Supporting Information

Nickel-Catalyzed Intramolecular Defluorinative [4+2] Cycloaddition for the Construction of Monofluoroarenes with *gem*-difluoroalkenes

Chuxing Wan, ‡ Min Cen, ‡ Tiantian Shi, Wangdong Wen, and Tao Wu*

School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi 330031, P. R. China.

taowu@ncu.edu.cn

目录

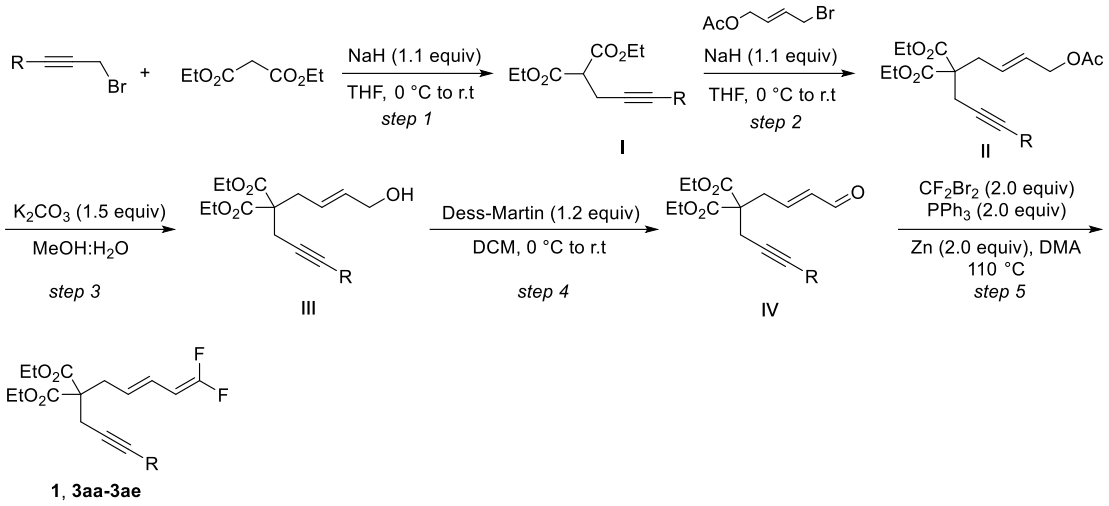
1. General information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Metal catalysts and ligands were obtained from Leyan, Bidepharm and Tansoole Chemical. All dry solvents were obtained from Energy Chemical. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas in dried glassware using standard vacuum-line techniques. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas in dried glassware using standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using silica gel HSGF254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200-300 mesh). Preparative thin-layer chromatography (PTLC) was performed using YanTai jiangyou chemical Plant HuangHai GF254 silica coated plates (0.20±0.03mm) prepared in our laboratory. Gas chromatography (GC) analysis was conducted on Agilent Technologies 7080A gaschromatography instrument with a FID detector with n-tetradecane as an internal standard. GC/MS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). The high-resolution mass spectra were conducted on 6545 Q-TOF LCMS instruments. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts for 1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual peak of $CDCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, td = triplet of doublets, q = quartet, m = multiplet, v = virtual coupling, br = broad signal), coupling constant (Hz), and integration.

2. General procedures for the synthesis of starting materials.

2.1 General procedure for the synthesis of *gem*-difluoroalkenes **1, 3aa-3ae** [1-4]



Diethyl malonate (1.0 equiv) was dissolved in anhydrous THF (10 mL) and added dropwise to a stirred suspension of NaH (1.1 equiv, 60% dispersion in mineral oil) in THF (40 mL) at 0 °C. After stirring for 30 min at the same temperature, propargyl bromide or an aryl-substituted propargyl bromide derivative (1.0 equiv) was added slowly. The mixture was stirred at 60 °C for 6 h, cooled to ambient temperature, and quenched with saturated aqueous sodium bicarbonate solution (10 mL). The mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford Compound **I**.

Compound I (1.0 equiv) was dissolved in anhydrous THF (10 mL) and added dropwise to a stirred suspension of NaH (1.1 equiv, 60% dispersion in mineral oil) in THF (40 mL) at 0 °C. After stirring for 30 min at the same temperature, (E)-4-bromobut-2-en-1-yl acetate (1.1 equiv) was added slowly. The mixture was stirred at 60 °C for 6 h, cooled to ambient temperature, and quenched with saturated aqueous sodium bicarbonate solution (10 mL). The mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford Compound II.

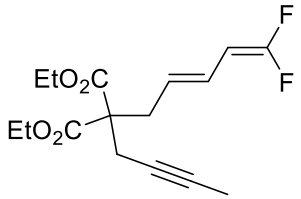
At room temperature, K_2CO_3 (1.5 equiv) was added to a solution of **II** (1.0 equiv) in MeOH: H_2O (9:1). The resulting mixture was stirred for 2 hours. After confirming complete consumption of the starting material by TLC, the mixture was concentrated to one-quarter of its original volume. The aqueous layer was extracted with EA (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to afford Compound **III**.

Compound III (1.0 equiv) was dissolved in anhydrous DCM (40 mL) and cooled to 0 °C. DMP (1.2 equiv) was added slowly. The mixture was stirred at ambient temperature for 2 h, then quenched by sequential addition of saturated aqueous sodium bicarbonate solution and saturated aqueous sodium thiosulfate solution. The mixture was extracted with DCM (3 × 20 mL). The

combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the enal product **IV**.

Compound IV (1.0 equiv) was dissolved in anhydrous DMA (20 mL) and cooled to 0 °C. A solution of CF_2Br_2 (2.0 equiv) in DMA (10 mL) was added, followed by the slow addition of solid PPh_3 (2.0 equiv). After stirring at 0 °C for 40 min, activated Zn powder (2.0 equiv) was introduced. The mixture was stirred at 110 °C for 2 h, then cooled to ambient temperature and quenched with H_2O (200 mL). After removal of the DMA, the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the gem-difluoroalkene product.

diethyl (E)-2-(but-2-yn-1-yl)-2-(5,5-difluoropenta-2,4-dien-1-yl) malonate (1)



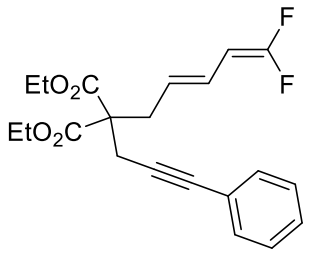
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.41 (dt, *J* = 15.0, 8.0 Hz, 1H), 4.88 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.16 (q, *J* = 8.0 Hz, 4H), 2.77 (s, 2H), 2.68 (d, *J* = 8.0 Hz, 2H), 1.72 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 156.2 (dd, *J* = 294.0, 289.0 Hz), 126.2 (dd, *J* = 12.0, 4.0 Hz), 123.1 (dd, *J* = 5.0, 2.0 Hz), 85.1, 81.8 (dd, *J* = 27.0, 17.0 Hz), 73.5, 61.5, 57.2, 35.6, 23.1, 14.1, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.3 (dd, *J* = 30.1, 3.8 Hz), -88.9 (d, *J* = 30.1 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{16}H_{29}F_2O_4$: 315.1402, found: 315.1401.

diethyl (E)-2-(5,5-difluoropenta-2,4-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl) malonate (3aa)



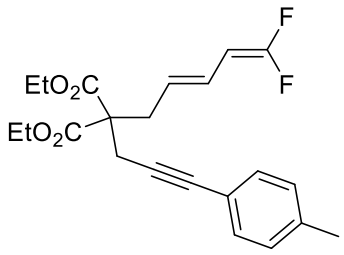
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.30 – 7.27 (m, 3H), 6.08 (dd, *J* = 16.2, 10.1 Hz, 1H), 5.49 (dt, *J* = 15.4, 7.7 Hz, 1H), 4.93 (dd, *J* = 24.4, 10.9 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 4H), 2.99 (s, 2H), 2.89 (d, *J* = 7.3 Hz, 2H), 1.6 (t, *J* = 8.0 Hz , 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 156.2 (dd, *J* = 294.0, 289.0 Hz), 131.6, 128.2, 128.0, 125.9 (dd, *J* = 12.0, 4.0 Hz), 123.3 (dd, *J* = 5.0, 2.0 Hz), 123.1, 84.1, 83.6, 81.7 (dd, *J* = 27.0, 17.0 Hz), 61.7, 57.2, 35.7, 23.6, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (dd, *J* = 30.1, 3.8 Hz), -87.5 (d, *J* = 30.1 Hz).

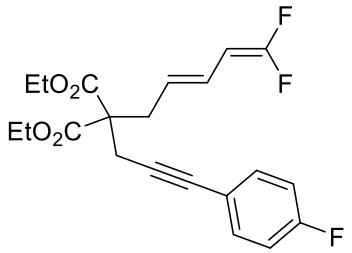
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{21}H_{22}F_2O_4Na$: 399.1378, found: 399.1377.

diethyl (E)-2-(5,5-difluoropenta-2,4-dien-1-yl)-2-(3-(p-tolyl) prop-2-yn-1-yl)malonate(3ab)



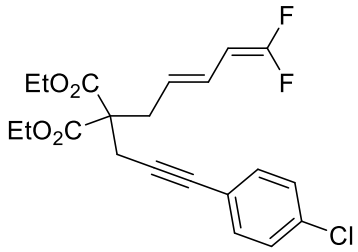
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J*= 8.0Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.06 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.49 (dt, *J* = 15.0, 8.0 Hz, 1H), 4.92 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 2.98 (s, 2H), 2.88 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 157.7 (dd, *J* = 292.0, 288.0 Hz), 138.1, 131.5, 129.0, 126.0 (dd, *J* = 11.0, 3.0 Hz), 123.3 (dd, *J* = 5.0, 1.0 Hz), 120.1, 83.8, 83.4, 81.8 (dd, *J* = 26.0, 16.0 Hz), 61.7, 57.3, 35.8, 23.8, 21.4, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -87.5 (d, *J* = 41.4 Hz), -90.4 (dd, *J* = 45.1, 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{24}F_2O_4Na$: 413.1535, found: 413.1530.

diethyl (E)-2-(5,5-difluoropenta-2,4-dien-1-yl)-2-(3-(4-fluorophenyl) prop-2-yn-1-yl)malonate (3ac)



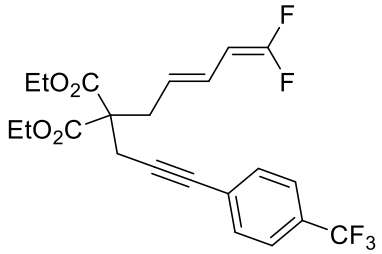
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.0, 6.0 Hz, 2H), 6.96 (dd, *J* = 9.0, 6.0 Hz, 2H), 6.07 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.49 (dt, *J* = 15.0, 8.0 Hz, 1H), 4.92 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 2.97 (s, 2H), 2.87 (d, *J* = 8.0 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 162.3 (d, *J* = 247.0 Hz), 156.2 (dd, *J* = 294.0, 289.0 Hz),133.4 (d, *J* = 8.0 Hz), 125.9 (dd, *J* = 11.0, 3.0 Hz), 123.3 (dd, *J* = 5.0, 2.0 Hz), 119.2 (d, *J* = 4.0 Hz), 115.4 (d, *J* = 22.0 Hz), 83.9, 82.6, 81.7 (dd, *J* = 27.0, 17.0 Hz), 61.6, 57.2, 35.8, 23.6, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -86.1 – -86.3 (m), -88.7 (dd, *J* = 29.1, 13.2 Hz), -111.5.
HRMS (ESI) $(M+H)^+$: Calcd for $C_{21}H_{22}F_3O_4$: 395.1465, found: 395.1462.

diethyl (E)-2-(3-(4-chlorophenyl)prop-2-yn-1-yl)-2-(5,5-difluoropenta-2,4-dien-1-yl)malonate (3ad)



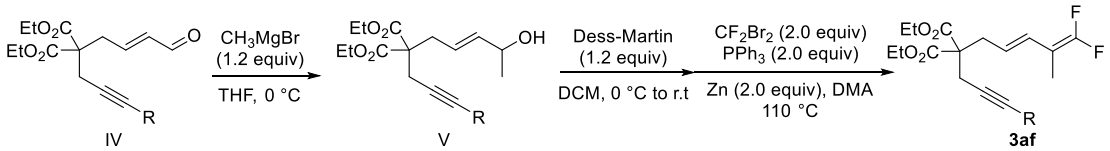
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.07 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.48 (dt, *J* = 16.0, 8.0 Hz, 1H), 4.92 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 2.98 (s, 2H), 2.87 (d, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 156.2 (dd, *J* = 294.0, 289.0 Hz),131.6, 128.2, 128.0, 125.9 (dd, *J* = 11.0, 3.0 Hz), 123.3 (dd, *J* = 4.0, 1.0 Hz), 123.1, 84.2, 83.7, 81.7 (dd, *J* = 26.0, 16.0 Hz), 61.7, 57.3, 35.8, 23.7, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (dd, *J* = 30.1, 26.3 Hz), -87.5 (d, *J* = 29.0 Hz).
HRMS (ESI) $(M+H)^+$: Calcd for $C_{21}H_{22}ClF_2O_4$: 411.1169, found: 411.1166.

diethyl (E)-2-(5,5-difluoropenta-2,4-dien-1-yl)-2-(3-(4-(trifluoromethyl) phenyl) prop-2-yn -1-yl) malonate(3ae)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.07 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.47 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.92 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 4H), 3.01 (s, 2H), 2.87 (d, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 156.3 (dd, *J* = 294.0, 289.0 Hz), 131.8, 129.7 (q, *J* = 32.7 Hz), 126.9, 125.7 (dd, *J* = 11.0, 3.0 Hz), 125.2 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 269.0 Hz), 123.5 (dd, *J* = 5.0, 2.0 Hz), 87.0, 82.4, 81.7 (dd, *J* = 27.0, 16.0 Hz), 61.8, 57.1, 35.8, 23.7, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9, -86.0 (dd, *J* = 30.1, 26.3 Hz), -88.5 (d, *J* = 30.1 Hz).
HRMS (ESI) $(M+H)^+$: Calcd for $C_{22}H_{22}F_5O_4$: 445.1433, found: 445.1425.

2.2 The procedure for the synthesis of *gem*-difluoroalkenes **3af** [5]

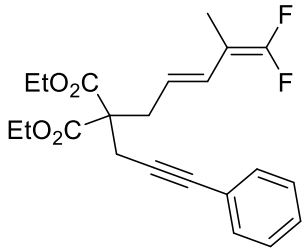


Under a N_2 atmosphere, a 250 mL round-bottom flask equipped with a stir bar was cooled to 0 °C. The aldehyde IV from procedure 2.1 (1.0 equiv) was added, followed by slow addition of CH_3MgBr (3.0 M in THF, 1.2 equiv). The mixture was stirred at 0 °C for 30 minutes and then allowed to warm to room temperature and stirred for 6 hours. The reaction was quenched with

saturated aqueous NH_4Cl solution (20 mL), and the organic layer was separated. The aqueous layer was extracted with EA (3×20 mL). The combined organic layers were washed with saturated NaCl solution (3×10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the alcohol compound **V**.

Following Steps 4 and 5 of General Procedure 2.1, Compound V was transformed into substrate **3af**.

diethyl (E)-2-(5,5-difluoro-4-methylpenta-2,4-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (3af)



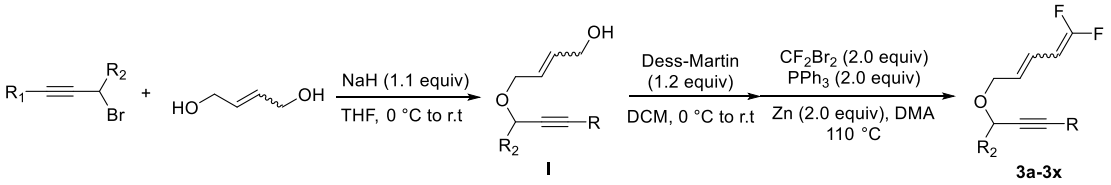
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.30-7.26 (m, 3H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.47 – 5.40 (m, 1H), 4.22 (q, *J*= 8.0 Hz 4H), 3.00 (s, 2H), 2.92 (d, *J* = 8.0 Hz, 2H), 1.66 (t, *J* = 3.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 156.2 (dd, *J* = 294.0, 289.0 Hz), 138.1, 131.6, 129.0, 126.1 (dd, *J* = 11.0, 3.0 Hz), 123.4(dd, *J* = 11.0, 3.0 Hz), 120.2, 83.8, 83.5, 81.8 (dd, *J* = 26.0, 16.0 Hz), 61.7, 57.4, 35.9, 23.8, 21.5, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.5 (d, *J* = 37.6 Hz), -92.8 (d, *J* = 37.6 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{24}F_2O_4Na$: 413.1535, found: 413.1533.

2.3 General procedure for the synthesis of *gem*-difluoroalkenes **3a** to **3x** [4,6]

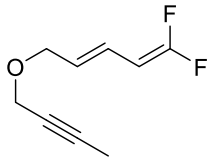


Under a nitrogen atmosphere, a dry 250 mL two-necked round-bottom flask equipped with a stir bar was cooled to 0 °C. A solution of trans or cis-2-butene-1,4-diol (5.0 equiv) in THF (10 mL) was added dropwise to a suspension of NaH (1.5 equiv, 60% dispersion in oil) in THF (40 mL). After addition, the mixture was stirred for an additional 30 minutes. Propargyl bromide aryl-substituted propargyl bromide (1.0 equiv) was then slowly added, and the reaction mixture was allowed to warm to room temperature and stirred overnight. Complete consumption of the starting material was confirmed by TLC. After cooling the reaction, it was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with EA (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to afford allylic alchols I.

Following Steps 4 and 5 of General Procedure 2.1, these allylic alcohols **I** was transformed

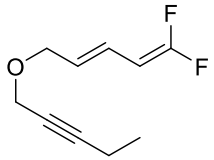
into substrate **3a-3x**.

(E)-5-(but-2-yn-1-yloxy)-1,1-difluoropenta-1,3-diene (3a)



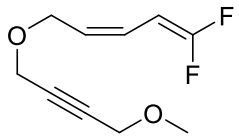
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.70 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.97 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.10 (s, 2H), 4.06 (d, *J* = 6.0 Hz, 2H), 1.86 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295, 289.0 Hz), 127.9 (dd, *J* = 10.0, 3.0 Hz), 122.2 (dd, *J* = 5.0, 2.0 Hz), 82.7, 81.4 (dd, *J* = 20.0, 10.0 Hz), 74.9, 69.6, 57.8, 3.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -87.5 (d, *J* = 41.3 Hz), -90.4 (dd, *J* = 45.1, 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_9H_{10}F_2ONa$: 195.0592, found: 195.0583.

(E)-1,1-difluoro-5-(pent-2-yn-1-yloxy) penta-1,3-diene (3b)



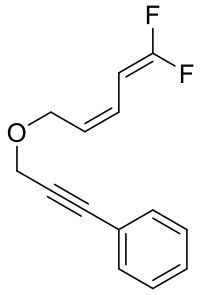
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.70 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.96 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.11 (s, 2H), 4.05 (d, *J* = 6.0 Hz, 2H), 2.23 (m, 2H), 1.20 (t, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0,289.0 Hz), 127.9 (dd, *J* = 11.0, 3.0 Hz), 122.2 (dd, *J* = 5.0, 2.0 Hz), 82.7, 81.5 (dd, *J* = 27.0, 16.0 Hz), 74.9, 69.6, 64.9, 57.8, 3.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (d, *J* = 41.3 Hz), -87.5 (dd, *J* = 45.1, 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{10}H_{12}F_2ONa$: 209.0748, found: 209.0753.

(Z)-1,1-difluoro-5-(4-methoxybut-2-yn-1-yl)oxy)penta-1,3-diene (3c)



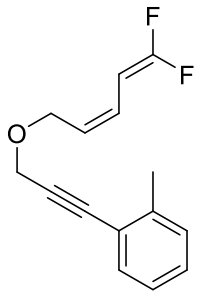
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.69 (dt, *J* = 12.0, 6.0 Hz, 1H), 4.98 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.20 (s, 2H), 4.15 (s, 2H), 4.08 (d, *J* = 6.0 Hz, 2H), 3.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (dd, *J* = 295.0, 289.0 Hz), 127.9 (dd, *J* = 20.0, 10.0 Hz), 122.1 (d, *J* = 10.0 Hz), 88.5, 81.5 (dd, *J* = 27.0, 17.0 Hz), 75.0, 69.5, 57.7, 13.7, 12.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (t, *J* = 26.3 Hz), -87.1 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{10}H_{12}F_2O_2Na$: 225.0698, found: 225.0694.

(Z)-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl) benzene (3d)



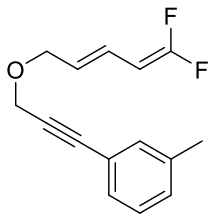
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.0, 3.0 Hz, 2H), 7.32 (dd, *J* = 5.0, 2.0 Hz, 3H), 6.24 (dd, *J* = 12.0, 11.0 Hz, 1H), 5.74 (dt, *J* = 12.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.38 (s, 2H), 4.16 (d, *J* = 6.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 131.7, 128.5, 128.3, 127.8 (dd, *J* = 11.0, 3.0 Hz), 122.6, 122.4 (dd, *J* = 5.0, 2.0 Hz), 86.4, 84.9, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.8, 57.9
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (t, *J* = 26.3 Hz), -87.5 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{14}H_{12}F_2ONa$: 257.0748, found: 257.0740.

(Z)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl)-2-methylbenzene (3e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7 Hz, 1H), 6.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.74 (dt, *J* = 12.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.42 (s, 2H), 4.18 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 140.3, 132.1, 129.4, 128.5, 127.8 (dd, *J* = 11.0, 3.0 Hz), 125.5, 122.4 (d, *J* = 4.0 Hz), 88.7, 85.3, 81.5 (dd, *J* = 27.0, 17.0 Hz), 69.6, 65.0, 58.0, 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{14}F_2ONa$: 271.0905, found: 271.0909.

(E)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl)-3-methylbenzene (3f)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.14 (t, *J* = 7.0 Hz,

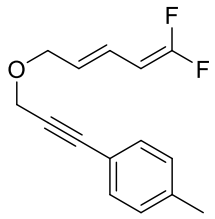
1H), 6.25 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.43 (s, 2H), 4.18 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 138.6, 131.7, 129.0, 127.8 (dd, *J* = 11.0, 3.0 Hz), 122.0 (dd, *J* = 5.0, 2.0 Hz), 121.3, 119.5, 86.6, 84.1, 81.5 (dd, *J* = 27.0, 17.0 Hz), 69.7, 64.9, 58.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.3 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{14}F_2ONa$: 271.0905, found: 271.0911.

(E)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl)-4-methylbenzene (3g)



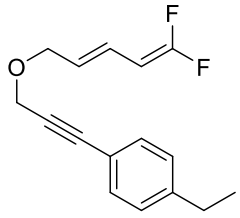
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.14 (td, *J* = 7.0, 2.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.75 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.43 (s, 2H), 4.18 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 290.0 Hz), 132.2, 132.0, 127.4 (dd, *J* = 11.0, 2.0 Hz), 122.6 (dd, *J* = 5.0, 1.0 Hz), 118.3, 111.9, 89.5, 84.7, 81.4 (dd, *J* = 27.0, 16.0 Hz), 70.1, 65.4, 57.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (dd, *J* = 26.3, 22.2 Hz), -87.3. (d, *J* = 26.3 Hz)

HRMS (ESI) $(M+K)^+$: Calcd for $C_{15}H_{14}F_2OK$: 287.0644, found: 287.0650.

(E)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl)-4-ethylbenzene (3h)



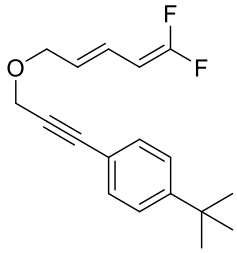
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.23 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.38 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 2H), 2.65 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 138.6, 131.7, 129.0, 127.8 (dd, *J* = 11.0, 3.0 Hz), 122.3 (dd, *J* = 5.0, 2.0 Hz), 119.5, 86.6, 84.1, 81.5 (dd, *J* = 28.0, 17.0 Hz), 69.7, 64.9, 58.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz).

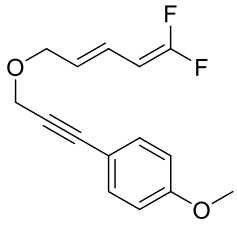
HRMS (ESI) $(M+K)^+$: Calcd for $C_{16}H_{16}F_2OK$: 301.0801, found: 301.0791.

(E)-1-(tert-butyl)-4-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl) benzene (3i)



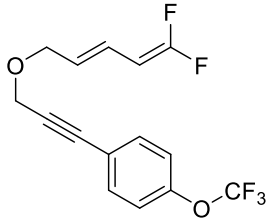
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 6.23 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.75 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.38 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 2H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 151.7, 131.5, 127.9 (dd, *J* = 11.0, 3.0 Hz), 125.3, 122.3 (dd, *J* = 5.0, 2.0 Hz), 119.5, 86.6, 84.1, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.7, 58.0, 34.7, 31.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.5 (t, *J* = 26.3 Hz), -87.5 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{18}H_{20}F_2ONa$: 313.1374, found: 313.1383.

(E)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl)-4-methoxybenzene (3j)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0, Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.25 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.36 (s, 2H), 4.14 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 290.0 Hz), 132.2, 132.0, 127.4 (dd, *J* = 11.0, 2.0 Hz), 122.6 (dd, *J* = 12.0 ,5.0 Hz), 118.3, 111.9, 89.5, 84.7, 81.5 (dd, *J* = 27.0, 16.0 Hz), 70.1, 65.4, 57.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{14}F_2O_2Na$: 287.0854, found: 287.0863.

(E)-1-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl)-4-(trifluoromethoxy) benzene (3k)



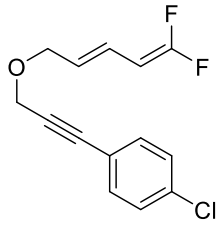
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.24 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.73 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.37 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 133.3, 127.6 (dd, *J* = 11.0, 3.0 Hz), 122.5 (dd, *J* = 5.0, 2.0 Hz), 120.8, 121.3, 120.4 (q, *J* = 215.0 Hz), 85.8, 85.0, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.9, 65.1, 57.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9, -85.2 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{12}F_5O_2$: 319.0752, found: 319.0744.

(E)-1-chloro-4-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl) benzene (3l)



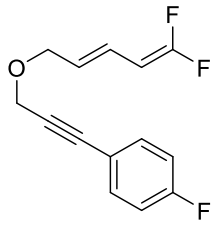
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.73 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.39 (s, 2H), 4.14 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz),131.8, 128.5, 128.3, 127.8 (dd, *J* = 11.0, 3.0 Hz), 122.6, 122.4 (dd, *J* = 5.0, 2.0 Hz), 86.4, 84.9, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.8, 57.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.5 (d, *J* = 41.3 Hz), -90.4 (dd, *J* = 45.1, 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{14}H_{11}ClF_2ONa$: 291.0359, found: 291.0352.

(E)-1-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl)-4-fluorobenzene (3m)



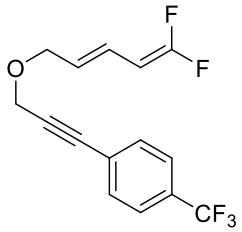
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.04 - 6.98 (m, 2H), 6.24 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.73 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 25.0, 11.0 Hz, 1H), 4.36 (s, 2H), 4.14 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 248.0 Hz), 156.7 (dd, *J* = 295.0, 290.0 Hz), 127.5 (dd, *J* = 11.0, 3.0 Hz), 122.5 (dd, *J* = 5.0, 2.0 Hz), 114.7 (d, *J* = 27.0 Hz), 104.5 (t, *J* = 25.0 Hz), 87.1, 84.1, 81.5 (dd, *J* = 27.0, 16.0 Hz), 70.0, 65.3, 57.6

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.11 – -86.3 (m), -88.7 (dd, *J* = 30.1, 11.3 Hz), -111.6.

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{14}H_{11}F_3ONa$: 275.0654, found: 275.0654.

(E)-1-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)prop-1-yn-1-yl)-4-(trifluoromethyl)benzene (3n)



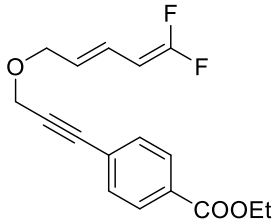
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.24 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.73 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.37 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 133.3, 127.6 (dd, *J* = 11.0, 3.0 Hz), 122.5 (d, *J* = 5.0 Hz), 120.8, 121.3, 121.2 (q, *J* = 215.0 Hz), 85.8, 85.0, 81.5 (dd, *J* = 28.0, 17.0 Hz), 69.9, 65.2, 57.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8, -85.0 (t, *J* = 26.3 Hz), -87.0 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{12}F_5O$: 303.0803, found: 303.0795.

ethyl (E)-4-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)prop-1-yn-1-yl)benzoate (3o)



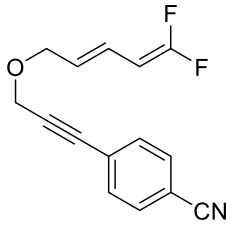
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.25 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.74 (dt, *J* = 15.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.39 -4.35 (m, 4H), 4.16 (d, *J* = 6.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 150.7 (dd, *J* = 295.0, 290.0 Hz), 131.7, 129.7, 129.5, 127.5 (dd, *J* = 11.0, 3.0 Hz), 125.4, 123.7, 122.6 (d, *J* = 5.0 Hz), 88.1, 85.6, 81.4 (dd, *J* = 27.0, 16.0 Hz), 70.0, 65.2, 57.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (t, *J* = 26.3 Hz), -87.0 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{17}H_{16}F_2O_3Na$: 329.0960, found: 329.0954.

(E)-4-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl) benzonitrile (3p)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.0 Hz, 2H), 7.53 (d, *J* = 6.0 Hz, 2H), 6.25 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.74 (dt, *J* = 15.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 25.0, 11.0 Hz, 1H), 4.38 (s, 2H), 4.15 (d, *J* = 5.0 Hz, 2H).

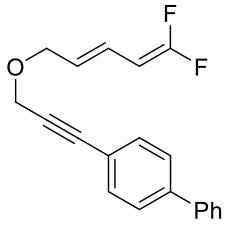
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 290.0 Hz), 132.2, 132.0, 127.4 (dd, *J* = 11.0, 3.0 Hz), 122.6 (dd, *J* = 5.0, 2.0 Hz), 118.3, 111.9, 89.5, 84.7, 81.5 (dd, *J* = 27.0, 17.0 Hz), 70.1,

65.4, 57.7

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9 (t, *J* = 26.3 Hz), -86.8 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{11}F_2NONa$: 282.0701, found: 282.0699.

(E)-4-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)prop-1-yn-1-yl)-1,1'-biphenyl (3q)



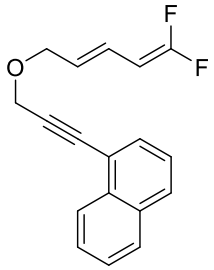
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 -7.51 (m, 6H), 7.47 - 7.43 (m, 2H), 7.37 (d, *J* = 7.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 11.0, 4.0 Hz, 1H), 5.76 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.40 (s, 2H), 4.17 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 141.2, 140.3, 132.2, 128.8, 127.8 (dd, *J* = 11.0, 4.0 Hz), 127.7, 127.0 (d, *J* = 3.0 Hz), 122.4 (d, *J* = 5.0 Hz), 121.5, 86.3, 85.5, 81.6 (dd, *J* = 27.0, 16.0 Hz), 69.8, 65.0, 58.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.5 (d, *J* = 41.3 Hz),-90.4 (dd, *J* = 45.1, 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{20}H_{16}F_2ONa$: 333.1061, found: 333.1058.

(E)-1-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl) naphthalene (3r)



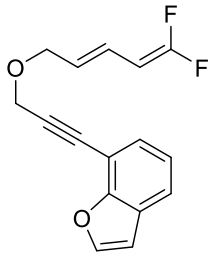
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.46 – 7.37 (m, 1H), 6.29 (dd, *J* = 16.0, 11.0 Hz, 1H), 5.79 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.01 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.54 (s, 2H), 4.25 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 289.0 Hz), 133.2, 130.7, 129.0, 128.3, 127.8 (dd, *J* = 11.0, 3.0 Hz), 126.8, 126.4, 126.0, 125.1, 122.5 (dd, *J* = 5.0, 1.0 Hz), 120.2, 89.8, 84.5, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.8, 65.1, 58.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (t, *J* = 26.3 Hz), -87.1 (d, *J* = 30.1 Hz).

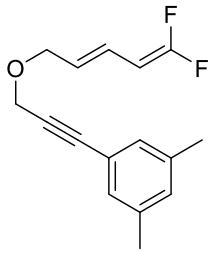
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{18}H_{14}F_2ONa$: 307.0905, found: 307.0904.

(E)-7-(3-(5,5-difluoropenta-2,4-dien-1-yl) oxy)prop-1-yn-1-yl) benzofuran (3s)



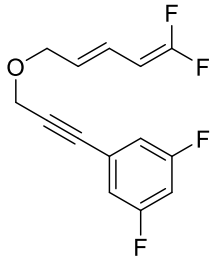
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.64 (s, 1H), 7.46 – 7.37 (m, 2H), 6.74 (s, 1H), 6.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.00 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.39 (s, 2H), 4.17 (d, *J* = 5.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 294.0, 287.0 Hz), 145.9, 128.2, 127.8 (dd, *J* = 11.0, 3.0 Hz), 127.5, 125.0, 122.5 (d, *J* = 6.0 Hz), 117.1, 111.6, 106.5, 86.8, 83.5, 81.6 (dd, *J* = 27.0, 17.0 Hz), 69.8, 58.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{12}F_2O_2Na$: 297.0698, found: 297.0691.

(E)-1-(3-((5,5-difluoropenta-2,4-dien-1-yl) oxy) prop-1-yn-1-yl)-3,5-dimethylbenzene (3t)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 6.96 (s, 1H), 6.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.36 (s, 2H), 4.15 (d, *J* = 7.0 Hz, 2H), 2.29 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 290.0 Hz), 132.2, 132.0, 127.4 (dd, *J* = 11.0, 3.0 Hz), 122.6 (dd, *J* = 5.0, 2.0 Hz), 118.3, 111.9, 89.5, 84.7, 81.5 (dd, *J* = 27.0, 17.0 Hz), 70.1, 65.4, 57.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.3 (d, *J* = 26.3 Hz).
HRMS (ESI) $(M+K)^+$: Calcd for $C_{16}H_{16}F_2OK$: 301.0801, found: 301.0804.

(E)-1-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)prop-1-yn-1-yl)-3,5-difluorobenzene (3u)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.88 (m, 2H), 6.79 (m, 2.0 Hz, 1H), 6.23 (dd, *J* = 15.0, 12.0 Hz, 1H), 5.72 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.35 (s, 2H), 4.13 (d, *J* =

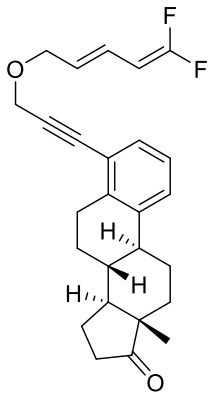
6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 248.0 Hz), 156.7 (dd, *J* = 295.0, 290.0 Hz), 127.5 (dd, *J* = 11.0, 3.0 Hz), 122.6 (dd, *J* = 5.0, 2.0 Hz), 114.7 (dd, *J* = 19.0, 8.0 Hz), 104.7 (t, *J* = 25.0 Hz), 87.1, 84.1 (t, *J* = 4.0 Hz), 81.5 (dd, *J* = 27.0, 16.0 Hz), 70.0, 65.3, 57.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (t, *J* = 26.3 Hz), -87.2 (d, *J* = 26.3 Hz), -109.7 (t, *J* = 7.5 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{14}H_{11}F_4O$: 271.0741, found: 271.0737.

(E)-4-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)prop-1-yn-1-yl)-13-methyl-6,7,8,9,11,12,13,14, 15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(3v)



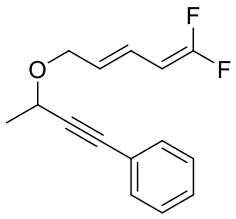
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.24 (s, 1H), 7.20 (s, 1H), 6.24 (dd, *J* = 15.5, 11.0 Hz, 1H), 5.74 (dt, *J* = 15.5, 6.2 Hz, 1H), 5.00 (dd, *J* = 12.0 Hz , 1H), 4.37 (s, 2H), 4.15 (d, *J* = 6.3 Hz, 2H), 2.89 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.33 – 2.27 (m, 1H), 2.21 – 2.12 (m, 1H), 2.09 – 1.95 (m, 3H), 1.66 – 1.59 (m, 2H), 1.55 – 1.41 (m, 4H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 157.8 (dd, *J* = 297.0, 289.0 Hz), 140.4, 136.6, 132.2, 129.0, 127.8 (dd, *J* = 11.0, 3.0 Hz), 125.3, 122.4 (dd, *J* = 5.0, 2.0 Hz), 119.8, 85.5, 84.1, 81.5 (dd, *J* = 27.0, 17.0 Hz), 69.7, 58.0, 50.4, 47.9, 44.4, 37.9, 35.8, 31.5, 29.0, 26.3, 25.5, 21.5, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (dd, *J* = 26.3, 22.2 Hz), -87.0 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{26}H_{28}F_2O_2Na$: 433.1950, found: 433.1956.

(E)-(3-((5,5-difluoropenta-2,4-dien-1-yl)oxy)but-1-yn-1-yl)benzene (3w)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.34 – 7.30 (m, 3H), 6.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 5.76 (dt, *J*=16.0, 6.0 Hz, 1H), 4.99 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.38 (d, *J*=6.0 Hz, 2H), 4.07 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 7.0 Hz, 3H).

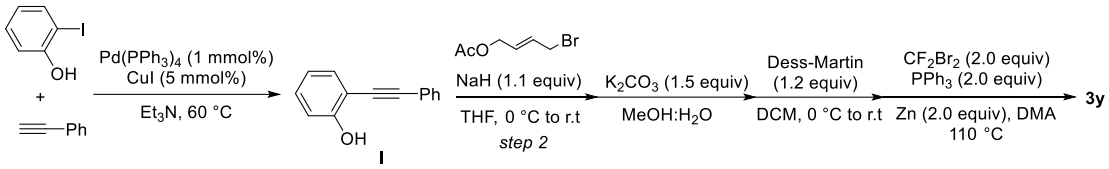
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 295.0, 290.0 Hz), 138.6, 131.6, 129.0, 127.8 (dd, *J* = 11.0, 3.0 Hz), 122.3 (dd, *J* = 5.0, 1.0 Hz), 86.6, 84.1, 81.5 (dd, *J* = 27.0, 16.0 Hz), 69.7, 64.9,

58.0, 21.4

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (dd, J = 26.3, 22.1 Hz), -87.5 (d, J = 30.0 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{14}F_2ONa$: 271.0905, found: 271.0898.

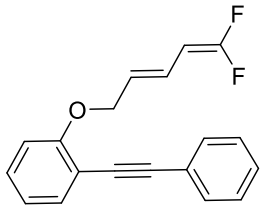
2.4 The procedure for the synthesis of *gem*-difluoroalkenes **3y**[7]



Iodobenzene (1.0 equiv), phenylacetylene (1.1 equiv), $Pd(PPh_3)_4$ (1 mol%), and CuI (5 mol%) were dissolved in anhydrous Et_3N (40 mL). The mixture was stirred at 60 °C for 6 h, then cooled to ambient temperature and quenched with saturated aqueous ammonium chloride solution. The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford phenol **I**.

Following Steps 3,4 and 5 of General Procedure 2.1, the phenol **I** was transformed into substrate **3y**.

(E)-1-((5,5-difluoropenta-2,4-dien-1-yl)oxy)-2-(phenylethynyl) benzene (3x)



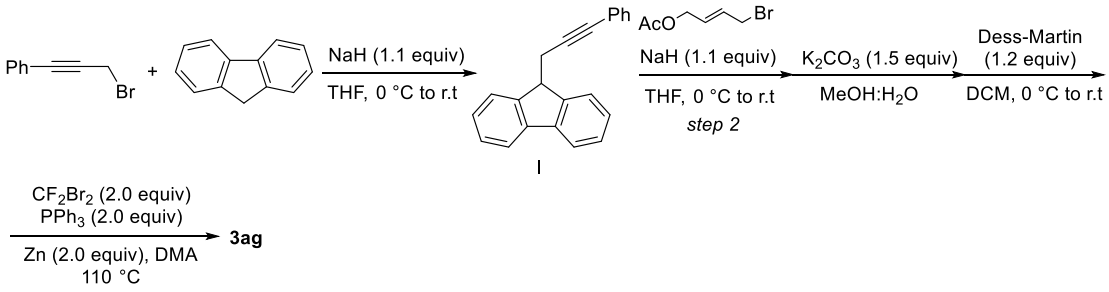
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.51 (m, 3H), 7.36 – 7.27 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.46 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.89 (dt, *J* = 16.0, 5.0 Hz, 1H), 5.04 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 156.7 (dd, *J* = 295.0, 289.0 Hz), 133.5, 131.6, 129.6, 128.3, 128.1, 126.7 (dd, *J* = 11.0, 3.0 Hz), 123.6, 121.5 (dd, *J* = 5.0, 2.0 Hz), 120.9, 113.1, 112.4, 93.7, 85.6, 81.7 (dd, *J* = 28.0, 17.0 Hz), 68.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (dd, *J* = 26.3, 22.2 Hz), -87.2 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{19}H_{15}F_2O$: 297.1085, found: 297.1080.

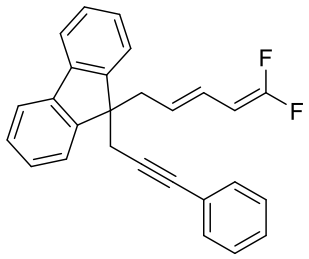
2.5 The procedure for the synthesis of *gem*-difluoroalkenes **3ag** [8]



Fluorene (1.0 equiv) was dissolved in anhydrous THF (10 mL) and added dropwise to a stirred suspension of NaH (1.1 equiv, 60% dispersion in mineral oil) in THF (40 mL) at 0 °C. After stirring for 30 min at the same temperature, (3-bromoprop-1-yn-1-yl)benzene (1.0 equiv) was added slowly. The mixture was stirred at 60 °C for 6 h, cooled to ambient temperature, and quenched with saturated aqueous sodium bicarbonate solution (10 mL). The mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford Compound **I**.

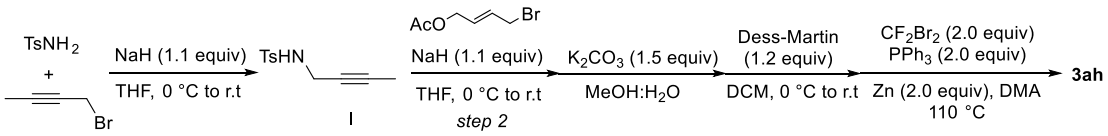
Following Steps 3,4 and 5 of General Procedure 2.1, compound **I** was transformed into substrate **3ag**.

(E)-9-(5,5-difluoropenta-2,4-dien-1-yl)-9-(3-phenylprop-2-yn-1-yl)-9H-fluorene (3ag)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.33 (m, 9H), 5.87 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.15 (dt, *J* = 15.0, 7.0 Hz, 1H), 4.68 (dd, *J* = 25.0, 11.0 Hz, 1H), 3.01 (d, *J* = 7.0 Hz, 2H), 2.85 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (dd, *J* = 293.0, 288.0 Hz), 148.9, 140.2, 133.7, 131.5, 128.5, 128.3, 127.9 (dd, *J* = 12.0, 4.0 Hz), 127.6, 127.2, 123.7, 121.8 (dd, *J* = 4.0, 2.0 Hz), 119.9, 87.2, 83.0, 81.8 (dd, *J* = 26.0, 17.0 Hz), 52.6, 40.4, 30.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -87.0 (dd, *J* = 33.8, 26.3 Hz), -89.6 (d, *J* = 33.8 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{27}H_{20}F_2Na$:405.1425, found: 405.1430.

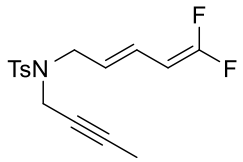
2.6 The procedure for the synthesis of *gem*-difluoroalkenes **3ah** [9]



In a dry 250 mL round-bottom flask equipped with a stir bar, p-toluenesulfonamide (4.0 equiv), methyl propargyl bromide (1.0 equiv), and K_2CO_3(1.1 equiv) were successively added. dry CH_3CN (20 mL) was introduced, and the mixture was heated under reflux in an oil bath for 4 hours. After confirming complete consumption of the starting material by TLC, the reaction was cooled to room temperature and quenched with H_2O (10 mL). The mixture was extracted with EA (3×25 mL), and the combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford Compound **I**.

