Supporting Information

Photoredox Relay-Catalyzed *gem*-Difluoroallylation of Alkyl Iodides

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Table of Contents

1. General information

Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. ^{19}F NMR spectra were recorded on a Varian 400 instrument spectrometer. Chemica shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (30 W, λ max = 470 nm) was purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

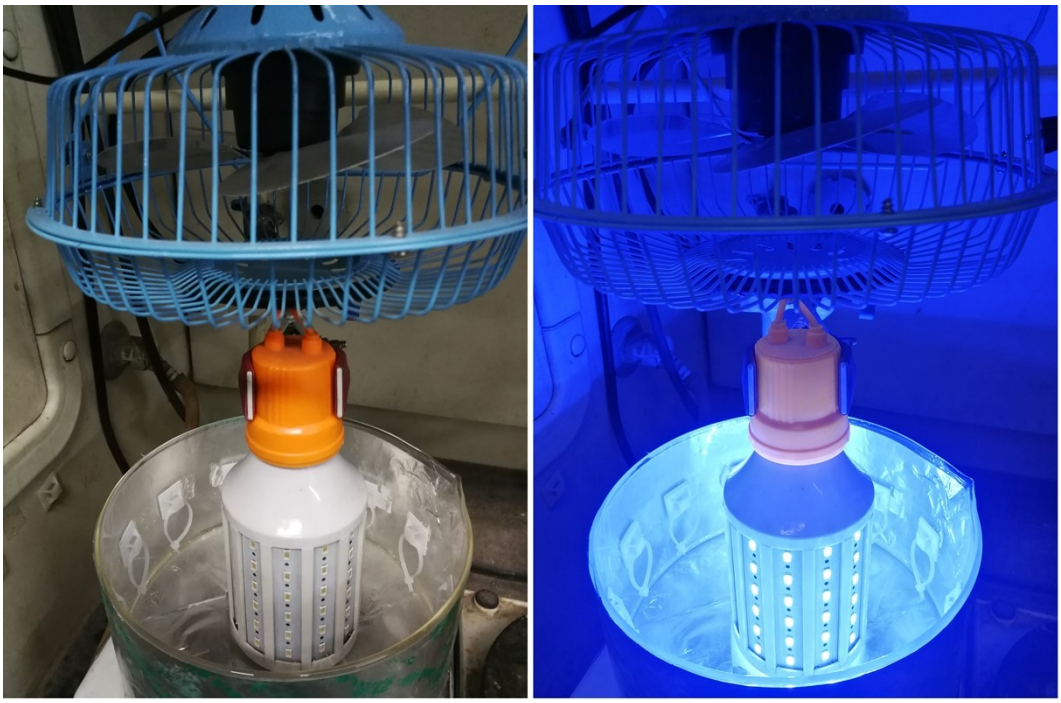
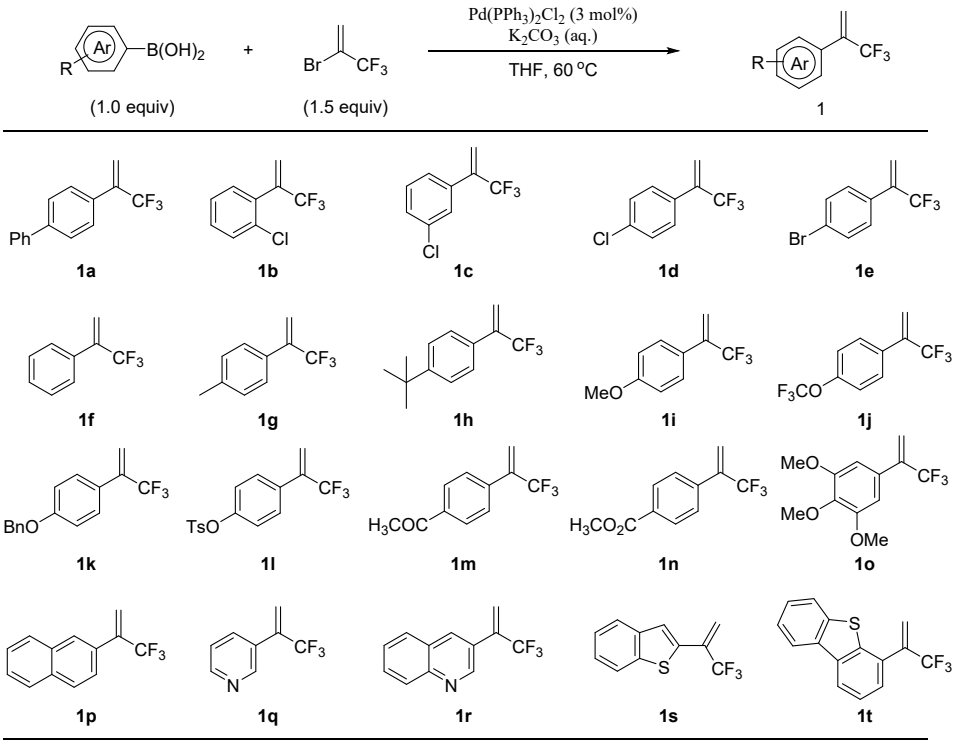


Figure S1 Photograph of the photocatalytic reactor

2. Preparation of photocatalyst $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$

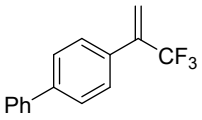
The photocatalyst was synthesized according to literature report.[1] The spectral data of the photocatalyst is consistent with the literature data. The other photocatalysts *fac*-$Ir(ppy)_3$, $[Ir(ppy)_2(dtbbpy)]PF_6$, $Ru(bpy)_3Cl_2 \cdot 6H_2O$, $Ru(bpy)_3(PF_6)_2$, Eosin Y, Mes-Acr^+-Me ClO_4^-, 4CzIPN and $Mn_2(CO)_{10}$ are commercially available.

3. General procedure for the preparation of trifluoromethyl alkenes



According to literature reports,[2] to a Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv., 3 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 0.09 mmol, 63.2 mg) were added. The vessel was evacuated and filled with argon (three times), and then aqueous K_2CO_3 (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.5 equiv., 4.5 mmol, 0.47 mL), the solution was stirred at 60 °C with heating mantle for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE - PE/EA).

4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**)



White solid, yield 77% (0.57 g).

R_f 0.55 (Petroleum ether).

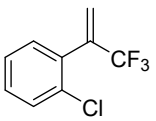
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 6.2 Hz, 4H), 7.57 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 6.01 (s, 1H), 5.86 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 140.3, 138.6 (q, $^2J_{C\text{-}F}$ = 29.9 Hz), 132.5, 128.9, 127.8, 127.7, 127.3, 127.1, 123.4 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 120.2 (q, $^3J_{C\text{-}F}$ = 5.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –64.56 (s, 3F).

The compound data is in agreement with the literature.[2]

1-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1b**)



Colorless oil, yield 48% (0.32 g).

R_f 0.70 (Petroleum ether).

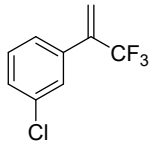
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.44 (m,1H), 7.33 – 7.23 (m, 3H), 6.20 (q, J = 0.4 Hz, 1H), 5.64 (q, J = 0.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3 (q, $^2J_{C\text{-}F}$ = 31.8 Hz), 134.0, 132.9, 131.1, 130.2, 130.0, 126.6, 124.6 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 122.8 (q, $^1J_{C\text{-}F}$ = 271.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.79 (s, 3F).

The compound data is in agreement with the literature.[3]

1-chloro-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1c**)



Colorless oil, yield 76% (0.50 g).

R_f 0.70 (Petroleum ether).

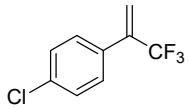
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.39 – 7.32 (m, 3H), 6.00 (d, J = 1.2 Hz, 1H), 5.79 (d, J = 1.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl3): δ 137.5 (q, $^2J_{C\text{-}F}$ = 31.5 Hz), 135.5, 134.6, 129.8, 129.3, 126.9, 125.6, 123.0 (q, $^1J_{C\text{-}F}$ = 273.8 Hz), 121.5 (q, $^3J_{C\text{-}F}$ = 5.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -64.85 (s, 3F).

The compound data is in agreement with the literature.[3]

1-chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1d**)



Colorless oil, yield 59% (0.39 g).

R_f 0.85 (Petroleum ether).

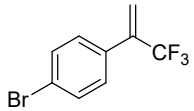
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 4H), 6.02 (s, 1H), 5.80 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (q, $^2J_{C\text{-}F}$ = 30.1 Hz), 135.2, 132.0, 128.8, 128.7, 123.2 (q, $^1J_{C\text{-}F}$ = 272.2 Hz),120.8 (q, $^3J_{C\text{-}F}$ = 5.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –64.97 (s, 3F).

The compound data is in agreement with the literature.[2]

1-bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1e**)



Colorless oil, yield 64% (0.48 g).

R_f 0.90 (Petroleum ether).

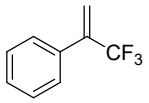
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.94 (s, 1H), 5.73 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (q, $^2J_{C\text{-}F}$ = 30.1 Hz), 132.5,131.8, 129.0, 123.4, 123.1 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 120.8 (q, $^3J_{C\text{-}F}$ = 5.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –64.91 (s, 3F).

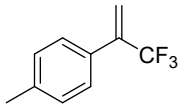
The compound data is in agreement with the literature.[2]

(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1f**)



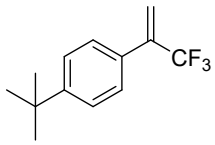
Colorless oil, yield 54% (0.28 g).
R_f 0.80 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.43 – 7.35 (m, 3H), 5.97 (s, 1H), 5.78 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (q, $^2J_{C\text{-}F}$ = 29.9 Hz), 133.7, 129.0, 128.6, 127.4, 123.4 (q, $^1J_{C\text{-}F}$ = 272.1 Hz),120.4 (q, $^3J_{C\text{-}F}$ = 5.7 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.79 (s, 3F).
The compound data is in agreement with the literature.[2]

1-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1g**)



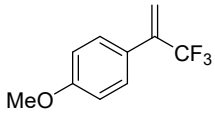
Colorless oil, yield 56% (0.31 g).
R_f 0.90 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.92 (s, 1H), 5.75 (s, 1H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.9 (q, $^2J_{C\text{-}F}$ = 29.3 Hz), 130.9, 129.4, 127.3, 123.6 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 119.6 (q, $^3J_{C\text{-}F}$ = 5.8 Hz), 21.2.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.84 (s, 3F).
The compound data is in agreement with the literature.[2]

1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1h**)



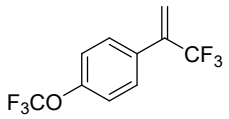
Colorless oil, yield 75% (0.51 g).
R_f 0.75 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 4H), 5.99 (s, 1H), 5.83 (s, 1H), 1.42 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 138.8 (q, $^2J_{C\text{-}F}$ = 29.5 Hz), 130.7, 127.0, 125.6, 123.5 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 119.4 (q, $^3J_{C\text{-}F}$ = 5.9 Hz), 34.6, 32.2.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.64 (s, 3F).
The compound data is in agreement with the literature.[4]

1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1i**)



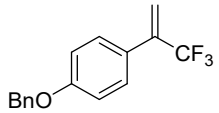
Colorless oil, yield 48% (0.29 g).
R_f 0.80 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 5.87 (q, J = 1.2 Hz, 1H), 5.70 (q, J = 1.6 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 138.2 (q, $^2J_{C\text{-}F}$ = 29.7 Hz), 128.6, 126.0, 123.5 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 118.8 (q, $^3J_{C\text{-}F}$ = 5.8 Hz), 114.0, 55.3.
^{19}F NMR (376 MHz, $CDCl_3$): δ –69.45 (s, 3F).
The compound data is in agreement with the literature.[2]

1-(trifluoromethoxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1j**)



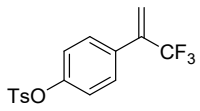
Colorless oil, yield 30% (0.22 g).
R_f 0.80 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.25 – 7.22 (m, 2H), 6.03 – 5.96 (m, 1H), 5.78 – 5.76 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 137.9 (q, $^2J_{C\text{-}F}$ = 30.4 Hz), 132.2, 129.0, 123.1 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 121.1 ($^3J_{C\text{-}F}$, J = 5.6 Hz), 120.9, 120.4 (q, $^1J_{C\text{-}F}$ = 256.4 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ –57.94 (s, 3F), –65.13 (s, 3F).
The compound data is in agreement with the literature.[4]

1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1k**)



White solid, yield 85% (0.71 g).
R_f 0.65 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 7H), 6.98 (d, J = 8.9 Hz, 2H), 5.87 (q, J = 1.2 Hz, 1H), 5.70 (q, J = 1.6 Hz, 1H), 5.09 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 138.3 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 136.7, 128.7, 128.1, 127.5, 126.3, 123.5 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 118.9 (q, $^3J_{C\text{-}F}$ = 5.6 Hz), 114.9, 70.1.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.76 (s, 3F).
The compound data is in agreement with the literature.[5]

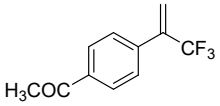
4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl 4-methylbenzenesulfonate (**1l**)



Colorless oil, yield 70% (0.72 g).
R_f 0.50 (Petroleum ether/EtOAc, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 5.96 (q, J = 0.8 Hz, 1H), 5.75 (q, J = 1.2 Hz, 1H), 2.45 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 145.6, 137.8 (q, $^2J_{C\text{-}F}$ = 30.1 Hz), 132.5, 132.3, 129.9, 128.8, 128.5,

123.1 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 122.6, 121.3 (q, $^{3}J_{C\text{-}F}$ = 5.8 Hz), 21.7.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.87 (s, 3F).
The compound data is in agreement with the literature.[5]

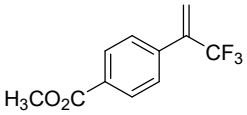
1-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one (**1m**)



Light yellow oil, yield 79% (0.51 g).
R_f 0.30 (Petroleum ether/EtOAc, 20/1).

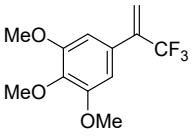
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 6.04 (d, J = 1.1 Hz, 1H), 5.86 (d, J = 1.5 Hz, 1H), 2.60 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 138.2 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz), 137.9, 137.3, 128.5, 127.6, 123.0 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 121.9 (q, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 26.6.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.64 (s, 3F).
The compound data is in agreement with the literature.[4]

methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (**1n**)



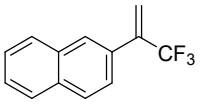
Colorless oil, yield 86% (0.59 g).
R_f 0.35 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 6.07 (s, 1H), 5.88 (s, 1H), 3.95 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 138.3 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz), 137.9, 130.6, 129.8, 127.4, 123.1 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 121.9 (q, $^{3}J_{C\text{-}F}$ = 5.7 Hz), 52.3.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.67 (s, 3F).
The compound data is in agreement with the literature.[2]

1,2,3-trimethoxy-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1o**)



Colorless oil, yield 75% (0.59 g).
R_f 0.20 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 2H), 5.92 (s, 1H), 5.73 (s, 1H), 3.87 (s, 6H), 3.86 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 138.828, 138.827 (q, $^{2}J_{C\text{-}F}$ = 30 Hz), 129.2, 123.3 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 120.3 (q, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 104.9, 60.9, 56.1.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.79 (s, 3F).
The compound data is in agreement with the literature.[4]

2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (**1p**)



Colorless oil, yield 75% (0.50 g).

R_f 0.50 (Petroleum ether).

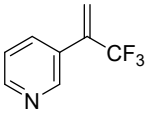
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91 – 7.86 (m, 3H), 7.60 (d, J = 8.5 Hz, 1H), 7.55 (dq, J = 6.8, 3.6 Hz, 2H), 6.08 (d, J = 1.1 Hz, 1H), 5.93 (d, J = 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1 (q, $^2J_{C\text{-}F}$ = 29.7 Hz), 133.3, 133.1, 130.9, 128.5, 128.3, 127.6, 127.0, 126.8, 126.6, 124.7, 123.5 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 120.7 (q, $^3J_{C\text{-}F}$ = 5.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –64.35 (s, 3F).

The compound data is in agreement with the literature.[2]

3-(3,3,3-trifluoroprop-1-en-2-yl)pyridine (**1q**)



Colorless oil, yield 37% (0.19 g).

R_f 0.80 (Petroleum ether/EtOAc, 5/1).

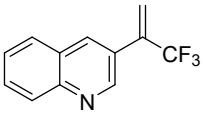
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.63 (d, J = 4.7 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.33 (dd, J = 7.9, 4.9 Hz, 1H), 6.06 (s, 1H), 5.84 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 148.5, 136.2 (q, $^2J_{C\text{-}F}$ = 29.0 Hz), 134.6, 129.6, 123.2, 122.9 (q, $^1J_{C\text{-}F}$ = 271.5 Hz), 122.0 (q, $^3J_{C\text{-}F}$ = 4.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –65.22 (s, 3F).

The compound data is in agreement with the literature.[2]

3-(3,3,3-trifluoroprop-1-en-2-yl)quinoline (**1r**)



White solid, yield 52% (0.35 g).

R_f 0.30 (Petroleum ether/EtOAc, 10/1).

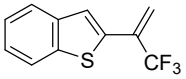
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 1.6 Hz, 1H), 8.23 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 6.15 (s, 1H), 5.98 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 147.9, 136.3 (q, $^2J_{C\text{-}F}$ = 30.5 Hz), 134.4, 130.4, 129.3, 128.3, 127.4, 127.2, 126.4, 123.1 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 122.1 (q, $^3J_{C\text{-}F}$ = 5.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –64.97 (s, 3F).

The compound data is in agreement with the literature.[4]

2-(3,3,3-trifluoroprop-1-en-2-yl)benzo[b]thiophene (**1s**)



White solid, yield 60% (0.41 g).

R_f 0.70 (Petroleum ether).

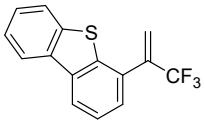
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.68 (m, 2H), 7.46 (s, 1H), 7.39 – 7.36 (m, 2H), 5.97 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 138.8, 135.5, 133.0 (q, $^2J_{C\text{-}F}$ = 31.3 Hz), 125.7, 124.8, 124.4, 123.9, 122.6 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 122.0, 119.6 (q, $^3J_{C\text{-}F}$ = 5.5 Hz), 118.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ –65.28 (s, 3F).

The compound data is in agreement with the literature.[6]

4-(3,3,3-trifluoroprop-1-en-2-yl)dibenzo[b,d]thiophene (**1t**)



White solid, yield 64% (0.53 g).

R_f 0.65 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.12 (m, 2H), 7.83 – 7.81 (m, 1H), 7.50 – 7.44 (m, 4H), 6.31 (s, 1H), 6.04 (s, 1H).

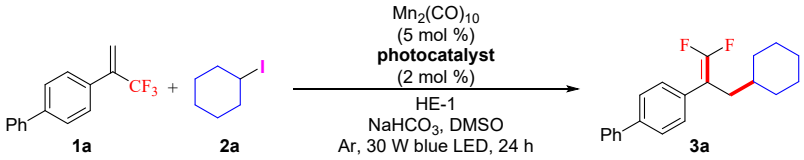
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.2, 137.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 136.4, 135.7, 128.7, 127.1, 126.5, 124.63, 124.59, 123.6 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 123.0 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 122.7, 122.0, 121.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ –65.88 (s, 3F).

The compound data is in agreement with the literature.[4]

4. Investigation of the key reaction parameters.

Table S1. Screening of photocatalysts.[a]

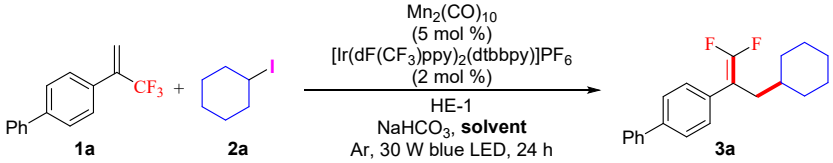


1a 2a 3a

Entry	Photocatalyst	Yield (%)[b]
1	*fac*-Ir(ppy)$_3$	0
2	[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$	67
3	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	0
4	Ru(bpy)$_3$Cl$_2$·6H$_2$O	0
5	Ru(bpy)$_3$(PF$_6$)$_2$	0
6	4CzIPN	48
7	EosinY	0
8	Mes-Acr$^+$-Me ClO$_4^-$	0

[a]Reaction conditions: **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), **photocatalyst** (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), and $NaHCO_3$ (0.3 mmol, 1 equiv.) in DMSO (0.1 M) were irradiated using a 30 W blue LED at room temperature under an argon atmosphere for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard.

Table S2. Screening of solvents.[a]

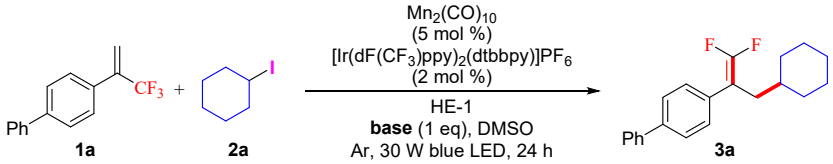


1a 2a 3a

Entry	Solvent	Yield (%)[b]
1	DMF	15
2	CH_3CN	0
3	MeOH	0
4	Acetone	0
5	DCM	0
6	THF	0
7	DMSO	67

[a]Reaction conditions: **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol %) (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), and $NaHCO_3$ (0.3 mmol, 1 equiv.) in **solvent** (0.1 M) were irradiated using a 30 W blue LED at room temperature under an argon atmosphere for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard.

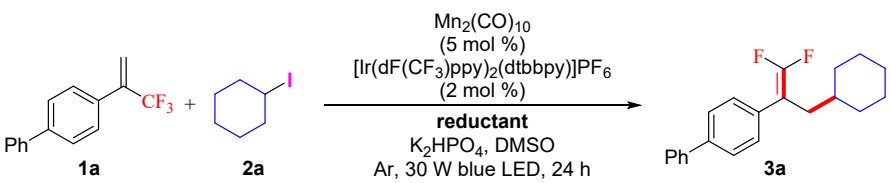
Table S3. Screening of bases.[a]



Entry	Base	Yield (%)[b]
1	$NaHCO_3$	67
2	Li_2CO_3	57
3	Na_2CO_3	51
4	K_2CO_3	69
5	Cs_2CO_3	34
6	**K_2HPO_4**	**88(83)**[c]
7	NaOH	42
8	AcONa	35
9	Et_3N	44
10	Pyridine	60

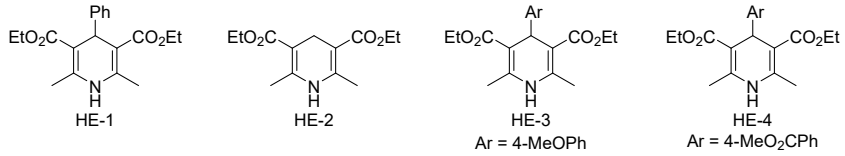
[a]Reaction conditions: **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol %) (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), and **base** (0.3 mmol, 1 equiv.) in DMSO (0.1 M) were irradiated using a 30 W blue LED at room temperature under an argon atmosphere for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c]Isolated yield.

Table S4. Screening of reductants.[a]



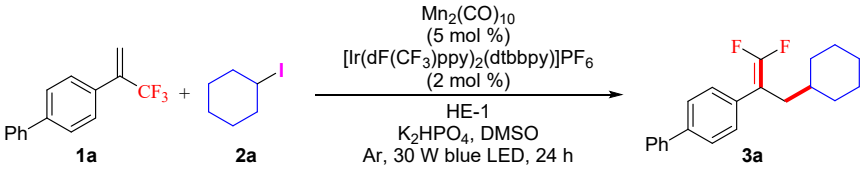
Entry	Reductant	Yield (%)[b]
1	HE-1	88
2	HE-2	23
3	HE-3	59

4	HE-4	58
5	Zn powder	46
	Mg powder	17
6	Et_3SiH	15



[a]Reaction conditions: **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol %) (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), **reductant** (0.45 mmol, 1.5 equiv.), and K_2HPO_4 (0.3 mmol, 1 equiv.) in DMSO (0.1 M) were irradiated using a 30 W blue LED at room temperature under an argon atmosphere for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard.

Table S5. Control experiments.[a]

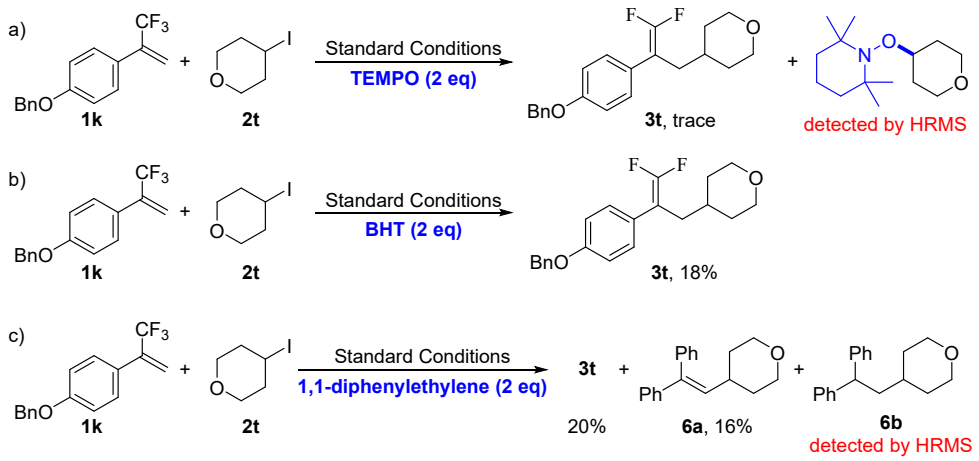


Entry	variation of standard conditions	Yield (%)[b]
1	under air	38
2	no K_2HPO_4	6
3	no HE-1	0
4	no light	0
5	no $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	0
6	no $Mn_2(CO)_{10}$	12
7	$Mn(CO)_5Br$ instead of $Mn_2(CO)_{10}$	81

[a]Reaction conditions,: **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), and K_2HPO_4 (0.3 mmol, 1 equiv.) in DMSO (0.1 M) were irradiated using a 30 W blue LED at room temperature under an argon atmosphere for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard.

5. Investigation of the mechamism.

5.1 Radical inhibition experiment



Scheme S1

To a 15 mL glass vial was added **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), K_2HPO_4 (0.3 mmol, 1 equiv.), DMSO (3 mL,0.1 M) and additive (TEMPO (93.8 mg, 0.6 mmol) or BHT (132 mg, 0.6 mmol) or 1,1-diphenylethylene (108 mg, 0.6 mmol)). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W Blue LED (approximately 5 cm away from the light source) at room temperature for 24 h. The isolated yield is given.

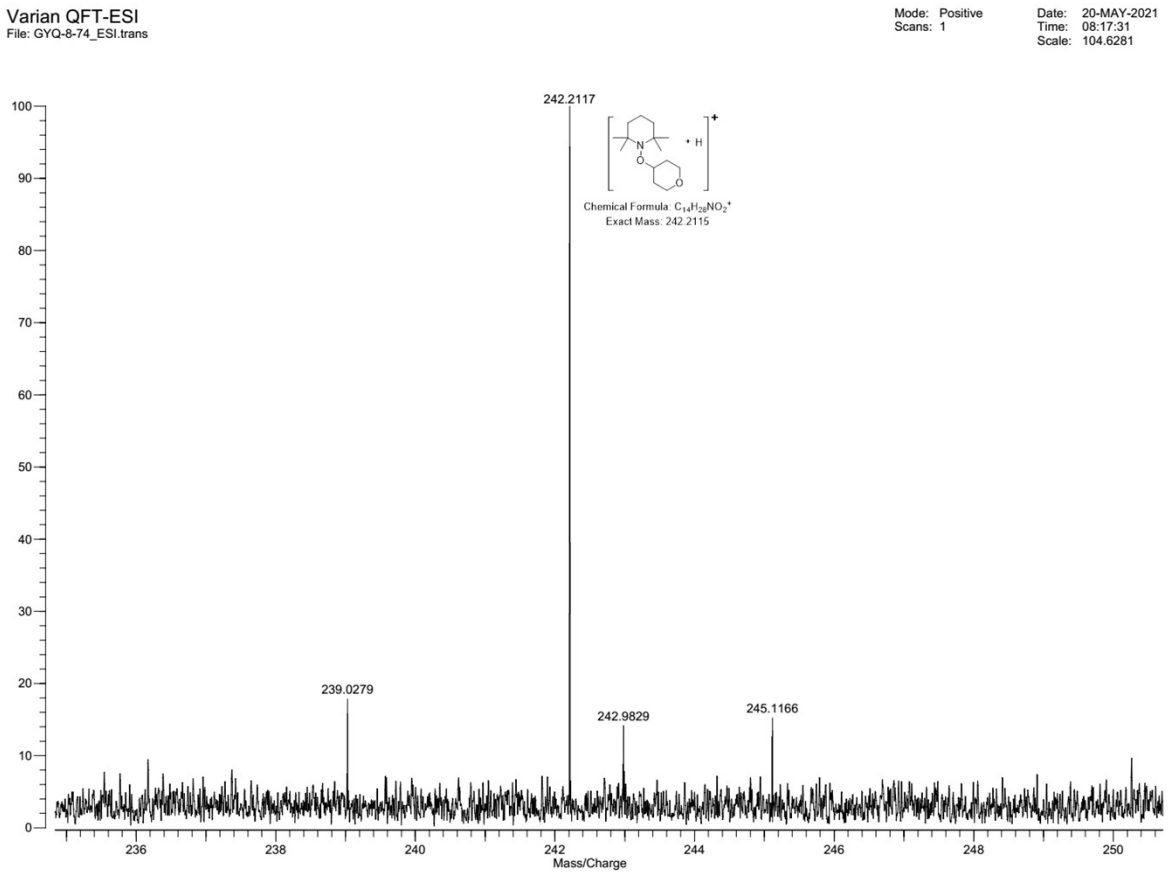


Figure S2 High resolution mass spectrum of TEMPO capture product.

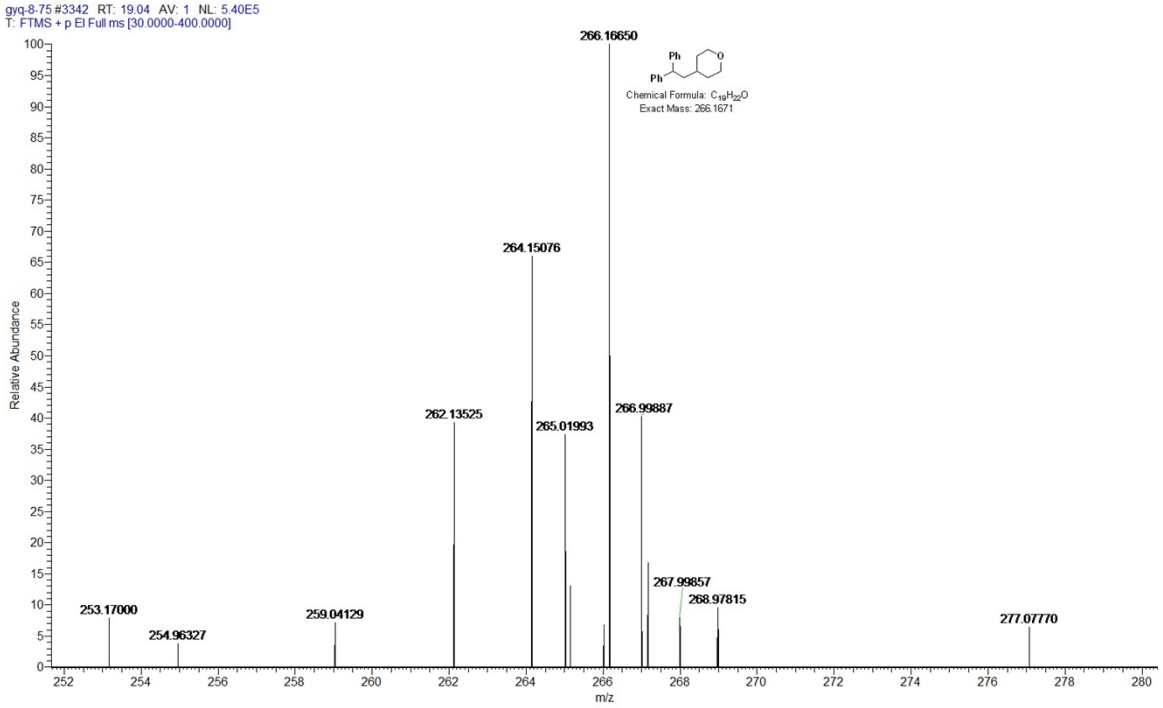
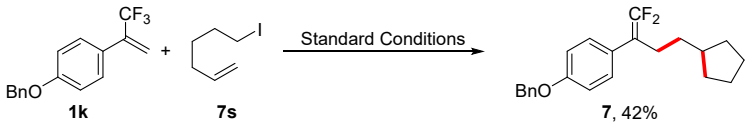


Figure S3 High resolution mass spectrum of **6b**.

5.2 Radical clock experiment



Scheme S2

To a 15 mL glass vial was added **1k** (0.3 mmol, 1 equiv.), **7s** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), K_2HPO_4 (0.3 mmol, 1 equiv.) and DMSO (3 mL,0.1 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W Blue LED (approximately 5 cm away from the light source) at room temperature for 24 h. When the reaction is completed, extracted with ethyl acetate (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether) to afford white solid **7** (43 mg, 42%).

5.3 Emission quenching experiments (Stern–Volmer studies)

For $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ emission quenching experiments: Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ solutions were excited at 350 nm and the emission intensity was collected at 475 nm. In a typical experiment, to a 3×10^{-6} M solution of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ in dimethyl sulfoxide was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 s, the emission of the sample was collected (Figure S4 (a)).

For $Mn_2(CO)_{10}$ emission quenching experiments: Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All $Mn_2(CO)_{10}$ solutions were excited at 355 nm and the emission intensity was collected at 710 nm. In a typical experiment, to a 3×10^{-6} M solution of $Mn_2(CO)_{10}$ in dimethyl

sulfoxide was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 s, the emission of the sample was collected (Figure S4 (b)).

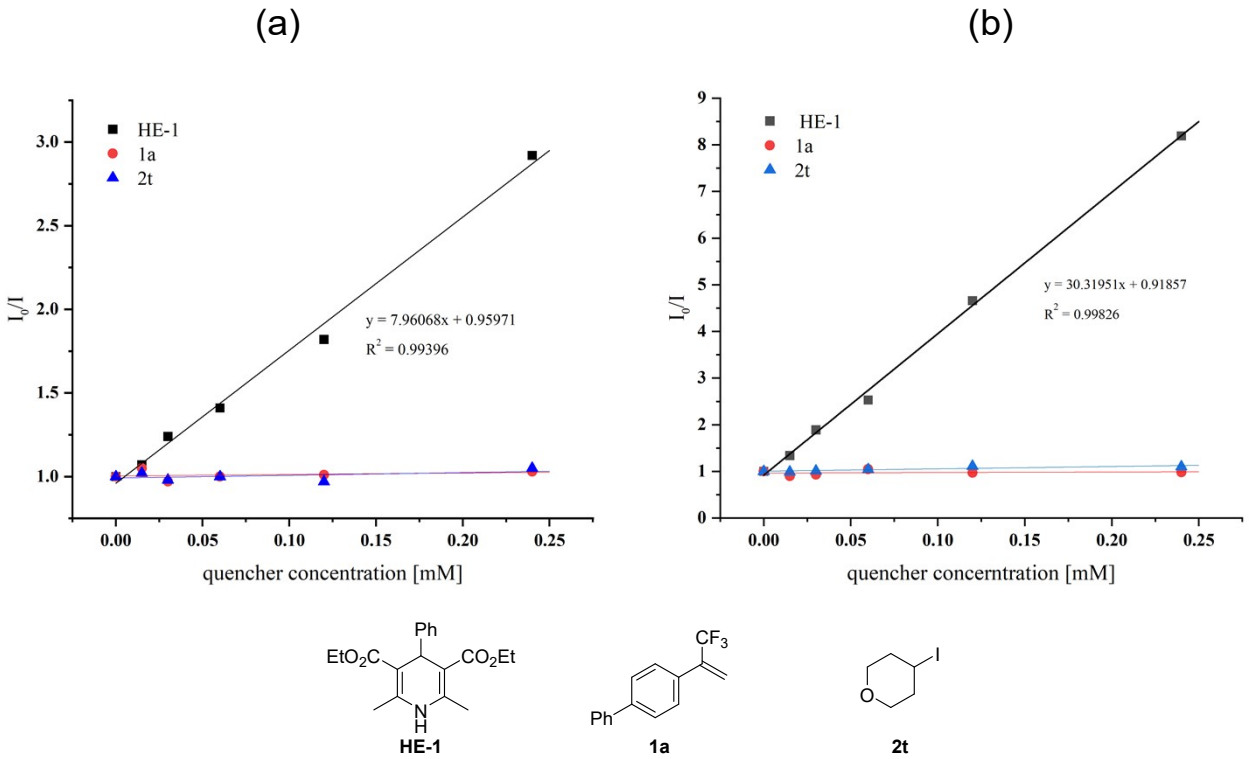
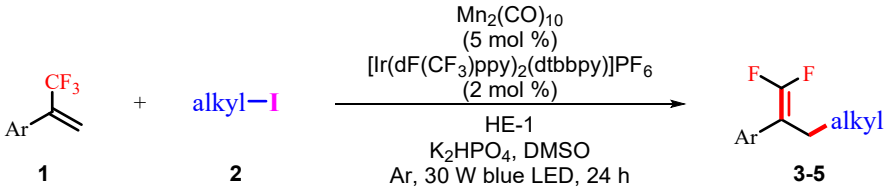


Figure S4 (a) $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ emission experiments. (b) $Mn_2(CO)_{10}$ emission experiments.

6. Experimental procedures and product characterization.

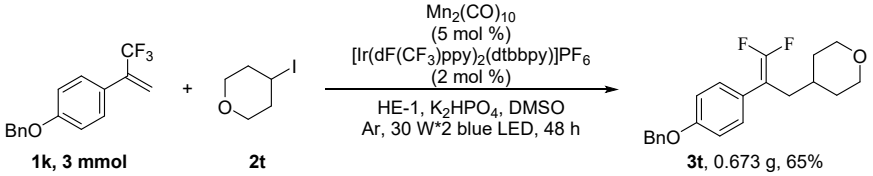
6.1 General procedure for difluoroallylation of alkyl iodides



1 **2** **3-5**

To a 15 mL glass vial was added **1** (0.3 mmol, 1 equiv.), **2** (0.6 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), $Mn_2(CO)_{10}$ (5 mol%), HE-1 (0.45 mmol, 1.5 equiv.), K_2HPO_4 (0.3 mmol, 1 equiv.) and DMSO (3 mL,0.1 M) or DMSO/dichloromethane (V/V = 1:1, 3 mL, 0.1 M, for **5c** and **5d**). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W Blue LED (approximately 5 cm away from the light source) at room temperature for 24 h. When the reaction is completed, extracted with ethyl acetate (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether/ethyl acetate) to afford the corresponding target compounds.

6.2 Gram scale

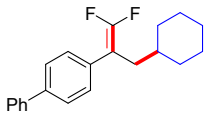


1k, 3 mmol **2t** **3t**, 0.673 g, 65%

To an oven-dried 100 mL Schlenk Tube with a stirring bar was added **1k** (835 mg, 3 mmol), **2t** (1270 mg, 6 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (67 mg, 2 mol%), $Mn_2(CO)_{10}$ (59 mg, 5 mol%), HE-1 (1480 mg, 4.5 mmol), K_2HPO_4 (520 mg, 3 mmol). Then, air was withdrawn and backfilled with Ar (three times). DMSO (30 mL) was added and the mixture was irradiated under 30 W × 2 blue LED (λ max = 470 nm, approximately 5 cm away from the light source) at room temperature for 48 h. When the reaction is completed, extracted with ethyl acetate (3 × 80 mL), washed with brine (3 × 100 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (hexane/ethyl acetate from 40/1 to 20/1) to afford white solid **3t** (673 mg, 65%).

6.3 Product Characterization

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (**3a**)



Light yellow solid, yield 83% (77.8 mg). M.p. = 56 – 58 °C.

R_f 0.70 (Petroleum ether/EtOAc, 40/1).

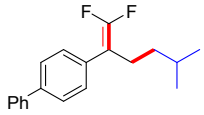
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, J = 8.5 Hz, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.42 – 7.32 (m, 3H), 2.32 (dt, J = 7.2, 2.4 Hz, 2H), 1.76 – 1.59 (m, 5H), 1.36 – 1.27 (m, 1H), 1.20 – 1.07 (m, 3H), 0.99 – 0.91 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, $^1J_{C\text{-}F}$ = 288.4 Hz, 284.2 Hz), 140.6, 139.9, 133.1 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 128.8, 128.6 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 127.4, 127.1, 127.0, 90.8 (dd, $^2J_{C\text{-}F}$ = 22.0, 12.1 Hz), 35.8, 35.1, 32.9, 26.4, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.68 (d, J = 43.5 Hz, 1F), -91.25 (d, J = 43.3 Hz, 1F).

HRMS (EI) calcd for $C_{21}H_{22}F_2$ $[M]^+$ 312.1690, found, 312.1681.

4-(1,1-difluoro-5-methylhex-1-en-2-yl)-1,1'-biphenyl (**3b**)



Colorless oil, yield 64% (55.0 mg).

R_f 0.70 (Petroleum ether).

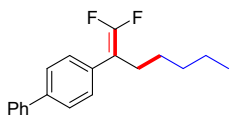
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 7.5 Hz, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.44 – 7.35 (m, 3H), 2.50 – 2.42 (m, 2H), 1.65 – 1.58 (m, 1H), 1.33 (dd, J = 15.7, 7.1 Hz, 2H), 0.93 (d, J = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6 (t, $^1J_{C\text{-}F}$ = 287.0 Hz), 140.6, 140.0, 132.9, 128.8, 128.6 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 127.4, 127.1, 127.0, 92.4 (dd, $^2J_{C\text{-}F}$ = 18.5, 15.5 Hz), 37.0, 27.7, 25.6, 22.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.35 (d, J = 44.0 Hz, 1F), -91.49 (d, J = 44.4 Hz, 1F).

The compound data is in agreement with the literature.[3]

4-(1,1-difluorohept-1-en-2-yl)-1,1'-biphenyl (**3c**)



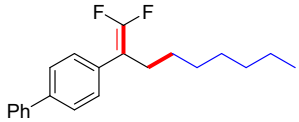
Colorless oil, yield 50% (42.8 mg).

R_f 0.65 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 2.45 – 2.38

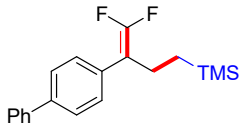
(m, 2H), 1.42 – 1.36 (m, 2H), 1.33 – 1.27 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (dd, $^1J_{C\text{-}F}$ = 288.4, 285.3 Hz), 140.6, 139.9, 132.9 (dd, $^3J_{C\text{-}F}$ = 3.4, 2.6 Hz), 128.8, 128.6 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 127.4, 127.11, 127.06, 92.2 (dd, $^2J_{C\text{-}F}$ = 20.9, 13.4 Hz), 31.3, 27.6, 27.5, 22.4, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.29 (d, J = 43.6 Hz, 1F), -91.46 (d, J = 43.6 Hz, 1F).
The compound data is in agreement with the literature.[7]

4-(1,1-difluorononon-1-en-2-yl)-1,1'-biphenyl (**3d**)



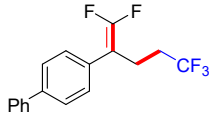
Colorless oil, yield 52% (48.6 mg).
R_f 0.65 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 7.4 Hz, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.40 – 7.30 (m, 3H), 2.42 (t, J = 7.3 Hz, 2H), 1.41 – 1.36 (m, 2H), 1.28 – 1.24 (m, 8H), 0.86 (t, J = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (dd, $^1J_{C\text{-}F}$ = 288.3, 285.2 Hz), 140.6, 139.9, 132.8 (dd, $^3J_{C\text{-}F}$ = 3.5, 2.3 Hz), 128.8, 128.6 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 127.4, 127.1, 127.0, 92.2 (dd, $^2J_{C\text{-}F}$ = 20.8, 13.5 Hz), 31.8, 29.02, 28.98, 27.8 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 27.5, 22.6, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.29 (d, J = 43.6 Hz, 1F), -91.48 (d, J = 43.6 Hz, 1F).
The compound data is in agreement with the literature.[5]

(3-([1,1'-biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)trimethylsilane (**3e**)



Colorless oil, yield 49% (46.4 mg).
R_f 0.70 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.3, 5.7 Hz, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.42 – 7.36 (m, 3H), 2.51 – 2.43 (m, 2H), 0.72 – 0.60 (m, 2H), 0.05 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 (dd, $^1J_{C\text{-}F}$ = 289.1, 284.4 Hz), 142.5, 141.8, 134.5 (t, $^3J_{C\text{-}F}$ = 4.1 Hz), 130.7, 130.5 (t, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.2, 129.0, 128.9, 96.4 (dd, $^2J_{C\text{-}F}$ = 21.7, 11.0 Hz), 23.8, 17.2, 0.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.65 (d, J = 44.7 Hz, 1F), -92.16 (d, J = 44.7 Hz, 1F).
HRMS (EI) calcd for $C_{19}H_{22}F_2Si$ $[M]^+$ 316.1459, found, 316.1450.

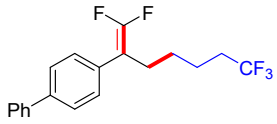
4-(1,1,5,5,5-pentafluoropent-1-en-2-yl)-1,1'-biphenyl (**3f**)



White solid, yield 51% (47.8 mg). M.p. = 48 – 50 °C.
R_f 0.45 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.8, 6.1 Hz, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 – 7.36 (m, 3H), 2.77 – 2.71 (m, 2H), 2.25 – 2.13 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (t, $^1J_{C\text{-}F}$ = 288.4 Hz), 140.7, 140.3, 131.1, 128.9, 128.5 (t, $^3J_{C\text{-}F}$ = 3.2 Hz),

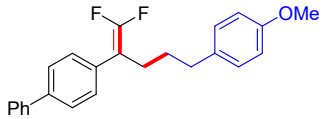
127.6, 127.5, 127.1, 126.6 (q, $^{1}J_{C\text{-}F}$ = 275.0 Hz), 89.9 (dd, $^{2}J_{C\text{-}F}$ = 19.9, 17.0 Hz), 32.1 (q, $^{2}J_{C\text{-}F}$ = 28.6 Hz), 20.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.63 (t, J = 10.9 Hz, 3F), -89.43 (s, 2F).
HRMS (EI) calcd for $C_{17}H_{13}F_5$ $[M]^+$ 312.0937, found, 312.0930.

4-(1,1,7,7,7-pentafluorohept-1-en-2-yl)-1,1'-biphenyl (**3g**)



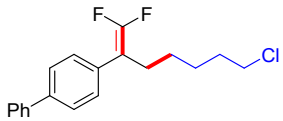
Colorless oil, yield 57% (58.4 mg).
R_f 0.60 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.48 (t, J = 7.5 Hz, 2H), 7.42 – 7.36 (m, 3H), 2.50 (t, J = 7.2 Hz, 2H), 2.13 – 2.01 (m, 2H), 1.66 – 1.57 (m, 2H), 1.54 – 1.46 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (dd, $^{1}J_{C\text{-}F}$ = 288.5, 286.1 Hz), 140.5, 140.2, 132.3 (t, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 128.9, 128.6 (t, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 127.5, 127.2, 127.1 (q, $^{1}J_{C\text{-}F}$ = 274.7 Hz), 127.0, 91.5 (dd, $^{2}J_{C\text{-}F}$ = 20.0, 14.9 Hz), 33.4 (q, $^{2}J_{C\text{-}F}$ = 28.3 Hz), 27.1, 26.8 (t, $^{3}J_{C\text{-}F}$ = 2.3 Hz), 21.3 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.39 (t, J = 11.3 Hz, 3F), -90.81 (m, 2F).
HRMS (EI) calcd for $C_{19}H_{17}F_5$ $[M]^+$ 340.1250, found, 340.1242.

4-(1,1-difluoro-5-(4-methoxyphenyl)pent-1-en-2-yl)-1,1'-biphenyl (**3h**)



Colorless oil, yield 61% (67.2 mg).
R_f 0.45 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.28 – 7.22 (m, 3H), 6.94 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 3.66 (s, 3H), 2.47 (t, J = 7.6 Hz, 2H), 2.39 – 2.31 (m, 2H), 1.63 – 1.55 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.7 (dd, $^{1}J_{C\text{-}F}$ = 288.4, 285.7 Hz), 140.6, 140.1, 133.9, 132.6 (t, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 129.3, 128.8, 128.6 (t, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 127.4, 127.15, 127.05, 113.8, 92.0 (dd, $^{2}J_{C\text{-}F}$ = 20.9, 13.6 Hz), 55.3, 34.4, 29.7, 27.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -90.84 (d, J = 42.9 Hz, 1F), -91.05 (d, J = 42.9 Hz, 1F).
HRMS (ESI) calcd for $C_{24}H_{23}F_2O$ $[M+H]^+$ 365.1717, found, 365.1711.

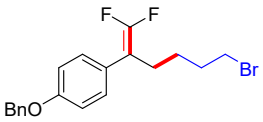
4-(7-chloro-1,1-difluorohept-1-en-2-yl)-1,1'-biphenyl (**3i**)



Colorless oil, yield 49% (47.3 mg).
R_f 0.20 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.6, 4.8 Hz, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 – 7.34 (m, 3H), 3.52 (t, J = 6.7 Hz, 2H), 2.48 – 2.46 (m, 2H), 1.80 – 1.73 (m, 2H), 1.52 – 1.37 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (t, $^{1}J_{C\text{-}F}$ = 287.0 Hz), 140.6, 140.1, 132.6, 128.8, 128.6 (t, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 127.4, 127.2, 127.0, 91.9 (dd, $^{2}J_{C\text{-}F}$ = 18.4, 16.2 Hz), 44.9, 32.3, 27.4, 27.1 (t, $^{3}J_{C\text{-}F}$ = 2.3 Hz), 26.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.00 (d, J = 43.2 Hz, 1F), -91.14 (d, J = 43.2 Hz, 1F).

HRMS (EI) calcd for $C_{19}H_{19}ClF_2$ $[M]^+$ 320.1143, found, 320.1135.

1-(benzyloxy)-4-(6-bromo-1,1-difluorohex-1-en-2-yl)benzene (**3j**)



Colorless oil, yield 41% (47.3 mg).

R_f 0.50 (Petroleum ether/EtOAc, 40/1).

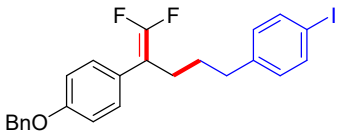
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 5H), 7.23 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 5.08 (s, 2H), 3.37 (t, J = 6.4 Hz, 1.6H), 3.15 (t, J = 6.8 Hz, 0.4H), 2.43 – 2.38 (m, 2H), 1.90 – 1.80 (m, 2H), 1.56 – 1.46 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 153.5 (dd, $^1J_{C\text{-}F}$ = 287.2, 285.1 Hz), 136.9, 129.4 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.1, 127.5, 125.7, 114.9, 91.3 (dd, $^2J_{C\text{-}F}$ = 20.7, 14.5 Hz), 70.1, 33.3, 31.9, 26.8, 26.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.09 (d, J = 45.9 Hz, 1F), -92.25 (d, J = 45.9 Hz, 1F).

HRMS (ESI) calcd for $C_{19}H_{20}BrF_2O$ $[M+H]^+$ 381.0666, found, 381.0659.

1-(benzyloxy)-4-(1,1-difluoro-5-(4-iodophenyl)pent-1-en-2-yl)benzene (**3k**)



Colorless oil, yield 53% (77.3 mg).

R_f 0.25 (Petroleum ether).

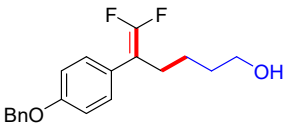
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.48 – 7.34 (m, 5H), 7.22 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 5.09 (s, 2H), 2.56 (t, J = 7.7 Hz, 2H), 2.43 – 2.39 (m, 2H), 1.72 – 1.63 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 153.5 (t, $^1J_{C\text{-}F}$ = 286.1 Hz), 141.5, 137.4, 136.9, 130.5, 129.4 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 128.7, 128.1, 127.5, 125.9, 114.9, 91.5 (dd, $^2J_{C\text{-}F}$ = 17.8, 17.0 Hz), 90.9, 70.1, 34.7, 29.2, 27.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.16 (s, 2F).

HRMS (ESI) calcd for $C_{24}H_{21}F_2INaO$ $[M+Na]^+$ 513.0503, found, 513.0492.

5-(4-(benzyloxy)phenyl)-6,6-difluorohex-5-en-1-ol (**3l**)



White solid, yield 59% (56.9 mg). M.p. = 58 – 60 °C.

R_f 0.40 (Dichloromethane).

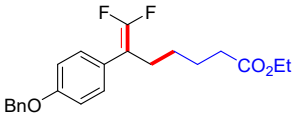
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 7.25 – 7.19 (m, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.05 (s, 2H), 3.58 (t, J = 6.5 Hz, 2H), 2.41 – 2.36 (m, 2H), 1.58 – 1.51 (m, 2H), 1.45 – 1.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.5 (t, $^1J_{C\text{-}F}$ = 285.8 Hz), 136.9, 129.4 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 128.6, 128.1, 127.5, 126.0, 114.8, 91.6 (dd, $^2J_{C\text{-}F}$ = 18.5, 16.6 Hz), 70.1, 62.6, 32.0, 27.5, 23.9 (t, $^3J_{C\text{-}F}$ = 2.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.48 (s, 2F).

HRMS (ESI) calcd for $C_{19}H_{20}F_2NaO_2$ $[M+Na]^+$ 341.1329, found, 341.1325.

ethyl 6-(4-(benzyloxy)phenyl)-7,7-difluorohept-6-enoate (**3m**)



Colorless oil, yield 57% (63.9 mg).

R_f 0.50 (Petroleum ether/Dichloromethane, 1/1).

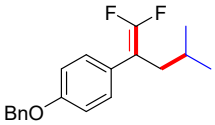
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 5H), 7.25 – 7.21 (m, 2H), 6.98 (d, J = 8.7 Hz, 2H), 5.08 (s, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.42 – 2.38 (m, 2H), 2.28 (t, J = 7.5 Hz, 2H), 1.64 (dt, J = 15.4, 7.5 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 158.0, 153.5 (t, $^1J_{C\text{-}F}$ = 286.0 Hz), 136.9, 129.4 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.0, 127.5, 125.9, 114.8, 91.5 (dd, $^2J_{C\text{-}F}$ = 19.4, 15.6 Hz), 70.0, 60.2, 34.0, 27.4, 27.2, 24.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.40 (s, 2F).

HRMS (ESI) calcd for $C_{22}H_{24}F_2NaO_3$ $[M+Na]^+$ 397.1591, found, 397.1586.

1-(benzyloxy)-4-(1,1-difluoro-4-methylpent-1-en-2-yl)benzene (**3n**)



White solid, yield 42% (38.1 mg). M.p. = 82 – 84 °C.

R_f 0.60 (Petroleum ether/EtOAc, 100/1).

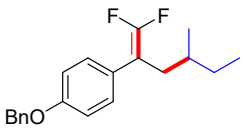
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 5.06 (s, 2H), 2.23 (d, J = 5.5 Hz, 2H), 1.61 – 1.54 (m, 1H), 0.87 (d, J = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.9 (dd, $^1J_{C\text{-}F}$ = 286.8, 283.9 Hz), 136.9, 129.4 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.0, 127.5, 126.42 (dd, $^3J_{C\text{-}F}$ = 4.2, 3.1 Hz), 114.7, 91.1 (dd, $^2J_{C\text{-}F}$ = 21.8, 13.1 Hz), 70.0, 36.7, 26.4, 22.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.45 (d, J = 46.3 Hz, 1F), -92.85 (d, J = 46.5 Hz, 1F).

HRMS (ESI) calcd for $C_{19}H_{21}F_2O$ $[M+H]^+$ 303.1560, found, 303.1555.

1-(benzyloxy)-4-(1,1-difluoro-4-methylhex-1-en-2-yl)benzene (**3o**)



White solid, yield 58% (55.0 mg). M.p. = 67 – 69 °C.

R_f 0.60 (Petroleum ether/EtOAc, 100/1).

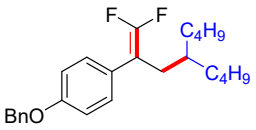
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 7.24 – 7.20 (m, 2H), 6.98 – 6.92 (m, 2H), 5.05 (s, 2H), 2.38 – 2.29 (m, 1H), 2.18 – 2.12 (m, 1H), 1.40 – 1.30 (m, 2H), 1.17 – 1.09 (m, 1H), 0.86 – 0.81 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.9 (dd, $^1J_{C\text{-}F}$ = 286.4, 283.9 Hz), 137.0, 129.5 (t, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.7, 128.1, 127.6, 126.4 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 114.8, 91.0 (dd, $^2J_{C\text{-}F}$ = 21.4, 13.7 Hz), 70.1, 34.7, 32.6, 29.1, 18.6, 11.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.44 (d, J = 46.4 Hz, 1F), -92.67 (d, J = 47.1 Hz, 1F).

HRMS (ESI) calcd for $C_{20}H_{23}F_2O$ $[M+H]^+$ 317.1717, found, 317.1710.

1-(benzyloxy)-4-(4-butyl-1,1-difluorooct-1-en-2-yl)benzene (**3p**)



Colorless oil, yield 74% (86.1 mg).

R_f 0.35 (Petroleum ether).

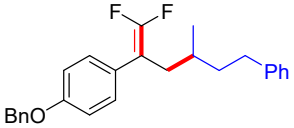
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H), 7.21 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.04 (s, 2H), 2.29 – 2.27 (m, 2H), 1.27 – 1.15 (m, 13H), 0.85 (t, J = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.8 (dd, $^1J_{C\text{-}F}$ = 285.9, 285.1 Hz), 137.0, 129.5 (t, $^3J_{C\text{-}F}$ = 3.0 Hz), 128.6, 128.0, 127.5, 126.4, 114.7, 91.2 (dd, $^2J_{C\text{-}F}$ = 19.3, 15.5 Hz), 70.0, 35.4, 32.7, 32.2, 28.5, 23.1, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.74 – -92.47 (m, 2F).

HRMS (ESI) calcd for $C_{25}H_{33}F_2O$ $[M+H]^+$ 387.2499, found, 387.2491.

1-(benzyloxy)-4-(1,1-difluoro-4-methyl-6-phenylhex-1-en-2-yl)benzene (**3q**)



Colorless oil, yield 57% (67.5 mg).

R_f 0.30 (Petroleum ether).

