Supporting Information

Rh-Catalyzed Allylic C-F Bond Activation: The Stereosynthesis of Trisubstituted Monofluoroal-kenes and A Mechanism Study

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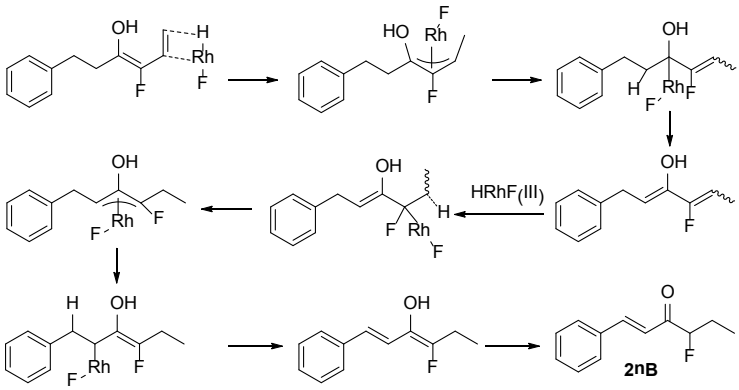
Contents

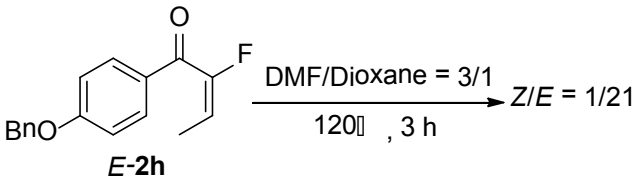
1. Proposed Mechanism for the Generation of 2nB (compare *Organometallics*, 2003, *22*, 1626):



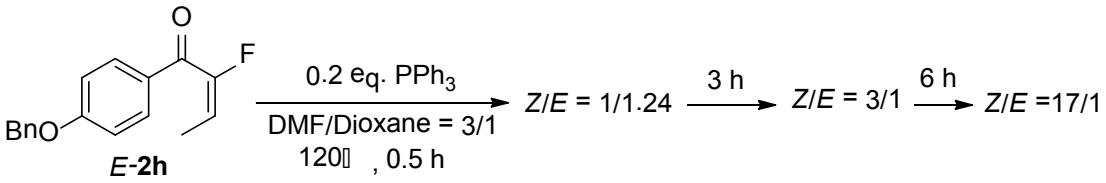
2nB HRMS(EI) calcd. for $C_{12}H_{13}OF$ $[M]^+$192.0950; found 192.0953.

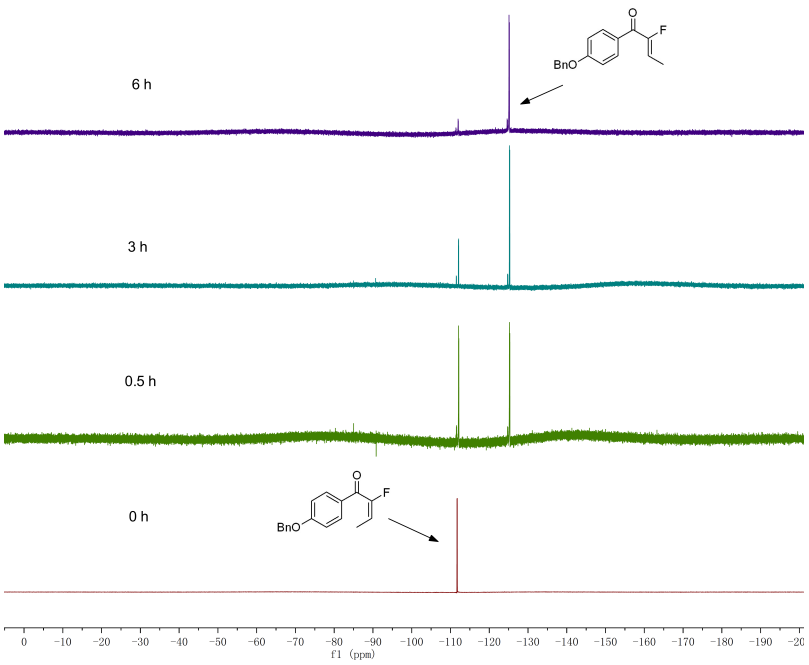
2. The Isomerization of α-Fluoro-α,β-unsaturated Ketones Mediated by Triphenylphosphine

In a glove box, *E*-**2h**(27 mg, 0.1 mmol), dioxane (0.1 mL) and DMF (0.3 mL) were added to an NMR tube, which was then heated at 120 °C for 3 h. The ratio of stereoisomers was determined by ^{19}F NMR.

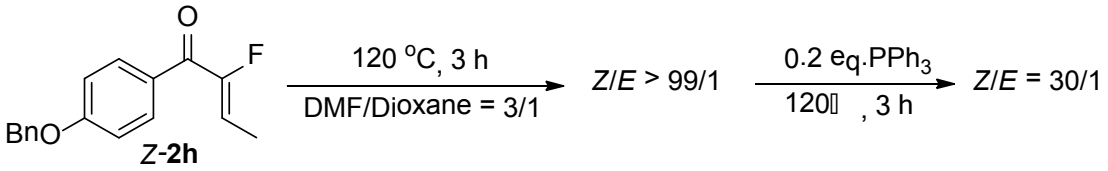


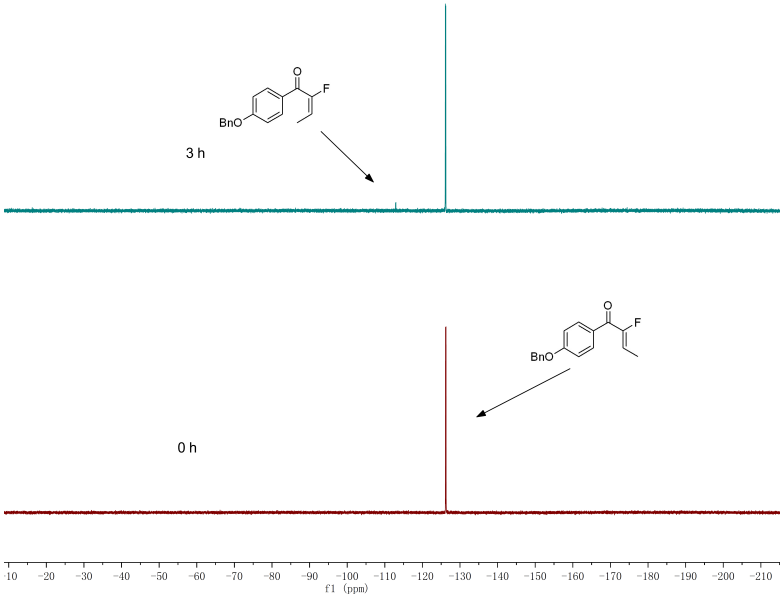
In a glove box, *E*-**2h** (27 mg, 0.1 mmol), dioxane (0.1 mL) and DMF (0.3 mL) were added to an NMR tube, which was then heated at 120°C. The ratio of stereoisomers was determined by ^{19}F NMR after 0, 0.5 h, 3 h and 6 h to be 1/0, 1/1.24, 1/3 and 1/17, respectively.



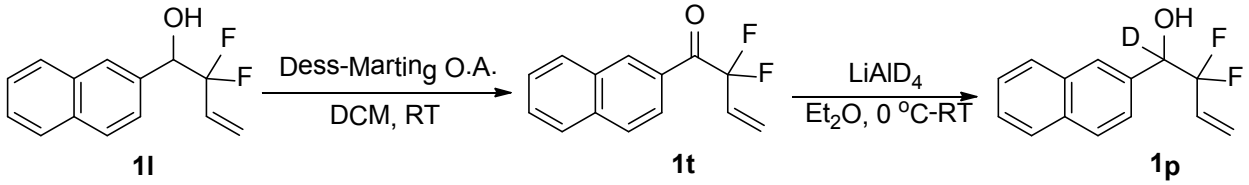


In a glove box, *Z*-**2h** (52 mg, 0.2 mmol), dioxane (0.2 mL) and DMF (0.6 mL) were added to an NMR tube, which was then heated at 120 °C for 3 h. The ratio of stereoisomers was determined by ^{19}FNMR.

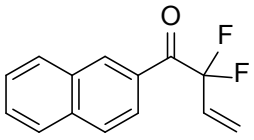




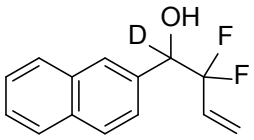
3. Deuterated experiments



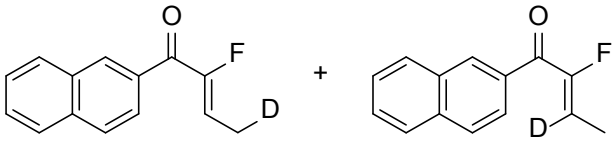
Into a 100 mL round bottom flask were added **1l** (702 mg, 3 mmol), DCM (30 mL) and Dess-Marting reagent (3.8g, 9 mmol). The mixture was stired at room temperature for overnight. Then the reaction was quenched with saturated $Na_2S_2O_3$ (50 mL). The mixture was extracted with 50 mL Et_2O, the organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford the product **1t**. Into a 25 mL round bottom flask were added $LiAlD_4$ (42 mg, 1 mmol) and Et_2O (5 mL). The mixture was cooled in an ice bath. Then **1t** (232 mg, 1 mmol) was added. The mixture was stirred at room temperature for 1h. Then the reaction was quenched with H_2O (10 mL). The mixture was extracted with 30 mL Et_2O, the organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford the product **1p.**



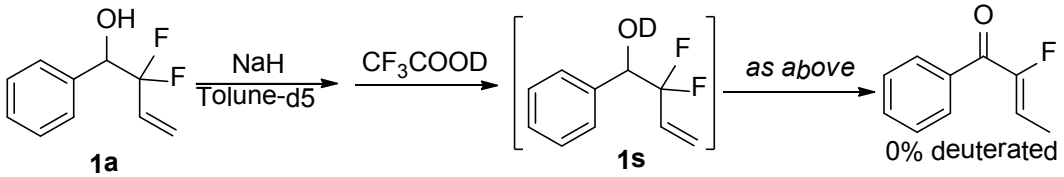
2,2-difluoro-1-(naphthalen-2-yl)but-3-en-1-one (**1t**): 94% yield. Colorless oil. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.63 (s, 1H), 8.08 – 8.01 (m, 1H), 7.95-7.91 (m, 1H), 7.87-7.80 (m, 2H), 7.62-7.50 (m, 2H), 6.36-6.21 (m, 1H), 5.93-5.86 (m, 1H), 5.67 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 188.61 (t, *J* = 30.8 Hz), 135.87 (s), 132.77 (t, *J* = 4.2 Hz), 132.12 (s), 129.95 (s), 129.86 (t, *J* = 25.2 Hz), 129.31 (s), 129.06 (t, *J* = 2.0 Hz), 128.48 (s), 127.67 (s), 126.94 (s), 124.69 (t, *J* = 2.1 Hz), 122.68 (t, *J* = 9.6 Hz), 115.62 (t, *J* = 250.6 Hz); ^{19}F NMR (376 MHz, cdcl$_3$) δ -99.20 (dd, *J* = 11.2, 2.1 Hz, 2F); IR (neat) ν = 3061, 1697, 1626, 1596, 1189, 1087, 967, 775 cm-1; HRMS(EI) calcd. for $C_{14}H_{10}F_2O$ $[M]^+$232.0700; found 232.0704.



2,2-difluoro-1-(naphthalen-2-yl)but-3-en-1-ol (**1p**): 81% yield. Colorless oil. ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.99 – 7.66 (m, 4H), 7.63 – 7.37 (m, 3H), 5.83 (m, 1H), 5.59-5.51 (m, 1H), 5.39 (d, *J* = 11.1 Hz, 1H), 2.97 (s, 1H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 133.44-133.34 (m), 133.06 (d, *J* = 54.6 Hz), 129.28 (t, *J* = 25.6 Hz), 128.11 (s), 127.84 (s), 127.61 (s), 127.07 (s), 126.35 (s), 126.19 (s), 124.96 (s), 121.62 (t, *J* = 9.2 Hz), 119.66 (t, *J* = 244.6 Hz); ^{19}F NMR (376 MHz, cdcl$_3$) δ -107.59 (dd, *J* = 246.8, 11.2 Hz, 1F), -108.93 (dd, *J* = 246.8, 12.4 Hz, 1F); IR (neat) ν = 3429, 3059, 1419, 1233, 1175, 1073, 985, 822 cm-1; HRMS(EI) calcd. for $C_{14}{}^{1}H_{11}F_2OD$ $[M]^+$235.0919; found 235.0916.



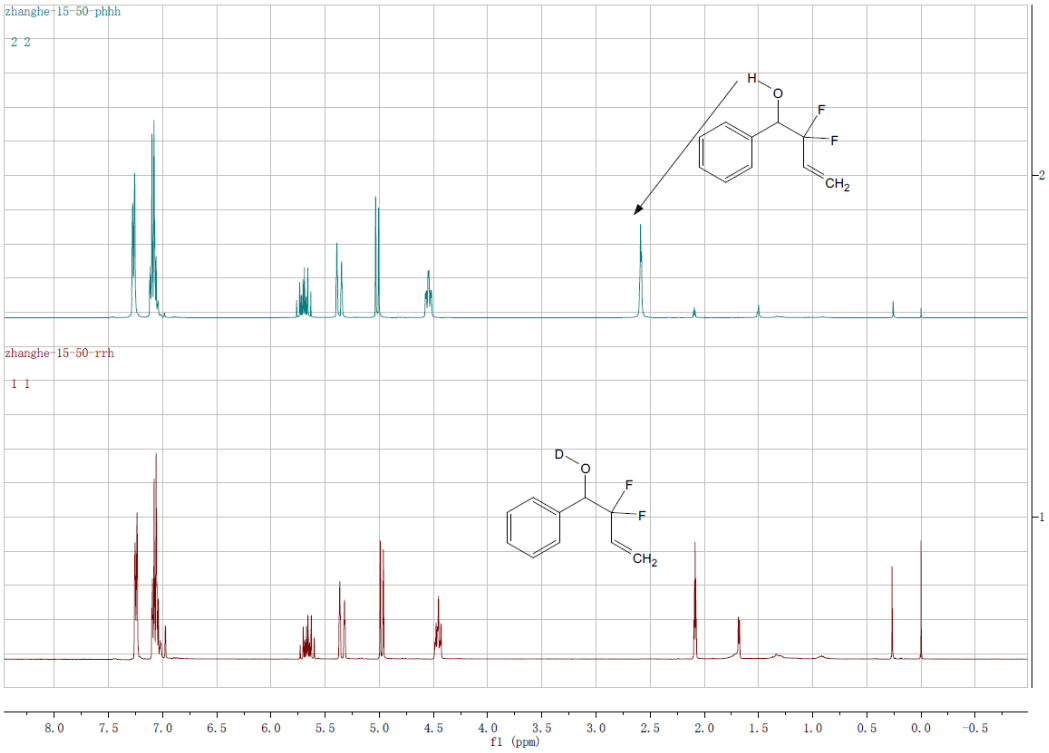
[(Z)-2-fluoro-1-(naphthalen-2-yl)but-2-en-1-one]-d1(**2q**+**2r**): colorless liquid. 75% yield. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.34 (s, 1.3H), 7.89 (m, 5.6H), 7.57 (m, 2.9H), 6.15 (dt, *J* = 33.9, 6.8 Hz, 1.0H), 1.96 – 1.84 (m, 3.1H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 187.25 (d, *J* = 28.0 Hz), 156.30 (d, *J* = 261.6 Hz), 135.33 (s), 133.42 (s), 132.21 (s), 130.87 (d, *J* = 4.9 Hz), 129.43 (s), 128.49 (s), 128.32 (s), 127.79 (s), 126.89 (s), 125.02 (d, *J* = 2.7 Hz), 119.10 (d, *J* = 13.5 Hz), 10.17 – 9.66 (td, *J* = 20.0 Hz, 5.0Hz); ^{19}F NMR (376 MHz, cdcl$_3$) δ -124.62 (d, *J* = 33.9 Hz, 3.1F), -125.02 (s, 1F); IR (neat) ν = 2923, 1655, 1627, 1466, 1354, 1296, 1120, 760 cm-1; IR (neat) ν = 3429, 3059, 1419, 1233, 1175, 1073, 985, 822 cm-1; HRMS(EI) calcd. for $C_{14}{}^{1}H_{10}F_1OD$ $[M]^+$215.0857; found 215.0860.



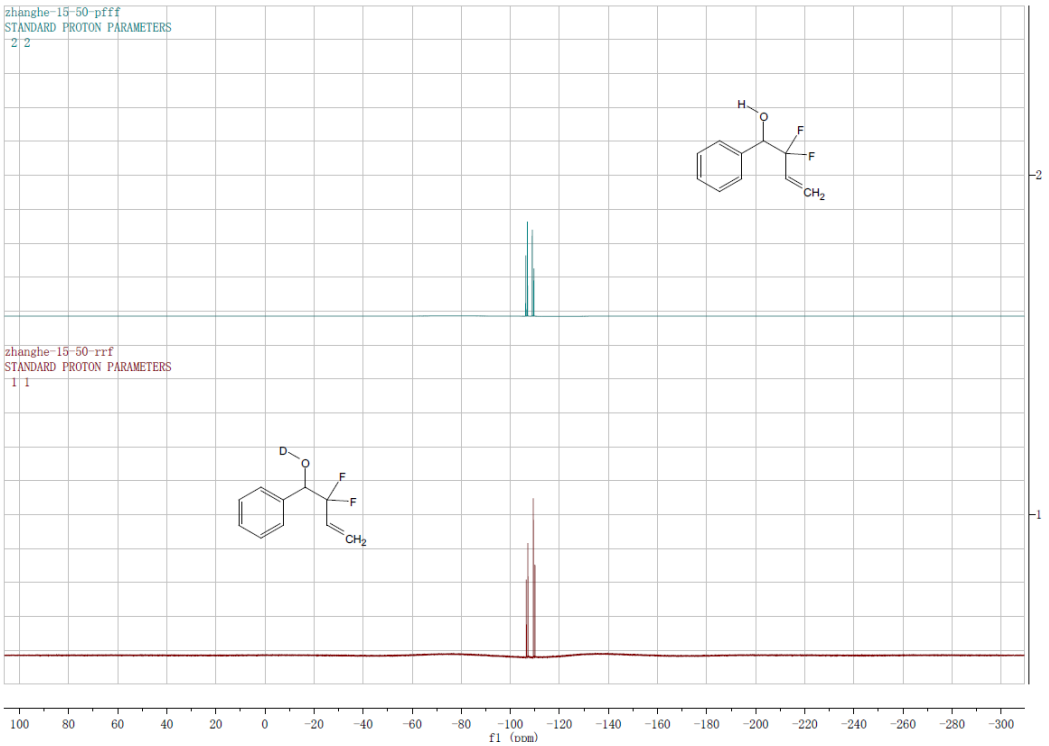
All of the tubes were dried before used. Under N_2, into a 25 mL schlenk tube were added NaH (30 mg, 0.72 mmol) (60% in oil, which was washed by pentane before used) and toluene-d$_5$ (2 mL) (dried by MS 4Å in a glove box before used). The mixture was stired for **1**h at room temperature. Then **1a** (100 μL, 0.6 mmol) was added to the mixure by syringe. The mixture was stired at room temprature for **1**h. Then the reaction was quenched with CF_3COOD (56 μL, 0.72 mmol), and stired for **1**h. The clean liquid was removed to a shlenk tube after filtration. The solvent was removed under reduced pressure. Took a sample of the residue and ran ^{1}H NMR (in toluene-d$_5$). Based on the NMR spectra, we can concluded that

the hydroxy group was deuterated. The deuterated alcohol **1s** was conducted under the standard condition. No deuterated product was detected by GCMS and ^{19}F NMR.

^{1}H NMR of substrate **1a** and the deuterated substrate **1s** (in toluene-d_5).

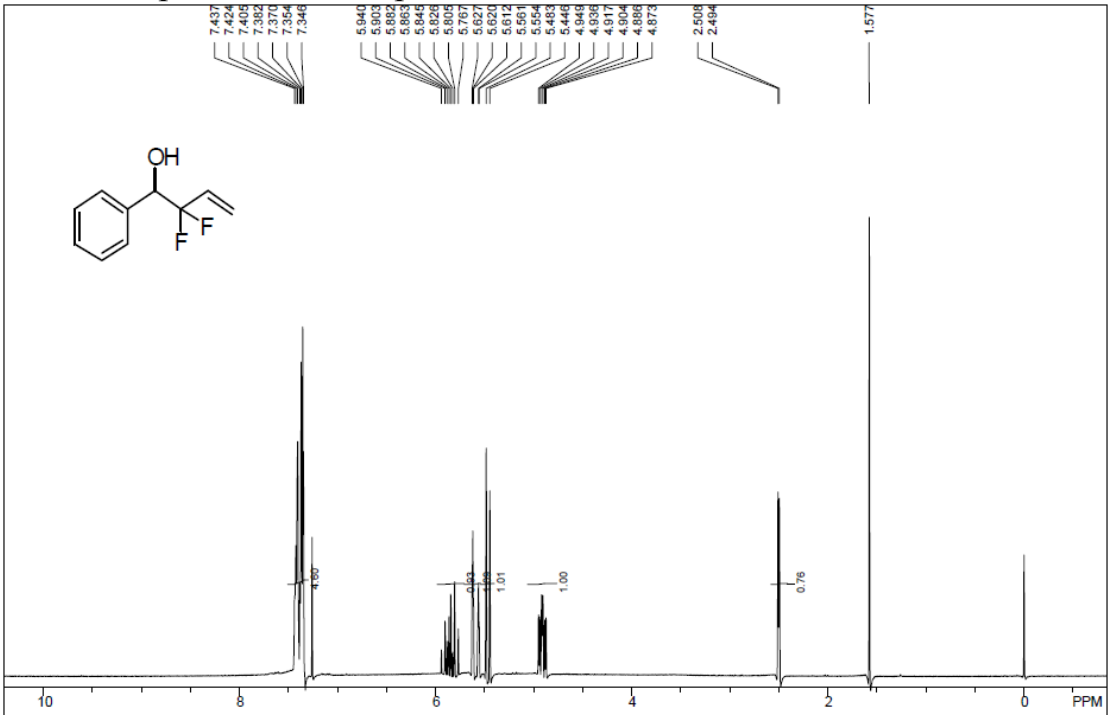


^{19}F NMR of substrate **1a** and the deuterated substrate **1s** (in toluene-d_5).

