.783306
H	5.339525	-3.455422	-6.508089
C	4.206044	-7.617222	-3.224072
H	3.773389	-8.478427	-3.747249
H	5.075124	-7.966913	-2.655038
H	3.445139	-7.240752	-2.518283

TS-6-FBpin

B3LYP-D3 SCF energy (au):	-5727.78736478
B3LYP-D3 enthalpy (au):	-5726.19244278
B3LYP-D3 free energy (au):	-5726.43569278
M06 SCF energy (au):	-5726.07236241
M06 enthalpy (au):	-5724.47744041
M06 free energy (au):	-5724.72069041

M06 free energy (quasi-harmonic) (au): -5724.69534863

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.306423	-1.564410	-0.469739
Fe	-3.616197	2.272255	0.674617
P	-2.184889	-2.314754	0.699037
P	-0.325741	0.621447	0.234301
C	-2.091824	1.013204	0.012781
C	-3.174069	0.224054	0.556417
C	-4.349695	0.533037	-0.191101
H	-5.334013	0.124472	-0.010417
C	-4.013044	1.488140	-1.194086
H	-4.701583	1.942280	-1.894392
C	-2.627651	1.789805	-1.071060
H	-2.065577	2.485865	-1.678160
C	-5.116772	2.990977	1.906334
H	-6.028761	2.451582	2.125884
C	-4.910569	3.878006	0.807299
C	-2.930856	3.737180	1.986589
H	-1.897947	3.866699	2.278863
C	-3.893265	2.902931	2.636550
H	-3.727049	2.298259	3.518674
C	0.531655	1.921895	-0.726476
C	0.777950	1.655209	-2.081303
H	0.473863	0.703955	-2.506657
C	1.436528	2.592410	-2.877795
H	1.631087	2.362320	-3.921249
C	1.861435	3.801479	-2.319368
C	1.622098	4.071208	-0.968088
H	1.957696	5.008671	-0.532545
C	0.957038	3.136574	-0.172063
H	0.784521	3.342065	0.880621
C	0.176755	0.889949	1.980822
C	-0.699209	1.317578	2.986967
H	-1.716683	1.575403	2.727365
C	-0.268189	1.404832	4.313524
H	-0.961339	1.734176	5.083398
C	1.045764	1.071467	4.647952
C	1.927080	0.648347	3.648282
H	2.951534	0.382049	3.892286
C	1.496331	0.547856	2.326247
H	2.186771	0.199996	1.567607
C	-3.558905	4.336443	0.855684

H	-3.082748	4.991978	0.138570
C	-3.017073	-0.854124	1.592460
H	-5.637664	4.122202	0.043835
C	-4.301754	-1.199196	2.348668
H	-4.692522	-0.300710	2.841454
H	-5.074012	-1.587278	1.678617
H	-4.108031	-1.959308	3.112153
H	-2.264526	-0.531364	2.316097
C	-3.589789	-3.046903	-0.207271
C	-3.829825	-2.570912	-1.503666
C	-4.482524	-3.961935	0.366055
C	-4.965134	-2.961096	-2.226648
H	-3.111344	-1.893479	-1.949197
C	-5.610125	-4.415084	-0.337879
H	-4.285775	-4.333754	1.368894
C	-5.832433	-3.886384	-1.621670
H	-6.708625	-4.220404	-2.176345
C	-1.752918	-3.488728	2.034704
C	-1.581253	-4.845945	1.720933
C	-1.352927	-3.032982	3.298477
C	-1.010589	-5.746968	2.633397
H	-1.871028	-5.192686	0.732724
C	-0.793840	-3.899109	4.251304
H	-1.446300	-1.977970	3.540773
C	-0.637421	-5.249367	3.894701
H	-0.191372	-5.932808	4.614784
H	2.385027	4.529730	-2.932974
H	1.378643	1.132255	5.680328
Si	2.789657	-3.148446	0.063015
C	1.667531	-3.226515	1.578928
H	1.041374	-4.122275	1.590282
H	2.287636	-3.232710	2.484540
H	1.008059	-2.355740	1.656202
C	4.060220	-4.544455	0.225167
H	3.555466	-5.518609	0.212854
H	4.795144	-4.536814	-0.586938
H	4.607282	-4.470392	1.172861
C	3.678902	-1.471359	0.160627
C	4.672787	-1.251759	1.133844
C	3.301801	-0.374242	-0.634891
C	5.258832	0.004643	1.306824
H	4.993623	-2.070542	1.775409
C	3.889356	0.884162	-0.477596
H	2.505513	-0.493483	-1.359795

C	4.868497	1.076538	0.498336
H	6.021576	0.147298	2.068853
H	3.562590	1.711862	-1.100452
H	5.321877	2.055347	0.633149
C	0.803144	-2.515563	-1.839777
C	1.907851	-3.271643	-1.611093
C	2.568345	-4.181714	-2.637125
H	2.094258	-4.132600	-3.617046
H	3.635550	-3.940172	-2.744963
H	2.528665	-5.226463	-2.298812
C	0.228320	-2.212164	-3.122994
F	-1.093193	-1.897710	-3.074375
F	0.012743	-3.701638	-4.081818
C	0.917946	-1.377113	-4.146738
C	2.284165	-1.079692	-4.053141
C	0.174463	-0.876026	-5.229363
C	2.894511	-0.269210	-5.009386
H	2.863929	-1.466993	-3.226133
C	0.789454	-0.067656	-6.181790
H	-0.864827	-1.158123	-5.336647
C	2.148178	0.245691	-6.071655
H	3.952066	-0.037974	-4.918455
H	0.208608	0.311195	-7.018049
H	2.623711	0.879326	-6.815827
B	-1.452293	-4.308984	-4.569699
O	-2.225211	-4.530143	-3.404152
O	-1.098194	-5.540016	-5.164801
C	-2.009585	-5.893535	-3.021771
C	-1.726353	-6.586108	-4.409678
C	-0.795339	-5.947950	-2.079488
C	-3.251571	-6.402274	-2.292344
C	-0.782164	-7.786715	-4.341691
C	-3.017025	-6.977784	-5.146005
H	-0.955898	-5.240502	-1.260388
H	-0.649182	-6.950922	-1.663921
H	0.114041	-5.640498	-2.597010
H	-3.173931	-7.477495	-2.089967
H	-3.363567	-5.876181	-1.339777
H	-4.156632	-6.215542	-2.873997
H	-1.191799	-8.572234	-3.694733
H	-0.645799	-8.206142	-5.344277
H	0.200822	-7.495683	-3.964022
H	-2.764348	-7.244750	-6.177073
H	-3.516293	-7.832950	-4.675700

H	-3.713782	-6.135889	-5.175570
Si	-5.326198	-2.253337	-3.945379
Si	-6.728428	-5.716111	0.447613
Si	-0.567153	-7.500714	2.075084
Si	-0.142641	-3.217416	5.890177
C	-4.048202	-0.926224	-4.349328
H	-3.993916	-0.153216	-3.573269
H	-3.065556	-1.395423	-4.445068
H	-4.285080	-0.437188	-5.302297
C	-7.064205	-1.491811	-3.867188
H	-7.357459	-1.073728	-4.838237
H	-7.816982	-2.239229	-3.587151
H	-7.108075	-0.684099	-3.125836
C	-5.278401	-3.621346	-5.243622
H	-5.737926	-3.295570	-6.185153
H	-4.235025	-3.882084	-5.442045
H	-5.804336	-4.522054	-4.904904
C	-7.966837	-6.348272	-0.832910
H	-7.453707	-6.765101	-1.707685
H	-8.597483	-7.138406	-0.407853
H	-8.630540	-5.548957	-1.183936
C	-7.641345	-4.950184	1.920320
H	-6.931561	-4.542261	2.650619
H	-8.293226	-4.129649	1.597326
H	-8.263439	-5.691323	2.437317
C	-5.629343	-7.130963	1.057709
H	-5.083158	-7.587335	0.224241
H	-4.883715	-6.767001	1.775124
H	-6.214954	-7.915321	1.552703
C	1.017620	-7.359726	1.046740
H	0.869256	-6.678315	0.201165
H	1.839172	-6.961155	1.654568
H	1.332516	-8.331046	0.645906
C	-1.967704	-8.216525	1.029928
H	-1.688328	-9.197229	0.625298
H	-2.882428	-8.343826	1.619752
H	-2.209669	-7.568436	0.181345
C	-0.259560	-8.591156	3.590235
H	-1.140117	-8.630167	4.242521
H	-0.027069	-9.617916	3.282536
H	0.585810	-8.229944	4.188064
C	1.650980	-2.671515	5.629913
H	2.276346	-3.516889	5.318522
H	1.706871	-1.907760	4.845998

H	2.083333	-2.250269	6.546305
C	-1.189611	-1.727433	6.405200
H	-1.106458	-0.912069	5.677442
H	-2.248956	-1.994178	6.499251
H	-0.855060	-1.336015	7.373937
C	-0.227284	-4.564001	7.215911
H	0.386338	-5.433609	6.951812
H	0.139551	-4.184728	8.177543
H	-1.255542	-4.914343	7.364180
F	-1.902562	-3.290892	-5.388649

TS-3a

B3LYP-D3 SCF energy (au):	-5216.56316685
B3LYP-D3 enthalpy (au):	-5215.16669585
B3LYP-D3 free energy (au):	-5215.38527085
M06 SCF energy (au):	-5215.02253705
M06 enthalpy (au):	-5213.62606605
M06 free energy (au):	-5213.84464105
M06 free energy (quasi-harmonic) (au):	-5213.82350120

Cartesian coordinates

ATOM	X	Y	Z
Cu	0.119388	0.674297	0.690157
Fe	-2.666840	1.236925	4.097872
P	-1.113706	-1.214821	1.110611
P	-1.346191	2.391070	1.123210
C	-2.764802	1.805313	2.106446
C	-3.220037	0.433886	2.242239
C	-4.332942	0.455196	3.143241
H	-4.880436	-0.422732	3.463909
C	-4.581797	1.796147	3.553294
H	-5.328008	2.116589	4.269157
C	-3.617554	2.627497	2.921842
H	-3.496212	3.691119	3.072509
C	-1.503041	-0.036751	5.262537
H	-1.353990	-1.084792	5.068380
C	-2.561397	0.514327	6.040503
C	-1.276163	2.257679	5.242289
H	-0.931055	3.253623	5.005315
C	-0.707938	1.037780	4.759859
H	0.139130	0.948959	4.090436
C	-2.116128	3.183573	-0.347871
C	-3.446862	2.965430	-0.725228

H	-4.095852	2.367128	-0.093483
C	-3.946638	3.519944	-1.907342
H	-4.980699	3.339814	-2.189767
C	-3.127772	4.308485	-2.716032
C	-1.801566	4.544553	-2.337975
H	-1.158349	5.161199	-2.960425
C	-1.298386	3.980787	-1.167604
H	-0.264154	4.157654	-0.882979
C	-0.733702	3.860187	2.052244
C	-1.411823	5.090859	2.042369
H	-2.313274	5.210589	1.447894
C	-0.923974	6.168730	2.781295
H	-1.456818	7.116205	2.770257
C	0.251161	6.031687	3.527815
C	0.936969	4.816252	3.526149
H	1.863926	4.707536	4.081490
C	0.450791	3.732080	2.791010
H	0.986307	2.787781	2.780422
C	-2.420346	1.934761	6.030452
H	-3.093673	2.645274	6.493182
C	-2.946297	-0.790608	1.386074
H	-3.356112	-0.044858	6.517978
C	-3.727686	-0.619326	0.063662
H	-4.735120	-0.251553	0.287944
H	-3.249864	0.110192	-0.599041
H	-3.825062	-1.566689	-0.470322
H	-3.383103	-1.644554	1.914643
C	-1.163064	-2.690155	-0.025773
C	-0.638746	-3.922422	0.399781
C	-1.665132	-2.611865	-1.336845
C	-0.669817	-5.069495	-0.404808
H	-0.187250	-3.992112	1.380221
C	-1.764694	-3.745581	-2.162892
H	-1.987720	-1.653745	-1.727706
C	-1.265143	-4.961641	-1.670598
H	-1.318774	-5.846294	-2.303742
C	-0.653352	-2.033083	2.692771
C	-1.472097	-3.000003	3.293289
C	0.592326	-1.742882	3.265357
C	-1.075113	-3.687163	4.450698
H	-2.427280	-3.246575	2.834511
C	1.022014	-2.387279	4.440269
H	1.200419	-0.965139	2.813340
C	0.177777	-3.360453	5.001599

H	0.497089	-3.874627	5.907064
H	-3.518472	4.740492	-3.633321
H	0.633394	6.874582	4.098137
Si	0.064293	-6.697399	0.209159
Si	-2.630464	-3.695950	-3.843019
Si	-2.245685	-4.958639	5.208361
Si	2.605148	-1.847932	5.330944
C	0.988184	-6.387802	1.831170
H	0.327453	-5.981980	2.606307
H	1.421735	-7.318840	2.216076
H	1.807212	-5.671497	1.693312
C	1.257801	-7.358110	-1.105088
H	1.643249	-8.348883	-0.835175
H	0.761945	-7.446387	-2.079438
H	2.115226	-6.686745	-1.231305
C	-1.326857	-7.952982	0.479645
H	-1.898639	-8.113785	-0.442452
H	-0.930085	-8.924427	0.800134
H	-2.025378	-7.604479	1.249090
C	-1.880317	-5.010375	-4.976832
H	-2.052321	-6.025156	-4.598565
H	-2.322520	-4.954829	-5.979135
H	-0.799271	-4.863454	-5.070858
C	-2.468260	-1.989824	-4.635203
H	-2.969928	-1.219325	-4.038482
H	-1.415301	-1.709867	-4.739392
H	-2.925947	-1.983870	-5.632107
C	-4.468468	-4.072957	-3.567494
H	-4.927396	-3.325282	-2.908705
H	-5.023239	-4.071163	-4.514212
H	-4.605246	-5.055168	-3.099320
C	-3.854839	-4.065257	5.655585
H	-3.667840	-3.278284	6.396374
H	-4.292207	-3.586586	4.770454
H	-4.603599	-4.751225	6.070095
C	-1.460915	-5.720847	6.748976
H	-2.126905	-6.468519	7.196218
H	-0.514336	-6.220262	6.510000
H	-1.255143	-4.960834	7.512179
C	-2.599608	-6.296939	3.916114
H	-1.693904	-6.872015	3.691205
H	-3.368937	-6.999891	4.258197
H	-2.946469	-5.851051	2.975658
C	3.678397	-0.820004	4.173358

H	4.050168	-1.413074	3.329760
H	3.103247	0.011127	3.752964
H	4.545743	-0.416003	4.711271
C	2.077011	-0.804569	6.820594
H	1.490295	0.061065	6.491194
H	1.448536	-1.384953	7.507265
H	2.943655	-0.437882	7.384842
C	3.529162	-3.390635	5.928462
H	3.837666	-4.018082	5.083745
H	4.431647	-3.113946	6.487476
H	2.907762	-4.005685	6.590928
Si	1.037580	0.368063	-2.999702
C	-0.767064	0.763756	-2.627700
H	-0.939131	1.842799	-2.670784
H	-1.424974	0.283827	-3.358111
H	-1.054664	0.428118	-1.627457
C	1.481244	1.210531	-4.640333
H	1.396086	2.300391	-4.545904
H	2.503666	0.978475	-4.958453
H	0.801410	0.899240	-5.442979
C	1.339578	-1.494182	-3.182077
C	1.324322	-2.140022	-4.431131
C	1.635986	-2.274746	-2.048231
C	1.584893	-3.508804	-4.546308
H	1.117575	-1.569473	-5.334514
C	1.899198	-3.640059	-2.156747
H	1.664698	-1.803438	-1.069240
C	1.870872	-4.262818	-3.406177
H	1.573704	-3.982818	-5.525166
H	2.116789	-4.218441	-1.263910
H	2.069691	-5.328280	-3.489119
C	1.869294	0.942146	-0.340540
C	2.221512	0.928511	-1.645437
C	3.649470	1.198037	-2.111161
H	4.329966	1.422771	-1.282835
H	4.054305	0.327426	-2.646564
H	3.686016	2.039785	-2.816232
C	2.738436	1.213879	0.733367
F	1.591215	0.958255	2.352038
F	3.544730	0.214820	1.132593
C	3.197697	2.550050	1.137877
C	4.086933	2.700916	2.213318
C	2.775991	3.678516	0.419394
C	4.546468	3.968013	2.560625

H	4.396342	1.824180	2.770611
C	3.241117	4.943672	0.769485
H	2.086921	3.547277	-0.408020
C	4.124679	5.091803	1.840820
H	5.233259	4.082588	3.394903
H	2.905458	5.814802	0.214193
H	4.481711	6.079911	2.118489

TS-4a

B3LYP-D3 SCF energy (au):	-5216.56612862
B3LYP-D3 enthalpy (au):	-5215.16962962
B3LYP-D3 free energy (au):	-5215.38947762
M06 SCF energy (au):	-5215.02469261
M06 enthalpy (au):	-5213.62819361
M06 free energy (au):	-5213.84804161
M06 free energy (quasi-harmonic) (au):	-5213.82619999

Cartesian coordinates

ATOM	X	Y	Z
Cu	0.132901	0.659418	0.804334
Fe	-2.629262	1.467005	4.137142
P	-1.167110	-1.132363	1.292228
P	-1.214905	2.460997	1.172870
C	-2.687191	1.981667	2.134899
C	-3.207516	0.634298	2.303644
C	-4.325175	0.731954	3.193204
H	-4.914567	-0.110729	3.533348
C	-4.516511	2.093275	3.563529
H	-5.253529	2.466987	4.262850
C	-3.511525	2.862671	2.917520
H	-3.345722	3.923205	3.043278
C	-1.552774	0.175681	5.361967
H	-1.479517	-0.889792	5.219611
C	-2.565056	0.837890	6.114376
C	-1.166673	2.446413	5.228459
H	-0.753201	3.402648	4.941775
C	-0.687134	1.168201	4.805557
H	0.152408	0.995916	4.143220
C	-1.889797	3.299493	-0.314759
C	-3.233434	3.214991	-0.699624
H	-3.947768	2.706092	-0.059333
C	-3.657702	3.779627	-1.906446
H	-4.702256	3.704069	-2.197452

C	-2.747563	4.440514	-2.732166
C	-1.405632	4.539144	-2.347433
H	-0.691377	5.052058	-2.986160
C	-0.977596	3.967227	-1.151442
H	0.070998	4.019543	-0.869375
C	-0.470773	3.874892	2.085610
C	-1.089387	5.134299	2.151334
H	-2.021136	5.310485	1.620618
C	-0.501574	6.169617	2.877500
H	-0.988975	7.139942	2.927640
C	0.718356	5.961281	3.529823
C	1.351132	4.719991	3.441342
H	2.306620	4.557852	3.933270
C	0.764915	3.675911	2.719752
H	1.254090	2.706897	2.653819
C	-2.326305	2.242760	6.033110
H	-2.946666	3.020095	6.461079
C	-2.984952	-0.631974	1.488911
H	-3.393584	0.360324	6.621821
C	-3.730622	-0.460843	0.146841
H	-4.727397	-0.050216	0.342540
H	-3.212341	0.234007	-0.521815
H	-3.857883	-1.416798	-0.365668
H	-3.473873	-1.443951	2.037810
C	-1.095744	-2.627916	0.182018
C	-0.318181	-3.718873	0.616595
C	-1.654530	-2.701460	-1.104679
C	-0.148351	-4.877135	-0.151189
H	0.161714	-3.669175	1.585061
C	-1.536743	-3.855652	-1.902487
H	-2.183056	-1.847322	-1.509504
C	-0.789025	-4.931269	-1.400146
H	-0.685611	-5.829480	-2.007130
C	-0.804188	-1.955365	2.895523
C	-1.655509	-2.938050	3.419551
C	0.420721	-1.701360	3.525474
C	-1.310906	-3.674551	4.562679
H	-2.585588	-3.166488	2.902527
C	0.790254	-2.385846	4.698278
H	1.069239	-0.939177	3.103469
C	-0.086054	-3.369829	5.186003
H	0.191825	-3.922641	6.082021
H	-3.078857	4.877174	-3.670382
H	1.177438	6.769726	4.093094

Si	0.882876	-6.313760	0.514044
Si	-2.403973	-3.984343	-3.580507
Si	-2.450686	-5.063085	5.143146
Si	2.347401	-1.899671	5.662212
C	1.418677	-5.933285	2.289650
H	0.551188	-5.737579	2.930726
H	1.964833	-6.783781	2.715801
H	2.070363	-5.054919	2.357617
C	2.394600	-6.550736	-0.604077
H	3.020196	-7.385998	-0.265950
H	2.086350	-6.761986	-1.635614
H	3.020623	-5.650498	-0.628092
C	-0.174627	-7.882805	0.496057
H	-0.559011	-8.094346	-0.509108
H	0.400972	-8.757186	0.823913
H	-1.035983	-7.775356	1.166271
C	-1.532571	-5.282395	-4.642798
H	-1.567622	-6.281405	-4.192058
H	-2.009725	-5.350647	-5.628158
H	-0.482206	-5.010864	-4.794490
C	-2.375321	-2.315608	-4.461770
H	-2.942030	-1.557488	-3.908860
H	-1.348030	-1.955817	-4.582026
H	-2.826883	-2.400787	-5.457981
C	-4.202851	-4.503193	-3.281004
H	-4.723930	-3.768345	-2.654822
H	-4.755006	-4.589624	-4.225251
H	-4.256921	-5.471806	-2.769678
C	-4.196919	-4.361782	5.351042
H	-4.215801	-3.583261	6.123204
H	-4.554236	-3.910375	4.417178
H	-4.913353	-5.140947	5.638543
C	-1.823199	-5.770155	6.779542
H	-2.479931	-6.573973	7.133415
H	-0.815095	-6.188950	6.675411
H	-1.787126	-5.001410	7.560668
C	-2.462026	-6.406653	3.806525
H	-1.473023	-6.870532	3.710734
H	-3.185742	-7.199747	4.031021
H	-2.720072	-5.980756	2.828943
C	3.535288	-0.968237	4.540363
H	3.953954	-1.633820	3.778140
H	3.040170	-0.145781	4.012971
H	4.371091	-0.555676	5.119534

C	1.792930	-0.804936	7.104599
H	1.270251	0.083162	6.730444
H	1.100398	-1.340081	7.765933
H	2.646707	-0.471620	7.707770
C	3.160228	-3.476996	6.329187
H	3.452617	-4.143384	5.508623
H	4.063262	-3.237650	6.904270
H	2.488579	-4.037308	6.991081
Si	0.773596	0.689740	-3.026762
C	-1.017717	0.659842	-2.451709
H	-1.424831	1.666144	-2.345155
H	-1.628884	0.111524	-3.174735
H	-1.094738	0.157982	-1.483968
C	0.948733	1.954004	-4.426600
H	0.696346	2.955050	-4.056454
H	1.966429	1.986742	-4.831439
H	0.263550	1.728304	-5.252989
C	1.231827	-1.032948	-3.679962
C	1.380878	-1.321882	-5.048290
C	1.439024	-2.083524	-2.765958
C	1.720760	-2.604479	-5.488029
H	1.233714	-0.536059	-5.786251
C	1.783357	-3.365607	-3.195304
H	1.332649	-1.895600	-1.701620
C	1.926734	-3.628602	-4.560252
H	1.830659	-2.803036	-6.551521
H	1.930484	-4.157063	-2.466220
H	2.199648	-4.625321	-4.898871
C	1.798305	0.865386	-0.353266
C	2.047365	1.008609	-1.673557
C	3.460901	1.220535	-2.210616
H	4.217249	1.224410	-1.418463
H	3.731779	0.437001	-2.932112
H	3.535517	2.178374	-2.743751
C	2.771618	0.821353	0.661940
F	1.699624	0.802614	2.355905
F	3.387002	1.960755	1.020479
C	3.517756	-0.404023	0.972552
C	4.871333	-0.331478	1.330068
C	2.908268	-1.659628	0.811094
C	5.611334	-1.501508	1.500615
H	5.337206	0.638706	1.461997
C	3.650268	-2.822054	0.987196
H	1.853293	-1.708170	0.567596

C	5.005615	-2.748177	1.329023
H	6.661123	-1.438098	1.773044
H	3.170824	-3.786772	0.857959
H	5.582692	-3.658640	1.465924

TS-3c

B3LYP-D3 SCF energy (au):	-5216.56542305
B3LYP-D3 enthalpy (au):	-5215.16940005
B3LYP-D3 free energy (au):	-5215.38942705
M06 SCF energy (au):	-5215.02769007
M06 enthalpy (au):	-5213.63166707
M06 free energy (au):	-5213.85169407
M06 free energy (quasi-harmonic) (au):	-5213.82952102

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.397620	-1.406266	-0.110114
Fe	-2.831938	2.283977	2.395132
P	-2.302053	-2.216896	0.887030
P	-0.800760	0.848817	-0.209618
C	-2.365744	1.222060	0.661258
C	-2.965340	0.354428	1.654770
C	-4.267814	0.871588	1.931461
H	-4.963524	0.466189	2.652599
C	-4.473979	2.049739	1.155659
H	-5.347910	2.687405	1.189706
C	-3.299774	2.279336	0.385882
H	-3.131344	3.099657	-0.298673
C	-2.769103	2.420900	4.458134
H	-3.237558	1.706563	5.122184
C	-3.394815	3.579930	3.906291
C	-1.247621	3.459346	3.066971
H	-0.356459	3.670554	2.498404
C	-1.443499	2.341456	3.932978
H	-0.724820	1.554411	4.120326
C	-1.082770	1.375766	-1.946395
C	0.031992	1.671413	-2.751445
H	1.021750	1.712639	-2.305744
C	-0.119901	1.920814	-4.114459
H	0.752976	2.153840	-4.718766
C	-1.386958	1.870892	-4.701256
C	-2.497608	1.563957	-3.914336
H	-3.485703	1.516379	-4.361644

C	-2.348230	1.309500	-2.549107
H	-3.216944	1.052591	-1.951955
C	0.435136	2.039150	0.445638
C	0.568655	3.354868	-0.022695
H	-0.050664	3.708908	-0.841613
C	1.502237	4.213999	0.559708
H	1.604058	5.231189	0.190025
C	2.295322	3.770131	1.622802
C	2.157354	2.463043	2.094962
H	2.781237	2.107744	2.909610
C	1.238669	1.592244	1.505830
H	1.156458	0.560419	1.840282
C	-2.450997	4.221137	3.047247
H	-2.631175	5.107641	2.453040
C	-2.354594	-0.886574	2.256707
H	-4.416797	3.892462	4.078235
C	-2.985477	-1.302392	3.589374
H	-2.858919	-0.494948	4.318710
H	-4.056604	-1.506945	3.502670
H	-2.500370	-2.200556	3.979957
H	-1.285176	-0.715919	2.431008
C	-4.015686	-2.185829	0.231528
C	-4.226432	-1.780690	-1.093172
C	-5.131898	-2.458364	1.038839
C	-5.522274	-1.649313	-1.626882
H	-3.357419	-1.565231	-1.709699
C	-6.442144	-2.354844	0.552854
H	-4.973231	-2.759899	2.067850
C	-6.605244	-1.950089	-0.783599
H	-7.616331	-1.859262	-1.179356
C	-2.087388	-3.789784	1.805494
C	-3.056621	-4.788873	1.947073
C	-0.819884	-3.978243	2.379330
C	-2.797485	-5.957578	2.681617
H	-4.015487	-4.674124	1.456488
C	-0.515109	-5.134207	3.116437
H	-0.072664	-3.199941	2.242043
C	-1.524826	-6.101494	3.262174
H	-1.311428	-6.999026	3.842830
H	-1.506304	2.065518	-5.763461
H	3.018745	4.441824	2.077695
Si	0.037295	-3.581072	-2.958566
C	-0.676409	-1.940870	-3.564159
H	0.114918	-1.288655	-3.950430

H	-1.406431	-2.092898	-4.367128
H	-1.168734	-1.396439	-2.751810
C	0.704116	-4.536026	-4.456272
H	1.497680	-3.975959	-4.966959
H	1.116305	-5.508007	-4.161190
H	-0.095893	-4.722642	-5.182691
C	-1.316392	-4.617473	-2.145921
C	-0.989491	-5.617630	-1.210841
C	-2.668016	-4.477133	-2.504638
C	-1.964733	-6.464368	-0.685049
H	0.039617	-5.725604	-0.875224
C	-3.654216	-5.310208	-1.970636
H	-2.962280	-3.700194	-3.204953
C	-3.299732	-6.315611	-1.070082
H	-1.689816	-7.217942	0.047012
H	-4.695086	-5.167904	-2.251201
H	-4.062216	-6.970821	-0.657094
C	1.213363	-2.494056	-0.665686
C	1.435231	-3.305644	-1.720883
C	2.776260	-3.984891	-1.960211
H	3.495922	-3.780234	-1.160107
H	2.656647	-5.075012	-2.032279
H	3.223775	-3.664778	-2.911402
C	2.095093	-2.170275	0.374368
F	2.474839	-3.157955	1.211545
F	0.866107	-1.436178	1.828234
C	3.005691	-1.019223	0.369570
C	2.999686	-0.129701	-0.716673
C	3.919216	-0.831074	1.417270
C	3.899345	0.931384	-0.755643
H	2.279884	-0.280796	-1.514421
C	4.815906	0.233445	1.373276
H	3.908564	-1.515957	2.257586
C	4.807306	1.117760	0.289960
H	3.884065	1.622189	-1.594069
H	5.520101	0.378617	2.188058
H	5.501249	1.953411	0.264937
Si	-5.849008	-1.023020	-3.380770
Si	-7.932016	-2.732143	1.652227
Si	-4.105342	-7.301591	2.873608
Si	1.227853	-5.354819	3.818973
C	-4.388870	-1.424235	-4.509010
H	-3.440649	-1.051048	-4.112272
H	-4.294957	-2.507394	-4.650453

H	-4.531325	-0.973096	-5.498958
C	-6.151712	0.847299	-3.304752
H	-6.276476	1.277666	-4.306444
H	-7.064369	1.059845	-2.734628
H	-5.330211	1.374925	-2.807935
C	-7.402338	-1.862128	-4.064457
H	-8.295774	-1.623045	-3.475661
H	-7.592594	-1.534881	-5.094115
H	-7.291439	-2.952894	-4.076064
C	-9.176325	-1.315023	1.489412
H	-9.501092	-1.185223	0.449913
H	-10.071743	-1.501172	2.095019
H	-8.736999	-0.366115	1.819642
C	-8.736237	-4.351189	1.094668
H	-8.035499	-5.189113	1.182359
H	-9.620827	-4.585401	1.699908
H	-9.054932	-4.290469	0.046926
C	-7.352870	-2.869723	3.448716
H	-6.641079	-3.691524	3.590821
H	-6.862892	-1.945965	3.780694
H	-8.202992	-3.053061	4.116708
C	-5.744925	-6.694880	2.145694
H	-6.106210	-5.808140	2.679574
H	-5.647899	-6.426167	1.087386
H	-6.518492	-7.468178	2.225197
C	-4.333741	-7.684270	4.713735
H	-5.060108	-8.491897	4.867444
H	-3.387982	-7.995126	5.173925
H	-4.690226	-6.801235	5.257293
C	-3.545436	-8.877372	1.983210
H	-2.571283	-9.212416	2.359946
H	-4.260624	-9.695451	2.134606
H	-3.443437	-8.716561	0.903913
C	2.324744	-6.132389	2.485009
H	2.362714	-5.494300	1.596853
H	3.351751	-6.275609	2.844460
H	1.934049	-7.112398	2.184482
C	1.894870	-3.669447	4.356290
H	2.961213	-3.735759	4.608373
H	1.772736	-2.917455	3.569556
H	1.363292	-3.313315	5.247682
C	1.150960	-6.525734	5.308457
H	0.476419	-6.143392	6.083946
H	0.801692	-7.526046	5.024359

H 2.144553 -6.642728 5.758704

TS-4c
B3LYP-D3 SCF energy (au): -5216.56411465
B3LYP-D3 enthalpy (au): -5215.16819565
B3LYP-D3 free energy (au): -5215.38942265
M06 SCF energy (au): -5215.02663155
M06 enthalpy (au): -5213.63071255
M06 free energy (au): -5213.85193955
M06 free energy (quasi-harmonic) (au): -5213.82861790

Cartesian coordinates
ATOM X Y Z
Cu -0.595051 -1.561646 -0.167220
Fe -2.452622 2.551892 2.157260
P -2.375914 -2.106340 1.148546
P -0.733293 0.701186 -0.415217
C -2.190887 1.319979 0.503499
C -2.869184 0.613392 1.573805
C -4.084108 1.321815 1.836751
H -4.805410 1.070944 2.601118
C -4.155719 2.458828 0.981182
H -4.936642 3.207981 0.984357
C -2.987677 2.469547 0.170946
H -2.737205 3.204371 -0.581572
C -1.448591 2.462675 3.970876
H -1.228862 1.543346 4.497708
C -2.639319 3.242759 4.094982
C -1.291730 4.236432 2.502433
H -0.929956 4.894395 1.724233
C -0.616798 3.078307 2.991037
H 0.338733 2.709734 2.650620
C -1.025007 1.286283 -2.134486
C -2.312939 1.304864 -2.691723
H -3.173462 1.085699 -2.070203
C -2.503905 1.602420 -4.041253
H -3.511436 1.614066 -4.447615
C -1.408379 1.874487 -4.862317
C -0.120141 1.842776 -4.322671
H 0.740692 2.047770 -4.953708
C 0.071950 1.547310 -2.972637
H 1.079554 1.520851 -2.568601
C 0.696482 1.702993 0.151135
C 0.822490 3.069016 -0.149217

H	0.082703	3.557164	-0.777626
C	1.895139	3.801096	0.356605
H	1.988145	4.858593	0.122664
C	2.848779	3.174585	1.167651
C	2.725738	1.816611	1.466166
H	3.463706	1.327666	2.096722
C	1.654127	1.073120	0.959370
H	1.533122	0.021603	1.212368
C	-2.541324	4.341048	3.186996
H	-3.300780	5.093345	3.016876
C	-2.394669	-0.612331	2.326183
H	-3.485988	3.017561	4.730696
C	-3.191298	-0.830723	3.619644
H	-3.168772	0.078761	4.230090
H	-4.238519	-1.068442	3.404138
H	-2.778947	-1.651849	4.208762
H	-1.330146	-0.487762	2.556415
C	-4.144719	-2.199515	0.670066
C	-4.525008	-1.538191	-0.503894
C	-5.132822	-2.842327	1.431564
C	-5.856531	-1.526254	-0.952649
H	-3.751895	-1.036243	-1.083231
C	-6.474912	-2.869087	1.023034
H	-4.842964	-3.342123	2.350096
C	-6.806833	-2.208883	-0.175637
H	-7.841739	-2.227846	-0.514611
C	-2.077265	-3.545848	2.248720
C	-2.663261	-4.797188	2.009795
C	-1.169495	-3.417780	3.312293
C	-2.425816	-5.892608	2.860735
H	-3.314076	-4.917646	1.147829
C	-0.925498	-4.472882	4.202273
H	-0.625003	-2.487401	3.421226
C	-1.577892	-5.694437	3.963998
H	-1.404809	-6.523729	4.647774
H	-1.555827	2.104825	-5.913855
H	3.683126	3.747569	1.563937
Si	-0.465241	-3.597192	-3.274319
C	-1.180385	-1.890584	-3.614637
H	-0.414616	-1.201298	-3.984984
H	-1.986761	-1.941906	-4.355137
H	-1.587341	-1.445142	-2.702136
C	0.170320	-4.353855	-4.892436
H	0.977407	-3.744549	-5.317852

H	0.564864	-5.366260	-4.747130
H	-0.633528	-4.413167	-5.635635
C	-1.851405	-4.707369	-2.610263
C	-3.032647	-4.151456	-2.089742
C	-1.745982	-6.111062	-2.615035
C	-4.071013	-4.948810	-1.599857
H	-3.154263	-3.075438	-2.068769
C	-2.779402	-6.919418	-2.136726
H	-0.849692	-6.586077	-3.010066
C	-3.946849	-6.339426	-1.629559
H	-4.968173	-4.479949	-1.202814
H	-2.679154	-8.001698	-2.163462
H	-4.753318	-6.970445	-1.265841
C	0.821445	-2.819180	-0.886018
C	0.935668	-3.561107	-2.008916
C	2.124355	-4.478776	-2.269614
H	2.867185	-4.442652	-1.465564
H	1.800673	-5.524530	-2.377200
H	2.630633	-4.215740	-3.208000
C	1.666640	-2.852944	0.237522
F	0.691199	-1.730292	1.628160
F	2.710289	-2.006221	0.261237
C	1.798153	-4.012656	1.123688
C	2.914435	-4.140057	1.964796
C	0.856434	-5.052851	1.052065
C	3.100036	-5.307582	2.702273
H	3.632998	-3.330160	2.021230
C	1.046782	-6.213787	1.793508
H	-0.016313	-4.940350	0.419355
C	2.171408	-6.348861	2.612747
H	3.970091	-5.406289	3.345702
H	0.311075	-7.008538	1.736746
H	2.320835	-7.260972	3.184371
Si	-6.296709	-0.637527	-2.561333
Si	-7.788103	-3.783416	2.030676
Si	-3.216724	-7.569955	2.506396
Si	0.201101	-4.188173	5.692226
C	-5.031582	-1.139626	-3.873875
H	-4.018020	-0.825011	-3.605198
H	-5.013849	-2.228993	-3.997970
H	-5.268130	-0.691692	-4.847158
C	-6.244978	1.233719	-2.266442
H	-6.323365	1.793716	-3.206834
H	-7.077600	1.542229	-1.622450

H	-5.319902	1.539153	-1.764368
C	-8.033761	-1.146268	-3.109602
H	-8.793982	-0.857044	-2.373975
H	-8.294845	-0.662923	-4.058870
H	-8.104634	-2.230334	-3.258070
C	-9.296815	-2.657725	2.230598
H	-9.707299	-2.361288	1.257689
H	-10.096099	-3.163267	2.786334
H	-9.036854	-1.741485	2.773854
C	-8.293538	-5.356330	1.107552
H	-8.671312	-5.119660	0.105396
H	-7.441421	-6.035571	0.992758
H	-9.084024	-5.895954	1.643902
C	-7.075624	-4.216029	3.728307
H	-6.188537	-4.854699	3.647583
H	-6.784916	-3.313931	4.280038
H	-7.815678	-4.752946	4.333933
C	-4.984147	-7.294713	1.885140
H	-5.625197	-6.910275	2.686685
H	-5.006566	-6.571079	1.063450
H	-5.428717	-8.228933	1.520305
C	-2.209568	-8.487170	1.191806
H	-1.230063	-8.786583	1.584332
H	-2.724453	-9.397162	0.858316
H	-2.043665	-7.852851	0.314508
C	-3.260435	-8.599596	4.094202
H	-3.767048	-9.556577	3.918638
H	-2.251819	-8.825841	4.460490
H	-3.797858	-8.078362	4.895254
C	1.441345	-2.827475	5.266790
H	1.911975	-3.018527	4.296903
H	0.953178	-1.847596	5.203084
H	2.227295	-2.757418	6.028880
C	1.090027	-5.793965	6.151124
H	1.742628	-6.122518	5.336178
H	1.707531	-5.653289	7.046827
H	0.381545	-6.603782	6.364094
C	-0.869041	-3.636508	7.157831
H	-1.606590	-4.403744	7.422998
H	-0.257468	-3.436766	8.046779
H	-1.418292	-2.718306	6.915590

TS-7
B3LYP-D3 SCF energy (au): -3832.51522861

B3LYP-D3 enthalpy (au): -3831.57156161
B3LYP-D3 free energy (au): -3831.73242961
M06 SCF energy (au): -3831.25482743
M06 enthalpy (au): -3830.31116043
M06 free energy (au): -3830.47202843
M06 free energy (quasi-harmonic) (au): -3830.45546982

Cartesian coordinates

ATOM	X	Y	Z
Cu	0.340198	0.436495	-0.315440
P	-1.481972	1.684122	0.354625
P	-0.549825	-1.643851	-0.607220
O	-4.575667	-0.751952	2.703348
O	-3.688169	-1.990311	4.451663
O	-5.127457	-2.075738	-0.365676
O	-6.287812	-0.943115	-2.025820
C	-1.531678	-1.894324	0.931625
C	-2.754706	-1.169748	1.091491
C	-3.379811	-1.307171	2.317338
C	-2.849674	-2.052327	3.367540
C	-1.661061	-2.736810	3.235960
C	-1.013307	-2.644609	1.991325
C	-4.718866	-1.059759	4.093989
C	-3.029147	0.972476	-0.361267
C	-3.748849	1.650928	-1.350878
C	-4.872745	1.089797	-1.985162
C	-5.248273	-0.170705	-1.575514
C	-4.548949	-0.849890	-0.581159
C	-3.423508	-0.341706	0.041511
C	-6.208355	-2.176498	-1.297021
C	-1.750251	-2.041777	-1.939726
C	0.729077	-2.964292	-0.644864
C	-1.855707	1.719401	2.153732
C	-3.110281	2.118985	2.644033
C	-1.511030	3.449456	-0.172797
H	-1.246124	-3.317340	4.052318
H	-0.072807	-3.166559	1.861036
H	-4.597642	-0.141424	4.681402
H	-5.697723	-1.519698	4.263980
H	-3.435807	2.645036	-1.649112
H	-5.417106	1.622256	-2.757203
H	-6.007769	-2.995830	-1.996797
H	-7.145481	-2.338172	-0.751874
H	-3.905611	2.381484	1.951899

C	1.748795	-4.984970	-1.519586
H	1.699236	-5.851489	-2.174167
C	2.879409	-4.765204	-0.731204
H	3.712990	-5.462007	-0.767807
C	2.939629	-3.639437	0.095090
H	3.821956	-3.453692	0.702105
C	1.880187	-2.732958	0.133466
H	1.933173	-1.837404	0.750951
C	0.676132	-4.091325	-1.476862
H	-0.185731	-4.268184	-2.110847
C	-3.343168	2.164238	4.018143
H	-4.311742	2.488153	4.391484
C	-2.335587	1.782520	4.911135
H	-2.520211	1.811862	5.982264
C	-1.100439	1.352429	4.423621
H	-0.322261	1.034470	5.112170
C	-0.853011	1.319407	3.048981
H	0.089438	0.940101	2.662060
C	-1.957041	-1.072950	-2.930910
H	-1.413008	-0.135919	-2.874365
C	-2.889132	-1.282935	-3.946592
H	-3.053316	-0.512567	-4.695079
C	-3.622671	-2.470978	-3.984130
H	-4.350990	-2.637105	-4.773327
C	-3.431052	-3.439162	-2.993393
H	-4.006946	-4.361092	-3.014000
C	-2.510802	-3.220648	-1.966994
H	-2.396789	-3.956258	-1.175915
C	-1.979812	4.497787	0.632201
H	-2.382662	4.289905	1.616717
C	-1.905964	5.819968	0.189774
H	-2.268085	6.620957	0.829391
C	-1.365175	6.111609	-1.063457
H	-1.304041	7.141127	-1.406644
C	-0.894090	5.074263	-1.871878
H	-0.465075	5.286748	-2.844099
C	-0.958043	3.752530	-1.429573
H	-0.557080	2.957257	-2.054452
Si	2.428030	0.769722	-3.527970
C	3.912859	0.868182	-4.705716
H	4.732199	0.220643	-4.369996
H	3.621450	0.545544	-5.712276
H	4.304775	1.889032	-4.784418
C	1.817966	-1.011845	-3.473983

H	2.541486	-1.649796	-2.955297
H	0.876276	-1.090538	-2.928545
H	1.664660	-1.412749	-4.483384
C	1.079880	1.878521	-4.264748
C	1.276386	3.267853	-4.376584
C	-0.111014	1.349272	-4.792954
C	0.332306	4.089194	-4.995357
H	2.185817	3.717851	-3.981833
C	-1.076415	2.168959	-5.384767
H	-0.287939	0.278454	-4.753408
C	-0.855966	3.542897	-5.489230
H	0.520188	5.156328	-5.090776
H	-1.992891	1.732733	-5.775652
H	-1.598130	4.183505	-5.958455
C	2.242153	1.115173	-0.718532
C	2.984040	1.358536	-1.819208
C	4.334159	2.062298	-1.728876
H	4.618035	2.279191	-0.693670
H	5.132936	1.459644	-2.180647
H	4.321508	3.014446	-2.279216
C	2.625867	1.239961	0.622347
F	1.336502	-0.081969	1.548672
F	3.660045	0.486948	1.039198
C	2.294243	2.344060	1.530833
C	1.649780	3.484948	1.033451
C	2.635210	2.271526	2.890483
C	1.334052	4.538692	1.889093
H	1.387199	3.530978	-0.017158
C	2.319744	3.326659	3.740439
H	3.115090	1.374853	3.264848
C	1.663524	4.459087	3.243948
H	0.816107	5.407968	1.496102
H	2.573140	3.264189	4.795289
H	1.407765	5.275091	3.914700

TS-8

B3LYP-D3 SCF energy (au):	-3832.52192731
B3LYP-D3 enthalpy (au):	-3831.57817931
B3LYP-D3 free energy (au):	-3831.73770231
M06 SCF energy (au):	-3831.25566456
M06 enthalpy (au):	-3830.31191656
M06 free energy (au):	-3830.47143956
M06 free energy (quasi-harmonic) (au):	-3830.45558825

Cartesian coordinates

ATOM	X	Y	Z
Cu	0.280380	0.346744	-0.213568
P	-1.621212	1.560831	0.205166
P	-0.488729	-1.811873	-0.310675
O	-4.968022	-0.766682	2.324871
O	-4.282788	-1.765708	4.304068
O	-5.043501	-2.373823	-0.657529
O	-5.890089	-1.496117	-2.632140
C	-1.660522	-1.911555	1.115827
C	-2.924218	-1.245183	1.031435
C	-3.711887	-1.297357	2.166029
C	-3.302907	-1.897583	3.354079
C	-2.077244	-2.517098	3.462046
C	-1.266071	-2.518194	2.312692
C	-5.322129	-0.988763	3.693997
C	-3.018691	0.725835	-0.658263
C	-3.535271	1.238235	-1.855184
C	-4.509511	0.560049	-2.610103
C	-4.953707	-0.643405	-2.107908
C	-4.444245	-1.167980	-0.922917
C	-3.451012	-0.552392	-0.183010
C	-5.957776	-2.611039	-1.732683
C	-1.463522	-2.523401	-1.696668
C	0.807059	-3.073619	0.048901
C	-2.155735	1.650253	1.964403
C	-3.444253	2.054986	2.343510
C	-1.662013	3.319966	-0.338103
H	-1.755336	-2.982304	4.387019
H	-0.297927	-3.002296	2.367521
H	-5.400418	-0.024208	4.208265
H	-6.265573	-1.544423	3.739037
H	-3.172518	2.188820	-2.227783
H	-4.893839	0.964782	-3.539704
H	-5.661587	-3.521074	-2.265351
H	-6.975250	-2.695645	-1.332483
H	-4.186109	2.296651	1.588679
C	1.838169	-5.259573	-0.170593
H	1.807149	-6.276097	-0.554877
C	2.938963	-4.823092	0.571270
H	3.766935	-5.500265	0.765818
C	2.972565	-3.513809	1.056890
H	3.827087	-3.158063	1.625584
C	1.916240	-2.639025	0.796271

H	1.935994	-1.619445	1.174672
C	0.776332	-4.391141	-0.431478
H	-0.058396	-4.737303	-1.031092
C	-3.789226	2.118116	3.692693
H	-4.785831	2.444633	3.980531
C	-2.857737	1.755404	4.671600
H	-3.132219	1.793436	5.722811
C	-1.578145	1.343746	4.295395
H	-0.854693	1.052970	5.052433
C	-1.217612	1.295434	2.946130
H	-0.223490	0.968178	2.646154
C	-1.357956	-1.933966	-2.962732
H	-0.711801	-1.076697	-3.102203
C	-2.071785	-2.449296	-4.044916
H	-1.975045	-1.981415	-5.020232
C	-2.894077	-3.564256	-3.873552
H	-3.447755	-3.968919	-4.716788
C	-3.004395	-4.159748	-2.612984
H	-3.640773	-5.030338	-2.473728
C	-2.303819	-3.635503	-1.526636
H	-2.422987	-4.077385	-0.541712
C	-2.831624	4.090230	-0.444575
H	-3.800241	3.639146	-0.252963
C	-2.761896	5.432133	-0.817301
H	-3.674405	6.016649	-0.901764
C	-1.522697	6.024869	-1.078552
H	-1.471066	7.071254	-1.367987
C	-0.354602	5.269782	-0.965592
H	0.612492	5.723582	-1.165629
C	-0.422939	3.923404	-0.599930
H	0.483263	3.331063	-0.522613
Si	1.590398	1.359636	-3.519063
C	-0.247587	1.795734	-3.431288
H	-0.400465	2.860961	-3.227689
H	-0.743598	1.546714	-4.378089
H	-0.745632	1.232346	-2.636738
C	2.361696	2.341739	-4.945705
H	2.268709	3.421089	-4.772601
H	3.426106	2.111915	-5.068612
H	1.861952	2.117542	-5.895734
C	1.739164	-0.489016	-3.906824
C	2.126990	-1.432260	-2.938303
C	1.392813	-0.973039	-5.182768
C	2.174374	-2.797946	-3.227747

H	2.360425	-1.099343	-1.932512
C	1.425522	-2.337726	-5.477312
H	1.086669	-0.277420	-5.962619
C	1.818985	-3.253566	-4.498237
H	2.469349	-3.501184	-2.455067
H	1.146702	-2.686373	-6.468987
H	1.843016	-4.316758	-4.723891
C	2.040636	1.273066	-0.740334
C	2.514126	1.736670	-1.915970
C	3.814277	2.525183	-2.018208
H	4.307056	2.637996	-1.046183
H	4.524801	2.040360	-2.702521
H	3.636514	3.530281	-2.425124
C	2.613308	1.336117	0.537576
F	1.353813	0.234333	1.661092
F	2.342035	2.430640	1.274868
C	3.776746	0.569615	1.006265
C	4.206513	0.691093	2.337908
C	4.475835	-0.267650	0.125186
C	5.322884	-0.012735	2.775941
H	3.644312	1.322636	3.015675
C	5.592914	-0.973409	0.570221
H	4.142424	-0.361670	-0.901742
C	6.018789	-0.849089	1.894385
H	5.649594	0.081783	3.807903
H	6.126447	-1.622947	-0.117968
H	6.888813	-1.400572	2.240983

27a

B3LYP-D3 SCF energy (au):	-585.499731839
B3LYP-D3 enthalpy (au):	-585.337866839
B3LYP-D3 free energy (au):	-585.386417839
M06 SCF energy (au):	-585.303574225
M06 enthalpy (au):	-585.141709225
M06 free energy (au):	-585.190260225
M06 free energy (quasi-harmonic) (au):	-585.188560386

Cartesian coordinates

ATOM	X	Y	Z
C	-2.594487	-0.492318	0.001057
F	-3.062598	0.148538	-1.126105
F	-3.067136	0.222717	1.080707
C	-3.146369	-1.903774	0.047554

C	-3.382911	-2.517981	1.280314
C	-3.381278	-2.598766	-1.141856
C	-3.856041	-3.829666	1.321511
H	-3.204634	-1.964983	2.196611
C	-3.854458	-3.910305	-1.096155
H	-3.201707	-2.108070	-2.092716
C	-4.091111	-4.527906	0.134462
H	-4.044750	-4.304788	2.280278
H	-4.041922	-4.448258	-2.021384
H	-4.460225	-5.549407	0.168281
C	-1.130646	-0.448314	0.002663
C	0.077198	-0.451344	0.005582
C	1.535622	-0.454387	0.009017
H	1.928404	-1.000676	-0.856846
H	1.934162	0.566448	-0.026994
H	1.924318	-0.936440	0.914043

27b

B3LYP-D3 SCF energy (au):	-1086.69602892
B3LYP-D3 enthalpy (au):	-1086.35859092
B3LYP-D3 free energy (au):	-1086.43297492
M06 SCF energy (au):	-1086.29973848
M06 enthalpy (au):	-1085.96230048
M06 free energy (au):	-1086.03668448
M06 free energy (quasi-harmonic) (au):	-1086.03073456

Cartesian coordinates

ATOM	X	Y	Z
C	-2.755101	0.231480	4.268541
C	-1.496225	0.474984	4.526942
C	-0.276434	0.726073	4.953766
F	0.764961	-0.045513	4.510503
C	0.114229	1.776123	5.905257
C	-0.834282	2.686704	6.407090
C	1.444076	1.868784	6.344594
C	-0.459990	3.654747	7.333864
H	-1.863203	2.630281	6.064341
C	1.812916	2.844521	7.271606
H	2.180410	1.172370	5.959838
C	0.866069	3.739098	7.772465
H	-1.205241	4.349749	7.712056
H	2.846192	2.902978	7.603610
H	1.156421	4.496888	8.494954

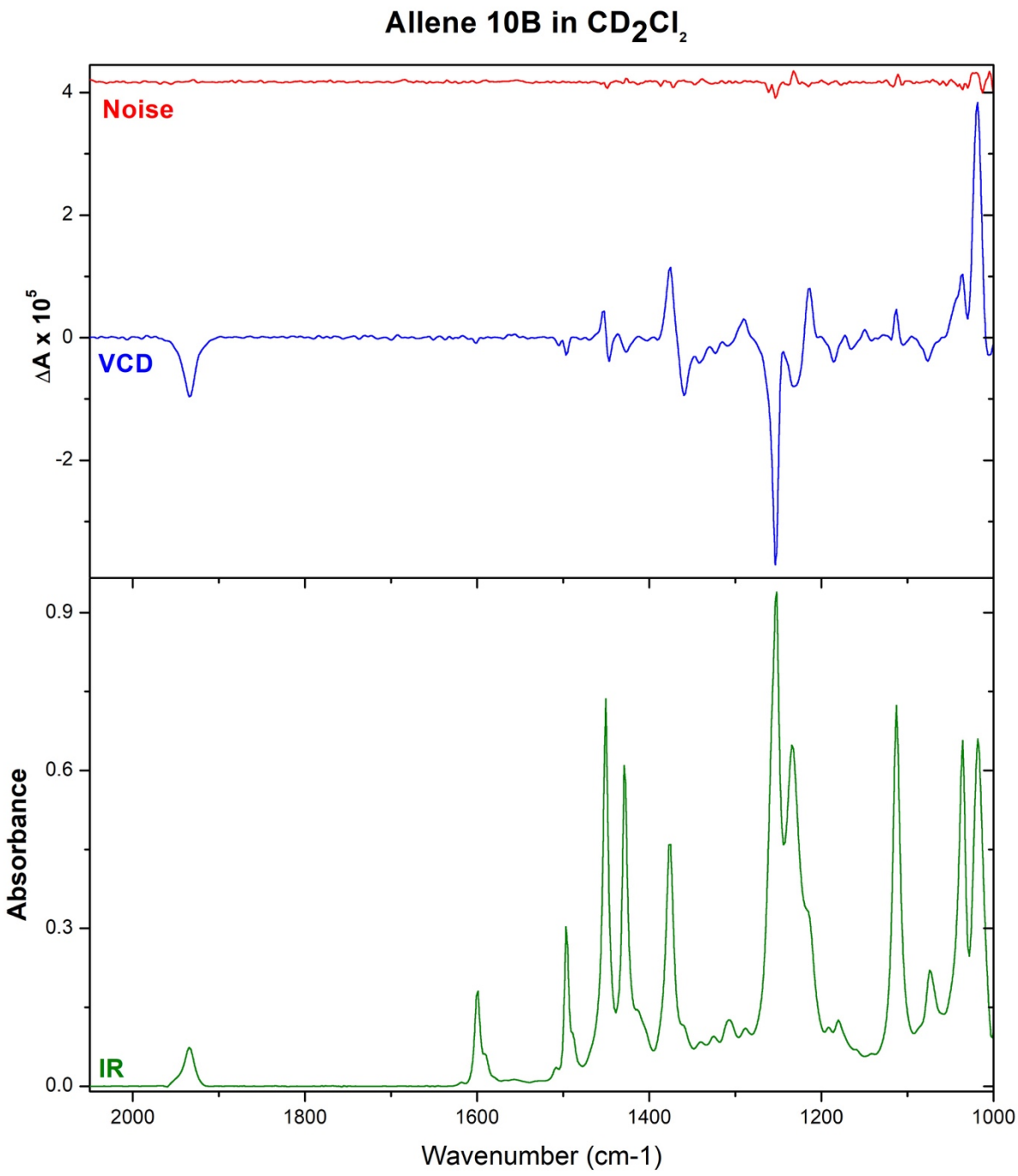
C	-3.505392	0.847956	3.100662
H	-3.879280	0.065119	2.428623
H	-4.380075	1.403226	3.463887
H	-2.874739	1.529863	2.522186
Si	-3.694990	-0.856034	5.519766
C	-4.816733	-2.053050	4.582878
H	-4.218695	-2.744279	3.977567
H	-5.422507	-2.650850	5.274190
H	-5.500930	-1.526621	3.907372
C	-2.453842	-1.770087	6.601833
H	-1.815292	-2.425803	5.999181
H	-1.799089	-1.067669	7.128812
H	-2.968476	-2.382765	7.350977
C	-4.725743	0.328399	6.566566
C	-6.122076	0.428652	6.438314
C	-4.089792	1.180771	7.490365
C	-6.856521	1.342865	7.198572
H	-6.649929	-0.215525	5.738512
C	-4.816713	2.096088	8.251800
H	-3.010048	1.136492	7.616361
C	-6.204376	2.179124	8.106204
H	-7.935904	1.401423	7.082520
H	-4.302394	2.742837	8.958347
H	-6.773534	2.891561	8.697846

2.5.10 VCD Analysis

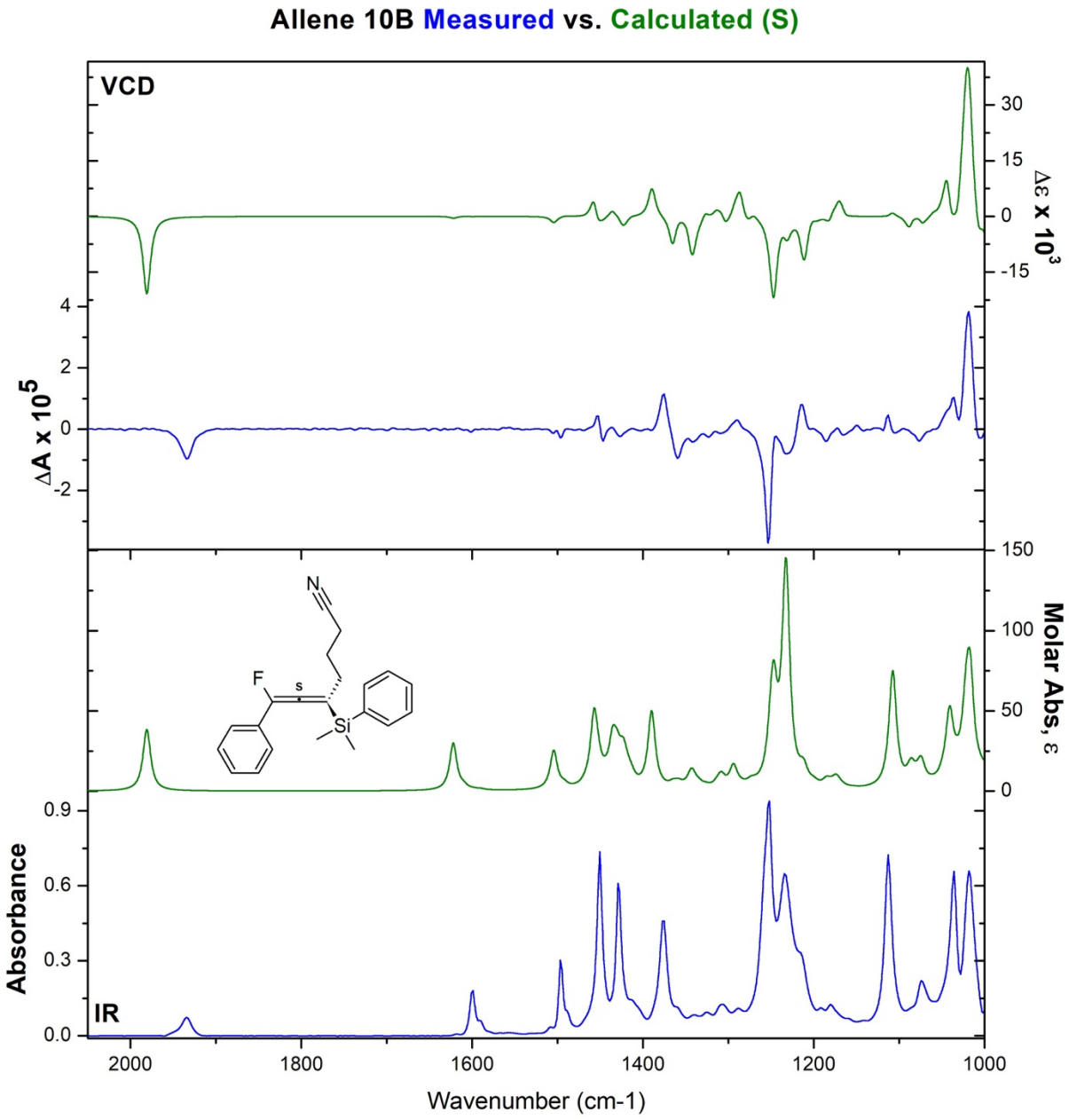
VCD Measurements: A 150uL solution containing 20mg of allene **10b** dissolved in CD_2Cl_2 was transferred to a BaF_2 IR cell with path length of 100 μm. Instrumentation was a BioTools (Jupiter, Florida) ChiralIR-2X DualPEM FT-VCD, resolution 4 cm^{-1}, PEM maximum frequency 1400 cm^{-1}. The sample was measured for 12 blocks of 1 hour each while purged with dry air to remove water vapor. The IR was processed by solvent subtraction and offset to zero at 2000cm^{-1}. The VCD blocks were averaged, then subtracted using a baseline of the racemic allene measured at the same concentration to produce the final spectrum.

VCD Calculations: Allene **10b** (S configuration) was subjected to a conformer search (GMMX, MMF94) using BioTools ComputeVOA software to find the lowest energy conformers in an 8 kcal/mol range. The geometries of a total of 46 conformers were optimized using Gaussian 09 at the B3LYP/6-31G(d) and B3PW91/6-31G(d) levels with CPCM solvent model in dichloromethane. IR and VCD were calculated at the same level, then duplicates were removed. The 35 lowest energy unique conformers were then re-calculated at the B3LYP/cc-pVTZ and B3PW91/cc-pVTZ levels, and the resulting spectra were Boltzmann averaged and plotted with a line width of 5 cm^{-1}. IR and VCD spectra were then frequency scaled and compared to the experimental data.

Measured VCD and IR Spectrum of 10b



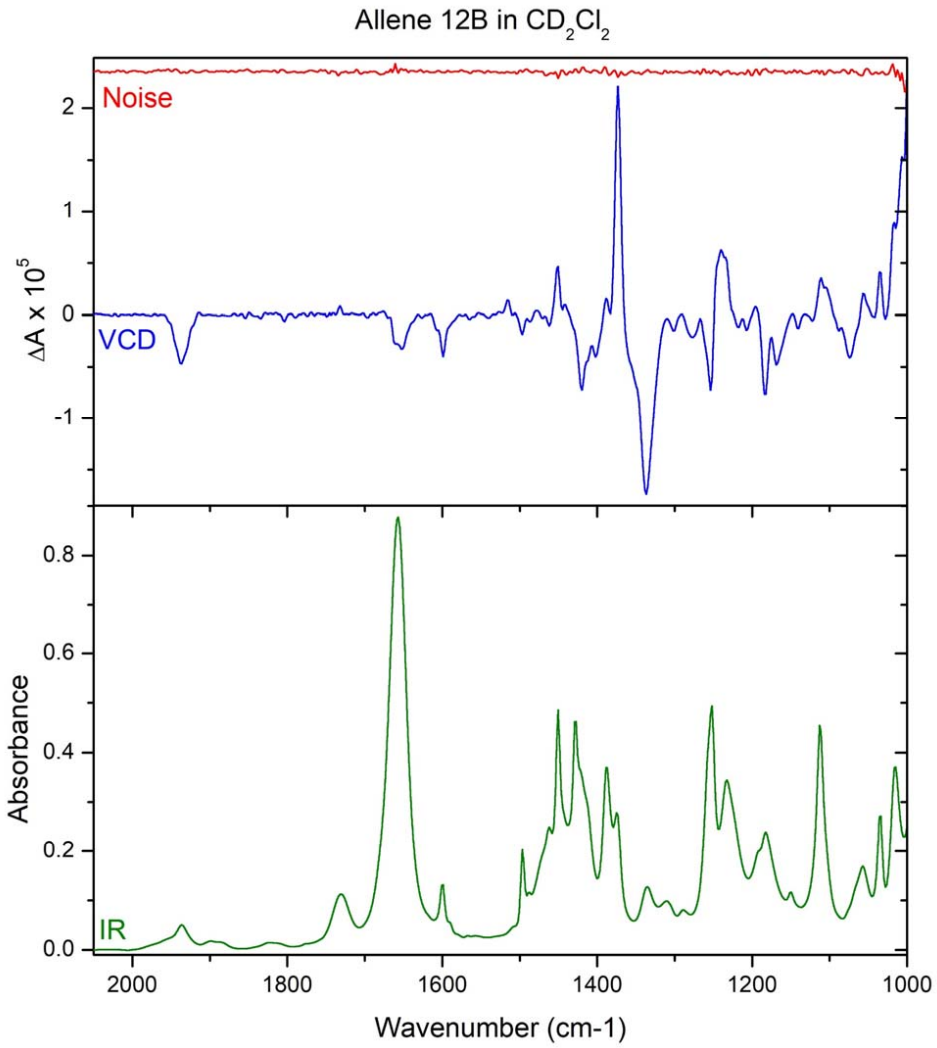
Measured and Calculated VCD and IR spectrum of 10b



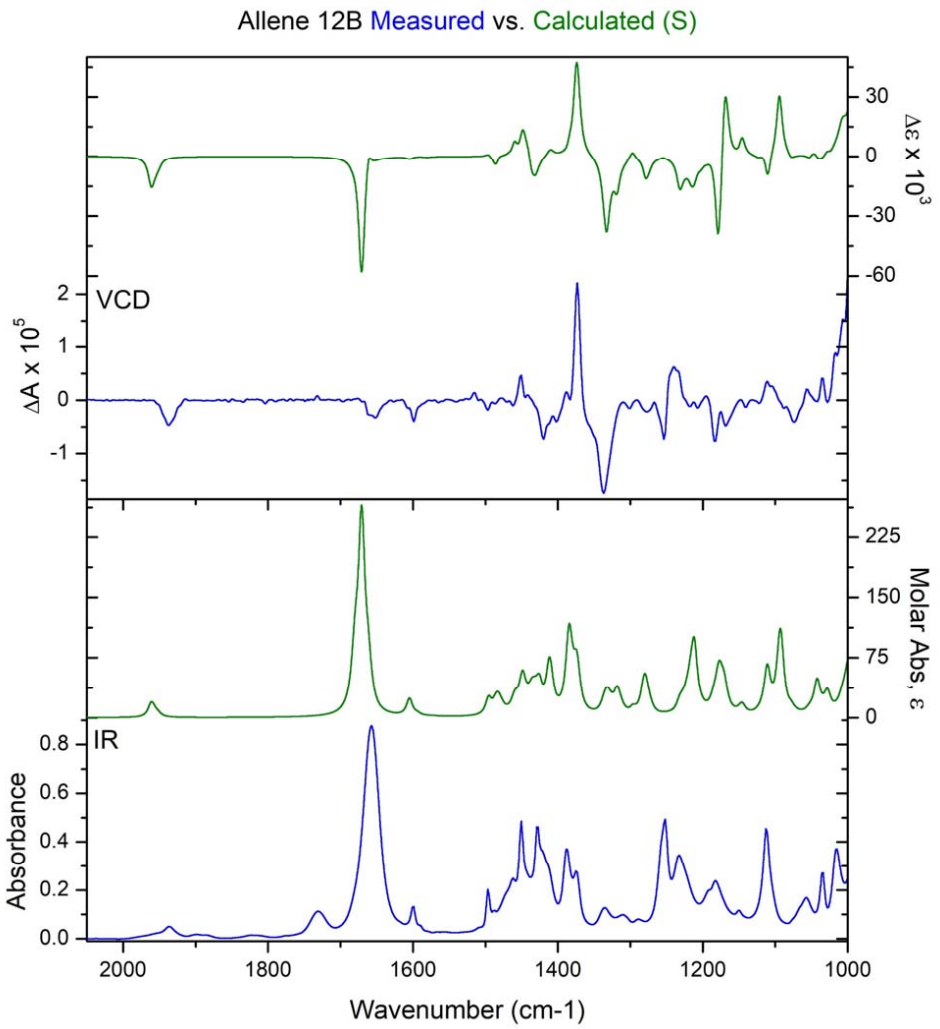
RESULTS	
Absolute Configuration of Allene 12B is (S)	Confidence Level: **91%**
MEASUREMENT PARAMETERS	
Concentration	12mg / 150uL
Solvent	CD_2Cl_2
Resolution	4 cm^{-1}
PEM setting	1400 cm^{-1}
Number of scans/Measurement time	22 hours enantiomer and solvent
Sample cell	BaF_2
Path length	100 µm
CALCULATION DETAILS	
Molecular Mechanics Force Field	**MMFF94 (Compute VOA)**
DFT Software version	**Gaussian '09**
Number of conformers used for Boltzmann sum	**81 (6-31G(d) / B3LYP)**
Methodology and basis sets for DFT calculations	**6-31Gd / B3LYP, B3PW91 / CPCM (CD_2Cl_2)**
Enantiomer used for calculation	**S**
Total calculated conformers	**214 (6-31Gd)**
Number of low-energy conformations shown in report	**4**

COMMENTS

The confidence level is a measure of the degree of congruence between a calculated and measured spectrum. If identical spectra are being compared the confidence level is 100%. The confidence level (CL) is not the likelihood that the assignment is correct. Rather it's a measure of quality or degree of agreement between calculated and measured spectra. With a CL of 91% for this molecule, the visual agreement between measured and calculated spectra is excellent – this is a very high confidence assignment. Two different calculations were performed, two functionals (B3LYP and B3PW91) each with the basis set 6-31G(d) – the CPCM solvent shell method was employed in both cases. While both methods indicated the same result for stereochemistry – the best overall match was 6-31G(d) / B3LYP. Of particular interest was the IR / VCD band observed at 1935 cm^{-1} which appears to be the allene asymmetric stretching mode. This was in fact an important band in assigning the absolute configuration. The slightly lower confidence level for this molecule is due to some minor intensity and frequency mismatches between experimental and calculated spectra. The visual agreement is very strong, this assignment is unambiguous.



IR (lower frame) and VCD (upper frame) spectra of **Allene 12B** in CD_2Cl_2; 100um path-length cell with BaF_2 windows; 22 h collection for enantiomer and solvent; instrument optimized at 1400 cm^{-1}. Solvent subtracted IR and racemic subtracted VCD spectra are shown. Uppermost trace is the VCD noise spectrum. The solvent absorbs strongly at and below 1000 cm^{-1} so the spectra are cut off at this point.

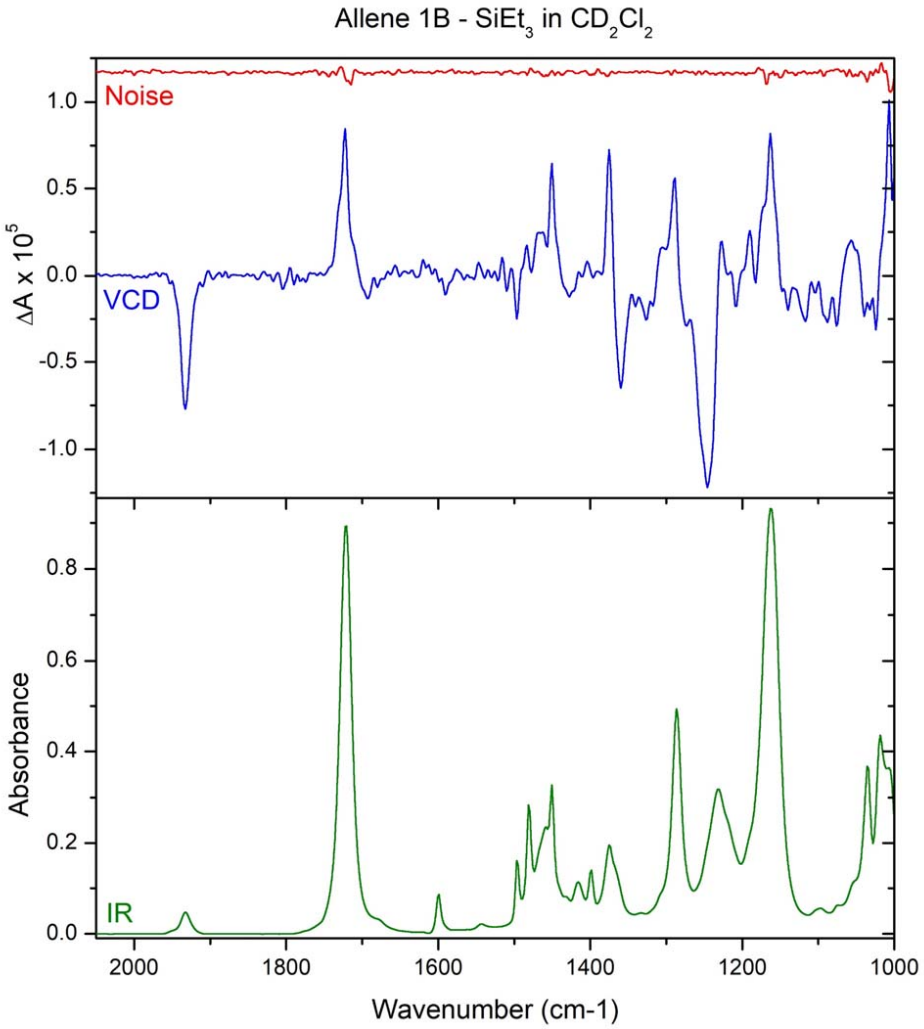


IR (lower frame) and VCD (upper frame) spectra observed for **Allene 12B** (left axes) compared with Boltzmann-averaged spectra of the calculated conformations for the **(S)** configuration, (right axes). Note the band at 1935 cm^{-1} in the experimental corresponding to the allene asymmetric stretch.

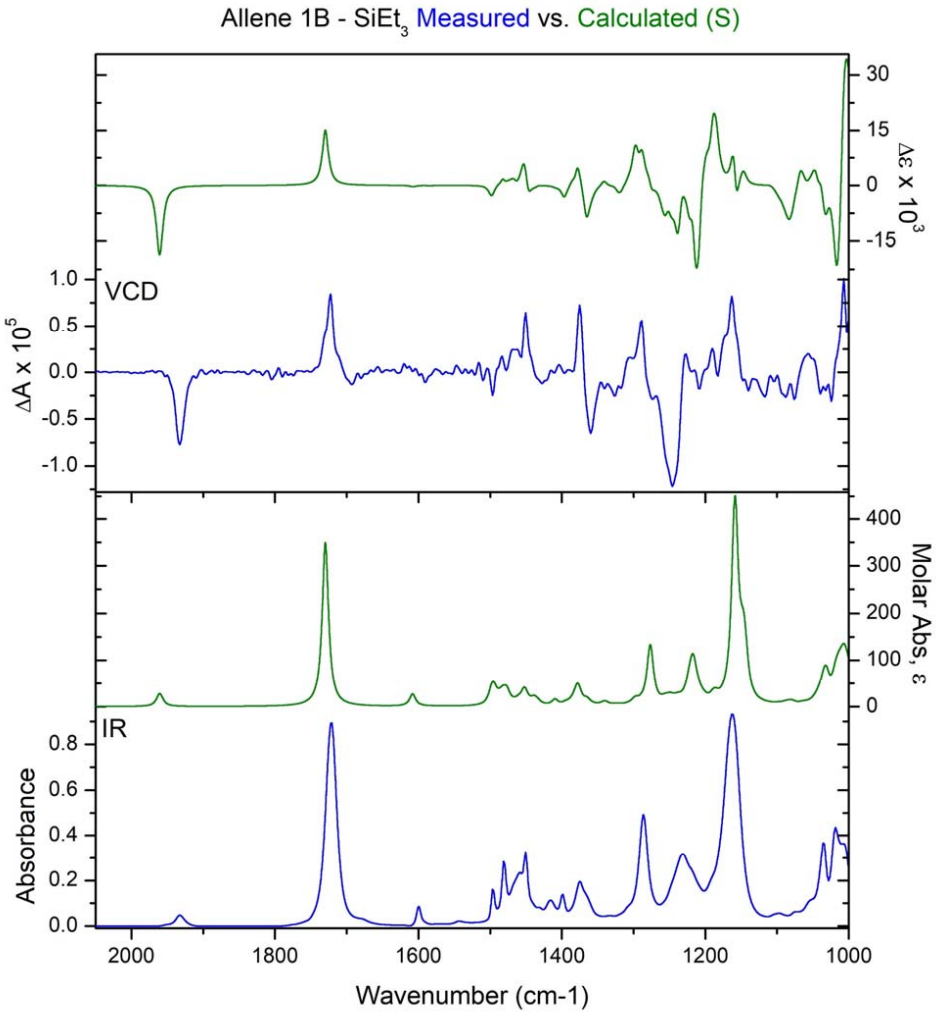
RESULTS	
Absolute Configuration of Allene 1B – $SiEt_3$ is (S)	Confidence Level: **94%**
MEASUREMENT PARAMETERS	
Concentration	14mg / 150uL
Solvent	CD_2Cl_2
Resolution	4 cm^{-1}
PEM setting	1400 cm^{-1}
Number of scans/Measurement time	22 hours enantiomer and solvent
Sample cell	BaF_2
Path length	100 µm
CALCULATION DETAILS	
Molecular Mechanics Force Field	**MMFF94 (Compute VOA)**
DFT Software version	**Gaussian '09**
Number of conformers used for Boltzmann sum	**382 (6-31G(d) / B3LYP)**
Methodology and basis sets for DFT calculations	**6-31Gd / B3LYP / CPCM (CD_2Cl_2)**
Enantiomer used for calculation	**S**
Total calculated conformers	**558 (6-31Gd / B3LYP)**
Number of low-energy conformations shown in report	**4**

COMMENTS

The confidence level is a measure of the degree of congruence between a calculated and measured spectrum. If identical spectra are being compared the confidence level is 100%. The confidence level (CL) is not the likelihood that the assignment is correct. Rather it's a measure of quality or degree of agreement between calculated and measured spectra. With a CL of 94% for this molecule, the visual agreement between measured and calculated spectra is excellent – this is a very high confidence assignment. Due to the large number of conformations, just one calculation was performed, using the B3LYP functional and the 6-31G(d) basis set – the CPCM solvent shell method was employed. Of particular interest was the IR / VCD band observed at 1938 cm^{-1} which appears to be the allene asymmetric stretching mode. This was in fact an important band in assigning the absolute configuration. The overall agreement was very good, with just a couple of small frequency / intensity mismatches between the experimental and calculated. This may have been corrected with a higher level calculation, however with over 100 important conformations it was not deemed a good use of time to do so.

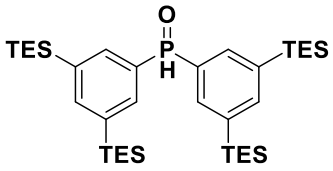


IR (lower frame) and VCD (upper frame) spectra of **Allene 1B – $SiEt_3$** in CD_2Cl_2; 100um path-length cell with BaF_2 windows; 22 h collection for enantiomer and solvent; instrument optimized at 1400 cm^{-1}. Solvent subtracted IR and racemic subtracted VCD spectra are shown. Uppermost trace is the VCD noise spectrum. The solvent absorbs strongly at and below 1000 cm^{-1} so the spectra are cut off at this point.

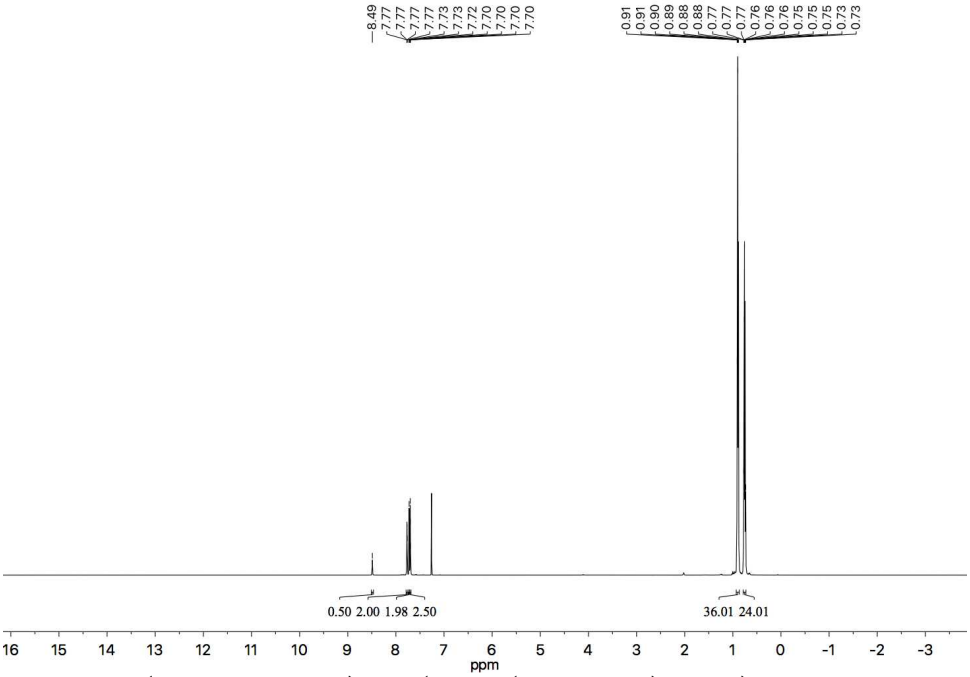


IR (lower frame) and VCD (upper frame) spectra observed for **Allene 1B – $SiEt_3$** (left axes) compared with Boltzmann-averaged spectra of the calculated conformations for the **(S)** configuration, (right axes). Note the band at 1938 cm^{-1} in the experimental corresponding to the allene asymmetric stretch.

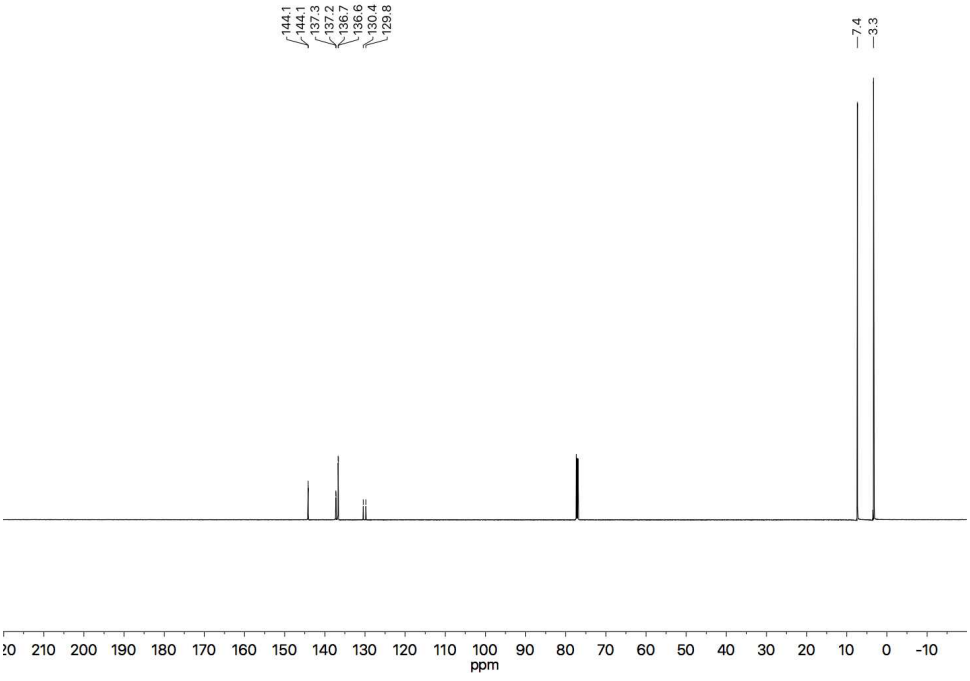
2.6 NMR Spectra



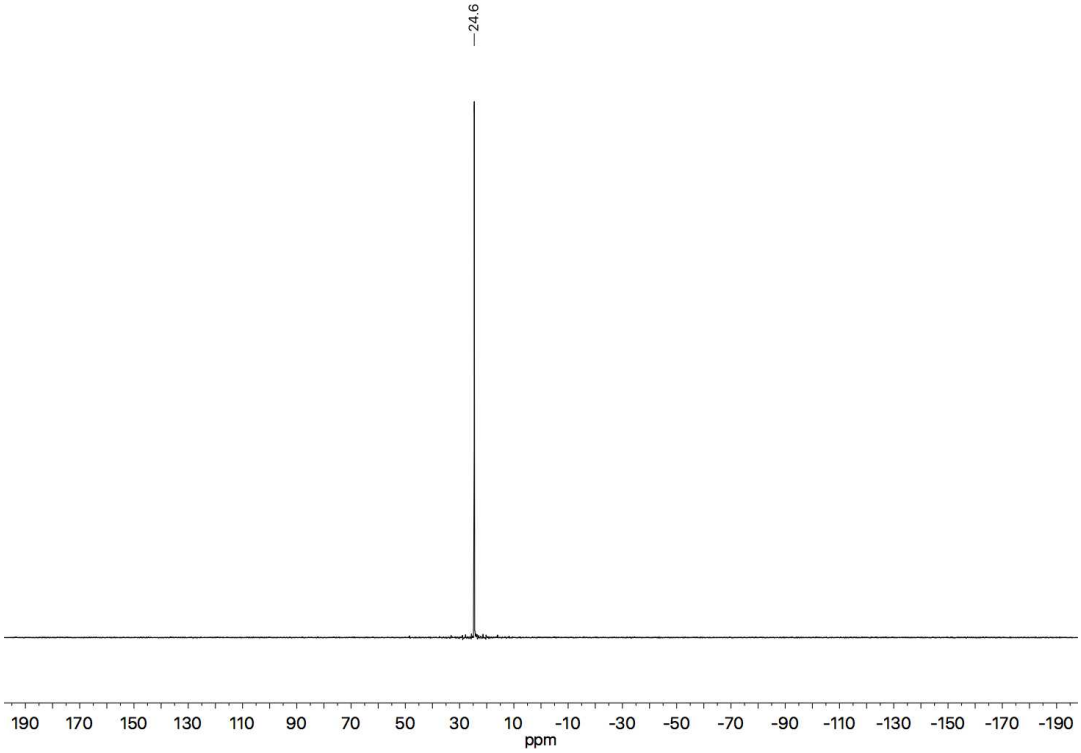
^{1}H NMR (600 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**



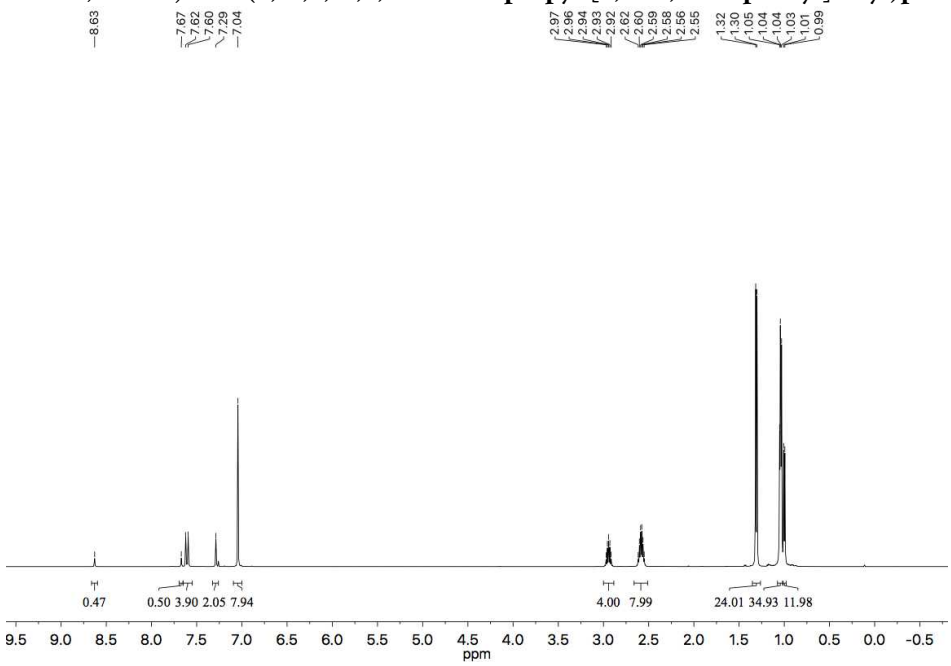
^{13}C NMR (151 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**



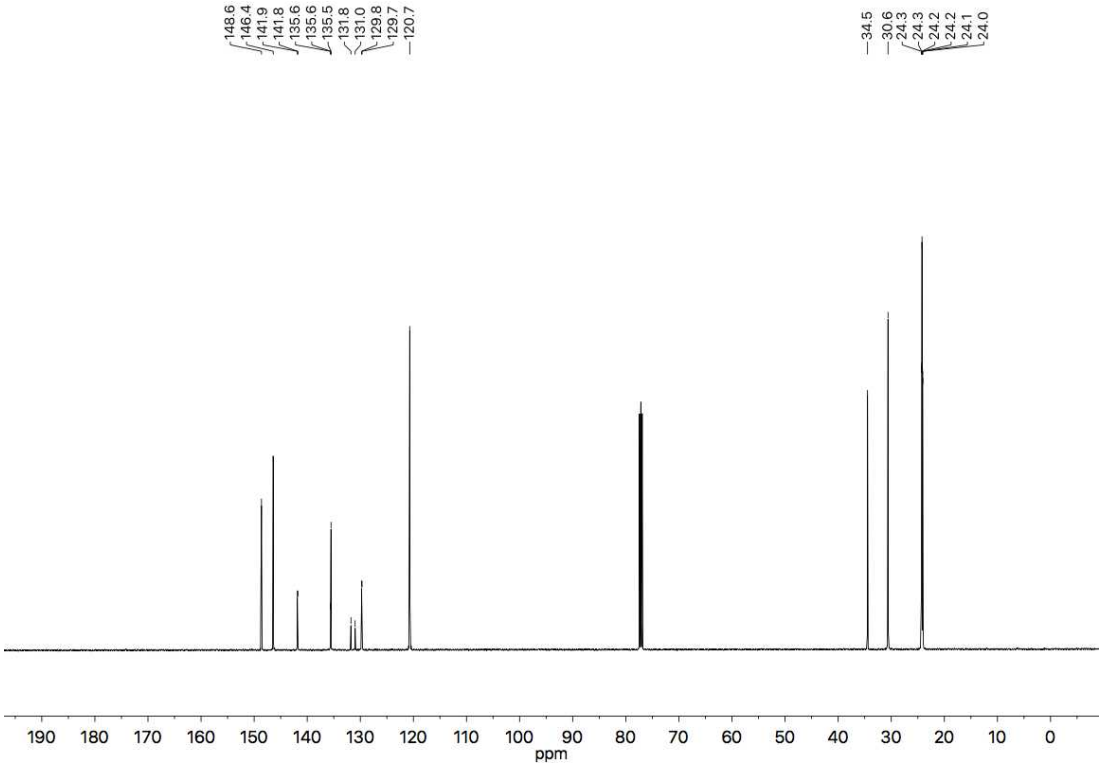
^{31}P NMR (243 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**



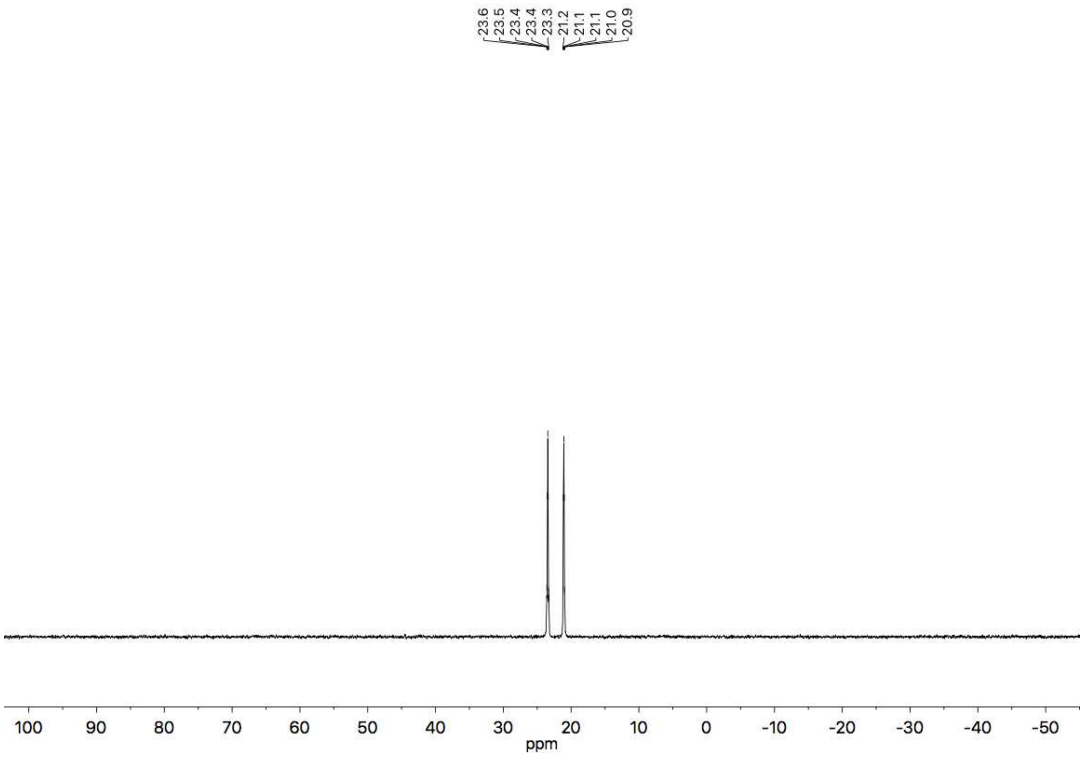
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**

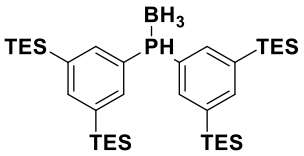


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**

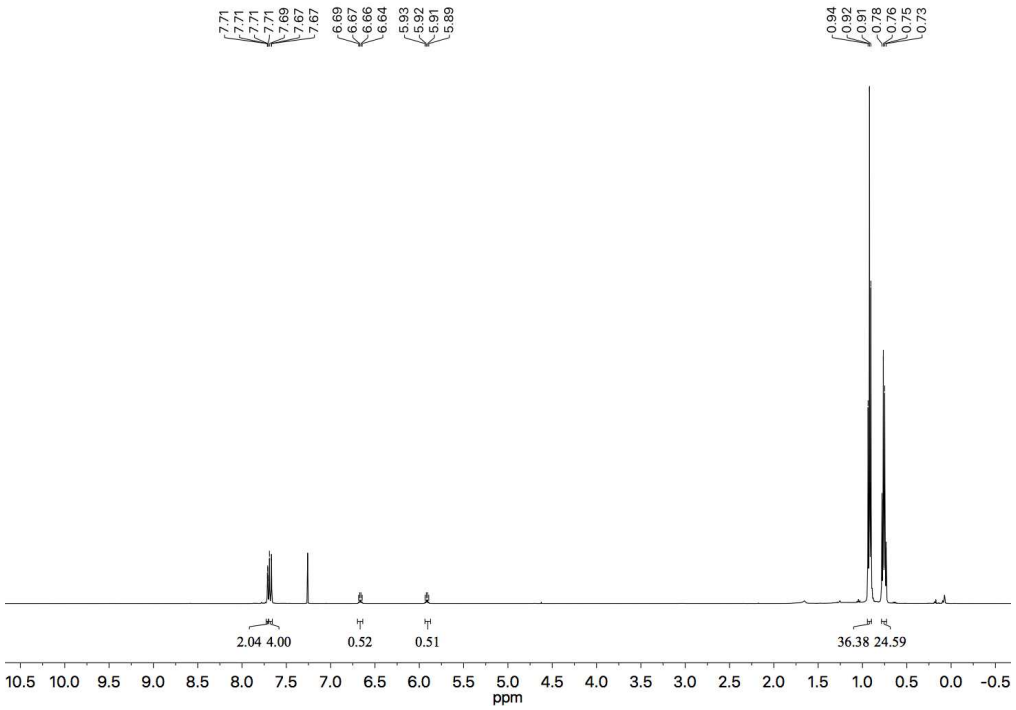


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**

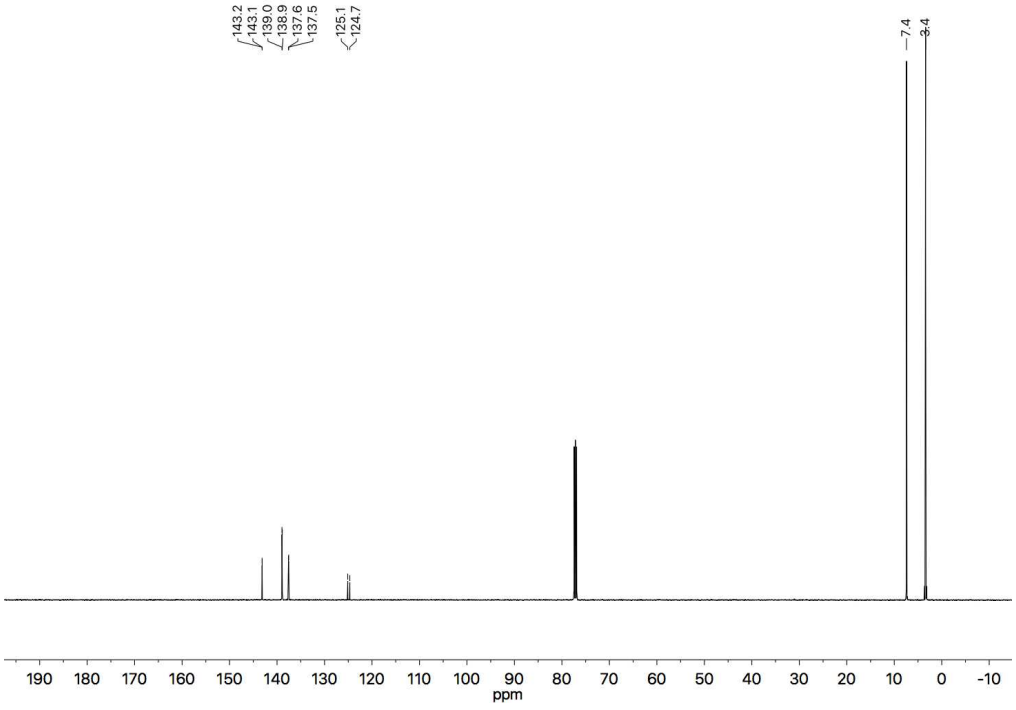




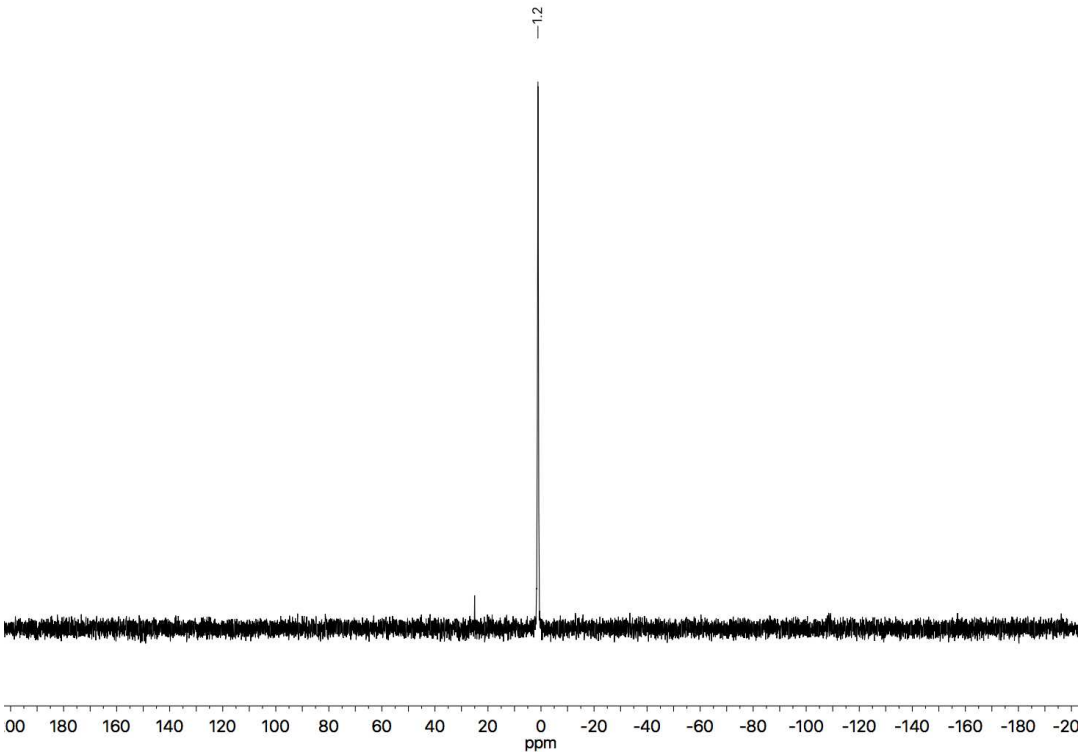
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine borane**



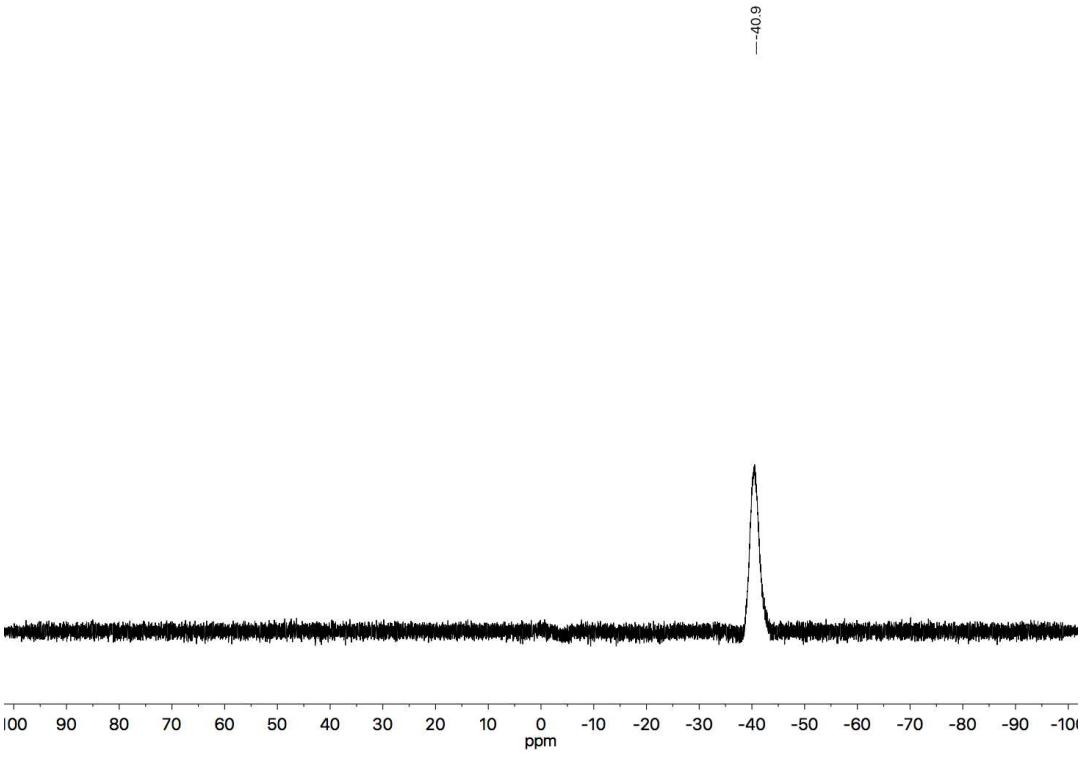
^{13}C NMR (126 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine borane**

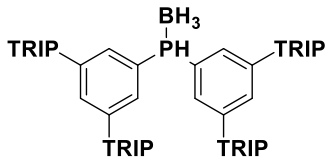


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine borane**

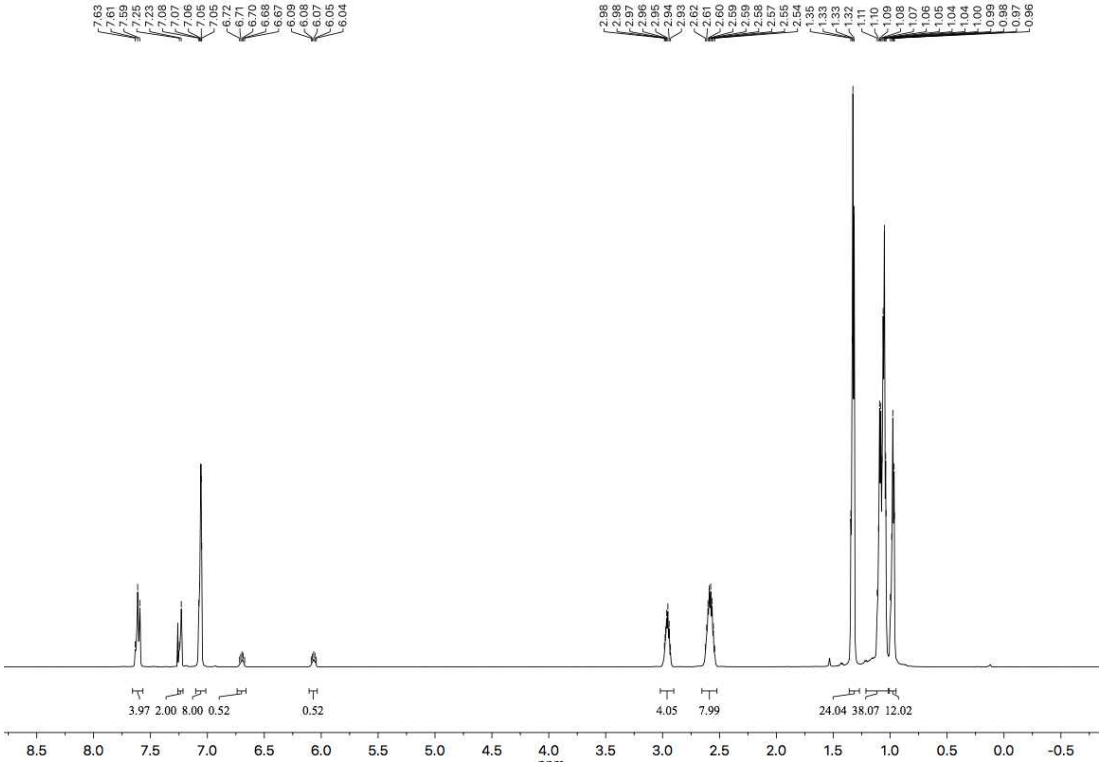


^{11}B NMR (160 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine borane**