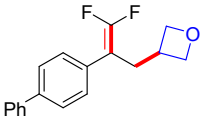
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 5H), 7.25 – 7.08 (m, 7H), 6.93 (d, J = 8.7 Hz, 2H), 5.04 (s, 2H), 2.65 – 2.57 (m, 1H), 2.55 – 2.44 (m, 1H), 2.42 – 2.36 (m, 1H), 2.21 (dd, J = 14.0, 7.6 Hz, 1H), 1.67 – 1.59 (m, 1H), 1.54 – 1.38 (m, 2H), 0.91 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.0 (dd, $^1J_{C\text{-}F}$ = 286.5, 284.8 Hz), 142.7, 137.0, 129.5 (t, $^3J_{C\text{-}F}$ = 2.8 Hz), 128.7, 128.3, 128.1, 127.5, 126.3, 125.7, 114.8, 90.9 (dd, $^2J_{C\text{-}F}$ = 20.6, 14.5 Hz), 70.1, 38.2, 34.9, 33.3, 30.8, 19.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.22 (d, J = 46.1 Hz, 1F), -92.39 (d, J = 46.2 Hz, 1F).

HRMS (ESI) calcd for $C_{26}H_{27}F_2O$ $[M+H]^+$ 393.2030, found, 393.2021.

3-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)oxetane (**3r**)



Colorless oil, yield 63% (53.9 mg).

R_f 0.30 (Petroleum ether/EtOAc, 10/1).

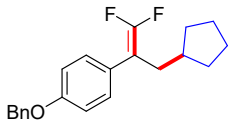
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.8, 3.0 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.40 – 7.29 (m, 3H), 4.69 (dd, J = 7.4, 6.3 Hz, 2H), 4.38 (t, J = 6.1 Hz, 2H), 3.09 – 3.02 (m, 1H), 2.83 (d, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, $^1J_{C\text{-}F}$ = 289.0, 285.8 Hz), 140.5, 140.4, 131.9 (dd, $^3J_{C\text{-}F}$ = 4.2, 3.1 Hz), 128.9, 128.6 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 127.5, 127.3, 127.0, 90.2 (dd, $^2J_{C\text{-}F}$ = 21.7, 14.4 Hz), 76.8, 33.8 (t, $^3J_{C\text{-}F}$ = 2.6 Hz), 31.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.14 (d, J = 42.0 Hz, 1F), -90.57 (d, J = 42.0 Hz, 1F).

HRMS (ESI) calcd for $C_{18}H_{16}F_2NaO$ $[M+Na]^+$ 309.1067, found, 309.1058.

1-(benzyloxy)-4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzene (**3s**)



White solid, yield 42% (41.2 mg). M.p. = 79 – 81 °C.

R_f 0.65 (Petroleum ether/EtOAc, 100/1).

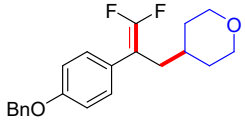
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 5H), 7.24 (d, J = 8.3 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.07 (s, 2H), 2.37 – 2.34 (m, 2H), 1.84 – 1.76 (m, 1H), 1.70 – 1.58 (m, 4H), 1.51 – 1.42 (m, 2H), 1.18 – 1.09 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.8 (dd, $^1J_{C\text{-}F}$ = 286.3, 283.6 Hz), 137.0, 129.5 (t, $^3J_{C\text{-}F}$ = 2.8 Hz), 128.6, 128.0, 127.5, 126.5 (t, $^4J_{C\text{-}F}$ = 2.6 Hz), 114.7, 91.7 (dd, $^2J_{C\text{-}F}$ = 21.6, 13.2 Hz), 70.0, 38.2, 33.7, 32.1, 25.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.95 (d, J = 47.3 Hz, 1F), -93.27 (d, J = 47.4 Hz, 1F).

HRMS (ESI) calcd for $C_{21}H_{23}F_2O$ $[M+H]^+$ 329.1717, found, 329.1713.

4-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**3t**)



White solid, yield 78% (80.3 mg). M.p. = 84 – 86 °C.

R_f 0.20 (Petroleum ether/EtOAc, 20/1).

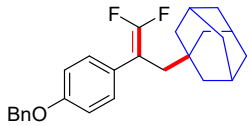
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 7.22 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.06 (s, 2H), 3.90 (dd, J = 11.4, 3.7 Hz, 2H), 3.25 (t, J = 11.1 Hz, 2H), 2.31 – 2.29 (m, 2H), 1.57 – 1.45 (m, 3H), 1.34 – 1.24 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.0 (dd, $^1J_{C\text{-}F}$ = 287.8, 284.3 Hz), 136.9, 129.4 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.7, 128.1, 127.6, 126.0 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 114.9, 89.8 (dd, $^2J_{C\text{-}F}$ = 21.7, 13.6 Hz), 70.0, 67.8, 34.8, 33.2 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.62 (d, J = 44.9 Hz, 1F), -91.93 (d, J = 45.1 Hz, 1F).

HRMS (ESI) calcd for $C_{21}H_{23}F_2O_2$ $[M+H]^+$ 345.1666, found, 345.1660.

1-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)adamantane (**3u**)



White solid, yield 64% (75.4 mg). M.p. = 133 – 135 °C.

R_f 0.75 (Petroleum ether/EtOAc, 40/1).

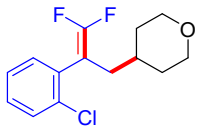
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 7.24 (d, J = 6.5 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 5.05 (s, 2H), 2.16 (s, 2H), 1.86 (s, 3H), 1.63 (d, J = 12.2 Hz, 3H), 1.56 – 1.51 (m, 3H), 1.38 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 154.3 (dd, $^1J_{C\text{-}F}$ = 287.5, 284.7 Hz), 136.9, 129.5 (t, $^4J_{C\text{-}F}$ = 2.9 Hz), 128.6, 128.4 (dd, $^3J_{C\text{-}F}$ = 4.6, 3.0 Hz), 128.0, 127.6, 114.6, 89.2 (dd, $^2J_{C\text{-}F}$ = 22.0, 12.7 Hz), 70.0, 42.7, 42.0, 36.9, 34.6 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 28.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.90 (d, J = 43.4 Hz, 1F), -92.93 (d, J = 43.7 Hz, 1F).

HRMS (EI) calcd for $C_{26}H_{28}F_2O$ $[M]^+$ 394.2108, found, 394.2100.

4-(2-(2-chlorophenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4b**)



Colorless oil, yield 73% (60.1 mg).

R_f 0.30 (Petroleum ether/EtOAc, 40/1).

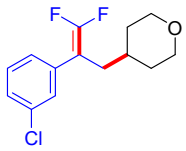
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dq, J = 7.3, 3.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 3.92 (dd, J = 11.1, 2.7 Hz, 2H), 3.29 (td, J = 11.7, 1.7 Hz, 2H), 2.39 – 2.24 (m, 2H), 1.63 (d, J = 13.1 Hz, 2H), 1.50 – 1.38 (m, 1H), 1.31 (ddd, J = 24.1, 11.9, 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (t, $^1J_{C\text{-}F}$ = 286.5 Hz), 134.2 (dd, $^4J_{C\text{-}F}$ = 2.7, 1.7 Hz), 132.9 (dd, $^3J_{C\text{-}F}$ = 5.6, 1.8 Hz), 131.3 (dd, $^4J_{C\text{-}F}$ = 2.9, 1.4 Hz), 130.0, 129.2, 126.8, 88.4 (dd, $^2J_{C\text{-}F}$ = 25.0, 16.4 Hz), 67.8, 35.8, 33.2 (t, $^3J_{C\text{-}F}$ = 2.6 Hz), 32.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.97 (d, J = 39.3 Hz, 1F), -92.36 (d, J = 39.4 Hz, 1F).

HRMS (ESI) calcd for $C_{14}H_{16}ClF_2O$ $[M+H]^+$ 273.0858, found, 273.0853.

4-(2-(3-chlorophenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4c**)



Colorless oil, yield 75% (61.2 mg).

R_f 0.35 (Petroleum ether/EtOAc, 40/1).

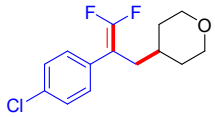
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 3H), 7.16 – 7.10 (m, 1H), 3.86 (dd, J = 11.3, 3.7 Hz, 2H), 3.21 (td, J = 11.8, 1.4 Hz, 2H), 2.28 – 2.26 (m, 2H), 1.53 – 1.37 (m, 3H), 1.24 (ddd, J = 15.3, 12.0, 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, $^1J_{C\text{-}F}$ = 289.9, 285.8 Hz), 135.6 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 134.4, 129.8, 128.3 (t, $^4J_{C\text{-}F}$ = 3.3 Hz), 127.6, 126.4 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 89.7 (dd, $^2J_{C\text{-}F}$ = 22.7, 12.9 Hz), 67.7, 34.6, 33.2, 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.40 (d, J = 39.8 Hz, 1F), -89.75 (d, J = 39.7 Hz, 1F).

HRMS (ESI) calcd for $C_{14}H_{16}ClF_2O$ $[M+H]^+$ 273.0858, found, 273.0851.

4-(2-(4-chlorophenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4d**)



Colorless oil, yield 78% (63.8 mg).

R_f 0.30 (Petroleum ether/EtOAc, 40/1).

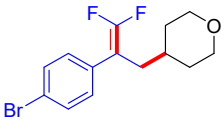
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 3.91 (dd, J = 11.6, 4.2 Hz, 2H), 3.25 (td, J = 11.8, 1.8 Hz, 2H), 2.32 (dt, J = 6.9, 2.3 Hz, 2H), 1.55 – 1.40 (m, 3H), 1.29 (ddd, J = 15.5, 11.9, 5.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, $^1J_{C\text{-}F}$ = 298.4, 285.6 Hz), 133.2, 132.1 (dd, $^3J_{C\text{-}F}$ = 4.4, 3.3 Hz), 129.5 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.8, 89.6 (dd, $^2J_{C\text{-}F}$ = 22.6, 13.1 Hz), 67.7, 34.6, 33.2 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.91 (d, J = 41.3 Hz, 1F), -90.35 (d, J = 41.1 Hz, 1F).

HRMS (ESI) calcd for $C_{14}H_{16}ClF_2O$ $[M+H]^+$ 273.0858, found, 273.0851.

4-(2-(4-bromophenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4e**)



Colorless oil, yield 75% (71.5 mg).

R_f 0.30 (Petroleum ether/EtOAc, 40/1).

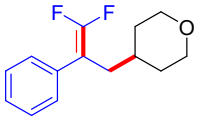
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 3.90 (dd, J = 11.5, 4.1 Hz, 2H), 3.25 (td, J = 11.8, 1.8 Hz, 2H), 2.32 (dt, J = 6.9, 2.3 Hz, 2H), 1.55 – 1.42 (m, 3H), 1.34 – 1.23 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (dd, $^1J_{C\text{-}F}$ = 289.7, 285.7 Hz), 132.6 (dd, $^3J_{C\text{-}F}$ = 4.4, 3.4 Hz), 131.7, 129.8 (t, $^4J_{C\text{-}F}$ = 3.3 Hz), 121.3, 89.7 (dd, $^2J_{C\text{-}F}$ = 22.6, 13.0 Hz), 67.7, 34.5, 33.2 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.75 (d, J = 41.1 Hz, 1F), -90.21 (d, J = 40.8 Hz, 1F).

HRMS (ESI) calcd for $C_{14}H_{16}BrF_2O$ $[M+H]^+$ 317.0353, found, 317.0345.

4-(3,3-difluoro-2-phenylallyl)tetrahydro-2H-pyran (**4f**)



Colorless oil, yield 61% (43.6 mg).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

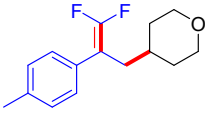
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.31 – 7.26 (m, 3H), 3.91 (dd, J = 11.3, 3.7 Hz, 2H), 3.26 (td, J = 11.8, 1.6 Hz, 2H), 2.38 – 2.31 (m, 2H), 1.60 – 1.54 (m, 2H), 1.52 – 1.45 (m, 1H), 1.35 – 1.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (dd, $^1J_{C\text{-}F}$ = 289.1, 284.8 Hz), 133.2 (t, $^3J_{C\text{-}F}$ = 3.3 Hz), 128.0, 127.7 (t, $^4J_{C\text{-}F}$ = 2.9 Hz), 126.8, 89.8 (dd, $^2J_{C\text{-}F}$ = 21.7, 13.3 Hz), 67.2, 34.2, 32.7, 32.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.83 (d, J = 42.8 Hz, 1F), -91.18 (d, J = 42.8 Hz, 1F).

HRMS (ESI) calcd for $C_{14}H_{17}F_2O$ $[M+H]^+$ 239.1247, found, 239.1241.

4-(3,3-difluoro-2-(p-tolyl)allyl)tetrahydro-2H-pyran (**4g**)



Colorless oil, yield 62% (46.9 mg).

R_f 0.30 (Petroleum ether/Dichloromethane, 1/1).

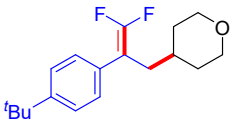
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 4H), 3.91 (dd, J = 11.3, 3.5 Hz, 2H), 3.26 (t, J = 11.6 Hz, 2H), 2.36 (s, 3H), 2.35 – 2.30 (m, 2H), 1.56 (d, J = 13.4 Hz, 2H), 1.53 – 1.43 (m, 1H), 1.30 (ddd, J = 15.1, 12.1, 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (dd, $^1J_{C\text{-}F}$ = 288.3, 284.7 Hz), 137.1, 130.6 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 129.2, 128.1 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 90.1 (dd, $^2J_{C\text{-}F}$ = 21.3, 13.7 Hz), 67.8, 34.7, 33.2 (t, $^3J_{C\text{-}F}$ = 2.3 Hz), 32.6, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.30 (d, J = 44.4 Hz, 1F), -91.55 (d, J = 44.6 Hz, 1F).

HRMS (ESI) calcd for $C_{15}H_{19}F_2O$ $[M+H]^+$ 253.1404, found, 253.1399.

4-(2-(4-(tert-butyl)phenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4h**)



Colorless oil, yield 75% (67.0 mg).

R_f 0.35 (Petroleum ether/EtOAc, 40/1).

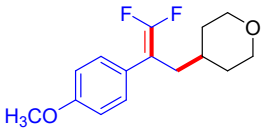
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 3.91 (dd, J = 11.3, 3.7 Hz, 2H), 3.27 (td, J = 11.8, 1.7 Hz, 2H), 2.36 – 2.30 (m, 2H), 1.58 – 1.47 (m, 3H), 1.33 (s, 9H), 1.29 – 1.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, $^1J_{C\text{-}F}$ = 288.8, 284.5 Hz), 150.2, 130.5 (t, $^3J_{C\text{-}F}$ = 3.5 Hz), 127.8 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 125.4, 90.0 (dd, $^2J_{C\text{-}F}$ = 21.6, 13.1 Hz), 67.8, 34.7, 34.5, 33.2 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 32.7, 31.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.85 (d, J = 43.5 Hz, 1F), -91.22 (d, J = 43.6 Hz, 1F).

HRMS (ESI) calcd for $C_{18}H_{25}F_2O$ $[M+H]^+$ 295.1873, found, 295.1866.

4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)tetrahydro-2H-pyran (**4i**)



Colorless oil, yield 69% (55.5 mg).

R_f 0.40 (Petroleum ether/EtOAc, 20/1).

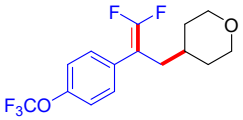
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.91 (dd, J = 11.3, 3.9 Hz, 2H), 3.81 (s, 3H), 3.26 (td, J = 11.8, 1.8 Hz, 2H), 2.31 (dt, J = 6.8, 2.3 Hz, 2H), 1.58 – 1.43 (m, 3H), 1.30 (ddd, J = 15.3, 12.0, 4.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.9 (dd, $^1J_{C\text{-}F}$ = 287.7, 284.1 Hz), 129.3 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 125.8 (dd, $^3J_{C\text{-}F}$ = 4.6, 2.8 Hz), 113.9, 89.8 (dd, $^2J_{C\text{-}F}$ = 21.8, 13.8 Hz), 67.8, 55.2, 34.8, 33.2 (t, $^3J_{C\text{-}F}$ = 2.7 Hz), 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.82 (d, J = 45.5 Hz, 1F), -92.12 (d, J = 45.4 Hz, 1F).

HRMS (ESI) calcd for $C_{15}H_{19}F_2O_2$ $[M+H]^+$ 269.1353, found, 269.1345.

4-(3,3-difluoro-2-(4-(trifluoromethoxy)phenyl)allyl)tetrahydro-2H-pyran (**4j**)



Colorless oil, yield 71% (68.5 mg).

R_f 0.45 (Petroleum ether/EtOAc, 40/1).

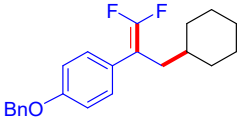
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 3.91 (dd, J = 11.2, 3.4 Hz, 2H), 3.27 (t, J = 11.1 Hz, 2H), 2.35 – 2.33 (m, 2H), 1.58 – 1.43 (m, 3H), 1.30 (ddd, J = 14.9, 12.0, 4.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, $^1J_{C\text{-}F}$ = 289.5, 285.4 Hz), 148.2, 132.4 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 129.61 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 121.0, 120.5 (q, J = 255.6 Hz), 89.5 (dd, $^2J_{C\text{-}F}$ = 22.9, 13.1 Hz), 67.7, 34.7, 33.2, 32.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.85 (s, 3F), -89.79 (d, J = 41.1 Hz, 1F), -90.37 (d, J = 41.4 Hz, 1F).

HRMS (ESI) calcd for $C_{15}H_{16}F_5O_2$ $[M+H]^+$ 323.1070, found, 323.1065.

1-(benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (**4k**)



White solid, yield 73% (74.6 mg). M.p. = 83 – 85 °C.

R_f 0.60 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 4H), 7.34 (t, J = 7.1 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 6.97 (d,

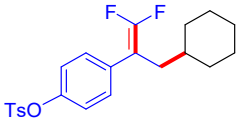
J = 8.7 Hz, 2H), 5.07 (s, 2H), 2.25 – 2.23 (m, 2H), 1.69 – 1.55 (m, 5H), 1.29 – 1.21 (m, 1H), 1.18 – 1.07 (m, 3H), 0.92 (dd, J = 21.4, 10.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.9 (dd, $^1J_{C\text{-}F}$ = 287.0, 283.4 Hz), 137.0, 129.4 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.0, 127.5, 126.6 (t, $^4J_{C\text{-}F}$ = 2.6 Hz), 114.7, 90.5 (dd, $^2J_{C\text{-}F}$ = 22.0, 12.9 Hz), 70.0, 35.7, 35.3, 32.9, 26.5, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.19 (d, J = 46.6 Hz, 1F), -92.62 (d, J = 46.8 Hz, 1F).

HRMS (ESI) calcd for $C_{22}H_{25}F_2O$ $[M+H]^+$ 343.1873, found, 343.1867.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl 4-methylbenzenesulfonate (**4l**)



White solid, yield 72% (88.3 mg). M.p. = 73 – 75 °C.

R_f 0.65 (Petroleum ether/EtOAc, 10/1).

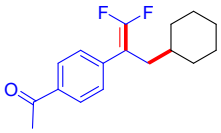
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 2.45 (s, 3H), 2.23 – 2.21 (m, 2H), 1.64 – 1.56 (m, 5H), 1.21 – 1.06 (m, 4H), 0.93 – 0.84 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (dd, $^1J_{C\text{-}F}$ = 289.3, 285.1 Hz), 148.4, 145.4, 133.1 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 132.4, 129.8, 129.5 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.5, 122.3, 90.2 (dd, $^2J_{C\text{-}F}$ = 23.0, 12.4 Hz), 35.7, 35.1, 32.8, 26.3, 26.0, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.14 (d, J = 41.7 Hz, 1F), -90.84 (d, J = 41.8 Hz, 1F).

HRMS (ESI) calcd for $C_{22}H_{24}F_2NaO_3S$ $[M+Na]^+$ 429.1312, found, 429.1309.

1-(4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (**4m**)



Colorless oil, yield 61% (51.0 mg).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

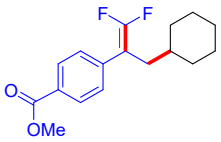
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.4 Hz, 2H), 2.60 (s, 3H), 2.30 (dt, J = 7.1, 2.3 Hz, 2H), 1.69 – 1.57 (m, 5H), 1.27 – 1.15 (m, 1H), 1.10 – 1.04 (m, 3H), 0.91 (dd, J = 21.1, 11.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 154.2 (dd, $^1J_{C\text{-}F}$ = 290.7, 286.0 Hz), 139.2 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 135.7, 128.5, 128.4 (t, $^4J_{C\text{-}F}$ = 3.5 Hz), 90.9 (dd, $^2J_{C\text{-}F}$ = 22.9, 11.7 Hz), 35.9, 34.8, 32.8, 26.6, 26.3, 26.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.72 (d, J = 38.8 Hz, 1F), -89.49 (d, J = 39.0 Hz, 1F).

The compound data is in agreement with the literature.[5]

methyl 4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoate (**4n**)



Colorless oil, yield 66% (58.6 mg).

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

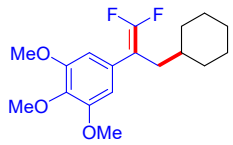
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.4 Hz, 2H), 3.91 (s, 3H), 2.30 (dt, J = 7.1, 2.3 Hz, 2H), 1.68 – 1.57 (m, 5H), 1.26 – 1.18 (m, 1H), 1.13 – 1.04 (m, 3H), 0.90 (dd, J = 21.8, 11.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 154.2 (dd, $^1J_{C\text{-}F}$ = 290.6, 285.7 Hz), 139.0 (dd, $^3J_{C\text{-}F}$ = 4.7, 3.7 Hz), 129.7, 128.8, 128.2 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 90.9 (dd, $^2J_{C\text{-}F}$ = 22.9, 11.8 Hz), 52.1, 35.8, 34.9, 32.8, 26.3, 26.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.02 (d, J = 39.2 Hz, 1F), -89.70 (d, J = 39.5 Hz, 1F).

HRMS (ESI) calcd for $C_{17}H_{21}F_2O_2$ $[M+H]^+$ 295.1510, found, 295.1503.

5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,2,3-trimethoxybenzene (**4o**)



Colorless oil, yield 77% (75.7 mg).

R_f 0.35 (Petroleum ether/EtOAc, 20/1).

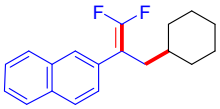
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 2H), 3.86 (s, 3H), 3.85 (s, 6H), 2.22 (dt, J = 7.0, 2.2 Hz, 2H), 1.69 – 1.59 (m, 5H), 1.32 – 1.23 (m, 1H), 1.16 – 1.11 (m, 3H), 0.97 – 0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 (dd, $^1J_{C\text{-}F}$ = 287.7, 284.4 Hz), 153.1, 137.2, 129.7 (dd, $^3J_{C\text{-}F}$ = 4.3, 2.9 Hz), 105.7 (t, $^4J_{C\text{-}F}$ = 3.0 Hz), 91.2 (dd, $^2J_{C\text{-}F}$ = 22.3, 12.7 Hz), 60.8, 56.2, 35.8, 35.5, 32.9, 26.4, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.15 (d, J = 45.1 Hz, 1F), -91.52 (d, J = 44.9 Hz, 1F).

HRMS (ESI) calcd for $C_{18}H_{25}F_2O_3$ $[M+H]^+$ 327.1772, found, 327.1766.

2-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)naphthalene (**4p**)



Colorless oil, yield 75% (64.8 mg).

R_f 0.65 (Petroleum ether).

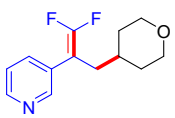
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 3H), 7.76 (s, 1H), 7.52 – 7.40 (m, 3H), 2.40 – 2.35 (m, 2H), 1.73 – 1.56 (m, 5H), 1.31 – 1.23 (m, 1H), 1.14 – 1.03 (m, 3H), 0.94 (dd, J = 22.8, 11.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, $^1J_{C\text{-}F}$ = 288.6, 284.6 Hz), 133.3, 132.4, 131.6 (t, $^3J_{C\text{-}F}$ = 3.8 Hz), 128.0, 127.9, 127.6, 127.3 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 126.3 (t, J = 2.8 Hz), 126.2, 126.0, 91.2 (dd, $^2J_{C\text{-}F}$ = 22.3, 12.5 Hz), 35.7, 35.3, 32.9, 26.4, 26.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.83 (d, J = 43.2 Hz, 1F), -91.54 (d, J = 43.3 Hz, 1F).

The compound data is in agreement with the literature.[3]

3-(1,1-difluoro-3-(tetrahydro-2H-pyran-4-yl)prop-1-en-2-yl)pyridine (**4q**)

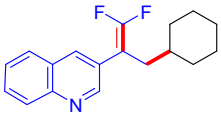


Colorless oil, yield 56% (40.0 mg).

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

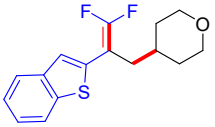
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.52 (d, J = 3.5 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.34 – 7.27 (m, 1H), 3.90 (dd, J = 11.4, 3.9 Hz, 2H), 3.24 (td, J = 11.8, 1.2 Hz, 2H), 2.39 – 2.34 (m, 2H), 1.57 – 1.44 (m, 3H), 1.30 (ddd, J = 15.7, 12.4, 4.8 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4 (dd, $^1J_{C\text{-}F}$ = 290.6, 286.9 Hz), 149.2 (t, $^4J_{C\text{-}F}$ = 3.5 Hz), 148.5, 135.5 (t, $^4J_{C\text{-}F}$ = 3.2 Hz), 129.8 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 123.4, 87.8 (dd, $^2J_{C\text{-}F}$ = 23.7, 13.2 Hz), 67.7, 34.3, 33.3, 32.
^{19}F NMR (376 MHz, $CDCl_3$) δ -88.41 (d, J = 38.6 Hz, 1F), -89.49 (d, J = 38.6 Hz, 1F).
HRMS (ESI) calcd for $C_{13}H_{16}F_2NO$ $[M+H]^+$ 240.1200, found, 240.1196.

3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)quinoline (**4r**)



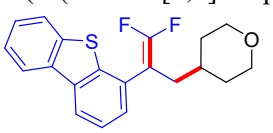
Colorless oil, yield 75% (65.0 mg).
R_f 0.50 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 1.7 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 2.40 (dt, J = 7.1, 2.2 Hz, 2H), 1.72 – 1.57 (m, 5H), 1.30 – 1.23 (m, 1H), 1.13 – 1.02 (m, 3H), 0.94 (dd, J = 22.4, 11.9 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (dd, $^1J_{C\text{-}F}$ = 289.9, 286.5 Hz), 150.3 (dd, $^3J_{C\text{-}F}$ = 4.0, 2.9 Hz), 146.9, 134.8 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 129.6, 129.2, 127.8, 127.7, 127.4 (t, $^4J_{C\text{-}F}$ = 4.2 Hz), 127.0, 88.7 (dd, $^2J_{C\text{-}F}$ = 23.8, 12.6 Hz), 35.8, 34.9, 32.8, 26.3, 26.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -88.77 (d, J = 40.0 Hz, 1F), -90.06 (d, J = 40.1 Hz, 1F).
HRMS (ESI) calcd for $C_{18}H_{20}F_2N$ $[M+H]^+$ 288.1564, found, 288.1557.

4-(2-(benzo[b]thiophen-2-yl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4s**)



Colorless oil, yield 64% (56.8 mg).
R_f 0.35 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.3 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.24 (s, 1H), 3.94 (dd, J = 11.1, 3.8 Hz, 2H), 3.31 (td, J = 11.9, 1.9 Hz, 2H), 2.44 – 2.39 (m, 2H), 1.87 – 1.74 (m, 1H), 1.64 (dd, J = 13.0, 1.6 Hz, 2H), 1.38 (ddd, J = 25.0, 12.3, 4.5 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (dd, $^1J_{C\text{-}F}$ = 295.6, 287.4 Hz), 139.6, 139.2, 136.2 (dd, $^3J_{C\text{-}F}$ = 7.2, 4.2 Hz), 124.5, 124.4, 123.3, 122.0 (t, $^4J_{C\text{-}F}$ = 5.4 Hz), 121.9, 86.9 (dd, $^2J_{C\text{-}F}$ = 26.9, 11.9 Hz), 67.8, 34.8, 34.0, 32.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -82.90 (d, J = 29.8 Hz, 1F), -87.26 (d, J = 29.9 Hz, 1F).
HRMS (ESI) calcd for $C_{16}H_{17}F_2OS$ $[M+H]^+$ 295.0968, found, 295.0965.

4-(2-(dibenzo[b,d]thiophen-4-yl)-3,3-difluoroallyl)tetrahydro-2H-pyran (**4t**)



Colorless oil, yield 83% (86.0 mg).

R_f 0.20 (Petroleum ether/EtOAc, 40/1).

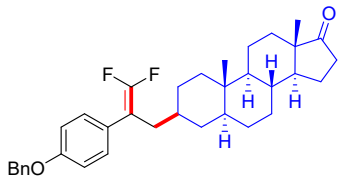
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 7.92 – 7.86 (m, 1H), 7.54 – 7.48 (m, 3H), 7.36 (d, J = 7.2 Hz, 1H), 3.95 (dd, J = 11.4, 2.6 Hz, 2H), 3.34 – 3.20 (m, 2H), 2.59 – 2.46 (m, 2H), 1.70 (d, J = 13.0 Hz, 2H), 1.52 – 1.31 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (t, $^1J_{C\text{-}F}$ = 288.3 Hz), 139.8 (t, $^4J_{C\text{-}F}$ = 2.6 Hz), 139.1, 136.1, 135.7, 128.9 (dd, $^3J_{C\text{-}F}$ = 5.0, 1.5 Hz), 127.4 (dd, J = 2.8, 1.2 Hz), 127.1, 124.8, 124.6, 122.8, 121.8, 121.1, 89.6 (dd, $^2J_{C\text{-}F}$ = 23.6, 15.7 Hz), 67.8, 35.4, 33.4 (t, $^3J_{C\text{-}F}$ = 2.5 Hz), 32.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.79 (d, J = 37.5 Hz, 1F), -90.74 (d, J = 37.4 Hz, 1F).

HRMS (ESI) calcd for $C_{20}H_{19}F_2OS$ $[M+H]^+$ 345.1125, found, 345.1119.

(5S,8R,9S,10S,13S,14S)-3-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (**5a**)



White solid, yield 85% (136.9 mg). M.p. = 106 – 108 °C.

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

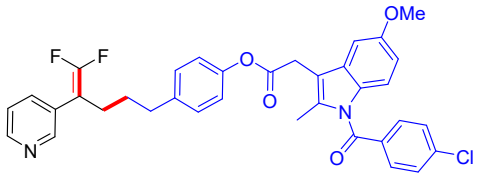
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 7.22 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.06 (s, 2H), 2.47 – 2.40 (m, 2H), 2.12 – 2.03 (m, 1H), 1.97 – 1.90 (m, 1H), 1.83 – 1.75 (m, 2H), 1.72 – 1.64 (m, 2H), 1.59 – 1.37 (m, 6H), 1.33 – 0.99 (m, 11H), 0.86 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.6, 157.9, 154.0 (t, $^1J_{C\text{-}F}$ = 285.2 Hz), 136.9, 129.5 (t, $^3J_{C\text{-}F}$ = 3.0 Hz), 128.6, 128.0, 127.5, 126.2, 114.7, 91.2 (t, $^2J_{C\text{-}F}$ = 17.4 Hz), 70.0, 54.8, 51.6, 47.9, 40.5, 36.6, 35.9, 35.1, 33.2, 32.1, 31.6, 30.9, 30.5 (t, $^3J_{C\text{-}F}$ = 2.1 Hz), 30.1, 28.6, 24.8, 21.8, 20.1, 13.9, 11.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.66 (s, 2F).

HRMS (ESI) calcd for $C_{35}H_{43}F_2O_2$ $[M+H]^+$ 533.3231, found, 533.3224.

4-(5,5-difluoro-4-(pyridin-3-yl)pent-4-en-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**5b**)



Colorless oil, yield 68% (125.3 mg).

R_f 0.20 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.51 (dd, J = 4.8, 1.4 Hz, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.08 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 9.0 Hz, 1H), 6.69 (dd, J = 9.0, 2.5 Hz, 1H), 3.89 (s, 2H), 3.83 (s, 3H), 2.59 (t, J = 7.6 Hz, 2H), 2.46 – 2.41 (m, 5H), 1.71 – 1.62 (m, 2H).

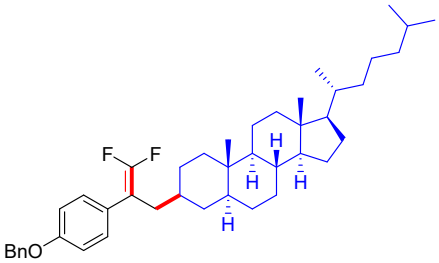
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.3, 156.1, 153.9 (dd, $^1J_{C\text{-}F}$ = 290.4, 287.0, Hz), 149.1 (t, $^4J_{C\text{-}F}$ = 3.4 Hz), 148.9, 148.3, 139.3, 139.2, 136.2, 135.7 (t, $^4J_{C\text{-}F}$ = 3.3 Hz), 133.9, 131.2, 130.9, 130.5, 129.6 (t, $^3J_{C\text{-}F}$ =

4.1 Hz), 129.22, 129.16, 123.4, 121.3, 115.0, 112.1, 111.8, 101.2, 89.5 (dd, $^{2}J_{C\text{-}F}$ = 23.4, 13.0 Hz), 55.7, 34.5, 30.5, 29.2, 26.7, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.09 (d, J = 39.4 Hz, 1F), -89.86 (d, J = 39.6 Hz, 1F).

HRMS (ESI) calcd for $C_{35}H_{30}ClF_2N_2O_4$ $[M+H]^+$ 615.1862, found, 615.1860.

(5S,8R,9S,10S,13R,14S,17R)-3-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (**5c**)



White solid, yield 54% (102.8 mg). M.p. = 103 – 105 °C.

R_f 0.65 (Petroleum ether/EtOAc, 40/1).

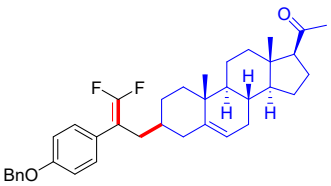
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 7.26 – 7.19 (m, 2H), 6.97 – 6.95 (m, 2H), 5.07 (s, 2H), 2.53 – 2.39 (m, 1H), 2.25 (d, J = 6.4 Hz, 1H), 1.97 (t, J = 11.5 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.72 – 1.62 (m, 2H), 1.55 – 0.87 (m, 37H), 0.76 (s, 3H), 0.66 & 0.65 (2×s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.8, 154.0 (t, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 153.9 (dd, $^{1}J_{C\text{-}F}$ = 287.0, 283.0 Hz), 137.0, 136.9, 129.5 (t, $^{4}J_{C\text{-}F}$ = 2.6 Hz), 129.4 (t, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 128.6, 128.0, 127.6, 127.5, 126.5 (t, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 126.3 (d, $^{3}J_{C\text{-}F}$ = 1.6 Hz), 114.9, 114.7, 91.3 (dd, $^{2}J_{C\text{-}F}$ = 19.6, 15.1 Hz), 90.5 (dd, $^{2}J_{C\text{-}F}$ = 21.8, 12.7 Hz), 70.0, 56.7, 56.6, 56.4, 56.3, 54.7, 54.6, 46.4, 42.7, 42.6, 40.5, 40.1, 39.6, 38.4, 36.4, 36.24, 36.15, 36.0, 35.9, 35.8, 35.59, 35.56, 35.3, 33.3, 32.3, 32.2, 30.6, 30.2, 29.0, 28.5, 28.3, 28.1, 24.8, 24.2, 23.93, 23.87, 22.9, 22.6, 21.1, 20.8, 18.7, 12.4, 12.1, 11.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.15 (d, J = 46.7 Hz, 0.3F), -92.48 – -92.70 (m, 1F), -92.77 (d, J = 47.1 Hz, 0.7F).

HRMS (ESI) calcd for $C_{43}H_{61}F_2O$ $[M+H]^+$ 631.4690, found, 631.4683.

1-((8S,9S,10R,13S,14S,17S)-3-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (**5d**)



White solid, yield 59% (98.8 mg). M.p. = 104 – 106 °C.

R_f 0.25 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 7.23 (dd, J = 8.6, 3.0 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.24 (d, J = 4.3 Hz, 1H), 5.06 (s, 2H), 2.58 – 2.49 (m, 1H), 2.42 – 2.38 (m, 0.7H), 2.32 – 2.27 (m, 2H), 2.24 – 2.14 (m, 1.3H), 2.14 & 2.12 (2×s, 3H), 2.08 – 1.92 (m, 3H), 1.80 – 1.58 (m, 7H), 1.49 – 1.38 (m, 4H), 1.31 – 1.18 (m, 3H), 1.14 – 1.06 (m, 1H), 0.98 & 0.97 (2×s, 3H), 0.63 & 0.62 (2×s, 3H).

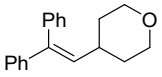
^{13}C NMR (100 MHz, $CDCl_3$) δ 209.71, 209.66, 158.6, 157.9, 153.9 (dd, $^{1}J_{C\text{-}F}$ = 287.6, 284.2 Hz), 153.7 (dd, $^{1}J_{C\text{-}F}$ = 287.0, 284.5 Hz), 142.7, 139.8, 136.9, 129.5 (t, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 129.4 (t, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.0,

127.53, 127.51, 126.4 (t, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 126.2 (t, $^{3}J_{C\text{-}F}$ = 4.3 Hz), 121.5, 119.4, 114.8, 114.7, 91.0 (dd, $^{2}J_{C\text{-}F}$ = 22.1, 13.1 Hz), 90.3 (dd, $^{2}J_{C\text{-}F}$ = 21.6, 13.2 Hz), 70.0, 63.8, 63.7, 57.0, 50.4, 50.2, 44.05, 44.02, 39.3, 39.1, 38.91, 38.89, 37.4, 37.1, 36.4, 35.1, 34.1, 32.0, 31.88, 31.85, 31.7, 31.60, 31.58, 29.1, 28.6, 25.4, 24.5, 22.84, 22.81, 20.9, 20.8, 19.5, 19.4, 13.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.90 – -92.11 (m, 1F), -92.35 (d, J = 46.0 Hz, 0.36F), -92.57 (d, J = 46.0 Hz, 0.64F).

HRMS (ESI) calcd for $C_{37}H_{45}F_2O_2$ $[M+H]^+$ 559.3388, found, 559.3381.

4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (**6a**)



White solid, yield 16% (26.0 mg). M.p. = 112 – 114 °C.

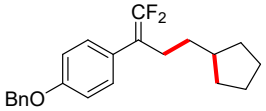
R_f 0.30 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 3H), 7.27 – 7.16 (m, 7H), 5.89 (d, J = 9.8 Hz, 1H), 3.91 (d, J = 11.1 Hz, 2H), 3.29 (td, J = 11.3, 3.9 Hz, 2H), 2.43 – 2.31 (m, 1H), 1.63 – 1.52 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.0, 140.2, 133.7, 129.7, 128.3, 128.2, 127.2, 127.11, 127.09, 67.4, 35.6, 32.9.

HRMS (EI) calcd for $C_{19}H_{20}O$ $[M]^+$ 264.1514, found, 264.1507.

1-(benzyloxy)-4-(4-cyclopentyl-1,1-difluorobut-1-en-2-yl)benzene (**7**)



White solid, yield 42% (43.0 mg). M.p. = 74 – 76 °C.

R_f 0.35 (Petroleum ether).

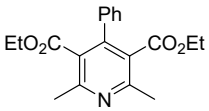
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 5H), 7.50 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 5.33 (s, 2H), 2.65 – 2.60 (m, 2H), 2.04 – 1.97 (m, 3H), 1.87 – 1.74 (m, 4H), 1.63 (dd, J = 15.2, 6.7 Hz, 2H), 1.36 – 1.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.4 (t, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 137.0, 129.4 (t, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 128.6, 128.1, 127.5, 126.4, 114.8, 92.1 (t, $^{2}J_{C\text{-}F}$ = 17.2 Hz), 70.0, 39.6, 34.3, 32.5, 27.0, 25.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.88 (s, 2F).

HRMS (ESI) calcd for $C_{22}H_{25}F_2O$ $[M+H]^+$ 343.1873, found, 343.1868.

diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (**G**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 3H), 7.30 – 7.23 (m, 2H), 4.01 (q, J = 7.1 Hz, 4H), 2.62 (s, 6H), 0.90 (t, J = 7.1 Hz, 6H).

The compound data is in agreement with the literature.[8]

7. References

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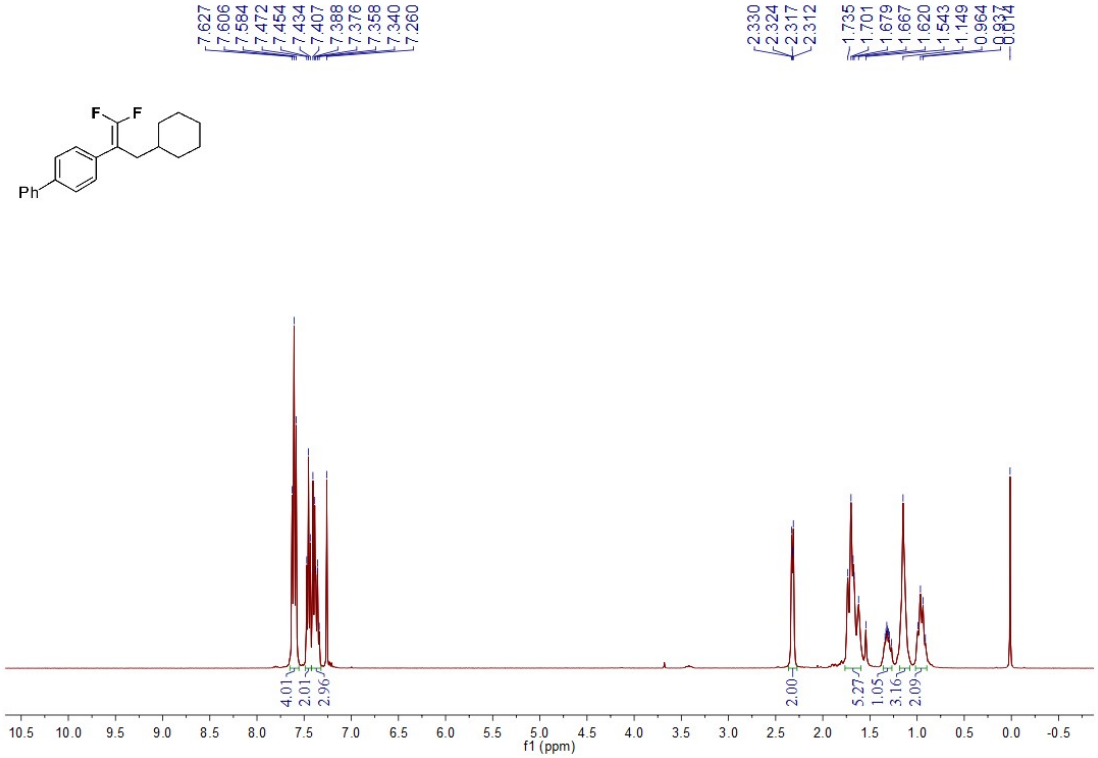
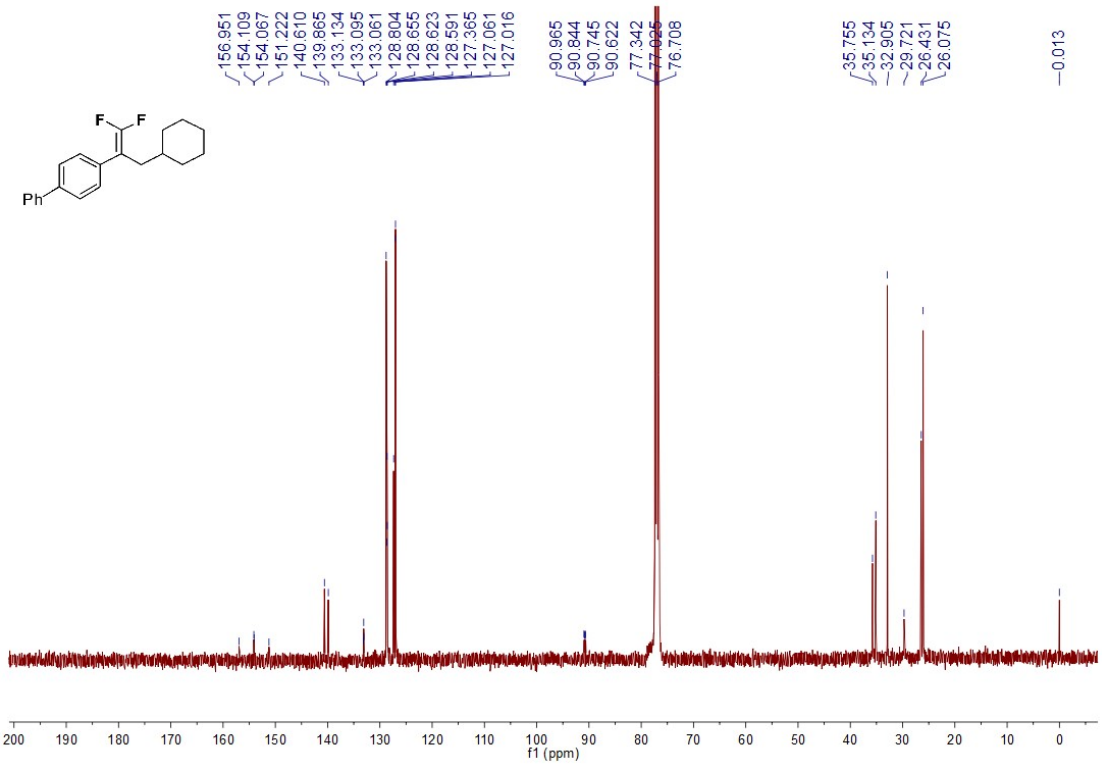
8. NMR spectra

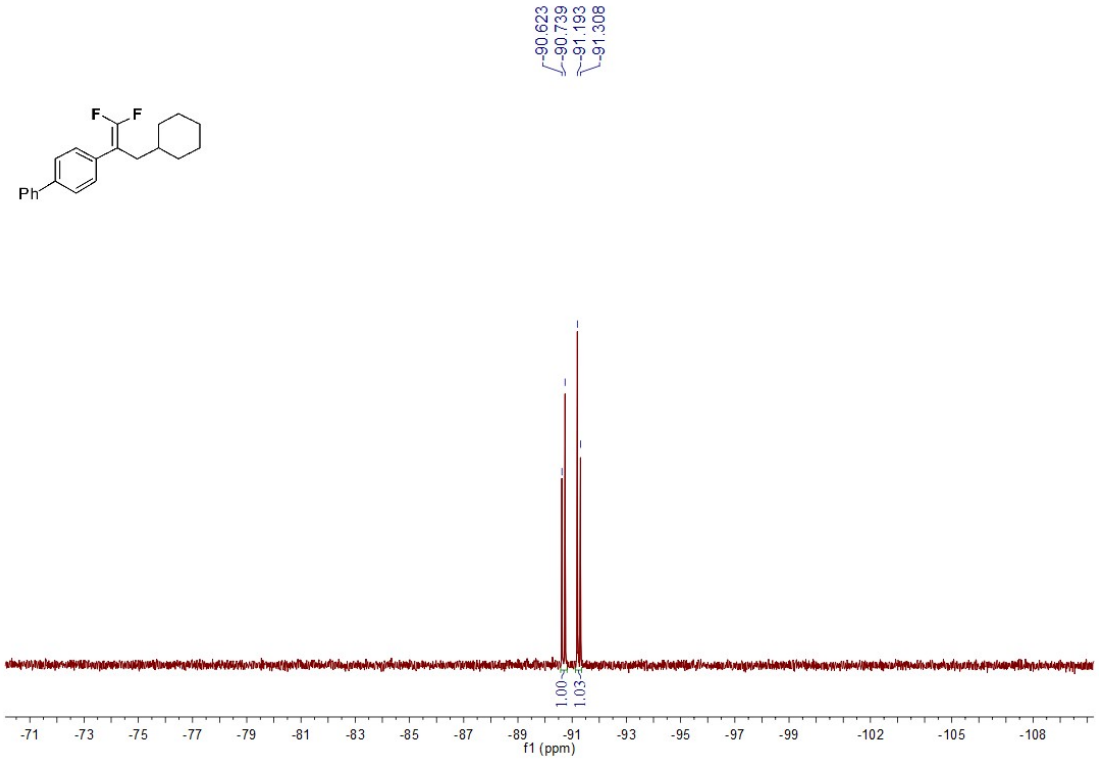
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**



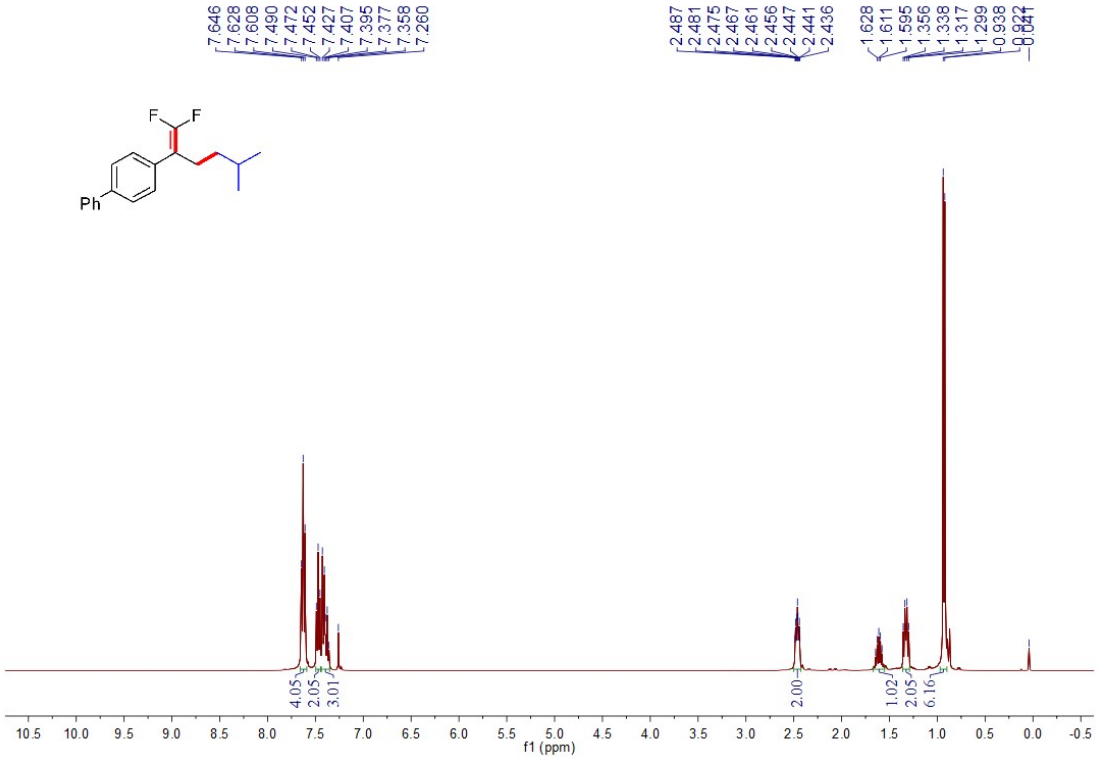
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3a**



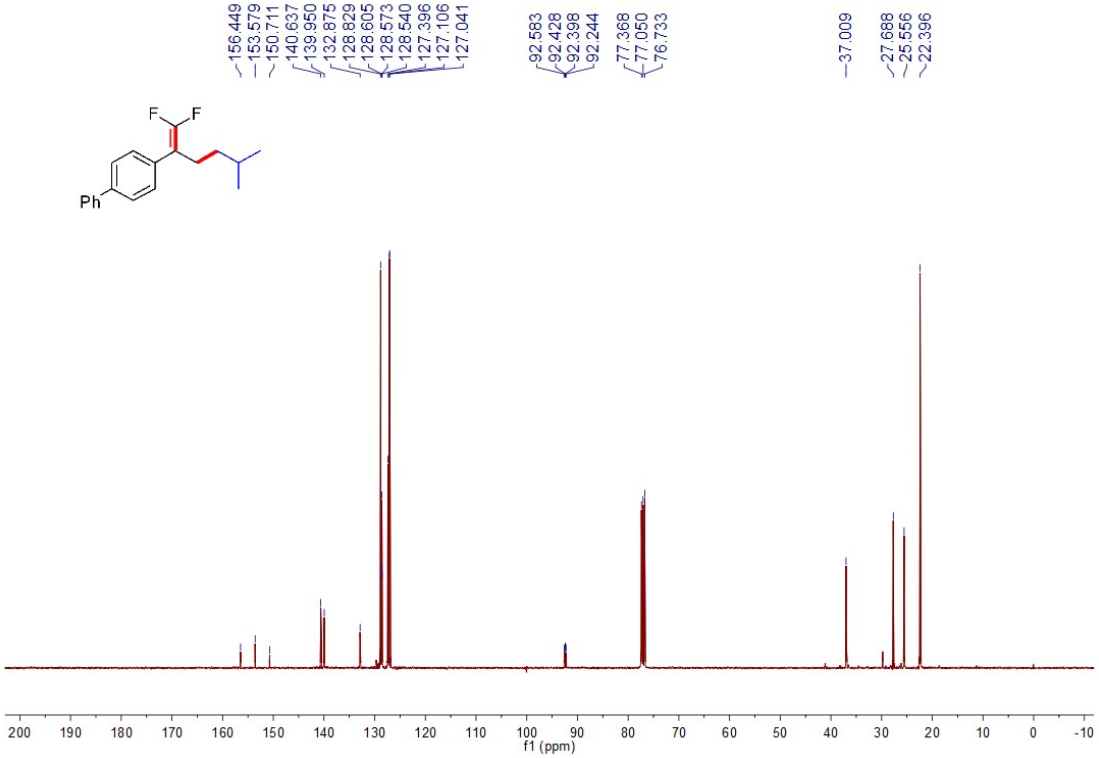
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3a**



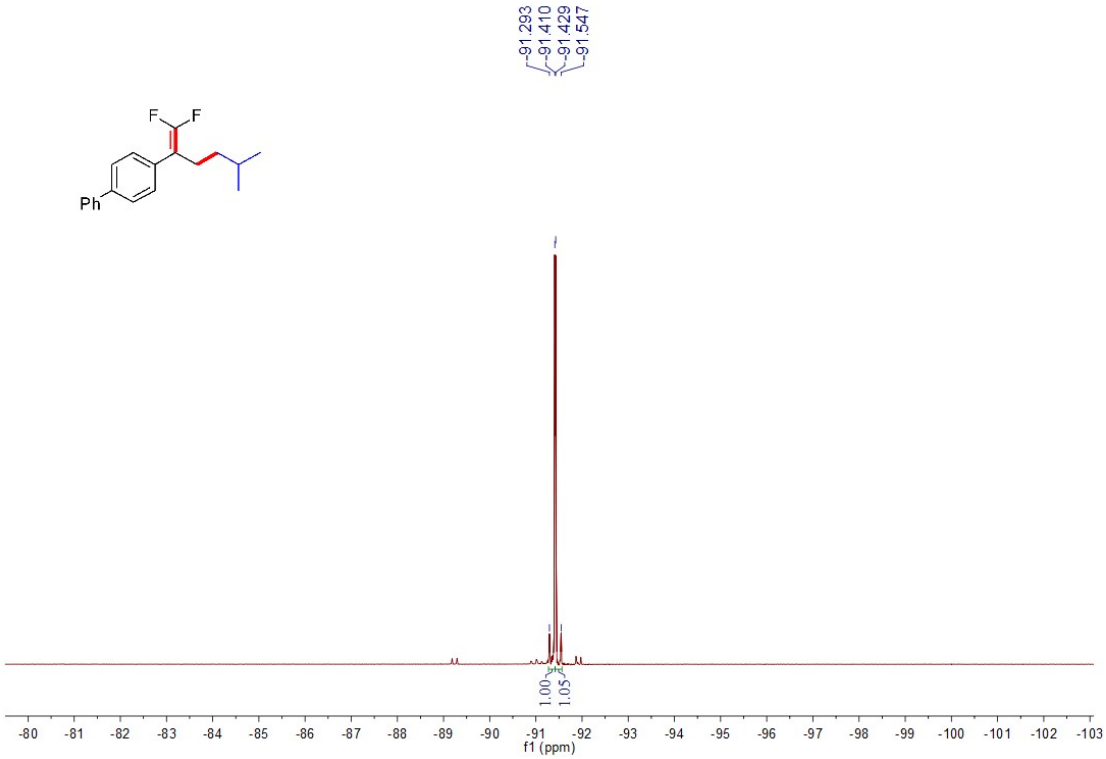
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**



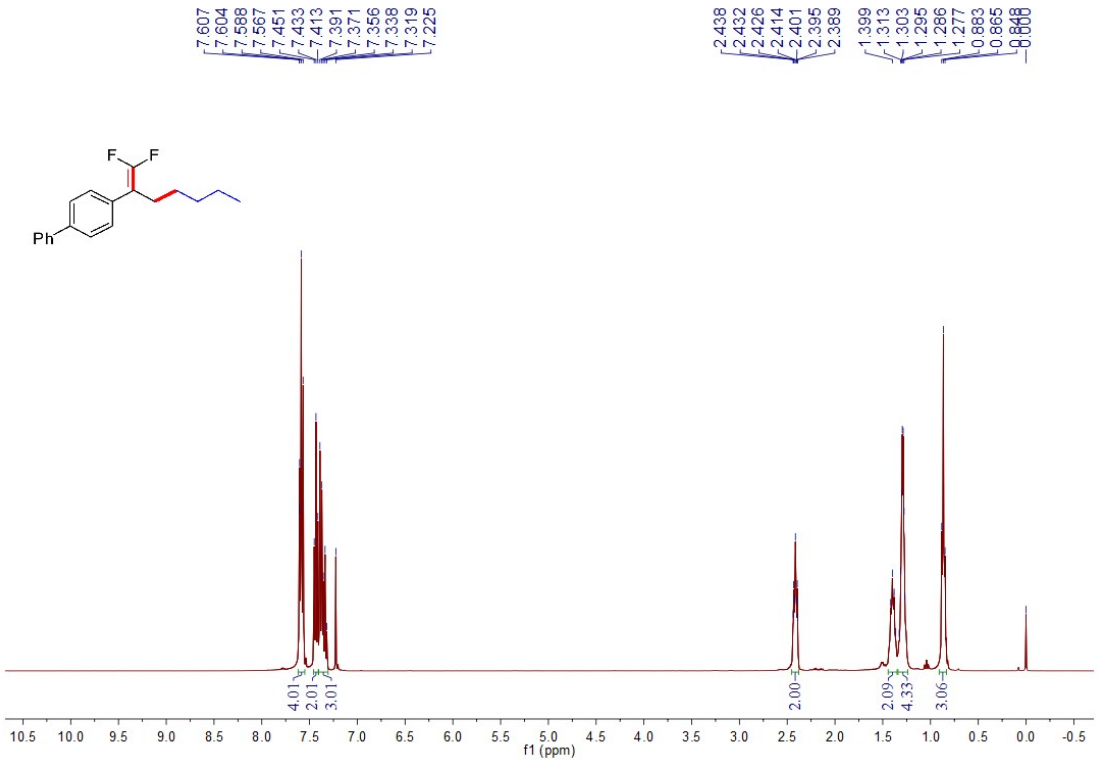
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3b**