Following Steps 3,4 and 5 of General Procedure 2.1, compound **I** was transformed into substrate **3ah**.

(E)-N-(but-2-yn-1-yl)-N-(5,5-difluoropenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (3ah)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.12 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.51 (dt, *J* = 16.0, 7.0 Hz, 1H), 4.95 (dd, *J* = 24.0, 11.0 Hz, 1H), 4.00 (s, 2H), 3.81 (d, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.55 (s, 3H).

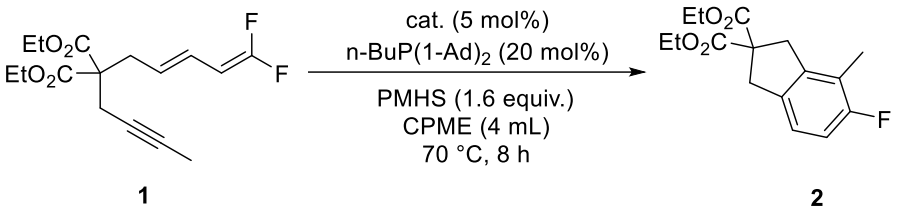
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (dd, J = 295.0, 290.0 Hz), 143.3, 136.1, 129.2, 127.8, 125.9 (dd, *J* = 11.0, 2.0 Hz), 123.4 (dd, *J* = 6.0, 2.0 Hz), 81.4 (dd, *J* = 27.0, 16.0 Hz), 71.5, 48.2, 43.0, 36.4, 21.5, 3.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (t, *J* = 26.3 Hz), -87.0 (d, *J* = 26.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{17}F_2NO_2SNa$:348.0840, found: 348.0837.

3. Optimization of reaction conditions.

Table S1. Optimization of metal catalyst

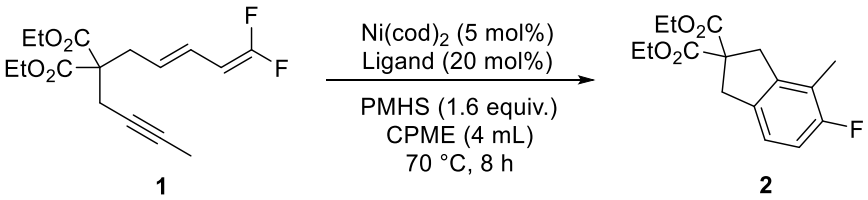


1 **2**

Entry	Metal cat.	Yield of **2**（%）
1	$[Rh(cod)Cl]_2$	17
2	$Ni(cod)_2$	77
3	$NiBr_2$	0
4	$Ni(acac)_2$	0
5	NiI_2	0
6	$NiCl_2(PPh_3)_2$	0

Reaction conditions: **1** (0.1 mmol) and CPME (4.0 mL) were combined with metal catalyst (0.01 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (0.04 mmol, 20 mol%), and PMHS (75 μL, 1.6 equiv). The reaction was conducted under N_2 at 70 °C for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

Table S2. Optimization of ligands



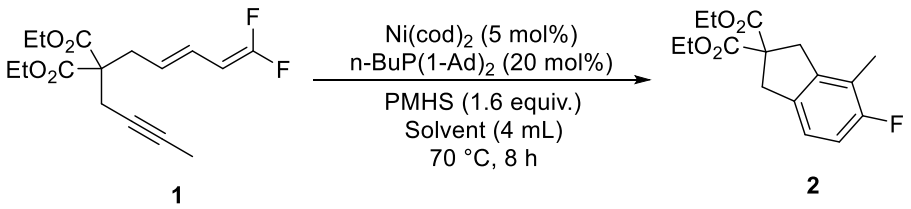
1 **2**

Entry	Ligand	Yield of **2**（%）
1	DPPM	2
2	DPEPhos	0
3	EDPP	0
4	DPPB	2
5	DPPP	3
6	DPPF	2
7	DPPBz	2
8	PPh_3	0
9	t-BuXPhos	0
10	BrettPhos	1
11	DPCP	0
12	t-BuPPh_2P	15

13	PCy_3	36
14	n-BuP(1-Ad)$_2$	77
15	(1-Ad)$_2$BnP	0
16	(1-Ad)$_3$P	3
17	tBu_3P	1
18	(3-OMePh)$_3$P	1
19	(2-OMePh)$_3$P	1
20	[2,6-(OMe)$_2$Ph]$_3$P	0
21	(2-Biphenyl)$_2$-1-AdP	0
22	DCyPFc	0
23	DPEPhos	0
24	rac-BINAP	0

Reaction conditions: **1** (0.1 mmol) and CPME (4.0 mL) were combined with Ni(cod)$_2$ (0.01 mmol, 5 mol%), Ligant (0.04 mmol, 20 mol%), and PMHS (75 μL, 1.6 equiv). The reaction was conducted under N_2 at 70 °C for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

Table S3. Optimization of solvents



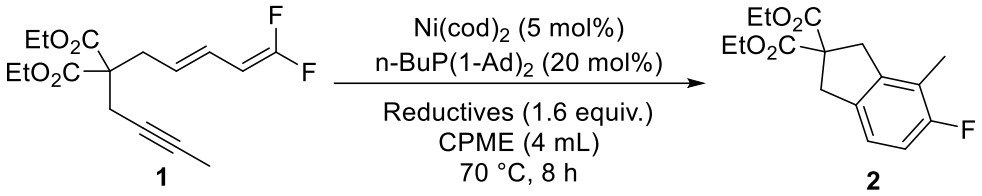
1 **2**

Entry	Solvent	Yield of **2**（%）
1	THF	36
2	n-Butyl ether	62
3	EA	30
4	DMF	17
5	CPME	77
6	Cyclohexane	34
7	1,4-Dioxane	54
8	m-Xylene	0
9	Cyclopentane	0
10	Methanol	0
11	CCl_4	0
12	MTBE	42
13	Acetonitrile	19
14	DMSO	0
15	Benzonitrile	14
16	Benzotrifluoride	0
17	2-MeTHF	22
18	Anisole	0

19	DCM	0
20	DCE	0

Reaction conditions: **1** (0.1 mmol) and solvent (4.0 mL) were combined with $Ni(cod)_2$ (0.01 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (0.04 mmol, 20 mol%), and PMHS (75 μL, 1.6 equiv). The reaction was conducted under N_2 at 70 °C for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

Table S4. Optimization of reductives

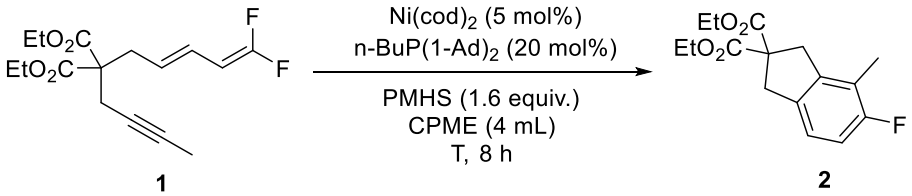


1 **2**

Entry	Reductives	Yield of **2**（%）
1	$(EtO)_2MeSiH$	30
2	Ph_3SiH	25
3	$PhMe_2SiH$	24
4	Ph_2MeSiH	27
5	$(EtO)_3SiH$	19
6	$PhSiH_3$	0
7	Ph_2SiH_2	0
8	Et_3SiH	23
9	PHMS	77
10	$EtMe_2SiH$	11
11	HBPin	0
12	B_2Pin_2+^{i}PrOLi	4
13	Zn	0

Reaction conditions: **1** (0.1 mmol) and CPME (4.0 mL) were combined with $Ni(cod)_2$ (0.01 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (0.04 mmol, 20 mol%), and reductives (1.6 equiv). The reaction was conducted under N_2 at 70 °C for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

Table S5. Optimization of reaction temperatures



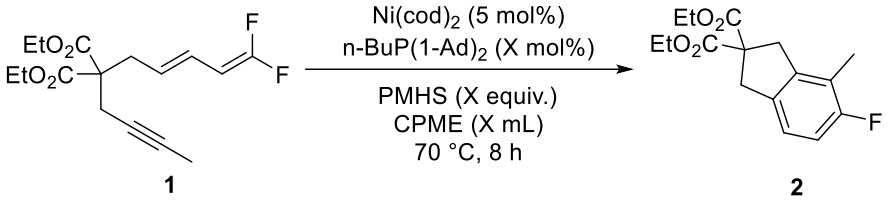
1 **2**

Entry	Temperature (℃)	Yield of **2**（%）
1	60	64
2	70	77
3	80	62
4	90	59

5	100	56
6	110	56

Reaction conditions: **1** (0.1 mmol) and CPME (4.0 mL) were combined with $Ni(cod)_2$ (0.01 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (0.04 mmol, 20 mol%), and PHMS (1.6 equiv). The reaction was conducted under N_2 at T for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

Table S6. Effects of other reaction factors.

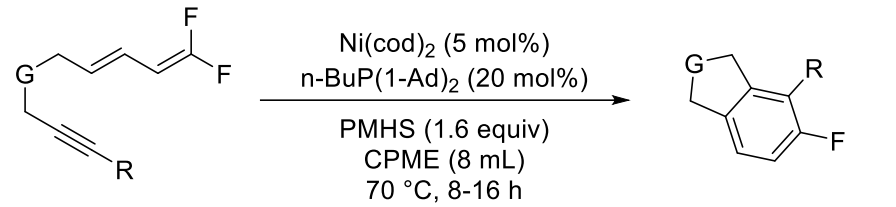


1 **2**

Entry	Variation	Yield of 2（%）
1	5 % n-BuP(1-Ad)$_2$ (1:1)	55
2	10 % n-BuP(1-Ad)$_2$ (1:2)	63
3	15 % n-BuP(1-Ad)$_2$ (1:3)	62
4	20 % n-BuP(1-Ad)$_2$ (1:4)	77
5	25 % n-BuP(1-Ad)$_2$ (1:5)	66
6	1 ml CPME	68
7	2 ml CPME	65
8	3 ml CPME	75
9	4 ml CPME	77
10	5 ml CPME	64
11	15 ul (1.0 equiv.)	68
12	20 ul (1.3 equiv.)	71
13	25 ul (1.6 equiv.)	77
14	30 ul (2.0 equiv.)	70
15	35 ul (2.3 equiv.)	61

Reaction conditions: 1 (0.2 mmol) and CPME (X mL) were combined with $Ni(cod)_2$ (0.01 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (X mol%), and PHMS (X equiv). The reaction was conducted under N_2 at T for 8 hours. The yield was determined by GC with 1-tetradecane as an internal standard.

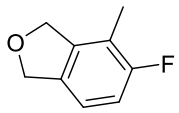
4. General Procedure for nickel catalyzed defluorinative cycloaddition of *gem*-difluoroalkenes



1, 3a-3y, 3aa-3ah **2, 4a-4y, 4aa-4ah**

Under N_2, $Ni(cod)_2$ (0.02 mmol, 5 mol%), n-BuP(1-Ad)$_2$ (0.08 mmol, 20 mol%), and PHMS (1.6 equiv), **1** or **3** (0.2 mmol), followed by CPME (8.0 mL). The resulting mixture was stirred at 70 °C for about 8-16 hours. Then, the solvent was removed under reduced pressure, and the residue was purified by short silica gel column chromatography to obtain the target products **2** or **4**.

5-fluoro-4-methyl-1,3-dihydroisobenzofuran (4a)



The title compound was obtained in 74 % (22.5 mg) yield according to general procedure, colorless oil.

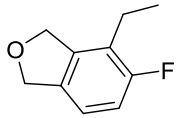
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 5.13 (s, 2H), 5.05 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J* = 243.0 Hz),137.8, 129.2, 128.8 (d, *J* = 2.0 Hz), 120.5 (d, *J* = 9.0 Hz), 115.2 (d, *J* = 24.0 Hz), 73.5, 73.3 (d, *J* = 3.0 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -124.3 (d, *J*= 11.3 Hz).

HRMS (ESI) $(M+K)^+$: Calcd for C_9H_9FOK :191.0269, found: 191.0262.

4-ethyl-5-fluoro-1,3-dihydroisobenzofuran(4b)



The title compound was obtained in 74 % (24.6 mg) yield according to general procedure, light yellow oil.

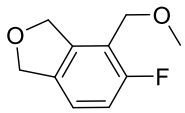
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.93 (t, *J* = 9.0 Hz, 2H), 5.11 (s, 2H), 5.08 (s, 2H), 2.57 (q, *J* = 8.0 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 243.0 Hz), 141.1, 134.9, 131.7, 121.3 (d, *J* = 9.0 Hz), 114.4 (d, *J* = 24.0 Hz), 72.9, 72.8 (d, *J*= 3.0 Hz), 65.9 (d, *J* = 4.0 Hz), 58.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -124.3 (d, *J*= 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{10}H_{11}FONa$:189.0686, found: 189.0679.

5-fluoro-4-(methoxymethyl)-1,3-dihydroisobenzofuran (4c)



The title compound was obtained in 63% (22.9 mg) yield according to general procedure, colorless oil.

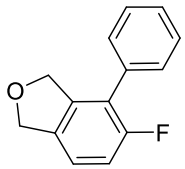
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.96 (t, *J* = 9.0 Hz, 1H), 5.16 (s, 2H), 5.06 (s, 2H), 4.51 (s, 2H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 243.0 Hz), 141.2 (d, *J* = 19.0 Hz), 134.9, 131.7, 121.3 (d, *J* = 9.0 Hz), 114.5 (d, *J* = 24.0 Hz), 73.0, 72.9 (d, *J*= 3.0 Hz), 65.9 (d, *J* = 4.0 Hz), 58.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.0 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{10}H_{11}FO_2Na$:205.0635, found: 205.0634.

5-fluoro-4-phenyl-1,3-dihydroisobenzofuran (4d)



The title compound was obtained in 67 % (28.7 mg) yield according to general procedure, colorless oil.

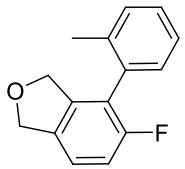
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.16 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.08 (t, *J* = 9.0 Hz, 1H), 5.13 (s, 2H), 5.02 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 246.0 Hz), 140.0, 138.4, 135.4, 132.3, 129.8 (d, *J* = 2.0 Hz), 122.1 (d, *J* = 9.0 Hz), 118.5, 115.4 (d, *J* = 24.0 Hz), 111.9, 73.5, 72.9 (d, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.8 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{14}H_{11}FONa$:237.0686, found: 237.0682.

5-fluoro-4-(o-tolyl)-1,3-dihydroisobenzofuran (4e)



The title compound was obtained in 68 % (31.0 mg) yield according to general procedure, light yellow oil.

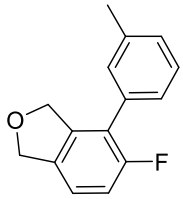
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.0 Hz, 2H), 7.25-7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 7.06 (t, *J*= 16.0 Hz, 1H), 5.15 (s, 2H), 4.95 (d, *J* = 13.0 Hz, 1H), 4.72 (d, *J* = 13.0 Hz, 1H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 242.0 Hz), 140.6, 136.4, 135.7, 134.4, 133.1, 130.2, 129.0, 128.4, 125.8, 120.9 (d, *J*= 9.0 Hz), 114.7 (d, *J*= 24.0 Hz), 73.7, 73.1 (d, *J*= 3.0 Hz), 19.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.4 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{14}FO$:229.1023, found: 229.1027.

5-fluoro-4-(m-tolyl)-1,3-dihydroisobenzofuran (4f)



The title compound was obtained in 71 % (32.4 mg) yield according to general procedure, colorless oil.

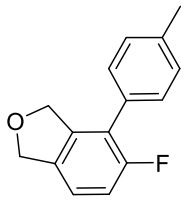
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.21 – 7.12 (m, 4H), 7.10-7.05 (m, 1H), 5.13 (s, 2H), 5.04 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 243.0 Hz), 138.1, 134.7, 133.5, 129.7, 129.6 128.8, 128.4, 126.0, 125.9, 120.7 (d, *J*= 10.0 Hz), 115.1 (d, *J*= 25.0 Hz), 73.6, 73.3 (d, *J*= 3.0 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.7 (dd, *J* = 11.3, 3.8 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{14}FO$:229.1023, found: 229.1020.

5-fluoro-4-(p-tolyl)-1,3-dihydroisobenzofuran (4g)



The title compound was obtained in 61 % (27.8 mg) yield according to General Procedure, yellow oil.

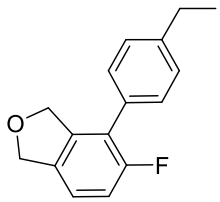
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 7.17 – 7.12 (m, 1H), 7.09 (t, *J* = 9.0 Hz, 1H), 5.15 (s, 2H), 5.07 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J* = 242.0 Hz), 143.8, 134.5, 133.1, 129.3, 128.4, 127.9, 124.1 (d, *J* = 18.0 Hz), 120.9 (d, *J* = 9.0 Hz), 115.0 (d, *J* = 25.0 Hz), 80.1, 71.7, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.8 (dd, *J* = 11.3, 3.4 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{14}FO$:229.1023, found: 229.1017.

4-(4-ethylphenyl)-5-fluoro-1,3-dihydroisobenzofuran (4h)



The title compound was obtained in 80 % (38.7 mg) yield according to general procedure, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 7.13 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 5.13 (s, 2H), 5.06 (s, 2H), 2.70 (q, *J*= 6.7 Hz, 2H), 1.28 (t, *J* = 6.0 Hz, 3H).

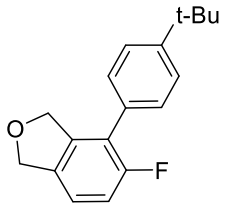
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 251.0 Hz), 144.1, 140.2 (d, *J*= 4.0 Hz), 134.7 (d, *J*=

3.0 Hz), 130.7, 128.9 (d, *J*= 2.0 Hz), 128.0,123.6 (d, *J*= 17.0 Hz), 120.6, 120.5, 115.2, 115.0, 73.5, 73.3 (d, *J*= 4.0 Hz), 28.6, 15.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.8 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{15}FONa$:265.0999, found: 265.0990.

4-(4-(tert-butyl)phenyl)-5-fluoro-1,3-dihydroisobenzofuran (4i)



The title compound was obtained in 76 % (41.1 mg) yield according to general procedure, colorless oil.

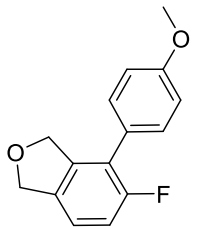
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 5.13 (s, 2H), 5.08 (s, 2H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J*= 244.0 Hz), 150.9, 140.2 (d, *J*= 4.0 Hz), 134.8 (d, *J*= 2.0 Hz), 130.5, 128.7, 128.6, 125.4, 120.5 (d, *J*= 9.0 Hz), 115.1 (d, *J*= 24.0 Hz), 73.5, 73.4 (d, *J*= 3.0 Hz), 31.3, 29.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.7 (dd, *J*= 7.5, 3.8 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{18}H_{19}FONa$:293.1312, found: 293.1306.

5-fluoro-4-(4-methoxyphenyl)-1,3-dihydroisobenzofuran (4j)



The title compound was obtained in 66 % (32.2 mg) yield according to general procedure, colorless oil.

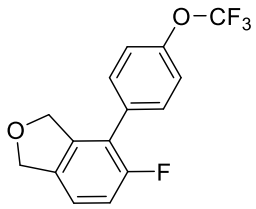
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.11 - 1.04 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 2H), 5.05 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J*= 246.0 Hz), 138.4, 135.4 (d, *J*= 2.0 Hz), 132.3, 129.8 (d, *J*= 2.0 Hz), 122.1 (d, *J*= 9.0 Hz), 118.5, 117.8 (d, *J*= 10.0 Hz), 115.4 (d, *J*= 24.0 Hz), 111.9, 73.5, 72.9, 72.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.4 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $CDCl_3)C_{15}H_{13}FO_2Na$:267.0792, found: 267.0794.

5-fluoro-4-(4-(trifluoromethoxy)phenyl)-1,3-dihydroisobenzofuran (4k)



The title compound was obtained in 68 % (40.5 mg) yield according to general procedure, yellow oil.

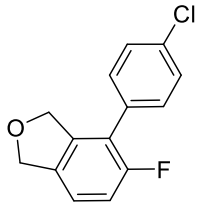
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, J=9.0, 5.0 Hz 1H), 7.11 (t, *J* = 9.0 Hz, 1H), 5.14 (s, 2H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, *J*= 245.0 Hz),145.1, 140.1 (d, *J*= 3.0 Hz), 137.3, 135.2, 129.5, 129.4, 126.7 (q, *J*= 219.0 Hz), 125.5 (q, *J*= 4.0 Hz), 121.7 (d, *J*= 9.0 Hz), 115.3 (d, *J*= 24.0 Hz), 73.5, 73.0 (d, *J*= 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -121.6 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{15}H_{10}F_4O_2Na$:321.0509, found: 321.0501.

4-(4-chlorophenyl)-5-fluoro-1,3-dihydroisobenzofuran (4l)



The title compound was obtained in 57 % (28.3 mg) yield according to general procedure, colorless oil.

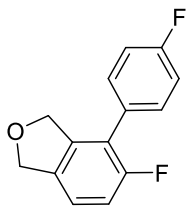
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.11 (t, *J* = 9.0 Hz, 1H), 5.14 (s, 2H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J*= 246.0 Hz), 140.0, 138.4, 135.4, 132.3, 129.8 (d, *J*= 2.0 Hz), 122.1 (d, *J*= 9.0 Hz), 118.5, 115.4 (d, *J*= 24.0 Hz), 111.9, 73.5, 72.9 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.7 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{14}H_{10}ClFONa$:271.0296, found: 271.0287.

5-fluoro-4-(4-fluorophenyl)-1,3-dihydroisobenzofuran (4m)



The title compound was obtained in 61 % (28.3 mg) yield according to general procedure, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.17 -7.06 (m, 4H), 5.13 (s, 2H), 5.02 (s, 2H).

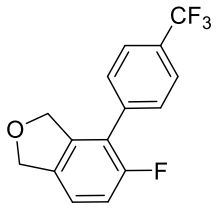
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J*= 246.0 Hz), 161.5 (d, *J*= 245.0 Hz), 134.9, 130.7 (d,

J= 2.0 Hz), 130.6 (d, *J*= 2.0 Hz) 129.5, 121.0 (d, *J*= 10.0 Hz), 115.6 (d, *J*= 22.0 Hz), 115.3, 115.1, 73.5, 73.1 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7, -121.9 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{14}H_{11}F_2O$:233.0772, found: 233.0778.

5-fluoro-4-(4-(trifluoromethyl) phenyl)-1,3-dihydroisobenzofuran (4n)



The title compound was obtained in 71 % (40.1 mg) yield according to general procedure, yellow oil.

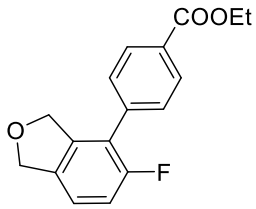
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.11 (t, *J* = 9.0 Hz, 1H), 5.14 (s, 2H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, *J*= 245.0 Hz), 140.2, 140.1, 137.3, 135.2 (d, *J*= 2.0 Hz), 129.4, 129.5, 126.7 (q, *J* = 220.0 Hz), 125.5 (q, *J*= 4.0 Hz), 121.7 (d, *J*= 9.0 Hz), 115.3 (d, *J*= 24.0 Hz), 73.5, 73.0 (d, *J*= 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -121.1 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{11}F_4O$:283.0741, found: 283.0738.

ethyl 4-(5-fluoro-1,3-dihydroisobenzofuran-4-yl)benzoate (4o)



The title compound was obtained in 66 % (37.8 mg) yield according to general procedure, light yellow oil.

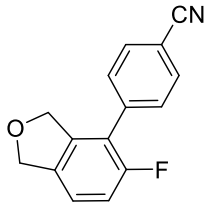
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.10 (t, *J* = 9.0 Hz, 1H), 5.13 (s, 2H), 5.03 (s, 2H), 4.41 (q, *J* = 6.7 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 242.0 Hz), 140.7, 136.4, 134.4, 133.1, 130.2, 129.0, 128.4, 125.8, 120.9 (d, *J*= 9.0 Hz), 114.7 (d, *J*= 24.0 Hz), 73.7, 73.1 (d, *J*= 3.0 Hz), 36.6, 19.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.4 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{17}H_{15}FO_3Na$:309.0897, found: 309.0887.

4-(5-fluoro-1,3-dihydroisobenzofuran-4-yl)benzonitrile (4p)



The title compound was obtained in 78 % (37.3 mg) yield according to general procedure, colorless oil.

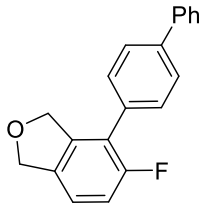
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.10 (t, *J* = 9.0 Hz, 1H), 5.12 (s, 2H), 5.01 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J*= 246.0 Hz), 140.0, 138.4, 135.4, 132.3, 129.8 (d, *J*= 2.0 Hz), 122.1 (d, *J*= 9.0 Hz), 118.5, 115.6, 115.3, 111.9, 73.5, 72.9 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.4 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{11}FNO$:240.0819, found: 240.0810.

4-([1,1'-biphenyl]-4-yl)-5-fluoro-1,3-dihydroisobenzofuran (4q)



The title compound was obtained in 67 % (38.9 mg) yield according to general procedure, colorless oil.

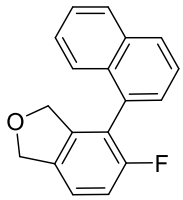
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 -7.63 (m, 4H), 7.49 – 7.45 (m, 4H), 7.40 -7.36 (m, 1H), 7.17 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.11 (t, *J*= 9.0 Hz 1H), 5.15 (s, 2H), 5.11 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 252.0 Hz), 141.4 (d, *J*= 4.0 Hz), 134.4 (d, *J*= 3.0 Hz), 133.6, 131.1 (d, *J*= 3.0 Hz), 128.6, 128.3, 127.0, 126.4, 126.0, 125.2, 125.1, 121.2 (d, *J*= 9.0 Hz), 114.8 (d, *J*= 24.0 Hz), 73.6, 73.1 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.6 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{20}H_{15}FONa$:313.0999, found: 313.1005.

5-fluoro-4-(naphthalen-1-yl)-1,3-dihydroisobenzofuran (4r)



The title compound was obtained in 67 % (35.4 mg) yield according to general procedure, colorless oil.

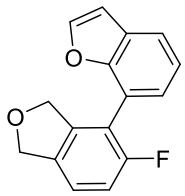
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.49 (m, 3H), 7.47 – 7.41 (m, 2H), 7.28 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.16 (t, *J* = 9.0 Hz, 1H), 5.20 (s, 2H), 4.90 (d, *J* = 13.0 Hz, 1H), 4.71 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, *J*= 243.0 Hz), 141.5, 134.6 (d, *J*= 3.0 Hz), 133.7, 131.2 (d, *J*= 3.0 Hz), 128.8, 128.5, 127.1, 126.5, 126.1, 125.3,125.2, 122.1, 121.9, 121.4 (d, *J*= 9.0 Hz), 114.9 (d, *J*= 24.0 Hz), 73.7, 73.2 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.6 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{18}H_{13}FONa$:287.0843, found: 287.0844.

7-(5-fluoro-1,3-dihydroisobenzofuran-4-yl)benzofuran (4s)



The title compound was obtained in 72 % (36.6 mg) yield according to general procedure, colorless oil.

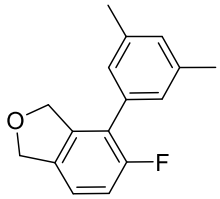
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.60 – 7.56 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 (m, 2H), 6.80 (s, 1H), 5.15 (s, 2H), 5.06 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J*= 244.0 Hz), 154.5, 145.6, 140.5 (d, *J*= 4.0 Hz), 134.7, 128.1, 127.7, 125.3, 124.0 (d, *J*= 18.0 Hz), 121.7 (d, *J*= 2.0 Hz), 120.6 (d, *J*= 9.0 Hz), 115.1 (d, *J*= 25.0 Hz), 111.4, 106.6, 73.6, 73.3 (d, *J*= 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.8 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{11}FO_2Na$:277.0635, found: 277.0632.

4-(3,5-dimethylphenyl)-5-fluoro-1,3-dihydroisobenzofuran (4t)



The title compound was obtained in 77 % (37.3 mg) yield according to general procedure, colorless oil.

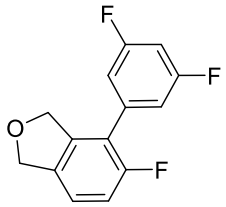
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.10 – 6.95 (m, 4H), 5.14 (s, 2H), 5.05 (s, 2H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J*= 243.0 Hz) , 140.3 (d, *J*= 4.0 Hz), 138.0, 134.7 (d, *J*= 2.0 Hz), 133.4, 129.7, 126.7 (d, *J*= 1.0 Hz), 124.0 (d, *J*= 18.0 Hz), 120.5 (d, *J*= 9.0 Hz), 115.0 (d, *J*= 25.0 Hz), 73.5, 73.3 (d, *J*= 4.0 Hz), 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.5 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{15}FONa$:265.0999, found: 265.0995.

4-(3,5-difluorophenyl)-5-fluoro-1,3-dihydroisobenzofuran (4u)



The title compound was obtained in 73 % (36.5 mg) yield according to General Procedure, colorless oil.

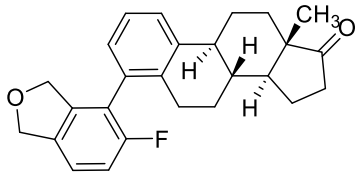
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.09 (t, J=9.0 Hz, 1H), 6.95 – 6.78 (m, 3H), 5.12 (s, 2H), 5.04 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J*= 247.0 Hz), 158.8 (d, *J*= 245.0 Hz),140.0, 136.6, 135.2, 121.9 (d, *J*= 9.0 Hz), 115.5 (d, *J*= 25.0 Hz), 112.2 (d, *J*= 2.0 Hz), 112.2 (d, *J*= 2.0 Hz), 103.6 (t, *J*= 25.0 Hz), 73.5, 72.9 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4 (t, *J* = 7.5 Hz), -121.2 (d, *J* = 7.5 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{14}H_{10}F_3O$: 251.0678, found: 251.0688.

(8R,9S,13S,14S)-4-(5-fluoro-1,3-dihydroisobenzofuran-4-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4v)



The title compound was obtained in 57 % (44.5 mg) yield according to General Procedure, colorless oil.

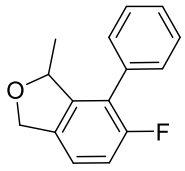
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.12 (m, 3H), 7.07 (t, *J* = 10.0 Hz, 1H), 5.12 (s, 2H), 5.06 (s, 2H), 2.95 (d, *J* = 5.0 Hz, 2H), 2.56 – 2.44 (m, 2H), 2.21 – 2.10 (m, 2H), 1.98 (s, 1H), 1.65 -1.51 (m, 8H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 159.1 (d, *J*= 244.0 Hz), 152.0, 140.2, 139.6, 136.7, 134.7, 131.0, 129.5, 126.3 (d, *J*= 2.0 Hz), 125.5, 120.6 (d, *J*= 9.0 Hz), 115.1 (d, *J*= 25.0 Hz), 73.5, 73.3 (d, *J*= 4 Hz), 50.5, 48.0, 44.4, 38.0, 35.9, 31.6, 29.4, 26.5, 25.6, 21.6, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.7 (d, *J* = 7.5 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{26}H_{28}FO_2$:391.2068, found: 391.2060.

6-fluoro-1-methyl-7-phenyl-1,3-dihydroisobenzofuran (4w)



The title compound was obtained in 71 % (32.4 mg) yield according to general procedure, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 5H), 7.14 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.08 (t, *J* = 9.0

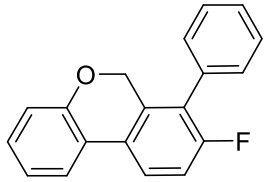
Hz, 1H), 5.54 (q, *J* = 7.0 Hz, 1H), 5.12 (s, 2H), 1.00 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J*= 242.0 Hz), 143.8 (d, *J*= 4.0 Hz), 134.5 (d, *J*= 2.0 Hz), 133.1, 129.3, 128.4, 127.9, 124.1 (d, *J*= 18.0 Hz), 120.9 (d, *J*= 9.0 Hz), 115.0 (d, *J*= 25.0 Hz), 80.1 (d, *J*= 3.0 Hz), 71.7, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.0 (dd, *J* = 7.5, 3.8 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{15}H_{14}FO$:229.1023, found: 229.1023.

8-fluoro-7-phenyl-6H-benzo[c]chromene (4x)



The title compound was obtained in 63 % (34.8 mg) yield according to general procedure, yellow oil.

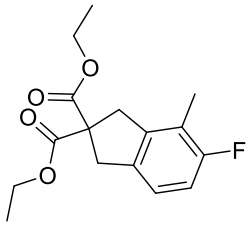
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.30 – 7.26 (m, 2H), 7.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.65 – 6.55 (m, 2H), 5.00 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J*= 241.0 Hz), 156.3, 134.7, 130.5 (d, *J*= 4.0 Hz), 130.2 (d, *J*= 3.0 Hz), 130.1, 129.2, 128.7, 128.6, 127.9, 126.4 (d, *J*= 17.0 Hz), 125.2 (d, *J*= 9.0 Hz), 122.8, 121.1, 117.4, 114.2 (d, *J*= 25.0 Hz), 69.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.2 (dd, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{19}H_{13}FONa$:299.0843, found: 299.0847.

diethyl 5-fluoro-4-methyl-1,3-dihydro-2H-indene-2,2-dicarboxylate (2)



The title compound was obtained in 77 % (45.3 mg) yield according to general procedure, colorless oil.

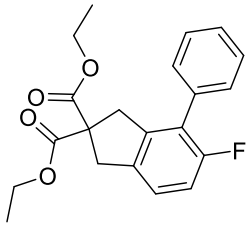
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.82 (t, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 4H), 3.54 (s, 2H), 3.51 (s, 2H), 2.17 (s, 3H), 1.26 (t, *J*= 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 159.0 (d, *J* = 240.0 Hz), 140.8, 135.6, 134.0, 129.5, 128.3, 127.6, 124.0 (d, *J* = 9.0 Hz), 114.5 (d, *J* = 24.0 Hz), 61.7, 60.7, 40.0, 39.9 (d, *J*= 3.0 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -122.1 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{16}H_{20}FO_4$:295.1340, found: 295.1333.

diethyl 5-fluoro-4-phenyl-1,3-dihydro-2H-indene-2,2-dicarboxylate (4aa)



The title compound was obtained in 89 % (63.4 mg) yield according to general procedure, colorless oil.

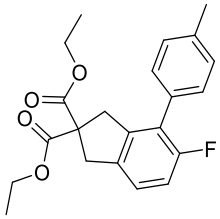
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 5H), 7.10 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.96 (t, *J* = 9.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 4H), 3.60 (s, 2H), 3.48 (s, 2H), 1.22 (t, *J* = 9.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 159.0 (d, *J*= 246.0 Hz), 140.8, 135.6, 134.0, 129.5 (d, *J* = 2.0 Hz), 128.3, 128.2, 127.6 (d, *J*= 3.0 Hz), 124.0 (d, *J*= 9.0 Hz), 114.5 (d, *J*= 24.0 Hz), 61.7, 60.8, 40.0, 39.9 (d, *J*= 3.0 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.2 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{21}H_{21}FO_4Na$:379.1316, found: 379.1315.

diethyl 5-fluoro-4-(p-tolyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4ab)



The title compound was obtained in 87 % (64.4 mg) yield according to general procedure, colorless oil.

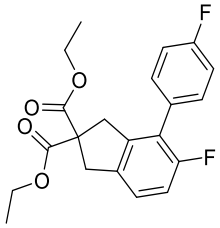
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 5.0 Hz, 4H), 7.03 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.89 (t, *J*=9.0 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 4H), 3.52 (s, 2H), 3.41 (s, 2H), 2.33 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 159.0 (d, *J*= 242.0 Hz), 140.7, 137.4, 135.5,130.9, 129.4, 129.0, 126.0, 123.8 (d, *J*= 10.0 Hz), 114.5 (d, *J*= 24.0 Hz), 61.8, 60.7, 40.0, 39.9 (d, *J* = 3.0 Hz), 21.3, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.2 (dd, *J* = 7.5, 3.8 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{22}H_{24}FO_4$:371.1653, found: 371.1648.

diethyl 5-fluoro-4-(4-fluorophenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4ac)



The title compound was obtained in 79 % (59.1 mg) yield according to general procedure, yellow

oil.

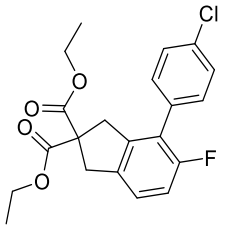
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J*= 8.0 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.10 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.96 (t, J= 9.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 3.60 (s, 2H), 3.46 (s, 2H), 1.23 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 162.2 (d, *J*= 245.0 Hz), 158.9 (d, *J*= 243.0 Hz), 140.8 (d, *J*= 4.0 Hz), 135.7 (d, *J*= 3.0 Hz), 131.2 (d, *J*= 8.0 Hz), 129.8 (d, *J*= 3.0 Hz), 127.4 (d, *J*= 15.0 Hz), 124.1 (d, *J*= 9.0 Hz), 115.3 (d, *J*= 21.0 Hz), 114.5 (d, *J*= 24.0 Hz), 61.8, 60.7, 40.0, 39.9 (d, *J*= 3.0 Hz), 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5, -121.3 (d, *J* = 11.3 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{21}H_{21}F_2O_4$:375.1402, found: 375.1399.

diethyl 4-(4-chlorophenyl)-5-fluoro-1,3-dihydro-2H-indene-2,2-dicarboxylate (4ad)



The title compound was obtained in 83 % (64.8 mg) yield according to general procedure, colorless oil.

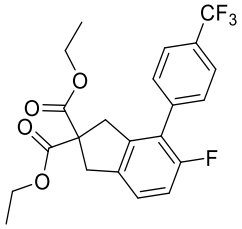
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.97 (t, *J* = 9.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 4H), 3.59 (s, 2H), 3.45 (s, 2H), 1.23 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 158.89 (d, *J*= 243.0 Hz), 140.7, 135.7, 133.7, 132.4, 130.9, 129.7, 128.6, 124.4 (d, *J*= 9.0 Hz), 114.6 (d, *J*= 24.0 Hz), 61.8, 60.8, 40.0, 39.0 (d, *J*= 3.0 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.1 (d, *J* = 7.5 Hz).

HRMS (ESI) $(M+H)^+$: Calcd for $C_{21}H_{21}ClF_2O_4$:391.1107, found: 391.1115.

Diethyl 5-fluoro-4-(4-(trifluoromethyl)phenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4ae)

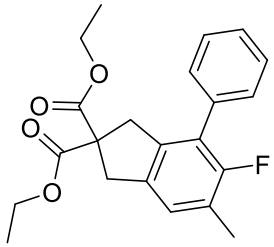


The title compound was obtained in 80 % (67.9 mg) yield according to general procedure, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.99 (t, *J* = 9.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 3.61 (s, 2H), 3.45 (s, 2H), 1.23 (t, *J* = 7.0 Hz, 6H).

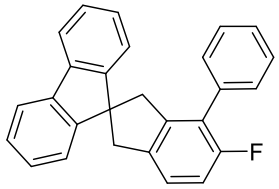
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 158.8 (d, *J*= 244.0 Hz), 140.7 (d, *J*= 3.0 Hz), 137.8, 135.9 (d, *J*= 3.0 Hz),129.9 (d, *J*= 1.0 Hz), 128.8, 126.6 (q, *J*= 215.0 Hz), 126.3, 125.3 (q, *J*= 4.0 Hz), 124.8 (d, *J*= 9.0 Hz), 114.7 (d, *J*= 24.0 Hz), 61.8, 60.8, 39.9, 39.8 (d, *J*= 3.0 Hz), 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -121.1 (d, *J* = 12.3 Hz).
HRMS (ESI) $(M+H)^+$: Calcd for $C_{22}H_{21}F_4O_4$:425.1370, found: 425.1366.

diethyl 5-fluoro-6-methyl-4-phenyl-1,3-dihydro-2H-indene-2,2-dicarboxylate(4af)



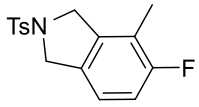
The title compound was obtained in 70 % (51.9 mg) yield according to general procedure, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.21 (m, 4H), 7.07 (dd, J= 8.0, 5.0 Hz, 1H), 6.92 (t, J= 9.0 Hz, 1H), 4.14 (q, J= 7.0 Hz, 4H), 3.55 (s, 2H), 3.45 (s, 2H), 2.37 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 159.0 (d, *J*= 242.0 Hz), 140.8, 137.4, 135.5,130.9, 129.4, 129.0, 126.0, 123.8 (d, *J*= 9.0 Hz), 114.5 (d, *J*= 24.0 Hz), 61.8, 60.7, 40.0, 39.9 (d, *J*= 3.0 Hz), 21.3, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -121.2 (dd, *J* = 7.5, 3.8 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{23}FO_4Na$:393.1473, found: 393.1470.

5'-fluoro-4'-phenyl-1',3'-dihydrospiro[fluorene-9,2'-indene] (4ag)



The title compound was obtained in 57 % (41.3 mg) yield according to general procedure, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.40 – 7.32 (m, 7H), 7.26 – 7.20 (m, 4H), 7.12 (t, *J*= 9.0 Hz, 1H), 3.52 (s, 2H), 3.45 (s, 1H), 3.36 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, *J*= 243.0 Hz), 141.5 (d, *J*= 4.0 Hz), 134.6 (d, *J*= 3.0 Hz), 133.7, 131.2 (d, *J*= 3.0 Hz), 128.8, 128.5, 127.1, 126.5, 126.1, 125.3, 125.2, 122.0 (d, *J*= 19.0 Hz), 121.4, 121.3, 114.9 (d, *J*= 24.0 Hz), 73.7, 73.2 (d, *J*= 4.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -121.0 (dd, *J* = 7.5, 3.8 Hz).
HRMS (ESI) $(M+H)^+$: Calcd for $C_{27}H_{20}F$:363.1544, found: 363.1551.

5-fluoro-4-methyl-2-tosylisoindoline (4ah)



The title compound was obtained in 86 % (52.5 mg) yield according to general procedure, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 2H), 6.93 (dd, J= 8.0, 5.0 Hz, 1H), 6.88 (t, J= 9.0 Hz, 1H), 4.58 (s, 2H), 4.54 (s, 2H), 2.40 (s, 3H), 2.11 (s, 3H).

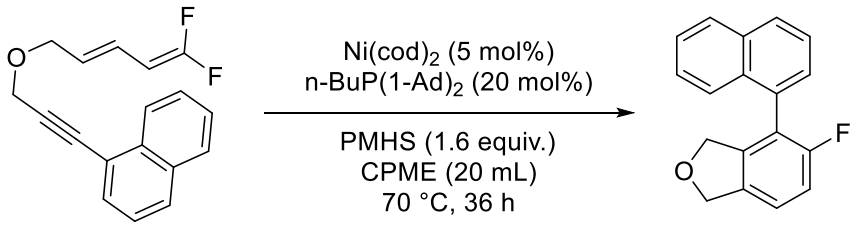
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, *J*= 242.0 Hz), 143.7, 137.4 (d, *J*= 6.0 Hz), 133.6, 129.8, 128.4, 127.9, 127.5, 120.7 (d, *J*= 9.0 Hz), 114.7 (d, *J*= 24.0 Hz), 53.6, 52.9 (d, *J*= 3.0 Hz), 21.5, 11.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.5.

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{16}H_{16}FNO_2SNa$:328.0778, found: 328.0778.

5. Gram-scale experiments and products derivatization

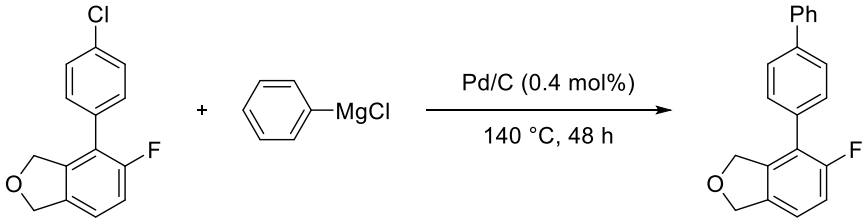
5.1 Scale-up reactions



3r **4r** 53%

Under N_2, $Ni(cod)_2$ (70 mg, 5 mol%), n-$BuP(1\text{-}Ad)_2$ (358 mg, 20 mol%), and PHMS (1.6 equiv) were added to **3r** (5.0 mmol), followed by CPME (20.0 mL). The resulting mixture was stirred at 70 °C for about 36 hours. Then, the solvent was removed under reduced pressure, and the residue was purified by short silica gel column chromatography to obtain the target product **4r** (0.7 g, 53%).

