Supporting Information for

Regioselective C−F Bond Transformations of Silyl Difluoroenolates

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General Information

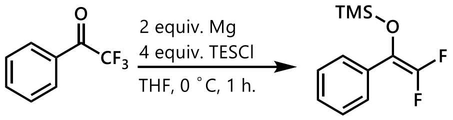
All reactions were performed under an atmosphere of nitrogen (1 atm) unless otherwise stated. Solvents were also purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (4Å MS). All other reagents were purified by standard procedures. Medium pressure column chromatography was carried out on a Biotage Flash Purification System Isolera One equipped with a 254 and 280 nm UV detector. The reaction mixture was heated by using an oil bath.

^{1}H NMR spectroscopy was recorded on Bruker Avance III 400 NMR spectrometer. Chemical shifts are reported in ppm from the solvent resonance as an internal standard ($CDCl_3$: δ= 7.26 ppm or C_6D_5H: δ= 7.16 ppm or THF-d_8: δ= 3.58 ppm). NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ^{19}F NMR spectroscopy was recorded on Bruker Avance III 400 NMR spectrometer. Chemical shifts are reported in ppm from the solvent resonance as an internal standard ((trifluoromethyl)cyclohexane: δ= −76.99 ppm or hexafluorobenzene: δ= −164.90 ppm).^{13}C NMR spectroscopy was recorded on Bruker Avance III 400 NMR spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the internal reference ($CDCl_3$: δ= 77.00 ppm). High-resolution mass spectrometry was performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. A single-crystal x-ray diffraction analysis was carried out using the Rigaku XtaLAB Synergy equipped with the HyPix-6000HE detector.

Experimental Details

Preparation of starting materials

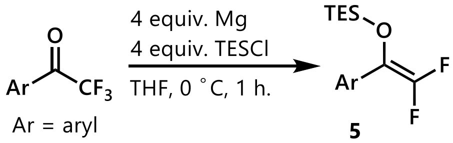
Synthesis of 1[1a]



1, 84%

To a dry 100 mL flask was placed magnesium turning (0.58 g, 24 mmol). The flask was heated using a heat gun under vacuum and was backfilled with N_2. Dry THF (40 mL) and freshly distilled TMSCl (6.11 mL, 48 mmol) were added, and the reactor was cooled with an ice bath. To the suspension was added α,α,α-trifluoroacetophenone (1.63 mL, 12 mmol) via a syringe. After the mixture was stirred at 0 °C for 1 h, all volatiles were removed under reduced pressure. Then, hexane was added to the residue to cause precipitation of magnesium salts which were removed by filtration through a short Celite pad. After drying under reduced pressure, the crude material was purified by Kugelrohr distillation to afford the **1** as a colorless oil (2.31 g, 10.1 mmol, 84 %).

General Procedure (GP1) for preparation of 5

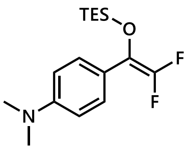


Ar = aryl

5

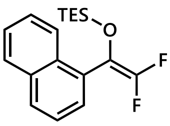
To a dry 100 mL flask was placed magnesium turnings (4 equiv.). The flask was heated using a heat gun under vacuum and was backfilled with N_2. Dry THF (0.33 M) and TESCl (4 equiv.) were added, and the reactor was cooled with an ice bath. To the suspension was added α,α,α-trifluoroacetophenone (1 equiv.) via a syringe. After the mixture was stirred at 0 °C for 1 h, all volatiles were removed under reduced pressure. Then NEt_3 was added to the crude product and stirred for 10 min. Addition of hexane caused precipitation of magnesium salts which were removed through a short Celite column. After drying under reduced pressure, the crude material was purified by silica gel column chromatography (3% of NEt_3 in hexane). Ar = Ph (**5a**), 4-tol (**5s**), 4-methoxyphenyl (**5t**), 4-fluorophenyl (**5v**), 2-naphthalene (**5w**) are known compounds and the spectrum data matched to that of reported ones. [1b,c]

5u



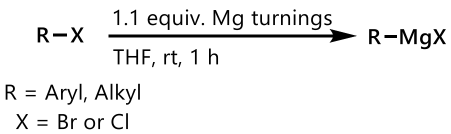
The reaction was performed at 3 mmol scale to afford **5u** in 37 % yield (0.35 g, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.32–7.30 (m, 2H), 7.24–7.22 (m, 3H), 7.18 (s, 5H), 0.96 (t, *J* = 7.9Hz, 9H), 0.55 (q, *J* = 8.1Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –106.8 (d, *J* = 76.4 Hz, 1F), –118.4 (d, *J* = 76.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 154.1 (t, *J* = 284.0 Hz), 149.9, 127.1 (dd, *J* = 3.3, 5.9 Hz), 120.4 (d, *J* = 6.9 Hz), 114.3 (dd, *J* = 18.4, 35.2 Hz), 111.8, 40.3 (q, *J* = 5.2 Hz), 6.5, 4.9. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}NOF_2Si$, 314.1746; found, 314.1751.

5x



The reaction was performed at 3 mmol scale to afford **5u** in 12 % yield (0.18 g, colorless oil).117.2 mg, ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18 (d, *J* = 8.23 Hz, 1H), 7.88 (d, *J* = 8.06 Hz, 2H), 7.56–7.45 (m, 4H), 0.83 (t, *J* = 7.95 Hz, 9H), 0.51 (q, *J* = 7.97 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ): –104.97 (d, *J* = 70.9 Hz, 1F), –115.09 (d, *J* = 72.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.6 (t, *J* = 277.6 Hz, 286.7 Hz), 133.8, 131.6 (d, *J* =2.35 Hz), 130.0 (q, *J* =2.33 Hz), 129.1 (d, *J* =127.04 Hz), 127.7, 126.5, 126.2, 126.0, 125.1, 113.2 (q, *J* =23.22 Hz), 6.4, 4.9. HRMS (EI): m/z $[M-H]^+$ calcd for $C_{18}H_{22}F_2OSi$, 320.1408 ; found, 320.1408.

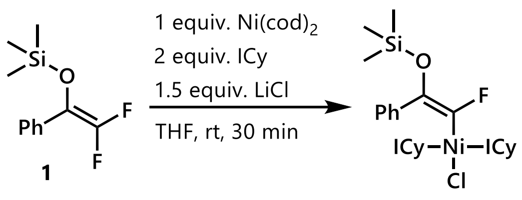
General Procedure (GP2) for preparation of Grignard reagent



A dry 50 mL two-necked flask equipped with a condenser was charged with magnesium turnings (0.16 g, 6.6 mmol) which was heated using a heat gun under vacuum. The flask was evacuated and backfilled with N_2 three times. Aryl bromide (6 mmol) in THF (6 mL) was added slowly with a syringe and stirred for 1 h. The concentration of the Grignard reagent was determined by titration.[2] All Grignard reagents were prepared in the same way.

Stoichiometric Reactions Using Ni(cod)₂

Synthesis of 2a



In the glove box, a solid mixture of Ni(cod)$_2$ (27.69 mg, 0.1 mmol), ICy (46.13 mg, 0.2 mmol) were added to THF in a screw test tube with a stir bar and the solution was stirred for several minutes. Then LiCl (6.21 mg, 0.15 mmol) was added to the solution and cooled to −20°C. Then, to the cold solution was added **1** (22.0 µL, 0.1 mmol) and gradually warmed to room temperature with stirring. After 30 minutes, all volatiles were removed under reduced pressure, and the residue was mixed with hexane and filtered. The desired product was reprecipitated using toluene/pentane, affording **(*E*)–2a** as a yellow solid (19.28 mg, 0.24 mmol, 24%). Single crystals for X-ray diffraction analysis were prepared by recrystallization from toluene/hexane at −35°C.

^{1}H NMR (400 MHz, CD_2Cl_2, δ/ppm): 7.99 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.85 (s, 4H), 5.68 (br, 4H), 2.56 (d, J = 11.6 Hz, 4H), 2.05-1.25 (m, 36H), −0.14 (s, 9 H). ^{19}F NMR (376 MHz, CD_2Cl_2, δ/ppm): –83.14 (s, 1F). ^{13}C NMR (100 MHz, CD_2Cl_2, δ/ppm): 176.2, 161.4 (d, J = 310.0 Hz), 140.3 (d, J = 15.5 Hz), 140.0 (d, J = 7.2 Hz), 128.0, 125.1, 124.8 (d, J = 2.5 Hz), 117.3, 117.2, 59.7, 35.4, 33.6, 26.5, 26.3, 26.0, 0.2. HRMS (EI): m/z $[M-H]^+$ calcd for $C_{41}H_{62}{}^{35}ClFN_4{}^{58}NiOSi$, 765.3635; found, 765.3656. Crystal Data for $C_{41}H_{62}ClFN_4NiOSi\cdot C_7H_8$ (M = 860.33 g/mol): Monoclinic, yellow, space group $P2_1/c$ (#14), a = 13.4345(4) Å, b = 29.7954(7) Å, c = 12.3795(4) Å, β = 110.828(4), V = 4631.5(3) Å^3, Z = 4, D_{calcd} = 1.234 g/cm^3, T = 123.15 K, R_1 (wR_2) = 0.049 (0.110).

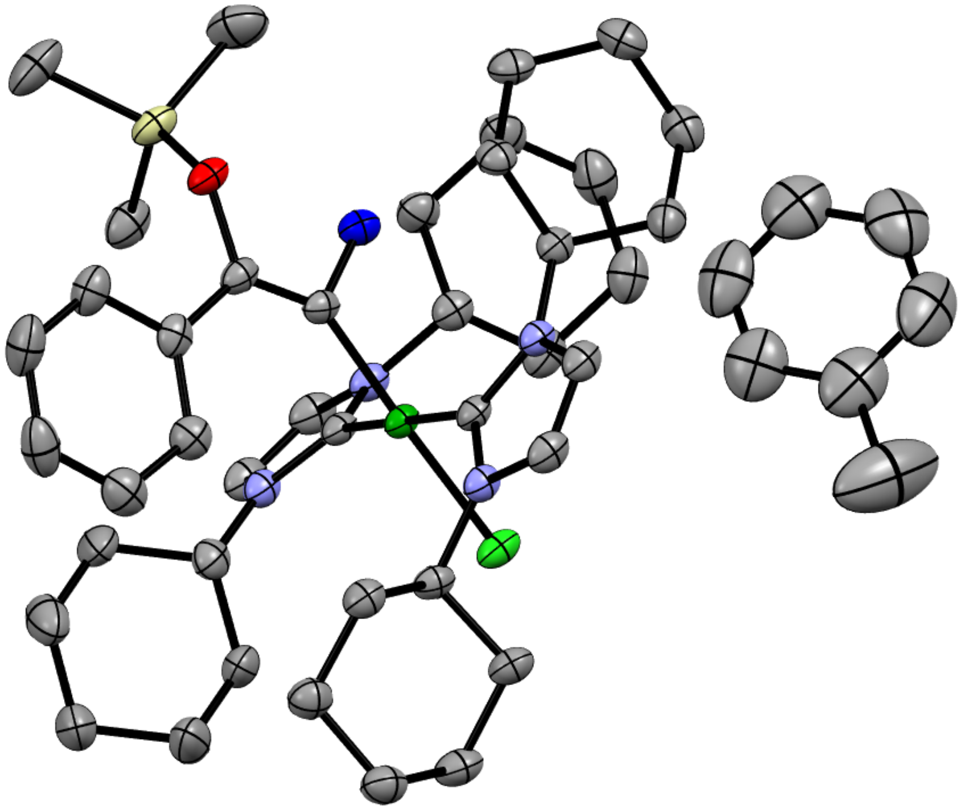
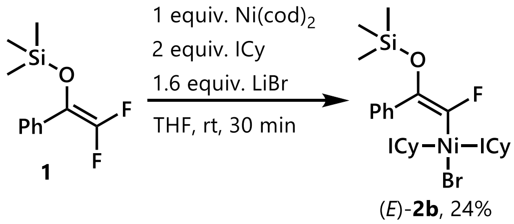


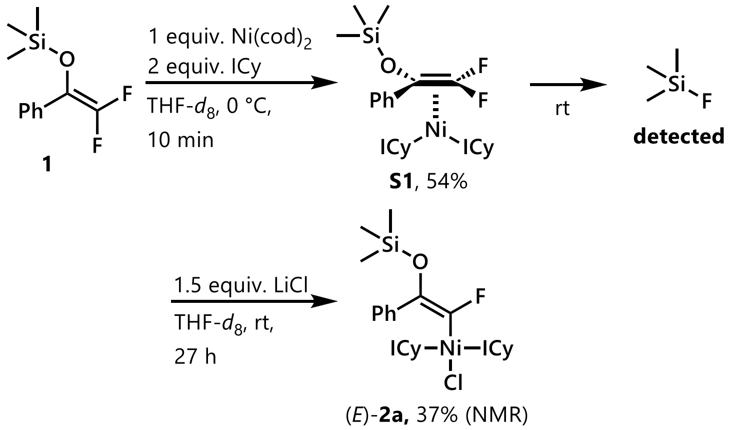
Figure S1. The thermal ellipsoid plot of 2a with 50% probability level.

Synthesis of 2b



The title compound was prepared in the same manner as that of **2a**. The reaction of $Ni(cod)_2$ (27.51 mg, 0.1 mmol), ICy (46.03 mg, 0.2 mmol), LiBr (14.05 mg, 0.16 mmol) and **1** (22.0 μL, 0.1 mmol) afforded **(*E*)–2b** as a yellow solid (19.50 mg, 0.24 mmol, 24%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ/ppm): 7.88 (d, J = 7.3 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 6.86 (s, 4H), 5.69 (br, 4H), 2.58 (d, J = 12.0 Hz, 4H), 1.95-1.27 (m, 36H), −0.15 (s, 9H). ^{19}F NMR (376 MHz, CD_2Cl_2, δ/ppm): –83.8 (s, 1F). ^{13}C NMR (100 MHz, CD_2Cl_2, δ/ppm): 175.9, 162.1 (d, J = 313 Hz), 140.9 (d, J = 15.8 Hz), 140.1 (d, J = 7.0 Hz), 128.0, 125.3, 125.2, 117.5, 117.4, 59.8, 35.1, 33.6, 26.5, 26.4, 25.9, 0.19. HRMS (EI): m/z $[M-H]^+$ calcd for $C_{41}H_{62}BrFN_4NiOSi$, 809.3130; found, 809.3131.

Reaction of 1 with Ni(cod)₂/ICy without Li salt

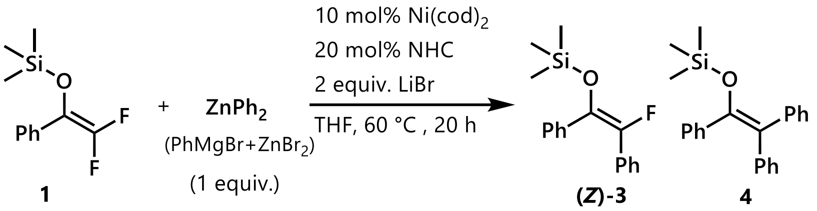


Scheme S1. Reaction of 1 without Li salt

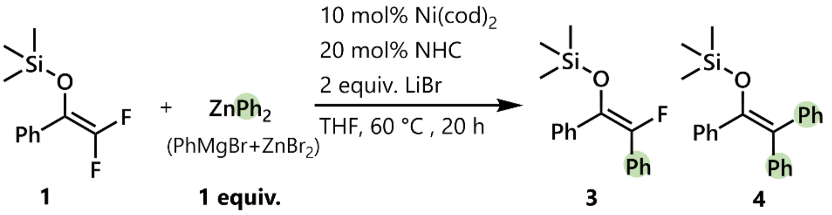
In the glove box, a solid mixture of Ni(cod)$_2$ (10.98 mg, 0.04 mmol), ICy (18.42 mg, 0.08 mmol) and 1,3,5-trimethoxybenzene (internal standard for ^{1}H NMR) were added to THF-d_8 in a screw test tube containing a stirring bar and the solution was stirred for several minutes. After the solution was cooled to 0 °C, **1** (10.14 mg, 0.044 mmol) and (trifluoromethyl)cyclohexane (internal standard for ^{19}F NMR) were added and stirring for 10 minutes. The solution was transferred into a J. Young NMR tube. ^{19}F NMR analysis showed a set of signals at –98.70 (d, J = 172.4 Hz, 1F) and –114.65 (d, J = 172.8 Hz, 1F) which were assigned to η^2-complex **S1**. This complex was decomposed with releasing trimethylsilyl fluoride at room temperature. When the solution prepared in another experiment was brought to the glove box again and LiCl (2.62 mg, 0.06 mmol) was added to it, **2a** was observed in 37% NMR yield.

Screening of NHC ligands

General Procedure (GP3) for preparation of diaryl zinc



$ZnBr_2$ (9.01 mg, 0.04 mmol) and LiBr (6.94 mg, 0.08 mmol) was mixed in THF charged in a vial containing a stirring bar. To the resulting solution was added PhMgBr solution (0.08 mmol based on titration using menthol and 1,10-phenanthroline) with stirring for 30 min at room temperature. The resulting solution containing diaryl zinc was used without titration.



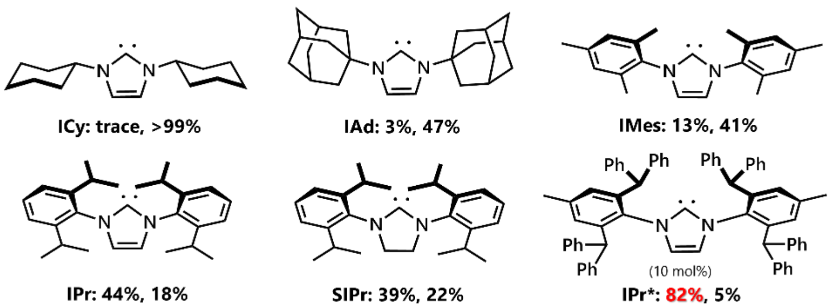
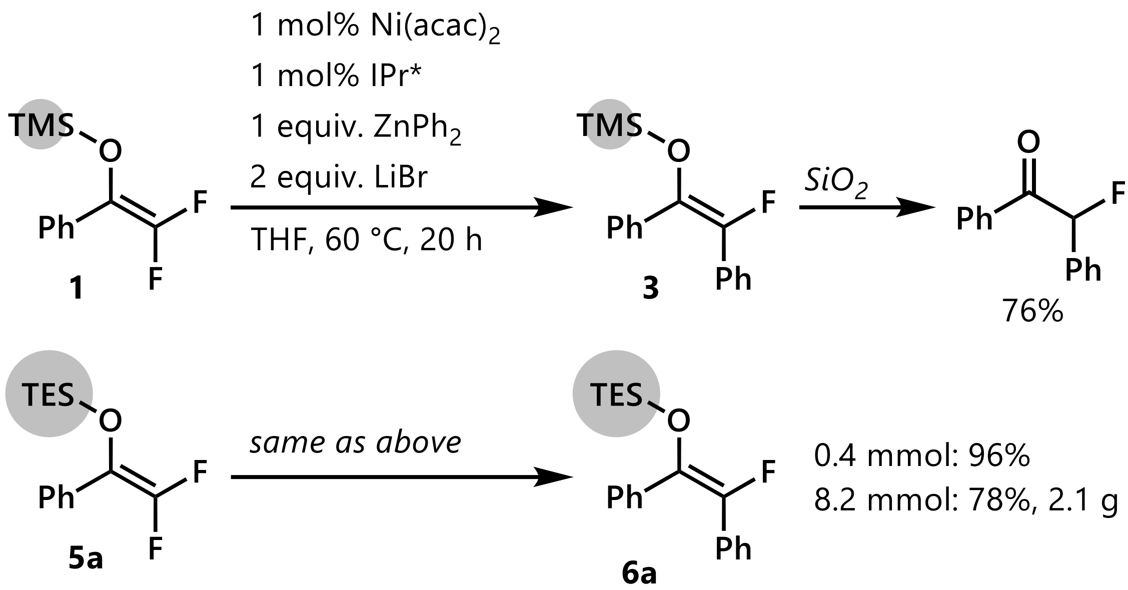


Figure S2. Result of screening of NHC ligands

$Ni(cod)_2$ (1.10 mg, 0.004 mmol), NHC ligand and 1,3,5-trimethoxybenzene (internal standard) were added to THF charged in a screw-capped test tube. Then, the $ZnPh_2$ solution prepared by following GP3 and **1** (8.8 μL, 0.04 mmol) was added. The tube was tightly capped and took out of the glove box. The reaction mixture was heated at 60 °C for 20 hours. The solution was brought to the glove box again, and (trifluoromethyl)cyclohexane as an internal standard and C_6D_6 were added. The solution was transferred into J. Young tube to determine the yields of **(*Z*)–3** and **4**. The results are summarized in Figure S1. The structure of products **(*Z*)–3** and **4** were estimated by ^{1}H NMR, ^{19}F NMR, GC-MS analysis. The geometric structure of **3** was estimated by ^{19}F NMR referring to the known analogues.[3]

Control experiments and further optimization were performed in the same manner. Isolated $ZnPh_2$ was prepared by following the literature.[4]

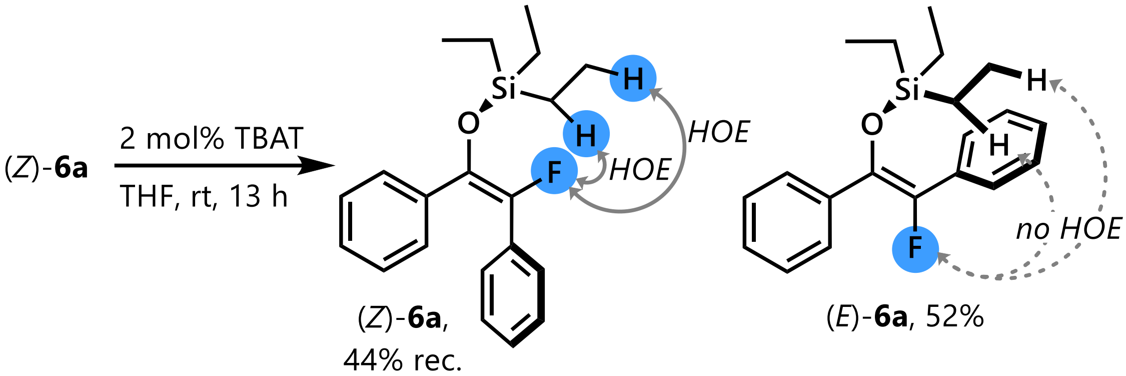
Trial for isolation of 3



Scheme S2. Isolation of silyl enolate using column chromatography

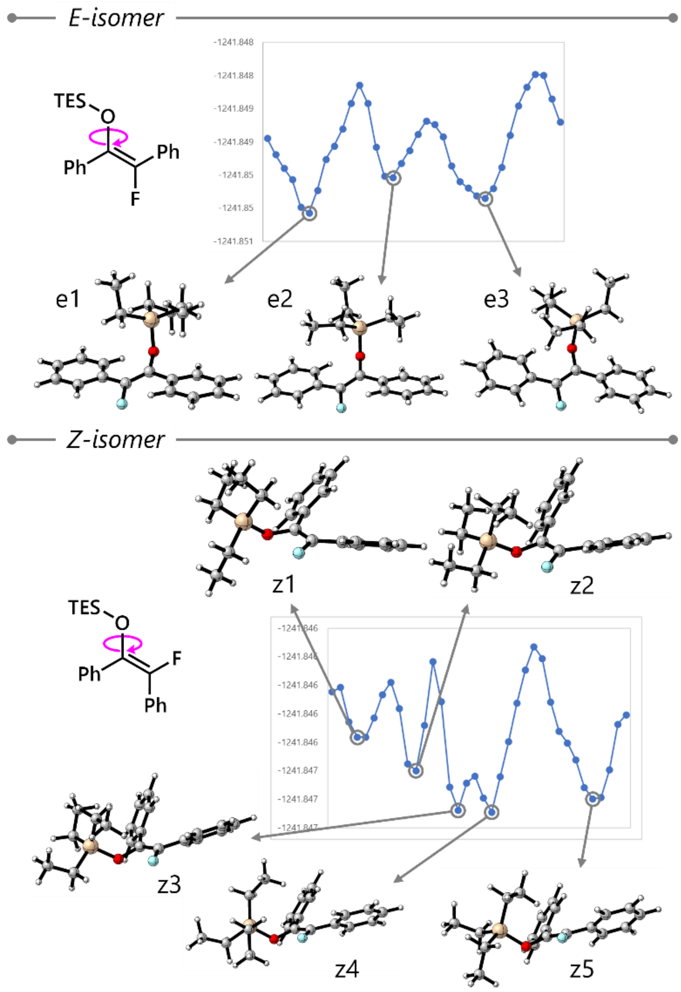
$Ni(acac)_2$ (1.05 mg, 0.004 mmol), IPr* (3.73 mg, 0.004 mmol) were added to THF charged in a screw-capped test tube. Then, the $ZnPh_2$ solution prepared by following GP3 and **1** (86.42 mg, 0.38 mmol) was added. The tube was tightly capped and took out of the glove box. The reaction mixture was heated at 60 °C for 20 hours. The solution was poured into hexane and precipitated metal salts were removed. Solvent was removed by evaporation. The crude mixture was purified by silica-gel column chromatography (0.5% of NEt_3 in hexane) to afford 2-fluoro-1,2-diphenylethan-1-one as a colorless oil (62.1 mg, 0.29 mmol, 76%). The spectrum data matched to that of previous report.[5]

Determination of geometry of 6a



Scheme S3. Isomerization of (*Z*)-6a and summary of ^{1}H-^{19}F HOESY

Table S1. H−F Bond lengths of rotamers

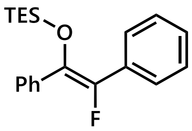


Conformer	The shortest distance (Å)	
	CH_2−F	CH_3−F
e1	4.05	4.87
e2	4.09	4.16
e3	4.25	3.62
Average for *E*-isomer:	4.13	4.21
z1	2.57	3.79
z2	2.64	2.41
z3	3.7	2.32
z4	2.58	2.56
z5	3.63	2.35
Average for *Z*-isomer:	3.02	2.69

The geometry of enolate moiety was determined by NMR. First, we treated isolated (*Z*)-**6a** with a catalytic amount of tetrabutylammonium difluorotriphenylsilicate (TBAT). As a result, isomerization of enolate occurred to give an equilibrium mixture of (*Z*)-**6a**:(*E*)-**6a** = 1:1.2 within 13 h. Both isomers of **6a** were analyzed by ^{1}H-^{19}F heteronuclear Overhauser effect spectroscopy (HOESY). The isomer obtained by our reaction ((*Z*)-**6a**) showed HOE between methylene and methyl protons of TES and fluorine while the isomer prepared by isomerization with TBAT showed no cross peaks. The assignment was corroborated by DFT calculations (for conditions, see "Computational Details" part). We scanned each isomer by rotating around C−O bond axis by 10° to find local minimum structures which were then optimized. The averages of shortest CH_2-F and CH_3-F distances of local minimum structures were 3.02 and 2.69 for *Z* isomer, and 4.13 and 4.22 for *E* isomer, respectively (Table S1). These calculations are in good agreement with the assignment of *E*/*Z* isomers by the absence and the presence of HOE between CH_2-F and CH_3-F. It is also worth noting that isomerization of **6a** indicate that our reaction is kinetically controlled to furnish the *Z* isomer selectively.

[Experimental Procedure] In the glove box, to a toluene (1 mL) solution of (*Z*)-**6a** (262.8 mg, 0.8 mmol) was added TBAT (8.6 mg, 0.016 mmol, 2 mol%) and the solution was stirred for 19 h. Toluene was evaporated in the glove box, and the residue was suspended in hexane which was then filtered through a pad of celite. The crude NMR yield was determined and 50 mg of the crude was used for HOESY. The residual crude was purified by column chromatography outside the glove box (hexane/(EtOAc/$CHCl_3$)=99/1 to 90/10) to afford (*E*)-**6a** (86.5 mg, 0.29 mmol, 37%) and (*Z*)-**6a** (81.6 mg, 0.28 mmol, 35%) both as colorless oil.

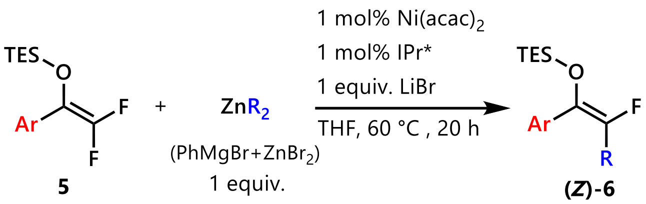
(*E*)-6a



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.90 (d, J = 7.4Hz, 2H), 7.69 (d, J = 8.2Hz, 2H), 7.46-7.42 (m, 4H), 7.39-7.32 (m, 2H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.51(q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –148.56 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 147.4 (d, *J* = 230.5 Hz), 137.9 (d, *J* = 41.8 Hz), 135.9 (d, *J* = 4.3 Hz), 132.3 (d, *J* = 26.1Hz), 128.2, 128.1, 127.9, 127.8, 127.7, 126.2 (d, *J* = 6.8 Hz), 6.5, 5.1. HRMS (EI): m/z $[M]^+$ calcd for $C_{20}H_{25}OFSi$, 328.1653; found, 328.1662.

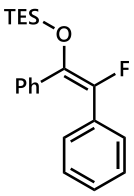
Cross-coupling reactions of silyl difluoroenolate 5

General Procedure (GP4):



In the glove box, $Ni(acac)_2$ (1.01 mg, 0.004 mmol) and IPr* (3.65 mg, 0.004 mmol) were added THF (0.5 mL) into a screw test tube. Then, the $ZnAr_2$ solution (1.5 mL) prepared by GP3 was transferred into the tube, and silyl difluoroenolate **5** (0.4 mmol) was added. The tube was tightly sealed and was heated at 60 °C for 20 hours. The reaction mixture was poured into hexane. The resulting suspension was filtered to remove metal salts. Then, the solvents were removed by evaporation under reduced pressure. The crude material was purified by silica gel column chromatography (typically, 2-3% of NEt_3 in hexane) to afford the corresponding silyl fluoroenolate **6**.

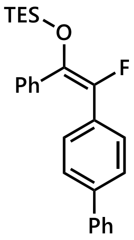
(*Z*)–6a



The reaction was conducted with 0.71M Grignard reagent solution in accordance with **GP1**. The product **6a** was obtained as a colorless oil (23.5 mg, 0.39 mmol, 96%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.24 (dd, *J* = 1.3, 9.1 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 2.87 (s, 6H), 0.84 (t, *J* = 4.5 Hz, 9H), 0.68 (q, *J* = 7.9Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –128.78 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.5 (d, *J* = 237.0 Hz), 136.0 (d, *J* = 2.3 Hz), 135.8 (d, *J* = 19.2 Hz), 132.3 (d, *J* = 25.7 Hz), 129.1 (d, *J* = 3.7 Hz), 128.3, 128.1, 127.9, 127.8, 127.8, 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{20}H_{25}OFSi$, 328.1653; found, 328.1663.

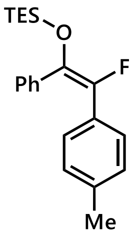
The reaction was also performed at 8 mmol scale to afford (*Z*)-**6a** in 2.1 g (78% yield).

(*Z*)–6b



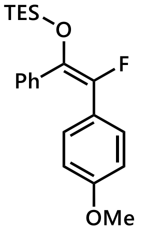
The reaction was conducted with 0.80M corresponding Grignard reagent solution in accordance with **GP1**. The product **6b** was obtained as a yellow oil (123.5 mg, 0.30 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.56 (d, *J* = 7.5 Hz, 2H), 7.43-7.23 (m, 14H), 0.97 (t, *J* = 7.9Hz, 9H), 0.68 (q, *J* = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –129.75 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.2 (d, *J* = 236.8 Hz), 140.33, 140.32, 136.1 (d, *J* = 2.9 Hz), 136.0 (d, *J* = 19.8 Hz), 131.3 (d, *J* = 25.8 Hz), 129.1 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 5.2 Hz), 128.7, 128.3, 128.2, 127.4, 126.9, 126.6, 6.6, 5.2 (d, *J* = 1.6 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{26}H_{29}OFSi$, 404.1966; found, 404.1958.

(*Z*)–6c



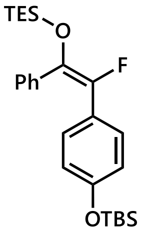
The reaction was conducted with 0.94M corresponding Grignard reagent solution in accordance with **GP1**. The product **6c** was obtained as a yellow oil (95.0 mg, 0.28 mmol, 69%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.32-7.30 (m, 2H), 7.24-7.22 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H), 0.96 (t, *J* = 8.0Hz, 9H), 0.68 (q, *J* = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –127.76 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.6 (d, *J* = 237.8 Hz), 137.8 (d, *J* = 1.4 Hz), 136.2 (d, *J* = 2.9 Hz), 135.2 (d, *J* = 19.9 Hz), 129.4 (d, *J* = 25.8 Hz), 129.0 (d, *J* = 2.9 Hz), 128.7, 128.1, 128.0, 127.8 (d, *J* = 4.4 Hz), 21.2 (q, *J* = 3.7 Hz), 6.6, 5.2 (d, *J* = 1.4 Hz). HRMS (EI): m/z $[M+H]^+$ calcd for $C_{21}H_{28}OFSi$, 343.1888; found, 343.1888.

(*Z*)–6d



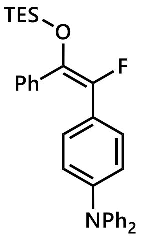
The reaction was conducted with 0.98M corresponding Grignard reagent solution in accordance with **GP1**. The product **6d** was obtained as a colorless oil (98.4 mg, 0.28 mmol, 69%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.31-7.28 (m, 2H), 7.22-7.21 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 3H), 0.96 (t, *J* = 7.9Hz, 9H), 0.67 (q, *J* = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –126.21 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 159.3, 146.5 (d, *J* = 238.6 Hz), 136.2 (d, *J* = 3.0 Hz), 134.5 (d, *J* = 19.9 Hz), 129.4 (d, *J* = 4.3 Hz), 128.9 (d, *J* = 3.0 Hz), 128.0, 127.9, 124.8 (d, *J* = 26.4 Hz), 113.5, 55.1 (q, *J* = 7.3 Hz), 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{27}O_2FSi$, 358.1759; found, 358.1744.

(*Z*)–6e



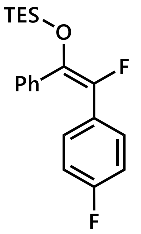
The reaction was conducted with 0.47M corresponding Grignard reagent solution in accordance with **GP1**. The product **6e** was obtained as a colorless oil (129.1mg, 0.28 mmol, 69%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.26-7.29 (m, 2H), 7.19-7.22 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.3 Hz, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.95 (s, 9H), 0.67 (q, *J* = 8.0 Hz, 6H), 0.16 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –126.16 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 155.4 (d, *J* = 1.4 Hz), 146.4 (d, *J* = 237.8 Hz), 136.1 (d, *J* = 2.9 Hz), 134.4 (d, *J* = 20.7 Hz), 129.3 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 3.0 Hz), 127.8, 127.4, 125.3 (d, *J* = 26.4 Hz), 119.5 (d, *J* = 3.9 Hz), 65.6, 25.4, 15.0 (d, *J* = 3.0 Hz), 6.3, 5.0. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{26}H_{39}O_2FSi_2$, 459.2545; found, 459.2563.

(*Z*)–6f



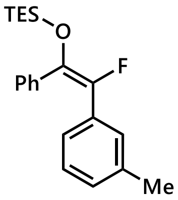
The reaction was conducted with 0.14M corresponding Grignard reagent solution in accordance with **GP1**. The product **6f** was obtained as a yellow oil (79.2 mg, 0.16 mmol, 39%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.36-7.34 (m, 2H), 7.26-7.22, m, 6H), 7.08-7.00 (m, 9H), 6.85 (d, *J* = 8.5Hz, 2H), 0.96 (t, *J* = 7.9Hz, 9H), 0.67 (q, J = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –128.39 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 147.5 (d, *J* = 33.6 Hz), 147.3 (d, *J* = 1.4 Hz), 147.3, 146.5 (d, *J* = 236.7 Hz), 136.3 (d, *J* = 2.9 Hz), 134.9 (d, *J* = 20.6 Hz), 129.3, 129.0 (d, *J* = 3.3 Hz), 128.5 (d, *J* = 4.3 Hz), 128.1, 125.6 (d, *J* = 26.4 Hz), 124.8, 123.2, 122.0, 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M+H]^+$ calcd for $C_{32}H_{35}NOFSi$, 496.2467; found, 496.2468.

(*Z*)–6g



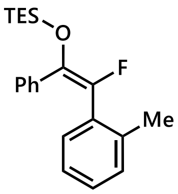
The reaction was conducted with 0.84M corresponding Grignard reagent solution in accordance with **GP1**. The product **6g** was obtained as a colorless oil (109.1 mg, 0.32 mmol, 77%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.30-7.35 (m, 5H), 7.17-7.13 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.67 (q, J = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –116.18- –116.27 (m, 1F), 128.11 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 162.2 (dd, *J* = 1.7, 248.2 Hz), 145.7 (d, *J* = 237.2 Hz), 135.9 (d, *J* = 2.3 Hz), 135.7 (d, *J* = 20.3 Hz), 129.8 (d, *J* = 4.3 Hz), 129.7 (d, *J* = 4.4 Hz), 129.0 (d, *J* = 2.9 Hz), 128.4, 128.2, 115.1 (d, *J* = 21.8 Hz), 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{20}H_{24}OF_2Si$, 346.1559; found, 346.1560.

(*Z*)–6h



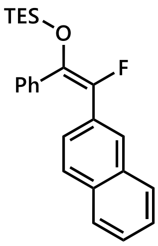
The reaction was conducted with 0.87M corresponding Grignard reagent solution in accordance with **GP1**. The product **6h** was obtained as a yellow oil (123.0 mg, 0.36 mmol, 90%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.31–7.30 (m, 2H), 7.24-7.22 (m, 3H), 7.06-6.99 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.23 (s, 3H), 0.96 (t, *J* = 7.9Hz, 9H), 0.68 (q, J = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –128.38 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 144.6 (d, *J* = 237.2 Hz), 137.6, 136.1 (d, *J* = 2.3 Hz), 135.6 (d, *J* = 19.9 Hz), 132.2 (d, *J* = 24.8 Hz), 129.0 (d, *J* = 2.9 Hz), 128.6, 128.3, 128.2, 128.0, 127.8, 125.1 (d, *J* = 5.1 Hz), 21.3 (q, *J* = 2.9 Hz), 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{27}OFSi$, 342.1810; found, 342.1806.

(*Z*)–6i



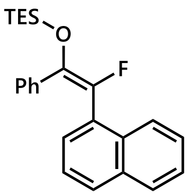
The reaction was conducted with 0.90M corresponding Grignard reagent solution in accordance with **GP1**. The product **6i** was obtained as a yellow oil (114.0 mg, 0.33 mmol, 83%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.24-7.18 (m, 2H), 7.12-7.09 m, 6H), 7.05-7.00 (m, 1H), 2.29 (d, *J* = 2.5 Hz, 3H), 0.99 (t, *J* = 7.9Hz, 9H), 0.75 (q, J = 7.9Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –119.18 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.3 (d, *J* = 242.1 Hz), 138.2, 136.0, 135.8 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 23.1 Hz), 131.4 (d, *J* = 2.2 Hz), 130.3 (d, *J* = 1.5 Hz), 129.2 (d, *J* = 2.3 Hz), 128.0 (d, *J* = 2.9 Hz), 127.7, 127.6, 125.7, 19.8 (m), 6.6, 5.2 (d, *J* = 1.4 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{27}OFSi$, 342.1810; found, 342.1822.

(*Z*)–6j



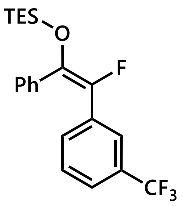
The reaction was conducted with 0.80M corresponding Grignard reagent solution in accordance with **GP1**. The product **6j** was obtained as a yellow oil (112.9 mg, 0.30 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.78-7.12 (m, 12H), 0.99 (t, *J* = 7.8Hz, 9H), 0.71 (q, *J* = 7.9Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –128.85 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.6 (d, *J* = 237.2 Hz), 136.3 (d, *J* = 19.9 Hz), 136.0 (d, *J* = 3.0 Hz), 133.0, 132.7, 129.9, 129.7, 129.2 (d, *J* = 3.0 Hz), 128.4, 128.2, 127.4 (d, *J* = 25.4 Hz), 126.7 (d, *J* = 2.1 Hz), 126.7 (d, *J* = 8.0 Hz), 126.3, 126.2, 125.5 (d, *J* = 4.2 Hz), 6.6, 5.3 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{24}H_{27}OFSi$, 378.1810; found, 378.1820.

(*Z*)–6k



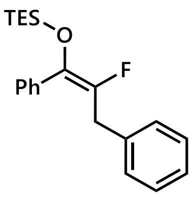
The reaction was conducted with 0.21M corresponding Grignard reagent solution in accordance to **GP1**. The NMR yield of crude reaction mixture was 45%. The product **6k** was obtained as a yellow oil (11.1 mg, 0.03 mmol, 7%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.13-8.10 (m, 1H), 7.88-7.81 (m, 2H), 7.58-7.50 (m, 2H), 7.28 (d, *J* = 5.8Hz, 2H), 7.12-7.01 (m, 5H), 1.04 (t, *J* = 7.8Hz, 9H), 0.79 (q, *J* = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –118.3 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 145.9 (d, *J* = 240.8 Hz), 137.2 (d, *J* = 19.5 Hz), 135.7 (d, *J* = 2.2 Hz), 133.7 (d, *J* = 1.5 Hz), 132.2, 130.1 (d, *J* = 3.7 Hz), 129.8 (d, *J* = 22.7 Hz), 129.8, 128.4, 128.0 (d, *J* = 2.8 Hz), 127.7, 127.6, 126.7, 126.1, 125.5, 125.3 (d, *J* = 1.4 Hz), 6.7, 5.3 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{24}H_{27}OFSi$, 378.1810; found, 378.1818.

(*Z*)–6l



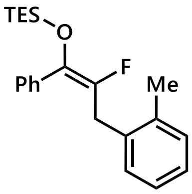
The reaction was conducted with 0.69M corresponding Grignard reagent solution in accordance with **GP1**. The NMR yield of crude reaction mixture was 38%. The product **6l** was obtained as a colorless oil (22.6 mg, 0.06 mmol), 14%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.42-7.39 (m, 2H), 7.32-7.24 (m, 7H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.67 (q, J = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –66.26 (s, 3F), –132.69 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 145.0 (d, *J* = 236.3 Hz), 137.4 (d, *J* = 18.6 Hz), 135.5 (d, *J* = 3.0 Hz), 133.3 (d, *J* = 26.4 Hz), 130.5 (d, *J* = 5.1 Hz) 130.5 (d, *J* = 32.3 Hz), 129.1 (d, *J* = 2.9 Hz), 128.9, 128.5, 128.3, 124.1 (d, *J* = 3.6 Hz), 124.2-123.9 (m), 123.8 (d, *J* = 272.8 Hz), 6.5, 5.2. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{21}H_{25}OF_4Si$, 397.1605; found, 397.1598.

(*Z*)–6m



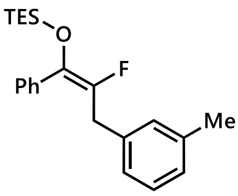
The reaction was conducted with 0.74M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from corresponding benzyl chloride. The product **6m** was obtained as a yellow oil (108.1 mg, 0.24 mmol, 79%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.42-7.39 (m, 2H), 7.35-7.31 (m, 5H), 7.24 (br, 2H), 3.68 (d, *J* = 24.5 Hz, 2H), 0.91 (t, *J* = 7.9Hz, 9H), 0.61 (q, *J* = 7.9Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –131.02 (t, *J* = 24.5Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.4 (d, *J* = 244.6 Hz), 137.6 (d, *J* = 2.9 Hz), 136.0 (d, *J* = 3.7 Hz), 135.1 (d, *J* = 16.8 Hz), 128.6, 128.19, 128.18, 128.14, 128.09, 126.5, 35.1 (dt, *J* = 5.1, 25.7 Hz), 6.5, 5.1. HRMS (EI): m/z $[M-H]^+$ calcd for $C_{21}H_{26}OFSi$, 341.1732; found, 341.1745.

(*Z*)–6n



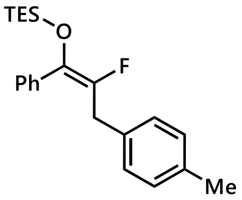
The reaction was conducted with 0.43M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from corresponding benzyl chloride. The product **7m** was obtained as a colorless oil (25.9 mg, 0.07 mmol, 19%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.40-7.37 (m, 2H), 7.34-7.30 (m,4H), 7.23-7.14 (m 3H), 3.65 (d, *J* = 23.7 Hz, 2H), 2.15 (s, 3H), 0.94 (t, *J* = 7.9Hz, 9H), 0.65 (q, *J* = 7.9Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): −130.26 (t, *J* = 23.7Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.0 (d, J = 244.7 Hz), 136.3, 136.1 (d, J = 3.3 Hz), 135.6 (d, J = 2.5 Hz), 135.3 (d, J = 16.7 Hz), 130.1, 128.2, 128.1, 128.02, 128.00, 127.97, 127.6, 126.1, 32.7 (d, J = 25.59), 19.5, 6.6, 5.1. HRMS (EI): m/z $[M]^+$ calcd for $C_{22}H_{29}FOSi$, 356.1966; found. 356.1977

(*Z*)–6o



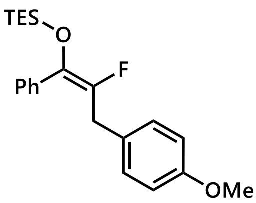
The reaction was conducted with 0.43M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from corresponding benzyl chloride. The product **6m** was obtained as a colorless oil (55.8 mg, 0.16 mmol, 39%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm):7.41-7.39 (m, 2H), 7.33-7.31 (m, 3H), 7.20 (t, *J* =7.5Hz, 1H), 7.06 (s, 1H), 7.04 (d, *J* =7.7Hz, 2H), 3.64 (d, *J* = 24.5Hz, 2H), 2.33 (s, 3H), 0.91 (t, *J* = 8.1Hz, 9H), 0.61 (q, *J* = 8.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): −130.31 (t, *J* = 24.5Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.5 (d, J = 244.63), 138.2, 137.4 (d, J = 2.5Hz), 136.0 (d, J = 3.3Hz), 135.1 (d, J = 16.8Hz), 123.0, 128.5, 128.3, 128.14, 128.10, 128.08, 125.2. HRMS (EI): m/z $[M]^+$ calcd for $C_{22}H_{29}FOSi$, 356.1966; found, 356.1974.

(*Z*)–6p



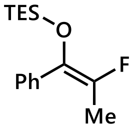
The reaction was conducted with 0.39M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from corresponding benzyl chloride. The product **6m** was obtained as a colorless oil (83.9 mg, 0.24 mmol, 59%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.46-7.44 (m, 2H), 7.38-7.32 (m, 3H), 7.20-7.14 (m, 4H), 3.68 (d, *J* = 24.4Hz, 2H), 2.37 (s, 3H), 0.96 (t, *J* = 7.9Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): −130.48 (t, *J* = 24.4Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.6 (d, *J* = 245.0Hz), 136.1, 136.0, 134.9 (d, *J* = 16.5Hz), 134.4 (d, *J* = 2.8Hz), 129.2, 128.1, 128.0, 34.7 (d, *J* = 25.02Hz), 21.0 (d, *J* = 5.0 Hz), 6.5, 5.1 (d, *J* =1.24 Hz), HRMS (EI): m/z $[M]^+$ calcd for $C_{22}H_{29}FOSi$, 356.1966; found, 356.1974.

(*Z*)–6q



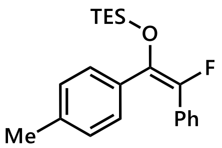
The reaction was conducted with 0.50M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from corresponding benzyl chloride. The product **7m** was obtained as a colorless oil (97.9 mg, 0.26 mmol, 65%) with *Z*/*E* =36:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.46-7.43 (m, 2H), 7.38-7.32 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.9 (d, *J* = 8.8Hz, 2H), 3,82 (s, 3H), 3.65 (d, *J* = 24.4Hz, 2H), 0.95 (t, *J* = 8.0Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): -130.78 (t, *J* = 24.4Hz, 1F), ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 158.3, 146.7 (d, J = 244.2 Hz), 136.0 (d, *J* = 3.1 Hz), 134.8 (d, J = 16.9 Hz), 129.5 (d, *J* = 2.4 Hz), 129.2, 128.1, 128.06, 114.0, 55.2 (d, J =7.9Hz), 34.2 (d, J =26.1 Hz), 6.5, 5.1. HRMS (EI): m/z $[M]^+$ calcd for $C_{22}H_{29}FO_2Si$, 372.1915; found 372.1916.

(*Z*)–6r



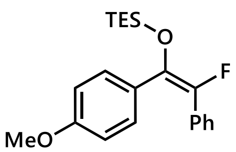
The reaction was conducted with 1.00M corresponding Grignard reagent solution in accordance with **GP1**. The Grignard reagent was prepared from iodomethane. The product **6r** was obtained as a colorless oil (95.6 mg, 0.36 mmol, 90%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.38-7.27 (m, 5H), 2.03 (d, *J* = 18.1 Hz, 3H), 0.91 (t, *J* = 7.9Hz, 9H), 0.59 (q, *J* = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –123.57 (q, *J* = 18.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 145.2 (d, *J* = 242.1 Hz), 136.3 (d, *J* = 3.6 Hz), 133.2 (d, *J* = 17.4 Hz), 128.2 (d, *J* = 3.0 Hz), 127.9, 127.7, 15.2 (d, *J* = 27.3 Hz), 6.5, 5.1. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{15}H_{24}OFSi$, 267.1575; found, 267.1583.

(*Z*)–6s



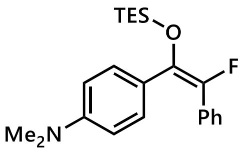
The reaction was conducted with 0.78M corresponding Grignard reagent solution in accordance with **GP1**. The product **6s** was obtained as a colorless oil (115.1 mg, 0.34 mmol, 79%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.33 (s, 1H), 7.28-7.24 br, 6H), 7.11 (d, J =7.8 Hz, 2H), 2.40 (s, 3H), 1.04 (t, *J* = 7.9Hz, 9H), 0.75 (q, J = 8.0Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –129.48 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 146.2 (d, *J* = 236.1 Hz), 138.1, 135.8 (d, *J* = 19.9 Hz), 133.1 (d, *J* = 2.3 Hz), 132.5 (d, *J* = 25.7 Hz), 128.9 (d, *J* = 3.0 Hz), 128.8, 127.9, 127.73, 127.68, 21.3 (q, *J* = 3.9 Hz), 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{27}OFSi$, 342.1810; found, 342.1827.