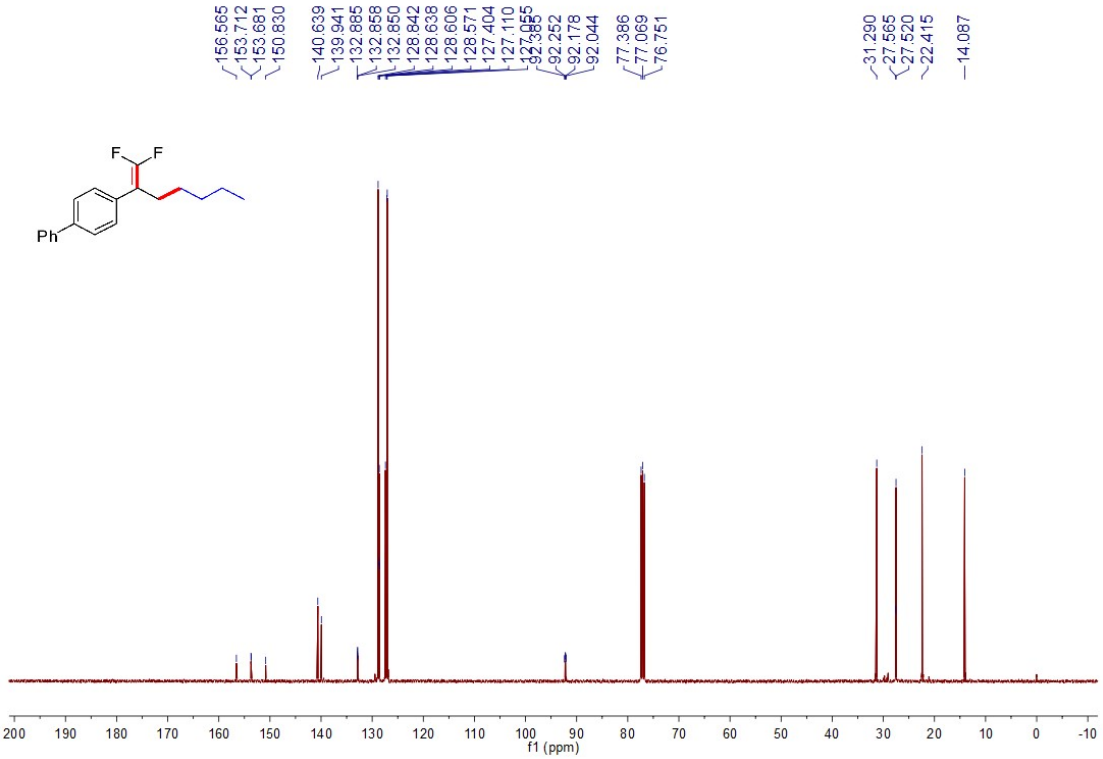
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3b**



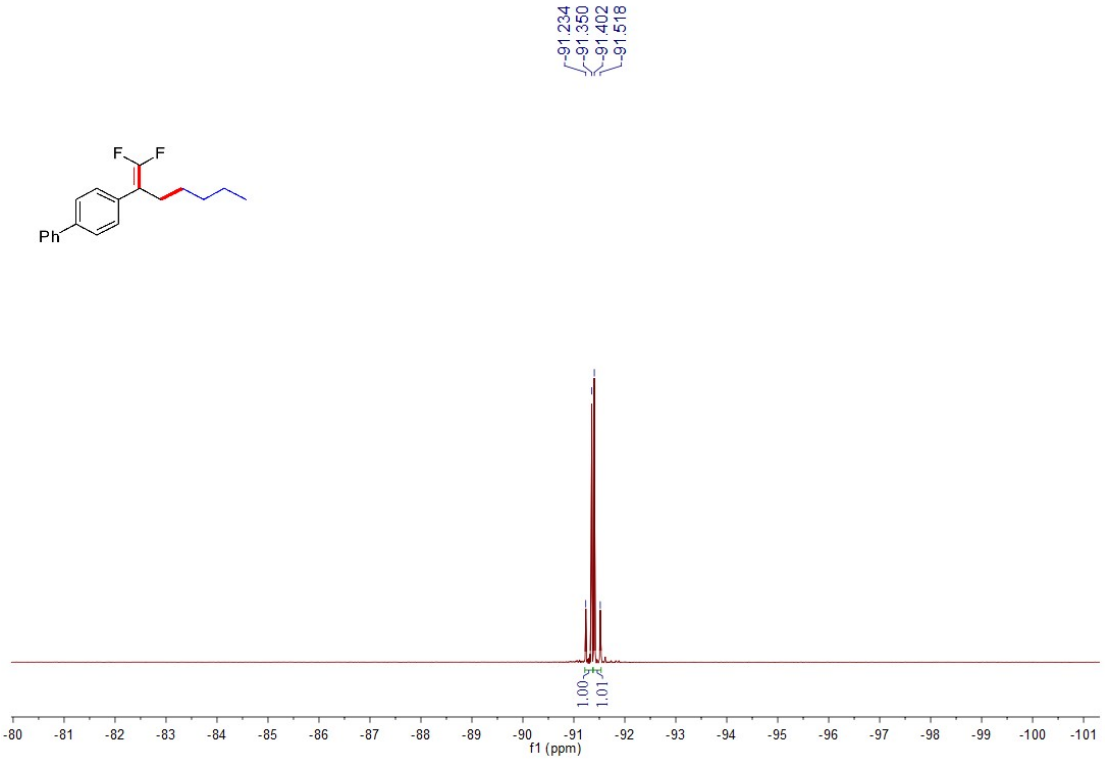
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3c**



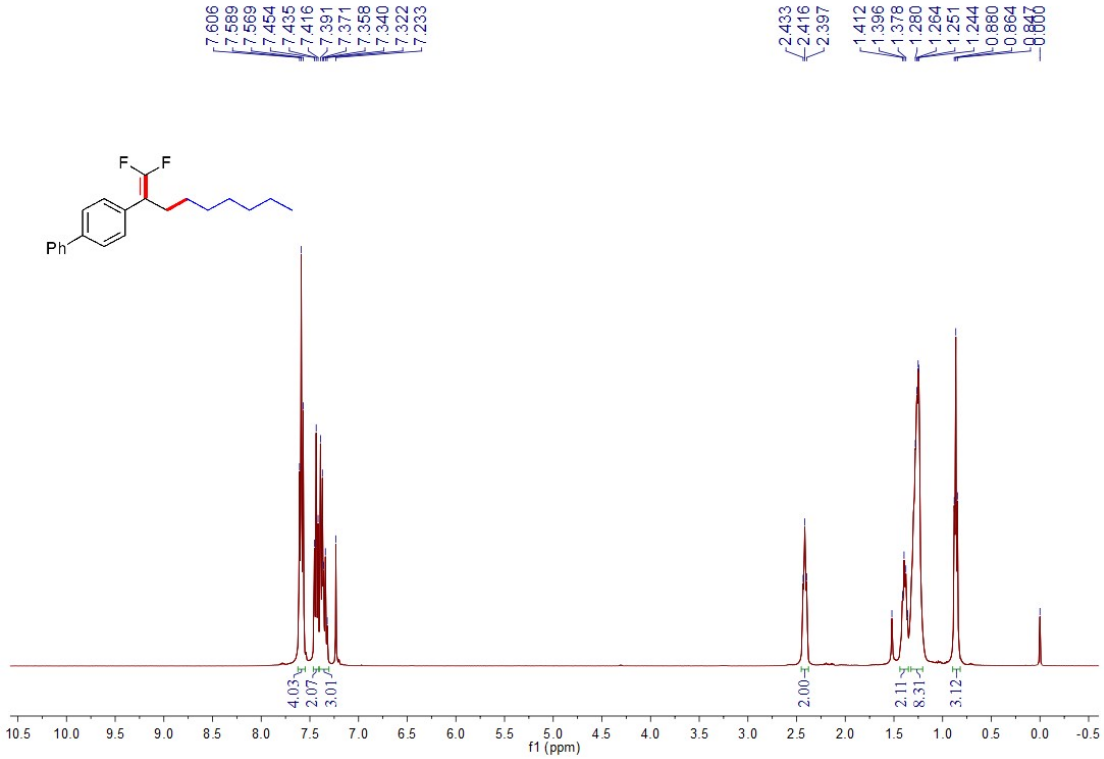
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3c**



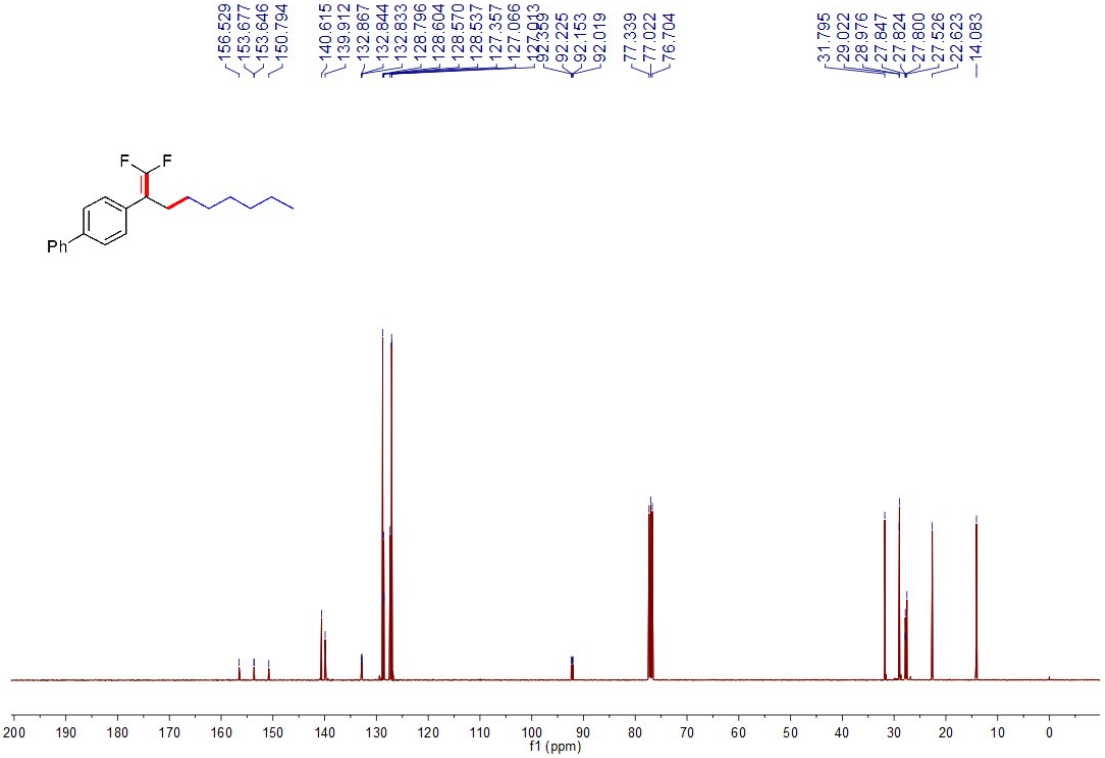
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3c**



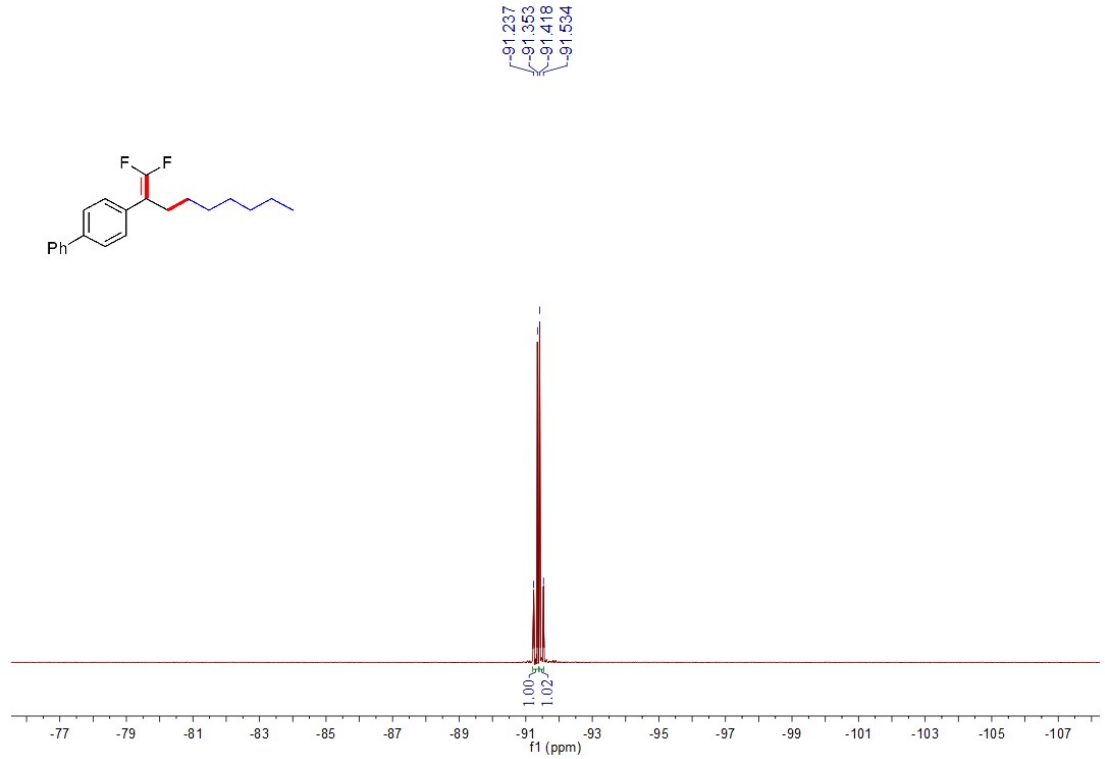
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**



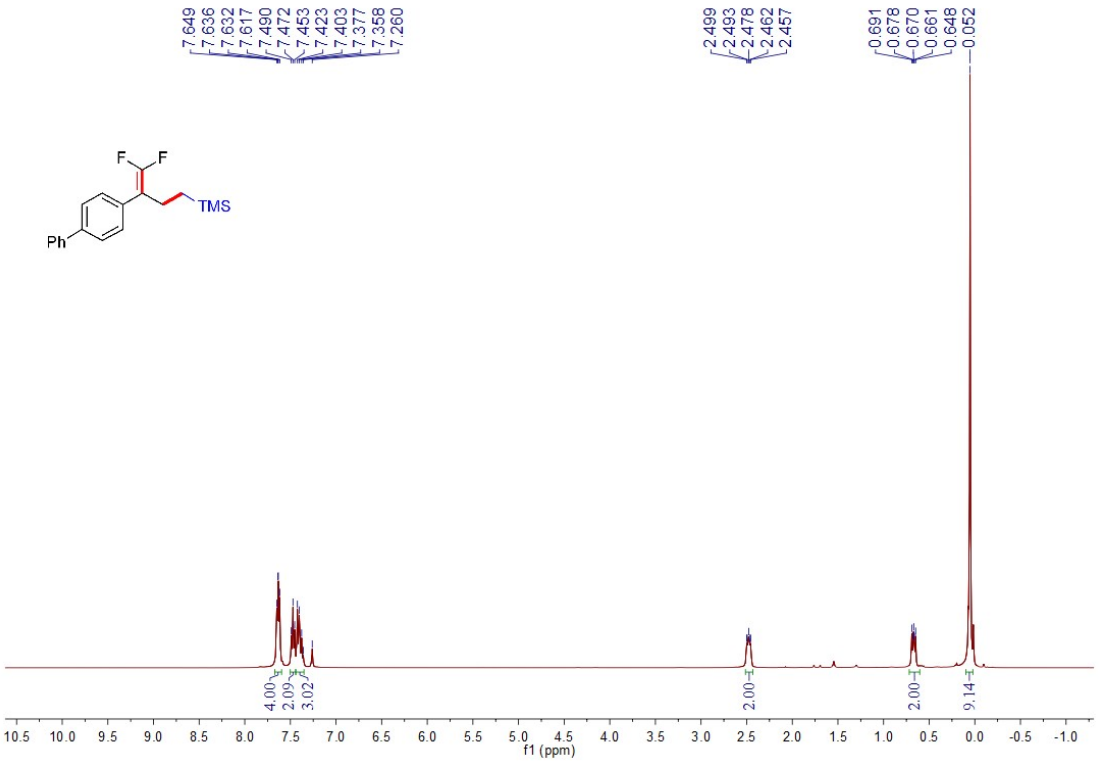
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3d**



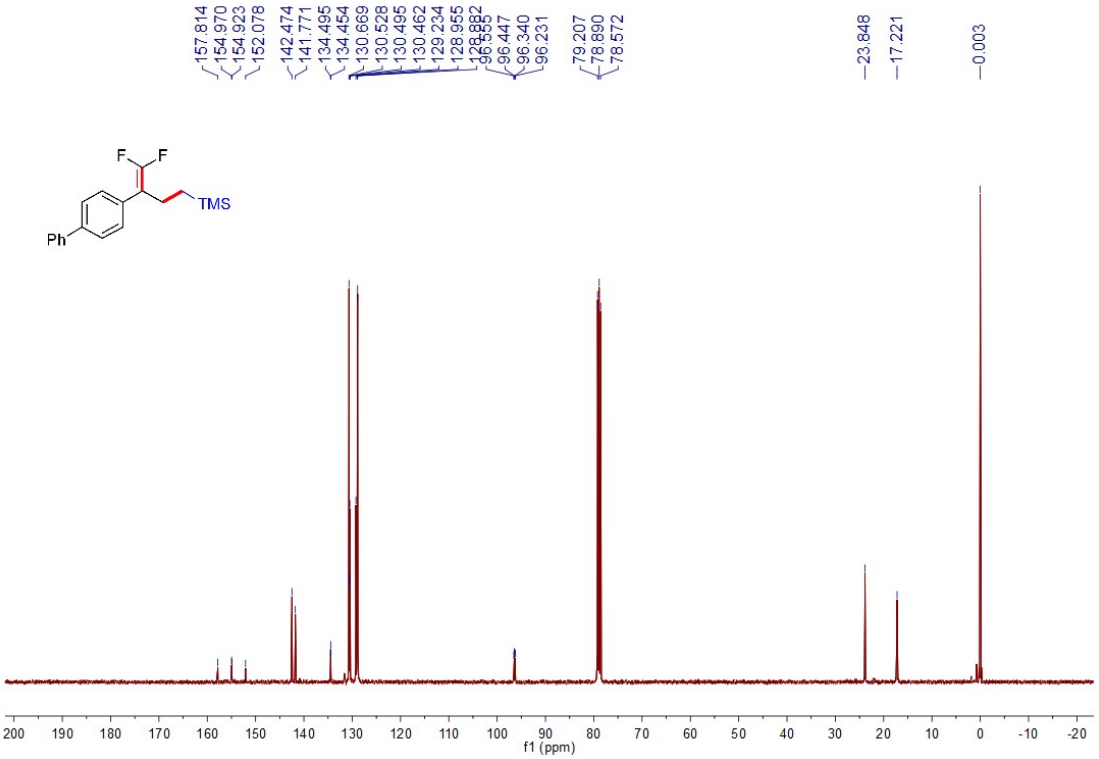
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3d**



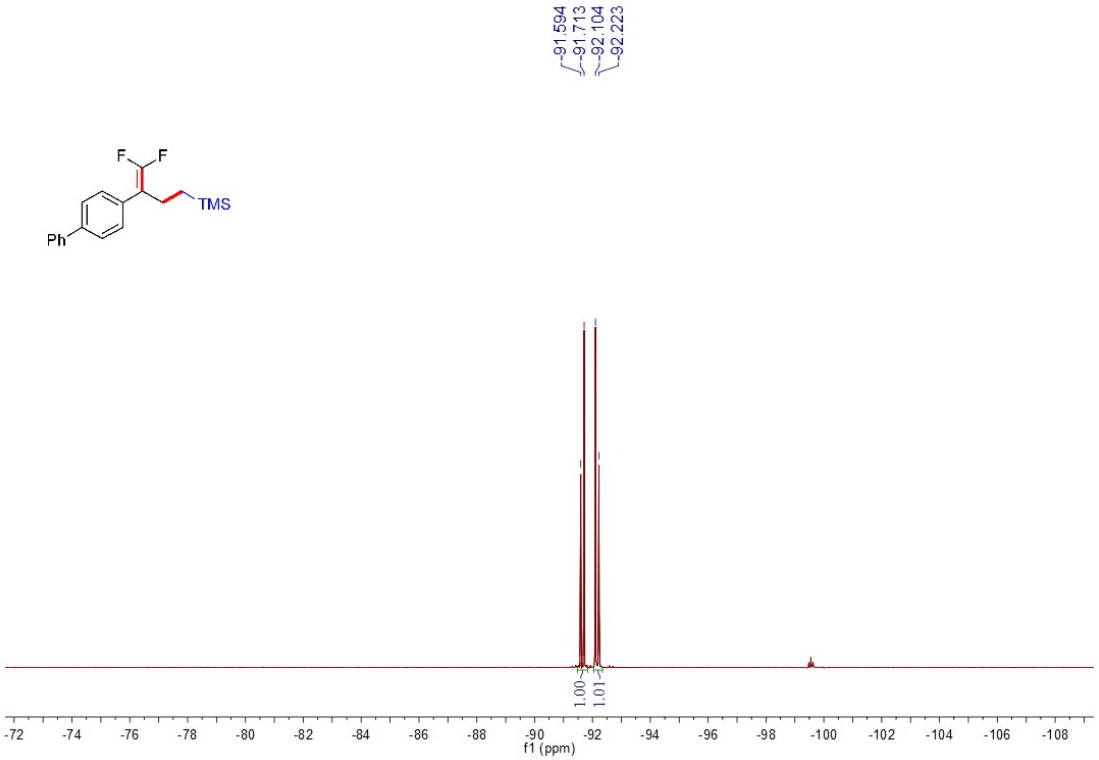
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e**



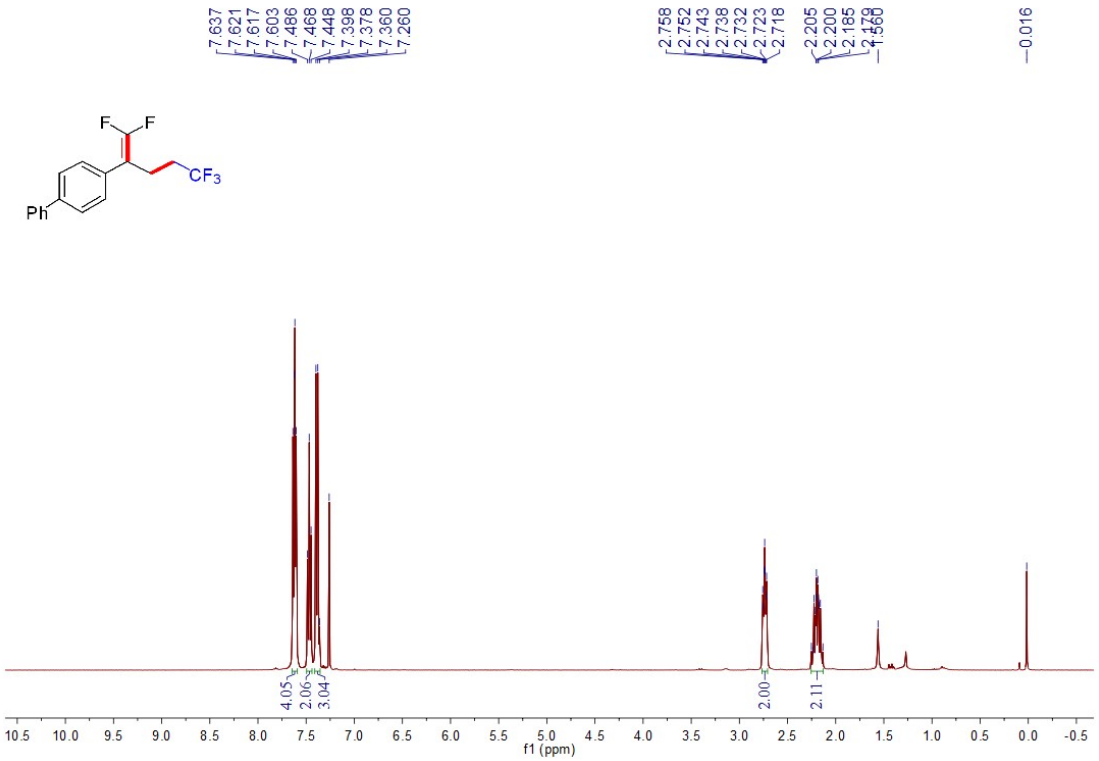
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3e**



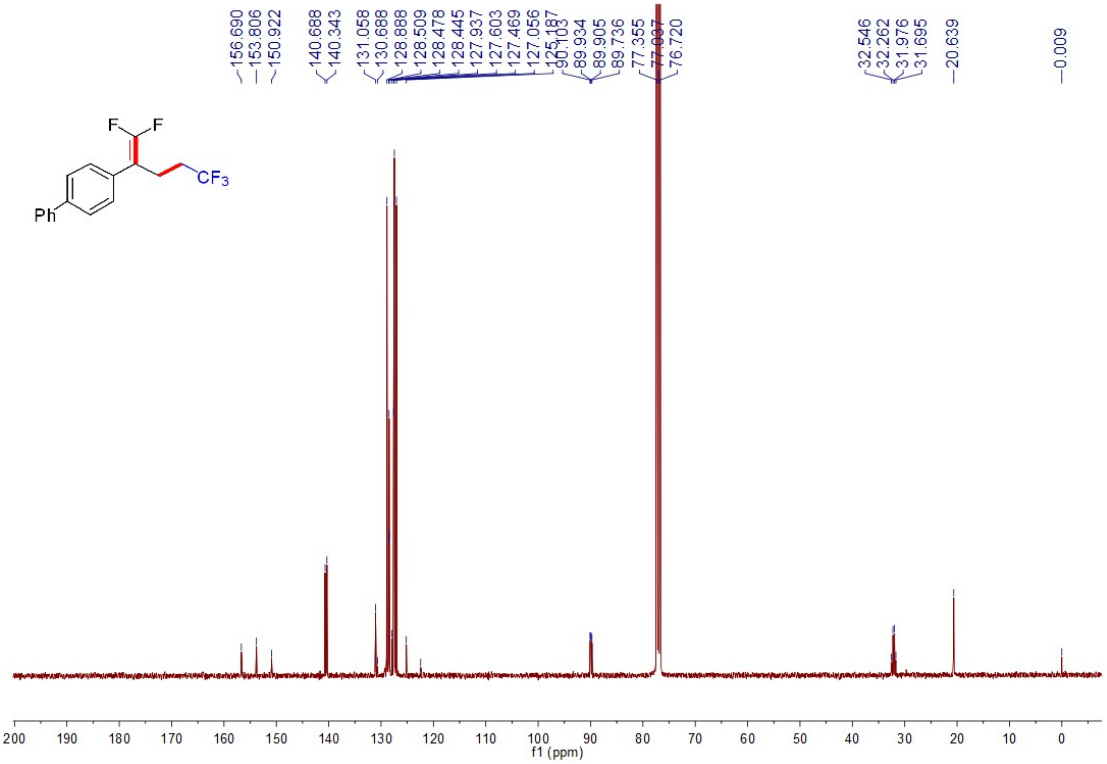
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3e**



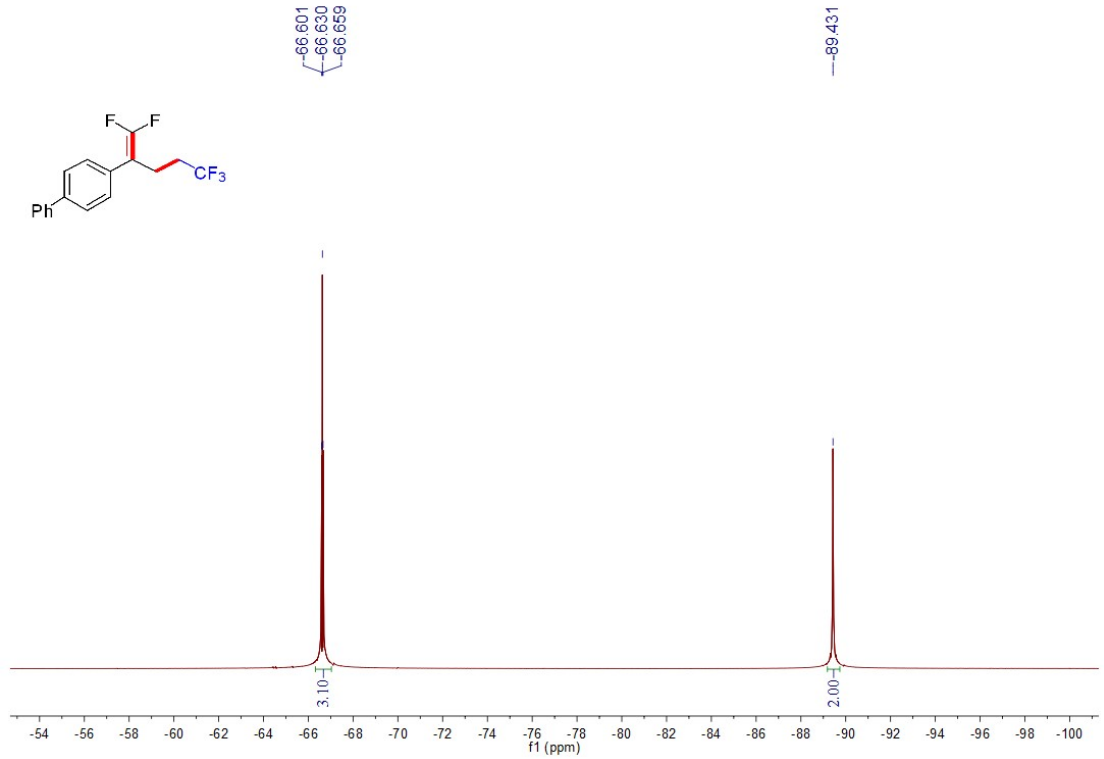
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3f**



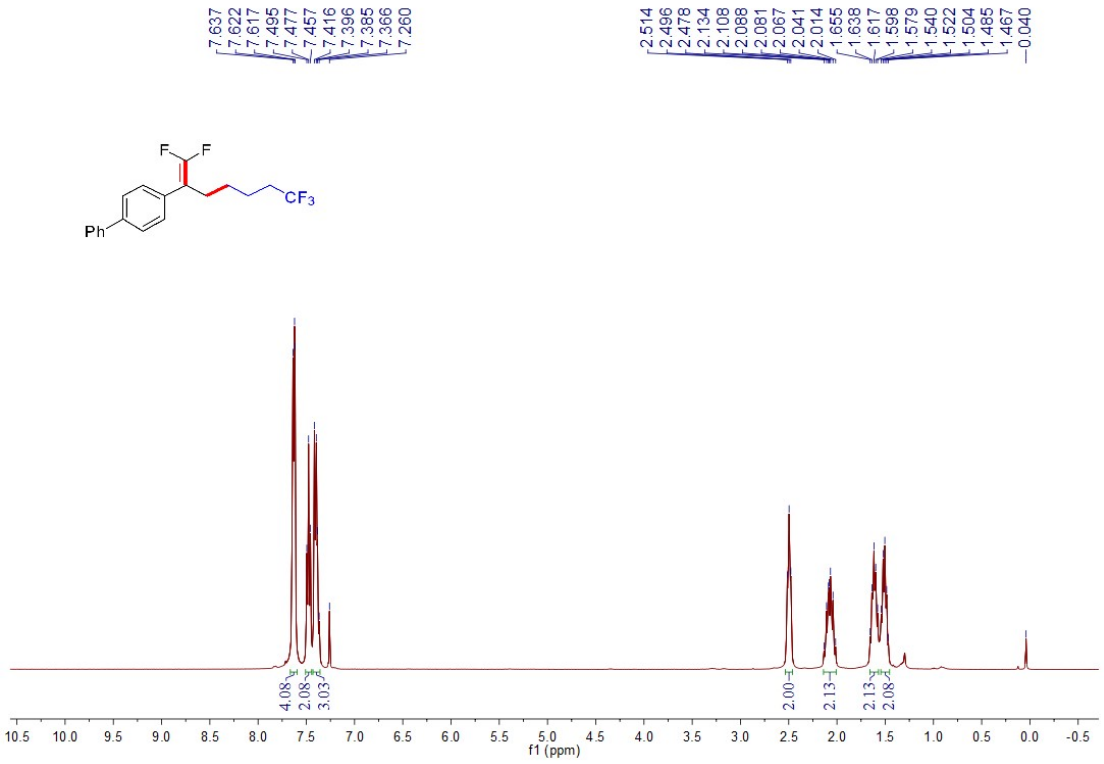
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3f**



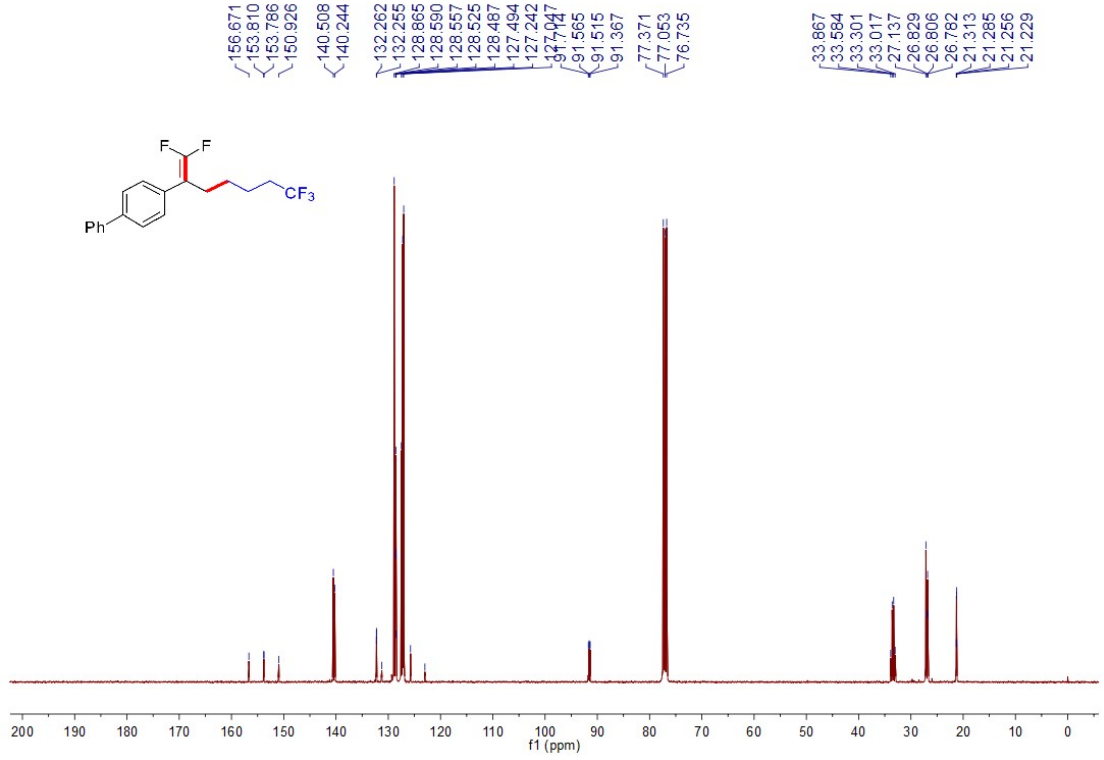
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3f**



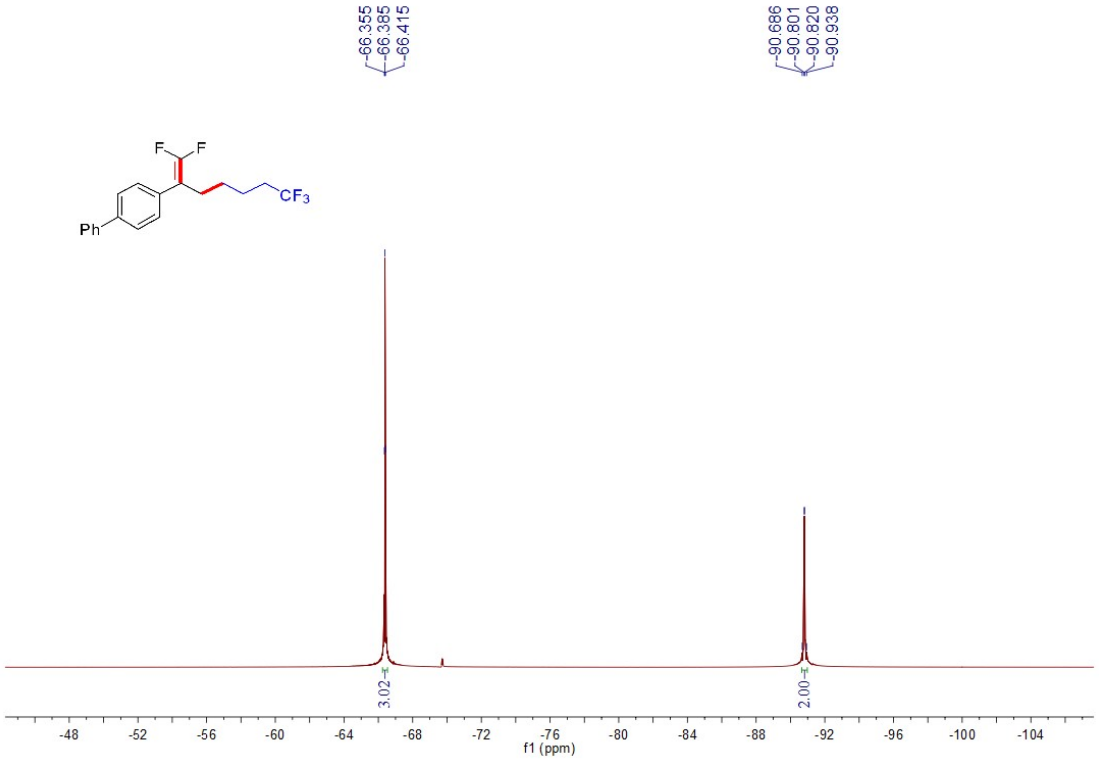
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3g**



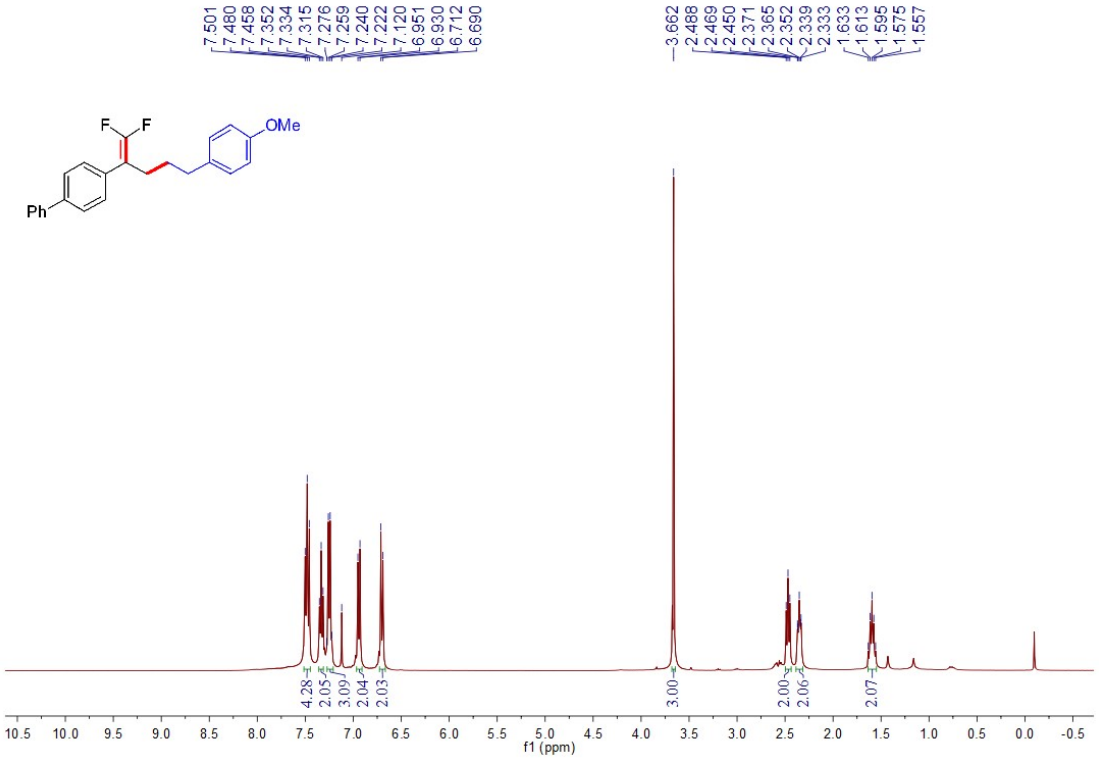
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3g**



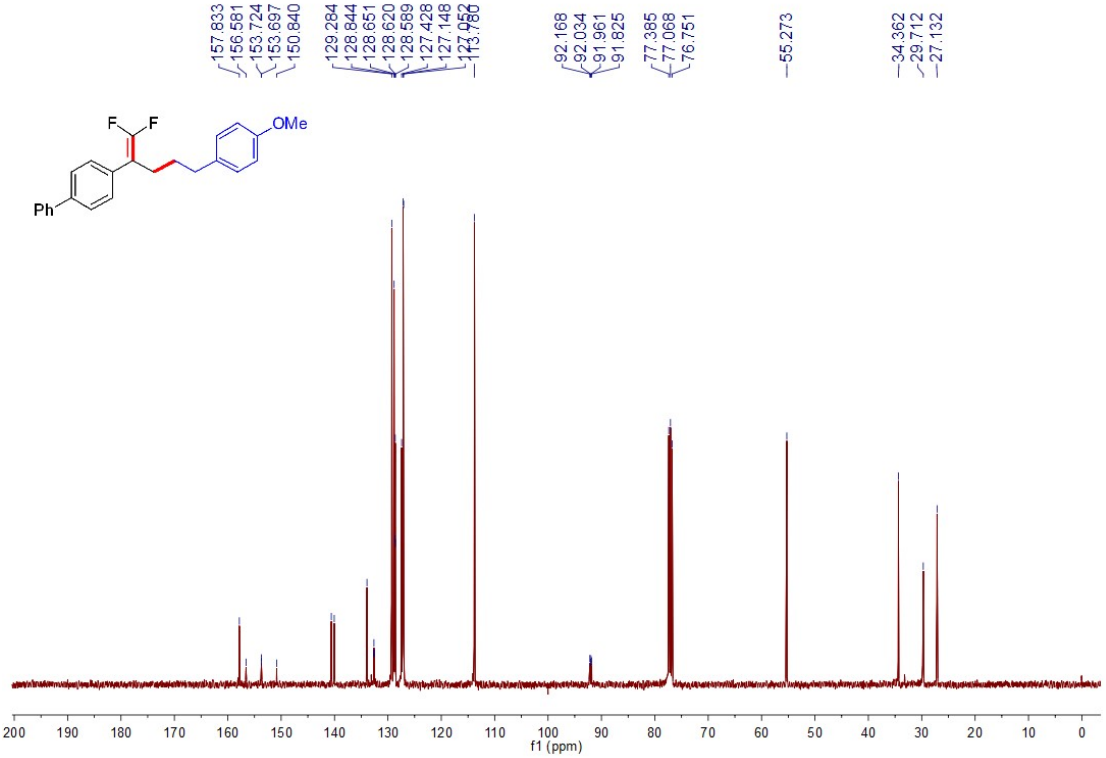
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3g**



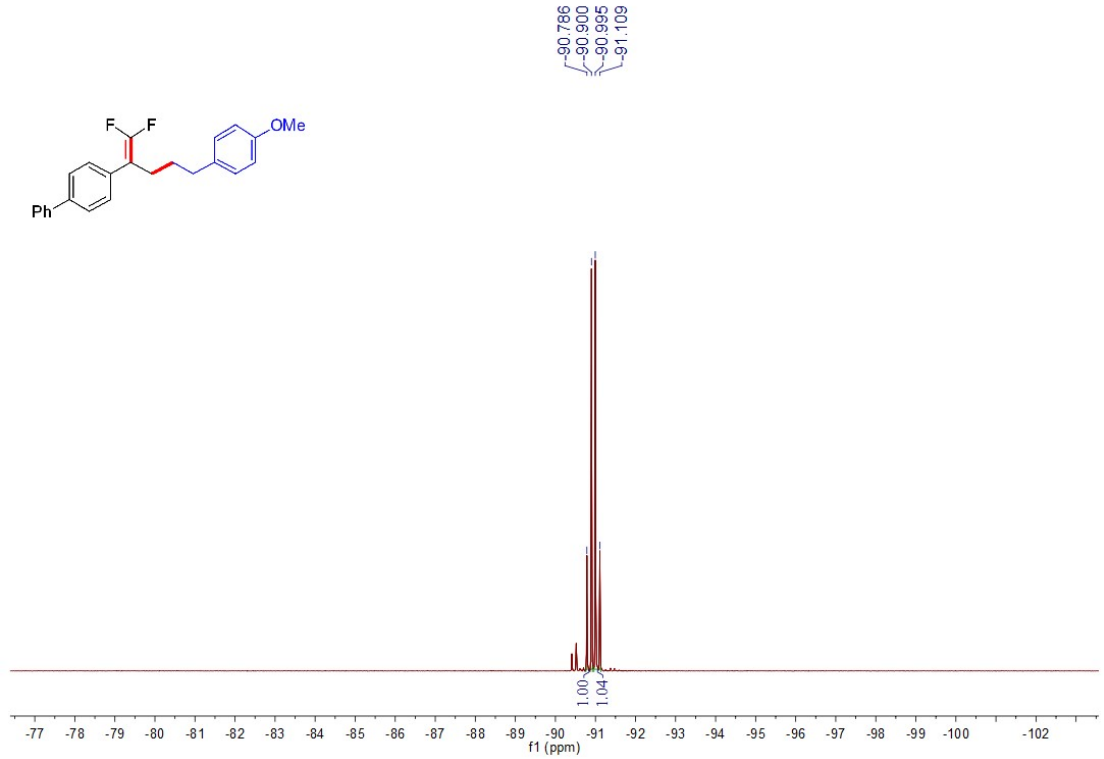
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3h**



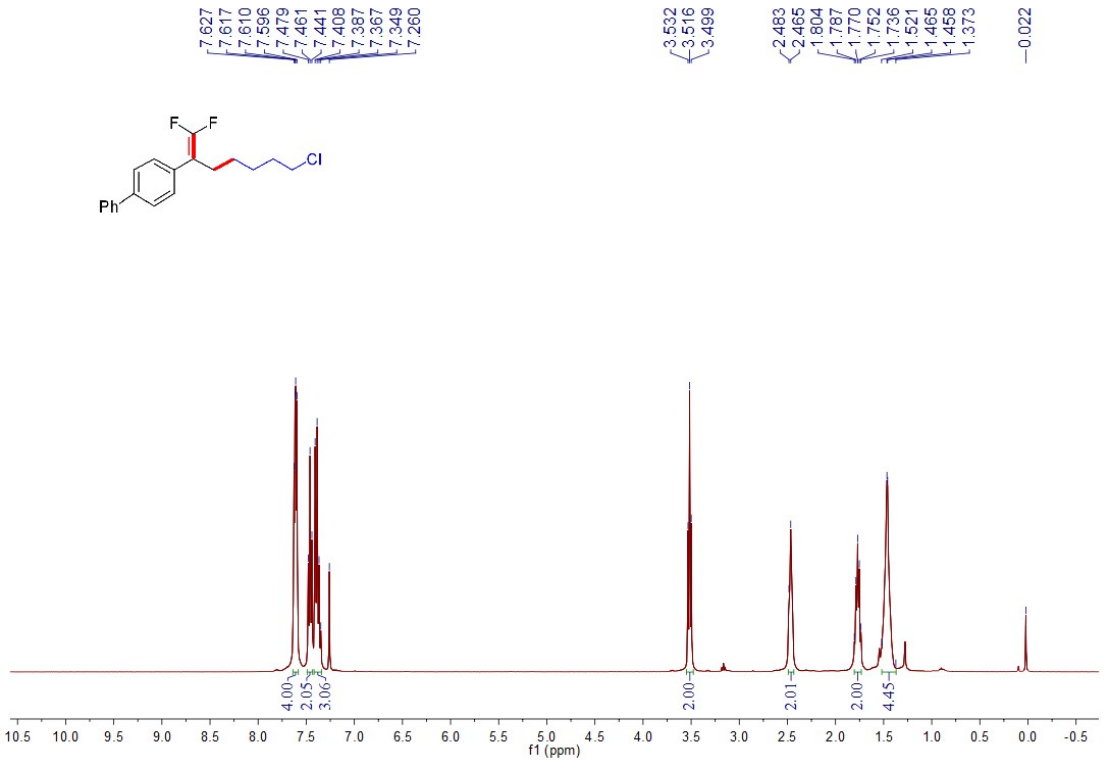
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3h**



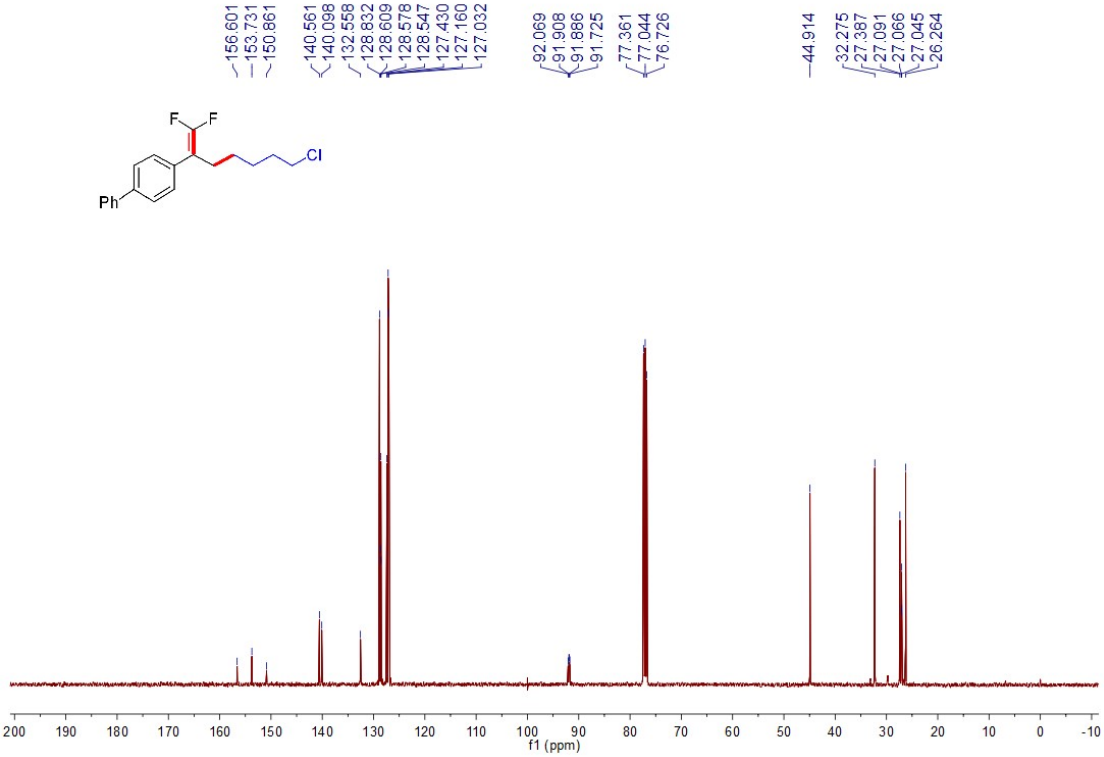
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3h**



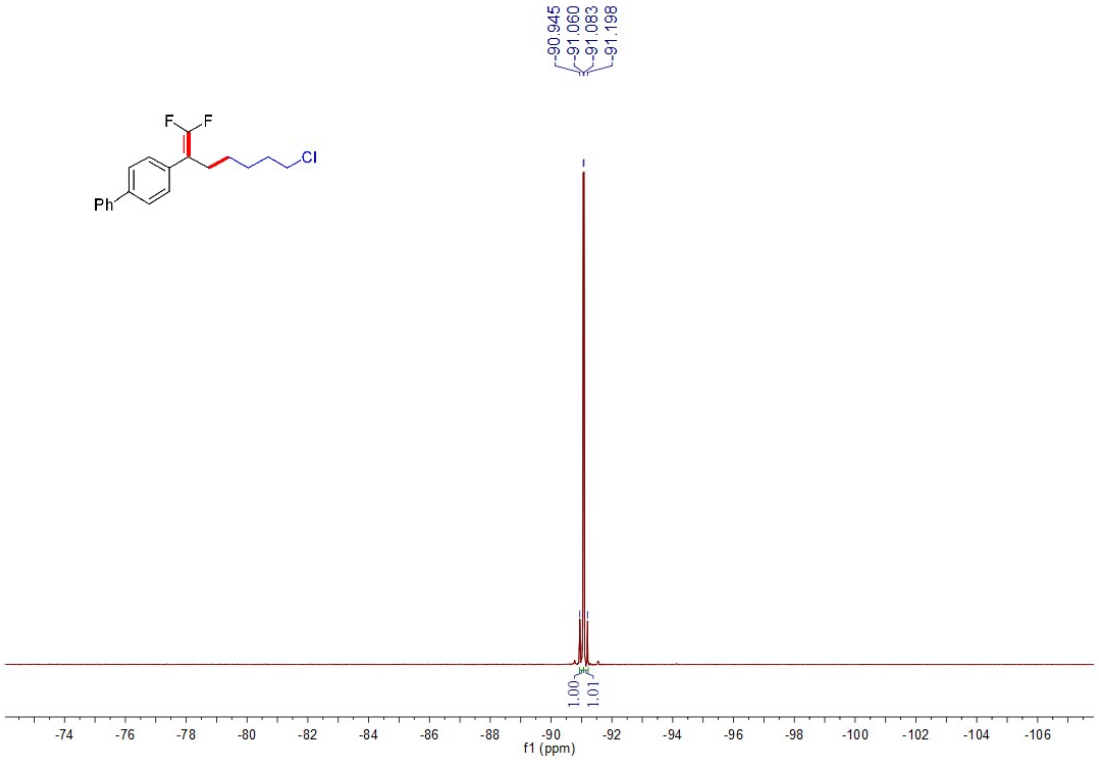
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3i**



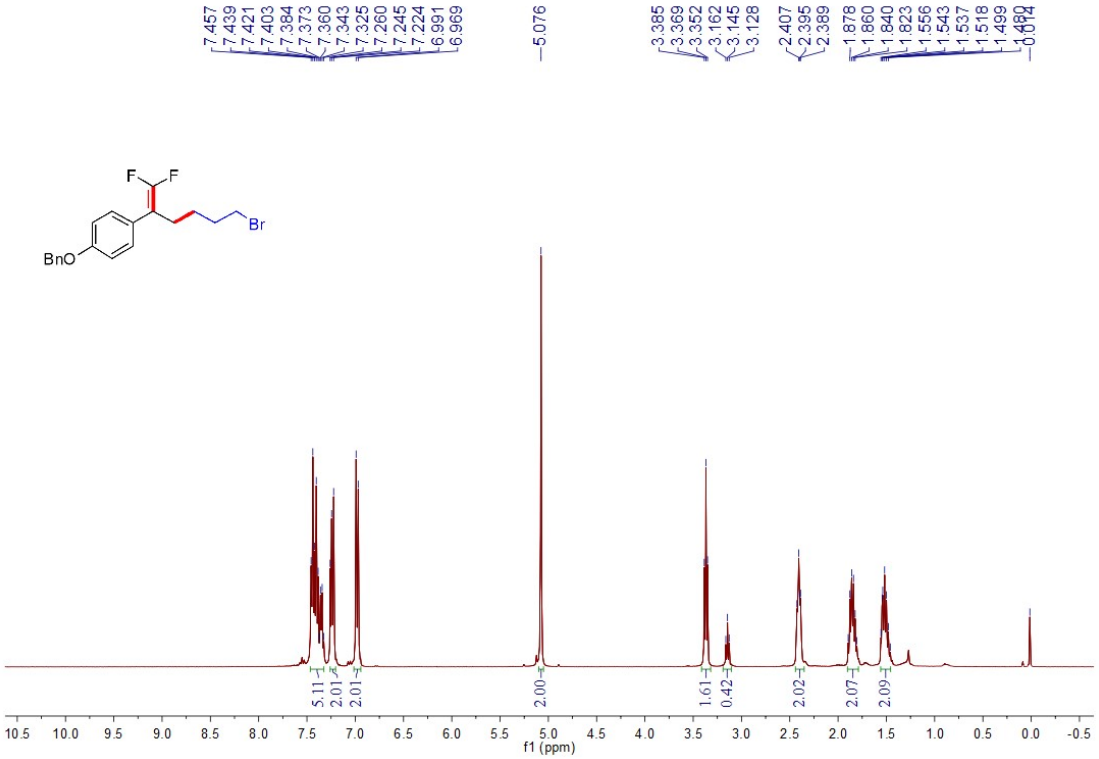
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3i**



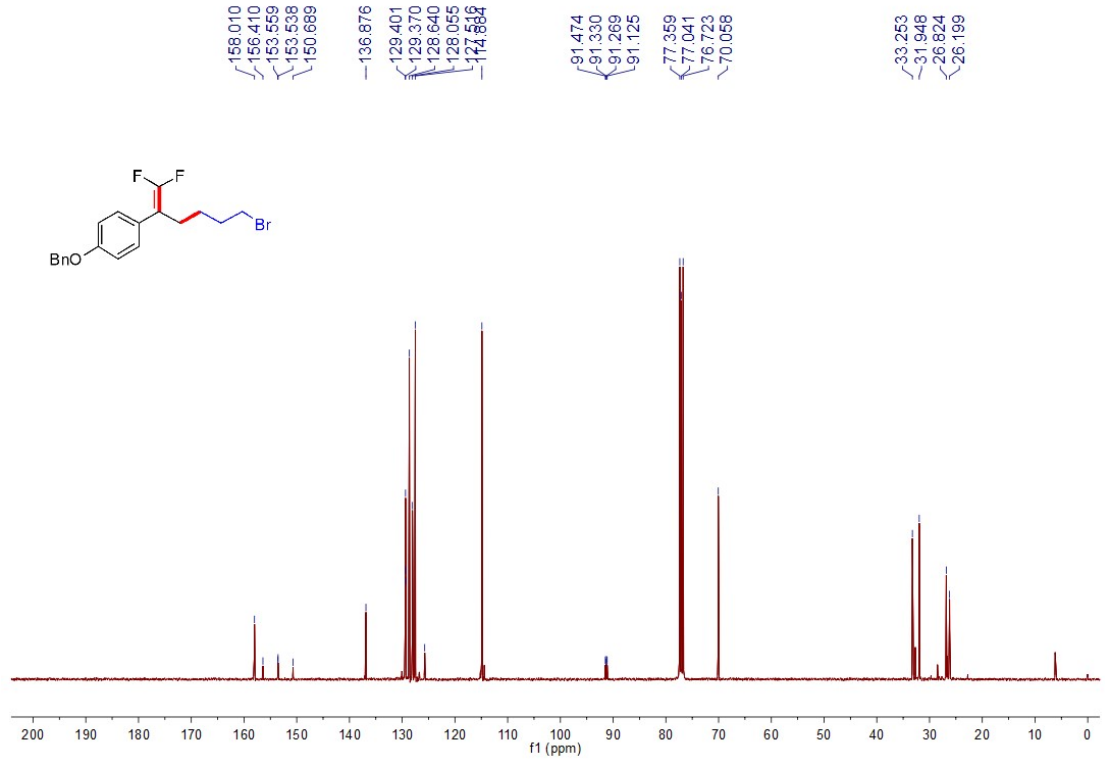
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3i**



