Supporting Information

Generation of Axially Chiral Fluoroallenes through a Copper–Catalyzed, Enantioselective *β*–Fluoride Elimination

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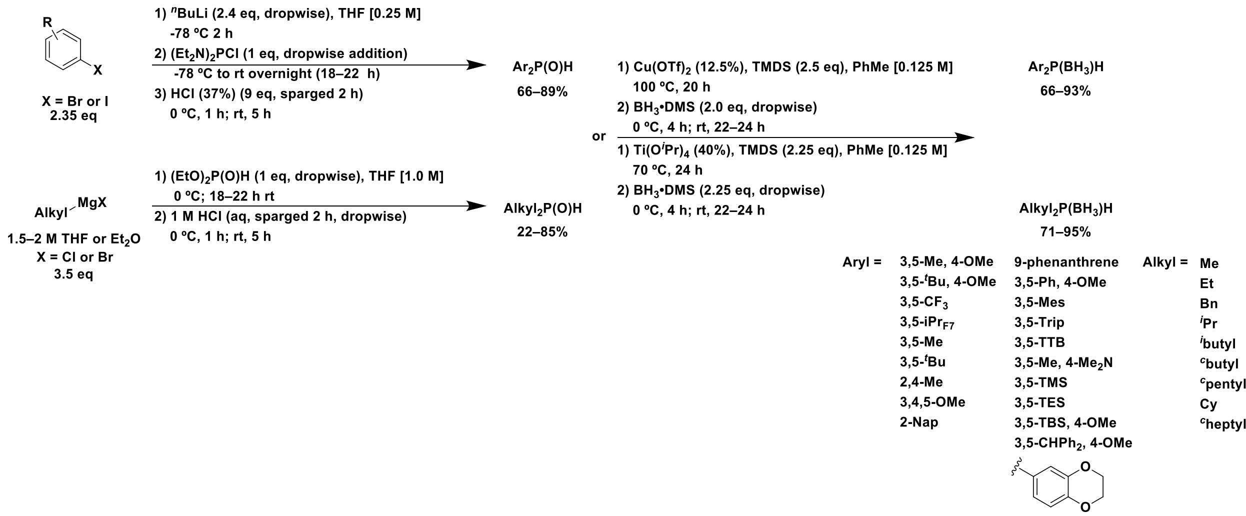
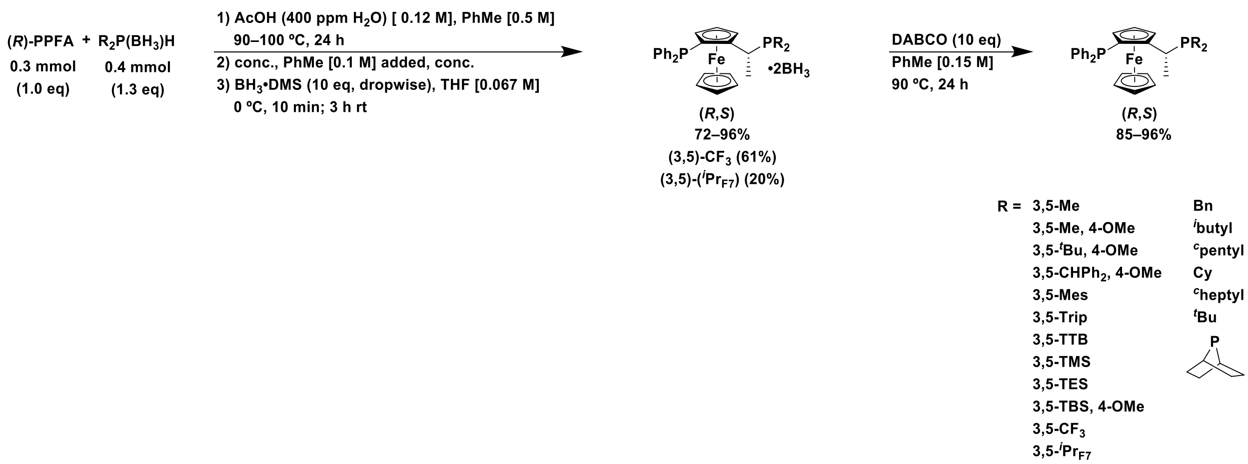
General Information

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 (^1H 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 ^1H 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.

1) General Ligand Synthesis:





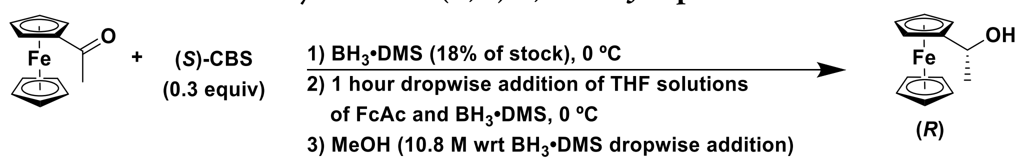
General notes for Josiphos synthesis

Aryl bromides or iodides were purchased or prepared following reported procedures.[1] 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.[2] 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.[3] 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.[4] The reduction of SPOs proceeded well with either $Cu(OTf)_2$[5] or $Ti(O^iPr)_4$[6], 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



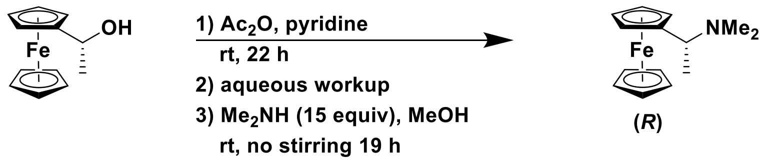
(*R*)-(1-Hydroxyethyl)ferrocene

Prepared from a modified literature procedure.[7]

(*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*).

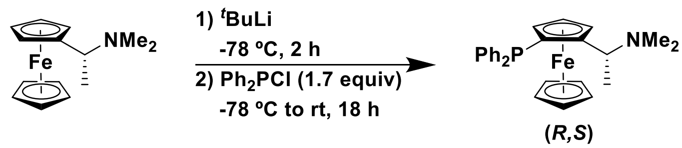
The spectra data were in agreement.[7]
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 4.58–4.51 (m, 1H), 4.24 – 4.21 (m, 9H), 4.17 (s, 1H), 1.85 (d, *J* = 4.0 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H).



(*R*)-Ugi's Amine
Prepared according to a modified literature procedure.[7]

(*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.

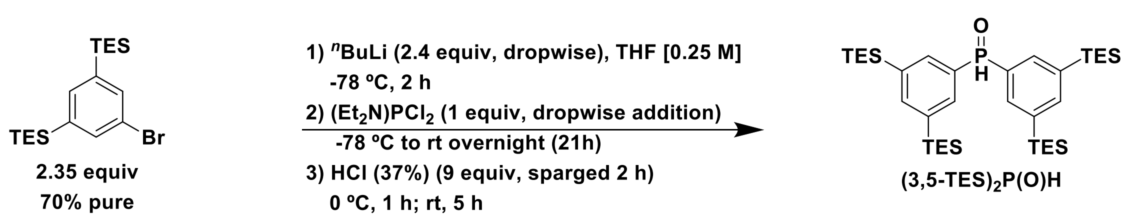
The spectra data were in agreement.[7]
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 4.14–4.12 (m, 1H), 4.11 (t, *J* = 1.9 Hz, 2H), 4.10 (s, 5H), 4.09 – 4.08 (m, 1H), 3.58 (q, *J* = 6.9 Hz, 1H), 2.07 (s, 6H), 1.43 (d, *J* = 6.9 Hz, 3H).



(R)-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine ((R)-PPFA)
Prepared according to a literature procedure.[8]

(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 ºC 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 ºC 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 ºC over the course of 5.5 hours and removed to rt. After 13 hours at rt, the reaction was cooled to 0 ºC, 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.[8]
^{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).

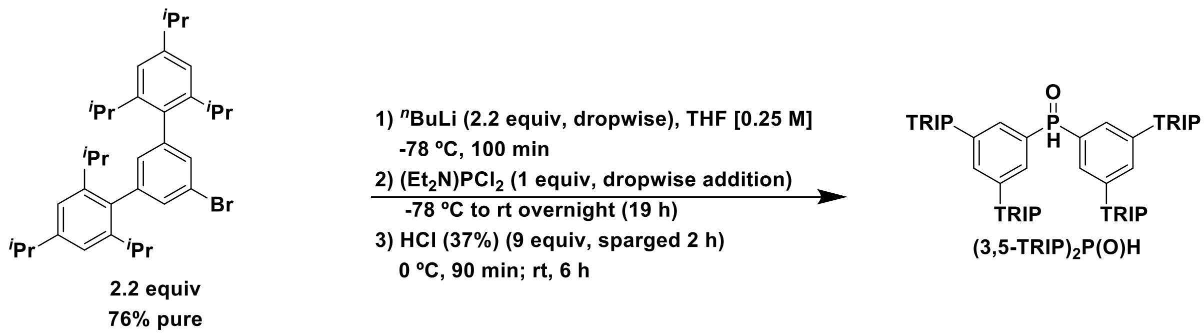


bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide

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 ºC 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 ºC 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 ºC solution of the aryl lithiate. The reaction was left in the -78 ºC 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%).

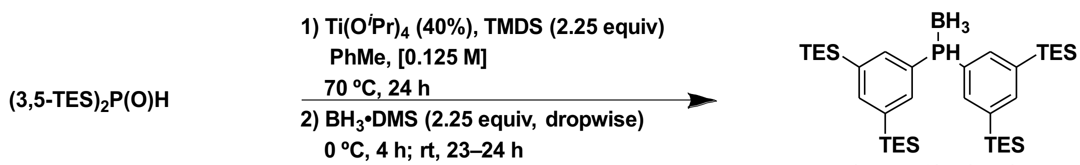
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 474.3 Hz, 1H), 7.79–7.76 (m, 2H), 7.71 (d, *J* = 13.6 Hz, 4H), 0.90 (t, *J* = 8.0 Hz, 36H), 0.76 (q, *J* = 8.1, 7.7 Hz, 24H).
^{31}P NMR (243 MHz, $CDCl_3$) δ 24.6 (s).
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1 (d, *J* = 2.6 Hz), 137.2 (d, *J* = 8.9 Hz), 136.7 (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)[9] 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.

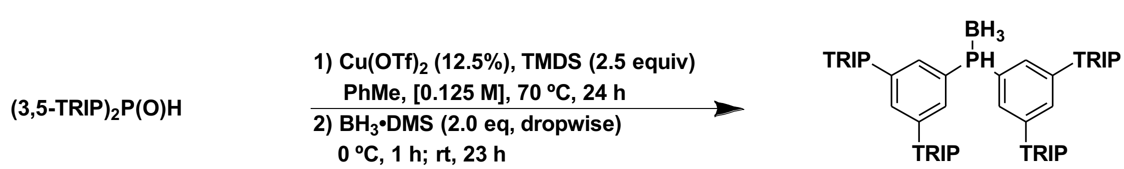


(3,5-TES)$_2$P(BH$_3$)H

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.



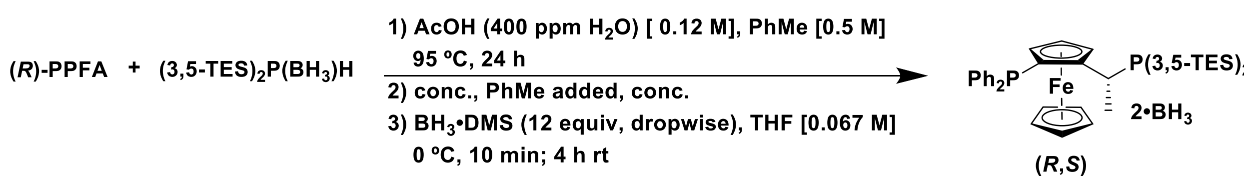
(3,5-TRIP)$_2$P(BH$_3$)H

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).

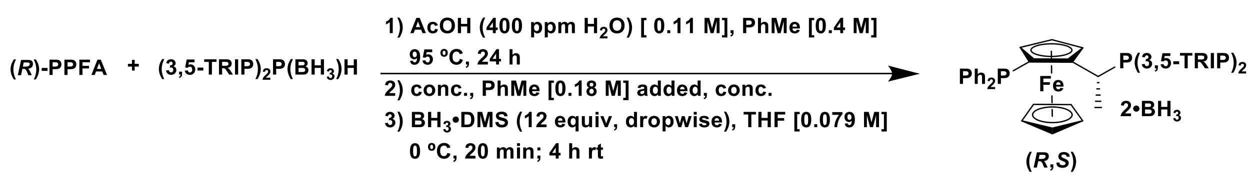


(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(3,5-bis(triethylsilyl)phenyl)phosphine• 2BH$_3$

(*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).

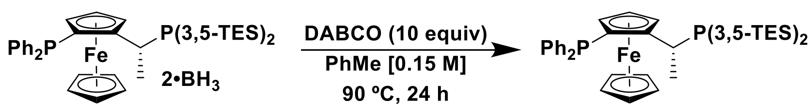
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.8 Hz, 2H), 7.75 (s, 1H), 7.72 (t, *J* = 9.0 Hz, 2H), 7.55 (s, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.5, 7.1 Hz, 2H), 7.26 (d, *J* = 10.3 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 2H), 6.82 – 6.71 (m, 2H), 5.44 (s, 1H), 4.58–4.50 (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.

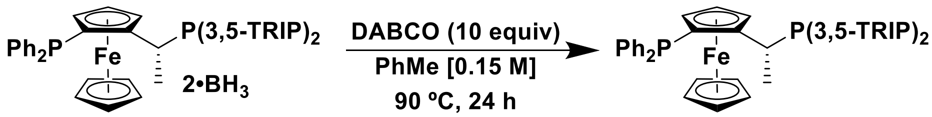


(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(3,5-bis(triethylsilyl)phenyl)phosphine (*R,S*)-(3,5-TES)Josiphos

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).

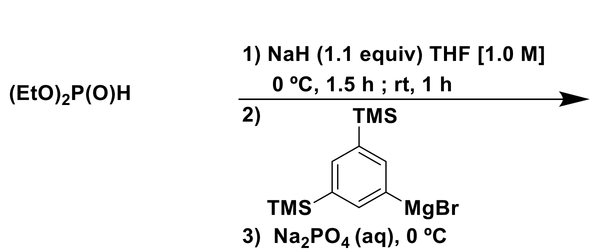


(*R*)-1-[(*S*$_p$)-2-(Diphenylphosphino)ferrocenyl]ethylbis(bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine
(*R*,*S*)-(3,5-TRIP)Josiphos

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.

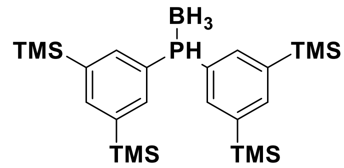
Selected Examples for Secondary Phosphine Borane Synthesis



bis(3,5-bis(trimethylsilyl)phenyl)phosphine oxide
Prepared according to a modified literature report.[4,10]

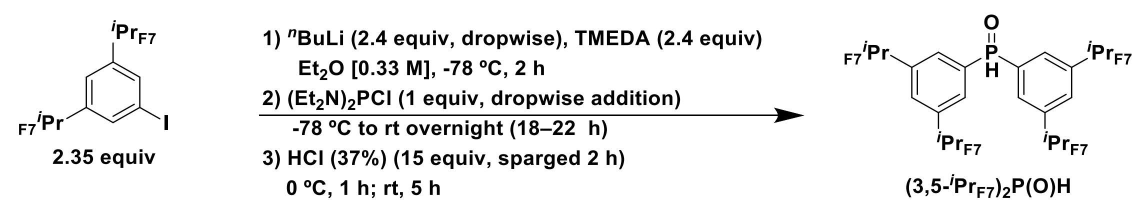
To a 250 mL Schlecnk round bottom flask was added NaH 60% in mineral oil (1.32 g, 33 mmol, 1.1 equiv), THF (30 mL, [1.0 M]), and the slurry cooled to 0 °C. Then, $(EtO)_2P(O)H$ (3.8 mL, 29.5 mmol, 1.0 equiv, distilled under nitrogen) was added dropwise. After 90 minutes at 0 °C, the slurry was removed 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-TMS)$_2$P(BH$_3$)H

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

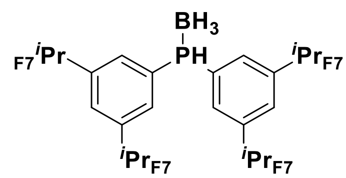
To a PhMe (50 mL, [0.4 M]) solution of the corresponding 3,5-TMS SPO (4.9 g, 10 mmol, 1.0 eq), Ti(O^{i}Pr)$_4$ 97% (1.2 mL, 40 mol%) and TMDS 97% (2.3 mL, 12.5 mmol, 1.25 equiv) were sequentially added under a positive flow of nitrogen at room temperature. After the addition, the reaction was placed 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.



bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine oxide
Prepared according to a modified literature procedure.[11]

1,3-Bis(perfluoropropan-2-yl)-iodo-benzene (12.42g, 23 mmol, 2.3 equiv) was added to Et$_2$O (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$_2$N)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$_2$N)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.[11]
^{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-^{i}Pr$_{F7}$)$_2$P(BH$_3$)H

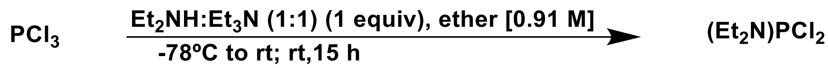
bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane

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,[12] or DIBAL–H[3,13] 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).

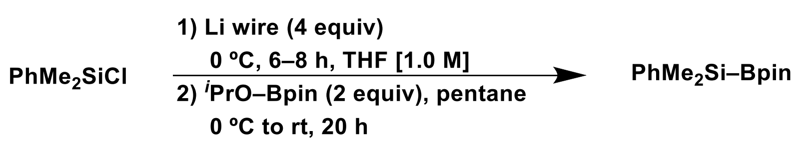
2) Synthesis of Reagents



Dichloro(diethylamino)phosphine
Prepared according to a modified literature procedure.[14]

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.[15]

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.[15]
^{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.[16]

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 °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 °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 °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).

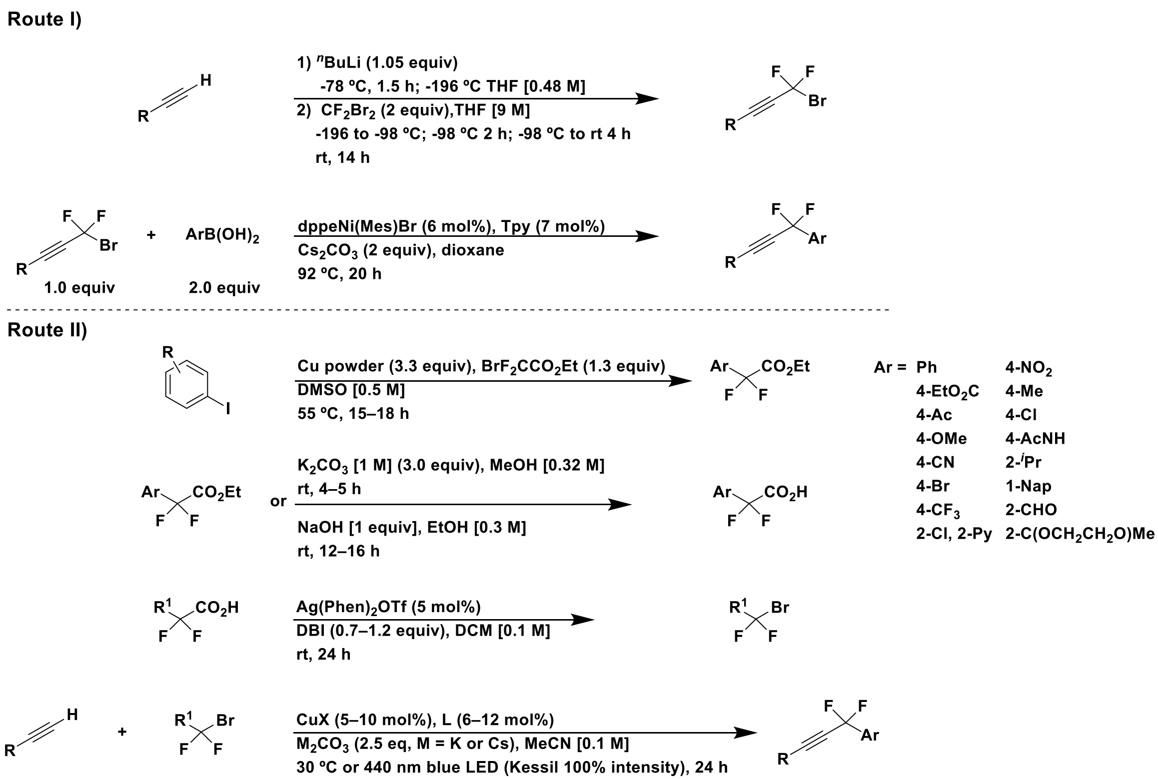
3) Synthesis of Substrates

General Routes:

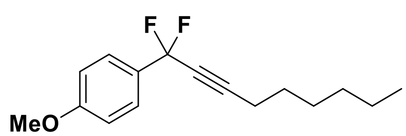
Two general routes were taken for the synthesis of the internal, difluoroalkynes.

Route (I) utilizes CF_2Br_2 as the fluorinated building block following literature reports.[17] Freezing the THF solution of the lithium acetylide with liquid nitrogen gave improved yields for alkynes bearing a 1° alkyl group relative to reaction conditions that utilize a -110 °C cooling bath (which works well for R = TIPS).[18] 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.[20] From the carboxylic acid intermediates, either decarboxylative bromination or decarboxylative alkynylation conditions were applied.[21] A photochemical procedure was developed to couple the bromodifluoroarenes with terminal alkynes. The difluoroalkynyl TIPS substrates were subsequently deprotected and arylated.



Route I



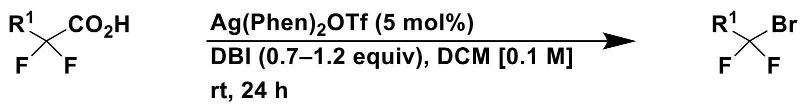
1-(1,1-difluoronon-2-yn-1-yl)-4-methoxybenzene (**2a**)

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-difluoronon-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 ºC 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.

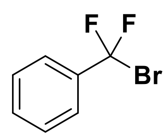
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.35 (tt, *J* = 7.2, 4.9 Hz, 2H), 1.60 (p, *J* = 7.3 Hz, 2H), 1.49–1.38 (m, 2H), 1.38–1.26 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -71.24 (s, 2F).
^{13}C NMR (151 MHz, $CDCl_3$) 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



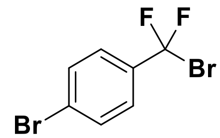
General Procedure A: Decarboxylative Bromination of Difluorocarboxylic Acids

To an oven-dried round bottom flask containing a large magnetic stir bar $Ag(Phen)_2OTf$ (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.)



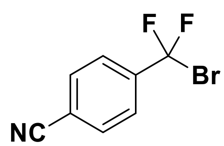
(bromodifluoromethyl)benzene **(1Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (3.9 g, 5 mol%), 2,2-difluoro-2-phenylacetic acid (12.0 g, 70 mmol , 1.0 equiv), and DBI (18.1 g, 63 mmol, 0.9 equiv), and CH_2Cl_2 (700 mL) were used. After anhydrous CH_2Cl_2 was poured into the vessel, the reaction 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.[22]
^{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).



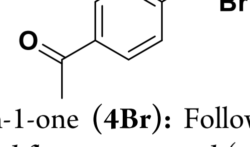
1-bromo-4-(bromodifluoromethyl)benzene **(2Br):** Following general procedure **A**, Ag(Phen)$_2$OTf (190 mg, 5 mol%), 2-(4-bromophenyl)-2,2-difluoroacetic acid (1.51 g, 6.0 mmol , 1.0 equiv), and DBI (1.55 g, 5.4 mmol, 0.9 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic 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.[23]
^{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).



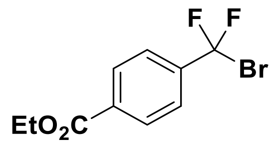
4-(bromodifluoromethyl)benzonitrile **(3Br):** Following general procedure **A**, Ag(Phen)$_2$OTf (190 mg, 5 mol%), 2-(4-cyanophenyl)-2,2-difluoroacetic acid (1.2 g, 6.0 mmol , 1.0 equiv), and DBI (2.0 g, 7.0 mmol, 1.17 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the difluoroacetic 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.[23]
^{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).



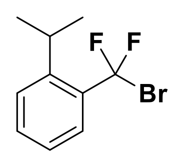
1-(4-(bromodifluoromethyl)phenyl)ethan-1-one **(4Br):** Following general procedure **A**, Ag(Phen)$_2$OTf (190 mg, 5 mol%), 2-(4-acetylphenyl)-2,2-difluoroacetic acid (1.3 g, 6.0 mmol , 1.0 equiv), and DBI (1.43 g, 5.0 mmol, 0.83 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the 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.



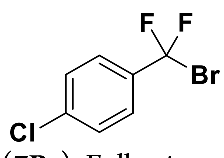
ethyl 4-(bromodifluoromethyl)benzoate **(5Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2-(4-(ethoxycarbonyl)phenyl)-2,2-difluoroacetic acid (1.47 g, 6.0 mmol , 1.0 equiv), and DBI (1.54 g, 5.4 mmol, 0.9 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the 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.[24]
^{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).



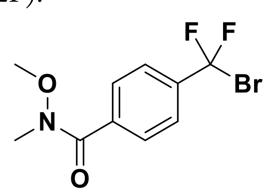
1-(bromodifluoromethyl)-2-isopropylbenzene **(6Br):** Following general procedure **A**, $Ag(Phen)_2OTf$ (190 mg, 5 mol%), 2,2-difluoro-2-(2-isopropylphenyl)acetic acid (1.3 g, 6.0 mmol , 1.0 equiv), and DBI (2.0 g, 7.0 mmol, 1.17 equiv), and CH_2Cl_2 (60 mL) were used. After CH_2Cl_2 was added, the 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).

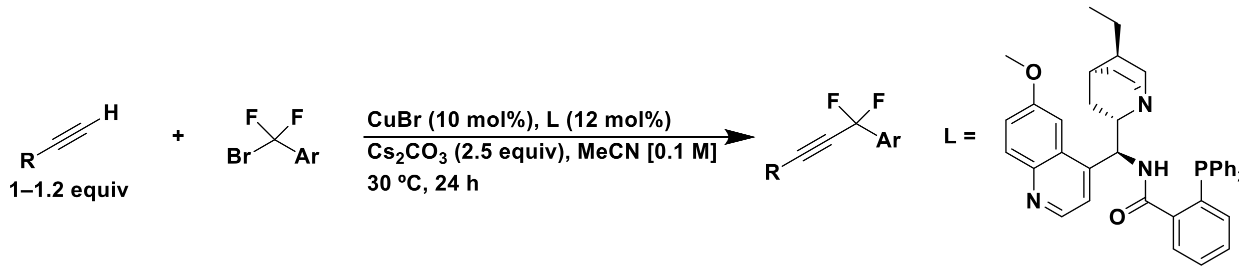
In accordance with previously reported spectra.[25]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -43.76 (s, 2F).



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.

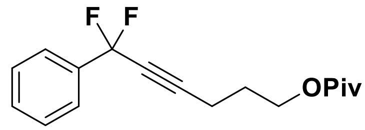


General Procedure B: Aryldifluoromethylation of Terminal Alkynes (Thermal Conditions)

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)

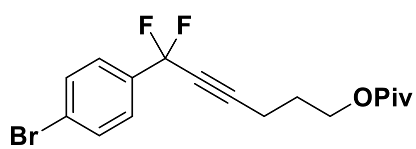
In a nitrogen filled glovebox, an oven-dried 50 mL Schleck round bottom reaction flask containing a large magnetic stir bar was charged with K_2CO_3 (2.5–3.0 eq), terpyridine (Tpy) (12 mol%), and $Cu(MeCN)_4BF_4$ (10 mol%). MeCN (0.1 M) (passed over an activated alumina column, degassed (3 freeze, pump, 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).

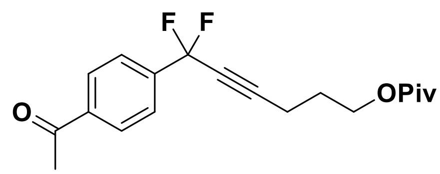
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.51–7.41 (m, 3H), 4.15 (t, J = 6.2 Hz, 2H), 2.45 (tt, J = 7.1, 4.8 Hz, 2H), 1.94 (p, J = 6.7 Hz, 2H), 1.20 (s, 9H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.15 (t, J = 4.6 Hz, 2F)
^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 136.6 (t, J = 28.1 Hz), 130.7 (d, 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 $C_{17}H_{20}FO_2^+$ $[M\text{-}F]^+$: 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).

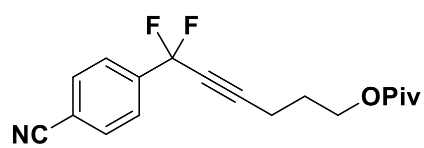
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 4.13 (t, J = 6.2 Hz, 2H), 2.43 (tt, J = 7.2, 4.9 Hz, 2H), 1.92 (p, J = 6.7 Hz, 2H), 1.19 (s, 9H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -74.43 (d, J = 4.4 Hz, 2F).

^{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).

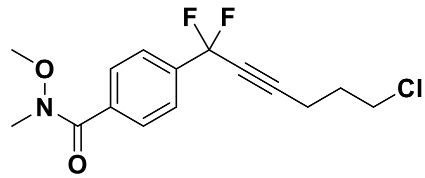
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 4.09 (t, J = 6.2 Hz, 2H), 2.57 (s, 3H), 2.41 (tt, J = 7.1, 4.8 Hz, 2H), 1.94–1.83 (m, 2H), 1.14 (s, 9H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.51 (d, J = 6.1 Hz, 2F).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 178.3, 140.5 (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%).

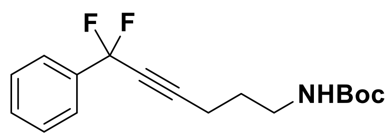
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.70 (m, 4H), 4.11 (t, J = 6.2 Hz, 2H), 2.42 (tt, J = 7.2, 5.0 Hz, 2H), 1.90 (p, J = 6.7 Hz, 2H), 1.16 (s, 9H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -76.02 (t, J = 5.1 Hz, 2F).

^{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.



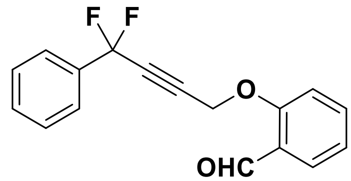
4-(6-chloro-1,1-difluorohex-2-yn-1-yl)-N-methoxy-N-methylbenzamide **(6a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuI (57 mg, 10 mol%), **8Br** (930 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (605 mg, 3.3 mmol, 1.1 equiv), and MeCN (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).

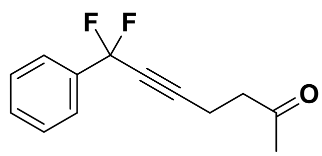
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.68–7.62 (m, 2H), 7.46–7.40 (m, 3H), 4.74 (s, 1H), 3.20 (q, *J* = 6.6 Hz, 2H), 2.37 (tt, *J* = 6.9, 4.8 Hz, 2H), 1.76 (t, *J* = 7.0 Hz, 1H), 1.43 (s, 9H).
^{19}**F NMR** (565 MHz, $CDCl_3$) δ -73.87 (m, 2F)
^{13}**C NMR** (151 MHz, $CDCl_3$) δ 156.1, 136.5 (t, *J* = 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).

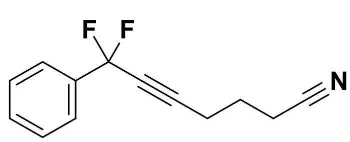
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.90–7.84 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.59–7.52 (m, 1H), 7.50–7.43 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.15–7.05 (m, 2H), 4.99–4.92 (m, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -76.64 (d, *J* = 108.0 Hz).
^{13}C NMR (151 MHz, $CDCl_3$) δ 189.3, 159.5, 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.



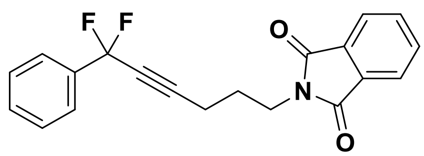
7,7-difluoro-7-phenylhept-5-yn-2-one **(9a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (400 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 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.



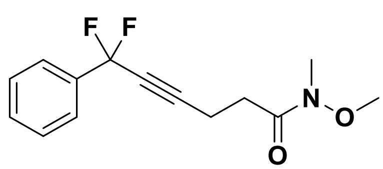
7,7-difluoro-7-phenylhept-5-ynenitrile (**10a**): Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (370 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. After 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 $C_{13}H_{11}FN^+$ $[M\text{-}F]^+$: 200.0870, found 200.867.



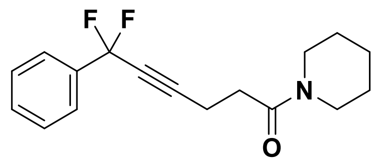
2-(6,6-difluoro-6-phenylhex-4-yn-1-yl)isoindoline-1,3-dione (**11a**): Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (850 mg, 3.9 mmol, 1.3 equiv), and MeCN (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 $C_{20}H_{15}FNO_2^+$ $[M\text{-}F]^+$: 320.1081, found 320.1078.



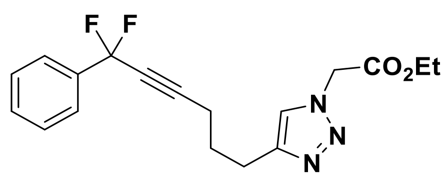
6,6-difluoro-N-methoxy-N-methyl-6-phenylhex-4-ynamide (**12a**): Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (487 mg, 3.45 mmol, 1.15 equiv), and MeCN (30 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-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).

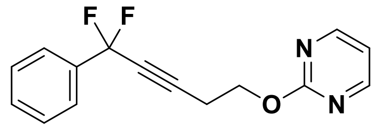
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.62 (m, 2H), 7.45–7.37 (m, 3H), 3.52 (d, *J* = 5.4 Hz, 2H), 3.34 (d, *J* = 5.4 Hz, 2H), 2.72–2.64 (m, 2H), 2.61–2.53 (m, 2H), 1.64–1.56 (m, 2H), 1.56–1.46 (m, 4H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -73.85 (t, *J* = 5.5 Hz, 2F).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 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-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).

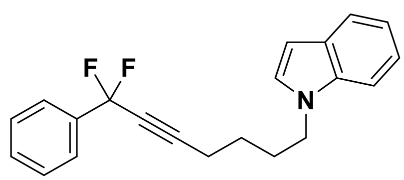
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.45–7.37 (m, 4H), 5.08 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.38 (tt, *J* = 7.0, 4.9 Hz, 2H), 2.00–1.94 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -73.68–-73.74 (m, 2F).
^{13}C NMR (151 MHz, $CDCl_3$) 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.



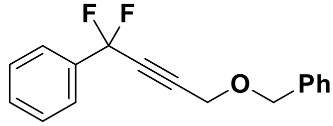
2-((5,5-difluoro-5-phenylpent-3-yn-1-yl)oxy)pyrimidine (**15a**): Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (600 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 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.



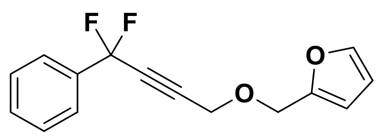
1-(7,7-difluoro-7-phenylhept-5-yn-1-yl)-1H-indole (**16a**): Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (650 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) were 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.



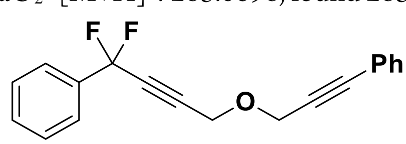
(4-(benzyloxy)-1,1-difluorobut-2-yn-1-yl)benzene **(17a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (587 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were 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).

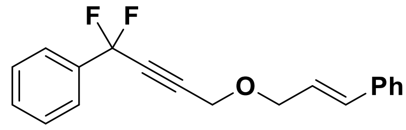
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.50–7.45 (m, 3H), 7.44 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.39 (d, *J* = 3.3 Hz, 1H), 6.37 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.58 (s, 2H), 4.30 (t, *J* = 4.2 Hz, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.78 (s, 2F).
^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 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).

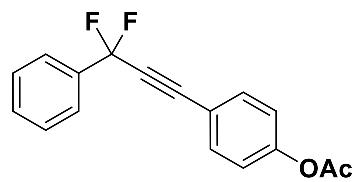
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.51–7.44 (m, 5H), 7.37–7.32 (m, 3H), 4.52 (s, 2H), 4.49 (t, *J* = 4.2 Hz, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.78–-75.92 (m, 2F).

^{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.



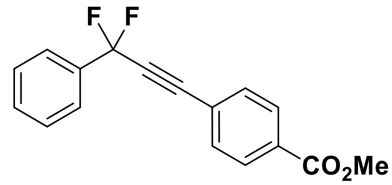
(4-(cinnamyloxy)-1,1-difluorobut-2-yn-1-yl)benzene **(20a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (700 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (570 mg, 3.3 mmol, 1.1 equiv), and MeCN (30 mL) 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.



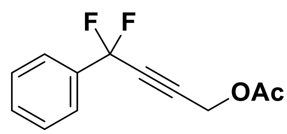
4-(3,3-difluoro-3-phenylprop-1-yn-1-yl)phenyl acetate **(21a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (724 mg, 3.5 mmol, 1.09 equiv), the corresponding terminal alkyne (570 mg, 3.2 mmol, 1.0 equiv), and MeCN (30 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.



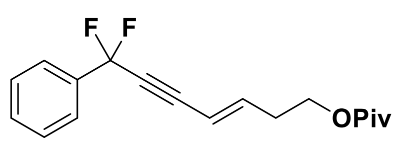
methyl 4-(3,3-difluoro-3-phenylprop-1-yn-1-yl)benzoate **(22a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (653 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (561 mg, 3.5 mmol, 1.17 equiv), and MeCN (30 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.



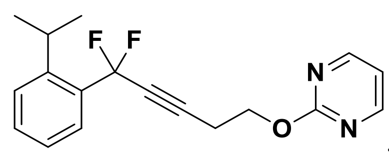
4,4-difluoro-4-phenylbut-2-yn-1-yl acetate **(23a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), $PhCF_2Br$ (621 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (390 mg, 3.9 mmol, 1.3 equiv), and MeCN (30 mL) were used. 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

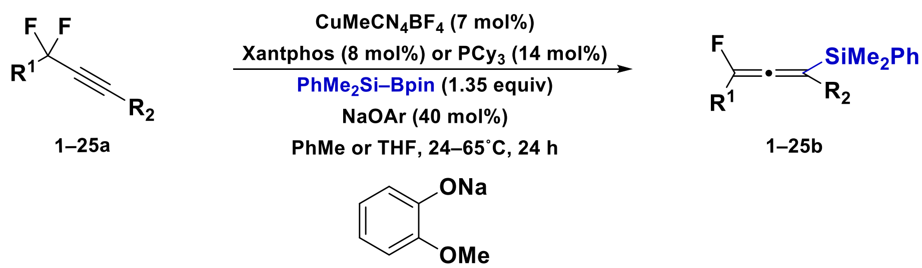


2-((5,5-difluoro-5-(2-isopropylphenyl)pent-3-yn-1-yl)oxy)pyrimidine **(25a):** Following general procedure **B**, Cs_2CO_3 (2.5 g, 7.5 mmol, 2.5 eq), L (221 mg, 12 mol%), CuBr (43 mg, 10 mol%), **6Br** (750 mg, 3.0 mmol, 1.0 equiv), the corresponding terminal alkyne (540 mg, 3.6 mmol, 1.2 equiv), and 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.

4) General Procedure for Alkyne Silylation

Notes: Although no deleterious effects of light were observed, all reactions were setup and conducted in the absence of light to ensure only thermal processes were occurring. 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$_2$Cy** 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.

5) 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).

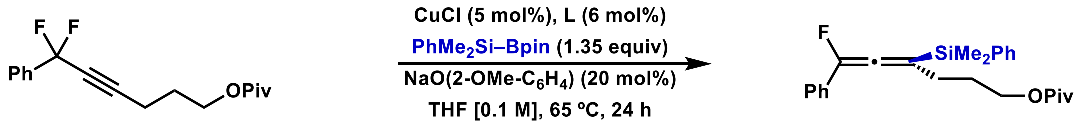
CsF(25%)-CaF_2 preparation:

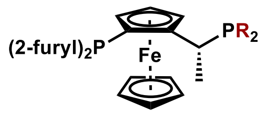
In air, CsF (99% from ChemImpex, dried at 180 °C for 5 days) (18.23 g, 120 mmol, 1 equiv), CaF_2 (99%) (28.1 g, 360 mmol, 4 equiv), and MeOH (new bottle from Sigma-Aldrich of optima filtered <0.07% H_2O) (400 mL) were added to a 1000 mL round bottom flask. The flask was sonicated for 5 minutes before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

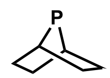
For Screening:

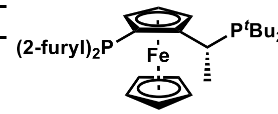
In a nitrogen filled glovebox, a stir bar, CuX (x mol%), ligand (x +1 mol%) were charged to a 1-dram vial. Solvent (500 μL) was added and the mixture was stirred at ambient temperature for 45–60 minutes. (If the ligand was an oil, then a 0.06 M solution was prepared and x + 1 mol% was added dropwise 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



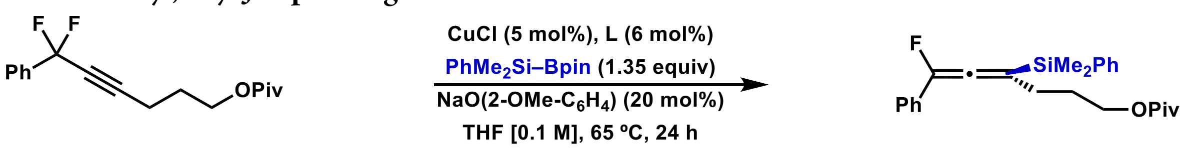


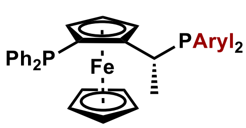
R	^{19}F NMR yield (SM %)	ee %
^{t}Bu	31% (63)	42
L0	27% (23)	-4
^{c}heptyl	9% (61)	5.5
Cy	68% (61)	33
^{c}pentyl	42% (<2)	44
^{i}butyl	41% (<1)	57
Bn	42% (<1)	60
	42% (<1)	70



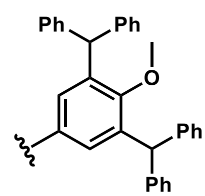
L0

Table S2. Aryl, Aryl Josiphos Ligands Examined

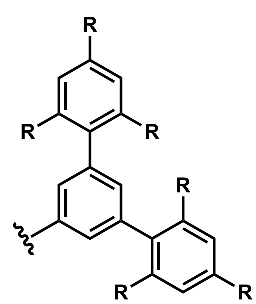




Aryl	^{19}F NMR yield (SM %)	ee %
3,5-Me	59% (23)	45
3,5-Me 4-OMe	31% (14)	44
3,5-^{t}Bu 4-OMe	41% (<1)	70
3,5-diBn 4-OMe	45% (33)	72
3,5-Ph 4-OMe	34% (3)	52
3,5-Mes	58% (38)	75
3,5-Trip	50% (32)	76
3,5-TTB	3% (79)	nd
3,5-TMS	73% (<1)	75
3,5-TES	66% (<1)	83
3,5-TBS 4-OMe	53% (43)	55
3,5-CF_3	43% (<2)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



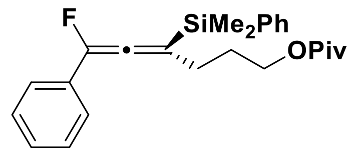
3,5-diBn 4-OMe



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

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**.



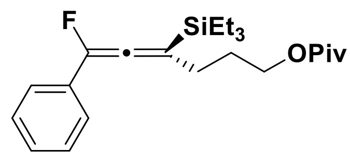
4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl pivalate (**1b**): Following general procedure D, but CuOTf·$0.5C_6H_6$ (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **1a** (54 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was purified 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*).

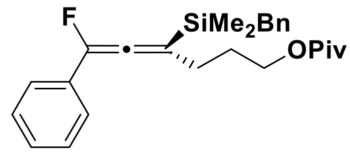
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.65–7.62 (m, 2H), 7.47–7.41 (m, 5H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 4.06 (td, *J* = 6.3, 2.2 Hz, 2H), 2.40 (ddd, *J* = 15.3, 9.0, 6.5 Hz, 2H), 1.95–1.81 (m, 2H), 1.19 (s, 9H), 0.53 (d, *J* = 5.0 Hz, 6H).
^{19}**F NMR** (565 MHz, CD_2Cl_2) 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.



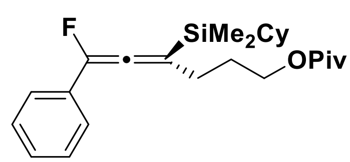
Large scale synthesis of **1b-SiEt$_3$**:
In a nitrogen filled glovebox, $(PPh_3)_3CuF{\cdot}2MeOH$ (224 mg, 8 mol%), (*R,S*)-3,5- Trip-Josiphos (376 mg, 9 mol%) and MTBE (45 mL) were charged to a 100 mL Schlenk round bottom flask. After 60 minutes, $Et_3SiBpin$ (981 mg, 4.05 mmol, 1.35 equiv), and **1a** (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$_2$SiBpin (1.2 g, 4.35 mmol, 1.45 eq) were added to the stirring solution. Once BnMe$_2$SiBpin 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*).

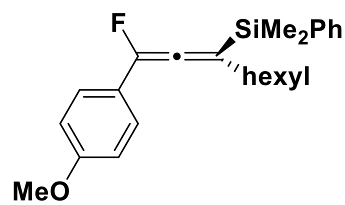
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.6, 6.7 Hz, 3H), 7.23–7.18 (m, 2H), 7.16–7.12 (m, 1H), 7.07 (d, *J* = 6.8 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 2.42–2.36 (m, 2H), 2.31 (q, *J* = 13.8 Hz, 2H), 1.97–1.79 (m, 2H), 1.21 (s, 9H), 0.19 (d, *J* = 18.4 Hz, 6H).
^{19}F 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$_2$SiBpin (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

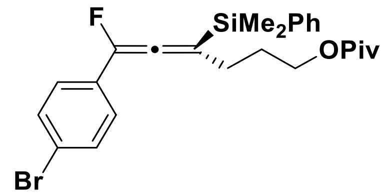
stirred for 8–10 minutes under N_2. After an ^{19}F NMR was acquired, the reaction was filtered over a pad of celite, rinsed with EtOAc (3 x 125 mL), and the filtrate was transferred to a separatory funnel with EtOAc and NH_4OH buffer (100 mL) was added. The layers were shaken and the aqueous phase disposed. 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)



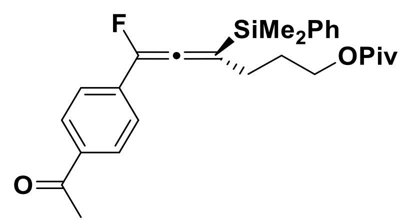
(1-fluoro-1-(4-methoxyphenyl)nona-1,2-dien-3-yl)dimethyl(phenyl)silane **(2b):** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **2a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 45 °C with MTBE as the solvent. The crude 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)



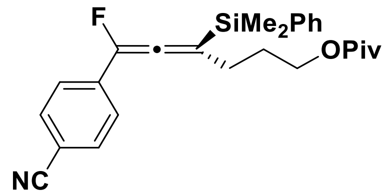
6-(4-bromophenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate **(3b):** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **3a** (75 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was 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)



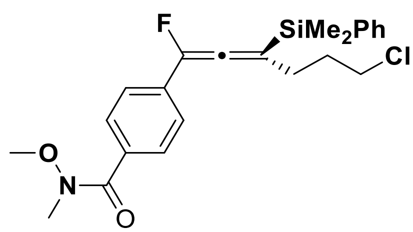
6-(4-acetylphenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate **(4b):** Following general procedure D, but CuOTf·0.5C_6H_6 (2.5 mg, 5 mol%), (*R,S*)-3,5- TES-Josiphos (220 μL, 0.06 M in PhMe, 6 mol%), and **4a** (70 mg, 0.2 mmol, 1.0 equiv) were used at 34 °C. The crude residue was 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)



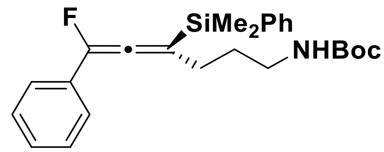
6-(4-cyanophenyl)-4-(dimethyl(phenyl)silyl)-6-fluorohexa-4,5-dien-1-yl pivalate **(5b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **5a** (68 mg, 0.2 mmol, 1.0 equiv) were used at 35 ºC. The crude residue 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)



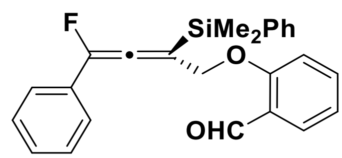
(R)-4-(6-chloro-3-(dimethyl(phenyl)silyl)-1-fluorohexa-1,2-dien-1-yl)-N-methoxy-N-methylbenzamide **(6b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240 μL, 0.06 M in PhMe, 6 mol%), and **6a** (63 mg, 0.2 mmol, 1.0 equiv) were used at 35 ºC. 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)



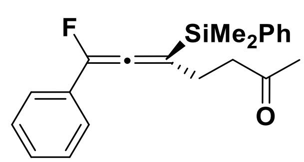
tert-butyl(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)carbamate (**7b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5- TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **7a** (62 mg, 0.2 mmol, 1.0 equiv) were used at 33 °C. The crude residue was 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)



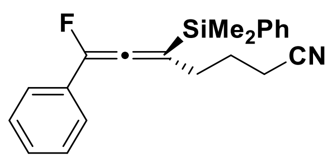
2-((2-(dimethyl(phenyl)silyl)-4-fluoro-4-phenylbuta-2,3-dien-1-yl)oxy)benzaldehyde (**8b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **8a** (58 mg, 0.2 mmol, 1.0 equiv) were used at 40 °C. The crude residue was 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)



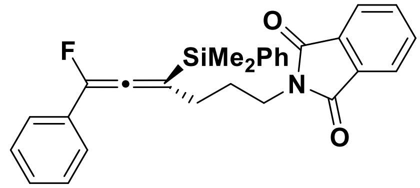
5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-5,6-dien-2-one **(9b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **9a** (44.5 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified 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)



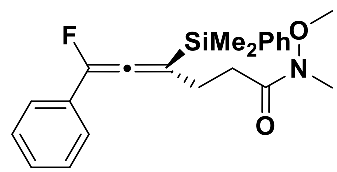
5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-5,6-dienenitrile **(10b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **10a** (44 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified 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)



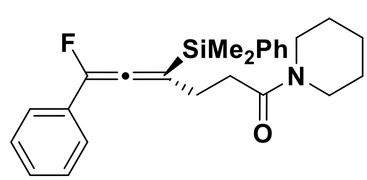
2-(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)isoindoline-1,3-dione **(11b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **11a** (68 mg, 0.2 mmol, 1.0 equiv) were used at 45 °C with MTBE 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)



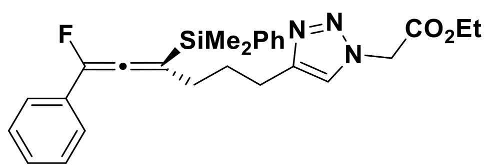
4-(dimethyl(phenyl)silyl)-6-fluoro-N-methoxy-N-methyl-6-phenylhexa-4,5-dienamide (**12b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R*,*S*)-3,5-TES-Josiphos (240 µL, 0.06 M in PhMe, 7 mol%), and **12a** (54 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue 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)



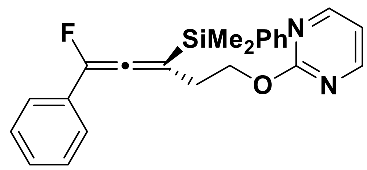
4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenyl-1-(piperidin-1-yl)hexa-4,5-dien-1-one (**13b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R*,*S*)-3,5-TES-Josiphos (240 µL, 0.06 M in PhMe, 7 mol%), and **13a** (58.5 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue 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)



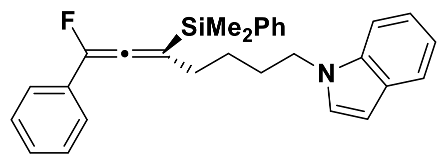
ethyl 2-(4-(4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl)-1H-1,2,3-triazol-1-yl)acetate **(14b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R*,*S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **14a** (70 mg, 0.2 mmol, 1.0 equiv) were used at 40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



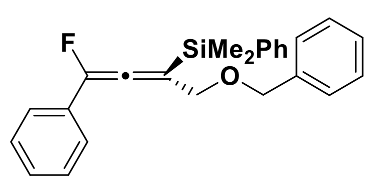
2-((3-(dimethyl(phenyl)silyl)-5-fluoro-5-phenylpenta-3,4-dien-1-yl)oxy)pyrimidine **(15b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R*,*S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **15a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue 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).

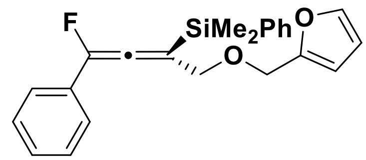
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.63–7.59 (m, 3H), 7.44–7.39 (m, 5H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 4.03 (t, *J* = 7.3 Hz, 2H), 2.37–2.27 (m, 2H), 1.88–1.78 (m, 2H), 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).

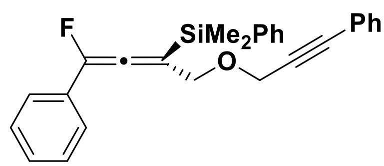
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 6.3 Hz, 2H), 7.45 (dt, *J* = 13.3, 6.3 Hz, 7H), 7.37–7.33 (m, 4H), 7.30 (d, *J* = 7.3 Hz, 2H), 4.57–4.48 (m, 2H), 4.35 (dd, *J* = 7.9, 4.2 Hz, 2H), 0.59 (d, *J* = 5.1 Hz, 6H).

^{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).

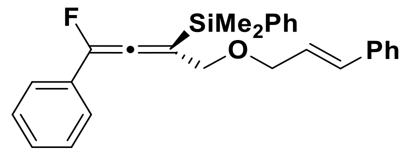
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.61 (d, *J* = 5.7 Hz, 2H), 7.43–7.36 (m, 5H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 4.40 (d, *J* = 2.5 Hz, 2H), 4.26 (dd, *J* = 7.8, 4.2 Hz, 2H), 0.52 (d, *J* = 4.4 Hz, 6H).
^{19}**F NMR** (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).

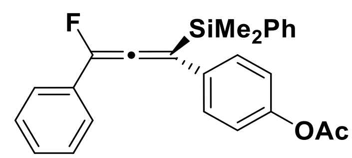
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 5.3 Hz, 2H), 7.43–7.33 (m, 12H), 7.29 (t, *J* = 7.0 Hz, 1H), 4.41 (dd, *J* = 8.1, 2.7 Hz, 2H), 4.35 (s, 2H), 0.56 (d, *J* = 4.3 Hz, 6H).
^{19}**F NMR** (565 MHz, CD_2Cl_2) δ -159.48 (t, *J* = 8.2 Hz, 1F).

^{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).

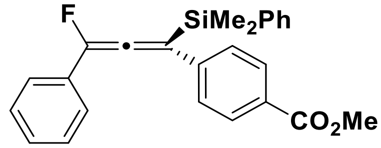
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.45–7.38 (m, 7H), 7.38–7.30 (m, 5H), 7.27 (t, *J* = 6.9 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.32 (dd, *J* = 8.0, 3.4 Hz, 2H), 4.12 (t, *J* = 4.3 Hz, 2H), 0.56 (d, *J* = 5.2 Hz, 6H).
^{19}**F NMR** (565 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).

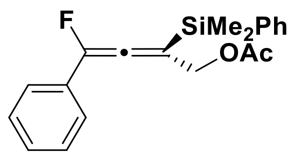
^{1}**H NMR** (600 MHz, CD_2Cl_2) δ 7.70–7.67 (m, 2H), 7.48–7.39 (m, 9H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 2.27 (s, 3H), 0.60 (d, *J* = 9.6 Hz, 6H).
^{19}**F NMR** (565 MHz, CD_2Cl_2) δ -157.86 (s, 1F).
^{13}**C NMR** (151 MHz, CD_2Cl_2) δ 202.0 (d, *J* = 28.4 Hz), 169.8, 151.2, 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)



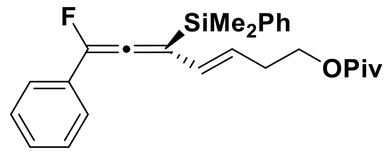
methyl 4-(1-(dimethyl(phenyl)silyl)-3-fluoro-3-phenylpropa-1,2-dien-1-yl)benzoate (**22b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **22a** (55 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was 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)



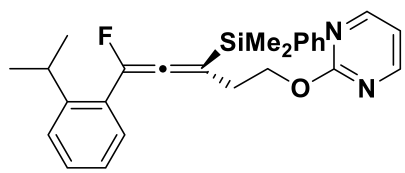
2-(dimethyl(phenyl)silyl)-4-fluoro-4-phenylbuta-2,3-dien-1-yl acetate (**23b**): Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **23a** (45 mg, 0.2 mmol, 1.0 equiv) were used at 35 °C. The crude residue was purified 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)



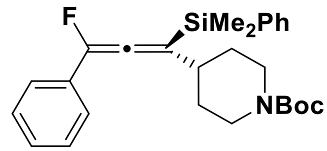
(*E*)-5-(dimethyl(phenyl)silyl)-7-fluoro-7-phenylhepta-3,5,6-trien-1-yl pivalate **(24b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 µL, 0.06 M in PhMe, 7 mol%), **24a** (62 mg, 0.2 mmol, 1.0 equiv), CsF (30 mg, 0.2 mmol, 1.0 equiv), and 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)



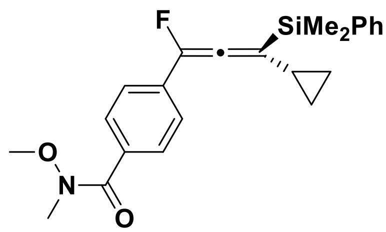
2-((3-(dimethyl(phenyl)silyl)-5-fluoro-5-(2-isopropylphenyl)penta-3,4-dien-1-yl)oxy)pyrimidine**(25b):** Following general procedure D, but $CuOTf{\cdot}0.5C_6H_6$ (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 µL, 0.06 M in PhMe, 7 mol%), and **25a** (63.5, 0.2 mmol, 1.0 equiv) were used at 45 °C with 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)



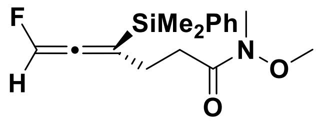
tert-butyl 4-(1-(dimethyl(phenyl)silyl)-3-fluoro-3-phenylpropa-1,2-dien-1-yl)piperidine-1-carboxylate **(26b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **26a** (67 mg, 0.2 mmol, 1.0 equiv) were used at 40 °C. The crude residue was purified by column chromatography on SiO_2 (EtOAc:hexanes 1:9) to afford the title compound as a colorless oil (56 mg, 62% yield).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.62 (d, *J* = 6.8 Hz, 2H), 7.45–7.35 (m, 7H), 7.30 (t, *J* = 7.4 Hz, 1H), 4.13–4.00 (m, 2H), 2.69 (s, 2H), 2.46–2.34 (m, 1H), 1.82–1.70 (m, 2H), 1.43 (s, 9H), 0.52 (d, *J* = 10.5 Hz, 9H).
^{19}F NMR (565 MHz, CD_2Cl_2) δ -159.51 (s, 1F).
^{13}C NMR (151 MHz, CD_2Cl_2) δ 197.0 (d, *J* = 27.8 Hz), 154.9, 143.8 (d, *J* = 224.9 Hz), 137.2, 134.4, 132.5 (d, *J* = 32.4 Hz), 130.2, 129.1, 128.8 (d, *J* = 12.9 Hz), 128.0, 123.6 (d, *J* = 3.4 Hz), 79.6, 44.3, 40.6, 33.3, 33.2, 28.7, -2.3 (d, *J* = 17.7 Hz).
HRMS (ESI+) calc'd for $C_{27}H_{34}FNNaO_2Si^+$ [M+Na]$^+$: 474.2235, found 474.2230.
Determination of enantiomeric ratio by HPLC analysis: IB column, 0.35 mL/min: hexanes:iPrOH 99.8:00.2; 36.20 min (major) and 37.59 min (minor)



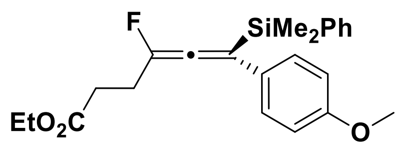
4-(3-cyclopropyl-3-(dimethyl(phenyl)silyl)-1-fluoropropa-1,2-dien-1-yl)-N-methoxy-N-methylbenzamide **(27b):** Following general procedure D, but CuOTf·0.5C_6H_6 (3.0 mg, 6 mol%), (*R,S*)-3,5-TES-Josiphos (240 μL, 0.06 M in PhMe, 7 mol%), and **27a** (59 mg, 0.2 mmol, 1.0 equiv, 95% pure) were used at 40 °C. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:1) to afford the title compound as a colorless oil (53 mg, 66% yield).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.63 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.41–7.38 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 3H), 3.33 (s, 3H), 1.48–1.42 (m, 1H), 0.89–0.79 (m, 2H), 0.63–0.55 (m, 2H), 0.52 (d, *J* = 6.1 Hz, 6H).
^{19}F NMR (565 MHz, CD_2Cl_2) δ -155.77 (s, 1F).
^{13}C NMR (151 MHz, CD_2Cl_2) δ 192.4 (d, *J* = 26.4 Hz), 169.8, 142.9 (d, *J* = 225.8 Hz), 137.0, 135.0 (d, *J* = 33.5 Hz), 134.5, 133.8, 130.4 (d, *J* = 12.8 Hz), 130.2, 129.1, 123.2 (d, *J* = 3.3 Hz), 61.5, 34.1, 12.8, 11.0 (d, *J* = 2.7 Hz), 10.7 (d, *J* = 3.3 Hz), -2.7 (d, *J* = 3.6 Hz).
HRMS (ESI+) calc'd for $C_{23}H_{26}FNNaO_2Si^+$ [M+Na]$^+$: 418.1609, found 418.1619.
Determination of enantiomeric ratio by HPLC analysis: ADH column, 0.3 mL/min: hexanes:iPrOH 99.5:0.5; 72.86 min (major) and 77.16 min (minor)



4-(dimethyl(phenyl)silyl)-6-fluoro-N-methoxy-N-methylhexa-4,5-dienamide (**28b**)**:** 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 **28a** (x, 0.2 mmol, 1.0 equiv, 95% pure) were used at 45 °C. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:1 to 2:1) to afford the title compound as a colorless oil (12 mg, 19% yield; with 2.5% **28a**).

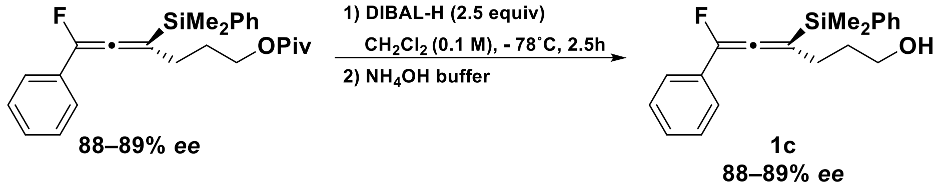
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.57–7.55 (m, 2H), 7.40–7.36 (m, 3H), 7.28 (dt, *J* = 89.2, 2.1 Hz, 1H), 3.63 (s, 3H), 3.11 (s, 3H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.51–2.37 (m, 2H), 0.46 (d, *J* = 3.5 Hz, 6H).
^{19}F NMR (565 MHz, CD_2Cl_2) δ -176.43 (dt, *J* = 89.1, 11.5 Hz, 1F).
^{13}C NMR (151 MHz, CD_2Cl_2) δ 196.5 (d, *J* = 13.6 Hz), 136.9 (d, *J* = 2.0 Hz), 134.5, 131.7 (d, *J* = 234.9 Hz), 130.1, 128.5, 123.4 (d, *J* = 14.4 Hz), 61.7, 32.6, 31.0, 26.8, -3.2 (d, *J* = 6.5 Hz).
HRMS (ESI+) calc'd for $C_{16}H_{22}FNNaO_2Si^+$ $[M+Na]^+$: 330.1296, found 330.1292.
Determination of enantiomeric ratio by HPLC analysis: OJ column, 0.4 mL/min: hexanes:iPrOH 99.6:00.4; 47.55 min (major) and 43.08 min (minor)



ethyl 6-(dimethyl(phenyl)silyl)-4-fluoro-6-(4-methoxyphenyl)hexa-4,5-dienoate (**29b**)**:** 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 **29a** (x, 0.2 mmol, 1.0 equiv, 95% pure) were used at 45 °C. The crude residue was purified by column chromatography on SiO_2 (Et_2O:hexanes 1:3) to afford the title compound as a colorless oil (41 mg, 52% yield).

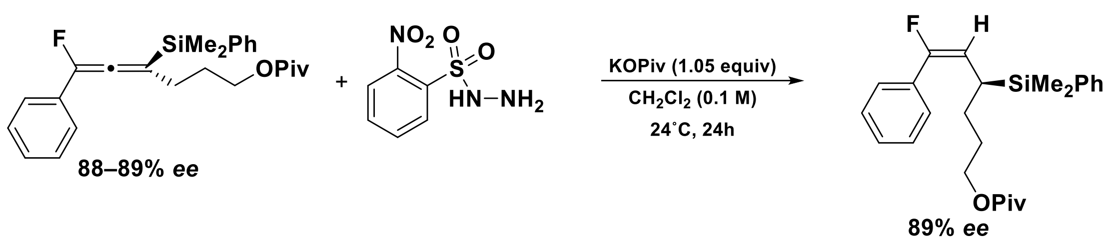
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.60–7.57 (m, 2H), 7.41–7.35 (m, 3H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.03 (dddd, *J* = 17.9, 10.8, 7.1, 3.6 Hz, 2H), 3.76 (s, 3H), 2.84–2.67 (m, 2H), 2.53–2.40 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.51 (d, *J* = 3.0 Hz, 6H).
^{19}F NMR (565 MHz, CD_2Cl_2) δ -144.57 (t, *J* =11.1 Hz, 1F).
^{13}C NMR (151 MHz, CD_2Cl_2δ 198.3 (d, *J* = 25.4 Hz), 172.6, 160.0, 142.8 (d, *J* = 232.8 Hz), 138.0, 134.5, 130.1 (d, *J* = 2.4 Hz), 130.0, 129.2, 128.5, 121.7 (d, *J* = 13.3 Hz), 114.4, 61.1, 55.8, 31.4 (d, *J* = 2.1 Hz), 26.5 (d, *J* = 34.9 Hz), 14.5, -1.5.
HRMS (ESI+) calc'd for $C_{23}H_{27}FNNaO_3Si^+$ $[M+Na]^+$: 421.1606, found 421.1610.
Determination of enantiomeric ratio by HPLC analysis: IA column, 0.4 mL/min: hexanes:iPrOH 99.9:00.1; 33.93 min (major) and 32.25 min (minor)

6) 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)

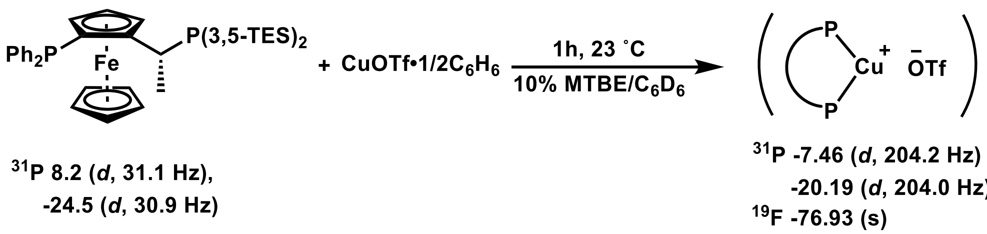


(*E*)-4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhex-5-en-1-yl pivalate (**2c**)**:** In a nitrogen filled glovebox, a 20 mL vial was charged with a stir bar, **1b** (189 mg, 0.46 mmol, 1.0 equiv), and CH_2Cl_2 (4.6 mL, 0.1 M). KOPiv (67 mg, 0.48 mmol, 1.05 eq) and 2-nitrobenzenesulfonylhydrazide (200 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).

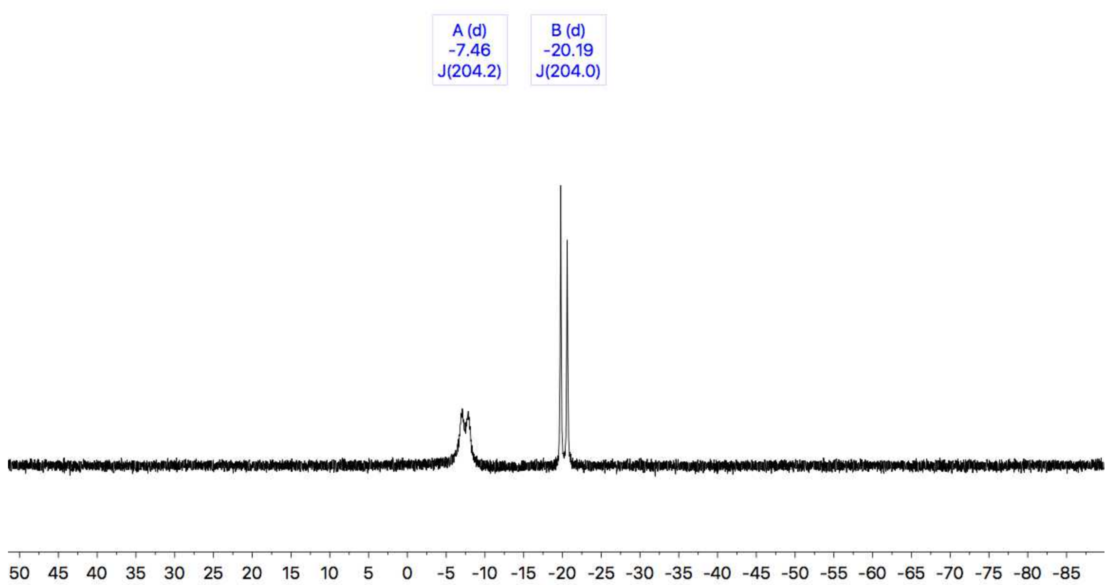
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.1 Hz, 2H), 7.38–7.31 (m, 8H), 5.20 (dd, *J* = 22.9, 12.7 Hz, 1H), 3.96 (t, *J* = 6.3 Hz, 2H), 2.04 (t, *J* = 12.2 Hz, 1H), 1.84–1.77 (m, 1H), 1.65–1.59 (m, 1H), 1.53–1.44 (m, 1H), 1.34–1.28 (m, 1H), 1.16 (s, 9H), 0.32 (d, *J* = 16.7 Hz, 6H).
^{19}**F 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)

7) Preliminary NMR Studies

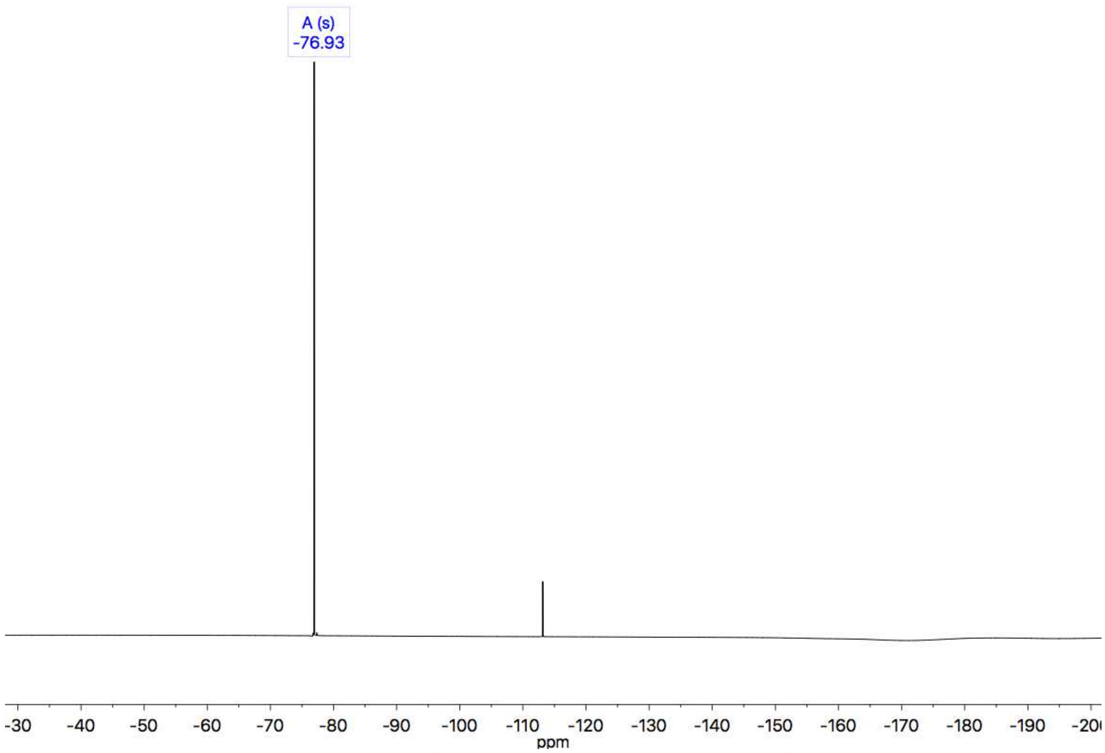
Formation of LCuOTf and LCu(^{t}BuCN)$_n$OTf:



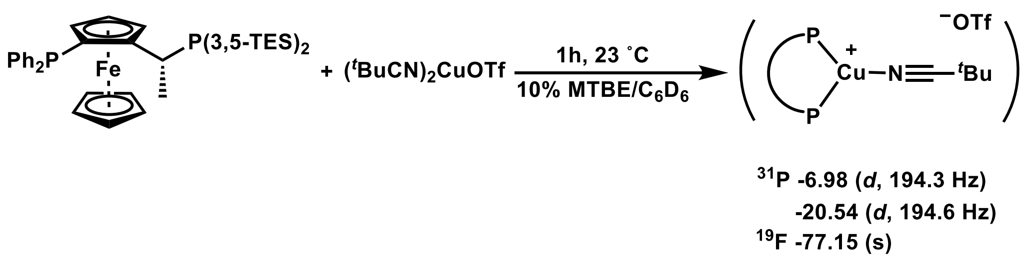
In a nitrogen filled glovebox, CuOTf·0.5C_6H_6 (7.0 mg, 0.028 mmol, 1 equiv) and a 20% MTBE/C_6D_6 solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (280 μL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 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.



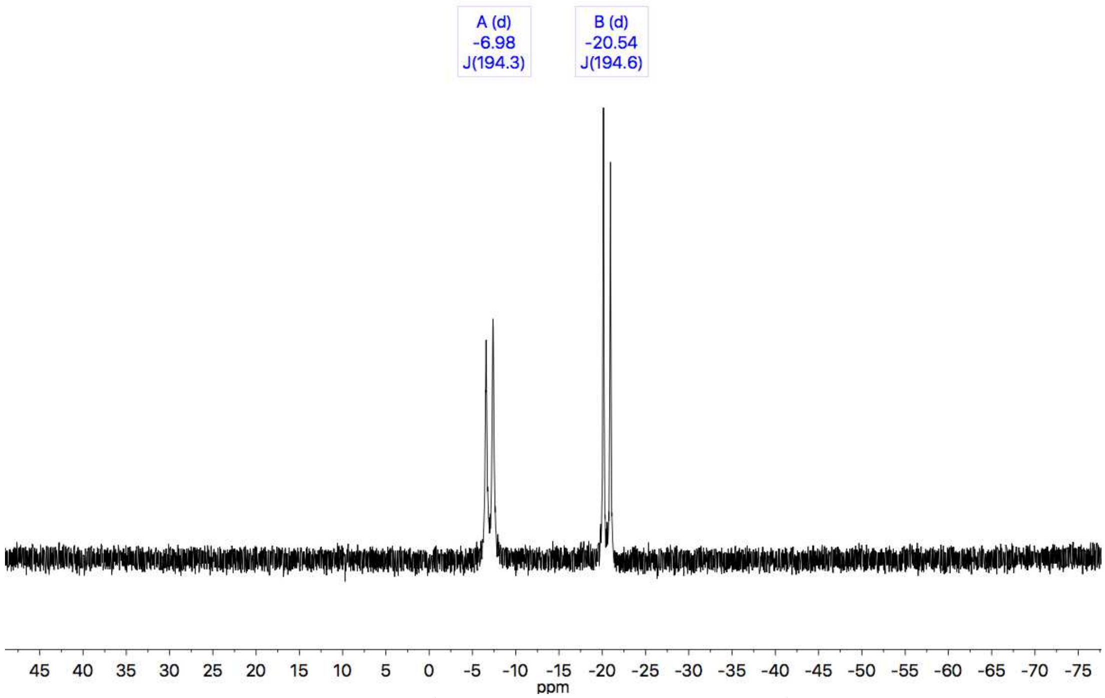
^{31}**P NMR** (243 MHz, 10% MTBE/C_6D_6)



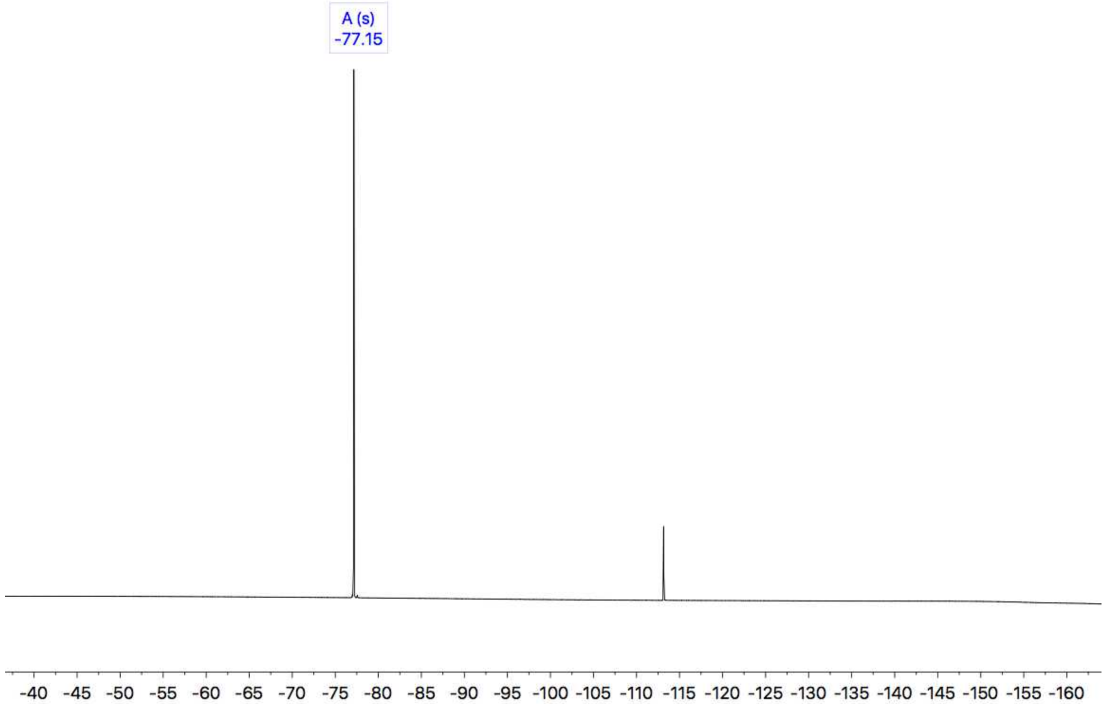
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



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.



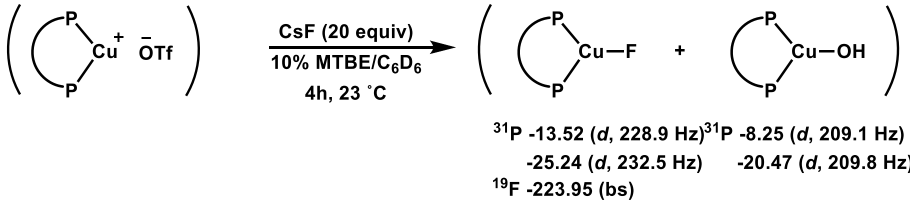
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

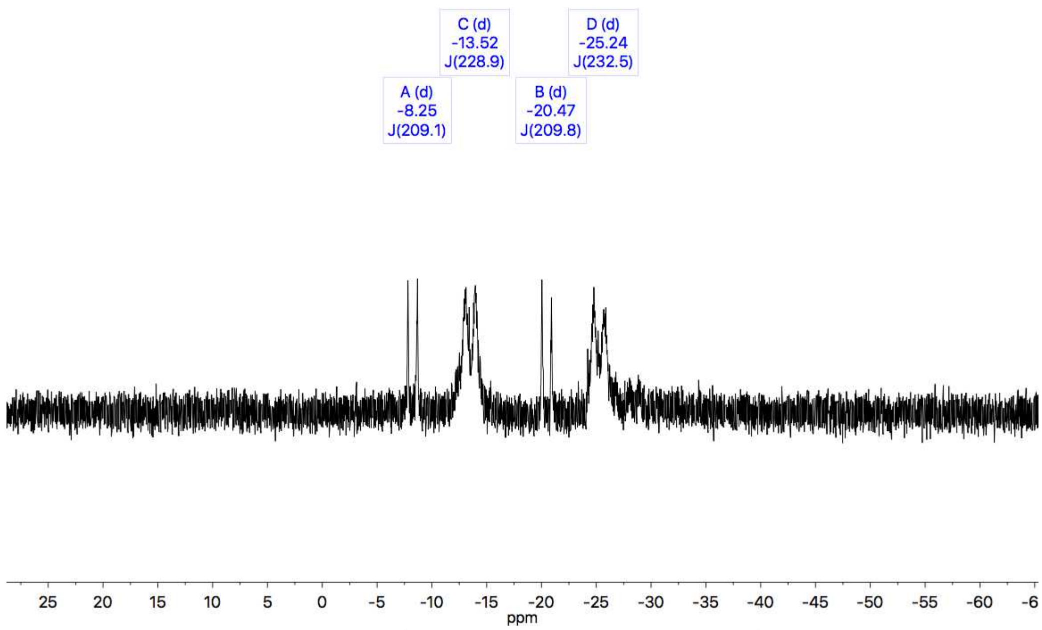


^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

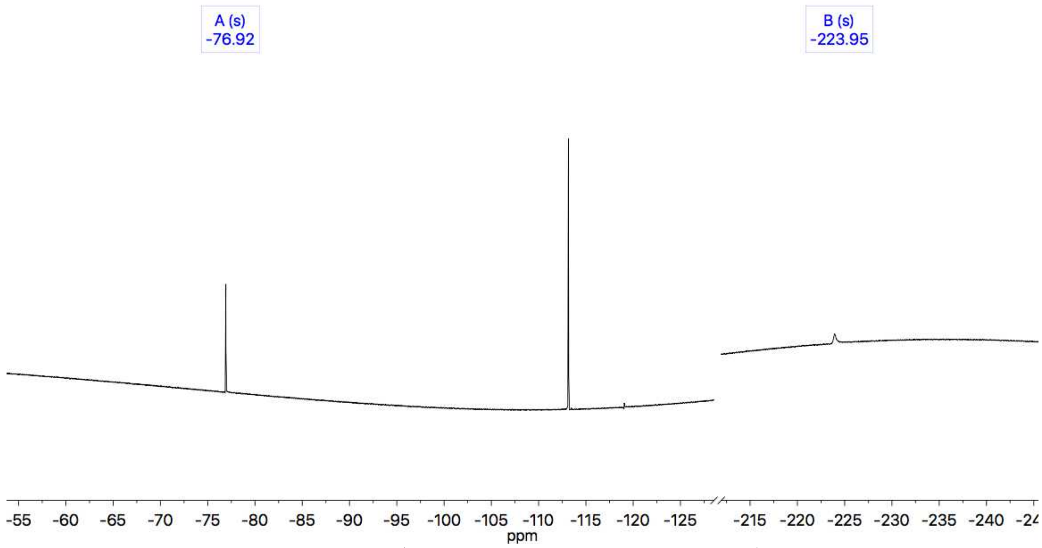
Formation of [LCuF] from LCuOTf and LCu(^{t}BuCN)$_n$OTf:

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.

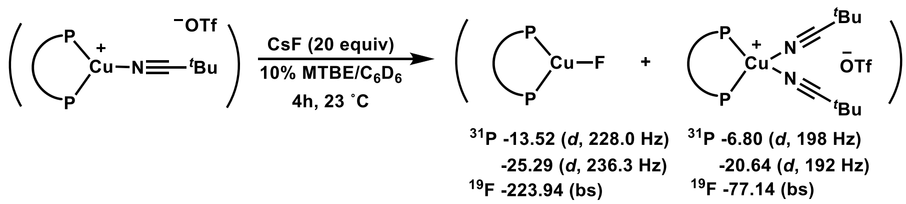


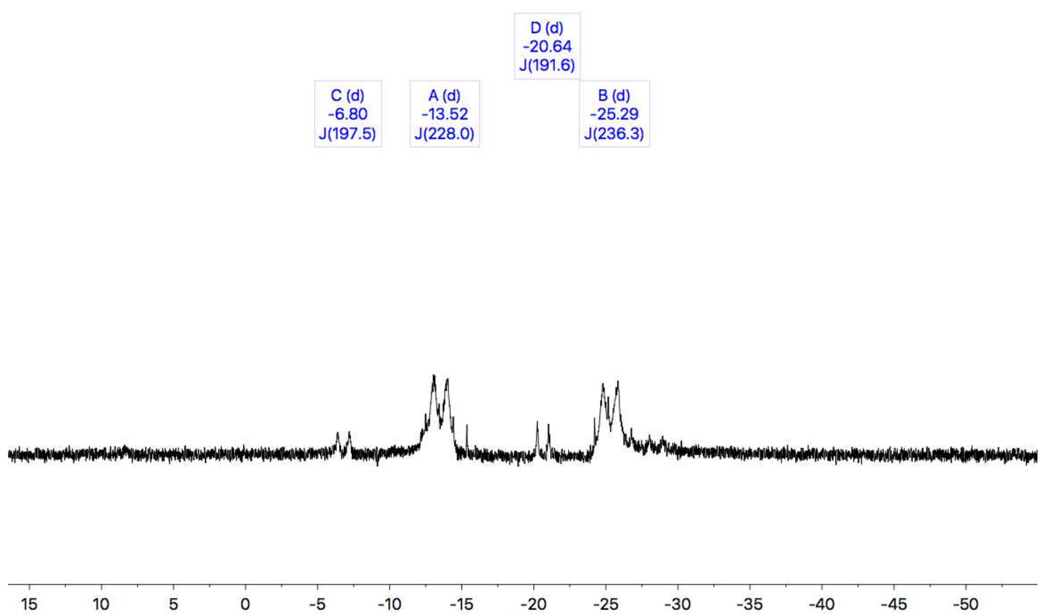


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

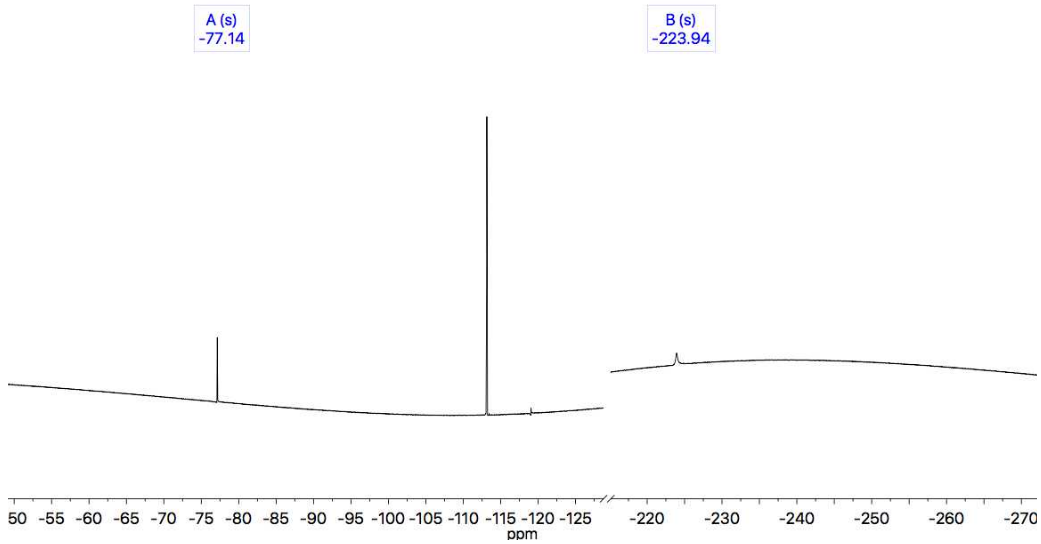


^{19}**F NMR** (565 MHz, 10% MTBE/C_6D_6)





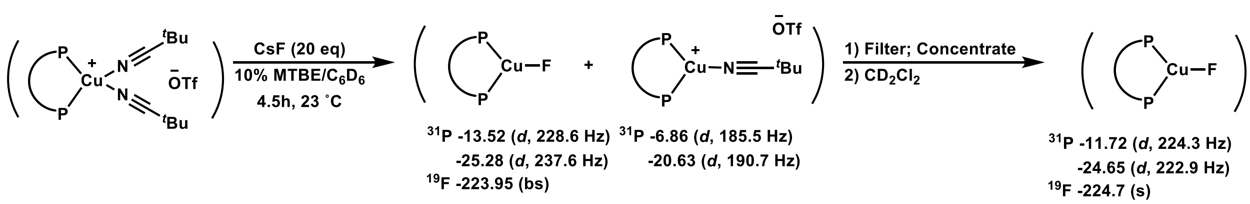
^{31}**P NMR** (243 MHz, 10% MTBE/C_6D_6)

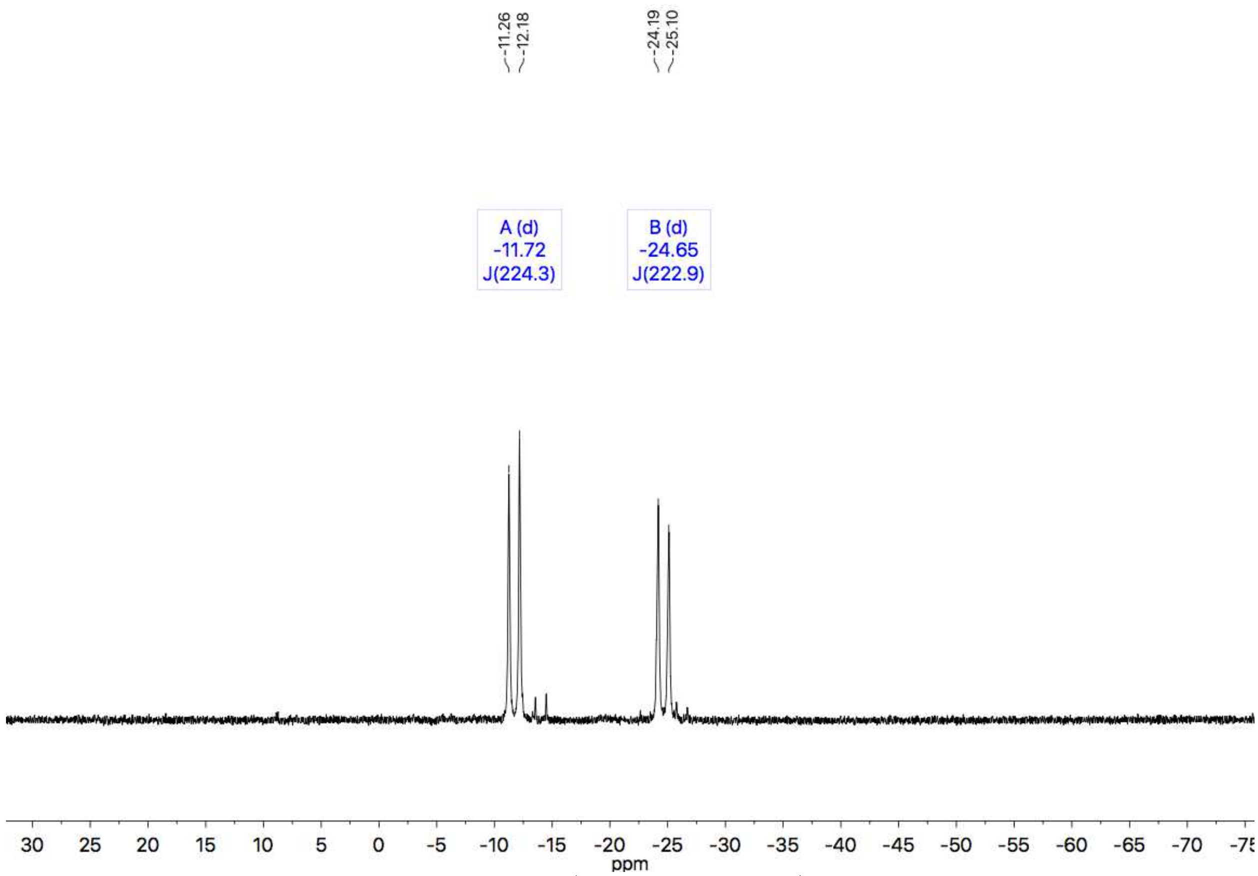


^{19} **F NMR** (565 MHz, 10% MTBE/C_6D_6)

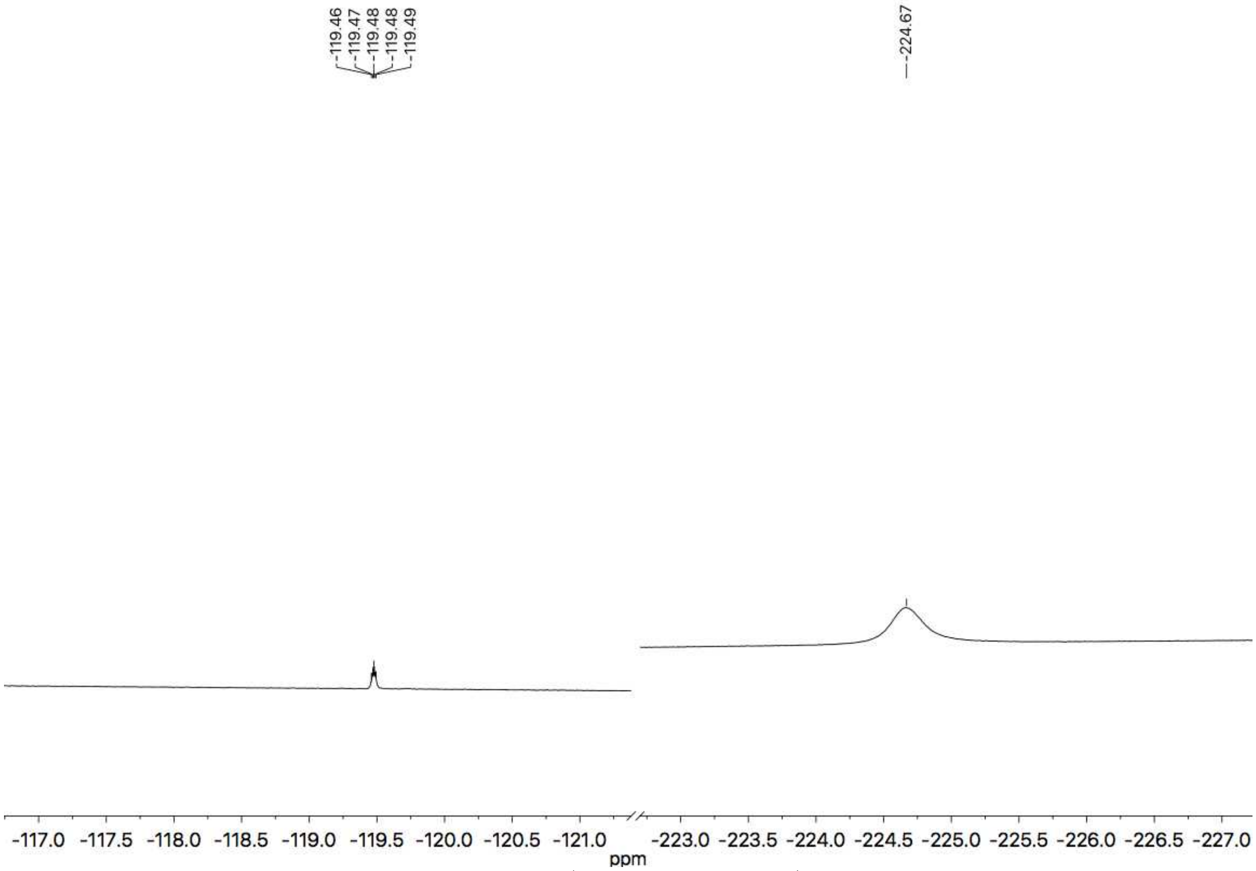
[LCuF] Speciation: Solvent Dependence

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, 0.56 mmol, 20 equiv) was added. The mixture was vigorously stirred (10/10 stir setting on an ika stirring plate) 4 hours. The slurry was filtered and concentrated inside the glovebox. The orange foam (30 mg) was redissolved in CD_2Cl_2 (500 μL), transferred to a J-Young NMR tube, and analyzed by NMR.

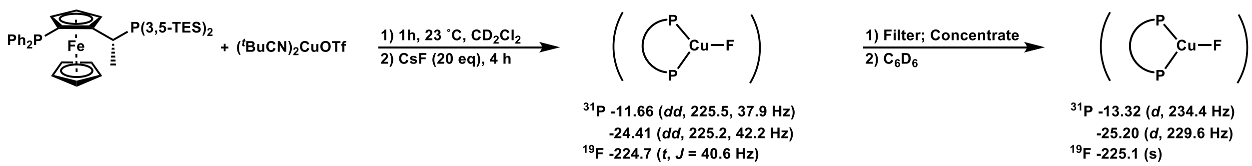




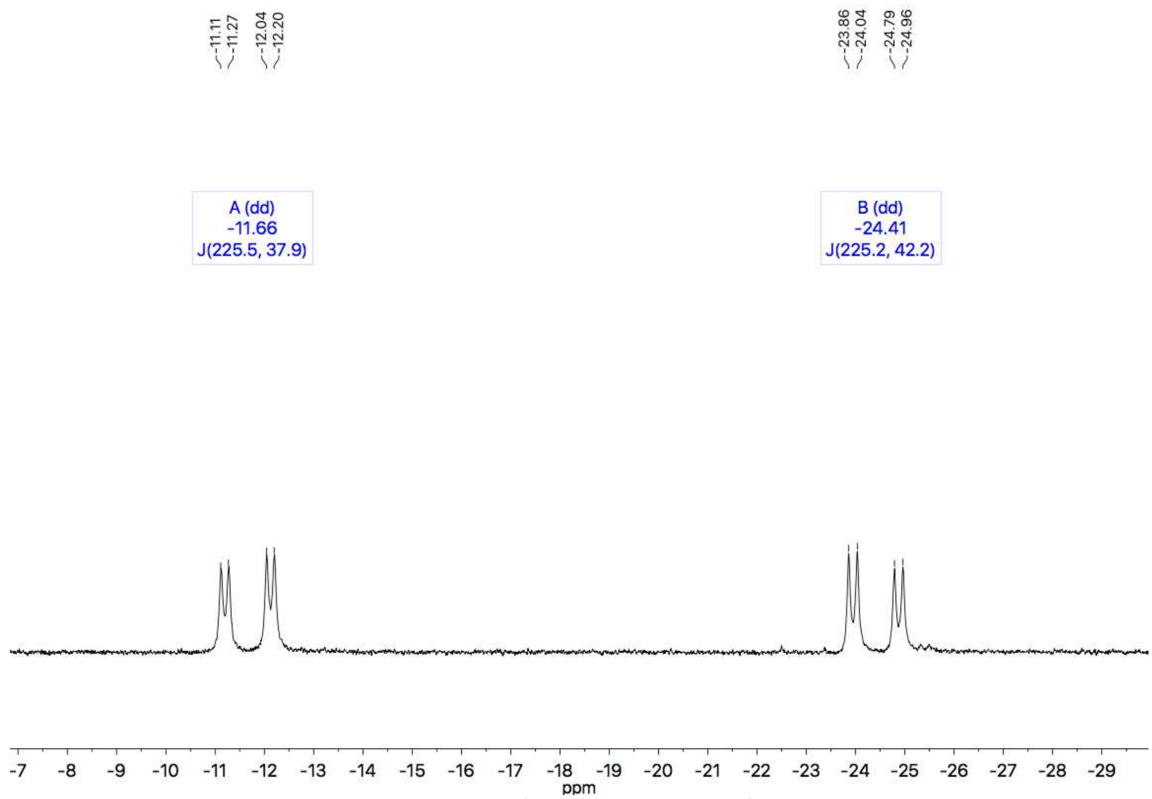
^{31}P NMR (243 MHz, CD_2Cl_2)



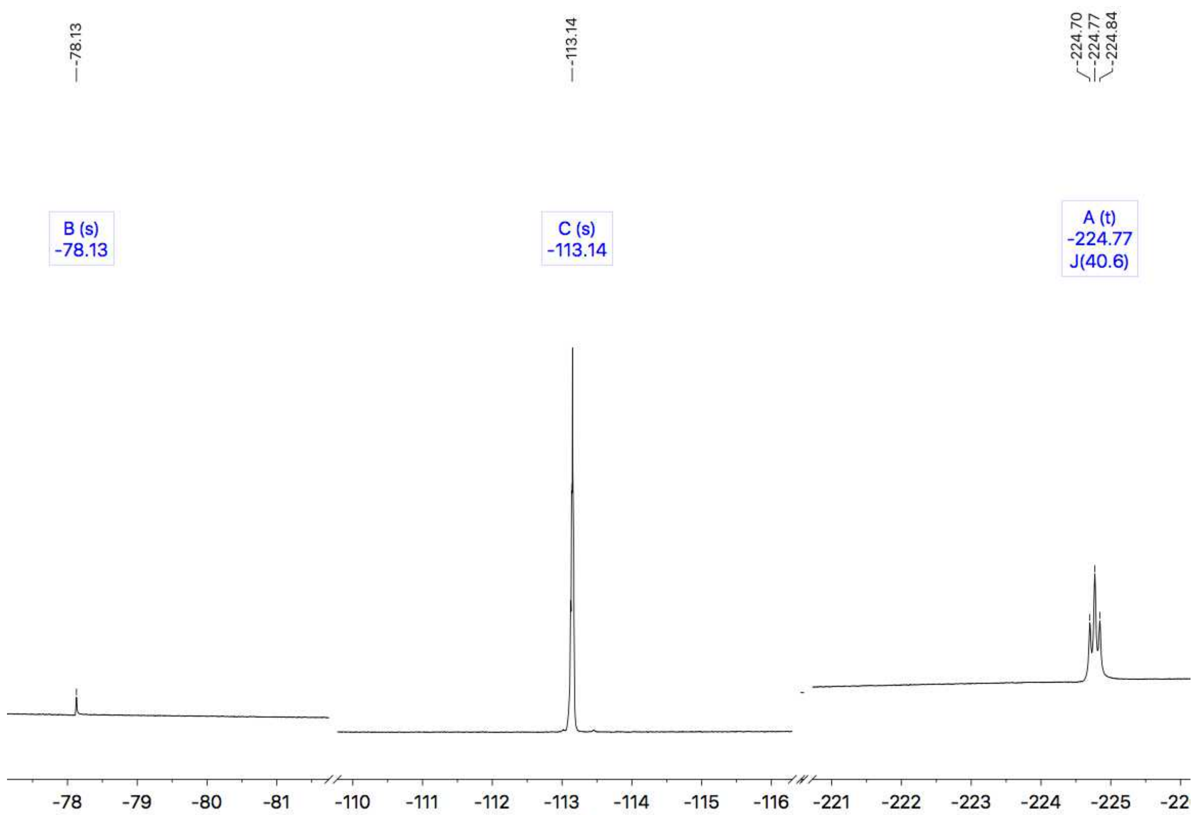
^{19}F NMR (565 MHz, CD_2Cl_2)



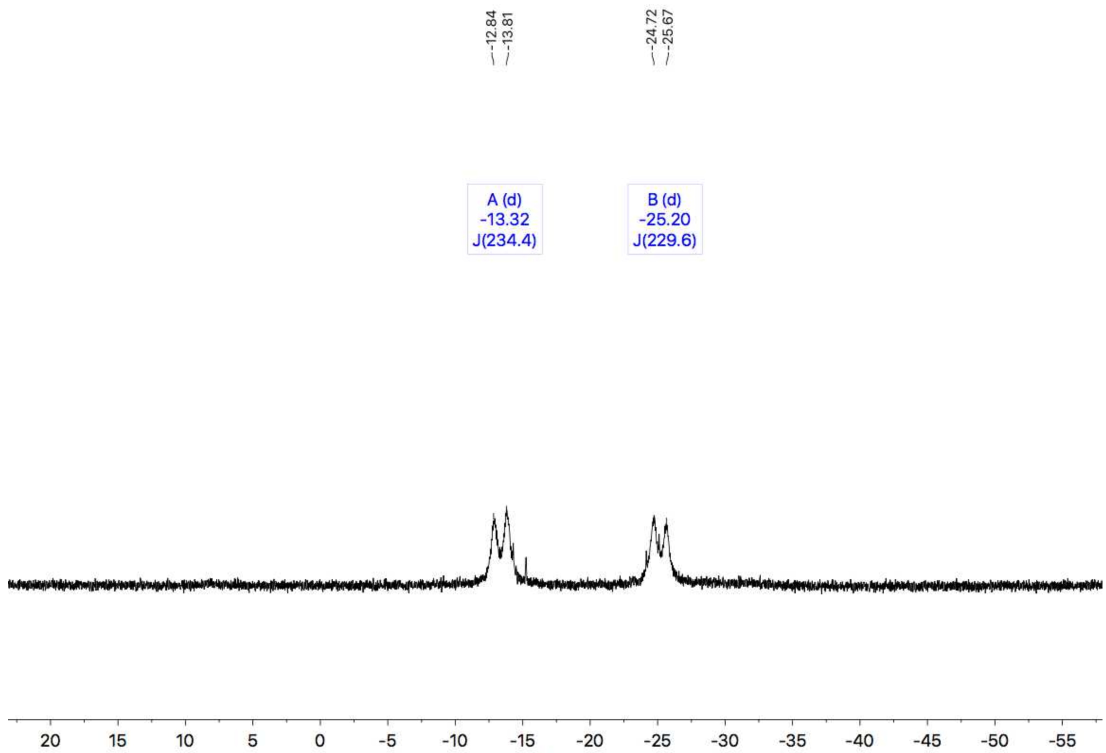
In a nitrogen filled glovebox, Cu(^{t}BuCN)$_2$OTf (10.6 mg, 0.028 mmol, 1 equiv) and a CD_2Cl_2 solution (1.3 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (280 μL (0.1 M in C_6D_6), 0.028 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, CsF (85 mg, 0.56 mmol, 20 equiv) was added. The mixture was vigorously stirred (10/10 stir setting on an ika stirring plate). After 4 hours, the solid was allowed to settle, an aliquot was transferred to a J-Young NMR tube, and the solution was analyzed by NMR. The sample was brought back inside the glovebox and the entire mixture was filtered and concentrated inside the glovebox. The orange foam (29 mg) was redissolved in C_6D_6 (500 μL), transferred to a J-Young NMR tube, and analyzed by NMR.



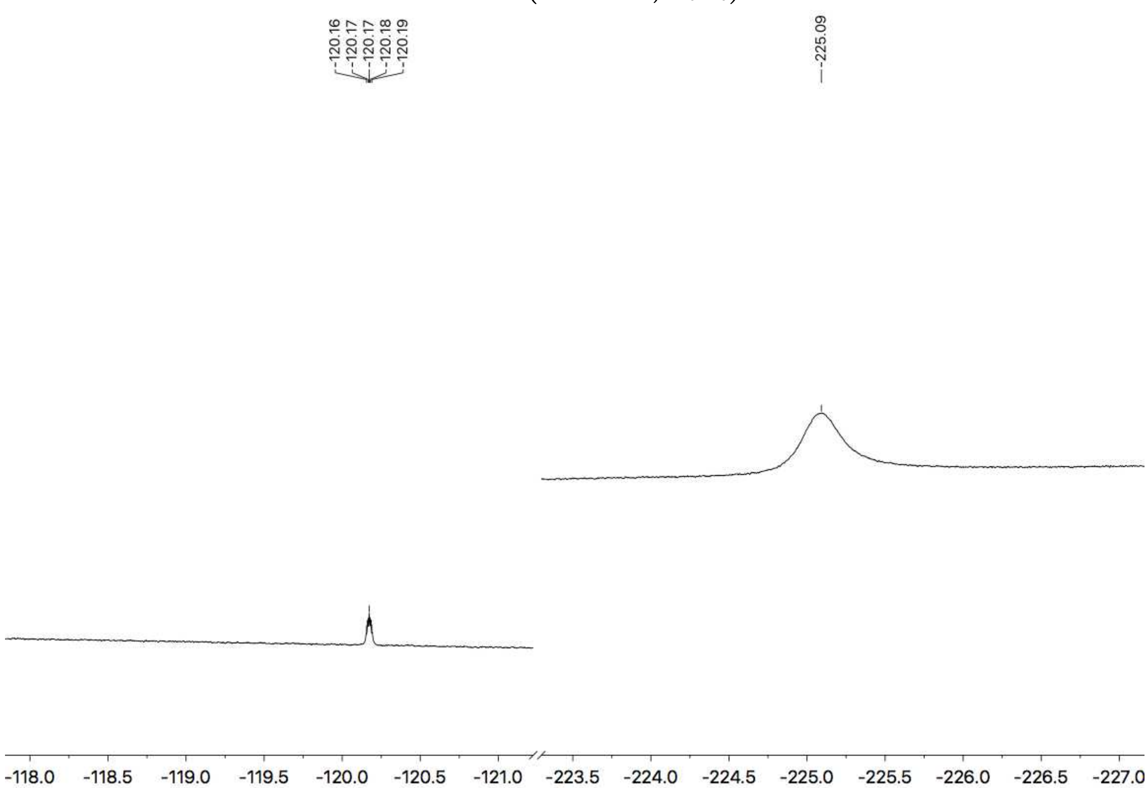
^{31}P NMR (243 MHz, CD_2Cl_2)



^{19}F NMR (565 MHz, CD_2Cl_2)



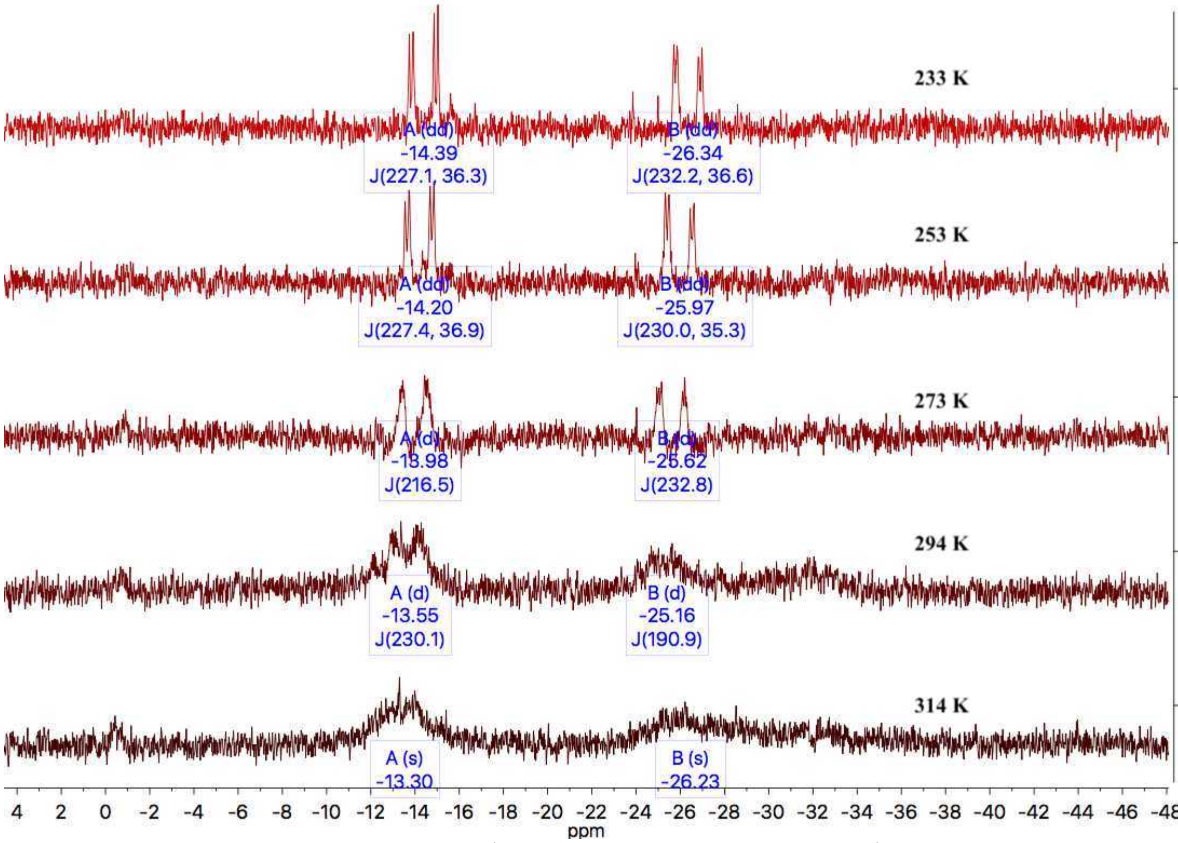
^{31}P NMR (243 MHz, C_6D_6)



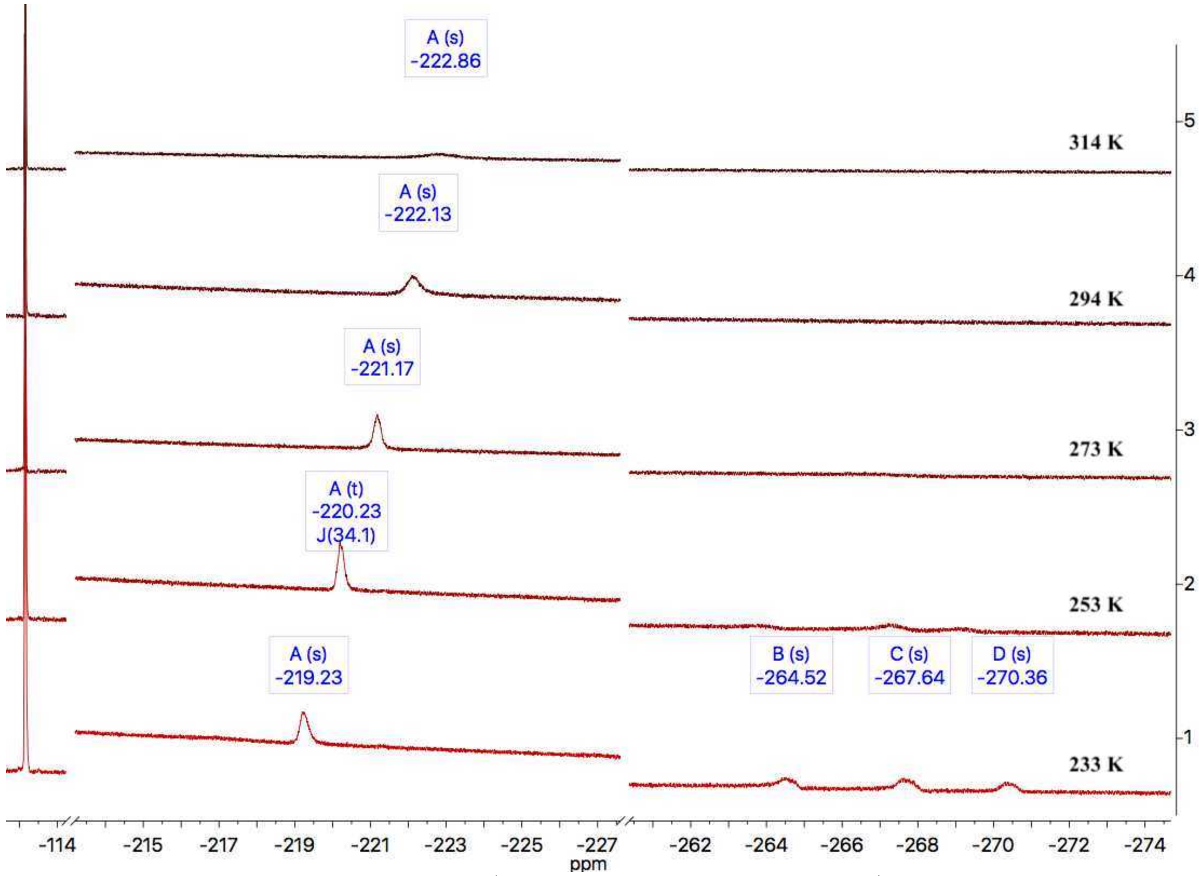
^{19}F NMR (565 MHz, C_6D_6)

[LCuF] Speciation: Temperature Dependence

In a nitrogen filled glovebox, Cu(^{t}BuCN)$_2$OTf (19.0 mg, 0.05 mmol, 1 equiv) and a 20% MTBE/PhMe$_{d8}$ solution (2.0 mL) were charged to a 1-dram vial containing a stir bar. (*R,S*)-3,5-TES-Josiphos (500 μL (0.1 M in PhMe$_{d8}$), 0.05 mmol, 1.0 equiv) was added dropwise to the stirring copper solution. After 1 h of stirring, CsF (152 mg, 1.0 mmol, 20 equiv) was added. The mixture was vigorously stirred (10/10 stir setting on an ika stirring plate). After 6 hours, the solid was allowed to settle, the mixture filter, PhF (4.7 μL, 0.05 mmol, 1 equiv) was added, an aliquot was transferred to a J-Young NMR tube, and the solution was analyzed by NMR. Acquisition began at 294 K and proceeded to 233 K. The last spectra were acquired at 314 K.



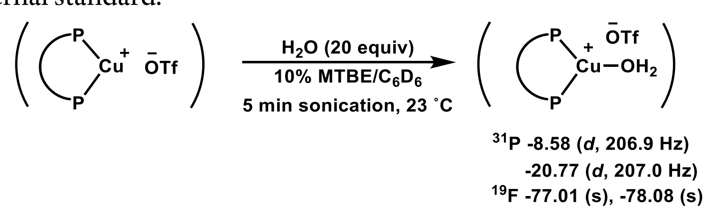
^{31}**P NMR** (202 MHz, 10% MTBE/PhMe$_{d8}$)

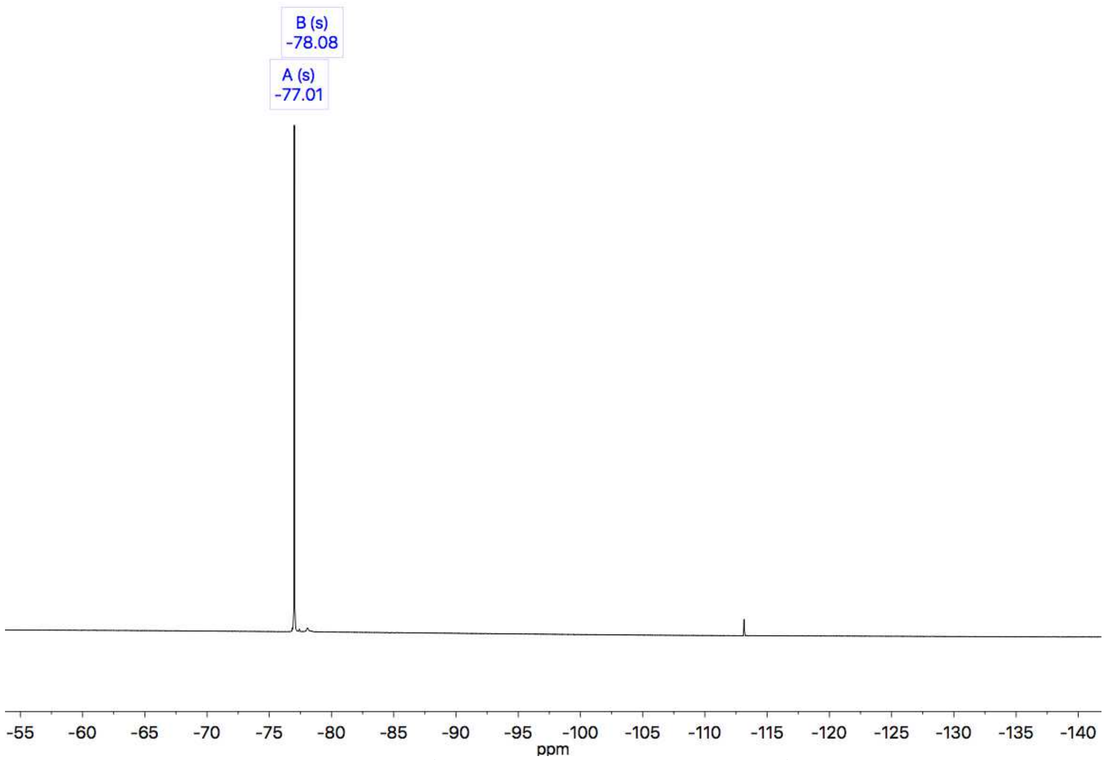


^{19}F NMR (470 MHz, 10% MTBE/PhMe$_{d8}$)

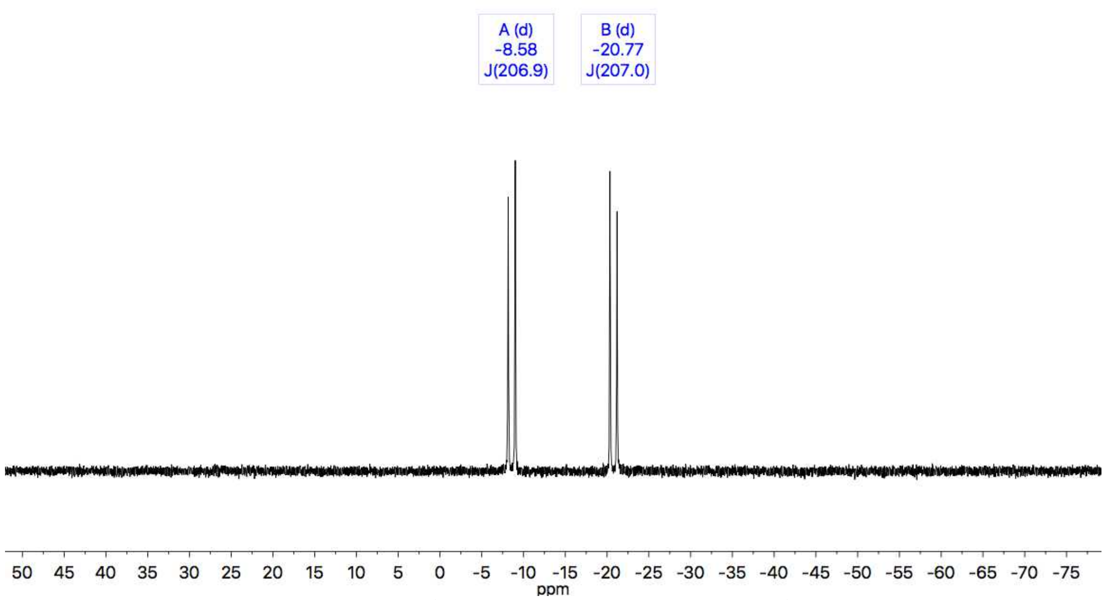
Formation of LCuOH and LCu(H_2O)OTf:

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, 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_2O (19 mg, 0.11 mmol, 8 equiv) and sonicated for 5 minutes before being analyzed. PhF was used as an internal standard.