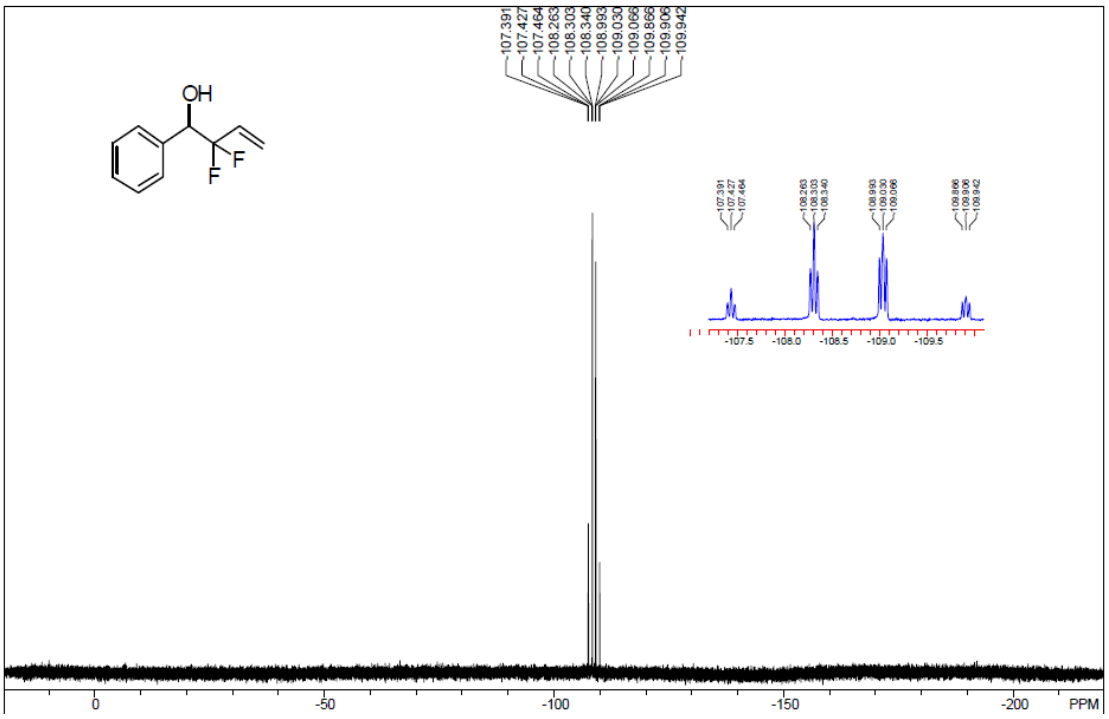


4. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra

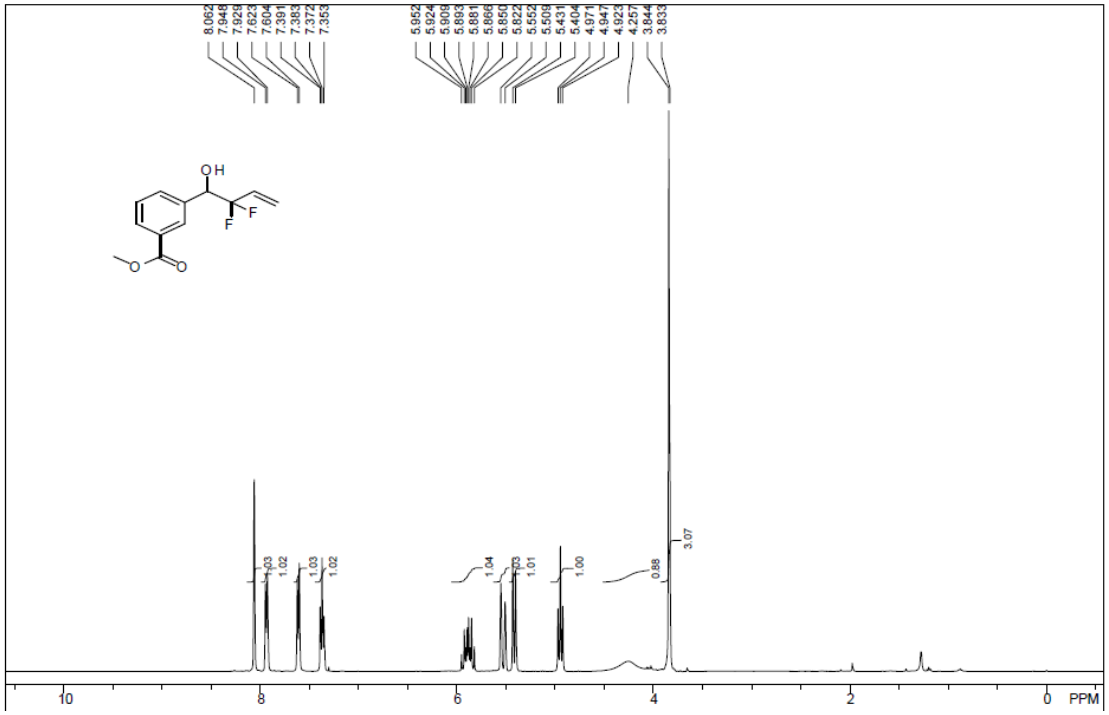
^{1}H NMR spectrum of compound **1a**



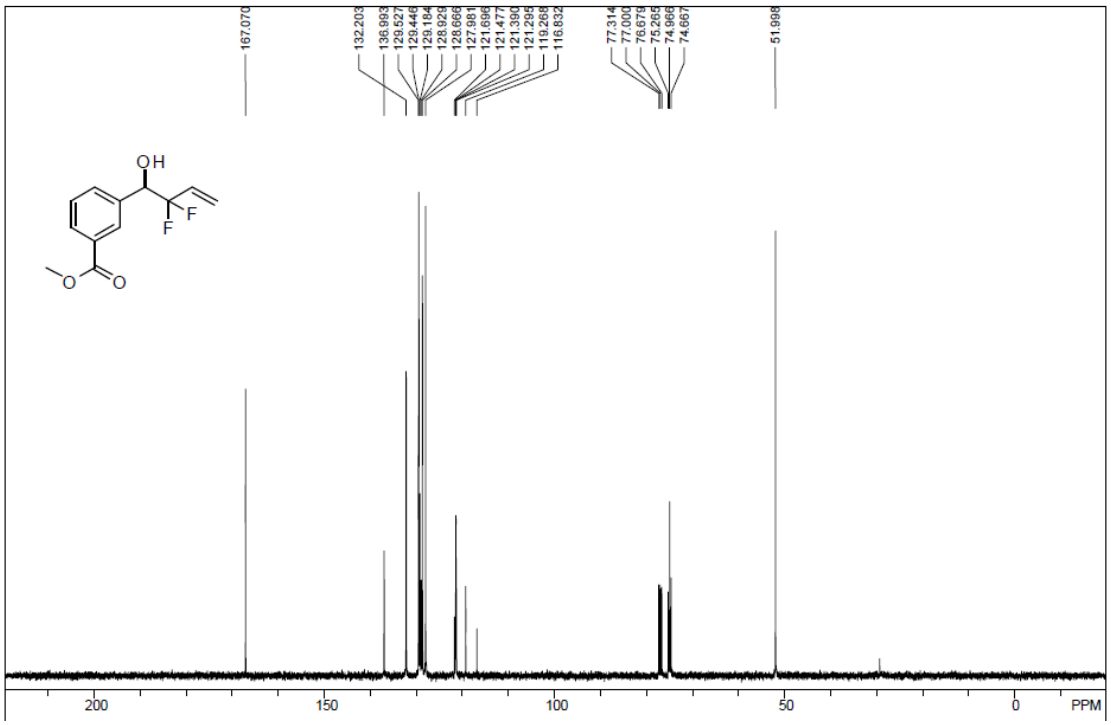
^{19}F NMR spectrum of compound **1a**



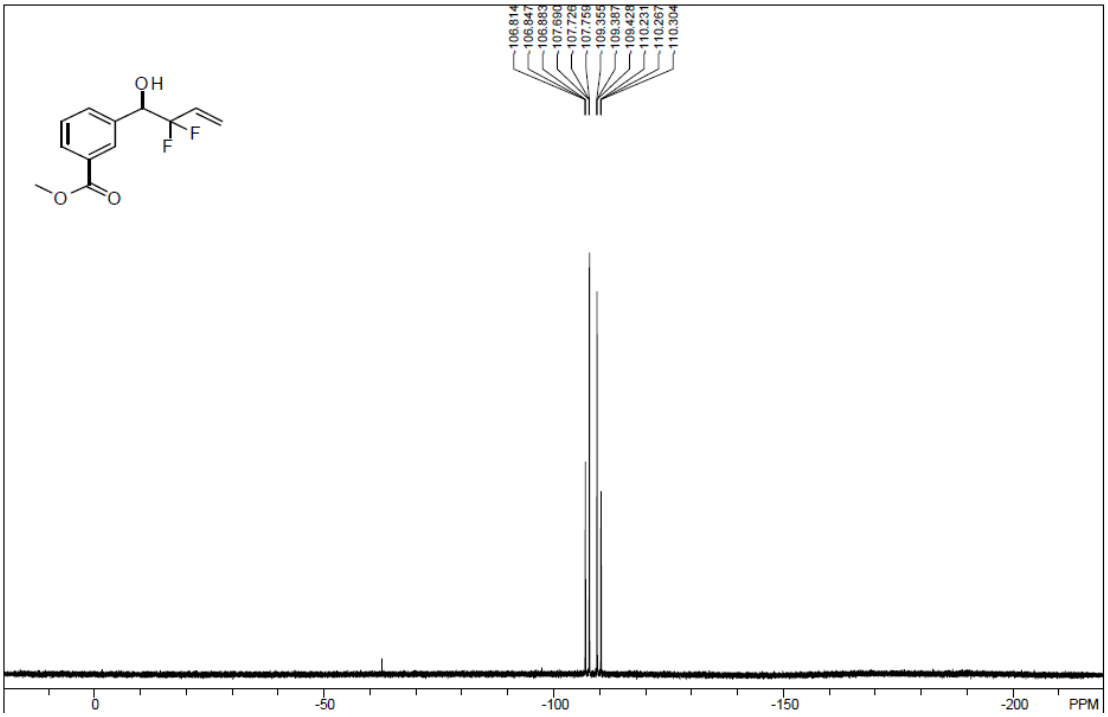
^{1}H NMR spectrum of compound **1b**



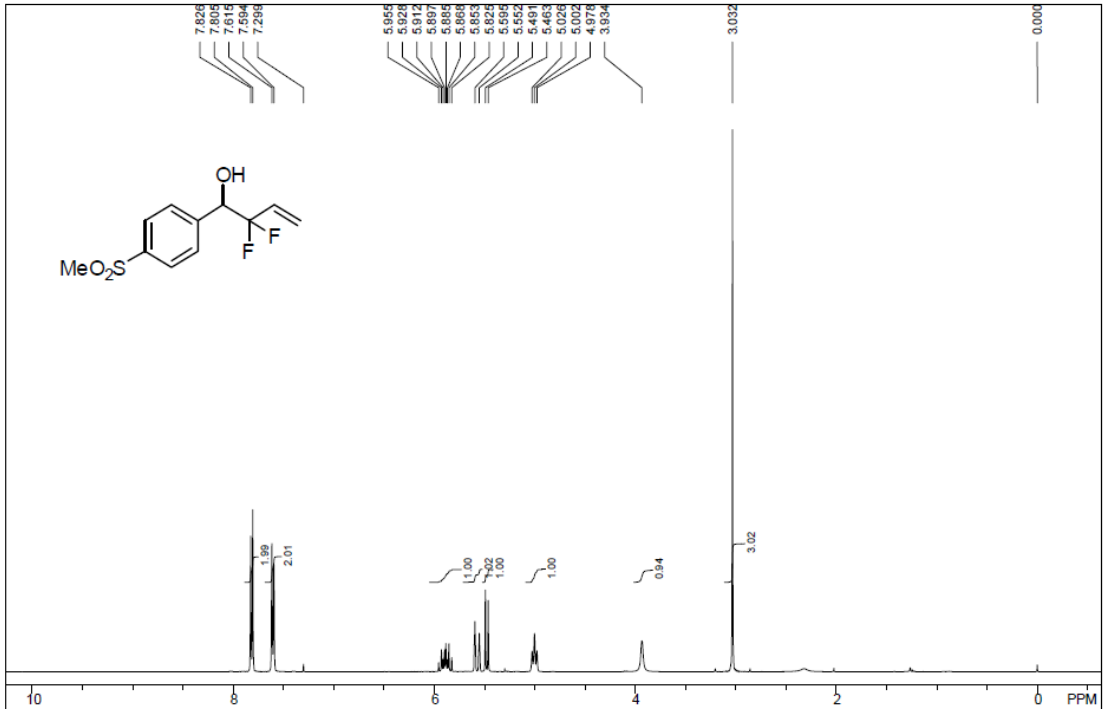
^{13}C NMR spectrum of compound **1b**



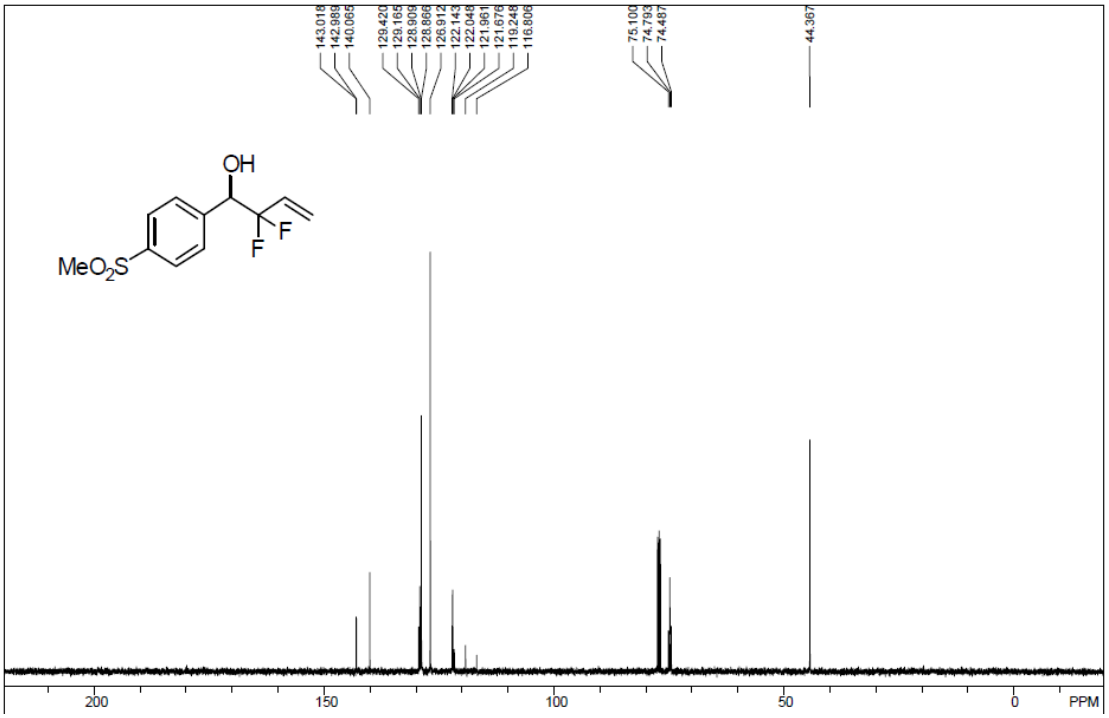
^{19}F NMR spectrum of compound **1b**



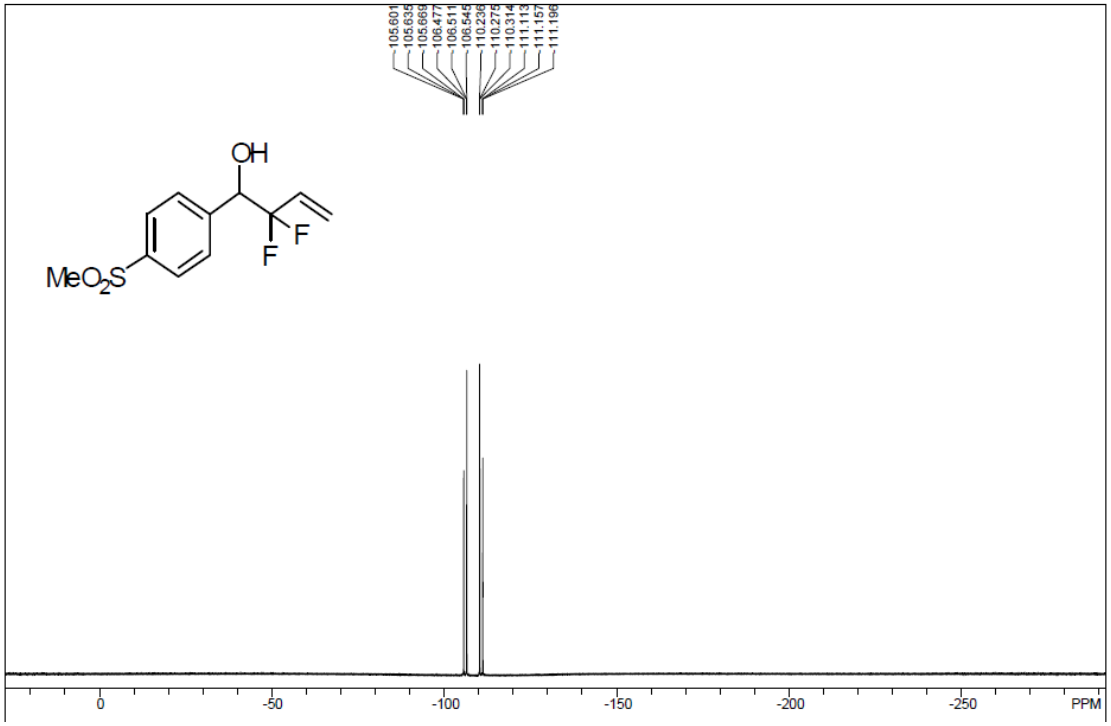
^{1}H NMR spectrum of compound **1c**



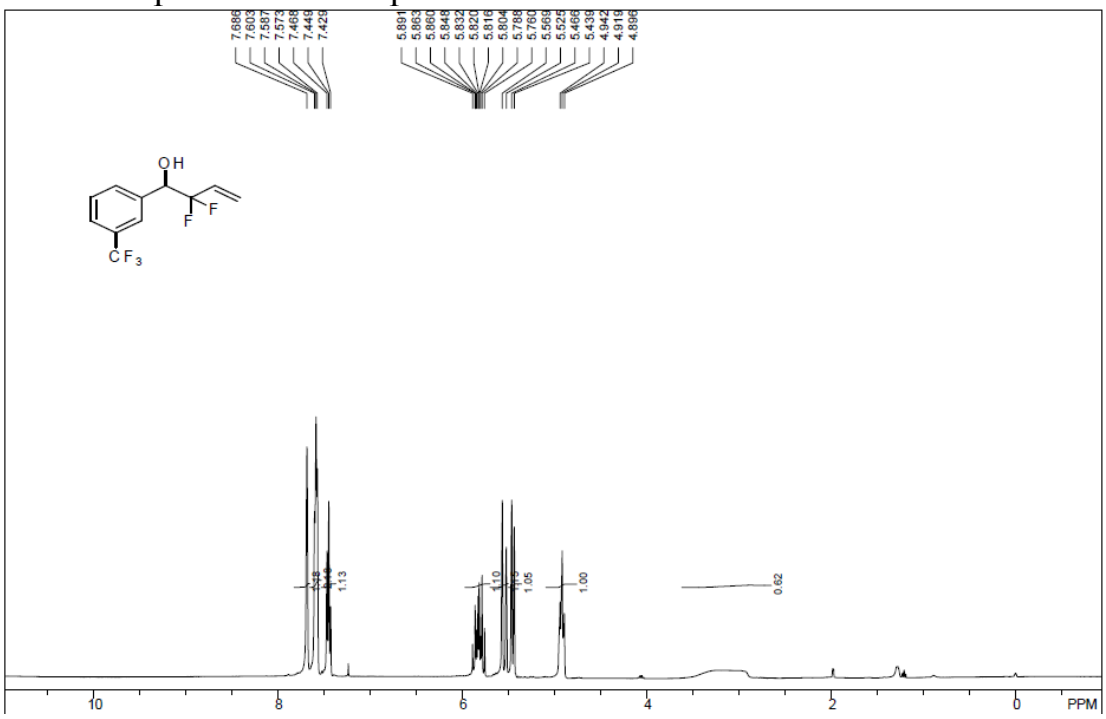
^{13}C NMR spectrum of compound **1c**



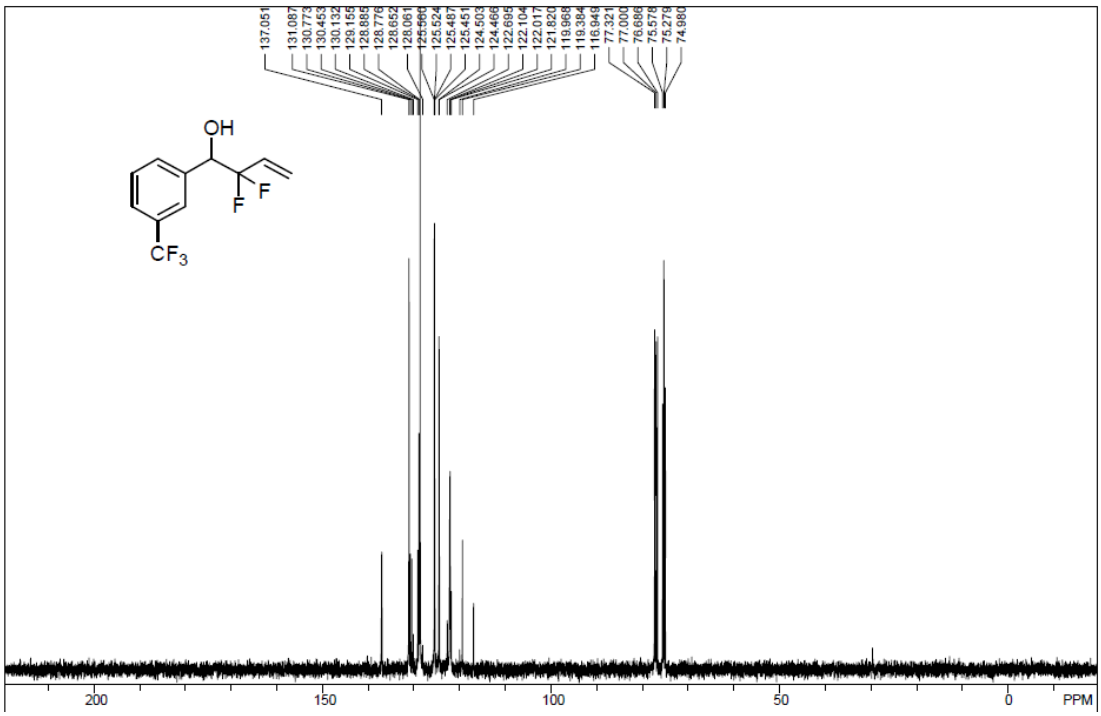
^{19}F NMR spectrum of compound **1c**



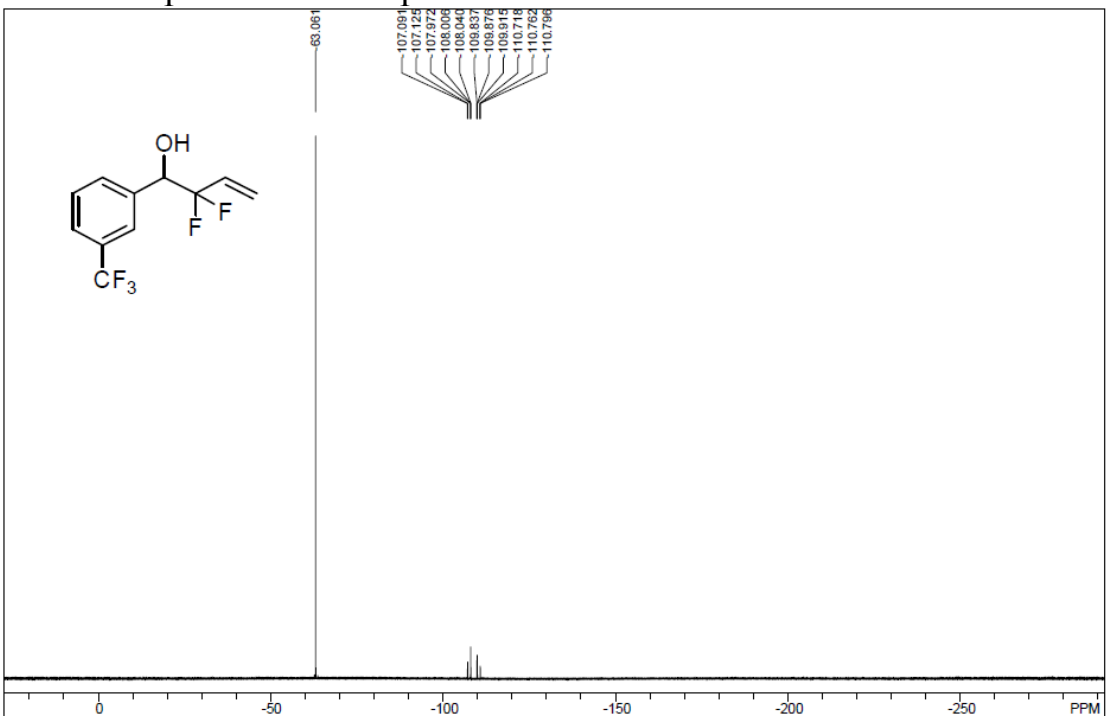
^{1}H NMR spectrum of compound **1d**



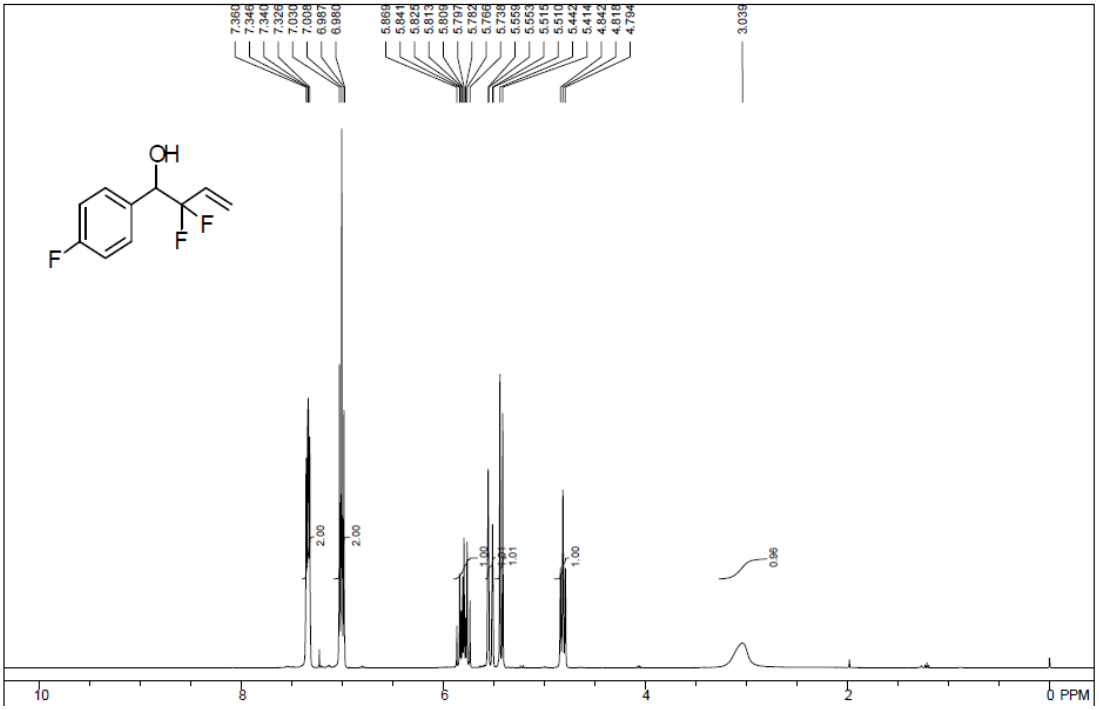
^{13}C NMR spectrum of compound **1d**



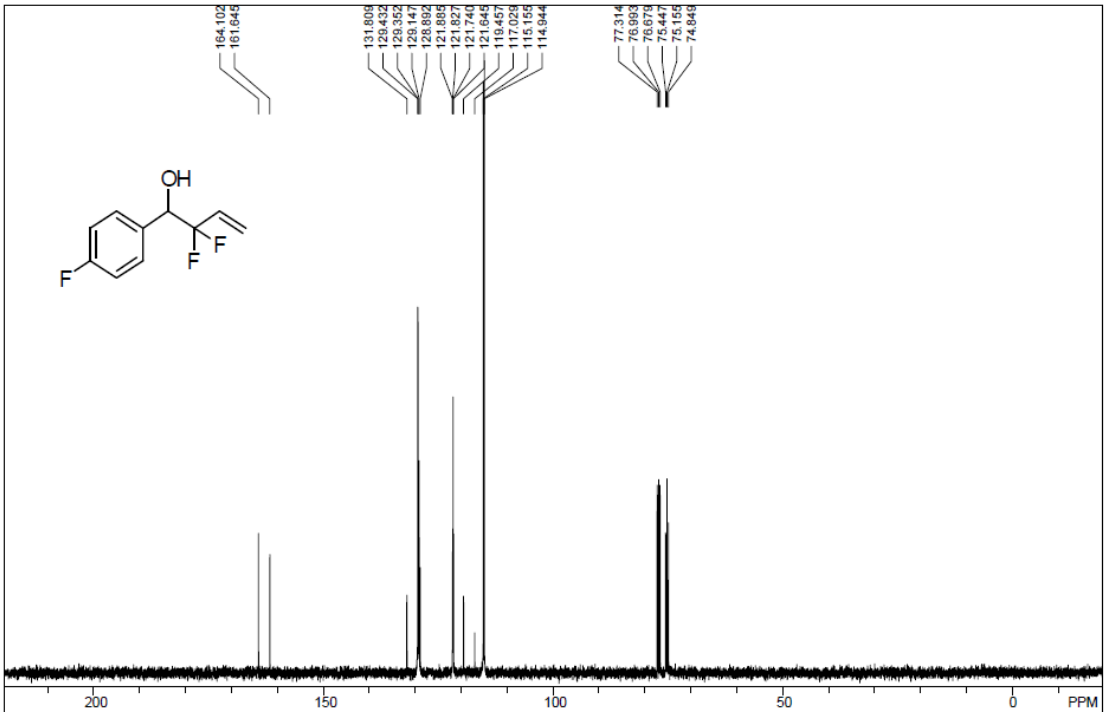
^{19}F NMR spectrum of compound **1d**



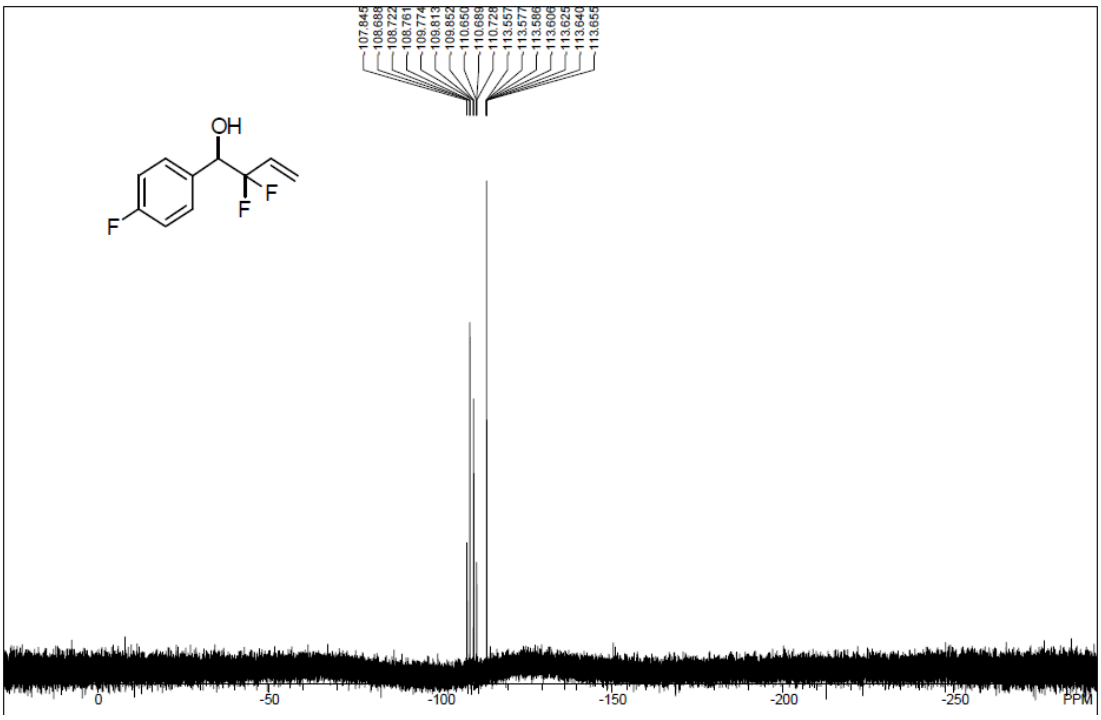
^{1}H NMR spectrum of compound **1e**



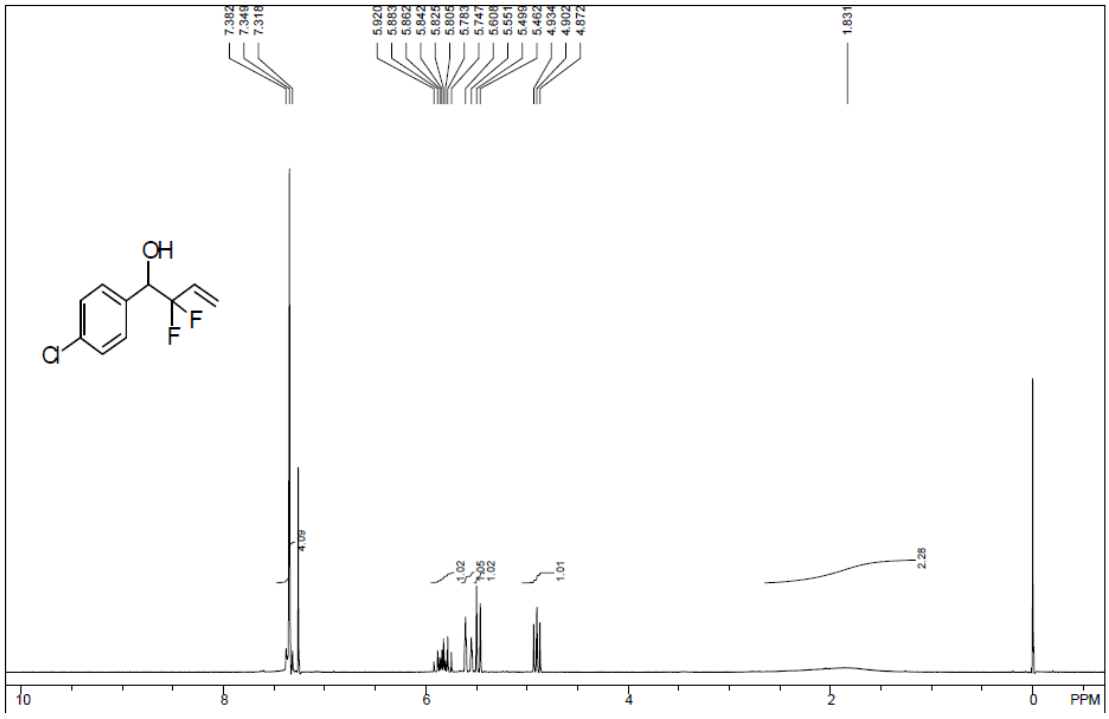