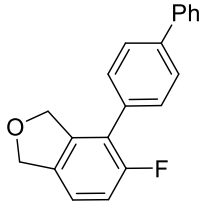
5.2 cross-coupling reaction of **4l** [9]



4l **4q** 61%

Place the stirrer into a pre-dried 25 mL Schlenk reaction tube, and then add Pd catalyst (11.2 mg, 0.4 mol% Pd/C) and **4l** (0.2 mmol, 1.0 equiv) sequentially under nitrogen. Then, Anhydrous toluene (2.0 mL) and phenylmagnesium chloride (0.3 mmol, 1.5 equiv, 3M in THF) were added to the mixture, sealed, and run at 140 ℃ for 48 hours. After that, the stirring was stopped, and the mixture was allowed to cool to room temperature. The reaction was quenched by adding saturated aqueous NH_4Cl solution, followed by extraction with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford the desired product **4q** (38.0 mg, 61% yield), yellow solid.

4-([1,1'-biphenyl]-4-yl)-5-fluoro-1,3-dihydroisobenzofuran(4q)



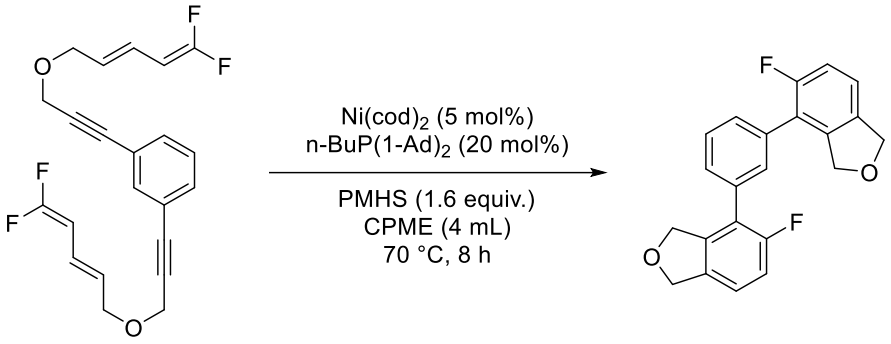
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 4H), 7.50 – 7.44 (m, 4H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.16 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.12 (t, *J* = 9.0 Hz, 1H), 5.15 (s, 2H), 5.11 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J*= 246.0 Hz), 140.8, 140.5, 134.9, 133.2, 132.5, 129.4 (d, *J*= 2.0 Hz), 128.8, 127.5, 127.2, 127.1, 126.5, 120.9 (d, *J*= 9.0 Hz), 115.2 (d, *J*= 25.0 Hz), 73.6, 73.3 (d, *J*= 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.6.

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{20}H_{15}FONa$:313.0999, found: 313.0991.

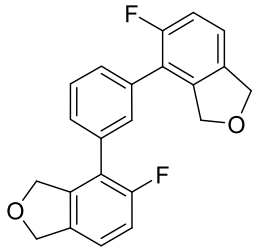
5.3 Double-defluorinative cycloaddition reaction of **5**



5 **6**, 63%

A pre-dried 25 mL Schlenk reaction tube, equipped with a magnetic stir bar, was charged with **5** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$ (1.4 mg, 0.005 mmol, 5 mol%), and n-$BuP(1\text{-}Ad)_2$ (7.3 mg, 0.020 mmol, 20 mol%) under a nitrogen atmosphere. CPME (4 mL) and PMHS (38 μL, 0.16 mmol, 1.6 equiv) were then added sequentially. The reaction vessel was sealed and stirred at 70 °C. Upon complete consumption of the starting material (about 8h), the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a short pad of silica gel to remove inorganic solids. The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to afford the title compound **6** (23.0 mg, 63% yield).

1,3-bis(5-fluoro-1,3-dihydroisobenzofuran-4-yl)benzene (6)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.09 (t, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 7.0 Hz, 3H), 6.84 (s, 1H), 5.12 (s, 4H), 5.04 (s, 4H).

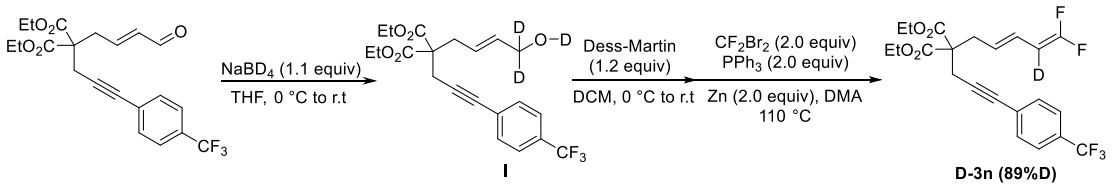
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J*= 246.0 Hz), 138.4, 135.4, 132.3, 129.8 (d, *J* = 2.0 Hz), 122.1 (d, *J*= 9 Hz), 118.5, 115.5, 115.2, 111.9, 73.5, 72.9 (d, *J*= 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.7 (dd, *J* = 11.3, 3.8 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{16}F_2O_2Na$:373.1011, found: 373.1009.

5.4 Synthesis of monodeuterated and monofluorinated aromatic rings

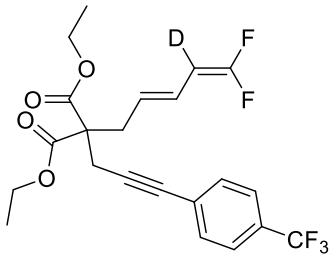
5.4.1 The synthesis of **D-3n**



Add a stirrer to a dried 25 mL round bottom flask, and then sequentially add aldehyde (3.0 mmol, 1.0 equiv) and THF (10 mL) to the flask under nitrogen. Then, add $NaBD_4$ (3.3 mmol, 1.1 equiv) in tetrahydrofuran solution dropwise at 0 ℃ and react at room temperature for 1 hour. After the substrate is completely consumed, quench with D_2O (2 mL), extract with ethyl acetate (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford the desired product I.

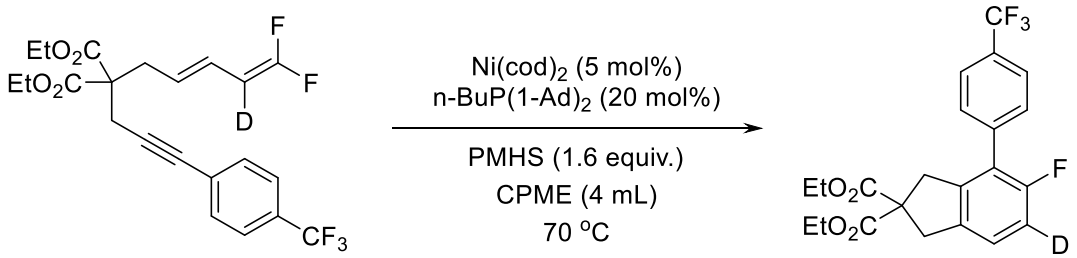
Following Steps 4 and 5 of General Procedure 2.1, compound **I** was transformed into substrate **D-3n** (89% D). The deuterium incorporation rate of compound D-3n was determined by ^{1}H NMR spectroscopy.

Diethyl(E)-2-(5,5-difluoropenta-2,4-dien-1-yl-4-d)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (D-3n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.07 (d, *J* = 15.0 Hz, 1H), 5.47 (dt, *J* = 15.0, 8.0 Hz, 1H), 4.95 (dd, *J* = 24.0, 8.0 Hz, 0.11H), 4.23 (q, *J* = 7.0 Hz, 4H), 3.01 (s, 2H), 2.87 (d, *J* = 9.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 156.3 (dd, *J* = 294.0, 289.0 Hz), 131.9, 130.0, 129.7, 126.3 (q, *J* = 238.0 Hz), 125.7 (dd, *J* = 11.0, 3.0 Hz), 125.2 (q, *J* = 4.0 Hz), 123.5 (dd, *J* = 5.0, 2.0 Hz), 87.1, 82.5, 81.7 (dd, *J* = 27.0, 16.0 Hz), 61.8, 57.1, 35.9, 23.7, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8, -86.1 (d, *J* = 30.1 Hz), -88.5 (d, *J* = 30.1 Hz).
HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{20}DF_5O_4Na$: 468.1315, found: 468.1317.

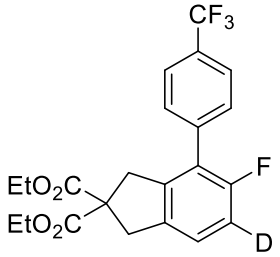
5.4.2 The reaction trial



D-3n (89%D) **D-4n (86%D), 69%**

A pre-dried 25 mL Schlenk reaction tube, equipped with a magnetic stir bar, was charged with **D-3n** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$ (1.4 mg, 0.005 mmol, 5 mol%), and n-$BuP(1\text{-}Ad)_2$ (7.3 mg, 0.020 mmol, 20 mol%) under a nitrogen atmosphere. CPME (4 mL) and PMHS (38 μL, 0.16 mmol, 1.6 equiv) were then added sequentially. The reaction vessel was sealed and stirred at 70 °C. Upon complete consumption of the starting material (about 8h), the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a short pad of silica gel to remove inorganic solids. The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to afford the title compound **6** (29.3 mg, 69% yield, 86%D). The deuterium incorporation rate of compound D-3n was determined by ^{1}H NMR spectroscopy.

Diethyl 5-fluoro-4-(4-(trifluoromethyl)phenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate-6-d (D-4n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 12.0 Hz, 0.14H),4.18 (q, J = 7.0 Hz, 4H), 3.61 (s, 2H), 3.45 (s, 2H), 1.23 (t, *J* = 7.0 Hz, 6H).

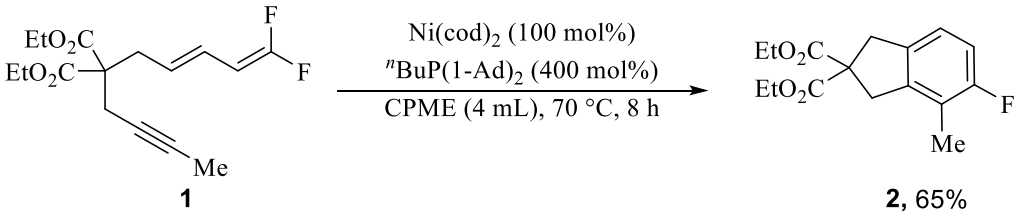
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 158.8 (d, *J*= 244.0 Hz), 140.7 (d, *J*= 3 Hz), 137.8, 135.9 (d, *J*= 3.0 Hz), 129.9, 128.8, 126.6 (q, *J*= 228.0 Hz), 126.3, 125.3 (q, *J*= 4.0 Hz), 124.8 (d, *J*= 9.0 Hz), 114.7 (d, *J*= 24.0 Hz), 61.8, 60.8, 39.9, 39.8 (d, *J*= 3.0 Hz), 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6, -121.4 (d, *J* = 7.5 Hz).

HRMS (ESI) $(M+Na)^+$: Calcd for $C_{22}H_{19}DF_4O_4Na$: 448.1253, found: 448.1248.

6. Control experiments

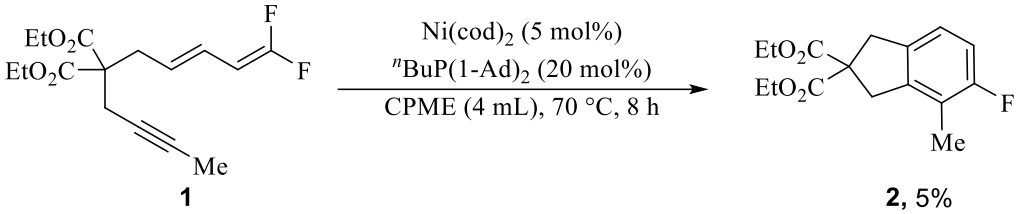
6.1 Experiments with Stoichiometric catalyst without Si-H



1 **2**, 65%

A pre-dried 25 mL Schlenk reaction tube, equipped with a magnetic stir bar, was charged with **1** (0.1 mmol, 1.0 equiv), Ni(cod)₂ (28 mg, 0.1 mmol, 100 mol%), and n-BuP(1-Ad)₂ (146 mg, 0.4 mmol, 400 mol%) under a nitrogen atmosphere. CPME (4 mL) was then added. The reaction vessel was sealed and stirred at 70 °C for 8 h. After the reaction, the reaction mixture was concentrated under reduced pressure, and the yield was determined by GC using n-tetradecane as an internal standard, 65% yield of **2**.

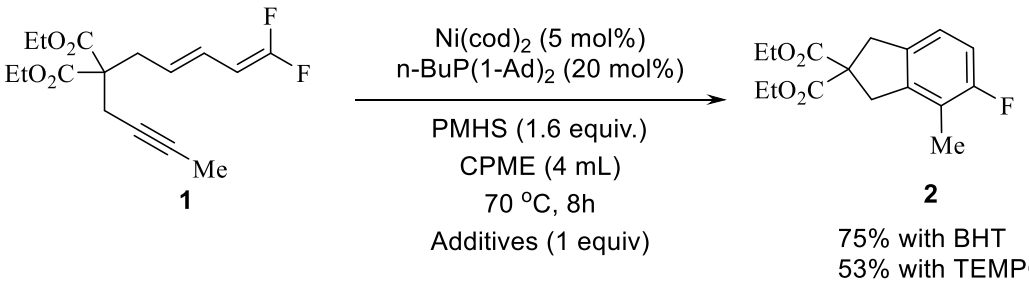
6.2 Experiments with catalytic catalyst without Si-H



1 **2**, 5%

A pre-dried 25 mL Schlenk reaction tube, equipped with a magnetic stir bar, was charged with **1** (0.1 mmol, 1.0 equiv), Ni(cod)₂ (1.4 mg, 0.005 mmol, 5 mol%), and n-BuP(1-Ad)₂ (7.3 mg, 0.020 mmol, 20 mol%) under a nitrogen atmosphere. CPME (4 mL) was then added. The reaction vessel was sealed and stirred at 70 °C. After 8 h, the reaction mixture was concentrated under reduced pressure, and the yield was determined by GC using n-tetradecane as an internal standard, 5% yield of **2**.

6.3 Experiments with radical scavengers TEMPO or BHT

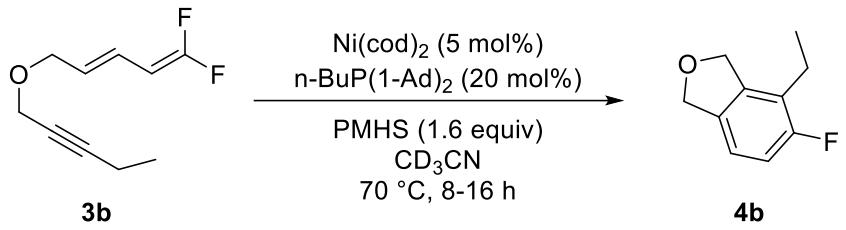


1 **2**

75% with BHT
53% with TEMPO

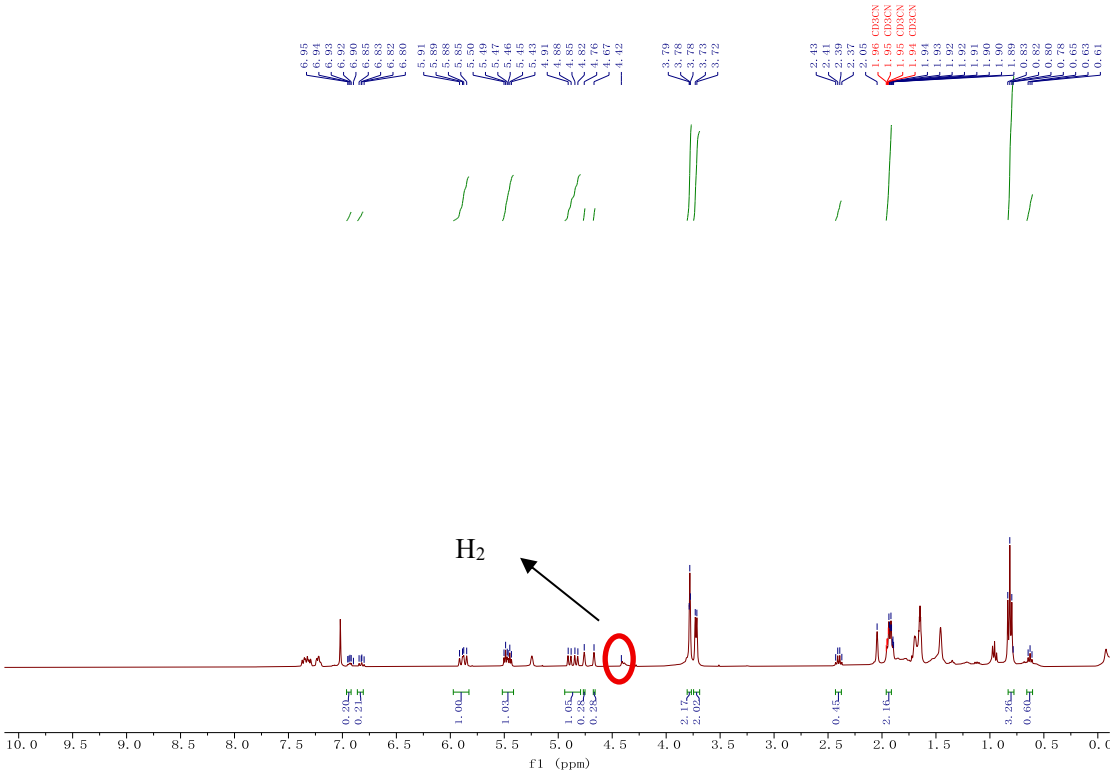
A pre-dried 25 mL Schlenk reaction tube, equipped with a magnetic stir bar, was charged with **1** (0.1 mmol, 1.0 equiv), Ni(cod)₂ (1.4 mg, 0.005 mmol, 5 mol%), and n-BuP(1-Ad)₂ (7.3 mg, 0.020 mmol, 20 mol%) under a nitrogen atmosphere. CPME (4 mL) and additives (1 equiv) were then added. The reaction vessel was sealed and stirred at 70 °C. After 8 h, the reaction mixture was concentrated under reduced pressure, and the yield was determined by GC using n-tetradecane as an internal standard.

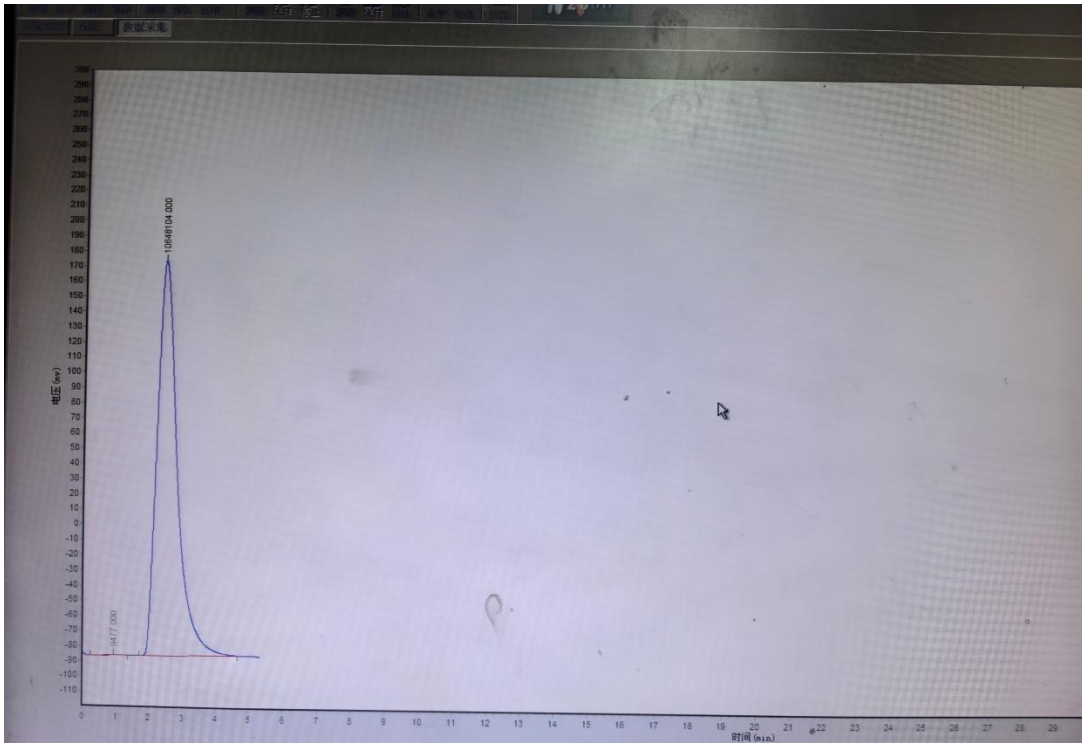
6.4 Hydrogen Detection Experiment



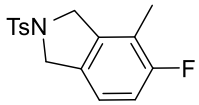
3b **4b**

Under a nitrogen atmosphere, **3b** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$ (1.4 mg, 0.005 mmol, 5 mol%), and n-BuP(1-Ad)$_2$ (7.3 mg, 0.020 mmol, 20 mol%) were sequentially added, followed by the addition of PMHS (1.6 equiv) and CD_3CN. The reaction tube was sealed and stirred at 70 °C for 8 hours. After the reaction was complete, the mixture was directly analyzed by crude NMR spectroscopy. According to the literature[10], the chemical shift of hydrogen gas (H_2) in ^1H NMR appears at 4.5 ppm. (The Si-H bond in PMHS was measured by NMR in deuterated acetonitrile solvent, with a chemical shift observed at 4.66 ppm). To further confirm whether hydrogen gas was generated during the reaction, we performed hydrogen measurements using an Agilent GC7890A equipped with a TCD detector, which confirmed the production of hydrogen gas.



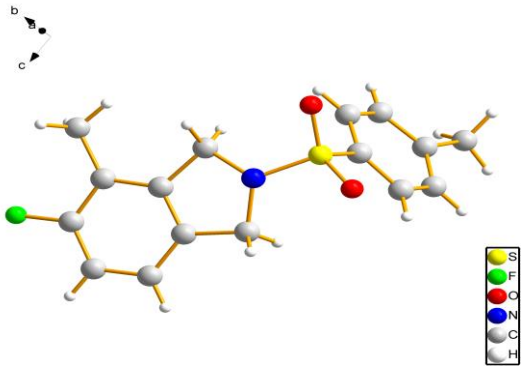

1064104.000
1417.000
电压 (mv)
时间 (min)

7. Test the single crystal structure of the product of 4ah



The data of compound 4ah was collected on a SuperNova diffractometer with graphite monochromated Mo Kα radiation (λ = 1.54184 Å) at 293 K. The data were modified for Lorentz and polarization effects. The structures were determined by immediate methods and refined with a full-matrix least-squares technique based on F2 with the SHELXL-2014 software package.10 Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Compound 4ah was taken in 1:2 acetonitrile: n-hexane (5 mL) and the solution was kept for 15 days at -20 ℃. The solvent was slowly evaporated and white needle crystals were formed.



CCDC: 2484178

Bond precision:	C-C = 0.0063 A		Wavelength=0.71073
Cell:	a=21.2486(11)	b=12.1534(6)	c=18.1236(10)
	alpha=90	beta=108.744(6)	gamma=90
Temperature	299 K		

	Calculated	Reported
Volume	4432.1(4)	4432.1(4)
Space group	C c	C c
Hall group	C -2yc	C -2yc
Moiety formula	C16 H16 F N O2 S	C16 H16 F N O2 S
Sum formula	C16 H16 F N O2 S	C16 H16 F N O2 S
Mr	305.36	305.36
Dx,g cm-3	1.373	1.373
Z	12	12
Mu (mm-1)	0.233	0.233
F000	1920.0	1920.0
F000’	1922.41	

h,k,lmax	30,17,26	30,17,26
Nref	14074[7041]	14074
Tmin,Tmax	0.954, 0.959	
Tmin’	0.954	

Correction method= Not given

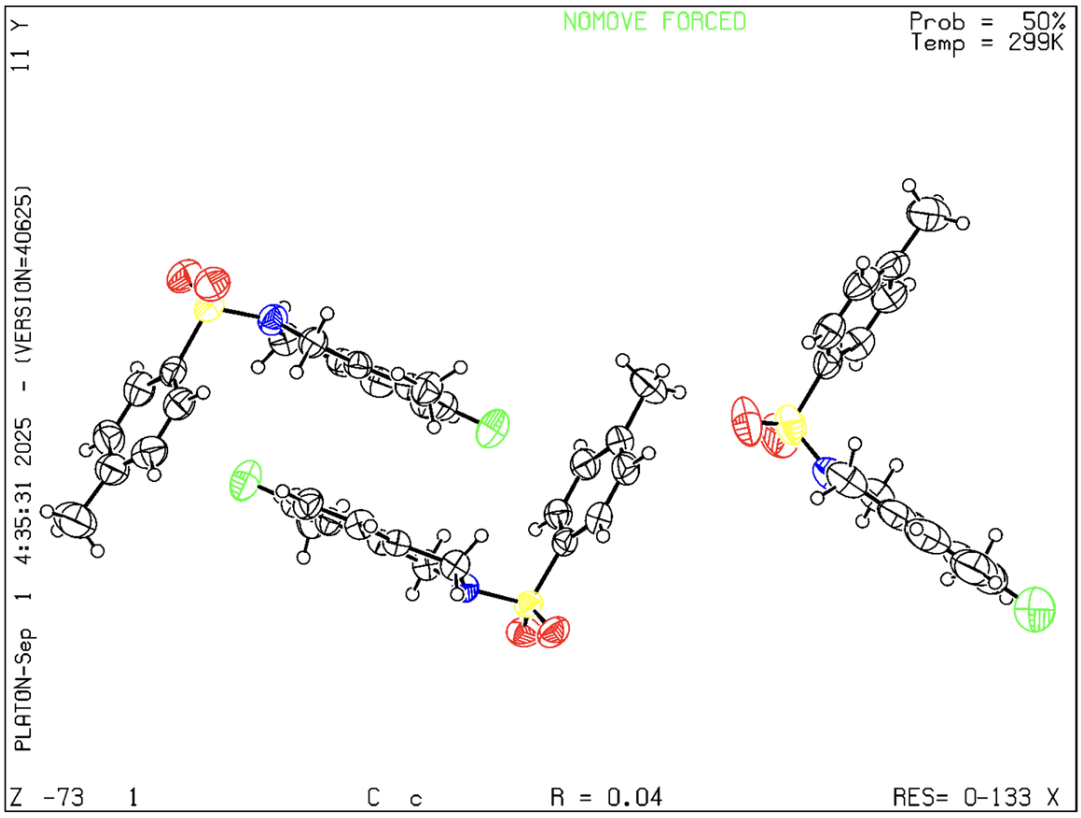
Data completeness= 2.00/1.00 Theta(max)= 30.922

R(reflections)= 0.0424(7735) wR2(reflections)= 0.1419(10167)

S = 0.959 Npar= 574

duplicate check

No duplication found



8. References

1. J. W. Jia, T. Morimoto, Y. Yamaguchi, H. Tanimoto, and K. Kakiuchi, *Org. Lett*, **2021**, *23,* 4893.

2. X. Z, Shu, C. M. Schienebeck, X. X. Li, X. Zhou, W. Z. Song, L.Q.Chen, I. A. Guzei, and W.P. Tang, *Org. Lett*, **2015**, *17,* 5128.

3. T. N. Van, K. N. De, *Tetrahedron*, **2000**, *56*, 7969.

4. N. Cini, F. Machetti, G. Menchi, E. Occhiato, and A. Guarna, *Eur. J. Org. Chem.* **2002,** *2002,* 873.

5. Y. P. Pan, Y. P. You, D. X. He, F. Chen, X.Y. Chang, M. Y. Jin, and X. Y. Xing, *Org. Lett,* **2020**, *22*, 7278.

6. L.G. Zhao, X. Y. Lu, W. Xu, *J. Org. Chem*, **2005**, *70*, 4059.

7. R. E. M. Brooner, T. J. Brown, R. A.Widenhoefer, *Angew. Chem. Int. Ed.,* **2013**, *52,* 6259.

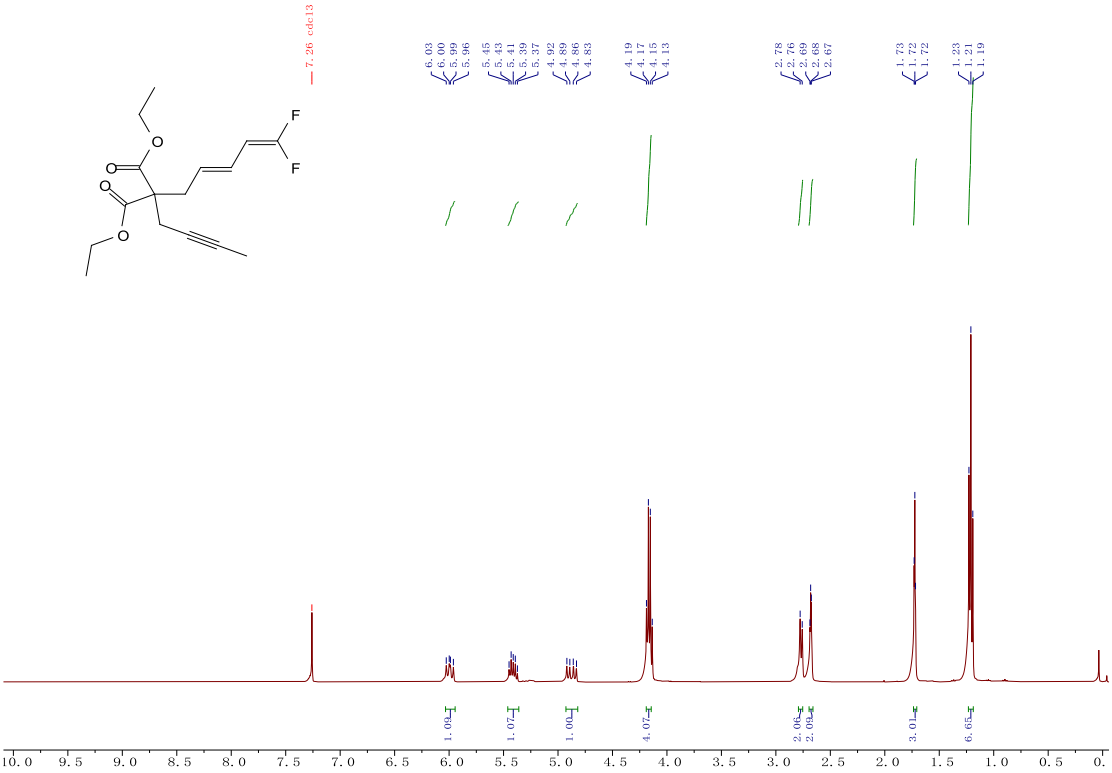
8. F. Ziyanak, M. Kuş, L. Artok, *Adv. Synth. Catal.* **2011**, *353*, 898.

9. X. Li, T. T. Zhu, Z. Q. Shao, Y. J. Li, H. H. Chang, W. C. Gao, Y. L. Zhang, and W. L. Wei, *Tetrahedron*, **2016**, *72*, 69.

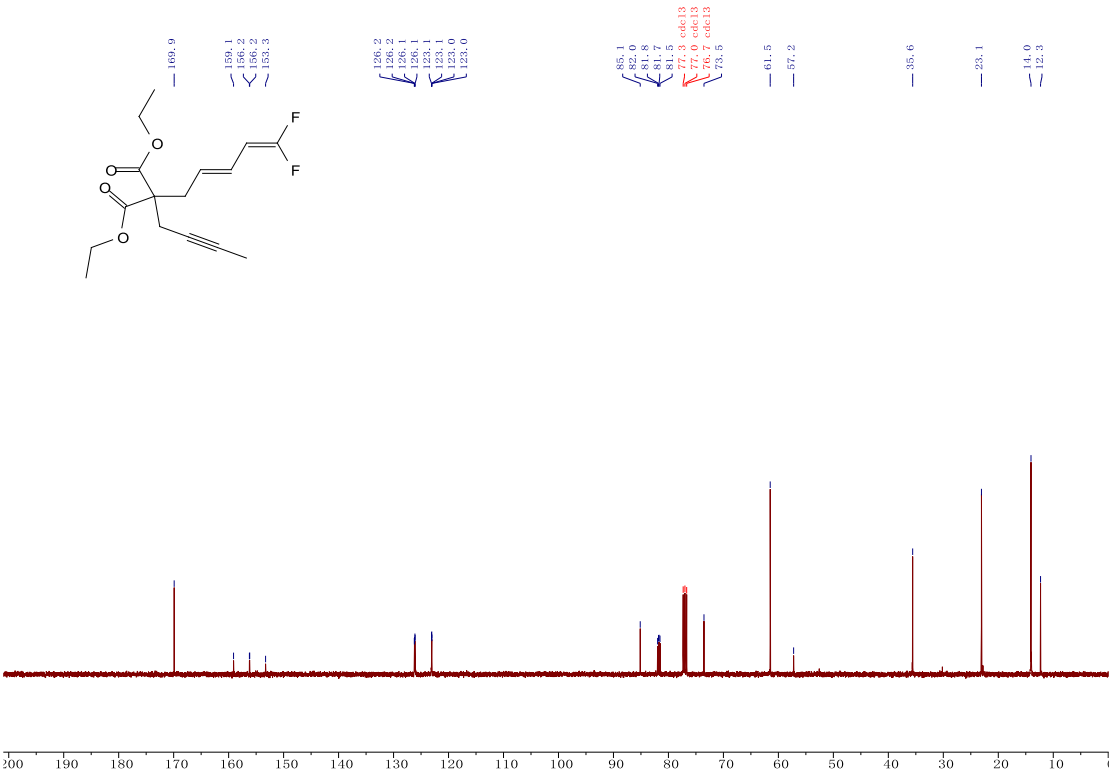
10. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, **2010**, *29*, 2176.

9. ^{1}H ^{19}F and ^{13}C NMR Spectra for Compounds

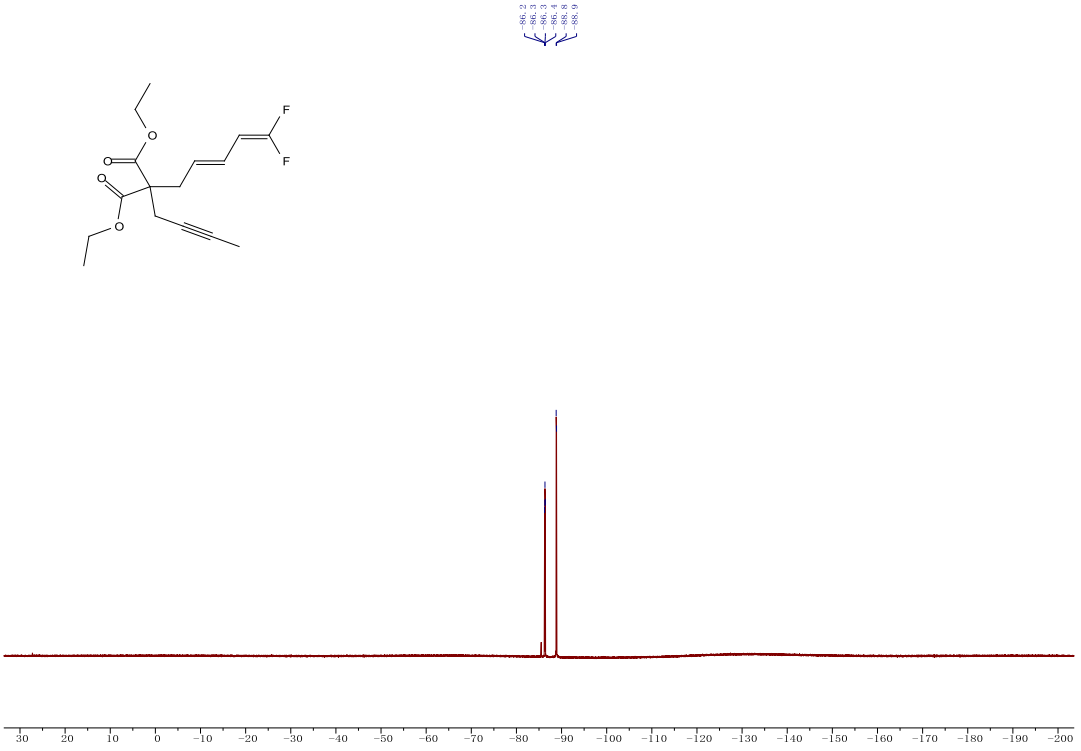
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**



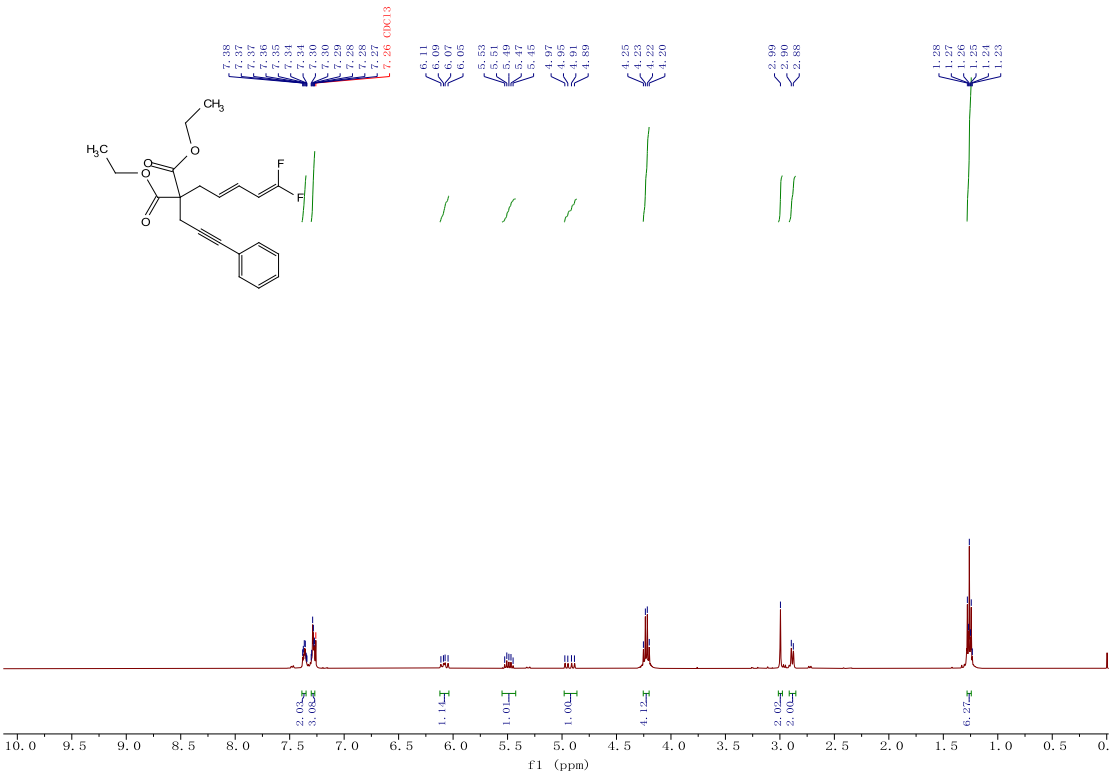
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1**



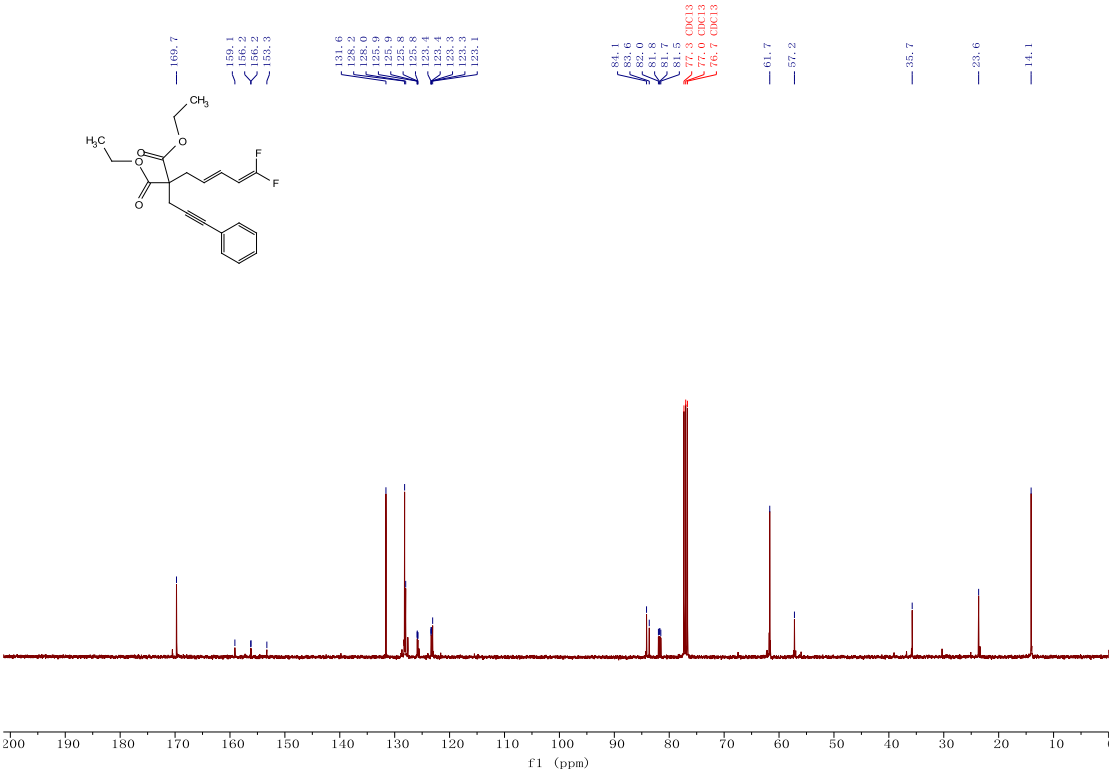
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1**



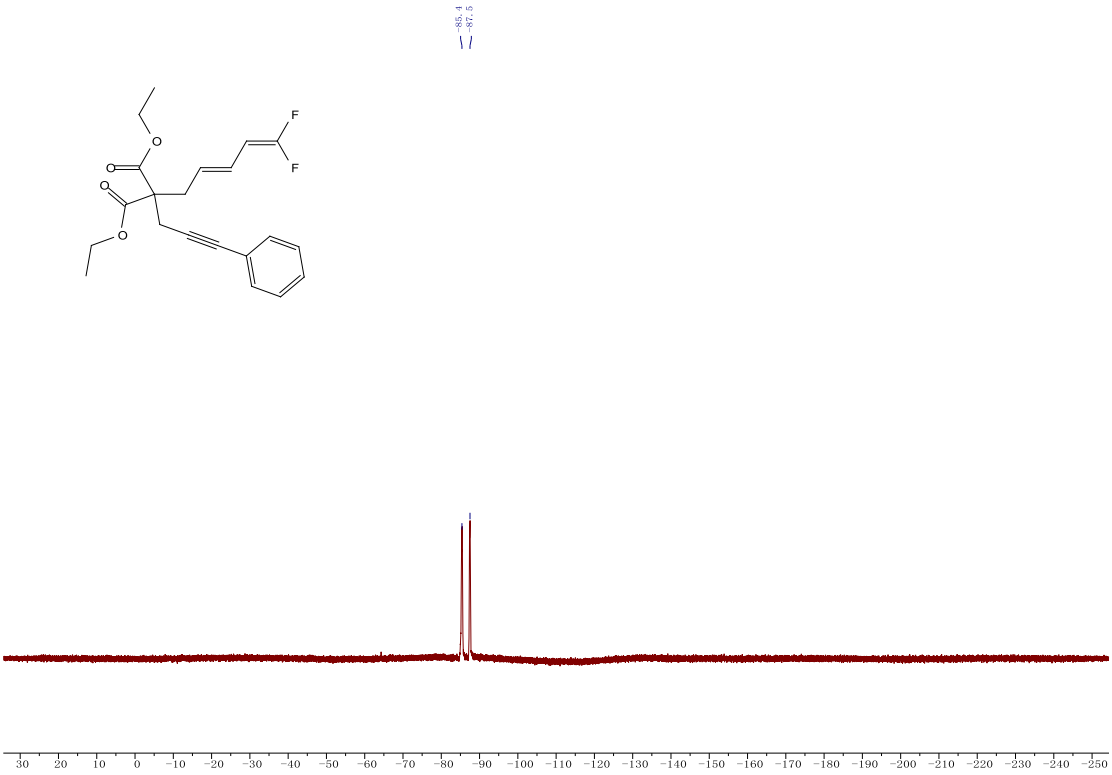
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