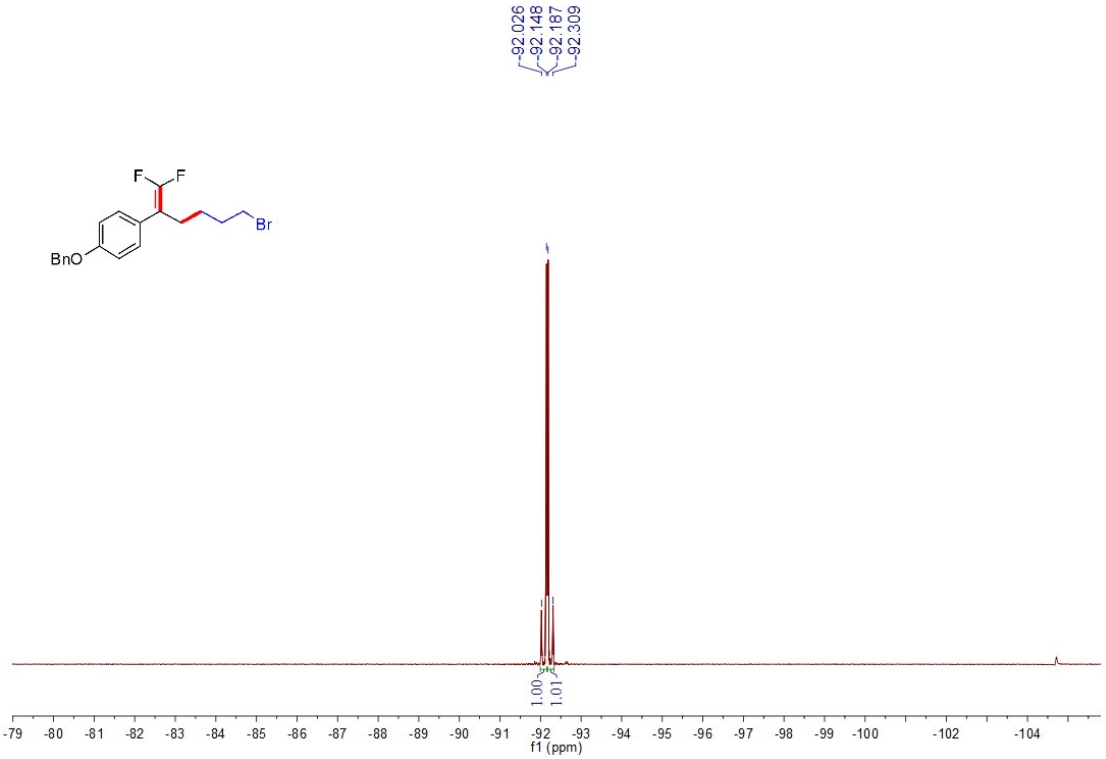
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3j**



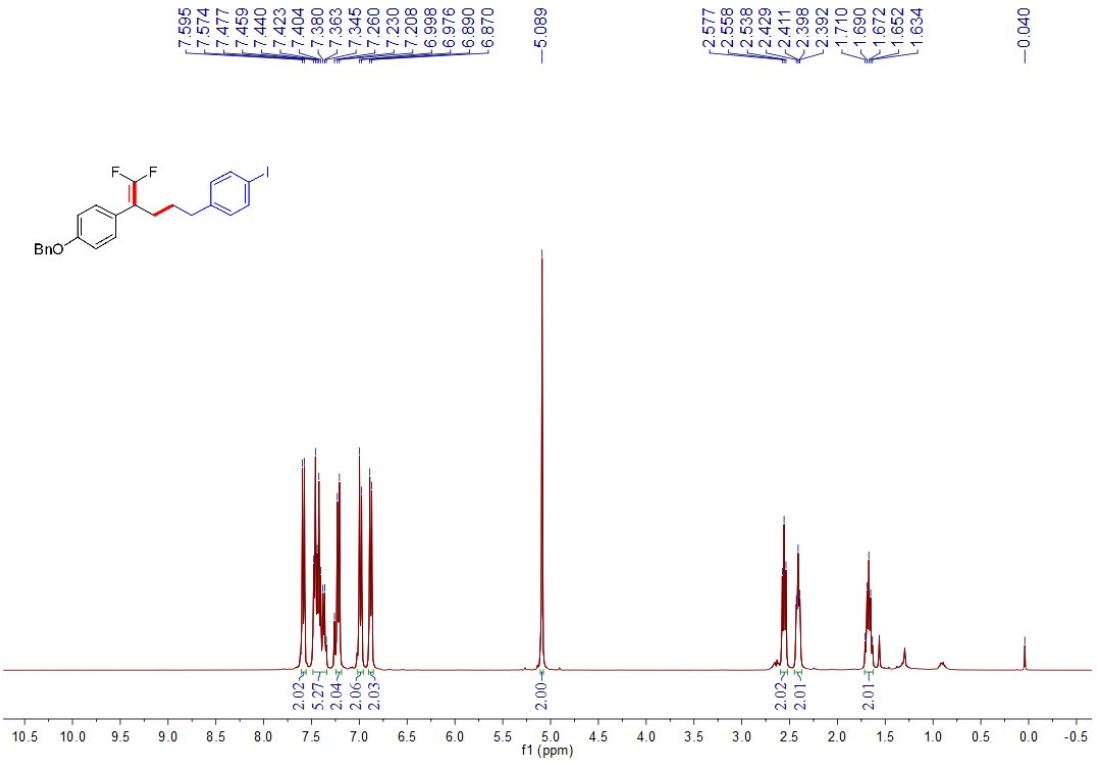
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3j**



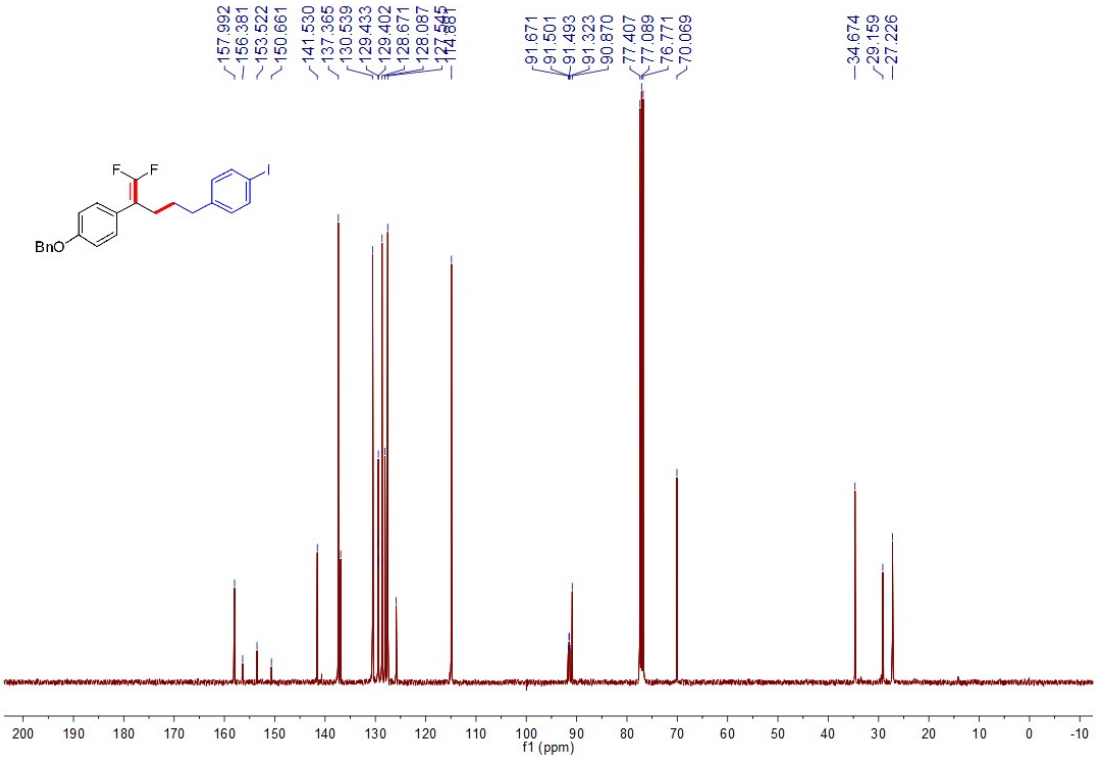
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3j**



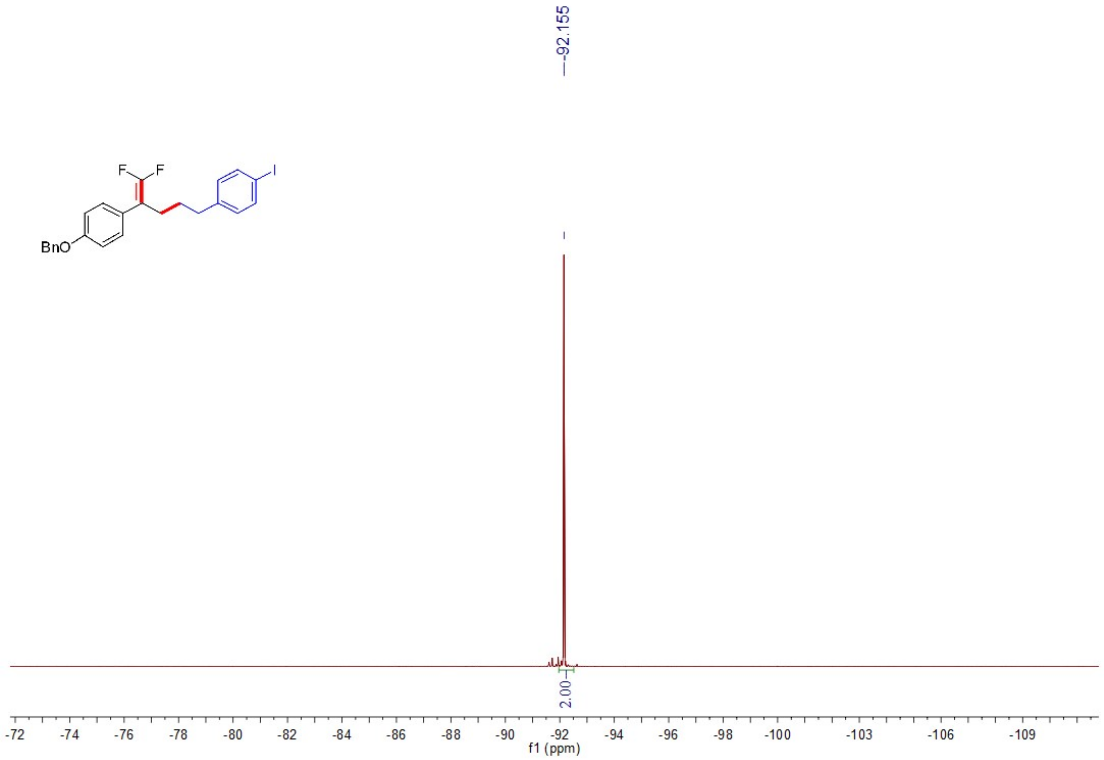
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3k**



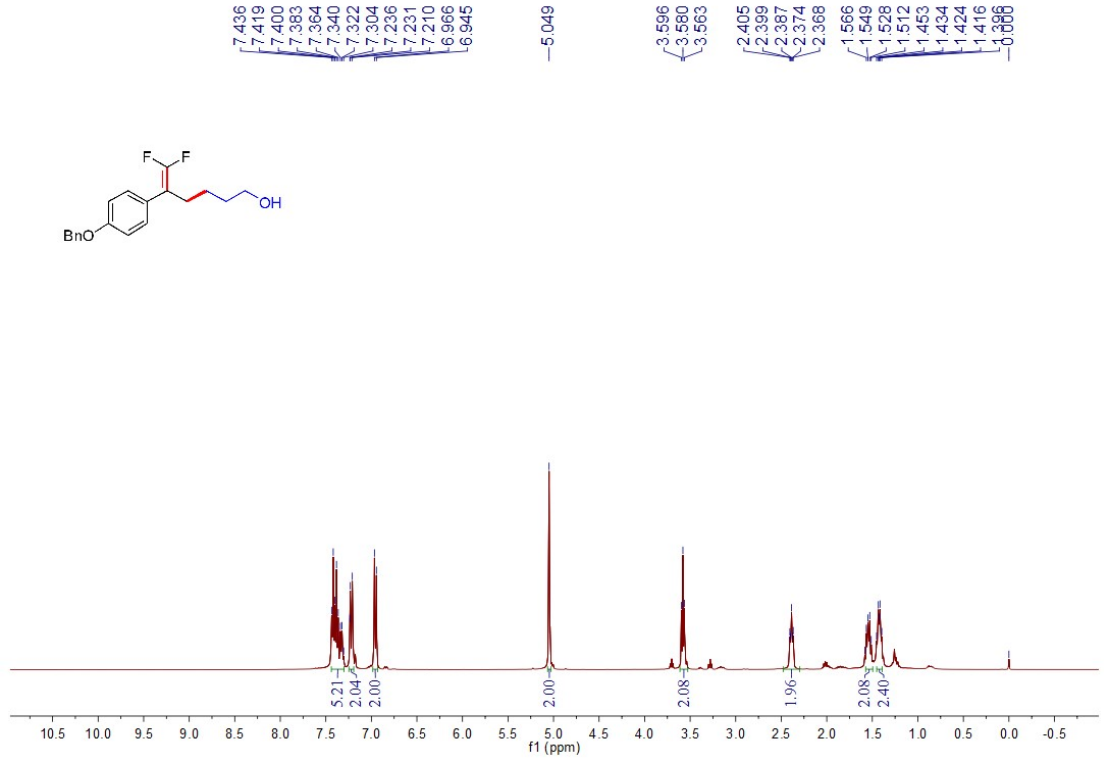
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3k**



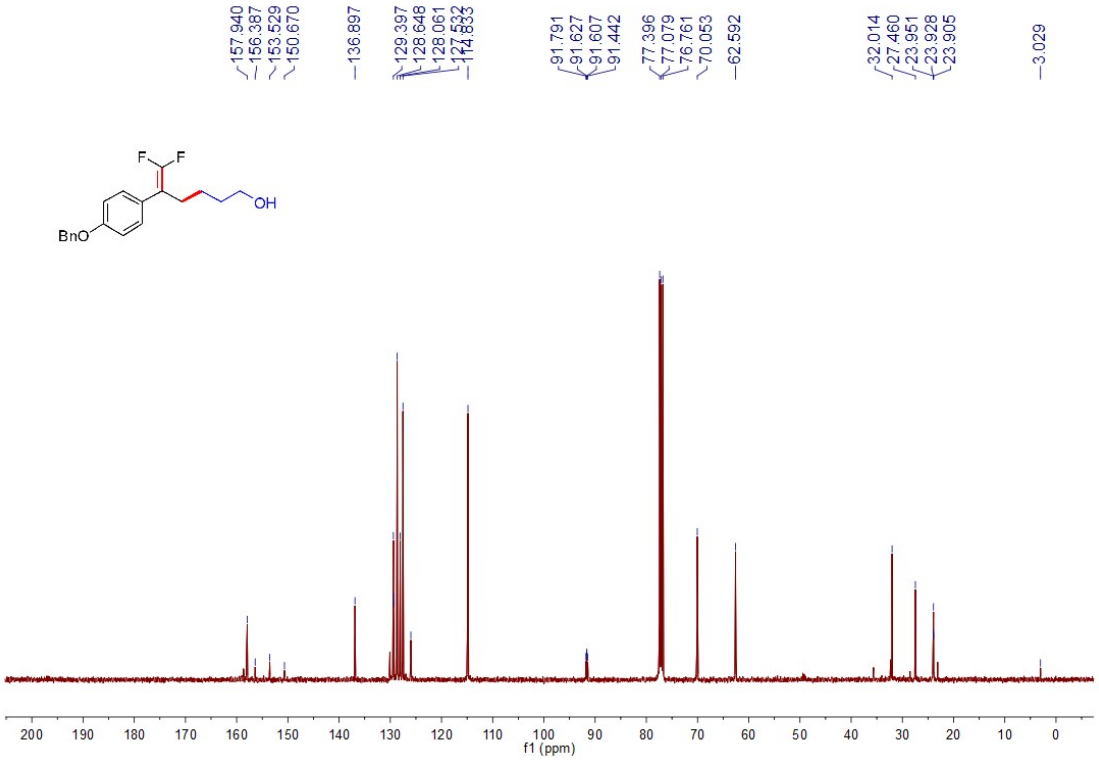
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3k**



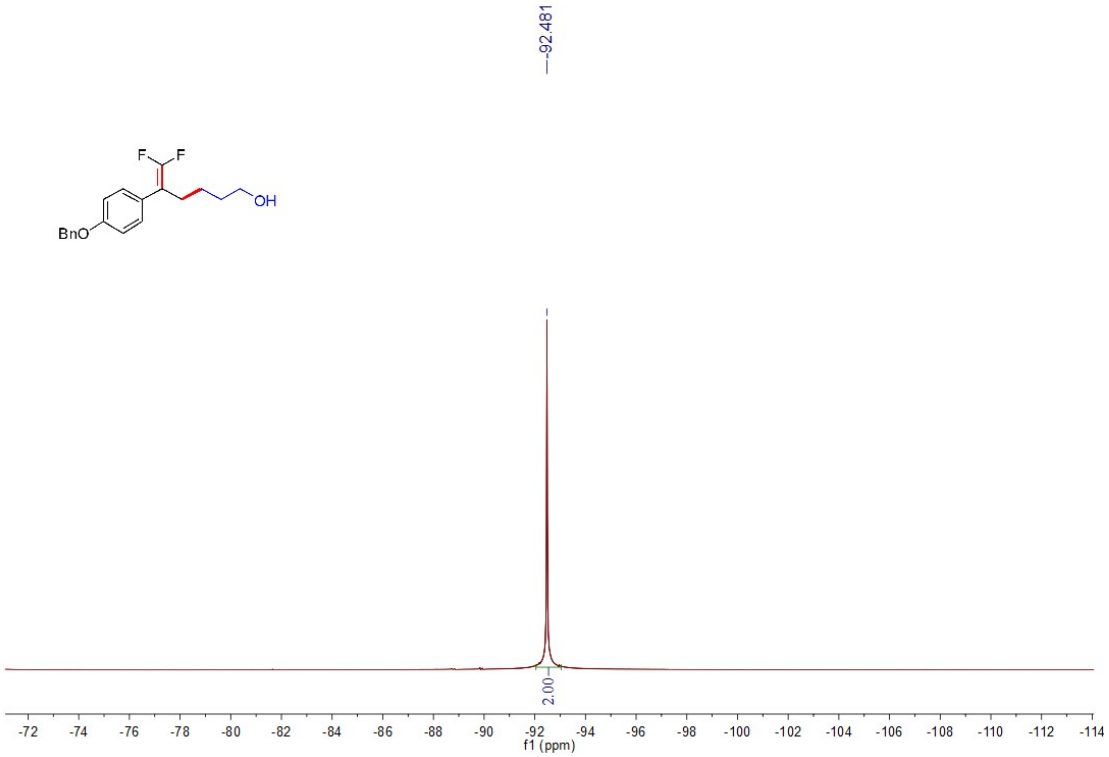
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3l**



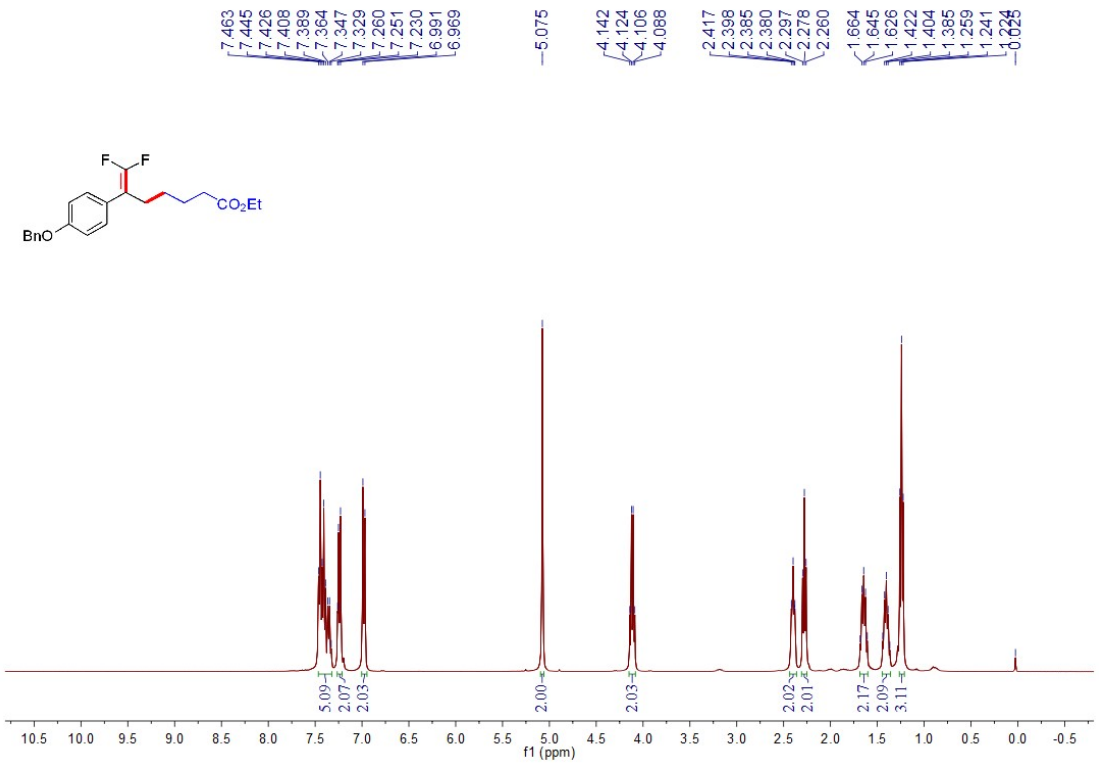
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3l**



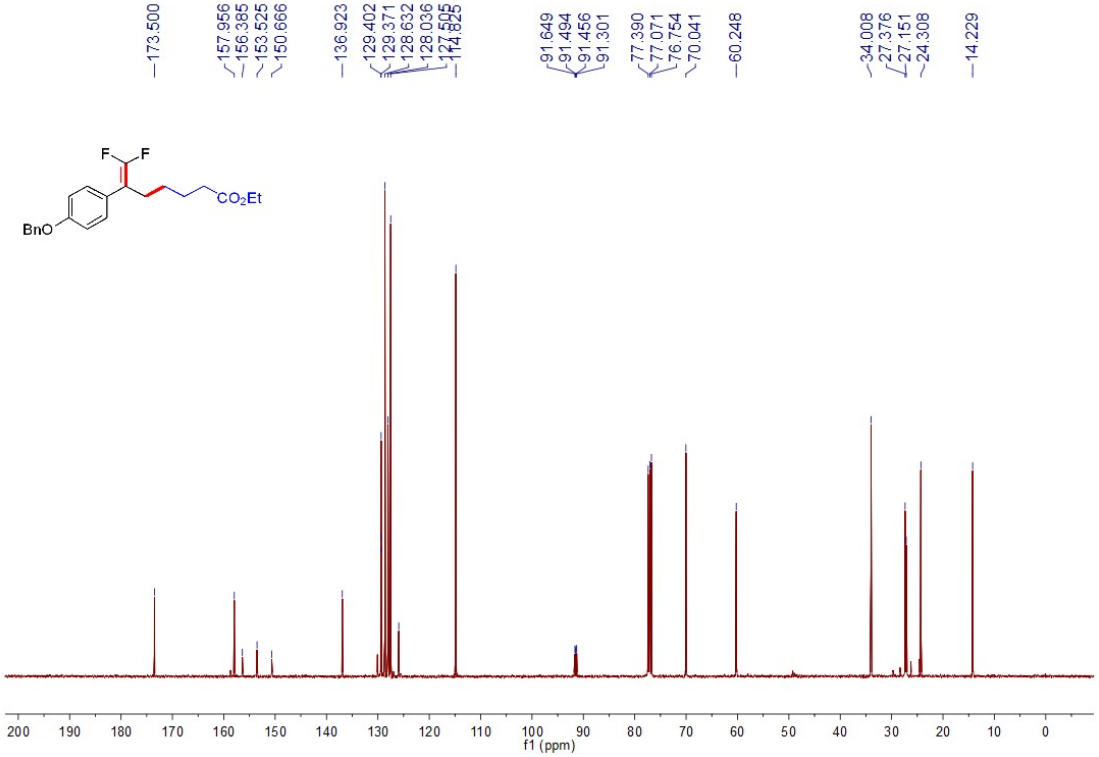
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3l**



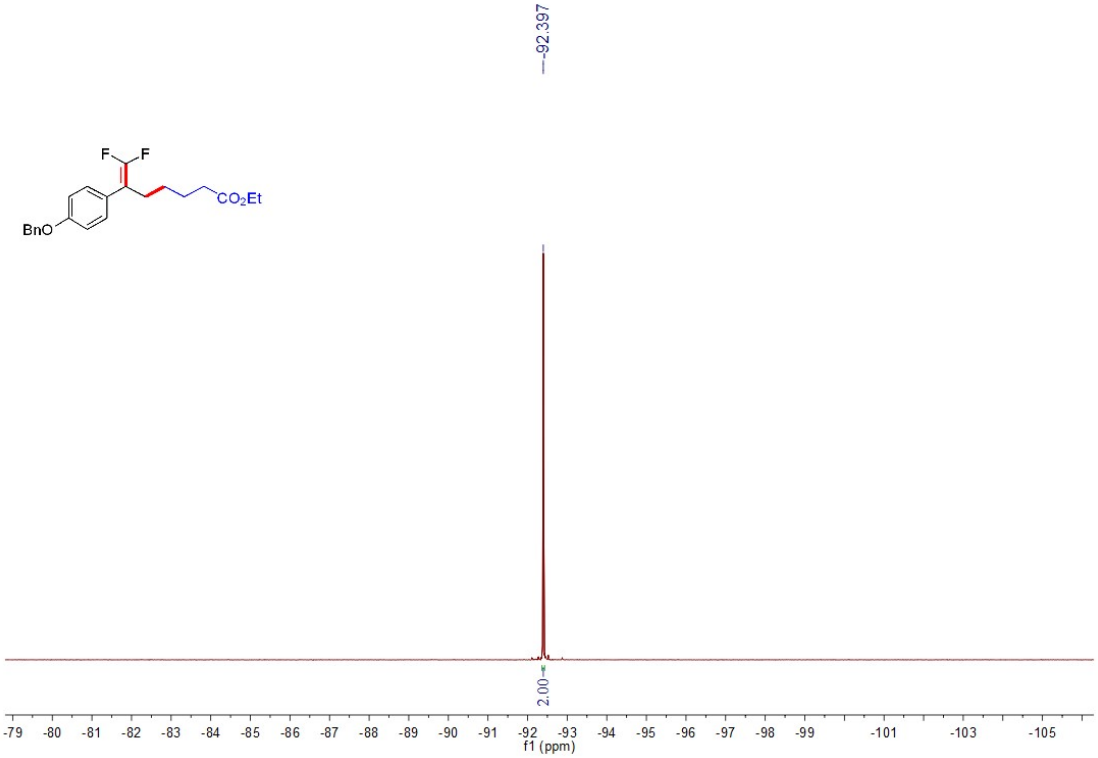
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3m**



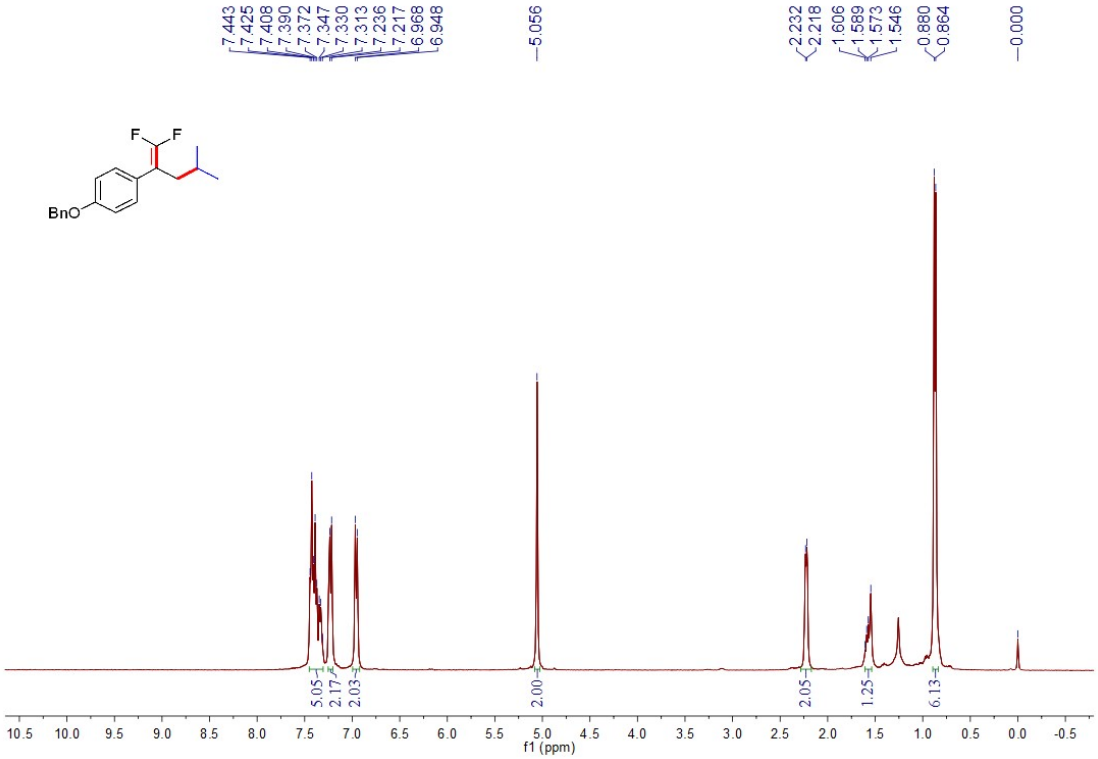
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3m**



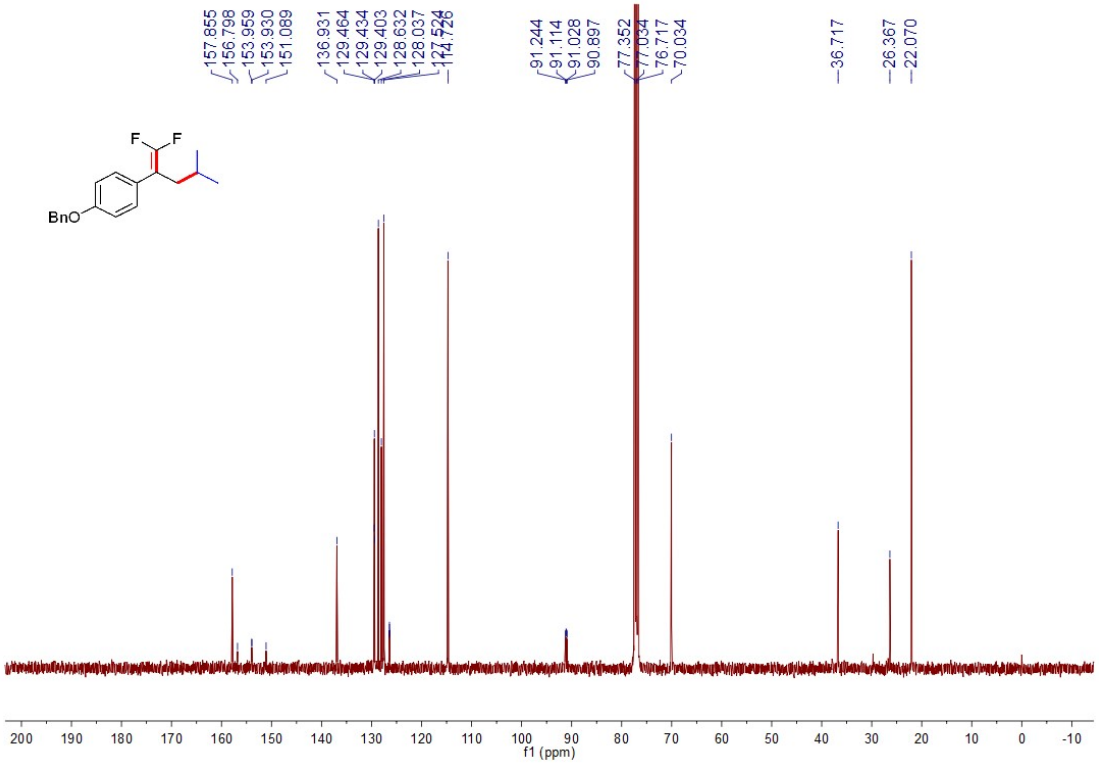
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3m**



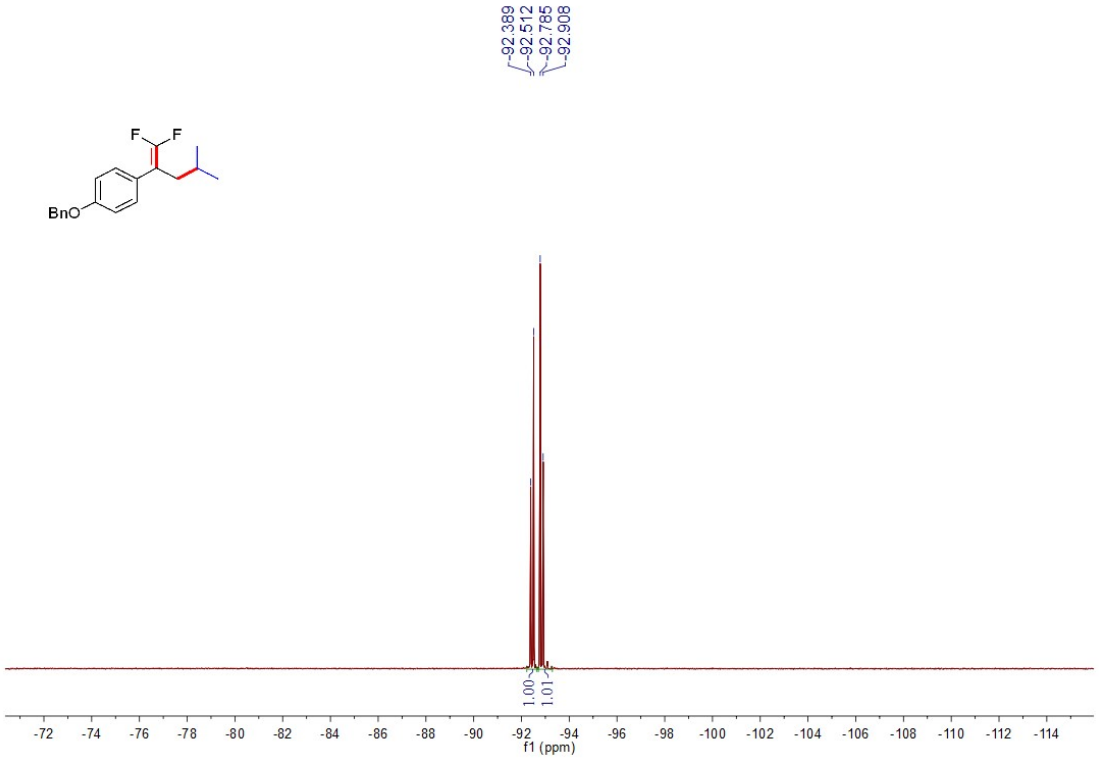
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3n**



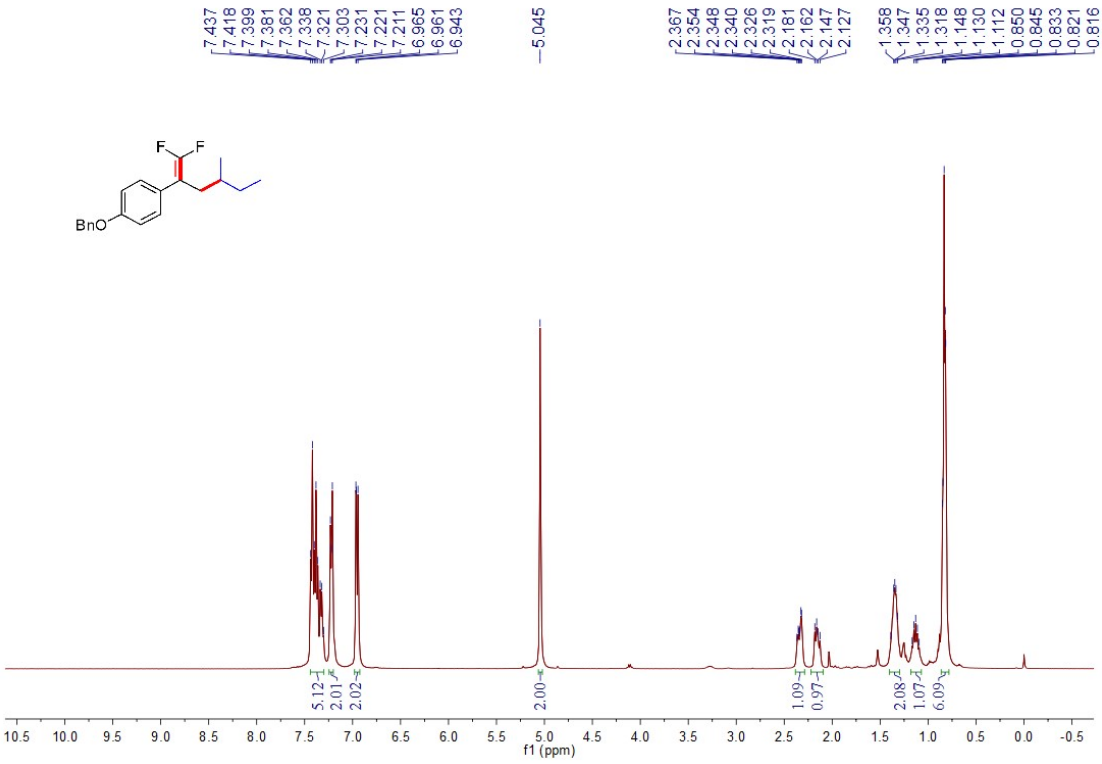
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3n**



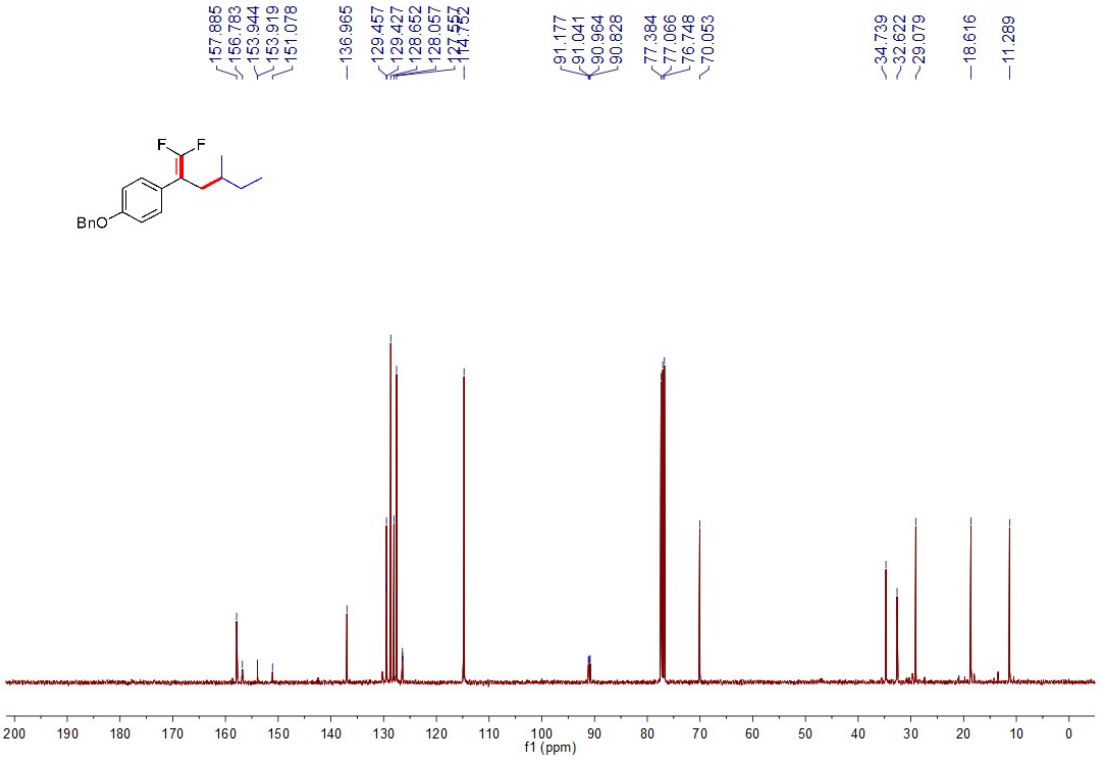
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3n**



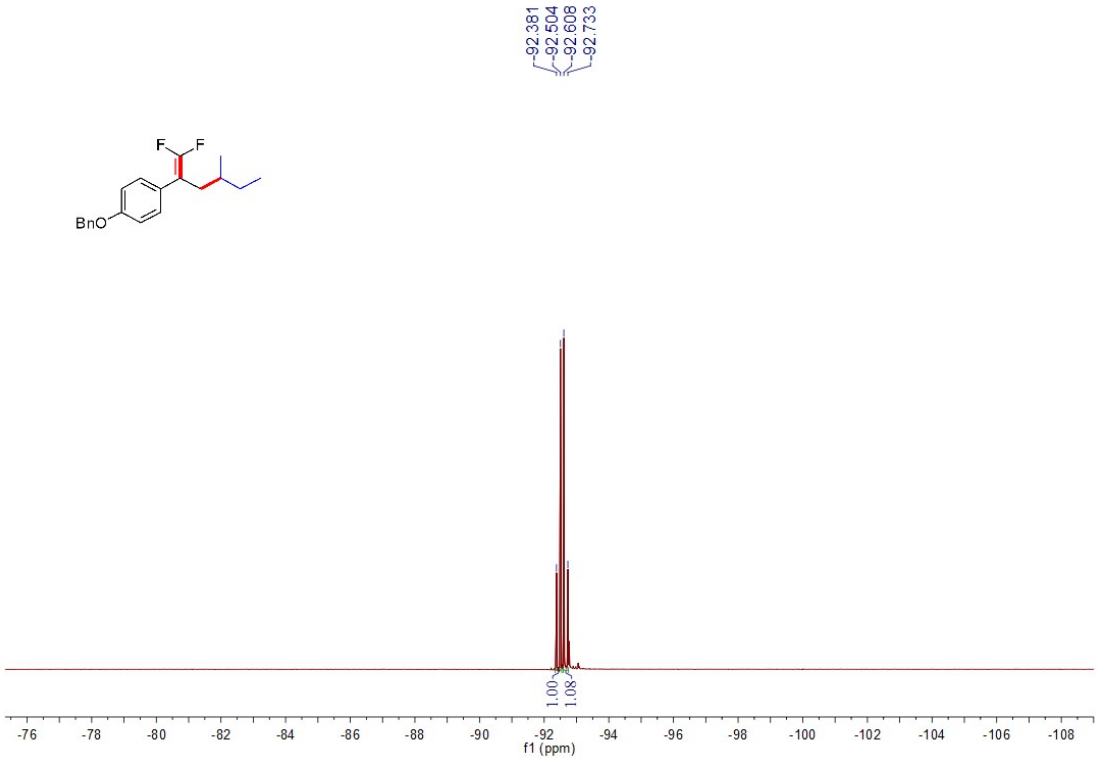
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3o**



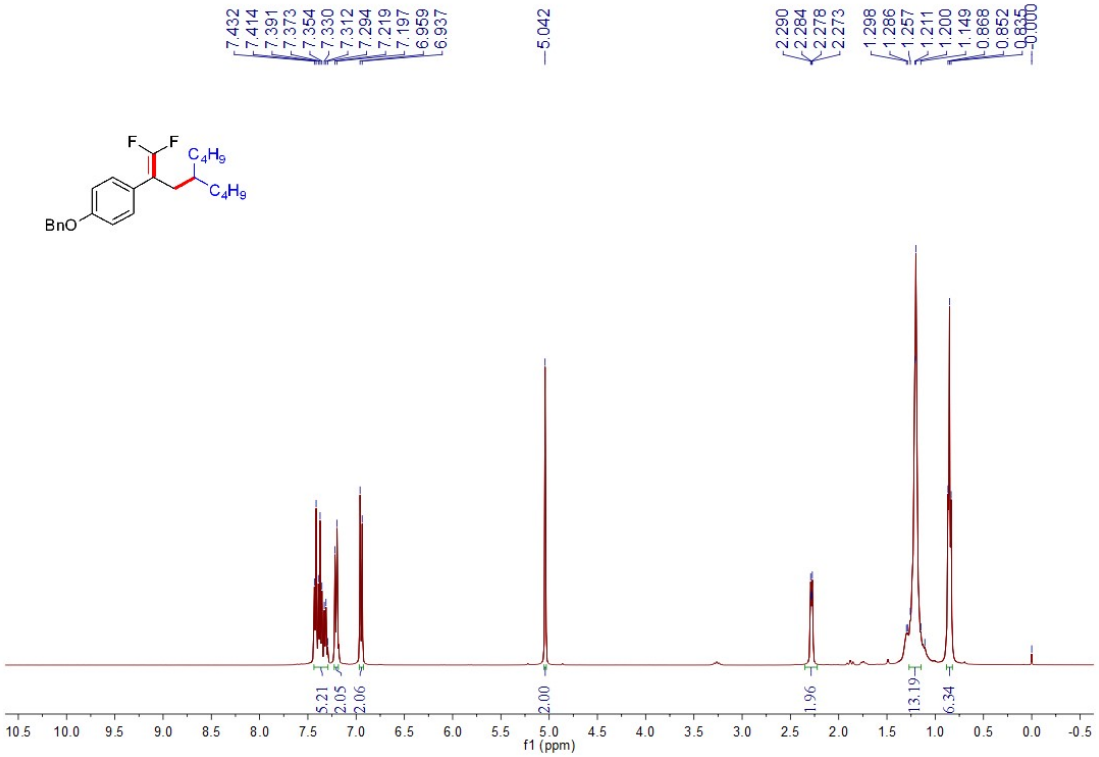
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3o**



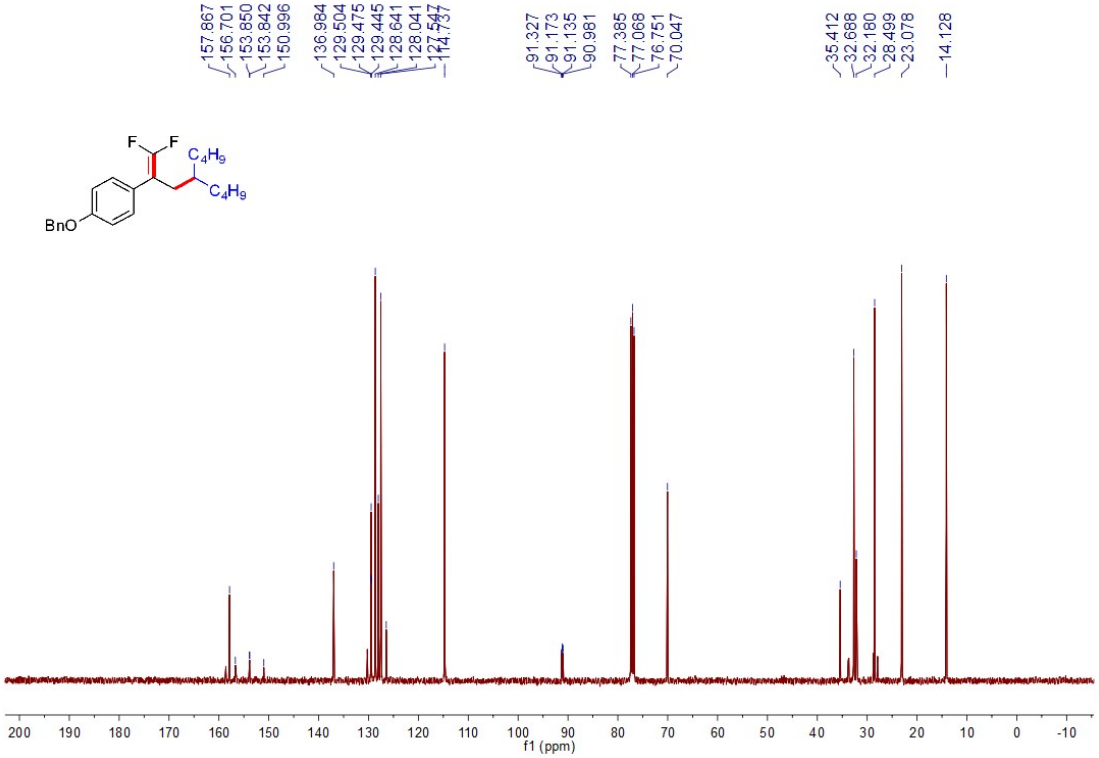
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3o**



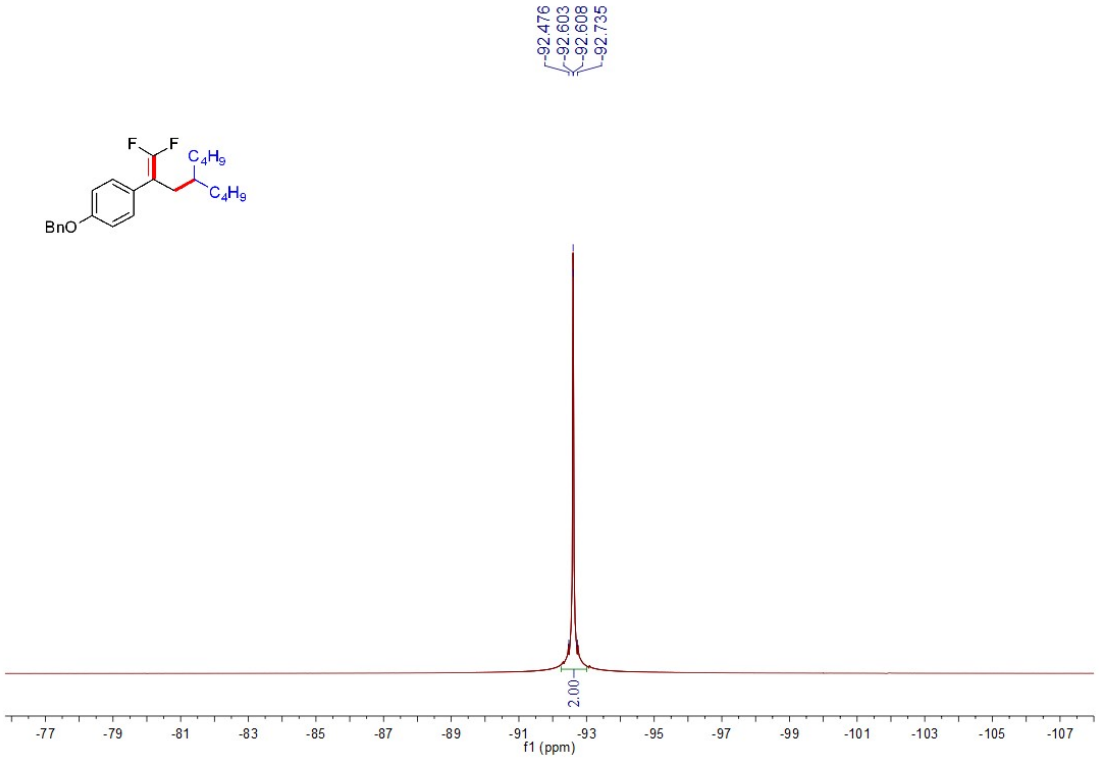
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3p**



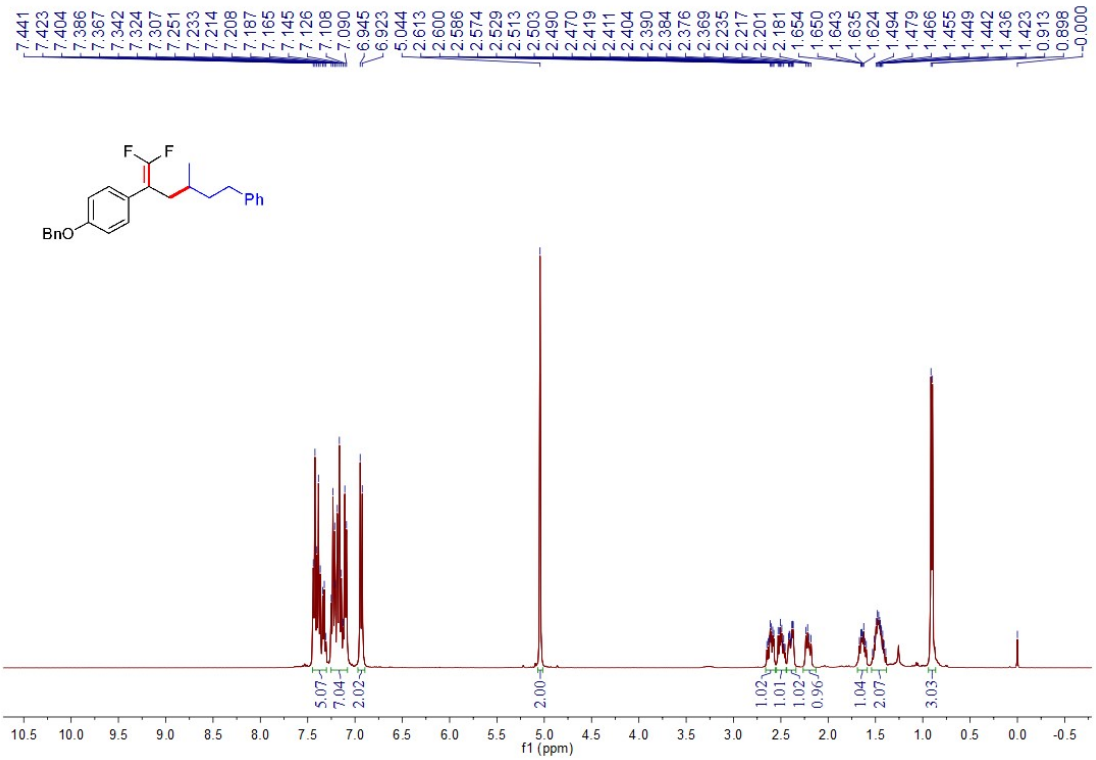
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3p**



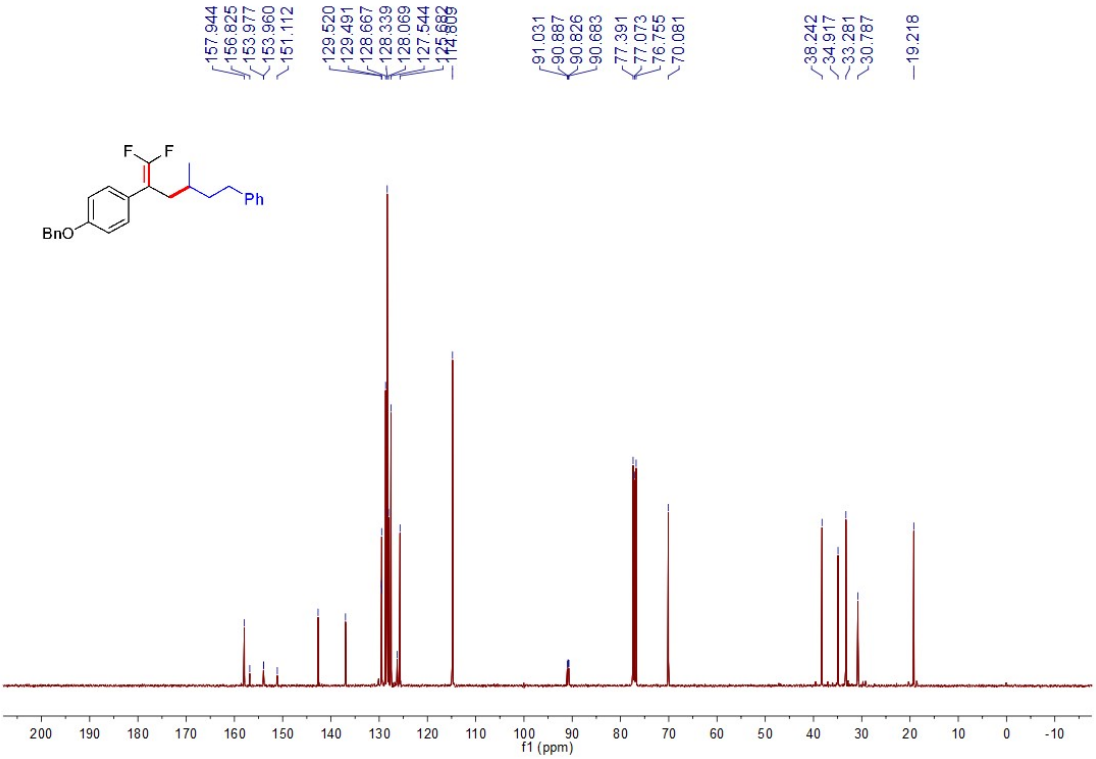
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3p**