(*Z*)–6t



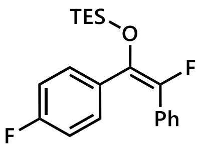
The reaction was conducted with 0.86M corresponding Grignard reagent solution in accordance with **GP1**. The product **6t** was obtained as a colorless oil (107.5 mg, 0.30 mmol, 73%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.23 (d, *J* = 8.7 Hz, 2H), 7.19-7.17 (m, 5H), 6.76 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 8.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –66.3 (s, 3F), –130.41 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 159.5, 145.8 (d, *J* = 235.8 Hz), 135.6 (d, *J* = 19.8 Hz), 132.6 (d, *J* = 25.7 Hz), 130.4 (d, *J* = 3.1 Hz), 128.3 (d, *J* = 2.3 Hz), 127.9, 127.61, 127.56, 113.5, 55.1 (q, *J* = 7.6 Hz), 6.6, 5.2 (d, *J* = 1.5 Hz). HRMS (EI): m/z $[M+H]^+$ calcd for $C_{21}H_{28}O_2FSi$, 359.1837; found, 359.1830.

(*Z*)–6u



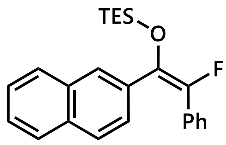
The reaction was conducted with 0.86M corresponding Grignard reagent solution in accordance to **GP1**. The product **6u** was obtained as a yellow oil (52.0 mg, 0.14 mmol, 34%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.26-7.14 (m, 7H), 6.56 (d, *J* = 8.9 Hz, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 2.95 (s, 6H), 0.68 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –132.12 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 150.2, 145.2 (d, *J* = 234.3 Hz), 136.3 (d, *J* = 19.2 Hz), 133.1 (d, *J* = 25.7 Hz), 123.0 (d, *J* = 3.1 Hz), 127.8, 127.4 (d, *J* = 5.2 Hz), 127.1, 123.3 (d, *J* = 2.2 Hz), 111.5 (d, *J* = 3.8 Hz), 40.2 (q, *J* = 5.0 Hz), 6.7, 5.3 (d, *J* = 1.4 Hz). HRMS (EI): m/z $[M+H]^+$ calcd for $C_{22}H_{31}NOFSi$, 372.2153; found, 372.2152.

(*Z*)–6v



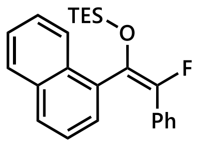
The reaction was conducted with 0.86M corresponding Grignard reagent solution in accordance to **GP1**. The product **6v** was obtained as a colorless oil (89.1 mg, 0.26 mmol, 64%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.30-7.26 (m, 2H), 7.21-7.15 (m, 5H), 6.92 (t, *J* = 8.8 Hz, 2H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –115.92, –116.02 (m, 1F), –128.35 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 162.5 (d, *J* = 248.1 Hz), 146.4 (d, *J* = 238.2 Hz), 134.8 (d, *J* = 19.8 Hz), 132.17 (t, *J* = 3.3 Hz), 132.15 (d, *J* = 25.7 Hz), 130.9 (dd, *J* = 3.0, 8.1 Hz), 128.1, 128.0, 127.8 (d, *J* = 4.4 Hz), 115.2 (d, *J* = 21.3 Hz), 6.6, 5.2 (d, *J* = 2.2 Hz). HRMS (EI): m/z $[M]^+$ calcd for $C_{20}H_{24}OF_2Si$, 346.1559; found, 346.1561.

(*Z*)–6w



The reaction was conducted with 0.86M corresponding Grignard reagent solution in accordance to **GP1**. The product **6w** was obtained as a yellow oil (99.9 mg, 0.26 mmol, 66%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.85 (br, 1H), 7.80–7.77 (m, 1H), 7.73–7.70 (m, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.49-7.42 (m, 2H), 7.34 (dd, *J* = 1.7, 8.6 Hz, 1H), 7.23-7.16 (m, 5H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): –127.7 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 147.0 (d, *J* = 238.7 Hz), 135.8 (d, *J* = 19.8 Hz), 133.6 (d, *J* = 2.9 Hz), 133.1 (d, *J* = 1.4 Hz), 132.3 (d, *J* = 25.7 Hz), 128.32, 128.31 (d, *J* = 6.6 Hz), 128.2, 128.0, 127.98, 127.92, 127.87, 127.6 (d, *J* = 4.5 Hz), 126.7 (d, *J* = 2.2 Hz), 126.4, 126.1, 6.6, 5.3. HRMS (EI): m/z $[M]^+$ calcd for $C_{24}H_{27}OFSi$, 378.1810; found, 378.1811.

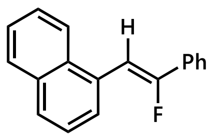
(*Z*)-6x



The reaction was conducted with 0.52M corresponding Grignard reagent solution in accordance to **GP3**. The NMR yield of crude reaction mixture was 27%. The product **6x** was obtained as a yellow oil (8.5 mg, 0.02 mmol, 11%) with *Z*/*E* = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.21–8.19 (m, 1H), 7.88–7.83 (m, 2H), 7.53–7.48 (m, 2H), 7.35–7.31 (m, 2H), 7.05–6.95 (m, 5H), 0.83 (t, *J* = 7.81 Hz, 9H), 0.56–0.50 (m, 6H) ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): 130.47 (s, 1F) ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 147.6 (d, *J* = 238.0 Hz), 135.0, 134.8, 134.0, 133.7, 133.6, 132.3, 132.2 (d, *J* =3.09 Hz), 132.1, 129.5, 128.6 (d, *J* =3.10 Hz), 128.4, 127.9, 127.4, 126.6, 126.5, 126.3 (d, *J* = 5.80 Hz) 125.5, 6.6, 5.3. HRMS (EI): m/z $[M]^+$ calcd for $C_{24}H_{27}FOSi$, 378.1810; found, 378.1810.

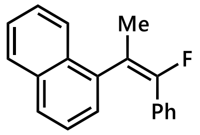
Reactions of gem-difluoroalkenes

8a



The reaction was conducted in accordance to **GP3**. The yields were determined by ^{1}H NMR (1,3,5-trimethoxybenzene as an internal standard) and ^{19}F NMR (trifluoromethylcyclohexane as an internal standard) of crude product. The products (*E*)-**8a**,[6] (*Z*)-**8a**,[6] and 1-(2,2-diphenylvinyl)naphthalene[7] were known compound.

8b



The reaction was conducted with 0.86M corresponding Grignard reagent solution in accordance to **GP3**. The NMR yield of crude reaction mixture was 96%. The product **8b** was isolated by column chromatography as a yellow oil (37.75 mg, 0.14 mmol, 36%) with *Z*/*E* > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03-8.01 (m, 1H), 7.94–7.91 (m, 1H), 7.86 (d, *J* = 8.26 Hz, 1H), 7.71 (d, *J* = 7.50 Hz, 2H), 7.58-7.43 (m, 7H), 2.28 (d, *J* = 3.03 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, δ): –98.99 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 153.0 (d, *J* = 241.20 Hz), 137.4 (d, *J* = 3.18 Hz), 134.0, 132.9, 132.6, 131.0, 129.1, 128.6, 128.6, 128.5, 128.4, 127.7, 126.2, 125.9, 125.7, 125.4, 114.4, 114.2, 20.1 (t, *J* = 3.38). HRMS (EI): m/z $[M]^+$ calcd for $C_{19}H_{15}F$, 262.1152; found, 262.1156.

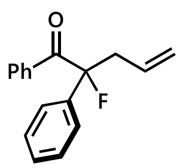
Asymmetric allylic alkylation of 6

(*S*)-*t*Bu-PHOX was prepared by following literature procedure.[8]

General Procedure (GP4)

In the glove box, $[Pd(C_3H_5)Cl]_2$ (1.5 mg, 4 μmol), (*S*)-*t*Bu-PHOX (3.9 mg, 10 μmol), and TBAT (108.0 mg, 0.2 mmol) were dissolved in 1 mL of toluene and stirred for 30 min. To the solution was added a toluene solution (1 mL) of silyl fluoroenolate (**6a** or **6m**, 0.2 mmol) and allyl ethyl carbonate (29.2 µL, 0.22 mmol). The reaction mixture was stirred at 40 °C for 17 h. After cooling to room temperature, NMR yield was obtained by using trifluoromethylcyclohexane as an internal standard for ^{19}F NMR analysis. The residue was mixed with brine and extracted with ethyl acetate three times. The combined organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography (hexane/$CHCl_3$=99/1 to 75/25). The enantiomer excess was determined by SFC analysis.

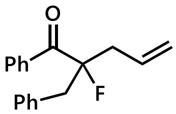
9



The reaction was performed at 0.3 mmol scale to afford 66.9 mg (86% yield) of **9** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 (d, J = 8.3 Hz, 2H), 7.52-7.46 (m, 3H), 7.42-7.30 (m, 5H), 5.78-5.67 (m. 1H), 5.15-5.08 (m, 2H), 3.18 (ddd, J = 7.0Hz, J = 14.8Hz, J = 25.6Hz, 1H) , 2.94 (ddd, J = 7.0 Hz ,J = 14.7Hz, J = 24.0 Hz, 1H) ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): −164.91 (t, J = 25.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 197.7 (d, J = 27.8 Hz), 138.4 (d, J = 22.2Hz), 134.8 (d, J = 3.4

Hz), 133.0, 131.1 (d, J = 3.1 Hz), 130.0 (d, J = 6.0 Hz), 128.7 (d, J = 1.2 Hz), 128.3, 128.1, 124.1 (d, J = 8.9 Hz), 119.7, 102.5 (d, J = 190.7 Hz), 44.0 (d, J = 23.0 Hz). HRMS (EI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}OF$, 255.1180; found, 255.1180.

10



The reaction afforded 38.9 mg (73 % yield) of **10** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.62 (d, J = 8.2Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.8Hz, 2H), 7.24-7.19 (m, 5H), 5.80(m, 1H), 5.16 (d, J = 17.5Hz, 1H), 5.14(d, J = 9.9Hz, 1H), 3.40 (dd, J = 14.4Hz, J = 30.1 Hz, 1H), 3.20 (dd, J = 14.3Hz , J = 18.1Hz, 1H), 2.90 (ddd, J = 7.3Hz, J = 14.4Hz , J = 27.7 Hz , 1H), 2.65 (ddd, J = 7.3Hz, J = 15.4Hz ,J = 15.4Hz , 1H). ^{19}F NMR (376 MHz, $CDCl_3$, δ/ppm): 163.47 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 202.5 (d, J = 27.0Hz), 136.2 (d, J = 3.8Hz), 134.7, 132.5, 130.9 (d, J = 3.4Hz), 130.7, 129.3 (d, J = 8.1Hz), 128.3, 127.9 (d, J = 1.0Hz), 127.0, 120.0, 104.0 (d, J = 193.5Hz), 43.7 (d, J = 21.1Hz), 42.5 (d, J = 22.09Hz) HRMS (EI): m/z $[M+H]^+$ calcd for $C_{18}H_{18}OF$, 269.1336; found, 269.1339.

Computational Details

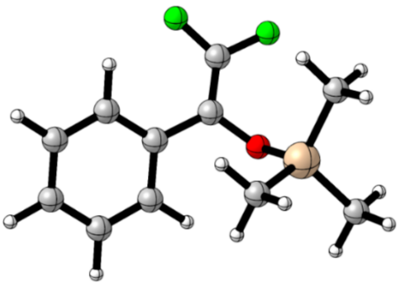
DFT calculations were performed with the Gaussian 16 package.[9] In optimizations and vibrational frequency calculations, we used B3LYP[10,11] with 6-31G(d) basis set. We applied Grimme's empirical dispersion correction (GD3)[12] for optimizations. Structures **A** to **H** showed no imaginary frequencies indicating they are ground states. Transition-states **TS1** and **TS2** had one imaginary frequency. Intrinsic reaction coordinate calculation was performed for each transition states at the same level of theory of the optimization study. Single point energies based on the structures obtained by optimization studies were calculated using M06[13]/6-311++G(2d,p). The calculated Gibbs free energies were obtained by adding the thermal correction given at frequency analysis. The computed structures were visualized by CYLview.[14]

Summary of DFT calculations

Structure	**Single Point Energy (hartree)**	**Thermal Correction (hartree)**	**Gibbs Free Energy (kcal/mol)**	**Imaginary frequency (cm^{-1})**
A	-991.79728	0.179732	-622249.9275	-
B	-5175.8187	1.053658	-3247216.812	-
C	-3423.8033	0.638004	-2148070.455	-
D	-4356.3933	0.859098	-2733141.267	-
E	-3323.748	0.63575	-2085286.168	-
F	-3784.2086	0.63647	-2374229.347	-
G	-3423.8176	0.637406	-2148079.804	-
TS1	-4356.3491	0.860326	-2733112.761	-266.45
TS2	-3423.7406	0.631829	-2148034.985	-142.64
LiCl(thf)$_2$	-1032.5	0.197316	-647780.2572	-
THF	-232.348	0.088877	-145744.9223	-
LiF	-107.43115	-0.017053	-67424.82186	-
COD	-311.84885	0.149139	-195594.6856	-

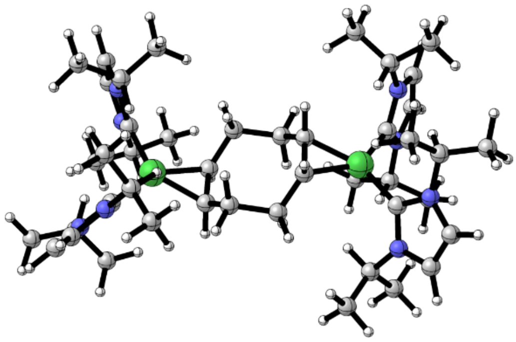
Optimized geometries

A



O	0.96958500	-0.08601400	-0.87794700
C	-1.37490700	0.12180600	-0.23567400
C	-0.04570100	0.73376800	-0.44050100
C	-2.36647000	0.69693600	0.57937900
H	-2.17525800	1.63531400	1.08612200
C	-1.64854800	-1.10680200	-0.86165600
H	-0.88799000	-1.55597900	-1.49083400
C	-3.59427600	0.06137100	0.75210800
H	-4.34600500	0.51866700	1.39006700
C	-2.87814700	-1.73752400	-0.68459700
H	-3.07103900	-2.68494300	-1.18108800
Si	2.03010400	-0.87049400	0.19636100
C	1.03025000	-1.93747400	1.38094600
H	1.68520500	-2.45189100	2.09509600
H	0.32046000	-1.32972700	1.95383600
H	0.44979600	-2.69470500	0.84266900
C	3.12567200	-1.89509400	-0.92937000
H	2.53398600	-2.61677600	-1.50393400
H	3.65923100	-1.25536700	-1.64125800
H	3.87185100	-2.45456700	-0.35244100
C	3.01260000	0.42130500	1.14724300
H	3.58534300	1.06164200	0.46840000
H	2.35112100	1.06887700	1.73386800
H	3.71341800	-0.05629700	1.84301800
C	-3.85810600	-1.15718000	0.12273700
H	-4.81625700	-1.64999100	0.26302500
C	0.23129700	2.03929800	-0.31107900
F	1.44083000	2.55819900	-0.49783600
F	-0.64682700	2.98605700	0.01458800

B



Ni	-3.34971700	-0.13238300	-0.16119100
C	-4.55152100	-1.57588600	0.12096600
N	-5.61921000	-1.90087000	-0.69070900
C	-4.18862400	1.53646900	0.16831900
N	-4.58115600	-2.57265100	1.06892000
N	-4.55430000	2.51742900	-0.72834900
C	-5.61378900	-3.47636700	0.84484200
H	-5.79986400	-4.32216600	1.48816100
C	-6.26103500	-3.05968400	-0.27031500
H	-7.11225100	-3.48010600	-0.78123400
N	-4.46578100	2.12110100	1.38228900
C	-5.01448500	3.66326700	-0.08800400
H	-5.34195100	4.54024500	-0.62458300
C	-4.95800900	3.41394900	1.24204800
H	-5.22422500	4.03289200	2.08473400
C	-1.59811400	0.51002300	-0.77054700
C	-1.62217600	-0.92906800	-0.74293600
C	1.59811100	0.51002500	0.77054900
C	-0.75777900	-1.75934600	0.19301000
C	1.62217100	-0.92906600	0.74294600
C	0.75777200	-1.75934900	-0.19299400
H	-1.69461600	-1.40464300	-1.72909000
H	-0.84204900	-1.40089400	1.22737600
H	1.64228500	0.95378600	1.77388000
H	1.69461100	-1.40463600	1.72910200
H	-1.64229000	0.95377800	-1.77388000

H	-1.13724500	-2.79043500	0.19595100	C	-4.19549300	1.45415700	2.65823100
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C	-0.76080000	1.36277100	0.16955400	H	5.19338500	-2.52374900	3.35482900
H	-0.88081700	1.01634800	1.20445300	H	5.19831200	-0.83177900	3.90740100
H	-1.15763400	2.38980000	0.15147300	H	3.97495800	-1.38243000	2.73270600
C	0.76079700	1.36276900	-0.16955700	C	7.41746800	-1.18392000	2.24662900
H	0.88081300	1.01634000	-1.20445500	H	7.63374100	-0.46173600	3.04098900
H	1.15763200	2.38979700	-0.15148300	H	7.69158000	-2.17613000	2.62496700
Ni	3.34971100	-0.13238400	0.16119600	H	8.05377400	-0.95126700	1.38610200
C	4.55151800	-1.57588300	-0.12096800	C	-5.65057000	2.59789600	-2.94464100
N	5.61921200	-1.90086400	0.69070300	H	-5.48929000	2.41755100	-4.01319200
C	4.18862700	1.53646300	-0.16832100	H	-6.42282200	1.90847000	-2.58805800
N	4.58115400	-2.57264900	-1.06892100	H	-6.03101300	3.62049100	-2.83315300
N	4.55431500	2.51742000	0.72834500	C	-3.23707900	3.35760200	-2.63494100
C	5.61378900	-3.47636400	-0.84484500	H	-2.32353200	3.17957200	-2.06106600
H	5.79986500	-4.32216100	-1.48816500	H	-3.01963500	3.20322800	-3.69782600
C	6.26103600	-3.05967900	0.27031100	H	-3.53719500	4.40381700	-2.49868700
H	7.11225500	-3.48009800	0.78122700	C	-5.46256500	1.37287600	3.51390600
N	4.46579100	2.12108900	-1.38229200	H	-5.81984100	2.37030800	3.79718600
C	5.01451300	3.66325100	0.08799800	H	-6.26371800	0.86258900	2.96910500
H	5.34199100	4.54022600	0.62457500	H	-5.26023900	0.81969400	4.43746100
C	4.95803500	3.41393100	-1.24205300	C	-3.02881800	2.12628400	3.38799300
H	5.22425800	4.03287000	-2.08474100	H	-2.78033200	1.57081700	4.29948100
C	4.34135200	2.40078400	2.17399400	H	-2.14605100	2.15495800	2.74314200
H	3.99012700	1.37420500	2.31020100	H	-3.28271200	3.15393100	3.67648700
C	4.19549100	1.45414800	-2.65823300	C	-4.35859900	-2.33287300	3.51362200
H	3.89343300	0.44552800	-2.35925100	H	-5.09251200	-3.11189300	3.75395100
C	5.93619000	-1.10292200	1.88000900	H	-3.63642100	-2.28385100	4.33642300
H	5.69961400	-0.07760400	1.58011100	H	-4.88694200	-1.37768900	3.45371300
C	3.64373700	-2.64091600	-2.19284500	C	-2.92140500	-3.99057600	2.23371900
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C	-5.93619300	-1.10292400	-1.88001100	C	-5.01837000	-1.48614000	-3.04592700
H	-5.69962900	-0.07760500	-1.58010500	H	-5.19830900	-0.83175900	-3.90739800
C	-4.34134600	2.40078500	-2.17399800	H	-3.97495400	-1.38240800	-2.73270200
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C	-7.41746800	-1.18393600	-2.24663800
H	-7.63374600	-0.46175000	-3.04099400
H	-7.69156600	-2.17614700	-2.62498400
H	-8.05378100	-0.95129500	-1.38611200
C	2.92139700	-3.99058500	-2.23369700
H	3.61110500	-4.80689700	-2.48151900
H	2.45652300	-4.20826800	-1.26889900
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C	4.35857800	-2.33288900	-3.51362400
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H	5.09249100	-3.11190900	-3.75395100
C	3.02881800	2.12628500	-3.38798800
H	3.28272000	3.15393000	-3.67648300
H	2.78032300	1.57082000	-4.29947500
H	2.14605500	2.15496500	-2.74313300
C	5.46255900	1.37285800	-3.51391500
H	5.26022400	0.81967800	-4.43746900
H	5.81984200	2.37028800	-3.79719500
H	6.26371000	0.86256400	-2.96911800
C	3.23708700	3.35760900	2.63492600
H	3.01963600	3.20324300	3.69781000
H	3.53721100	4.40382200	2.49866700
H	2.32354200	3.17958100	2.06104600
C	5.65057200	2.59789000	2.94464400
H	6.03102100	3.62048300	2.83315500
H	5.48928400	2.41755000	4.01319400
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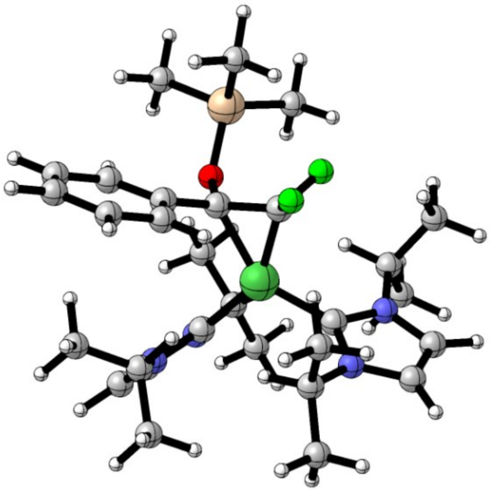
C



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C	-1.35048400	-0.29127400	-0.65525300
C	4.30511500	-1.13523800	-1.09692300
C	4.40467300	0.17942300	-1.41120300
H	5.02002900	-1.93691300	-1.19413300
H	5.22032500	0.73844100	-1.84111300
N	3.03300400	-1.32596700	-0.56894900
N	3.19581000	0.76351500	-1.05094800
C	2.32449800	-0.15658800	-0.53673000
C	2.77179500	2.13595100	-1.35649400
H	1.92631100	2.29956600	-0.68439800
C	0.01660500	1.18020800	3.83585600
C	-0.20651000	2.38946900	3.26771400
H	-0.02641200	0.86919300	4.86752400
H	-0.47199800	3.33636500	3.71014000
N	0.33477700	0.31041100	2.80044300
N	-0.03123800	2.22416100	1.89899600
C	0.30329600	0.93589900	1.58414300
C	-0.20614100	3.29820100	0.91015700
H	-0.13353400	2.79455600	-0.05750800
Ni	0.49527600	0.09787800	-0.13612200
O	-1.85922700	-1.34265200	0.15311300
Si	-2.68131900	-2.71079300	-0.38438600
C	-1.57767300	-4.22314700	-0.13951000

H	-2.12291300	-5.15692100	-0.32573700
H	-0.71379800	-4.18457900	-0.80884200
H	-1.20737100	-4.25486300	0.89326400
C	-4.17124600	-2.88261000	0.76388400
H	-3.85585100	-2.87413900	1.81456500
H	-4.87984600	-2.05887600	0.62086600
H	-4.70736700	-3.82321000	0.58504500
C	-3.23441700	-2.49991800	-2.17030200
H	-2.36818300	-2.38270300	-2.82804900
H	-3.81703300	-3.36391900	-2.51305200
H	-3.85878000	-1.60482300	-2.27163300
C	-2.31374600	0.80004400	-0.91136300
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C	-3.51579500	0.85697200	-0.17606600
C	-3.01333200	2.85539100	-2.03548800
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C	-4.21313200	2.87986100	-1.31782600
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C	0.91355600	4.33614500	1.04425200
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H	0.84025800	5.07708400	0.24047500
H	0.84055700	4.86890200	1.99990200
C	-1.59859200	3.92104000	1.01854200
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H	-1.74872600	4.63400700	0.20257500
H	-2.36933400	3.15174300	0.93921700
C	3.87102300	3.14926300	-1.03890600
H	4.72616500	3.04661900	-1.71732000
H	3.47923500	4.16449100	-1.15789500
H	4.22889900	3.03408200	-0.01028900
C	2.26695200	2.22745600	-2.80036500
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H	1.47338900	1.49362700	-2.96660800
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C	2.49214000	-3.60979500	-1.34744900
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H	1.99574800	-4.54093400	-1.05329900
C	3.21827600	-3.17443700	1.05709800
H	3.21088900	-2.44424100	1.87142100
H	2.73767700	-4.09433000	1.40774200
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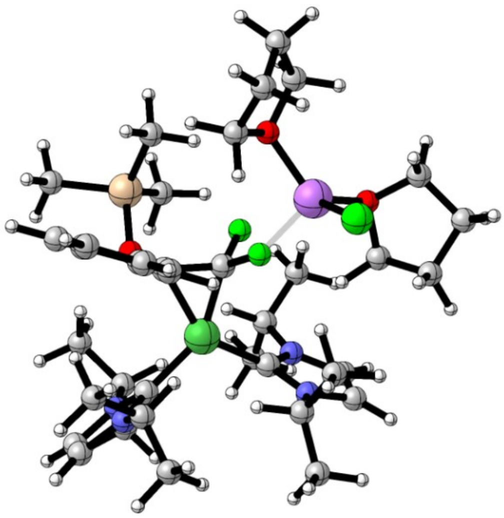
D



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C	-4.91599100	-0.82528000	-1.75582600	Cl	4.13149800	0.48768900	-2.25734100
H	-6.29412400	-0.60197800	-0.03677200	Li	3.27421500	0.19094800	-0.22485200
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N	-4.20982600	-0.02687400	0.16685500	O	3.60955200	1.81249300	0.84594000
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H	-1.70266800	-0.53334900	-2.66488400	H	1.75921300	2.37980300	0.14621100
Ni	-1.29963500	0.37910700	-0.08672100	H	2.43961600	3.44797000	1.39391300
O	-1.03725000	-1.84573500	1.52640000	H	5.47744800	2.31729400	1.61092200
Si	-0.25342900	-2.43133400	2.89655100	H	5.46060100	1.60554600	-0.03714200
C	-0.27613100	-1.10953800	4.24511800	H	4.94692200	4.48437400	0.77176700
H	0.00612600	-1.52709800	5.21969500	H	5.58942600	3.86636400	-0.76327400
H	0.40618400	-0.28934500	4.00742100	H	2.97298000	4.69269400	-0.66149000
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C	-1.33061200	-3.87062600	3.47300200	C	3.67066400	-2.55192800	-0.47262000
H	-2.36902400	-3.54925500	3.61876300	O	3.79242500	-1.51058800	0.53387100
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C	-0.81282600	-3.70769800	-0.51242800	H	5.64847700	-3.70832200	1.11771900
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C	-3.10862300	0.21857500	-4.12440900
H	-3.09384800	1.25403500	-3.77160300
H	-2.41048100	0.12442300	-4.96313900
H	-4.11610700	0.00141100	-4.49901000
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C	-4.16279800	-0.93869600	2.45547300
H	-3.32803500	-1.57999200	2.16185000
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C	-2.26557800	3.26901100	3.10231300
H	-2.47540500	2.84179800	4.08899100
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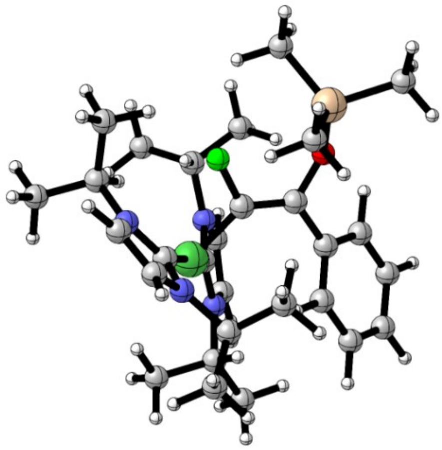
E



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N	2.17174200	-2.15139600	-1.42379500
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H	0.03134900	0.75373600	2.46252100
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C	1.77927700	-1.73344700	-0.19022900
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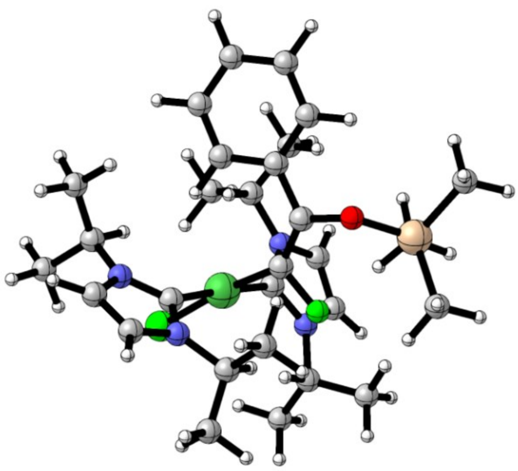
C	-2.89305700	-2.43294300	-0.11200600
H	-2.29518800	-2.08934700	-0.96068200
C	-0.29626000	1.57117400	-0.57439400
C	2.97872500	-1.34909900	1.98236200
H	1.99026400	-0.93198800	2.19186600
C	-3.26180800	0.09692600	2.47913400
H	-3.71102900	0.72599300	3.23052100
C	-1.79797400	0.21209000	-2.07328500
H	-0.97820600	-0.47628300	-2.23873300
C	3.53063400	-2.40491000	-1.44981700
H	4.04569000	-2.74517400	-2.33350800
C	-2.62883000	2.26073300	-1.10715400
H	-2.46156200	3.15071900	-0.50979600
C	-3.03081000	-0.00176900	-2.69088900

H	-3.17126200	-0.86897800	-3.33121900
C	-3.86270900	2.04340100	-1.71549300
H	-4.66308900	2.76553100	-1.58055900
Si	1.56913100	3.65727900	-0.74669400
C	1.13587500	5.25325000	-1.63032000
H	2.02776500	5.87185600	-1.78753100
H	0.68568300	5.05451700	-2.60932100
H	0.42072100	5.84416900	-1.04658400
C	2.32630400	4.02314800	0.93500000
H	1.64529800	4.63778200	1.53577800
H	2.53188600	3.10342100	1.49044700
H	3.26572100	4.57958300	0.83011700
C	2.66837900	2.55786800	-1.80812200
H	2.86090800	1.59644500	-1.32194800
H	2.20435100	2.36523200	-2.78255500
H	3.63358800	3.04446400	-1.99332000
C	1.28177800	-2.16298200	-2.60468200
H	0.27273100	-2.18057100	-2.17983400
C	-4.07216600	0.90930100	-2.50683900
H	-5.03009000	0.75171900	-2.99435000
C	3.99877800	-2.15108600	-0.19753600
H	4.99335000	-2.23986300	0.20935400
C	0.40048700	0.59655200	0.04498700
F	1.56349200	1.01129700	0.68827900
C	-1.24512900	2.44782200	2.75225200
H	-2.22014300	2.70681600	3.17991700
H	-0.48542500	3.04243800	3.26929800
H	-1.23229000	2.72552900	1.69610900
C	-0.87325700	0.52928700	4.39898400
H	-0.64471100	-0.53852700	4.48405600
H	-0.09382100	1.09480100	4.91919100
H	-1.82217800	0.71967600	4.91226500
C	-4.32840100	-2.62970100	-0.59029900
H	-4.97148400	-3.02746000	0.20249600
H	-4.74825100	-1.69021200	-0.96148000
H	-4.33446900	-3.35382800	-1.41011800
C	-2.27758400	-3.71774900	0.45361700
H	-2.81810000	-4.05428100	1.34445200
H	-2.30729700	-4.51540600	-0.29538900
H	-1.22781100	-3.55865200	0.73685500
C	1.48275400	-3.42634400	-3.44147200
H	0.72893200	-3.45889300	-4.23384600
H	2.46451200	-3.43910300	-3.92691600
H	1.38412600	-4.32909900	-2.83029600
C	1.47053900	-0.86917400	-3.40120400
H	2.48500800	-0.81116000	-3.81044000
H	0.76225900	-0.83121200	-4.23494100
H	1.30430400	0.00002900	-2.75826000
C	4.02479800	-0.25410300	2.19615300
H	3.83632900	0.59112100	1.53011200
H	3.97678900	0.09785400	3.23129000
H	5.04039700	-0.62591100	2.02159900
C	3.20845700	-2.58316500	2.85725000
H	4.18145700	-3.04095700	2.64698600
H	3.19206700	-2.29955000	3.91426800
H	2.43093900	-3.33537100	2.68667600

F

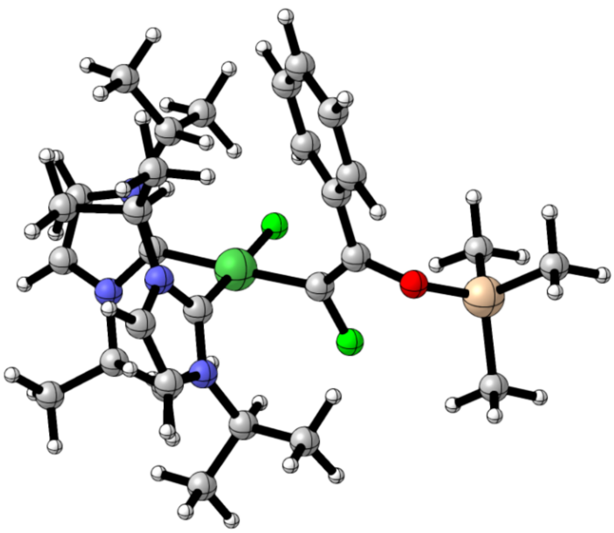


Ni	0.88967200	-0.54072000	0.47921800
O	-2.26975700	0.77081800	-2.03499600
N	2.32980800	-1.20548900	-2.03913900
N	-1.14881500	-1.86211000	2.11578000
N	-0.94249700	0.20499000	2.67536300
N	3.37373500	0.33210100	-0.95692400
C	2.25911500	-0.45250700	-0.90447700

C	1.35032400	-2.23616400	-2.43282900	C	-0.25582400	5.04303800	-0.34702500
H	0.71427800	-2.36649600	-1.56021000	H	-0.04857900	6.08122200	-0.10210500
C	-0.80436300	2.33058900	-0.96205500	C	-2.01587000	-1.64945100	3.18024000
C	-0.46969800	-0.72586900	1.81048100	H	-2.64515700	-2.42791200	3.58023700
C	4.11482900	0.07608600	-2.10144700	C	-0.51712600	-0.14977100	-0.69836400
H	5.03436200	0.59273400	-2.32388900	F	-1.16910800	-1.35574400	-1.05674800
C	3.81625700	1.26976100	0.09426400	Cl	2.42331600	-1.23540800	2.08129600
H	3.00120400	1.28385000	0.82069900	C	-1.57629900	2.59699800	2.61990900
C	-1.15640500	0.92353500	-1.21967200	H	-2.25123100	2.55681400	3.48335800
C	-0.90462600	-3.16396800	1.46728500	H	-1.16159000	3.60761100	2.55693200
H	-0.27295100	-2.92650700	0.60998100	H	-2.15173400	2.41431200	1.70792600
C	3.45567100	-0.88968700	-2.78483500	C	0.43046400	1.76688200	3.98934200
H	3.68661000	-1.37211400	-3.72066000	H	1.24002300	1.02993100	3.98788700
C	0.42468400	2.71893400	-0.39647100	H	0.86390600	2.77303800	3.99930100
H	1.16370300	1.95534600	-0.19458300	H	-0.15974400	1.64293400	4.90540400
C	-1.88650900	-0.34572300	3.53143900	C	4.02615000	2.66991200	-0.49147700
H	-2.38032100	0.23135200	4.29654000	H	4.22163100	3.38059100	0.31867700
C	-1.73299600	3.34820500	-1.25542800	H	4.89114300	2.69469400	-1.16460400
H	-2.67038100	3.08328100	-1.72962300	H	3.14768100	3.00677200	-1.04751400
C	0.68957200	4.04848500	-0.07999800	C	5.06944300	0.73371100	0.79137100
H	1.64342900	4.30984500	0.37102500	H	5.91148500	0.66790500	0.09152300
C	-1.46242500	4.68125200	-0.94778600	H	5.35651200	1.41088000	1.60318100
H	-2.20392200	5.44225800	-1.17905100	H	4.86662500	-0.25183900	1.21508100
Si	-3.72762900	0.02331400	-1.64059300	C	2.05367400	-3.56460700	-2.72402900
C	-5.05865400	1.16902100	-2.32616500	H	2.68316800	-3.50857400	-3.61974200
H	-6.05965100	0.73695000	-2.20281000	H	2.67952100	-3.86714700	-1.87822100
H	-5.04790900	2.14046400	-1.81785900	H	1.30306600	-4.34262400	-2.89851500
H	-4.90303300	1.35054000	-3.39621900	C	0.48644800	-1.74270400	-3.59582000
C	-3.86414100	-1.64503400	-2.50445200	H	-0.02381700	-0.81478200	-3.32742200
H	-3.73849400	-1.52212500	-3.58700600	H	1.09511100	-1.57030900	-4.49174400
H	-3.09250700	-2.33588100	-2.15397600	H	-0.27370900	-2.49293700	-3.83764500
H	-4.84734400	-2.10141500	-2.33344400	C	-0.13064000	-4.08103200	2.41606600
C	-3.88230600	-0.12404700	0.23008100	H	-0.72100200	-4.30946900	3.31179500
H	-3.02889200	-0.66176400	0.64937400	H	0.10389200	-5.02650800	1.91449000
H	-3.91164800	0.86712100	0.69795200	H	0.80332900	-3.59704800	2.71678200
H	-4.79861600	-0.65623600	0.51325500	C	-2.21140200	-3.76703500	0.95038000
C	-0.43664500	1.58644500	2.74186900	H	-1.99797100	-4.69695500	0.41286200
H	0.19629800	1.68454600	1.86017500	H	-2.90001000	-4.00876900	1.76855900

H	-2.70695400	-3.07471600	0.26477200

G



F	-0.32983600	0.49383700	-2.32557000
F	1.81043900	-1.65625100	-1.10624200
C	1.36047900	-0.45314700	-0.53572700
C	2.35029600	0.27811600	0.01489100
C	-0.49179600	-2.02457100	3.05279200
C	-0.95770400	-0.79744700	3.38461900
H	-0.26614100	-2.88159800	3.66649400
H	-1.22386300	-0.37974700	4.34197900
N	-0.31252900	-2.02675000	1.67620700
N	-1.04610800	-0.07293300	2.20379800
C	-0.64561800	-0.81701500	1.13193200
C	-1.55563100	1.30776200	2.12598700
H	-1.33803700	1.62564100	1.10575200
C	-4.67796000	-0.31409200	-1.24953700
C	-4.43121000	0.99314100	-1.51608700
H	-5.59458000	-0.87768200	-1.30182600
H	-5.09286900	1.77836400	-1.84477900
N	-3.46818900	-0.86740000	-0.84847500
N	-3.08132300	1.20347000	-1.27840000
C	-2.46654400	0.05691200	-0.87978600
C	-2.38337500	2.48111900	-1.53179400
H	-1.38297900	2.33080700	-1.13179400
Ni	-0.53028700	-0.21216200	-0.64770800
O	3.65304900	-0.18767000	0.16308300
Si	4.69849700	-0.55825900	-1.10894900
C	6.35197000	0.21426800	-0.63464900
H	7.13137300	-0.02092100	-1.37040300
H	6.26747300	1.30509600	-0.56656000
H	6.69070900	-0.15565200	0.34063700
C	4.89299500	-2.42930200	-1.22139800
H	5.24024500	-2.84193400	-0.26625000
H	3.93073400	-2.89147300	-1.46062700
H	5.61906600	-2.71364500	-1.99345200
C	4.03591500	0.17171400	-2.70903000
H	3.94513600	1.26160700	-2.63277200
H	4.69885200	-0.05613900	-3.55298200
H	3.04068500	-0.22718300	-2.92937100
C	2.11789700	1.64140900	0.52112600
C	1.20242600	2.49659900	-0.12533500
C	2.84349400	2.14362400	1.61577200
C	0.97716600	3.78741500	0.35182400
H	0.71876200	2.13837500	-1.02907600
C	2.62756000	3.44229300	2.07782700
H	3.58013500	1.50355300	2.09139900
C	1.68499800	4.26795000	1.45741300
H	0.26986600	4.43360400	-0.16452800
H	3.19649800	3.81220000	2.92777900
H	1.51978700	5.27961800	1.81941400
C	0.26983000	-3.16140100	0.93345800
H	0.20800900	-2.87212100	-0.11518600
C	-3.06152900	3.63188000	-0.78591200
H	-4.06596900	3.83804500	-1.17421500
H	-3.14303200	3.41970500	0.28446600
H	-2.46726600	4.54301900	-0.91042200
C	-2.25952600	2.72191000	-3.03645800
H	-3.24580300	2.80500100	-3.50990200
H	-1.71431800	3.65484200	-3.21794700
H	-1.69770300	1.89322600	-3.46998400
C	-3.06998300	1.31117400	2.35520000
H	-3.31428200	0.93535100	3.35588800
H	-3.46556900	2.32888900	2.27467100

H	-3.57255400	0.68190500	1.61441600
C	-0.79492200	2.22326800	3.08457900
H	-1.09712200	3.26112800	2.91545100
H	-1.00560100	1.97859100	4.13277100
H	0.28093500	2.15244000	2.90852600
C	1.74447400	-3.33800100	1.30982800
H	2.29873400	-2.41171800	1.14965400
H	1.84559800	-3.64162200	2.35909400
H	2.19411100	-4.11631400	0.68477600
C	-0.54701600	-4.43722400	1.16166300
H	-1.60362900	-4.28885500	0.91734600
H	-0.15653800	-5.23832400	0.52577300
H	-0.48255800	-4.77961400	2.20110800
C	-3.21506100	-2.28968400	-0.54791200
H	-2.50814200	-2.27527900	0.28348600
C	-4.48463500	-3.00682100	-0.09211600
H	-5.20337900	-3.12600300	-0.91100800
H	-4.22178400	-4.00991400	0.25854000
H	-4.97331100	-2.47396800	0.73057800
C	-2.55130700	-2.96927800	-1.74985600
H	-2.30710500	-4.01027400	-1.51108200
H	-3.22062900	-2.95904200	-2.61762300
H	-1.62970900	-2.44287000	-2.01727000

TS1

The structure is depicted in Figure 1D.

F	-0.45029800	1.62615900	-1.31296400
F	1.15117400	0.21853100	-0.27549600
C	-0.59065000	0.68262700	-0.32133200
C	-0.98376600	1.20532800	0.90230600
C	1.76934200	-2.71539200	-2.76250200
C	1.55063900	-3.59849800	-1.75823500
H	2.53458400	-2.70403900	-3.51793100
H	2.06793500	-4.50814800	-1.50199300
N	0.85367000	-1.69249100	-2.60195100
N	0.51177800	-3.08340800	-0.99555800
C	0.06465700	-1.90245900	-1.50916700
C	-0.02002800	-3.73767600	0.20843600
H	-0.75949600	-3.03803100	0.60675500
C	-5.19353900	0.87266500	-0.83259900
C	-5.32286200	-0.01240900	0.18968500
H	-5.88113200	1.61045100	-1.21416200
H	-6.14858600	-0.18819700	0.85872800
N	-3.92678500	0.68663800	-1.36031100
N	-4.12701700	-0.70742000	0.26648200
C	-3.24890800	-0.28516800	-0.69015300
C	-3.80768900	-1.81023800	1.20076200
H	-2.79682800	-1.60411200	1.55552200
Ni	-1.39622800	-0.85933900	-0.93199100
O	-1.47576500	2.51031700	0.94320200
Si	-0.48115200	3.83577600	1.28784800
C	-0.08015100	4.72366800	-0.32547000
H	0.61908200	5.55447300	-0.16960100
H	0.36245400	4.02924700	-1.04498400
H	-0.99229000	5.13235000	-0.77697900
C	-1.52214400	4.95521500	2.38906500
H	-1.74232800	4.46492300	3.34451800
H	-1.00668200	5.89955900	2.60367100
H	-2.47748800	5.19736400	1.90825400
C	1.06584200	3.24003900	2.17096200
H	1.63135600	2.54168500	1.54785000
H	1.72401600	4.07852300	2.43083300
H	0.79714300	2.71606200	3.09569100
C	-1.15154000	0.39925400	2.08435600
C	-0.44499000	-0.81948600	2.24626000
C	-2.02710000	0.79503900	3.12246800
C	-0.65158400	-1.61883800	3.36665500
H	0.28585600	-1.09186200	1.49469500
C	-2.21852900	-0.01053600	4.24229400
H	-2.56486500	1.73170100	3.01980900
C	-1.54660300	-1.23082400	4.37174700
H	-0.08730300	-2.54175600	3.47147300
H	-2.90544900	0.31394100	5.02121300
H	-1.69727200	-1.85463600	5.24856200
C	0.74019300	-0.48268600	-3.44515200
H	0.63803000	0.33801500	-2.73677100

C	-3.35048600	1.48740600	-2.45589500
H	-2.34514700	1.08700800	-2.58696400
Cl	4.42424600	-1.03369800	-1.56543500
Li	2.87893900	-0.17138400	-0.12919400
C	5.00167100	1.91068600	0.09248200
O	3.56914800	1.74772500	0.14774400
C	3.00059300	2.65370600	-0.81377300
C	3.95844100	2.58975500	-2.00253100
C	5.33980700	2.41492000	-1.32985000
H	5.30512200	2.63059600	0.86608900
H	5.43768700	0.93270900	0.30238400
H	1.99049700	2.29896500	-1.01767000
H	2.95226500	3.66538200	-0.38082200
H	3.73246900	1.70499200	-2.60233700
H	3.89820400	3.47917000	-2.63845800
H	5.94283700	1.68037500	-1.86713300
H	5.88995400	3.36128200	-1.28622800
C	4.23906300	-1.91243600	1.87112100
O	3.10224500	-1.04151100	1.66879900
C	2.97045400	-0.13333400	2.79781200
C	4.09918200	-0.49908600	3.77166600
C	5.13584200	-1.15894500	2.84829400
H	3.88998300	-2.86150100	2.30583200
H	4.68089000	-2.09569100	0.88949400
H	3.07248200	0.88391500	2.41072600
H	1.97042900	-0.25060000	3.22276800
H	4.48435800	0.37602800	4.30404000
H	3.74677900	-1.22046800	4.51898400
H	5.71338500	-0.39770200	2.31107800
H	5.83541300	-1.81496100	3.37564800
C	-4.74049400	-1.81913300	2.40800400
H	-4.37435600	-2.55674100	3.12741900
H	-4.74289700	-0.84531700	2.90552100
H	-5.76638300	-2.09424500	2.13416900
C	-3.80935300	-3.14125700	0.44428200
H	-3.10048100	-3.09429100	-0.38973200
H	-3.50467000	-3.95651000	1.10914200
H	-4.80389600	-3.36701400	0.04287000
C	-0.71626100	-5.05181800	-0.15847800
H	-1.17604600	-5.49539000	0.73133400
H	-1.49758100	-4.88382600	-0.90645400
H	-0.00152600	-5.77548900	-0.56638800
C	1.08926300	-3.92847100	1.24713600
H	1.85392400	-4.62523800	0.88563600
H	1.57546600	-2.97594400	1.47497300
H	0.66643700	-4.34782500	2.16614500
C	-3.23464200	2.95456900	-2.03750300
H	-2.67919900	3.03014200	-1.09994800
H	-2.70124200	3.51731800	-2.81103400
H	-4.22368900	3.41097700	-1.90843900
C	-4.14491700	1.28094600	-3.74704600
H	-3.66532800	1.82437000	-4.56786100
H	-4.18810800	0.21934200	-4.01257700
H	-5.17101900	1.65528300	-3.65165800
C	2.00097300	-0.25546700	-4.27670600
H	1.93383800	0.72795100	-4.75381400
H	2.89697900	-0.28636500	-3.64869800
H	2.09883800	-1.00122100	-5.07560000
C	-0.51927400	-0.56880600	-4.31530400
H	-0.65385700	0.36242700	-4.87711600
H	-0.44319200	-1.39743500	-5.02916400
H	-1.40598300	-0.72916200	-3.69250600

TS2

The structure is depicted in Figure 1D.