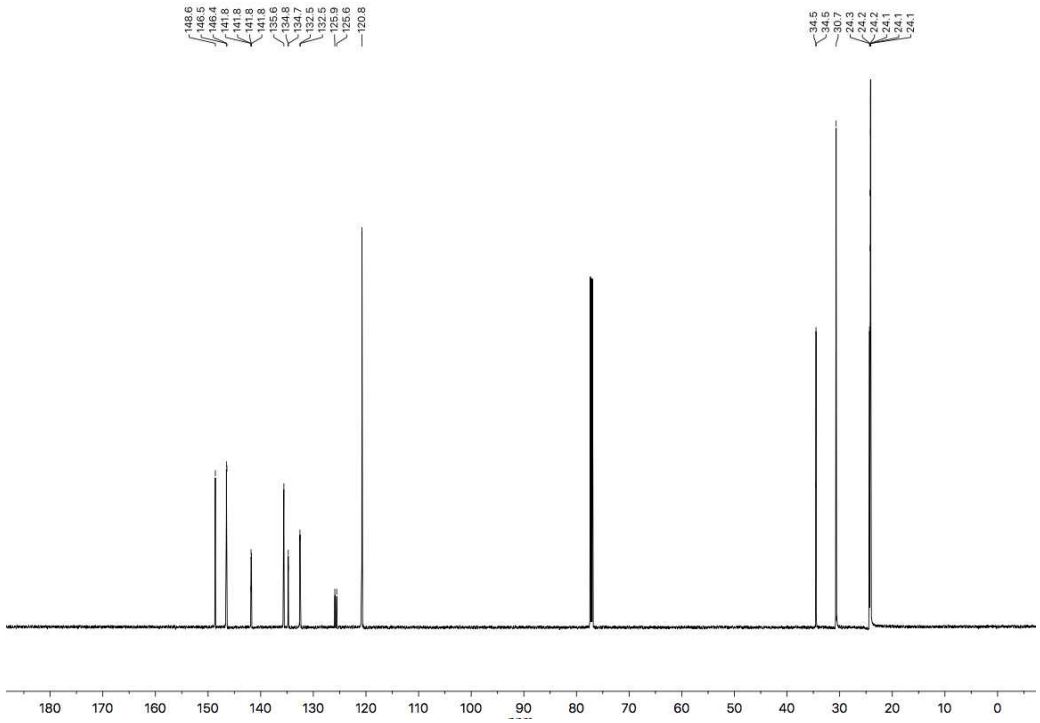




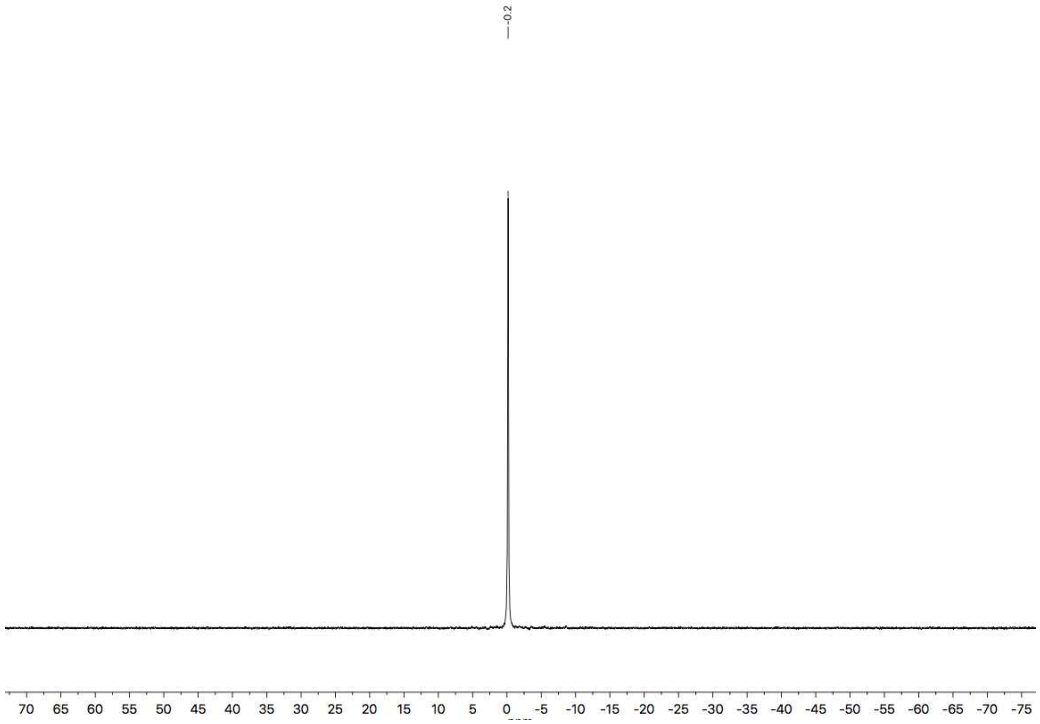
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



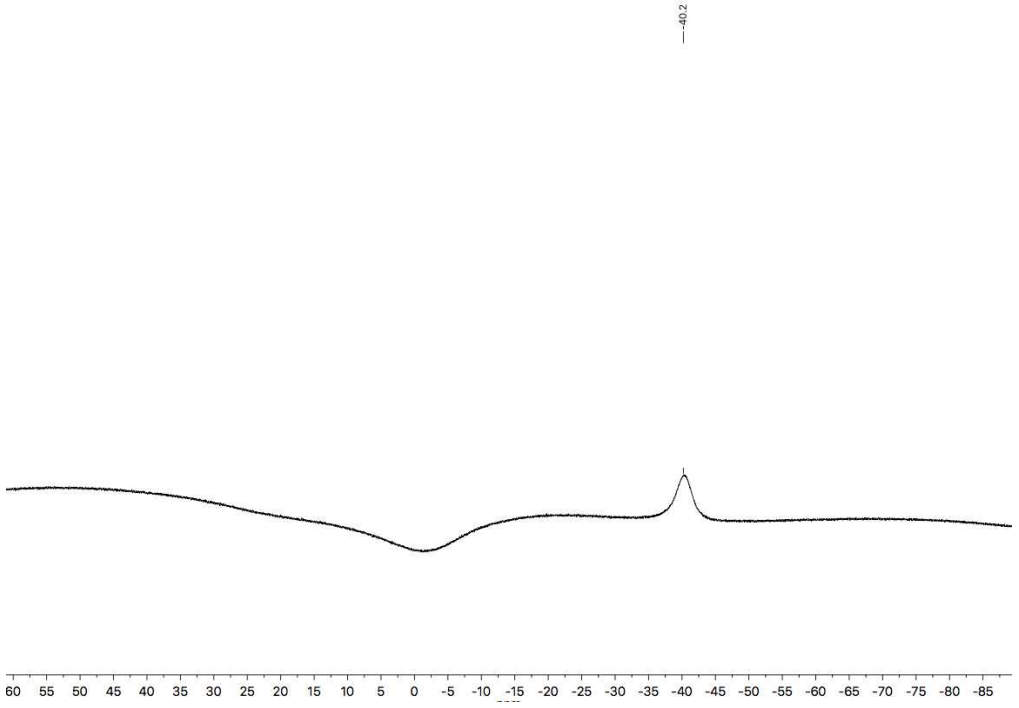
^{13}C NMR (126 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**

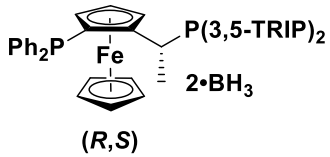


^{31}P NMR (202 MHz, $CDCl_3$) – – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



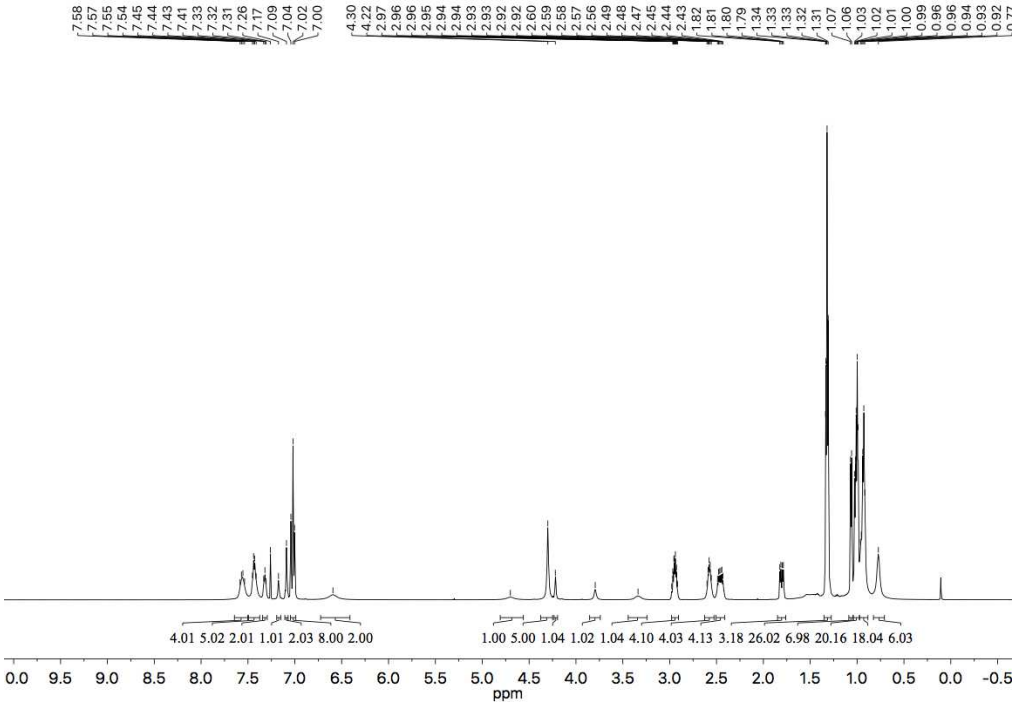
^{11}B NMR (160 MHz, $CDCl_3$) – – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



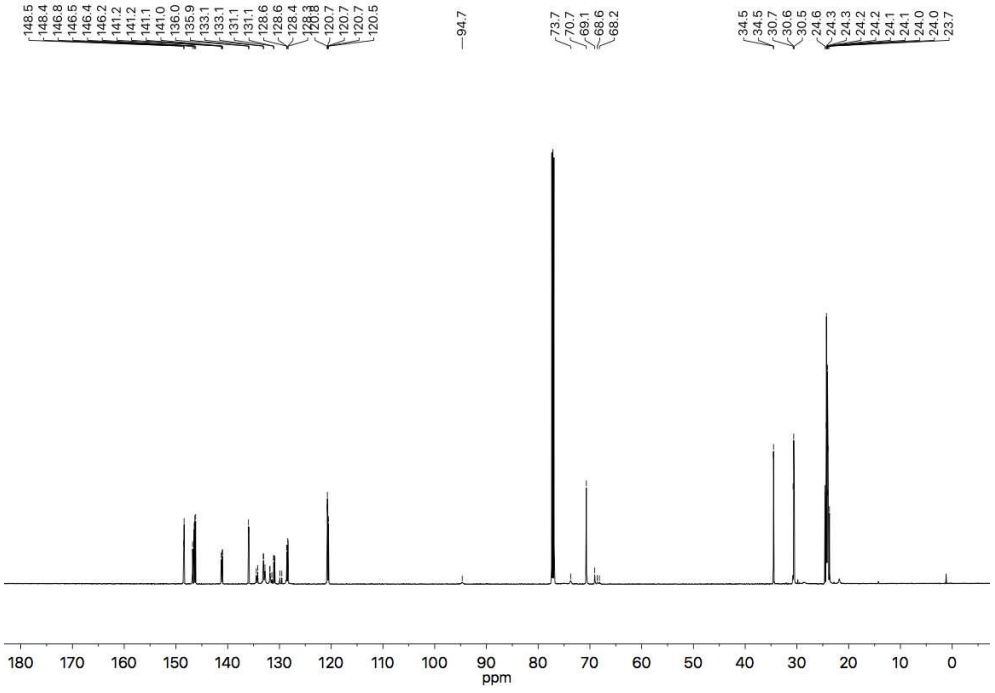


(*R*,*S*)

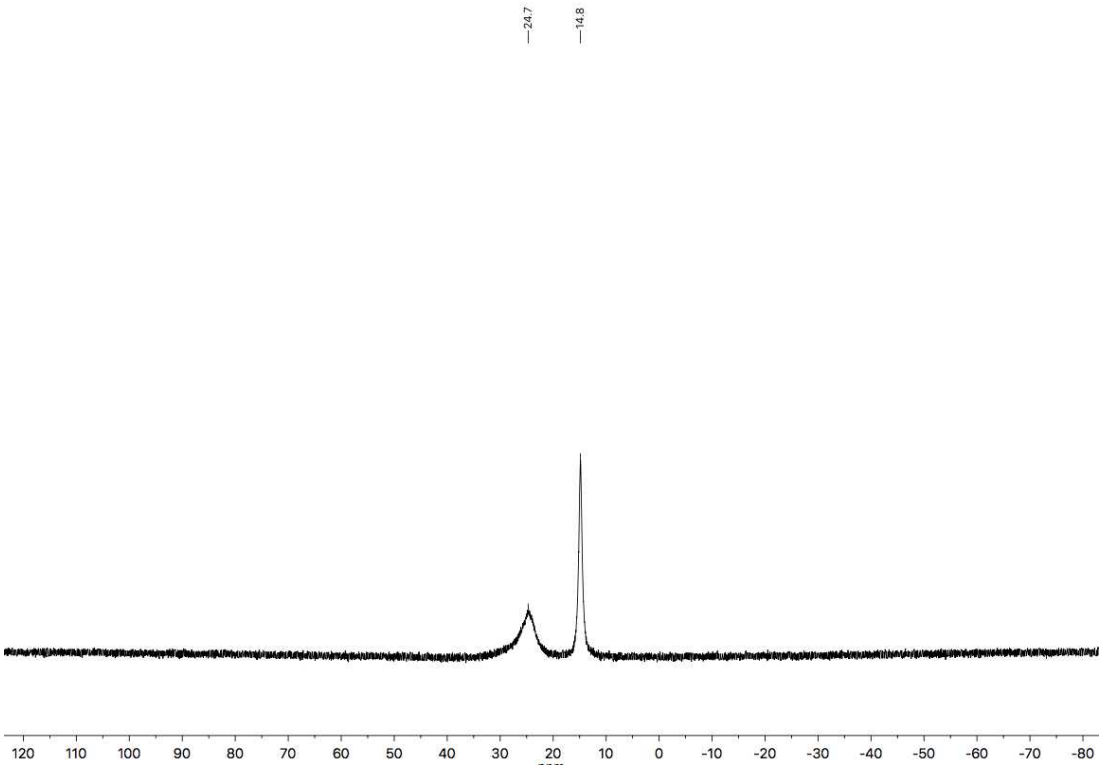
^{1}H NMR (500 MHz, $CDCl_3$) – (***R*,*S***)-(**3,5-TRIP**)**Josiphos•2BH$_3$**



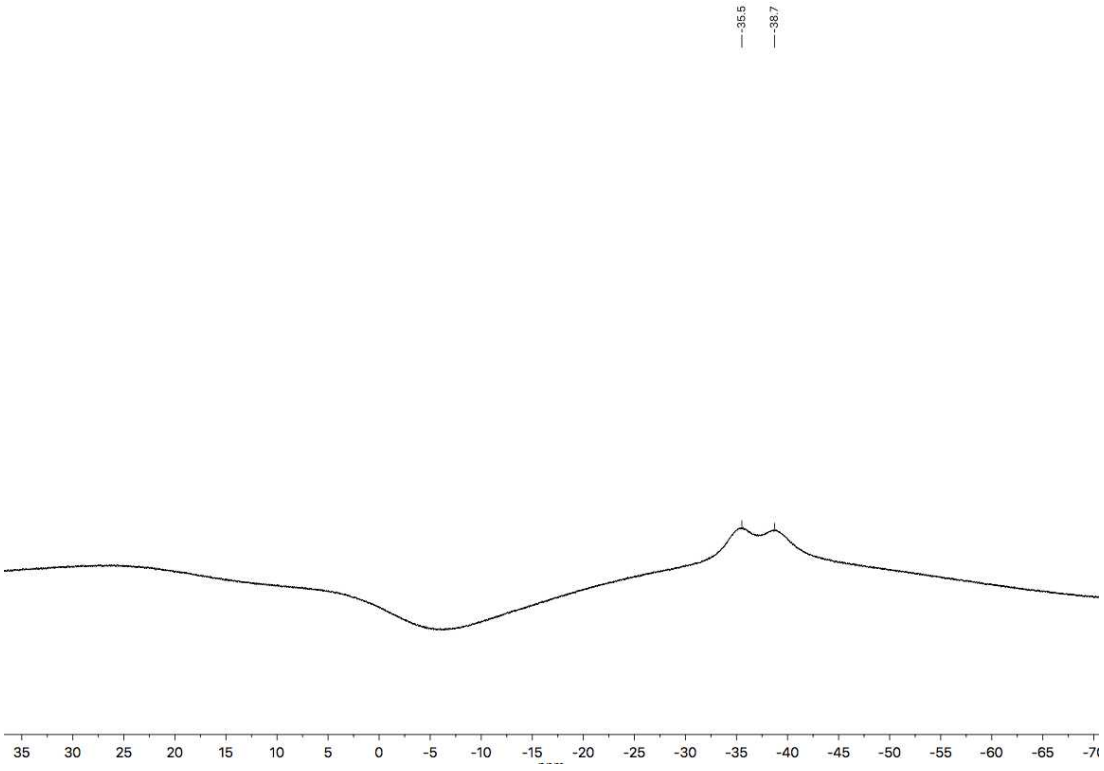
^{13}C NMR (151 MHz, CD_2Cl_2) – (***R*,*S***)-(**3,5-TRIP**)**Josiphos•2BH$_3$**

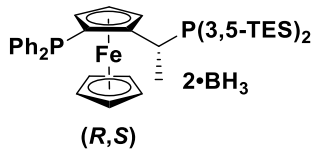


^{31}P NMR (202 MHz, $CDCl_3$) – **(*R,S*)-(3,5-TRIP)Josiphos•2BH$_3$**



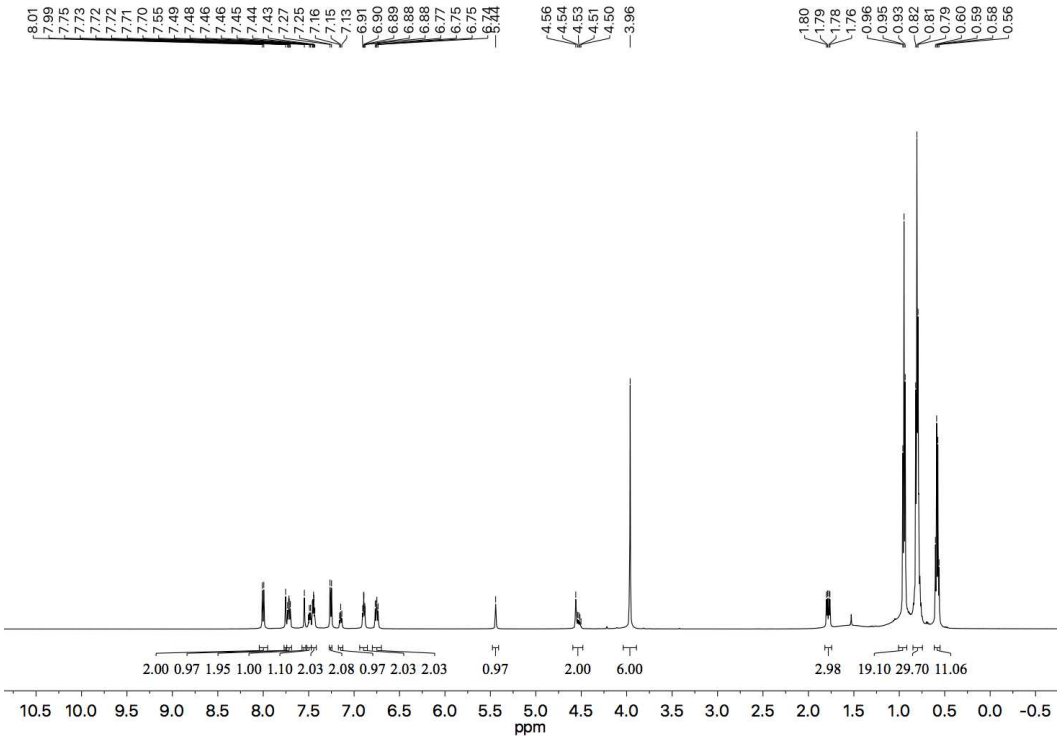
^{11}B NMR (160 MHz, $CDCl_3$) – **(*R,S*)-(3,5-TRIP)Josiphos•2BH$_3$**



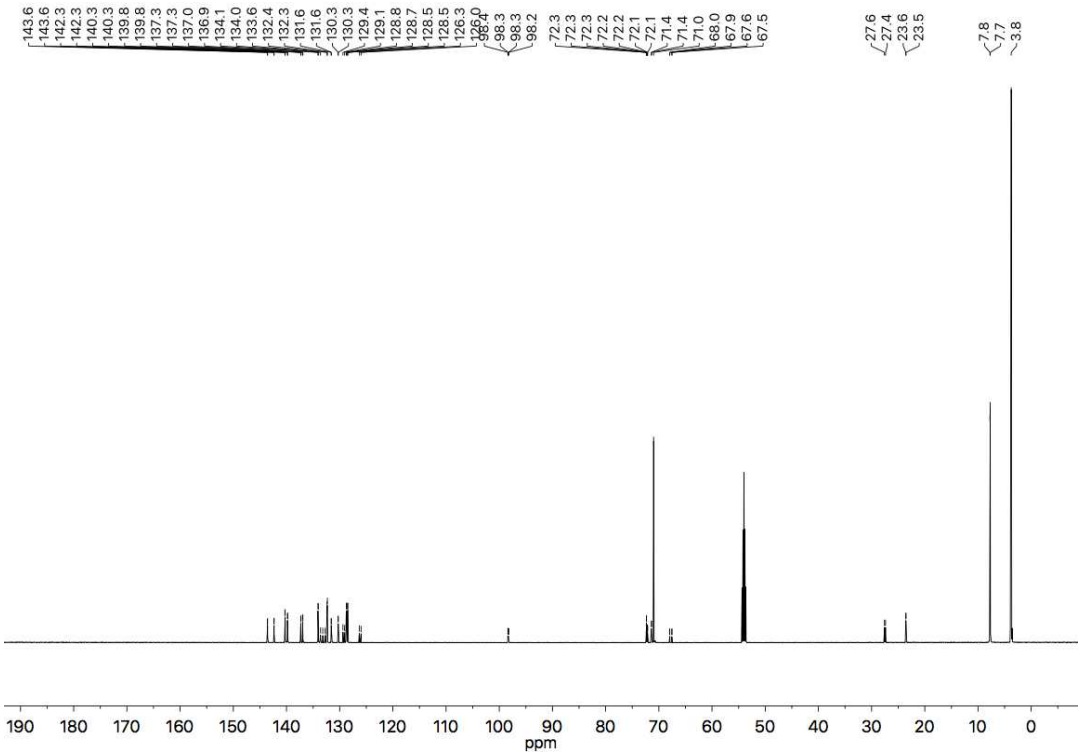


(*R*,*S*)

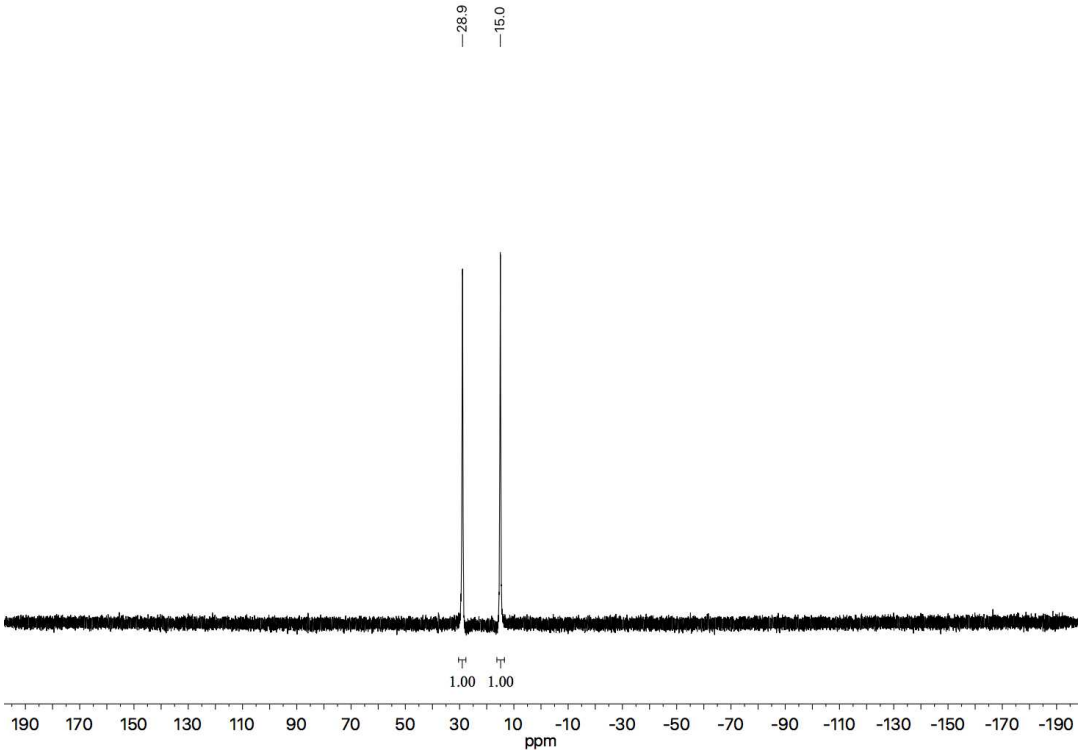
^{1}H NMR (500 MHz, $CDCl_3$) – (***R*,*S***)-(**3,5-TES**)**Josiphos•2BH$_3$**



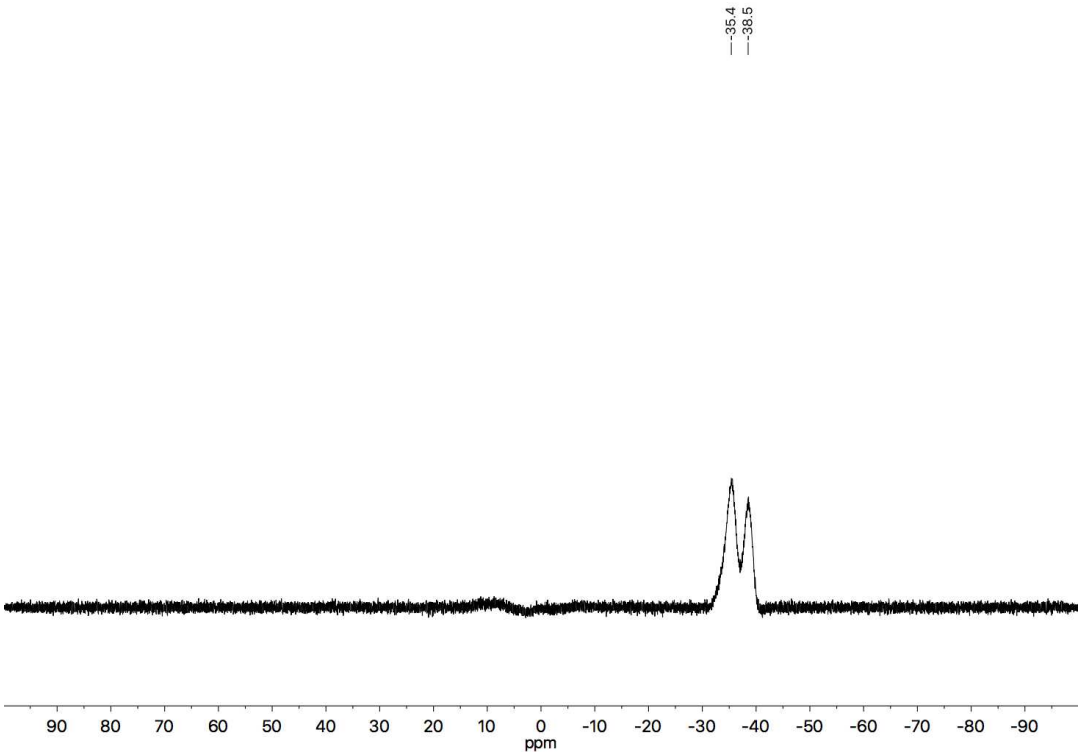
^{13}C NMR (151 MHz, CD_2Cl_2) – (***R,S***)-(**3,5-TES**)**Josiphos•2BH$_3$**

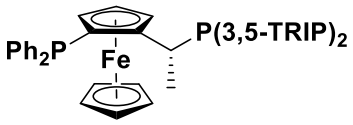


^{31}P NMR (202 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos•2BH$_3$**

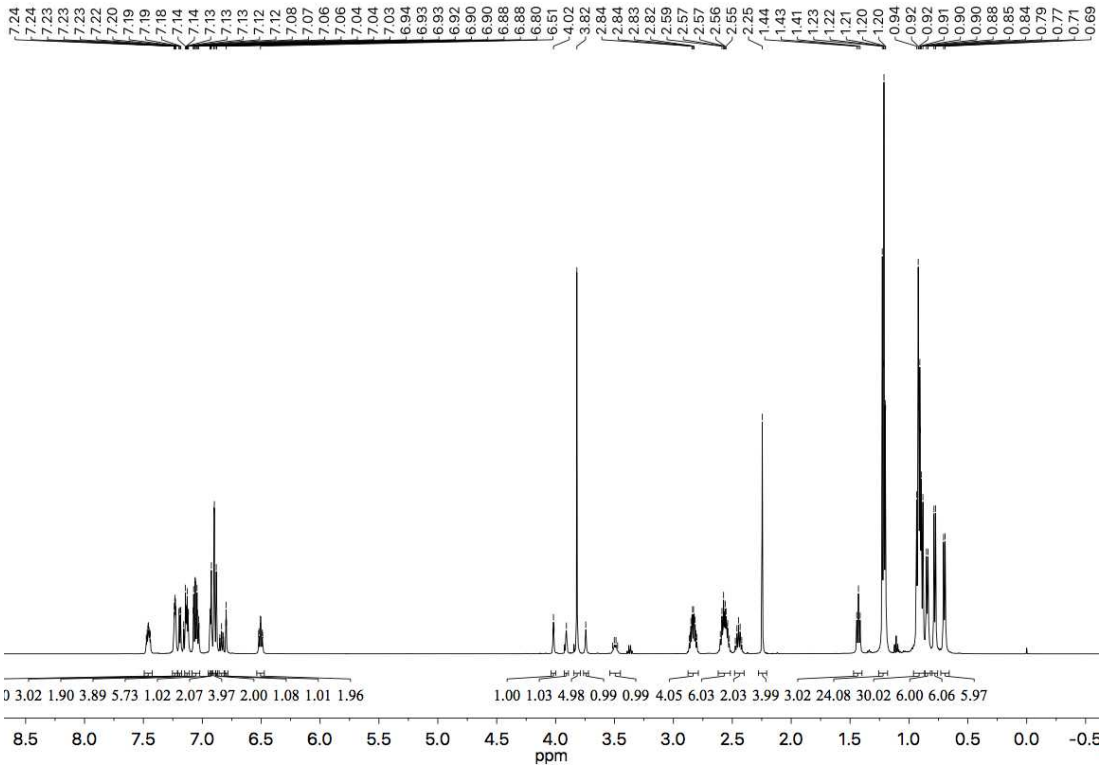


^{11}B NMR (160 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos•2BH$_3$**

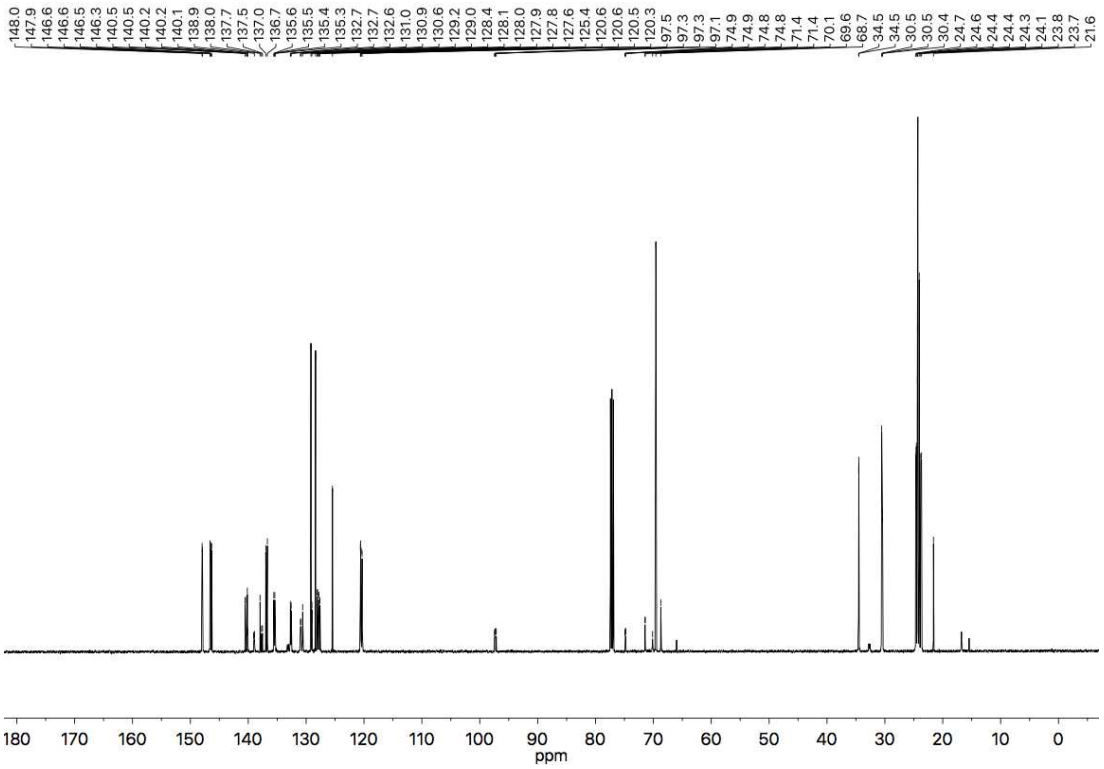




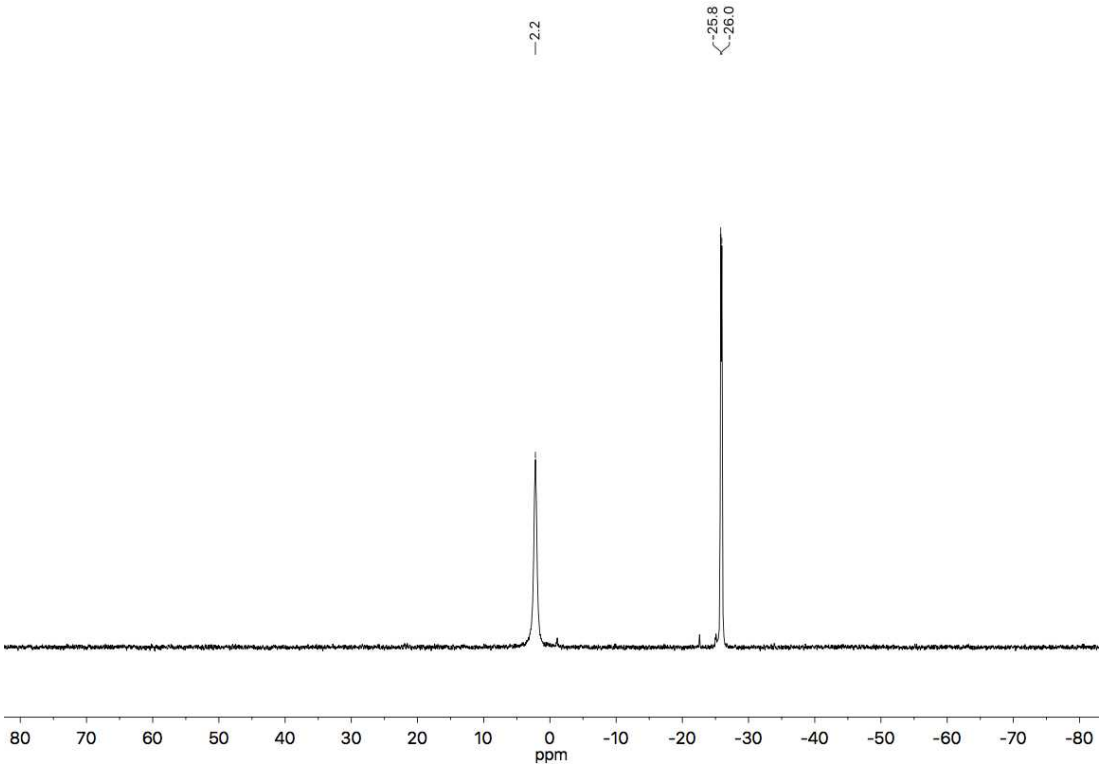
^{1}H NMR (500 MHz, $CDCl_3$) – **(*R,S*)-(3,5-TES)Josiphos**

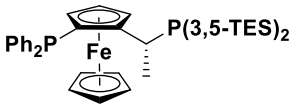


^{13}C NMR (126 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TRIP**)**Josiphos**



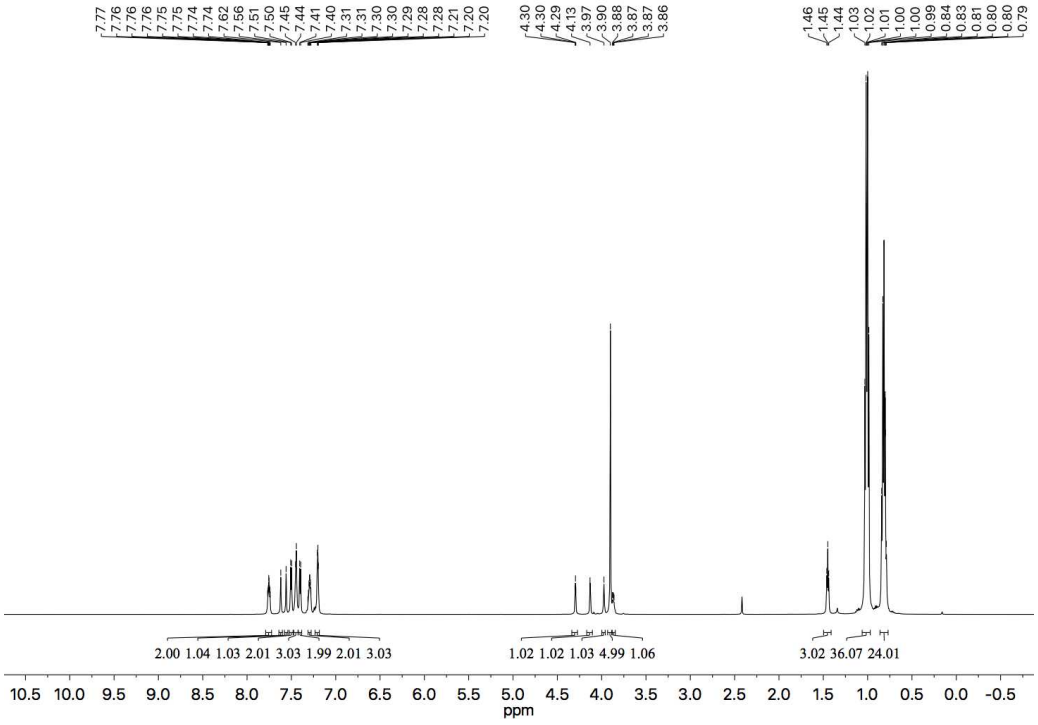
^{31}P NMR (202 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TRIP**)**Josiphos**



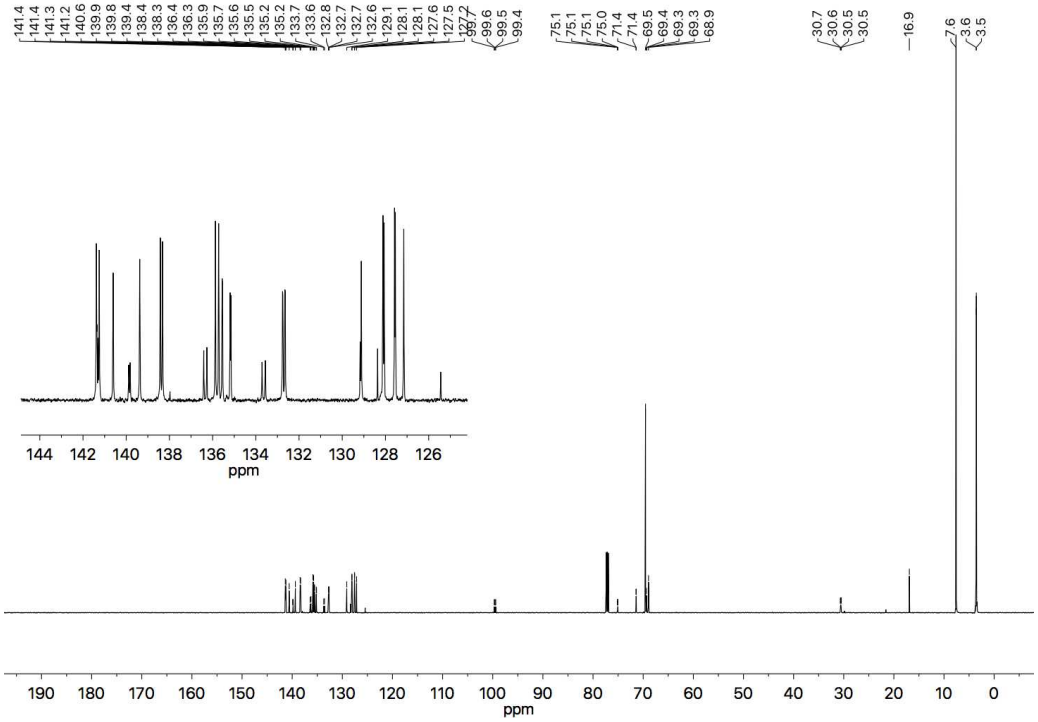


(*R*,*S*)

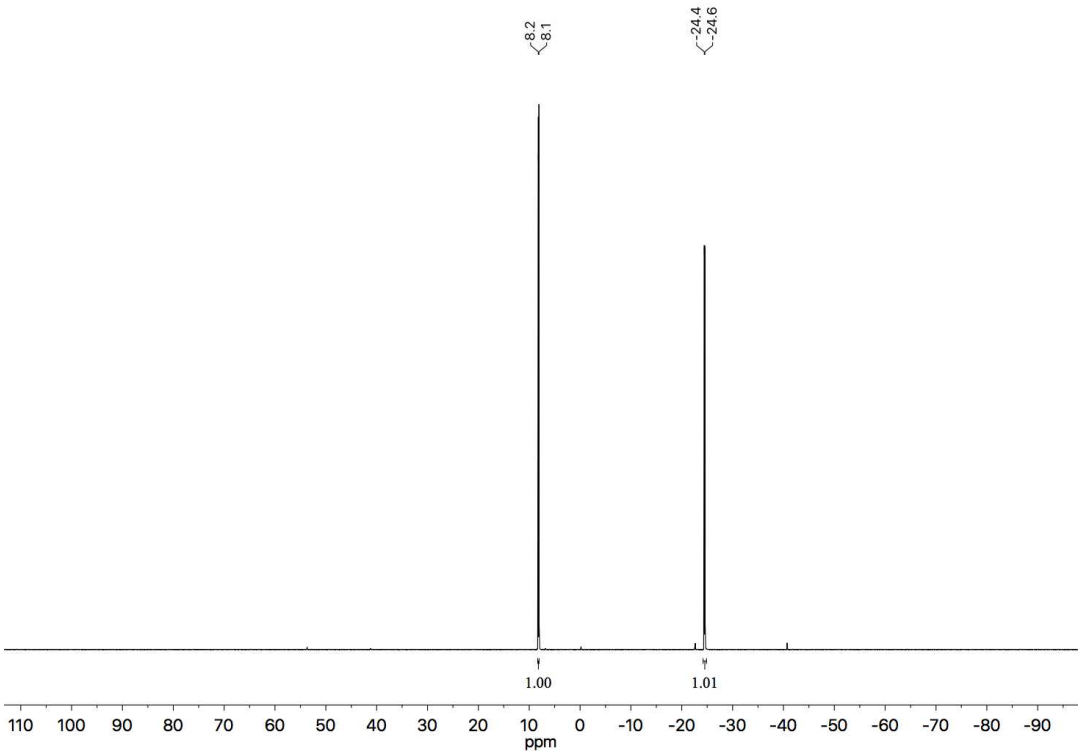
^{1}H NMR (600 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

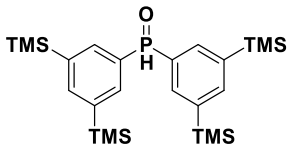


^{13}C NMR (151 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

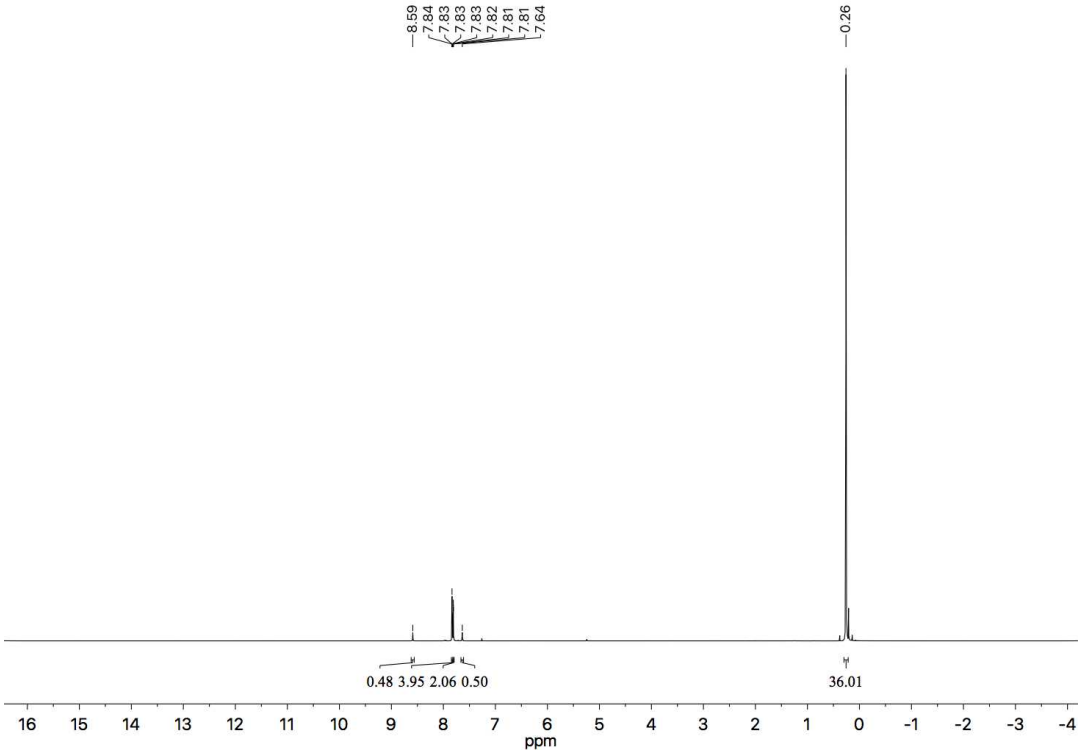


^{31}P NMR (243 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

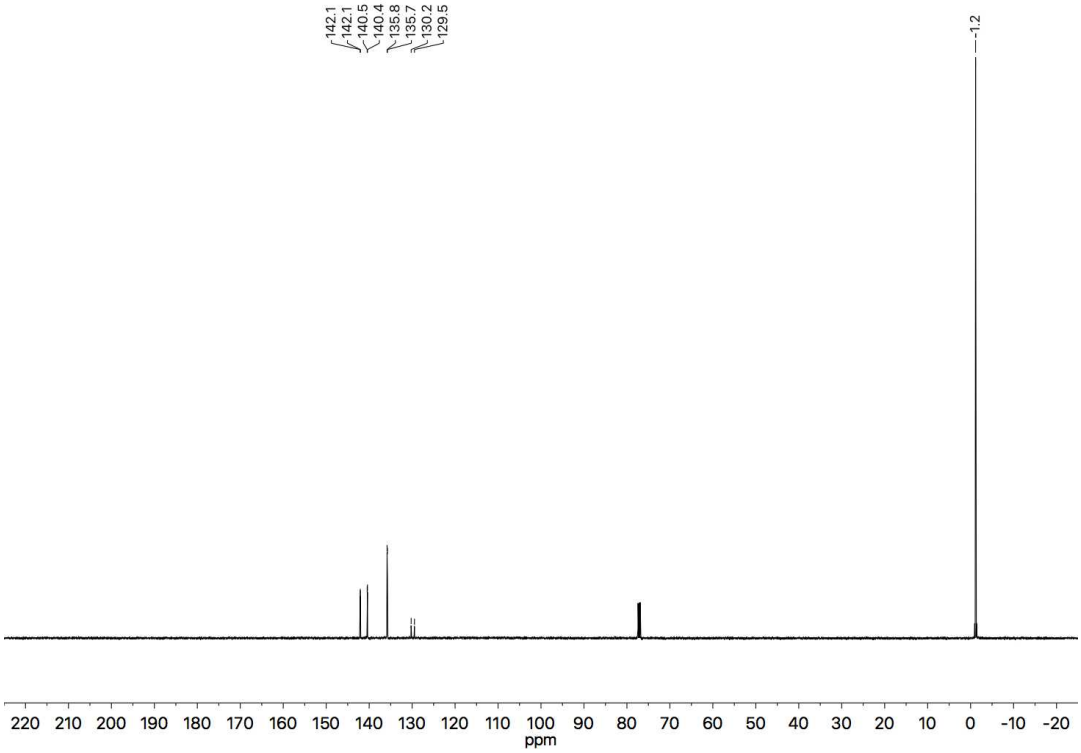




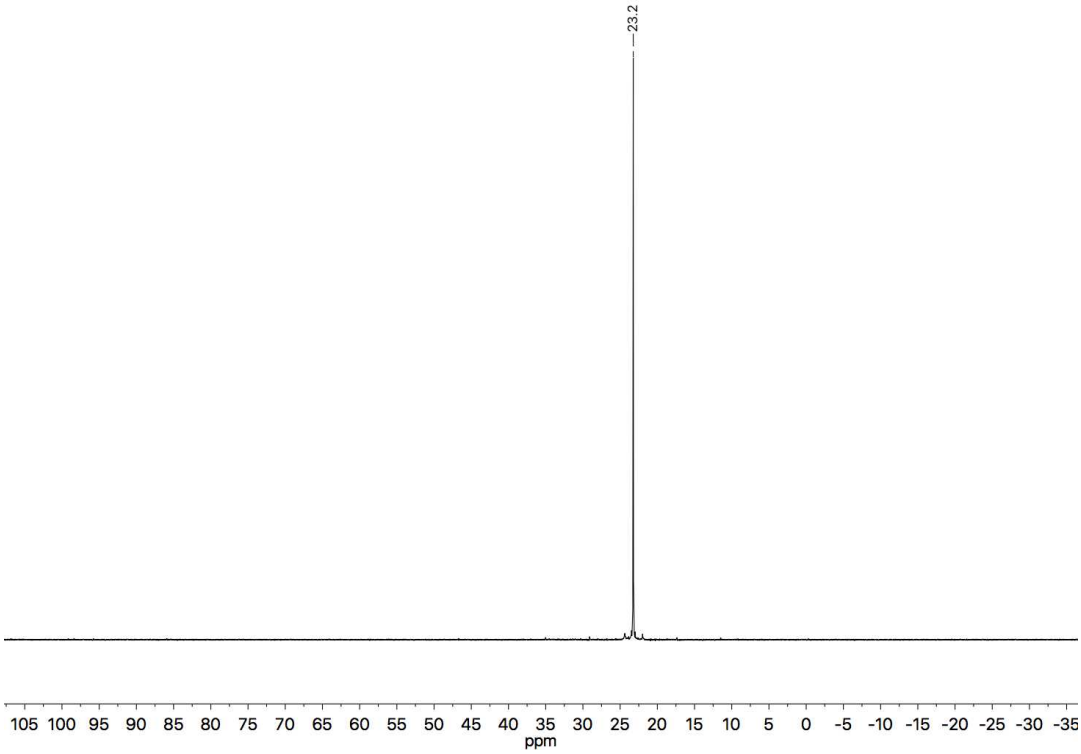
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

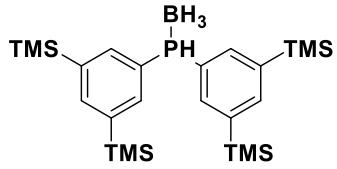


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

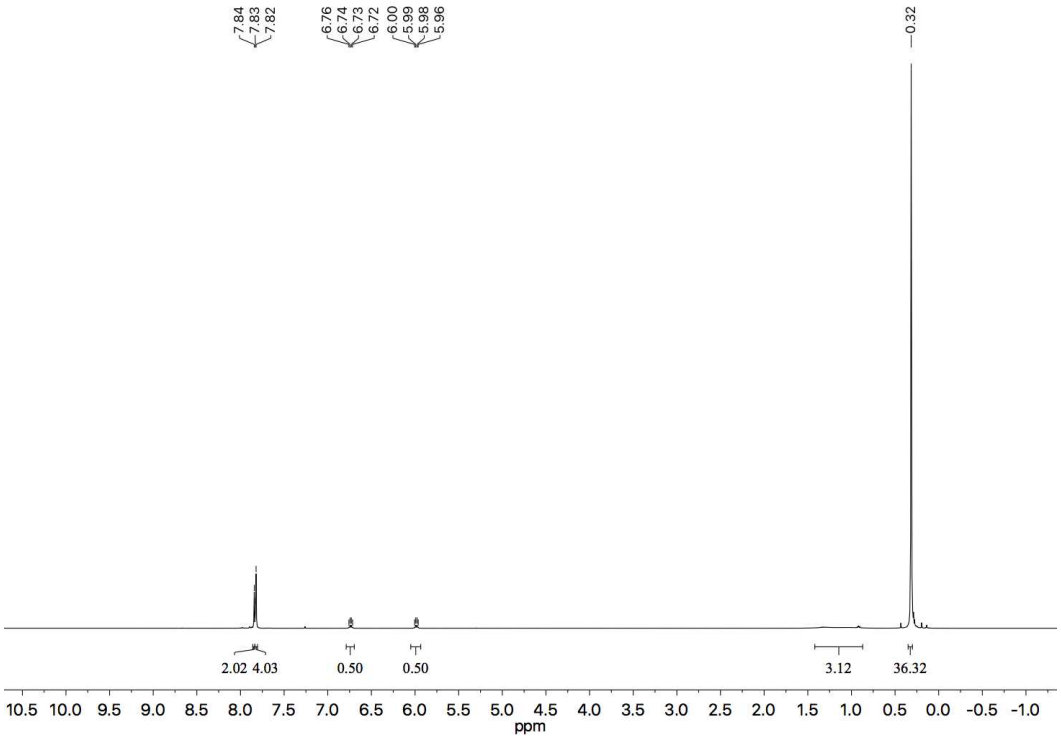


^{31}P NMR (203 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

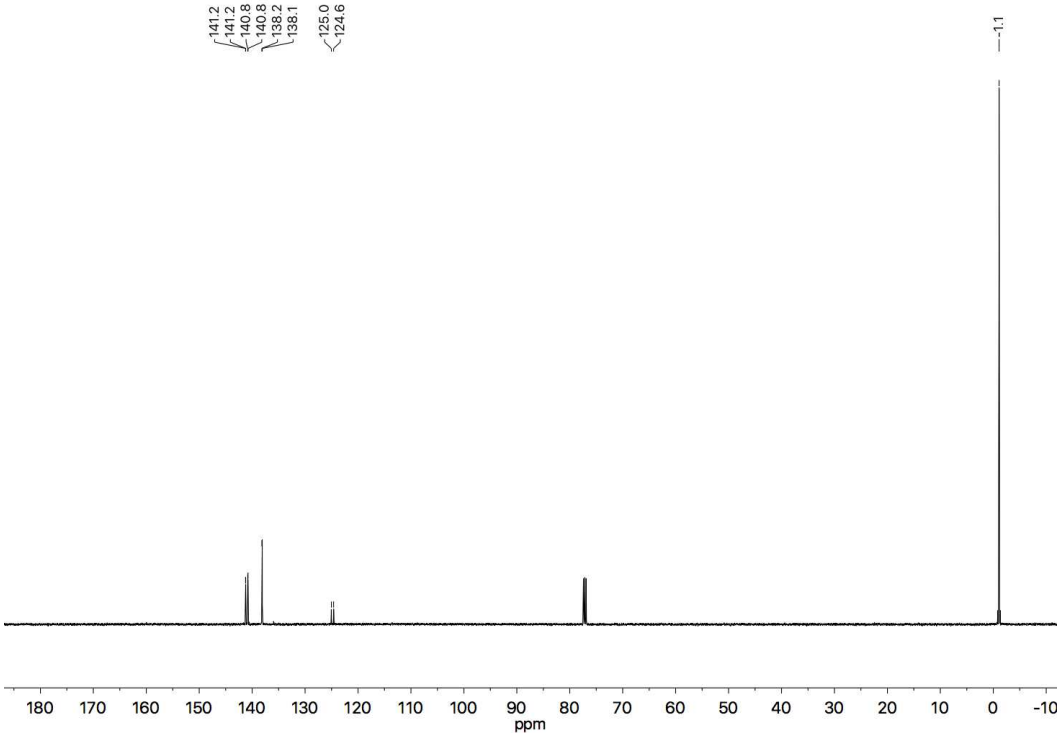




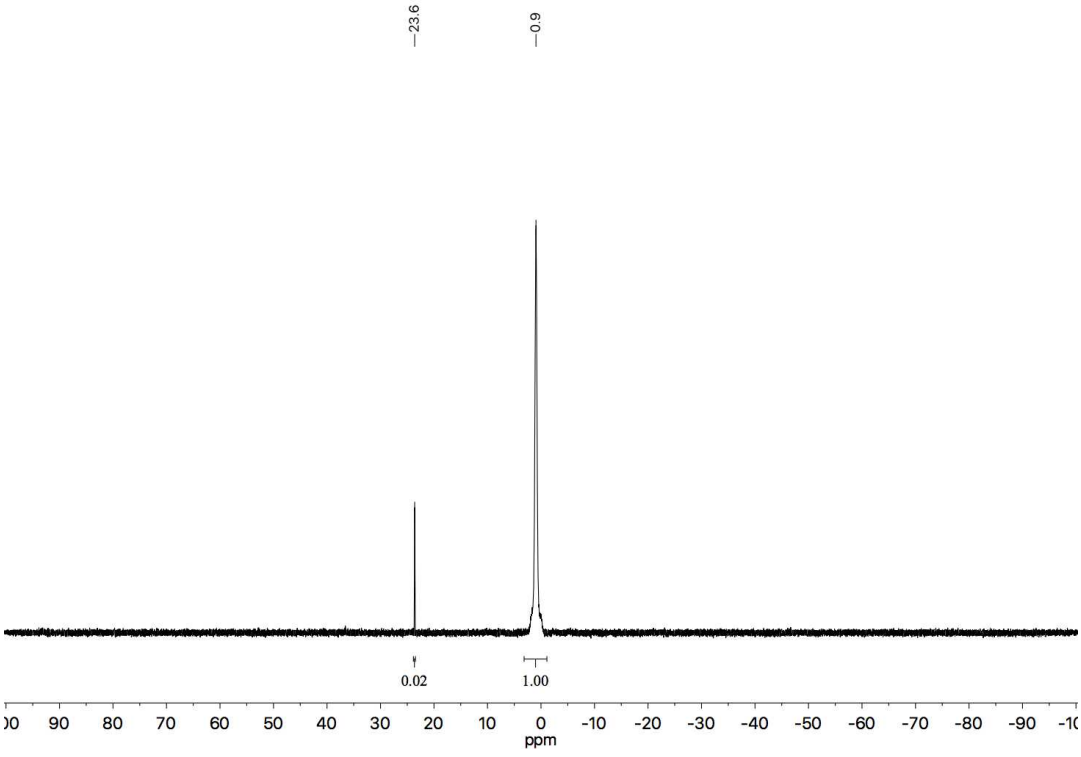
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

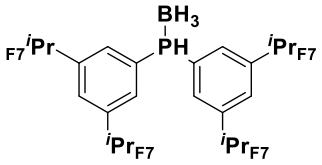


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

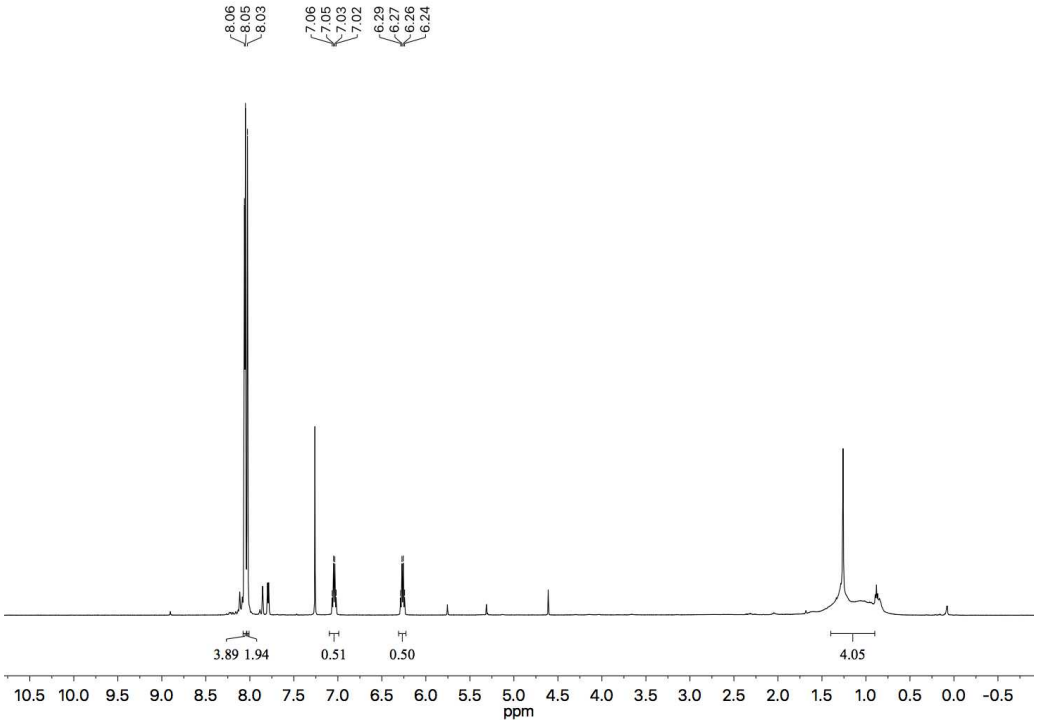


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

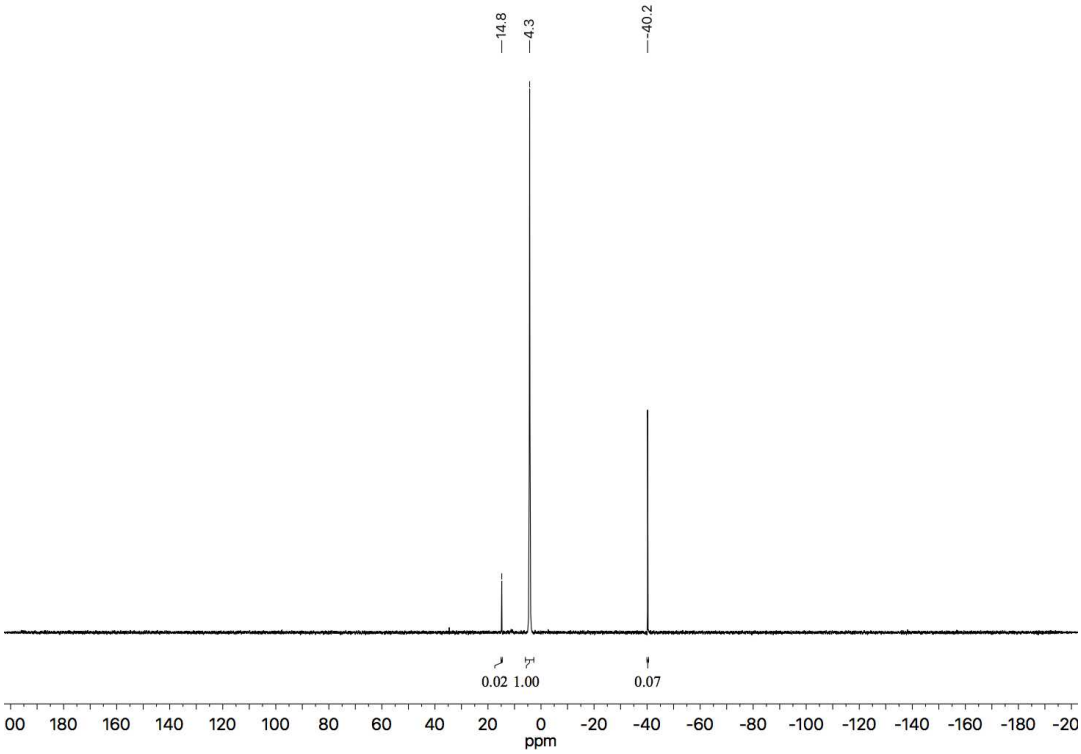




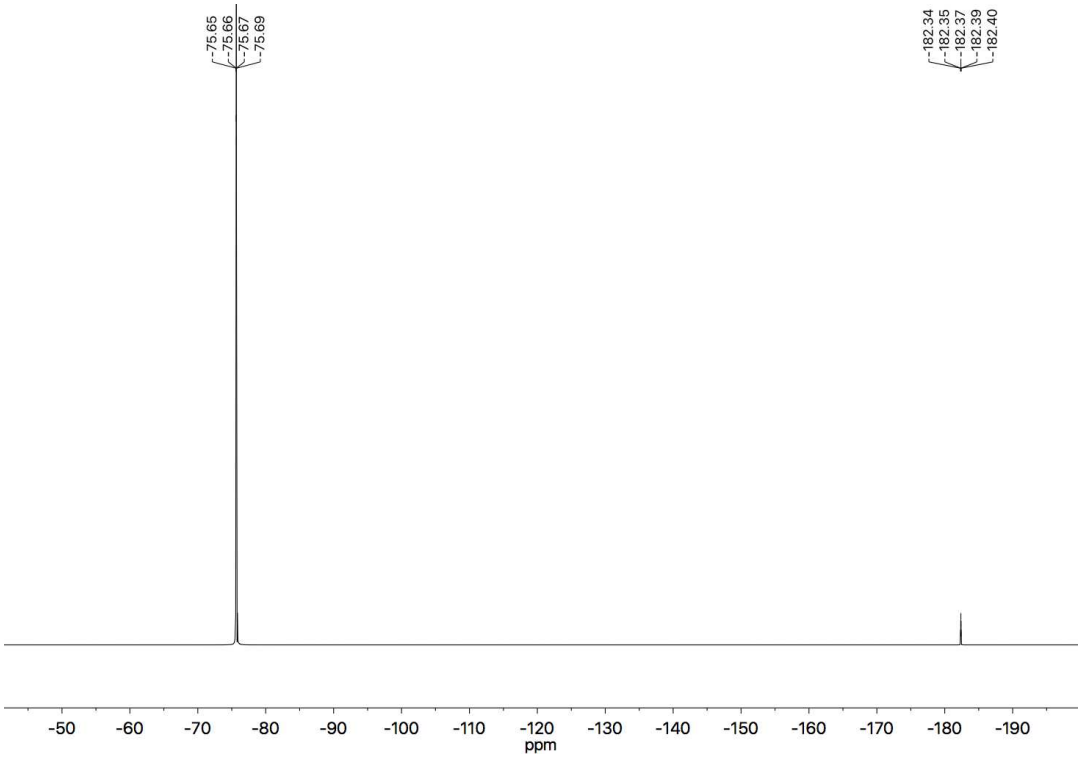
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

