Supporting Information

Catalytic C-F Bond Activation of gem-Diflurocyclopropanes by Nickel(I) Complexes via a Radical based Mechanism

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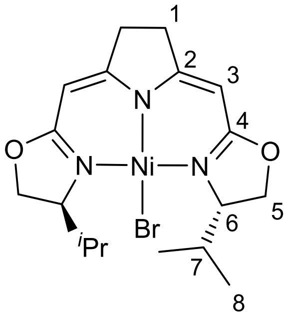
Contents:

I. General Information

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were predried over activated 4 Å molecular sieves and were refluxed over magnesium (methanol), sodium (toluene), potassium (hexane), sodium-potassium alloy (tetrahydrofurane, diethyl ether) or calcium hydride (dichloromethane) under an argon atmosphere and collected by distillation. ^{1}H and ^{13}C^{1} NMR spectra were recorded on a Bruker Avance III 600, Bruker Avance II 400 and Bruker DRX 200 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane.[2] ^{19}F NMR was measured at 376 MHz, and 1,4-bis(trifluoromethyl)benzene (−63.39 ppm) was used as an internal standard. All NMR spectra were recorded at room temperature (295 K). Mass spectra were recorded by the mass spectrometry service at the Organic Chemistry Laboratory of the University Heidelberg and the elemental analyses were measured by the analytical services of the University of Heidelberg. Compounds **4a, 7a, 8a, 9a, 10a** and complexes **2a/b** and **3a/b** were synthesized according to the literature procedures.[3] Me_2NHBH_3 was purchased from Sigma Aldrich, sublimated in vacuum and stored in under argon. All other reagents were purchased and used as received.

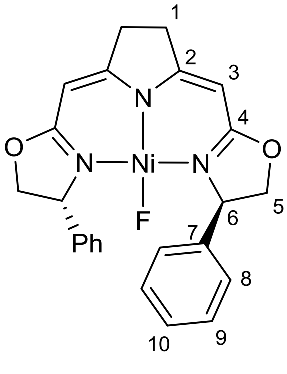
II. a) Preparation of the Complexes and Reagents

1. (S)-Lig$_{iPr}$(iso)NiBr



To a solution of the protioligand (**(S)-Lig$_{iPr}$H**) (370 mg, 1.16 mmol) in 10 ml THF, tBuLi (1.28 mmol, 1.1 eq) was added at −78 °C and stirred for 10 min. The solution was subsequently canulated to a suspension of $NiBr_2$(dme) (2.32 mmol, 2 eq) and 5 ml THF at low temperature. The mixture was allowed to reach room temperature and was stirred for an additional hour. After the removal of the solvents, the residue was treated with a toluene/pentane (1/1) mixture and the inorganic metal salts were removed by filtration. After the evaporation of the solvents, the crude was was dissolved in 20 ml toluene and heated to 90 °C for 48 h. At room temperature, the solution was filtrated and the solvents were removed. After crystallization from a toluene/pentane mixture, the product was obtained as brown crystalline solid in 80% yield (422 mg). **^{1}H NMR (600 MHz, C_6D_6)**: δ [ppm] = 14.30 (d, 2 H, H^6), 4.64 (b, 2 H, H^5), 4.22 (b, 2 H, H^7), 3.27 (b, 2 H, $H^{5'}$), 2.65 (b, 6 H, H^8), 1.61 (b, 6 H, $H^{8'}$), −1.03 (b, 2 H, H^1), −1.36 (m, 2 H, H^3), −2.09 (m, 2 H, $H^{1'}$). **^{13}C NMR (600 MHz, C_6D_6)**: δ [ppm] = 176.8 (C^2), 126.9 (C^4), 122.3 (C^6), 117.7 (C^3), 111.7 (C^1), 96.0 (C^5), 41.7 (C^7), 27.5 (C^8), 19.8 ($C^{8'}$). **HRMS(FAB$^+$):** Anal. for $C_{18}H_{26}{}^{19}FN_3{}^{58}NiO_2$ (m/z) calcd.: 453.0562; found: 453.0572. **Elemental analysis [%]**: calculated for $C_{18}H_{26}FN_3NiO_2$: 47.51, H 5.76, N 9.23 found: C 47.51; H 5.70, N: 9.05.

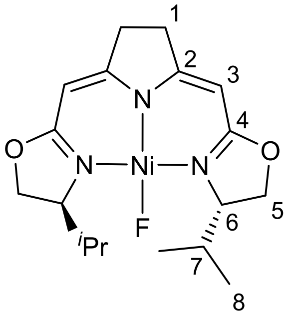
2. (R)-Lig$_{Ph}$(iso)NiF 1a



To a solution of complex Lig$_{Ph}$(iso)NiOH (850 mg, 1.85 mmol) in 20 ml THF, an excess of NH_4F and a drop of water were added and stirred for 20 h. After removal of the solvents, the residue was treated with a toluene/pentane (1/1) mixture and filtrated. After removal of the solvents, the crude was recrystallized from a toluene/pentane mixture to give the product in 68% yield (588 mg). **^{1}H NMR (600 MHz, C_6D_6)**: δ [ppm] = 7.46 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H, H^8), 7.21 (dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.0 Hz, 4 H, H^9), 7.07 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, H^{10}), 4.92 (m, 2 H, H^6), 4.81 (s, 2 H, H^3), 3.79-3.62(m, 4 H, $H^{5,5'}$), 1.86 (m, 4 H, H^1). **^{13}C NMR (600 MHz, C_6D_6)**: δ [ppm] = 170.2 (C^2), 164.1 (C^4), 145.1 (C^7), 128.7 (C^9), 127.4 (C^{10}), 126.7 (C^8), 81.5 (C^3), 75.0 (C^5), 63.0 (C^6), 30.0 (C^1). **^{19}F NMR**

(400 MHz, C_6D_6): δ [ppm] = −444.0 (s). **HRMS(FAB$^+$):** Anal. for $C_{24}H_{22}{}^{19}FN_3{}^{58}NiO_2$ (m/z) calcd.: 463.1050, found: 463.1049. **Elemental analysis [%]**: calculated for $C_{24}H_{22}FN_3NiO_2$ H_2O: C 60.03, H 5.04, N 8.75 found: C 60.59, H 5.21, N 8.34.

3. (S)-Lig$_{iPr}$(iso)NiF 1b



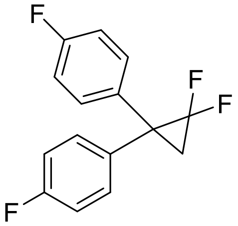
To a solution of Lig$_{iPr}$(iso)NiBr (1.175 g, 2.58 mmol) in 30 ml THF and a catalytic amount of water, CsF (430 mg, 1.1 eq.) was added and the suspension was stirred over night at room temperature. The solvent was removed, the product extracted with toluene and filtered over celite®. After evaporation of the solvent, the crude was recrystallized from a dichloromethane/pentane mixture to give the product as red crystalline solid in 90% yield (915 mg). **^{1}H NMR (600 MHz, C_6D_6)**: δ [ppm] = 4.77 (s, 2 H, H^3), 4.13 (ddd, $^3J_{H,H}$ = 3.2 Hz, $^3J_{H,H}$ = 3.1 Hz, $^3J_{H,H}$ = 9.0 Hz, 2 H, H^6), 3.80 (dd, $^3J_{H,H}$ = 3.3 Hz, $^2J_{H,H}$ = 8.6 Hz, 2 H, H^5), 3.65 (dd, $^2J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 8.8 Hz, 2 H, H$^{5'}$), 2.86 (sd, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 2.9 Hz, 2 H, H^7), 1.85-1.75 (m, 4 H, H^1), 0.89 (d, $^3J_{H,H}$ = 7.1 Hz, 6 H, H^8), 0.73 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, H$^{8'}$). **^{13}C NMR (600 MHz, C_6D_6)**: δ [ppm] = 169.5 (C^4), 163.2 (C^2), 81.3 (C^3), 67.6 (C^5), 64.9 (d, $^3J_{C,F}$ = 7.4 Hz, C^6), 31.6 (C^7), 29.8 (C^1), 19.3 (C$^{8'}$), 14.6 (C^8). **^{19}F NMR (400 MHz, C_6D_6)**: δ [ppm] = −452.1 (s). **HRMS(FAB$^+$):** Anal. for $C_{18}H_{26}{}^{19}FN_3{}^{58}NiO_2$ (m/z) calcd.: 393.1363; found: 393.1357. **Elemental analysis [%]**: calculated for $C_{18}H_{26}FN_3NiO_2$: 54.86, H 6.65, N 10.66 found: 54.54; H 6.66, N: 10.26.

II. b) General Procedure for the Synthesis of gem-Difluorinated Cyclopropanes

The gem-Difluorocyclopropanes **4a, 7a, 8a, 9a, 10a** were synthesized according to literature procedures.[3-4]

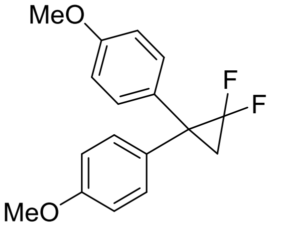
To a suspension of anhydrous NaI (0.2 eq) in THF the corresponding alkene (1 eq) and $TMSCF_3$ were added in that order under inert atmosphere. The mixture was heated to 65 °C for a period of 16 hours. The reaction mixture was evaporated to dryness under reduced pressure. The crude was purified on a silica gel column to obtain the pure *gem*-difluorocyclopropane product.

1. 4,4'-(2,2-Difluorocyclopropane-1,1-diyl)bis(fluorobenzene) 5a



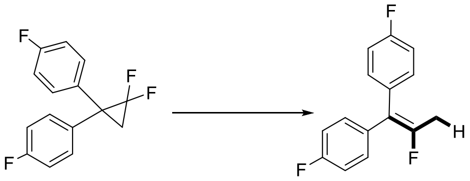
The crude was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 95:5, R_f = 0.25) to give the product as a colorless solid in 47% (2.5 g) yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ [ppm] = 7.34 (dd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,F}$ = 5.3 Hz, 4 H), 7.01 (dd, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,F}$ = 8.7 Hz, 4H), 2.04 (t, $^3J_{H,F}$ = 8.5 Hz, 2H). **^{13}C NMR (600 MHz, $CDCl_3$)**: δ [ppm] = 162.0 (d, $^1J_{C,F}$ = 246.9 Hz), 134.3, 130.4 (d, $^2J_{C,F}$ = 8.3 Hz), 115.7 (d, $^2J_{C,F}$ = 21.6 Hz), 112.6 (t, $^1J_{C,F}$ = 288.2 Hz), 38.6 (t, $^2J_{C,F}$ = 10.5 Hz), 23.9 (t, $^2J_{C,F}$ = 10.0 Hz). **^{19}F NMR (400 MHz, $CDCl_3$)**: δ [ppm] = −114.6 (tt, $J_{F,H}$ = 8.6 Hz, 5.3 Hz, 2 F), −130.2 (t, $^3J_{F,H}$ = 8.5 Hz, 2 F).), **HRMS(EI$^+$):** Anal. for $C_{15}H_{10}F_4$ (m/z) calcd.: 266.0719, found: 266.0711

2. 4,4'-(2,2-Difluorocyclopropane-1,1-diyl)bis(methoxybenzene) 6a



The crude was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 95:5, R_f = 0.3) to give the product as a colorless solid in 80% (1.5 g) yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ [ppm] = 7.30 (d, $^3J_{H,H}$ = 8.9 Hz, 4H), 6.84 (d, $^3J_{H,H}$ = 8.9 Hz, 4H), 3.77 (s, 6H), 2.00 (t, $^3J_{H,F}$ = 8.5 Hz, 2H). **^{13}C NMR (400 MHz, $CDCl_3$)**: δ [ppm] = 158.8, 131.3, 129.9, 114.1, 113.4 (t, $^1J_{C,F}$ = 288.2 Hz), 55.4, 38.8 (t, $^2J_{C,F}$ = 10.6 Hz), 23.92 (t, $^2J_{C,F}$ = 9.7 Hz). **^{19}F NMR (400 MHz, $CDCl_3$)**: δ [ppm] = −130.2 (t, $^3J_{F,H}$ = 8.5 Hz). **HRMS(EI$^+$):** Anal. for $C_{17}H_{16}F_2O_2$ (m/z) calcd.: 290.1118, found: 290.1091.

III. Catalytic Hydrodefluoration of gem-Difluorocyclopropanes



5a

5b

Entry	Catalyst	Solvent	Temperature	Hydride source	Time	Yield[a]
1	none	THF/Tol/$CHCl_3$	100 °C	Me_2NHBH_3	48 h	-
2	none	neat	70 °C	Me_2NHBH_3	48 h	-
3	none	THF/Tol/$CHCl_3$	100 °C	$PhSiH_3$/Ph_2SiH_2	48 h	-
4	(dme)$NiCl_2$	THF/Tol/$CHCl_3$	100 °C	Me_2NHBH_3	48 h	-
5	1a (10 mol%)	THF	50 °C	2 eq Me_2NHBH_3	72 h	<1 %
6	1a (10 mol%)	THF	60 °C	2 eq Me_2NHBH_3	72 h	> 95%
7	1a (10 mol%)	THF	60 °C	$LiEt_3BH$	16 h	decomposition
8	1a (10 mol%)	Tol	80 °C	2 eq Me_2NHBH_3	16 h	99%
9	1a (2.5 mol%)	Tol	80 °C	2 eq Me_2NHBH	16 h	99%
10	1a (10 mol%)	Tol	80 °C	$PhSiH_3$	16 h	>95%
11	1a (5mol%)	Tol	80 °C	Ph_2SiH_2	16 h	>95%

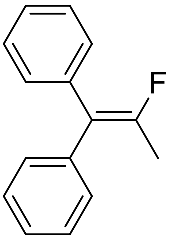
[a] determined by ^{19}F-NMR before work-up using 1,4-bis(trifluoromethyl)benzene as internal standard.

General Procedure for the Activation of gem-Difluorinated Cyclopropanes

A Young NMR tube was charged with the catalyst (**(R)-Lig$_{Ph}$(iso)NiF 1a** or **(S)-Lig$_{iPr}$(iso)NiF 1b,** 2.5 mol%), the geminal-difluorocyclopropane (0.4 mmol), Me_2NHBH_3 (0.8 mmol, 2 eq.) and 1,4-bis(trifluoromethyl)benzene as internal standard in 0.5 ml toluene-d_8. The reaction mixture was heated to 80 °C for 16 h. The NMR-yield and the diastereomeric ratio were determined directly from ^{19}F NMR spectrum of the reaction mixture after the reaction. The crude products were purified by column chromatography and the isolated yields were determined for each reaction.

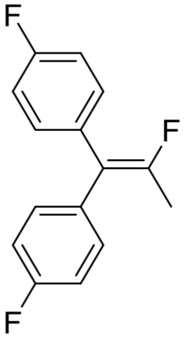
Analytical Data of Fluoroalkenes 4b-11b

1. (2-Fluoroprop-1-ene-1,1-diyl)dibenzene 4b



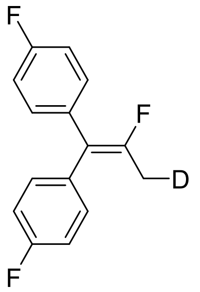
The crude was purified by flash column chromatography on silica gel (petroleum ether, $R_f = 0.1$) to give the product as a colourless solid in 89% yield (NMR yield: 95%). **^{1}H NMR (CD_2Cl_2, 600 MHz):** δ [ppm] = 7.37-7.19 (m, 10 H), 2.03 (d, $^3J_{H,F}$ = 17.8 Hz, 3 H). **^{13}C NMR (CD_2Cl_2, 600 MHz):** δ [ppm] = 155.4 (d, $^1J_{C,F}$ = 256.8 Hz), 139.6 (d, $^3J_{C,F}$ = 8.2 Hz), 138.2, 130.6 (d, $^4J_{C,F}$ = 3.1 Hz), 129.9 (d, $^4J_{C,F}$ = 4.5 Hz), 128.7, 128.3, 127.5, 127.7, 120.7 (d, $^2J_{C,F}$ = 15.3 Hz), 17.1 (d, $^2J_{C,F}$ = 30.0 Hz). **^{19}F NMR (400 MHz, CD_2Cl_2)**: δ [ppm] = −97.3 (q, $^3J_{F,H}$ = 17.8 Hz). **HRMS(EI$^+$):** Anal. for $C_{15}H_{13}F$ (m/z) calcd.: 212.1001, found: 212.1012.

2. 4,4'-(2-Fluoroprop-1-ene-1,1-diyl)bis(fluorobenzene) 5b



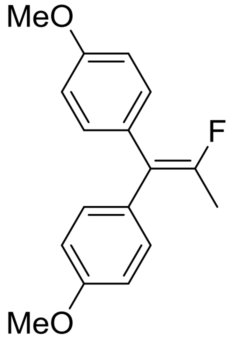
The crude was purified by flash column chromatography on silica gel (petroleum ether/ethylacetate 50:1, $R_f = 0.1$) to give the product as a colorless solid in 86% yield (NMR yield: 99%). **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ [ppm] = 7.29-7.24 (m, 2 H), 7.21-7.18 (m, 2 H), 7.11-7.07 (m, 2 H),7.04-7.00 (m, 2 H), 2.08 (d, $^3J_{H,F}$ = 17.9 Hz, 3 H), **^{13}C NMR ($CDCl_3$, 600 MHz):** δ [ppm] = 162.1 (d, $^1J_{C,F}$ = 246.8 Hz), 161.7 (dd, $^1J_{C,F}$ = 246.8 Hz, $^6J_{C,F}$ = 1.4 Hz), 155.2 (d, $^1J_{C,F}$ = 258.0 Hz), 135.0 (dd, $^3J_{C,F}$ = 8.3 Hz, $^4J_{C,F}$ = 3.6 Hz), 133.5 (d, $^4J_{C,F}$ = 3.6 Hz), 132.0 (dd, $^3J_{C,F}$ = 7.7 Hz, $^4J_{C,F}$ = 3.3 Hz), 131.3 (dd, $^3J_{C,F}$ = 7.7 Hz, $^4J_{C,F}$ = 5.0 Hz), 118.7 (d, $^2J_{C,F}$ = 15.4 Hz), 115.6 (d, $^2J_{C,F}$ = 21.5 Hz), 115.0 (d, $^2J_{C,F}$ = 21.5 Hz), 17.1 (d, $^2J_{C,F}$ = 30.0 Hz) **^{19}F NMR (400 MHz, $CDCl_3$)**: δ [ppm] = −96.3 (q, $^3J_{F,H}$ = 17.9 Hz, 1 F), −114.7 (tt, $J_{F,H}$ = 8.6 Hz, 5.3 Hz, 1 F), −115.1 (tt, $J_{F,H}$ = 8.6 Hz, 5.3 Hz, 1 F). **HRMS(EI$^+$):** Anal. for $C_{15}H_{11}F$ (m/z) calcd.: 248.0846, found: 248.0827.

3. 4,4'-(2-fluoroprop-1-ene-1,1-diyl-3-d)bis(fluorobenzene) 5b*



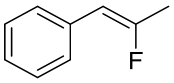
^{1}H NMR (CDCl$_3$, 600 MHz): δ [ppm] = 7.21-7.19 (m, 2 H), 7.15-7.13 (m, 2 H), 7.05-7.07 (m, 2 H), 6.99-9.96 (m, 2 H), 2.09 (dt, $^{3}J_{H,F}$ = 17.6 Hz, $^{2}J_{H,D}$ = 2.2 Hz 2 H), **^{2}H NMR (CHCl$_3$, 600 MHz)**: δ [ppm] = 2.05 (bs, 1H)), **^{13}C NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 162.1 (d, $^{1}J_{C,F}$ = 246.8 Hz), 161.7 (dd, $^{1}J_{C,F}$ = 246.8 Hz, $^{6}J_{C,F}$ = 1.4 Hz), 155.2 (d, $^{1}J_{C,F}$ = 257.7 Hz), 135.0 (dd, $^{3}J_{C,F}$ = 8.3 Hz, $^{4}J_{C,F}$ = 3.3 Hz), 133.5 (d, $^{4}J_{C,F}$ = 3.6 Hz), 132.0 (dd, $^{3}J_{C,F}$ = 8.0 Hz, $^{4}J_{C,F}$ = 3.0 Hz), 131.3 (dd, $^{3}J_{C,F}$ = 8.0 Hz, $^{4}J_{C,F}$ = 5.0 Hz), 118.7 (d, $^{2}J_{C,F}$ = 15.4 Hz), 115.6 (d, $^{2}J_{C,F}$ = 21.5 Hz), 115.0 (d, $^{2}J_{C,F}$ = 21.5 Hz), 17.1 (dt, $^{2}J_{C,F}$ = 30.0 Hz, $^{1}J_{C,D}$ =20 Hz); **^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −96.5 (t, $^{3}J_{F,H}$ = 17.4 Hz, 1 F), −114.7 (tt, $J_{F,H}$ = 8.7 Hz, 5.5 Hz, 1 F), −115.1 (tt, $J_{F,H}$ = 8.7 Hz, 5.5 Hz, 1 F). **HRMS(EI^{+}):** Anal. for $C_{15}H_{11}F$ (m/z) calcd.: 249.0876, found: 249.0878.

4. 4,4'-(2-Fluoroprop-1-ene-1,1-diyl)bis(methoxybenzene) 6b



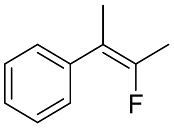
The crude was purified by flash column chromatography on silica gel (petroleum ether/ethylacetate 50:1, R_f = 0.1) to give the product as a colourless solid in 92% yield (NMR yield: 98%). **^{1}H NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 7.21 (d, $^{3}J_{H,H}$ = 8.3 Hz, 2 H), 7.12 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2 H), 6.89 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H), 6.84 (d, $^{3}J_{H,H}$ = 7.9 Hz, 2 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 2.04 (d, $^{3}J_{H,F}$ = 17.8 Hz, 3 H). **^{13}C NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 158.7, 158.3, 154.1 (d, $^{1}J_{C,F}$ = 255.8 Hz), 131.5 (d, $^{4}J_{C,F}$ = 3.0 Hz), 131.8 (d, $^{3}J_{H,F}$ =8.4 Hz), 130.8 (d, $^{4}J_{C,F}$ = 4.9 Hz), 130.5, 113.8, 113.8, 119.3 (d, $^{2}J_{C,F}$ = 15.0 Hz), 55.4, 55.3, 17.2 (d, $^{2}J_{C,F}$ = 30.3 Hz). **^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −98.4 (q, $^{3}J_{F,H}$ = 17.8 Hz). **HRMS(EI^{+}):** Anal. for $C_{17}H_{17}F$ (m/z) calcd.: 272.1213, found: 272.1198.