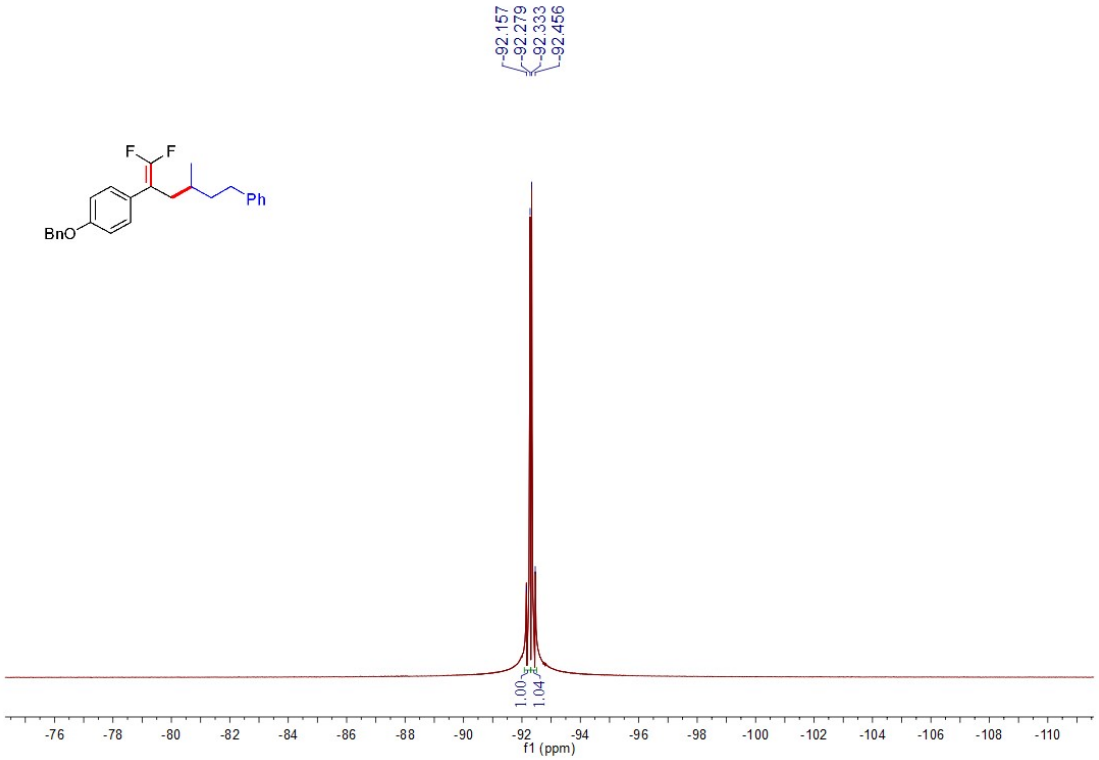
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3q**



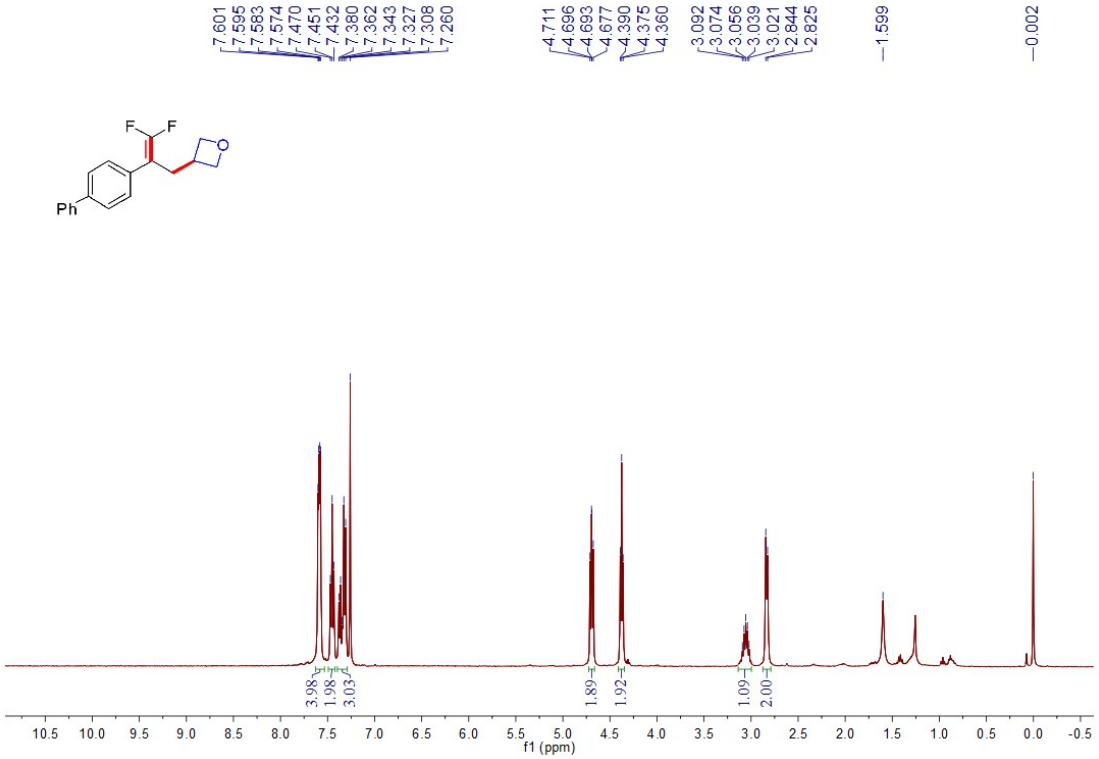
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3q**



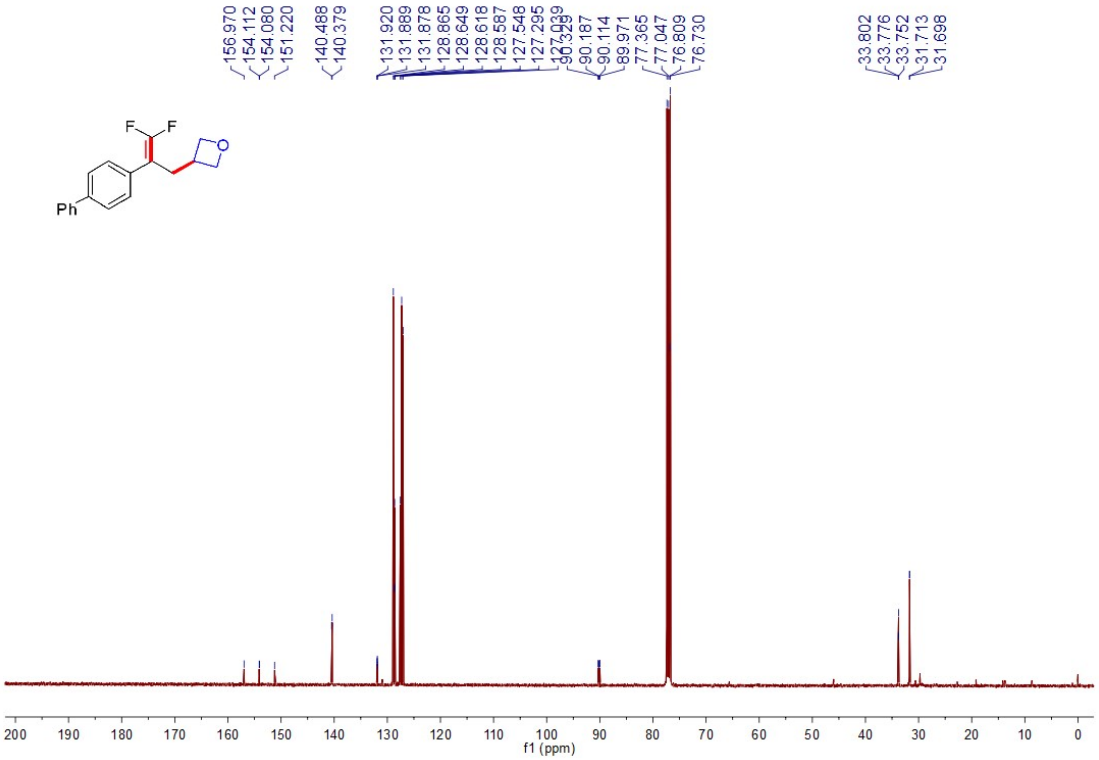
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3q**



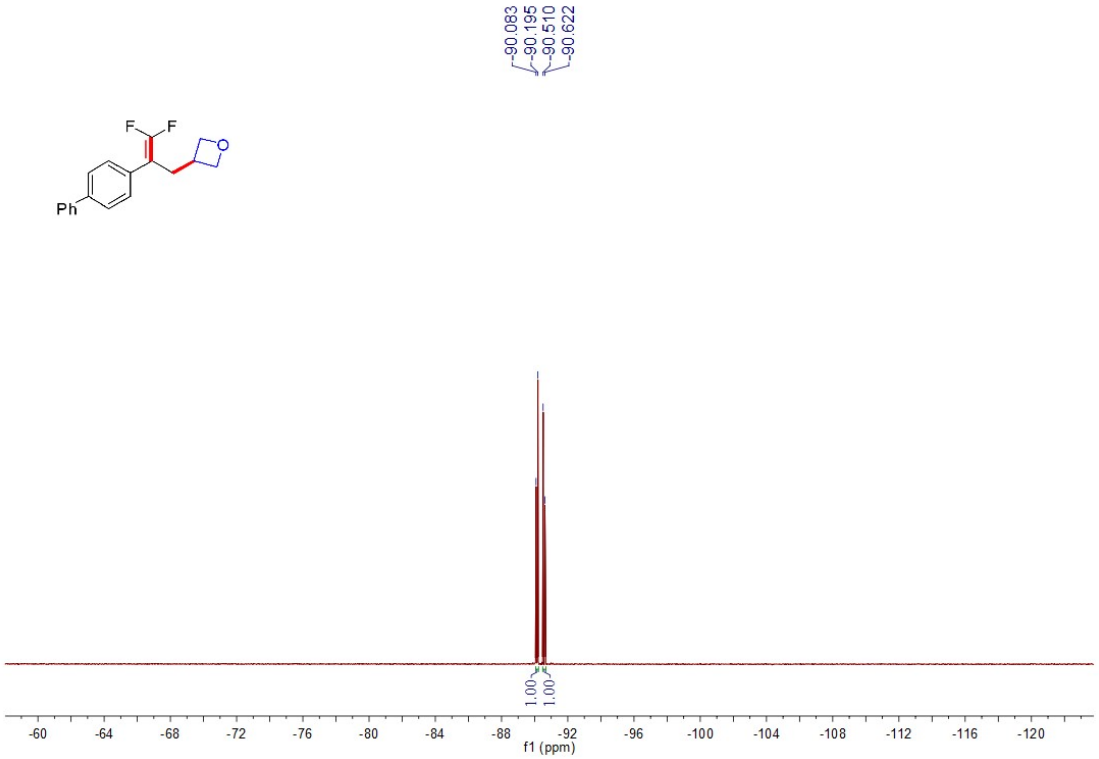
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3r**



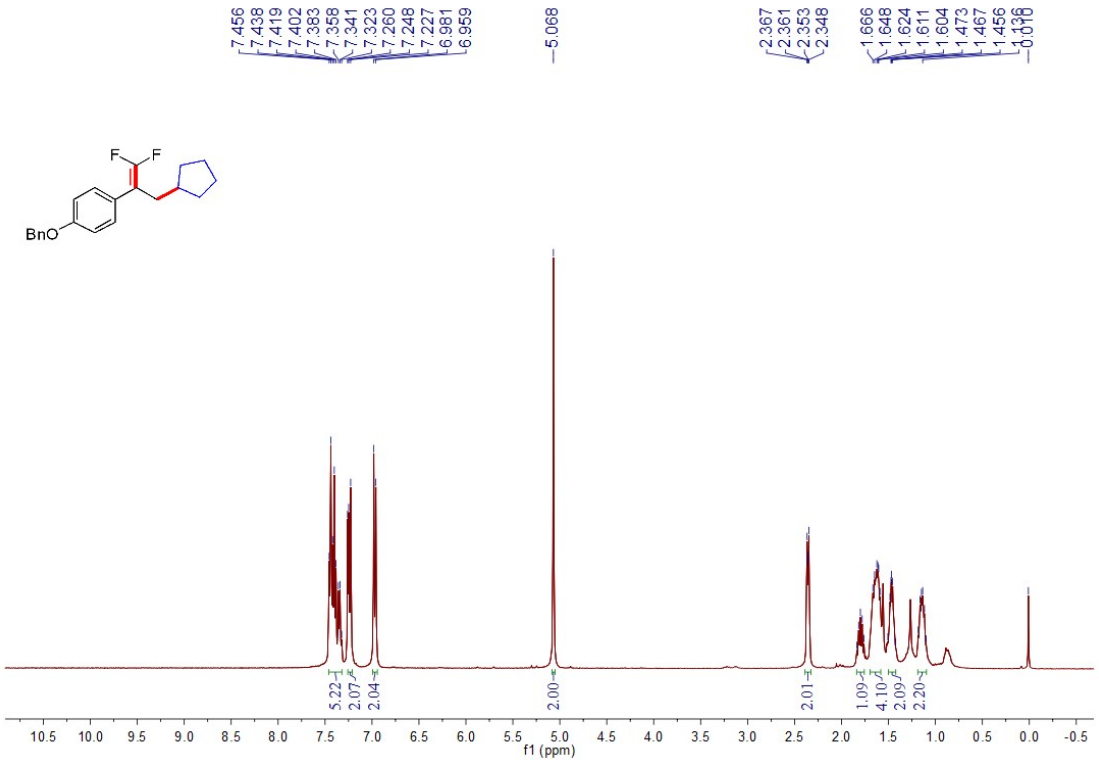
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3r**



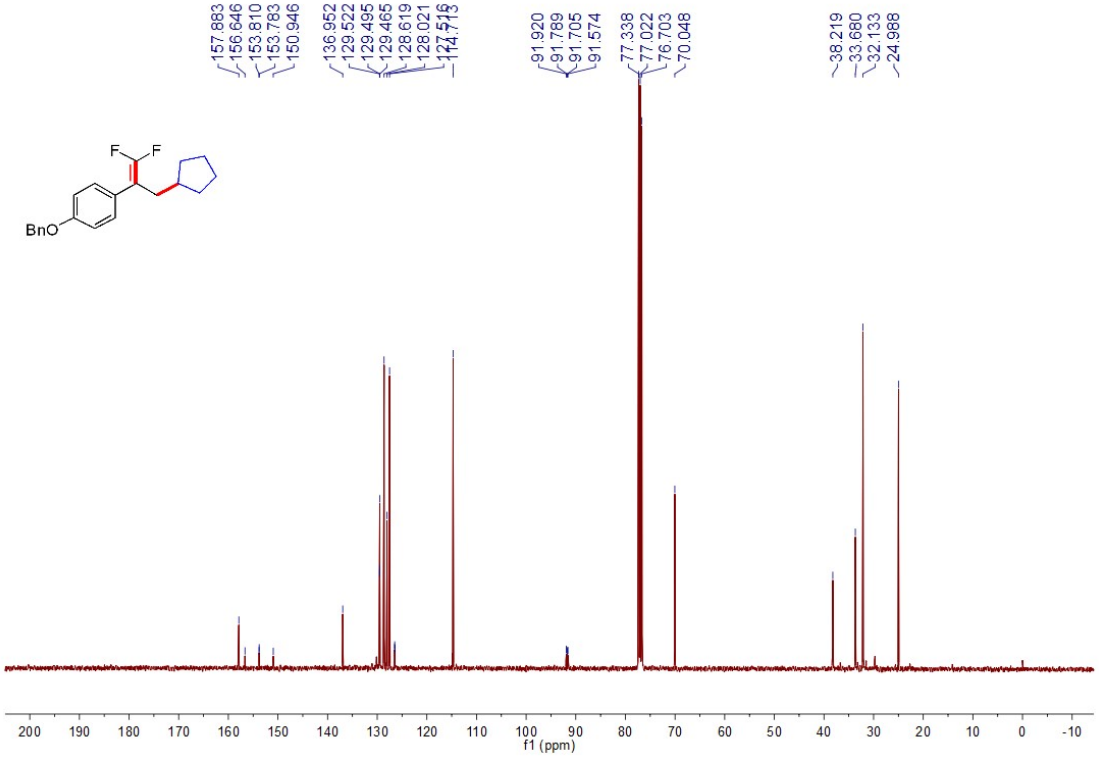
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3r**



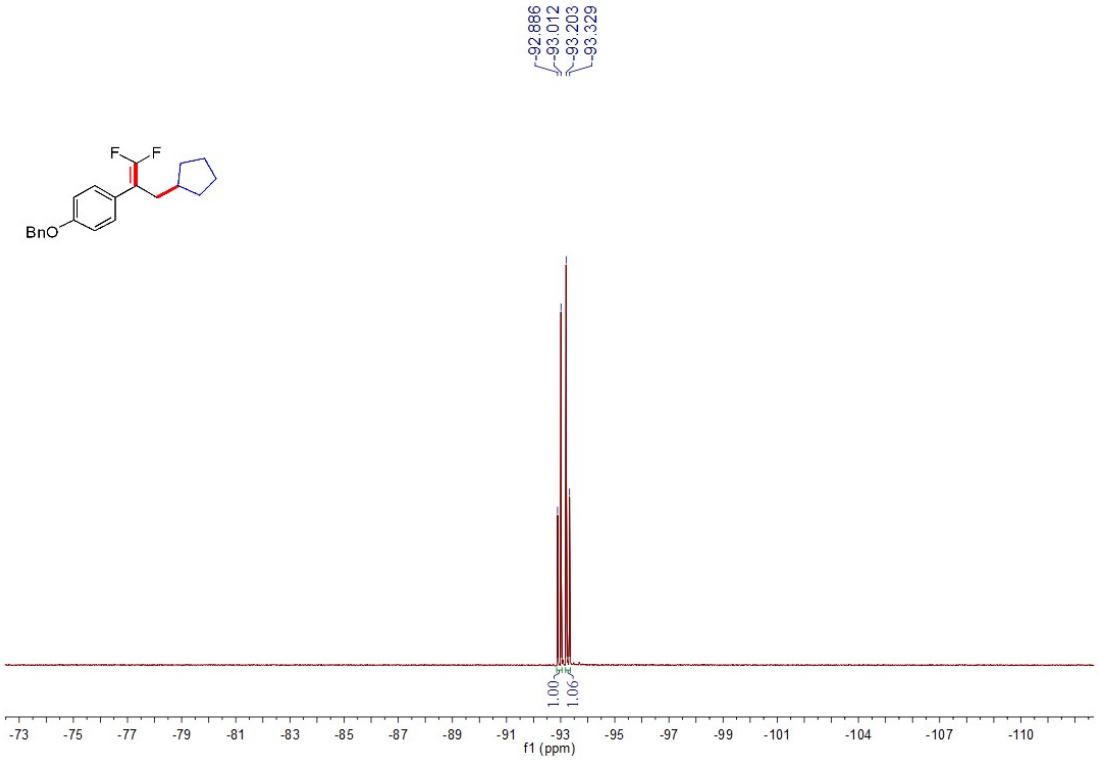
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3s**



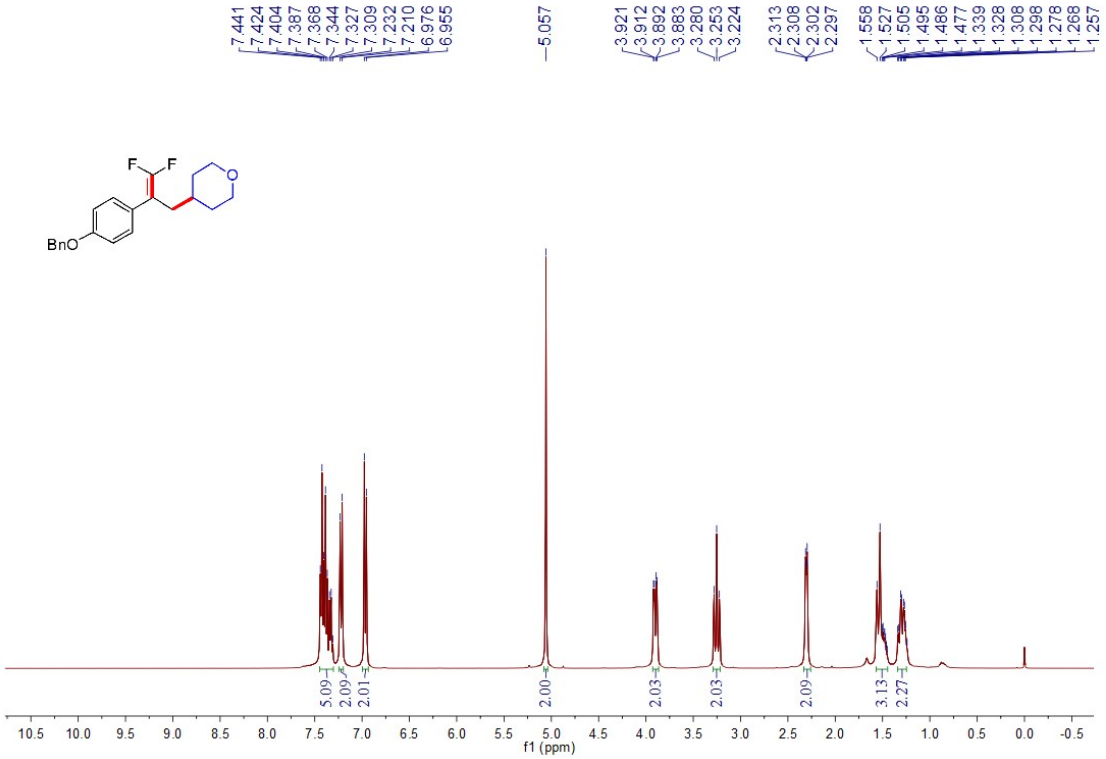
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3s**



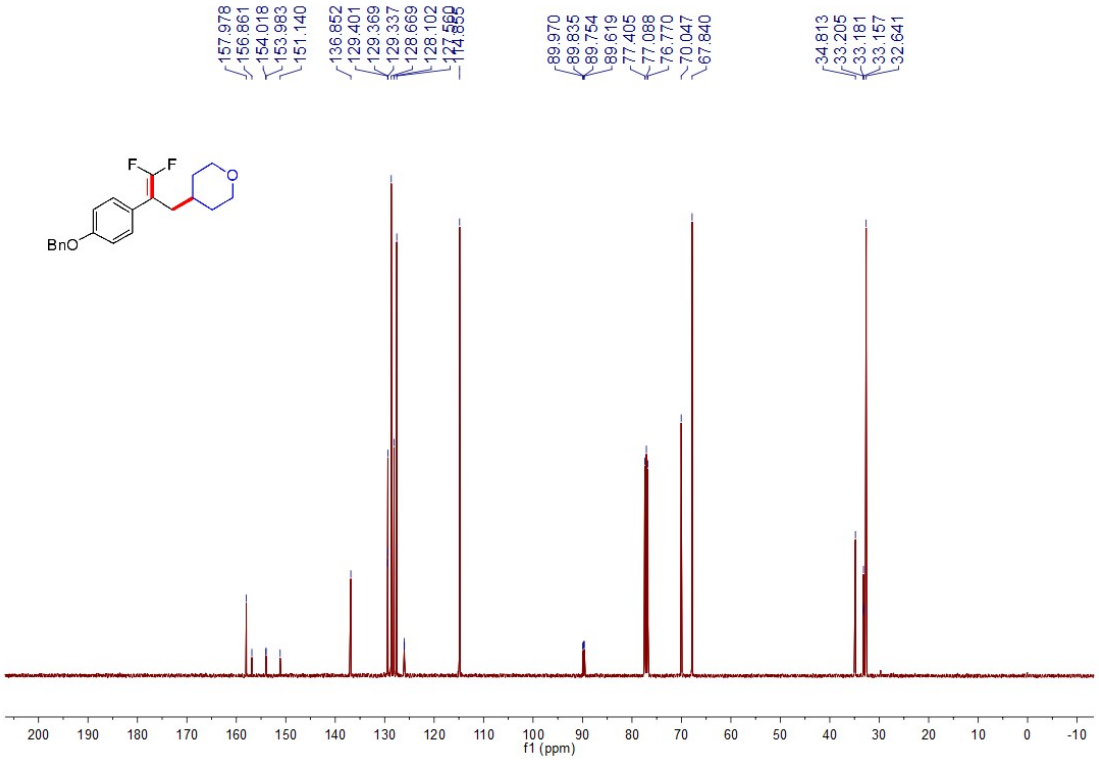
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3s**



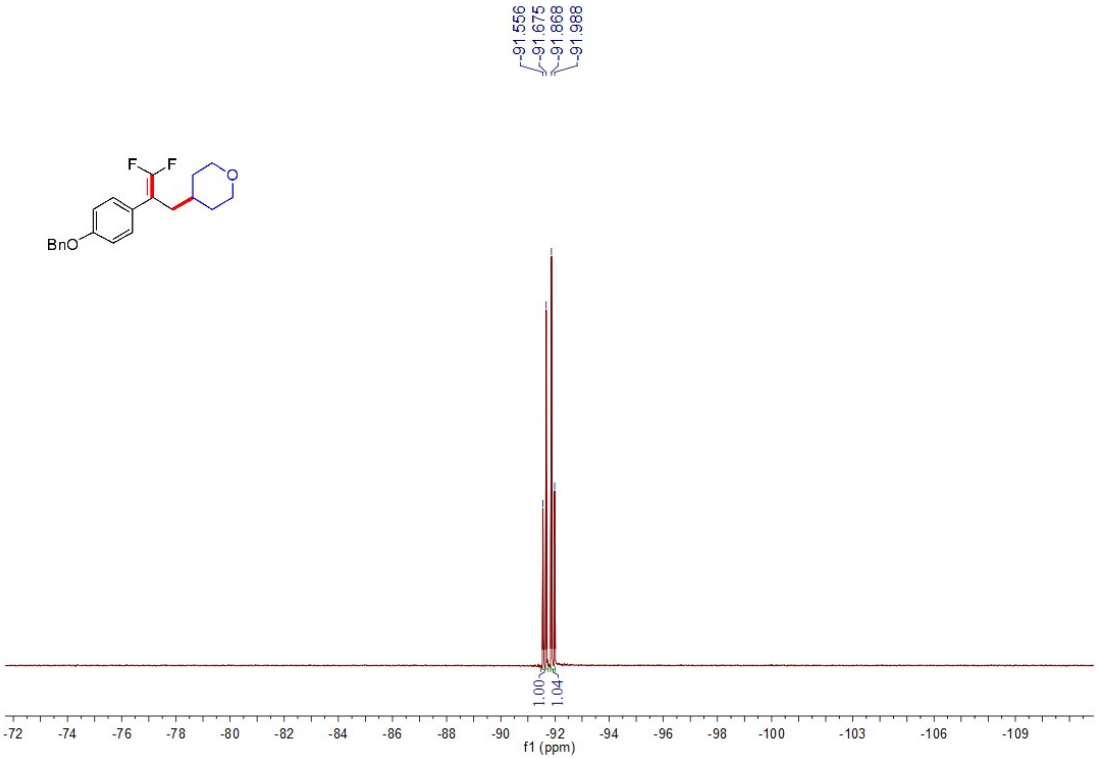
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3t**



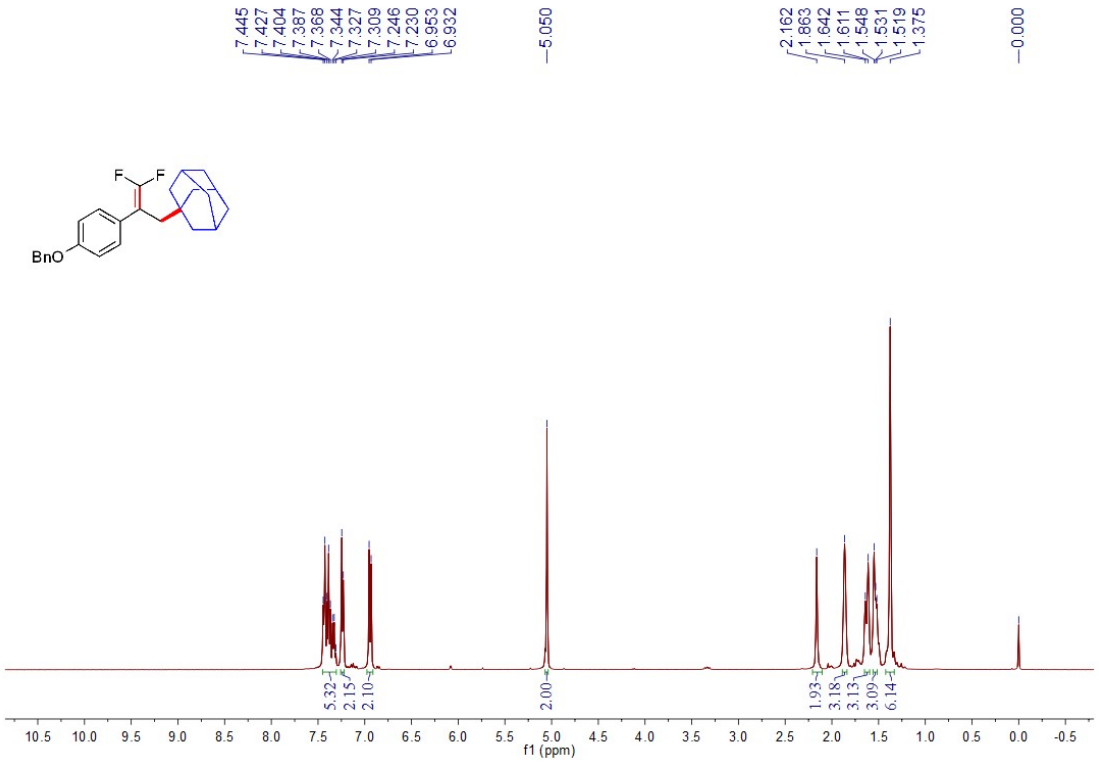
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3t**



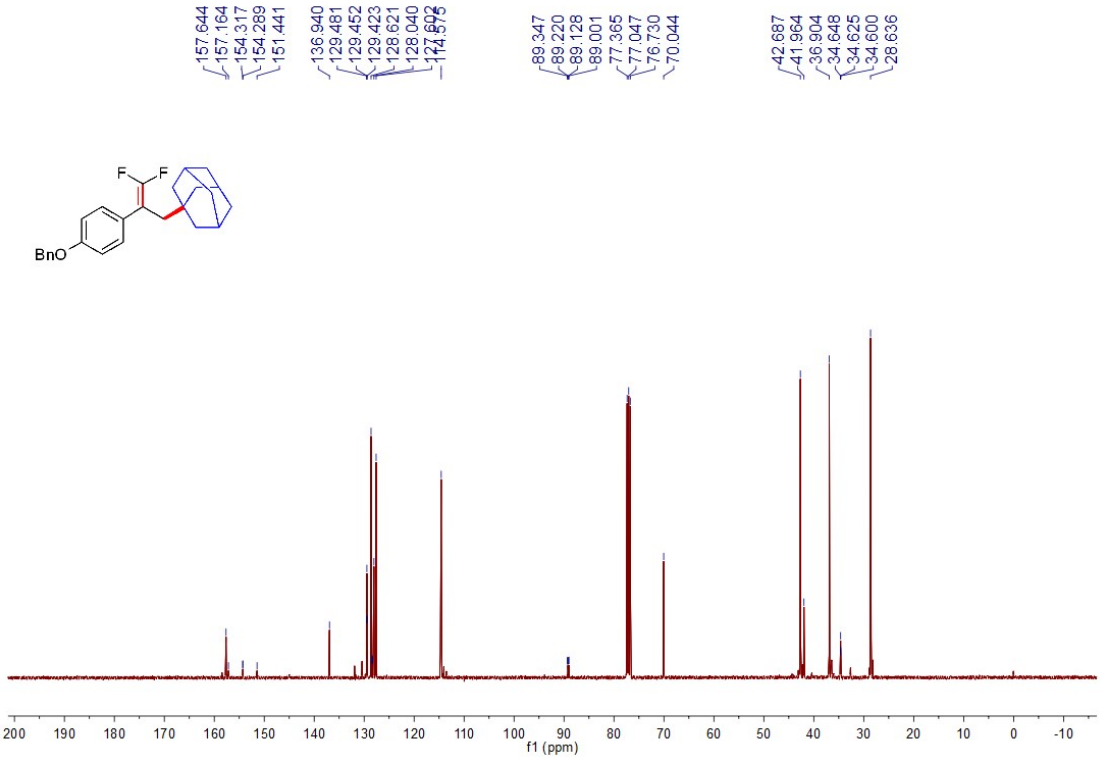
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3t**



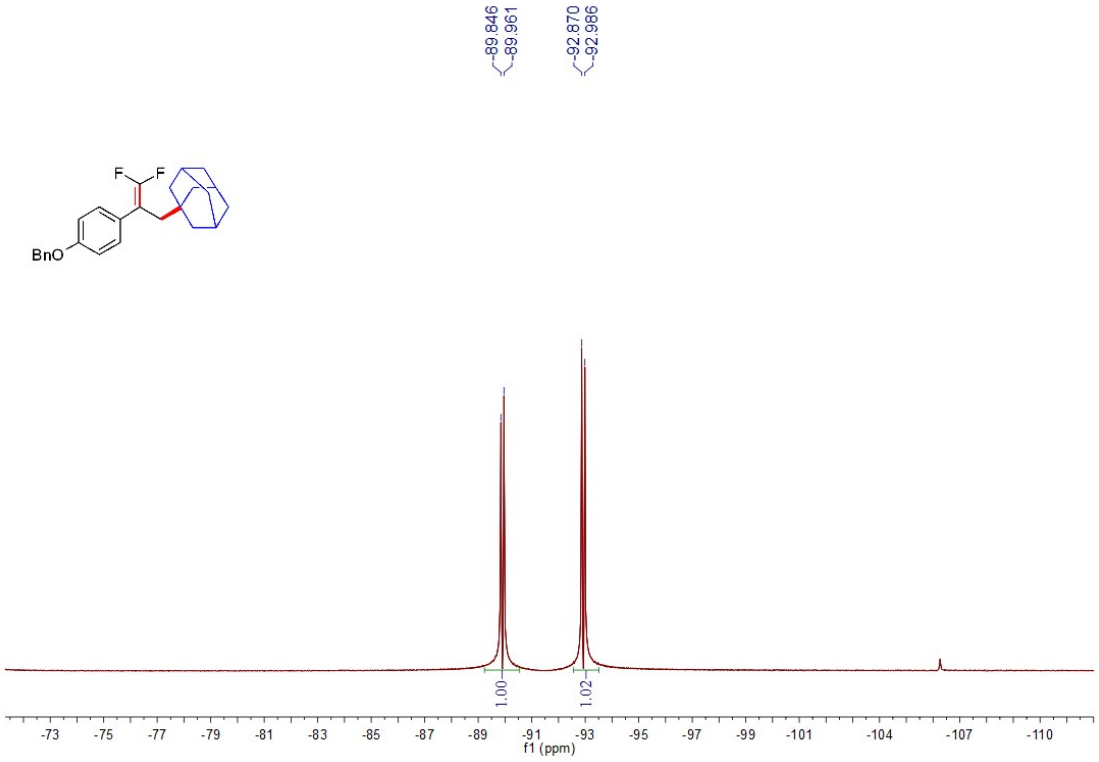
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3u**



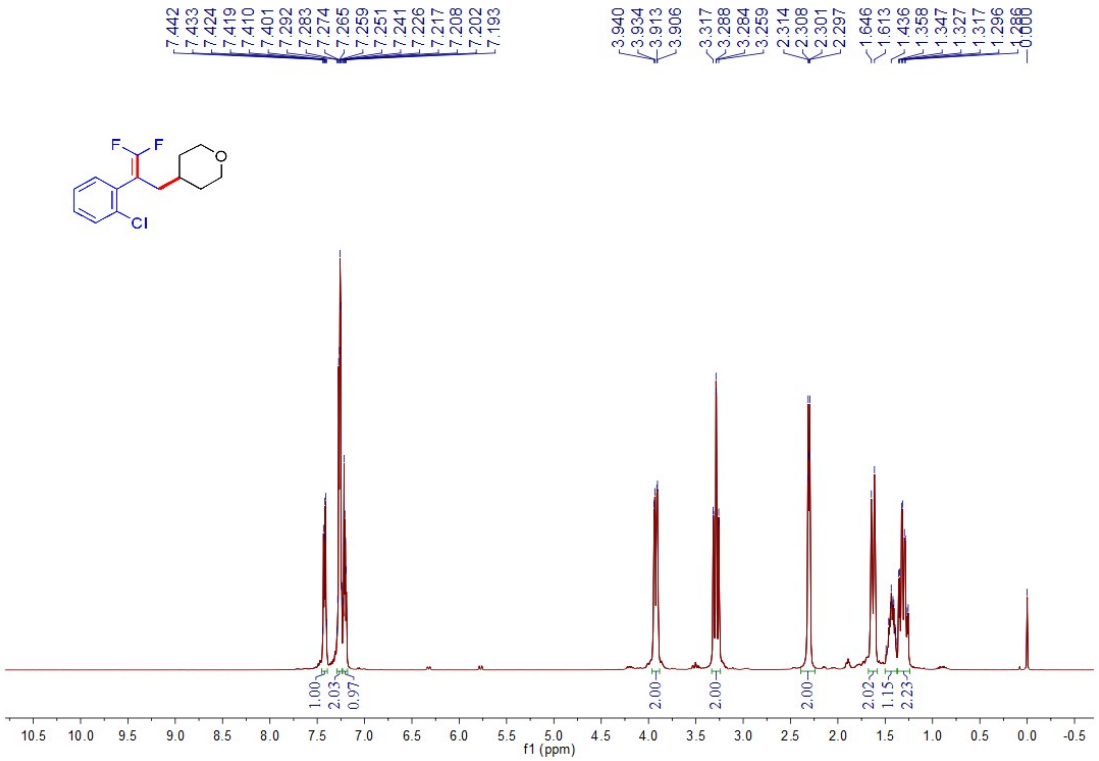
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3u**



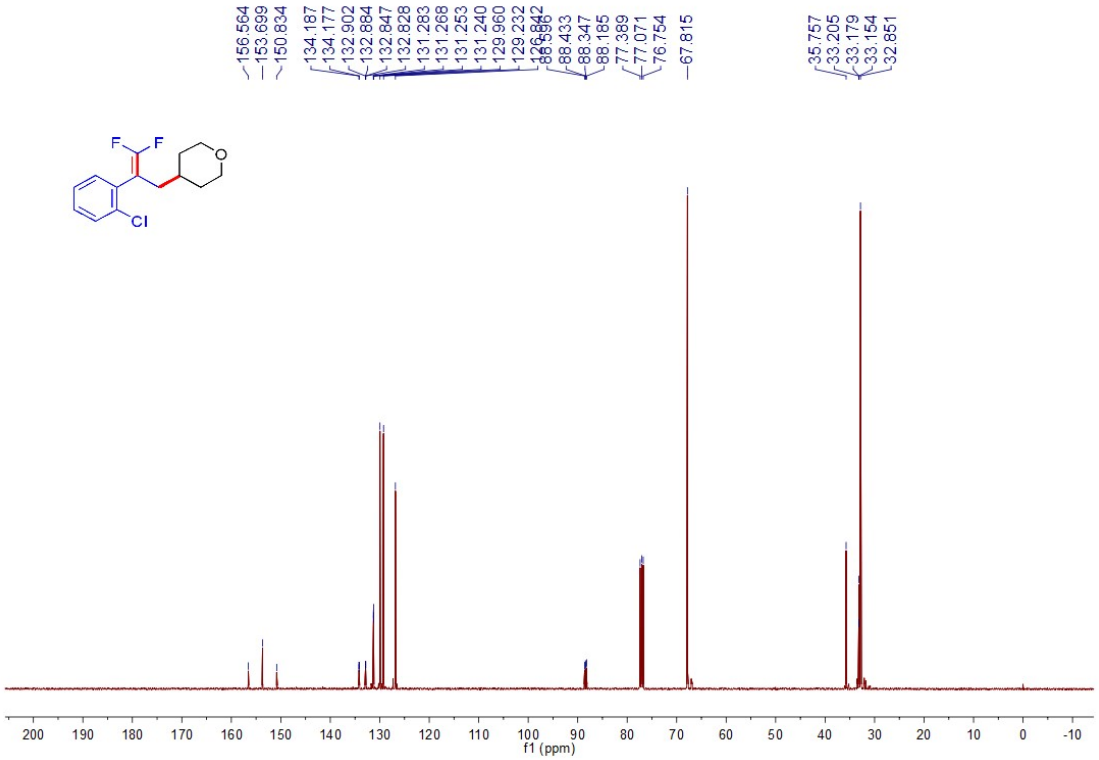
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3u**



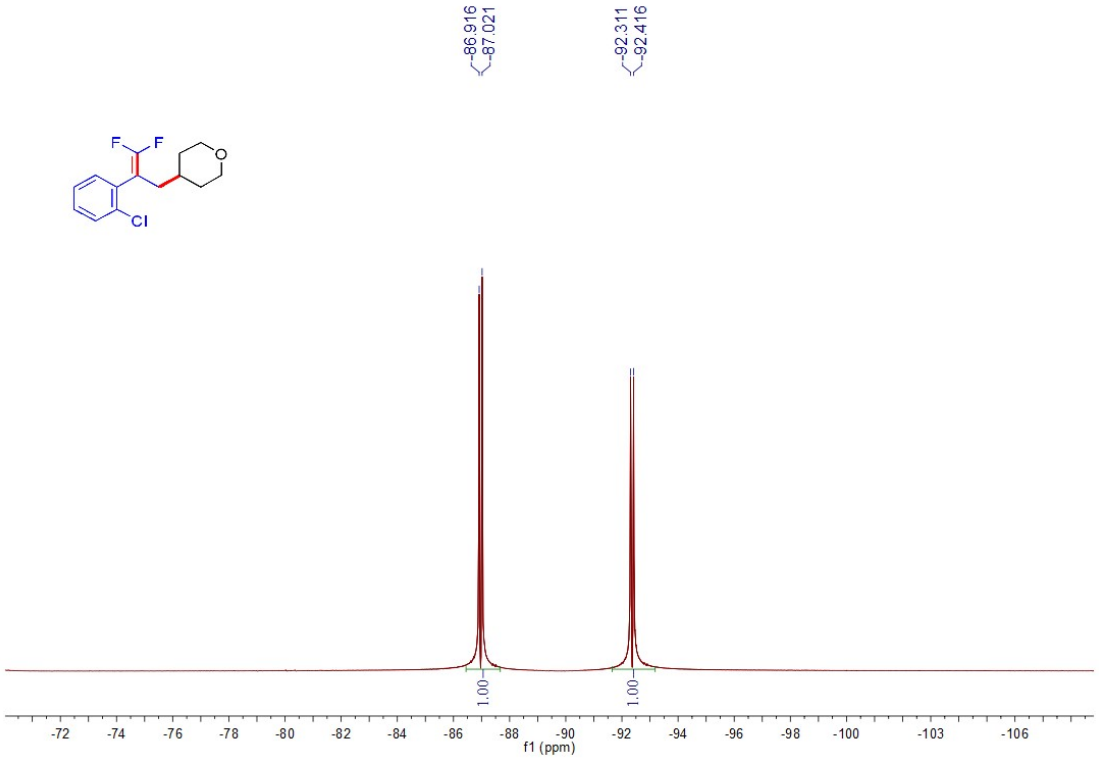
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4b**



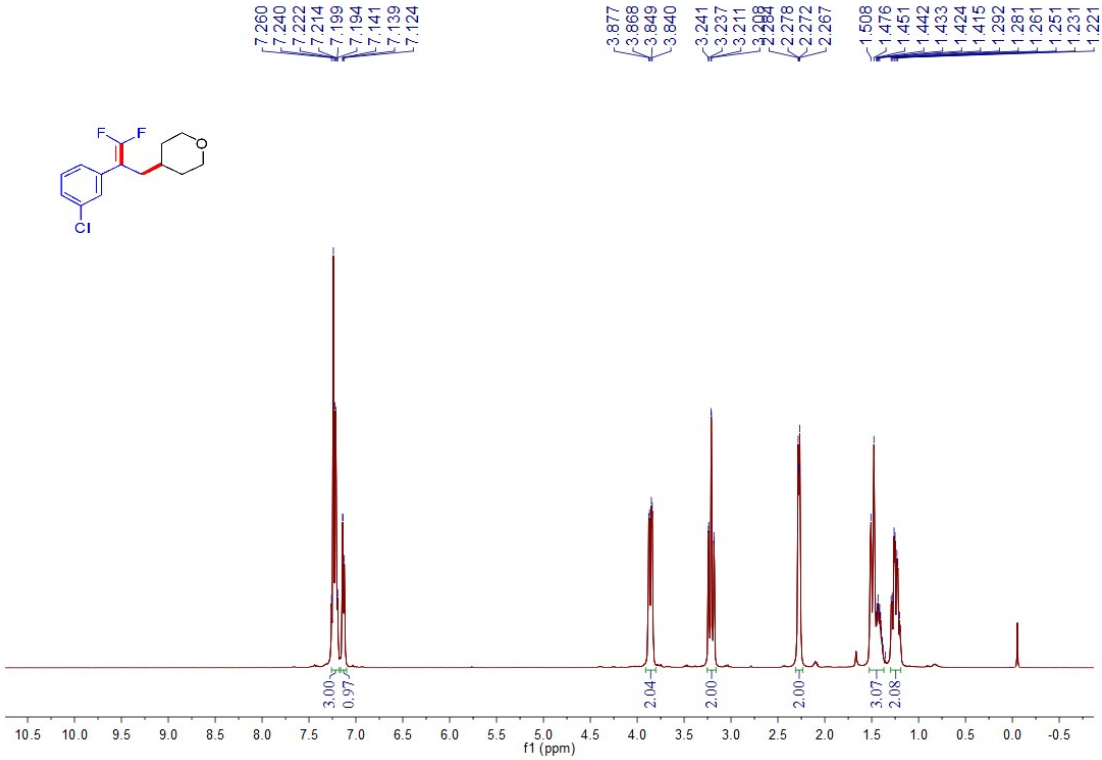
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4b**



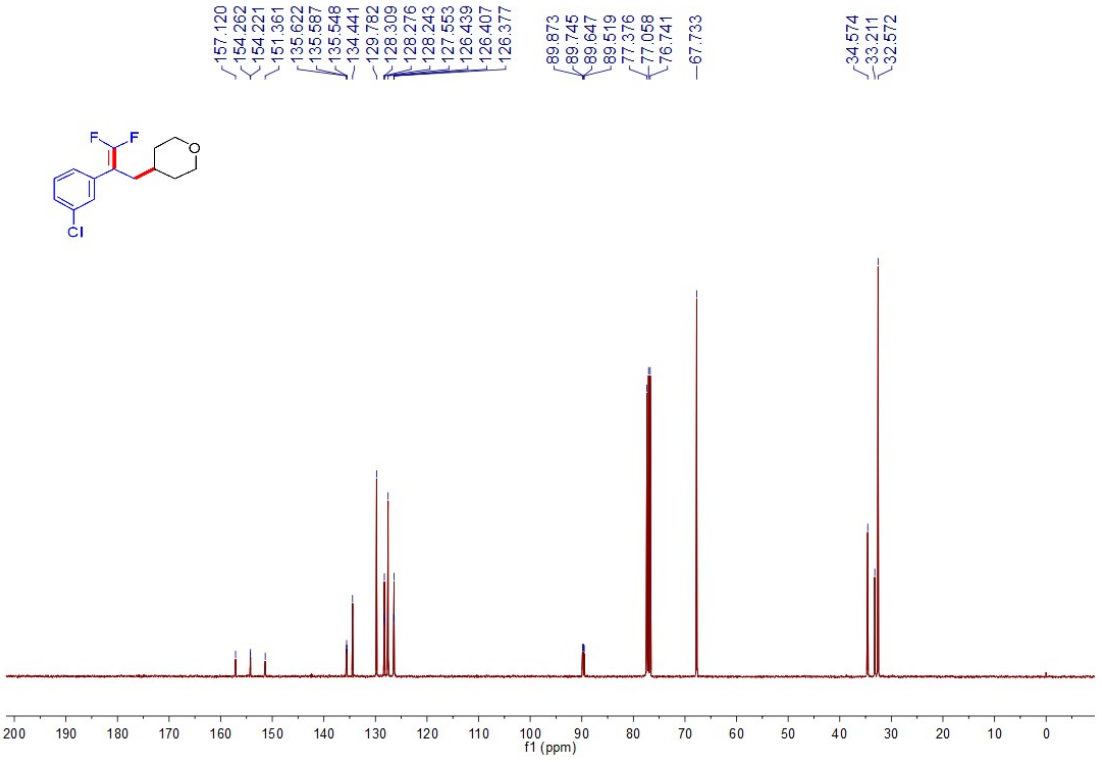
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4b**



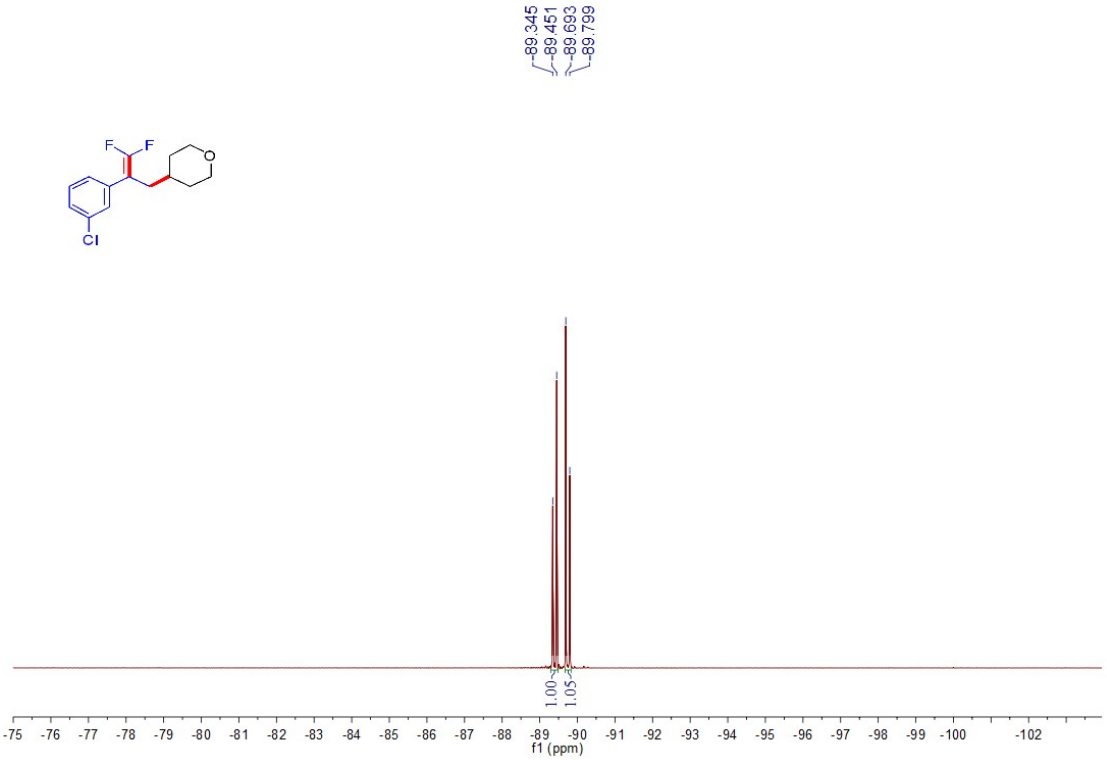
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**



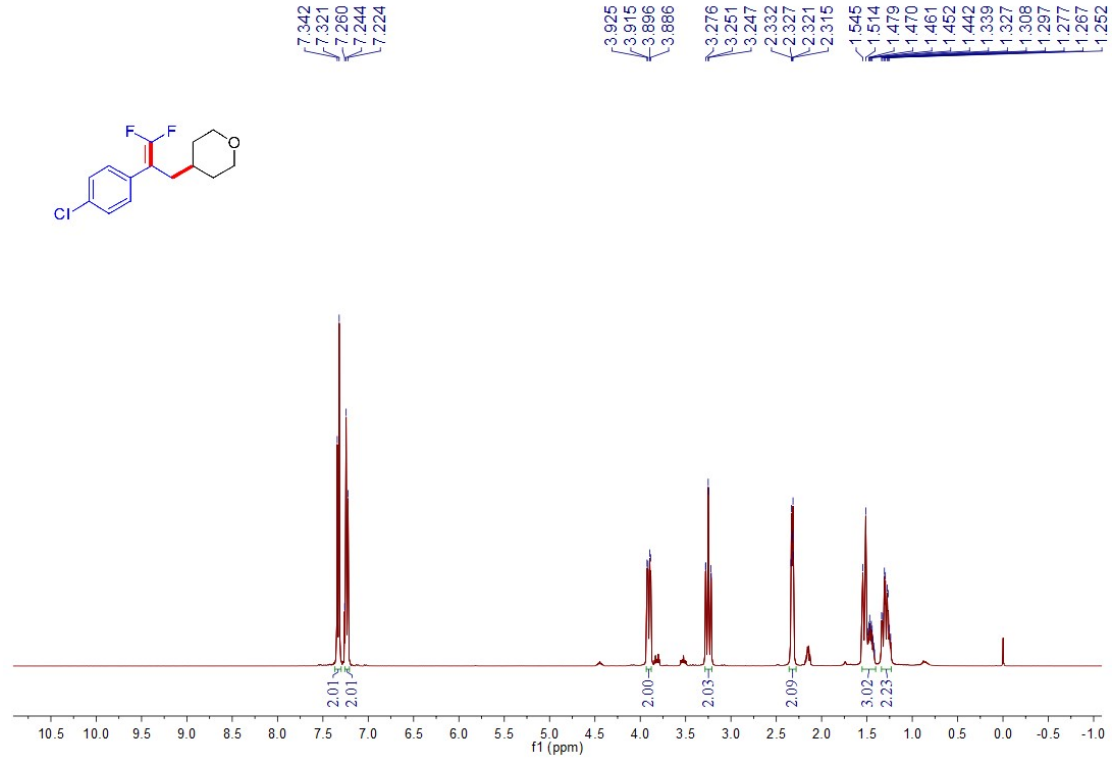
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4c**



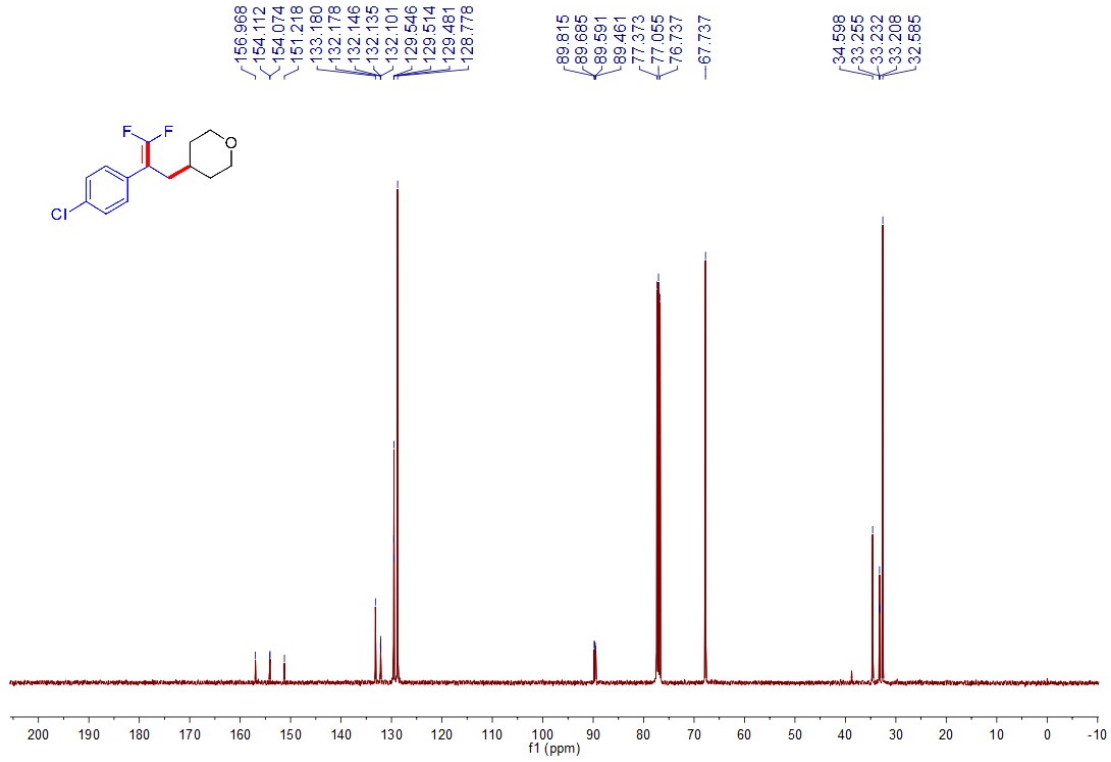
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4c**



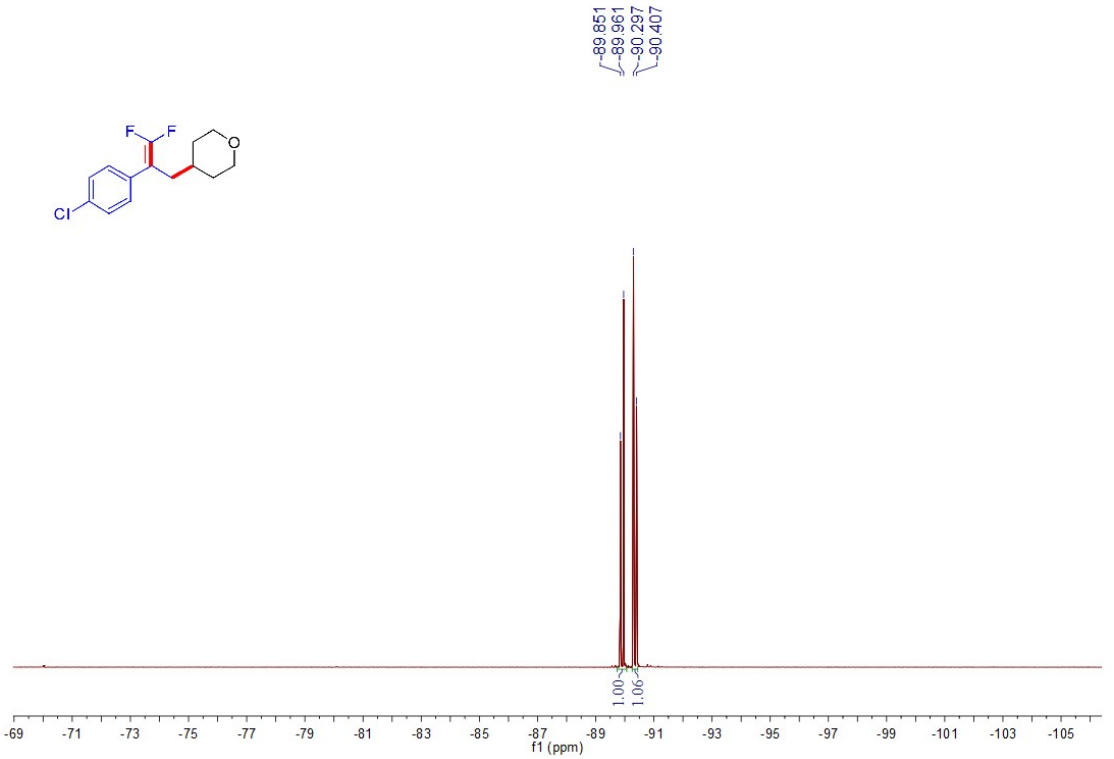
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d**