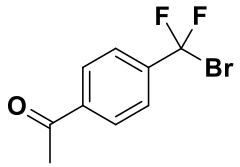


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

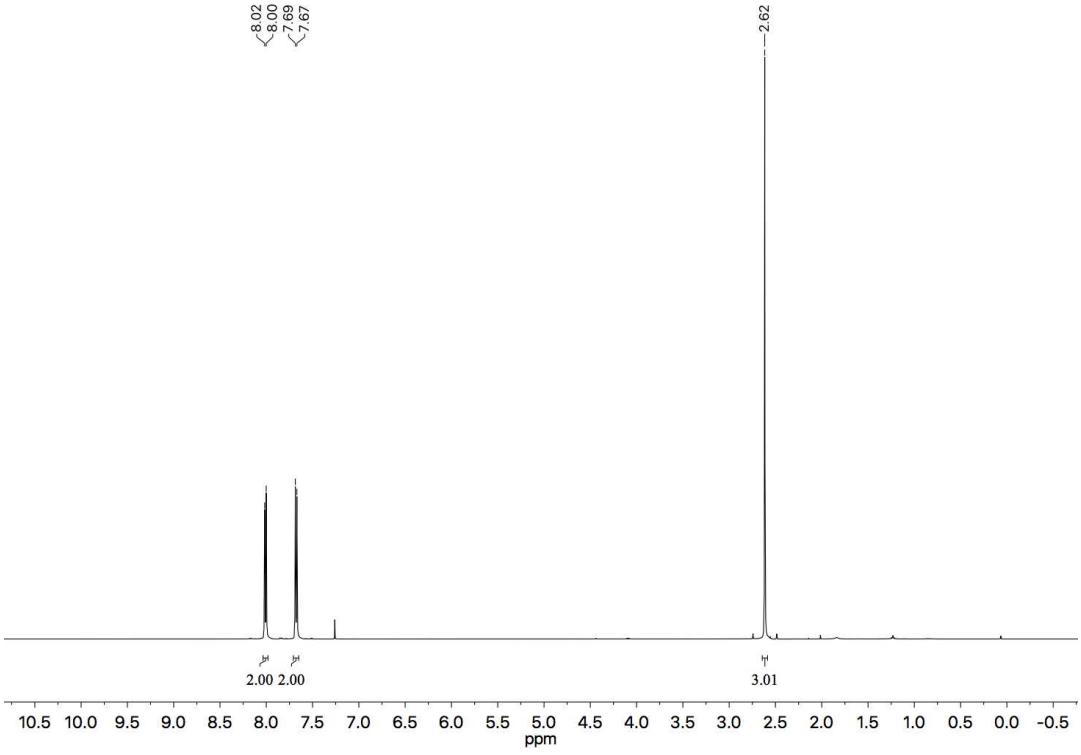


^{19}F NMR (470 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

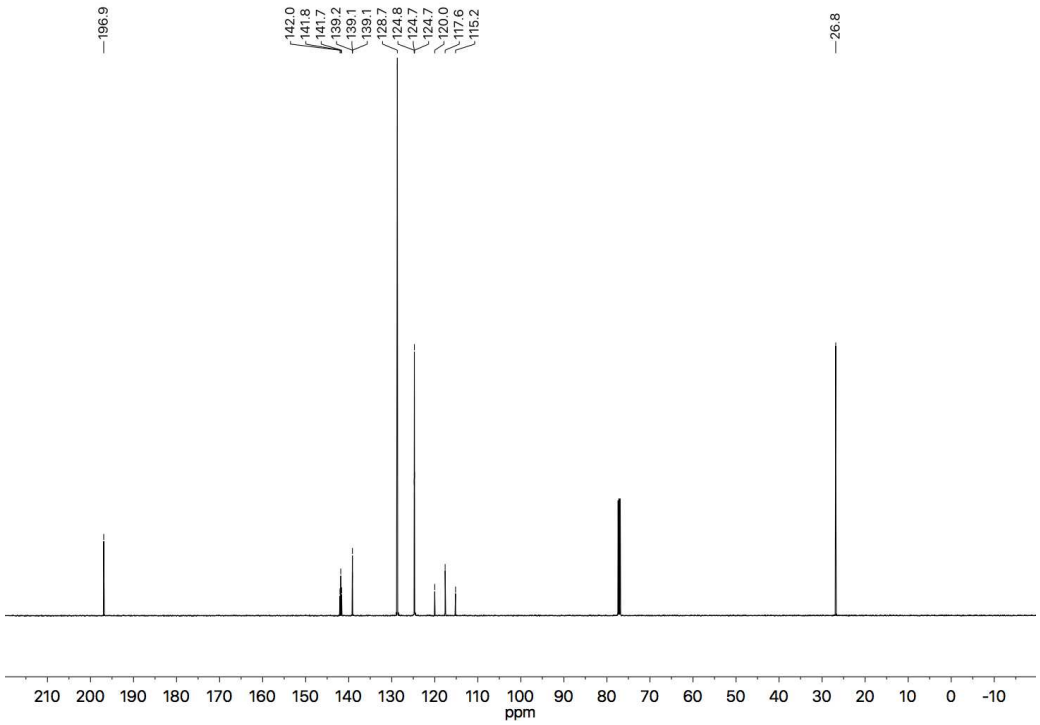




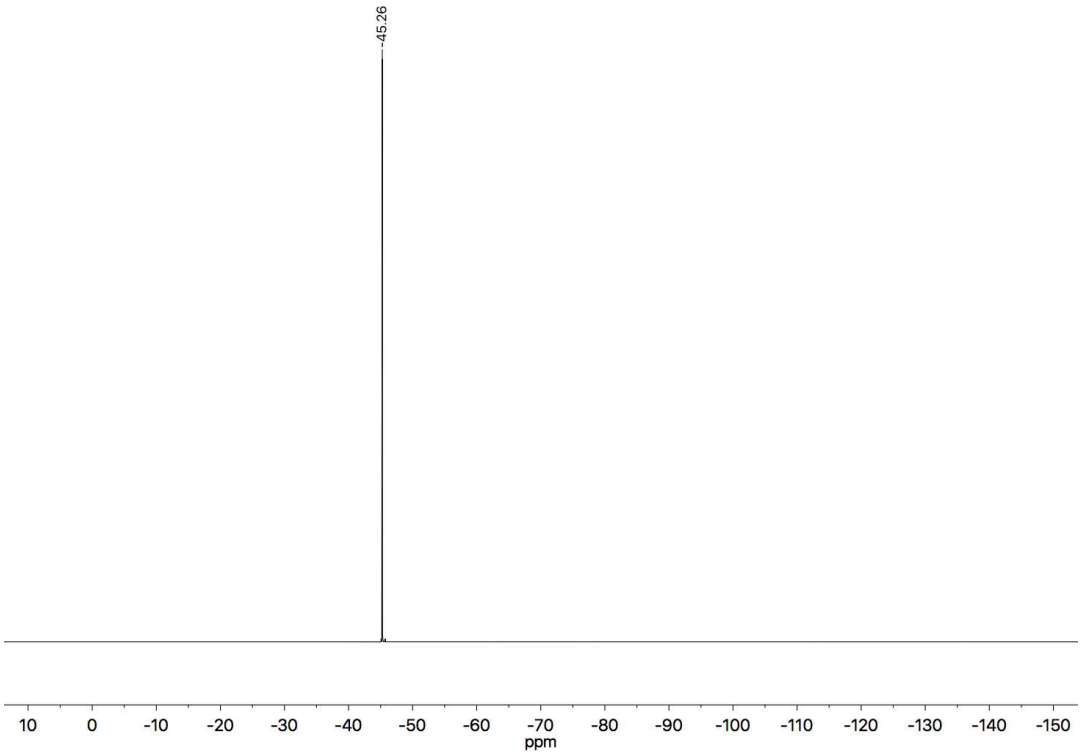
^{1}H NMR (500 MHz, $CDCl_3$) – **4Br**

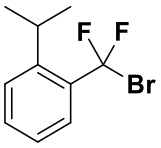


^{13}C NMR (126 MHz, $CDCl_3$) – **4Br**

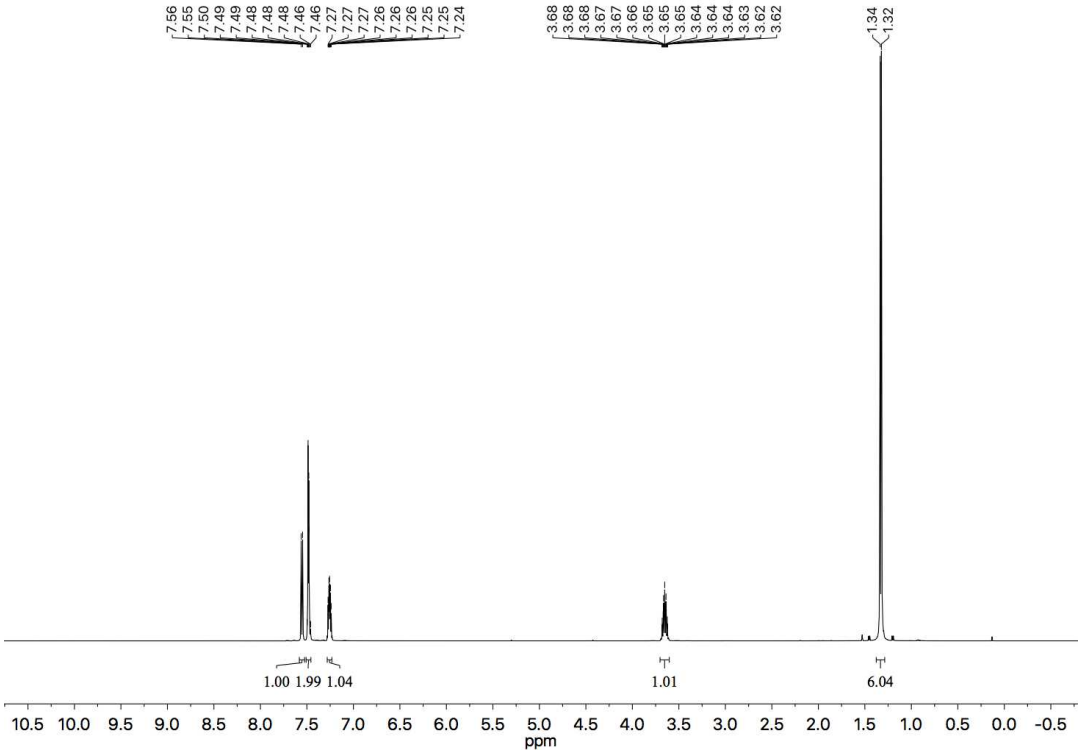


^{19}F NMR (470 MHz, $CDCl_3$) – **4Br**

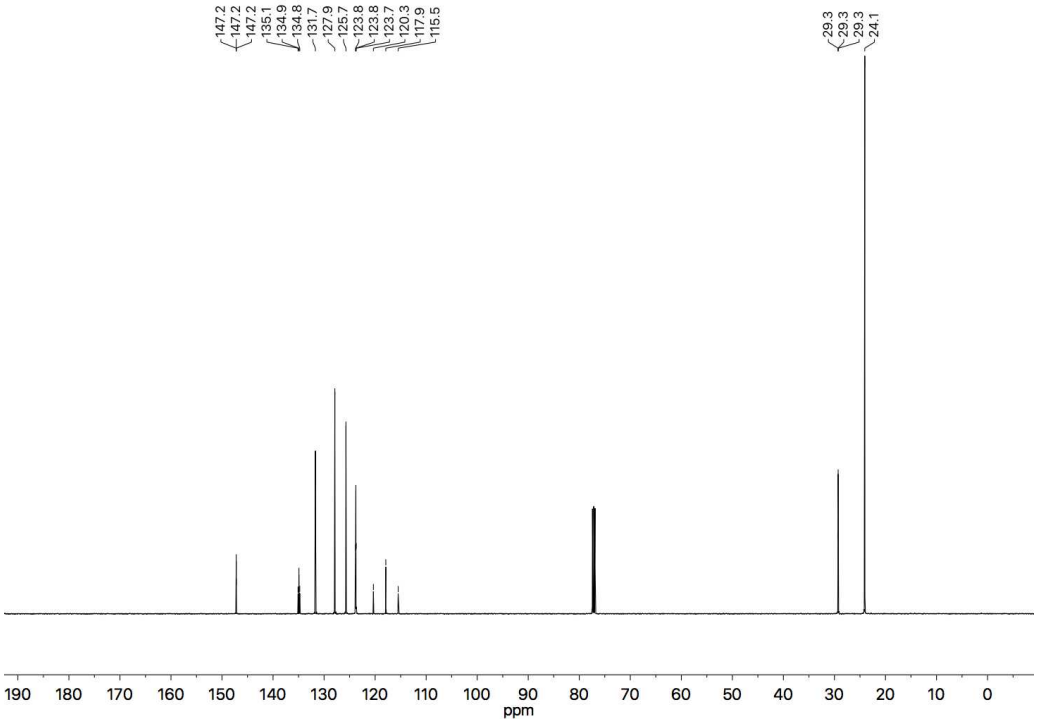




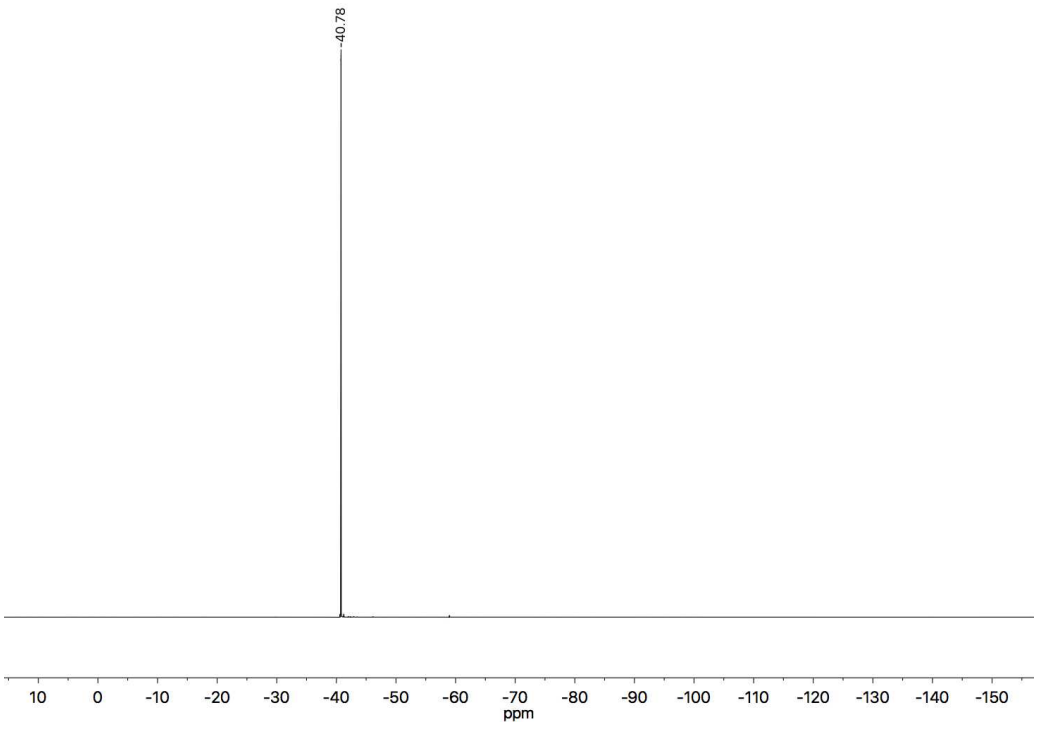
^{1}H NMR (500 MHz, $CDCl_3$) – **6Br**

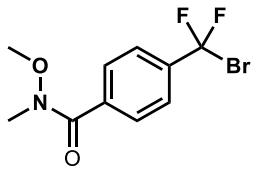


^{13}C NMR (126 MHz, $CDCl_3$) – **6Br**

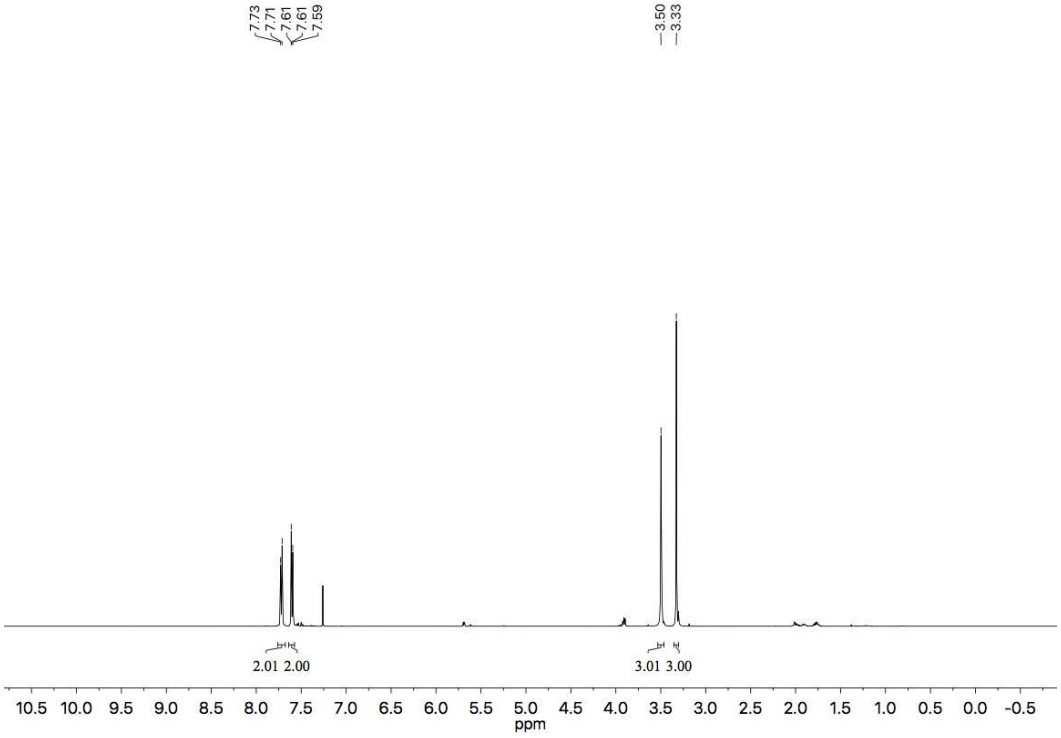


^{19}F NMR (470 MHz, $CDCl_3$) – **6Br**

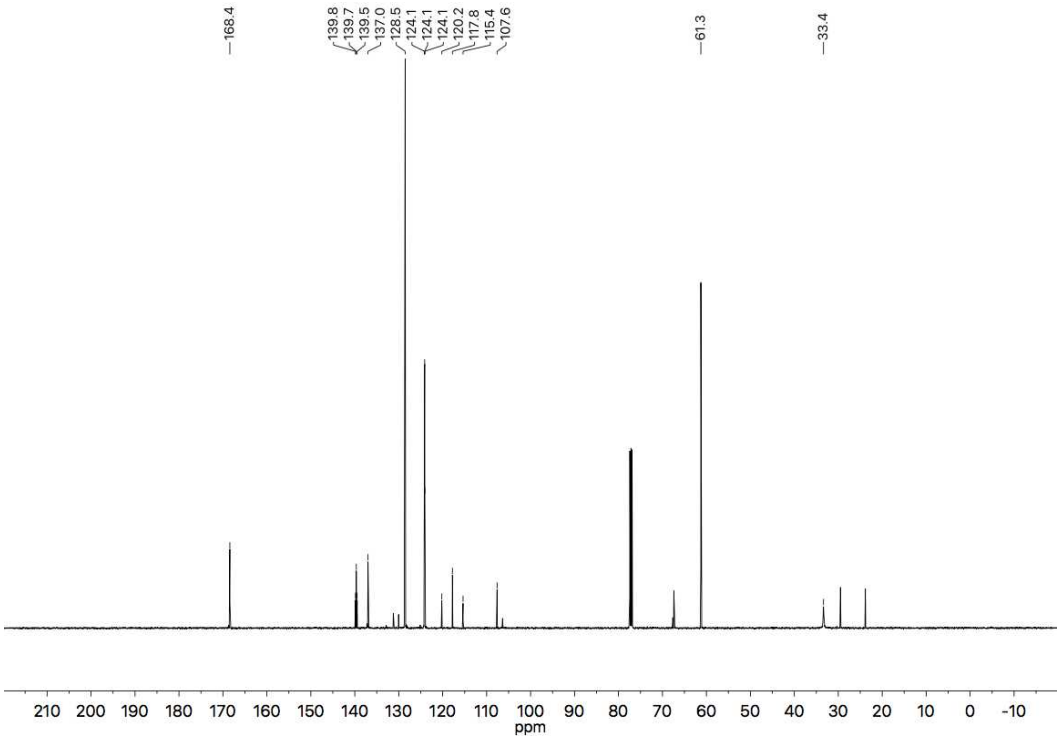




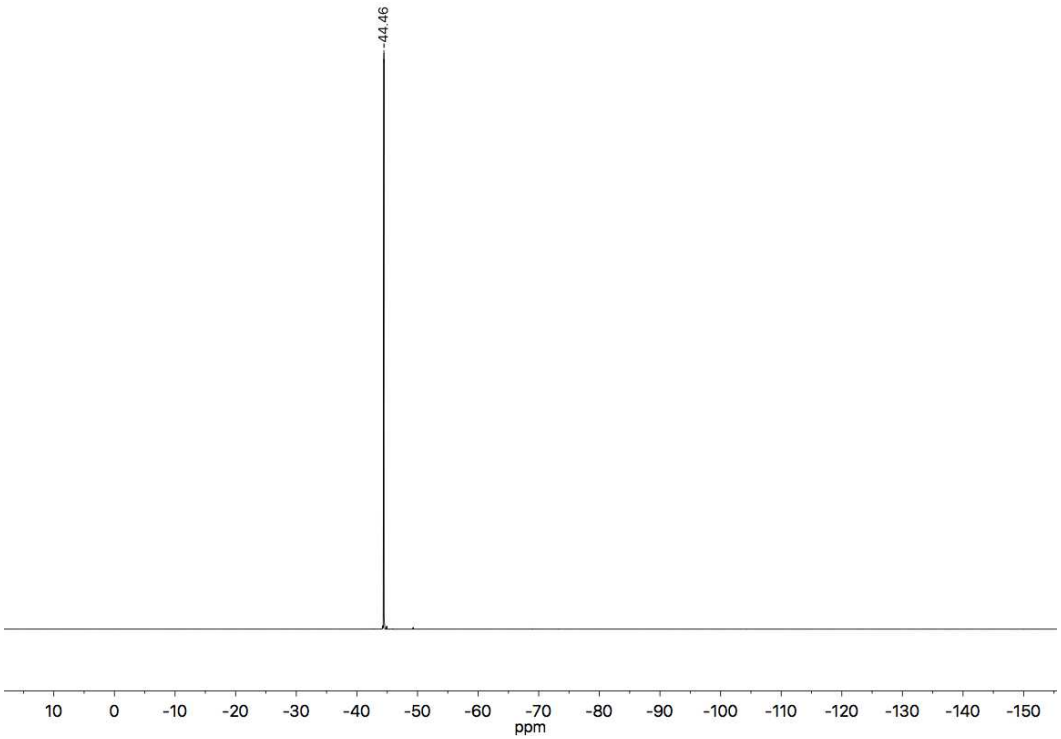
^{1}H NMR (500 MHz, $CDCl_3$) – **8Br**

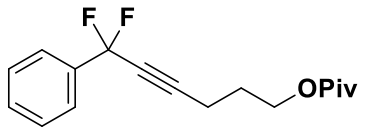


^{13}C NMR (126 MHz, $CDCl_3$) – **8Br**

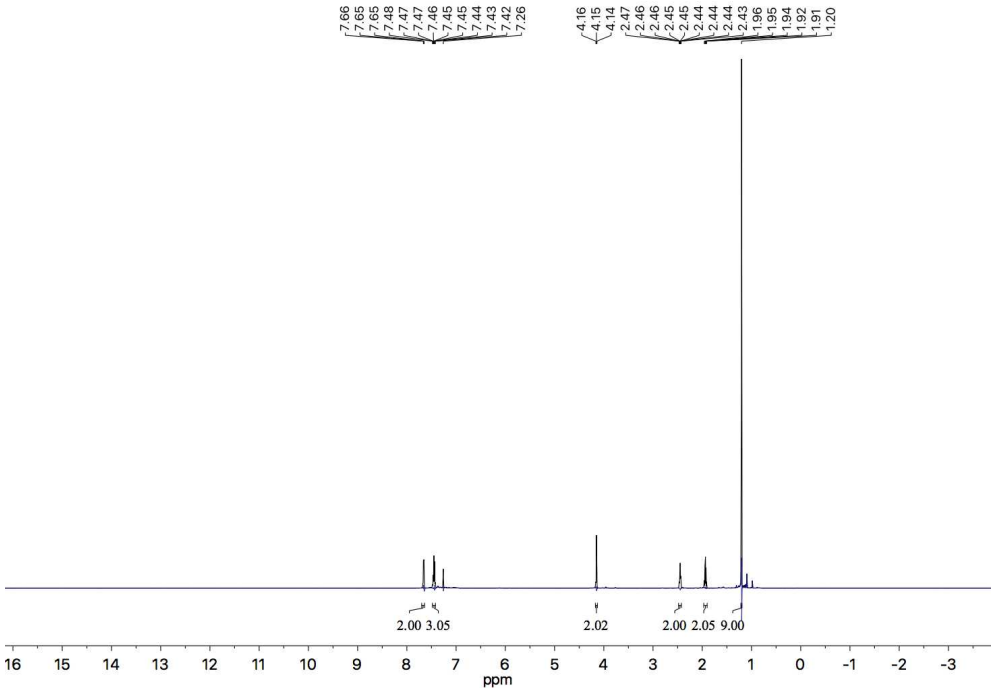


^{19}F NMR (470 MHz, $CDCl_3$) – **8Br**

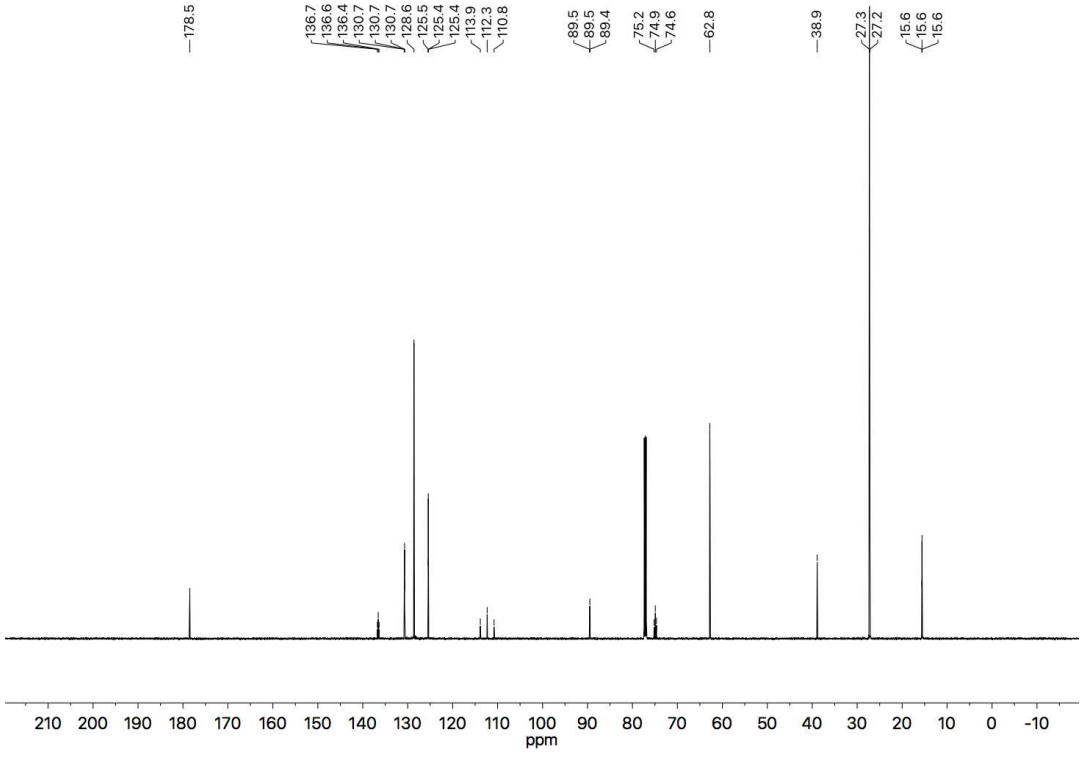




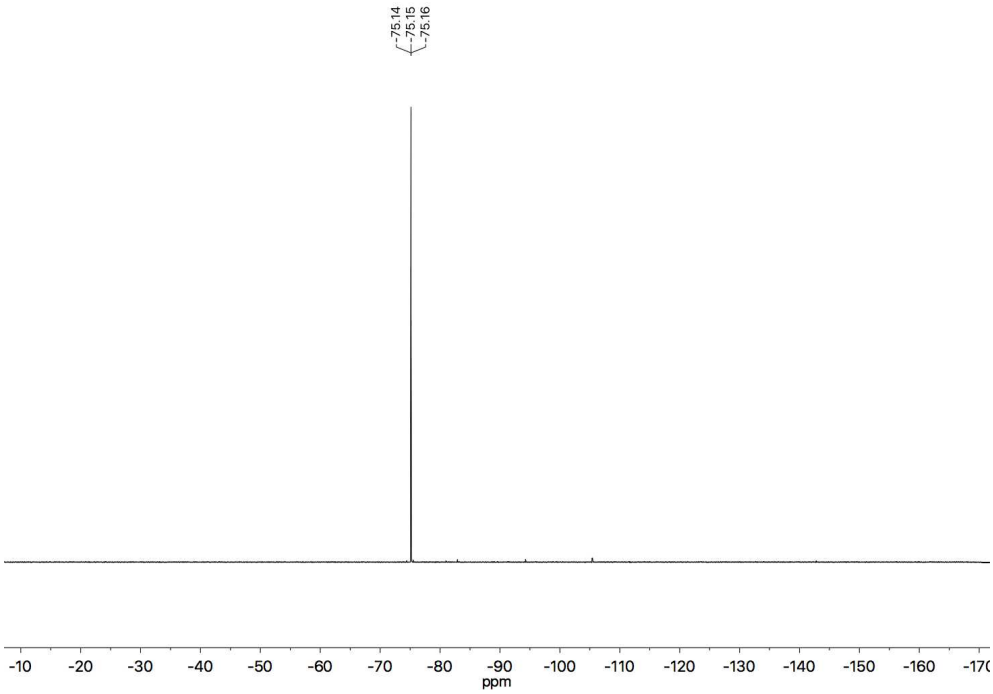
^{1}H NMR (600 MHz, $CDCl_3$) – **1a**

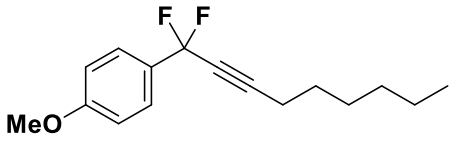


^{13}C NMR (151 MHz, $CDCl_3$) – **1a**

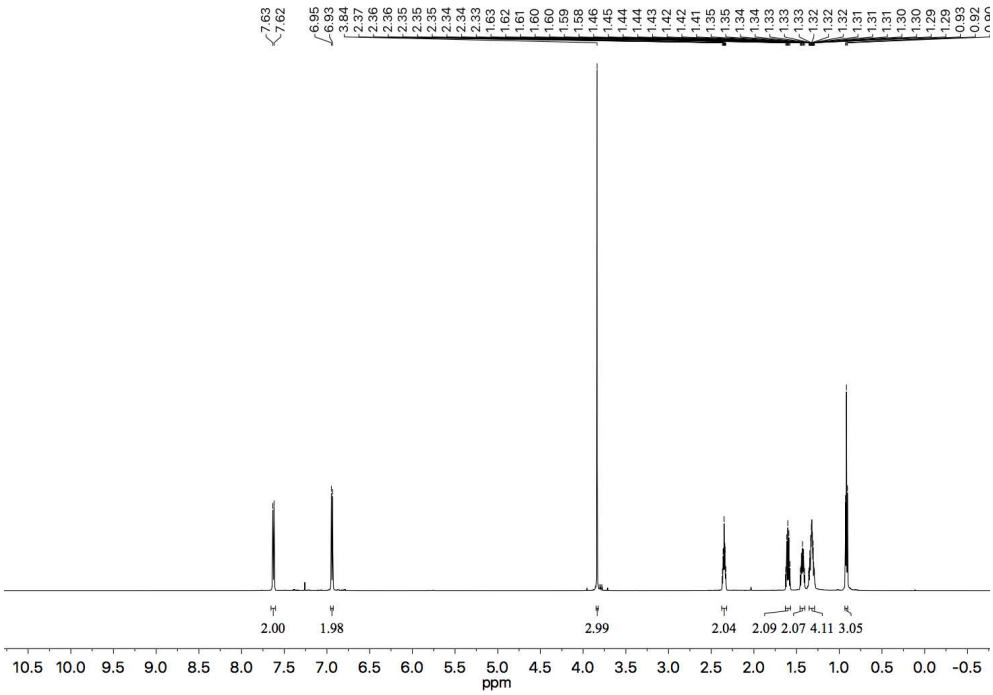


^{19}F NMR (565 MHz, $CDCl_3$) – **1a**

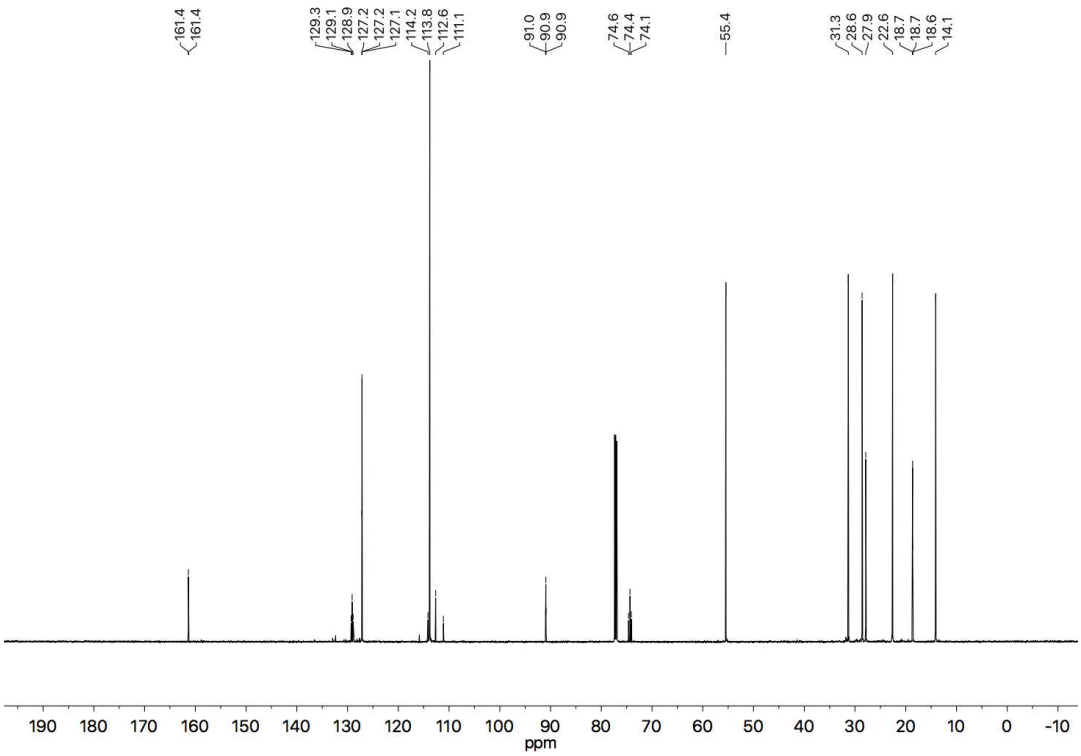




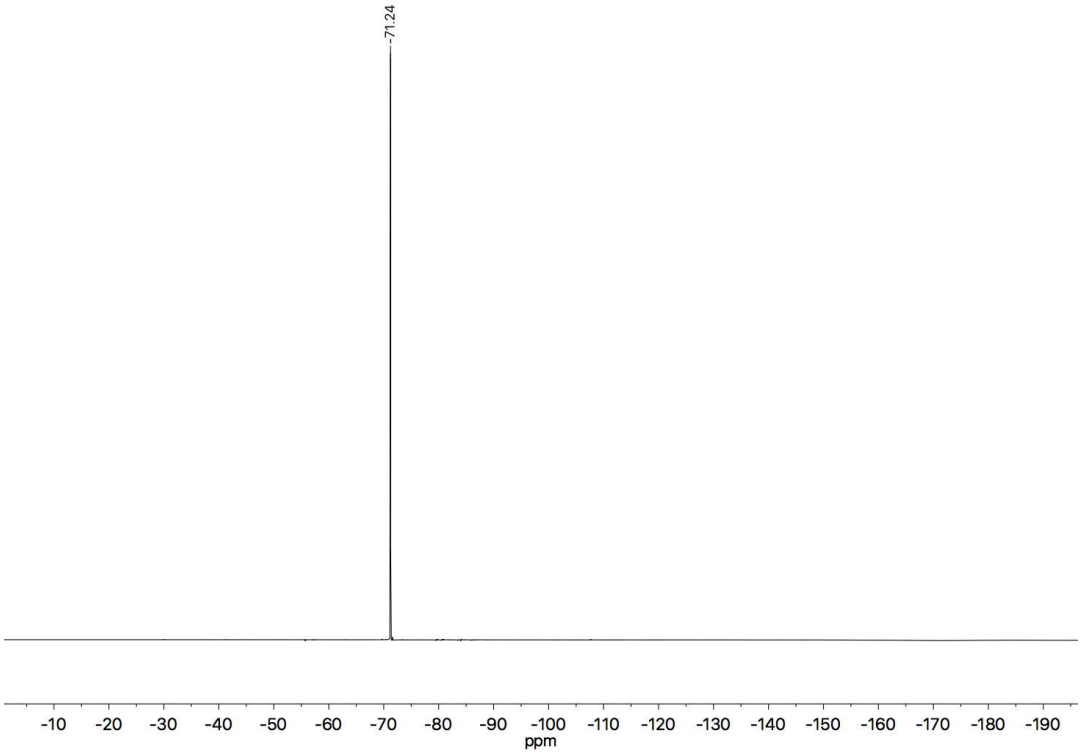
^{1}H NMR (600 MHz, $CDCl_3$) – **2a**

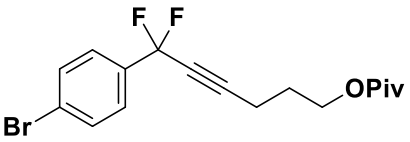


^{13}C NMR (151 MHz, $CDCl_3$) – **2a**

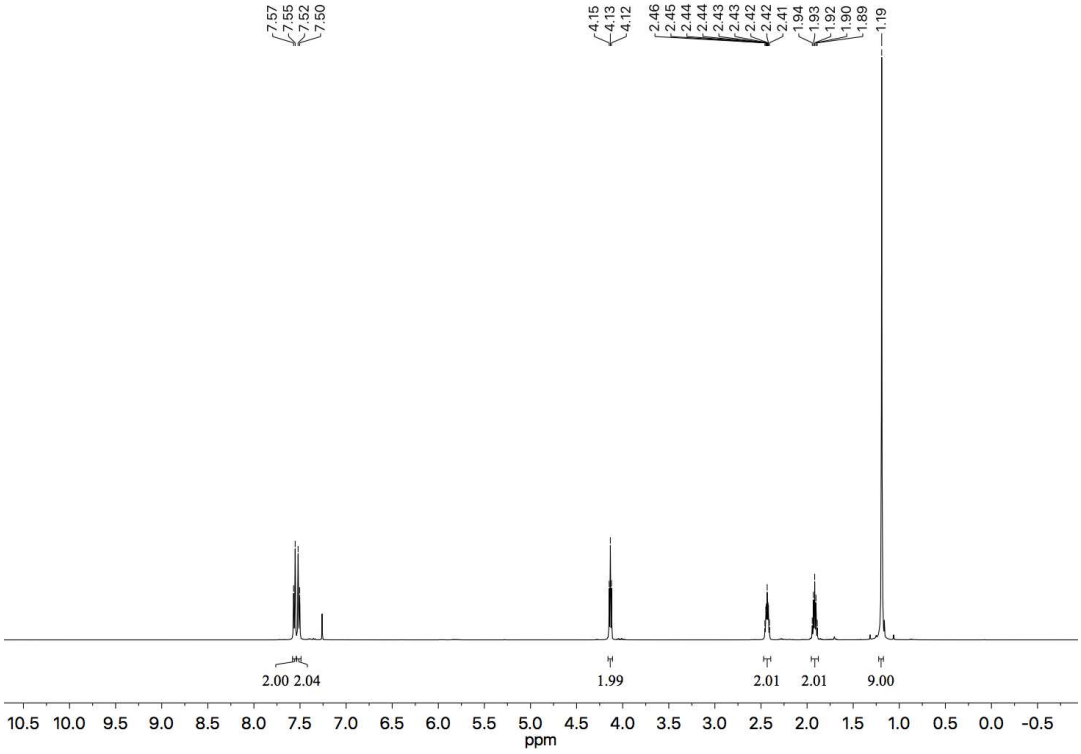


^{19}F NMR (565 MHz, $CDCl_3$) – **2a**

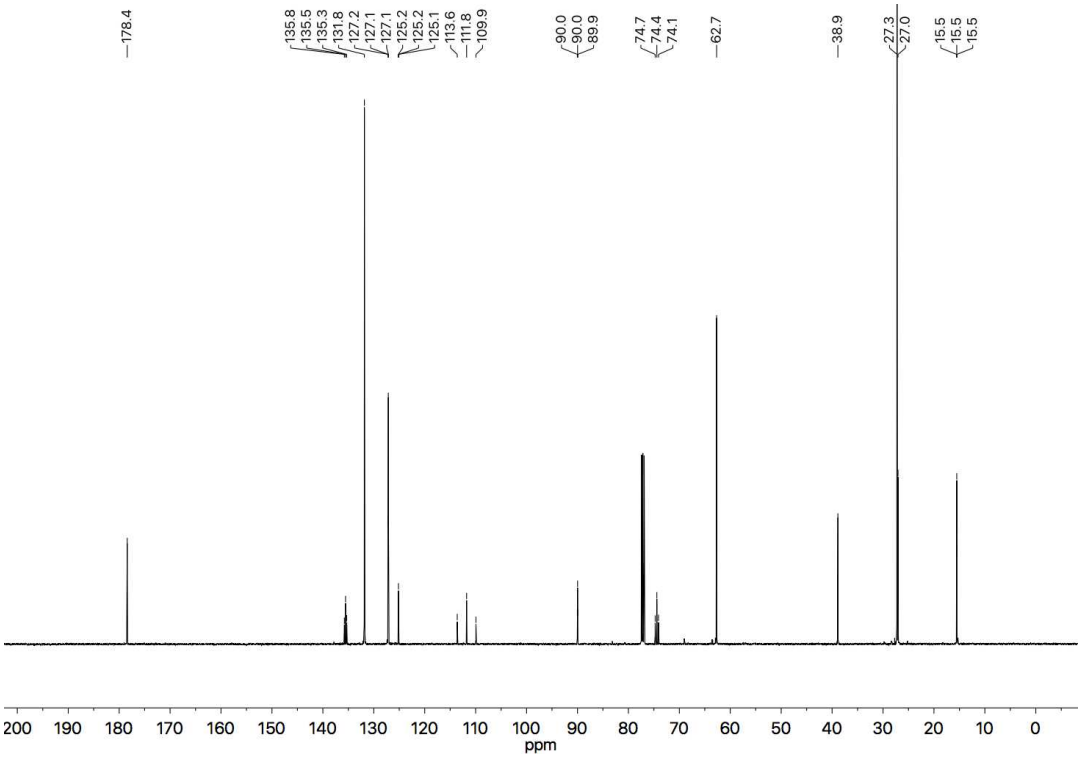




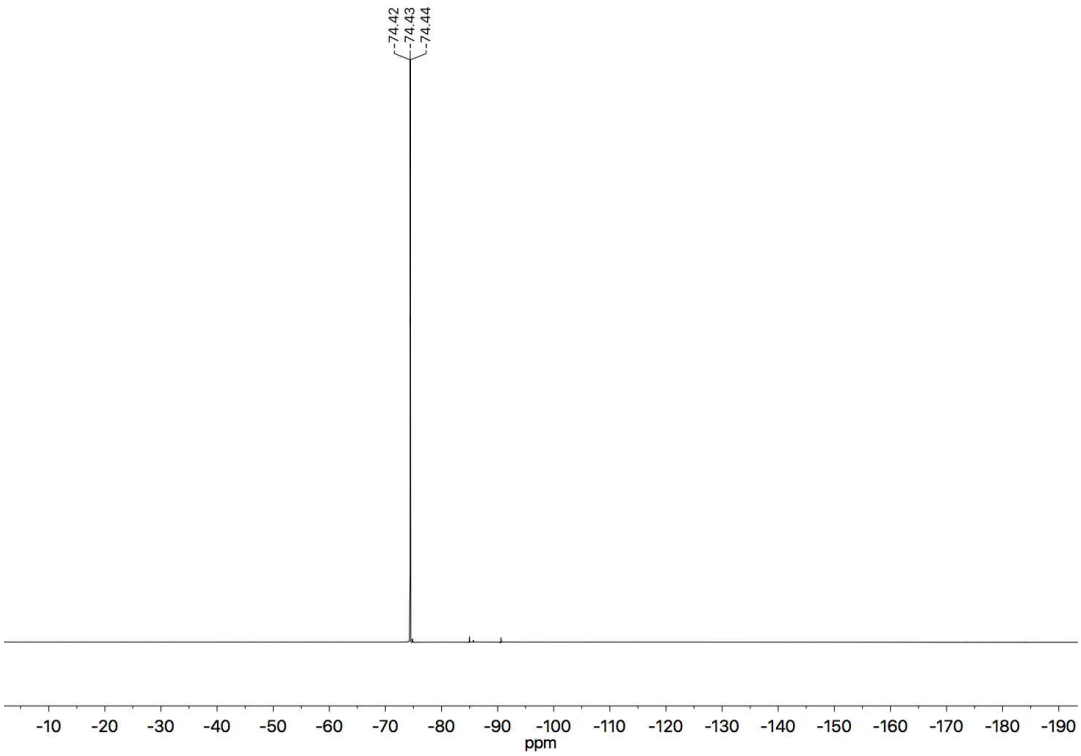
^{1}H NMR (500 MHz, $CDCl_3$) – **3a**

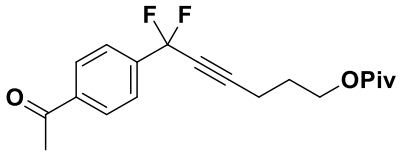


^{13}C NMR (126 MHz, $CDCl_3$) – **3a**

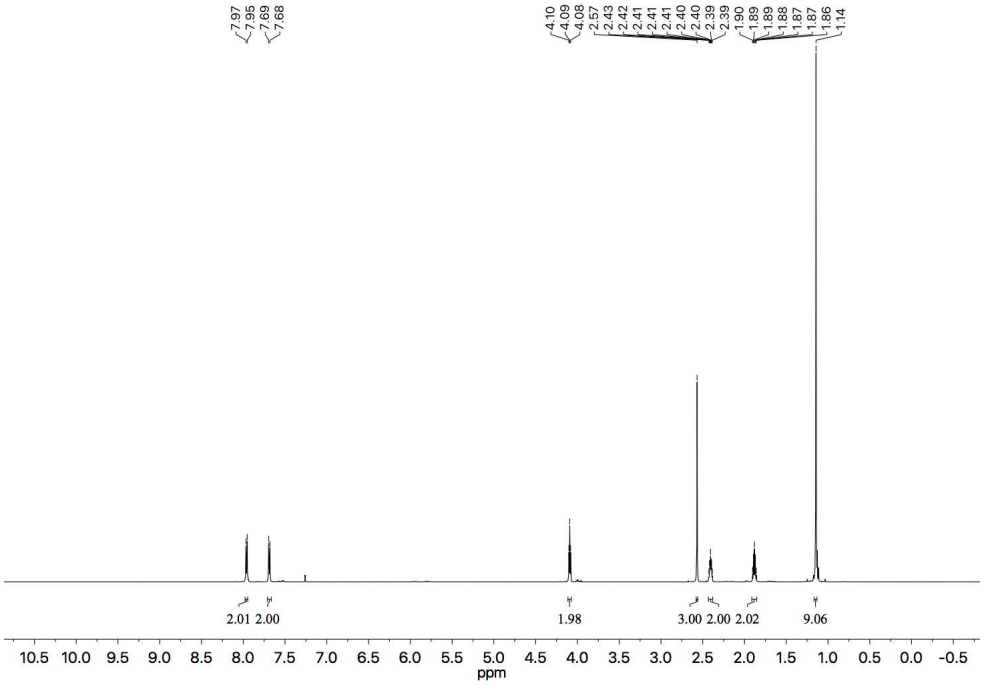


^{19}F NMR (470 MHz, $CDCl_3$) – **3a**

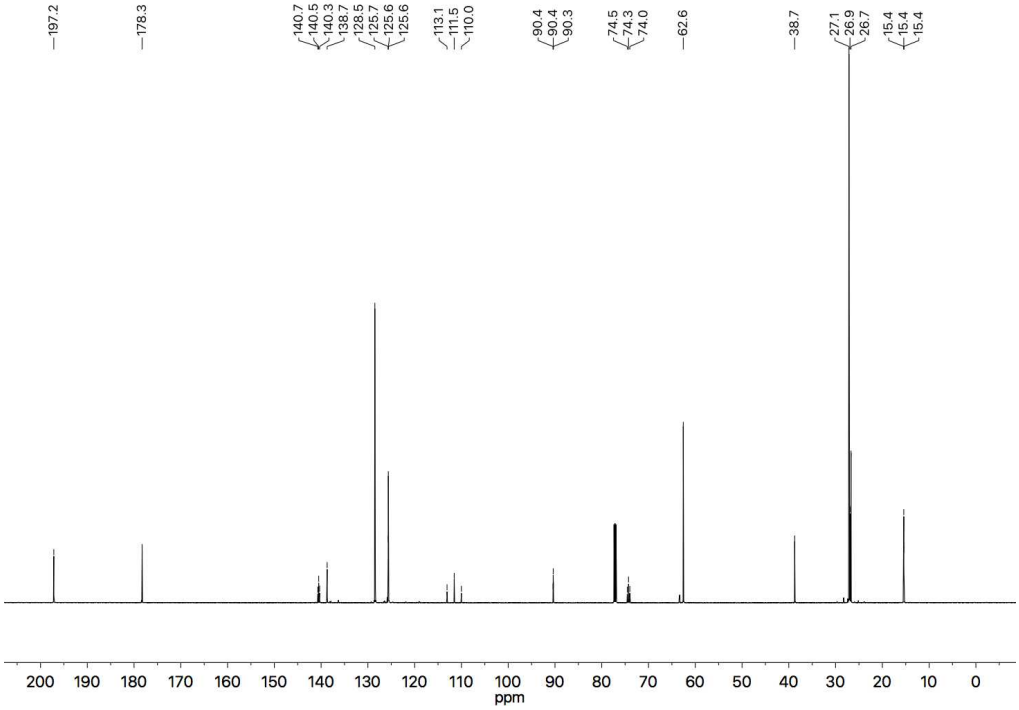




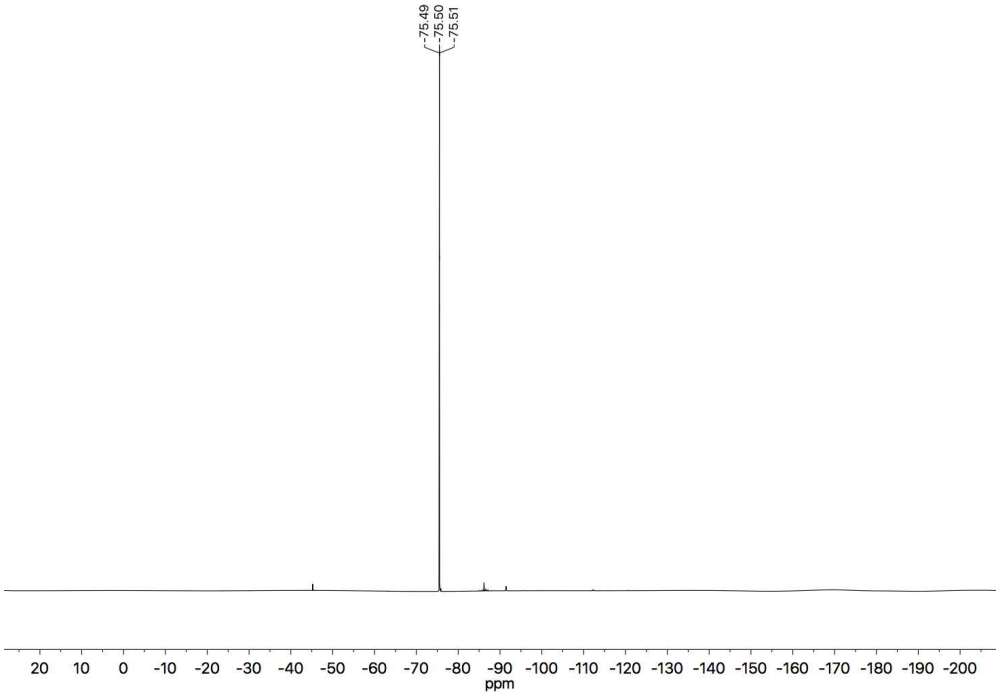
^{1}H NMR (600 MHz, $CDCl_3$) – **4a**

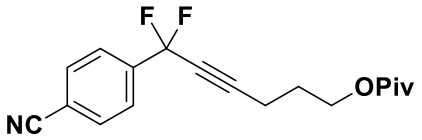


^{13}C NMR (151 MHz, $CDCl_3$) – **4a**

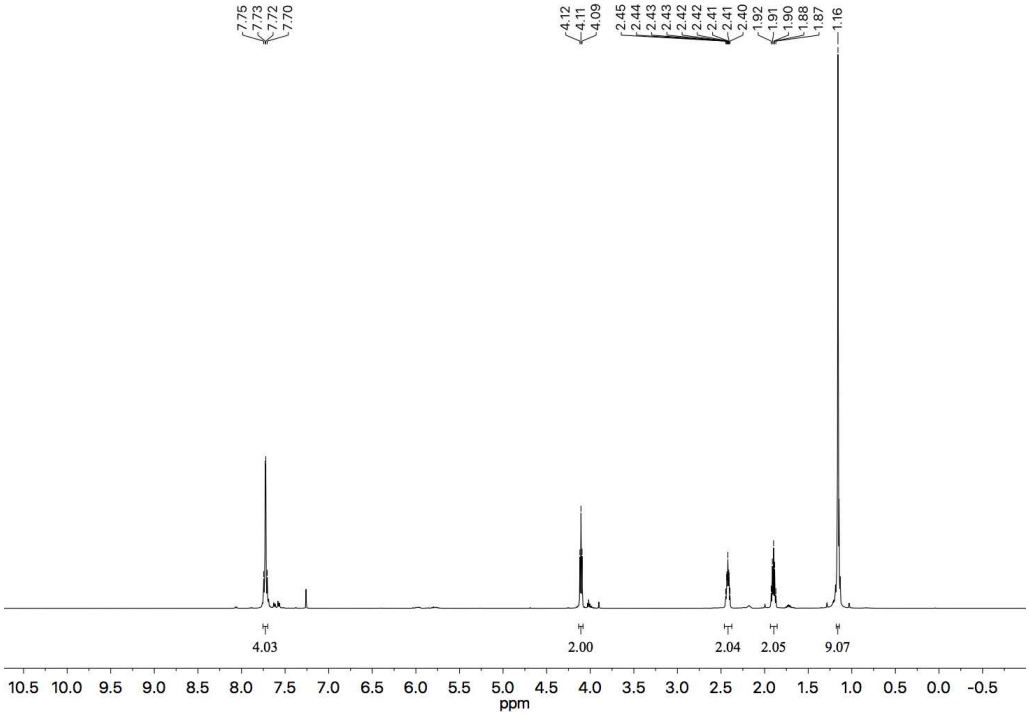


^{19}F NMR (565 MHz, $CDCl_3$) – **4a**

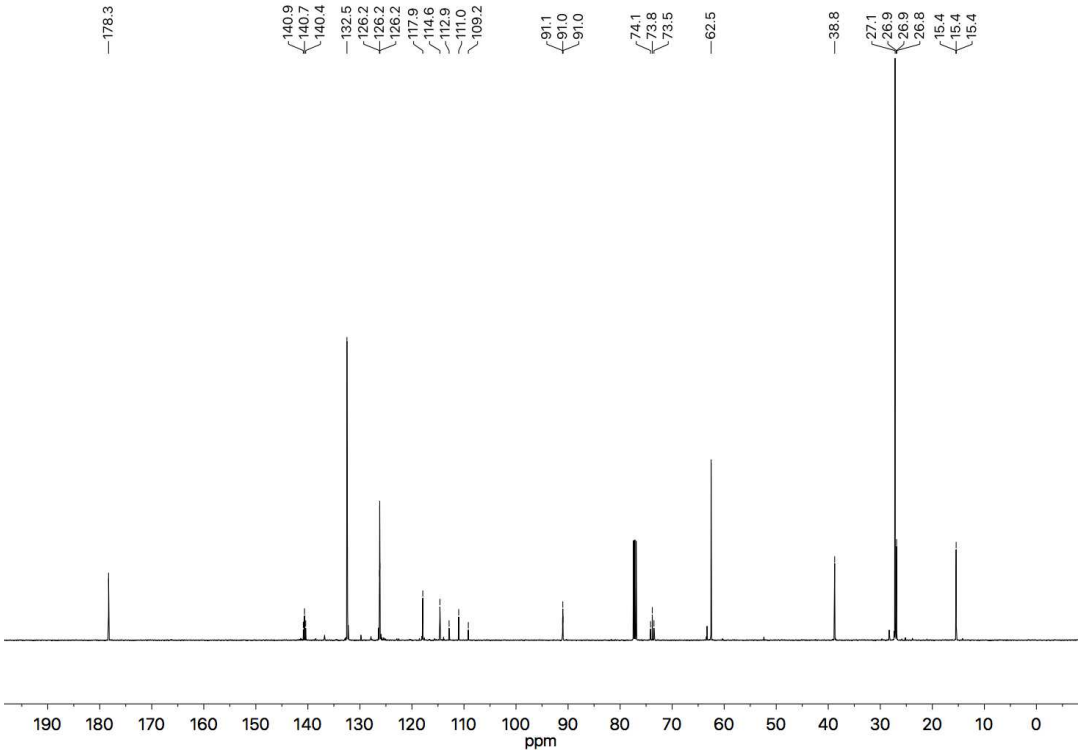




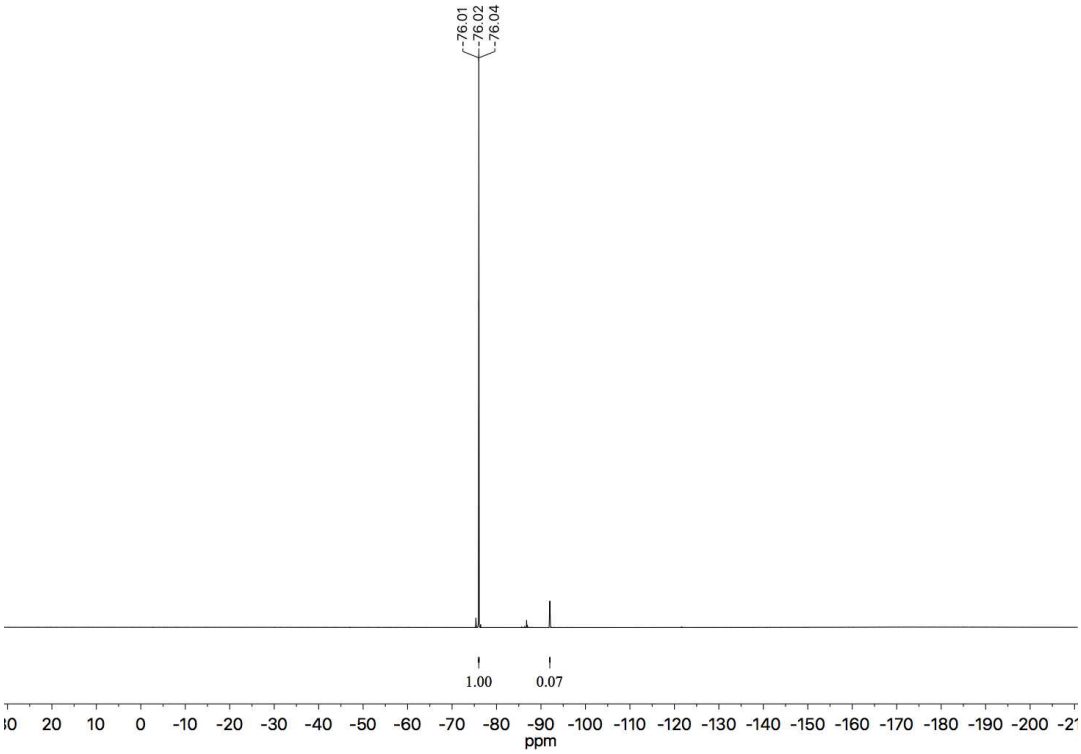
^{1}H NMR (500 MHz, $CDCl_3$) – **5a**

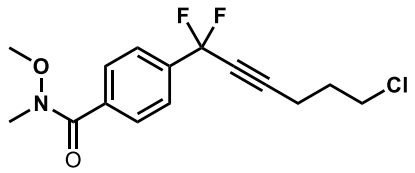


^{13}C NMR (126 MHz, $CDCl_3$) – **5a**

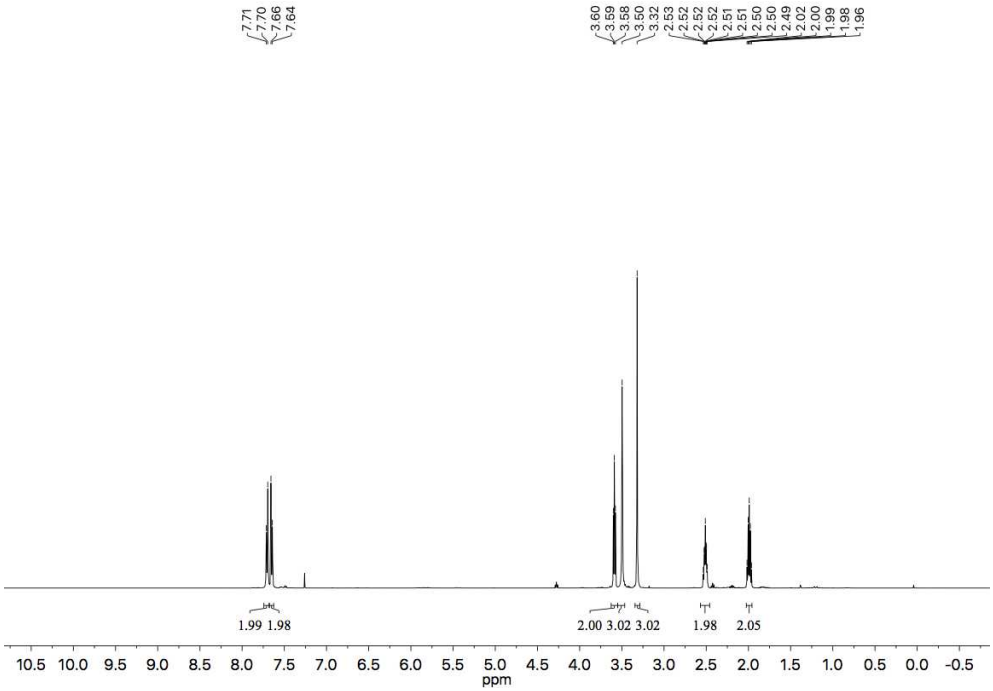


^{19}F NMR (470 MHz, $CDCl_3$) – **5a**

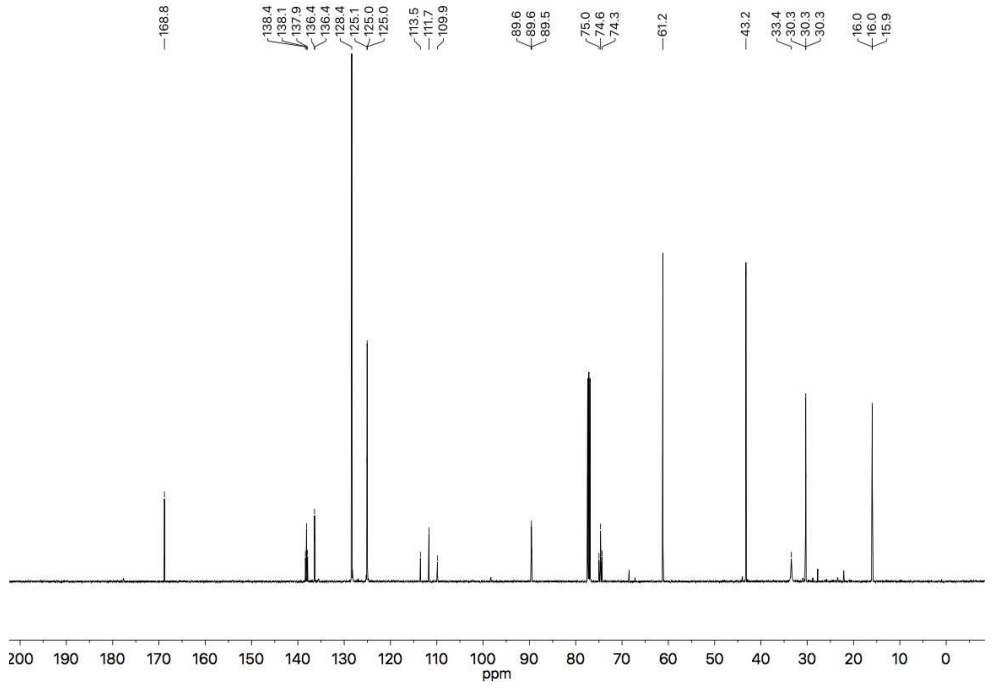




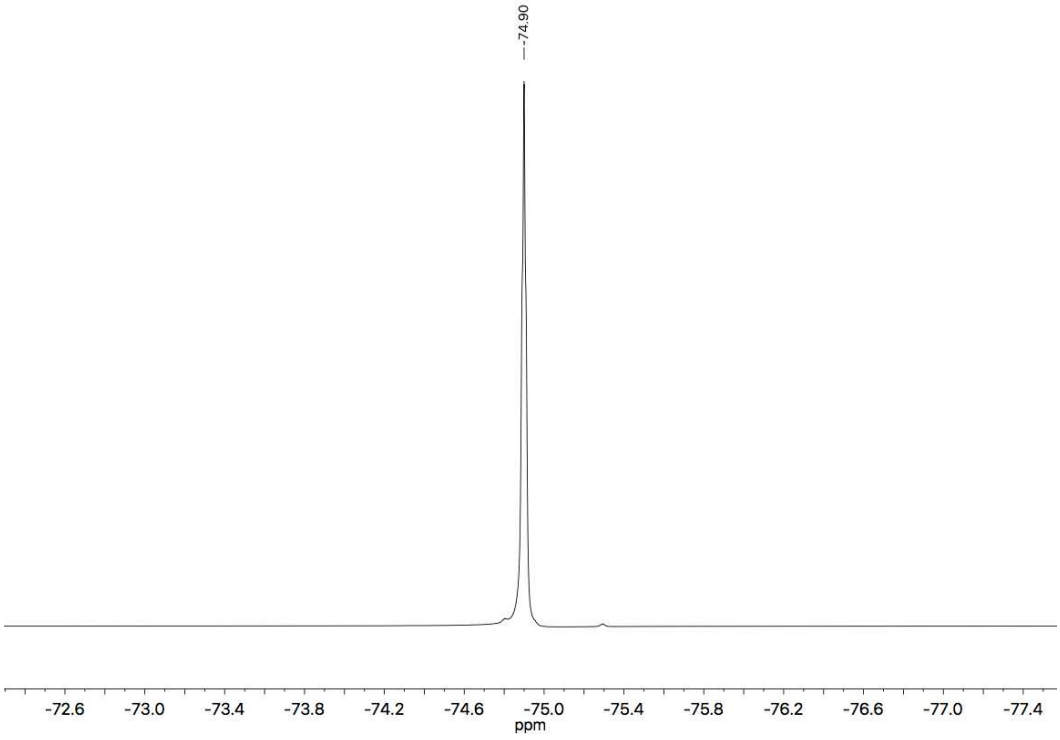
^{1}H NMR (500MHz, $CDCl_3$) – **6a**

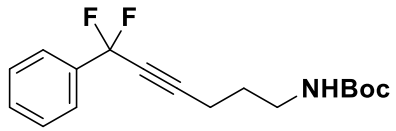


^{13}C NMR (126 MHz, $CDCl_3$) – **6a**

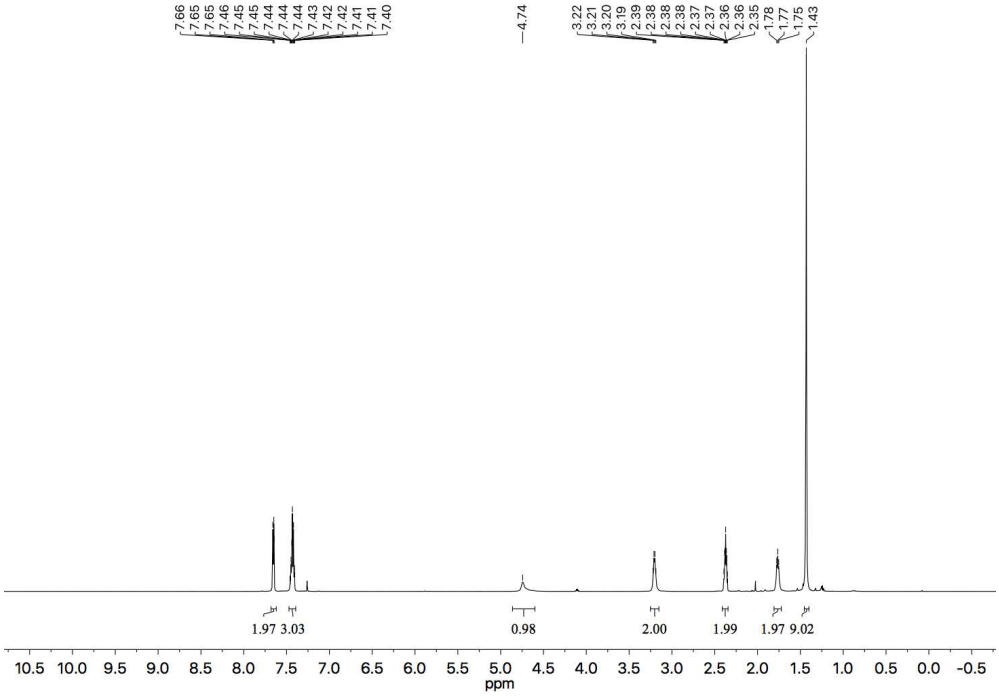


^{19}F NMR (470 MHz, $CDCl_3$) – **6a**

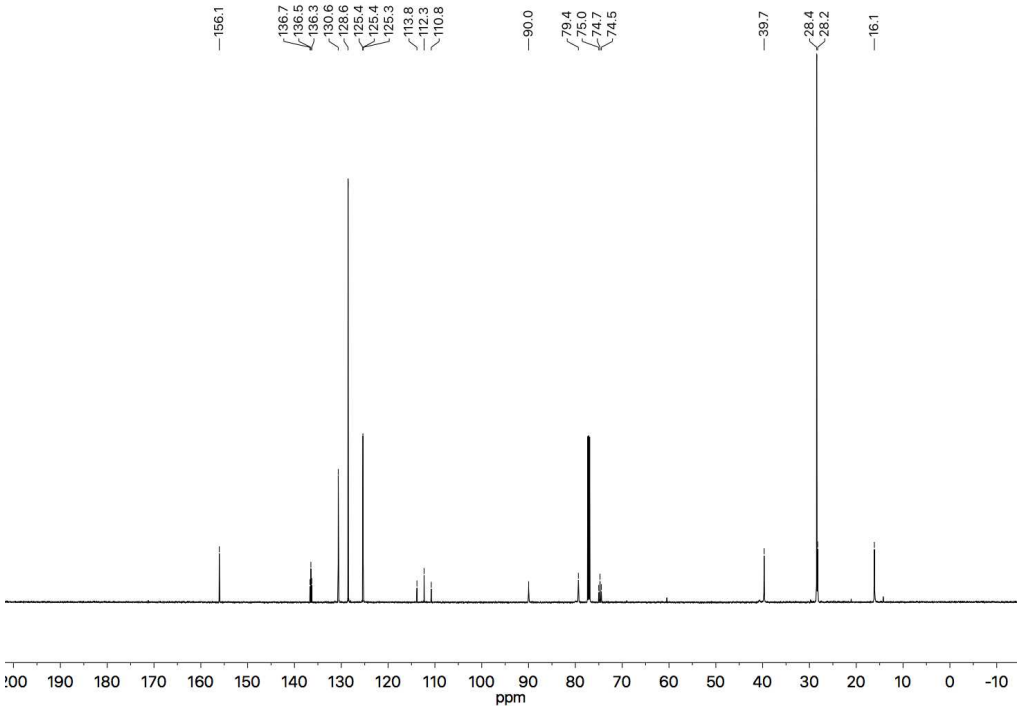




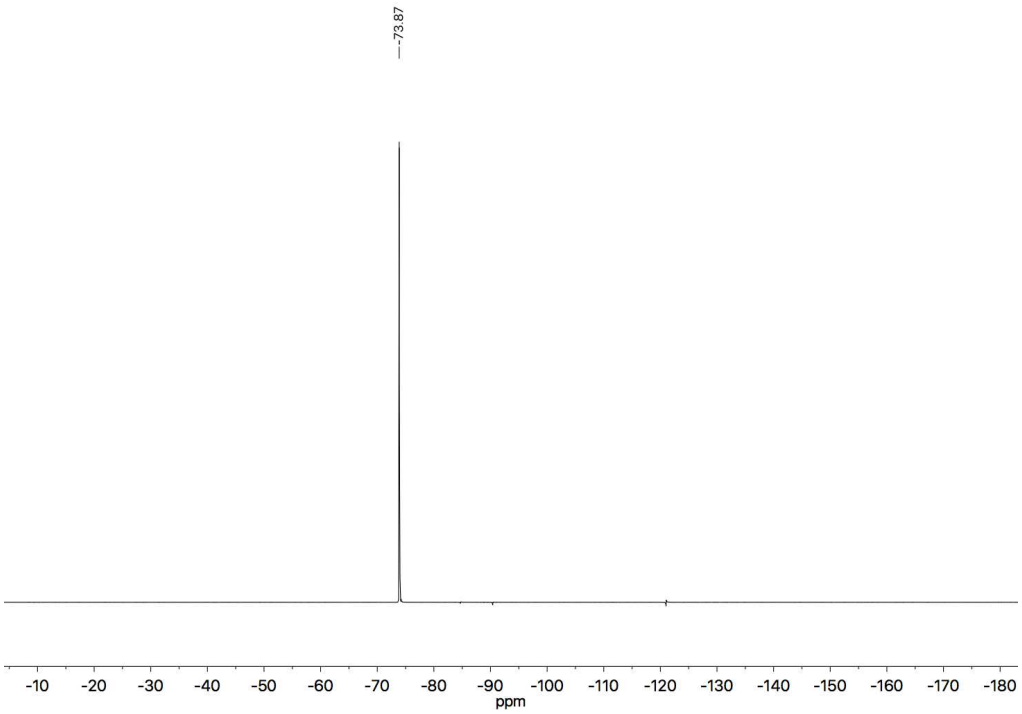
^{1}H NMR (600 MHz, $CDCl_3$) – **7a**

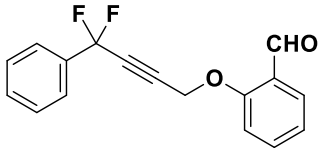


^{13}C NMR (151 MHz, $CDCl_3$) – **7a**

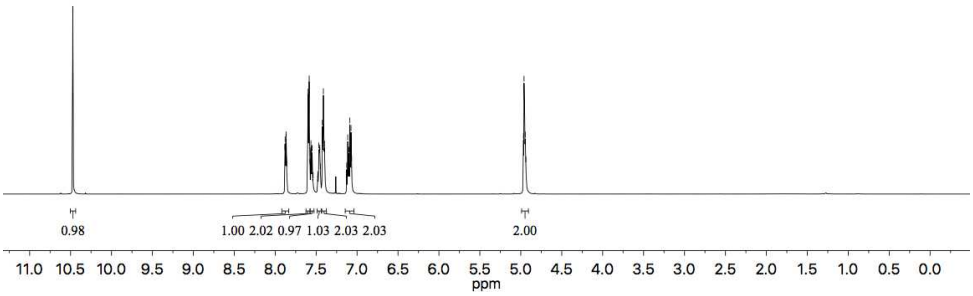


^{19}F NMR (565 MHz, $CDCl_3$) – **7a**

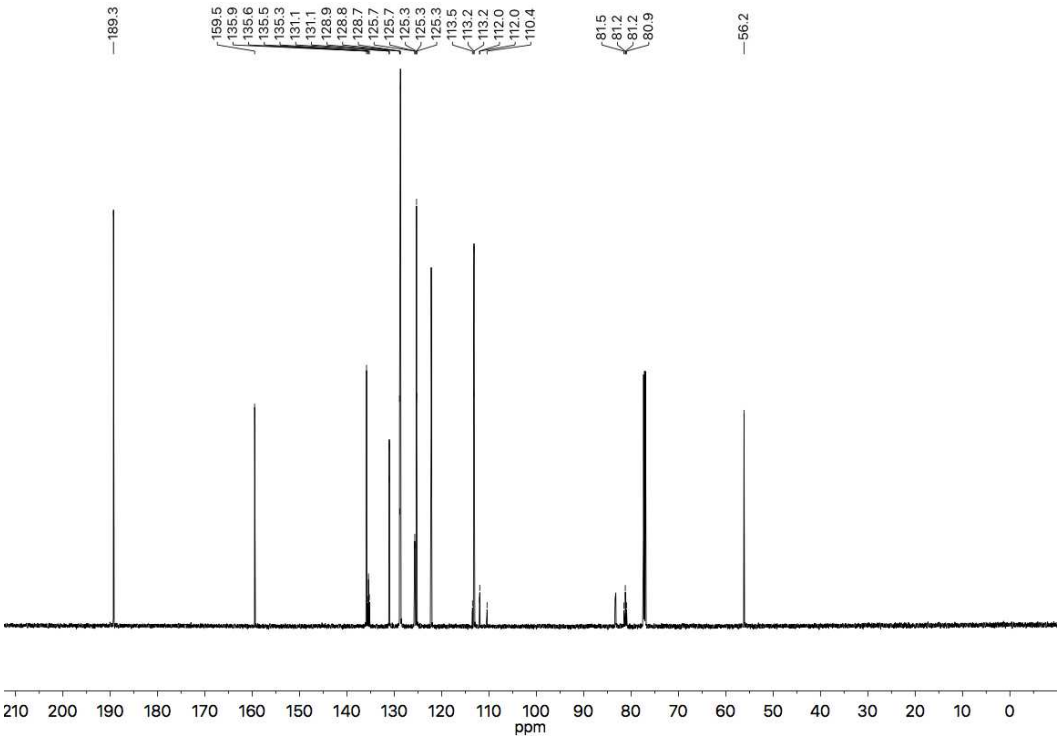




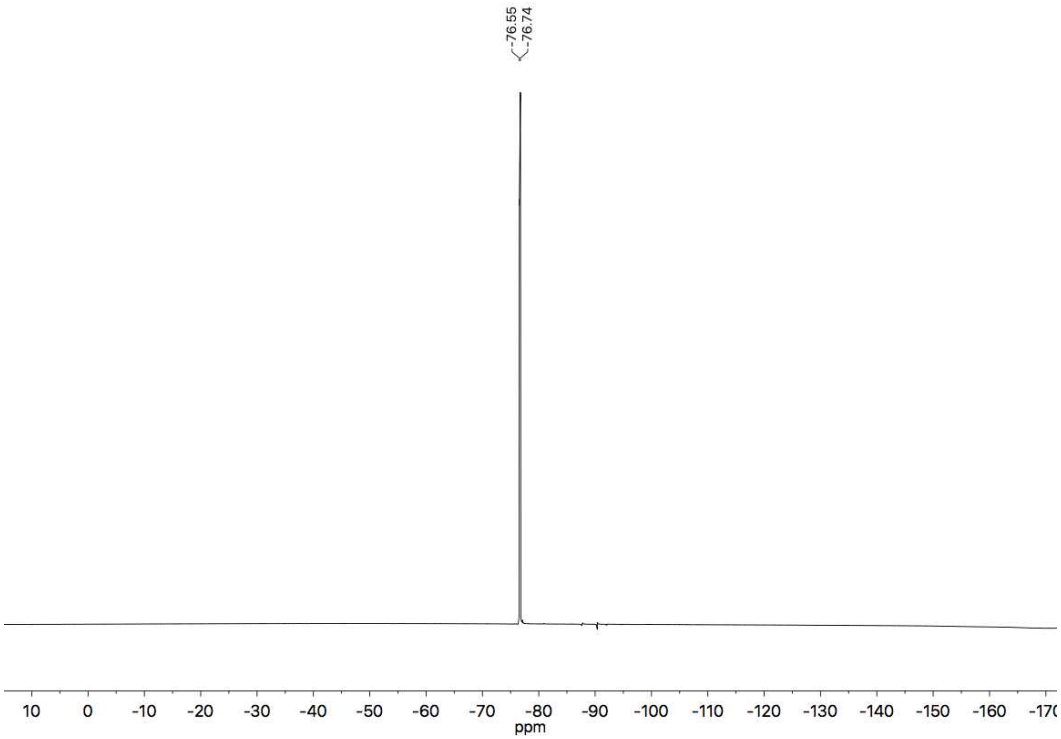
^{1}H NMR (600 MHz, $CDCl_3$) – **8a**

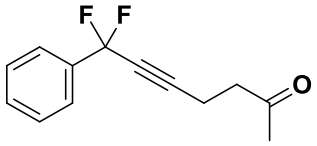


^{13}C NMR (151 MHz, $CDCl_3$) – **8a**

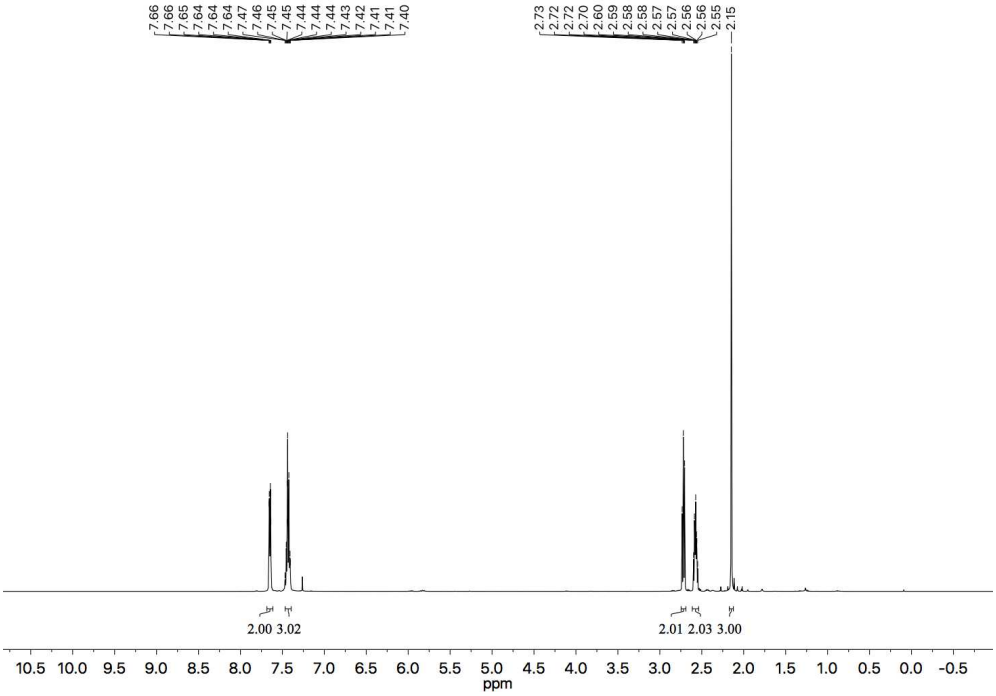


^{19}F NMR (565 MHz, $CDCl_3$) – **8a**

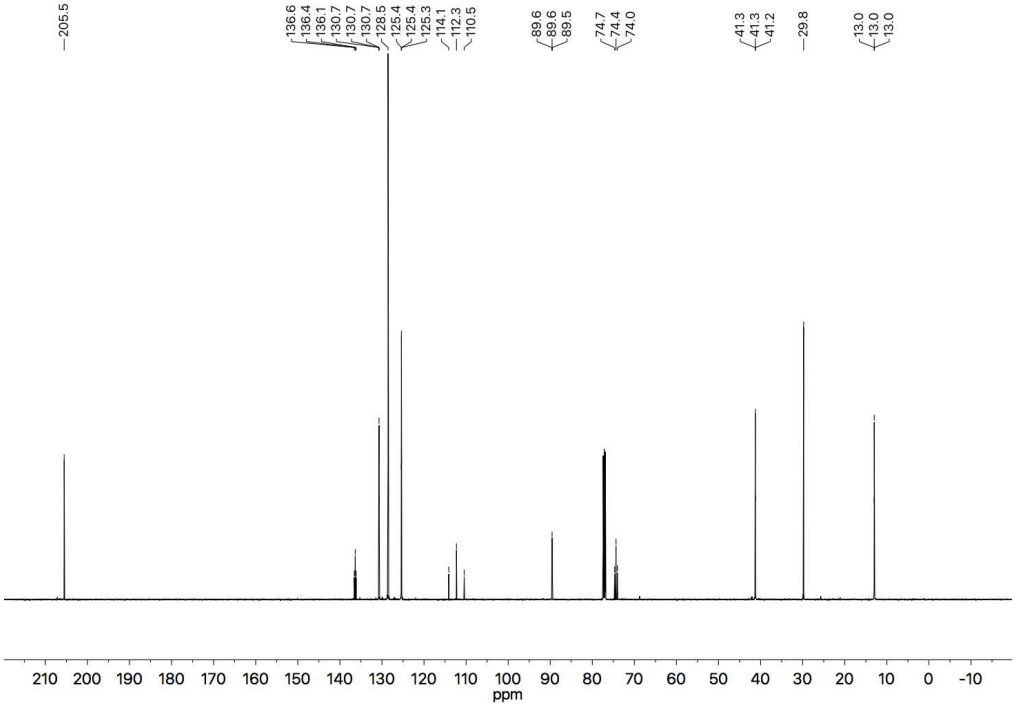




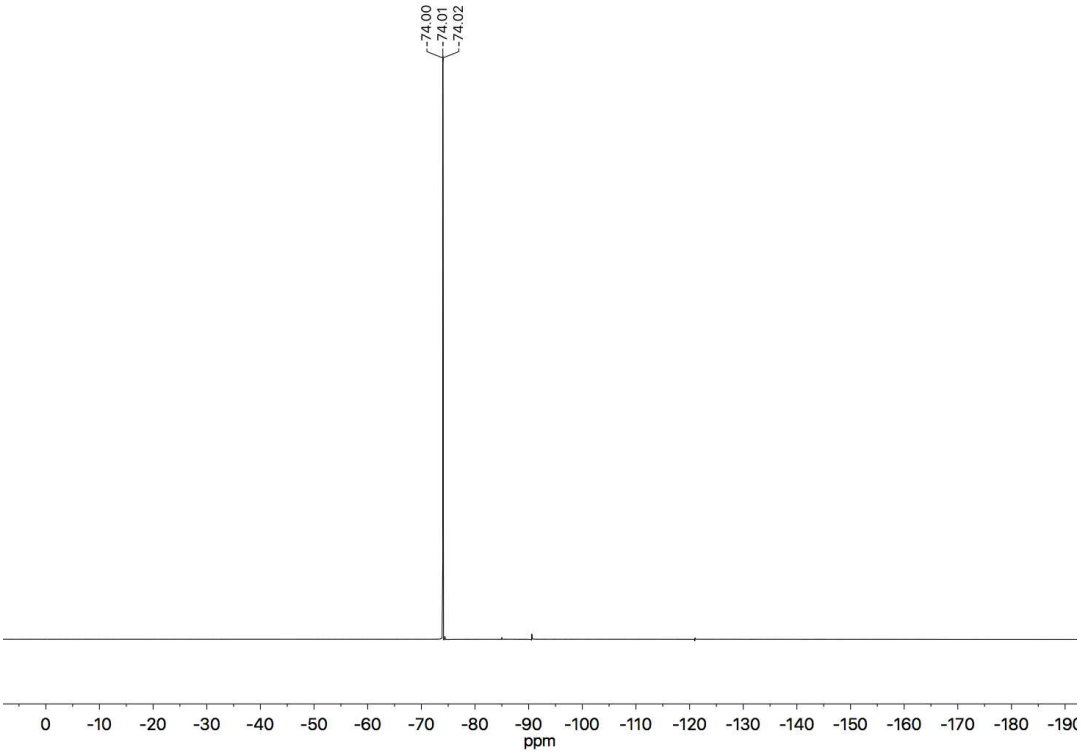
^{1}H NMR (500 MHz, $CDCl_3$) – **9a**

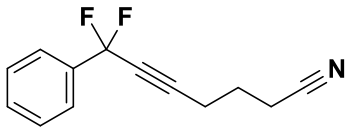


^{13}C NMR (126 MHz, $CDCl_3$) – **9a**

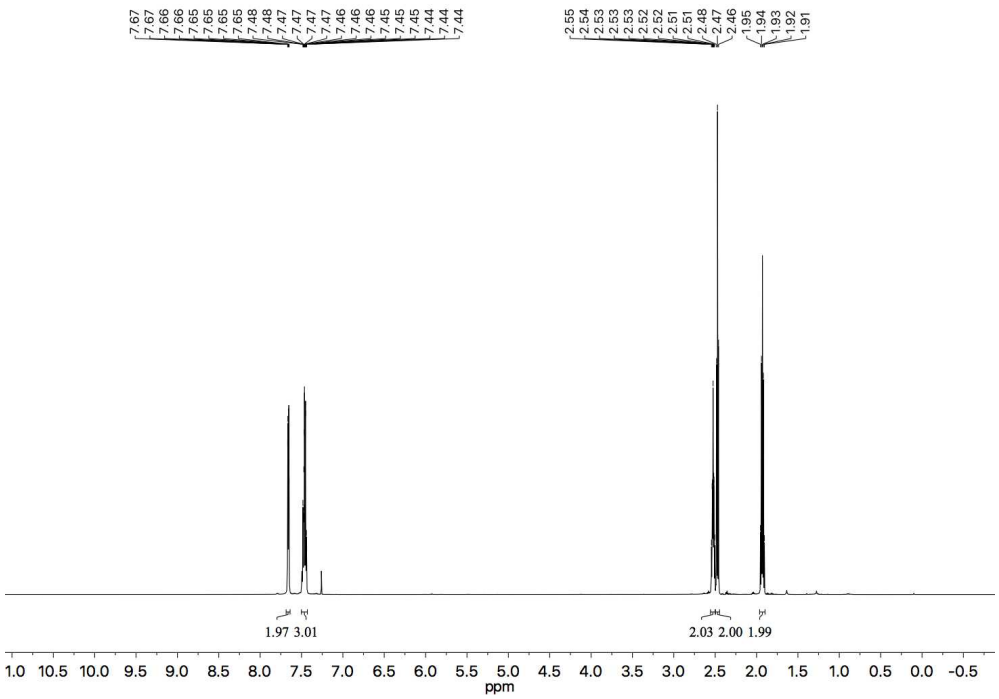


^{19}F NMR (470 MHz, $CDCl_3$) – **9a**

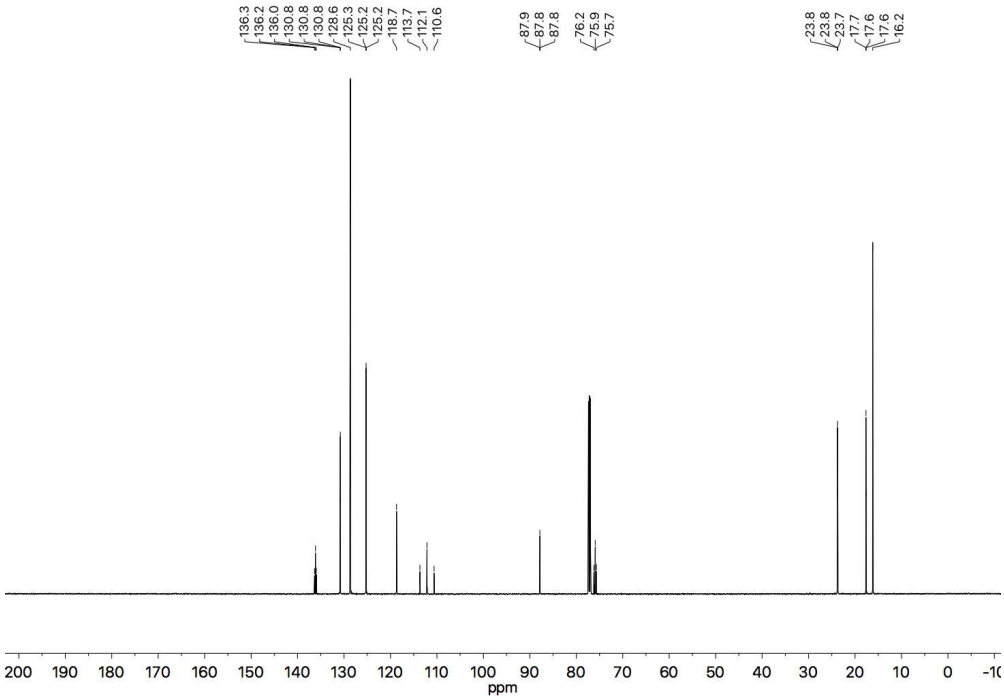




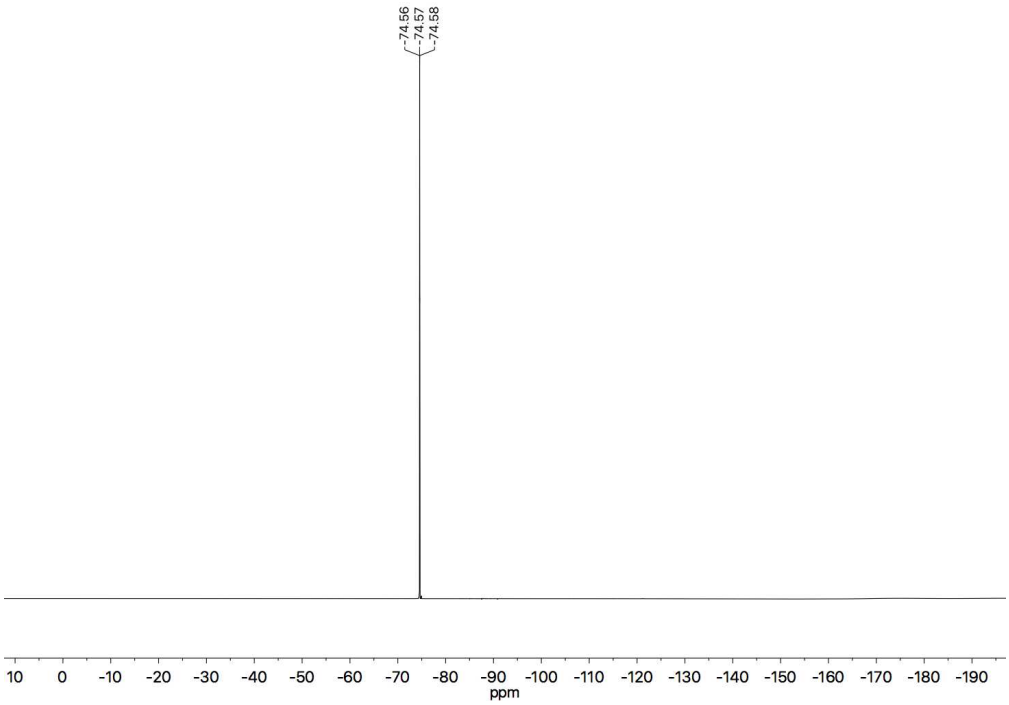
^{1}H NMR (600 MHz, $CDCl_3$) – **10a**

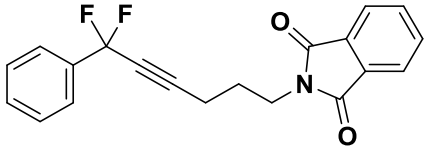


^{13}C NMR (151 MHz, $CDCl_3$) – **10a**

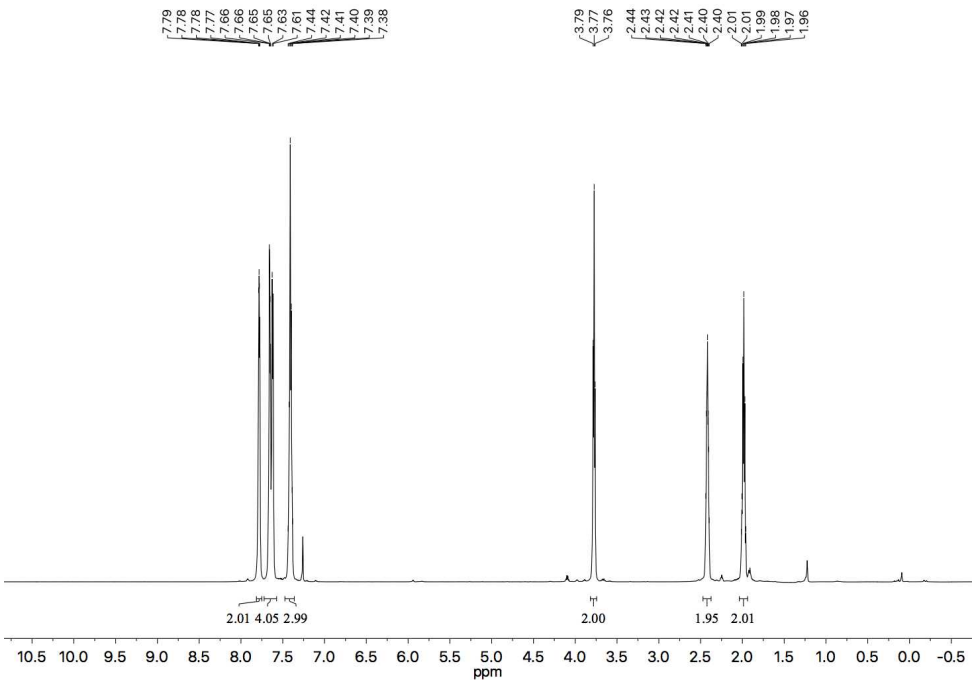


^{19}F NMR (565 MHz, $CDCl_3$) – **10a**

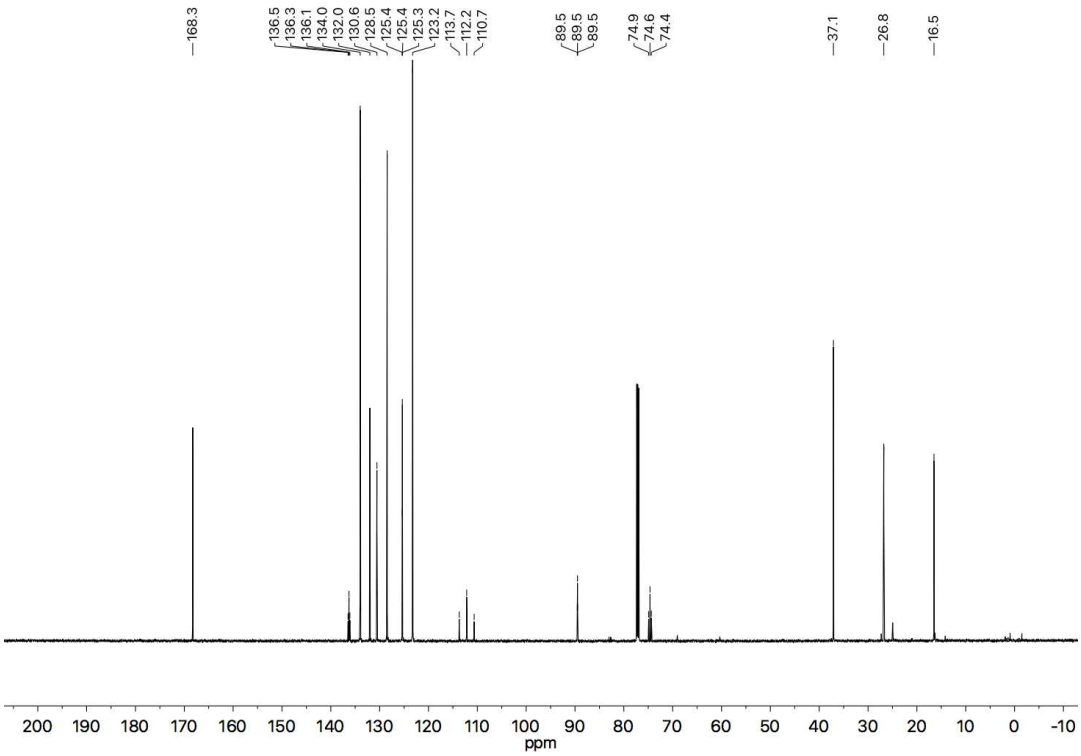




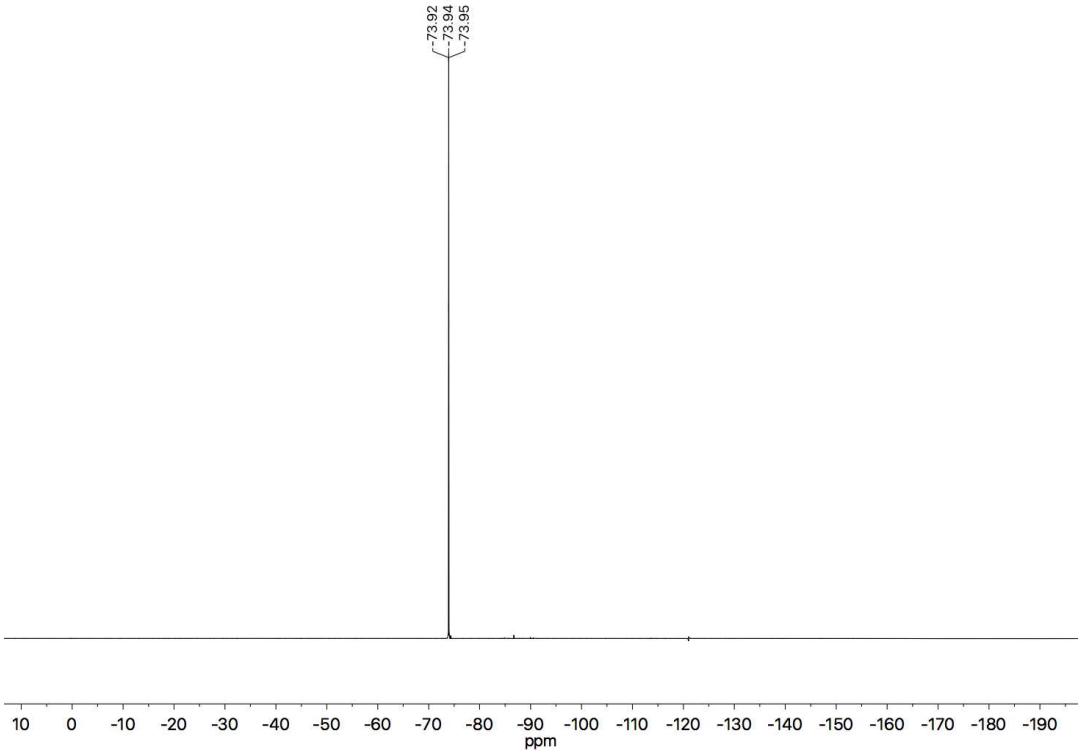
^{1}H NMR (600 MHz, $CDCl_3$) – **11a**

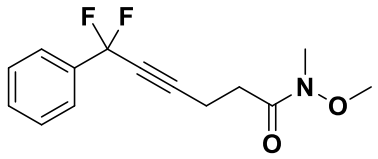


^{13}C NMR (151 MHz, $CDCl_3$) – **11a**

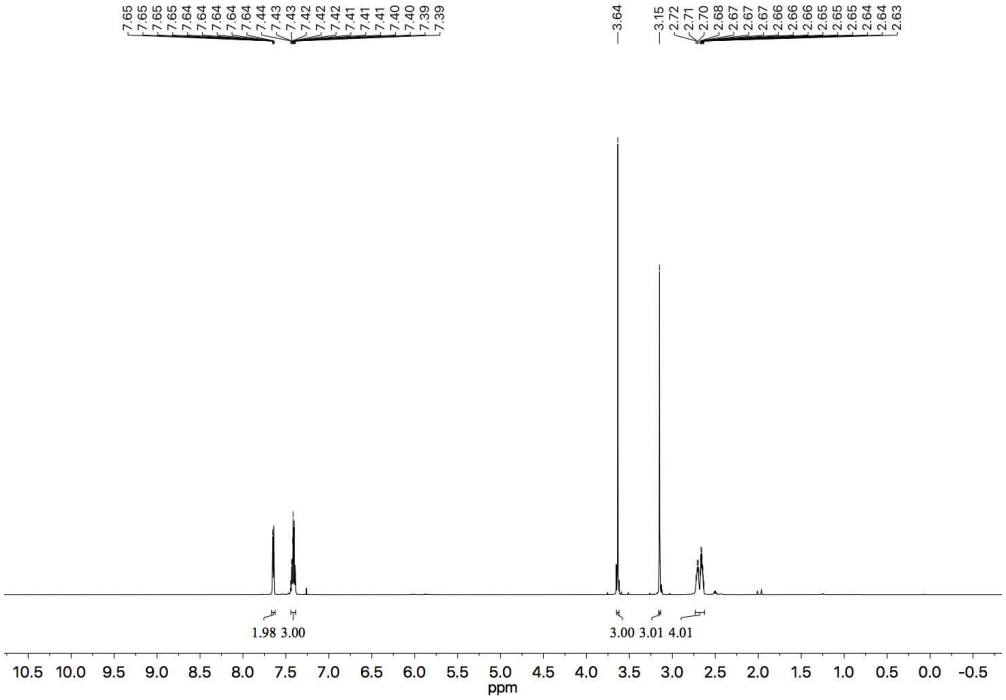


^{19}F NMR (470 MHz, $CDCl_3$) – **11a**

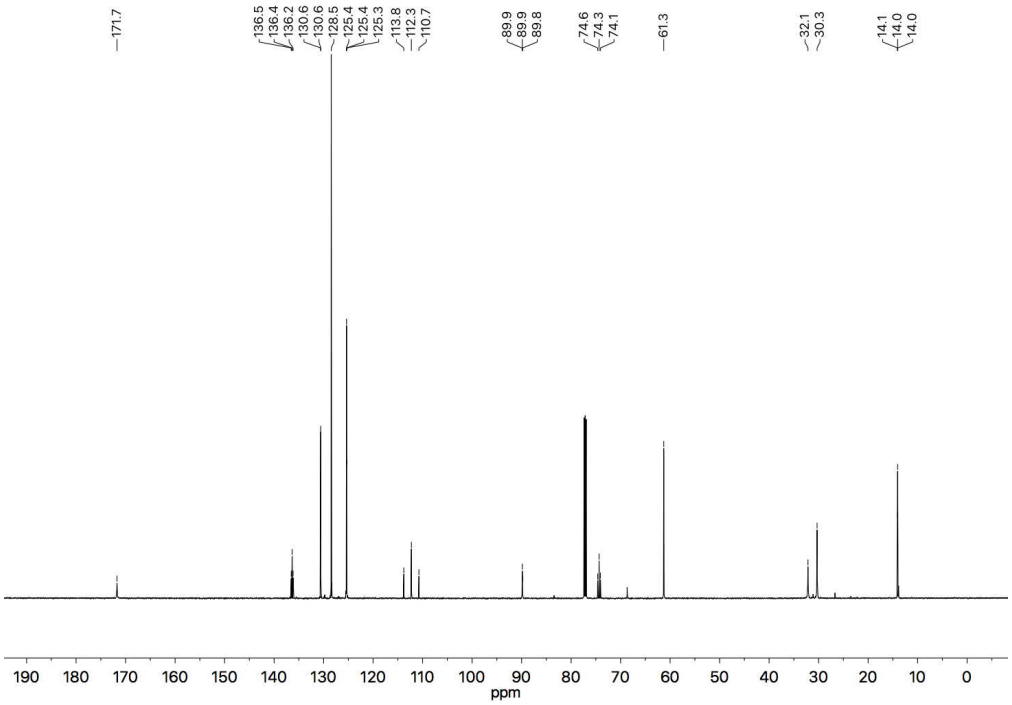




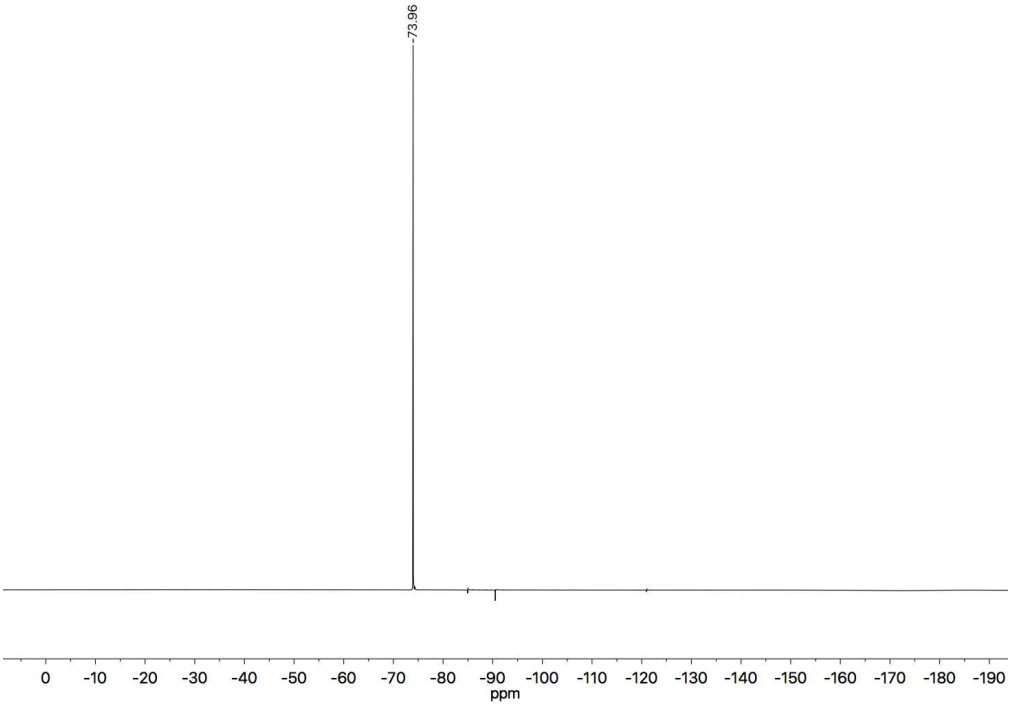
^{1}H NMR (600 MHz, $CDCl_3$) – **12a**

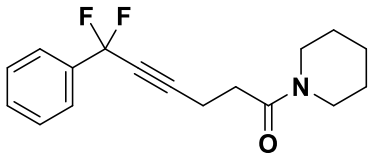


^{13}C NMR (151 MHz, $CDCl_3$) –**12a**

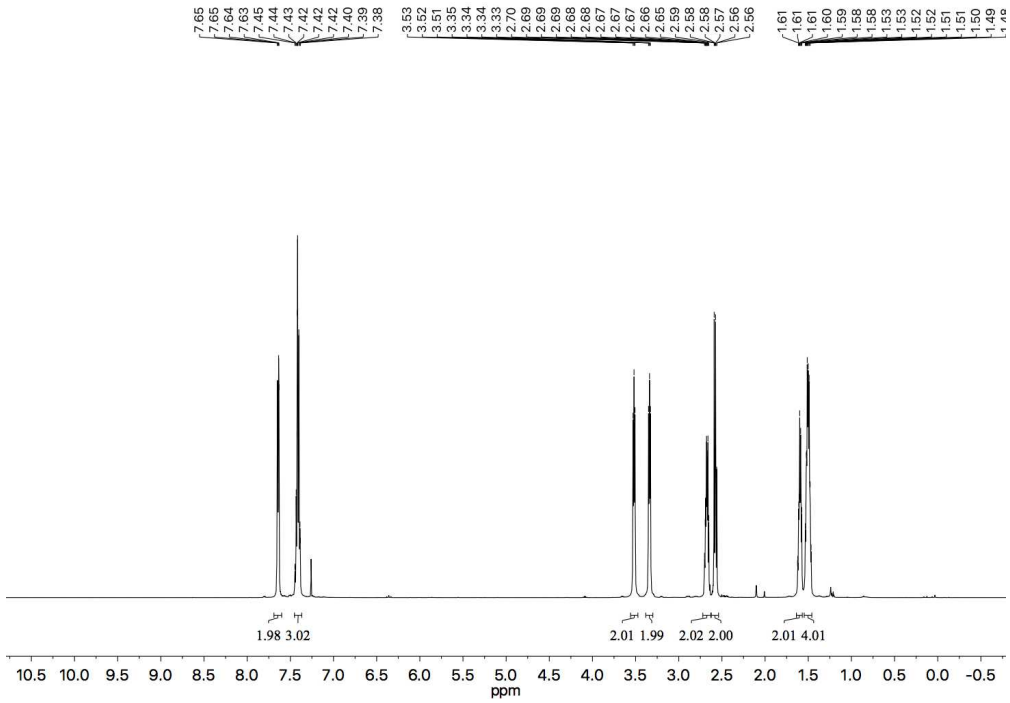


^{19}F NMR (565 MHz, $CDCl_3$) – **12a**

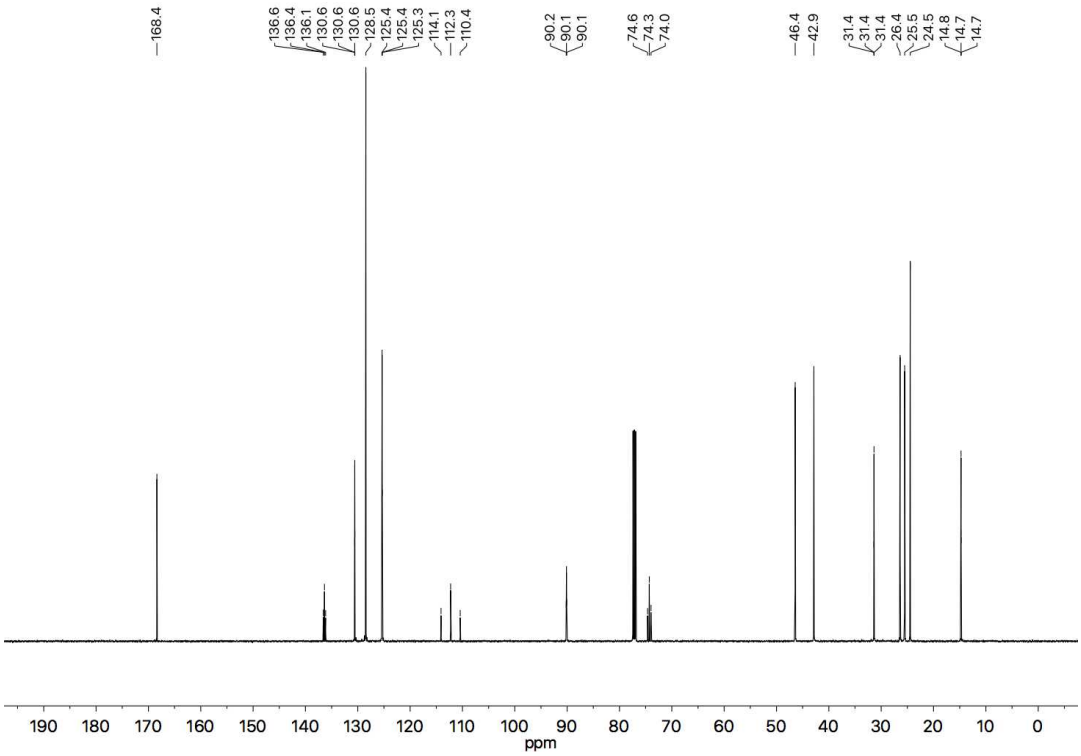




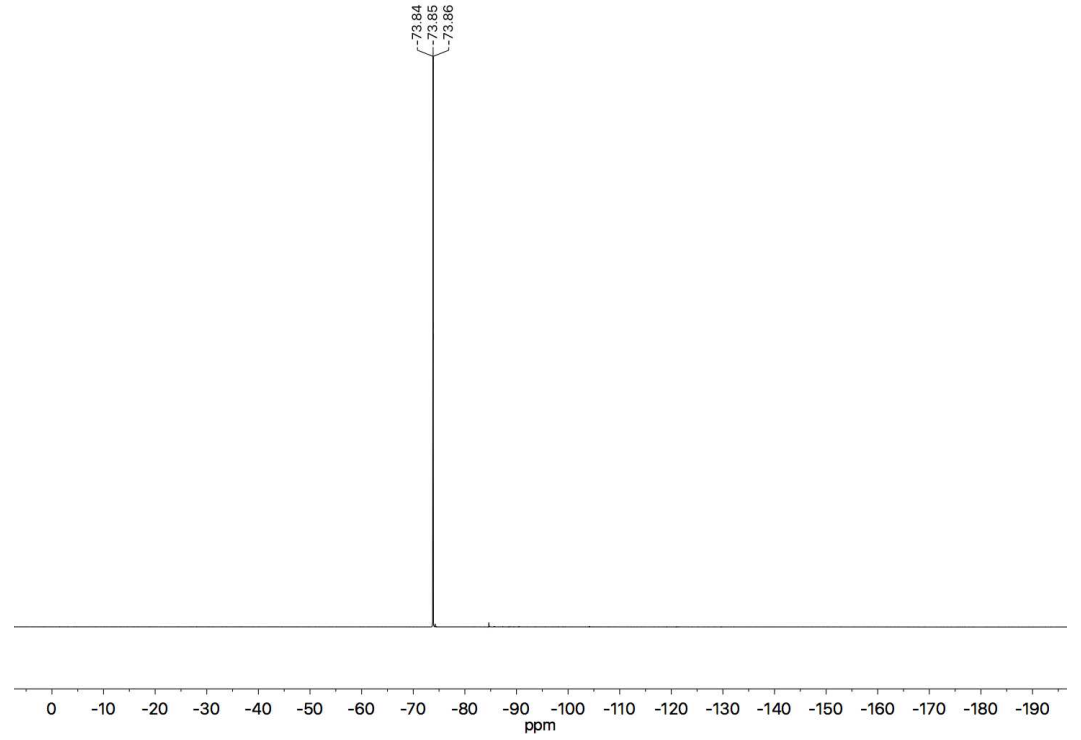
^{1}H NMR (500 MHz, $CDCl_3$) – **13a**

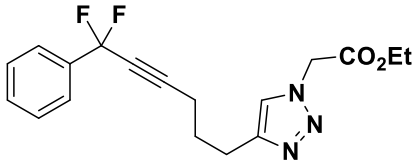


^{13}C NMR (126 MHz, $CDCl_3$) – **13a**

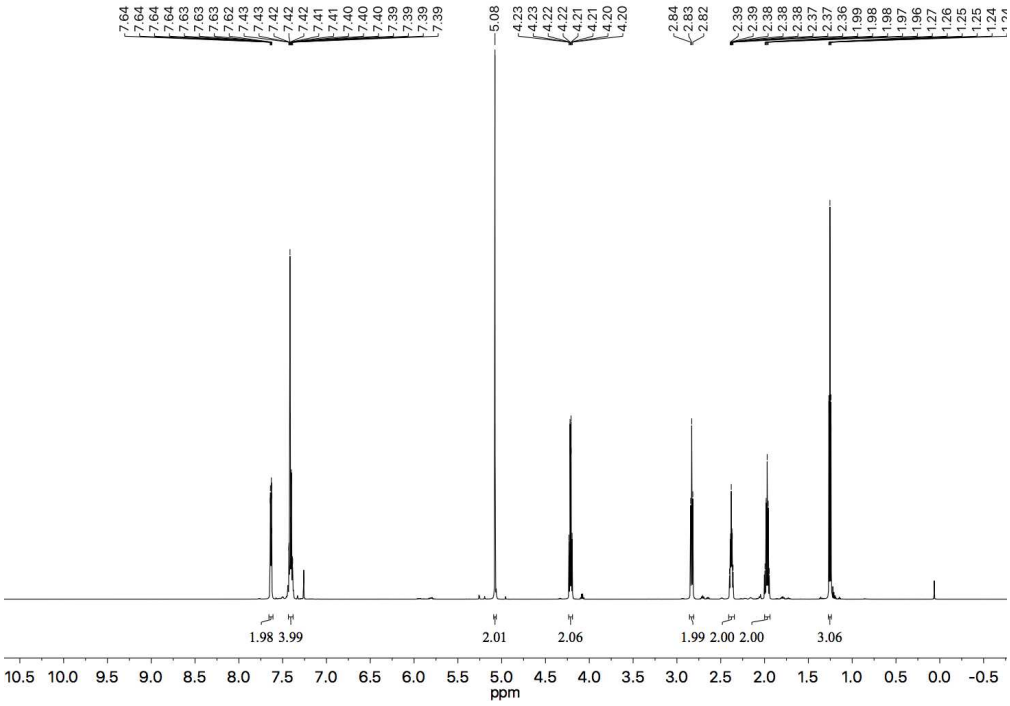


^{19}F NMR (470 MHz, $CDCl_3$) – **13a**

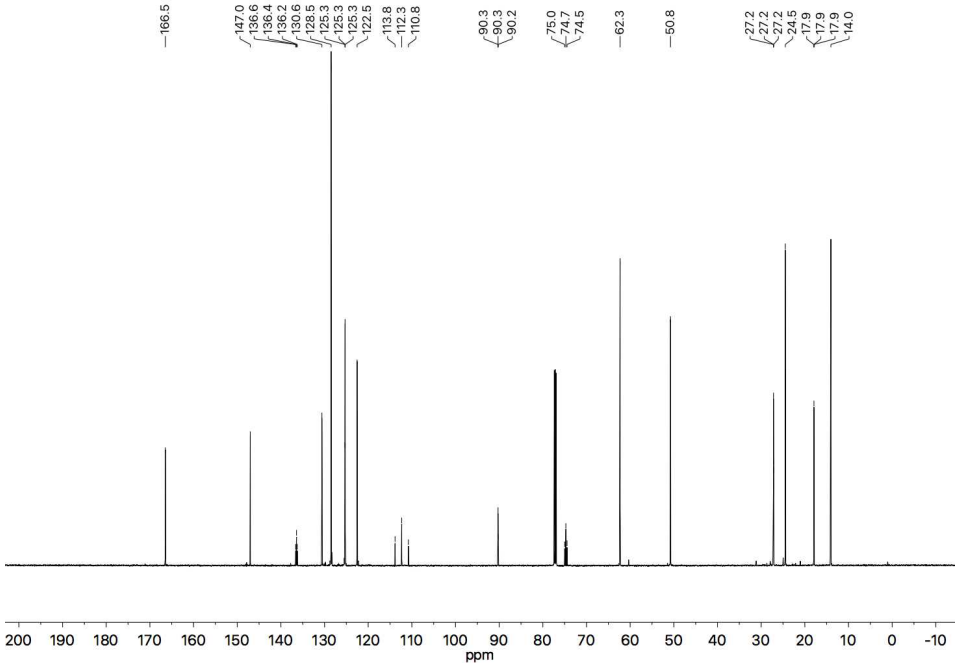




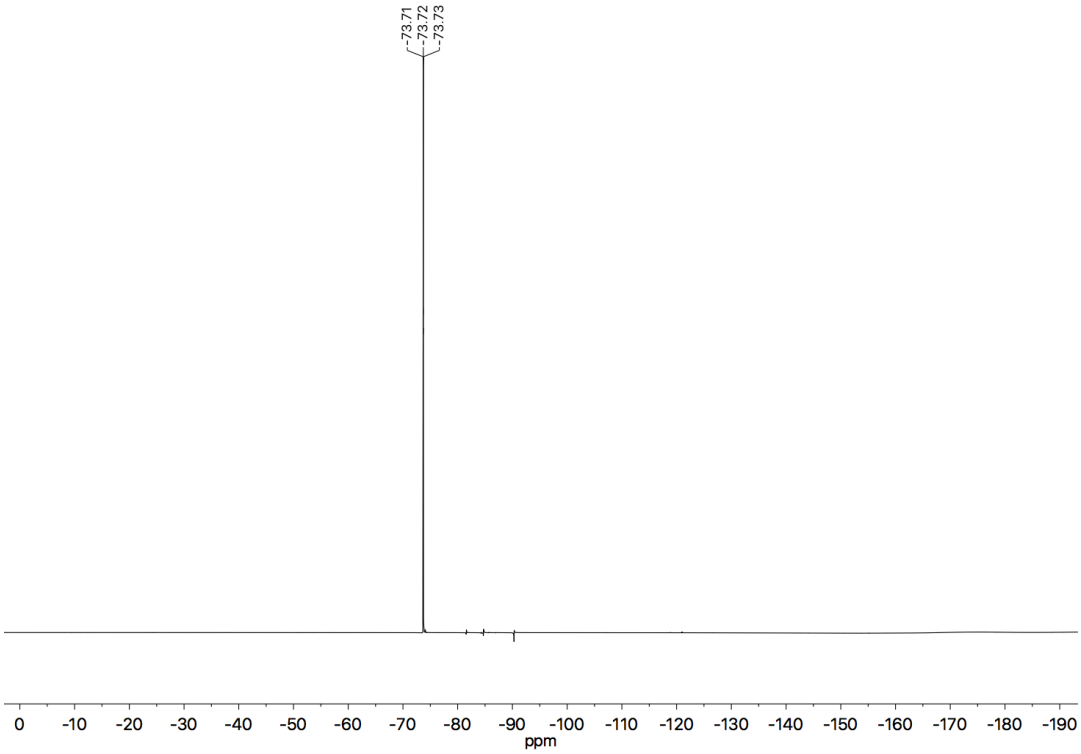
^{1}H NMR (600 MHz, $CDCl_3$) – **14a**

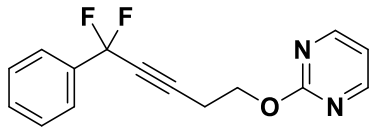


^{13}C NMR (151 MHz, $CDCl_3$) – **14a**

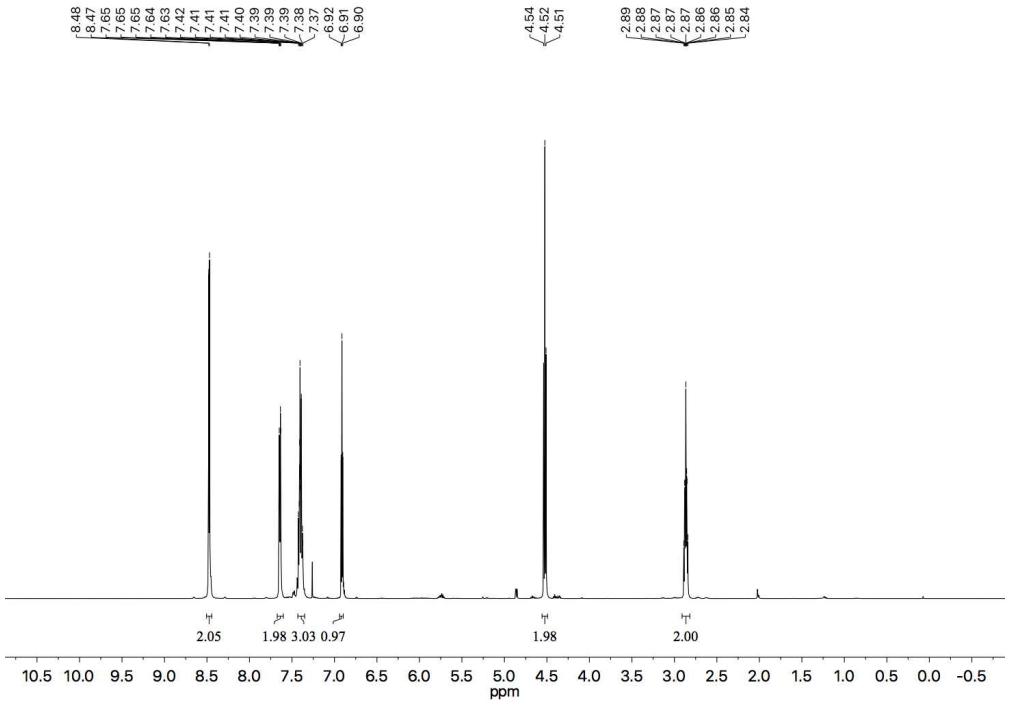


^{19}F NMR (565 MHz, $CDCl_3$) – **14a**

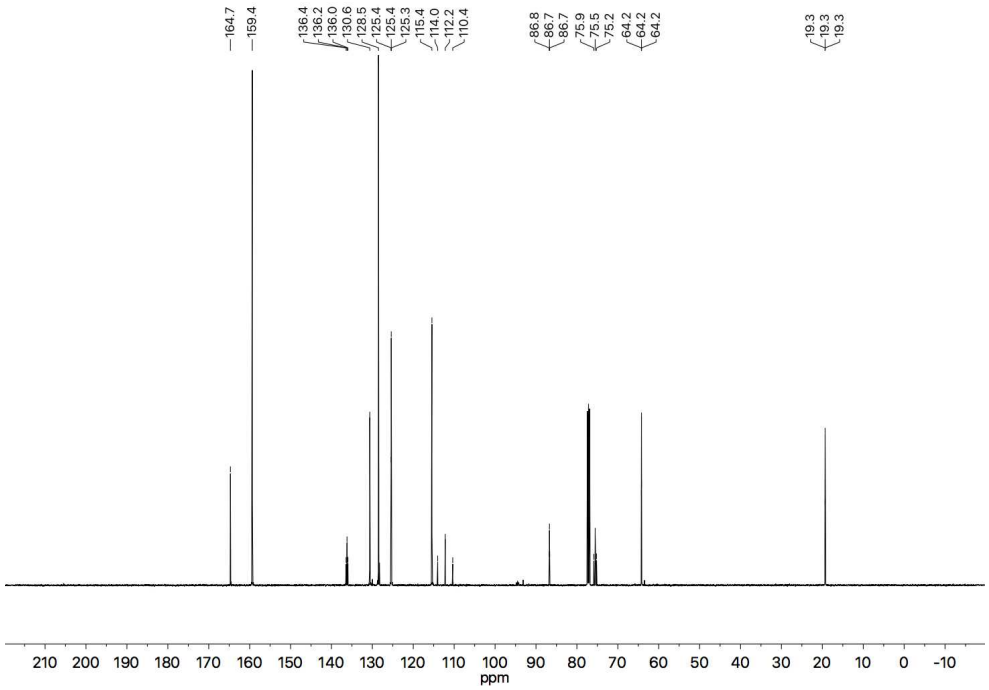




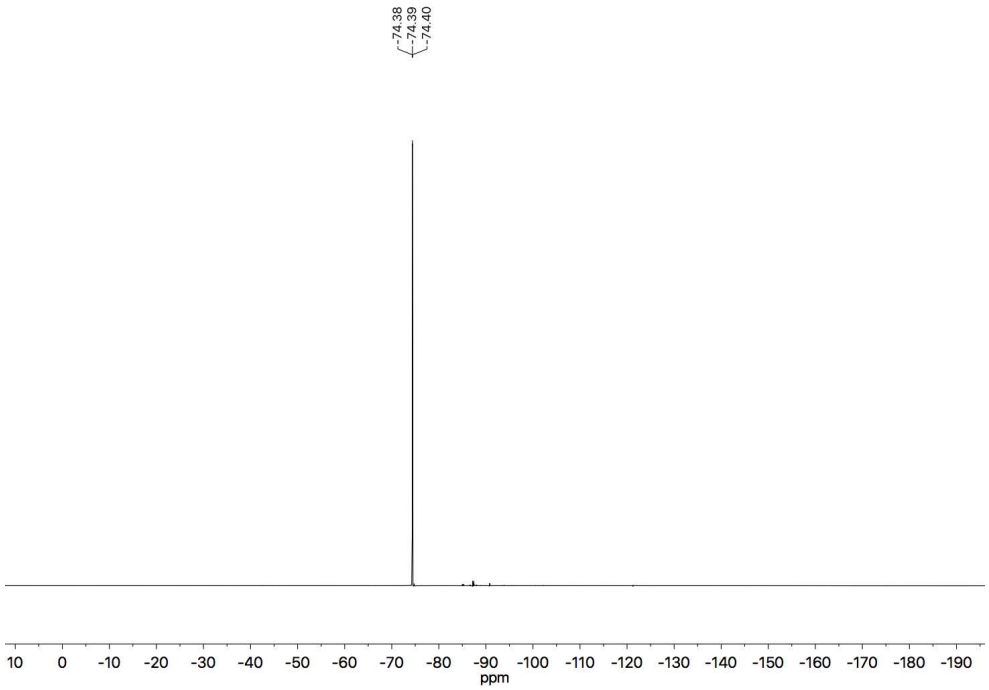
^{1}H NMR (500 MHz, $CDCl_3$) – **15a**



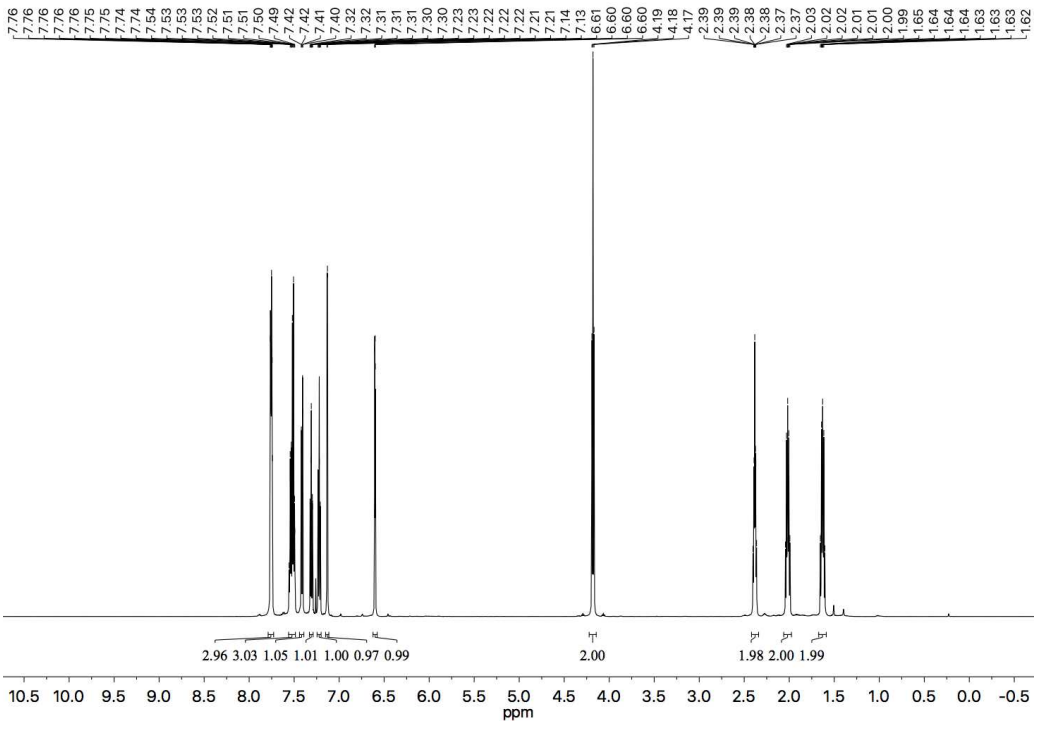
^{13}C NMR (126 MHz, $CDCl_3$) – **15a**



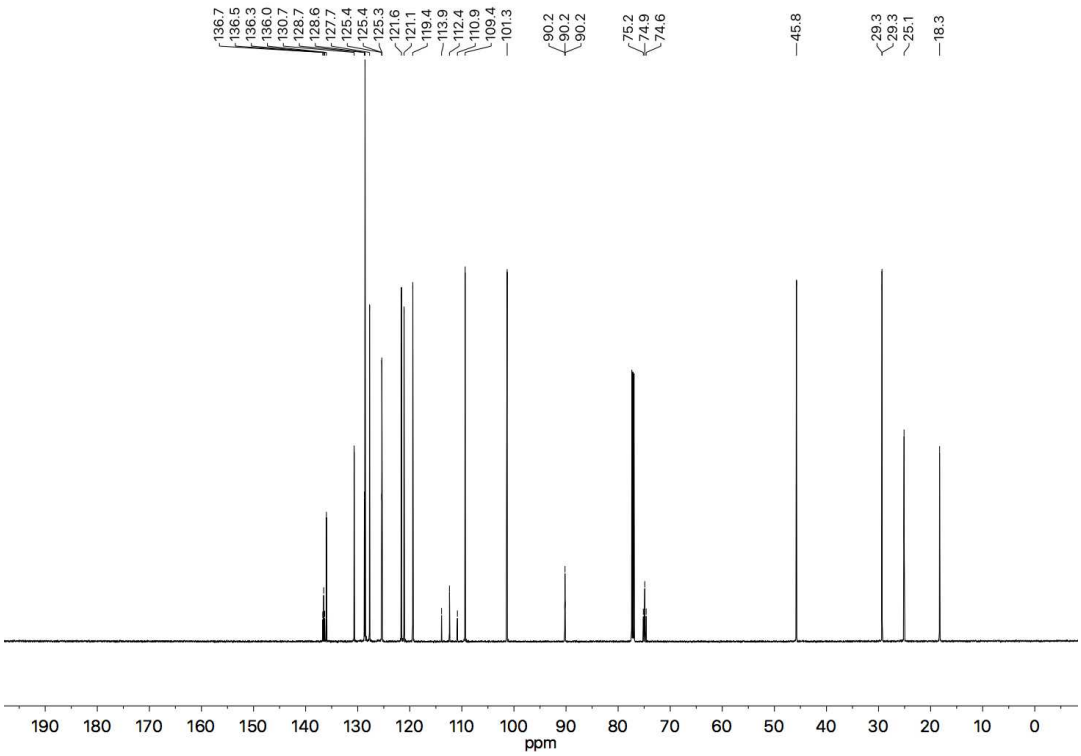
^{19}F NMR (470 MHz, $CDCl_3$) – **15a**