5. (Z)-(2-Fluoroprop-1-en-1-yl)benzene 7b



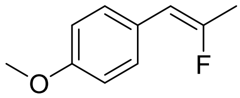
The crude was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 200:1, $R_f = 0.3$) to give the product as a colourless oil in 67% yield (NMR yield (E+Z): 90%). Diastereomeric ratio (Z:E): 9:1. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ [ppm] = 7.47 (d, $^3J_{H,H} = 7.3$ Hz, 2 H), 7.33 (t, $^3J_{H,H} = 7.8$ Hz, 2 H), 7.21 (t, $^3J_{H,H} = 7.4$ Hz, 1 H), 5.48 (d, $^3J_{H,F} = 38.9$ Hz, 1 H), 2.09 (dd, $^3J_{H,F} = 16.7$ Hz, $^4J_{H,H} = 0.7$ Hz, 3 H). **^{13}C NMR (600 MHz, CDCl$_3$)**: δ [ppm] = 157.9 (d, $^1J_{C,F} = 263.8$ Hz), 134.0 (d, $^3J_{C,F} = 2.5$ Hz), 128.5, 128.3 (d, $^4J_{C,F} = 7.4$ Hz), 126.7 (d, $^6J_{C,F} = 2.8$ Hz), 106.4 (d, $^2J_{C,F} = 8.5$ Hz), 19.2 (d, $^2J_{C,F} = 29.1$ Hz). **^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −94.5 (dq, $^3J_{F,H} = 38.8$ Hz, 16.6 Hz). **HRMS(EI$^+$):** Anal. for C_9H_9F (m/z) calcd.: 136.0688, found: 136.0688.

6. (Z)-(3-Fluorobut-2-en-2-yl)benzene 8b



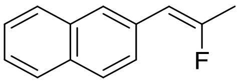
The crude was purified by flash column chromatography on silica gel (petroleum ether, $R_f = 0.3$) to give the product as a colourless oil in 65% yield (NMR yield (Z+E): 74%). Diastereomeric ratio (Z:E): 7:3. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ [ppm] = 7.42-7.36 (m, 4 H), 7.30-7.25 (m, 1 H), 2.13 (dd, $^3J_{H,F} = 17.6$ Hz, $^4J_{H,H} = 0.8$ Hz, 3 H), 2.01-2.00 (m, 3 H). **^{13}C NMR (400 MHz, CDCl$_3$)**: δ [ppm] = 152.3 (d, $^1J_{C,F} = 248.8$ Hz), 138.7 (d, $^3J_{C,F} = 1.3$ Hz), 128.2 ($^5J_{C,F} = 4.3$ Hz), 128.1, 126.6, 111.9 (d, $^2J_{C,F} = 13.7$ Hz), 17.6 (d, $^3J_{C,F} = 5.0$ Hz), 15.7 (d, $^2J_{C,F} = 31.1$ Hz). **^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −98.8 (qq, $^2J_{F,H} = 17.6$ Hz, 2.9 Hz). The absolute configuration was determined by NOESY experiments. **HRMS(EI$^+$):** Anal. for $C_{10}H_{11}F$ (m/z) calcd.: 150.0845, found: 150.0858.

7. (Z)-1-(2-fluoroprop-1-en-1-yl)-4-methoxybenzene 9b



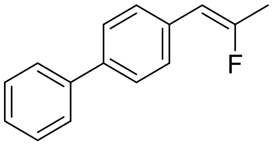
The crude was purified by flash column chromatography on silica gel (petroleum ether/ethylacetate 200:1, $R_f = 0.3$) to give the product as a colourless oil in 61% yield (NMR yield (Z+E): 78%). Diastereomeric ratio (Z:E): 19:1. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ [ppm] = 7.40 (dm, $^3J_{H,H} = 8.9$ Hz, 2 H), 6.86 (dm, 2 H, $^3J_{H,H} = 8.9$ Hz, 2 H), 5.41 (d, $^3J_{H,F} = 39.2$ Hz, 1 H), 3.81 (s, 3 H), 2.06 (d, $^3J_{H,F} = 16.7$ Hz, 3 H). **^{13}C NMR (CDCl$_3$, 400 MHz):** δ [ppm] = 158.3 (d, $^6J_{C,F} = 2.9$ Hz), 156.5 (d, $^1J_{C,F} = 260.8$ Hz), 129.5 (d, $^5J_{C,F} = 7.5$ Hz), 126.8 (d, $^3J_{C,F} = 2.5$ Hz), 113.9, 105.8 (d, $^2J_{C,F} = 9.1$ Hz), 55.4, 19.1 (d, $^2J_{C,F} = 29.4$ Hz).**^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −97.4 (dq, $^3J_{H,F} = 39.2$ Hz, 16.8 Hz), **HRMS(EI$^+$):** Anal. for $C_{10}H_{11}F$ (m/z) calcd.: 166.0794, found: 166.0812.

8. (Z)-2-(2-Fluoroprop-1-en-1-yl)naphthalene 10b



The crude was purified by flash column chromatography on silica gel (petroleum ether, R_f = 0.1) to give the product as a colourless solid in 89% yield (NMR yield (Z+E): 96%). Diastereomeric ratio (Z:E): 9:1.**^{1}H NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 7.87 (s, 1 H), 7.82-7.77 (m, 3 H), 7.64-7.63 (m, 1 H), 7.41-7.47 (m, 2 H), 5.63 (d, $^{3}J_{F,H}$ = 38.5 Hz, 1 H), 2.14 (d, $^{3}J_{F,H}$ = 16.8 Hz, 3 H). **^{13}C NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 158.3 (d, $^{1}J_{C,F}$ = 264.4 Hz), 133.6, 132.3 (d, $J_{C,F}$ = 1.6 Hz), 131.60 (d, $J_{C,F}$ = 2.8 Hz), 128.1, 128.0, 127.6, 126.9 (d, $J_{C,F}$ = 7.4 Hz), 126.6 (d, $J_{C,F}$ = 7.7 Hz), 126.1, 125.8, 106.6 (d, $^{2}J_{C,F}$ = 8.5 Hz) 19.36 (d, $^{2}J_{C,F}$ = 29.1 Hz).**^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −93.9 (dq, $^{3}J_{F,H}$ = 38.2 Hz, 16.8 Hz), **HRMS(EI^{+}):** Anal. for $C_{13}H_{11}F$ (m/z) calcd.: 186.0845, found: 186.0860.

9. (Z)-4-(2-Fluoroprop-1-en-1-yl)-1,1'-biphenyl 11b



The crude was purified by flash column chromatography on silica gel (petroleum ether, R_f = 0.1) to give the product as a colourless solid in 81% yield (NMR yield (Z+E): 99%). Diastereomeric ratio (Z:E): 9:1. **^{1}H NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 7.62-7.28 (m, 9 H), 5.52 (d, $^{3}J_{H,F}$ = 38.9 Hz, 1 H), 2.11 (dd, $^{3}J_{H,F}$ = 16.8 Hz, 3 H). **^{13}C NMR (CDCl$_3$, 600 MHz):** δ [ppm] = 158.2 (d, $^{1}J_{C,F}$ = 264.4 Hz), 140.9, 139.4 (d, $J_{C,F}$ = 2.3 Hz), 133.1 (d, $J_{C,F}$ = 2.6 Hz), 128.95, 128.90, 128.7 (d, $J_{C,F}$ = 7.4 Hz), 127.5, 127.4, 127.3, 127.2, 127.1, 127.1, 106.1 (d, $^{2}J_{C,F}$ = 9.6 Hz), 19.3 (d, $^{2}J_{C,F}$ = 29.2 Hz). **^{19}F NMR (400 MHz, CDCl$_3$)**: δ [ppm] = −93.7 (dq, $^{3}J_{F,H}$ = 39.2 Hz, 16.7 Hz), **HRMS(EI^{+}):** Anal. for $C_{15}H_{131}F$ (M^{+}) calcd.: 212.1001, found: 212.1007.

Stoichiometric reactions

A Young NMR tube was charged with (R)Lig$_{Ph}$(iso)Ni(I) **3a** (30 mg, 0.067 mmol, 2 eq.), 4,4'-(2,2-Difluorocyclopropane-1,1-diyl)bis(fluorobenzene) (9 mg, 0.033 mmol, 1 eq) and 1,4-bis(trifluoromethyl) benzene as internal standard in 0.5 ml toluene-d$_8$. The reaction mixture was heated to 80 °C for 3 h. The NMR spectrum showed clean conversion to one compound which was identified by comparison of NMR and GC-MS spectra as 4,4'-(propa-1,2-diene-1,1-diyl)bis(fluorobenzene).[5]

A Young NMR tube was charged with preformed (R)Lig$_{Ph}$(iso)NiH **2a** (25 mg, 0.054 mmol, 1.6 eq) and ,4'-(2,2-Difluorocyclopropane-1,1-diyl)bis(fluorobenzene) (9 mg, 0.034 mmol, 1 eq) and 1,4-bis(trifluoromethyl) benzene as internal standard in 0.5 ml toluene-d$_8$. The reaction mixture was heated to 80 °C for 12 h. The NMR spectrum showed clean conversion to one compound which was identified by comparison of NMR and GC-MS spectra as 4,4'-(2-Fluoroprop-1-ene-1,1-diyl)bis(fluorobenzene).

A Young NMR tube was charged with preformed (R)Lig$_{Ph}$(iso)NiD **2a*** (18 mg, 0.040 mmol, 1.6 eq and ,4'-(2,2-Difluorocyclopropane-1,1-diyl)bis(fluorobenzene) (6.7 mg, 0.025 mmol, 1 eq). The reaction mixture was heated to 80 °C for 12 h. The NMR spectrum showed clean conversion to one compound. The crude was purified by flash column chromatography on silica gel (petroleum ether/ethylacetate 50:1, $R_f = 0.1$) to give the 4,4'-(2-fluoroprop-1-ene-1,1-diyl-3-d)bis(fluorobenzene) as a colorless solid (NMR yield: 95%).

A Young NMR tube was charged with (R)Lig$_{Ph}$(iso)Ni(I) **3a** (26 mg, 0.058 mmol, 10 eq.), perfluorodecahydronaphthalene (2.7 mg, 0.0058 mmol) 0.5 ml tetrahydrofurane-d$_8$. After 3 days at roomtemperature the ^{19}F NMR spectrum showed clean conversion to one compound which was identified by comparison of NMR and GC-MS spectra as perfluoronaphthalene. The solvent was removed in vacuo, the residue was washed with pentane to give **1a** (25 mg, 0.054°mmol, 94 %).

IV. Crystallographic Data

X-ray Crystal Structure Determinations

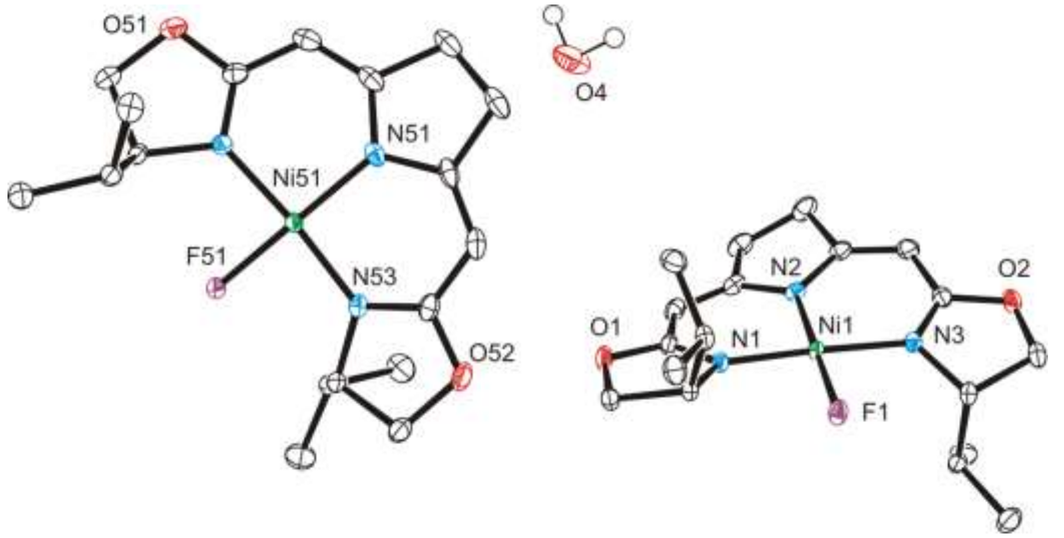
Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Cu-K_α radiation, microfocus X-ray tube, multilayer mirror optics; 1,1-diphenyl-2-fluoro-prop-1-ene) or a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, sealed X-ray tube, graphite monochromator; all other compounds). Data were corrected for air and detector absorption, Lorentz and polarization effects;[#1,#2] absorption by the crystal was treated numerically (Gaussian grid)[#2,#3] (compound **4b**) or with a semiempirical multiscan method (all other compounds).[#4,#5] The structures were solved by the charge flip procedure[#6] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[#7] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data the positions of most hydrogen atoms (except those of the methyl groups, which were calculated and then treated as variable metric rigid groups) were taken from difference Fourier syntheses and refined. Crystals of **4a** were twinned; after de-twinning[#8] (approx. twin fractions 0.66:0.34) refinement was carried out against all singles and composites of both domains.

CCDC 1427461-1427465 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

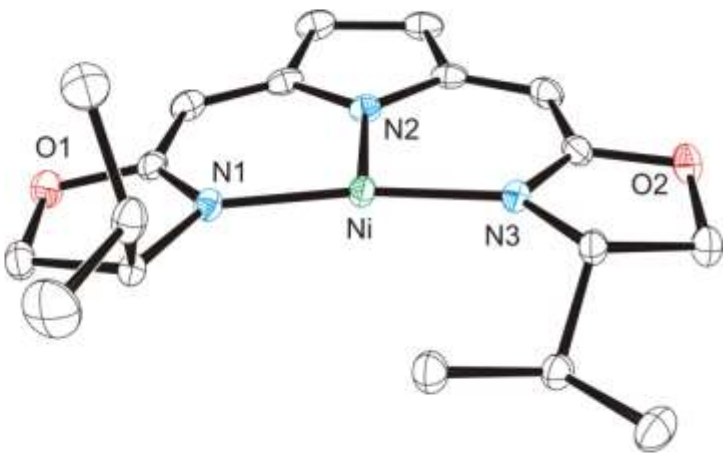
Table S1. Details of the crystal structure determinations of **1b**·0.5 H_2O, **3b**, **4a** and **4b**.

	1b·0.5 H_2O	**3b**	**4a**	**4b**
formula	$C_{21.50}H_{31}FN_3NiO_{2.50}$	$C_{18}H_{26}N_3NiO_2$	$C_{15}H_{12}F_2$	$C_{15}H_{13}F$
M_r	449.20	375.13	230.25	212.25
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P\ 2_1\ 2_1\ 2_1$	$P\ 2_12_12_1$	$C\ 2/c$	$C\ c$
a /Å	10.777(8)	5.790(3)	24.870(15)	7.74284(13)
b /Å	10.970(8)	10.095(5)	5.944(4)	17.2689(2)
c /Å	36.58(3)	29.897(14)	16.266(10)	8.39473(13)
β /°			107.995(7)	91.1751(15)
V /Å^3	4325(5)	1747.5(14)	2287(2)	1122.23(3)
Z	8	4	8	4
F_{000}	1904	796	960	448
d_c /Mg·m^{-3}	1.380	1.426	1.337	1.256
X-radiation, λ /Å	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073	Cu-$K\alpha$, 1.54184
μ /mm^{-1}	0.930	1.125	0.099	0.661
max., min. transmission factors	0.8623, 0.7854	0.8623, 0.7985	0.7464, 0.6511	0.980, 0.937
data collect. temperat. /K	100(1)	100(1)	100(1)	120(1)
θ range /°	1.1 to 32.4	2.1 to 32.6	1.7 to 32.4	5.1 to 70.8
index ranges h,k,l	-16 ... 16, -15 ... 16, -53 ... 53	-8 ... 8, -14 ... 14, -44 ... 45	-36 ... 34, -8 ... 8, -24 ... 24	-9 ... 9, -20 ... 20, -10 ... 10
reflections measured	110129	45811	34259	20879
unique [R_{int}]	14769 [0.0455]	6139 [0.0535]	5453 [0.0470]	2047 [0.0441]
observed [$I \geq 2\sigma(I)$]	13565	5551	4459	2020
Data / restraints / parameters	14769 / 0 / 648	6139 / 0 / 267	5453 / 0 / 191	2047 / 2 / 177
GooF on F^2	1.053	1.035	1.067	1.080
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0297, 0.0640	0.0313, 0.0657	0.0466, 0.1099	0.0255, 0.0654
R indices (all data) $R(F)$, $wR(F^2)$	0.0356, 0.0666	0.0390, 0.0682	0.0639, 0.1185	0.0258, 0.0656
absolute structure parameter	0.011(3)	0.012(5)		-0.06(5)
Difference density: max, min /e·Å^{-3}	0.544, -0.368	0.601, -0.315	0.371, -0.280	0.126, -0.127

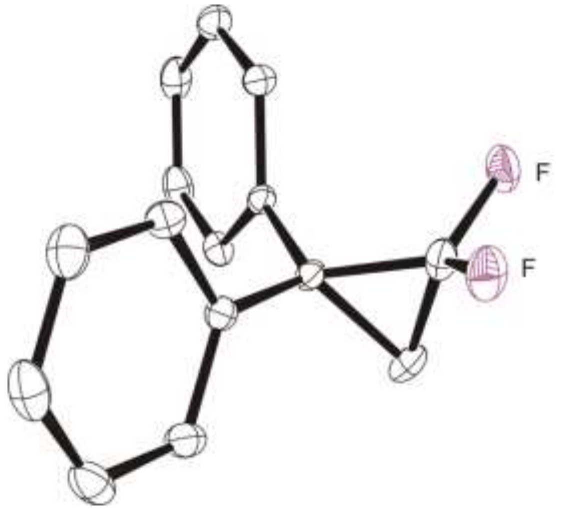
1b 0.5 H_2O



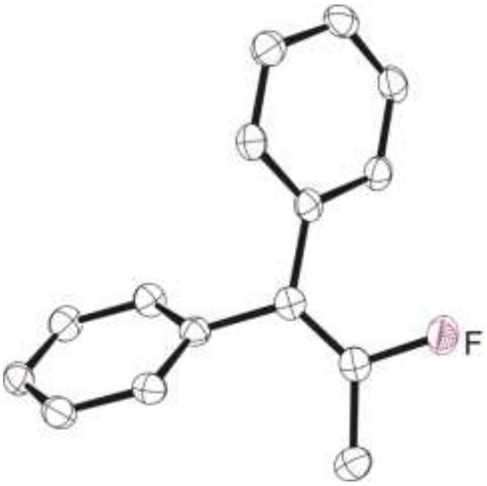
3b



4a



4b



#1 *SAINT*, Bruker AXS GmbH, Karlsruhe, Germany **1997-2013**.

#2 *CrysAlisPro*, Agilent Technologies UK Ltd., Oxford, UK **2011**-**2014**.

#3 W. R. Busing, H. A. Levy, *Acta Cryst.* **1957**, *10*, 180.

#4 (a) G. M. Sheldrick, *SADABS*, Bruker AXS GmbH, Karlsruhe, Germany **2004-2014**; (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3.

#5 R. H. Blessing, *Acta Cryst.* **1995**, *A51*, 33.

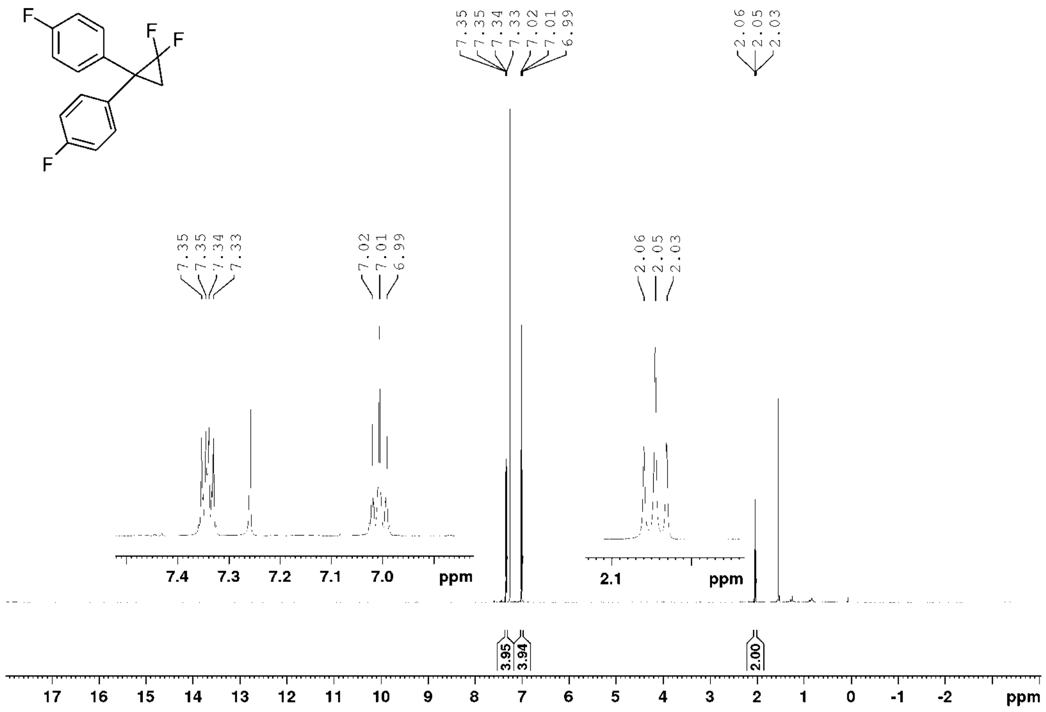
#6 (a) L. Palatinus, *SUPERFLIP*, EPF Lausanne, Switzerland and Fyzikální ústav AV ČR, v. v. i., Prague, Czech Republic, **2007**-**2014**; (b) L. Palatinus, G. Chapuis, *J. Appl. Cryst.* **2007**, 40, 786.