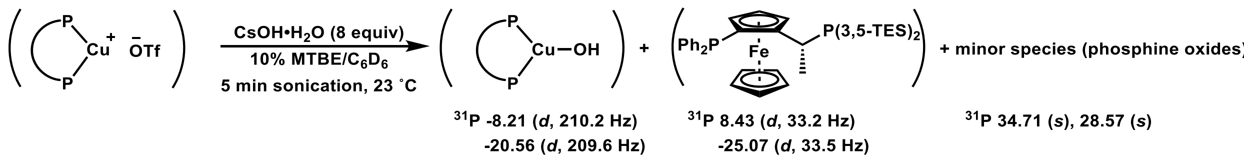


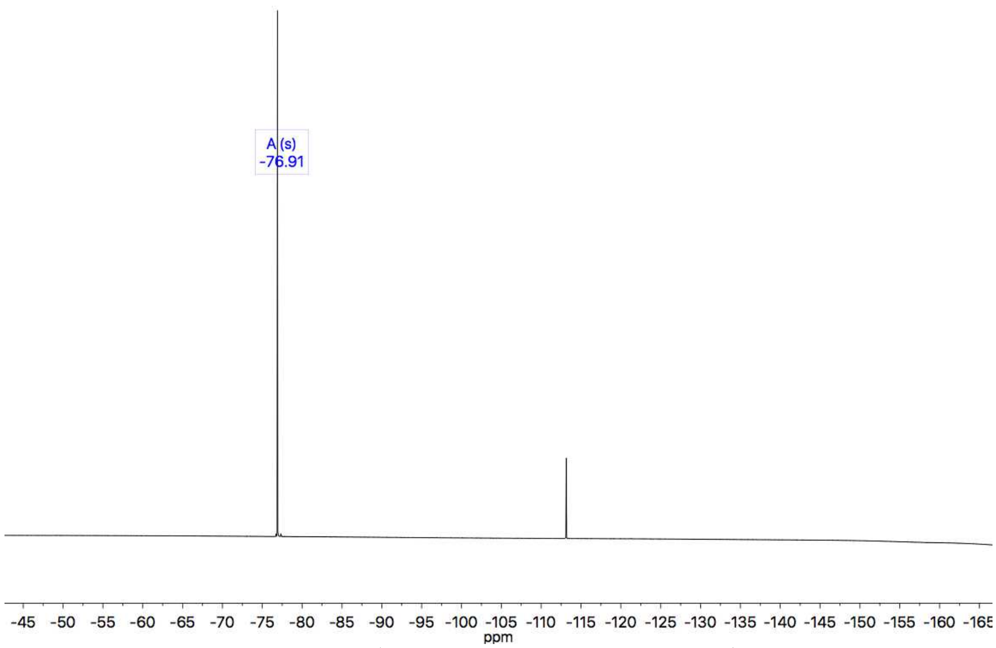


^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

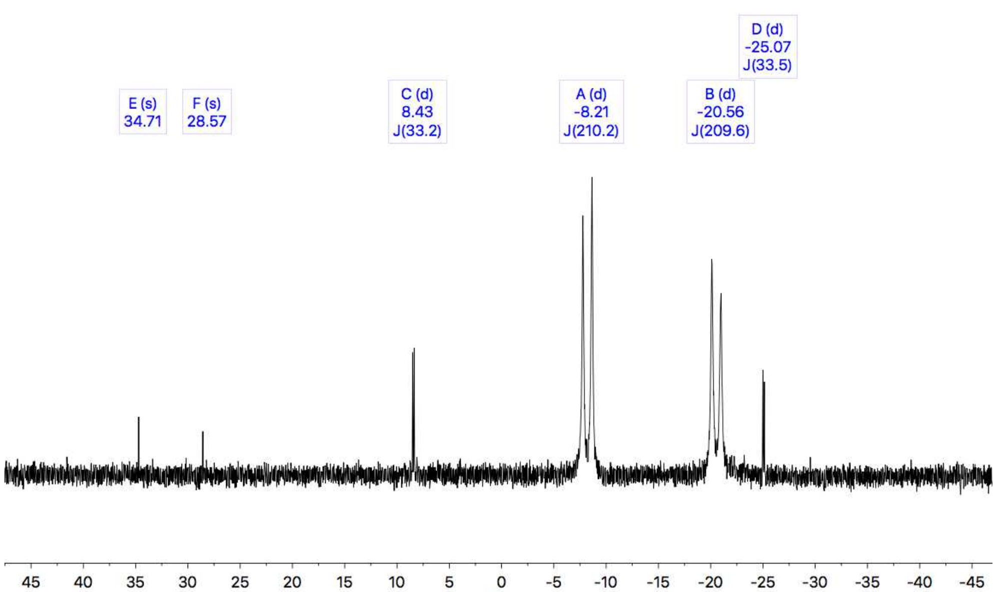


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)





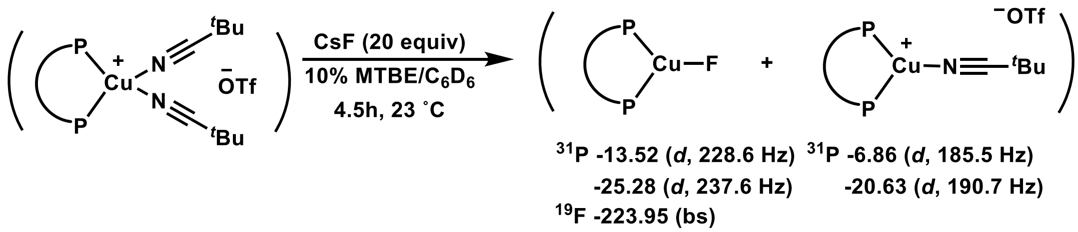
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

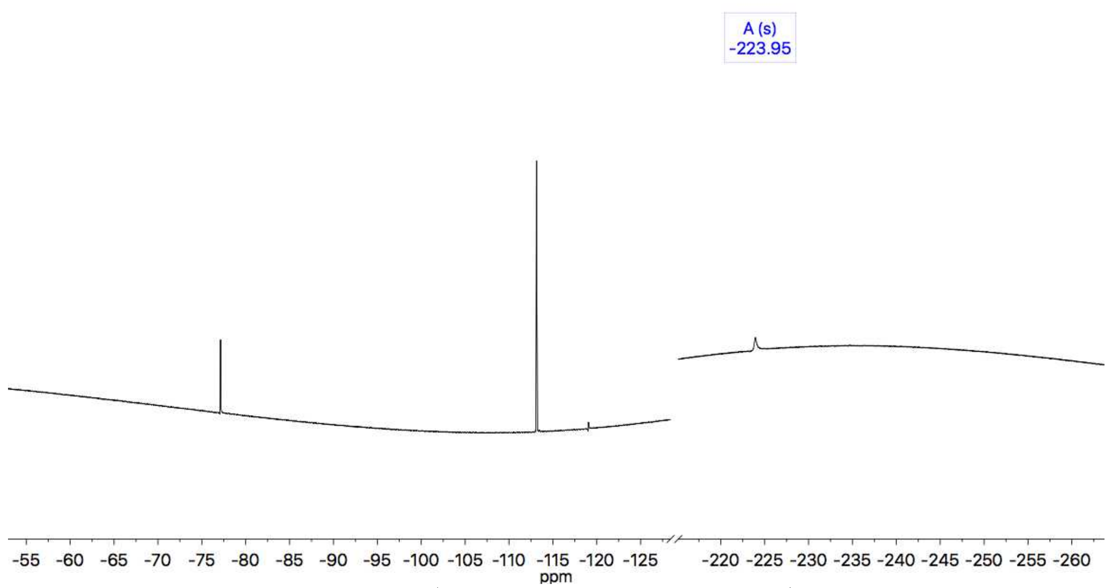


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

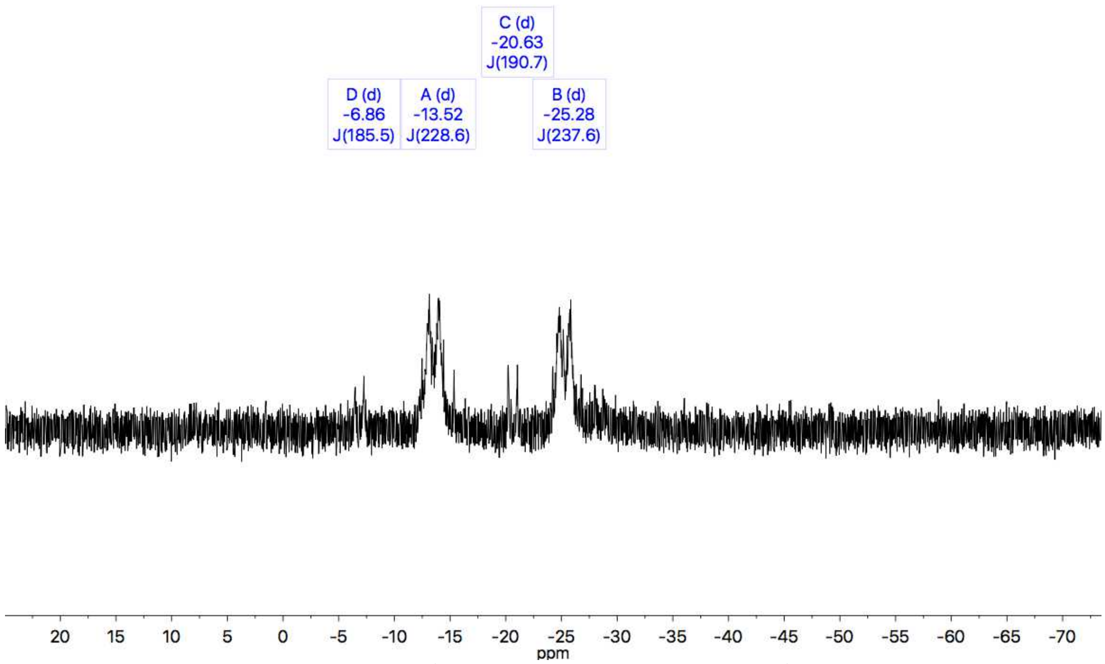
Reactivity of LCuF and $LCuSiMe_2Ph$: Generation of $LCuF_2Bpin$ FBpin

In a nitrogen filled glovebox, $Cu(^{t}BuCN)_2OTf$ (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.



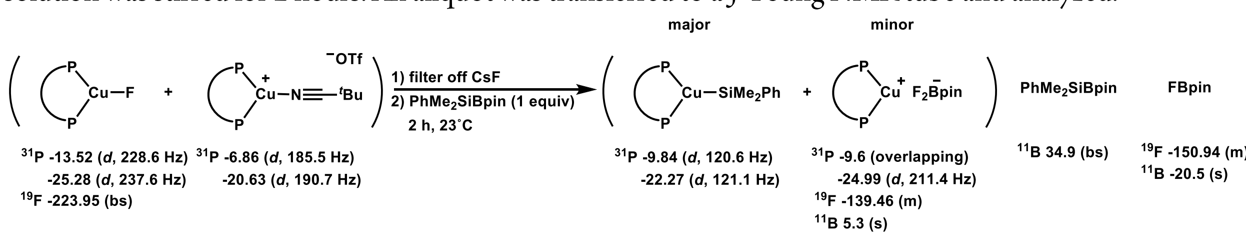


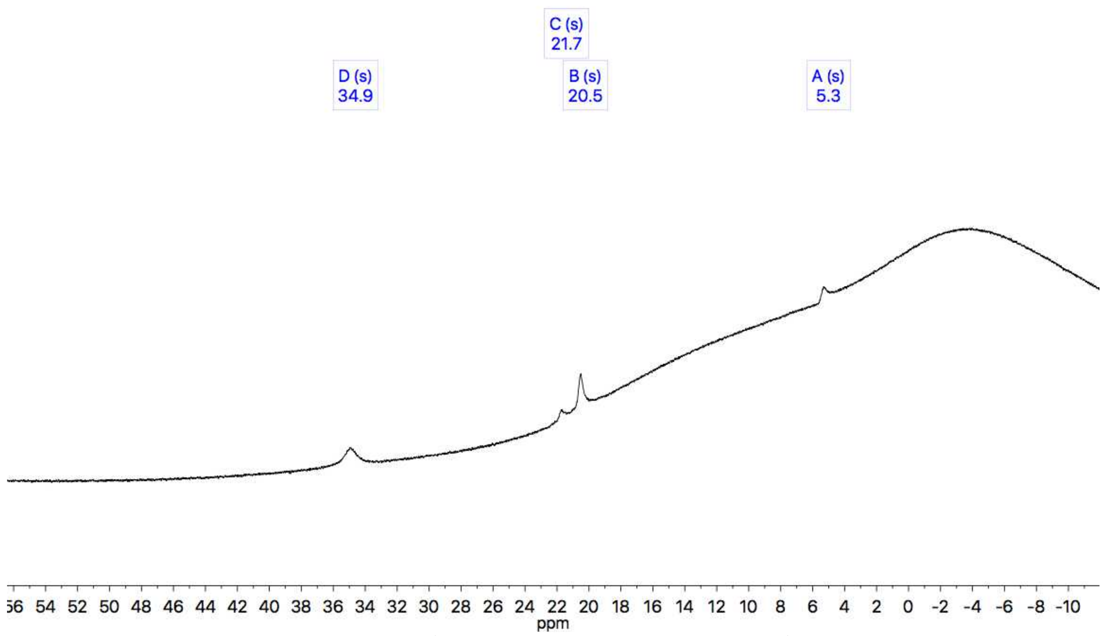
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



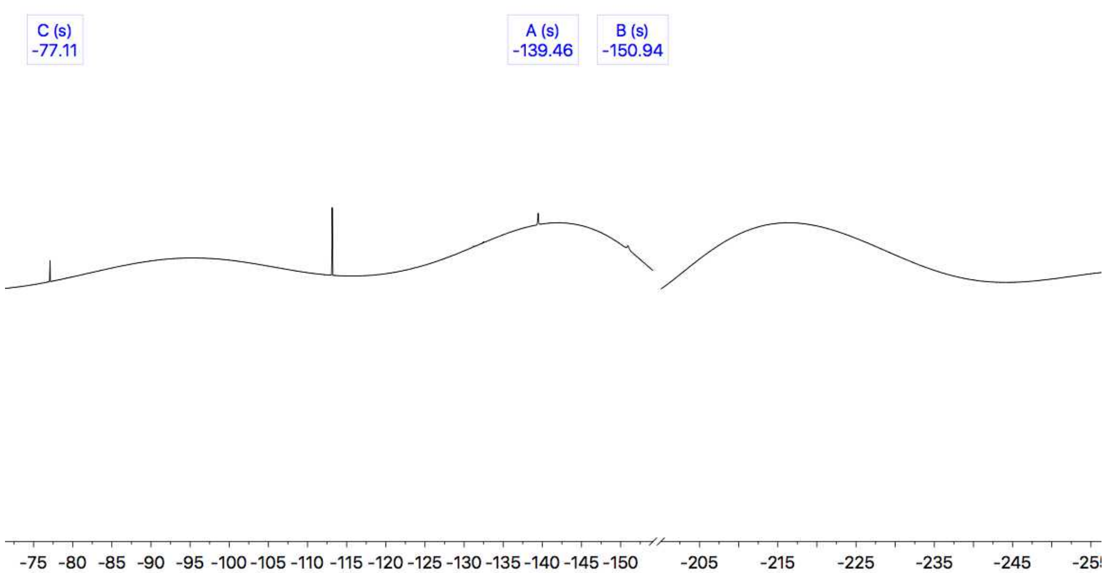
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

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.

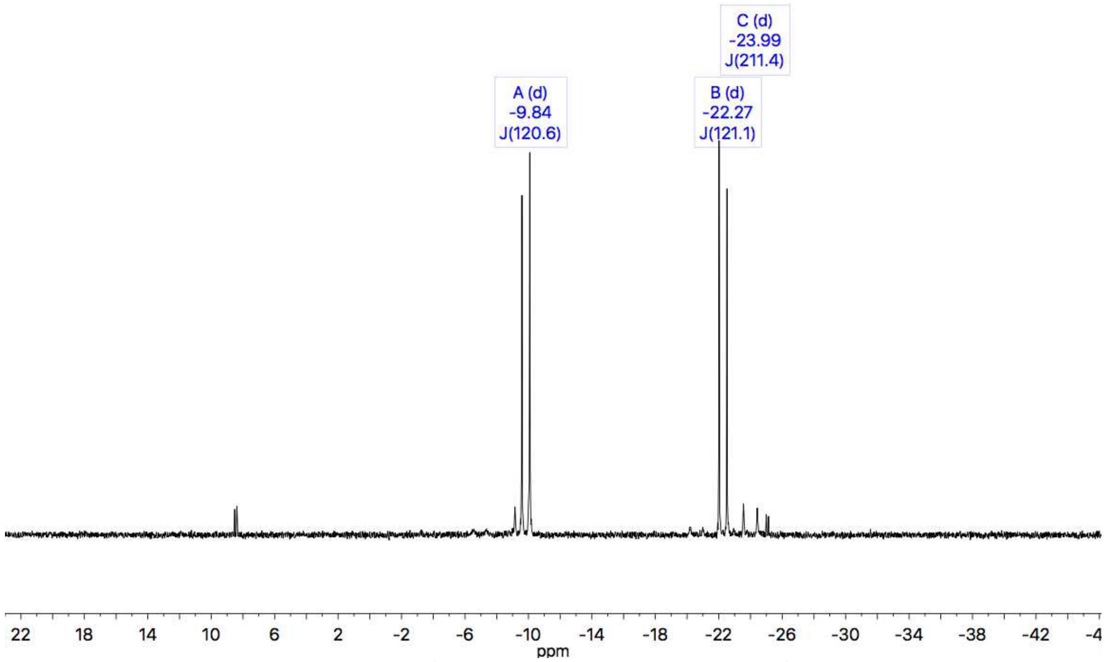




[11]B NMR (193 MHz, 10% MTBE/C_6D_6)

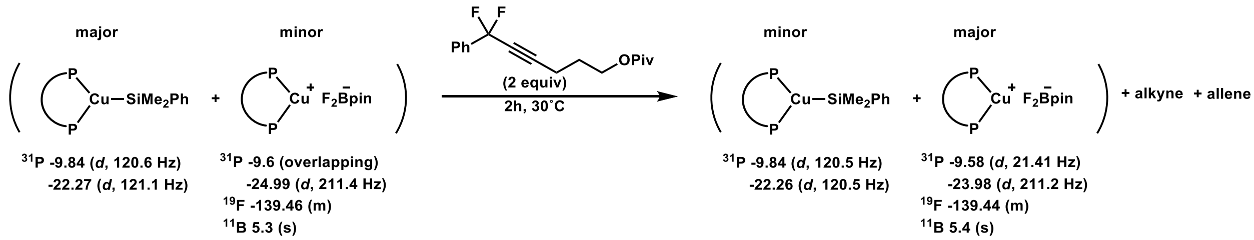


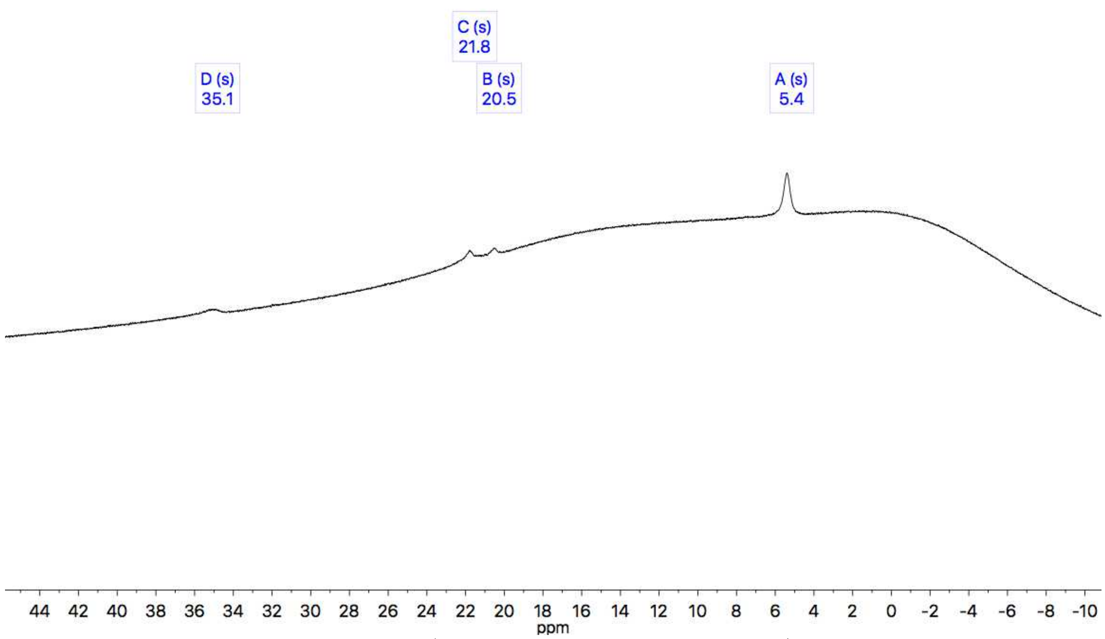
[19]F NMR (565 MHz, 10% MTBE/C_6D_6)



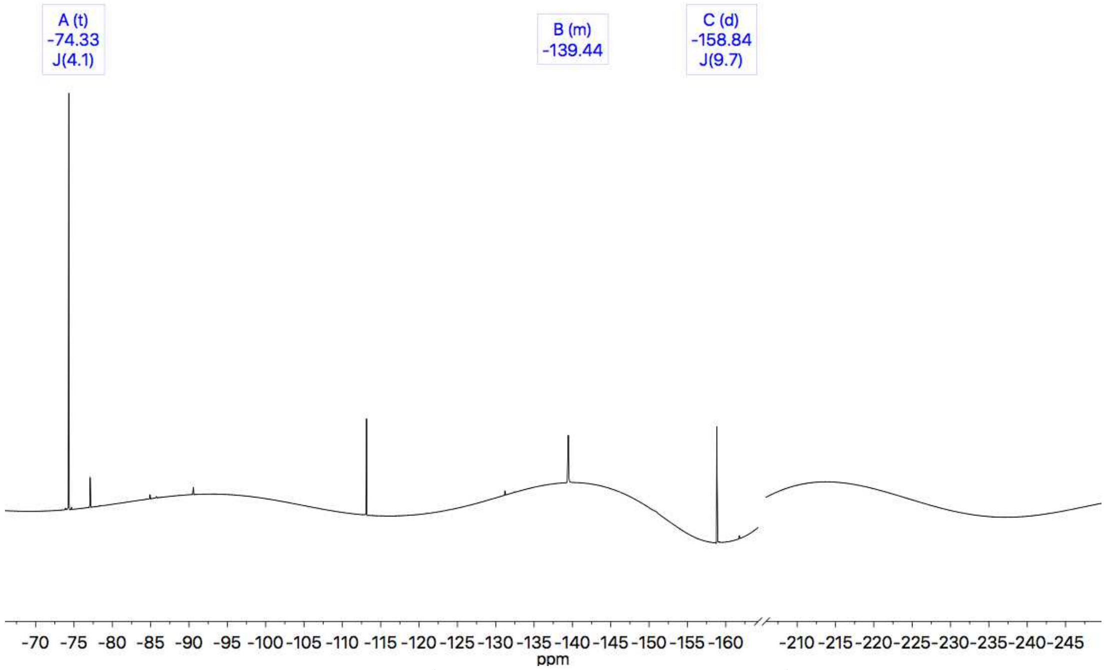
^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

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.

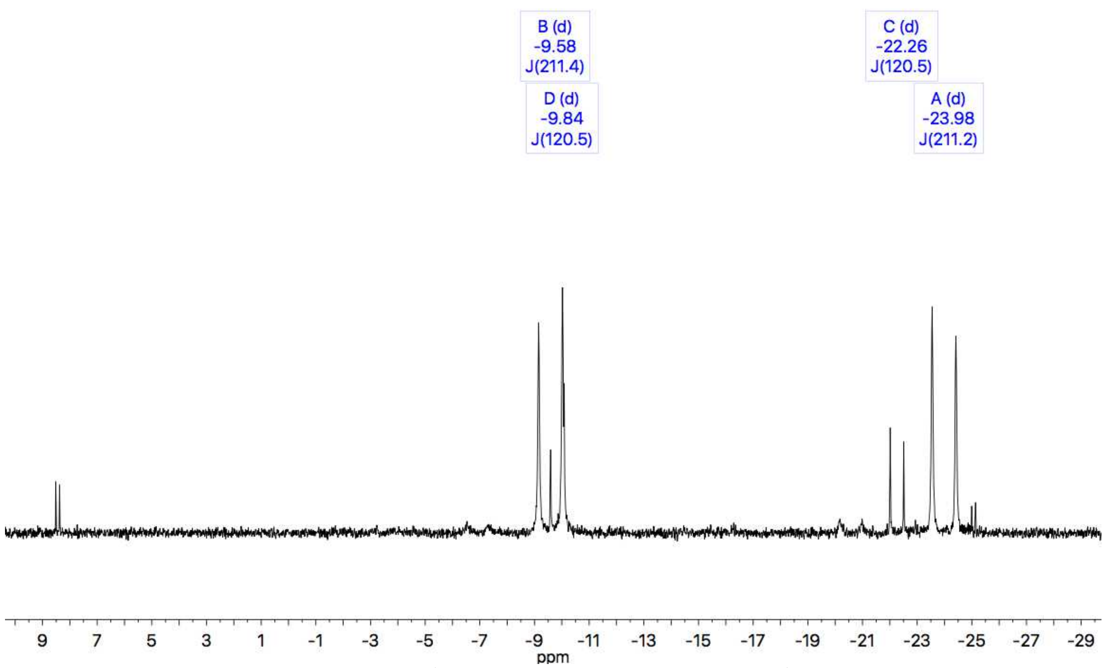




^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



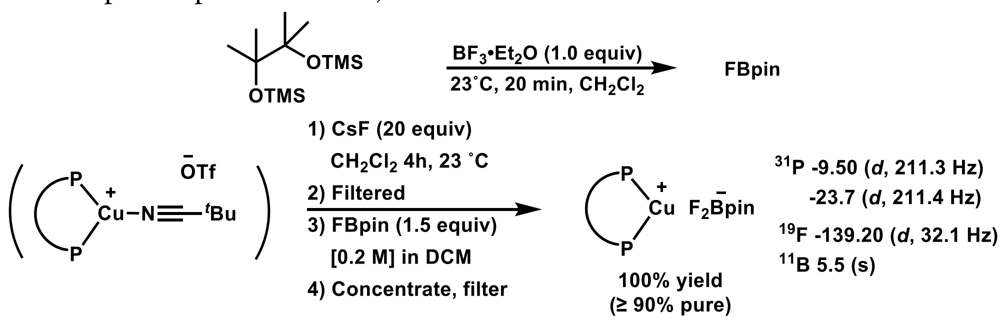
^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)

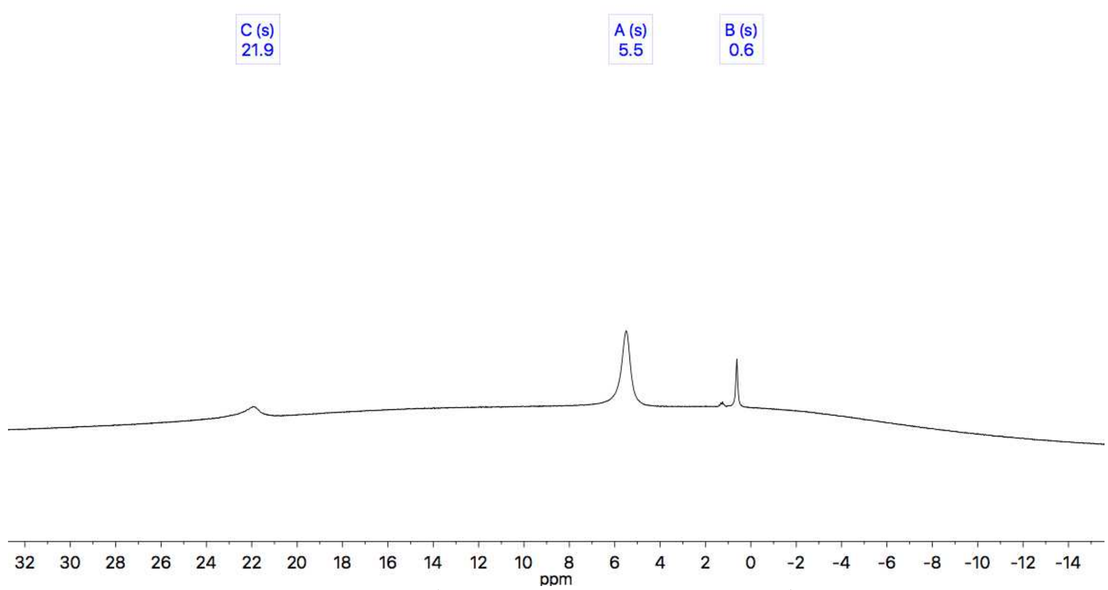


^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

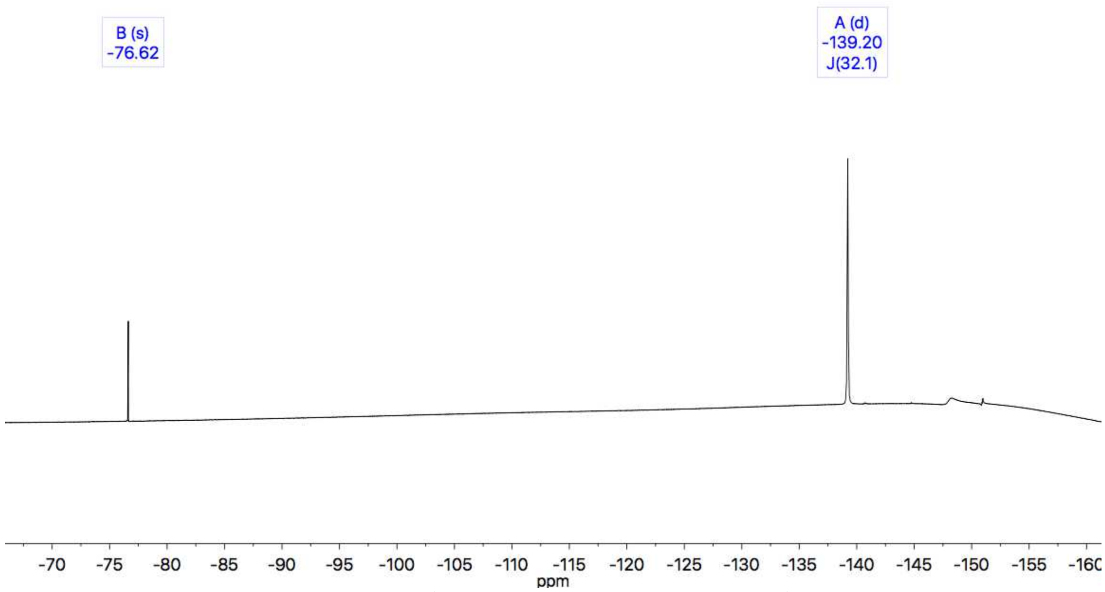
Preparation of (*R,S*)-3,5-TES-JosiphosCuF$_2$Bpin:

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 $BF_3{\cdot}Et_2O$ (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.)

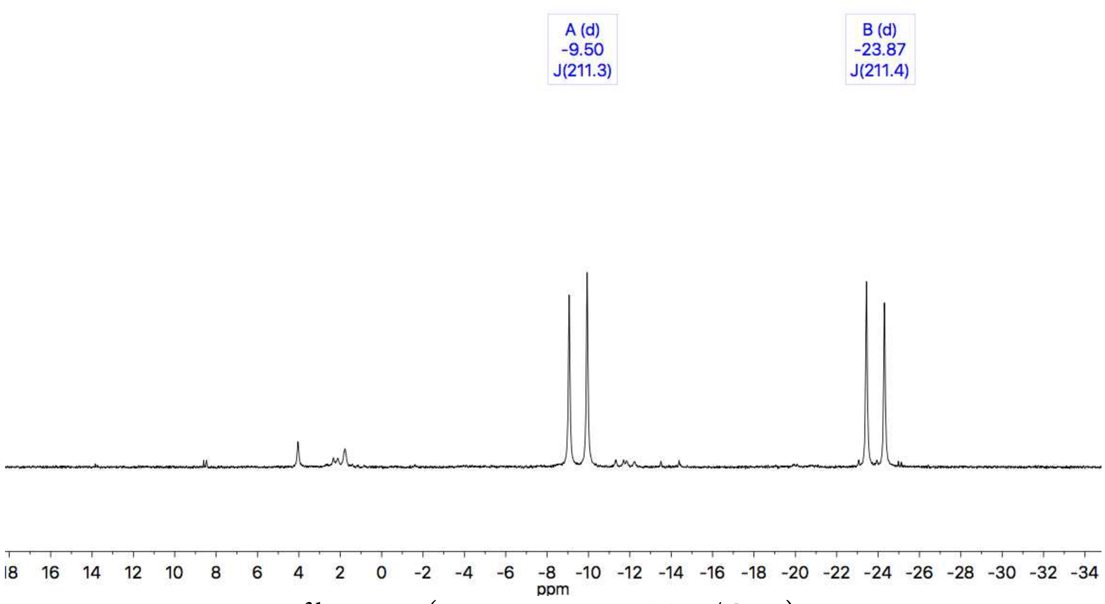




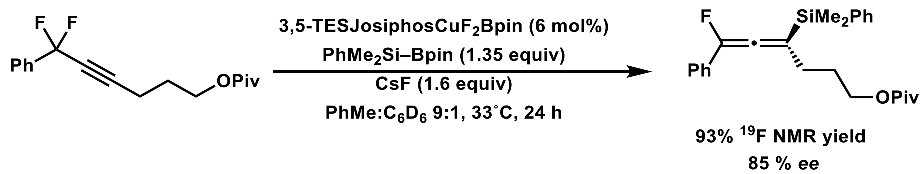
^{11}B NMR (193 MHz, 10% MTBE/C_6D_6)



^{19}F NMR (565 MHz, 10% MTBE/C_6D_6)



^{31}P NMR (243 MHz, 10% MTBE/C_6D_6)

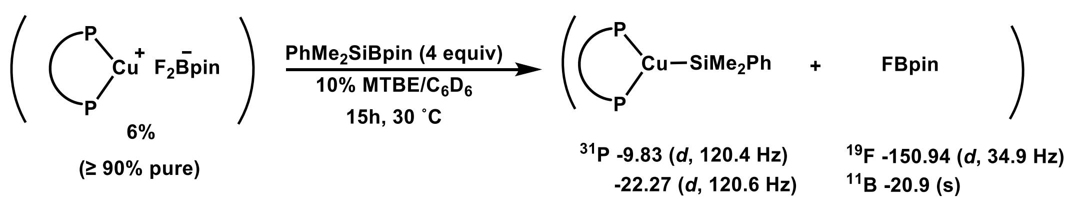


(*R,S*)-3,5-TES-JosiPhosCuF_2Bpin as a catalyst:

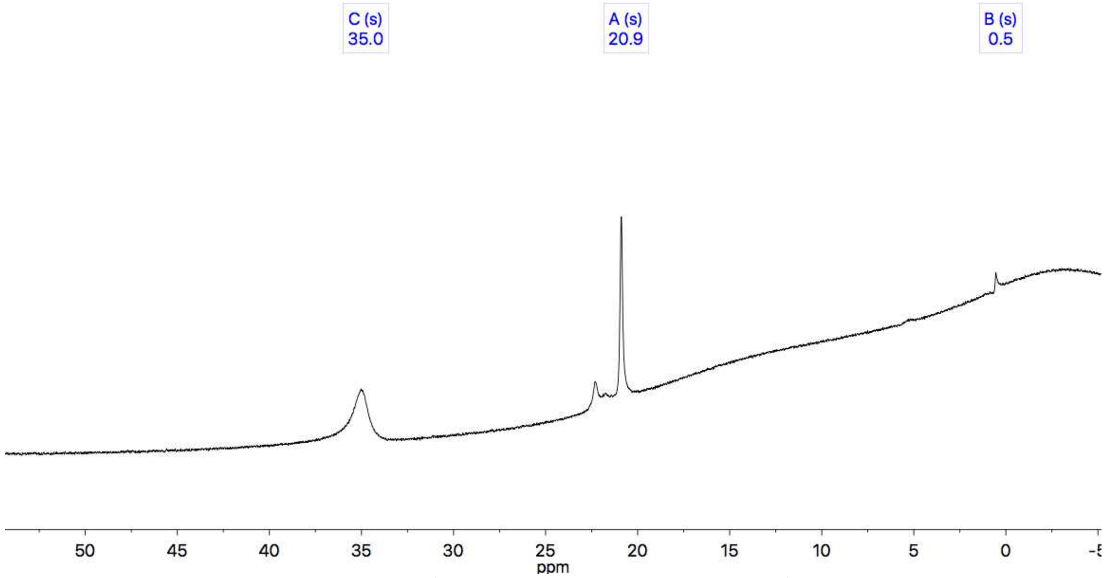
4-(dimethyl(phenyl)silyl)-6-fluoro-6-phenylhexa-4,5-dien-1-yl pivalate **(1b):**

Crude (*R,S*)-3,5-TES-JosiphosCuF_2Bpin (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.

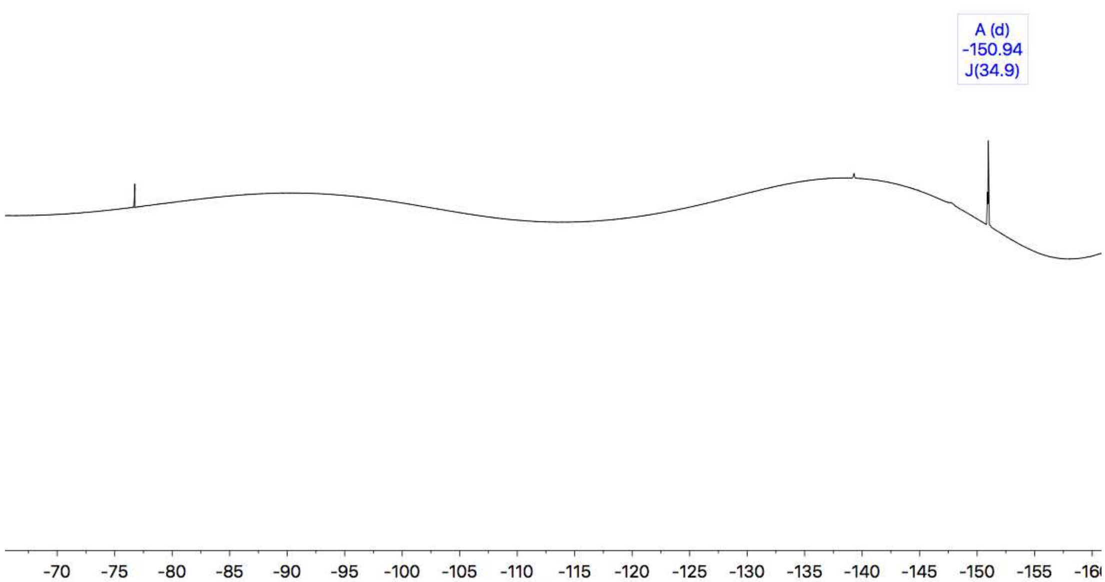
(*R,S*)-3,5-TES-JosiPhosCuF_2Bpin + $PhMe_2$SiBPin:



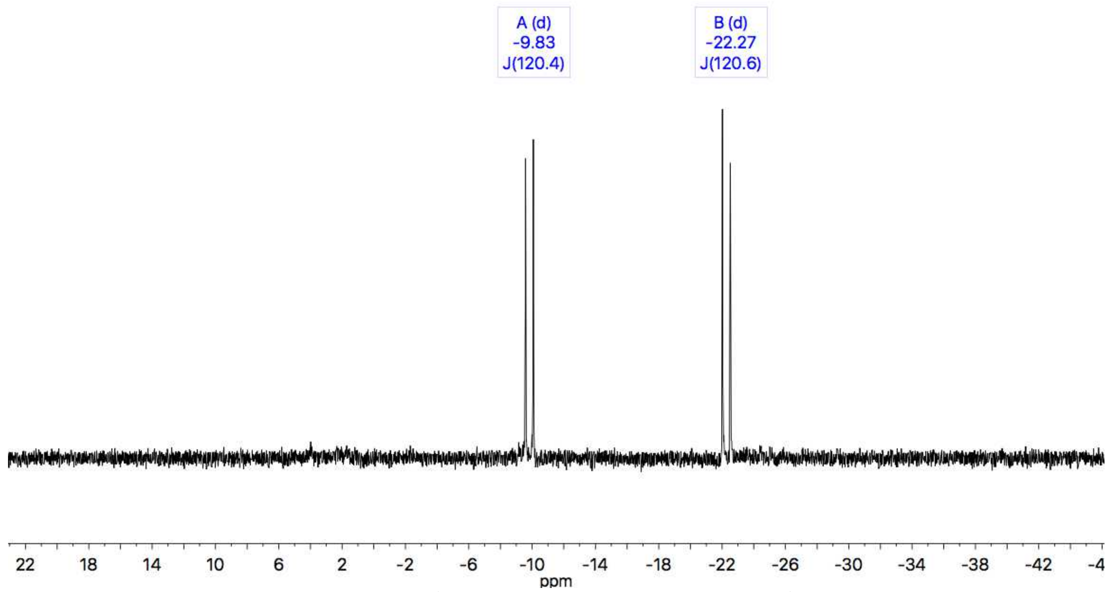
In a nitrogen filled glovebox, crude (*R,S*)-3,5-TES-JosiphosCuF_2Bpin (570 µL, 0.035 M in C_6D_6, 0.02 mmol), was diluted MTBE (150 µL) and C_6D_6 (750 µL) in a 1-dram vial with a stir bar. $PhMe_2$SiBpin (21 µL, 0.08 mmol, 4.0 equiv) was added, the vial sealed, and heated at 30 °C in the glovebox. 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)



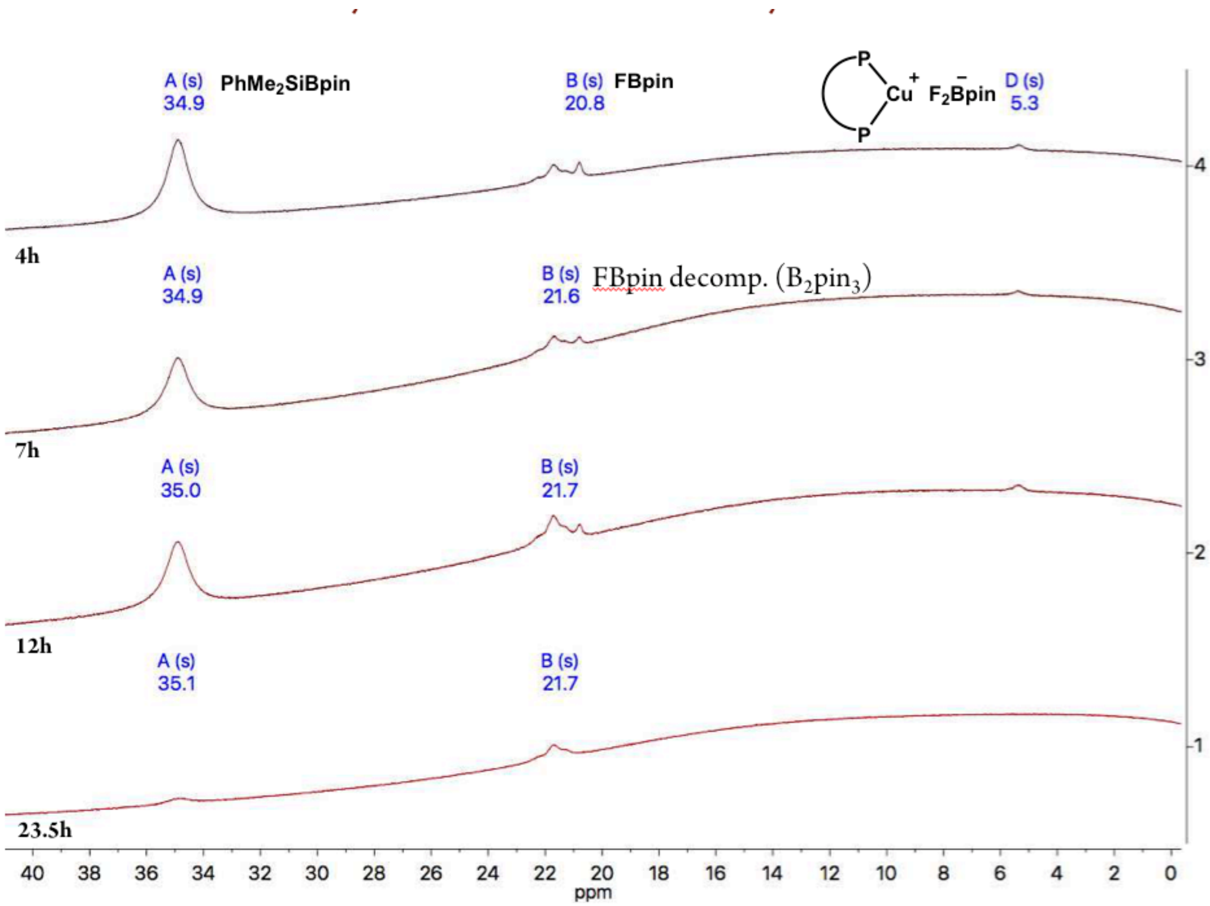
[19]F NMR (565 MHz, 10% MTBE/C_6D_6)



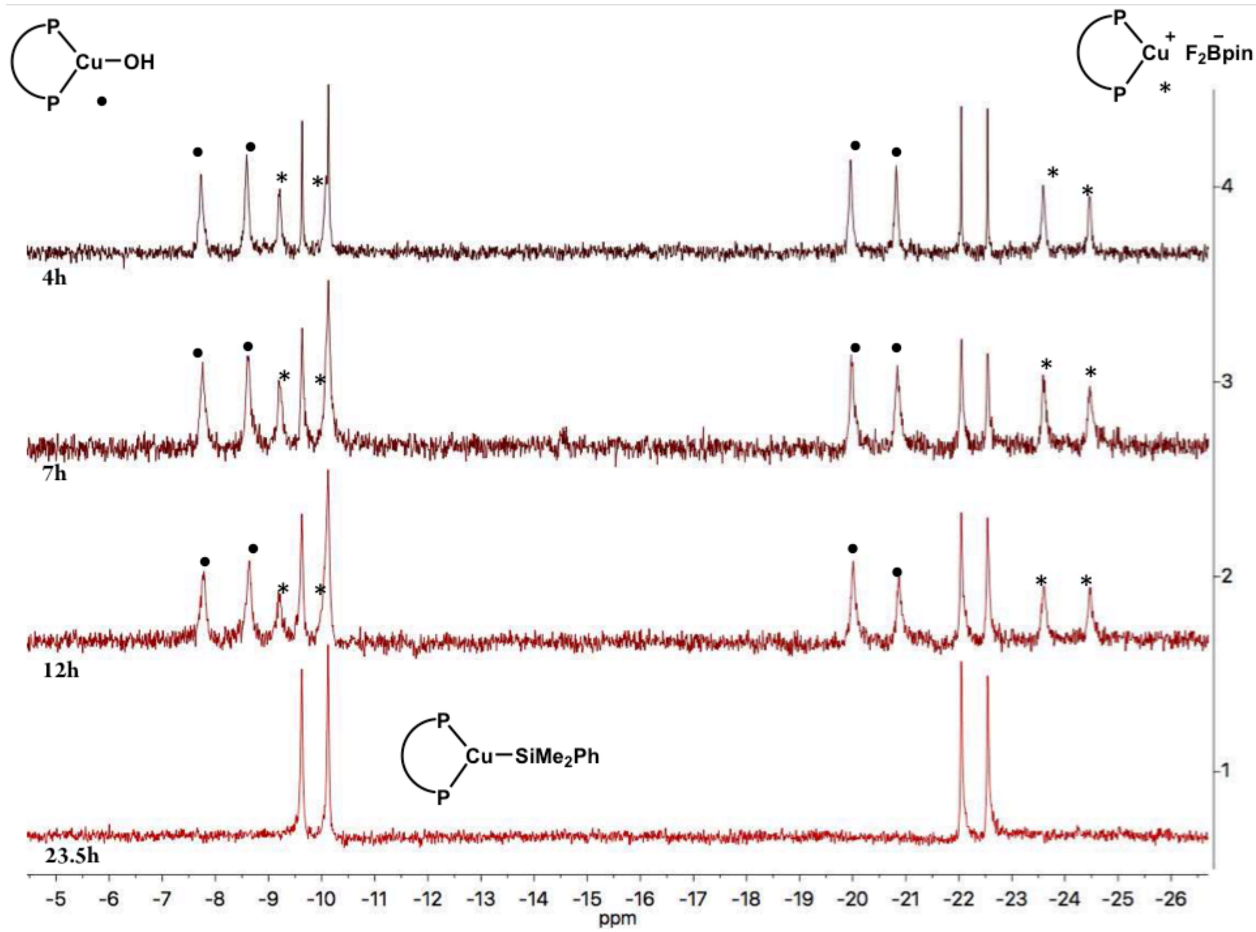
^{31}**P NMR** (243 MHz, 10% MTBE/C_6D_6)

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.



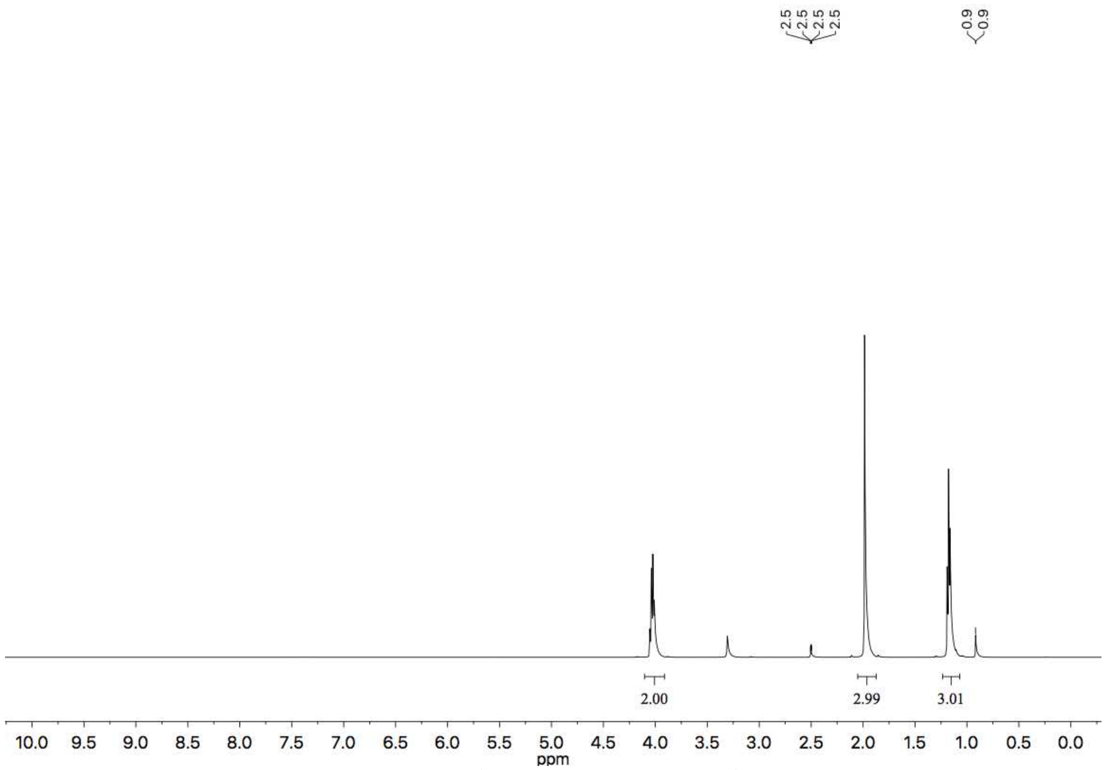
^{11}**B NMR** (193 MHz, 10% MTBE/C_6D_6)



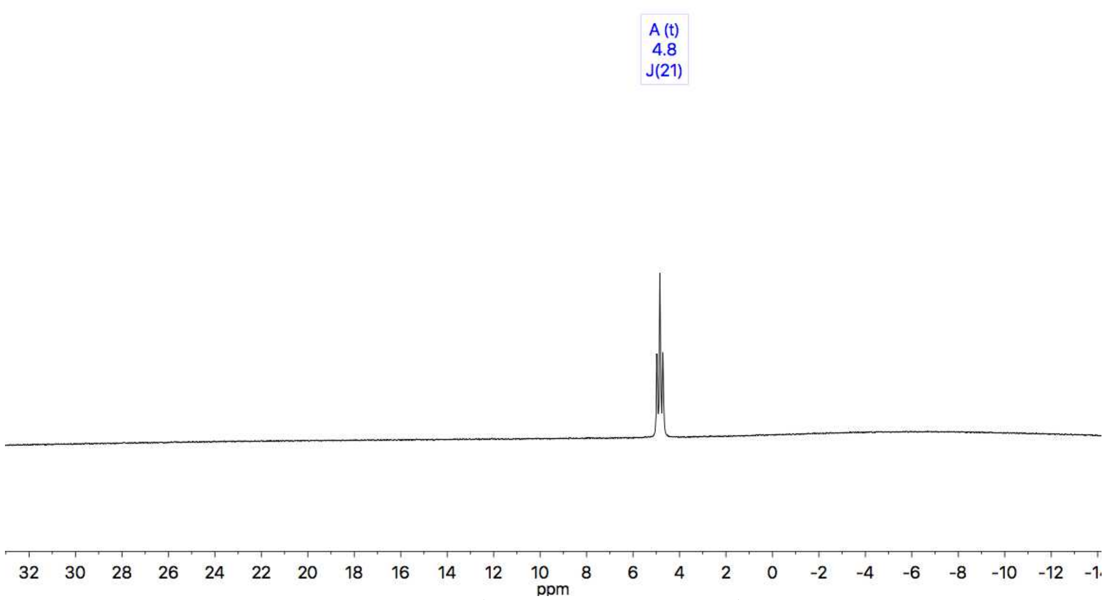
^{31}**P NMR** (243 MHz, 10% MTBE/C_6D_6)

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)

8) Computational Studies

I. Computational Methods

Density functional theory (DFT) calculations were carried out using the Gaussian 16 program[26] on Pitt CRC, XSEDE,[27] and the TACC Frontera supercomputers. Geometries of all stationary points were fully optimized using the dispersion-corrected with zero-damping[28] B3LYP-D3(zero) functional.[29] The SDD basis set was used for copper, iron, and cesium 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[30] were performed using the GoodVibes package,[31] 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[32] with the SDD basis set for copper, iron, and cesium and 6-311+G(d,p) basis set for other atoms. Solvation energy corrections were calculated using the SMD solvation model[33] 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)[34] algorithm, which is implemented in Q-Chem 5.3 package.[35] Following a similar procedure reported by our group,[36] 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

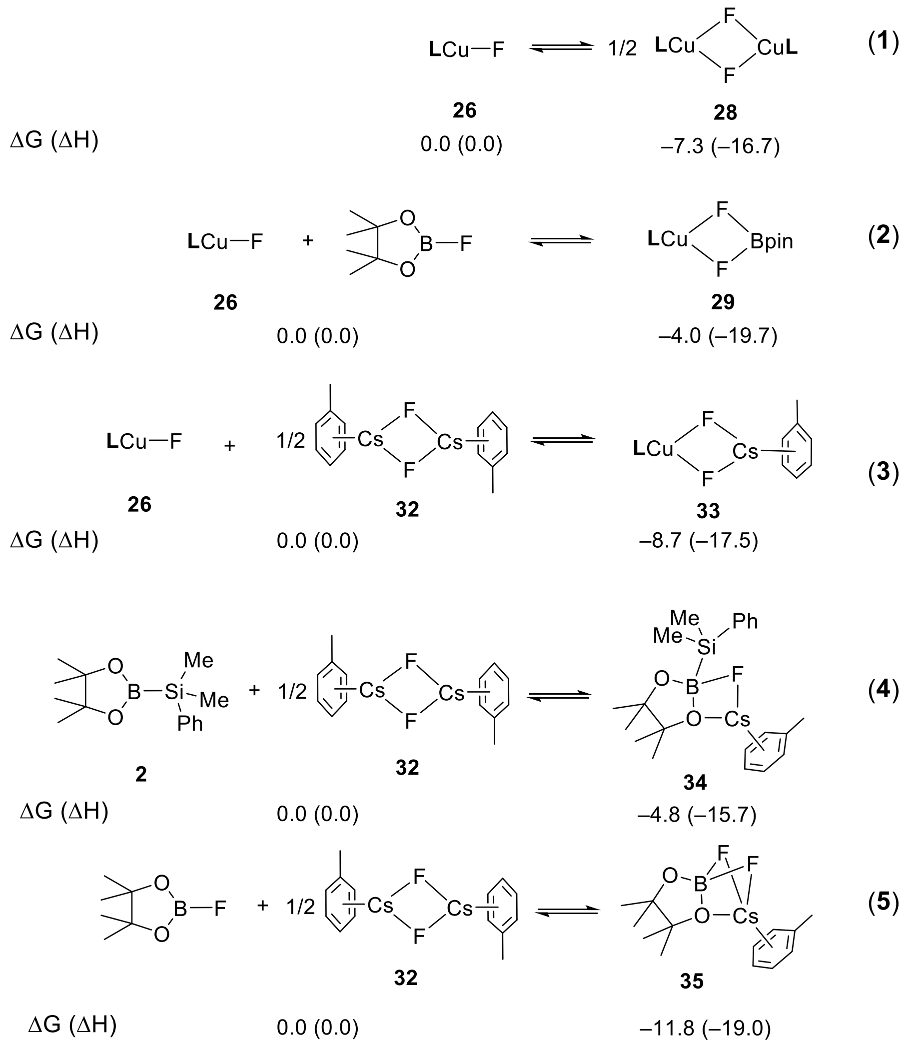


Figure S1. Reaction Gibbs free energies and enthalpies to form possible off-cycle complexes with LCuF and BPinF. L = (*R*,*S*)-3,5-TMS-Josiphos.

Because the $LCuF_2Bpin$ heterodimer was observed experimentally as a potential LCuF reservoir, we computed the reaction energies to form several possible dimeric and heterodimeric species of LCuF (eqs. 1-3, Figure S1). From monomeric $Cu^{I}F$ species **26**, the dimerization to form dimeric species **28**, and the association with FBpin and CsF to form heterodimers **29** and **33** are all exergonic. Indicating the equilibrium should favor the dimeric and heterodimeric species over the monomeric LCuF. This is consistent with the experimental results that monomeric LCuF **26** was not observed. It should be noted that the exact catalyst resting state depends on the relative concentrations of LCuF, FBpin, and CsF, considering the computed exergonicity of equations 1-3 are comparable. Therefore, either **28**, **29**, or **33** may be an off-cycle complex before the σ-bond metathesis with $PhMe_2SiBpin$. The relatively low energy required to dissociate the dimer and heterodimers indicate that the dissociation to the catalytically active monomeric LCuF is feasible under the catalytic conditions. 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 ($\Delta G^{\ddagger}$ = 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.

Next, we investigated the possibility of the fluoride salt (CsF) binding to the Lewis acidic $PhMe_2SiBpin$ and FBpin species (eqs. 4-5, Figure S1). The formation of complexes **34** and **35** are both exergonic, indicating the binding of $PhMe_2SiBpin$ and FBpin with CsF are both thermodynamically favorable. The binding of CsF to the more Lewis acidic FBpin is much stronger than the binding to $PhMe_2SiBpin$, indicating that the formation of **35** provides thermodynamic driving force for the product formation.

For simplicity, the catalytically active monomeric species (*i.e.* LCuF, FBpin, $PhMe_2SiBpin$) and the dimer of CsF [*i.e.* $Cs_2F_2(tol)_2$, **32**] were used as the energy references in the computed reaction energy profile (Figure 2, main manuscript). Although the aforementioned off-cycle complexes may be formed, the dissociations to form the monomeric species are all relatively facile and are only uphill by several kcal/mol. Therefore, these off-cycle complexes are not expected to affect the predicted reaction mechanism, the rate-determining step (**TS2**, alkyne migratory insertion), or the origin of regio- and enantioselectivity.

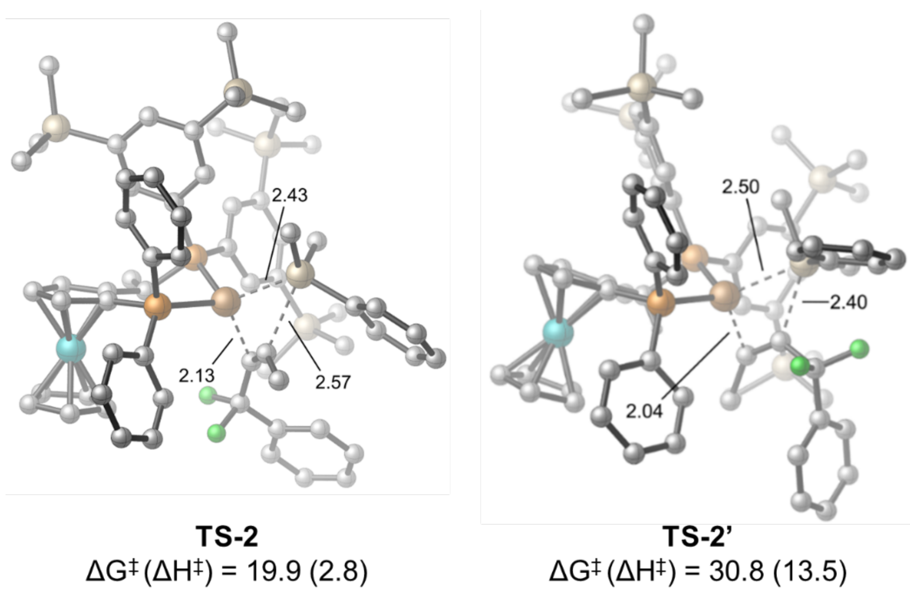
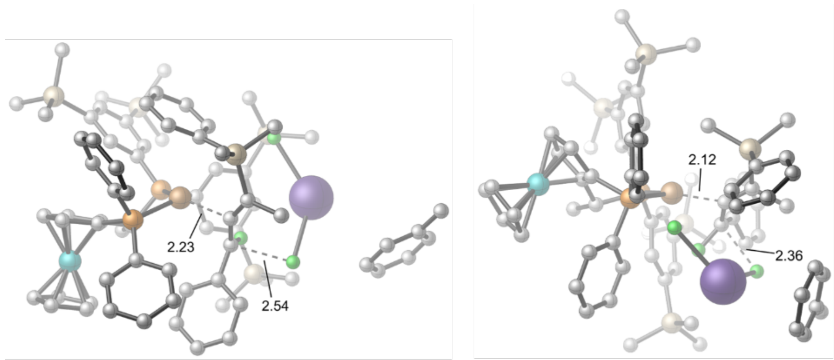
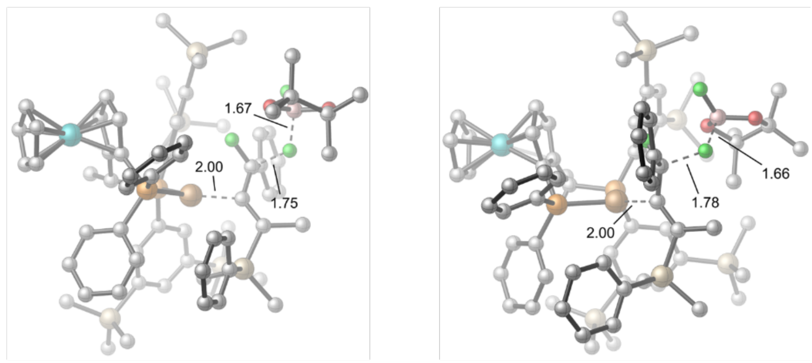


Figure S2. Optimized structures of the alkyne insertion transition states. Gibbs free energies and enthalpies (kcal/mol) are with respect to **30**.



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** ($\Delta G^{‡}$ = 14.6 kcal/mol with respect to **31**).

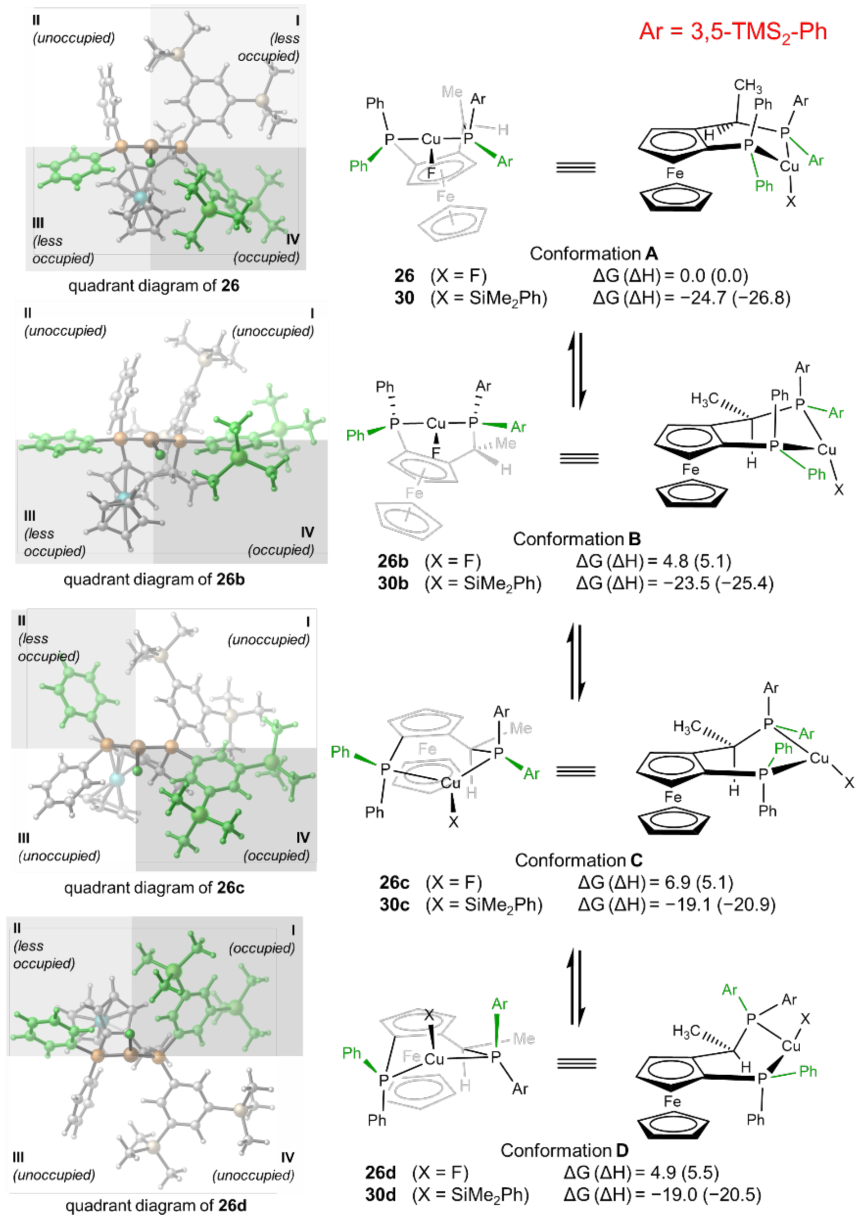


Figure S4. Conformers of LCu^{I}F and LCuSiMe$_2$Ph complexes supported by the (*R,S*)-3,5-TMS-Josiphos ligand. The *P*-phenyl and *P*-aryl groups "proximal" to the Cu center are highlighted in green. Gibbs free energies and enthalpies (in kcal/mol) are with respect to **26**.

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.

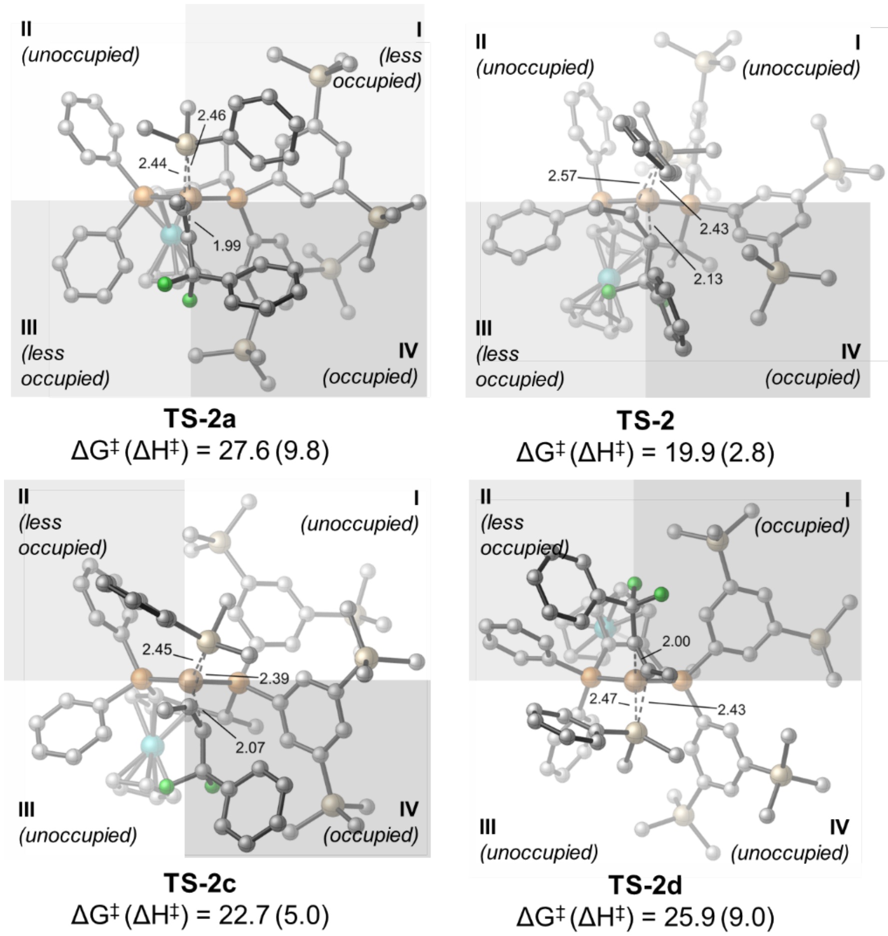


Figure S5. Conformers of the alkyne migratory insertion transition states with different conformations of the (*R,S*)-3,5-TMS-Josiphos ligand. Gibbs free energies and enthalpies (kcal/mol) are with respect to **30**.

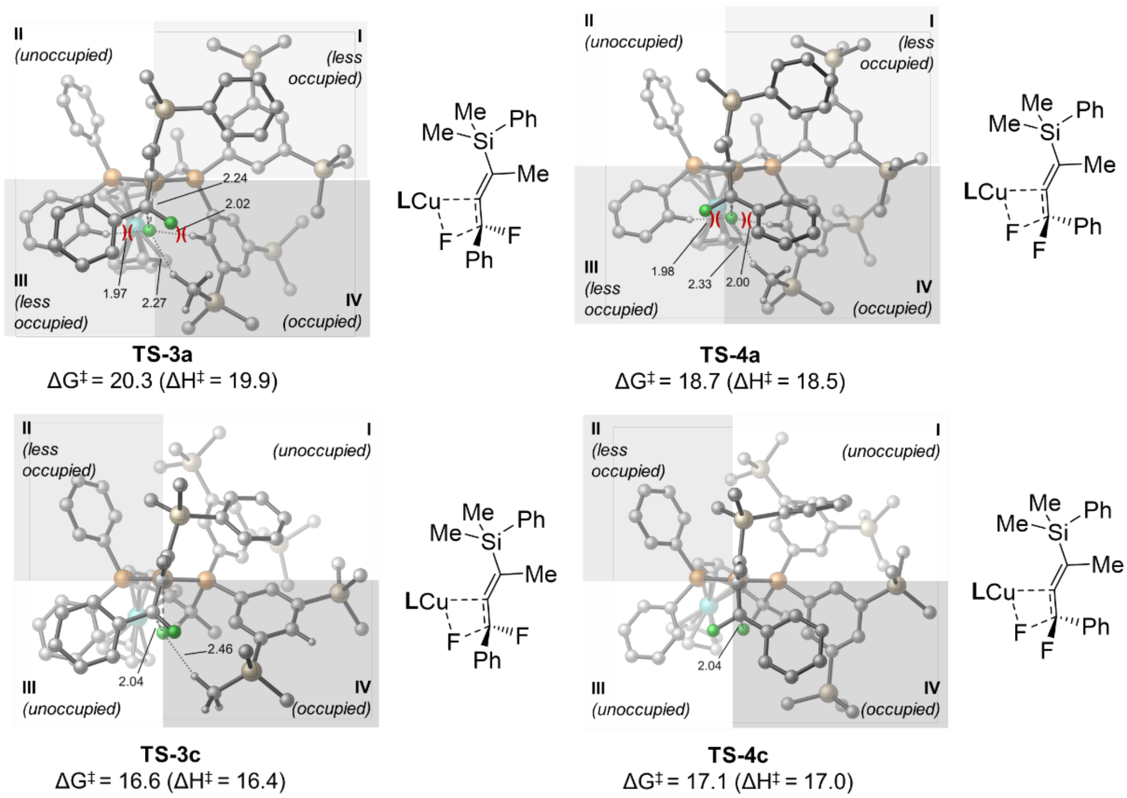
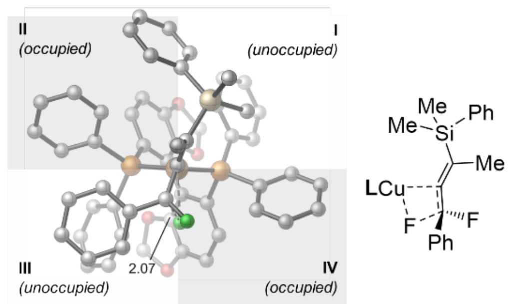
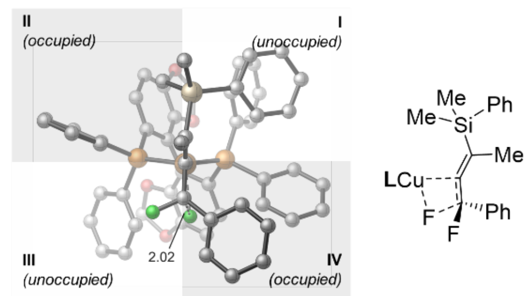


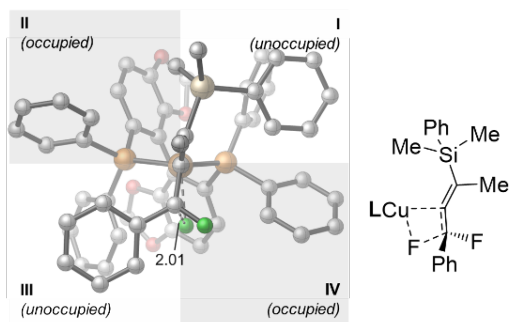
Figure S6. Optimized structures of *β*-fluoride elimination transition states with different conformations of the (*R,S*)-3,5-TMS-Josiphos ligand. Gibbs free energies and enthalpies (kcal/mol) are with respect to **31**. See Figure 3 in the manuscript for the optimized transition state structures with the most favorable ligand conformation (**B**).



TS-7
ΔΔG‡ = 0.0 (ΔΔH‡ = 0.0)



TS-8
ΔΔG‡ = 0.2 (ΔΔH‡ = −0.2)



TS-7'
ΔΔG‡ = 0.4 (ΔΔH‡ = −0.2)

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
H	0.289426	1.039062	3.870580
C	-2.959311	2.136683	-0.460454
C	-4.355821	2.262599	-0.419847
H	-4.862882	2.330479	0.538593
C	-5.096046	2.278724	-1.604178
H	-6.178221	2.370082	-1.562472
C	-4.450128	2.172789	-2.838265
C	-3.058761	2.047494	-2.888024
H	-2.552335	1.950314	-3.844077
C	-2.319319	2.022081	-1.705467
H	-1.238359	1.903532	-1.741282
C	-1.481349	3.767832	1.467648
C	-2.340723	4.855839	1.256842
H	-3.306716	4.701090	0.782864
C	-1.953539	6.138532	1.647677
H	-2.621824	6.979692	1.482420
C	-0.706417	6.340202	2.246667
C	0.159268	5.260751	2.442041
H	1.135591	5.418687	2.892425
C	-0.218307	3.974696	2.048620
H	0.458132	3.130552	2.184192
C	-1.964190	2.119530	6.116788

H	-2.579282	2.850880	6.625835
C	-3.103595	-1.152558	2.051715
H	-2.692346	0.173197	6.959670
C	-4.054934	-1.285292	0.842661
H	-5.080149	-1.075574	1.167768
H	-3.806705	-0.568968	0.053287
H	-4.022603	-2.290024	0.412915
H	-3.351941	-1.947902	2.763470
C	-1.367988	-2.613768	0.181562
C	-1.273004	-4.002094	0.332638
C	-1.529672	-2.081392	-1.107121
C	-1.353480	-4.868674	-0.770548
H	-1.116327	-4.414269	1.325199
C	-1.634277	-2.905198	-2.238159
H	-1.576633	-0.998344	-1.216002
C	-1.539962	-4.295275	-2.040661
H	-1.601540	-4.951398	-2.906633
C	-0.552606	-2.327111	2.979098
C	-1.187713	-3.359324	3.680961
C	0.723787	-1.907941	3.385871
C	-0.569110	-3.988784	4.775325
H	-2.180544	-3.684117	3.372554
C	1.366203	-2.481183	4.493834
H	1.188769	-1.078436	2.858728
C	0.702366	-3.525625	5.161865
H	1.185765	-3.990164	6.020090
H	-5.028554	2.177028	-3.757994
H	-0.406131	7.339997	2.549384
Si	-1.231048	-6.735221	-0.491084
Si	-1.920053	-2.128204	-3.938172
Si	-1.468864	-5.394004	5.659099
Si	2.987629	-1.720957	5.120109
C	0.194390	-7.073692	0.706254
H	0.049257	-6.547939	1.657764
H	0.275150	-8.144787	0.929228
H	1.152370	-6.742486	0.288754
C	-0.929266	-7.606078	-2.142321
H	-0.817226	-8.686964	-1.994219
H	-1.762436	-7.454833	-2.839247
H	-0.016822	-7.239373	-2.627210
C	-2.846970	-7.354130	0.278682
H	-3.703943	-7.151926	-0.374678
H	-2.810093	-8.435116	0.462432
H	-3.035788	-6.861689	1.240205
C	-1.649858	-3.429220	-5.283920
H	-2.366876	-4.254763	-5.199845
H	-1.774557	-2.986156	-6.279428
H	-0.640886	-3.855425	-5.233106
C	-0.704034	-0.695247	-4.160455
H	-0.811895	0.039246	-3.354326
H	0.333247	-1.049682	-4.150141
H	-0.873338	-0.173881	-5.110941
C	-3.693790	-1.472262	-4.017411
H	-3.872890	-0.726978	-3.234154

H	-3.897589	-0.993793	-4.983861
H	-4.419943	-2.283056	-3.884301
C	-3.048444	-4.701547	6.441203
H	-2.810676	-3.941845	7.195440
H	-3.684281	-4.227212	5.683203
H	-3.638559	-5.488027	6.927510
C	-0.351818	-6.143066	6.986095
H	-0.854567	-6.976705	7.491007
H	0.579952	-6.528243	6.555215
H	-0.086108	-5.404629	7.751960
C	-1.931610	-6.700665	4.367974
H	-1.038362	-7.116398	3.886894
H	-2.491807	-7.531277	4.814321
H	-2.557913	-6.266226	3.578798
C	3.802076	-0.759569	3.717595
H	4.120170	-1.432287	2.911209
H	3.121574	-0.018415	3.279097
H	4.693105	-0.232268	4.081288
C	2.549674	-0.558999	6.549404
H	1.853151	0.216940	6.211108
H	2.066420	-1.102876	7.370485
H	3.442820	-0.064702	6.951595
C	4.115888	-3.107535	5.748102
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

ATOM	X	Y	Z
Cu	0.265027	-0.637047	0.639961
Fe	-1.798434	2.253731	2.702490
P	-1.645731	-1.876707	0.860701
P	-0.704671	1.072038	-0.353932
C	-2.051253	1.495569	0.807808
C	-2.674830	0.631869	1.806491
C	-3.680327	1.422614	2.453353
H	-4.309867	1.091169	3.266259
C	-3.668588	2.740220	1.913041
H	-4.280541	3.568014	2.246893
C	-2.673115	2.788115	0.902984
H	-2.385646	3.658594	0.329790
C	-0.878154	1.598229	4.436834
H	-1.114910	0.659964	4.922779

C	-1.530829	2.848080	4.668945
C	0.046178	3.153032	3.011213
H	0.632310	3.606169	2.224712
C	0.097545	1.780124	3.411649
H	0.723005	0.996966	2.990908
C	-1.563914	0.630380	-1.917972
C	-2.790409	1.175138	-2.323137
H	-3.296152	1.901080	-1.692101
C	-3.380282	0.765325	-3.519987
H	-4.331747	1.189929	-3.823922
C	-2.760169	-0.201066	-4.314795
C	-1.543845	-0.757007	-3.912968
H	-1.064528	-1.520361	-4.520184
C	-0.950987	-0.344258	-2.720107
H	-0.018399	-0.795270	-2.388250
C	0.136998	2.664807	-0.715724
C	-0.395186	3.670960	-1.535719
H	-1.356776	3.526336	-2.019970
C	0.316356	4.852381	-1.749831
H	-0.103115	5.627650	-2.385652
C	1.568519	5.034940	-1.155791
C	2.115635	4.027373	-0.357588
H	3.096281	4.157527	0.091994
C	1.406076	2.843925	-0.144427
H	1.828066	2.049404	0.467744
C	-0.954106	3.810849	3.787339
H	-1.255282	4.846046	3.690371
C	-2.342372	-0.796569	2.244582
H	-2.343822	3.023662	5.361746
C	-3.461942	-1.450861	3.071130
H	-3.629372	-0.889526	3.997453
H	-4.407894	-1.496522	2.523875
H	-3.181039	-2.469337	3.351447
H	-1.456798	-0.740576	2.888184
C	-3.036362	-2.172248	-0.294615
C	-2.898025	-3.169096	-1.274836
C	-4.212654	-1.412768	-0.274688
C	-3.913890	-3.437493	-2.201612
H	-1.981099	-3.753715	-1.298483
C	-5.262863	-1.646974	-1.178528
H	-4.317958	-0.620575	0.456393
C	-5.090718	-2.667806	-2.125653
H	-5.897387	-2.874484	-2.828933
C	-1.366141	-3.486873	1.689755
C	-2.252543	-4.568889	1.653781
C	-0.148439	-3.614786	2.375941
C	-1.936792	-5.788697	2.276973
H	-3.192621	-4.463725	1.117660
C	0.194708	-4.804263	3.036976
H	0.539622	-2.770048	2.375786
C	-0.713010	-5.877106	2.966044
H	-0.456310	-6.815344	3.455577
H	-3.231290	-0.531924	-5.236228
H	2.121895	5.954379	-1.327030

F	1.530827	-0.946145	1.959650
Si	-3.715084	-4.768760	-3.526377
Si	-6.847337	-0.622764	-1.062042
Si	-3.150859	-7.225164	2.119213
Si	1.879956	-4.891147	3.897910
C	-2.061125	-5.651548	-3.287245
H	-1.214696	-4.960512	-3.380849
H	-2.001842	-6.122391	-2.298708
H	-1.930051	-6.439335	-4.038782
C	-3.770119	-3.928777	-5.223197
H	-2.954207	-3.202833	-5.319662
H	-3.677865	-4.655583	-6.039379
H	-4.712741	-3.385403	-5.362529
C	-5.137792	-6.006970	-3.374723
H	-6.111647	-5.505745	-3.432061
H	-5.100987	-6.756961	-4.174399
H	-5.090820	-6.535904	-2.415421
C	-6.776640	0.861469	-2.236416
H	-6.645316	0.541926	-3.276769
H	-7.700067	1.451042	-2.178814
H	-5.939597	1.520498	-1.978421
C	-8.322703	-1.714935	-1.521050
H	-8.394898	-2.584112	-0.856815
H	-9.262507	-1.154527	-1.445098
H	-8.245593	-2.088297	-2.549437
C	-7.028280	0.014482	0.711296
H	-7.023579	-0.809599	1.434877
H	-6.213618	0.698438	0.979728
H	-7.971372	0.561378	0.832367
C	-3.611814	-7.394389	0.287522
H	-4.028198	-6.455985	-0.099295
H	-2.730983	-7.638955	-0.318389
H	-4.359299	-8.181544	0.129303
C	-2.351189	-8.819609	2.745787
H	-2.091367	-8.748867	3.808879
H	-3.034147	-9.669752	2.629025
H	-1.433192	-9.050436	2.192409
C	-4.714872	-6.844903	3.116487
H	-5.463715	-7.639057	3.005880
H	-4.487260	-6.742401	4.184170
H	-5.172140	-5.905181	2.783306
C	1.808266	-6.190443	5.274868
H	1.585244	-7.189249	4.879744
H	2.769199	-6.253122	5.800136
H	1.038278	-5.944610	6.015945
C	3.187429	-5.385524	2.620891
H	4.184368	-5.447026	3.075083
H	2.961188	-6.358855	2.168968
H	3.230837	-4.642091	1.815839
C	2.284555	-3.182052	4.591994
H	2.253033	-2.414935	3.807505
H	1.568350	-2.893181	5.371520
H	3.286645	-3.170330	5.039004

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
Cu	-0.483895	-1.268642	0.211108
Fe	-2.658480	2.564658	2.328087
P	-2.420544	-2.045218	1.118079
P	-0.819595	0.894081	-0.265052
C	-2.331023	1.409826	0.634375
C	-3.022320	0.645635	1.658043
C	-4.257035	1.317507	1.918525
H	-4.988339	1.021781	2.657428
C	-4.331439	2.486726	1.106657
H	-5.126742	3.220560	1.121639
C	-3.146725	2.551731	0.324505
H	-2.896820	3.317972	-0.396513
C	-1.668267	2.426340	4.147276
H	-1.414130	1.494086	4.634506
C	-2.891250	3.150085	4.296040
C	-1.571501	4.275724	2.769737
H	-1.229872	4.986773	2.030335
C	-0.853620	3.123091	3.208110
H	0.120320	2.812286	2.861022
C	-1.146459	1.438955	-1.991266
C	-2.421717	1.299435	-2.565460
H	-3.252439	0.945829	-1.961328
C	-2.631291	1.620855	-3.907531
H	-3.623305	1.515282	-4.335434
C	-1.572958	2.071476	-4.699825
C	-0.299269	2.195562	-4.142291
H	0.532389	2.541583	-4.750282
C	-0.085661	1.879933	-2.799922
H	0.909020	1.986422	-2.377842
C	0.542005	1.985031	0.303297
C	0.530183	3.375484	0.108350
H	-0.284193	3.837979	-0.442411
C	1.555823	4.164179	0.625272
H	1.541433	5.240621	0.474900
C	2.600808	3.569182	1.342177
C	2.622011	2.185962	1.527752
H	3.436938	1.721855	2.076636
C	1.598846	1.385567	1.006809
H	1.614722	0.303848	1.147405
C	-2.830443	4.294945	3.444484
H	-3.618477	5.023420	3.303505
C	-2.544496	-0.603186	2.365460

H	-3.733154	2.859320	4.911071
C	-3.326538	-0.905247	3.649711
H	-3.254505	-0.052753	4.334225
H	-4.387796	-1.081153	3.454025
H	-2.921384	-1.789132	4.149026
H	-1.493201	-0.456198	2.642984
C	-4.097621	-2.127857	0.386891
C	-4.223451	-1.869361	-0.986092
C	-5.259291	-2.379741	1.133175
C	-5.476370	-1.856997	-1.623070
H	-3.318445	-1.670816	-1.556718
C	-6.530528	-2.405532	0.540333
H	-5.170569	-2.570898	2.196745
C	-6.608546	-2.135780	-0.836886
H	-7.587415	-2.142715	-1.314177
C	-2.176692	-3.508013	2.196996
C	-3.126269	-4.491979	2.494938
C	-0.884473	-3.620202	2.738851
C	-2.826661	-5.559149	3.360272
H	-4.110486	-4.441668	2.039529
C	-0.540225	-4.673671	3.598798
H	-0.126423	-2.896896	2.437750
C	-1.531295	-5.623686	3.903857
H	-1.282009	-6.447419	4.570339
H	-1.740496	2.320658	-5.744029
H	3.397341	4.186018	1.749949
F	1.083028	-1.806306	1.092994
Si	-5.651214	-1.437389	-3.459484
Si	-8.043360	-2.856723	1.581367
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
Cu	-0.822977	0.793549	-2.051378
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
H	-2.100818	4.508598	-1.766798
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
C	-3.006788	4.587486	1.434490
H	-3.630566	4.270431	2.279399
H	-2.203881	3.849486	1.315326
H	-2.546897	5.549208	1.693925
C	-8.070788	-0.704043	1.204026
H	-7.381430	-1.522221	0.960380
H	-7.720409	-0.241963	2.134787
H	-9.056715	-1.144703	1.396665
C	-8.764160	-0.286855	-1.772235
H	-8.832935	0.421540	-2.606159
H	-8.085158	-1.092106	-2.078836
H	-9.756671	-0.729348	-1.623324
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
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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
C	-0.764241	-2.086572	-6.902908
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
H	1.019248	3.570842	-3.698286
C	2.013628	2.881336	-1.908841
C	2.186394	1.817811	-1.020504
H	2.880633	1.908022	-0.189795
C	1.488649	0.623465	-1.213283
H	1.652986	-0.228472	-0.554223
C	-2.809190	2.816937	-0.115761
H	-3.271884	3.565446	-0.746146
C	-2.450847	-2.238179	0.195871
H	-4.509845	2.128240	1.174335
C	-3.602628	-2.576084	1.153349

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
C	-2.392568	-4.311052	-1.990718
C	-1.599020	-5.011314	-2.913111
C	-3.739178	-4.073957	-2.289552
C	-2.132845	-5.529114	-4.101579
H	-0.537298	-5.112493	-2.698255
C	-4.303018	-4.517641	-3.498618
H	-4.347079	-3.505023	-1.593890
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	1.039957	-6.029234	-3.993107
H	0.420471	-7.607856	-3.502037
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H	-0.042393	-4.730789	-6.630828
H	-0.094350	-6.249955	-7.548861
H	-1.561561	-5.271078	-7.356141
C	-1.974451	-8.154869	-5.671692
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H	-2.185017	-8.731851	-4.763213
C	-5.962296	-3.026945	-5.578892
H	-5.477672	-3.595633	-6.382270
H	-6.953967	-2.723130	-5.935909
H	-5.369126	-2.119216	-5.412607
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H	-7.161993	-6.221830	-3.388080
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H	-6.605262	-6.250311	-5.066866
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H	-6.910012	-3.581238	-1.671102
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H	-7.867935	-2.719970	-2.884854
C	-5.216972	-8.232097	0.516399

H	-5.225770	-7.448124	-0.250804
H	-4.557419	-9.031373	0.161494
H	-6.232818	-8.639147	0.591139
C	-4.442256	-8.955280	3.437757
H	-4.108618	-8.582007	4.413466
H	-5.401491	-9.464638	3.590409
H	-3.717444	-9.703416	3.096955
C	-5.868193	-6.269993	2.804545
H	-6.869184	-6.702874	2.923309
H	-5.560444	-5.859570	3.773622
H	-5.947301	-5.431571	2.101274
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H	1.244739	-9.035001	2.798678
H	1.843380	-8.861803	4.459000
H	0.107739	-9.044511	4.159400
C	2.463341	-6.008662	2.880024
H	3.314875	-6.203122	3.543012
H	2.668438	-6.494627	1.922560
H	2.409331	-4.928275	2.700732
C	0.578694	-5.959606	5.340806
H	0.499192	-4.867465	5.281703
H	-0.351351	-6.338069	5.782229
H	1.398821	-6.200424	6.028908
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
C	5.637387	-4.428746	-3.122632
C	5.125906	-5.757209	-3.406535
C	5.948487	-6.301095	-4.445863
H	5.815352	-7.265137	-4.914626
C	6.932311	-5.339709	-4.819553
H	7.660389	-5.452432	-5.612608
C	6.742566	-4.188327	-4.012299
H	7.308653	-3.269863	-4.070457
C	3.199884	-4.894576	-6.003947
H	2.588000	-5.764434	-5.817118
C	4.232548	-4.792260	-6.985669
C	4.165035	-2.812231	-5.798770
H	4.417732	-1.828203	-5.431945
C	3.157482	-3.676359	-5.262937
H	2.526075	-3.497651	-4.399312
C	6.485530	-3.137365	-0.685270
C	7.669443	-3.875574	-0.805615
H	7.771924	-4.612402	-1.593854
C	8.716073	-3.686452	0.100237
H	9.622164	-4.277694	-0.000399
C	8.597922	-2.748110	1.125933
C	7.413946	-2.014583	1.260199
H	7.309647	-1.289743	2.063582
C	6.360566	-2.217422	0.370407
H	5.435072	-1.658078	0.488484
C	5.070759	-1.637890	-2.631358
C	6.262279	-0.965651	-2.947892

H	7.218169	-1.396021	-2.663014
C	6.226104	0.261863	-3.608089
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C	4.996158	0.838288	-3.939562
C	3.808389	0.191809	-3.595931
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H	5.665300	-3.126706	-7.433203
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C	3.773864	-7.902457	-3.343420
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C	6.435266	-7.189048	-0.852004
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H	4.807440	-5.408983	1.528225
C	7.657993	-7.422140	-0.204151
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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
H	4.962418	1.799724	-4.445363
F	1.610131	-4.102520	-2.451468
Si	6.946994	-5.725010	3.591399
Si	9.084365	-8.283178	-1.088879
Si	4.095795	-11.264790	1.571721
Si	-0.901289	-9.638514	-0.722697
C	5.902780	-4.183881	3.908168
H	6.207054	-3.367815	3.245169
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H	9.390608	-6.269706	3.844393
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H	6.394629	-6.903500	5.744897
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H 11.407061 -7.502325 -1.674197
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C 9.604969 -9.806195 -0.093270
H 8.779484 -10.524643 -0.021556
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C 8.530752 -8.783778 -2.826026
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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

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C	-3.367186	1.622638	3.158552
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C	-3.490666	2.936600	2.622157
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C	-2.800494	2.966892	1.383518
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H	0.201374	0.731438	4.359474
C	-0.647954	2.779679	4.741664
C	0.176624	3.684450	2.781218
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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
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C	-4.891426	1.150028	-2.490866
H	-5.933422	1.412329	-2.329686
C	-4.496206	0.566249	-3.694797
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H	-1.186885	0.143068	-3.022000
C	-0.425967	2.772276	-0.841284
C	-1.068889	3.872482	-1.429643
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C	-0.350194	5.034756	-1.711280
H	-0.852915	5.884750	-2.165306
C	1.015165	5.102472	-1.415822
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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
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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
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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
H	-4.635592	-2.232446	-3.905202
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

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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

BpinSiMe2Ph **2**

B3LYP-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 **32**

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

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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

CuF2Cs **33**
B3LYP-D3 SCF energy (au): -4521.56216236
B3LYP-D3 enthalpy (au): -4520.36059336
B3LYP-D3 free energy (au): -4520.56560536
M06 SCF energy (au): -4520.24685949
M06 enthalpy (au): -4519.04529049
M06 free energy (au): -4519.25030249
M06 free energy (quasi-harmonic) (au): -4519.22678013

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.313421	1.259498	1.109201
Fe	-2.784438	0.986529	4.502600
P	-0.975188	-0.868490	1.451418
P	-2.166036	2.441253	1.445454
C	-3.286479	1.543291	2.570468
C	-3.367470	0.099346	2.696400
C	-4.322224	-0.175624	3.726292
H	-4.587636	-1.167195	4.072283
C	-4.833067	1.054395	4.232393
H	-5.533545	1.165861	5.050340
C	-4.198230	2.112115	3.522438
H	-4.320183	3.171015	3.707806
C	-1.202258	0.019250	5.452280
H	-0.849090	-0.970121	5.211184
C	-2.234812	0.319390	6.388894
C	-1.507299	2.303417	5.461489
H	-1.435990	3.349865	5.200745

C	-0.751722	1.244411	4.869976
H	-0.008170	1.357969	4.088985
C	-3.194171	2.738355	-0.050126
C	-4.580834	2.951040	-0.014612
H	-5.106045	2.941773	0.937079
C	-5.293034	3.147670	-1.198822
H	-6.367544	3.309899	-1.164009
C	-4.626196	3.128152	-2.426936
C	-3.248712	2.898184	-2.468940
H	-2.733187	2.861519	-3.425198
C	-2.528687	2.694199	-1.288796
H	-1.464519	2.455936	-1.314036
C	-1.944995	4.085826	2.237386
C	-2.912401	5.100511	2.256054
H	-3.867853	4.949690	1.761247
C	-2.647161	6.314262	2.893629
H	-3.402417	7.096154	2.904176
C	-1.411051	6.525160	3.511247
C	-0.435823	5.524703	3.478194
H	0.532114	5.690550	3.944562
C	-0.693817	4.310466	2.838083
H	0.068860	3.533220	2.793971
C	-2.422402	1.734323	6.397014
H	-3.164358	2.275567	6.970558
C	-2.832058	-0.985282	1.779496
H	-2.803278	-0.402932	6.961120
C	-3.608344	-0.956800	0.443538
H	-4.684954	-0.932848	0.645530
H	-3.360861	-0.065769	-0.142885
H	-3.384208	-1.837600	-0.165168
H	-3.028233	-1.947223	2.268374
C	-0.692499	-1.969069	-0.003717
C	-0.556878	-3.363008	0.043914
C	-0.533519	-1.316570	-1.237314
C	-0.269300	-4.115607	-1.108282
H	-0.650136	-3.872642	0.999384
C	-0.253003	-2.028337	-2.416370
H	-0.560363	-0.227372	-1.250377
C	-0.127958	-3.425447	-2.327426
H	0.099765	-3.992843	-3.228460
C	-0.169668	-1.782419	2.822595
C	-0.638968	-2.961620	3.415131
C	1.024424	-1.217880	3.293557
C	0.071409	-3.598146	4.448013
H	-1.583256	-3.387846	3.080113
C	1.770213	-1.815555	4.322505
H	1.315086	-0.246170	2.894893
C	1.276410	-3.008860	4.877055
H	1.832281	-3.484765	5.682865
H	-5.182214	3.278713	-3.348999
H	-1.205648	7.471149	4.005887
Si	-0.057780	-5.983805	-0.938941
Si	-0.043998	-1.023939	-4.003736
Si	-0.642723	-5.164518	5.224392

Si	3.330777	-0.930060	4.918733
C	1.296576	-6.307359	0.346302
H	1.067006	-5.794844	1.288566
H	1.399993	-7.377699	0.563526
H	2.268904	-5.938460	-0.002486
C	0.424028	-6.734272	-2.606625
H	0.564616	-7.818396	-2.519107
H	-0.349747	-6.560998	-3.364124
H	1.361197	-6.307211	-2.983446
C	-1.679612	-6.742415	-0.324182
H	-2.496291	-6.566013	-1.034002
H	-1.583885	-7.825778	-0.180585
H	-1.974319	-6.306694	0.638207
C	0.425519	-2.174190	-5.431955
H	-0.348681	-2.930269	-5.610775
H	0.555557	-1.607961	-6.362208
H	1.366300	-2.701457	-5.230817
C	1.300168	0.273008	-3.701038
H	1.038657	0.862029	-2.812349
H	2.280050	-0.199401	-3.544542
H	1.397128	0.957317	-4.553552
C	-1.675228	-0.137751	-4.363625
H	-1.978091	0.463498	-3.498233
H	-1.587181	0.533790	-5.227049
H	-2.481498	-0.851348	-4.571463
C	-2.261530	-4.708120	6.093642
H	-2.080877	-3.986455	6.899367
H	-2.964281	-4.245691	5.389376
H	-2.752557	-5.587006	6.529208
C	0.587436	-5.890983	6.461867
H	0.192416	-6.812860	6.905441
H	1.542498	-6.135740	5.981846
H	0.793797	-5.192209	7.281354
C	-0.998774	-6.409812	3.842255
H	-0.079184	-6.694918	3.317840
H	-1.461200	-7.324424	4.232985
H	-1.684089	-5.986379	3.097469
C	4.709143	-1.203980	3.635774
H	4.923647	-2.269954	3.494301
H	4.419128	-0.791180	2.661100
H	5.638618	-0.706285	3.939276
C	2.965660	0.914396	5.053196
H	2.550167	1.311445	4.117665
H	2.223004	1.102658	5.837946
H	3.872707	1.480088	5.303086
C	3.880547	-1.660575	6.574509
H	4.118890	-2.728050	6.491253
H	4.776441	-1.150268	6.948322
H	3.095328	-1.550690	7.331934
F	1.280218	1.698630	2.267614
F	0.325307	1.555600	-0.810951
Cs	2.857938	0.491364	0.103676
C	3.665770	4.323249	-0.142842
C	2.440745	4.165161	-0.806796

C	2.450732	3.569088	-2.080662
C	3.643556	3.149828	-2.671300
C	4.860400	3.310027	-1.994702
C	4.866024	3.899364	-0.726946
H	3.676859	4.776031	0.846058
H	1.505620	3.404918	-2.588711
H	3.622772	2.688902	-3.656000
H	5.792202	2.993162	-2.457317
H	5.804499	4.040793	-0.195371
C	1.132031	4.551355	-0.168220
H	1.270220	4.992602	0.822290
H	0.580698	5.267137	-0.791091
H	0.514574	3.653068	-0.068071

CsFBpinSi **34**
B3LYP-D3 SCF energy (au): -1403.98499876
B3LYP-D3 enthalpy (au): -1403.47467776
B3LYP-D3 free energy (au): -1403.56780876
M06 SCF energy (au): -1403.44703535
M06 enthalpy (au): -1402.93671435
M06 free energy (au): -1403.02984535
M06 free energy (quasi-harmonic) (au): -1403.02224759

Cartesian coordinates

ATOM	X	Y	Z
B	-3.301426	-1.458752	0.780881
O	-3.366450	-0.071579	0.214541
O	-4.203384	-2.244582	-0.035304
C	-4.229502	-0.085602	-0.921210
C	-5.121502	-1.354218	-0.661640
C	-4.999344	1.238125	-0.974143
C	-3.364289	-0.228348	-2.183649
C	-6.282613	-1.064191	0.311940
C	-5.669694	-2.018640	-1.925385
H	-4.301643	2.069420	-1.139672
H	-5.730524	1.245164	-1.791166
H	-5.535580	1.418923	-0.036988
H	-3.952863	-0.150014	-3.105127
H	-2.608293	0.565335	-2.184818
H	-2.846251	-1.190314	-2.174637
H	-7.067402	-0.447247	-0.144002
H	-6.722755	-2.018886	0.616290
H	-5.909477	-0.572954	1.214325
H	-6.281978	-2.884107	-1.649818
H	-6.296143	-1.325500	-2.501100
H	-4.858211	-2.374849	-2.564369
Si	-1.379039	-2.215560	0.848617
C	-1.258187	-3.939687	1.649125
H	-1.810347	-4.664671	1.038480
H	-0.223840	-4.293591	1.744354
H	-1.716772	-3.949331	2.645380
C	-0.501650	-2.305071	-0.841711
H	-1.036038	-3.006736	-1.494399

H -0.498925 -1.333859 -1.350816
H 0.537180 -2.648465 -0.757615
C -0.322553 -1.037396 1.939246
C -0.317629 -1.145716 3.346745
C 0.366351 0.064889 1.390512
C 0.317618 -0.202280 4.162105
H -0.827392 -1.984195 3.816937
C 1.004887 1.016362 2.193888
H 0.400292 0.186270 0.309828
C 0.977932 0.890579 3.587569
H 0.310545 -0.325478 5.243622
H 1.536142 1.847621 1.733864
H 1.485667 1.618937 4.215925
F -3.752132 -1.356969 2.177114
Cs -2.939525 1.455475 2.679957
C -4.027202 4.976270 4.137765
C -4.904063 4.861905 3.055225
C -5.970745 3.947495 3.079784
C -6.133437 3.150336 4.223530
C -5.259142 3.260509 5.310498
C -4.200944 4.173820 5.271622
H -3.218422 5.701965 4.103031
H -4.769586 5.499080 2.183543
H -6.958462 2.443089 4.266542
H -5.413521 2.641418 6.190490
H -3.529763 4.272294 6.120624
C -6.901639 3.816995 1.896431
H -6.439250 3.236073 1.088233
H -7.832303 3.311296 2.171233
H -7.156758 4.798248 1.481200

CsF2Bpin **35**
B3LYP-D3 SCF energy (au): -902.881826290
B3LYP-D3 enthalpy (au): -902.541846290
B3LYP-D3 free energy (au): -902.618179290
M06 SCF energy (au): -902.546042507
M06 enthalpy (au): -902.206062507
M06 free energy (au): -902.282395507
M06 free energy (quasi-harmonic) (au): -902.276026217

Cartesian coordinates
ATOM X Y Z
B -0.888800 -1.845042 -0.516487
O -2.037256 -2.692219 -0.636455
O -0.026183 -2.432867 0.537645
C -2.059035 -3.572094 0.481745
C -0.528558 -3.740041 0.807962
C -2.821230 -2.887688 1.631804
C -2.771599 -4.865093 0.083093
C -0.215251 -4.105513 2.259290
C 0.161562 -4.731279 -0.145829
H -3.810866 -2.596649 1.265495
H -2.949666 -3.546352 2.499244

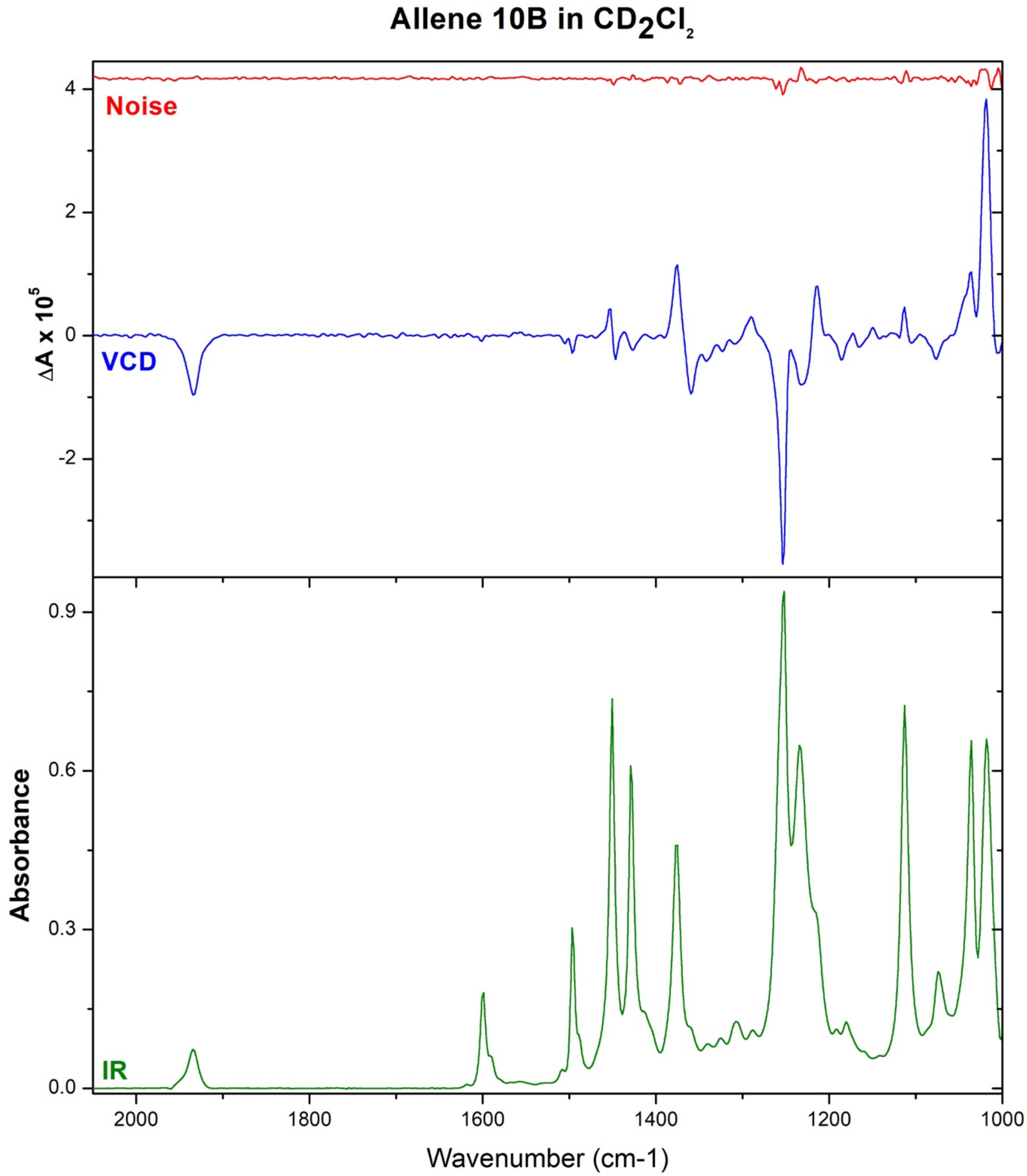
H	-2.297702	-1.979732	1.945286
H	-2.712974	-5.613837	0.882940
H	-3.829151	-4.657428	-0.113249
H	-2.339775	-5.285859	-0.828300
H	-0.683264	-5.057008	2.538291
H	0.868907	-4.212757	2.393182
H	-0.566556	-3.329557	2.944474
H	1.247876	-4.642531	-0.021310
H	-0.122582	-5.770602	0.055036
H	-0.085415	-4.487115	-1.182633
F	-0.164202	-1.733543	-1.744593
F	-1.176254	-0.487867	-0.124648
Cs	1.860755	-0.255287	0.141315
C	2.680979	2.473650	-2.742326
C	1.283366	2.430749	-2.676285
C	0.571296	1.281939	-3.056272
C	1.303172	0.171629	-3.513441
C	2.697480	0.212822	-3.591049
C	3.395619	1.362869	-3.201634
H	3.207843	3.381015	-2.455660
H	0.734451	3.304752	-2.331050
H	0.768961	-0.736140	-3.772310
H	3.240432	-0.654333	-3.960124
H	4.479738	1.399522	-3.275653
C	-0.929928	1.209261	-2.923040
H	-1.379846	2.208145	-2.935949
H	-1.370120	0.621513	-3.734803
H	-1.206860	0.711400	-1.986904

9) VCD Analysis

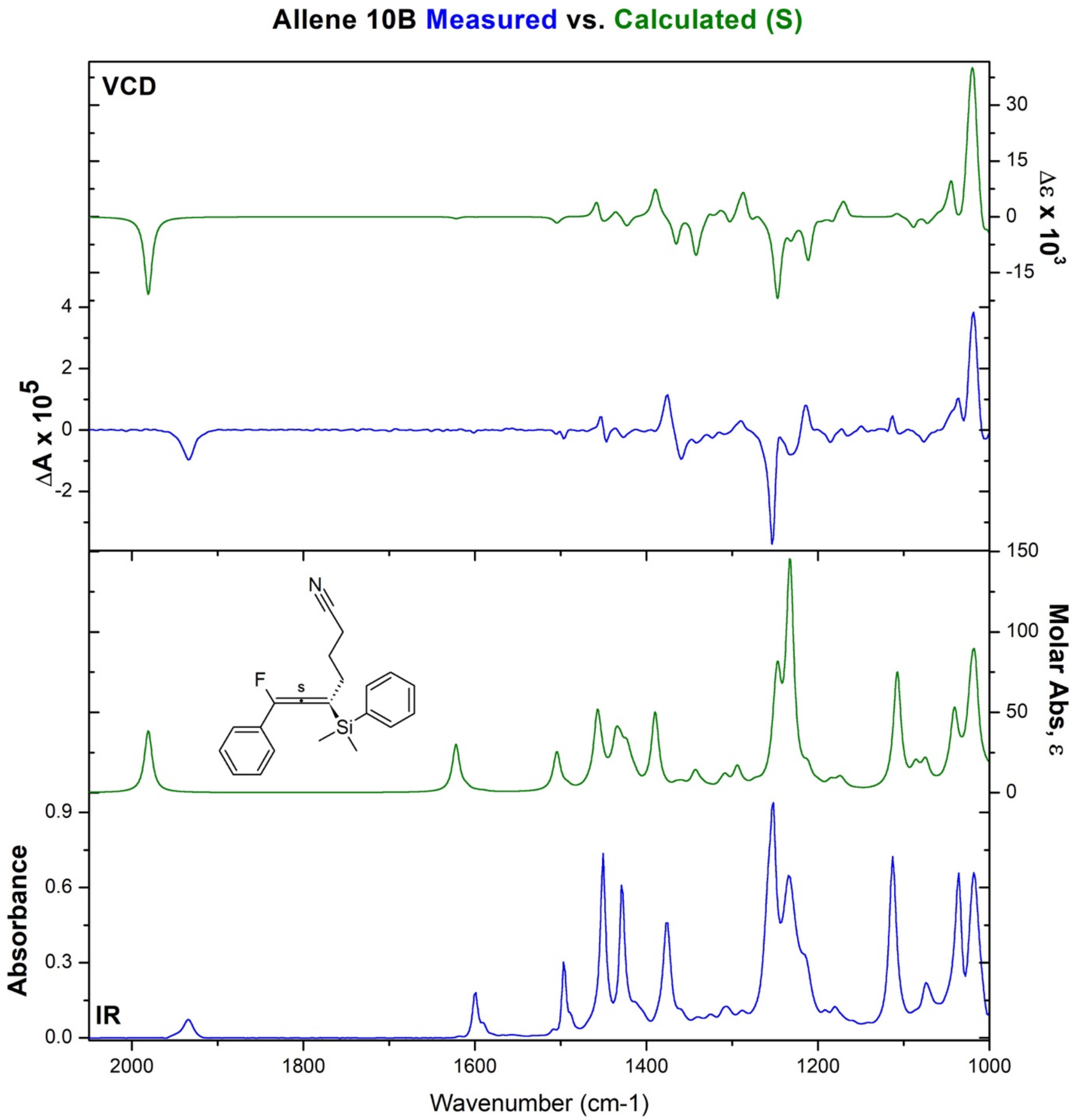
VCD Measurements: A 150uL solution containing 20 mg of allene **10b** dissolved in CD_2Cl_2 was transferred to a BaF_2 IR cell with path length of 100 μm. Instrumentation was a BioTools (Jupiter, Florida) ChiralIR-2X DualPEM FT-VCD, resolution 4 cm^{-1}, PEM maximum frequency 1400 cm^{-1}. The sample 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. Allenes **1b-Et3Si**, **12b**, **17b**, and **25b** were measured in a similar manner to **10b**.

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. Allenes **1b-Et3Si**, **12b**, **17b**, and **25b** were analyzed in a similar manner.