F	-1.41311800	-1.46709500	-1.33798200
F	0.02562600	0.10402900	-2.10548200
C	-0.85219900	-0.26042200	-0.95783600
C	-1.80369100	0.73415700	-0.61486800
C	4.57369100	0.88484000	-1.47335000
C	4.58533300	1.39932600	-0.21575200
H	5.29335900	0.96932400	-2.27232100
H	5.31817300	2.01149300	0.28596600
N	3.39529900	0.16539800	-1.59539200
N	3.41140300	0.98344200	0.39013900
C	2.64941900	0.22608000	-0.45218600

C	2.99421000	1.30019400	1.76407000
H	2.11310800	0.67103000	1.90555100
C	-0.45266400	-3.21734200	2.53019600
C	-0.78268800	-2.09040200	3.20735900
H	-0.57971400	-4.25690800	2.78820500
H	-1.25140200	-1.96002300	4.16978400
N	0.12366200	-2.80653400	1.33460200
N	-0.40190800	-1.01625800	2.41287800
C	0.16449100	-1.44343500	1.24342300
C	-0.62210100	0.39881300	2.76713300
H	-0.25458700	0.96161000	1.90468900
Ni	0.81836400	-0.44694100	-0.16708000
O	-3.02192000	0.24028200	-0.12807200
Si	-4.27296100	-0.29729800	-1.12169600
C	-4.54987300	-2.12946200	-0.77519000
H	-5.42718200	-2.51651500	-1.30841700
H	-3.67437700	-2.71047400	-1.08293900
H	-4.70583300	-2.30010600	0.29688300
C	-5.80419200	0.67737700	-0.60786300
H	-5.99314400	0.56735400	0.46692800
H	-5.67087400	1.74561200	-0.81473200
H	-6.70050300	0.33760600	-1.14182900
C	-3.84262100	0.01186800	-2.92608500
H	-2.93734800	-0.54021800	-3.19734000
H	-4.65693200	-0.30024900	-3.59174000
H	-3.64597500	1.07619500	-3.09714200
C	-1.52951200	2.12297000	-0.40193600
C	-0.27850600	2.73724500	-0.70486900
C	-2.53669200	2.97851700	0.12616000
C	-0.07417000	4.09766000	-0.51739900
H	0.53196300	2.12973300	-1.09205900
C	-2.31025900	4.33738500	0.32128300
H	-3.49857900	2.54974000	0.38346200
C	-1.08138500	4.92245200	0.00221200
H	0.89512100	4.52225700	-0.77453500
H	-3.11143600	4.95065700	0.73017100
H	-0.90921000	5.98394200	0.15626400
C	2.94647400	-0.52735000	-2.81586900

H	2.05871600	-1.07999200	-2.50101500
C	0.56663600	-3.69983600	0.25518200
H	0.92437100	-3.01470500	-0.52045800
C	-2.11253000	0.69909300	2.93831700
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H	3.69805200	1.02942800	3.78957300
H	4.34098100	-0.16616000	2.64186400
H	4.97807600	1.49373300	2.66297800
C	2.58607000	2.76888300	1.88970700
H	1.77311400	3.00479600	1.19696700
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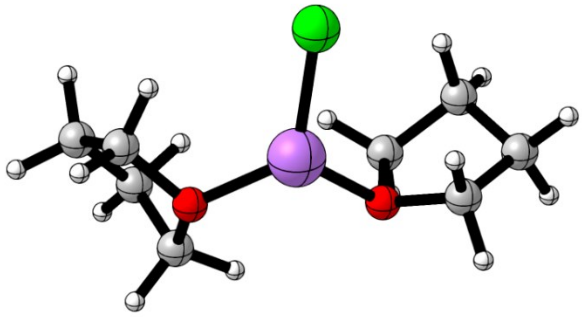
H	3.43321400	3.43311000	1.67932300
C	-0.61377100	-4.50090500	-0.29870900
H	-1.40255800	-3.81959100	-0.62632400
H	-0.28999800	-5.10448900	-1.15362300
H	-1.02383600	-5.18077400	0.45765500
C	1.72770500	-4.57986800	0.72394100
H	2.09577500	-5.19242600	-0.10620300
H	2.55248600	-3.96328400	1.09639500
H	1.41448100	-5.25776600	1.52702100
C	2.53694700	0.48730400	-3.88575700
H	2.14741100	-0.03409200	-4.76649900
H	1.75370500	1.14419800	-3.50037800
H	3.39353300	1.09594600	-4.19996200
C	4.00955900	-1.51585600	-3.30056200
H	3.61946300	-2.09114700	-4.14650600
H	4.91628600	-1.00169100	-3.64051100
H	4.28701900	-2.21346700	-2.50340300

LiCl(thf)$_2$



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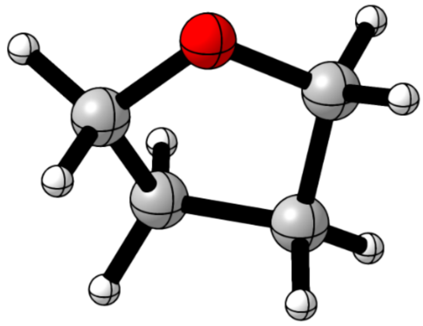
Li	0.00297500	0.57617600	-0.79976100
C	2.78760600	0.81600100	-0.39660200
O	1.77986800	-0.07115600	-0.96974300
C	2.09855700	-1.42529600	-0.59817600
C	2.67137400	-1.29281900	0.81007300
C	3.50928700	-0.00252700	0.69771200
H	3.46570900	1.12980400	-1.19749000
H	2.24761400	1.68526200	-0.01274200
H	1.17614900	-2.00779800	-0.66897500
H	2.83781000	-1.83601800	-1.30097300
H	1.85426400	-1.16045600	1.52819500
H	3.26028700	-2.16282500	1.11507600
H	3.56168200	0.54168200	1.64420600
H	4.53336400	-0.23875400	0.38990500
C	-1.46505800	-1.12170700	0.77546600
O	-1.32274500	-0.81378600	-0.64006000
C	-2.60107400	-0.33795700	-1.16402300
C	-3.62353500	-0.57168400	-0.05049400
C	-2.75815400	-0.44059300	1.21222100
H	-1.50586000	-2.21319000	0.88754700
H	-0.58164200	-0.73606100	1.29415900
H	-2.49497000	0.73093500	-1.38388000
H	-2.81064300	-0.89015300	-2.08476400
H	-4.43931000	0.15556500	-0.08730400
H	-4.05416600	-1.57756100	-0.12469000
H	-2.55248200	0.61306300	1.42517700
H	-3.20224100	-0.91275600	2.09355400

THF



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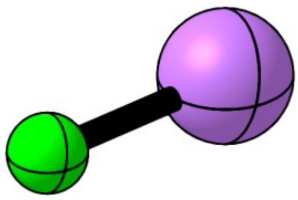
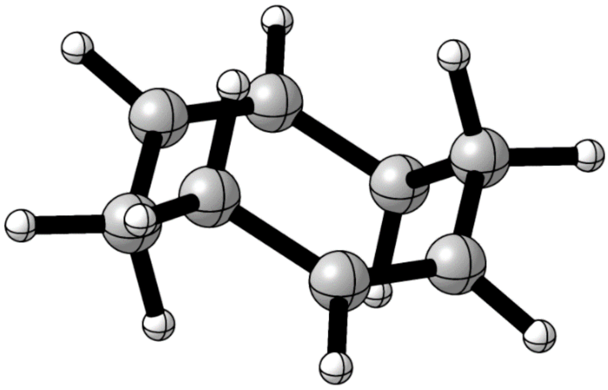
O	0.00000000	1.25210700	0.00000000
C	1.16446600	0.42958000	-0.13429200
C	0.73218100	-0.99597600	0.23174300
C	-0.73218100	-0.99597700	-0.23174200
H	-1.52864300	0.47554300	1.17282800
H	-1.95211000	0.82377400	-0.51884500
H	1.52864200	0.47554300	-1.17282800
H	1.95211000	0.82377500	0.51884400
H	1.34569600	-1.76394400	-0.24946900
H	0.78660300	-1.14541900	1.31693600
H	-0.78660300	-1.14542000	-1.31693600
H	-1.34569600	-1.76394400	0.24947000

LiF



Li	0.00000000	0.00000000	-1.16405900
F	0.00000000	0.00000000	0.38802000

COD



C	0.47214800	-1.61130300	0.81744500
C	1.06154100	-1.48937900	-0.37688100
C	-1.06154100	1.48937900	0.37688100
C	1.33539100	-0.19889300	-1.11720000
C	-0.47214800	1.61130300	-0.81744500
C	0.04683400	0.48487100	-1.68352700
H	1.34803000	-2.40459800	-0.89507000
H	1.84945500	0.51576300	-0.46080800
H	-1.34803000	2.40459800	0.89507000
H	-0.31315100	2.61874800	-1.20215100
H	0.31315100	-2.61874800	1.20215100
H	2.02232100	-0.40889000	-1.94491400
H	0.26164600	0.88150700	-2.68233600
H	-0.72685500	-0.28335200	-1.81439200
C	-0.04683400	-0.48487100	1.68352700
H	0.72685500	0.28335200	1.81439200
H	-0.26164600	-0.88150700	2.68233600
C	-1.33539100	0.19889300	1.11720000
H	-1.84945500	-0.51576300	0.46080800
H	-2.02232100	0.40889000	1.94491400

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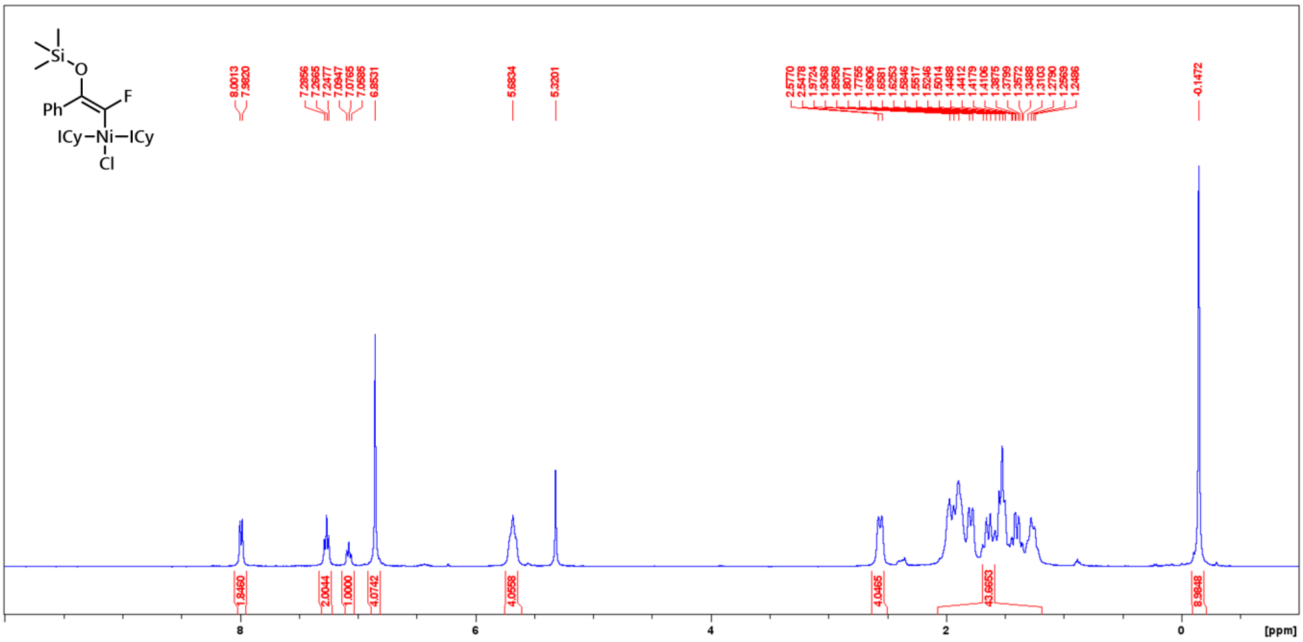
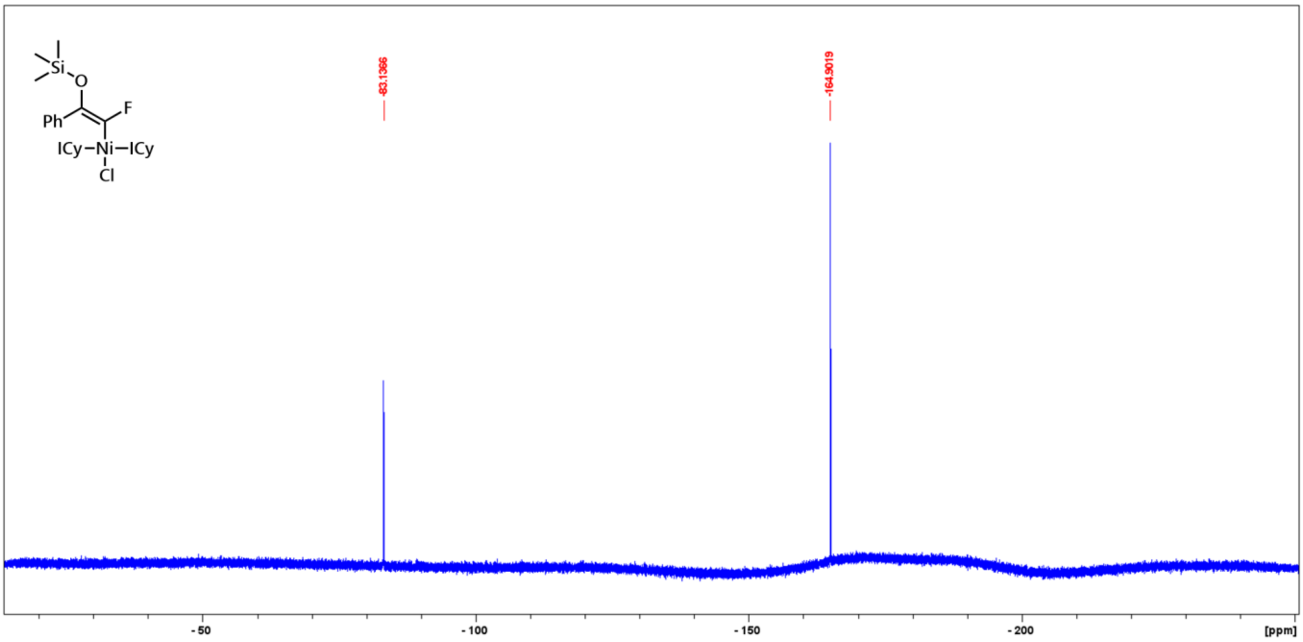
Spectrum Data

2a

^{1}H NMR (400 MHz, CD_2Cl_2)



^{19}F NMR (376 MHz, CD_2Cl_2)



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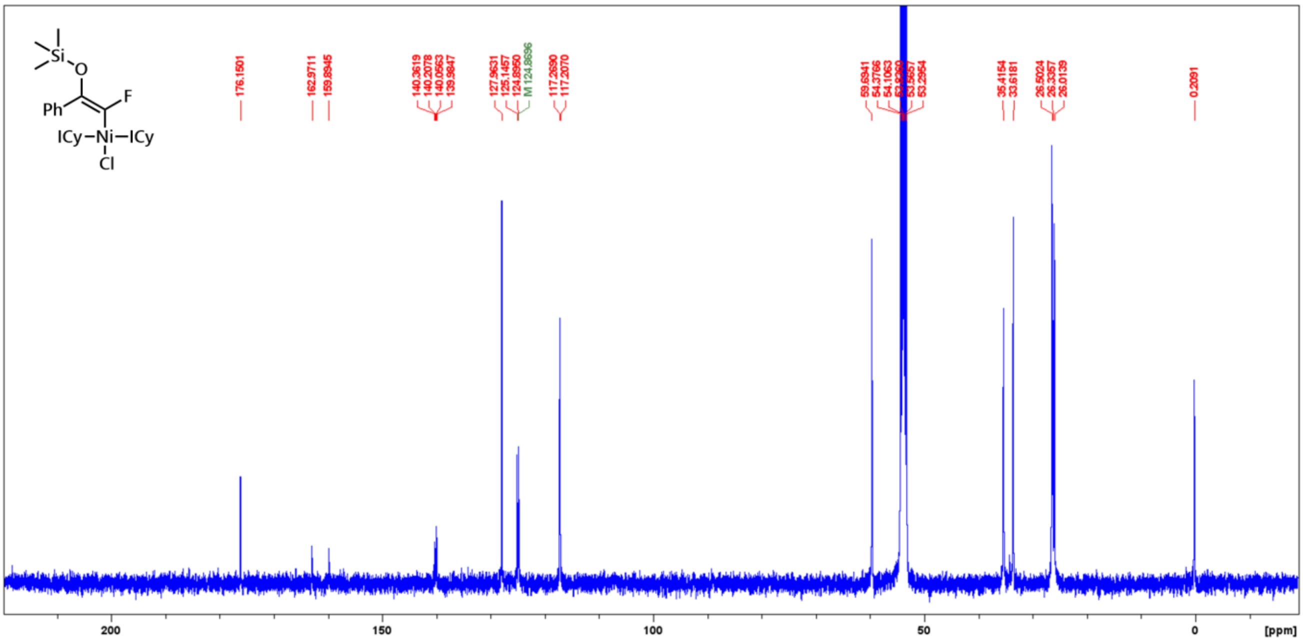

2b

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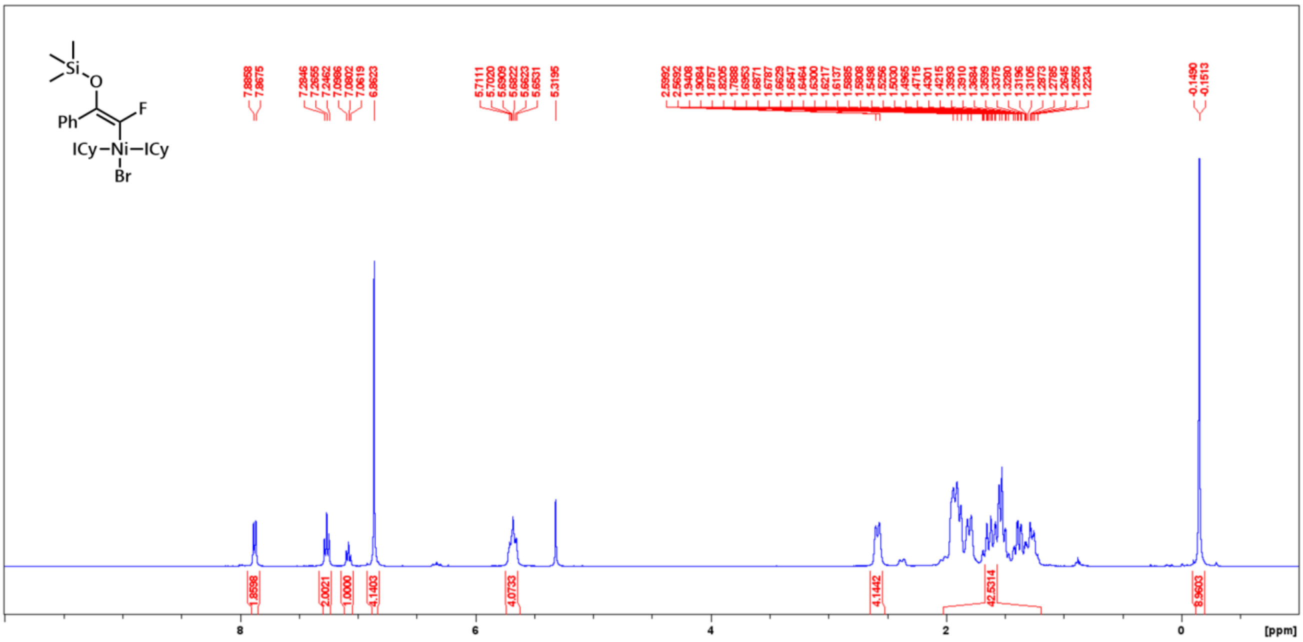

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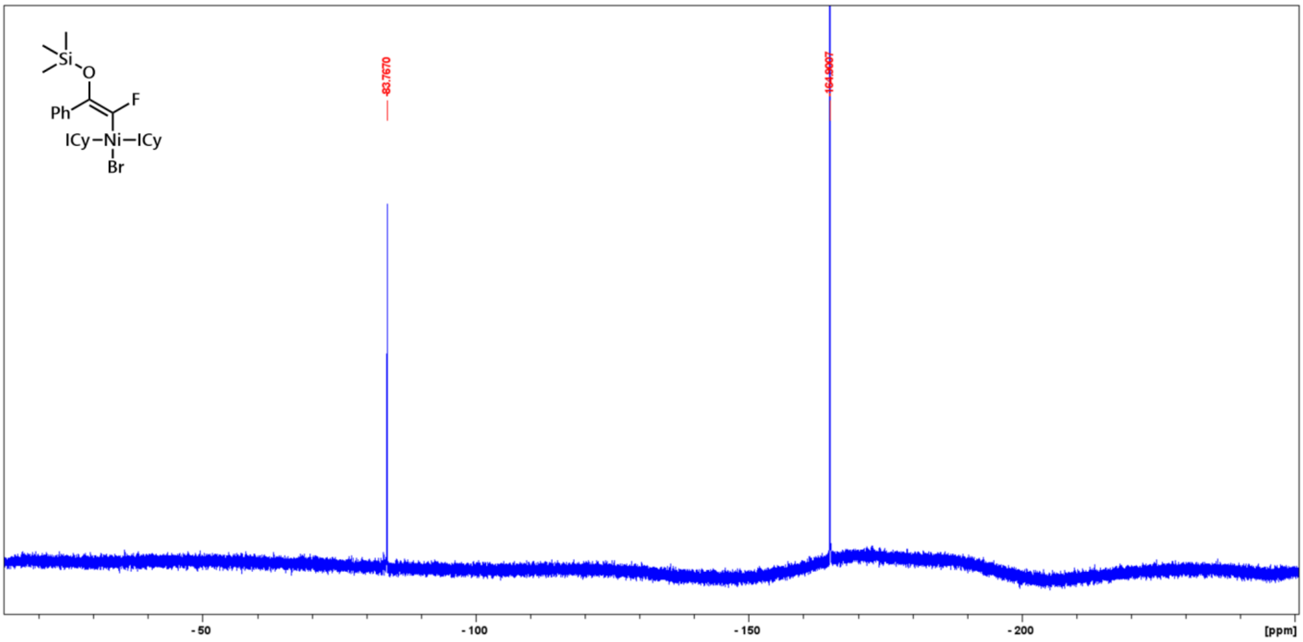

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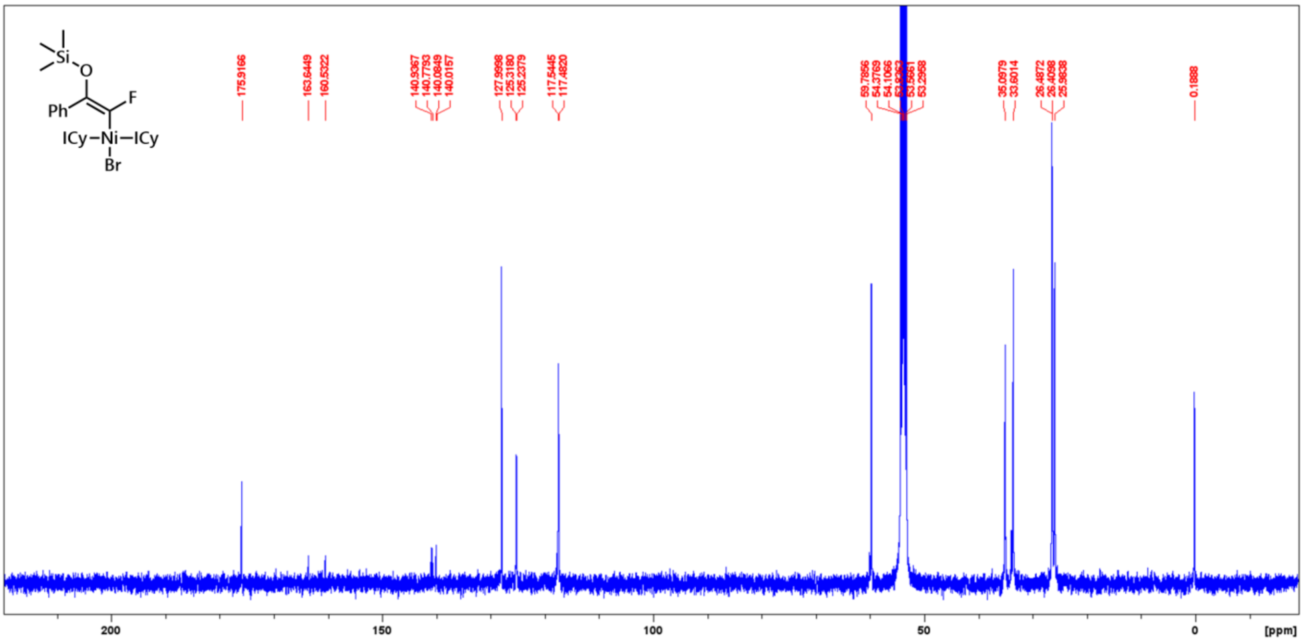
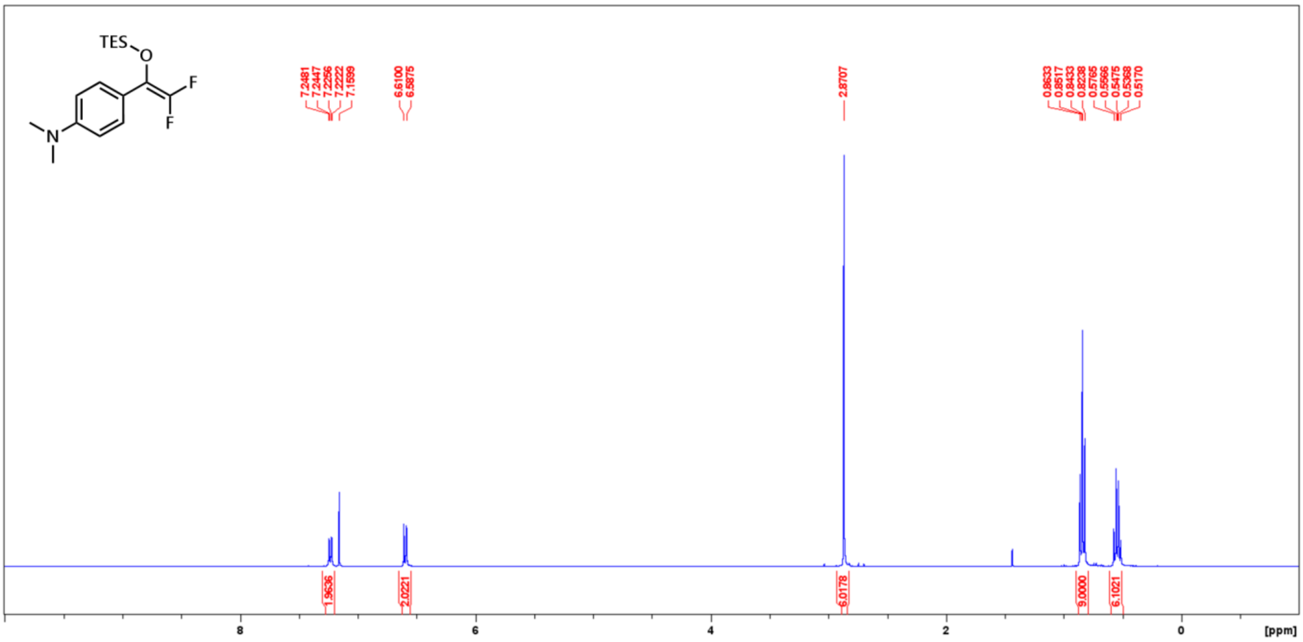


5u

^{1}H NMR (400 MHz, $CDCl_3$)



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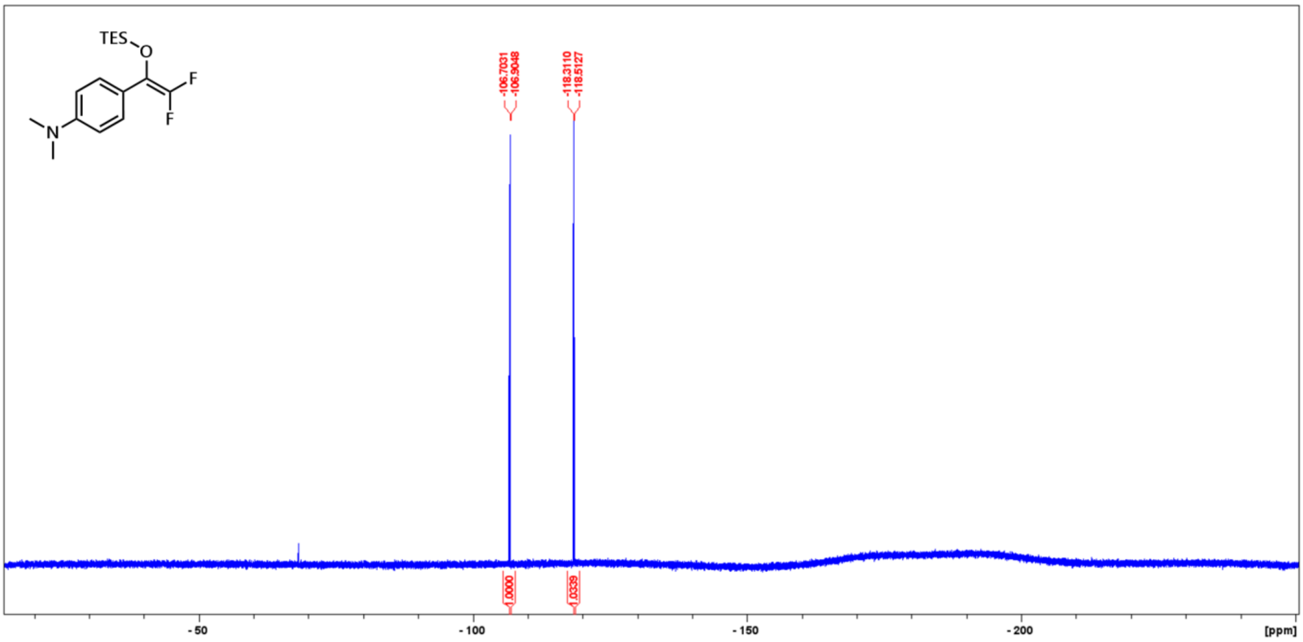

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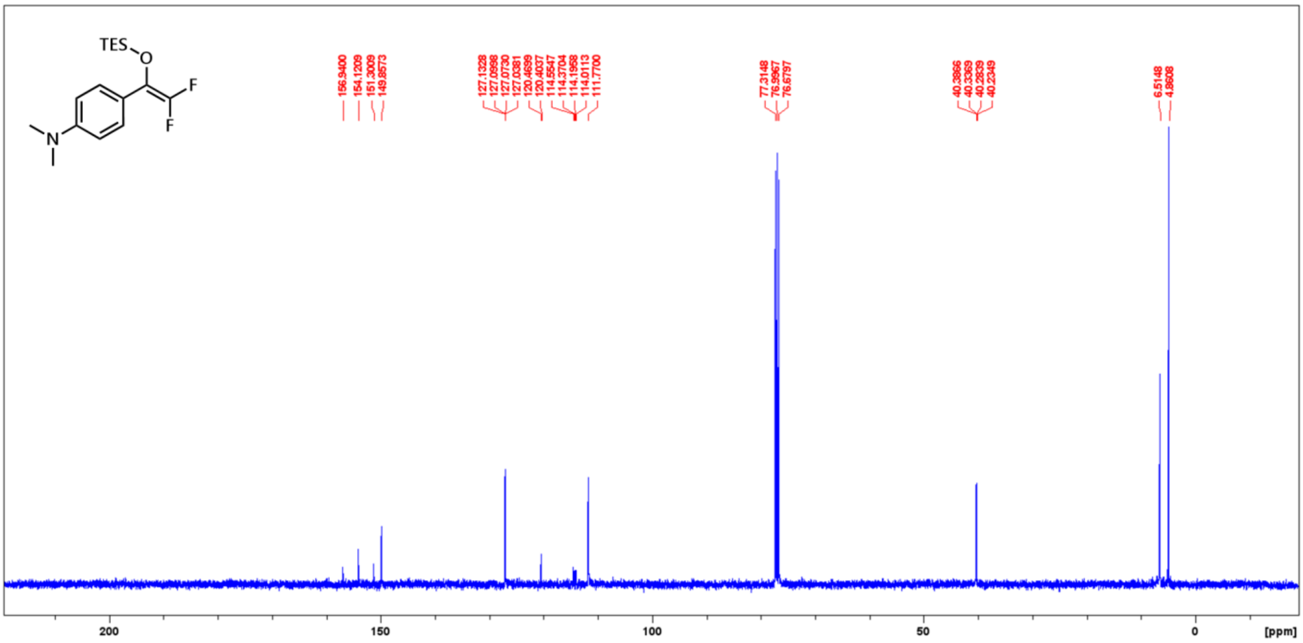

5x

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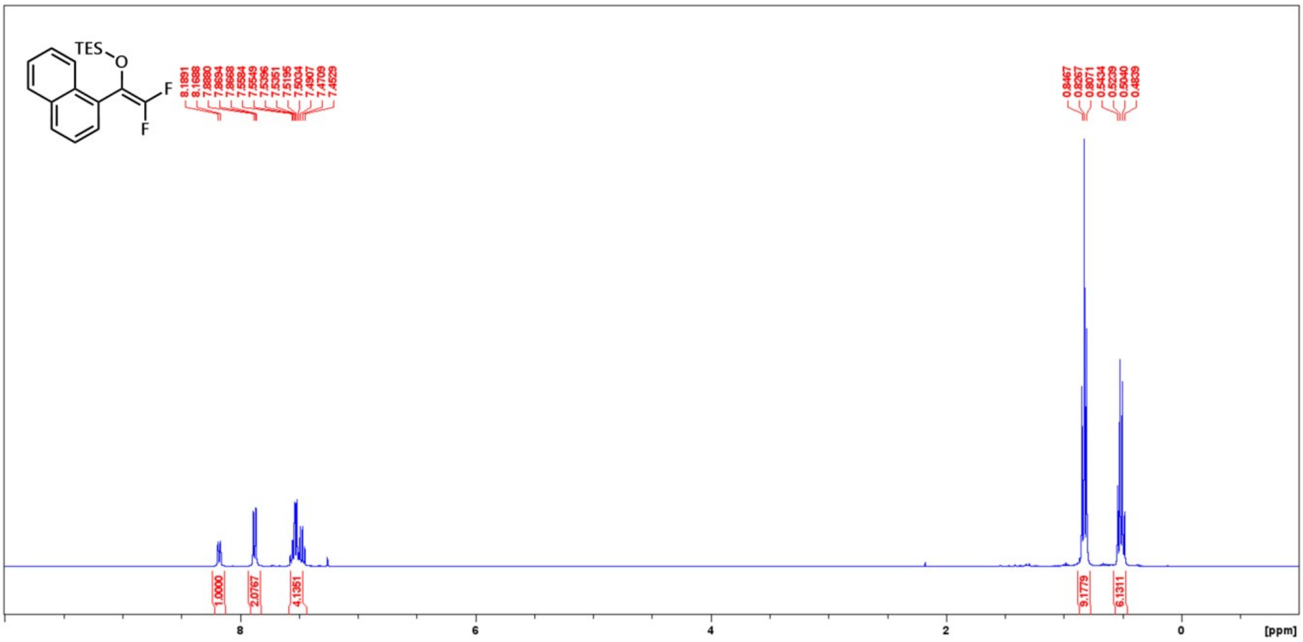

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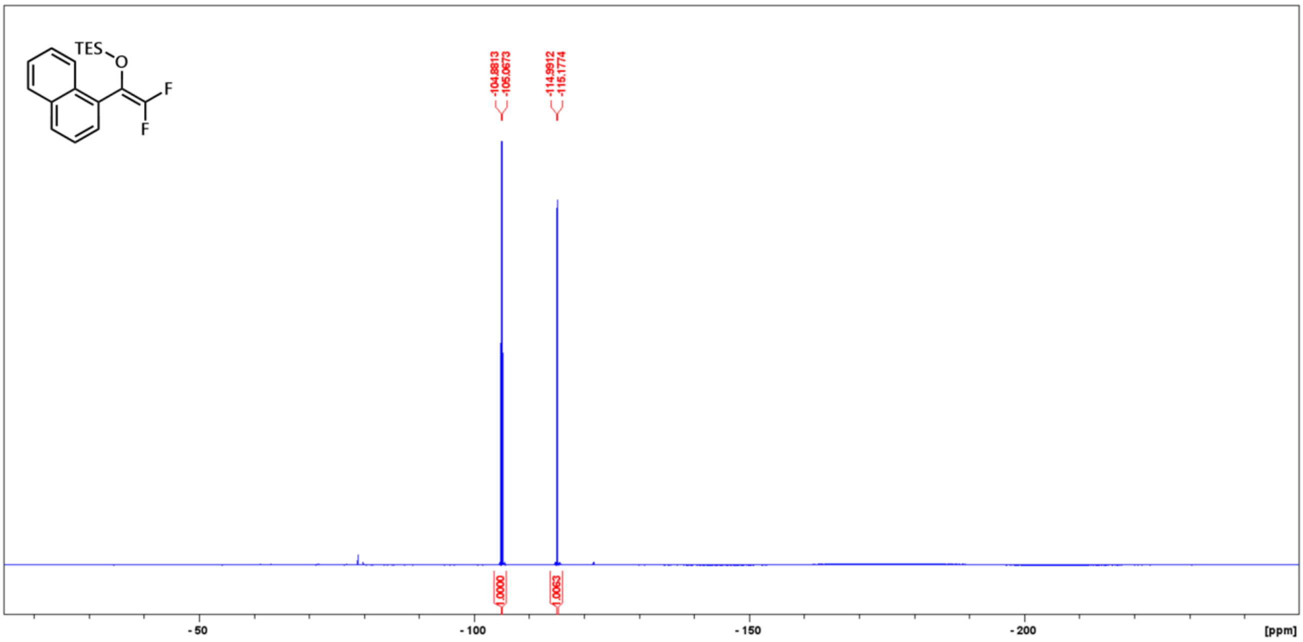

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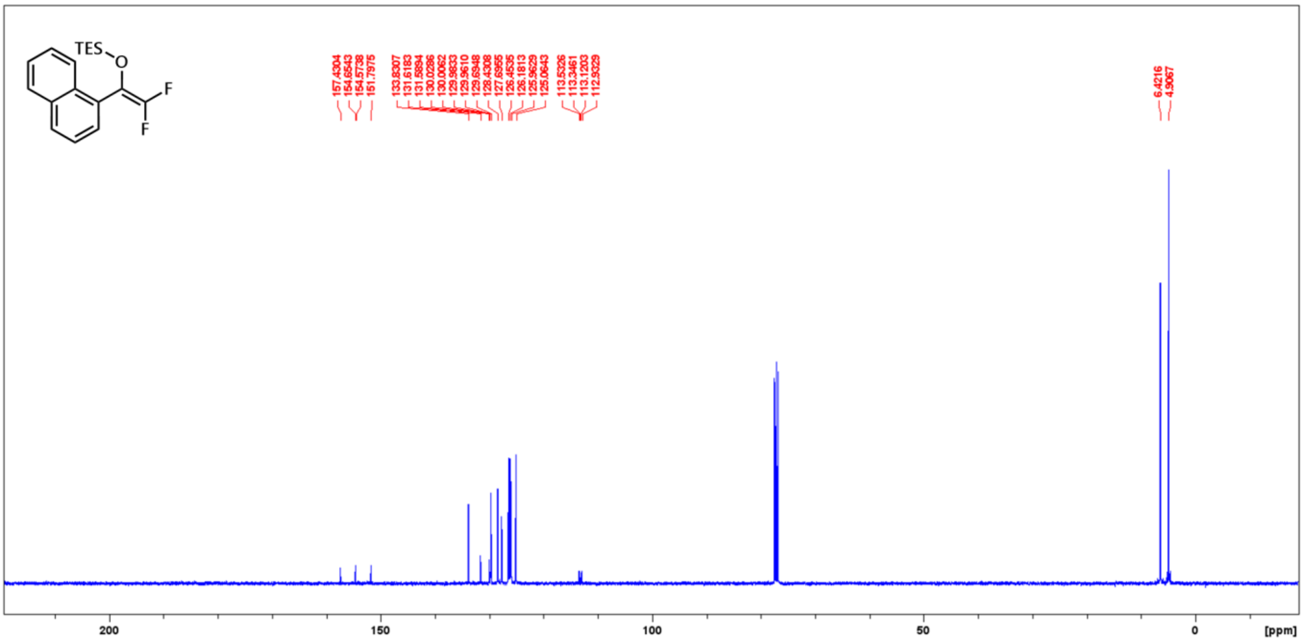

(Z)-6a

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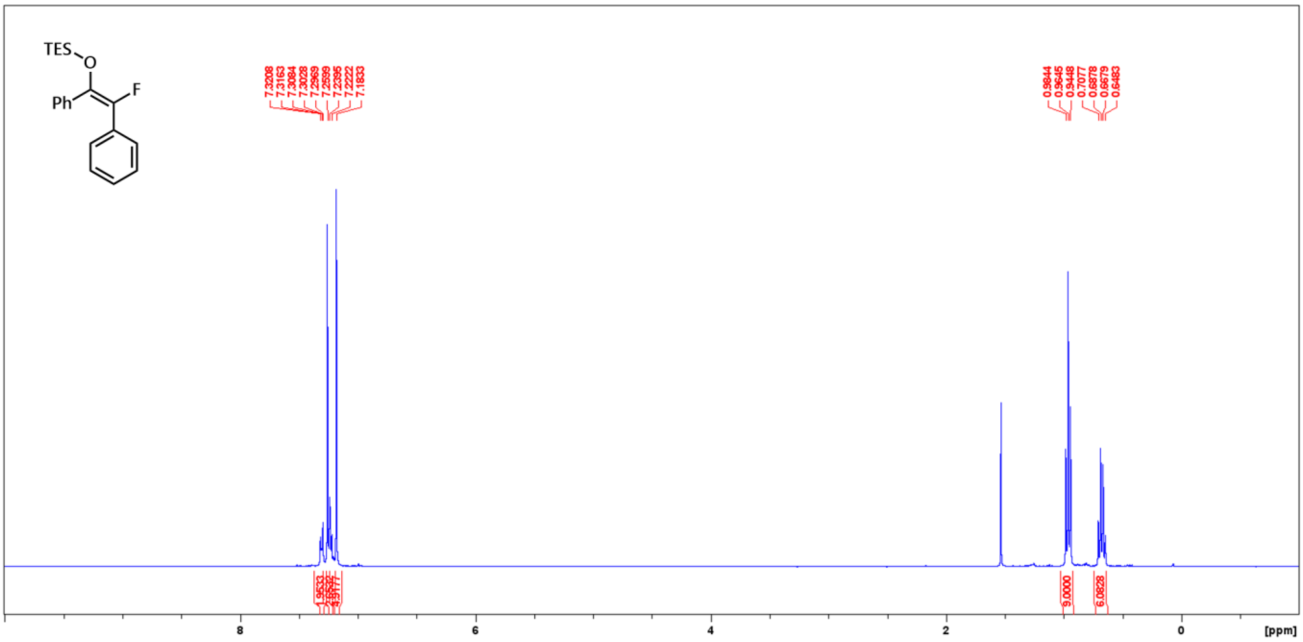

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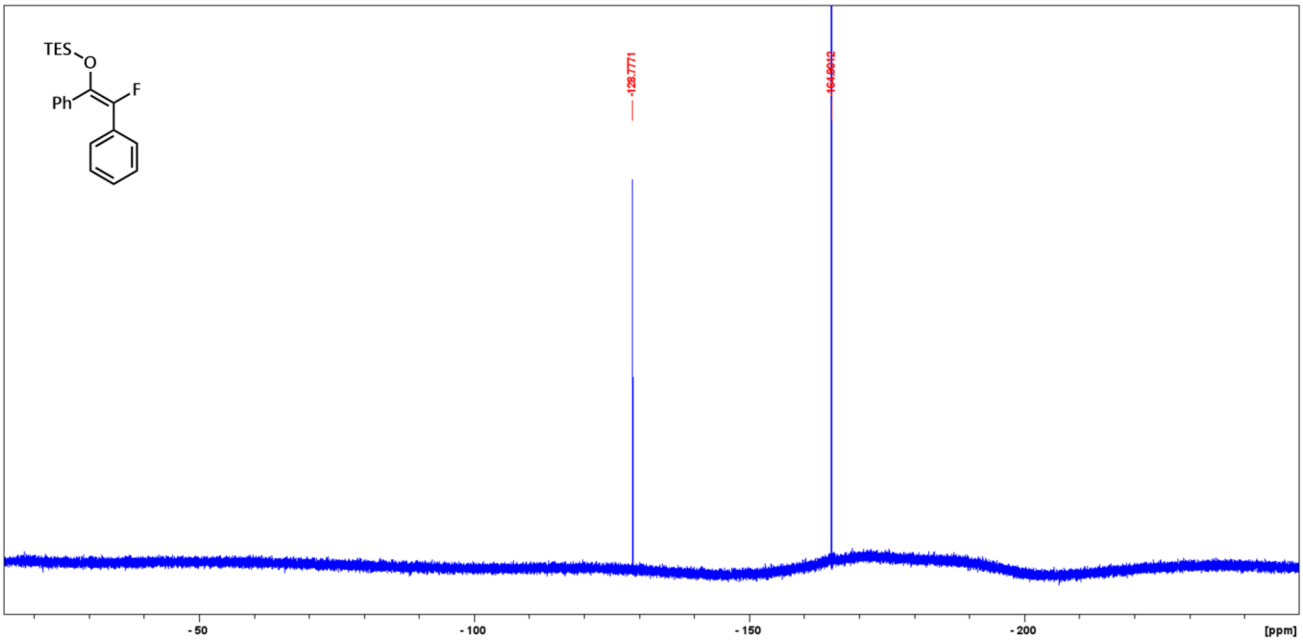
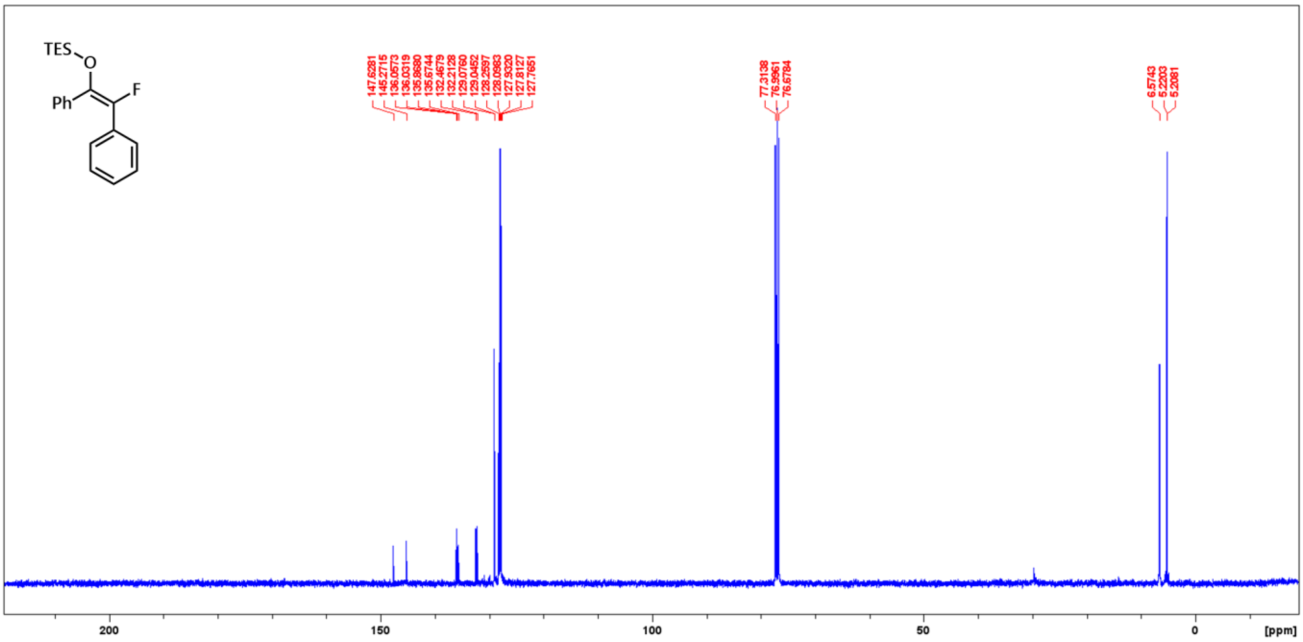


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)



(E)-6a

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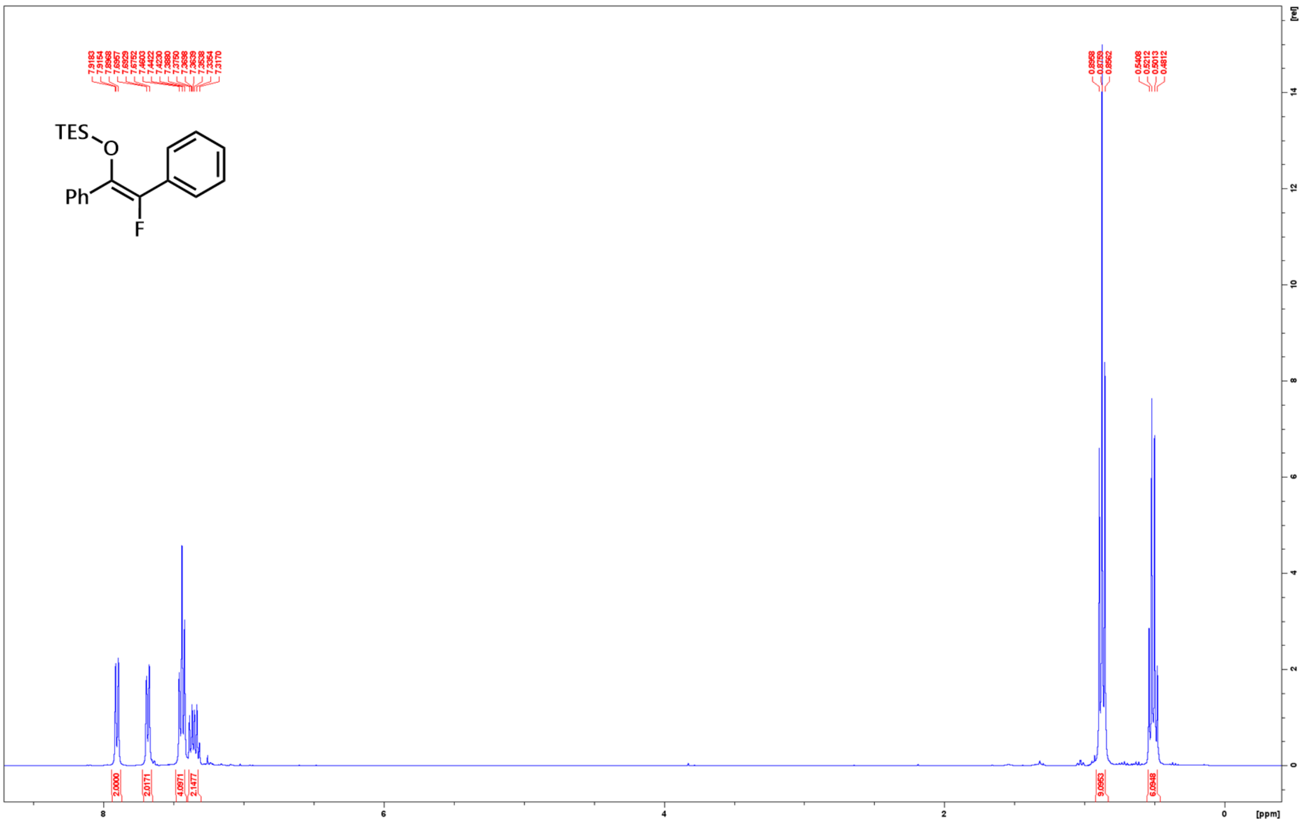