#7 (a) G. M. Sheldrick, *SHELXL-20xx*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany **2012**-**2014**; (b) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112; (c) G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

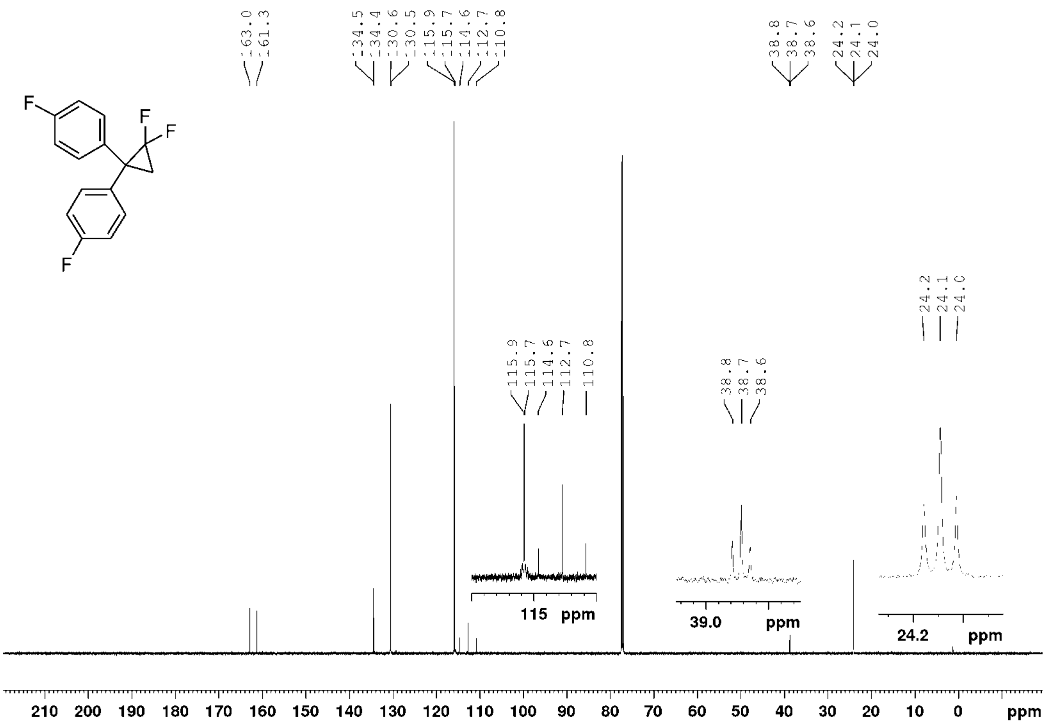
#8 G. M. Sheldrick, *TWINABS*, Bruker AXS GmbH, Karlsruhe, Germany **2004-2012**.

VI. NMR Spectra of new compounds (^{1}H NMR, ^{13}C NMR, ^{19}F {^{1}H}, ^{19}F NMR)

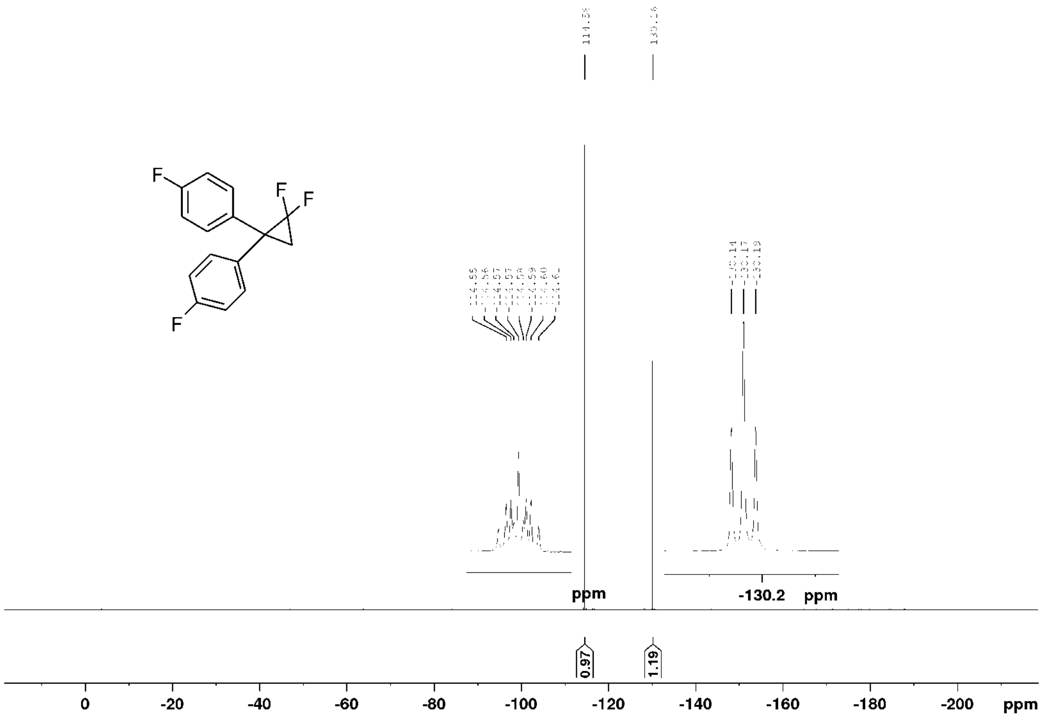
^{1}H NMR spectrum of **5a** (CDCl$_3$)



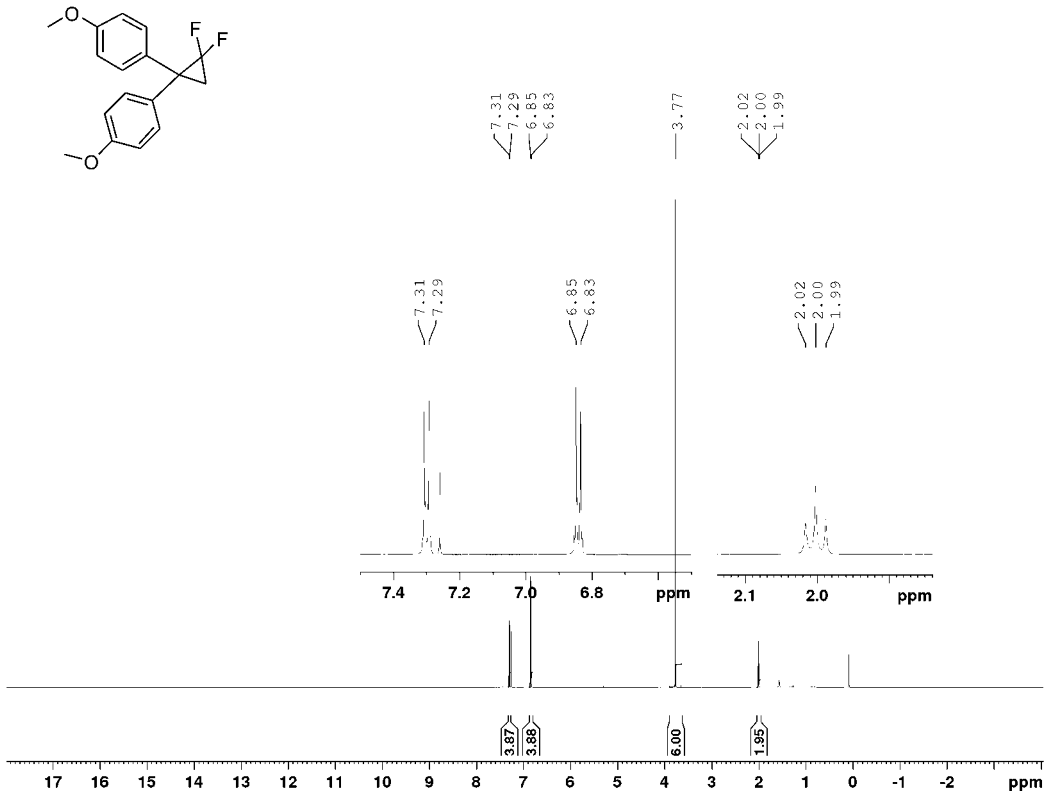
^{13}C NMR spectrum of **5a** (CDCl$_3$)



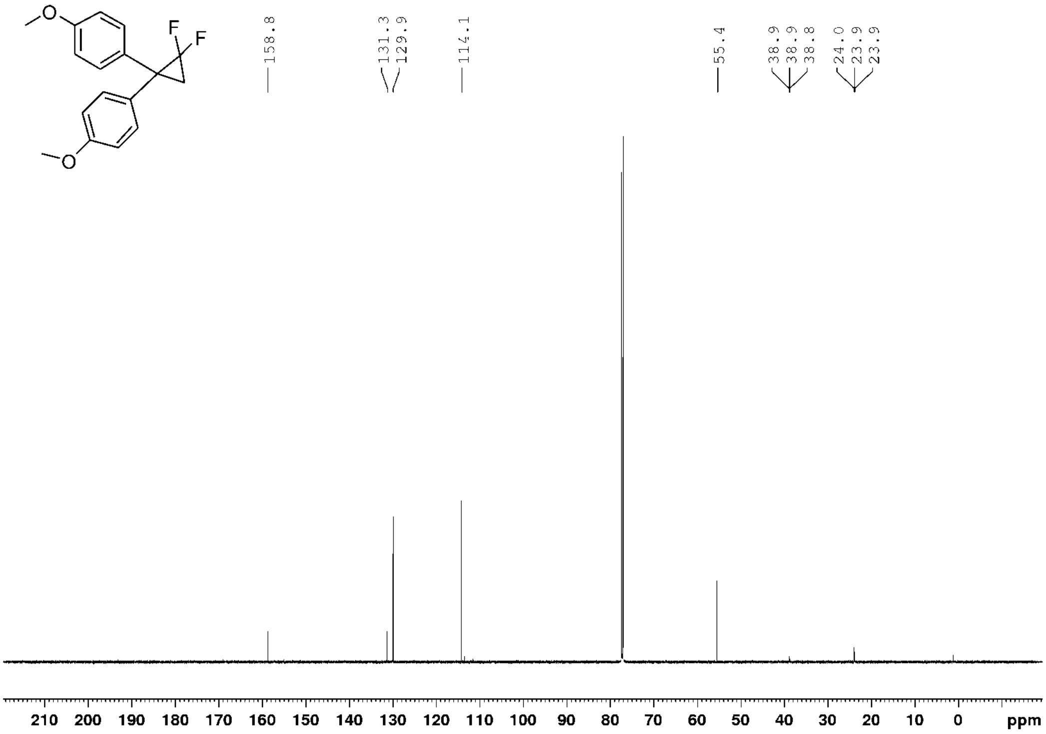
^{19}F NMR spectrum of **5a** ($CDCl_3$)



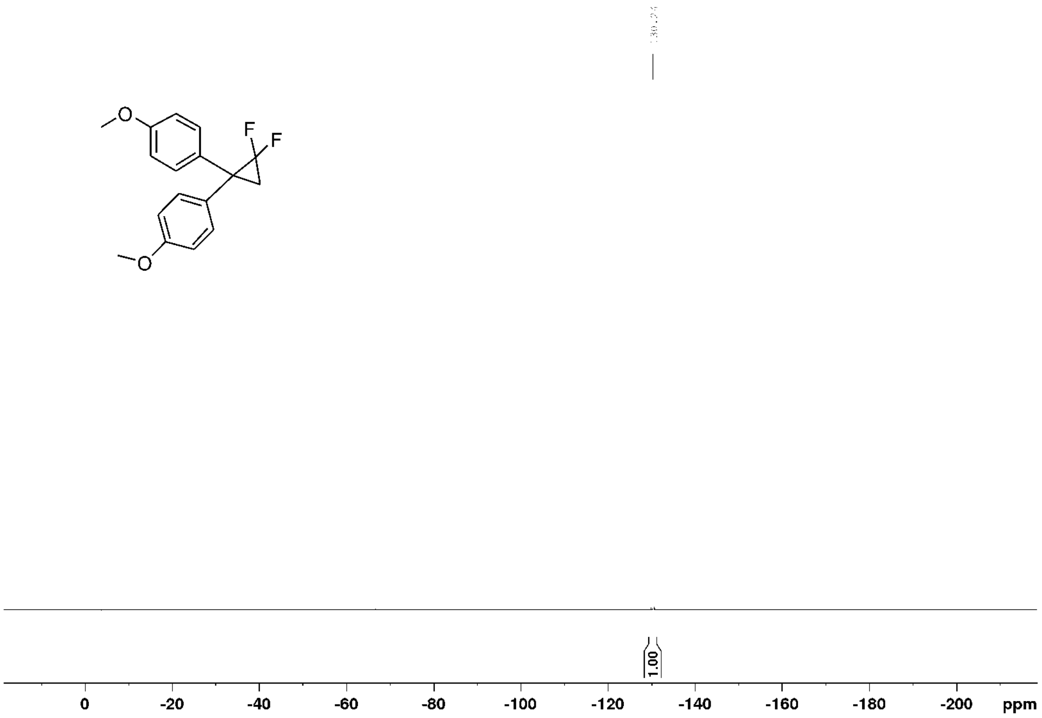
^{1}H NMR spectrum of **6a** ($CDCl_3$)



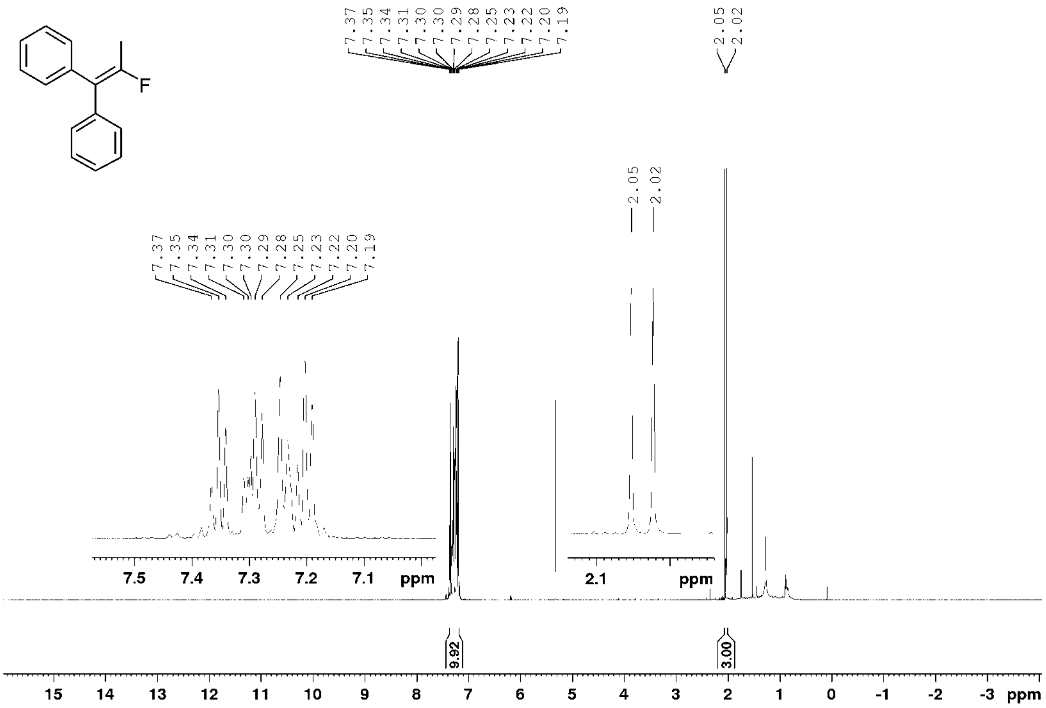
^{13}C NMR spectrum of **6a** ($CDCl_3$)



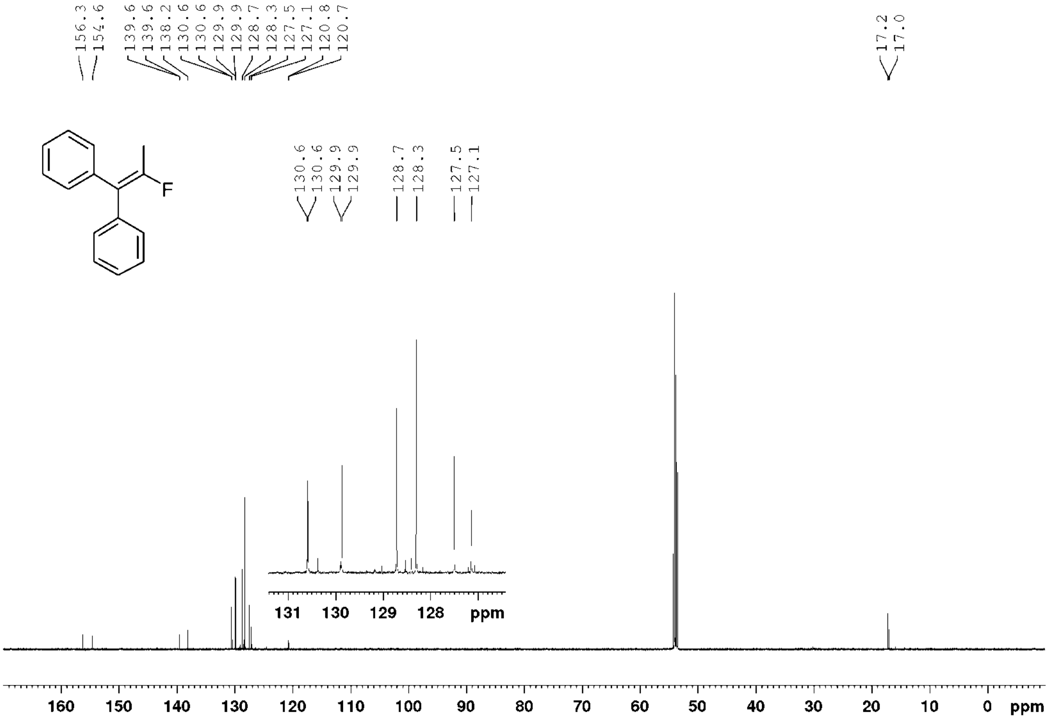
^{19}F NMR spectrum of **6a** ($CDCl_3$)



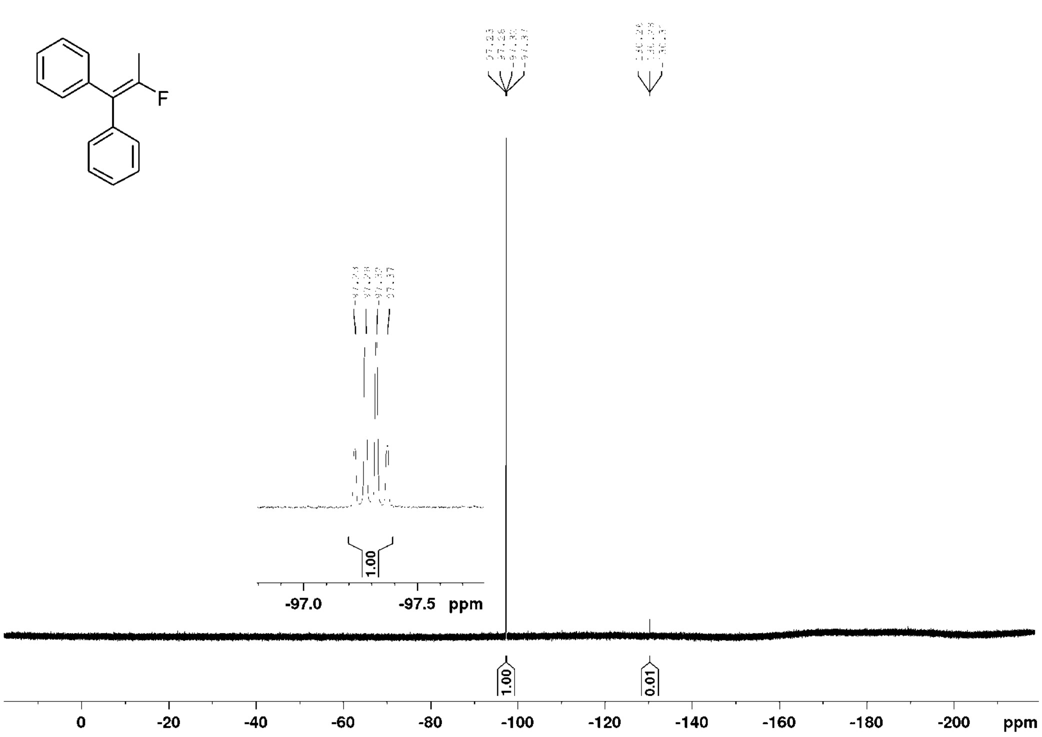
^{1}H NMR spectrum of **4b** (CD$_2$Cl$_2$)



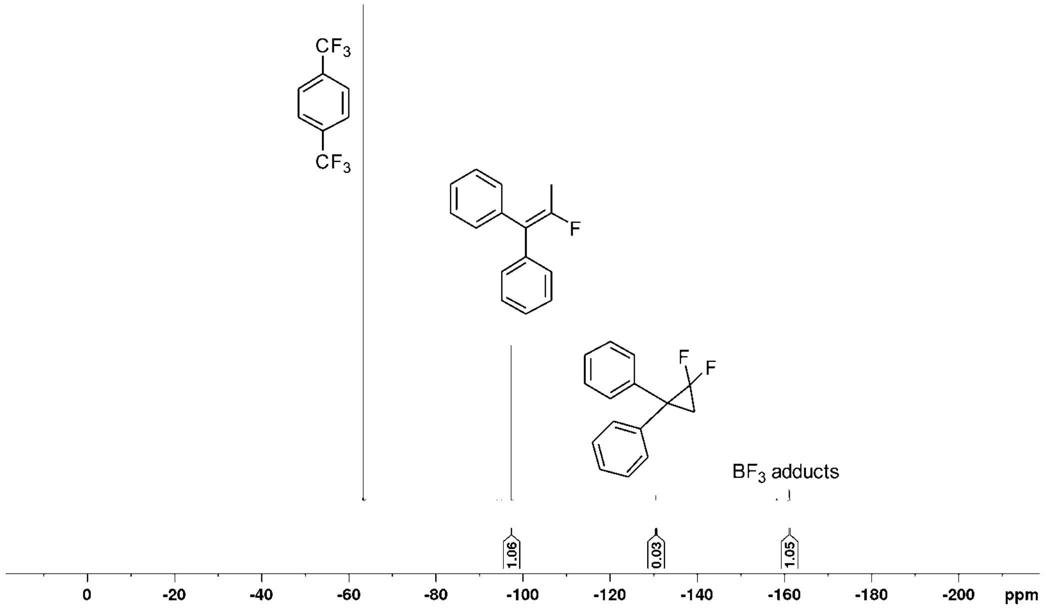
^{13}C NMR spectrum of **4b** (CD$_2$Cl$_2$)