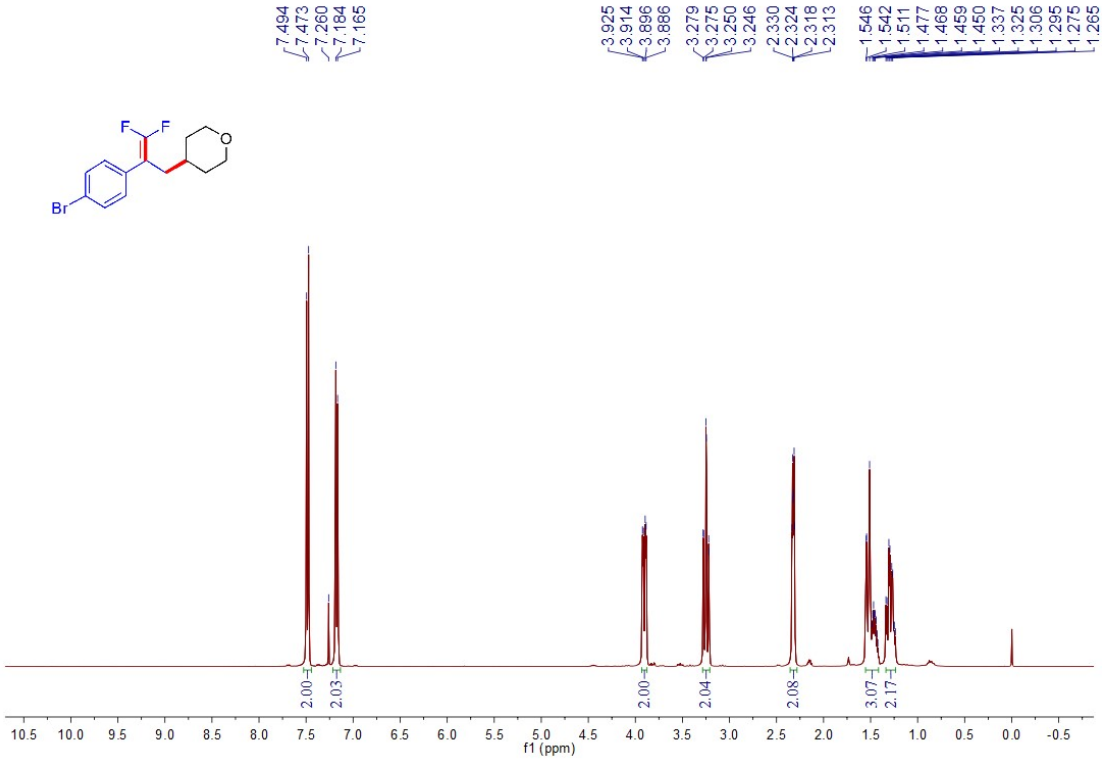
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4d**



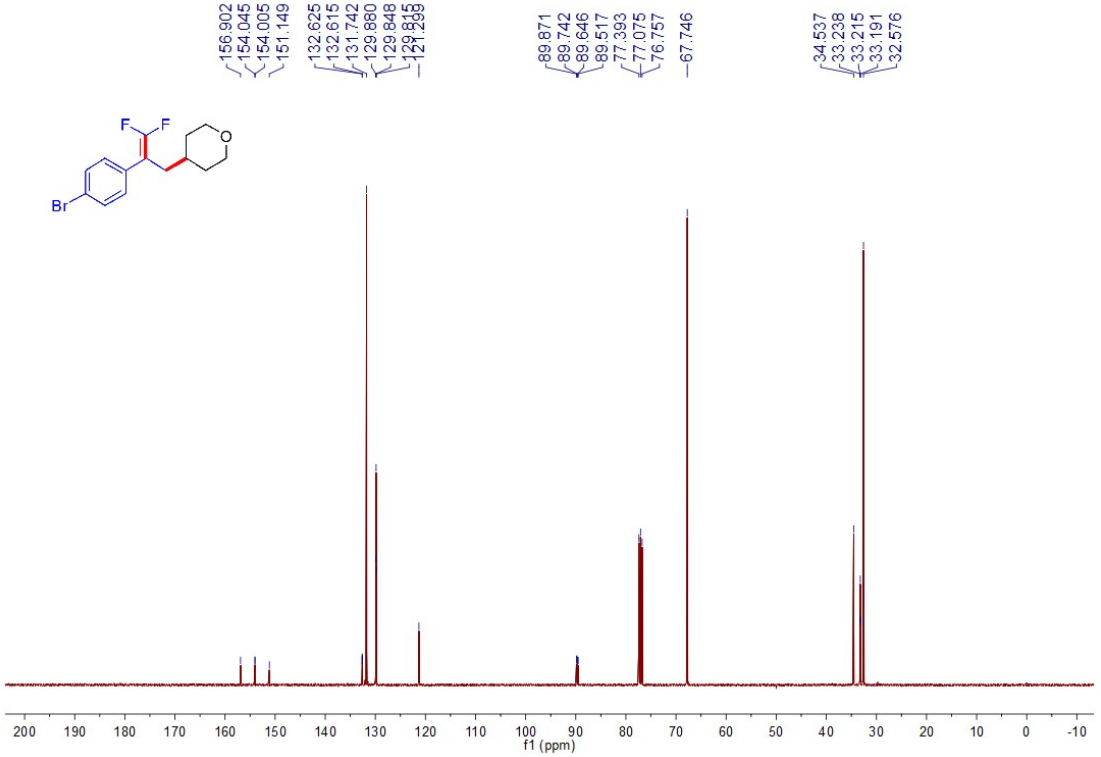
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4d**



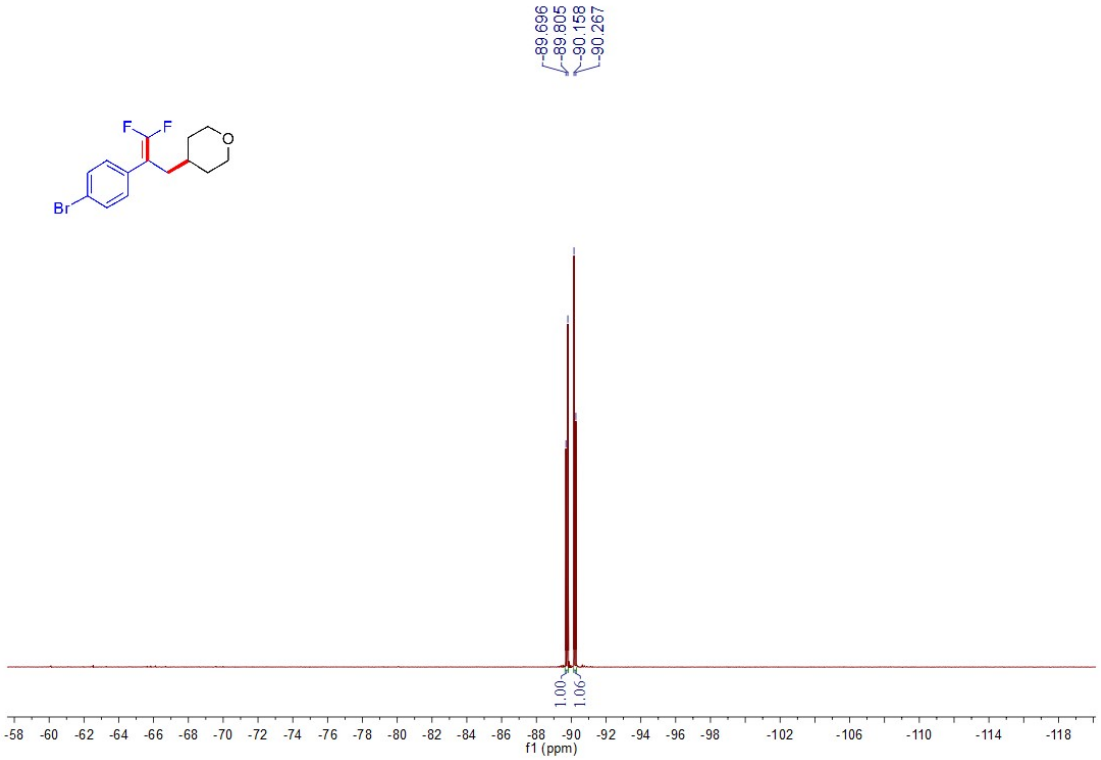
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4e**



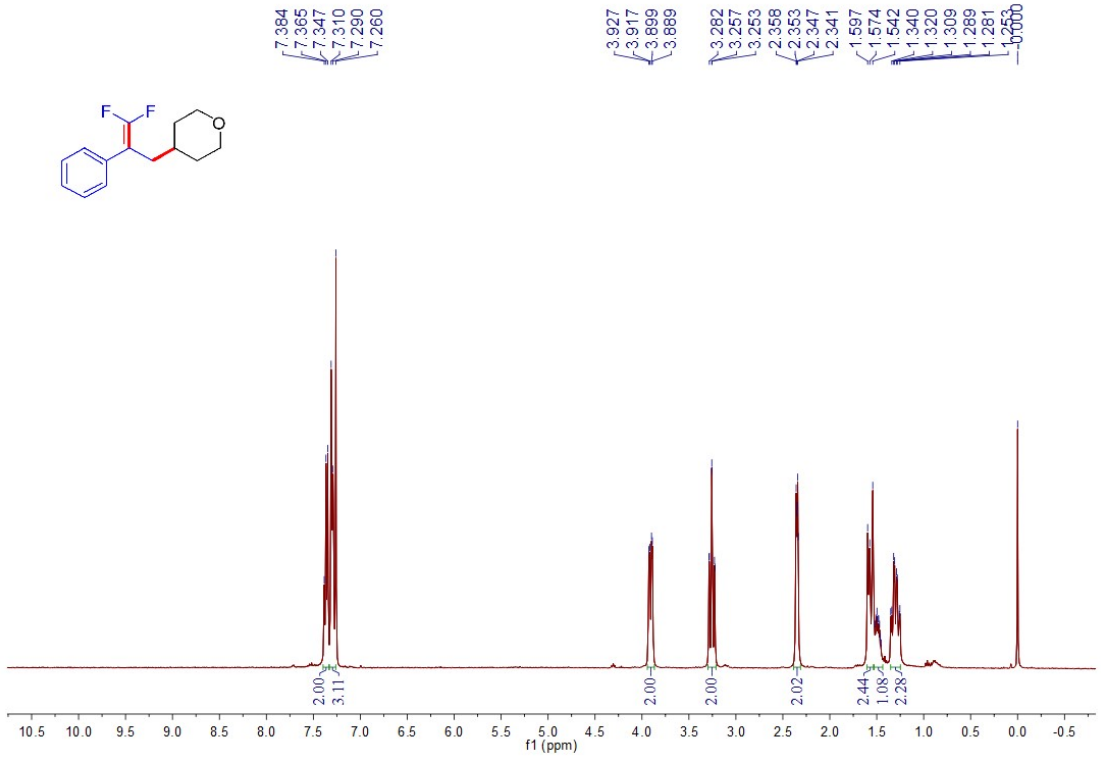
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4e**



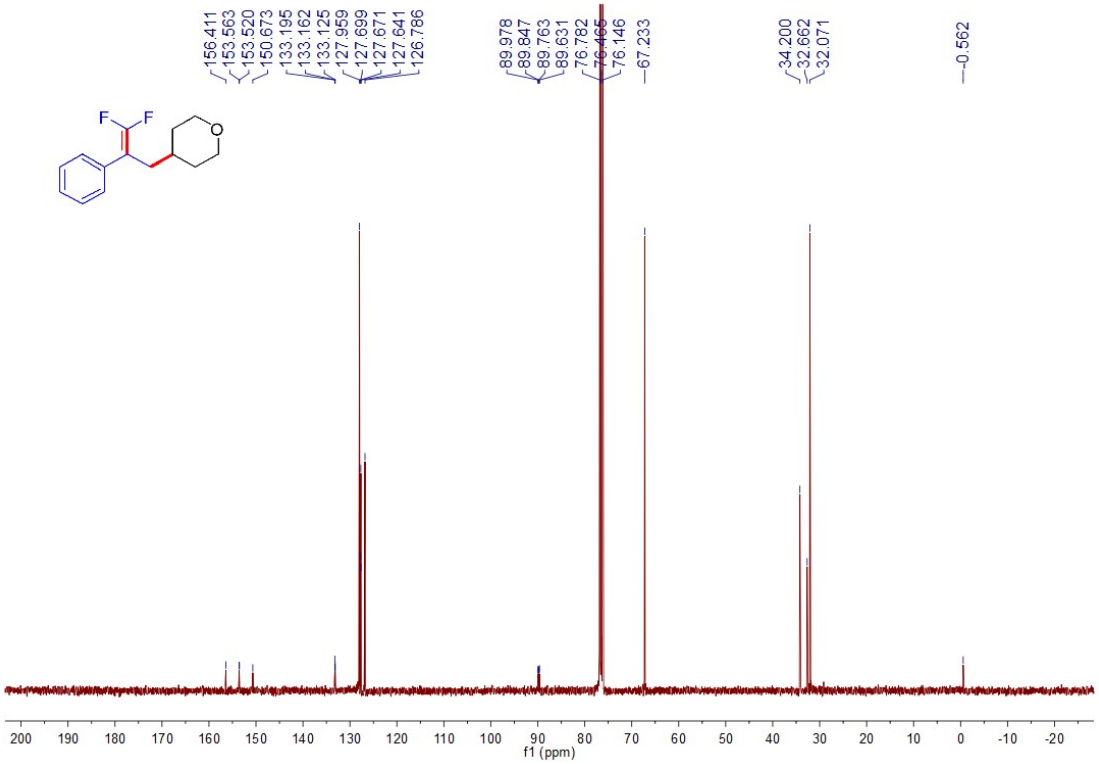
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4e**



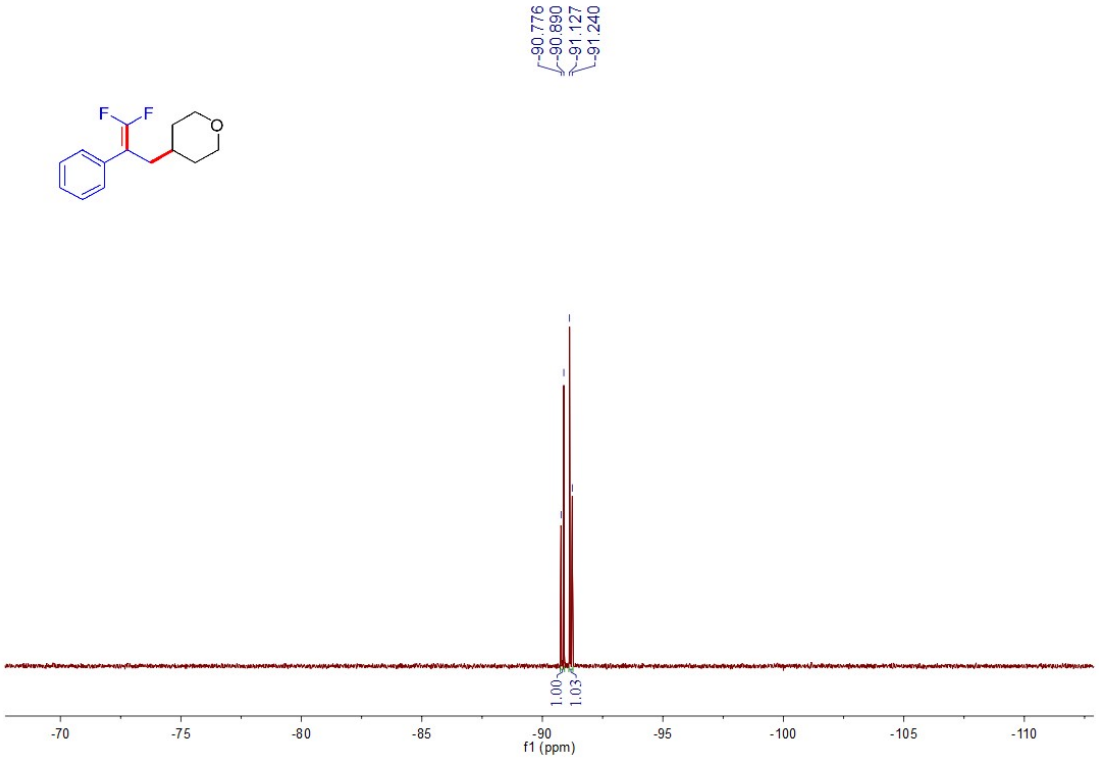
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4f**



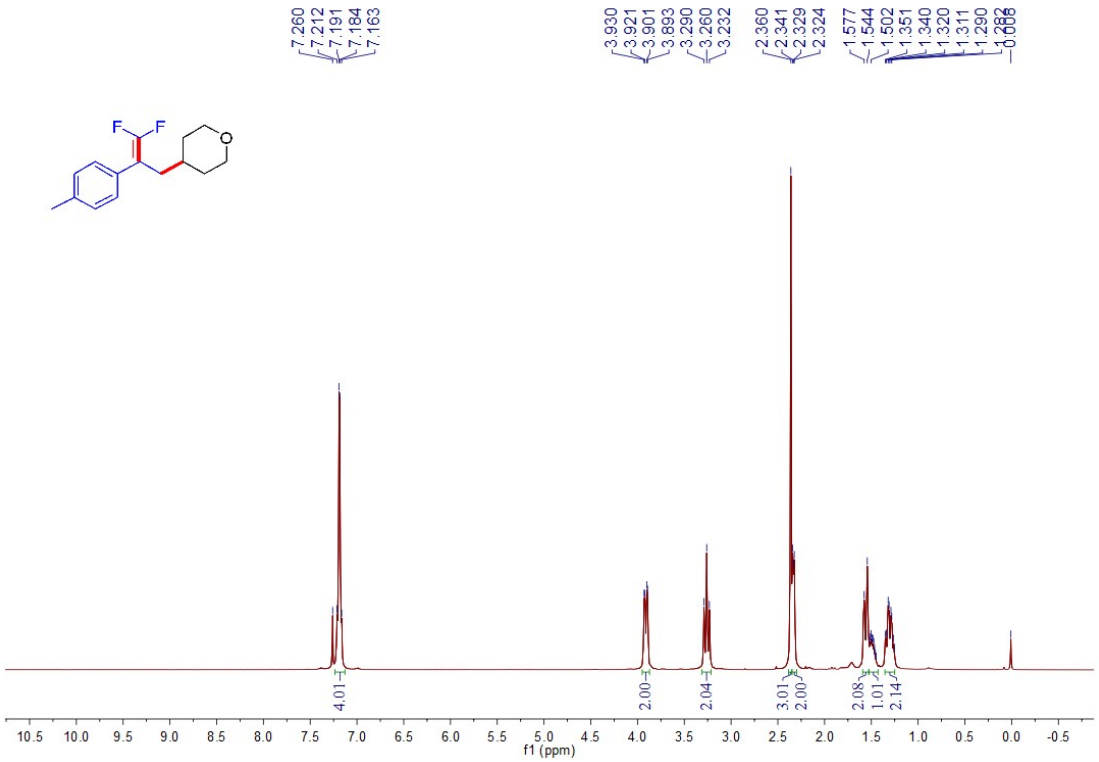
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4f**



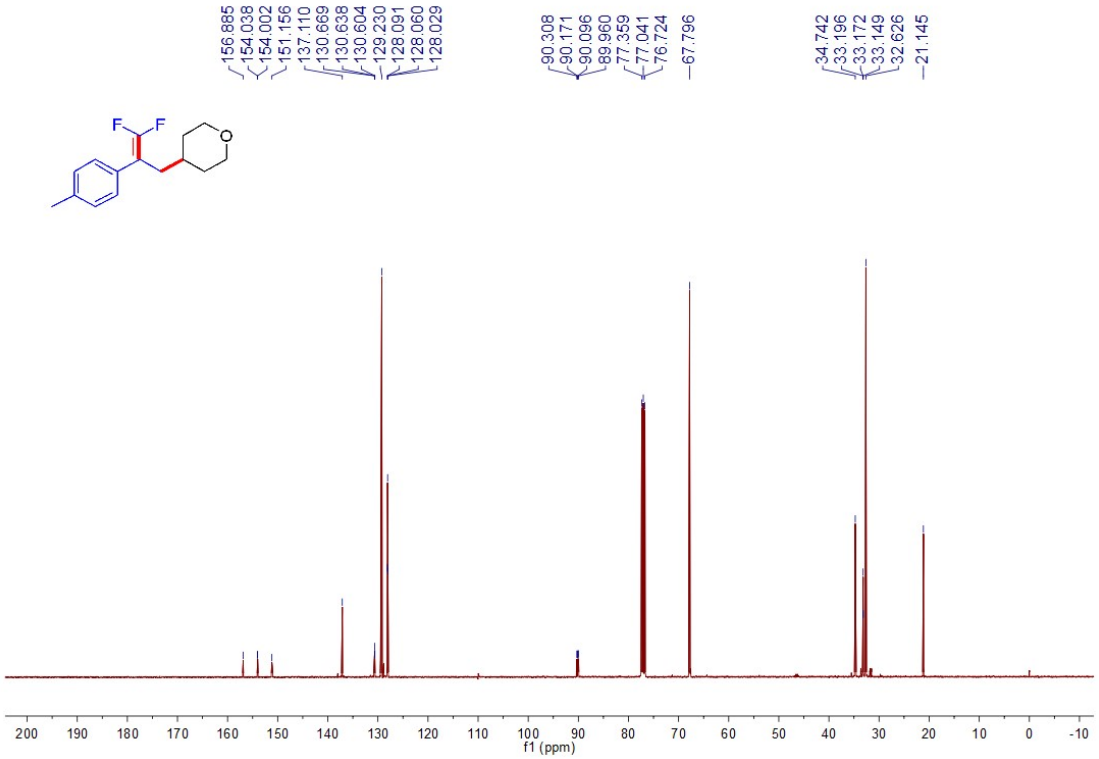
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4f**



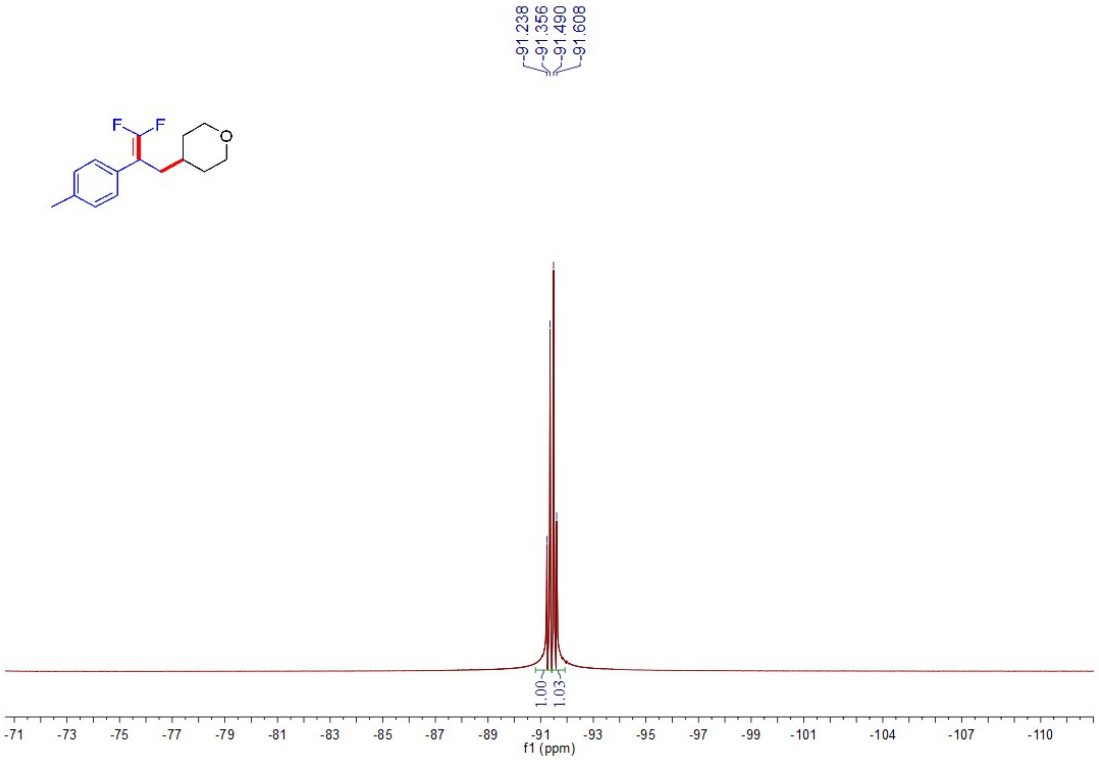
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4g**



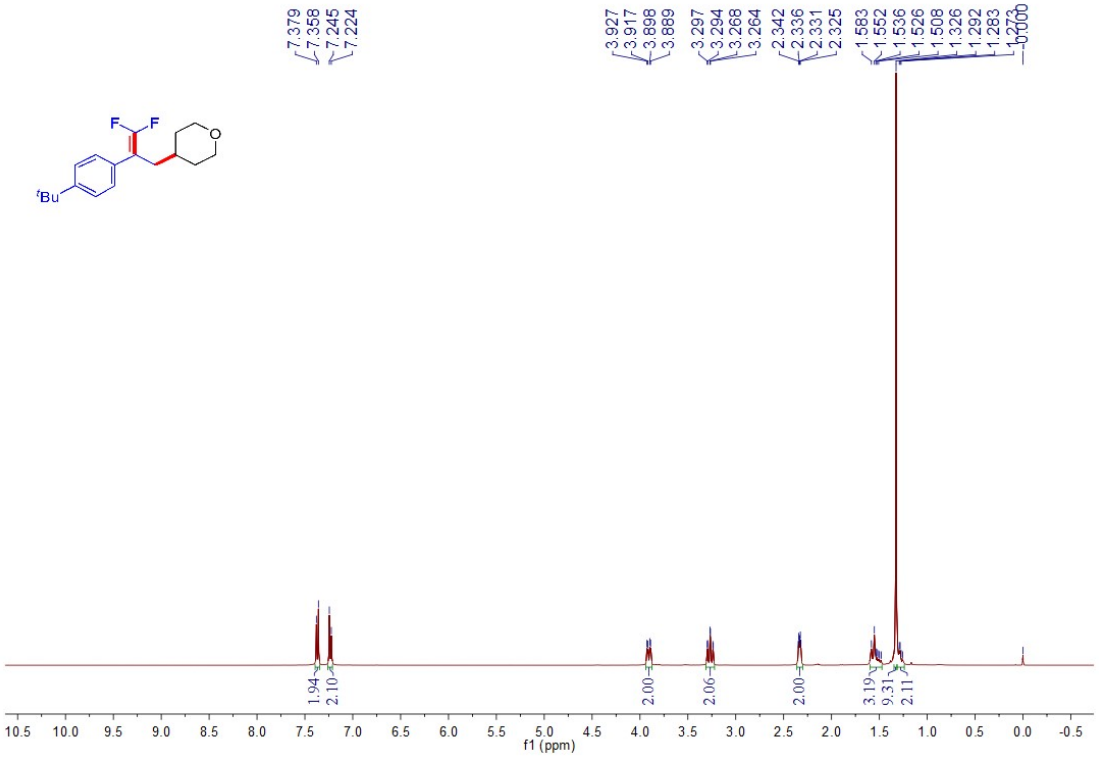
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4g**



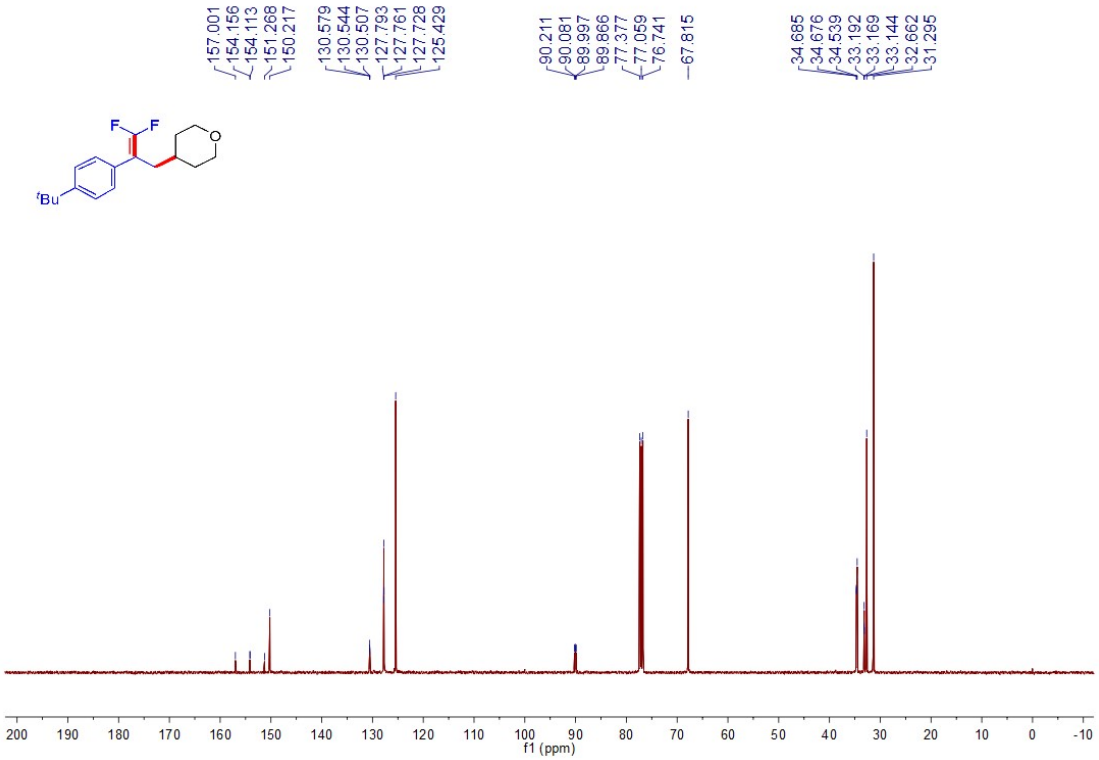
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4g**



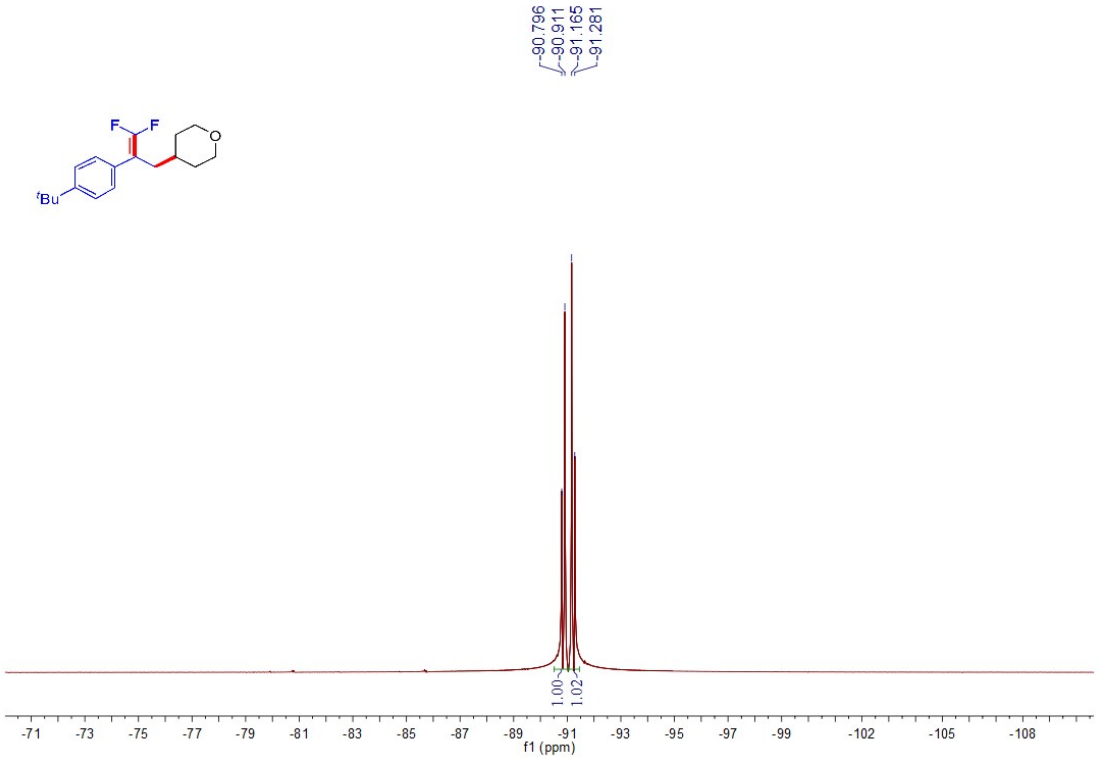
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4h**



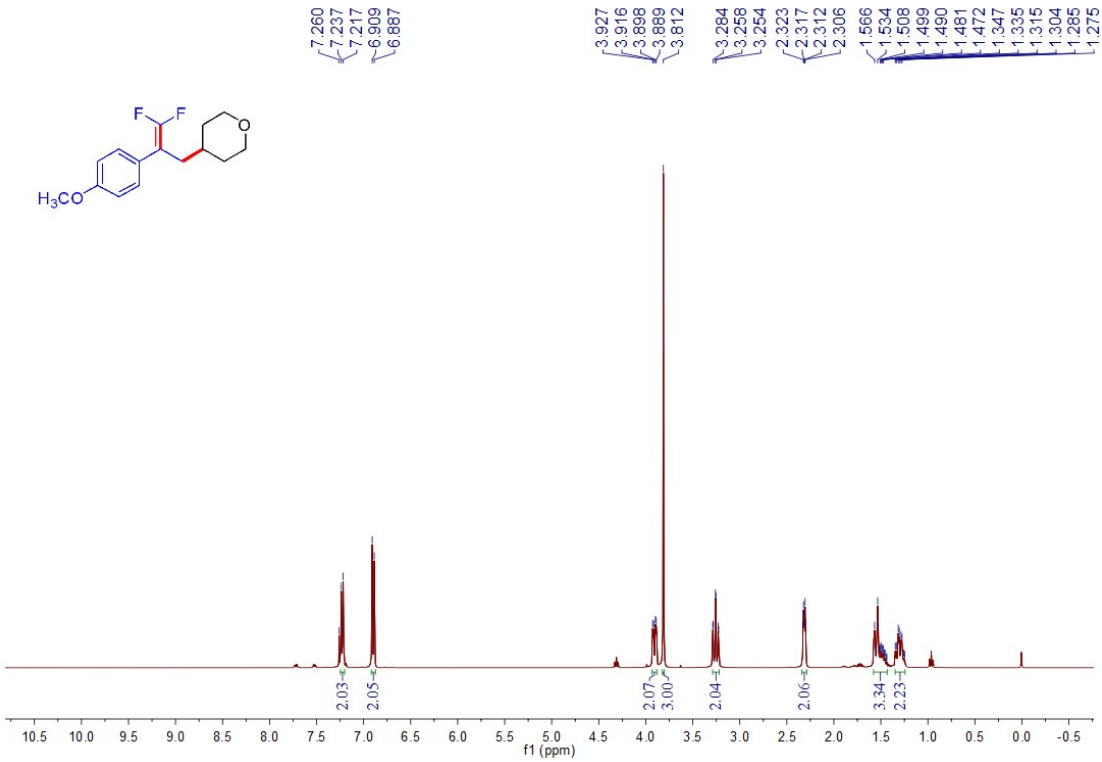
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4h**



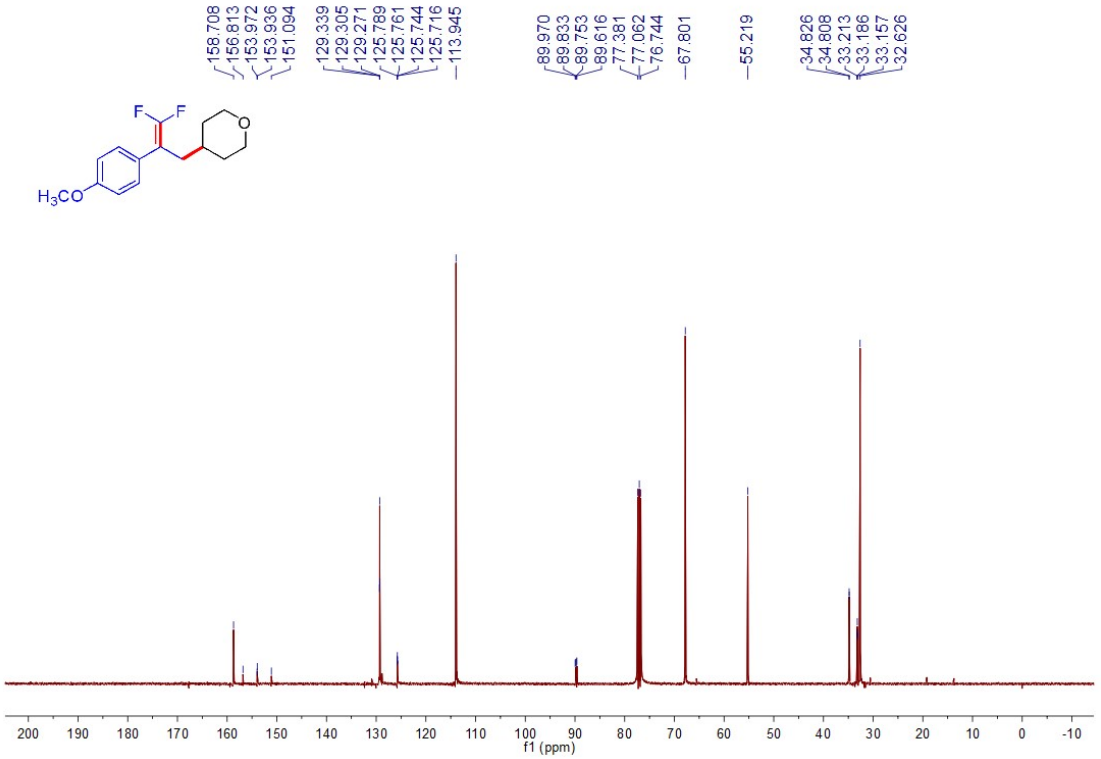
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4h**



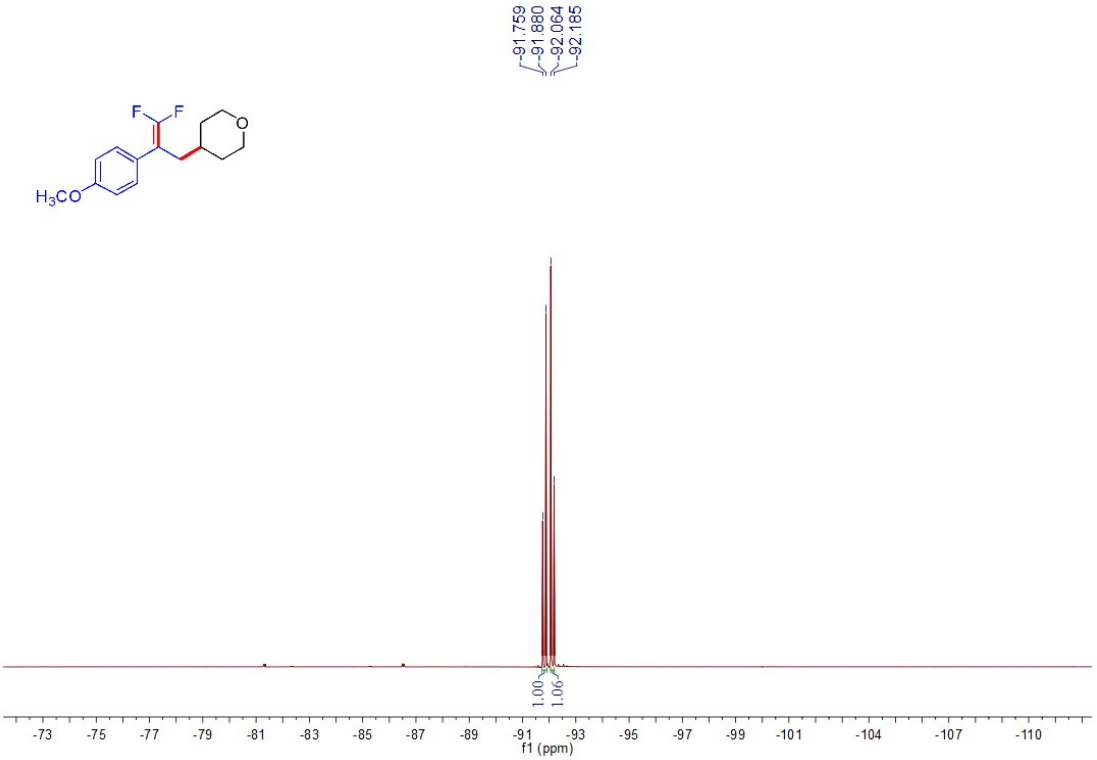
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4i**



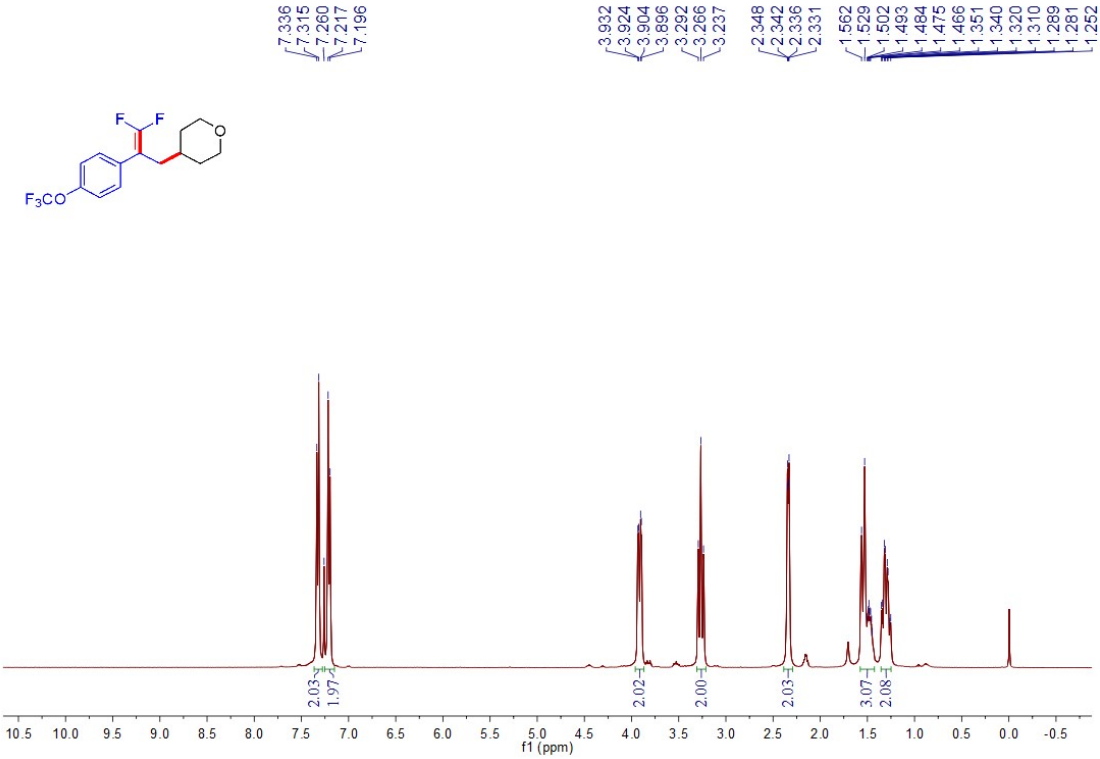
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4i**



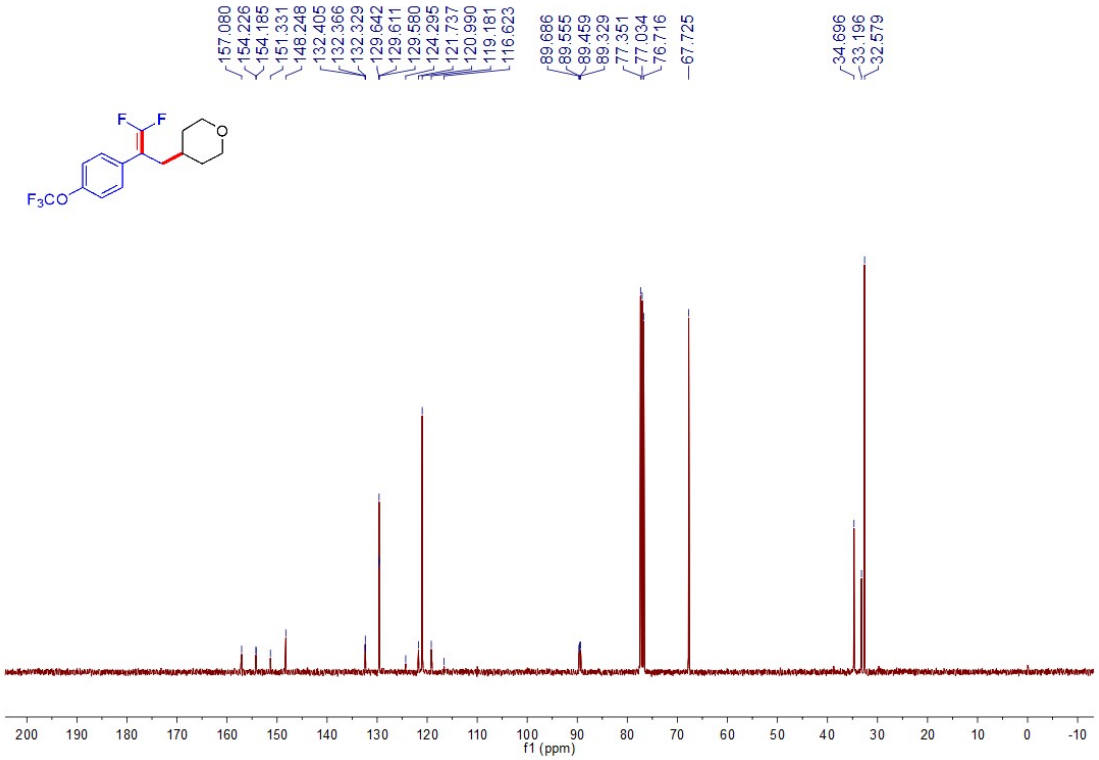
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4i**



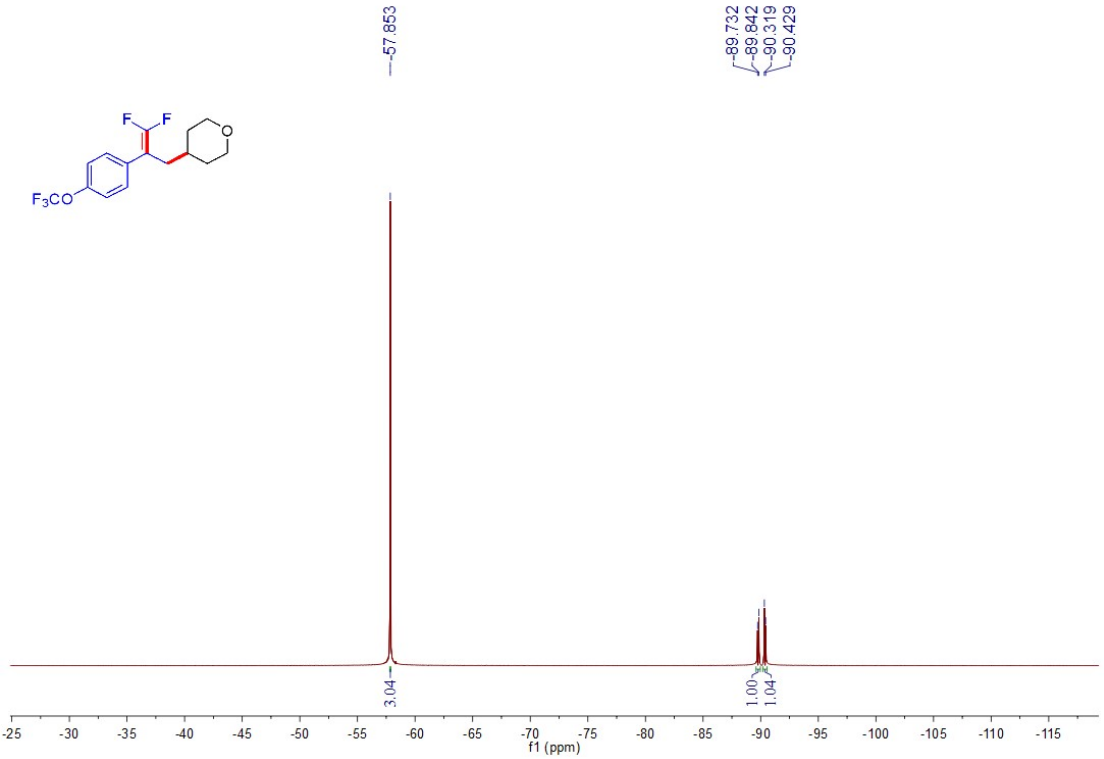
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4j**



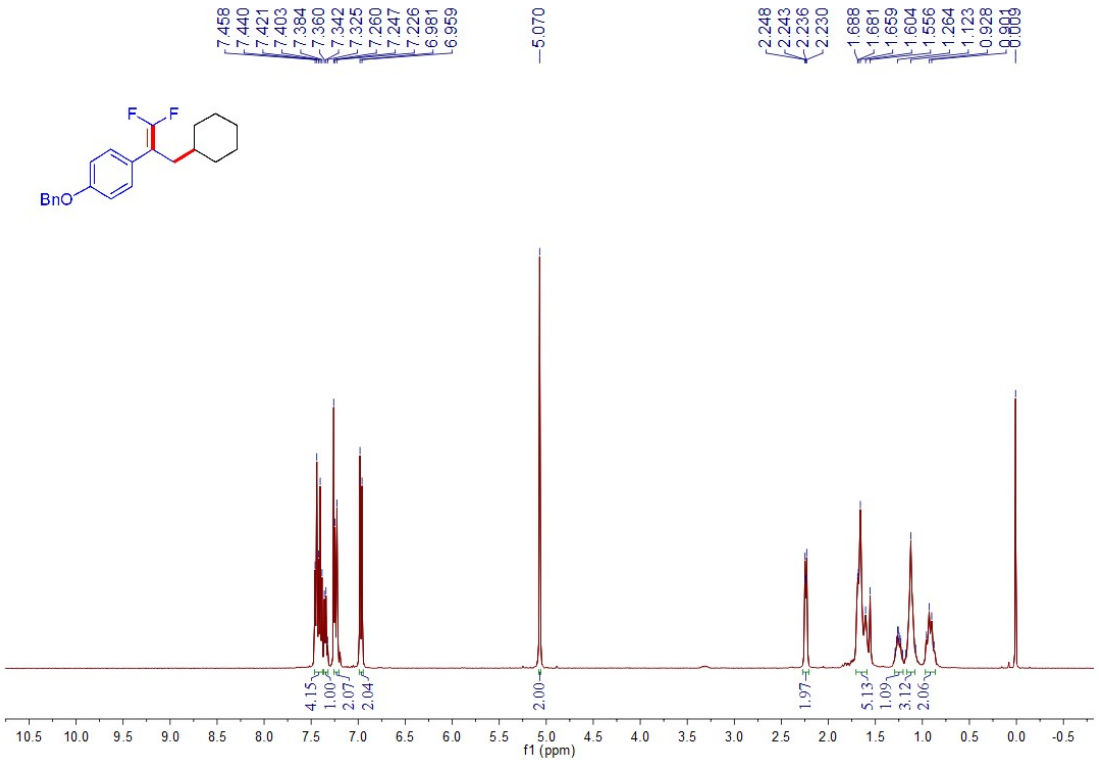
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4j**



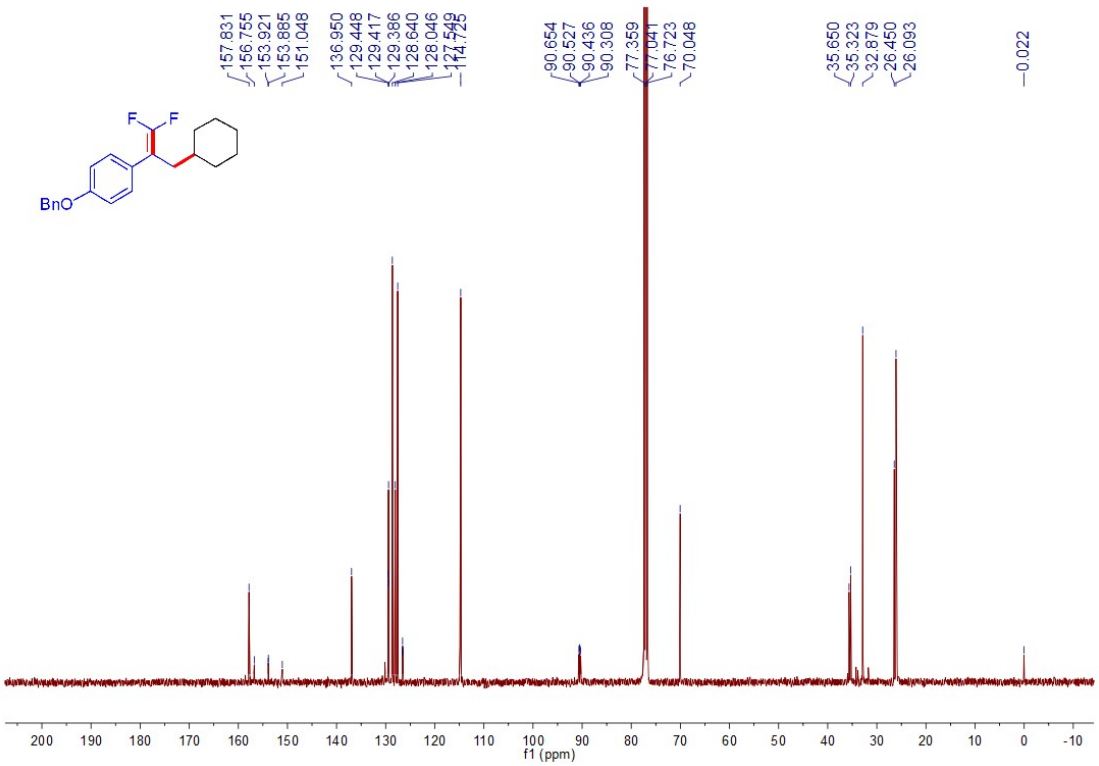
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4j**



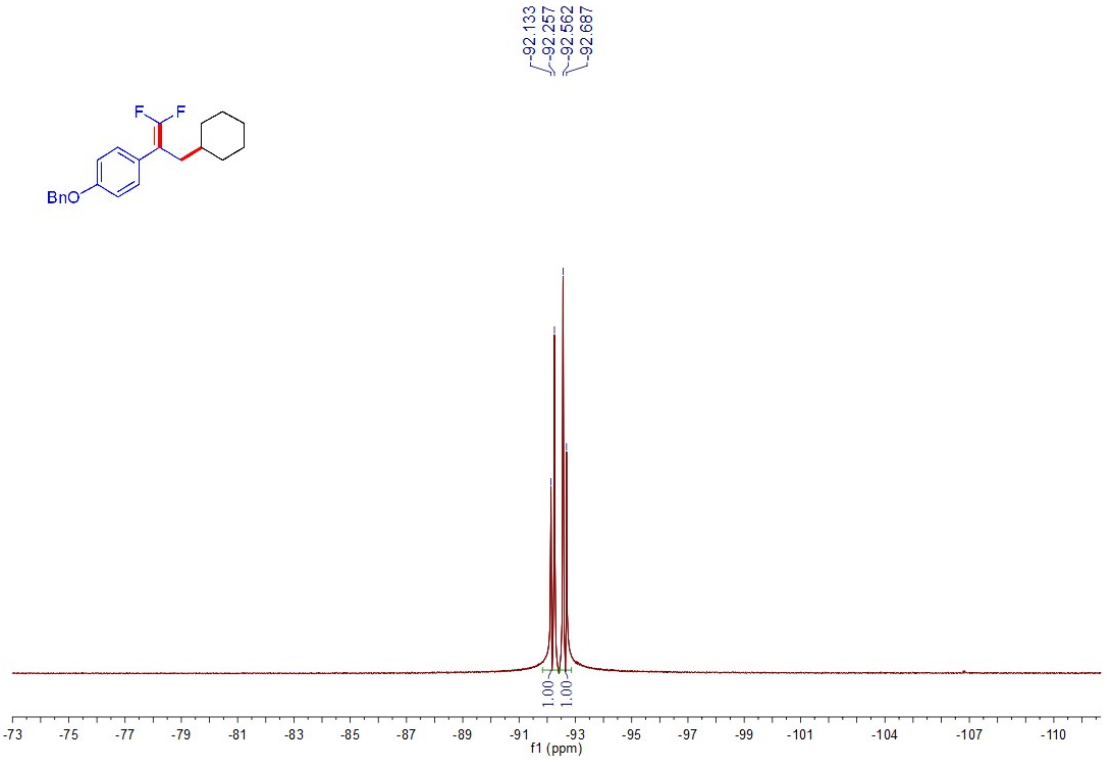
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4k**



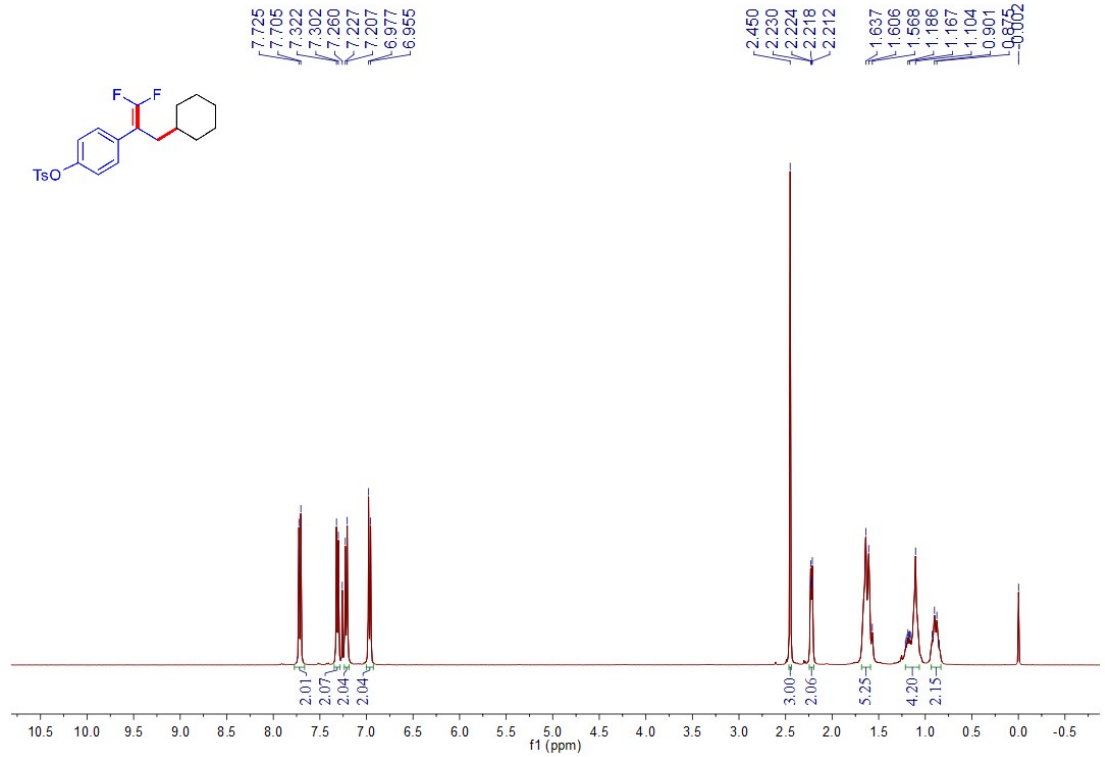
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4k**