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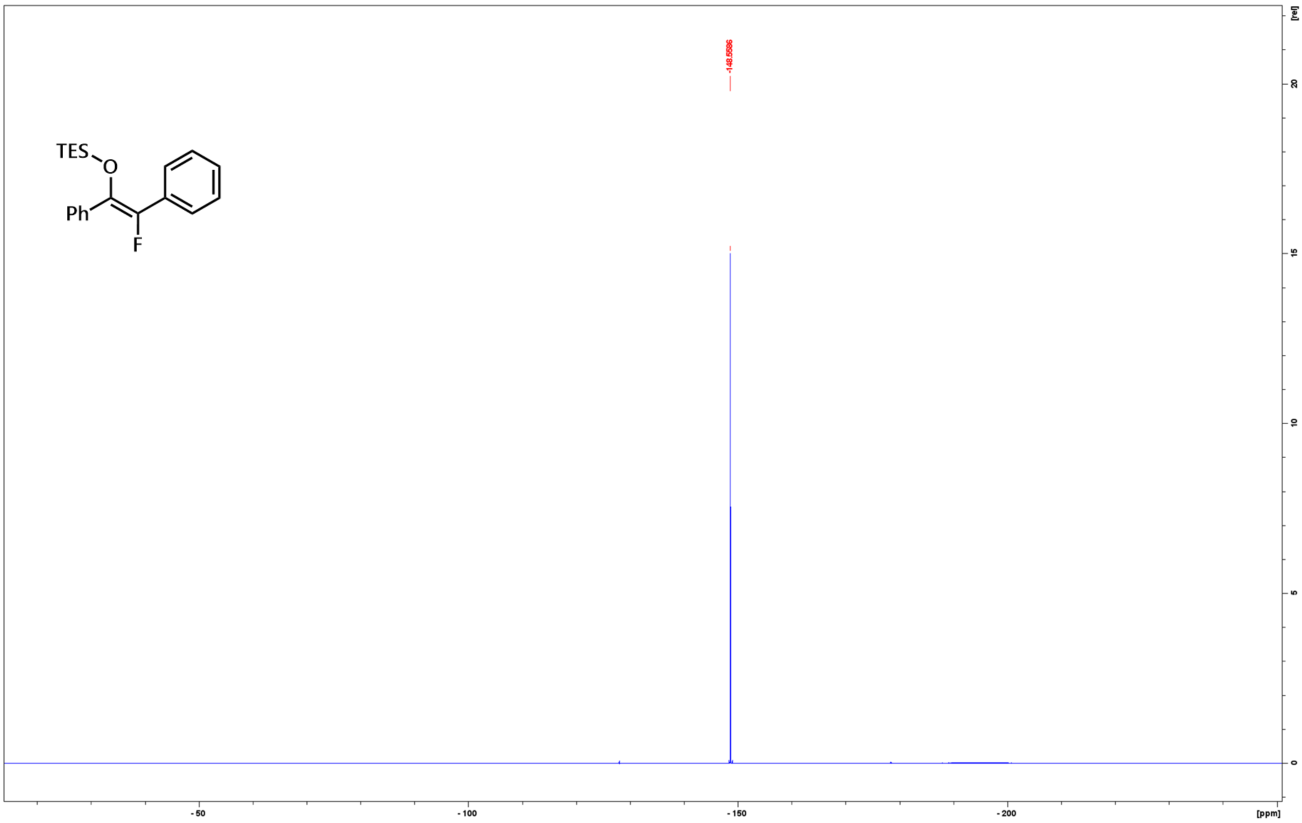

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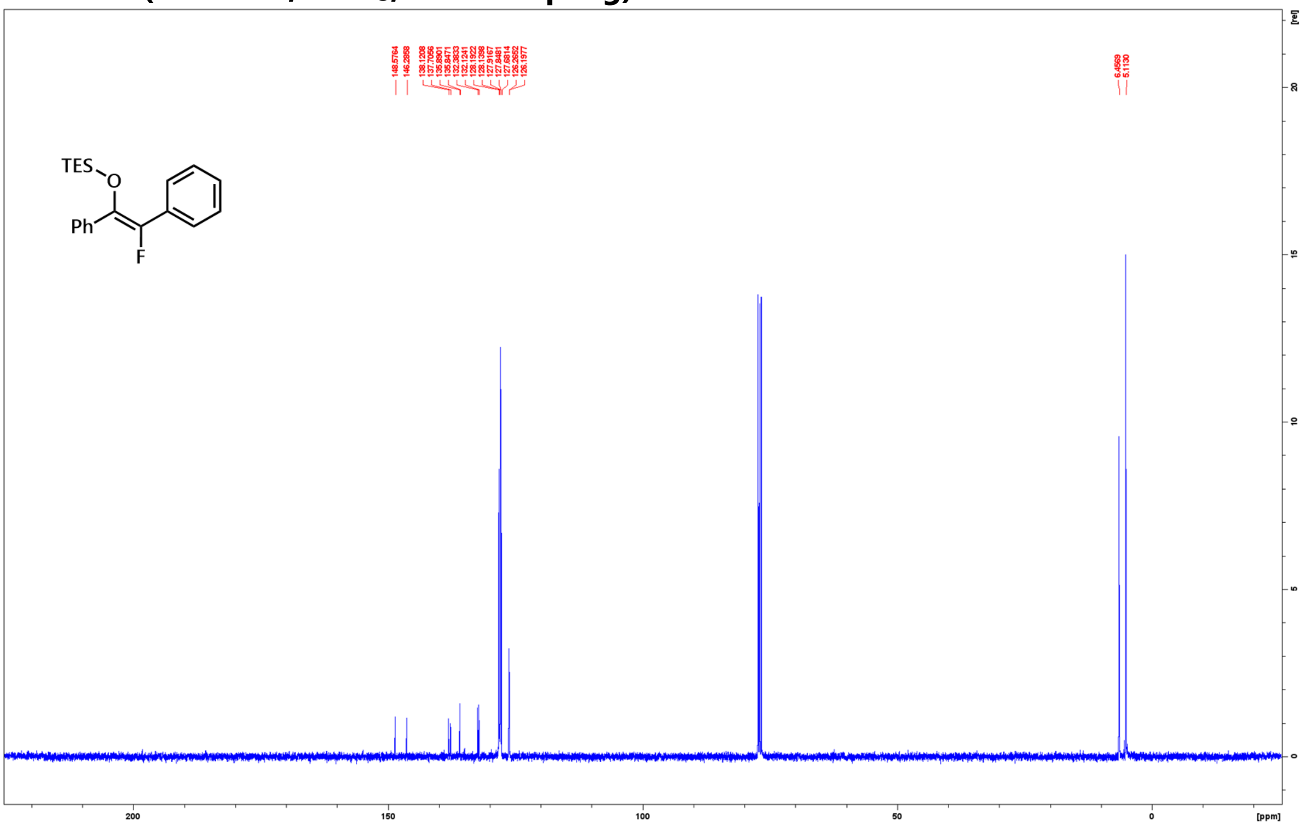
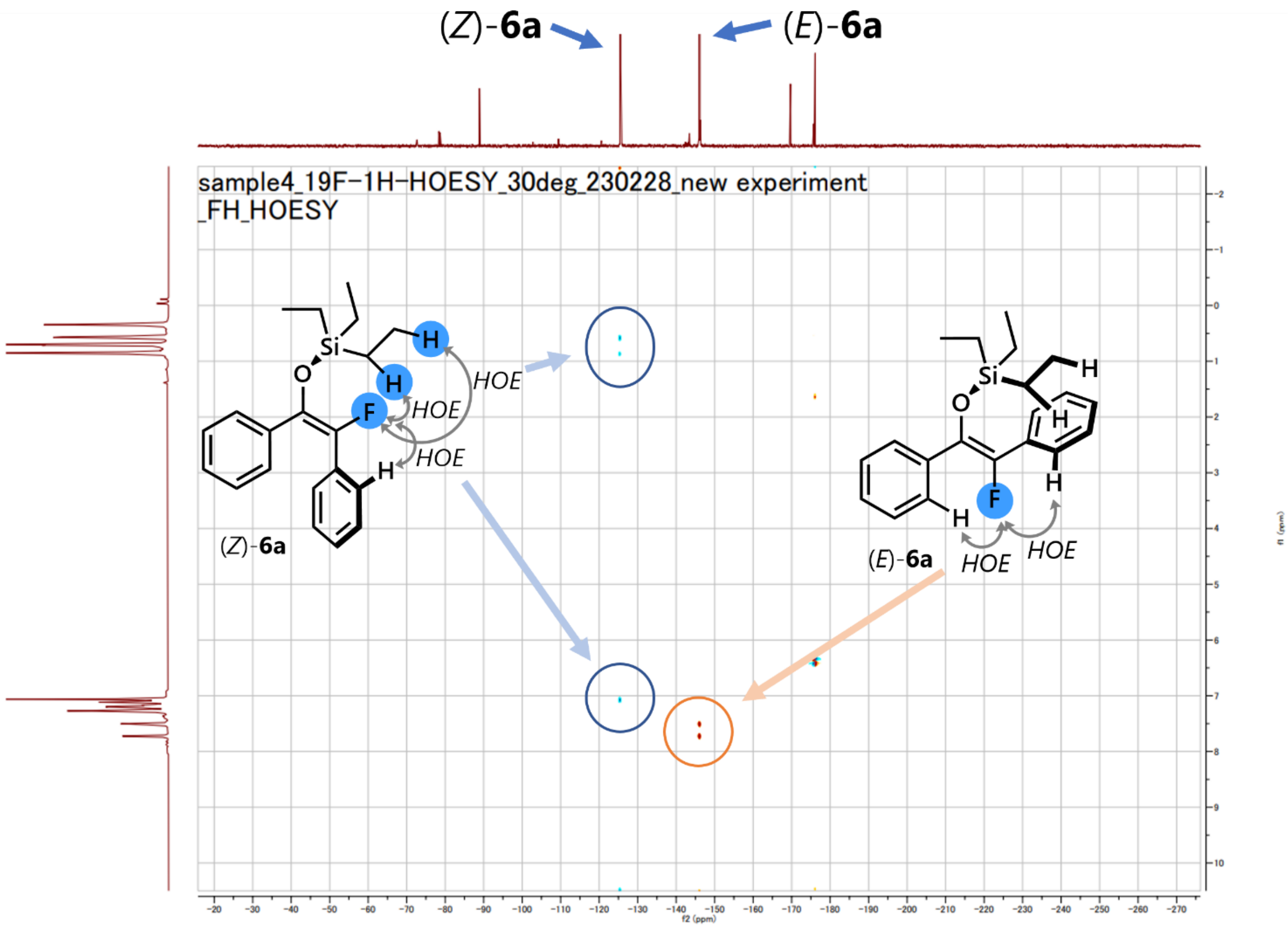


^{1}H-^{19}F HOESY (mixture of (*E*)-6a and (*Z*)-6a, $CDCl_3$)



(Z)-6b

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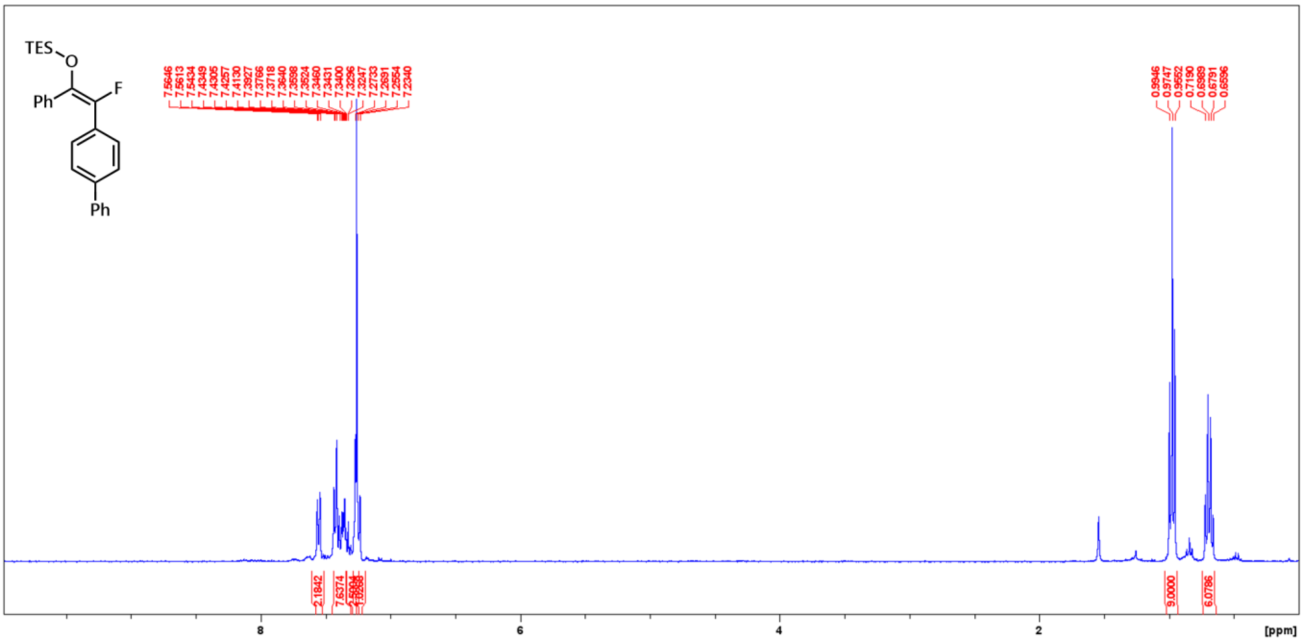

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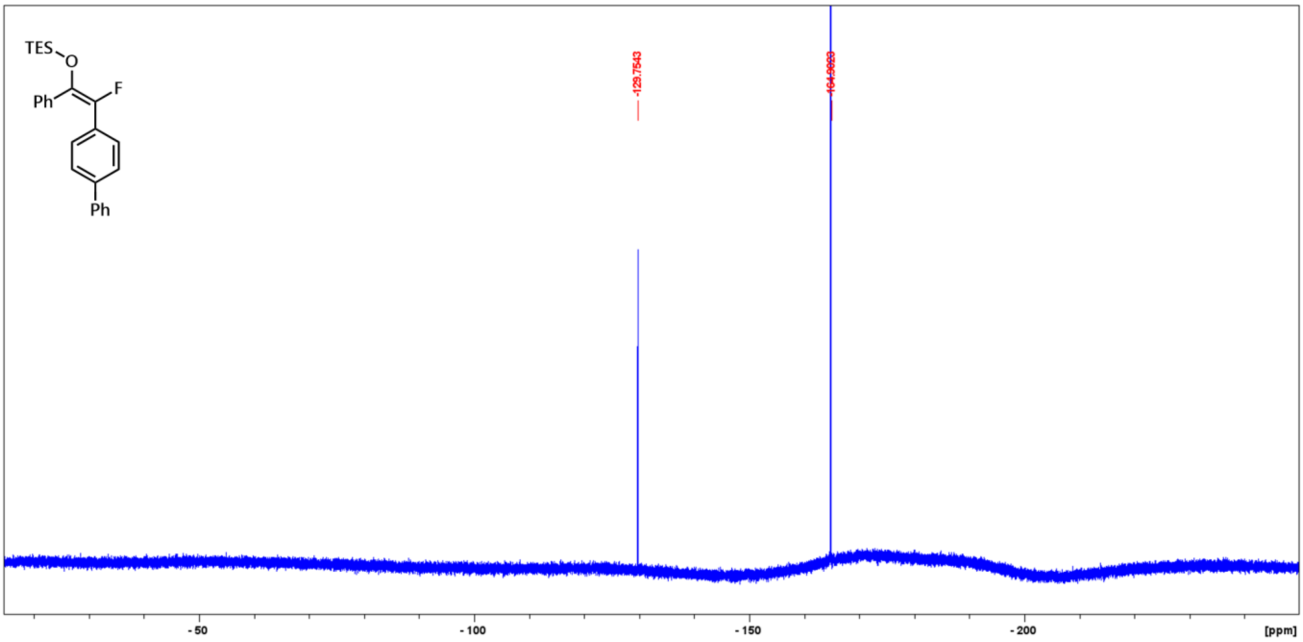

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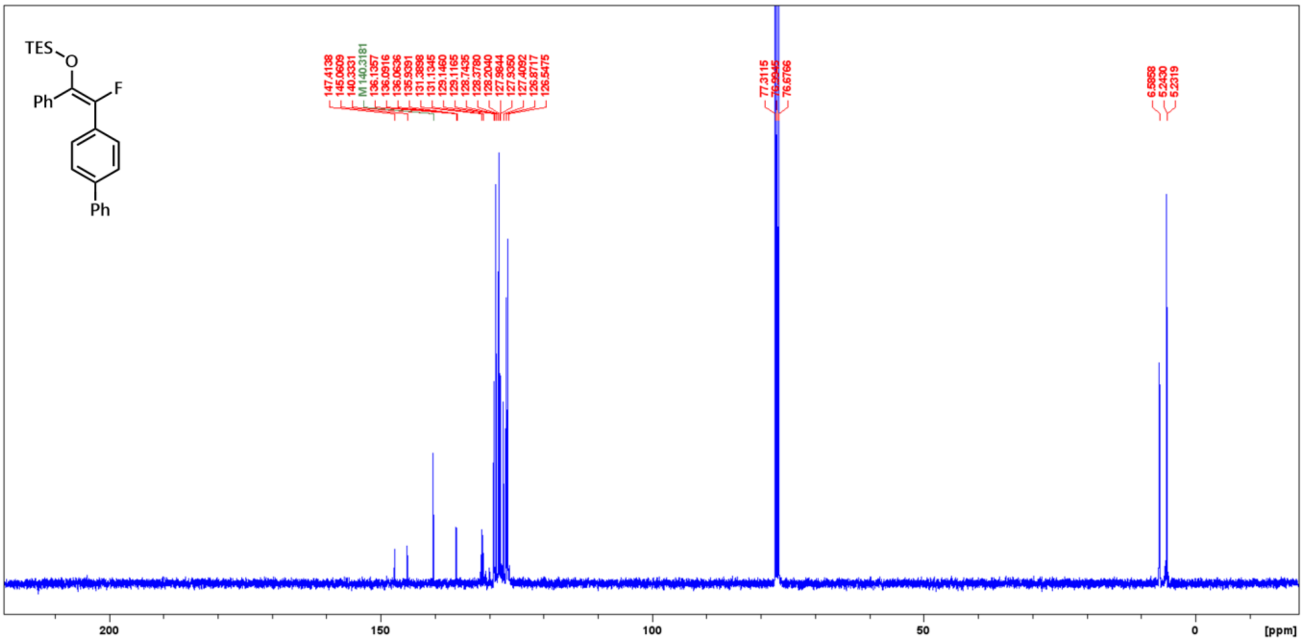

(Z)-6c

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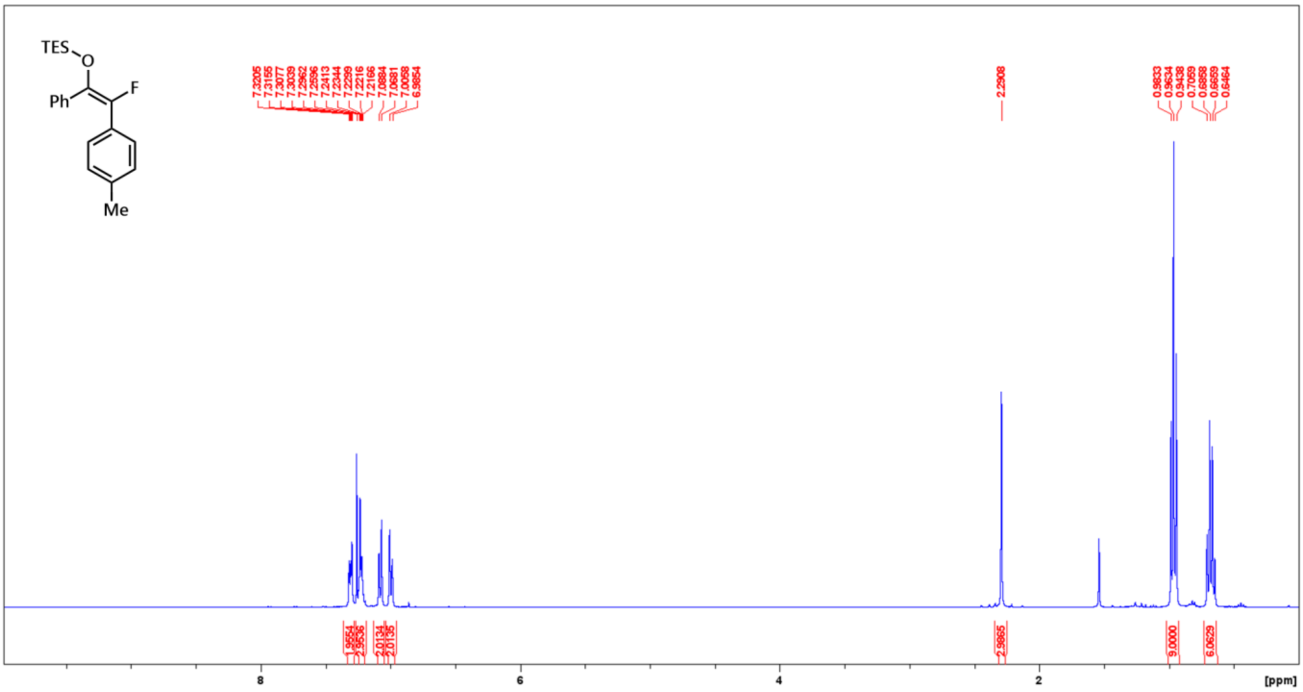
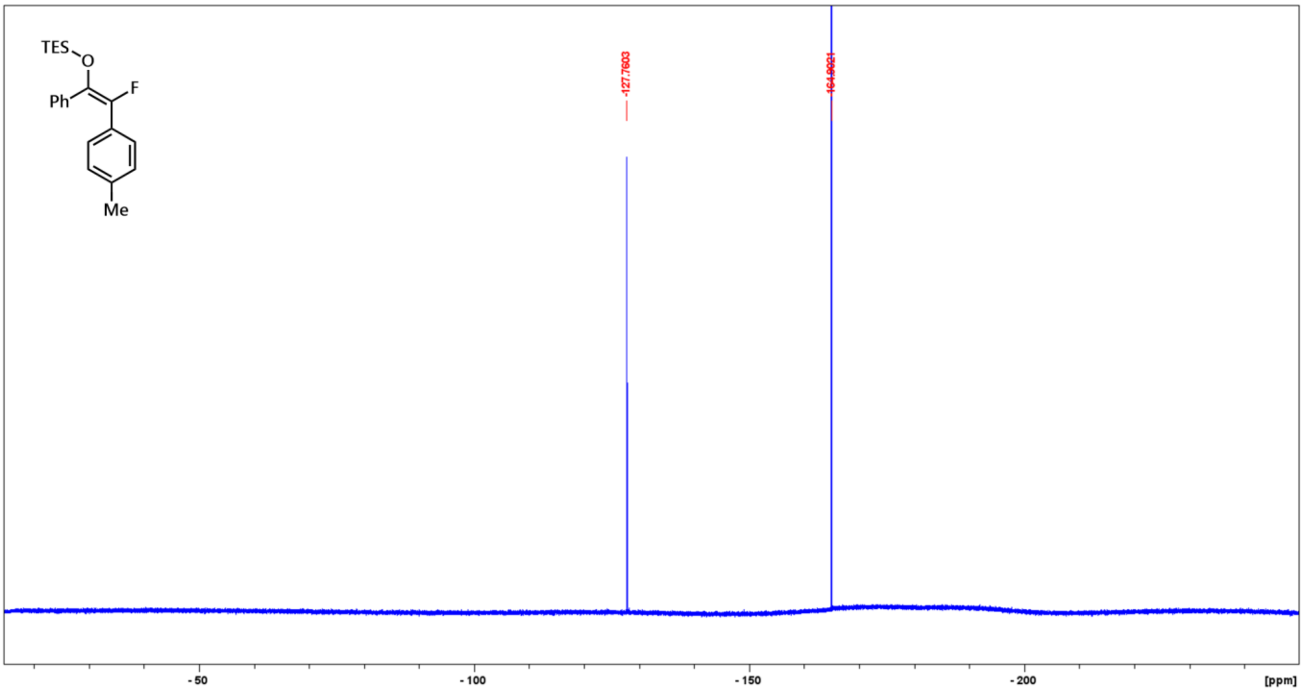
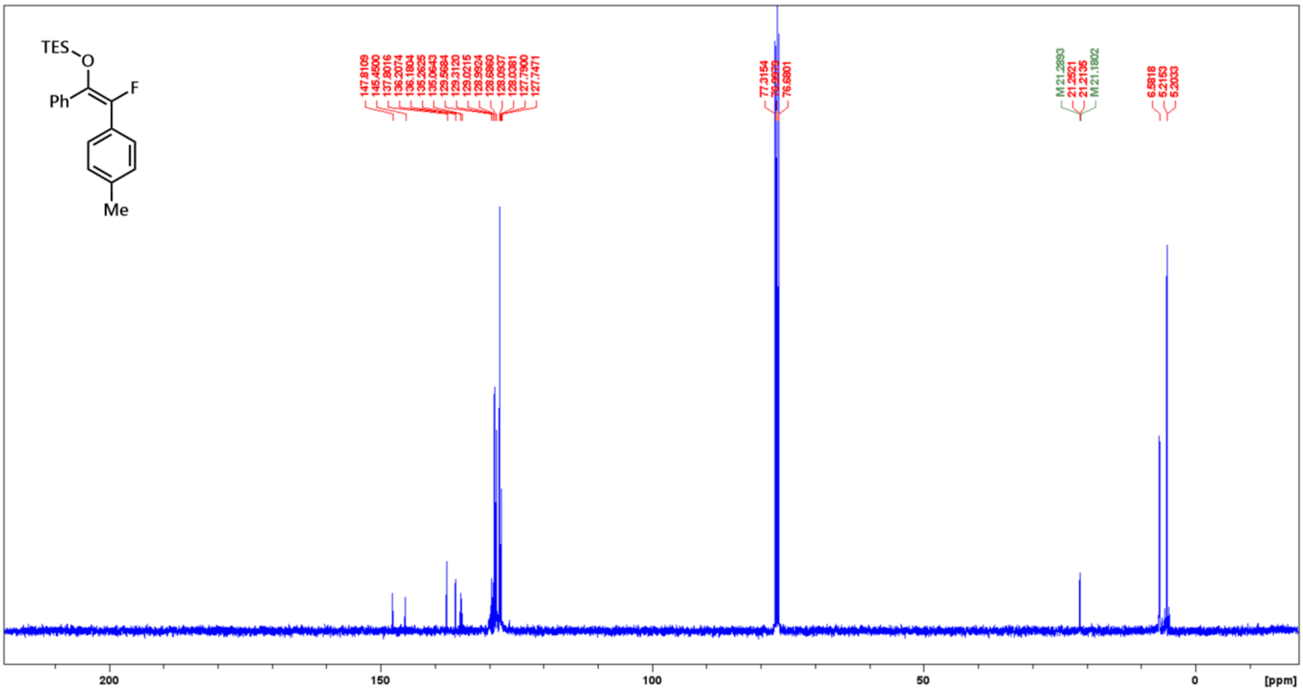


^{19}F NMR (376 MHz, $CDCl_3$)

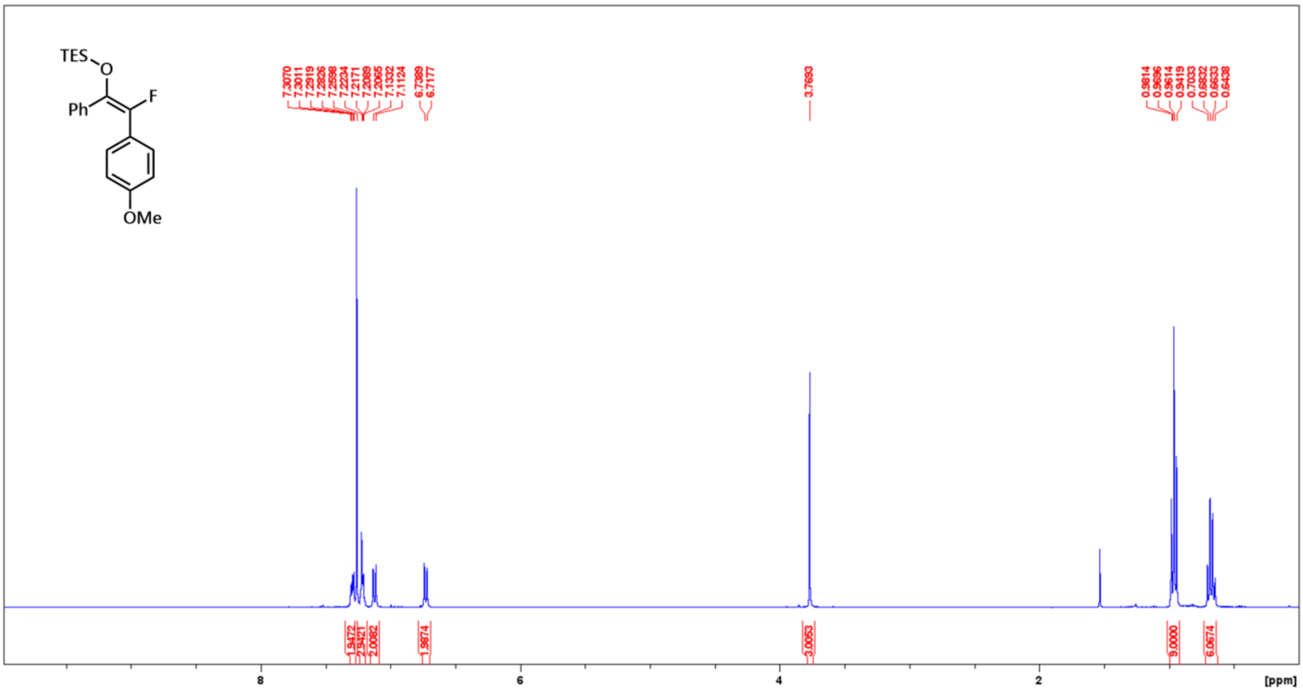


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

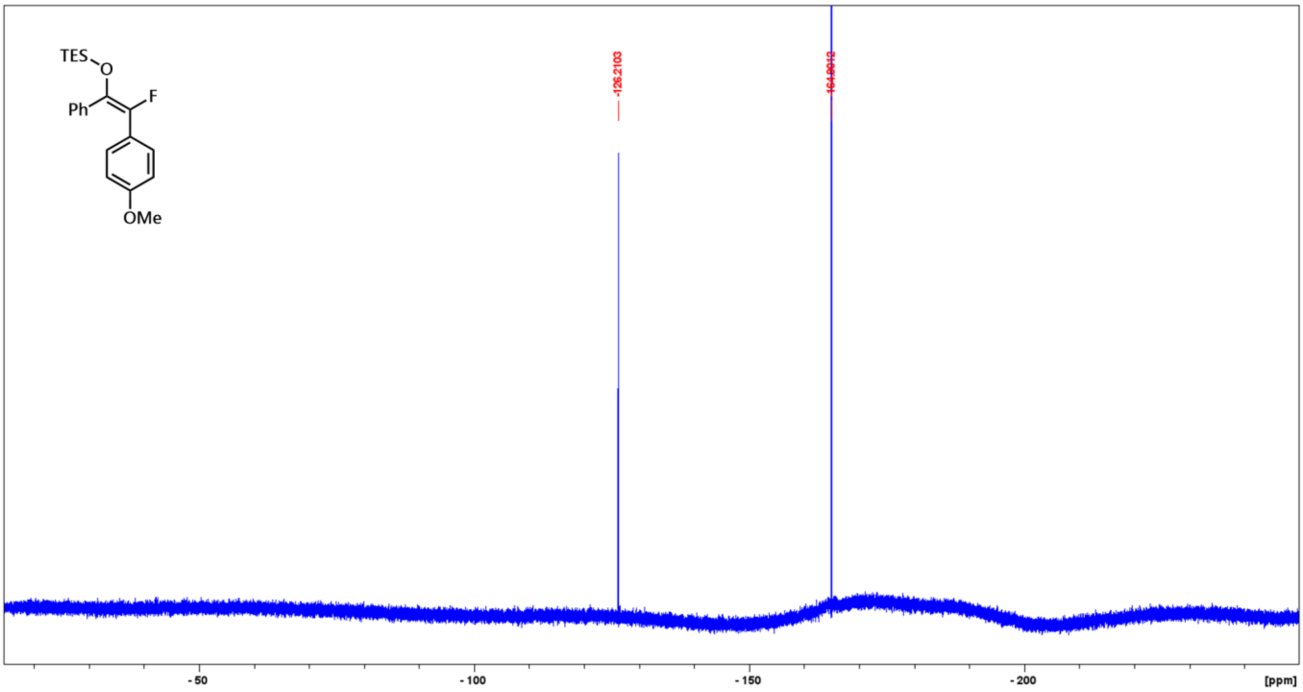


(Z)-6d

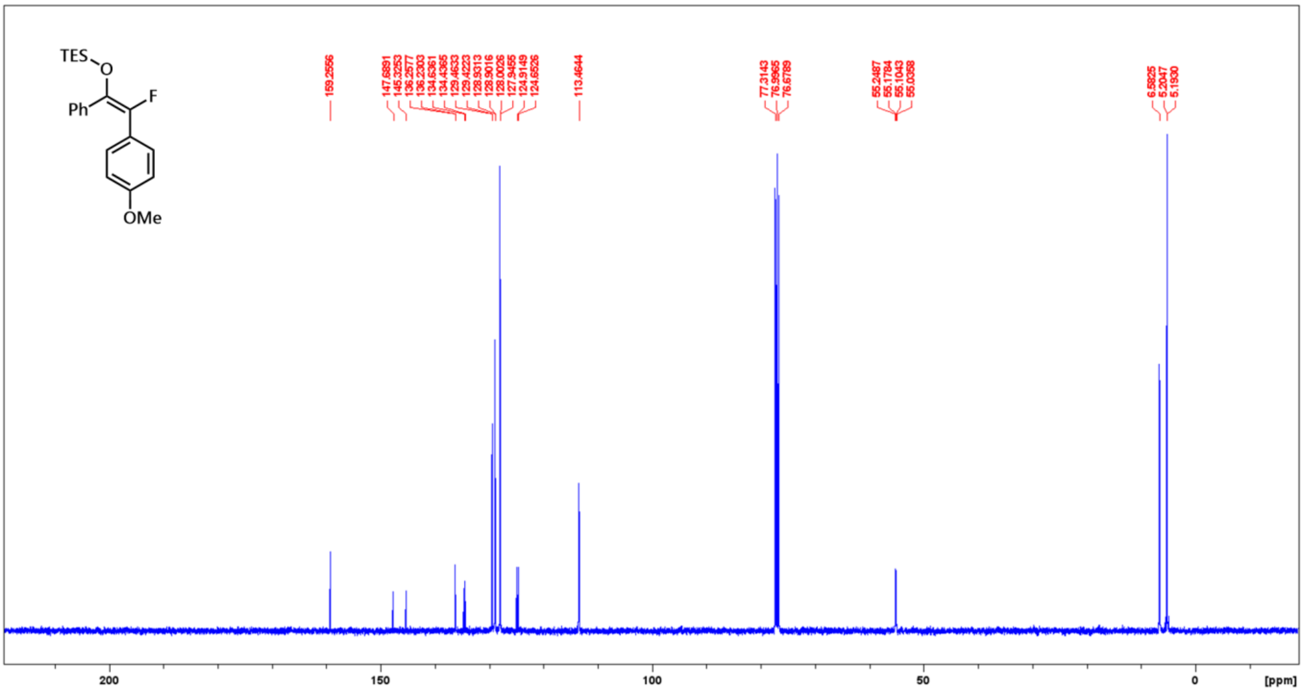
^{1}H NMR (400 MHz, $CDCl_3$)



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

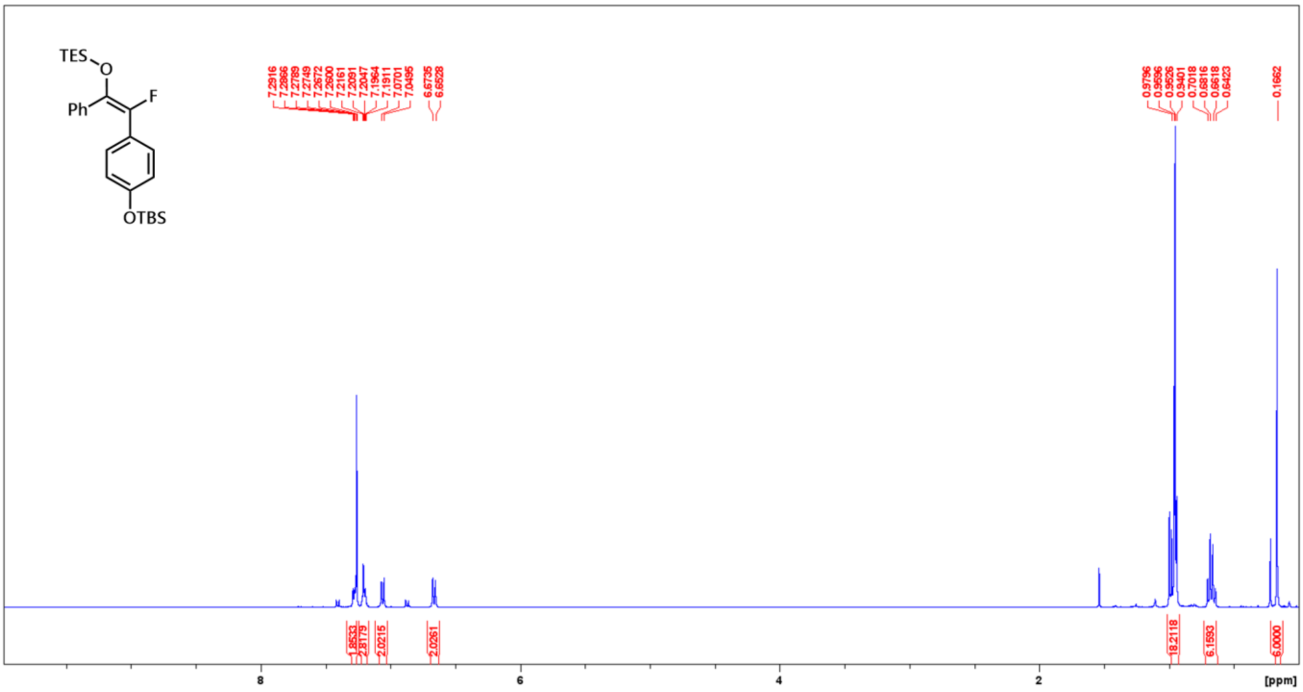


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

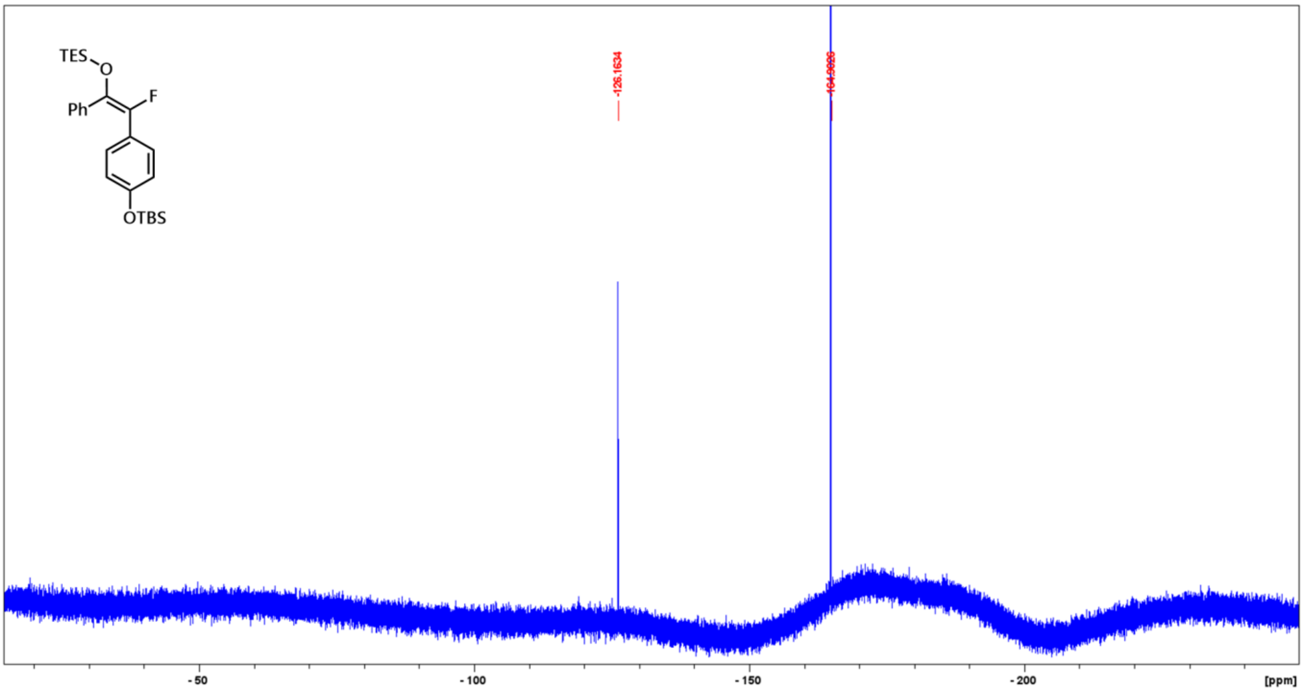


(Z)-6e

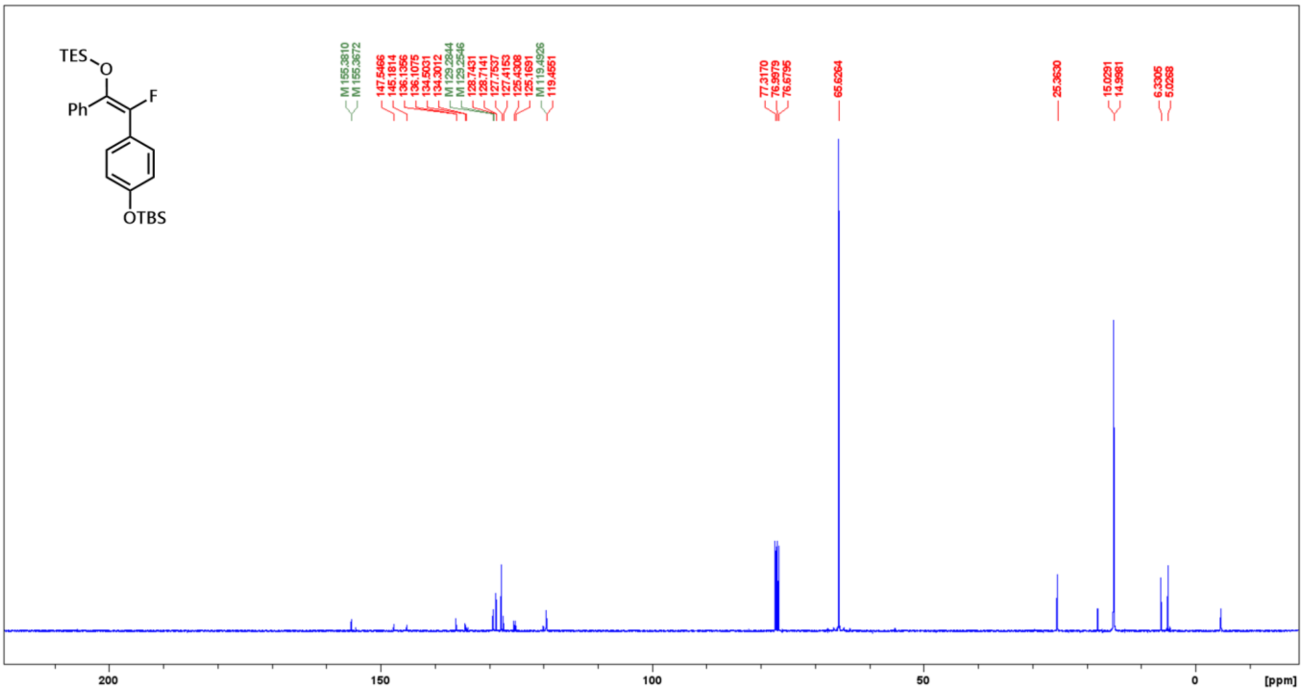
^{1}H NMR (400 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

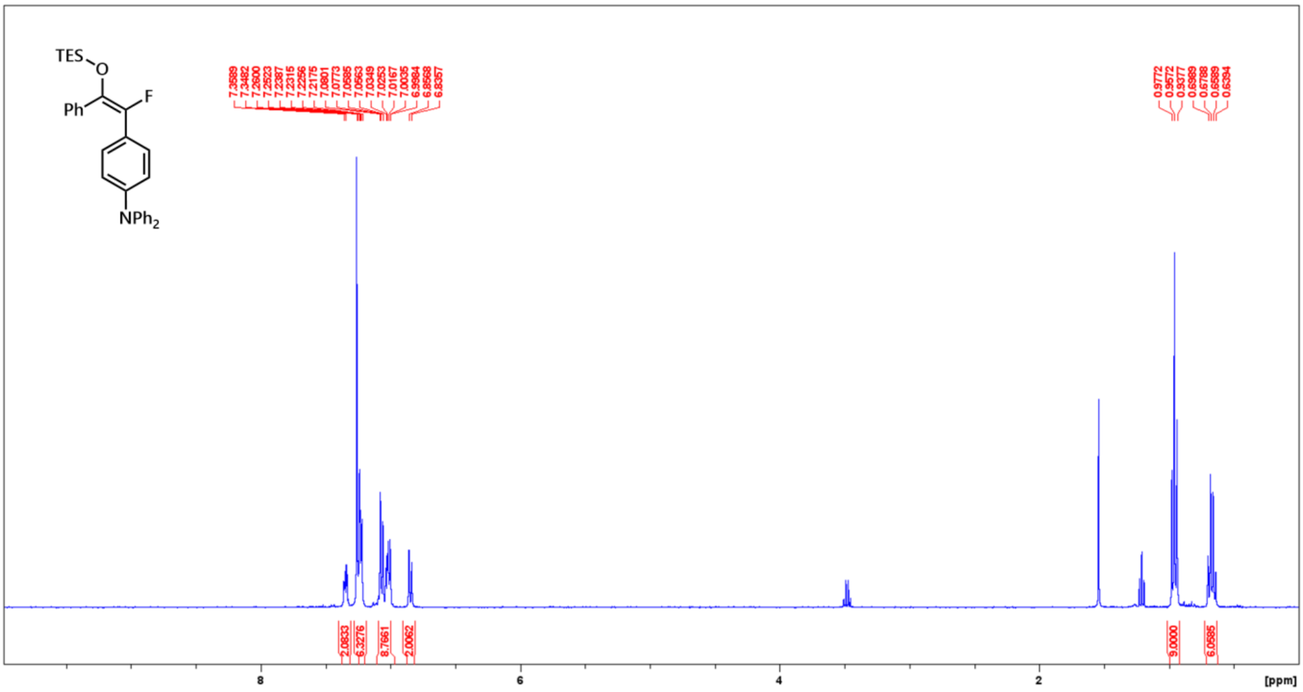


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

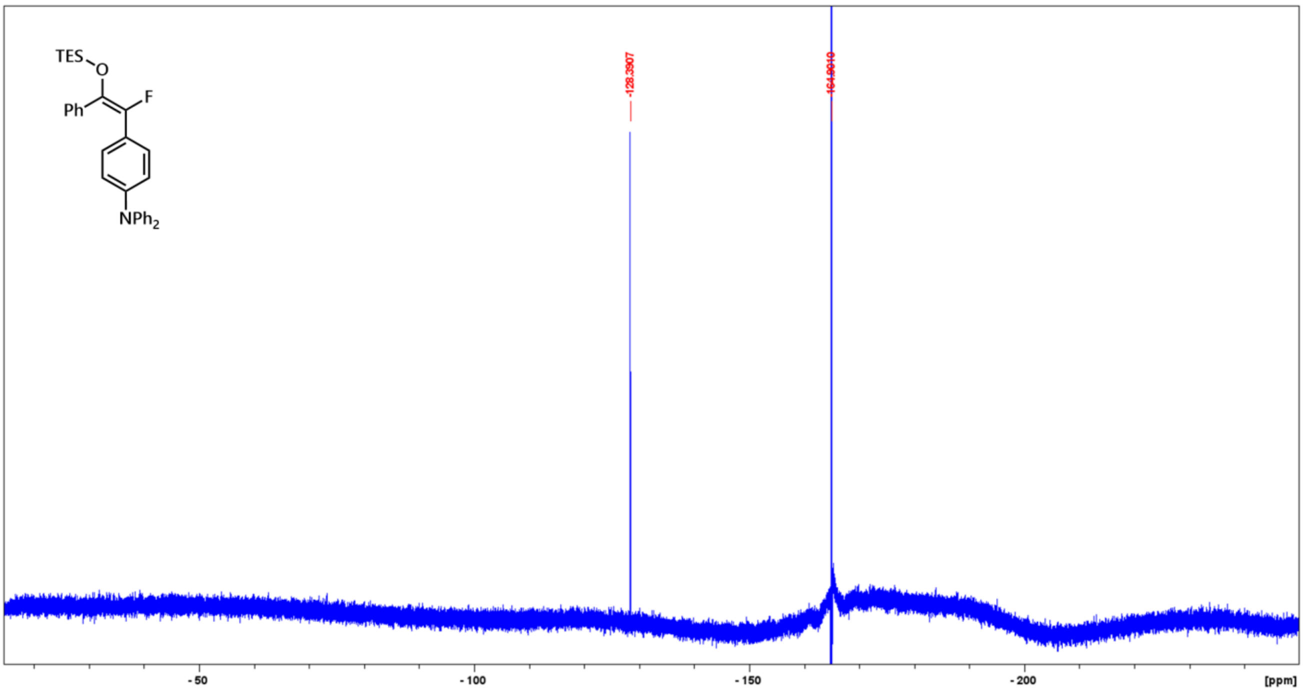


(Z)-6f

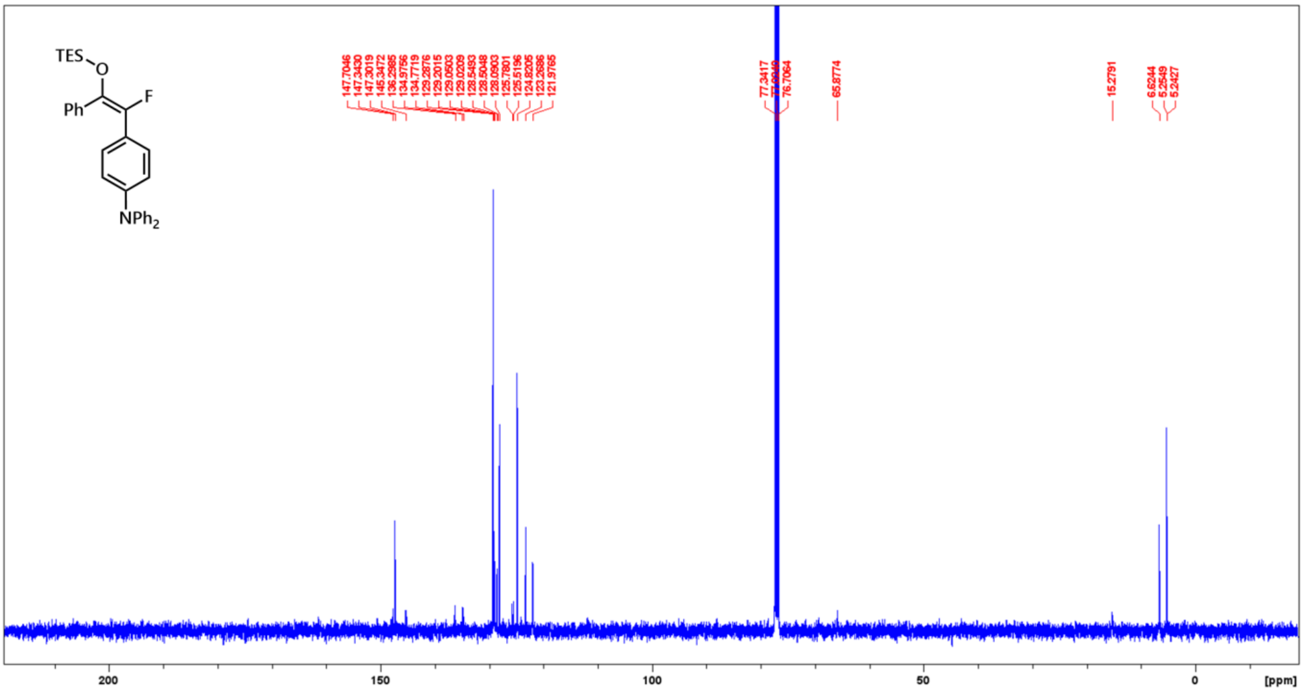
^{1}H NMR (400 MHz, $CDCl_3$)