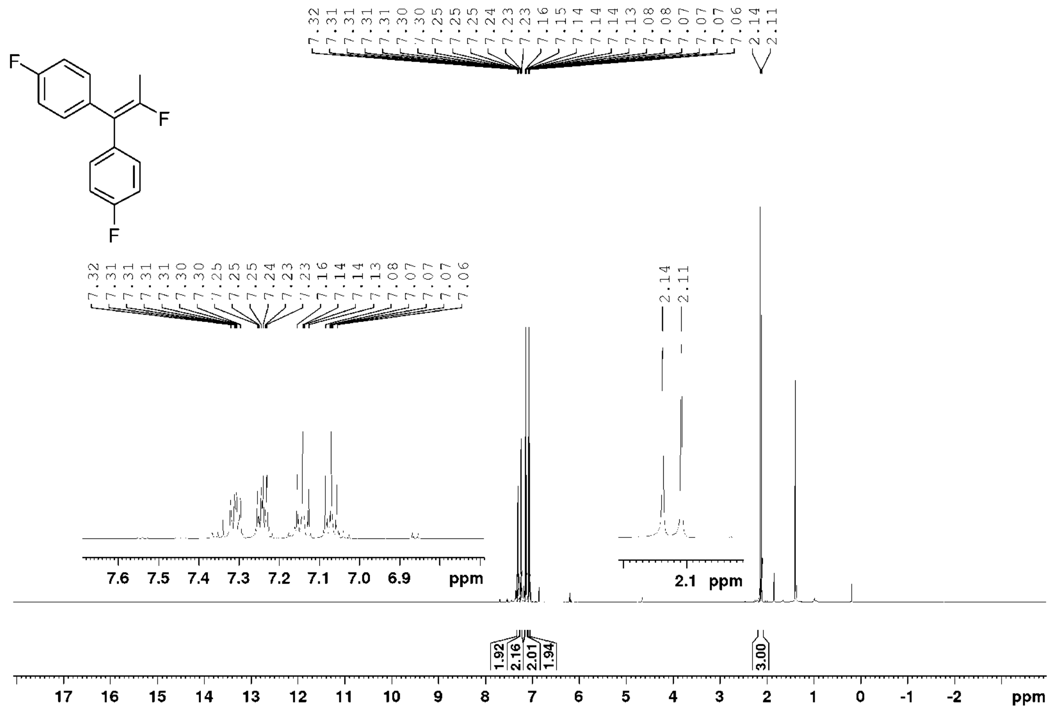
^{19}F NMR spectrum of **4b** after purification (CD_2Cl_2)



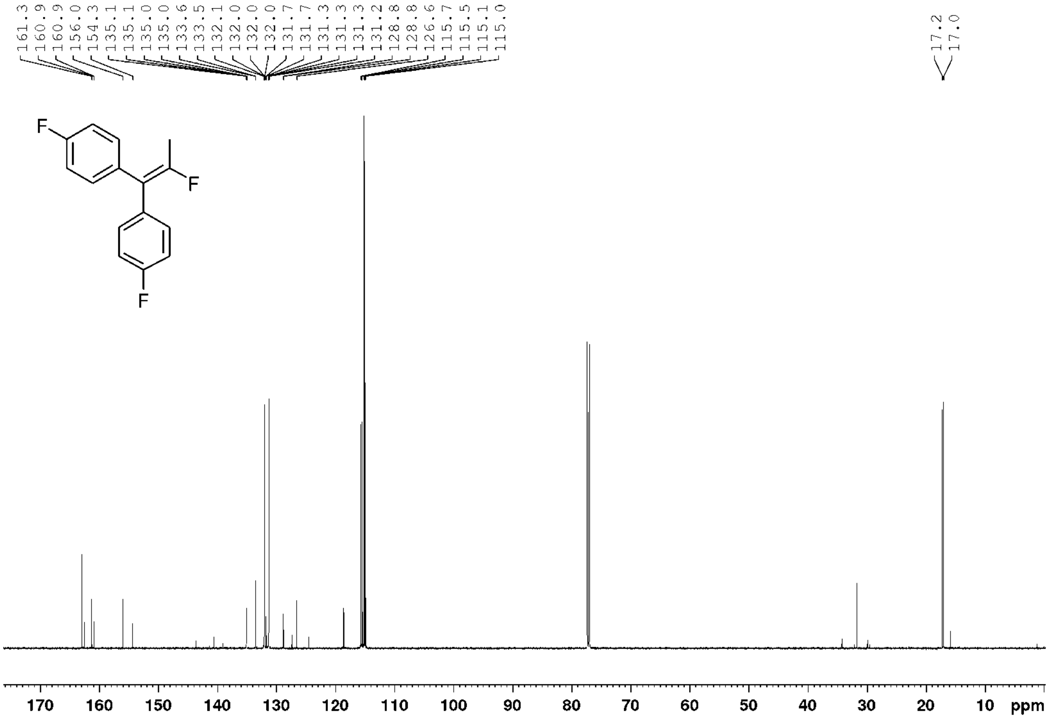
$^{19}F\{^1H\}$ NMR spectrum of **4b** reaction solution (d_8-Toluene)



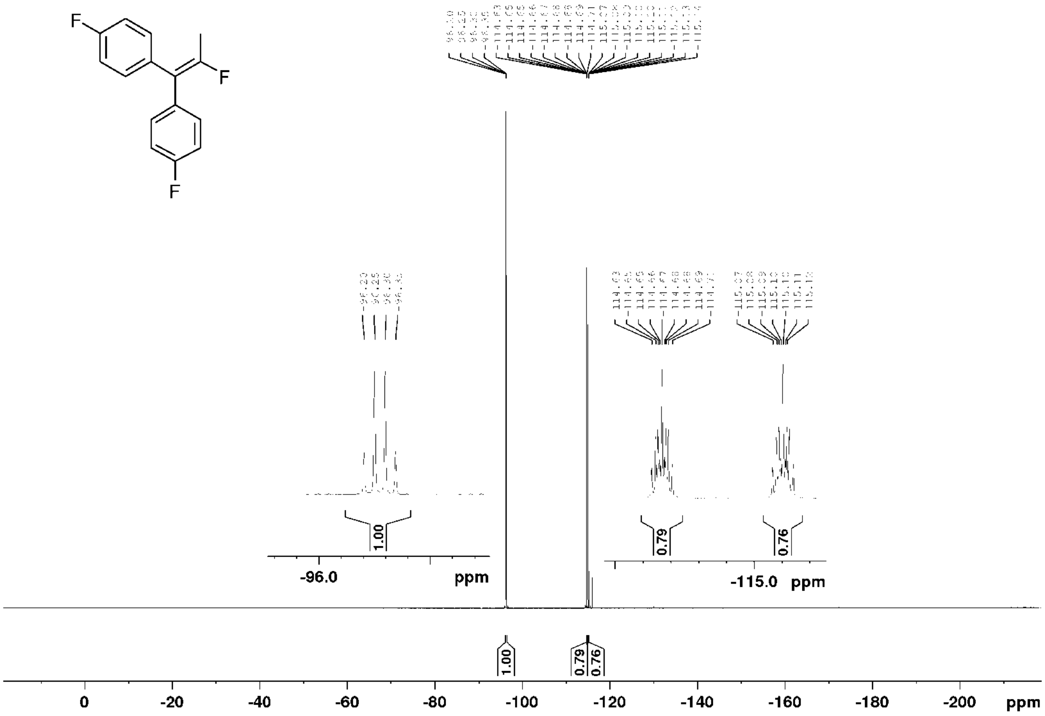
^{1}H NMR spectrum of **5b** (CDCl$_3$)



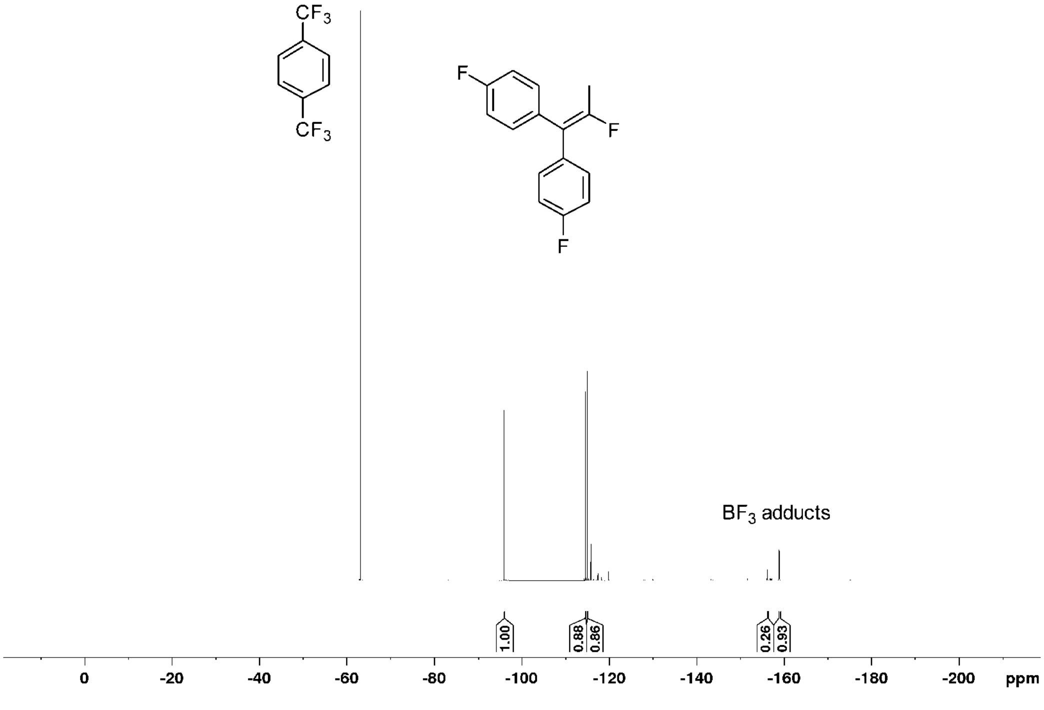
^{13}C NMR spectrum of **5b** (CDCl$_3$)



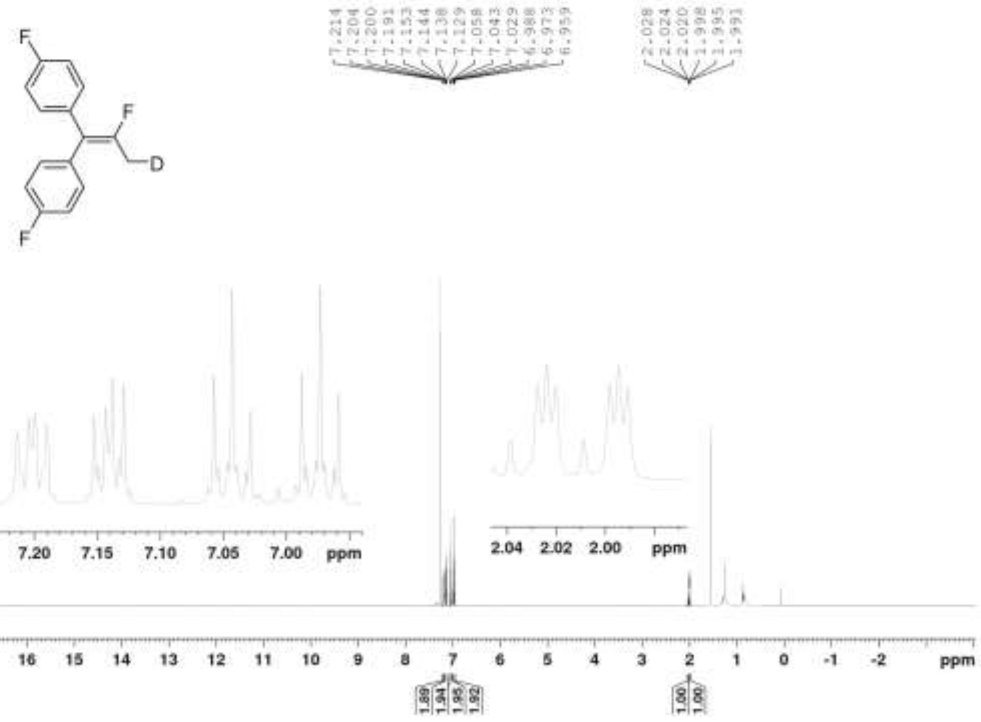
^{19}F NMR spectrum of **5b** after purification (CDCl$_3$)



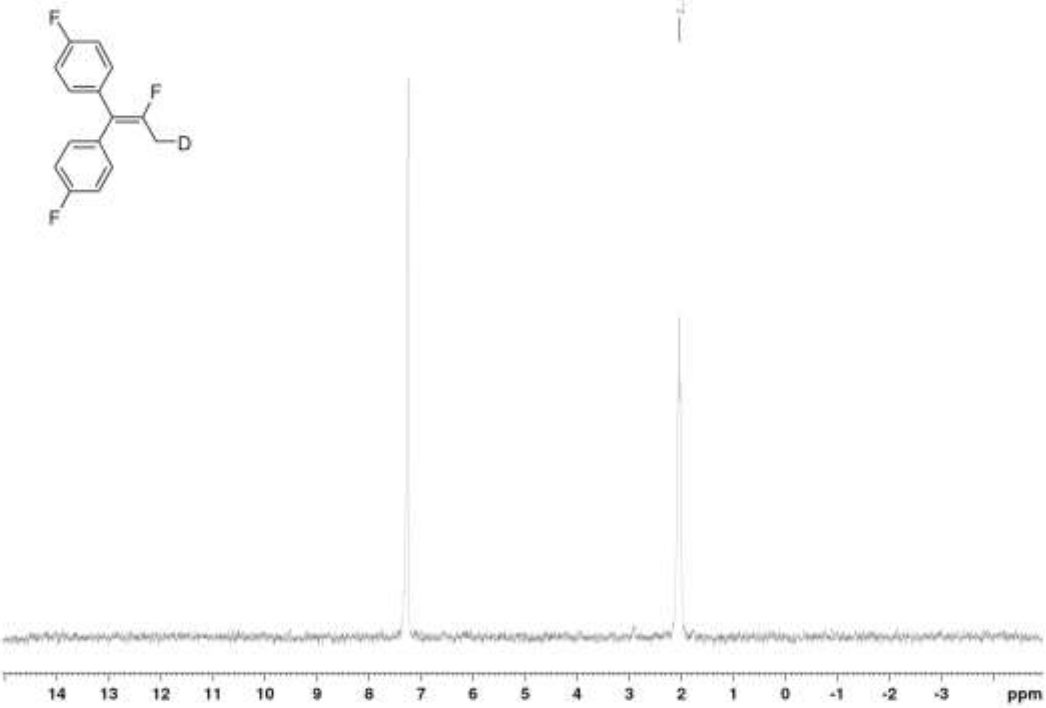
^{19}F{^{1}H} NMR spectrum of **5b** reaction solution (d$_8$-Toluene)



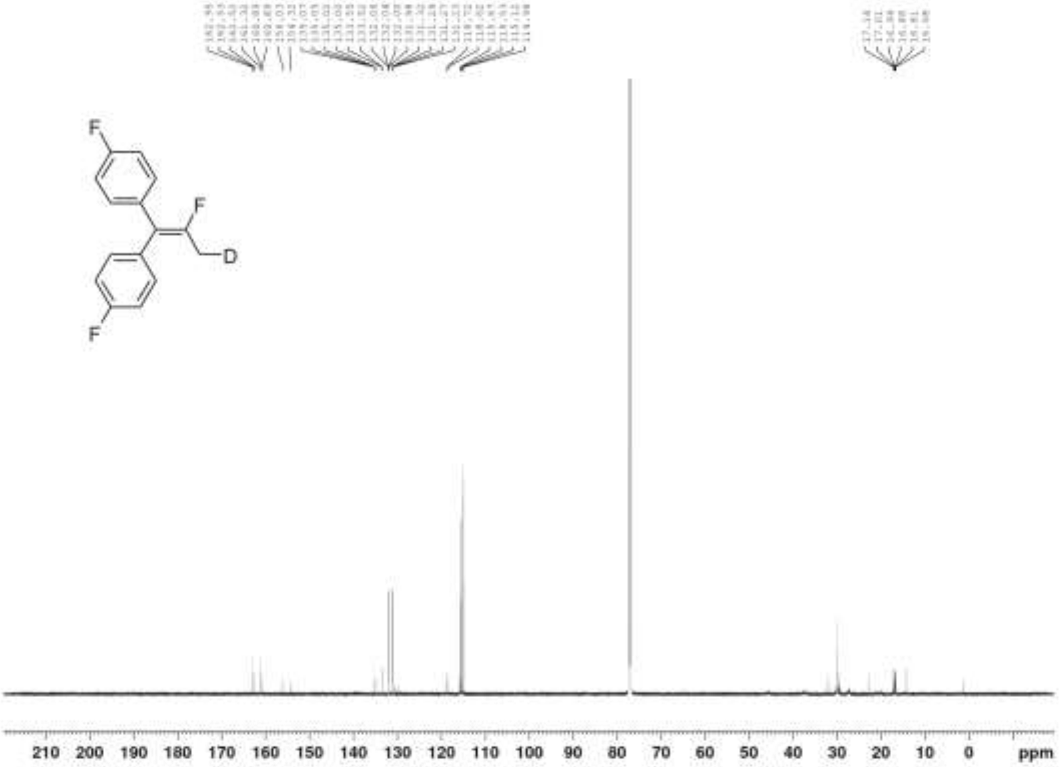
^{1}H NMR spectrum of **5b*** ($CDCl_3$)



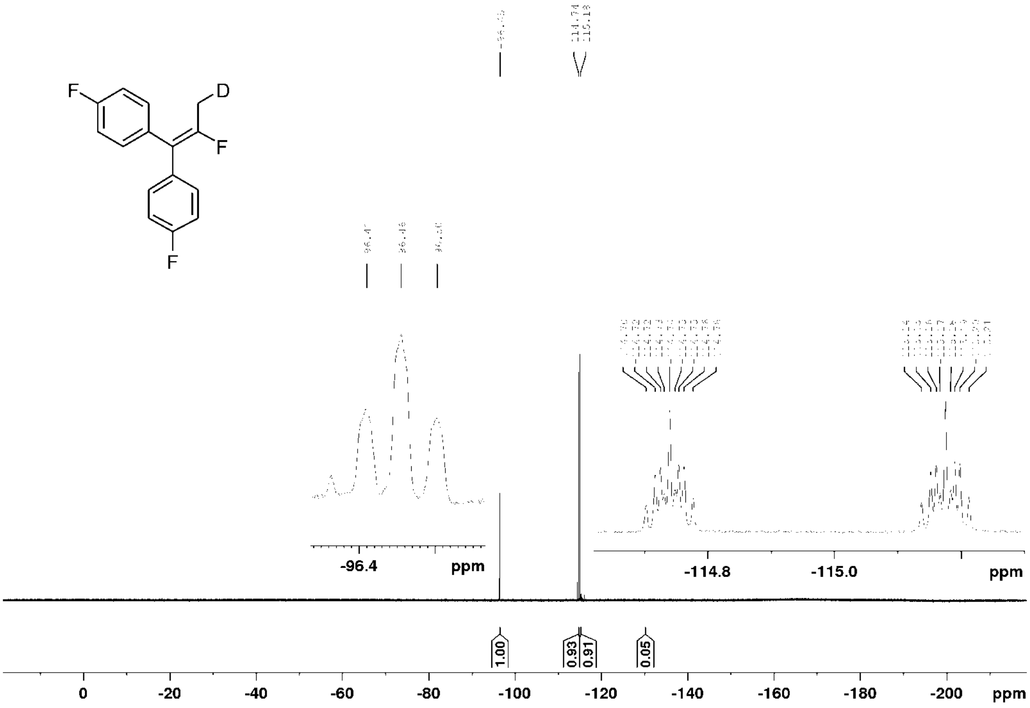
^{2}H NMR spectrum of **5b*** ($CHCl_3$)



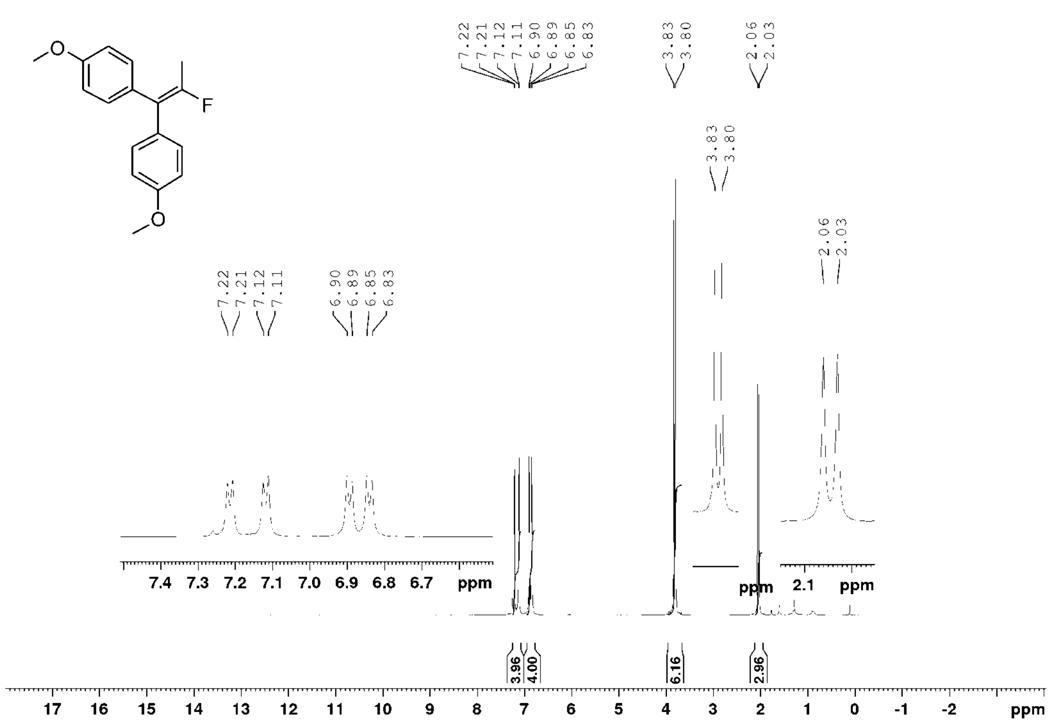
^{13}C NMR spectrum of **5b*** (CDCl$_3$)



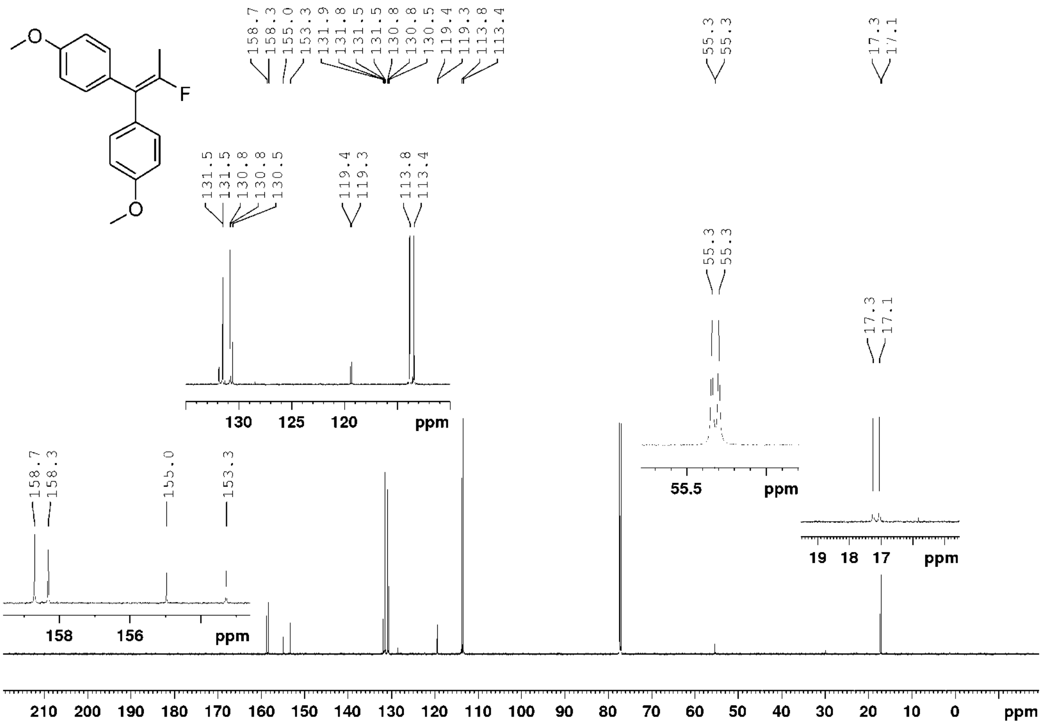
^{19}F NMR spectrum of **5b*** (CDCl$_3$)