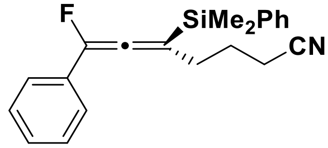
Measured VCD and IR Spectrum of 10b

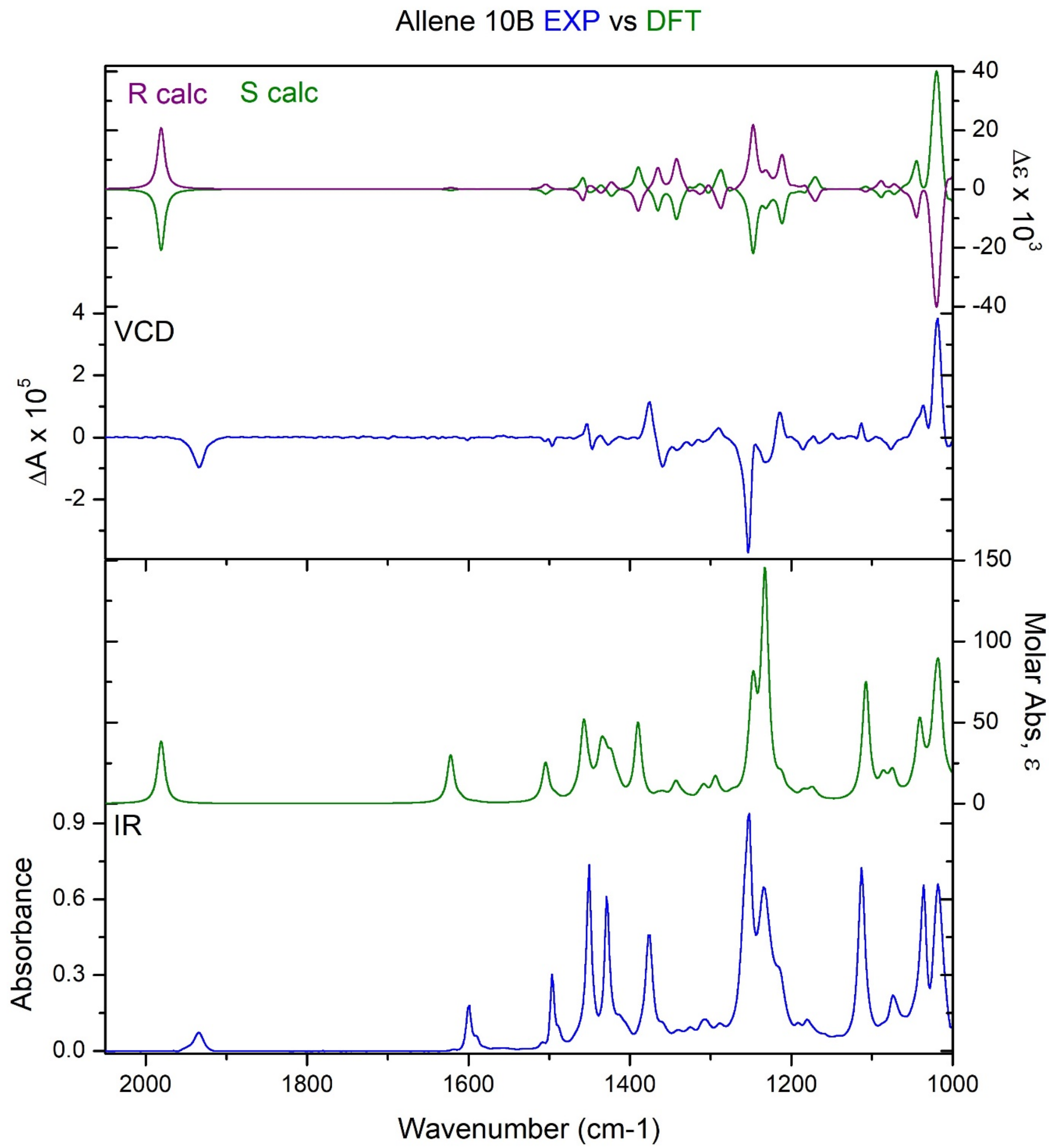


Measured and Calculated VCD and IR spectrum of 10b

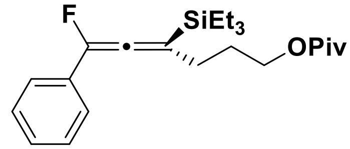


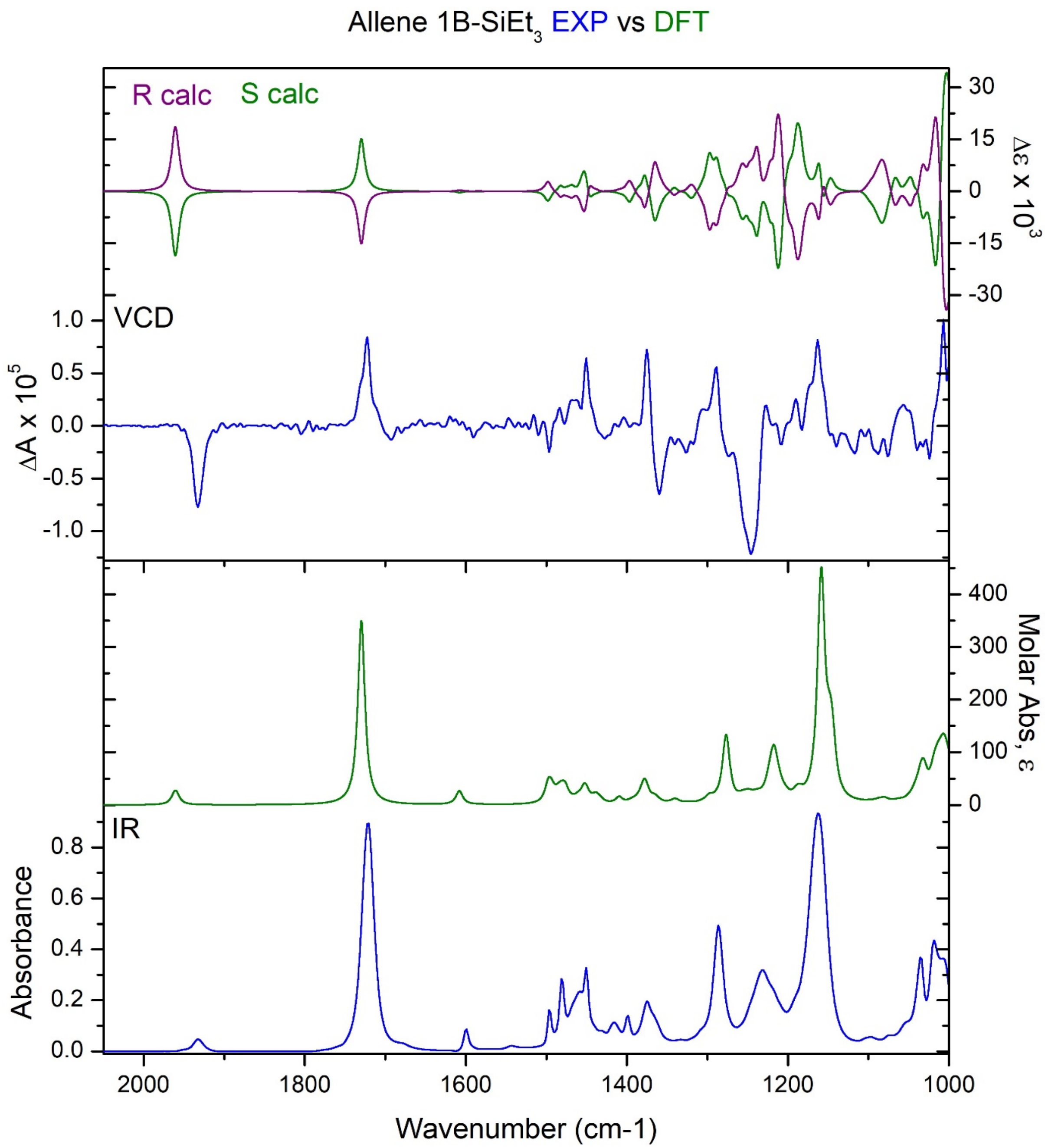
Experimental vs Calculated VCD and IR spectrum of 10b



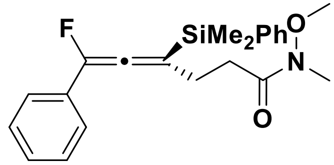


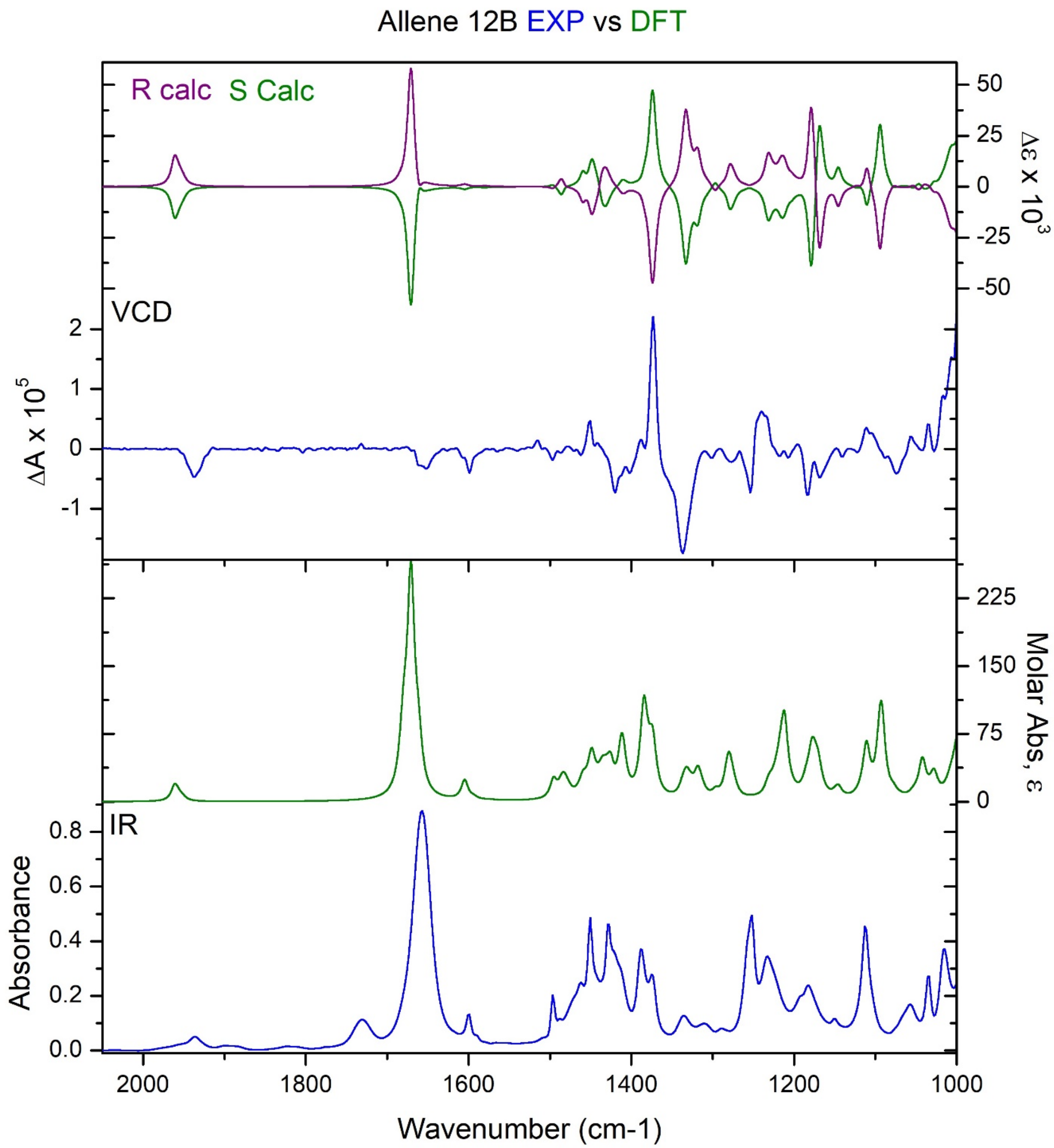
Experimental vs Calculated VCD and IR spectrum of 1b-SiEt$_3$



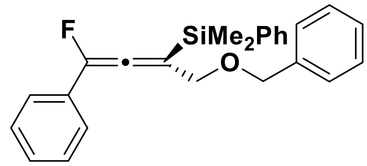


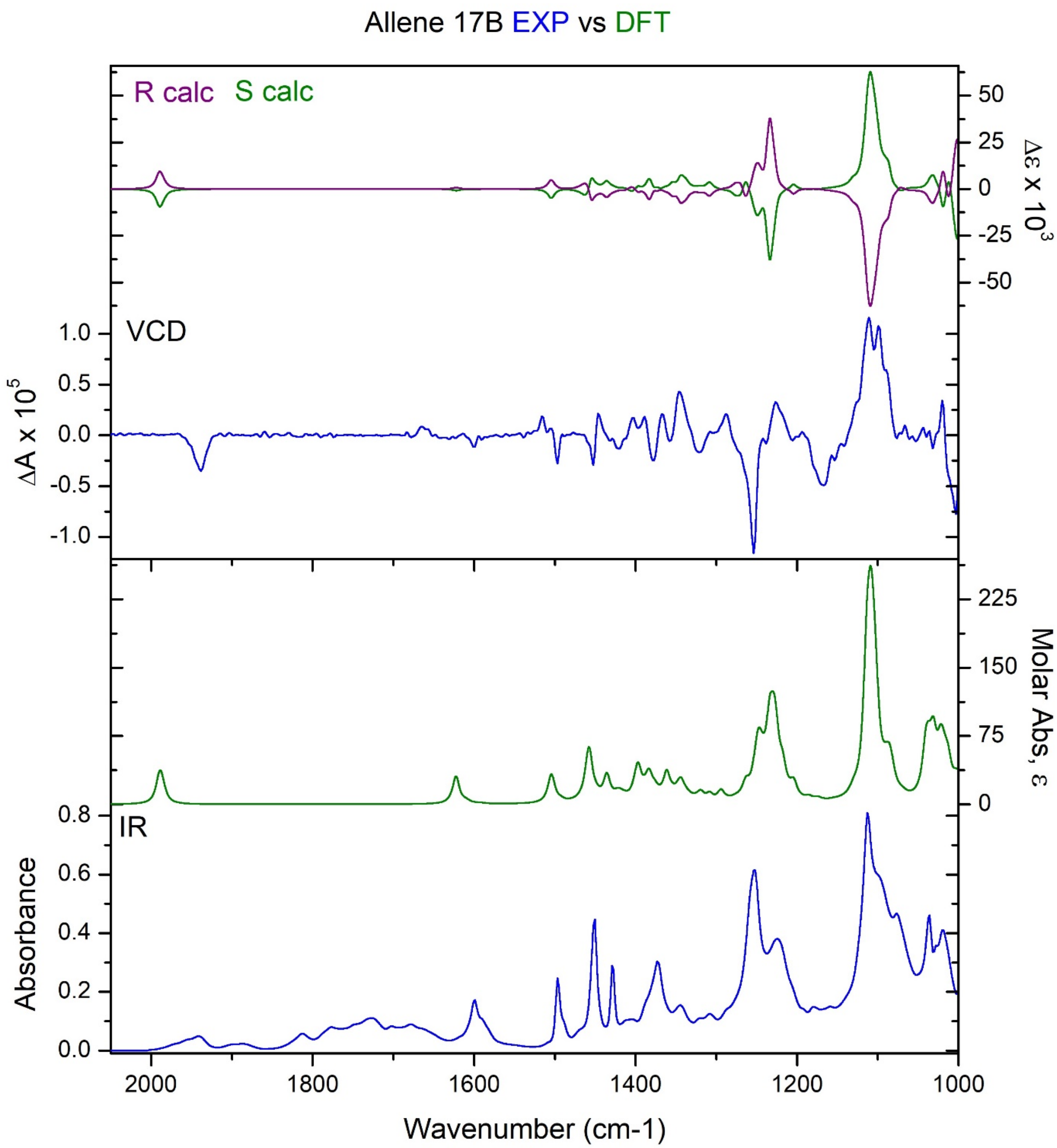
Experimental vs Calculated VCD and IR spectrum of 12b



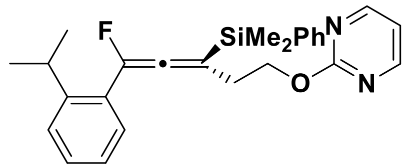


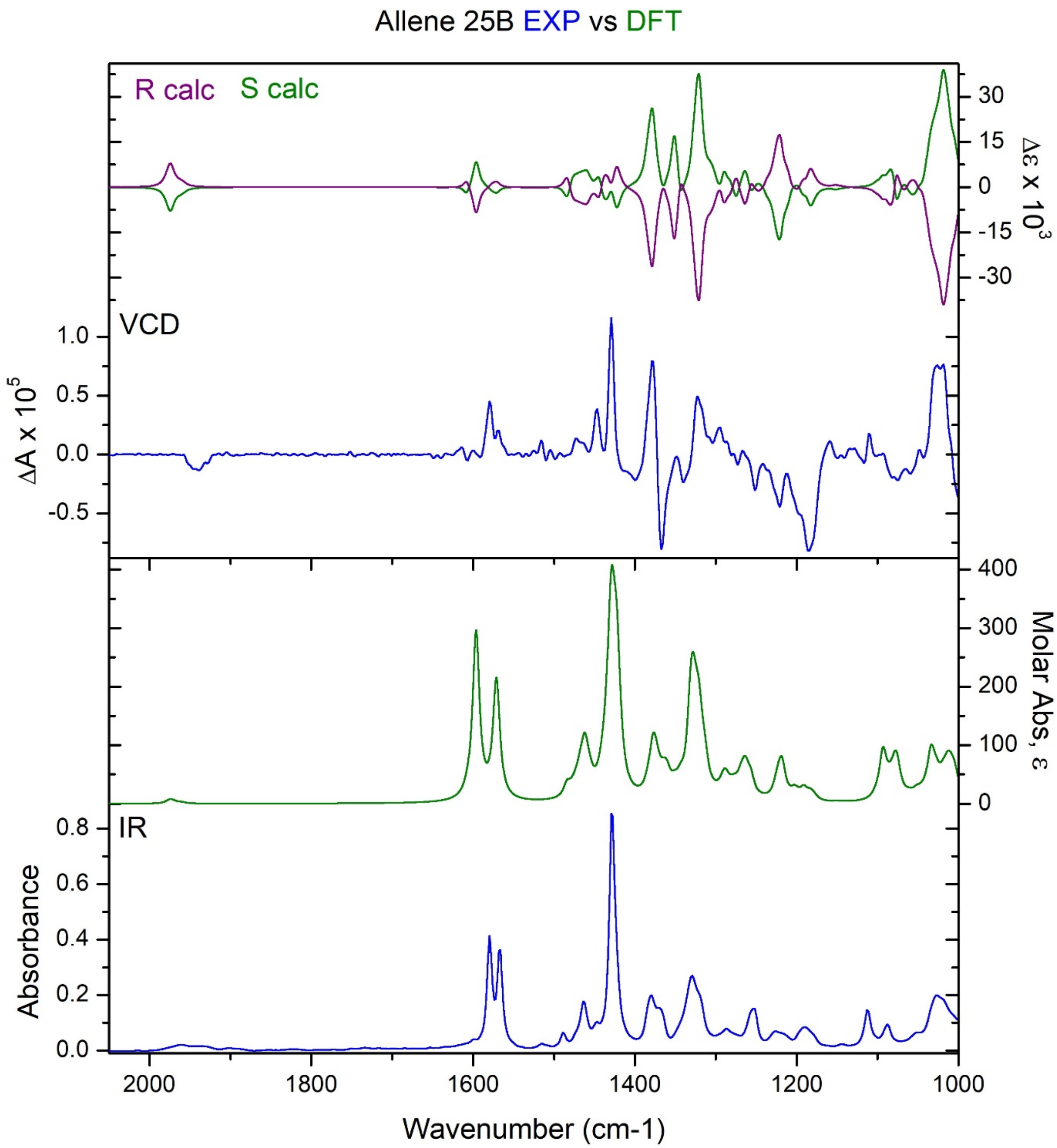
Experimental vs Calculated VCD and IR spectrum of 17b





Experimental vs Calculated VCD and IR spectrum of 25 b





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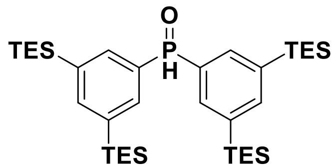
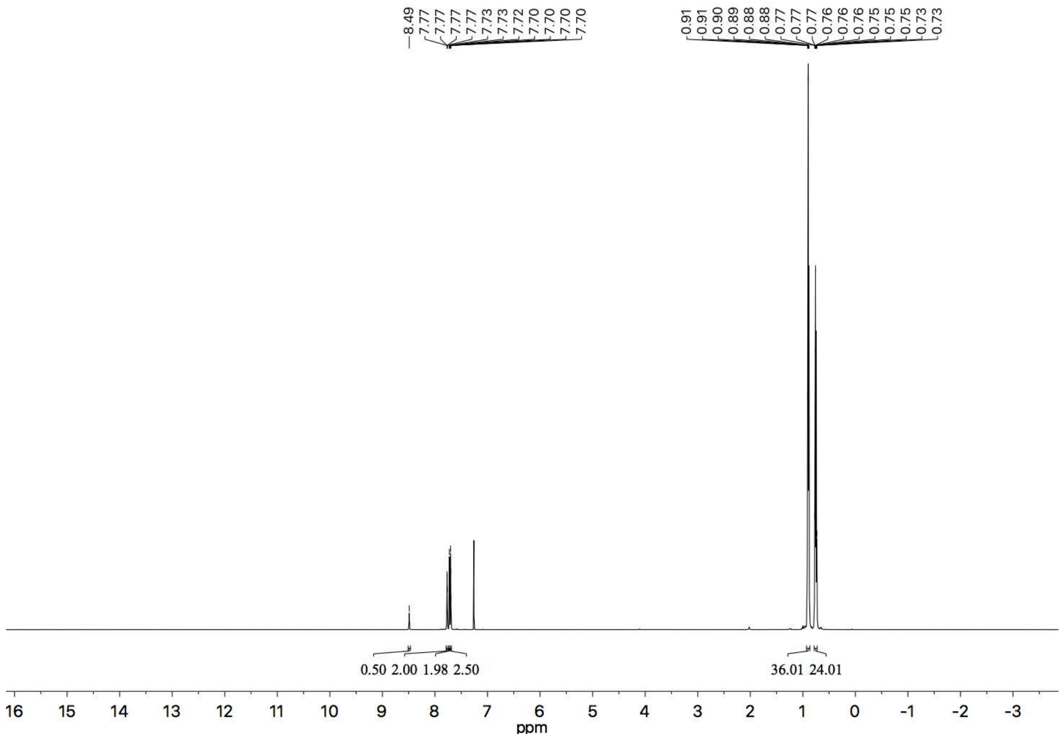
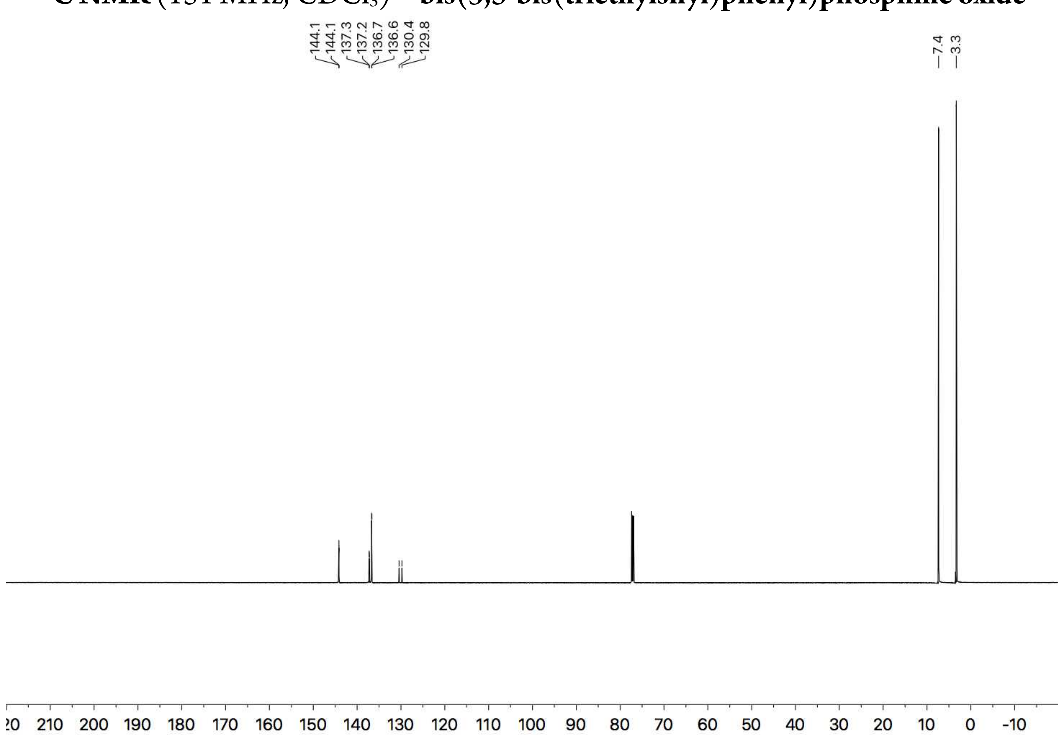
Supporting Information – NMR Spectra



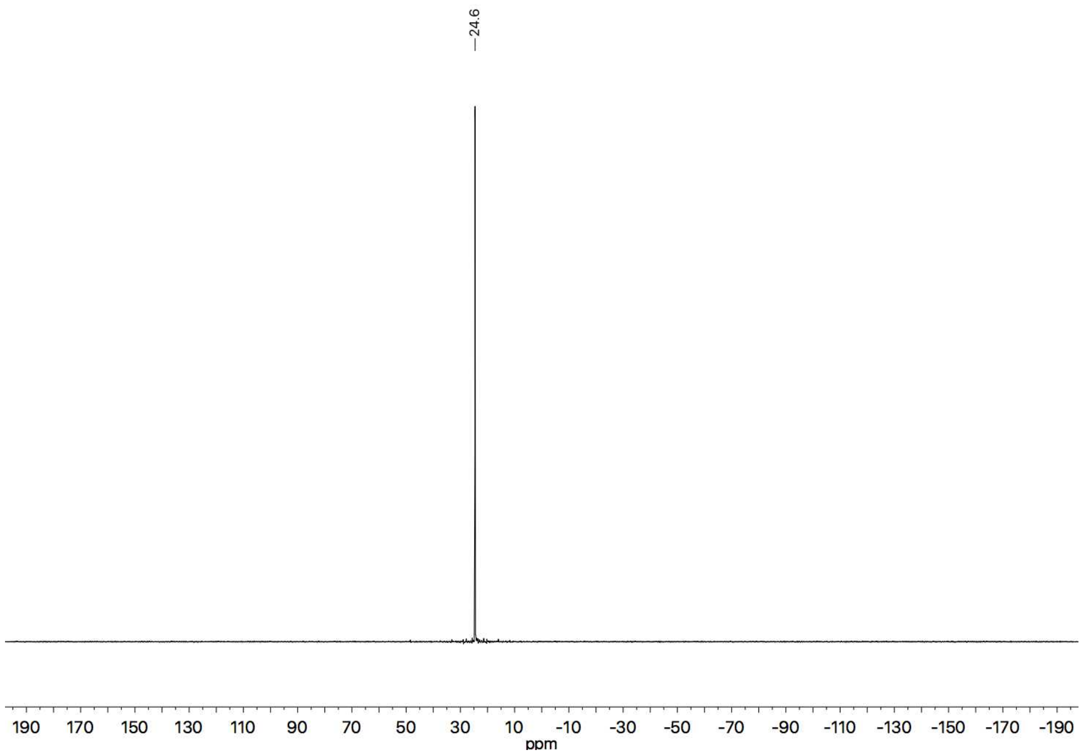
^{1}H NMR (600 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**

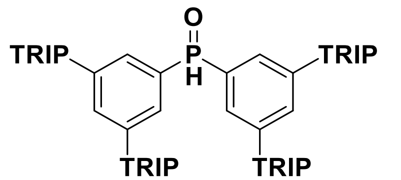


^{13}C NMR (151 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**

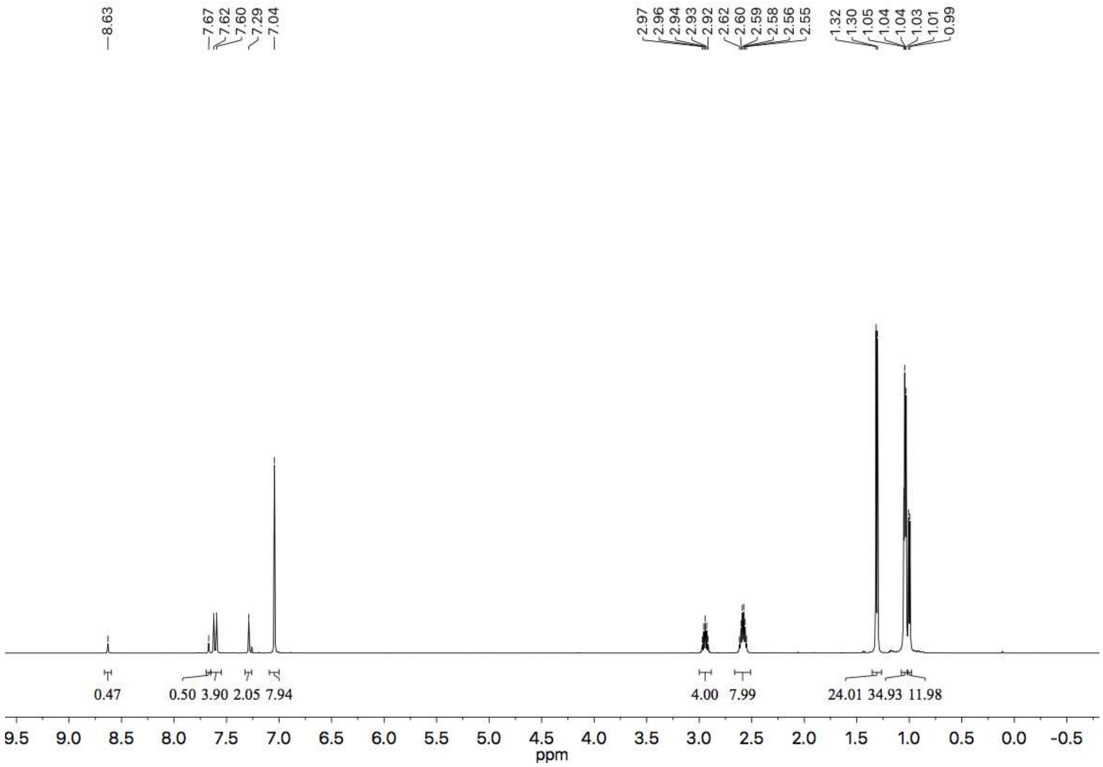


^{31}P NMR (243 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine oxide**

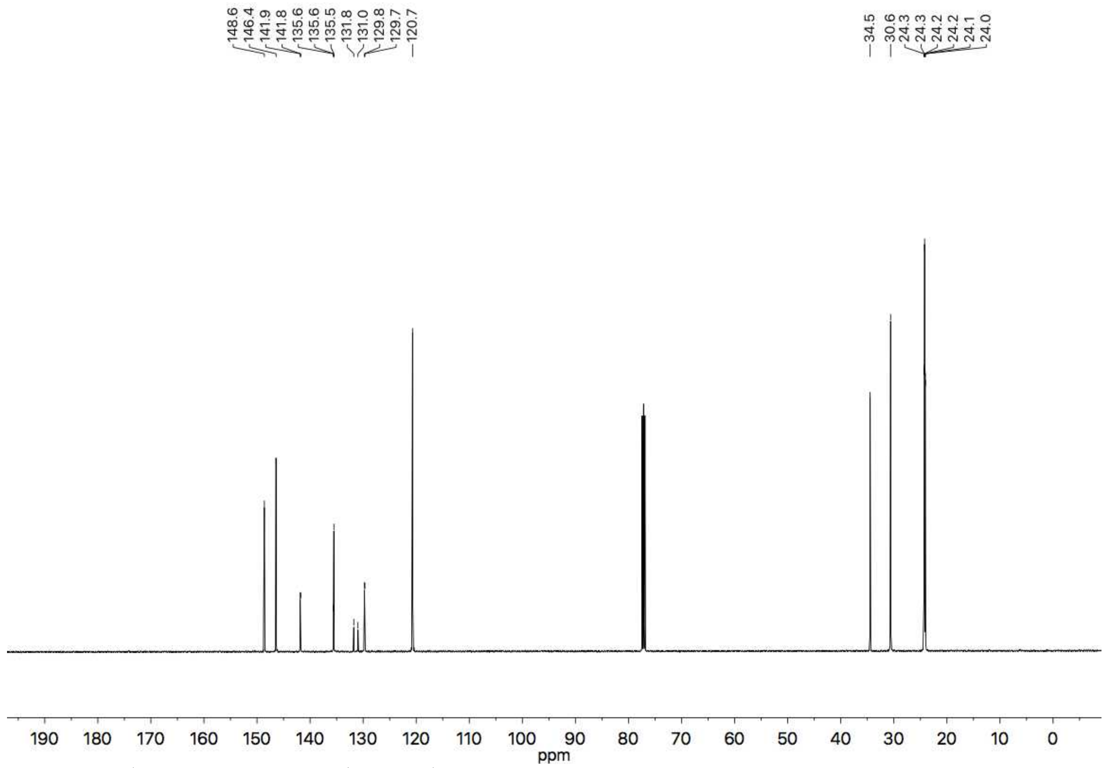




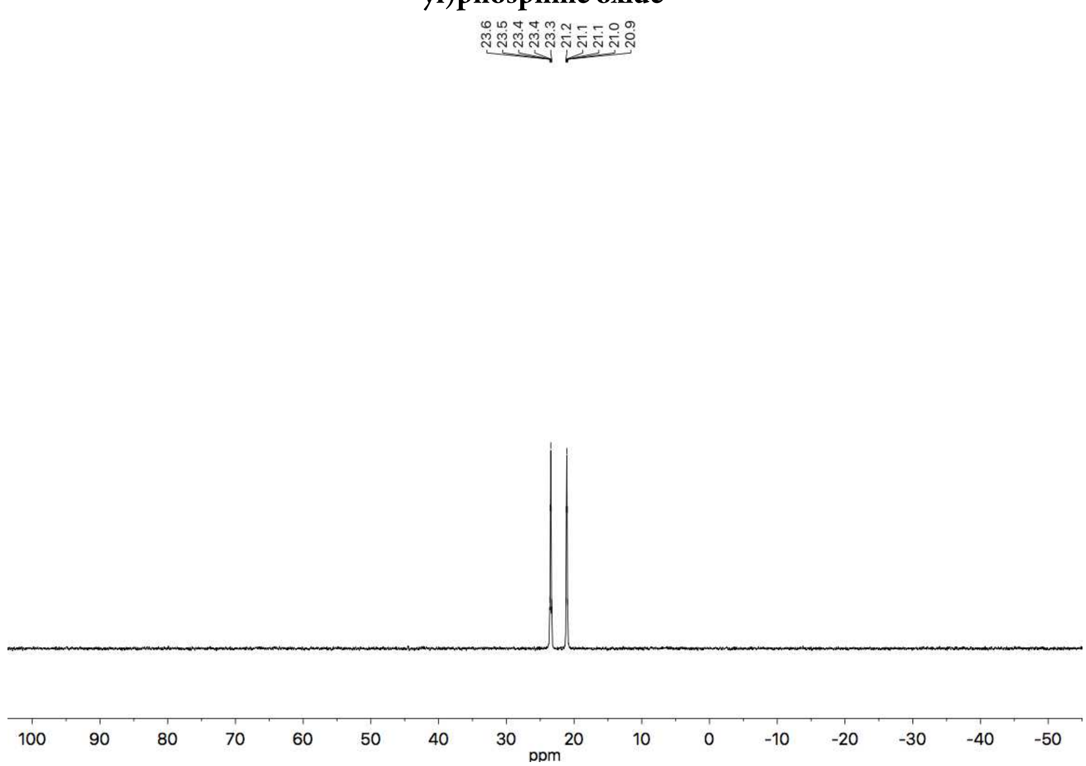
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**

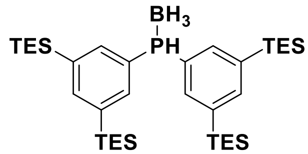


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**



^{31}P NMR (202 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine oxide**





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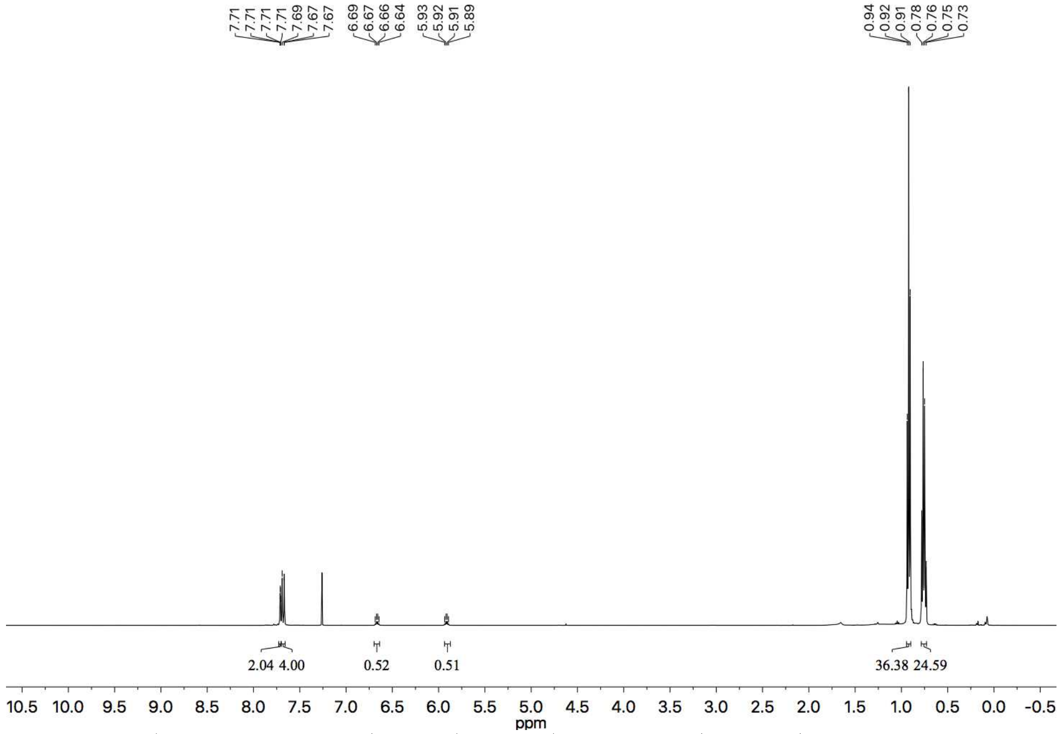

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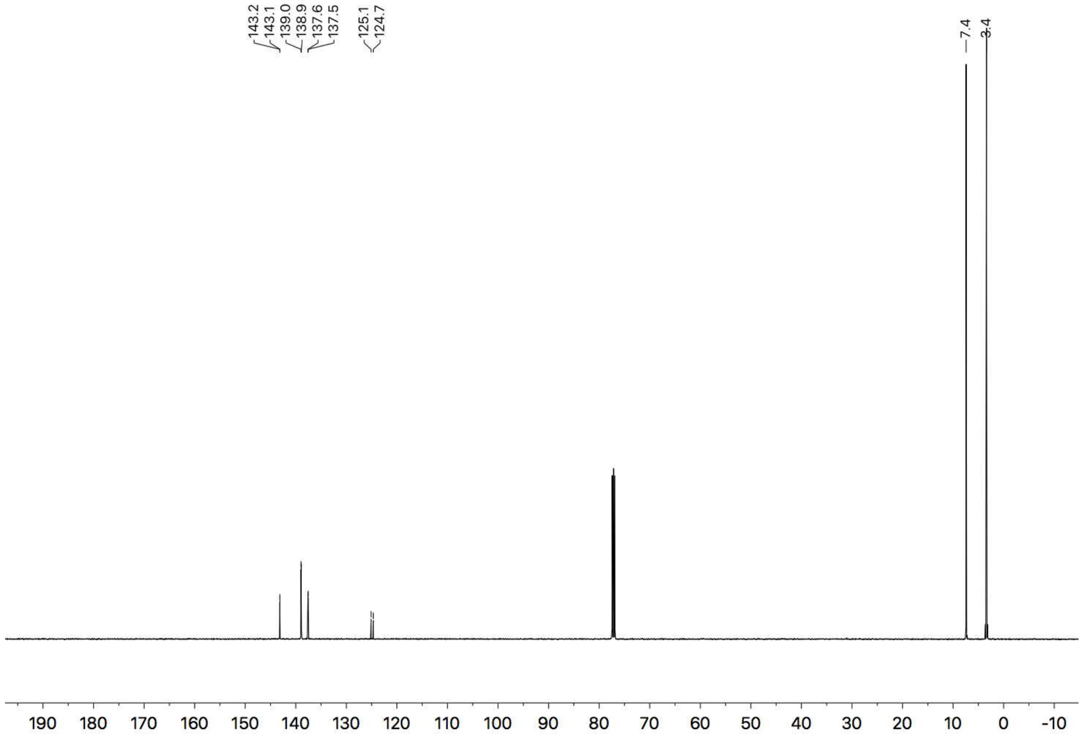

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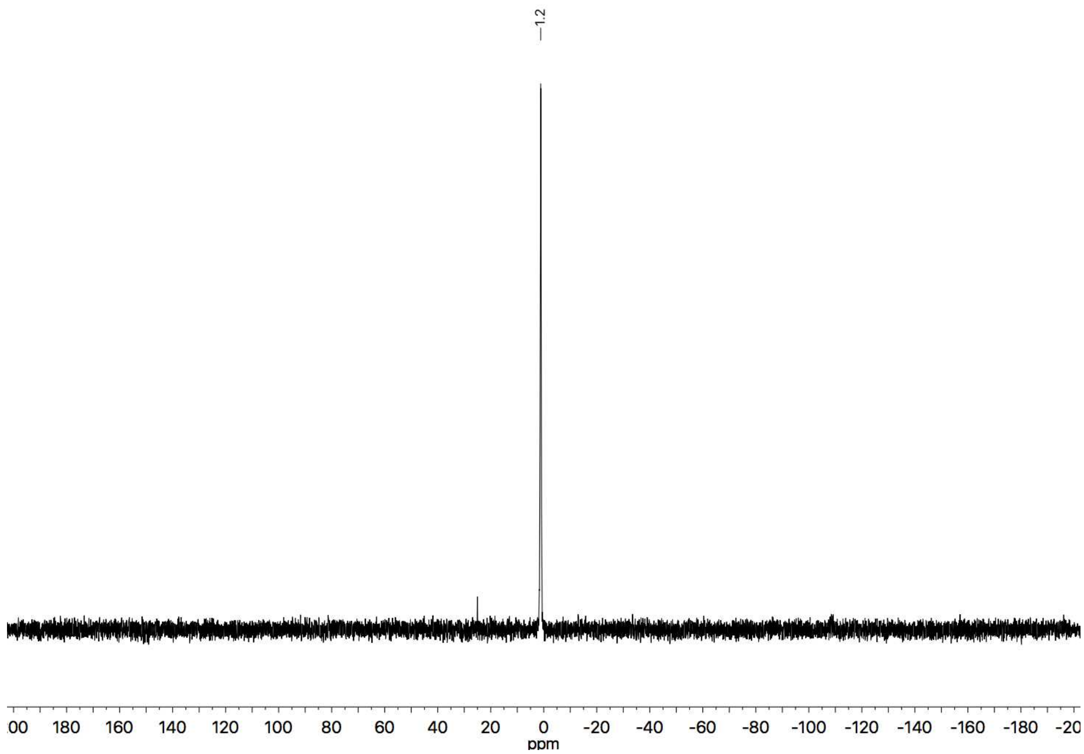
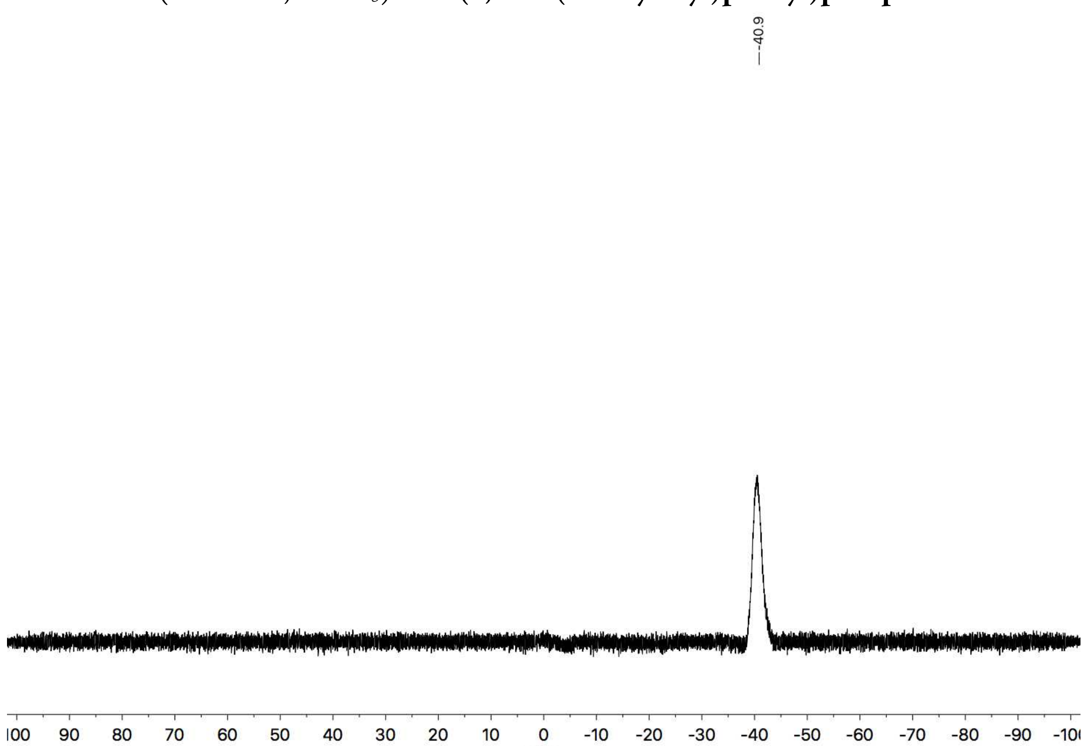
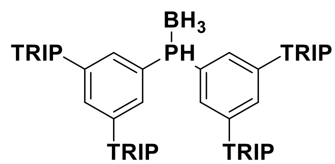
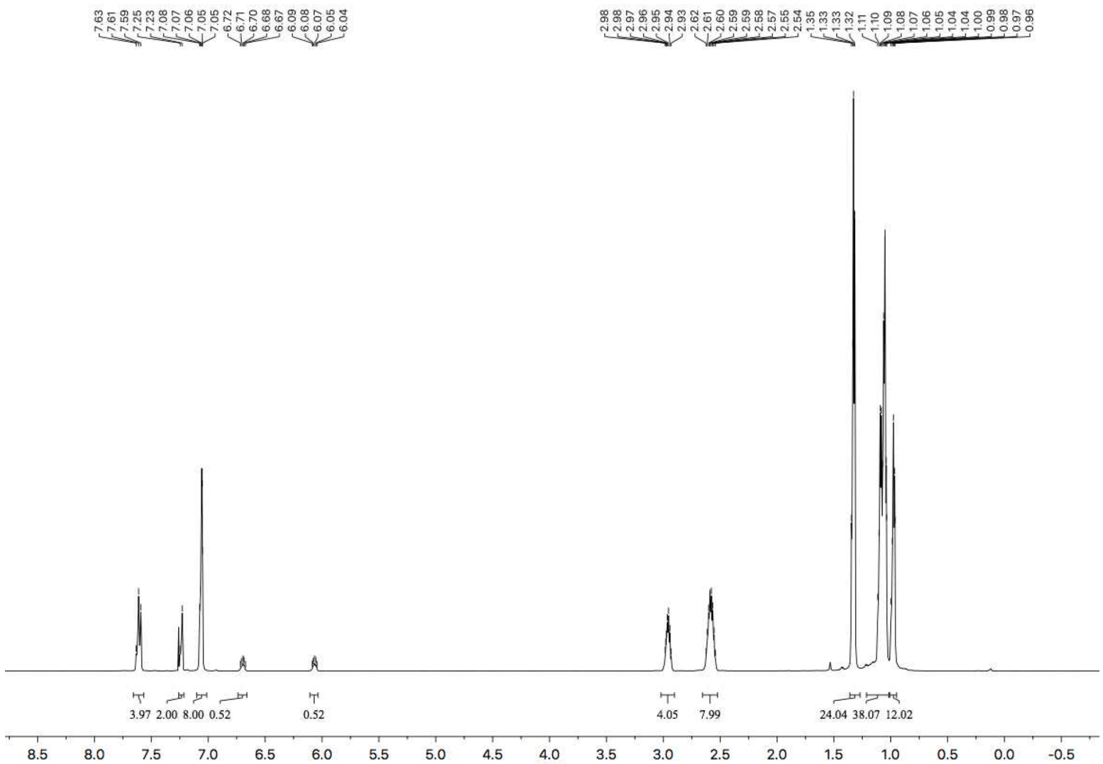


^{11}B NMR (160 MHz, $CDCl_3$) – **bis(3,5-bis(triethylsilyl)phenyl)phosphine borane**





^{1}H NMR (500 MHz, $CDCl_3$) – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



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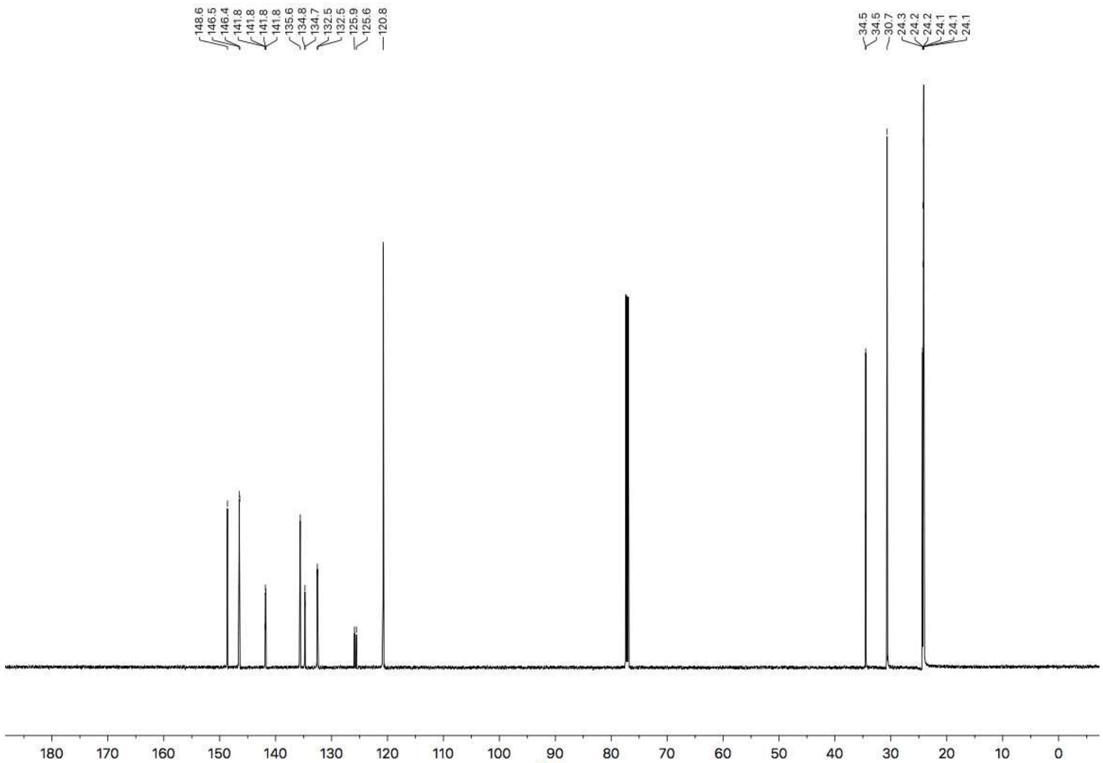
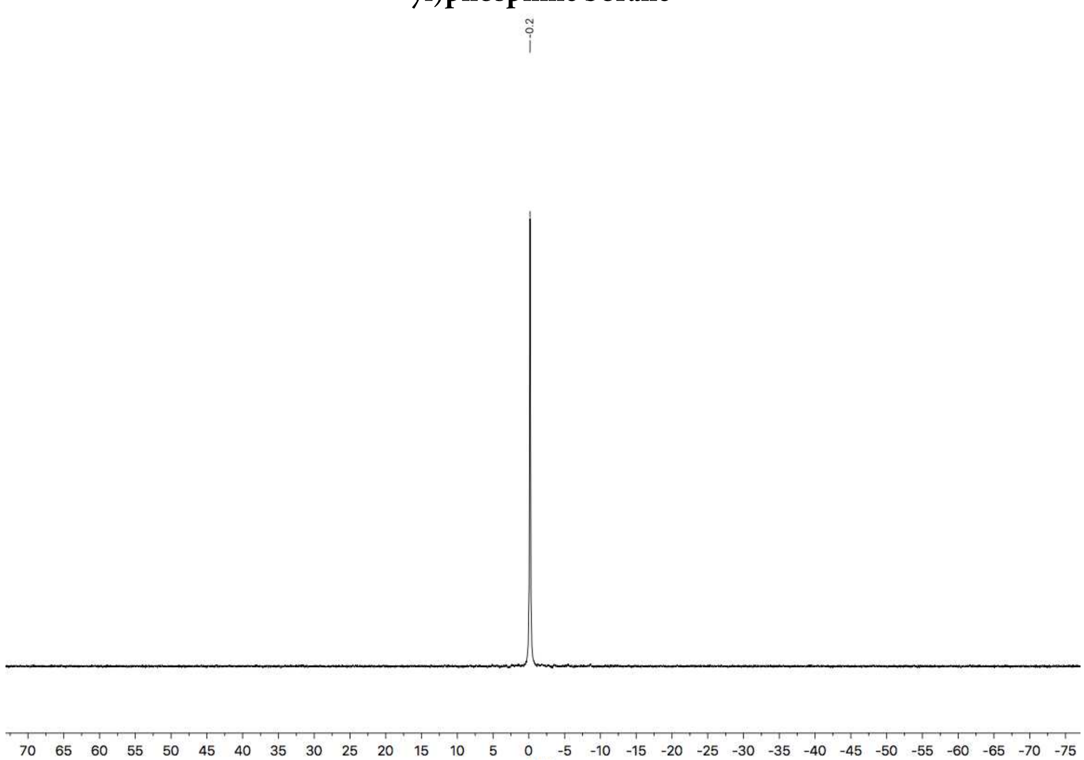
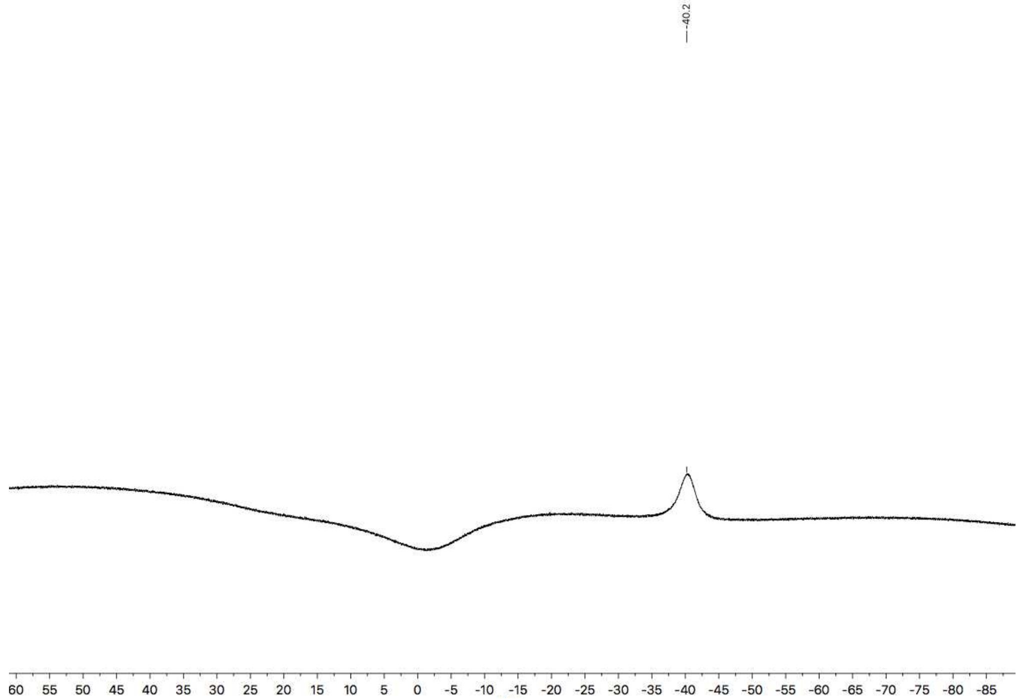
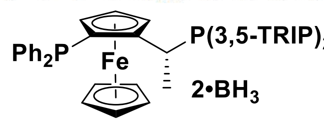


^{31}P NMR (202 MHz, $CDCl_3$) – – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



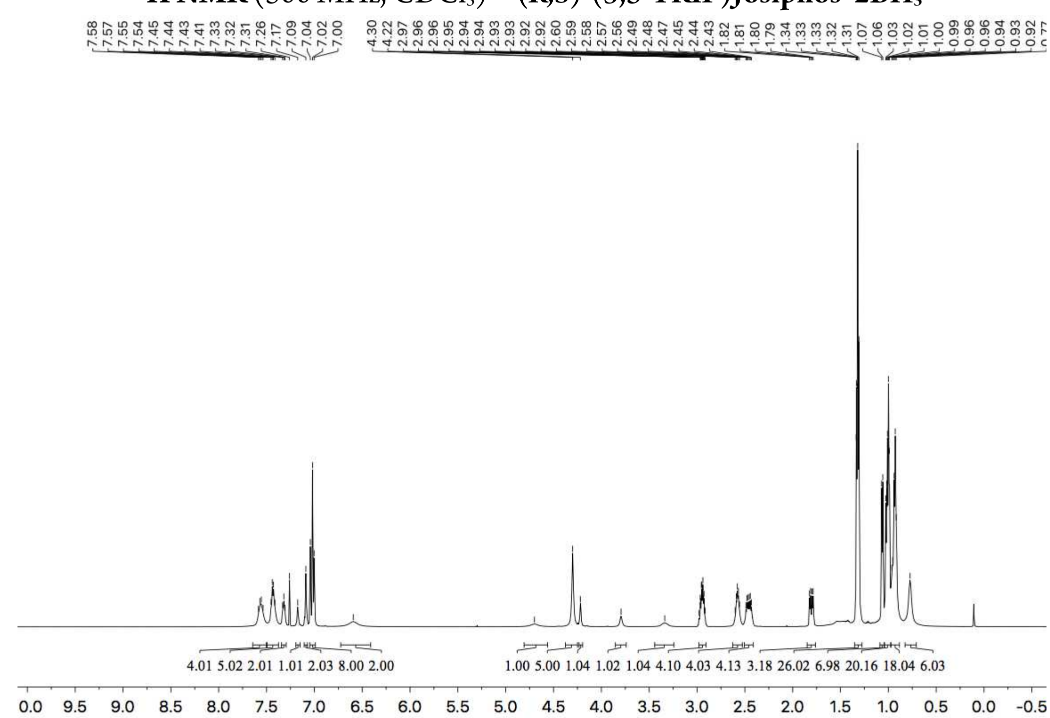
^{11}B NMR (160 MHz, $CDCl_3$) – – **bis(2,2'',4,4'',6,6''-hexaisopropyl-[1,1':3',1''-terphenyl]-5'-yl)phosphine borane**



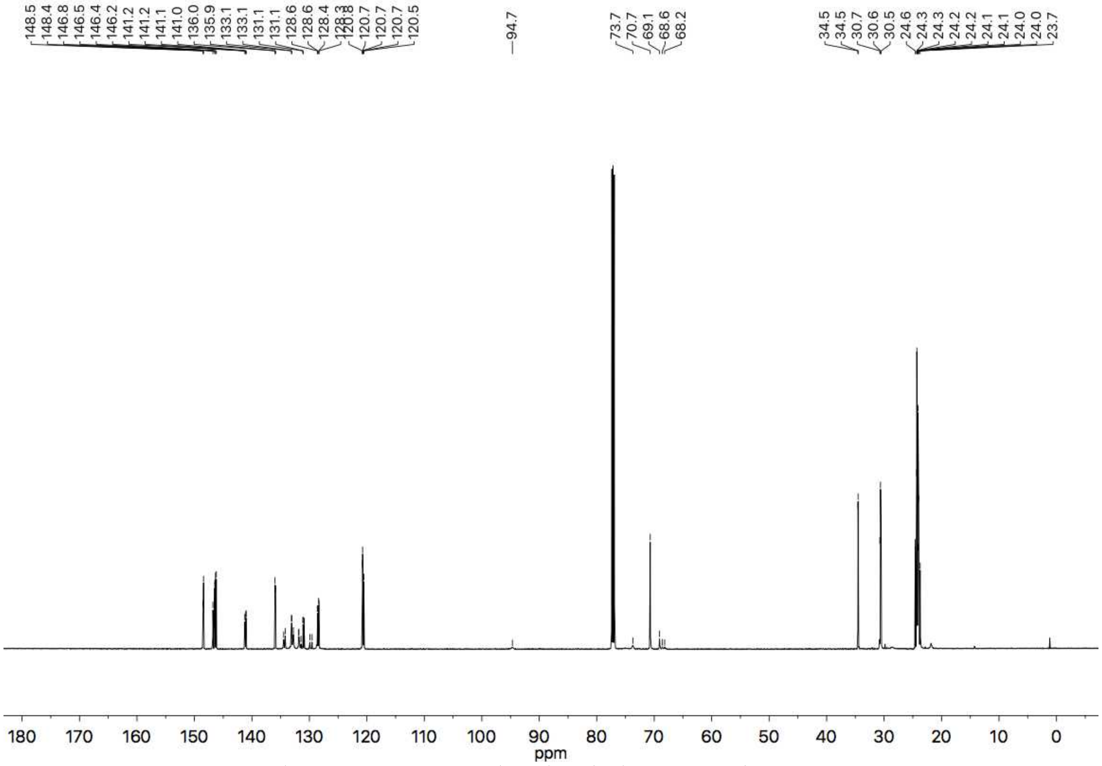


(*R*,*S*)

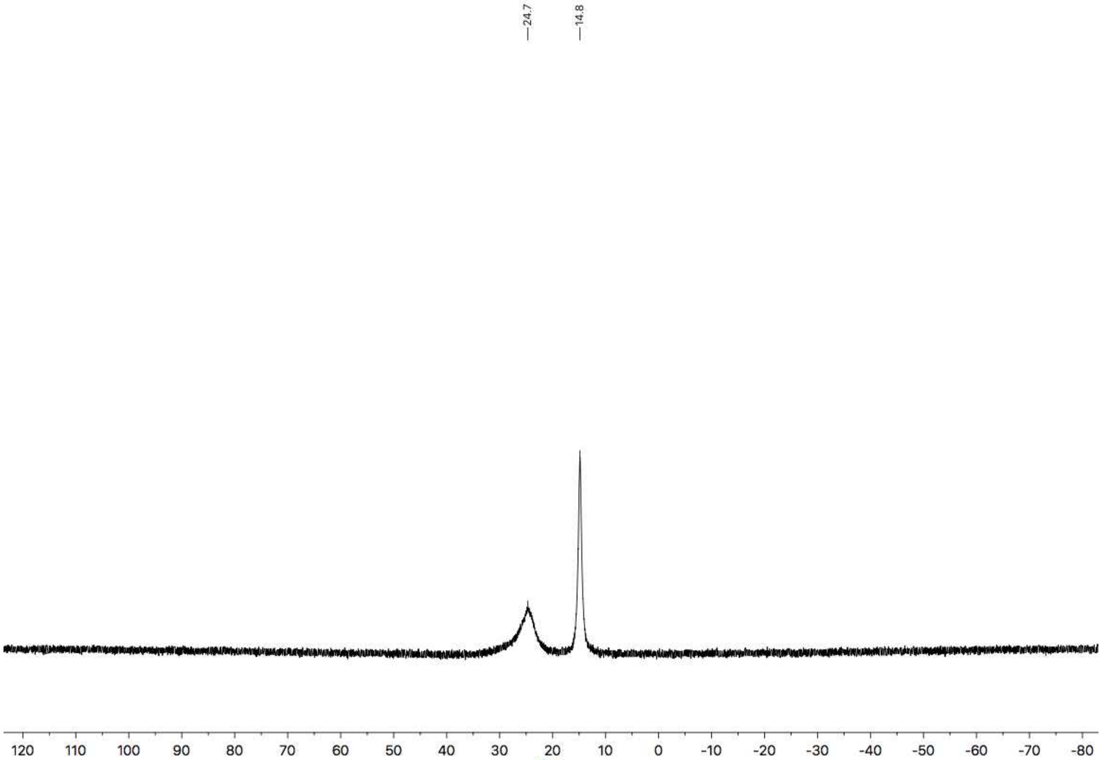
^{1}H NMR (500 MHz, $CDCl_3$) – **(*R,S*)-(3,5-TRIP)Josiphos•2BH$_3$**



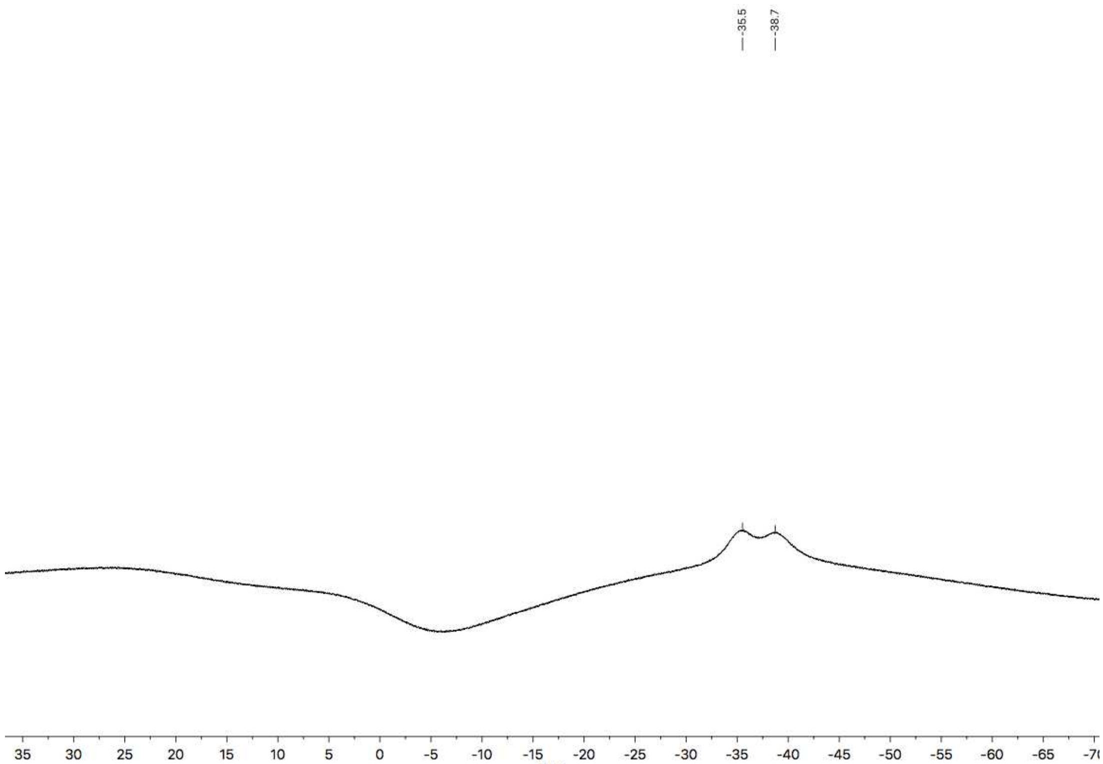
^{13}C NMR (151 MHz, CD_2Cl_2) – (***R,S***)-(**3,5-TRIP**)**Josiphos•2BH$_3$**

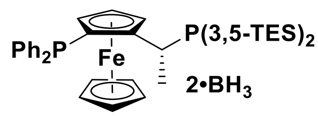


^{31}P NMR (202 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TRIP**)**Josiphos•2BH$_3$**



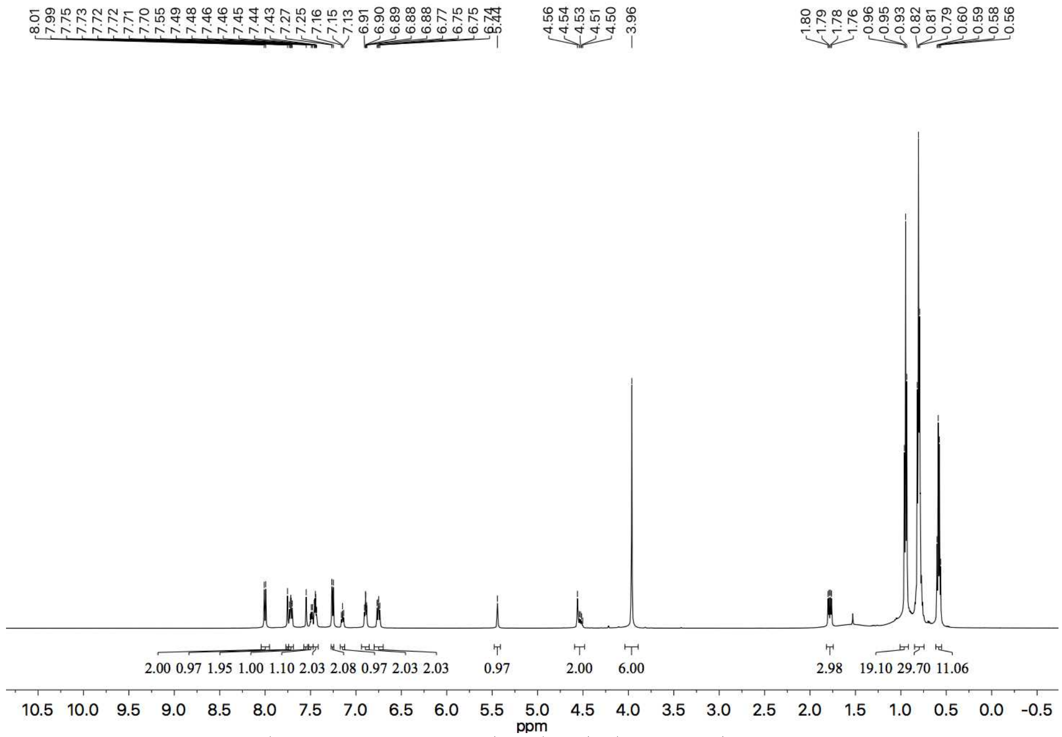
^{11}B NMR (160 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TRIP**)**Josiphos•2BH$_3$**


-35.5
-38.7
35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65

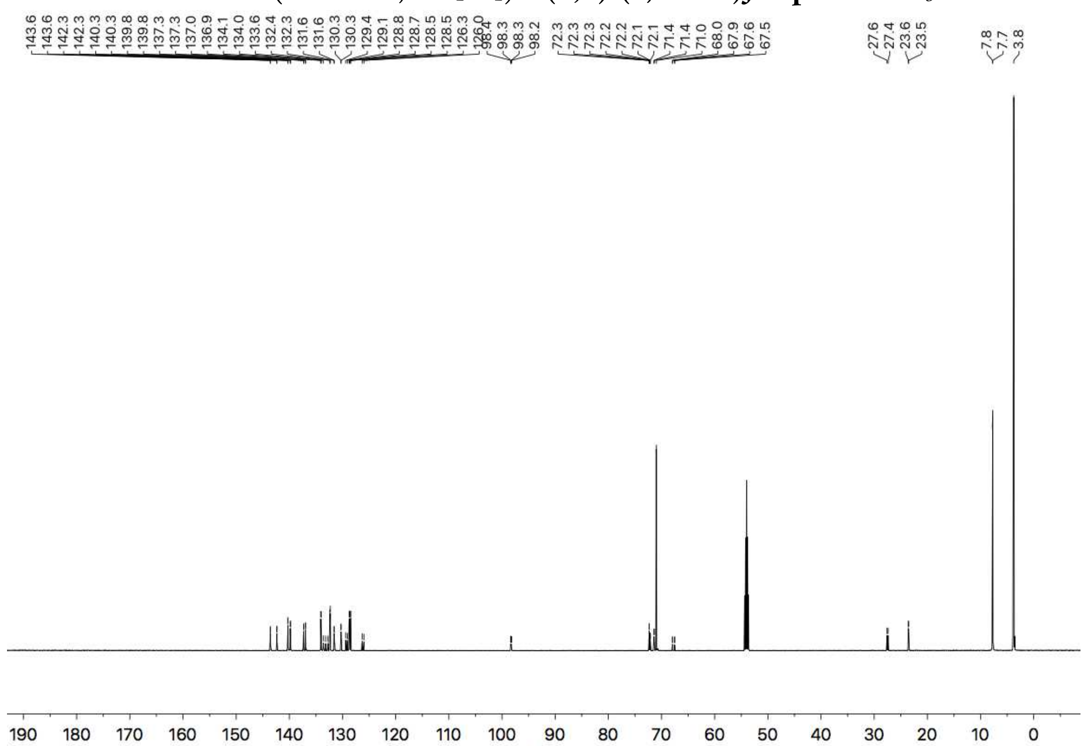


(*R*,*S*)

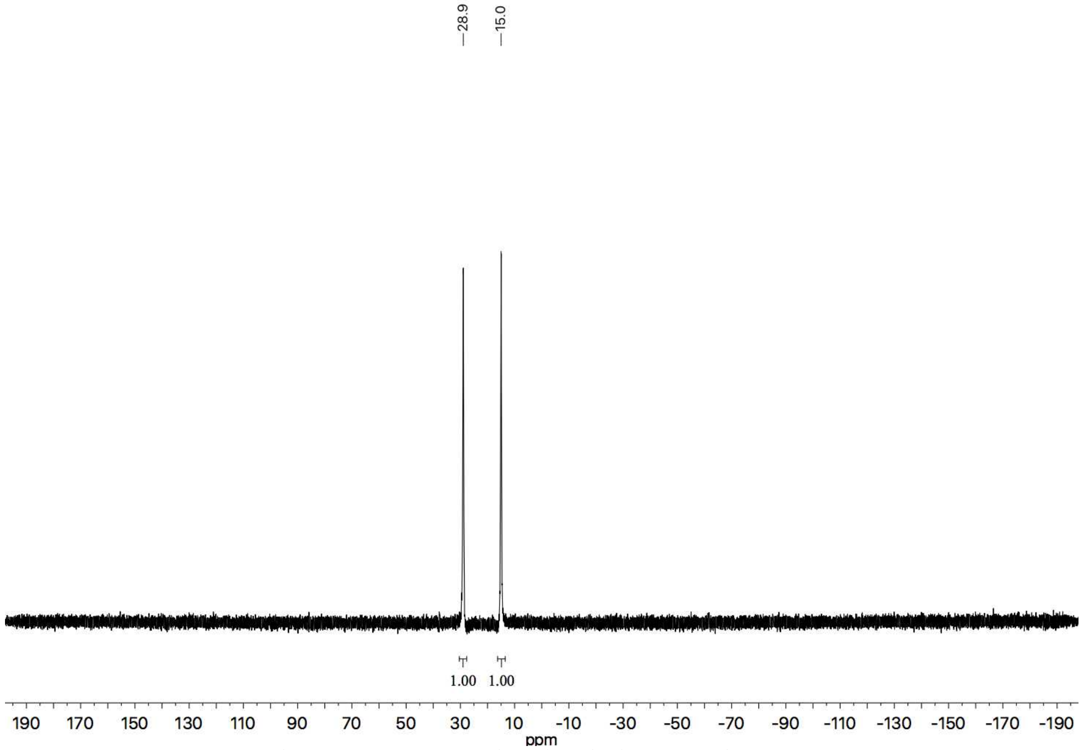
^{1}H NMR (500 MHz, $CDCl_3$) – (***R*,*S***)-**(3,5-TES)Josiphos•2BH$_3$**



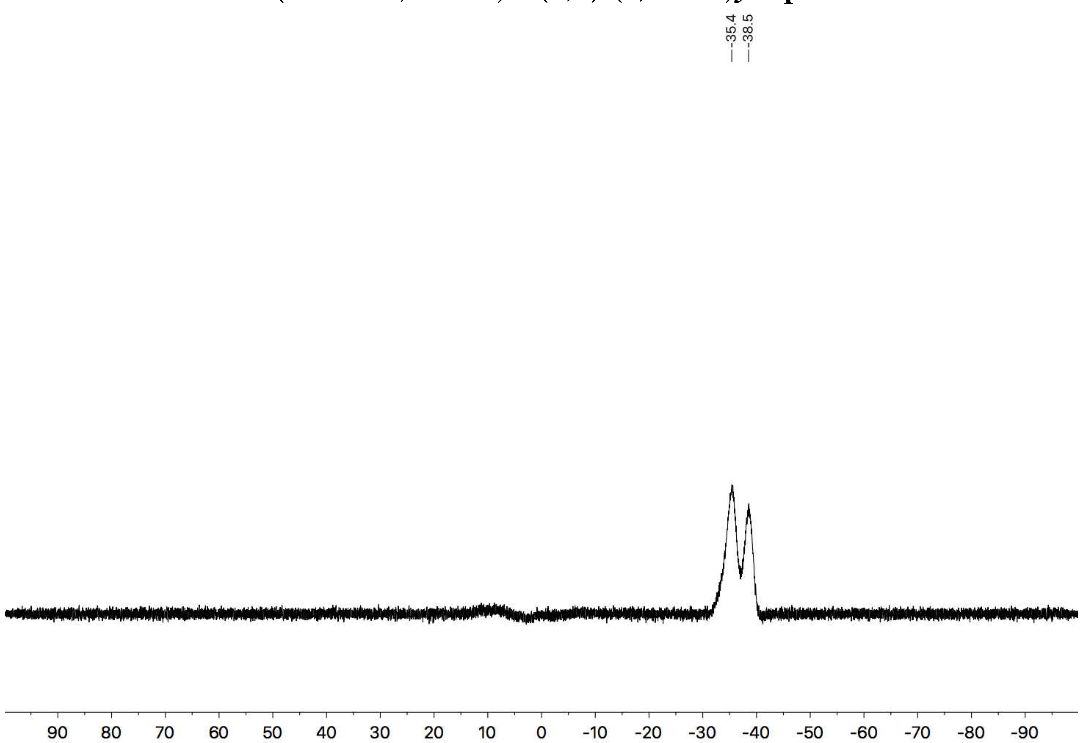
^{13}C NMR (151 MHz, CD_2Cl_2) – (***R*,*S***)-**(3,5-TES)Josiphos•2BH$_3$**

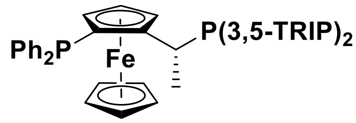


^{31}P NMR (202 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES)Josiphos•2BH$_3$**

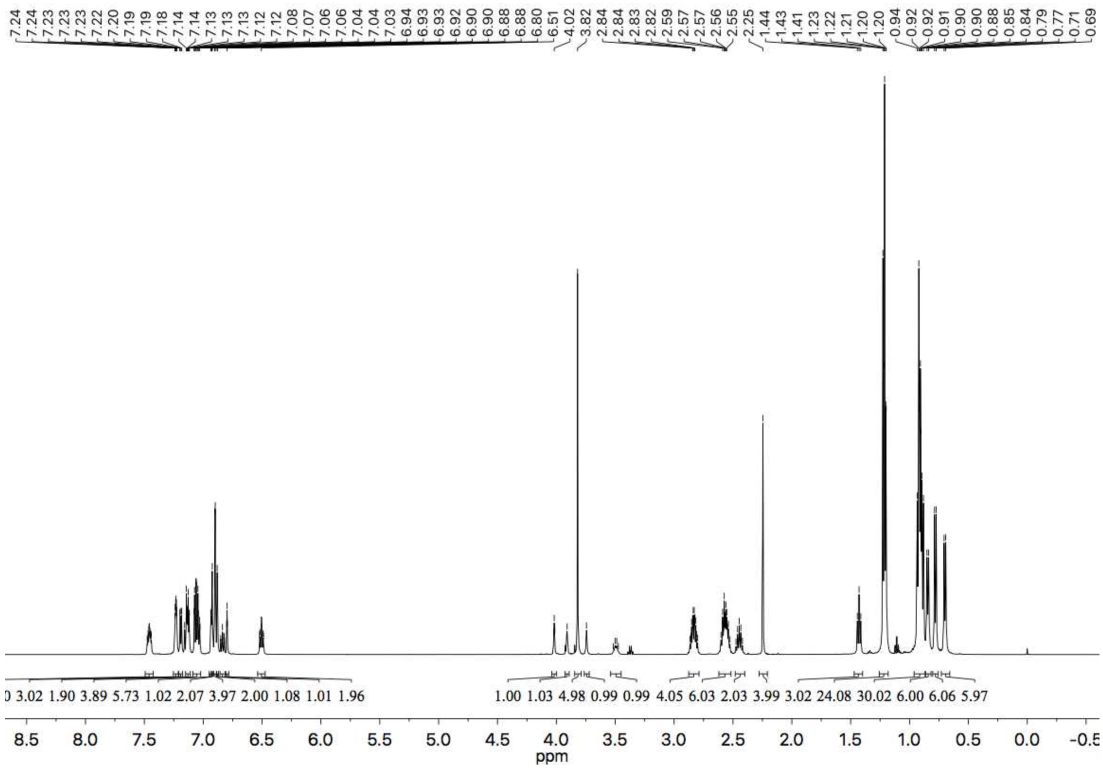


^{11}B NMR (160 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES)Josiphos•2BH$_3$**

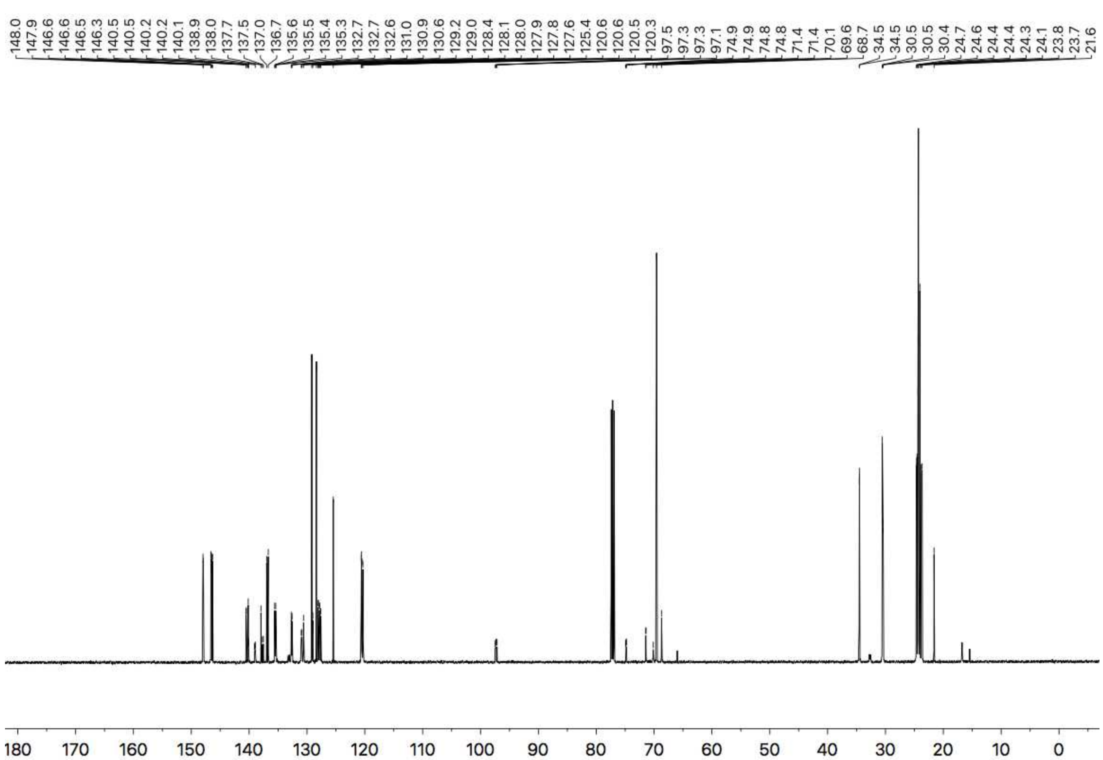




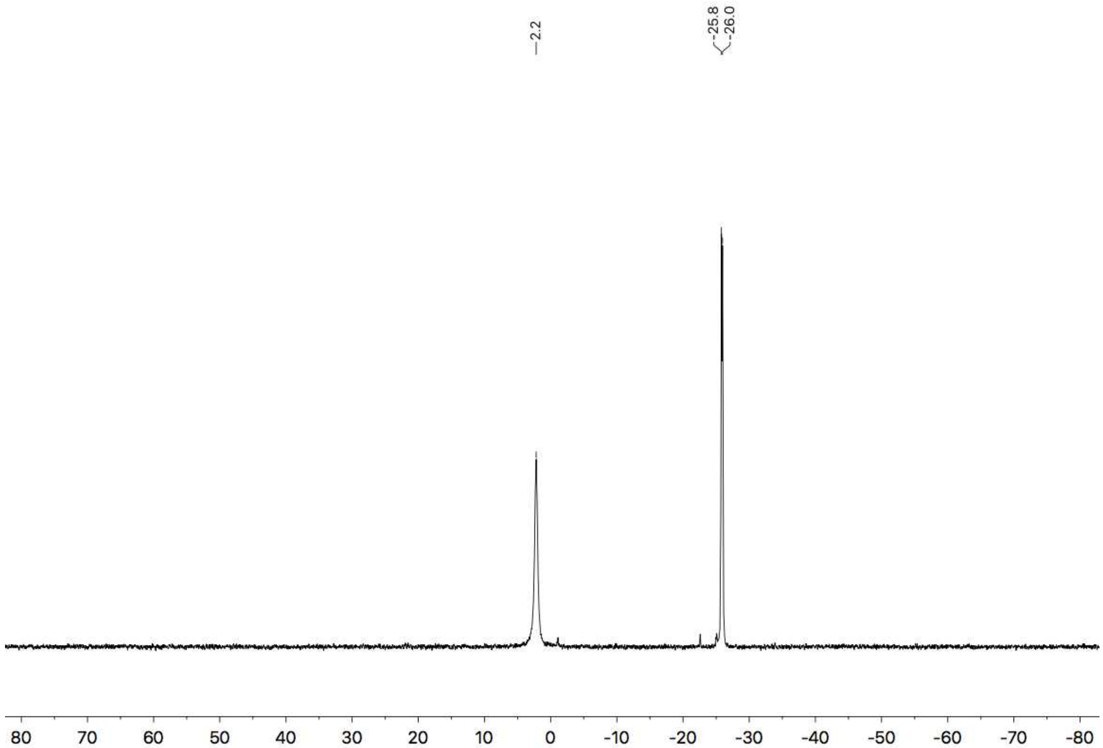
¹H NMR (500 MHz, CDCl₃) – (***R,S***)-(**3,5-TES**)**Josiphos**

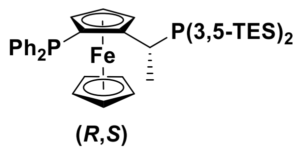


¹³C NMR (126 MHz, CDCl₃) – (***R,S***)-(**3,5-TRIP**)**Josiphos**

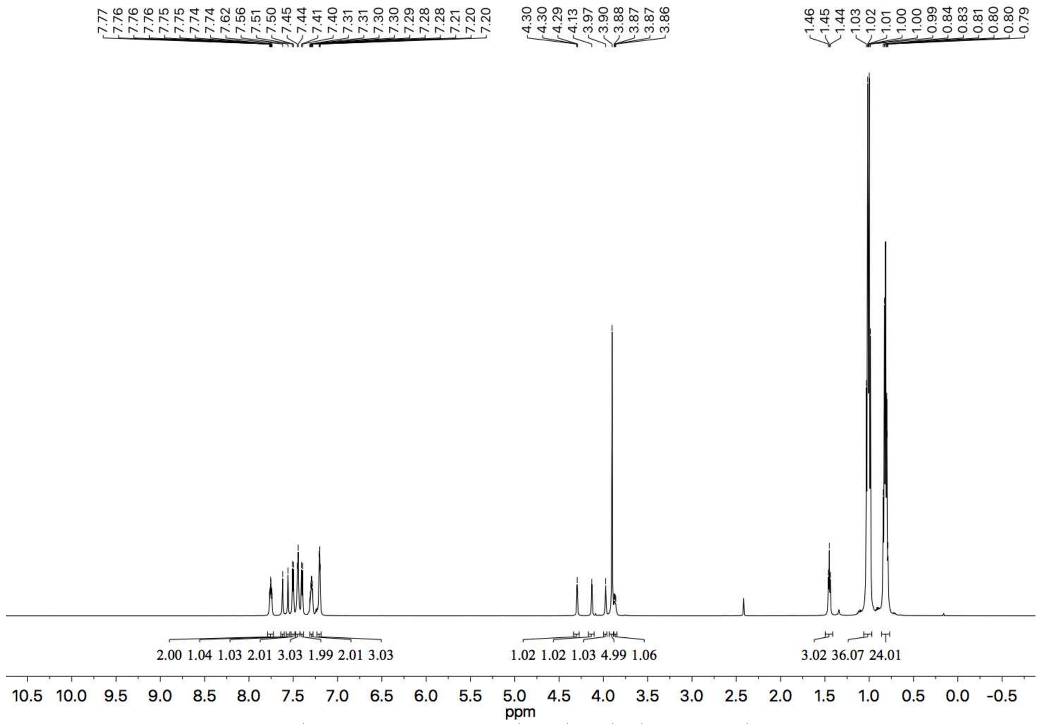


^{31}P NMR (202 MHz, $CDCl_3$) – ***(R,S)*-(3,5-TRIP)Josiphos**

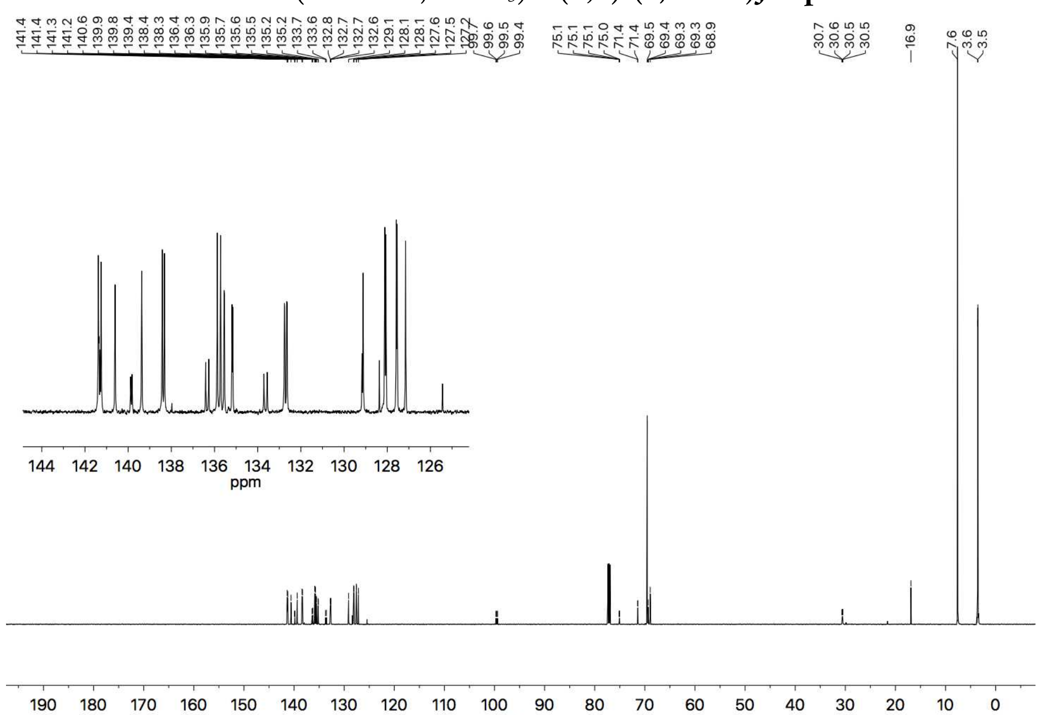




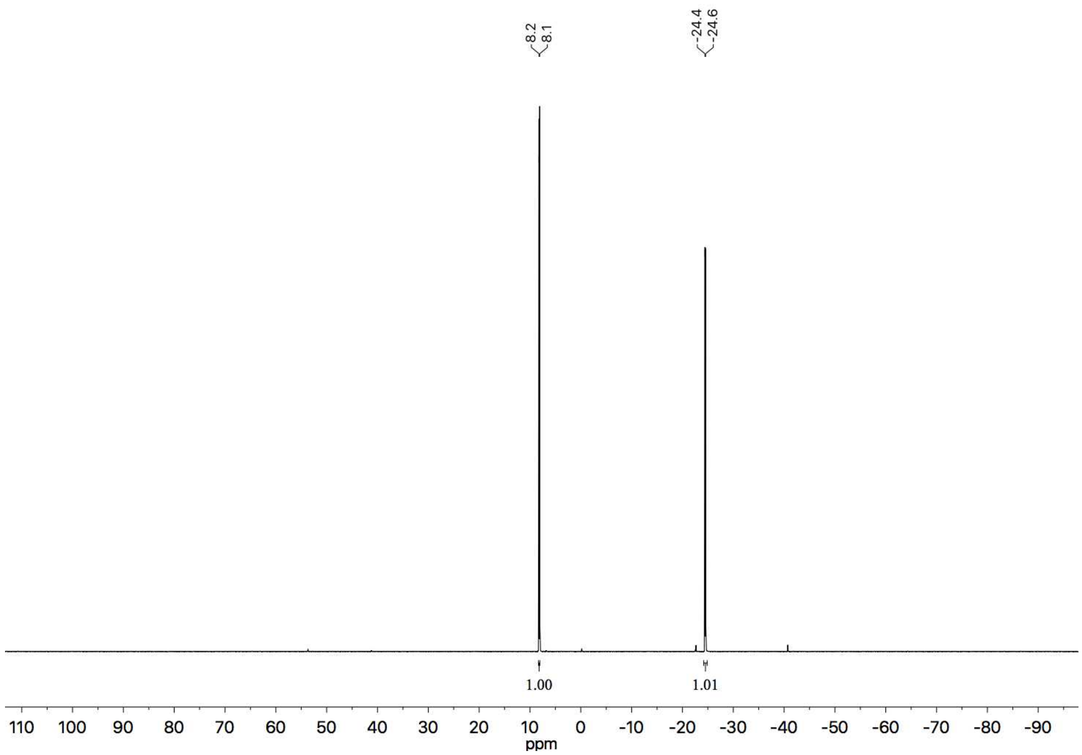
^{1}H NMR (600 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

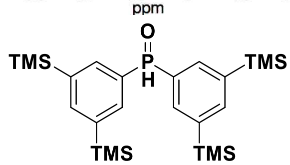


^{13}C NMR (151 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

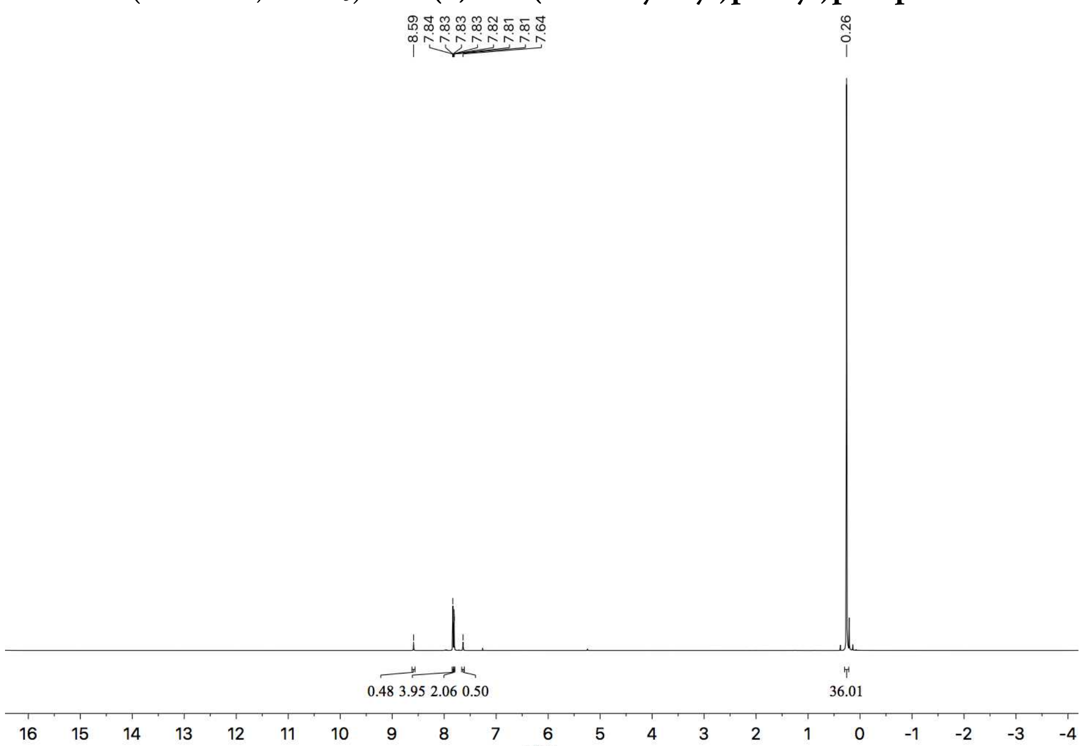


^{31}P NMR (243 MHz, $CDCl_3$) – (***R,S***)-(**3,5-TES**)**Josiphos**

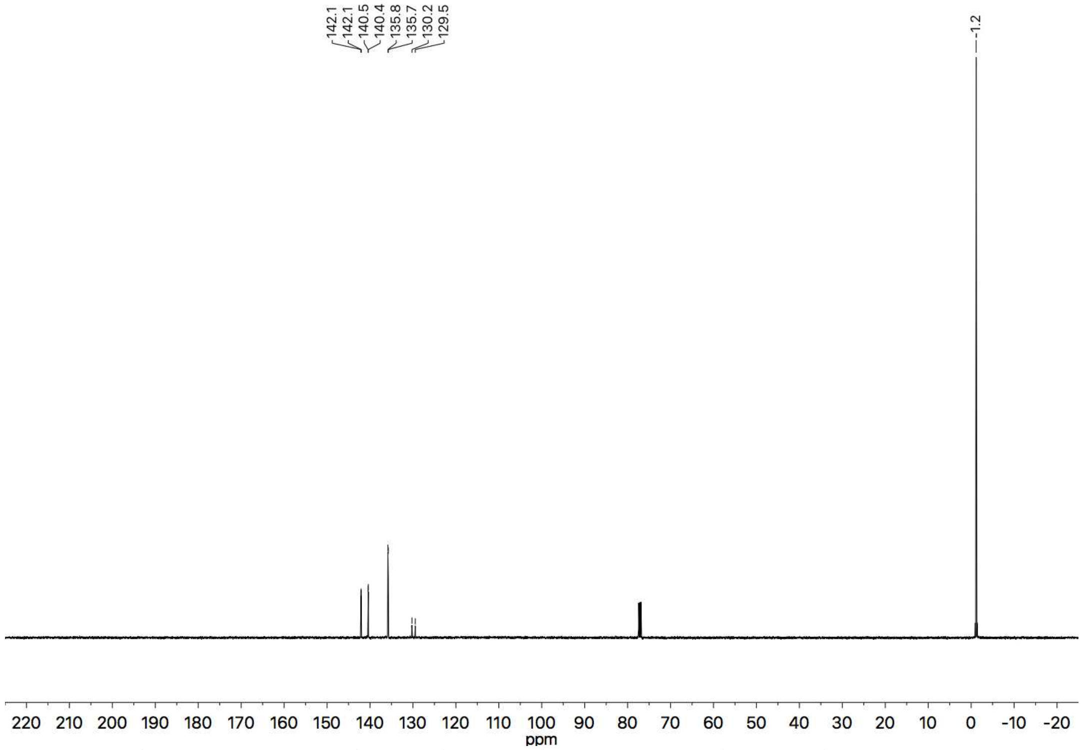




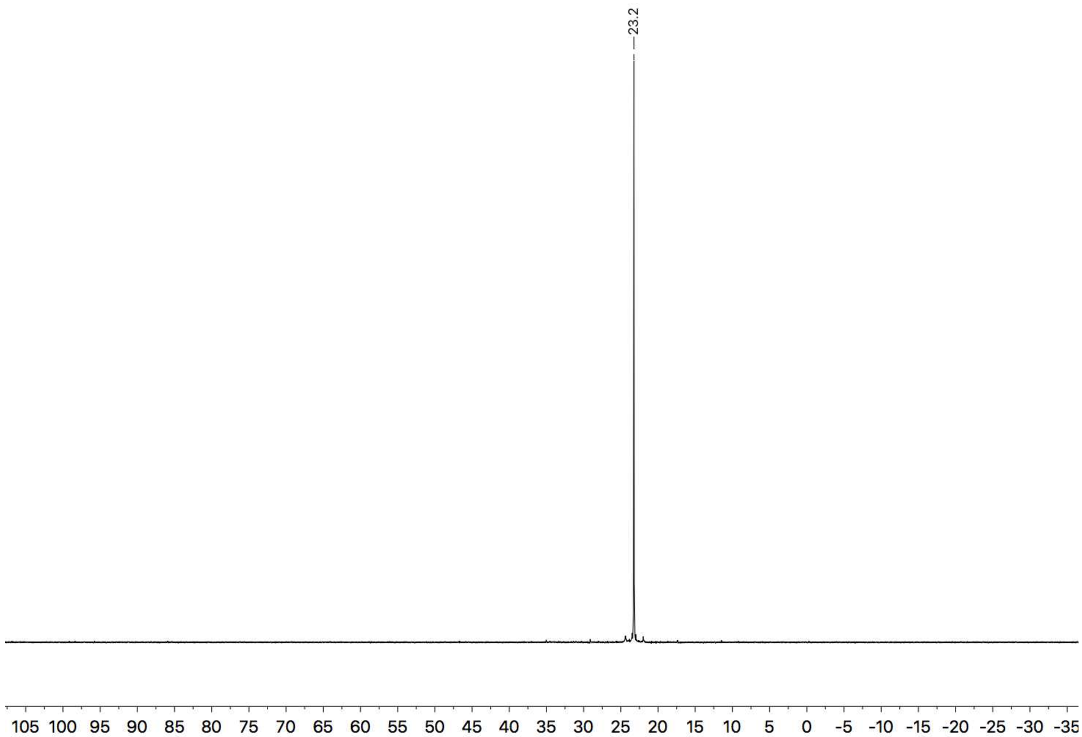
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

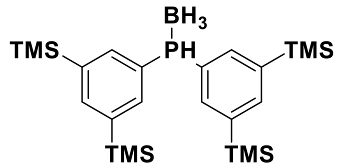


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

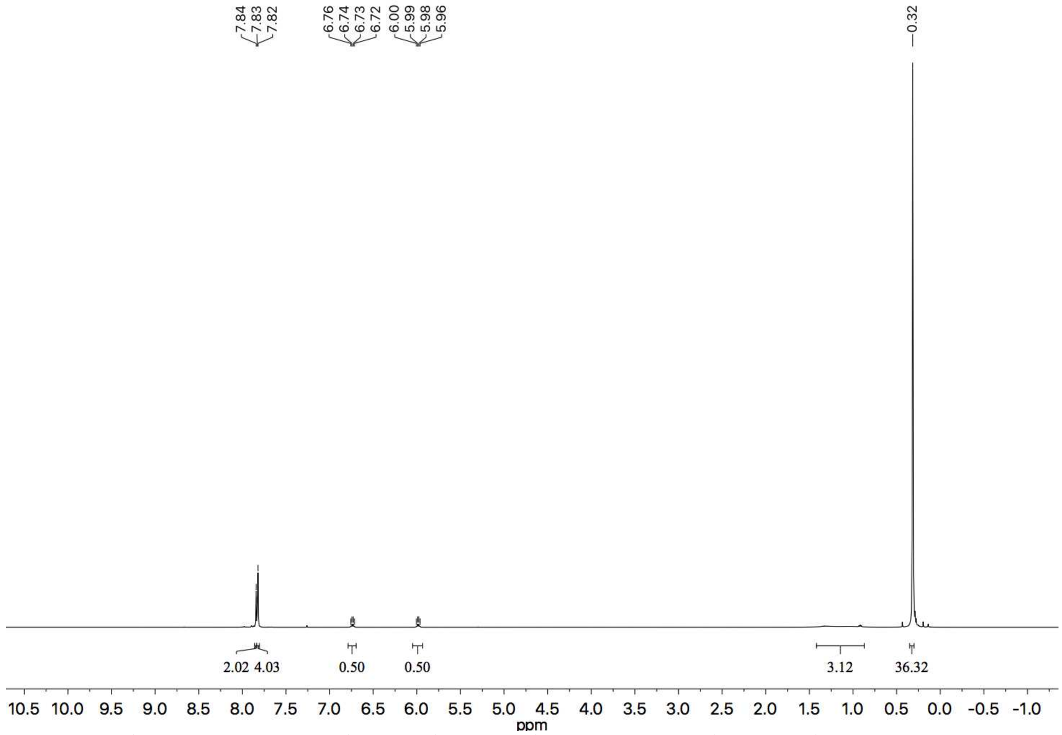


^{31}P NMR (203 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

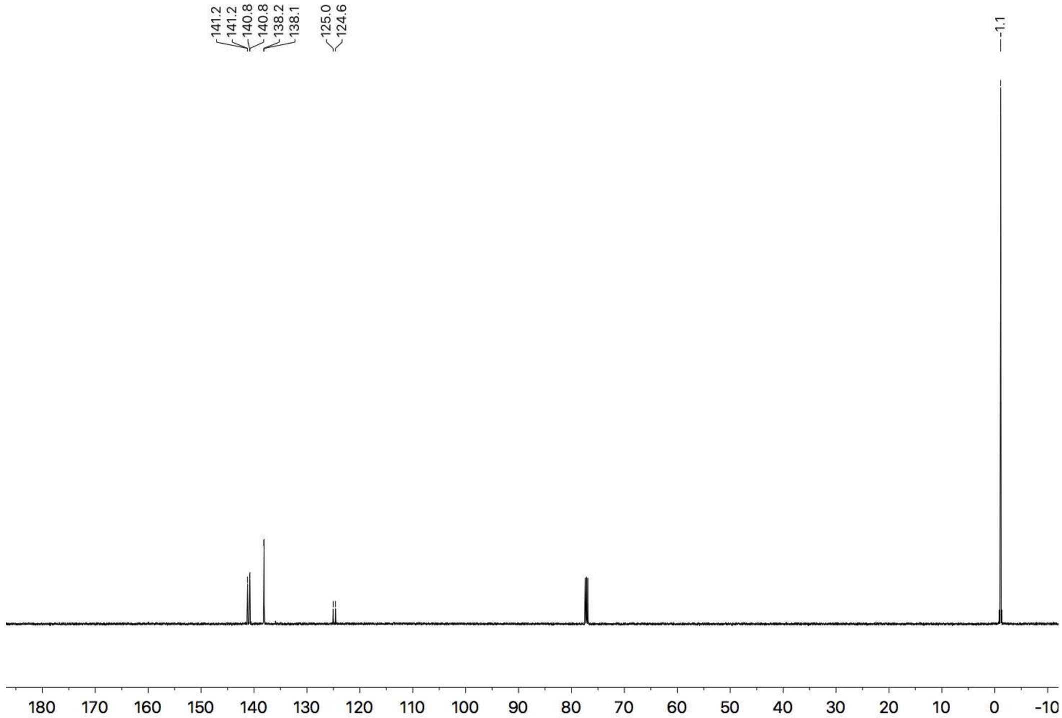




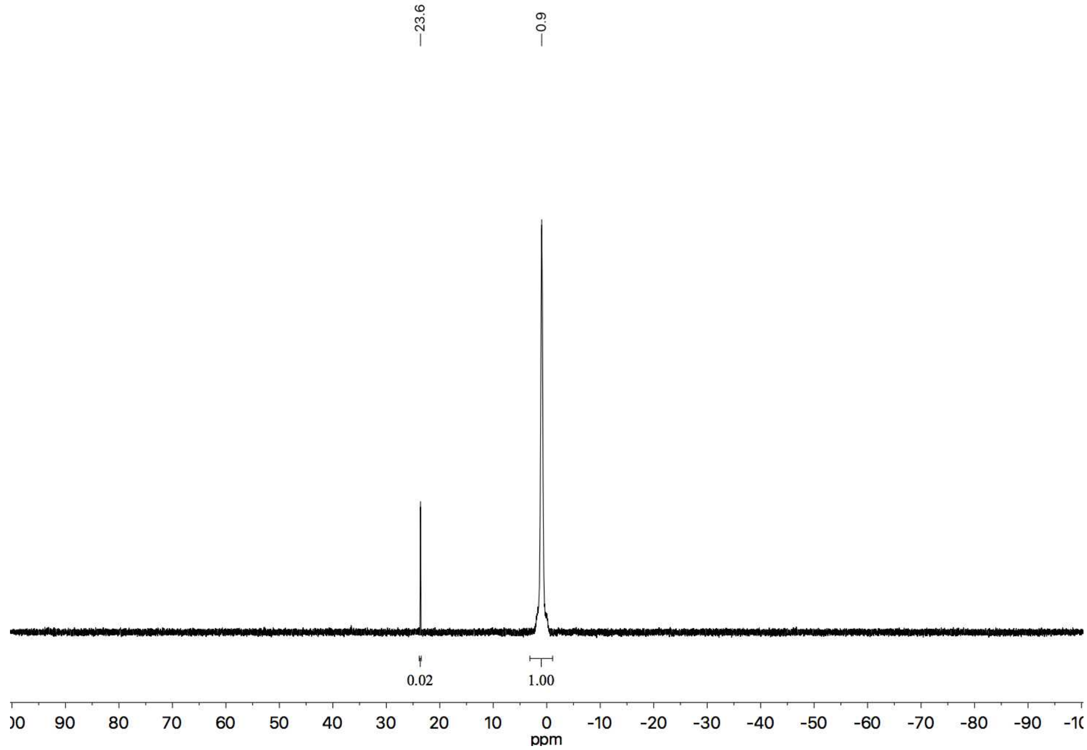
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

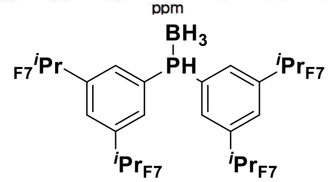


^{13}C NMR (126 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

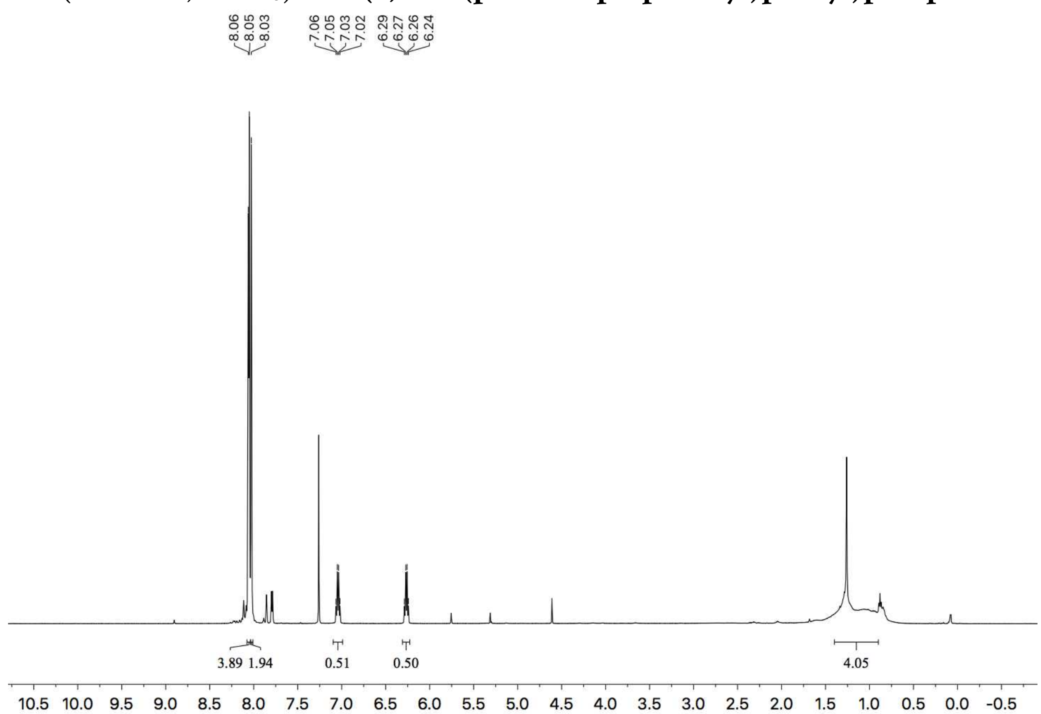


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(3,5-bis(trimethylsilyl)phenyl)phosphine borane**

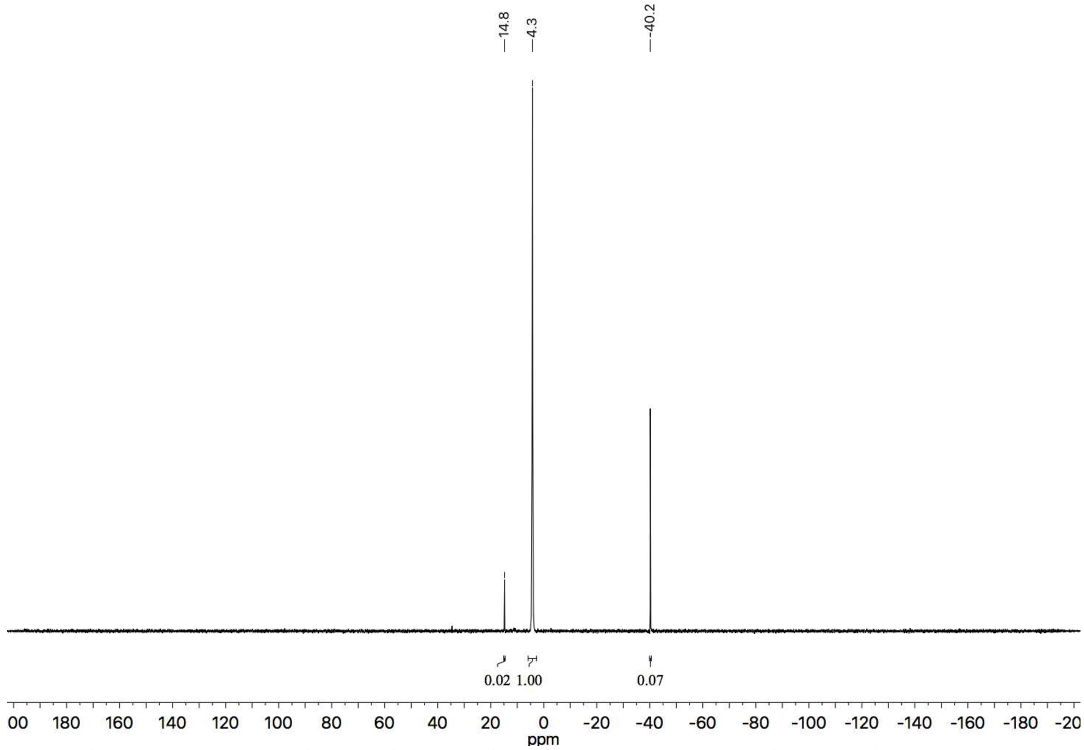




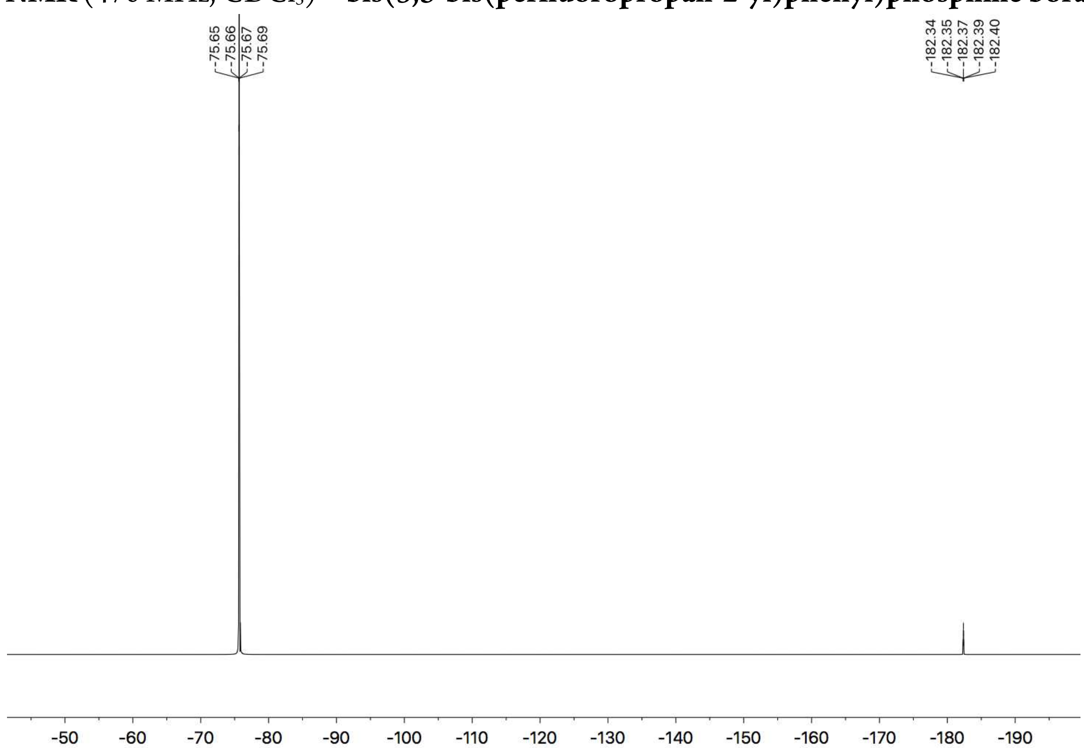
^{1}H NMR (500 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

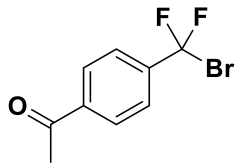


^{31}P NMR (202 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

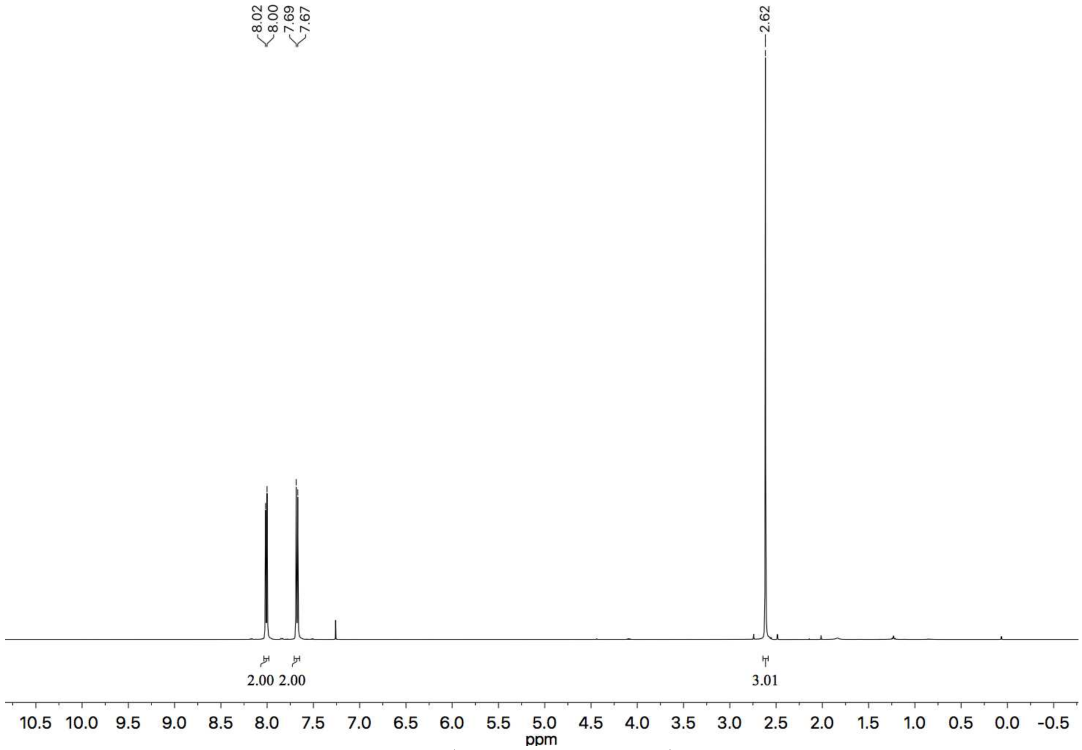


^{19}F NMR (470 MHz, $CDCl_3$) – **bis(3,5-bis(perfluoropropan-2-yl)phenyl)phosphine borane**

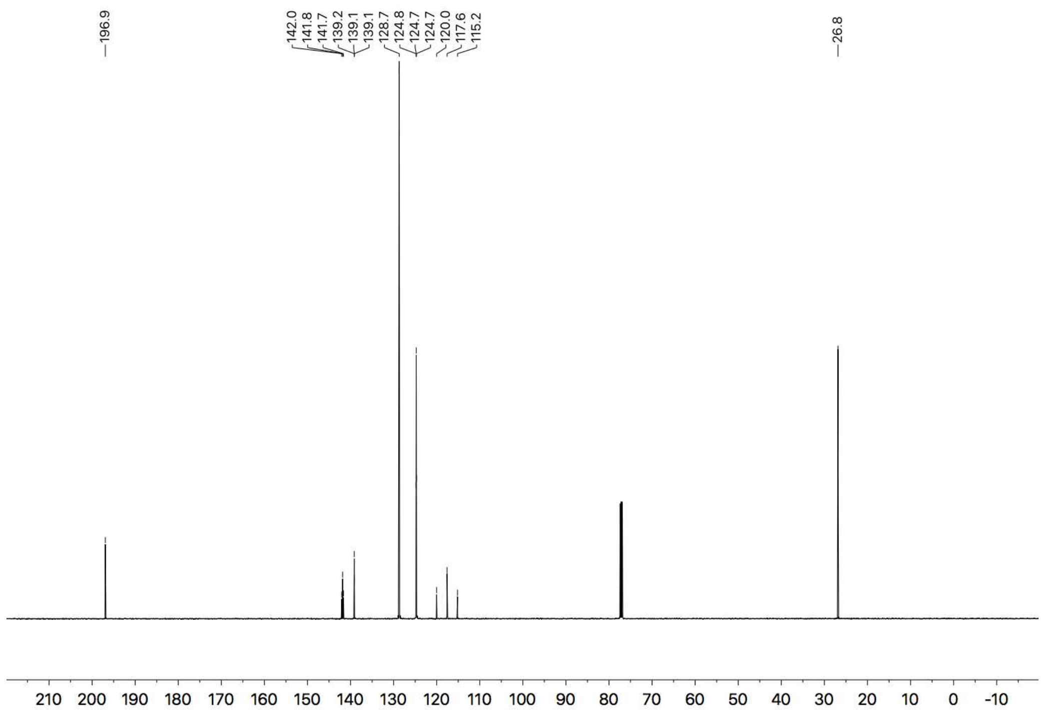




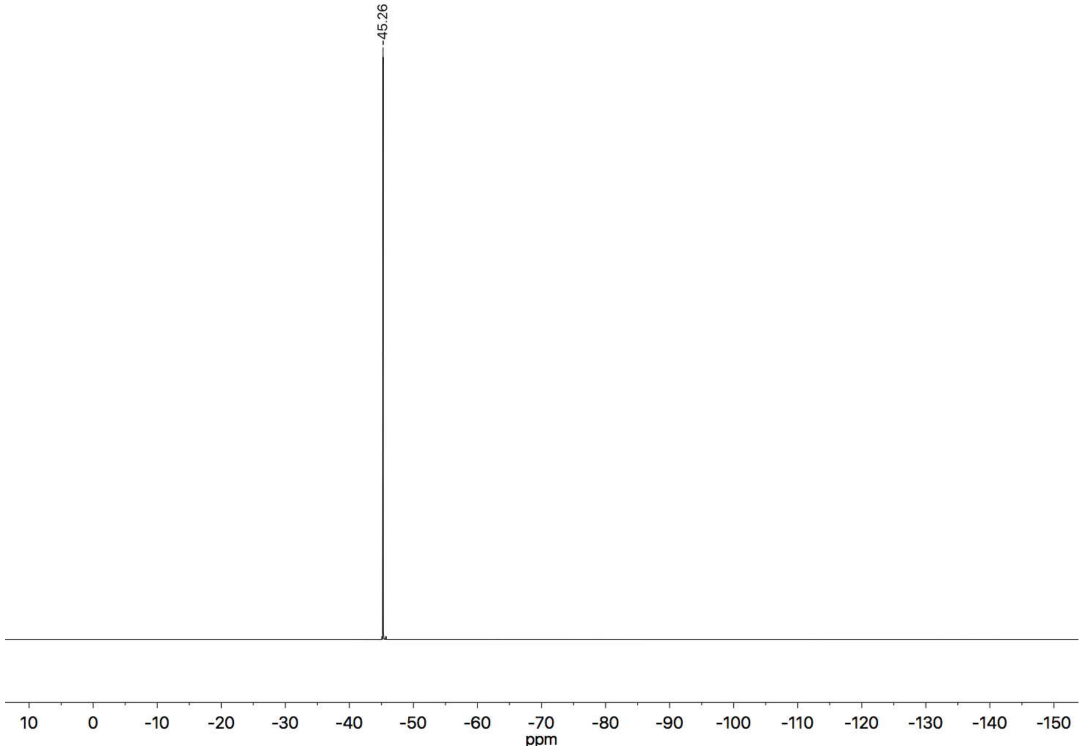
^{1}H NMR (500 MHz, $CDCl_3$) – **4Br**

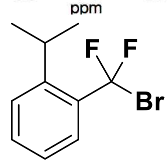


^{13}C NMR (126 MHz, $CDCl_3$) – **4Br**

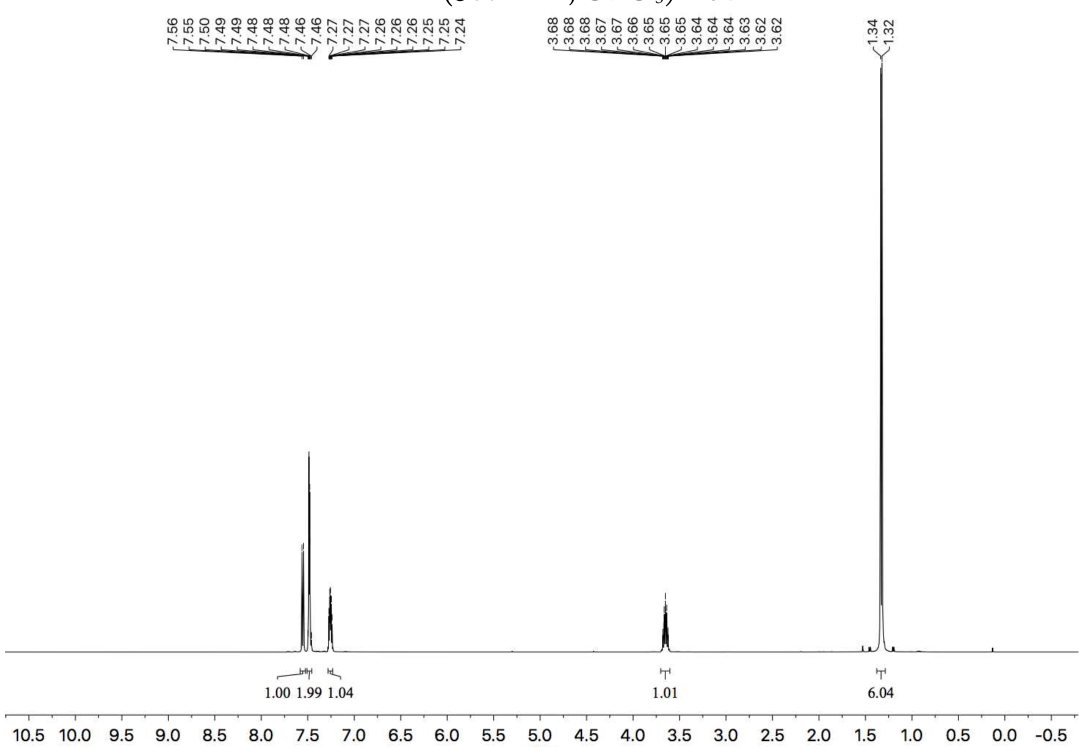


^{19}F NMR (470 MHz, $CDCl_3$) – **4Br**

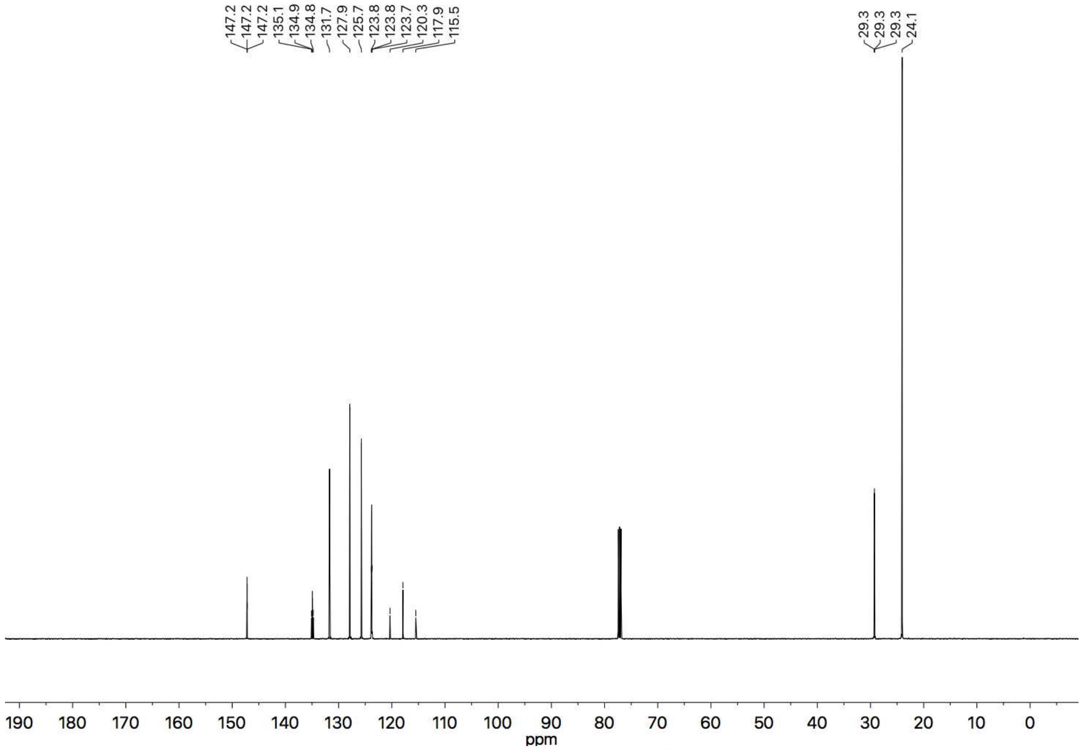




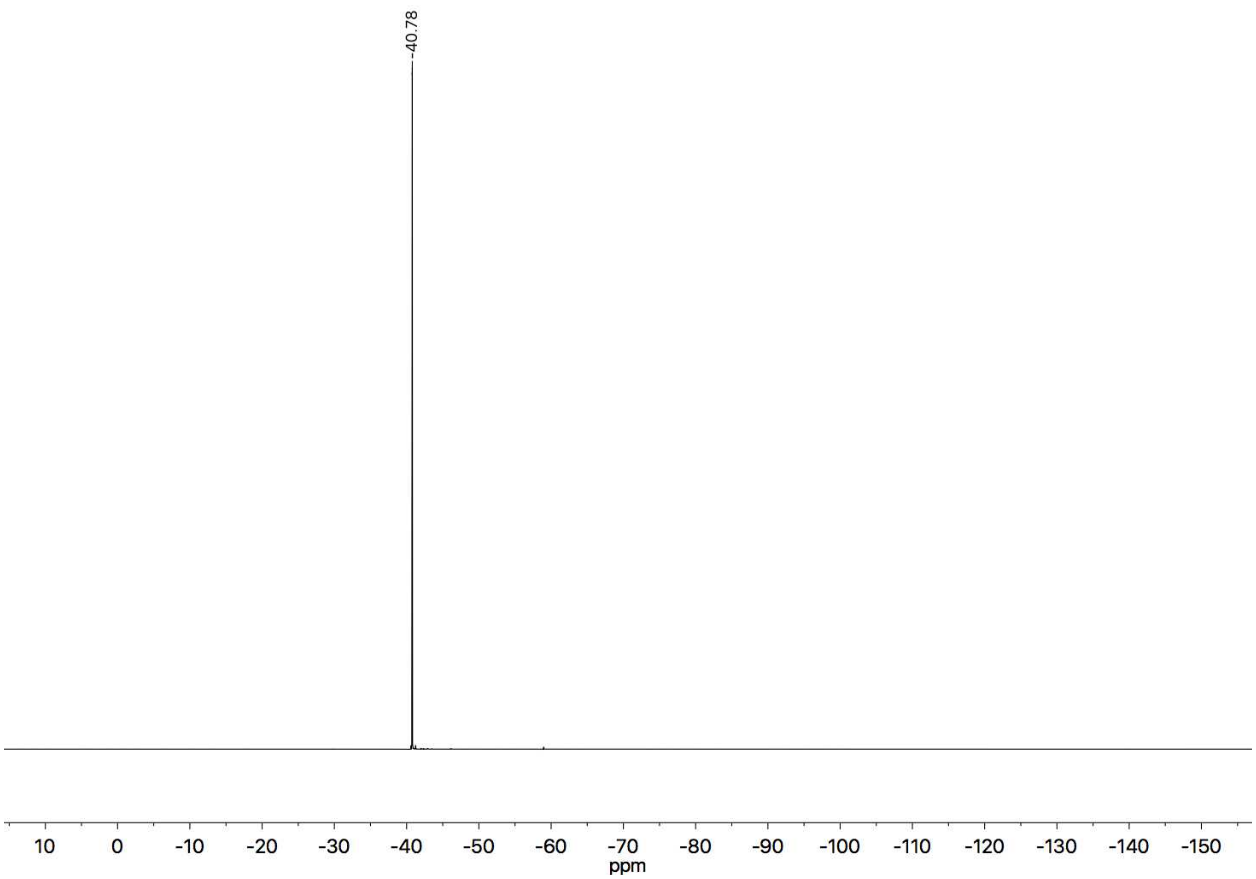
^{1}H NMR (500 MHz, $CDCl_3$) – **6Br**

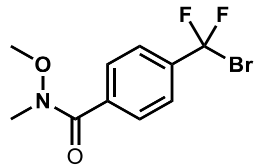


^{13}**C NMR** (126 MHz, $CDCl_3$) – **6Br**

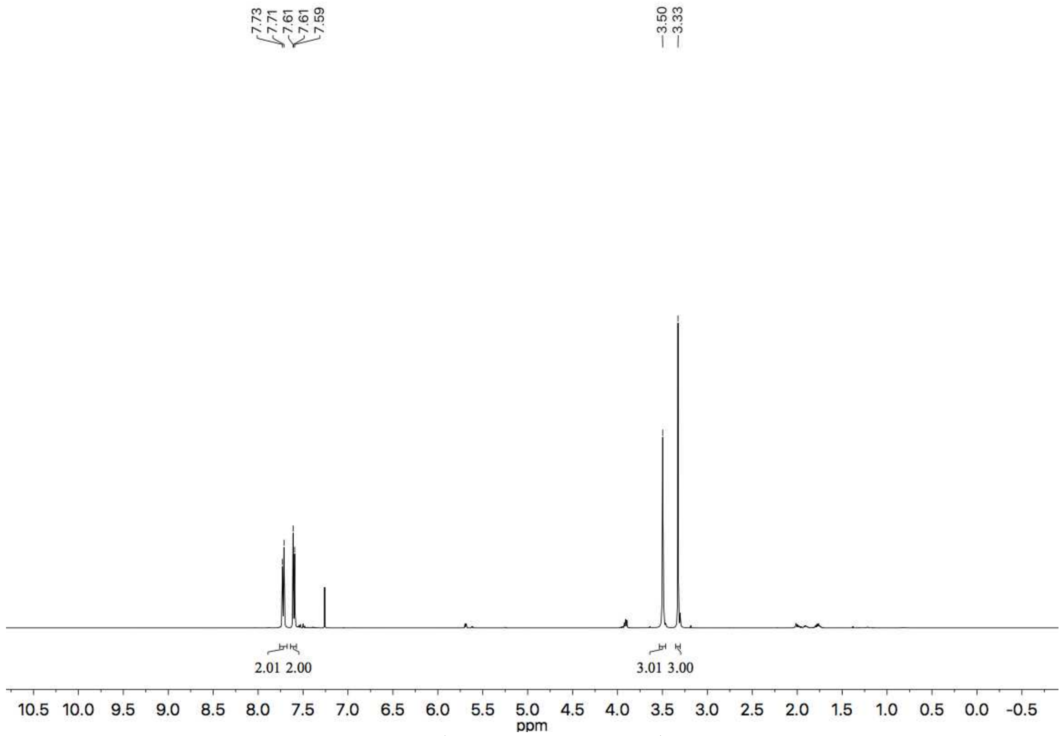


^{19}**F NMR** (470 MHz, $CDCl_3$) – **6Br**

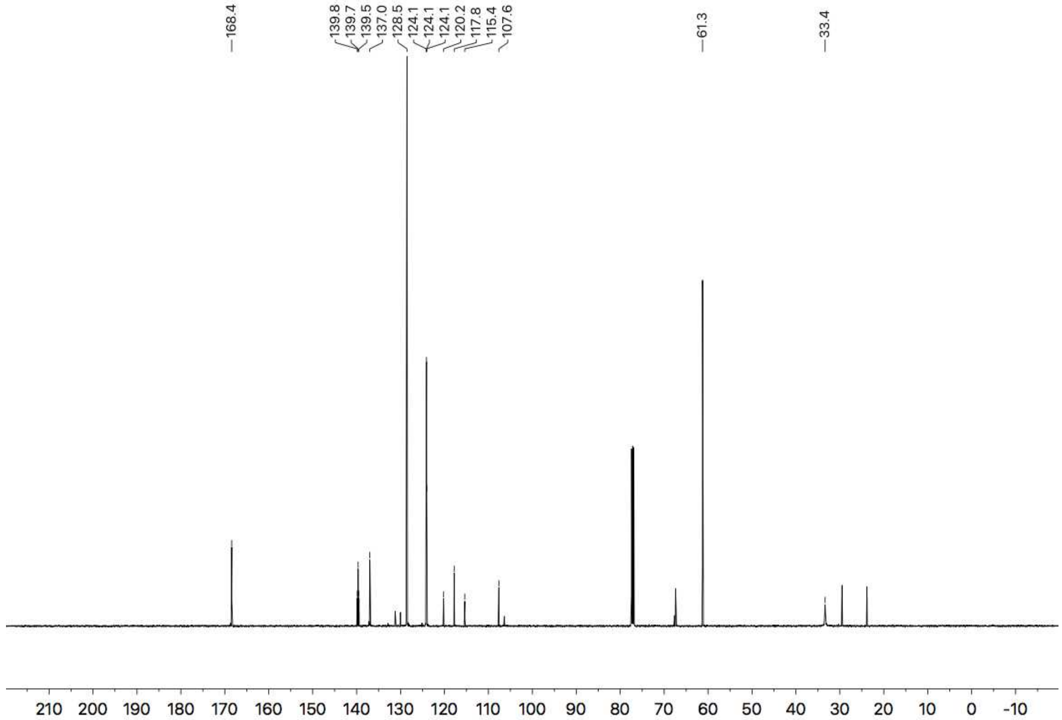




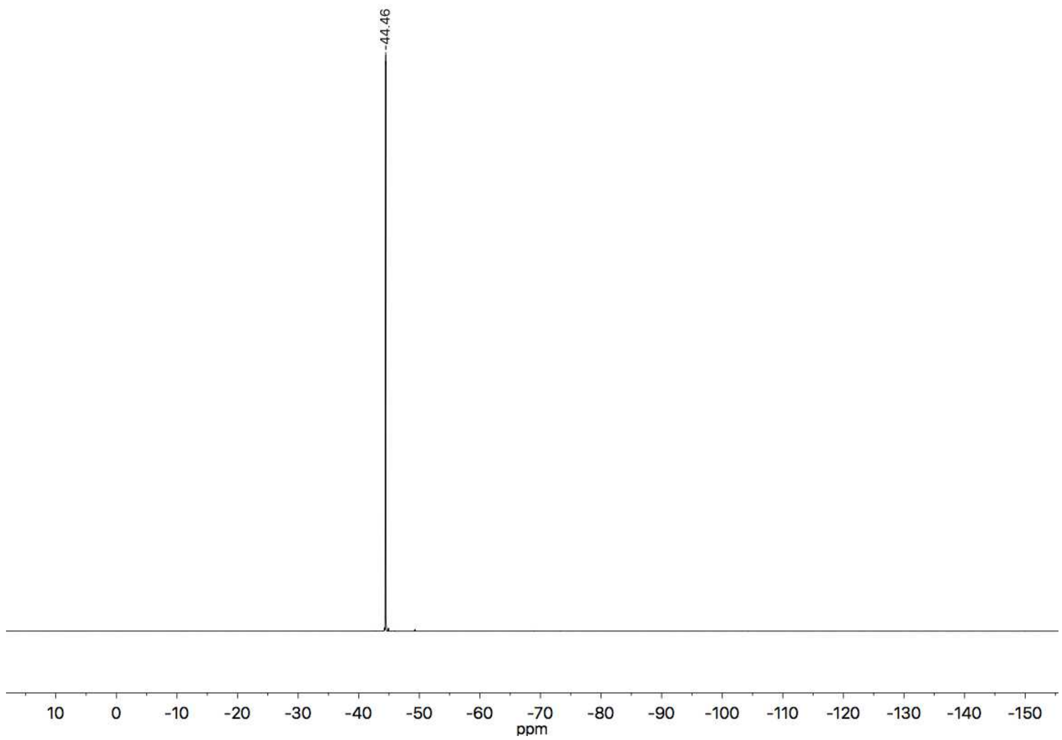
^{1}**H NMR** (500 MHz, $CDCl_3$) – **8Br**