^{13}C NMR spectrum of compound **1e**



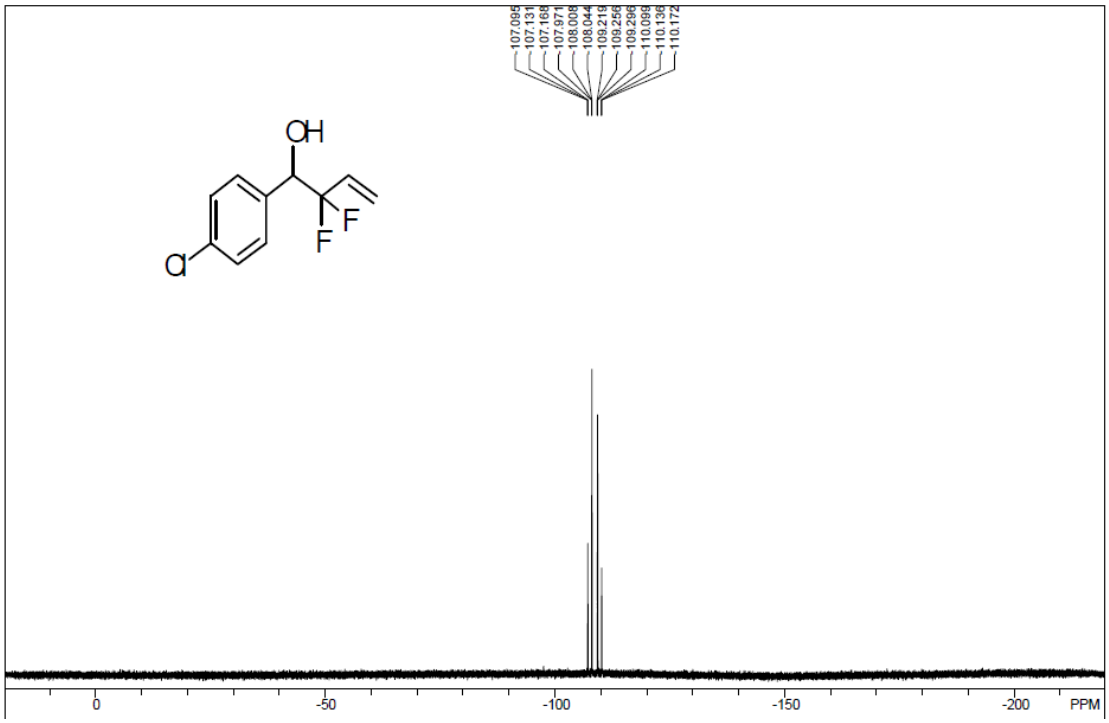
^{19}F NMR spectrum of compound **1e**



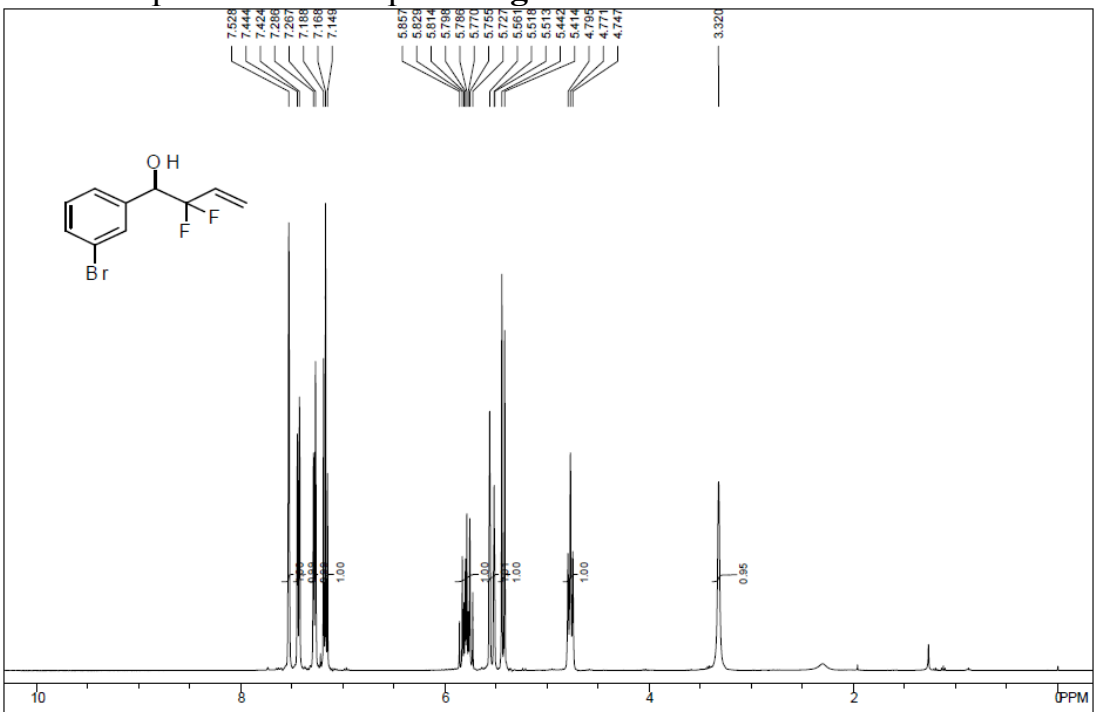
^{1}H NMR spectrum of compound **1f**



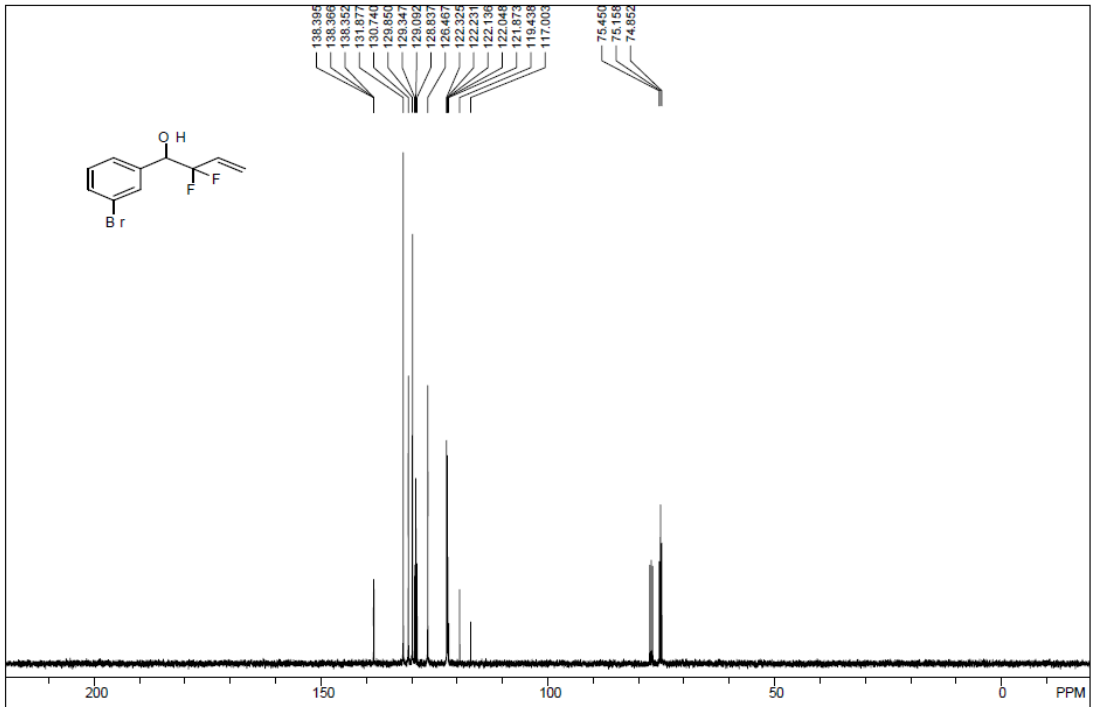
^{19}F NMR spectrum of compound **1f**



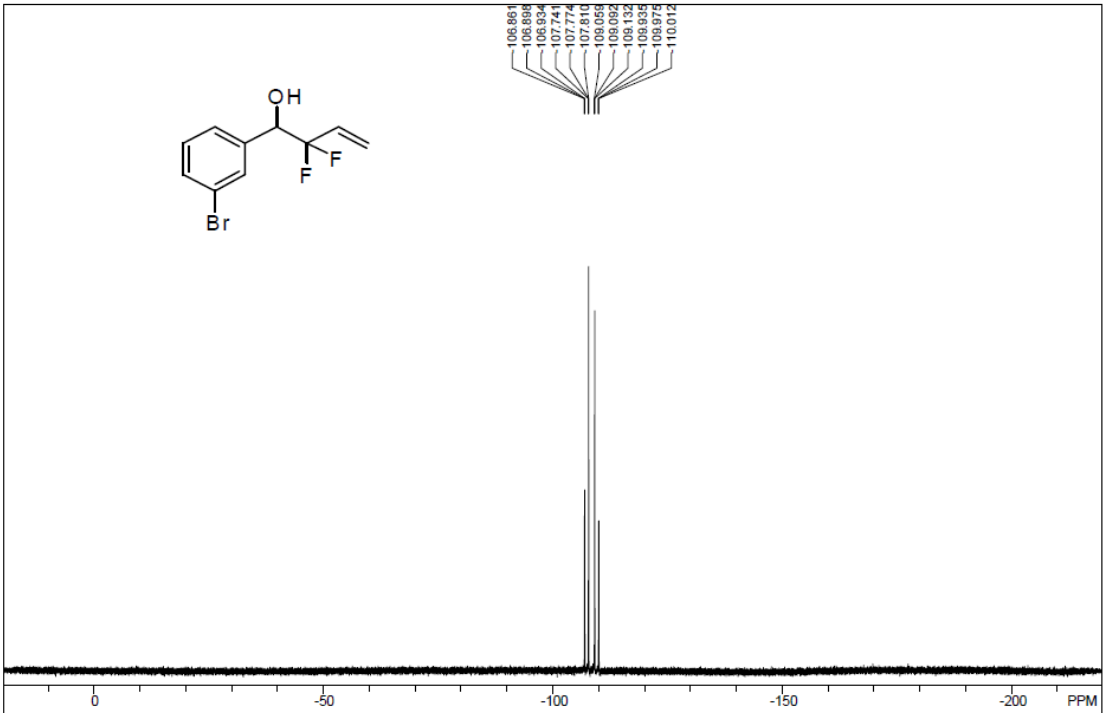
^{1}H NMR spectrum of compound **1g**



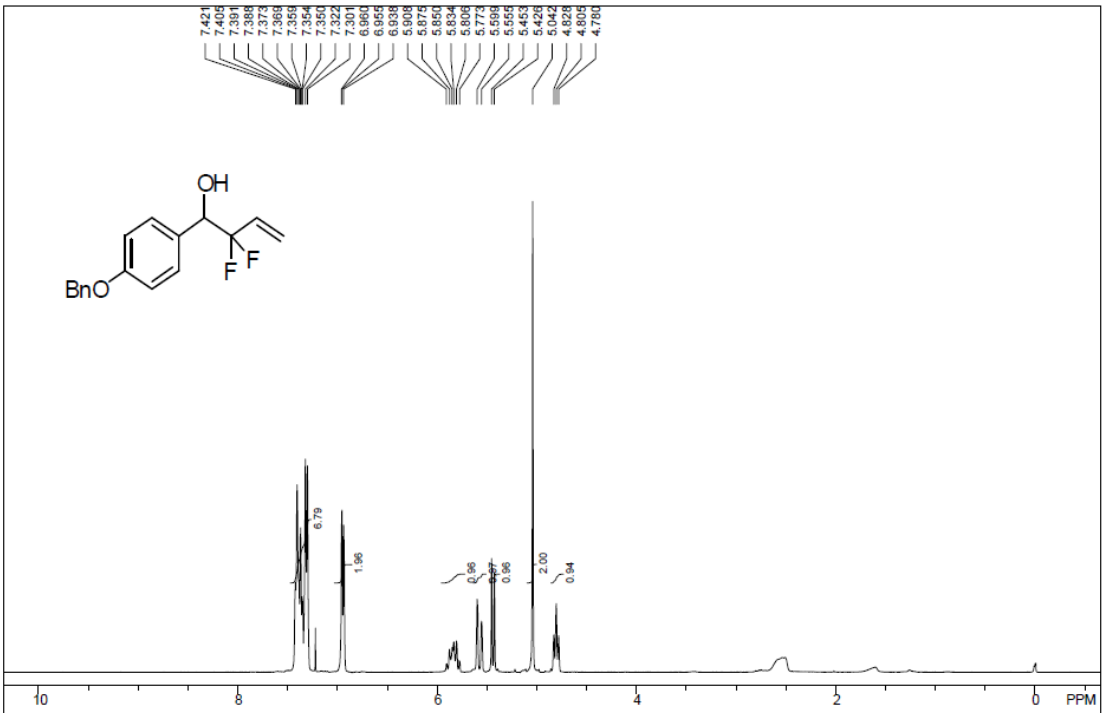
^{13}C NMR spectrum of compound **1g**



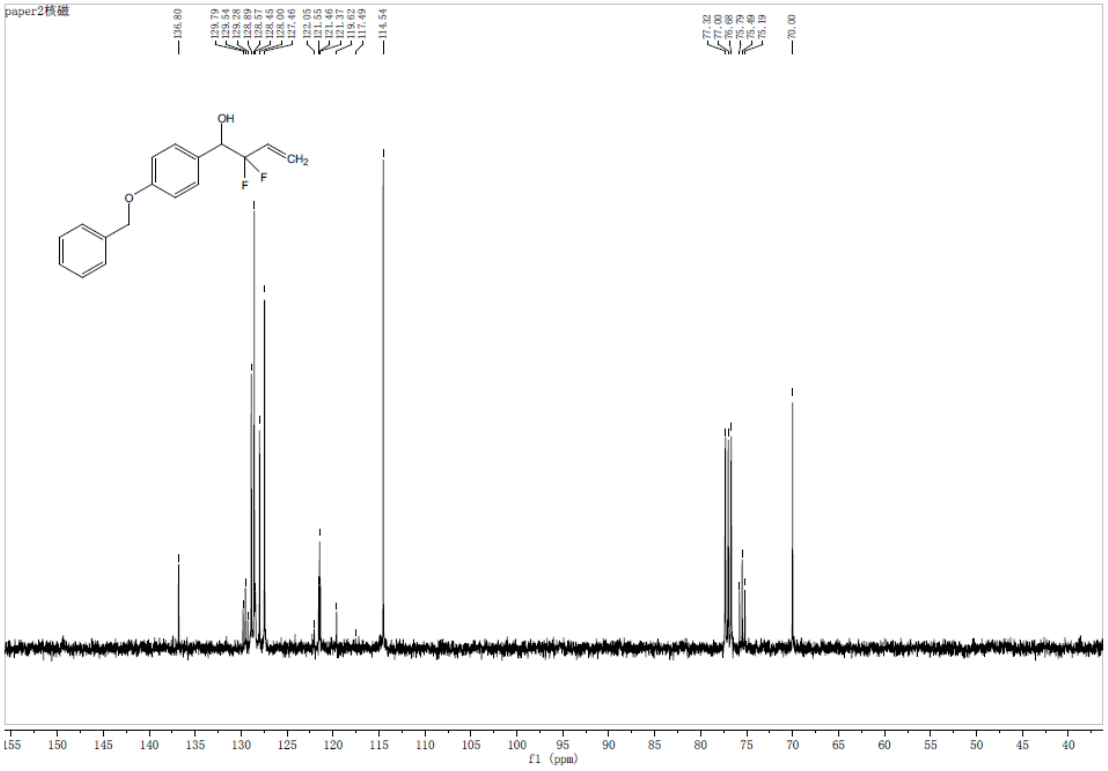
^{19}F NMR spectrum of compound **1g**



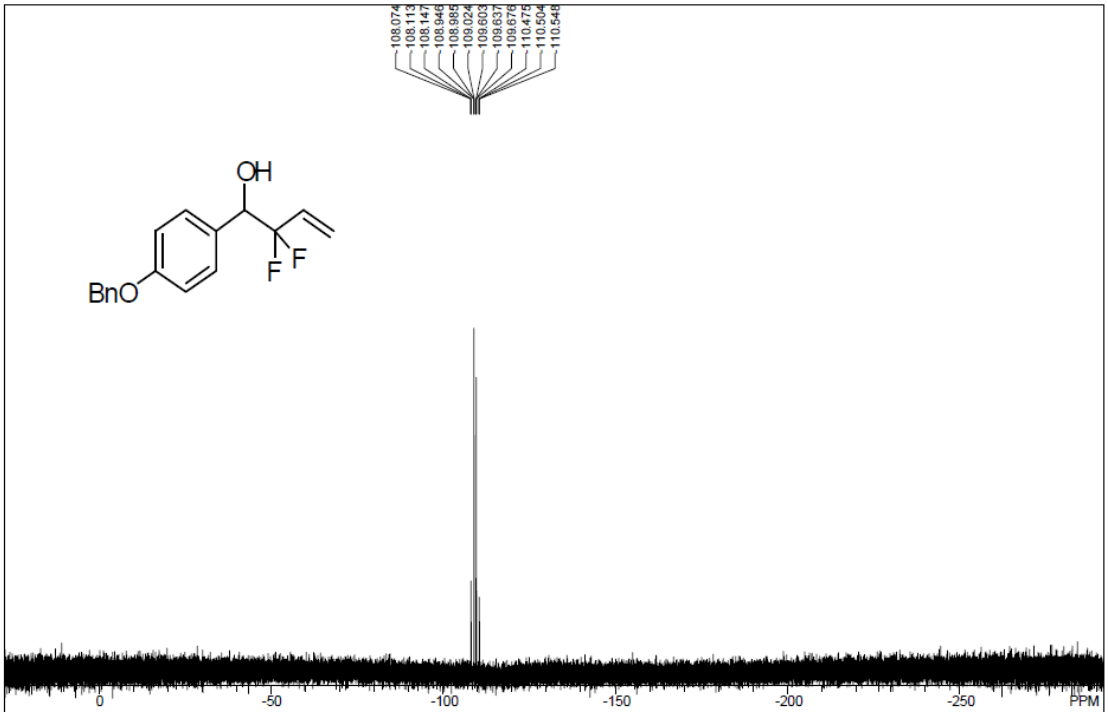
^{1}H NMR spectrum of compound **1h**



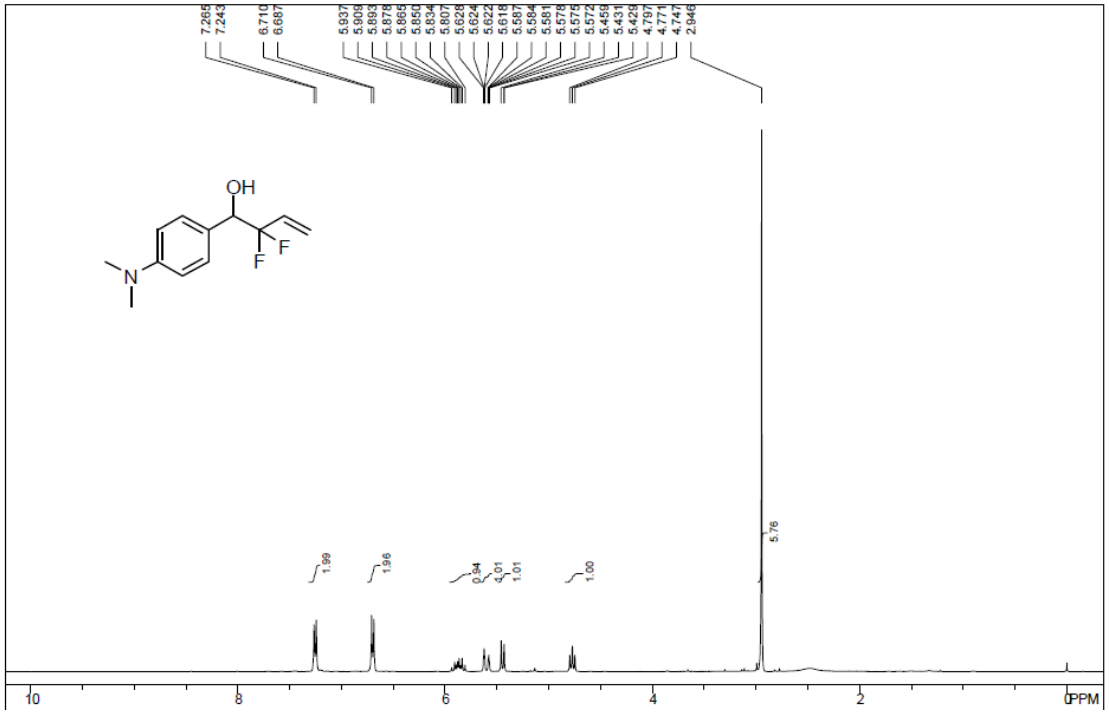
^{13}C NMR spectrum of compound **1h**



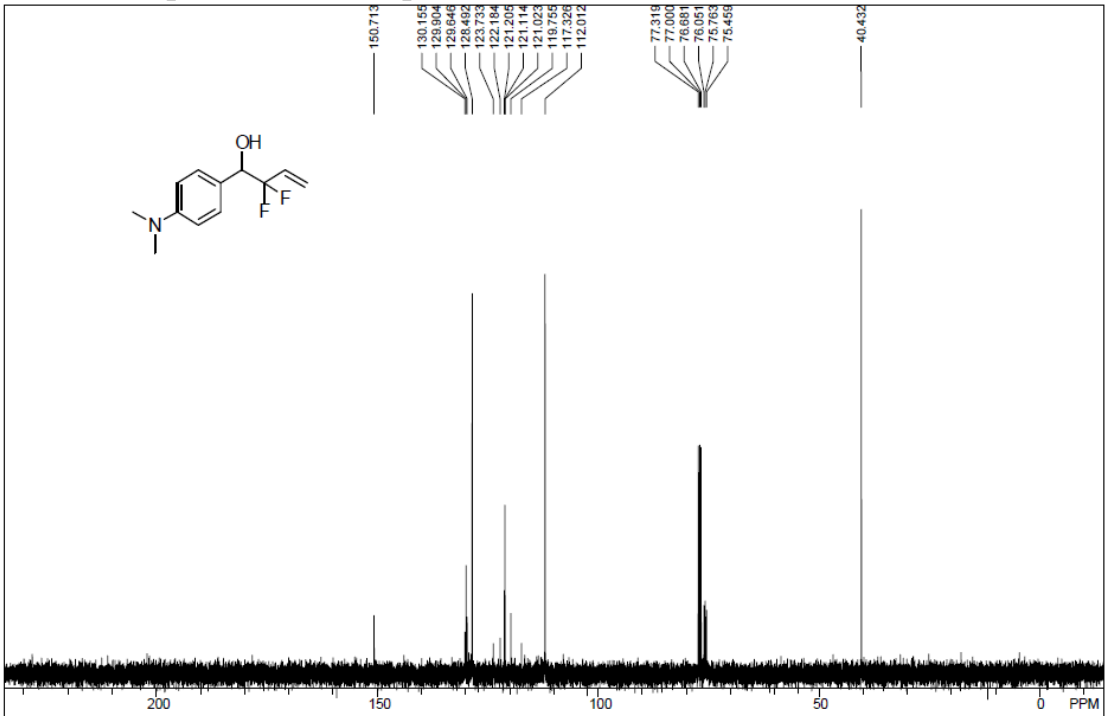
^{19}F NMR spectrum of compound **1h**



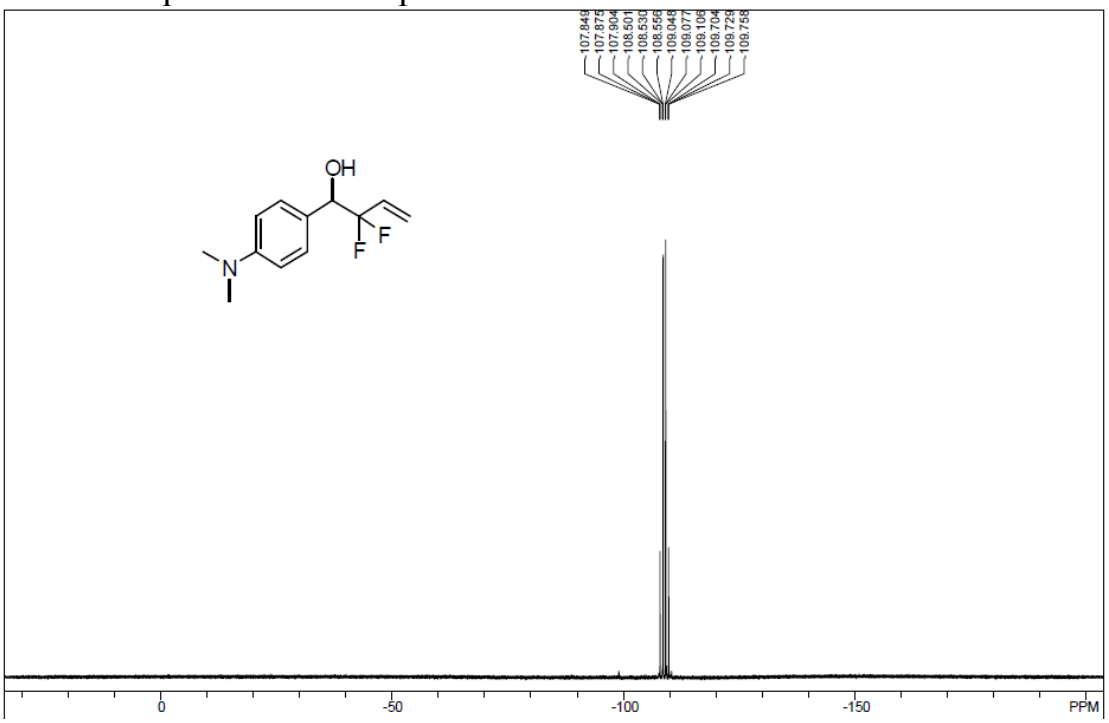
^{1}H NMR spectrum of compound **1i**



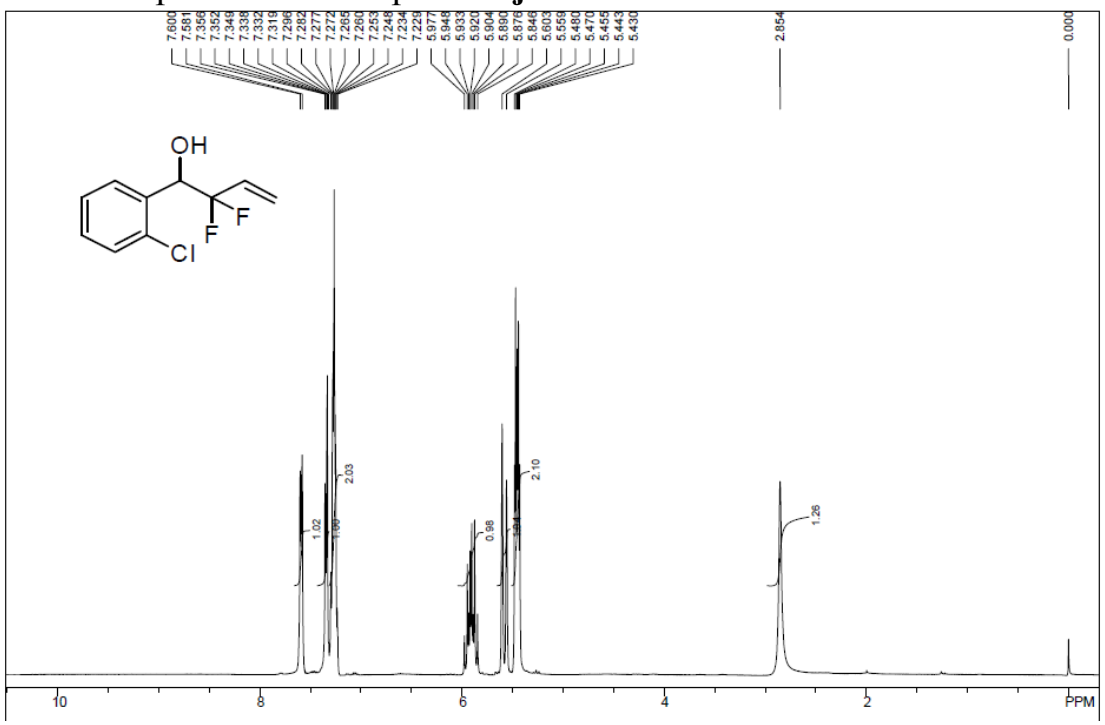
^{13}C NMR spectrum of compound **1i**



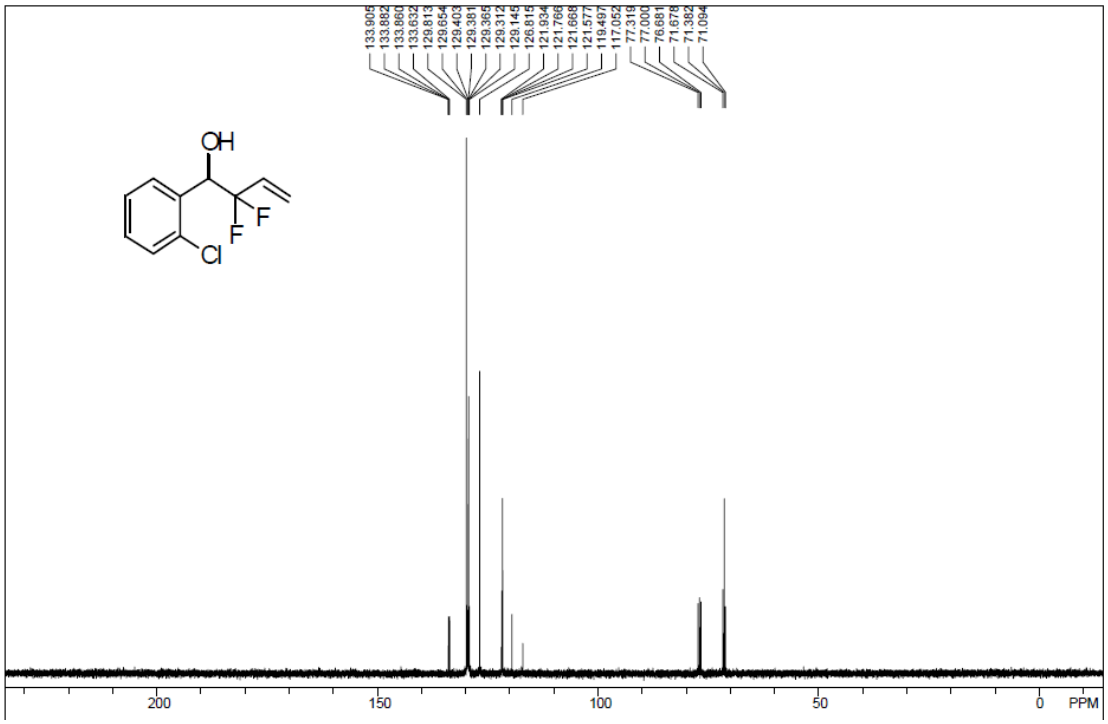
^{19}F NMR spectrum of compound **1i**



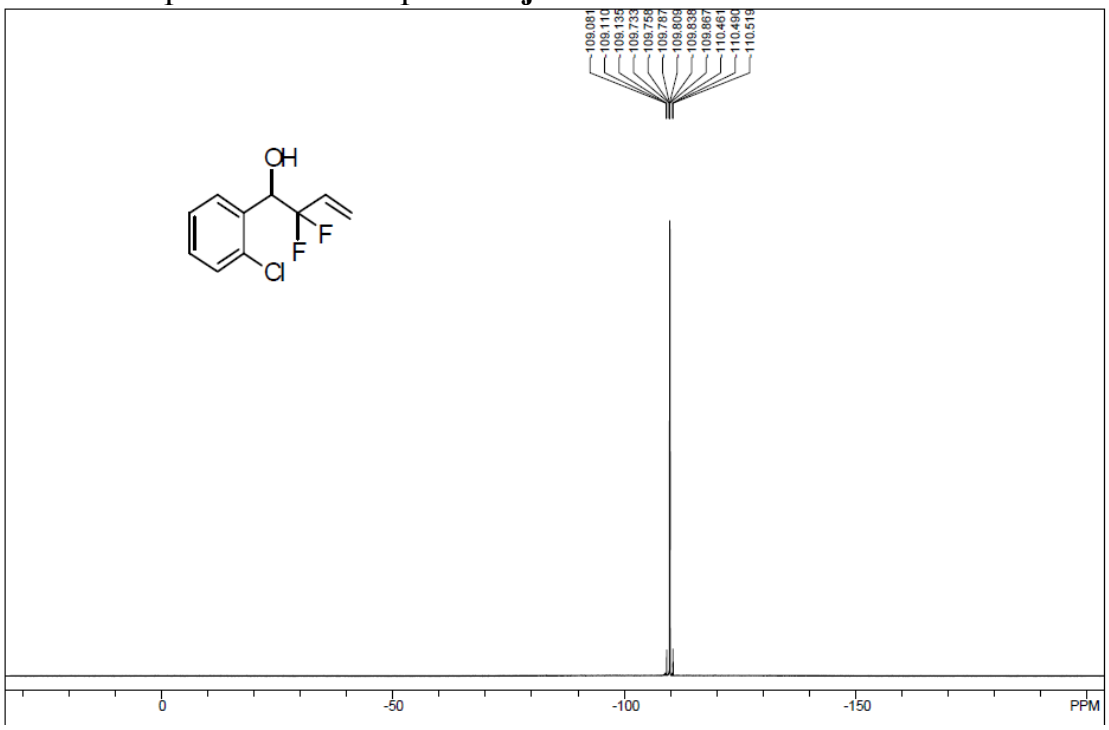
^{1}H NMR spectrum of compound **1j**