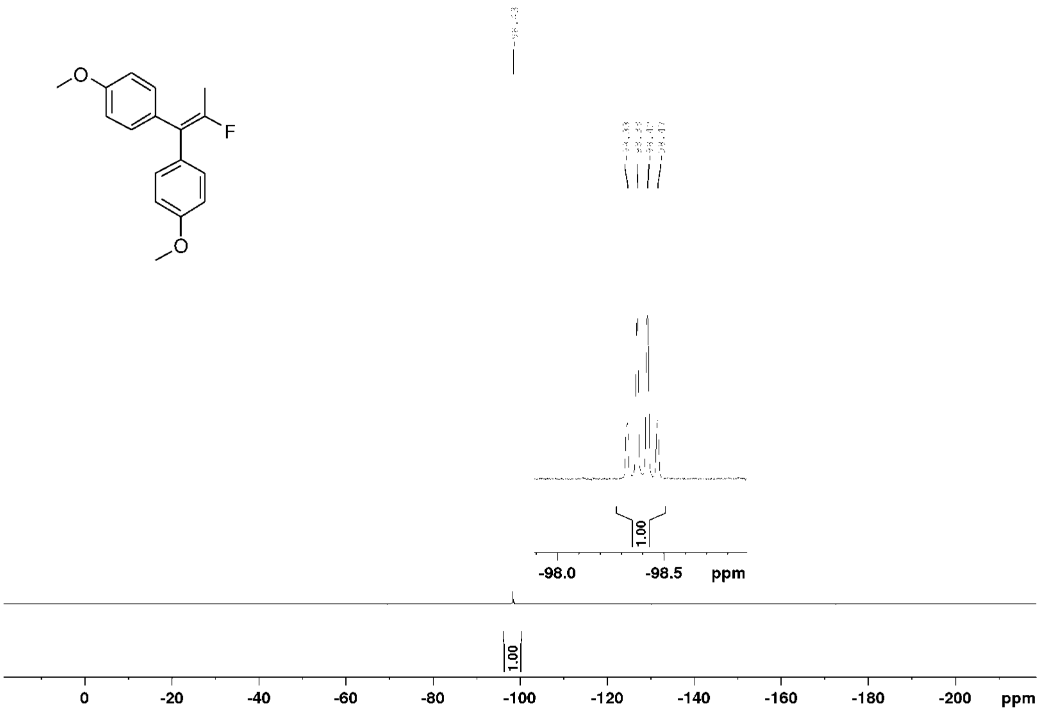
^{1}H NMR spectrum of **6b** (CDCl$_3$)



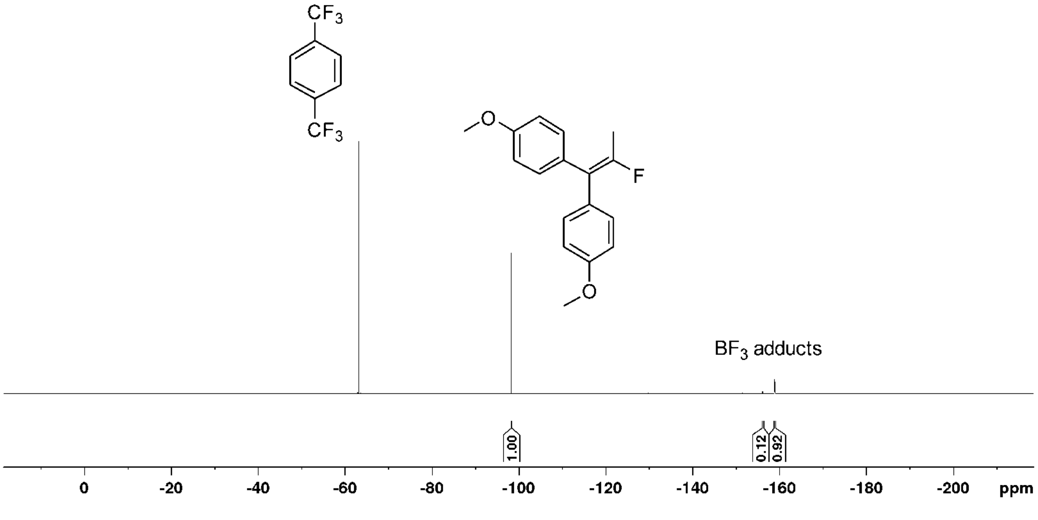
^{13}C NMR spectrum of **6b** (CDCl$_3$)



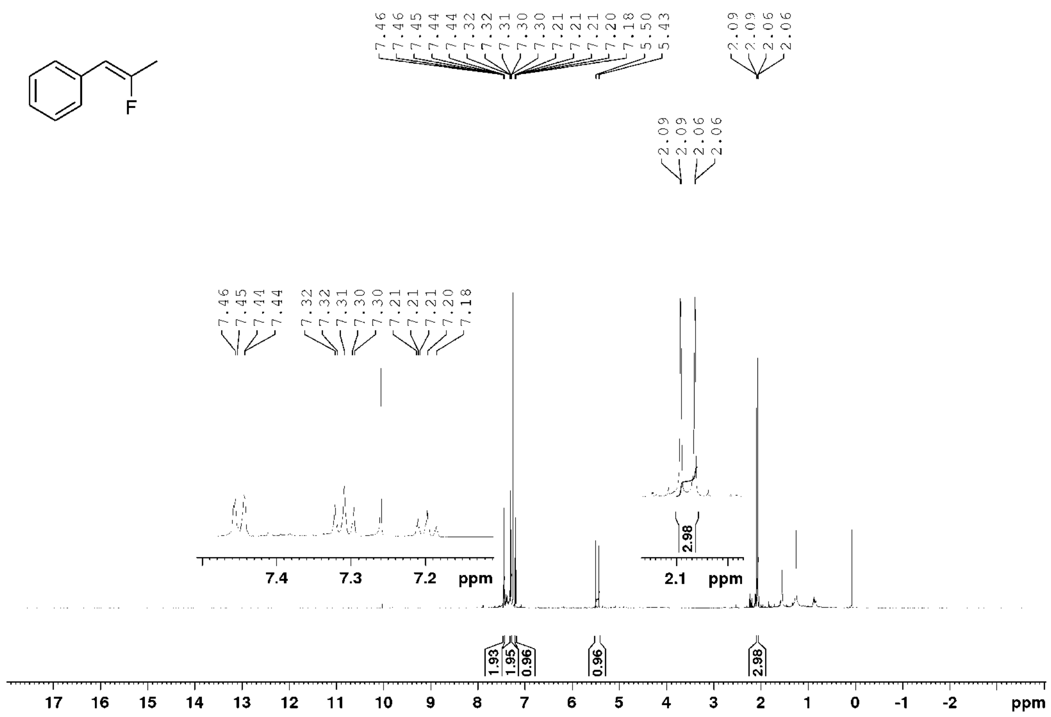
^{19}F NMR spectrum of **6b** after purification ($CDCl_3$)



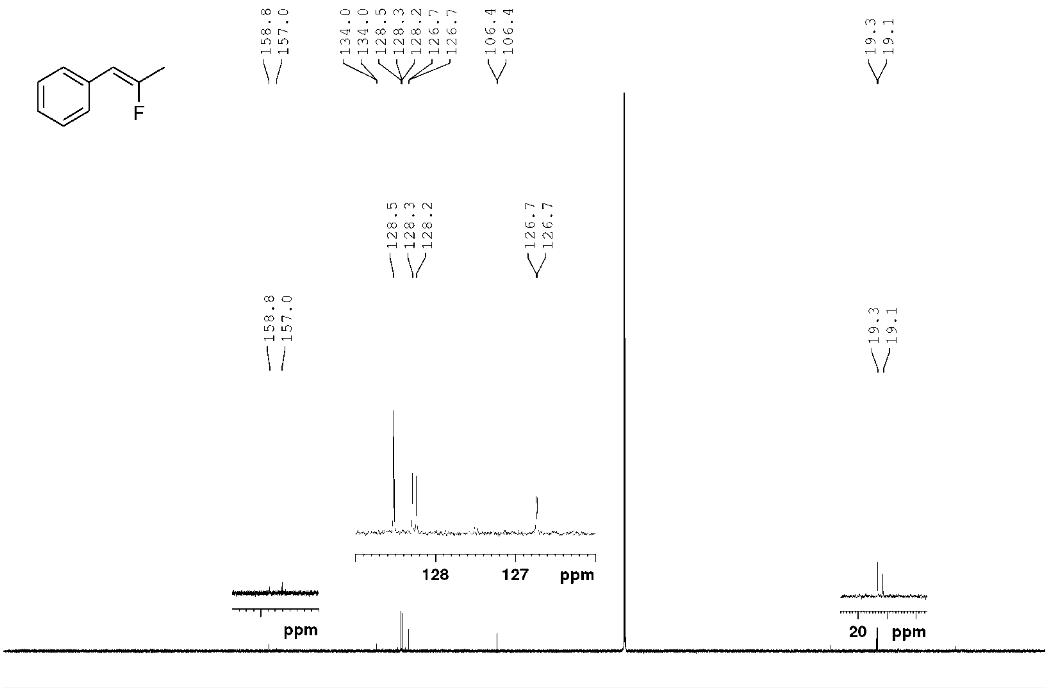
^{19}F{^{1}H} NMR spectrum of **6b** reaction solution (d_8-Toluene)



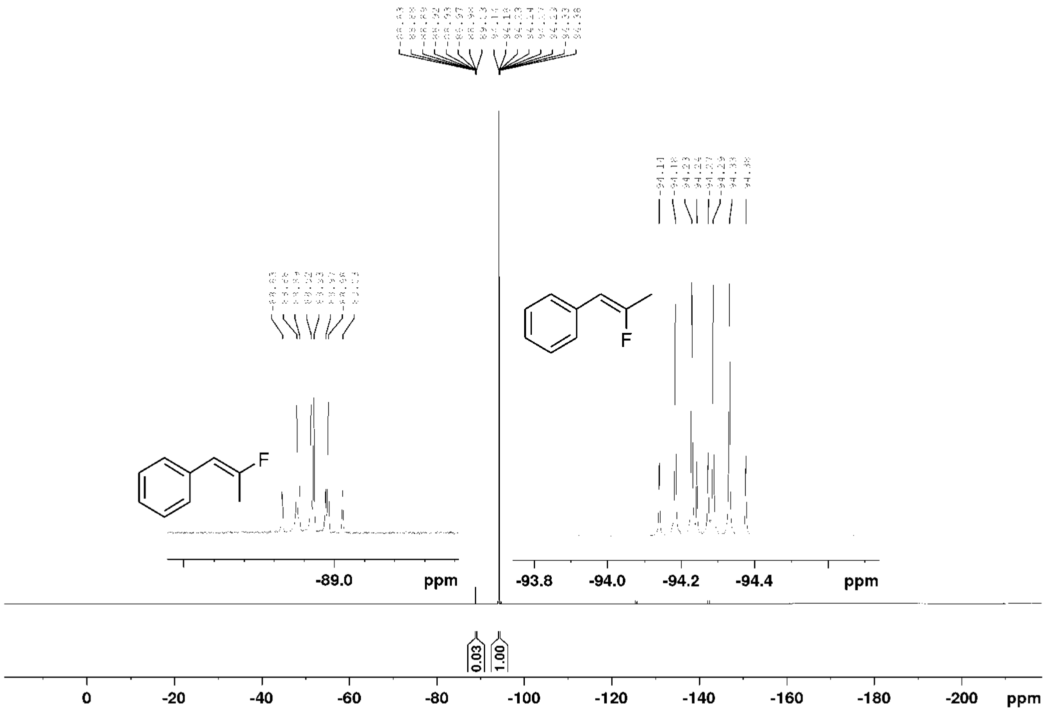
^{1}H NMR spectrum of **7b** (CDCl$_3$)



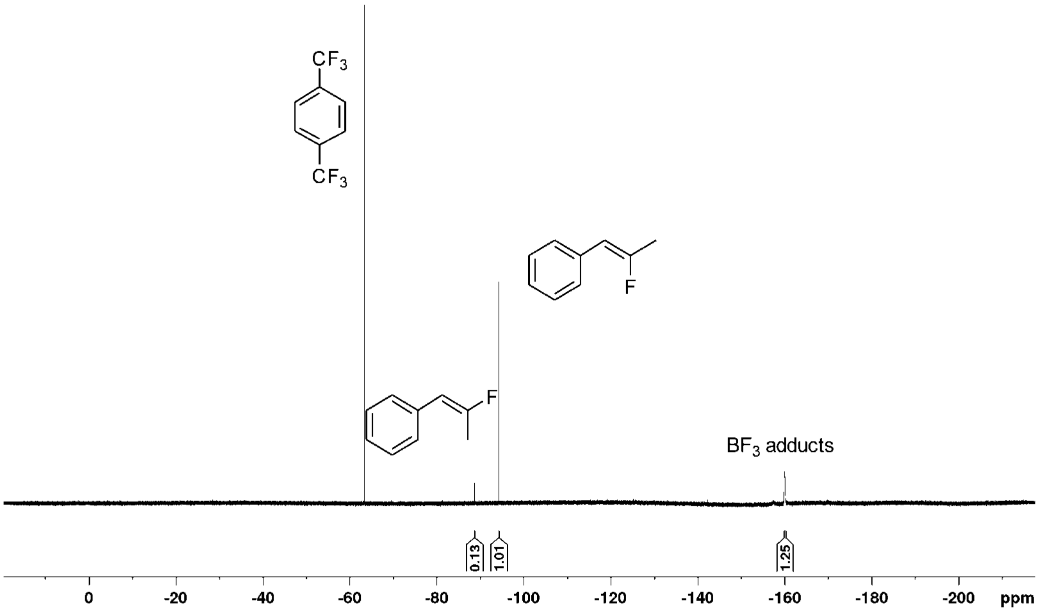
^{13}C NMR spectrum of **7b** (CDCl$_3$)



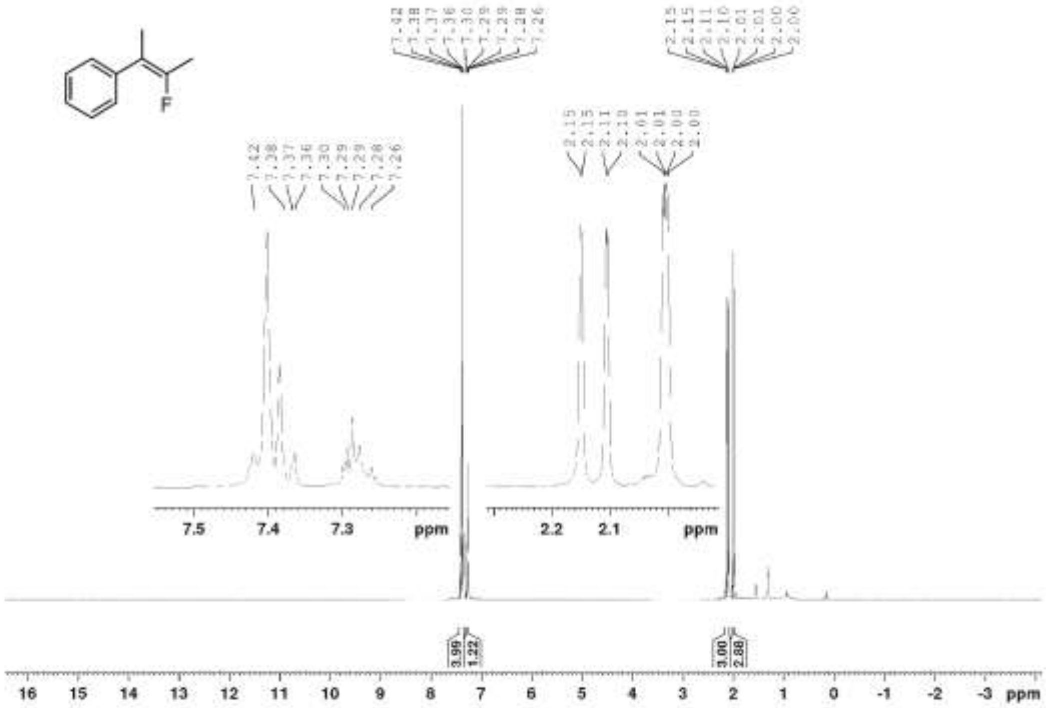
^{19}F NMR spectrum of **7b** after purification ($CDCl_3$)



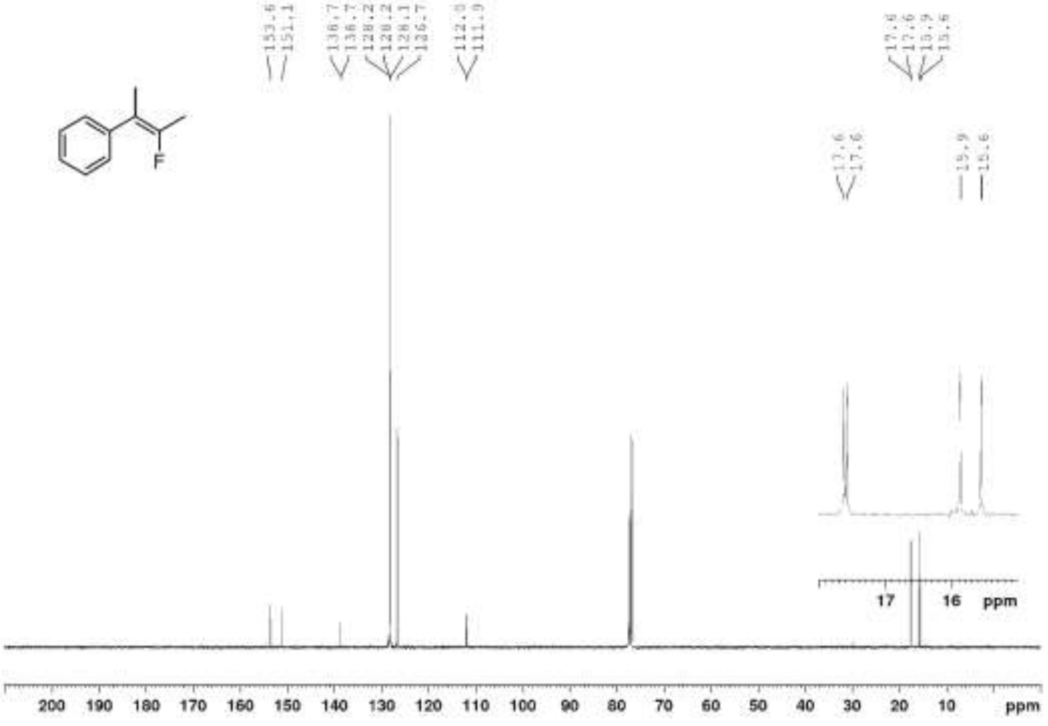
^{19}F{^{1}H} NMR spectrum of **4b** reaction solution (d_8-Toluene)



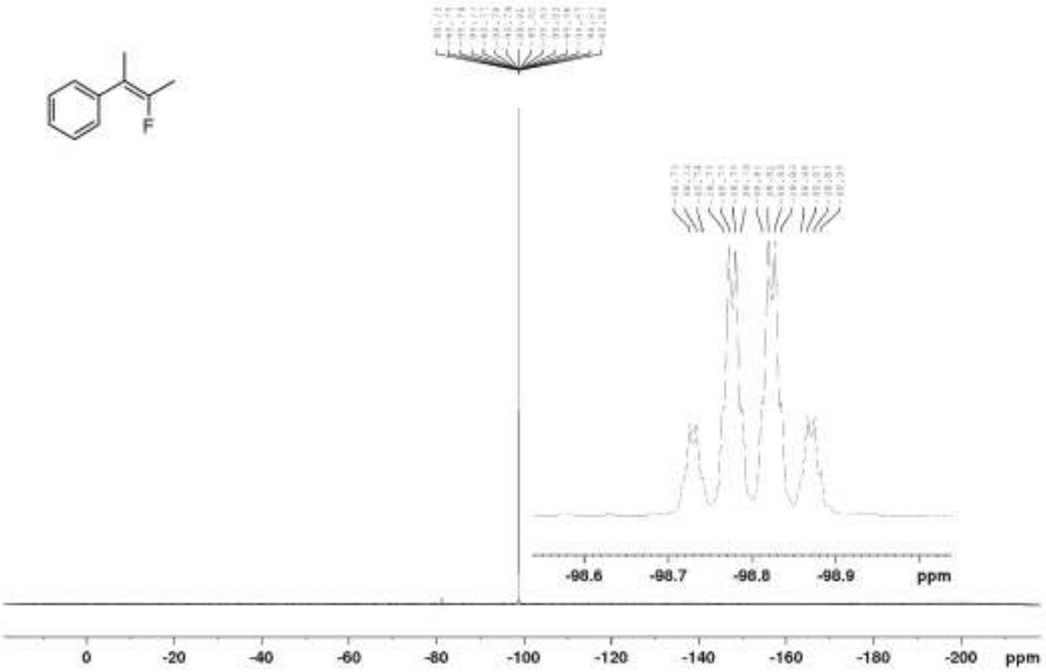
^{1}H NMR spectrum of **8b** (CDCl$_3$)