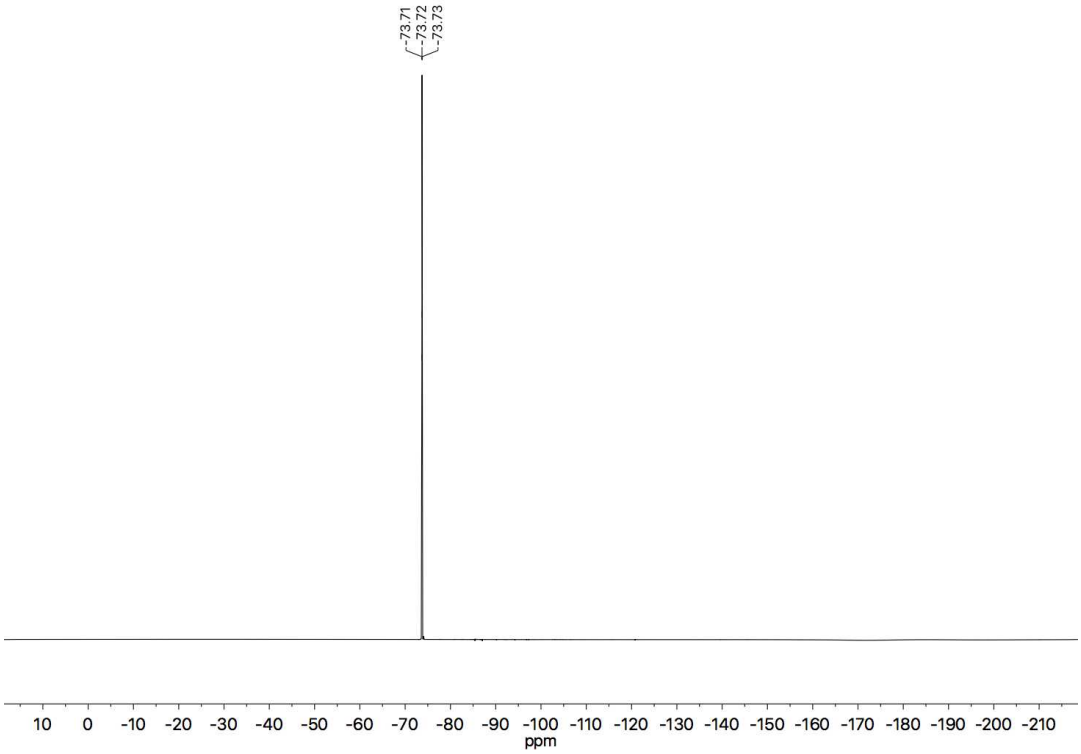
^{1}H NMR (600 MHz, $CDCl_3$) – **16a**

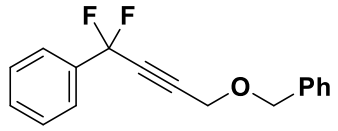


^{13}C NMR (151 MHz, $CDCl_3$) – **16a**

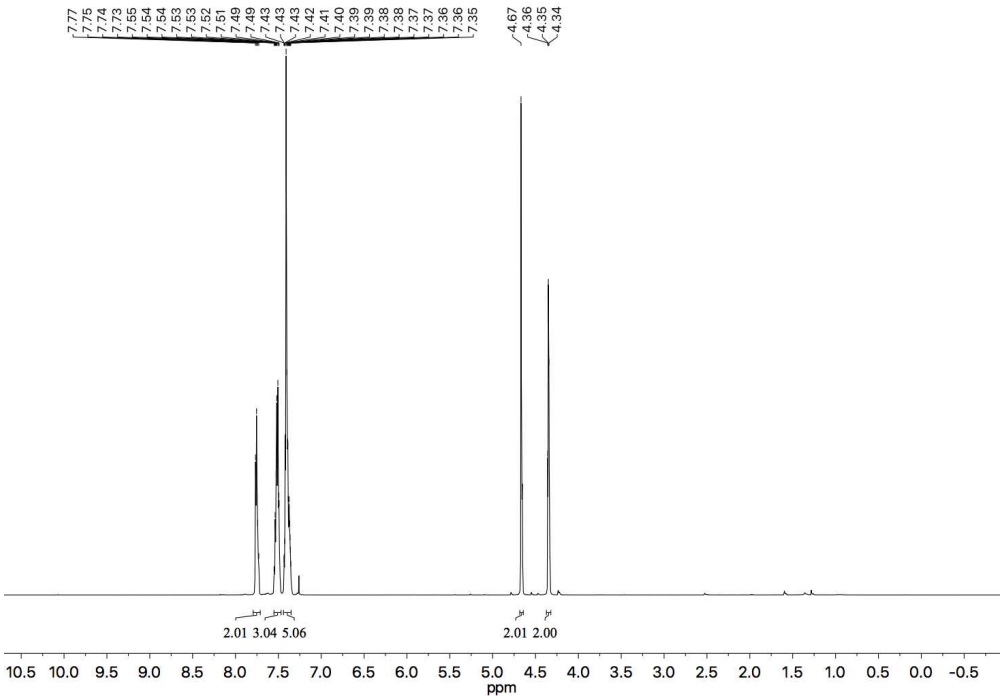


^{19}F NMR (565 MHz, $CDCl_3$) – **16a**

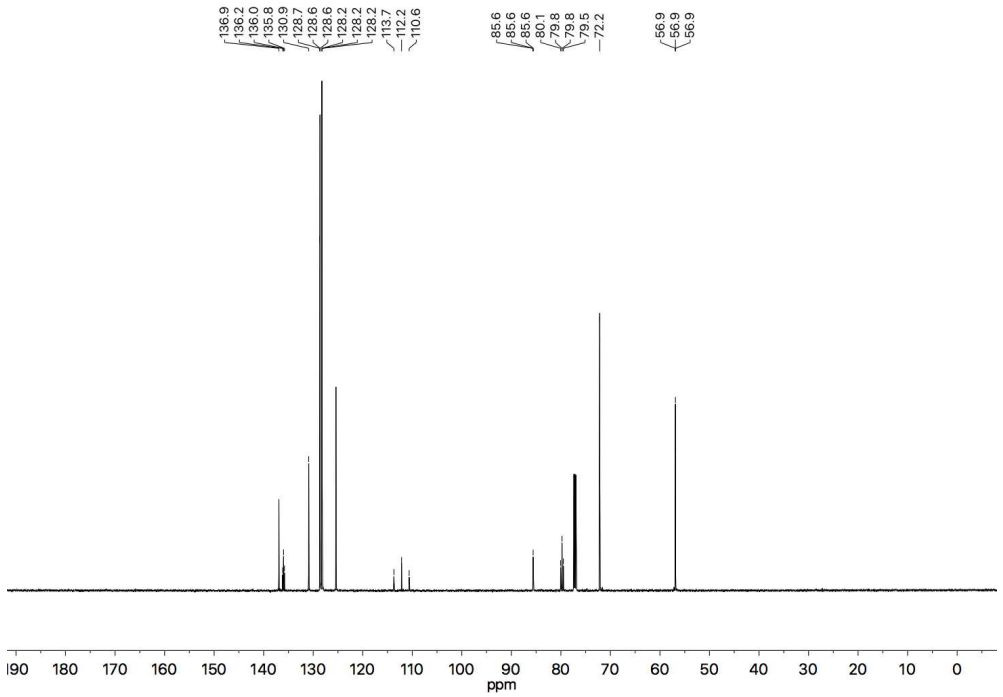




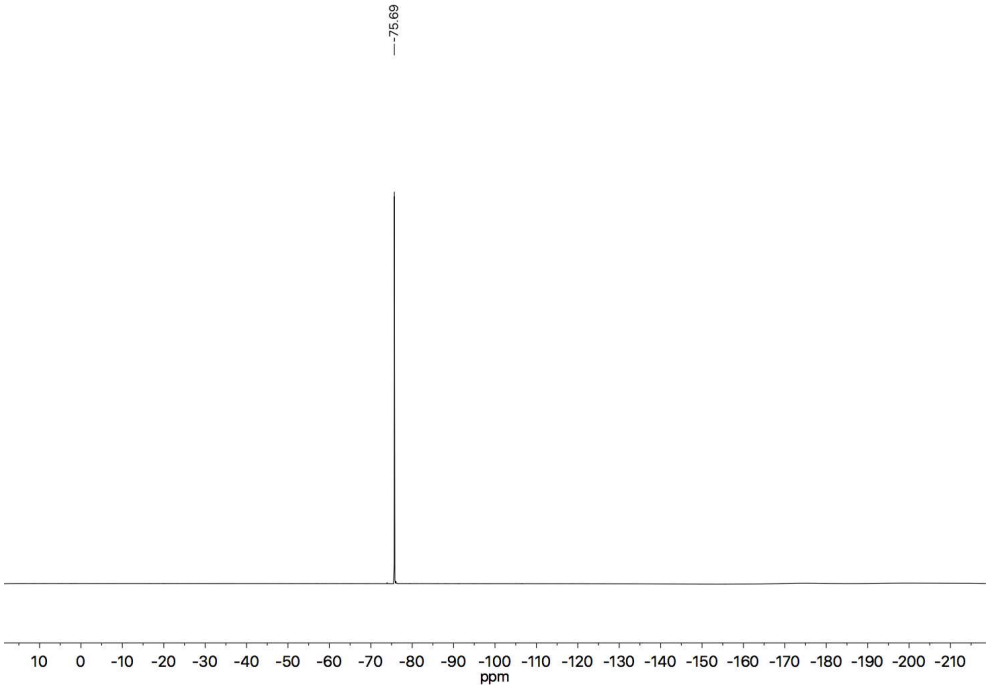
^{1}H NMR (600 MHz, $CDCl_3$) – **17a**

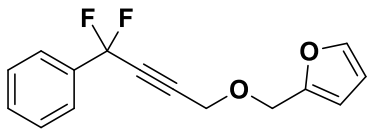


^{13}C NMR (151 MHz, $CDCl_3$) – **17a**

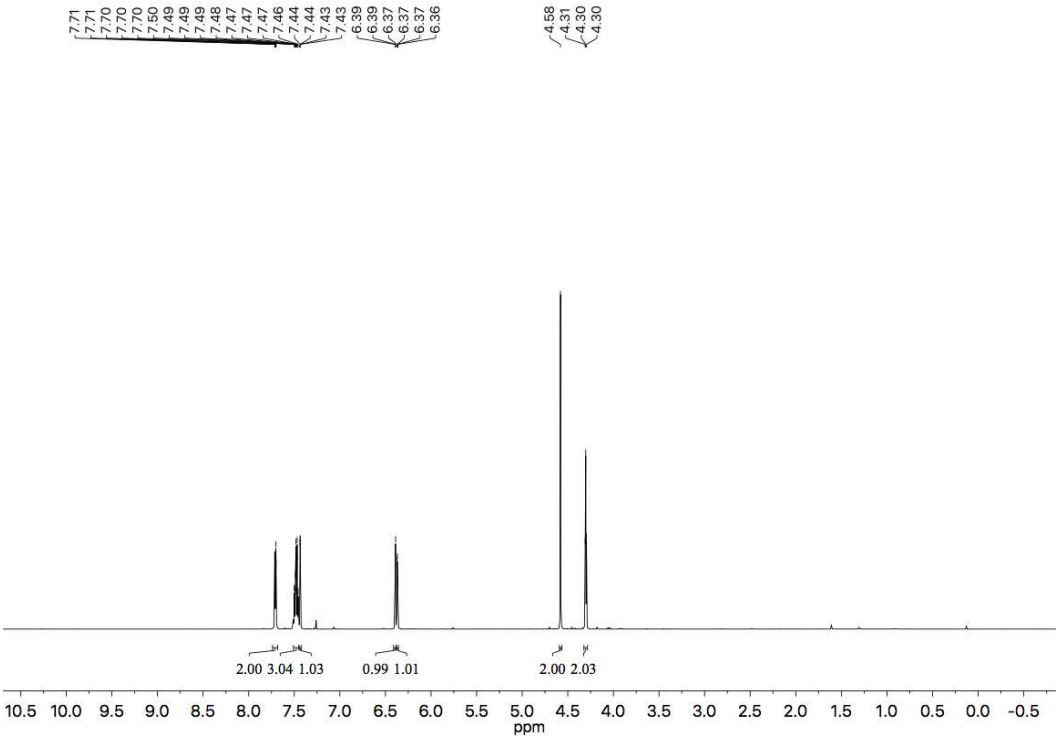


^{19}F NMR (565 MHz, $CDCl_3$) – **17a**

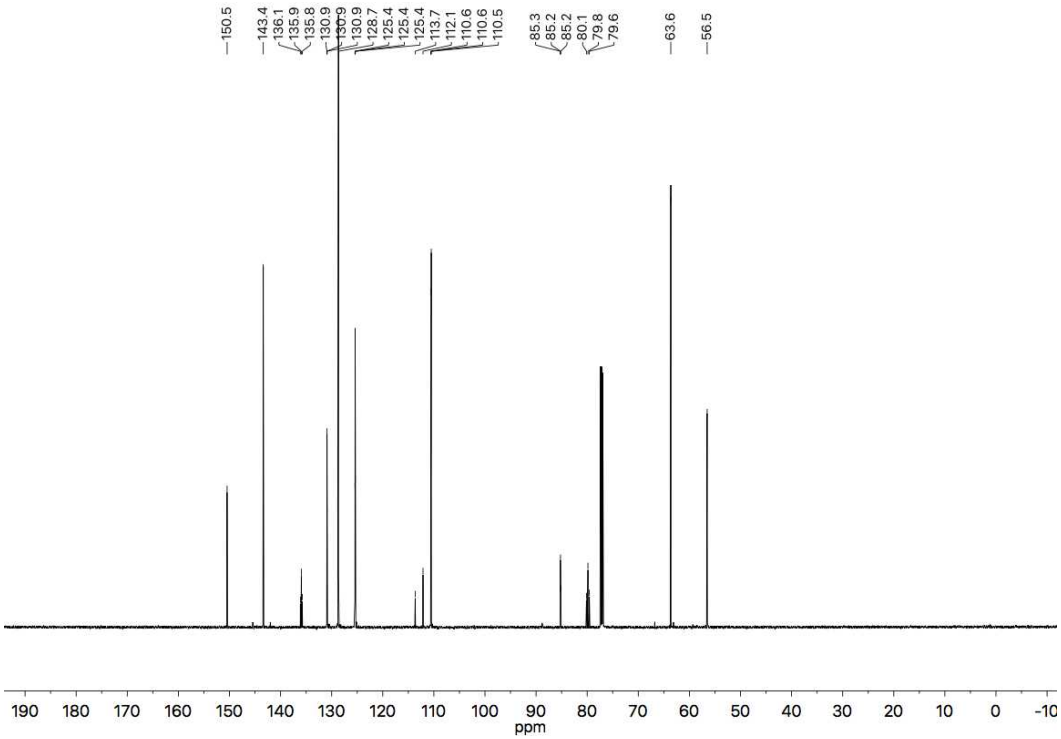




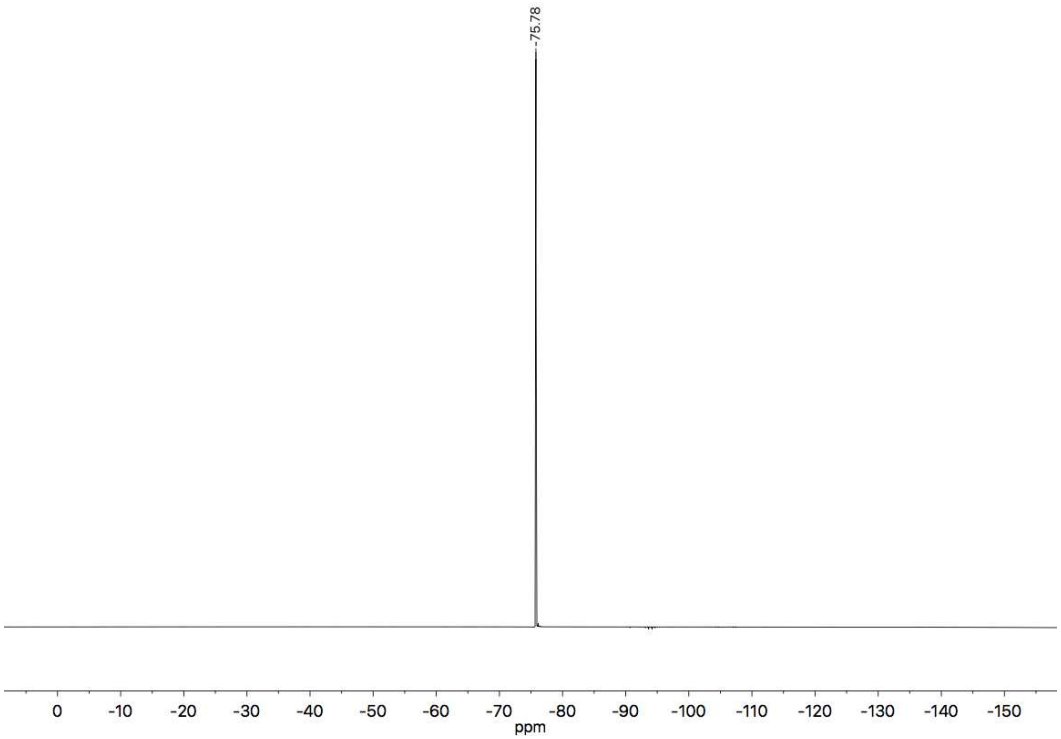
^{1}H NMR (600 MHz, $CDCl_3$) – **18a**

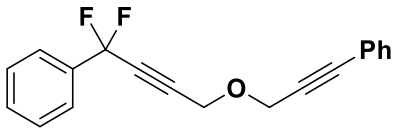


^{13}C NMR (151 MHz, $CDCl_3$) – **18a**

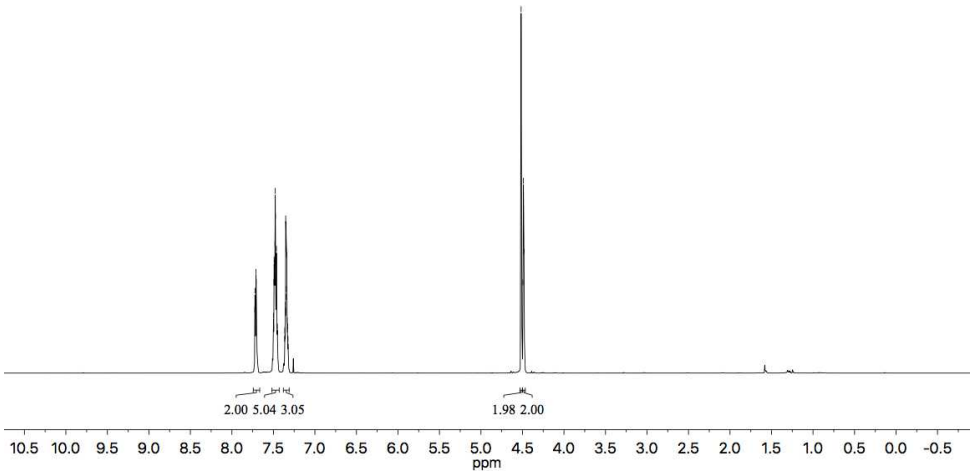


^{19}F NMR (565 MHz, $CDCl_3$) – **18a**

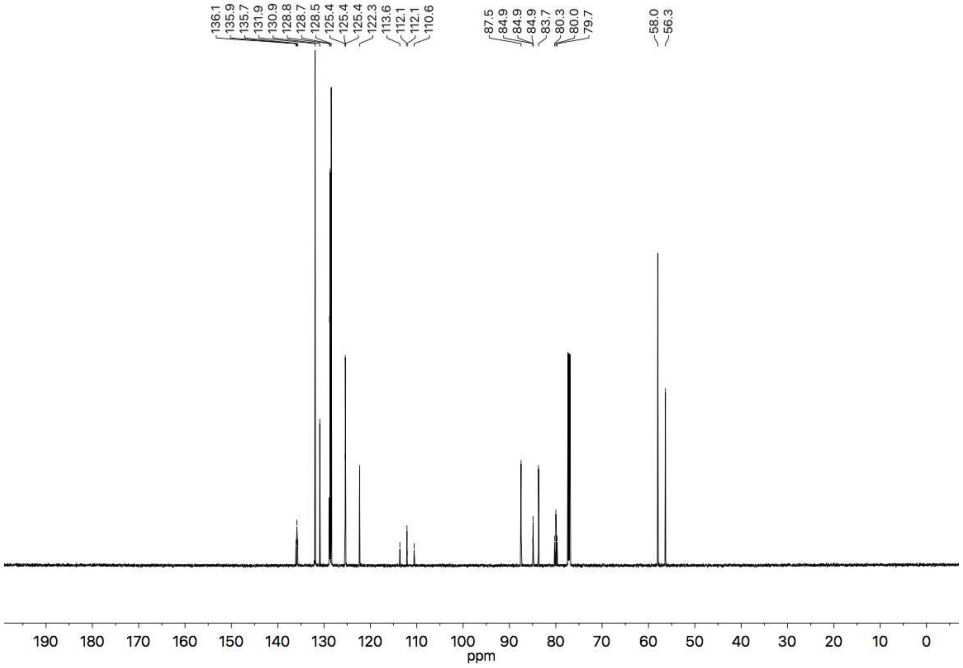




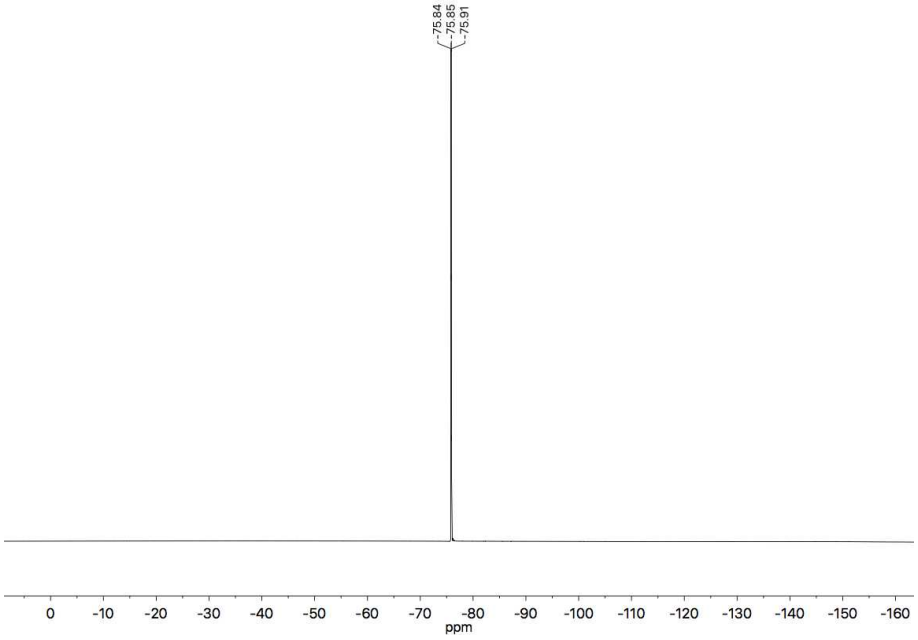
^{1}H NMR (600 MHz, $CDCl_3$) – **19a**

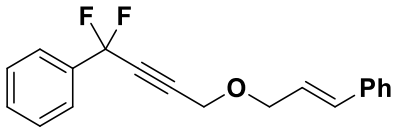


^{13}C NMR (151 MHz, $CDCl_3$) – **19a**

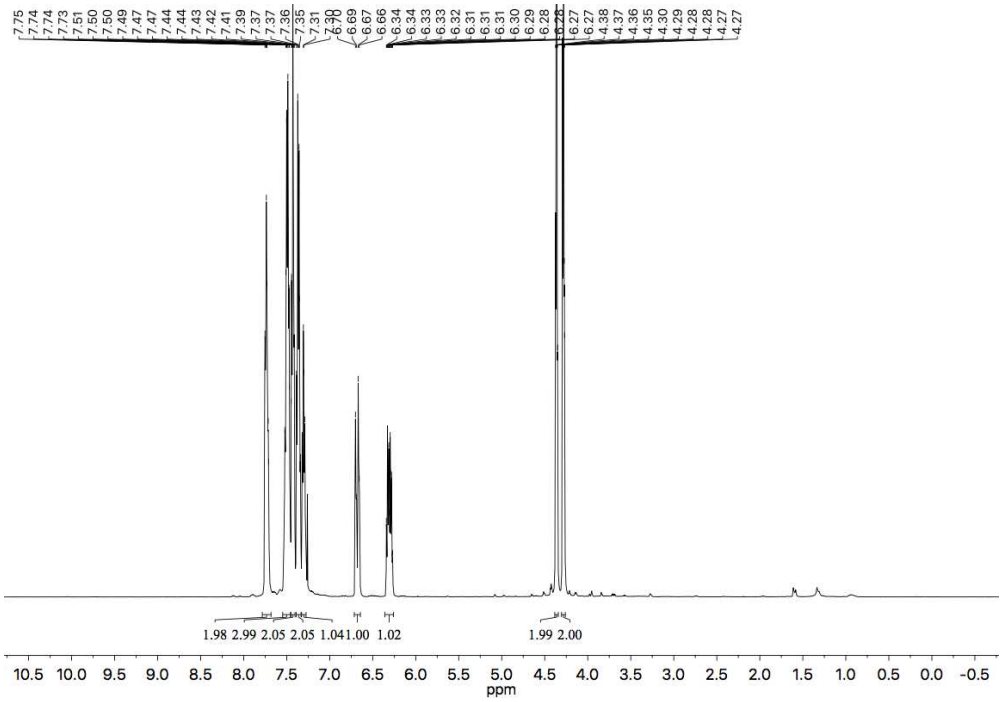


^{19}F NMR (565 MHz, $CDCl_3$) – **19a**

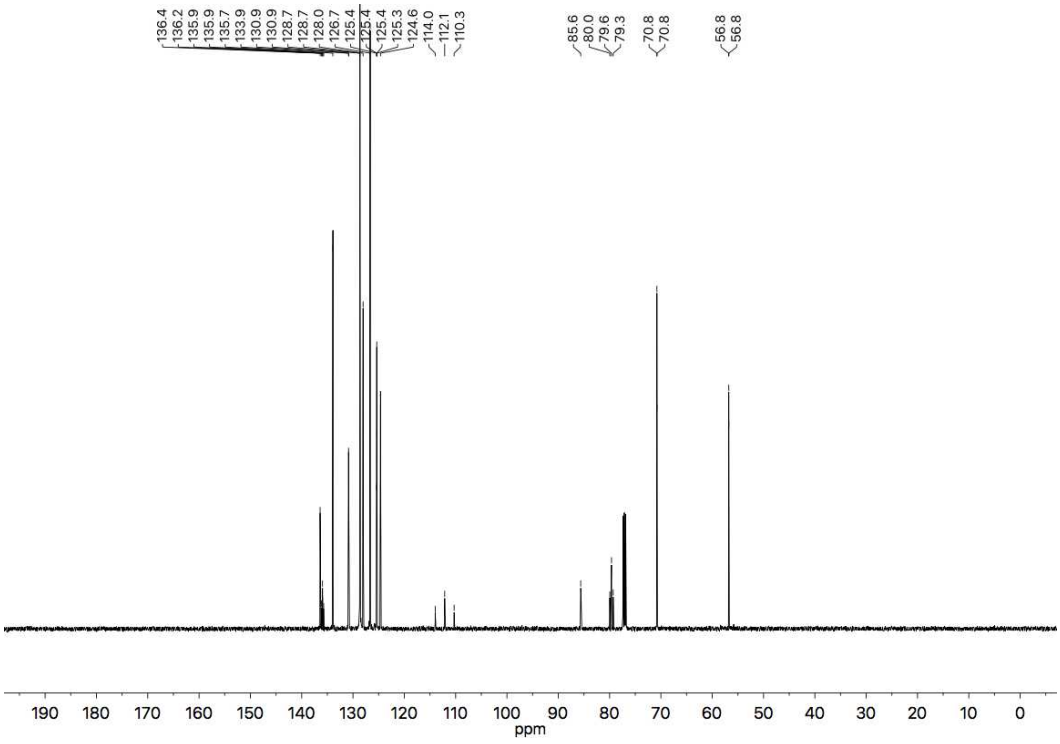




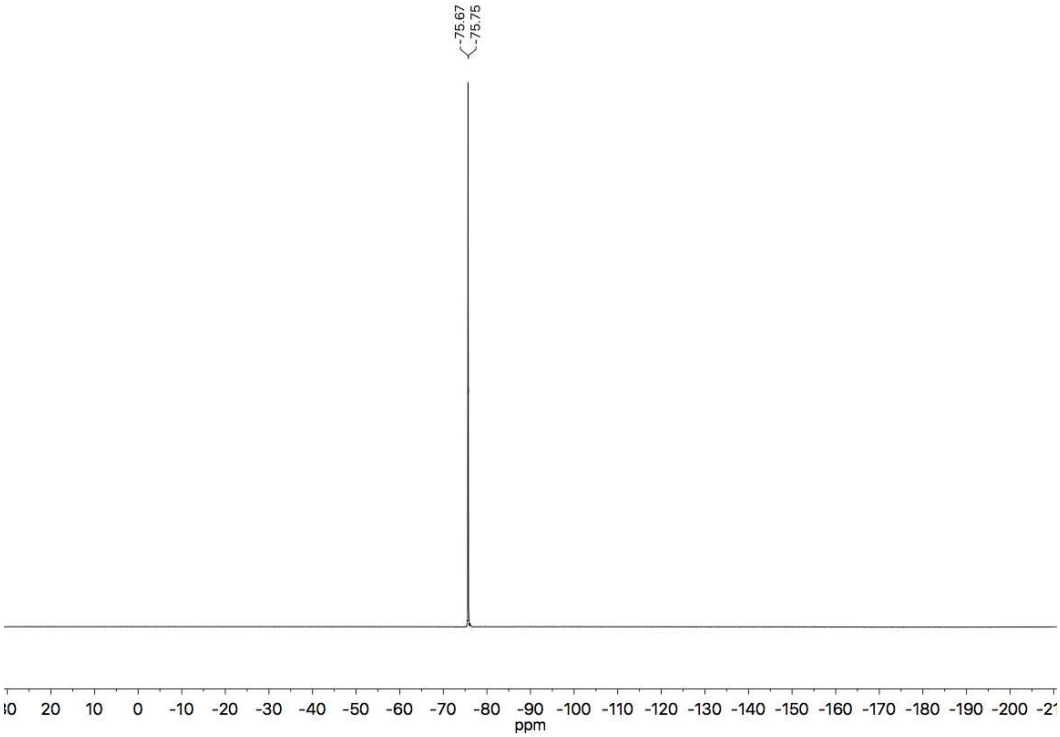
^{1}H NMR (500 MHz, $CDCl_3$) – **20a**

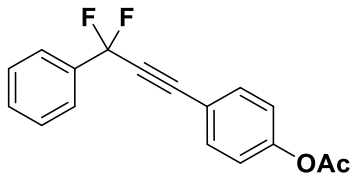


^{13}C NMR (126 MHz, $CDCl_3$) – **20a**

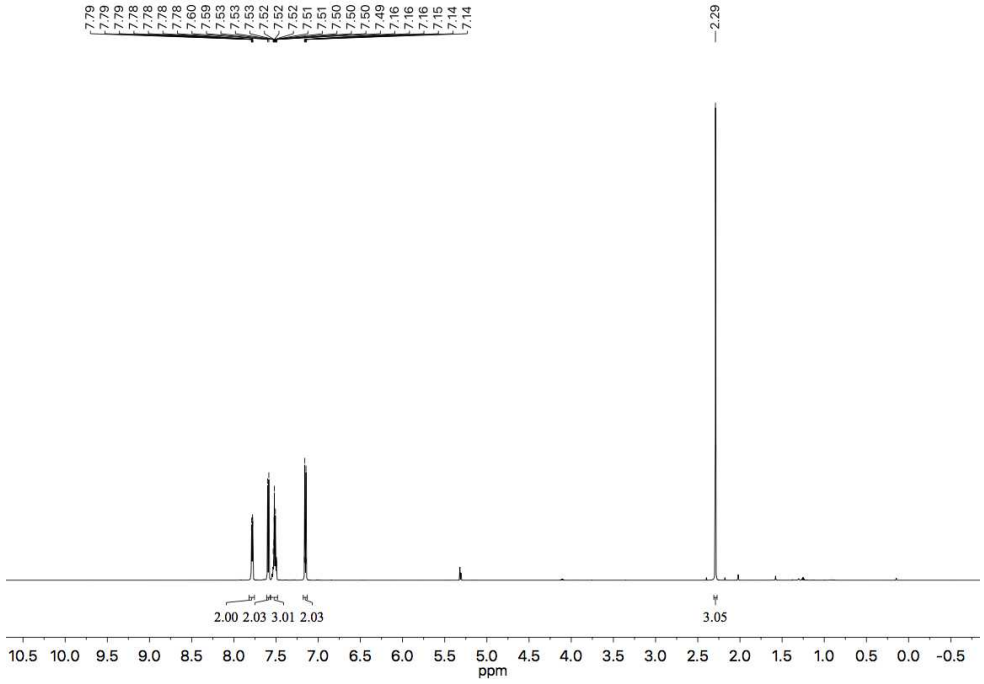


^{19}F NMR (470 MHz, $CDCl_3$) – **20a**

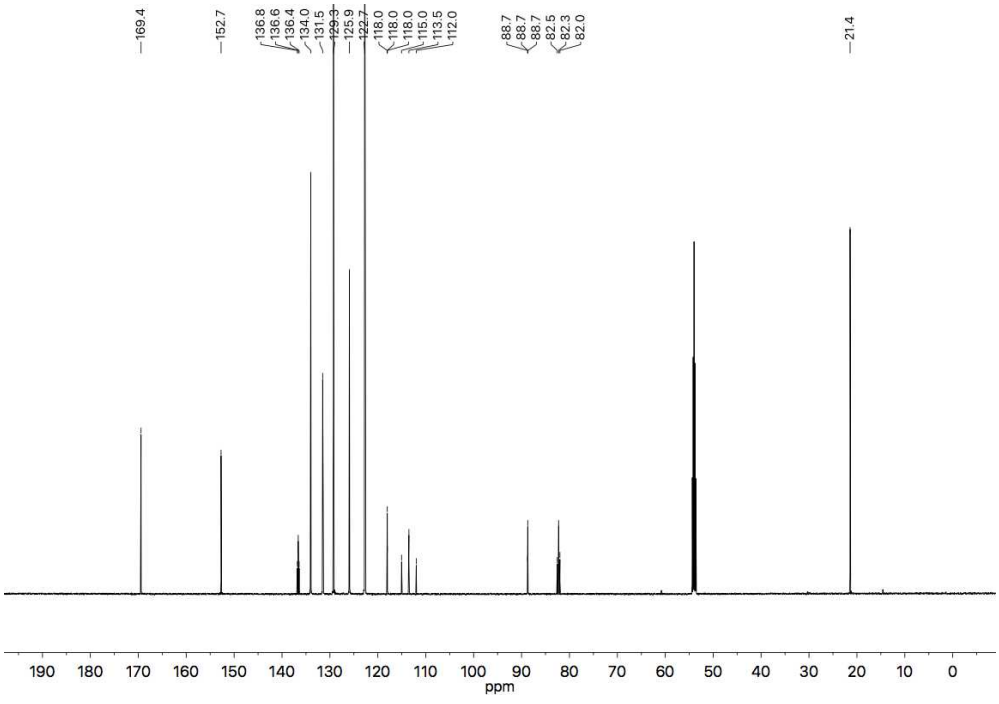




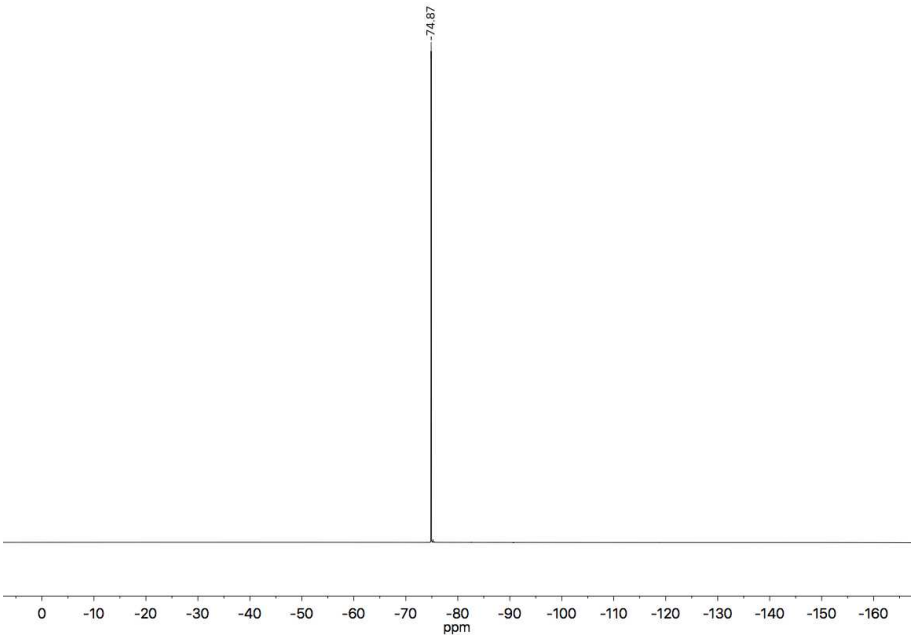
^{1}H NMR (600 MHz, CD_2Cl_2) – **21a**

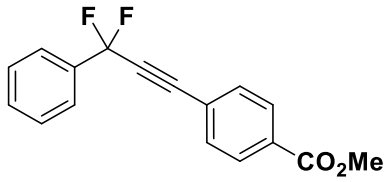


^{13}C NMR (151 MHz, CD_2Cl_2) – **21a**

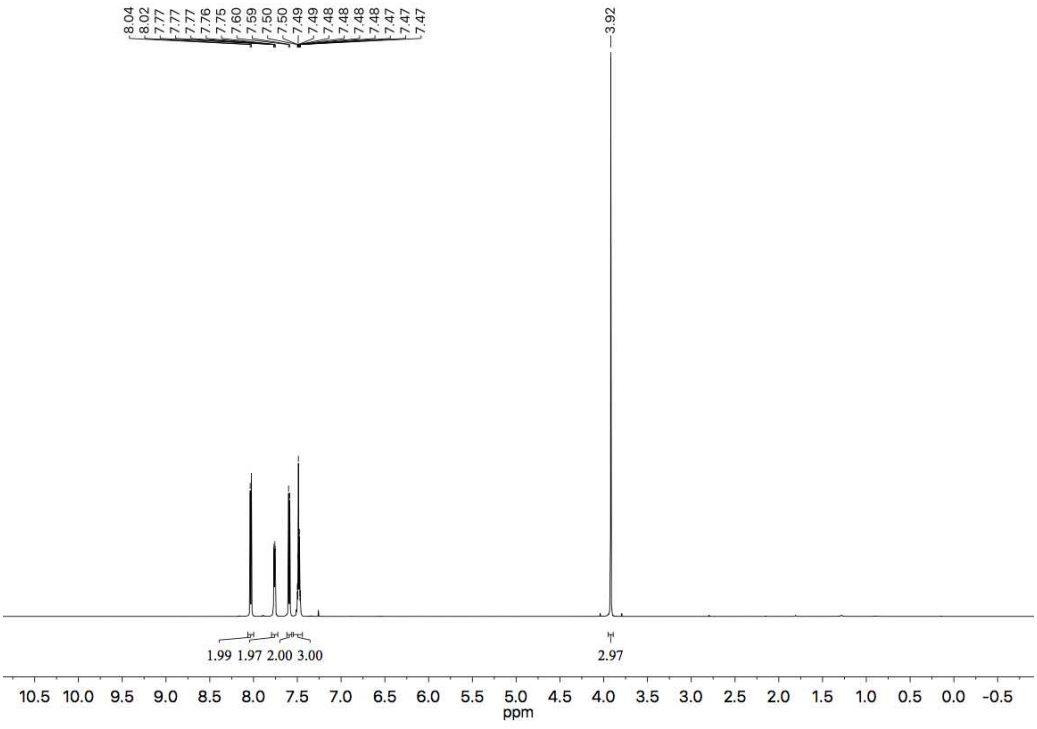


^{19}F NMR (565 MHz, CD_2Cl_2) – **21a**

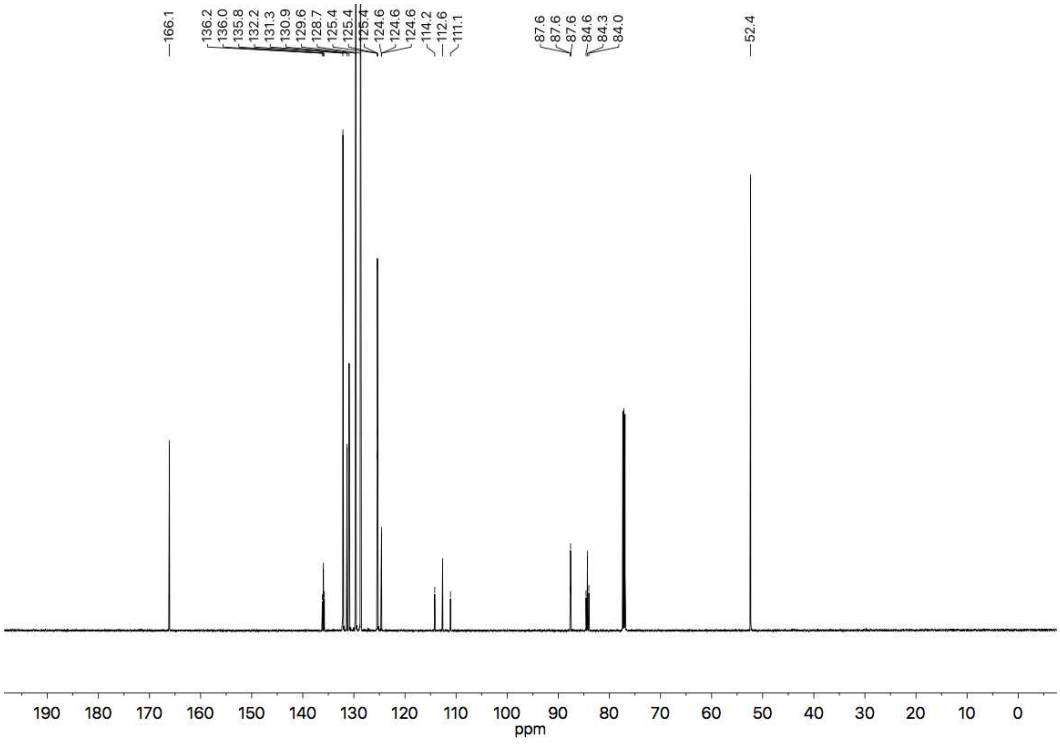




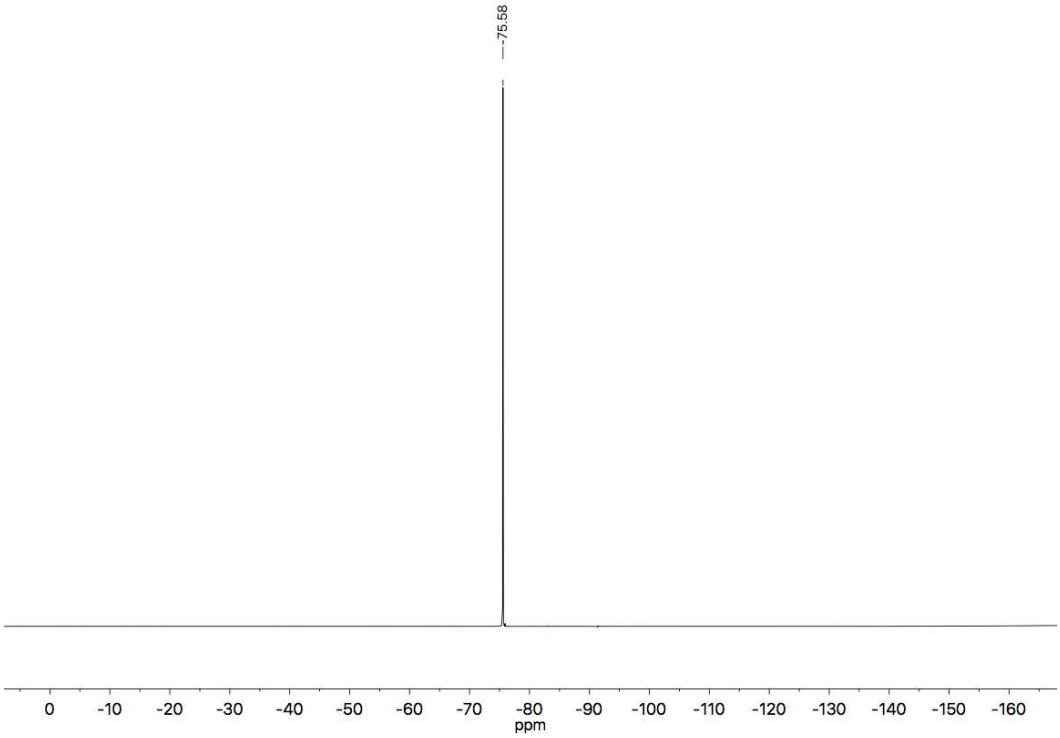
^{1}H NMR (600 MHz, $CDCl_3$) – **22a**

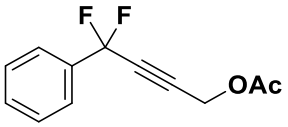


^{13}C NMR (151 MHz, $CDCl_3$) – **22a**

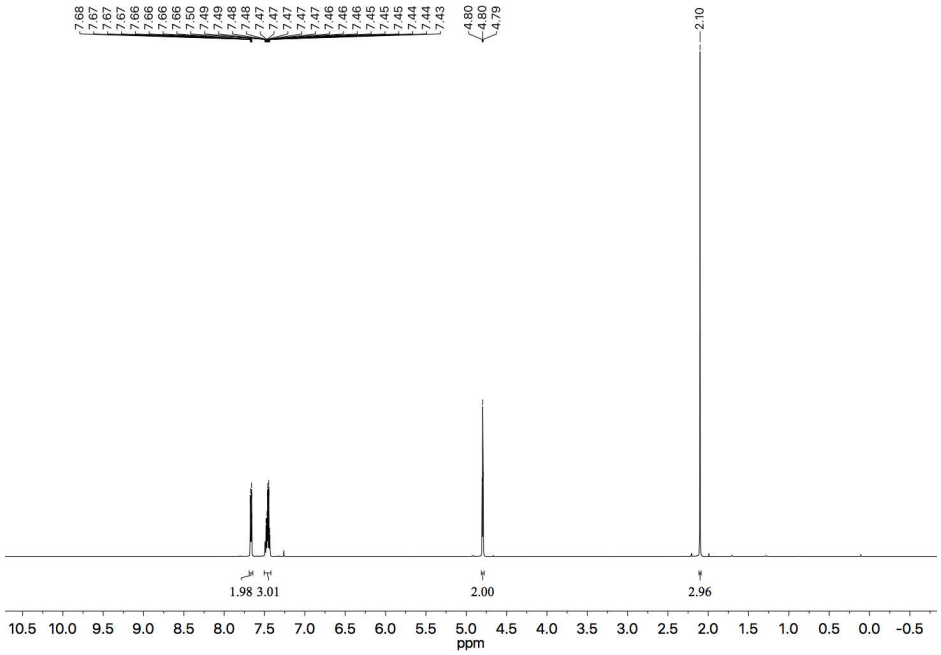


^{19}F NMR (565 MHz, $CDCl_3$) – **22a**

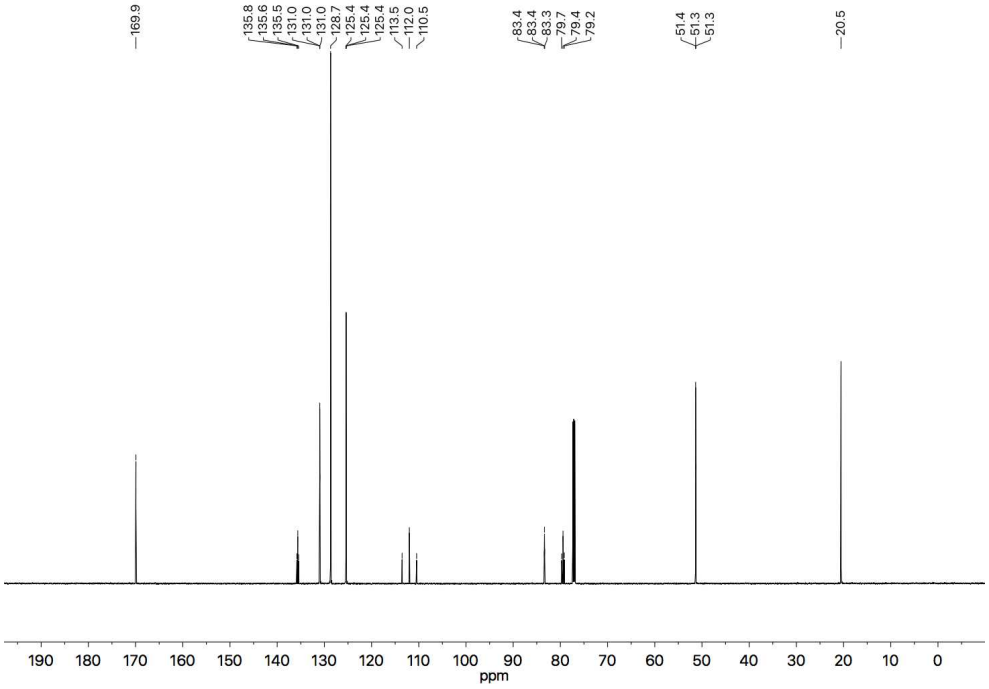




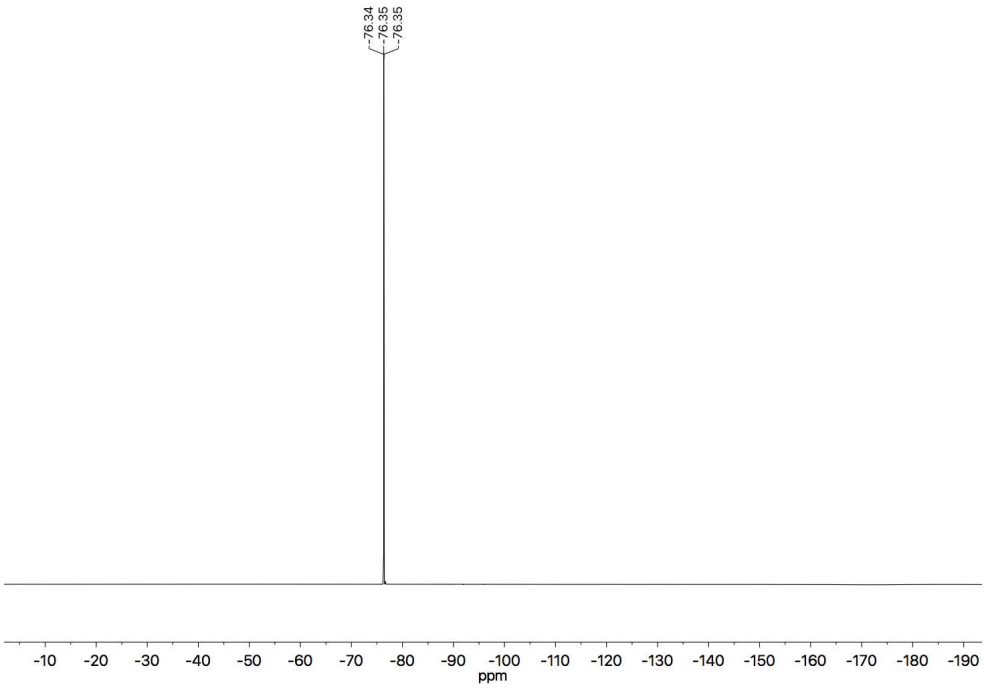
^{1}H NMR (600 MHz, $CDCl_3$) – **23a**

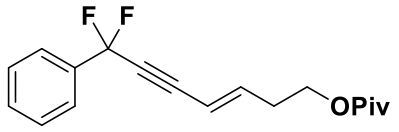


^{13}C NMR (151 MHz, $CDCl_3$) – **23a**

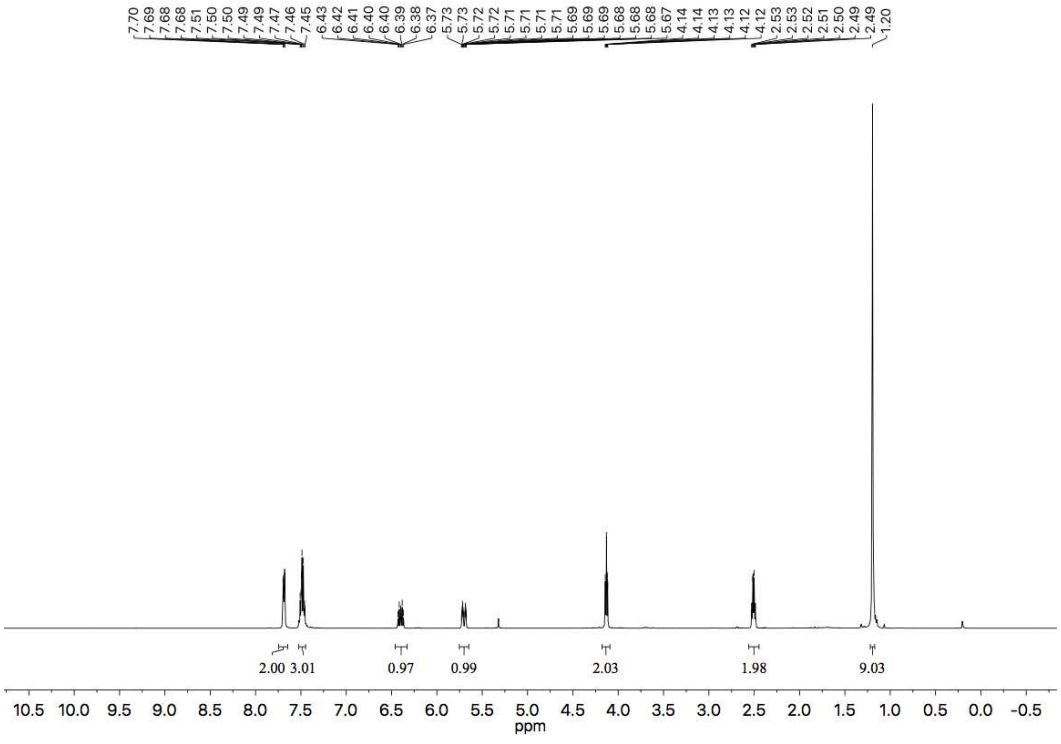


^{19}F NMR (565 MHz, $CDCl_3$) – **23a**

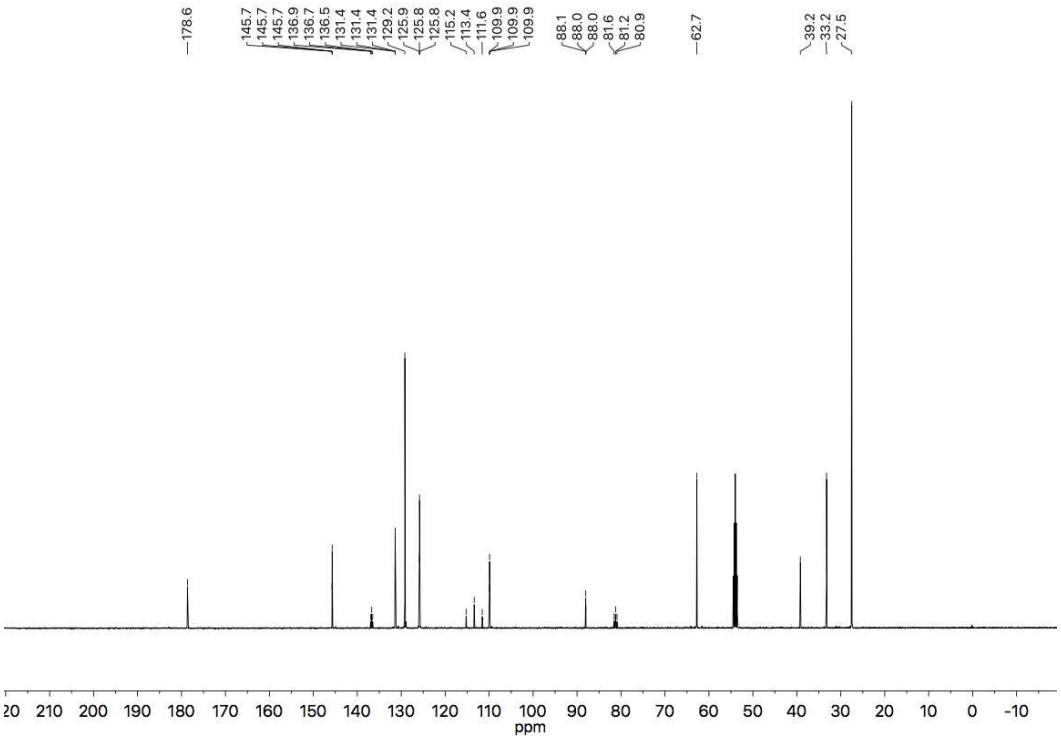




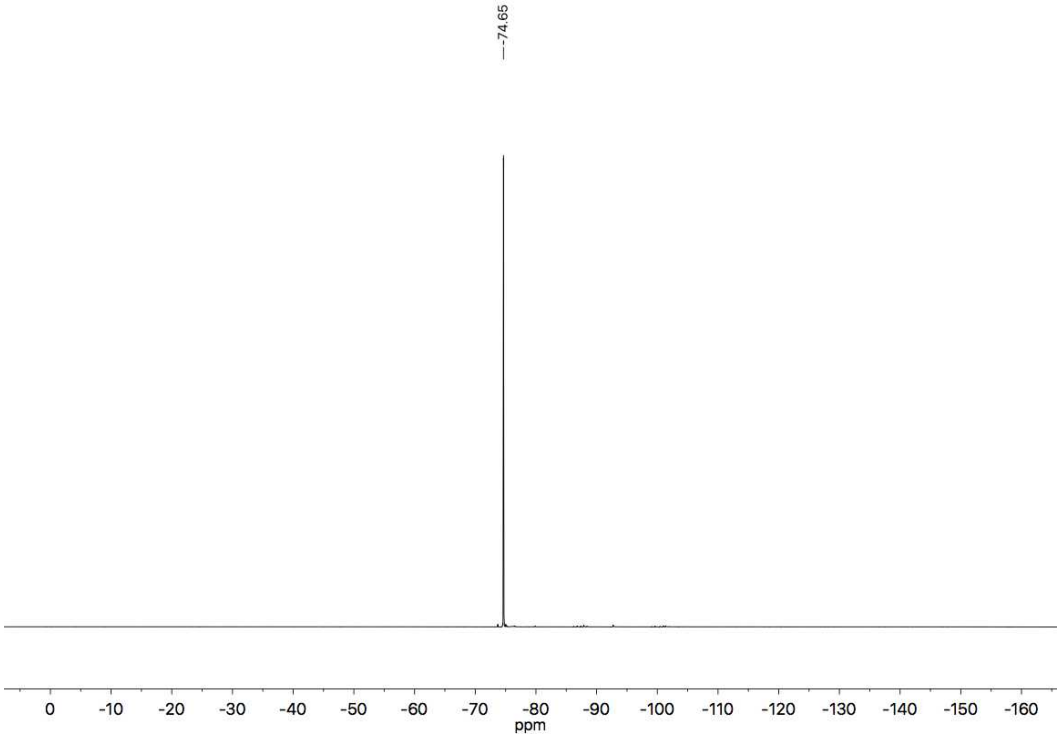
^{1}H NMR (500 MHz, CD_2Cl_2) – **24a**

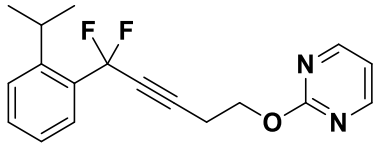


^{13}C NMR (126 MHz, CD_2Cl_2) – **24a**

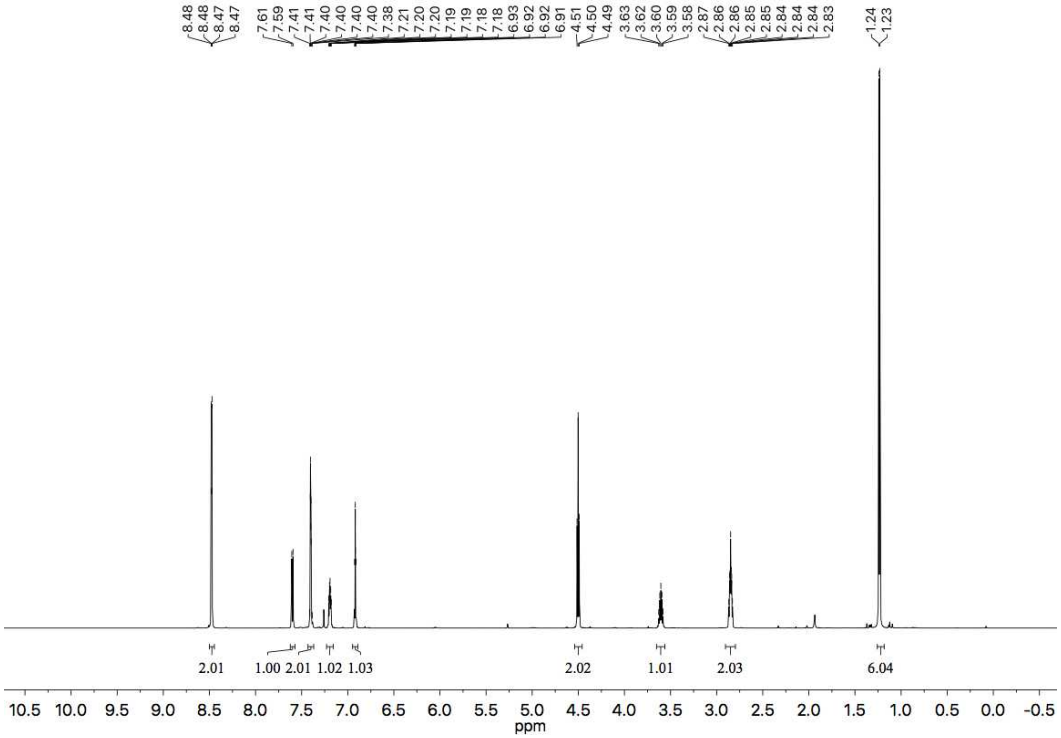


^{19}F NMR (470 MHz, CD_2Cl_2) – **24a**

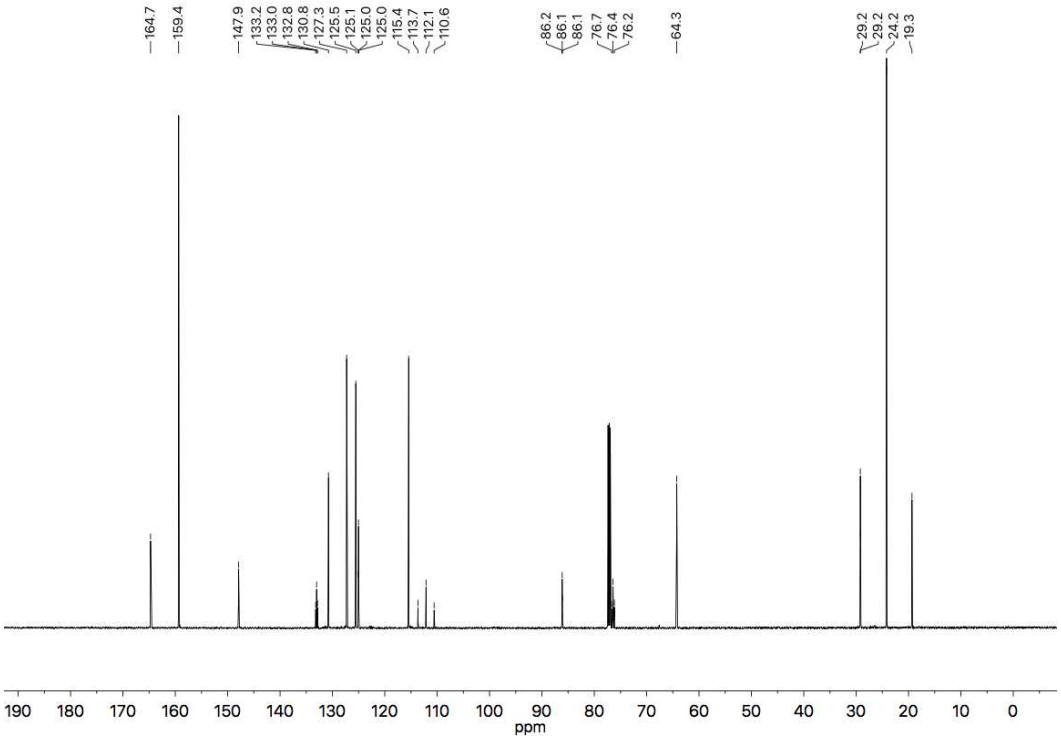




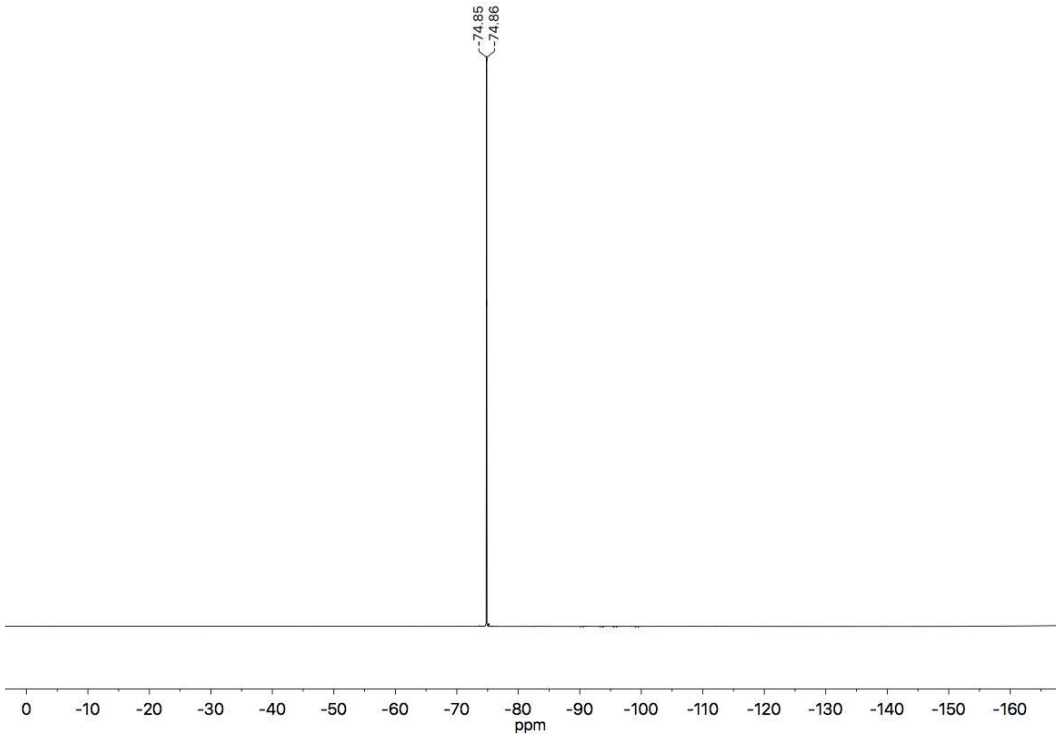
^{1}H NMR (600 MHz, $CDCl_3$) – **25a**

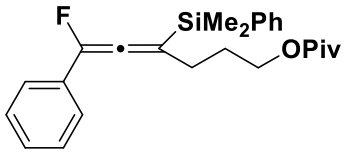


^{13}C NMR (151 MHz, $CDCl_3$) – **25a**

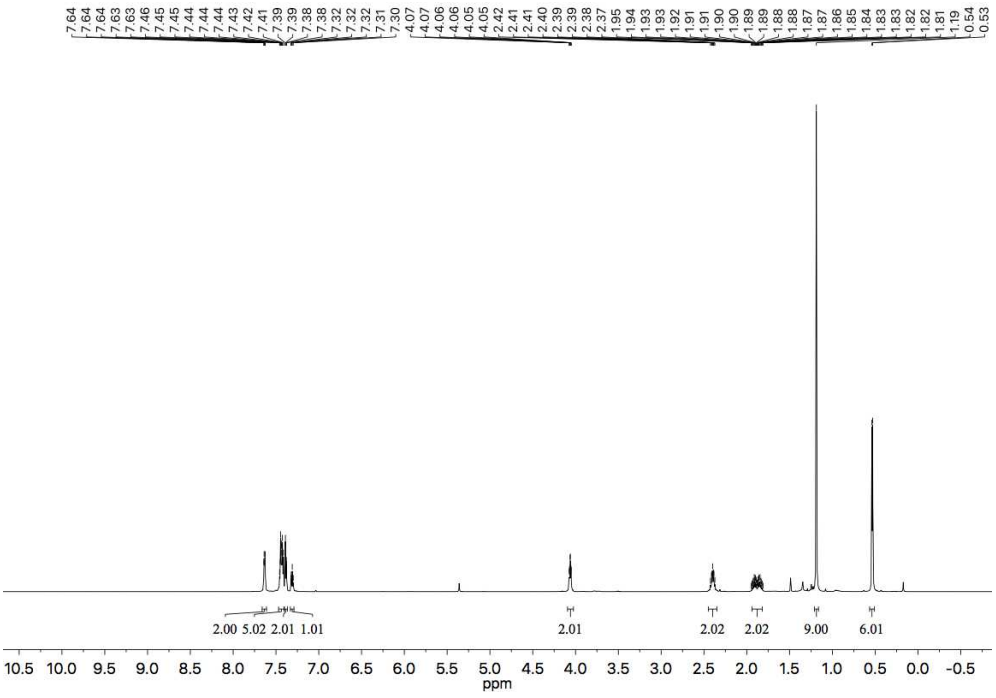


^{19}F NMR (565 MHz, $CDCl_3$) – **25a**

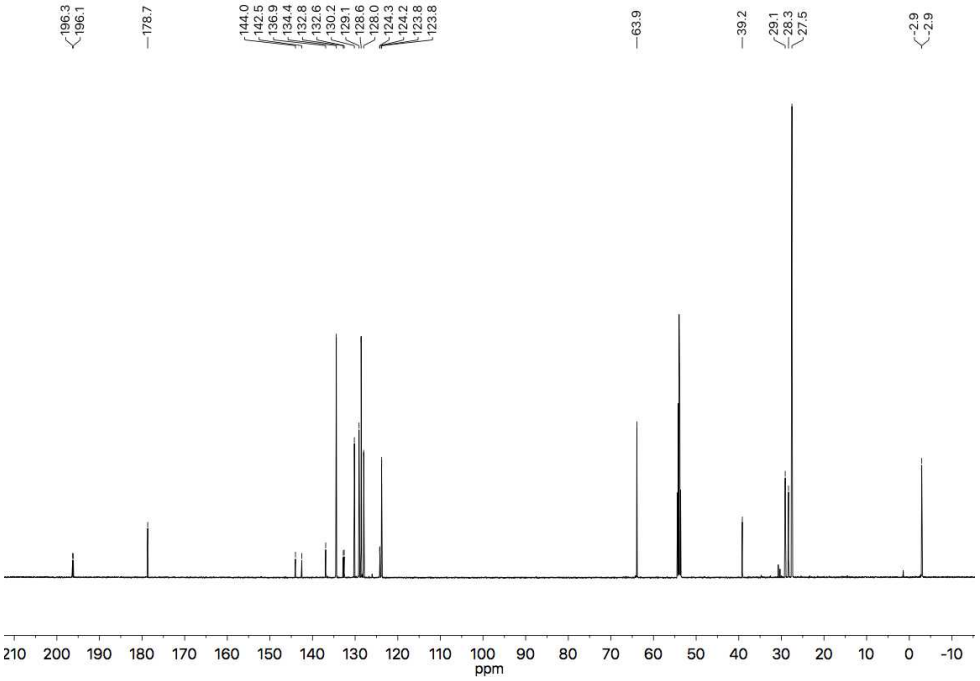




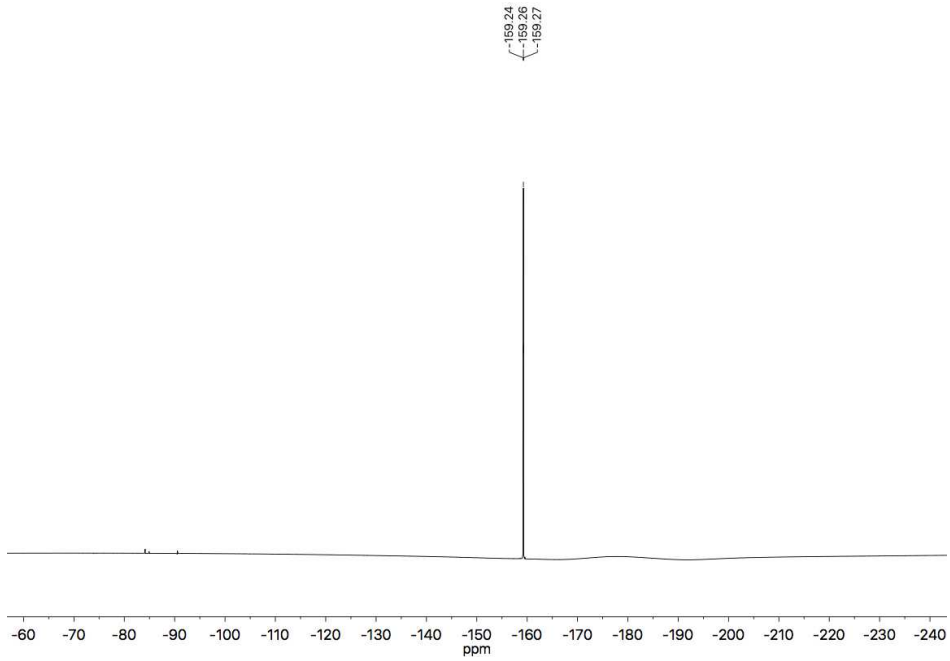
^{1}H NMR (600 MHz, CD_2Cl_2) – **1b**

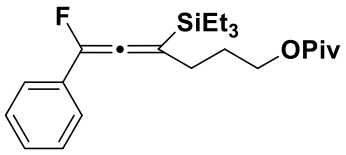


^{13}C NMR (151 MHz, CD_2Cl_2) – **1b**

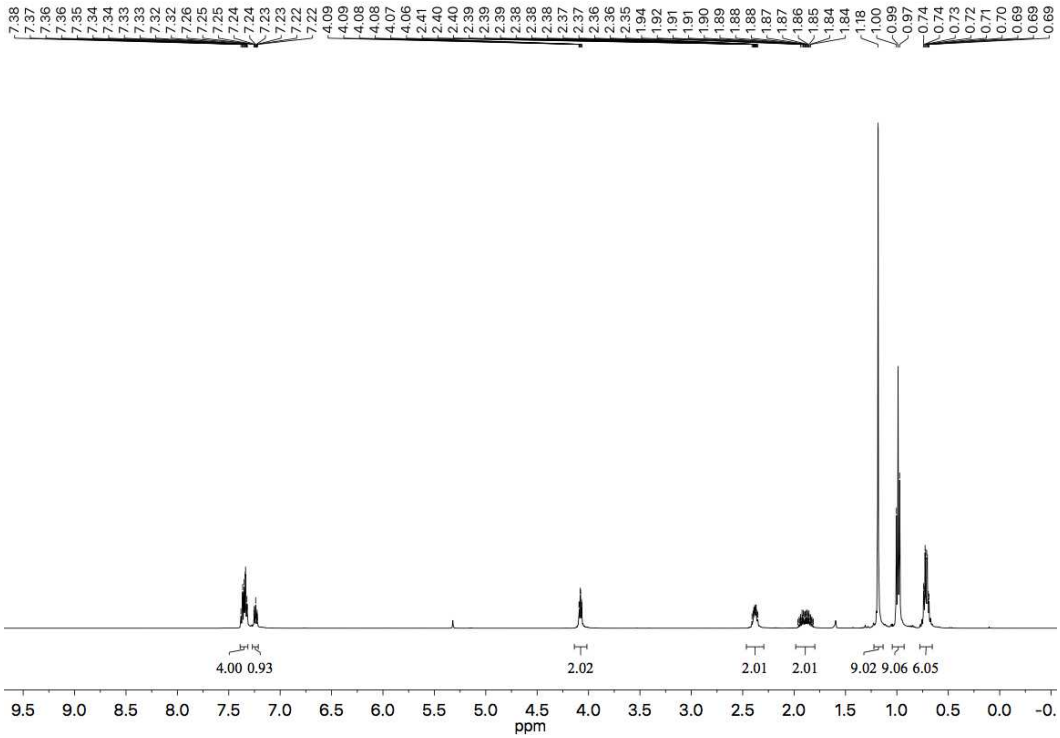


^{19}F NMR (565 MHz, CD_2Cl_2) – **1b**

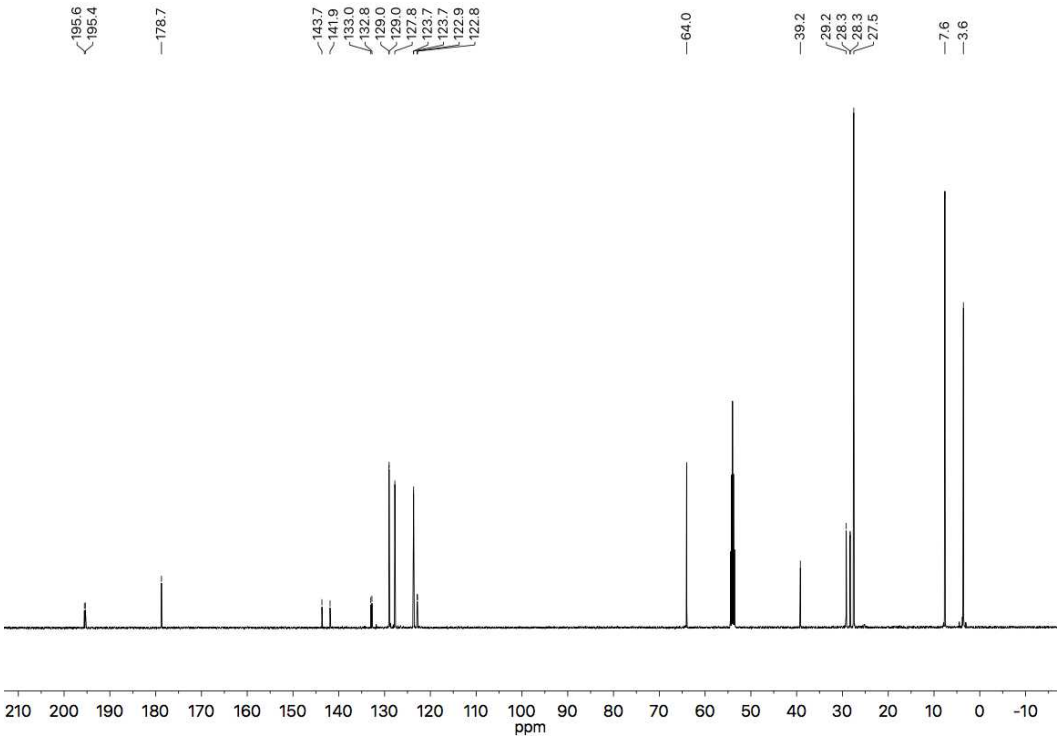




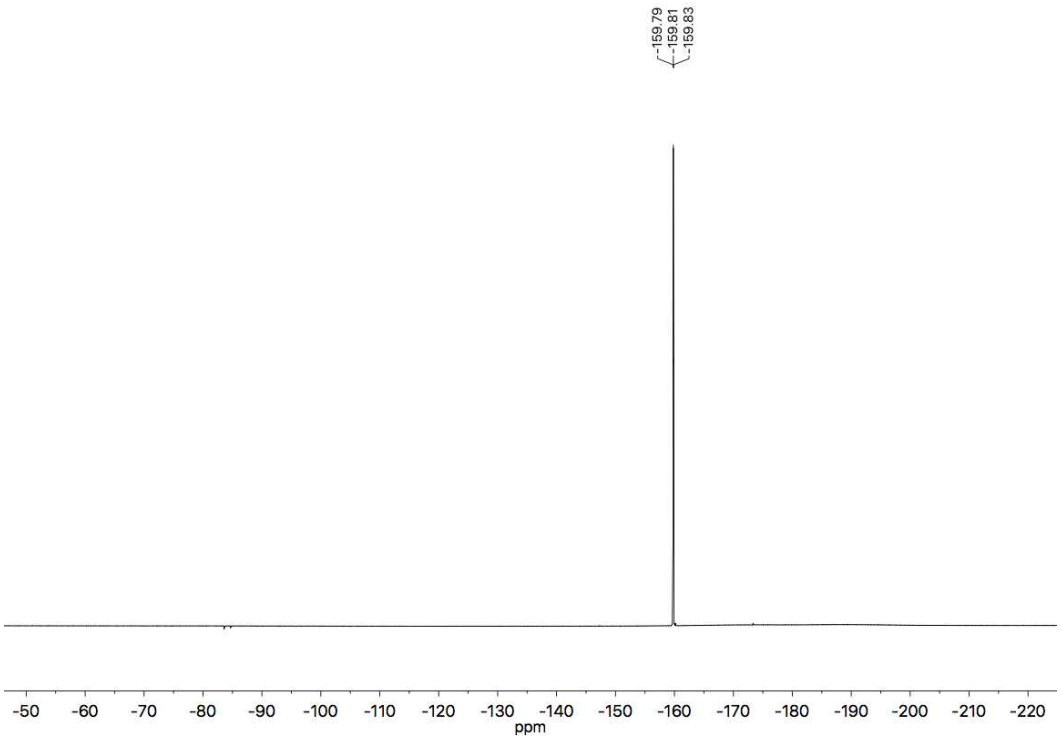
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

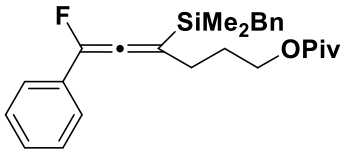


^{13}C NMR (126 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

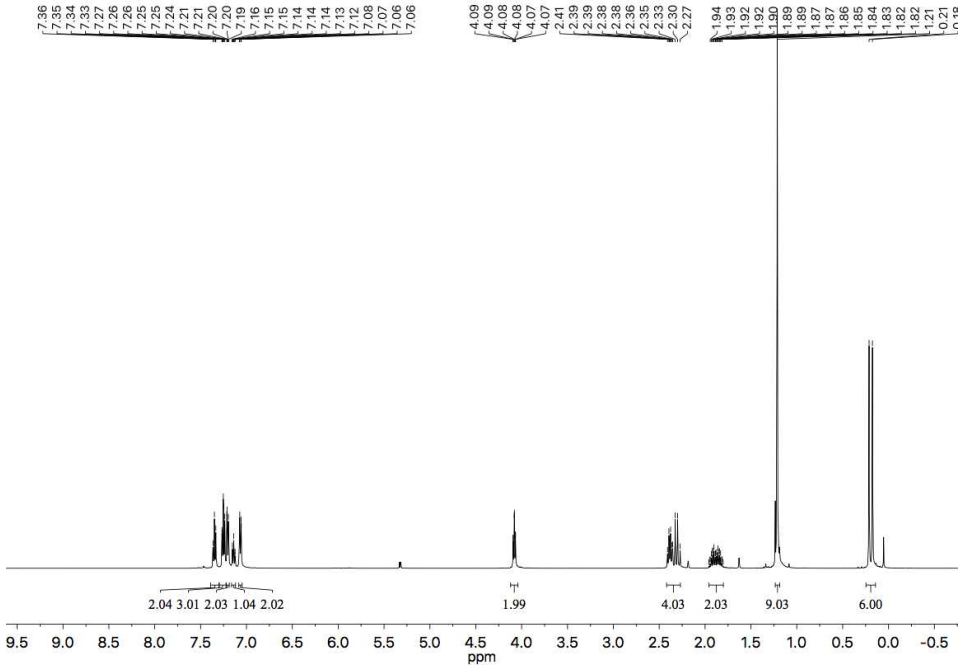


^{19}F NMR (470 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

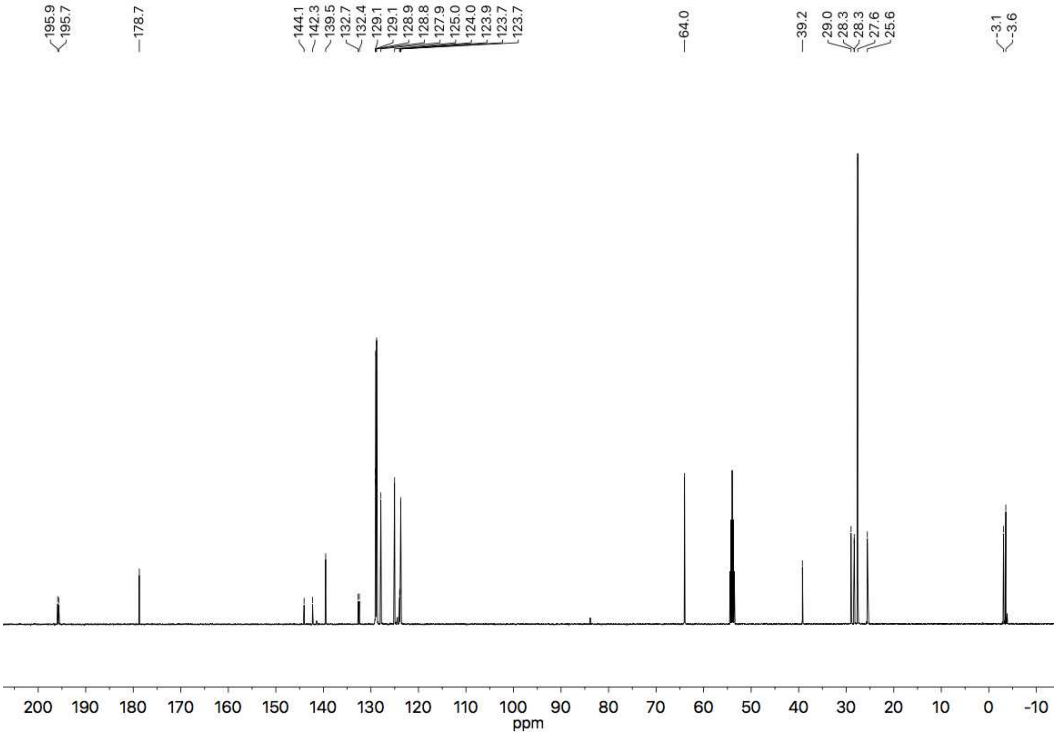




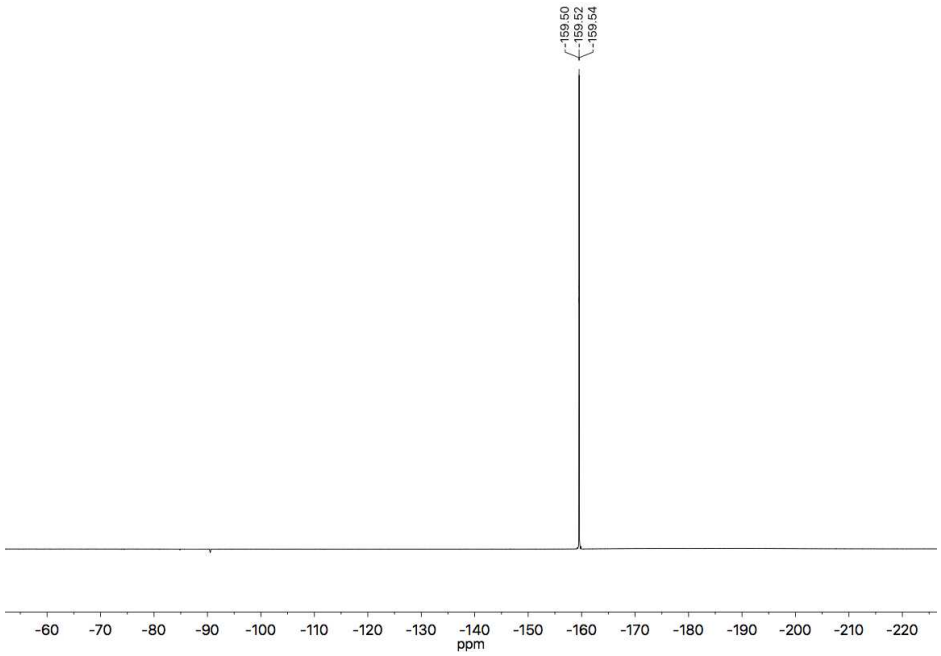
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b-SiMe$_2$Bn**



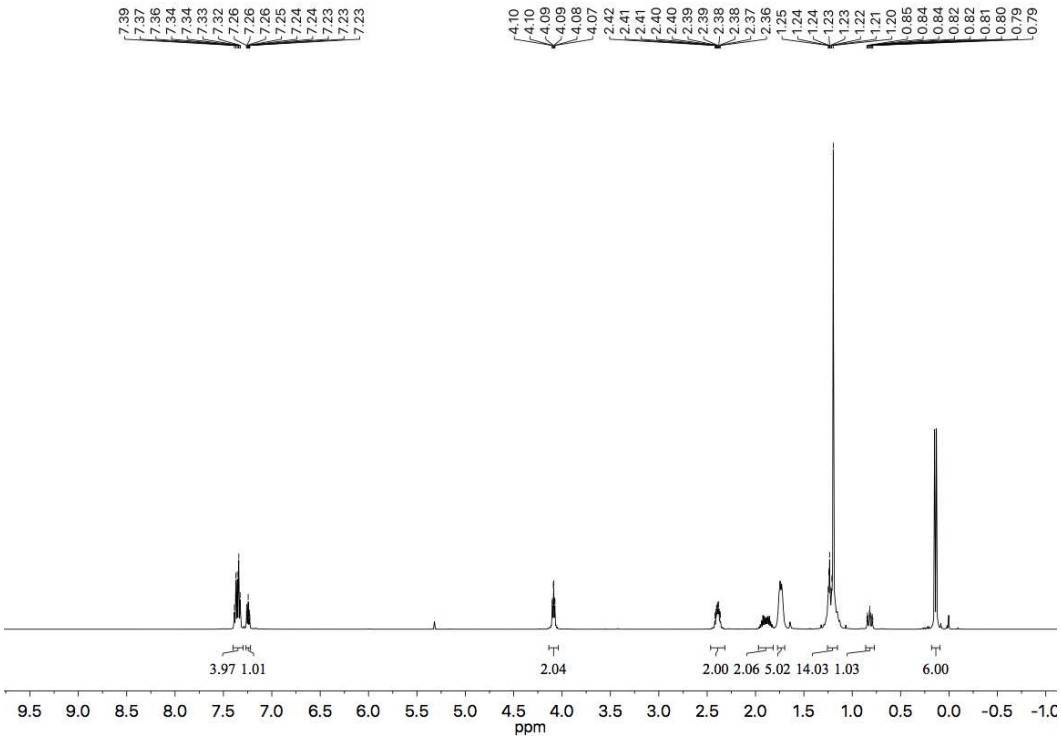
^{13}C NMR (126 MHz, CD_2Cl_2) – **2b- SiMe$_2$Bn**



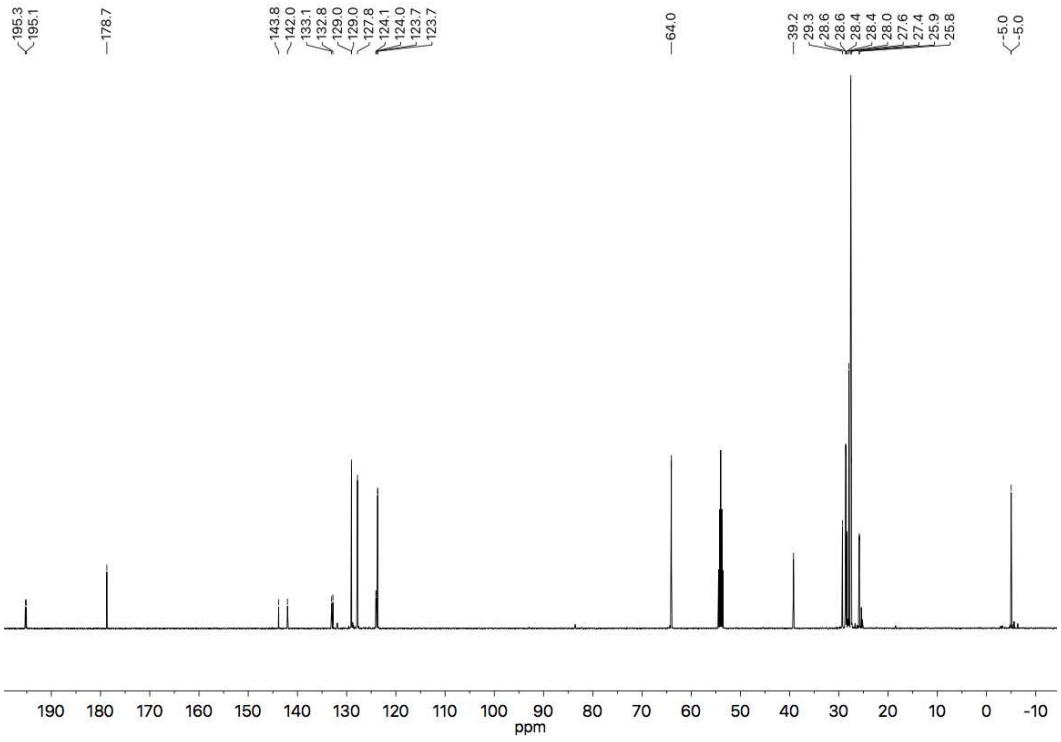
^{19}F NMR (470 MHz, CD_2Cl_2) – **2b- $SiMe_2Bn$**



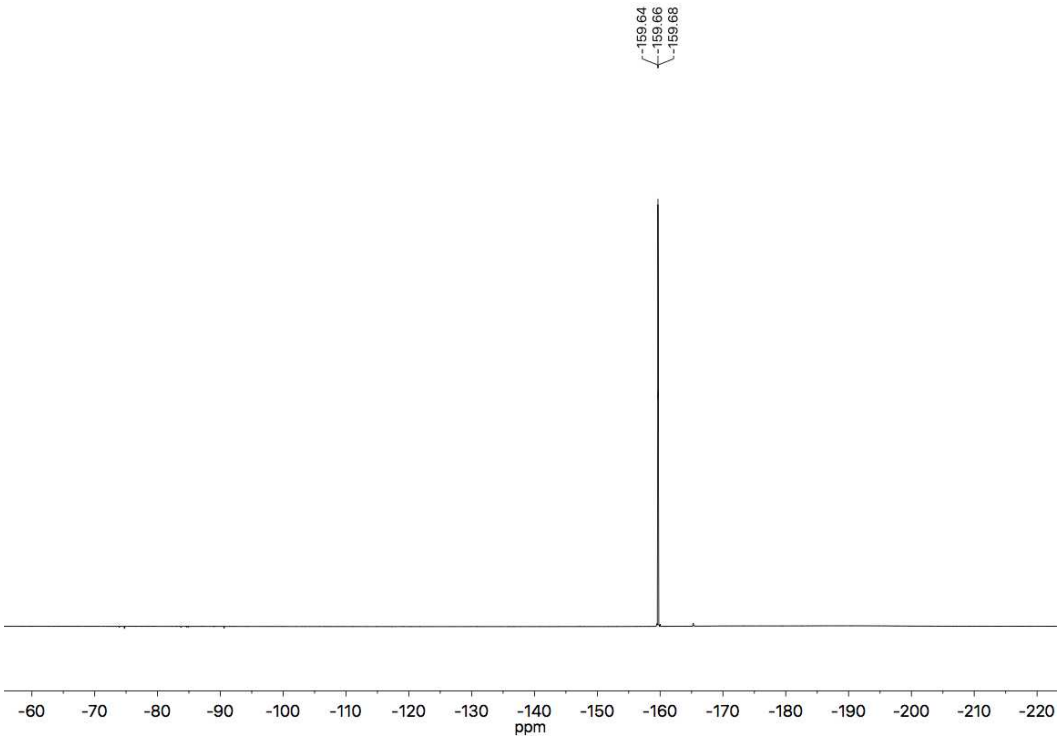
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b- $SiMe_2Cy$**