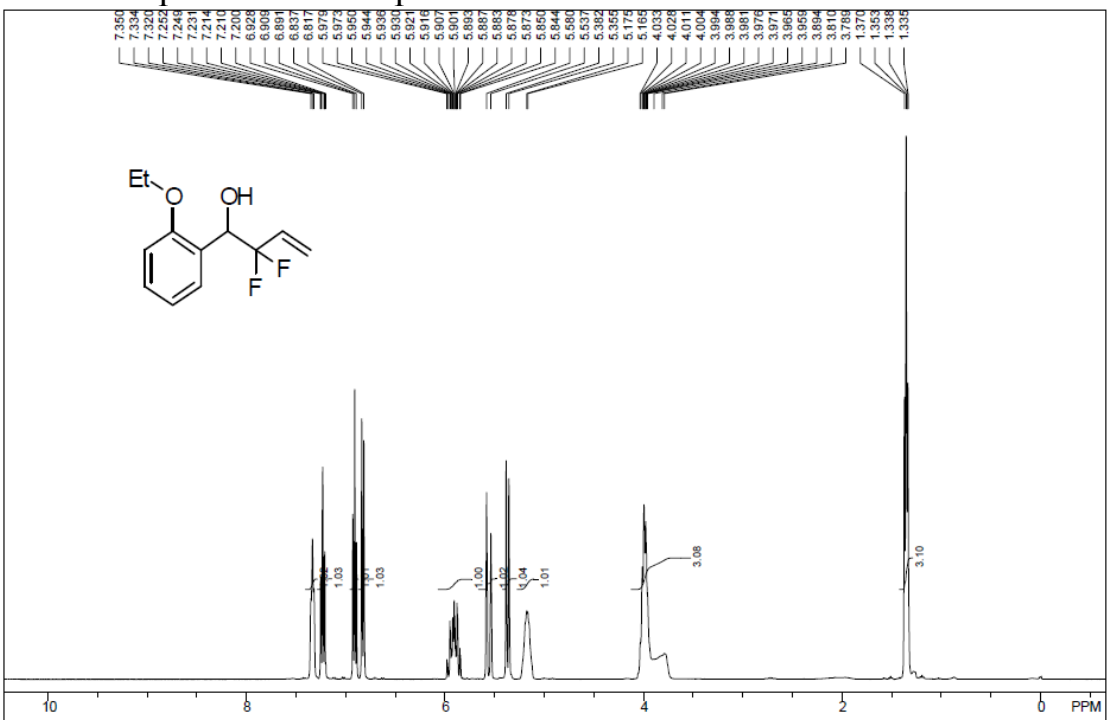
^{13}C NMR spectrum of compound **1j**



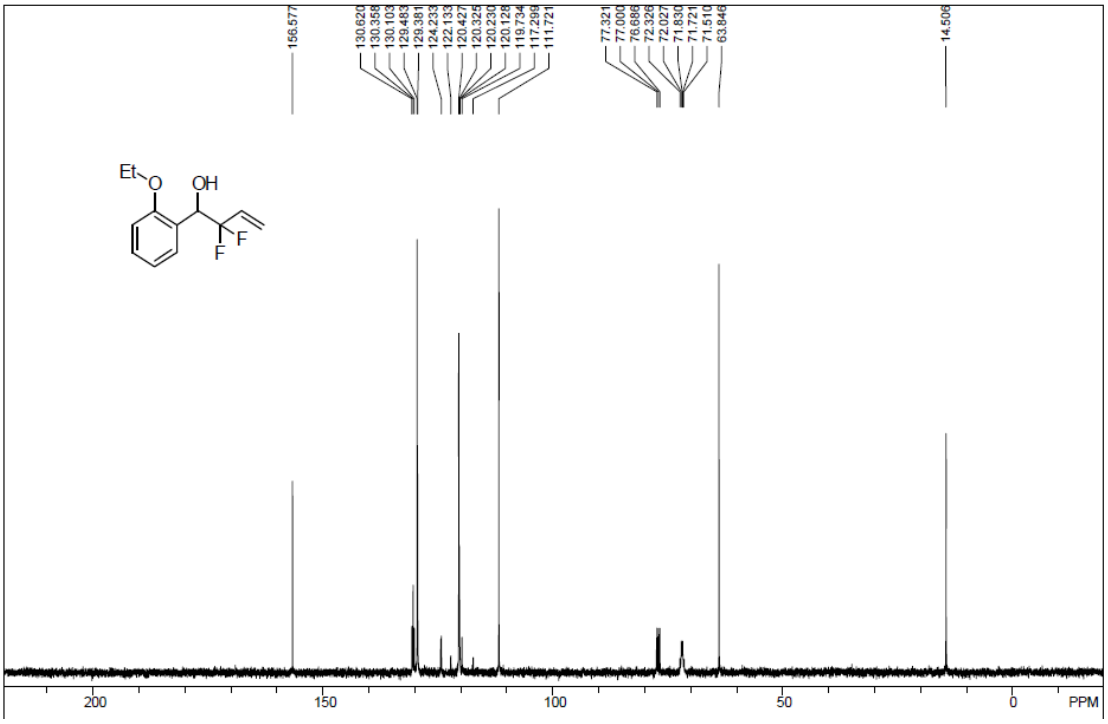
^{19}F NMR spectrum of compound **1j**



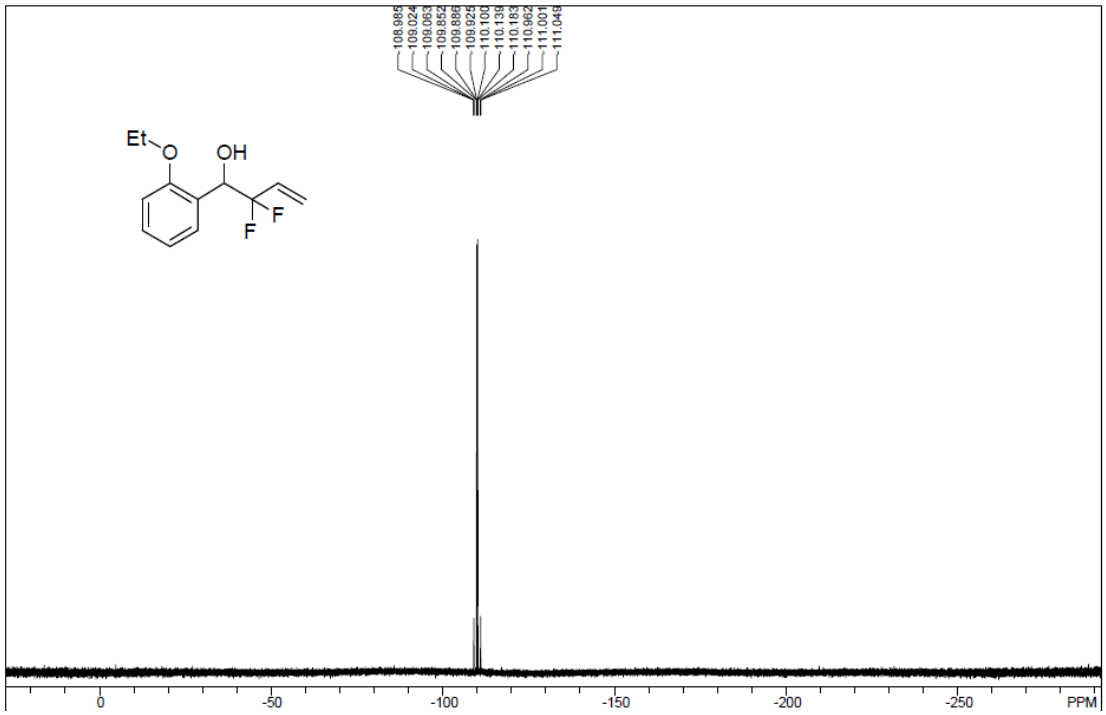
^{1}H NMR spectrum of compound **1k**



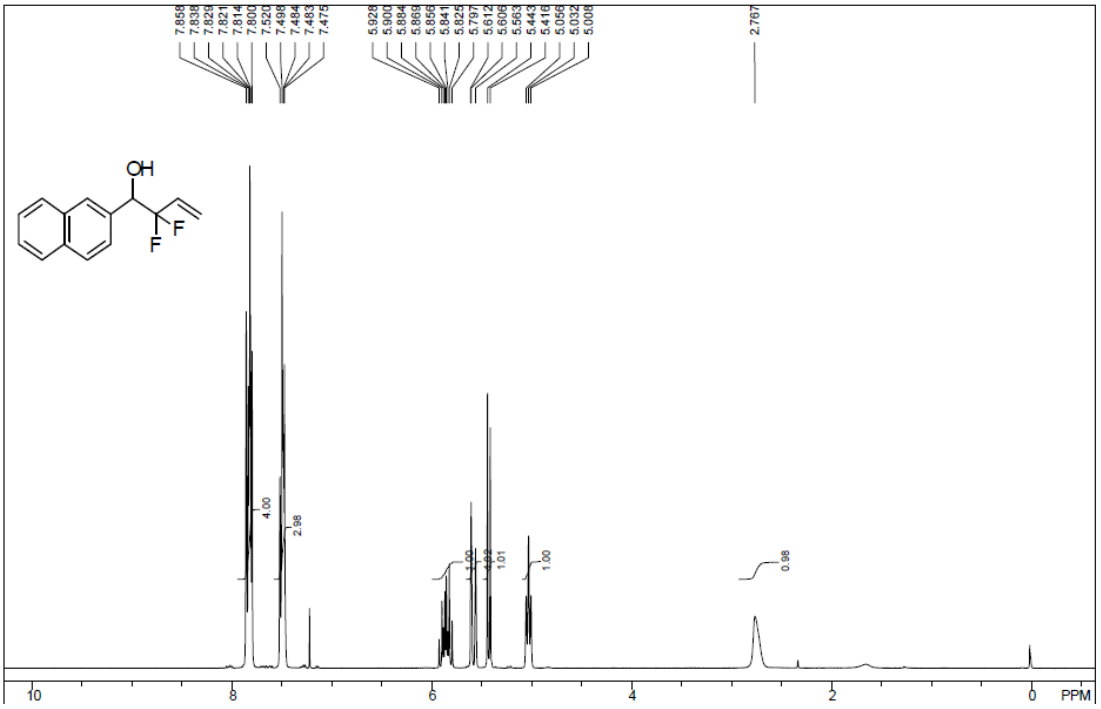
^{13}C NMR spectrum of compound **1k**



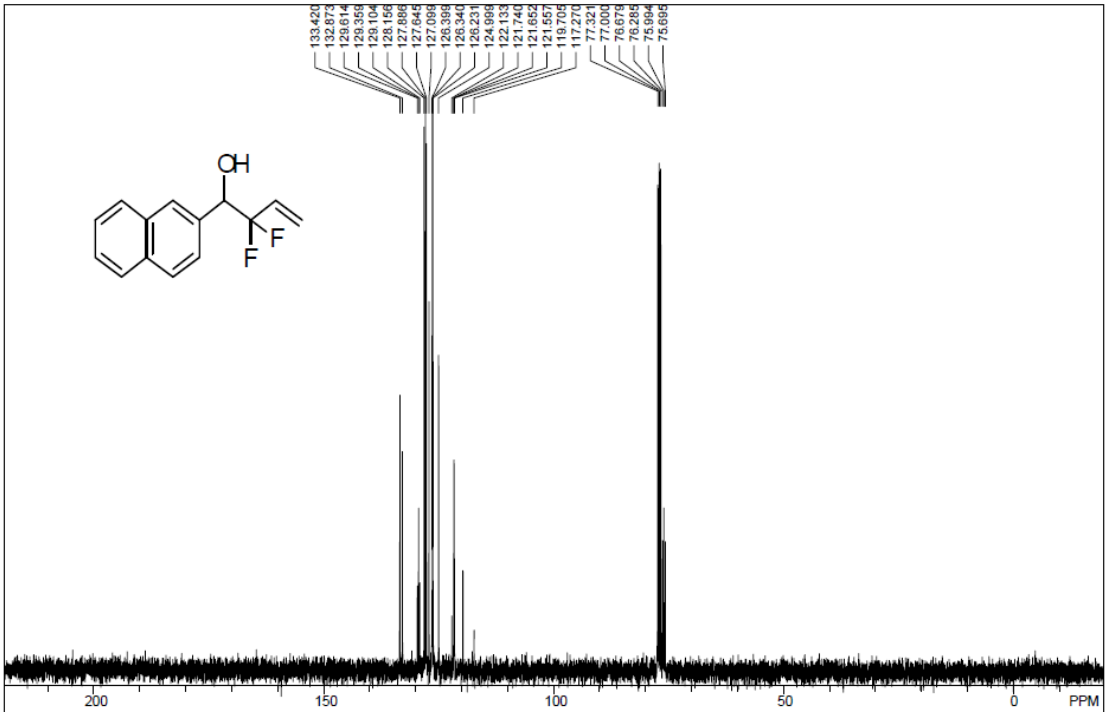
^{19}F NMR spectrum of compound **1k**



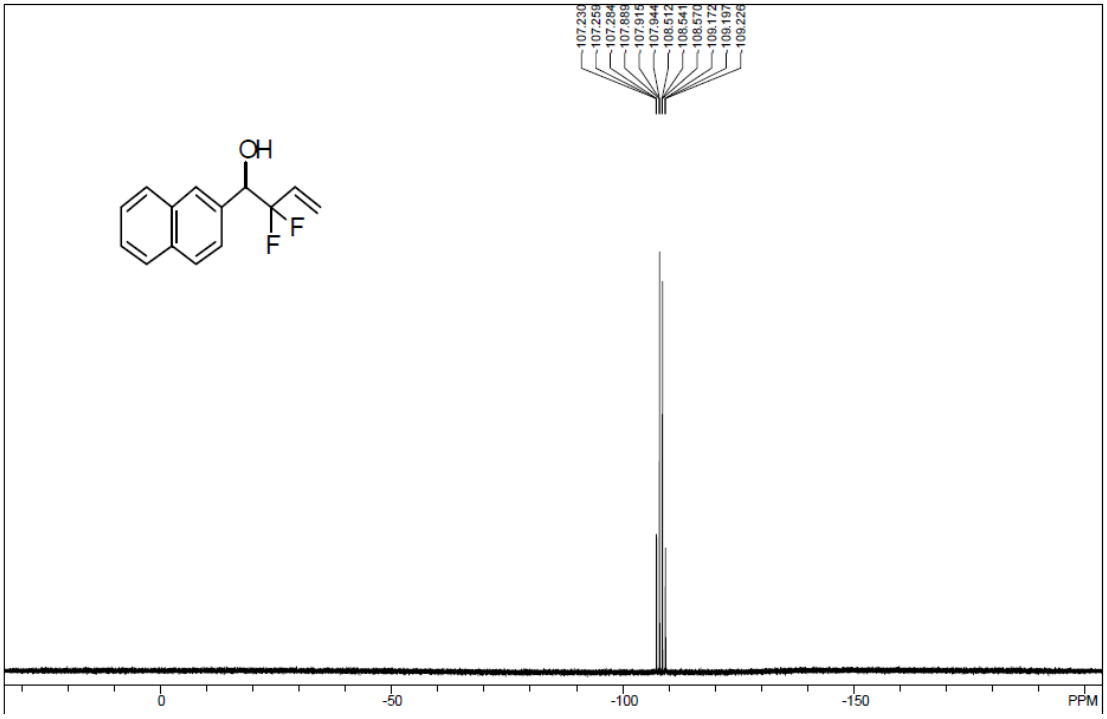
^{1}H NMR spectrum of compound **1l**



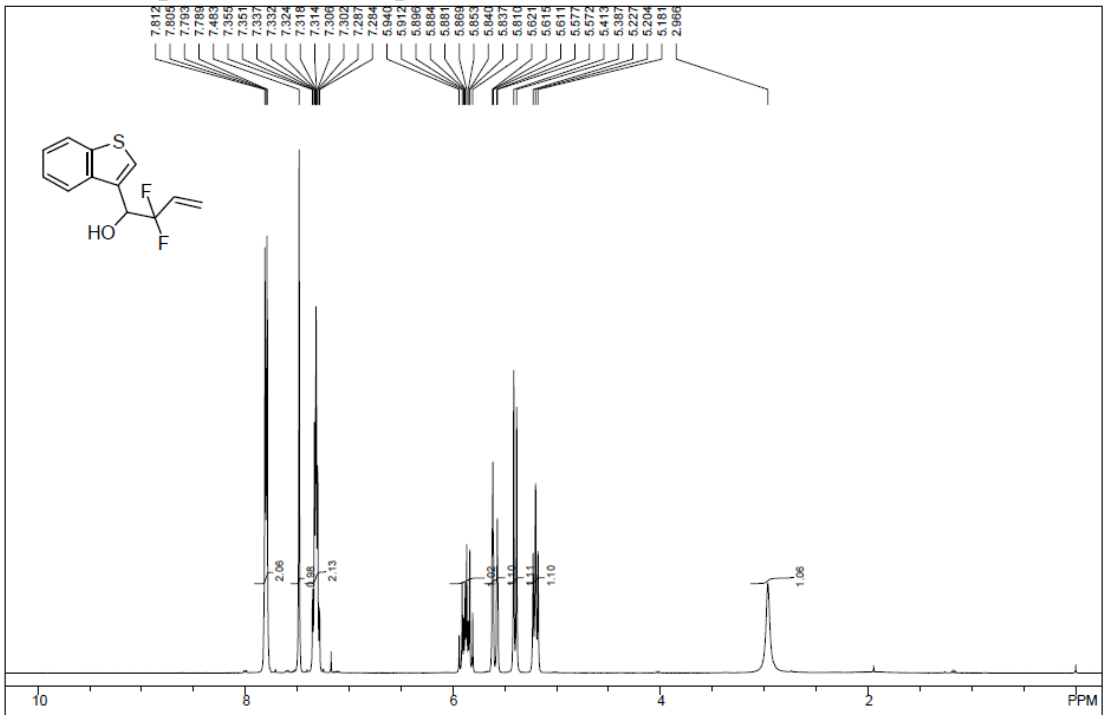
^{13}C NMR spectrum of compound **1l**



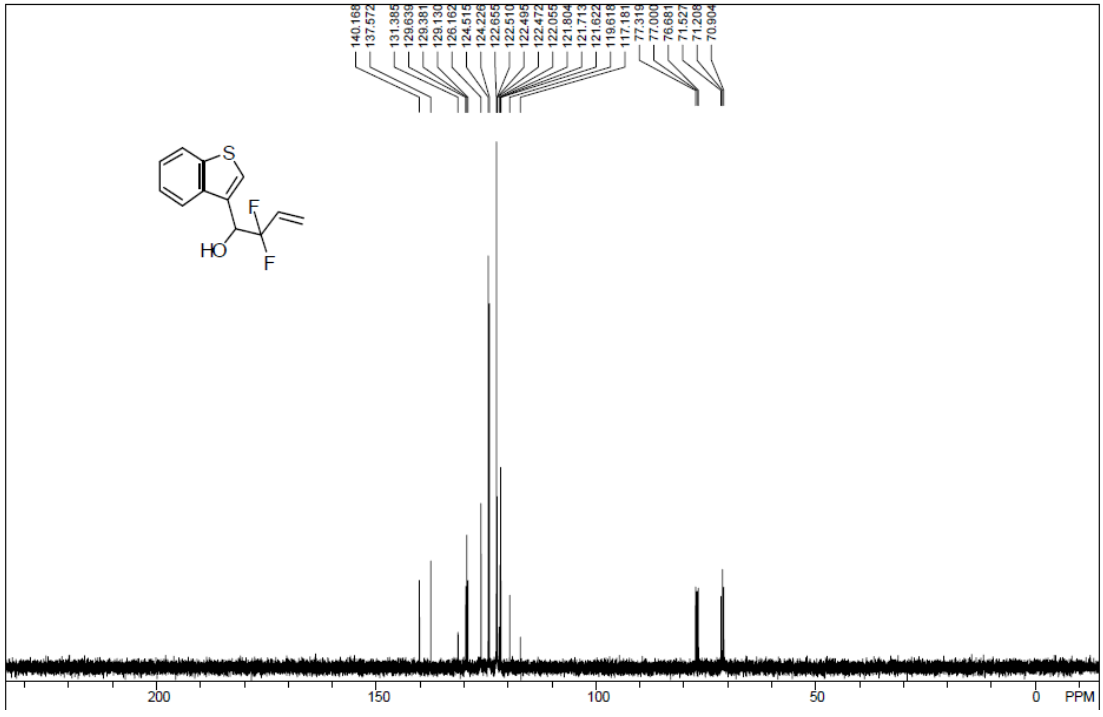
^{19}F NMR spectrum of compound **1l**



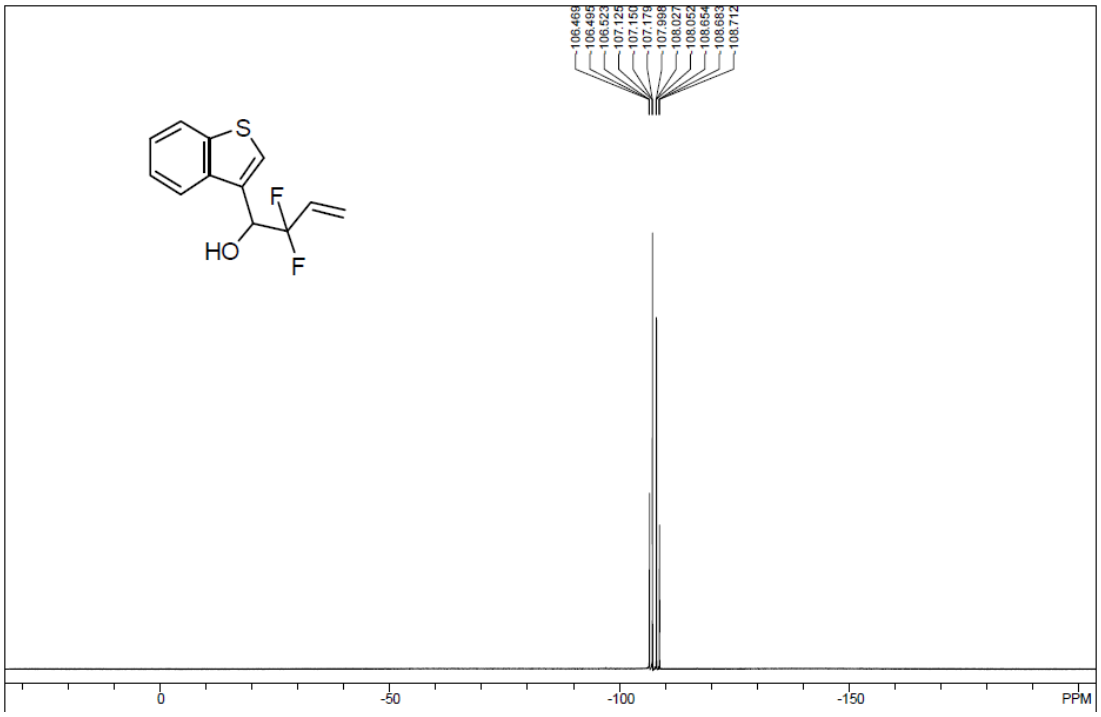
^{1}H NMR spectrum of compound **1m**



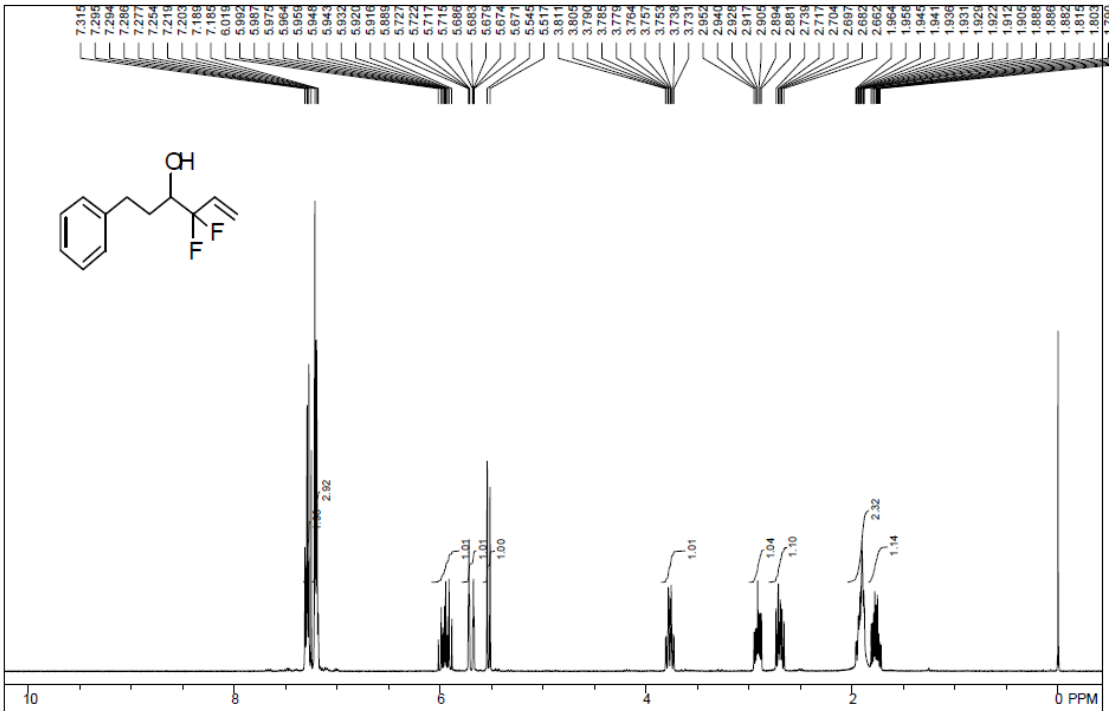
^{13}C NMR spectrum of compound **1m**



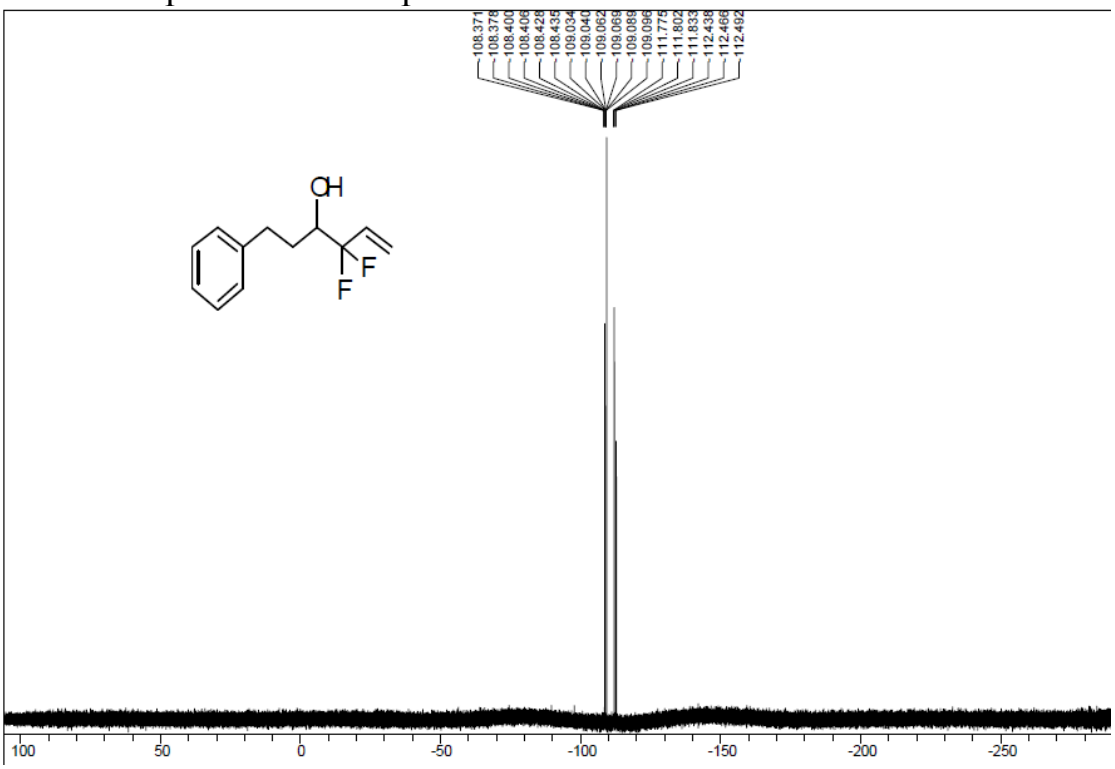
^{19}F NMR spectrum of compound **1m**



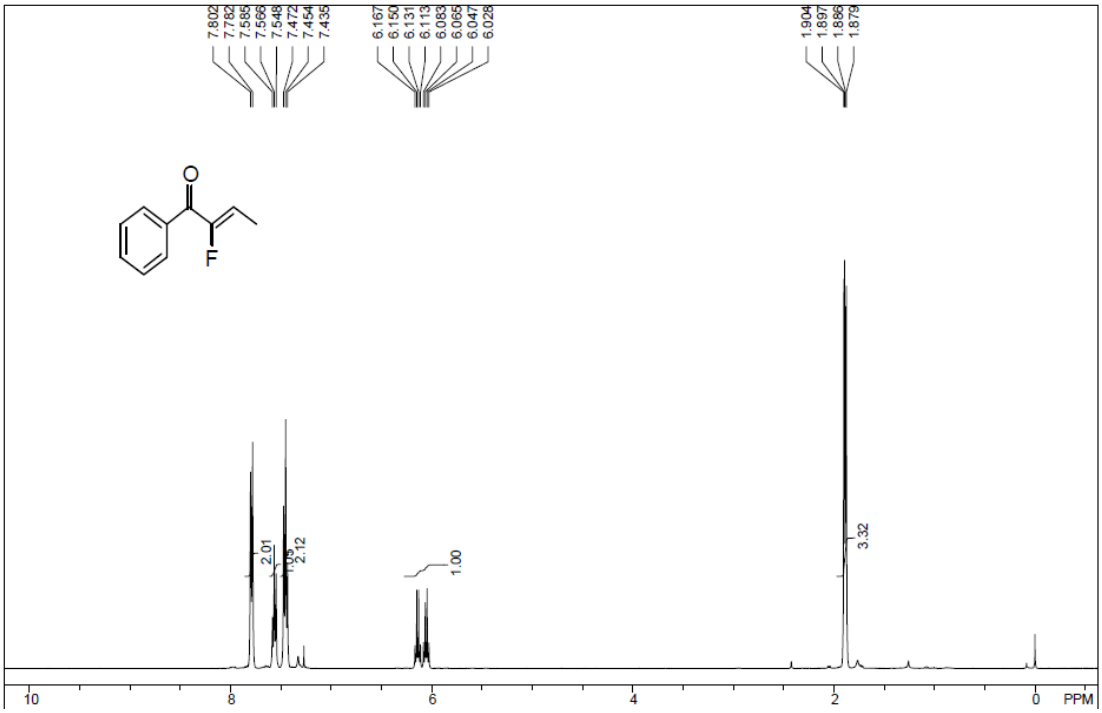
^{1}H NMR spectrum of compound **1n**



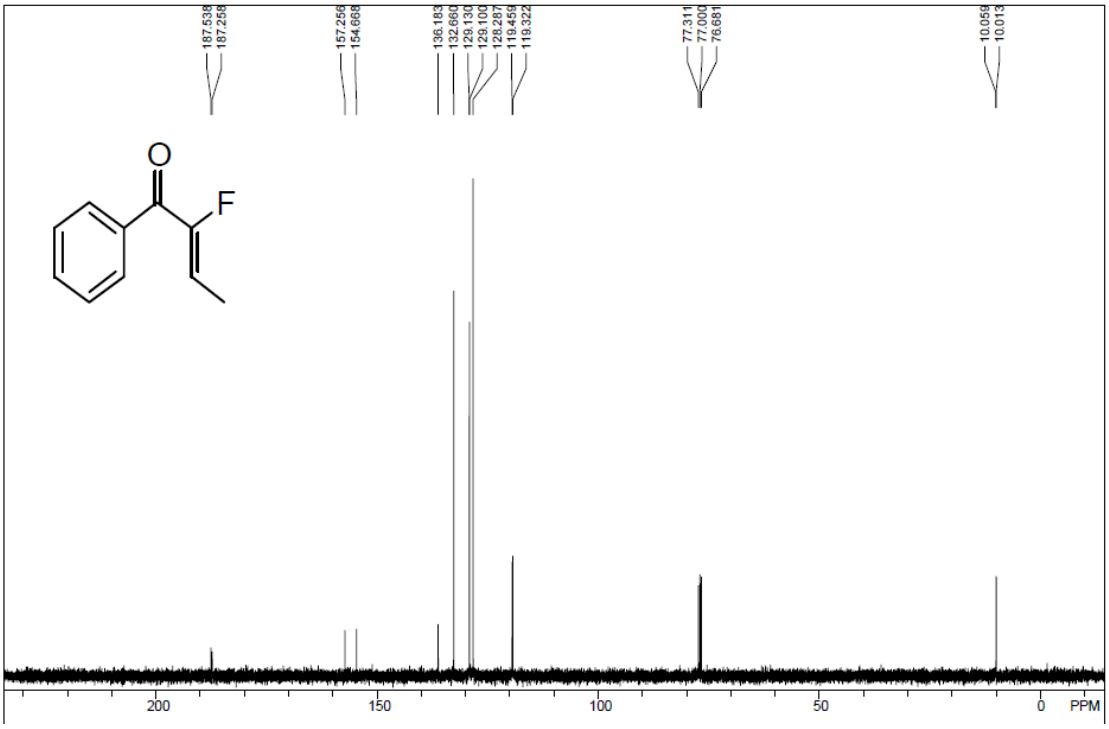
^{19}F NMR spectrum of compound **1n**



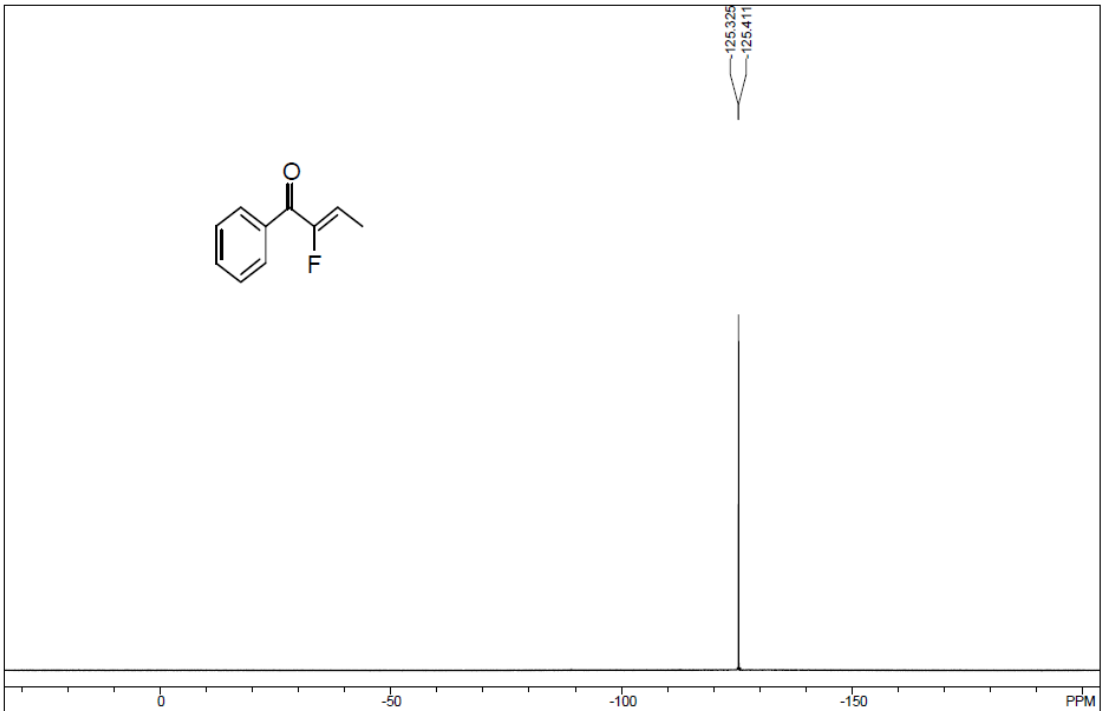