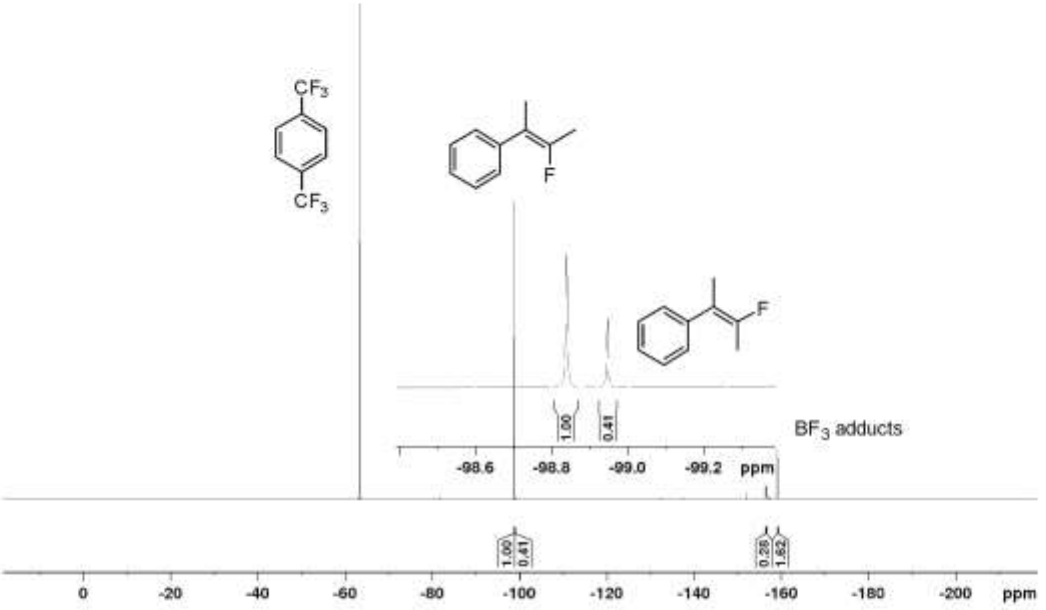
^{13}C NMR spectrum of **8b** (CDCl$_3$)



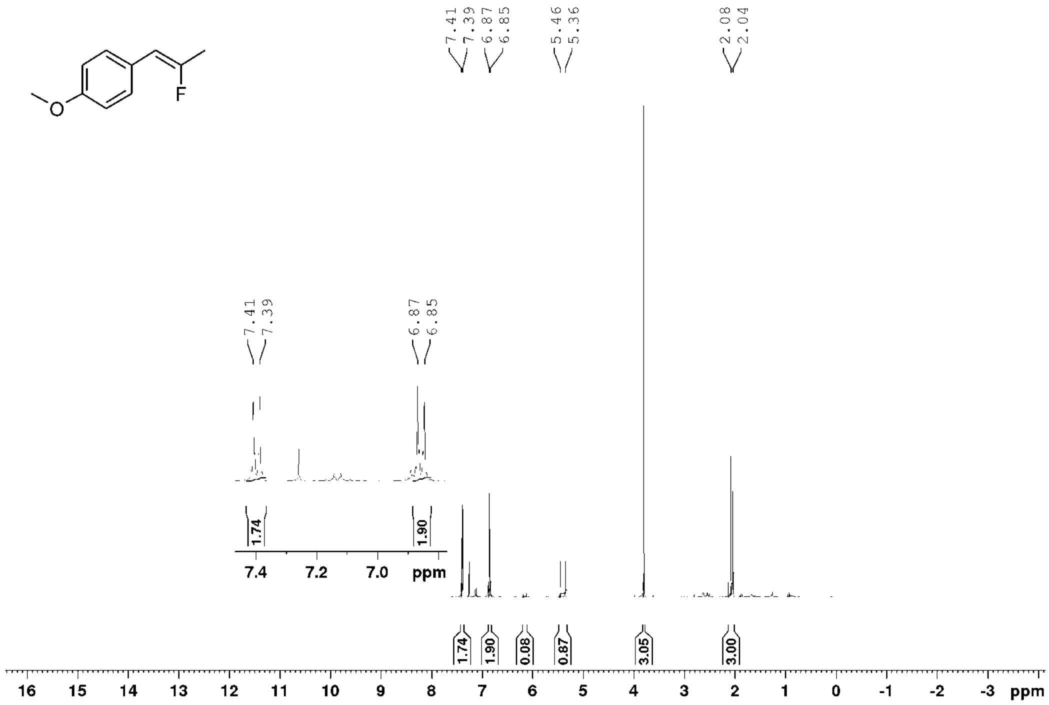
^{19}F NMR spectrum of **8b** after purification ($CDCl_3$)



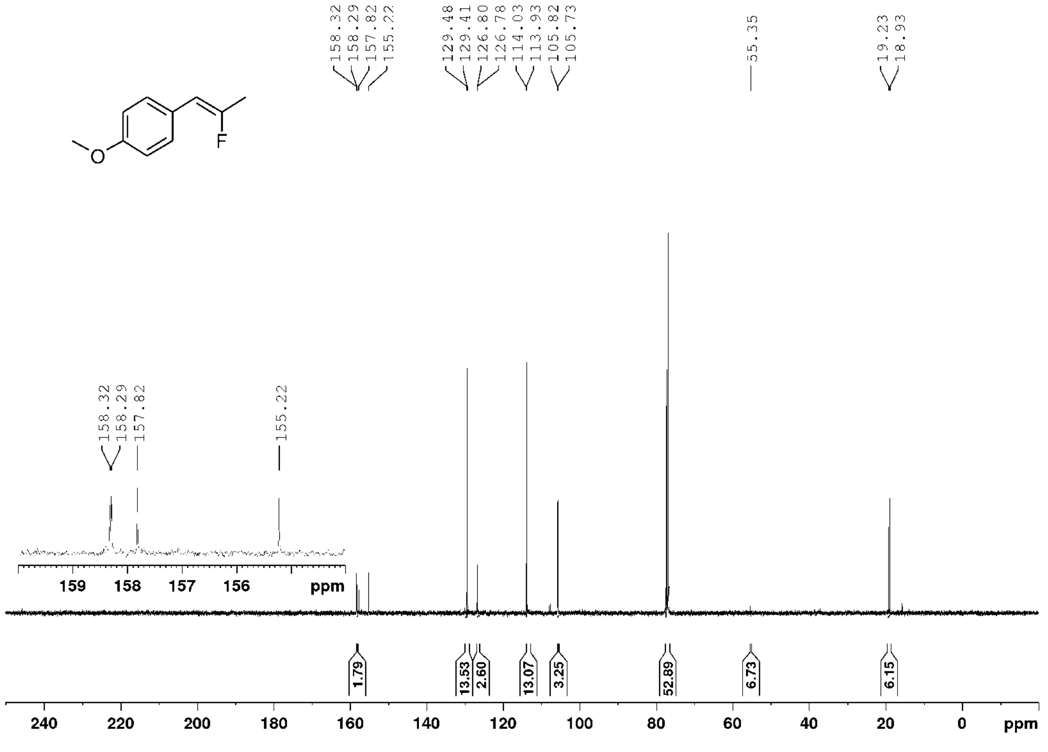
^{19}F{^{1}H} NMR spectrum of **8b** reaction solution (d_8-Toluene)



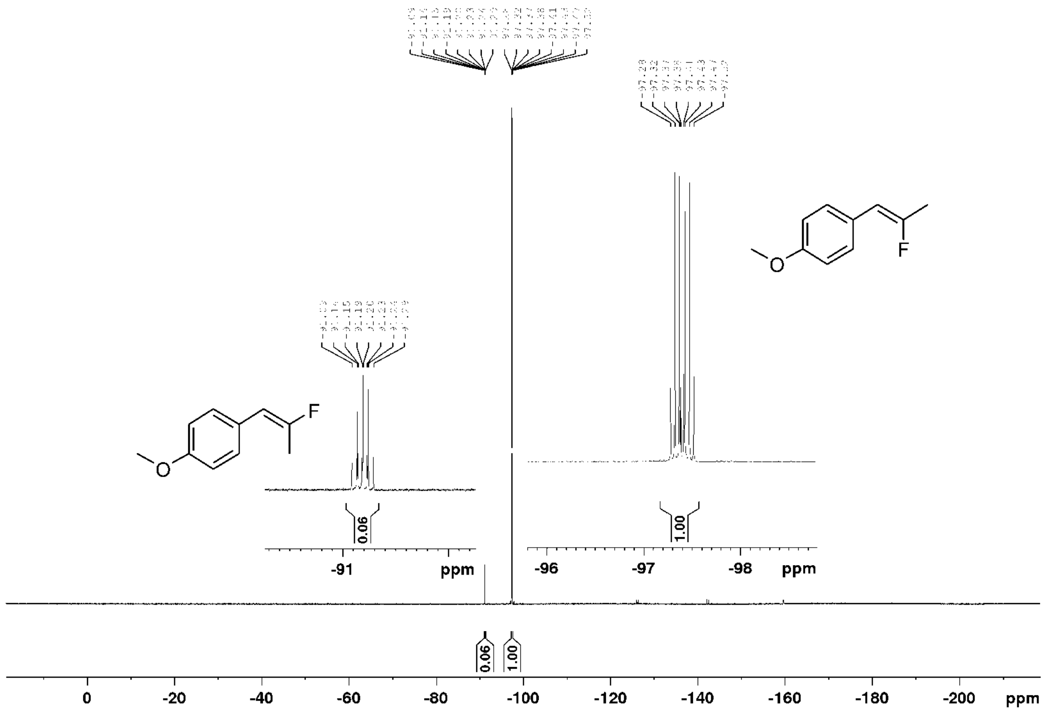
^{1}H NMR spectrum of **9b** (CDCl$_3$)



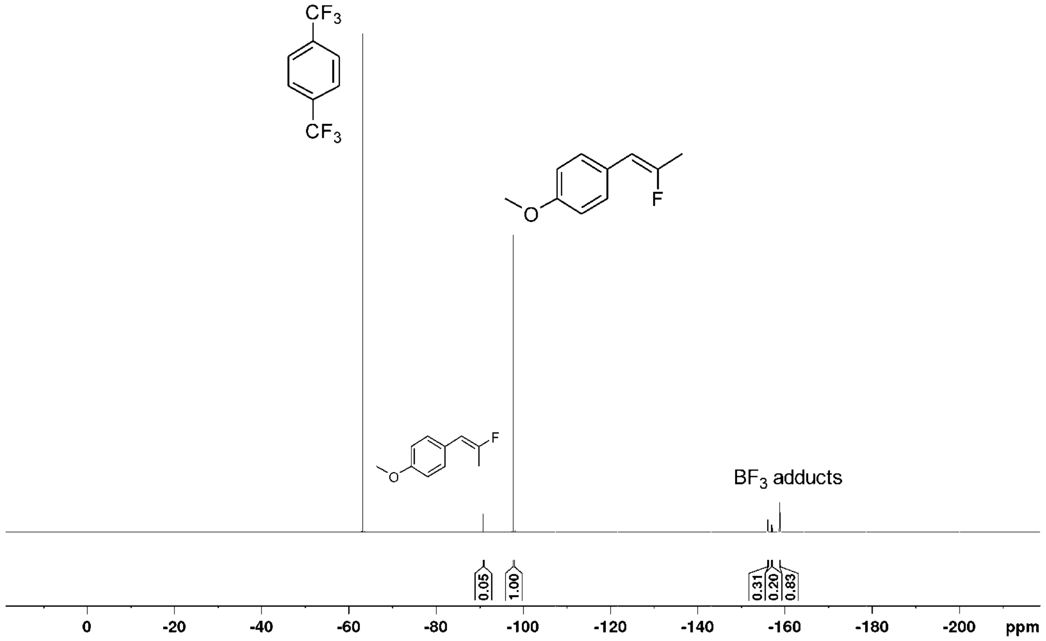
^{13}C NMR spectrum of **9b** (CDCl$_3$)



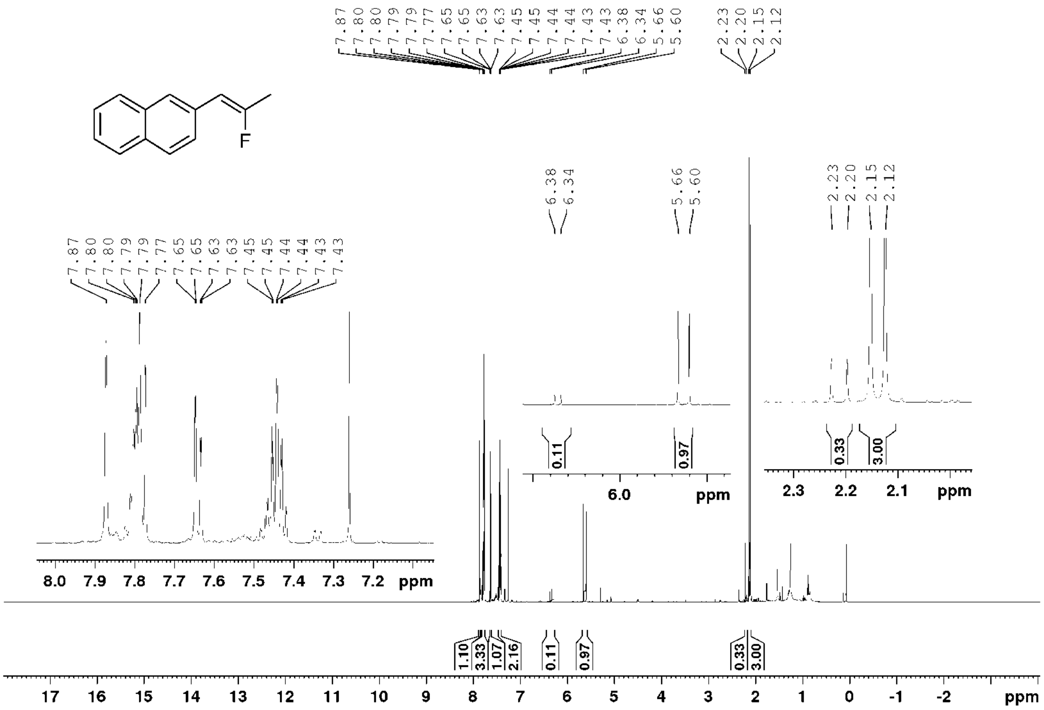
^{19}F NMR spectrum of **9b** after purification ($CDCl_3$)



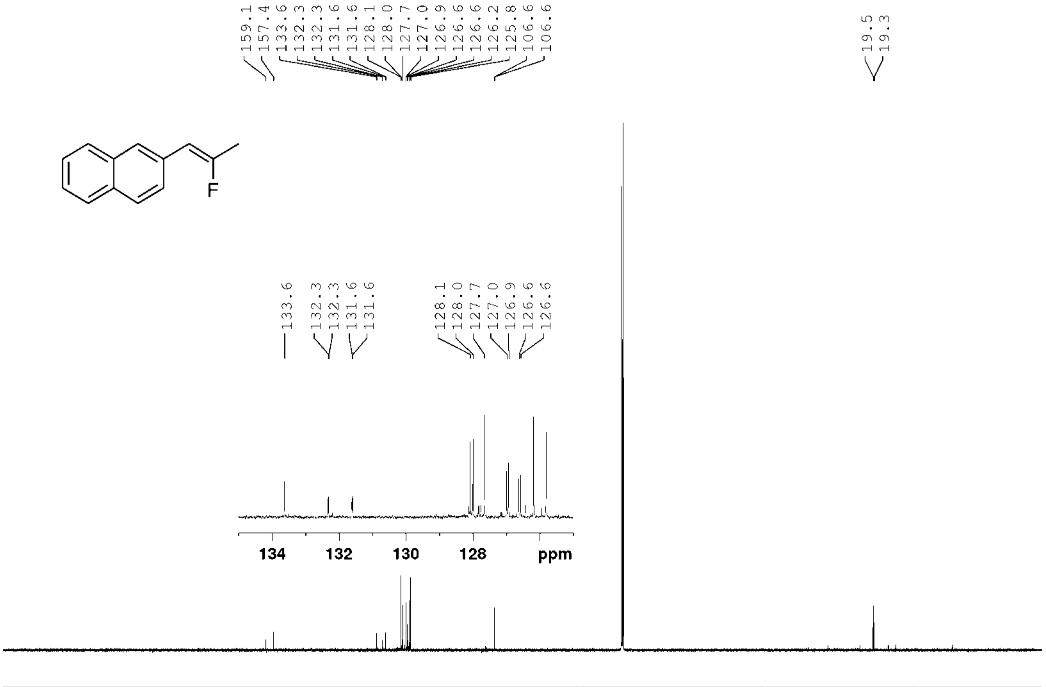
^{19}F{^{1}H} NMR spectrum of **9b** reaction solution (d_8-Toluene)



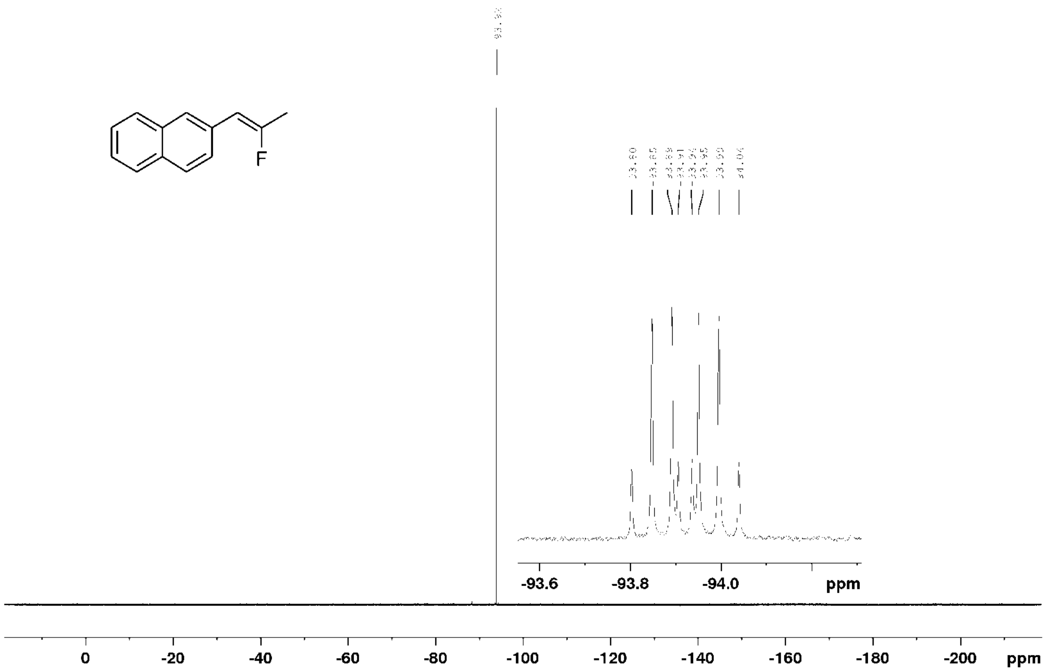
^{1}H NMR spectrum of **10b** (CDCl$_3$)



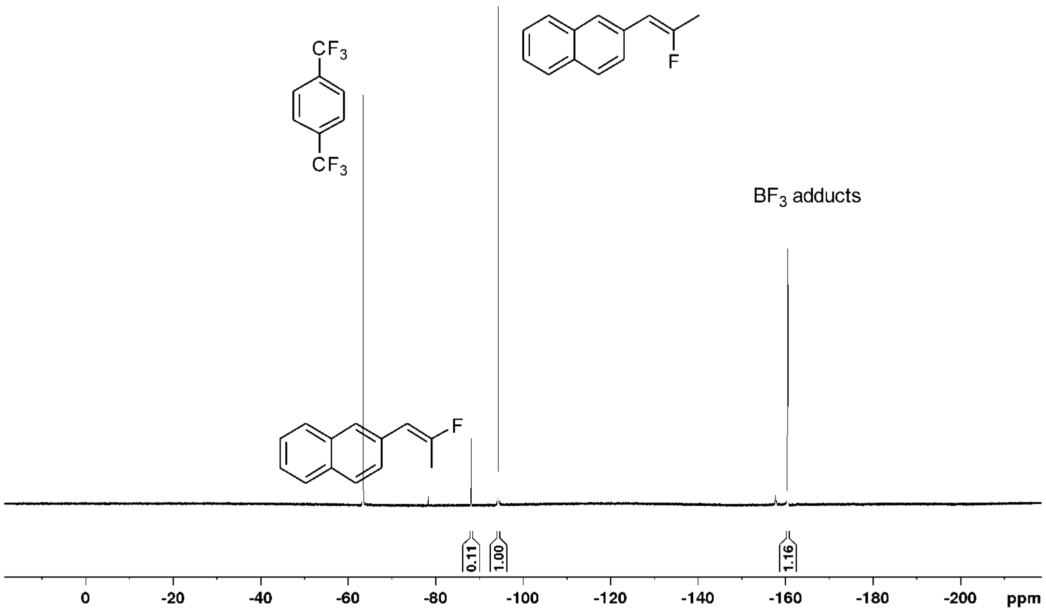
^{13}C NMR spectrum of **10b** (CDCl$_3$)



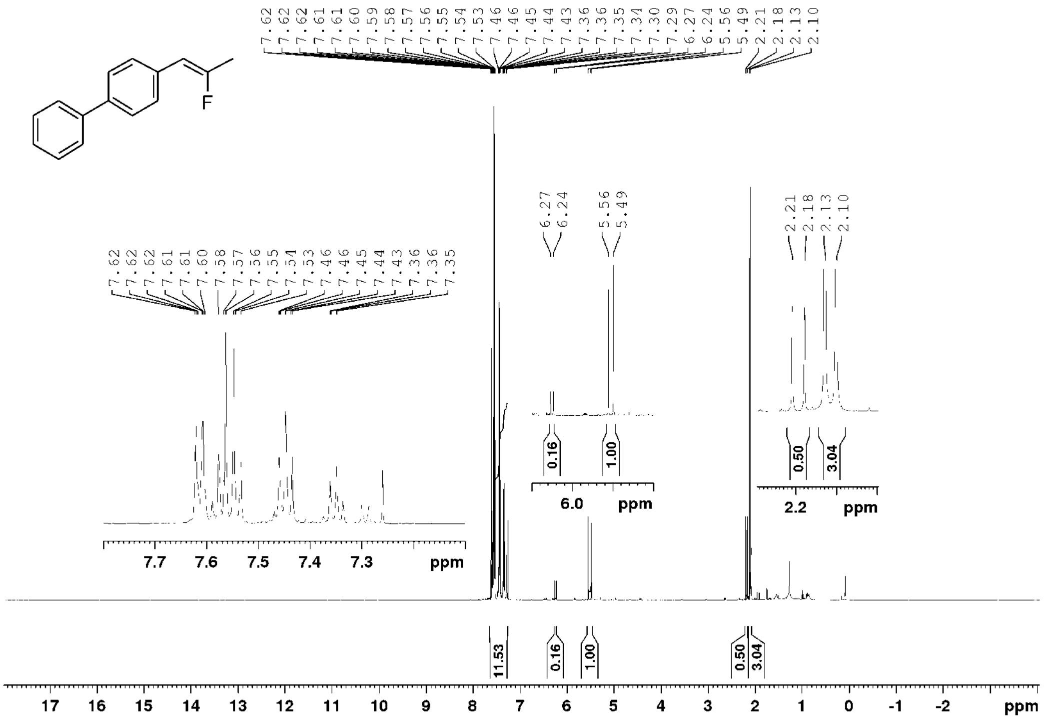
^{19}F NMR spectrum of **10b** after purification ($CDCl_3$)