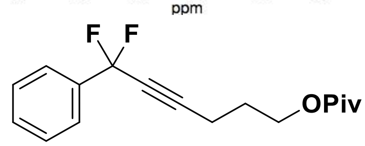


^{13}**C NMR** (126 MHz, $CDCl_3$) – **8Br**

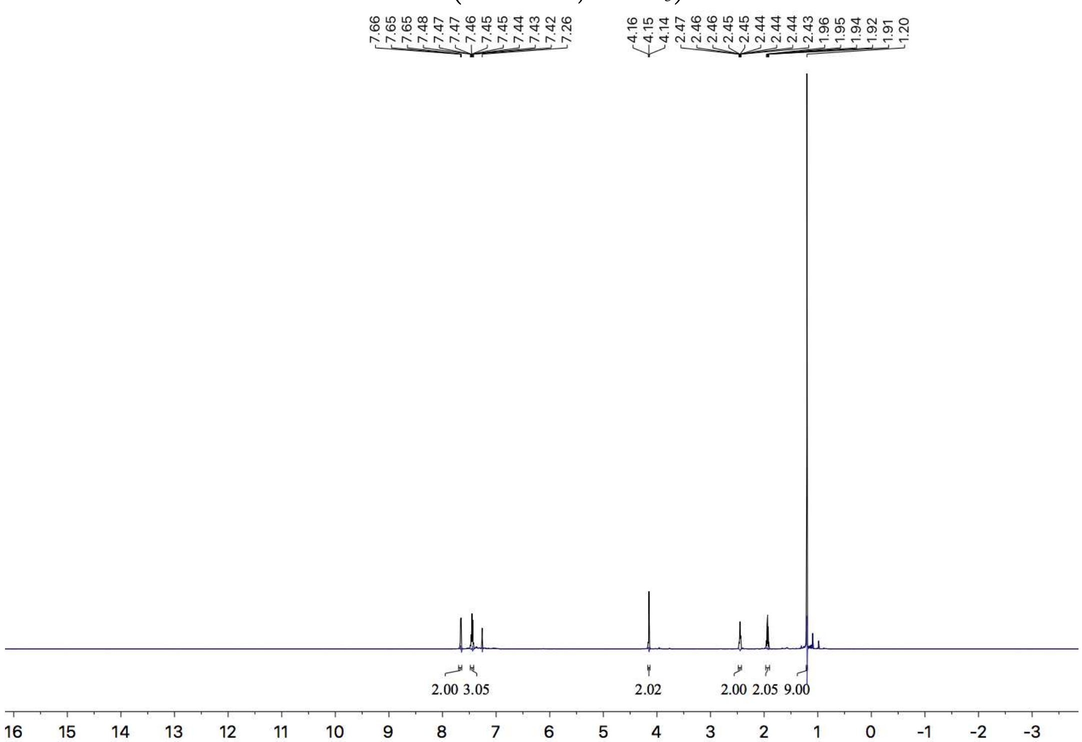


^{19}F NMR (470 MHz, $CDCl_3$) – **8Br**

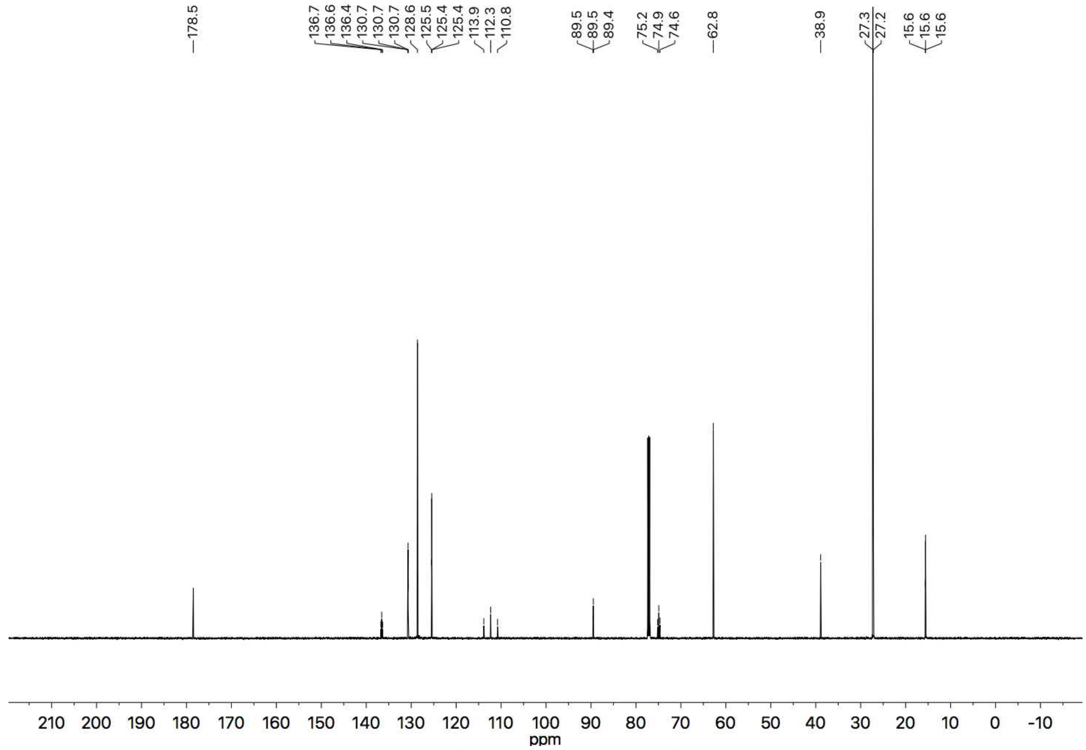




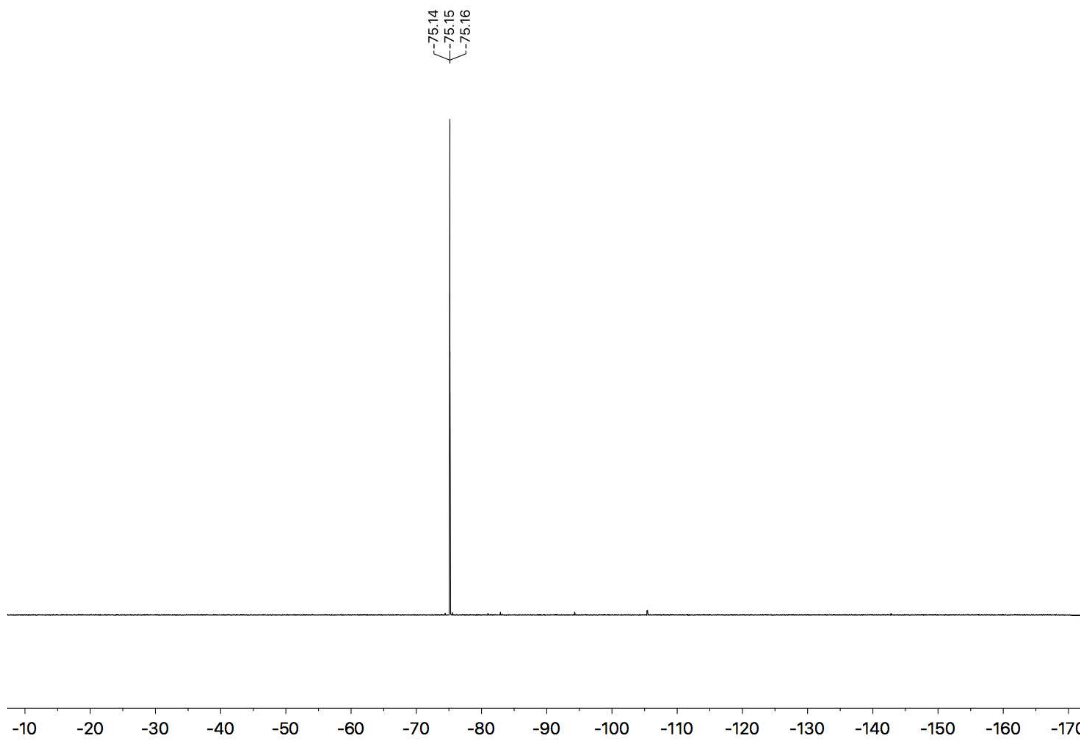
^{1}H NMR (600 MHz, $CDCl_3$) – **1a**

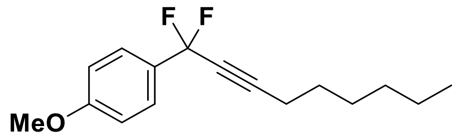


^{13}C NMR (151 MHz, $CDCl_3$) – **1a**

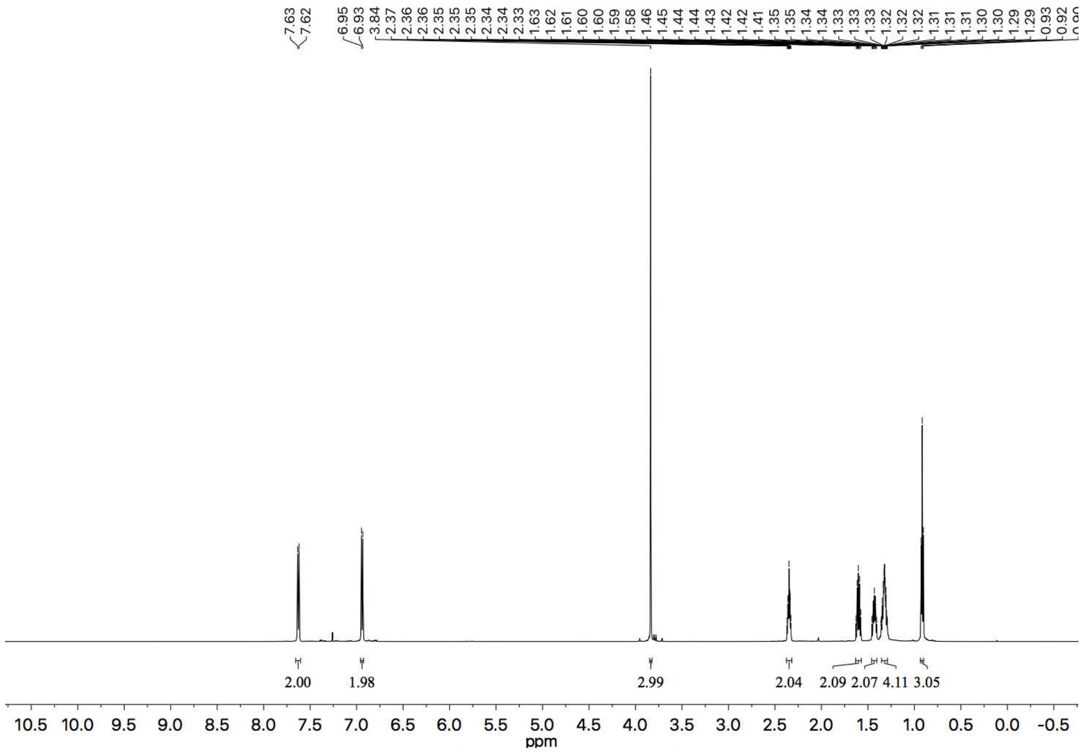


^{19}F NMR (565 MHz, $CDCl_3$) – **1a**

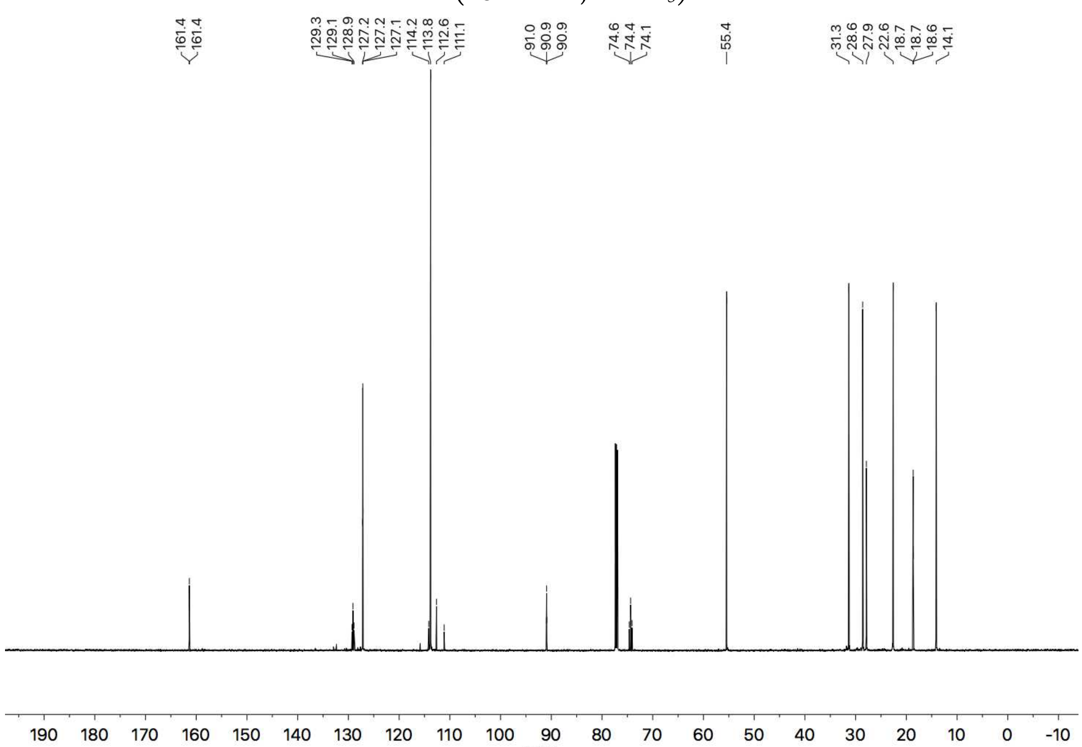




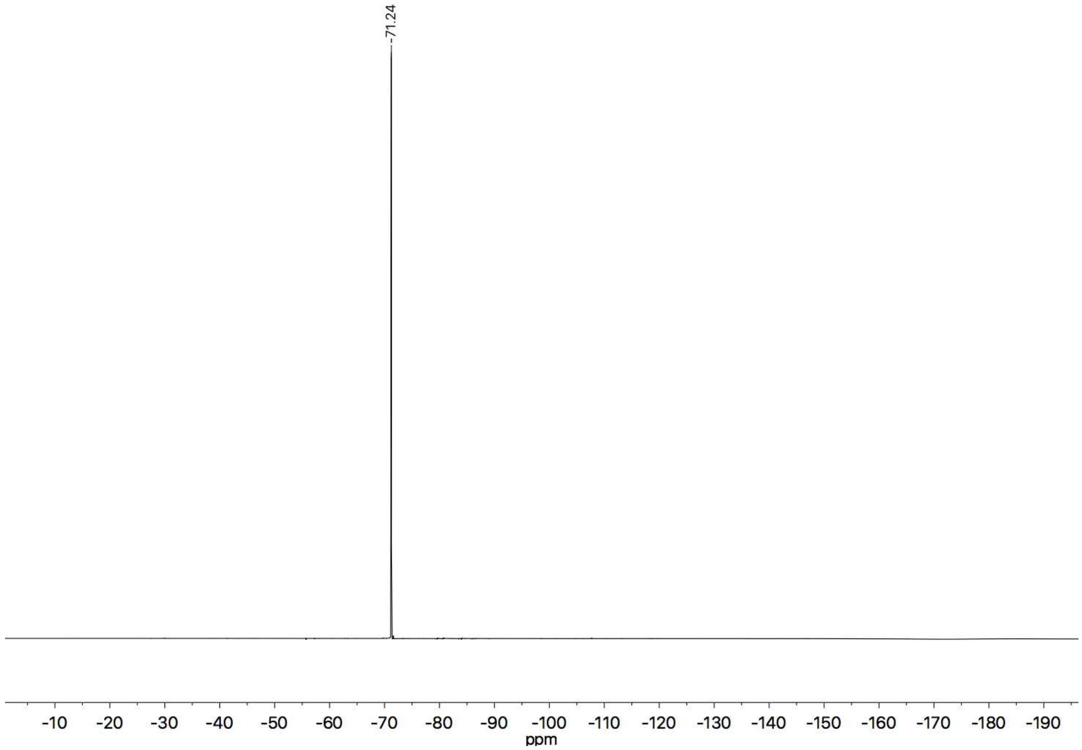
[1]H NMR (600 MHz, $CDCl_3$) – **2a**

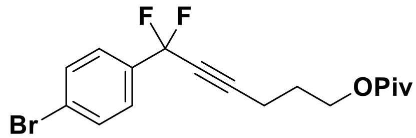


[13]C NMR (151 MHz, $CDCl_3$) – **2a**

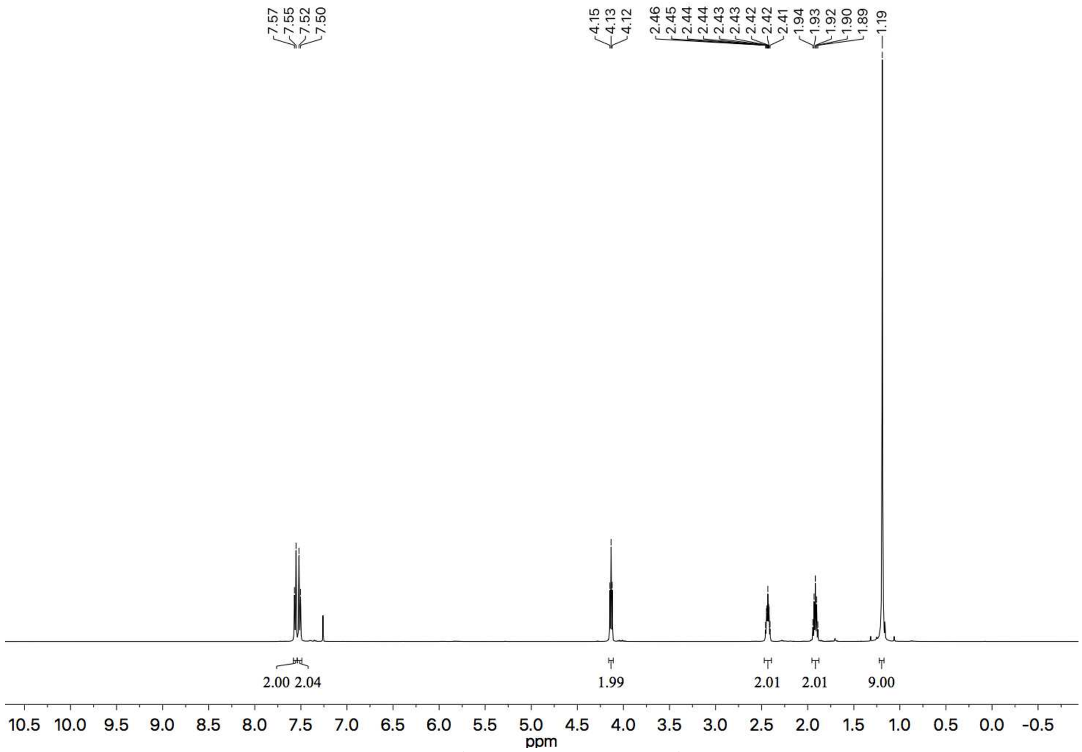


^{19}F NMR (565 MHz, $CDCl_3$) – **2a**

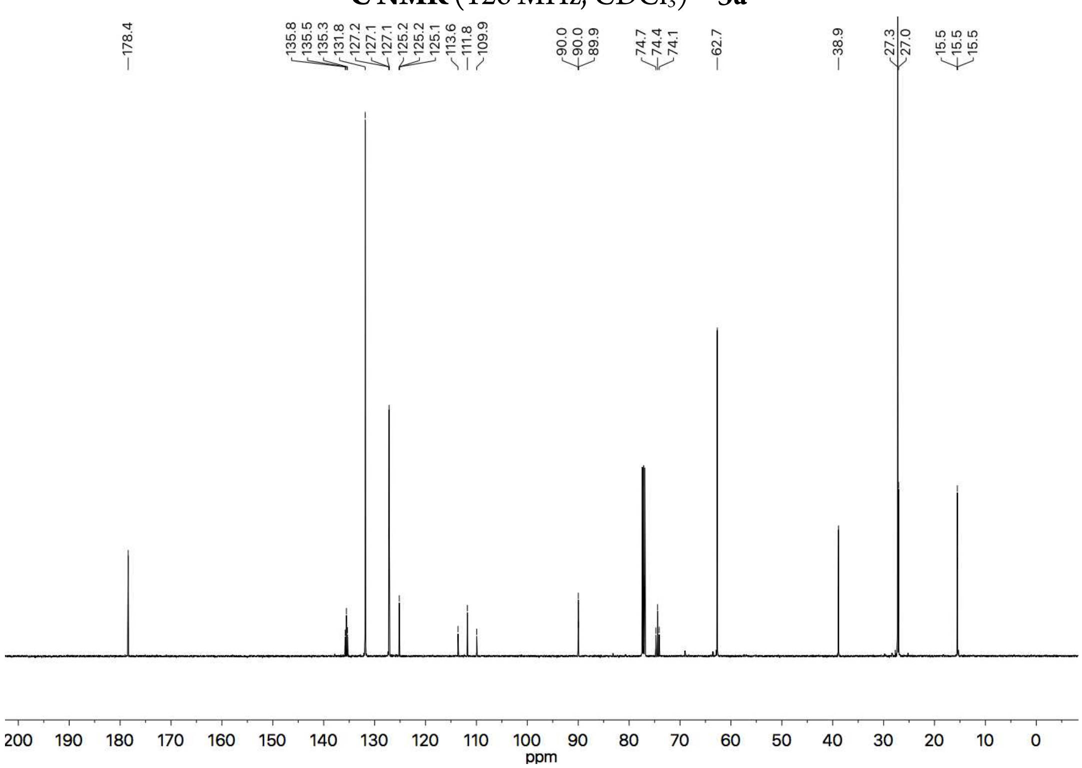




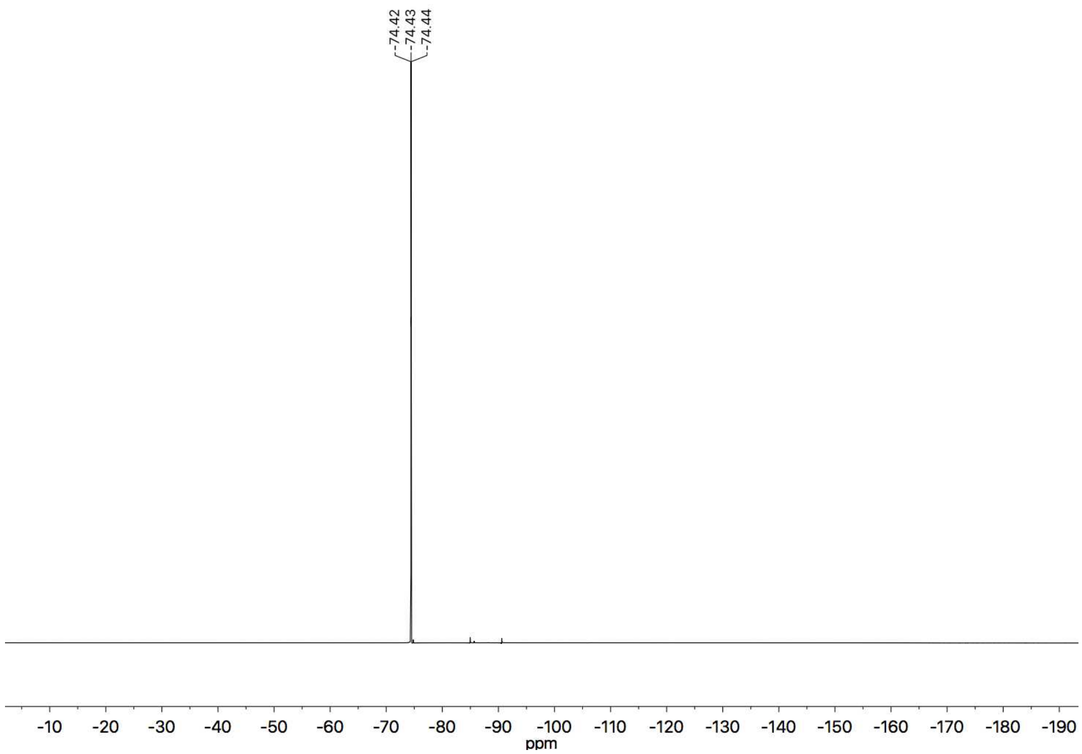
^{1}H NMR (500 MHz, $CDCl_3$) – **3a**

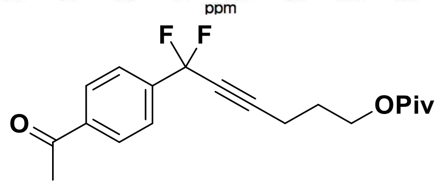


^{13}C NMR (126 MHz, $CDCl_3$) – **3a**

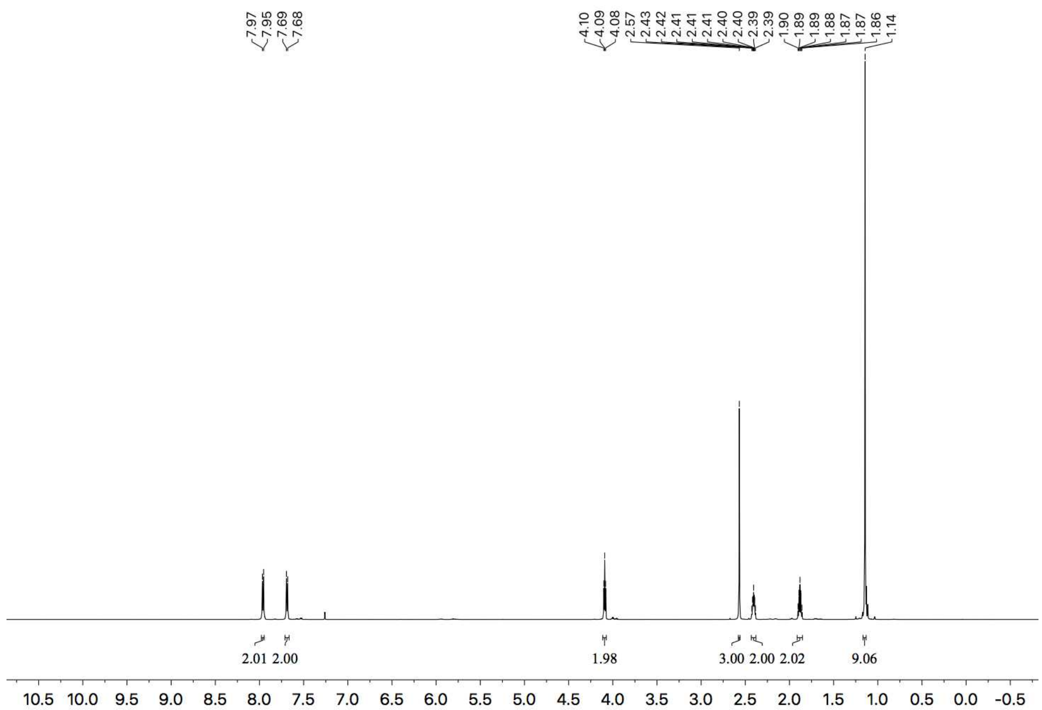


^{19}F NMR (470 MHz, $CDCl_3$) – **3a**

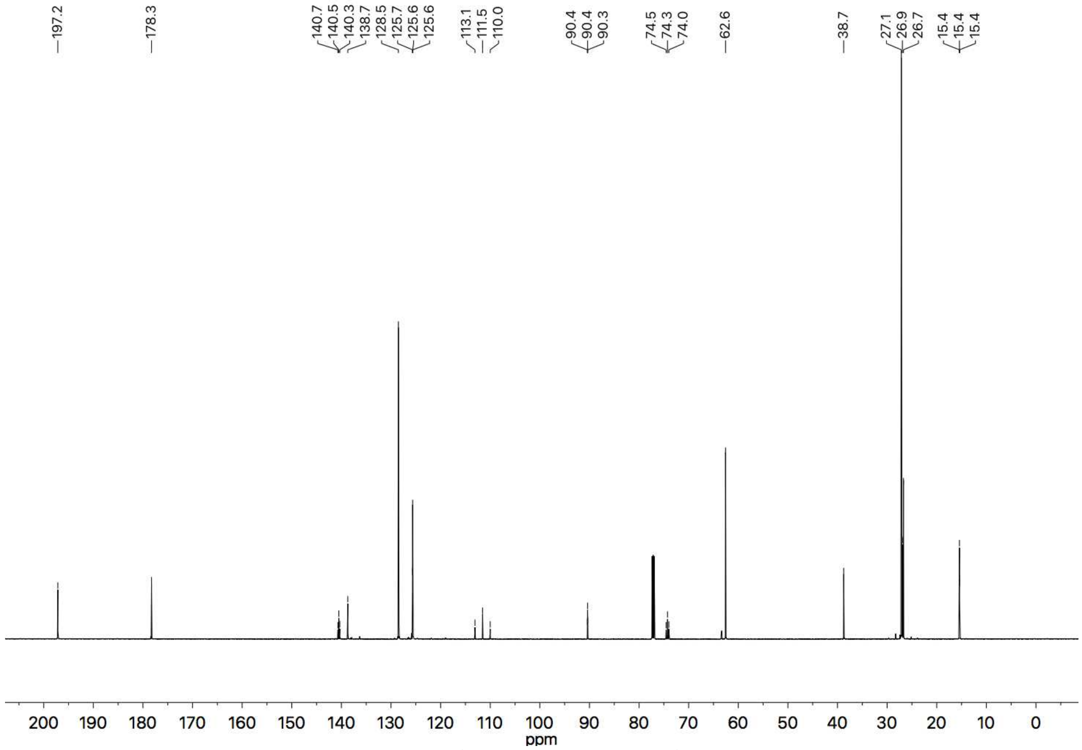




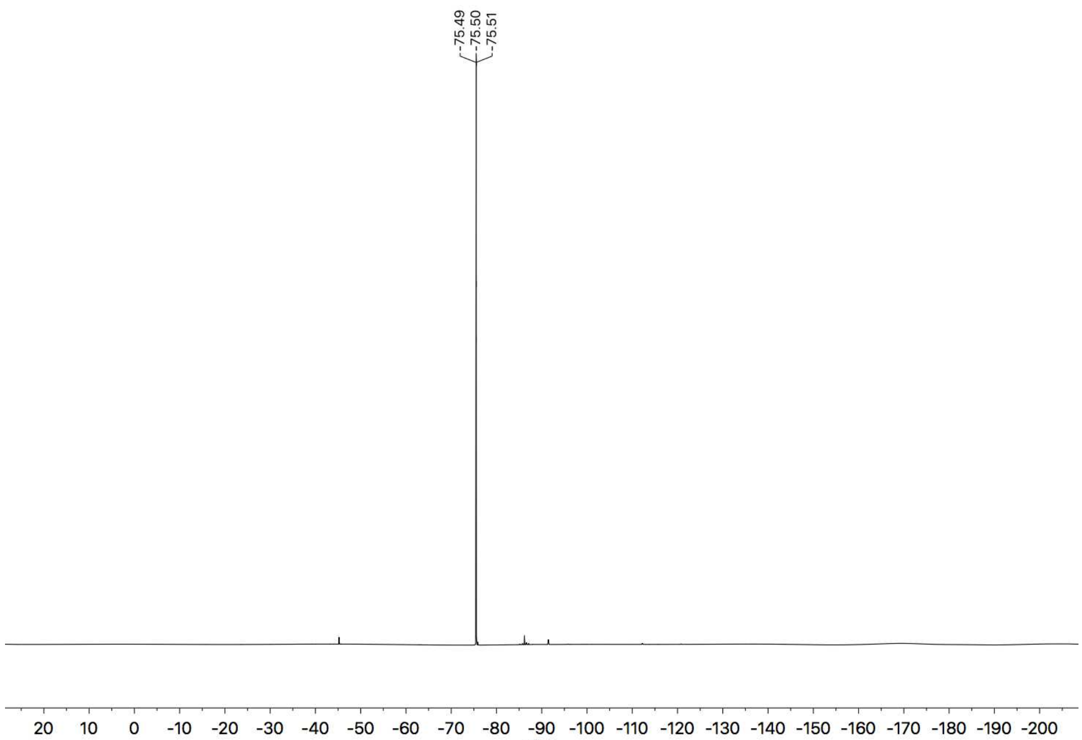
^{1}H NMR (600 MHz, $CDCl_3$) – **4a**

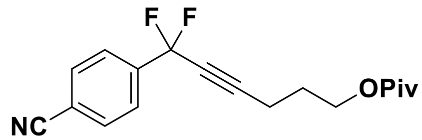


^{13}C NMR (151 MHz, $CDCl_3$) – **4a**

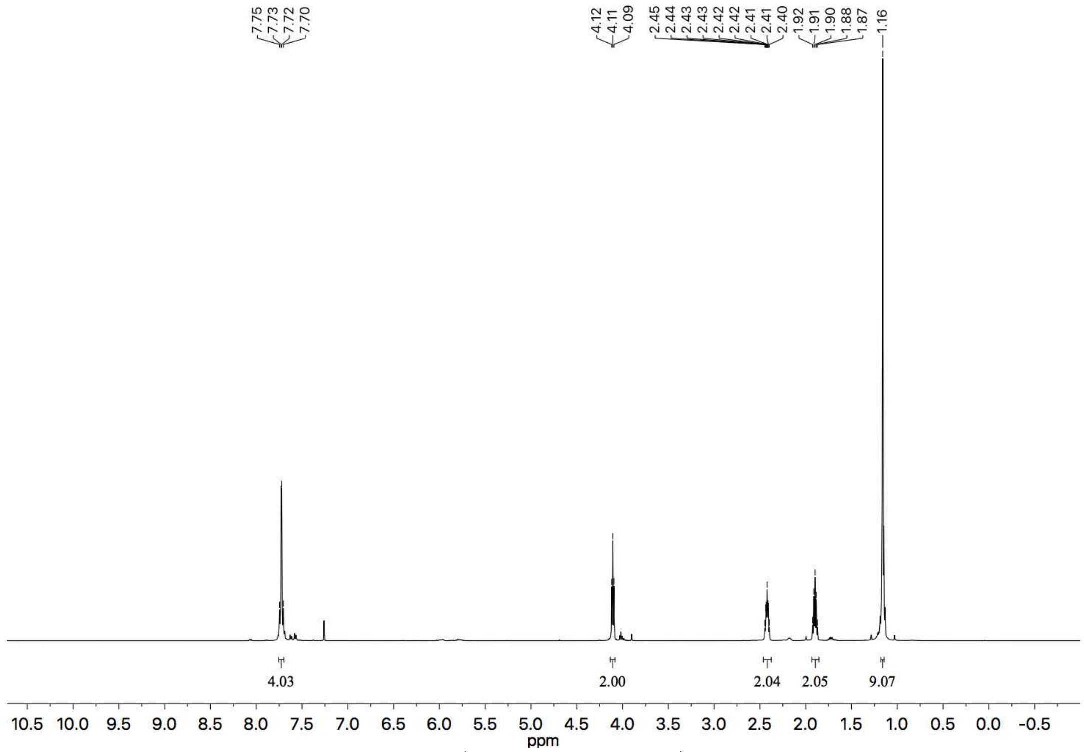


^{19}F NMR (565 MHz, $CDCl_3$) – **4a**

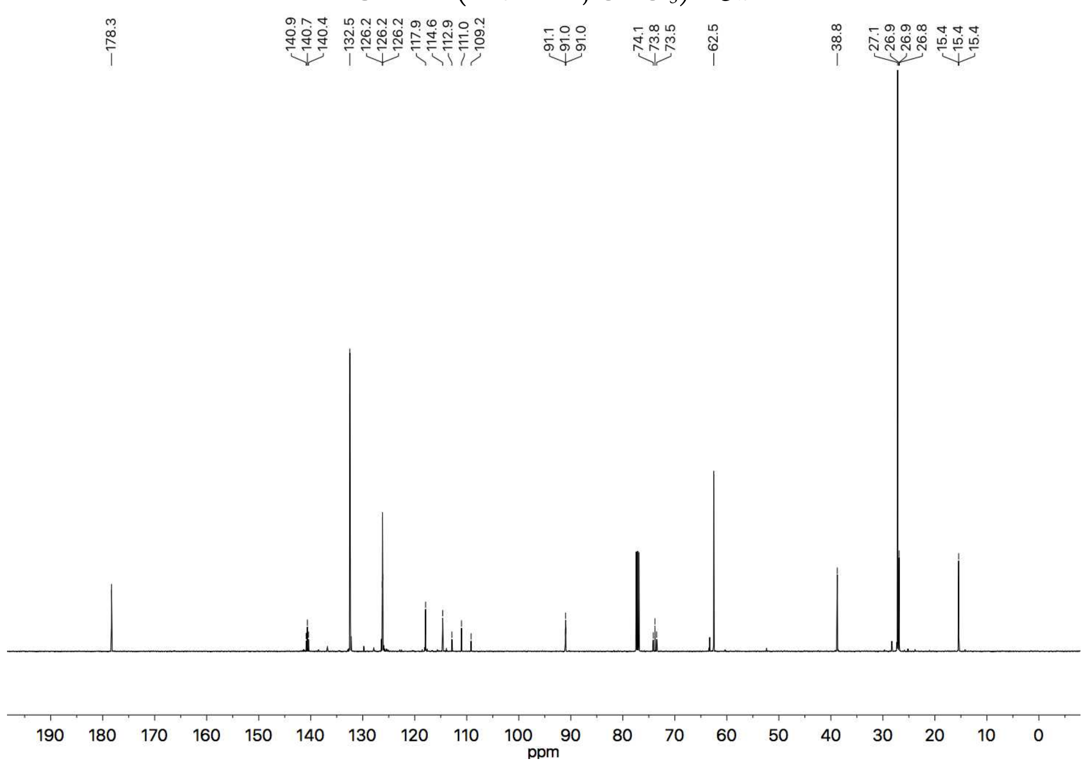




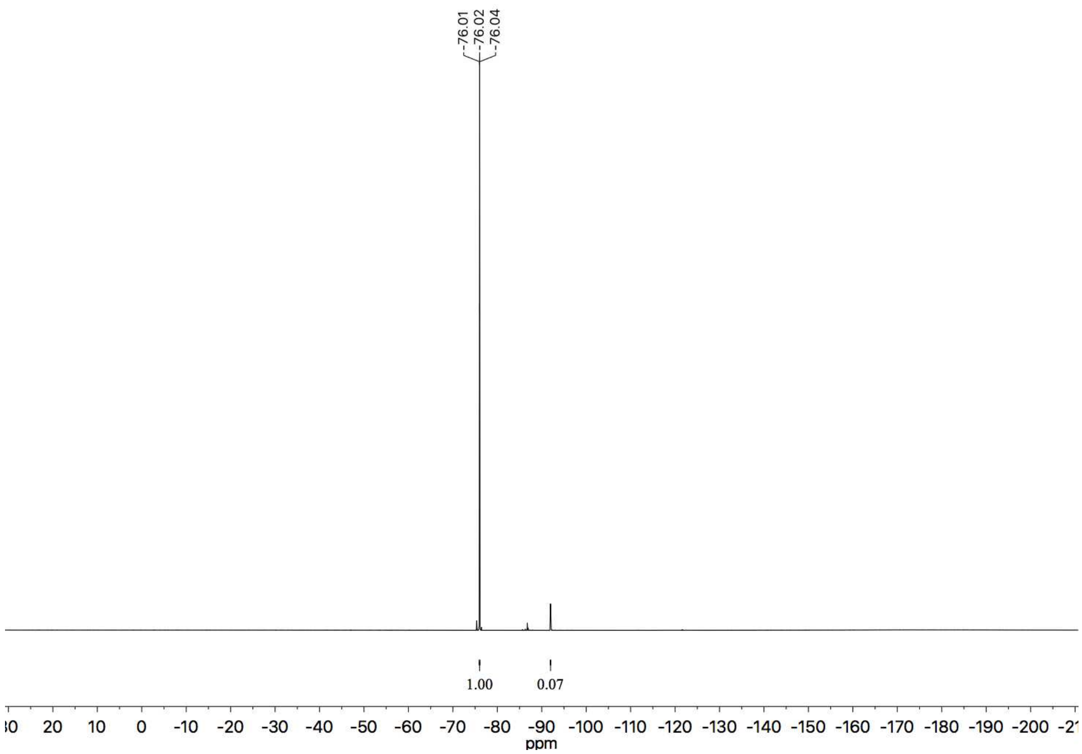
[1]H NMR (500 MHz, $CDCl_3$) – **5a**

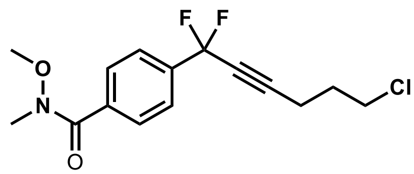


[13]C NMR (126 MHz, $CDCl_3$) – **5a**

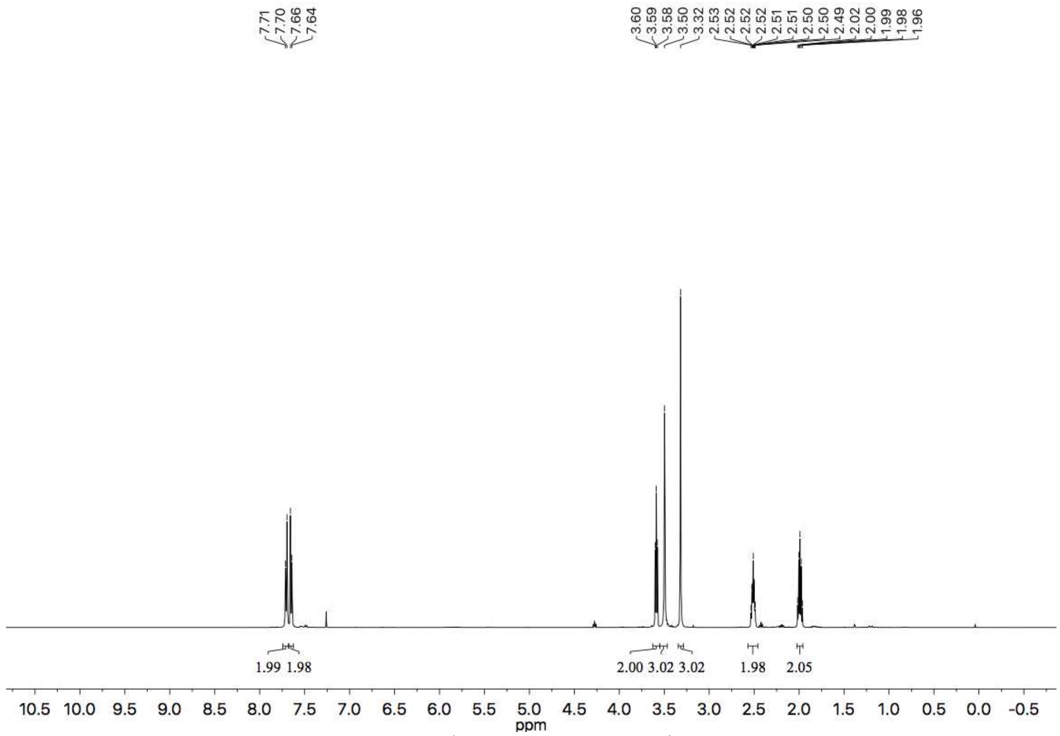


^{19}F NMR (470 MHz, $CDCl_3$) – **5a**

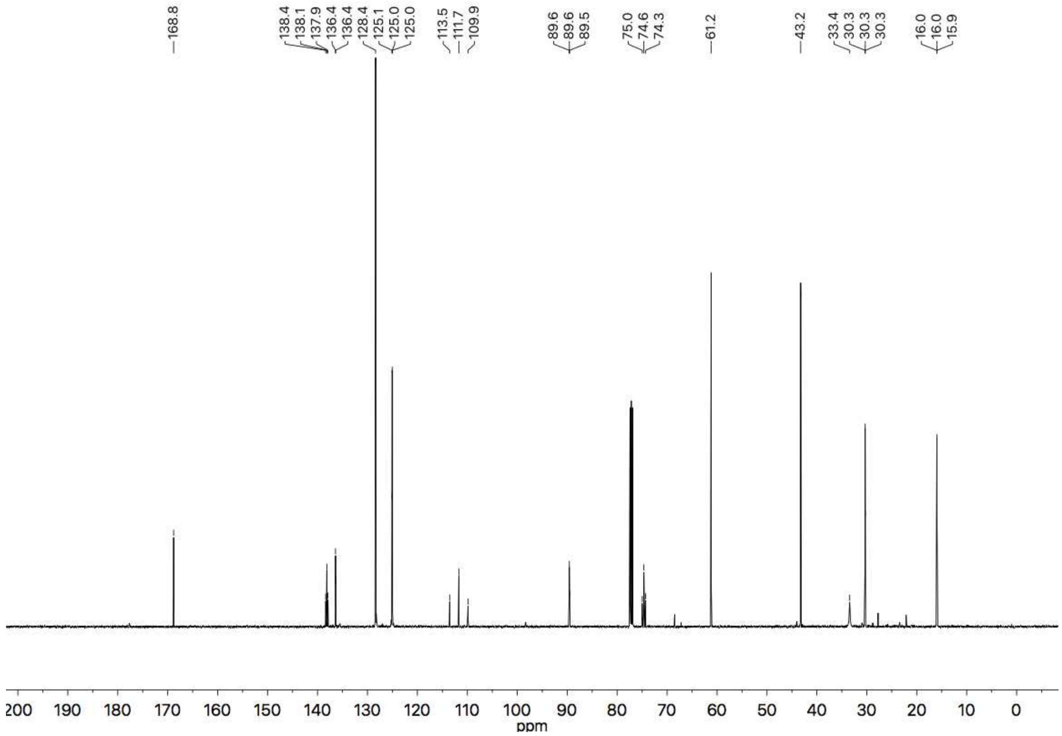




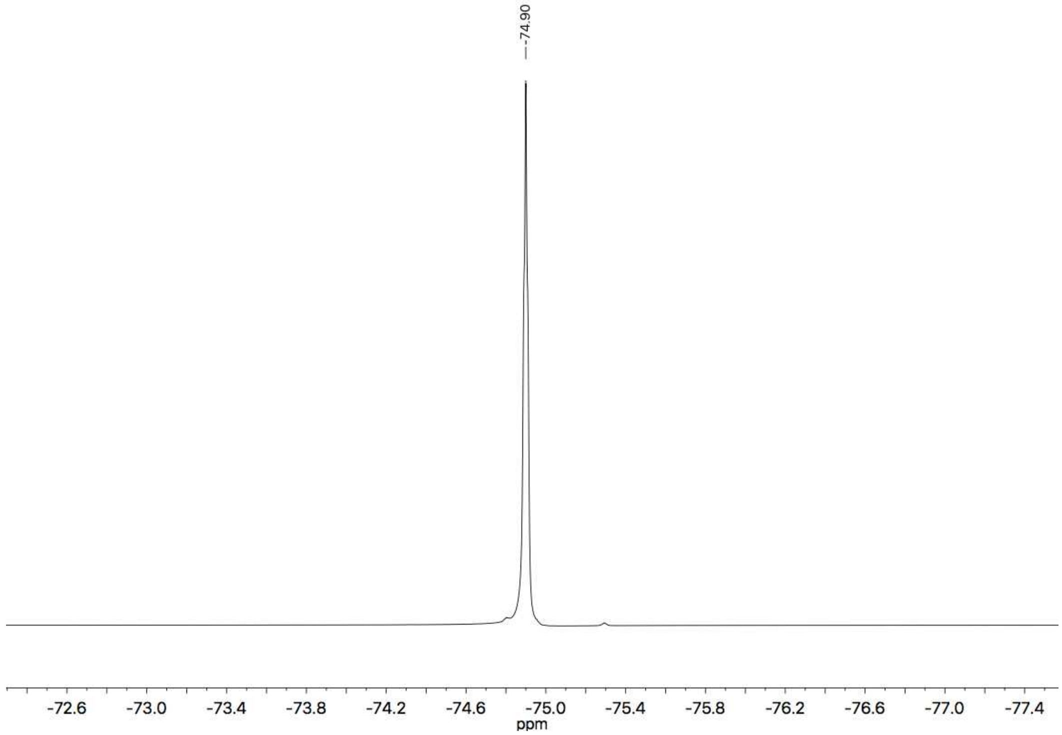
[1]H NMR (500MHz, $CDCl_3$) – **6a**

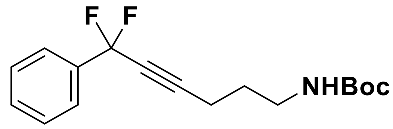


[13]C NMR (126 MHz, $CDCl_3$) – **6a**

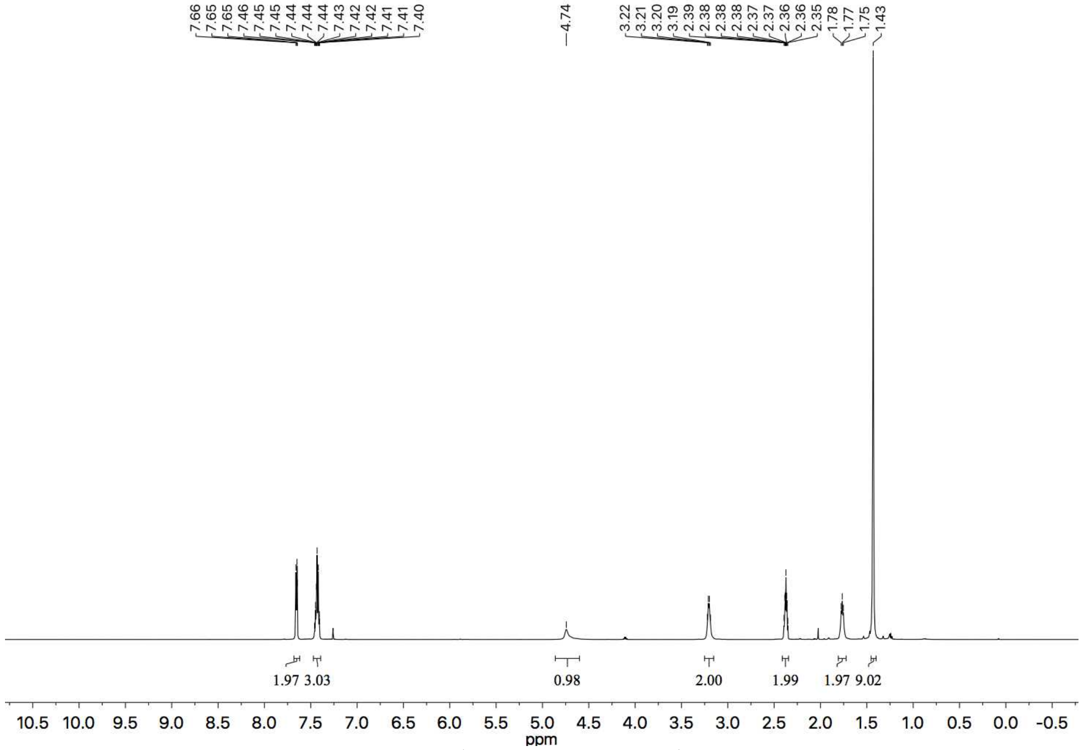


^{19}F NMR (470 MHz, $CDCl_3$) – **6a**

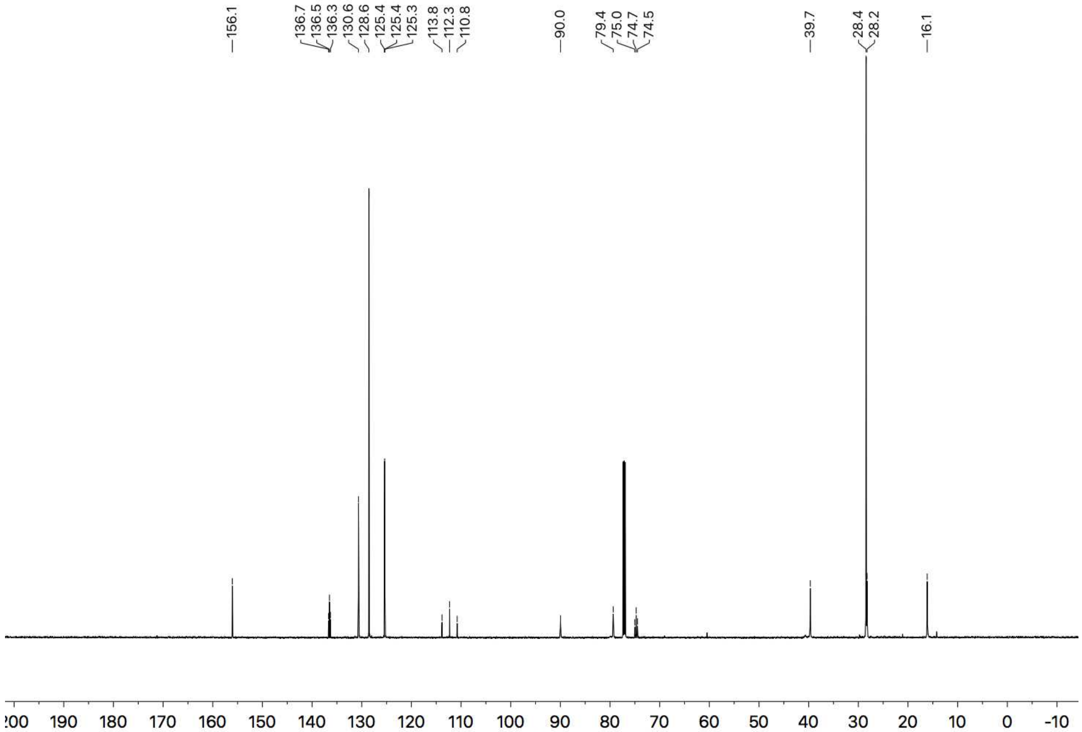




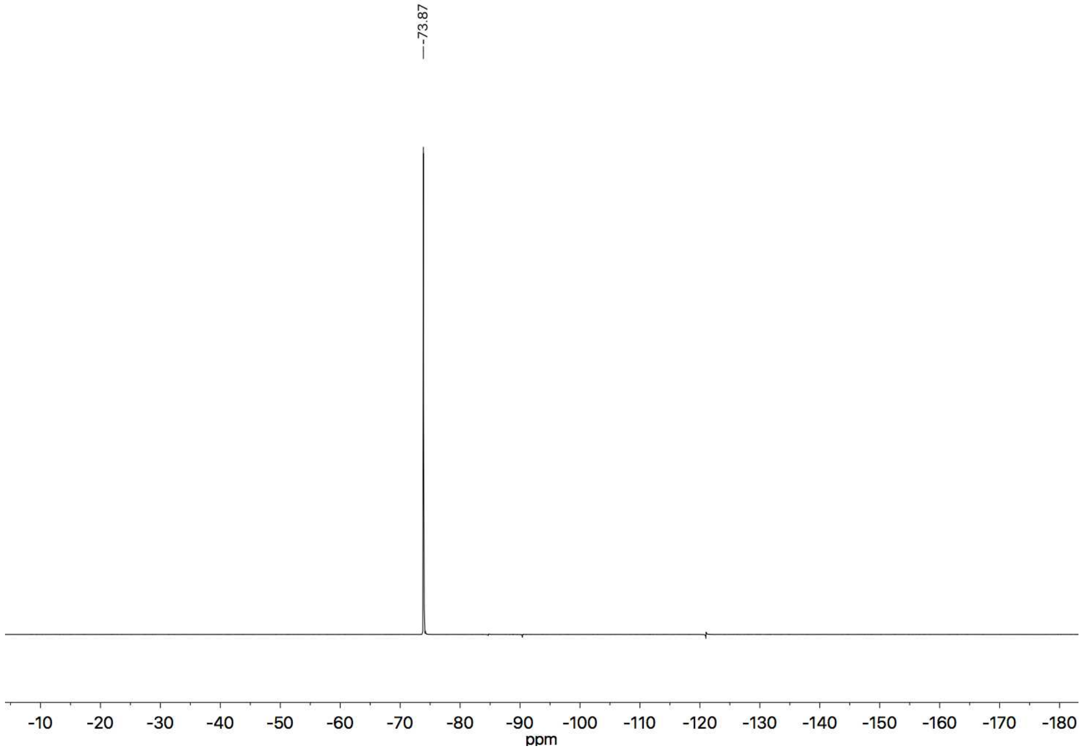
^{1}H NMR (600 MHz, $CDCl_3$) – **7a**

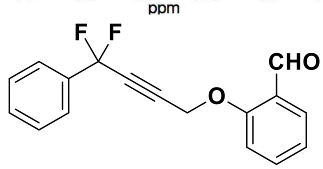


^{13}C NMR (151 MHz, $CDCl_3$) – **7a**

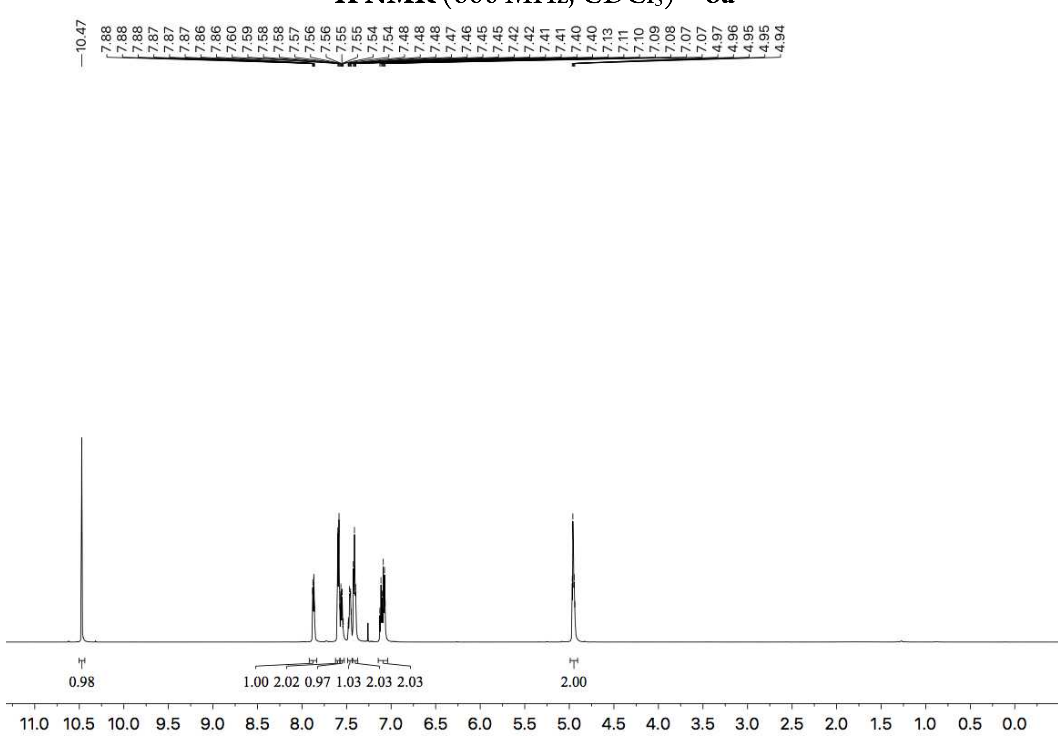


^{19}F NMR (565 MHz, $CDCl_3$) – **7a**

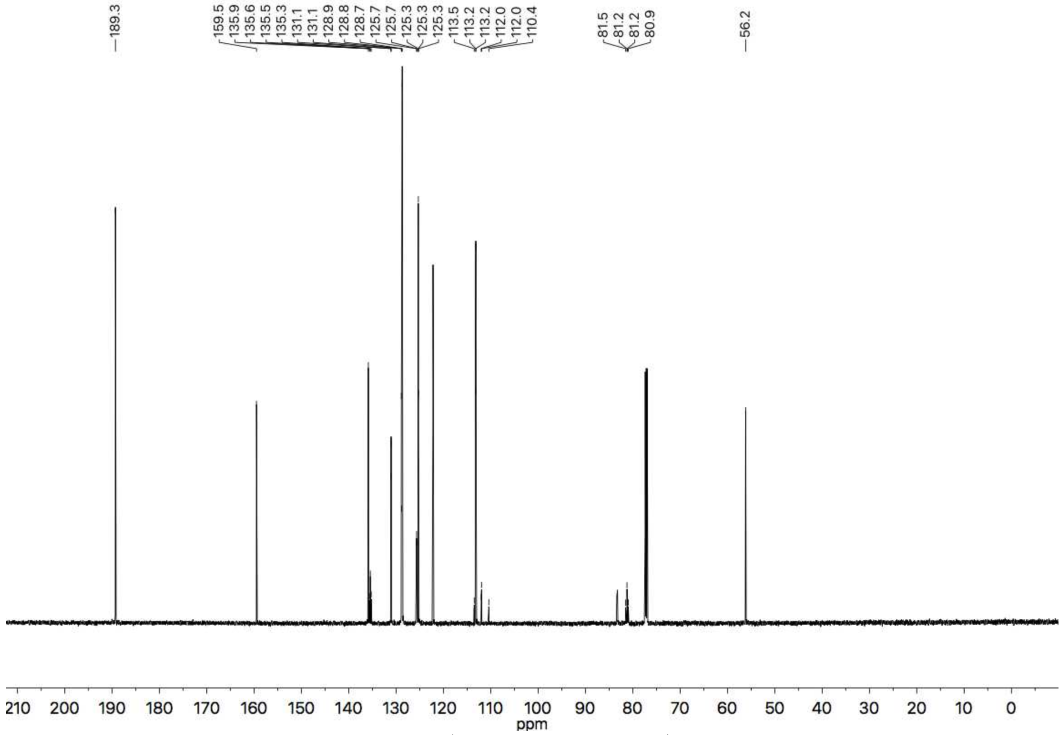




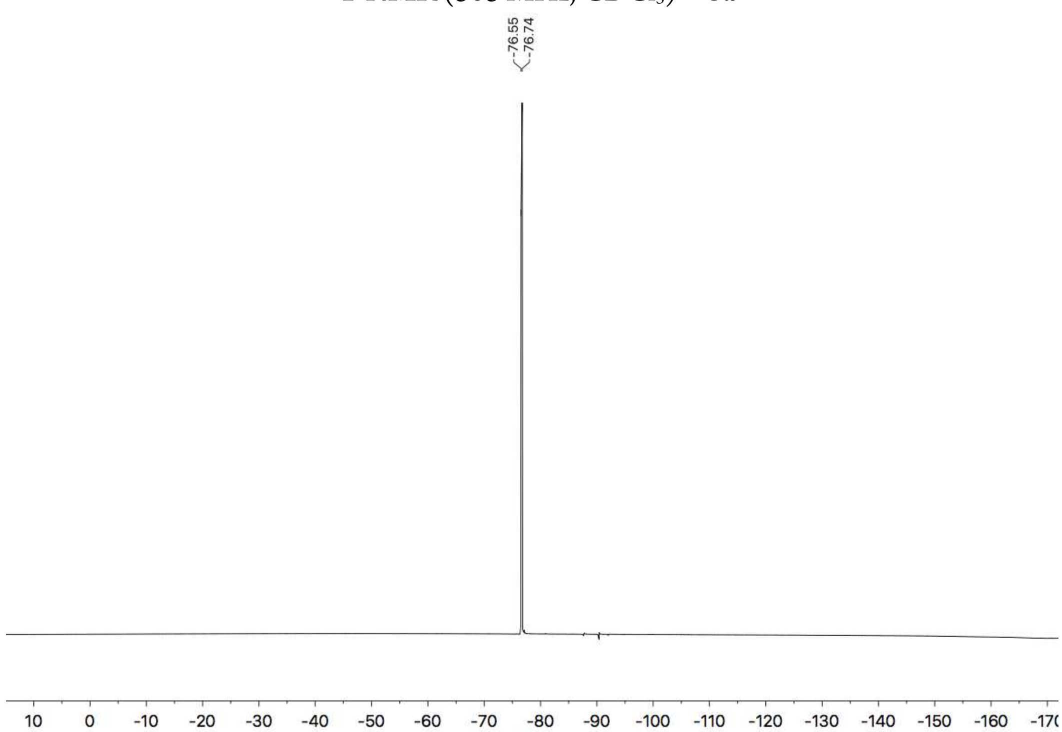
^{1}H NMR (600 MHz, $CDCl_3$) – **8a**

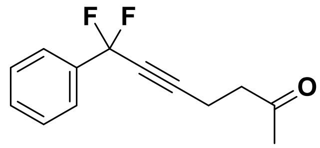


^{13}C NMR (151 MHz, $CDCl_3$) – **8a**

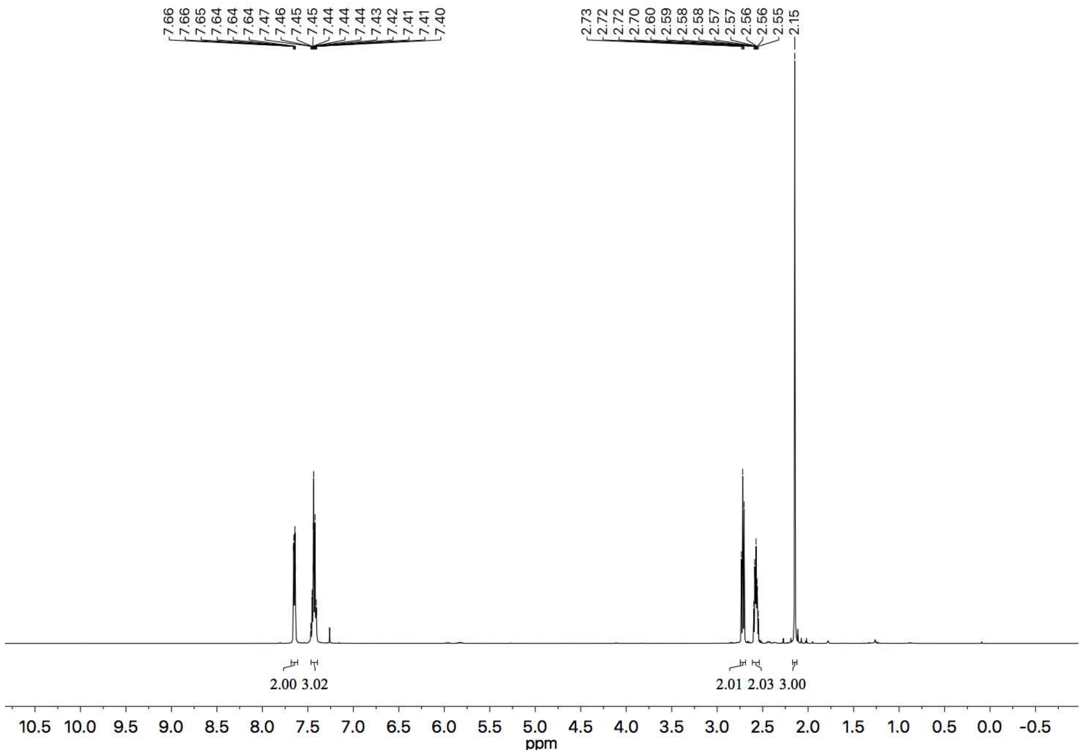


^{19}F NMR (565 MHz, $CDCl_3$) – **8a**

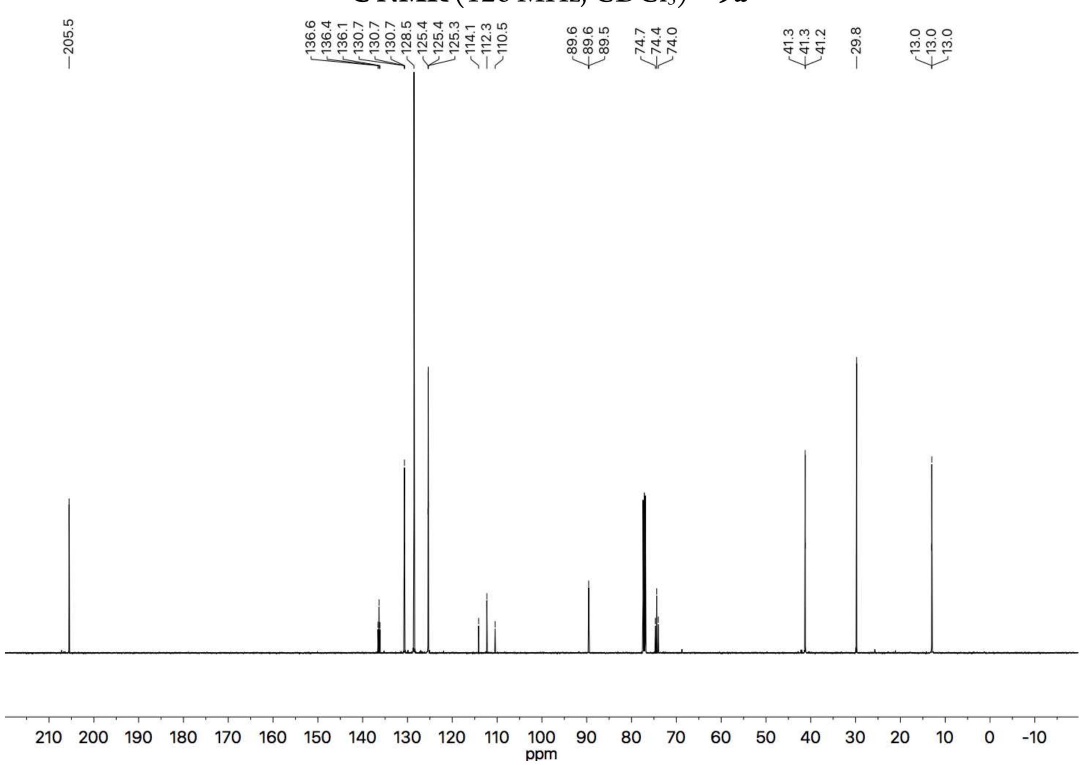




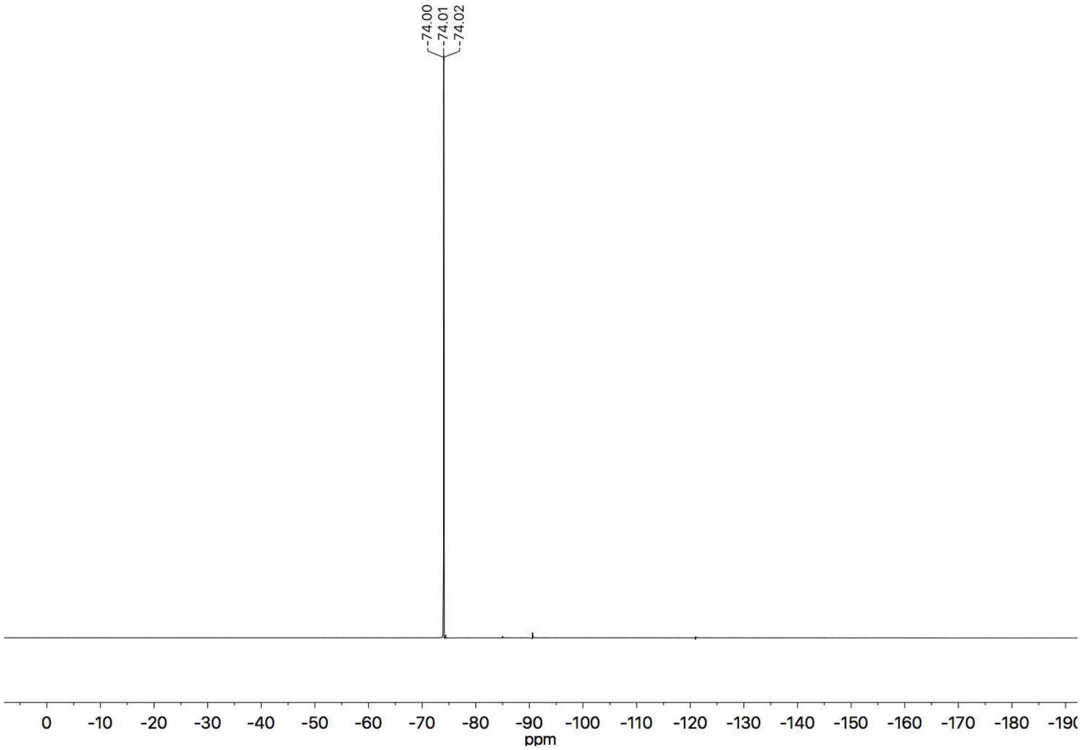
^{1}H NMR (500 MHz, $CDCl_3$) – **9a**

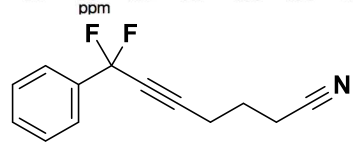


^{13}C NMR (126 MHz, $CDCl_3$) – **9a**

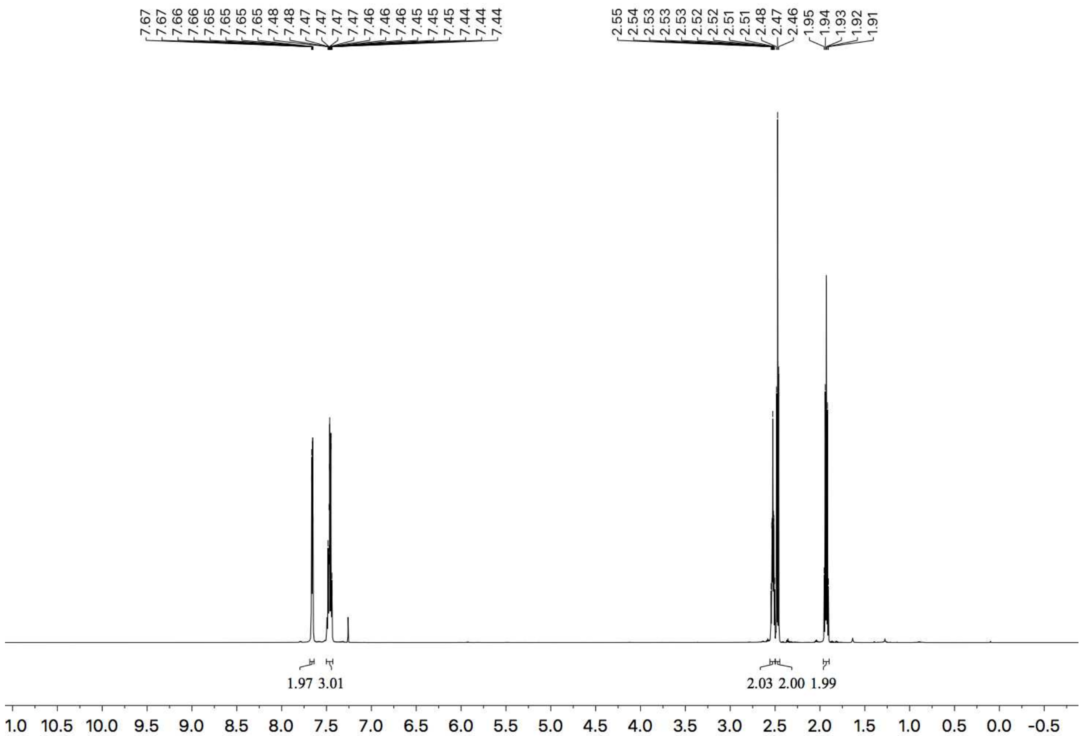


^{19}F NMR (470 MHz, $CDCl_3$) – **9a**

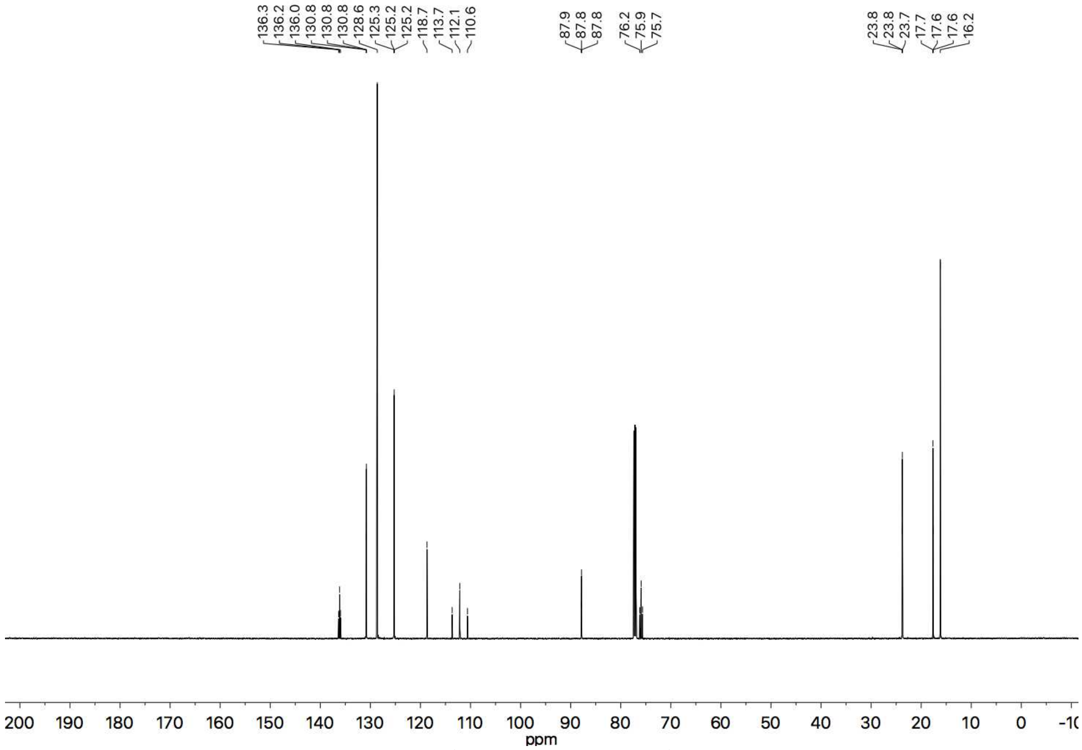




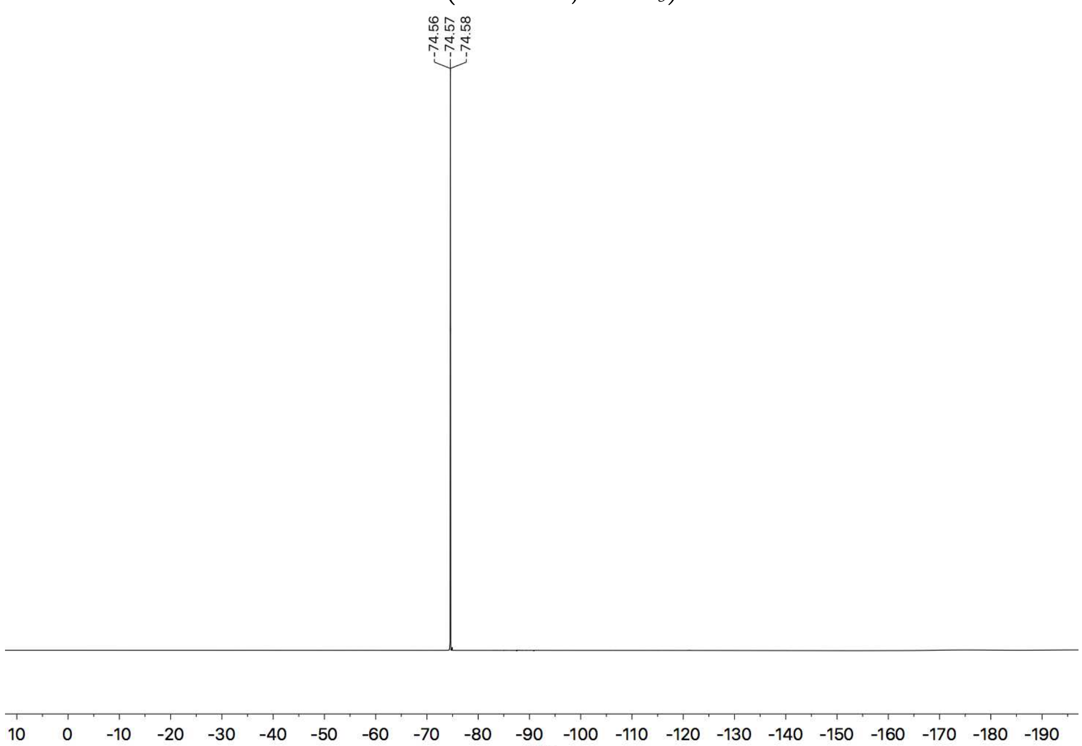
^{1}H NMR (600 MHz, $CDCl_3$) – **10a**

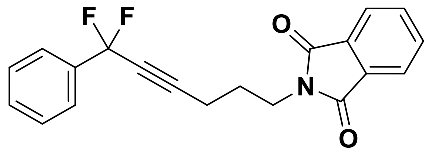


^{13}C NMR (151 MHz, $CDCl_3$) – **10a**

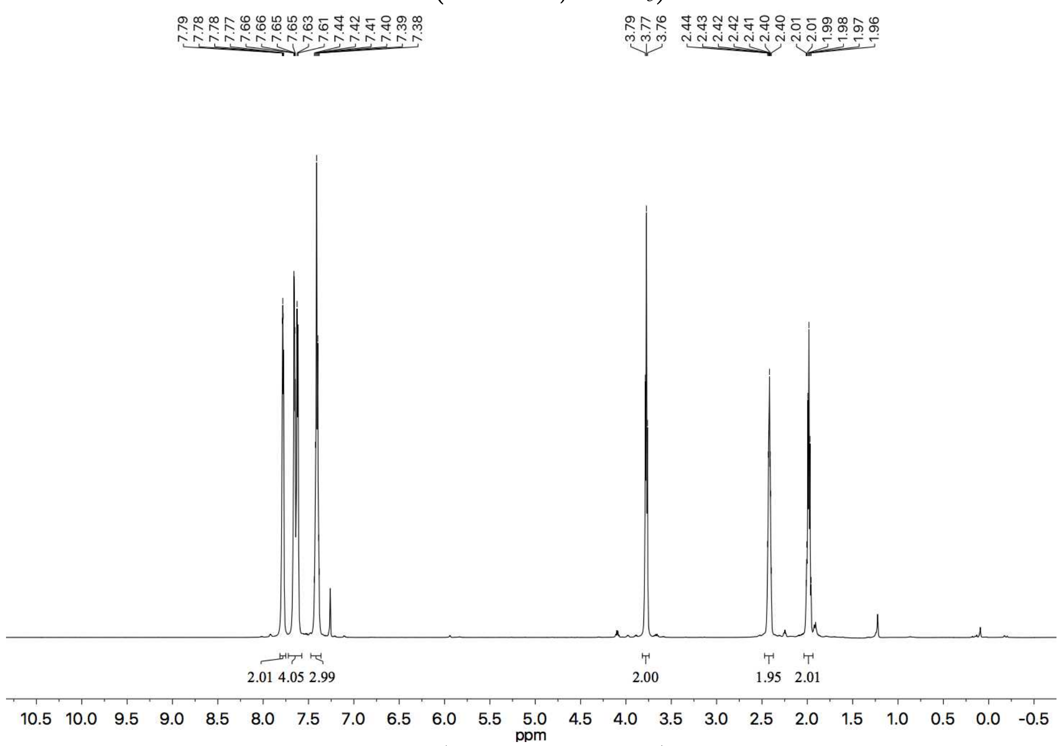


^{19}F NMR (565 MHz, $CDCl_3$) – **10a**

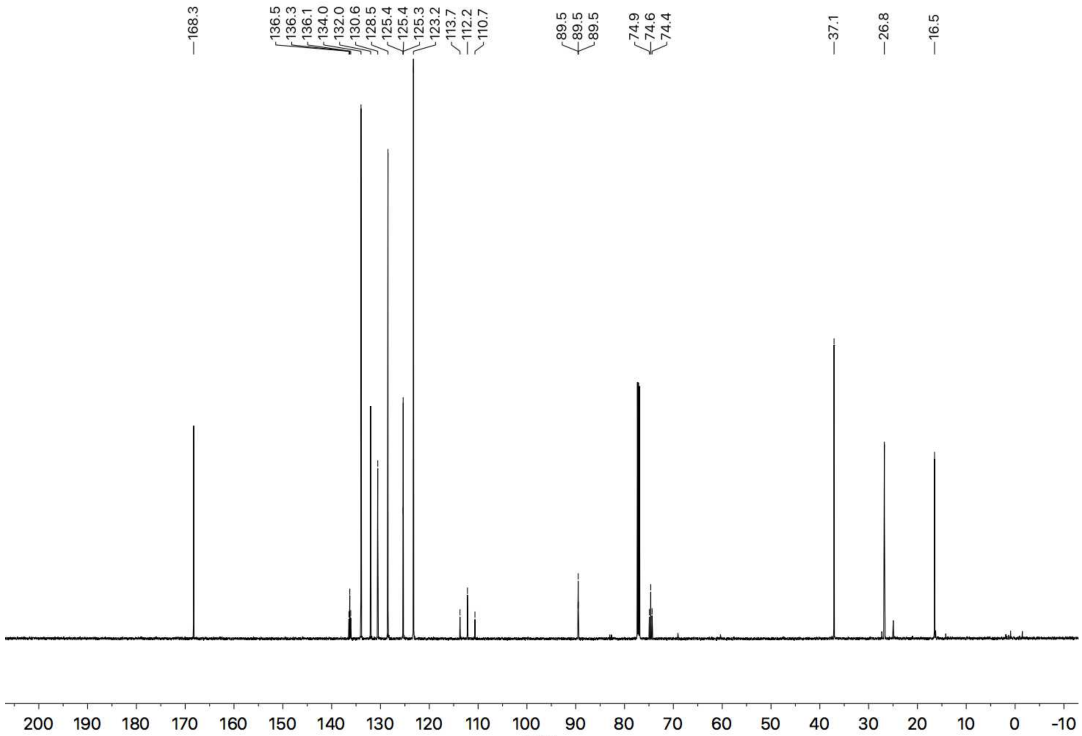




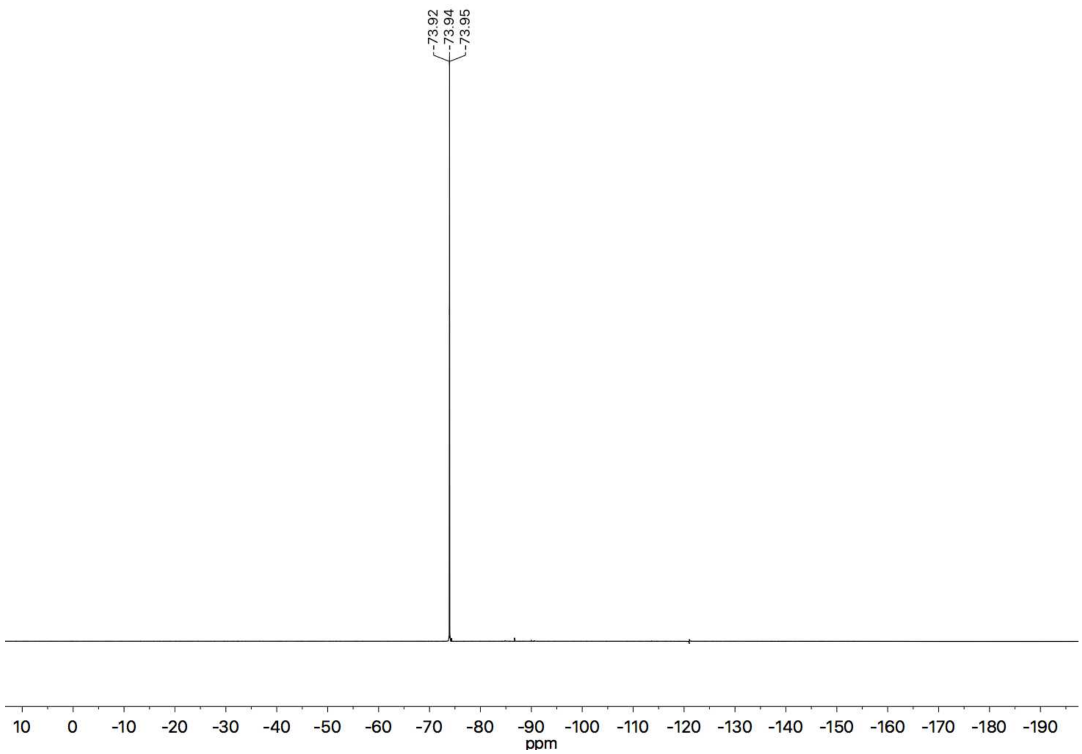
[1]H NMR (600 MHz, $CDCl_3$) – **11a**

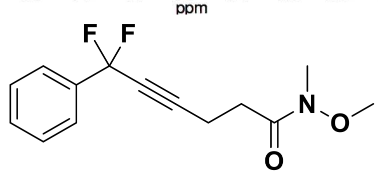


[13]C NMR (151 MHz, $CDCl_3$) – **11a**

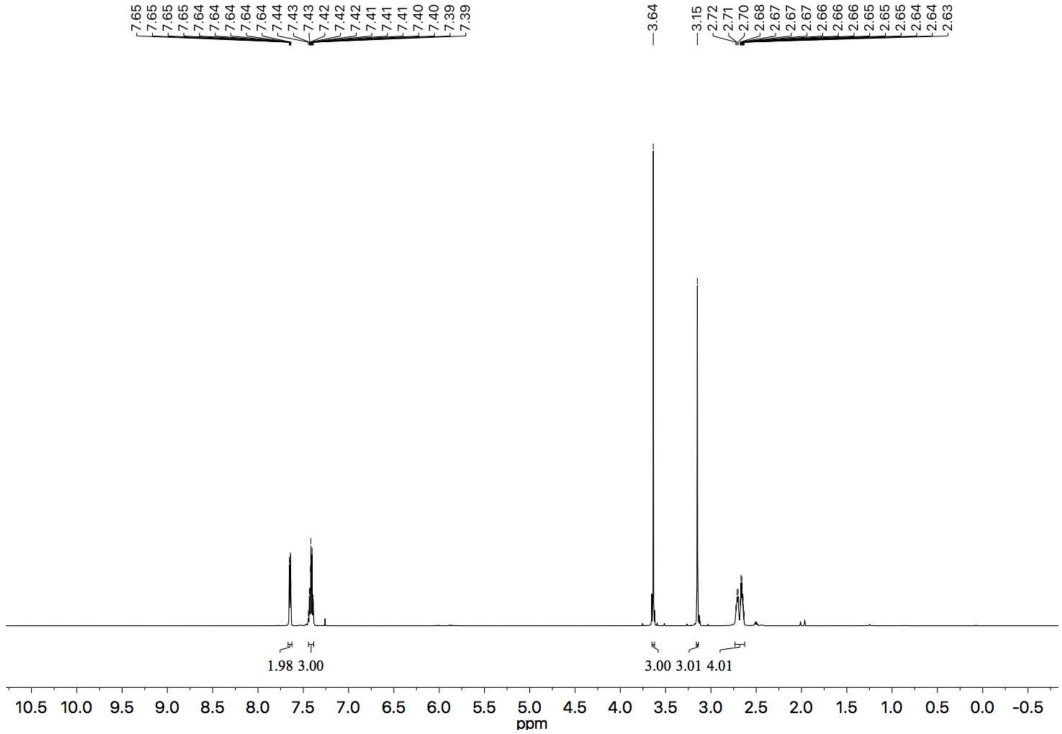


^{19}F NMR (470 MHz, $CDCl_3$) – **11a**

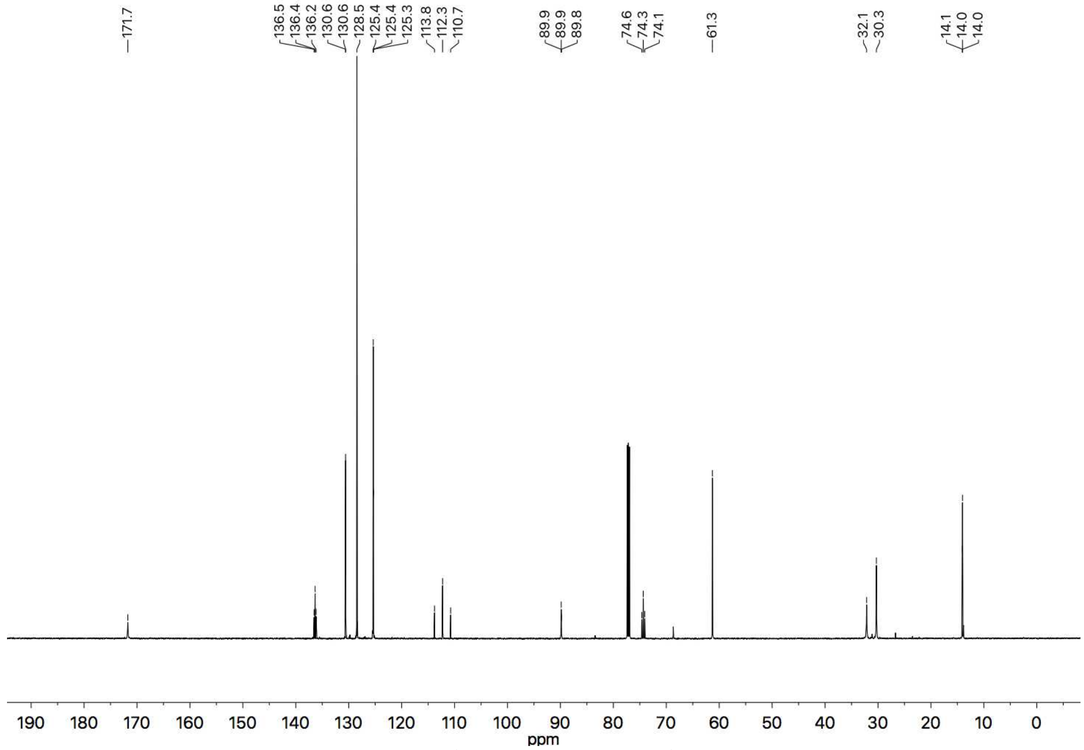




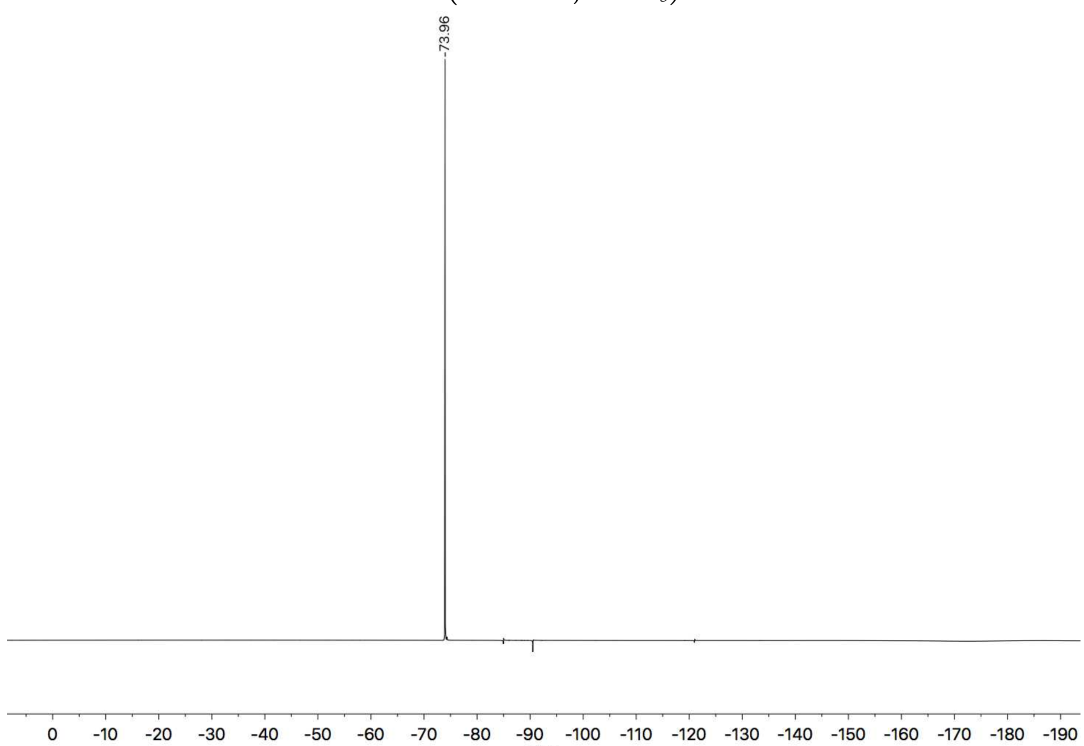
^{1}H NMR (600 MHz, $CDCl_3$) – **12a**

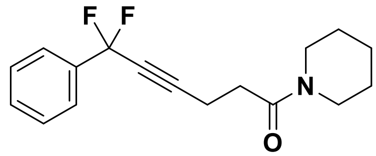


^{13}C NMR (151 MHz, $CDCl_3$) –**12a**

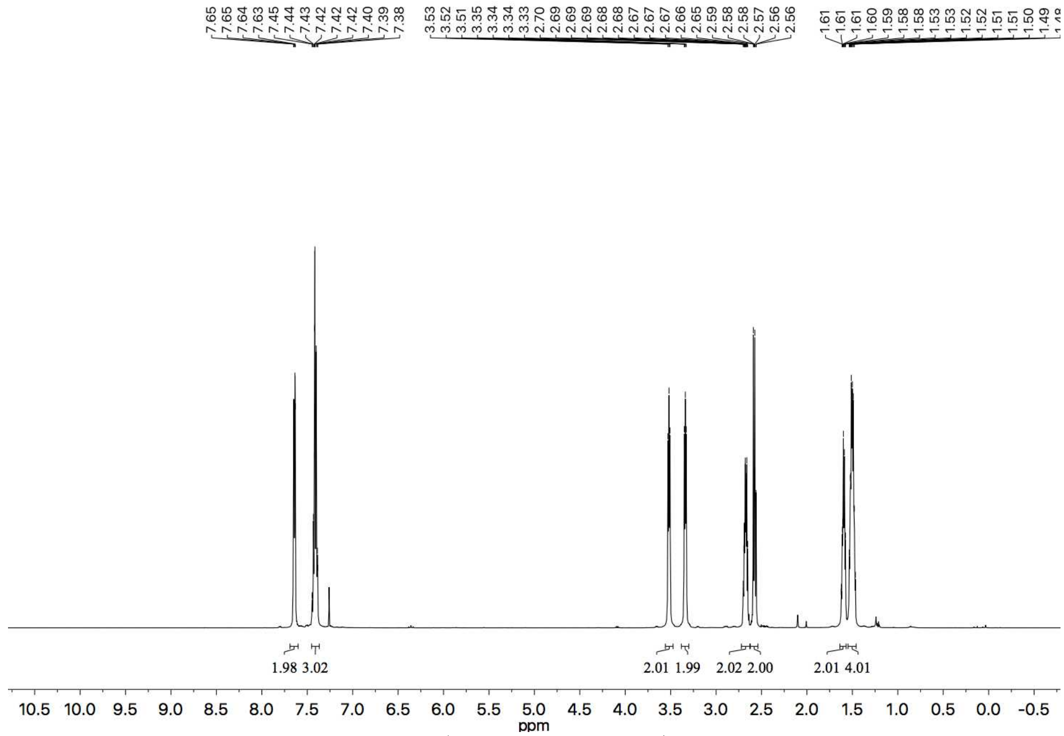


^{19}F NMR (565 MHz, $CDCl_3$) – **12a**

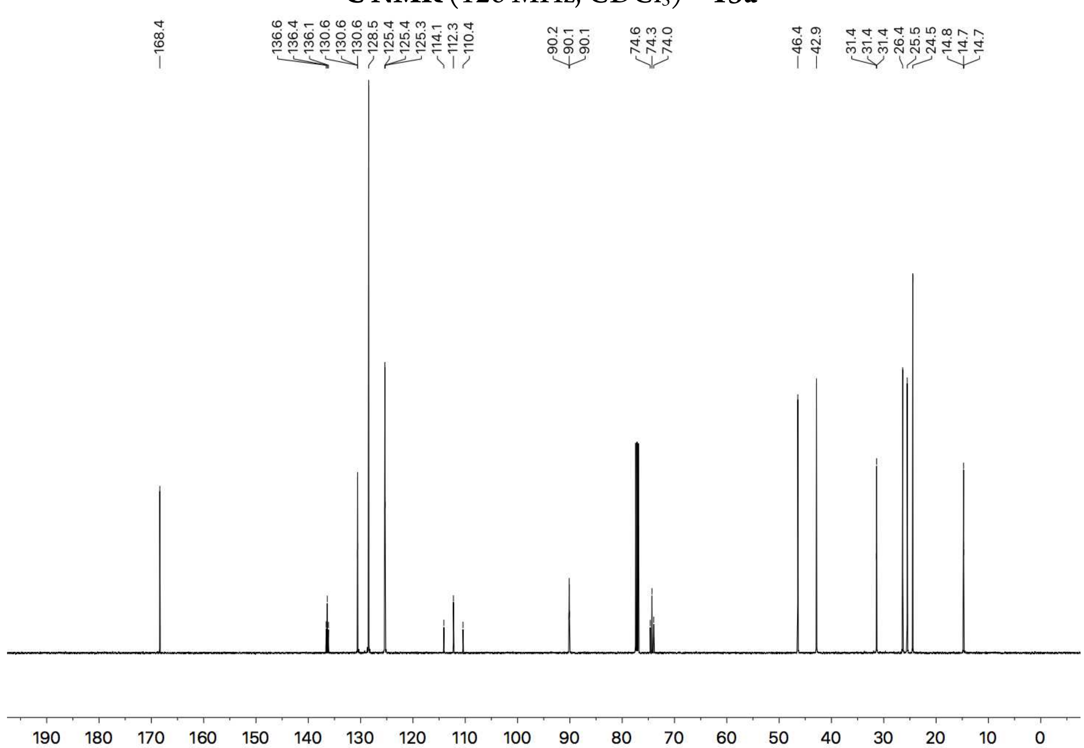




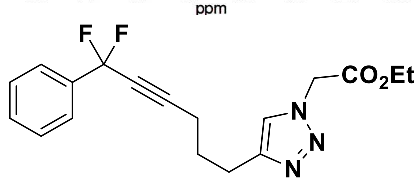
^{1}**H NMR** (500 MHz, $CDCl_3$) – **13a**



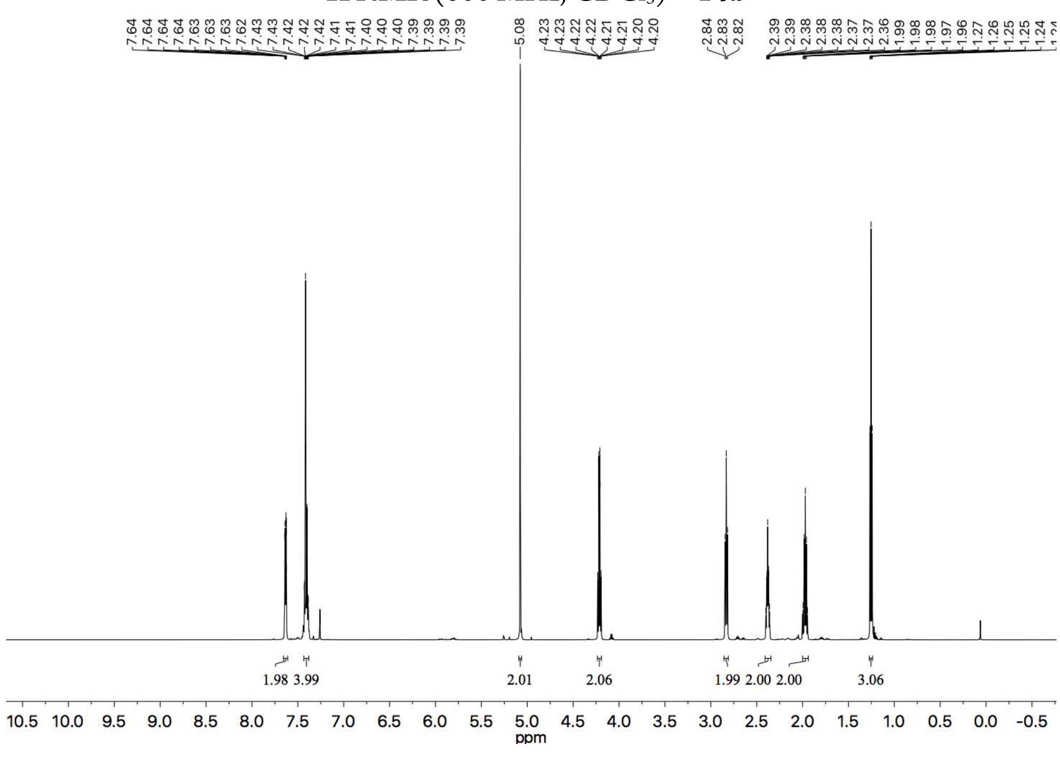
^{13}**C NMR** (126 MHz, $CDCl_3$) – **13a**



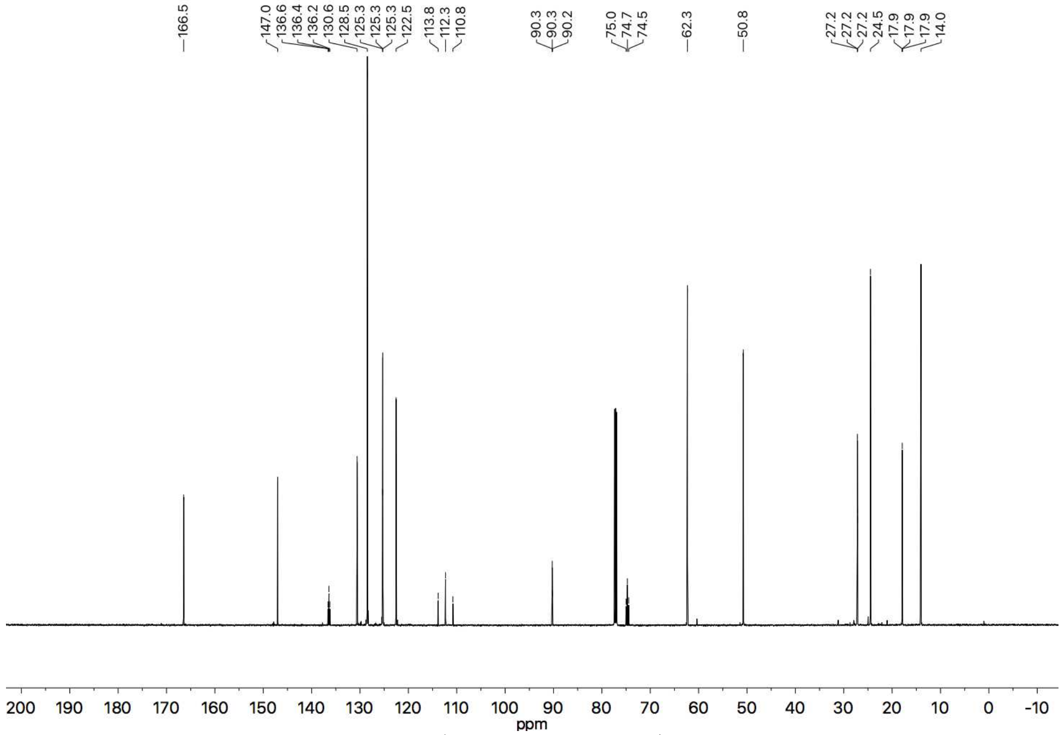
^{19}F NMR (470 MHz, $CDCl_3$) – **13a**