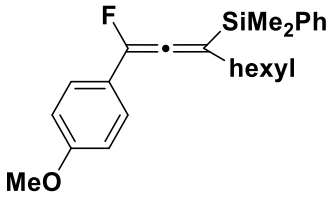


^{13}C NMR (126 MHz, CD_2Cl_2) – **2b- $SiMe_2Cy$**

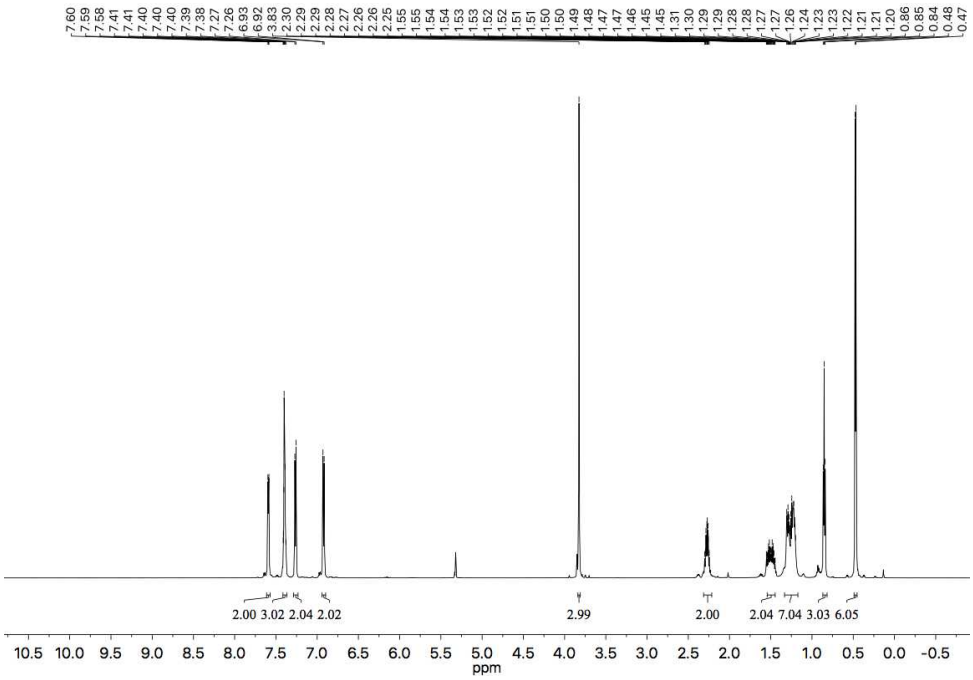


^{19}F NMR (470 MHz, CD_2Cl_2) – **2b- $SiMe_2Cy$**

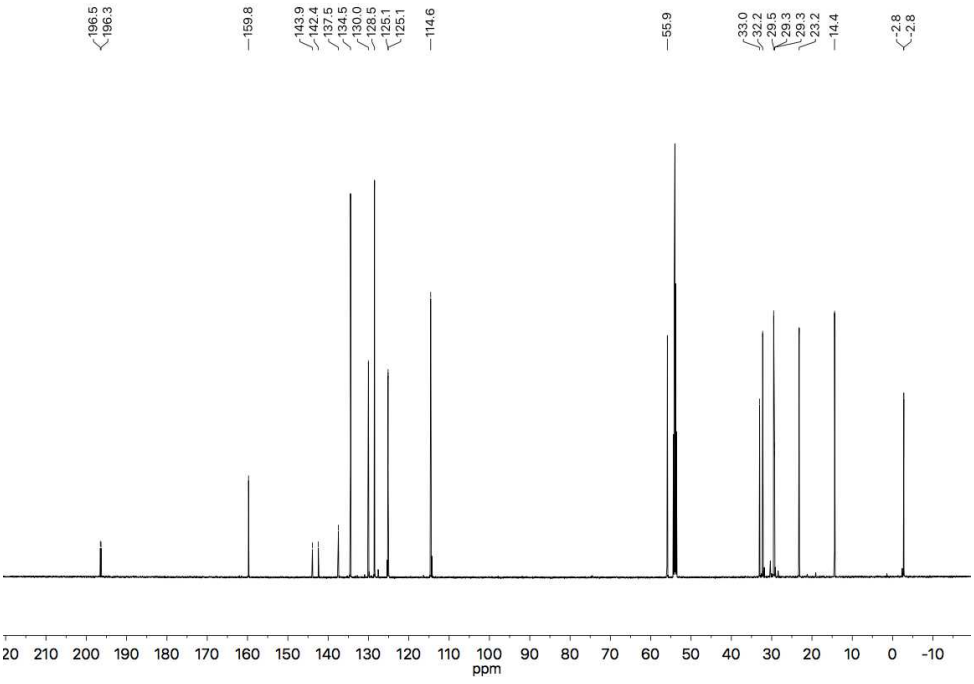




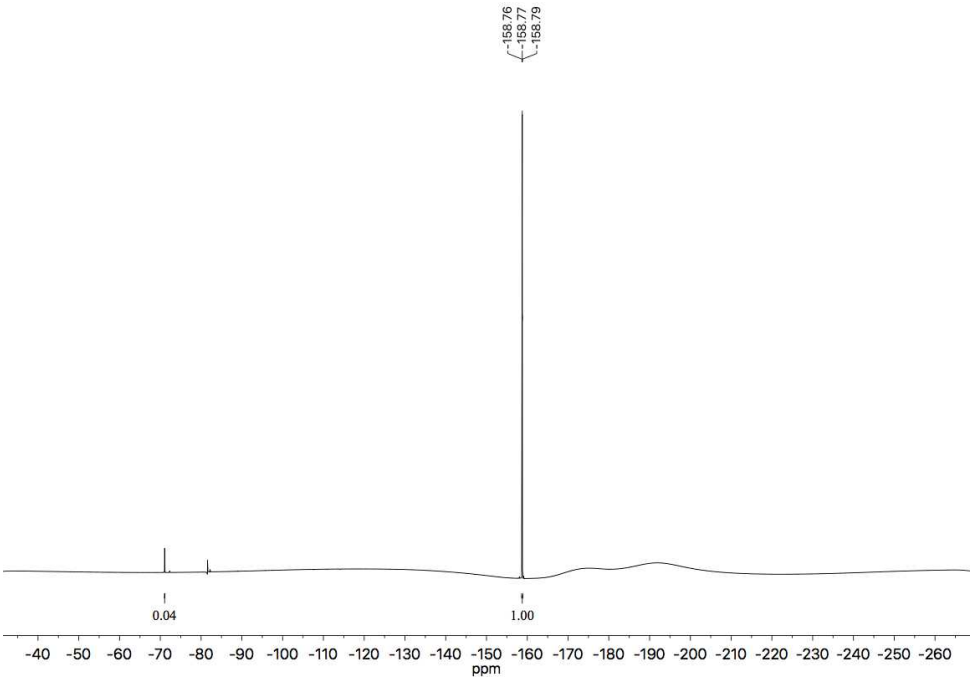
^{1}H NMR (600 MHz, CD_2Cl_2) – **2b**

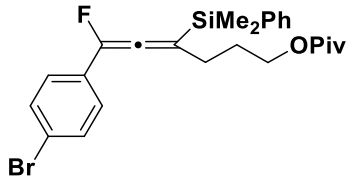


^{13}C NMR (151 MHz, CD_2Cl_2) – **2b**

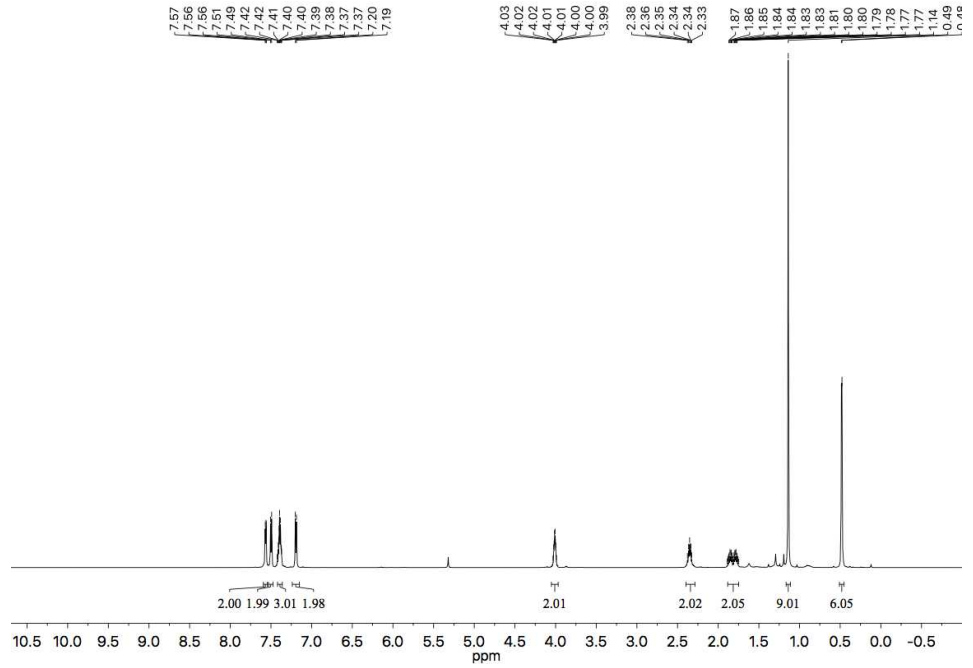


^{19}F NMR (565 MHz, CD_2Cl_2) – **2b**

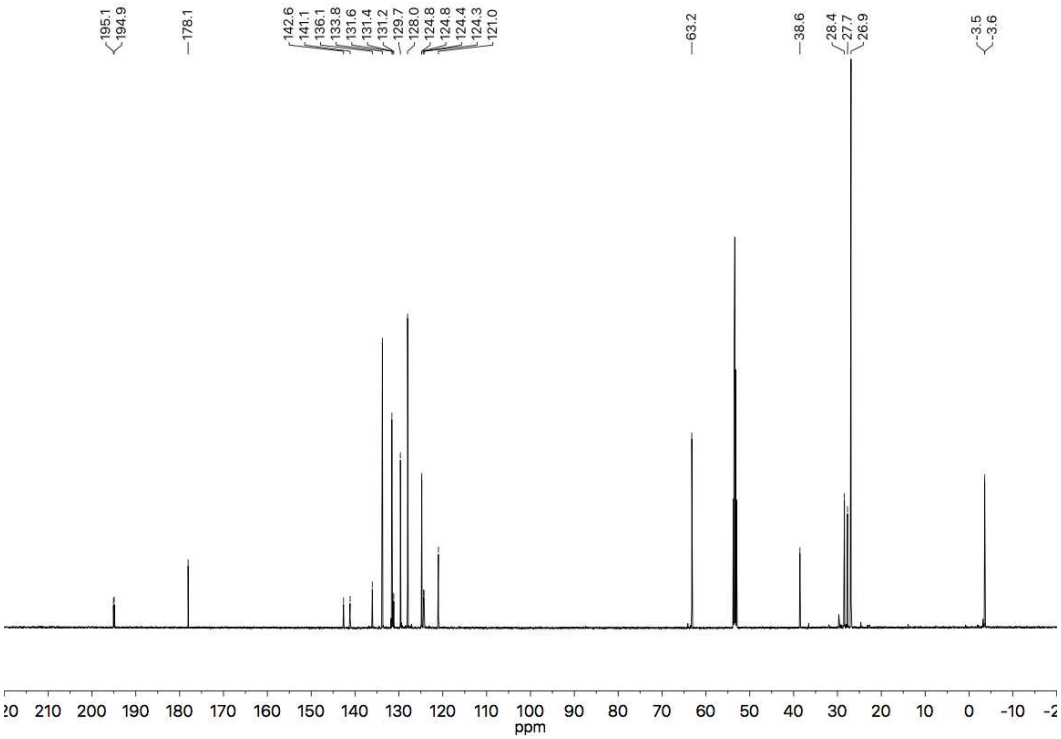




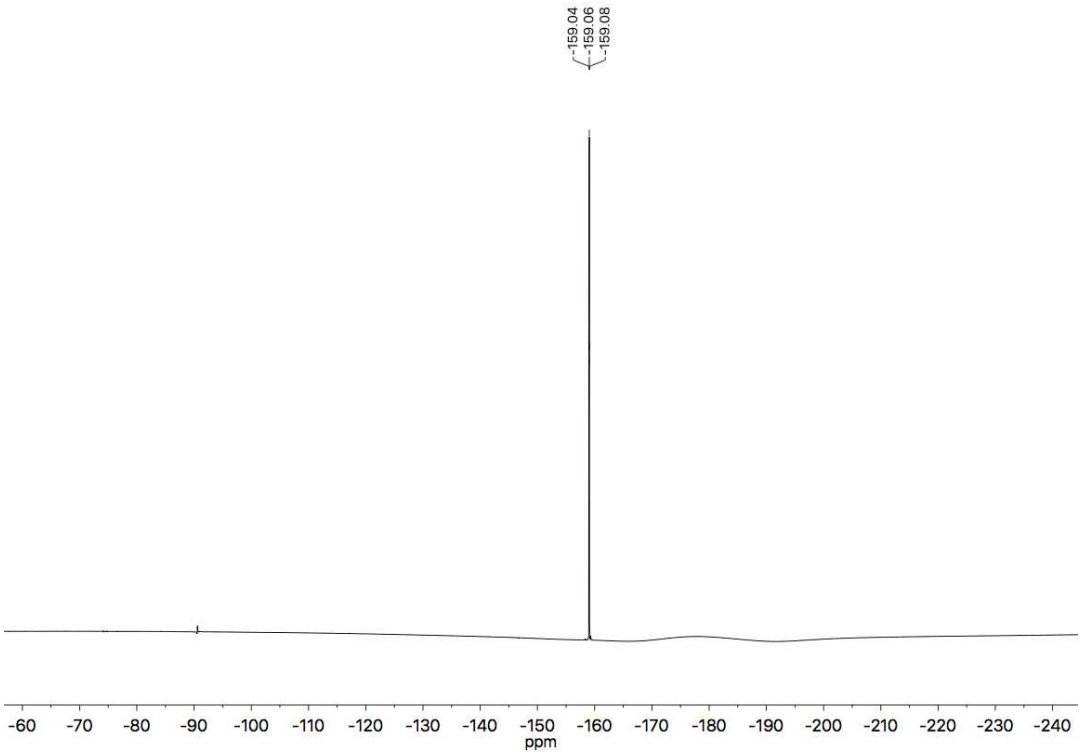
^{1}H NMR (600 MHz, CD_2Cl_2) – **3b**

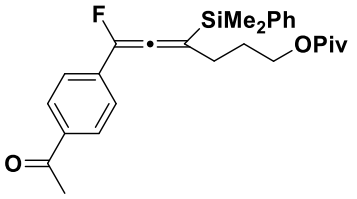


^{13}C NMR (151 MHz, CD_2Cl_2) – **3b**

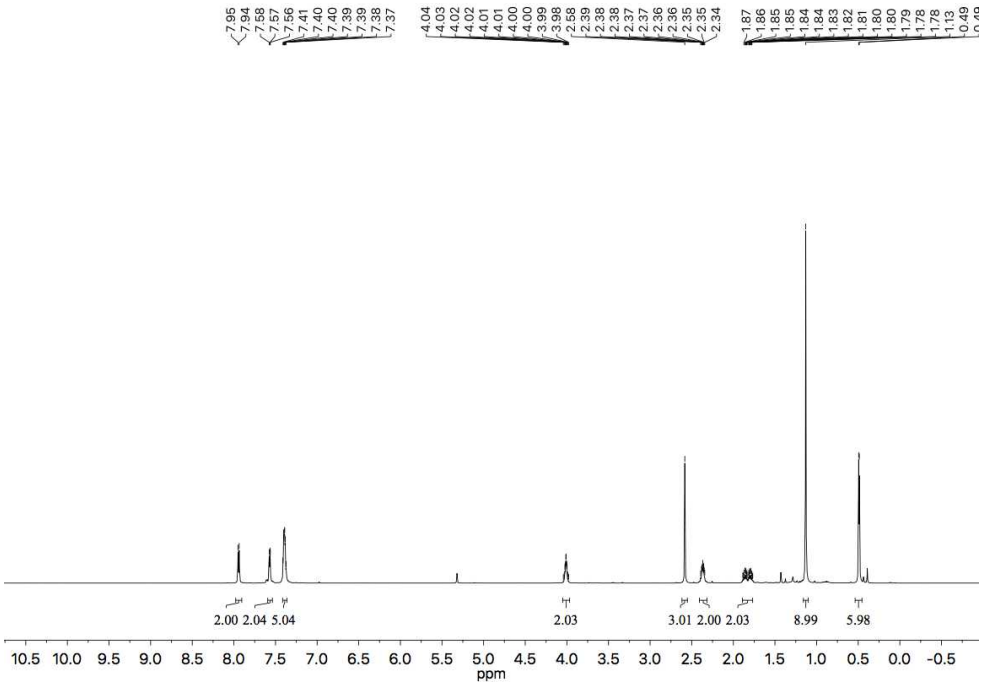


^{19}F NMR (565 MHz, CD_2Cl_2) – **3b**

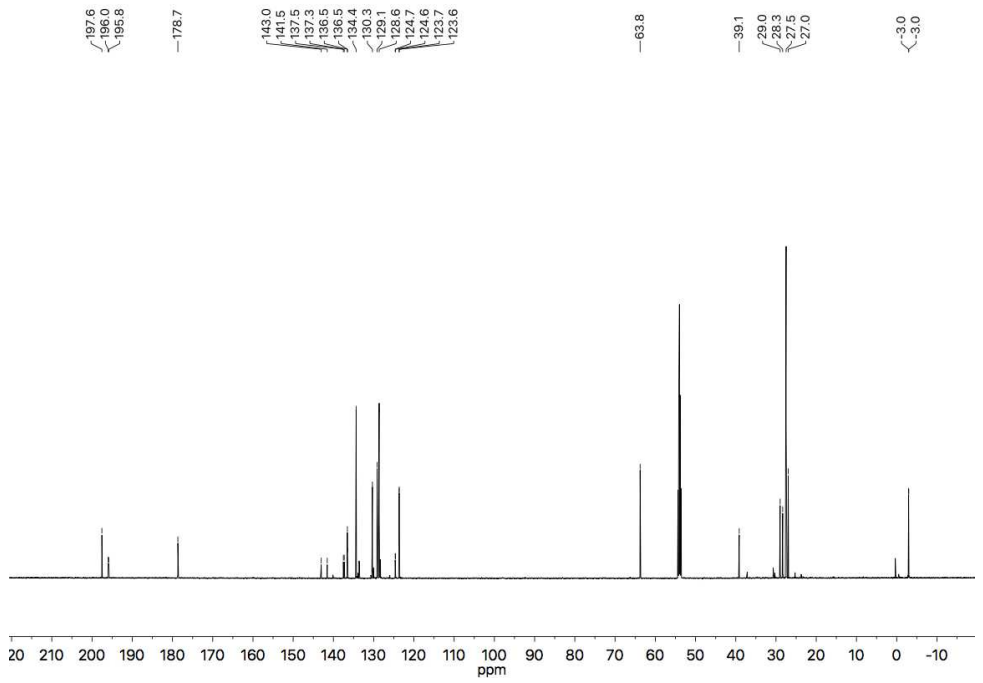




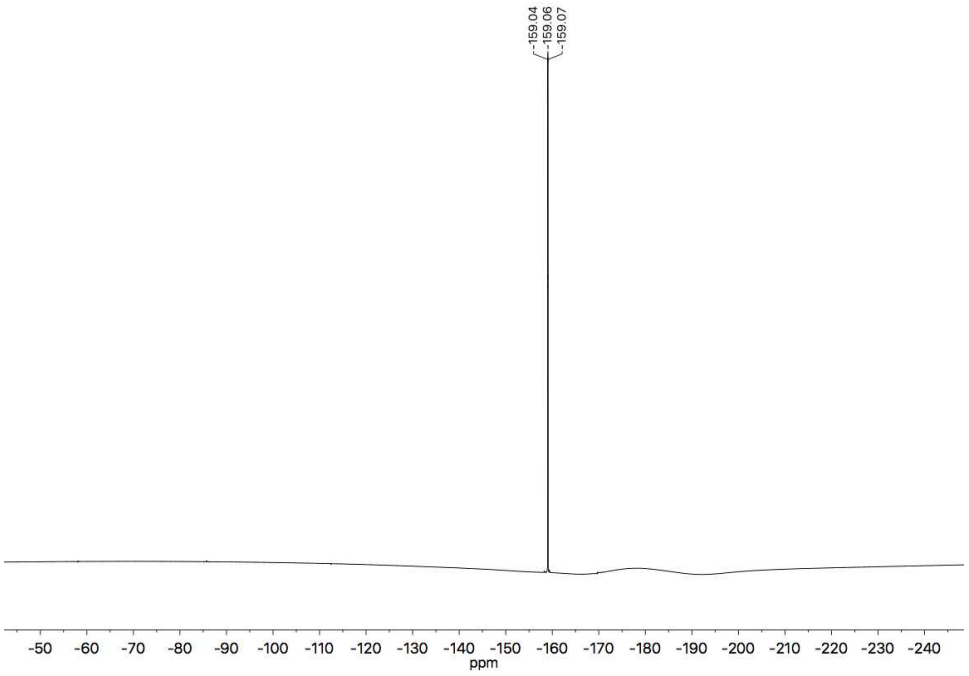
^{1}H NMR (600 MHz, CD_2Cl_2) – **4b**

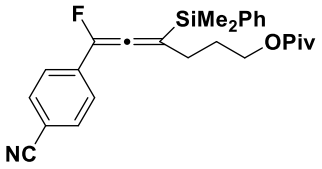


^{13}C NMR (151 MHz, CD_2Cl_2) – **4b**

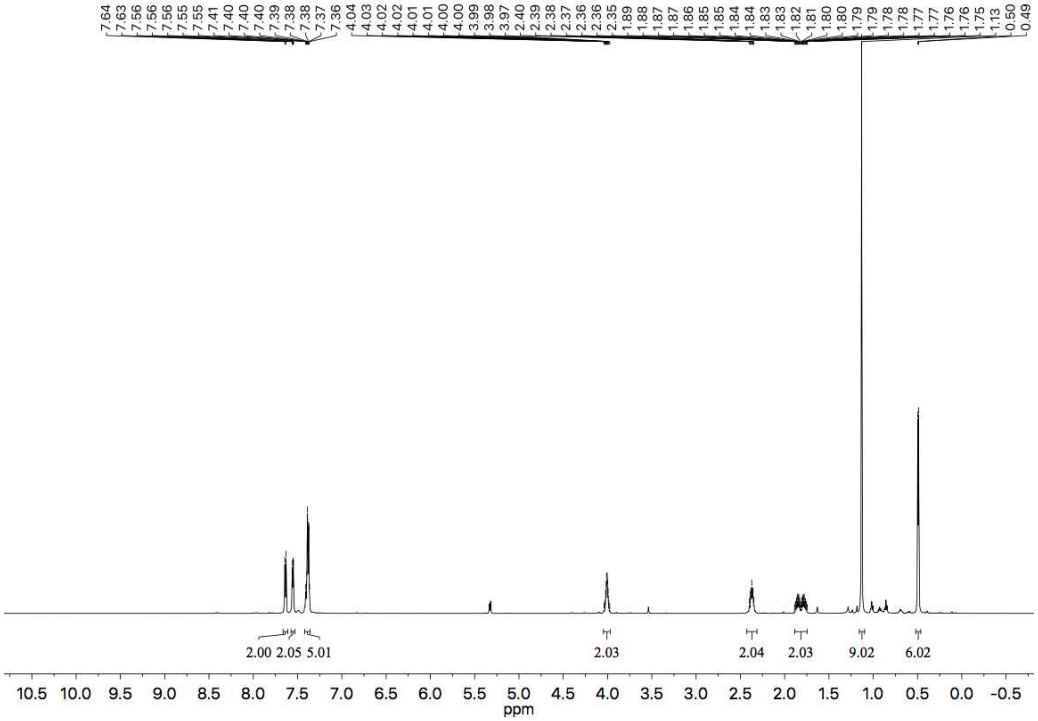


^{19}F NMR (565 MHz, CD_2Cl_2) – **4b**

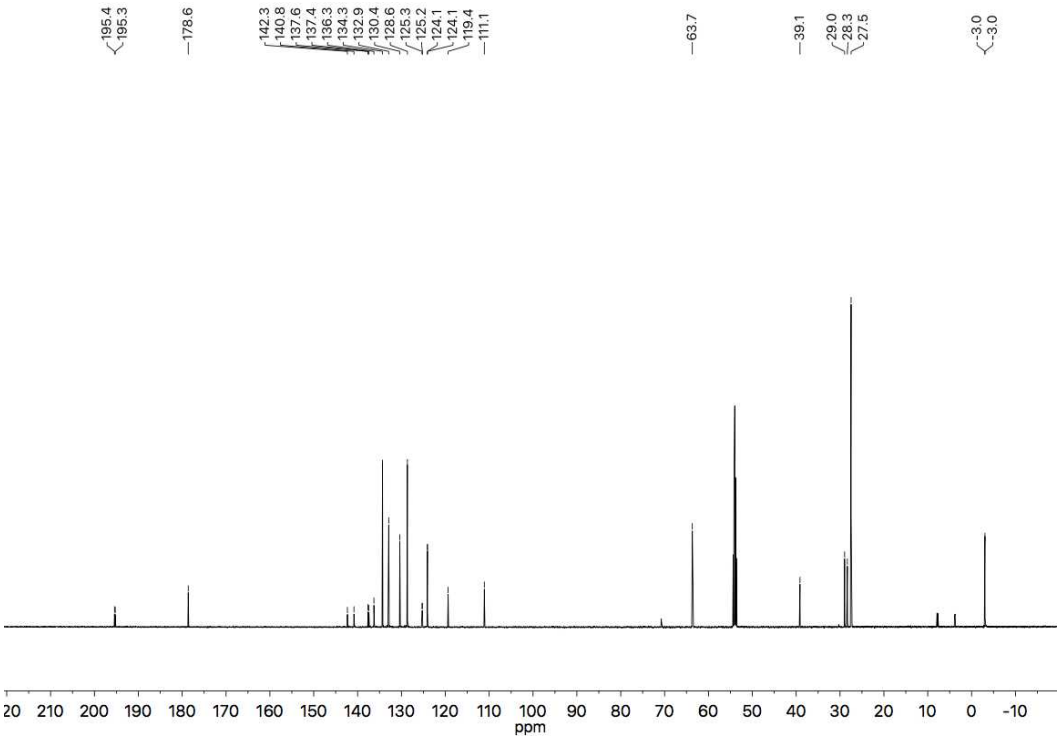




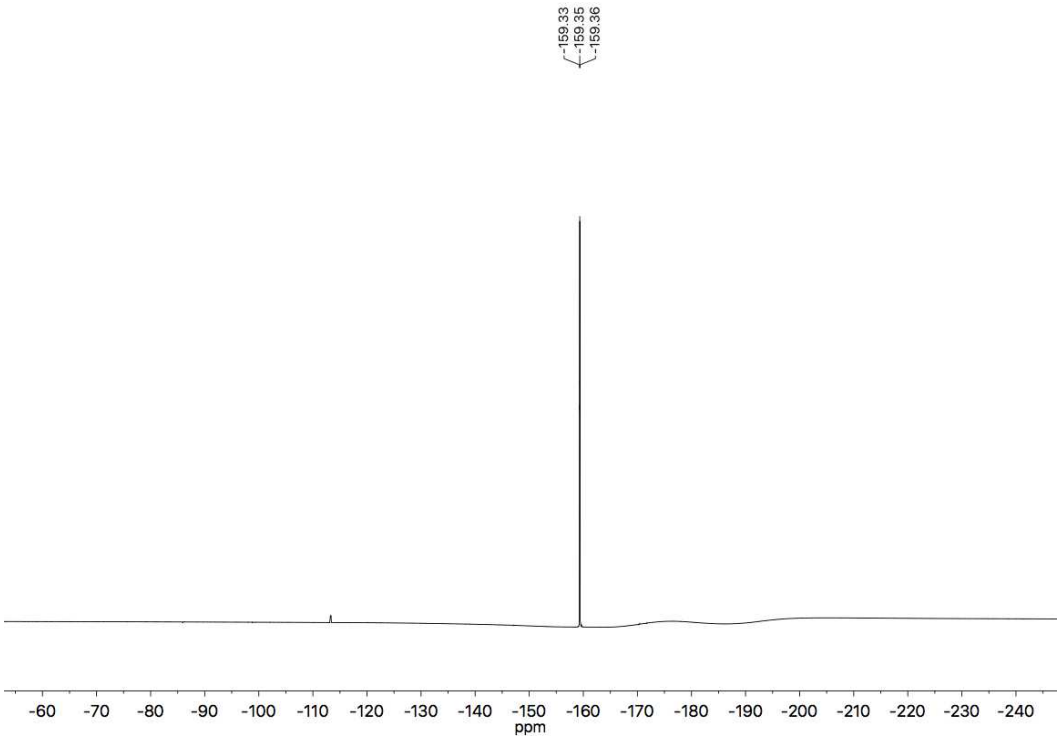
^{1}H NMR (600 MHz, CD_2Cl_2) – **5b**

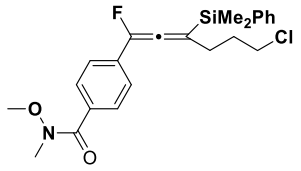


^{13}C NMR (151 MHz, CD_2Cl_2) – **5b**

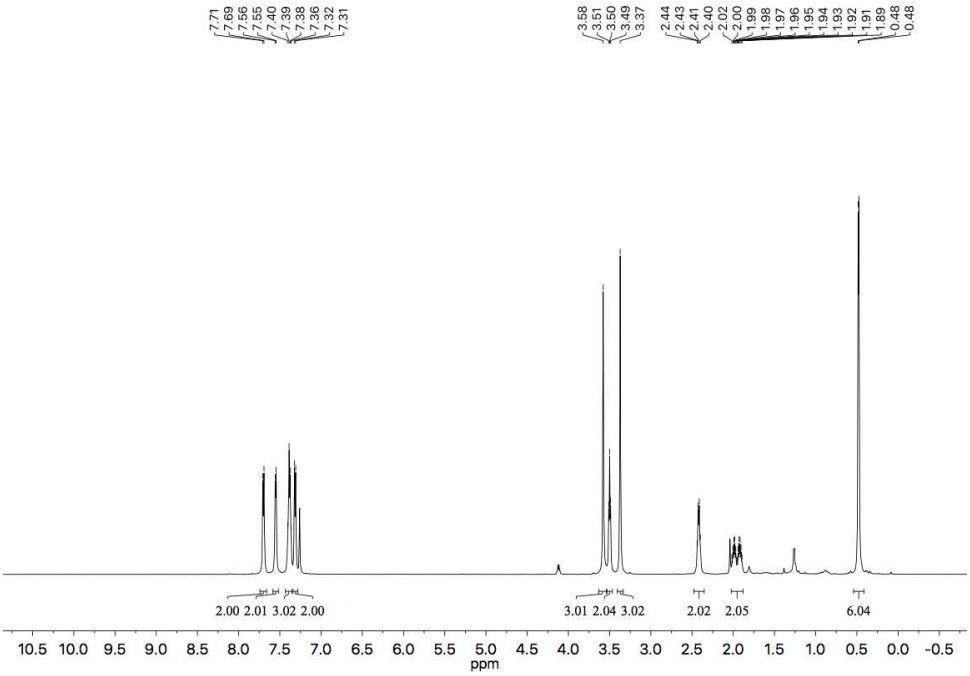


^{19}F NMR (565 MHz, CD_2Cl_2) – **5b**

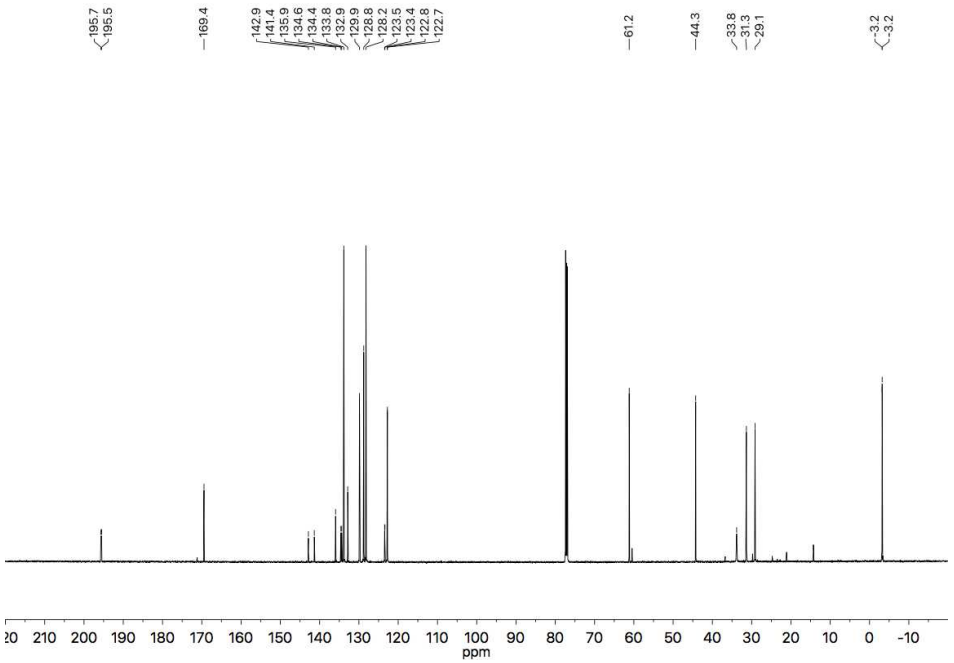




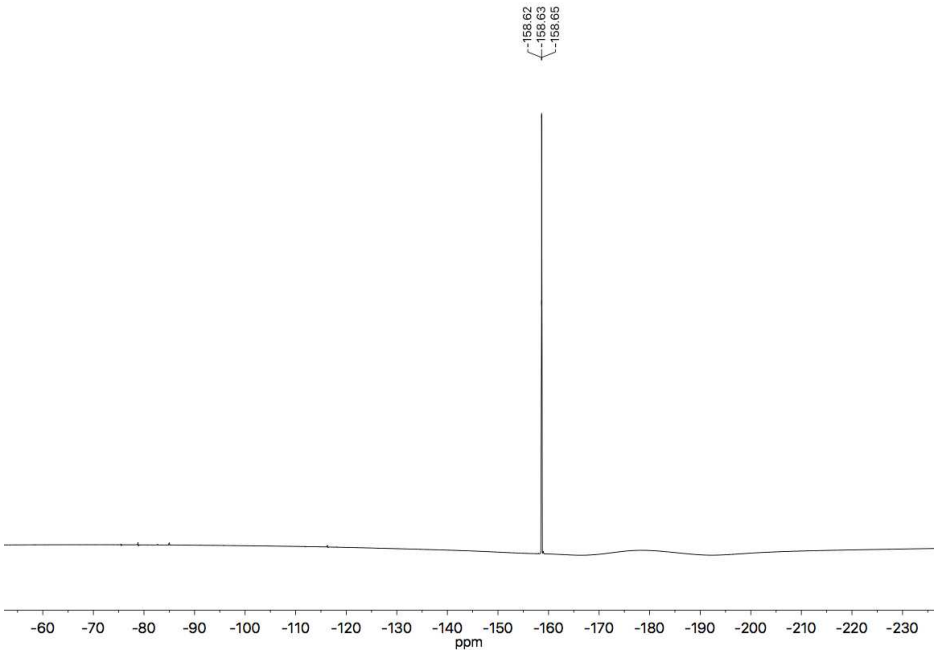
^{1}H NMR (600 MHz, CD_2Cl_2) – **6b**

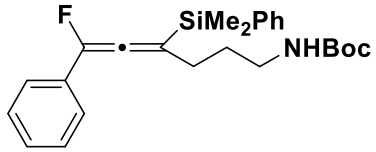


^{13}C NMR (151 MHz, CD_2Cl_2) – **6b**

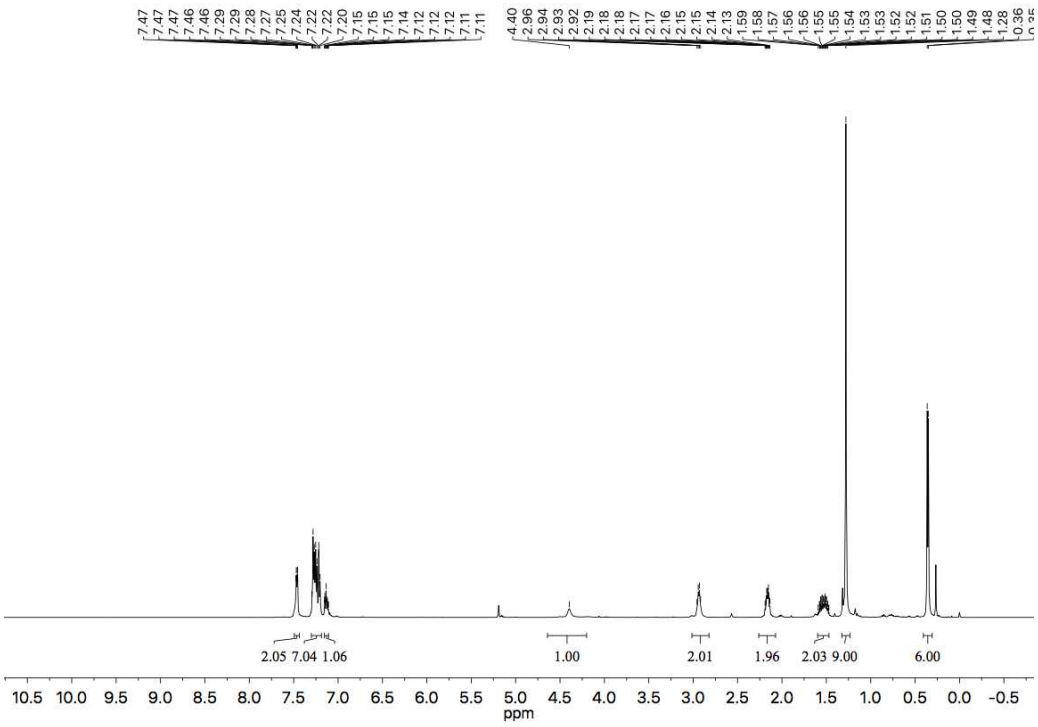


^{19}F NMR (565 MHz, CD_2Cl_2) – **6b**

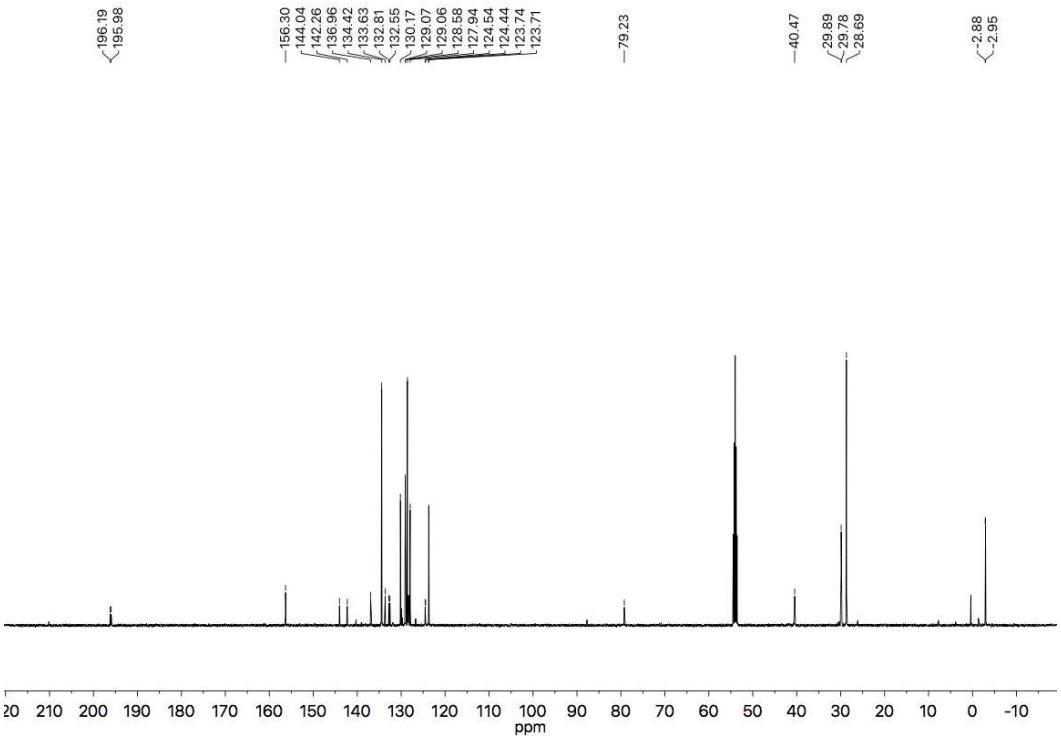




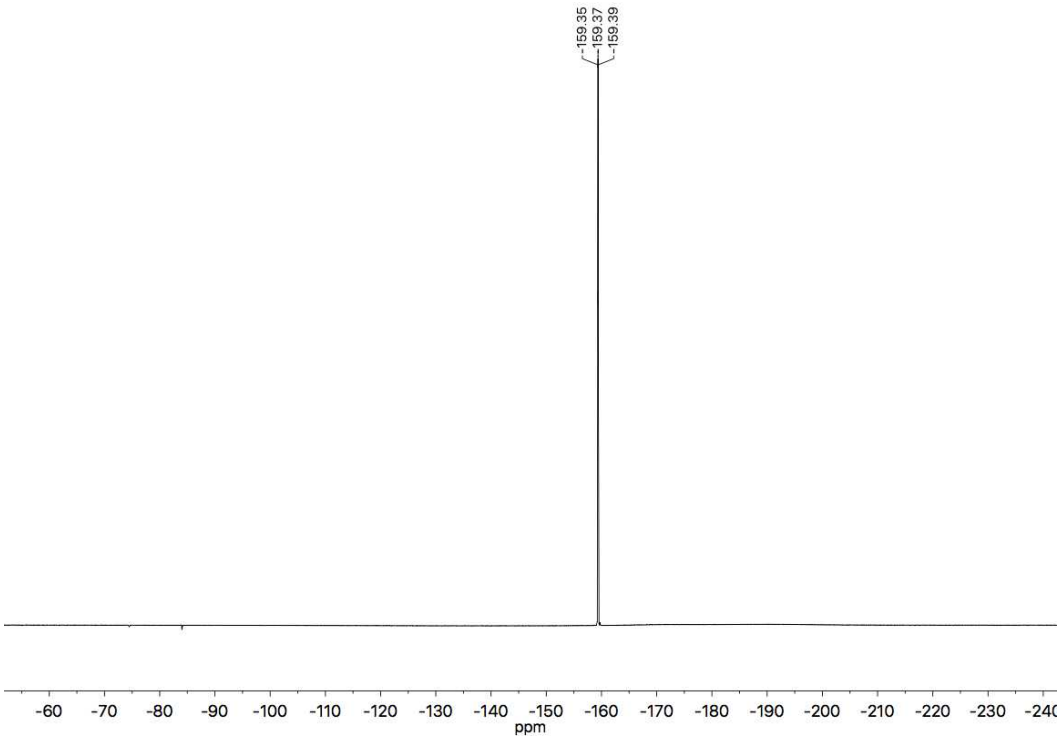
^{1}H NMR (500 MHz, CD_2Cl_2) – **7b**

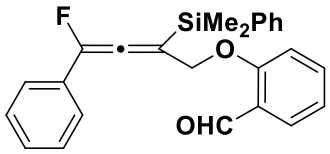


^{13}C NMR (126 MHz, CD_2Cl_2) – **7b**

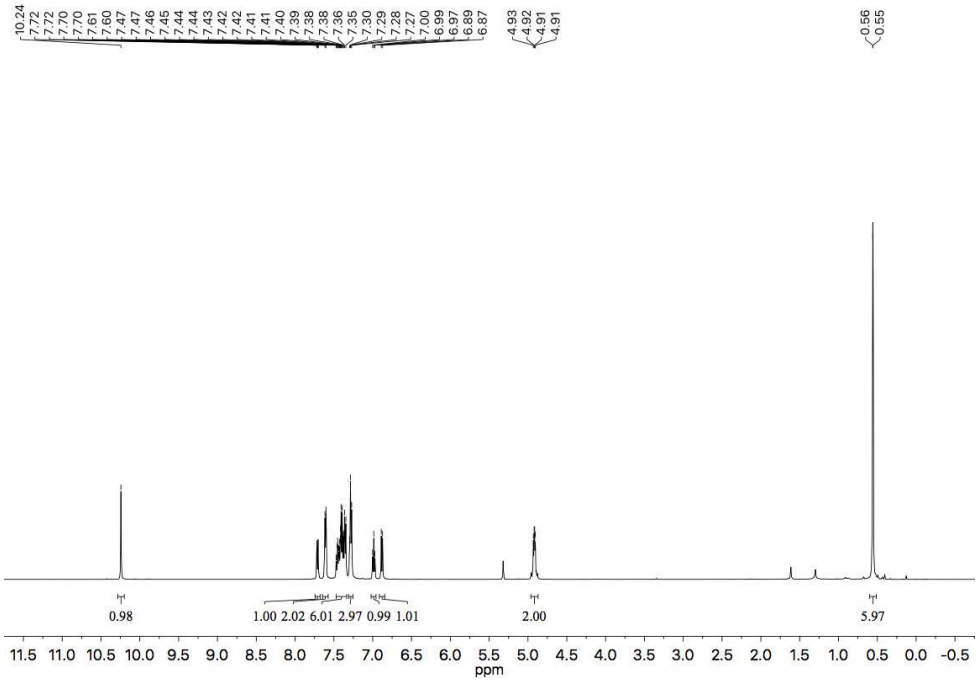


^{19}F NMR (470 MHz, CD_2Cl_2) – **7b**

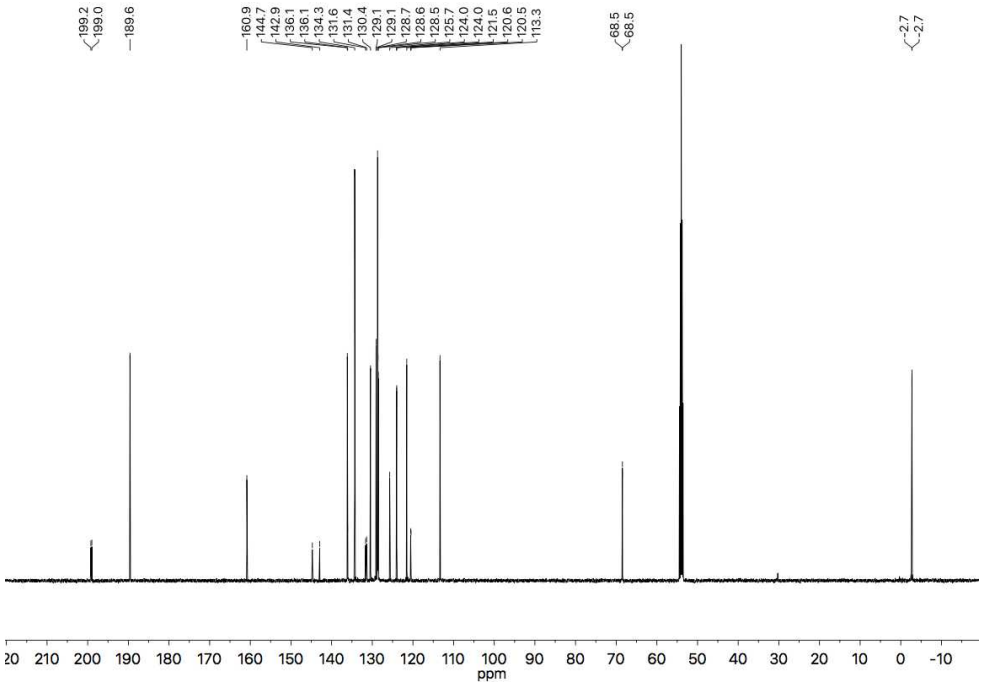




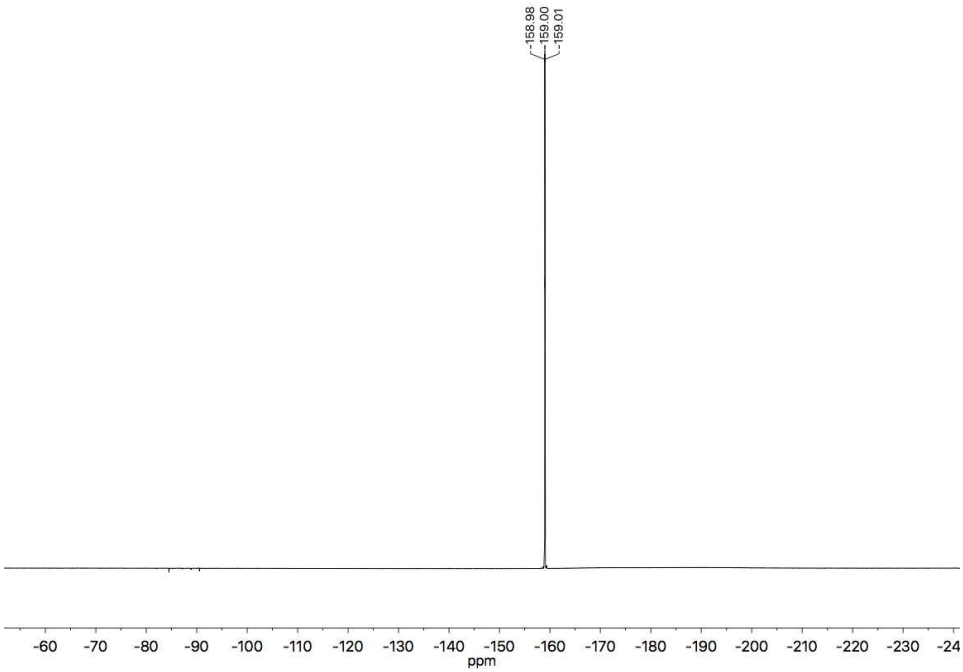
^{1}H NMR (500 MHz, CD_2Cl_2) – **8b**

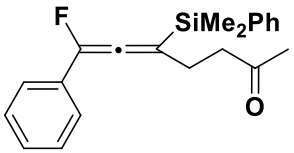


^{13}C NMR (126 MHz, CD_2Cl_2) – **8b**

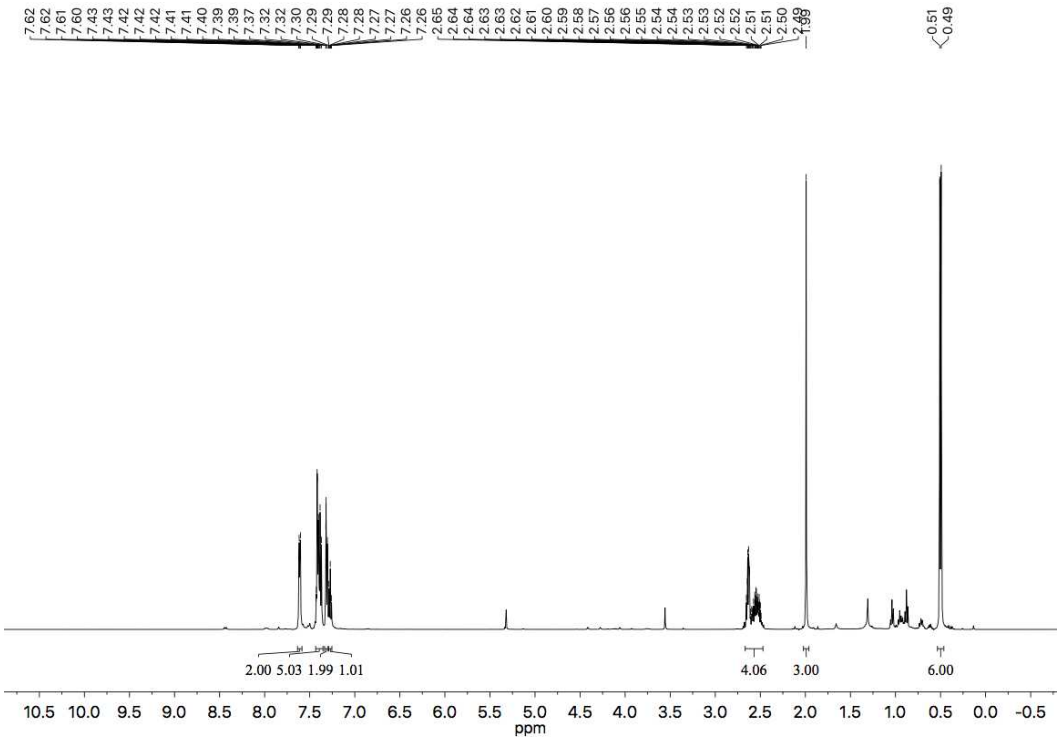


^{19}F NMR (470 MHz, CD_2Cl_2) – **8b**

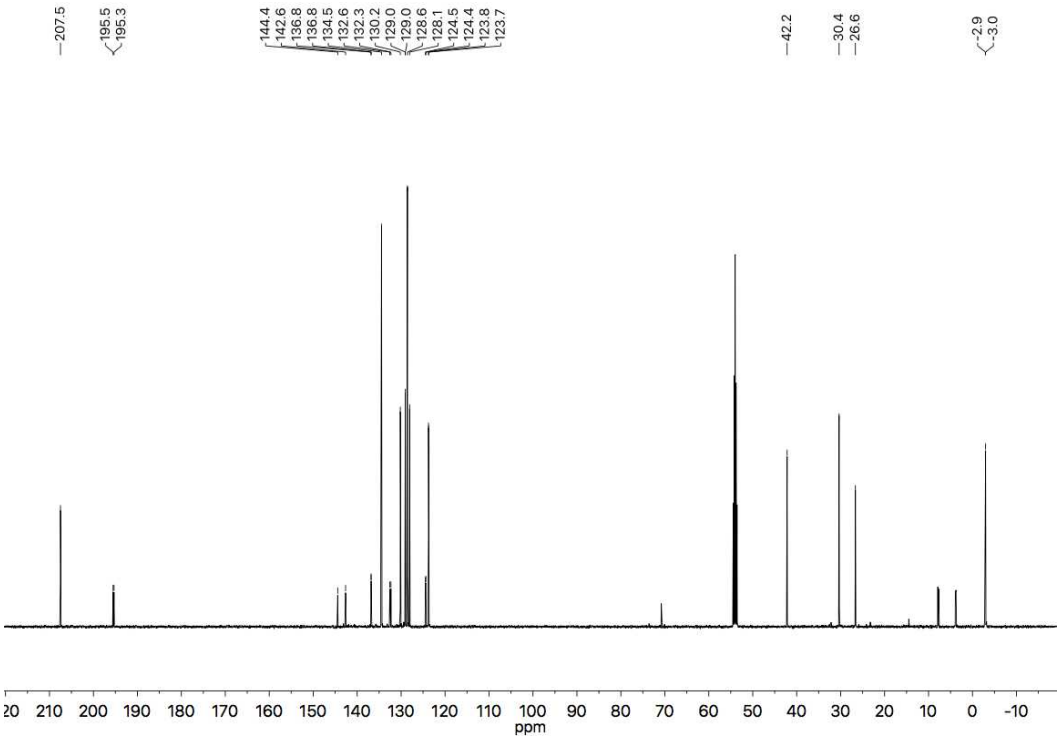




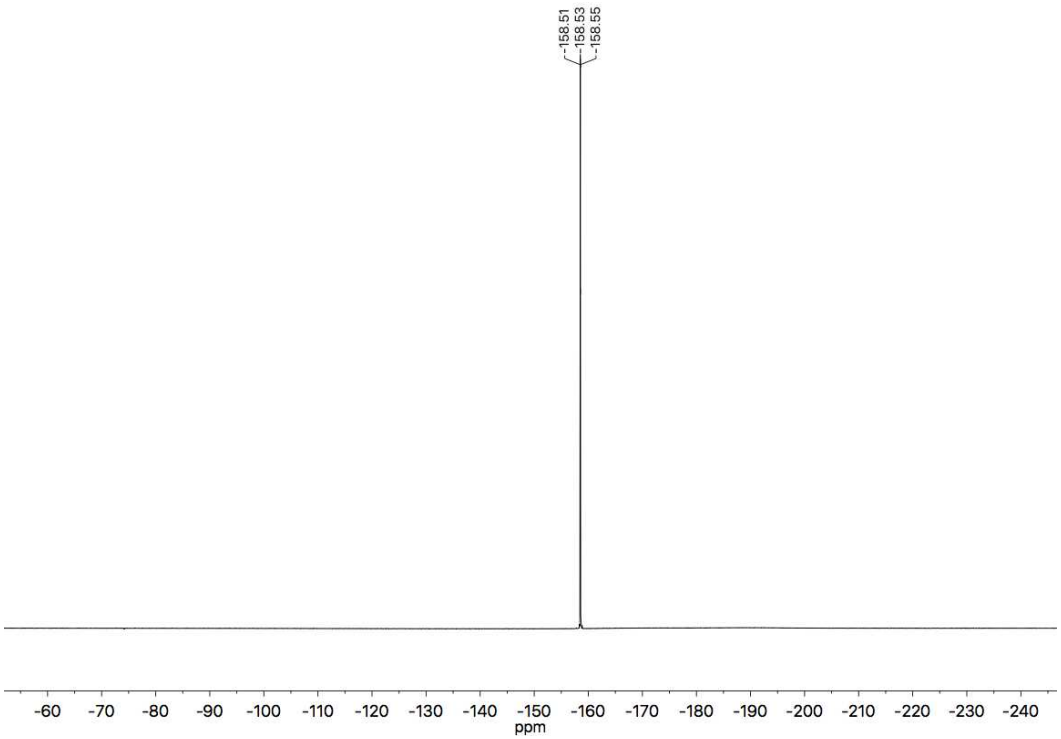
^{1}H NMR (500 MHz, CD_2Cl_2) – **9b**

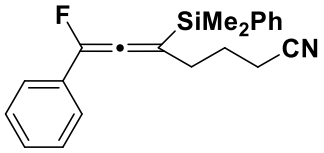


^{13}C NMR (126 MHz, CD_2Cl_2) – **9b**

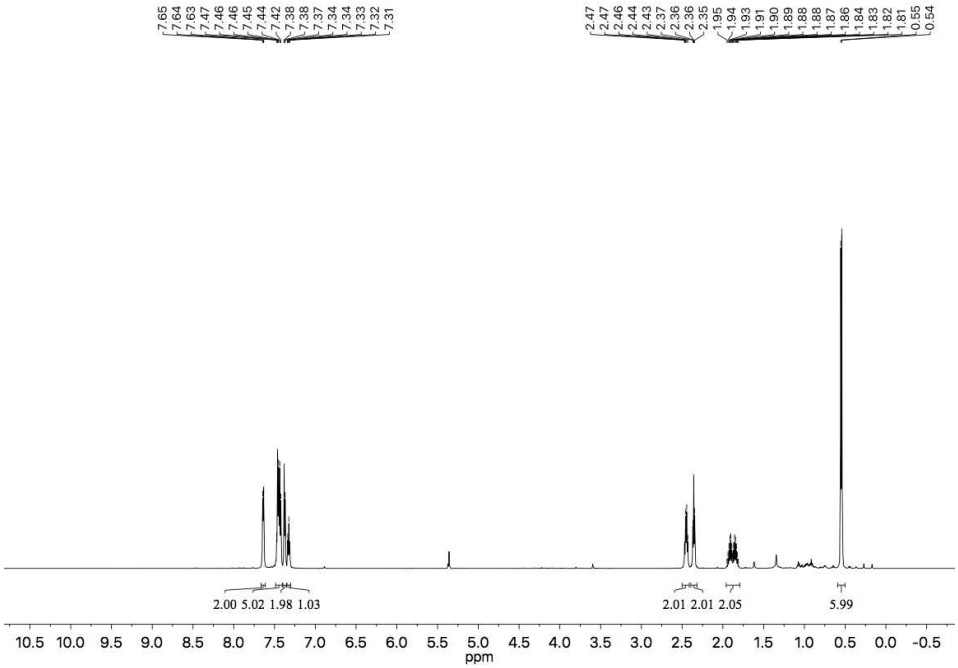


^{19}F NMR (470 MHz, CD_2Cl_2) – **9b**

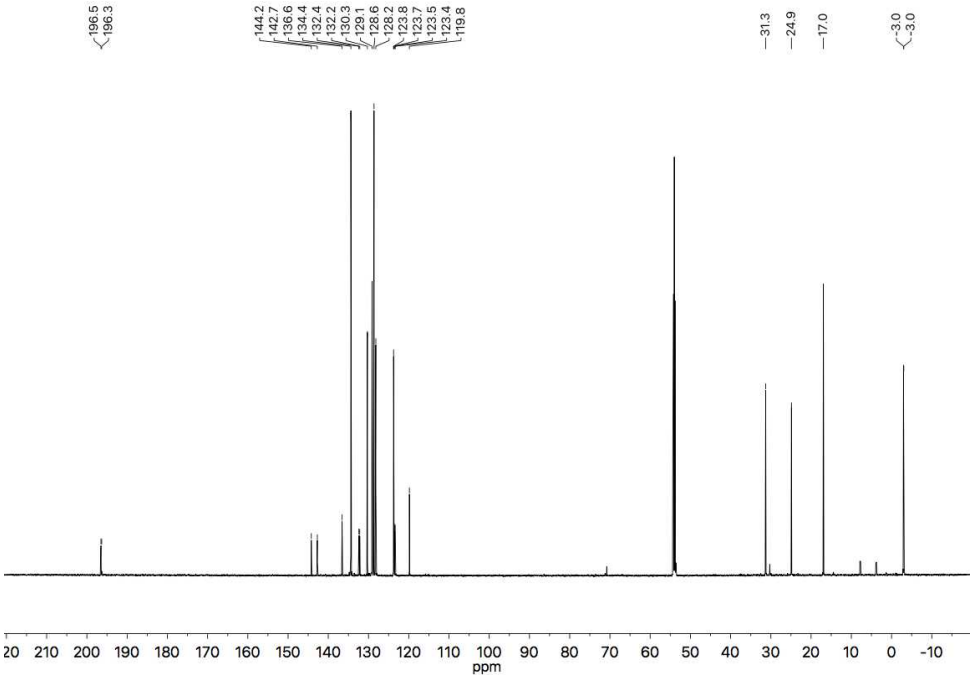




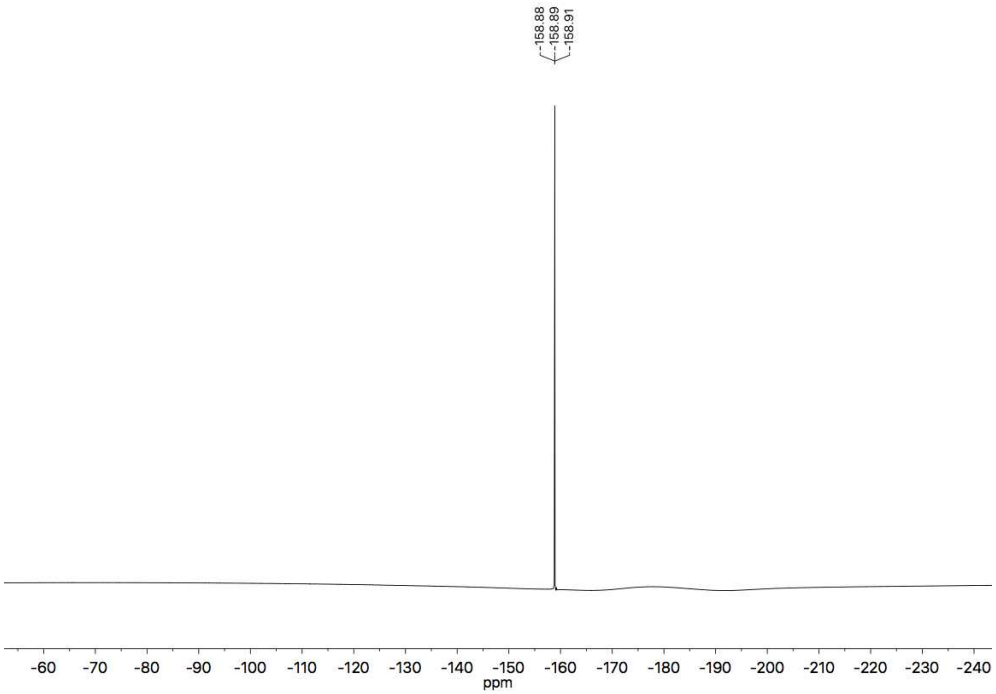
^{1}H NMR (600 MHz, CD_2Cl_2) – **10b**

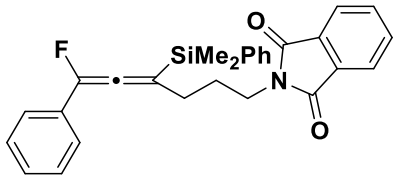


^{13}C NMR (151 MHz, CD_2Cl_2) – **10b**

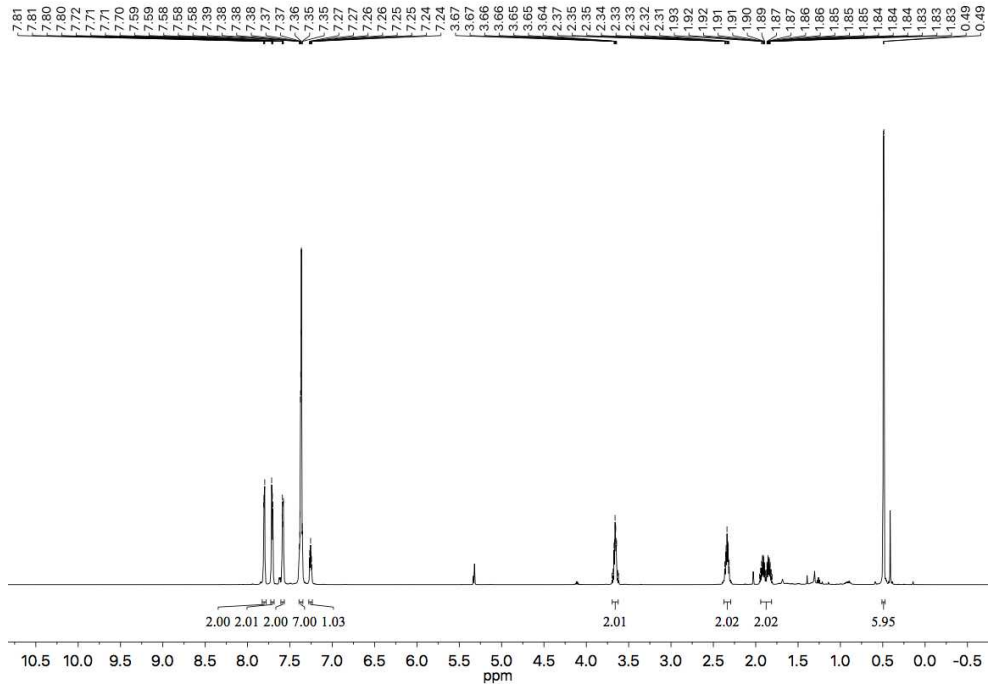


^{19}F NMR (565 MHz, CD_2Cl_2) – **10b**

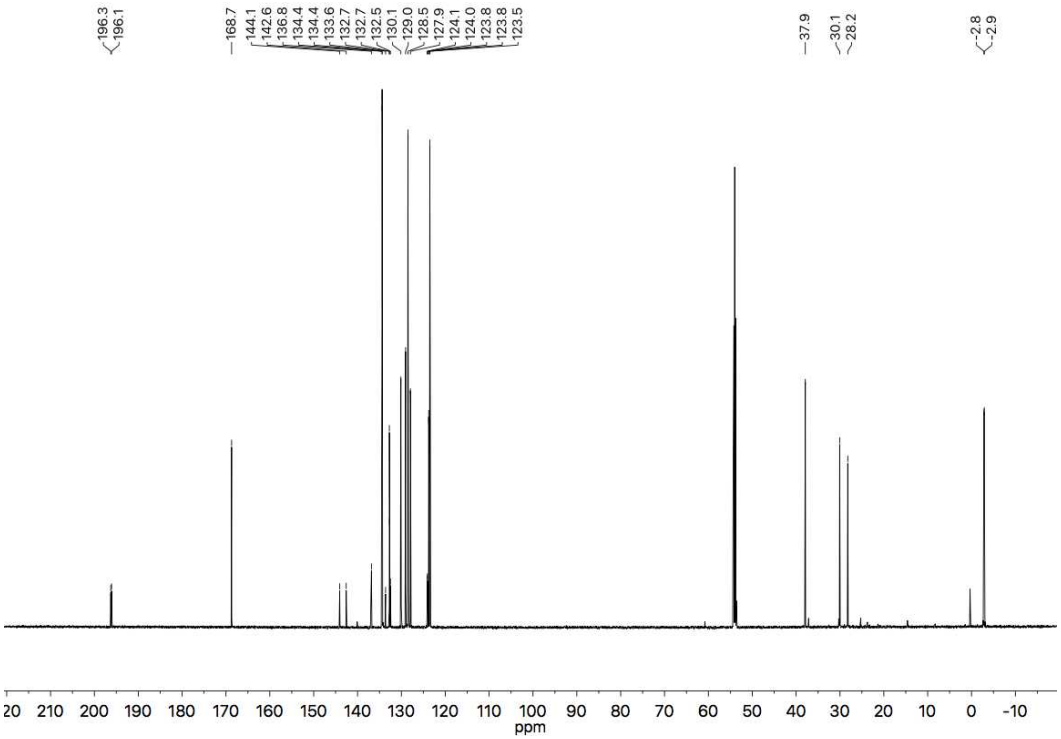




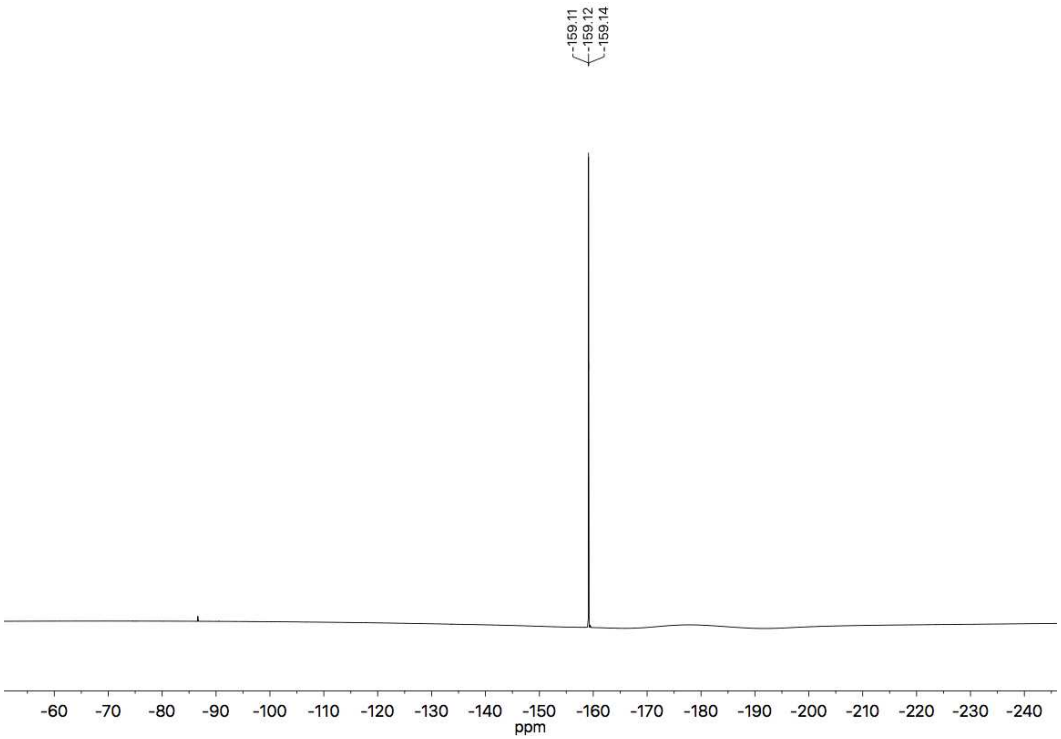
^{1}H NMR (600 MHz, CD_2Cl_2) – **11b**

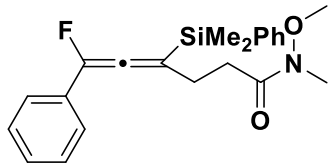


^{13}C NMR (151 MHz, CD_2Cl_2) – **11b**

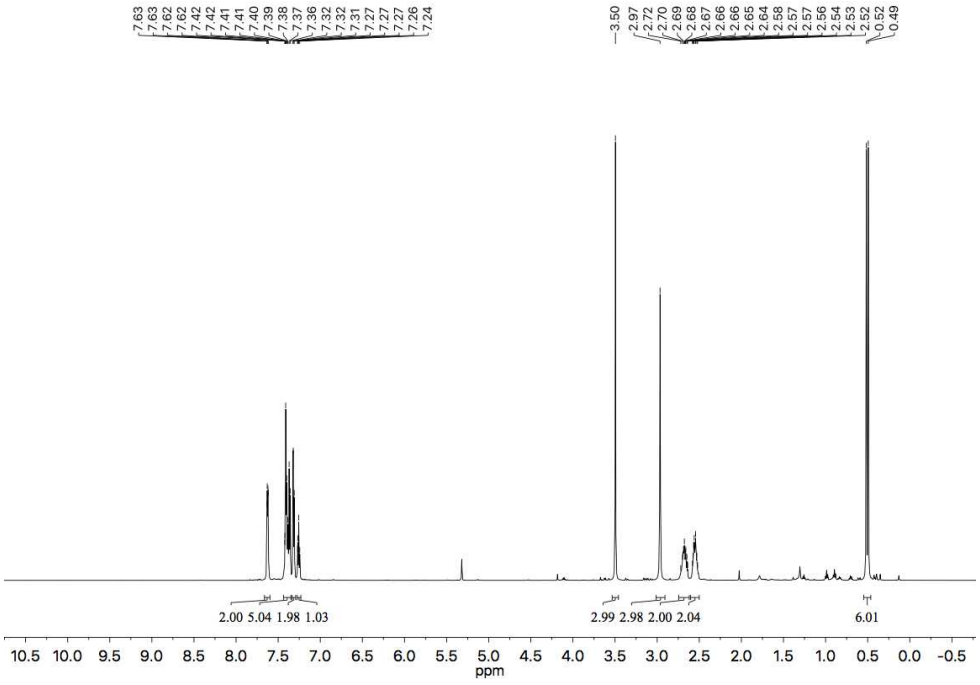


^{19}F NMR (565 MHz, CD_2Cl_2) – **11b**

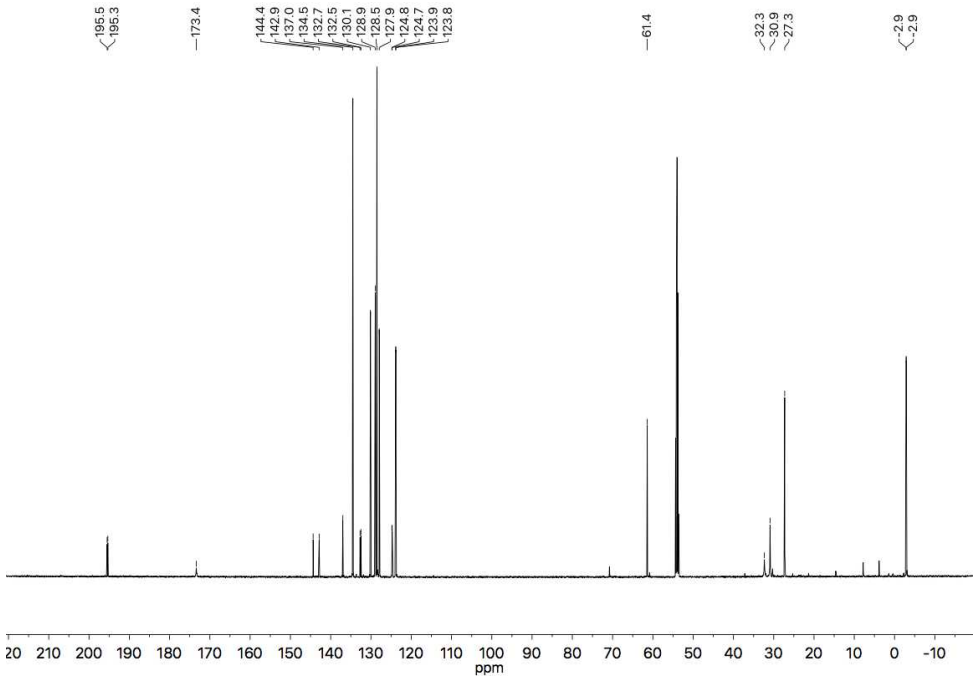




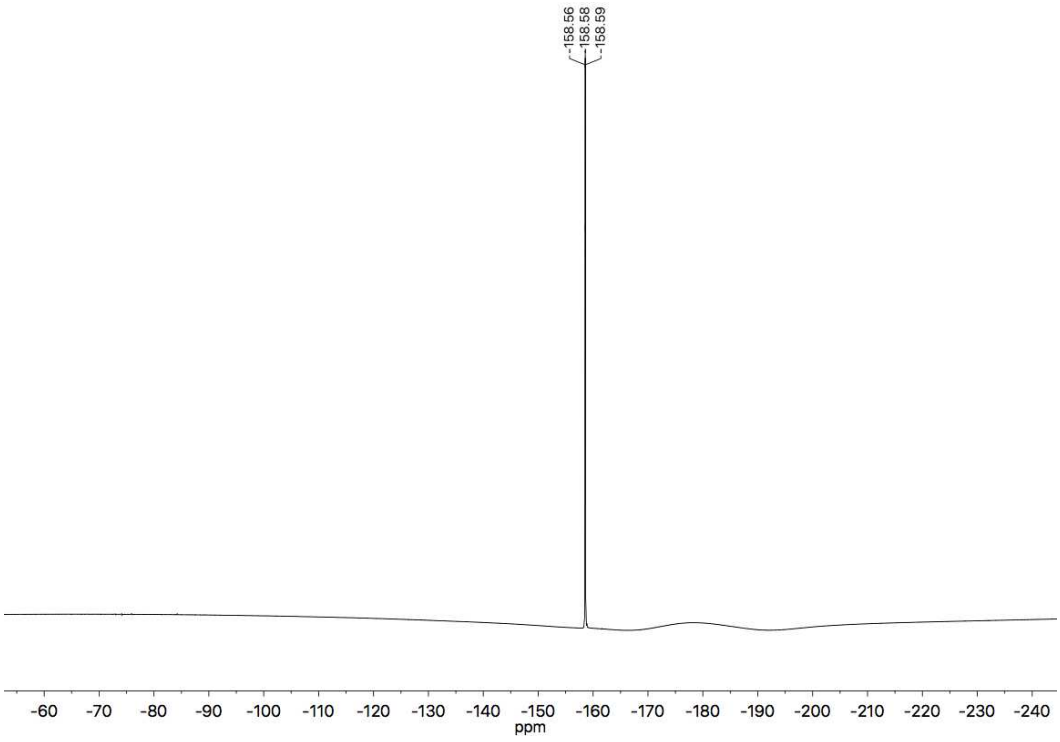
^{1}H NMR (600 MHz, CD_2Cl_2) – **12b**

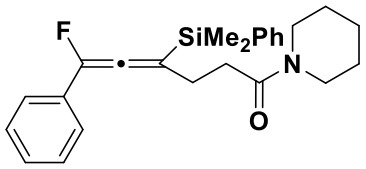


^{13}C NMR (151 MHz, CD_2Cl_2) – **12b**

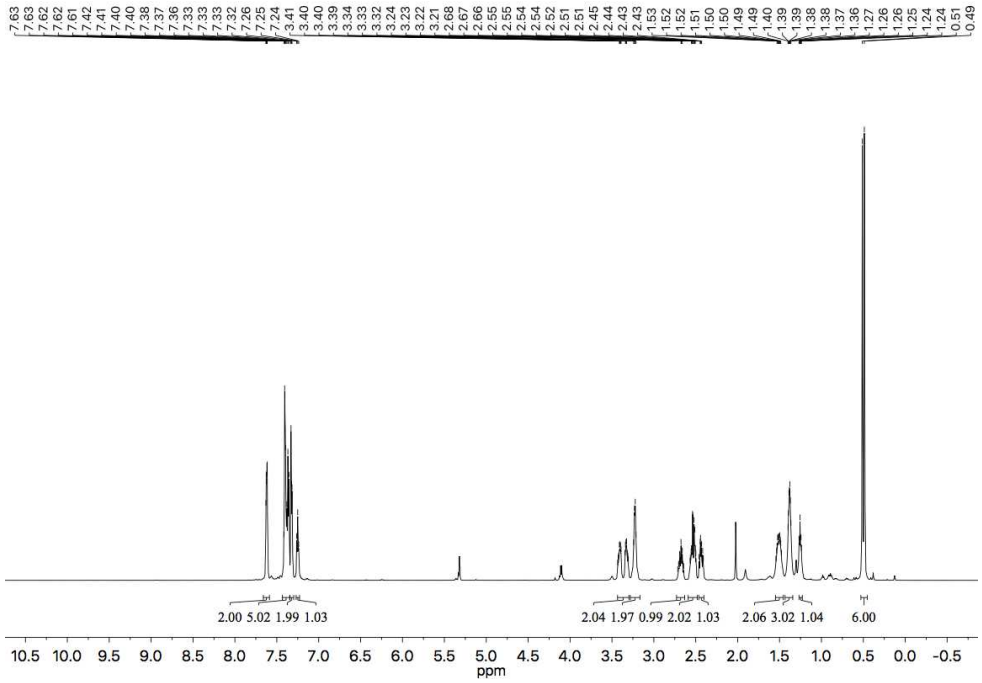


^{19}F NMR (565 MHz, CD_2Cl_2) – **12b**

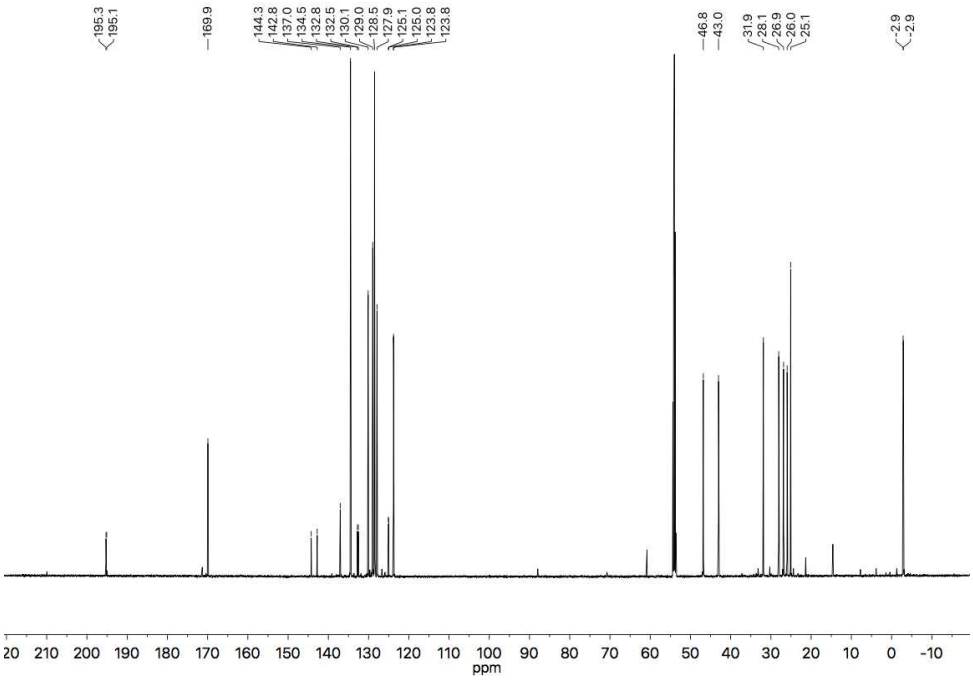




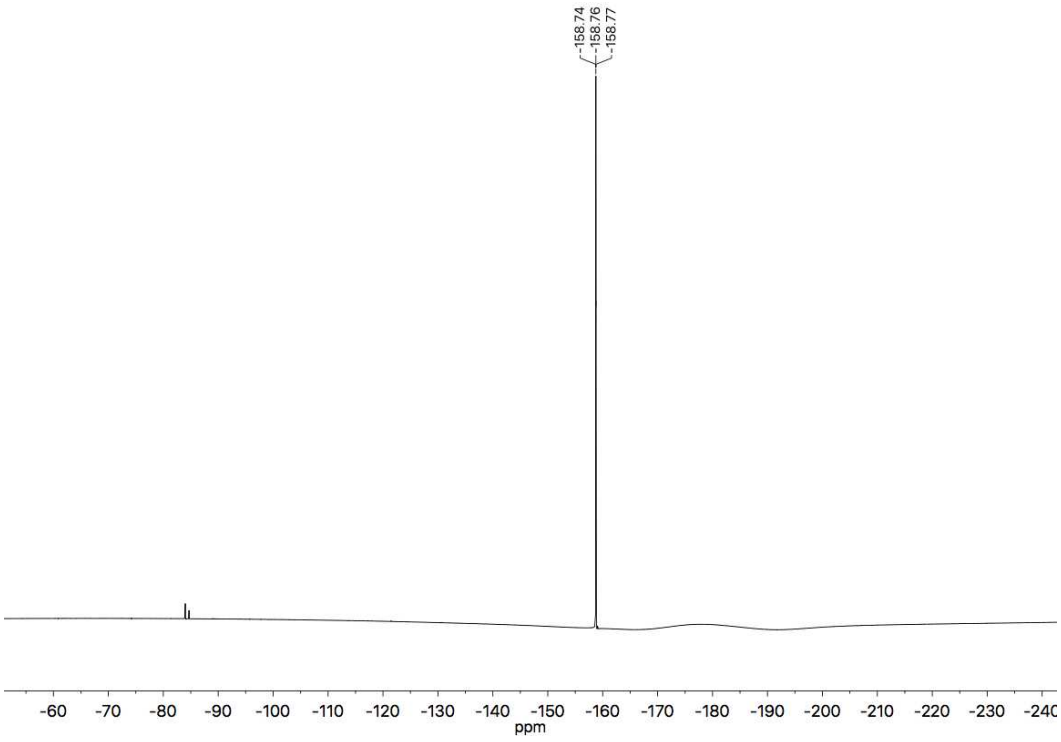
^{1}H NMR (600 MHz, CD_2Cl_2) – **13b**

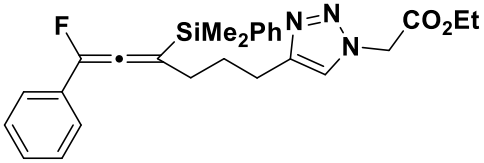


^{13}C NMR (151 MHz, CD_2Cl_2) – **13b**

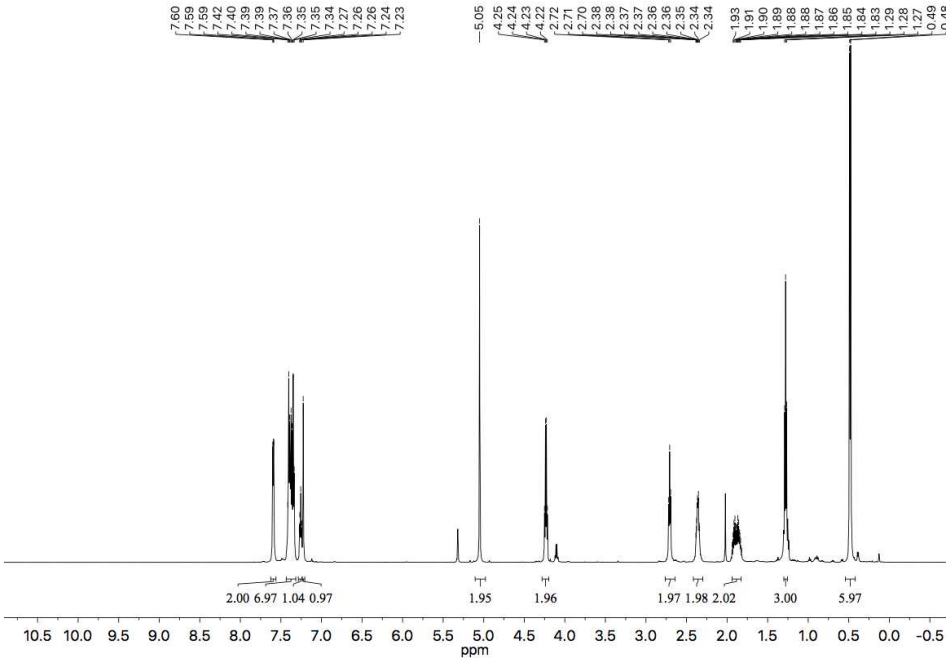


^{19}F NMR (565 MHz, CD_2Cl_2) – **13b**

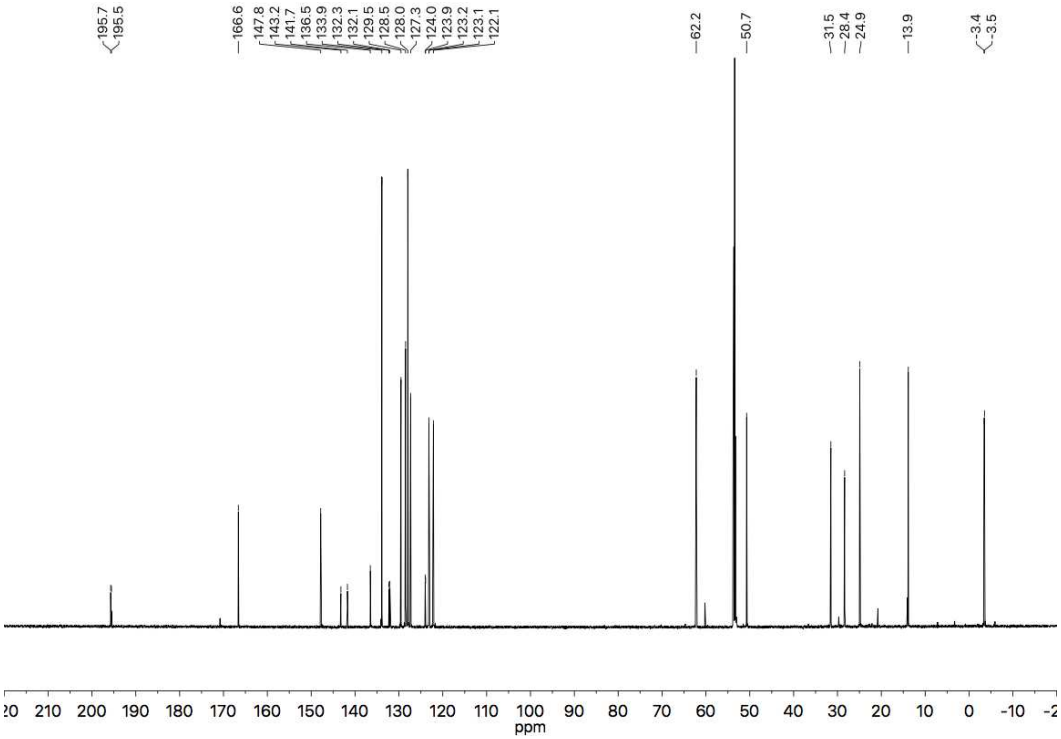




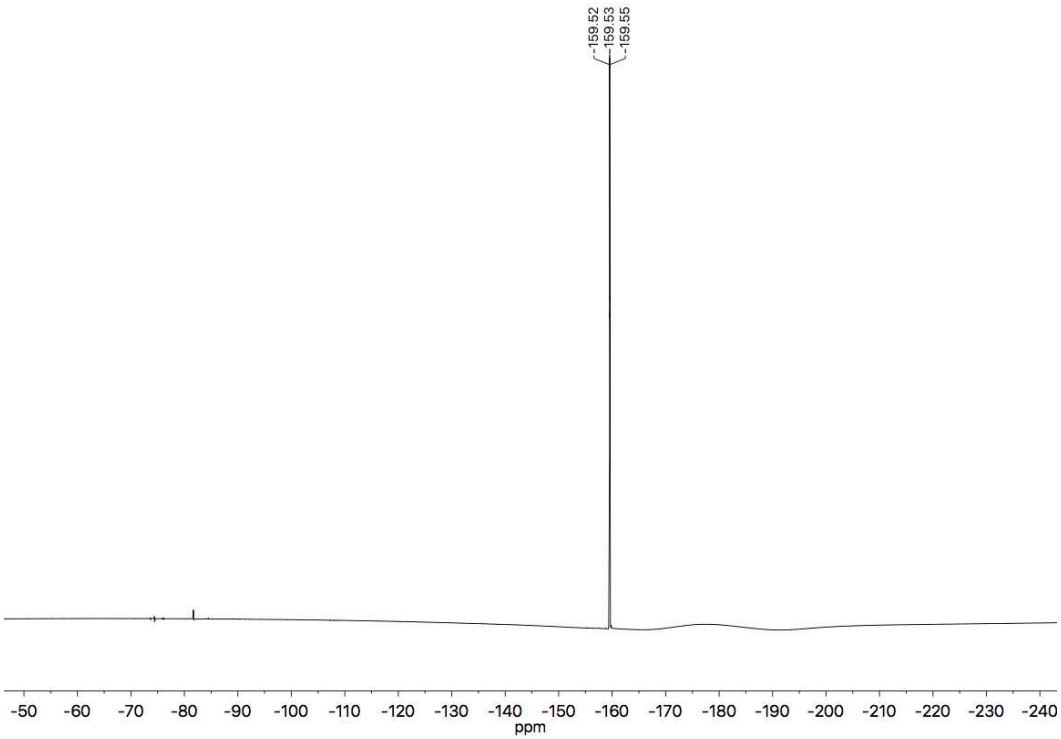
^{1}H NMR (600 MHz, CD_2Cl_2) – **14b**

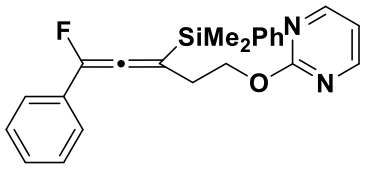


^{13}C NMR (151 MHz, CD_2Cl_2) – **14b**

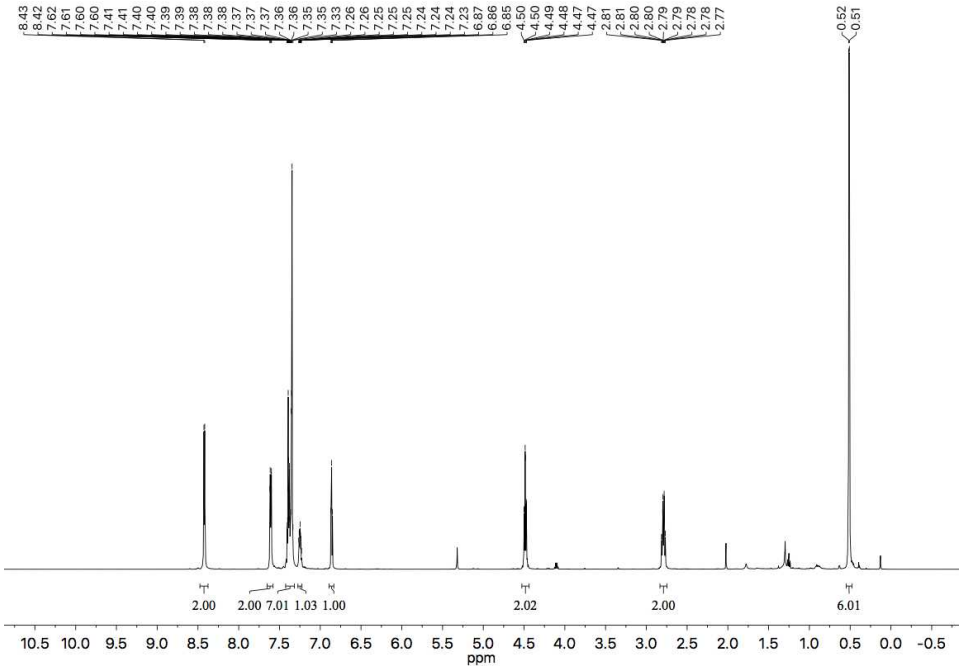


^{19}F NMR (565 MHz, CD_2Cl_2) – **14b**

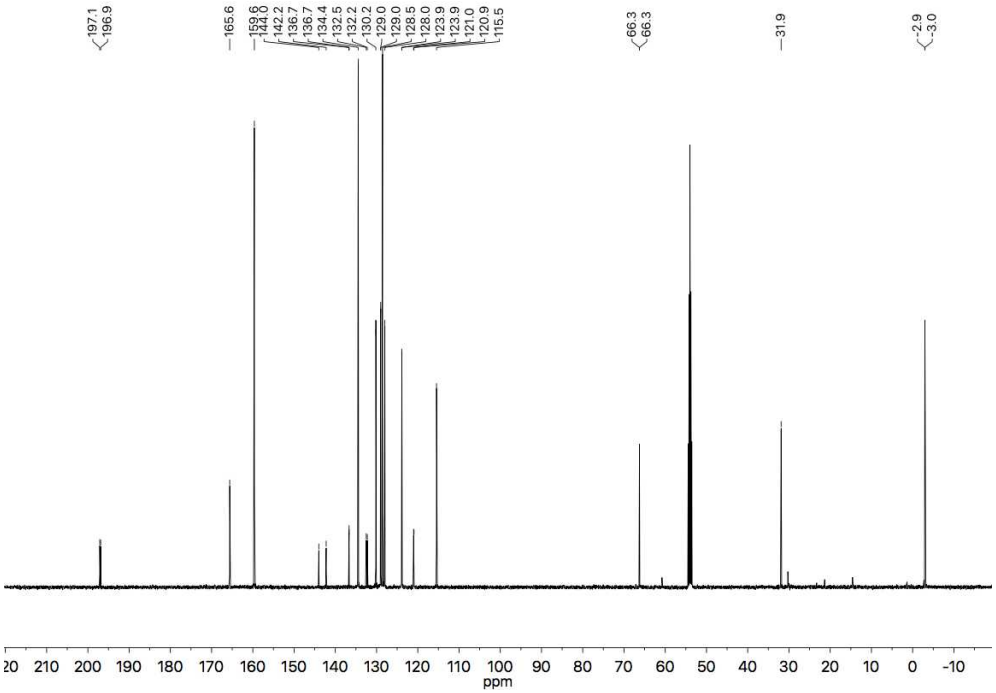




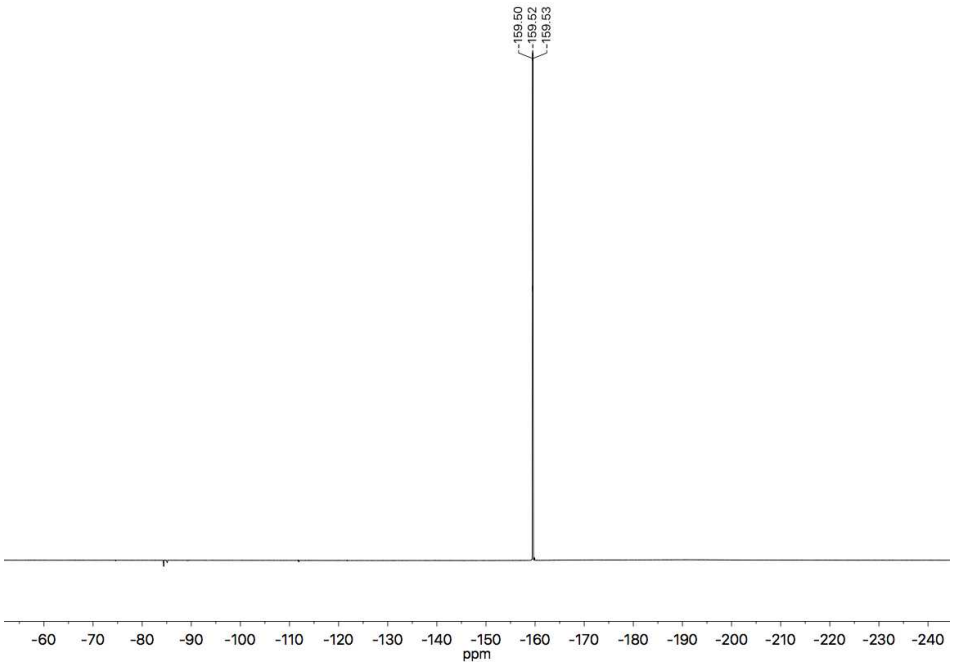
^{1}H NMR (500 MHz, CD_2Cl_2) – **15b**

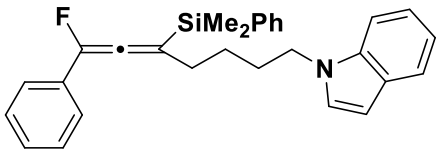


^{13}C NMR (126 MHz, CD_2Cl_2) – **15b**

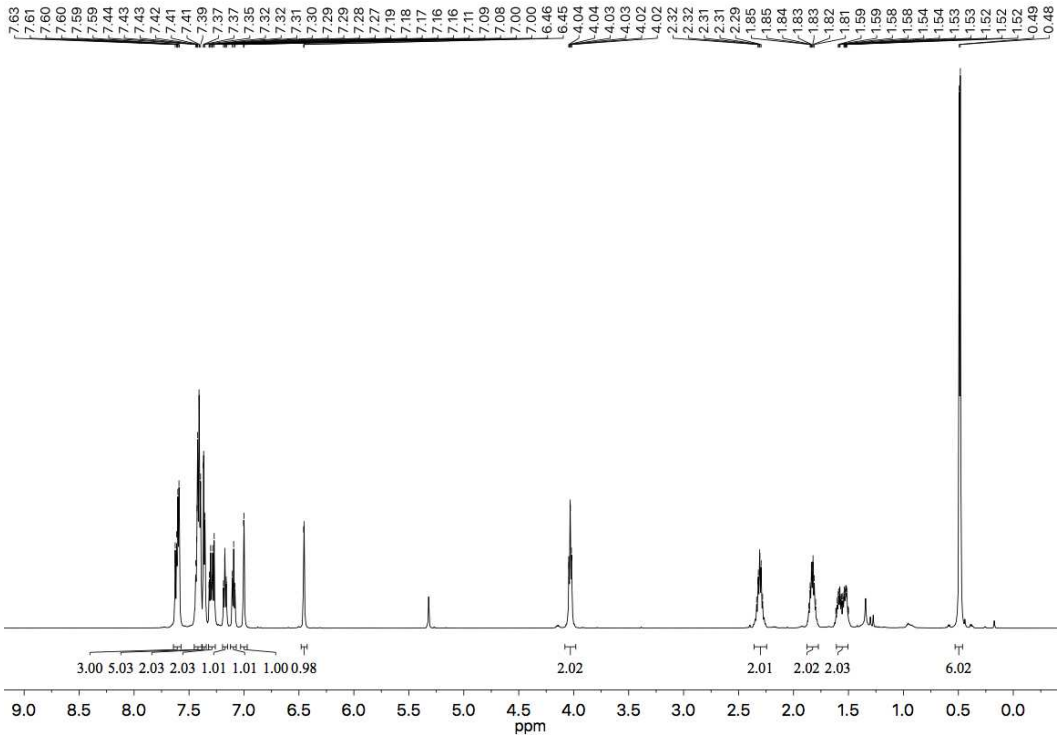


^{19}F NMR (470 MHz, CD_2Cl_2) – **15b**

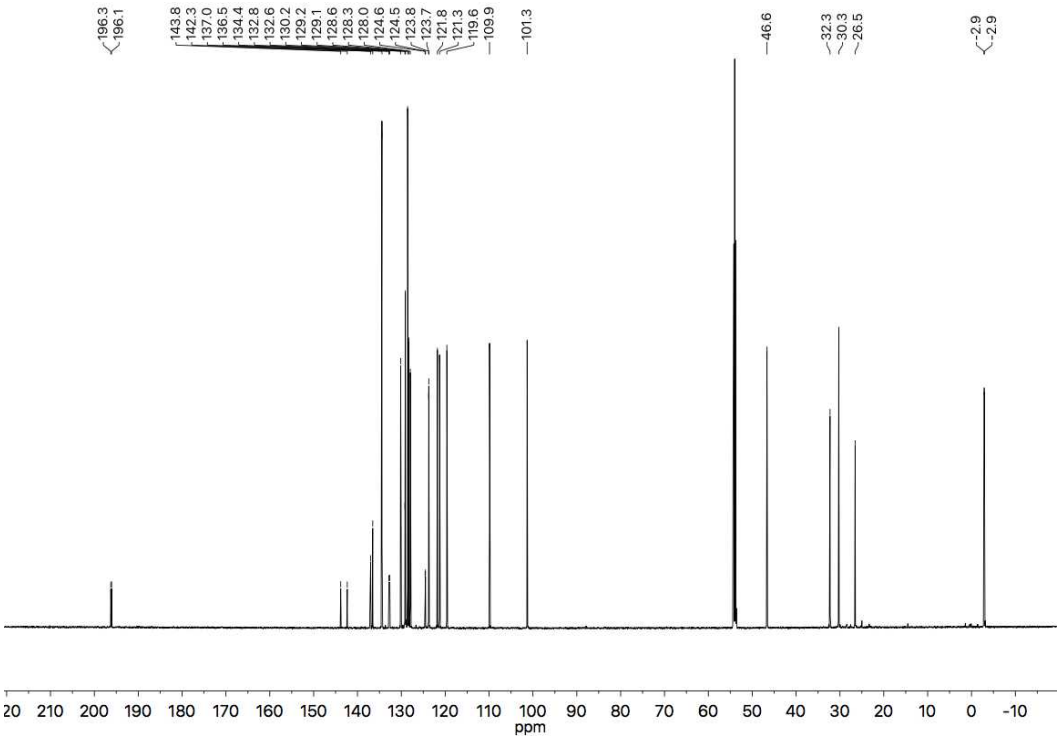




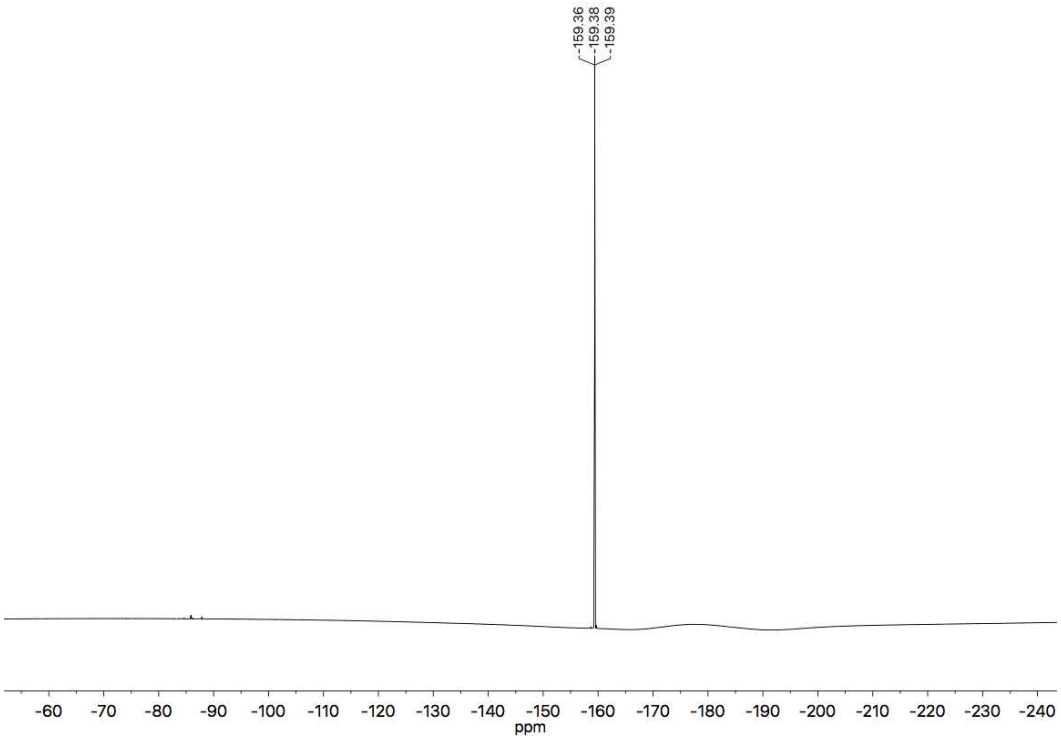
^{1}H NMR (600 MHz, CD_2Cl_2) – **16b**

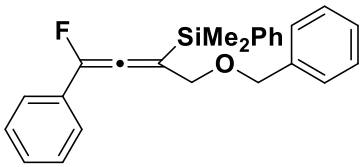


^{13}C NMR (151 MHz, CD_2Cl_2) – **16b**

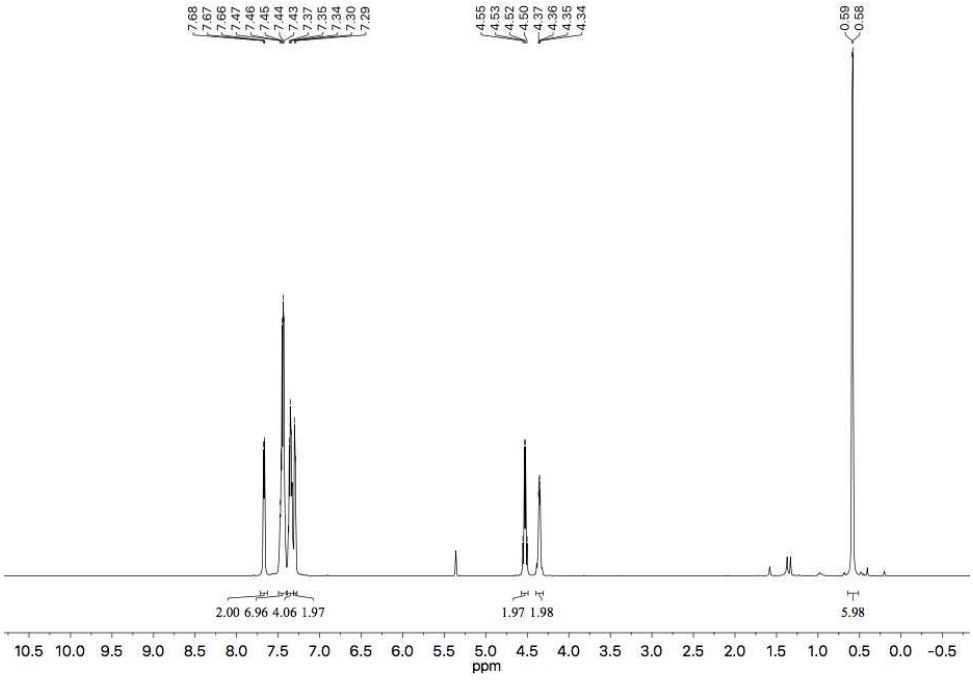


^{19}F NMR (565 MHz, CD_2Cl_2) – **16b**

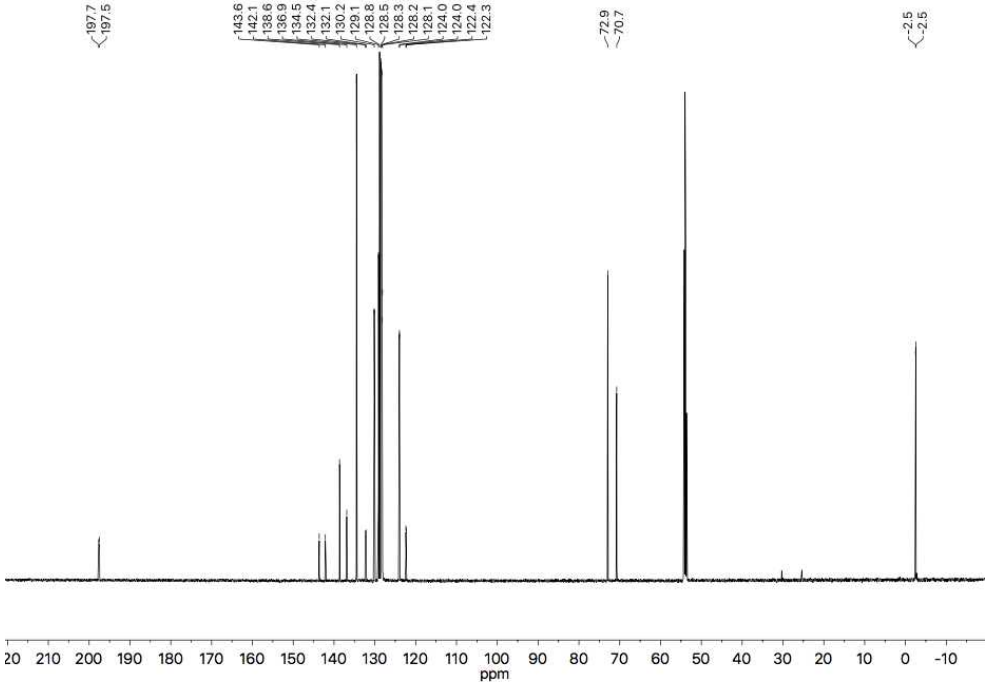




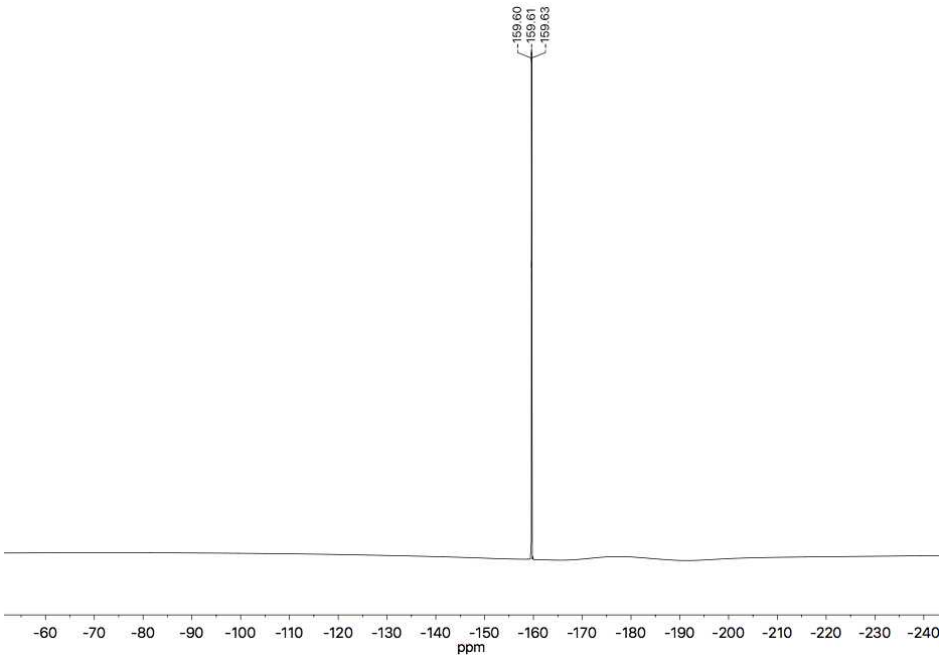
^{1}H NMR (600 MHz, CD_2Cl_2) – **17b**

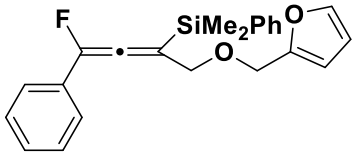


^{13}C NMR (151 MHz, CD_2Cl_2) – **17b**

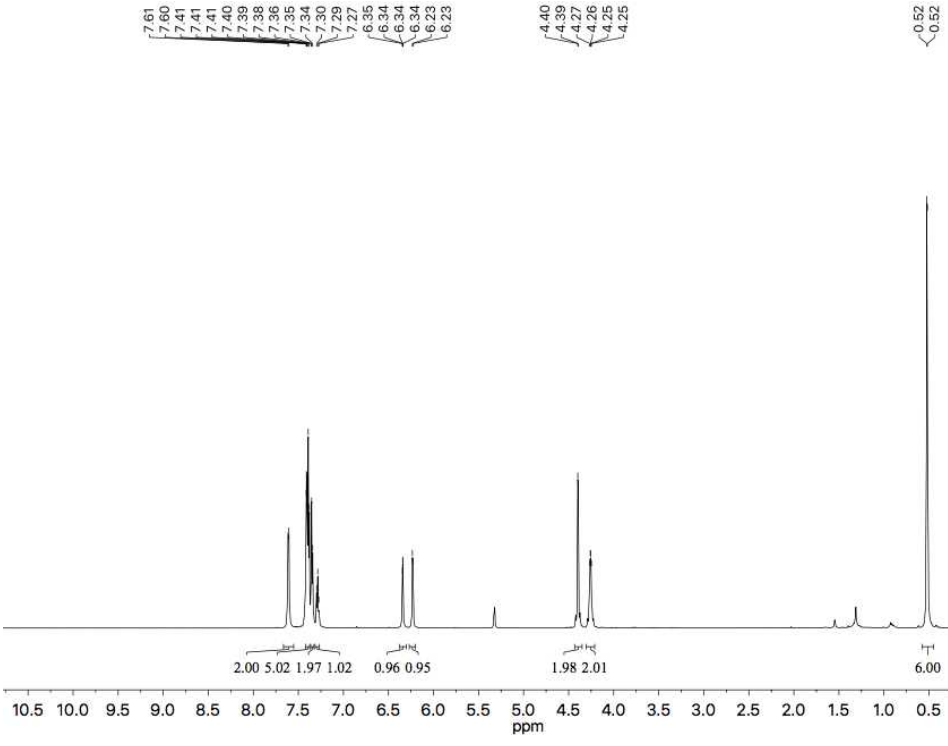


^{19}F NMR (565 MHz, CD_2Cl_2) – **17b**

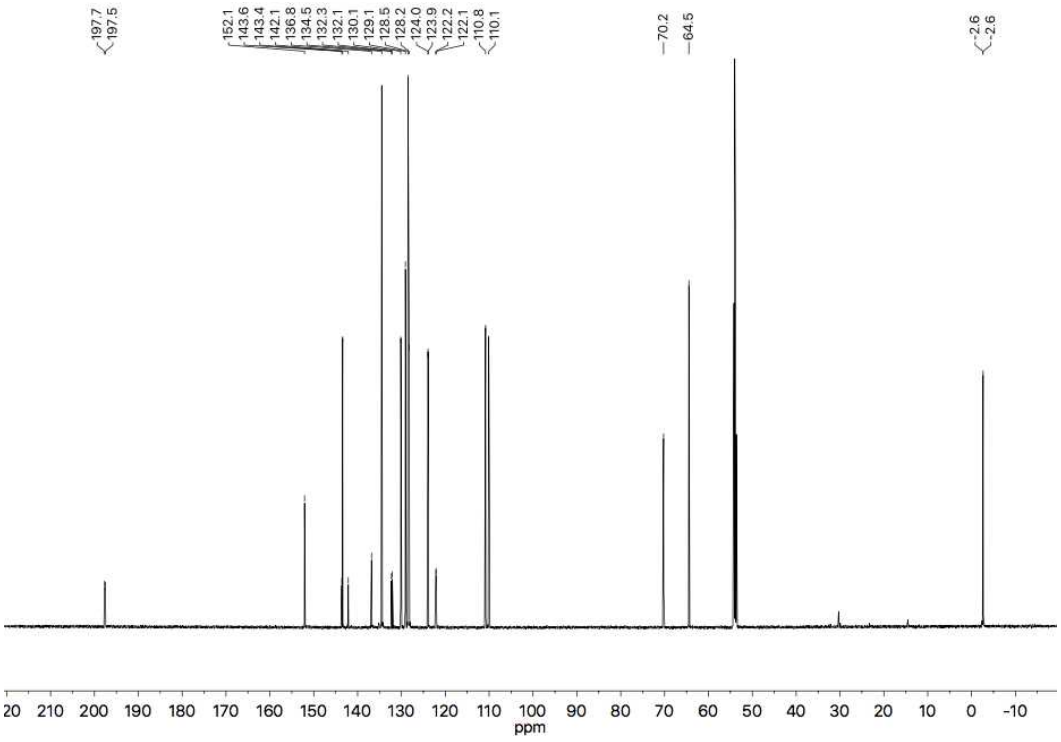




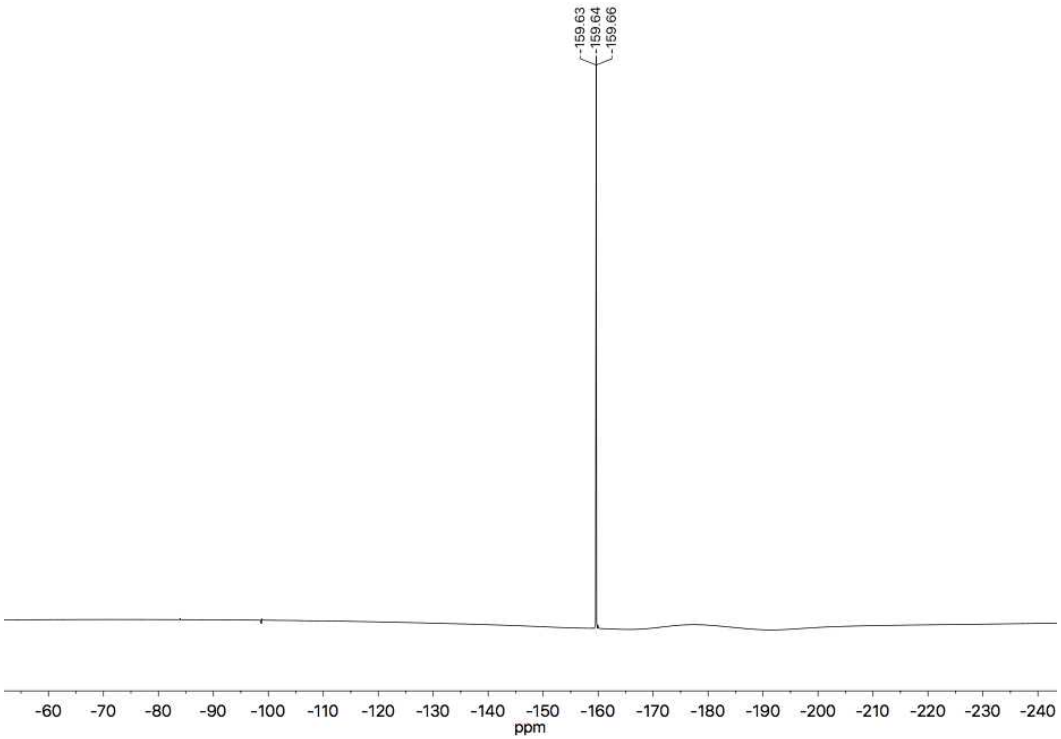
^{1}H NMR (600 MHz, CD_2Cl_2) – **18b**