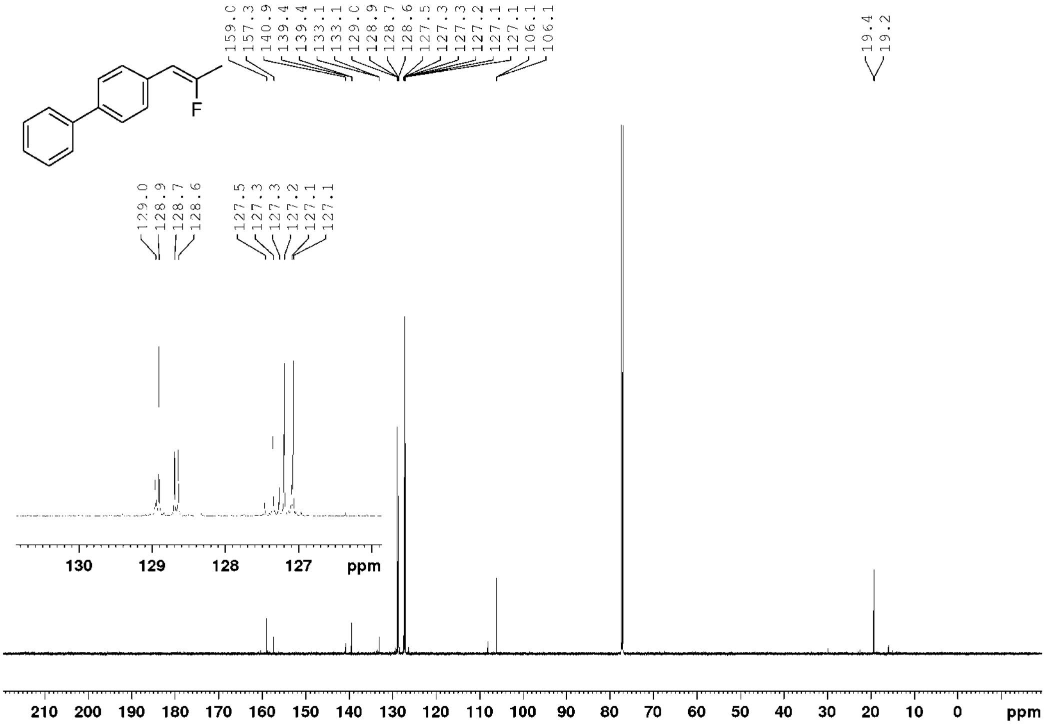
^{19}F{^{1}H} NMR spectrum of **10b** reaction solution (d_8-Toluene)



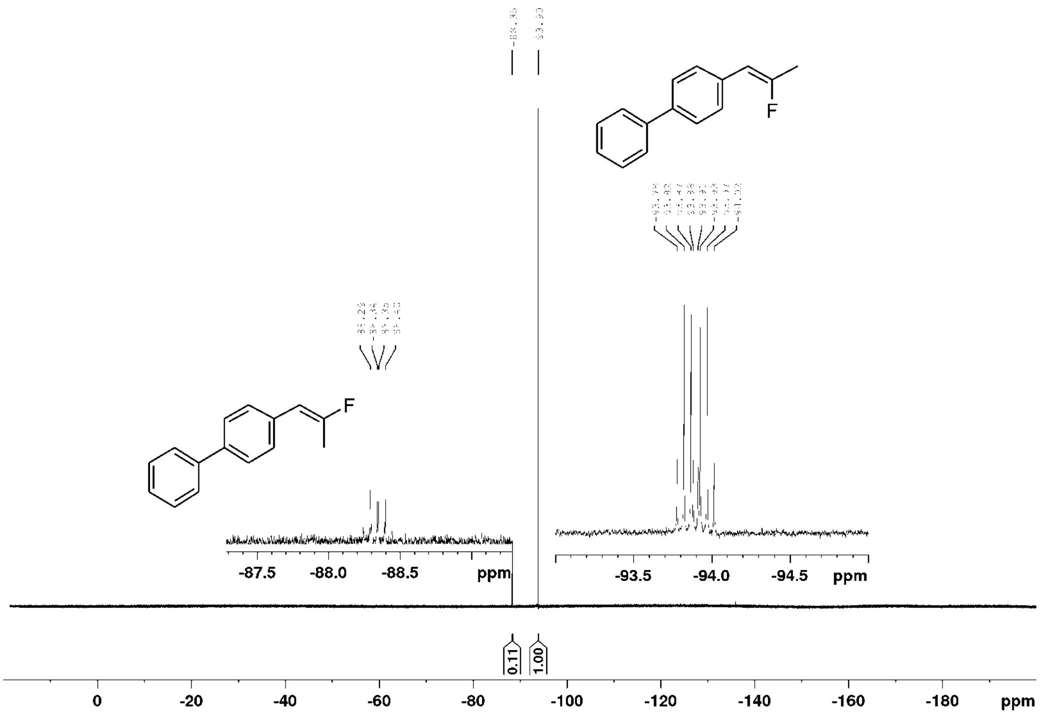
^{1}H NMR spectrum of **11b** ($CDCl_3$)



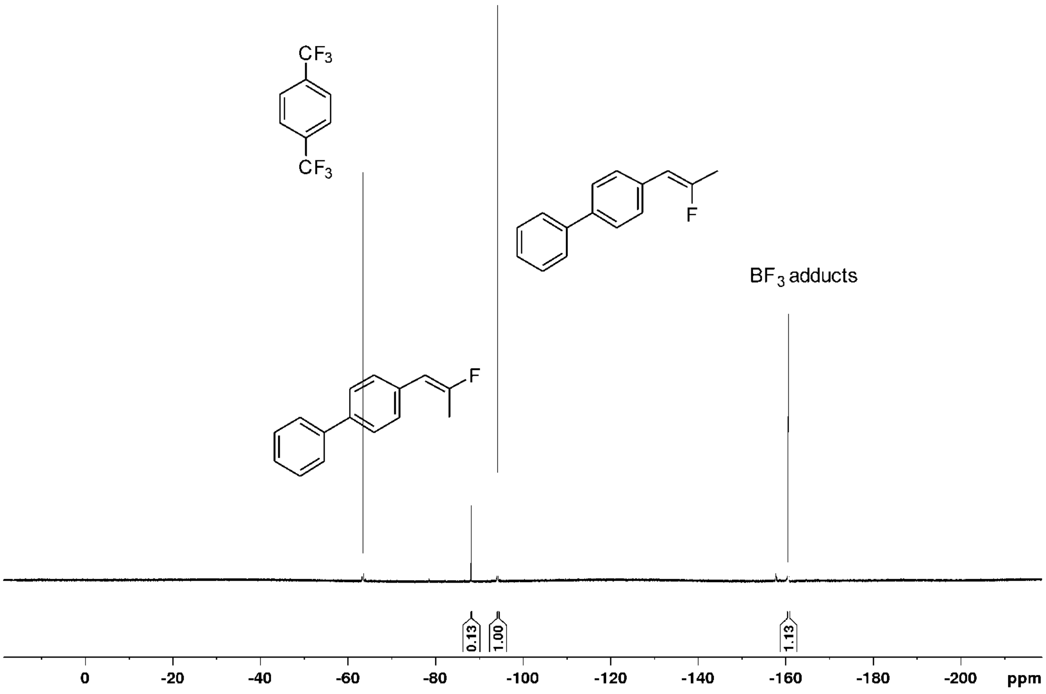
^{13}C NMR spectrum of **11b** ($CDCl_3$)



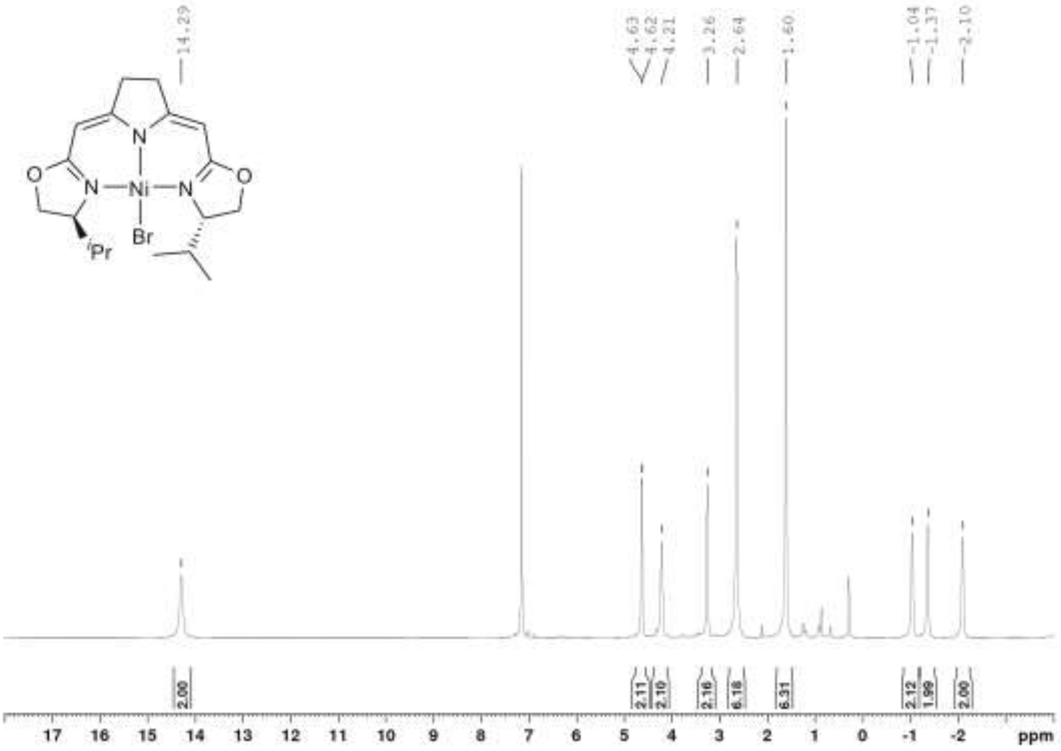
^{19}F NMR spectrum of **11b** after purification ($CDCl_3$)



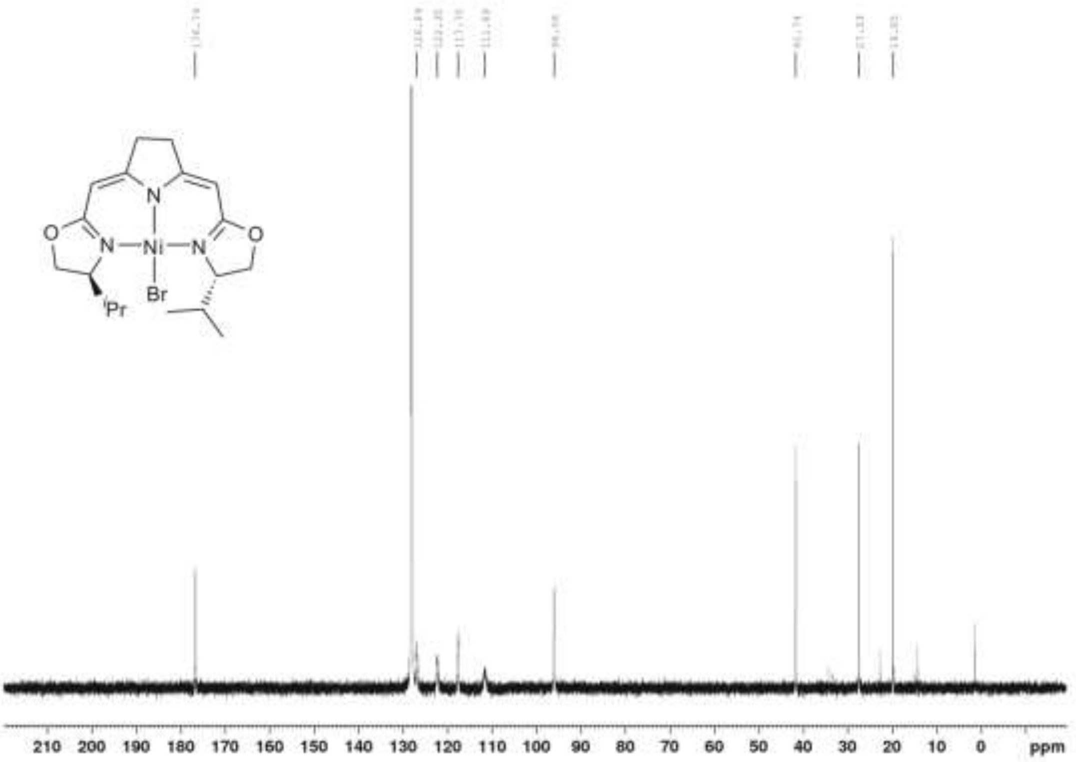
^{19}F{^{1}H} NMR spectrum of **11b** reaction solution (d_8-Toluene)



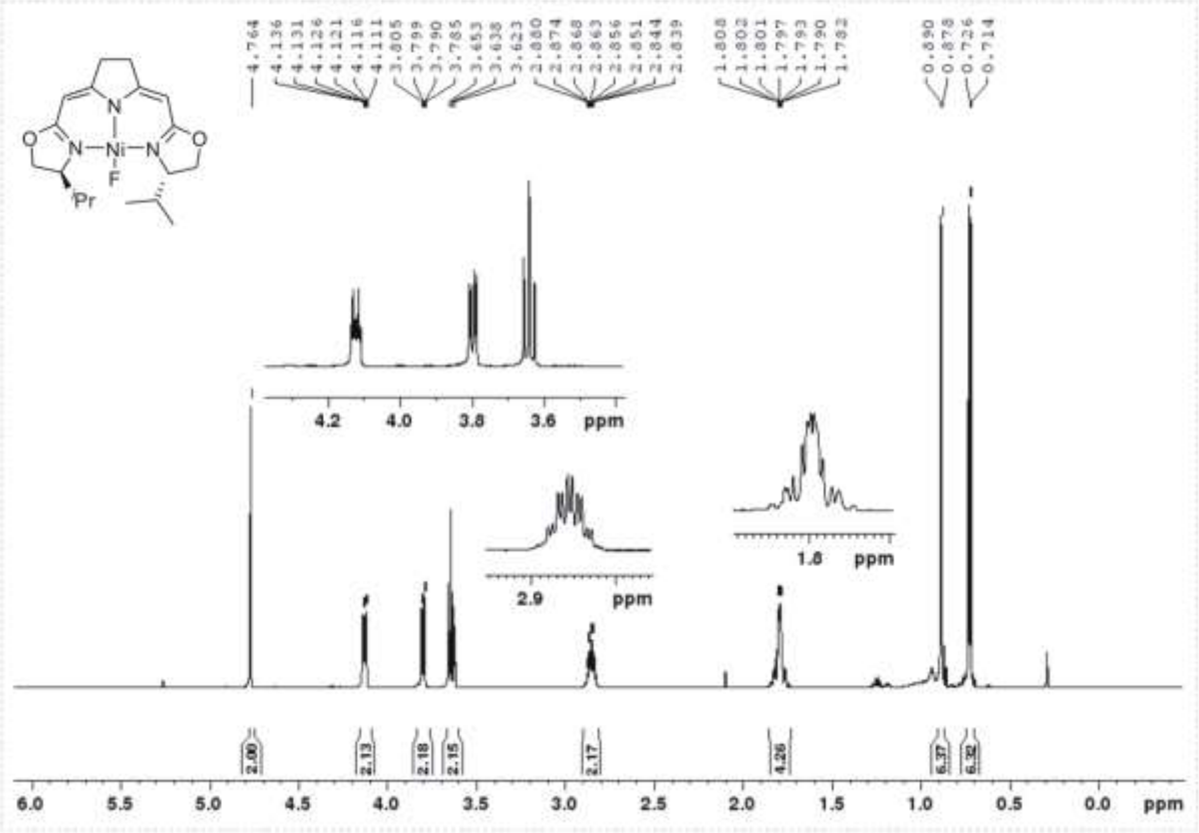
^{1}H NMR spectrum of **(S)-Lig$_{iPr}$(iso)NiBr**



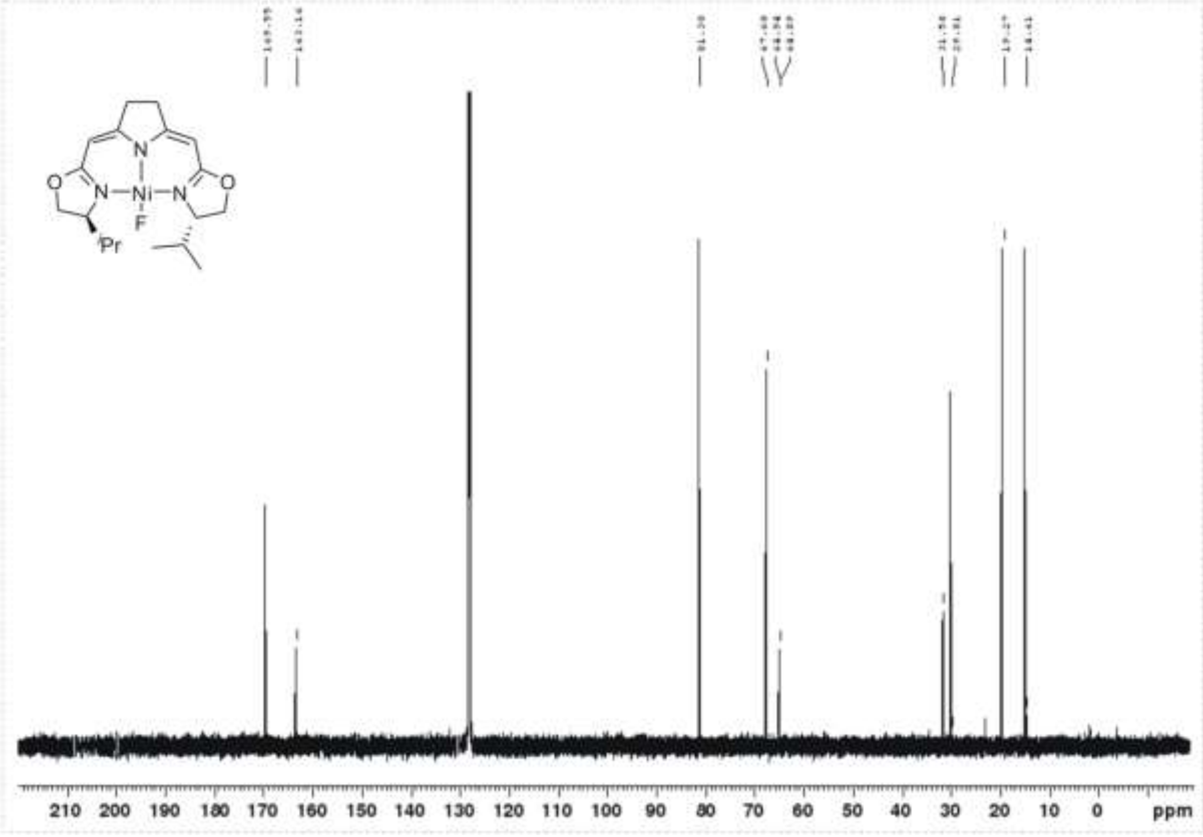
^{13}C NMR spectrum of **(S)-Lig$_{iPr}$(iso)NiBr**