^{1}H NMR spectrum of compound **2a**



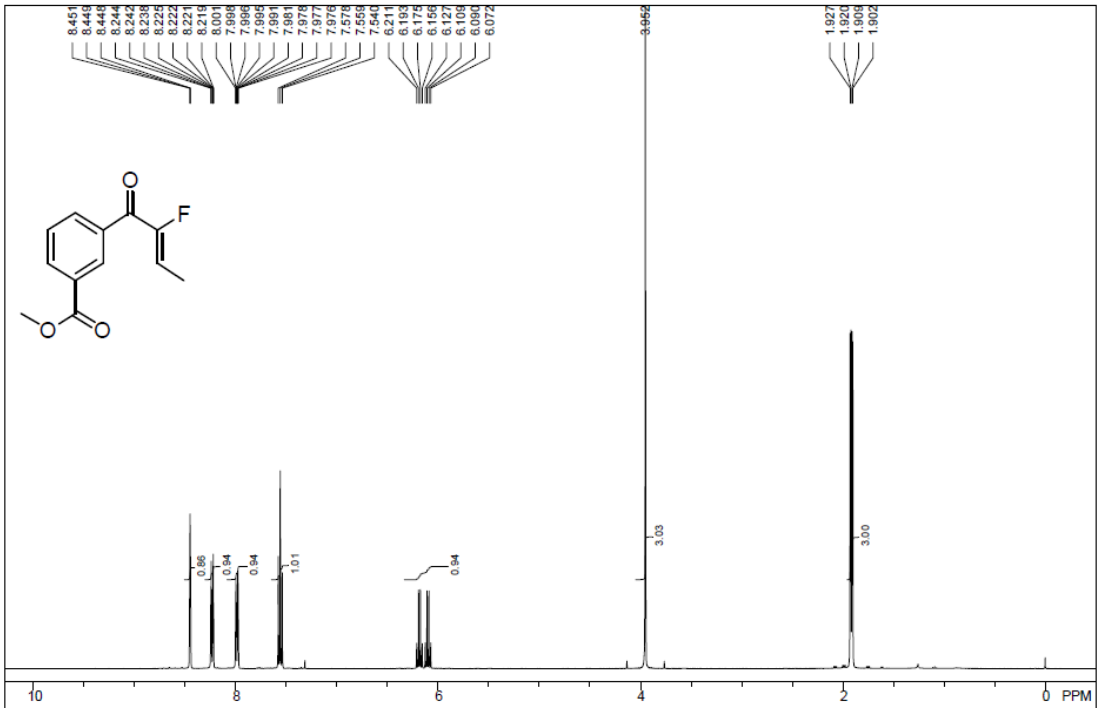
^{13}C NMR spectrum of compound **2a**



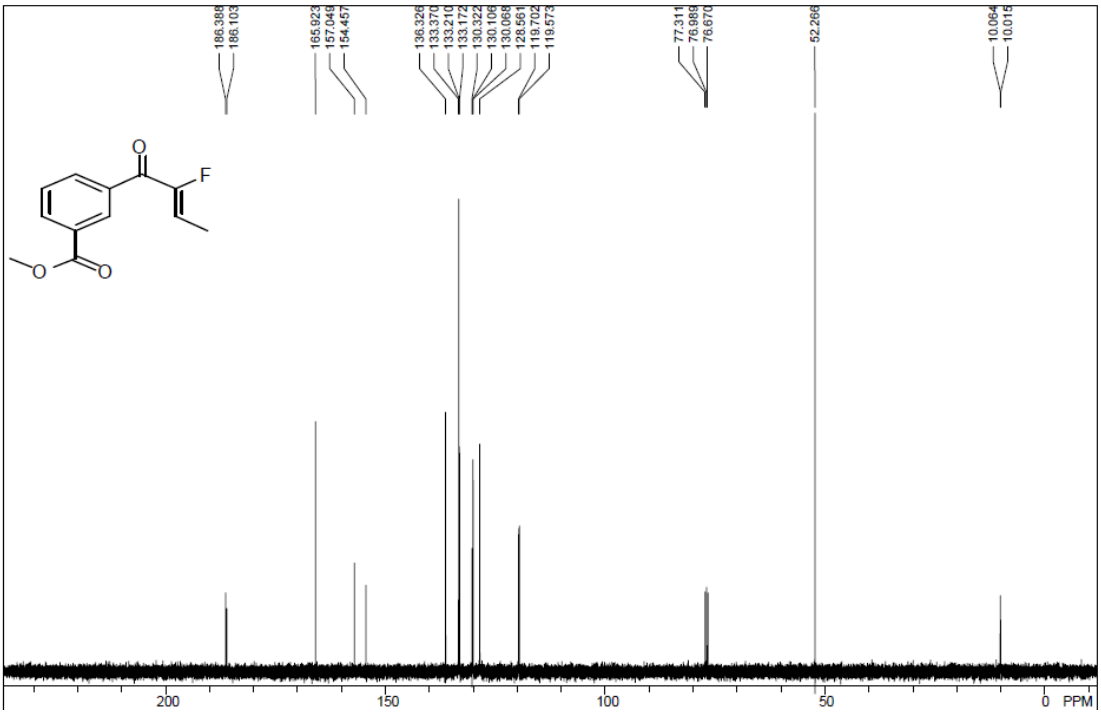
^{19}F NMR spectrum of compound **2a**



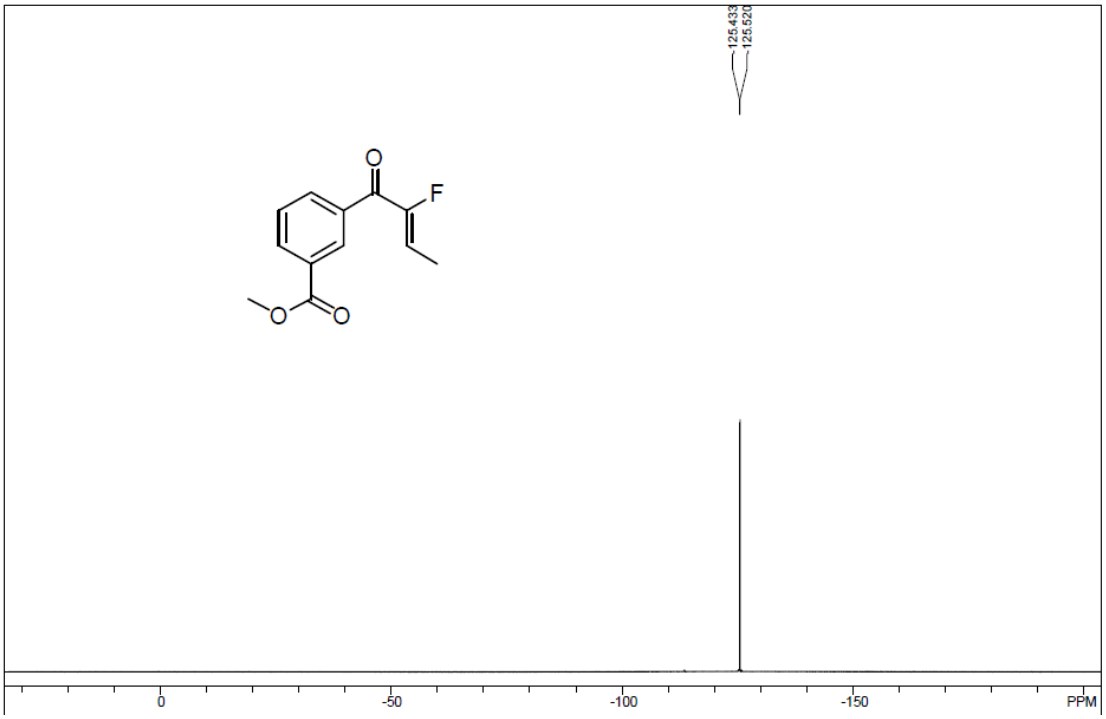
^{1}H NMR spectrum of compound **2b**



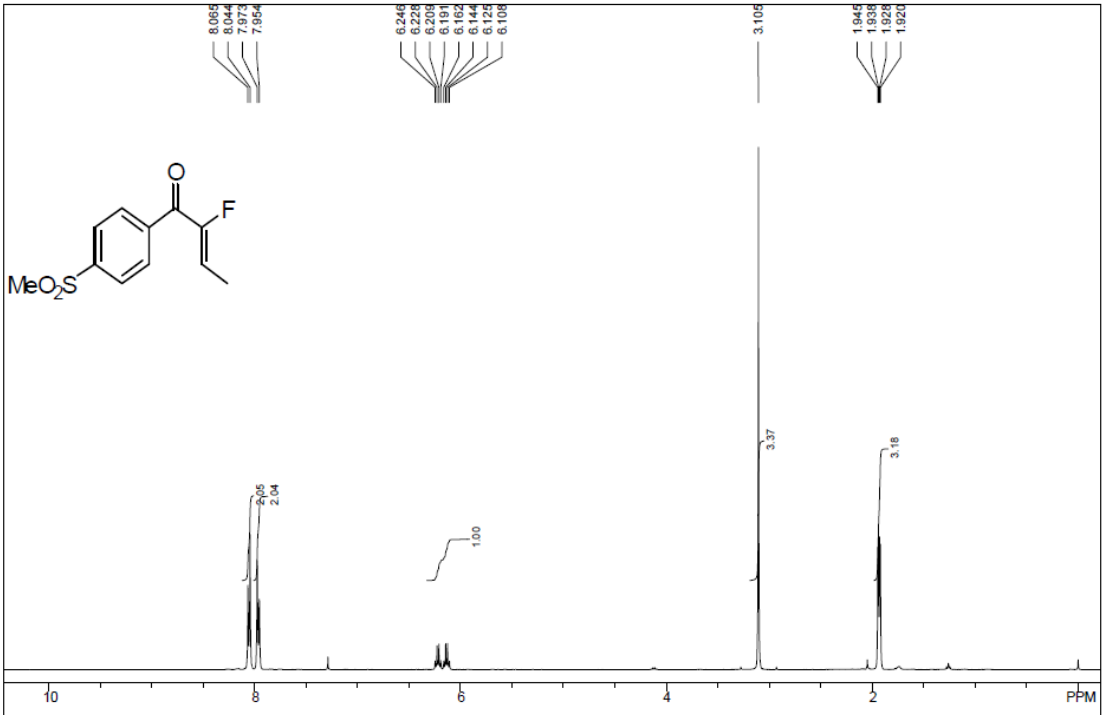
^{13}C NMR spectrum of compound **2b**



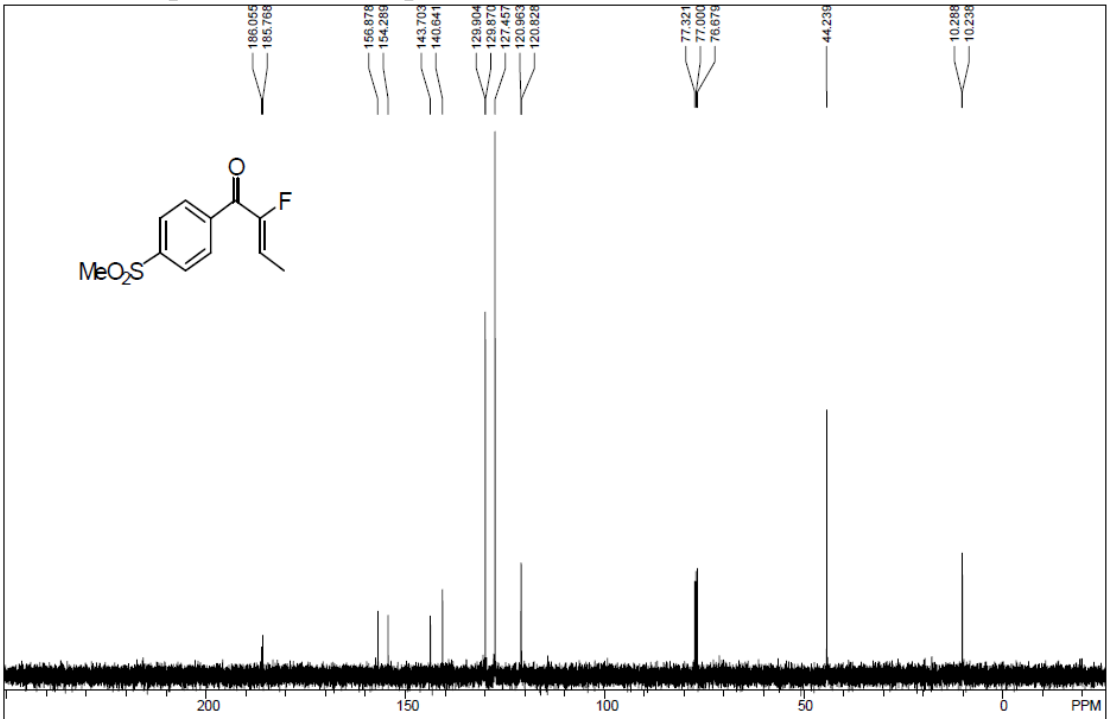
^{19}F NMR spectrum of compound **2b**



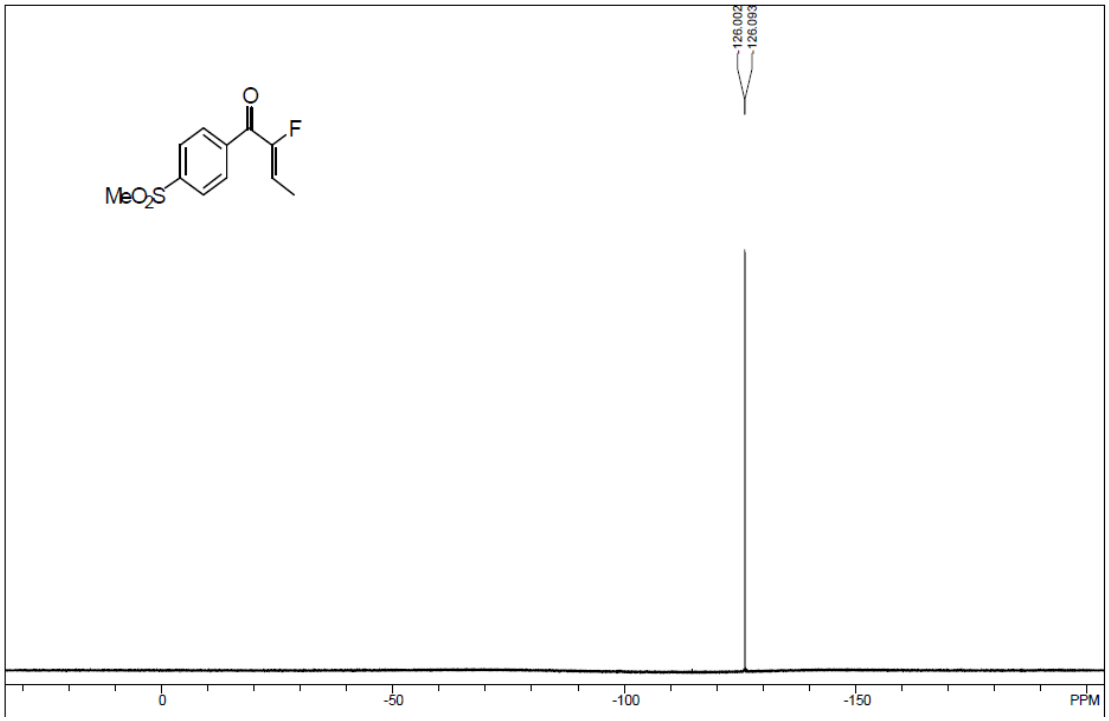
^{1}H NMR spectrum of compound **2c**



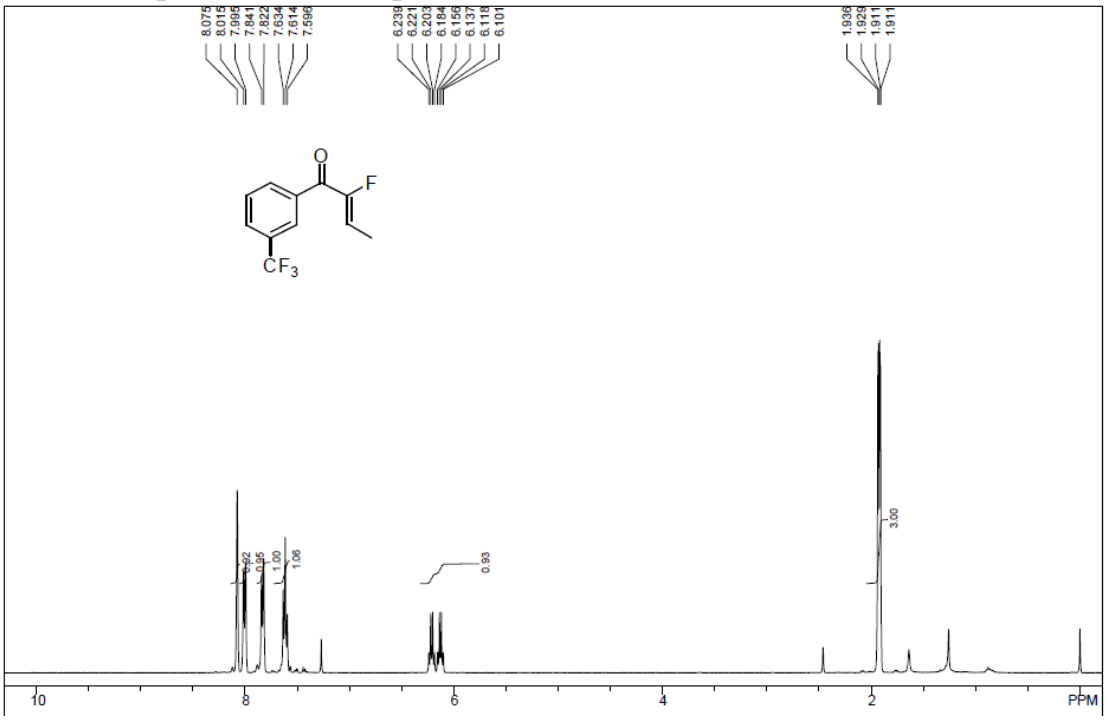
^{13}C NMR spectrum of compound **2c**



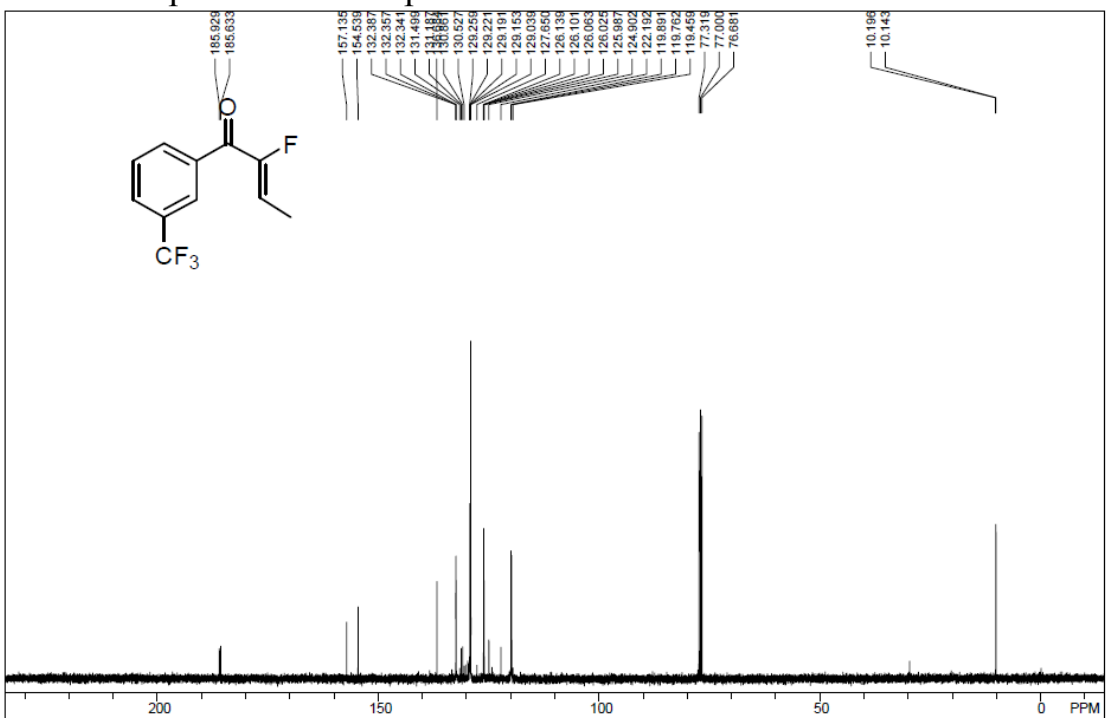
^{19}F NMR spectrum of compound **2c**



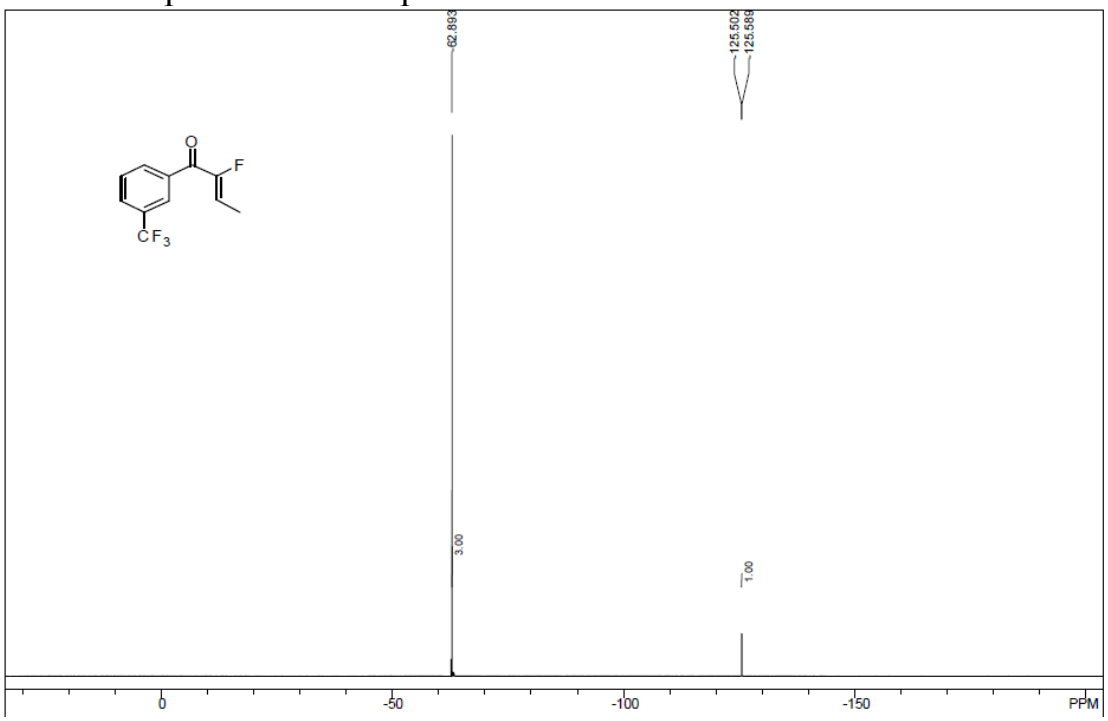
^{1}H NMR spectrum of compound **2d**



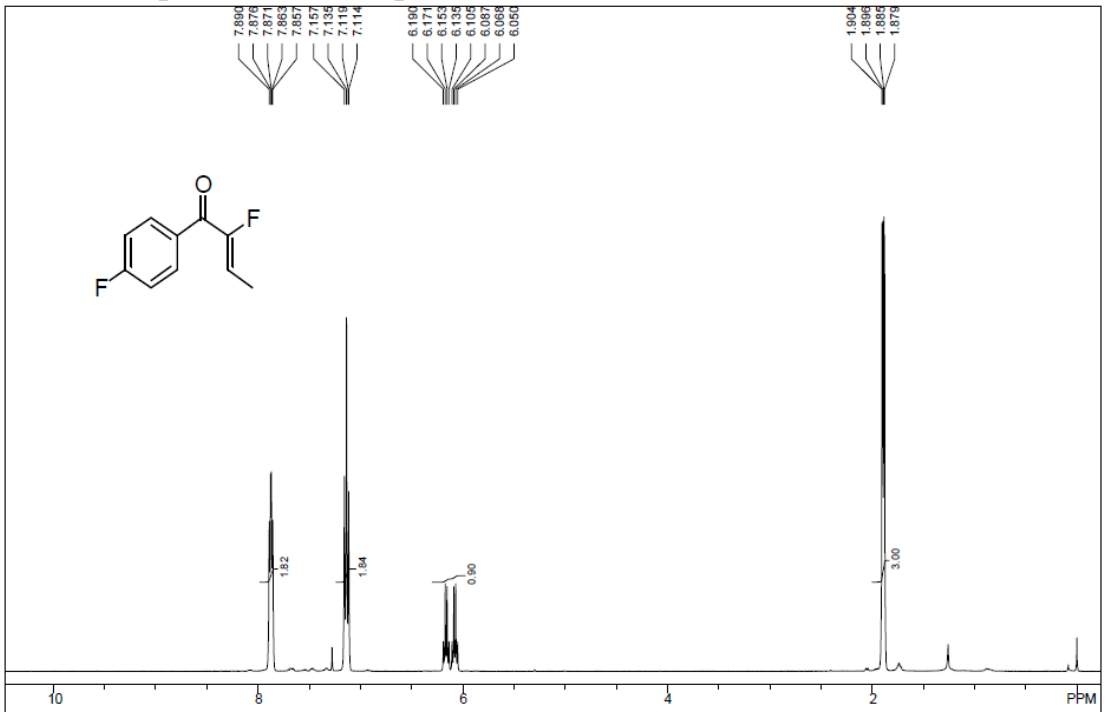
^{13}C NMR spectrum of compound **2d**



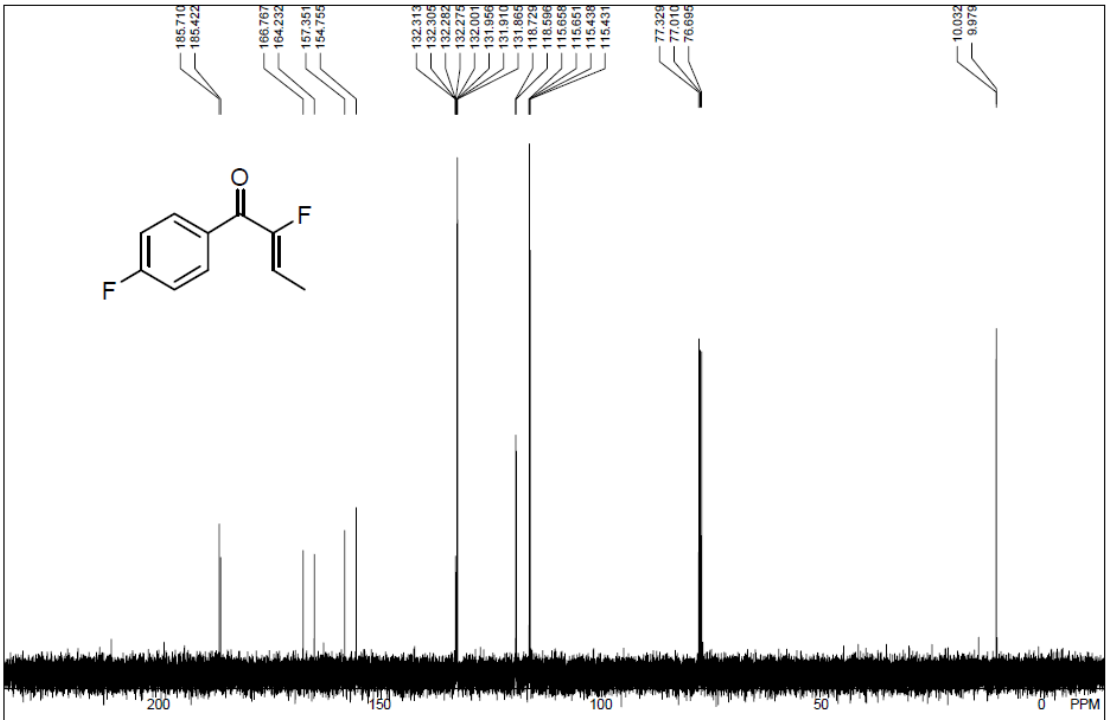
^{19}F NMR spectrum of compound **2d**



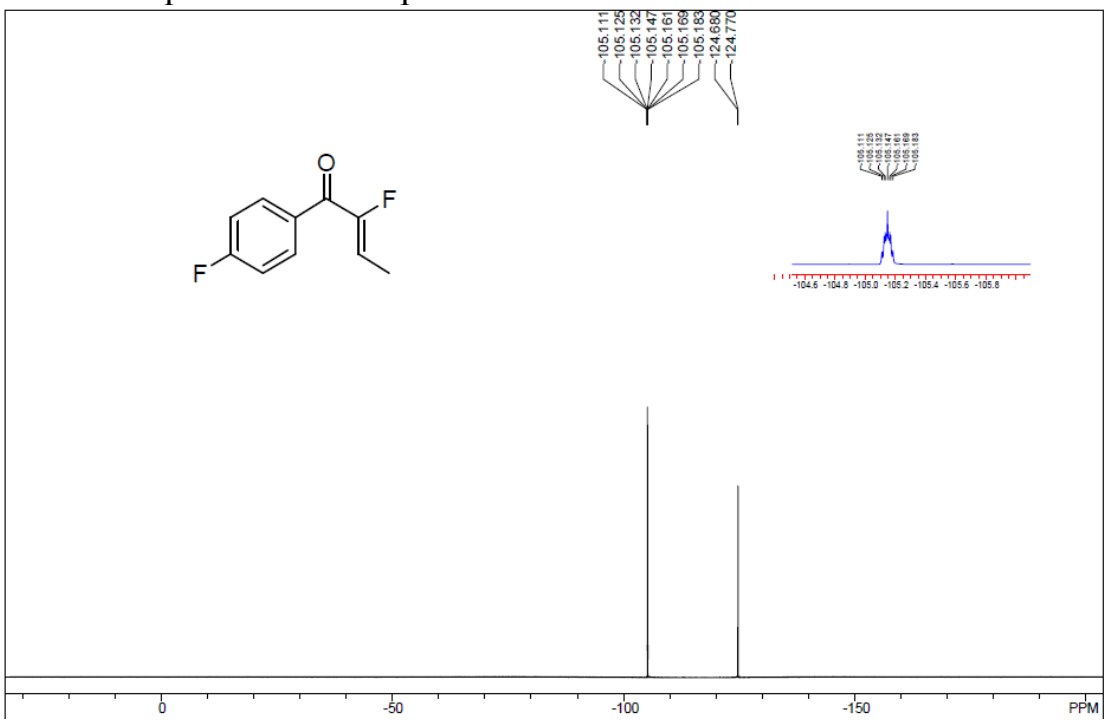
^{1}H NMR spectrum of compound **2e**



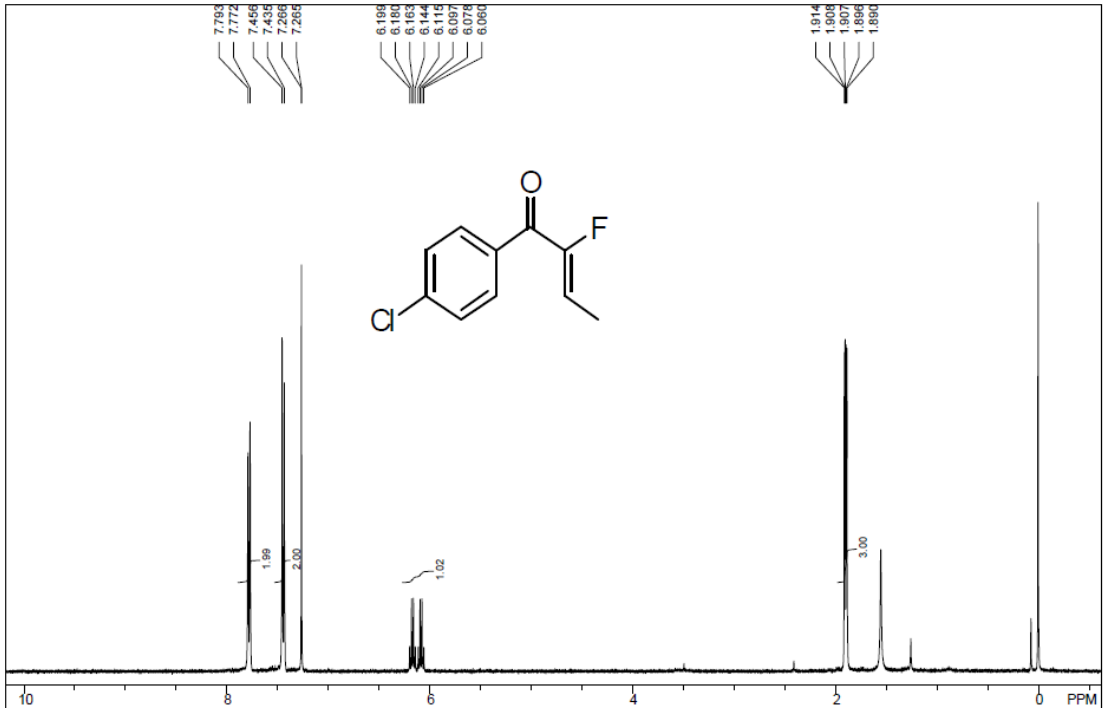
^{13}C NMR spectrum of compound **2e**