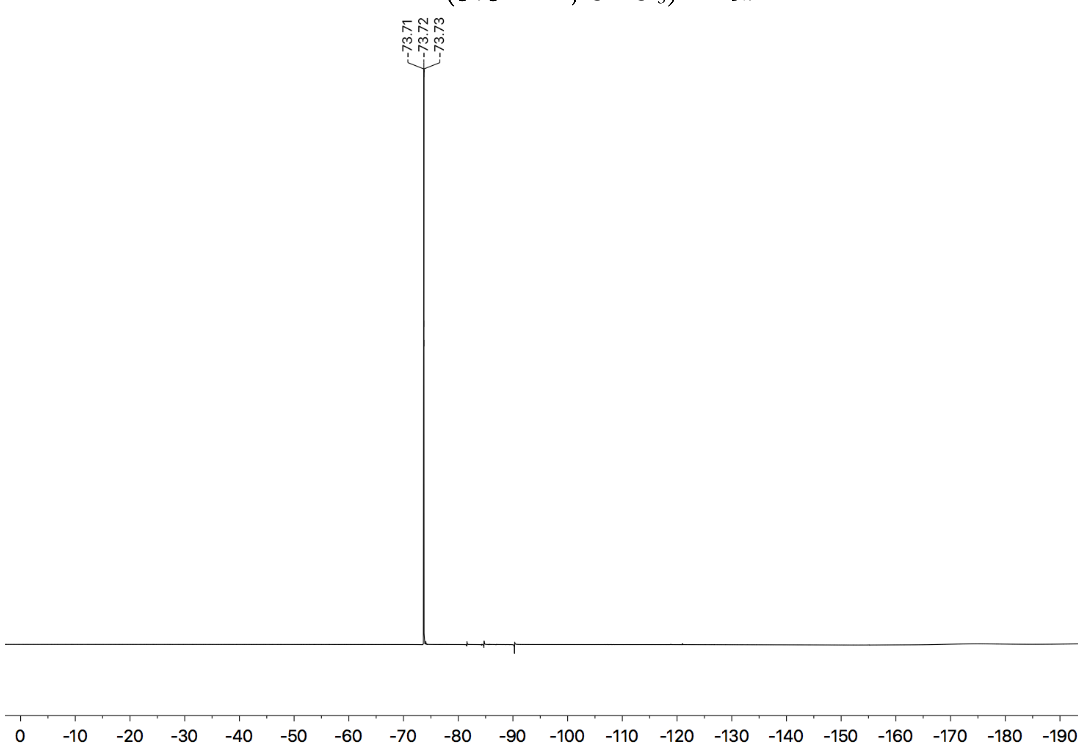
^{1}H NMR (600 MHz, $CDCl_3$) – **14a**

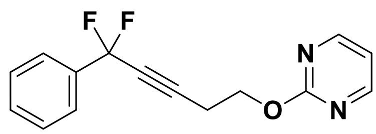


^{13}C NMR (151 MHz, $CDCl_3$) – **14a**

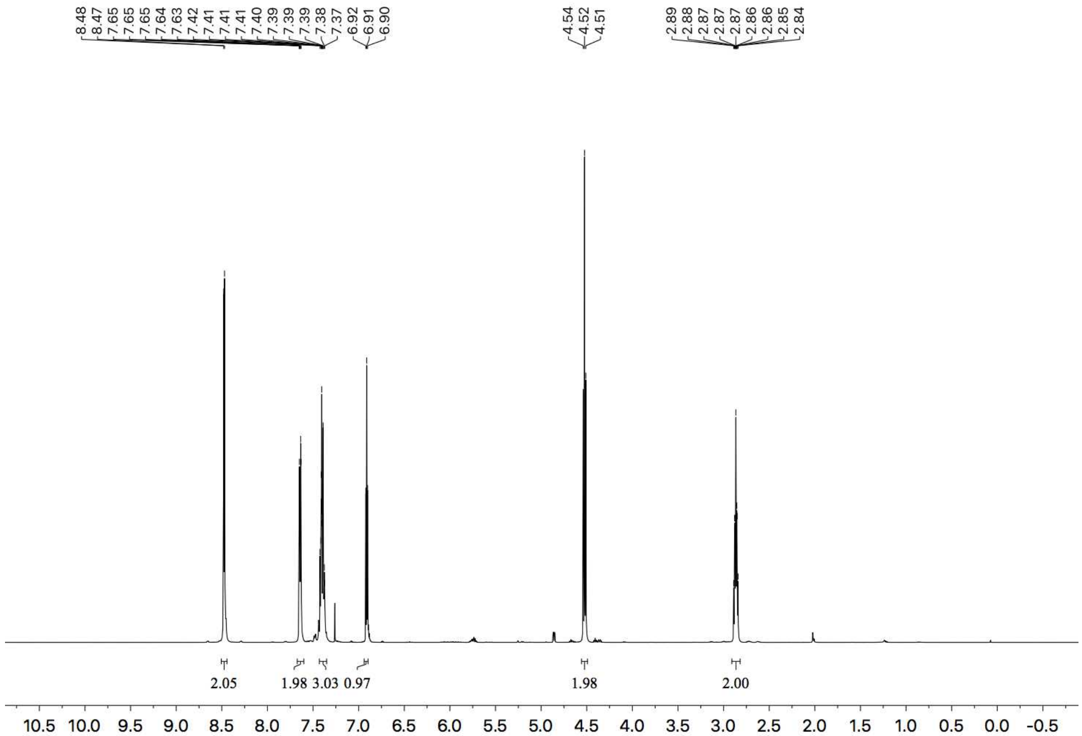


^{19}F NMR (565 MHz, $CDCl_3$) – **14a**

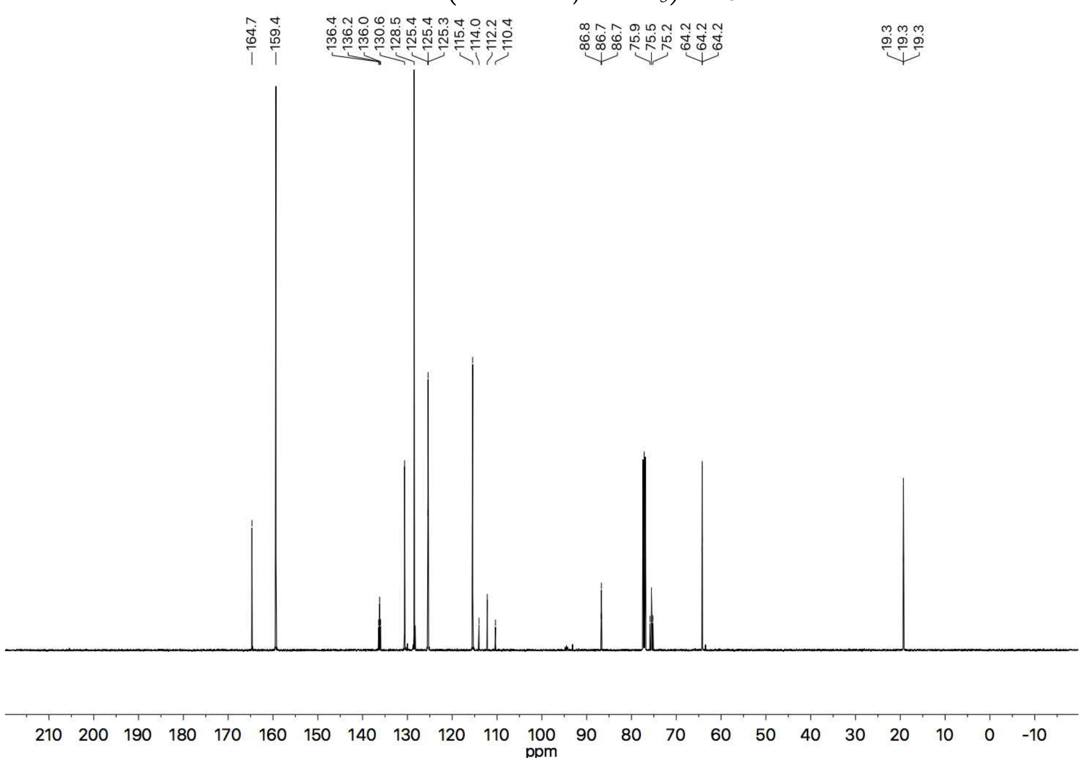




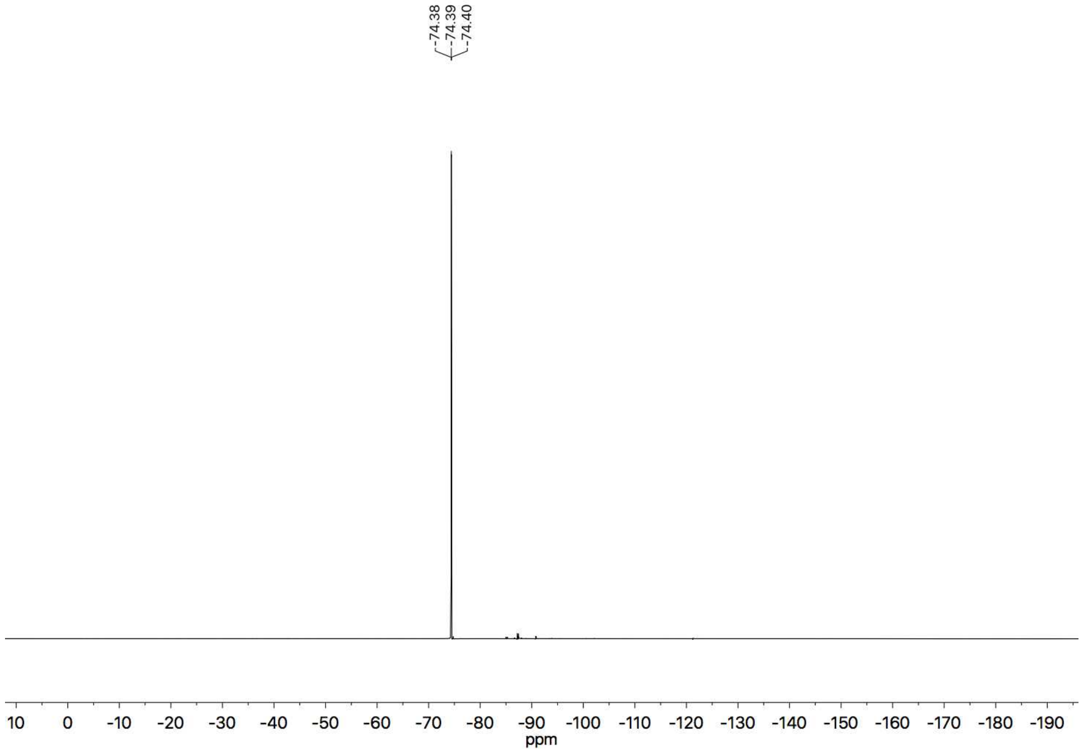
[1]H NMR (500 MHz, $CDCl_3$) – **15a**

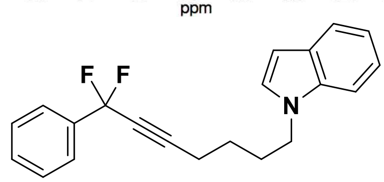


[13]C NMR (126 MHz, $CDCl_3$) – **15a**

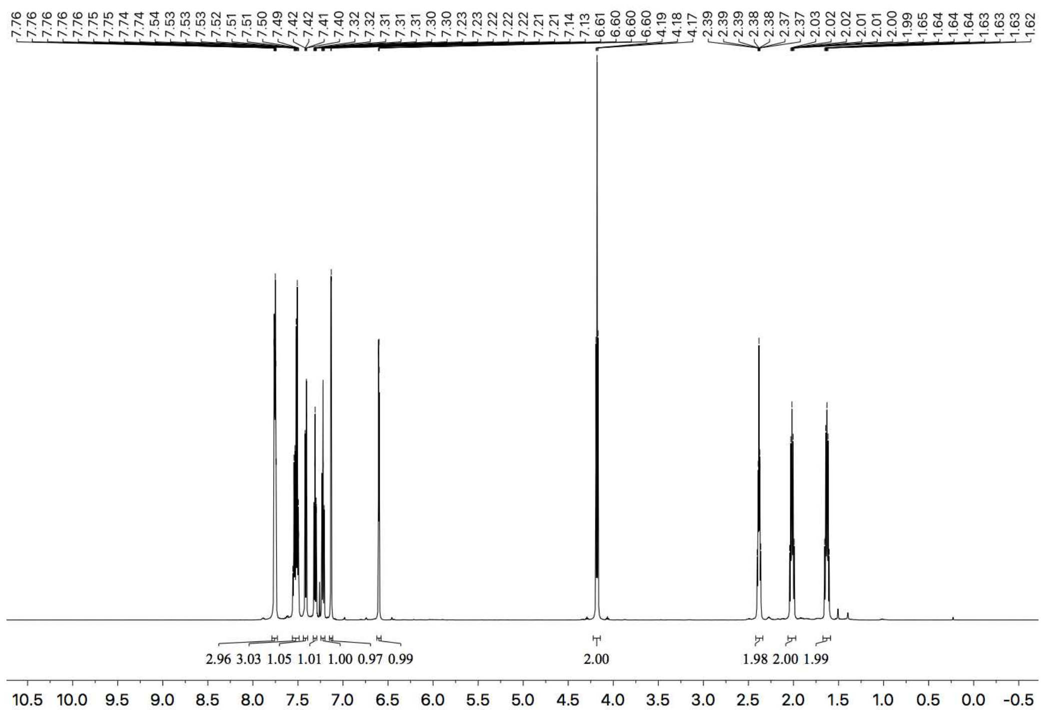


^{19}F NMR (470 MHz, $CDCl_3$) – **15a**

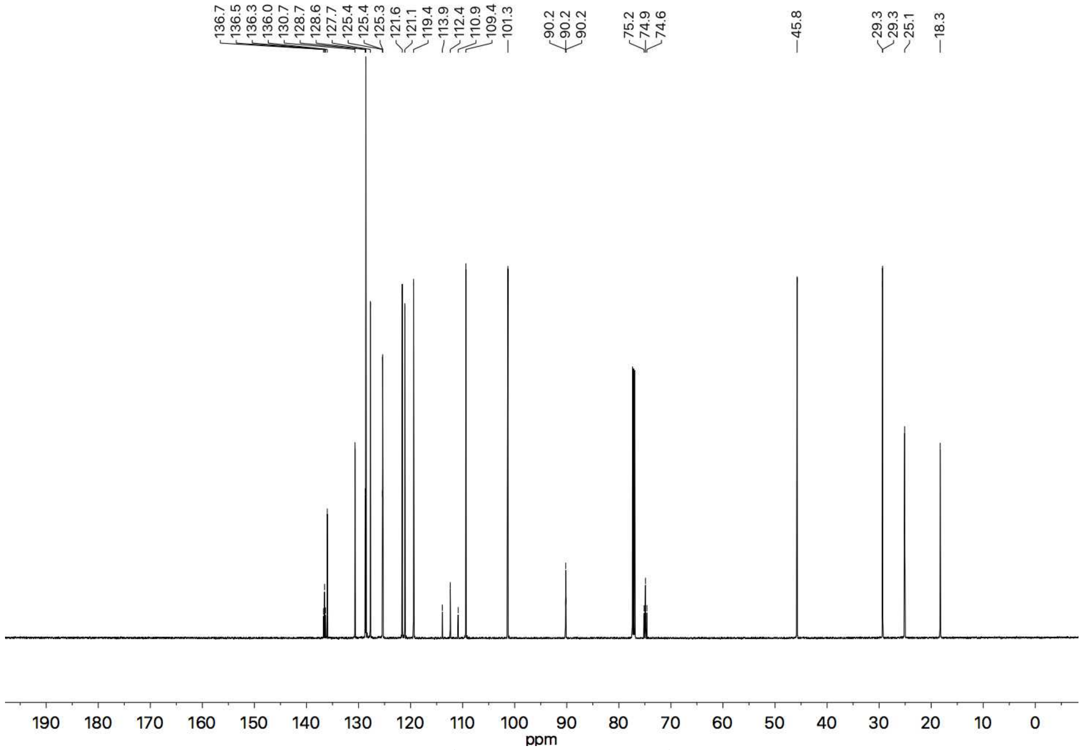




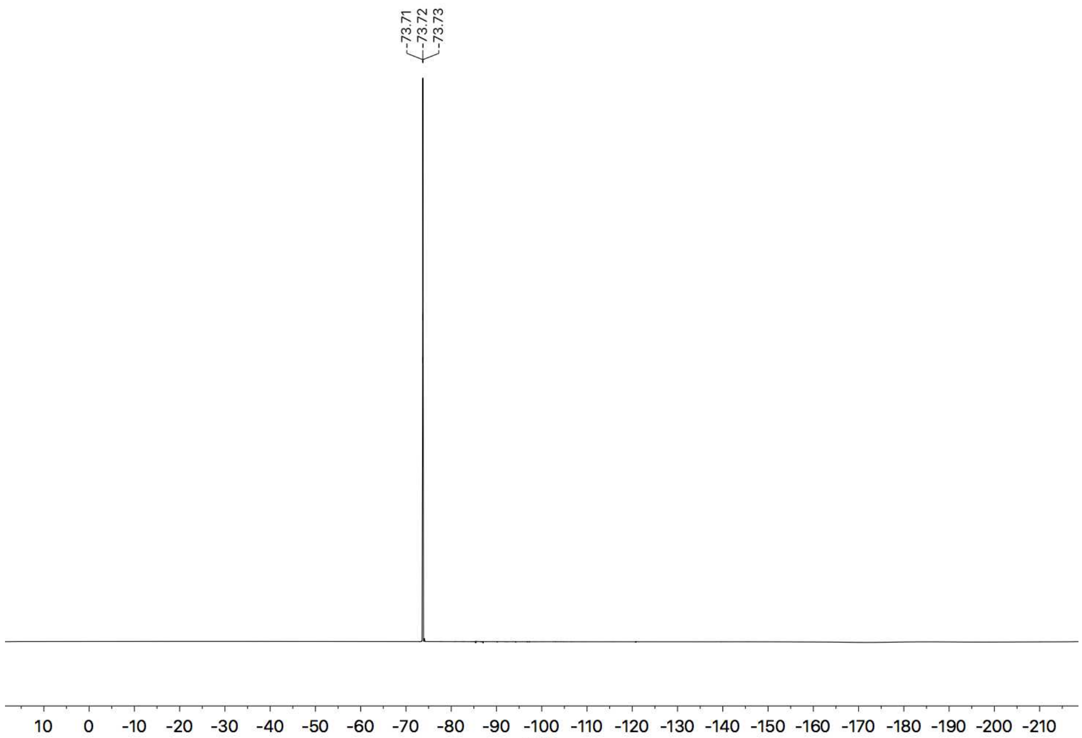
^{1}H NMR (600 MHz, $CDCl_3$) – **16a**

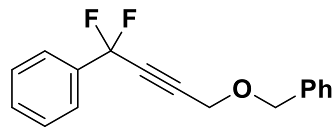


^{13}C NMR (151 MHz, $CDCl_3$) – **16a**

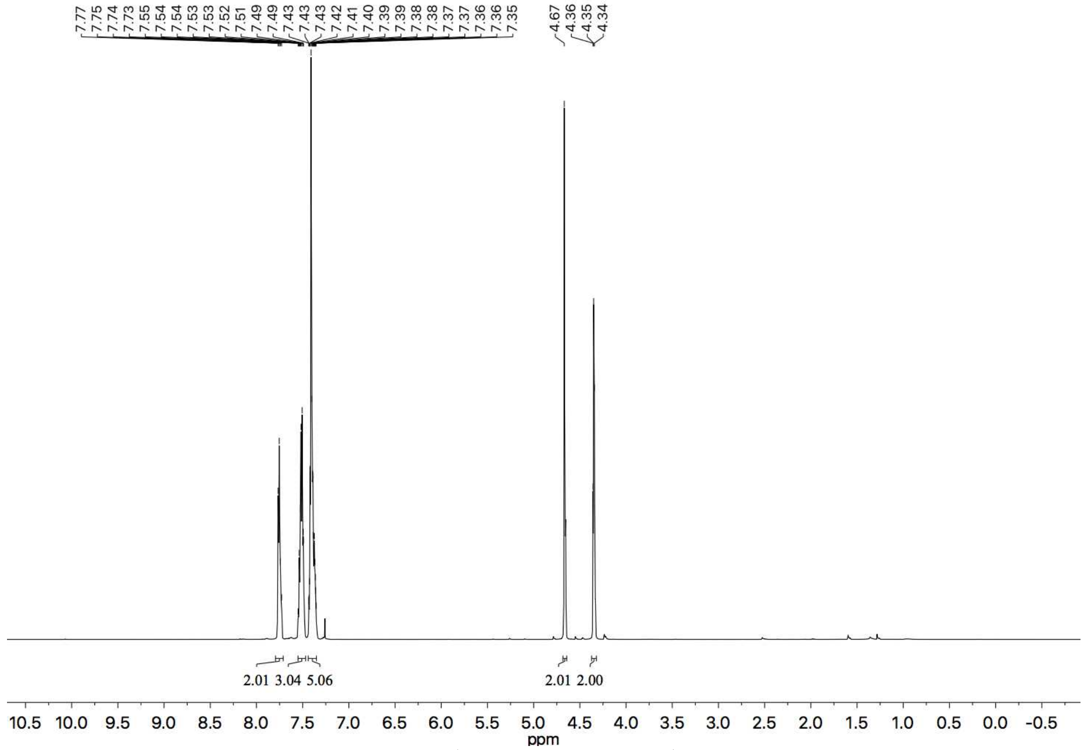


^{19}F NMR (565 MHz, $CDCl_3$) – **16a**

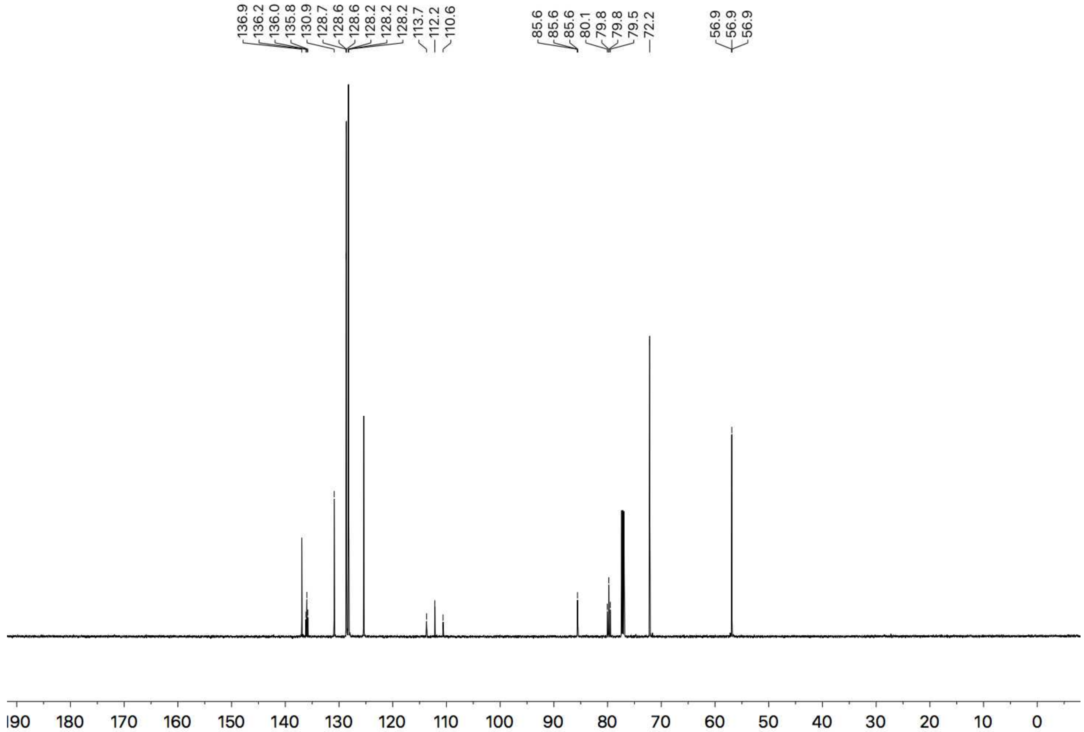




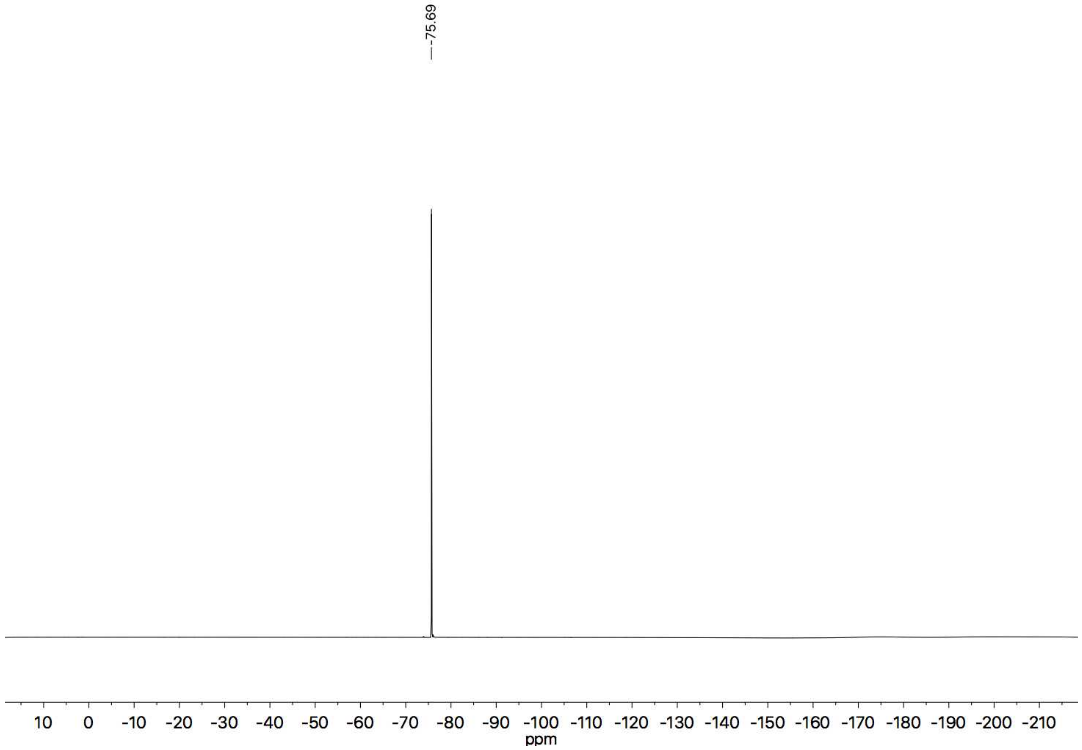
^{1}H NMR (600 MHz, $CDCl_3$) – **17a**

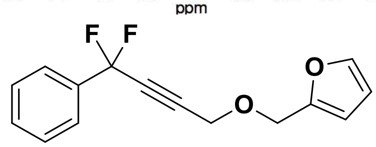


^{13}C NMR (151 MHz, $CDCl_3$) – **17a**

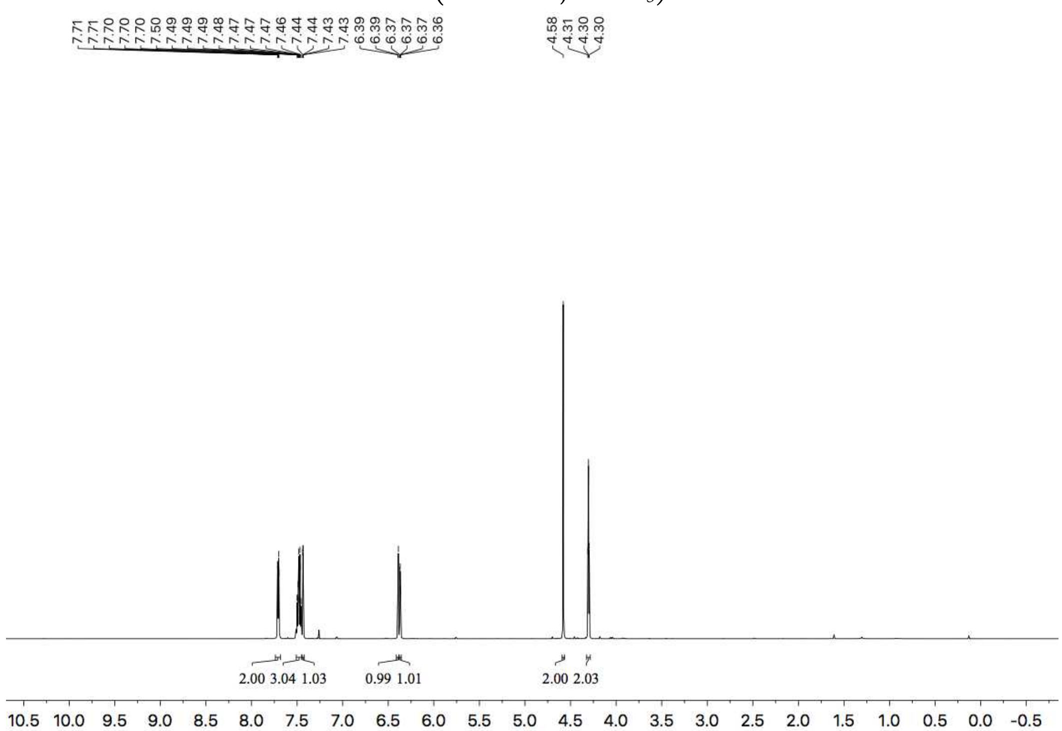


^{19}F NMR (565 MHz, $CDCl_3$) – **17a**

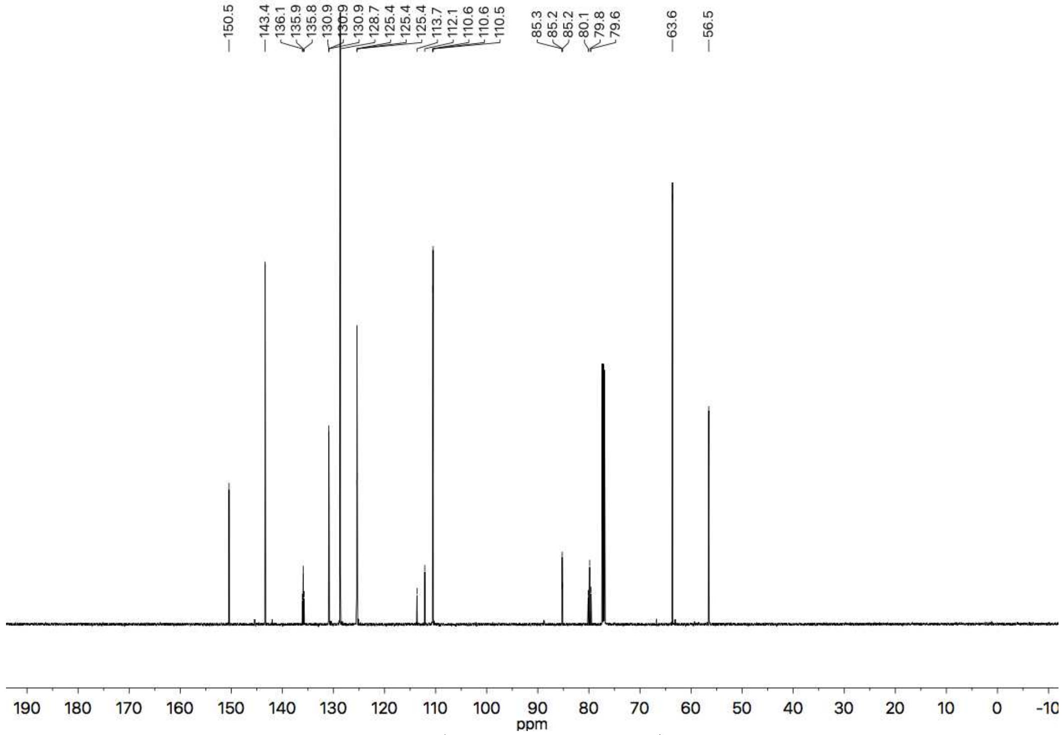




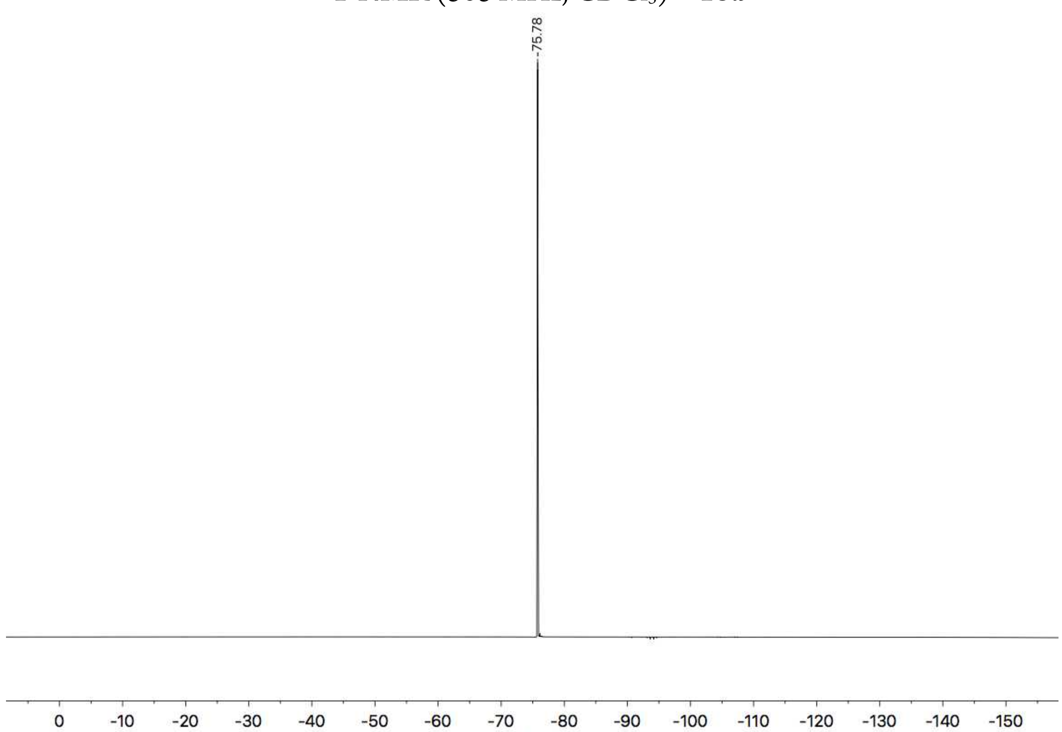
^{1}H NMR (600 MHz, $CDCl_3$) – **18a**

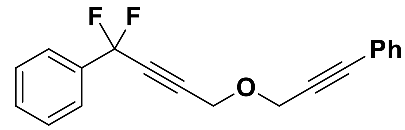


^{13}C NMR (151 MHz, $CDCl_3$) – **18a**

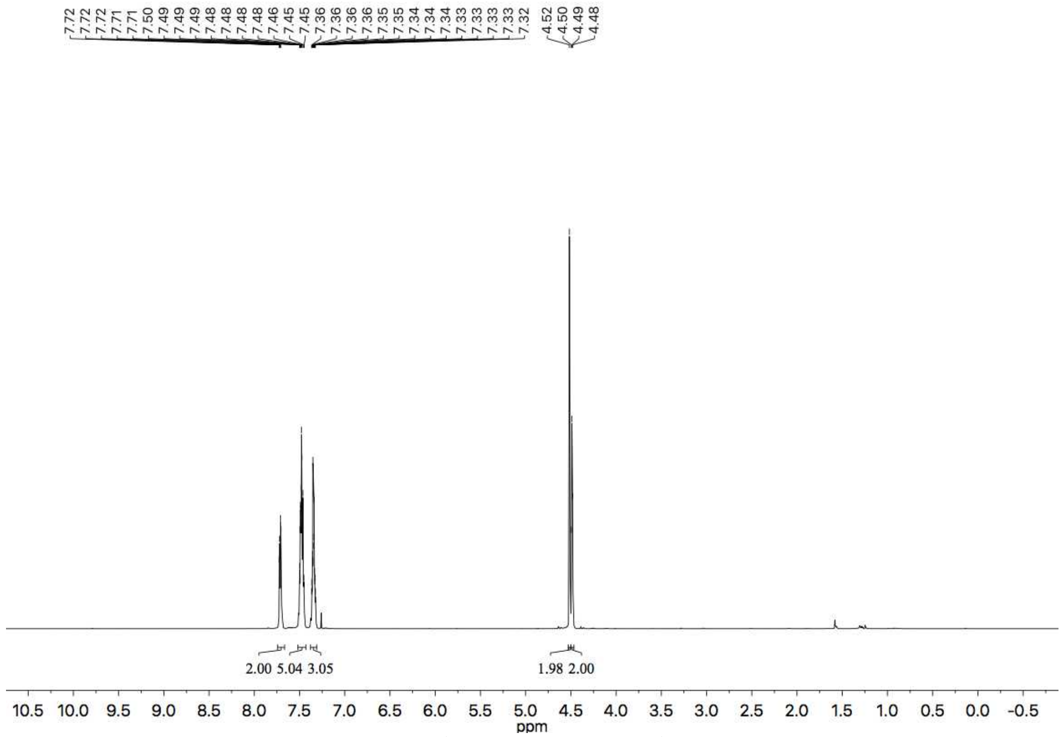


^{19}F NMR (565 MHz, $CDCl_3$) – **18a**

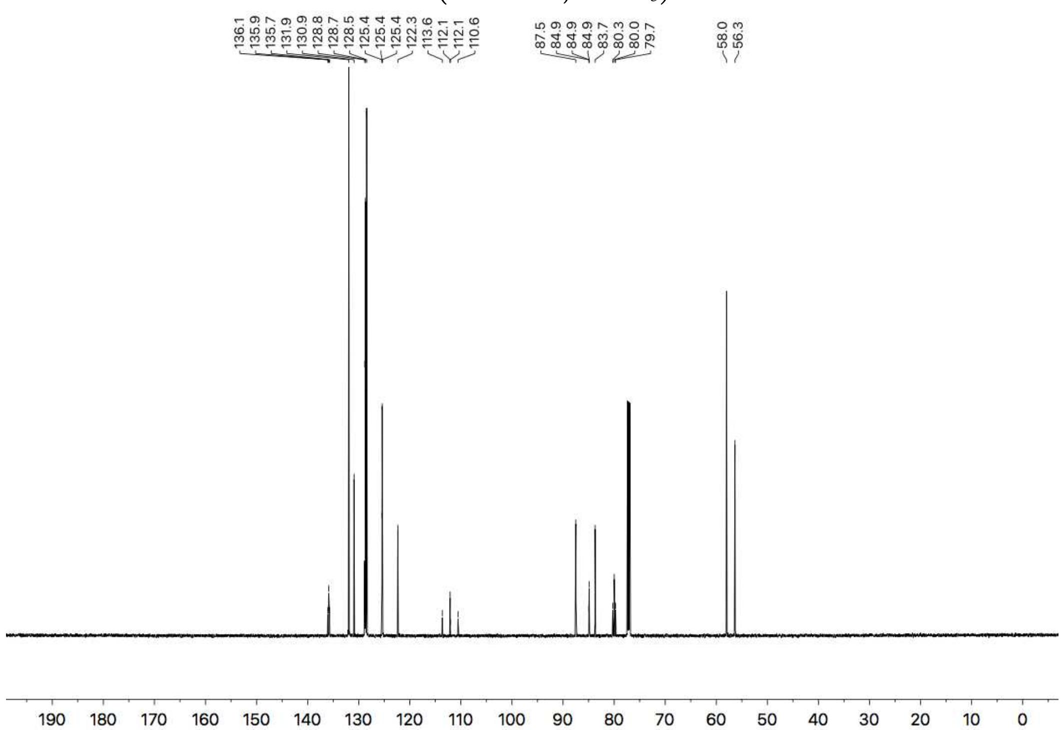




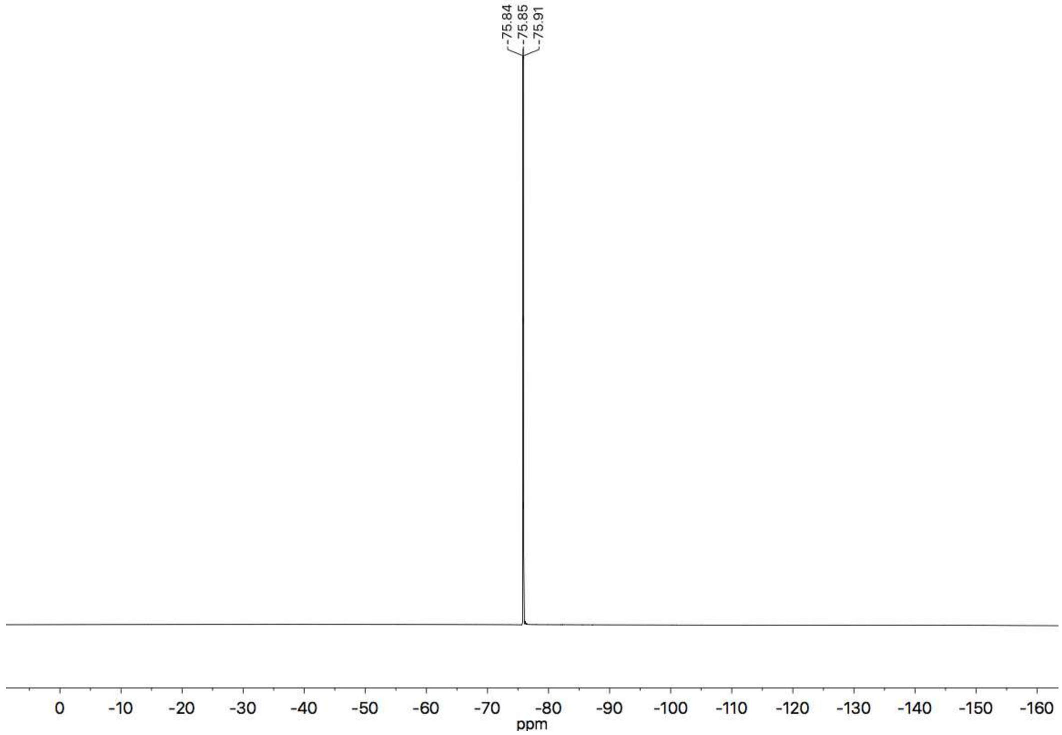
^{1}H NMR (600 MHz, $CDCl_3$) – **19a**

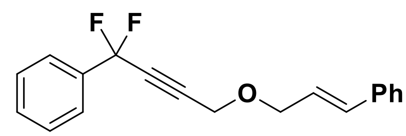


^{13}C NMR (151 MHz, $CDCl_3$) – **19a**

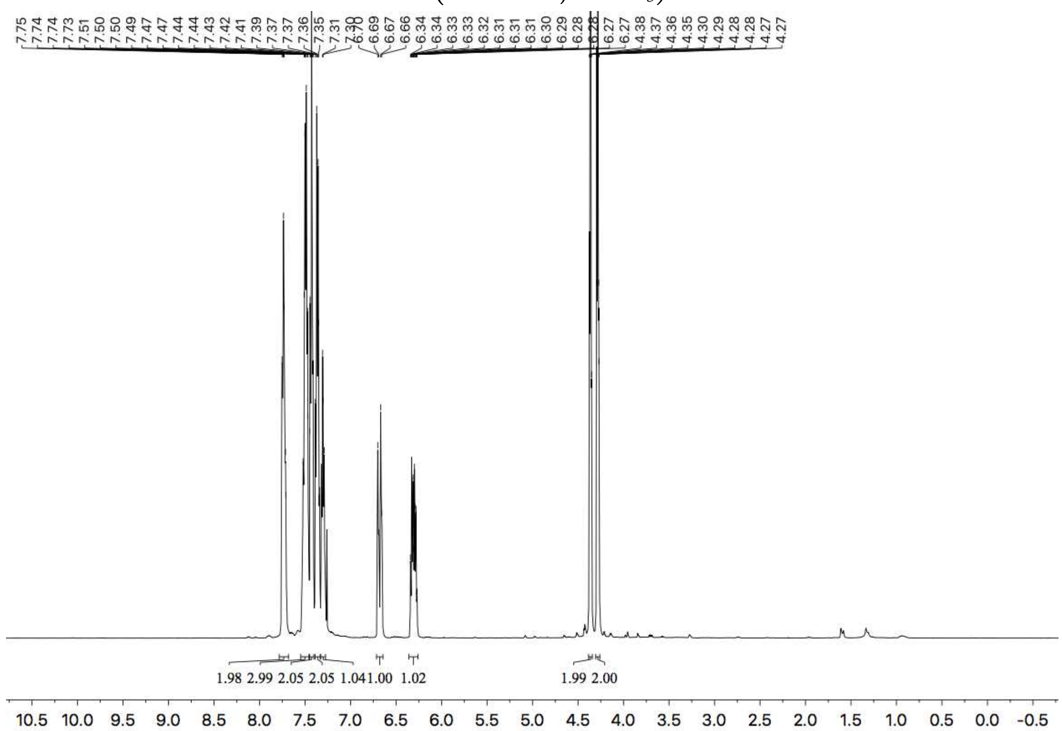


^{19}F NMR (565 MHz, $CDCl_3$) – **19a**

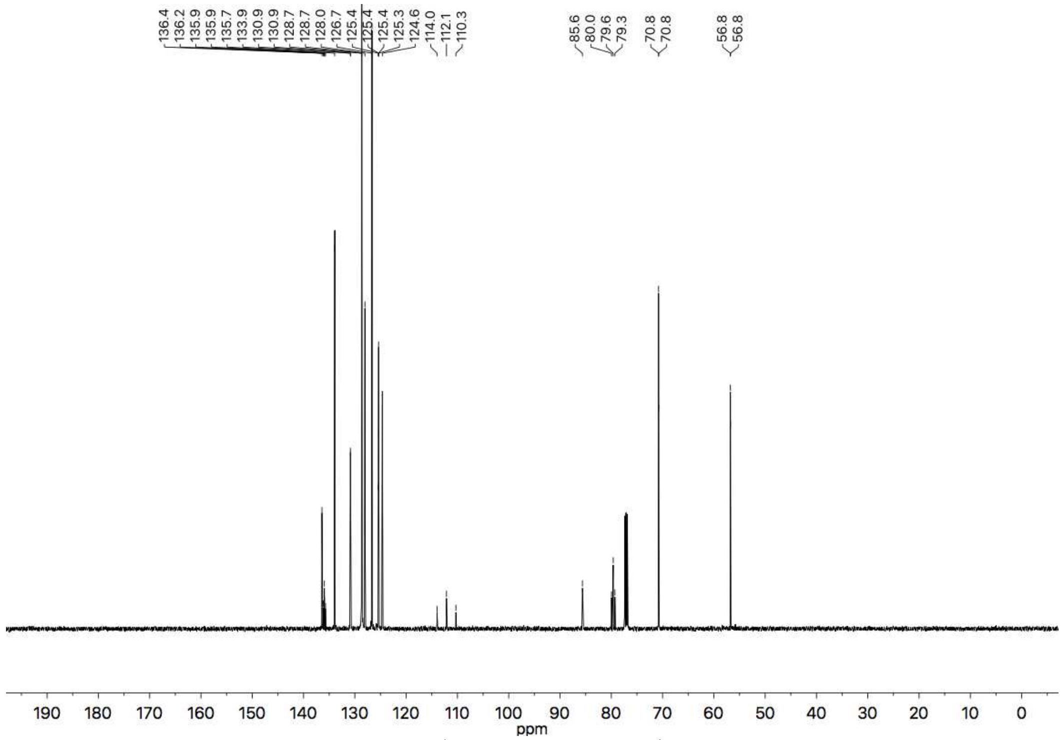




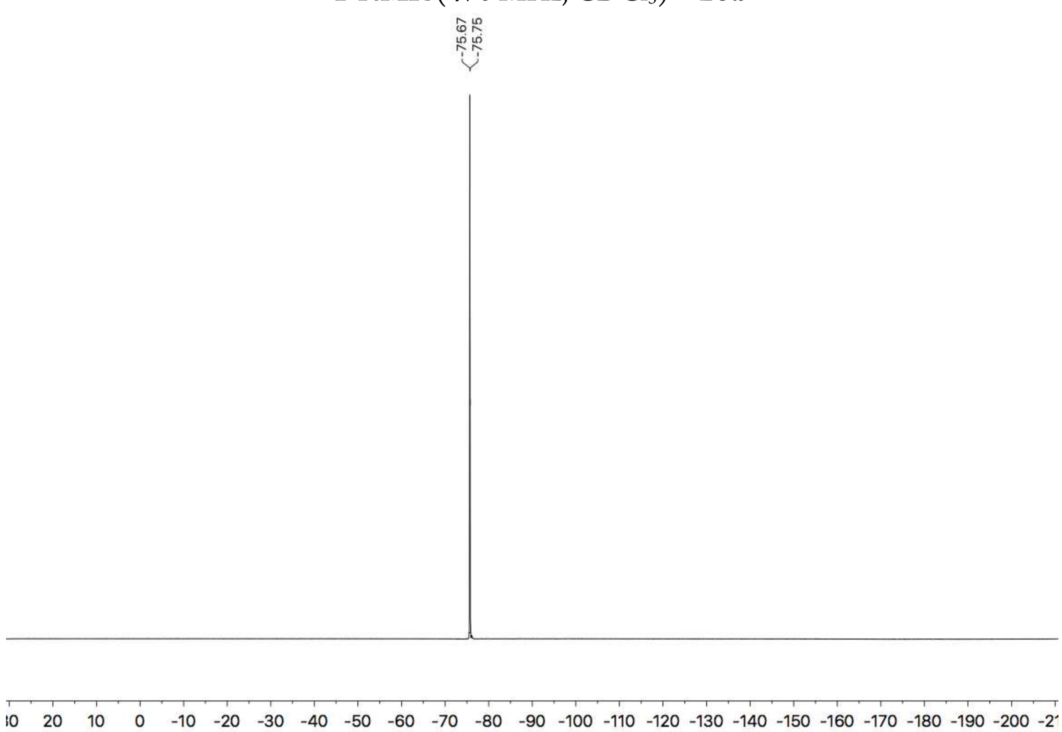
^{1}H NMR (500 MHz, $CDCl_3$) – **20a**

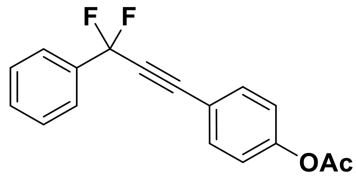


^{13}C NMR (126 MHz, $CDCl_3$) – **20a**

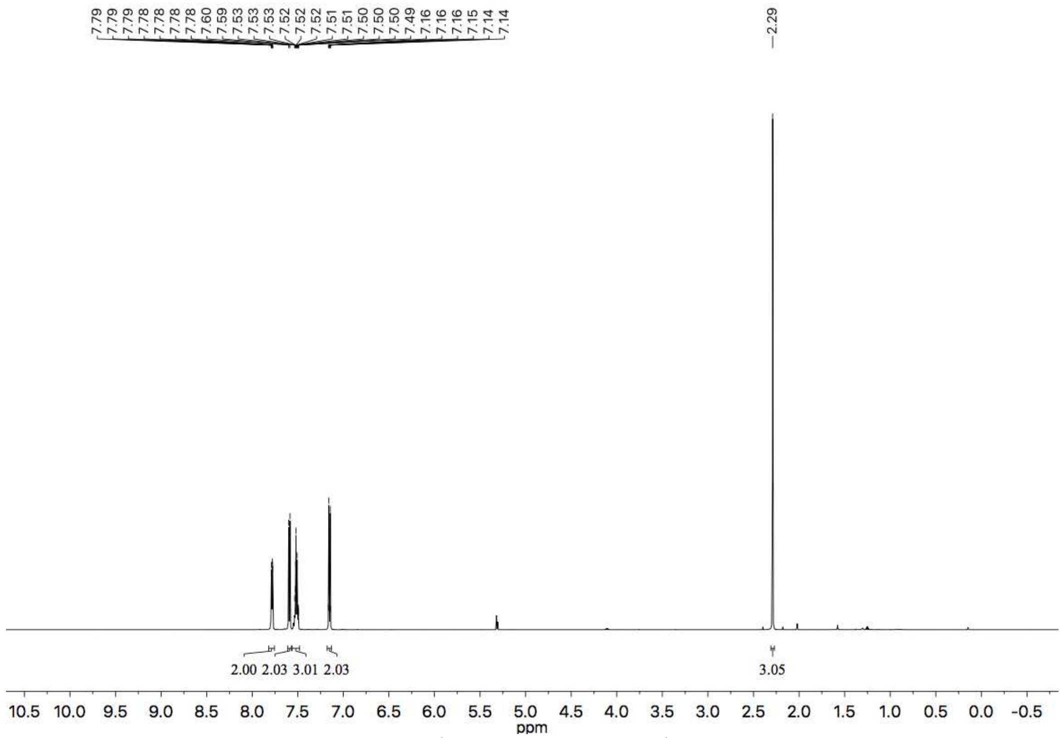


^{19}F NMR (470 MHz, $CDCl_3$) – **20a**

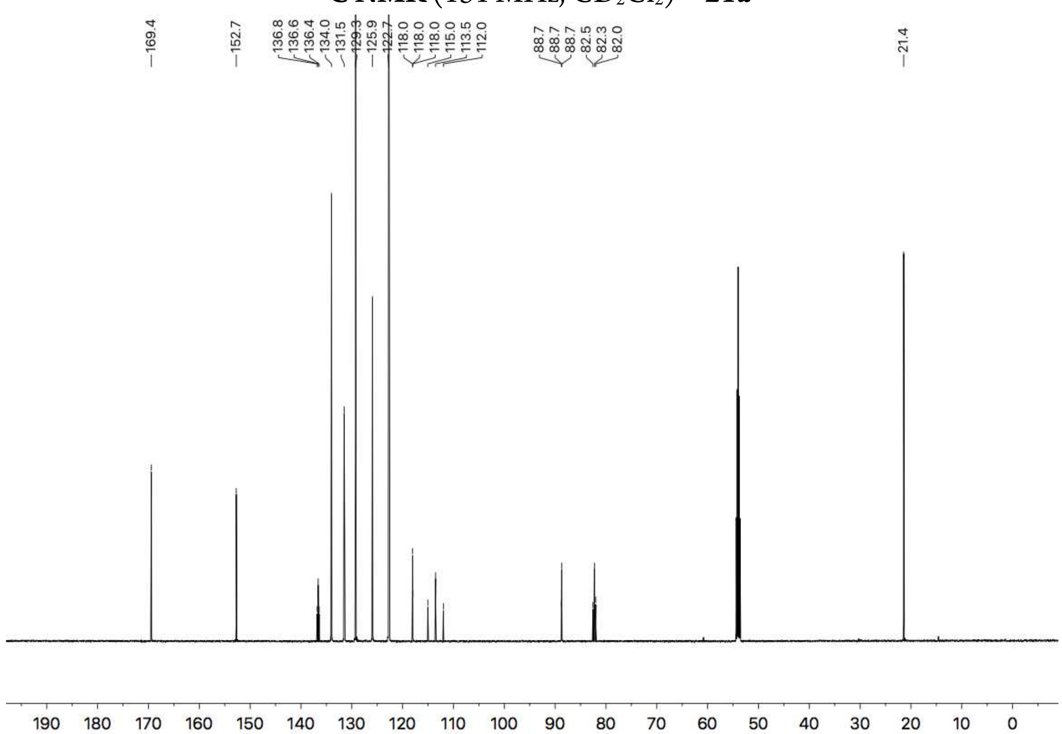




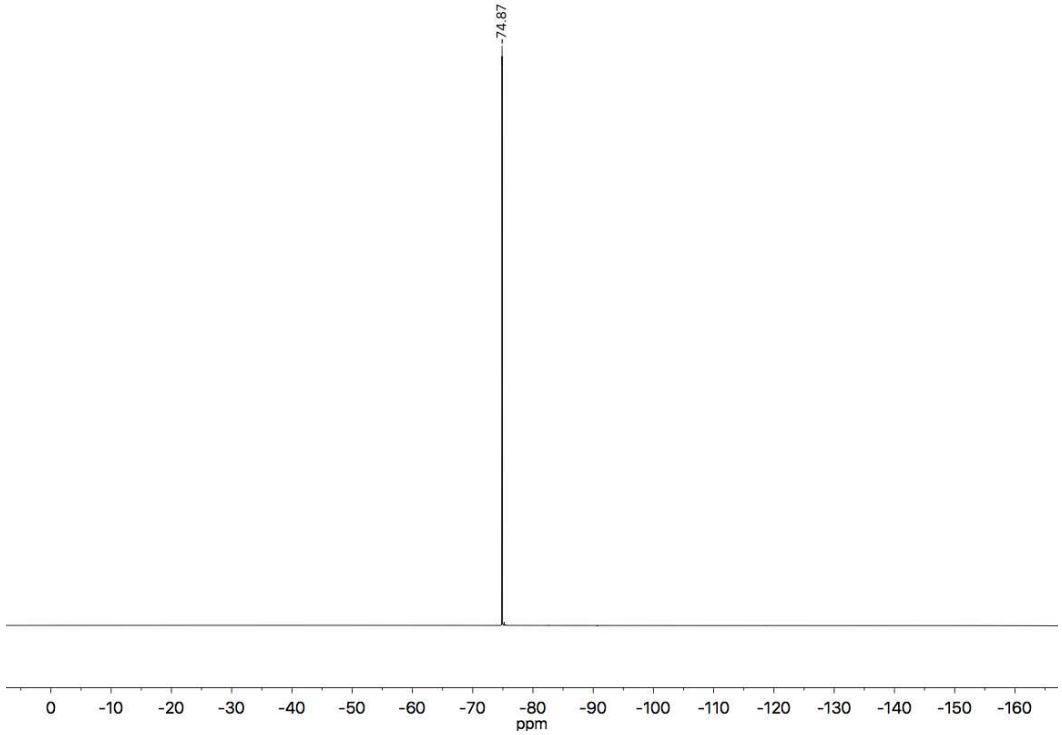
^{1}**H NMR** (600 MHz, CD_2Cl_2) – **21a**

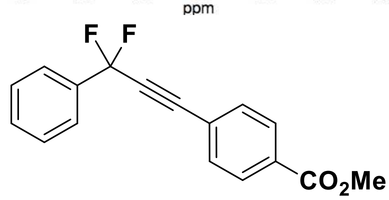


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **21a**

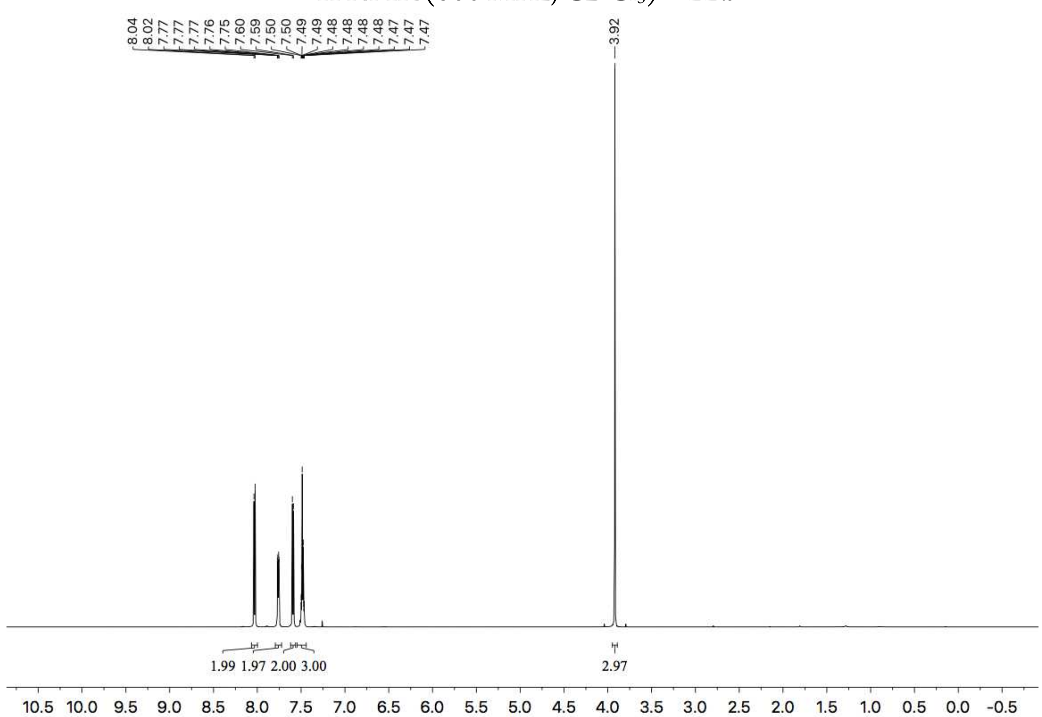


^{19}F NMR (565 MHz, CD_2Cl_2) – **21a**

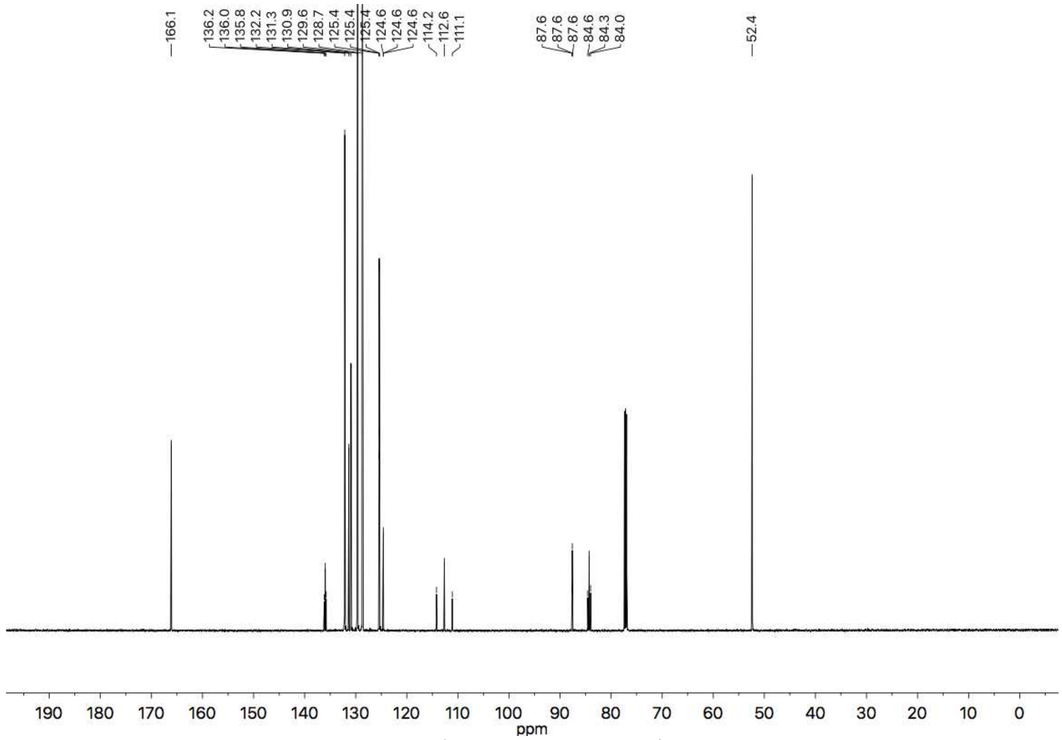




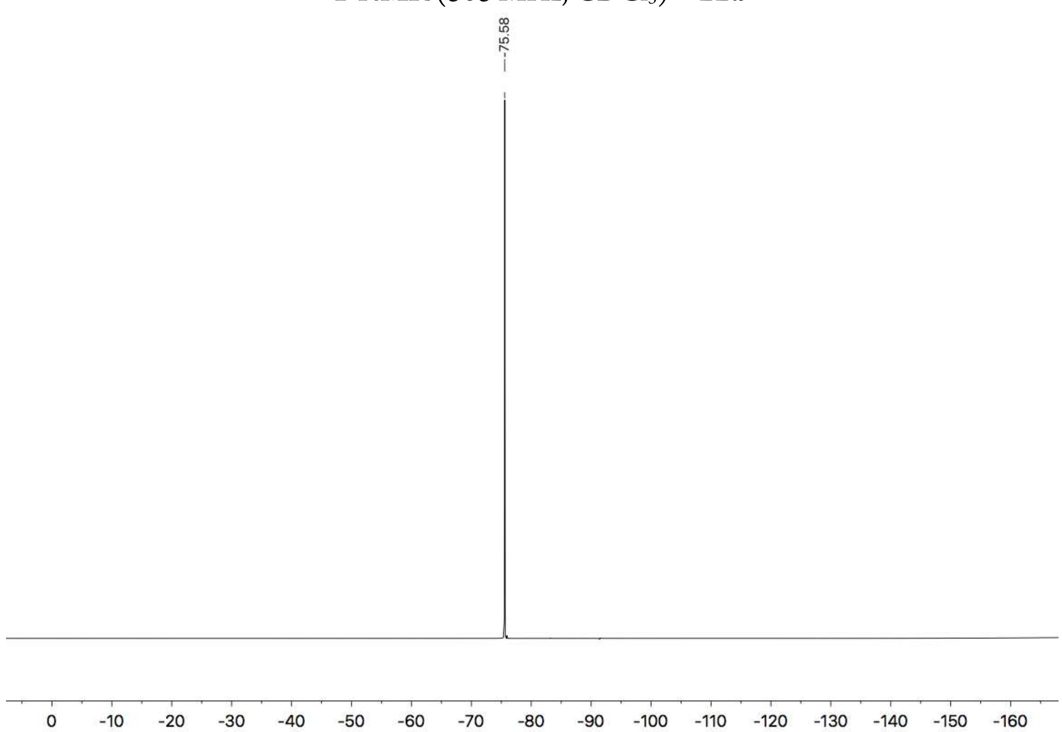
^{1}H NMR (600 MHz, $CDCl_3$) – **22a**

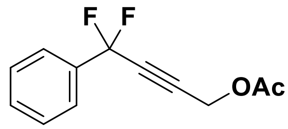


^{13}C NMR (151 MHz, $CDCl_3$) – **22a**

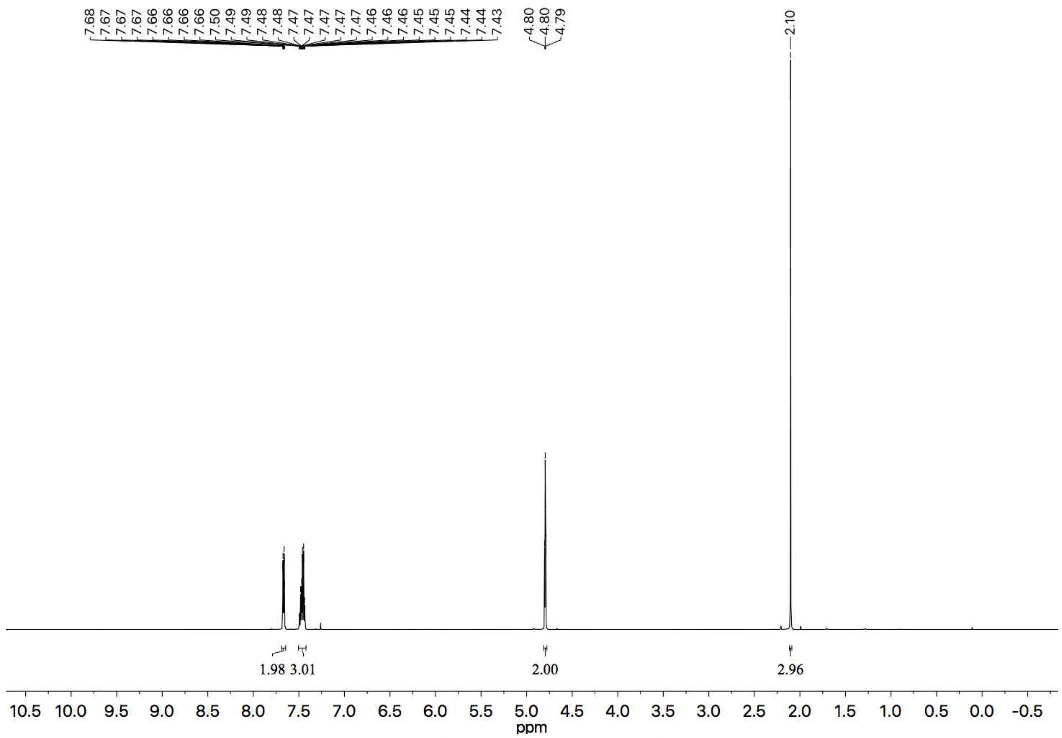


^{19}F NMR (565 MHz, $CDCl_3$) – **22a**

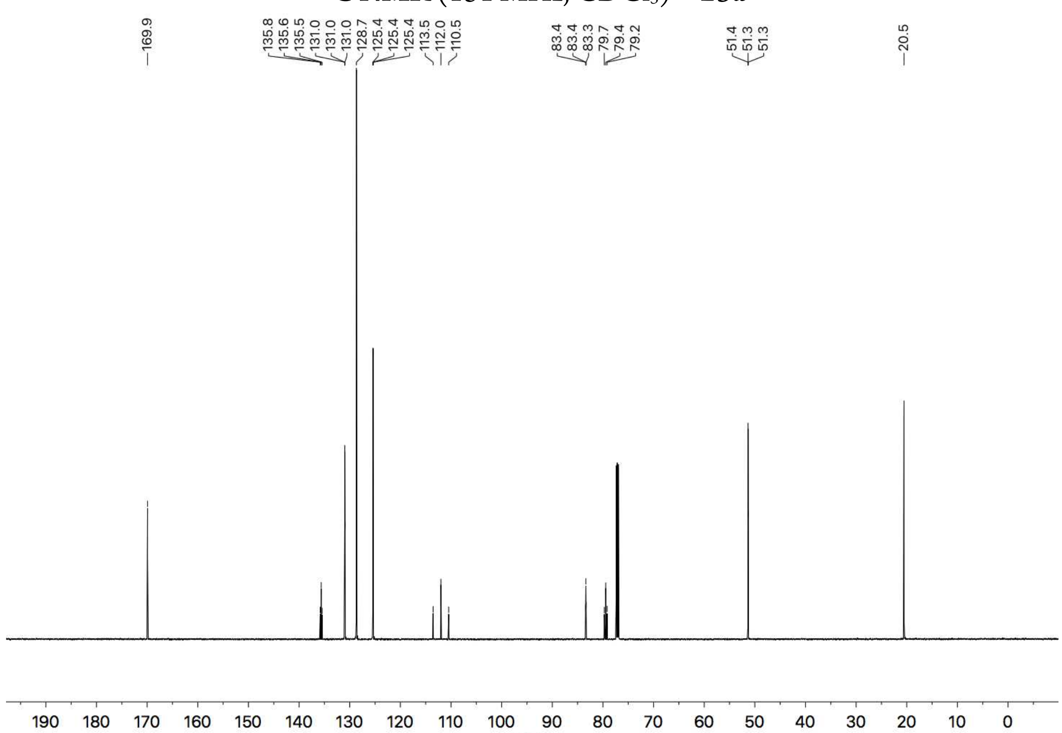




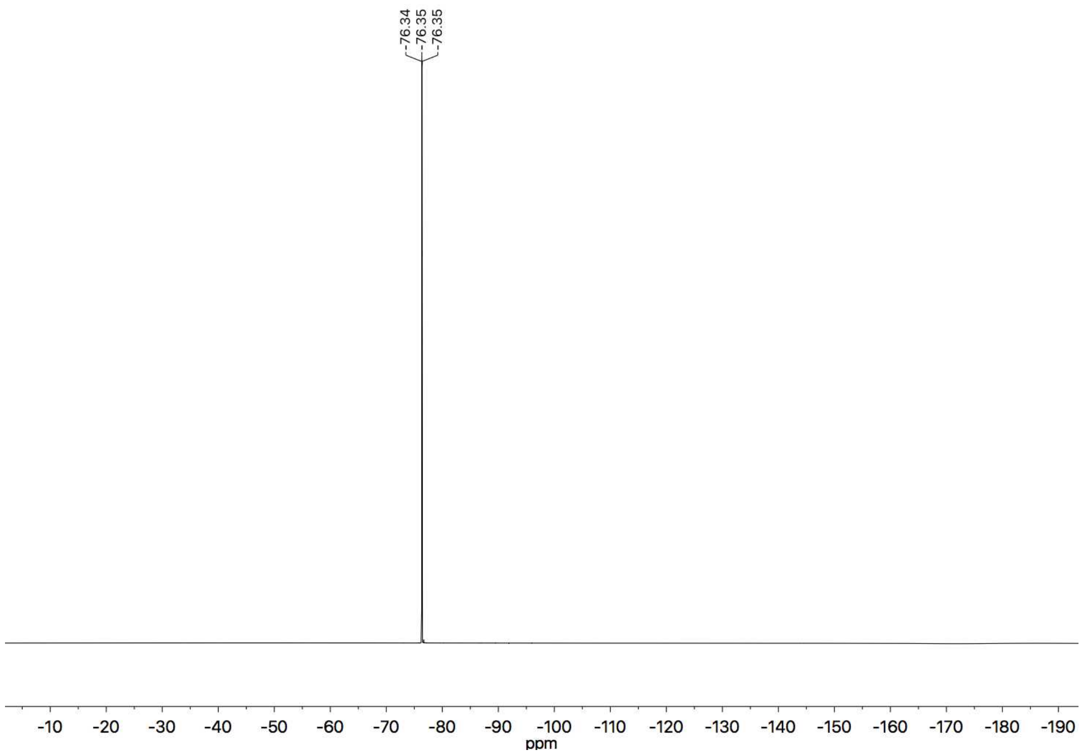
^{1}H NMR (600 MHz, $CDCl_3$) – **23a**

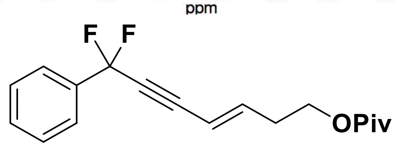


^{13}C NMR (151 MHz, $CDCl_3$) – **23a**

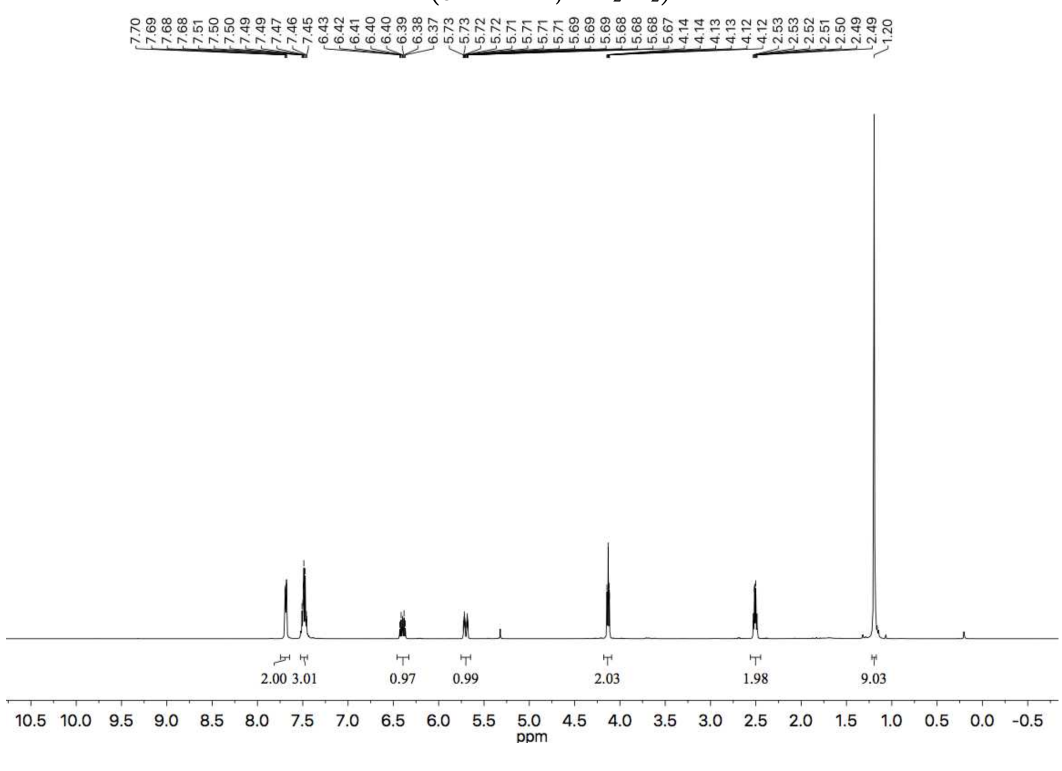


¹⁹F NMR (565 MHz, $CDCl_3$) – **23a**

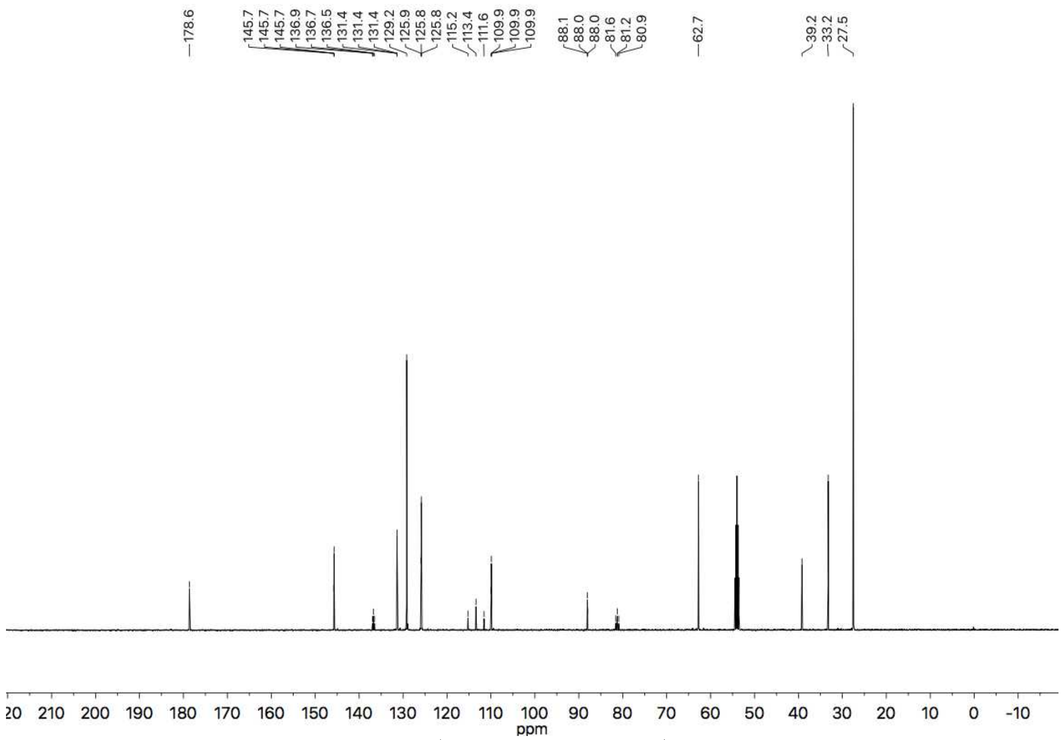




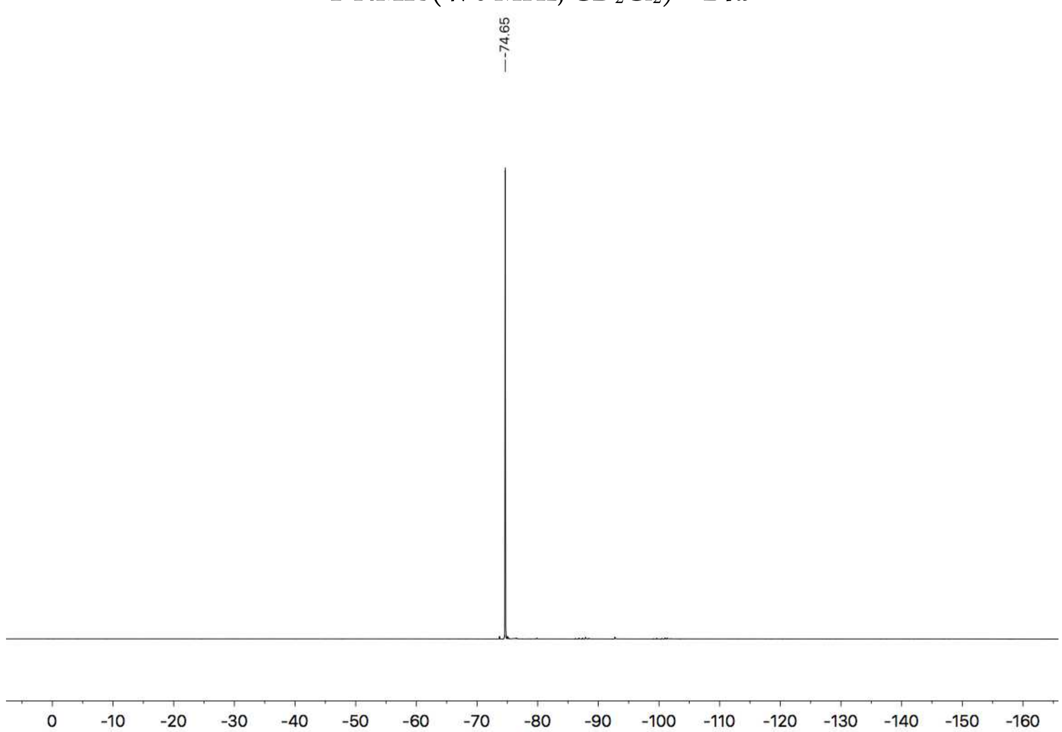
¹H NMR (500 MHz, CD_2Cl_2) – **24a**

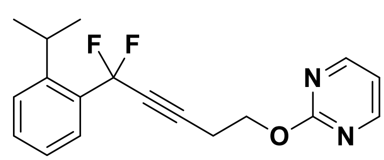


^{13}C NMR (126 MHz, CD_2Cl_2) – **24a**

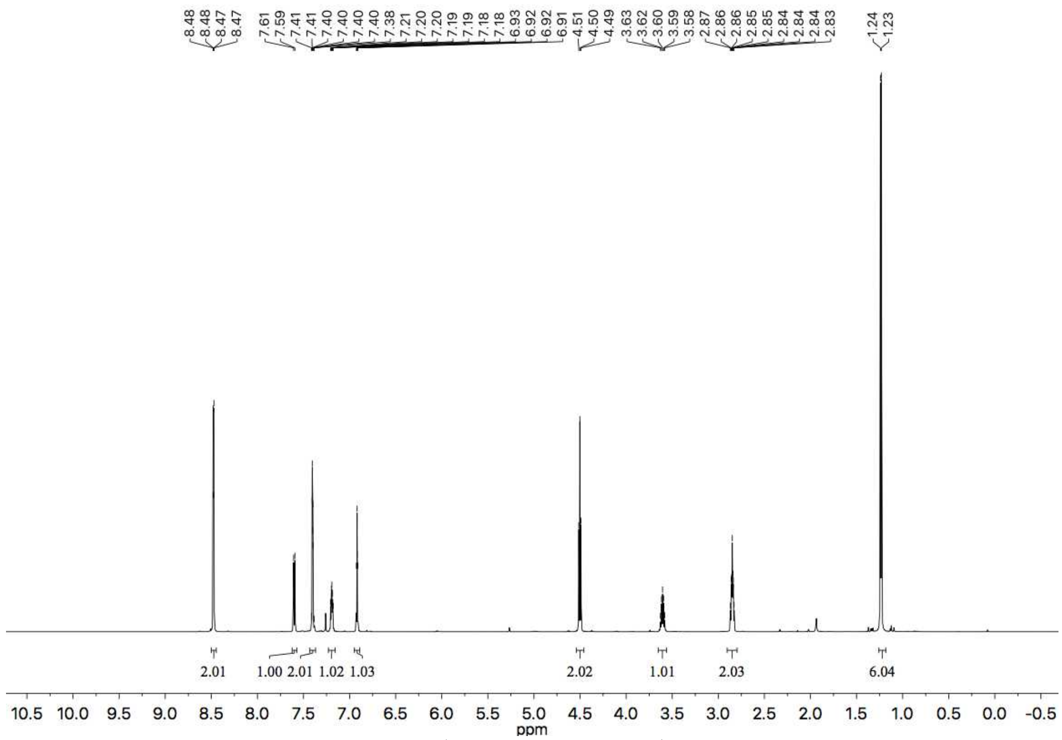


^{19}F NMR (470 MHz, CD_2Cl_2) – **24a**

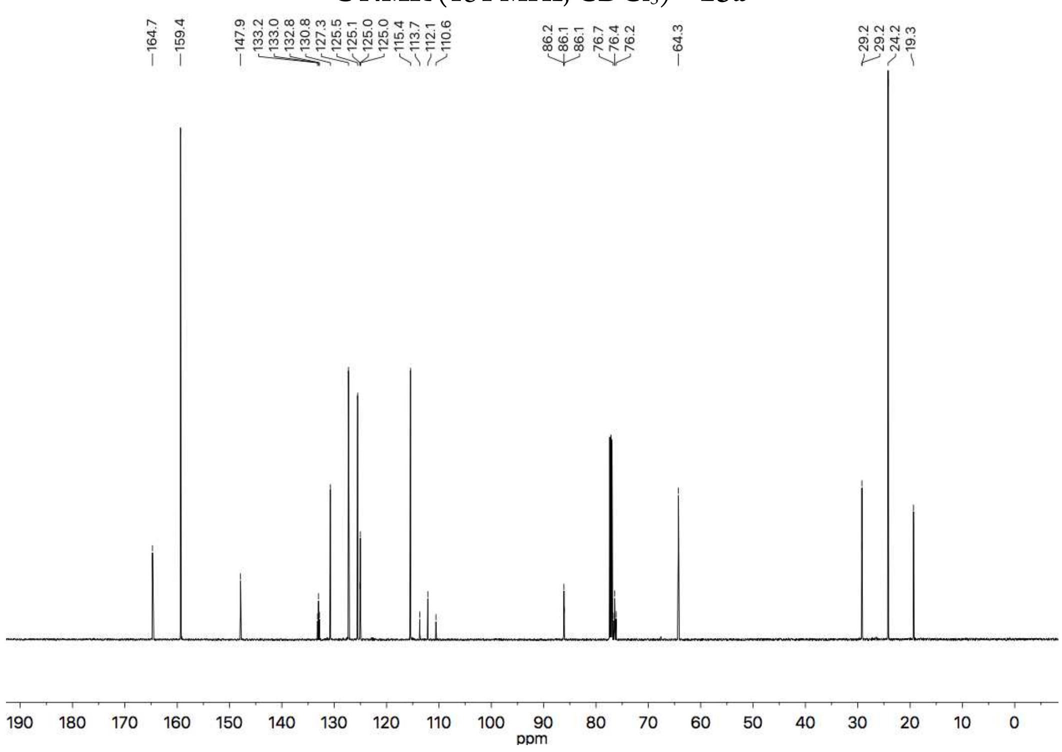




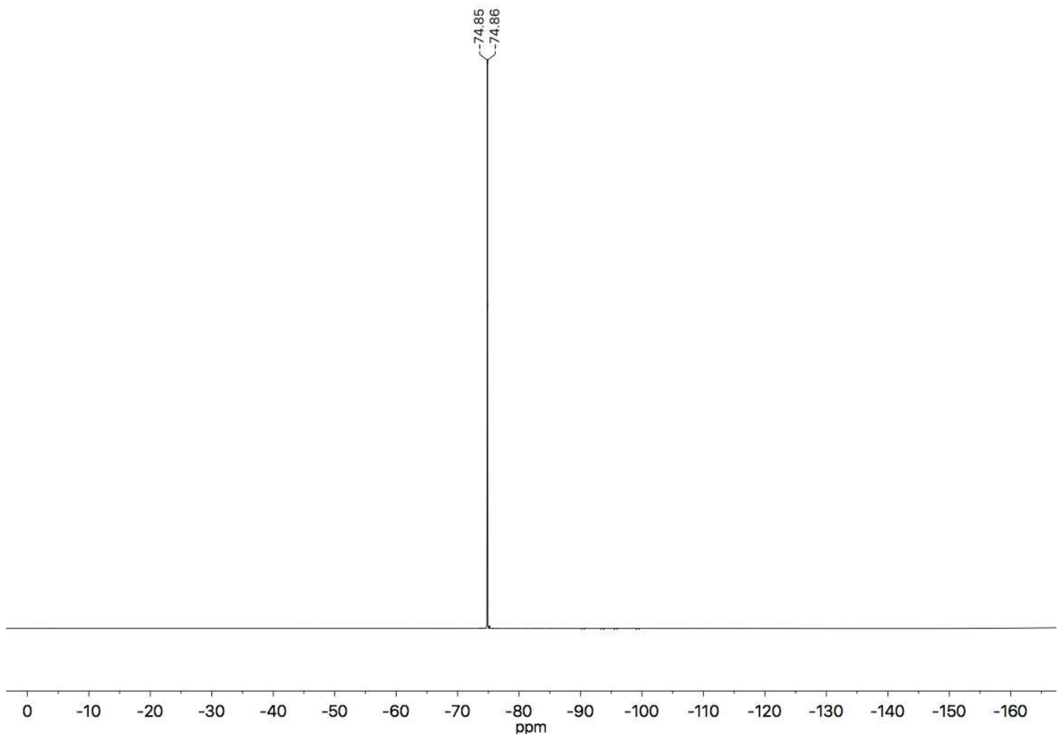
^{1}H NMR (600 MHz, $CDCl_3$) – **25a**

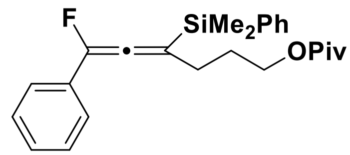


^{13}C NMR (151 MHz, $CDCl_3$) – **25a**

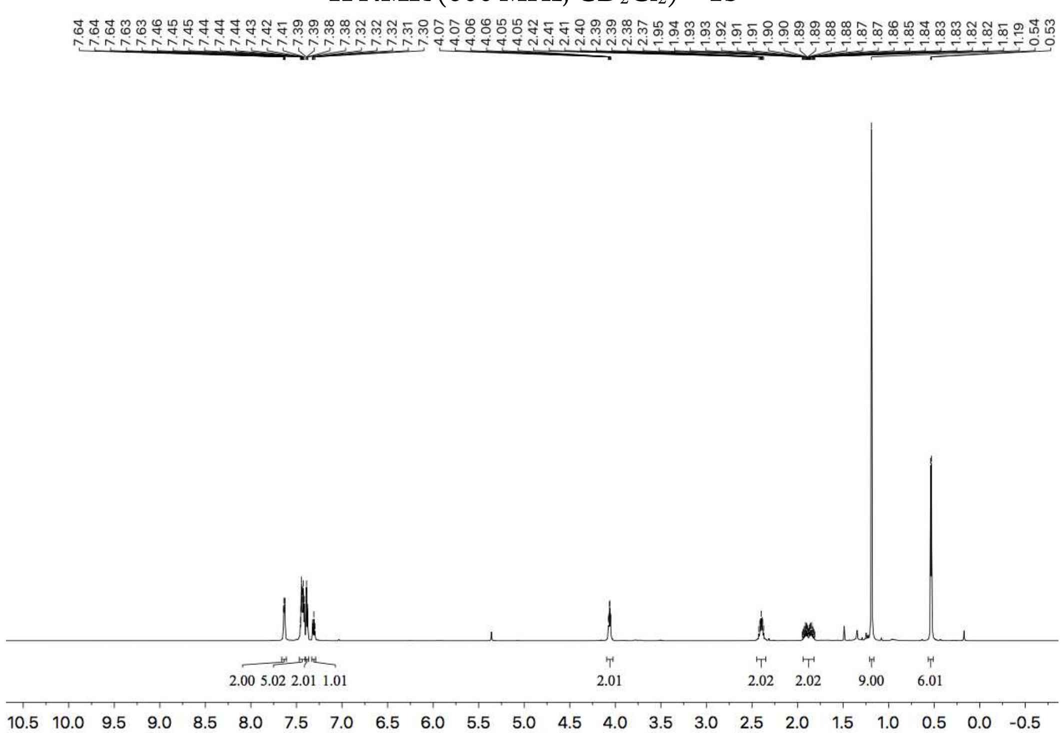


^{19}F NMR (565 MHz, $CDCl_3$) – **25a**

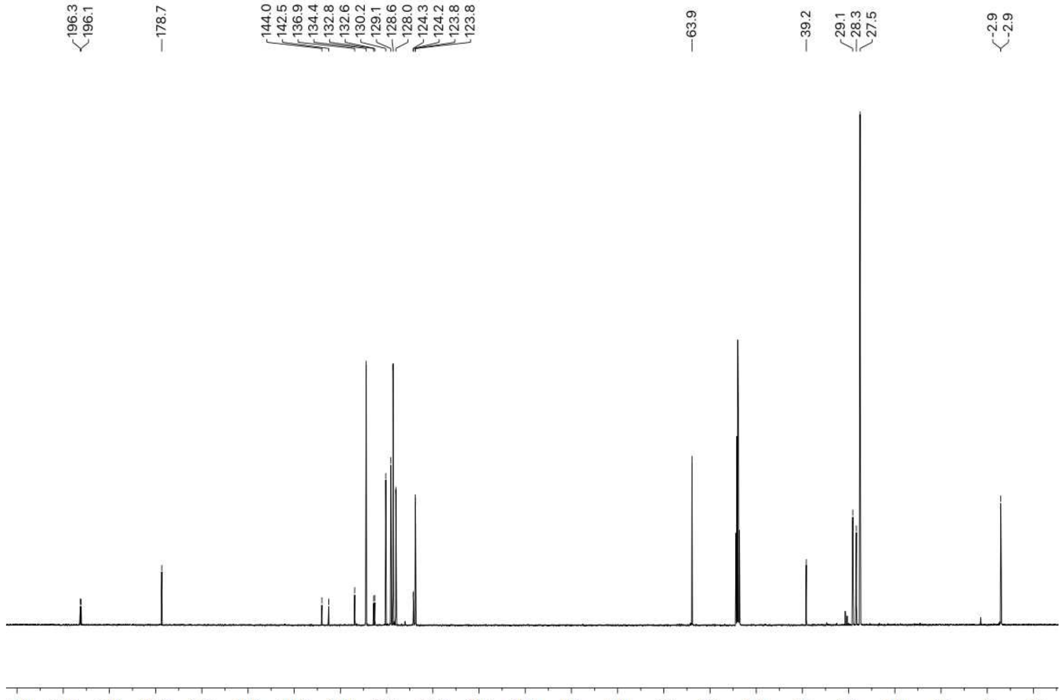




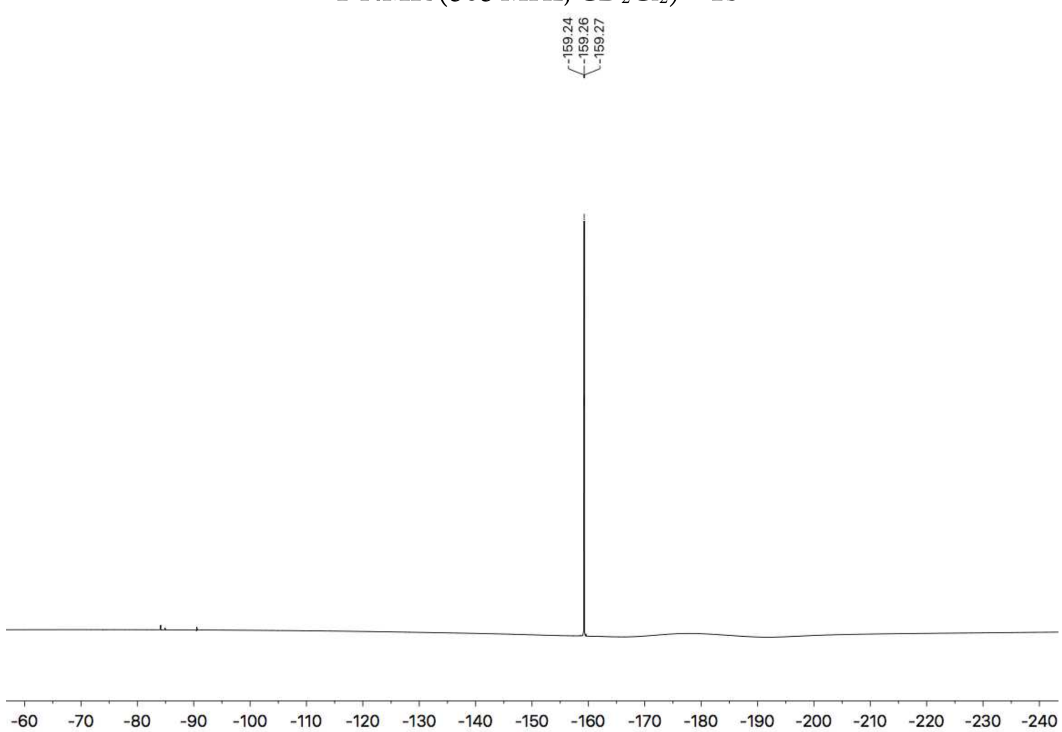
^{1}H NMR (600 MHz, CD_2Cl_2) – **1b**

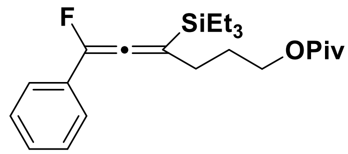


^{13}C NMR (151 MHz, CD_2Cl_2) – **1b**

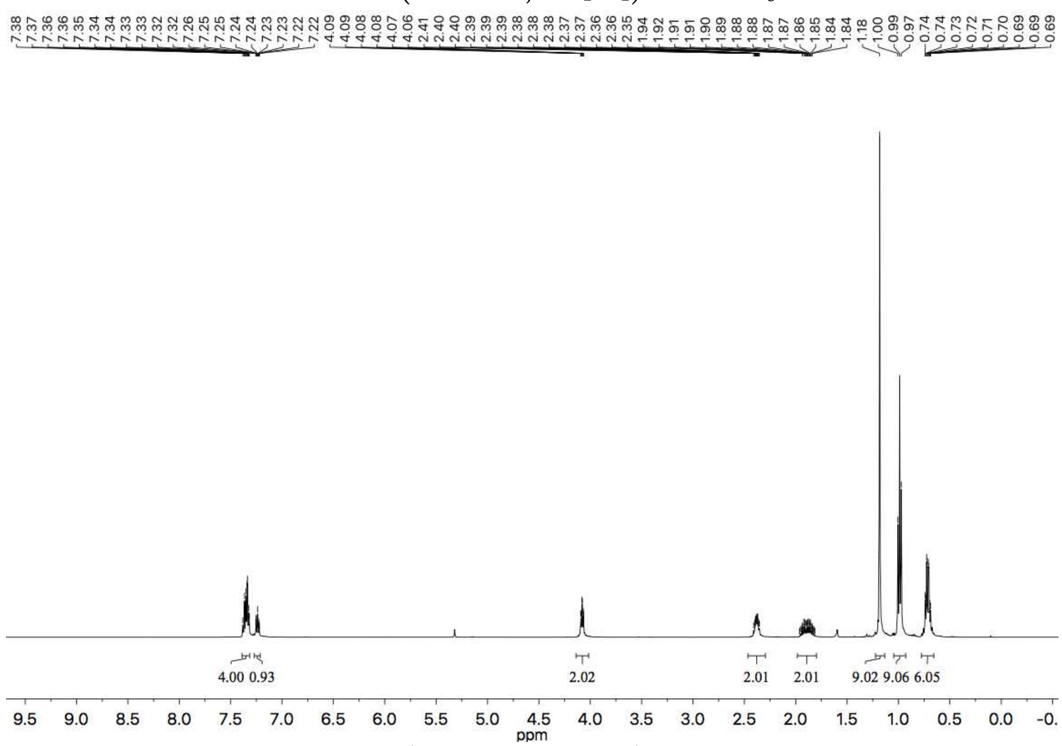


^{19}F NMR (565 MHz, CD_2Cl_2) – **1b**

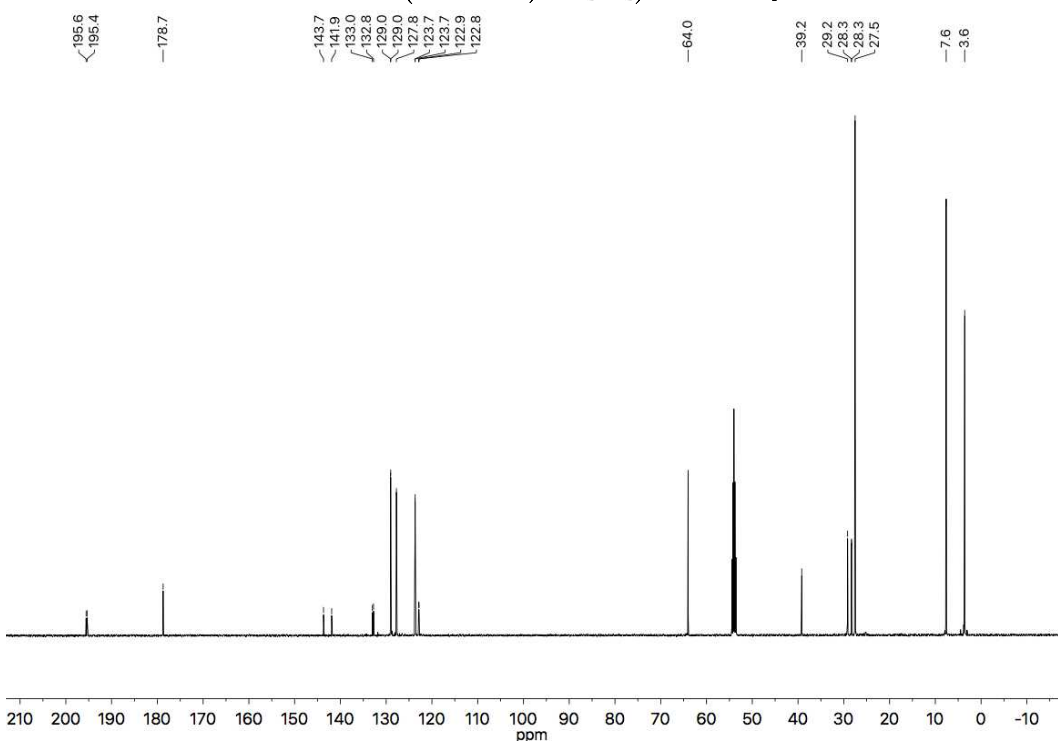




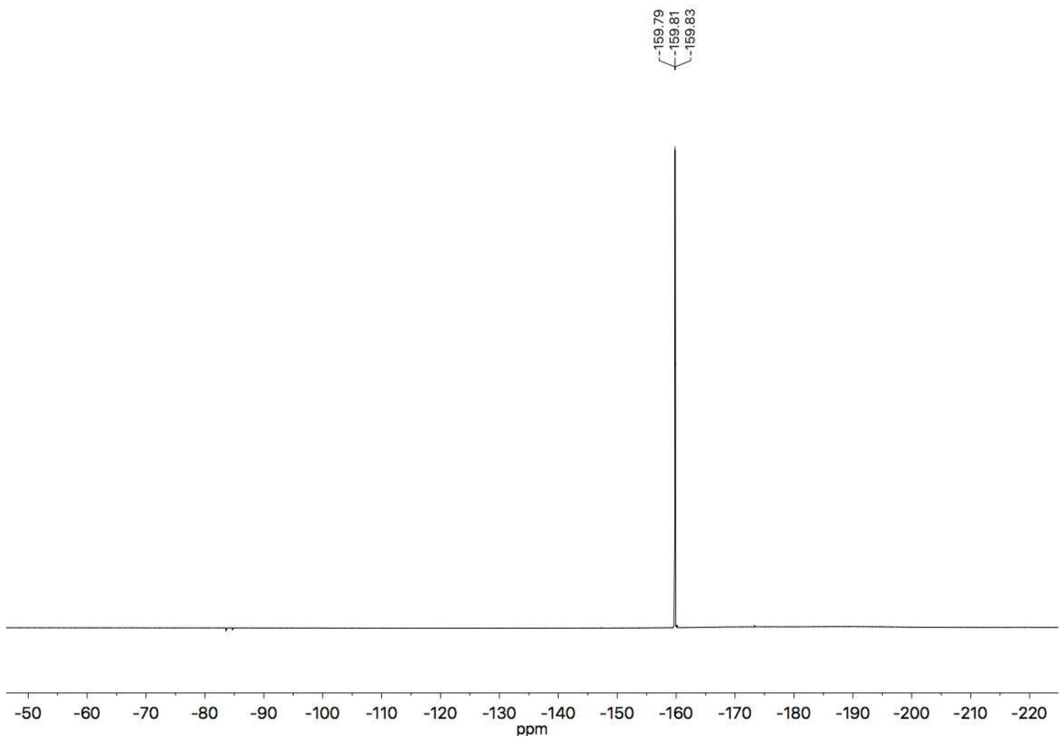
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

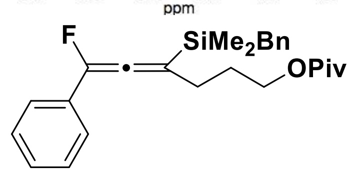


^{13}C NMR (126 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

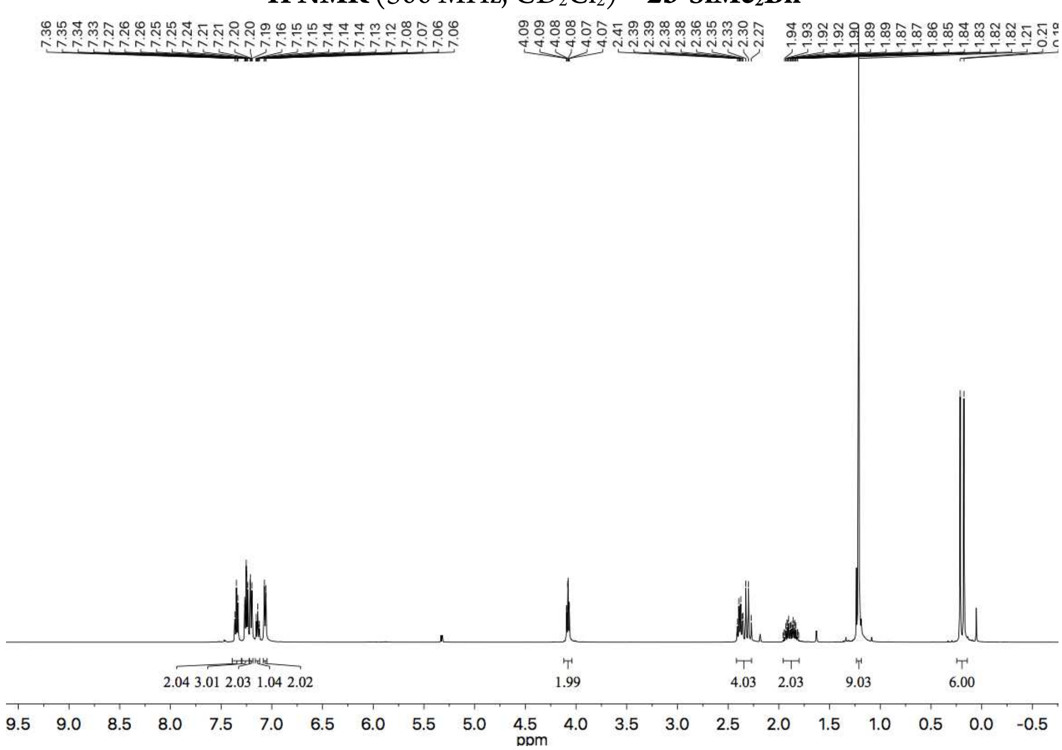


^{19}F NMR (470 MHz, CD_2Cl_2) – **2b-SiEt$_3$**

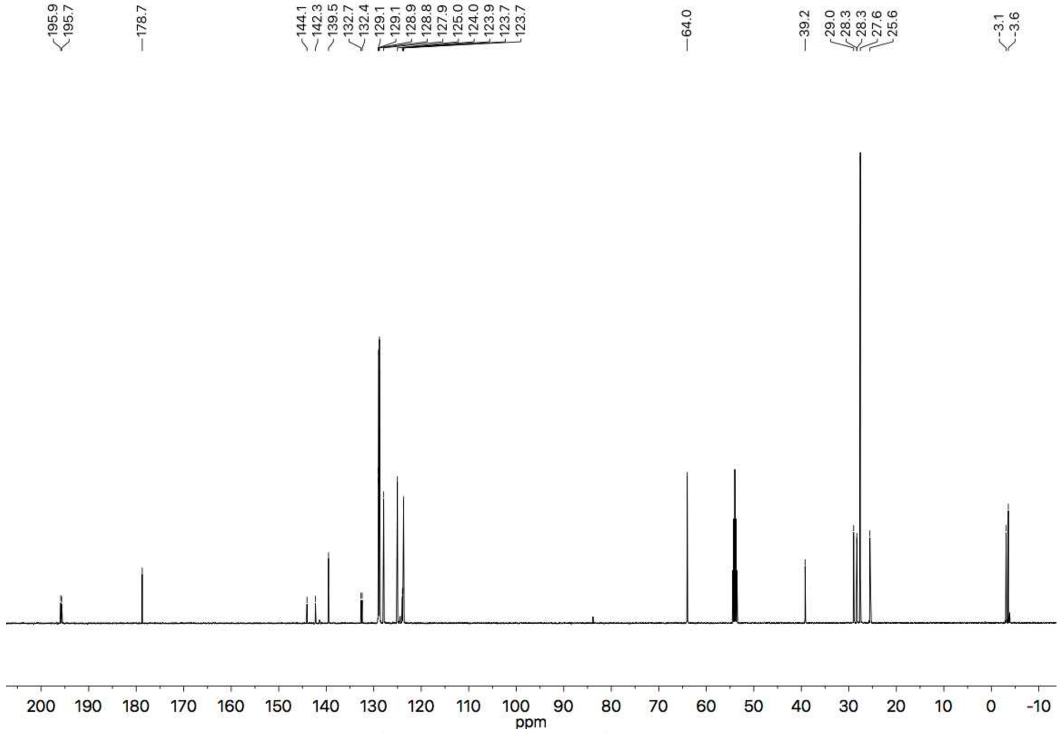




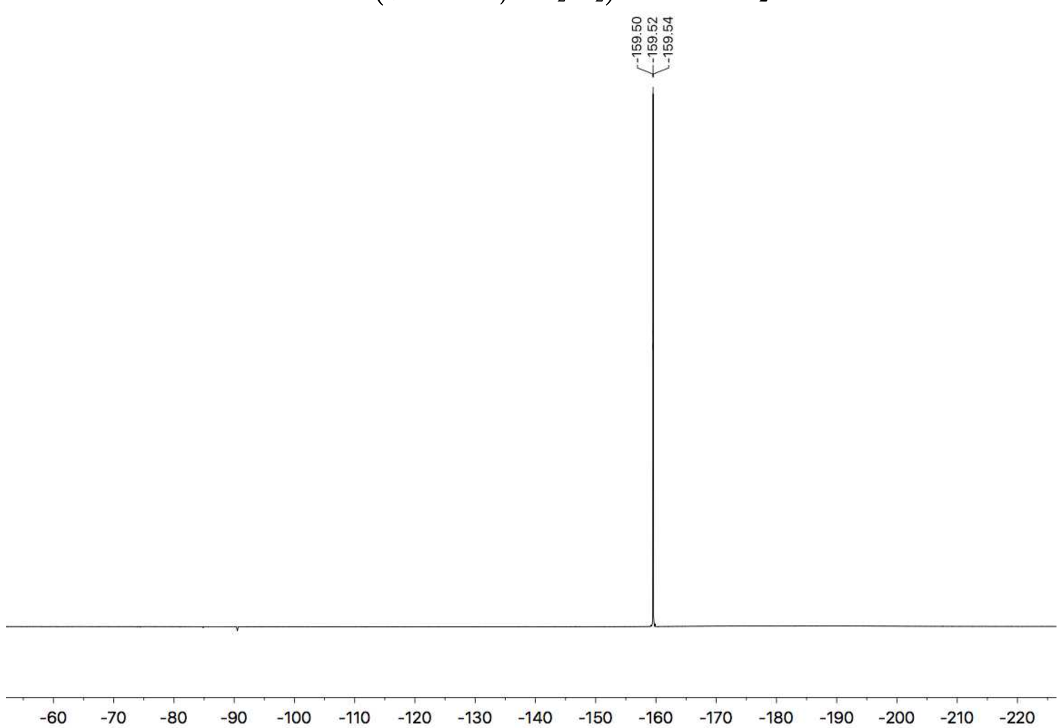
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b-SiMe$_2$Bn**

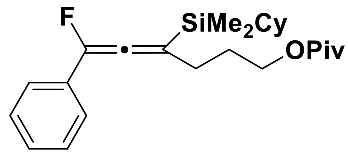


^{13}C NMR (126 MHz, CD_2Cl_2) – **2b- SiMe$_2$Bn**

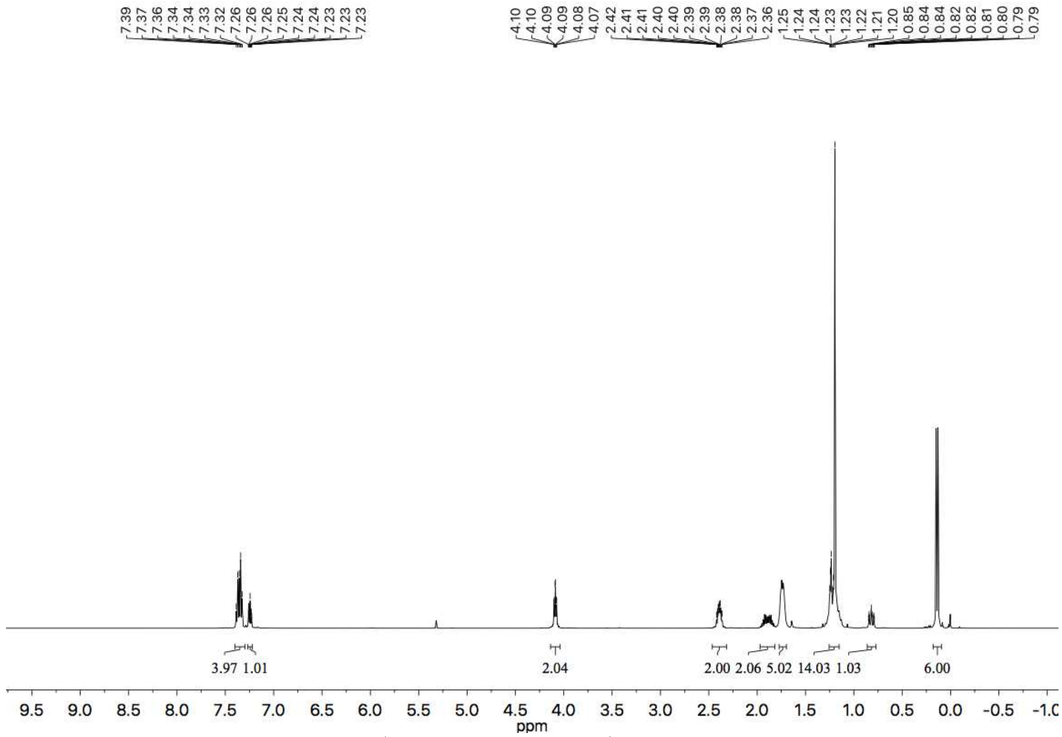


^{19}F NMR (470 MHz, CD_2Cl_2) – **2b- SiMe$_2$Bn**

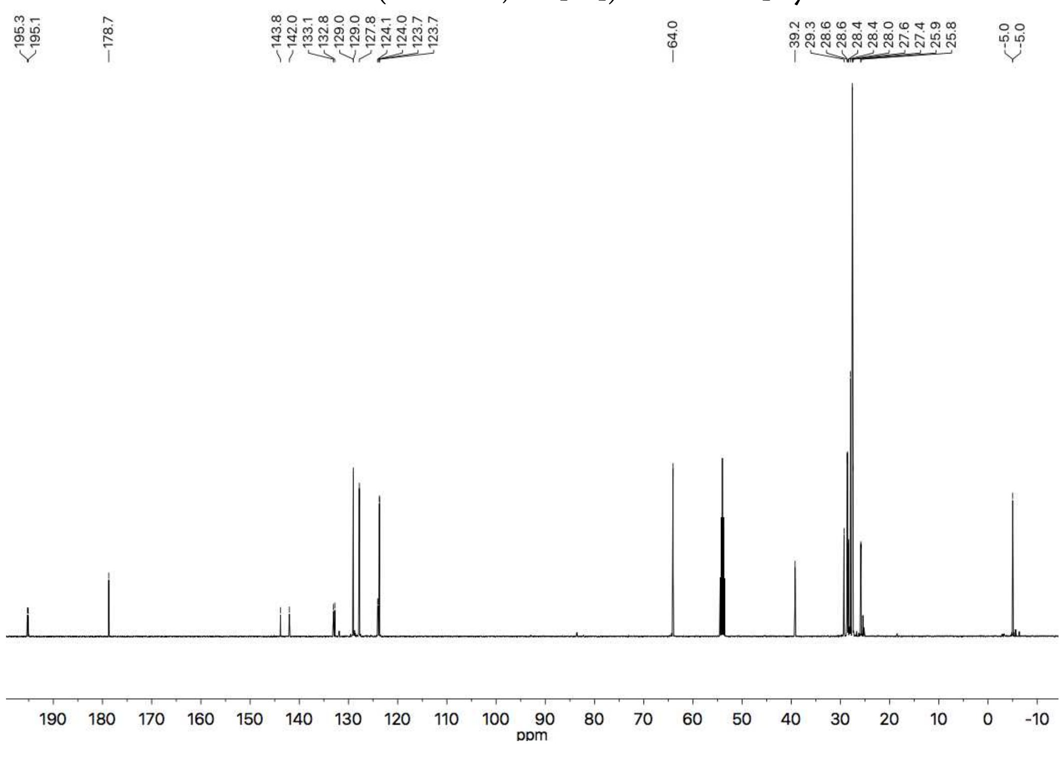




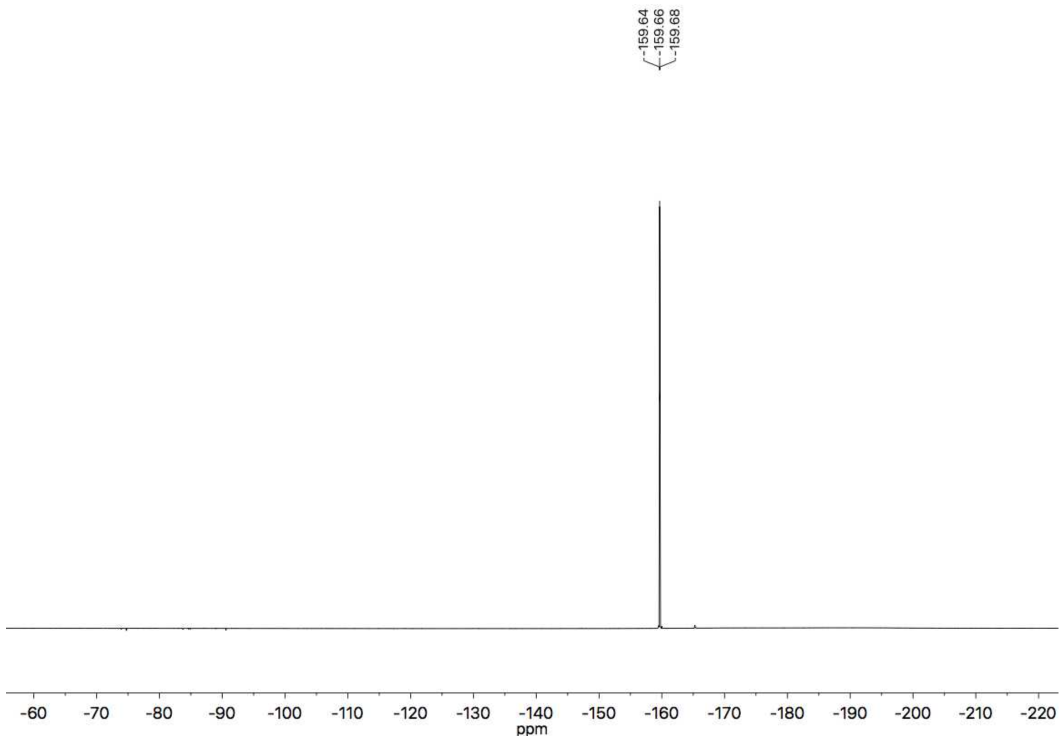
^{1}H NMR (500 MHz, CD_2Cl_2) – **2b- SiMe$_2$Cy**

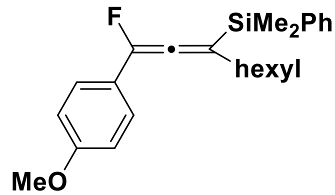


^{13}C NMR (126 MHz, CD_2Cl_2) – **2b- SiMe$_2$Cy**

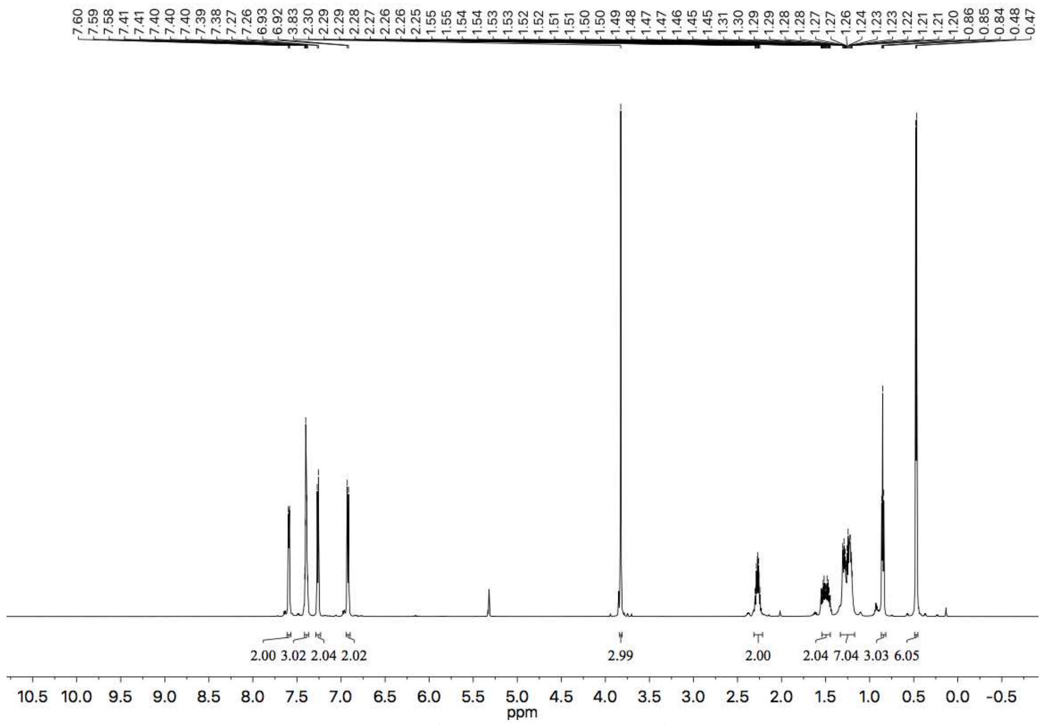


^{19}F NMR (470 MHz, CD_2Cl_2) – **2b- $SiMe_2Cy$**

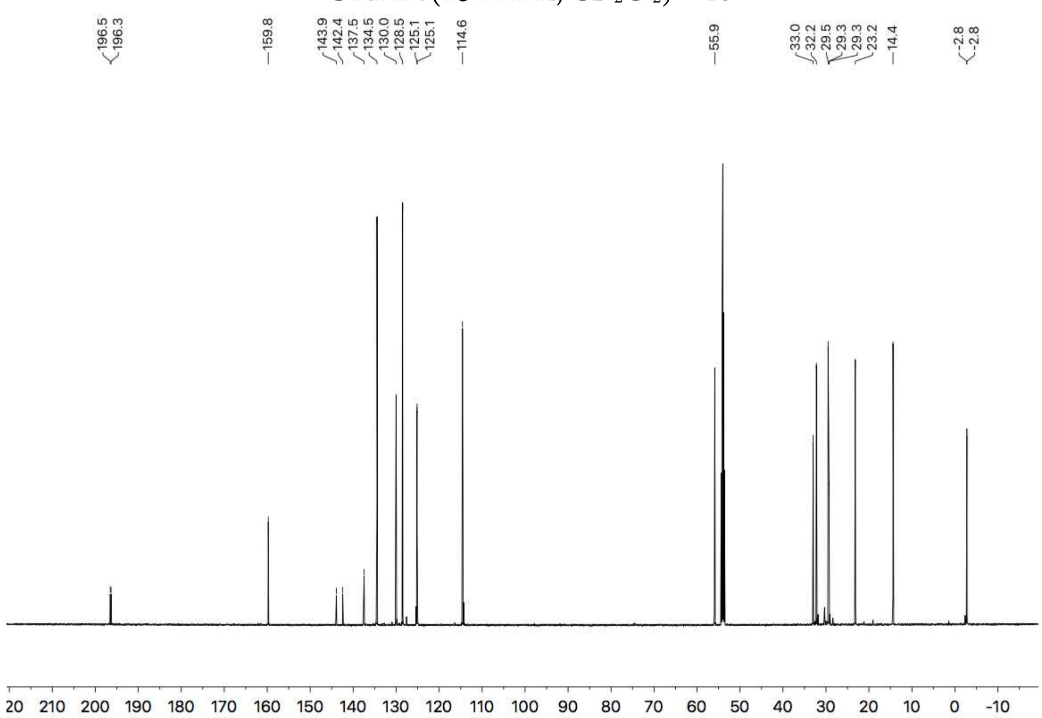




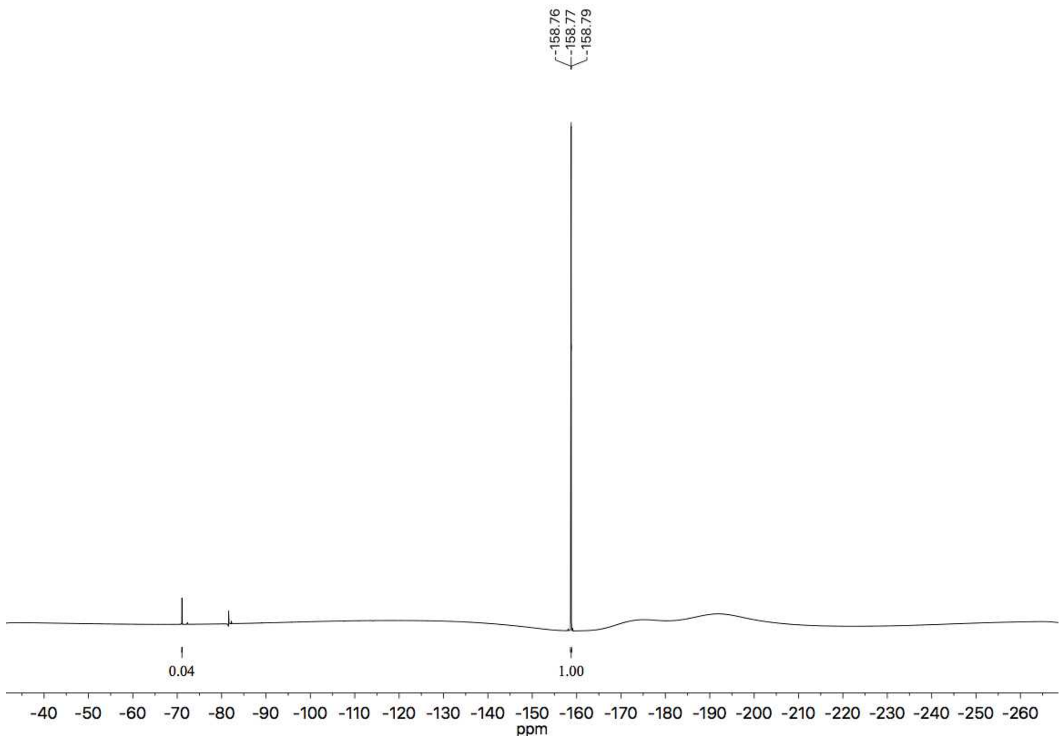
[1]H NMR (600 MHz, CD_2Cl_2) – **2b**

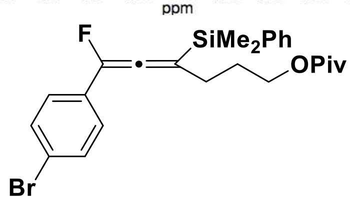


[13]C NMR (151 MHz, CD_2Cl_2) – **2b**

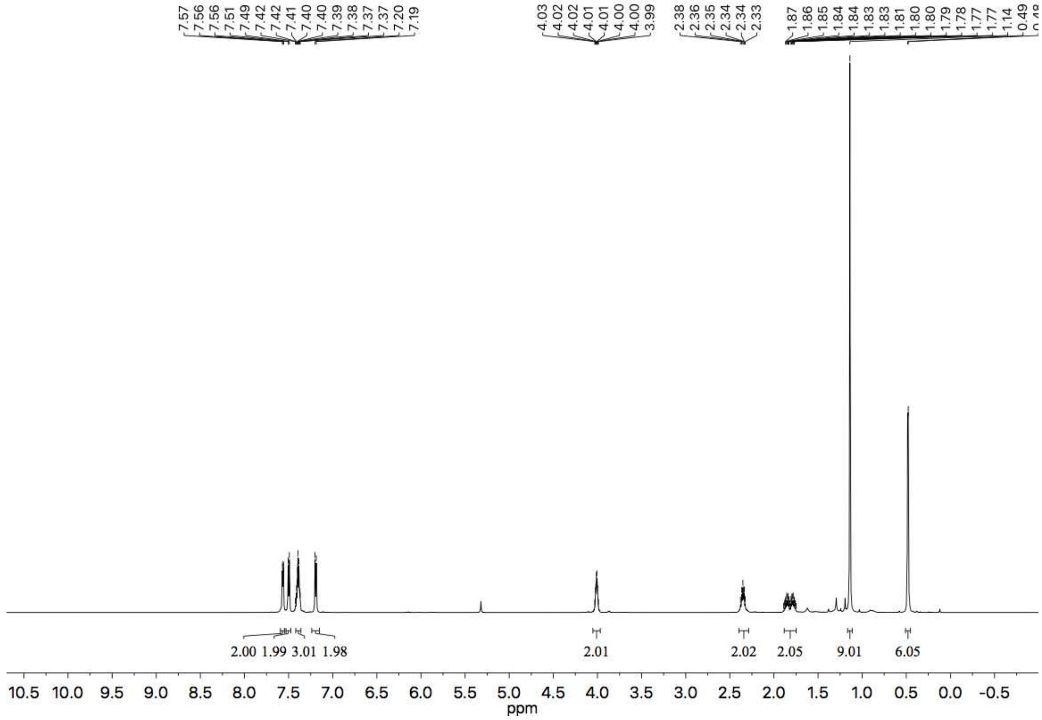


^{19}F NMR (565cMHz, CD_2Cl_2) – **2b**

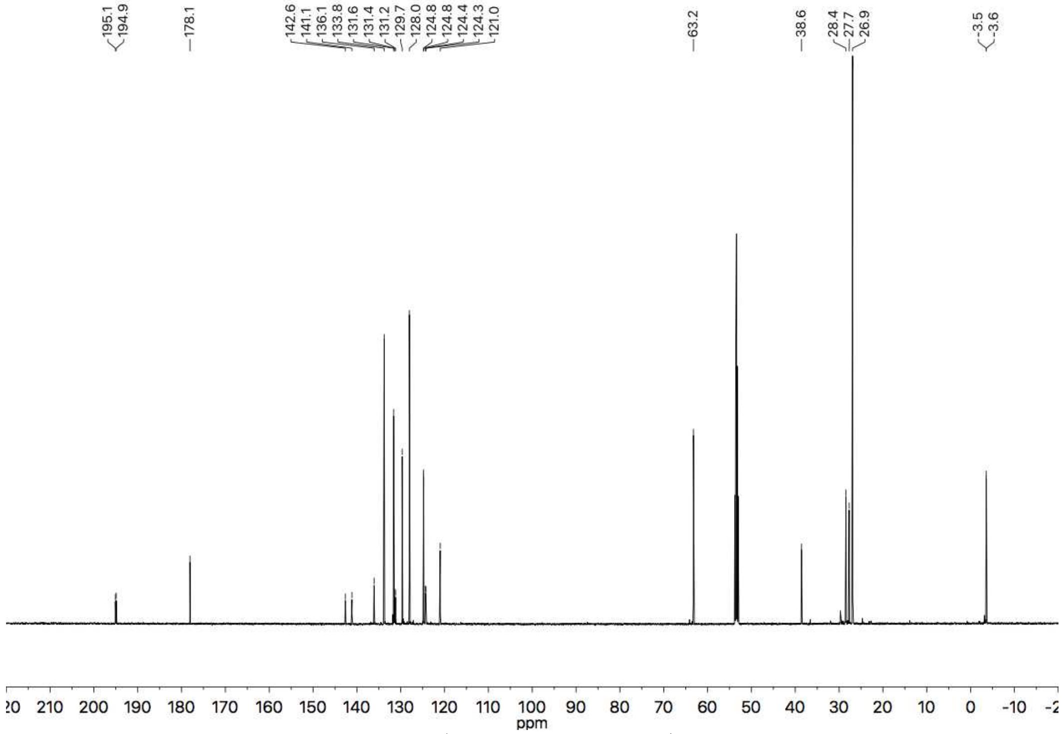




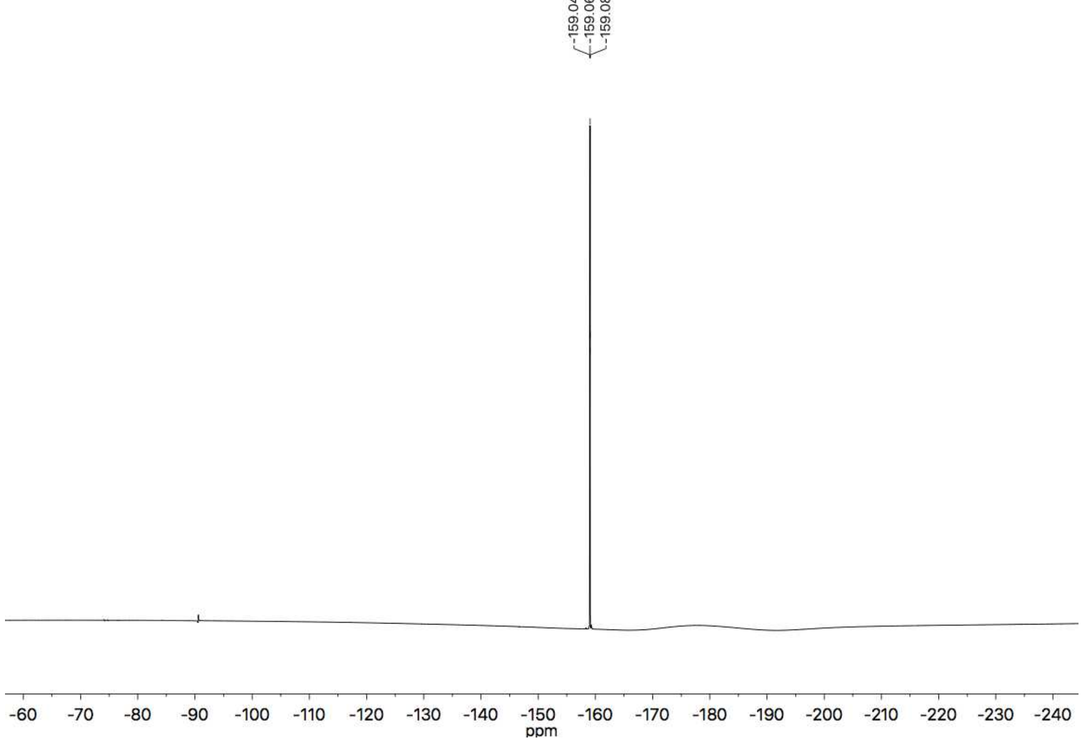
^{1}H NMR (600 MHz, CD_2Cl_2) – **3b**

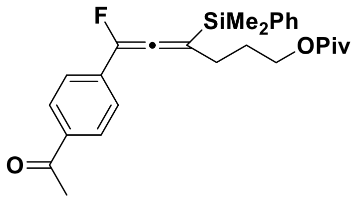


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **3b**

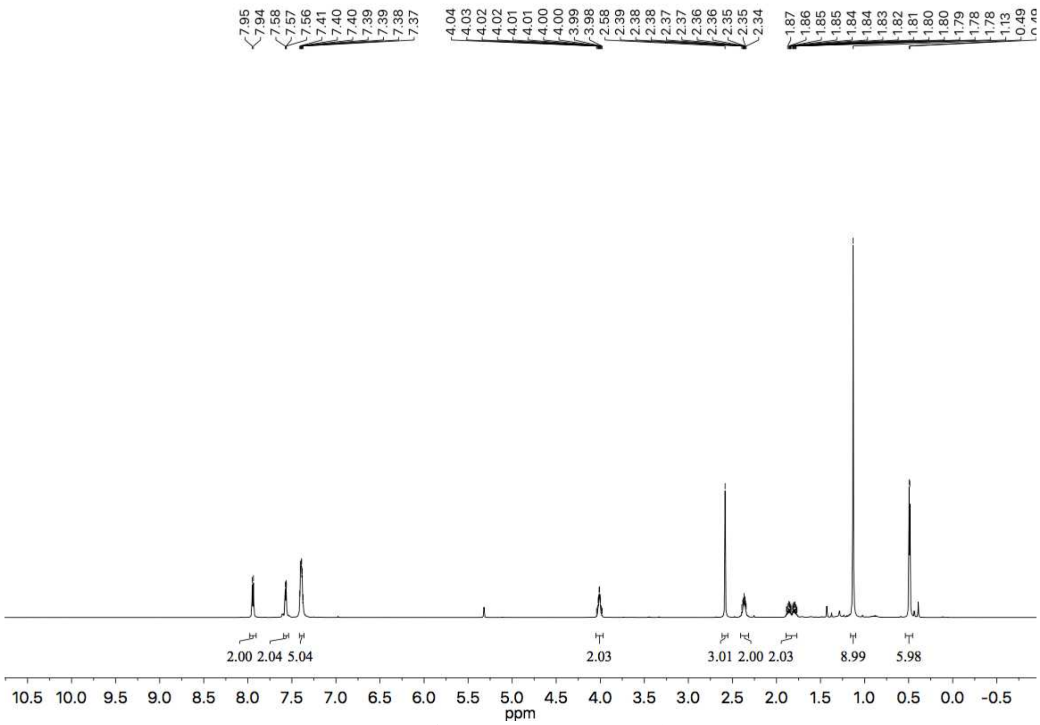


^{19}**F NMR** (565 MHz, CD_2Cl_2) – **3b**

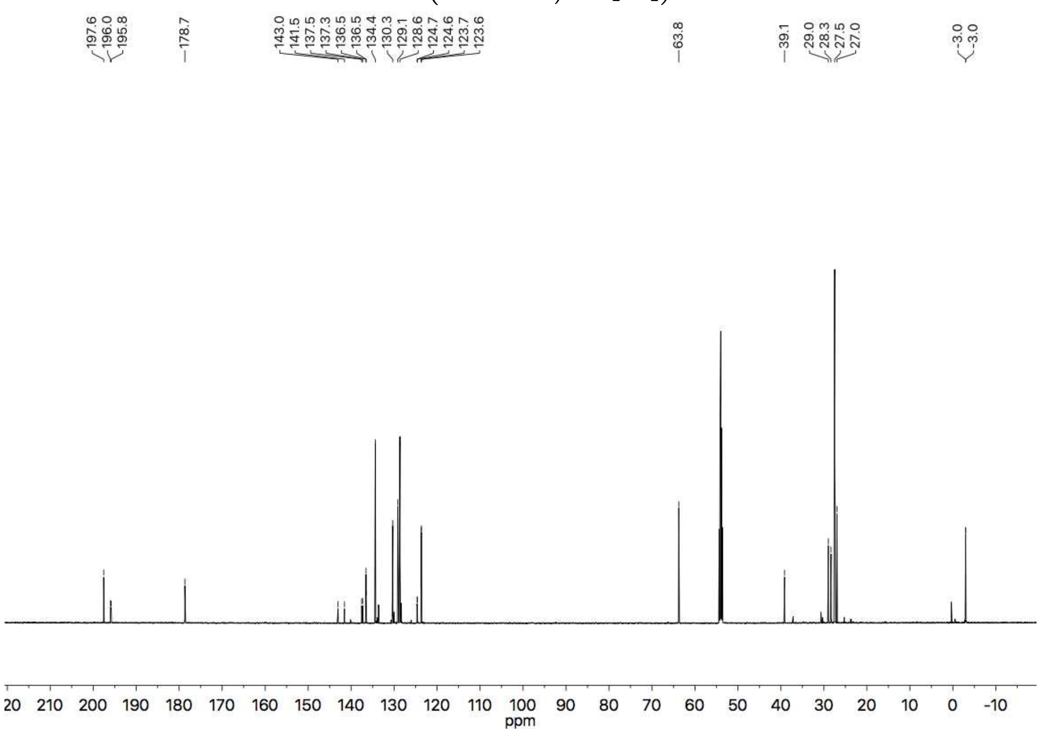




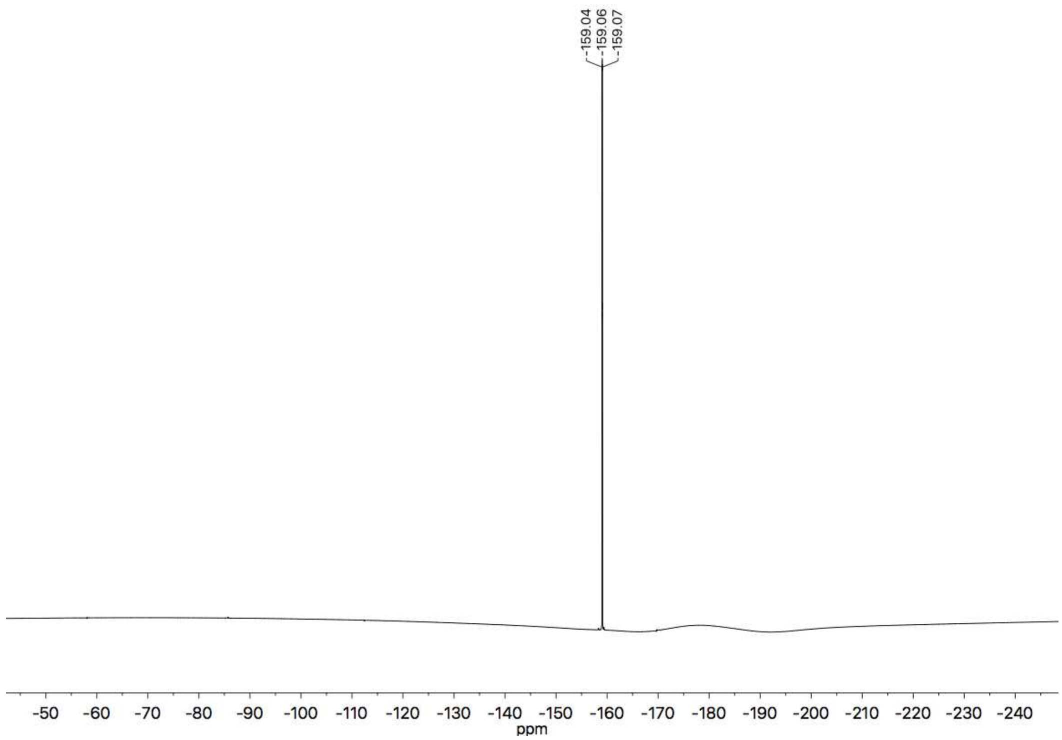
[1]H NMR (600 MHz, CD_2Cl_2) – **4b**

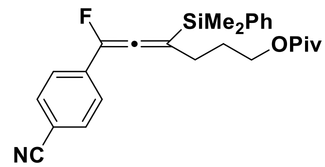


[13]C NMR (151 MHz, CD_2Cl_2) – **4b**

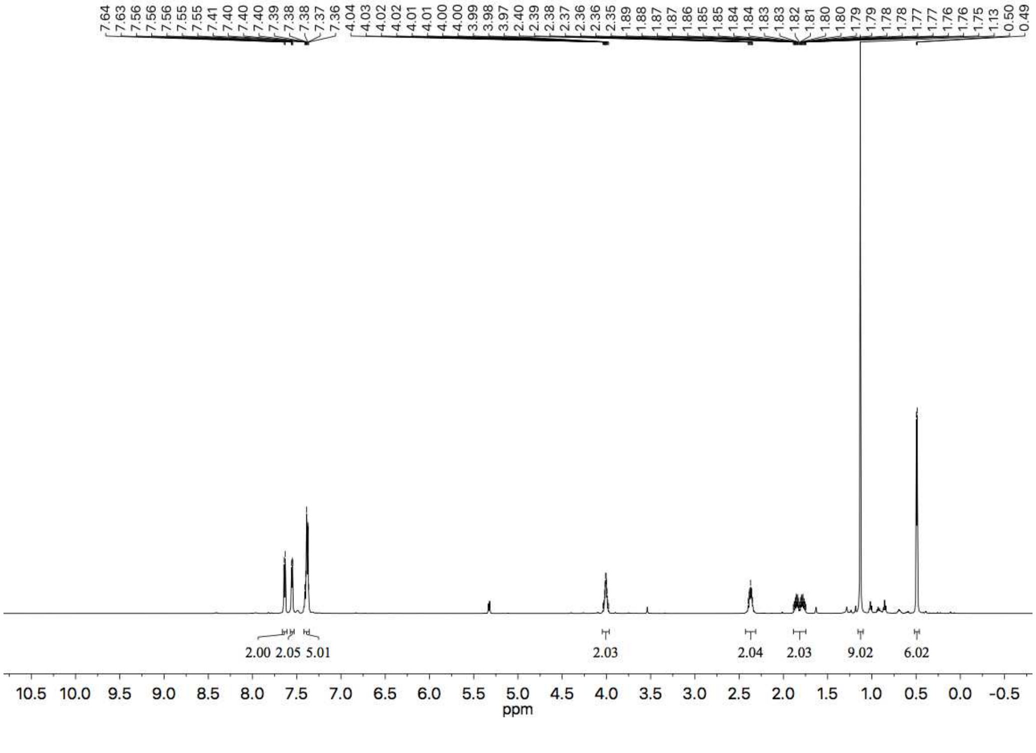


^{19}F NMR (565 MHz, CD_2Cl_2) – **4b**

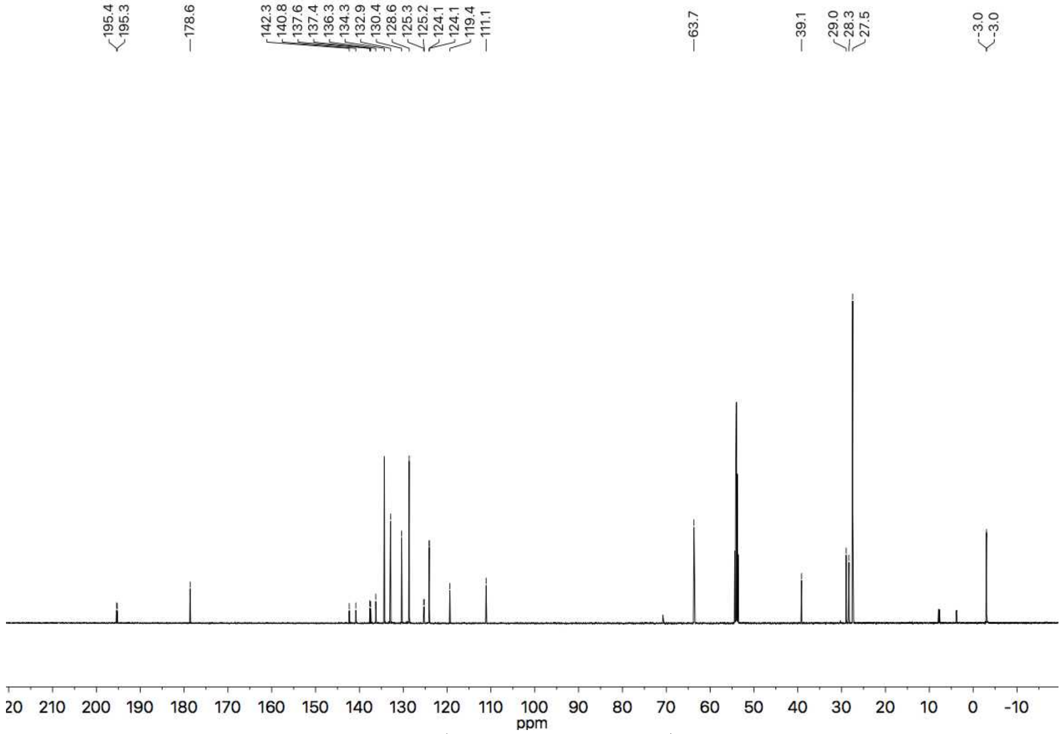




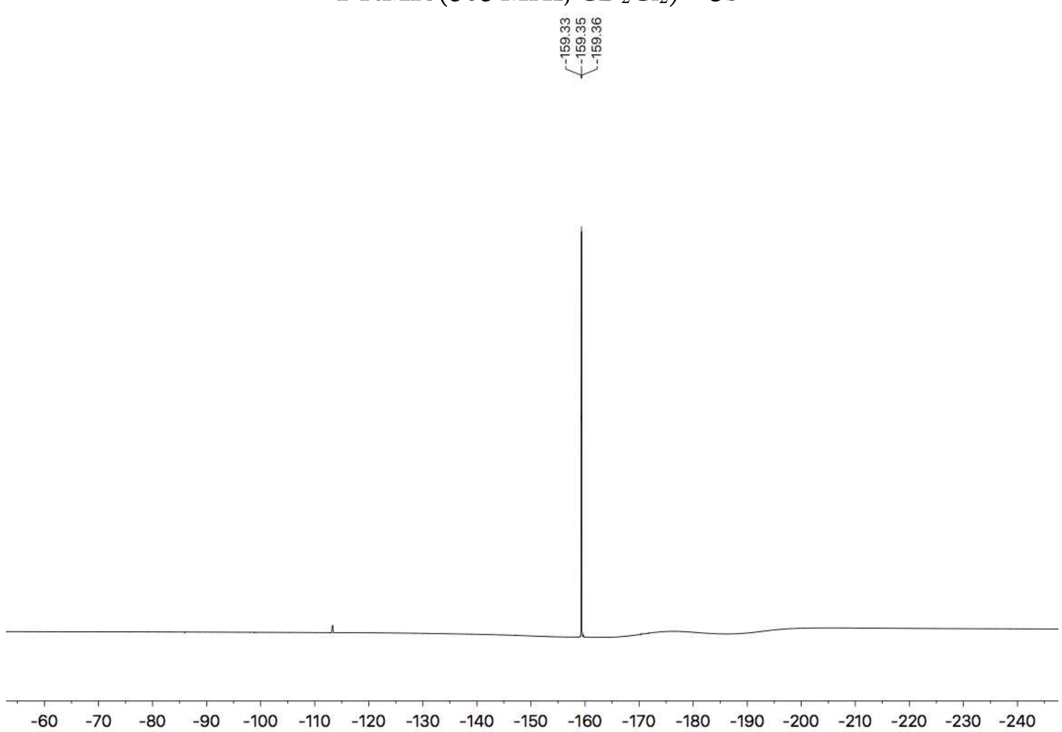
^{1}H NMR (600 MHz, CD_2Cl_2) – **5b**

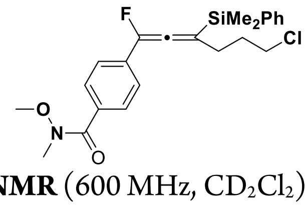


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **5b**

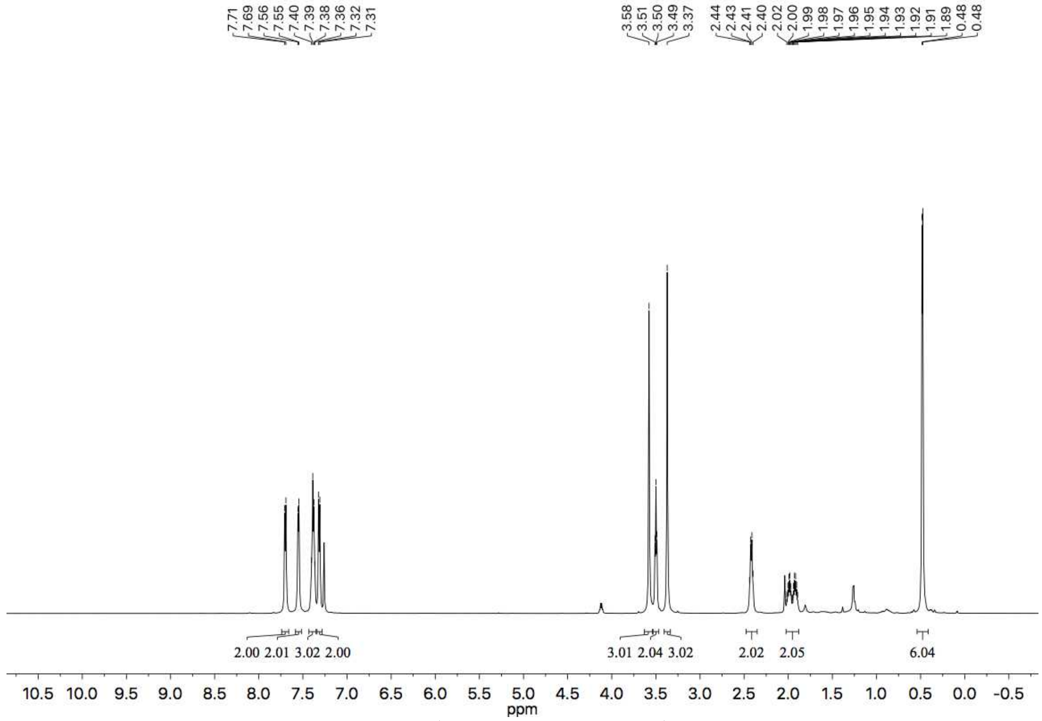


^{19}**F NMR** (565 MHz, CD_2Cl_2) – **5b**

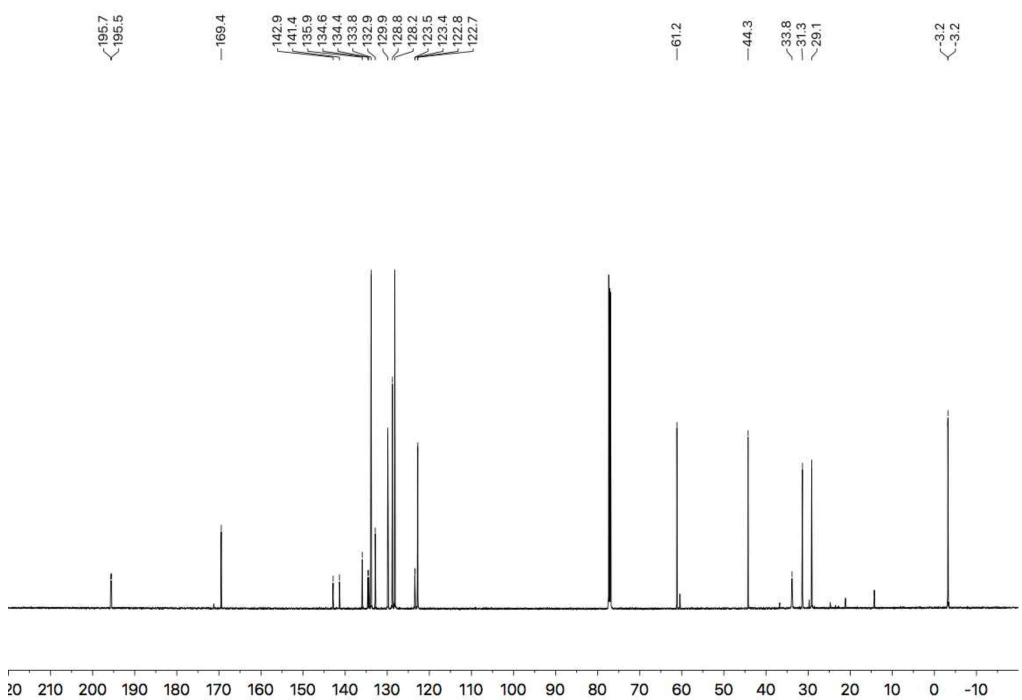




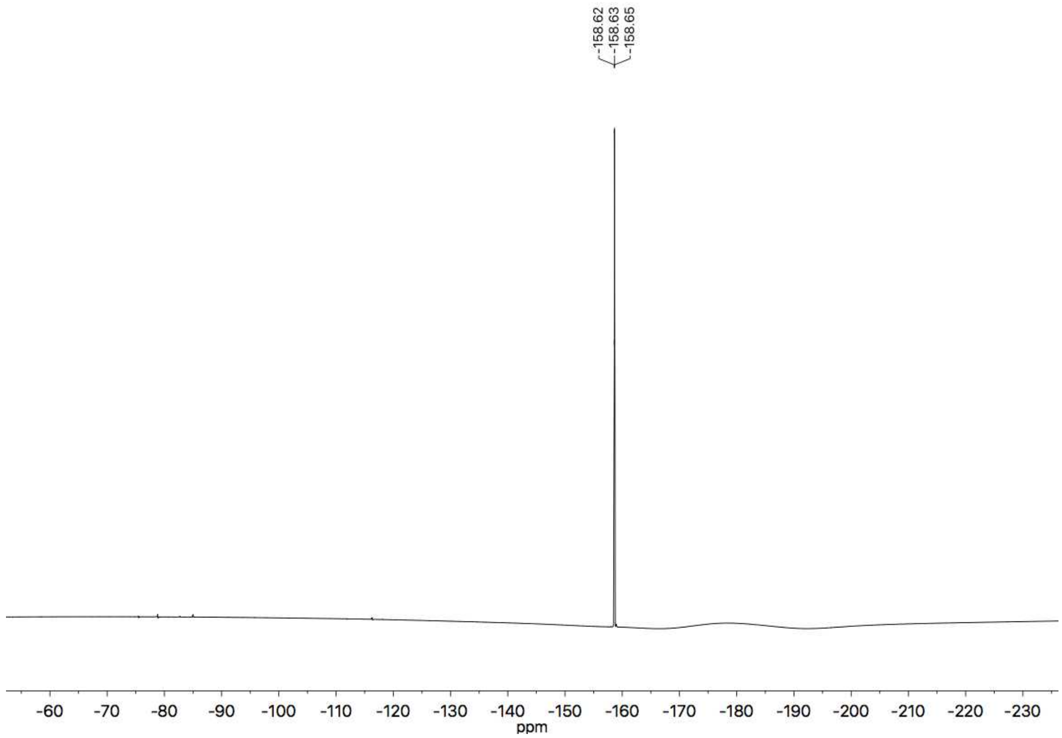
^{1}**H NMR** (600 MHz, CD_2Cl_2) – **6b**