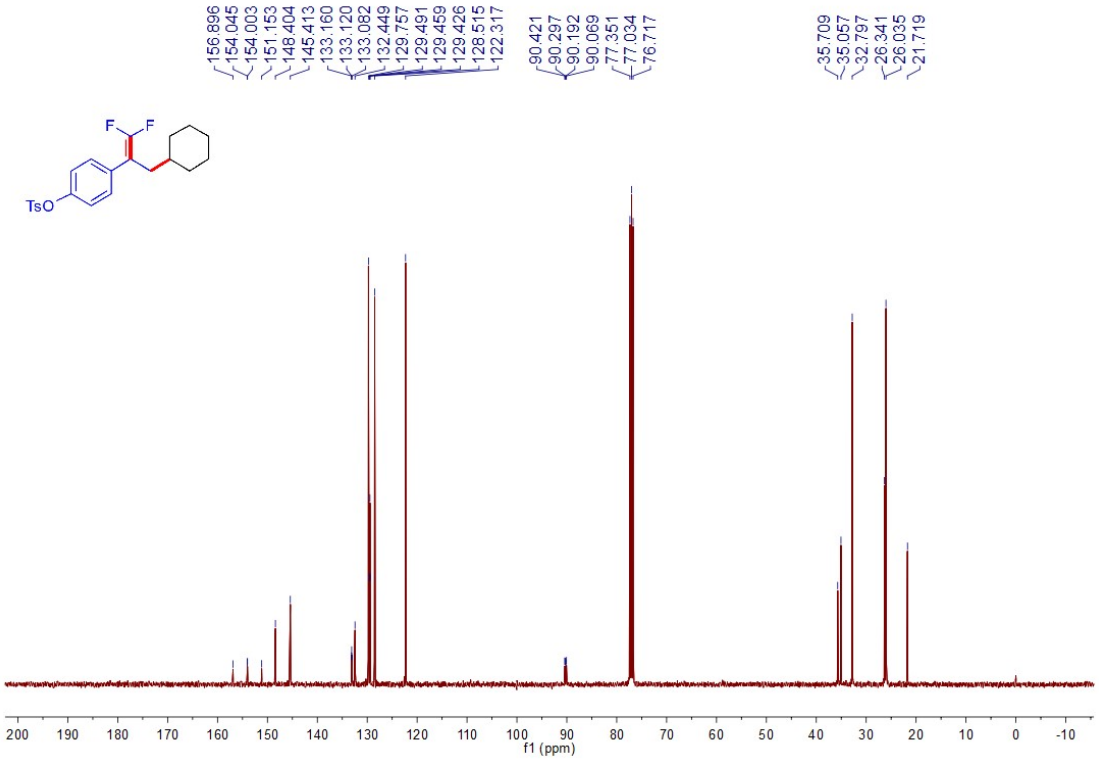
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4k**



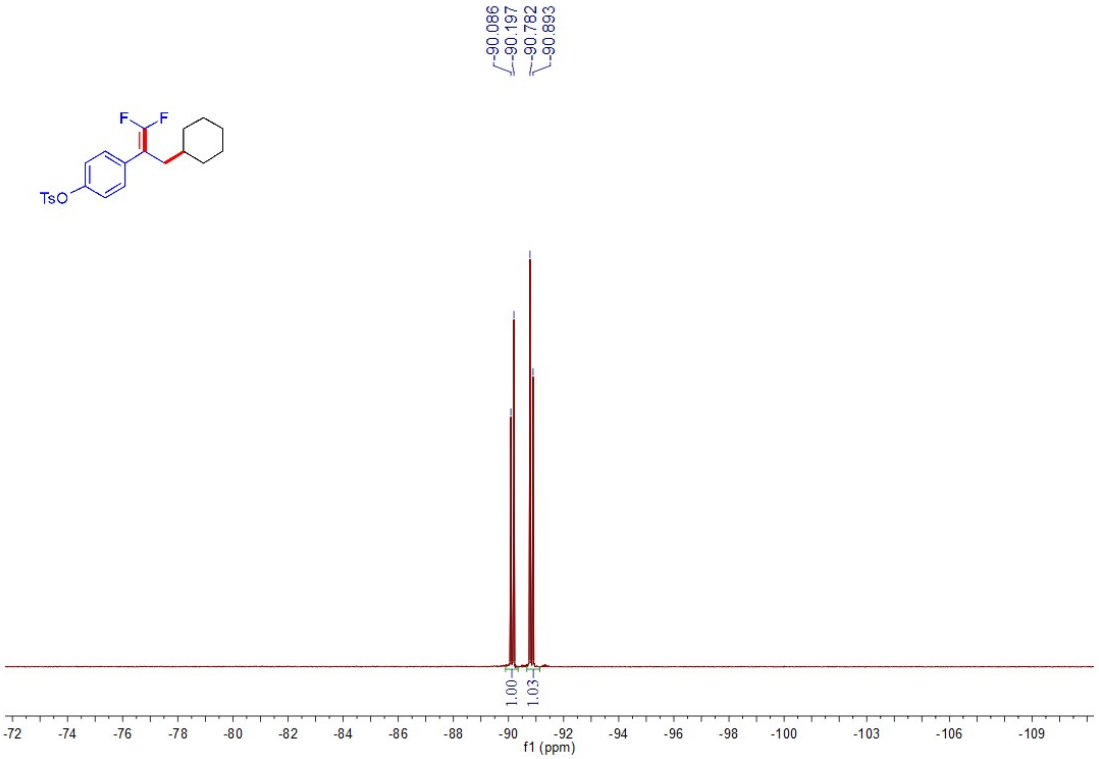
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4l**



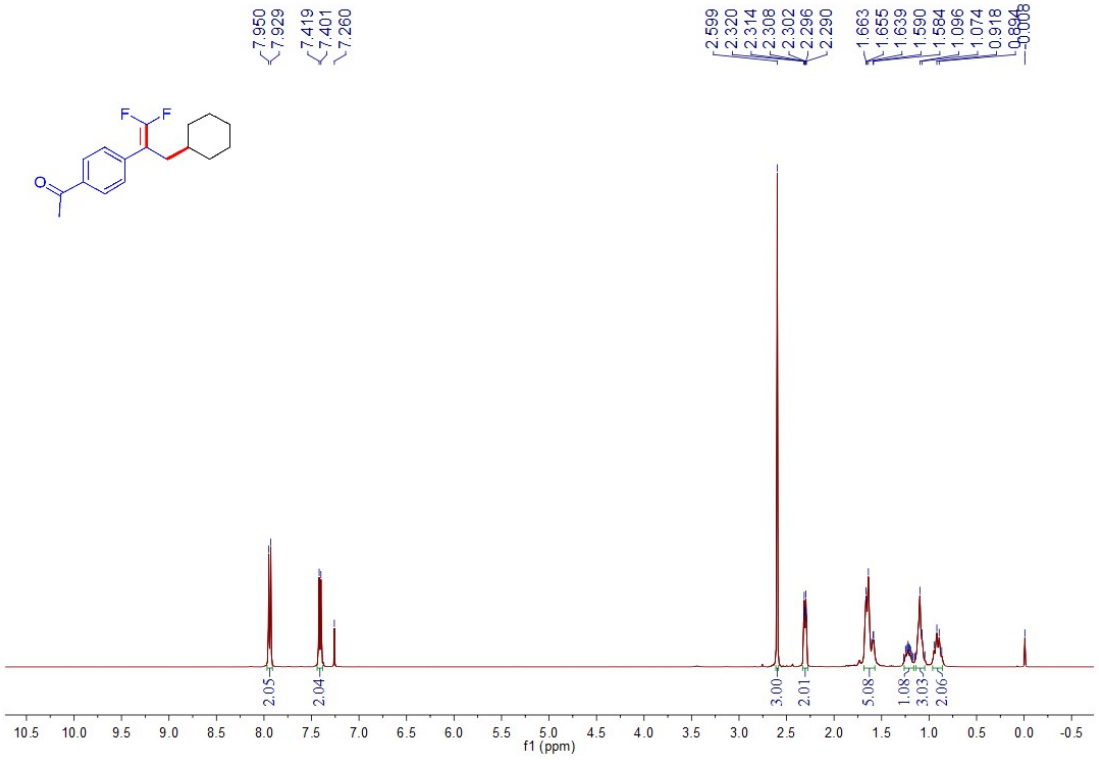
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4l**



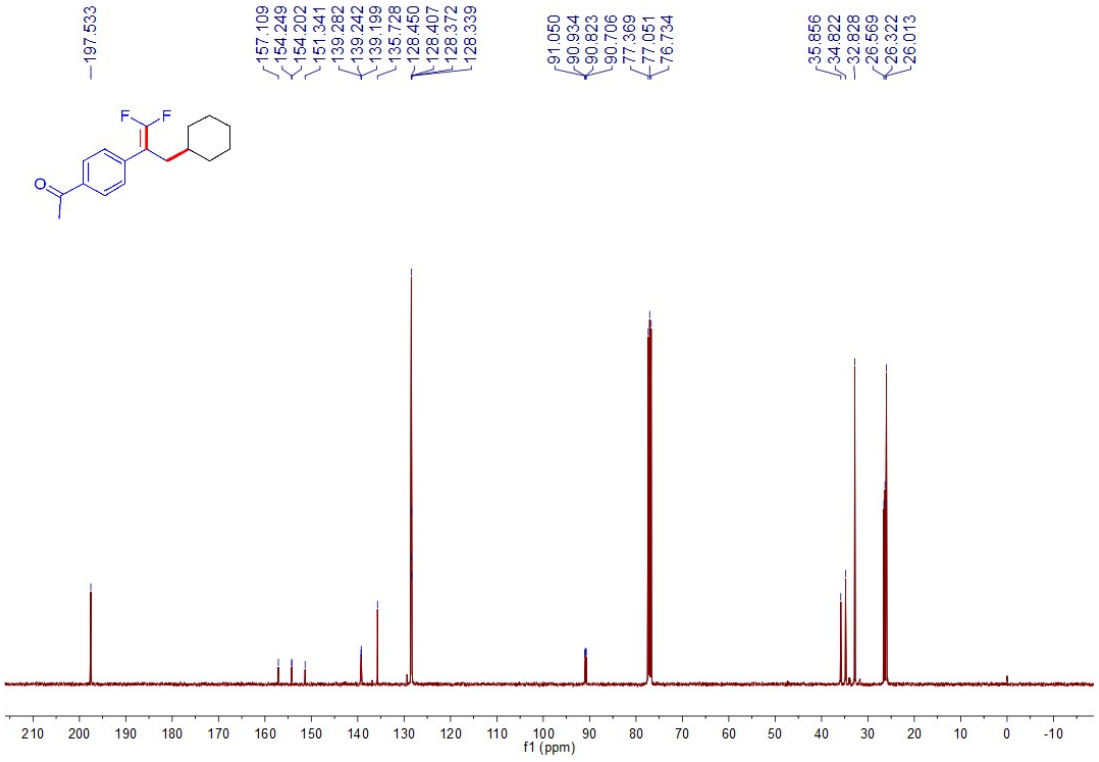
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4l**



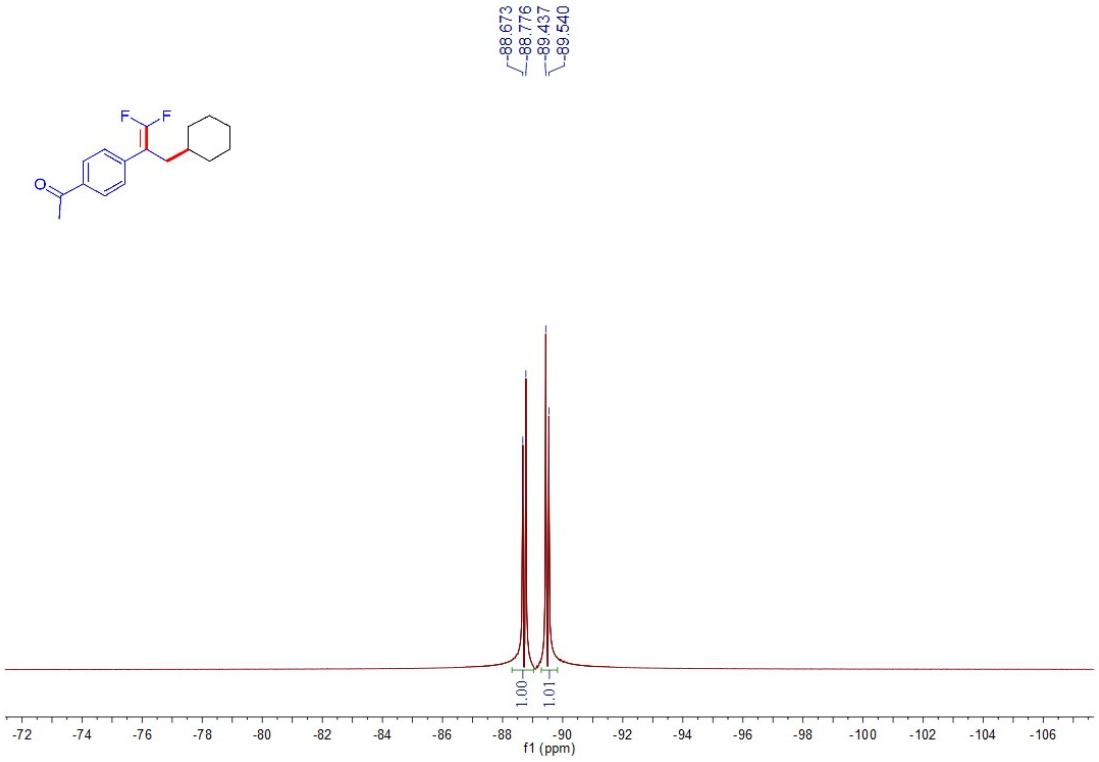
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4m**



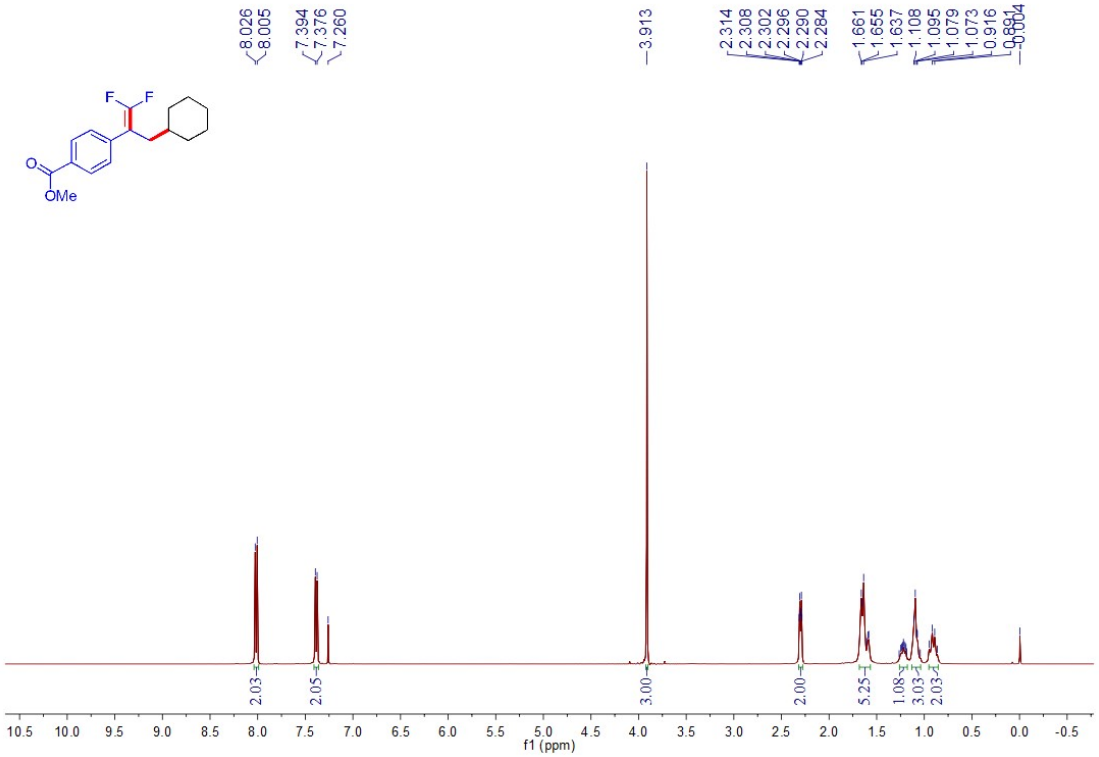
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4m**



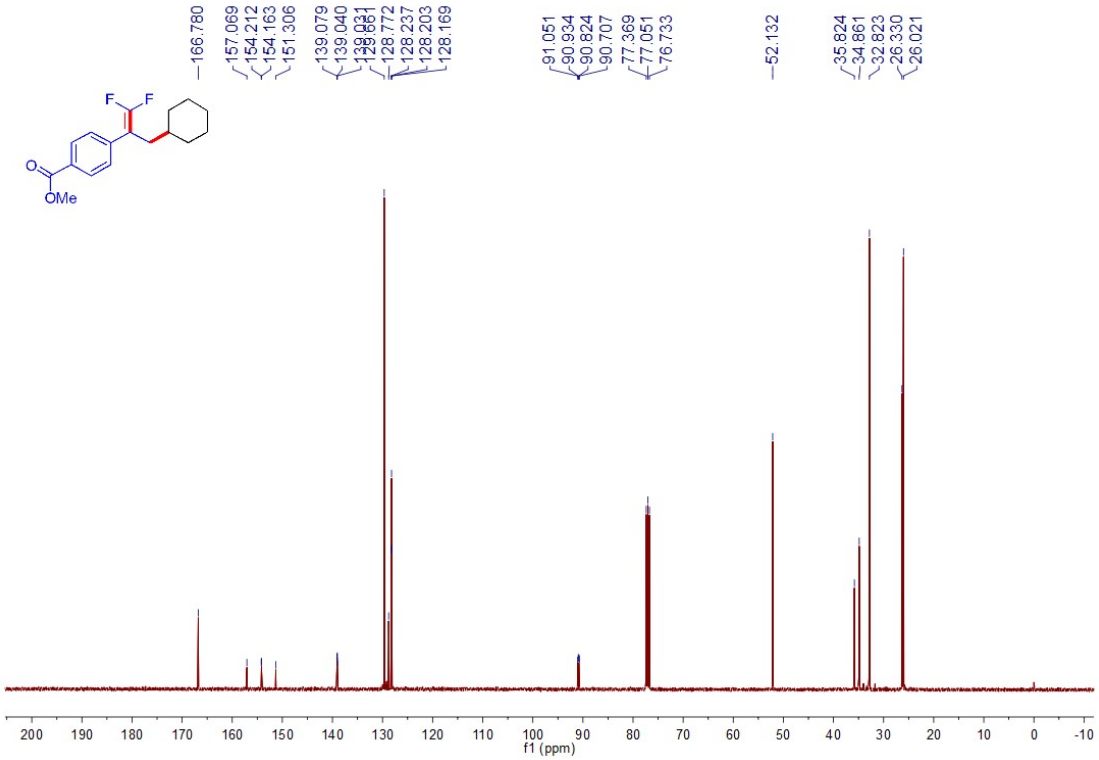
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4m**



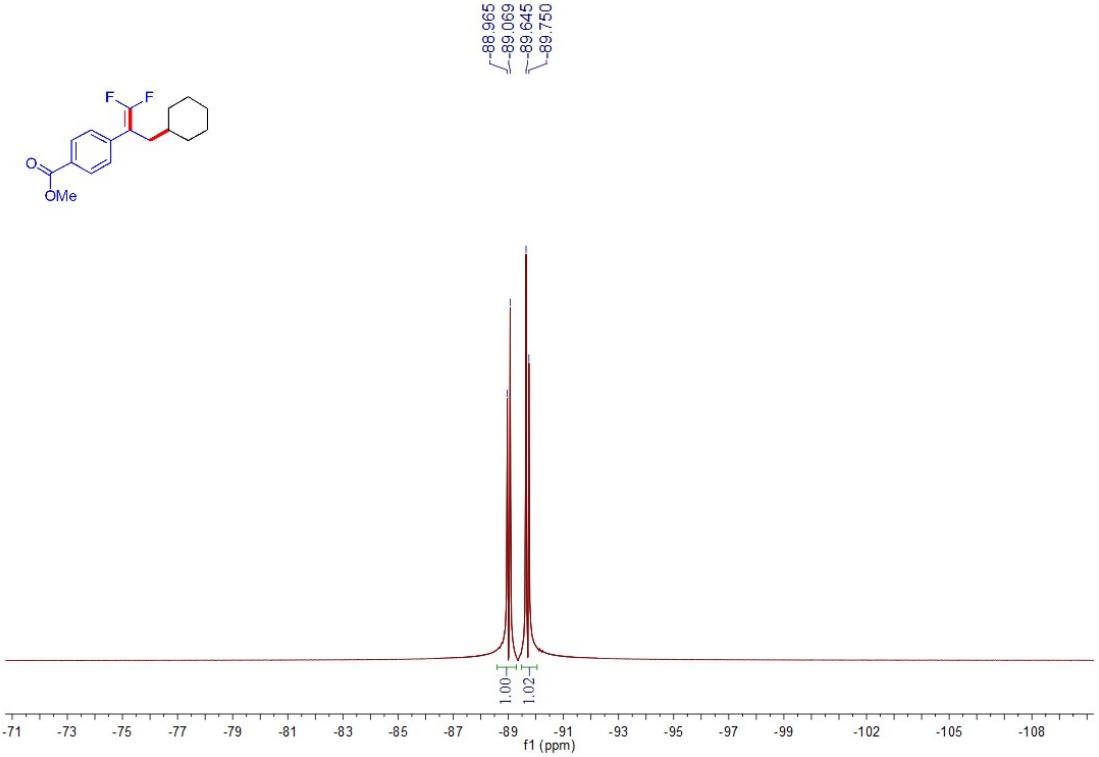
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4n**



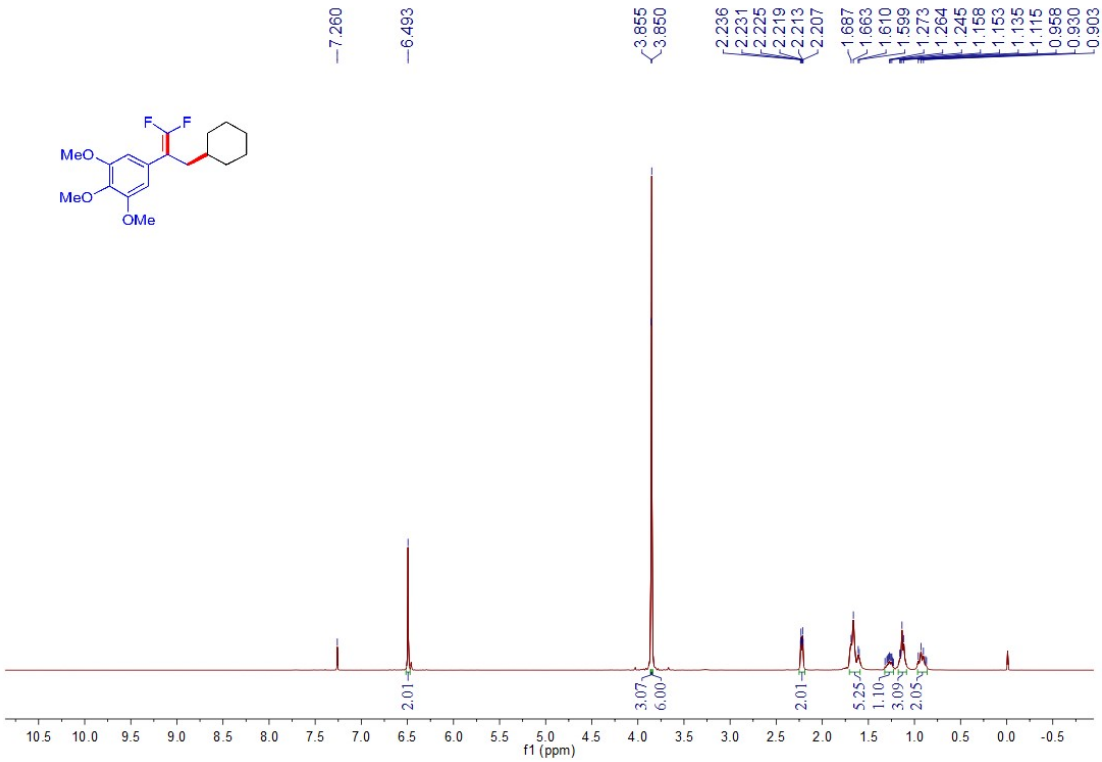
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4n**



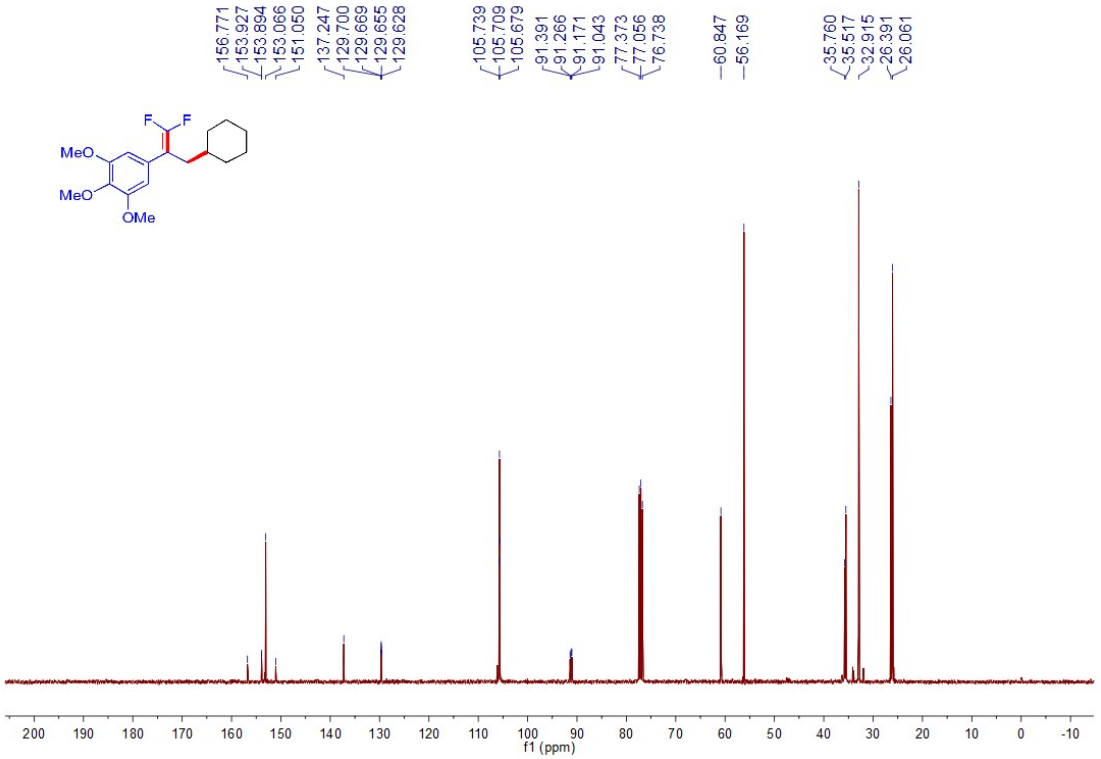
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4n**



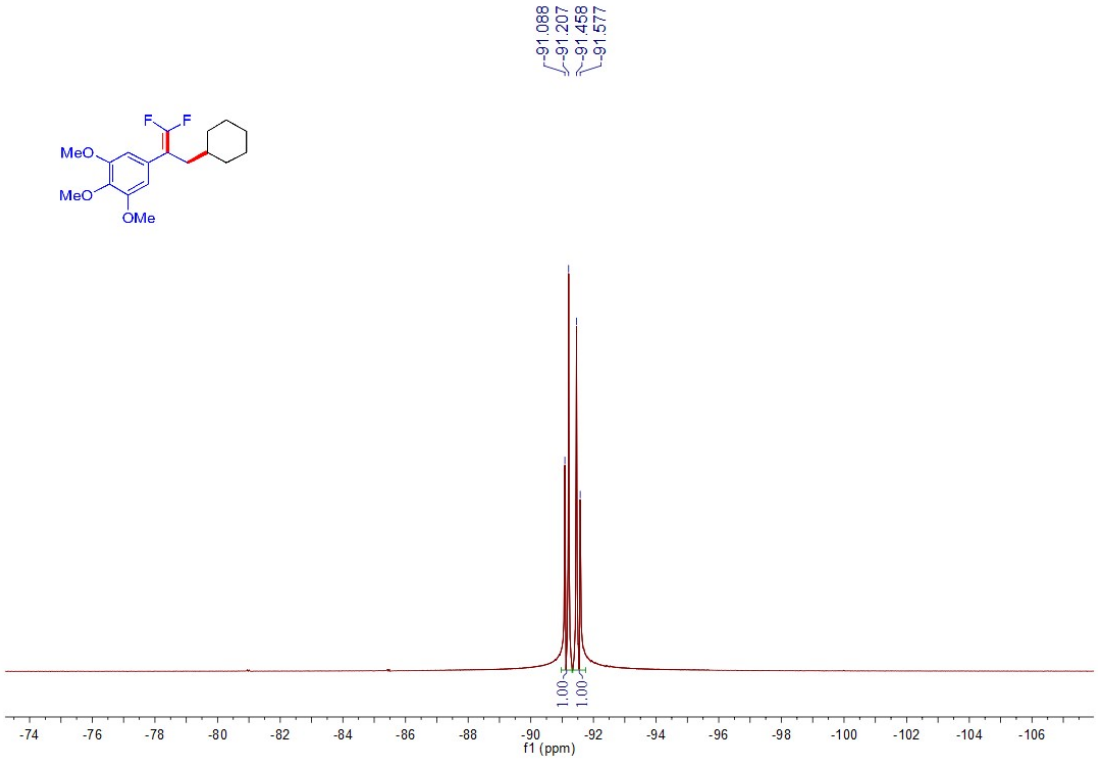
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4o**



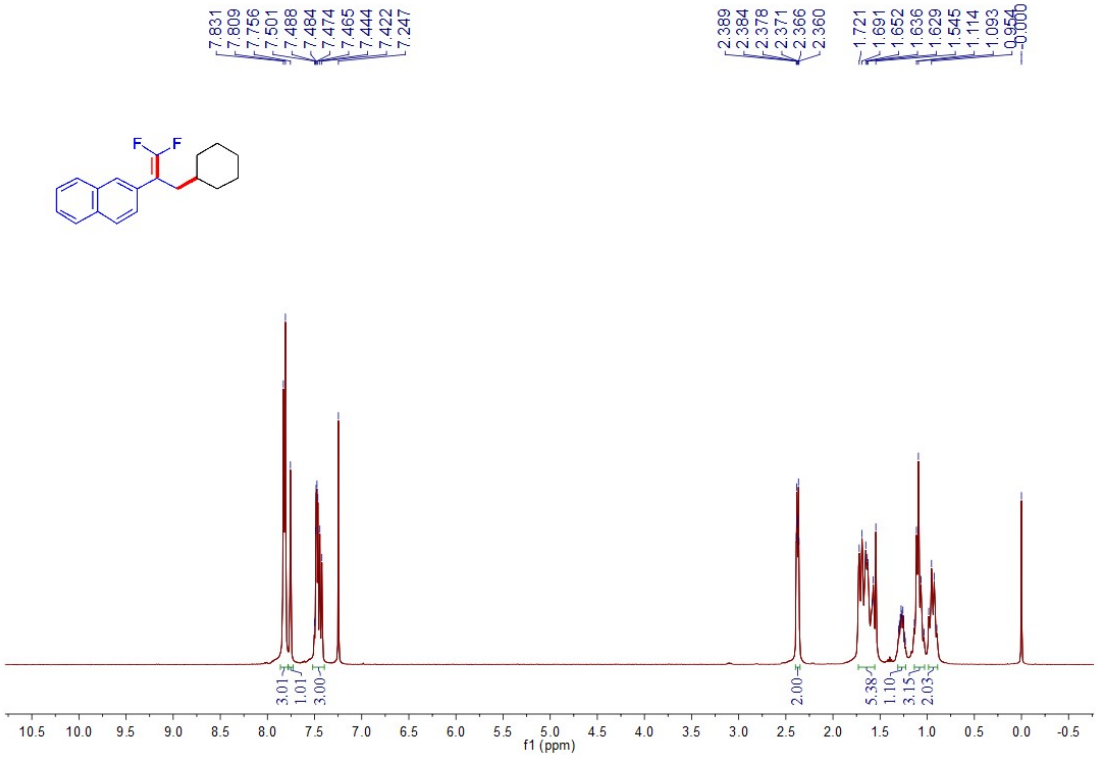
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4o**



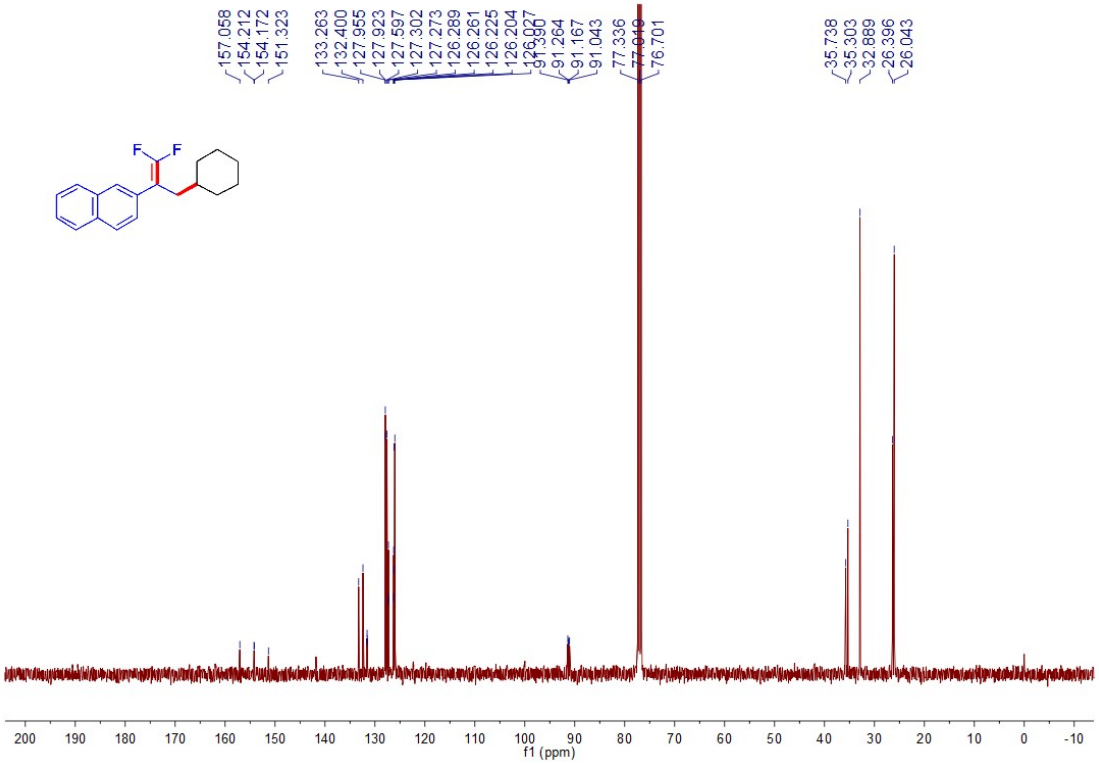
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4o**



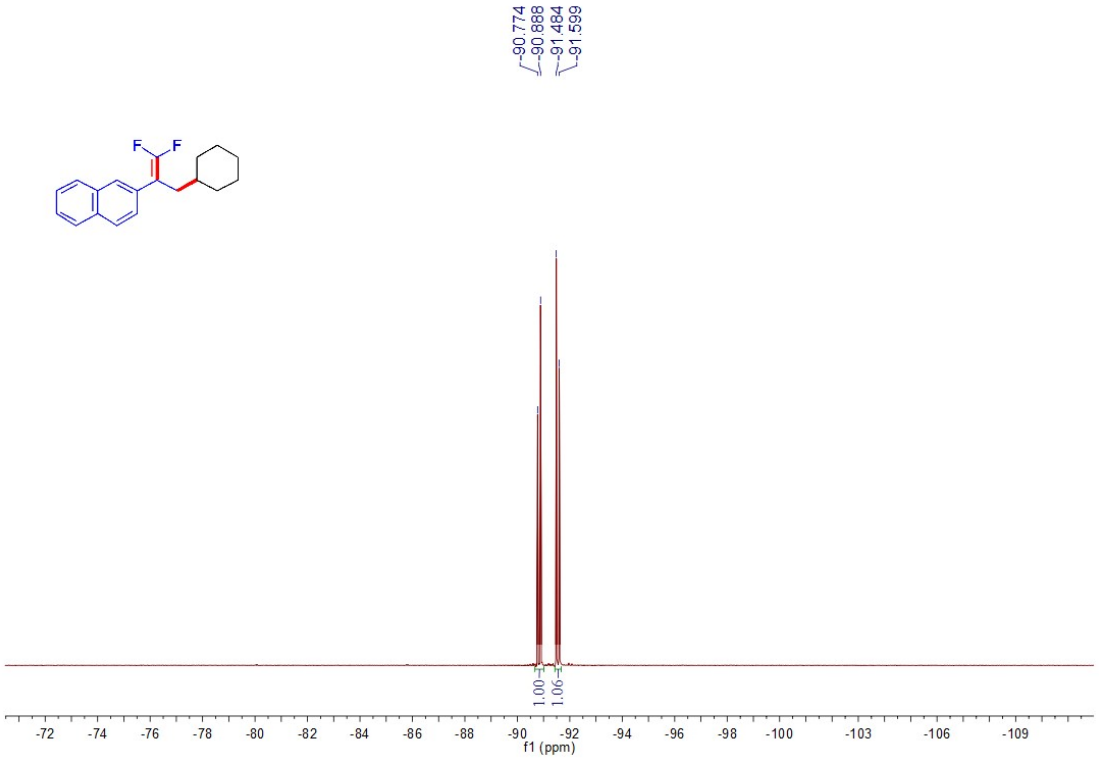
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4p**



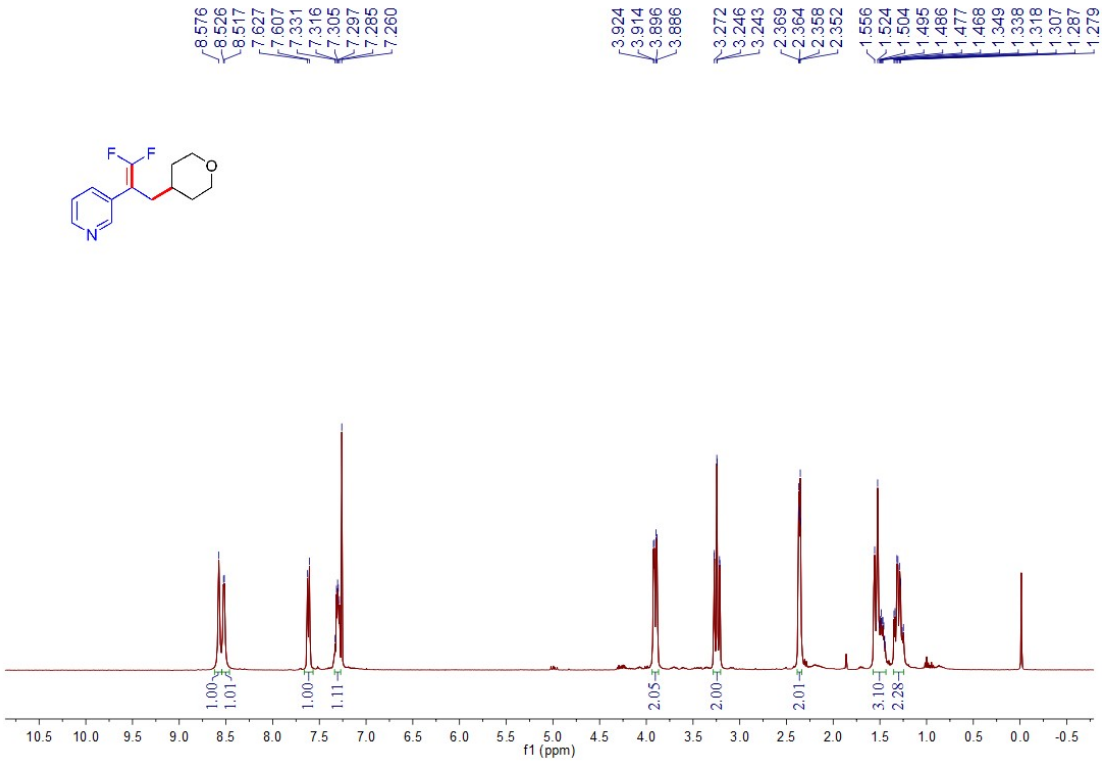
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4p**



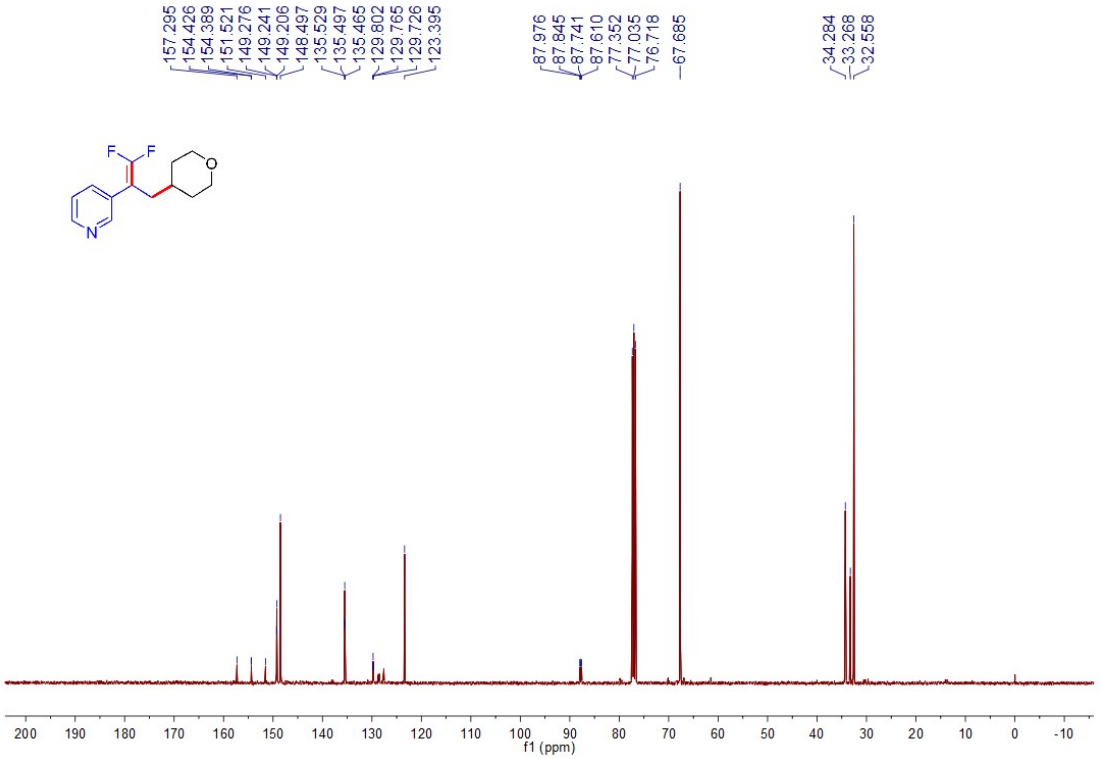
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4p**



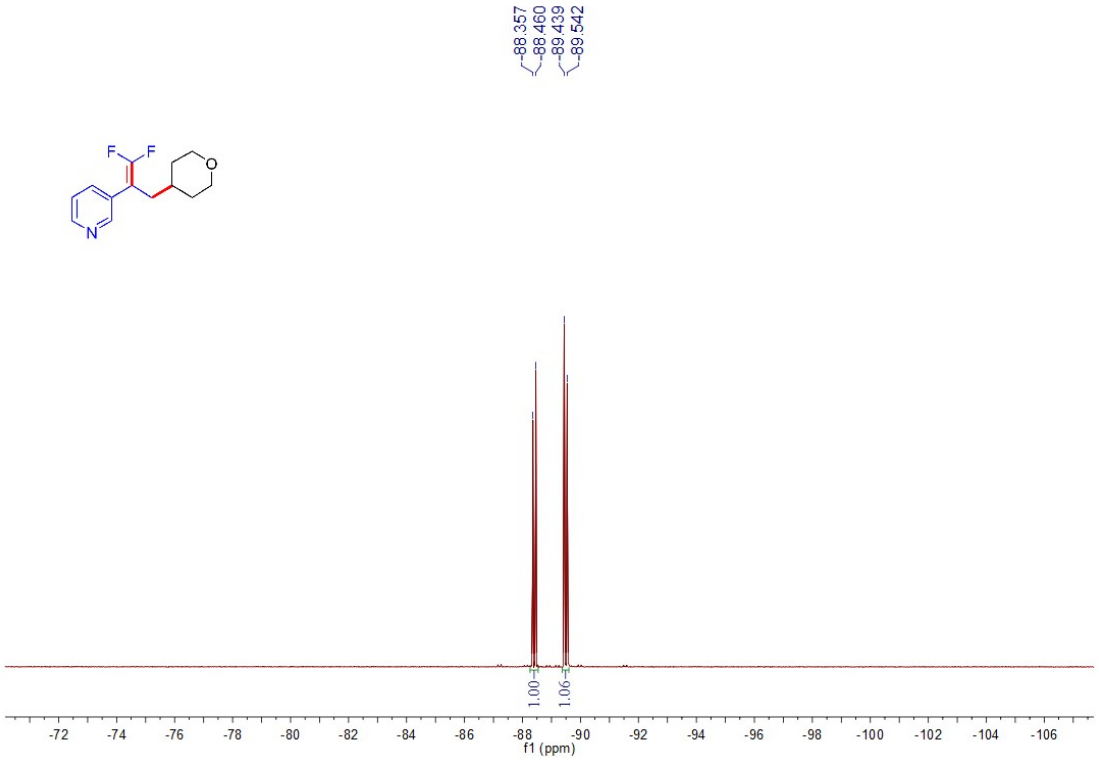
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4q**



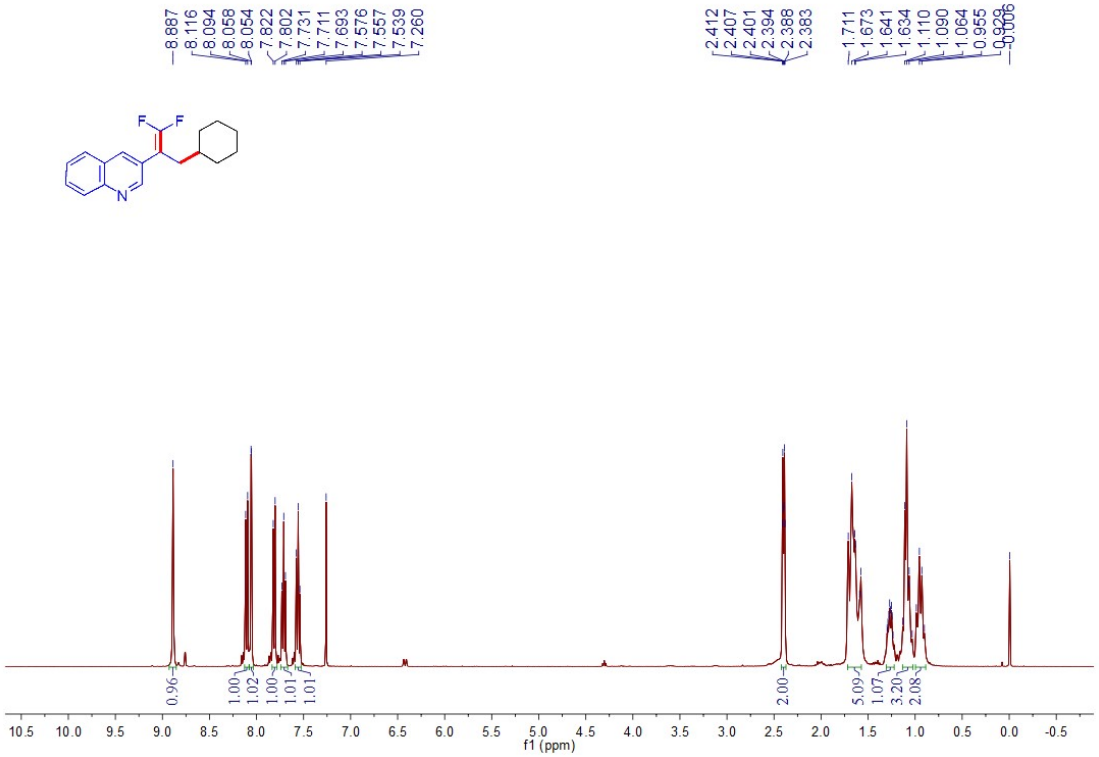
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4q**



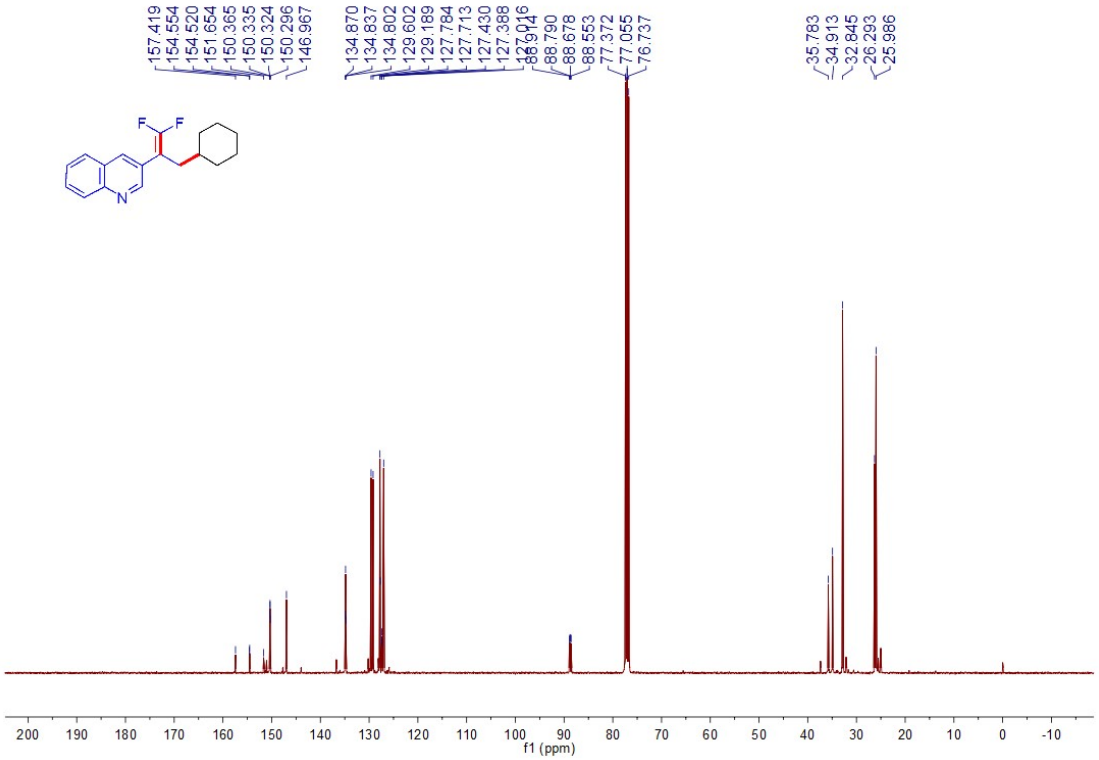
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4q**



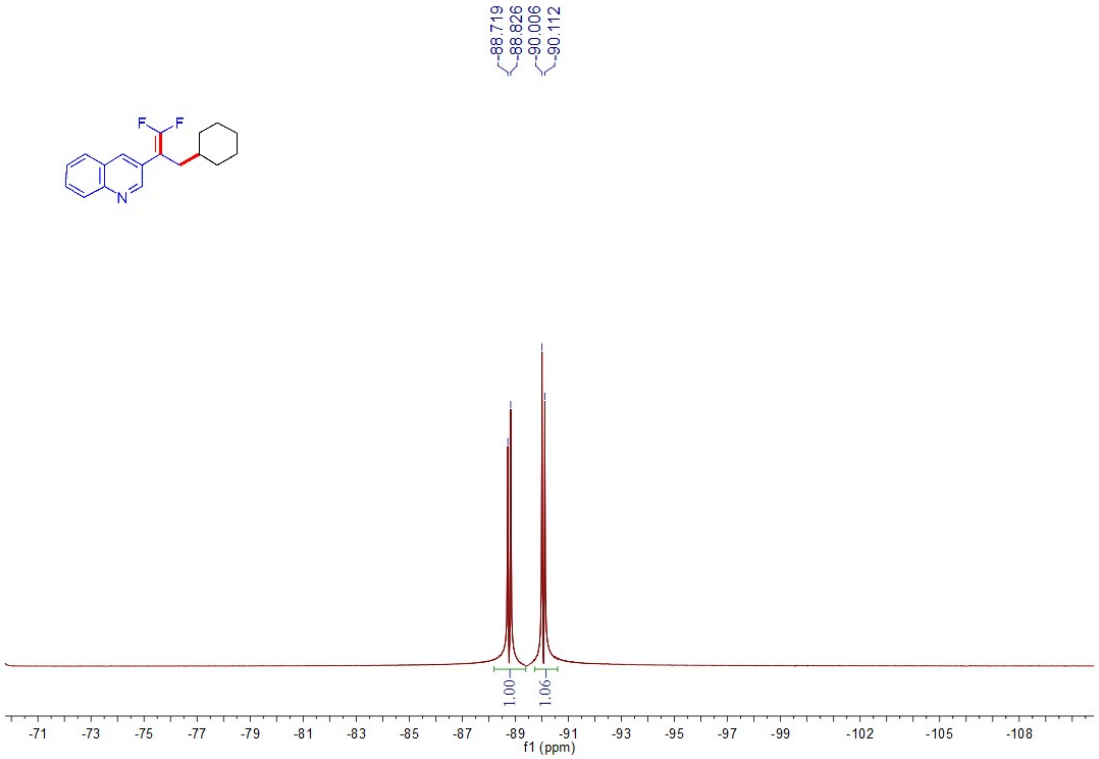
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4r**



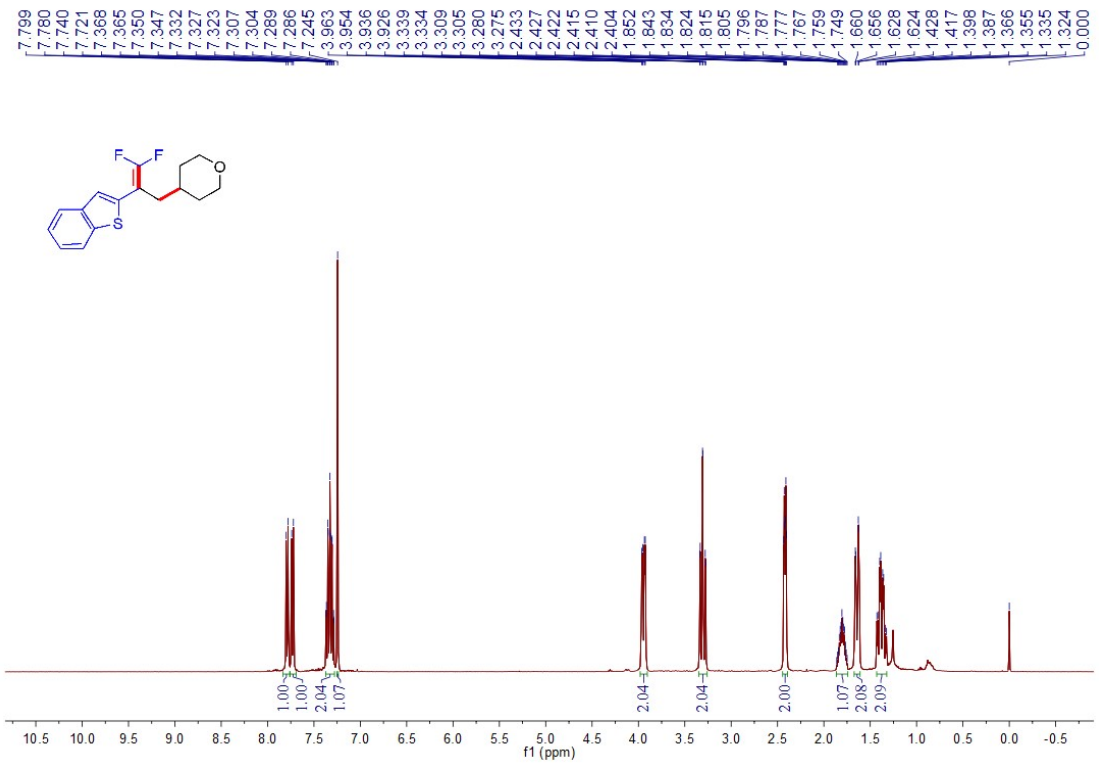
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4r**