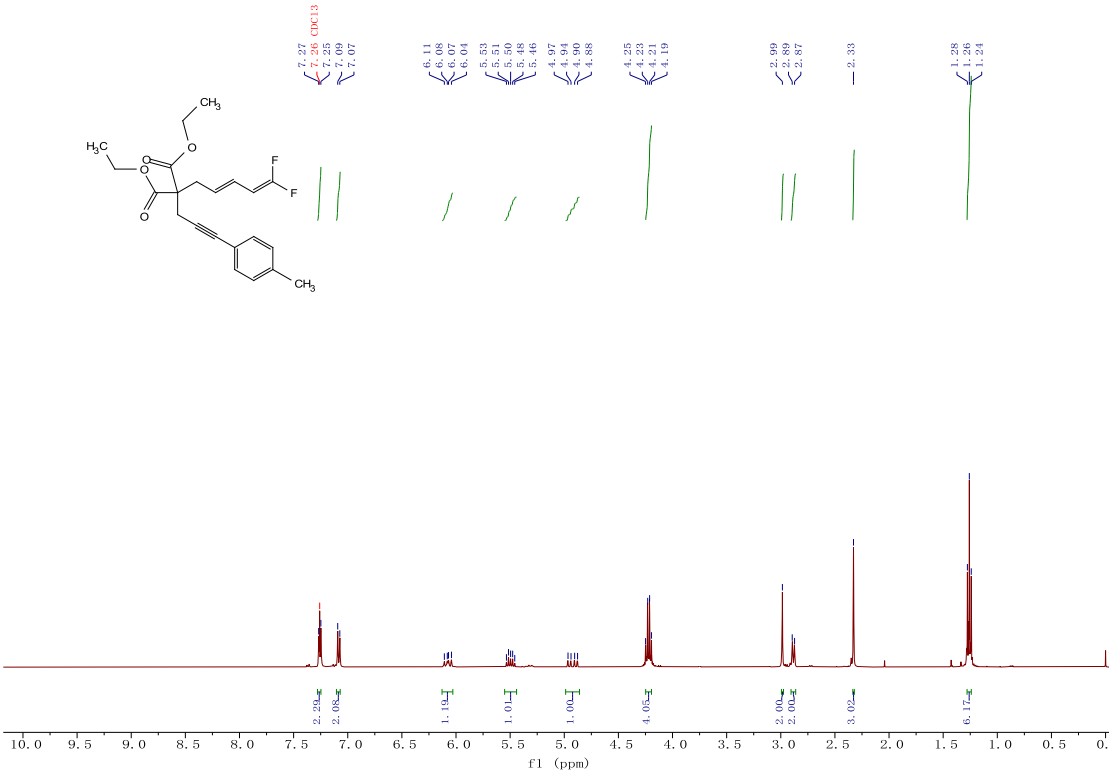
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3aa**



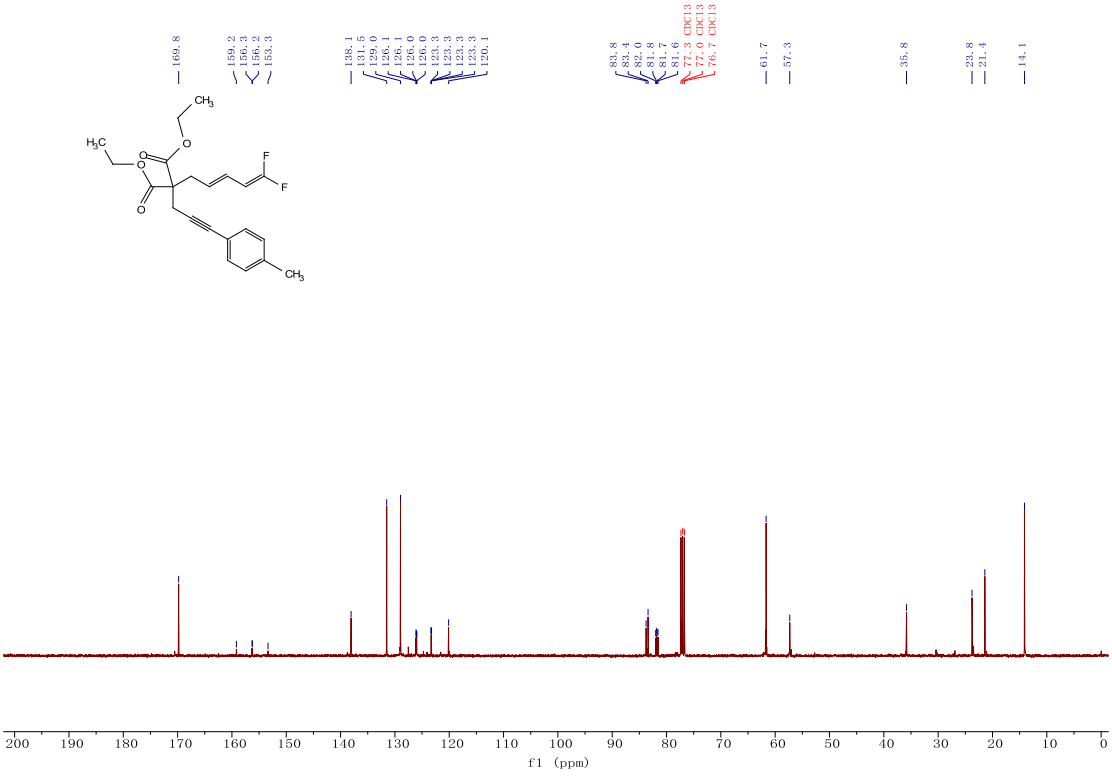
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3aa**



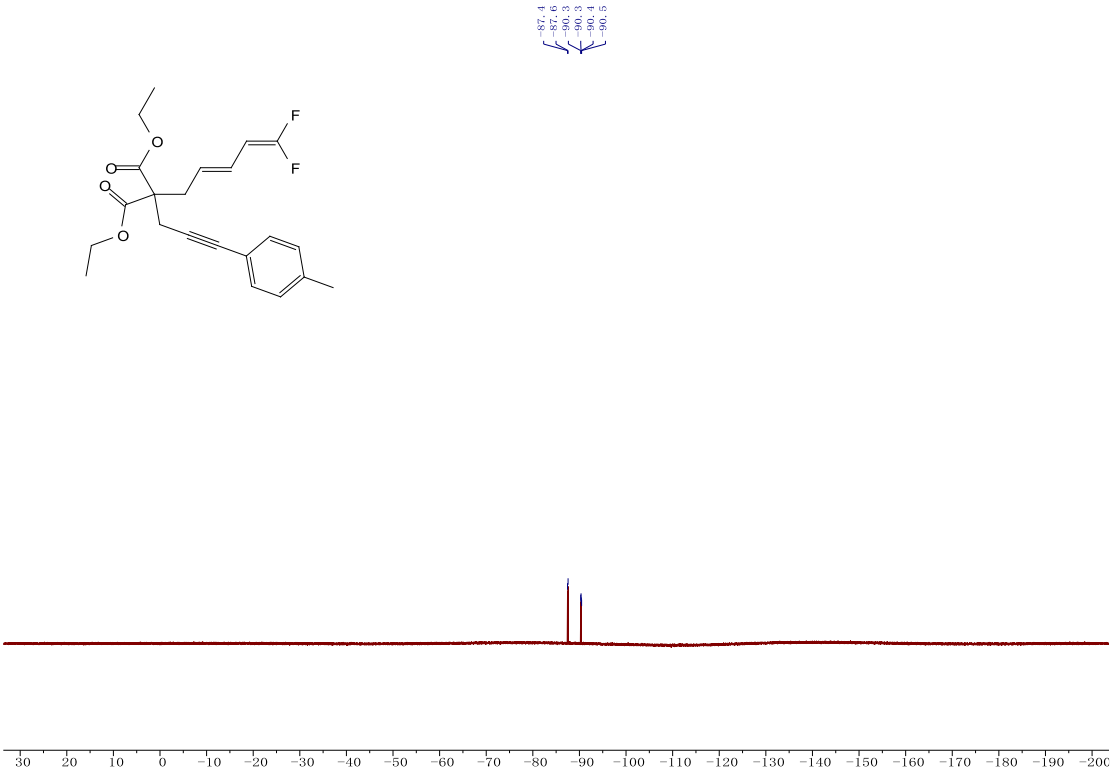
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



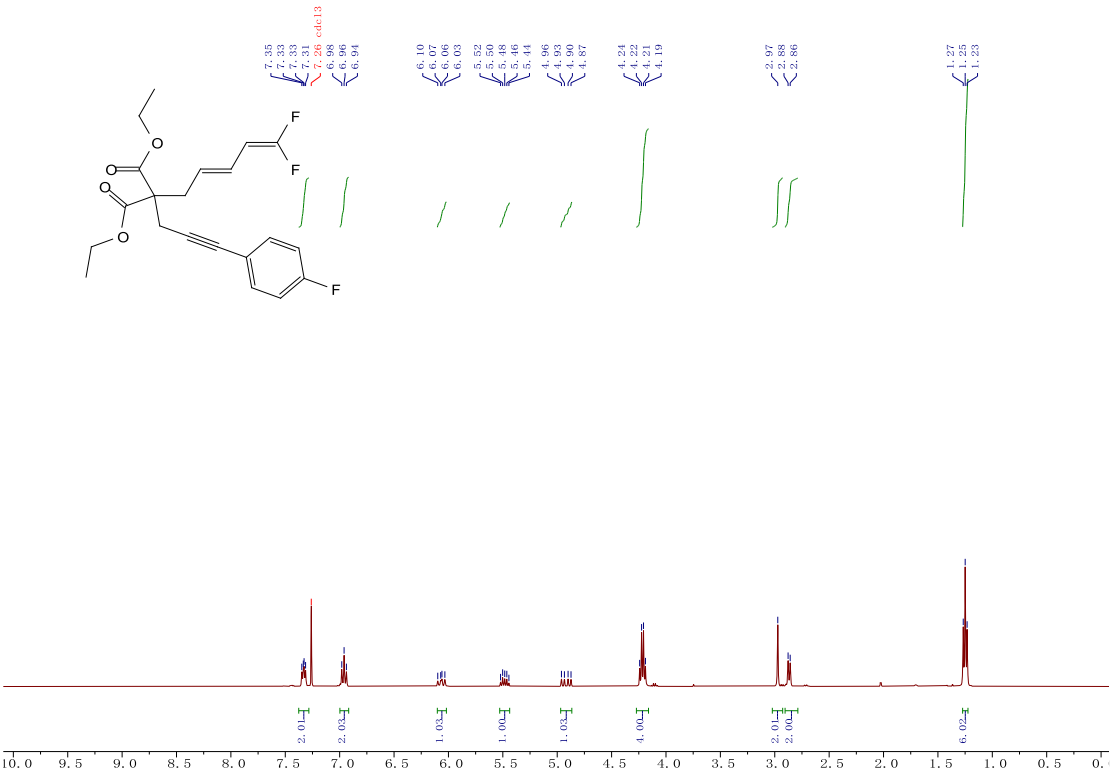
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ab**



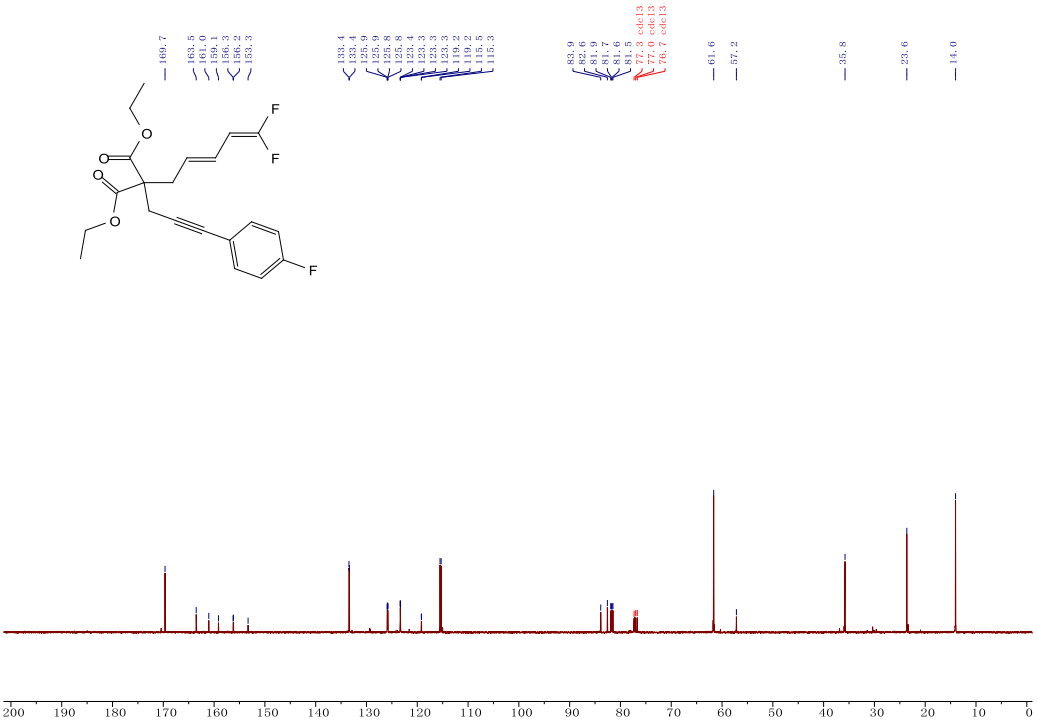
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ab**



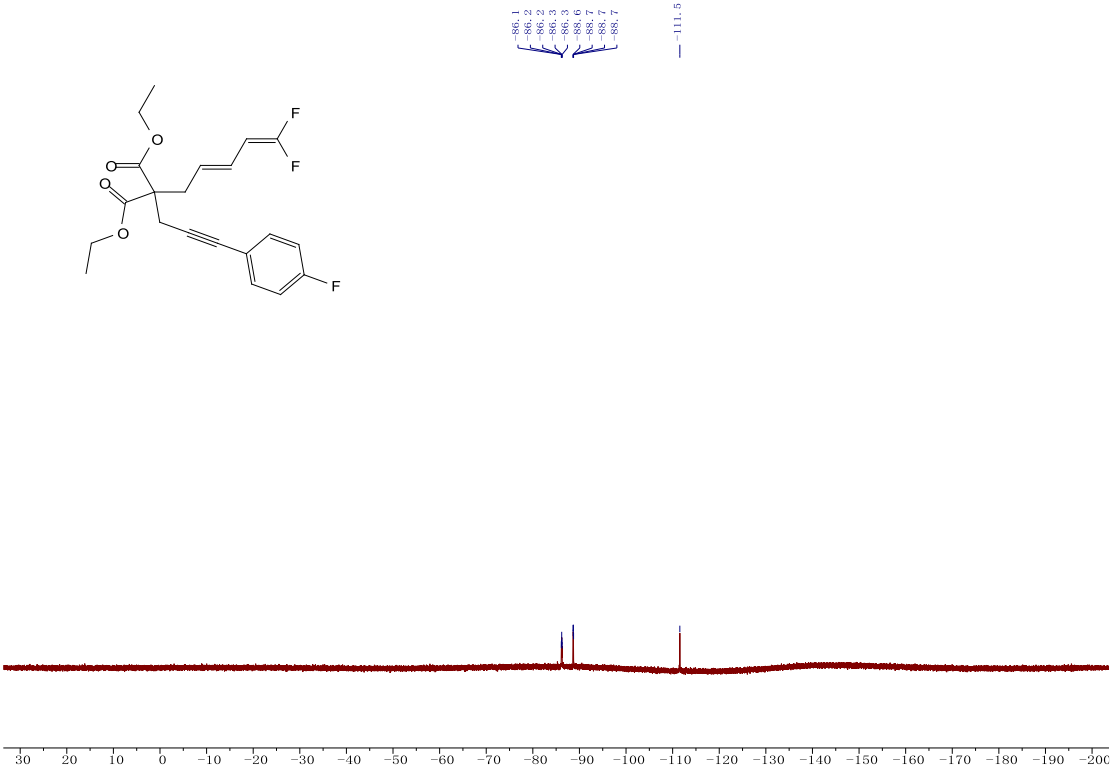
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



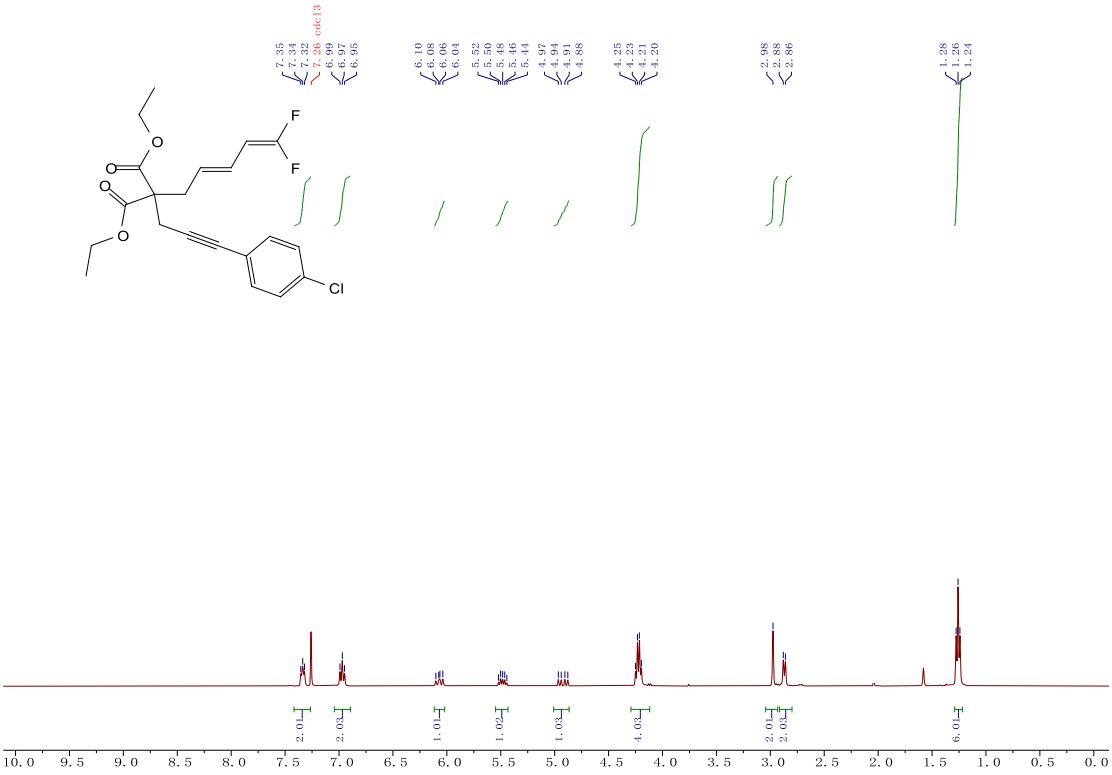
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ac**



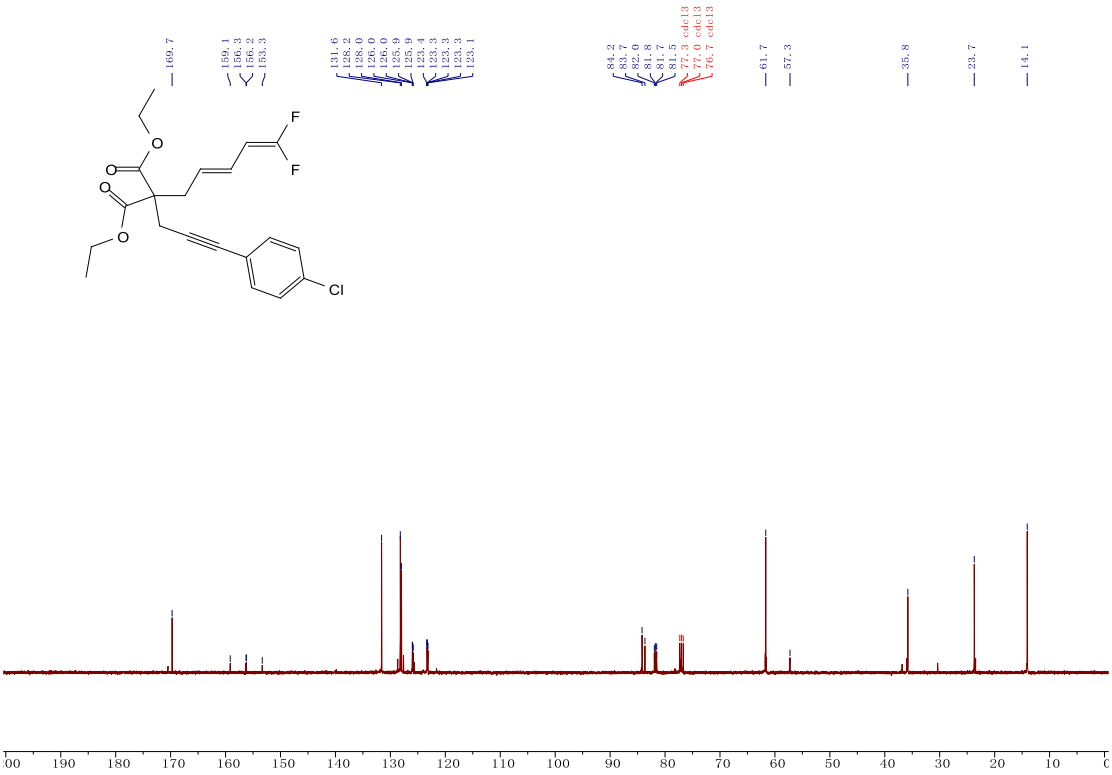
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ac**



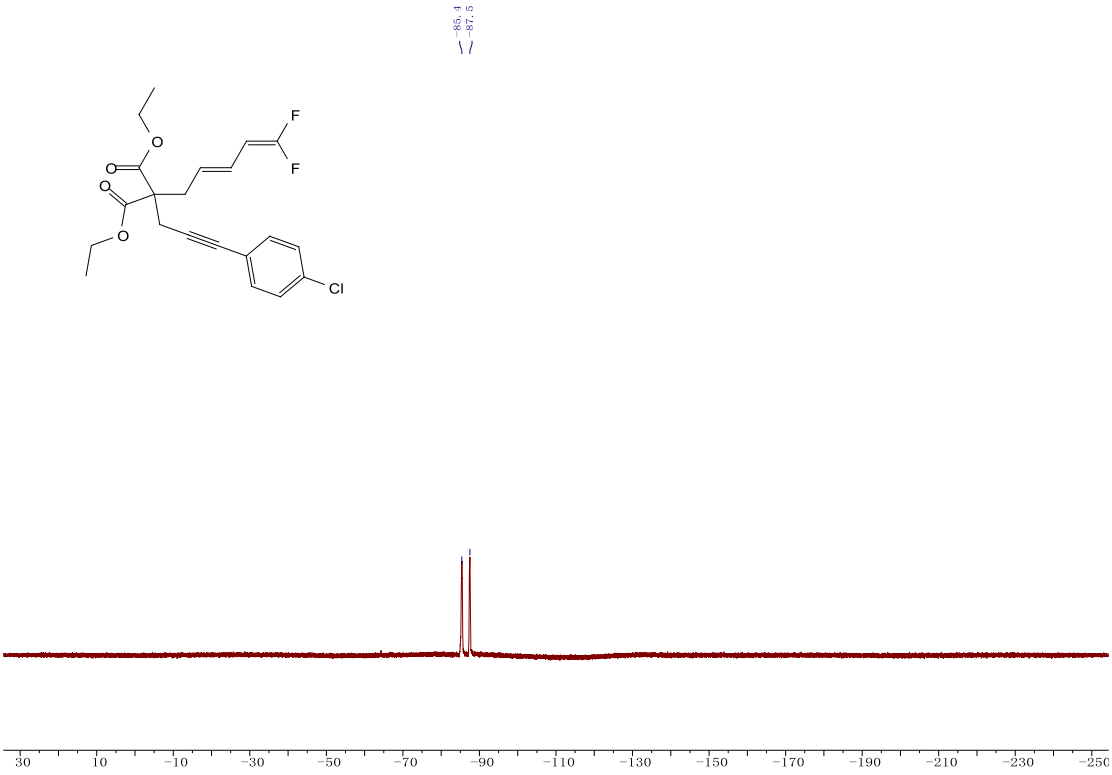
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



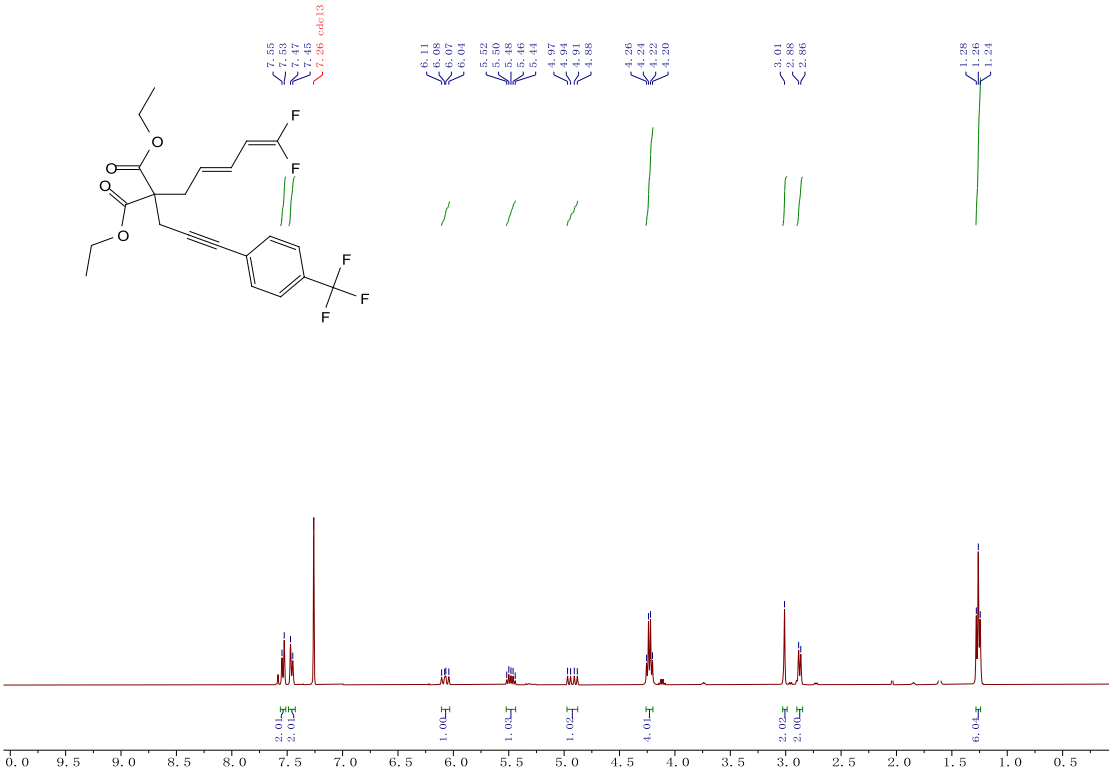
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ad**



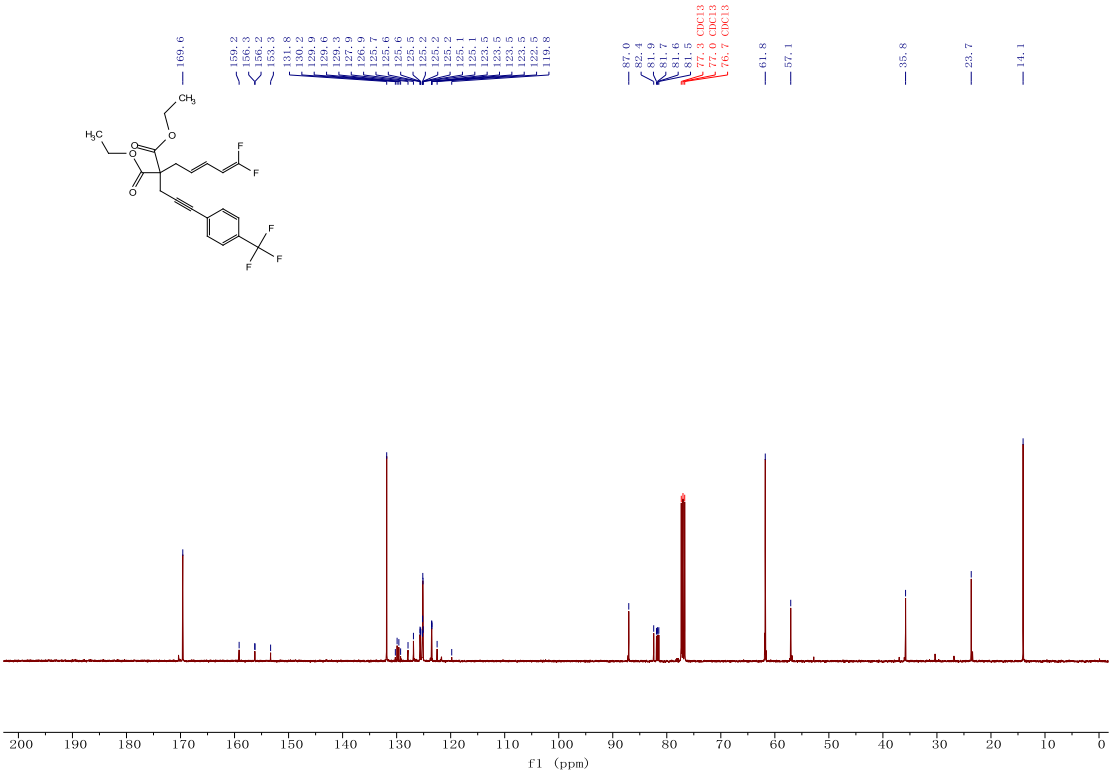
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ad**



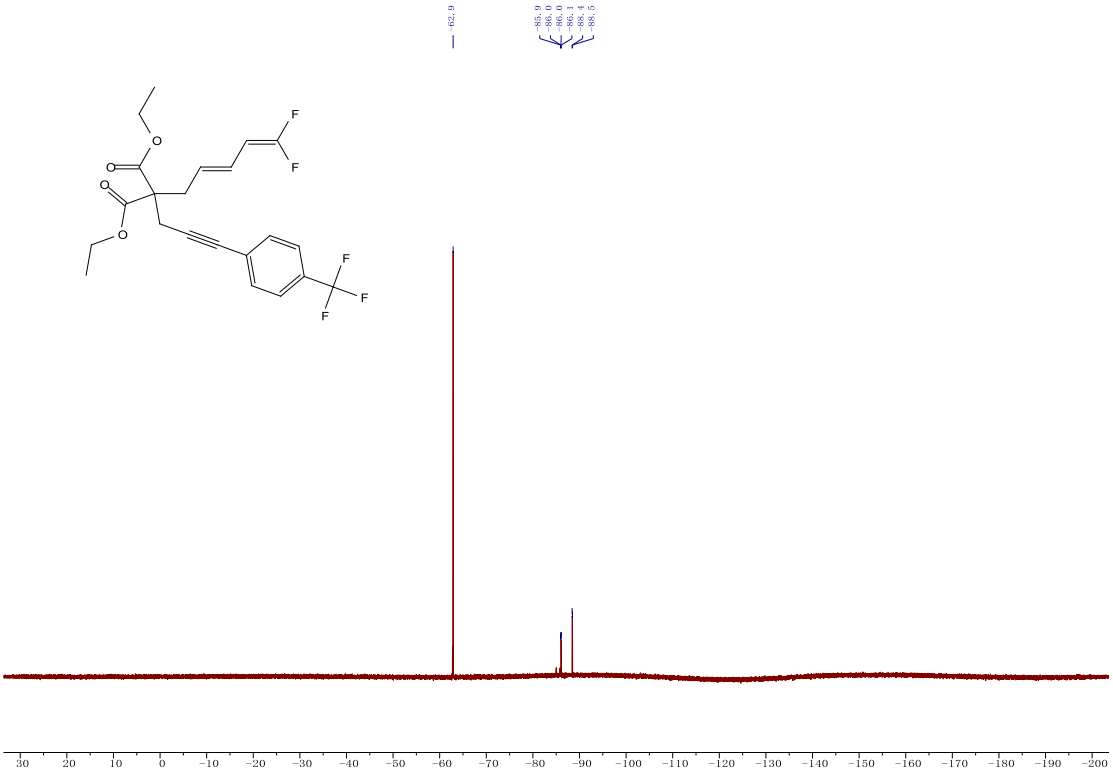
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



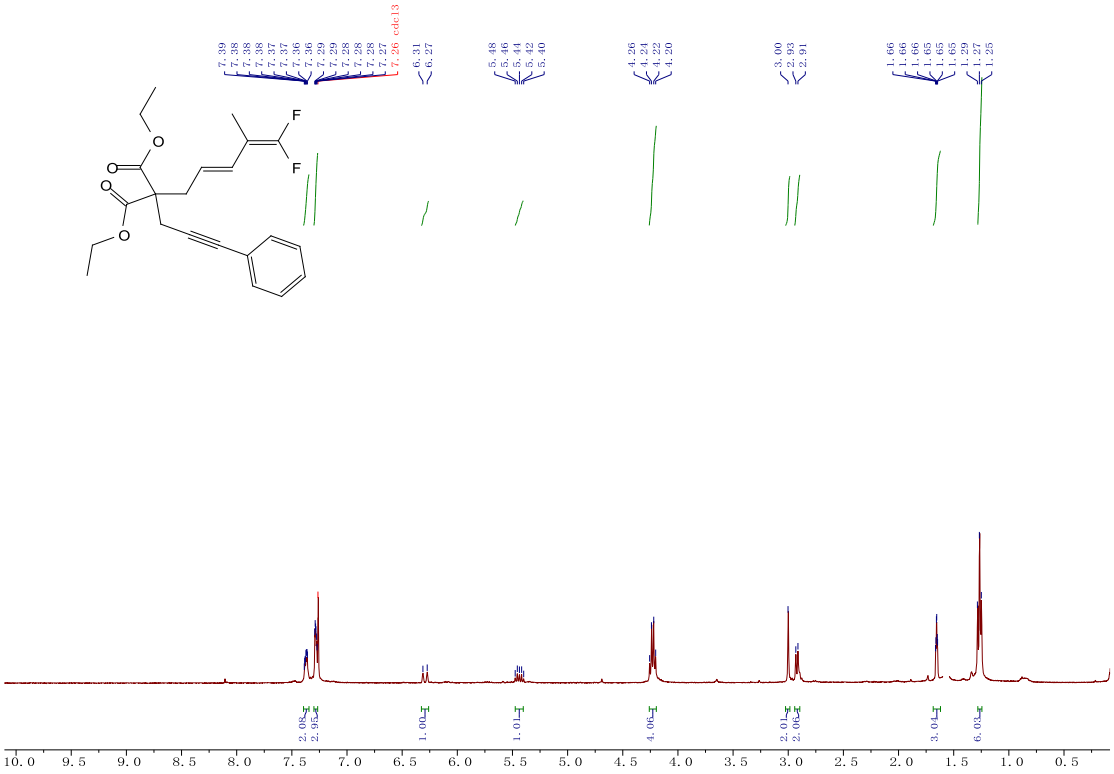
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ae**



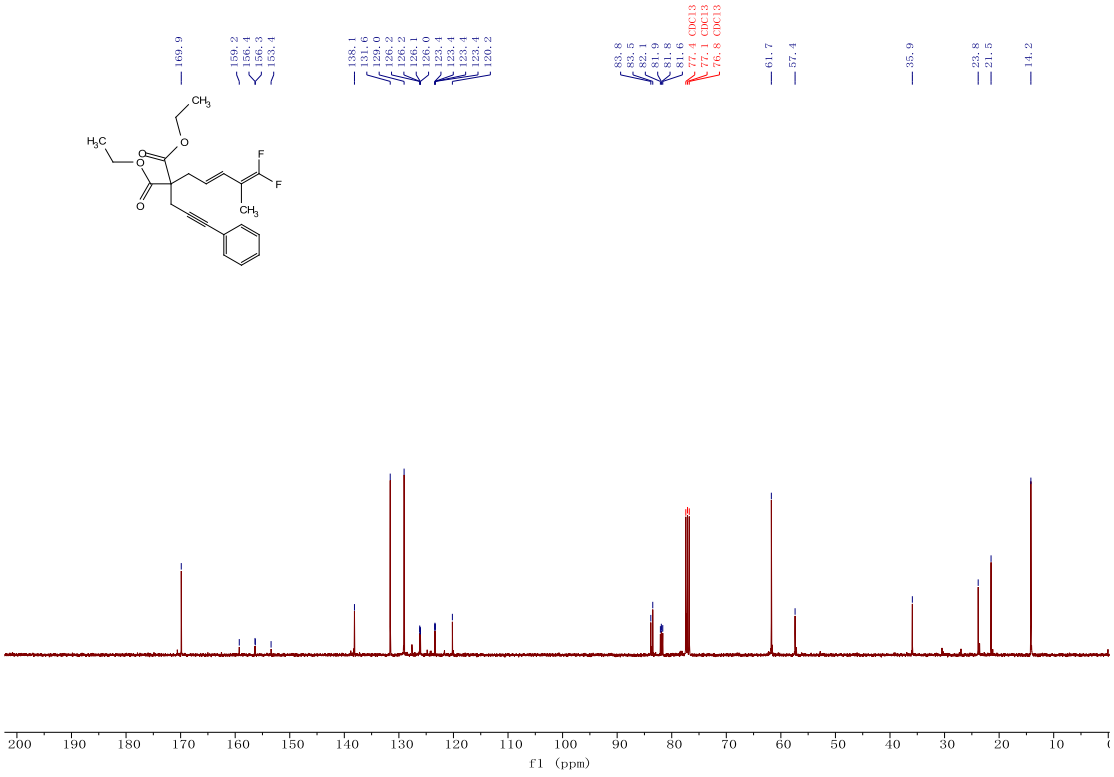
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ae**



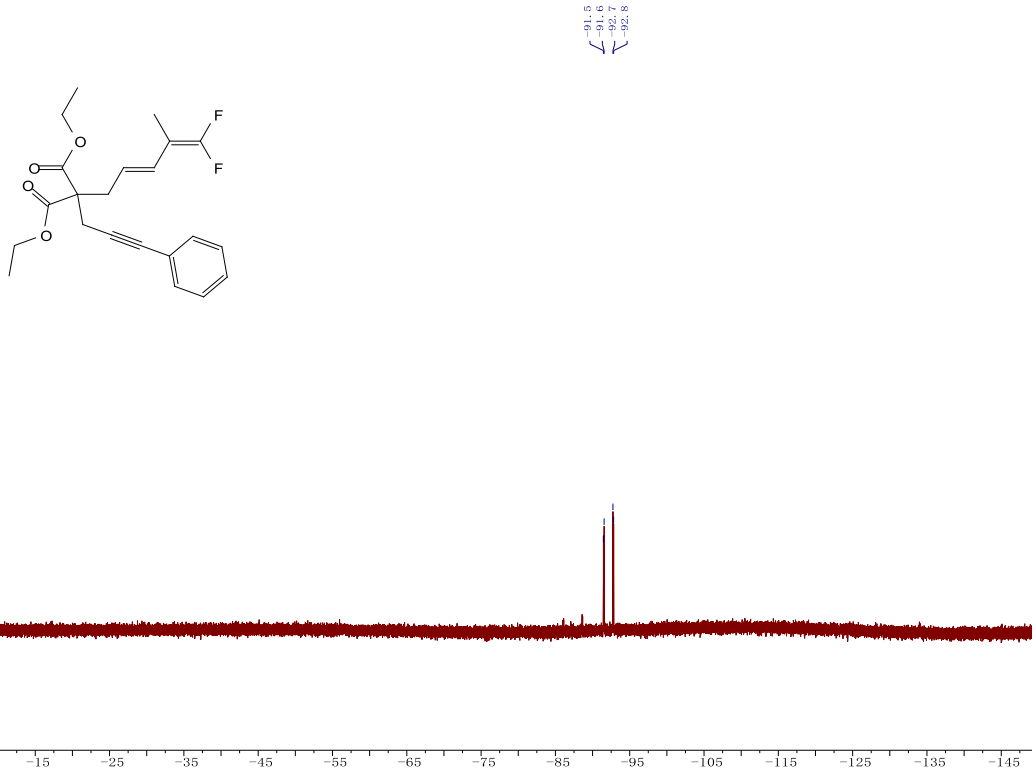
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



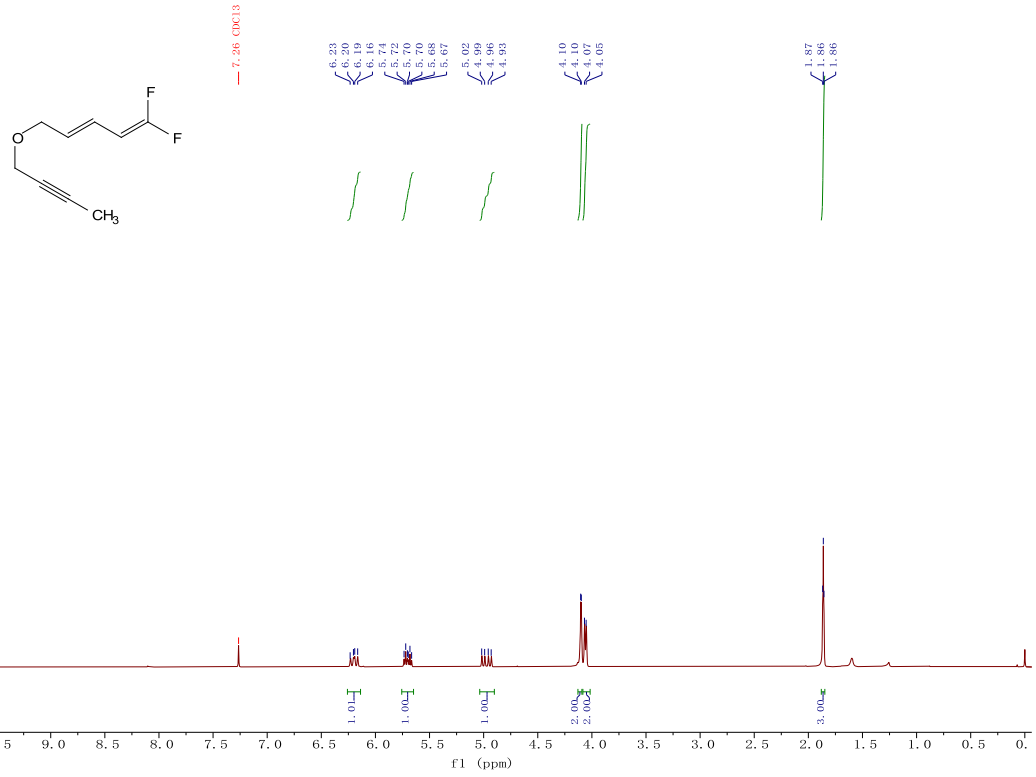
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3af**



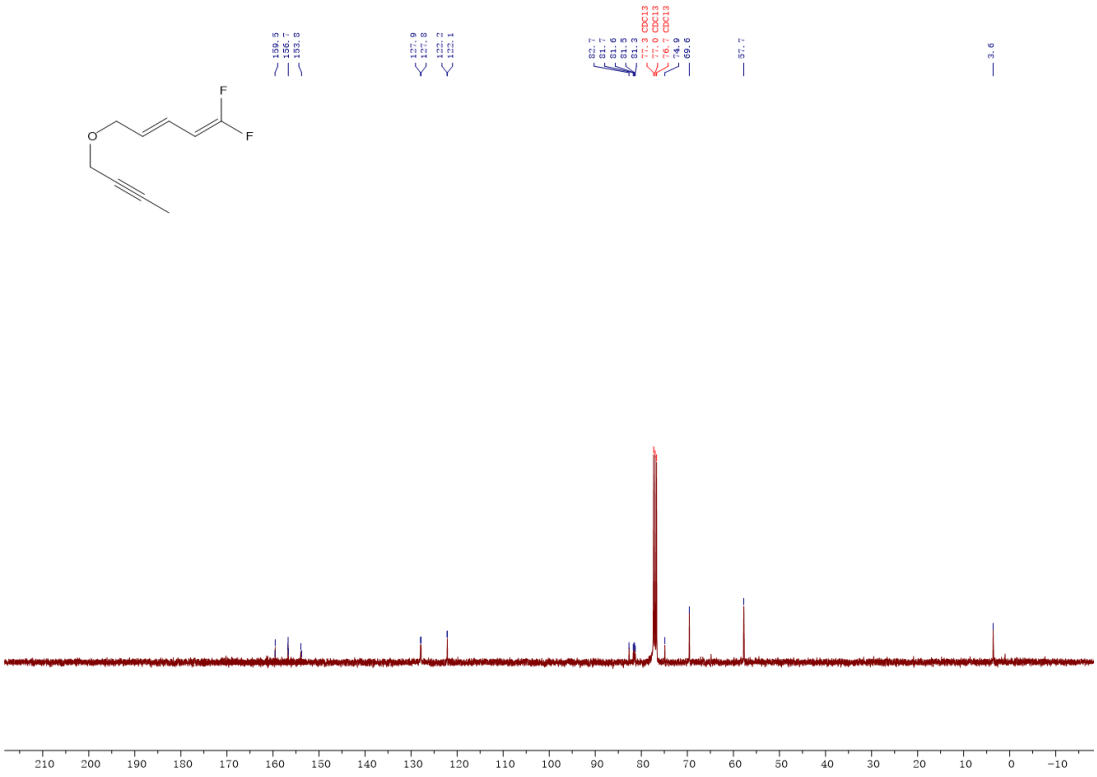
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3af**