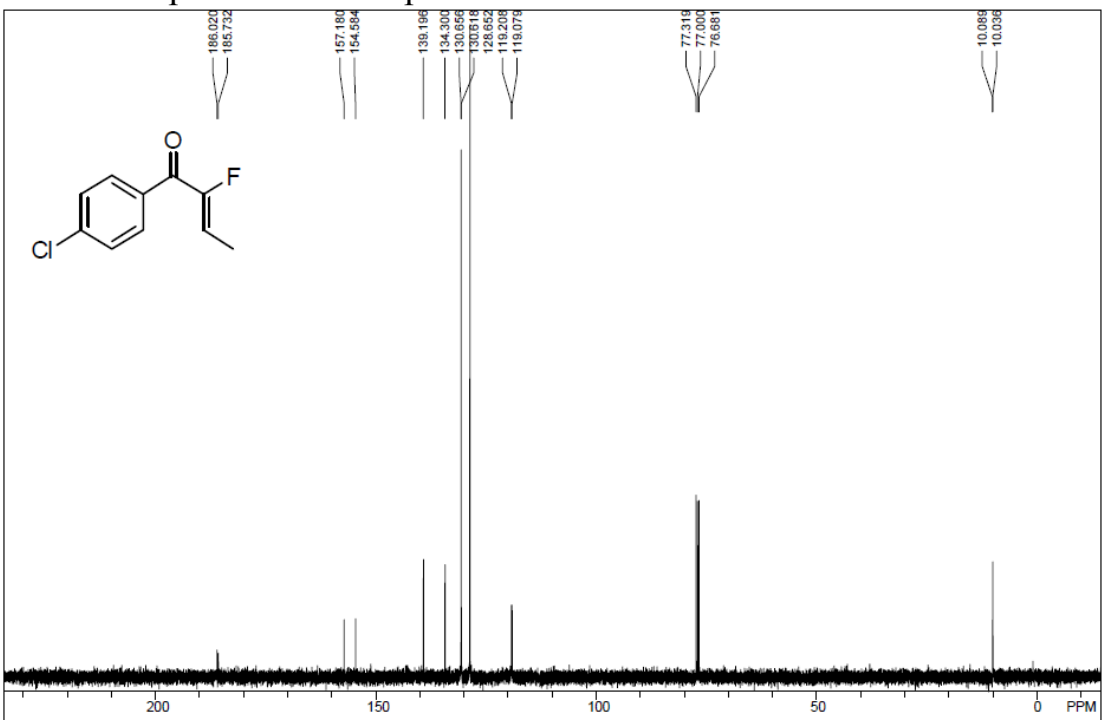
^{19}F NMR spectrum of compound **2e**



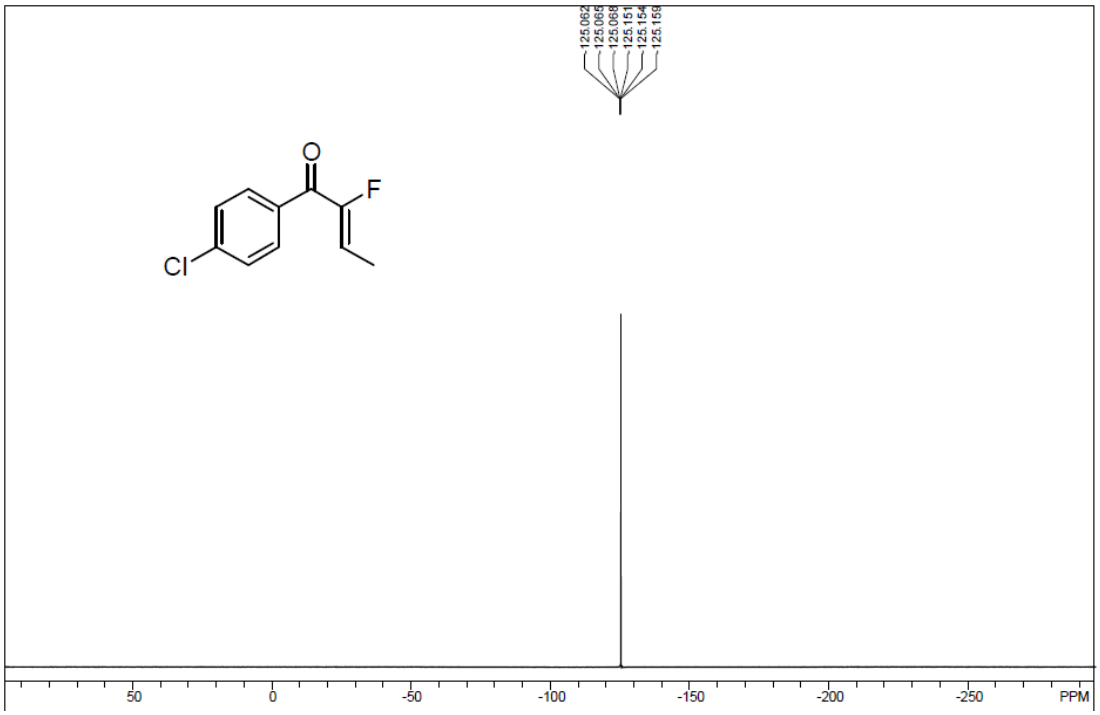
^{1}H NMR spectrum of compound **2f**



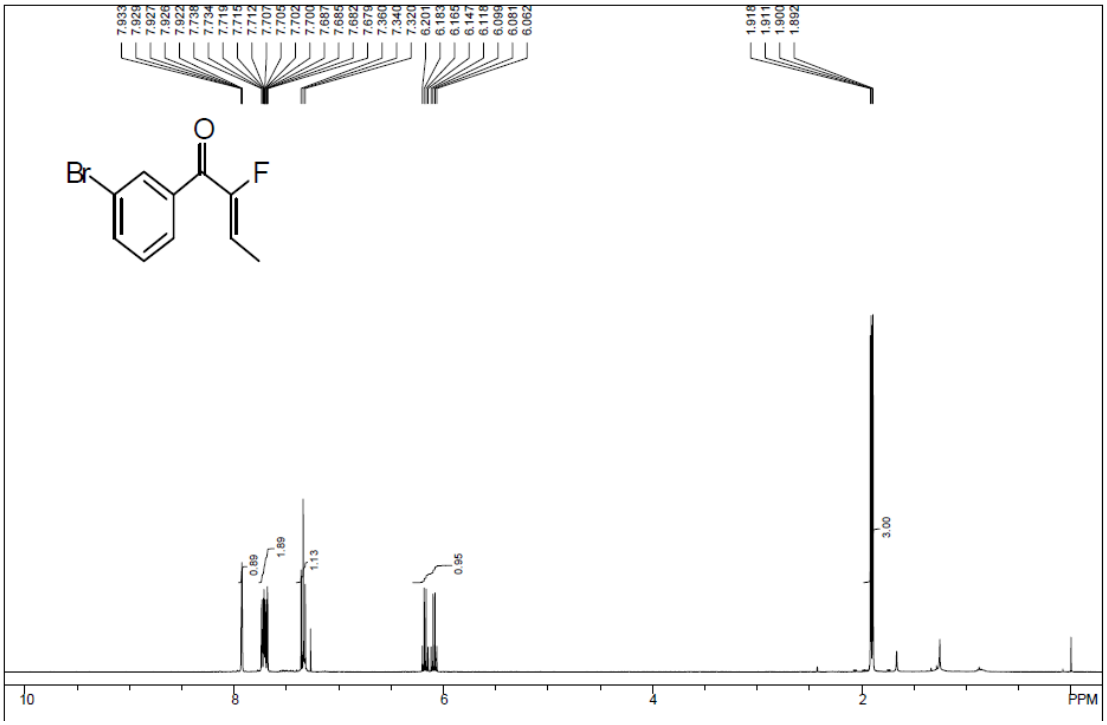
^{13}C NMR spectrum of compound **2f**



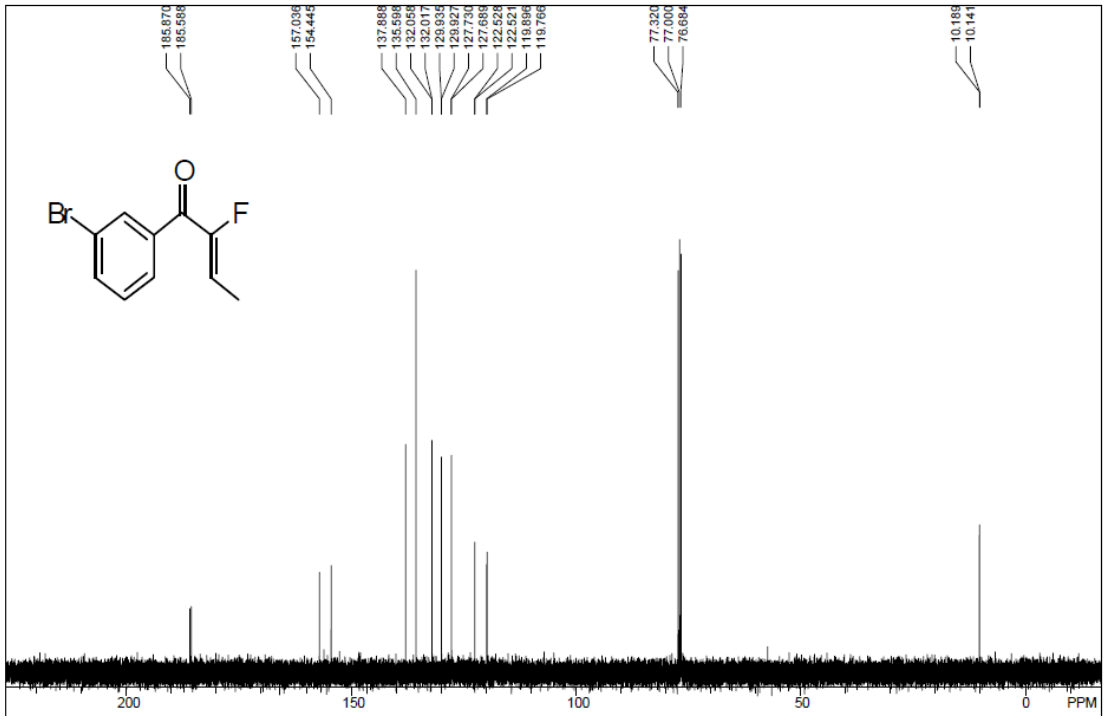
^{19}F NMR spectrum of compound **2f**



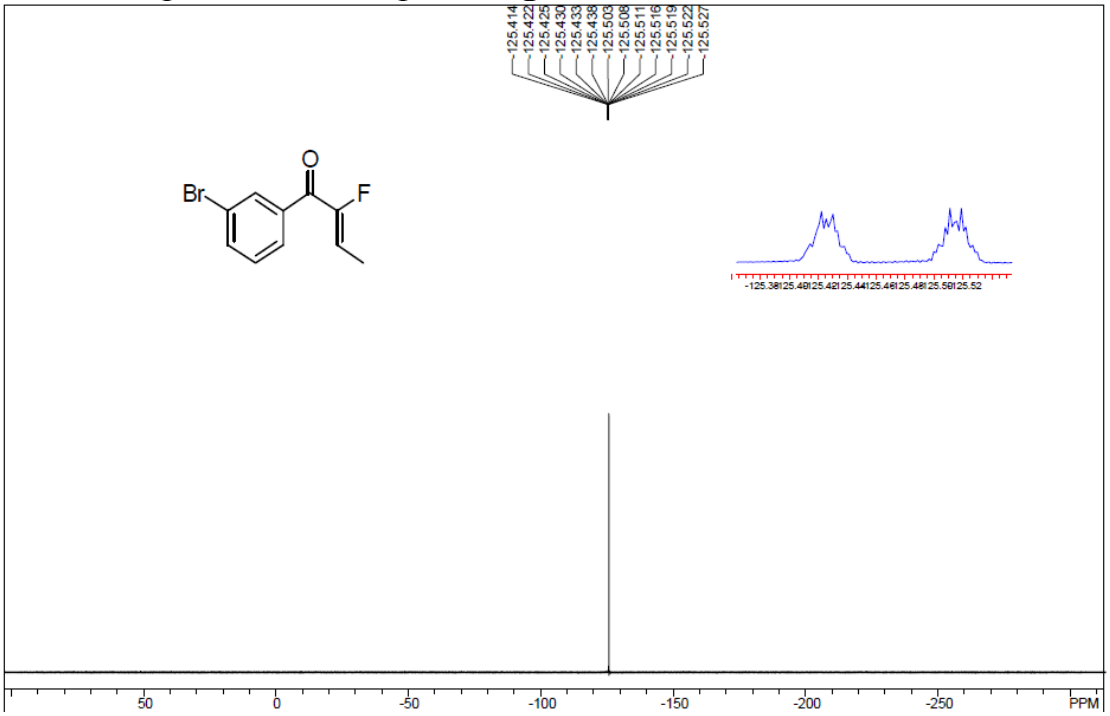
^{1}H NMR spectrum of compound **2g**



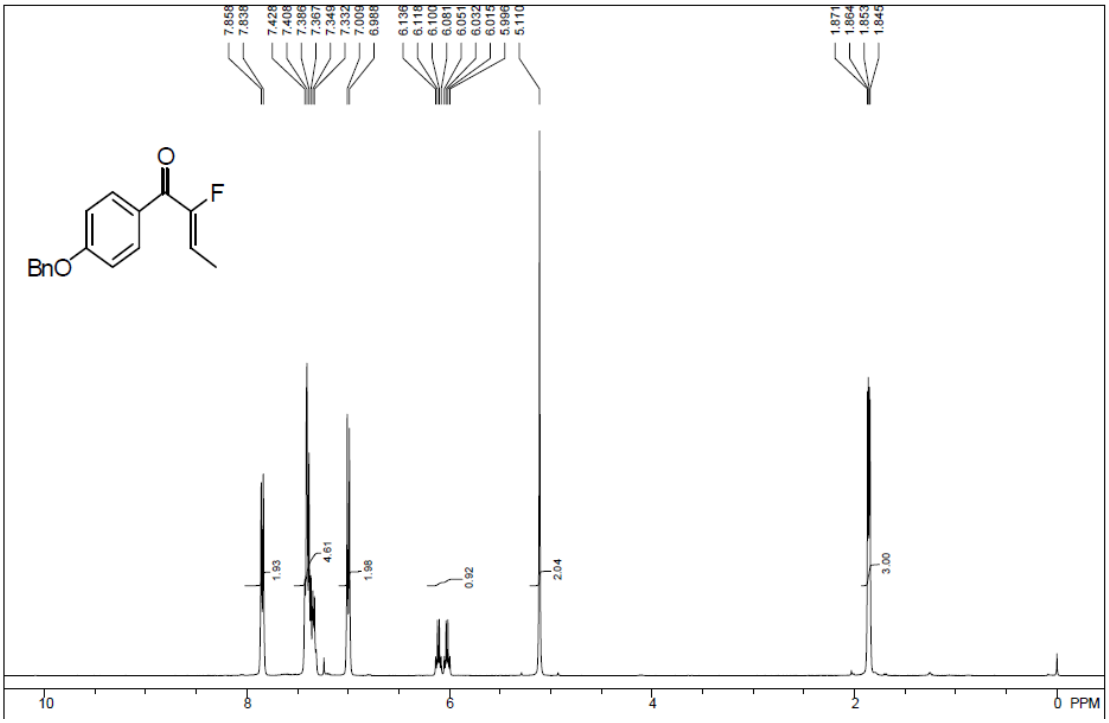
^{13}C NMR spectrum of compound **2g**



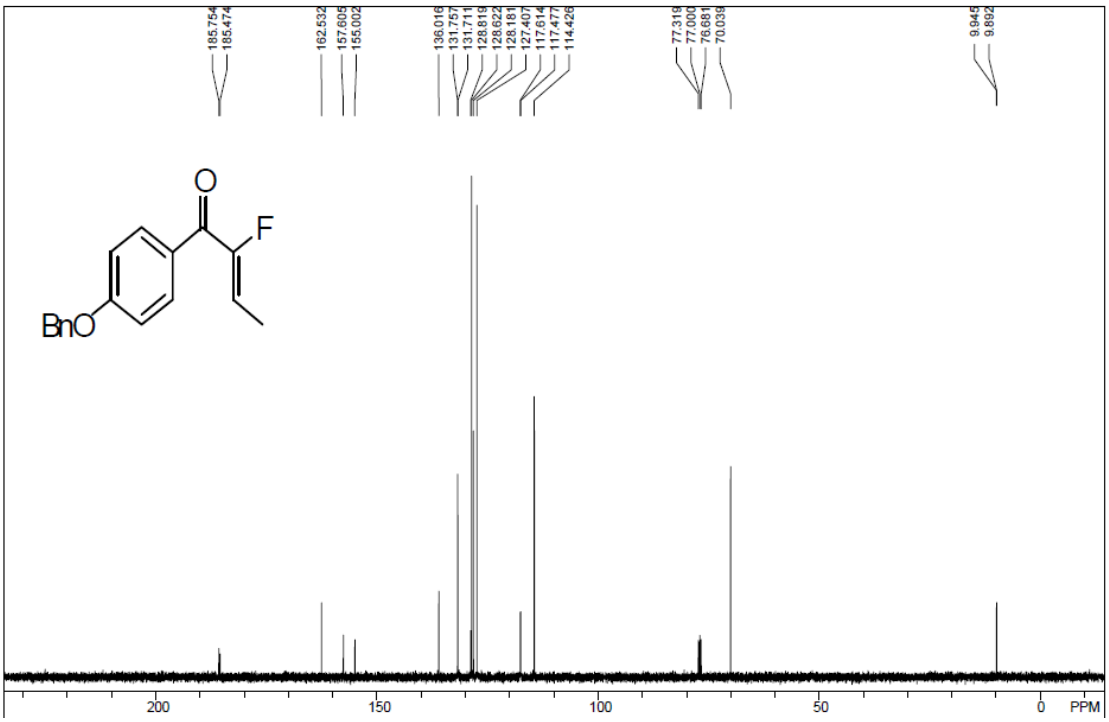
^{19}F NMR spectrum of compound **2g**



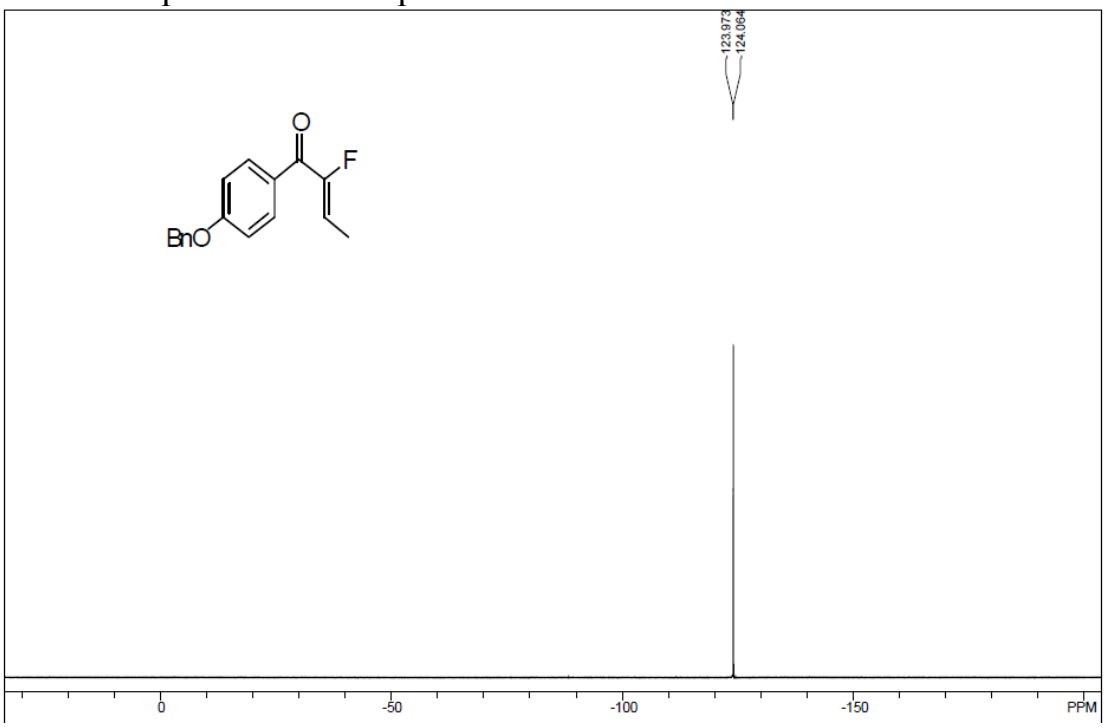
^{1}H NMR spectrum of compound ***Z*-2h**



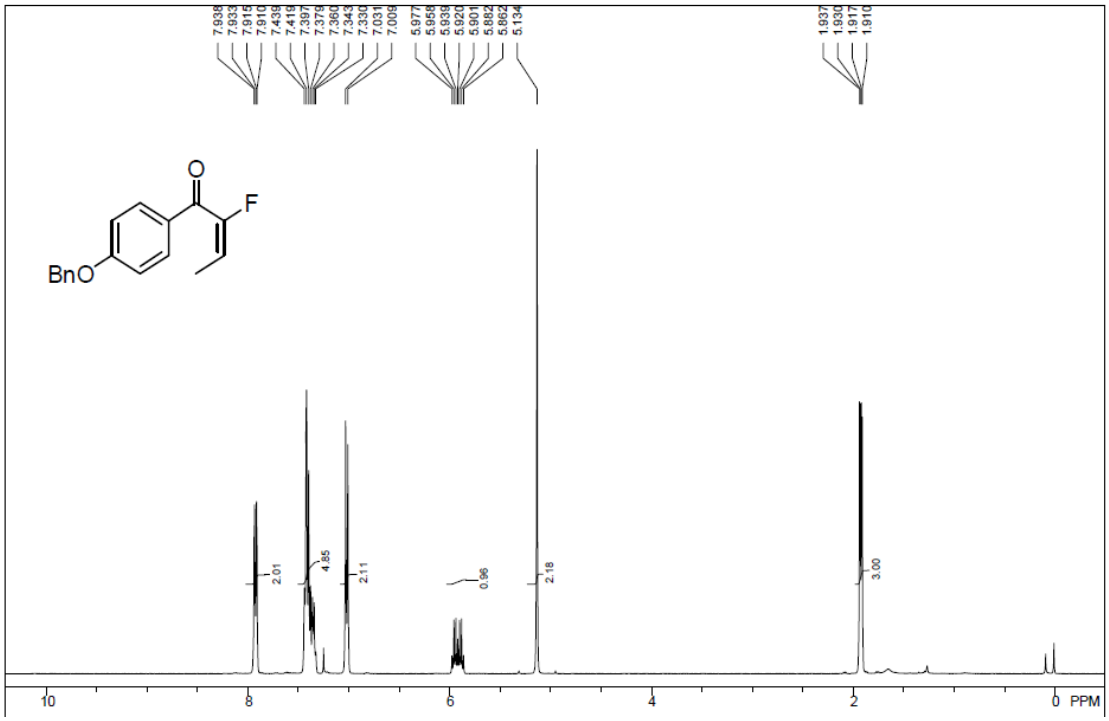
^{13}C NMR spectrum of compound ***Z*-2h**



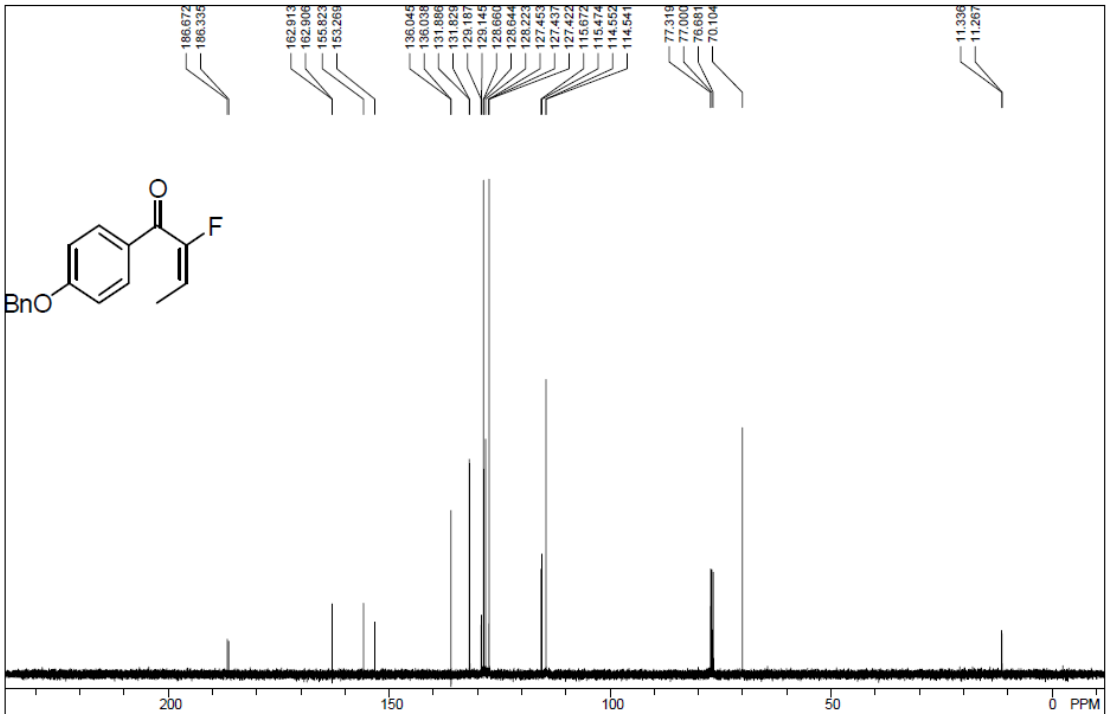
^{19}F NMR spectrum of compound ***Z*-2h**



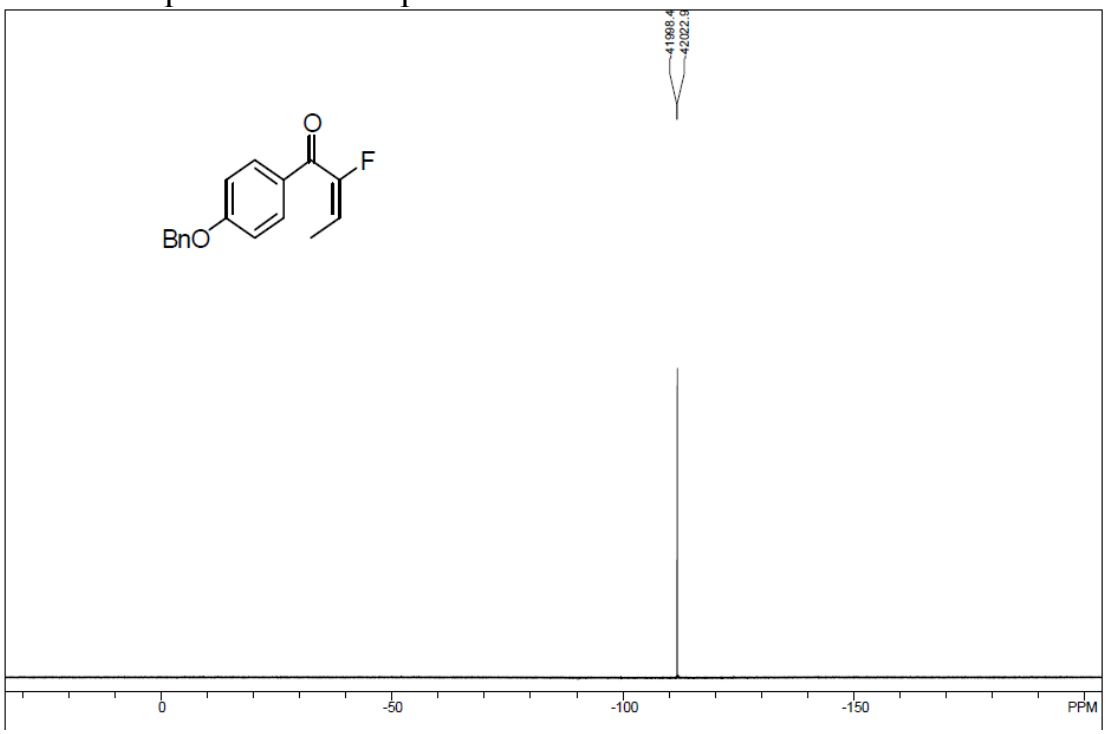
^{1}H NMR spectrum of compound *E*-**2h**



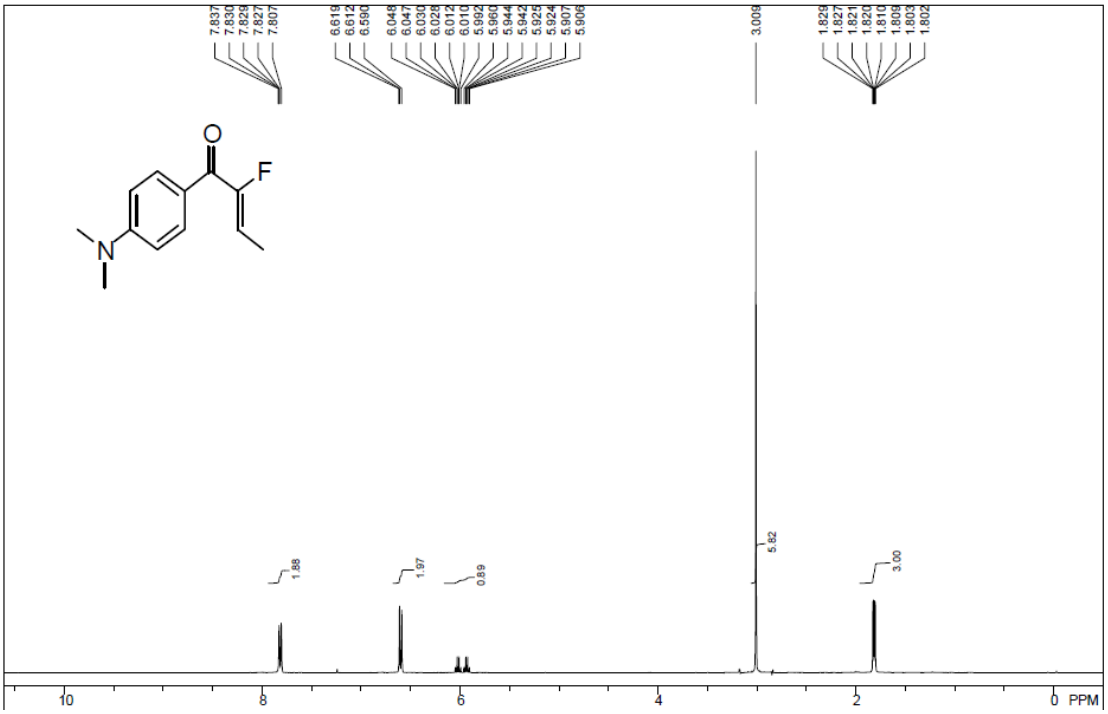
^{13}C NMR spectrum of compound *E*-**2h**



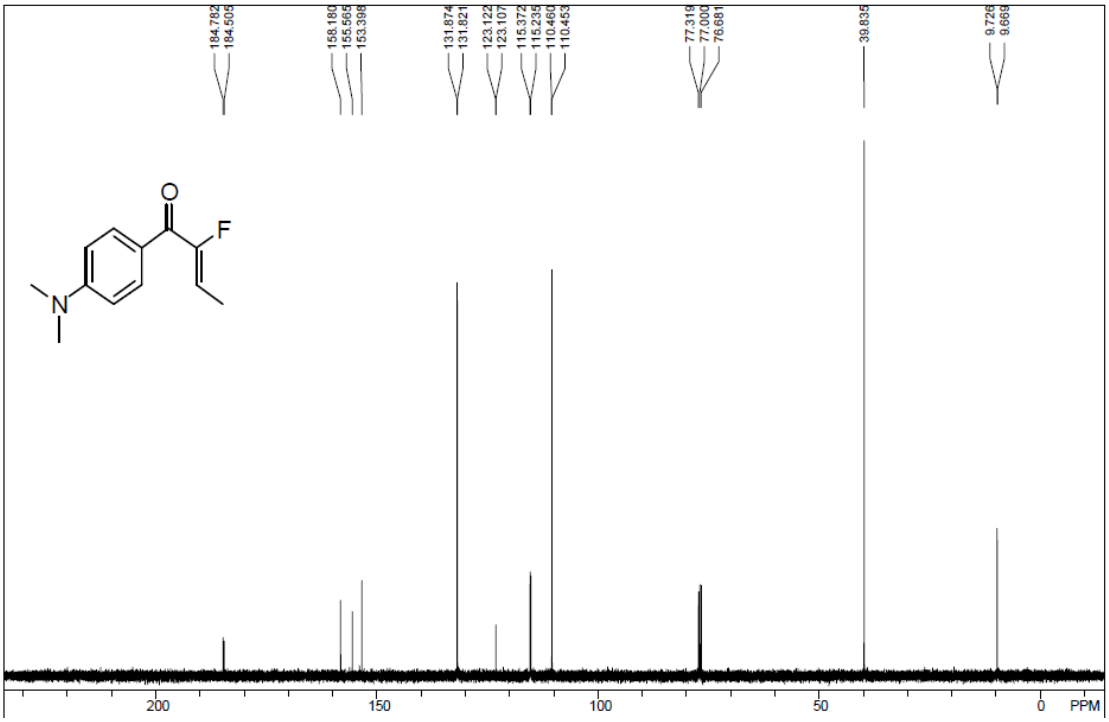
^{19}F NMR spectrum of compound ***E*-2i**