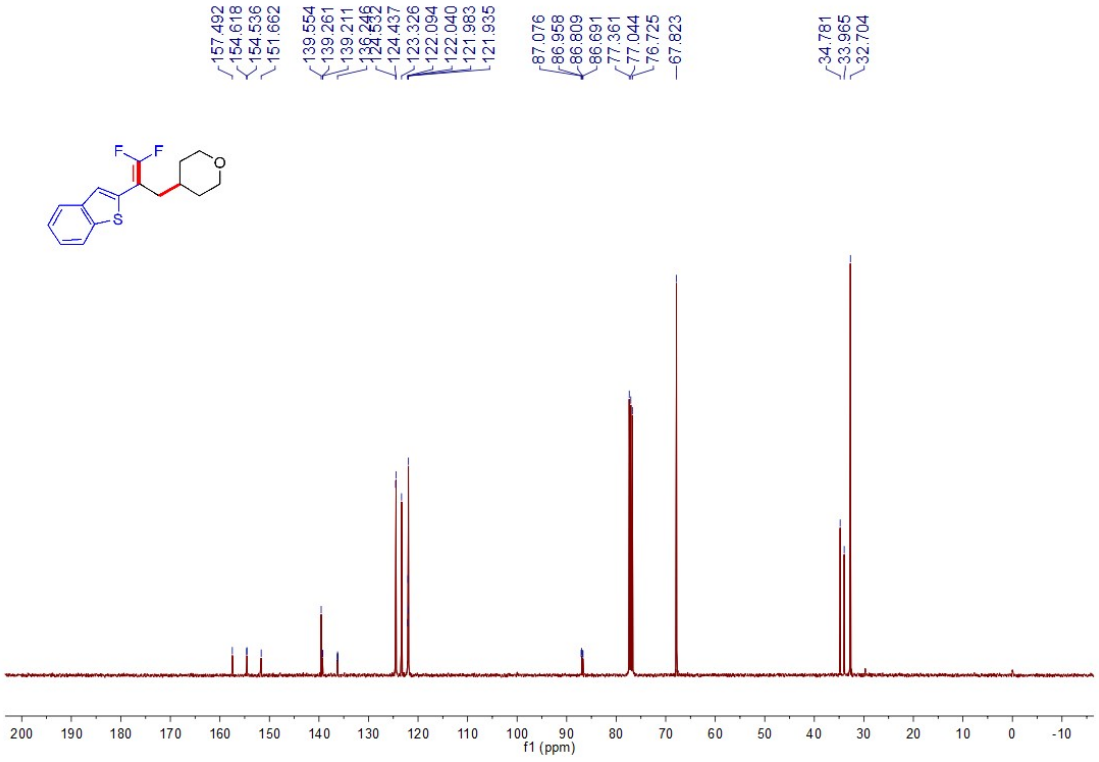
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4r**



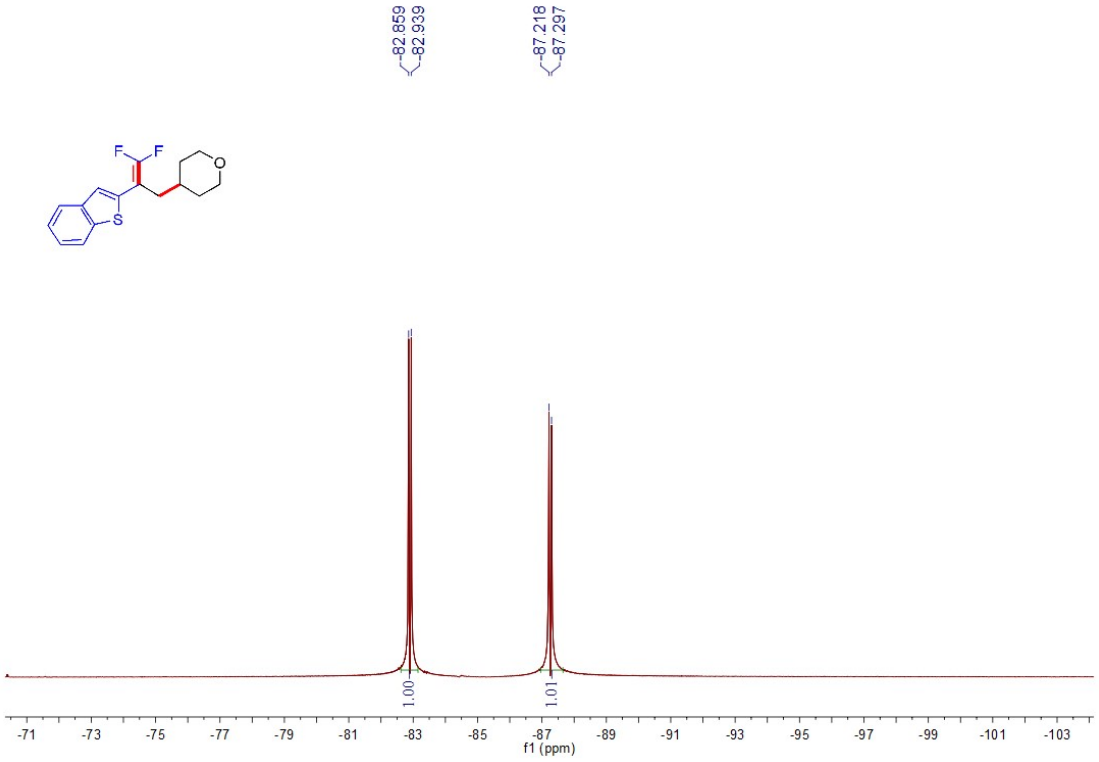
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4s**



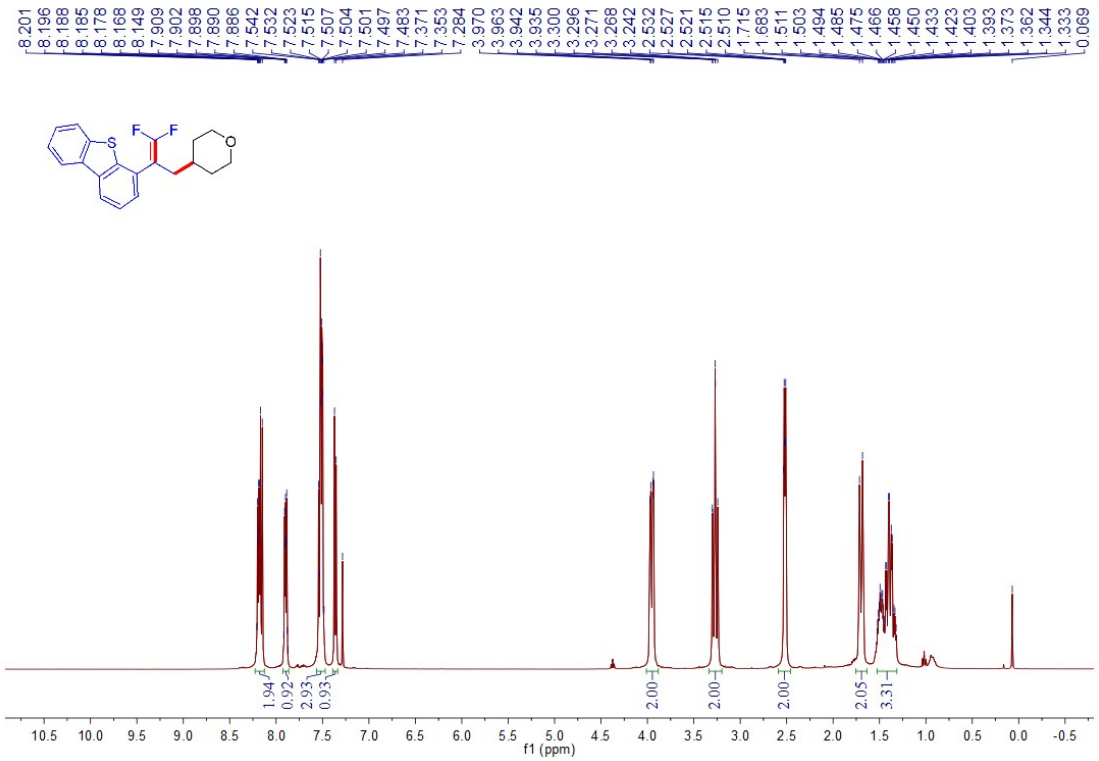
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4s**



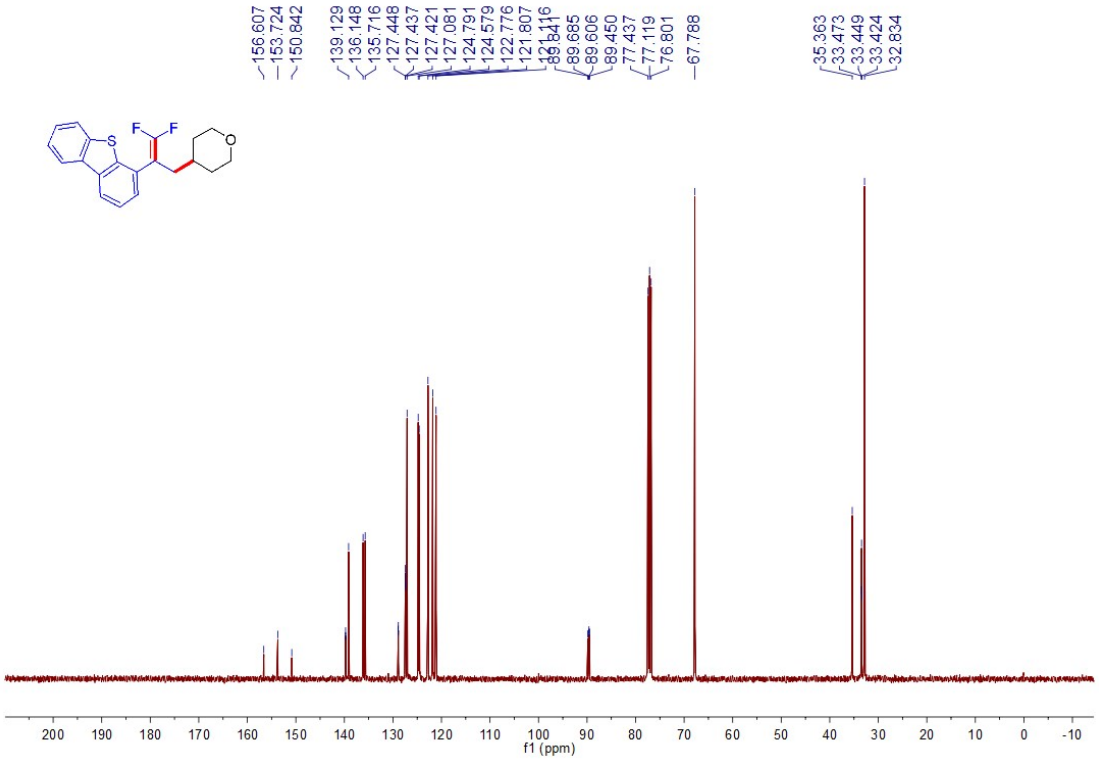
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4s**



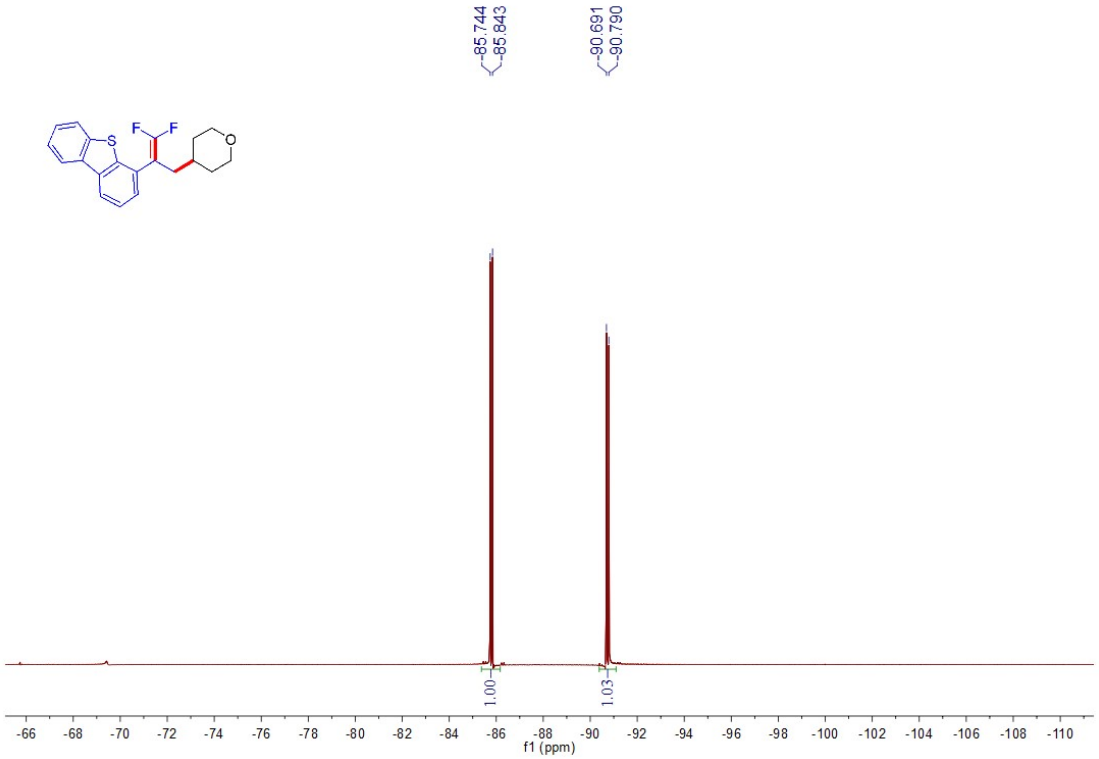
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4t**



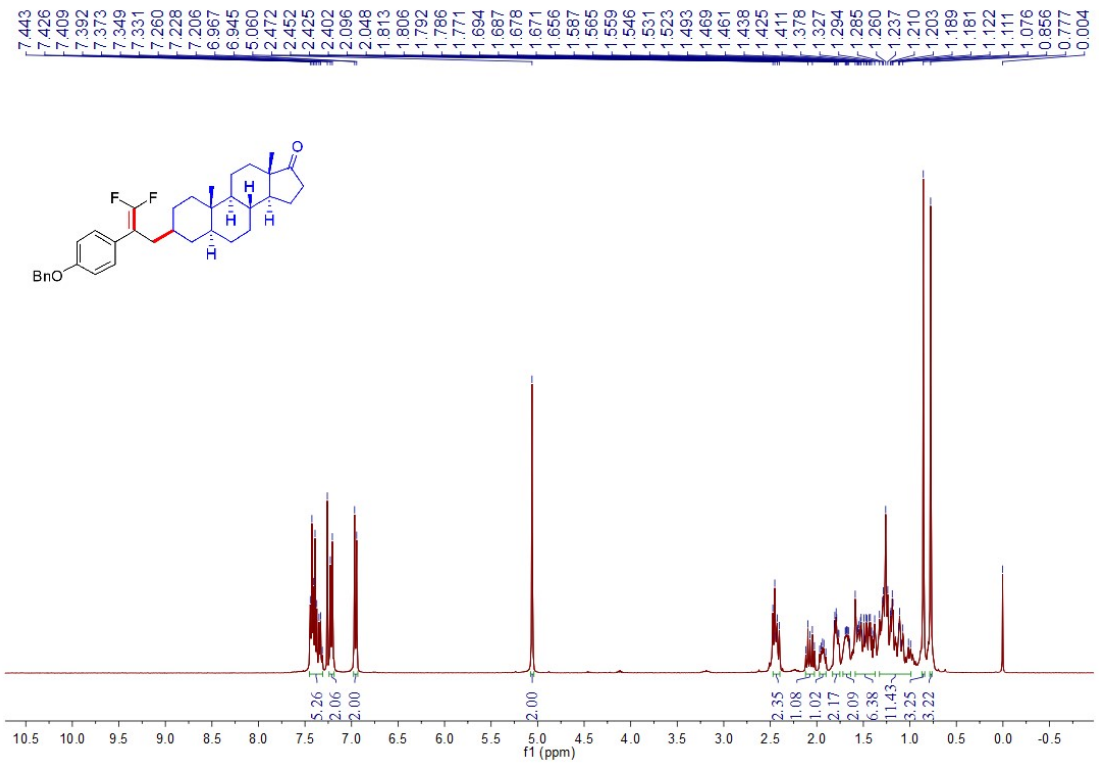
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4t**



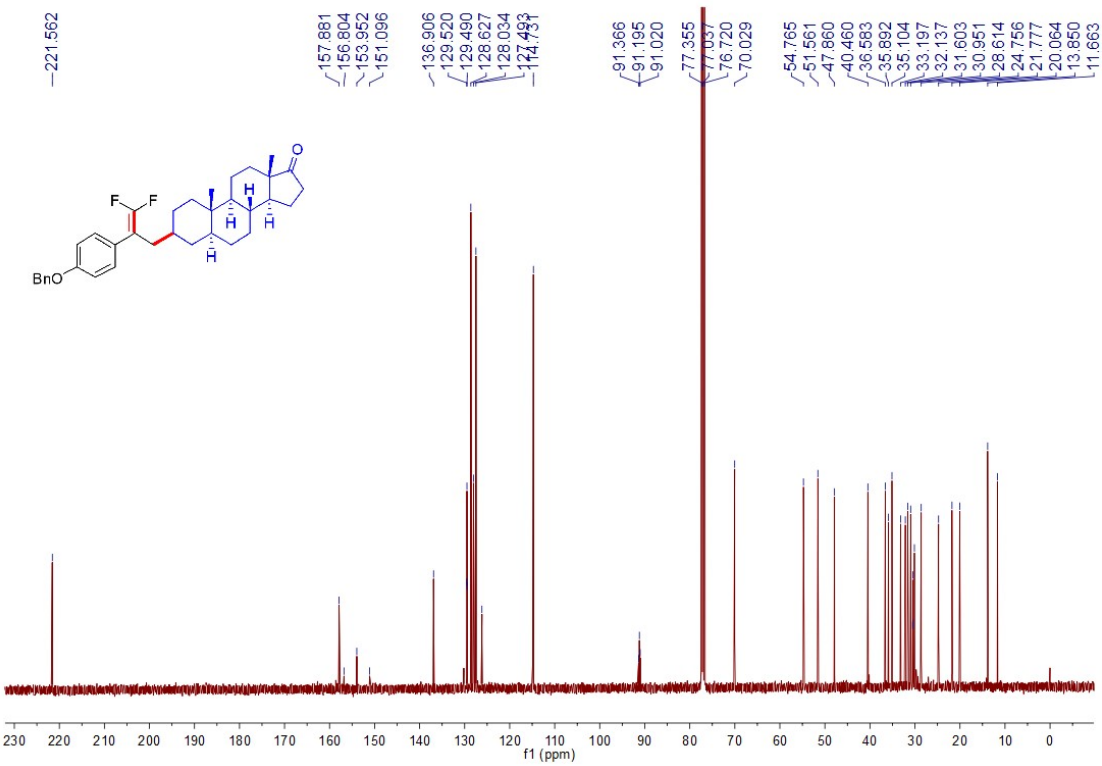
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4t**



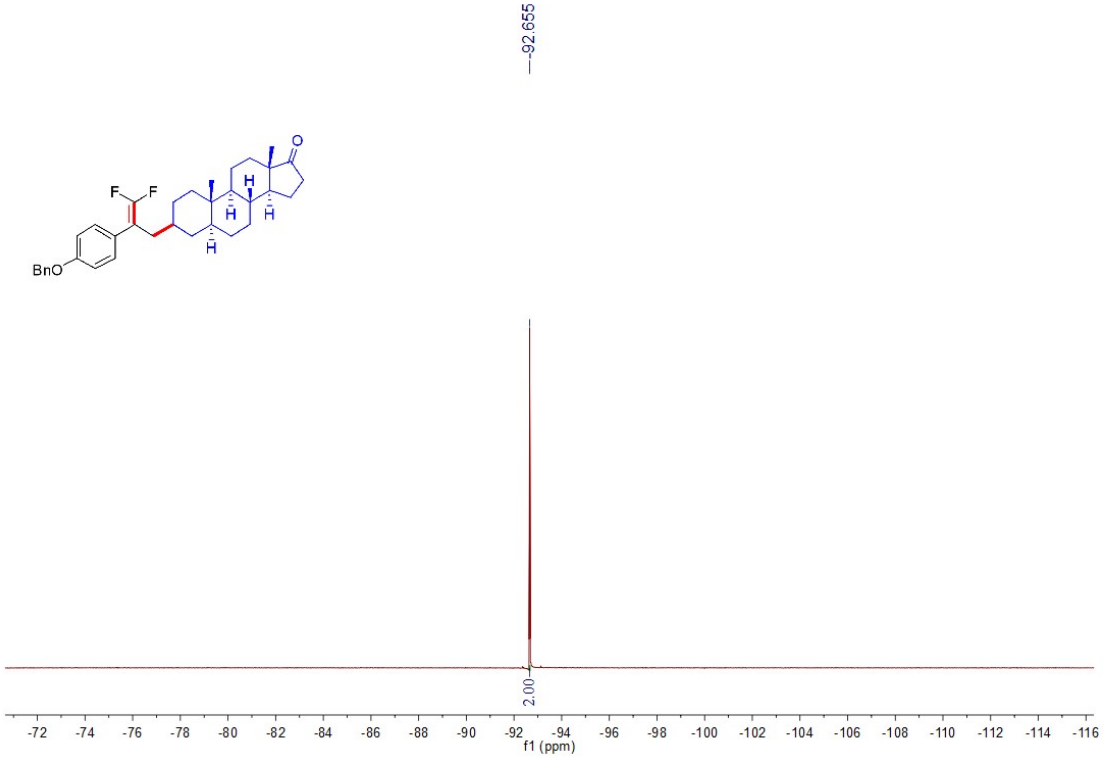
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a**



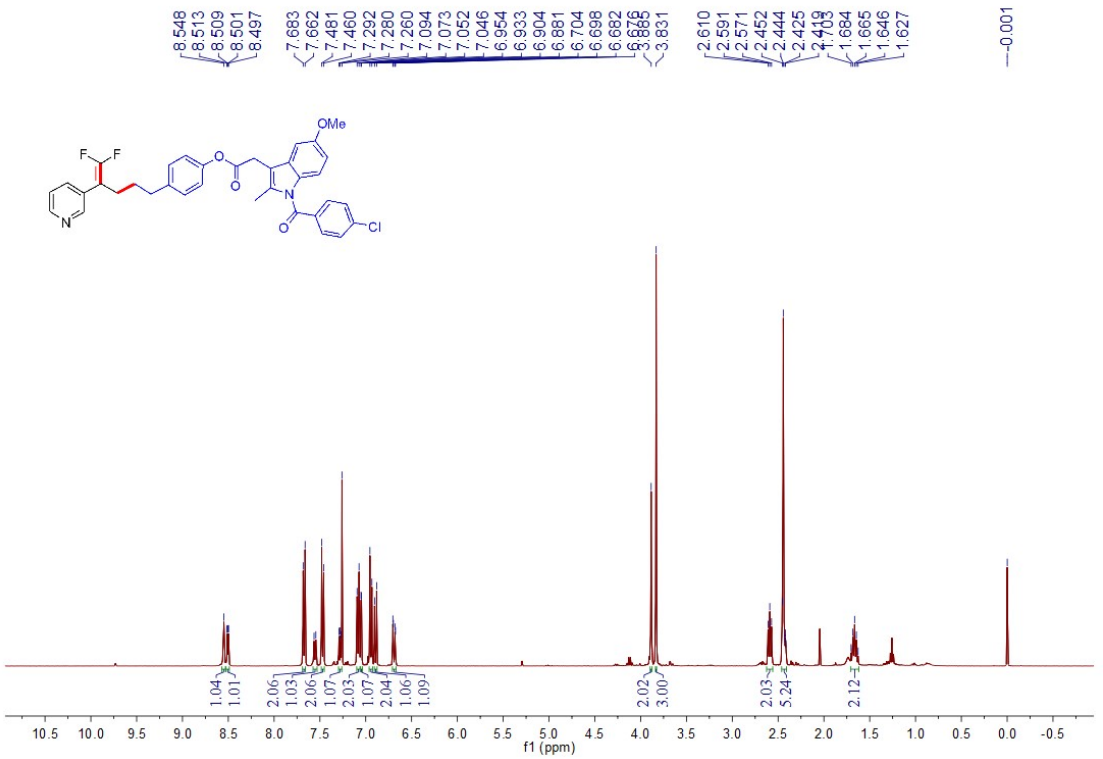
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5a**



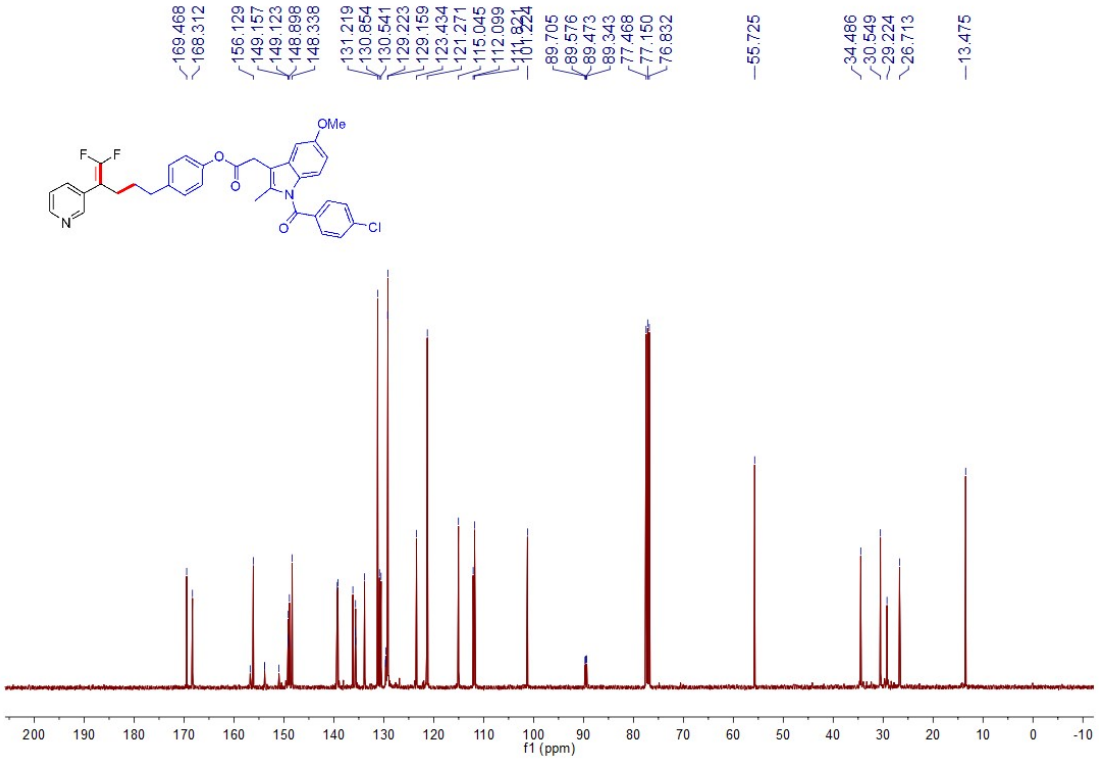
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5a**



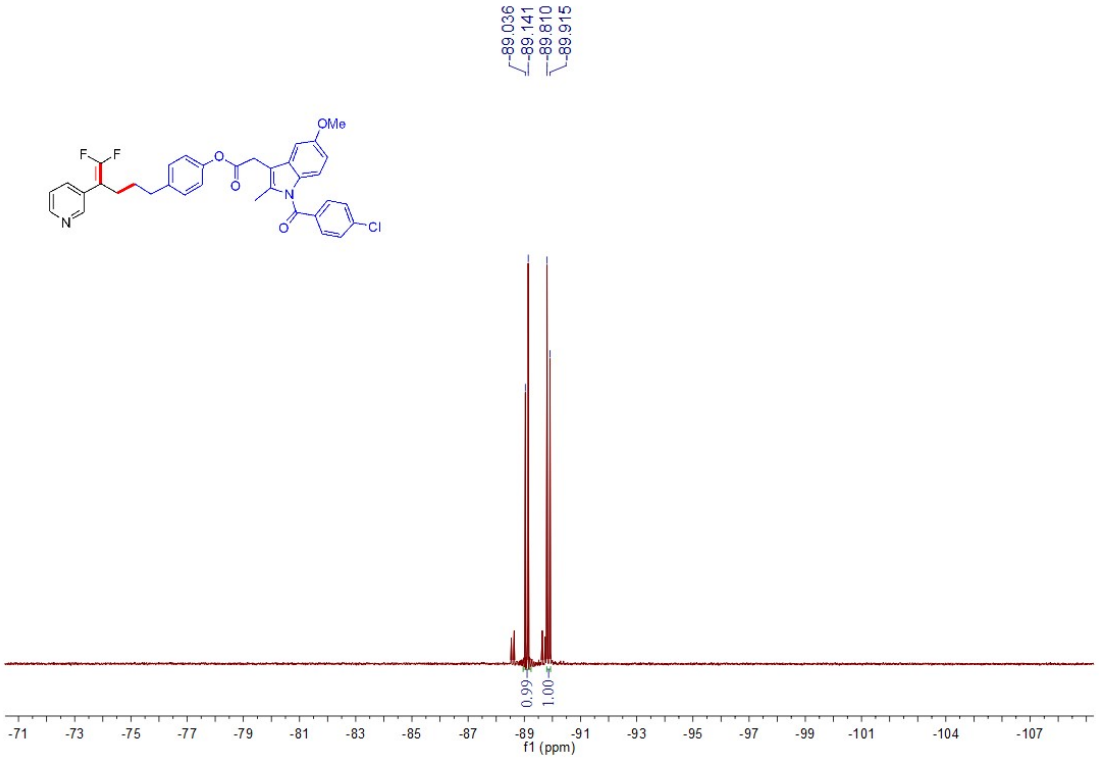
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b**



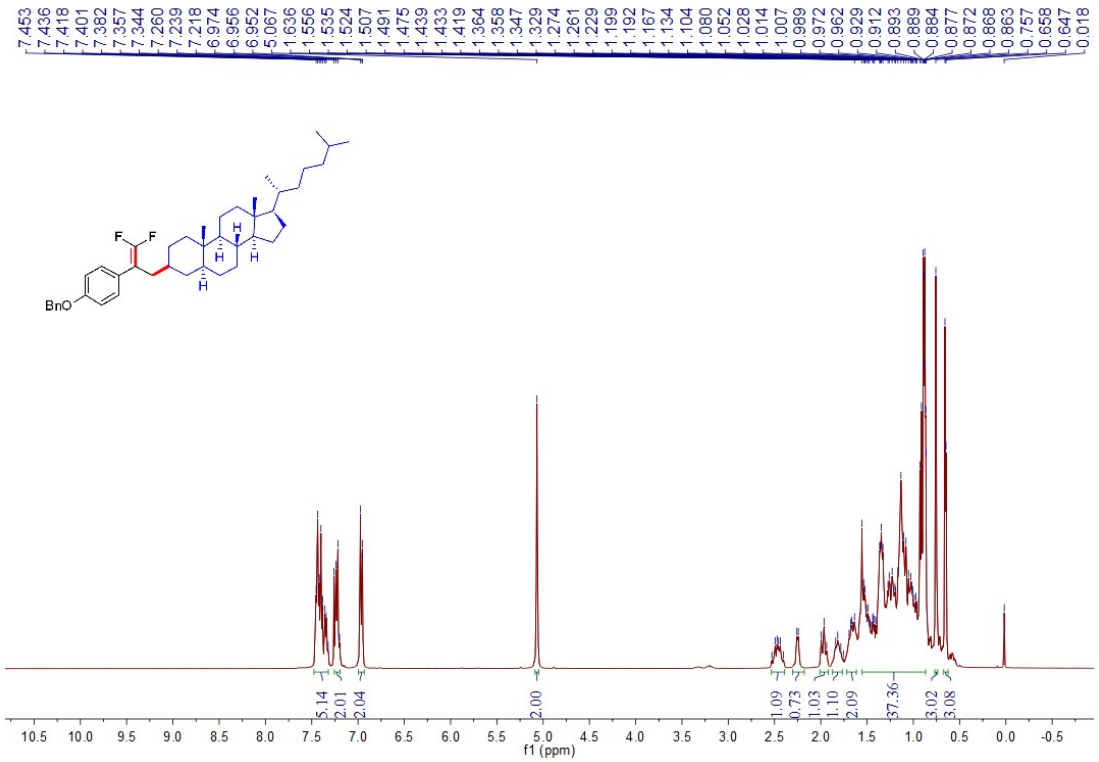
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5b**



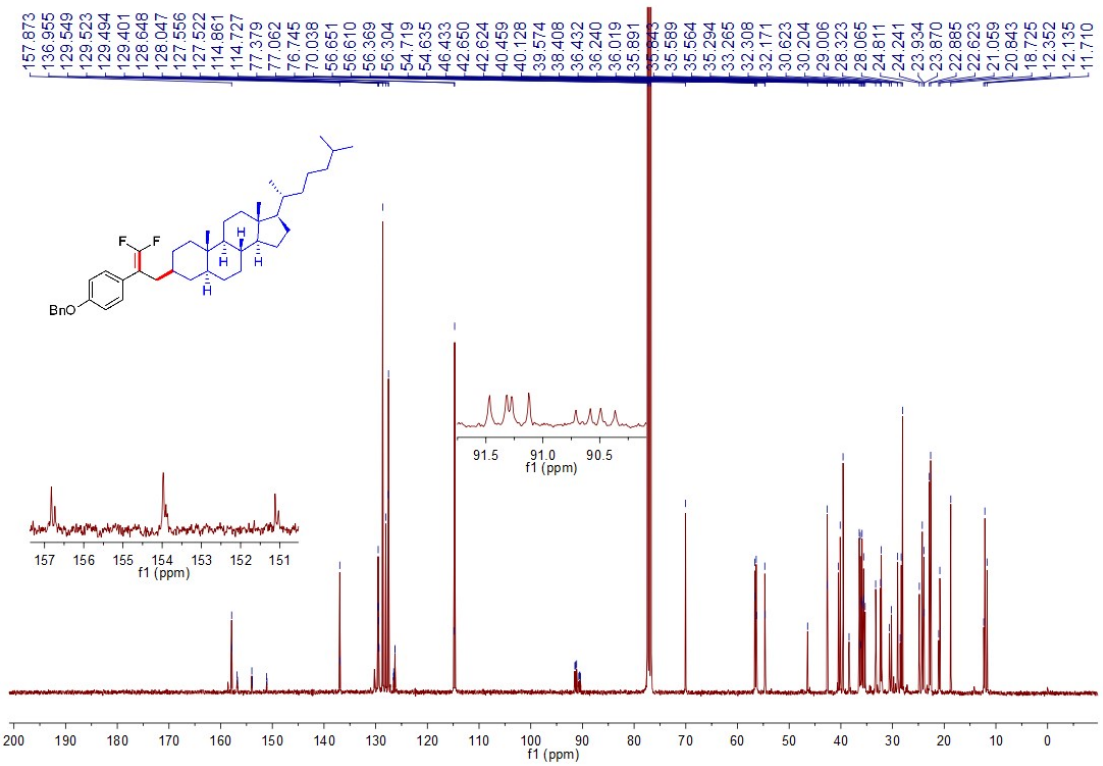
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5b**



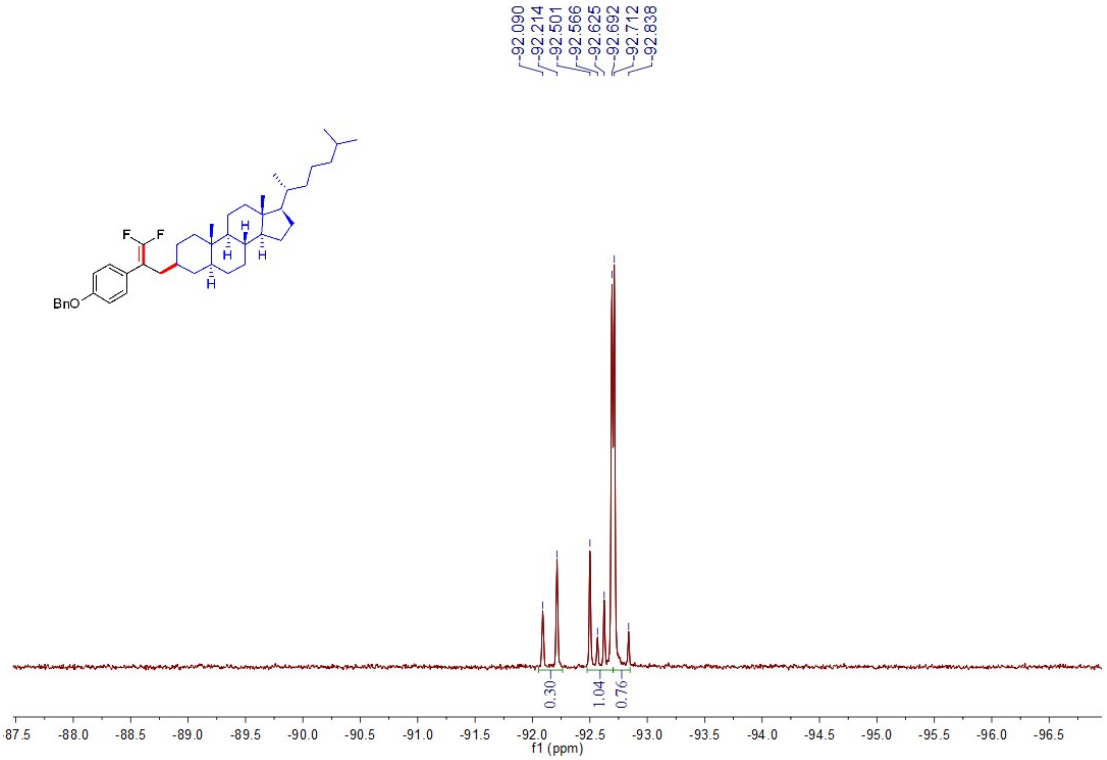
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5c**



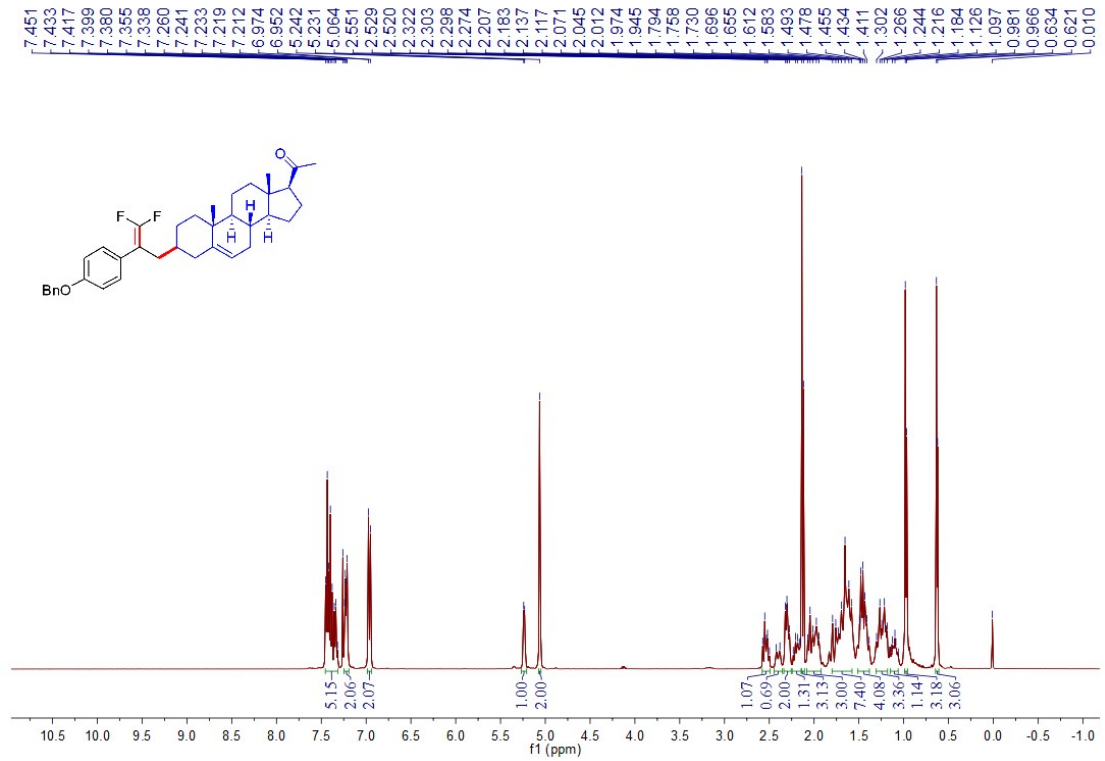
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5c**



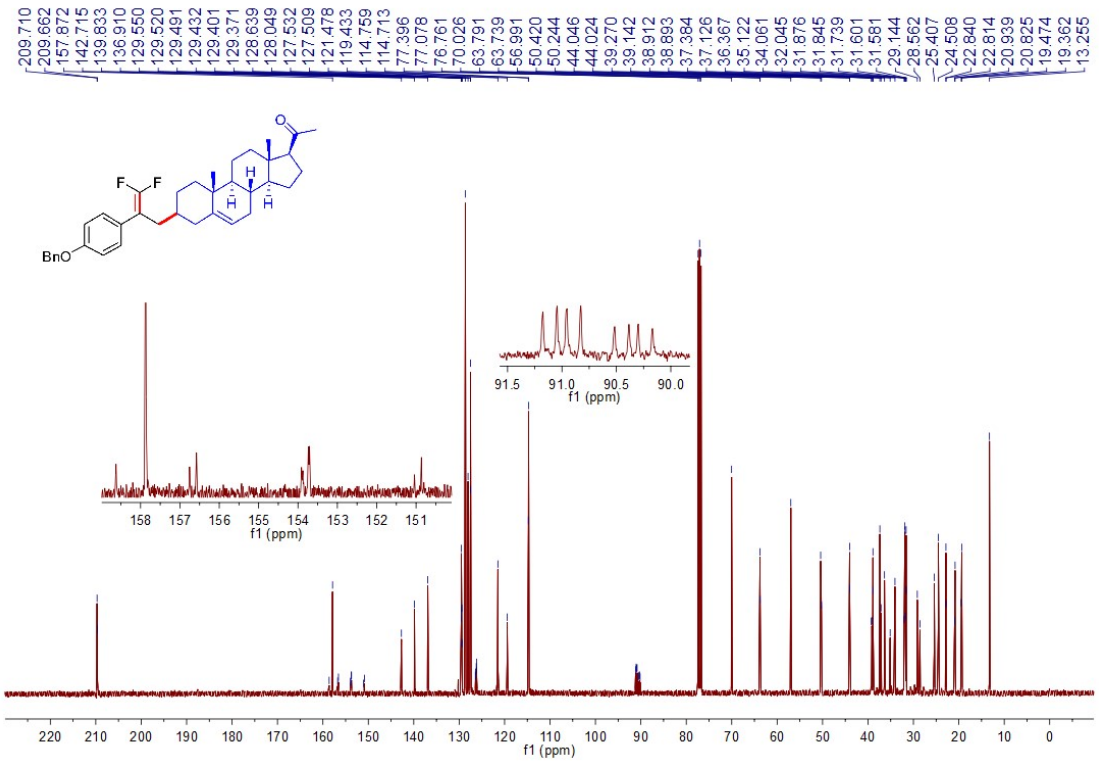
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5c**



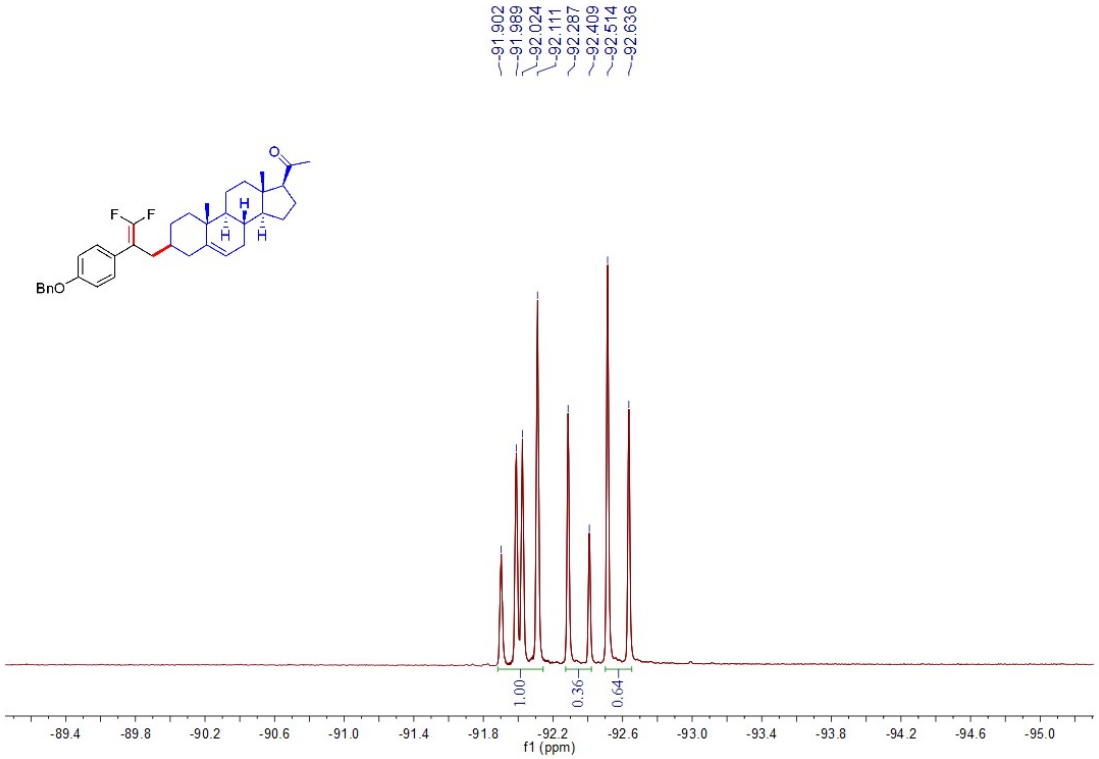
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5d**



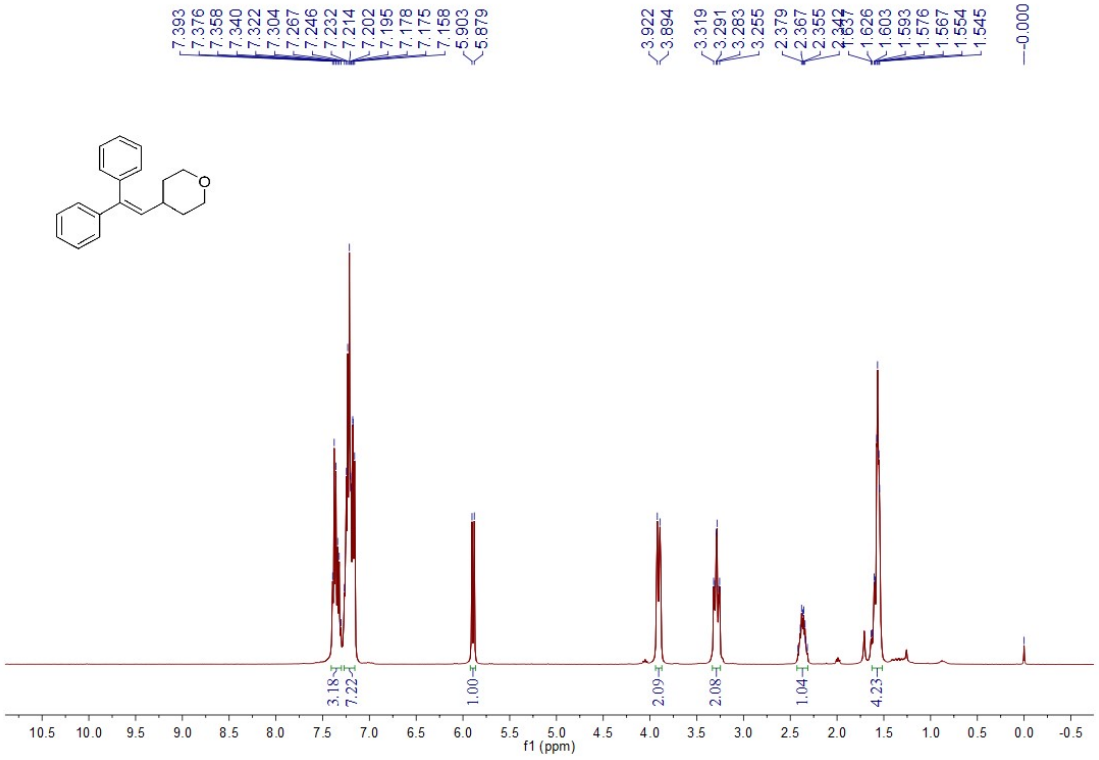
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5d**



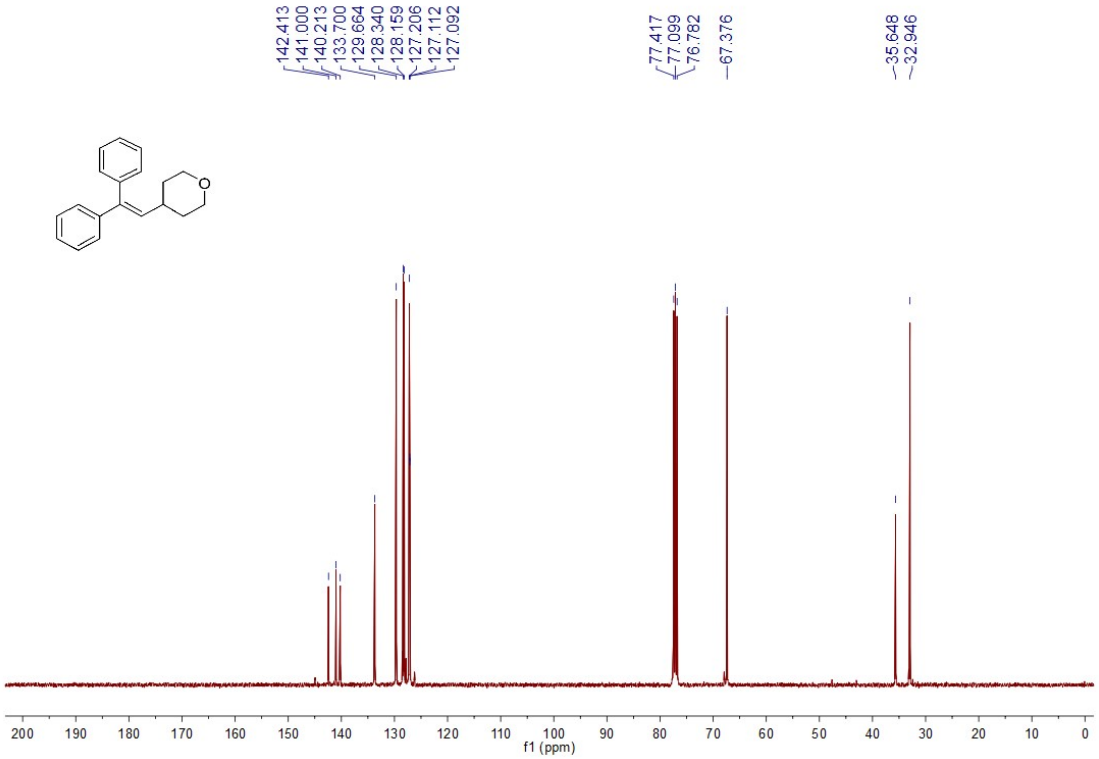
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5d**



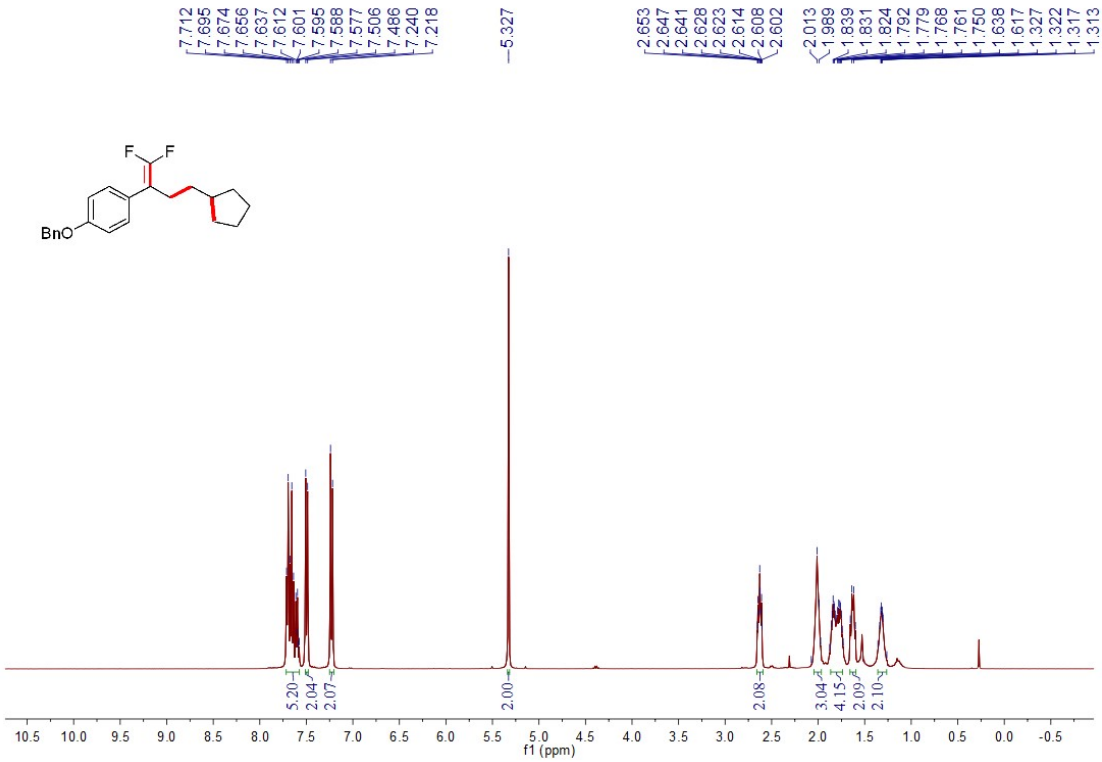
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6a**



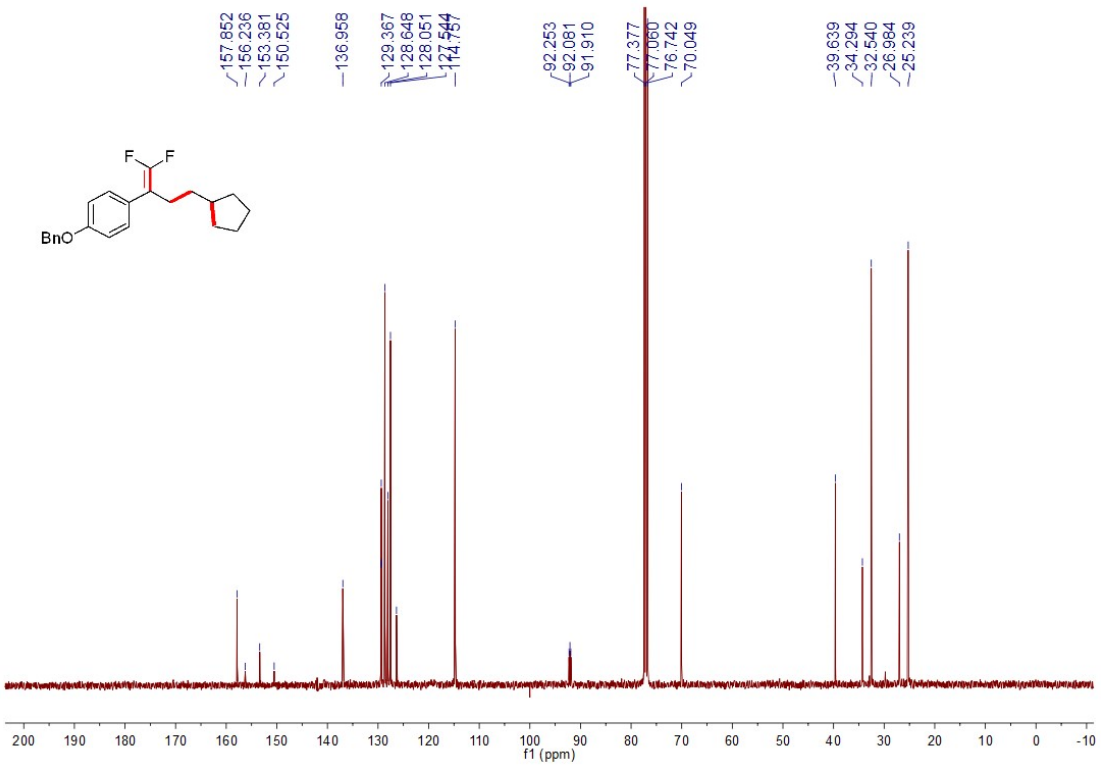
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6a**



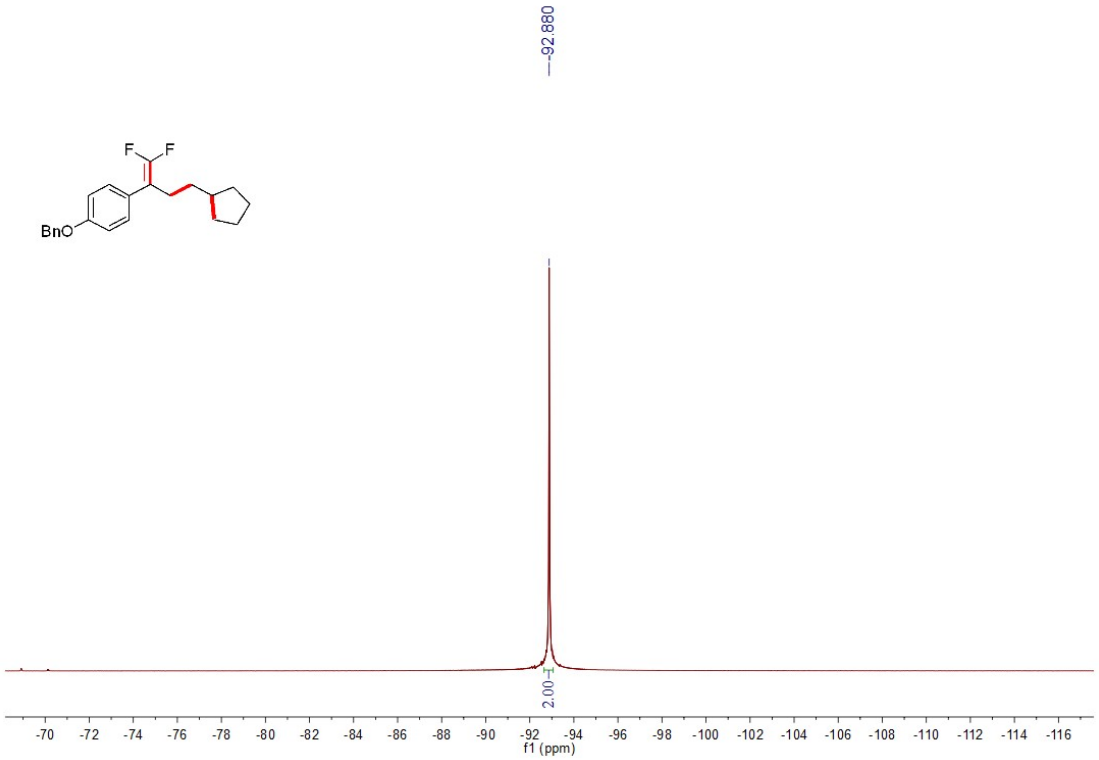
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **7**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **7**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **G**