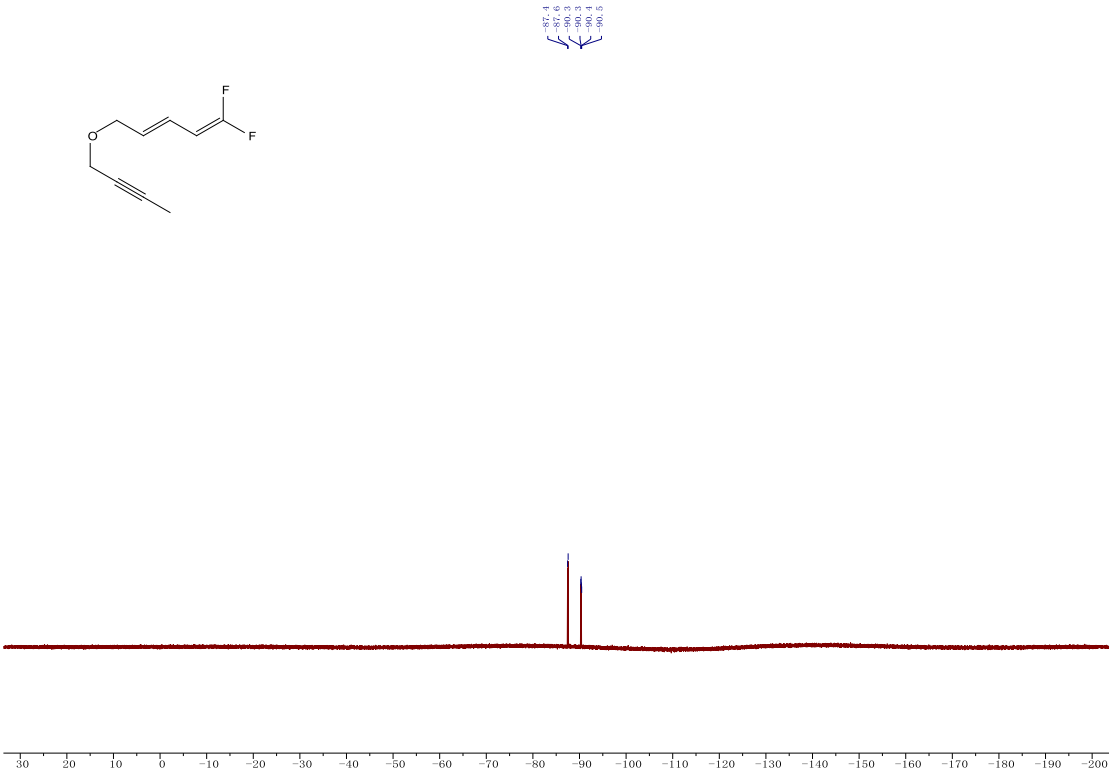
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



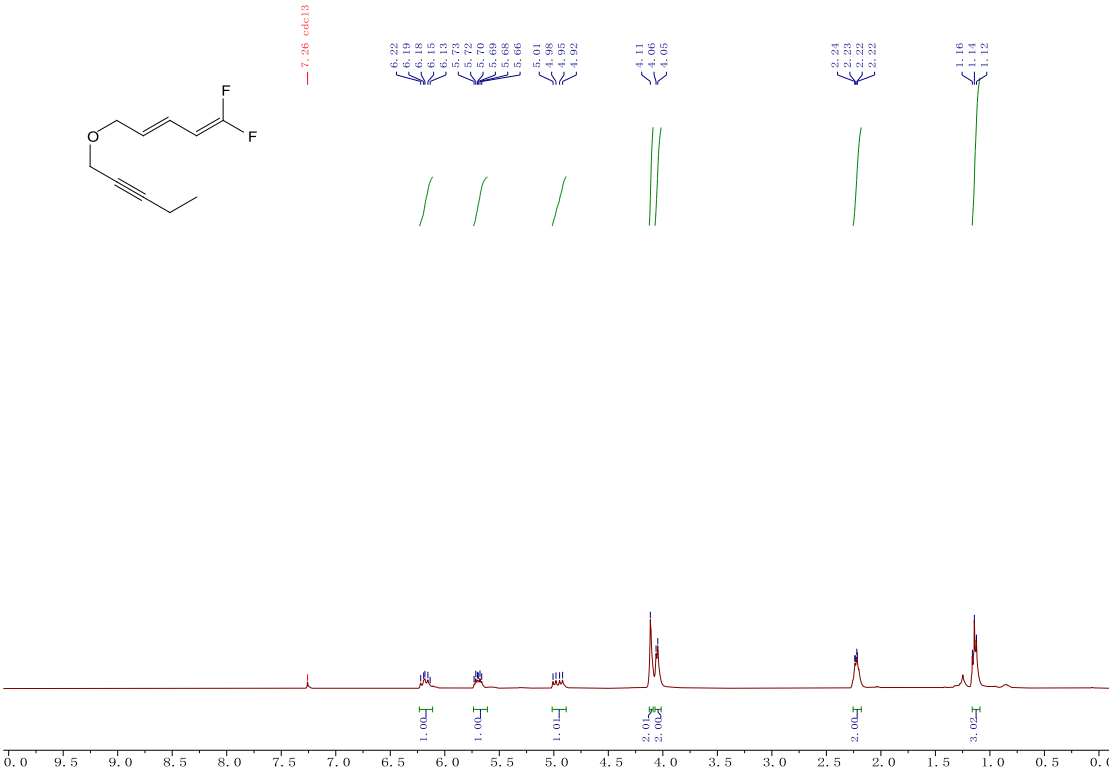
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3a**



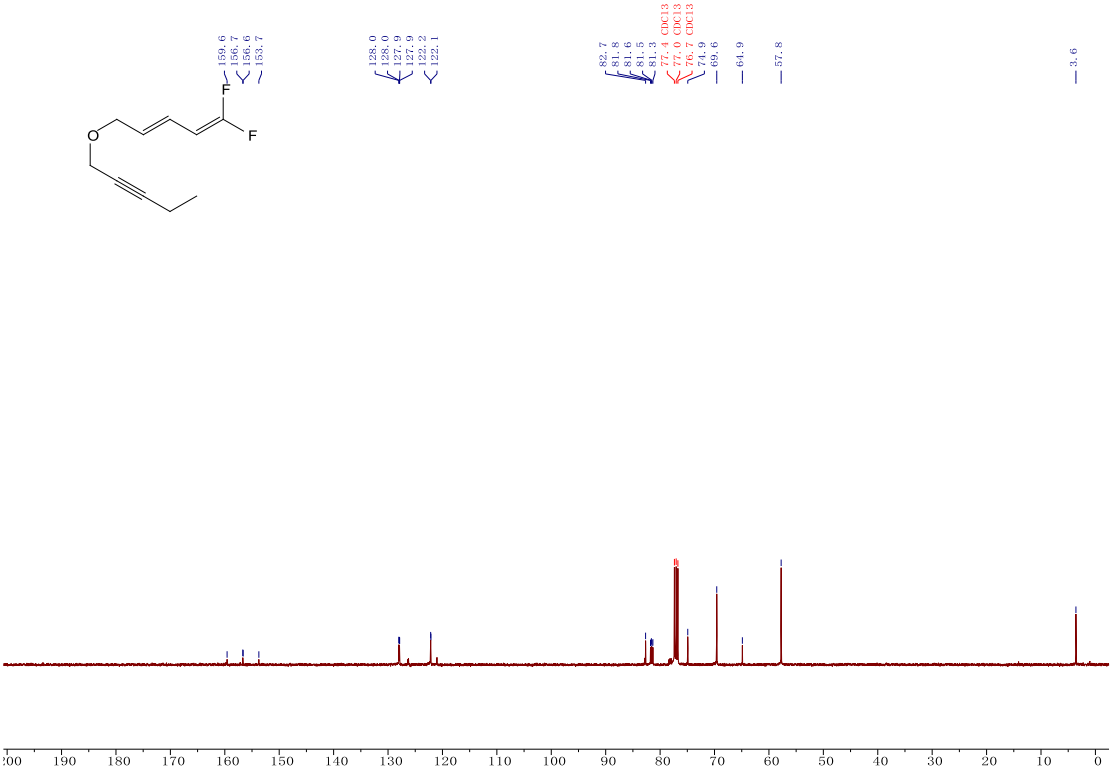
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3a**



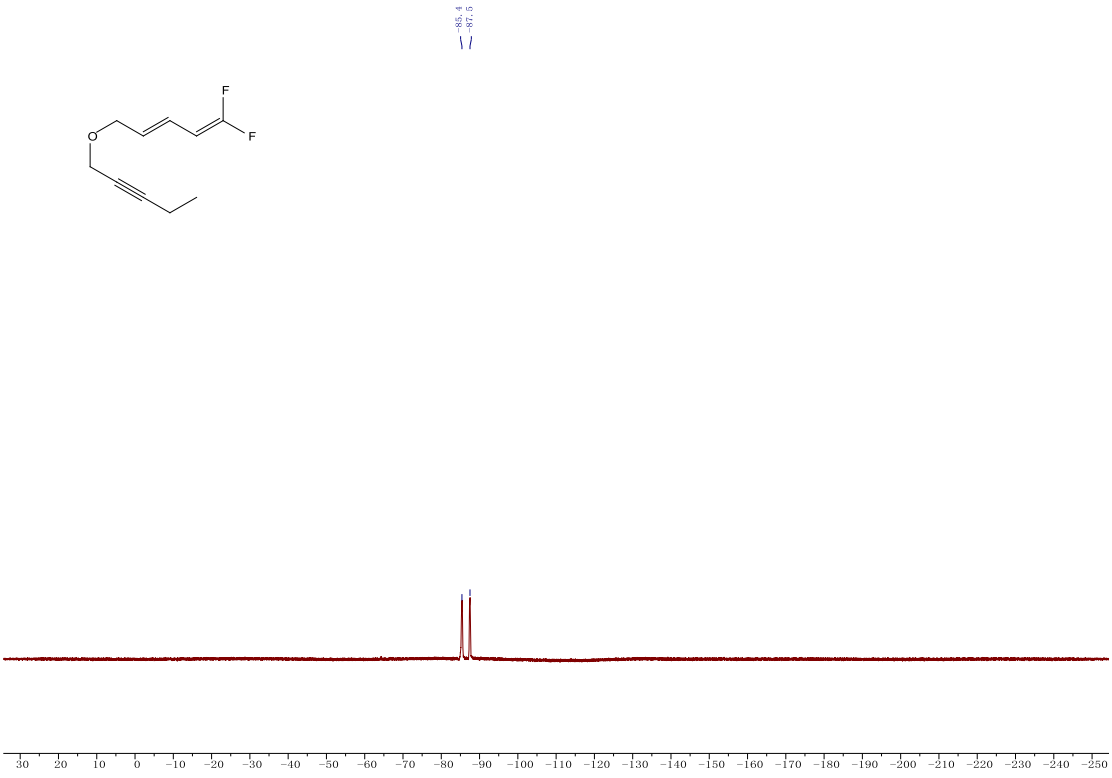
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



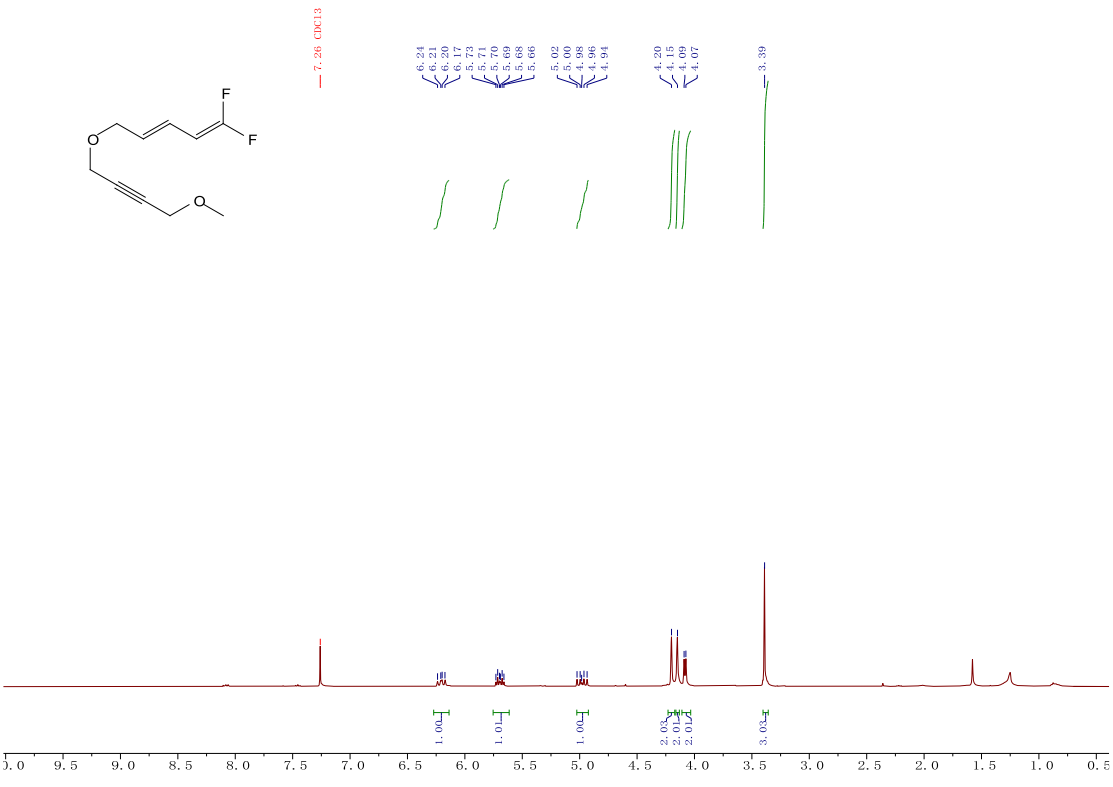
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b**



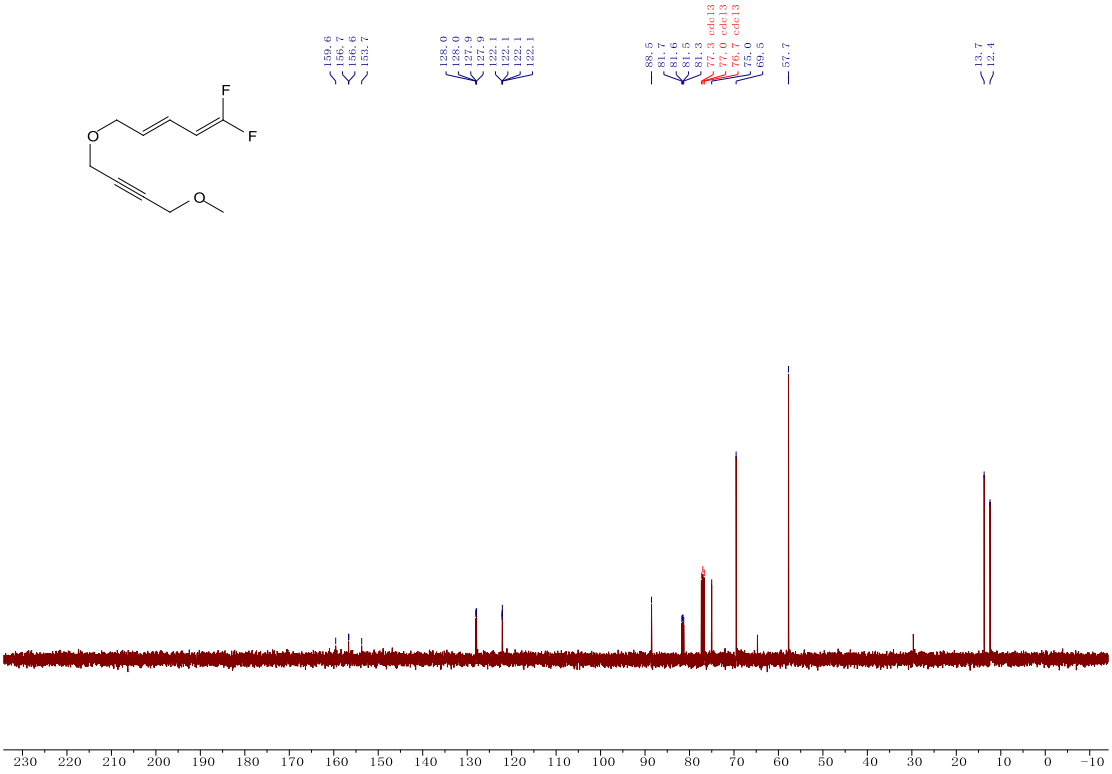
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3b**



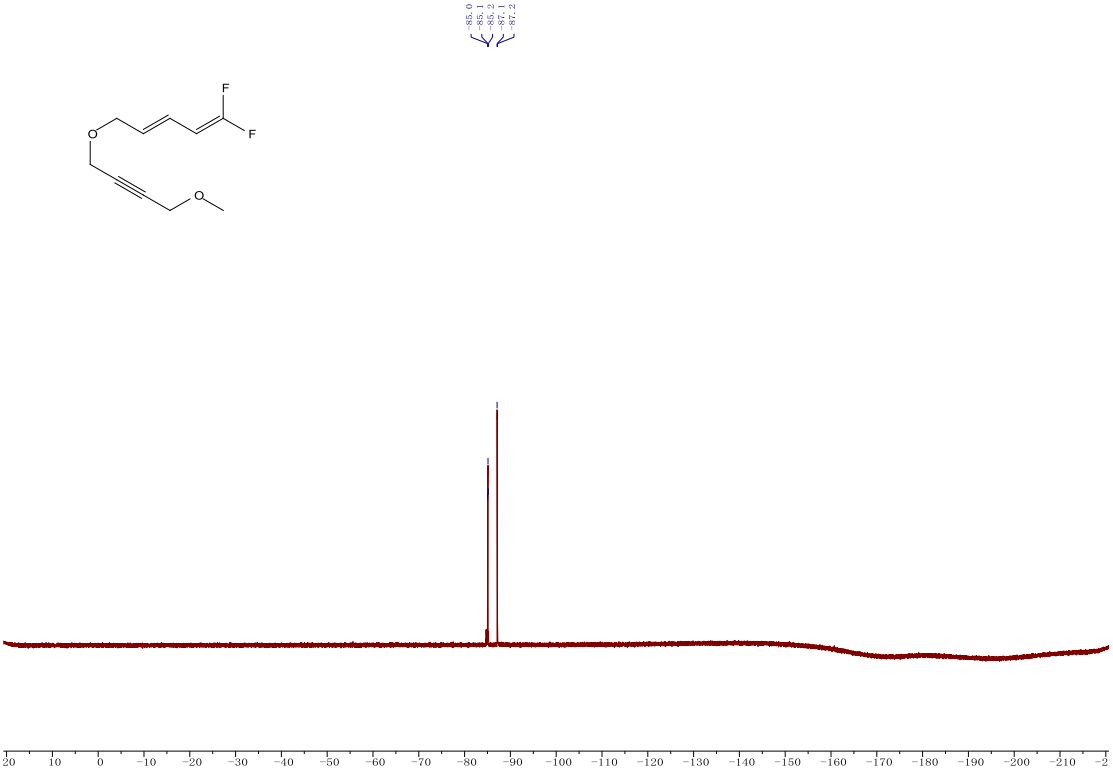
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



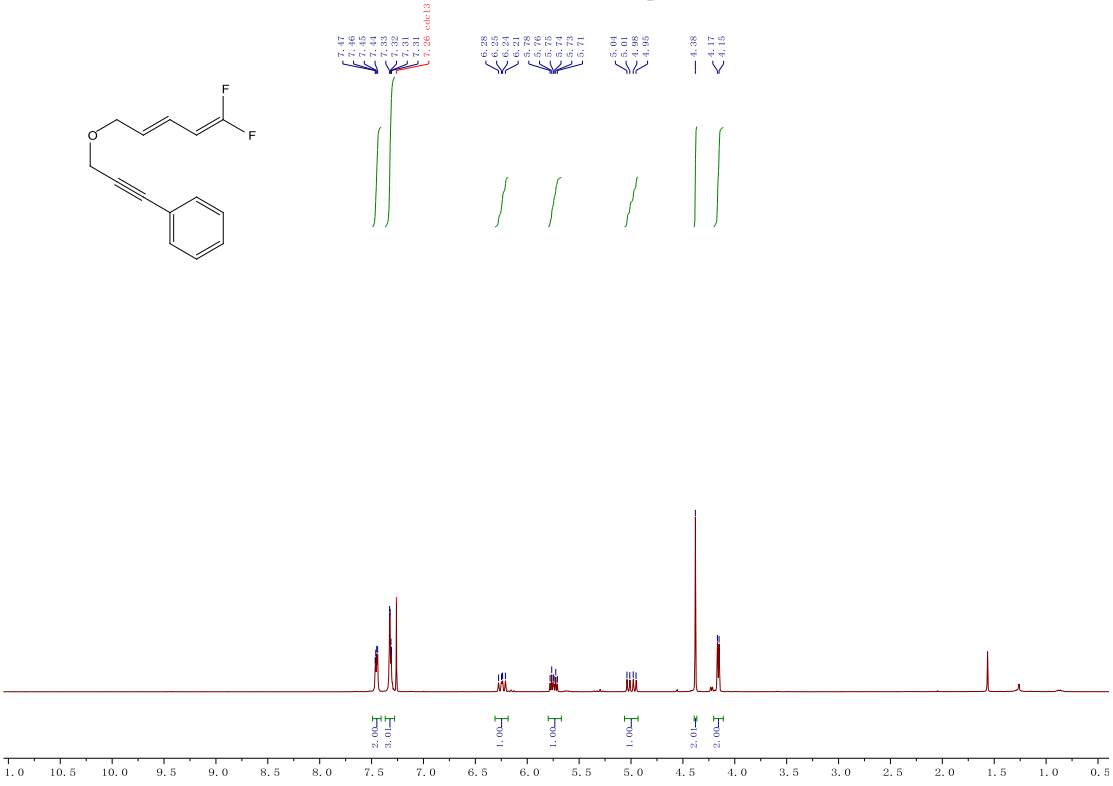
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c**



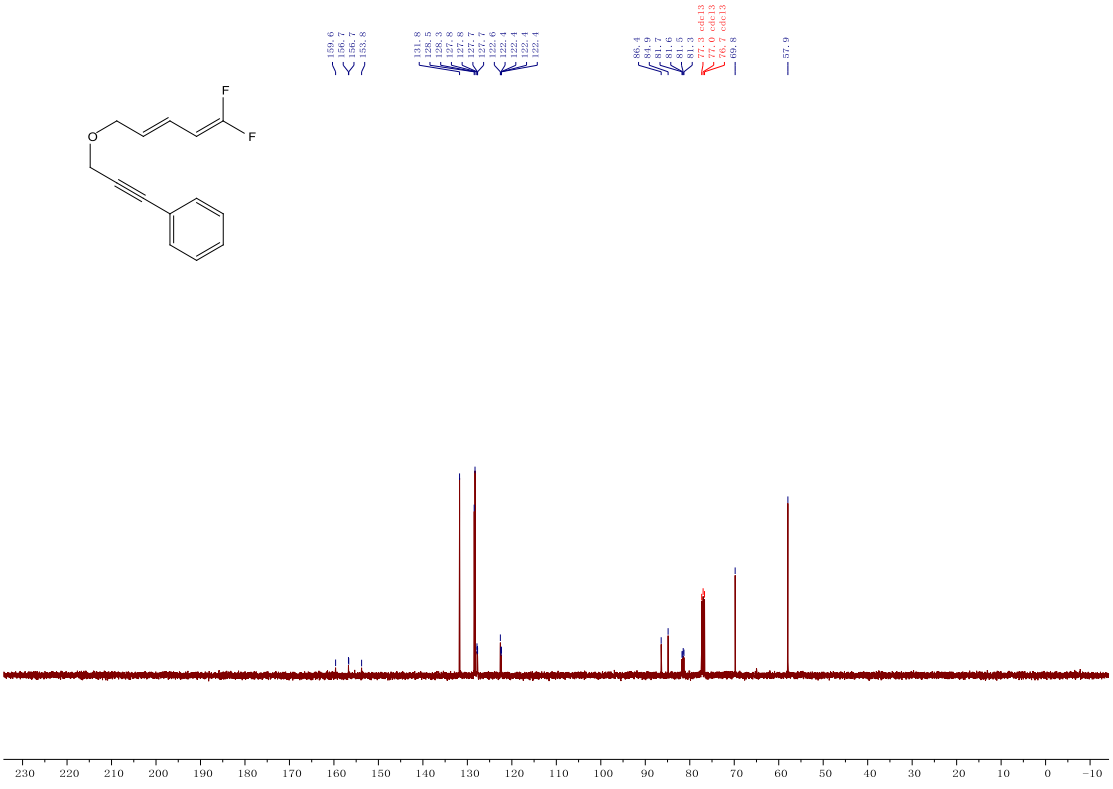
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3c**



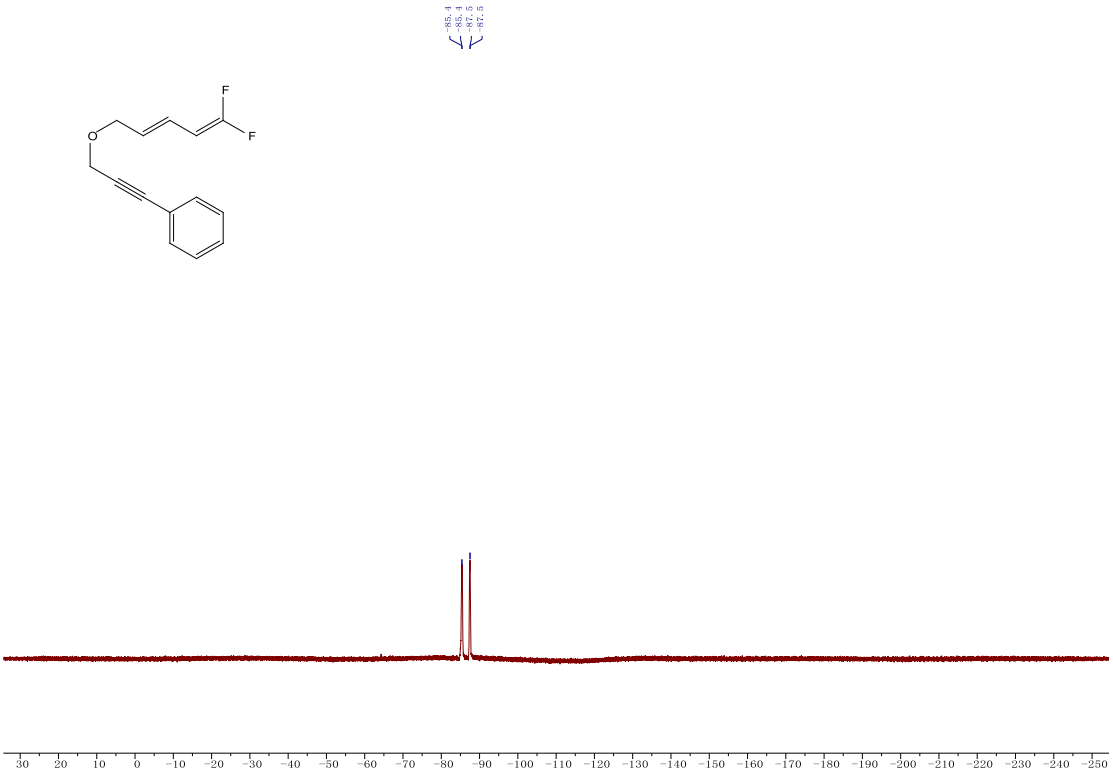
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



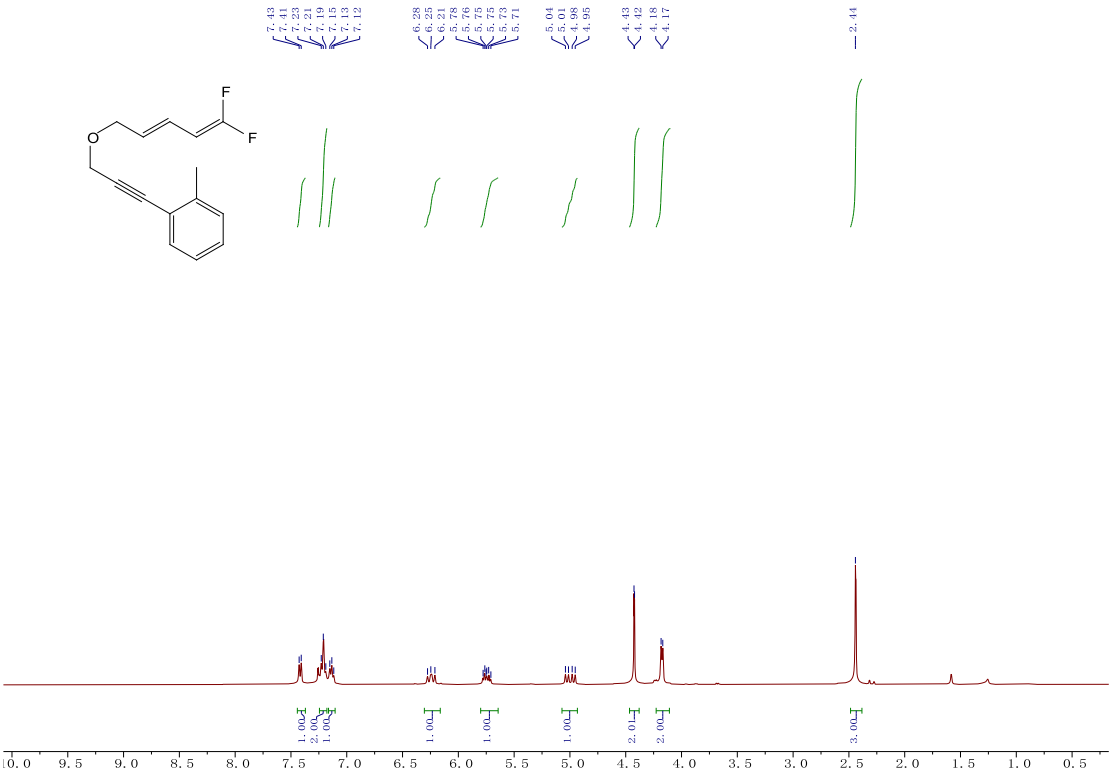
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3d**



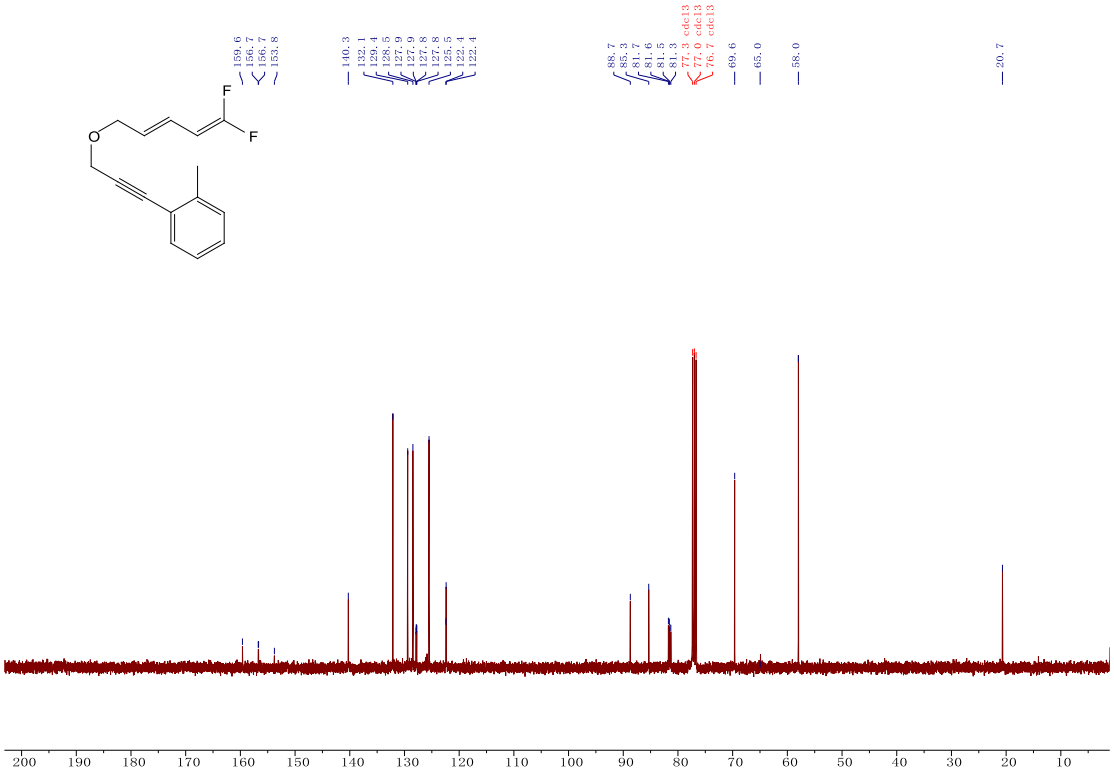
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3d**



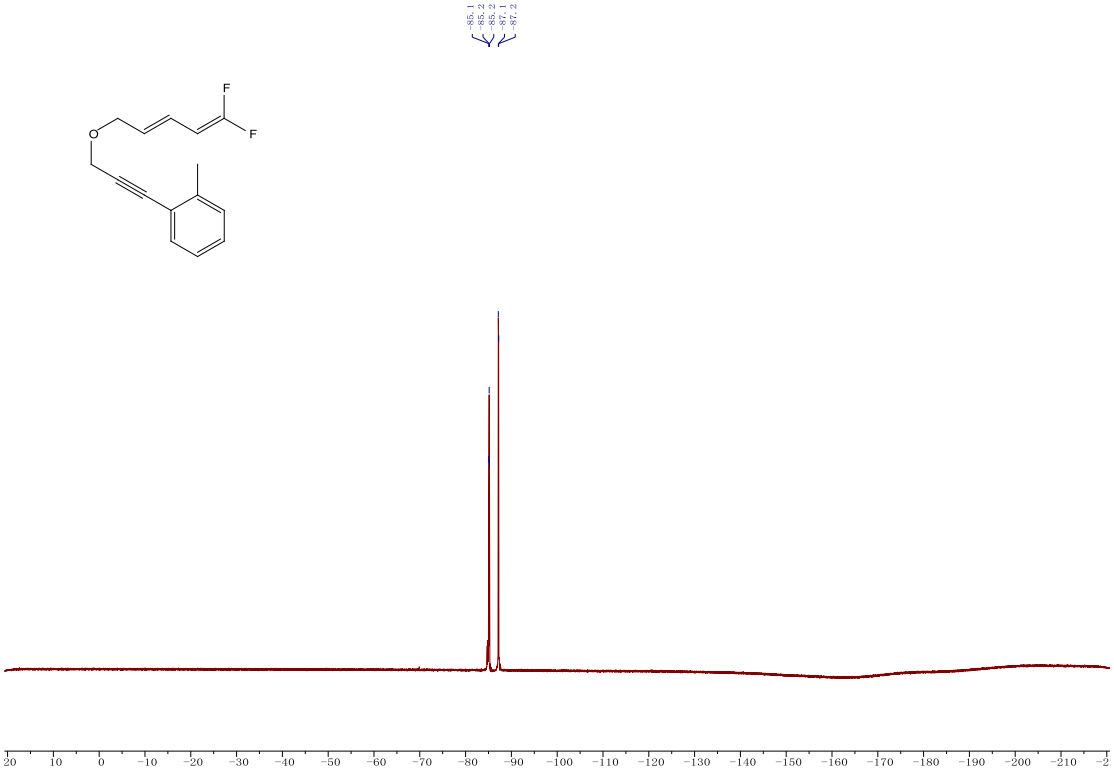
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



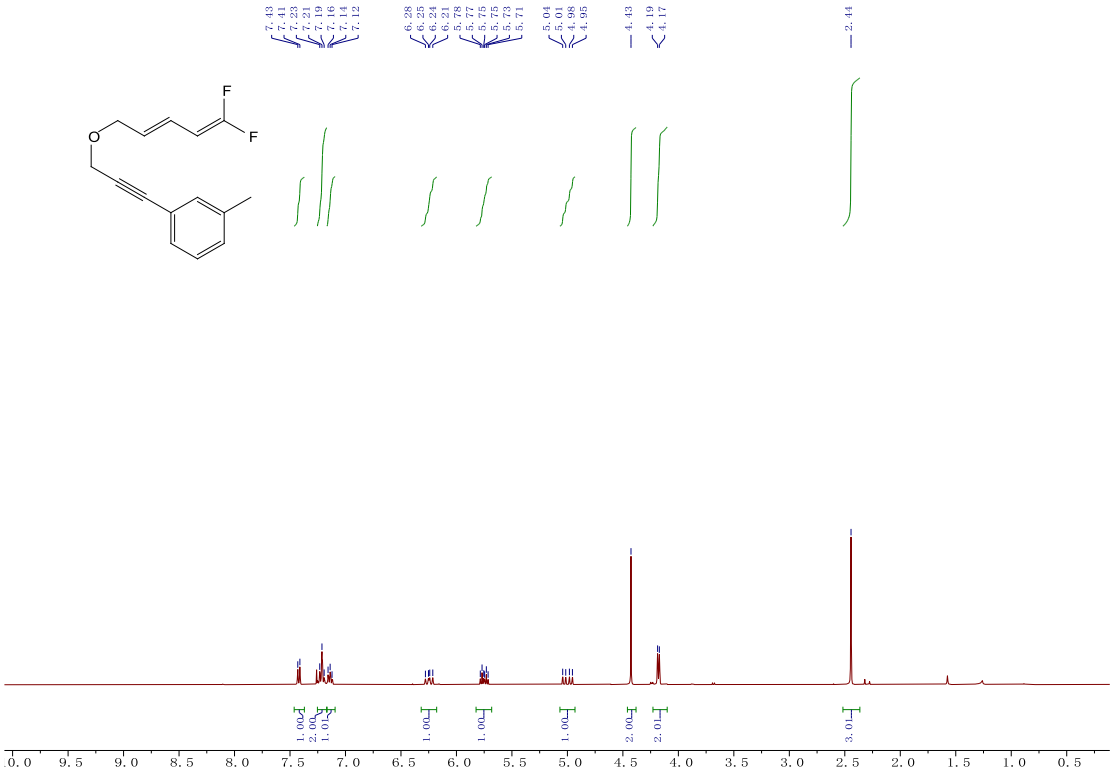
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3e**



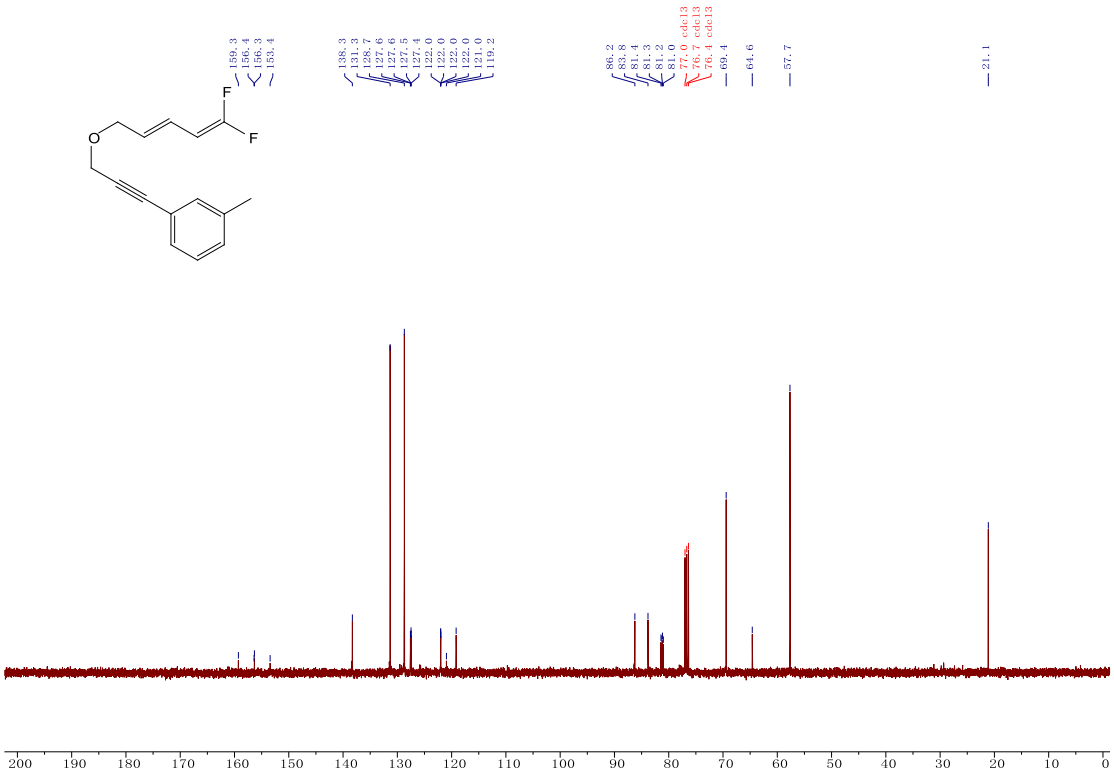
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3e**



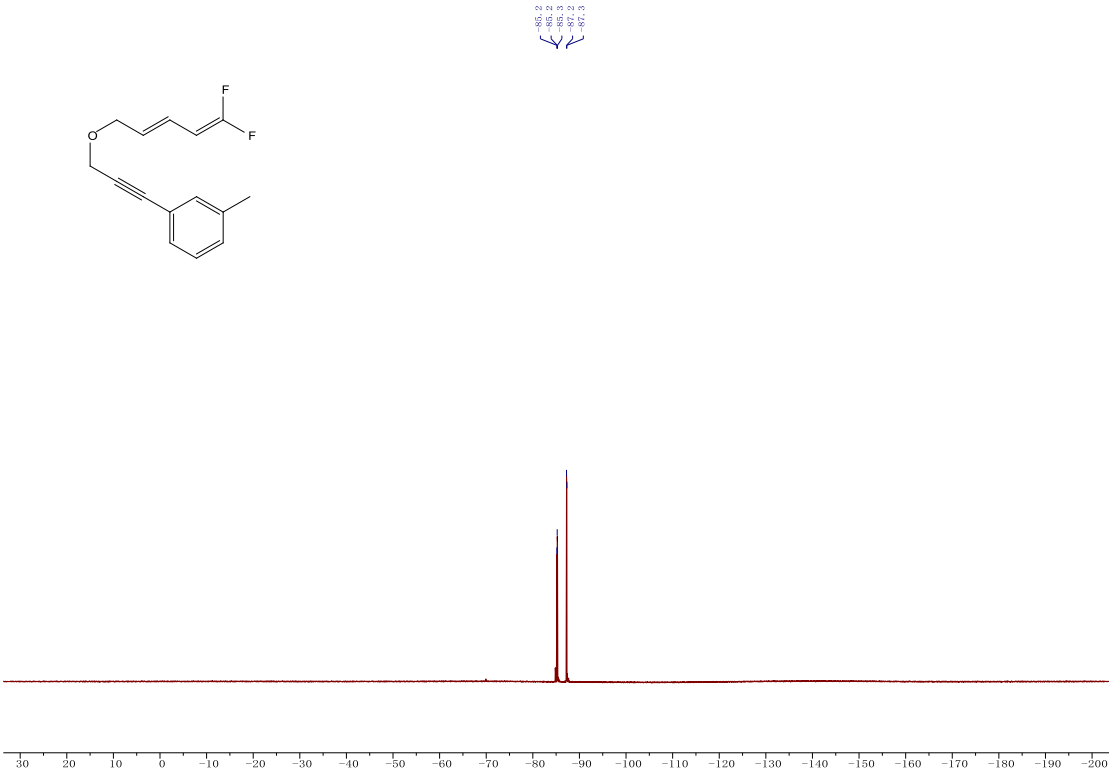
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