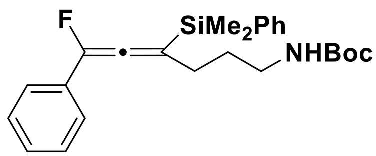


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **6b**

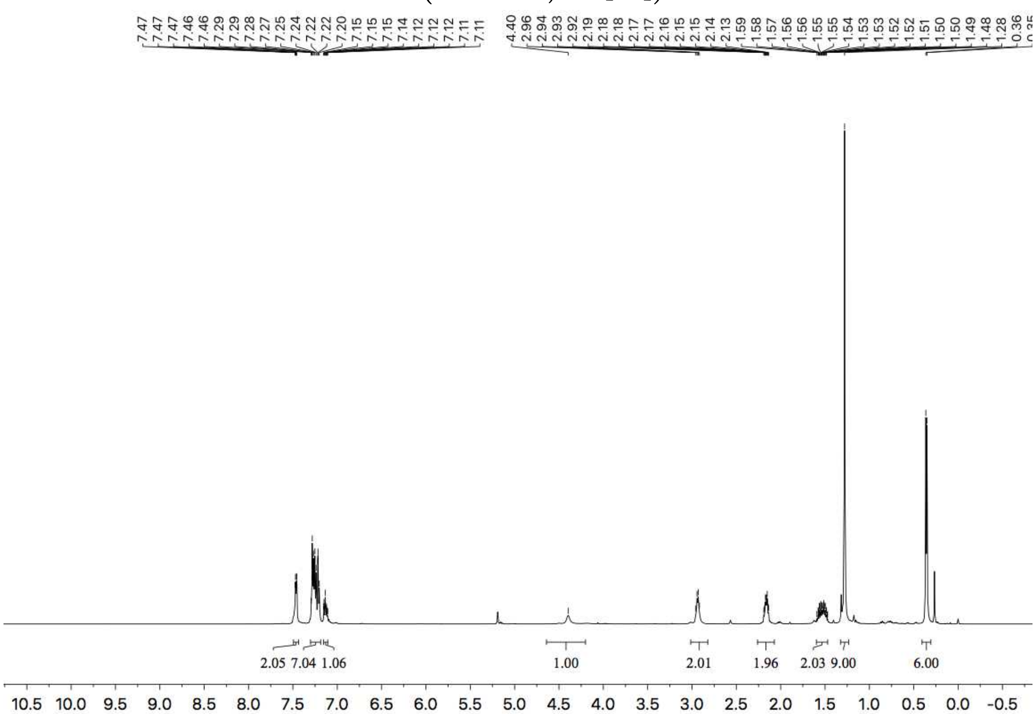


^{19}F NMR (565 MHz, CD_2Cl_2) – **6b**

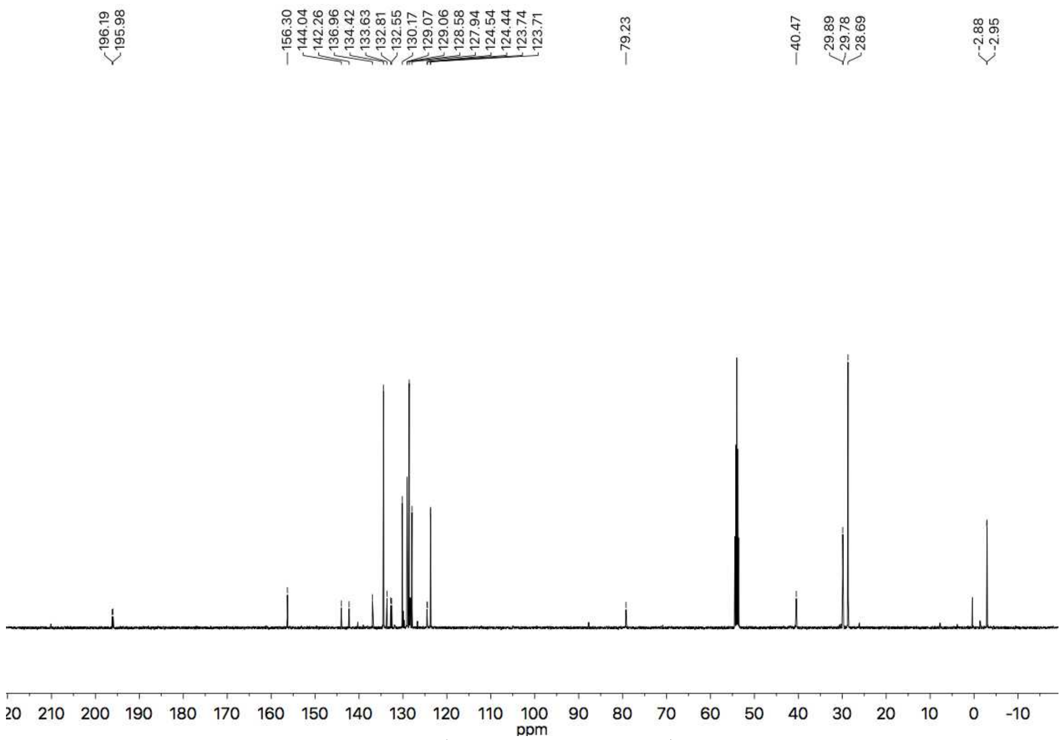




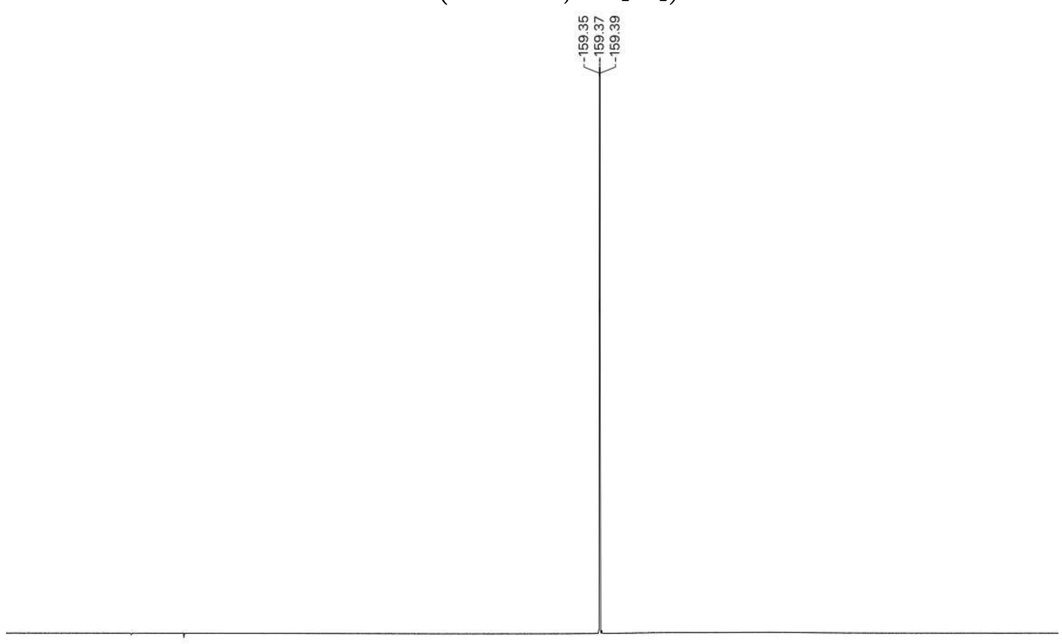
^{1}H NMR (500 MHz, CD_2Cl_2) – **7b**

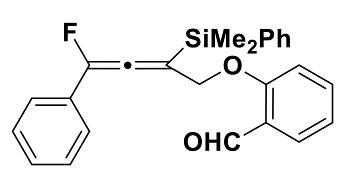


^{13}C NMR (126 MHz, CD_2Cl_2) – **7b**

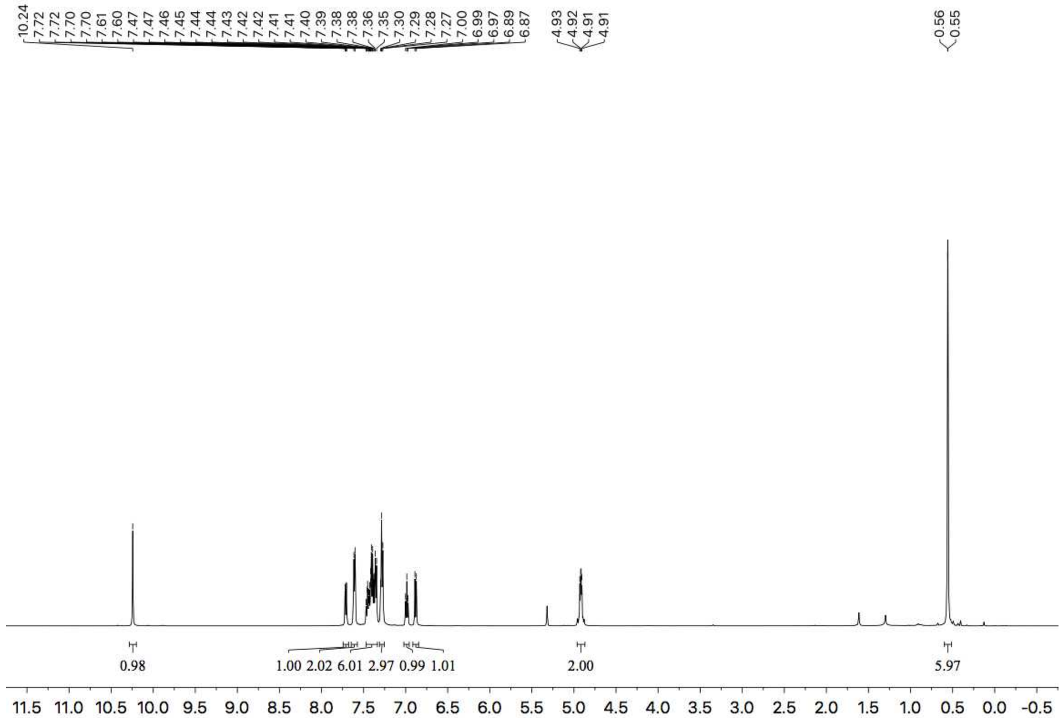


^{19}F NMR (470 MHz, CD_2Cl_2) – **7b**

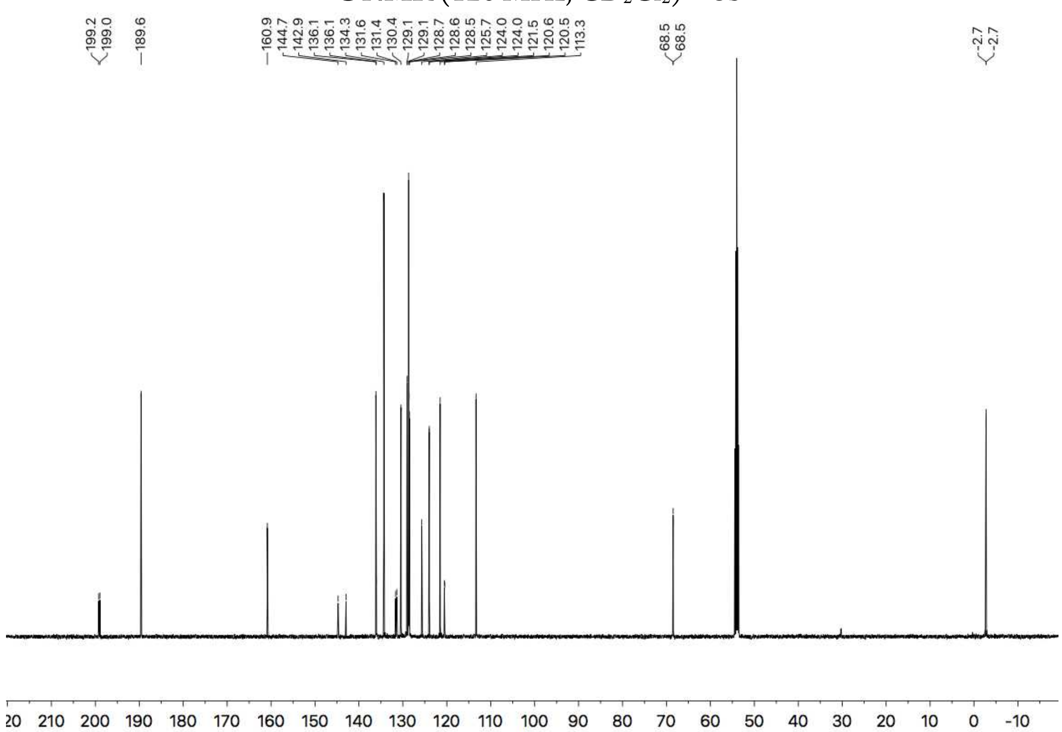




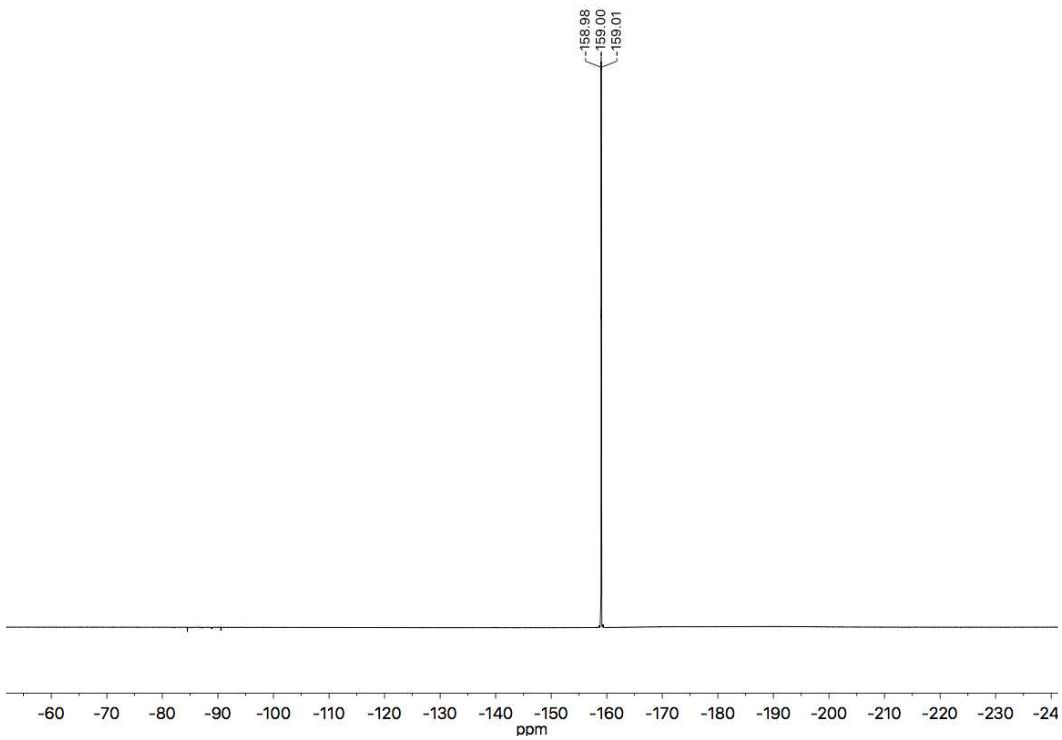
^{1}H NMR (500 MHz, CD_2Cl_2) – **8b**

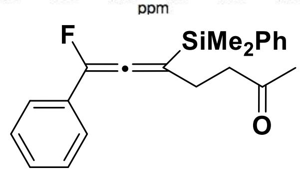


^{13}C NMR (126 MHz, CD_2Cl_2) – **8b**

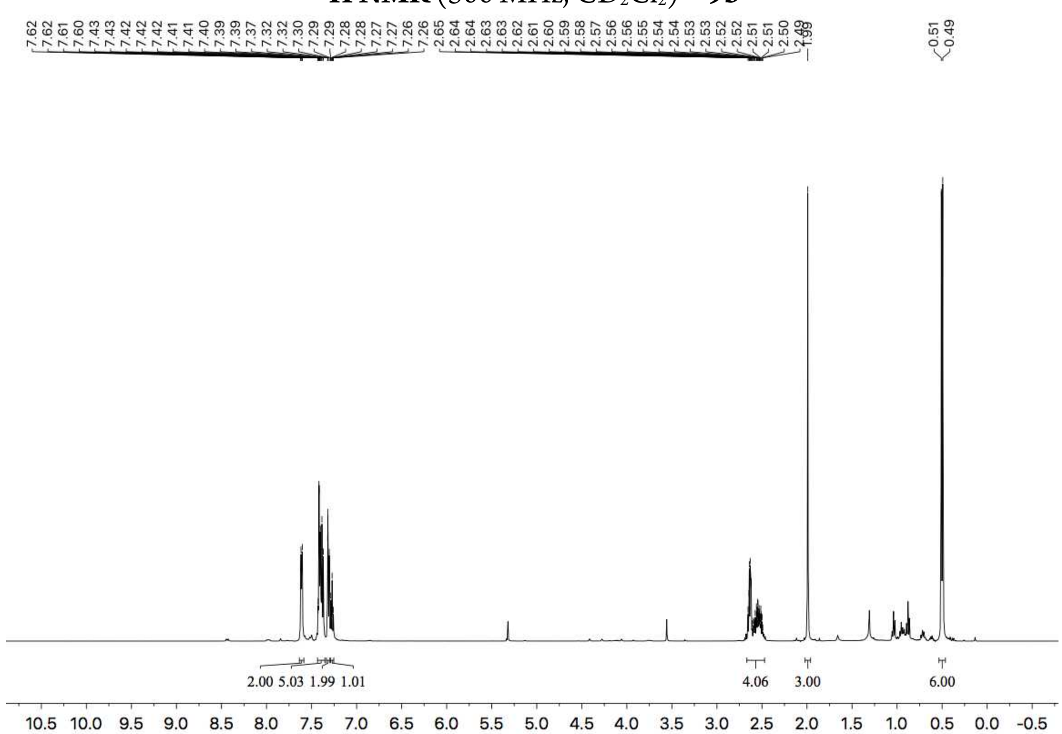


^{19}F NMR (470 MHz, CD_2Cl_2) – **8b**

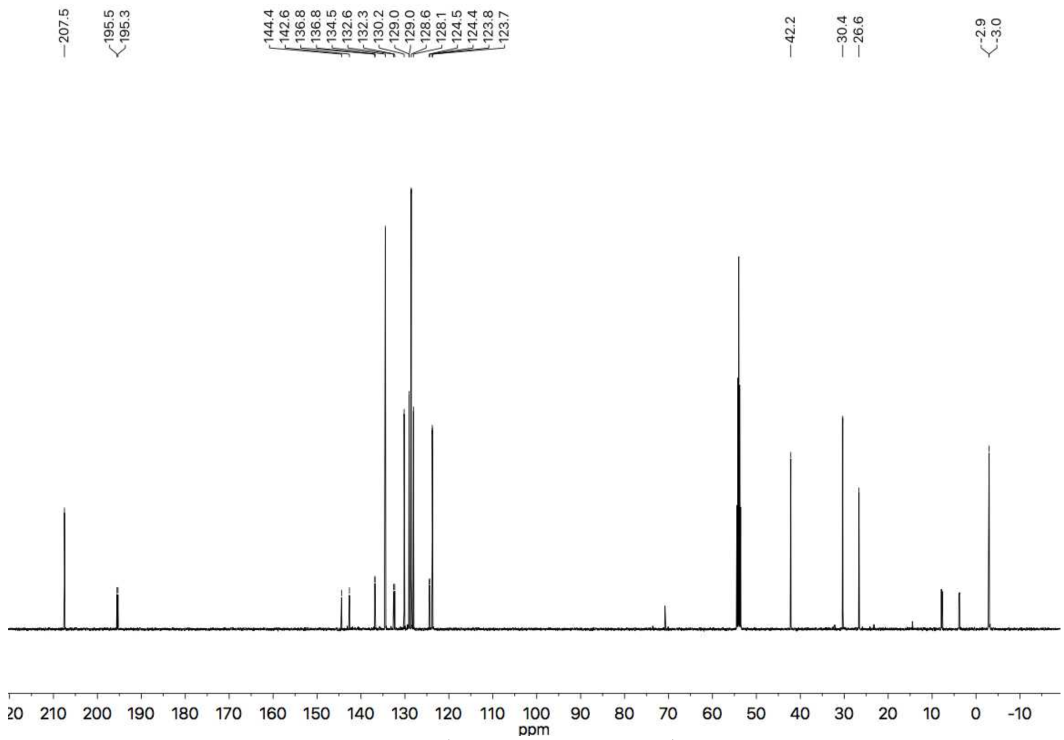




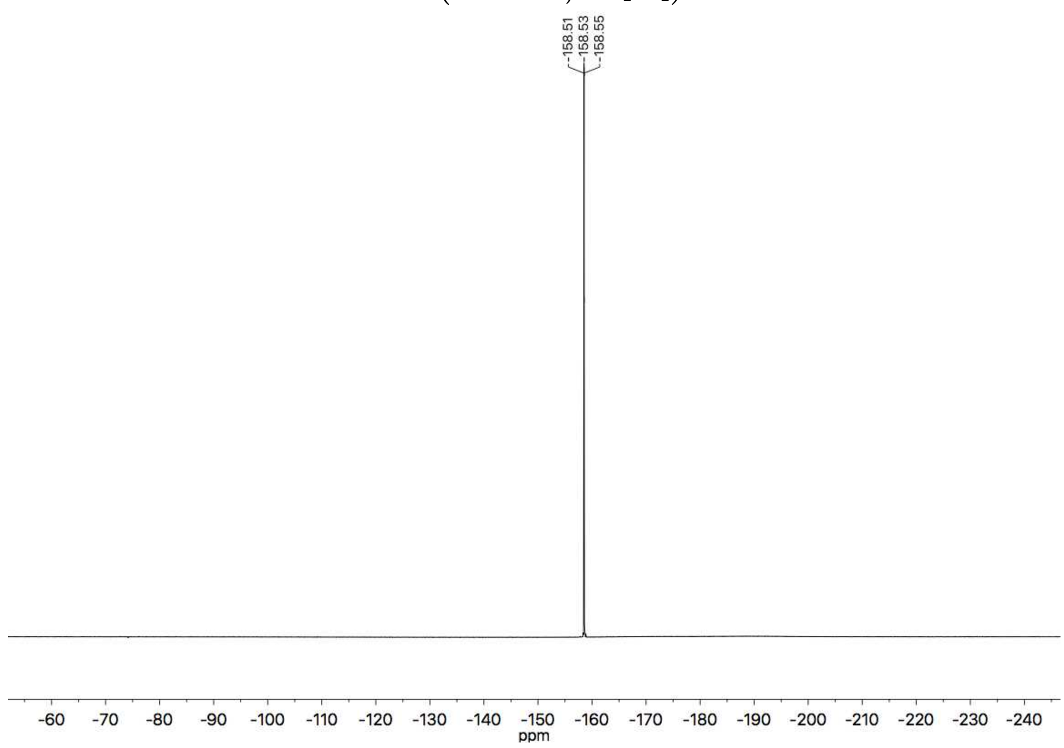
^{1}H NMR (500 MHz, CD_2Cl_2) – **9b**

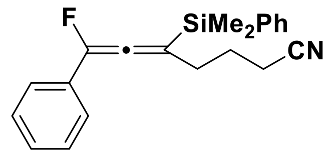


^{13}C NMR (126 MHz, CD_2Cl_2) – **9b**

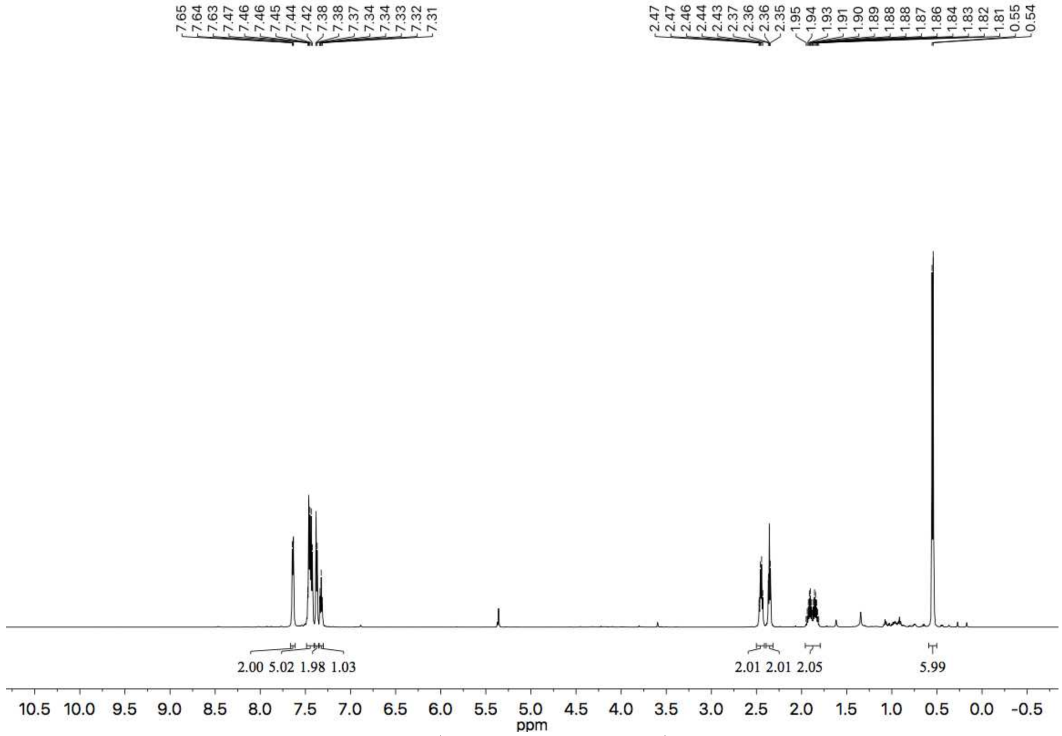


^{19}F NMR (470 MHz, CD_2Cl_2) – **9b**

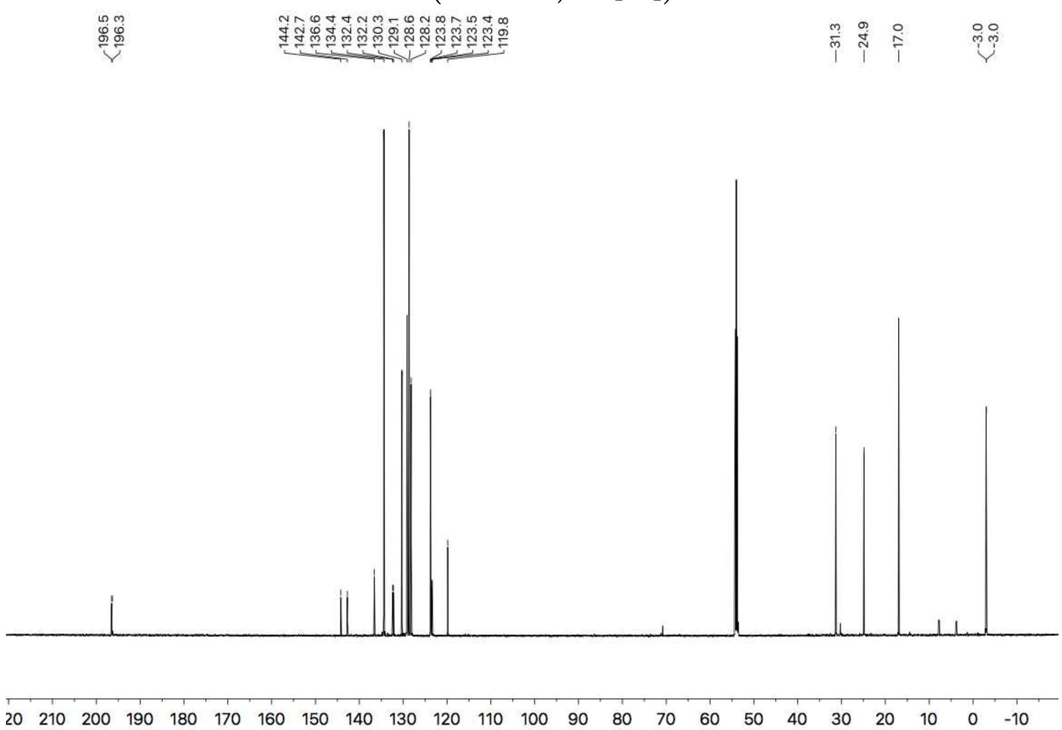




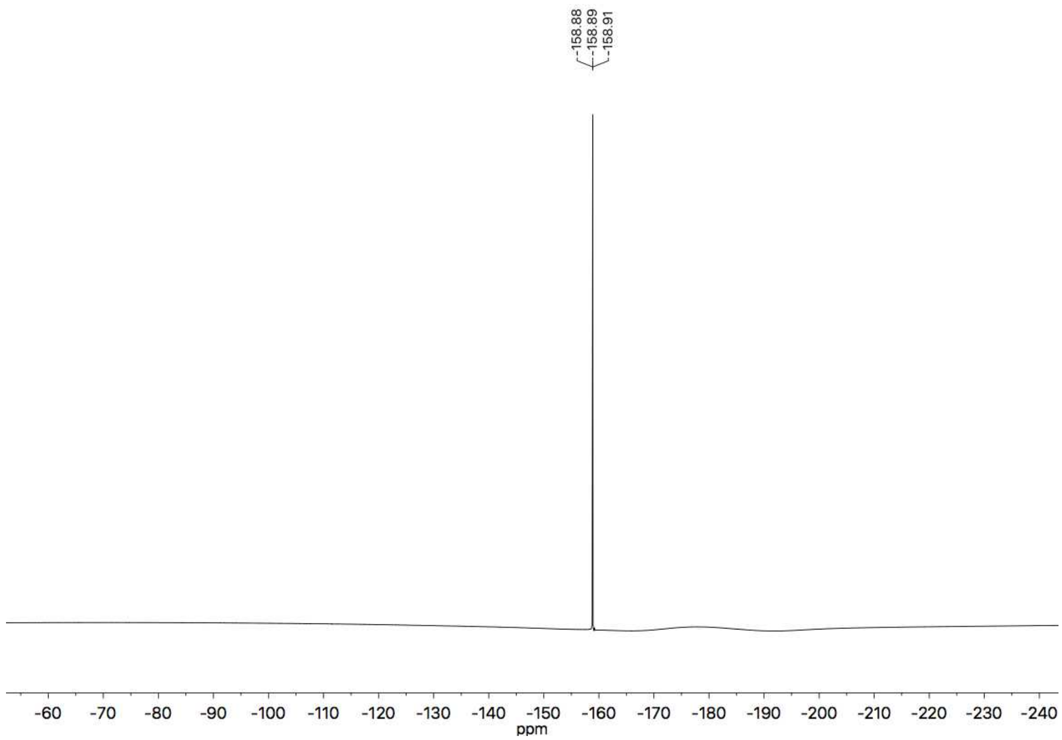
^{1}H NMR (600 MHz, CD_2Cl_2) – **10b**

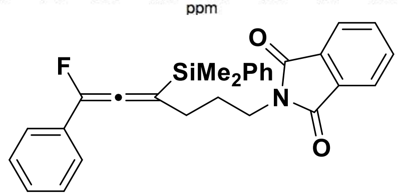


^{13}C NMR (151 MHz, CD_2Cl_2) – **10b**

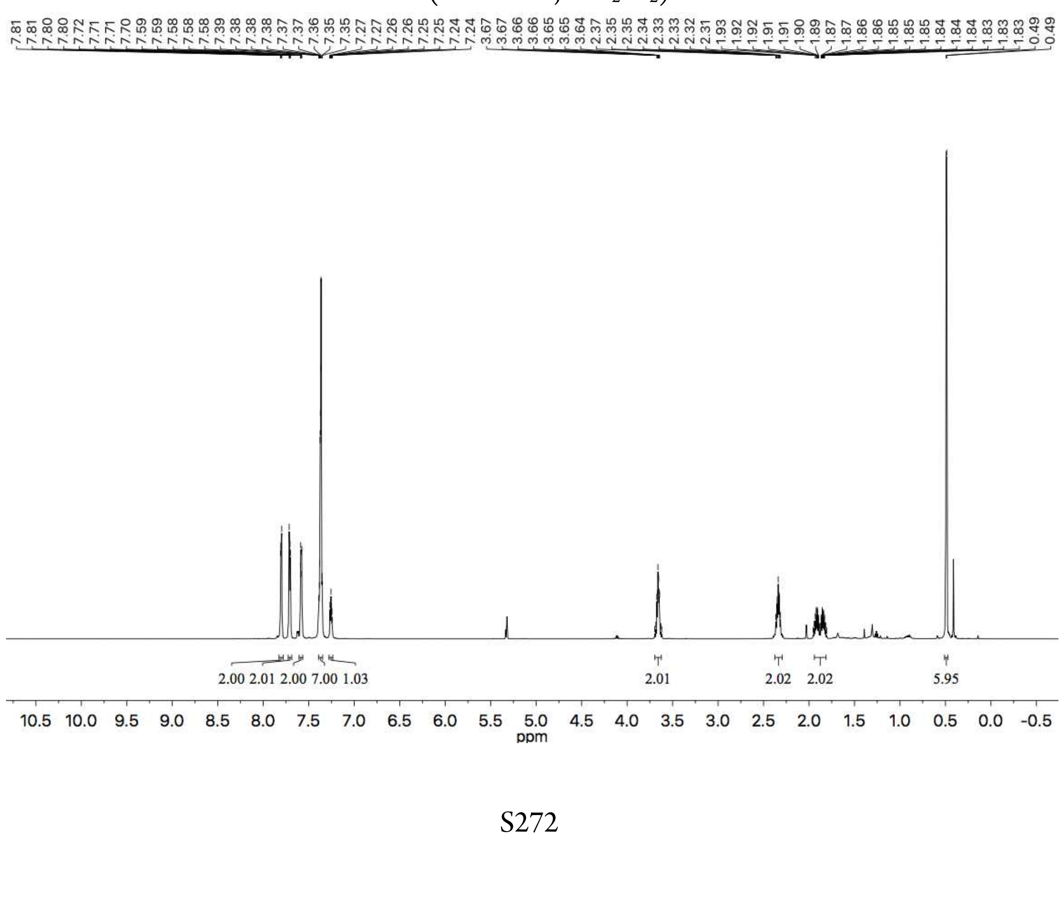


^{19}F NMR (565 MHz, CD_2Cl_2) – **10b**

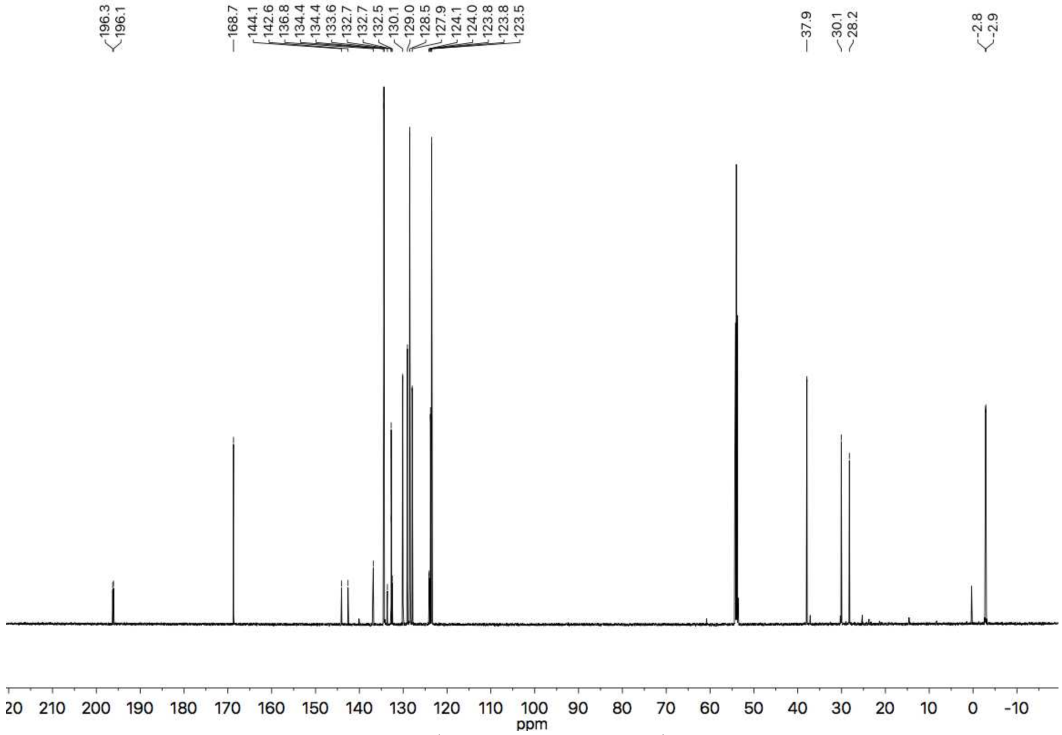




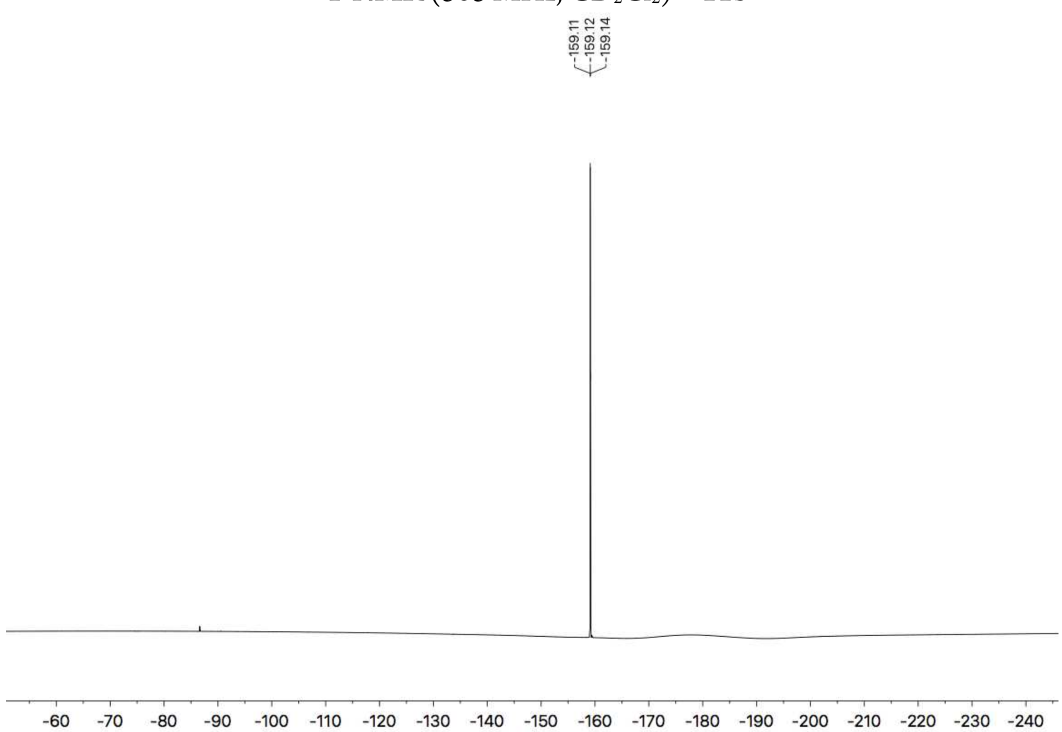
^{1}H NMR (600 MHz, CD_2Cl_2) – **11b**

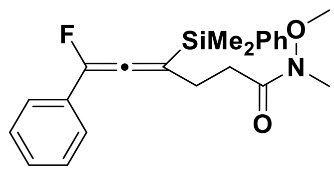


[13]C NMR (151 MHz, CD_2Cl_2) – **11b**

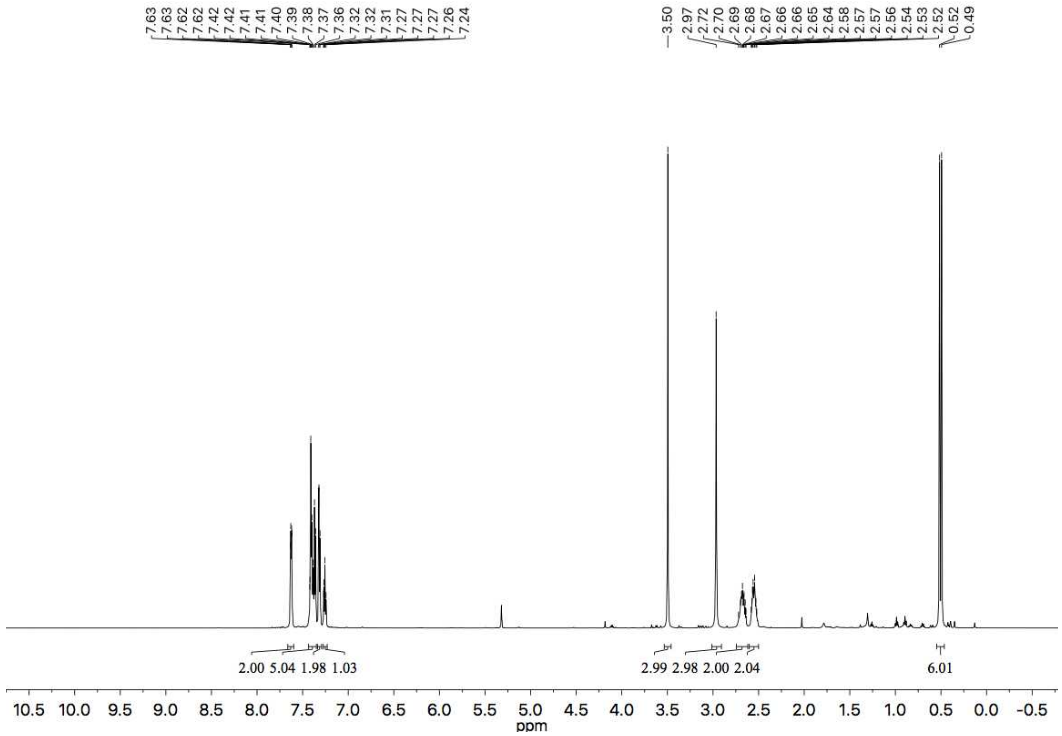


[19]F NMR (565 MHz, CD_2Cl_2) – **11b**

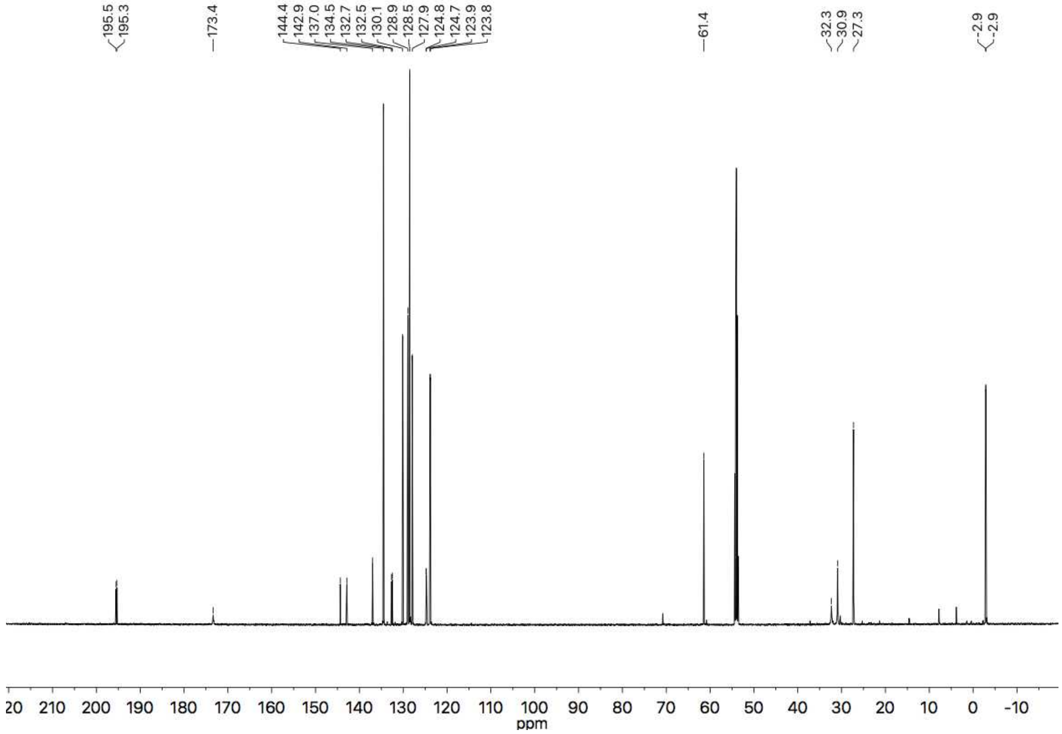




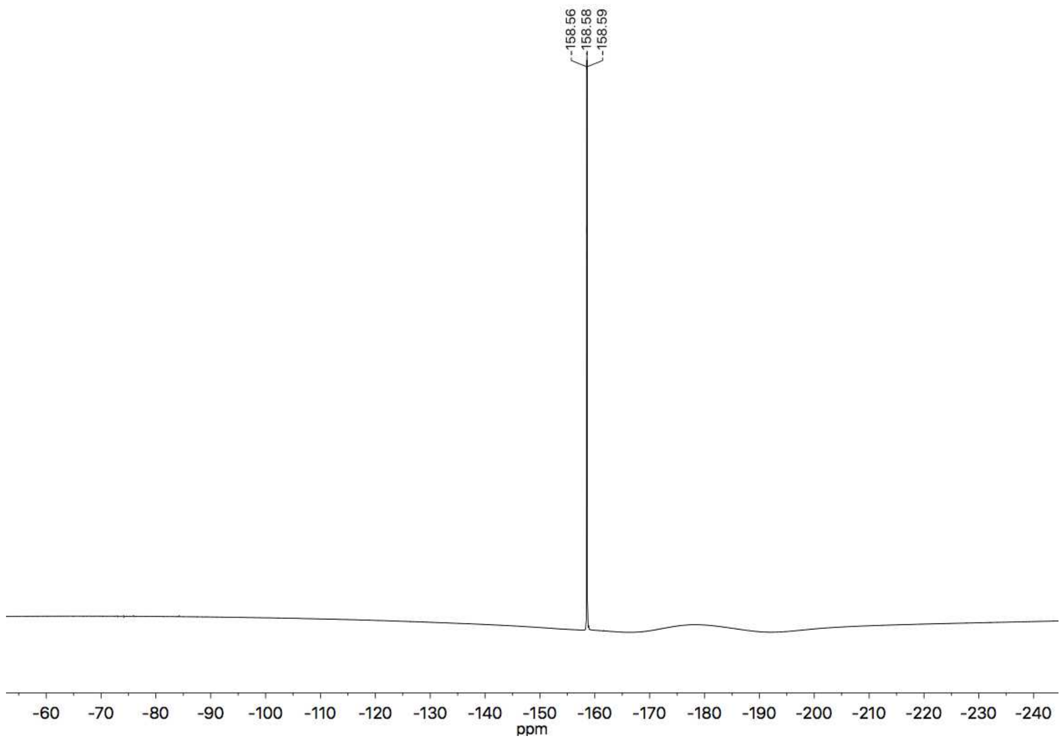
[1]H NMR (600 MHz, CD_2Cl_2) – **12b**

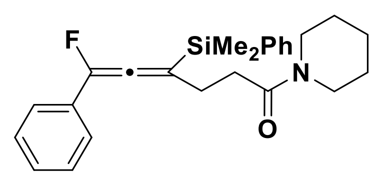


[13]C NMR (151 MHz, CD_2Cl_2) – **12b**

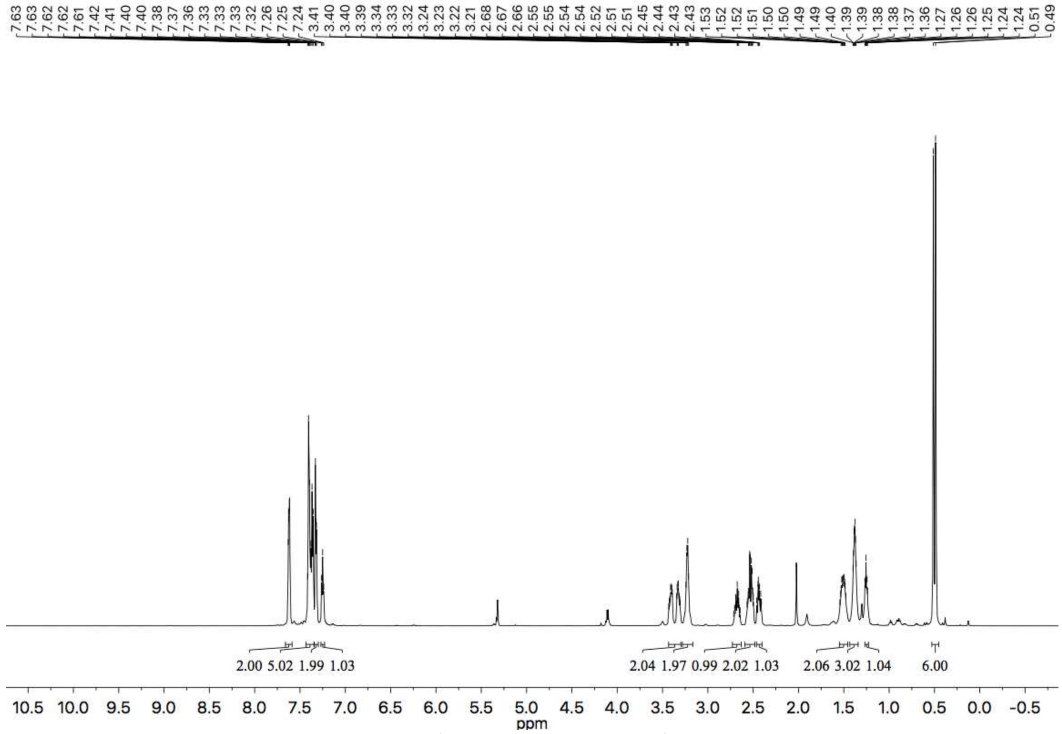


^{19}F NMR (565 MHz, CD_2Cl_2) – **12b**

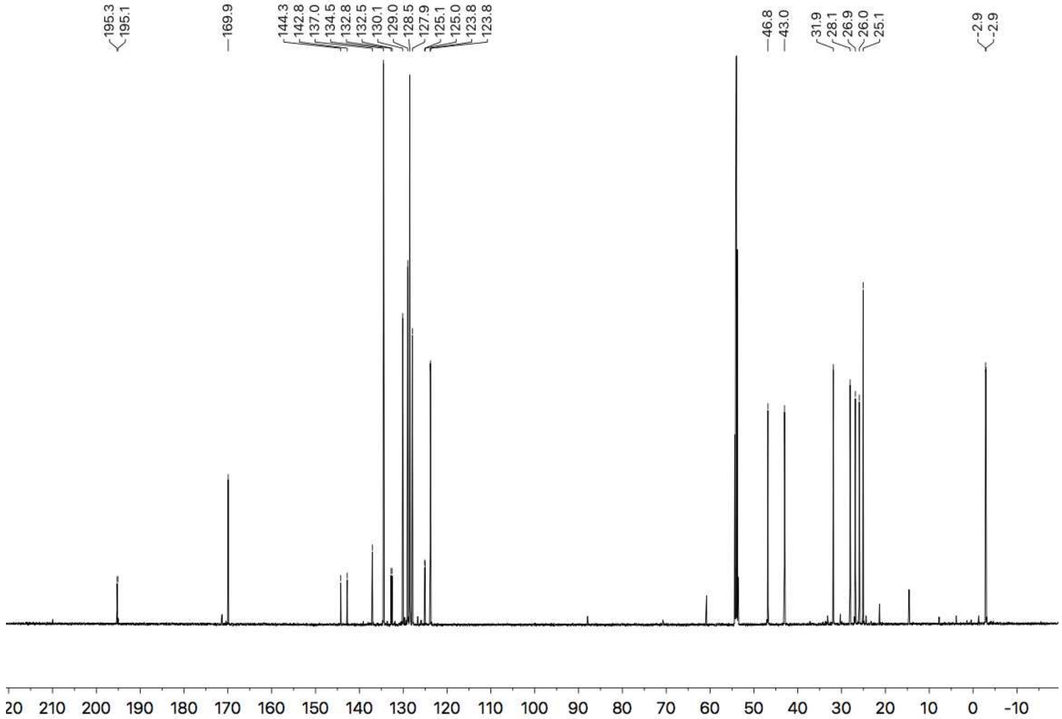




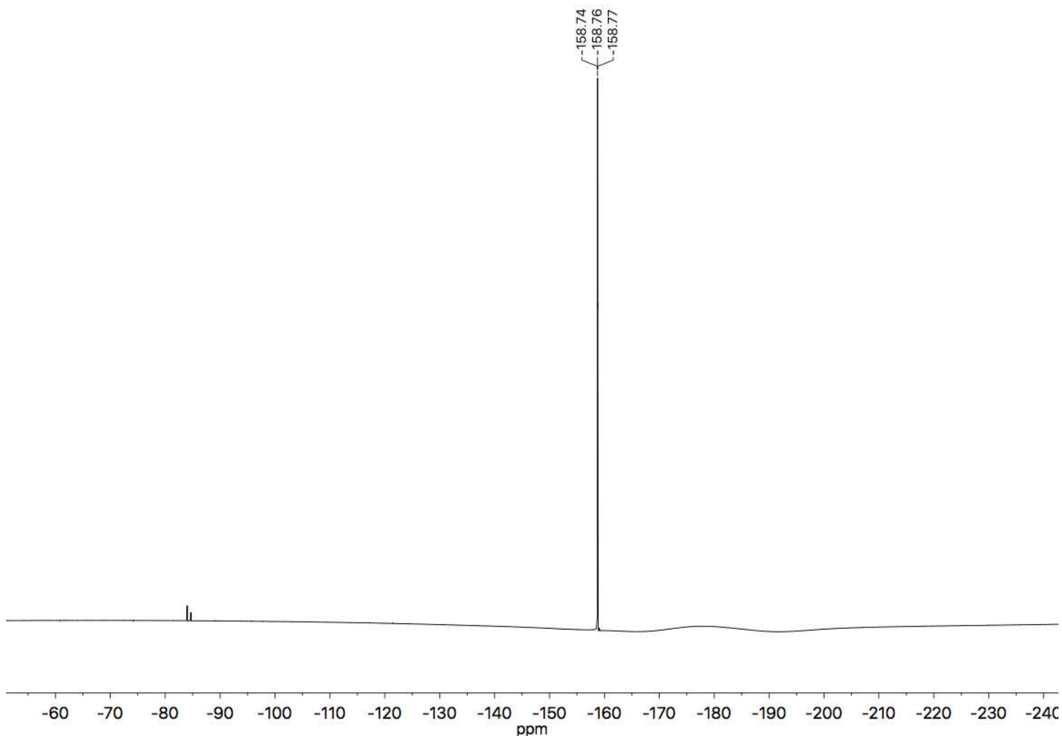
^{1}H NMR (600 MHz, CD_2Cl_2) – **13b**

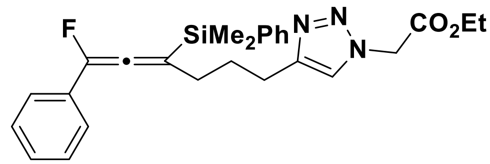


^{13}C NMR (151 MHz, CD_2Cl_2) – **13b**

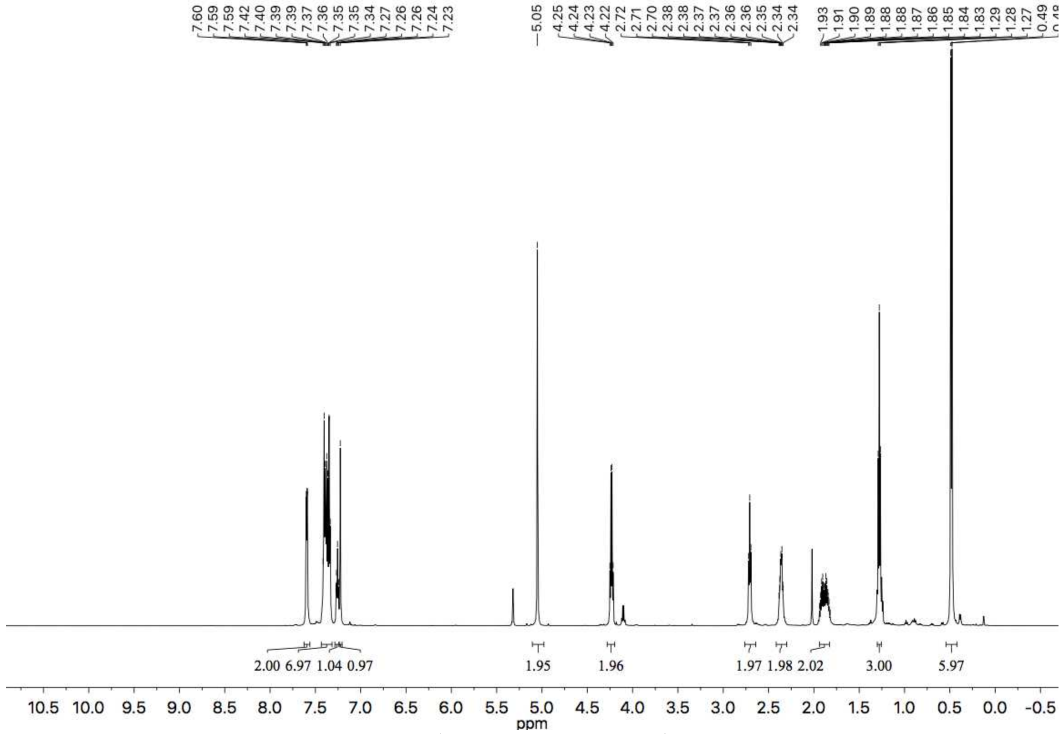


^{19}F NMR (565 MHz, CD_2Cl_2) – **13b**

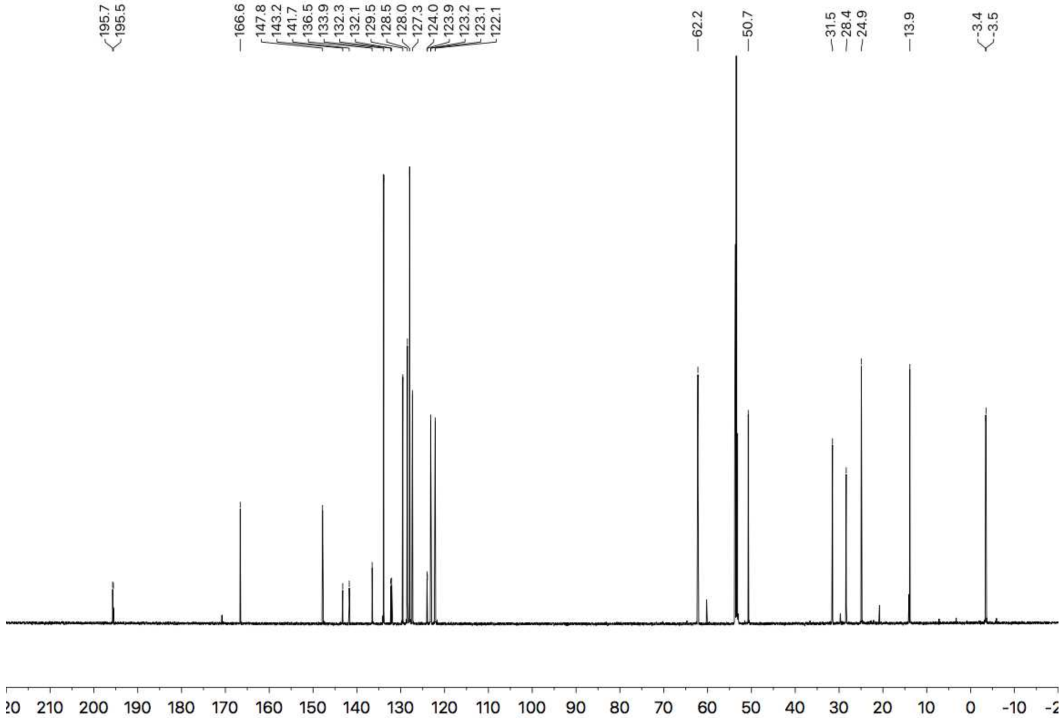




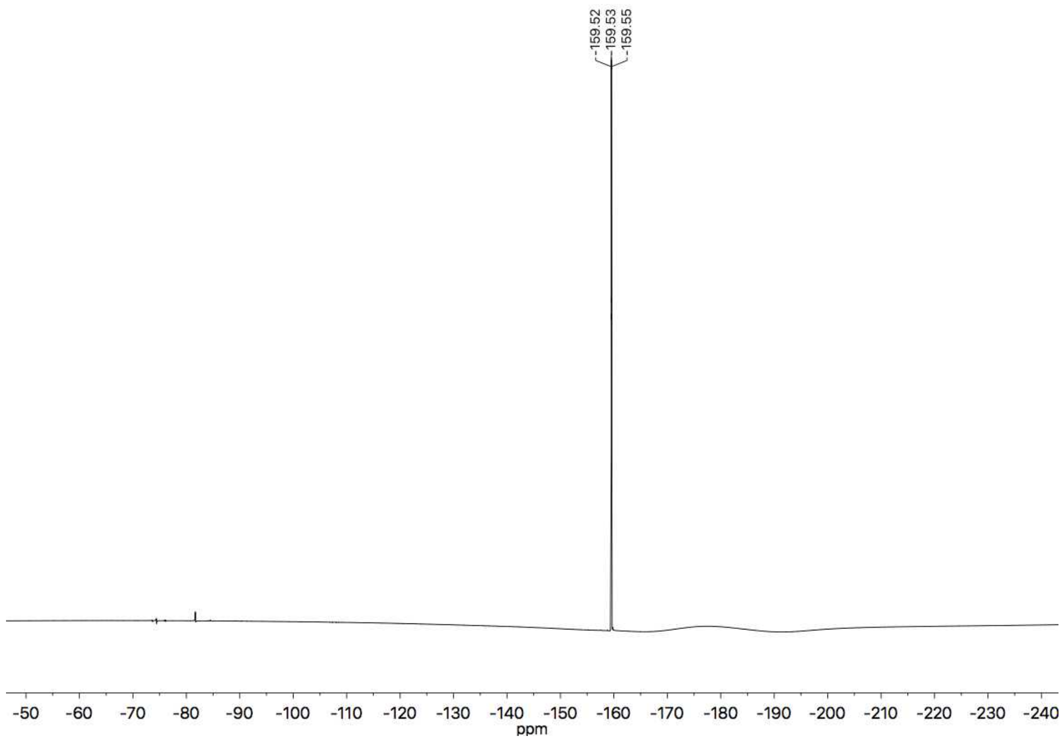
^{1}H NMR (600 MHz, CD_2Cl_2) – **14b**

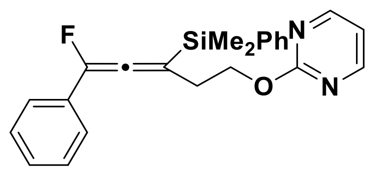


^{13}C NMR (151 MHz, CD_2Cl_2) – **14b**

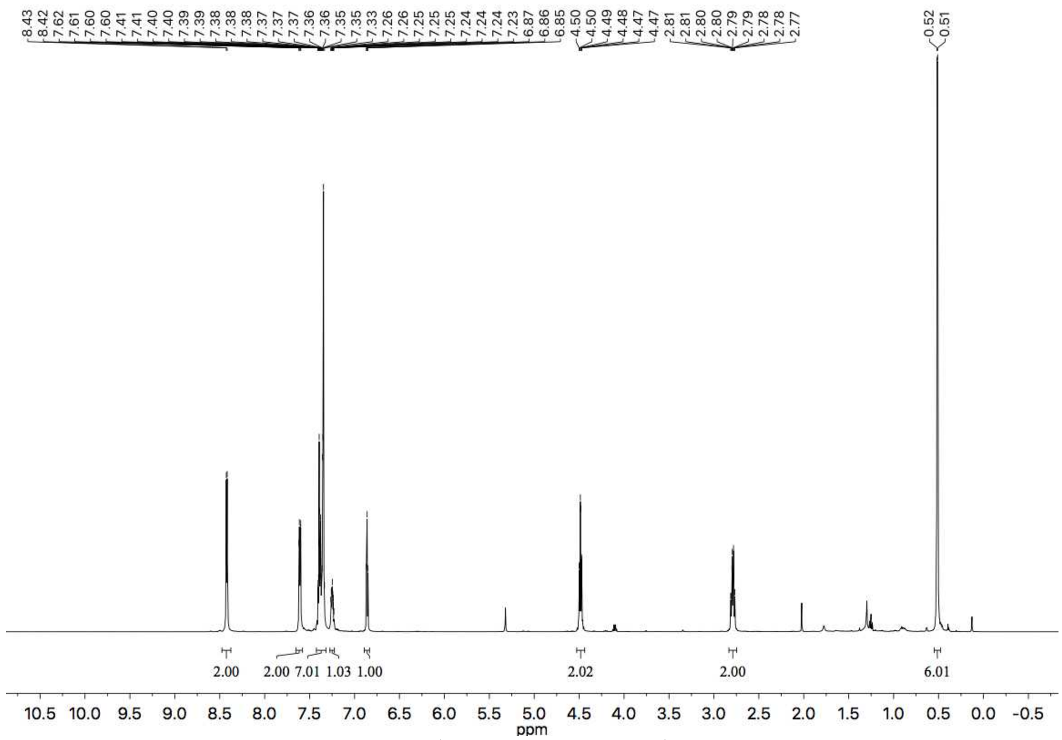


^{19}F NMR (565 MHz, CD_2Cl_2) – **14b**

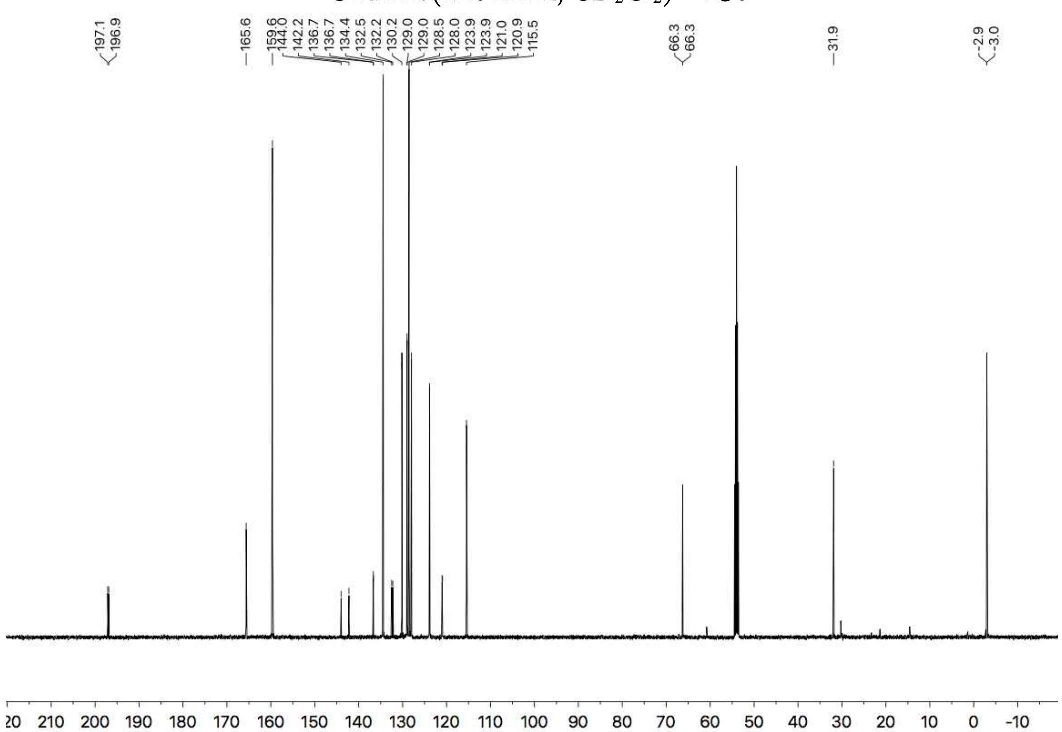




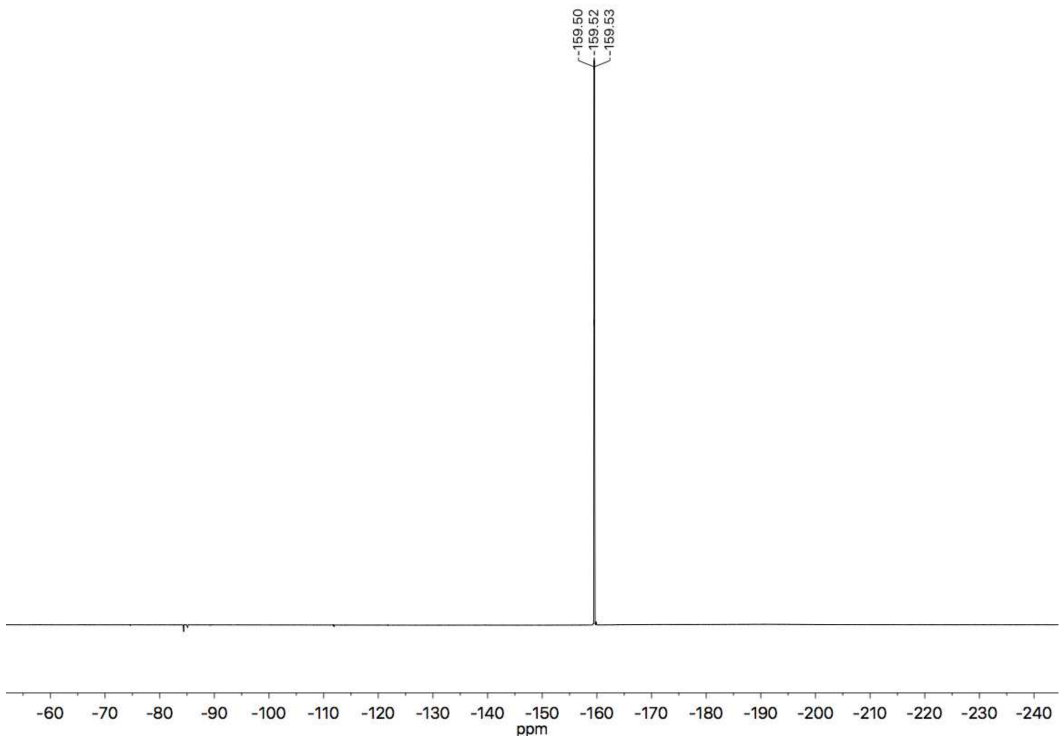
^{1}H NMR (500 MHz, CD_2Cl_2) – **15b**

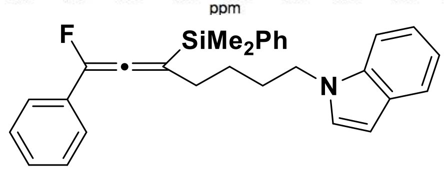


^{13}C NMR (126 MHz, CD_2Cl_2) – **15b**

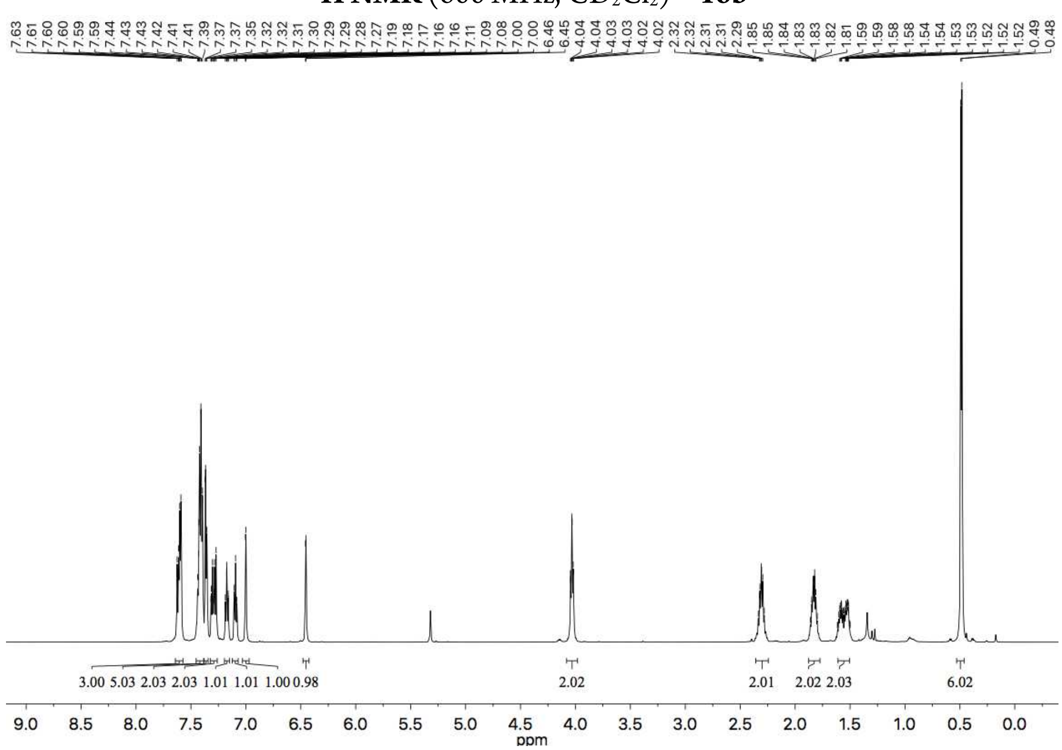


^{19}F NMR (470 MHz, CD_2Cl_2) – **15b**

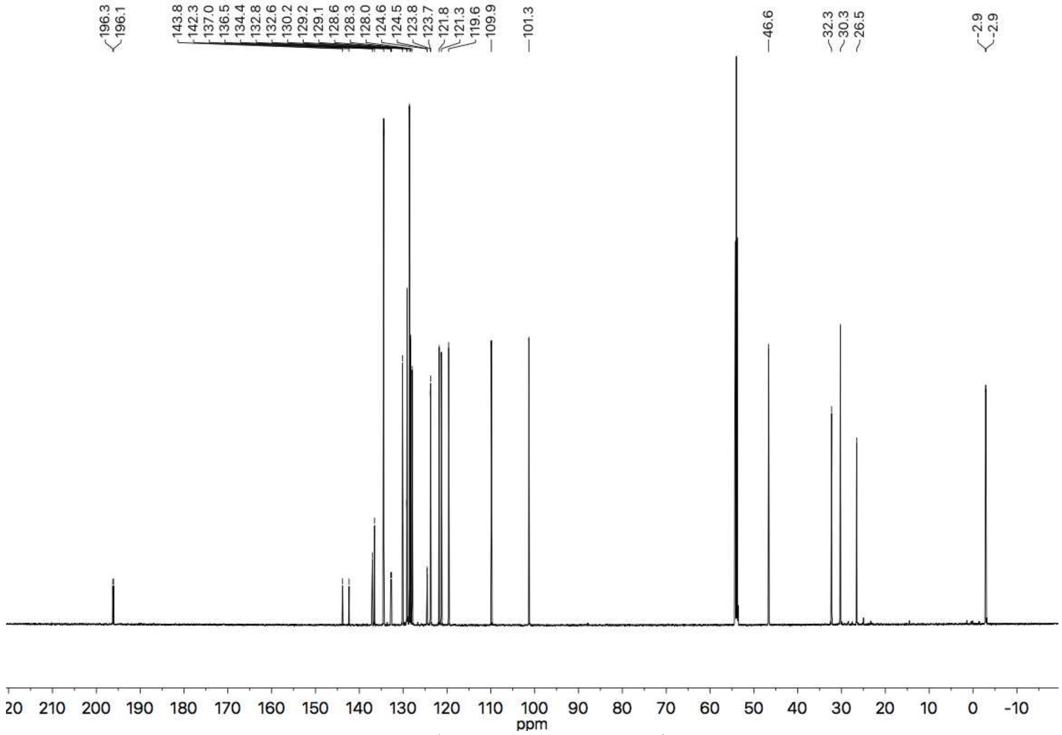




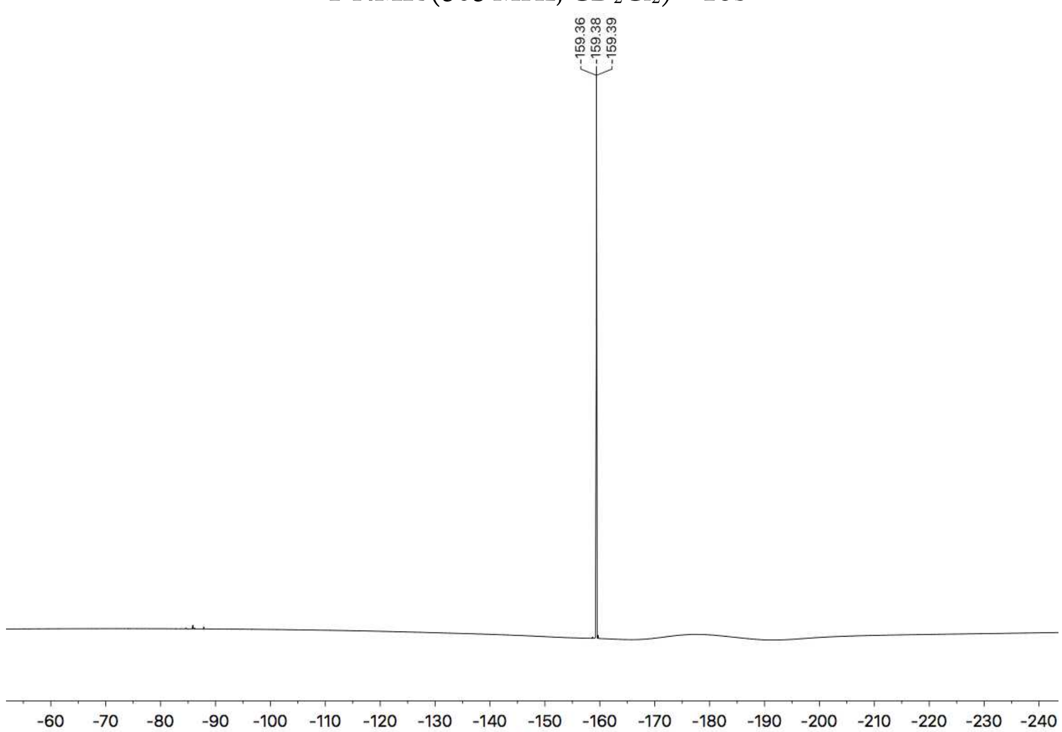
^{1}H NMR (600 MHz, CD_2Cl_2) – **16b**

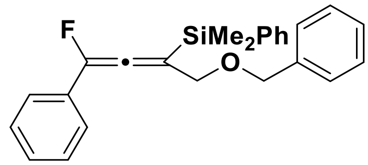


^{13}C NMR (151 MHz, CD_2Cl_2) – **16b**

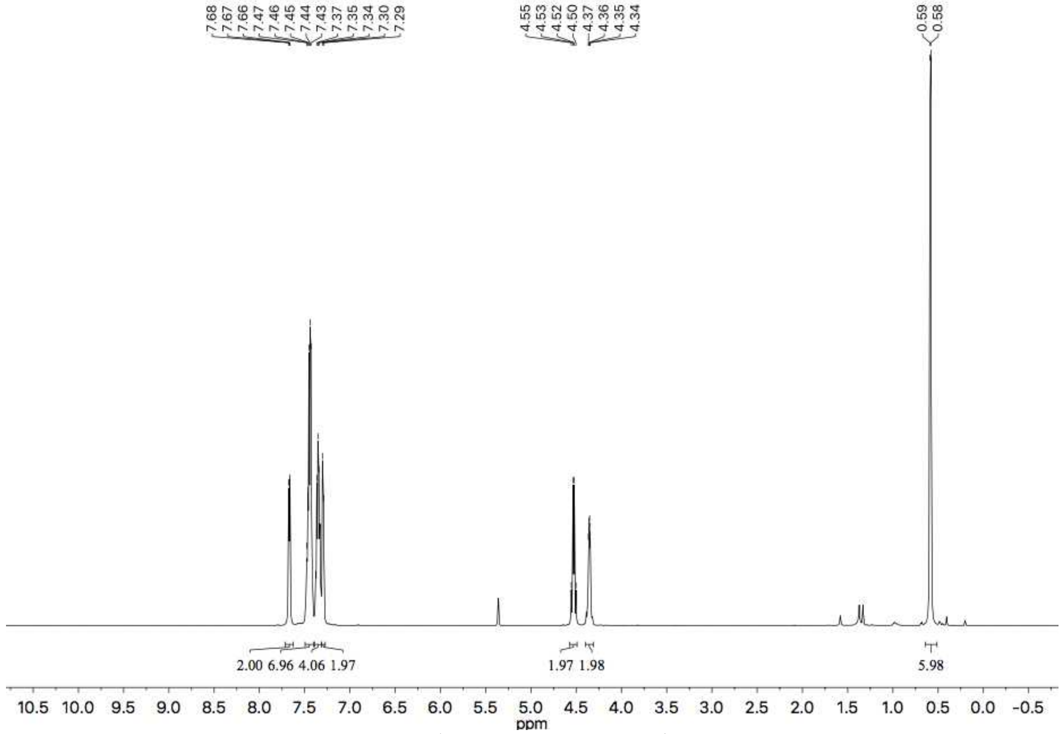


^{19}F NMR (565 MHz, CD_2Cl_2) – **16b**

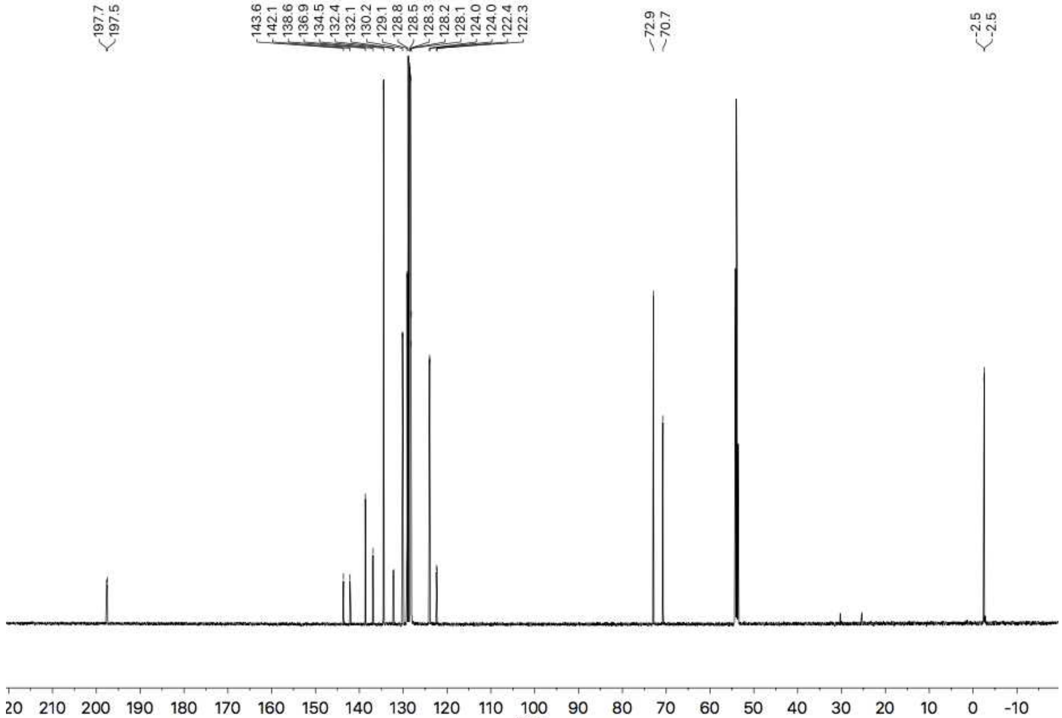




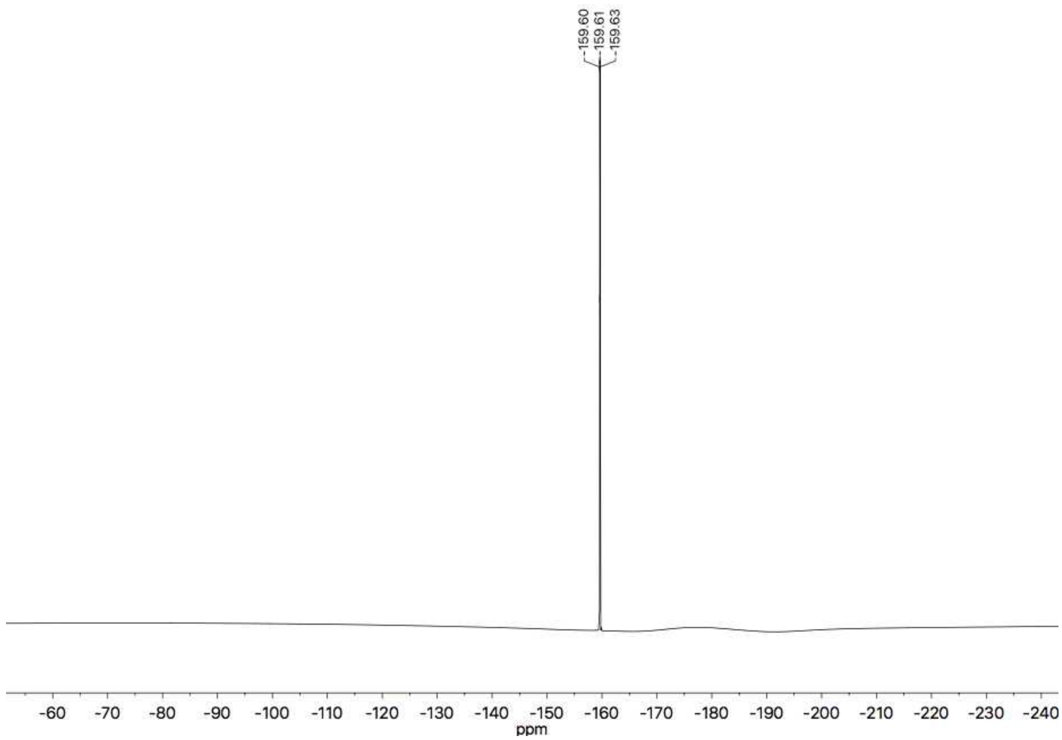
^{1}H NMR (600 MHz, CD_2Cl_2) – **17b**

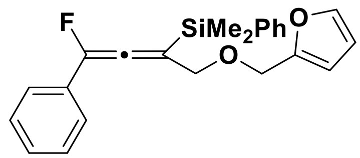


^{13}C NMR (151 MHz, CD_2Cl_2) – **17b**

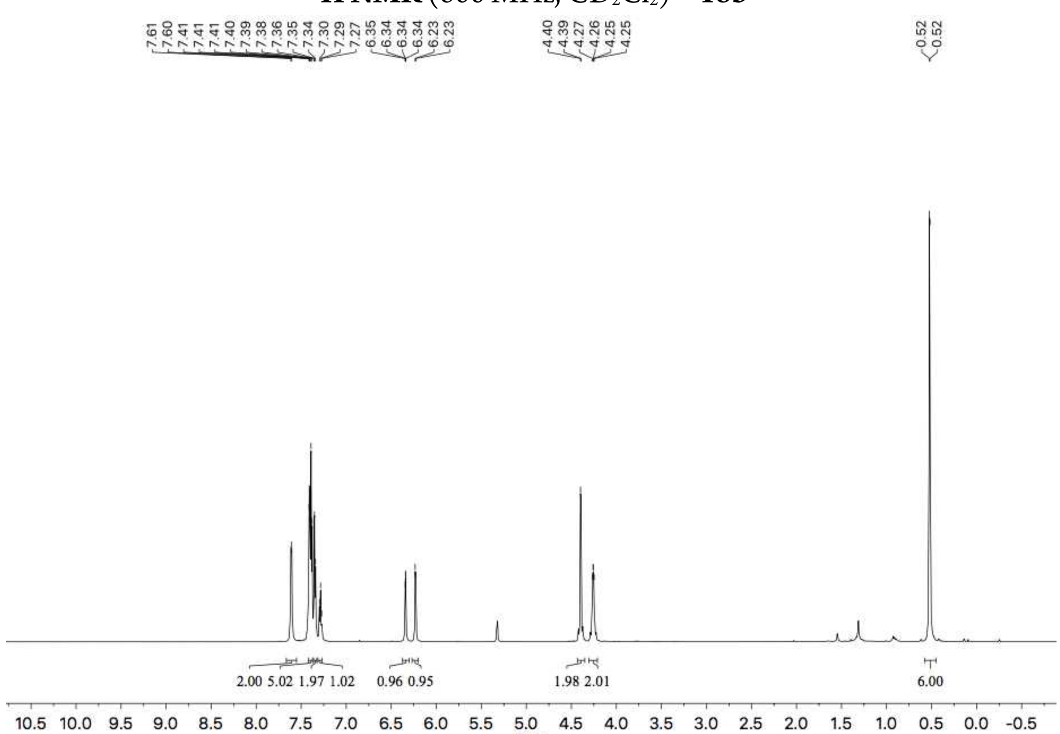


^{19}F NMR (565 MHz, CD_2Cl_2) – **17b**

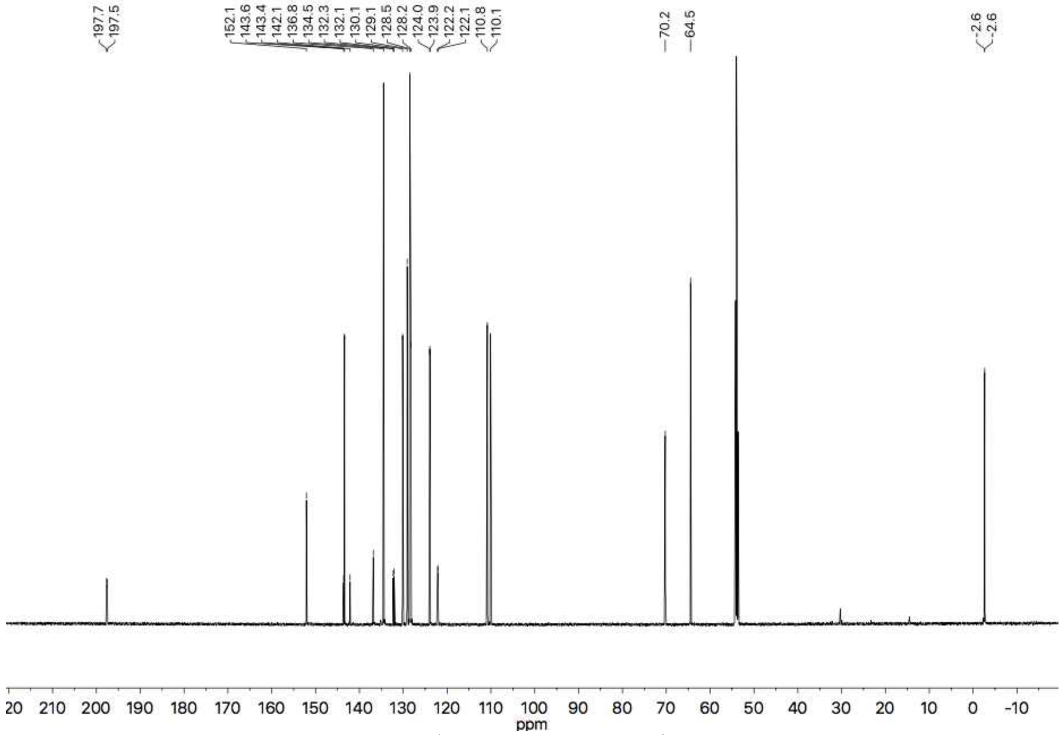




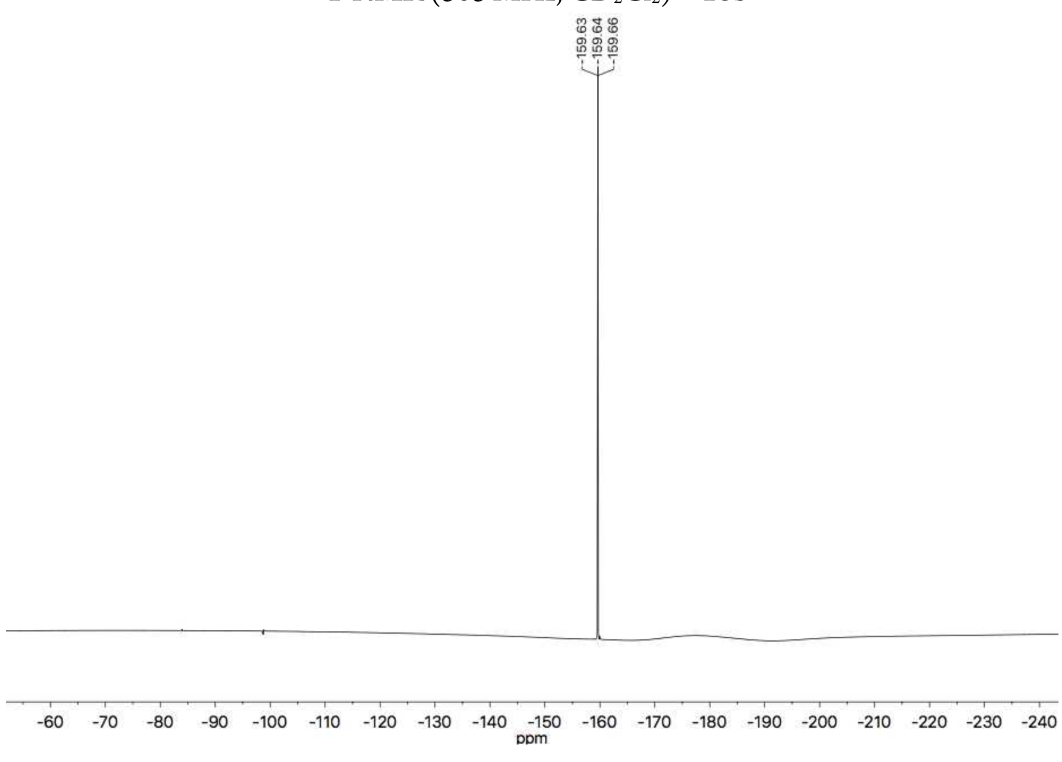
^{1}H NMR (600 MHz, CD_2Cl_2) – **18b**

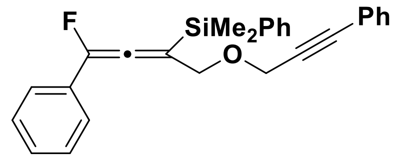


^{13}C NMR (151 MHz, CD_2Cl_2) – **18b**

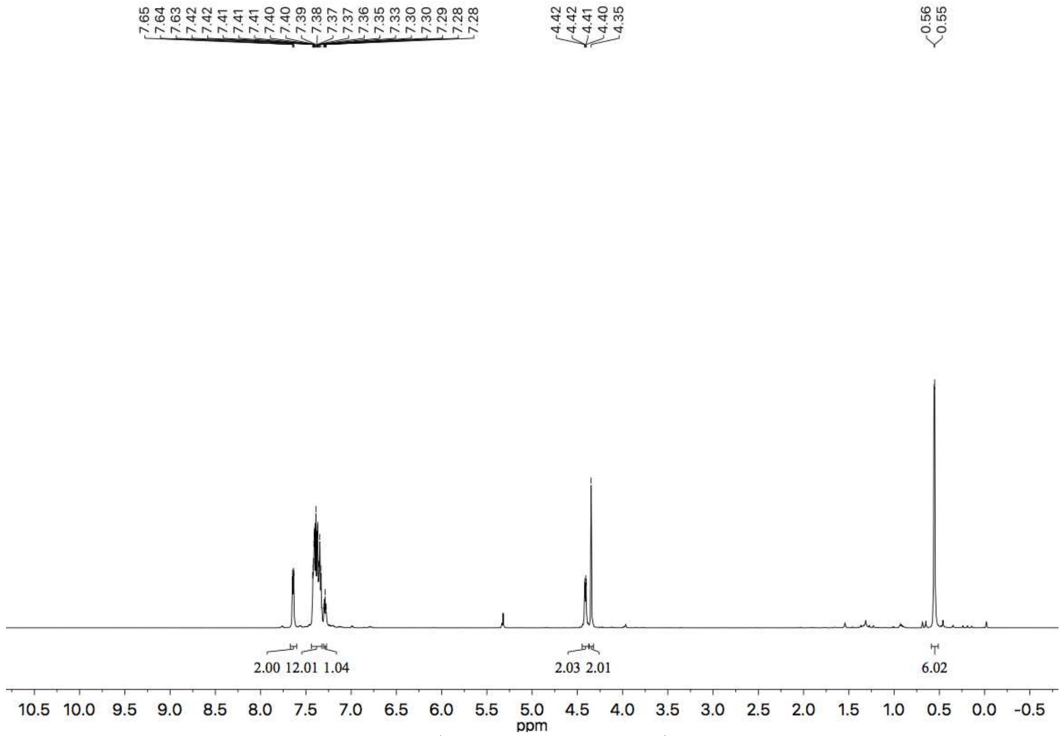


^{19}F NMR (565 MHz, CD_2Cl_2) – **18b**

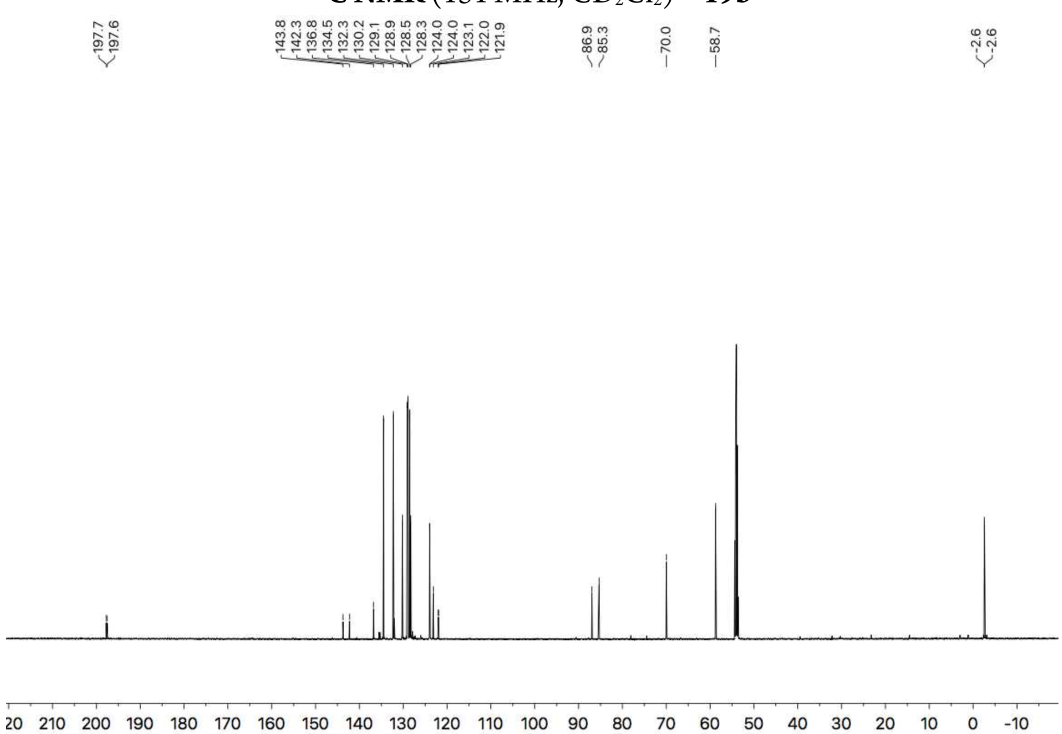




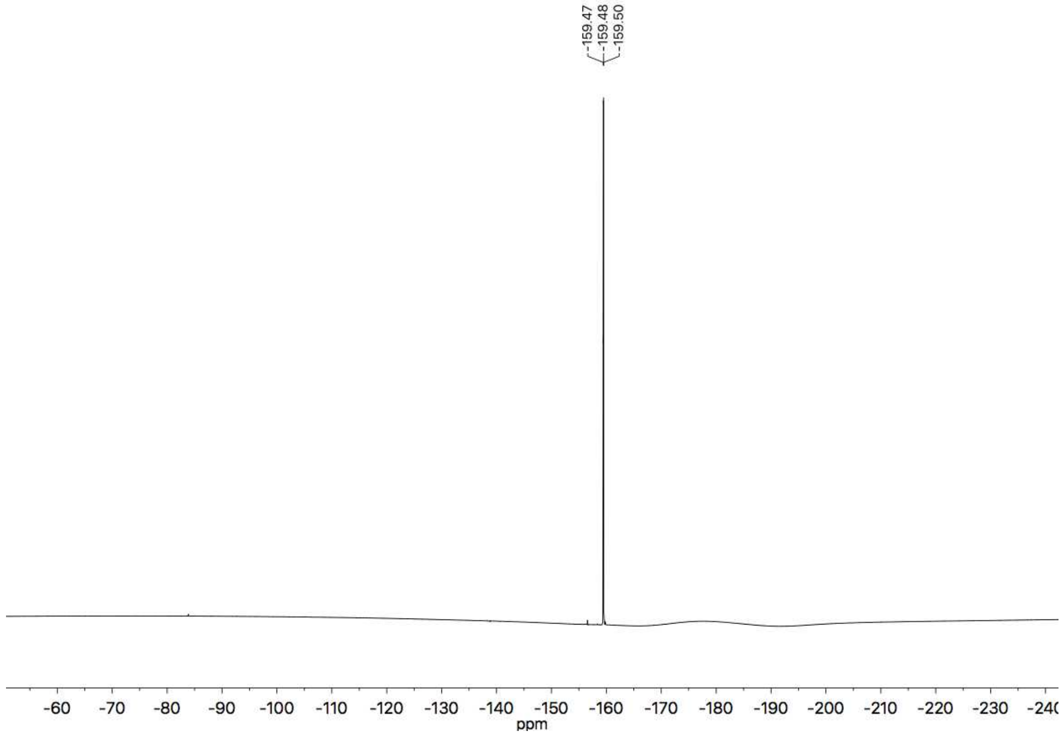
[1]H NMR (600 MHz, CD_2Cl_2) – **19b**

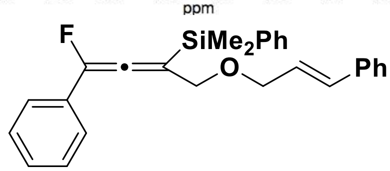


[13]C NMR (151 MHz, CD_2Cl_2) – **19b**

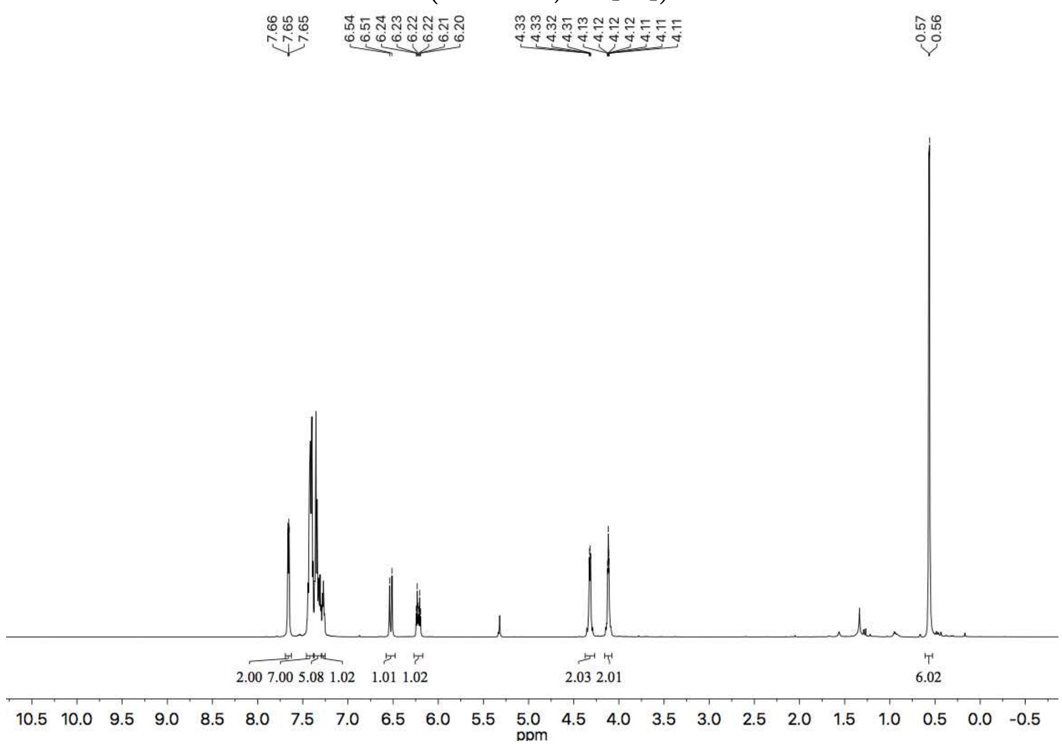


^{19}F NMR (565 MHz, CD_2Cl_2) – **19b**

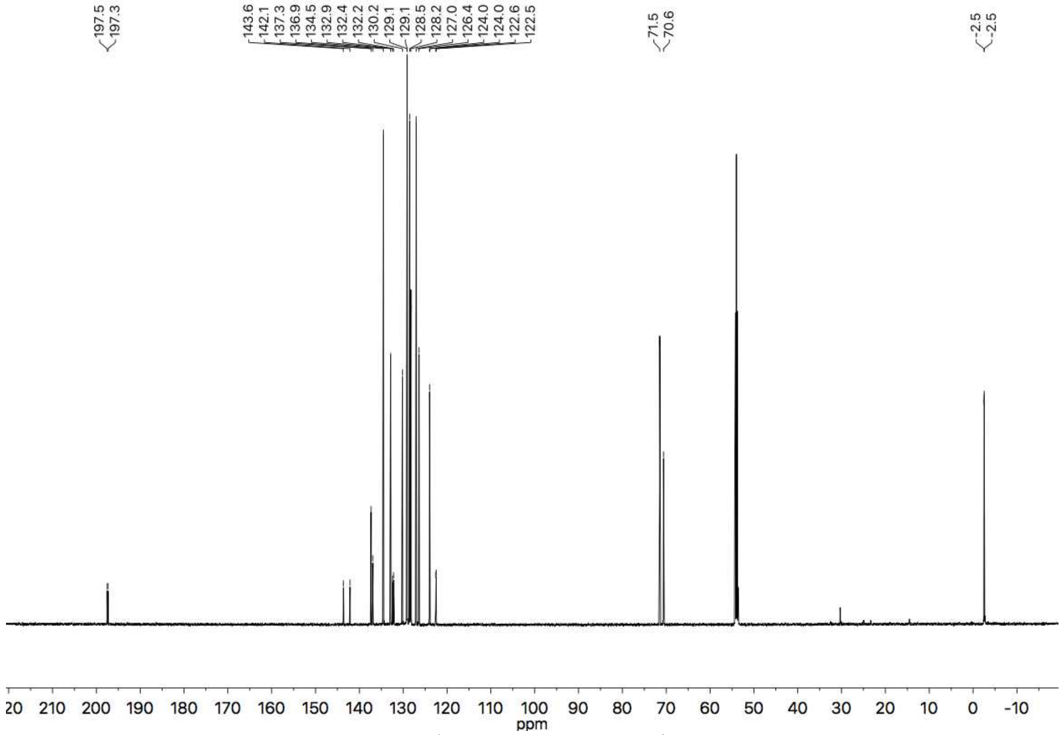




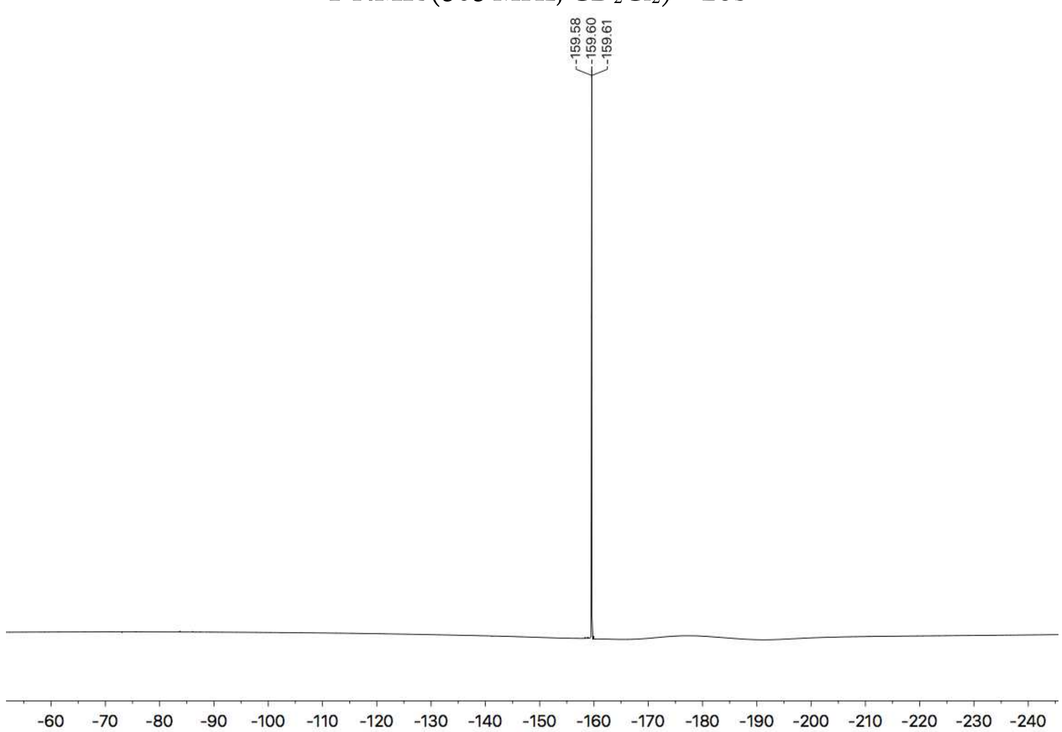
^{1}H NMR (600 MHz, CD_2Cl_2) – **20b**

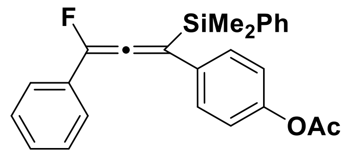


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **20b**



^{19}**F NMR** (565 MHz, CD_2Cl_2) – **20b**





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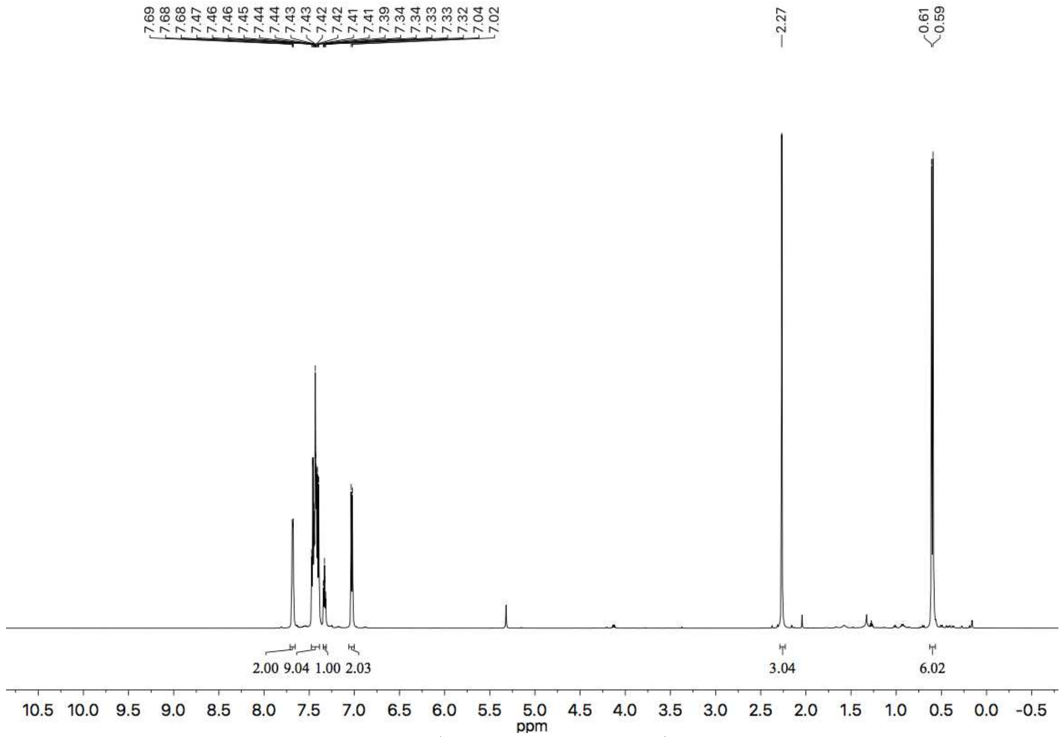
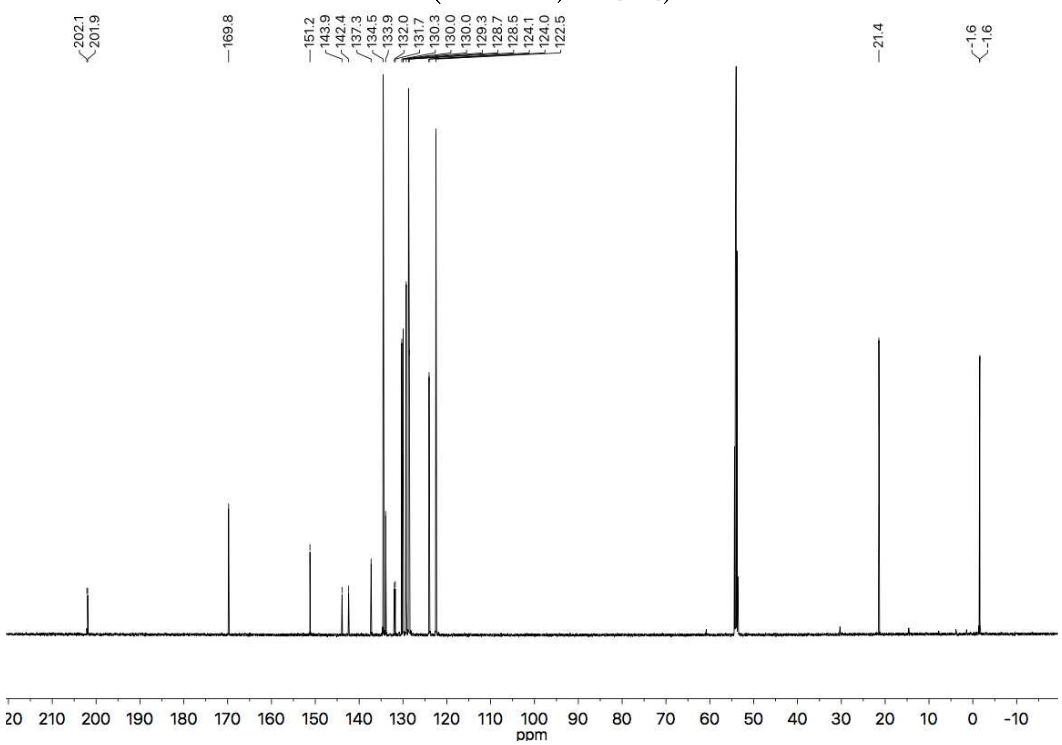
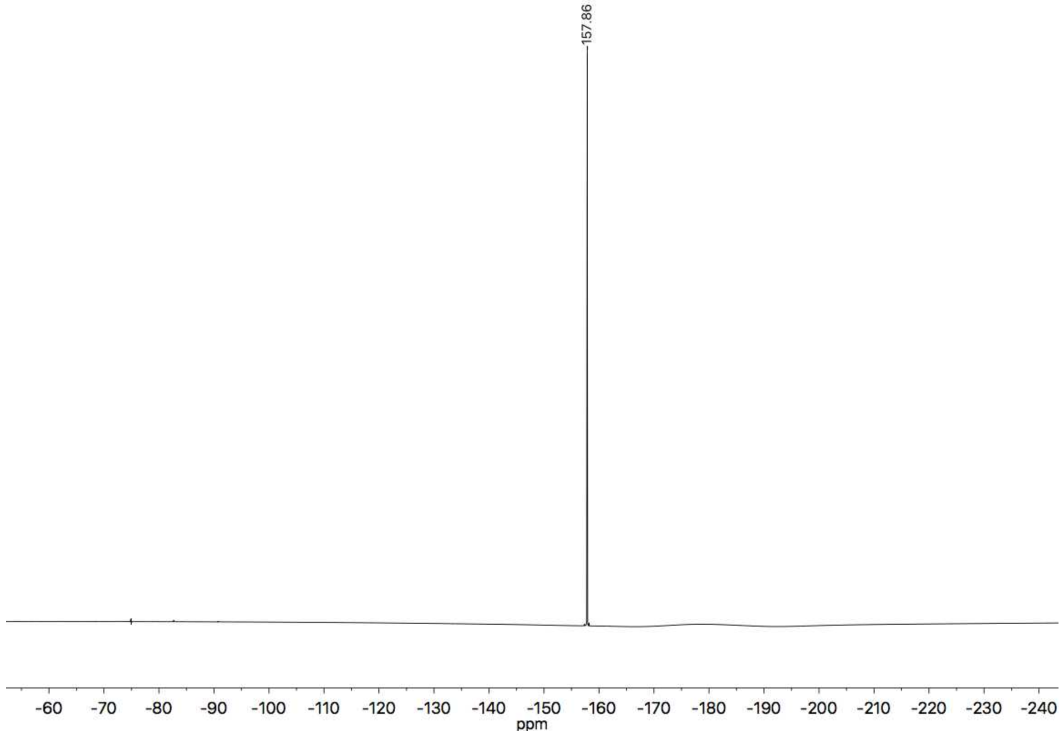
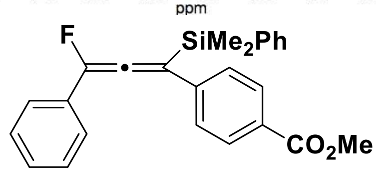