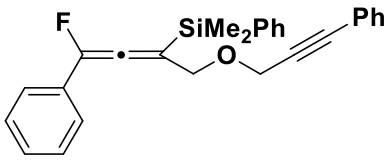


^{13}C NMR (151 MHz, CD_2Cl_2) – **18b**

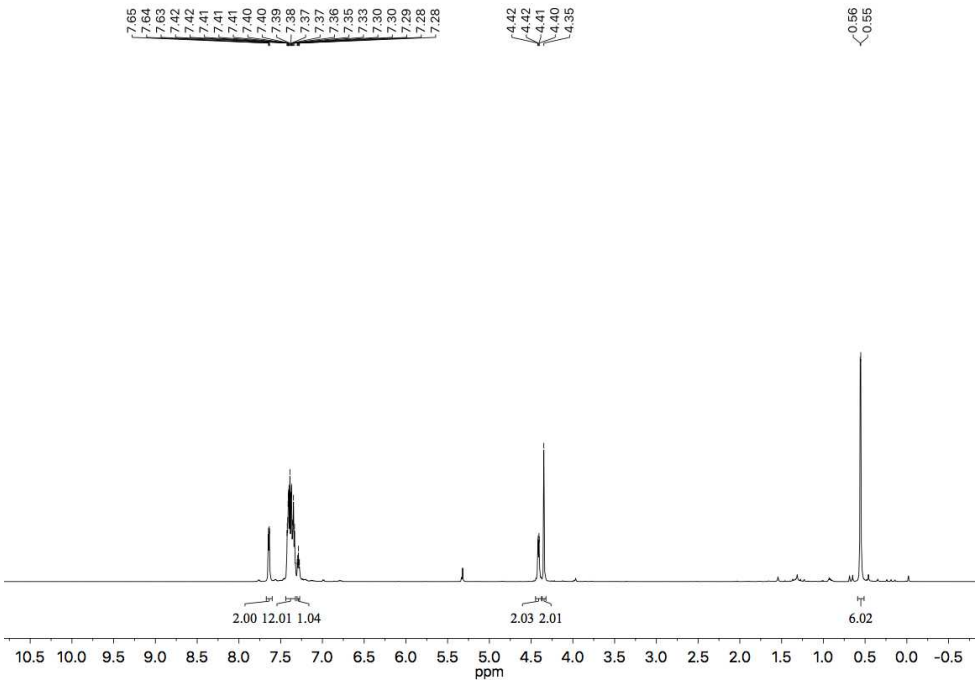


^{19}F NMR (565 MHz, CD_2Cl_2) – **18b**

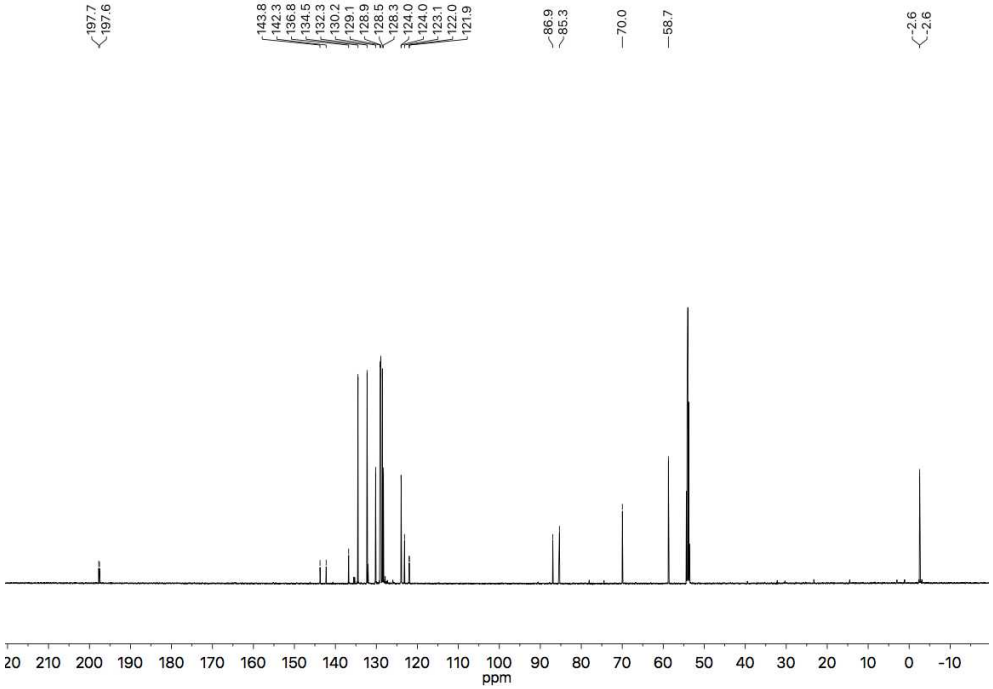




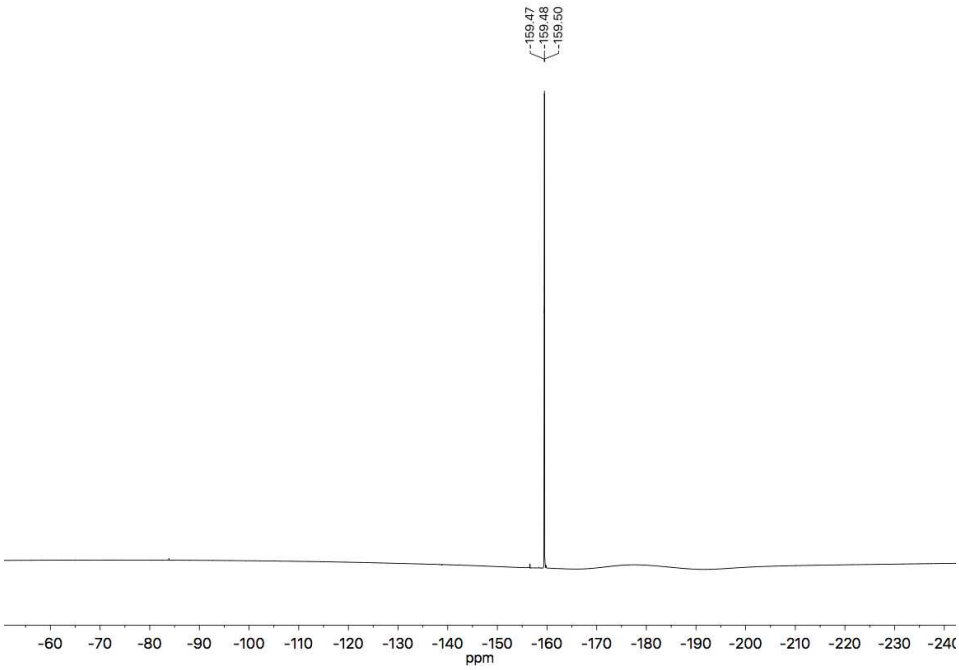
^{1}H NMR (600 MHz, CD_2Cl_2) – **19b**

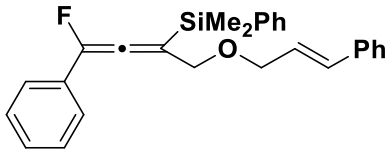


^{13}C NMR (151 MHz, CD_2Cl_2) – **19b**

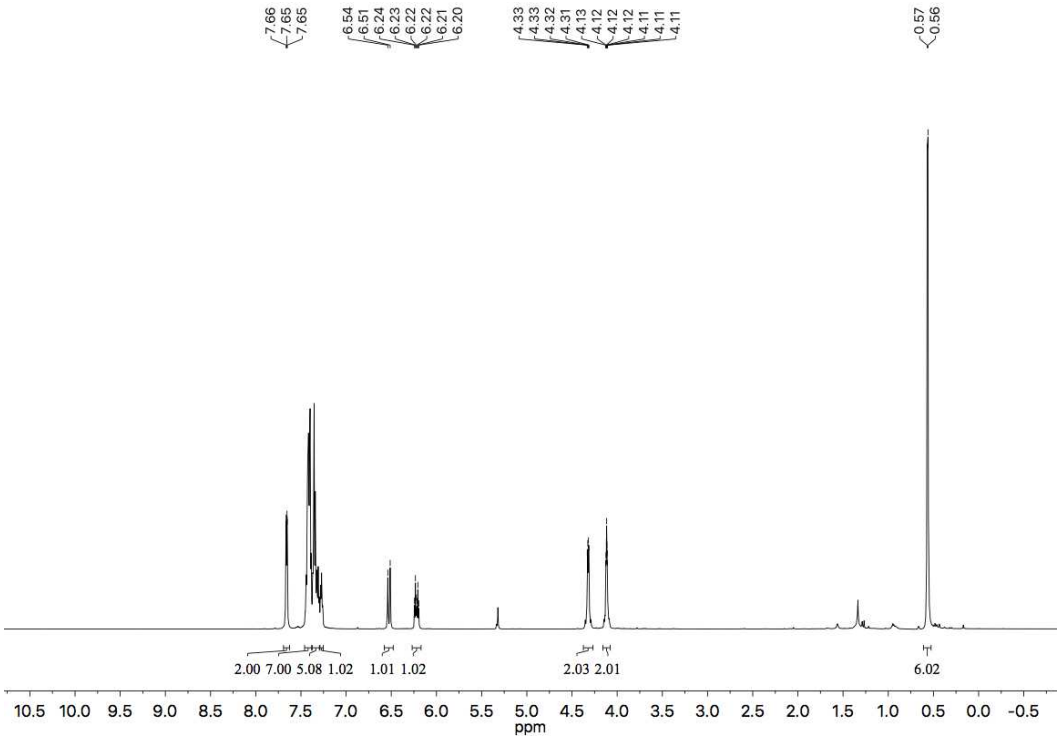


^{19}F NMR (565 MHz, CD_2Cl_2) – **19b**

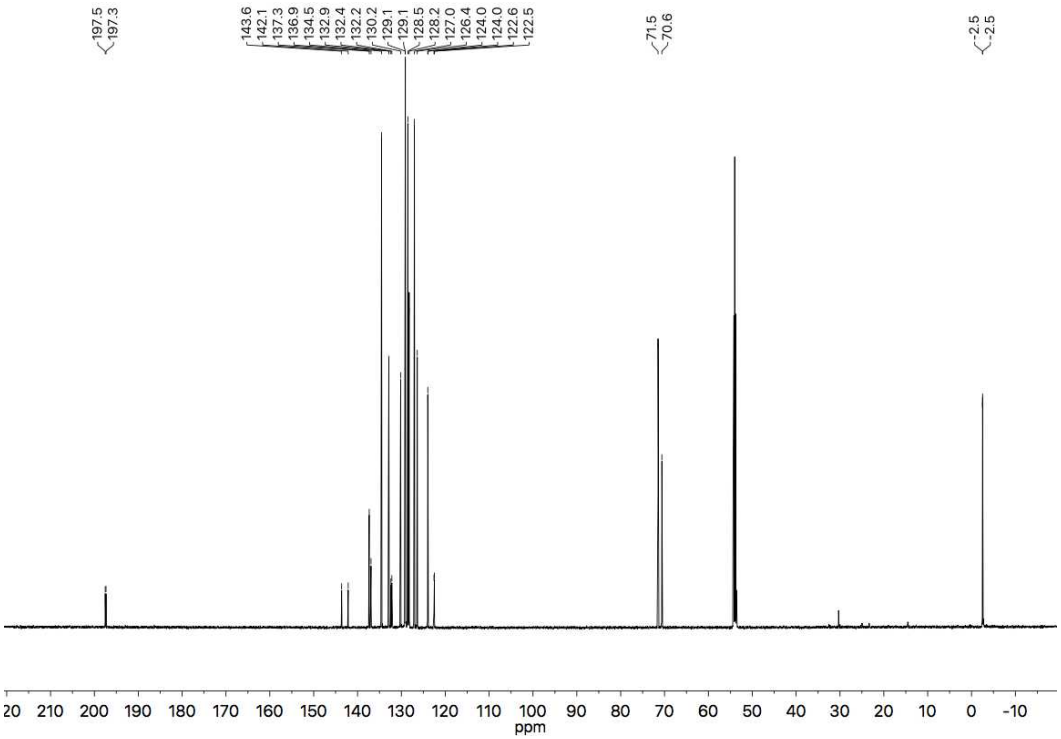




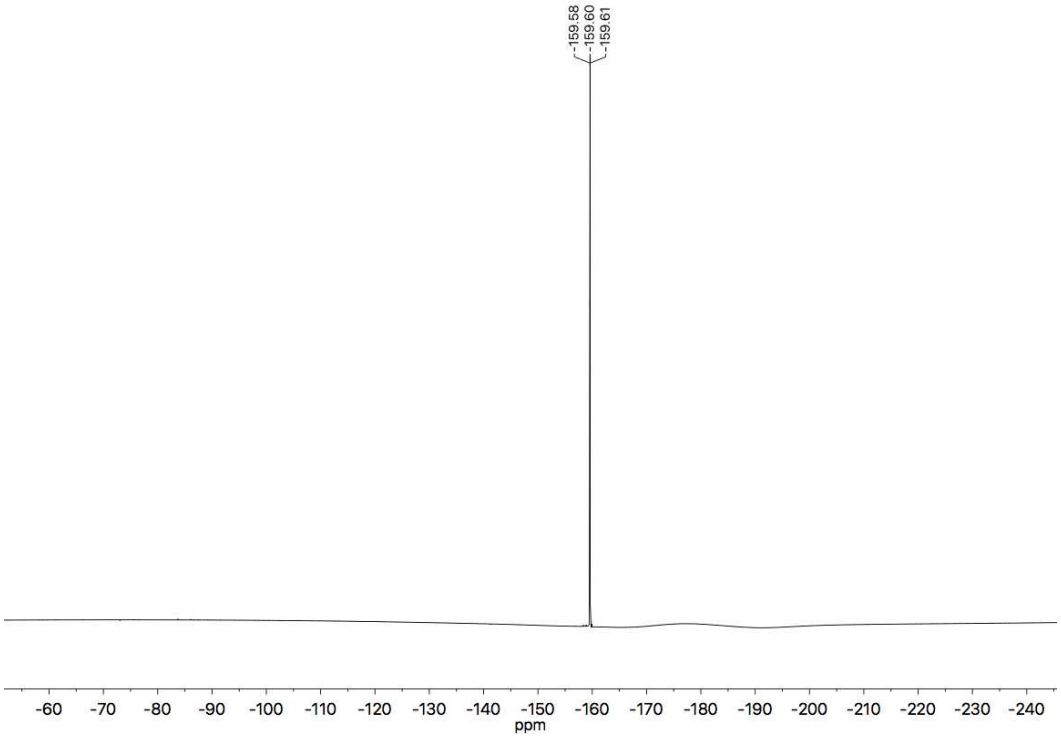
^{1}H NMR (600 MHz, CD_2Cl_2) – **20b**

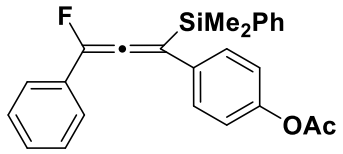


^{13}C NMR (151 MHz, CD_2Cl_2) – **20b**

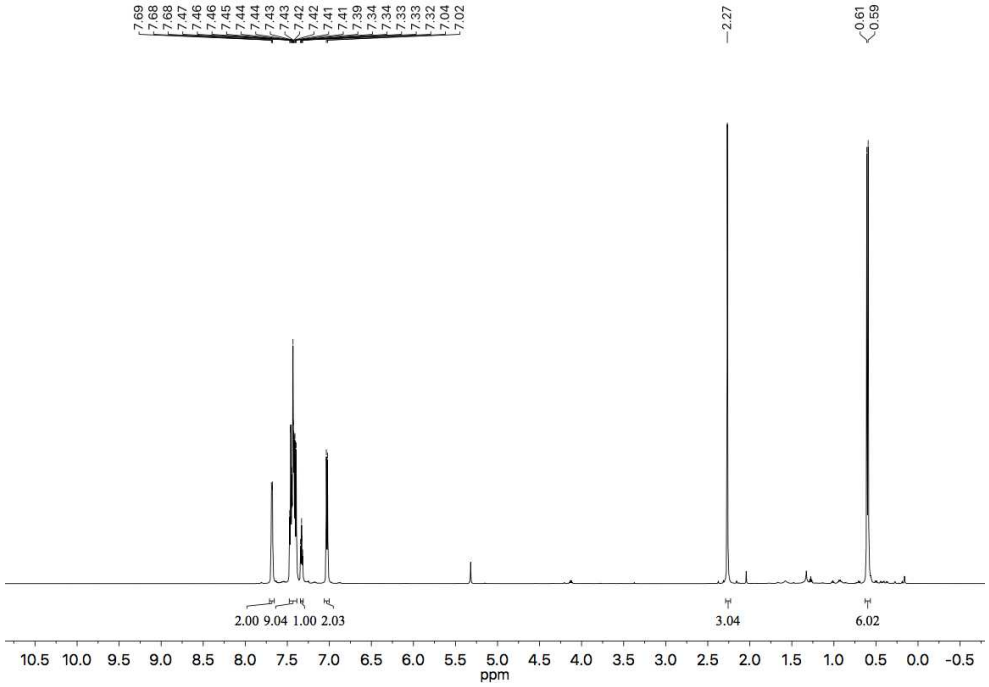


^{19}F NMR (565 MHz, CD_2Cl_2) – **20b**

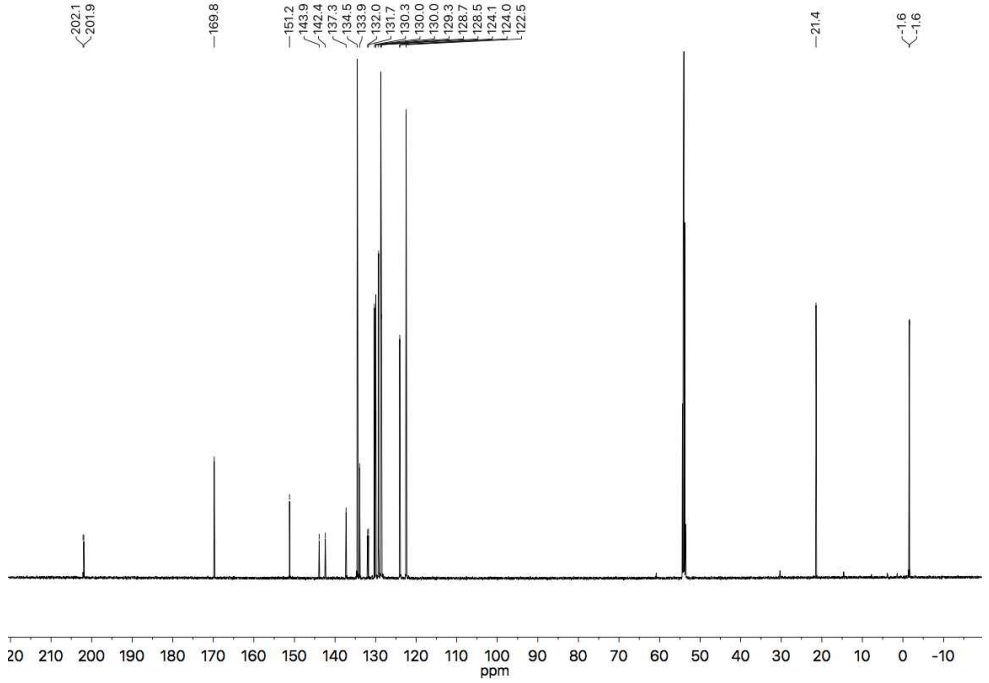




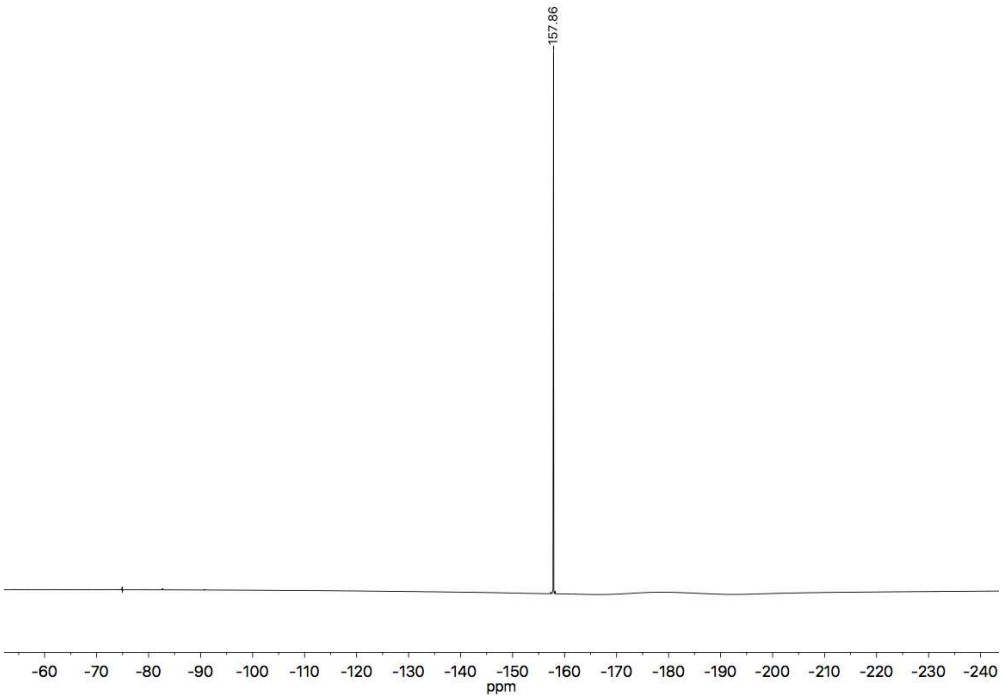
^{1}H NMR (600 MHz, CD_2Cl_2) – **21b**

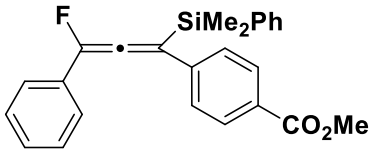


^{13}C NMR (151 MHz, CD_2Cl_2) – **21b**

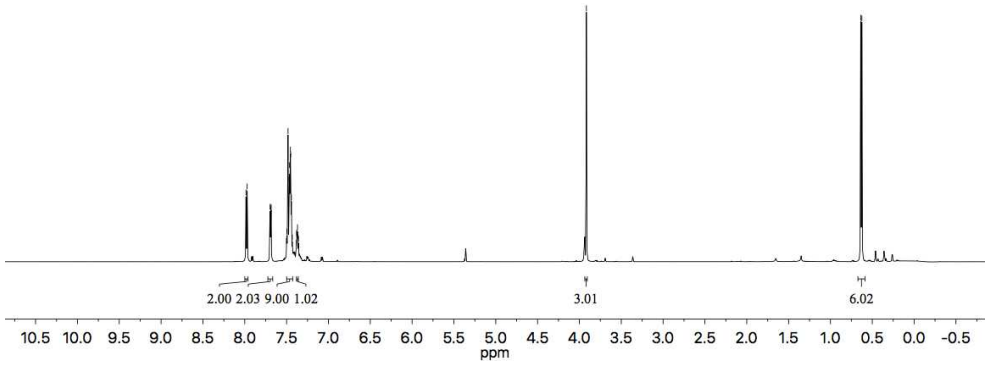


^{19}F NMR (565 MHz, CD_2Cl_2) – **21b**

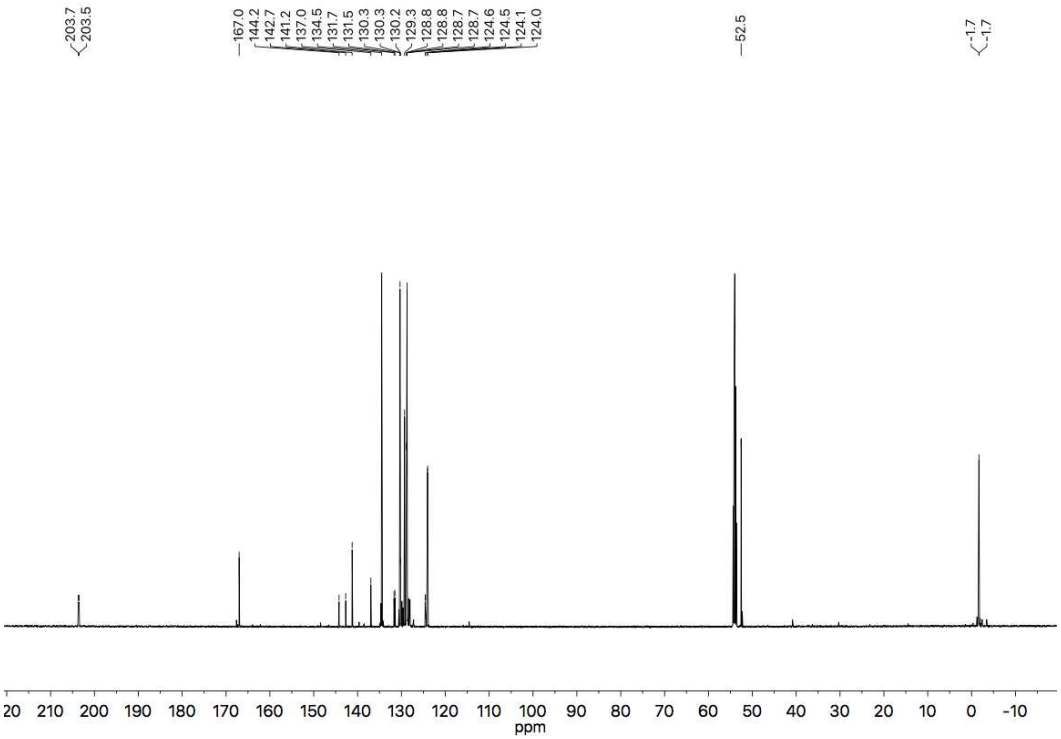




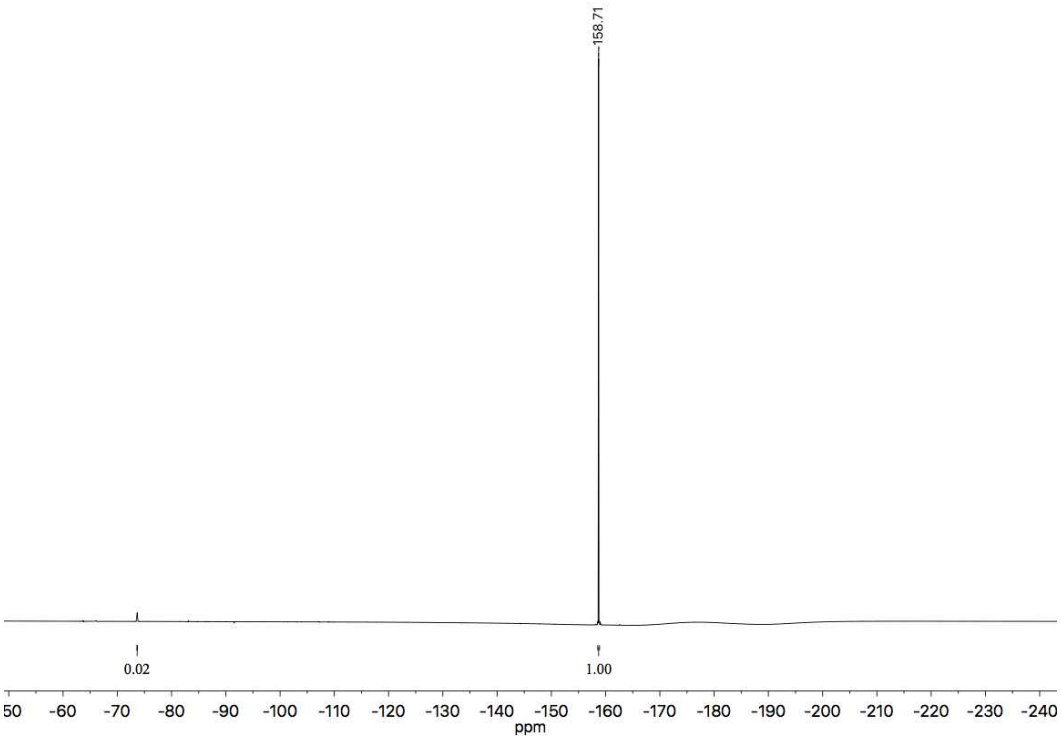
^{1}H NMR (600 MHz, CD_2Cl_2) – **22b**

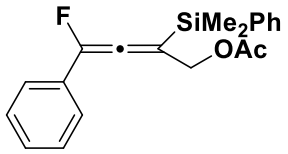


^{13}C NMR (151 MHz, CD_2Cl_2) – **22b**

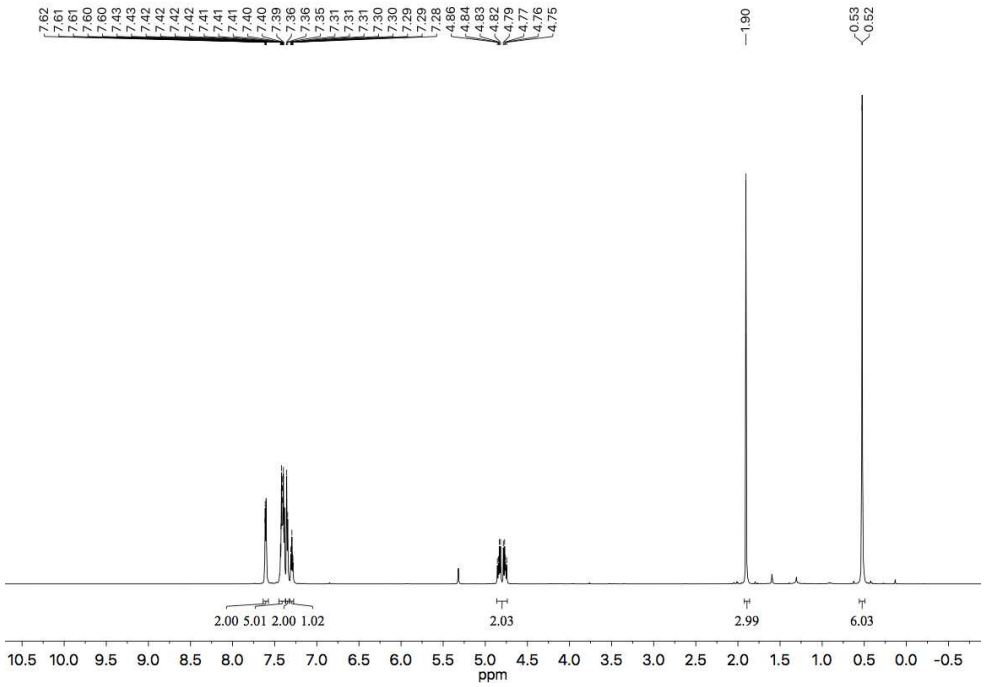


^{19}F NMR (565 MHz, CD_2Cl_2) – **22b**

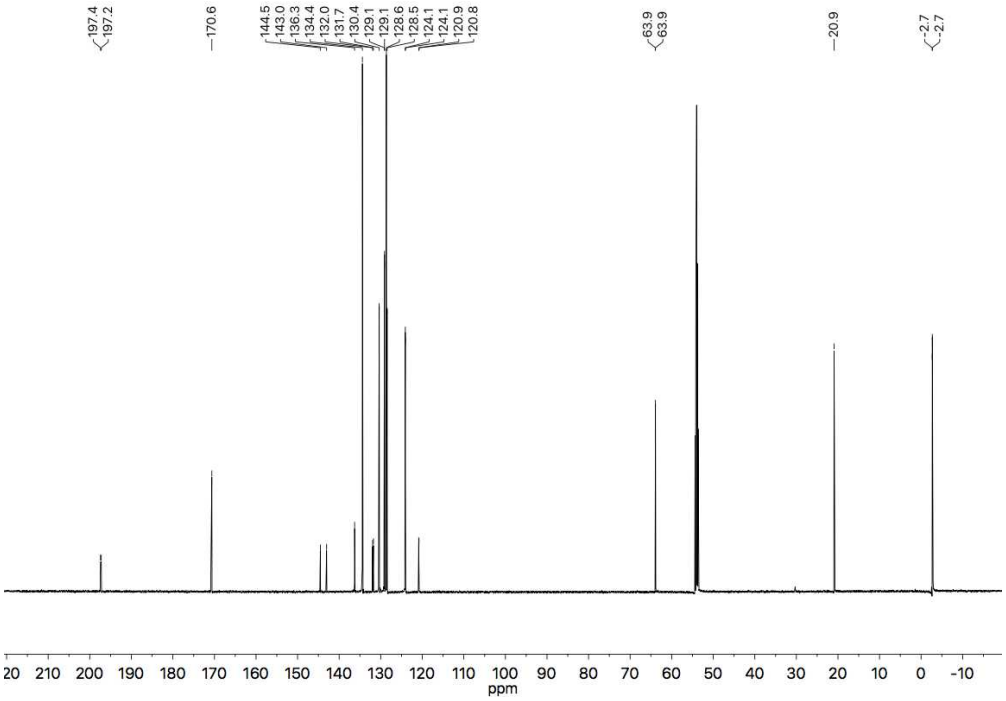




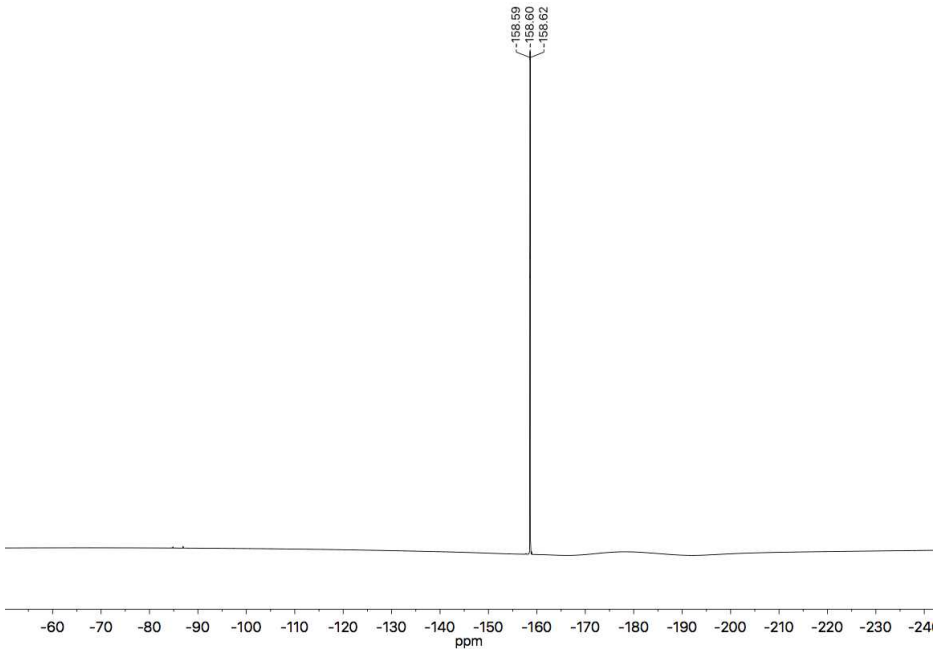
^{1}H NMR (600 MHz, CD_2Cl_2) – **23b**

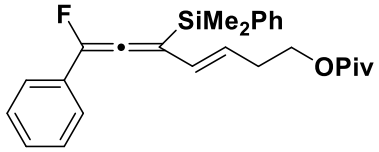


^{13}C NMR (151 MHz, CD_2Cl_2) – **23b**

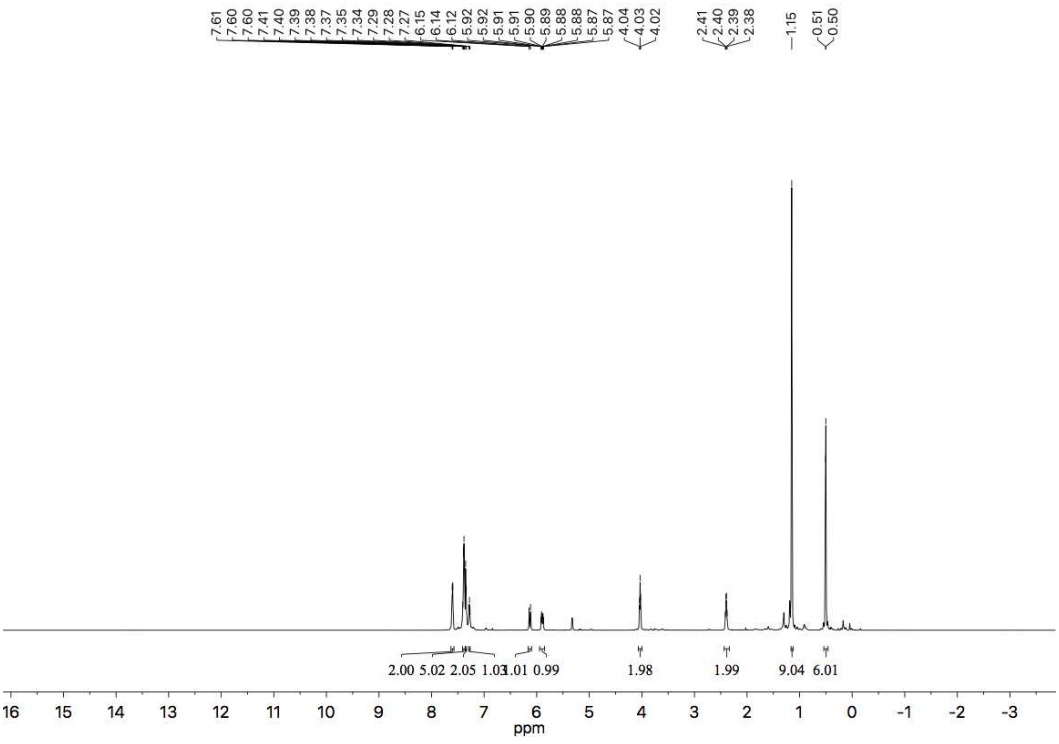


^{19}F NMR (565 MHz, CD_2Cl_2) – **23b**

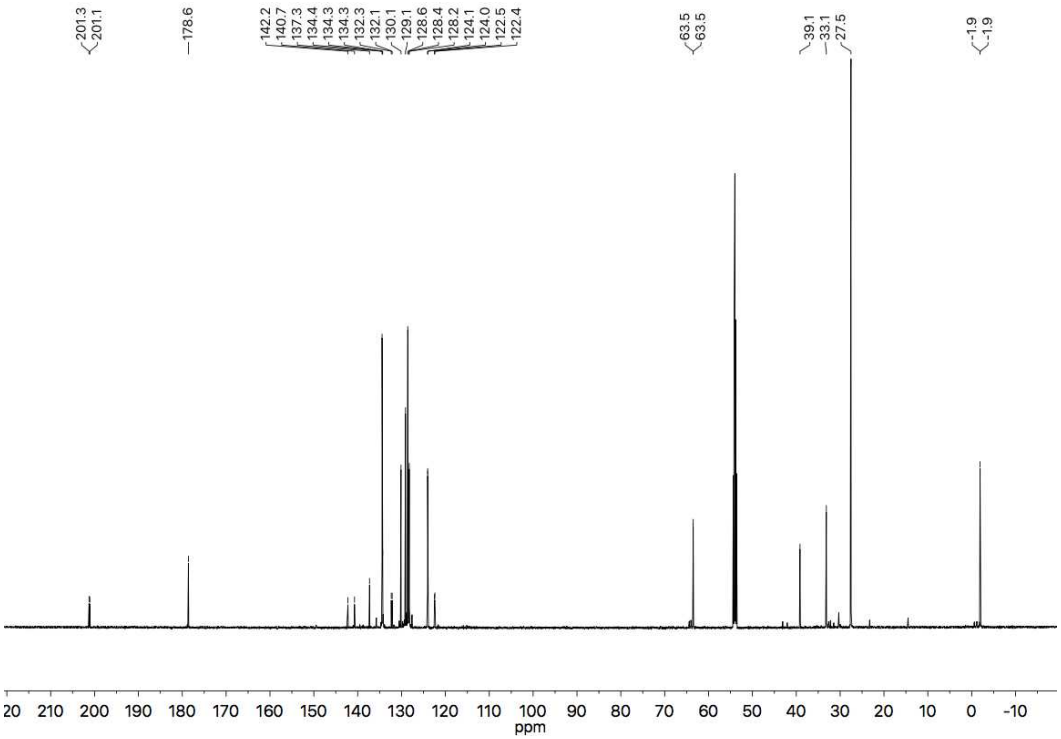




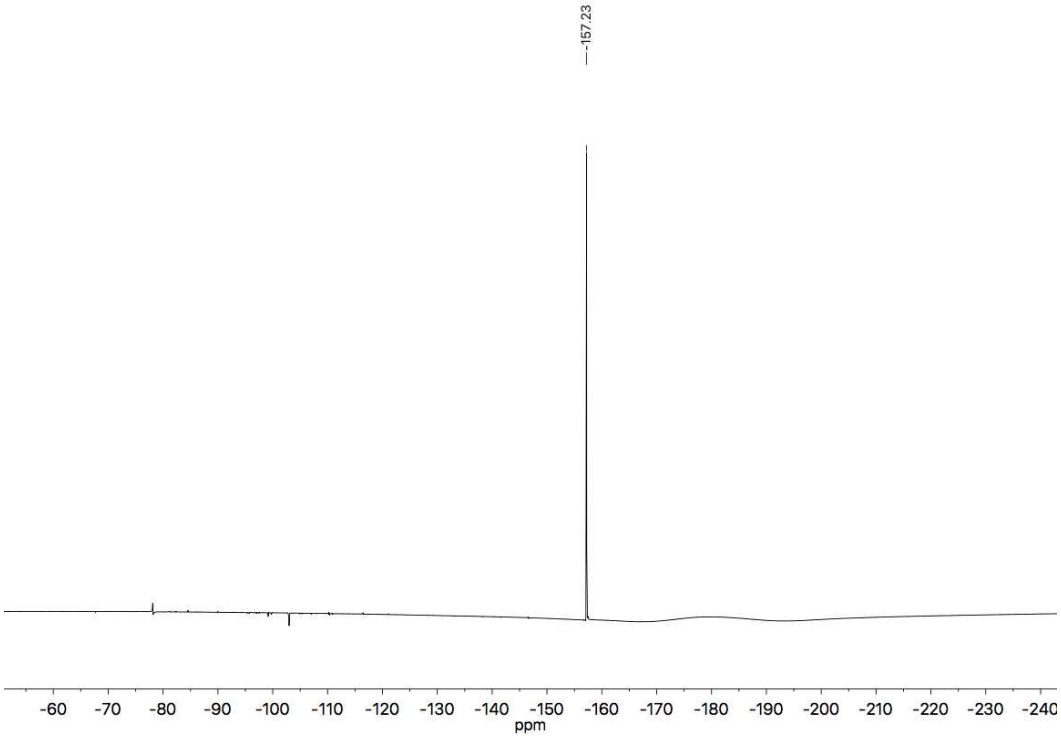
^{1}H NMR (600 MHz, CD_2Cl_2) – **24b**

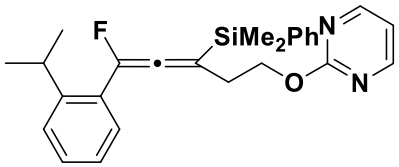


^{13}C NMR (151 MHz, CD_2Cl_2) – **24b**

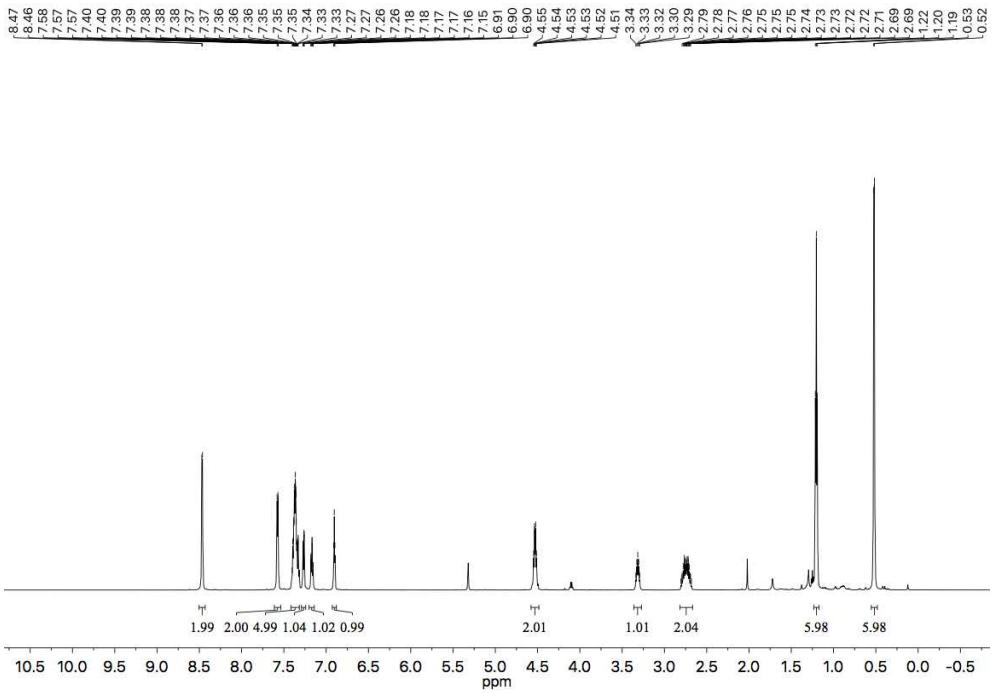


^{19}F NMR (565 MHz, CD_2Cl_2) – **24b**

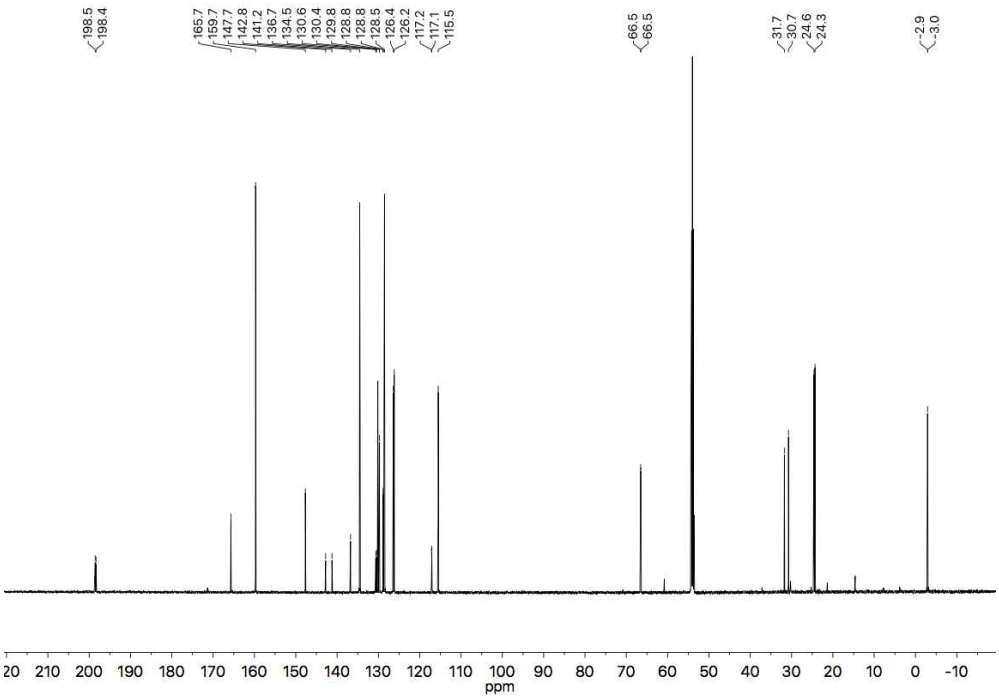




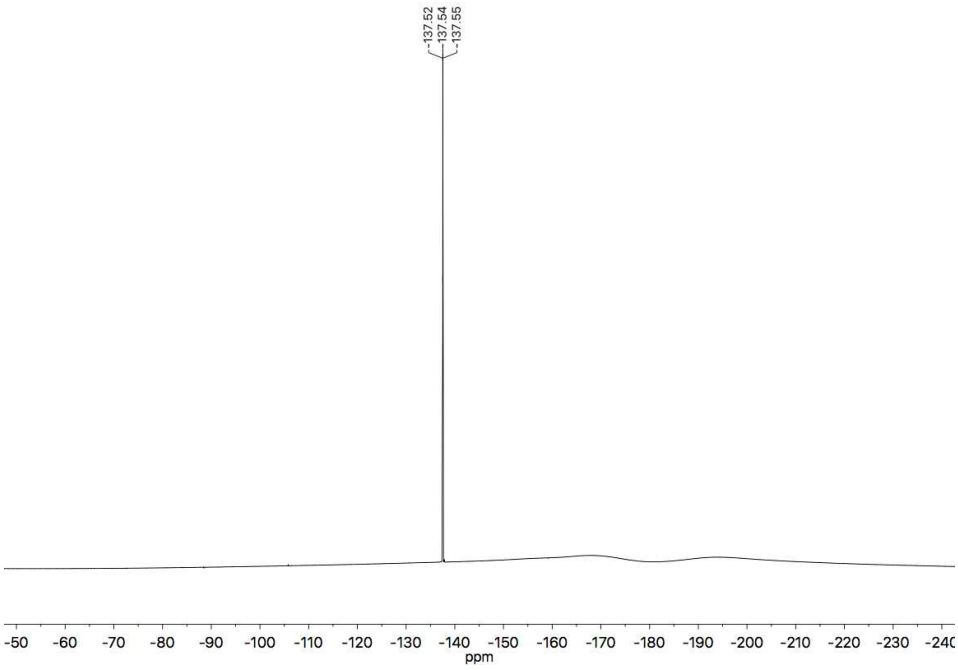
^{1}H NMR (600 MHz, CD_2Cl_2) – **25b**

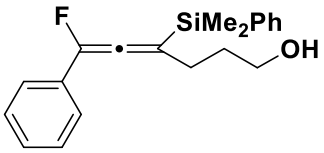


^{13}C NMR (151 MHz, CD_2Cl_2) – **25b**

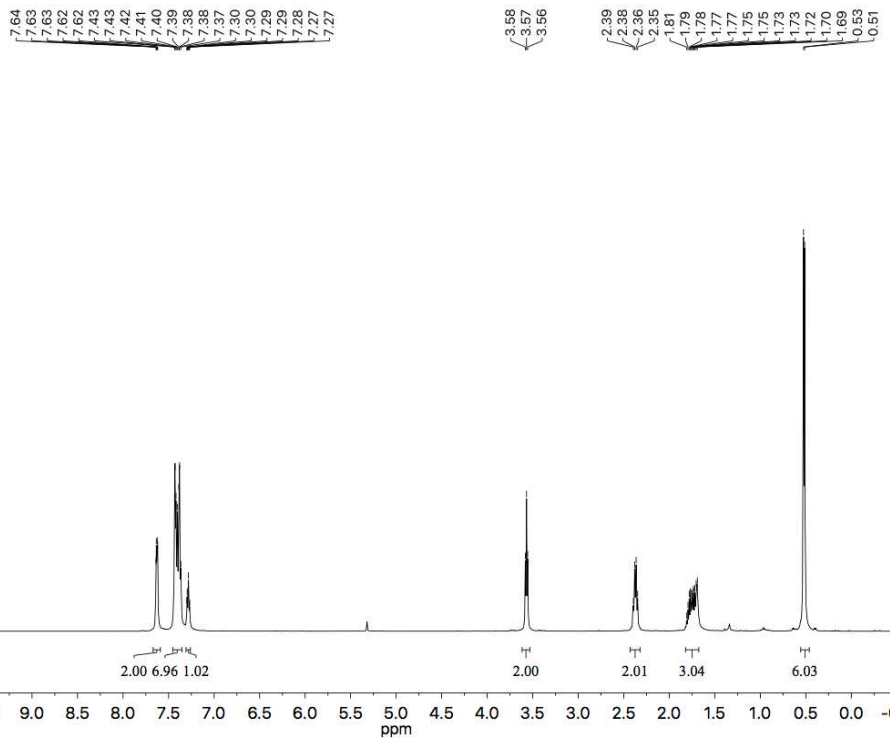


^{19}F NMR (565 MHz, CD_2Cl_2) – **25b**

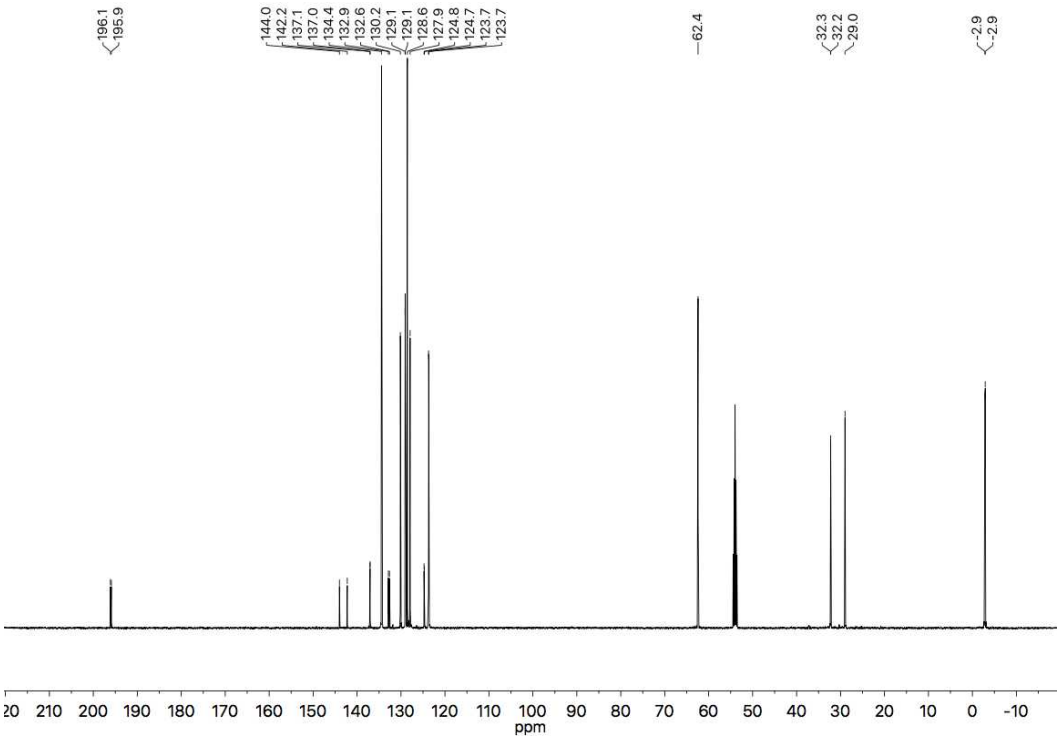




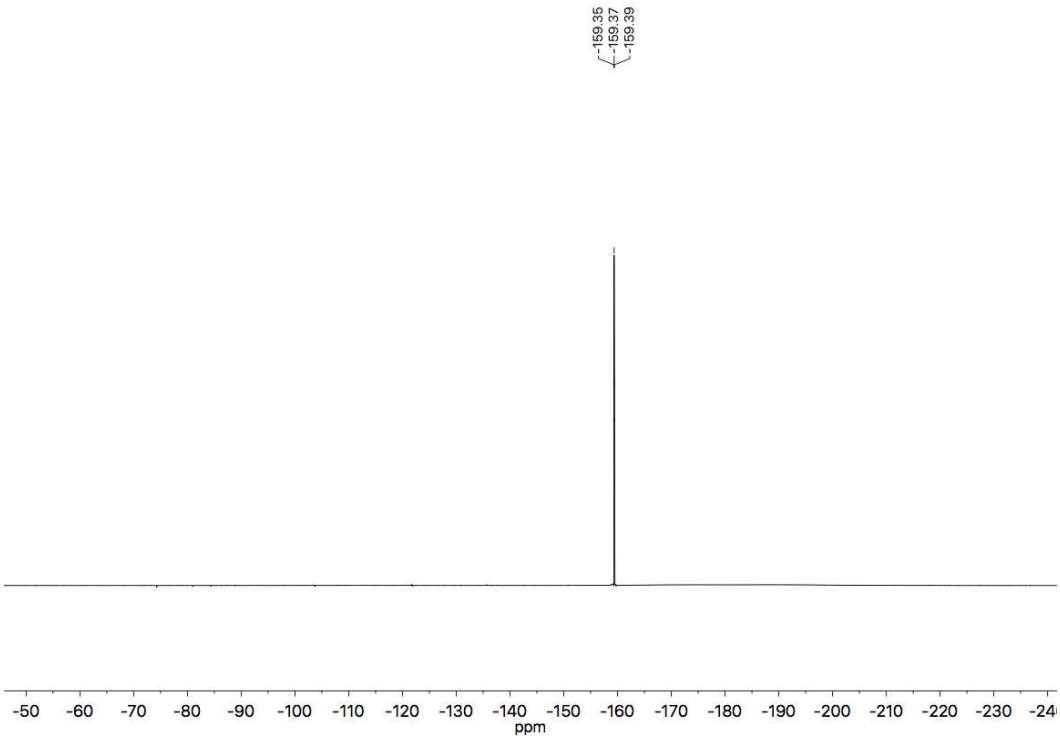
^{1}H NMR (600 MHz, CD_2Cl_2) – **1c**

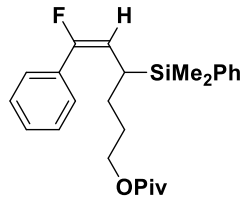


^{13}C NMR (151 MHz, CD_2Cl_2) – **1c**

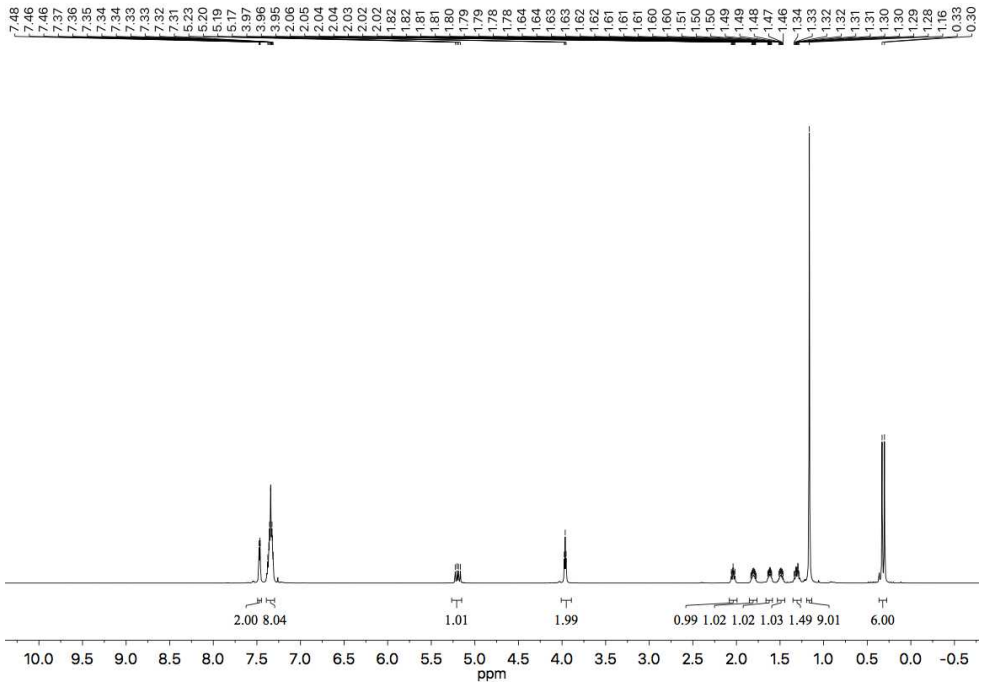


^{19}F NMR (565 MHz, CD_2Cl_2) – **1c**

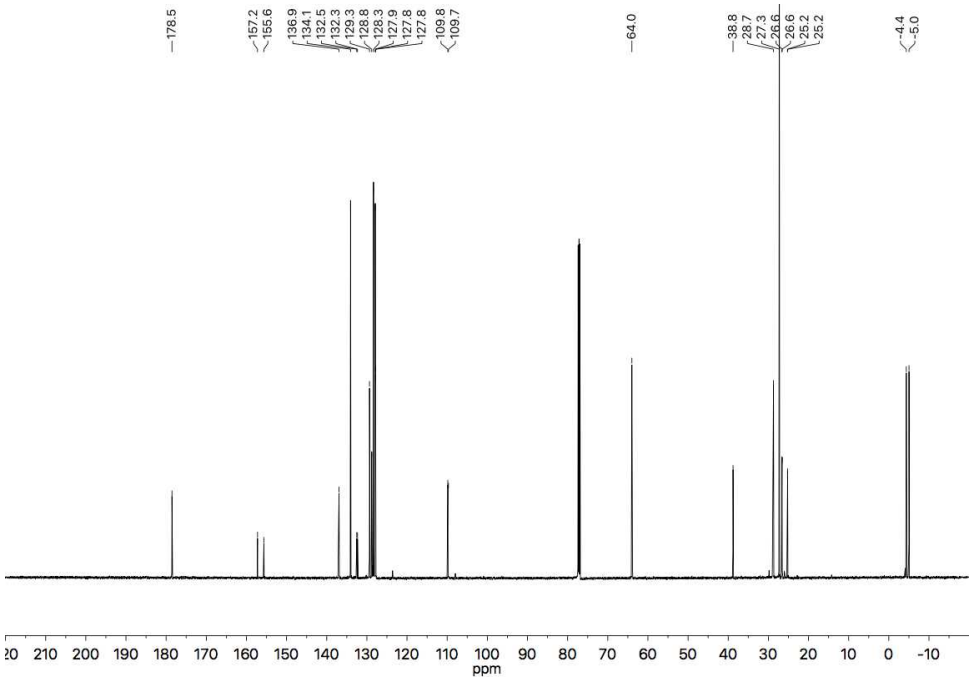




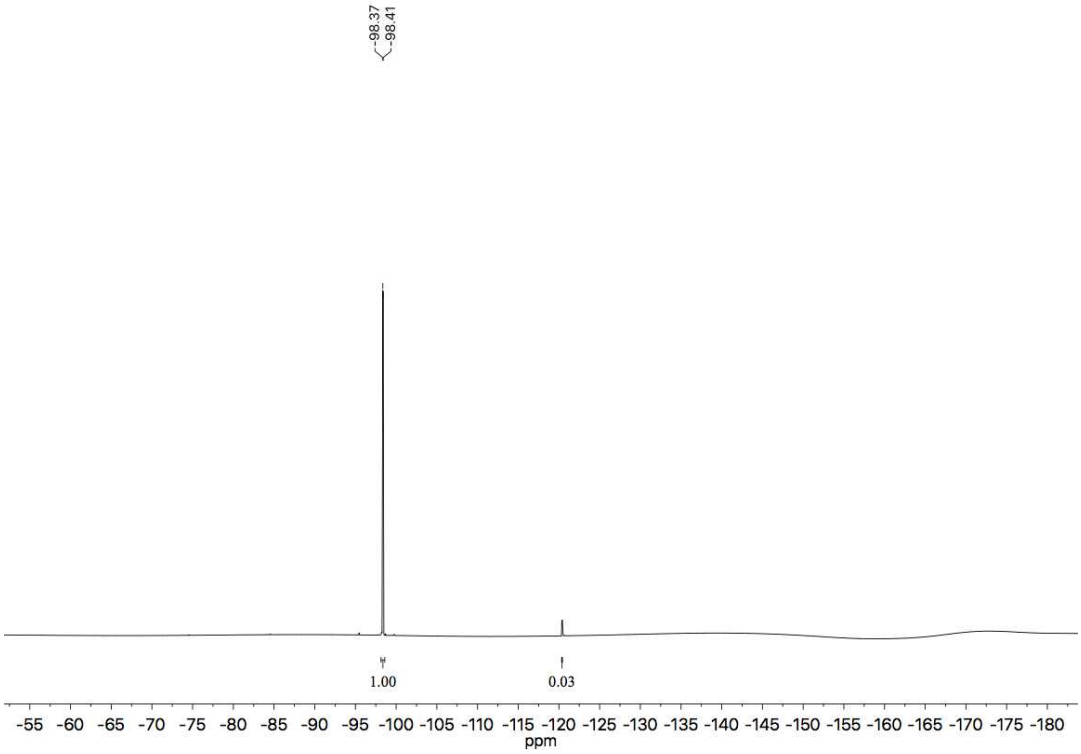
^{1}H NMR (600 MHz, $CDCl_3$) – **2c**



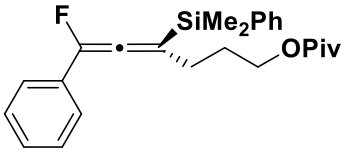
^{13}C NMR (151 MHz, $CDCl_3$) – **2c**



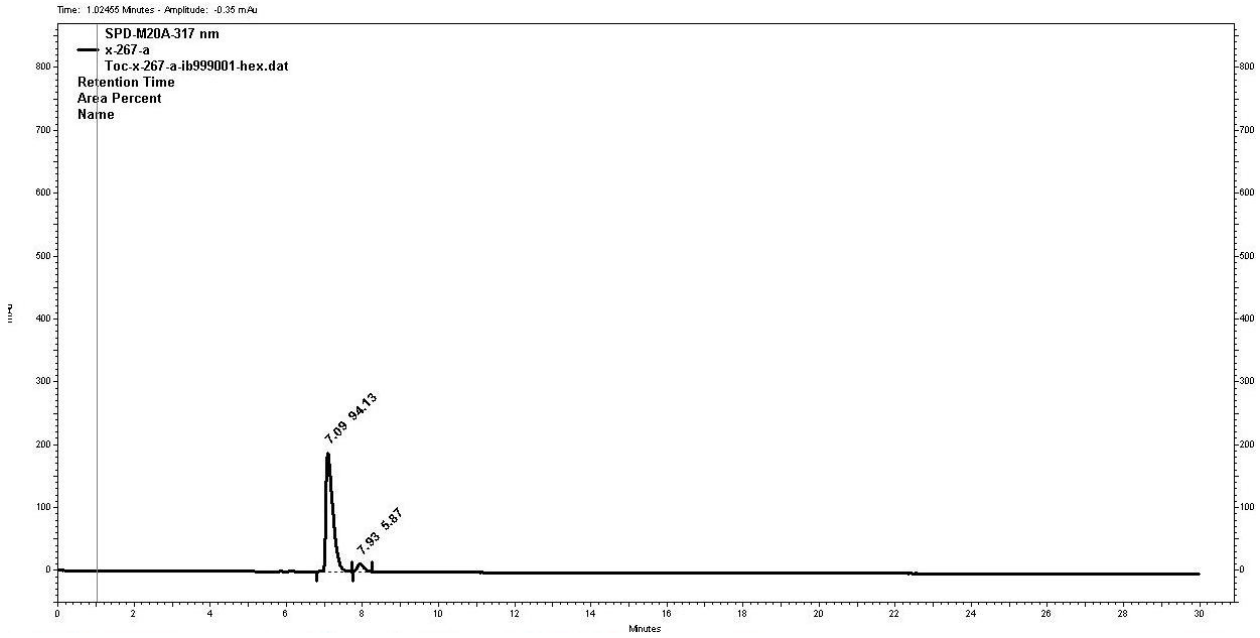
^{19}F NMR (565 MHz, $CDCl_3$) – **2c**

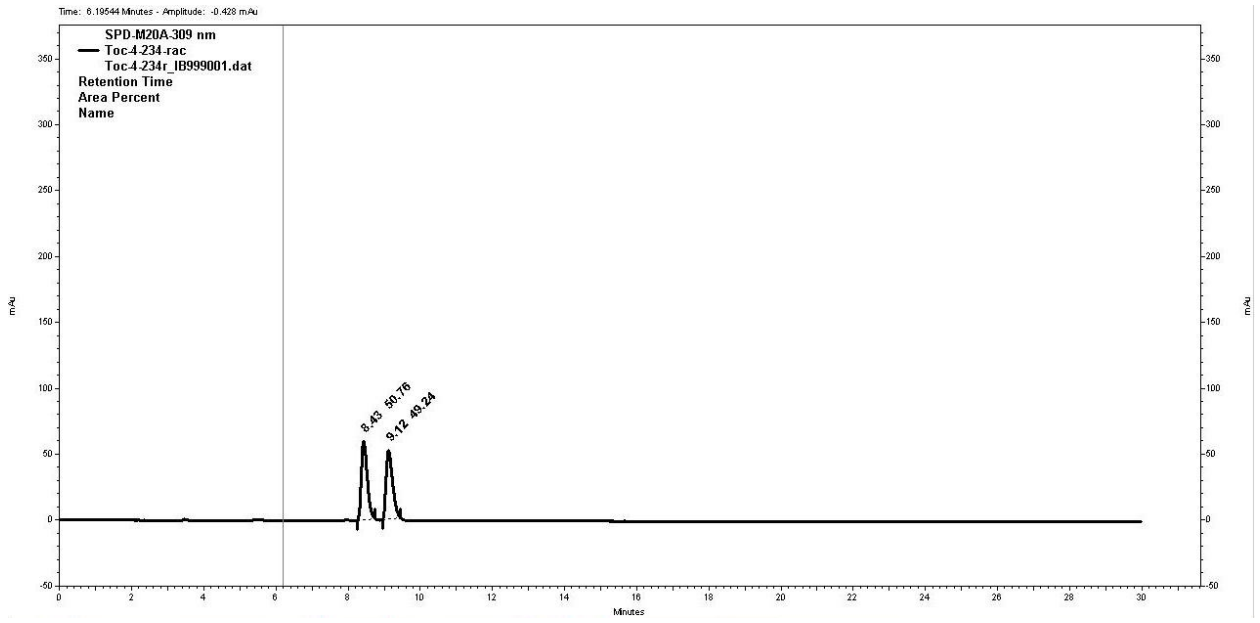


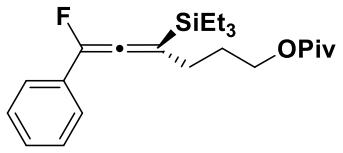
2.7 HPLC Spectra



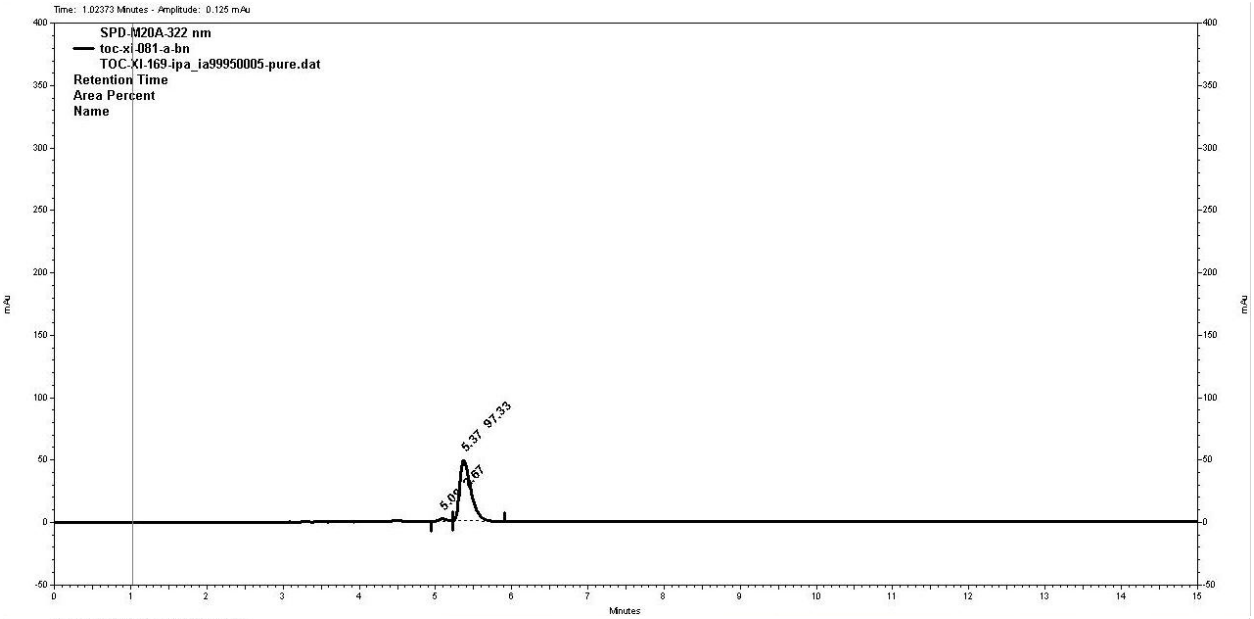
1b: IB column, 1.0 mL/min: 99.9:00.1 hexanes:iPrOH; 7.09 min (major) and 7.93 min (minor)

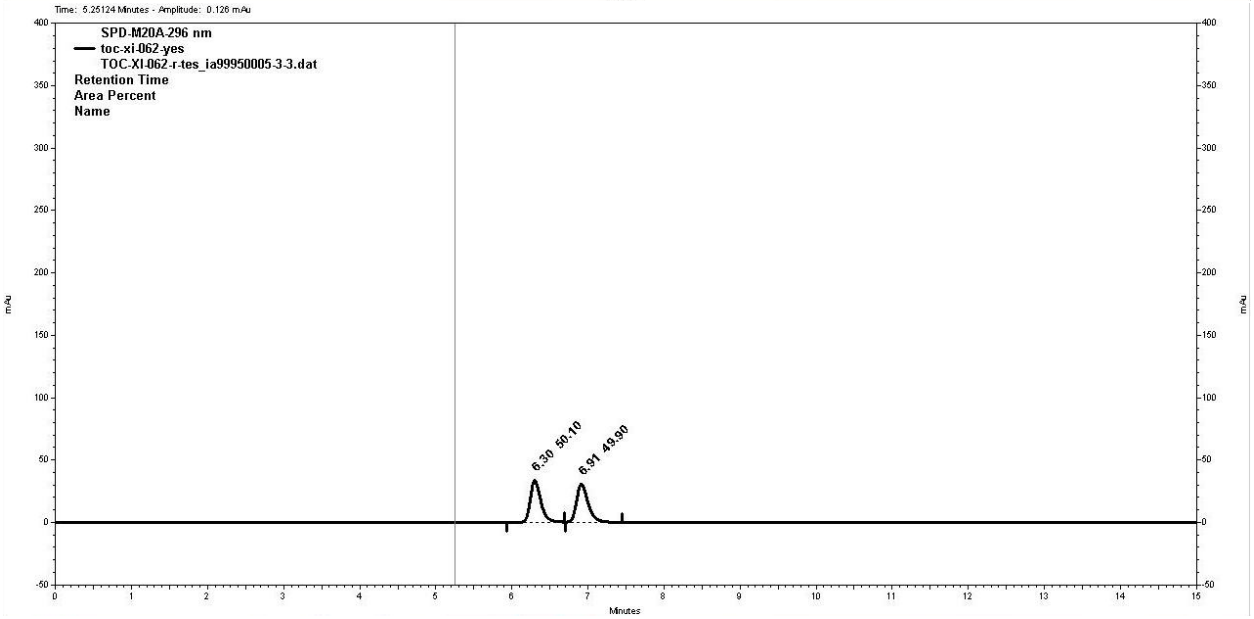


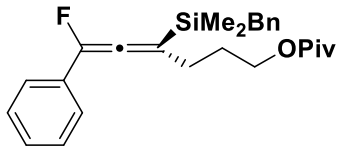




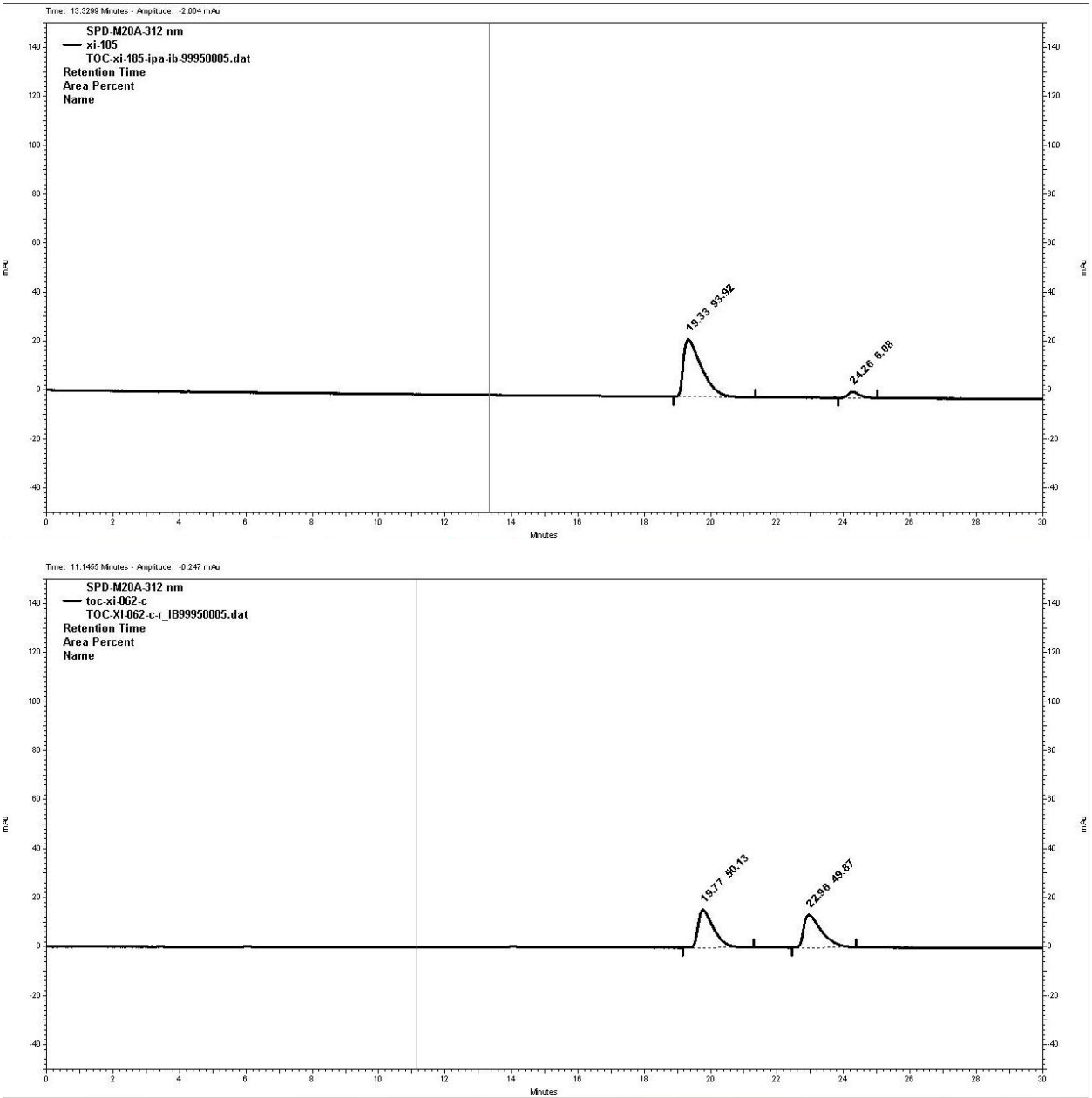
1b-SiEt$_3$: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 6.91 min (major) and 6.30 min (minor)

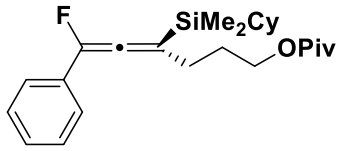




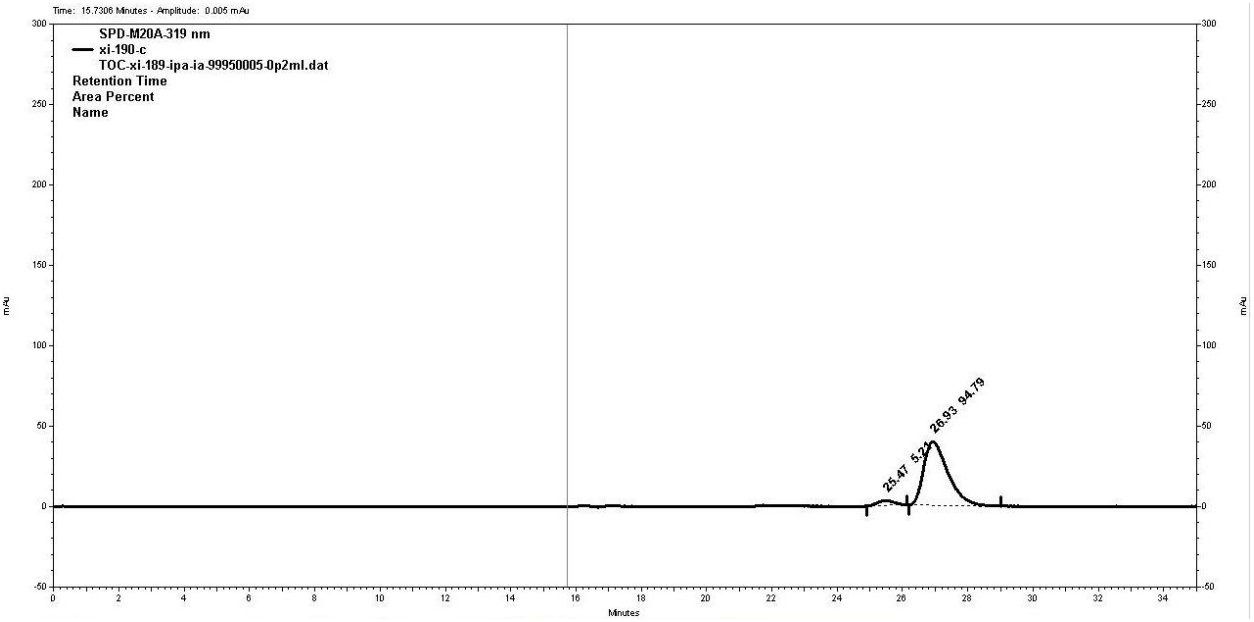


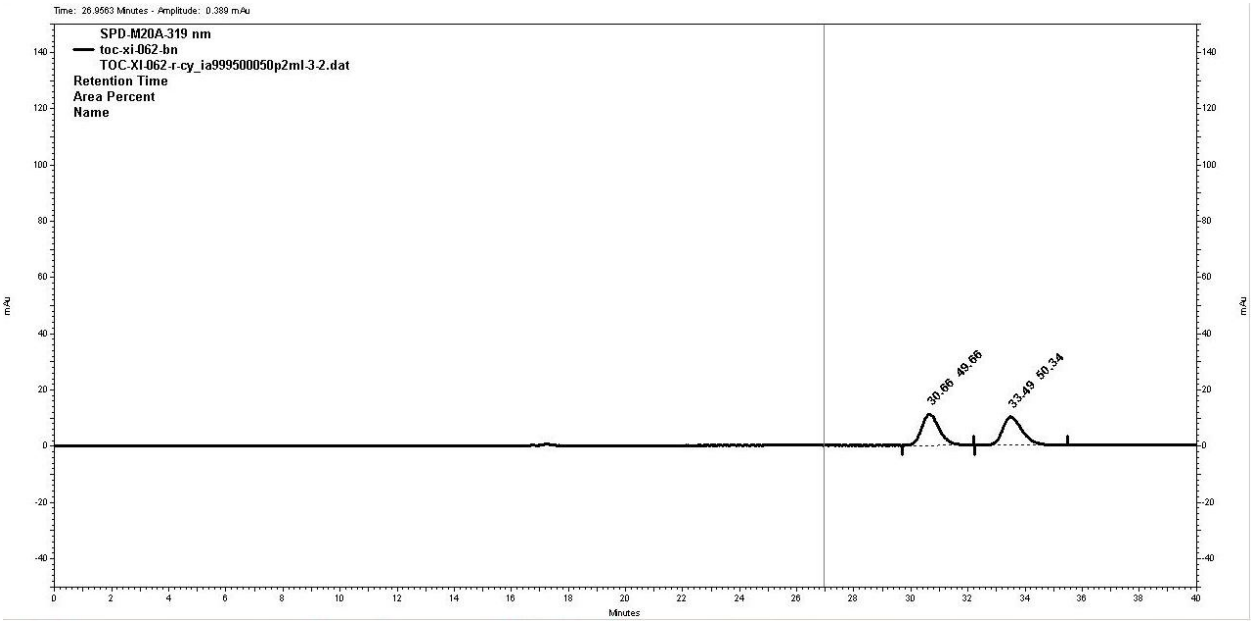
1b-SiMe$_2$Bn: IB column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 19.77 min (major) and 22.96 min (minor)

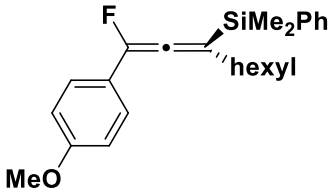




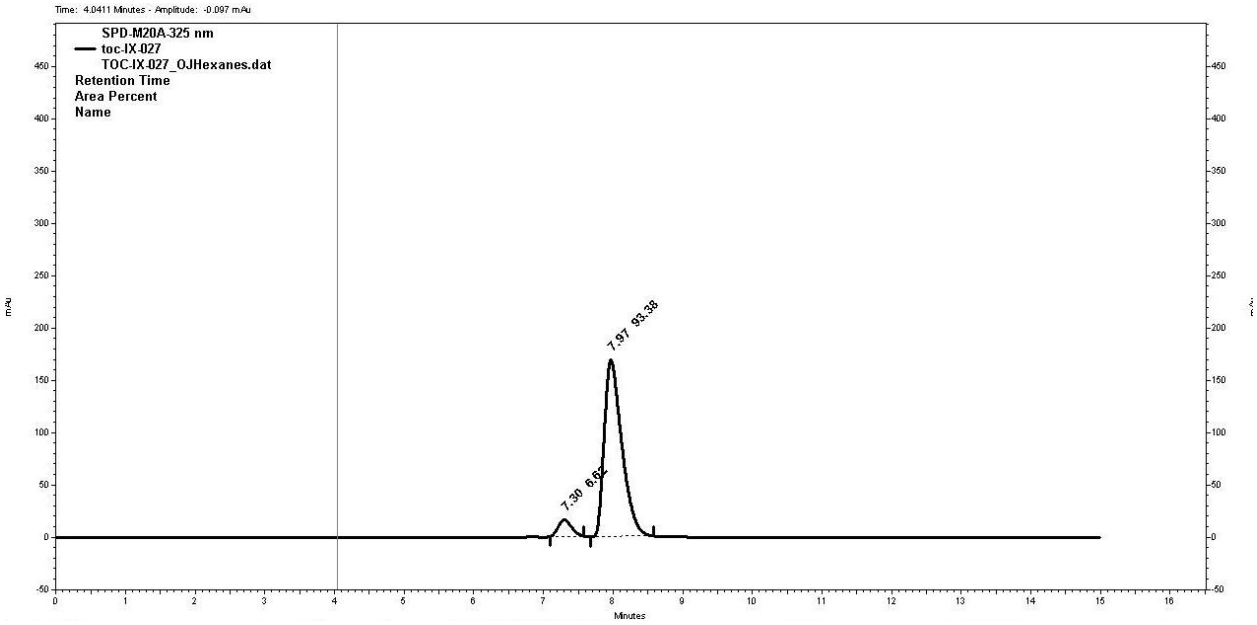
1b-SiMe$_2$Bn: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 33.49 min (major) and 30.66 min (minor)

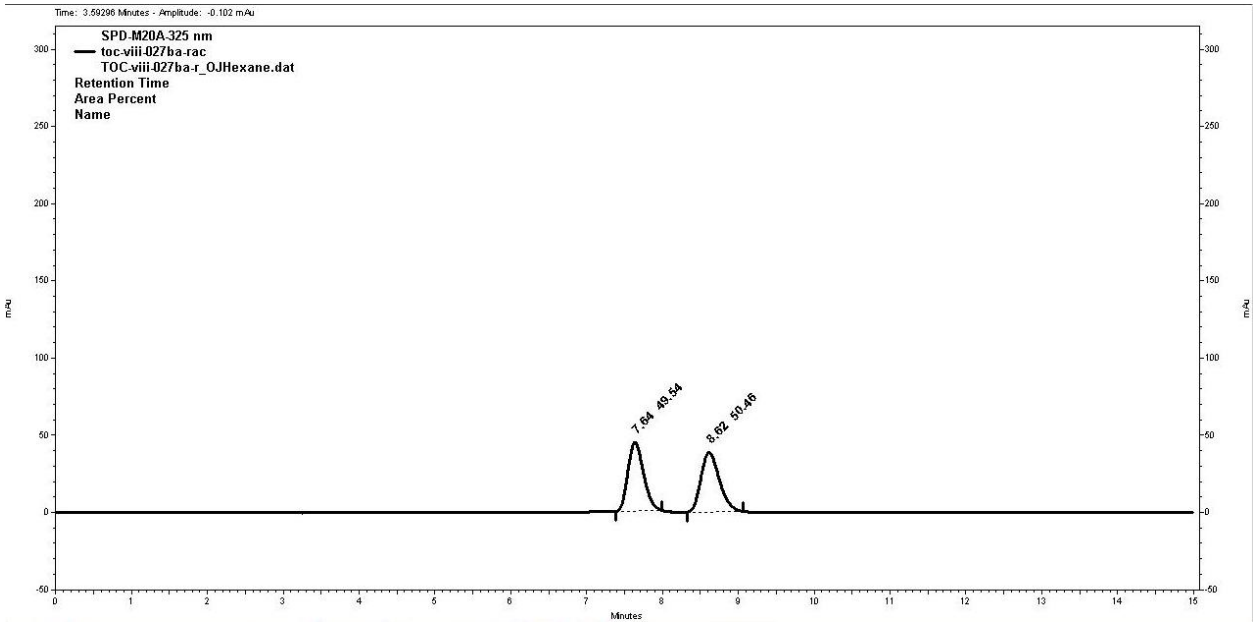


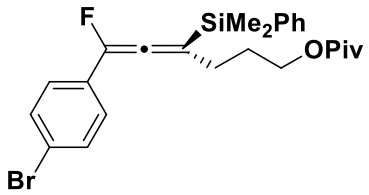




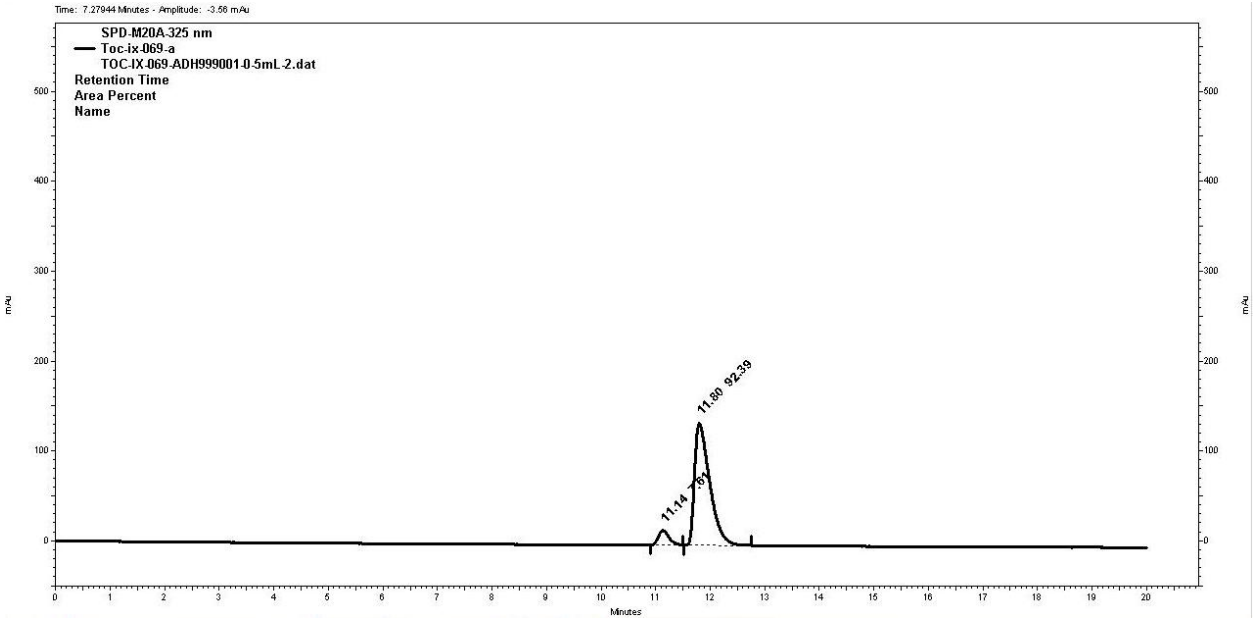
2b: OJ column, 1.0 mL/min: hexanes; 7.97 min (major) and 7.30 min (minor)

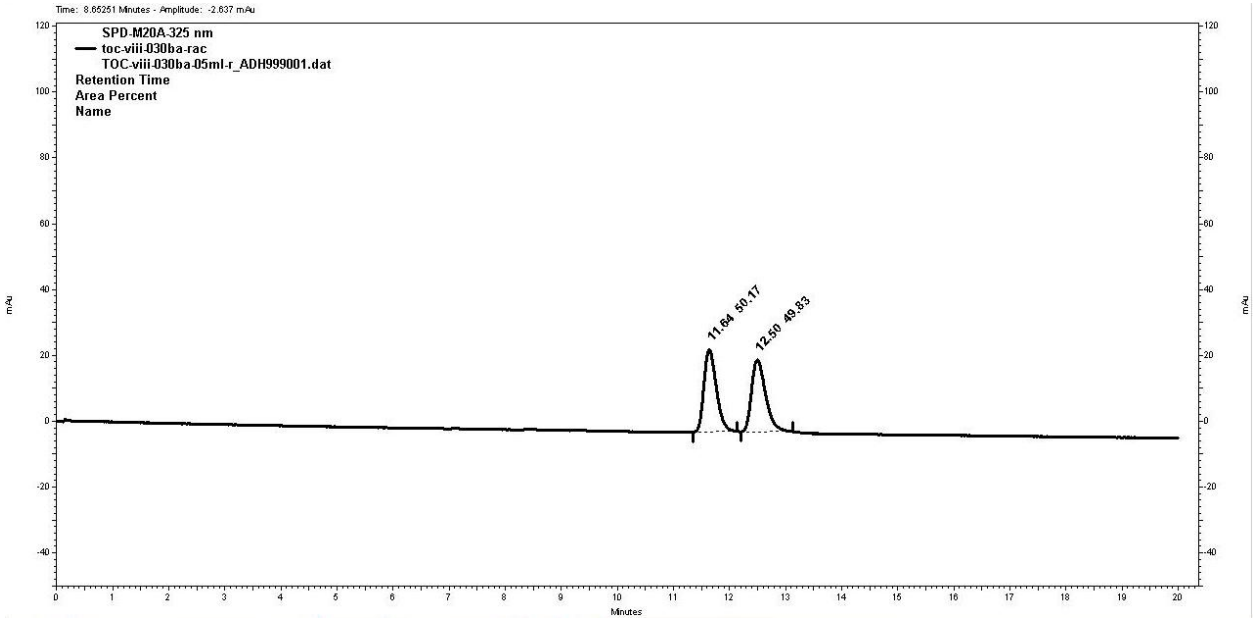


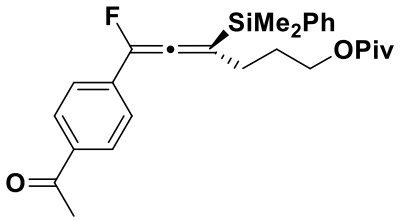




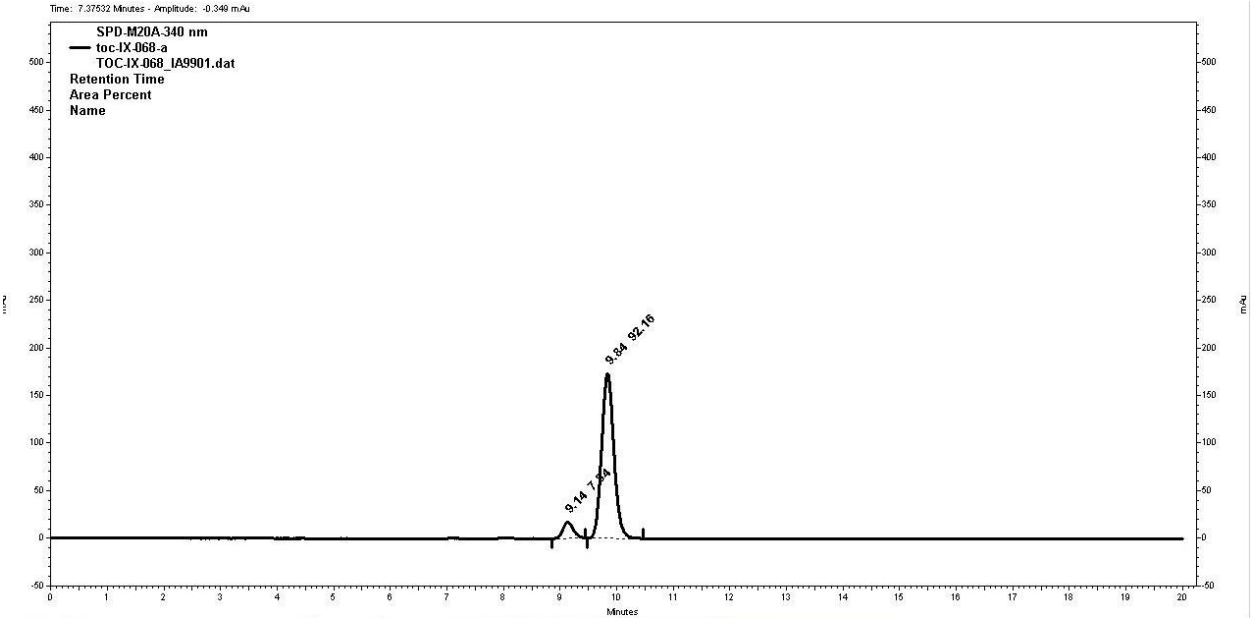
3b: ADH column, 0.5 mL/min: hexanes:iPrOH 99.9:00.1; 11.80 min (major) and 11.14 min (minor)

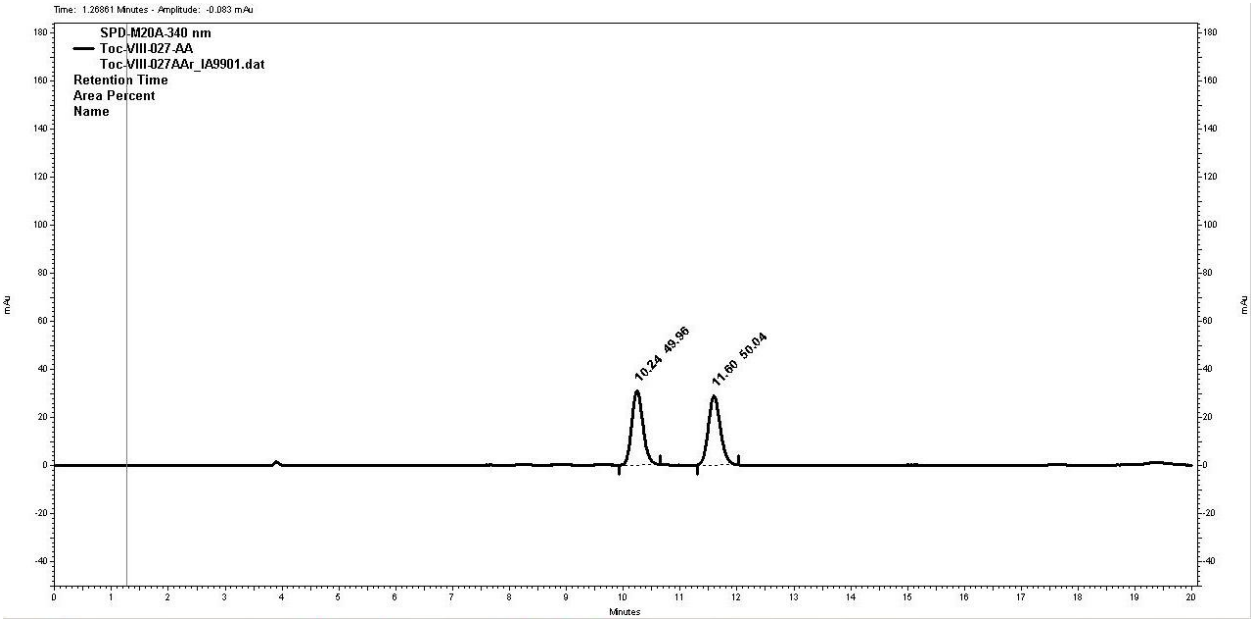


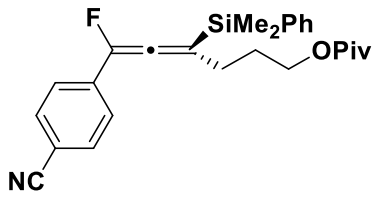




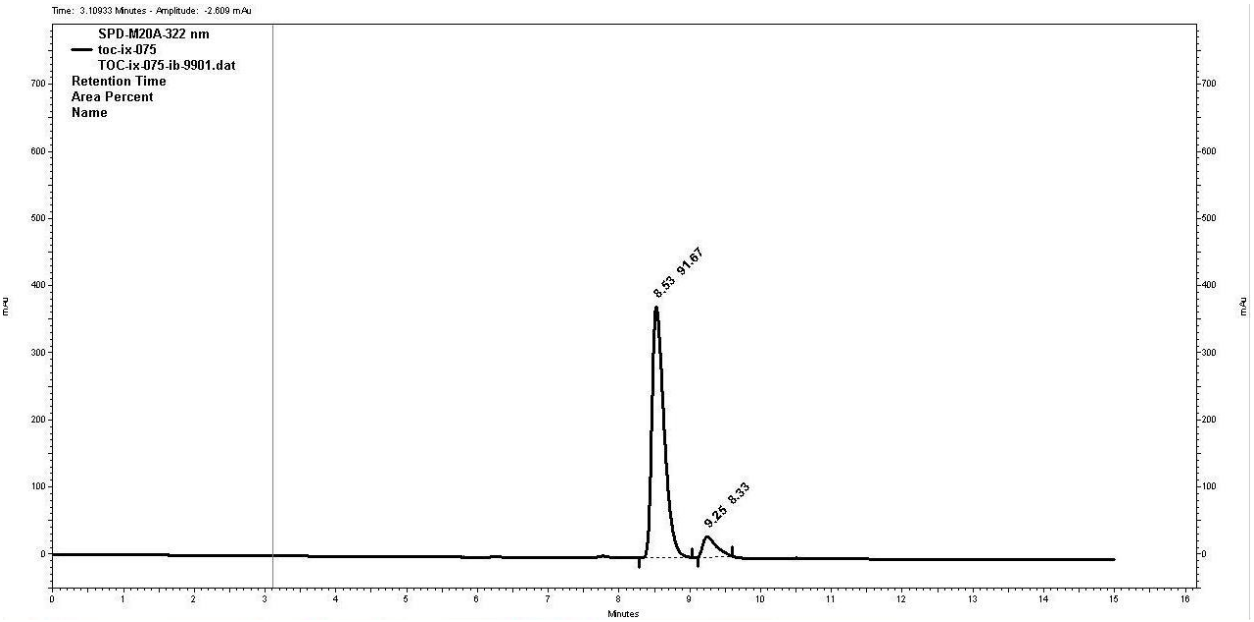
4b: IA column, 1.0 mL/min: hexanes:iPrOH 99:1; 9.84 min (major) and 9.14 min (minor)

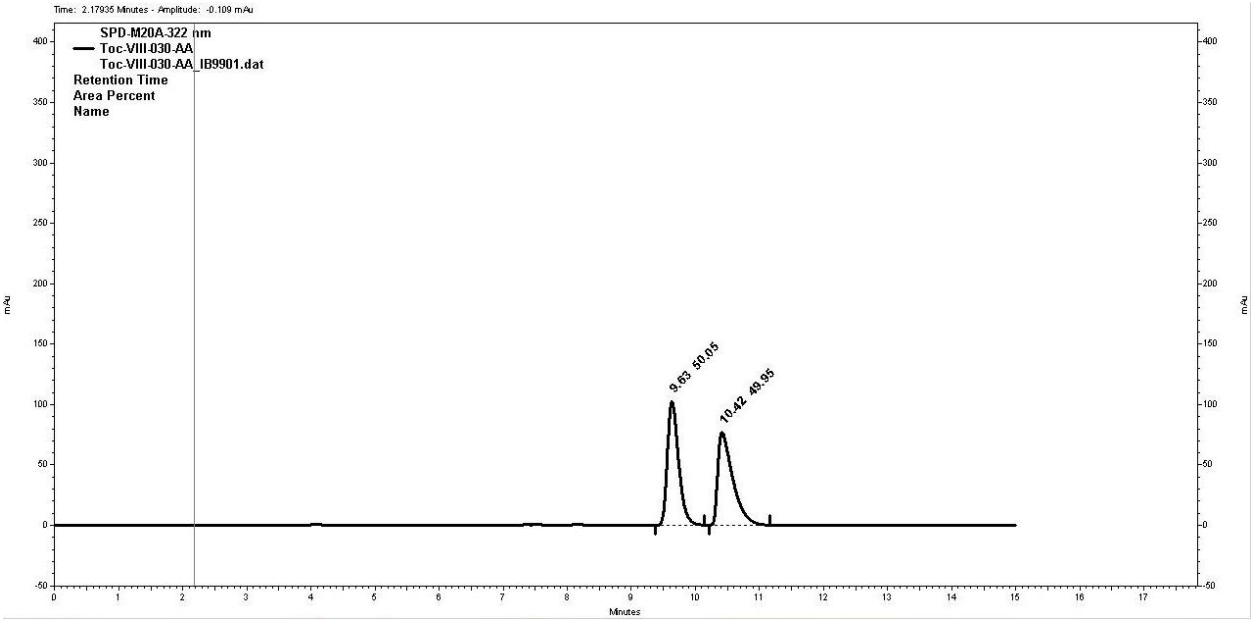


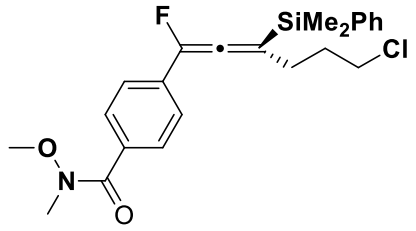




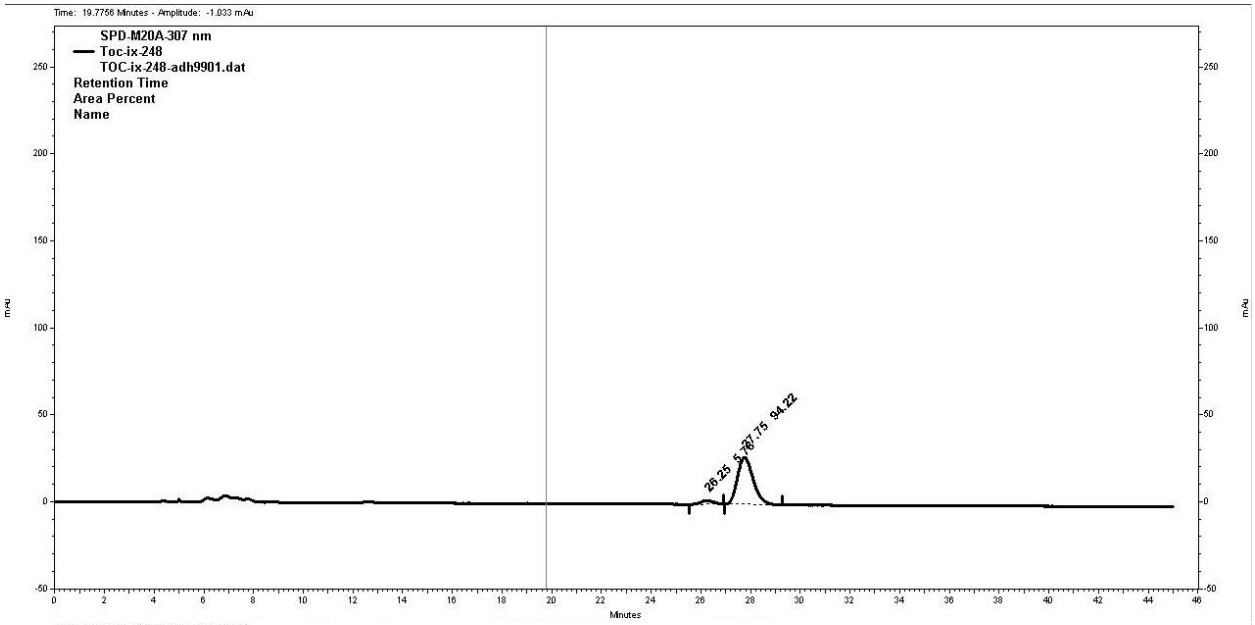
5b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 8.53 min (major) and 9.25 min (minor)

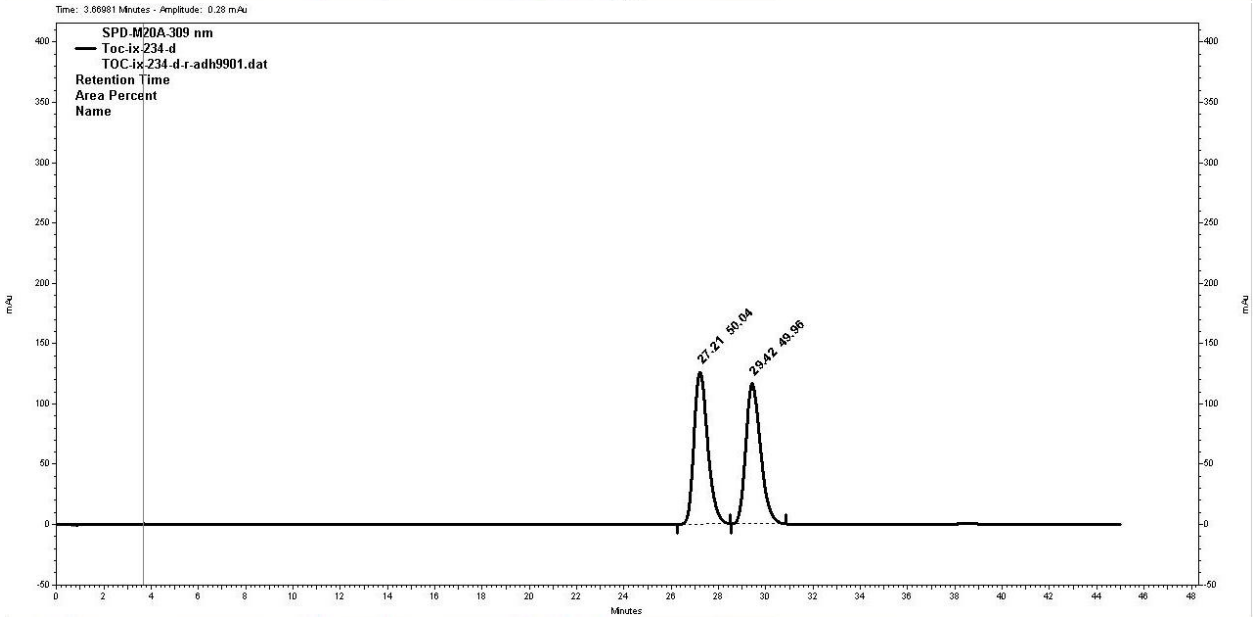


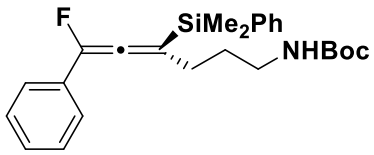




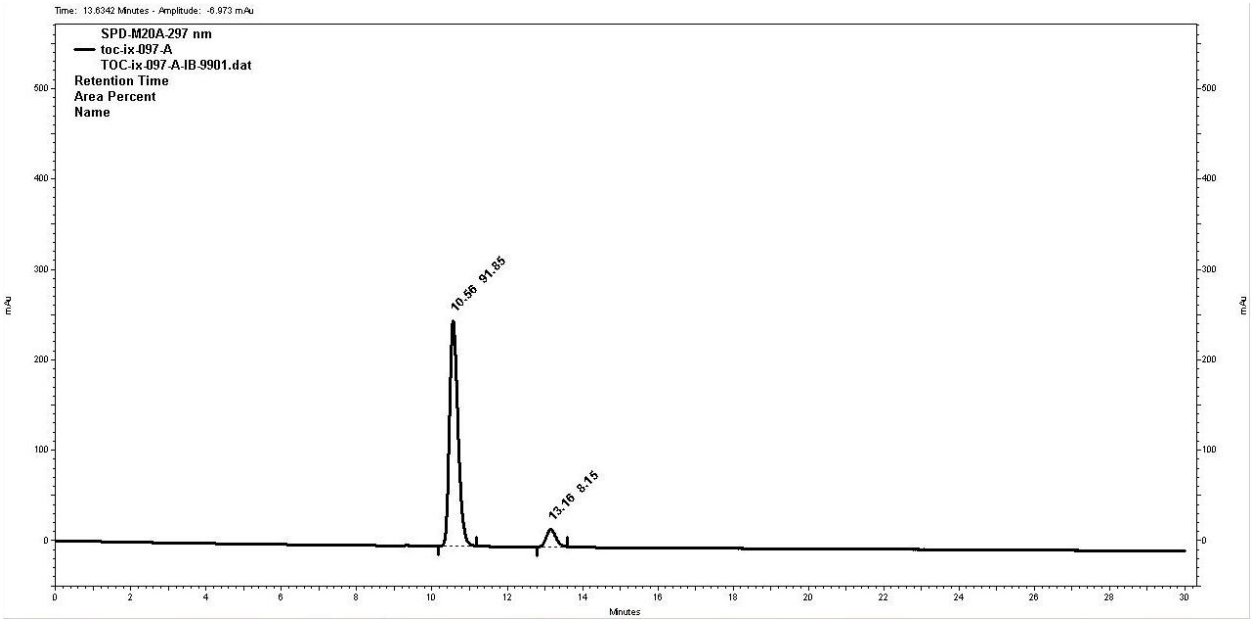
6b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 27.75 min (major) and 26.25 min (minor)

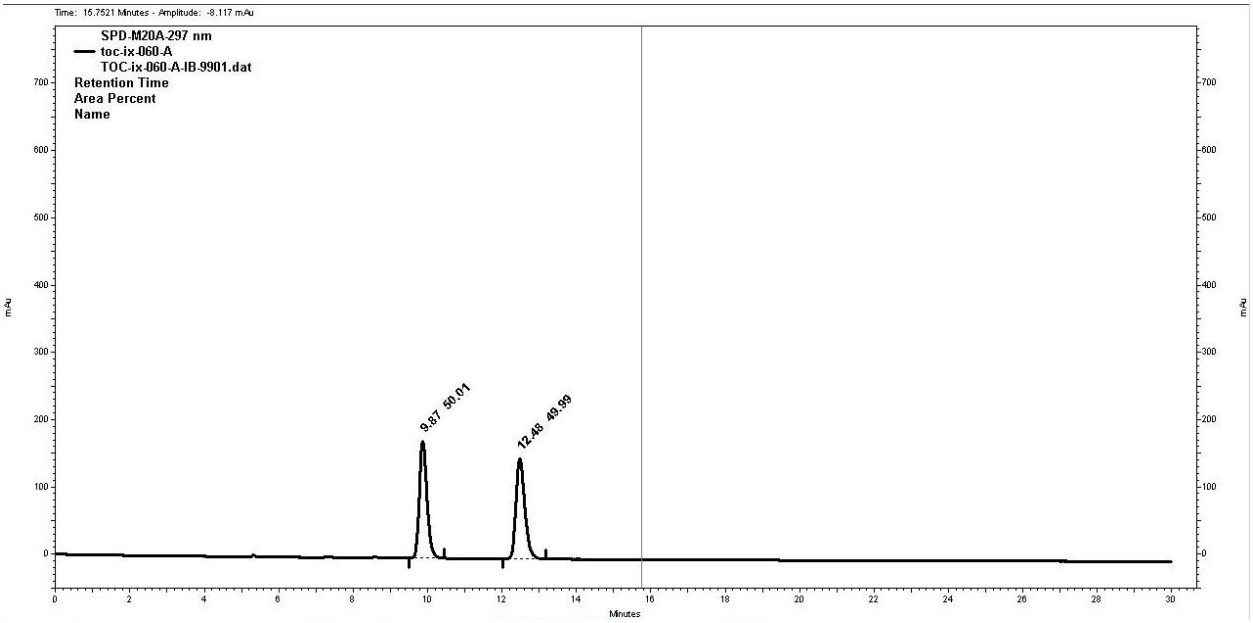


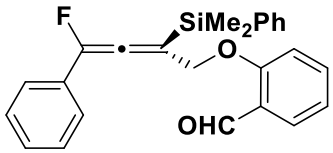




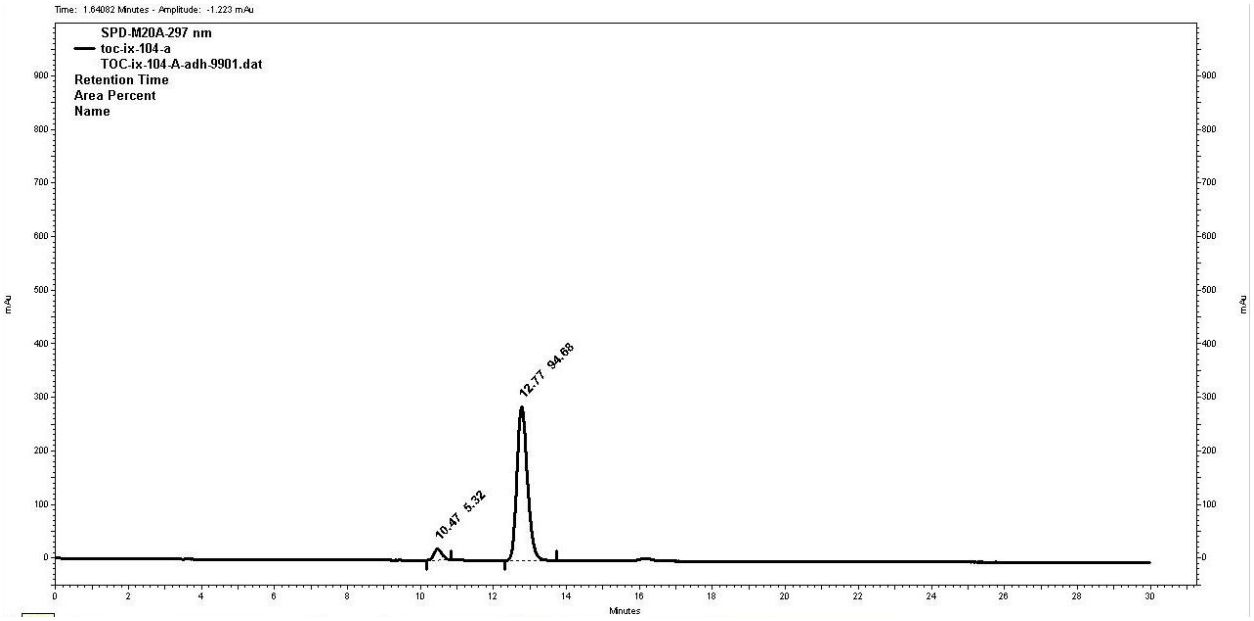
7b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 10.56 min (major) and 13.16 min (minor)