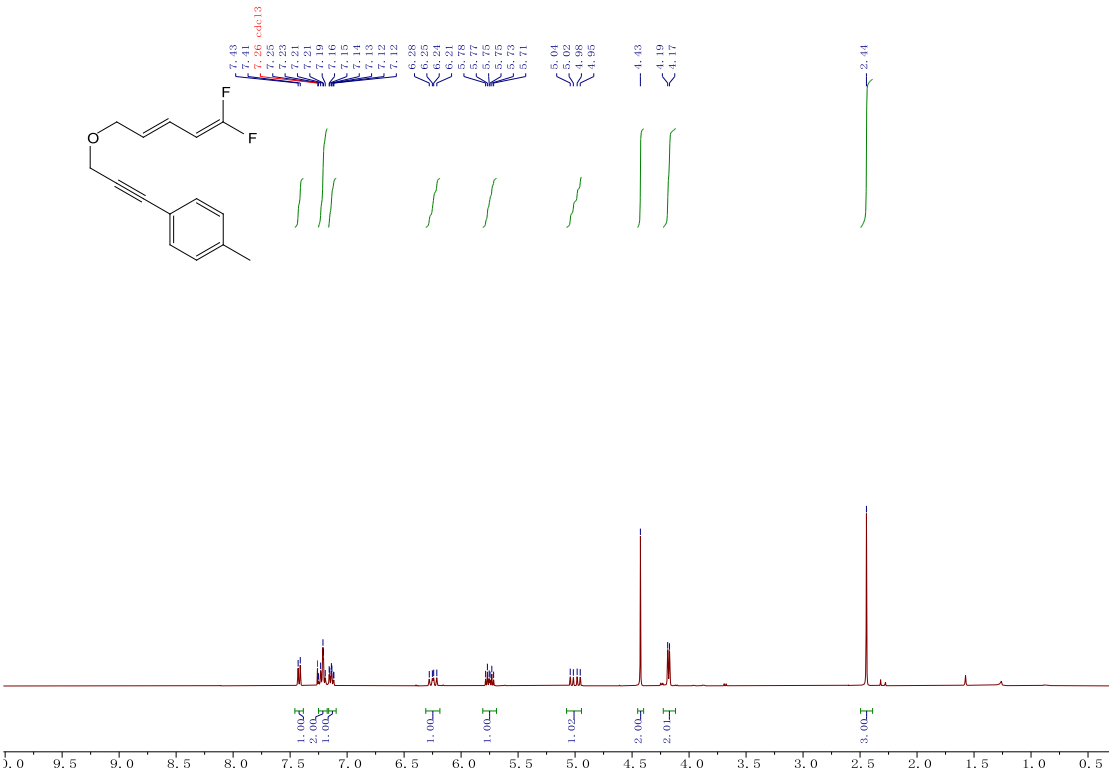
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3f**



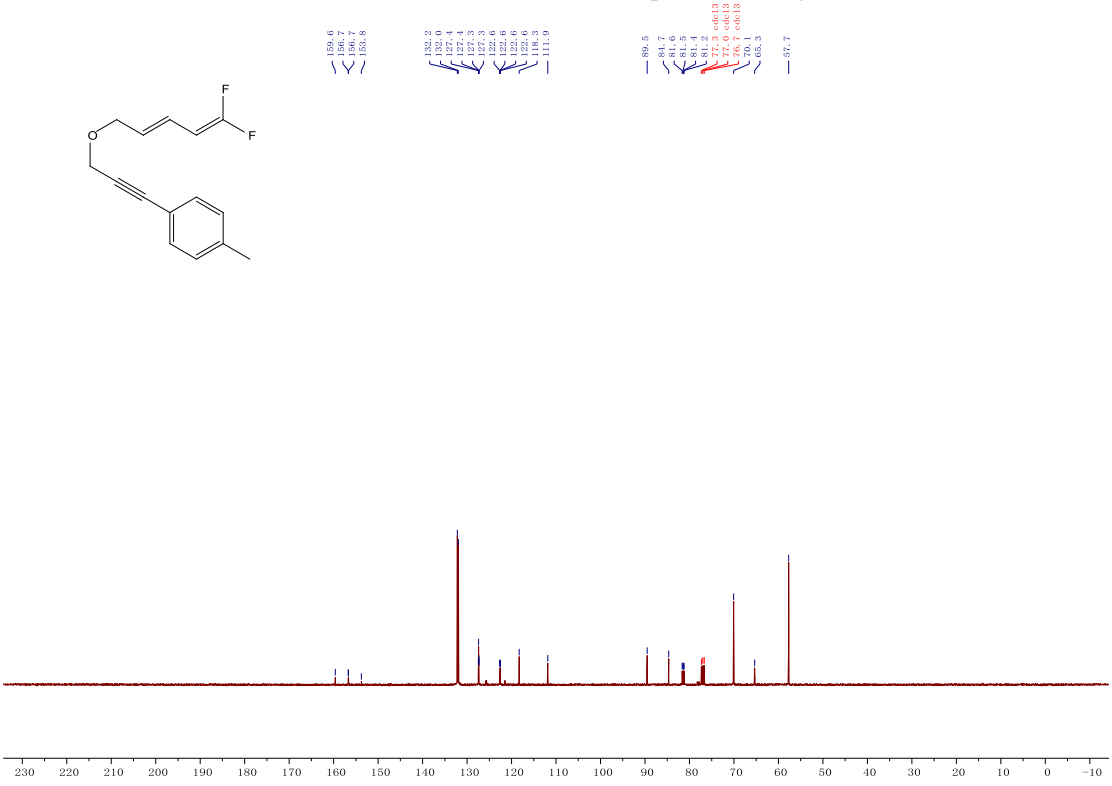
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3f**



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

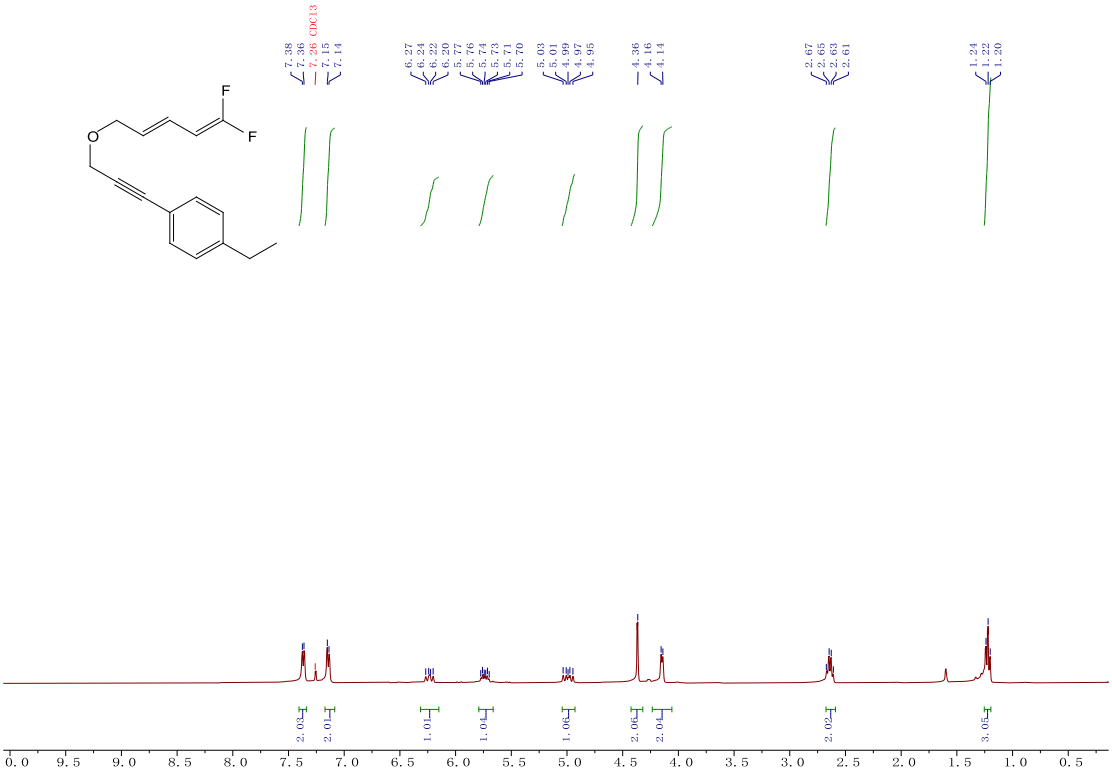


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3g**

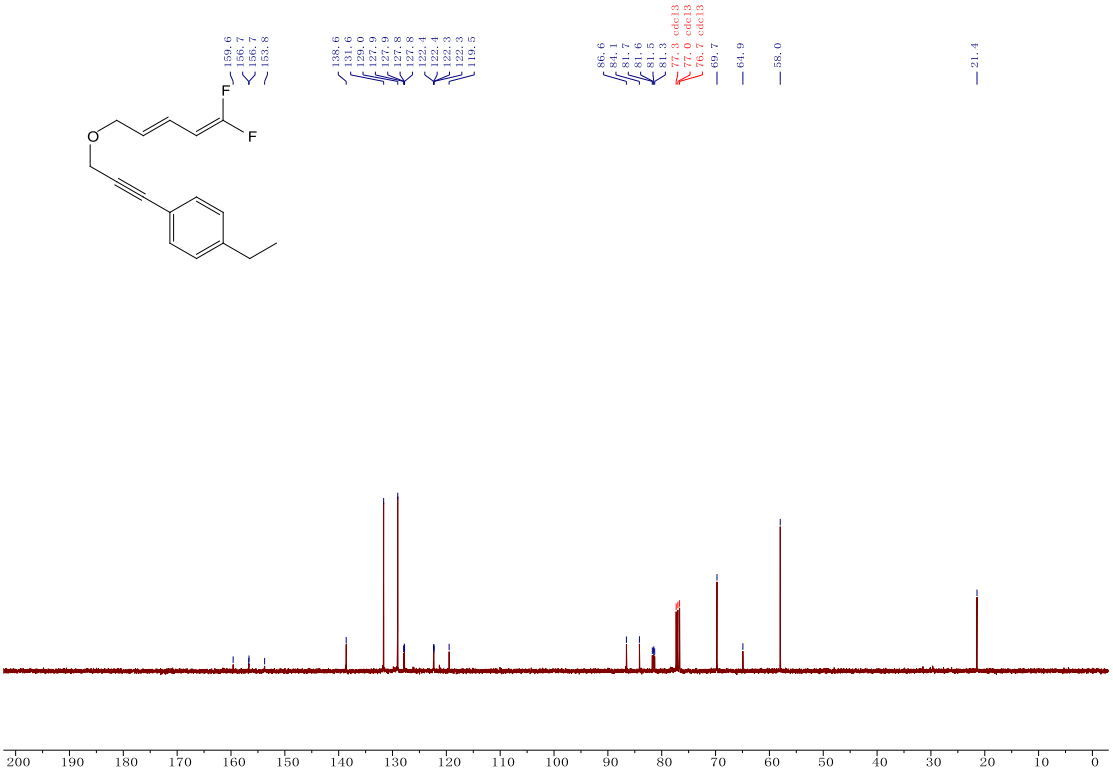


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3g**

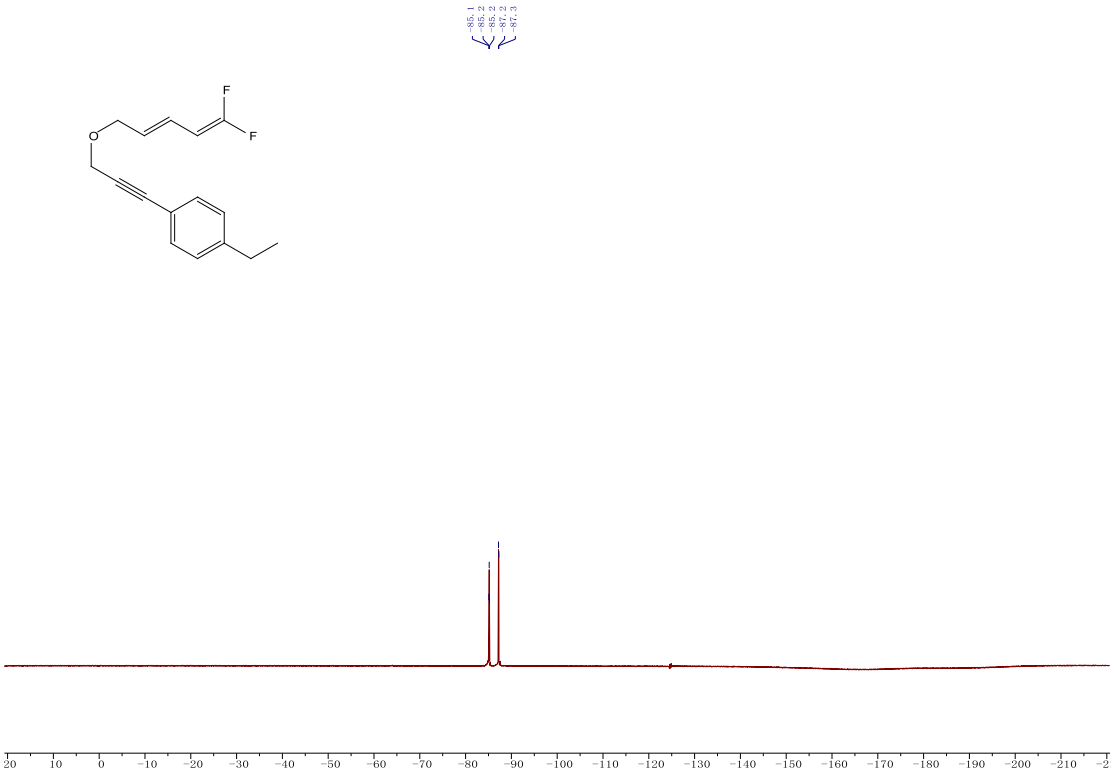
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



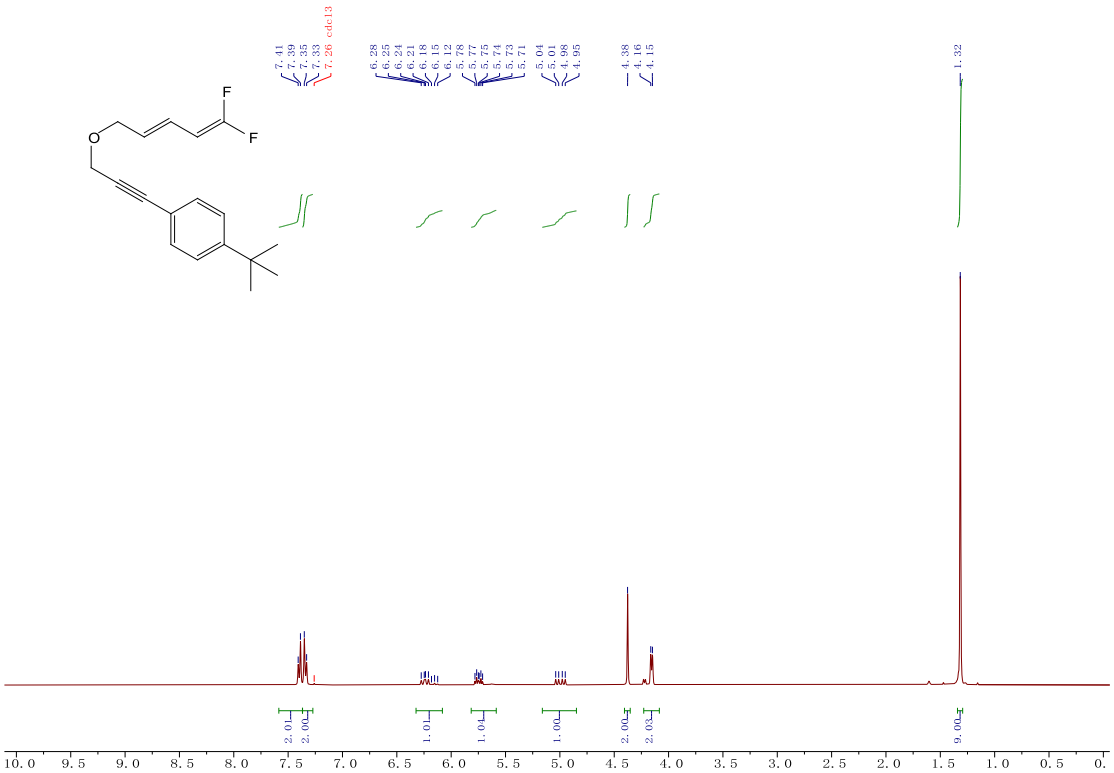
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3h**



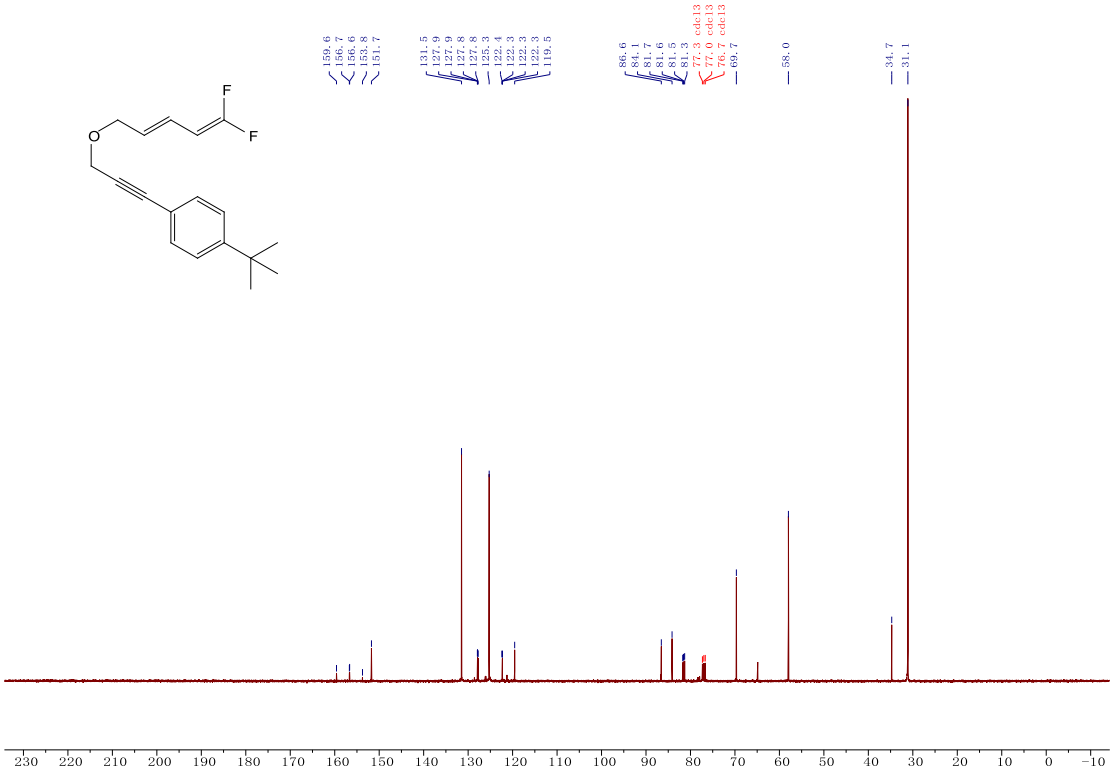
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3h**



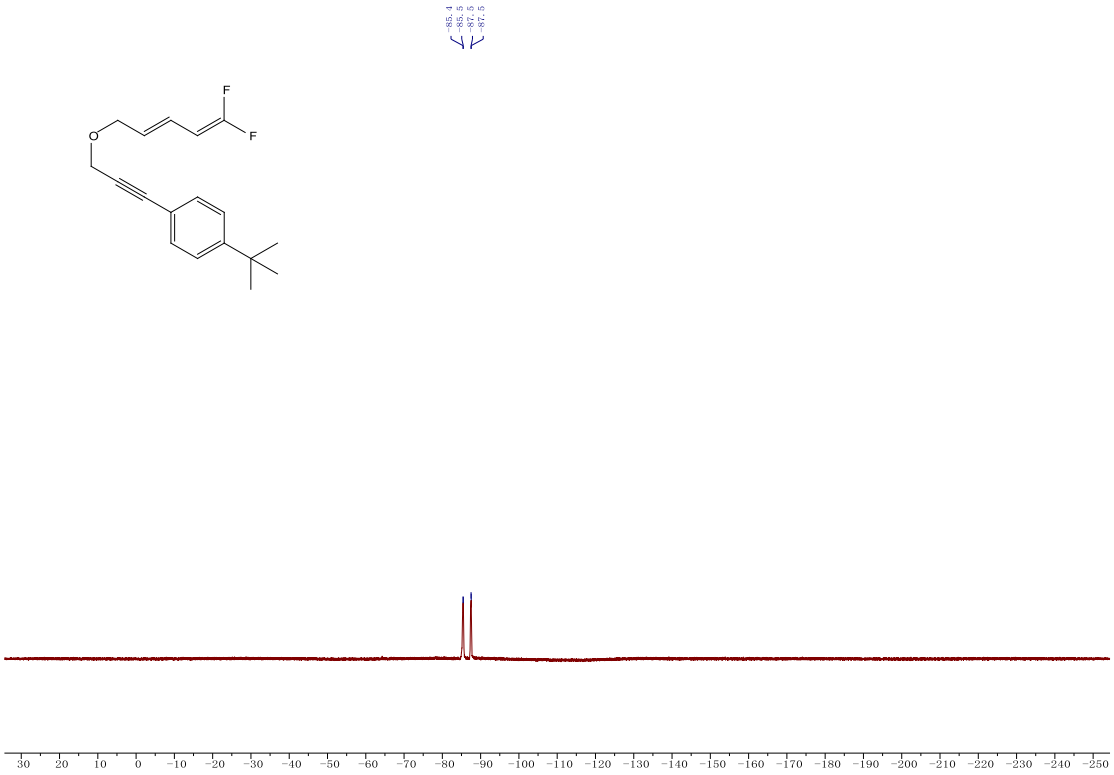
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**



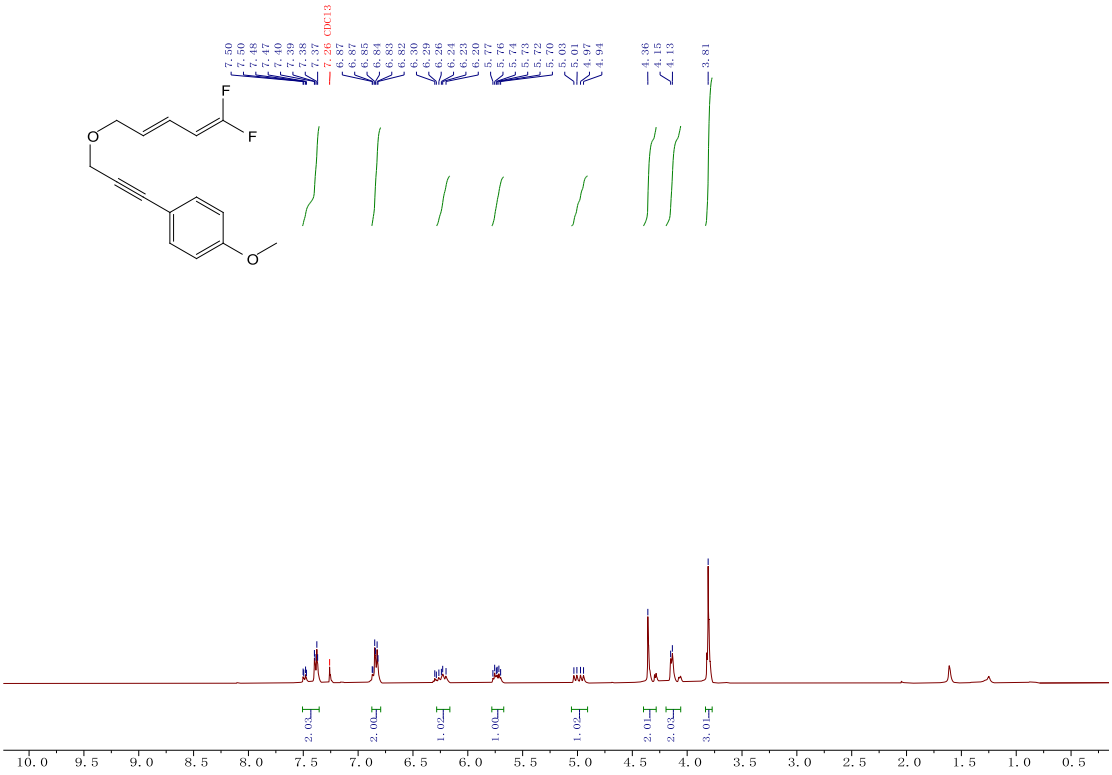
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3i**



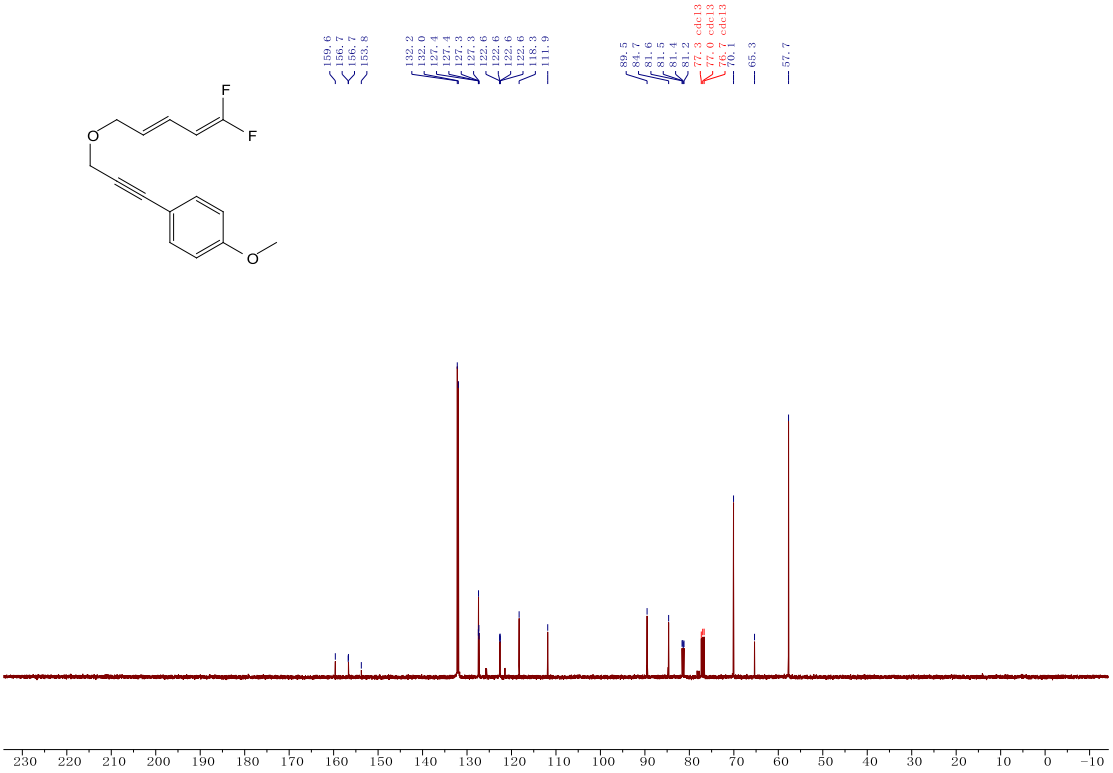
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3i**



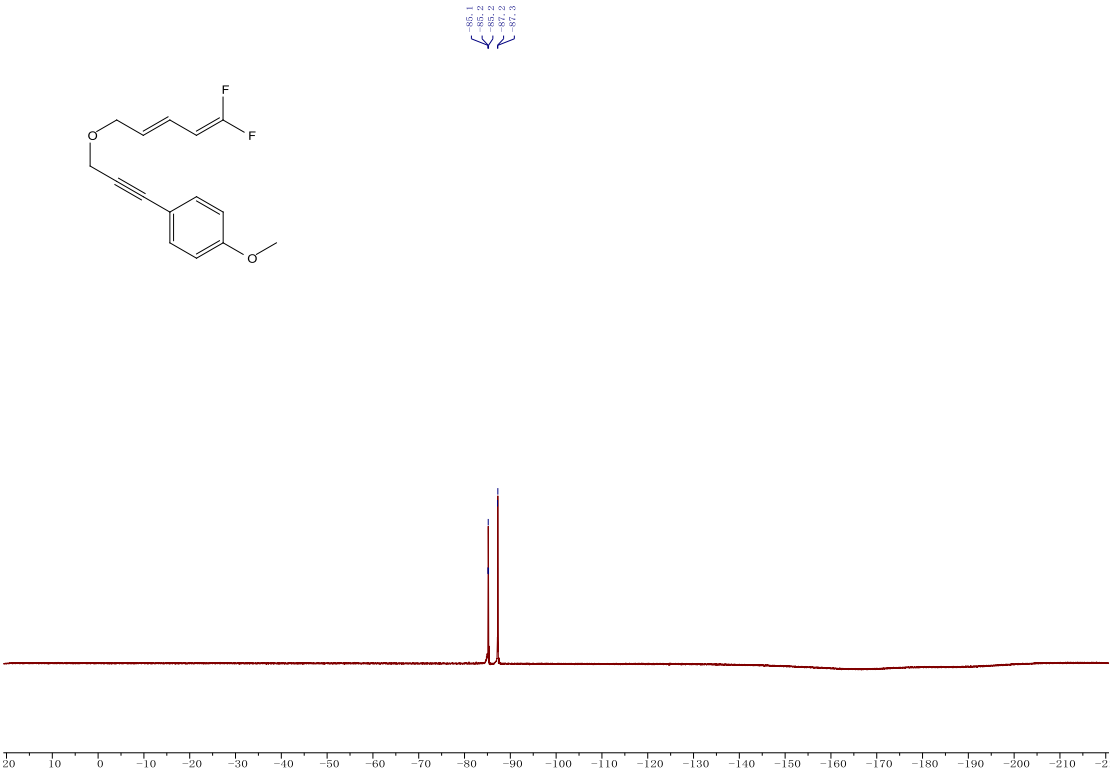
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**



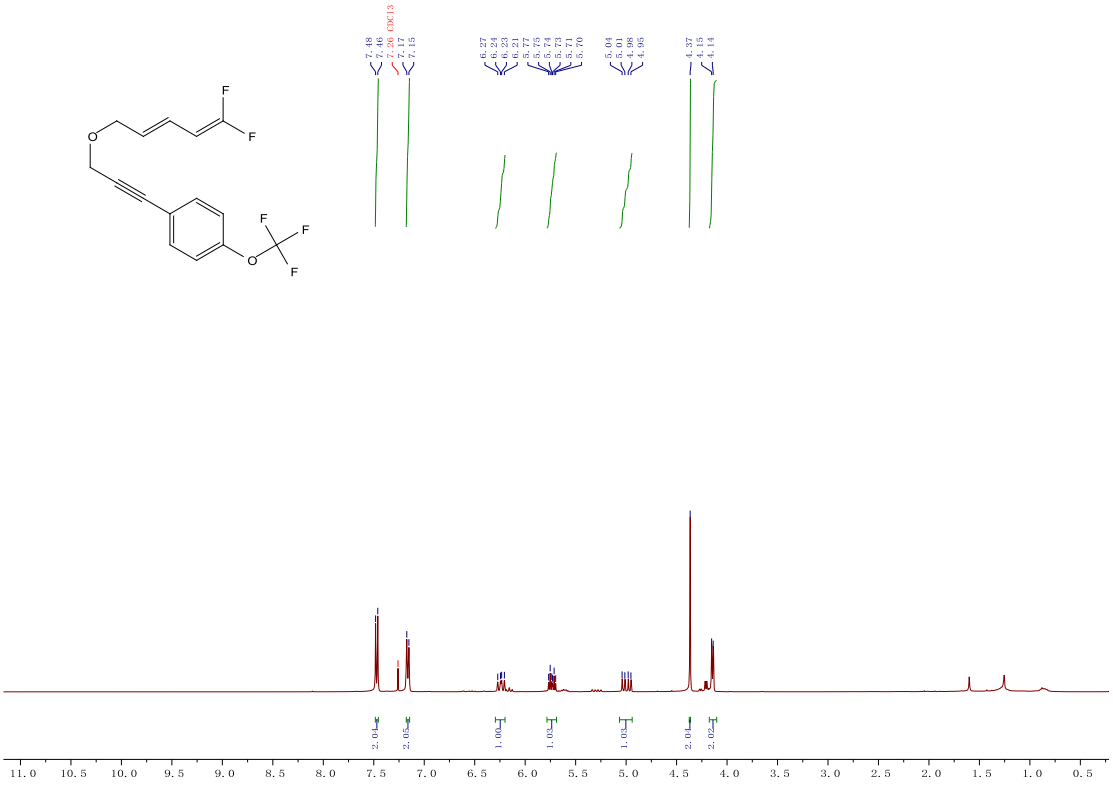
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3j**



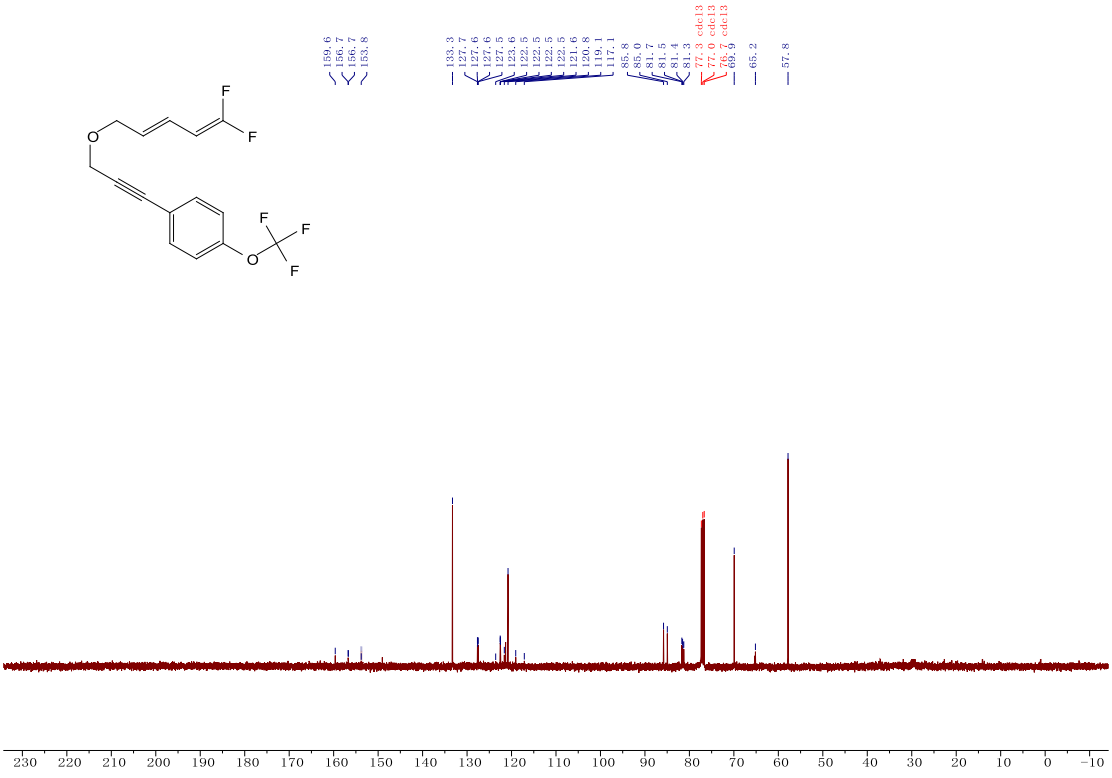
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3j**



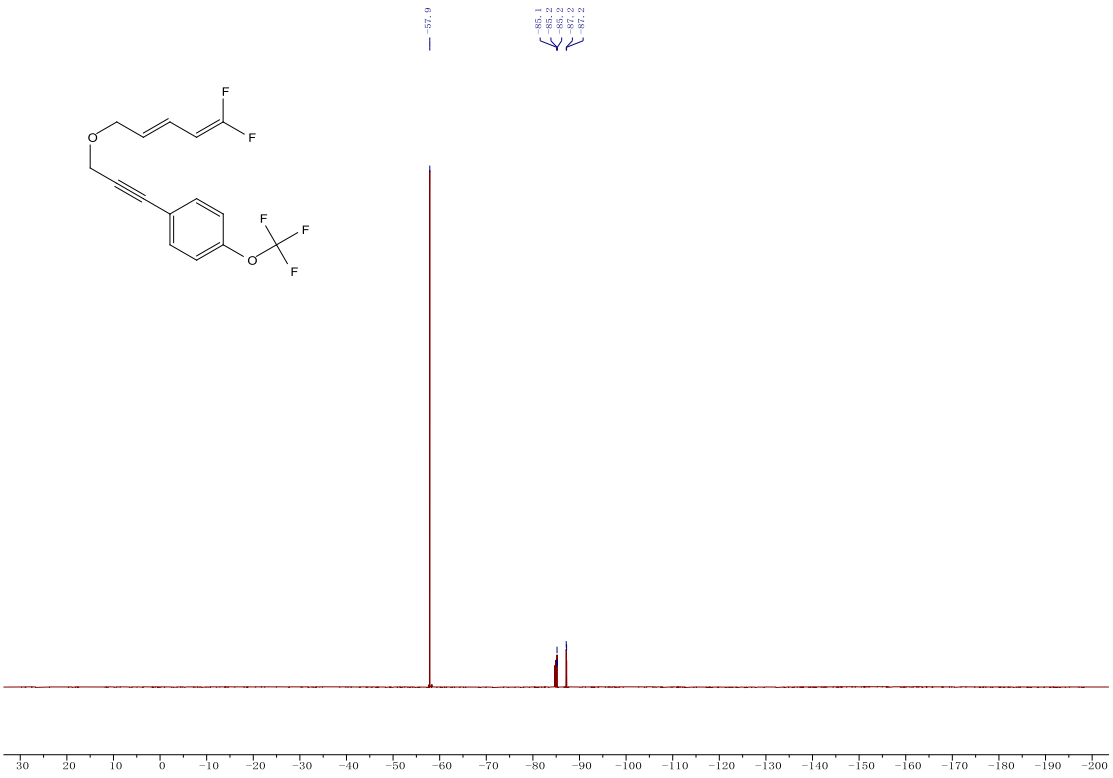
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**



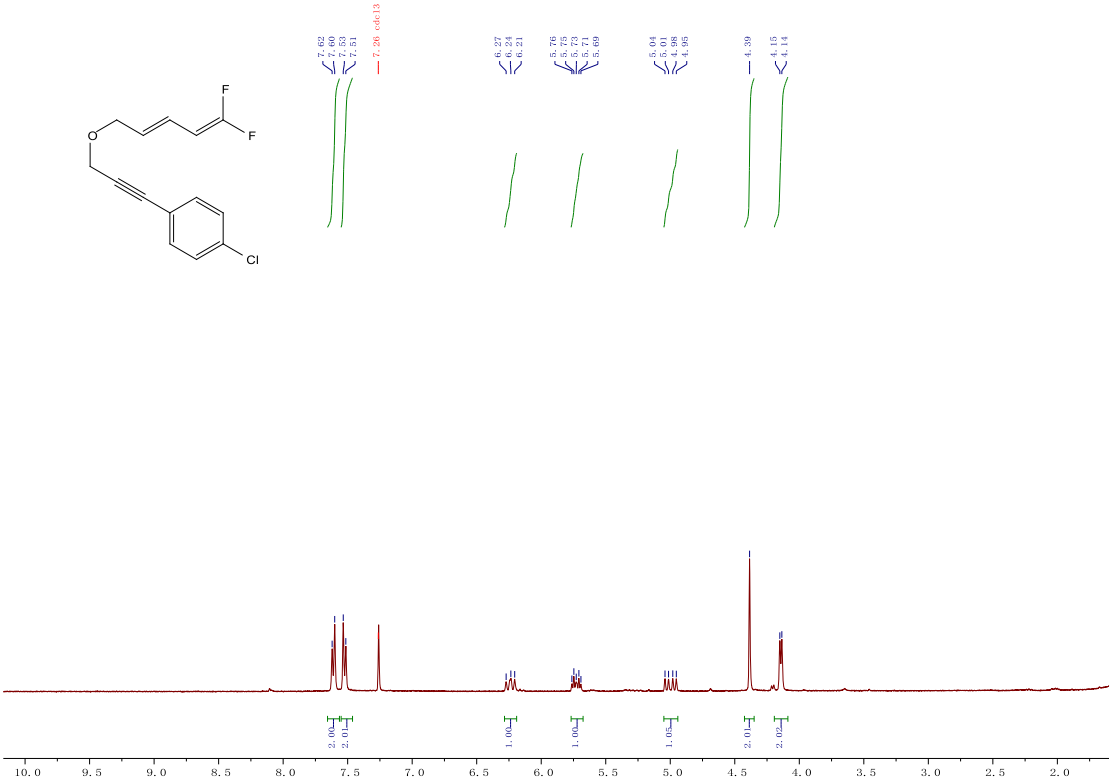
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3k**



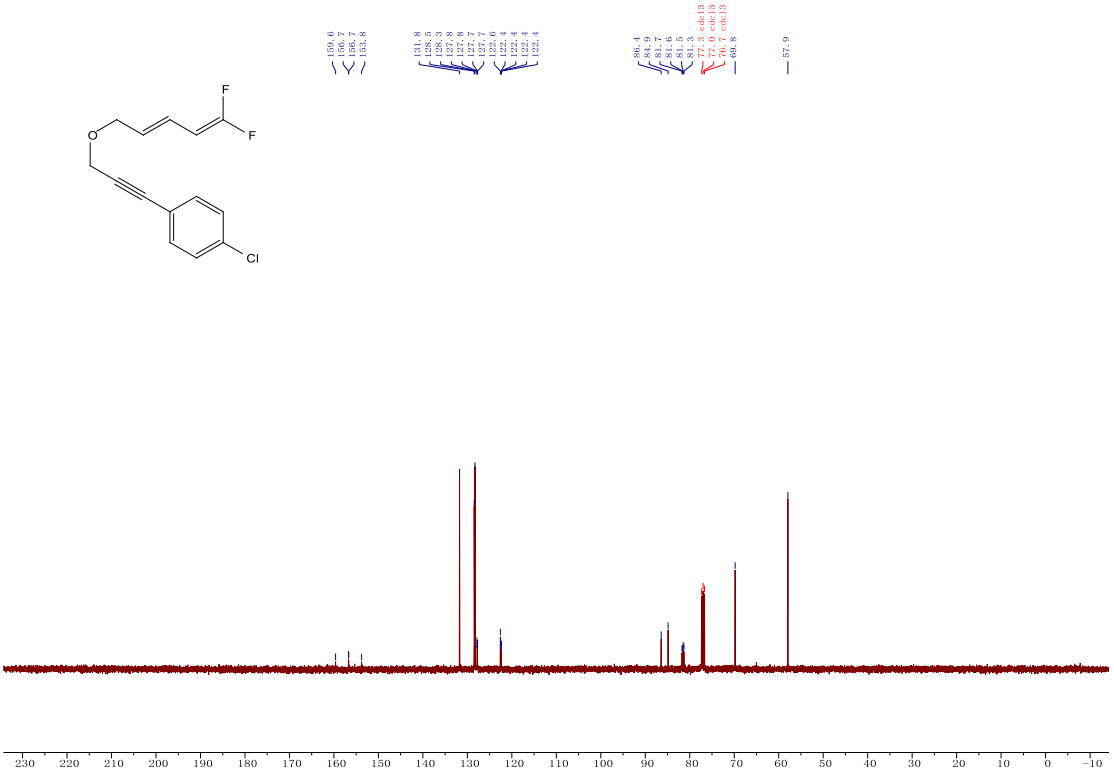
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3k**