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

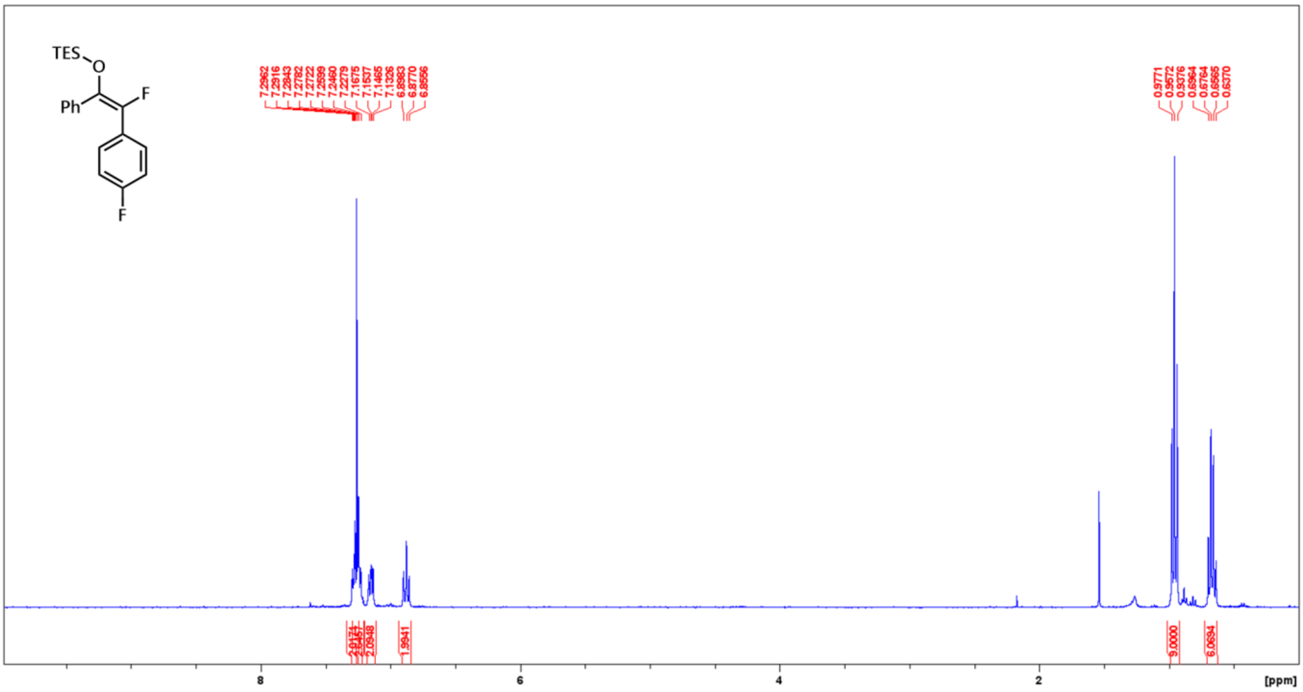


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

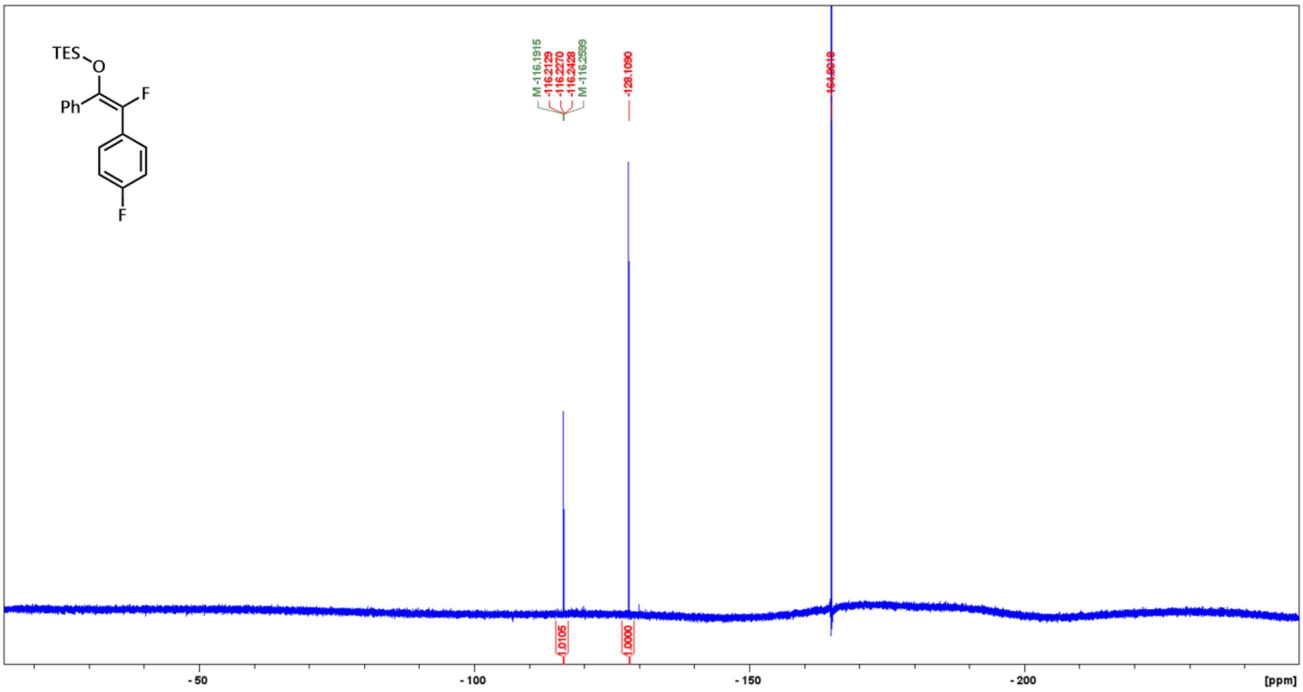


(Z)-6g

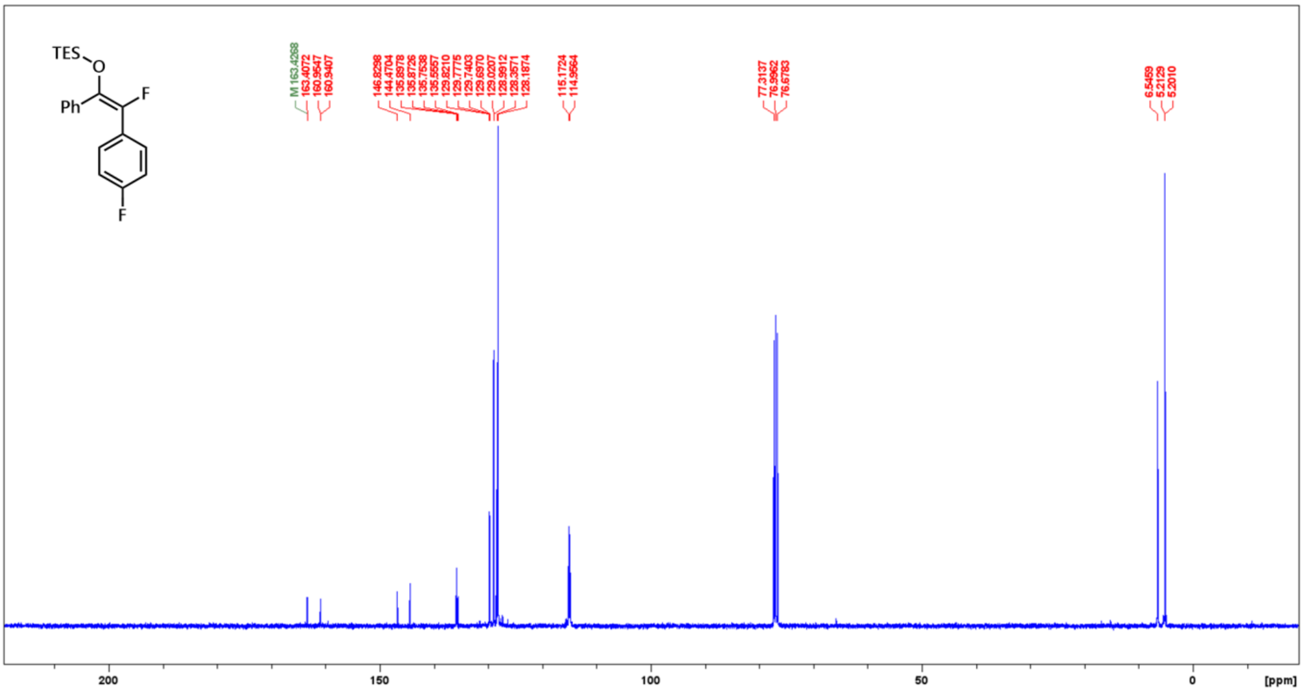
^{1}H NMR (400 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

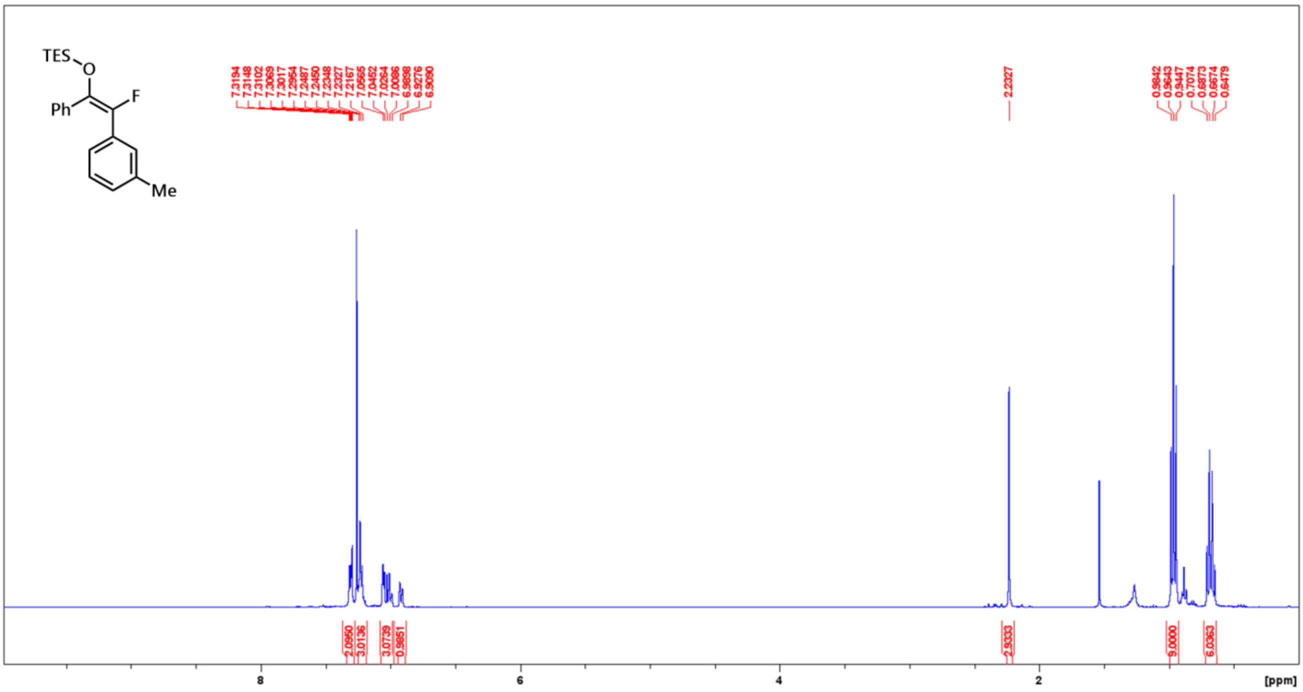


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

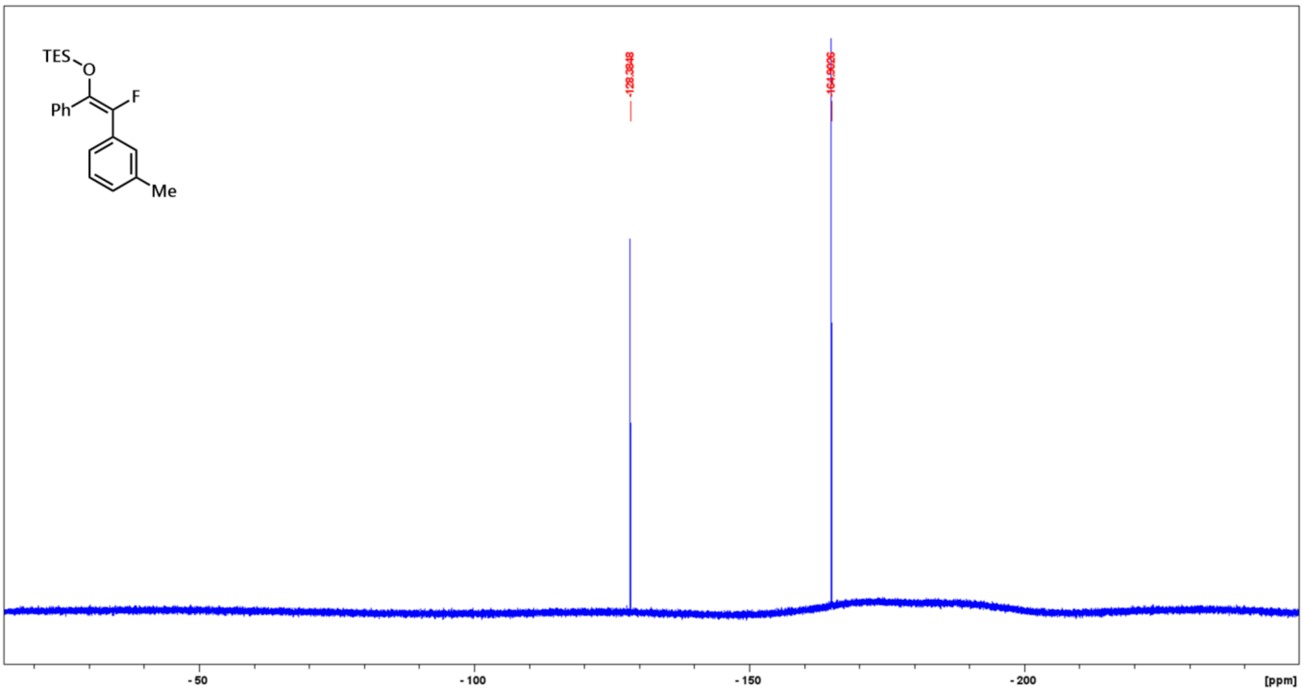


(Z)-6h

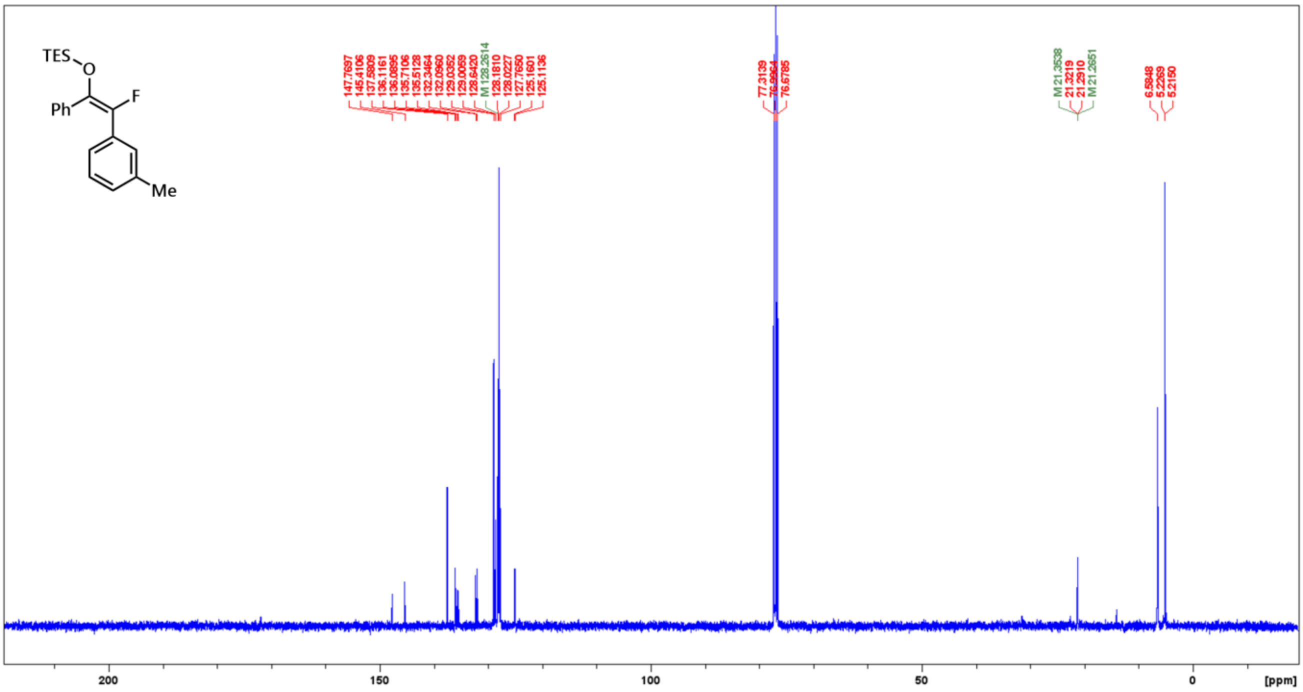
^{1}H NMR (400 MHz, $CDCl_3$)



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

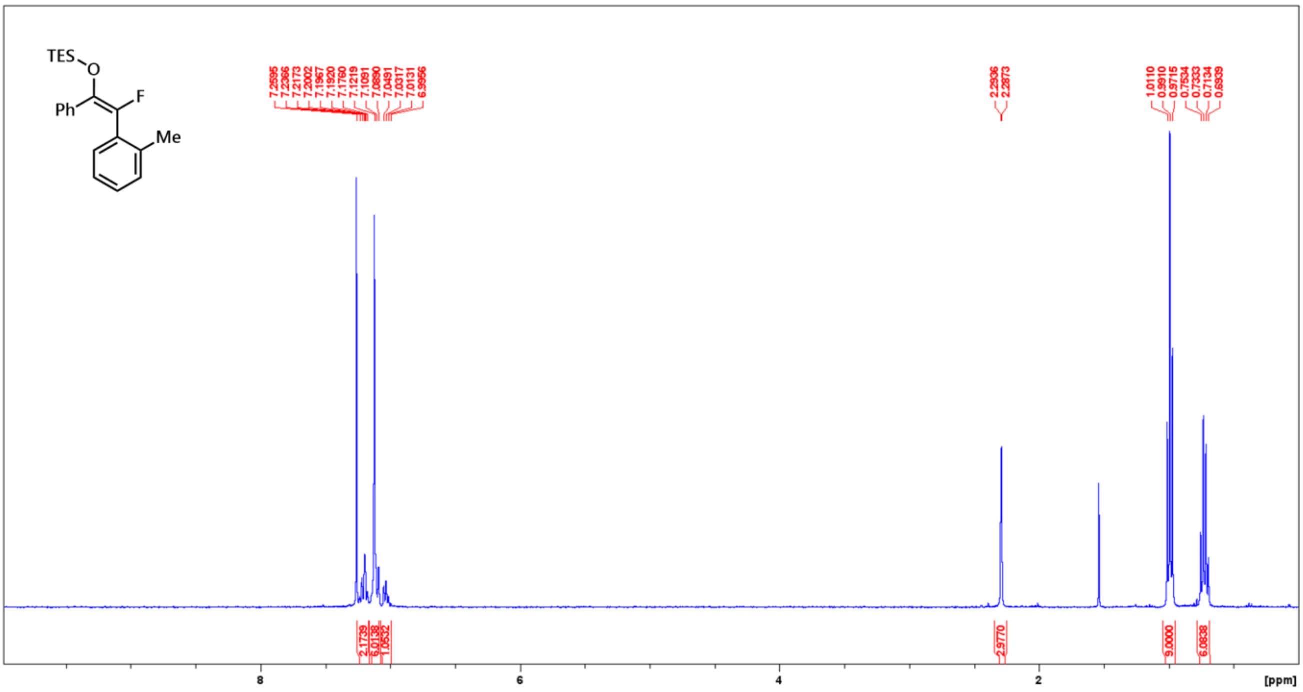


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

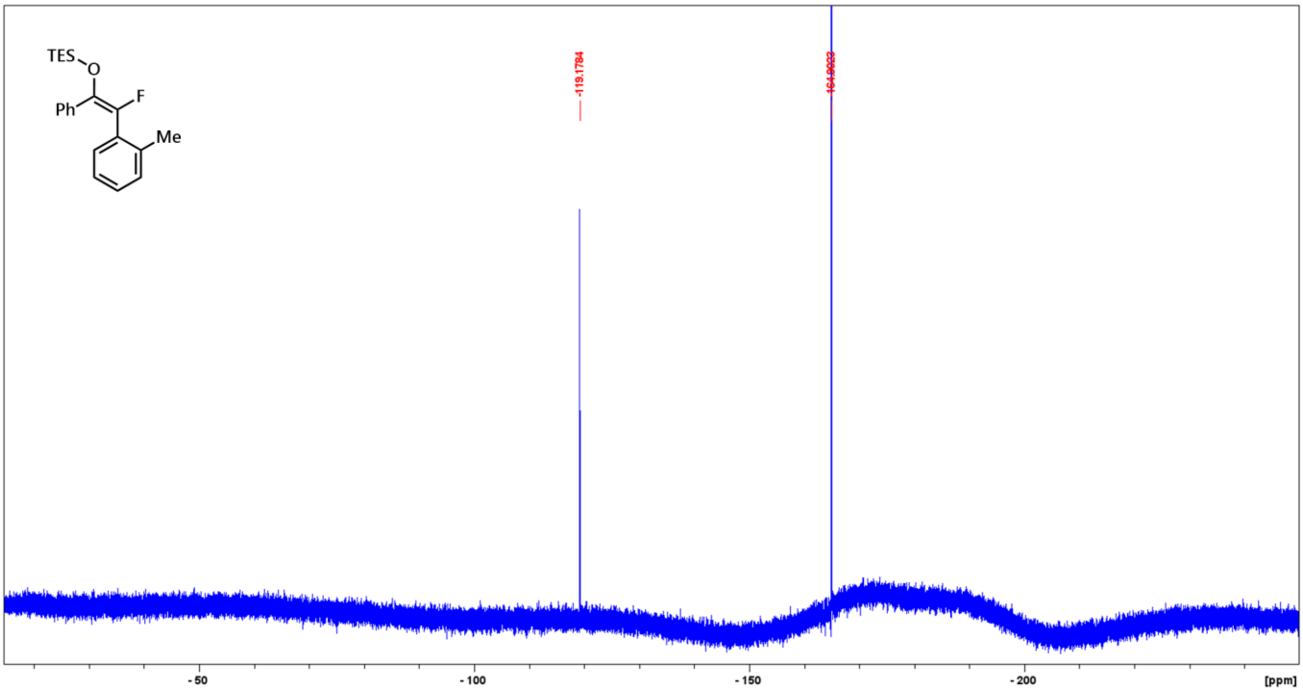


(Z)-6i

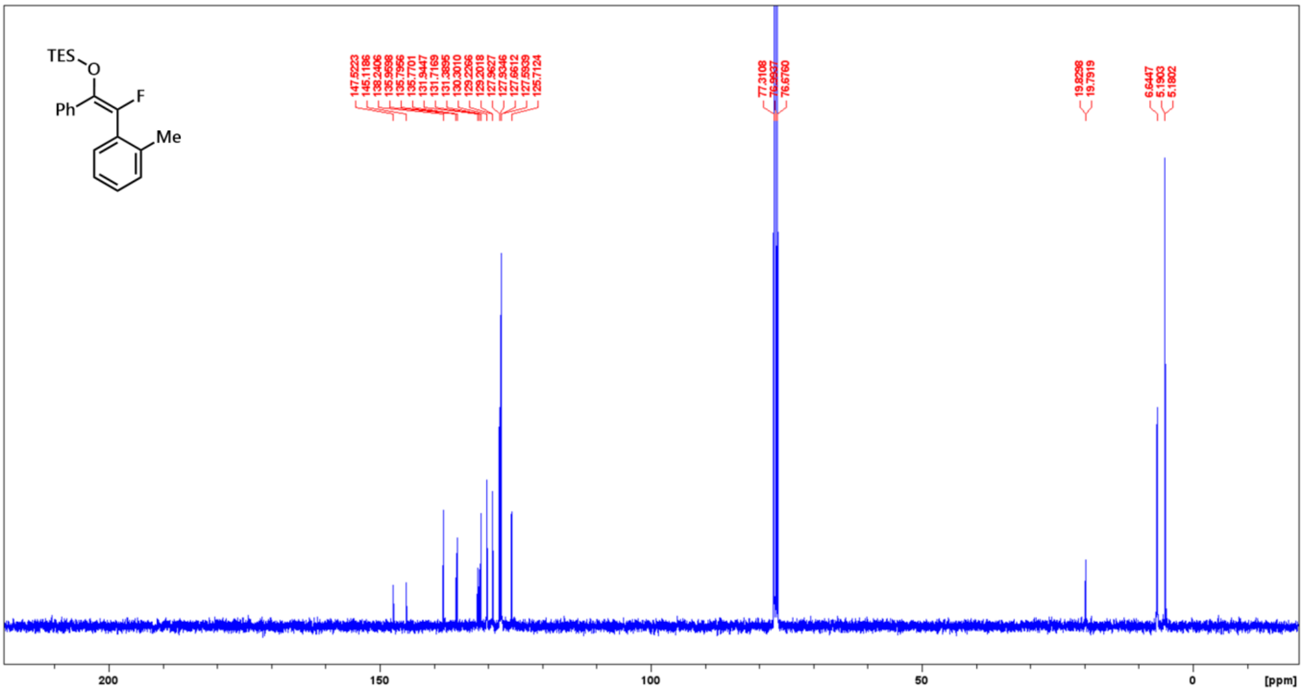
^{1}H NMR (400 MHz, $CDCl_3$)



[19]F NMR (376 MHz, CDCl₃)

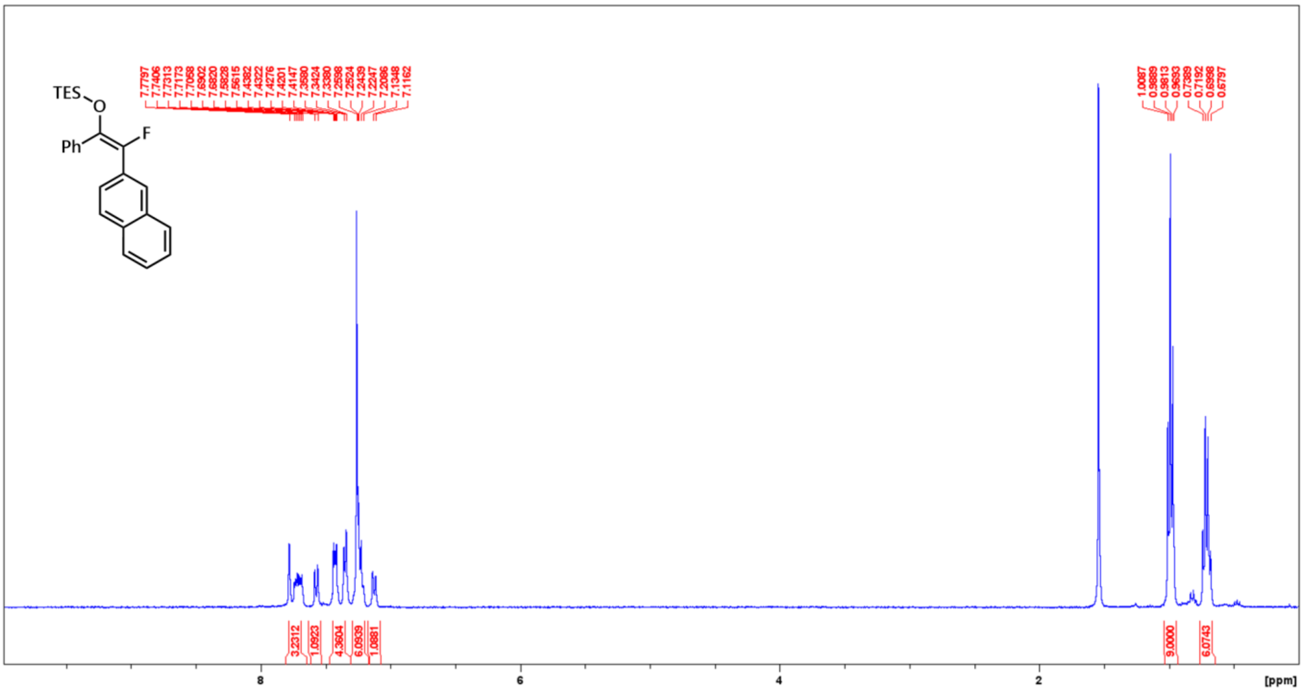


[13]C NMR (100 MHz, CDCl₃, [1]H decoupling)

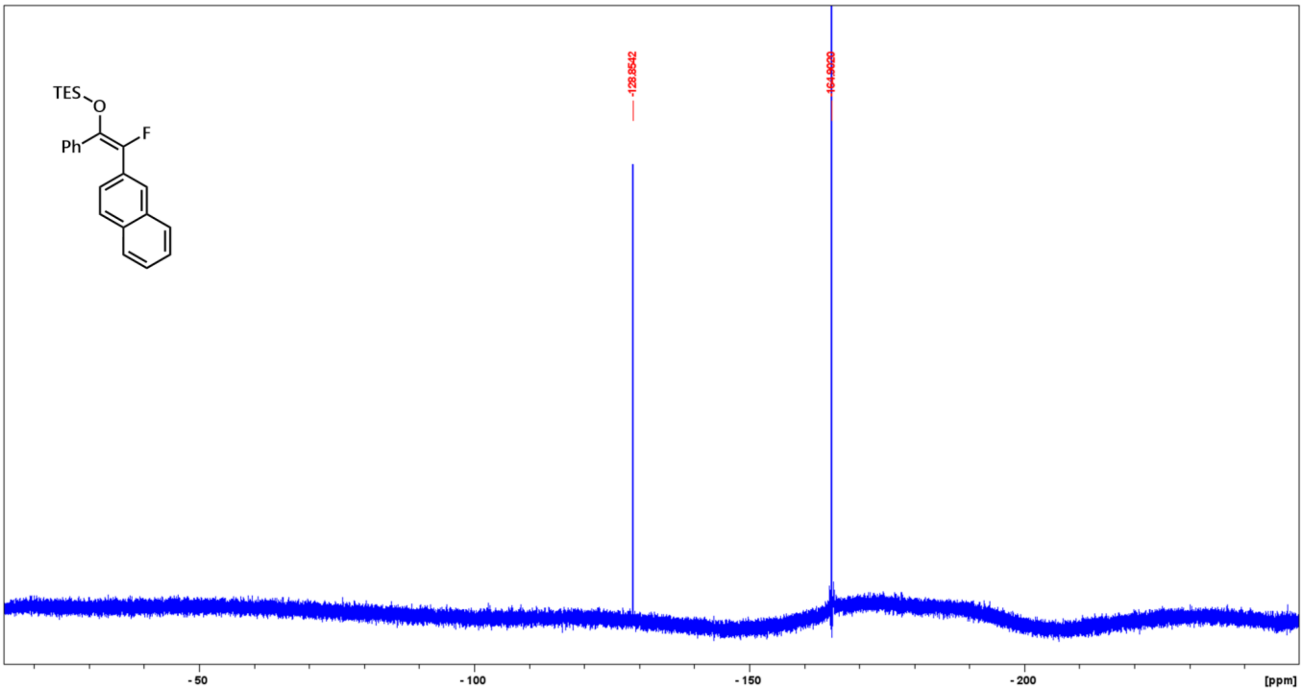


(Z)-6j

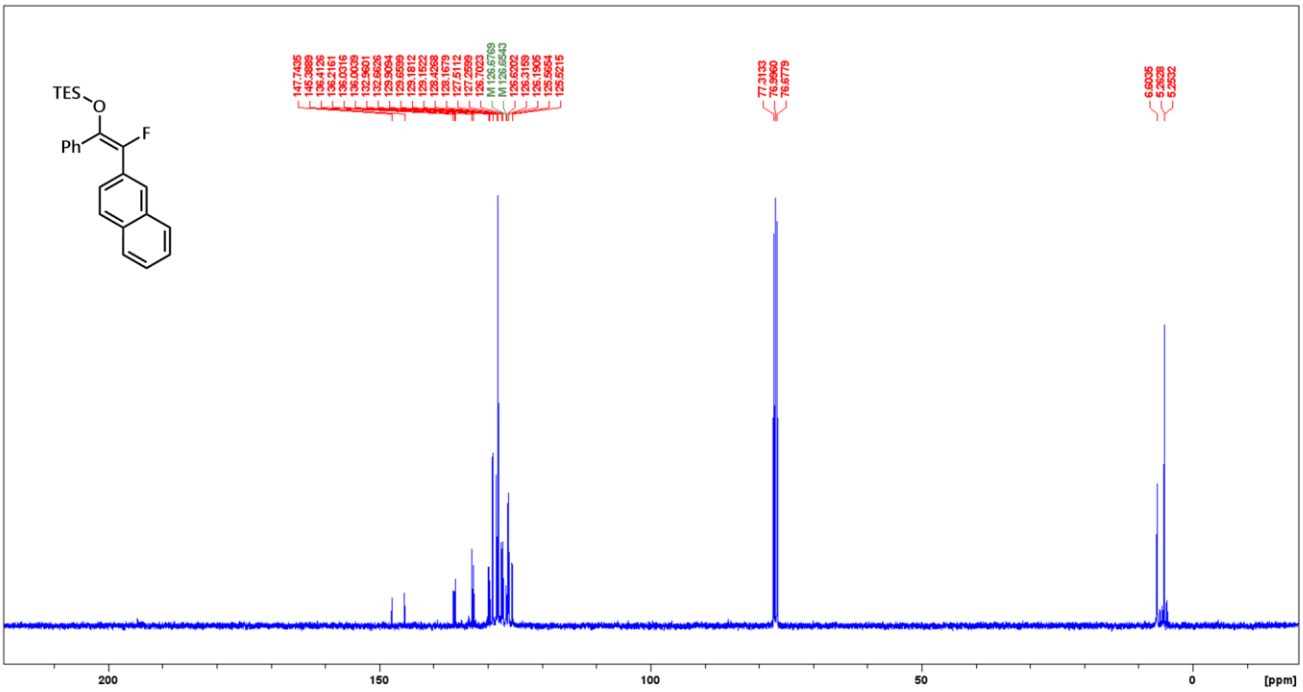
^{1}H NMR (400 MHz, CDCl$_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

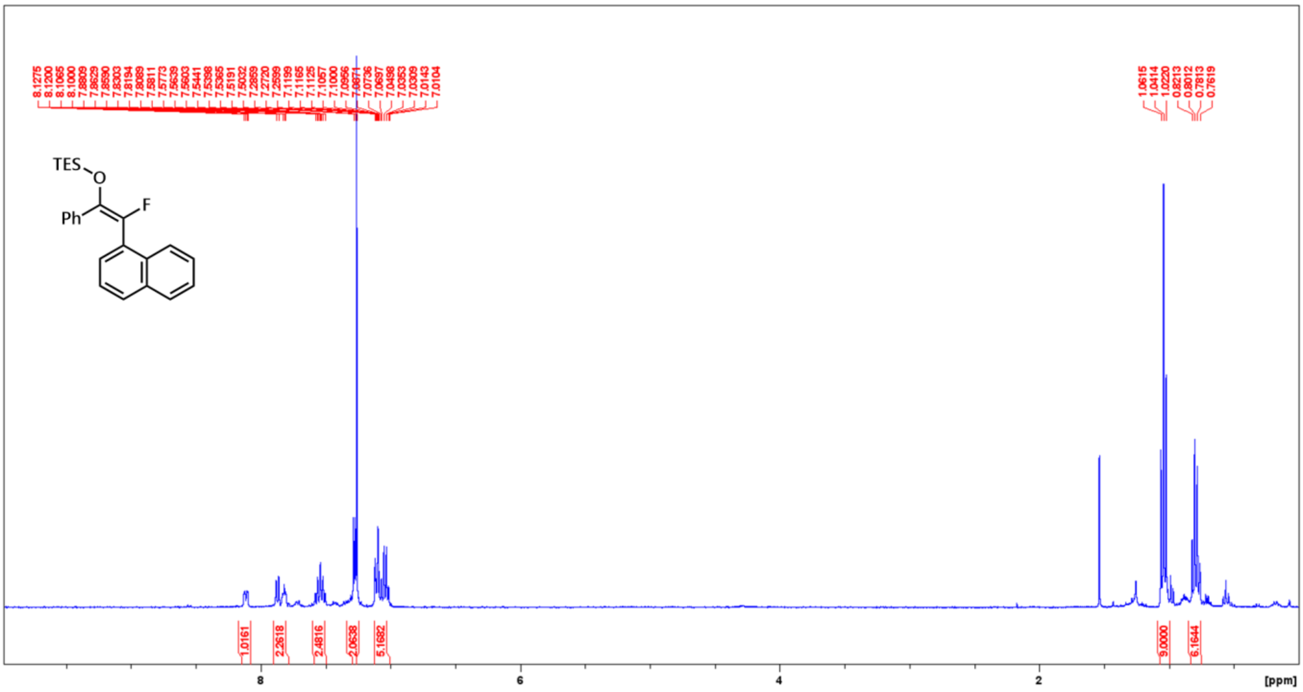


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

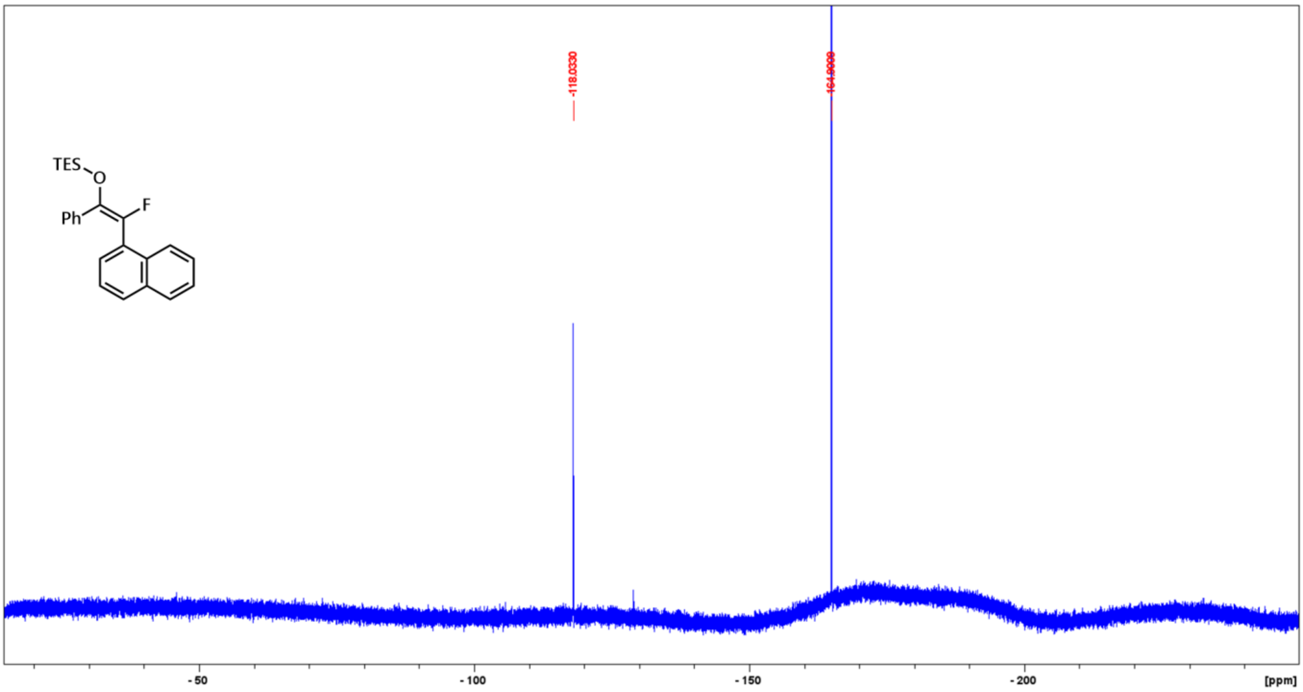


(Z)-6k

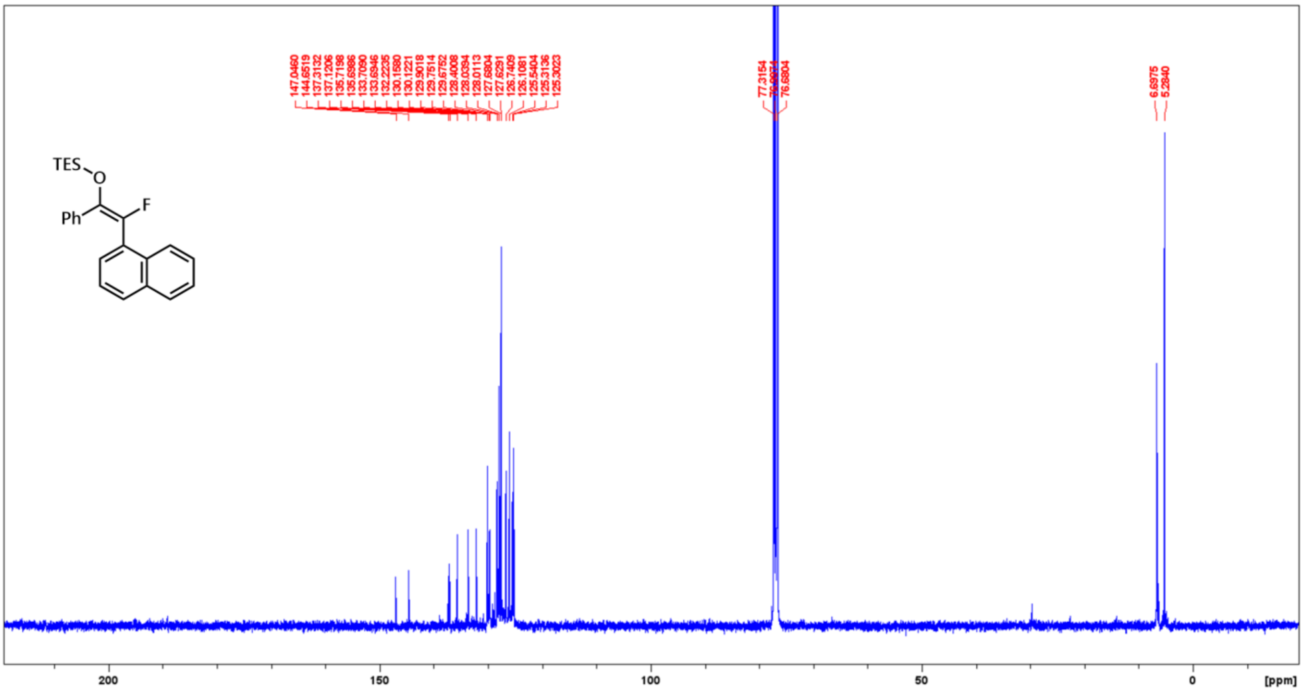
^{1}H NMR (400 MHz, CDCl$_3$)



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

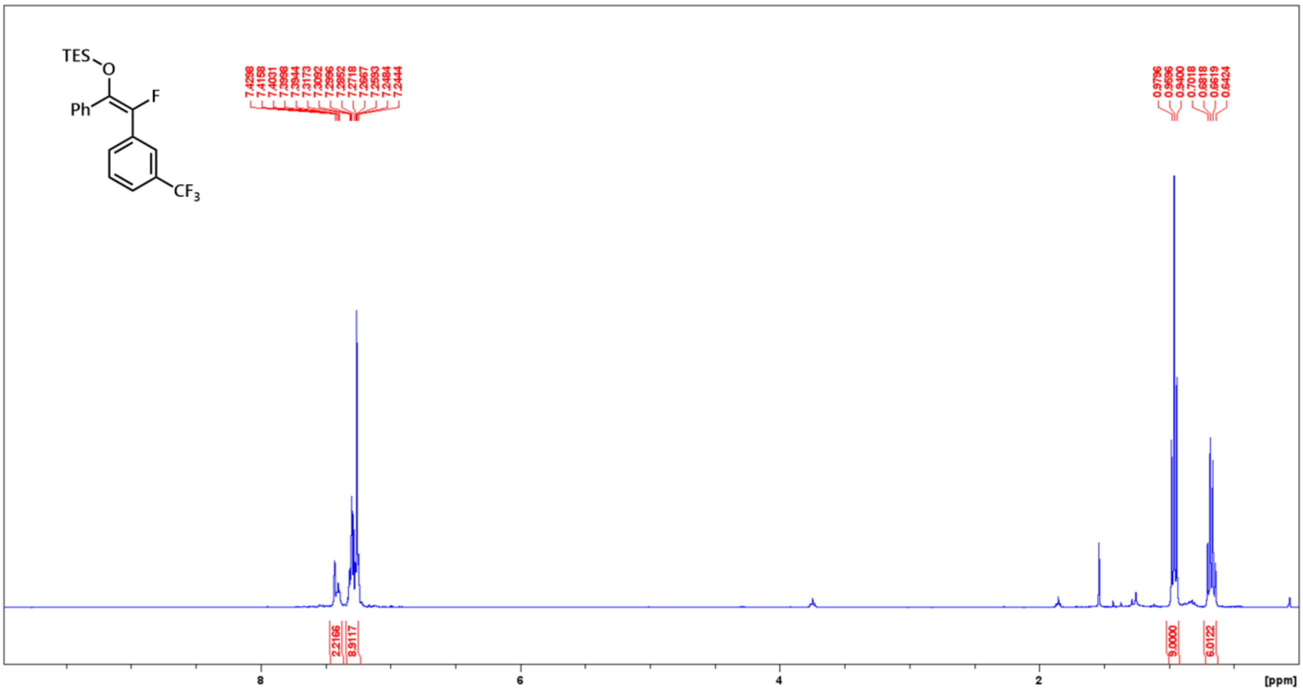


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

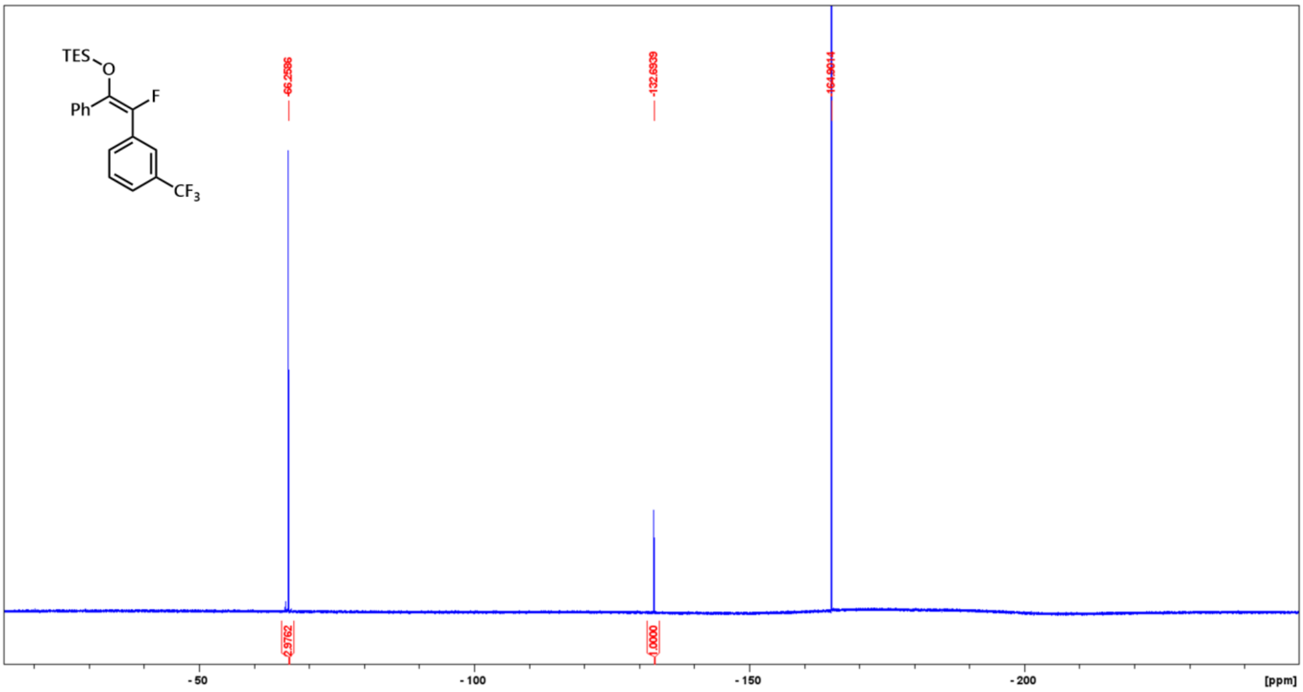


(Z)-6l

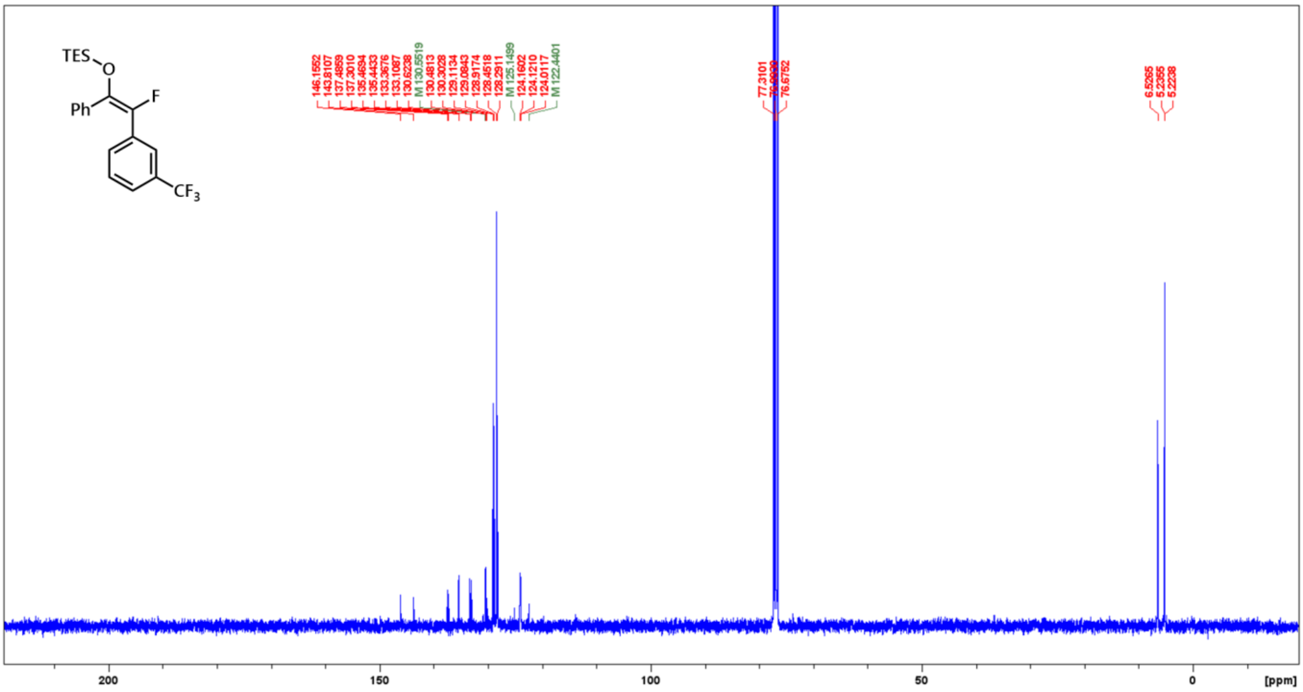
^{1}H NMR (400 MHz, $CDCl_3$)