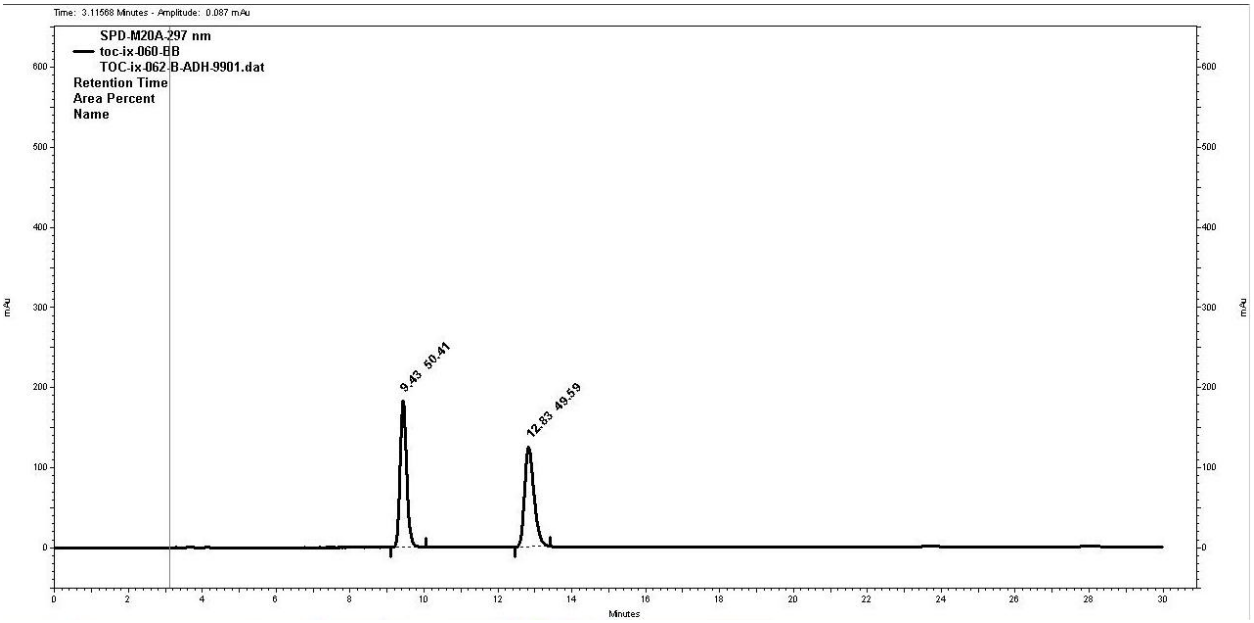


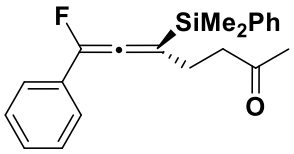




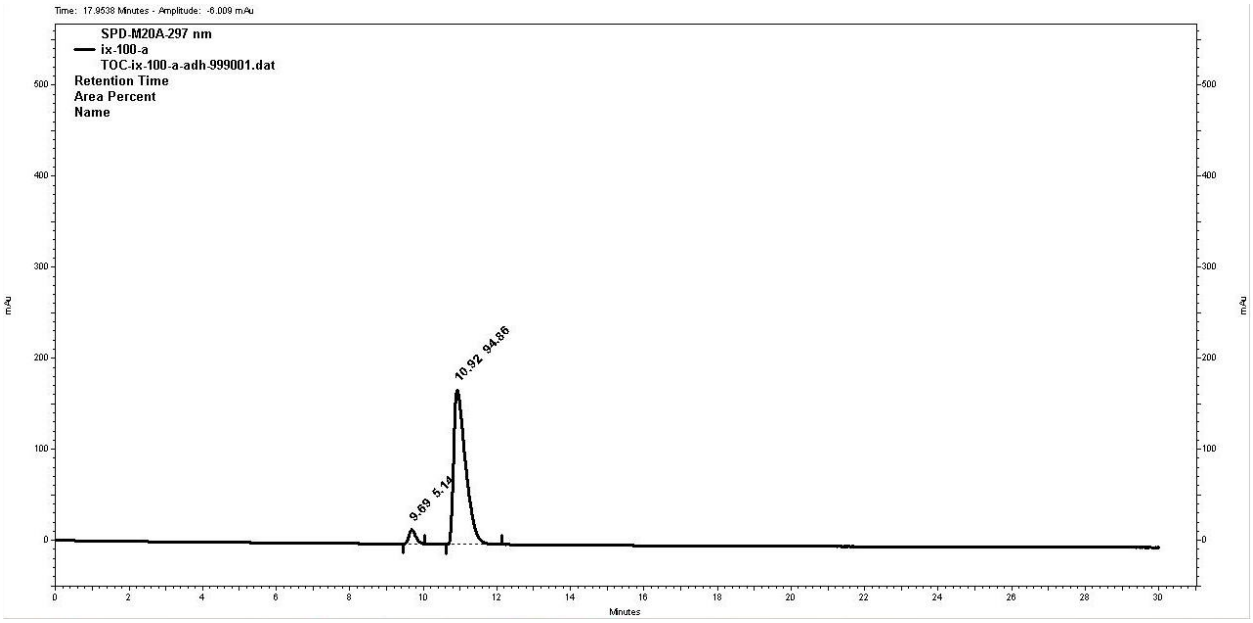
8b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.77 min (major) and 10.47 min (minor)

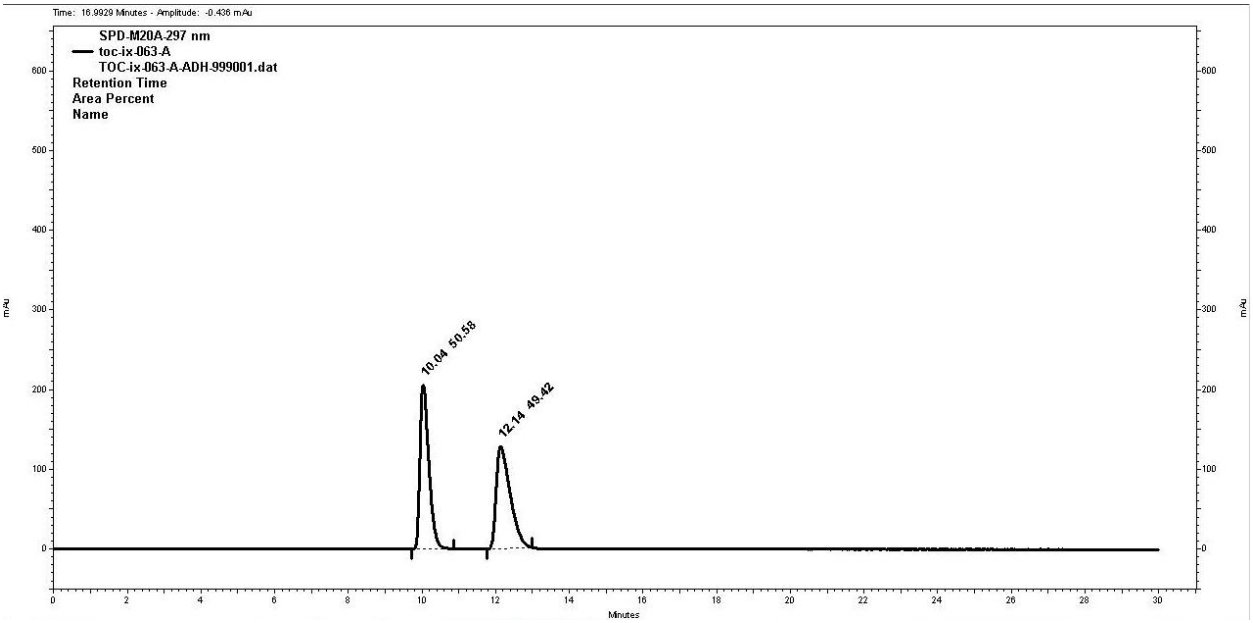


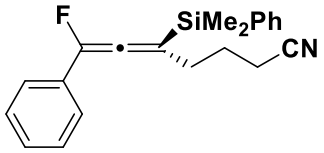




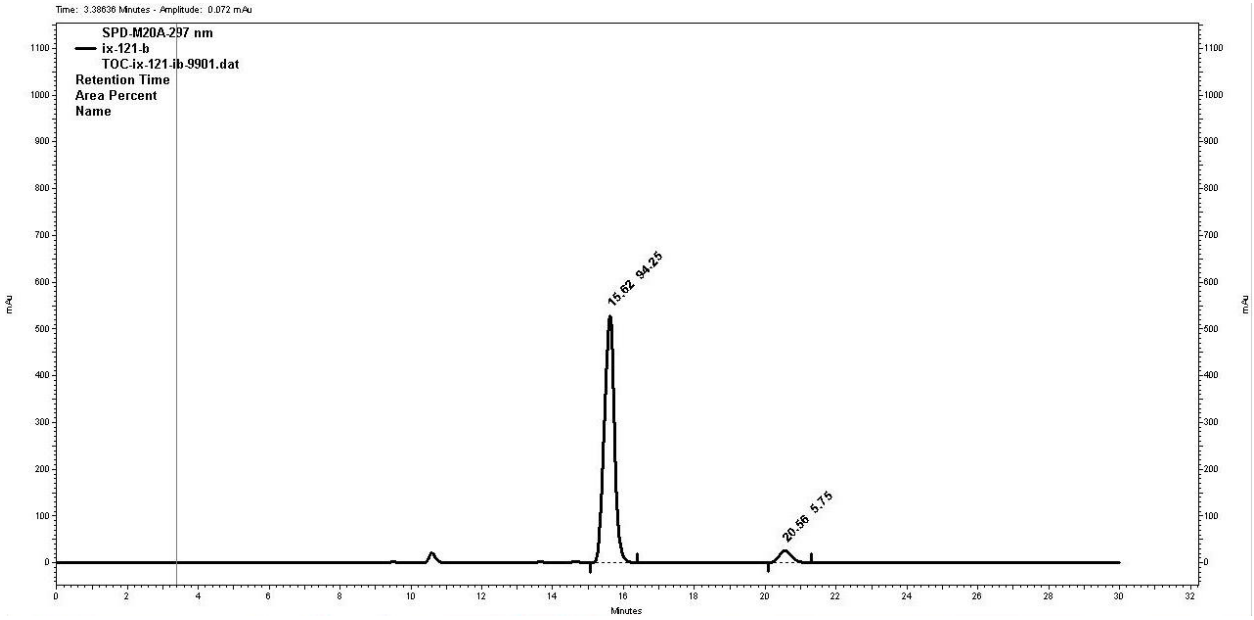
9b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 10.92 min (major) and 9.69 min (minor)

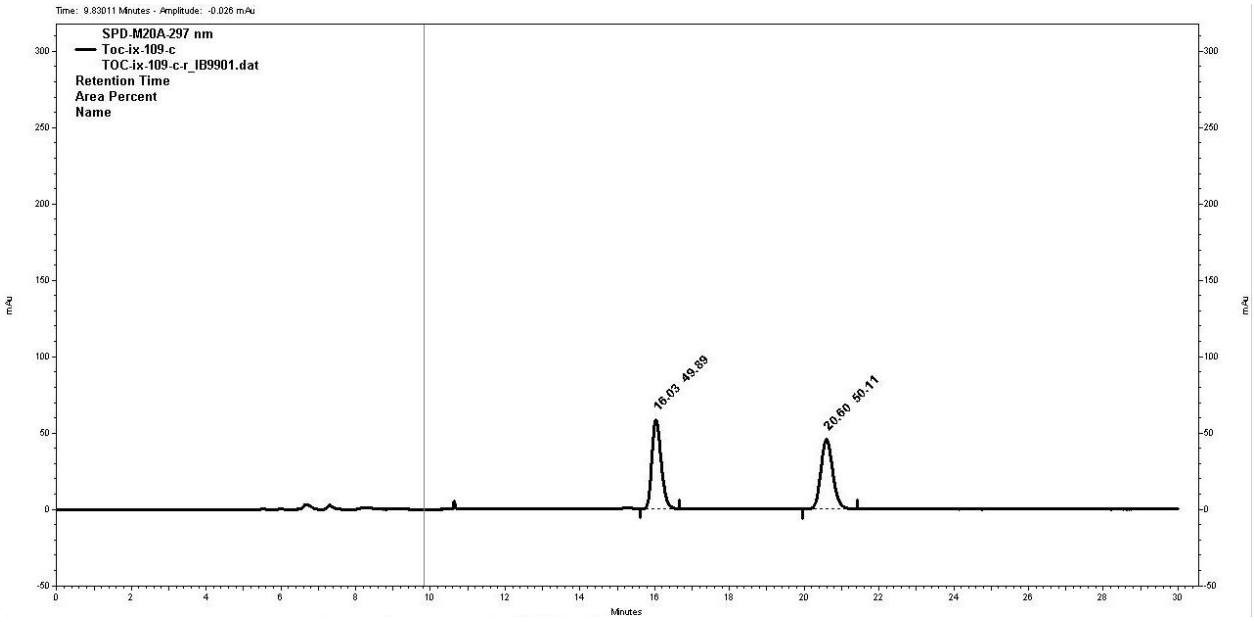


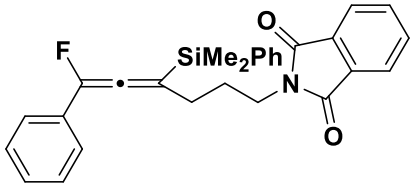




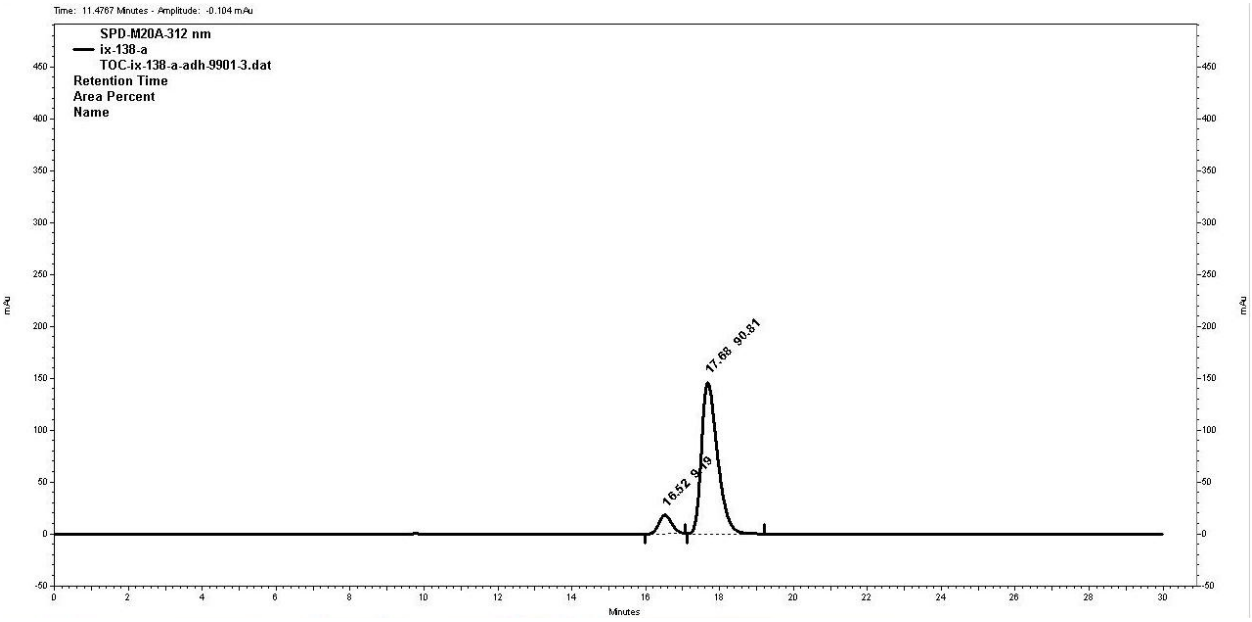
10b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 15.62 min (major) and 20.56 min (minor)

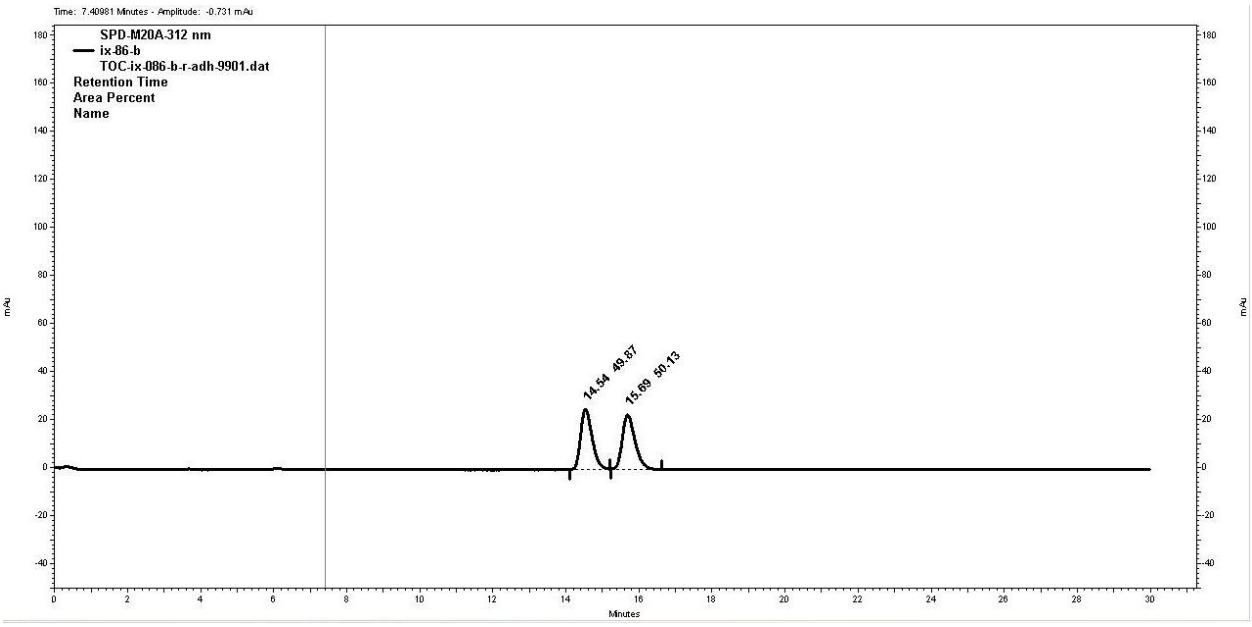


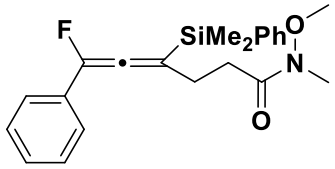




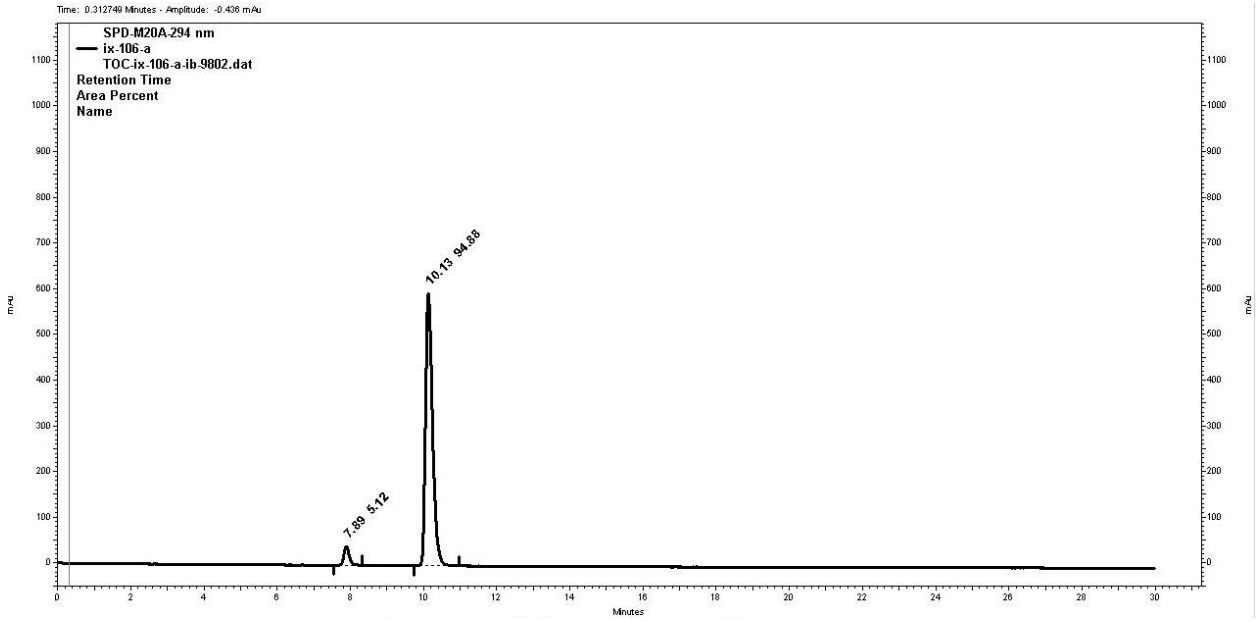
11b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 17.68 min (major) and 16.52 min (minor)

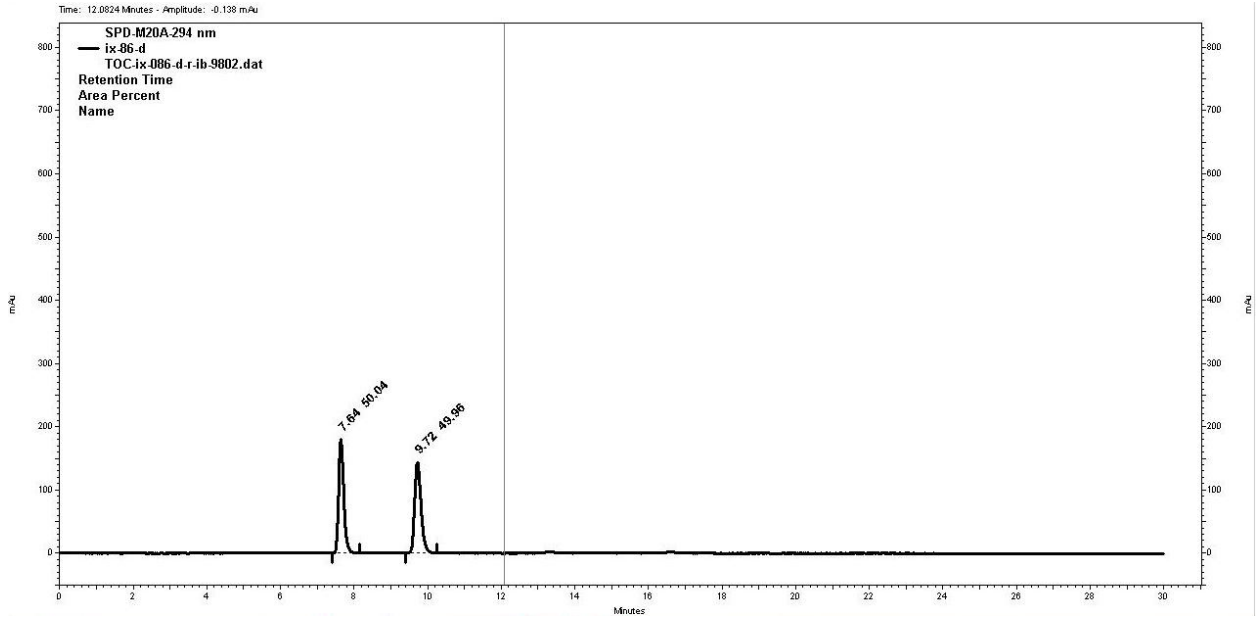


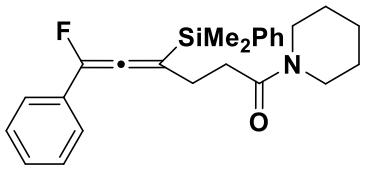




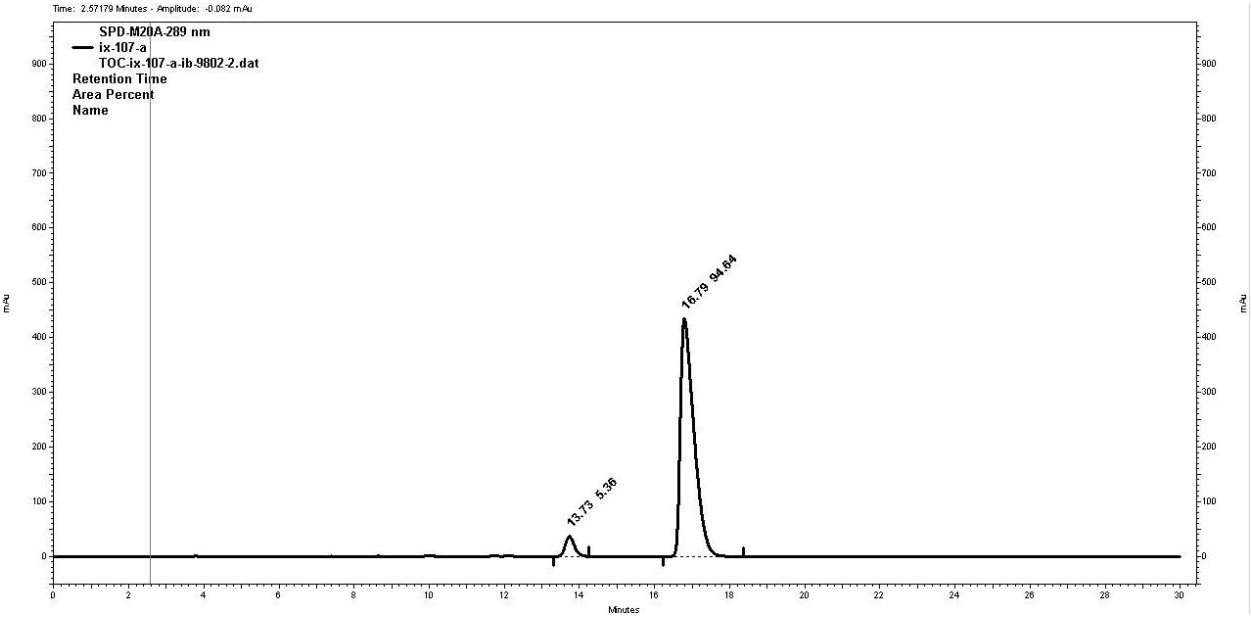
12b: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 10.13 min (major) and 7.89 min (minor)

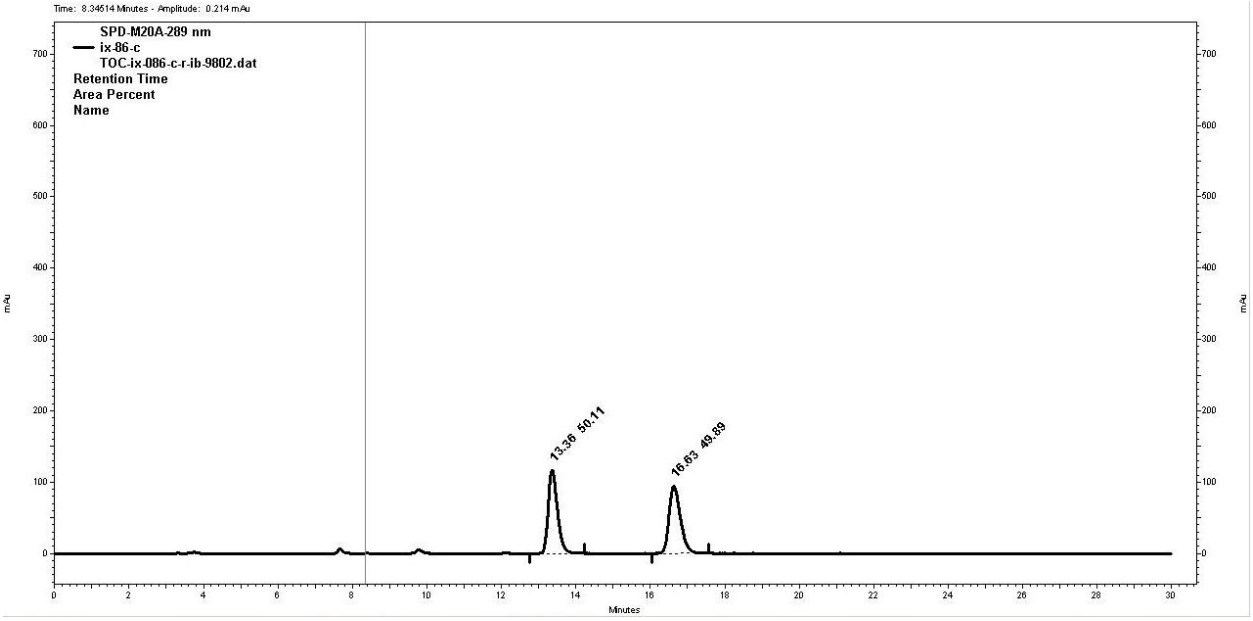


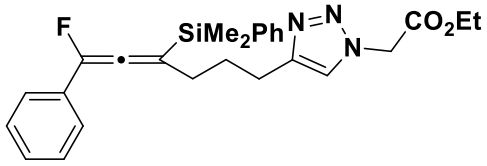




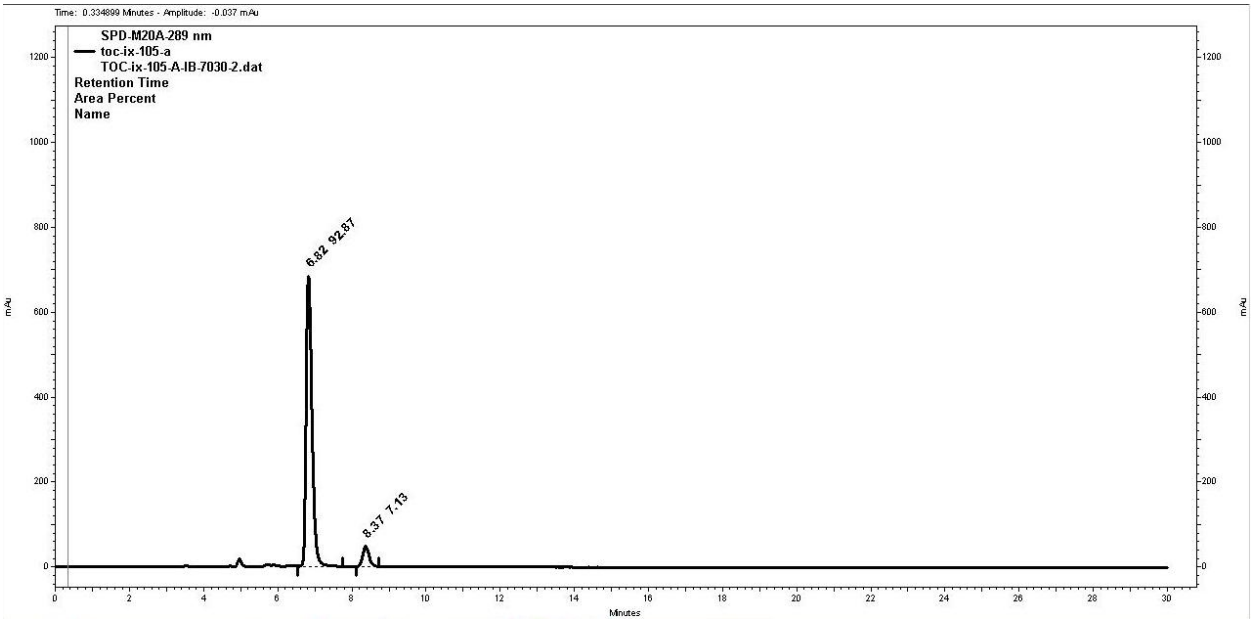
13b: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 16.79 min (major) and 13.73 min (minor)

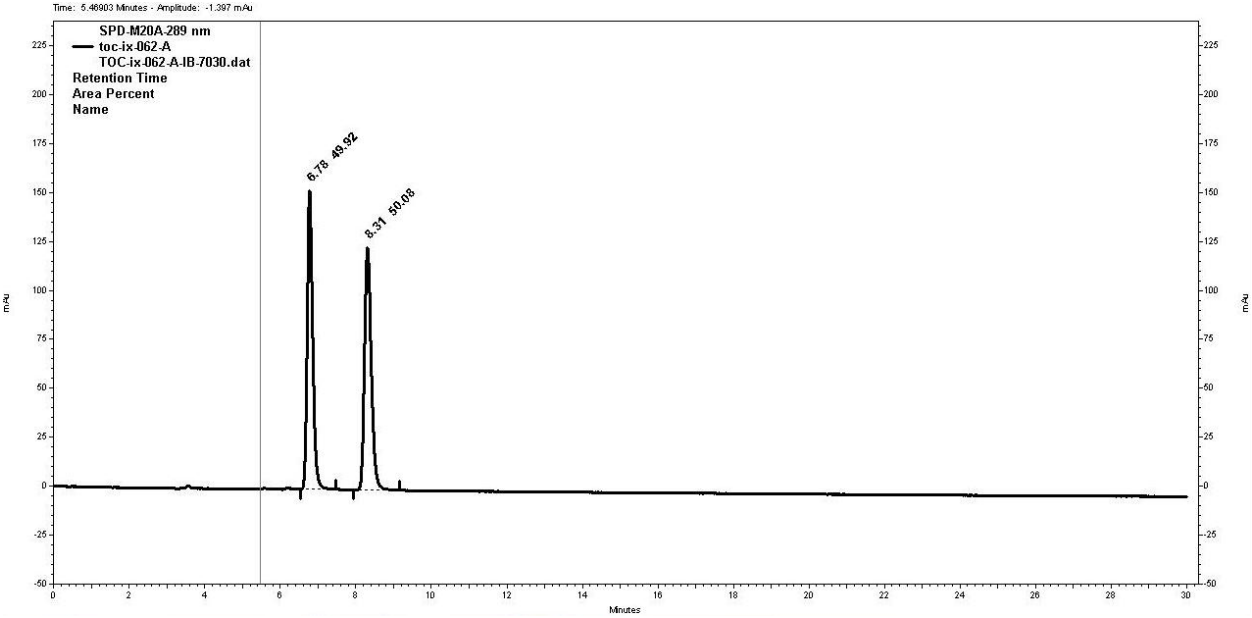


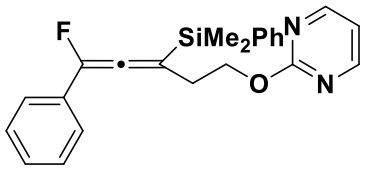




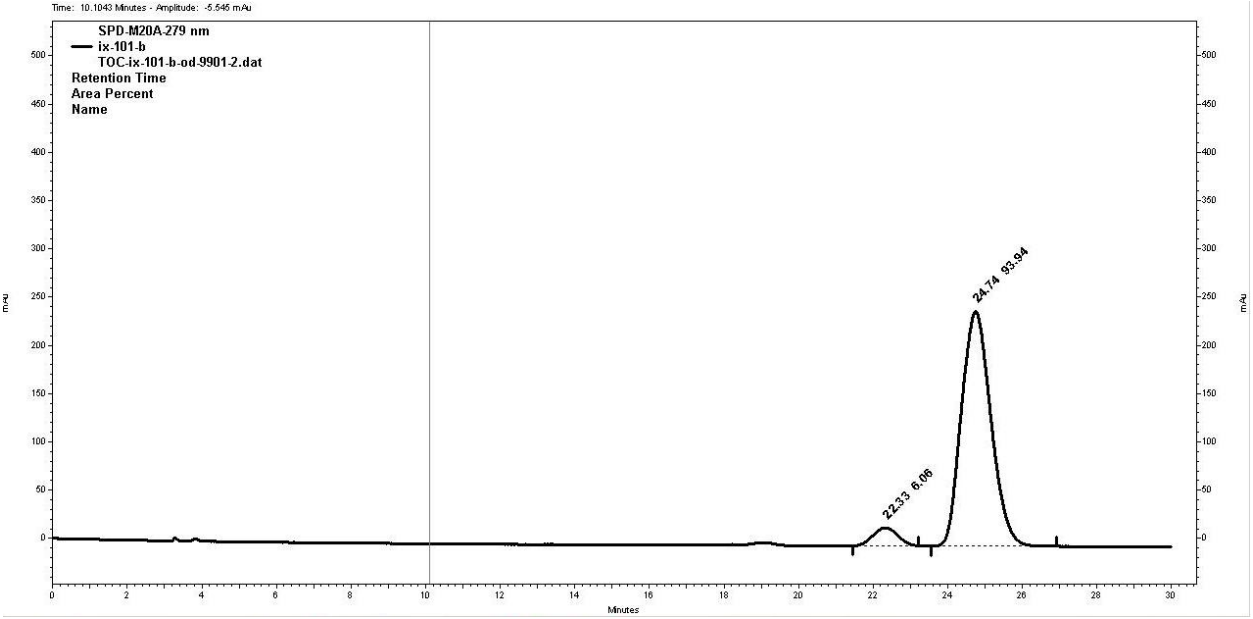
14: IB column, 1.0 mL/min: hexanes:iPrOH 70:30; 6.82 min (major) and 8.37 min (minor)

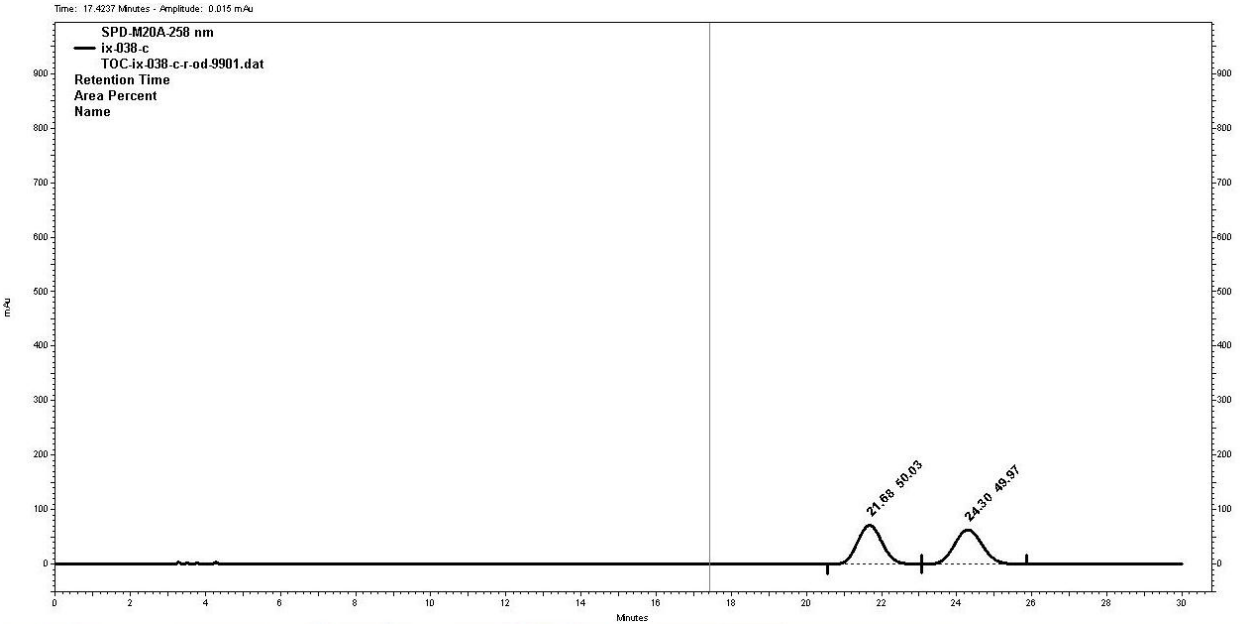


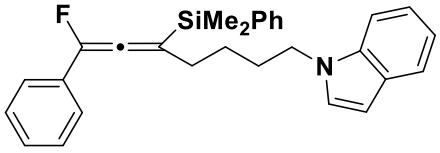




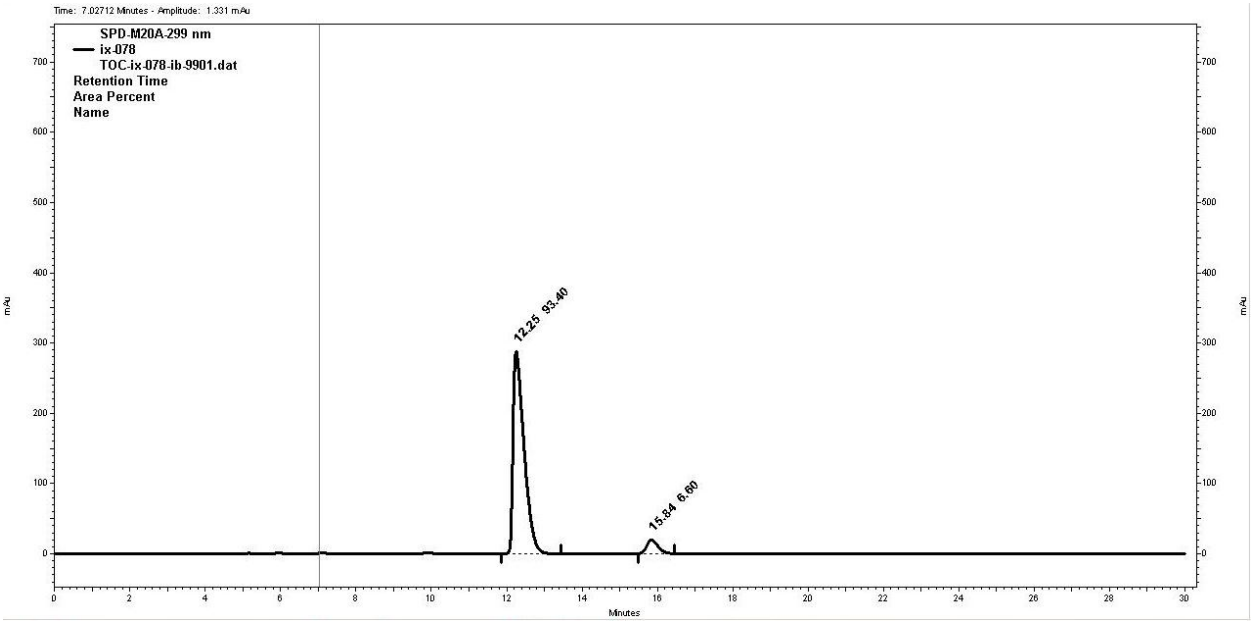
15b: OD column, 1.0 mL/min: hexanes:iPrOH 99:01; 24.74 min (major) and 22.33 min (minor)

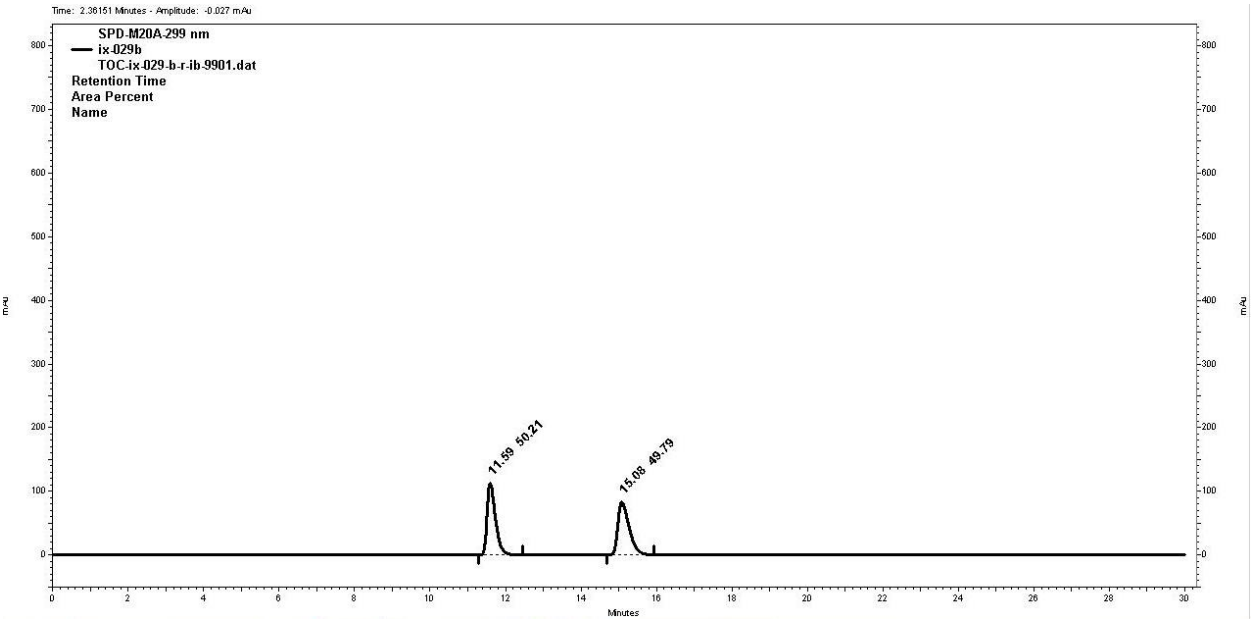


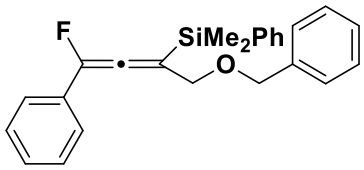




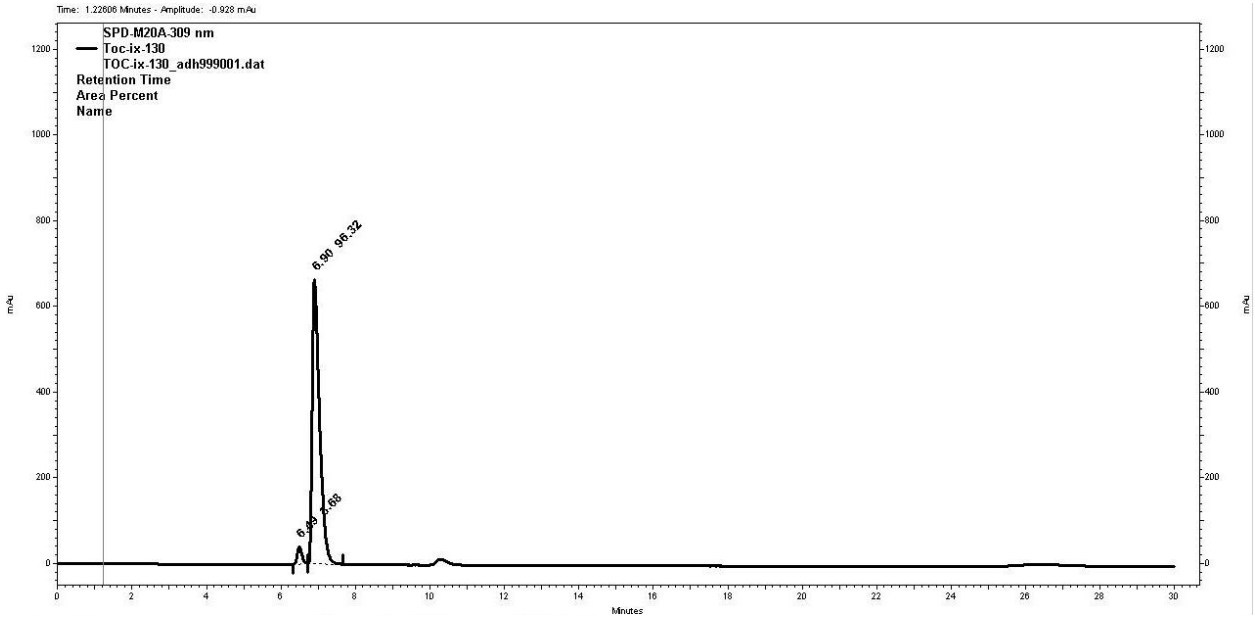
16b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.25 min (major) and 15.84 min (minor)

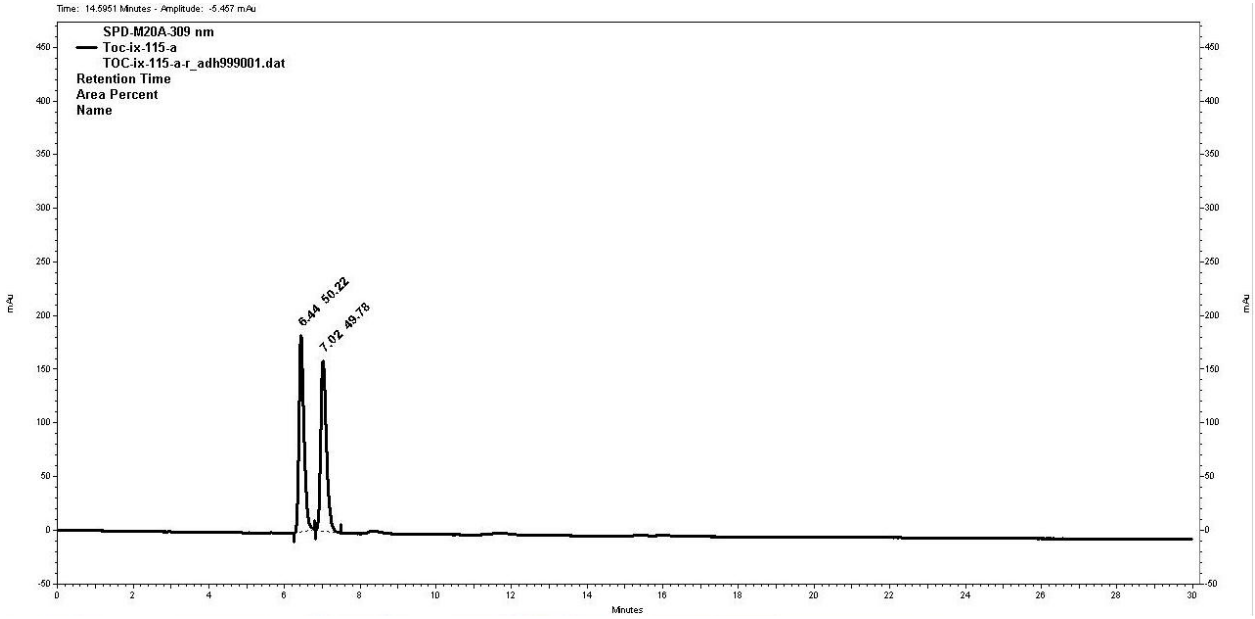


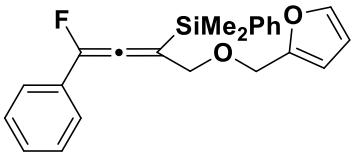




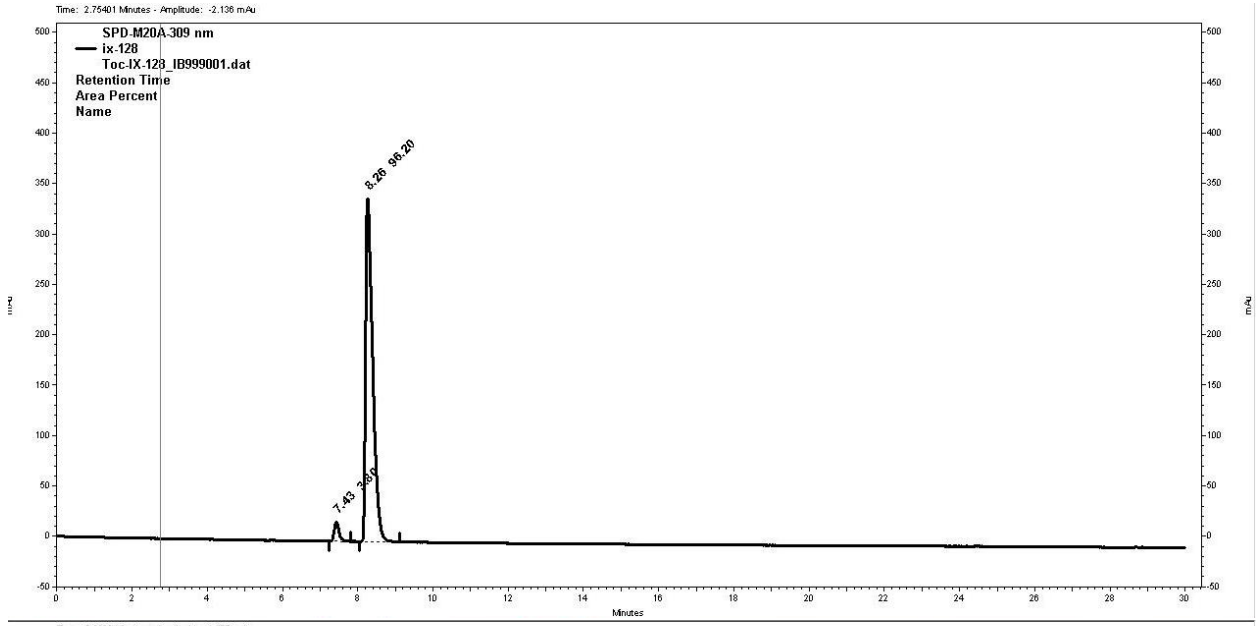
17: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 6.90 min (major) and 6.49 min (minor)

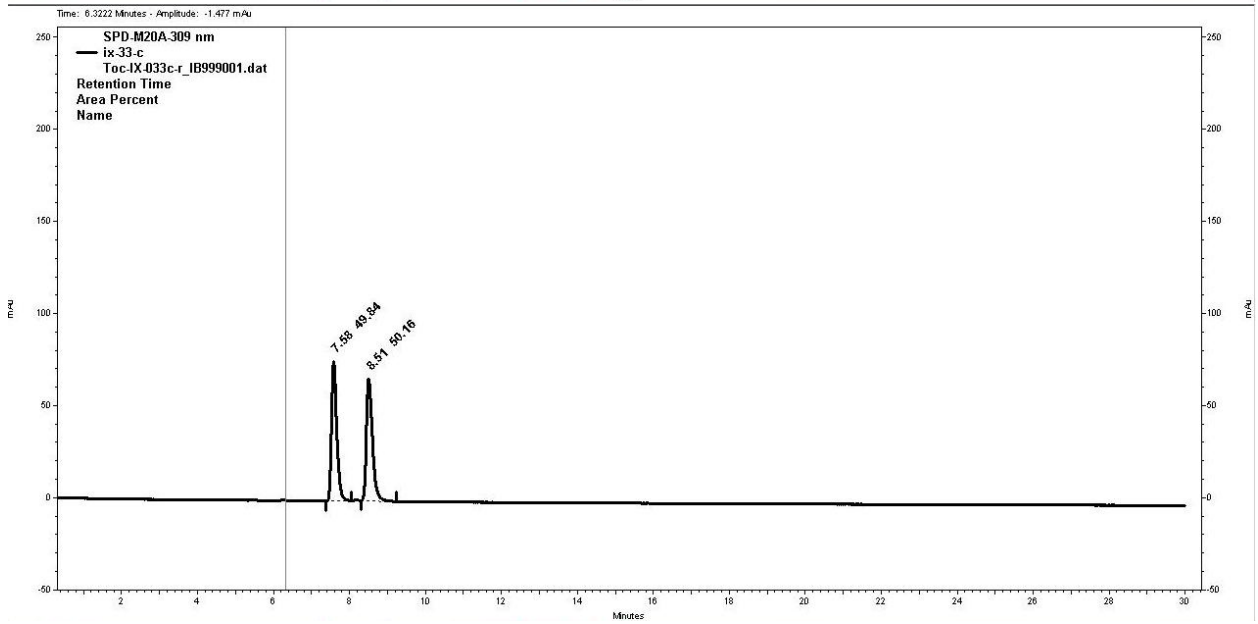


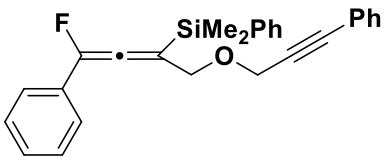




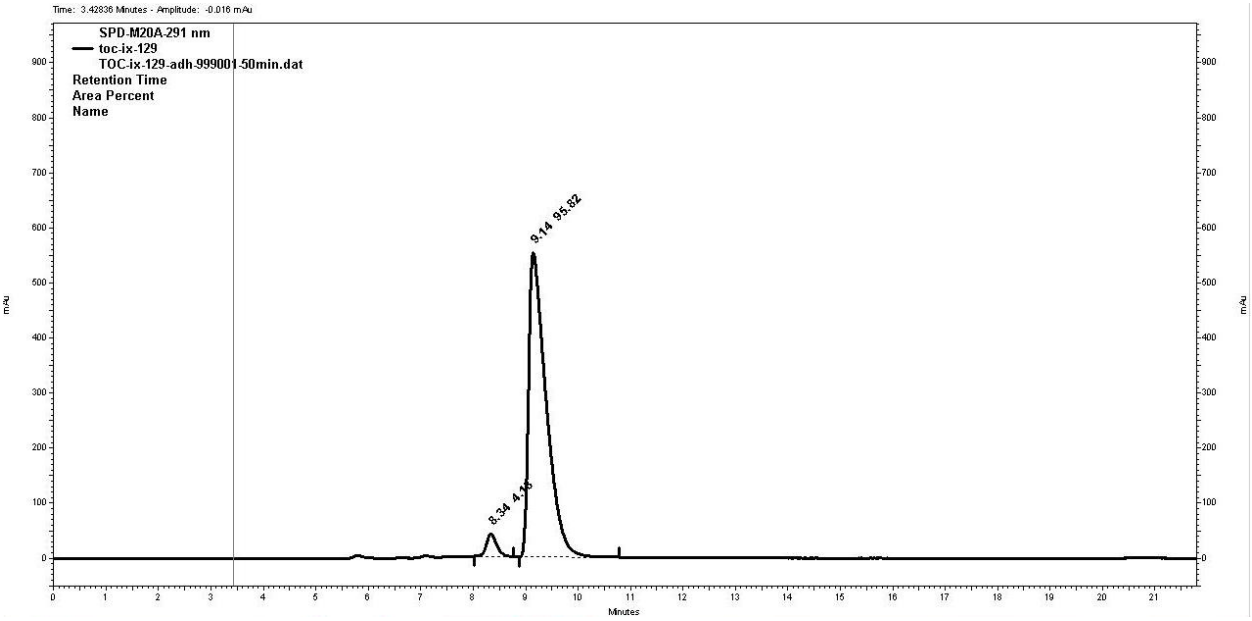
18b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 8.26 min (major) and 7.43 min (minor)

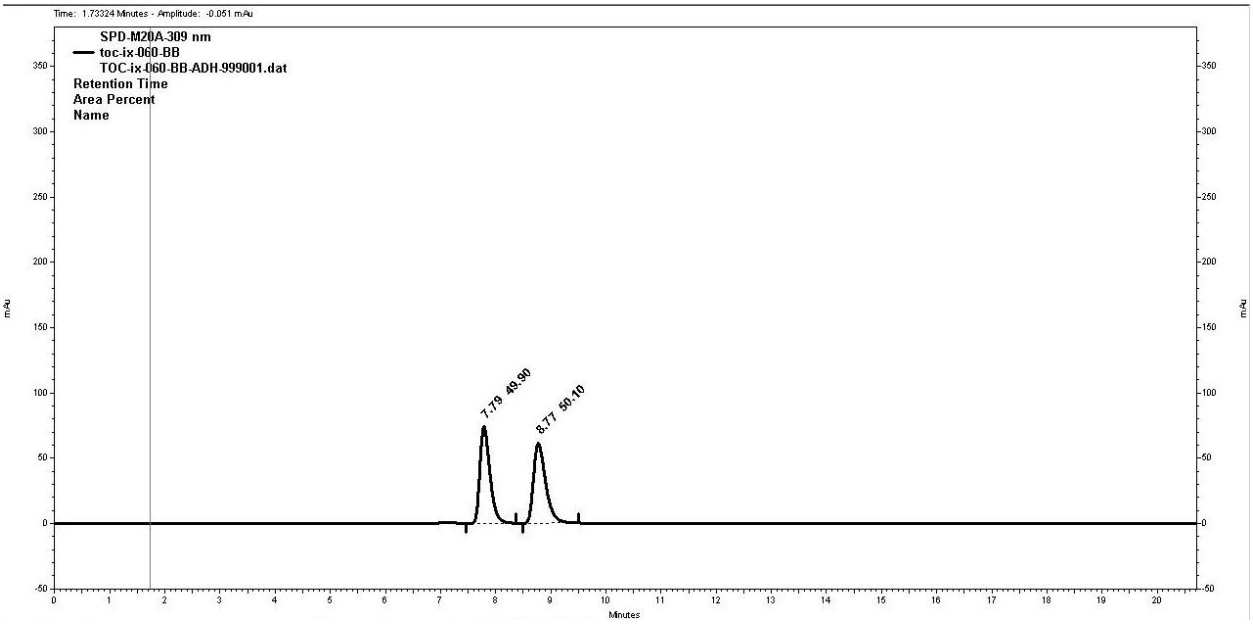


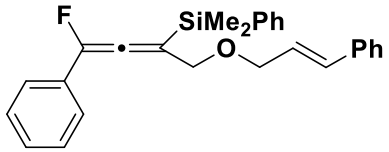




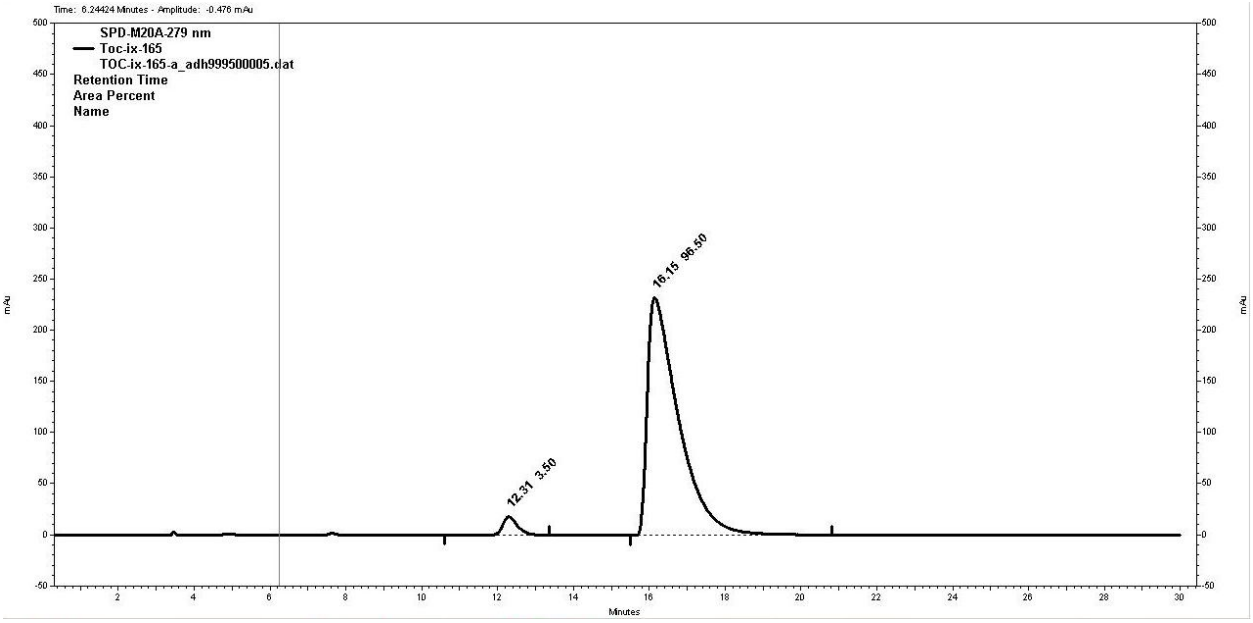
19b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 9.14 min (major) and 8.34 min (minor)

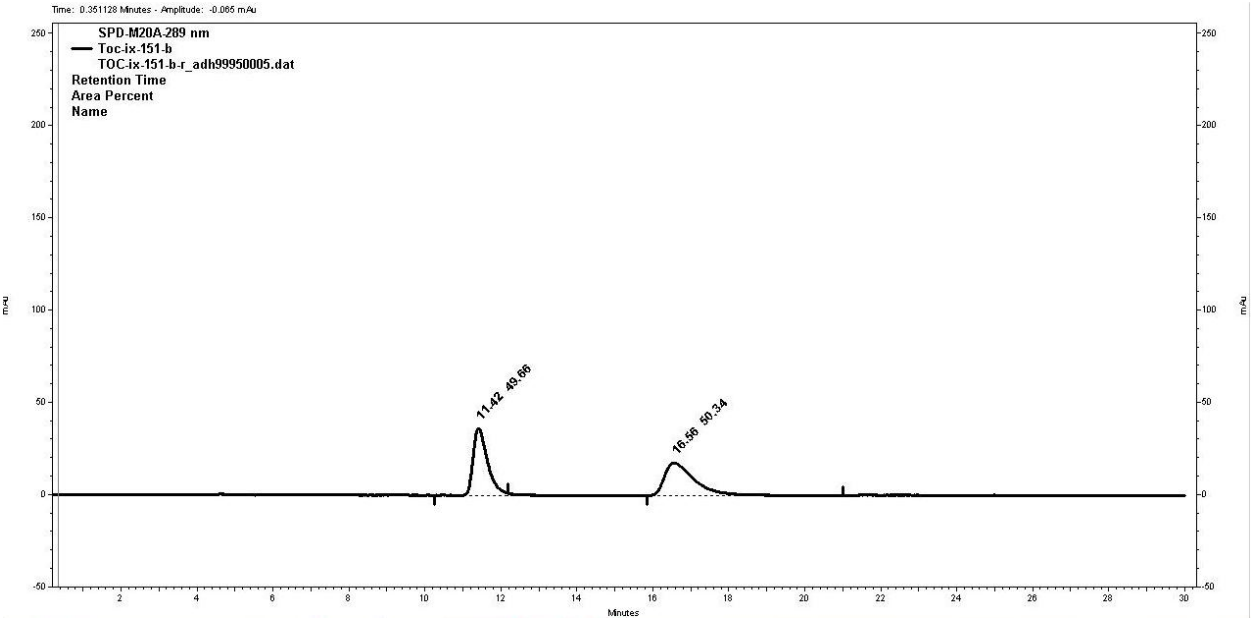


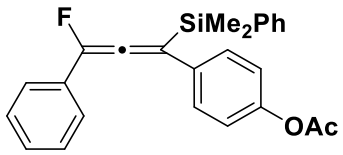




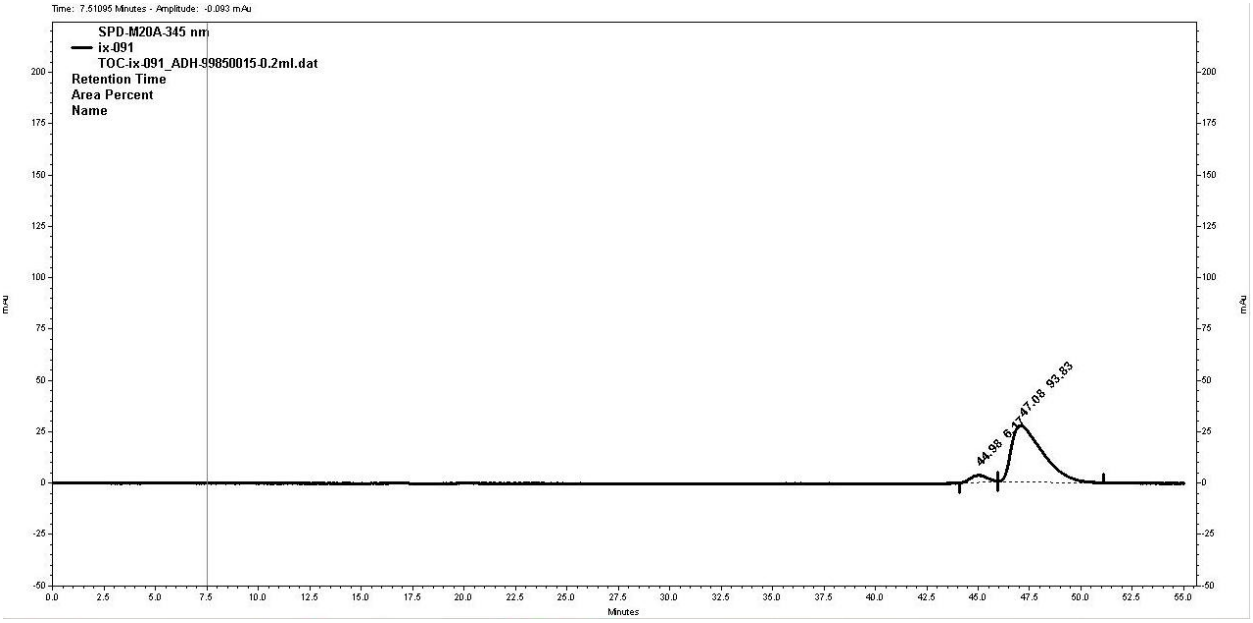
20b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.95:00.05; 16.15 min (major) and 12.31 min (minor)

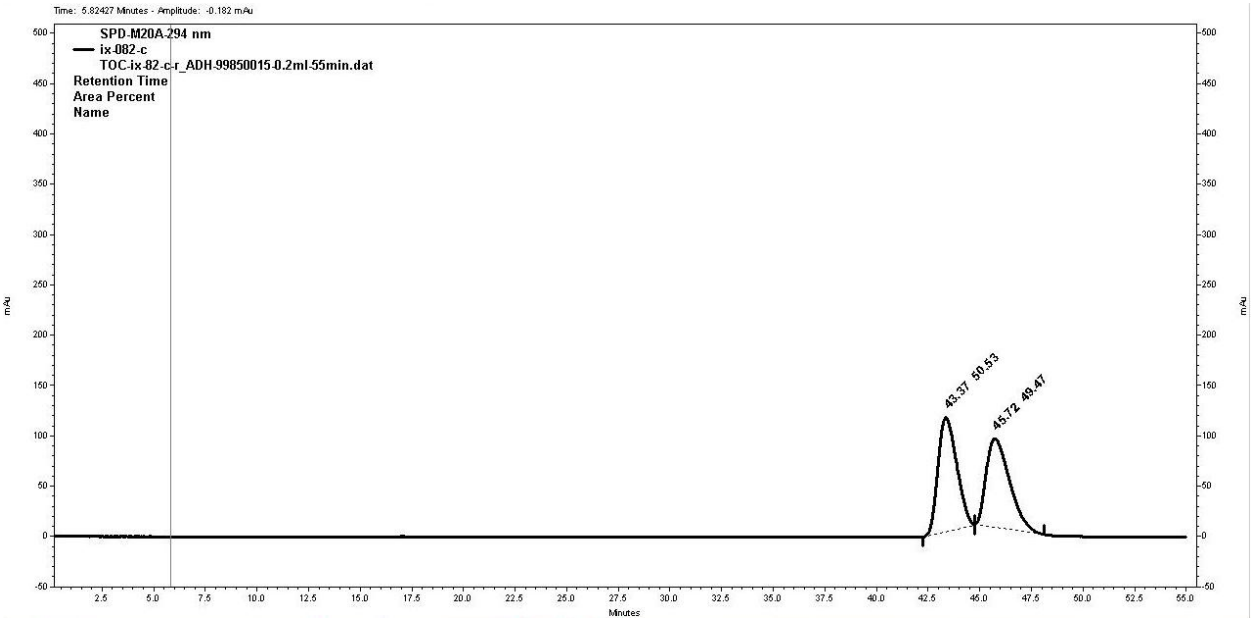


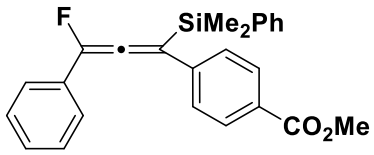




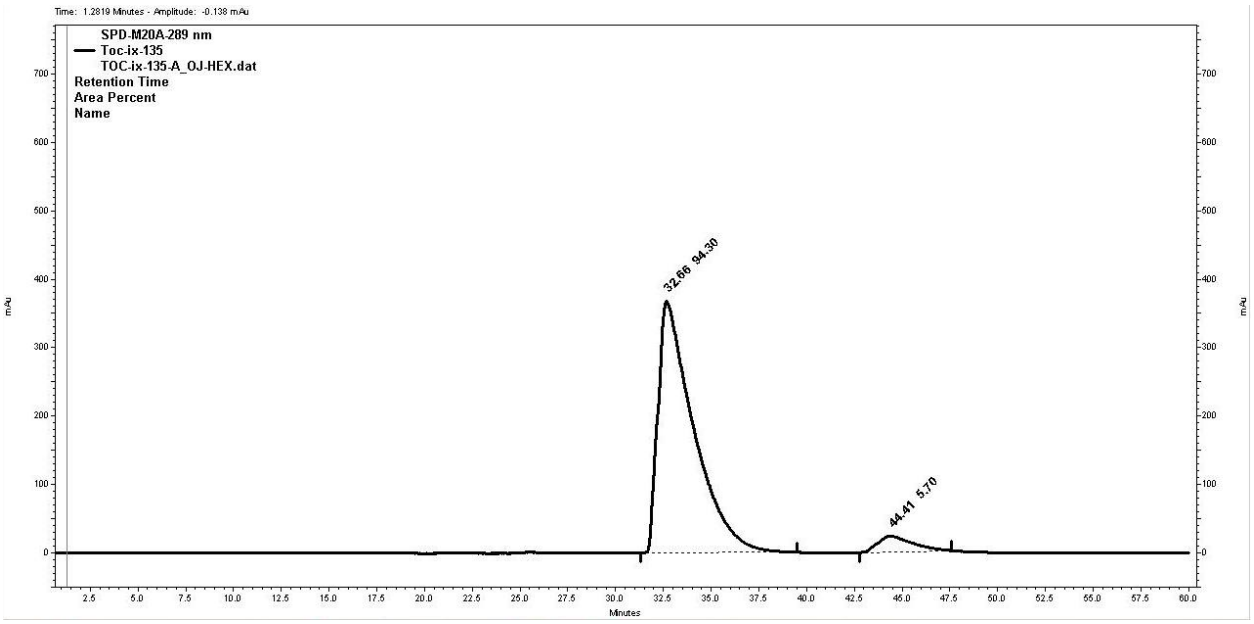
21b: ADH column, 0.2 mL/min: hexanes:iPrOH 99.85:00.15; 47.08 min (major) and 44.98 min (minor)

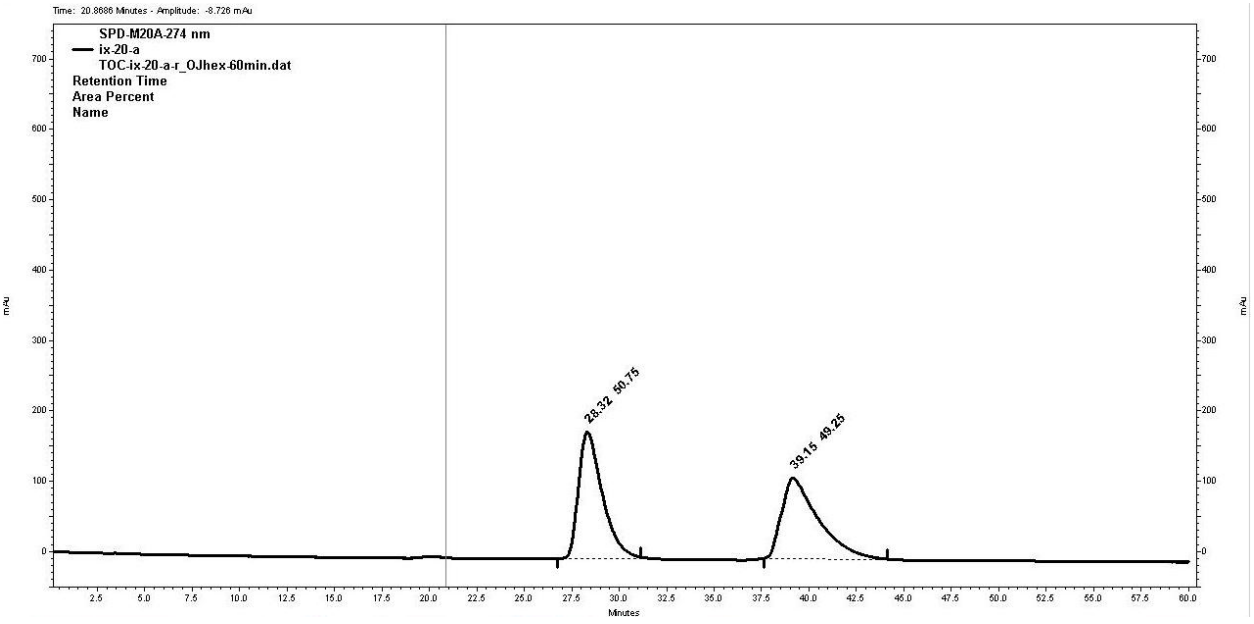


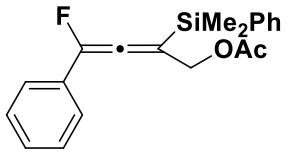




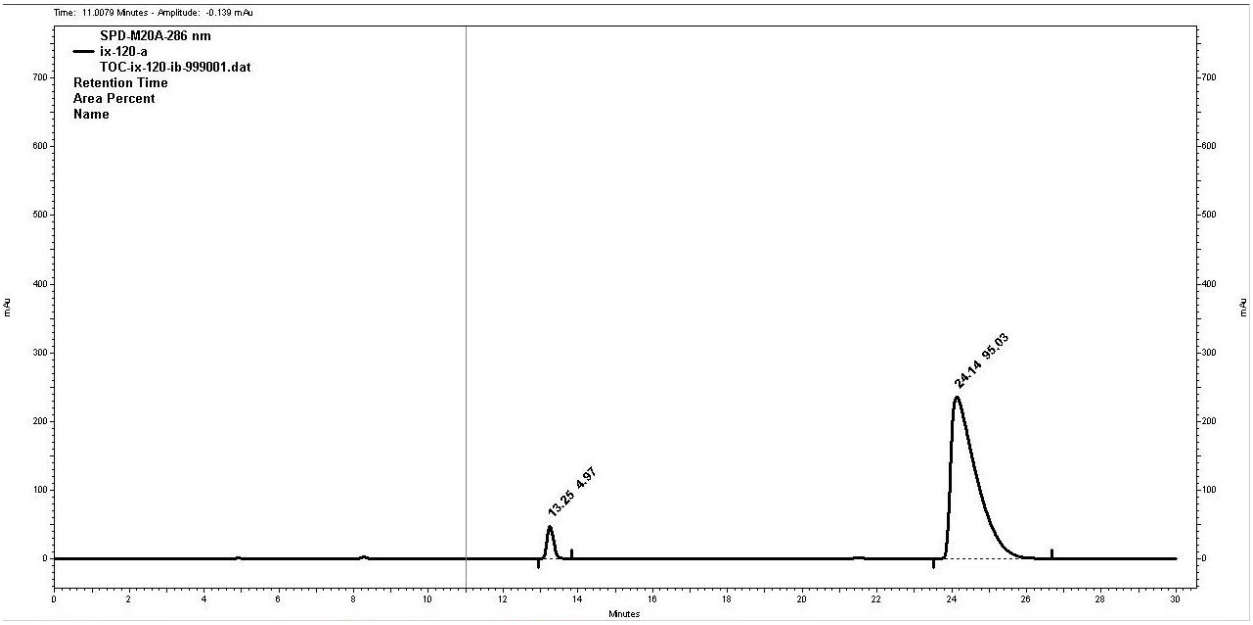
22b: OJ column, 1.0 mL/min: hexanes; 32.66 min (major) and 44.41 min (minor)

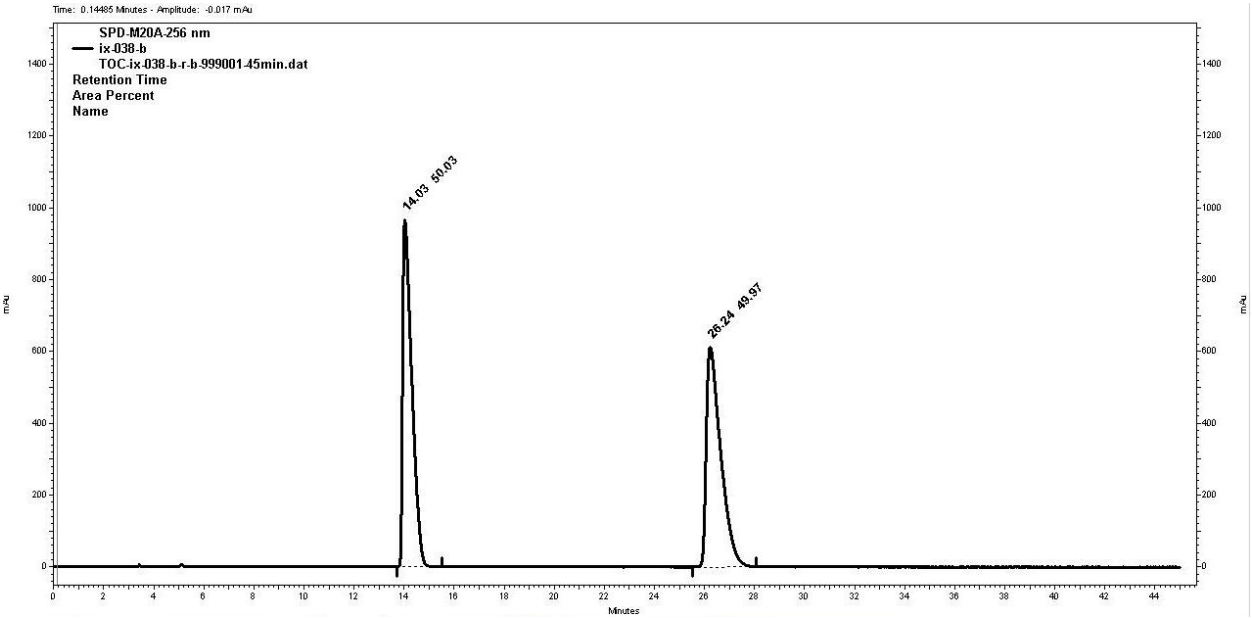


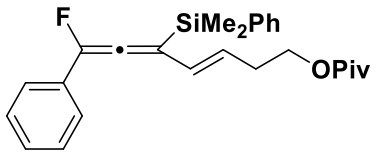




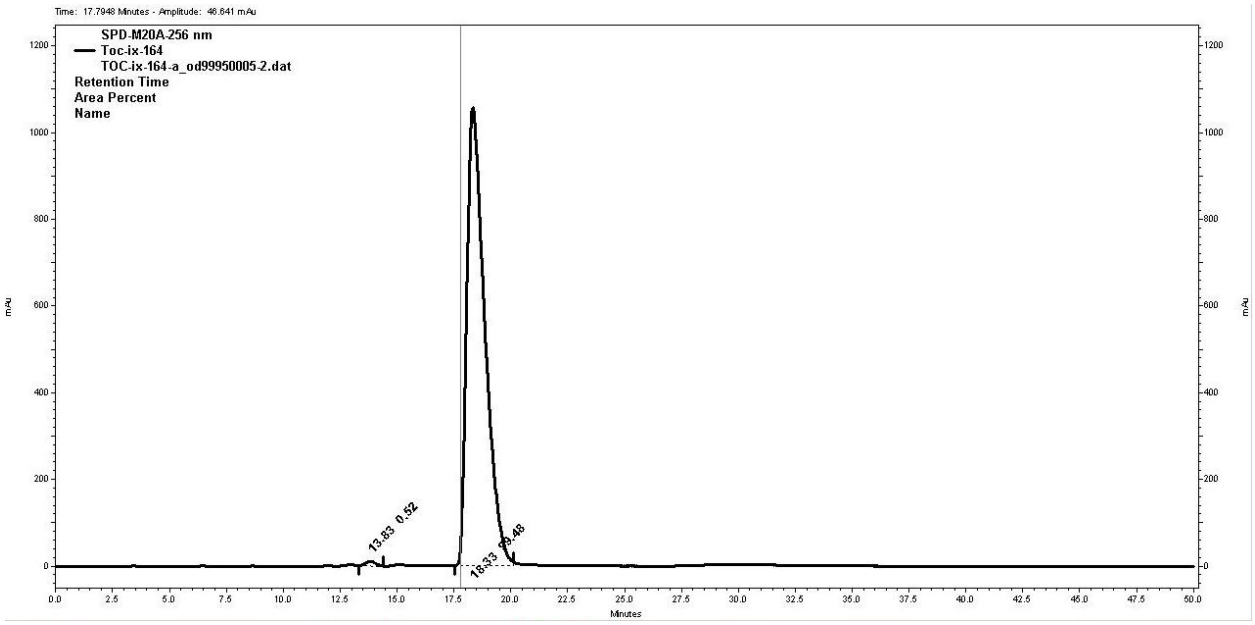
23b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 21.14 min (major) and 13.25 min (minor)

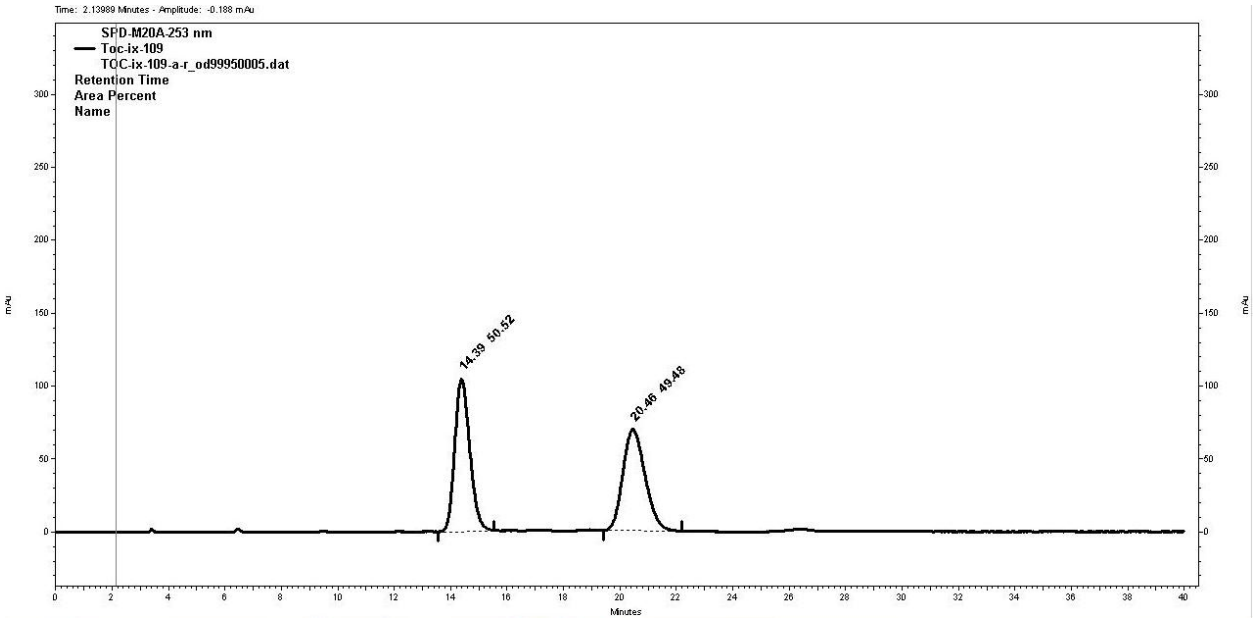


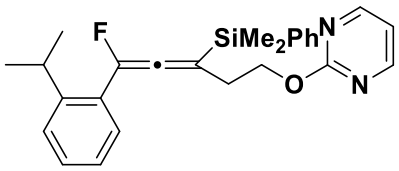




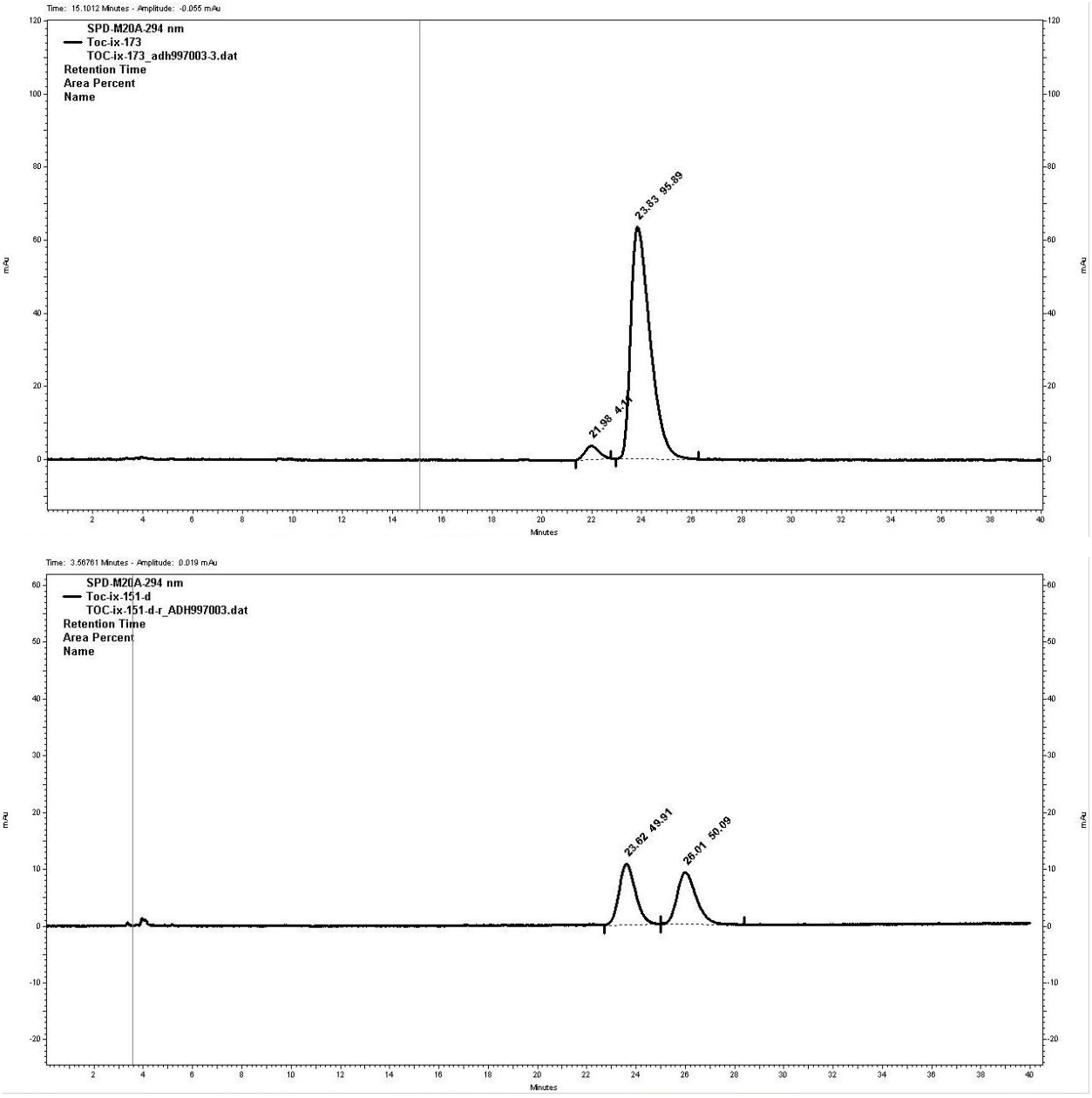
24b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 18.33 min (major) and 13.83 min (minor)

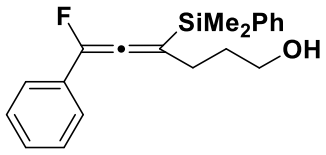




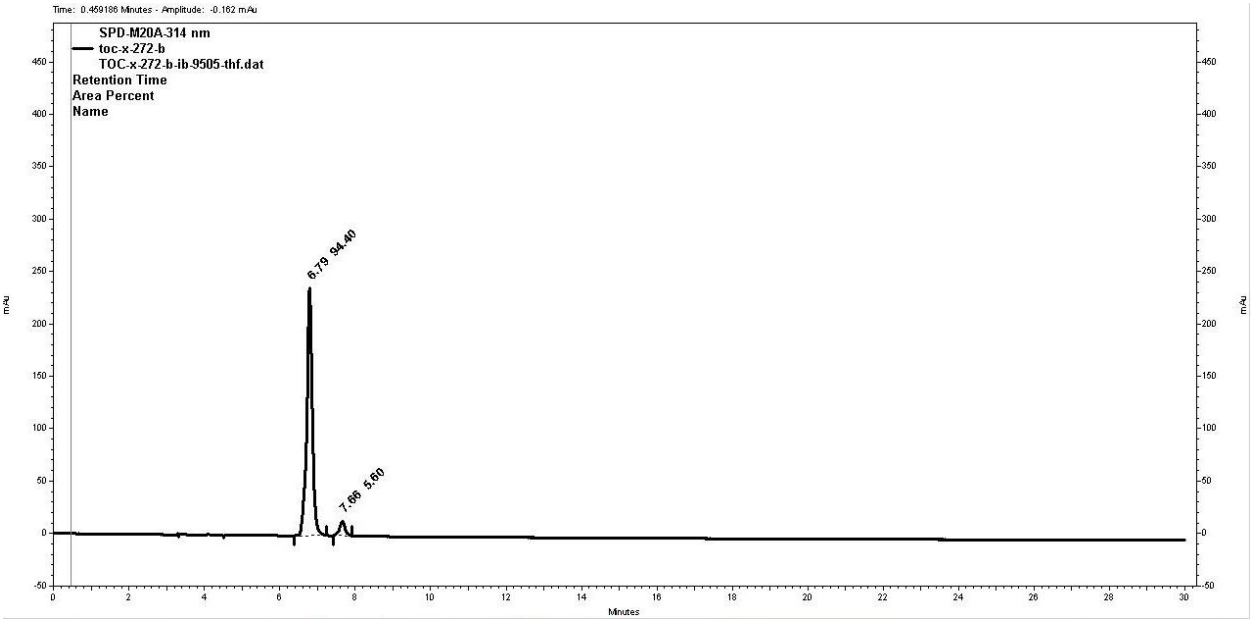


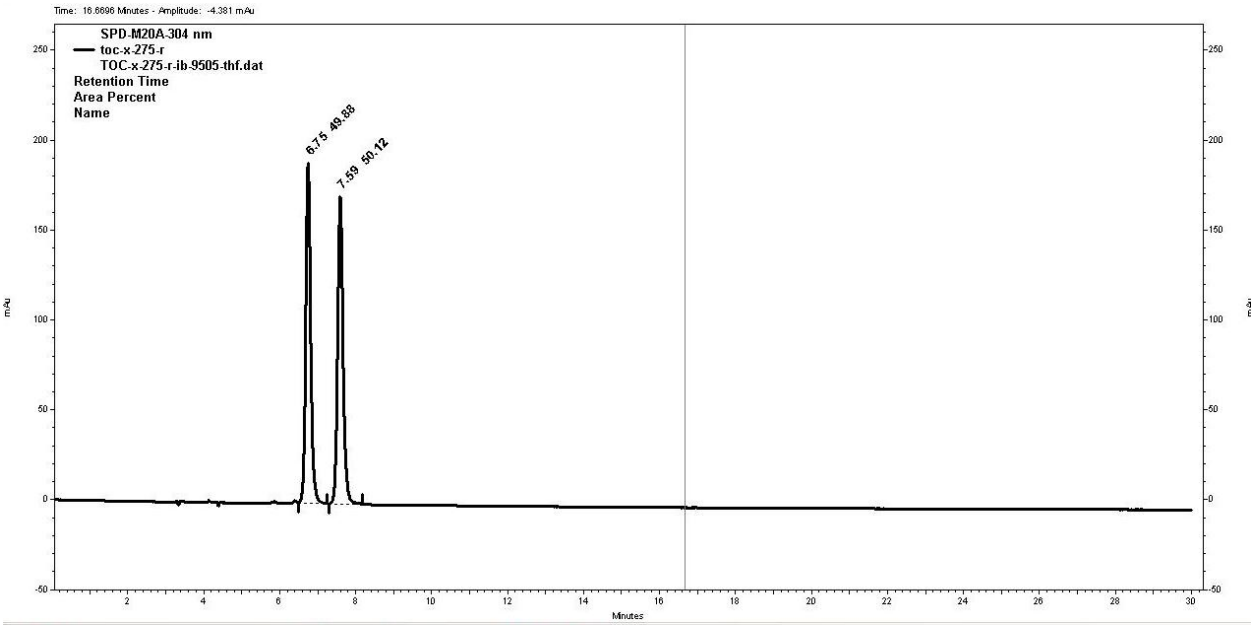
25b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.7:00.3; 23.83 min (major) and 21.98 min (minor)

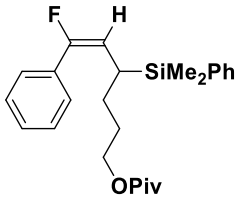




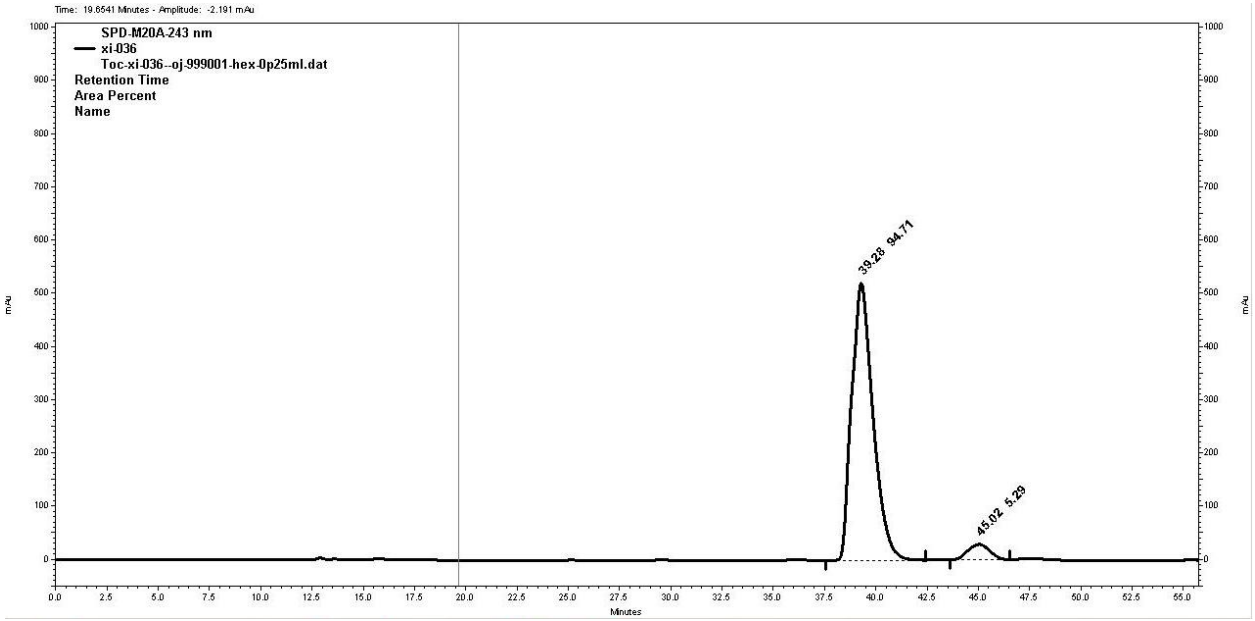
1c: IB column, 1.0 mL/min: hexanes:iPrOH 95:05; 6.79 min (major) and 7.66 min (minor)

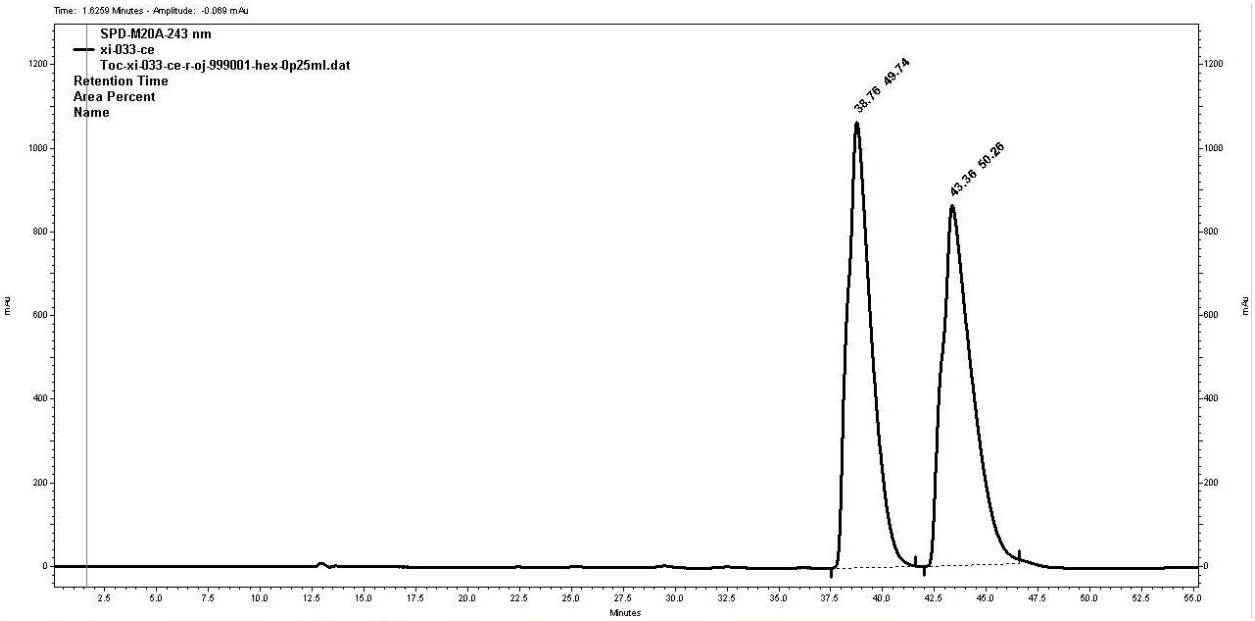






2c: OJ column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 39.28 min (major) and 45.02 min (minor)





2.8 References

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Chapter 3

Creation of Fluorine-Containing Quaternary Centers: Copper-Catalzyed Kinetic Resolution of Tetrasubstituted Monofluoro, Allenylsilanes

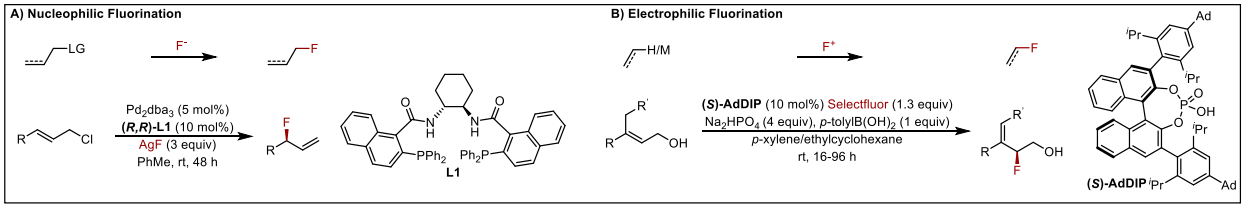
This chapter describes unpublished results and current research efforts are ongoing.

3.1 Introduction

3.1.1 Creation of Fluorine-Containing Stereocenters from Fluorine-Containing Building Blocks

As the applications of fluorinated molecules in both agrochemical and pharmaceutical industries have grown, improved methods to synthesize existing and new fluorinated motifs have become desirable.[1] Specifically, in the development of therapeutics the iterative process of synthesis, biological assays, and molecular redesign of target compounds has become a fundamental technique in drug discovery. The selective incorporation of fluorine into a compound of interest can alter its pharmacokinetics in dramatic ways, as the introduction of fluorine is known to change a molecule's bioavailability, lipophilicity, and oxidative stability.[1c,2] Thus, the introduction of fluorine to increase a drug's potency against and selectivity for target enzymes is a popular strategy employed by medicinal chemists. Although less than 10 fluorine-containing natural products have been isolated, approximately 35% of agrochemicals and 20% pharmaceuticals contain a fluorine.[3] Since there is a dearth of chiral fluorinated building blocks from nature and given the benefits of fluorine incorporation into organic molecules, there has been drive toward developing stereoselective methods to create fluorine-containing stereocenters.

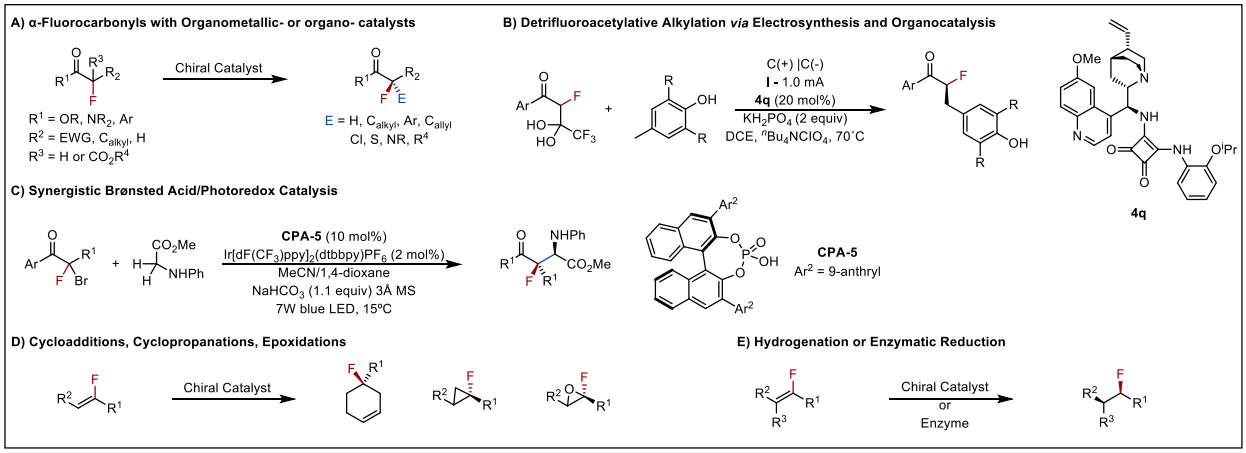
There are two complimentary strategies for the creation of fluorine-containing stereocenters (Scheme 3.1). The first strategy utilizes nonfluorinated starting material and creates a C–F bond in an enantioselective manner. Enantioselective fluorination has been achieved with both nucleophilic (Scheme 3.1A)[4] and electrophilic (Scheme 3.1B)[5] fluorination reagents. These methods typically employ chiral auxiliaries, stoichiometric chiral reagents, or, ideally, chiral metal or organic catalysts to set the new stereocenter.[1a,1b] The second approach employs fluorinated building blocks and creates C–C or C–X (X = H, Cl, N, S, and C) bonds to set a fluorine-containing stereocenter (Scheme 3.2).[6] This strategy has become popular as achiral fluorinated building blocks are readily available and allows the valorization of prochiral fluorine-containing molecules.[1d]



Scheme 3.1 Enantioselective Nucleophilic and Electrophilic Fluorination

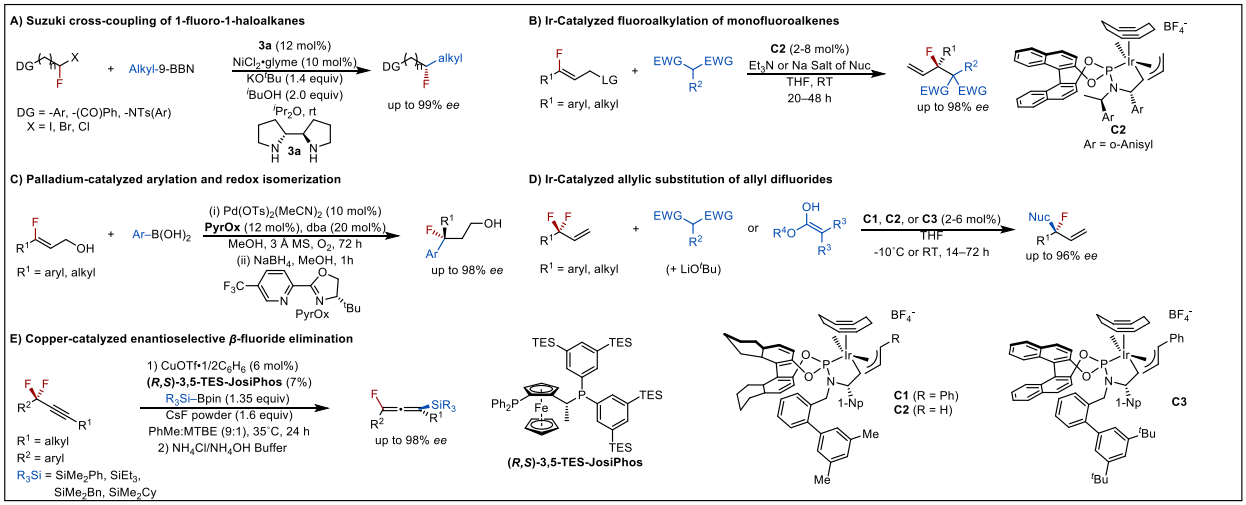
The most well-established fluorinated precursor used to create C–F stereocenters are *α*-fluorocarbonyl compounds (Scheme 3.2A). Methods that utilize these precursors often leverage the reactivity of fluoroenolates and their synthetic equivalents. One of first reports that highlighted this strategy was of the enantioselective aldol reaction where bromofluoroketene silyl acetals were utilized by Kobayashi and coworkers in 1999.[7] Since then, numerous reports of transition metal catalyzed and organocatalyzed transformations have expanded upon this initial discovery by either changing the identity of the carbonyl moiety, moving to less acidic esters and amides from aldehydes and ketones precursors, or by introducing a new electrophile forming C–C, C–H, C–Cl, C–Cl, or C–S bonds.[8,9] New approaches have also been applied to create chiral alkyl fluorides from *α*-fluorocarbonyl compounds such as electrochemistry[9q] and visible light catalysis[9p] (Scheme 3.2B and C). In addition to *α*-fluorocarbonyl

compounds, the [4+2] and [3+3] cycloaddition[10], cyclopopanation[11], epoxidation[12] as well as reduction[13,14] of fluoroalkenes has generated both secondary and tertiary fluorine stereocenters (Scheme 3.2D and E).