[13]C NMR (151 MHz, CD_2Cl_2) – **21b**

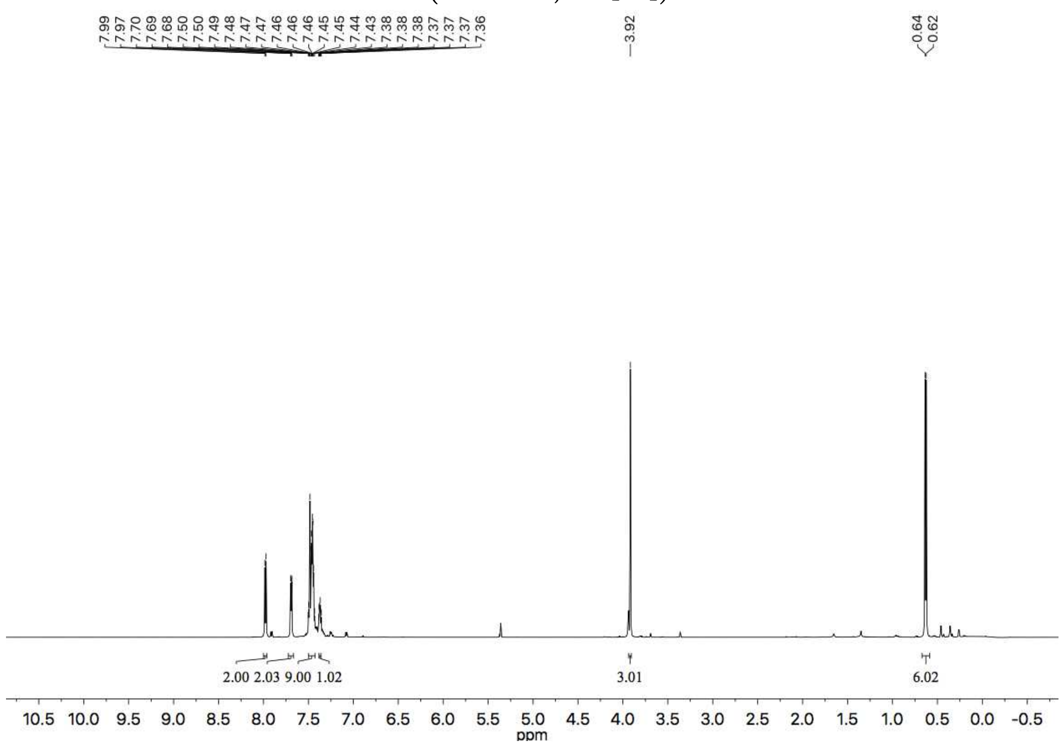


^{19}F NMR (565 MHz, CD_2Cl_2) – **21b**

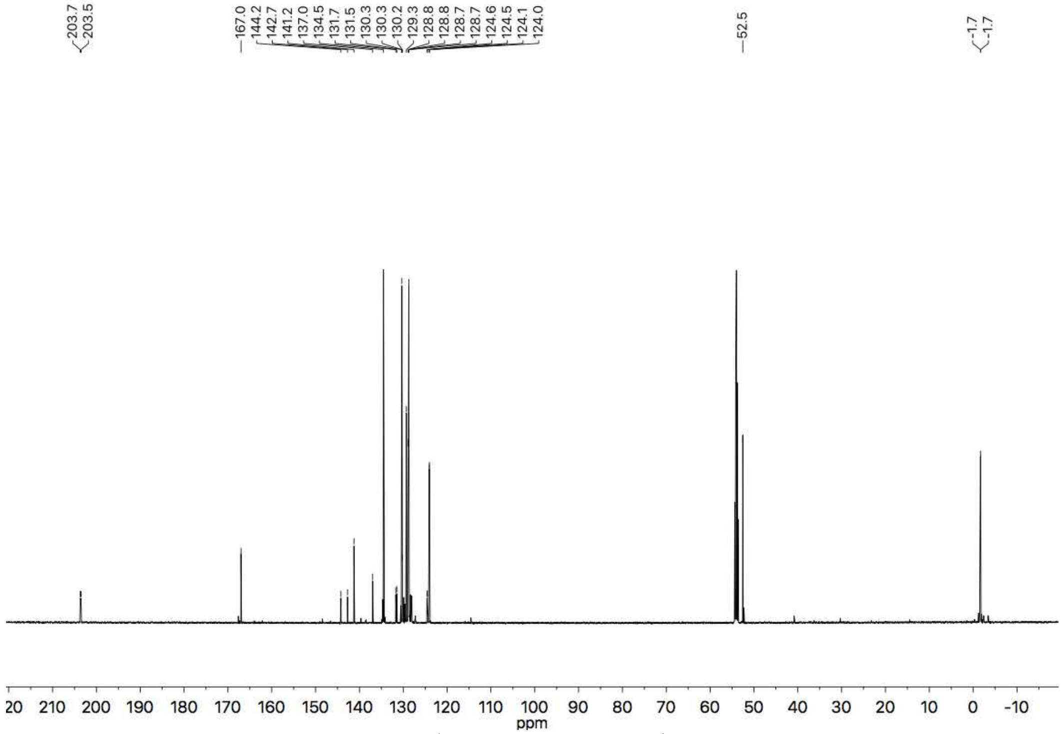




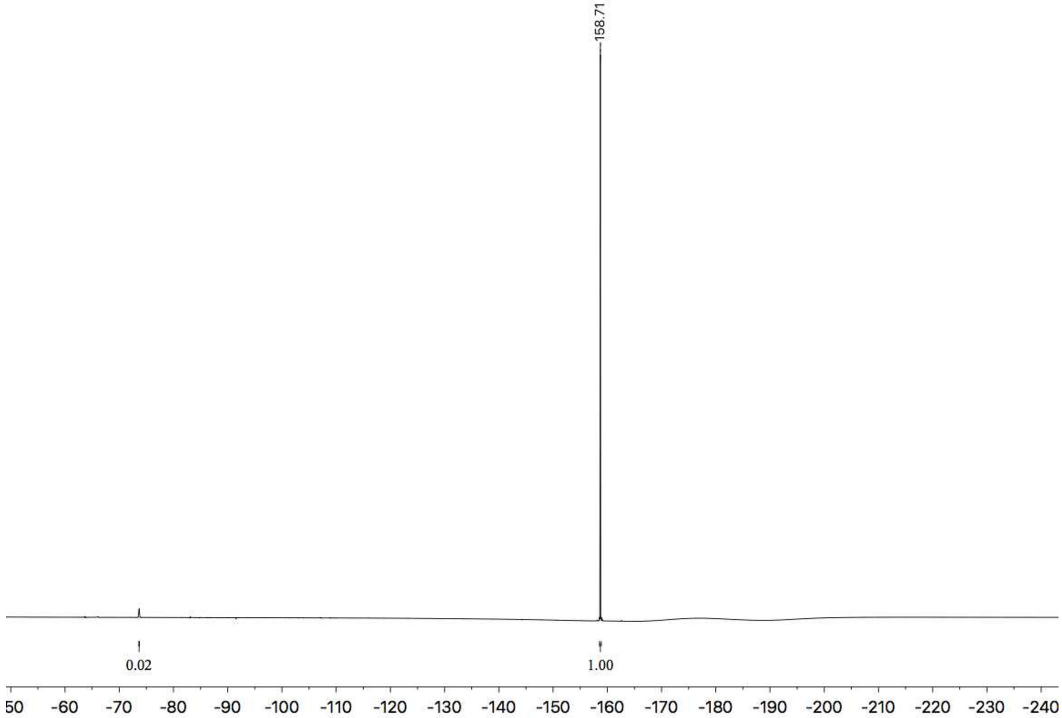
^{1}H NMR (600 MHz, CD_2Cl_2) – **22b**

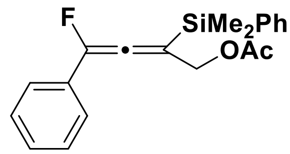


^{13}C NMR (151 MHz, CD_2Cl_2) – **22b**

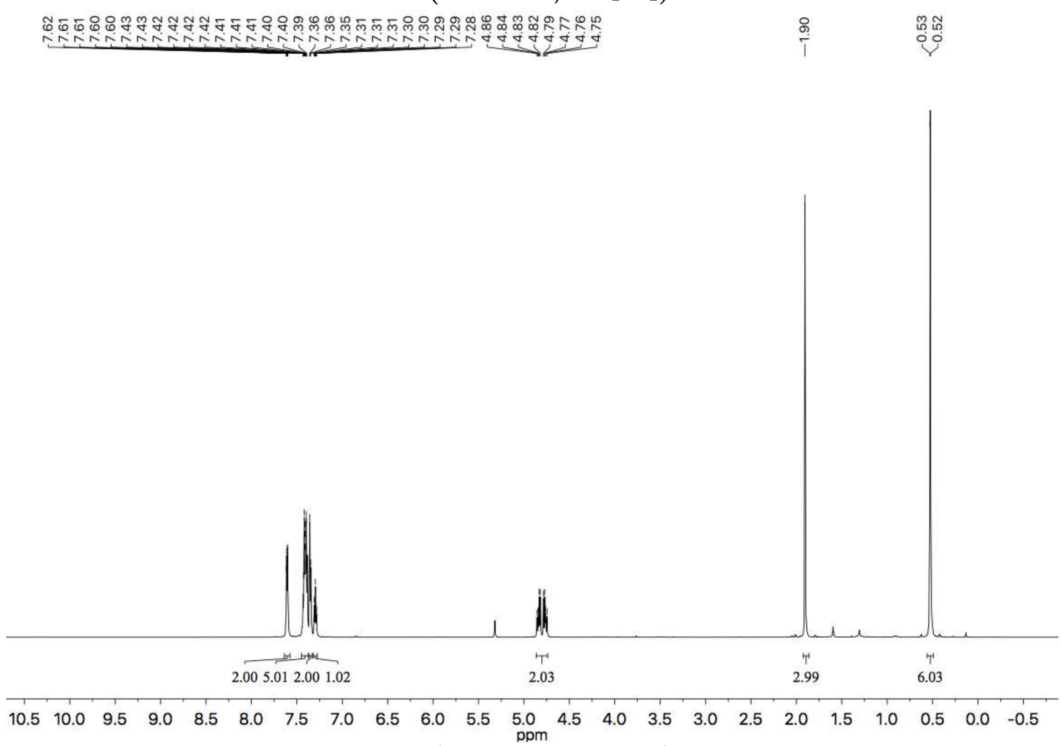


^{19}F NMR (565 MHz, CD_2Cl_2) – **22b**

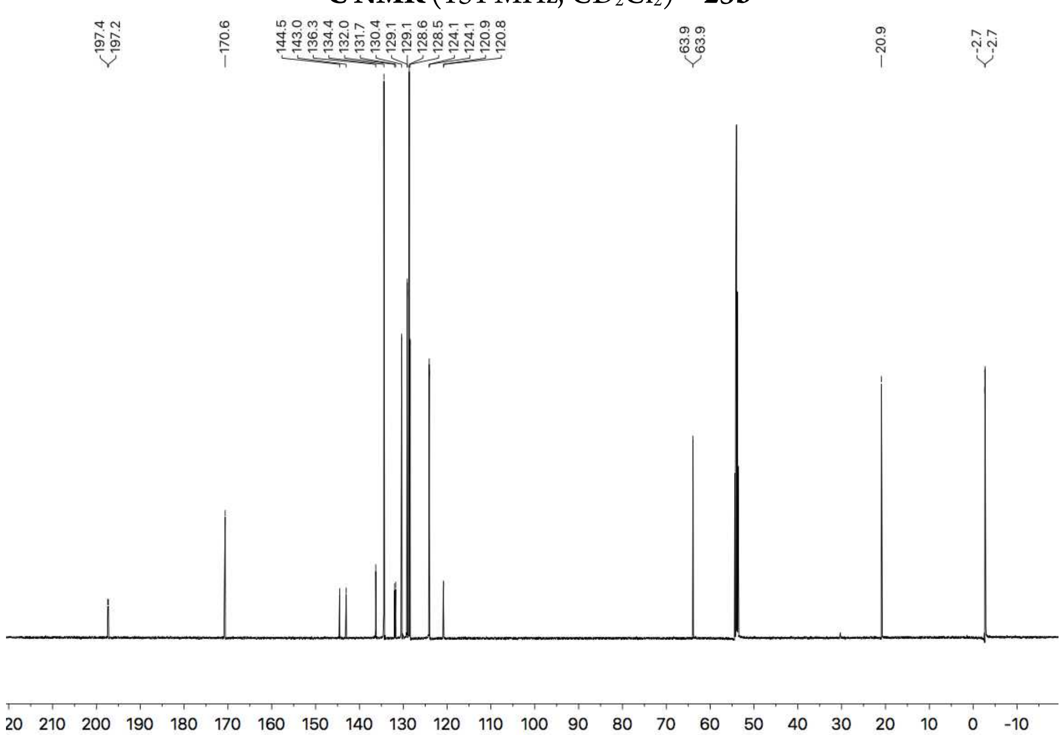




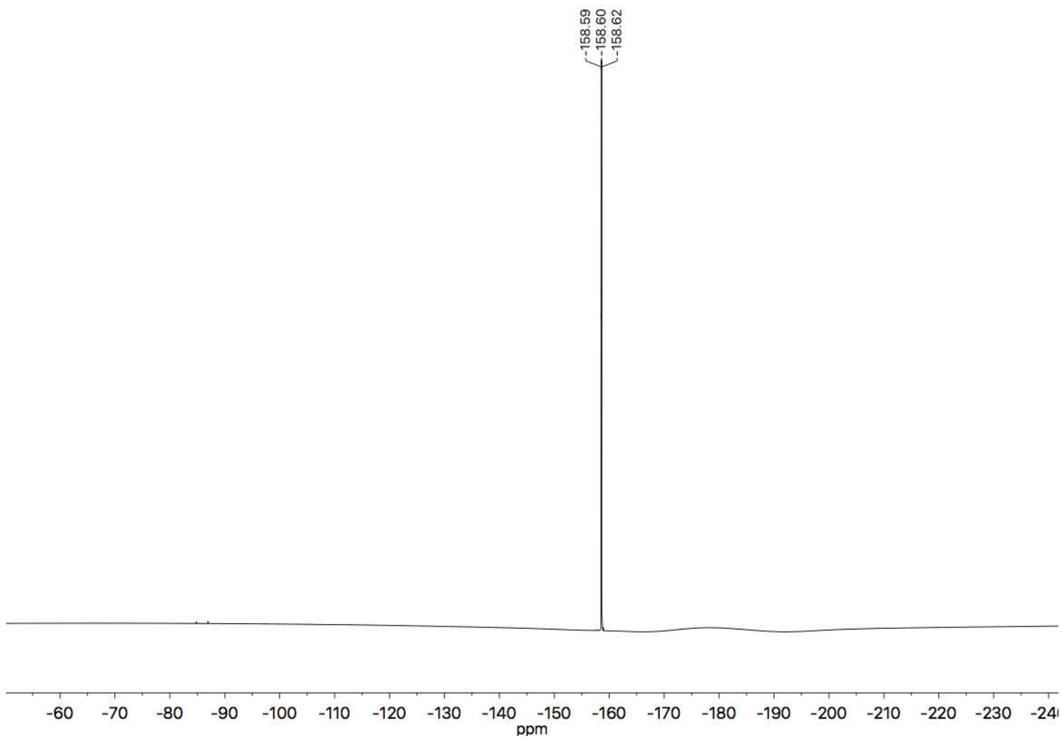
^{1}**H NMR** (600 MHz, CD_2Cl_2) – **23b**

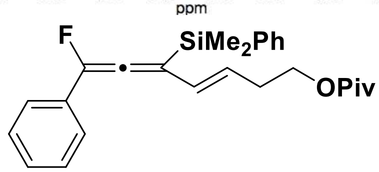


^{13}**C NMR** (151 MHz, CD_2Cl_2) – **23b**



^{19}**F NMR** (565 MHz, CD_2Cl_2) – **23b**





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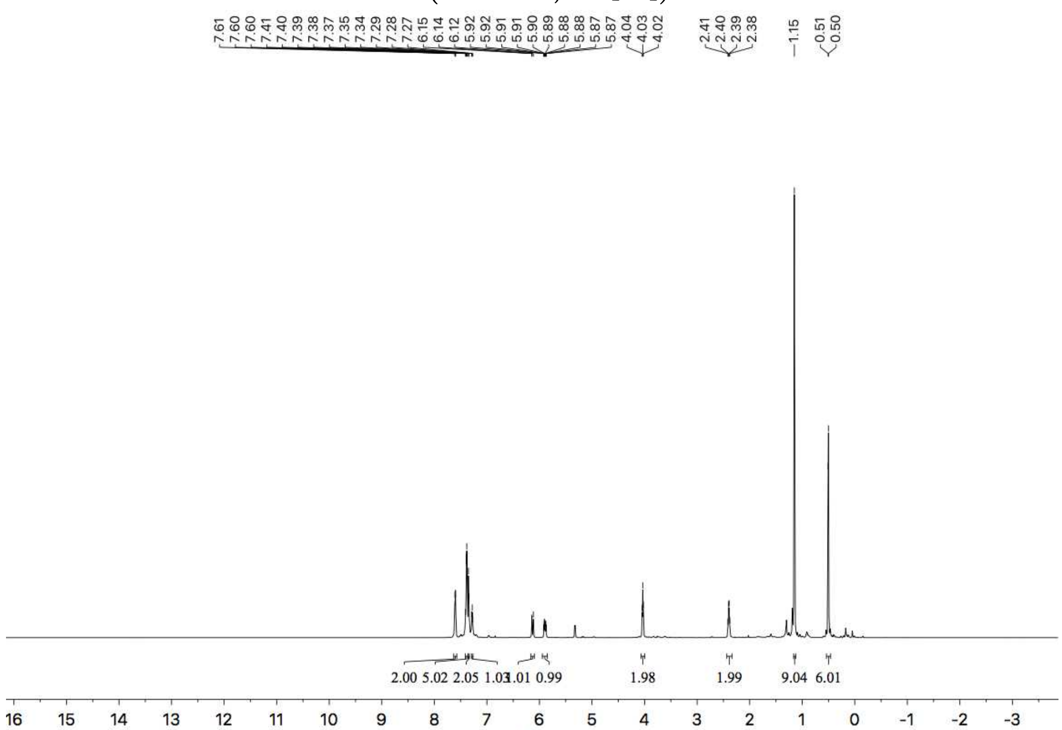
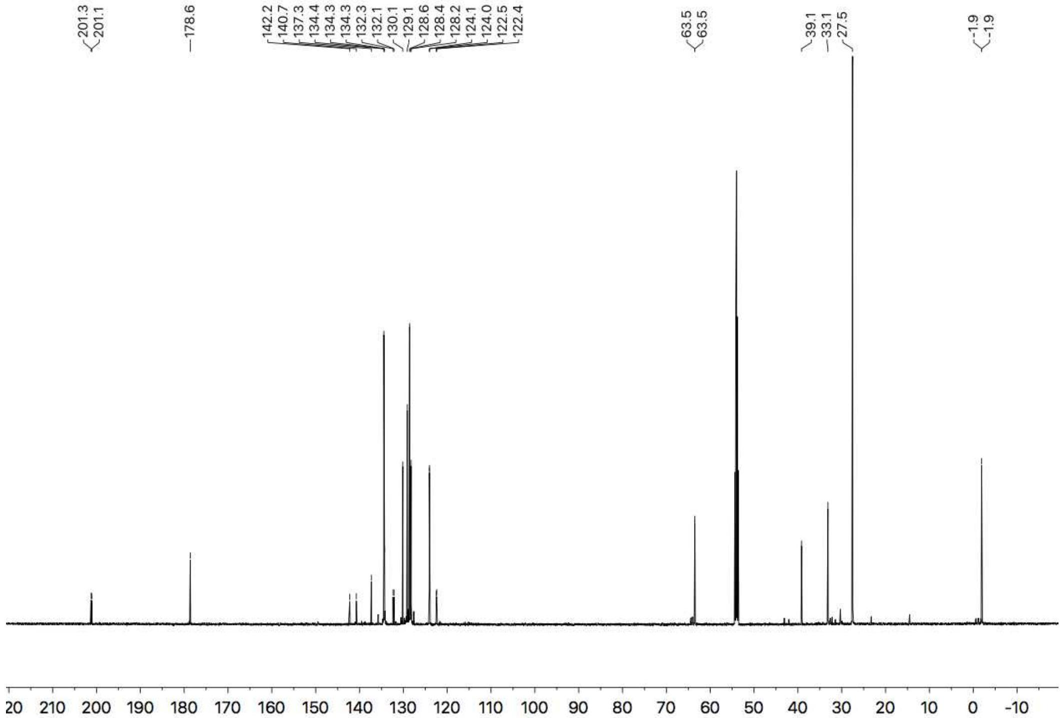
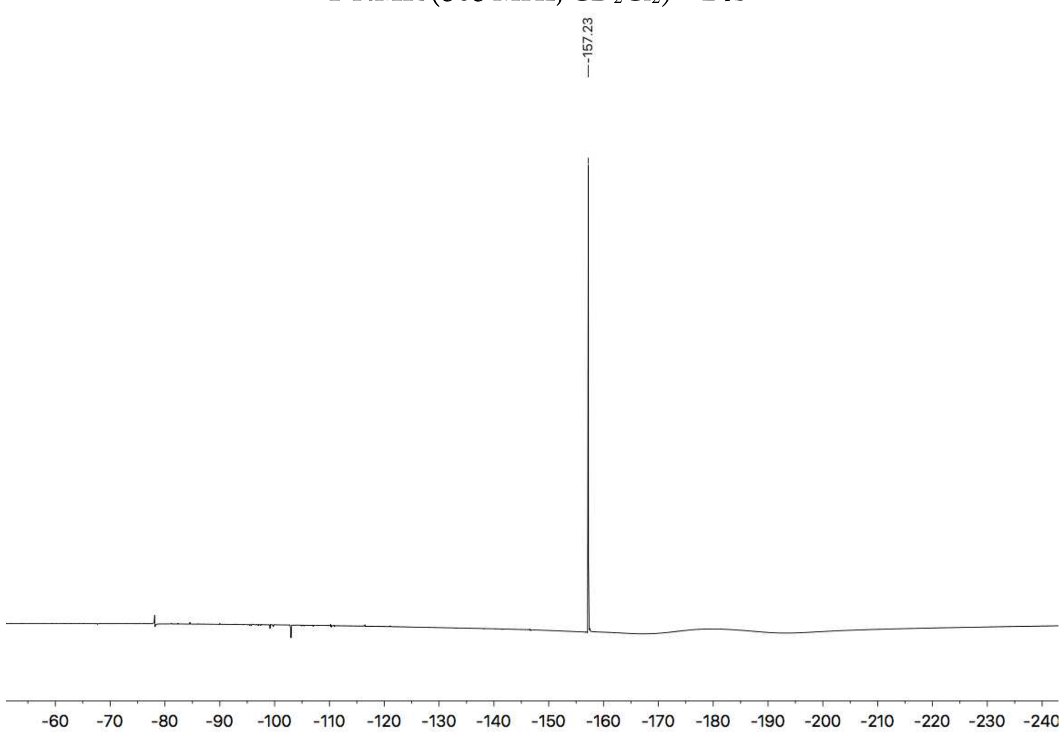
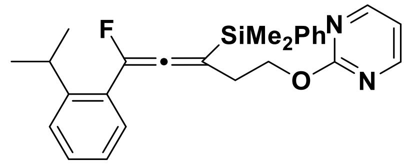


^{13}C NMR (151 MHz, CD_2Cl_2) – **24b**

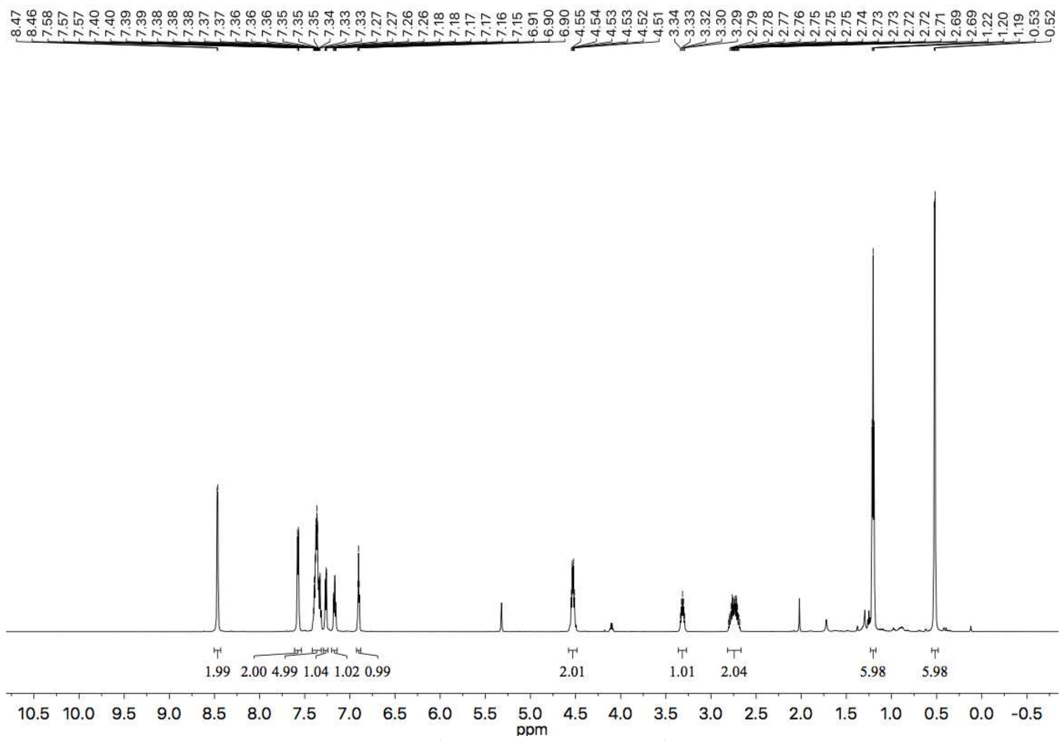


^{19}F NMR (565 MHz, CD_2Cl_2) – **24b**

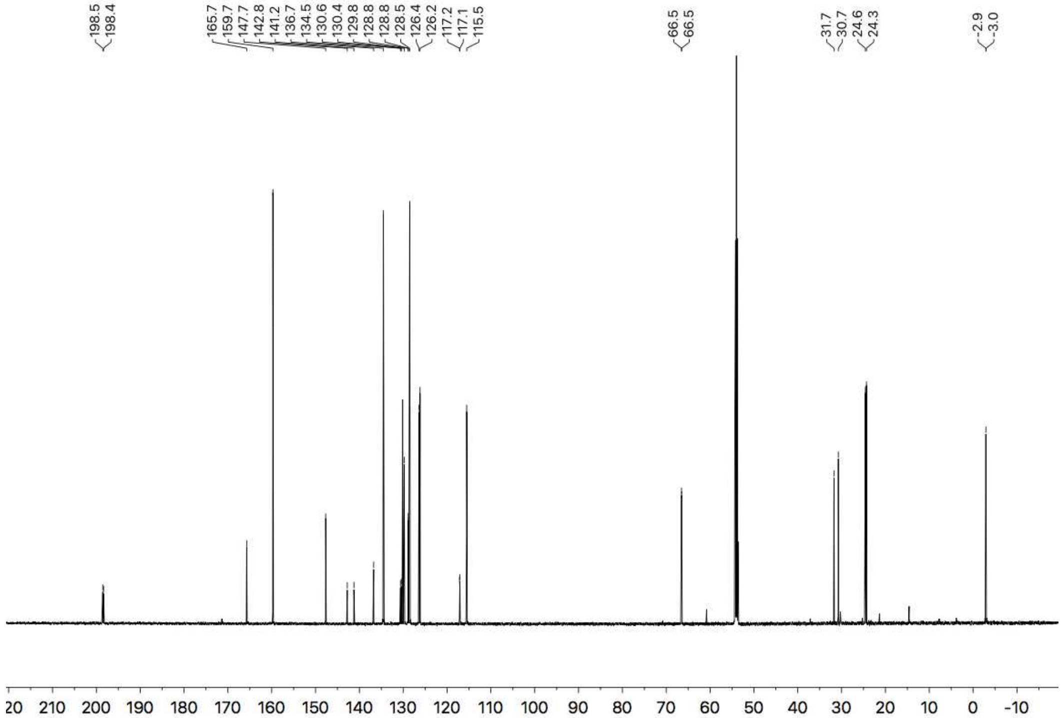




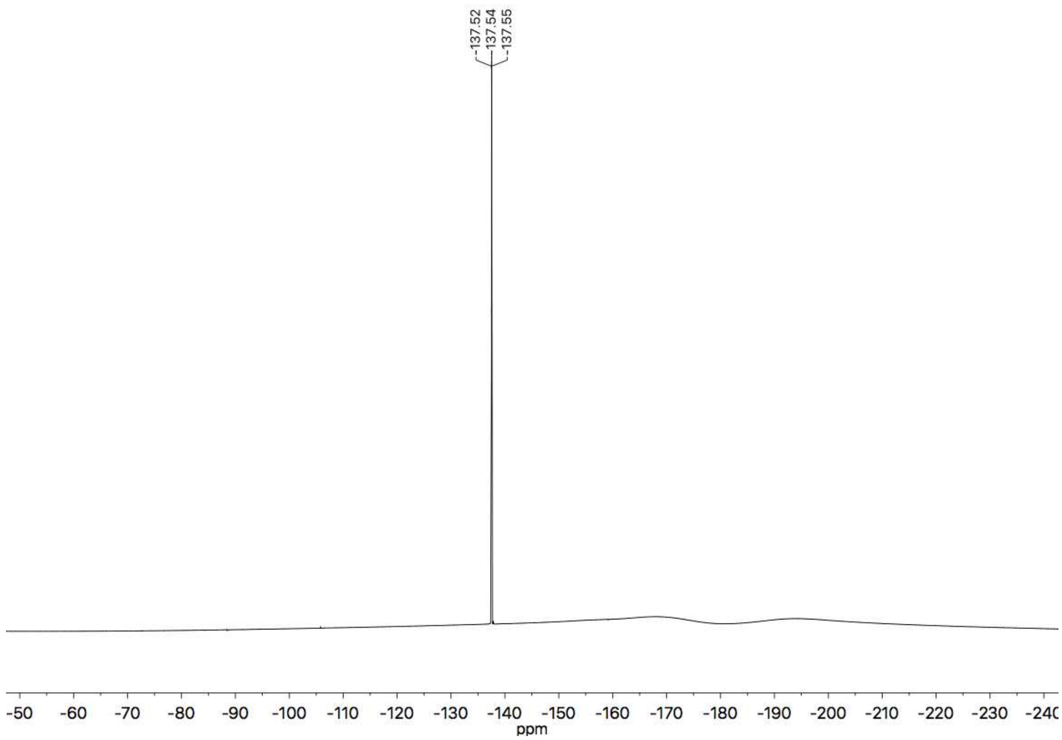
^{1}H NMR (600 MHz, CD_2Cl_2) – **25b**

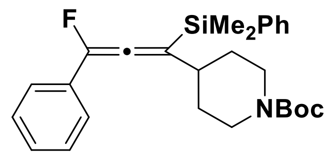


^{13}C NMR (151 MHz, CD_2Cl_2) – **25b**



^{19}F NMR (565 MHz, CD_2Cl_2) – **25b**





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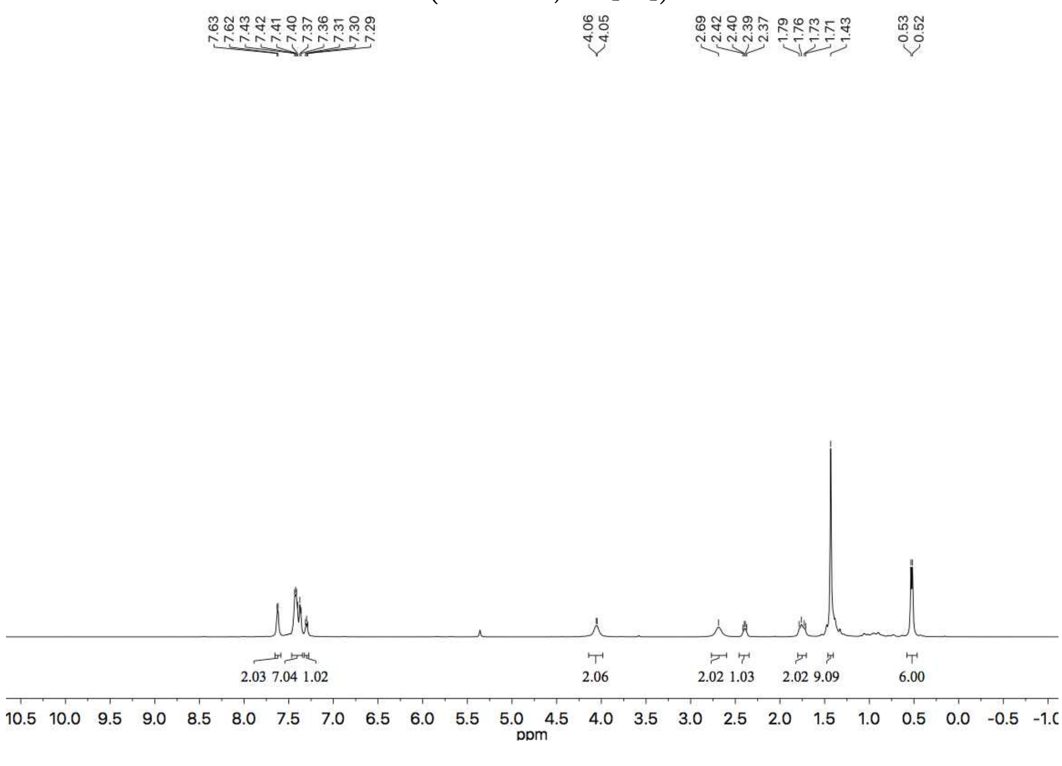
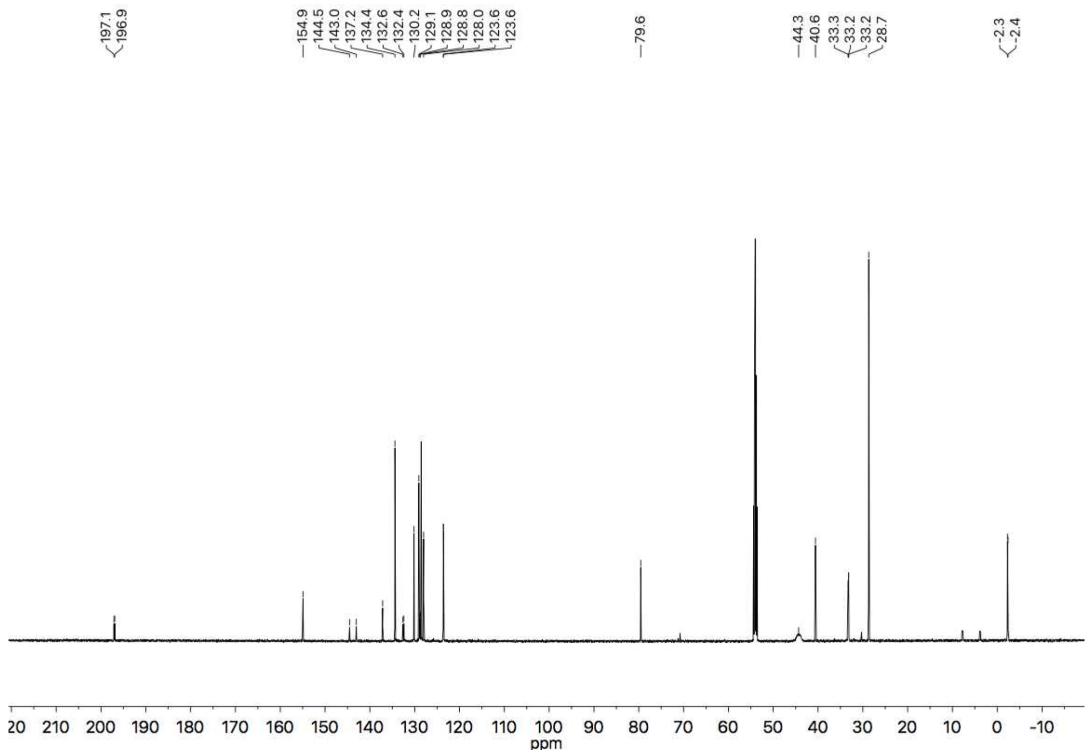
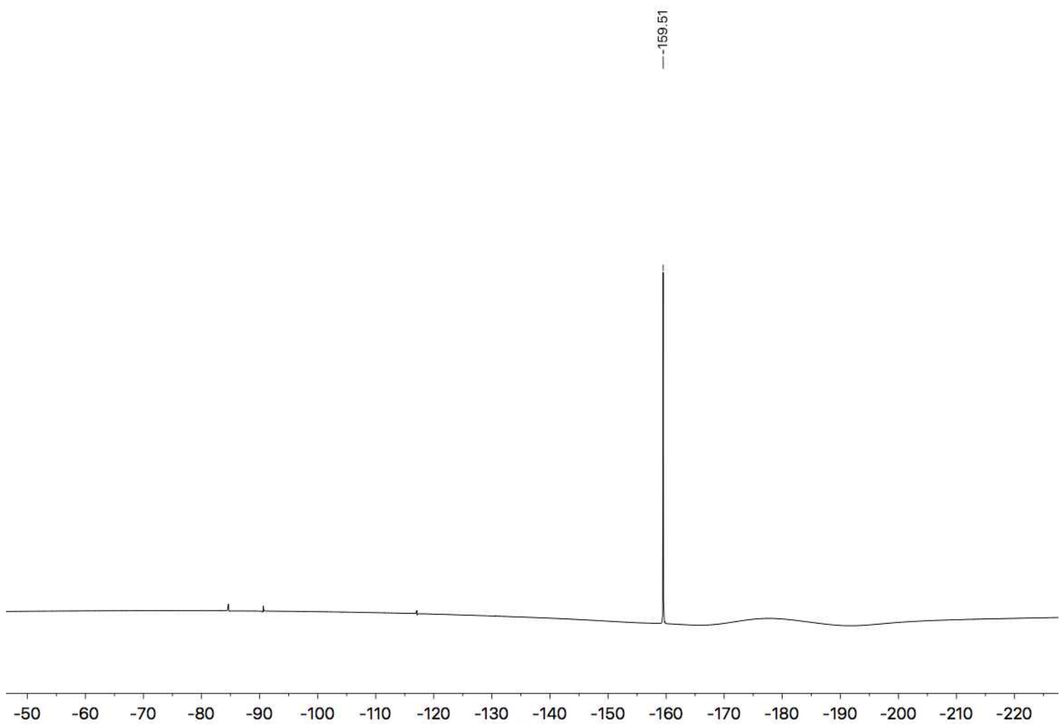
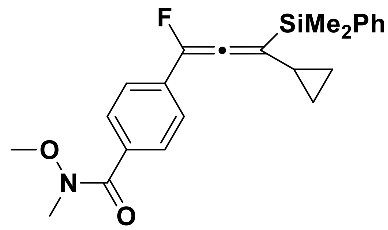


[13]C NMR (151 MHz, CD_2Cl_2) – **26b**



[19]F NMR (565 MHz, CD_2Cl_2) – **26b**





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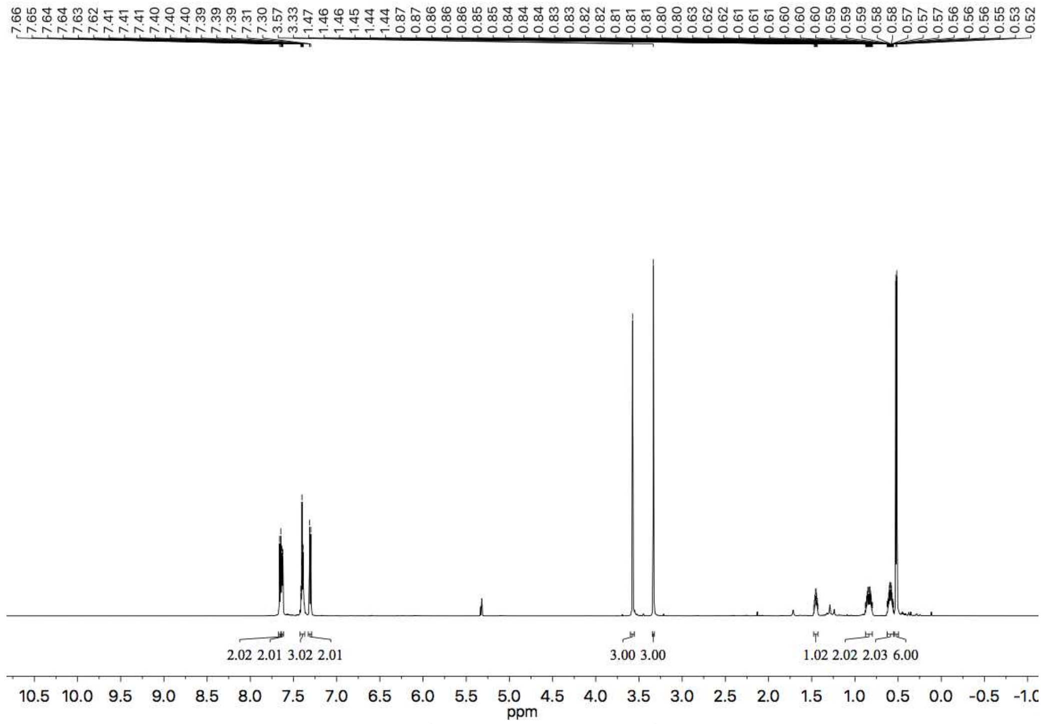
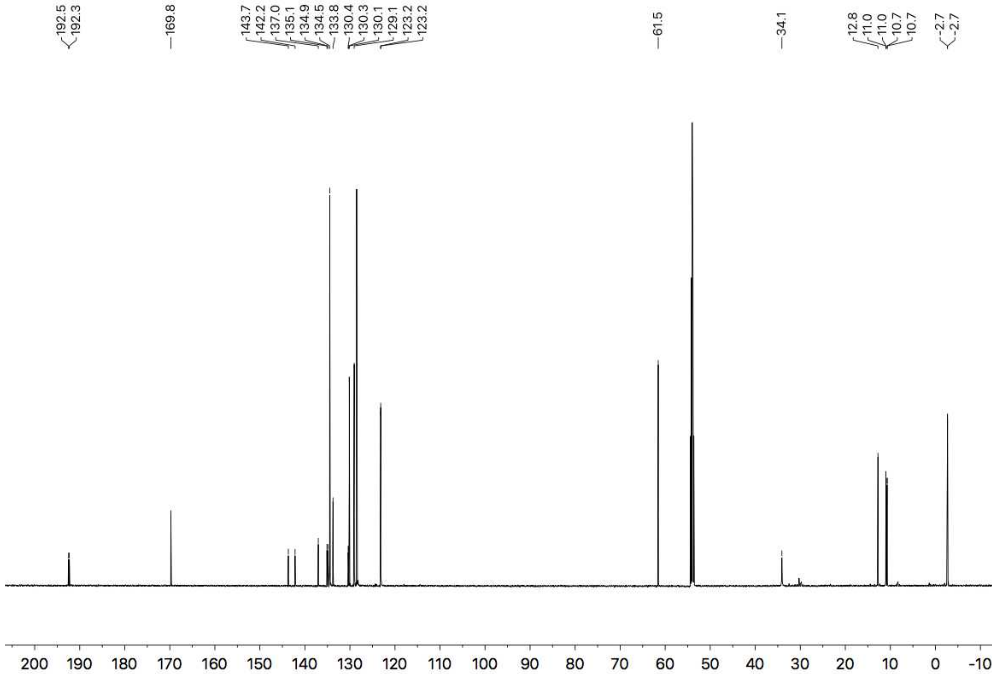
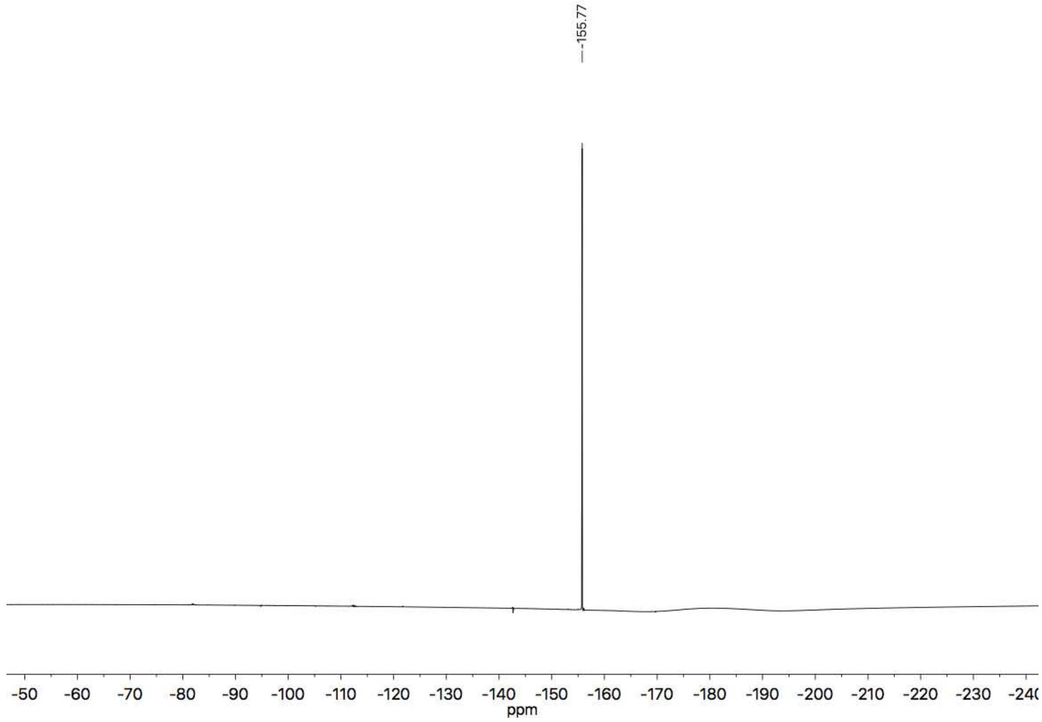
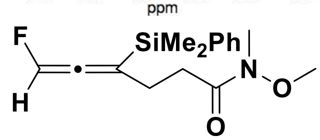


[13]C NMR (151 MHz, CD_2Cl_2) – **27b**

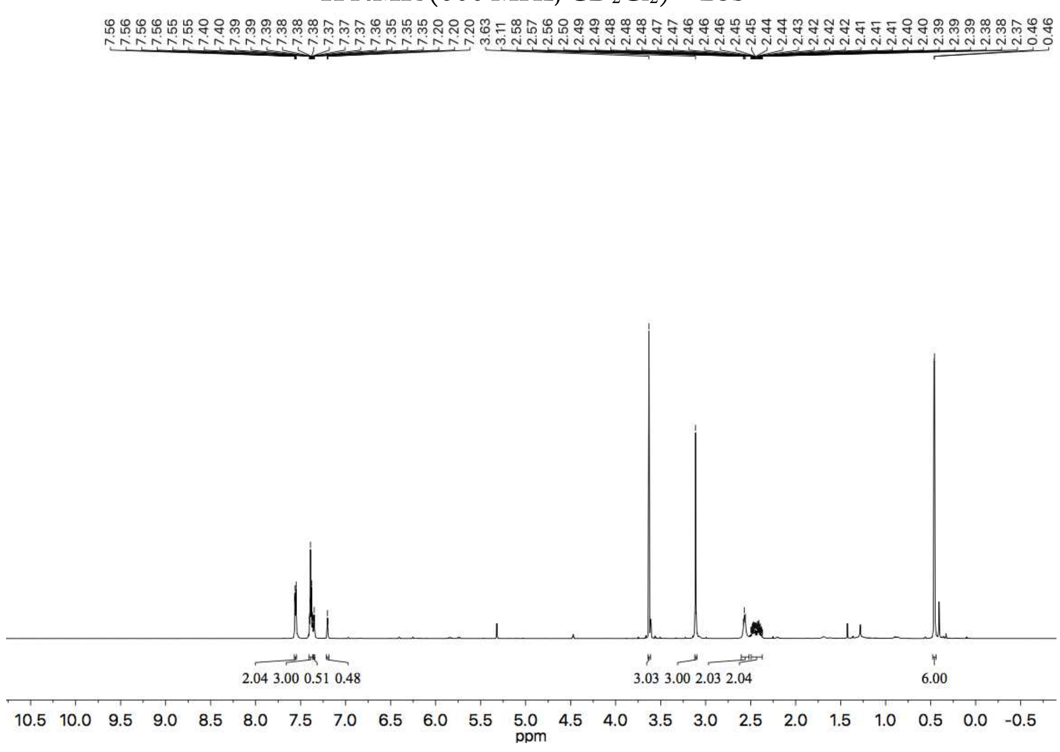


^{19}F NMR (565 MHz, CD_2Cl_2) – **27b**

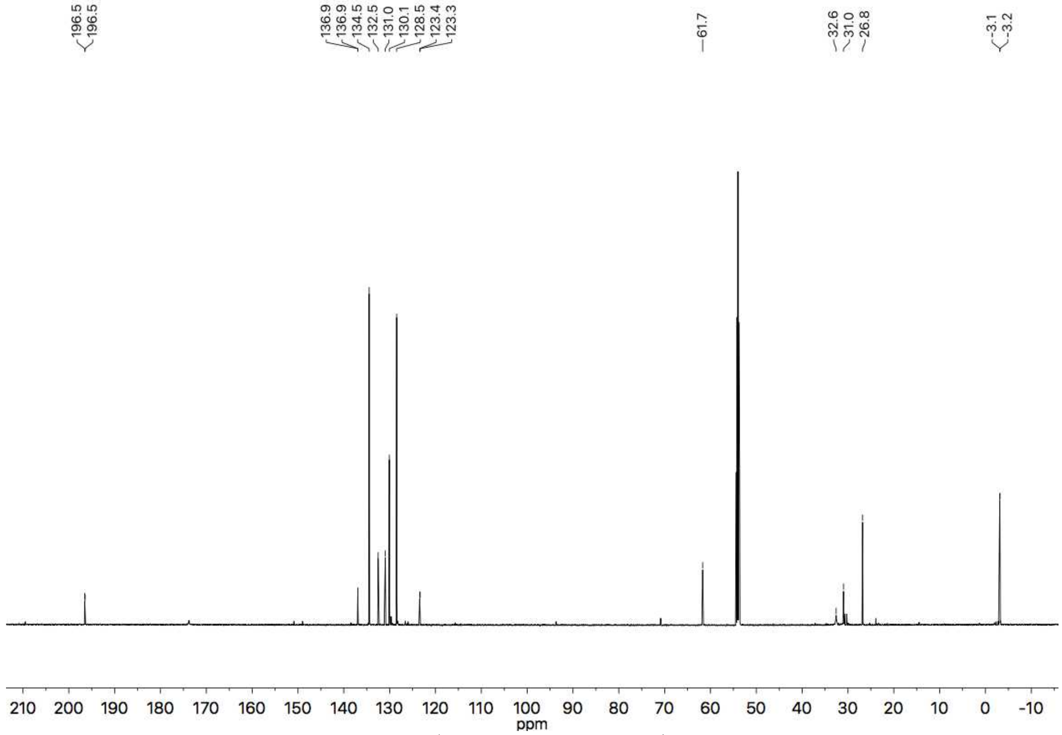




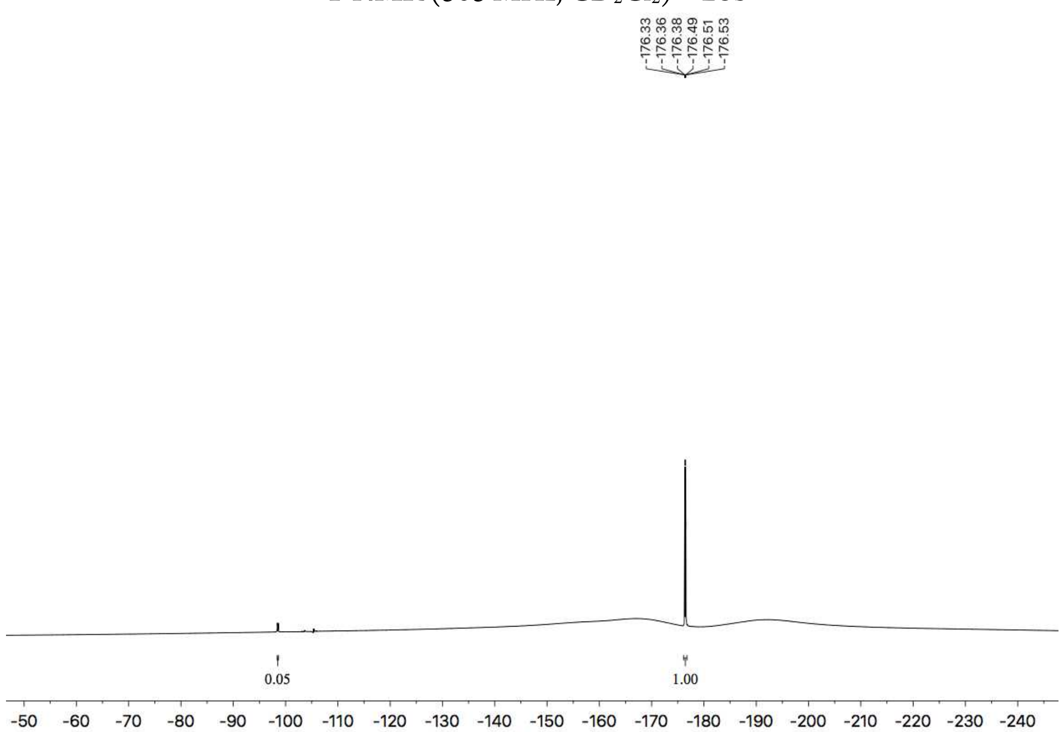
^{1}H NMR (600 MHz, CD_2Cl_2) – **28b**

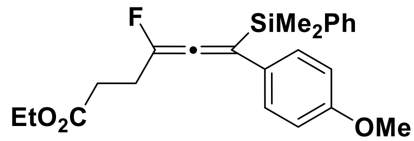


^{13}C NMR (151 MHz, CD_2Cl_2) – **28b**

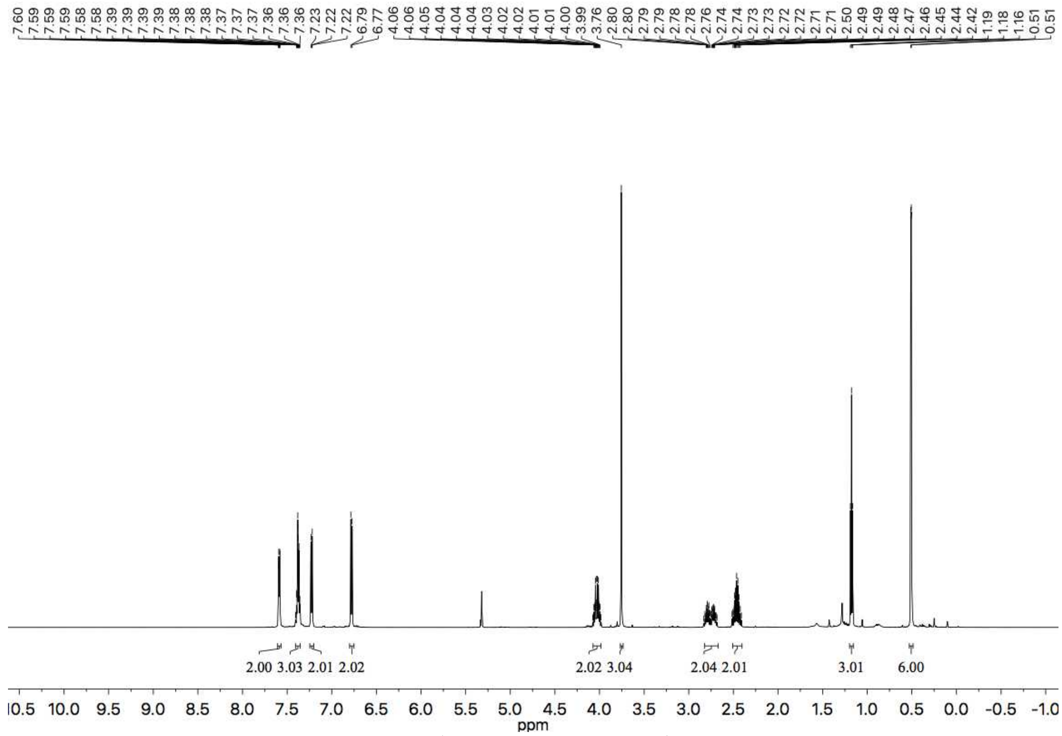


^{19}F NMR (565 MHz, CD_2Cl_2) – **28b**

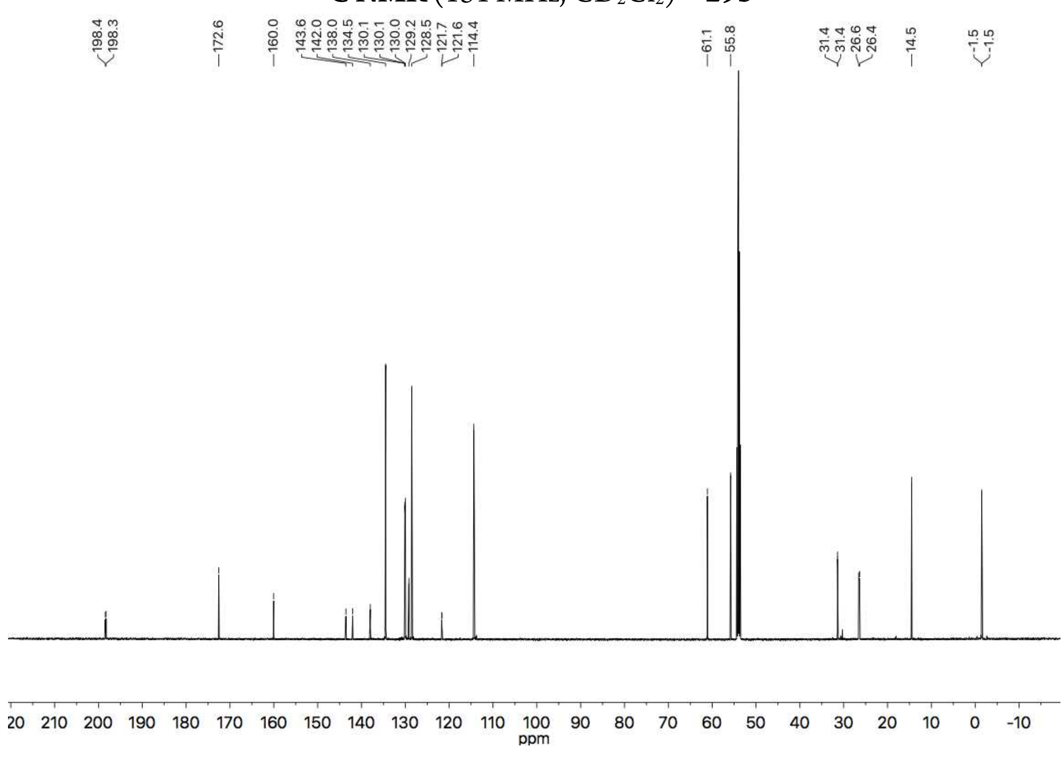




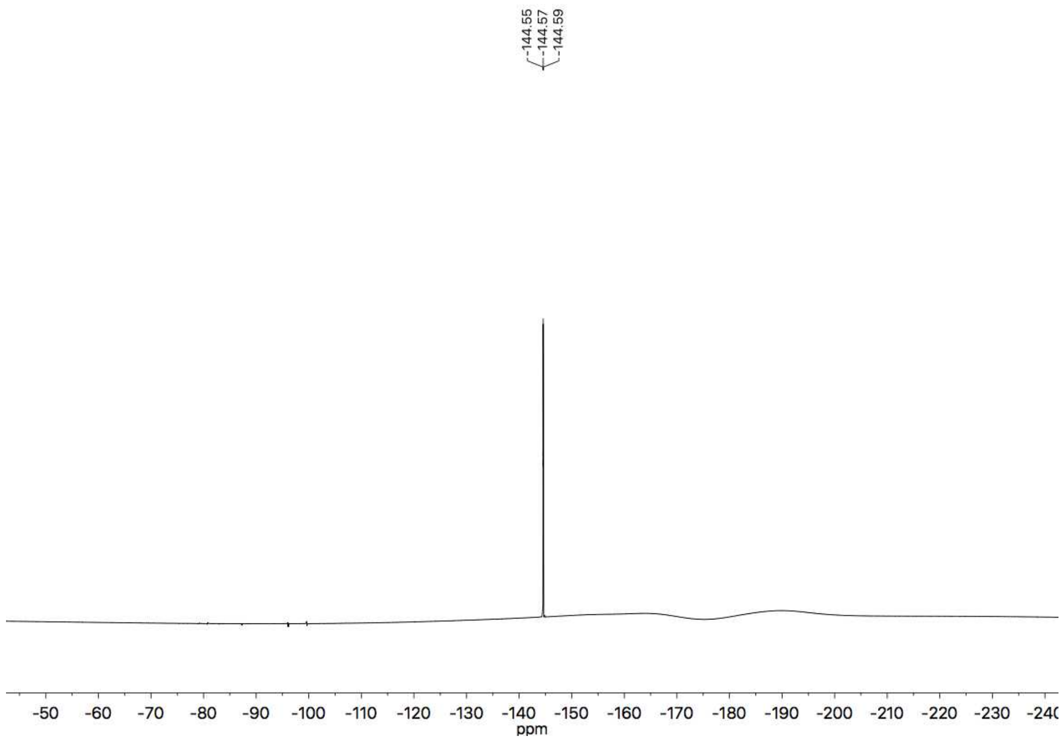
^{1}H NMR (600 MHz, CD_2Cl_2) – **29b**

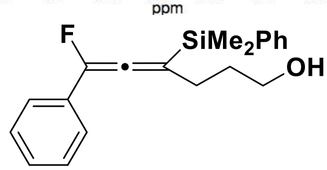


^{13}C NMR (151 MHz, CD_2Cl_2) – **29b**

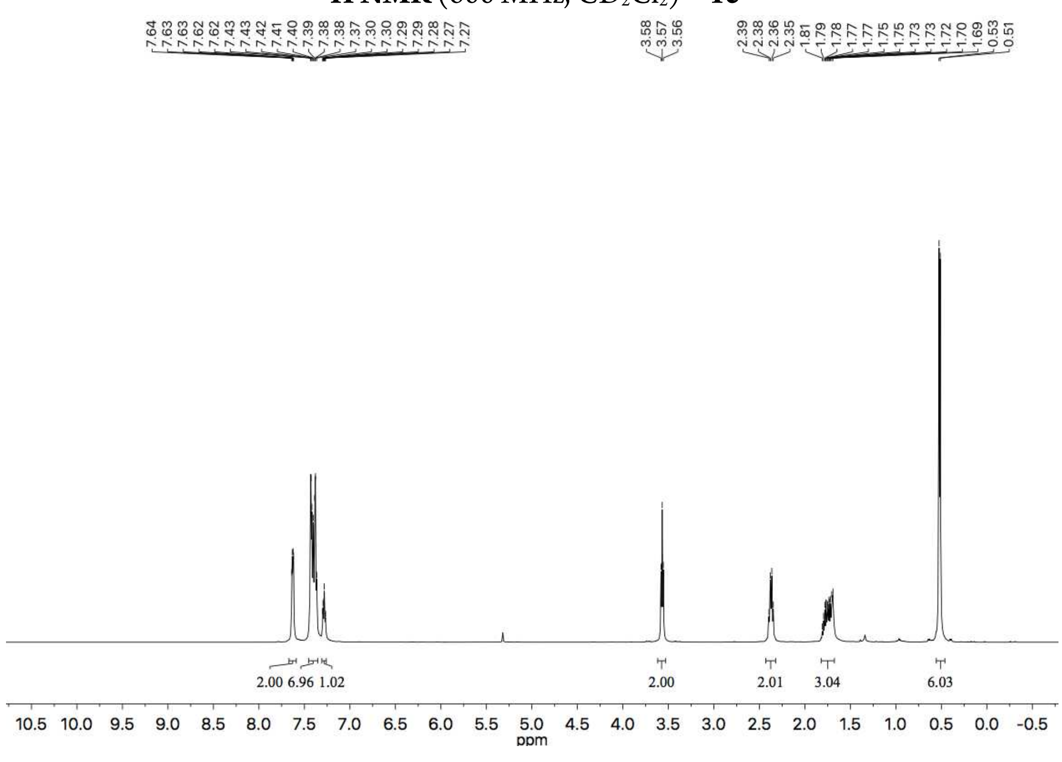


^{19}F NMR (565 MHz, CD_2Cl_2) – **29b**

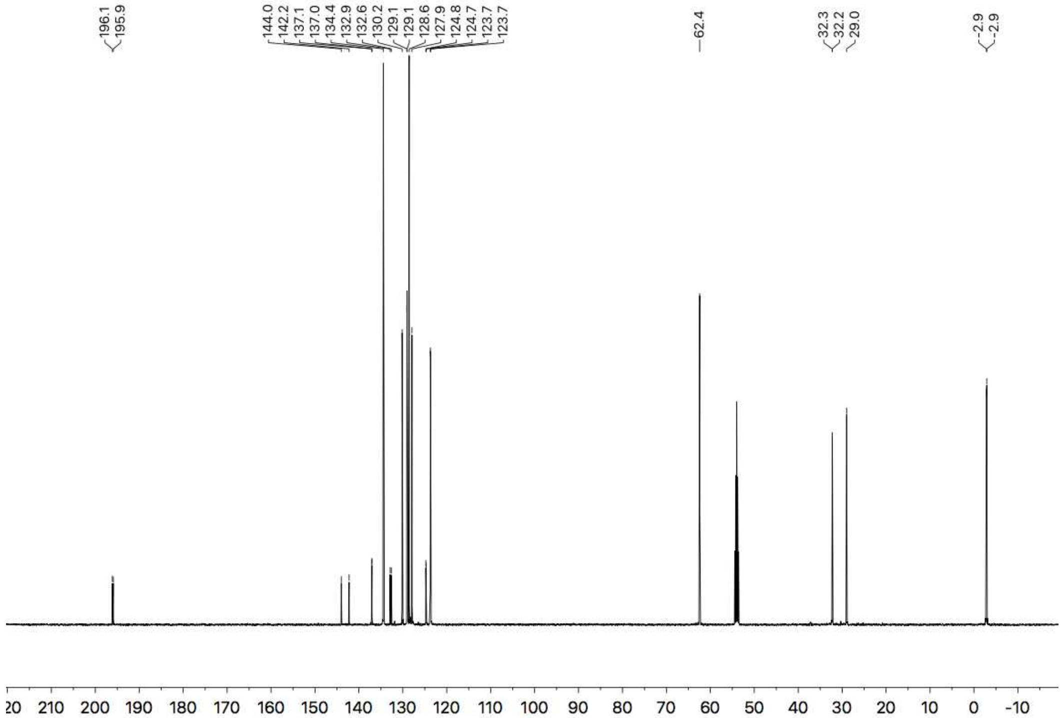




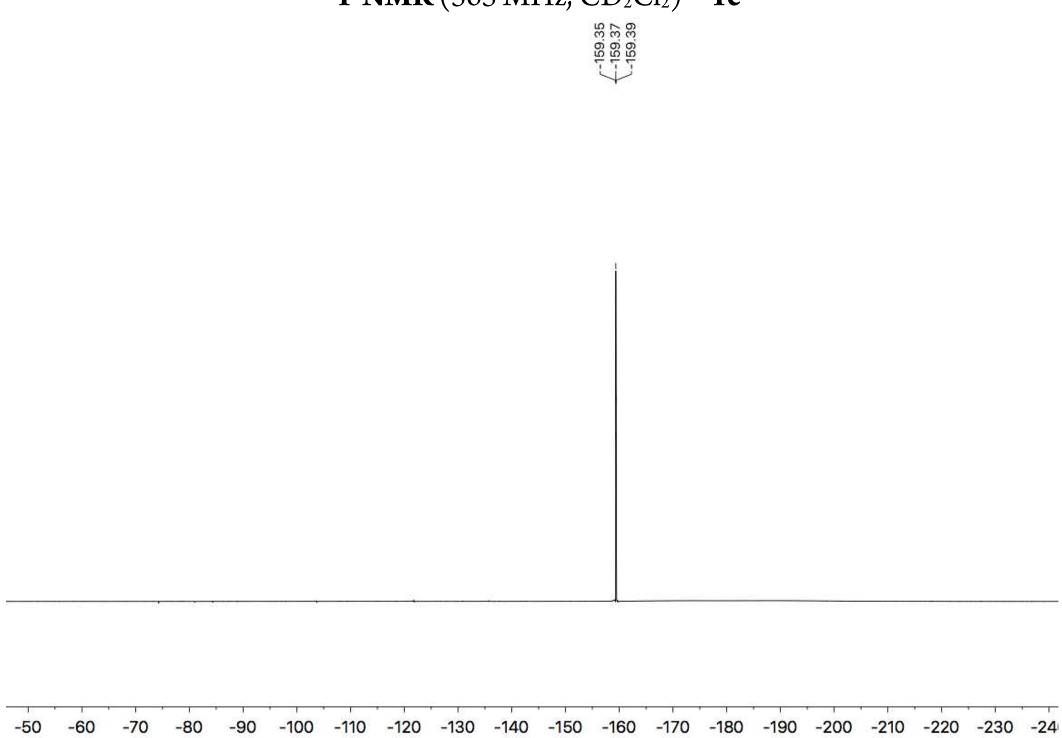
^{1}H NMR (600 MHz, CD_2Cl_2) – **1c**

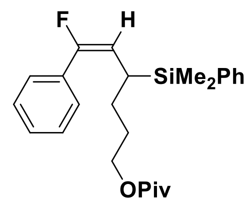


^{13}C NMR (151 MHz, CD_2Cl_2) – **1c**

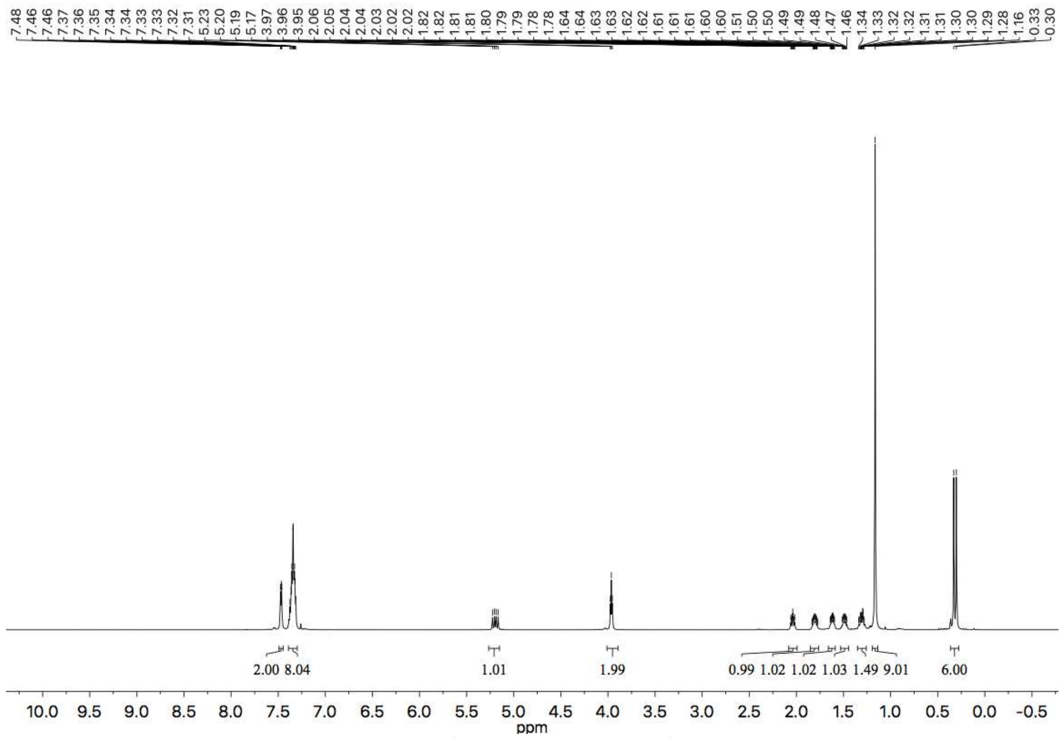


^{19}F NMR (565 MHz, CD_2Cl_2) – **1c**

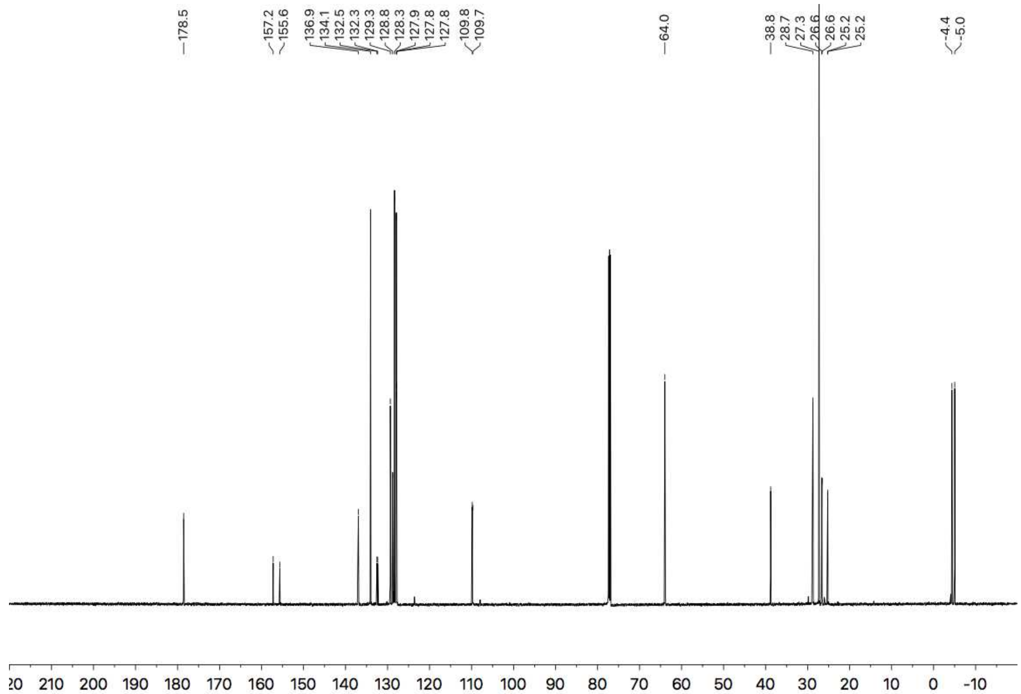




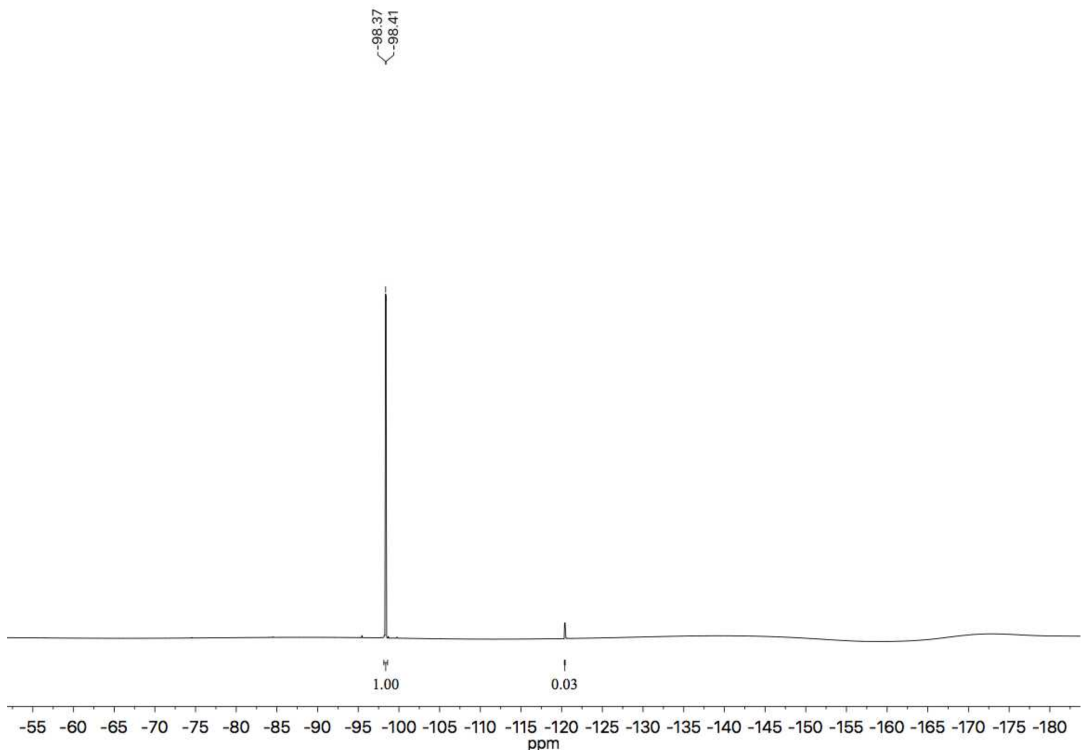
^{1}H NMR (600 MHz, $CDCl_3$) – **2c**



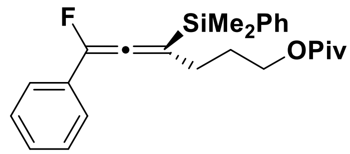
^{13}C NMR (151 MHz, $CDCl_3$) – **2c**



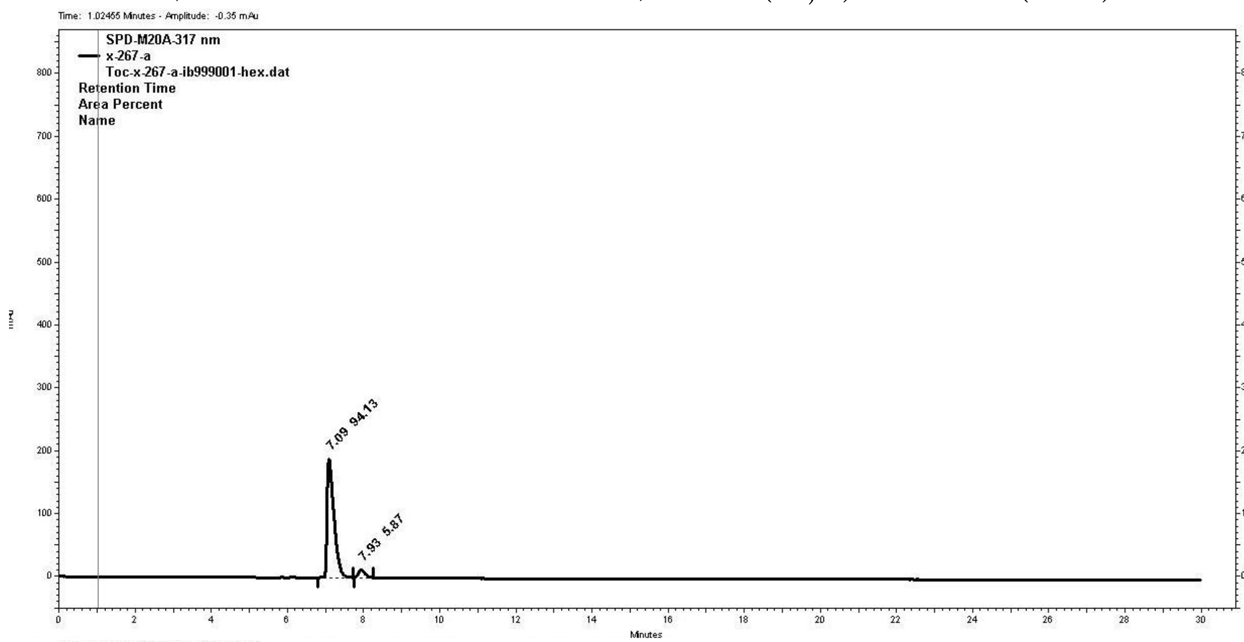
^{19}F NMR (565 MHz, $CDCl_3$) – **2c**

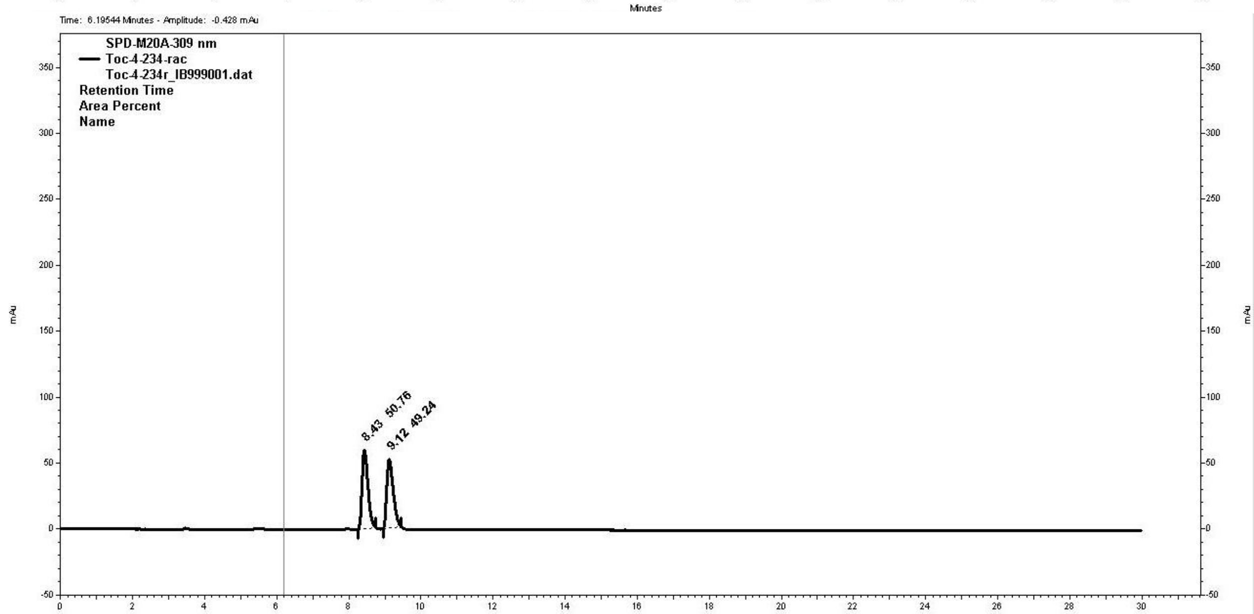


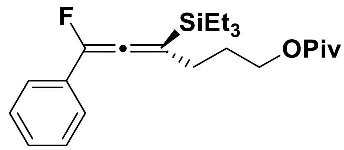
Supporting Information – HPLC Data



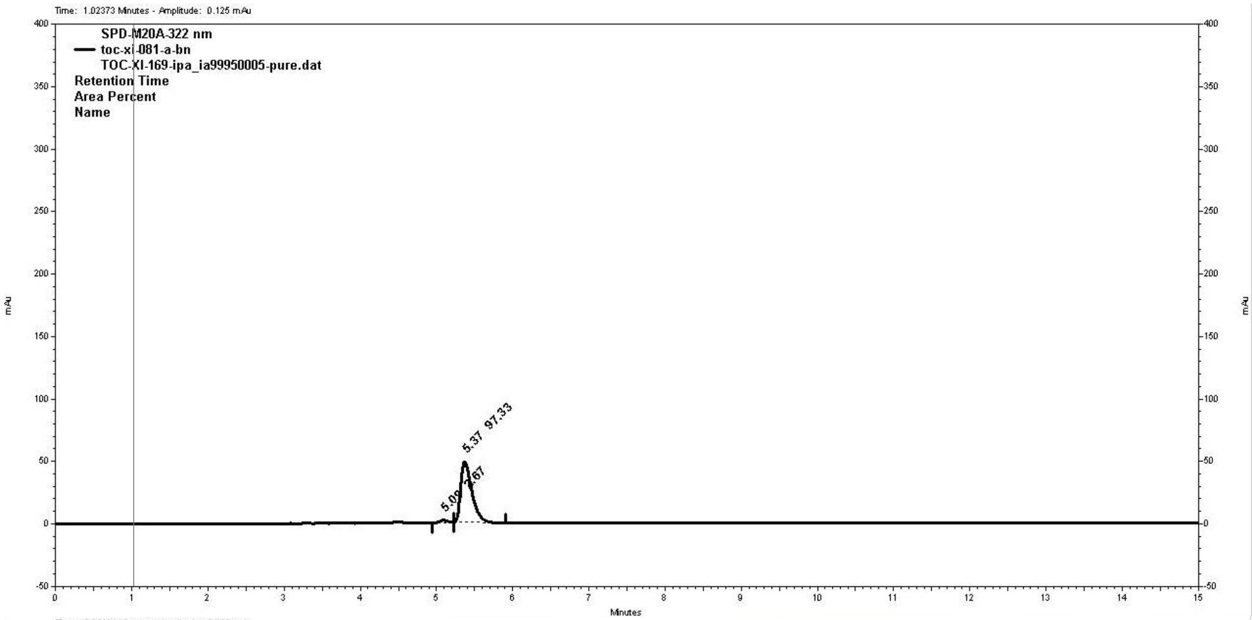
1b: IB column, 1.0 mL/min: 99.9:00.1 hexanes:iPrOH; 7.09 min (major) and 7.93 min (minor)

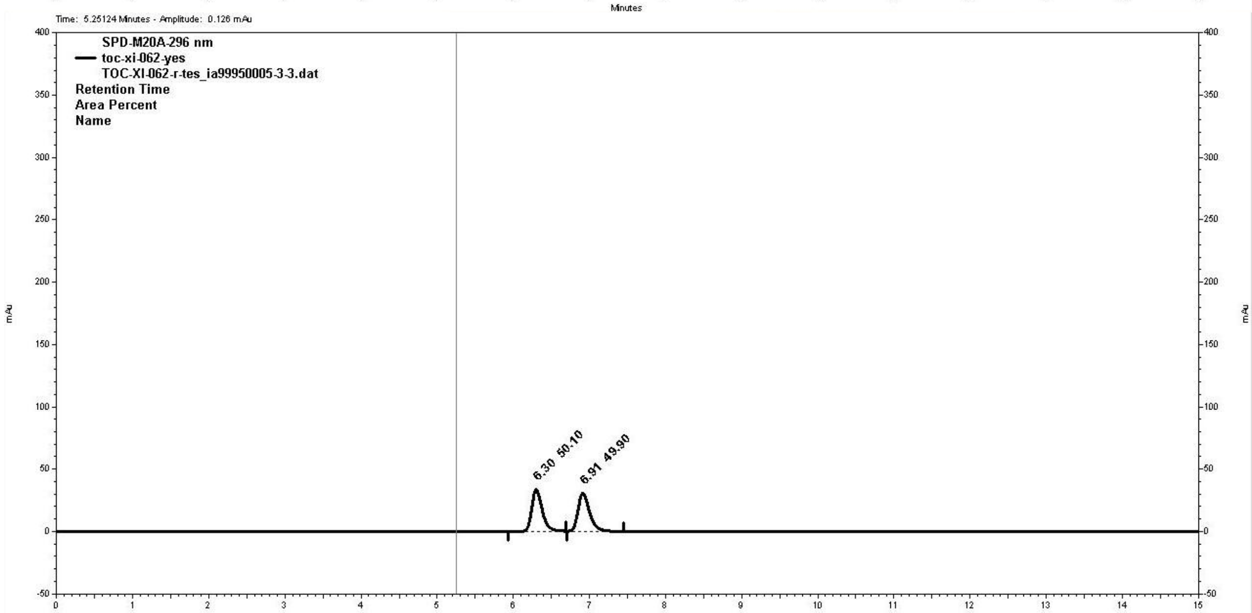


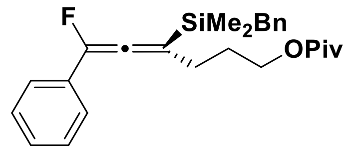




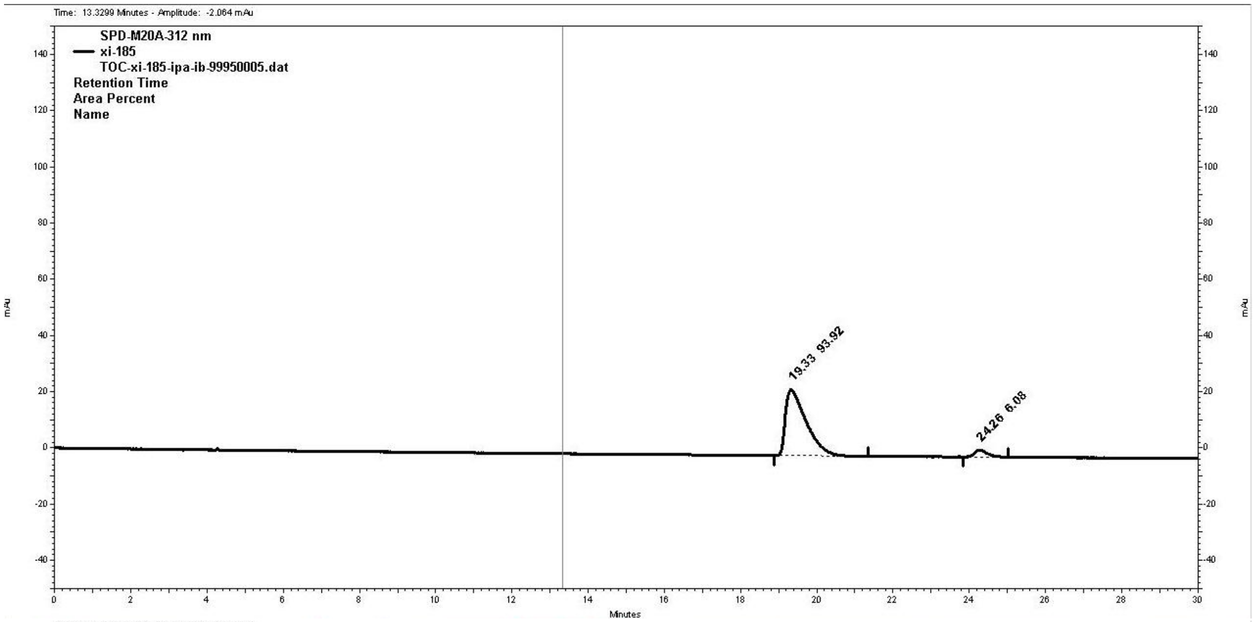
1b-SiEt$_3$: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 6.91 min (major) and 6.30 min (minor)

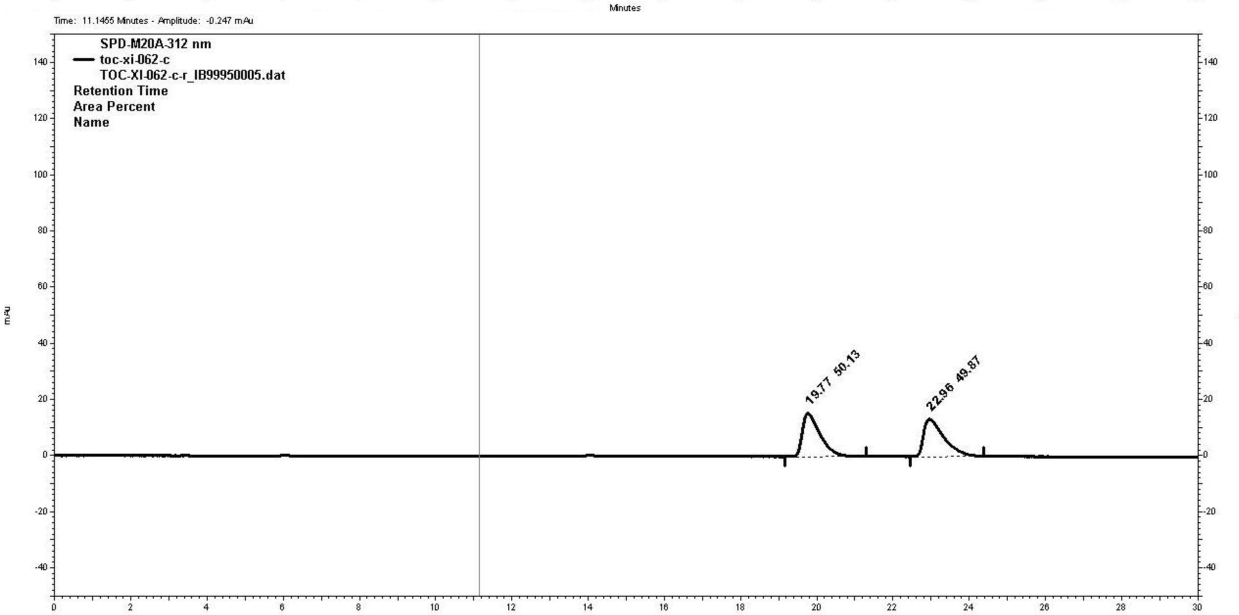


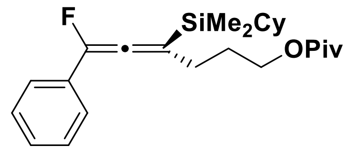




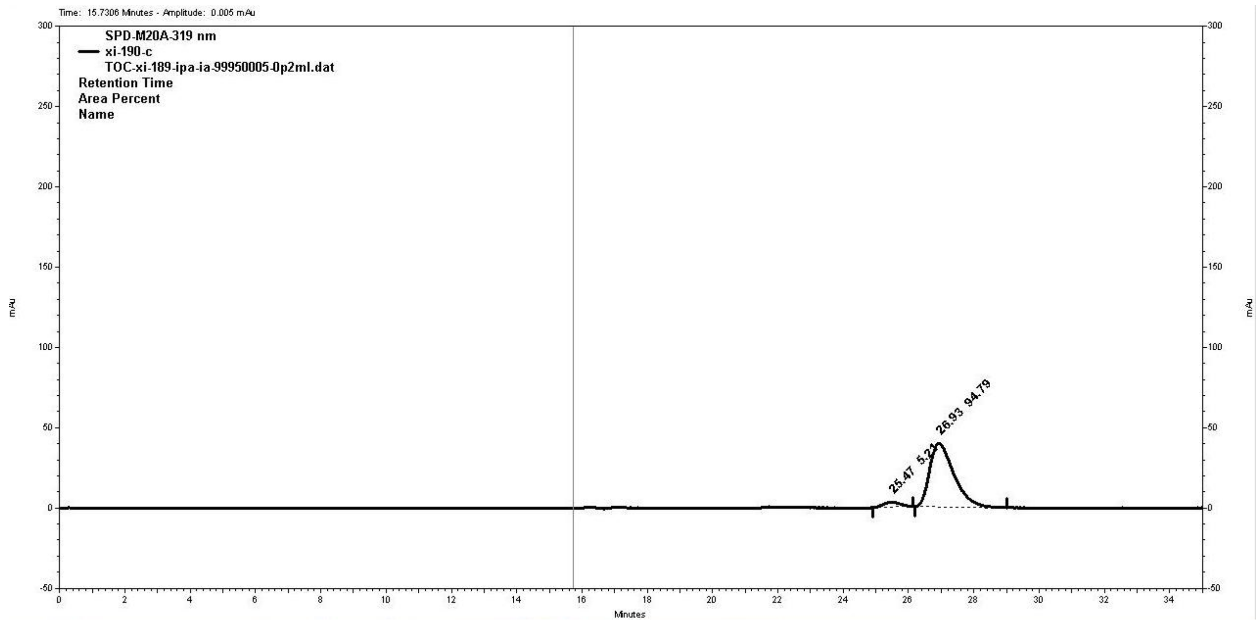
1b-SiMe$_2$Bn: IB column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 19.77 min (major) and 22.96 min (minor)

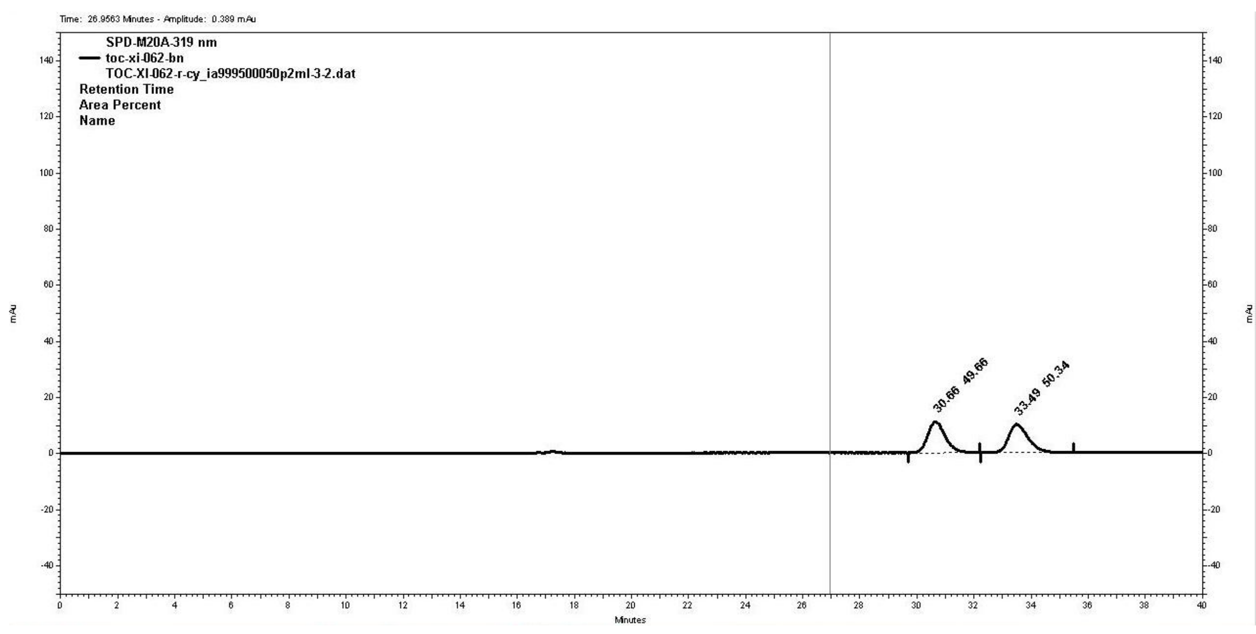


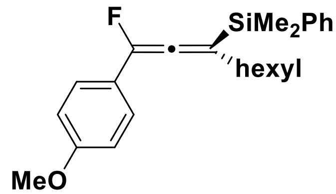




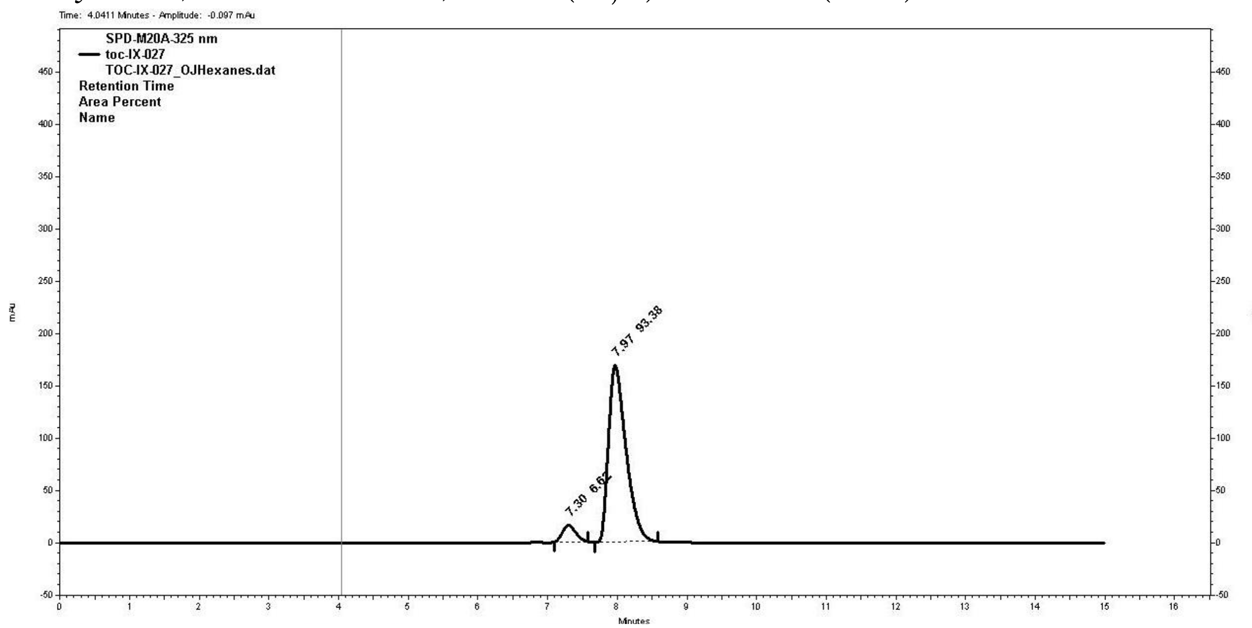
1b-SiMe₂Bn: IA column, 1.0 mL/min: 99.95:00.05 hexanes:iPrOH; 33.49 min (major) and 30.66 min (minor)

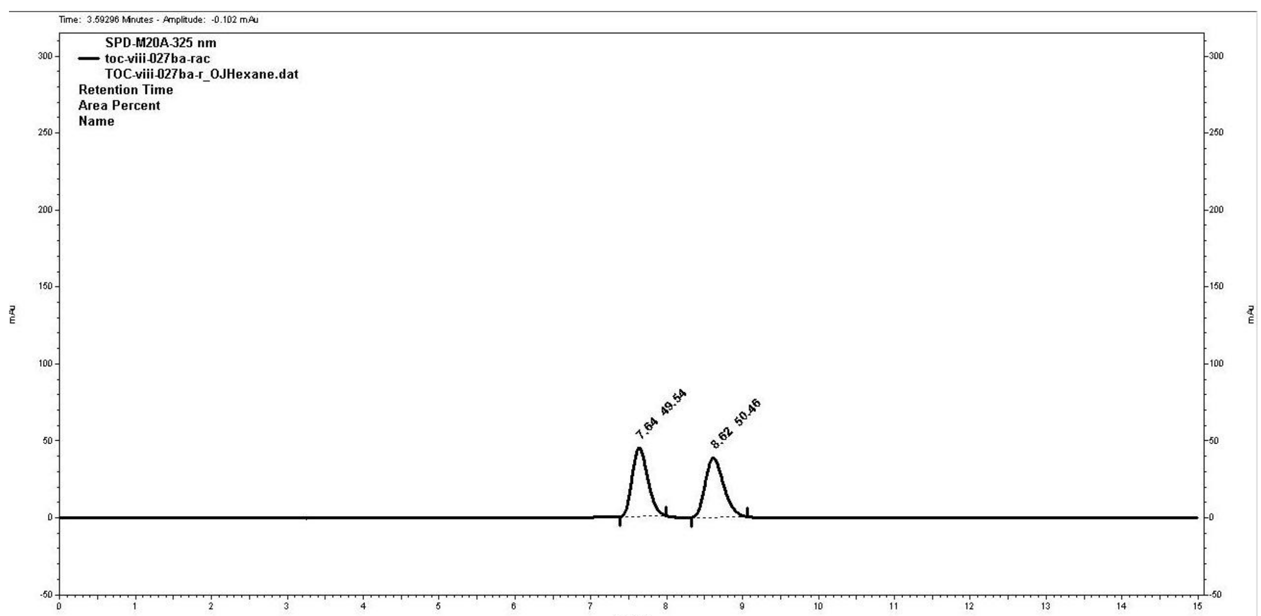


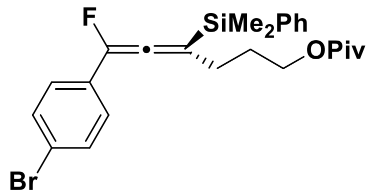




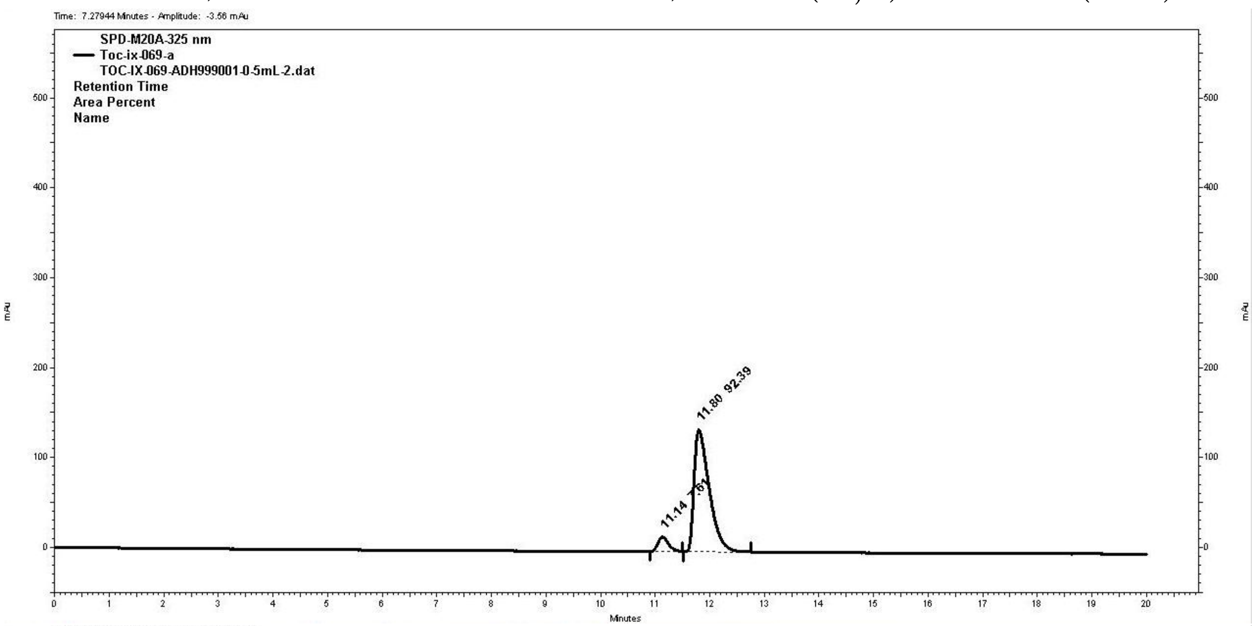
2b: OJ column, 1.0 mL/min: hexanes; 7.97 min (major) and 7.30 min (minor)

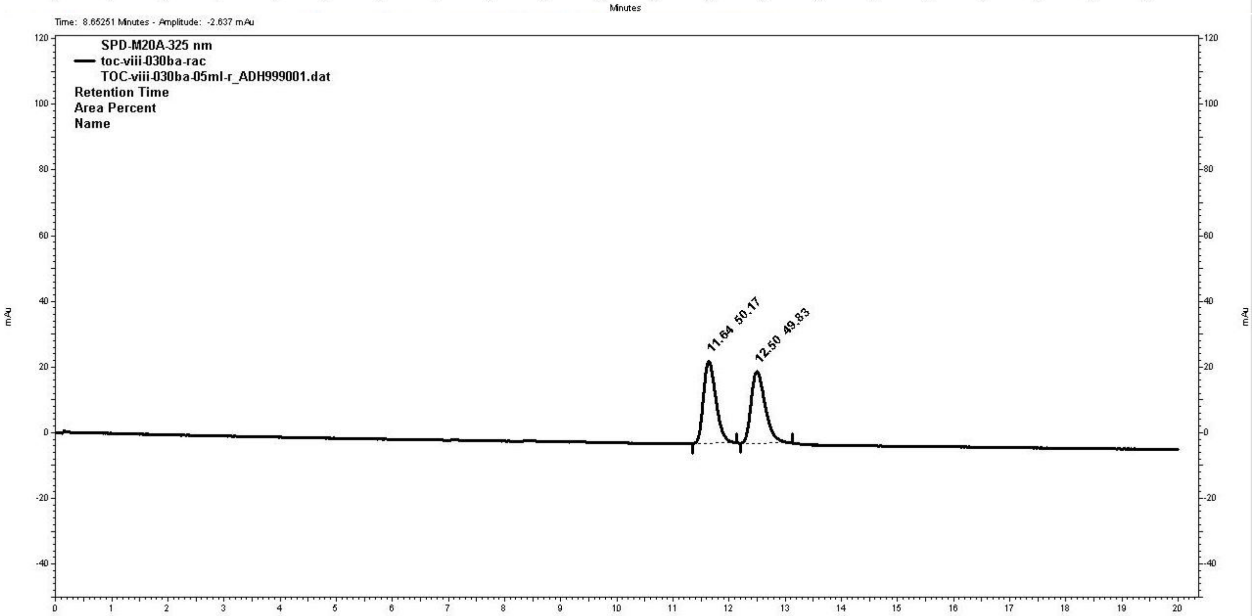


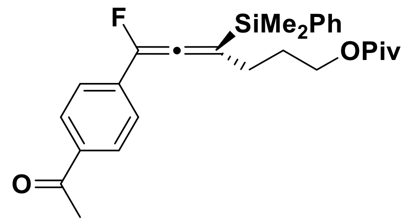




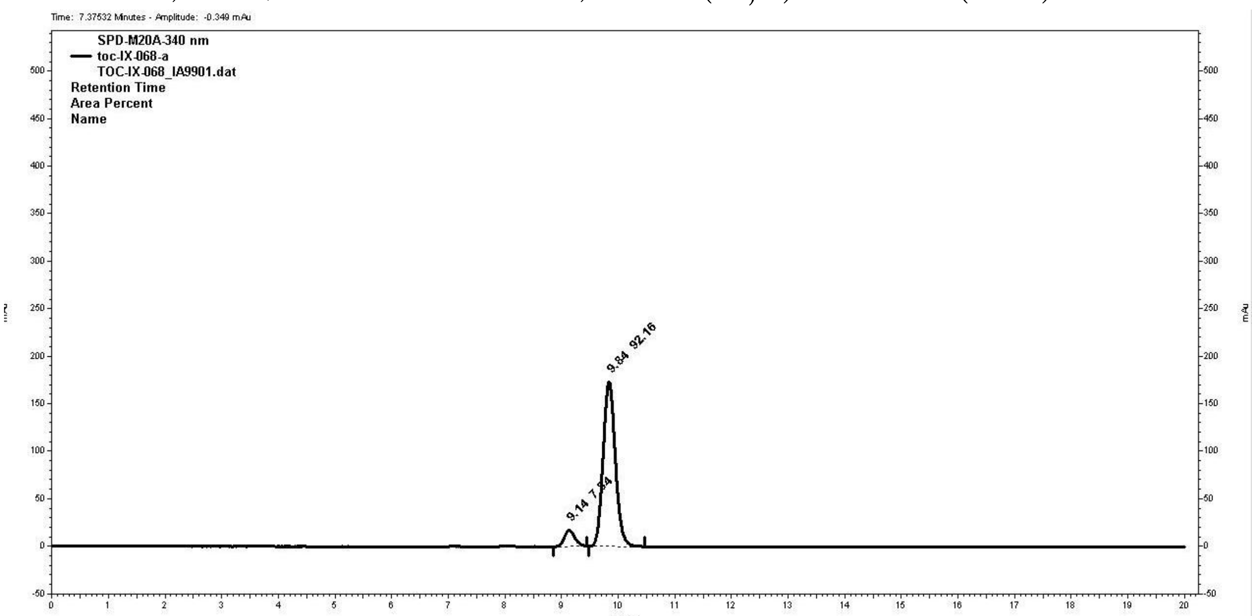
3b: ADH column, 0.5 mL/min: hexanes:iPrOH 99.9:00.1; 11.80 min (major) and 11.14 min (minor)

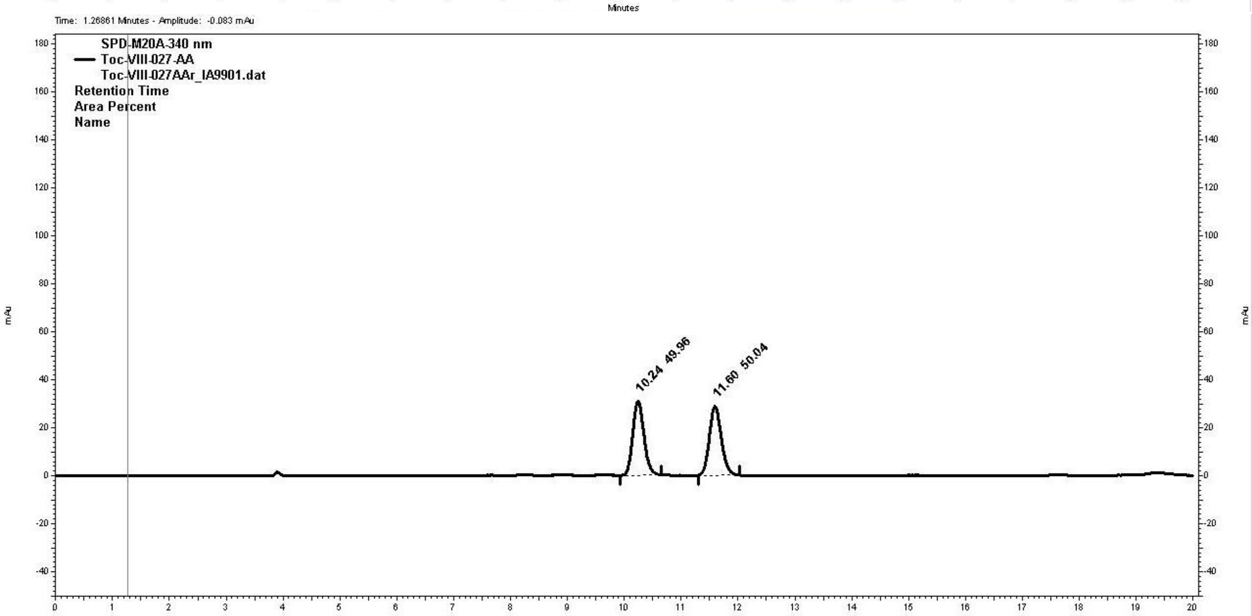


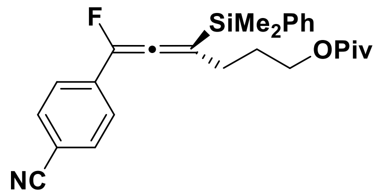




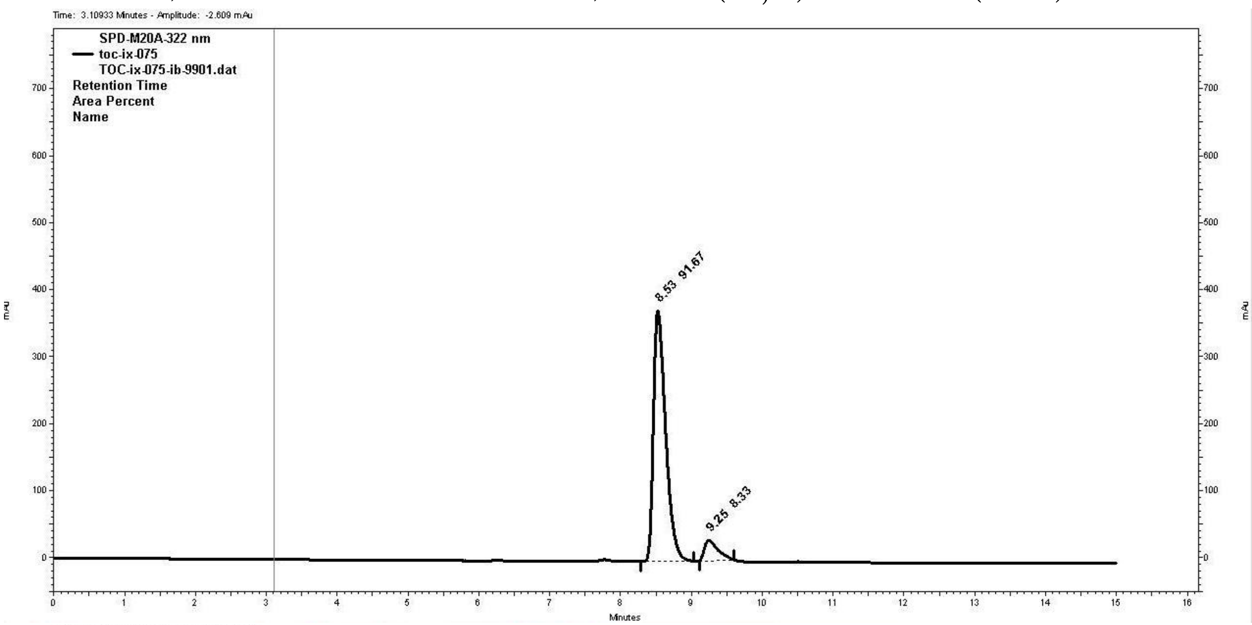
4b: IA column, 1.0 mL/min: hexanes:iPrOH 99:1; 9.84 min (major) and 9.14 min (minor)

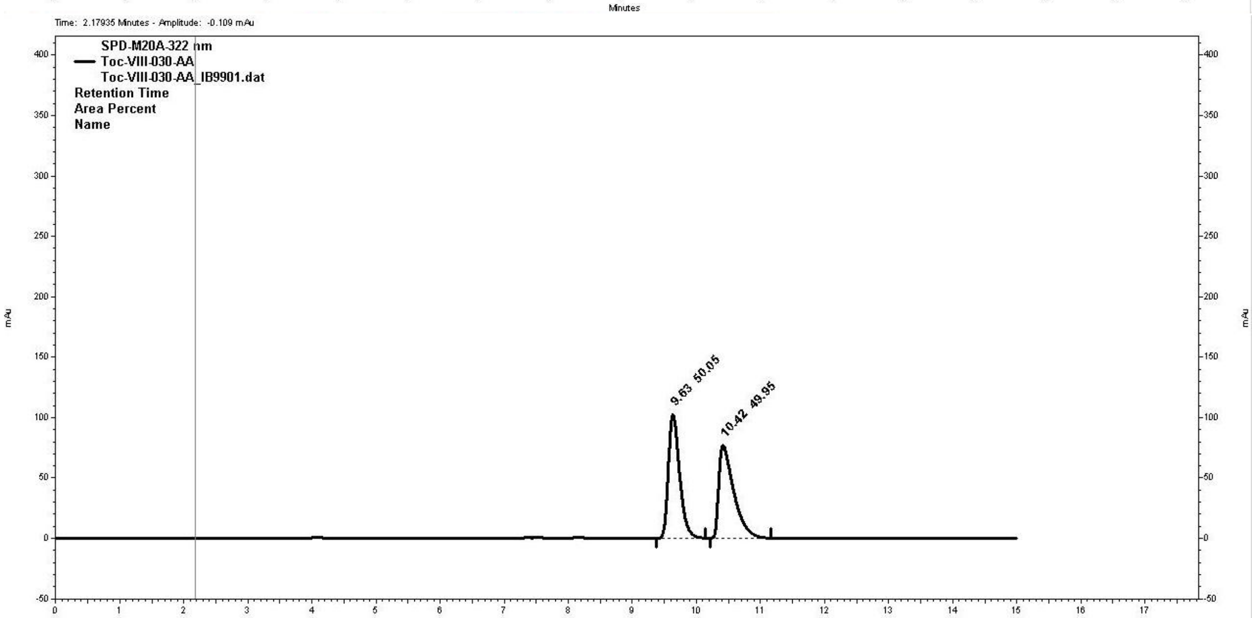


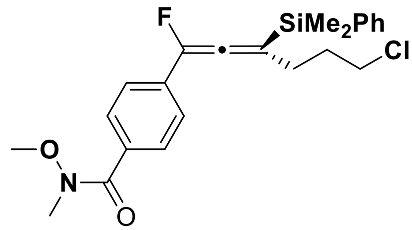




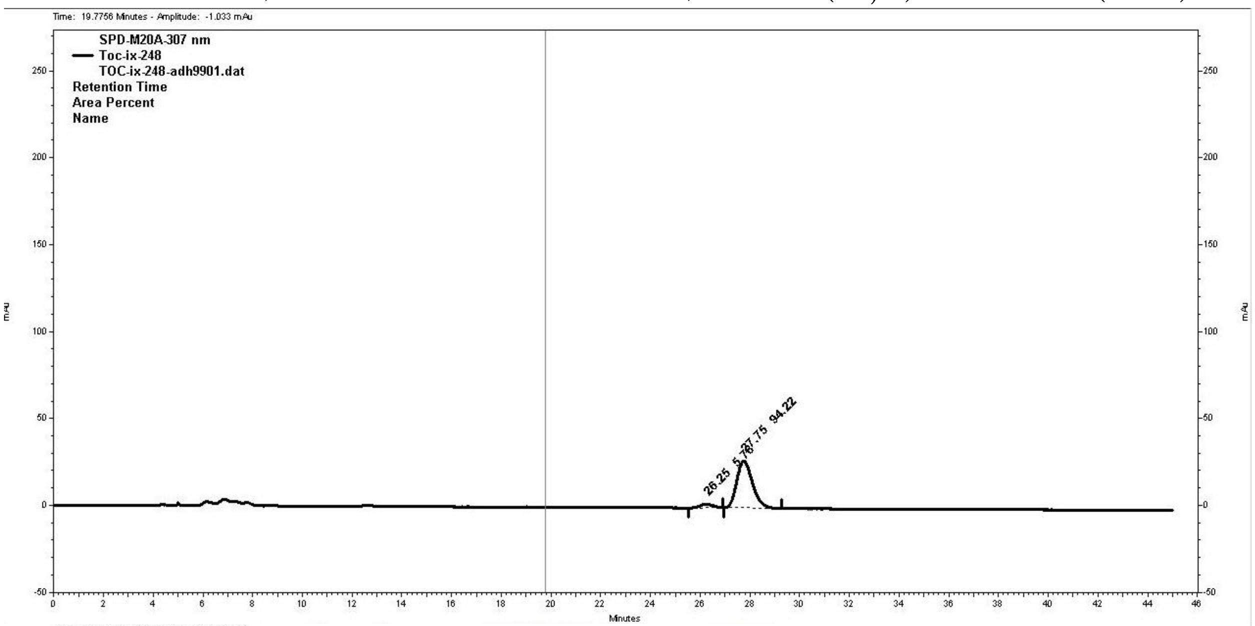
5b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 8.53 min (major) and 9.25 min (minor)