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

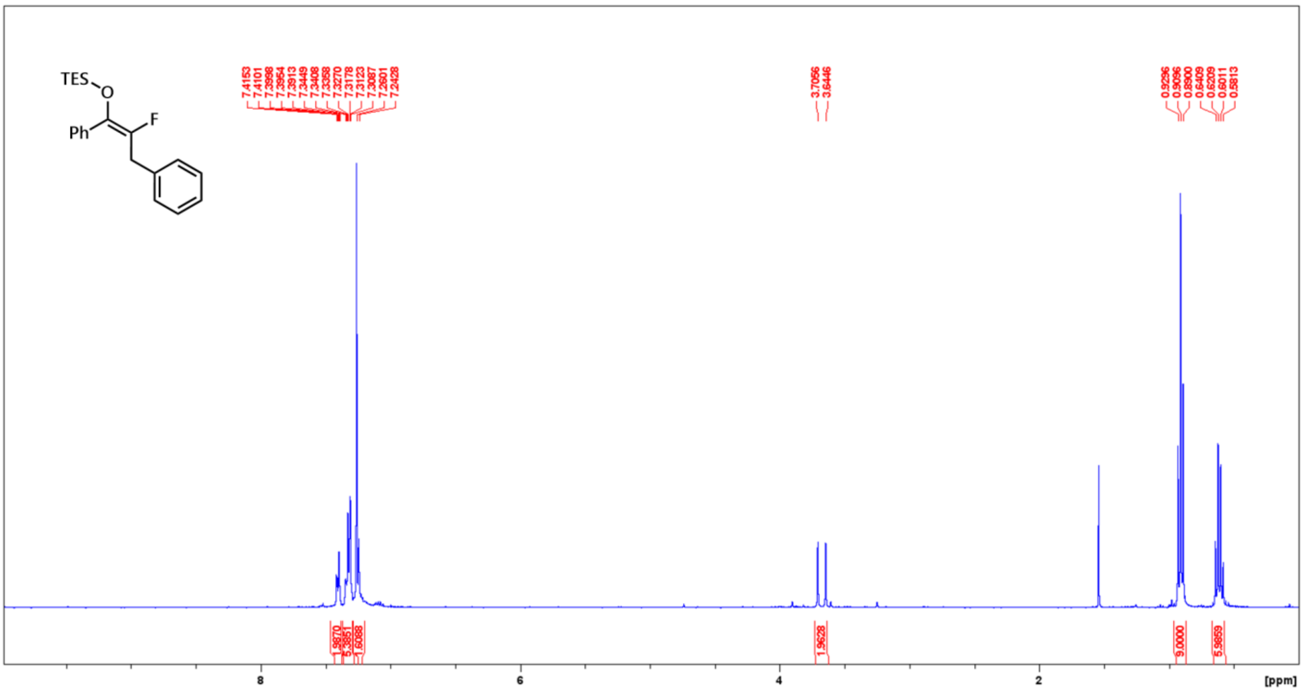


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

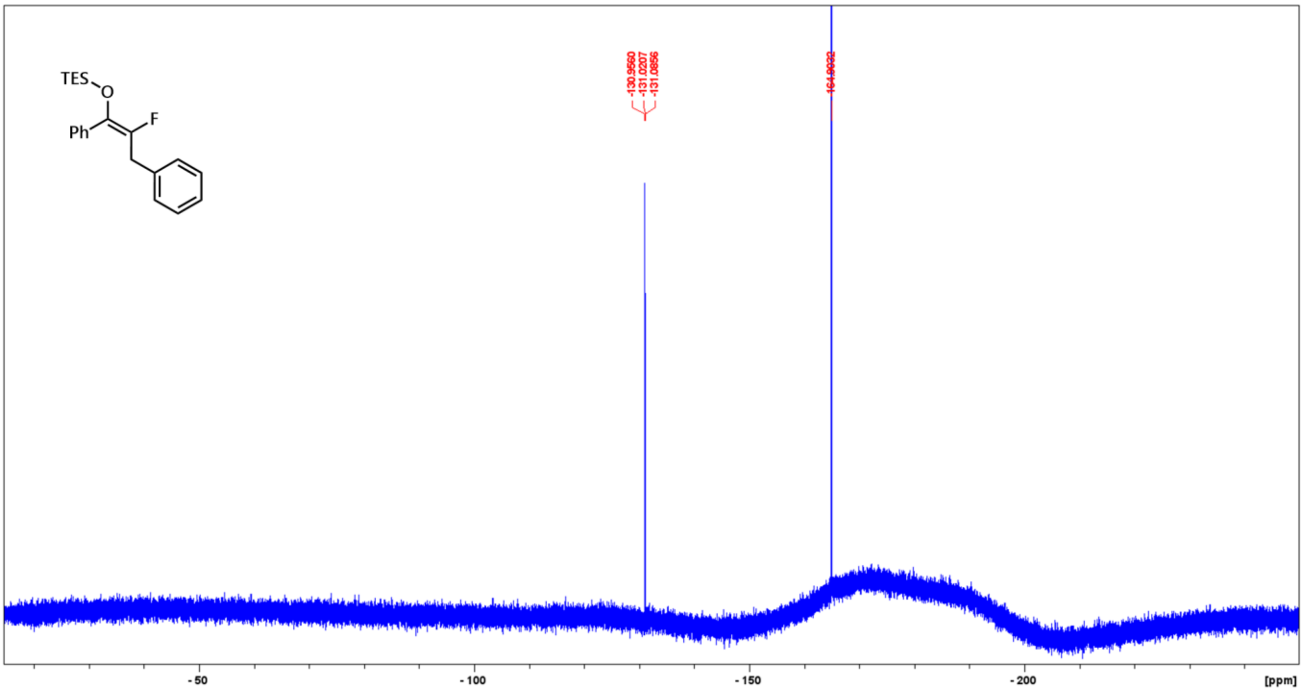


(Z)-6m

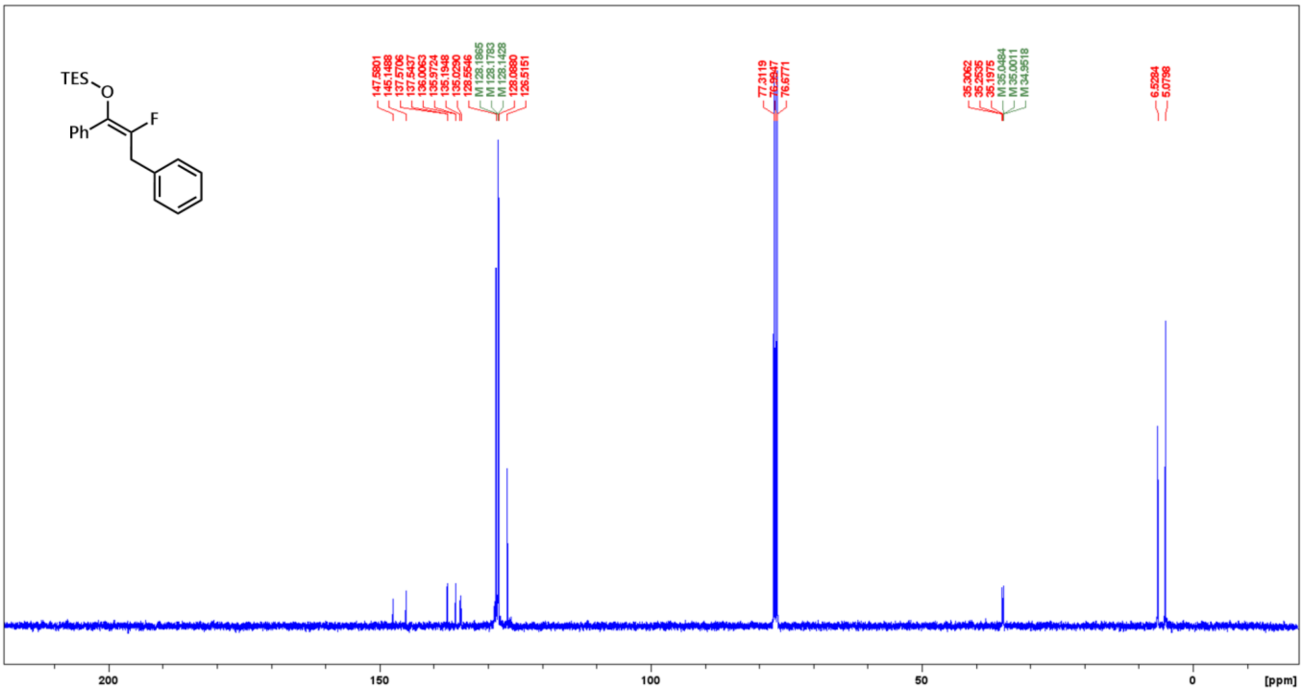
^{1}H NMR (400 MHz, $CDCl_3$)



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

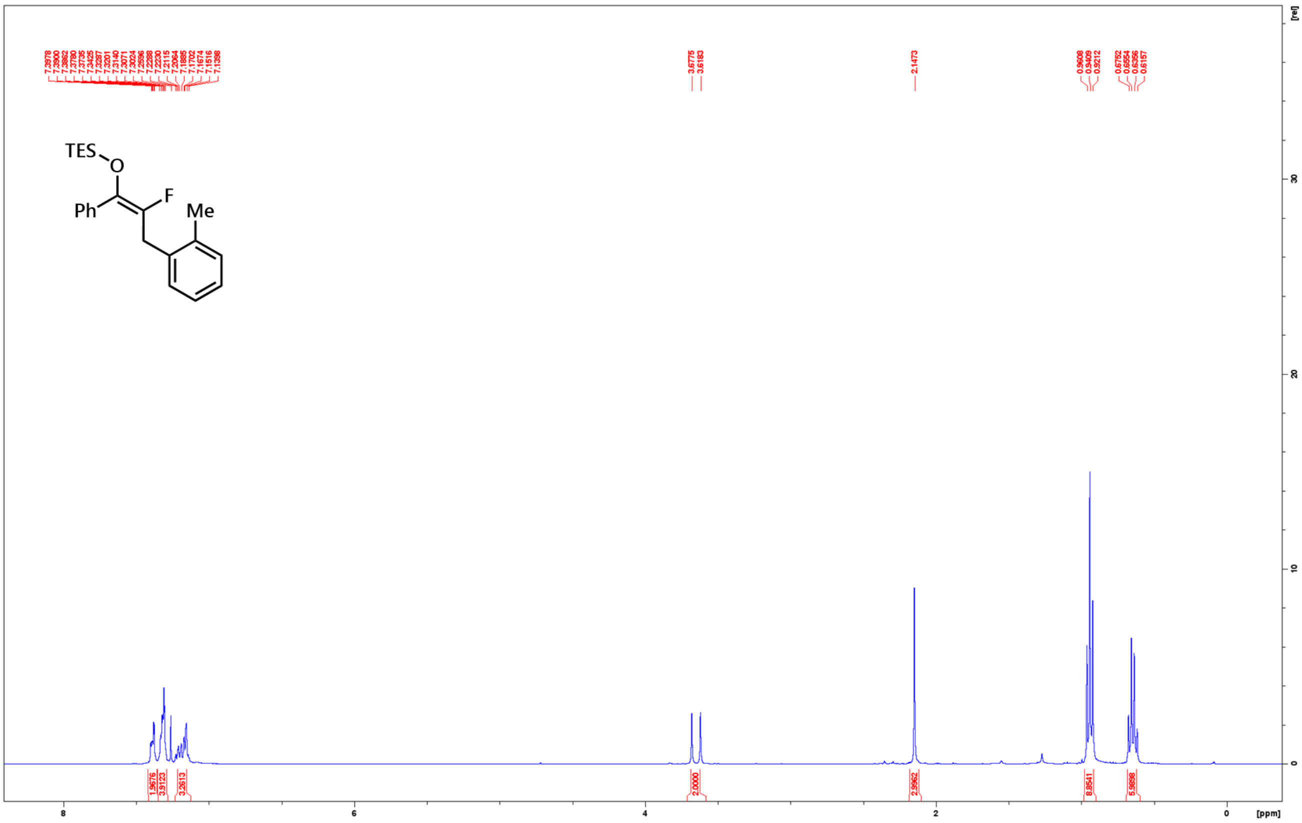


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

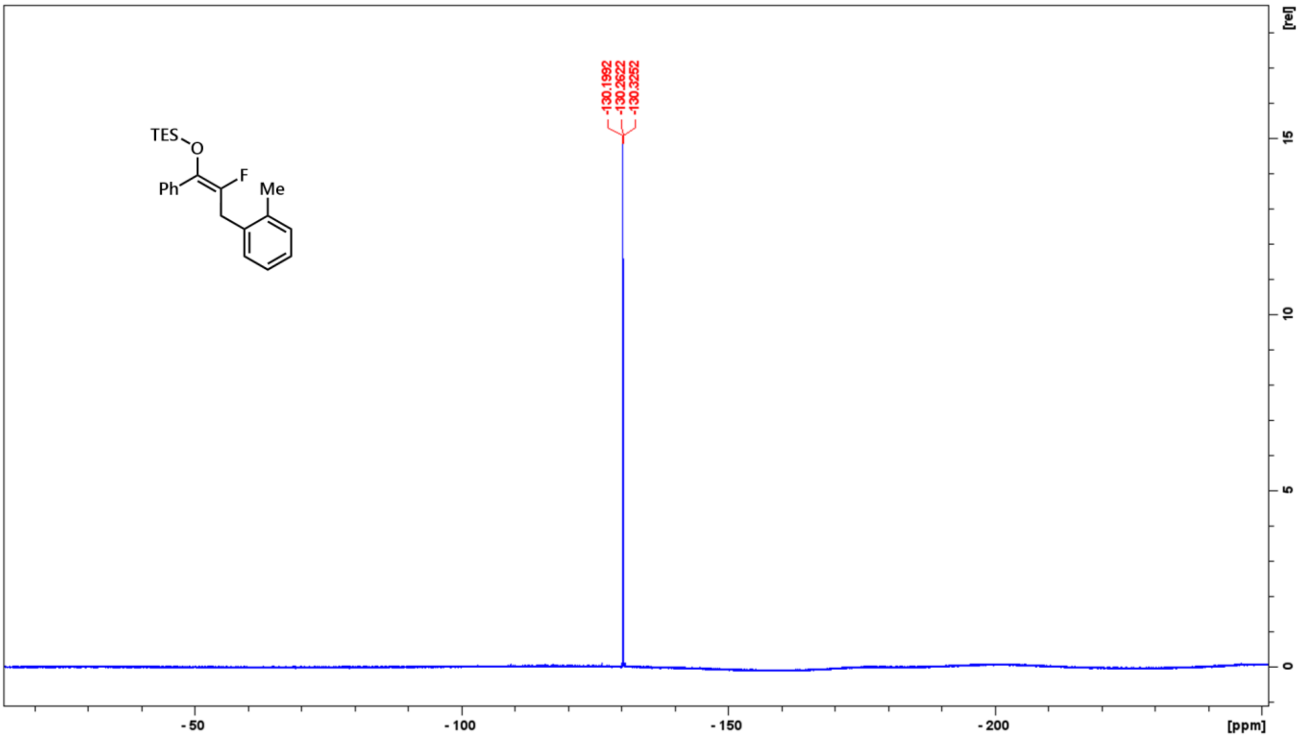


(Z)-6n

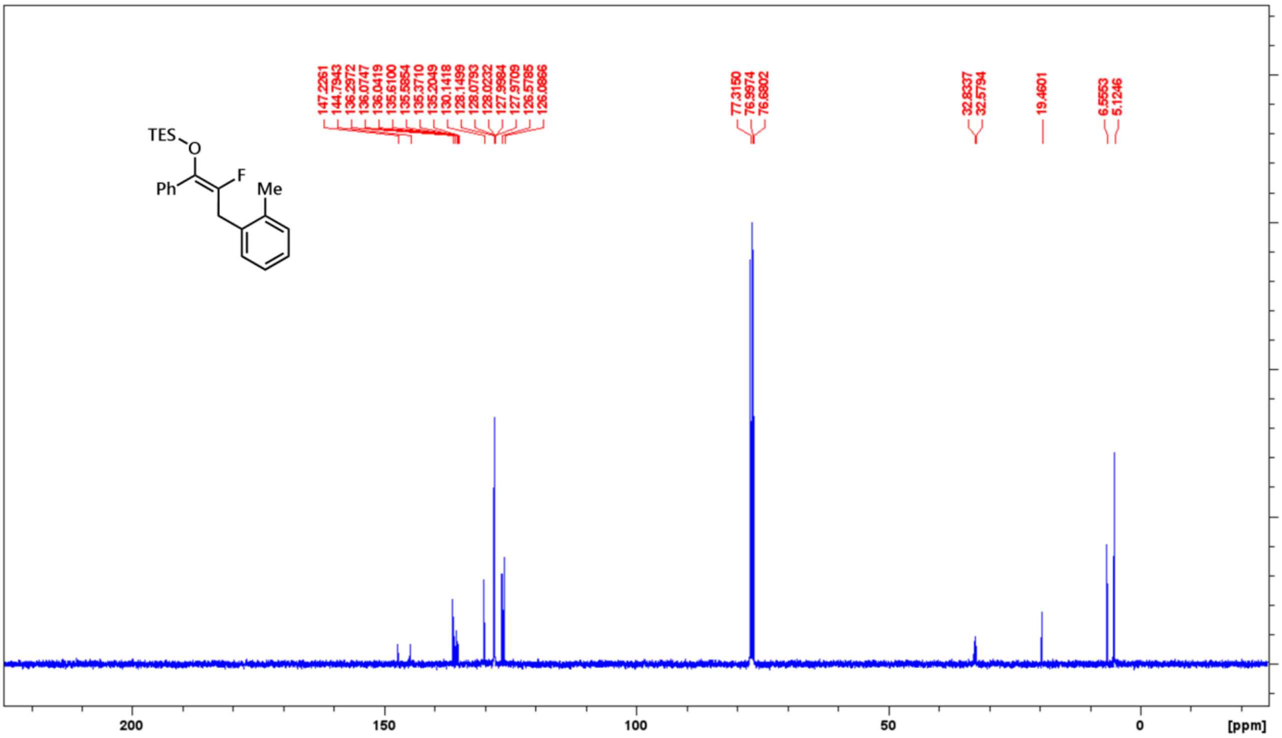
[1]H NMR (400 MHz, CDCl₃)



[19]F NMR (376 MHz, CDCl₃)

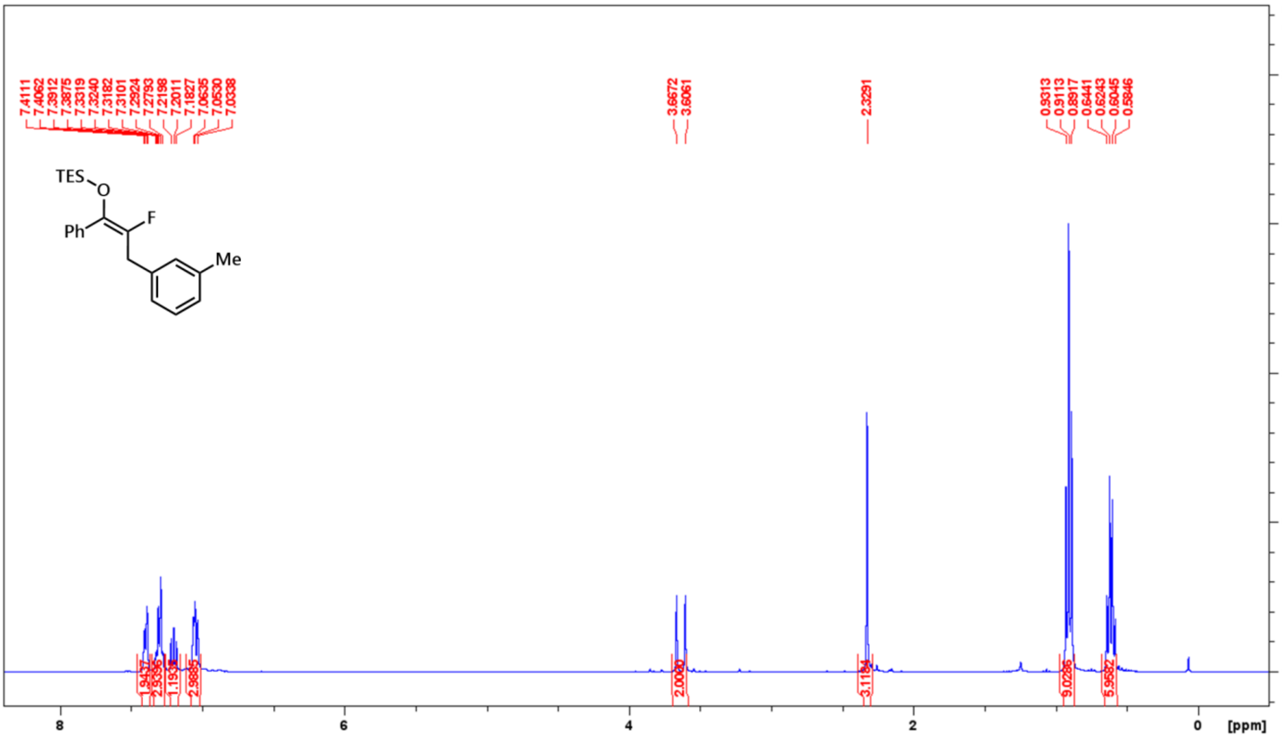


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

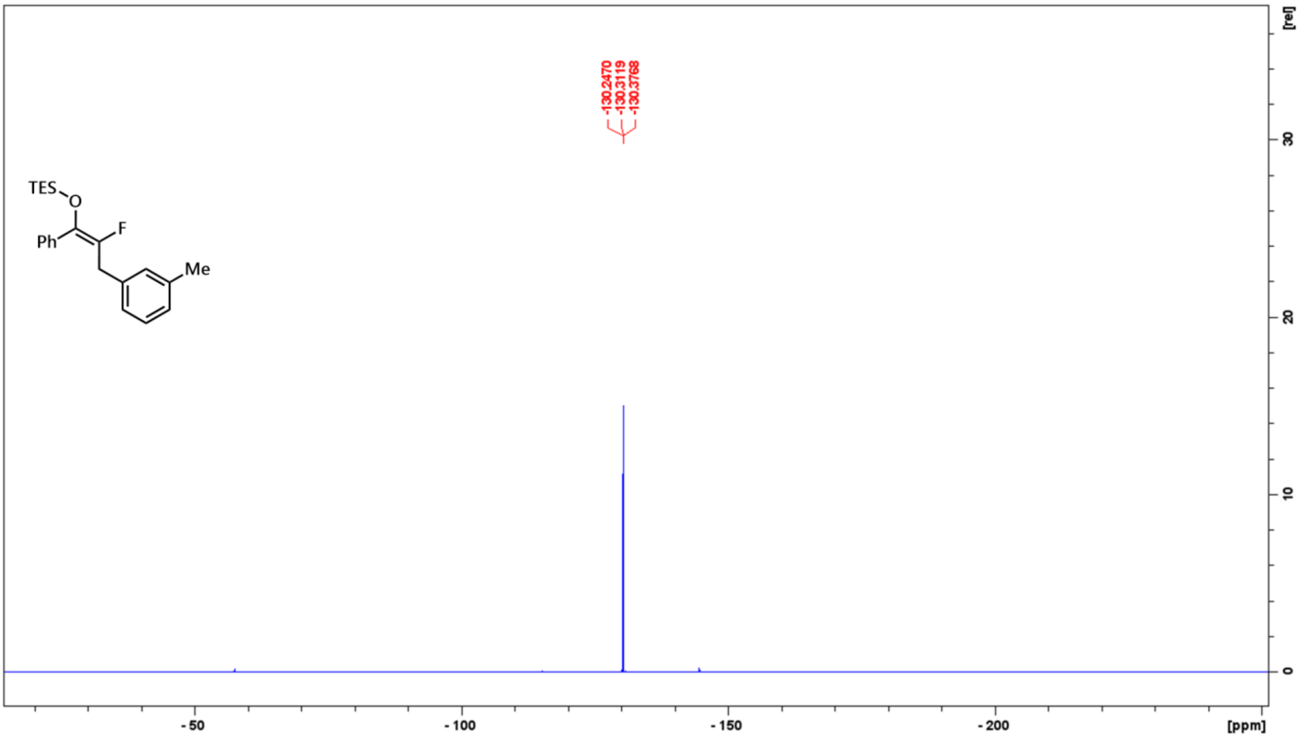


(Z)-6o

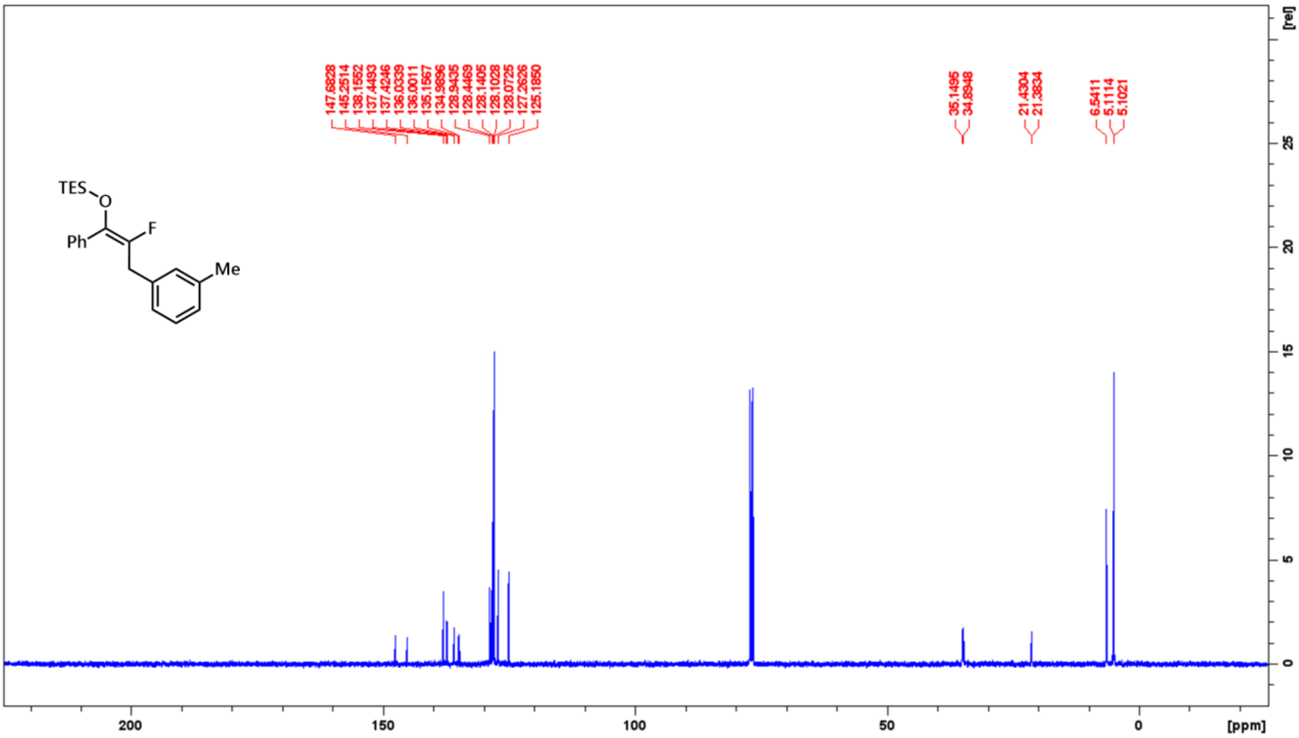
^{1}H NMR (400 MHz, $CDCl_3$)



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

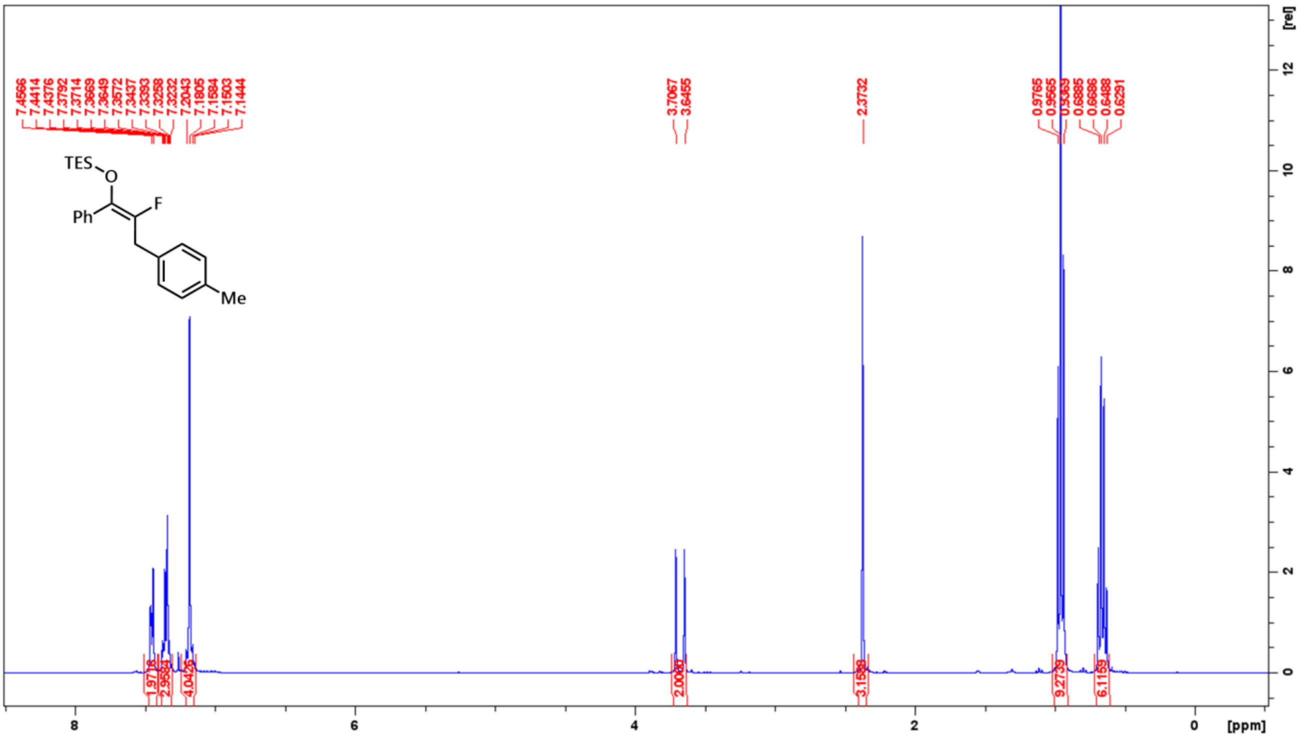


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

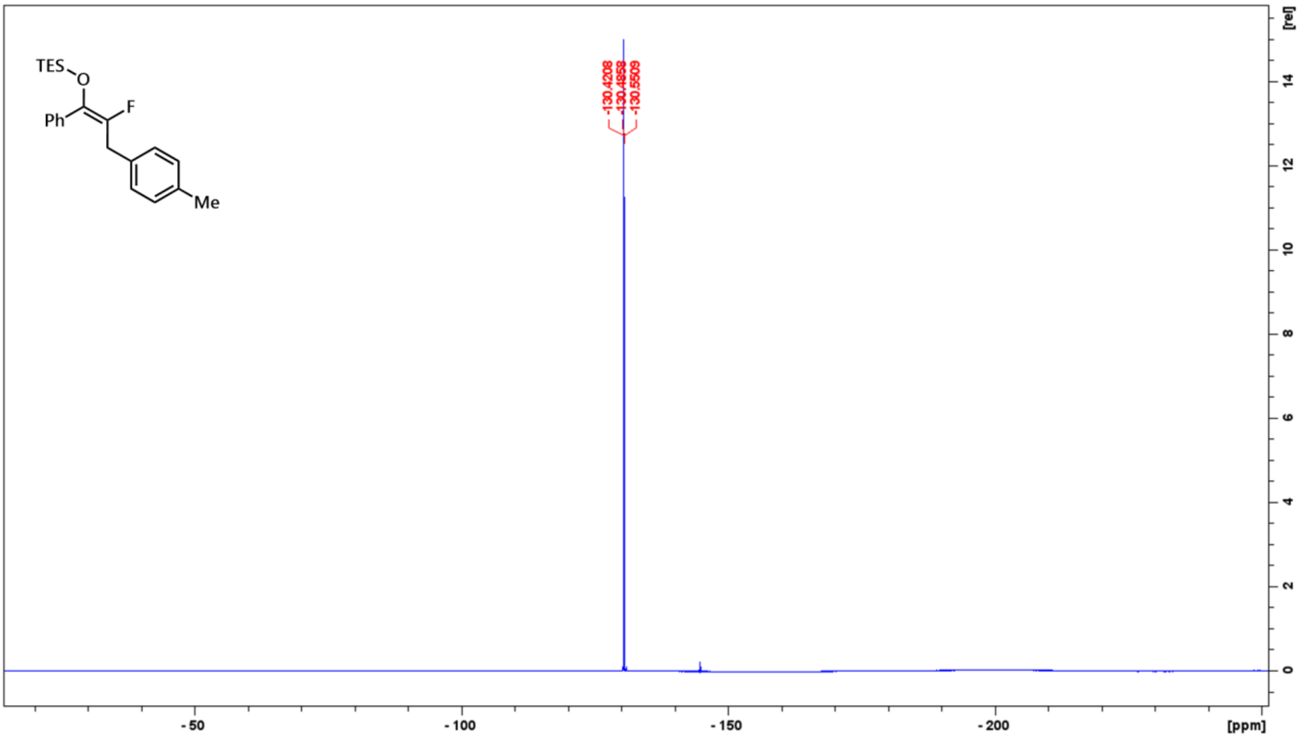


(Z)-6p

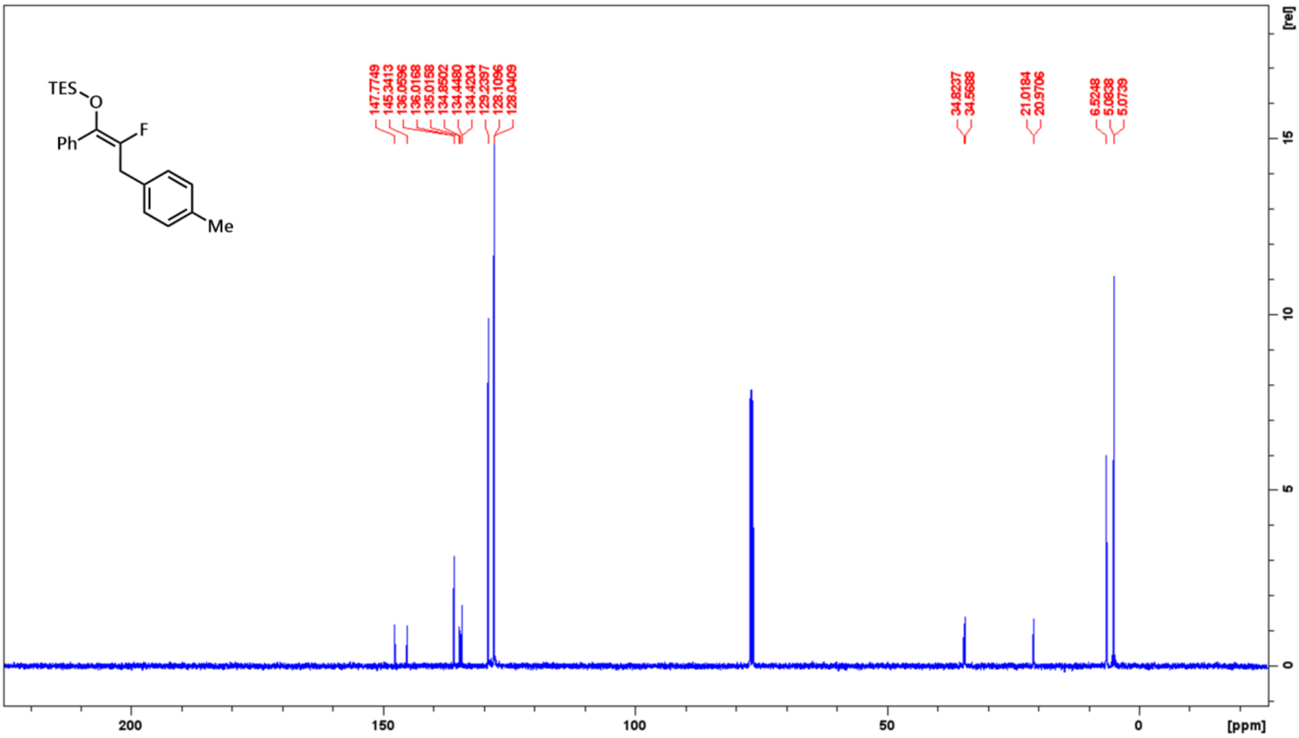
^{1}H NMR (400 MHz, $CDCl_3$)



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

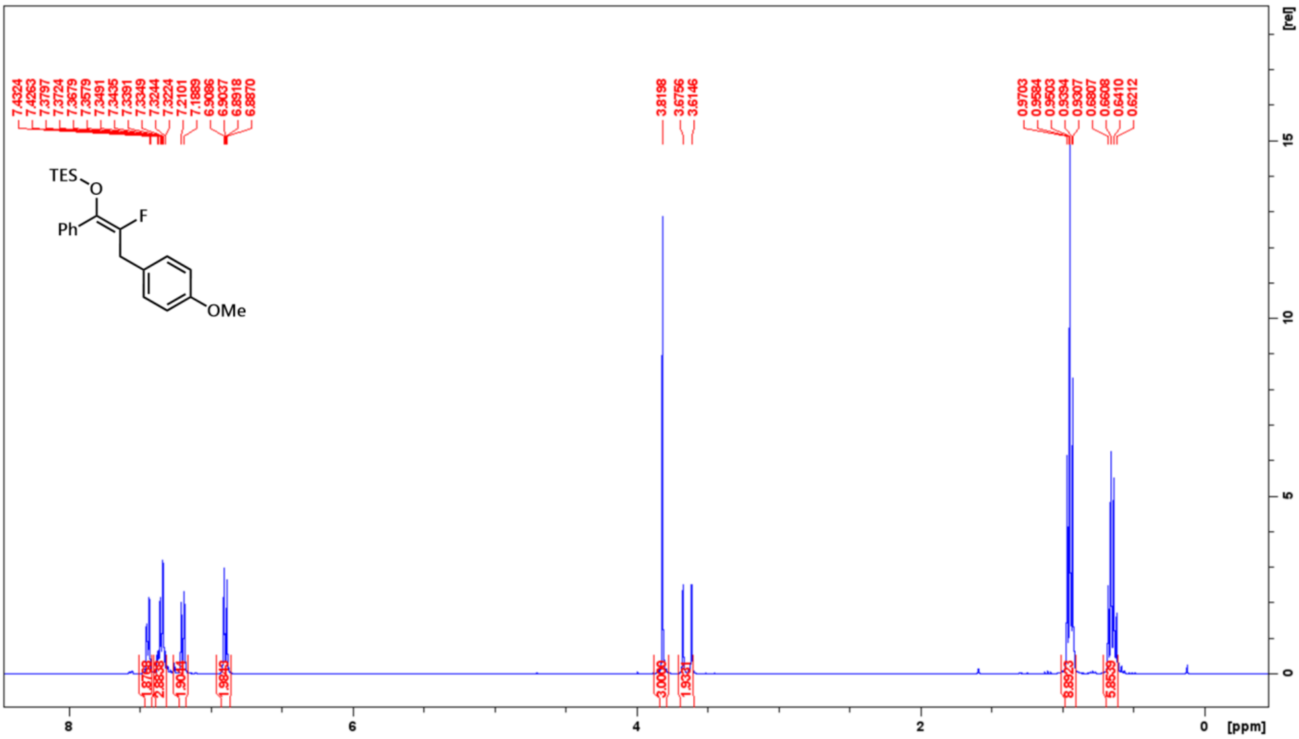


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

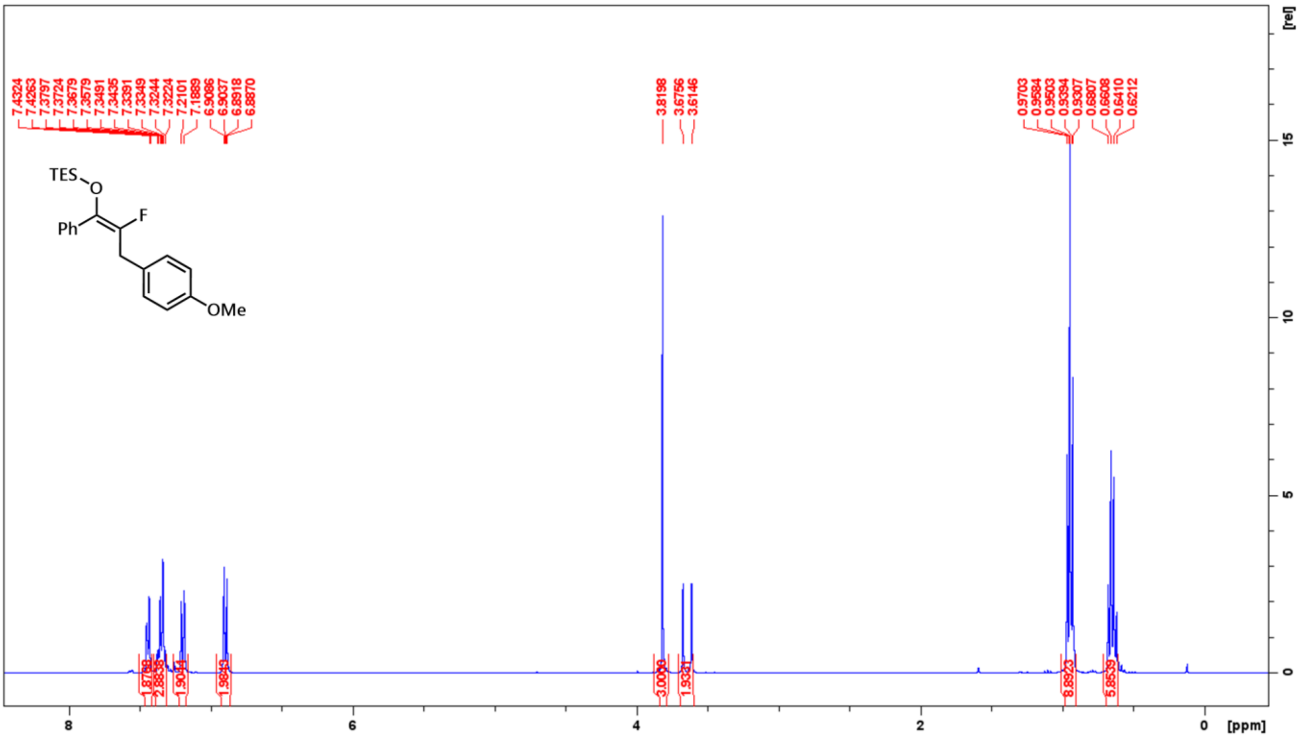


***(Z)*-6q**

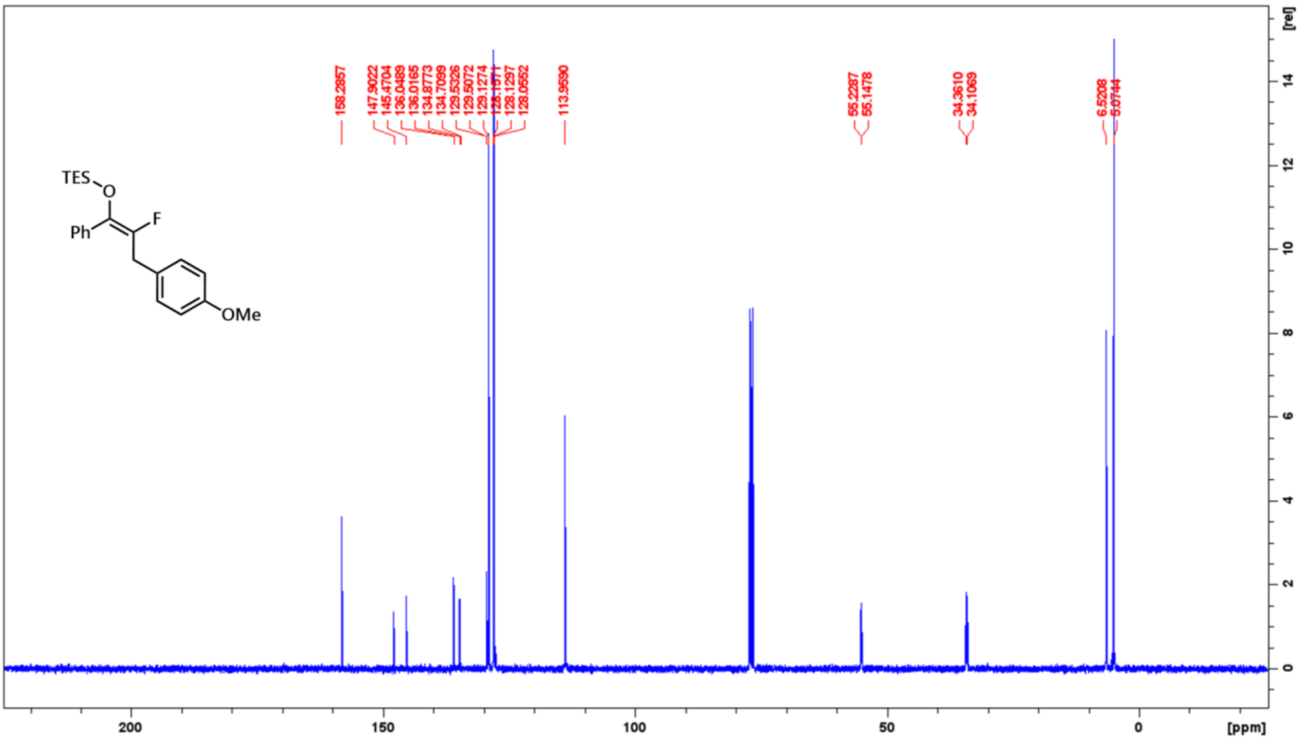
^{1}H NMR (400 MHz, $CDCl_3$)