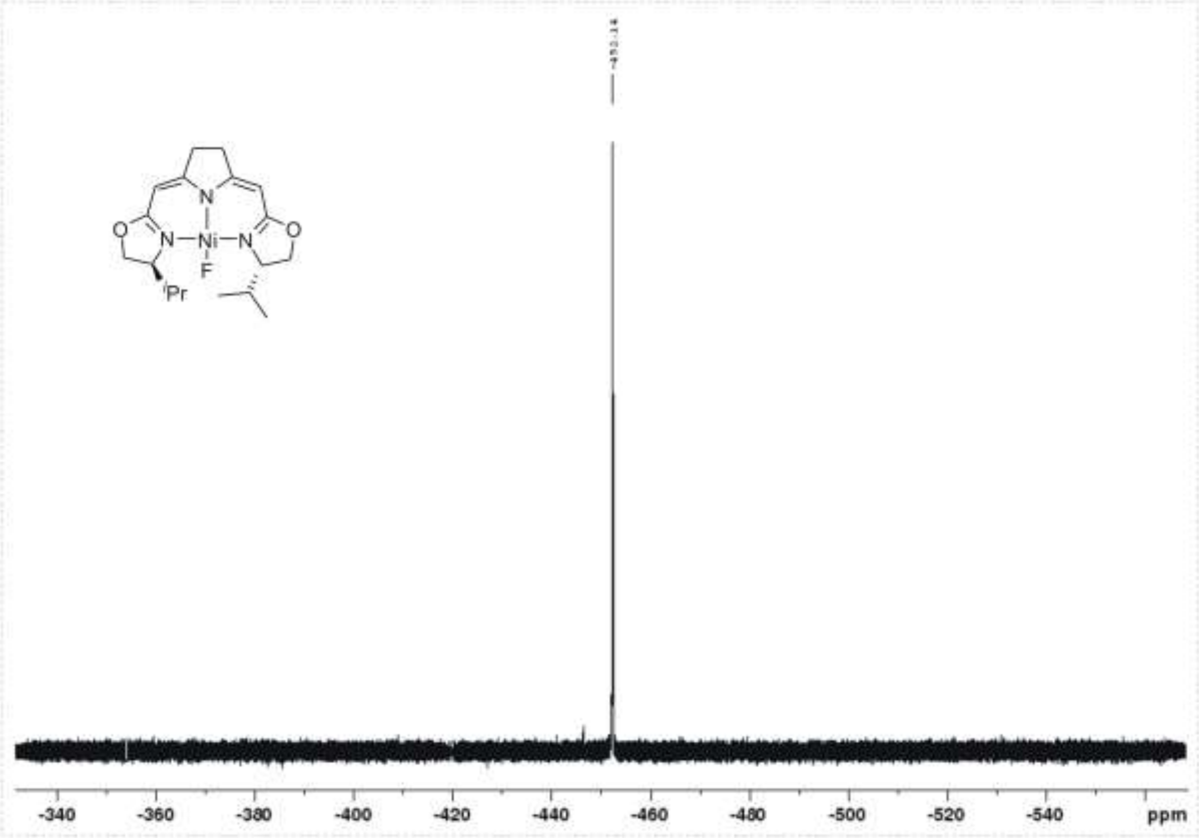
^{1}H NMR spectrum of **1b**



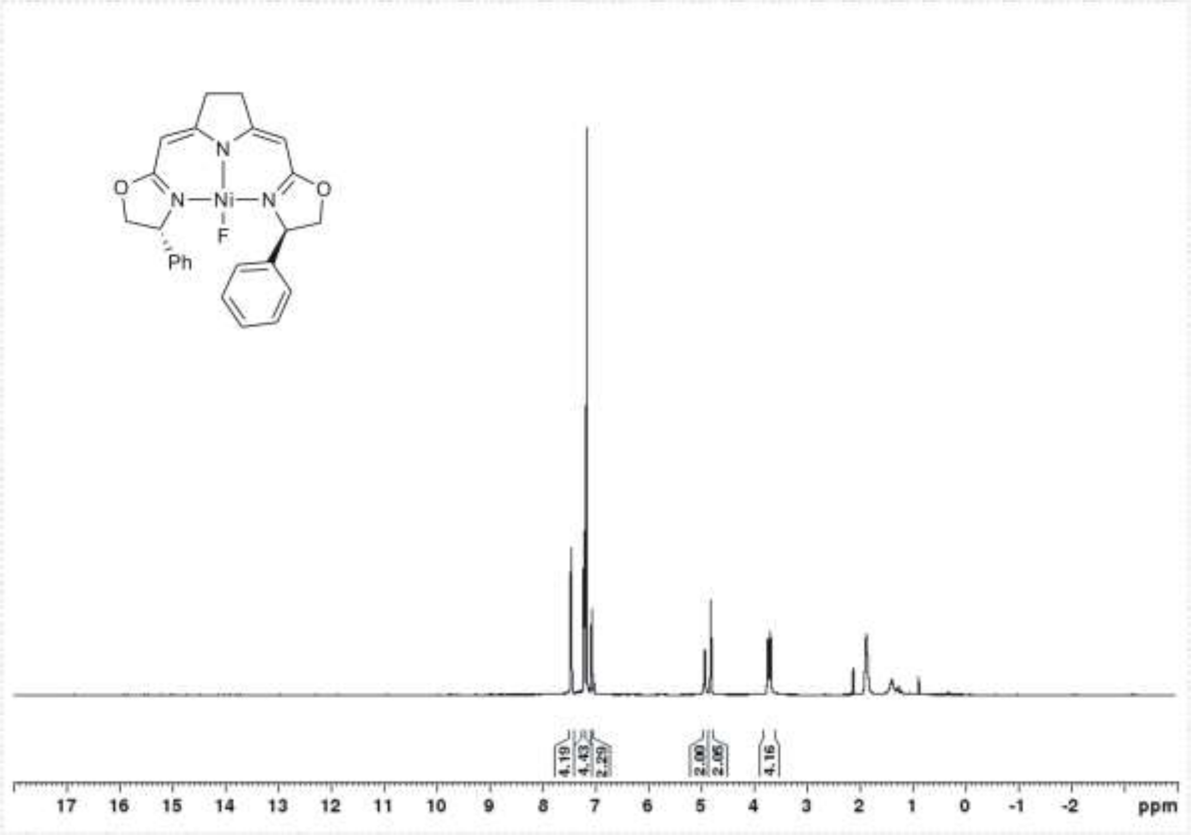
^{13}C NMR spectrum of **1b**



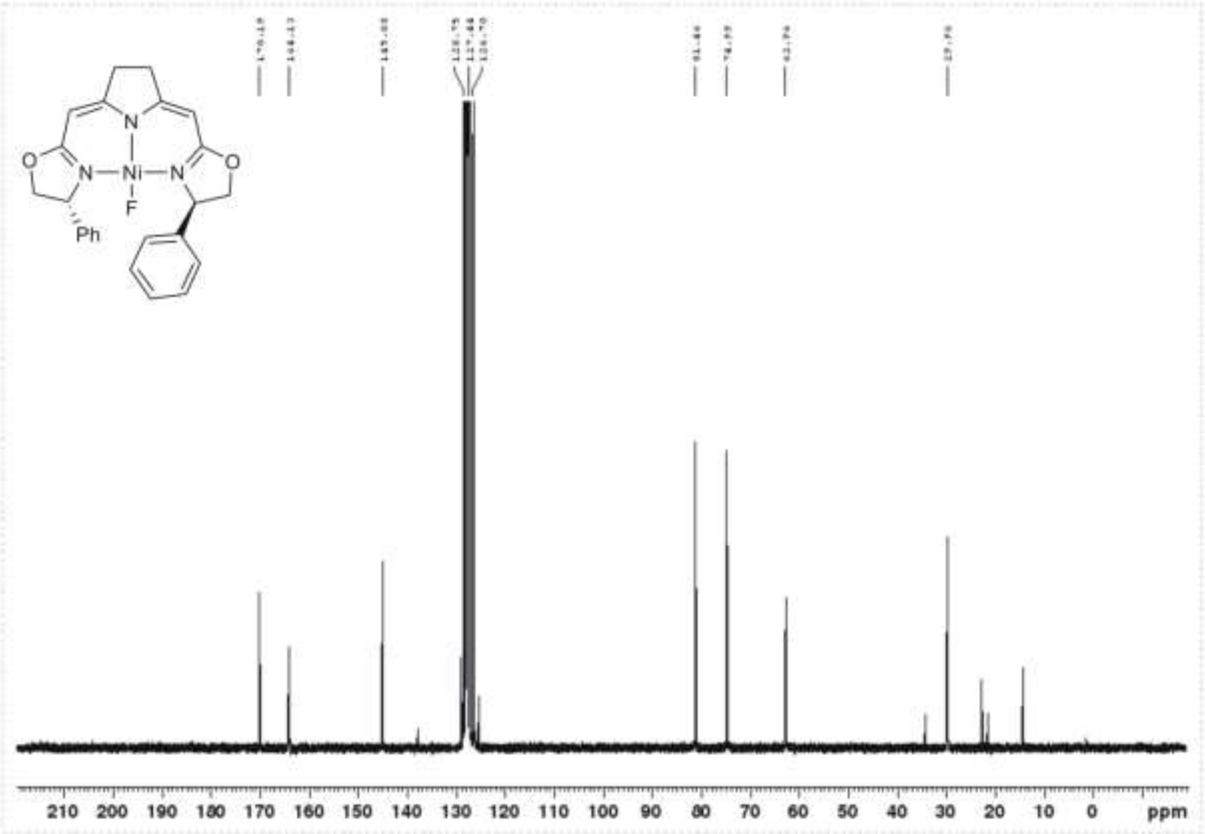
^{19}F NMR spectrum of **1b**



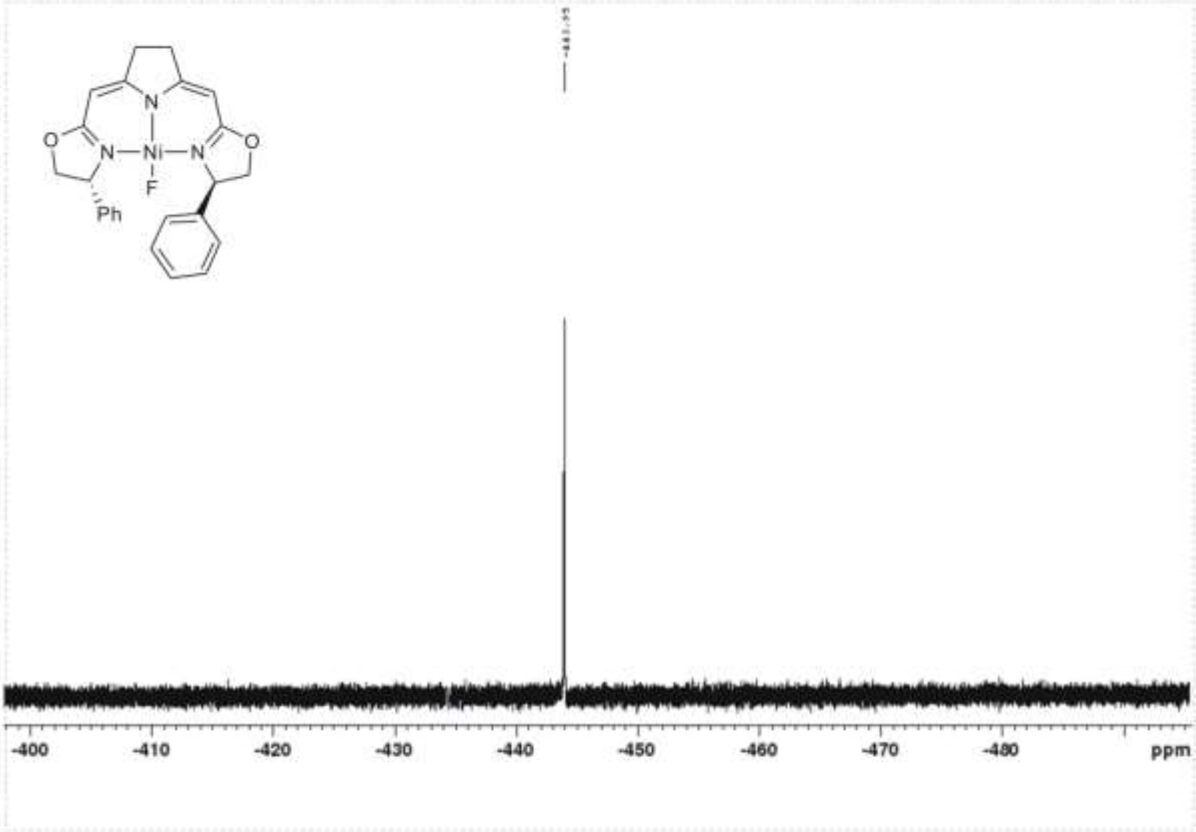
^{1}H NMR spectrum of **1a**



^{13}C NMR spectrum of **1a**



^{19}F NMR spectrum of **1a**



VII. Computational studies

DFT calculations at the D3[6]-B3LYP[7] /TZVP[8] level of theory were carried out using the Gaussian 09 program package. [9] All optimized geometries were confirmed as minimal energy structures by frequency analysis.

Table 1 Summary of DFT studies

	ΔG [kJ/mol]
7b-E	0
7b-Z	-7,45
8b-E	0
8b-Z	+6,41
9b-E	0
9b-Z	-8,24
10b-E	0
10b-Z	-7,35
11b-E	0
11b-Z	-8,50

Cartesian Coordinates of the Optimized Structure **7b**

7b-E **G [HA] = -448,25733900**				**7b-Z** **G [HA] = -448,26018500**			
H	-2.42671700	2.30531400	-0.51298800	H	-3.42363500	-1.81385100	0.00024400
C	-2.10922500	1.29194000	-0.29836600	C	-2.68525300	-1.02114400	0.00012800
C	-3.04168500	0.34049800	0.10276100	C	-3.08814300	0.31053000	0.00004200
H	-4.08475200	0.61037500	0.21218500	H	-4.14112100	0.56390100	0.00009500
C	-2.62497600	-0.96566800	0.34566700	C	-2.12323800	1.31418800	-0.00011500
H	-3.34404000	-1.71764600	0.64740700	H	-2.42640900	2.35439300	-0.00019200
C	-1.28763100	-1.31078200	0.20147900	C	-0.77015700	1.00043200	-0.00018000
H	-0.97084400	-2.32921200	0.39472500	H	-0.04175500	1.79654300	-0.00030700
C	-0.33124000	-0.35781700	-0.17799500	C	-0.34624300	-0.33964400	-0.00008600
C	-0.77083000	0.94596300	-0.44515400	C	-1.33378300	-1.33882600	0.00006200
H	-0.06527800	1.68632000	-0.79902200	H	-1.03208500	-2.38031600	0.00012600
C	1.07203200	-0.77169800	-0.31708500	C	1.05481400	-0.76471200	-0.00014500
C	2.15436800	-0.06817900	0.00735000	C	2.17818400	-0.04633700	0.00002100
H	1.25209500	-1.77182200	-0.69764500	H	1.21342400	-1.83710000	-0.00033600
F	3.37040300	-0.64503500	-0.23198000	C	3.58055400	-0.54061400	-0.00004500
C	2.30894900	1.26447100	0.64769500	H	3.60953700	-1.62912400	-0.00021600
H	1.36530900	1.61355700	1.06165000	H	4.11329600	-0.17335300	0.88142100
H	2.67665100	2.00561900	-0.06770500	H	4.11331700	-0.17307900	-0.88138500
H	3.04537700	1.19043300	1.45111000	F	2.13500200	1.31652700	0.00027300

Cartesian Coordinates of the Optimized Structure **8b**

8b-E				**8b-Z**			
G [HA] = -487,56372800				**G [HA] = -487,56129000**			
H	-2.77779700	-1.87746700	1.34560800	H	-2.69519200	-2.18361200	0.91185000
C	-2.35569800	-1.06955100	0.76005200	C	-2.31514300	-1.25050600	0.51345000
C	-3.17683200	-0.29211500	-0.04992700	C	-3.18941100	-0.32633400	-0.05106200
H	-4.23967200	-0.49359100	-0.10312800	H	-4.25092100	-0.53616000	-0.09926600
C	-2.62344500	0.75107100	-0.78739800	C	-2.68672000	0.87061800	-0.54961700
H	-3.25481700	1.36125100	-1.42206800	H	-3.35580700	1.59885600	-0.99218300
C	-1.26003100	1.01169000	-0.71676300	C	-1.32457100	1.14039900	-0.48179300
H	-0.83875300	1.82054600	-1.30154400	H	-0.95445800	2.07722900	-0.87832600
C	-0.42001100	0.23010600	0.08486100	C	-0.43072100	0.21524000	0.07285300
C	-0.99127400	-0.80721100	0.82914200	C	-0.95334700	-0.98350800	0.57517600
H	-0.35732900	-1.40492200	1.47270500	H	-0.28511100	-1.70887900	1.01794300
C	1.03464400	0.53073000	0.16870400	C	1.01936000	0.53541600	0.15869000
C	1.94701900	-0.38435300	-0.15758600	C	1.96317600	-0.36274100	-0.13613100
F	3.27446900	-0.06485300	-0.02414600	C	3.44867200	-0.26778800	-0.12234200
C	1.79338800	-1.75944100	-0.70505800	H	3.80150600	0.69876300	0.22635800
H	0.75152200	-1.98758800	-0.91605900	H	3.84026600	-0.43743900	-1.12909700
H	2.18279600	-2.50119100	-0.00222400	H	3.86415900	-1.04635500	0.52324300
H	2.37148800	-1.84970400	-1.62847300	F	1.58753800	-1.61200300	-0.55554200
C	1.41715000	1.90799400	0.64871900	C	1.36953800	1.94401100	0.57917300
H	1.01968700	2.08288600	1.65234800	H	0.78949600	2.22808400	1.45987500
H	0.98707500	2.67589500	0.00029200	H	1.12943900	2.66348900	-0.20849900
H	2.49611100	2.04405200	0.67137500	H	2.42378300	2.06521700	0.81759700

Cartesian Coordinates of the Optimized Structure **9b**

9b-E **G [HA] = -562,79636700**				**9b-Z** **G [HA] = -562,79950300**			
H	-1.55525600	2.23450300	-0.63835700	H	-2.48003600	1.87919200	0.00042300
C	-1.20700000	1.23316900	-0.42021400	C	-1.76462700	1.06933300	0.00023200
C	-2.14843700	0.26012600	-0.07421900	C	-2.17799600	-0.26233100	0.00002700
C	-1.72173100	-1.04511100	0.17402700	C	-1.21509700	-1.27631200	-0.00021600
H	-2.42496300	-1.82434800	0.43076200	H	-1.55116600	-2.30527900	-0.00038100
C	-0.36780800	-1.35420400	0.08843000	C	0.13254000	-0.97137100	-0.00025000
H	-0.05096600	-2.37176000	0.28628900	H	0.84999400	-1.77748900	-0.00044100
C	0.59299800	-0.39040300	-0.23011600	C	0.57657500	0.36573500	-0.00004200
C	0.13514700	0.90910300	-0.50341600	C	-0.40505600	1.36363400	0.00019200
H	0.83853300	1.67061600	-0.81374400	H	-0.10173200	2.40468200	0.00035100
C	2.00787800	-0.77760100	-0.30579300	C	1.98044900	0.77528800	-0.00006500
C	3.06263500	-0.05520300	0.06471300	C	3.09655500	0.04603600	-0.00007300
H	2.22445300	-1.77194900	-0.68299600	H	2.15035300	1.84619600	-0.00005100
F	4.30012200	-0.60707900	-0.12897900	C	4.50483200	0.52291700	-0.00008600
C	3.16465500	1.27821300	0.71410700	H	4.54632200	1.61127900	-0.00004100
H	2.20002000	1.60031700	1.10109000	H	5.03417300	0.15036400	-0.88163000
H	3.53428200	2.03362800	0.01459300	H	5.03421100	0.15028800	0.88140200
H	3.87732600	1.21931200	1.53995100	F	3.03692700	-1.31884500	-0.00007000
O	-3.44547100	0.67888800	-0.02029800	O	-3.47809600	-0.67459200	0.00004500
C	-4.45149400	-0.26876500	0.30999100	C	-4.50196200	0.31035500	0.00024200
H	-5.39214500	0.27722100	0.29362500	H	-5.44217900	-0.23671900	0.00018700
H	-4.29585100	-0.68896900	1.30910700	H	-4.45242600	0.94221000	-0.89275700
H	-4.49382500	-1.08189100	-0.42217400	H	-4.45236300	0.94191900	0.89344400

Cartesian Coordinates of the Optimized Structure **10b**

10b-E				**10b-Z**			
G [HA] = -601,90962300				**G [HA] = -601,91242000**			
C	2.42224400	0.66981400	-0.39034400	C	-2.40871800	0.73076100	-0.00028200
C	3.28037400	-0.25459800	0.03575300	C	-3.30788800	-0.25458700	0.00000400
C	3.07477800	-1.49287400	0.83151500	C	-0.94609200	0.67985200	-0.00016000
H	2.07918300	-1.51374500	1.26992800	C	-0.24951800	1.92408400	0.00003600
H	3.20669400	-2.38579600	0.21381700	C	1.11688800	1.98304700	0.00016400
H	3.81945100	-1.53286900	1.62969700	C	1.89633600	0.80017800	0.00009300
F	4.60295600	-0.05935700	-0.24687000	C	1.21603500	-0.45607000	-0.00012200
C	0.96271300	0.66235400	-0.22808800	C	-0.19734100	-0.48464000	-0.00024800
C	0.30557600	1.89492300	0.04808700	C	1.98786200	-1.64735000	-0.00020500
C	-1.05097800	1.95571500	0.21491900	C	3.35839900	-1.59799200	-0.00008000
C	-1.85317300	0.79170000	0.10839800	C	4.02846700	-0.35356900	0.00013500
C	-1.21222600	-0.44856500	-0.19291800	C	3.31226200	0.81706100	0.00021800
C	0.19248500	-0.47521200	-0.36255100	H	-0.82376000	2.84365100	0.00009200
C	-2.00941400	-1.61420100	-0.32199300	H	1.62005500	2.94332700	0.00031900
C	-3.36990200	-1.55758300	-0.15413900	H	-0.68864900	-1.44617600	-0.00042100
C	-4.00168800	-0.33095900	0.14905000	H	1.47349400	-2.60156400	-0.00036900
C	-3.25895400	0.81626600	0.27539300	H	3.93460800	-2.51524100	-0.00014400
H	0.90207600	2.79534300	0.13694600	H	5.11133300	-0.32879200	0.00023200
H	-1.53043400	2.90346700	0.43231500	H	3.82396100	1.77294600	0.00038400
H	0.65850400	-1.41503600	-0.63210400	H	-2.83963700	1.72539400	-0.00060800
H	-1.52508700	-2.55566000	-0.55559900	C	-4.79020200	-0.14107100	-0.00009900
H	-3.96682200	-2.45588800	-0.25409600	F	-2.91011000	-1.55862000	0.00046200
H	-5.07647400	-0.30027200	0.27914300	H	-5.09961000	0.90295600	-0.00043700
H	-3.74156000	1.75953700	0.50495800	H	-5.20991000	-0.63330400	0.88154400
H	2.85686500	1.53445600	-0.88165800	H	-5.20983200	-0.63385100	-0.88147400

Cartesian Coordinates of the Optimized Structure **11b**

11b-E **G [HA] = -679,32185500**				**11b-Z** **G [HA] = -679,32509000**			
H	0.52431100	1.66331000	1.06436800	H	0.51858300	-1.86981800	0.50874300
C	0.08504600	0.78047200	0.61624200	C	0.09106300	-0.91237100	0.23699900
C	0.91869400	-0.19165300	0.05149800	C	0.94183800	0.16441800	-0.04272200
C	0.31450000	-1.34756100	-0.45876700	C	0.34837500	1.39228100	-0.35715600
H	0.92908400	-2.11394800	-0.91481200	H	0.97386700	2.24177400	-0.60263300
C	-1.06072500	-1.51480400	-0.41898300	C	-1.02965800	1.53060800	-0.39093600
H	-1.50040700	-2.41486100	-0.83314600	H	-1.45711000	2.49336200	-0.64821200
C	-1.89914700	-0.53032500	0.12262400	C	-1.88550900	0.45320000	-0.11111900
C	-1.29145700	0.61281200	0.65866700	C	-1.28813700	-0.77817900	0.20653900
H	-1.89873700	1.36225800	1.14928400	H	-1.90480300	-1.63260800	0.43924600
C	-3.34987400	-0.75396500	0.14070300	C	-3.32762800	0.68787100	-0.16919600
C	-4.30734400	0.15291700	-0.04284800	C	-4.34890800	-0.14284400	0.04461100
H	-3.68603300	-1.77489100	0.29014500	H	-3.62325600	1.69836000	-0.42781000
F	-5.60157100	-0.27789900	0.04401100	C	-5.80317600	0.15651200	-0.02945600
C	-4.24352400	1.59860800	-0.38246600	H	-5.97239500	1.19896500	-0.29509200
H	-3.24256800	1.88343300	-0.69961900	H	-6.28260500	-0.04493000	0.93252900
H	-4.53382900	2.21836500	0.47072400	H	-6.28553900	-0.48085700	-0.77573700
H	-4.94652100	1.80548000	-1.19258400	F	-4.12835700	-1.44685200	0.37782300
C	2.38768300	-0.01014900	0.00861200	C	2.41366600	0.00982200	-0.00710100
C	2.94896300	1.23851100	-0.28770800	C	3.02853200	-1.14632900	-0.50469600
H	2.29818800	2.07508500	-0.51102100	H	2.41905100	-1.92690800	-0.94315500
C	4.32736700	1.41027400	-0.32926100	C	4.41022900	-1.29128000	-0.47189200
H	4.73996900	2.38296800	-0.56872100	H	4.86477400	-2.19042500	-0.87028400
C	5.17572900	0.33659500	-0.07579400	C	5.20913300	-0.28318500	0.05956800
H	6.25000800	0.47012500	-0.10831300	H	6.28597200	-0.39617600	0.08518900
C	4.63241500	-0.90998900	0.22026200	C	4.61248700	0.87124400	0.55777400
H	5.28395700	-1.75025900	0.42793400	H	5.22420600	1.65851300	0.98181000
C	3.25398200	-1.08112400	0.26232300	C	3.23074500	1.01572500	0.52483400
H	2.84286700	-2.04968800	0.51904600	H	2.77614800	1.90744800	0.93868700

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