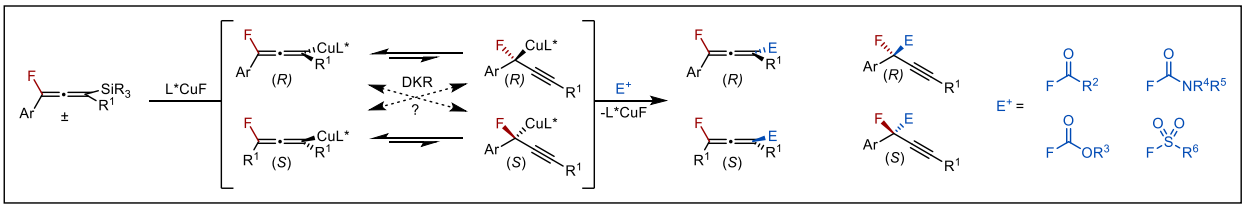
Scheme 3.2 Fluorine-containing Stereocenters from Fluorinated Building Blocks

Although a majority of the aforementioned reports that generate fluorine stereocenters focus on *α*-fluorocarbonyl precursors, recent publications have leveraged alternative strategies to utilize noncarbonyl-based fluorinated building blocks. Expanding upon the work from the Fu lab who reported the nickel-catalyzed Negishi cross-coupling of *α*-bromo, *α*-fluoro ketones with aryl zinc nucleophiles that generated chiral tertiary alkyl fluorides,[15] Gandelman and Jiang achieved the Suzuki cross-coupling of unactivated 1-fluoro-1-haloalkanes with alkyl-9BBN reagents (Scheme 3.3A).[16] Compared to earlier work, the creation of chiral secondary fluorides was achieved in positions remote from directing groups. The creation of fluorine-containing quaternary centers is a challenging endeavor, especially distal from a carbonyl-based directing group, but Gandelman's and Jiang's efforts have generated a new strategy to access this motif.[1a,1b] The iridium-catalyzed allylic fluoroalkylation reported by Butcher and Hartwig created fluorine-containing quaternary stereocenters from trisubstituted monofluoroalkenes. This transformation highlights that asymmetric addition of nucleophilic reagents to monofluoroalkenes could circumvent undesired defluorination pathways (Scheme 3.3B).[17] A complementary approach was presented by Toste and Sigman where a palladium-catalyzed arylation of trisubstituted monofluoroalkenes and subsequent chain-walking process furnished alcohols bearing a chiral tertiary fluoride (Scheme 3.3C).[18] A new approach to the creation of fluorine stereocenters was presented by Butcher and Hartwig through the desymmetrization of difluoromethylene groups by an iridium catalyzed allylic substitution of difluoroallylic electrophiles (Scheme 3.3D). This method highlighted that the selective replacement of one of the two enantiotopic C–F bonds was a viable strategy to create fluorine-containing quaternary stereocenters. Rather than point chirality, O'Connor and Toste demonstrated that axial chirality could be achieved *via* a copper-catalyzed enantioselective *β*-fluoride elimination from an alkenyl copper intermediate, generating tetrasubstituted monofluoroallenes (Scheme 3.3E). Not only did this report achieve the desymmetrization of propargylic difluorides, but it also demonstrated for the first time that alkenyl copper species can undergo *β*-fluoride elimination and that this elimination could be achieved in an enantioselective fashion.



Scheme 3.3 New Approaches toward the Generation of Fluorine-containing Stereocenters

Despite these advancements, the pool of achiral fluorinated building blocks that can be used to create C–F stereocenters is still limited. For instance, the creation of chiral fluorine-containing quaternary stereocenters is still largely limited to *α*-fluorocarbonyl compounds. One way to address this shortcoming would be the employment of tetrasubstituted monofluoroallenes. It was hypothesized that allenyl copper species could be accessed from monofluoroallenyl silanes and that the resulting organocopper species could be trapped by a suitable electrophile, generating a fluorine-containing quaternary stereocenter (Scheme 3.4). Furthermore, since attempts at achieving chirality transfer of this fluorinated substrate were previously unsuccessful, as detailed in chapter 2, it was envisioned that a dynamic kinetic resolution could be achieved provided that a suitable electrophile was selected.[19]



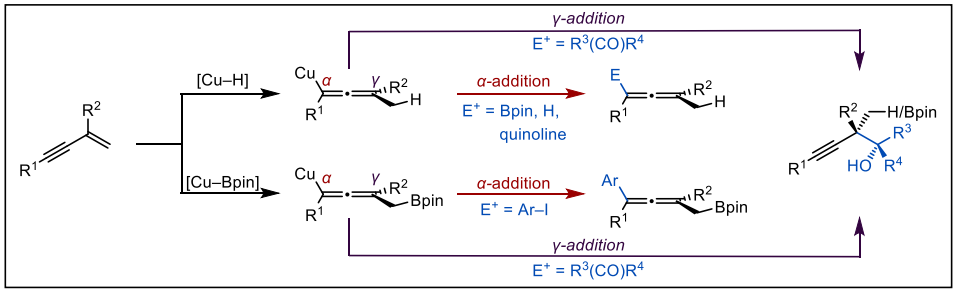
Scheme 3.4 Proposed Reactivity of Chiral, Monofluoroallenyl Copper Complexes

3.2 Kinetic Resolution of Tetrasubstituted Monofluoro, Allenylsilanes: Copper-Catalyzed Acylation

3.2.1 Results and Discussion

Although propargylations of **1b** did not proceed under Lewis acidic conditions, it was hypothesized that by utilizing racemic **1b** in the presence of a chiral copper fluoride catalyst that a chiral allenyl copper species could be generated (Scheme 3.4). Allenyl copper species are known to react with electrophiles and that the product distributions (allenylation vs propargylation) are dictated by both the ligand and the electrophile (Scheme 3.5).[20] It was envisioned that by employing acyl fluorides and analogs as an electrophile that propargylation would be the dominant pathway for the allenyl copper species and that in the presence of a suitable chiral ligand that the acylation of racemic monofluoro, allenylsilanes

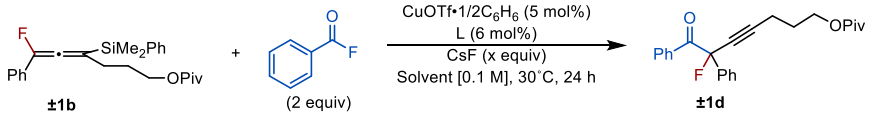
would generated fluorine-containing quaternary stereocenters. Several potential obstacles toward achieving this transformation included controlling the regioselectivity of addition (propargylation or allenylation), preventing unproductive protodesilylation of the starting material, and avoiding defluorination of the product. Herein, the kinetic resolution of tetrasubstituted, monofluoro allenylsilanes via copper-catalyzed acylation is demonstrated. Ongoing studies are aimed at achieving dynamic kinetic resolution through both ligand design and tuning the electrophilicity of the fluoroelectrophile.



Scheme 3.5 Reported Reactivity Trends of Allenylcopper Species

The investigation began by determining if a LCuF species could undergo transmetallation with **±1b**. Initial experiments revealed that bidentate phosphine ligands and CuF, generated *in situ* from CsF and LCuOTf, could not only desilylate **±1b** but also afforded the desired propargylation product in modest yields (Table 3.1 entries 1-3, 7). By decreasing the concentration of the reaction (entry 5) the mass balance of the reaction improved, but increasing the equivalents of benzoyl fluoride had a negative effect on the yield of **±1d** (entry 6). Ultimately, employing 1,2-bis(dicyclohexylphosphino)ethane (dcype) and a solvent combination of MTBE and PhMe generated **±1d** in 73% yield (entry 9).

Table 3.1 Optimization of Copper-Catalyzed Desilylative Acylation[a]



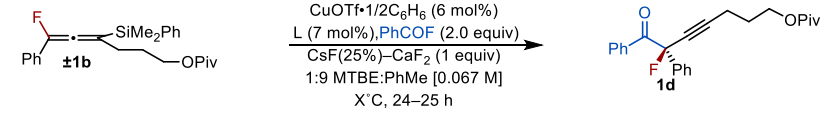
Entry	L	Solvent	CsF (equiv)	^{19}F NMR yield (SM)
1	dppBz[b]	PhMe	1.5	47% (0)
2	XantPhos[b]	PhMe	1.5	34% (32)
3	PCy_3[b]	PhMe	1.5	7% (84)
4	dppBz	PhMe	1.0	49% (0)
5	dppBz[c]	PhMe	0.25	48% (13)
6	dppBz[d]	PhMe	0.25	35% (32)
7	dcype	PhMe	1.0	30% (62)
8	dcype	MTBE	1.0	33% (0)
9	dcype	9:1 PhMe:MTBE	1.0	73% (0)
10	dcype	9:1 PhMe:MTBE	2.0	53% (23)

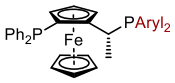
[a]Standard conditions: **±1b** (0.10 mmol, 1.0 equiv), PhC(O)F (0.20 mmol, 2.0 equiv), CuOTf·1/2C6H6 (5 mol%), L (6 mol%), solvent (1.0 mL), 30°C, 24 h. 19F NMR yields were determined using PhF as an internal standard; b 40°C; c 0.07 M; d PhC(O)F (4 equiv)

With suitable conditions for the racemic transformation in hand, an initial survey of Josiphos ligands was conducted to ascertain if a similar 3,5-substituent trend that was observed in chapter 2 would emerge with this new transformation (Table 3.2). Although sterically more demanding 3,5-substituents were more effective with respect the enantiomeric excess of **1d**, the trend was not as strong as observed in

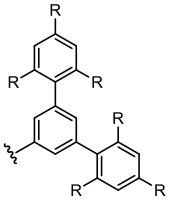
the copper-catalyzed, asymmetric *β*-fluoride elimination reaction. Other suitable chiral ligands were examined under the optimized reaction conditions to determine if another chiral ligand structure would prove more suitable for the asymmetric acylation of allenylsilane **1b** (Table 3.3). Although **1d** was observed in the presence of all of the ligands examined, the class of ligands that generated **1d** in the greatest enantiomeric excess were pyridine-oxazoline (PyOx) ligands (Table 3.3, last row) where ^{t}Bu-PyOx-CF_3 generated **1d** in 74% *ee*.

Table 3.2 Enantioselective Copper-Catalyzed Desilylative Acylation – Josiphos[a]





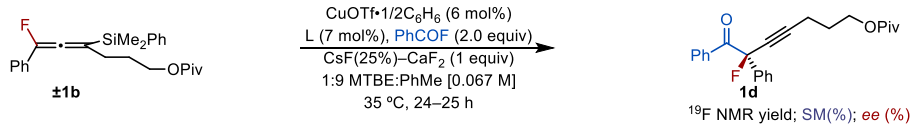
Aryl	X°C	^{19}F NMR yield (SM)	*ee* (%)
3,5-CF_3	35	18% (47)	+23
3,5-Me 4-OMe	35	46% (0)	+1
3,5-^{t}Bu 4-OMe	35	28% (41)	+4
3,5-TMS	35	31% (42)	+16
3,5-TES	40	28% (43)	+28
3,5-TES	30	15% (58)	+40
3,5-TES[b]	30	34% (22)	+28
Mes	40	20% (48)	+24
Trip	40	27% (44)	+10

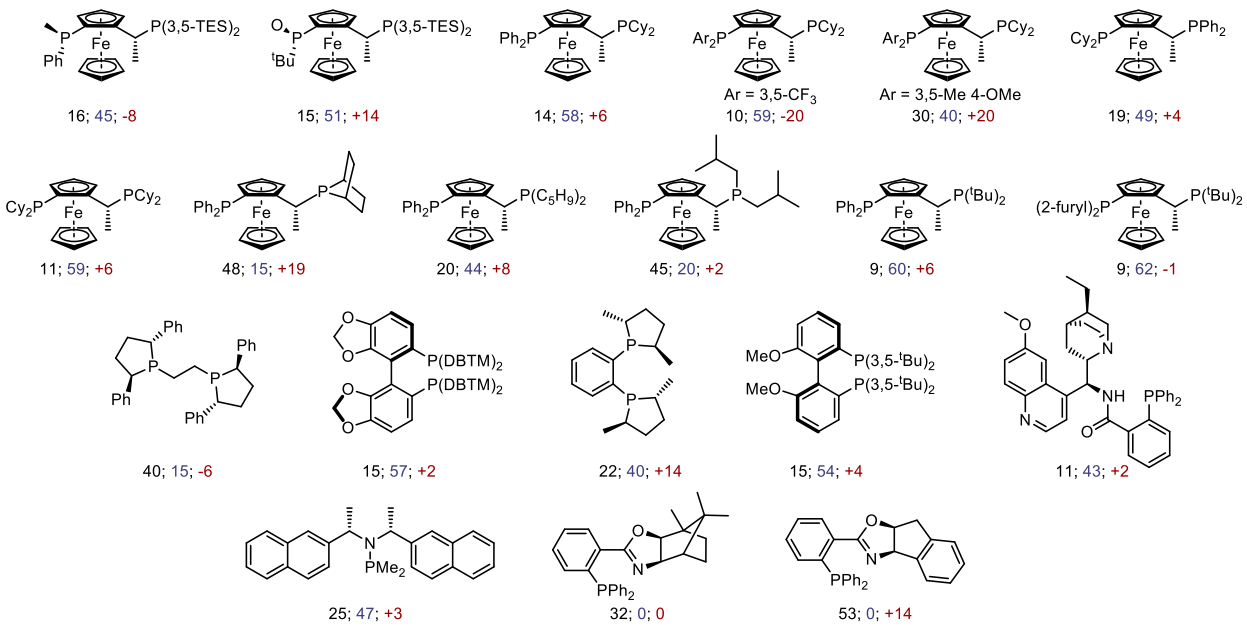


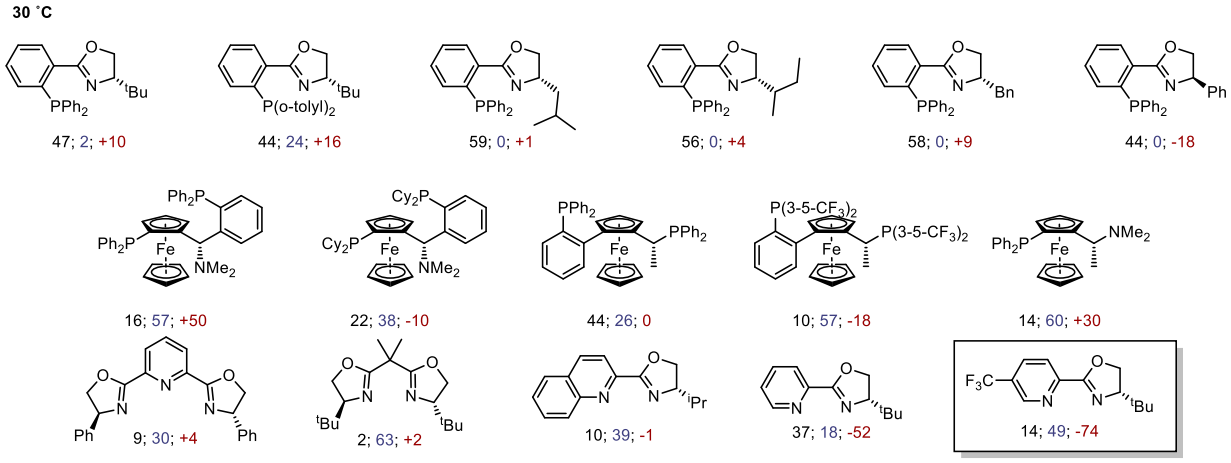
Mes = R = Me
Trip = R = ^{i}Pr

[a]Standard conditions: **±1b** (0.10 mmol, 1.0 equiv), PhC(O)F (0.20 mmol, 2.0 equiv), CuOTf·1/2C_6H_6 (5 mol%), L (6 mol%), solvent (1.5 mL), 24 h; 19F NMR yields were determined using PhF as an internal standard; enantiomeric excess determined by HPLC with a chiral stationary phase; [b]$(PPh3)_3$CuF·2MeOH (6 mol%)

Table 3.3 The Effect of Chiral Ligand on Copper-Catalyzed Desilylative Acylation[a]





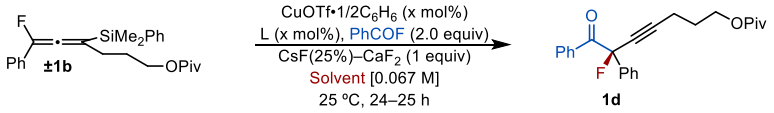


[a]Standard conditions: **±1b** (0.10 mmol, 1.0 equiv), PhC(O)F (0.20 mmol, 2.0 equiv), CuOTf·1/2C_6H_6 (6 mol%), L (7 mol%), solvent (1.5 mL), 24 h; ^{19}F NMR yields were determined using PhF as an internal standard; enantiomeric excess determined by HPLC with a chiral stationary phase.

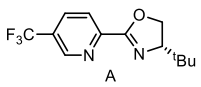
Further optimization with the PyrOx ligands led to enhancements to both the chemical yield and enantiomeric excess of **1d** (Table 3.4). Increasing the catalyst loading of the ligand and copper had a positive effect on the *ee* % of **1d** (entries 1-3). The transformation was found to be very sensitive to solvent effects, suggesting that in more polar solvents that an uncatalyzed pathway mediated by CsF becomes operative (entries 4-10). Ultimately with both ^{t}Bu-PyOx-CF_3 and ^{t}Bu-PyOx as the ligand and cyclohexane as the solvent **1b** could be obtained in 88–90% *ee* and 39–62% yield (entries 11 and 14). The allenyl TES,

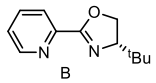
±1d-Et$_3$Si, was subjected to similar conditions, but gave inferior results compared to **±1d** (See Table S1 and S2).

Table 3.4 PyOx-Copper-Catalyzed Desilylative Acylation[a]



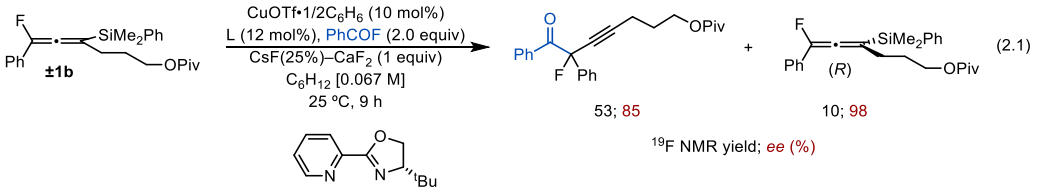
entry	Cu (%)	L (%)	Solvent	yield (SM)[a]	ee (%)[b]
1	6	A (7)	PhMe:MTBE 9:1	11% (54)	-45
2	6	A (12)	PhMe:MTBE 9:1	13% (50)	-62
3	10	A (12)	PhMe:MTBE 9:1	23% (37)	-75
4	6	A (7)	DCM	24% (32)	-4
5	6	A (7)	1,2-DCE	20% (39)	+2
6	6	A (7)	Et_2O	11% (40)	-46
7	6	A (7)	MTBE	12% (38)	-57
8	6	A (7)	C_6H_{12}	39% (28)	-90
9	6	A (7)	1,4-Dioxane	27% (0)	0
10	10	A (12)	PhMe	27% (34)	-82
11	10	A (12)	C_6H_{12}	44% (17)	-88
12	10	A (20)	C_6H_{12}	36% (24)	-84
12[c]	10	A (12)	C_6H_{12}	28% (35)	-74
13	10	B (12)	PhMe	27% (34)	-60
14	10	B (12)	C_6H_{12}	62% (3)	-88





[a]Standard conditions: **±1b** (0.10 mmol, 1.0 equiv), PhC(O)F (0.20 mmol, 2.0 equiv), CuOTf·1/2C_6H_6 (6 mol%), L (7 mol%), solvent (1.5 mL), 24 h; ^{19}F NMR yields were determined using PhF as an internal standard; enantiomeric excess determined by HPLC with a chiral stationary phase.

At this point it was unclear if the current reaction was a kinetic resolution or a dynamic kinetic resolution. When the reaction was quenched at 90% conversion of **±1b**, the unreacted **1b** was recovered and analyzed by chiral HPLC. The enantiomeric excess of the unreacted allene was determined to be 98% (Equation 3.1). Interestingly, the recovered allene was the (*R*) enantiomer, suggesting that the (*S*)-PyOx copper catalyst reacts preferentially or productively with the (*S*) enantiomer of the allene. Although there a several reports of allenyl copper species, there has been only one study that examined the configurational stability of these species.[20] DFT calculations by Hovedya and coworkers indicated that the 1,3 isomerization of the allenyl copper species to the propargyl copper species is stereospecific.[20f] However, these calculations were only performed with bidentate phosphine ligands. Other reports in the literature suggest that copper species can racemization chiral allenes.[20f,21] Currently, other electrophiles are being explored that would alter the energy landscape of the current transformation. Several alternative electrophiles would be sulfonyl fluorides, fluoroformates, and carbamoyl fluorides (Figure 3.1). If there is a viable pathway for racemization, then by decreasing the electrophilicity of the electrophile the relative rates of electrophile trapping and racemization could become competitive, allowing for dynamic kinetic resolution to become operative. However, changing the electrophilicity of the electrophile could also influence the α:γ ratio.[20] Provided that a copper catalyzed racemization could be realized, it would highlight a new mechanism for the dynamic kinetic resolution of internal allenes, which is largely limited to the generation of allyl metal intermediates resulting from the addition of metal hydrides into allenes or displacement of allenyl electrophiles.[22]



3.3 Conclusion

In conclusion, attempts at product diversification of the monofluoroallenes described in chapter 2 led to the discovery of the kinetic resolution of tetrasubstituted, monofluoro allenyl silanes *via* copper-catalyzed acylation. The resulting propargyl, fluorine-containing quaternary centers are highly desirable and cannot be obtained with current technologies. Ongoing research include optimization of the kinetic resolution by machine learning in collaboration with the Sigman Group at Utah and examining if dynamic kinetic resolution can be achieved by rationally tuning the electrophile (Figure 3.1).

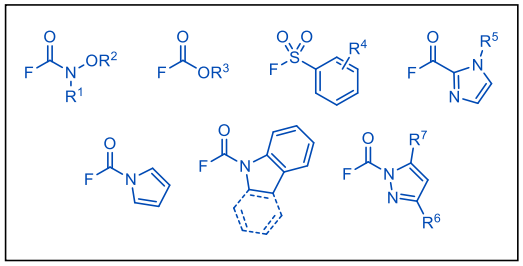


Figure 3.1 Potential Fluoroelectrophiles with Differing Electrophilicities

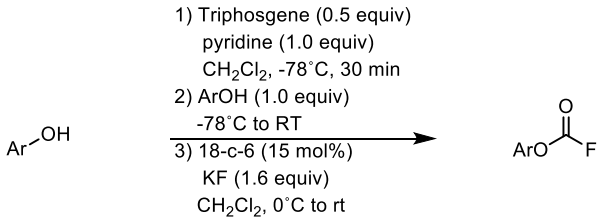
3.4 Supporting Information

3.4.1 General Information

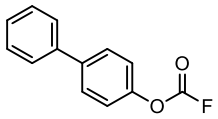
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Vessels used in air-free reactions were oven-dried and cooled under dynamic vacuum (once at ambient temperature, vessels were refilled with nitrogen and evacuated two more times) prior to use. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed using ICN SiliTech 32-63D 60Å silica gel. Commercial grade solvents were used for reactions without further purification except as indicated below. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), toluene (PhMe), benzene (C_6H_6), diethyl ether (Et_2O), dimethyl formamide (DMF), triethylamine (Et_3N) and tetrahydrofuran (THF) were dried by passing commerically available pre-dried, oxygen-free formulations through activated alumina columns under argon. Trifluorotoluene ($PhCF_3$), cyclohexane (C_6H_{12}), methyl tert-butyl ether (MBTE), acetic acid (AcOH), trifluoroacetic acid (TFA), pyridine, diethylamine (Et_2NH) and 1,2-dichloroethane (DCE) were distilled under a nitrogen atmosphere from either CaH_2 or P_2O_5 as described in literature. All solvents employed in alkyne silylation reactions were degassed by freeze-pump-thaw cycles (three cycles) using liquid nitrogen and stored over activated 3 Å molecular sieves. Thin layer chromatography analysis was performed using Merck 60 pre-coated silica gel plates with F254 indicator. Visualization was accomplished by iodine, p-anisaldehyde, potassium permanganate, Dragendorff-Munier, cerium ammonium molybdate, and/or UV light (254 nm). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AVQ-400, DRX-500, Neo-500 and AV-600 instruments with 400, 500 and 600 MHz frequencies. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker DRX-500, Neo-500, and AV-600 instruments with a ^{13}C operating frequency of 126 and 150 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded on Bruker AVQ-400, DRX-500, Neo-500, and AV-600 instruments with 376, 471, and 565 MHz frequencies. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$, δ 5.32 for CH_2Cl_2) was used as an internal reference for ^{1}H spectra. For ^{13}C spectra, chemical shifts are reported relative to the δ 77.16 resonance of $CDCl_3$ and relative to the δ 53.84 for CD_2Cl_2. For ^{19}F spectra, chemical shifts are reported in relative to the δ -113.15 resonance of PhF. Coupling constants are reported in Hz. Mass spectral data were obtained from either the UC-Berkeley Catalysis Center operated by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI (or APCI) mode or the QB3/Chemistry Mass Spectrometry Facility at UC-Berkeley. Monofluoroallenes were synthesized as described in chapter 2. Acyl fluorides were prepared according to literature procedures and their spectra match those reported in the literature.[23]

3.4.2 Substrate Synthesis

Fluoroformates



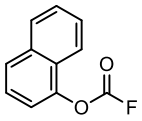
To a cycled 3-neck round bottom flask equipped with an additional funnel, triphosgene (0.5 equiv) was added followed by CH_2Cl_2 [0.57 M]. Once the solid was dissolved, the flask was placed in a -78˚C bath. Pyridine (1.0 equiv) was added dropwise and after 30 minutes a solution of phenol (1.0 equiv) in CH_2Cl_2 [0.92 M] was added dropwise. After 12 hours, the reaction was removed from the warmed cooling bath and allowed to stir at room temperature. The reaction was monitored (by GC-MS) until full consumption of the phenol. Once the phenol was completely consumed, the reaction was poured onto water, diluted with EtOAc and Et_2O, and shaken vigorously in a fumehood. The aqueous layer was disposed of (neutralize with NaOH before disposing into aqueous waste container), and the organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude mixture was transferred with anhydrous CH_2Cl_2 [1.25 M] to a cycled round bottom flask equipped with an addition funnel and cooled to 0˚C. Spray dried KF (1.6 equiv) was weighed in a glovebox and added to the solution. 18-c-6 (15 mol%) was charged to the additional funnel and dissolved in CH_2Cl_2 [0.75 M wrt 18-c-6], which was added dropwise to the 0˚C slurry. The reaction was stirred vigorously and was allowed to reach ambient temperate overnight. Once full conversion of the chloroformate had been achieved (monitored by GC-MS), the reaction was filtered over a short pad of SiO_2 and concentrated. The crude mixture was purified by distillation. Note: Fluoroformates streak on SiO_2 and could not be successfully purified by column chromatography.



[1,1'-biphenyl]-4-yl carbonofluoridate

Utilizing 4-phenylphenol (35.2 g, 207 mmol, 1 equiv) triphosgene (30.69 g, 103 mmol, 0.5 equiv), pyridine (17.0 mL, 207 mmol, 1.0 equiv), KF (18.6 g, 320 mmol, 1.6 equiv), and 18c-6 (8.0 g, 15 mol%) , the fluoroformate was isolated by distillation (140-143˚C, 400 mtorr). Upon reaching room temperature, the oil solidified to a colorless solid. Yield 41% (18.0 g) over two-steps. The major byproduct was the carbonate (from the first step in the sequence).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72–7.65 (m, 2H), 7.61 (t, *J* = 6.3 Hz, 2H), 7.51 (q, *J* = 7.5 Hz, 2H), 7.48–7.42 (m, 1H), 7.38 (dd, *J* = 8.6, 3.6 Hz, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -15.20 (s, 1F).
^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 143.9 (dd, *J* = 286.5, 2.4 Hz), 140.6, 139.8, 129.0, 128.6, 127.9, 127.3, 120.4.

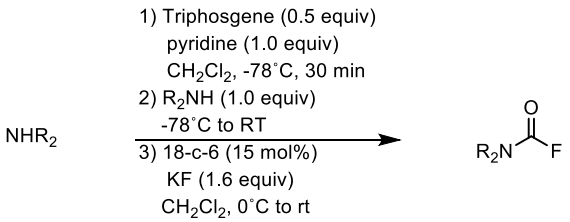


naphthalen-1-yl carbonofluoridate

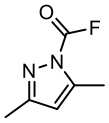
Utilizing 1-naphthalenol (18.5 g, 127 mmol, 1 equiv), triphosgene (15.5 g, 51 mmol, 0.5 equiv), pyridine (10.2 mL, 127 mmol, 1.0 equiv), KF (8.8 g, 152 mmol, 1.6 equiv), and 18c-6 (5.0 g, 20 mol%), the fluoroformate was isolated by distillation (88-91˚C, 110 mtorr)as a colorless oil. Yield 59% (11.4 g) over two-steps. The major byproduct was the carbonate (from the first step in the sequence).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85–7.80 (m, 1H), 7.65–7.56 (m, 2H), 7.50 (d, *J* = 5.0 Hz, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -15.40 (s, 1F).
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 145.3–142.6 (m), 134.7, 128.2, 127.5, 127.3, 127.1, 125.5, 125.2, 120.3, 116.7.

Carbamoyl Fluorides



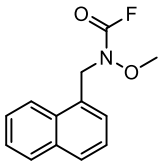
To a cycled 3-neck round bottom flask equipped with an additional funnel, triphosgene (0.5 equiv) was added followed by CH_2Cl_2 [0.4 M]. Once the solid was dissolved, the flask was placed in a -78˚C bath. Pyridine (1.0 equiv) was added dropwise and after 30 minutes a solution of amine (1.0 equiv) in CH_2Cl_2 [2.0 M] was added dropwise. After 12 hours, the reaction was removed from the warmed cooling bath and allowed to stir at room temperature. The reaction was monitored (by GC-MS) until full consumption of the amine. The temperature was raised to 40˚C to achieve full conversion. Once the amine was completely consumed, the reaction was poured onto water, diluted with EtOAc and Et_2O, and shaken vigorously in a fumehood. The aqueous layer was disposed of (neutralize with NaOH before disposing into aqueous waste container), and the organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude mixture was transferred with anhydrous CH_2Cl_2 [0.85 M] to a cycled round bottom flask and cooled to 0˚C. Spray dried KF (2.0 equiv) was weighed in a glovebox and added to the solution followed by 18-c-6 (20 mol%). The reaction was stirred vigorously and was allowed to reach ambient temperate overnight. Once full conversion of the carbamoyl chloride had been achieved (monitored by GC-MS), the reaction was filtered over a short pad of SiO_2 and concentrated. The crude mixture was purified by distillation or column chromatography. Note: Carbamoyl fluorides based on heterocycles streak on SiO_2 and could not be successfully purified by column chromatography.



3,5-dimethyl-1*H*-pyrazole-1-carbonyl fluoride

Utilizing 3,5-dimethylpyrazole (19.4 g, 200 mmol, 1 equiv), triphosgene (30.0 g, 100 mmol, 0.5 equiv), pyridine (20.0 mL, 200 mmol, 1.0 equiv), KF (21.4 g, 368 mmol, 1.6 equiv), and 18c-6 (9.7 g, 20 mol%), the carbamoyl fluoride was isolated by distillation (50-70˚C, 110 mtorr)as a colorless solid that was subsequentially recrystallized from Et_2O and pentane at -20˚C to remove residual 18-c-6. Yield 16% (4.5 g) over two-steps. The major byproduct was the urea (from the first step in the sequence). The reaction had to be heated at 40˚C for the formation of the carbamoyl chloride to occur.

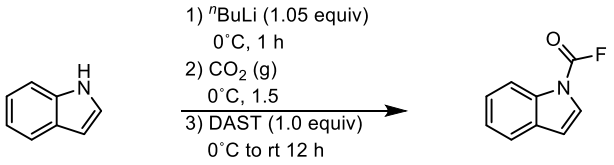
^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.03 (s, 1H), 2.45 (s, 3H), 2.26–2.13 (m, 3H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -4.97 (s, 1F).
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 146.1, 140.2 (d, *J* = 307.1 Hz), 112.6 (d, *J* = 5.2 Hz), 13.8 (d, *J* = 3.3 Hz), 13.4.



methoxy(naphthalen-1-ylmethyl)carbamic fluoride

Utilizing *O*-methyl-*N*-(naphthalen-1-ylmethyl)hydroxylamine (18.0 g, 96 mmol, 1 equiv), triphosgene (14.24 g, 48 mmol, 0.5 equiv), pyridine (8.0 mL, 96 mmol, 1.0 equiv), KF (6.2 g, 103 mmol, 1.07 equiv), and 18c-6 (2.53 g, 10 mol%), the carbamoyl fluoride was purified by silica gel column chromatography (1:13 to 1:9 EtOAc:Hexanes) to afford the desired carbamoyl fluoride as a colorless oil that turned orange over time (14.32 g, 64%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.99–7.90 (m, 2H), 7.66–7.62 (m, 1H), 7.61–7.50 (m, 3H), 5.17 (s, 2H), 3.49 (s, 3H).
^{19}F NMR (470 MHz, CD_2Cl_2) δ -24.82 (s, 1F).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.2 (d, *J* = 295.0 Hz), 134.4, 132.0, 130.6, 129.9, 129.4, 128.4, 127.4, 126.7, 125.9, 123.6, 63.6, 51.6.

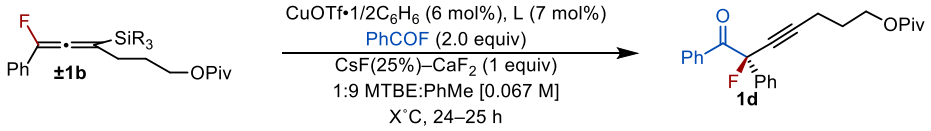


1*H*-indole-1-carbonyl fluoride

To a cycled 3-neck round bottom flask equipped with an additional funnel, indole (11.7 g, 100 mmol, 1.0 equiv) was added followed by THF [0.3 M]. Once the solid was dissolved, the flask was placed in a 0°C ice bath. ^{n}BuLi (42ml, 105mmol, 1.05 equiv; 2.5 M in Hexanes) was added dropwise over 10 minutes and after an additional 60 minutes of stirring, CO_2 (generated from dry ice and passed through a drying column) was sparged through the solution for 30 minutes. After an addition hour under a CO_2 atmosphere, DAST (13.5 ml, 100 mmol, 1 equiv) was added. The reaction was allowed to reach room temperate overnight (12 hours). The reaction was poured onto $NaHCO_3$ (sat.), diluted with EtOAc and Et_2O (1:1, 1000 mL total), and shaken vigorously. The aqueous layer was disposed of and the organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude mixture was quickly purified by silica gel column chromatography (1:15 to 1:10 EtOAc:Hexanes) to afford the desired carbamoyl fluoride as a colorless solid that was subsequently recrystallized from pentane at -20°C (3.3 g, 20%). Note: The carbamoyl fluoride appears pone to hydrolysis (observed decomposition when dissolved in old, wet bottles of $CDCl_3$). By NMR a mixture of rotamers is present.

^{1}H NMR (600 MHz, C_6D_6) δ 8.13 (s, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.03 (m, 2.5H), 6.64 (s, 1H), 6.07 (s, 1H).
^{19}F NMR (565 MHz, C_6D_6) δ -5.29 (s, 1F), -7.22 (s, 0.25F).
^{13}C NMR (151 MHz, C_6D_6) δ 140.1 (d, *J* = 301.3 Hz), 135.6, 130.9 (d, *J* = 3.8 Hz), 128.4, 125.7, 124.7, 124.5, 121.6, 115.0 (d, *J* = 7.6 Hz), 111.4, 110.5.

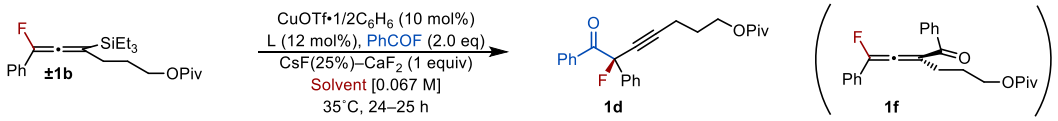
3.4.3 General Procedure for Copper-Catalyzed Kinetic Resolution: Screening Tables



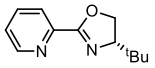
In a nitrogen filled glovebox, a stir bar, CuX (x mol%), and ligand (x +1 mol%) were charged to a 1-dram vial. Solvent (1.5 mL) was added and the mixture was stirred at ambient temperature for 45–60 minutes. (If the ligand was an oil, then a 0.2 M solution in PhMe was prepared and x + 1 mol% was added dropwise to a stirring solution (1.4 mL) of the copper salt.) Then racemic allenylsilane (0.1 mmol, 1.0 equiv) and acyl fluoride (0.2 mmol, 2.0 equiv) were added. The mixture was stirred for 2–4 minutes before the addition of CsF(25%)–CaF_2 (38 mg, 0.1 mmol, 1.0 equiv). The vial was sealed with a ptfe-lined, thermal-rated cap, secured with electrical tape, removed from the glovebox, and placed in a preheated, heating block set at 900 rpm. After 24–25 h, the reaction was removed to ambient temperature, diluted with EtOAc (500 μL) and PhF (9.5 μL, 0.1 mmol, 1.0 equiv) and the NH_4Cl (1 mL) were added. The contents were vigorously stirred for 4 minutes and the layers were allowed to separate. An ^{19}F NMR was acquired. The organic phase was diluted

with EtOAc (4 mL), dried over Na_2SO_4, concentrated, and purified by preparative TLC. The enantiomeric excess was determined by a chiral HPLC.

Table S1. Utilization of Allenyl TES Precursors

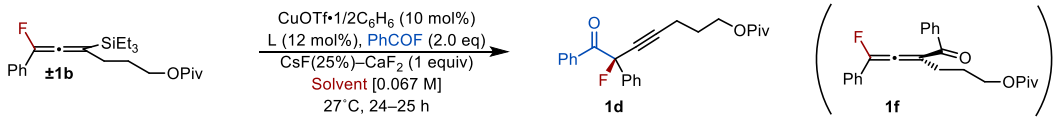


entry	Solvent	1d yield (SM)[a]	1d *ee* (%)[b]	1b *ee* (%)[b]	1f yield(*ee*)[a]
1	MTBE	15% (69)	+59	+1	0%
2	3:1 PhMe:MTBE	9% (83)	+62	+2	0%
3	3:1 C_6H_{12}:MTBE	8% (92)	+17	-5	0%
4	dioxane	12% (61)	nd	nd	6%
5	EtOAc	28% (0)	+2	nd	26%(2)

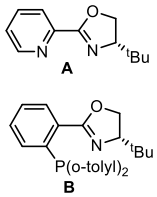


[a]Yield was determined by 19F NMR of crude reaction mixture, using PhF as an internal standard.
[b]Determined by HPLC analysis using a chiral stationary phase

Table S2. Solvent Effect for Allenyl TES

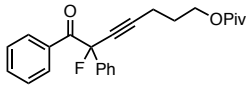


entry	L	Solvent	1d yield (SM)[a]	1d *ee* (%)[b]	1f yield[a]
1	A	EtOAc	28% (0)	+4	22%
2	A	1:1 EtOAc:C_6H_{12}	10% (57)	+9	7%
3	A	1:4 EtOAc:C_6H_{12}	9% (84)	+66	0%
4[c]	A	EtOAc	0% (100)	-	-
5	B	EtOAc	38% (0)	+9	36%
6	A	DME	40% (0)	+4	28%
7	A	THF	26% (0)	+4	22%
8	A	MeCN	48% (0)	+4	7% or 15%



[a]Yield was determined by 19F NMR of crude reaction mixture, using PhF as an internal standard.
[b]Determined by HPLC analysis using a chiral stationary phase
[c] KF (1 equiv)

3.4.4 Characterized Alkynes

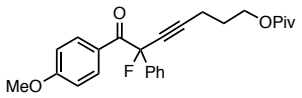


6-fluoro-7-oxo-6,7-diphenylhept-4-yn-1-yl pivalate (**1d**)(purity ≥95%):

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.00 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.64 (ddd, *J* = 6.8, 3.7, 1.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.39 (t, *J* = 7.9 Hz, 2H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.49 (q, *J* = 6.9 Hz, 2H), 1.93–1.85 (m, 2H), 1.18 (s, 9H).
^{19}F NMR (470 MHz, CD_2Cl_2) δ -124.19 (t, *J* = 5.2 Hz, 1F).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 191.2 (d, *J* = 27.1 Hz), 178.0, 136.7 (d, *J* = 23.9 Hz), 133.4, 133.0 (d, *J* = 1.5 Hz), 130.2 (d, *J* = 2.4 Hz), 129.8 (d, *J* = 2.7 Hz), 128.8, 128.2, 126.8 (d, *J* = 4.0 Hz), 94.7 (d, *J* = 8.7 Hz), 93.7 (d, *J* = 182.9 Hz), 76.0 (d, *J* = 29.0 Hz), 62.5, 38.6, 27.2 (d, *J* = 2.5 Hz), 26.9, 15.78 (d, *J* = 2.9 Hz).

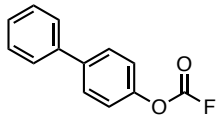
Determination of enantiomeric ratio by HPLC analysis: IA column, 1.0 mL/min: hexanes:iPrOH 99.5:0.5; 13.94 min (major) and 17.66 min (minor)



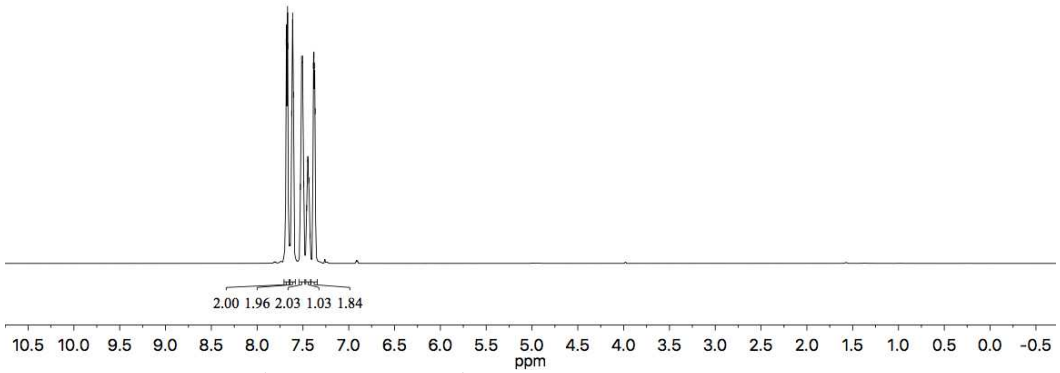
6-fluoro-7-(4-methoxyphenyl)-7-oxo-6-phenylhept-4-yn-1-yl pivalate (**2d**):

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.65–7.61 (m, 2H), 7.43 (dd, *J* = 5.1, 2.0 Hz, 3H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.08 (t, *J* = 6.2 Hz, 2H), 3.83 (s, 3H), 2.49 (q, *J* = 6.9 Hz, 2H), 1.93–1.85 (m, 2H), 1.18 (s, 9H).
^{19}F NMR (470 MHz, CD_2Cl_2) δ -123.45 (t, *J* = 6.6 Hz, 1F).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 190.0 (d, J = 26.5 Hz), 178.6, 164.3, 137.6 (d, *J* = 23.8 Hz), 133.3, 133.3, 130.2 (d, *J* = 2.8 Hz), 129.3, 127.4, 127.4, 126.1 (d, *J* = 2.0 Hz), 114.0, 94.9, 94.1 (d, *J* = 173.1 Hz), 76.8 (d, *J* = 29.0 Hz), 63.1, 56.1, 39.2, 27.8 (d, *J* = 2.2 Hz), 27.5, 16.3 (d, *J* = 2.9 Hz).
Determination of enantiomeric ratio by HPLC analysis: IA column, 1.0 mL/min: hexanes:iPrOH 97:03; 14.21 min and 15.38 min

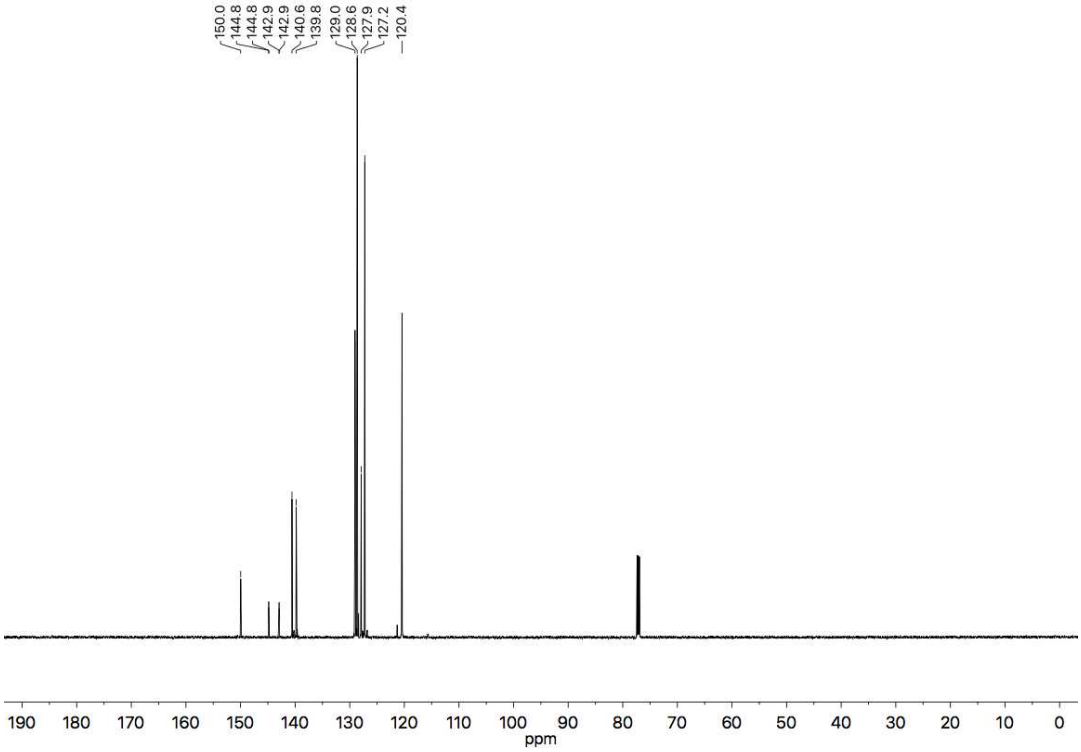
3.4.5 NMR Spectra



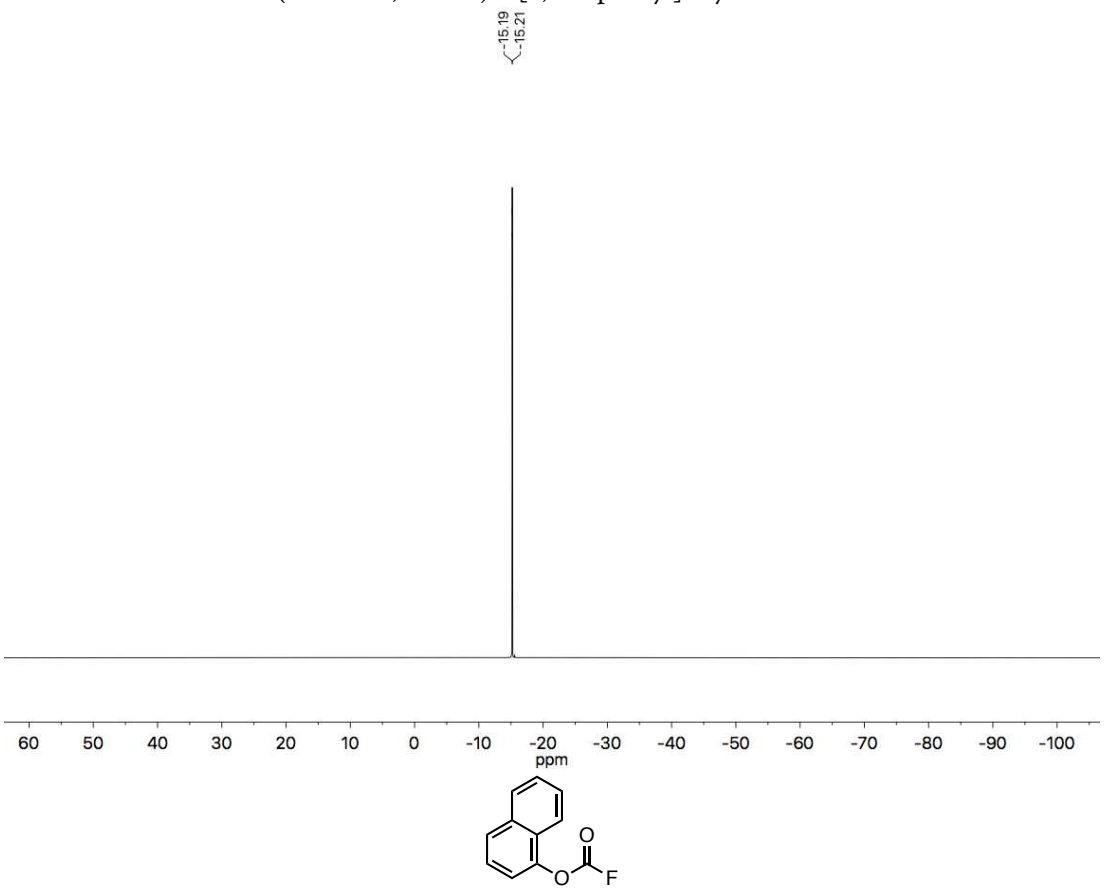
^{1}H NMR (600 MHz, $CDCl_3$) – [1,1'-biphenyl]-4-yl carbonofluoridate



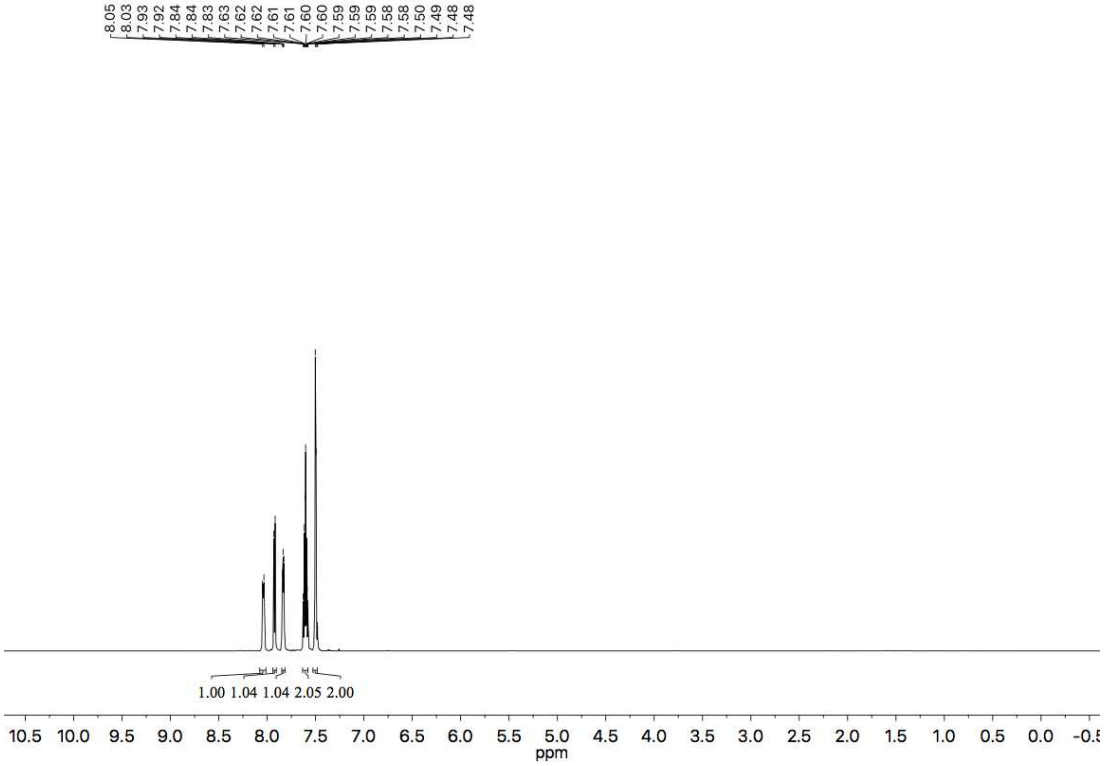
^{13}C NMR (151 MHz, $CDCl_3$) – [1,1'-biphenyl]-4-yl carbonofluoridate



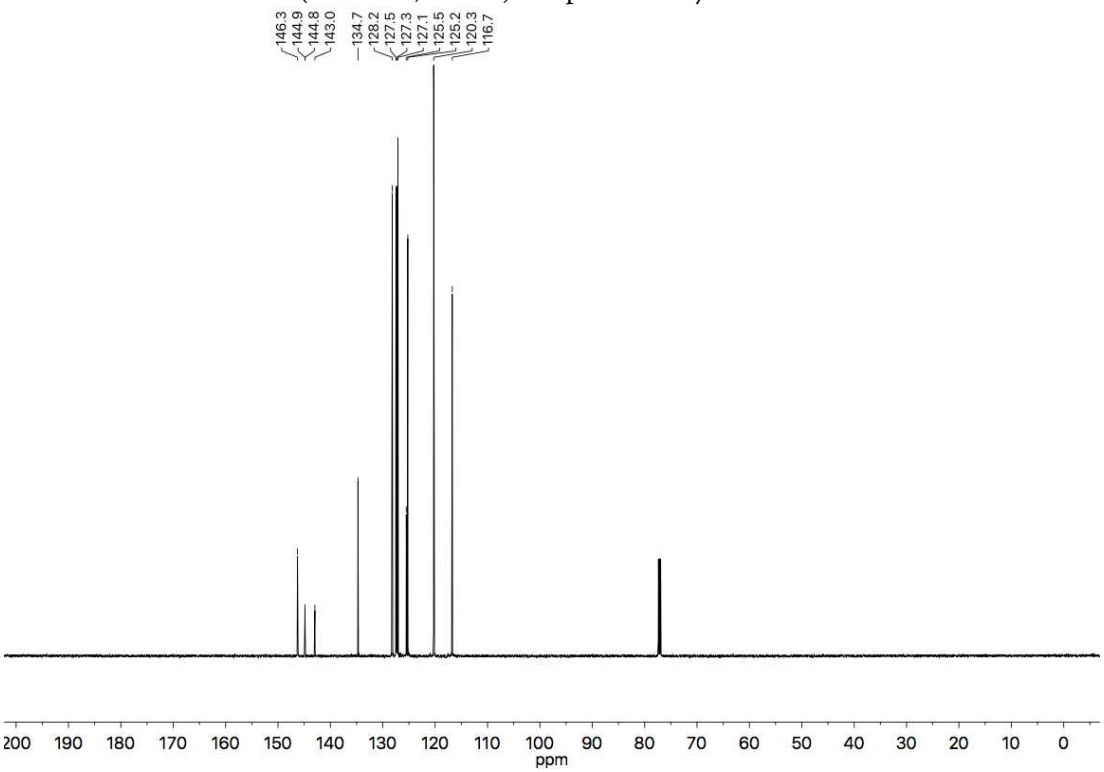
^{19}F NMR (565 MHz, $CDCl_3$) – [1,1'-biphenyl]-4-yl carbonofluoridate



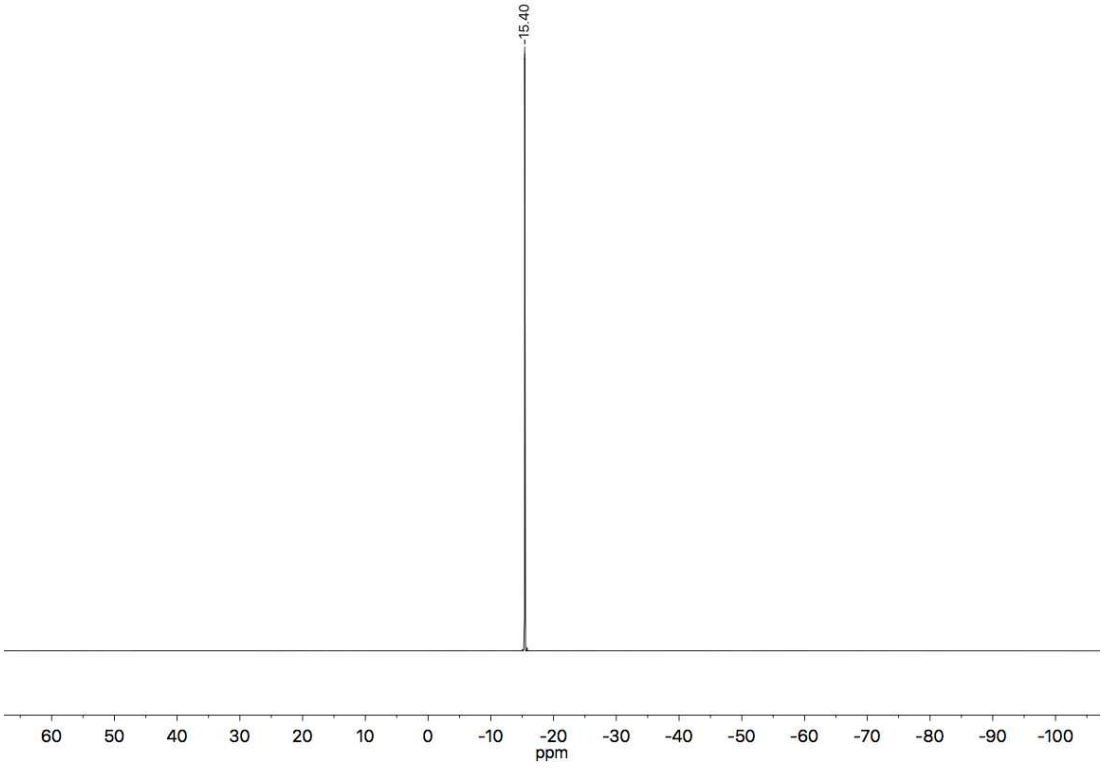
^{1}H NMR (600 MHz, $CDCl_3$) – naphthalen-1-yl carbonofluoridate

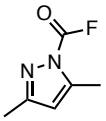


^{13}C NMR (151 MHz, $CDCl_3$) – naphthalen-1-yl carbonofluoridate

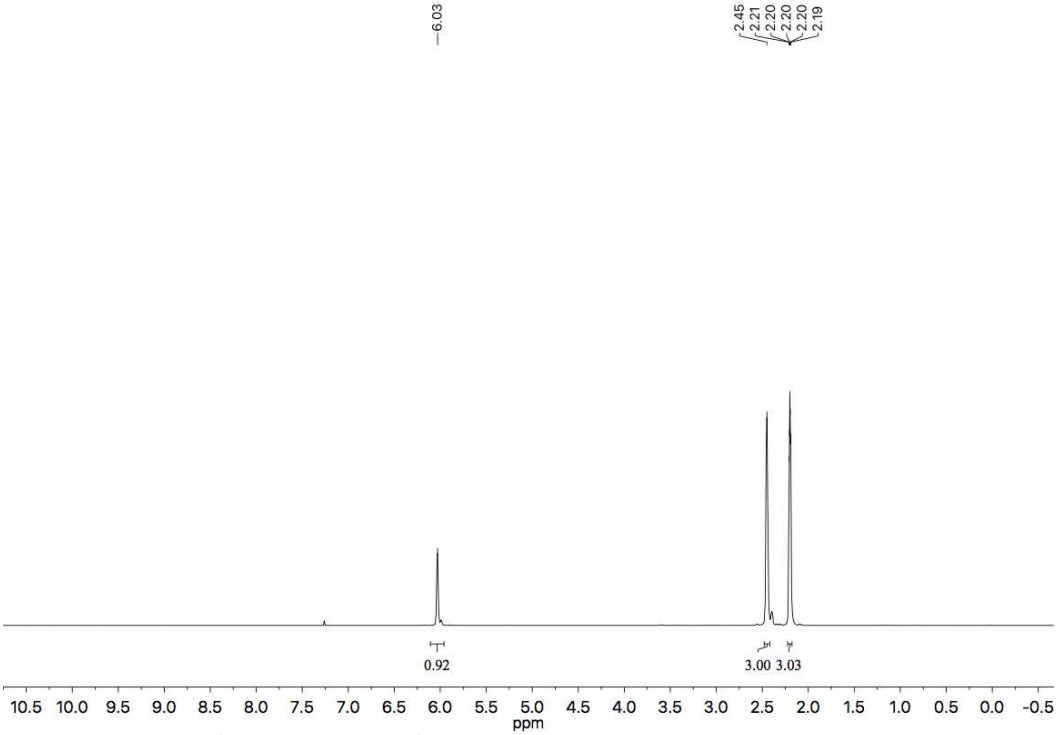


^{19}F NMR (565 MHz, $CDCl_3$) – naphthalen-1-yl carbonofluoridate

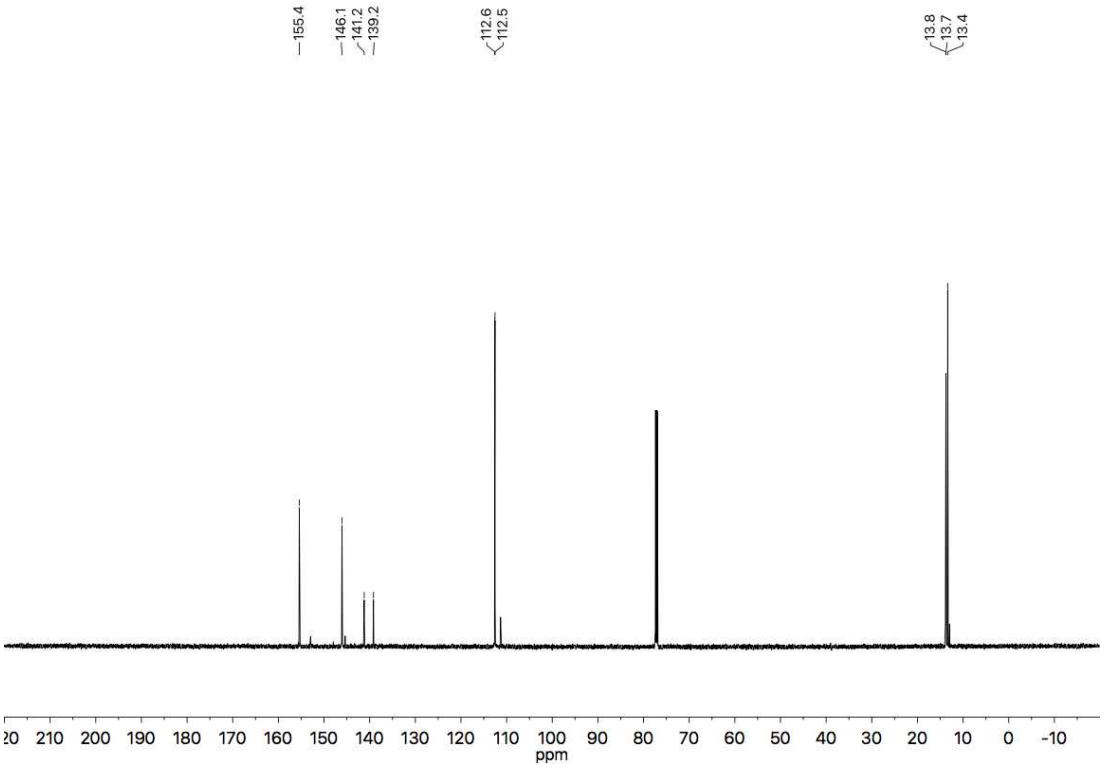




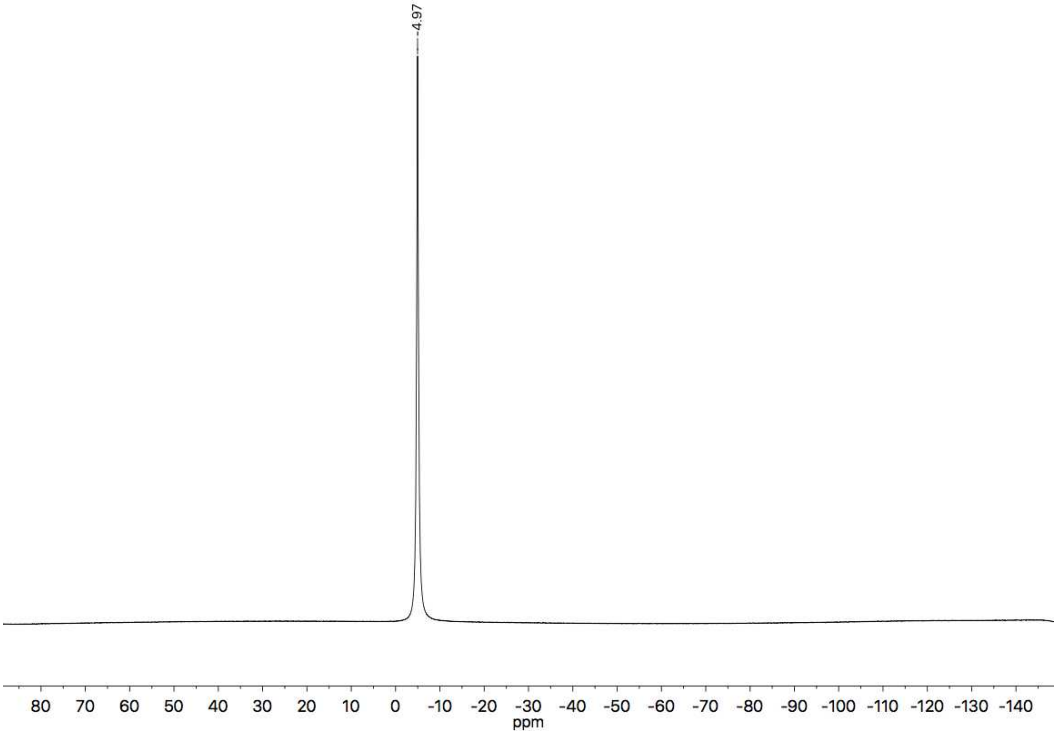
^{1}H NMR (500 MHz, CD_2Cl_2) – 3,5-dimethyl-1*H*-pyrazole-1-carbonyl fluoride

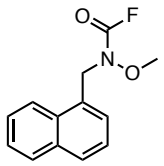


^{13}C NMR (151 MHz, $CDCl_3$) – 3,5-dimethyl-1*H*-pyrazole-1-carbonyl fluoride

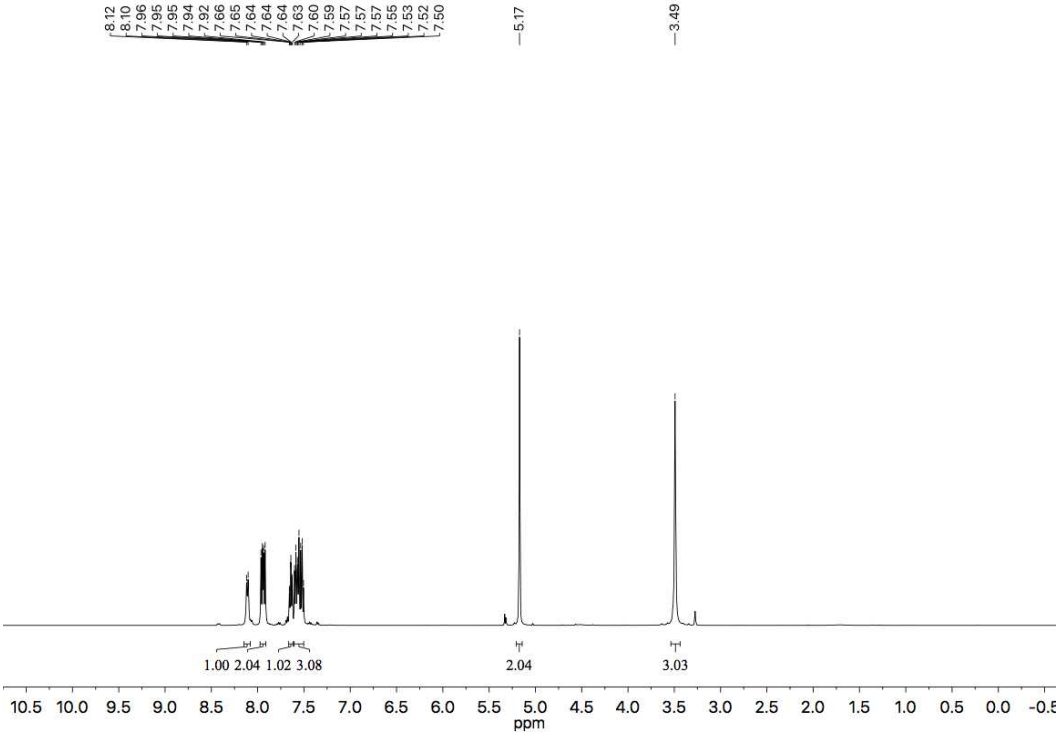


^{19}F NMR (565 MHz, $CDCl_3$) – 3,5-dimethyl-1*H*-pyrazole-1-carbonyl fluoride

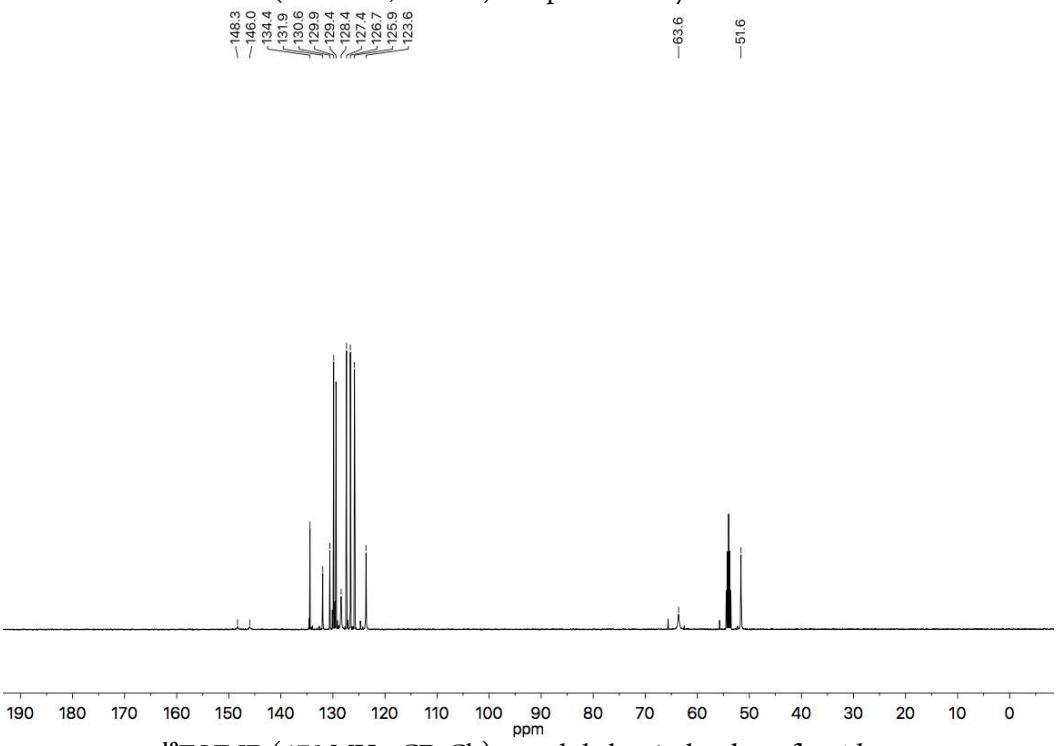




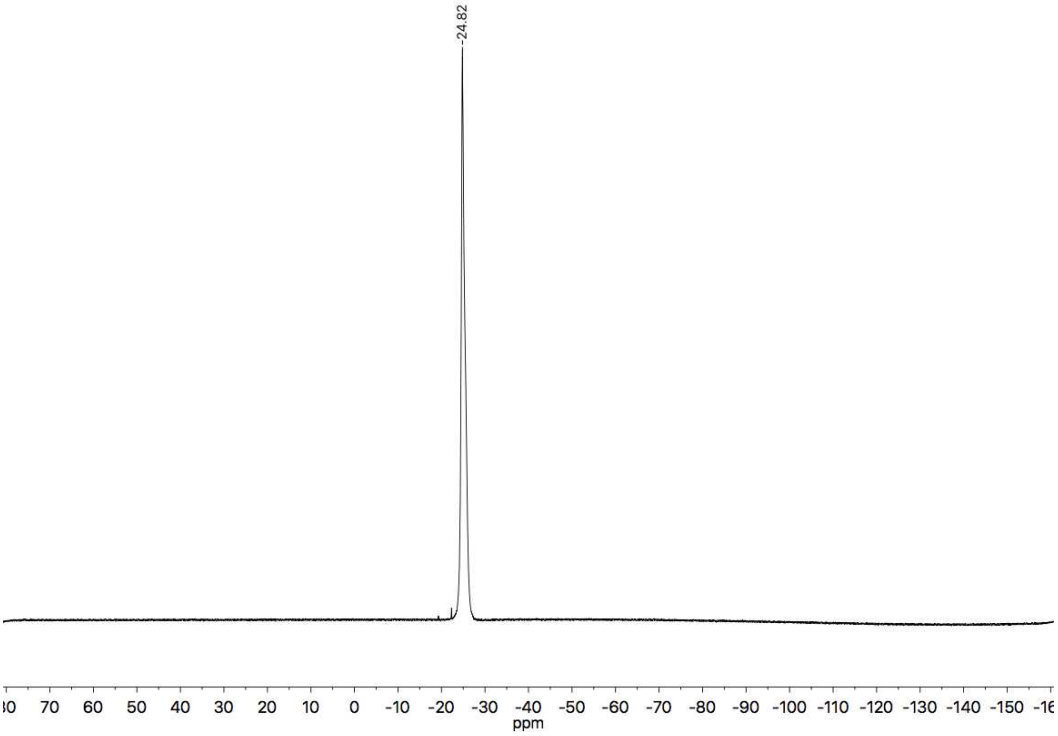
^{1}H NMR (500 MHz, CD_2Cl_2) – naphthalen-1-yl carbonofluoridate

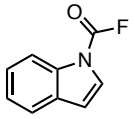


^{13}C NMR (126 MHz, CD_2Cl_2) – naphthalen-1-yl carbonofluoridate

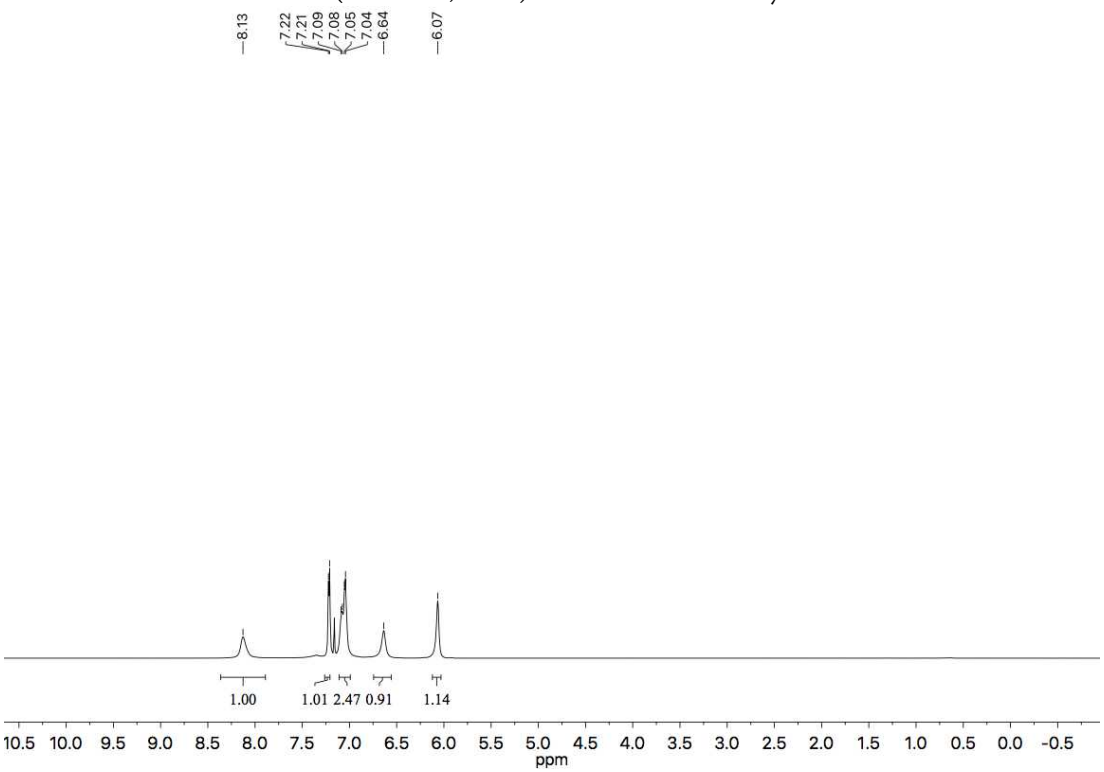


^{19}F NMR (470 MHz, CD_2Cl_2) – naphthalen-1-yl carbonofluoridate

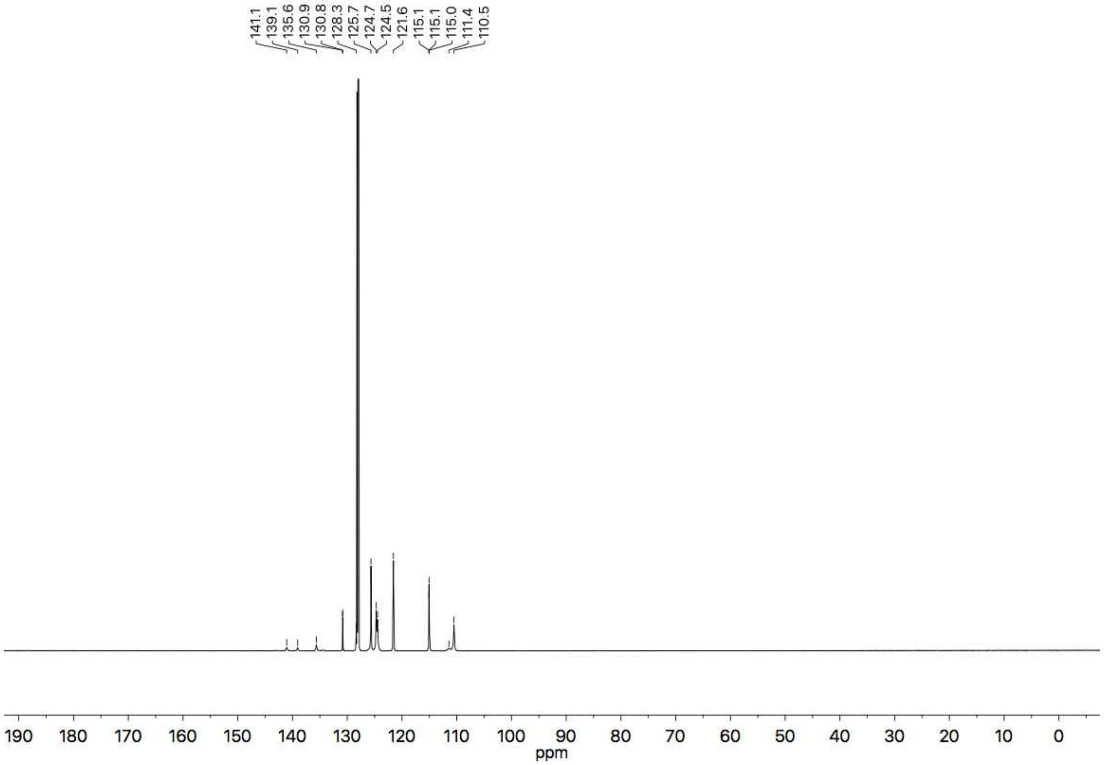




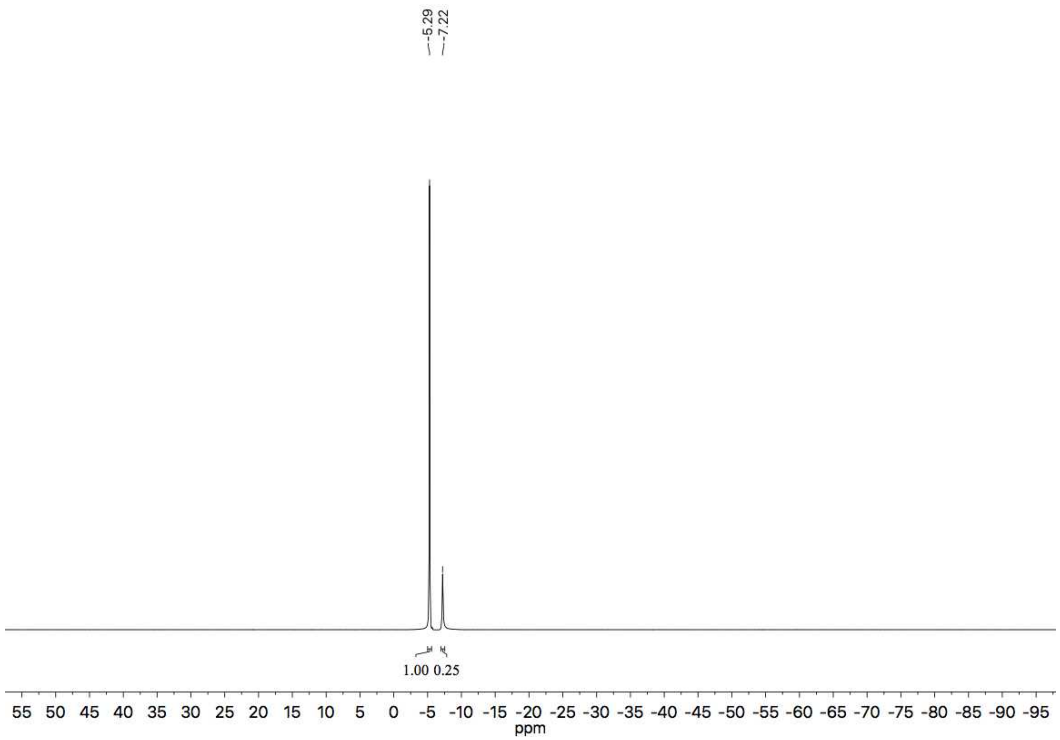
^{1}H NMR (600 MHz, C_6D_6) – 1*H*-indole-1-carbonyl fluoride

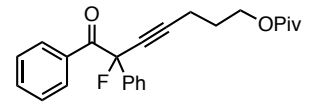


^{13}C NMR (151 MHz, C_6D_6) – 1*H*-indole-1-carbonyl fluoride

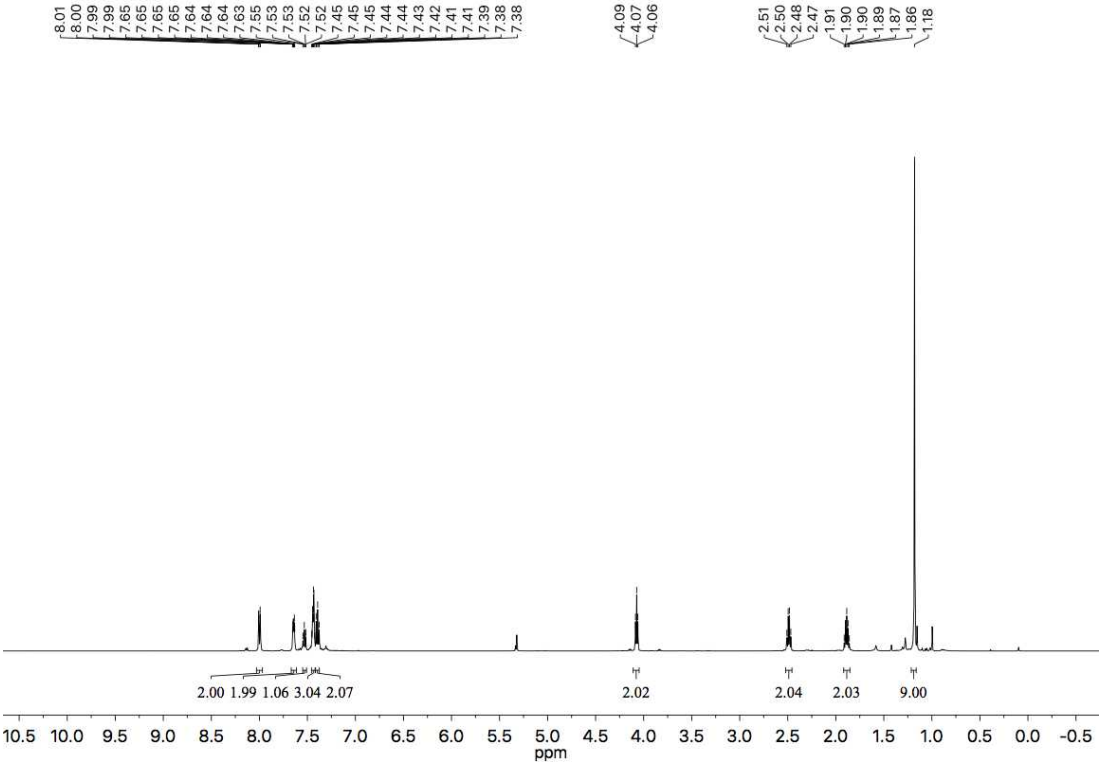


^{19}F NMR (565 MHz, C_6D_6) – 1*H*-indole-1-carbonyl fluoride

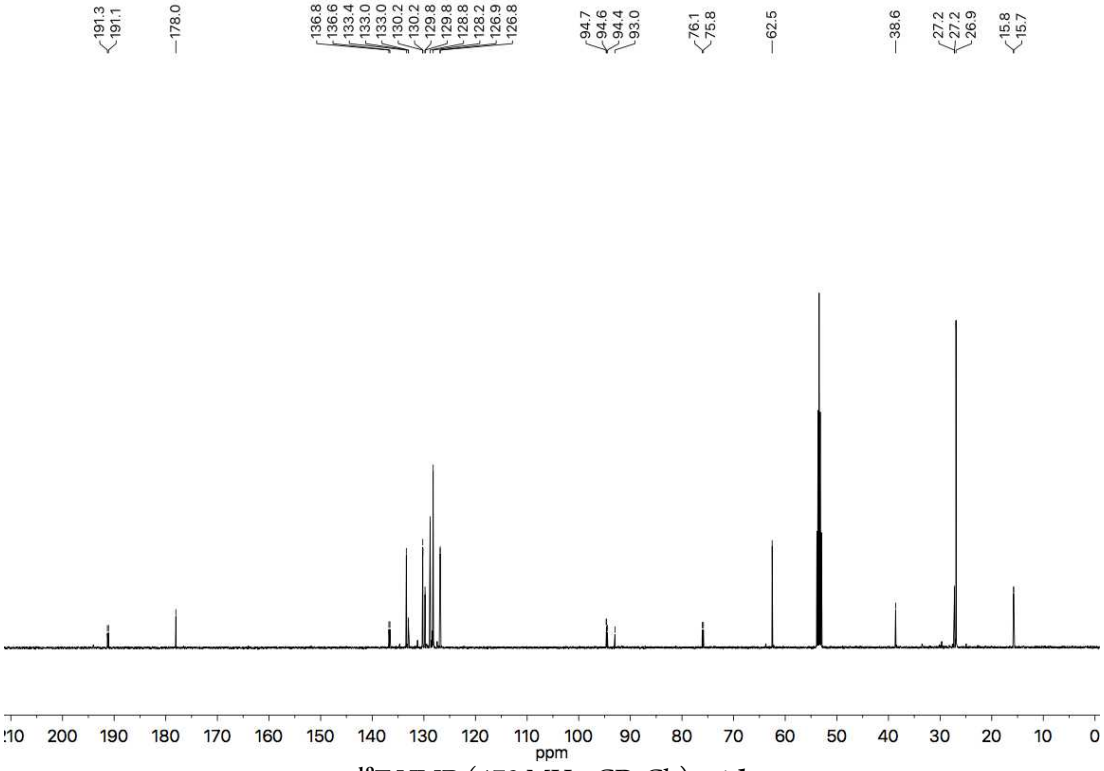




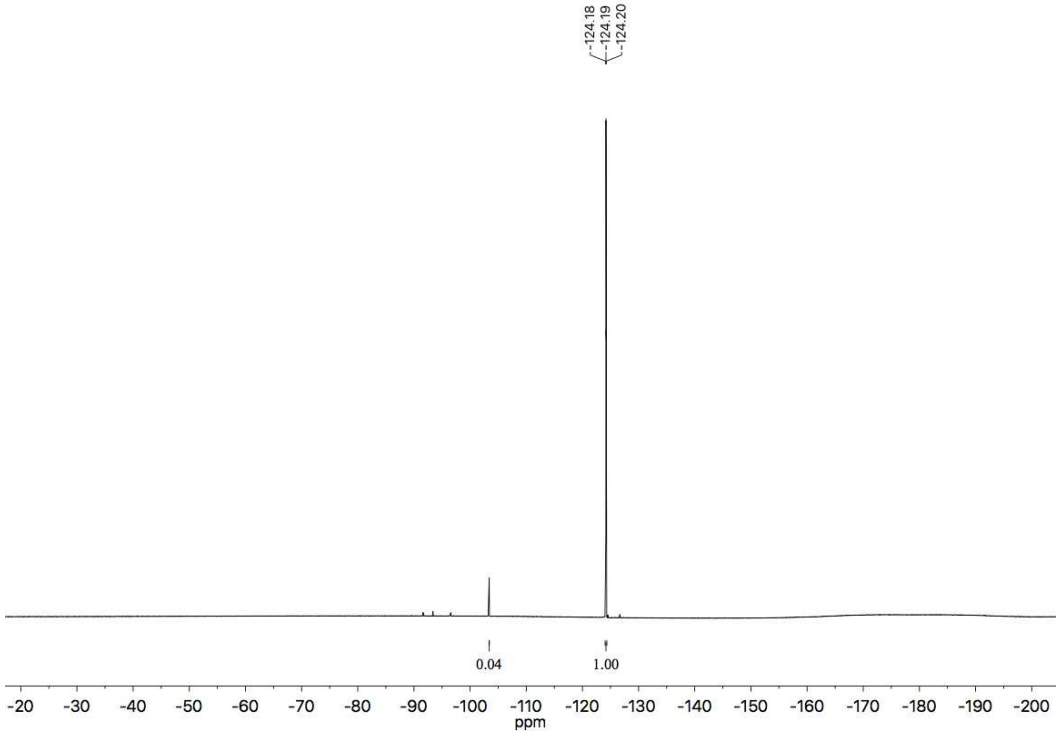
^{1}H NMR (500 MHz, CD_2Cl_2) – **1d**

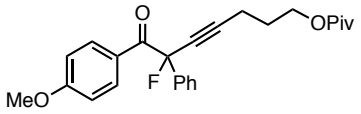


^{13}C NMR (126 MHz, CD_2Cl_2) – **1d**

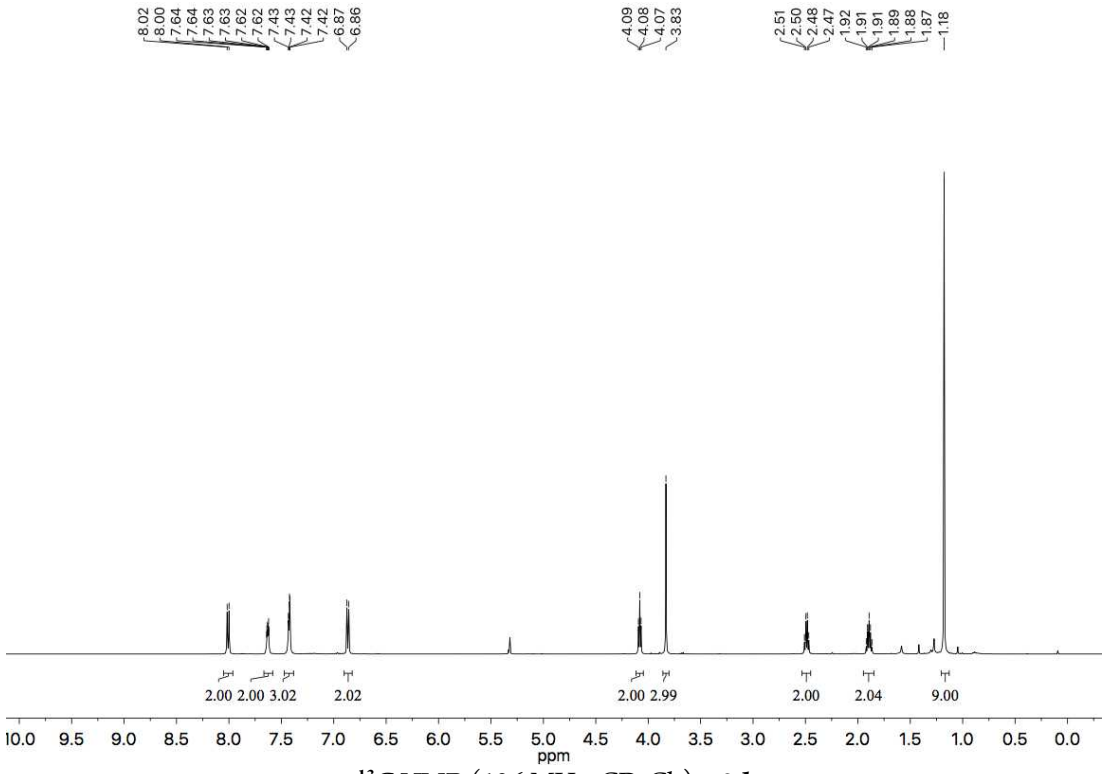


^{19}F NMR (470 MHz, CD_2Cl_2) – **1d**

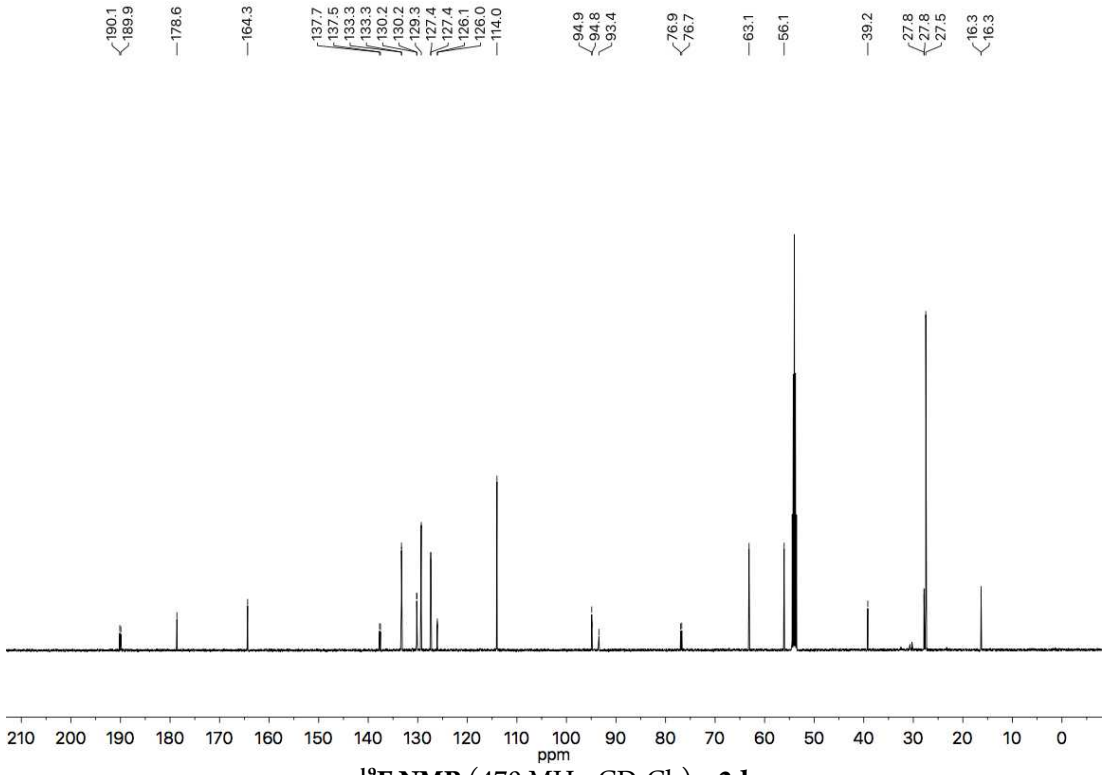




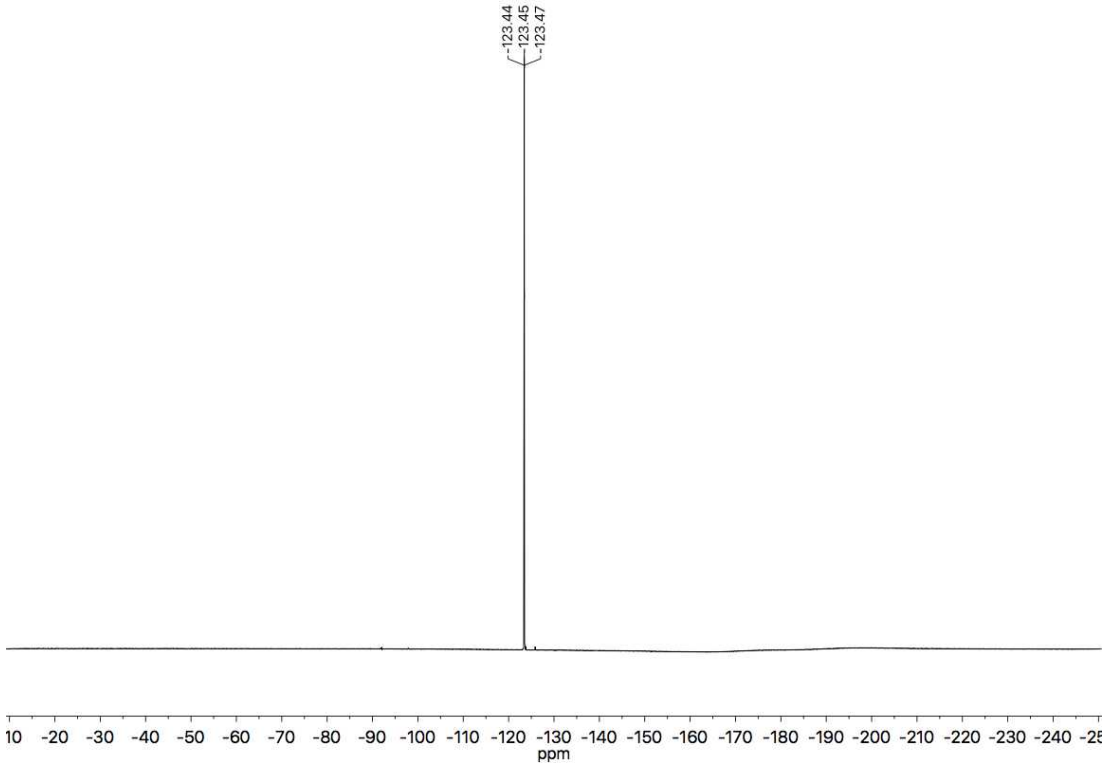
^{1}H NMR (500 MHz, CD_2Cl_2) – **2d**



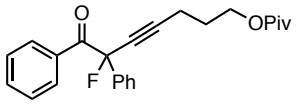
^{13}C NMR (126 MHz, CD_2Cl_2) – **2d**



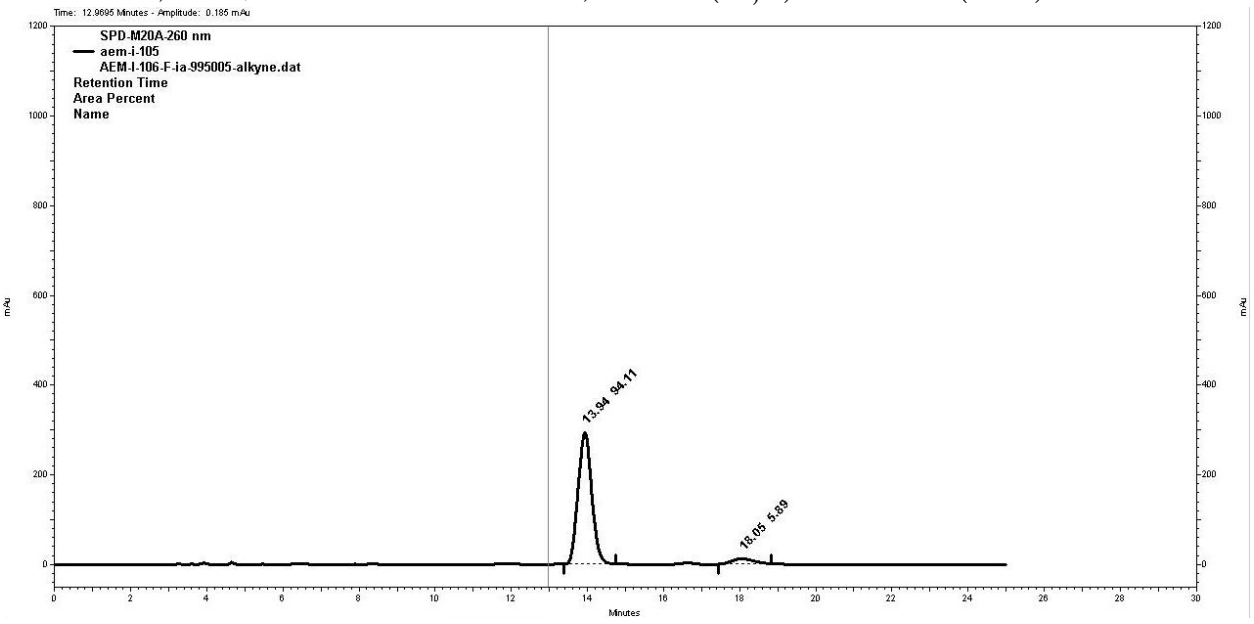
^{19}F NMR (470 MHz, CD_2Cl_2) – **2d**

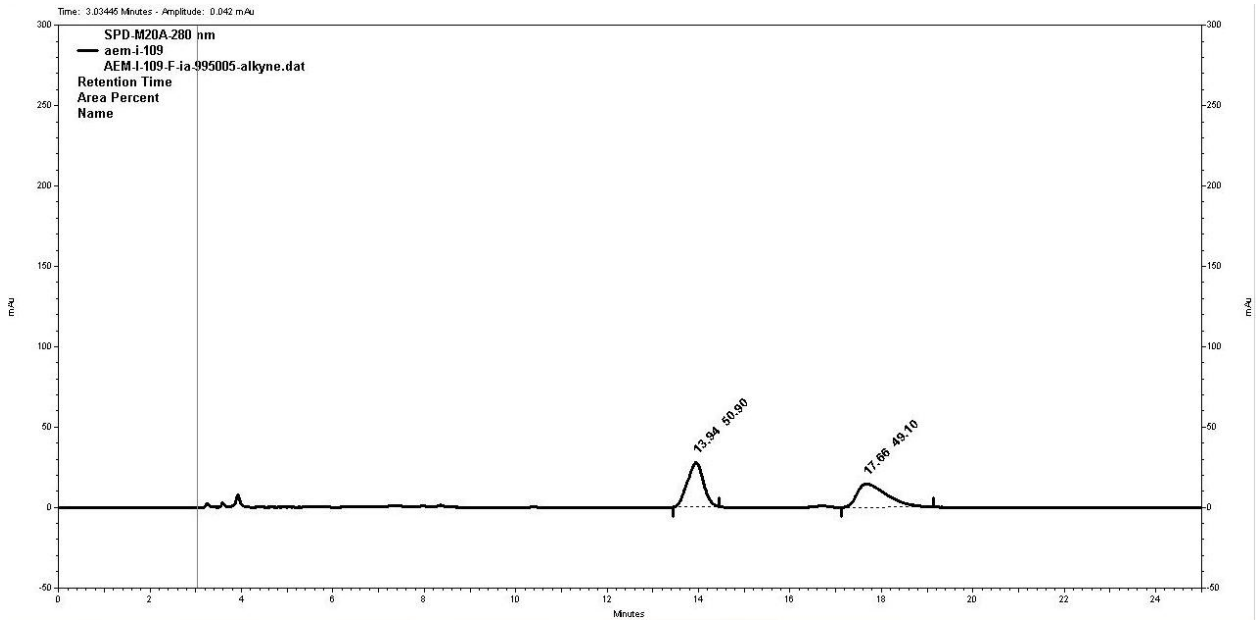


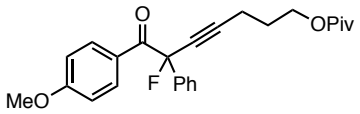
3.4.6 HPLC Spectra



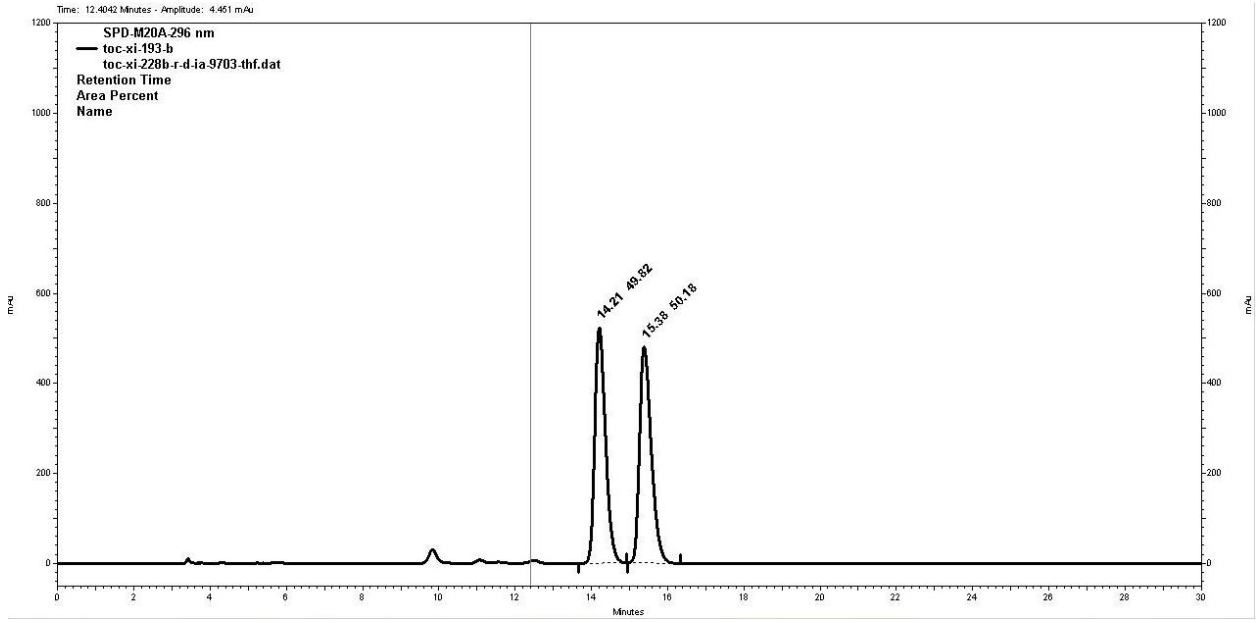
1d: IA column, 1.0 mL/min: 99.5:00.5 hexanes:iPrOH; 13.94 min (major) and 17.66 min (minor)







2d: IA column, 1.0 mL/min: 97:03 hexanes:iPrOH; 14.21 min and 15.38 min



3.5 References

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