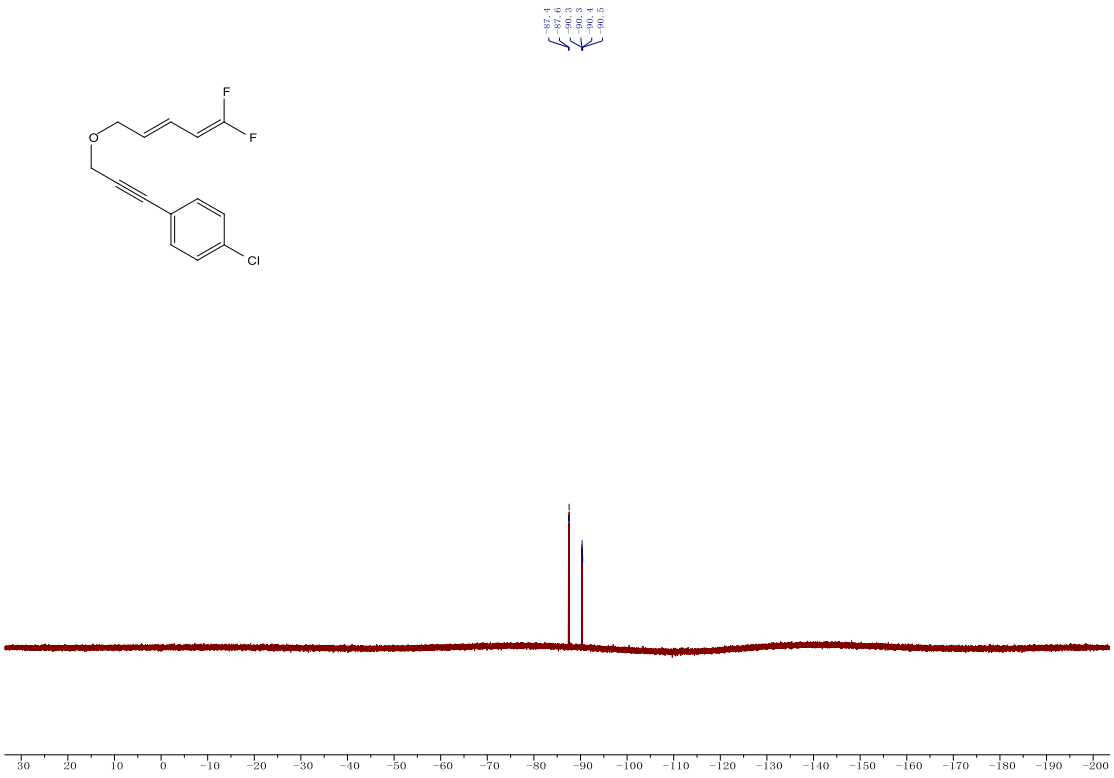
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



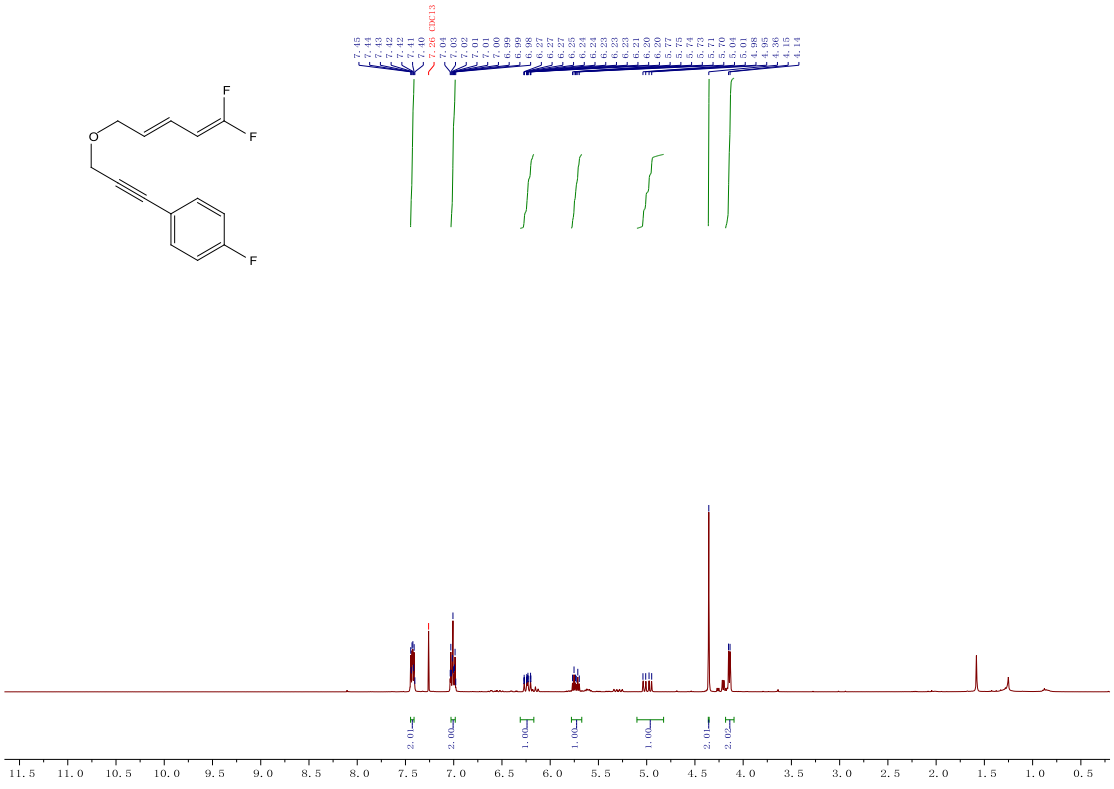
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3l**



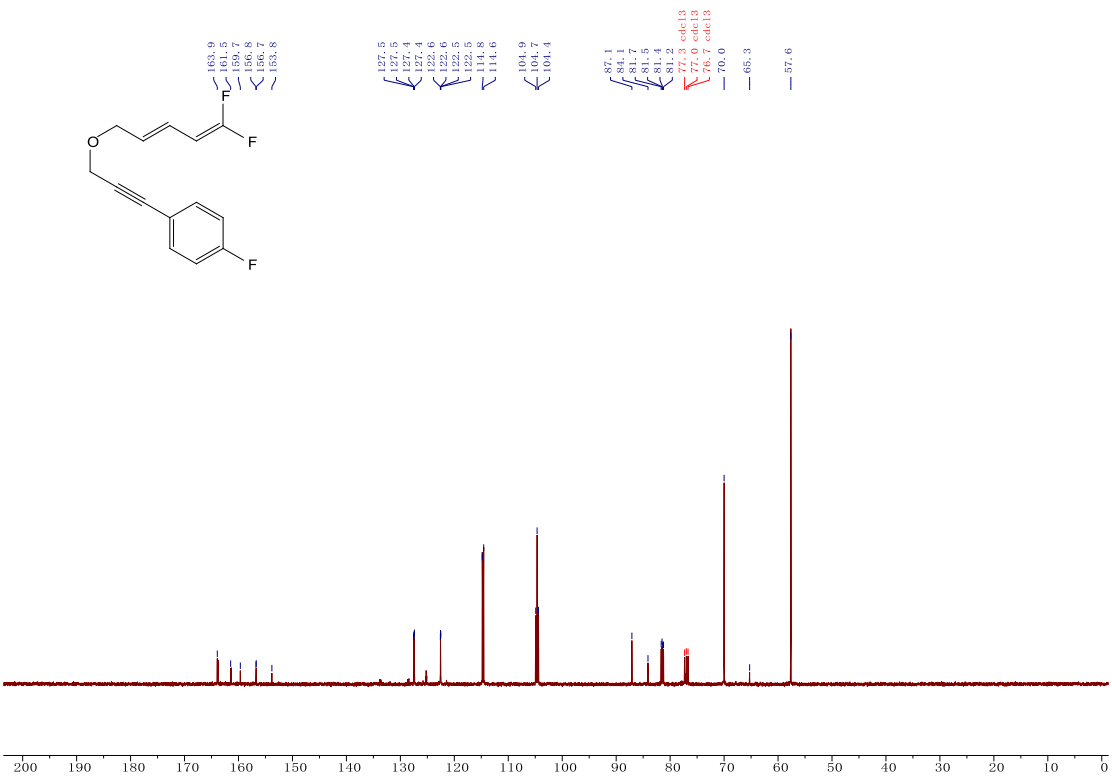
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3l**



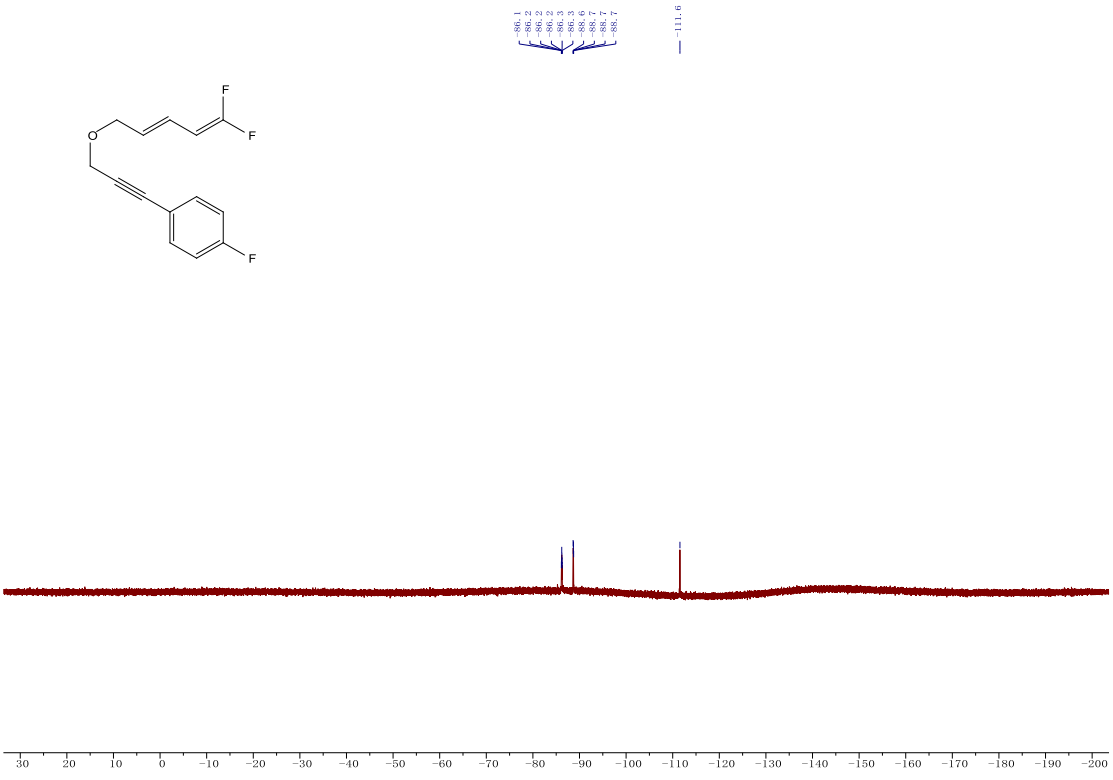
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



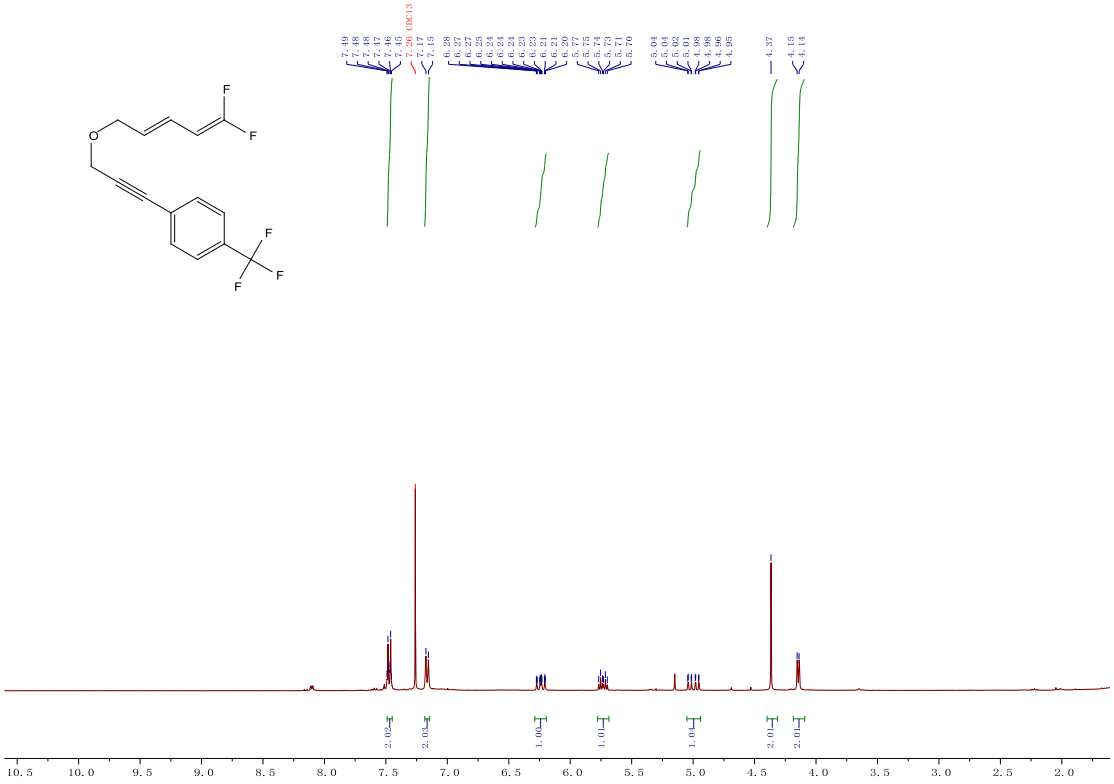
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3m**



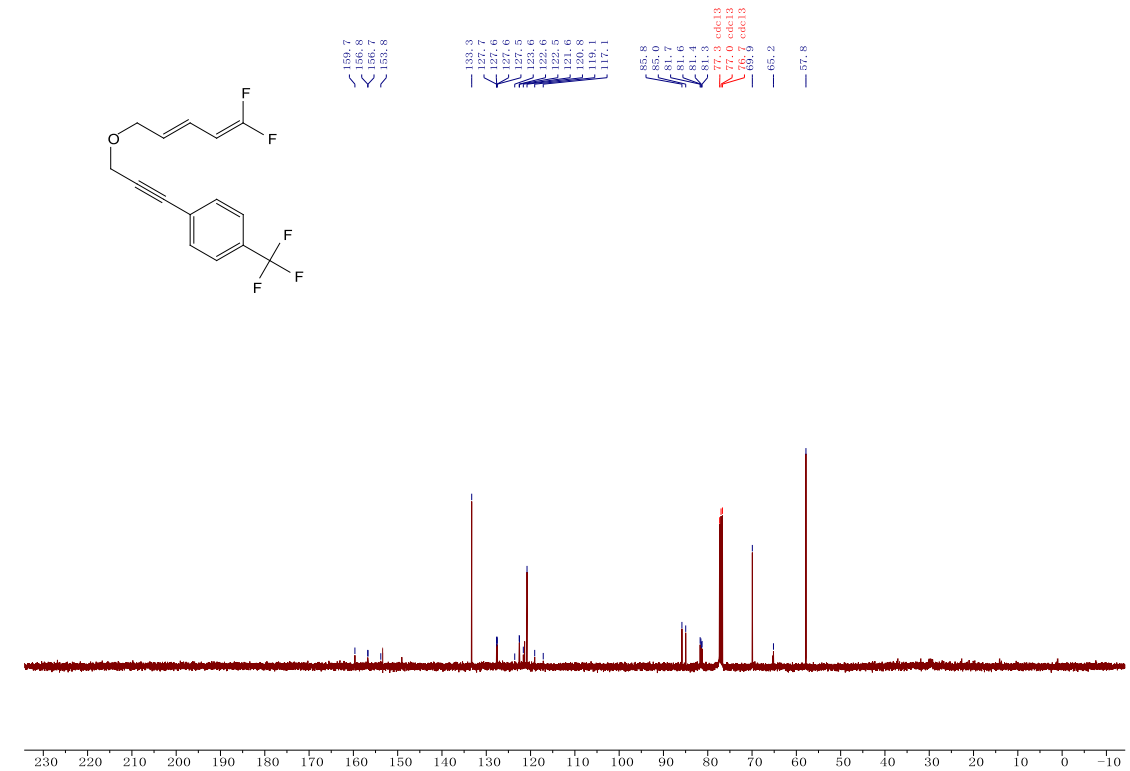
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3m**



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

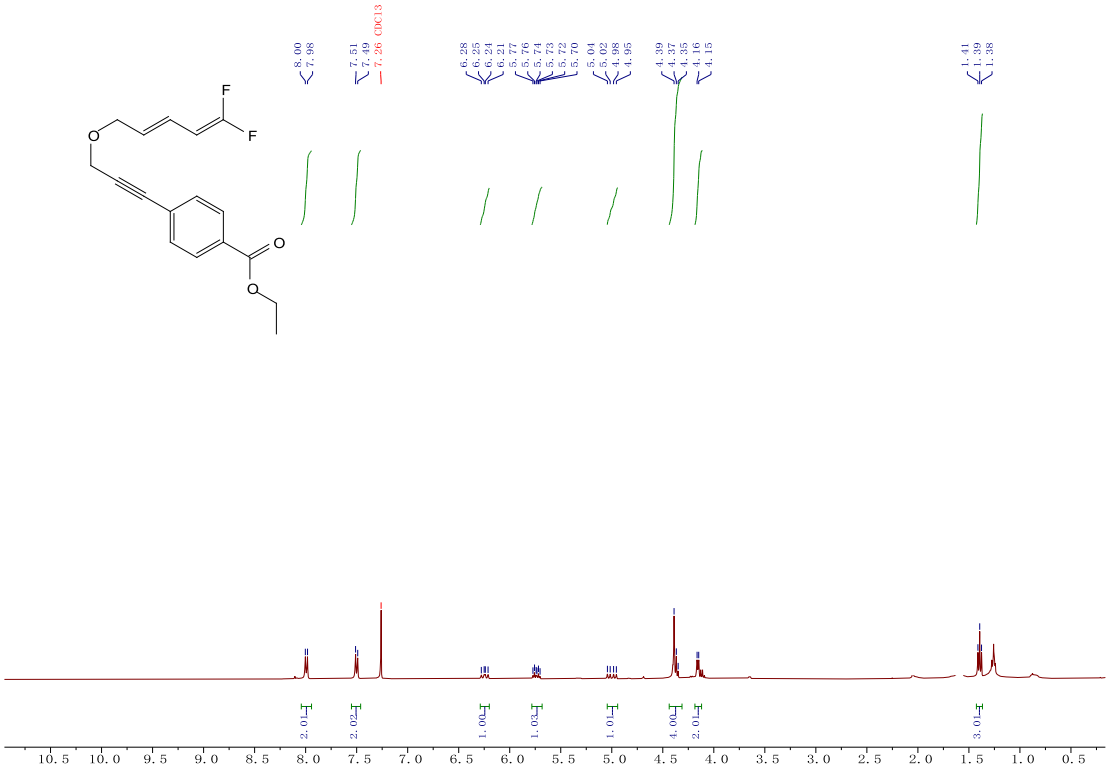


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3n**

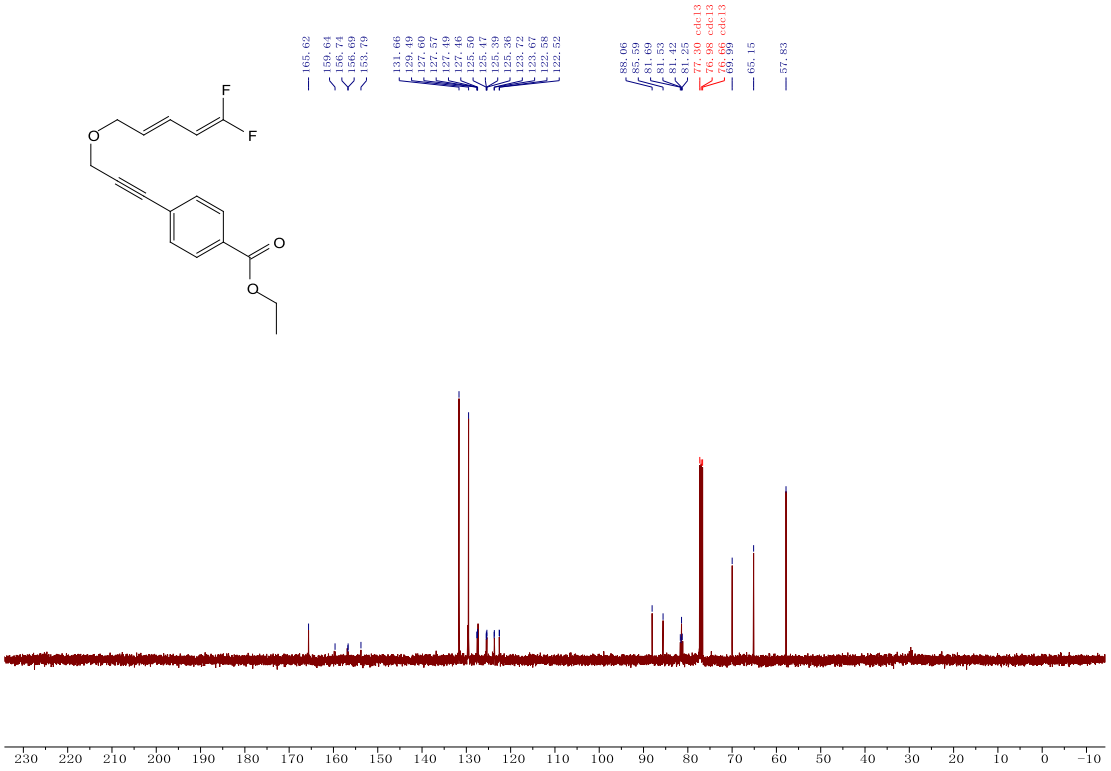


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3n**

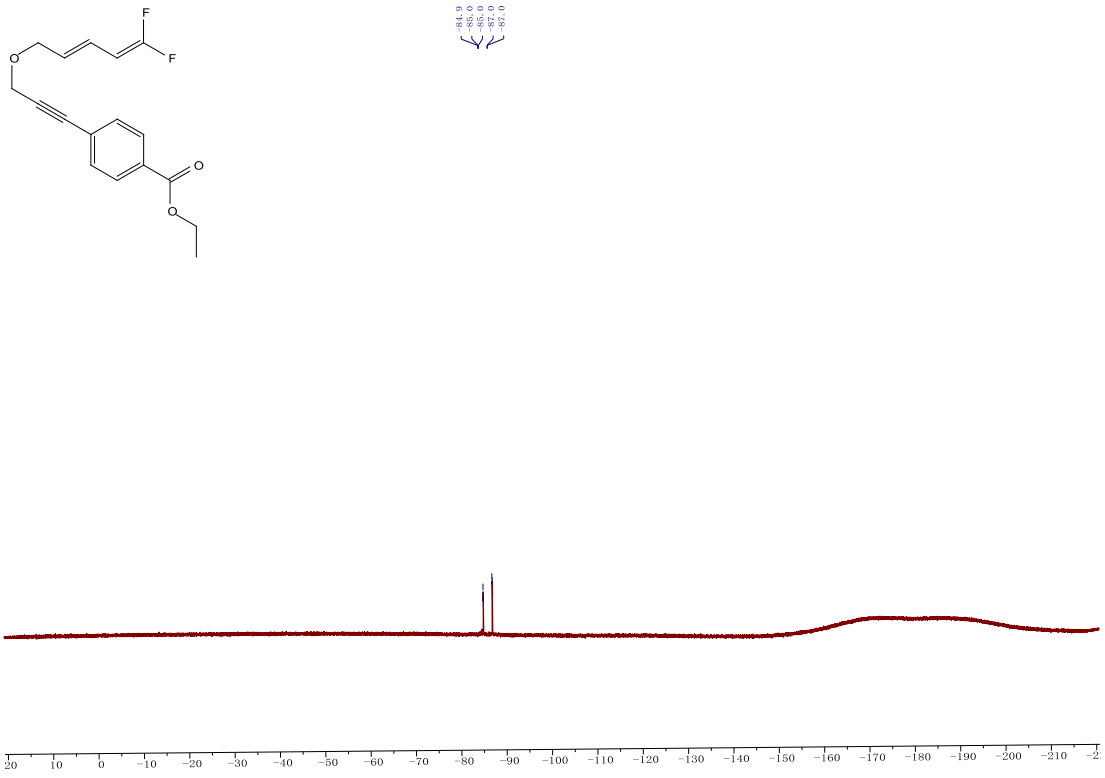
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**



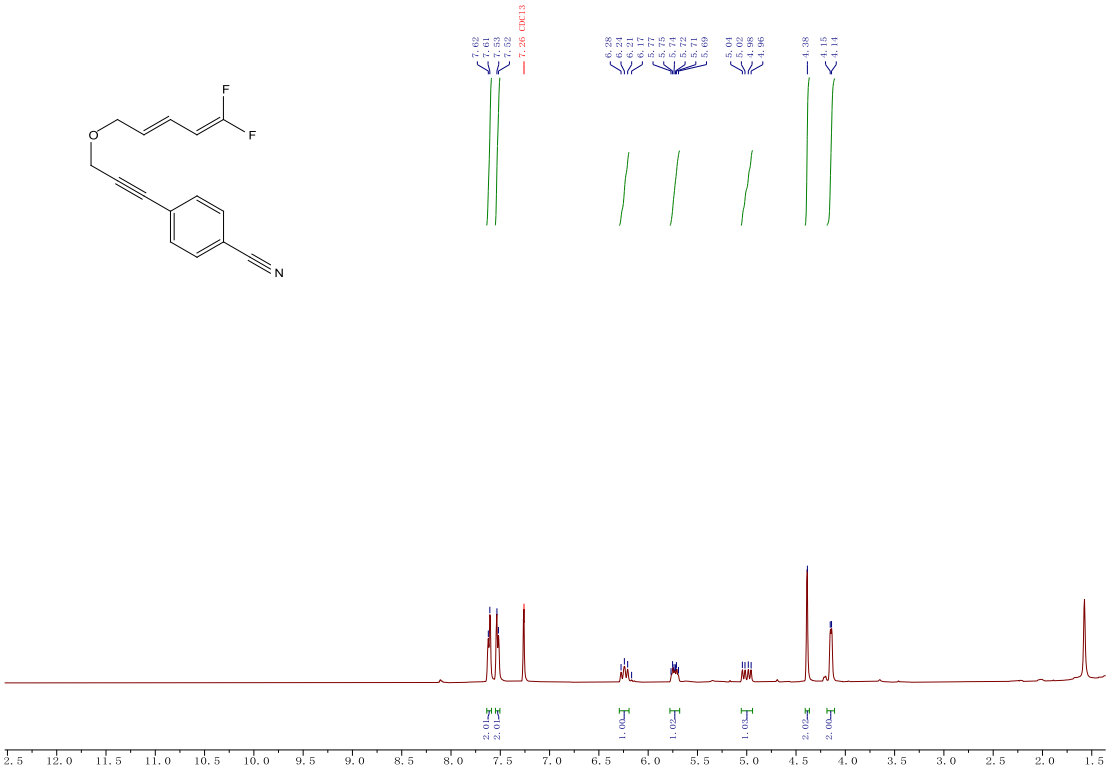
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3o**



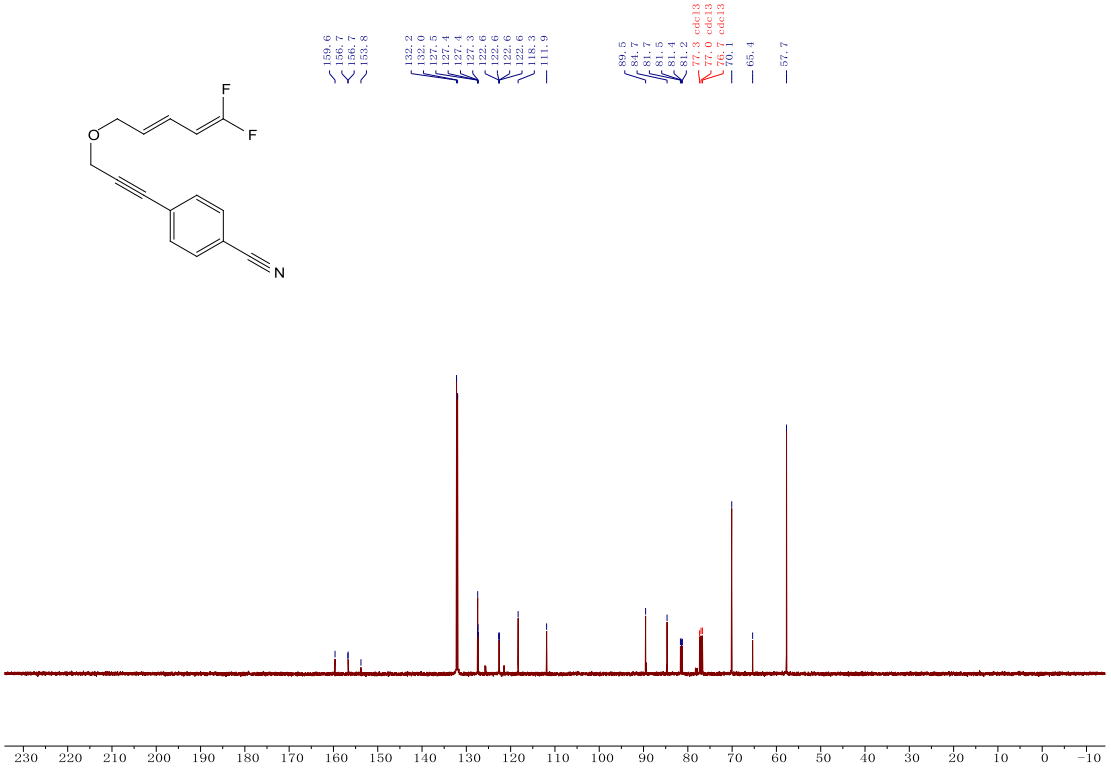
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3o**



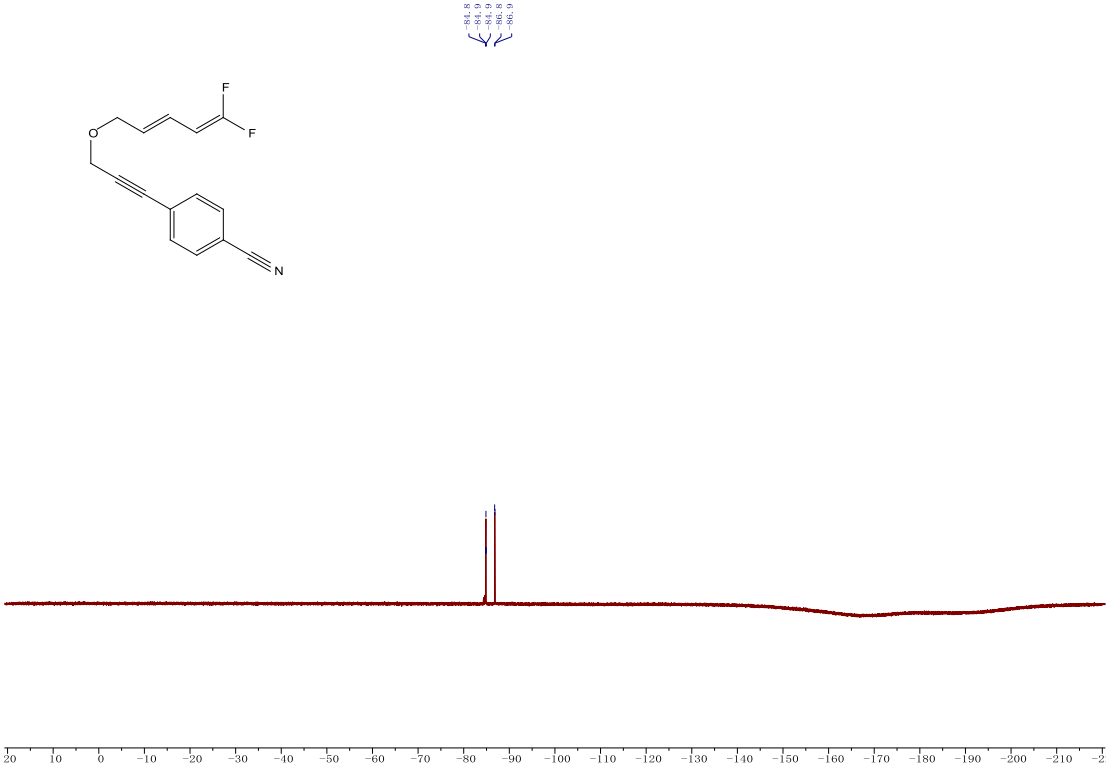
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**



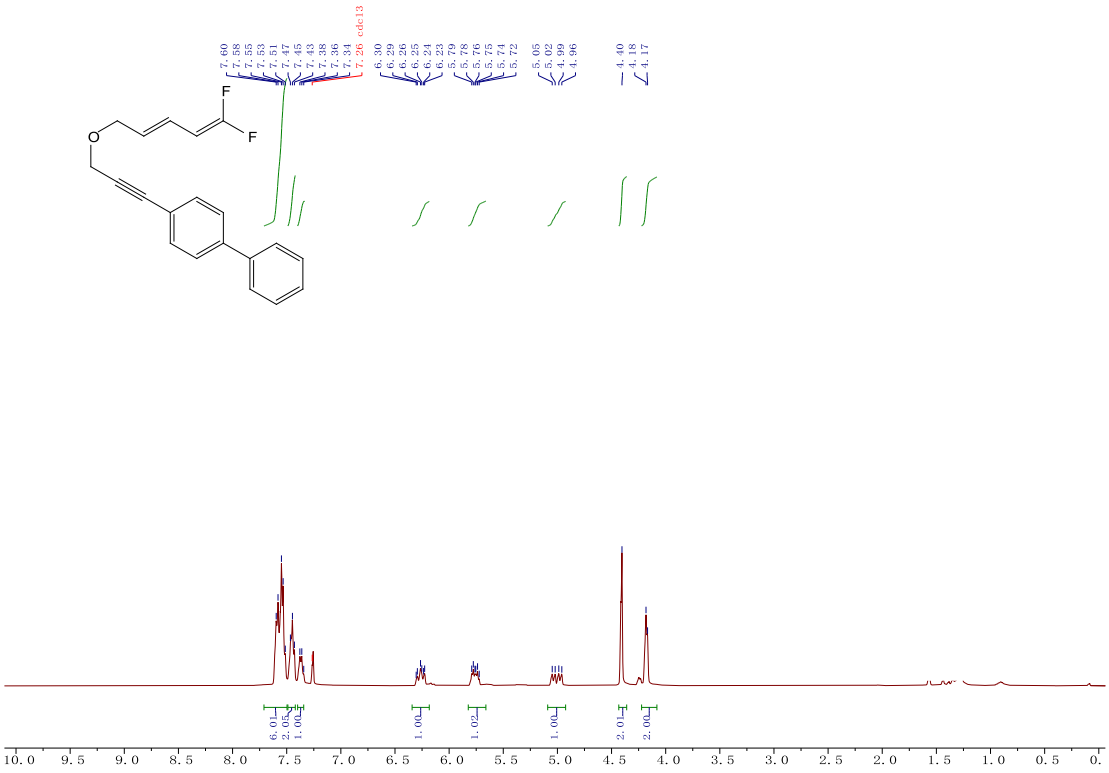
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3p**



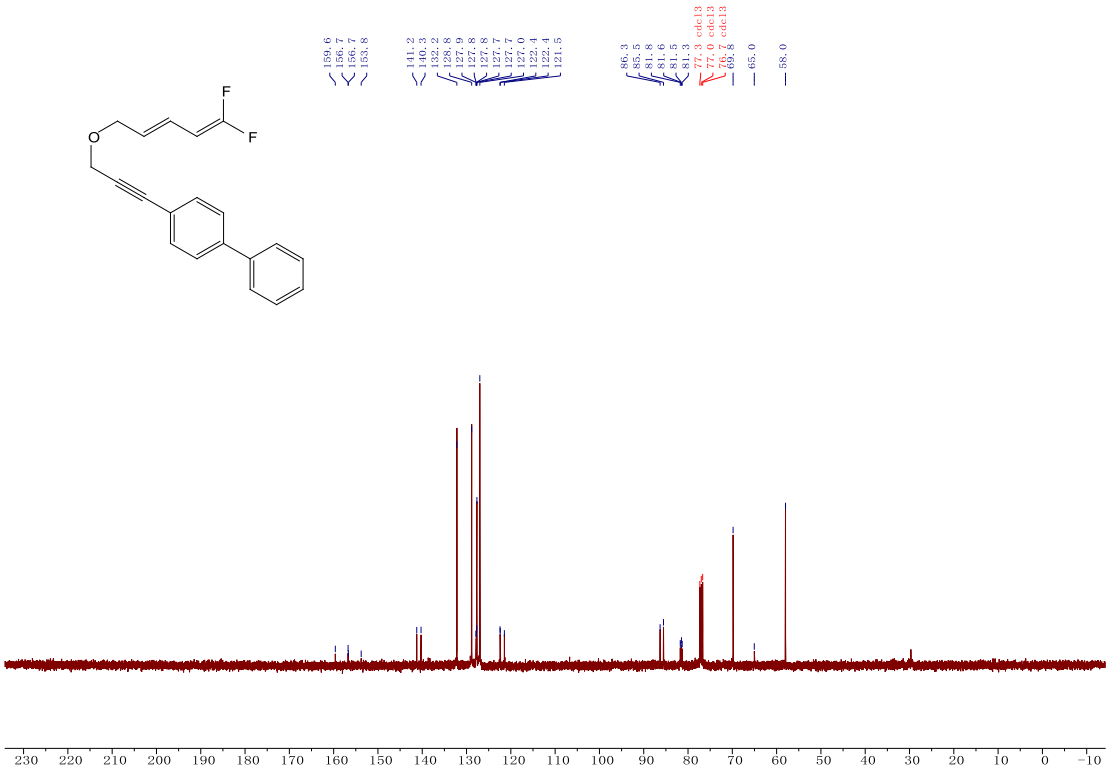
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3p**



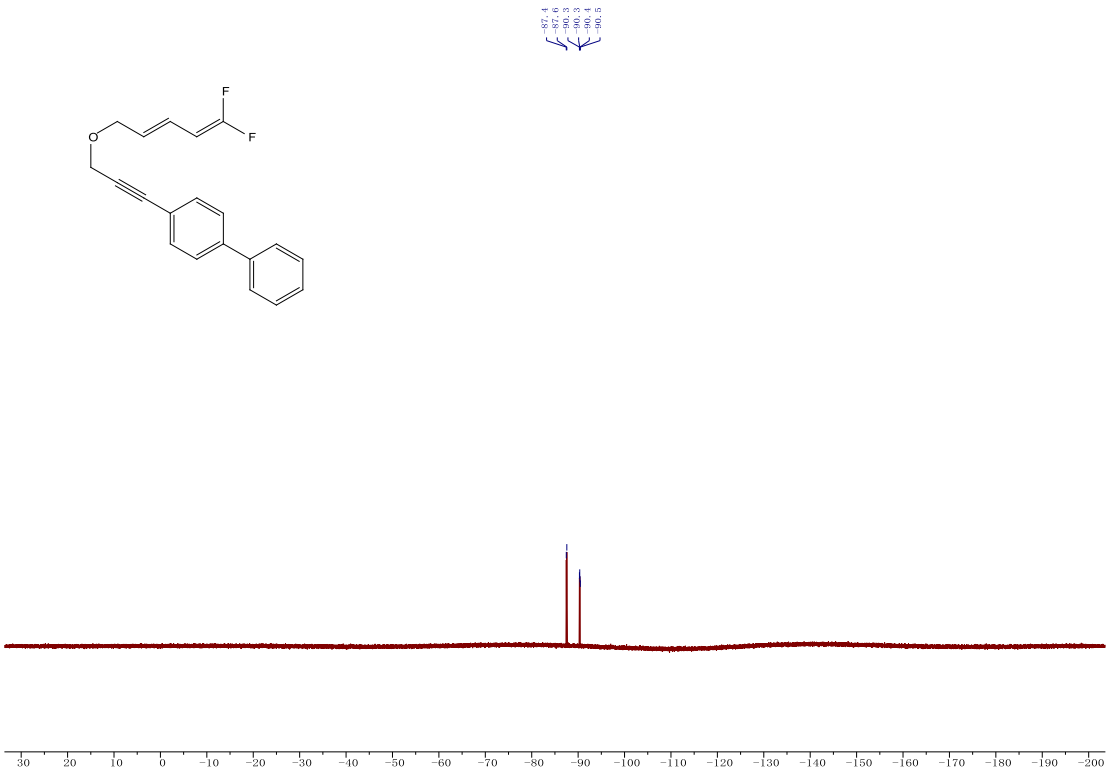
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**



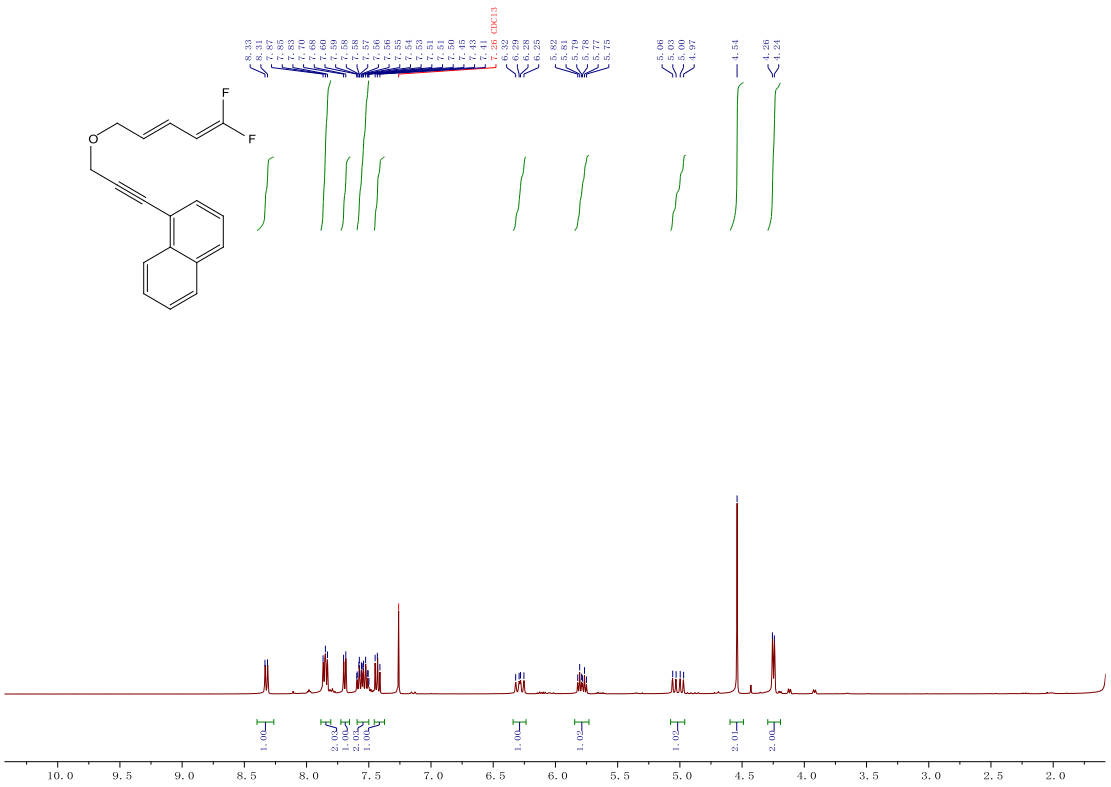
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3q**



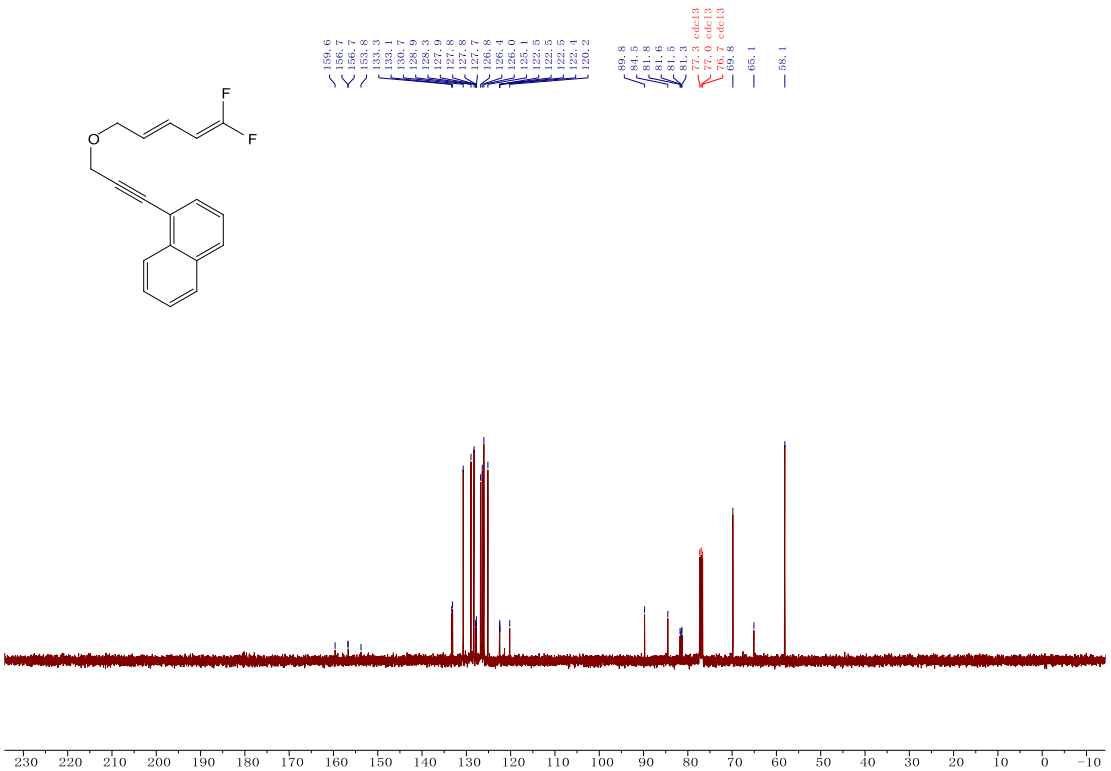
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3q**