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

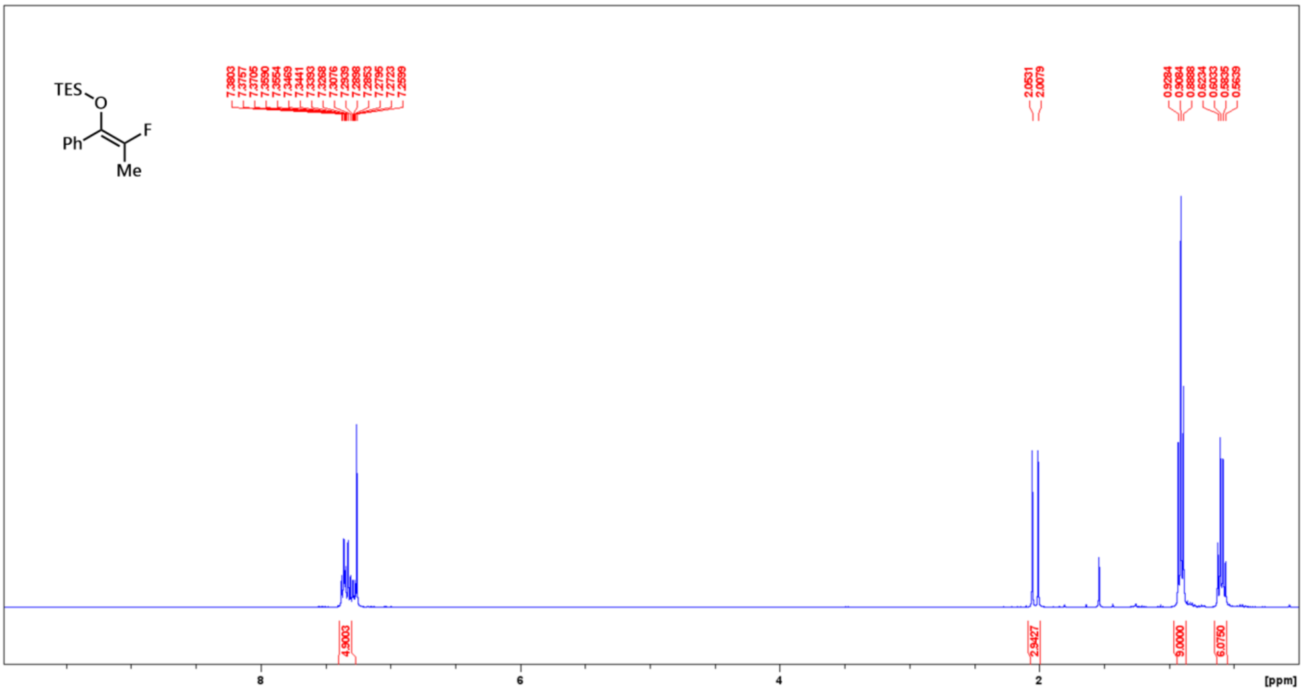


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

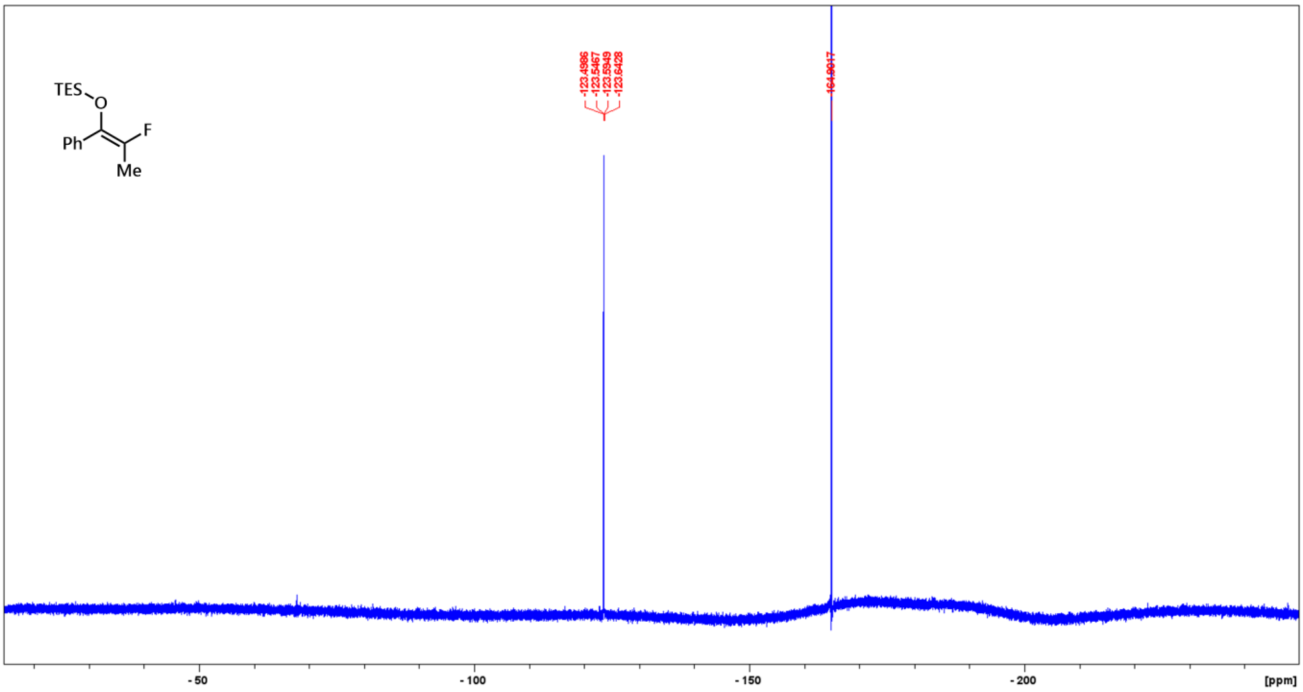


(Z)-6r

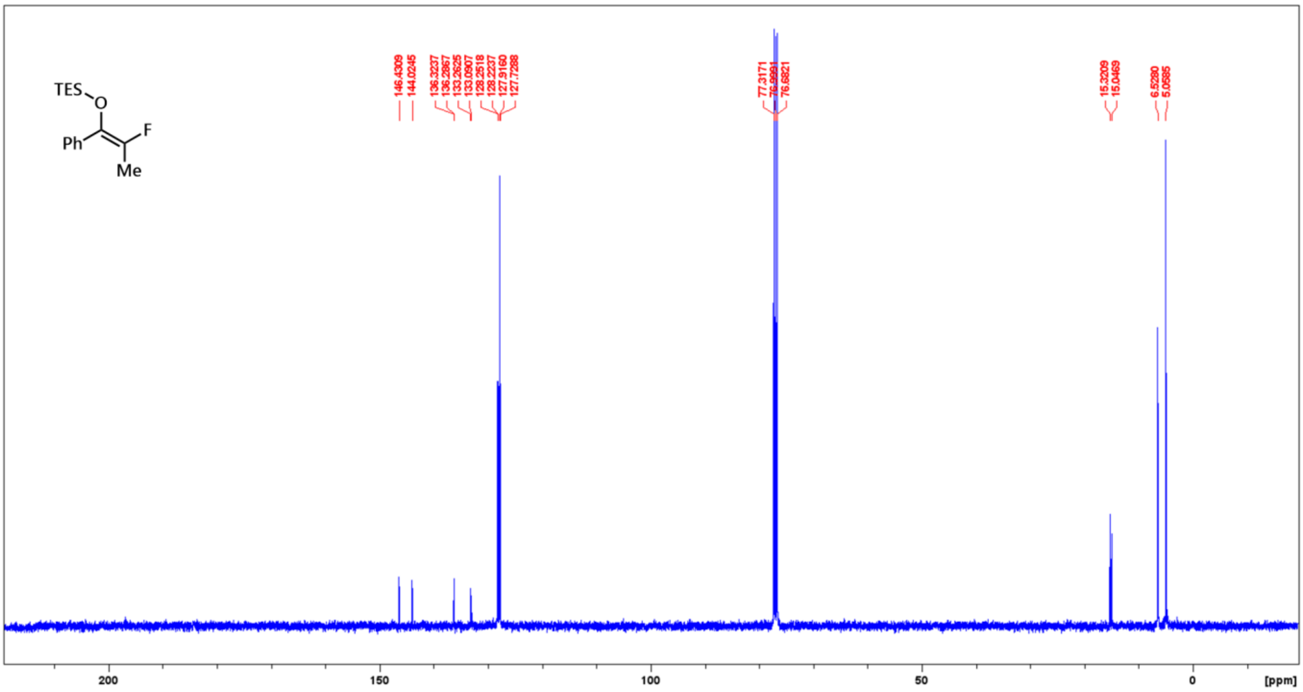
^{1}H NMR (400 MHz, $CDCl_3$)



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

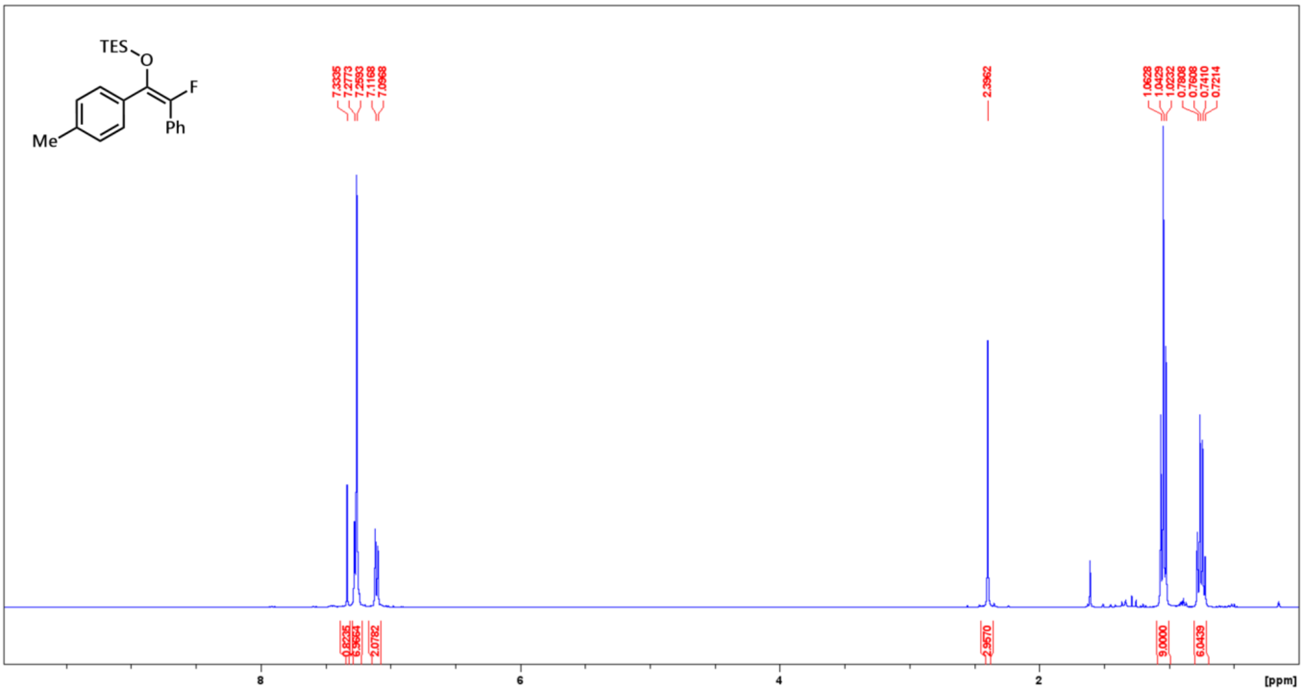


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

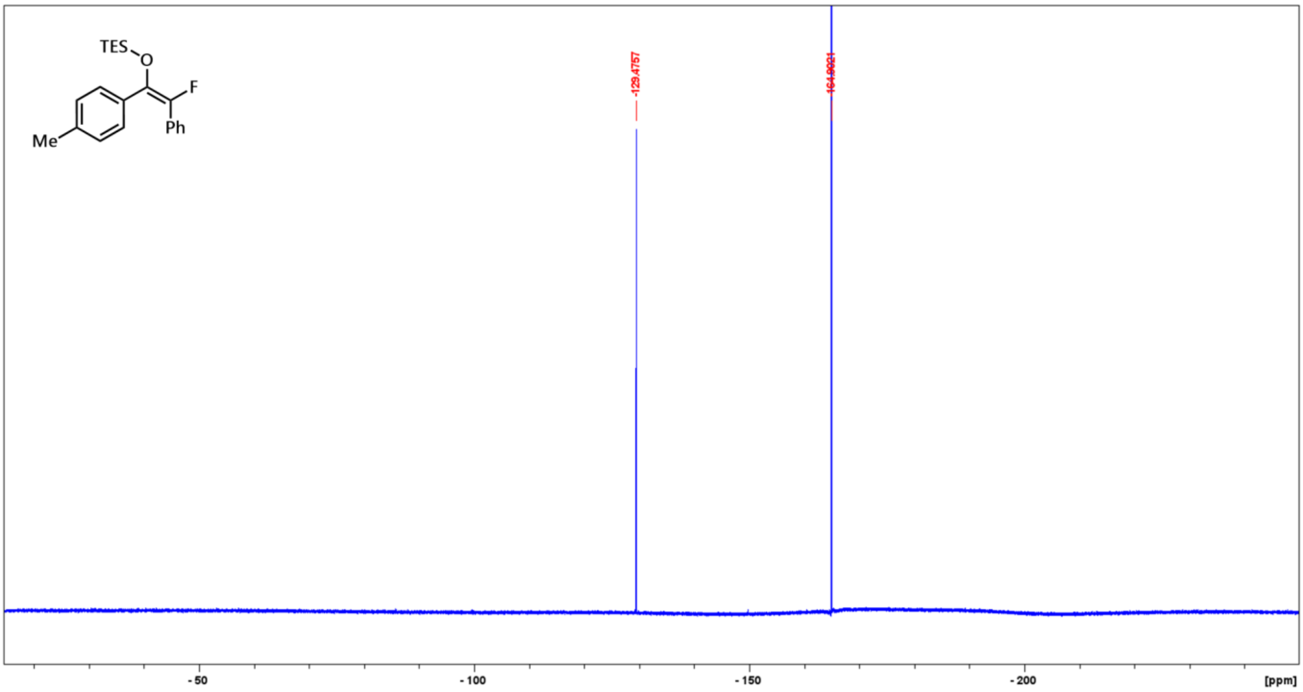


(Z)-6s

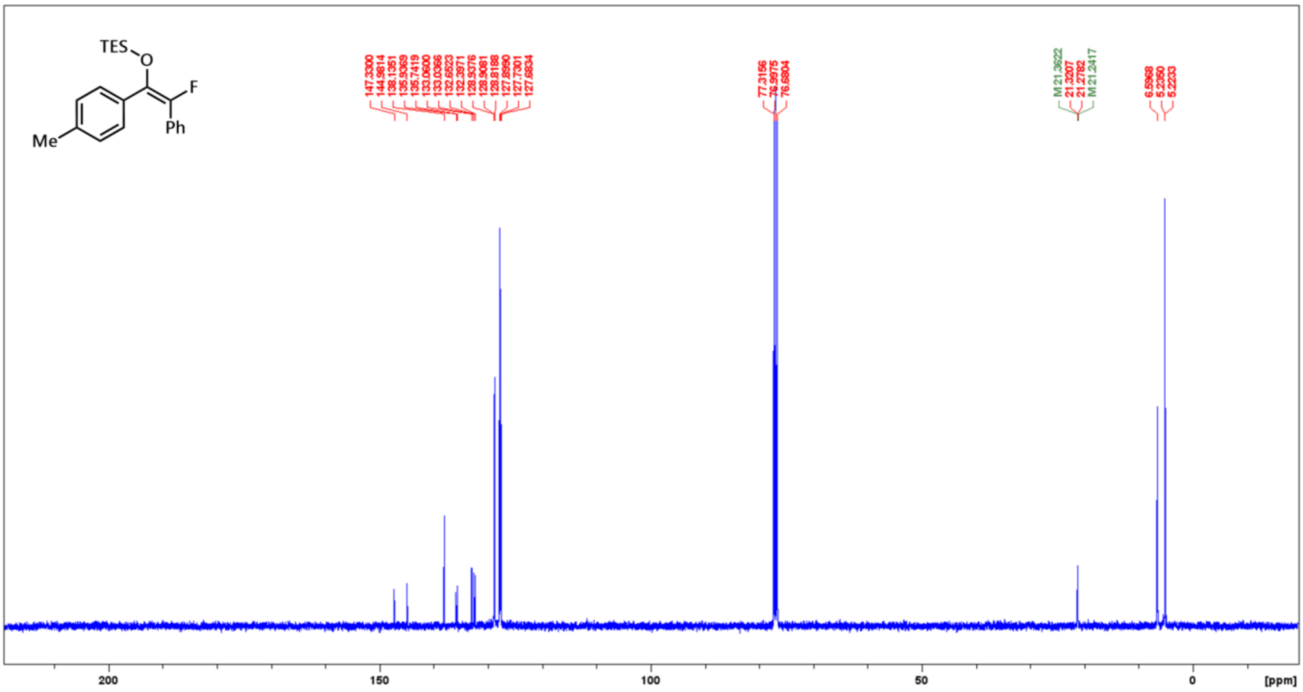
^{1}H NMR (400 MHz, CDCl$_3$)



[19]F NMR (376 MHz, CDCl$_3$)

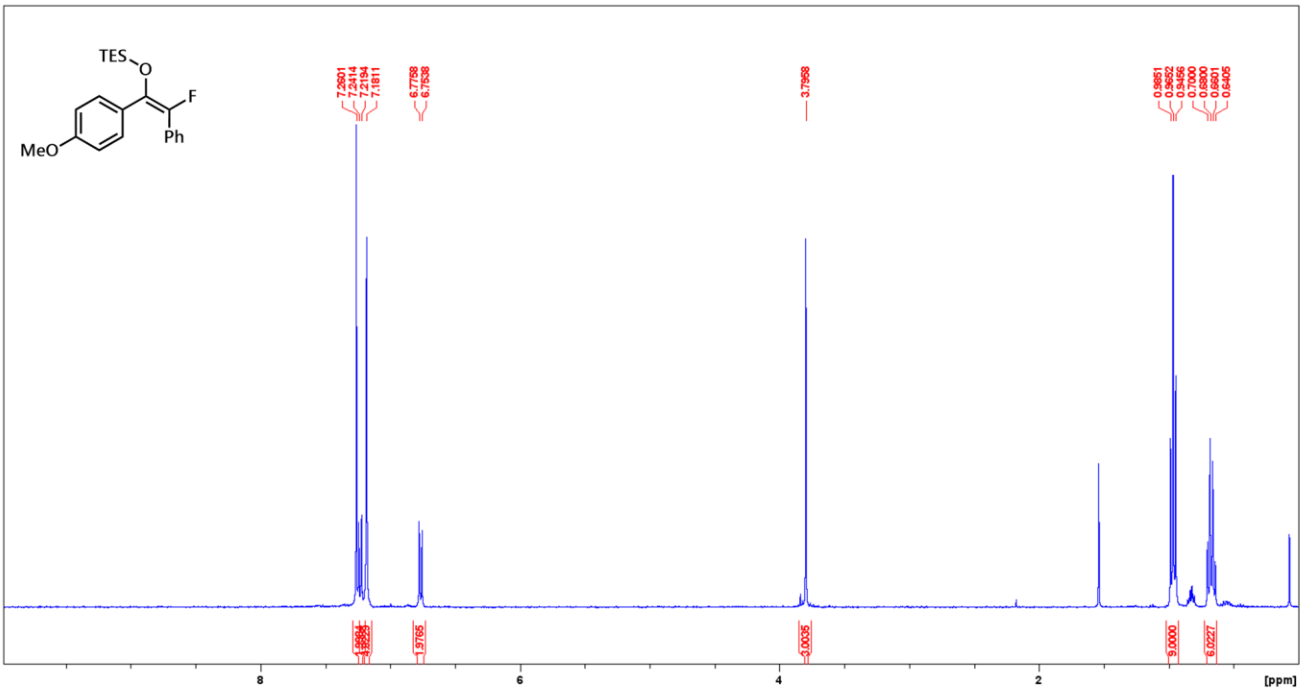


[13]C NMR (100 MHz, CDCl$_3$, [1]H decoupling)

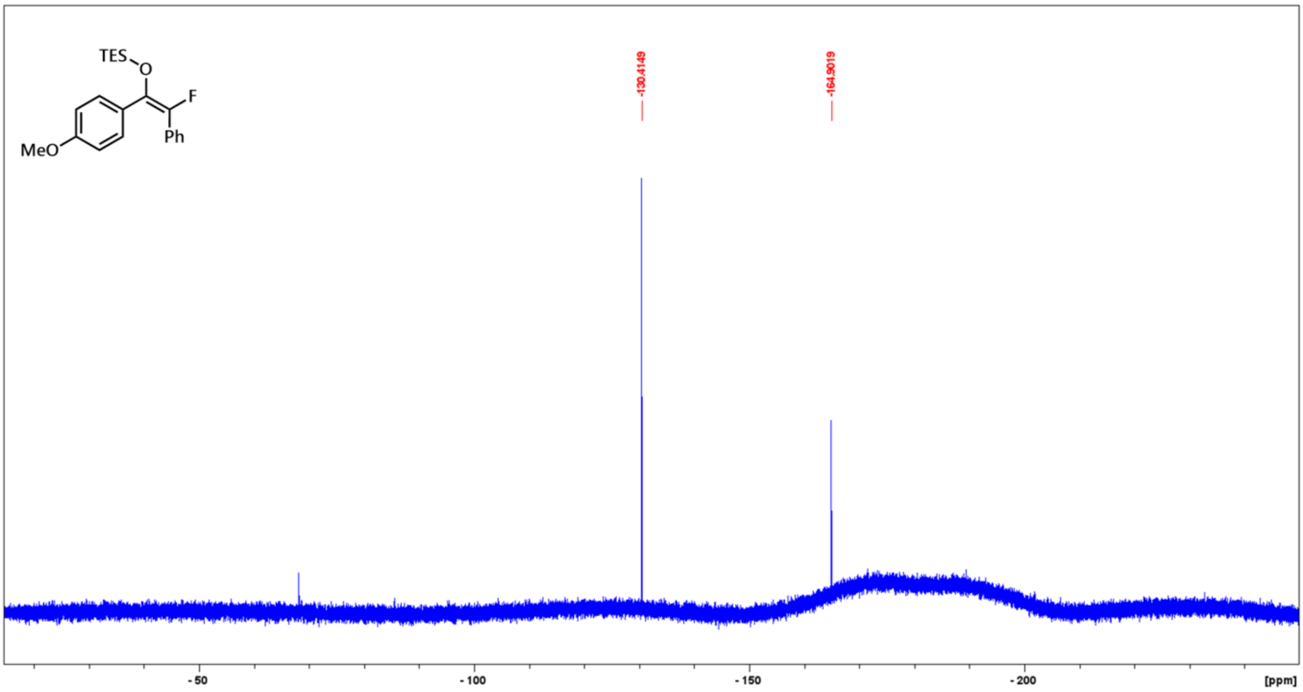


(Z)-6t

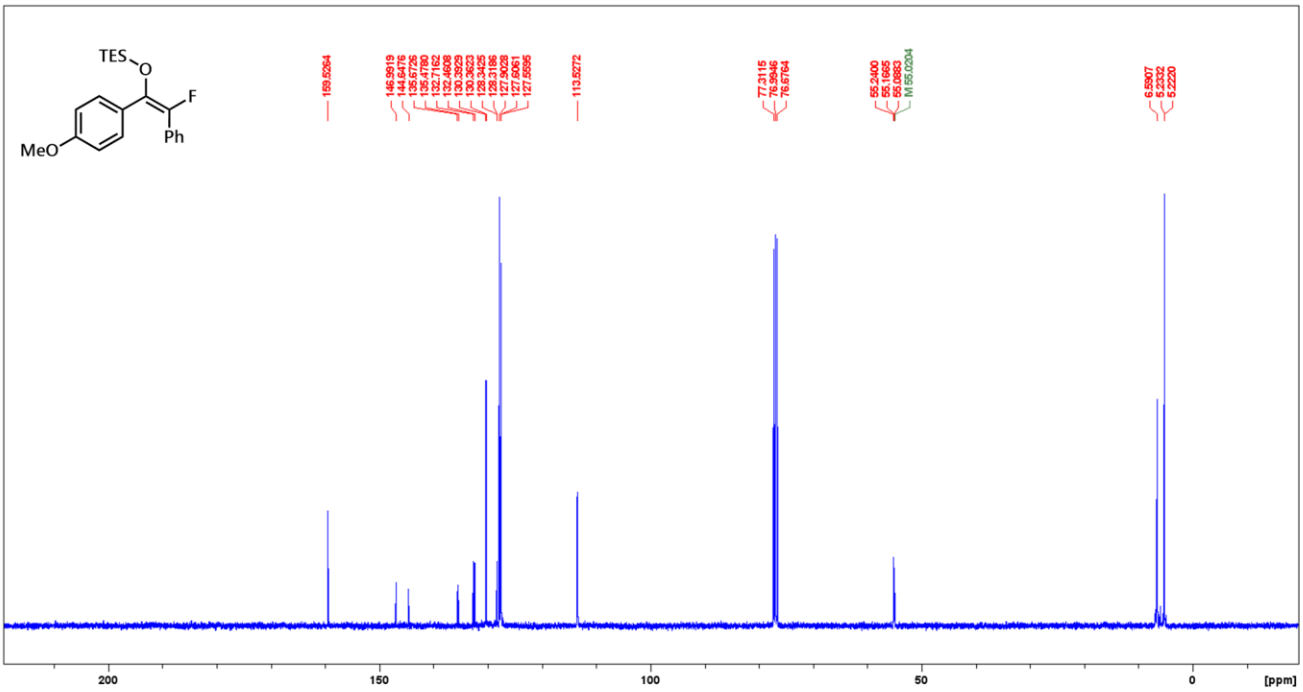
^{1}H NMR (400 MHz, CDCl$_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

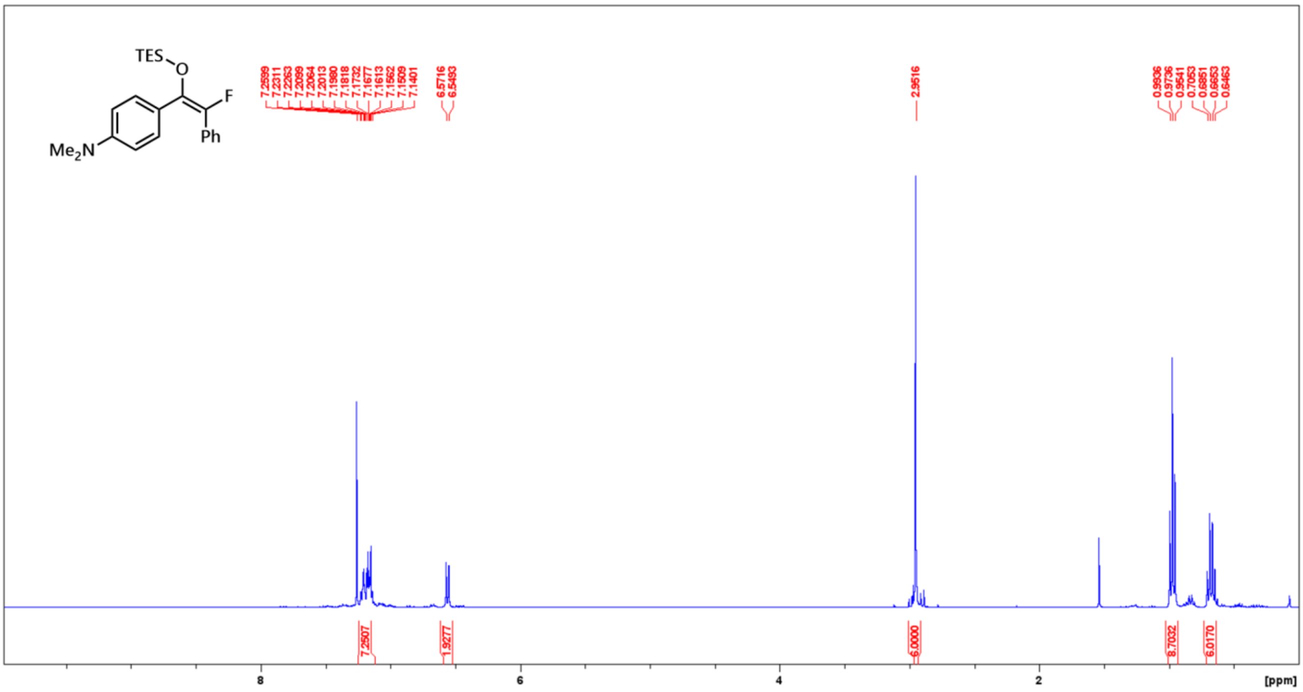


^{13}C NMR (100 MHz, $CDCl_3$, ^1H decoupling)

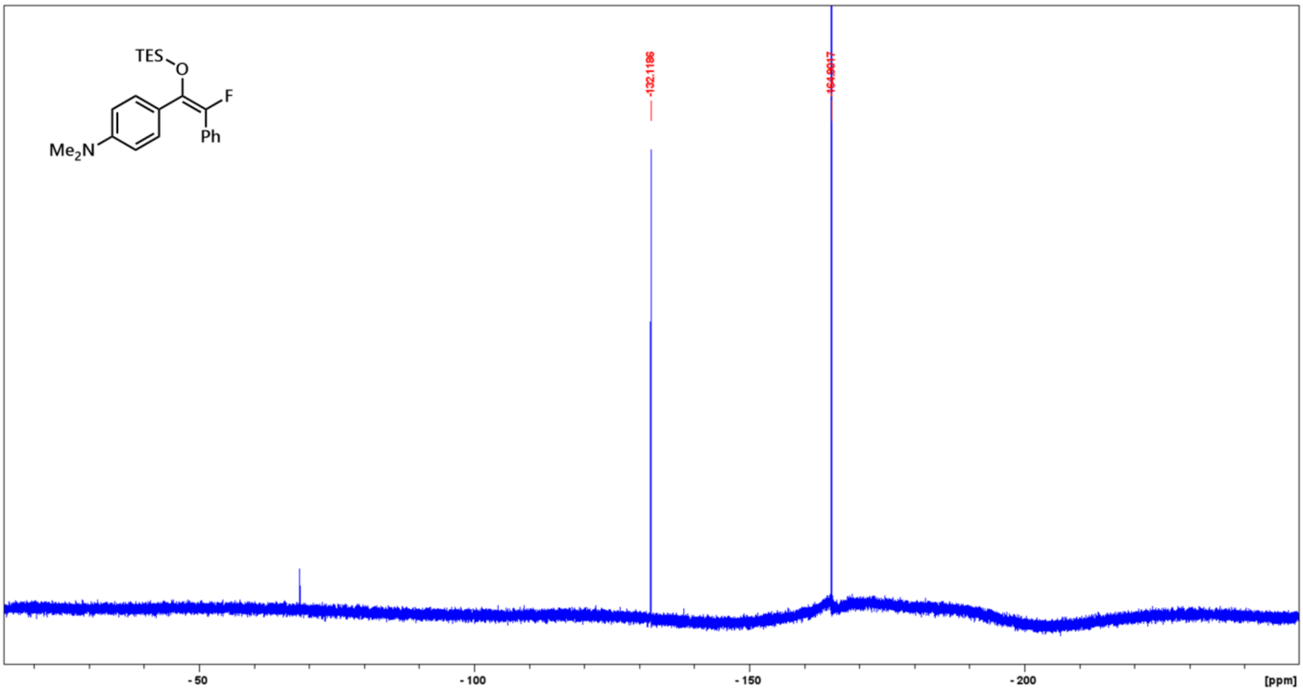


(Z)-6u

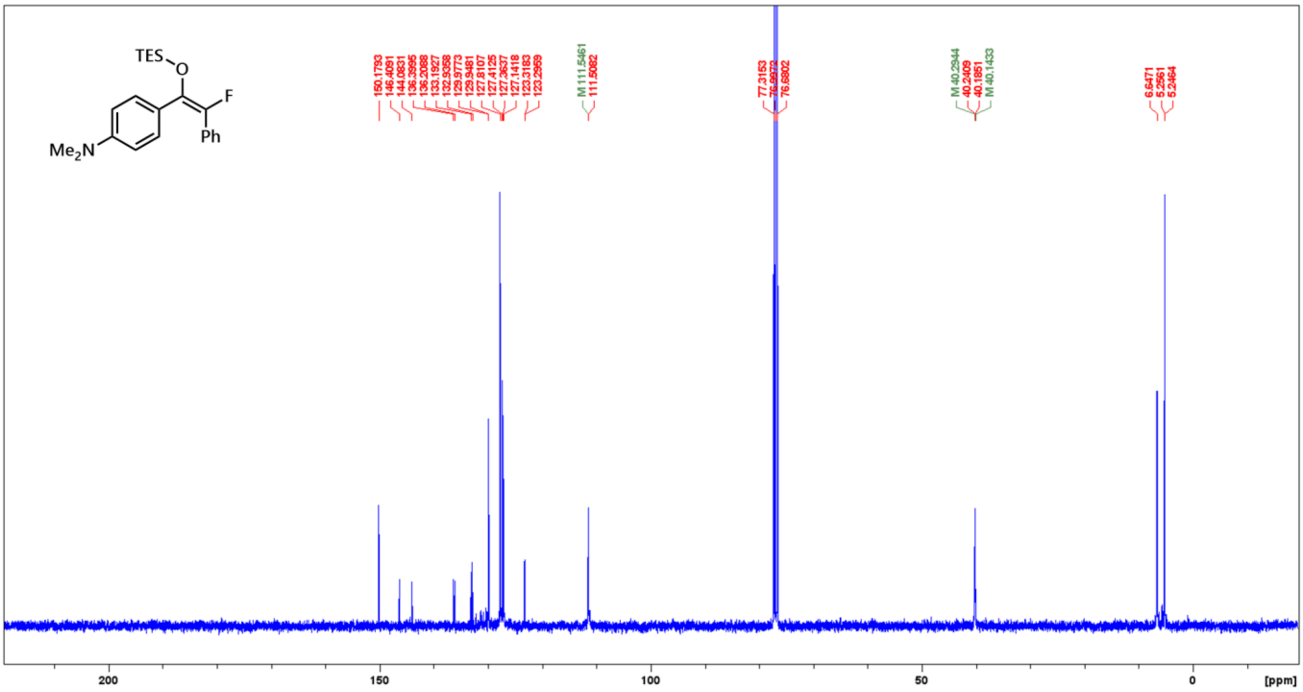
^1H NMR (400 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

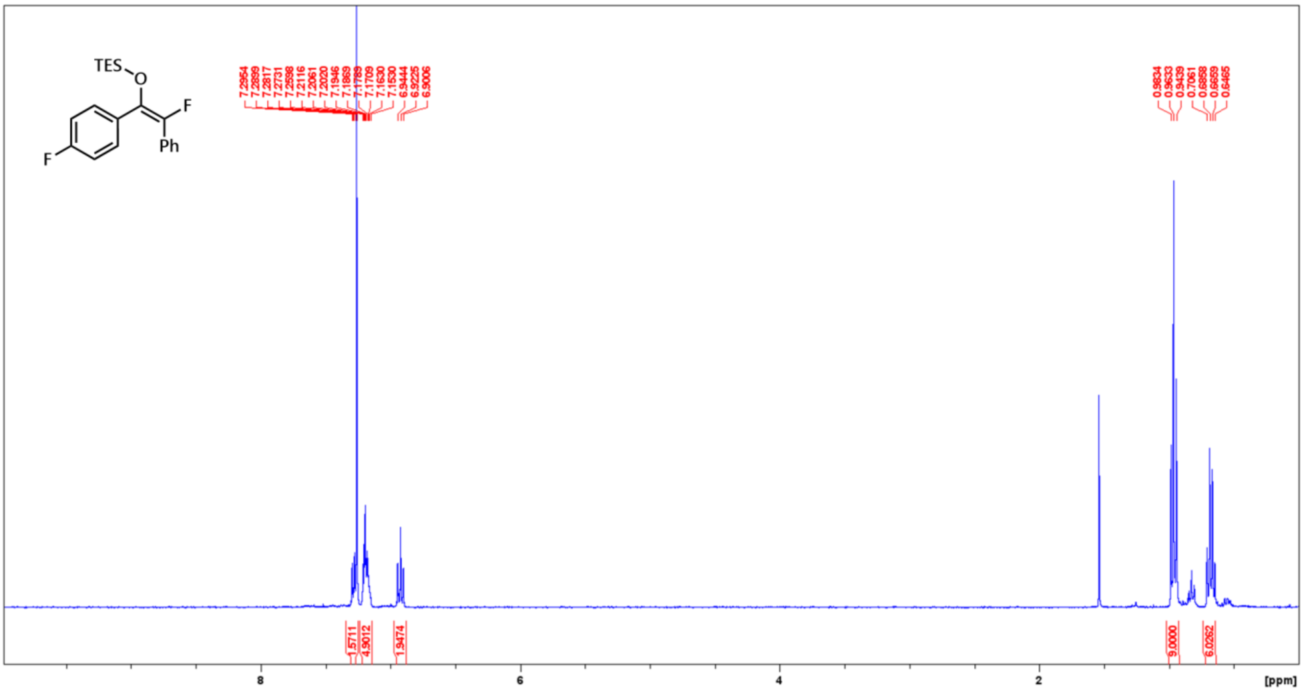


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

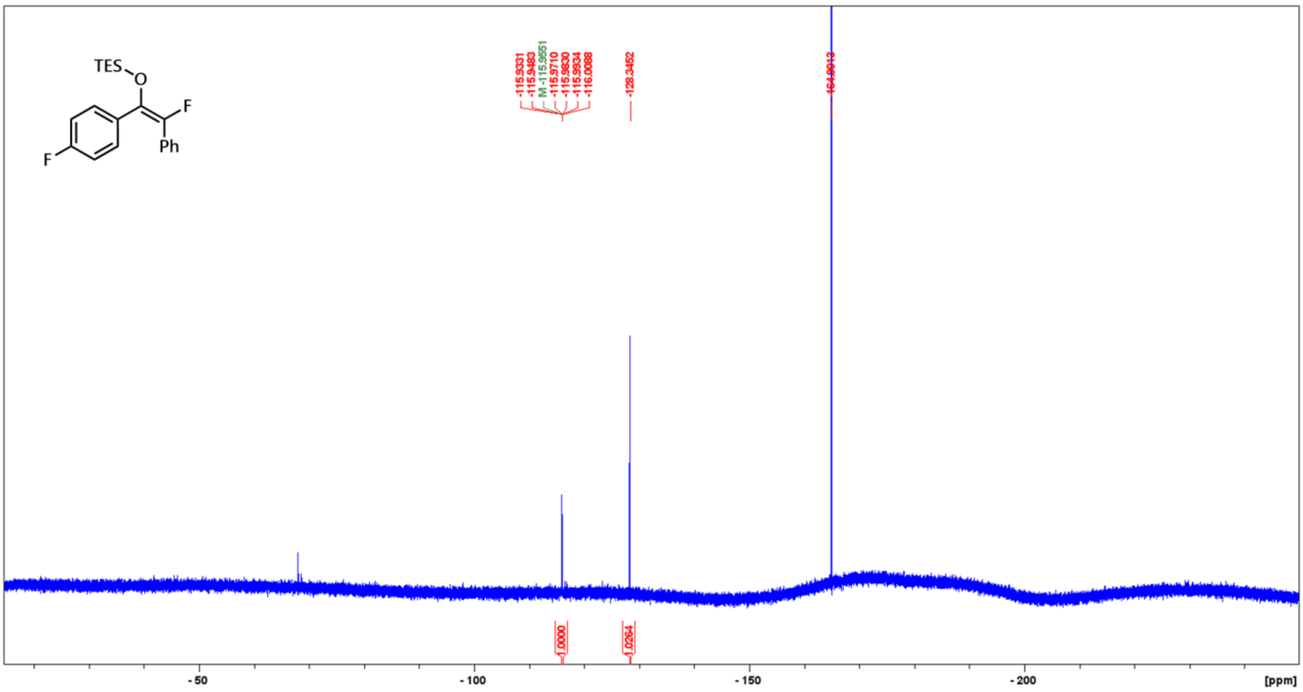


(Z)-6v

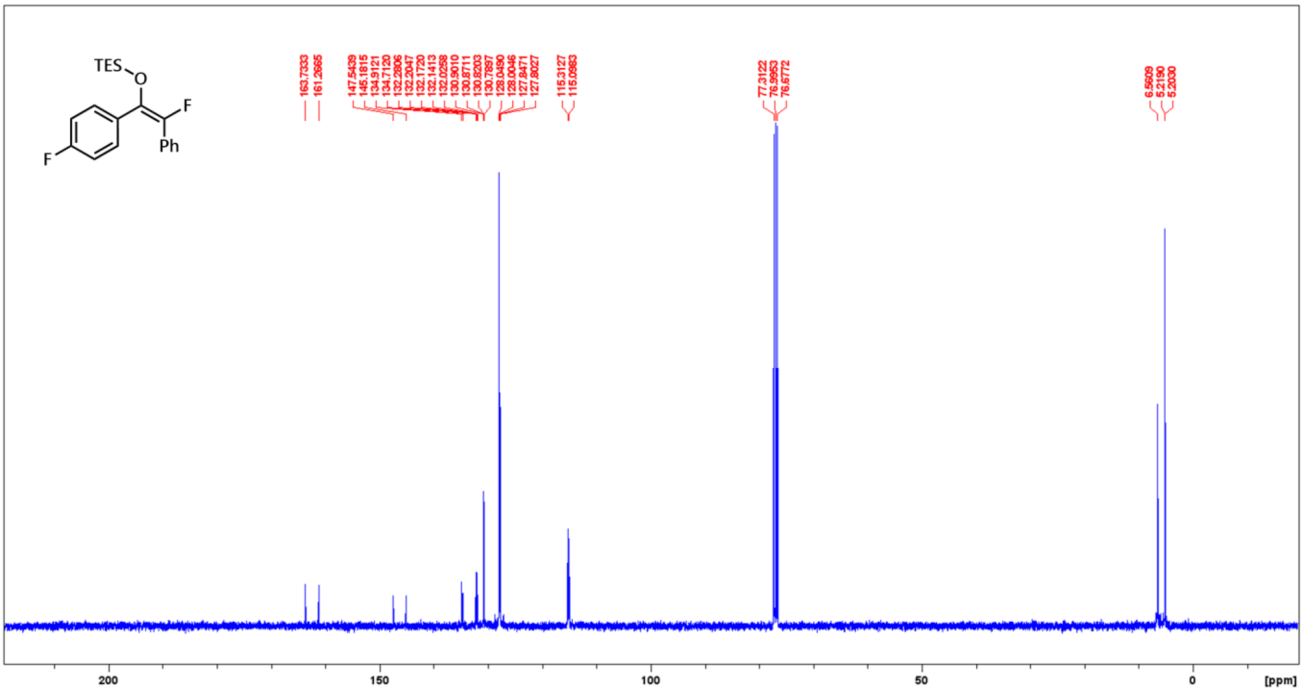
^{1}H NMR (400 MHz, $CDCl_3$)



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

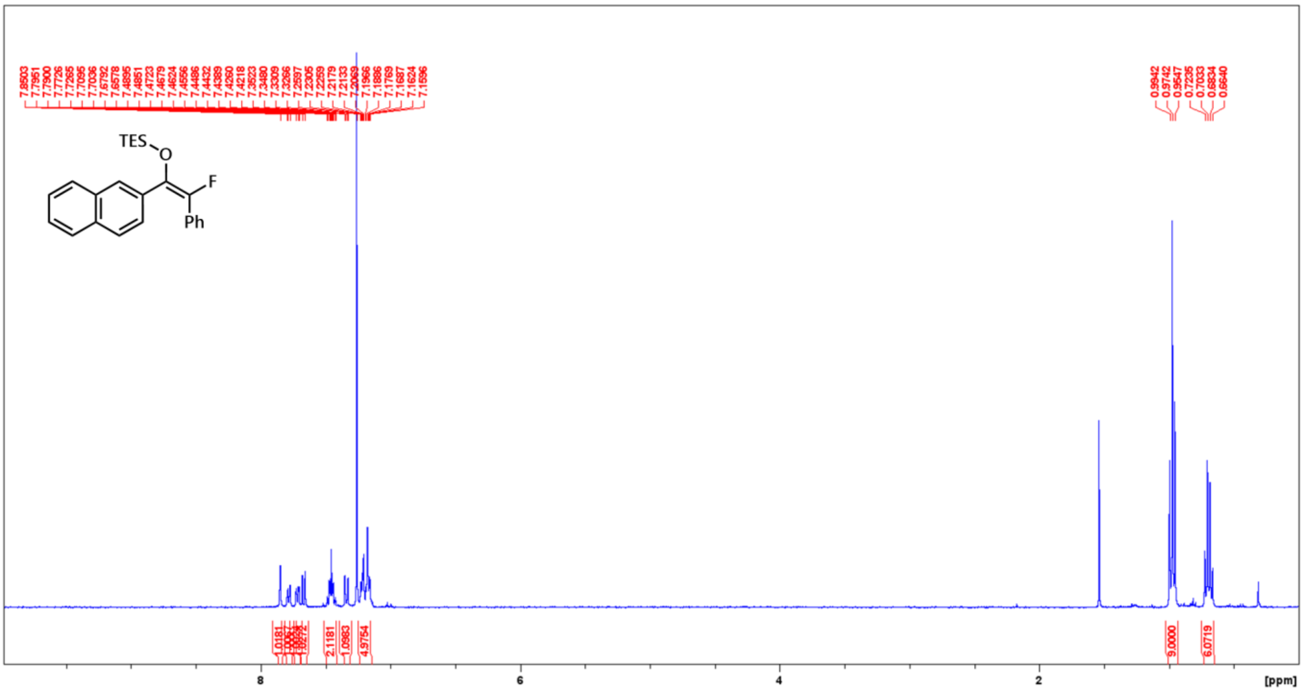


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)

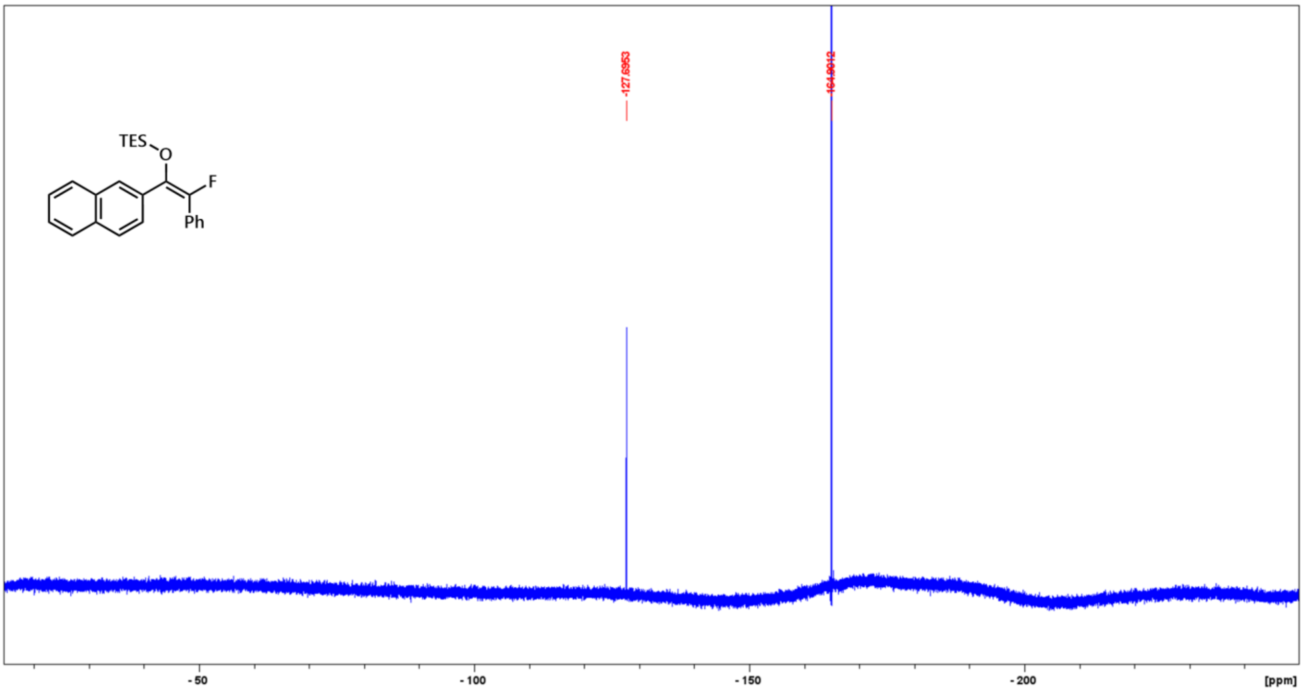


(Z)-6w

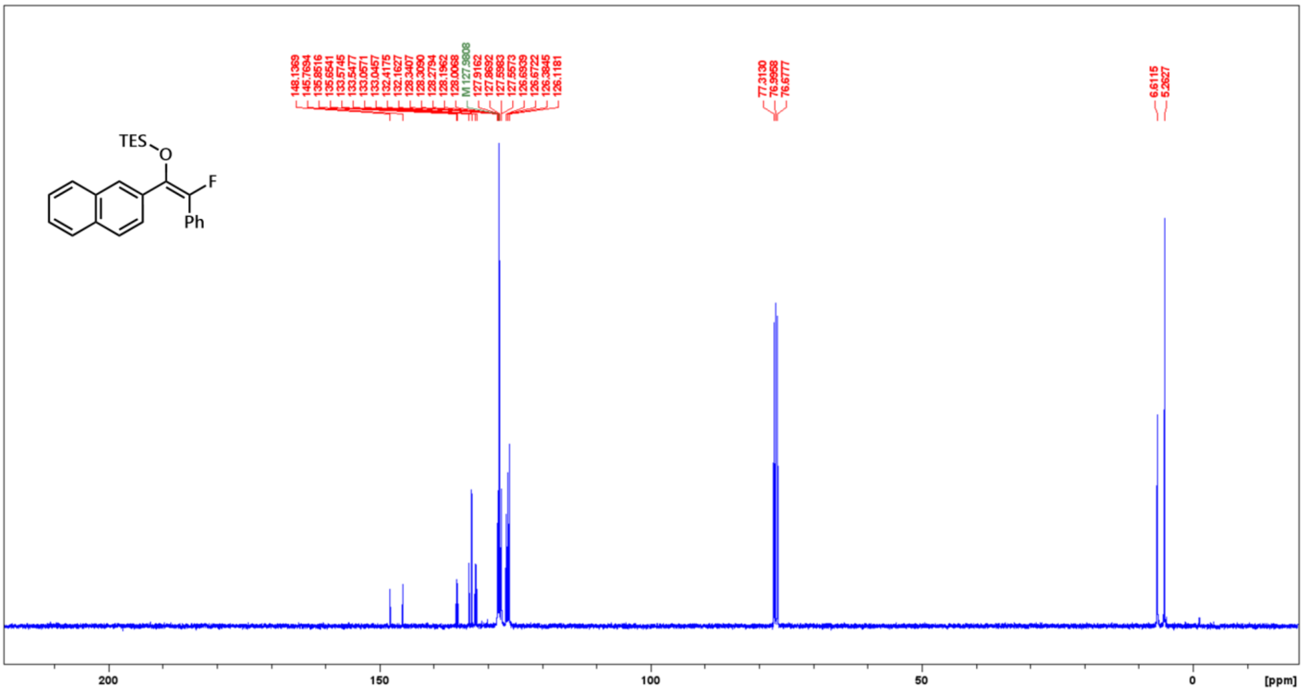
^{1}H NMR (400 MHz, $CDCl_3$)



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

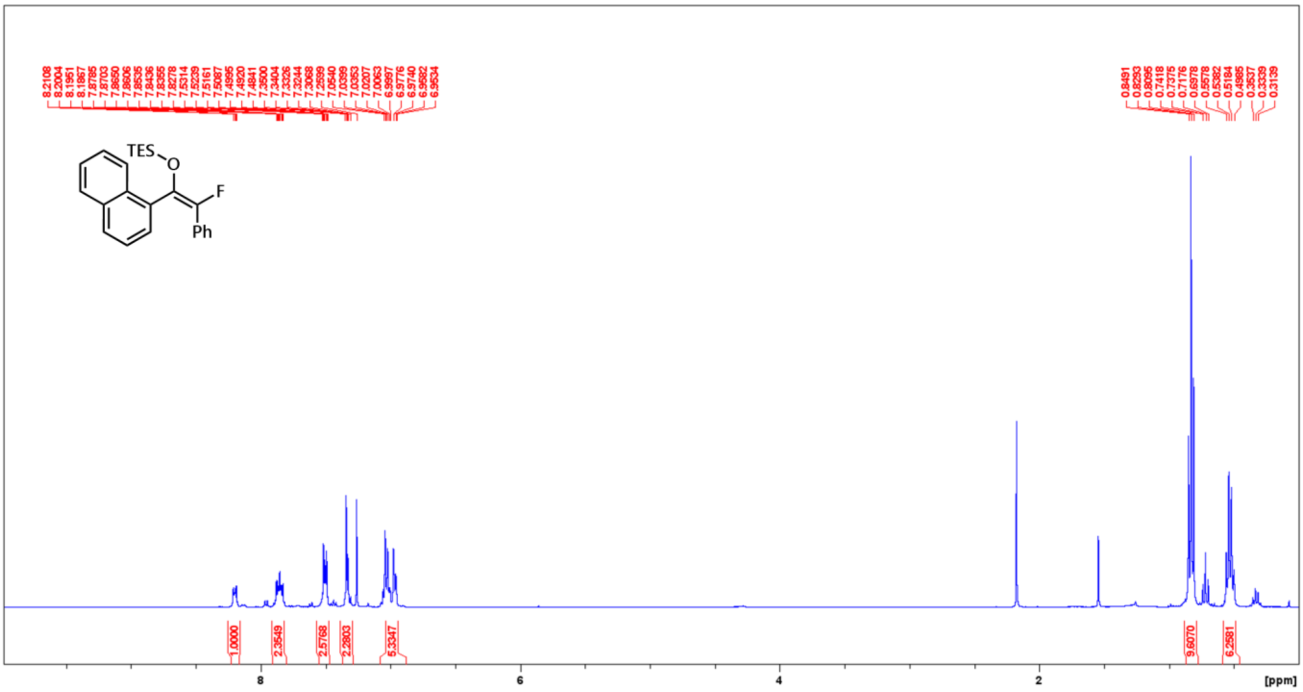


^{13}C NMR (100 MHz, $CDCl_3$, ^1H decoupling)