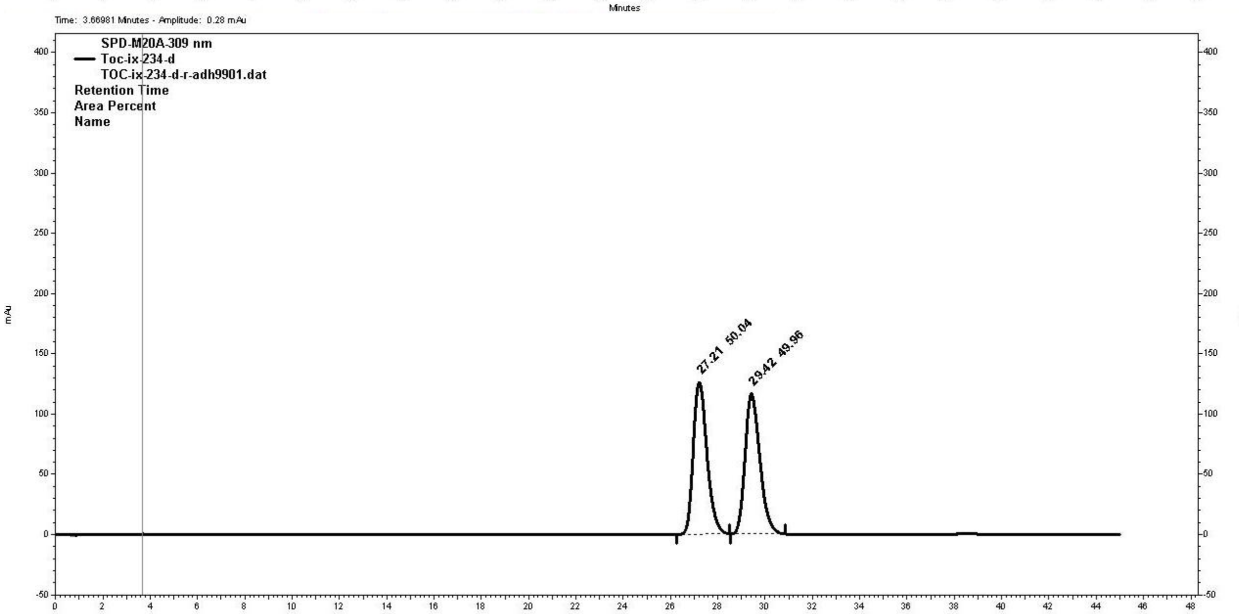


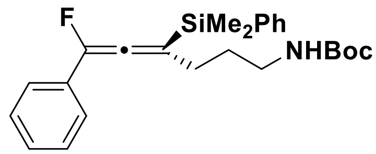




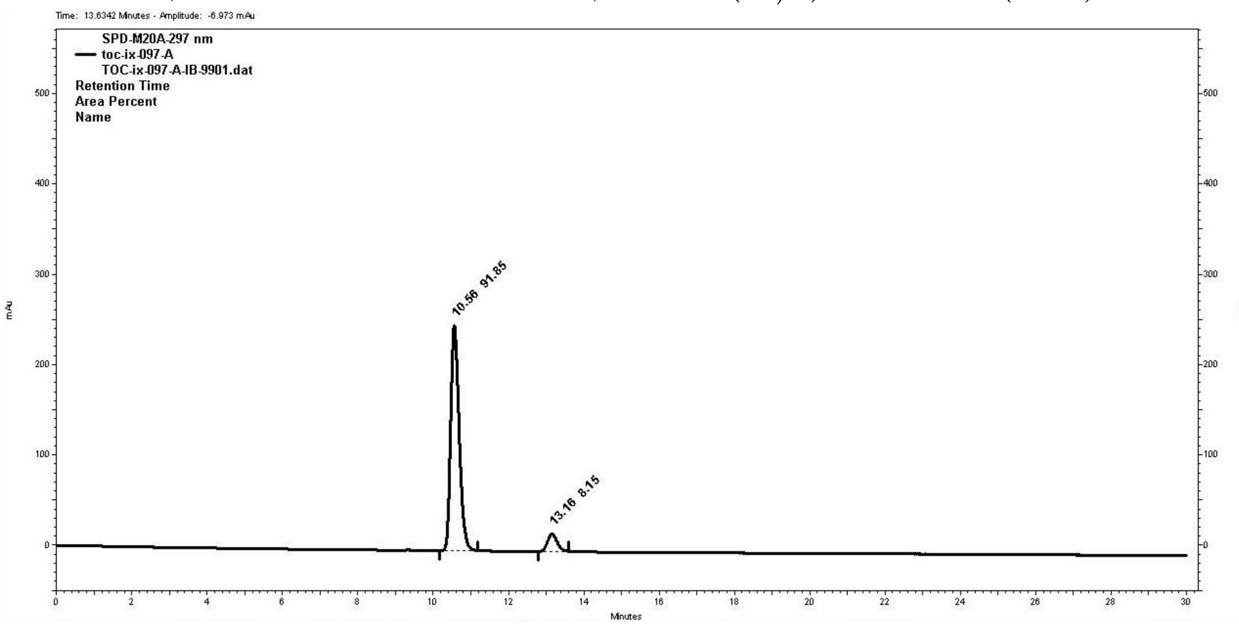
6b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 27.75 min (major) and 26.25 min (minor)

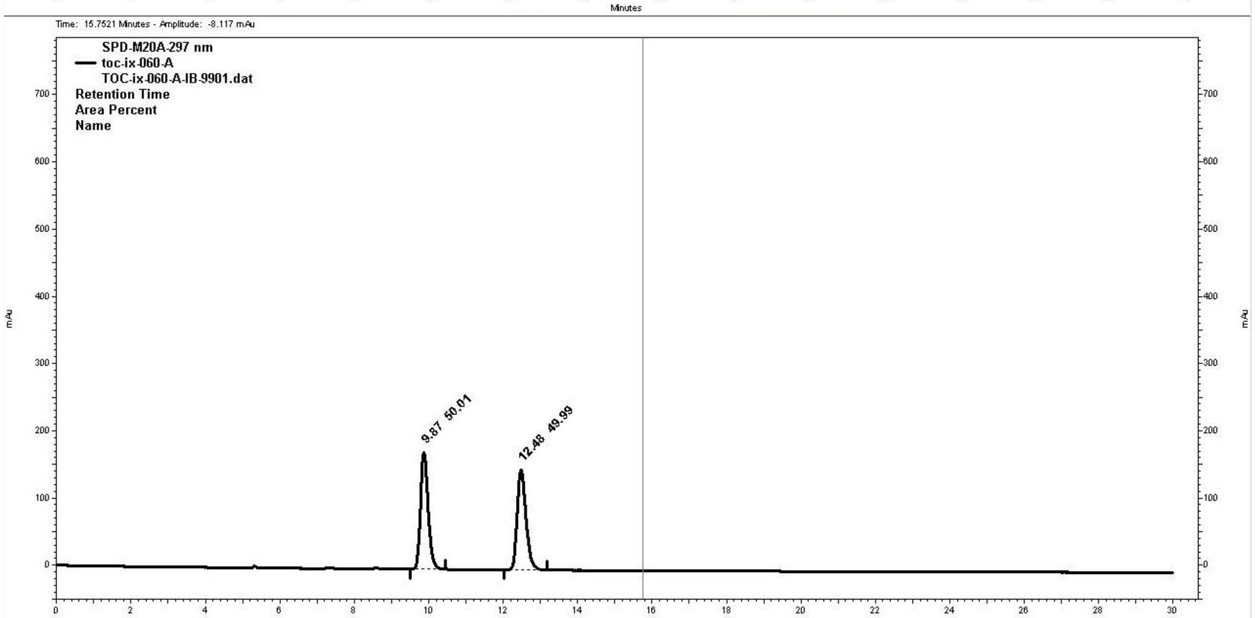


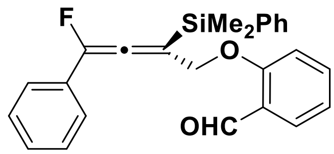




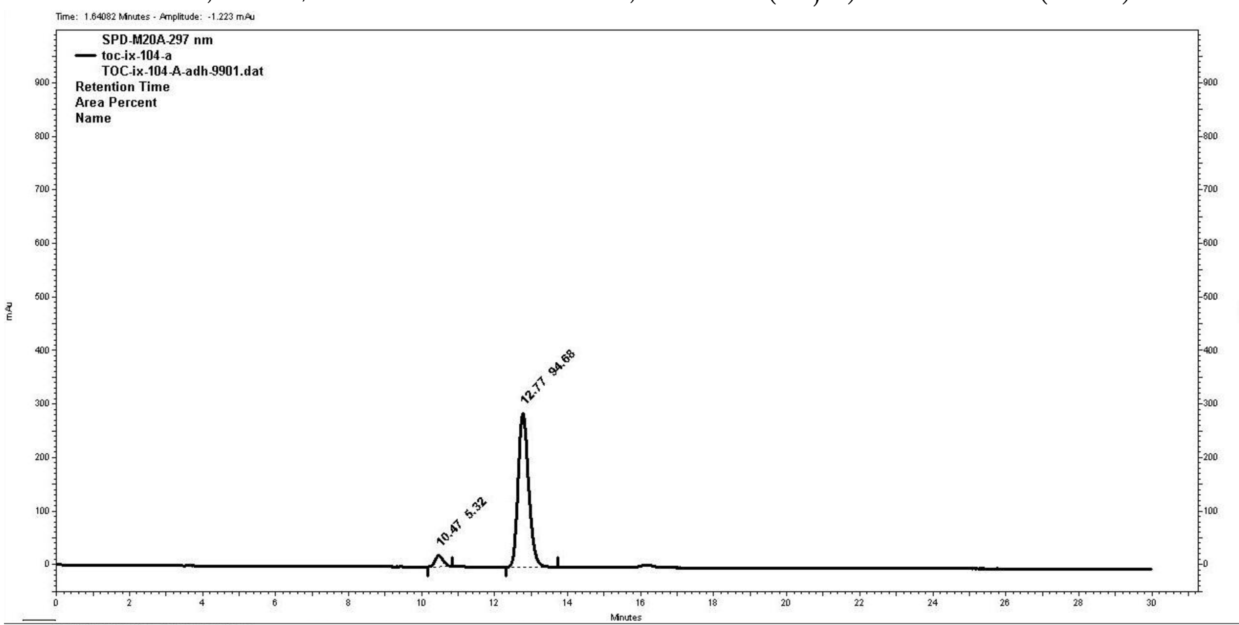
7b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 10.56 min (major) and 13.16 min (minor)

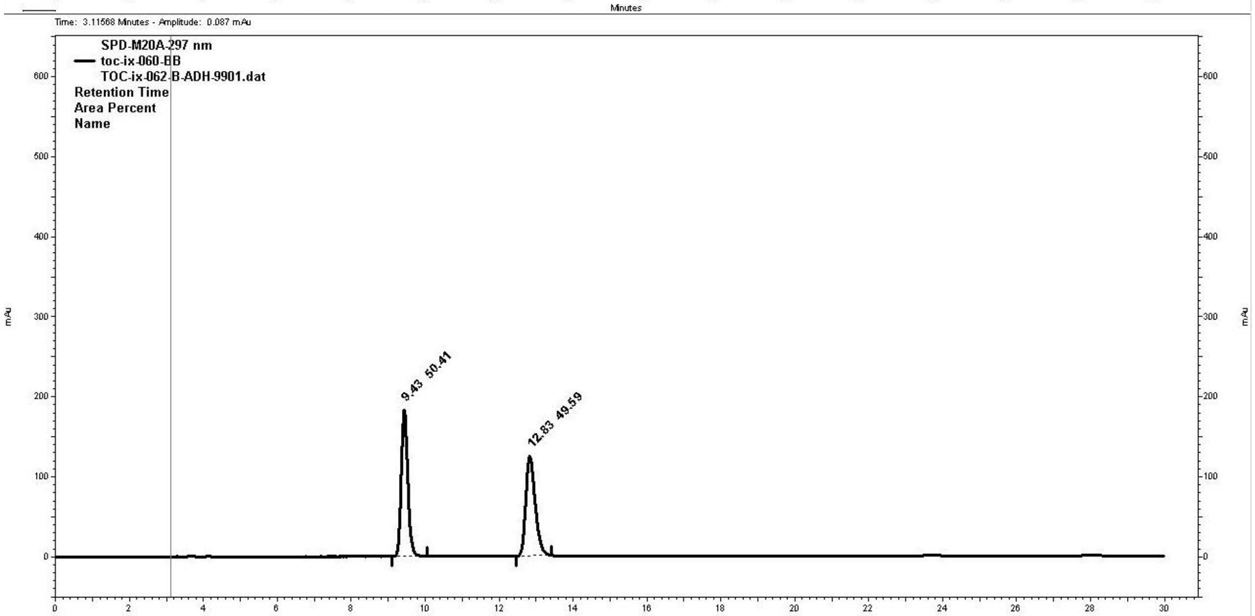


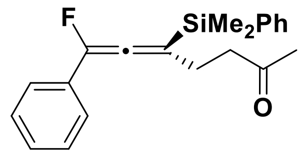




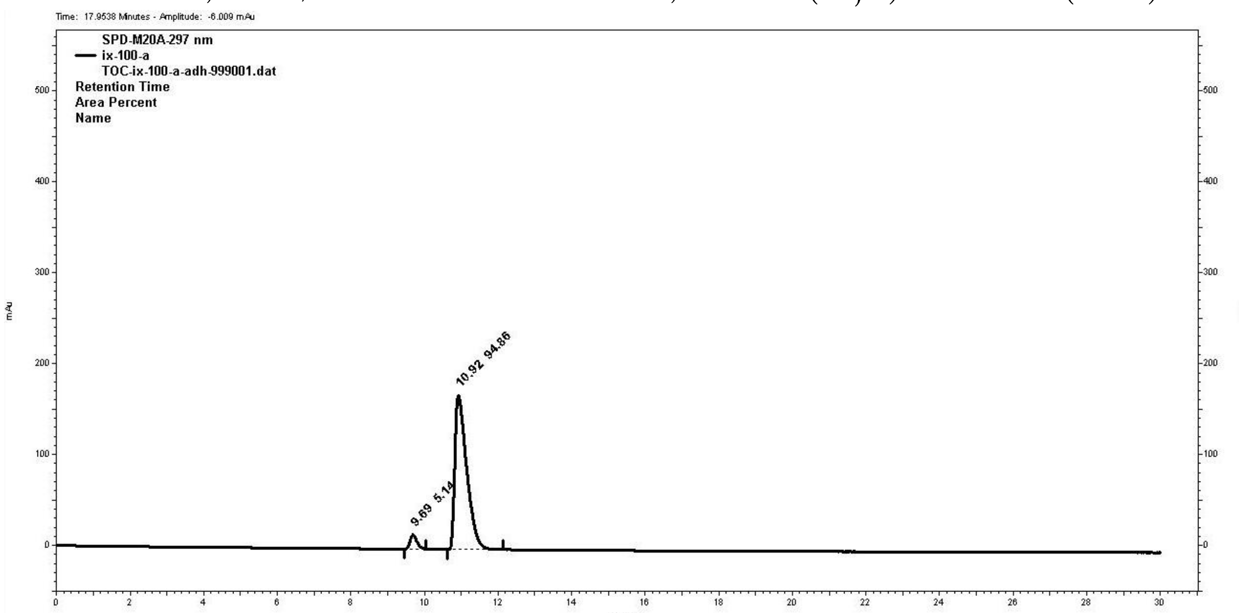
8b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.77 min (major) and 10.47 min (minor)

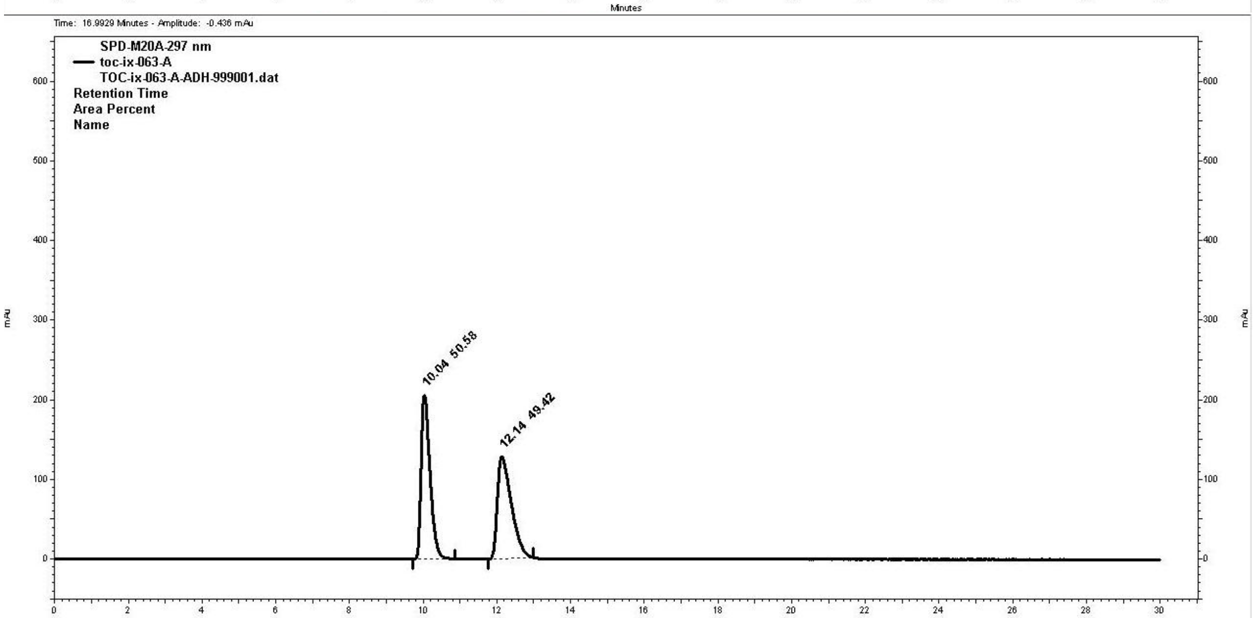


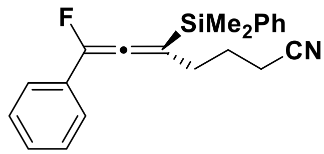




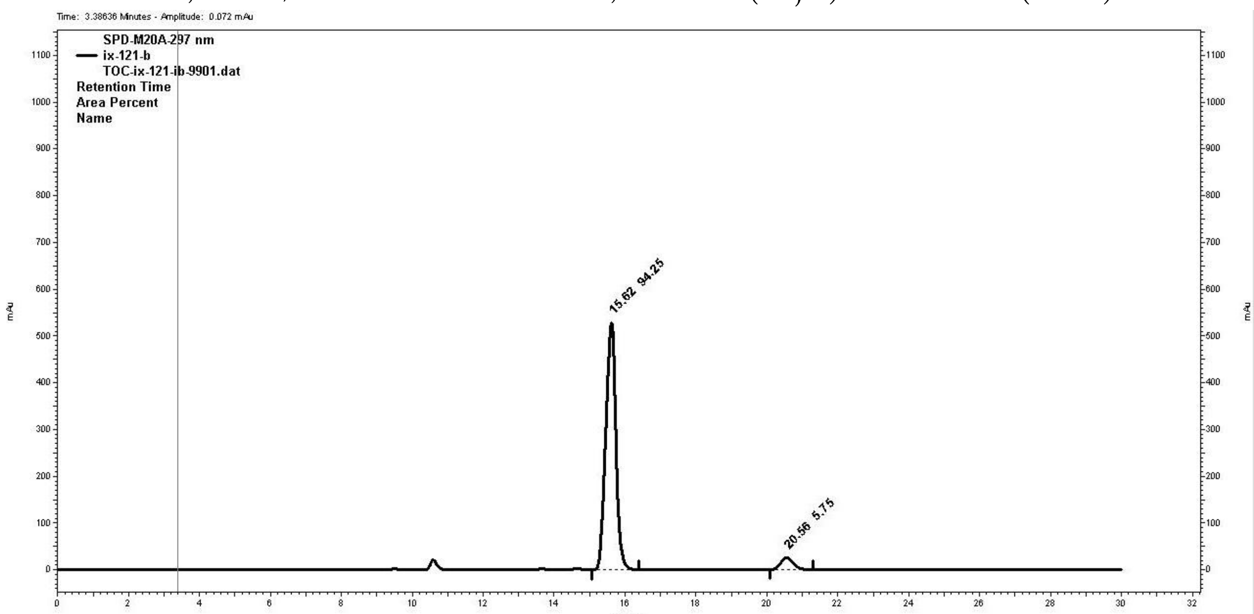
9b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 10.92 min (major) and 9.69 min (minor)

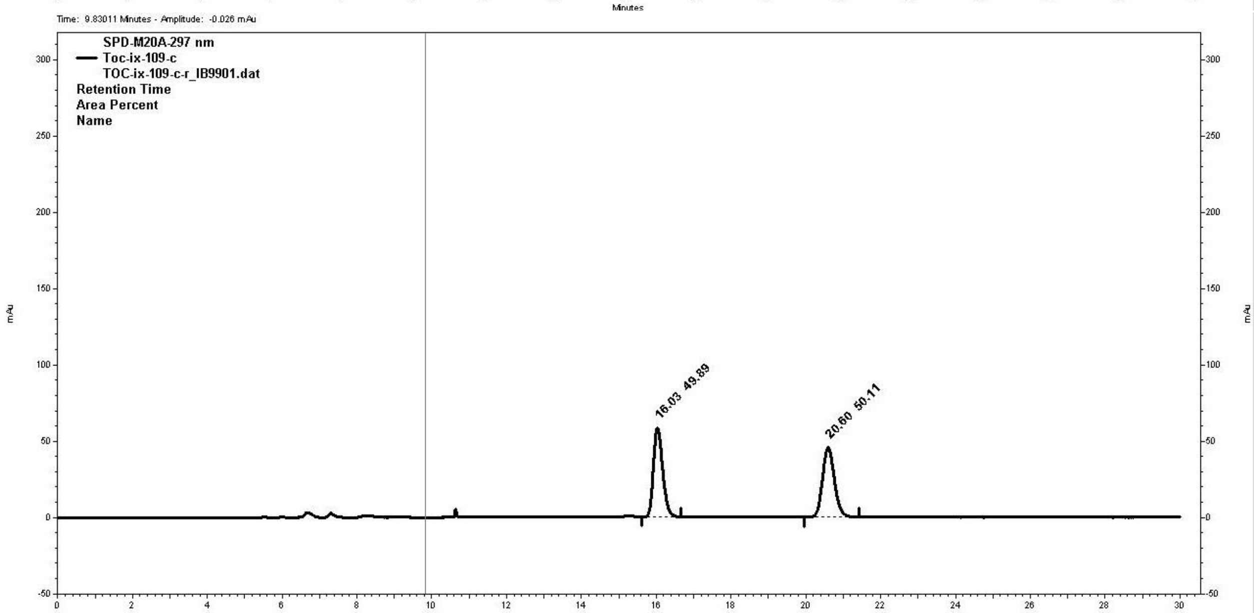


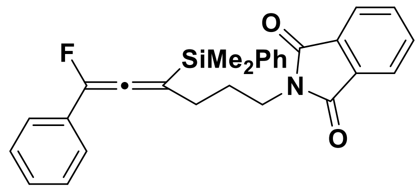




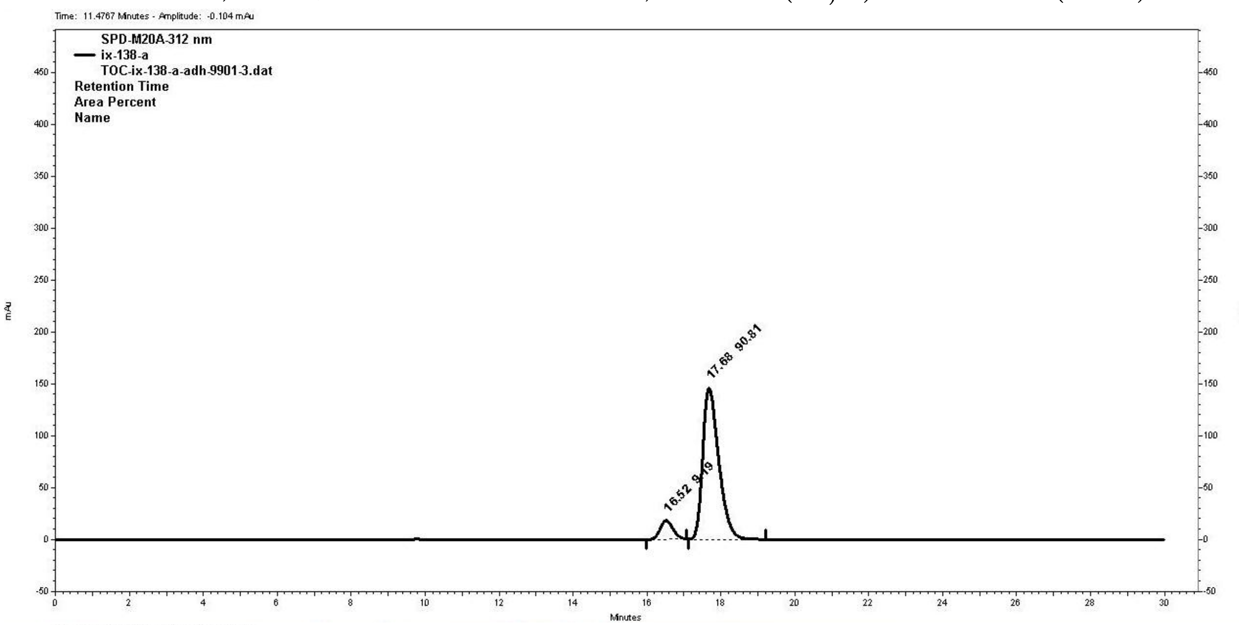
10b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 15.62 min (major) and 20.56 min (minor)

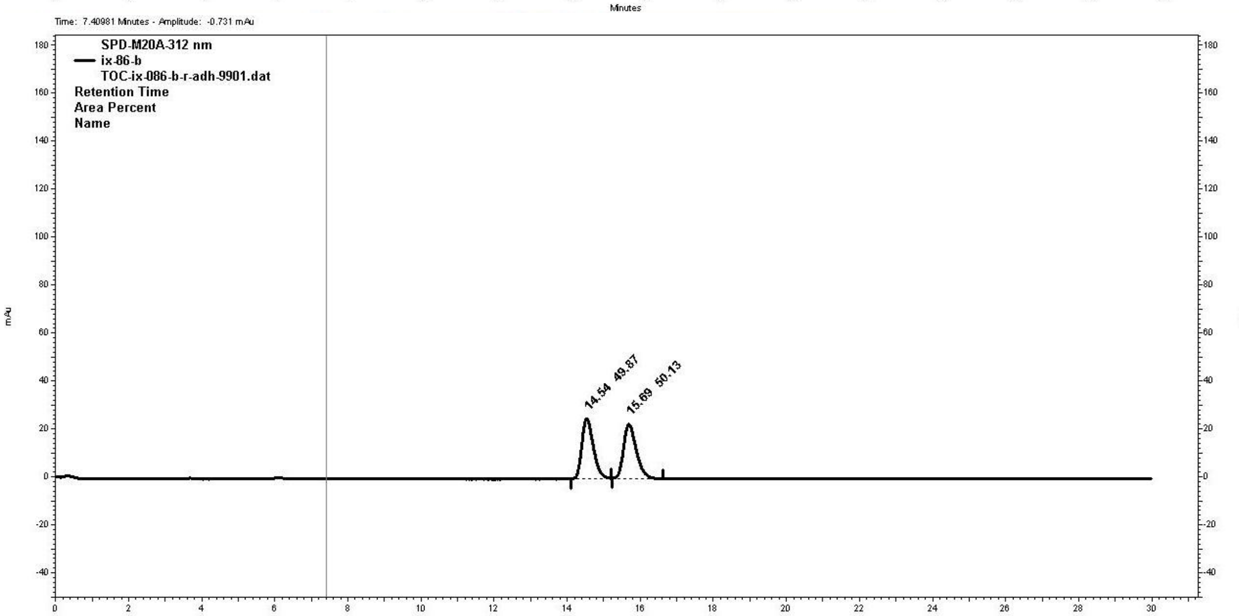


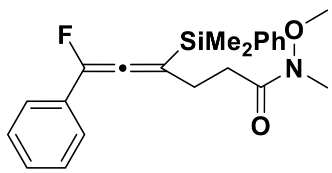




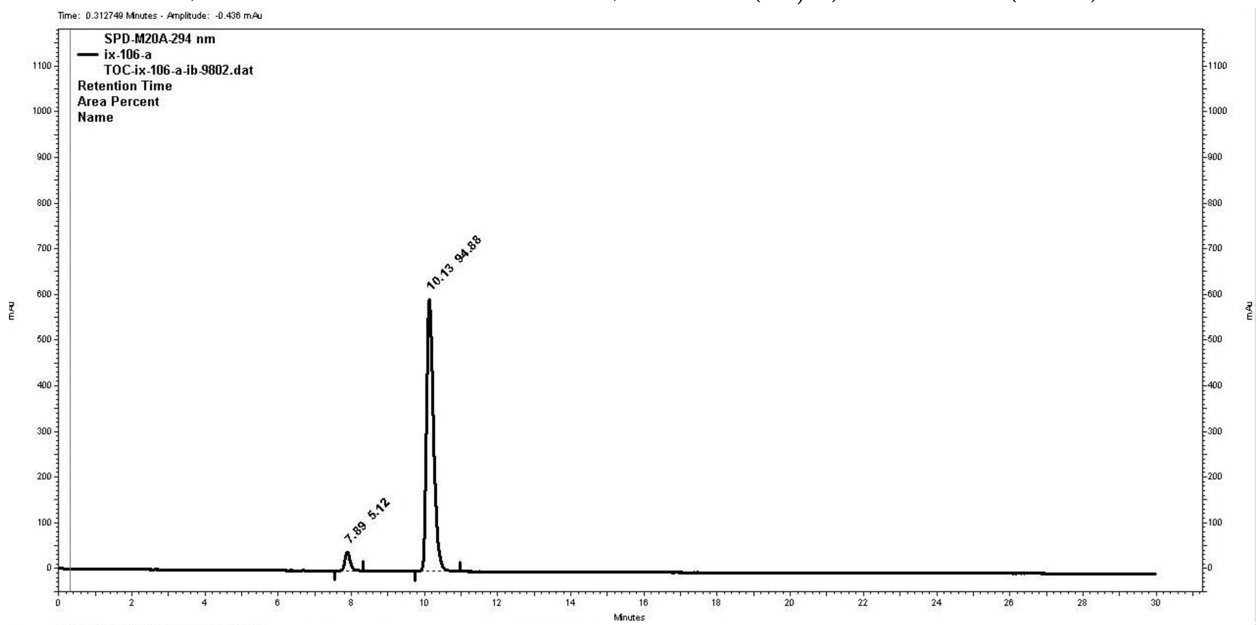
11b: ADH column, 1.0 mL/min: hexanes:iPrOH 99:01; 17.68 min (major) and 16.52 min (minor)

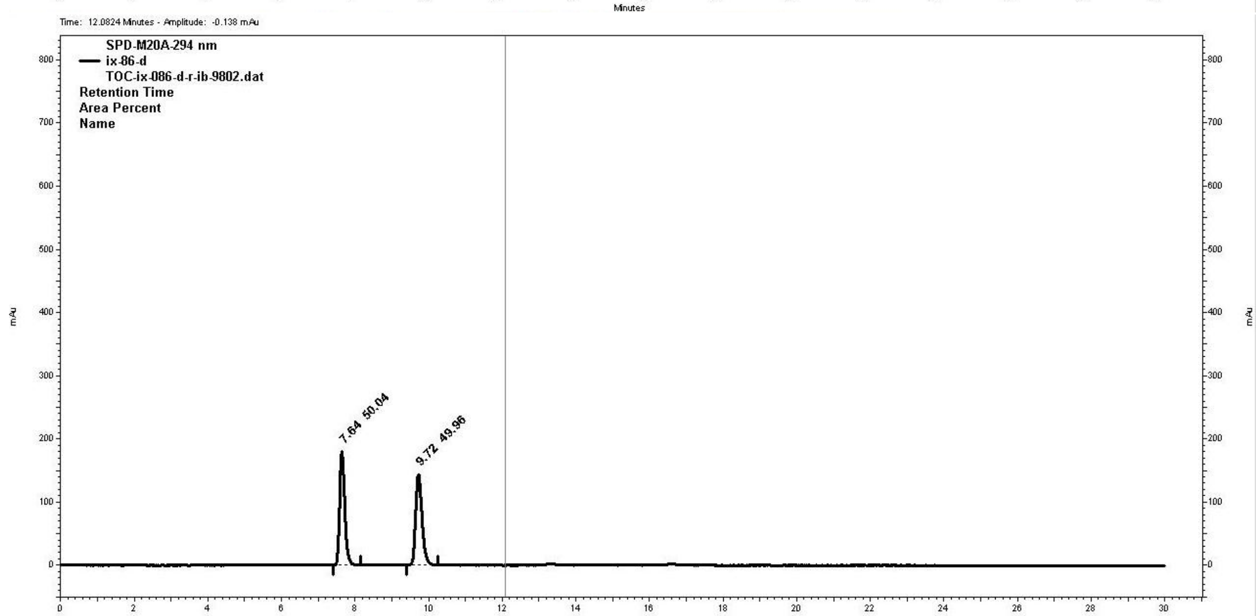


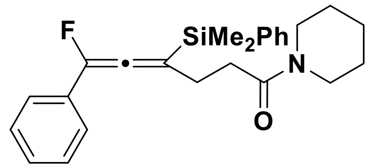




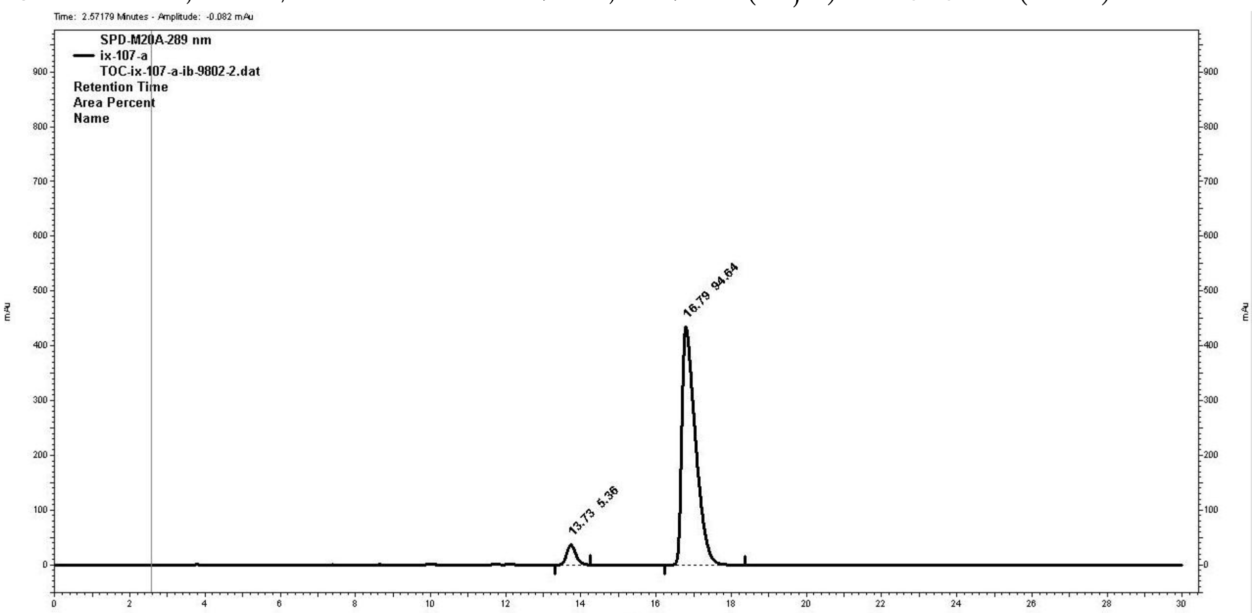
12b: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 10.13 min (major) and 7.89 min (minor)

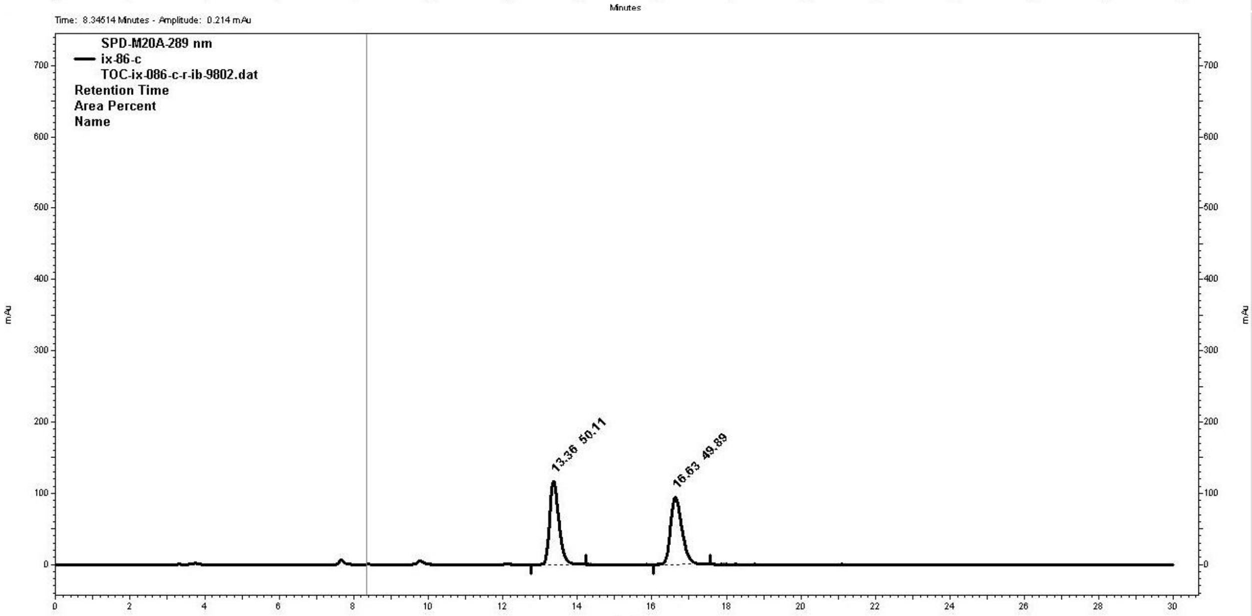


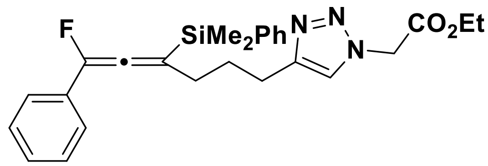




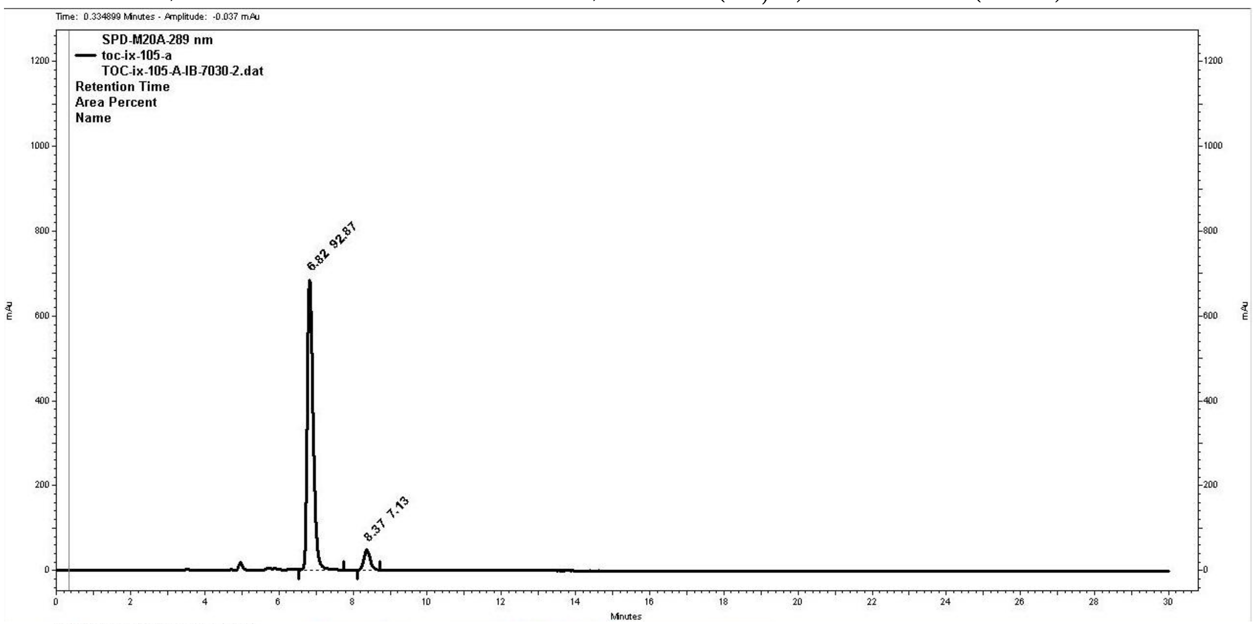
13b: IB column, 1.0 mL/min: hexanes:iPrOH 98:02; 16.79 min (major) and 13.73 min (minor)

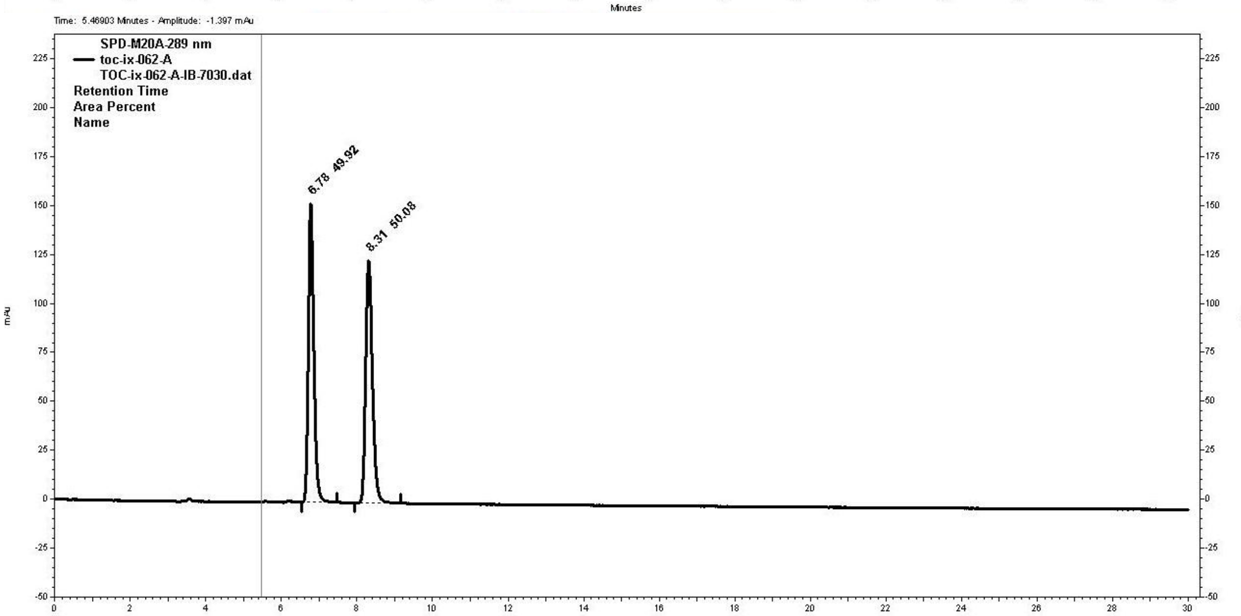


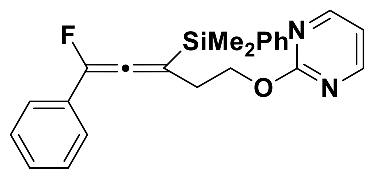




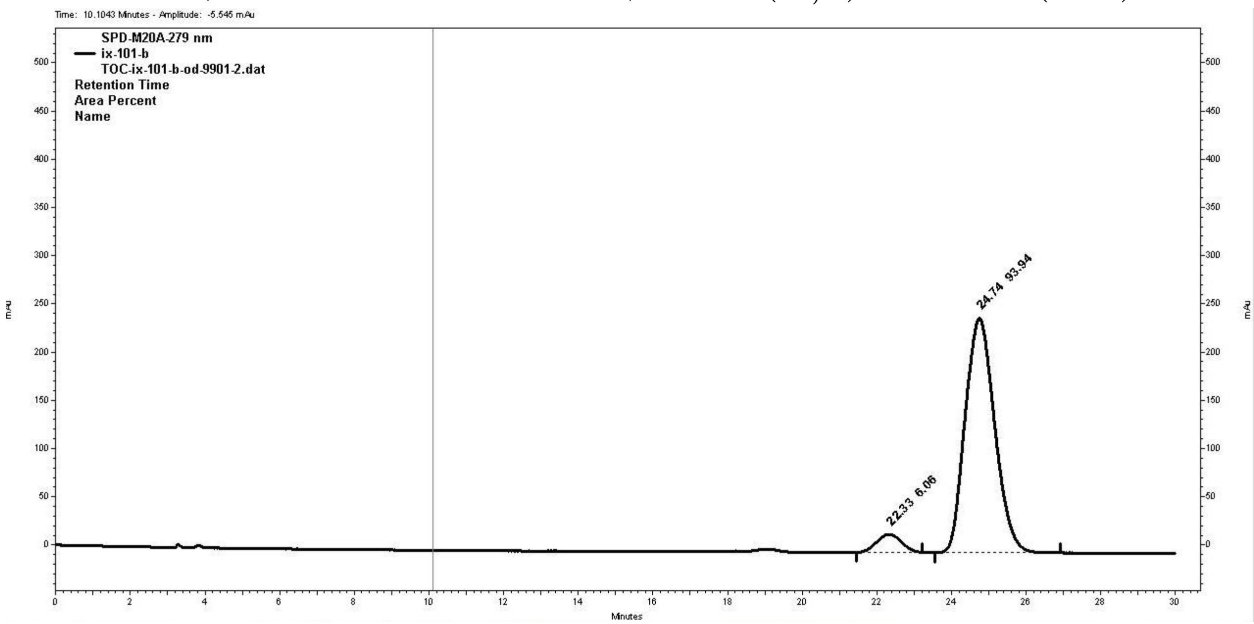
14: IB column, 1.0 mL/min: hexanes:iPrOH 70:30; 6.82 min (major) and 8.37 min (minor)

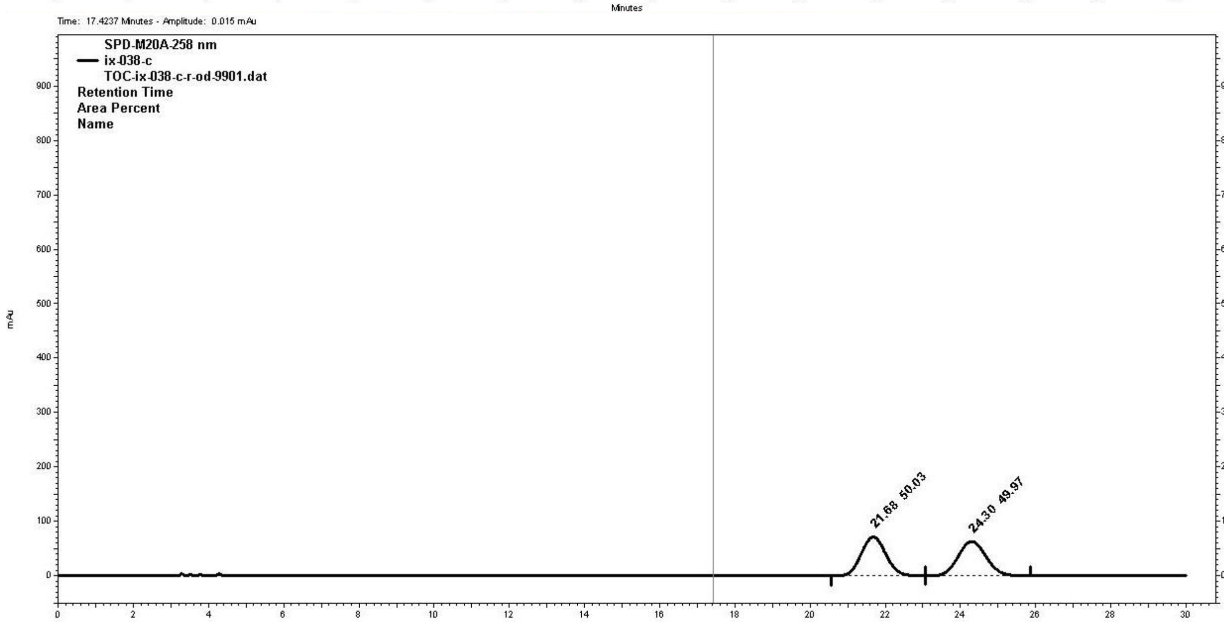


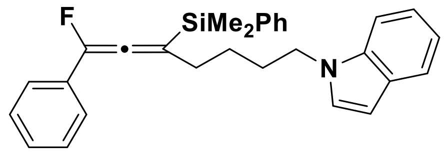




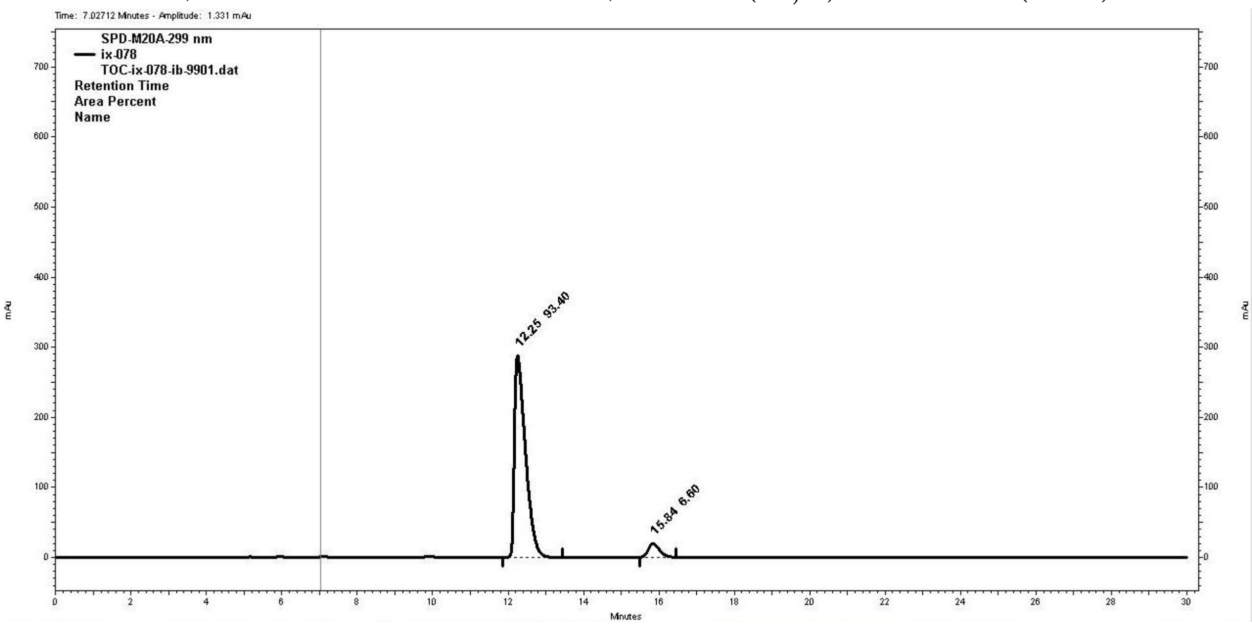
15b: OD column, 1.0 mL/min: hexanes:iPrOH 99:01; 24.74 min (major) and 22.33 min (minor)

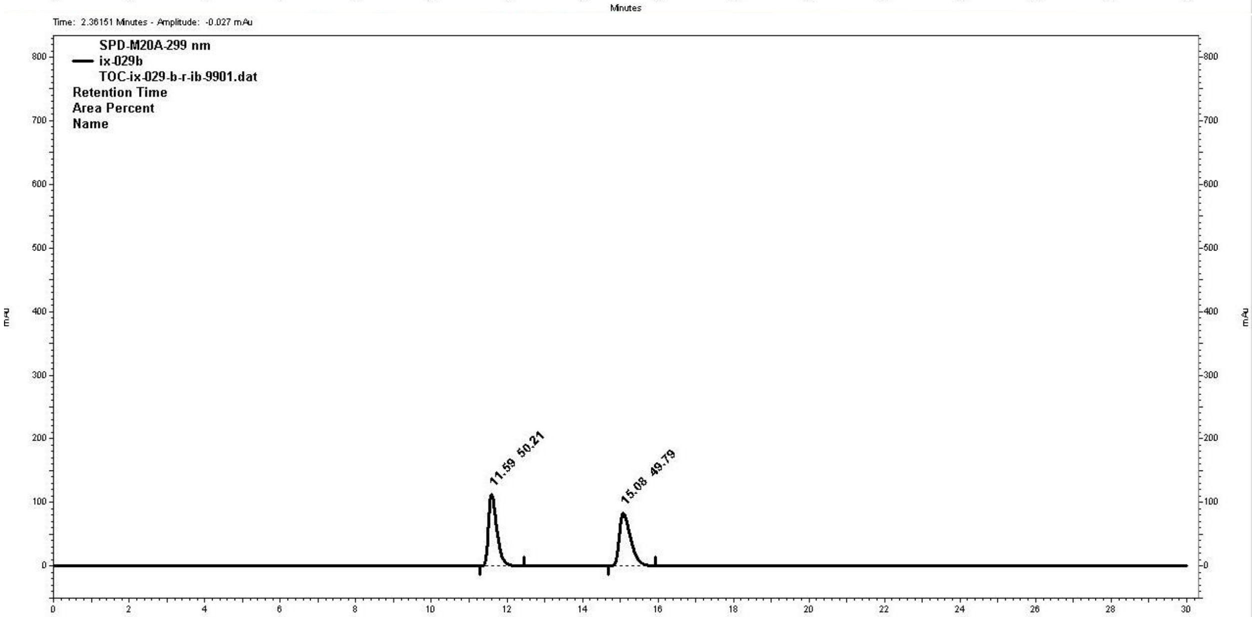


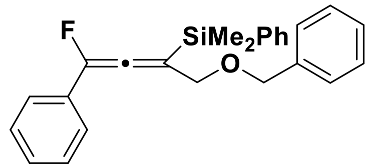




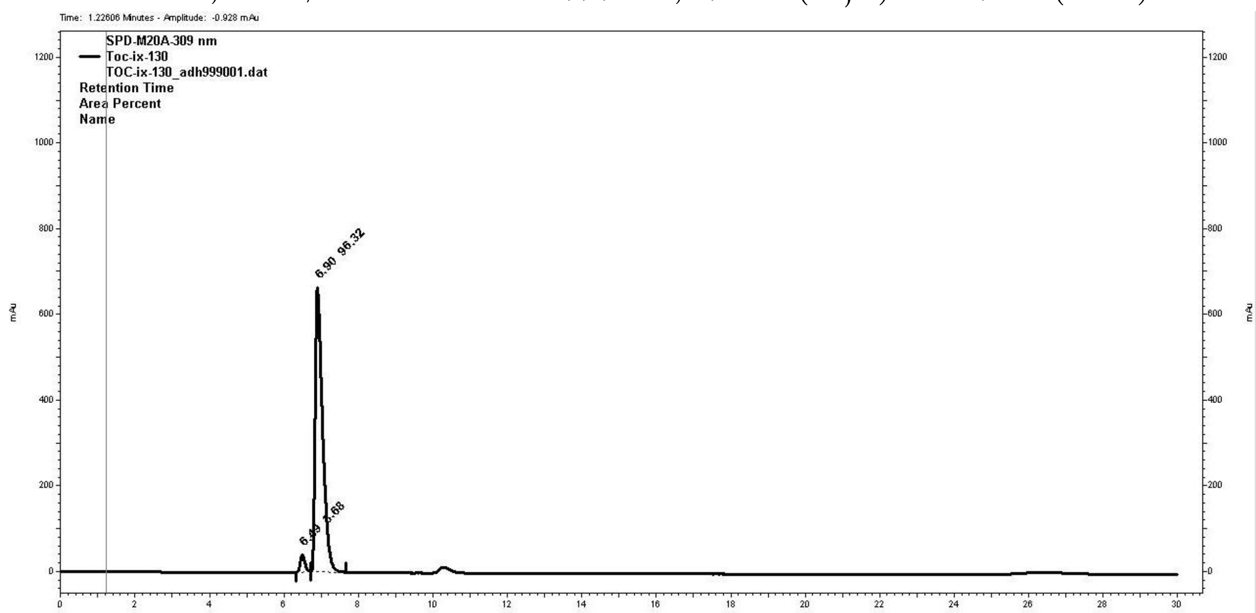
16b: IB column, 1.0 mL/min: hexanes:iPrOH 99:01; 12.25 min (major) and 15.84 min (minor)

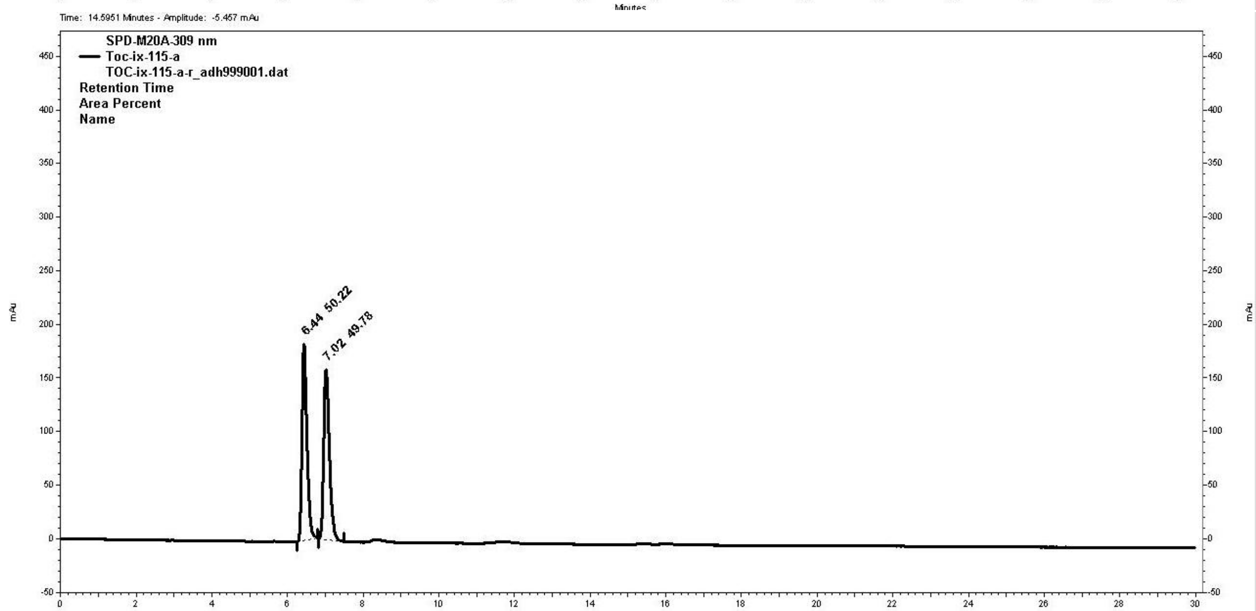


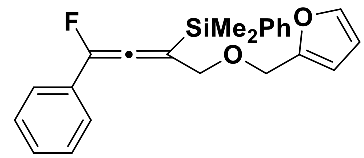




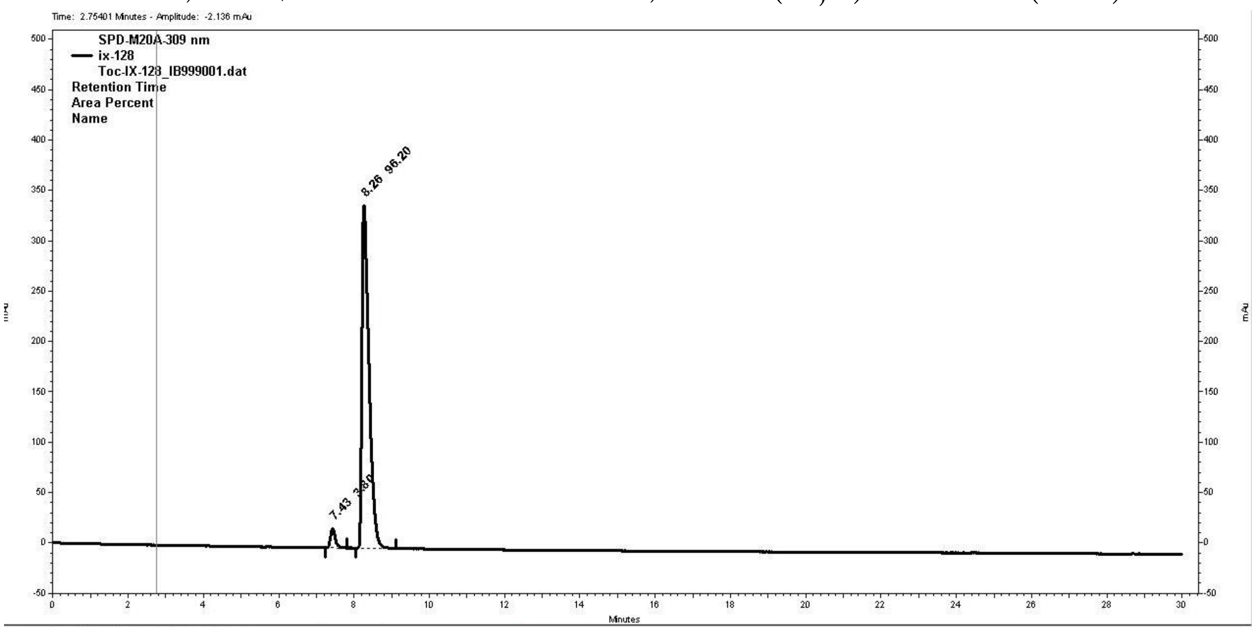
17: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 6.90 min (major) and 6.49 min (minor)

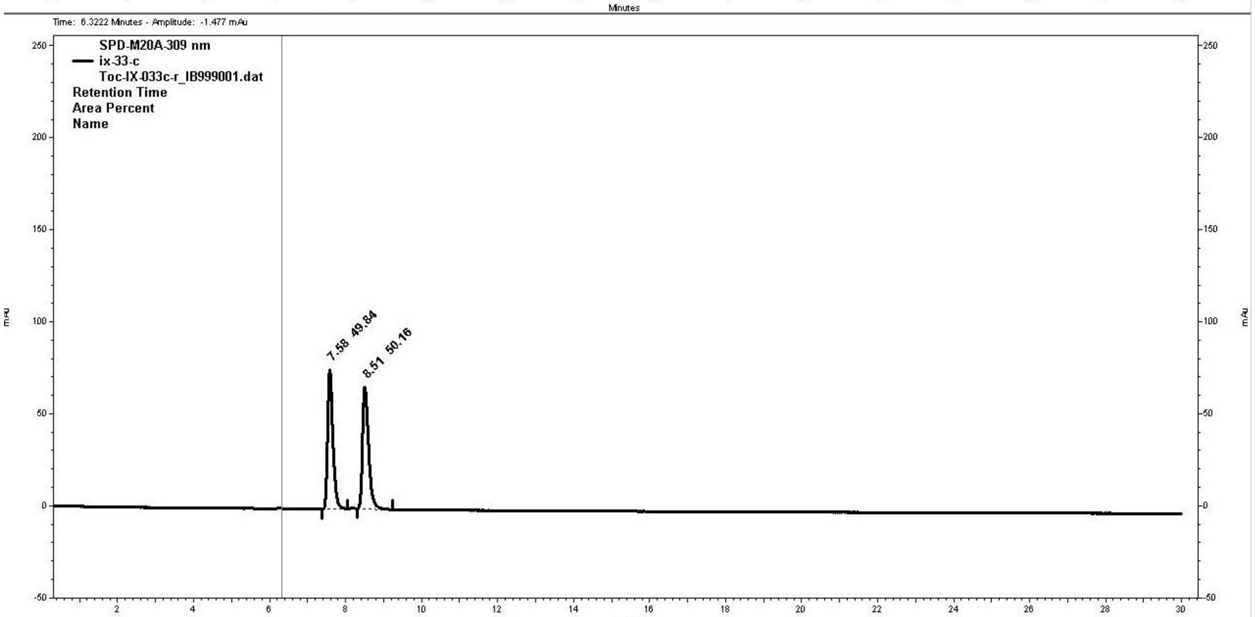


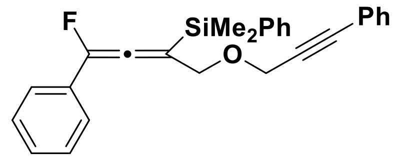




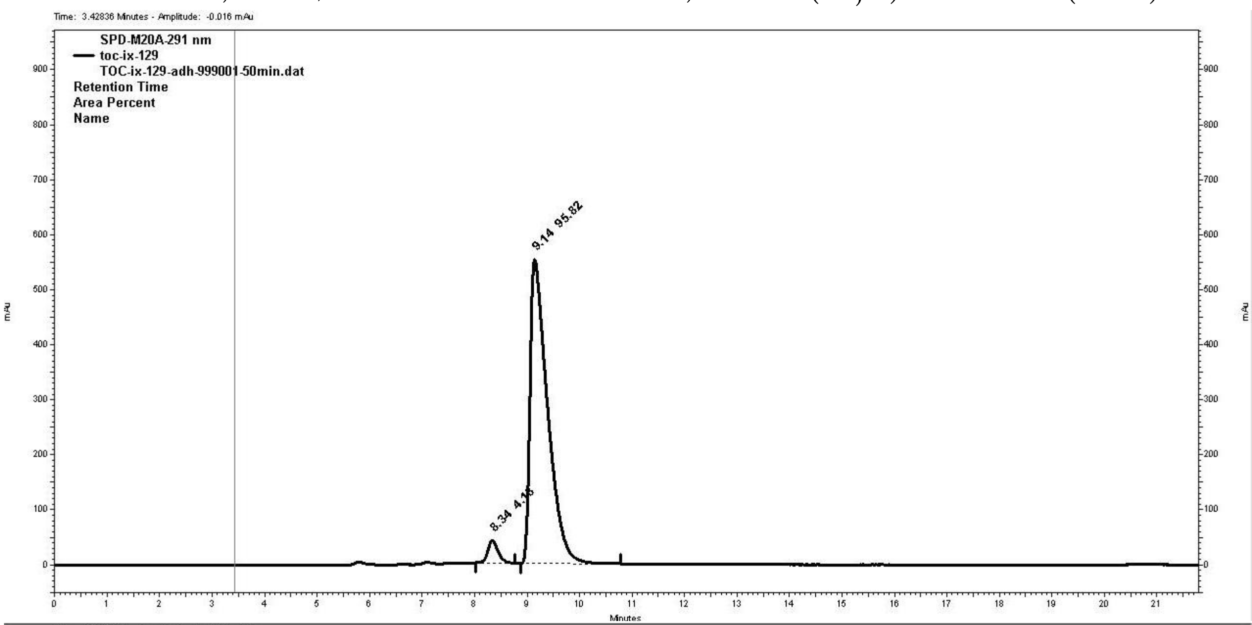
18b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 8.26 min (major) and 7.43 min (minor)

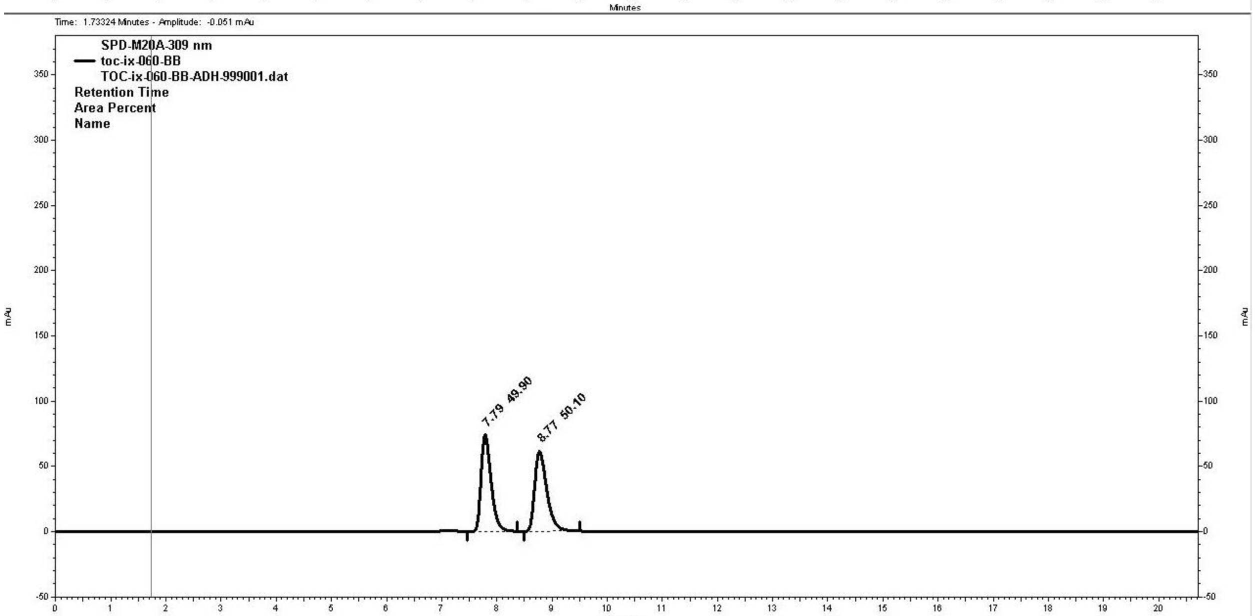


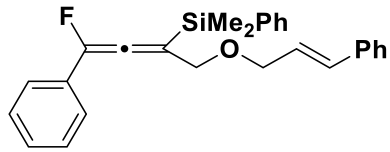




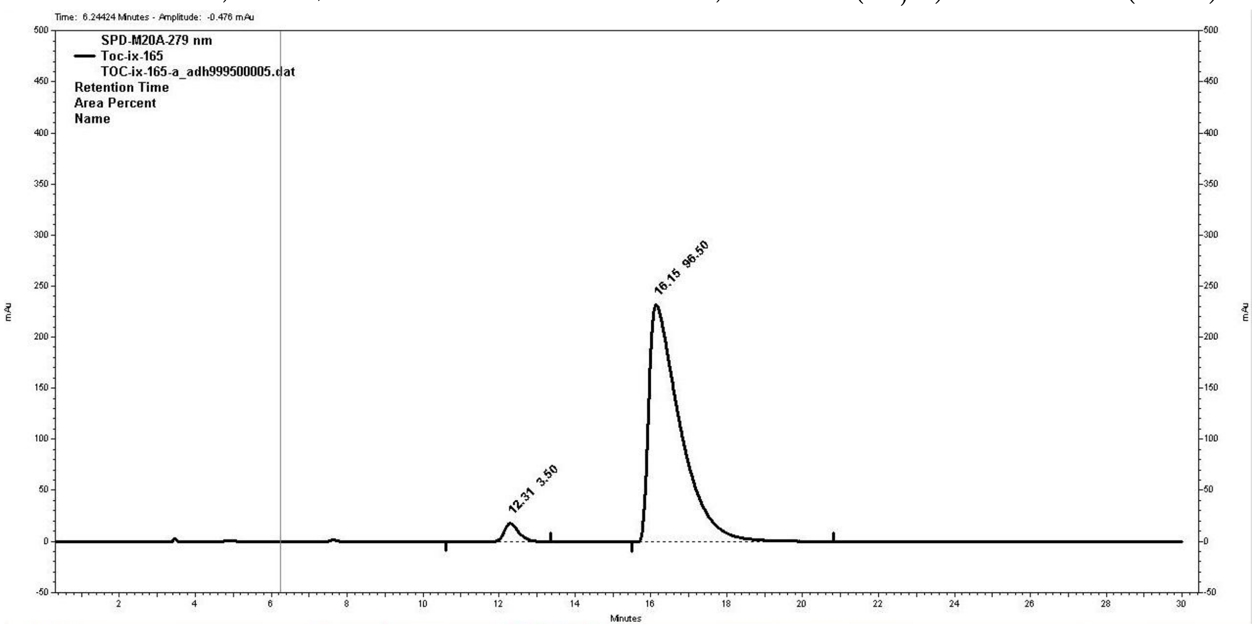
19b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 9.14 min (major) and 8.34 min (minor)

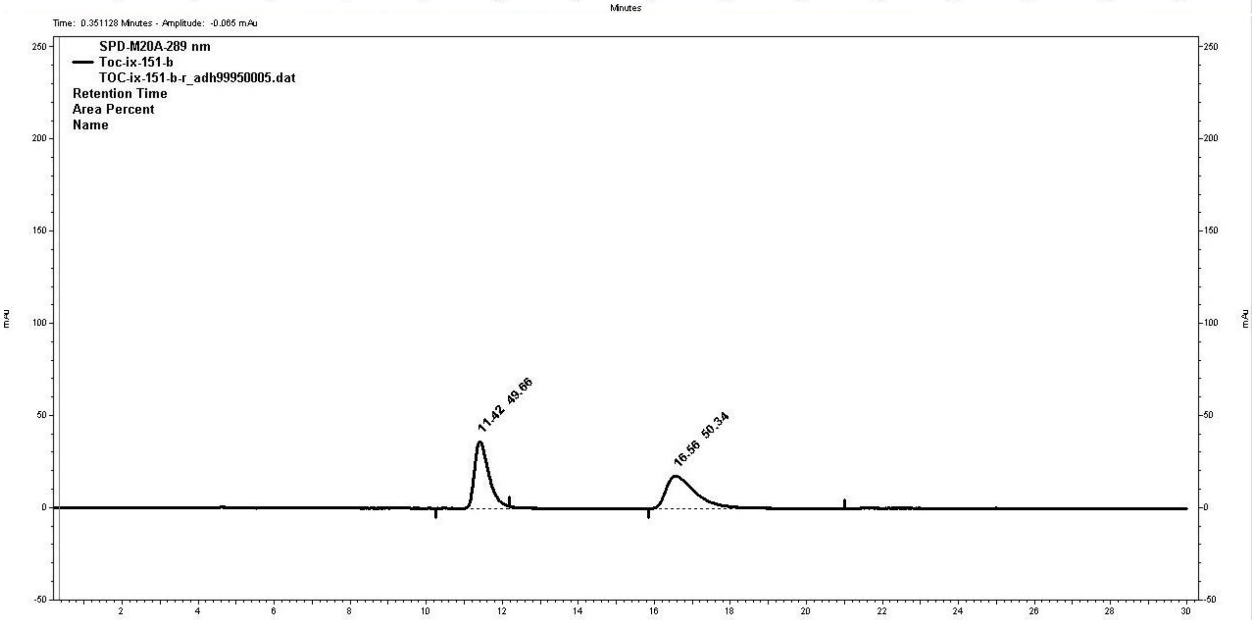


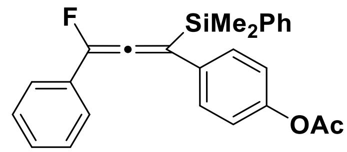




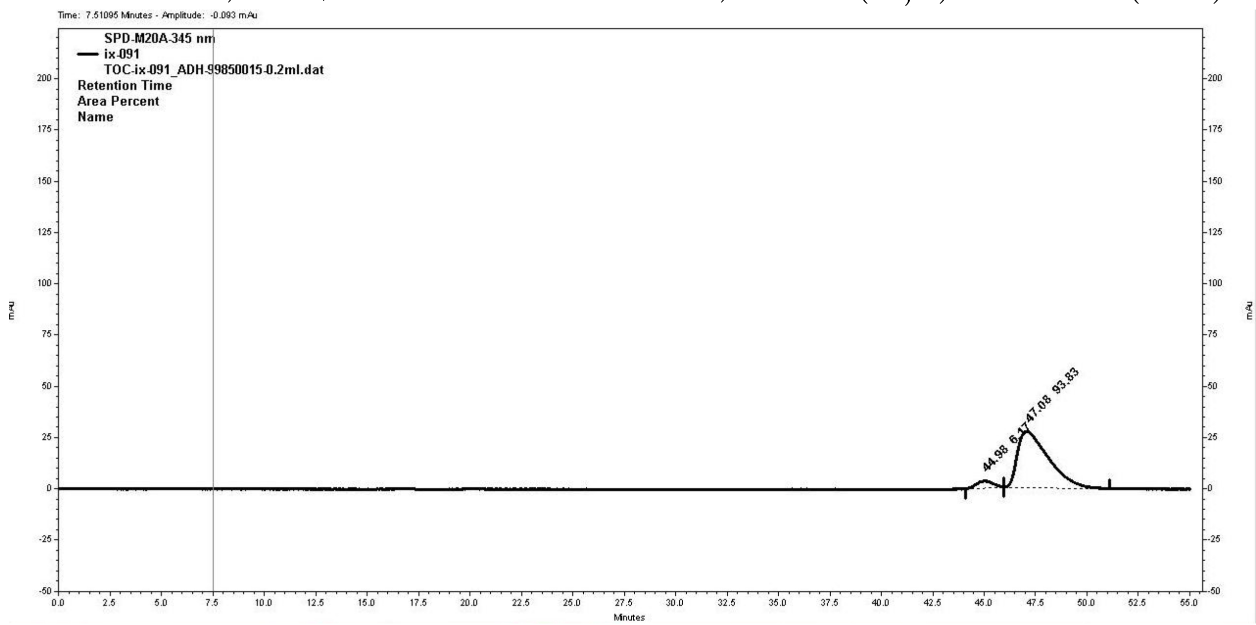
20b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.95:00.05; 16.15 min (major) and 12.31 min (minor)

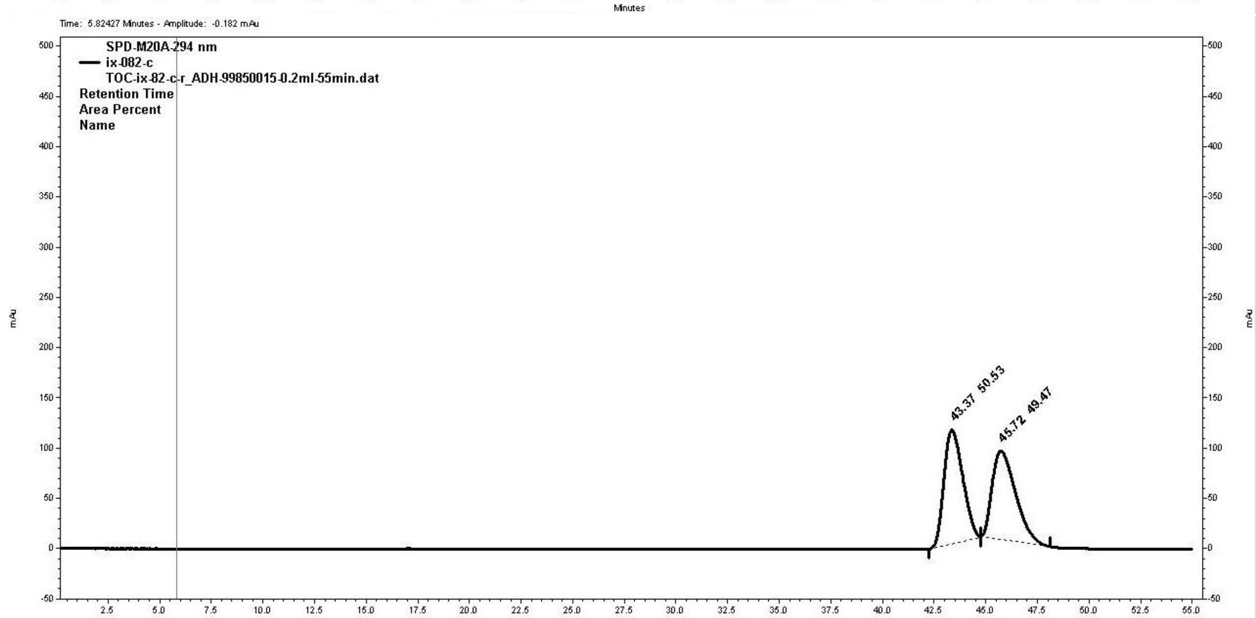


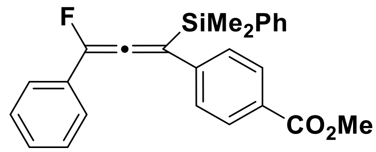




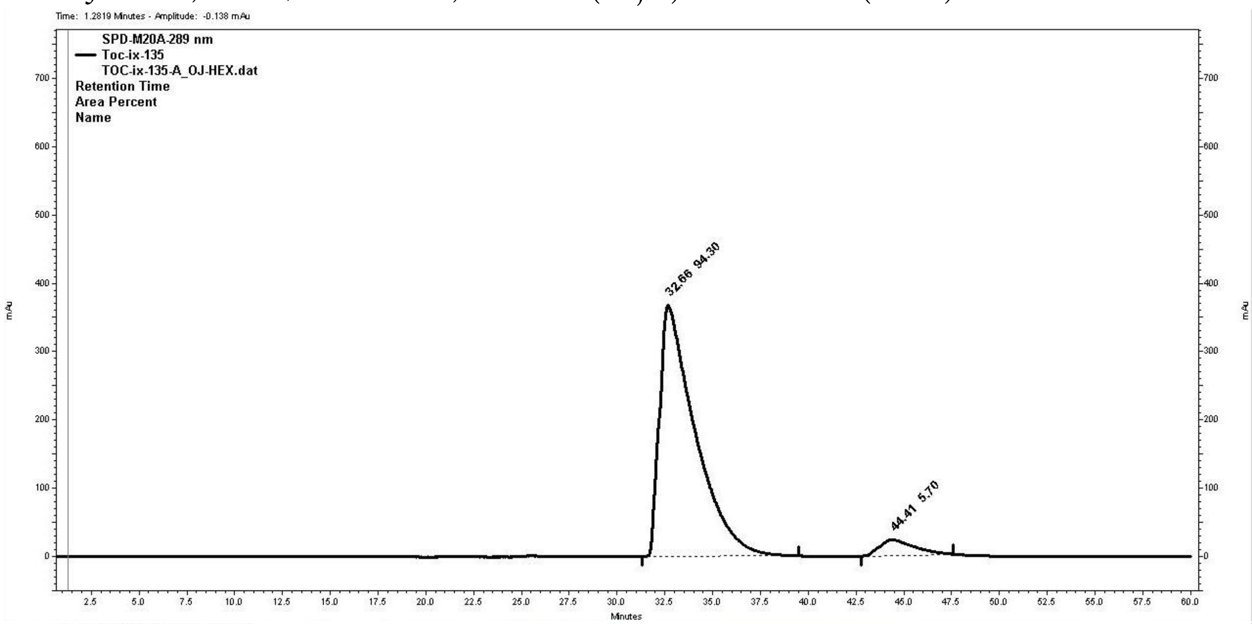
21b: ADH column, 0.2 mL/min: hexanes:iPrOH 99.85:00.15; 47.08 min (major) and 44.98 min (minor)

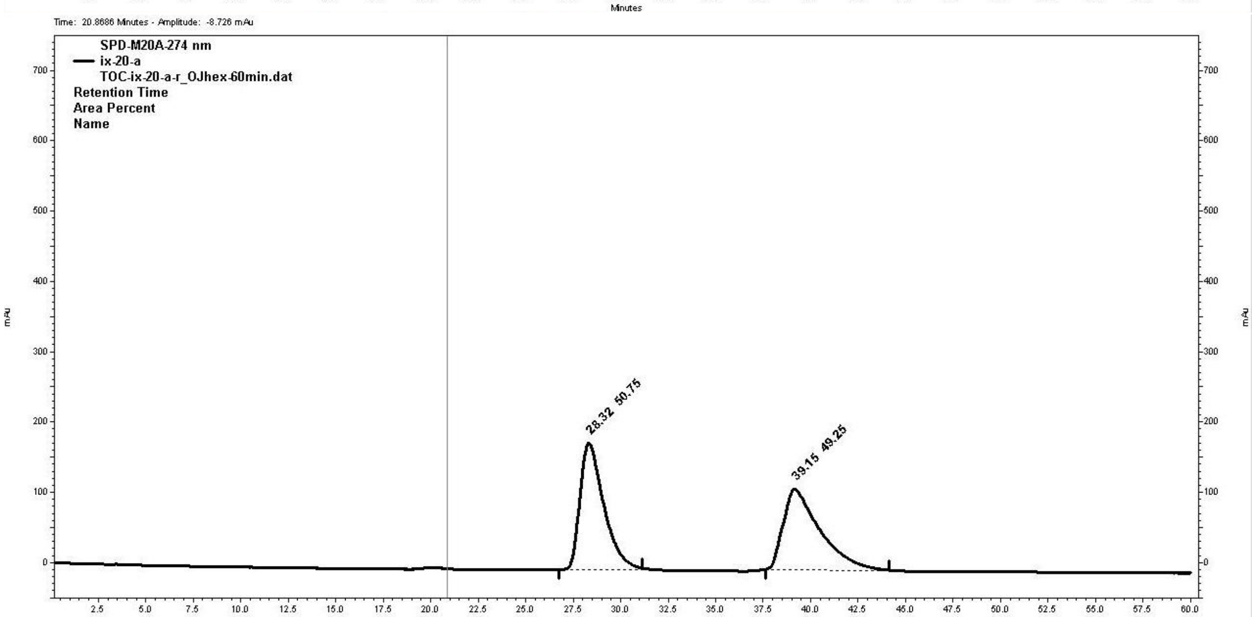


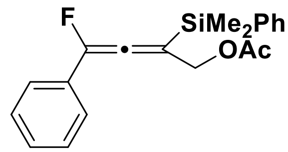




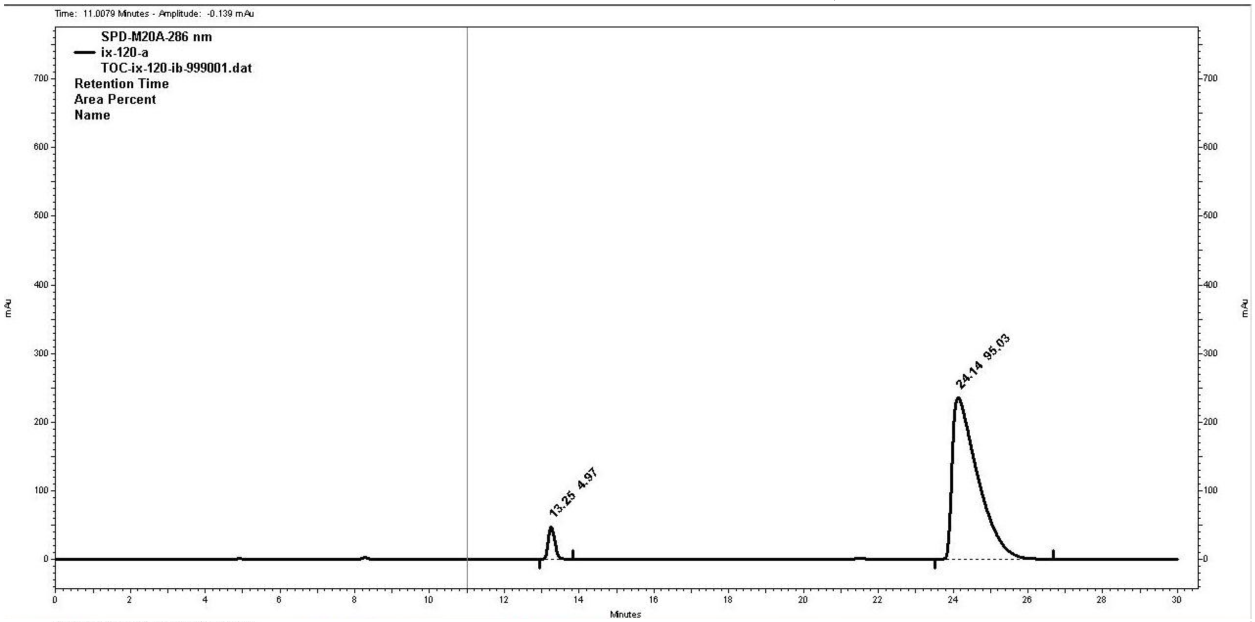
22b: OJ column, 1.0 mL/min: hexanes; 32.66 min (major) and 44.41 min (minor)

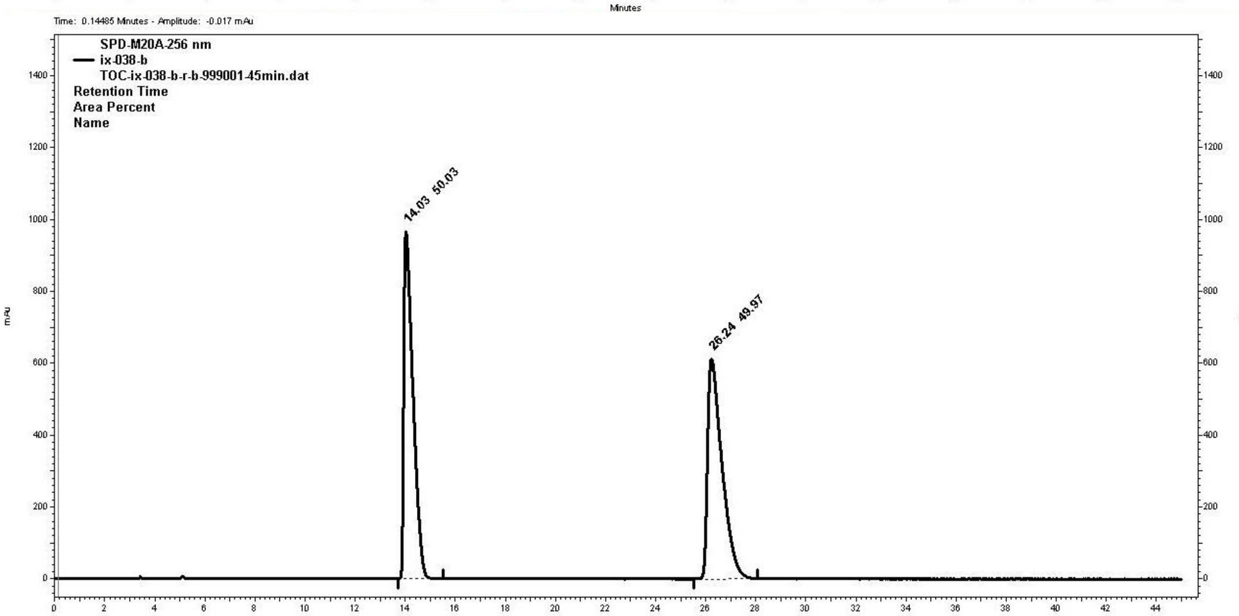


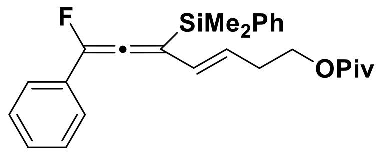




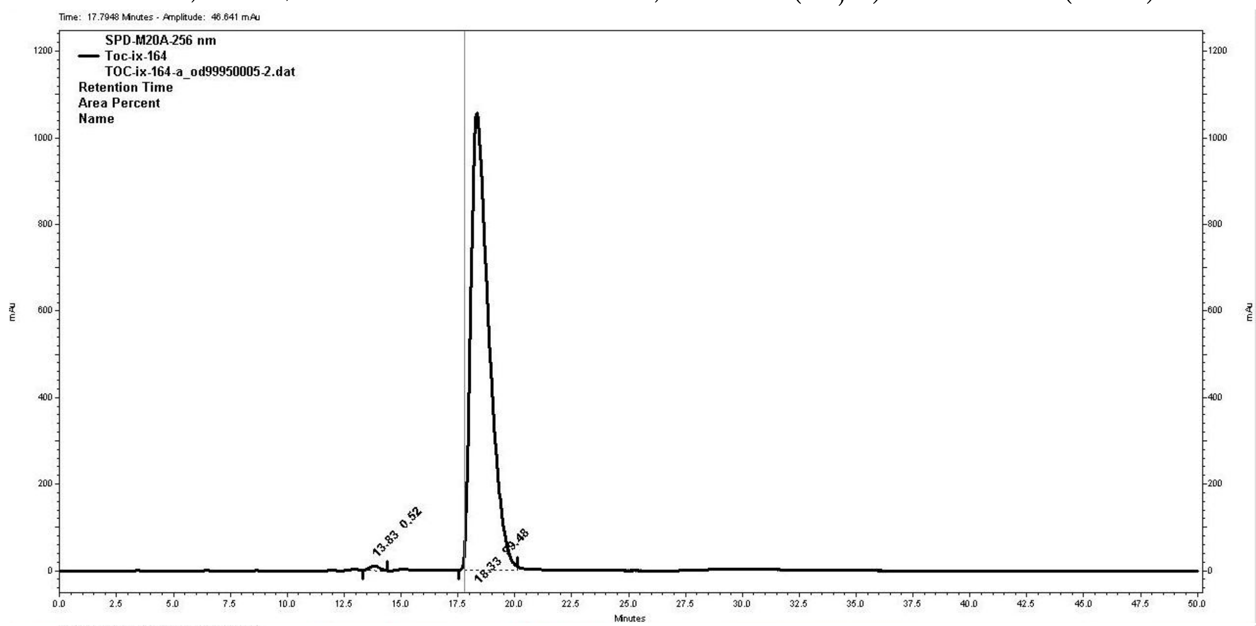
23b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 21.14 min (major) and 13.25 min (minor)

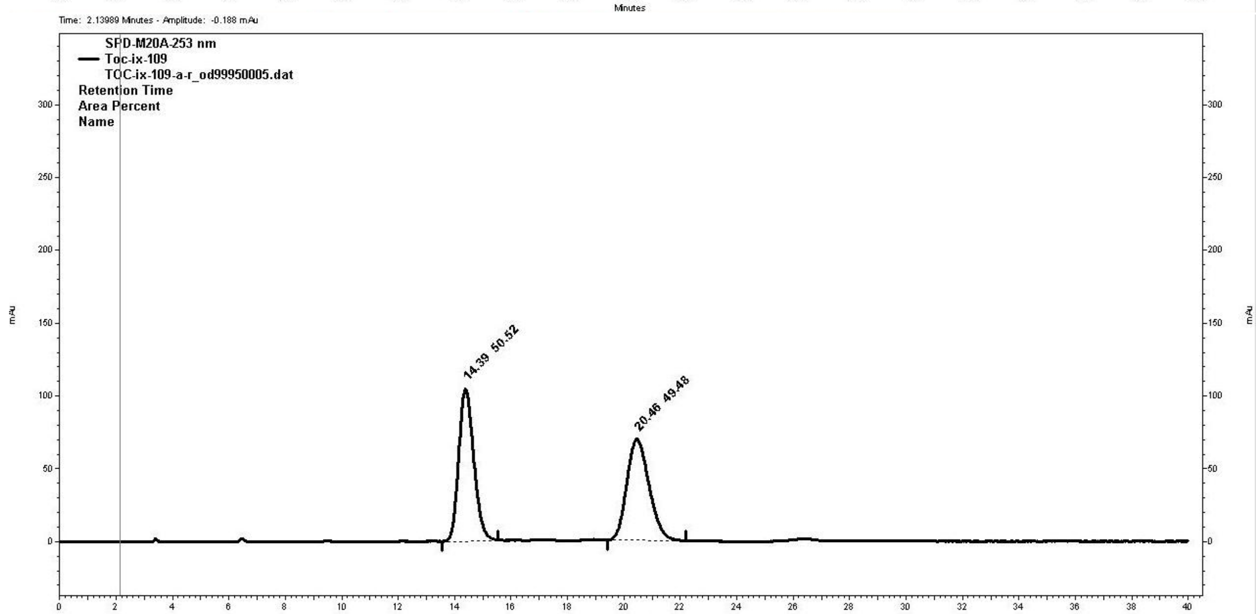


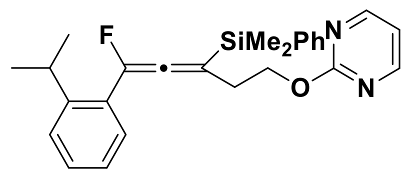




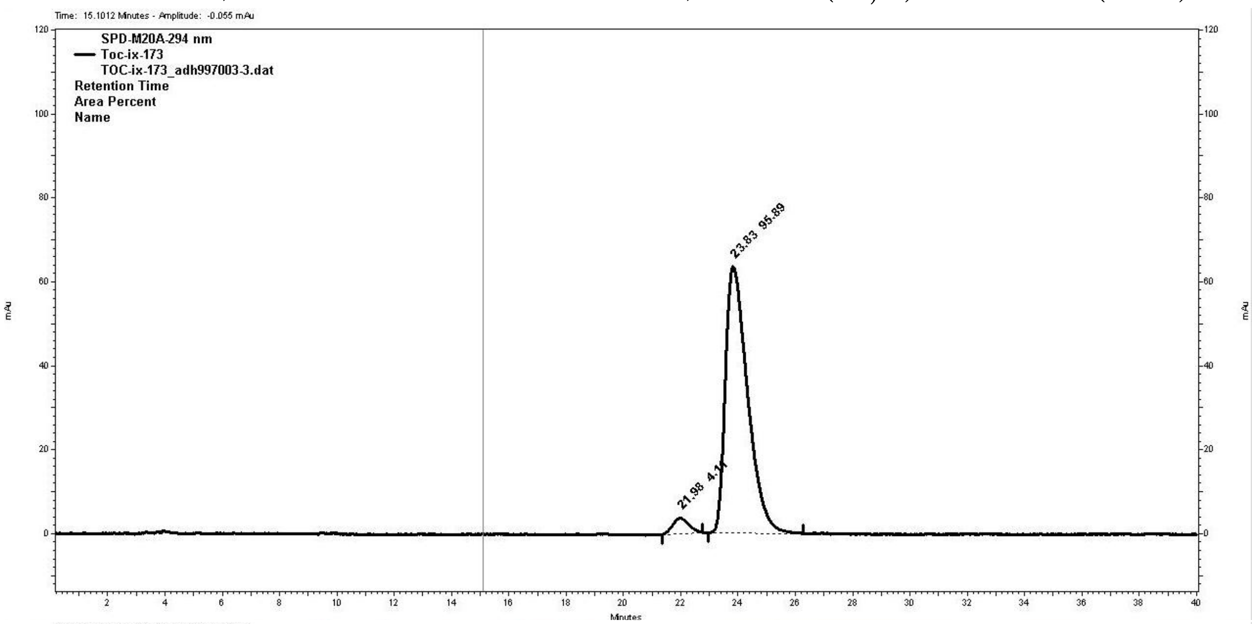
24b: IB column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 18.33 min (major) and 13.83 min (minor)

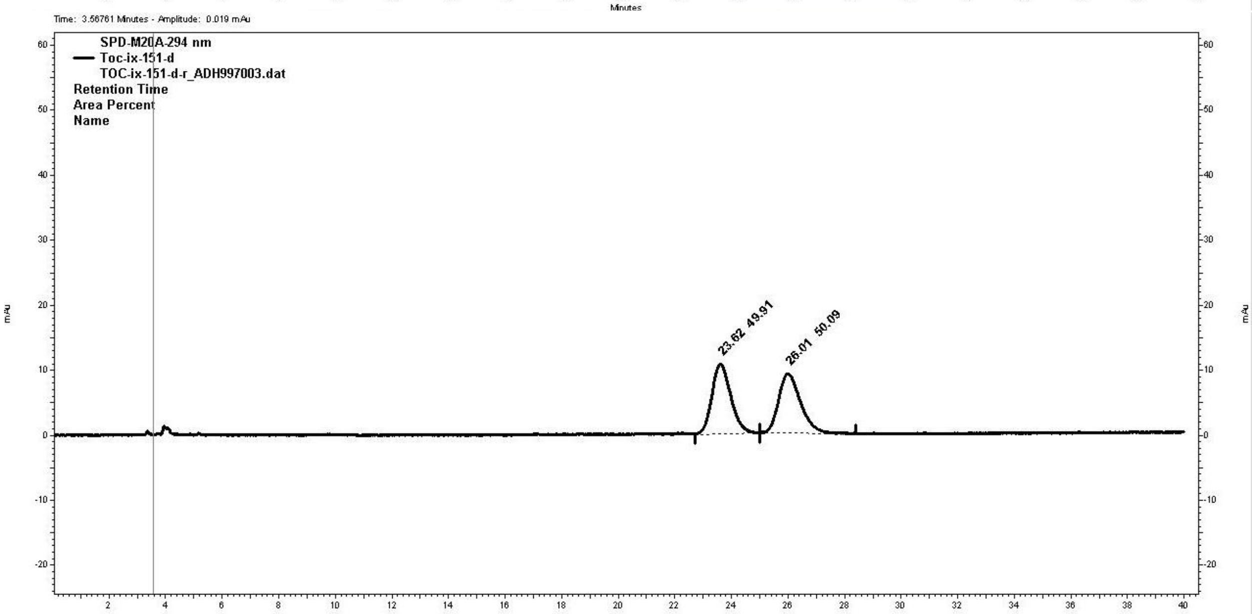


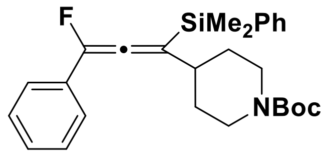




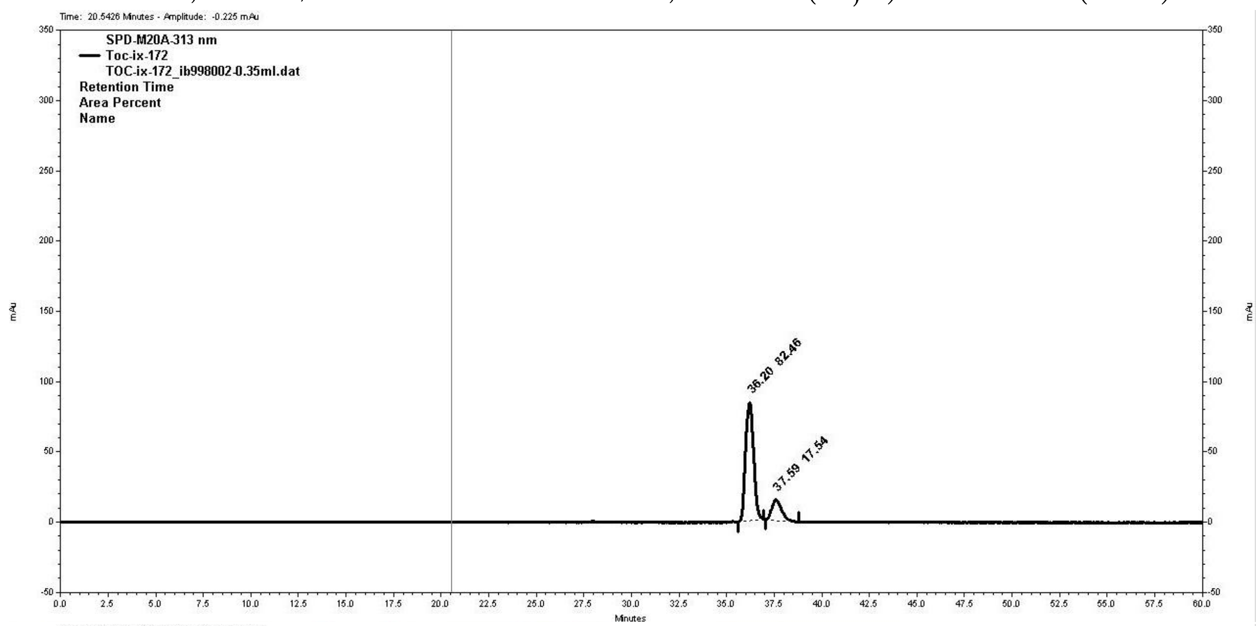
25b: ADH column, 1.0 mL/min: hexanes:iPrOH 99.7:00.3; 23.83 min (major) and 21.98 min (minor)

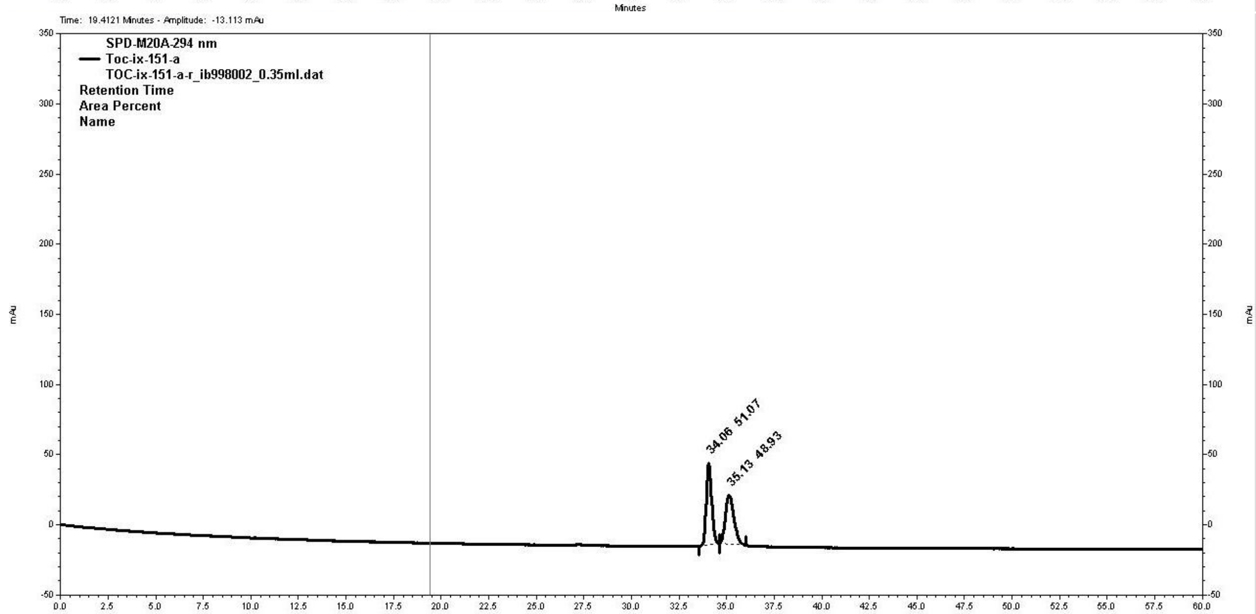


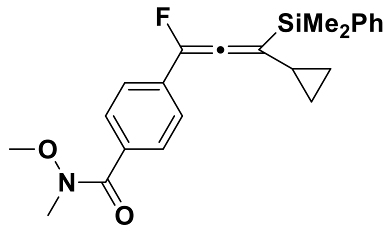




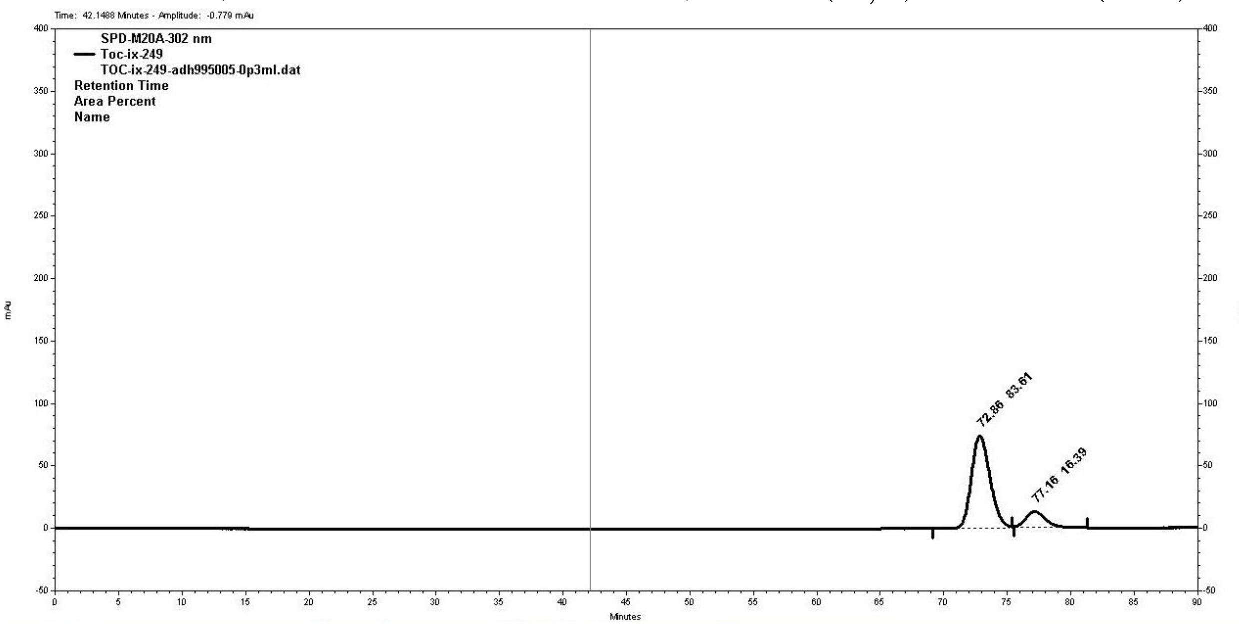
26b: IB column, 0.35 mL/min: hexanes:iPrOH 99.8:00.2; 36.20 min (major) and 37.59 min (minor)

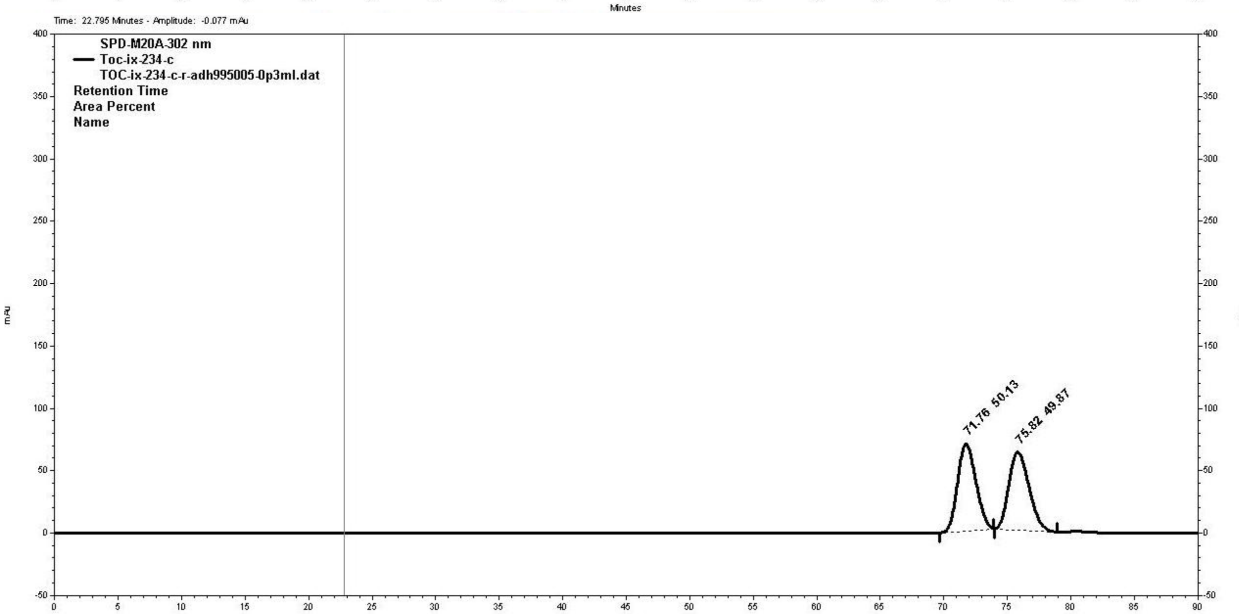


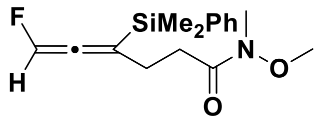




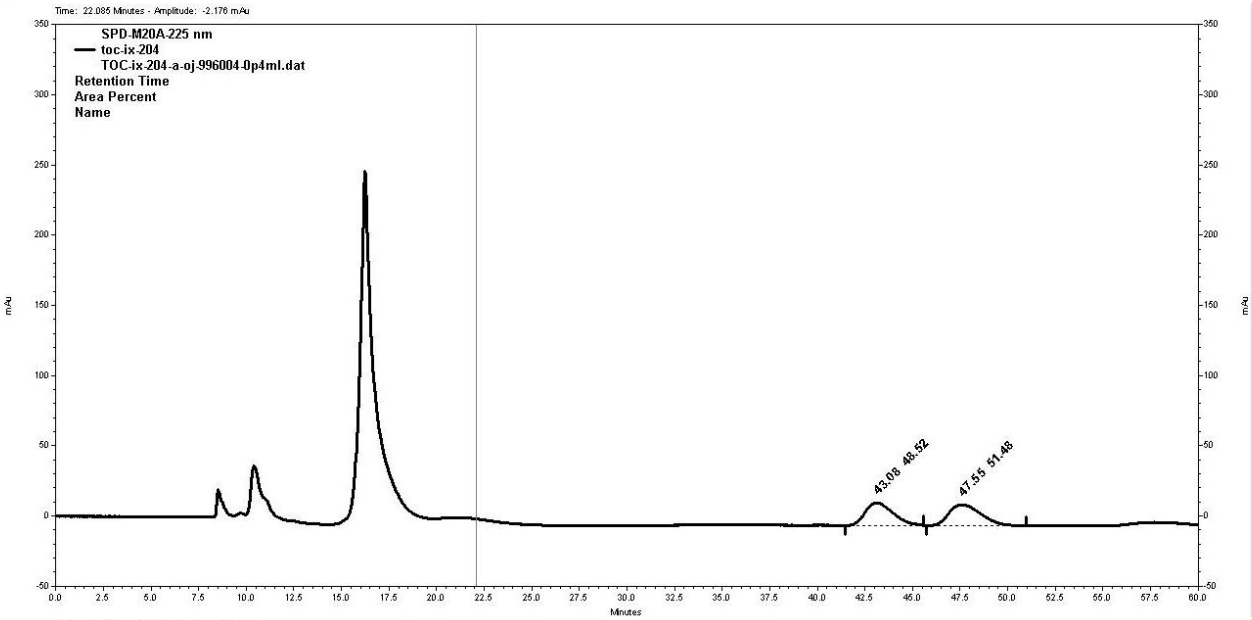
27b: ADH column, 0.3 mL/min: hexanes:iPrOH 99.8:00.2; 72.86 min (major) and 77.16 min (minor)

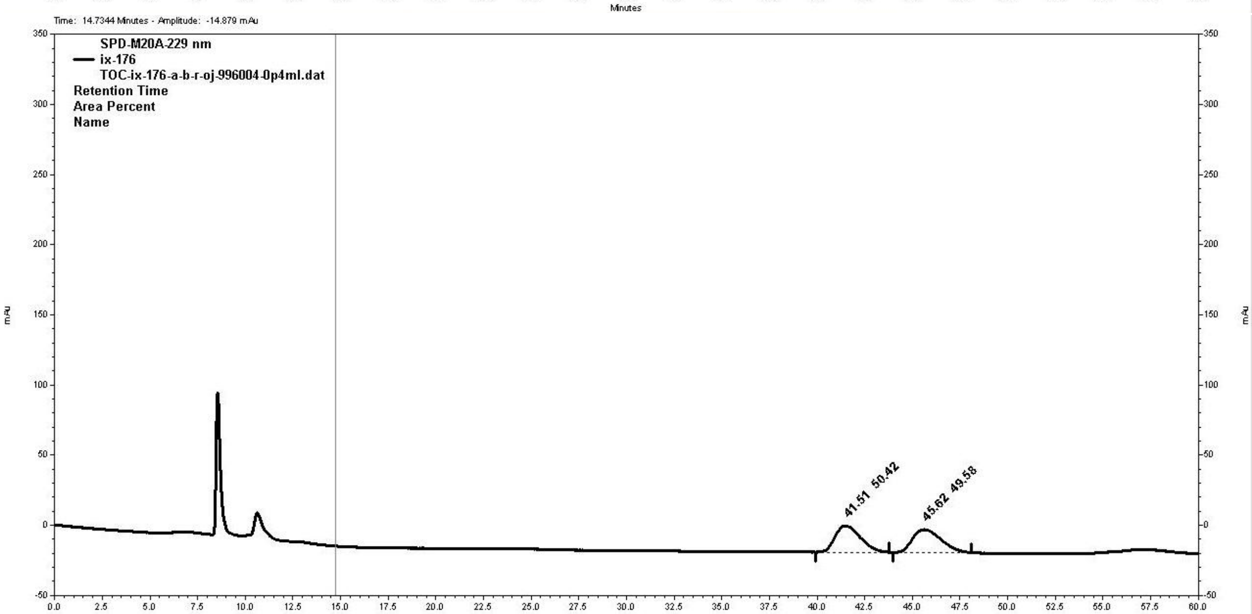


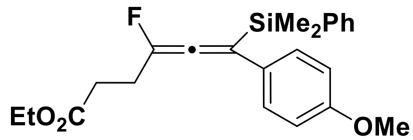




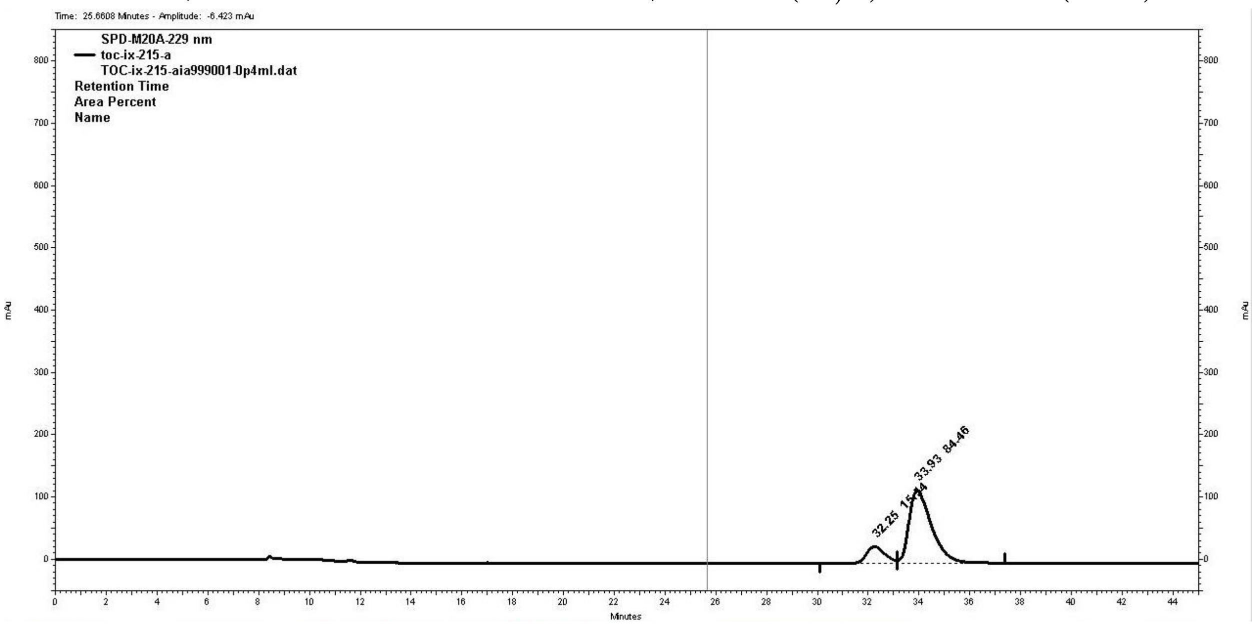
28b: OJ column, 0.4 mL/min: hexanes:iPrOH 99.6:00.4; 47.55 min (major) and 43.08 min (minor)

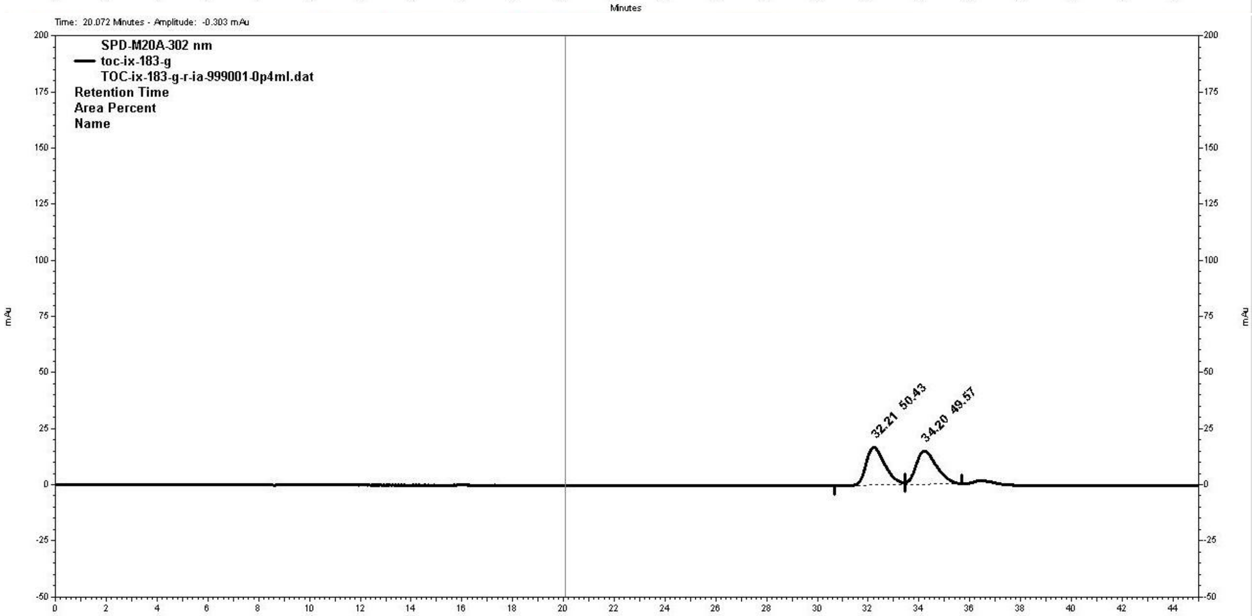


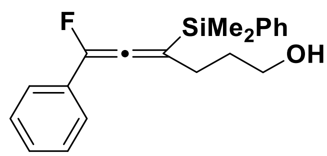




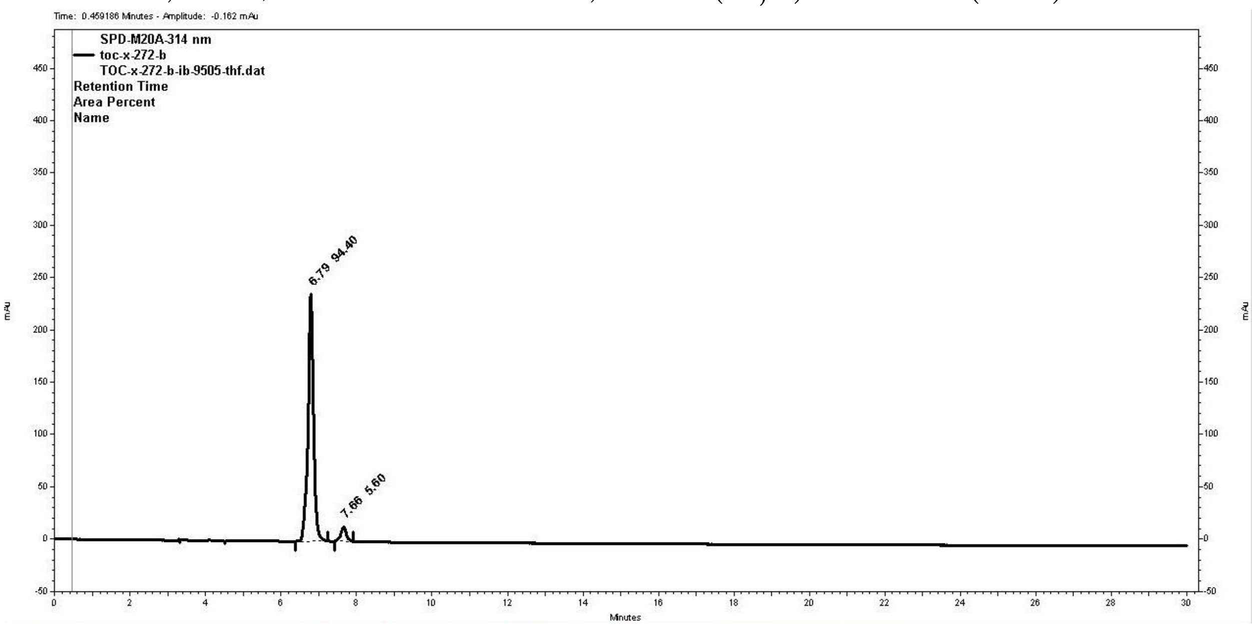
29b: IA column, 0.4 mL/min: hexanes:iPrOH 99.6:00.4; 33.93 min (major) and 32.25 min (minor)

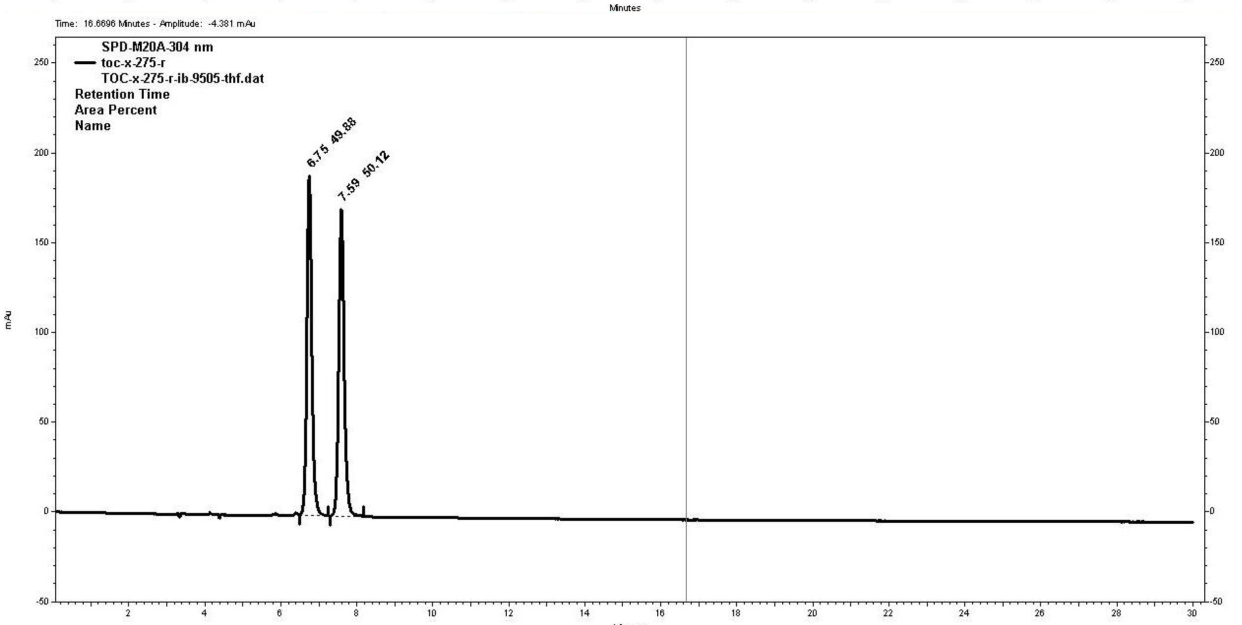


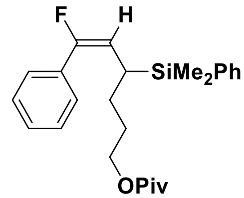




1c: IB column, 1.0 mL/min: hexanes:iPrOH 95:05; 6.79 min (major) and 7.66 min (minor)







2c: OJ column, 1.0 mL/min: hexanes:iPrOH 99.9:00.1; 39.28 min (major) and 45.02 min (minor)