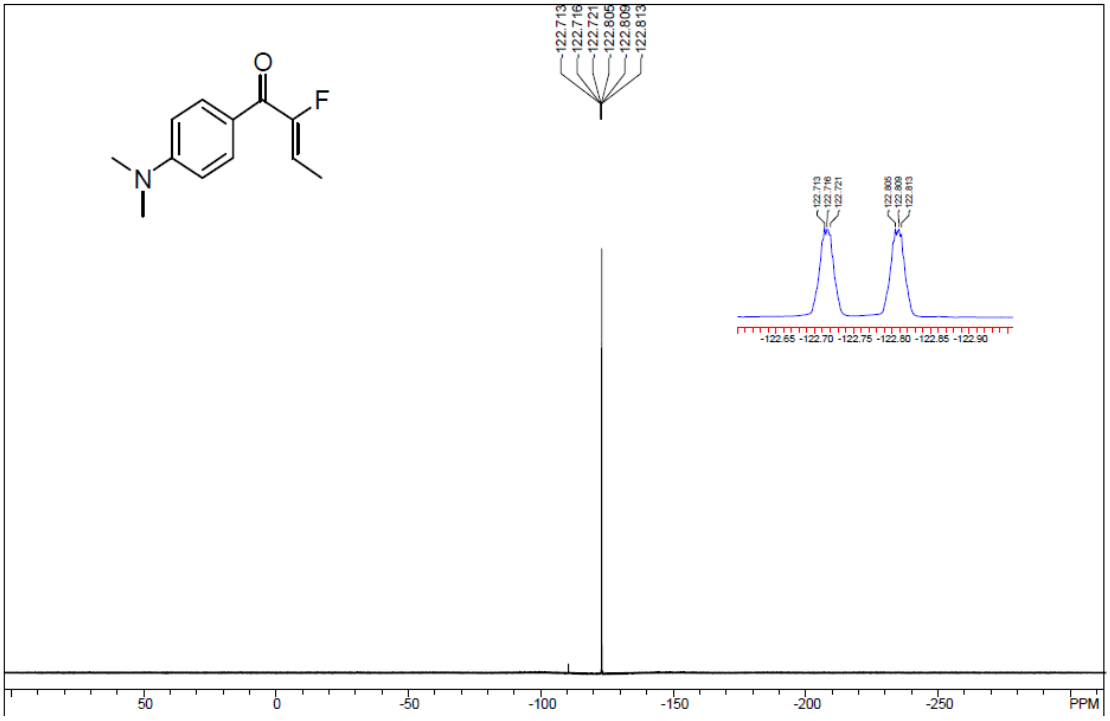
^{1}H NMR spectrum of compound *Z*-**2i**



^{13}C NMR spectrum of compound *Z*-**2i**

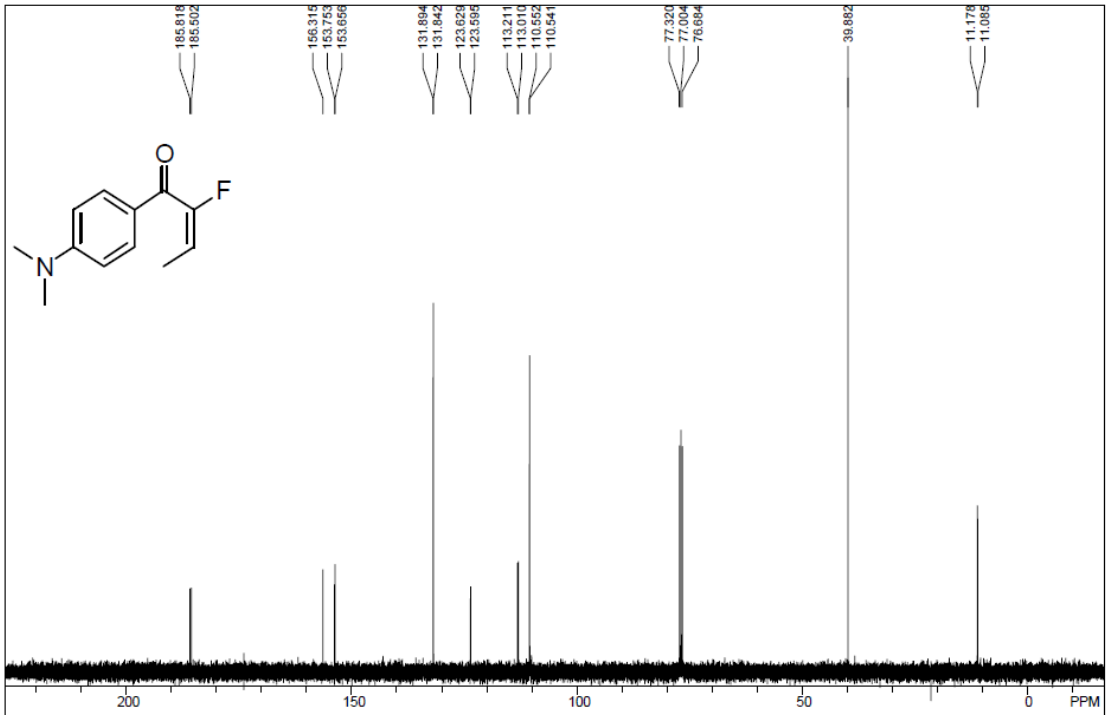


^{19}F NMR spectrum of compound *Z*-**2i**

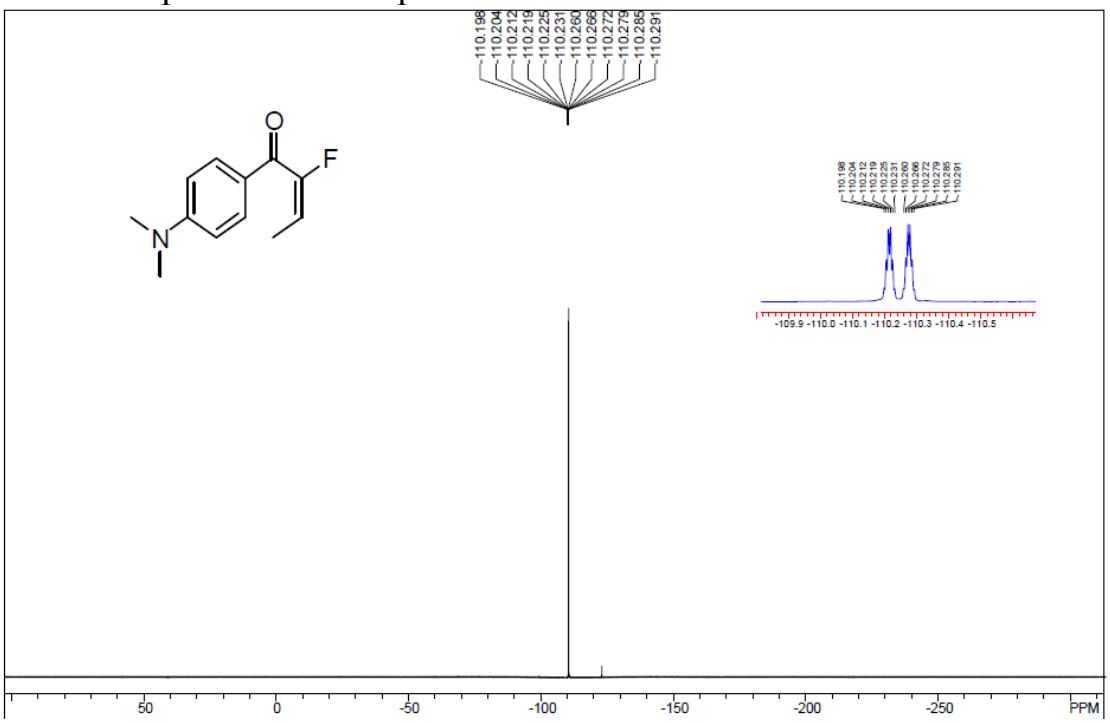


^{1}H NMR spectrum of compound *E*-**2i**

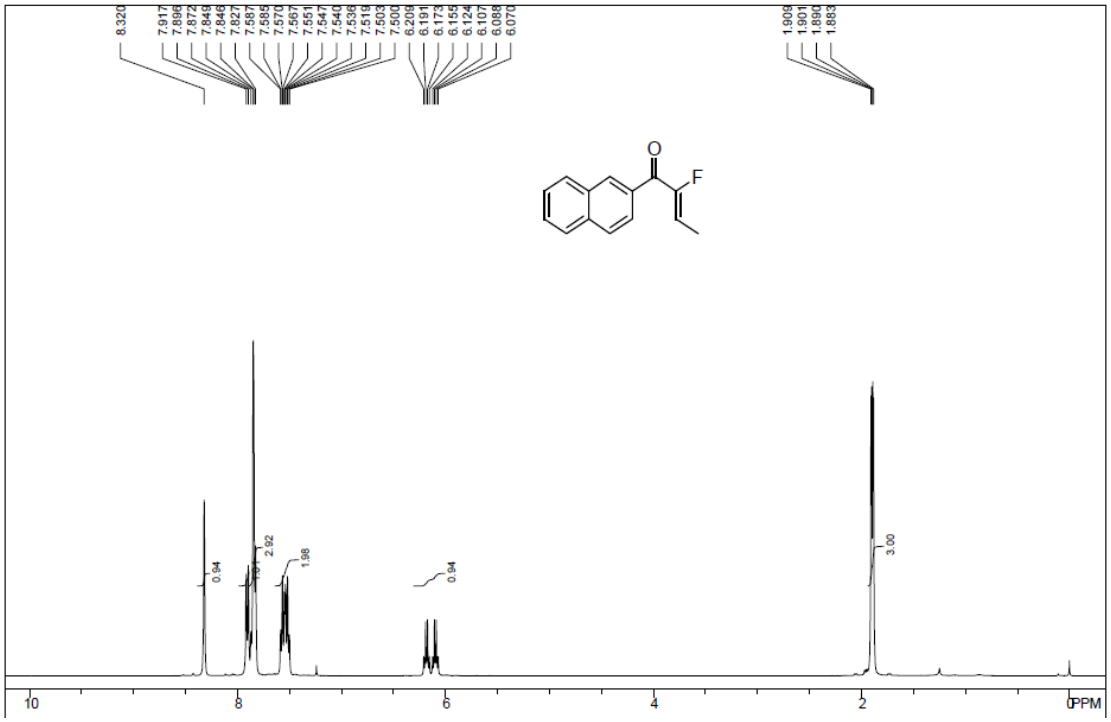
^{13}C NMR spectrum of compound *E*-**2i**



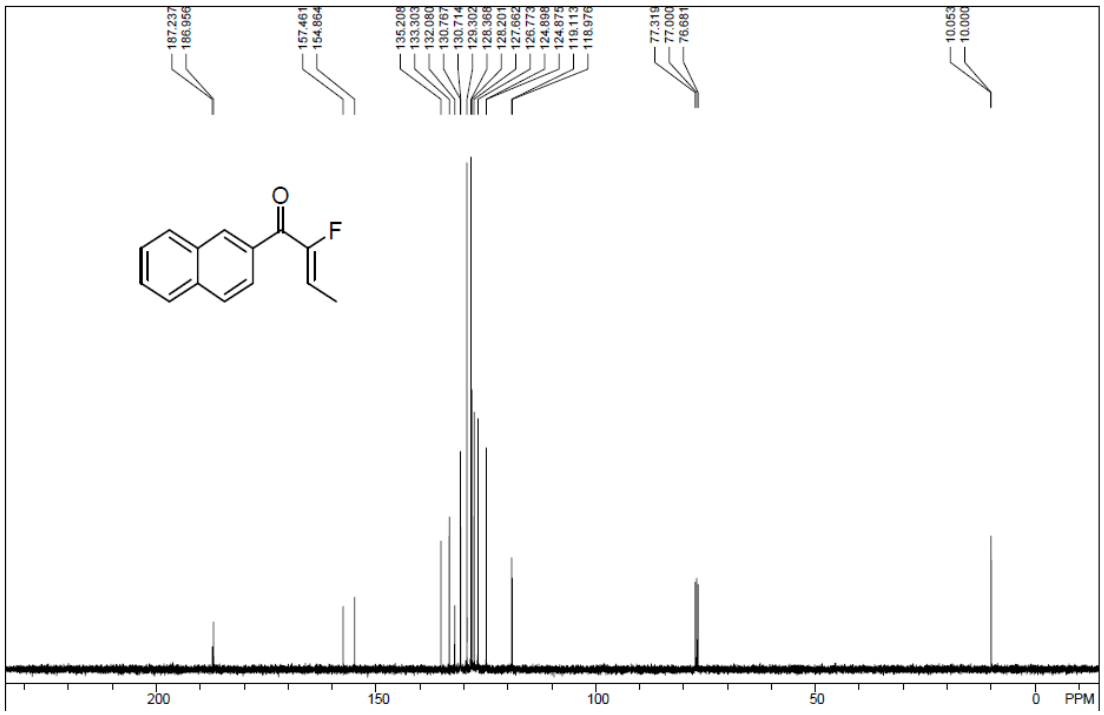
^{19}F NMR spectrum of compound *E*-**2i**



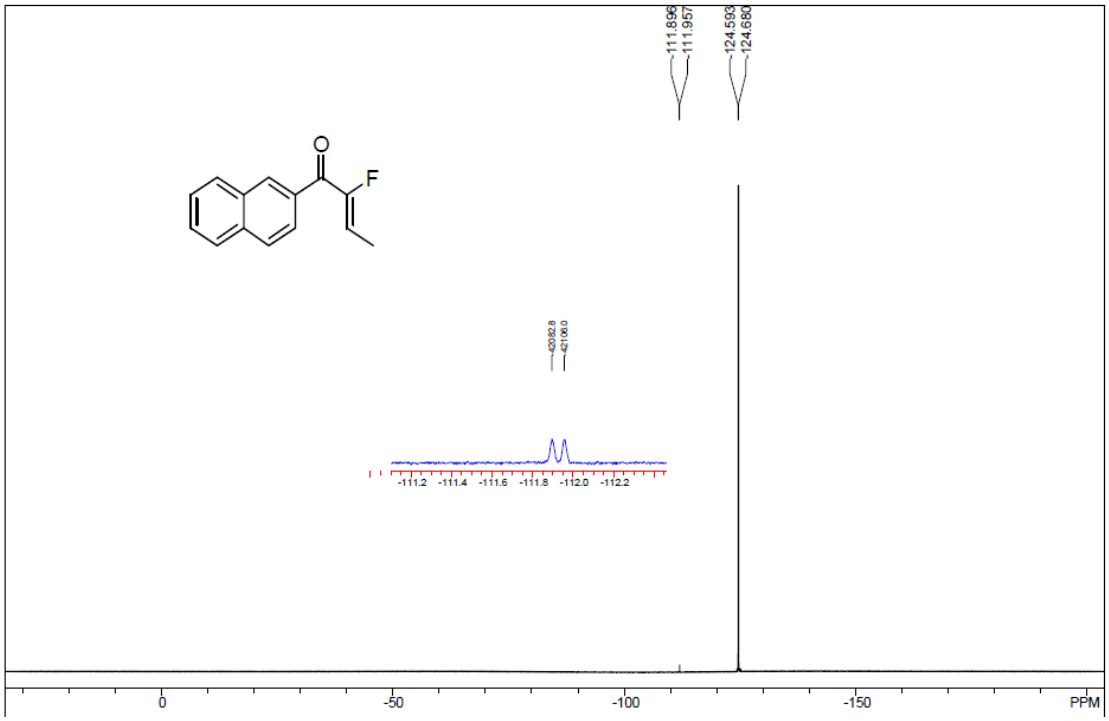
^{1}H NMR spectrum of compound **2l**



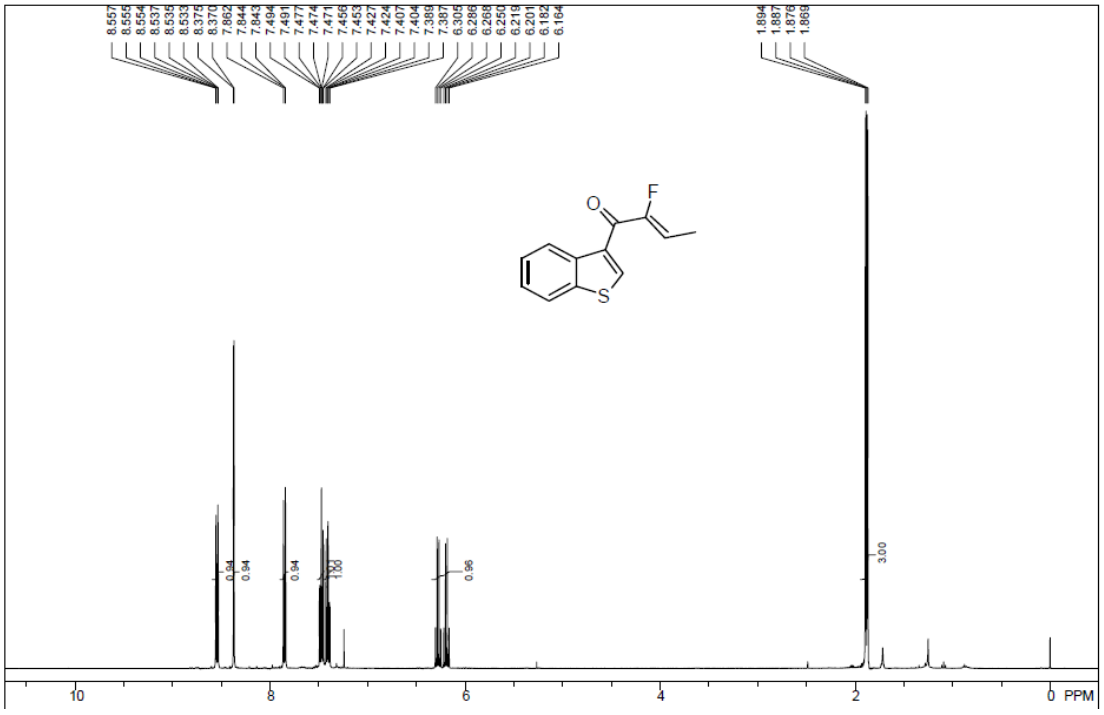
^{13}C NMR spectrum of compound **2l**



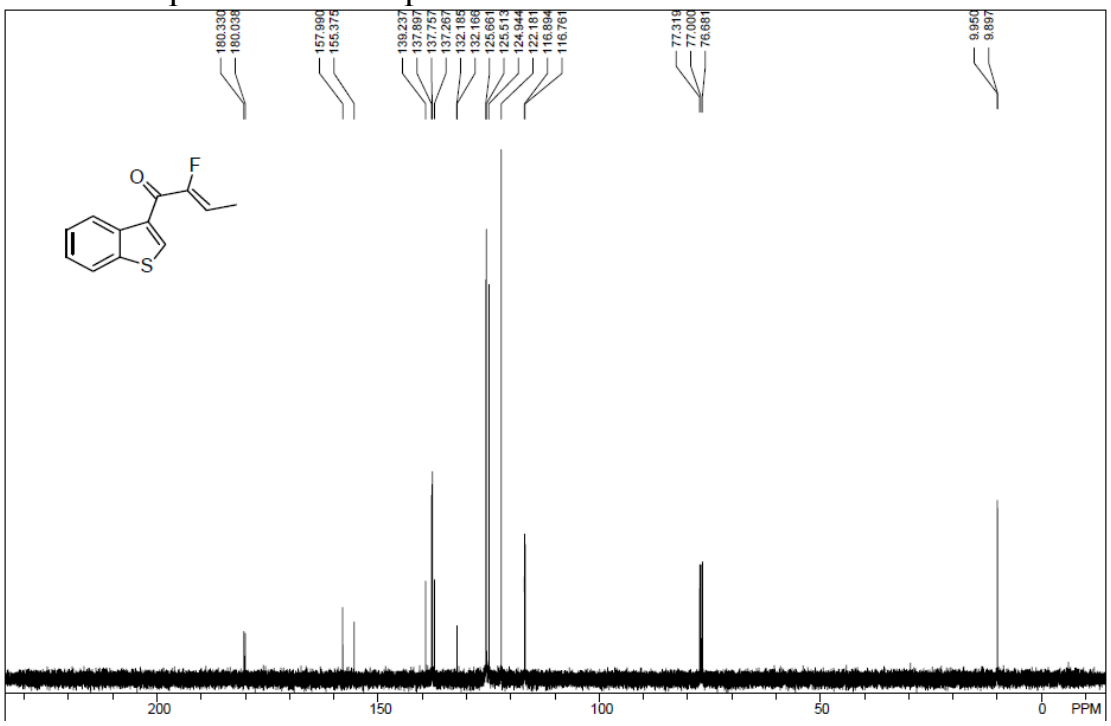
^{19}F NMR spectrum of compound **2l**



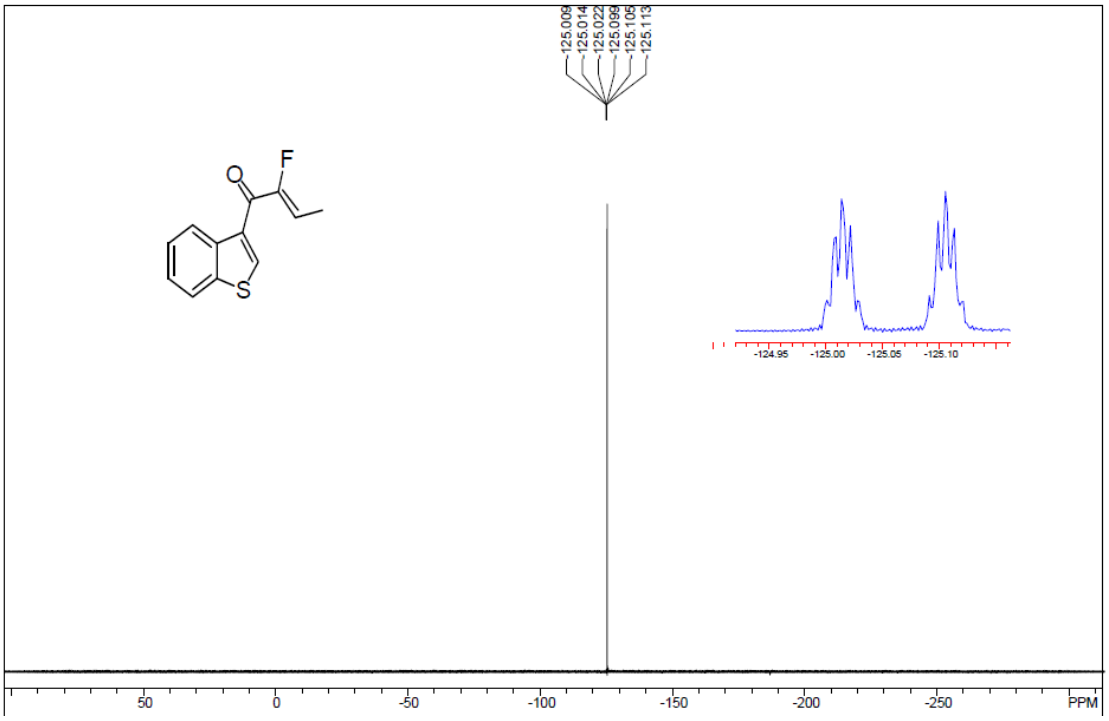
^{1}H NMR spectrum of compound **2m**



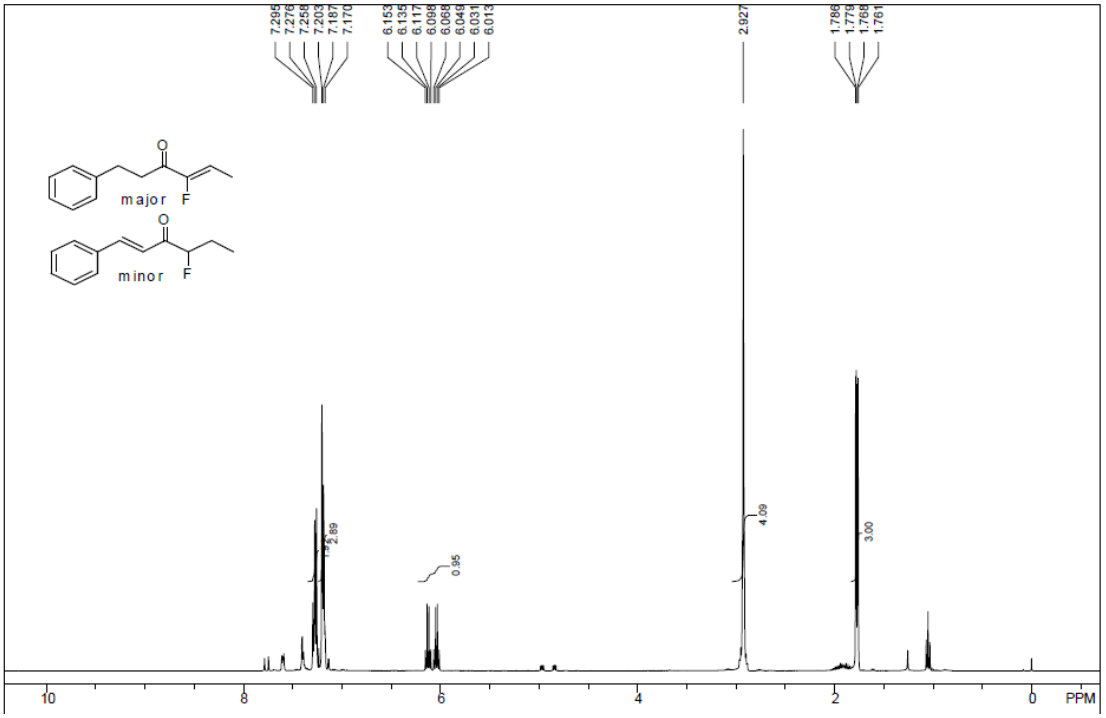
^{13}C NMR spectrum of compound **2m**



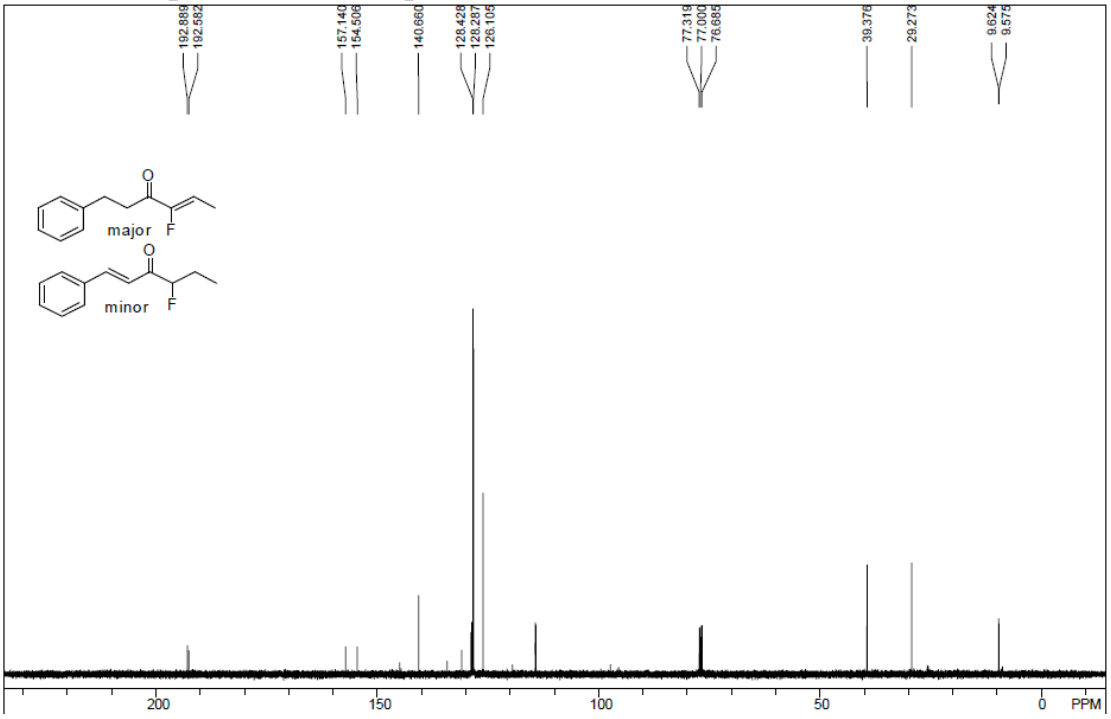
^{19}F NMR spectrum of compound **2m**



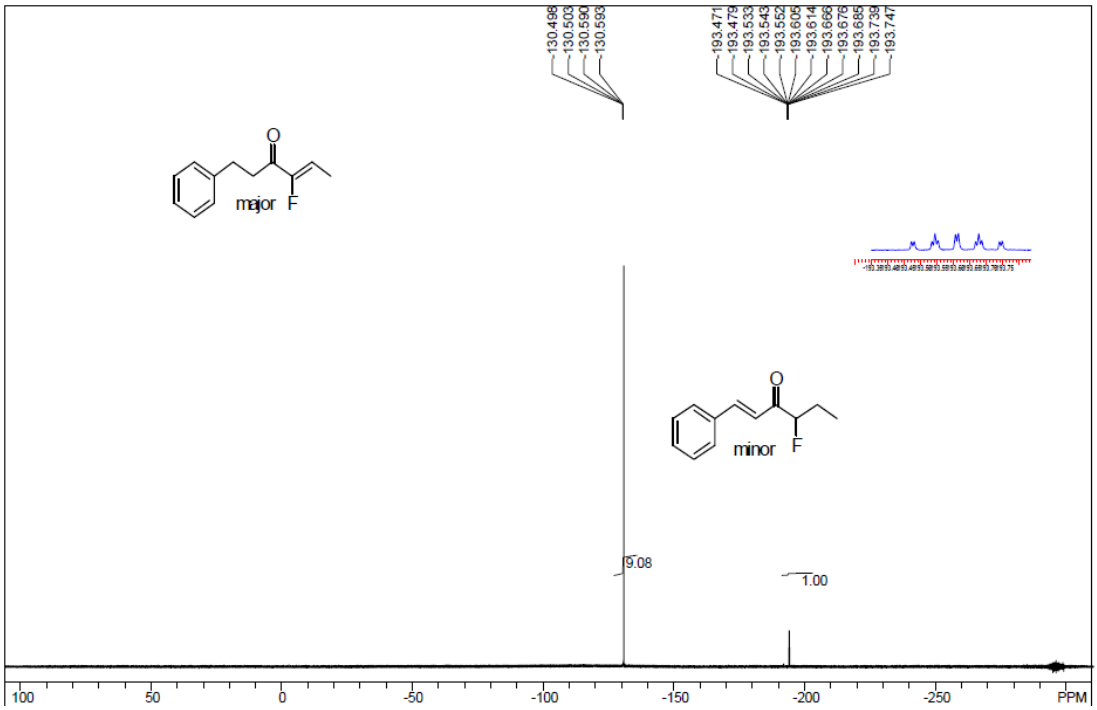
^{1}H NMR spectrum of compound **2nA+2nB**