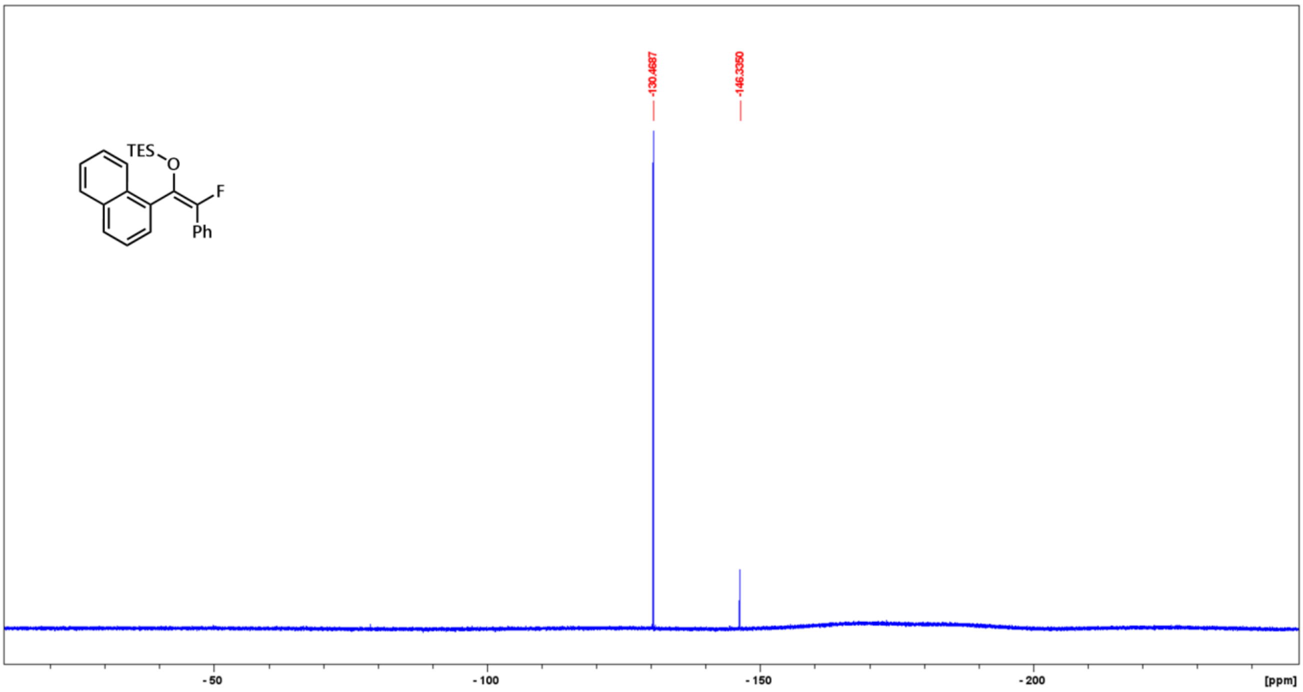


(Z)-6x

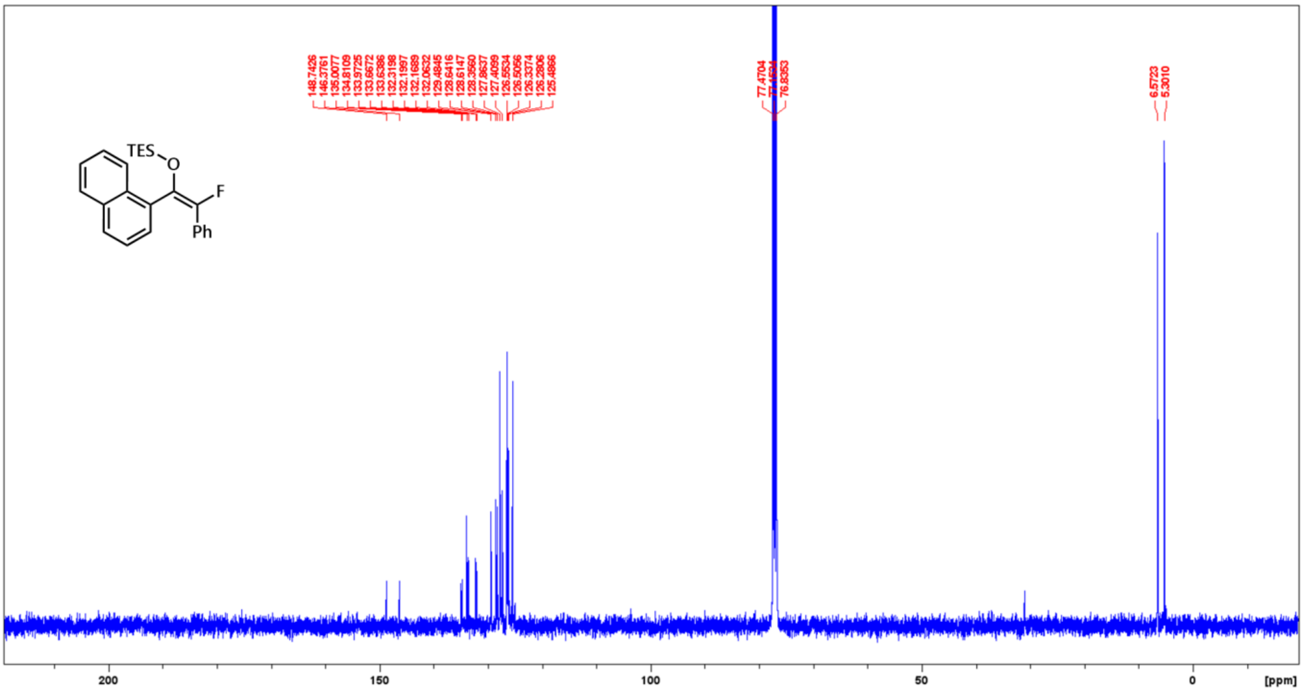
^{1}H NMR (400 MHz, $CDCl_3$)



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

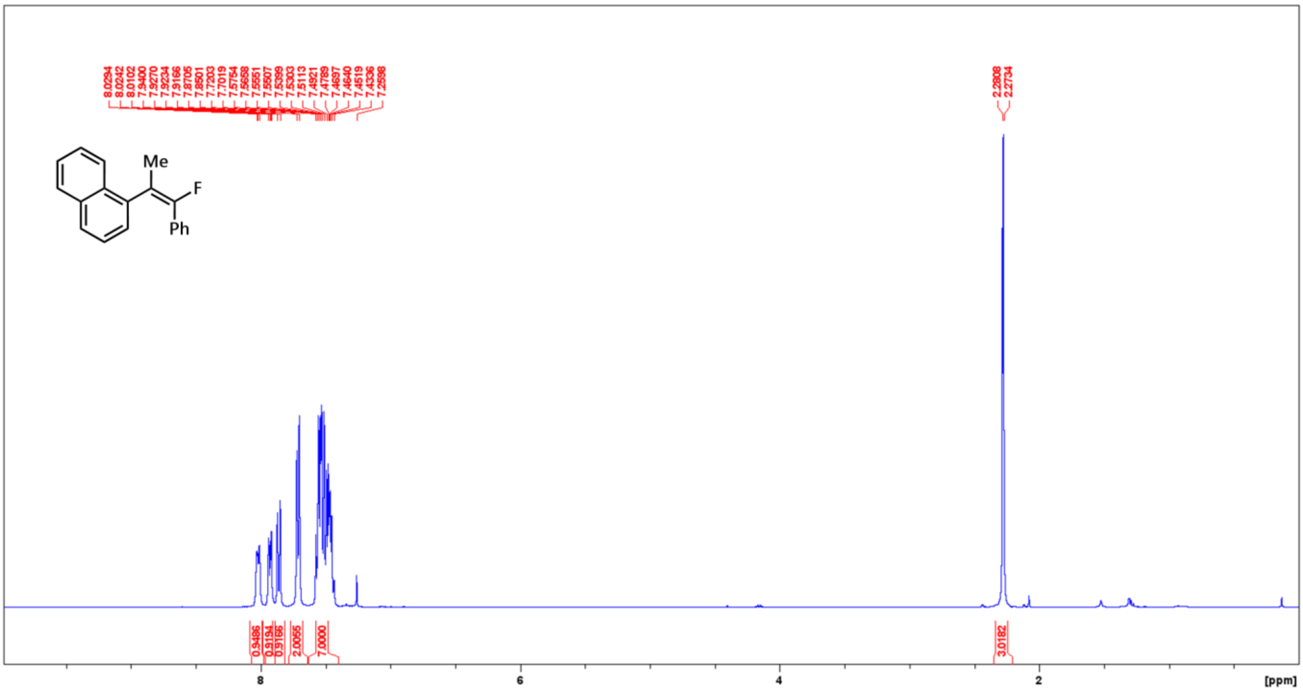


^{13}C NMR (100 MHz, CDCl$_3$, ^{1}H decoupling)

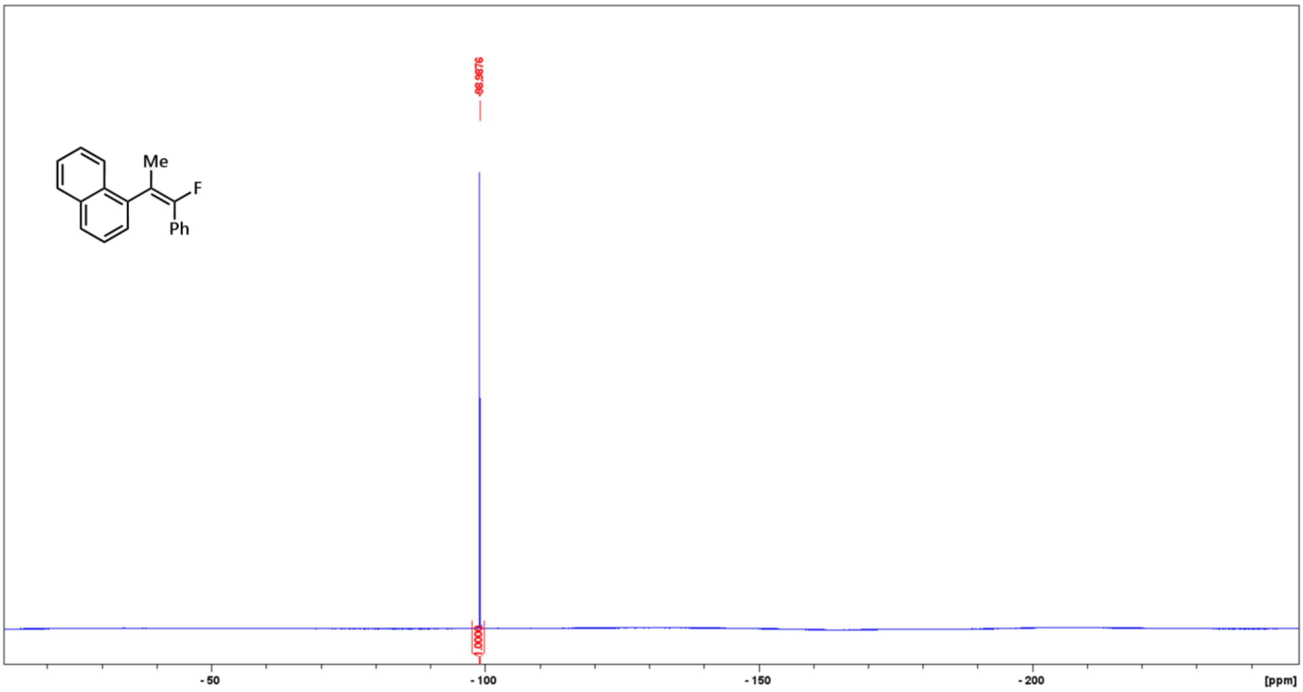


(E)-8b

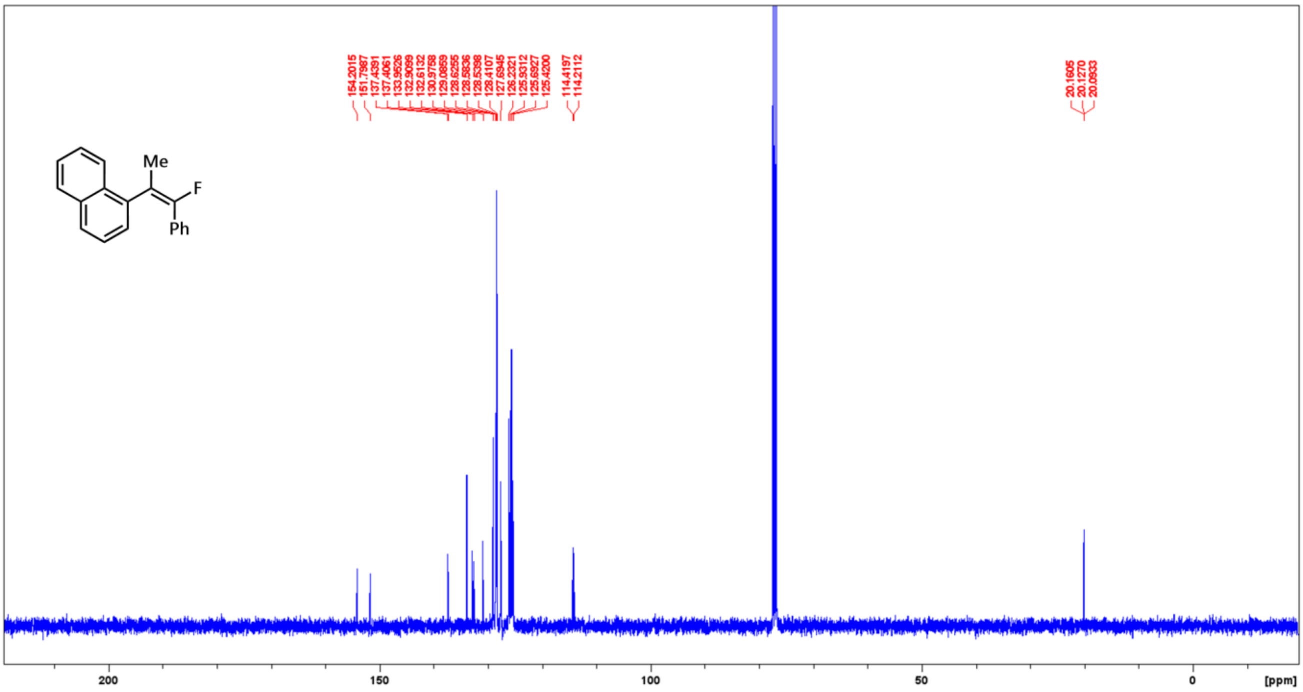
^{1}H NMR (400 MHz, CDCl$_3$)



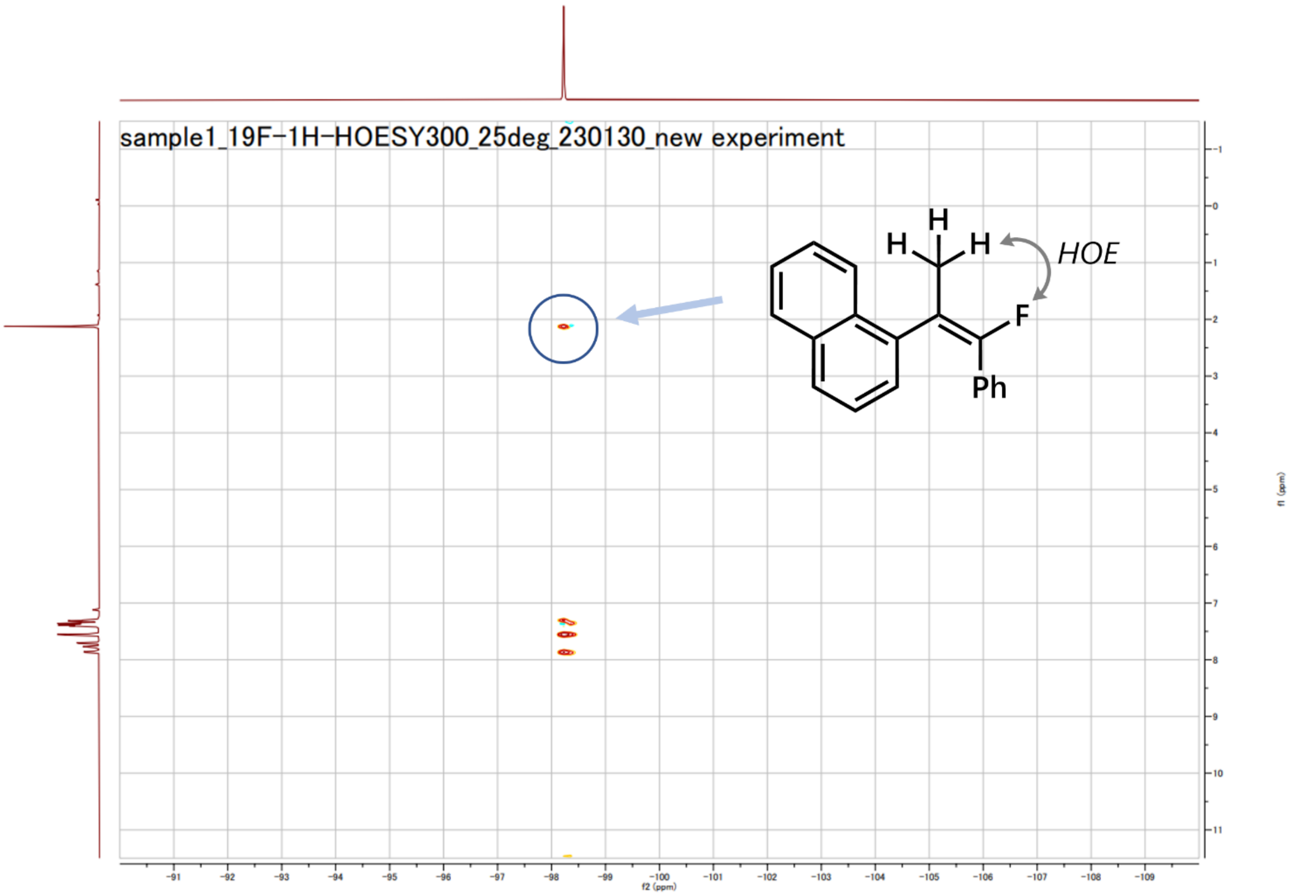
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)



^{1}H-^{19}F HOESY ($CDCl_3$)



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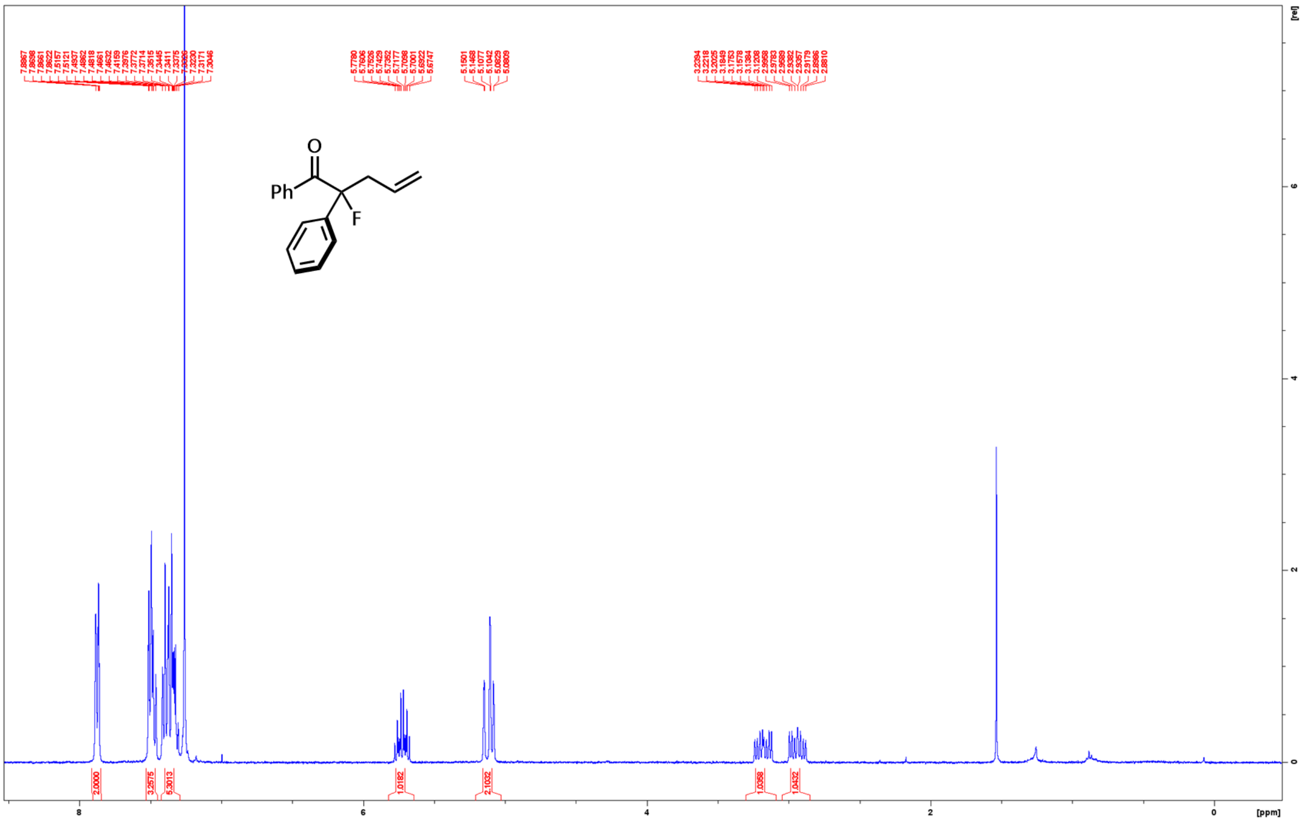
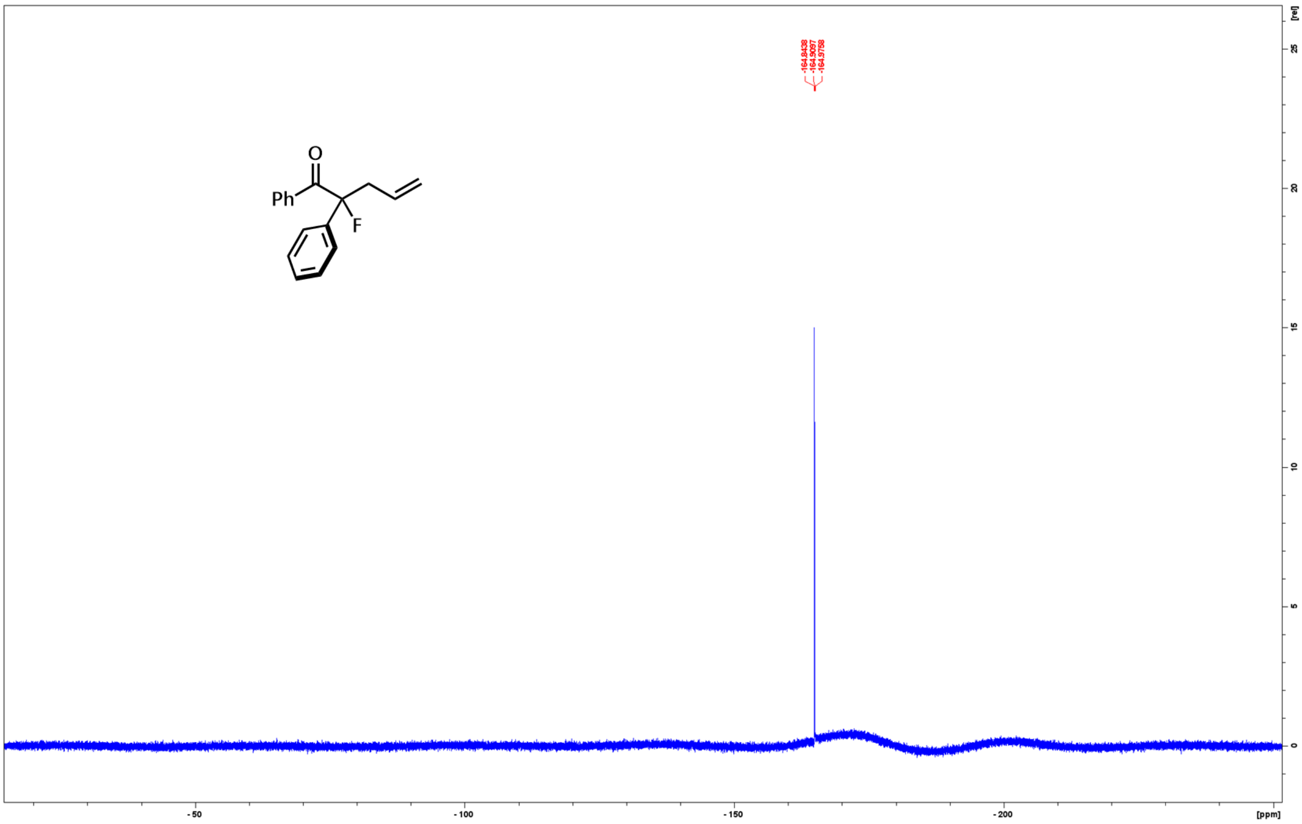
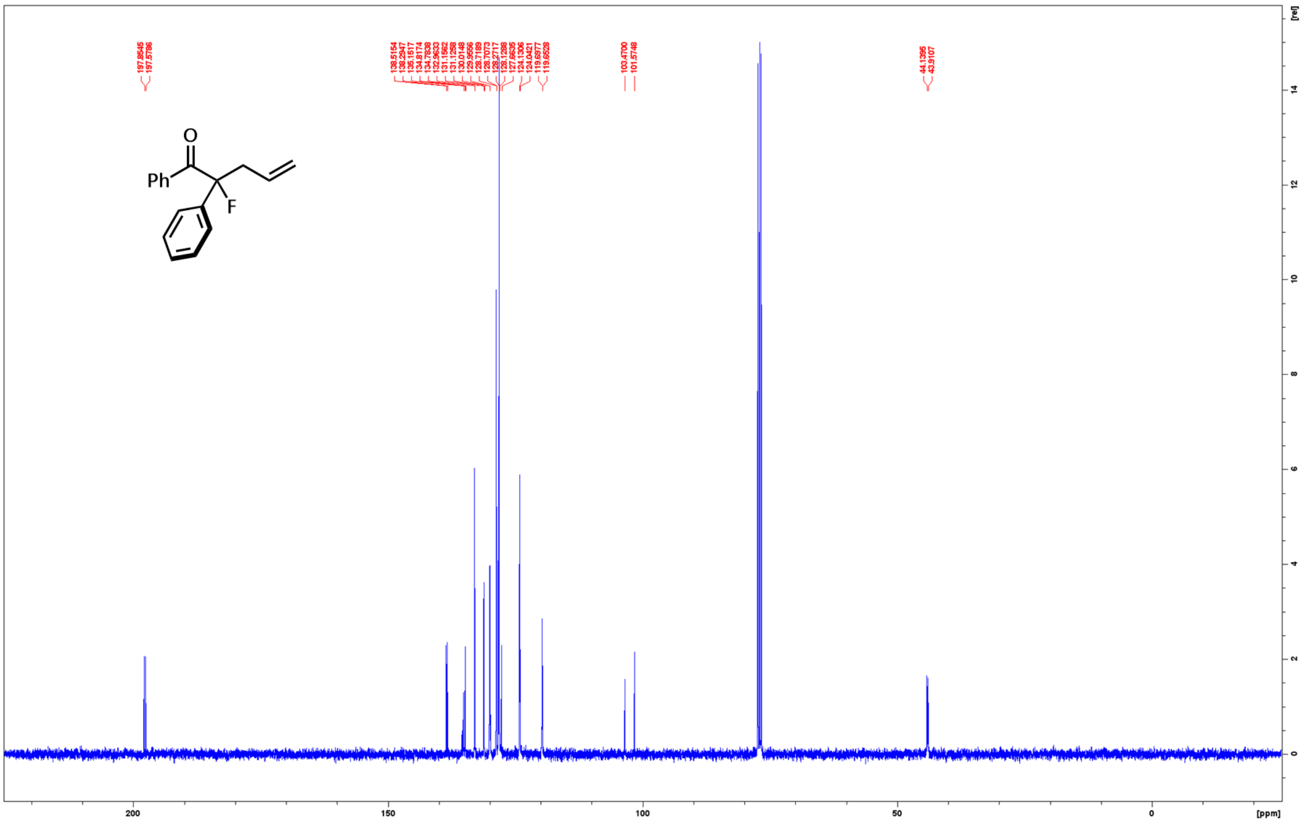
^{1}H NMR (400 MHz, CDCl$_3$)



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

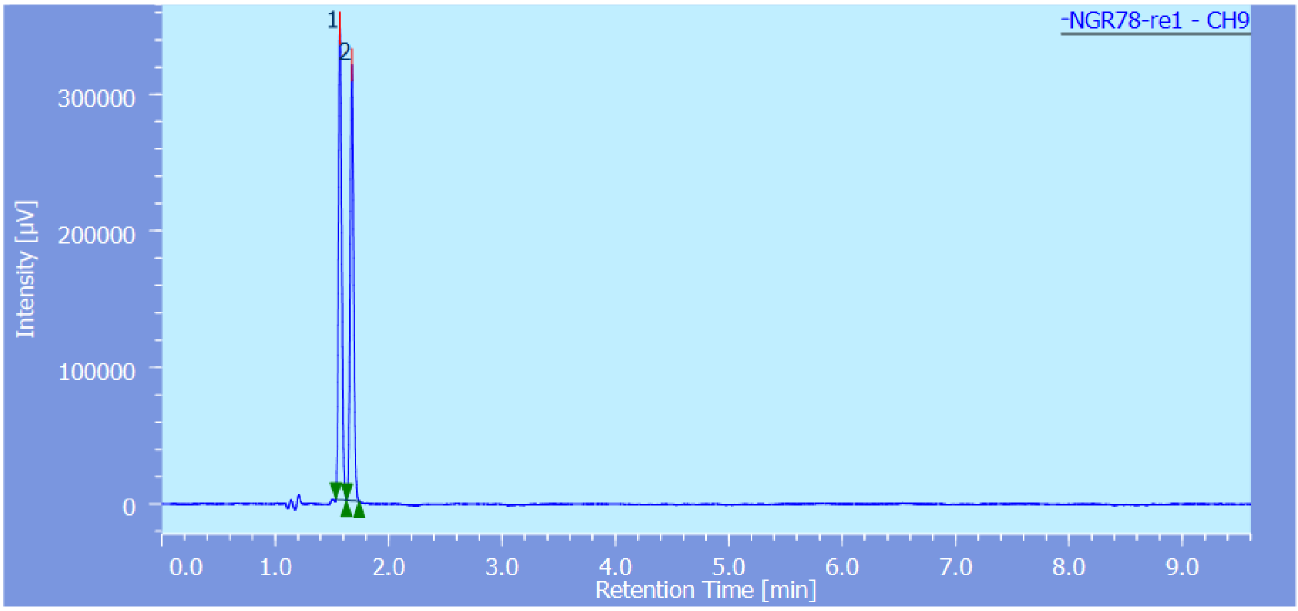


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)



SFC (Table 2, entry 1)

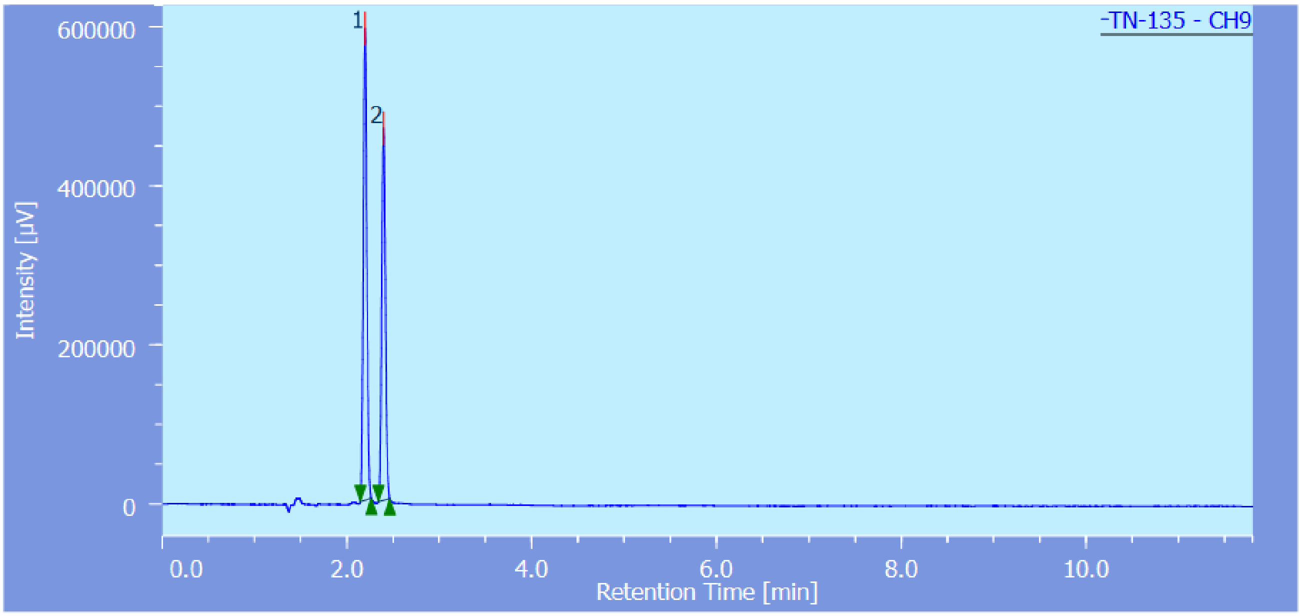
$scCO_2$, 2.4 mL/min, MeOH 1.0 mL/min, sample charge: Et_2O



Peak	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
#1	1.572	678591	345035	50.560	51.945
#2	1.675	663566	319201	49.440	48.055

SFC (Table 2, entry 2)

$scCO_2$, 2.4 mL/min, MeOH 0.3 mL/min, sample charge: Et_2O



Peak	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
#1	2.197	1575981	592130	55.329	55.902
#2	2.397	1272381	467100	44.671	44.098

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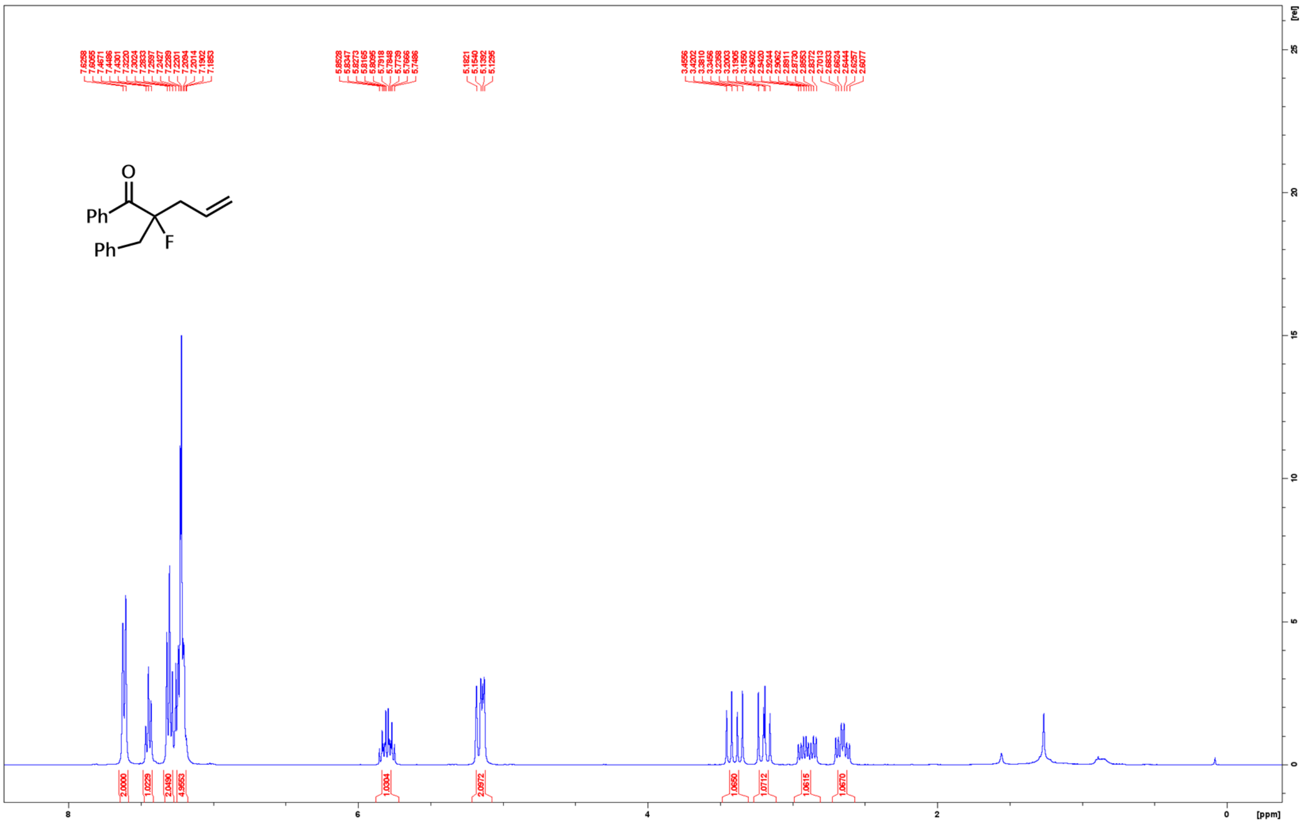
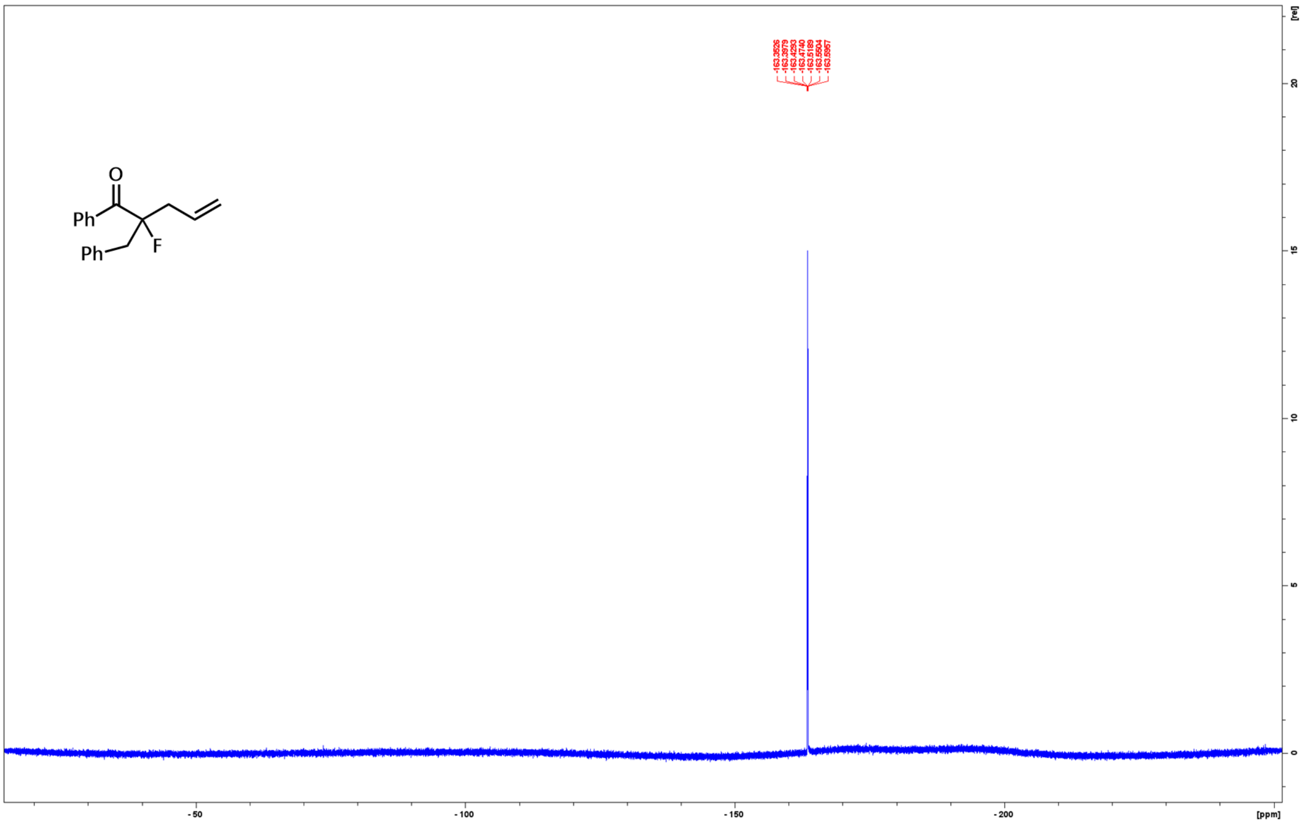
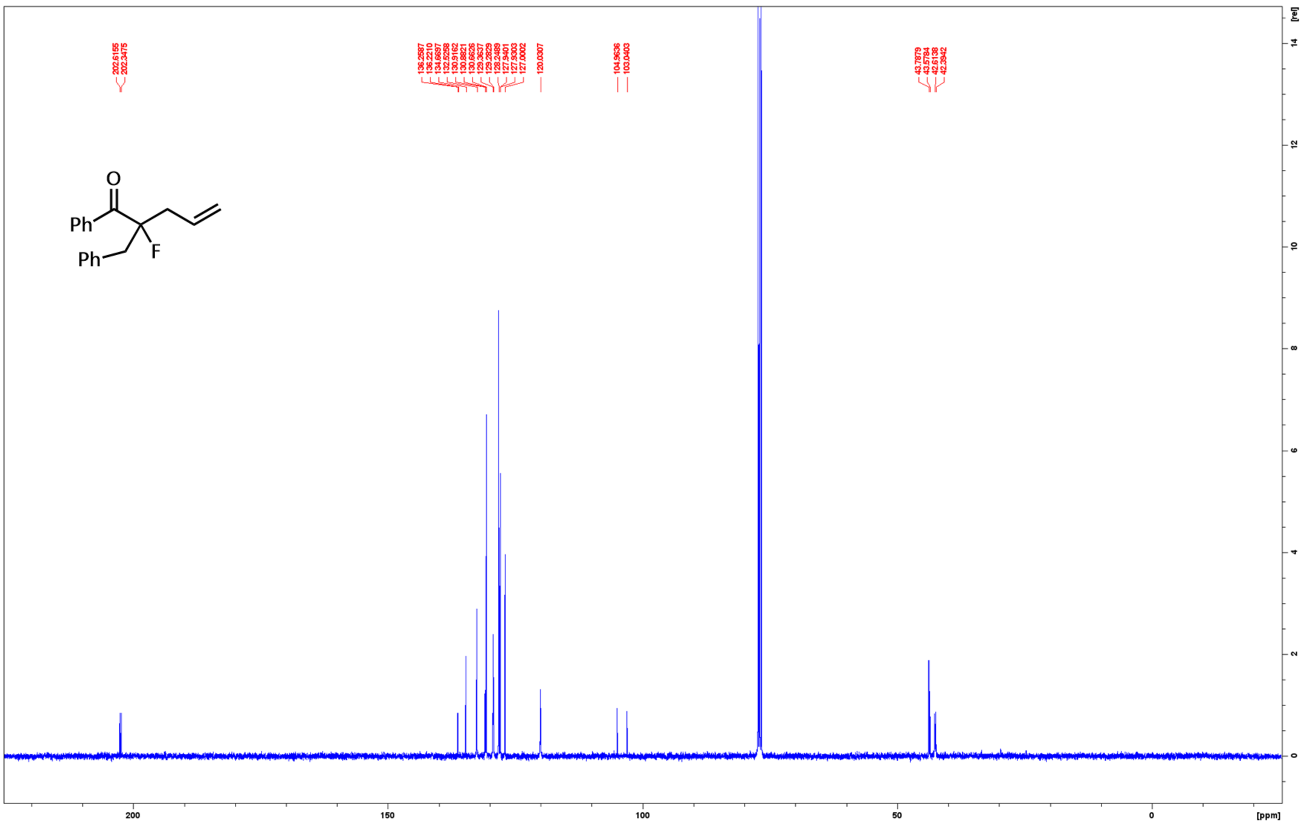
¹H NMR (400 MHz, CDCl₃)



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

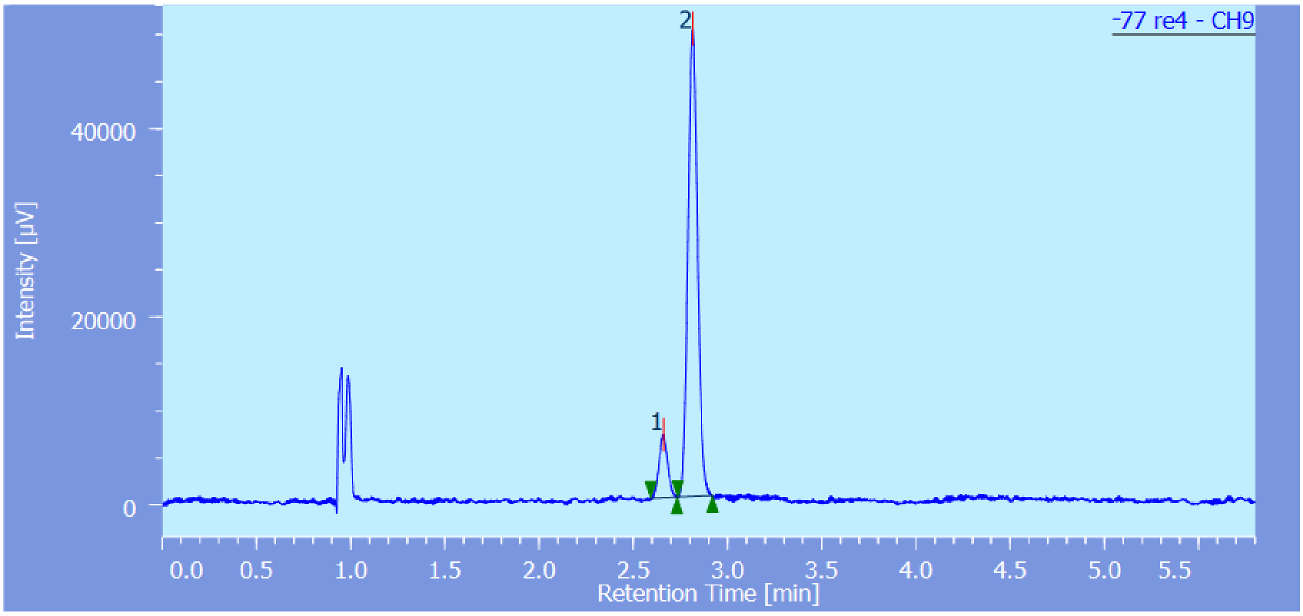


^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H decoupling)



SFC (Table 2, entry 3)

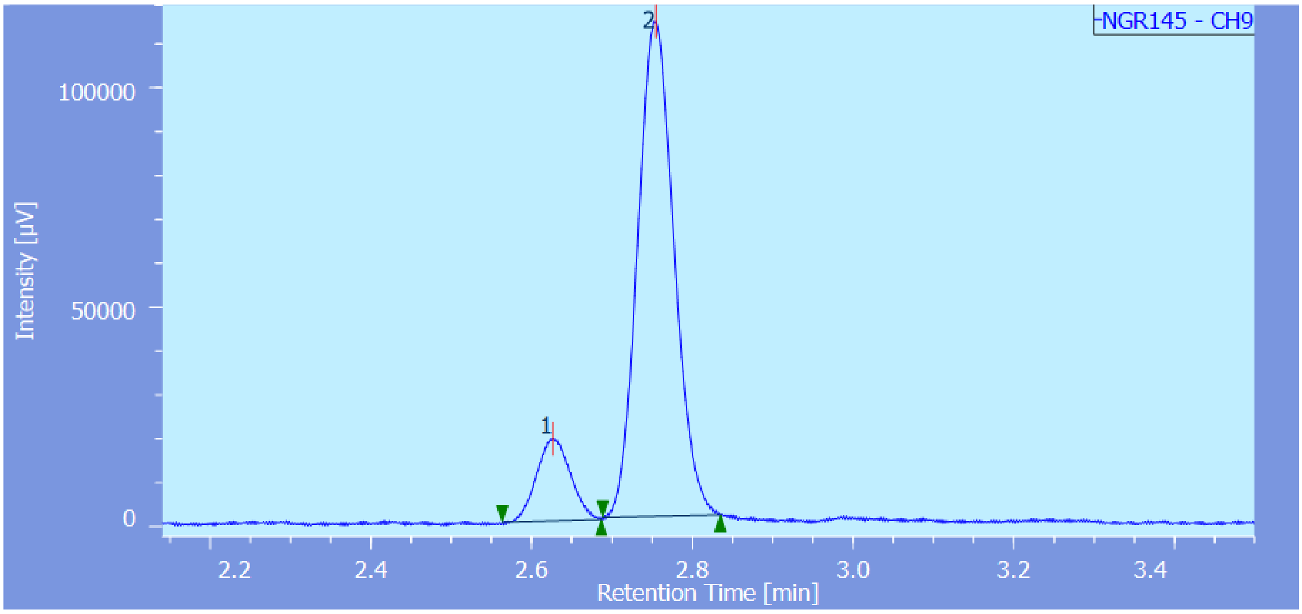
$scCO_2$, 4.0 mL/min, MeOH 0.09 mL/min, sample charge: hexane



Peak	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
#1	2.660	21123	6688	10.687	11.861
#2	2.815	176532	49700	89.313	88.139

SFC (Table 2, entry 4)

$scCO_2$, 4.0 mL/min, MeOH 0.09 mL/min, sample charge: hexane



Peak	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
#1	2.627	54729	18689	13.375	14.224
#2	2.755	354455	112701	86.625	85.776