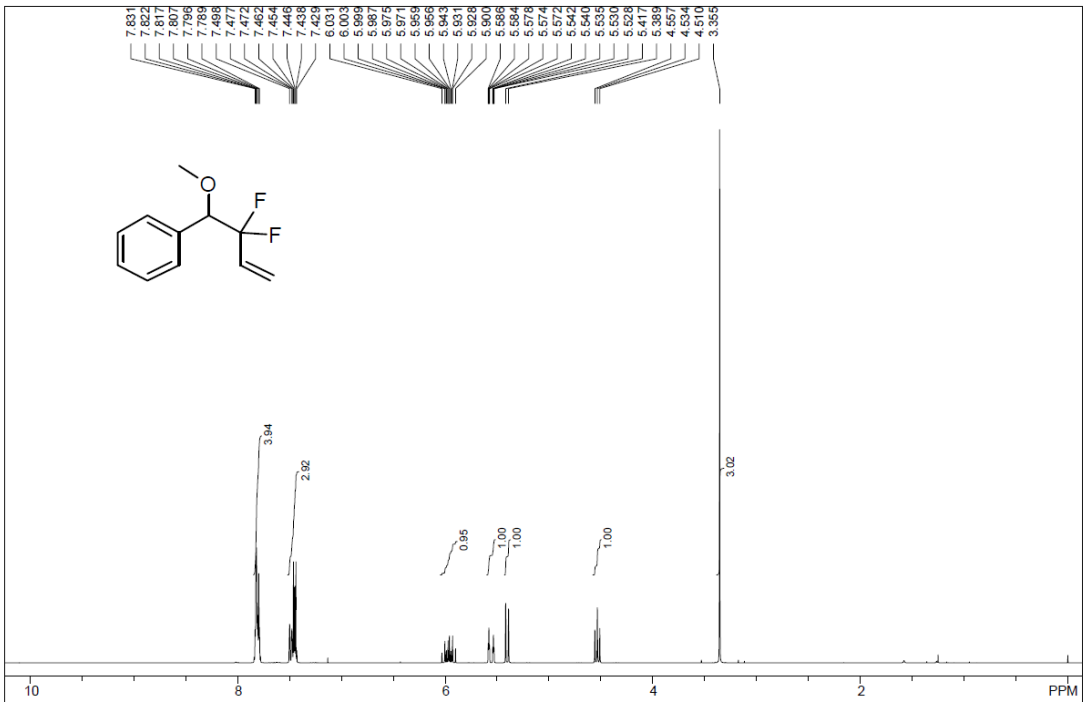
^{13}C NMR spectrum of compound **2nA+2nB**



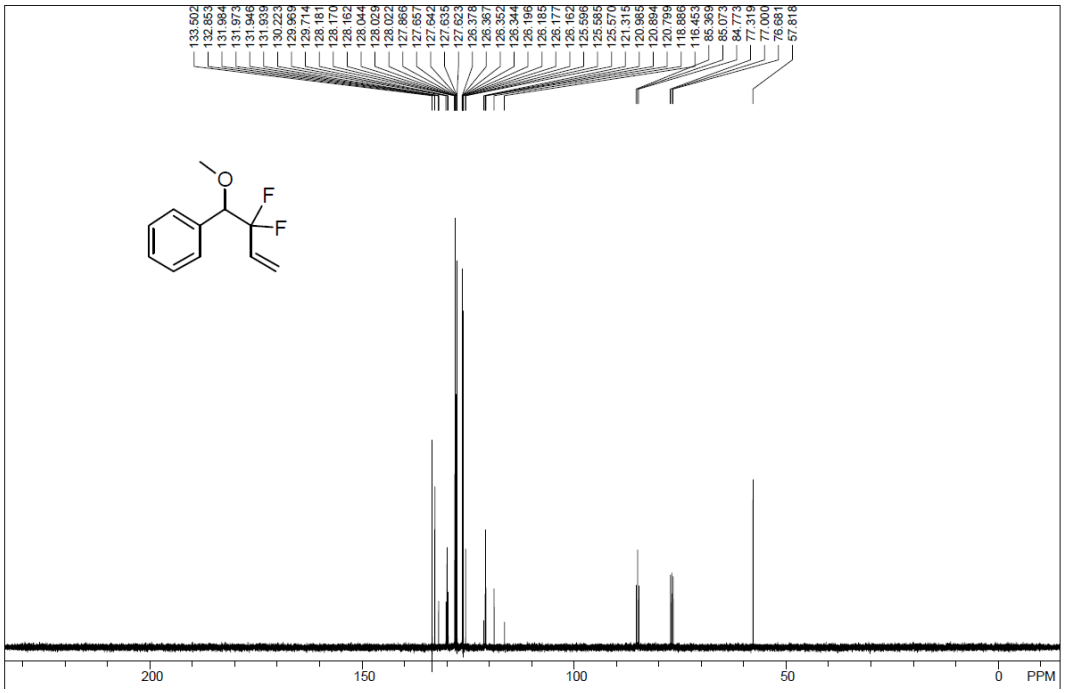
^{19}F NMR spectrum of compound **2nA+2nB**



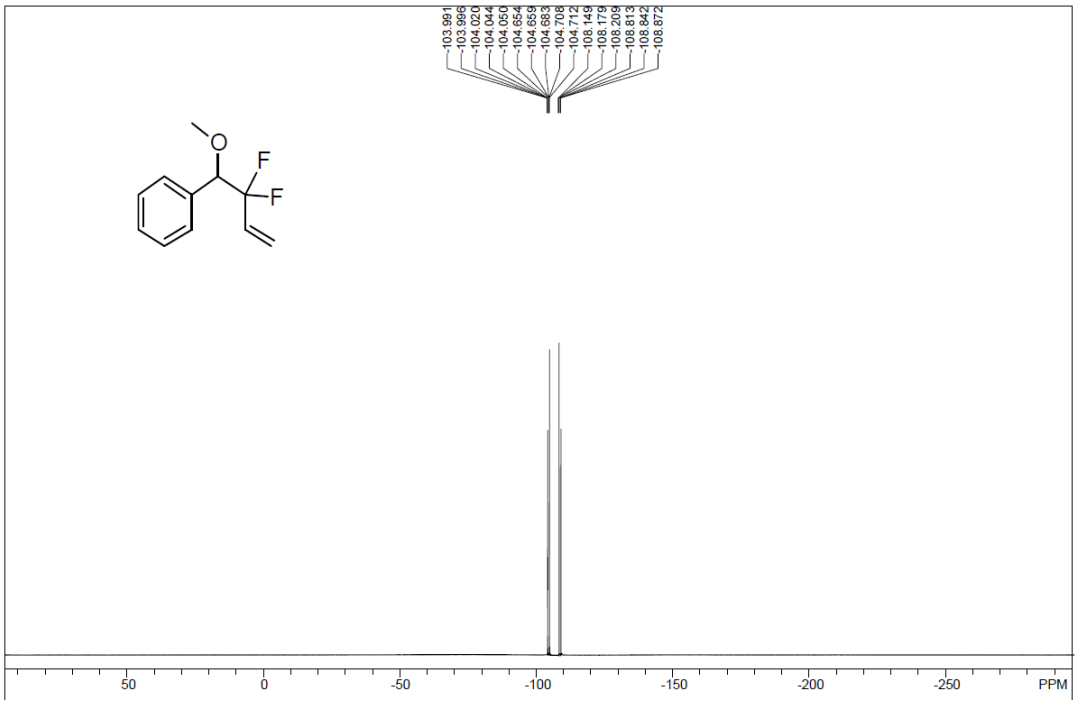
^{1}H NMR spectrum of compound **1o**



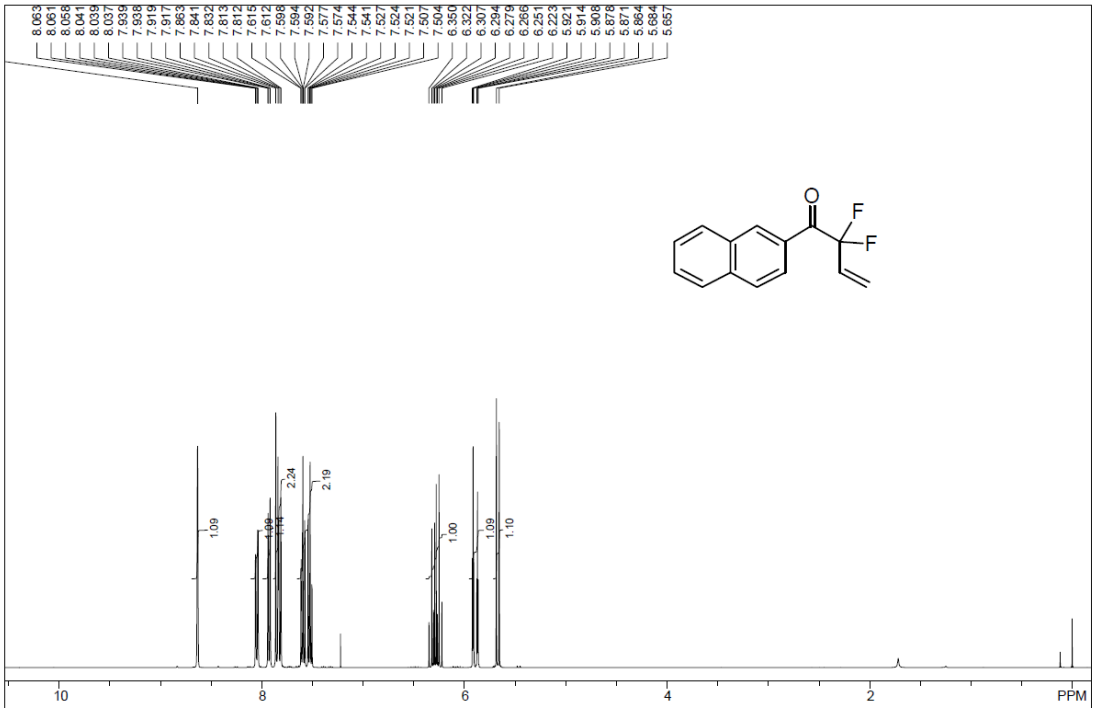
^{13}C NMR spectrum of compound **1o**



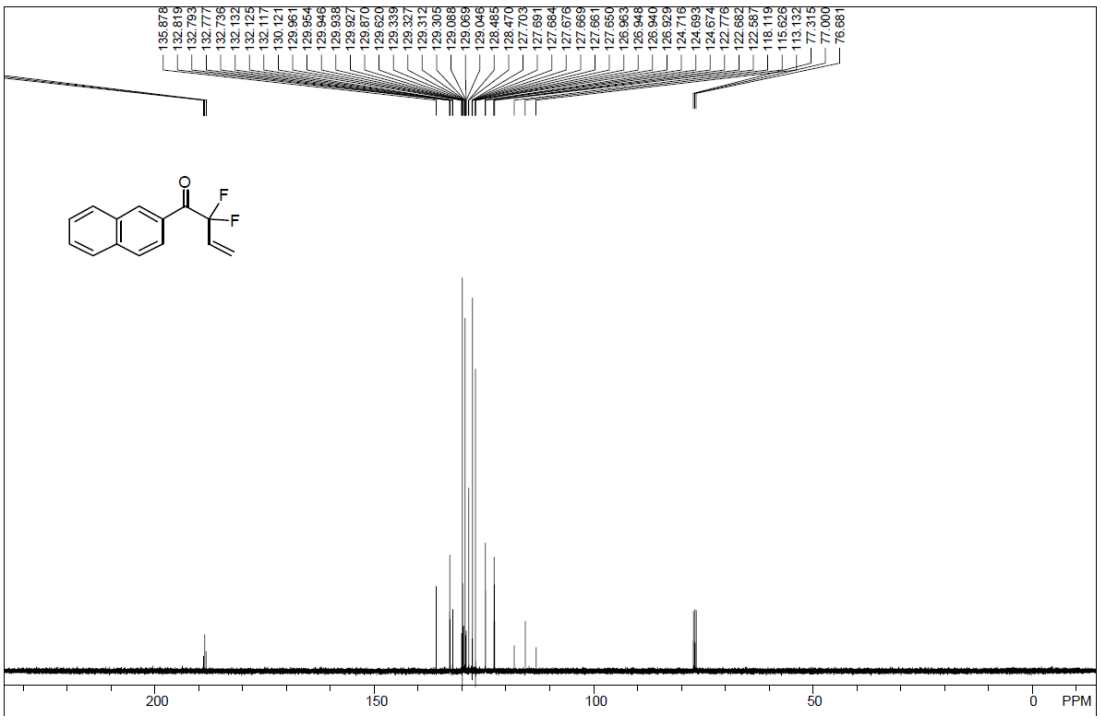
^{19}F NMR spectrum of compound **1o**



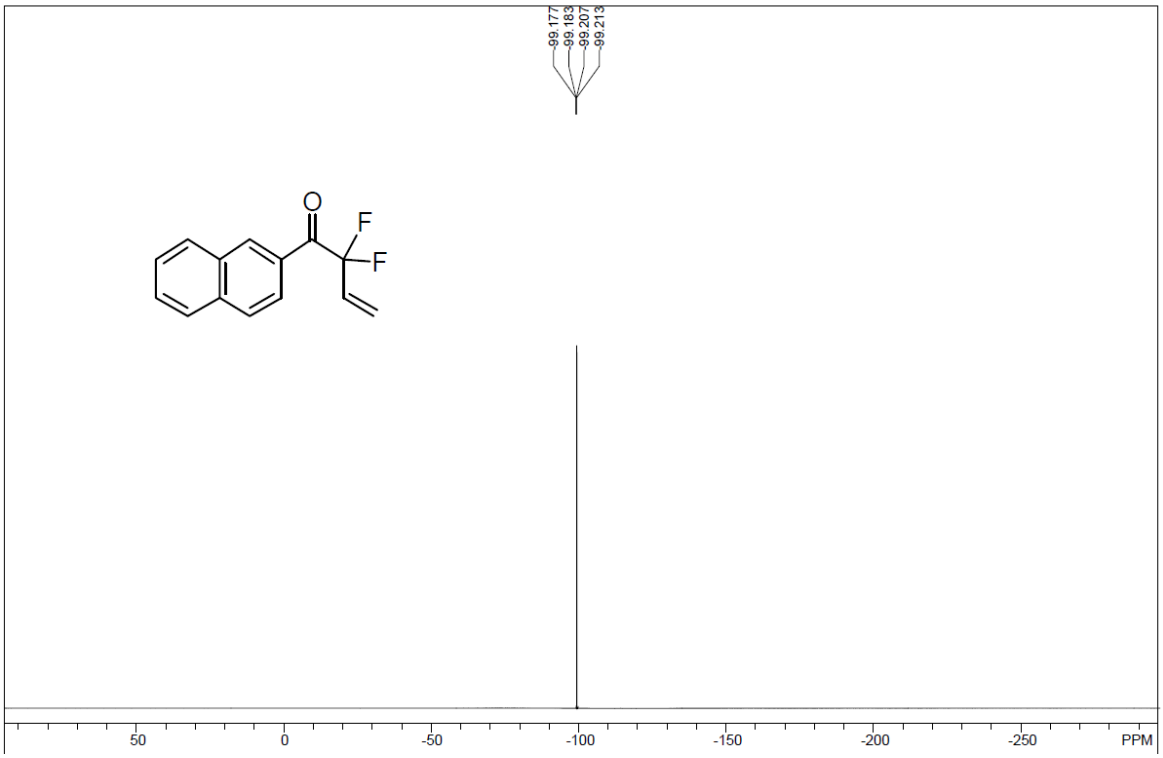
^{1}H NMR spectrum of compound **1t**



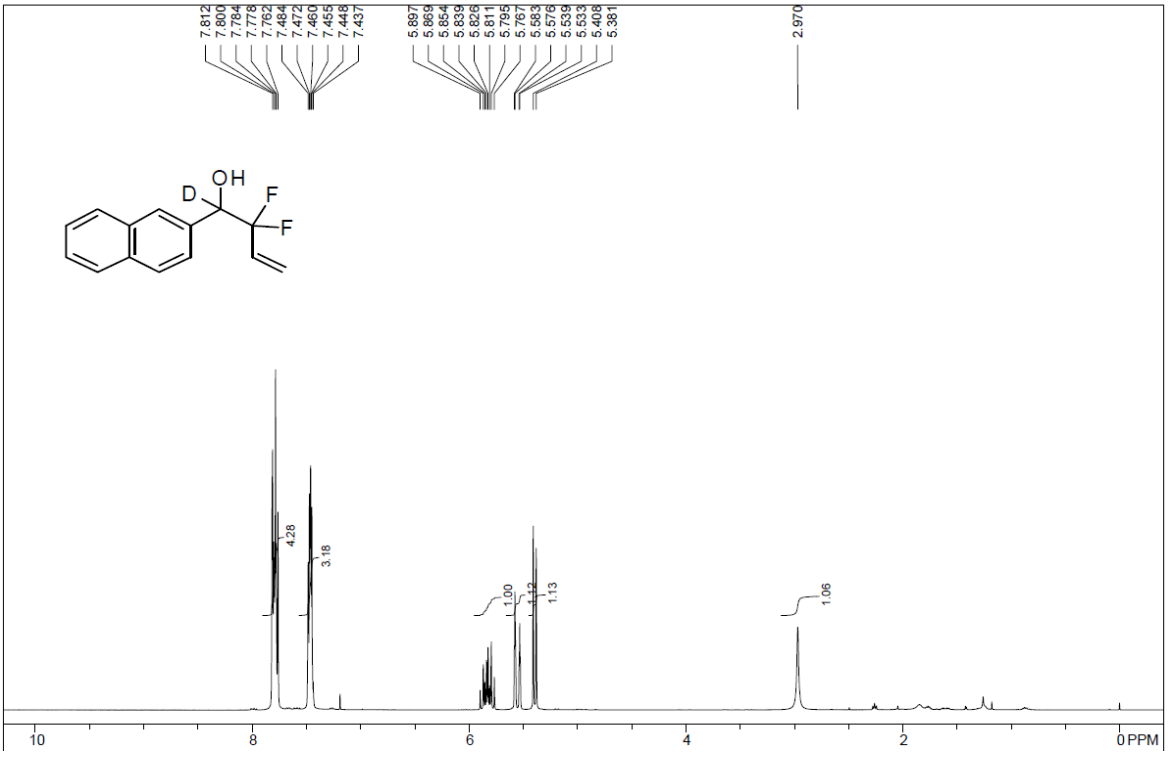
^{13}C NMR spectrum of compound **1t**



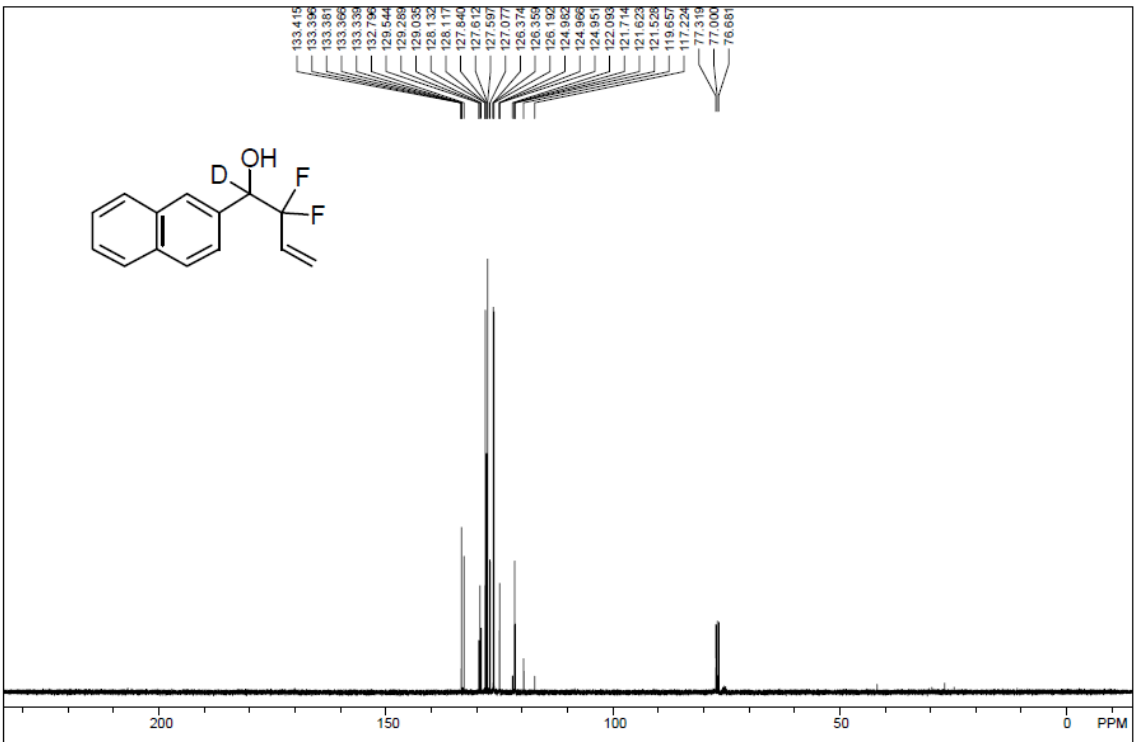
^{19}F NMR spectrum of compound **1t**



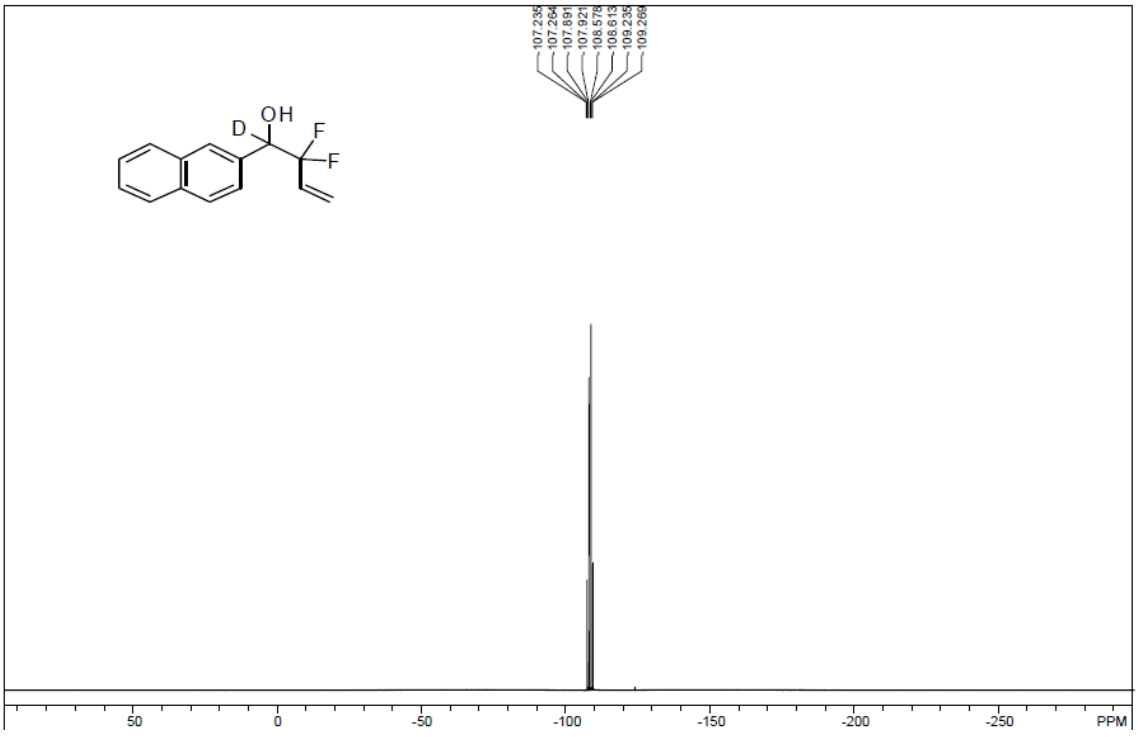
^{1}H NMR spectrum of compound **1n**



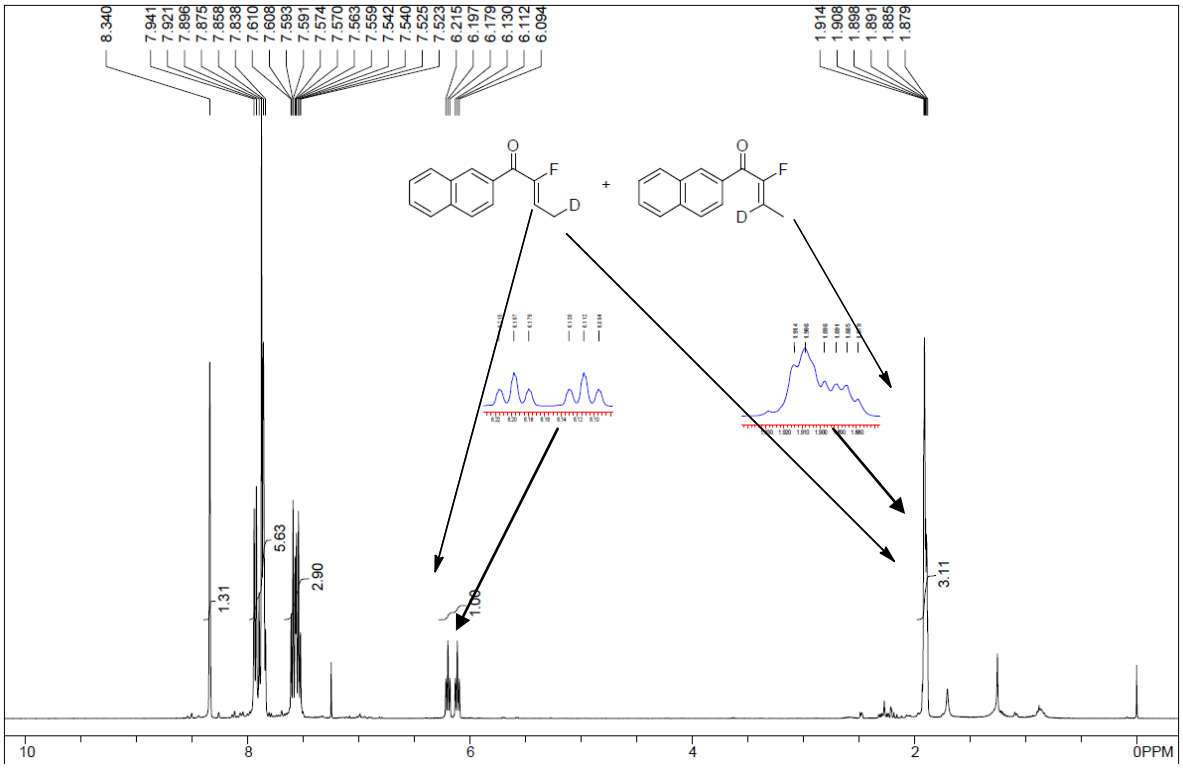
^{13}C NMR spectrum of compound **1p**



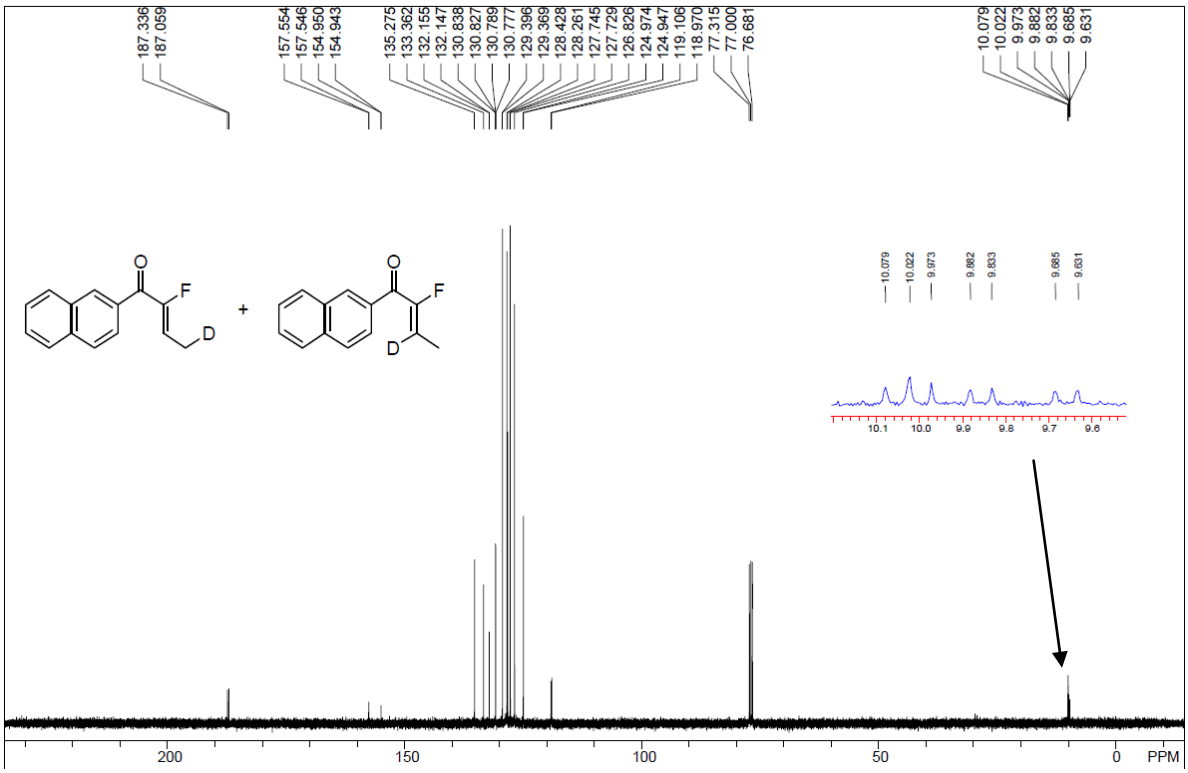
^{19}F NMR spectrum of compound **1p**



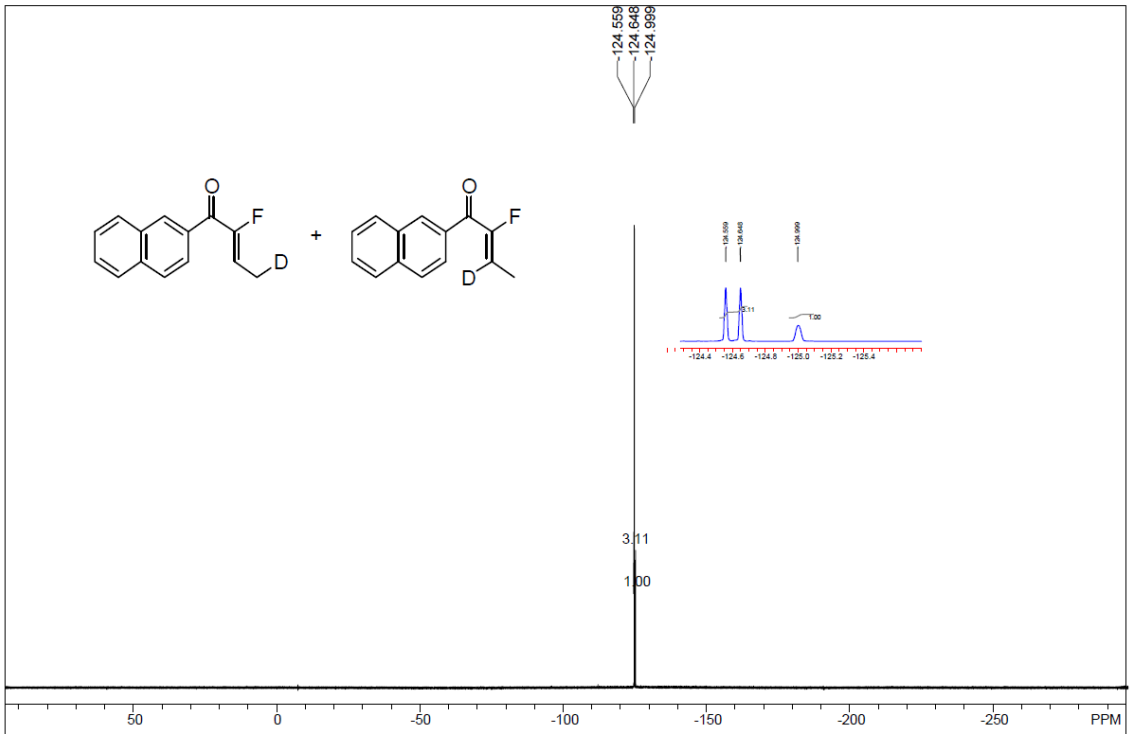
^{1}H NMR spectrum of compound **2q+2r**



^{13}C NMR spectrum of compound **2q+2r**



^{19}F NMR spectrum of compound **2q+2r**



^{2}D NMR spectrum of compound **2q+2r**