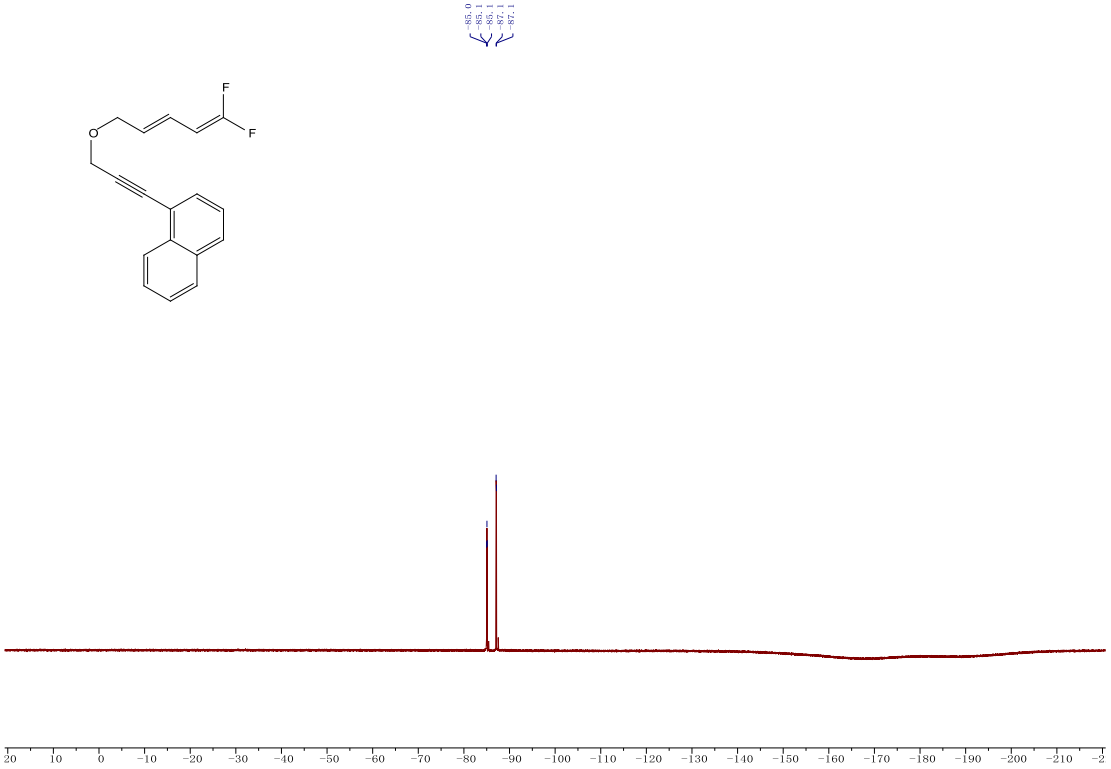
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**



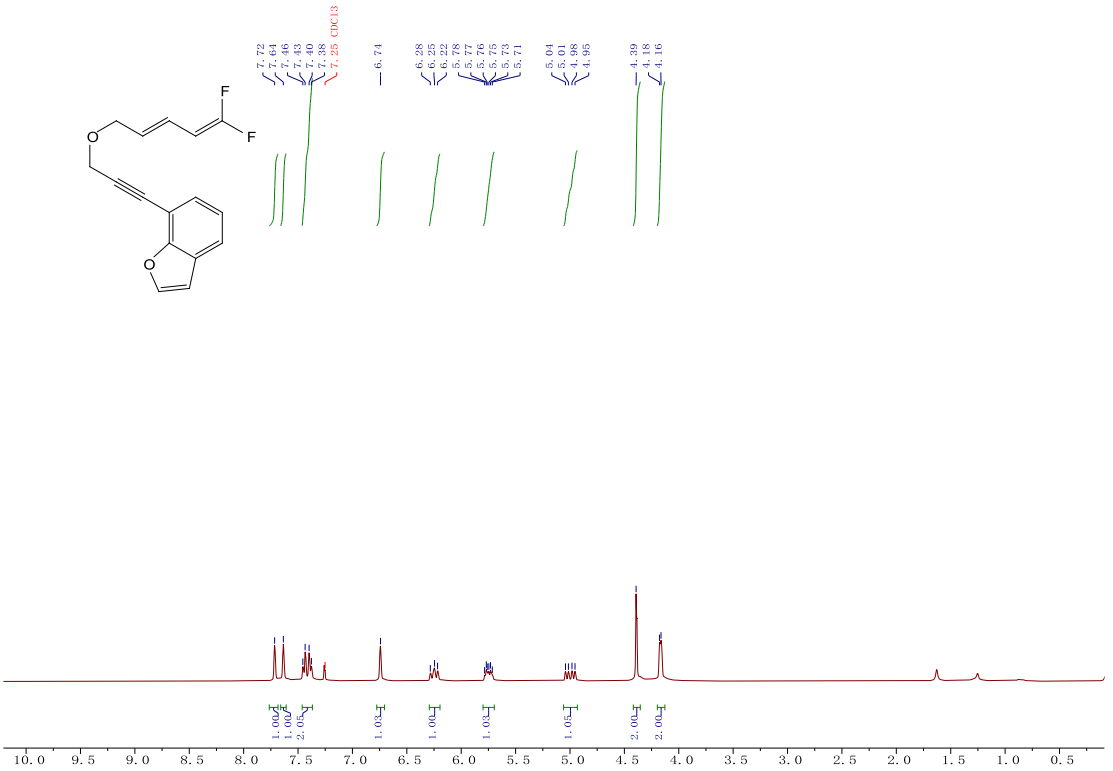
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3r**



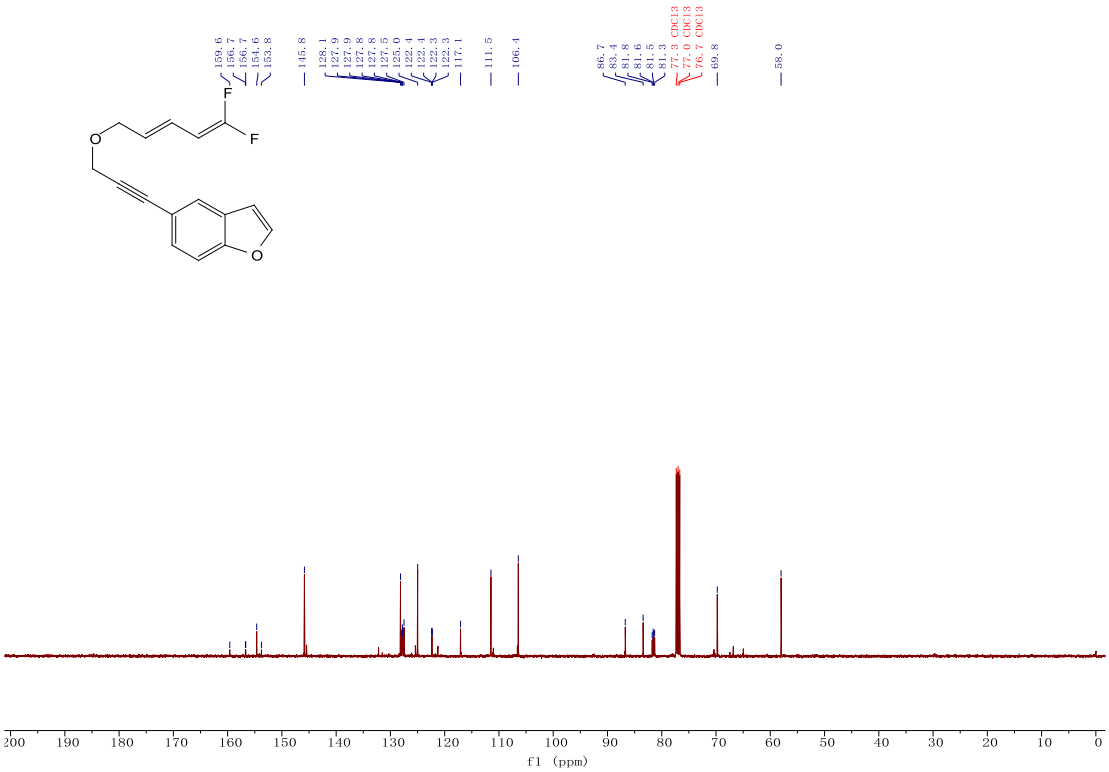
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3r**



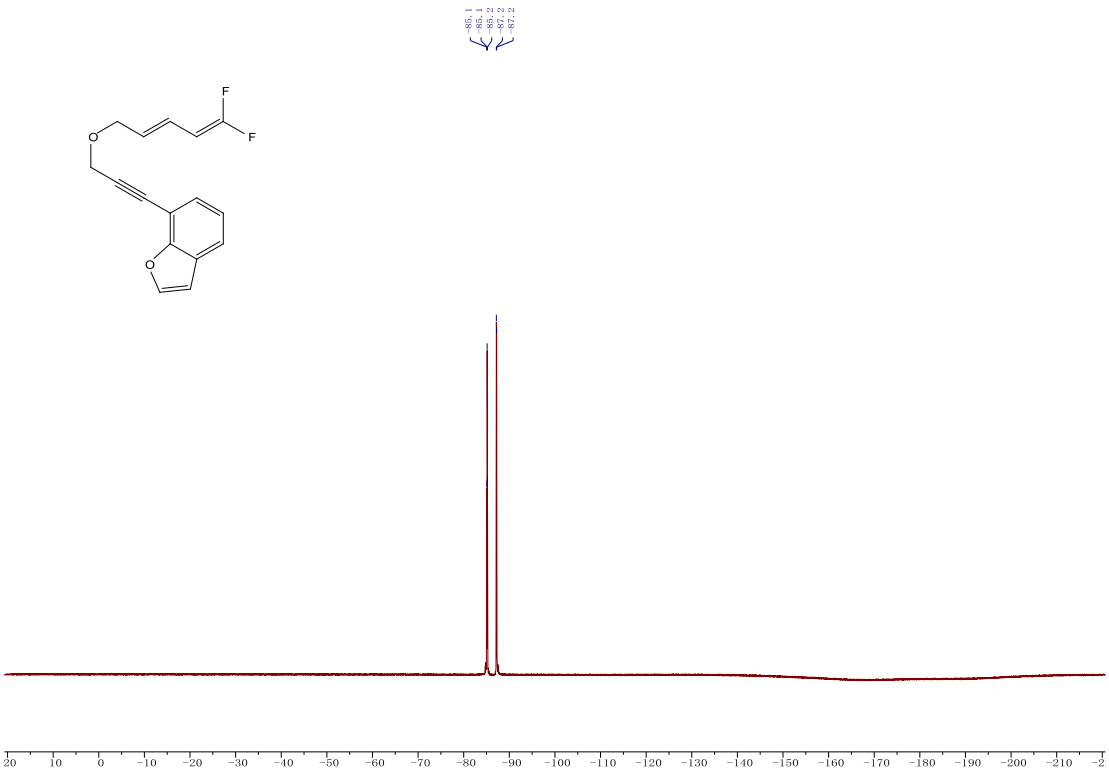
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s**



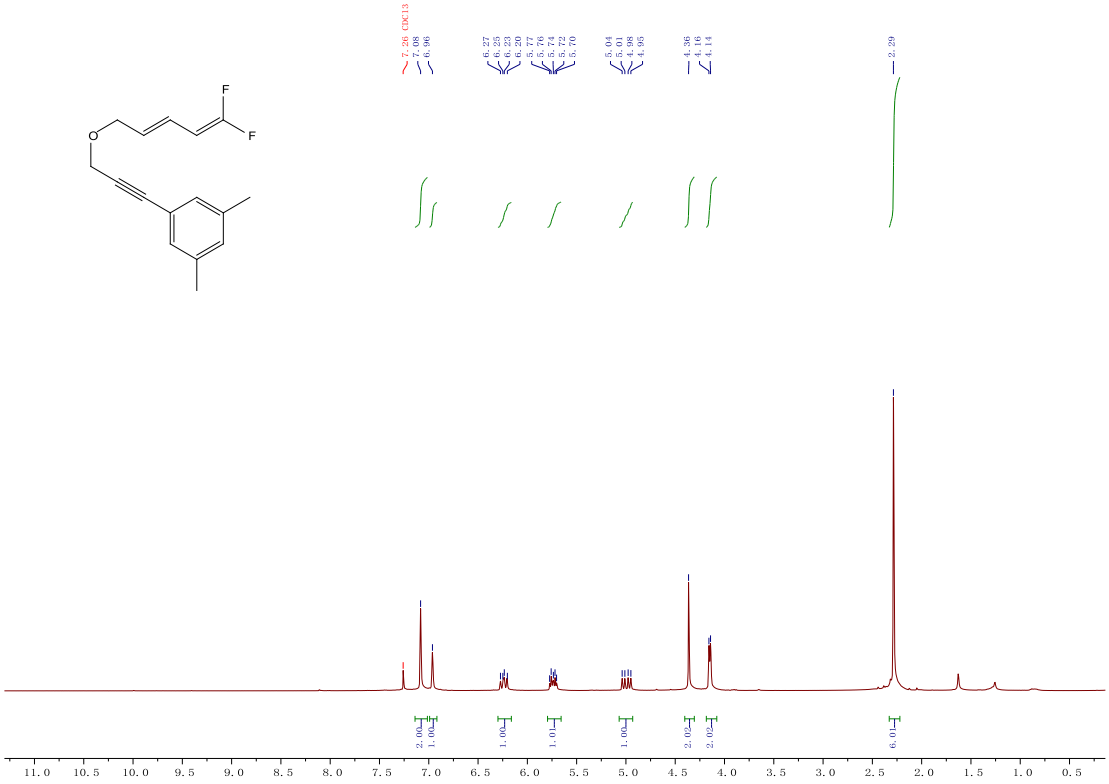
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3s**



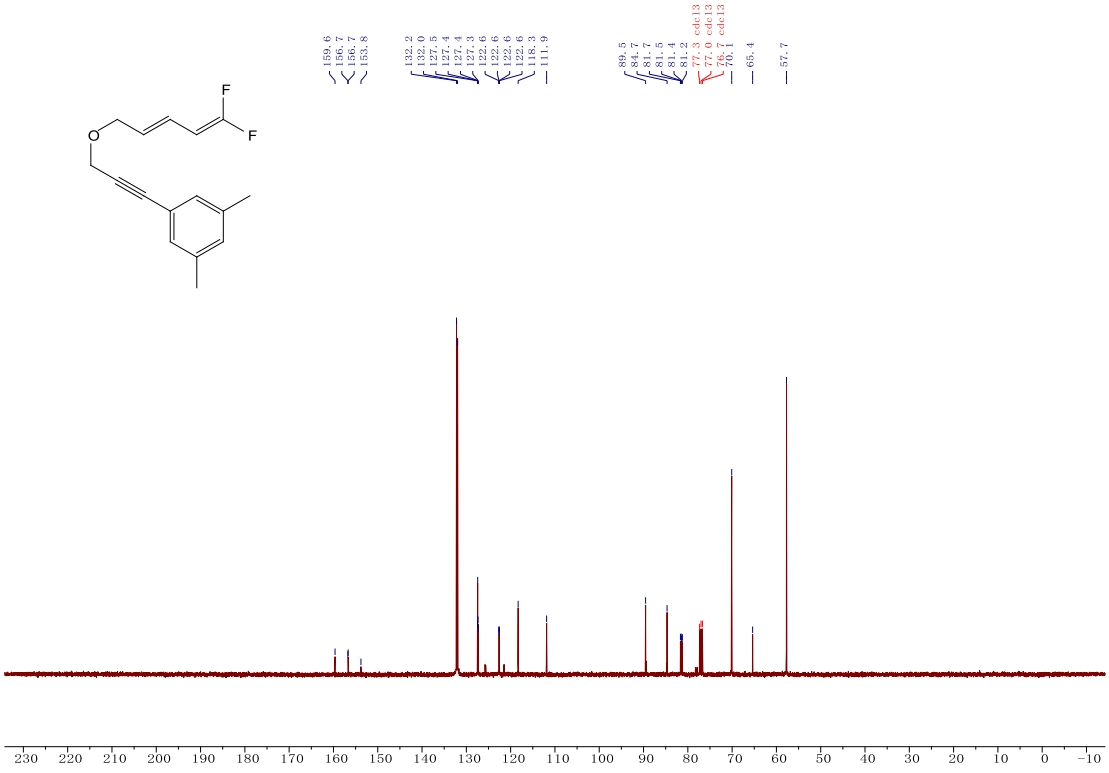
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3s**



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

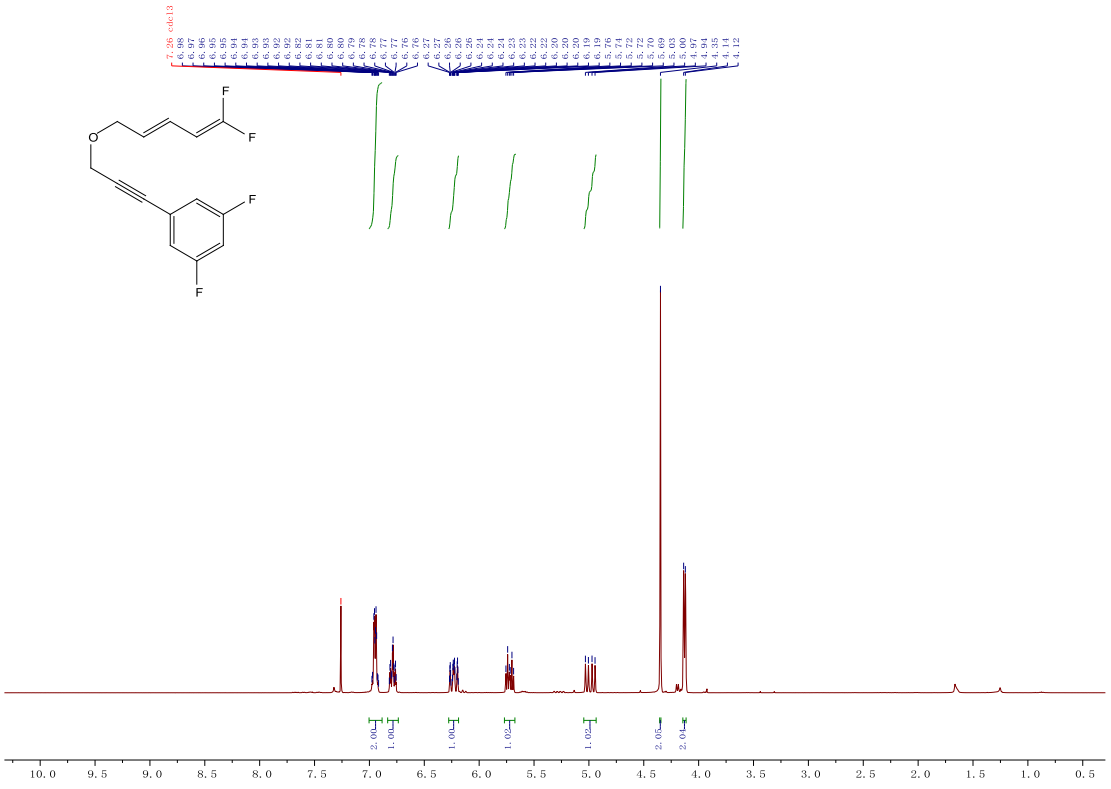


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3t**

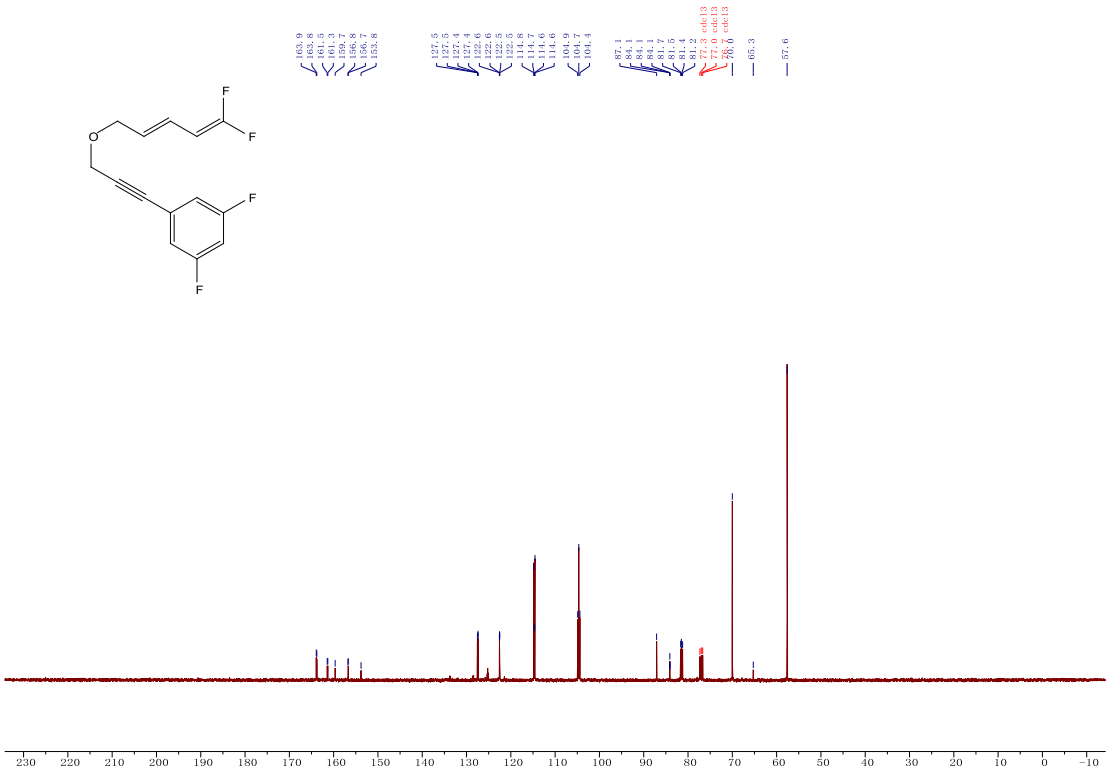


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3t**

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

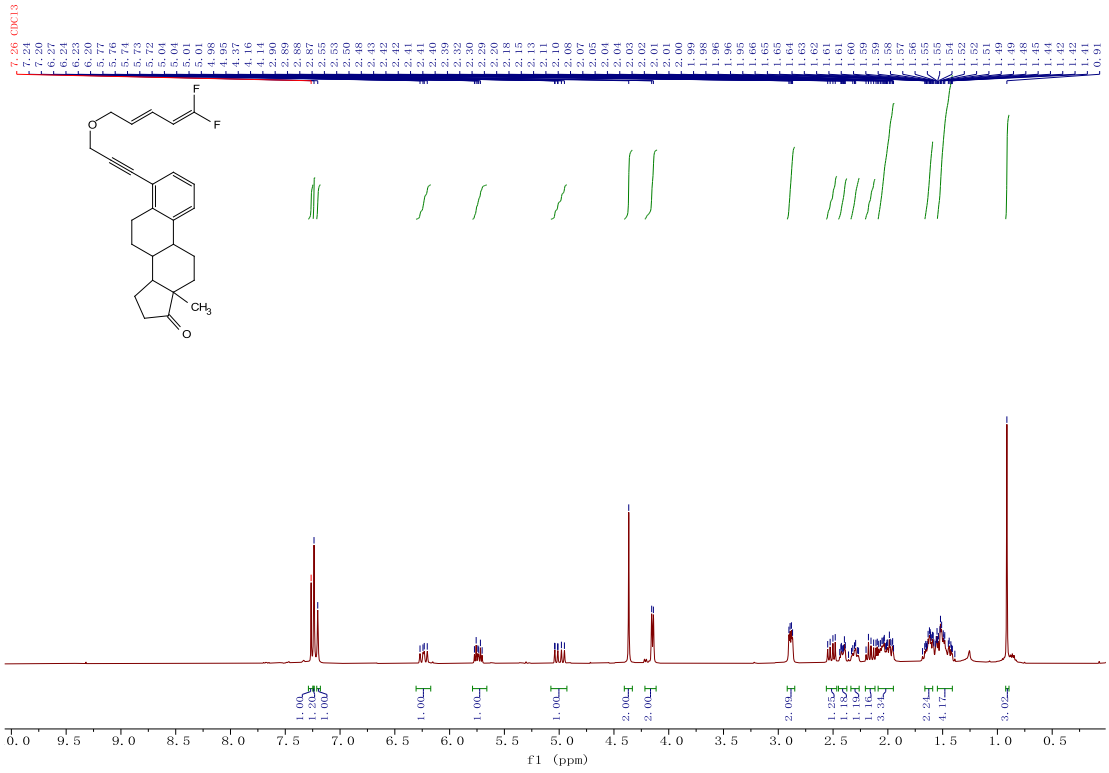


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3u**

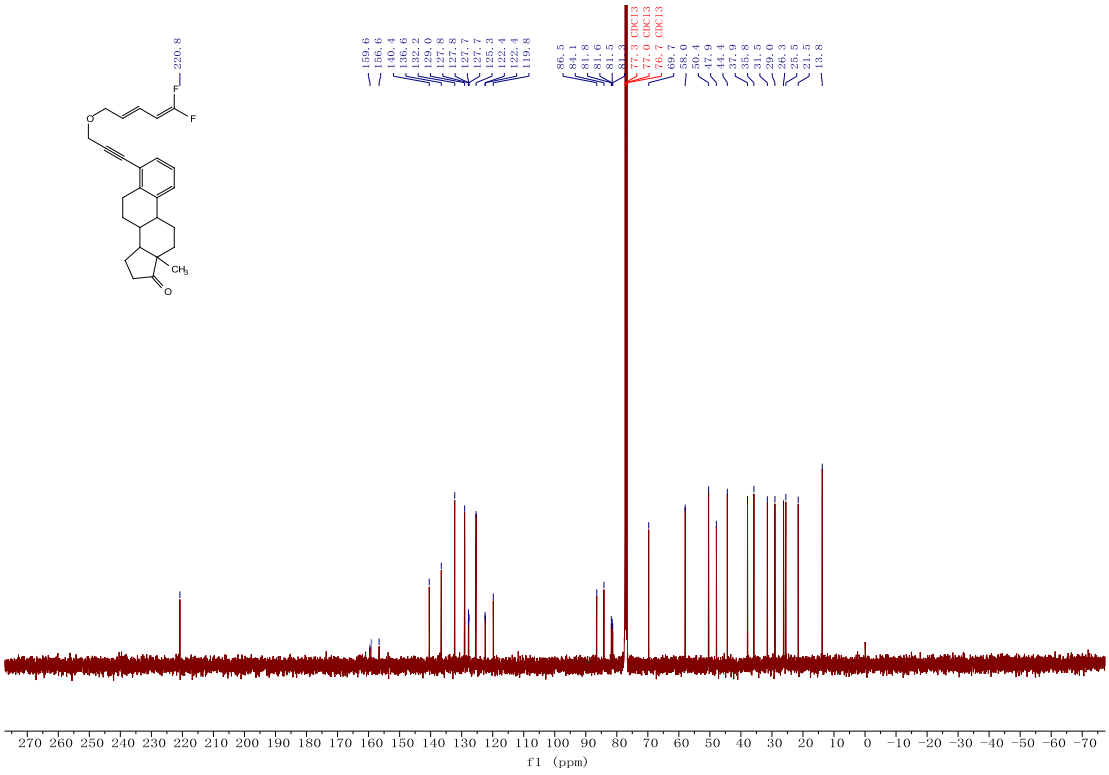


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3u**

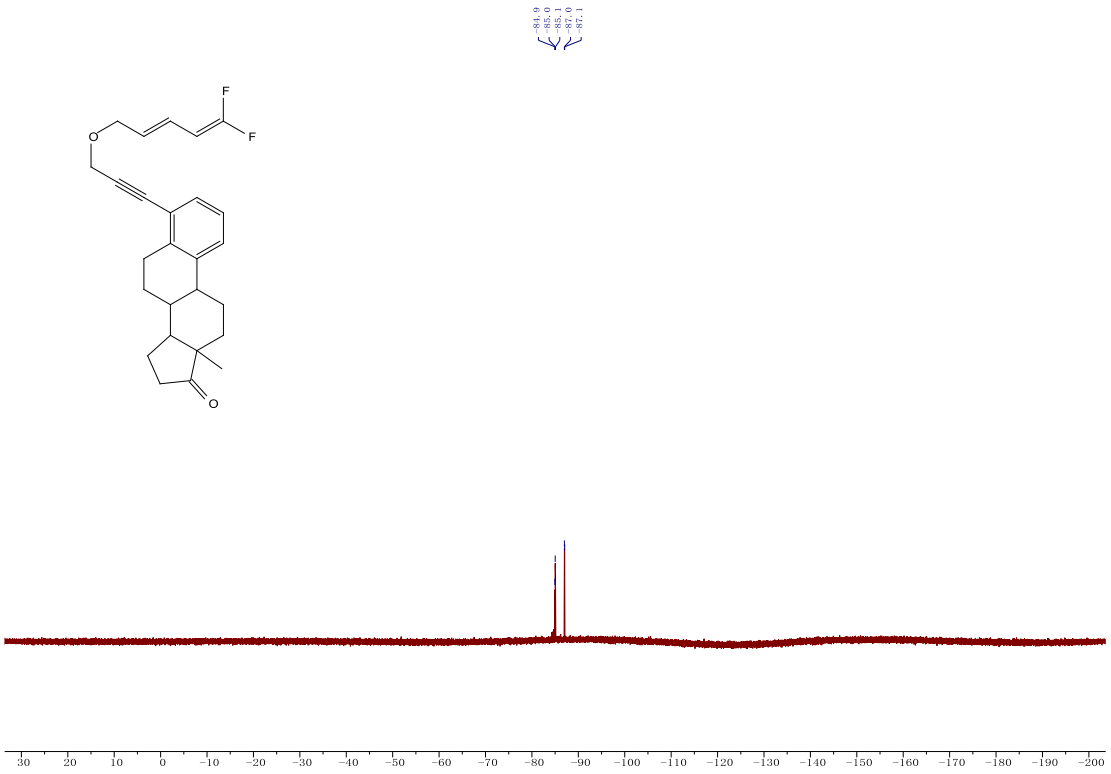
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3v**



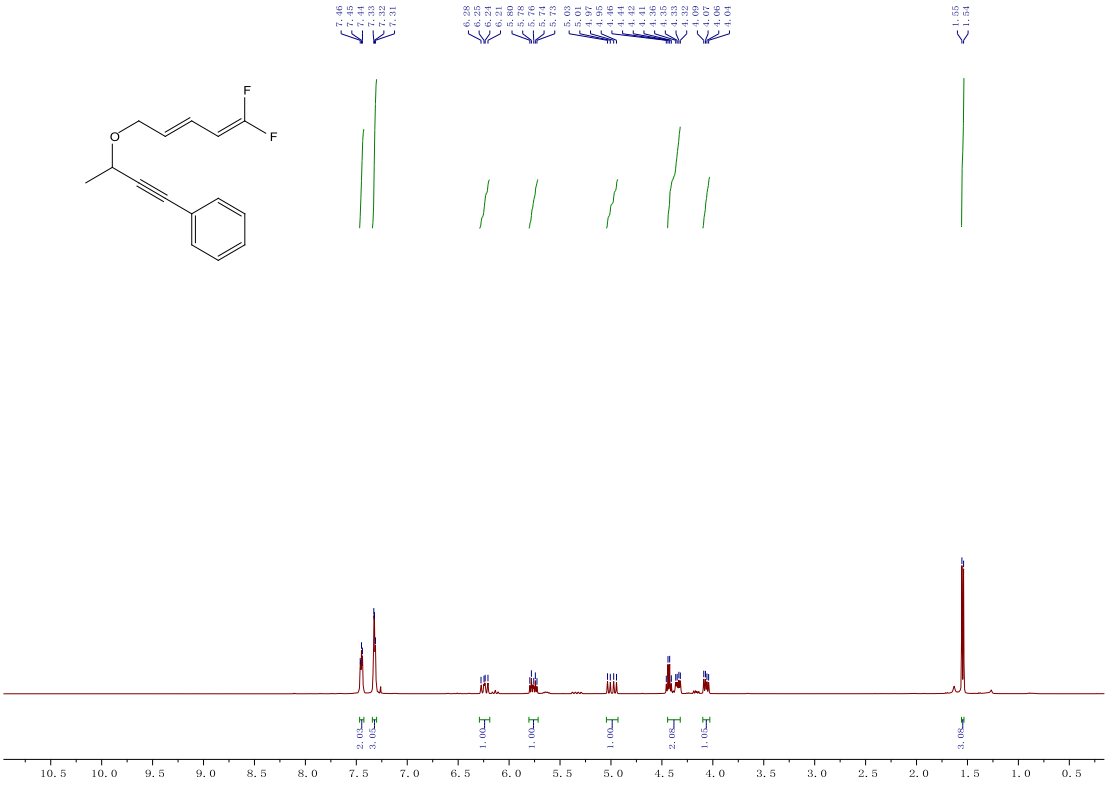
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3v**



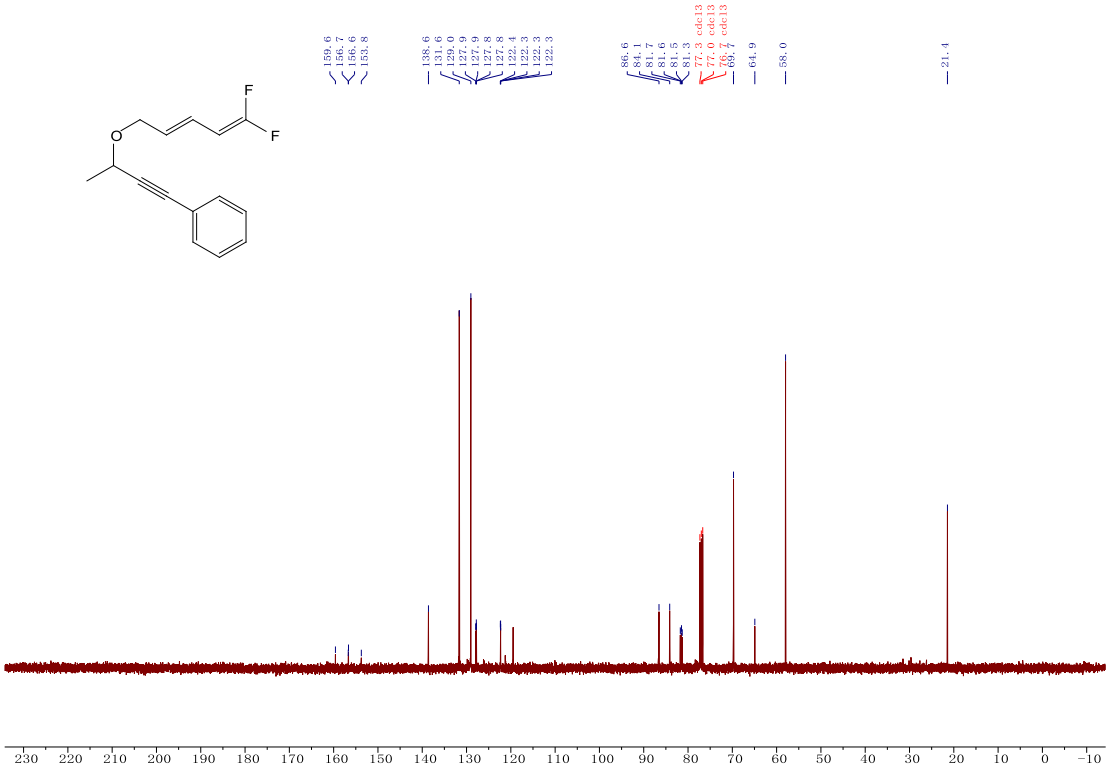
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3v**



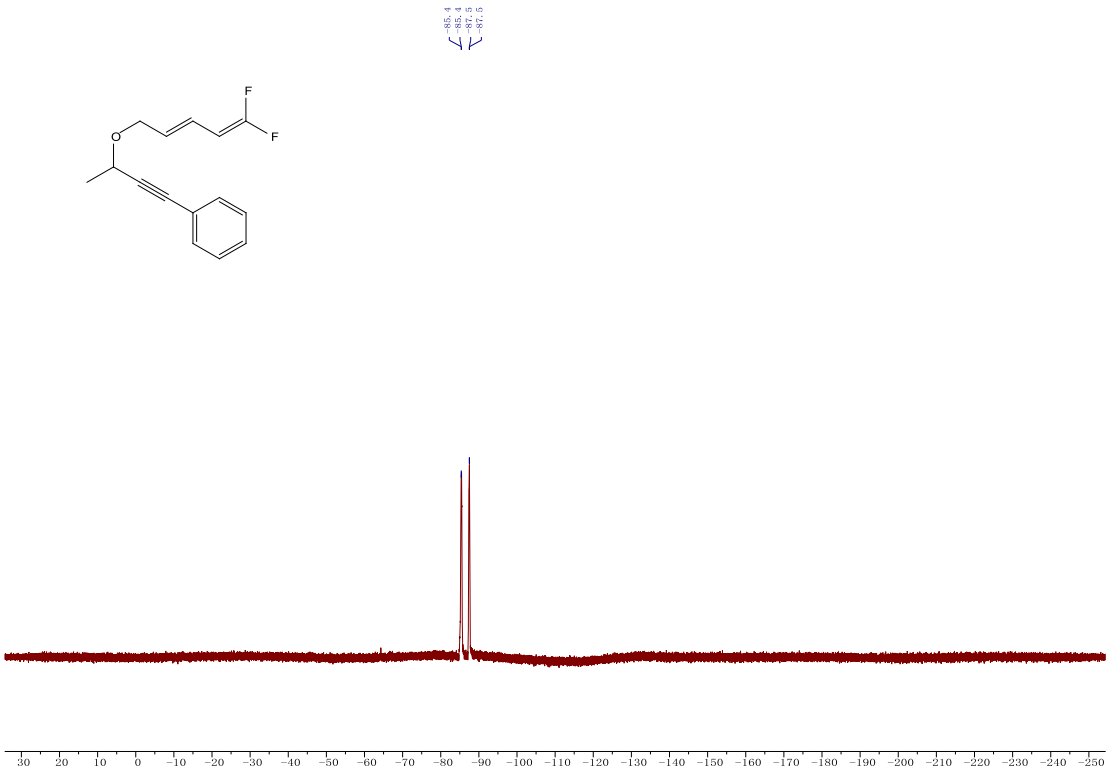
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3w**



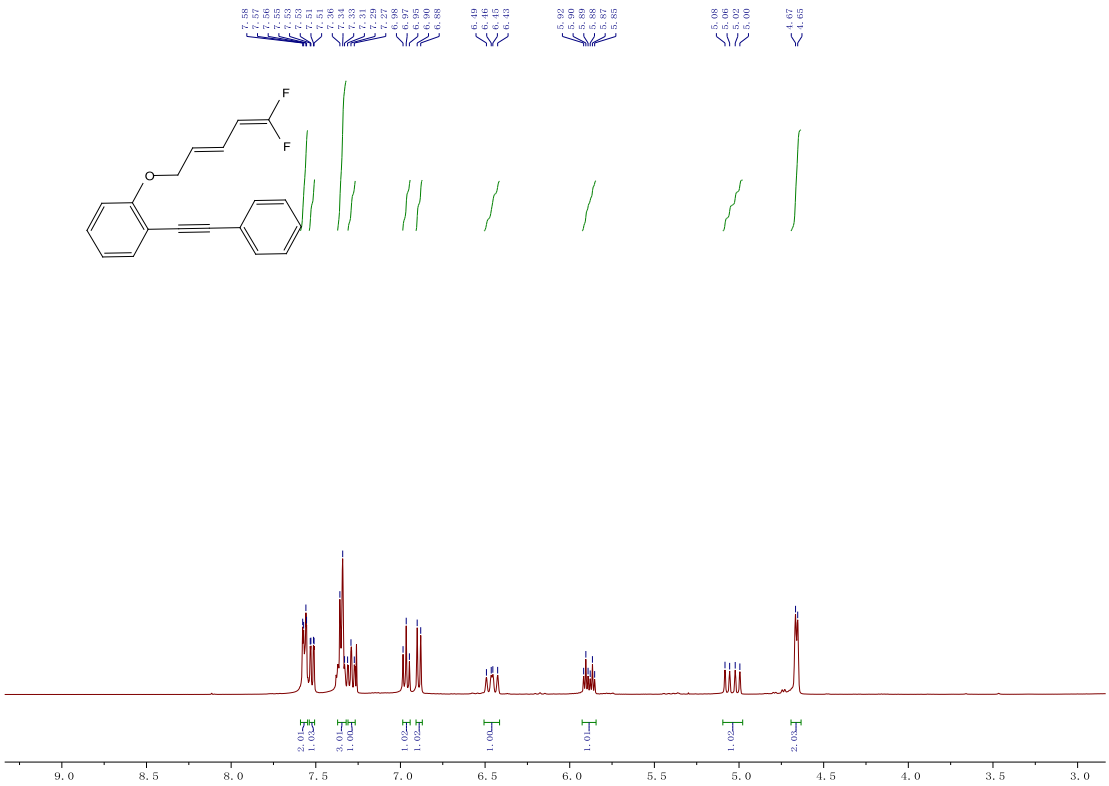
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3w**



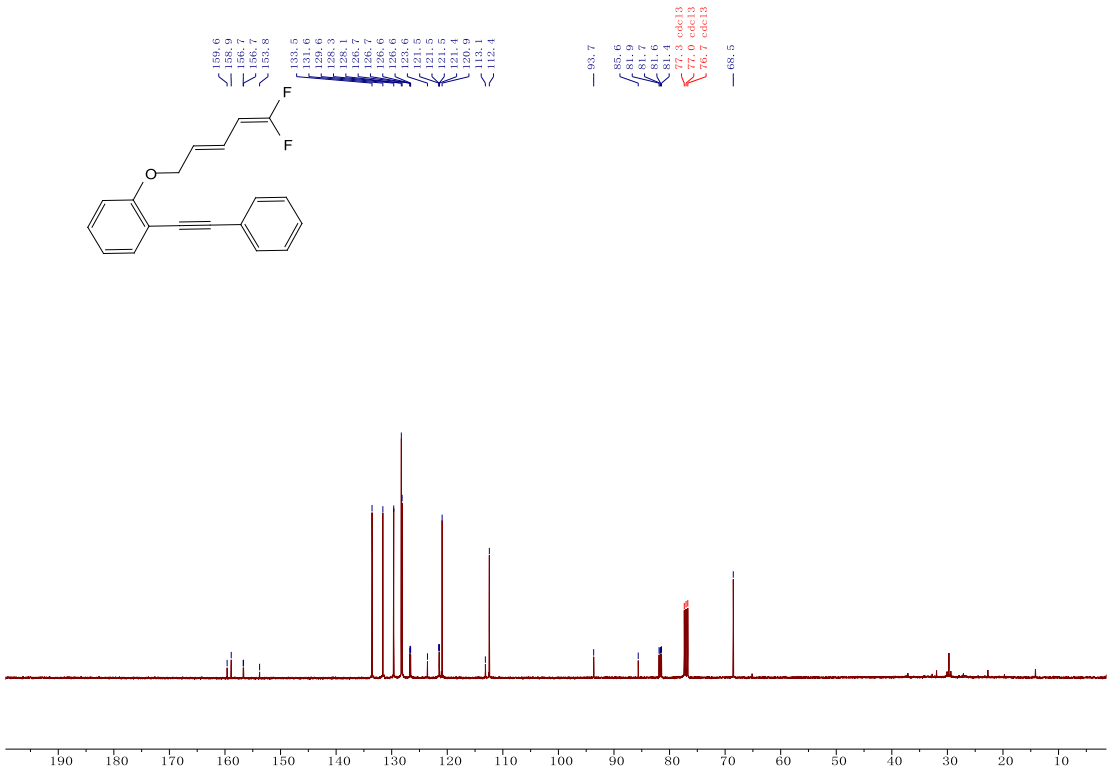
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3w**



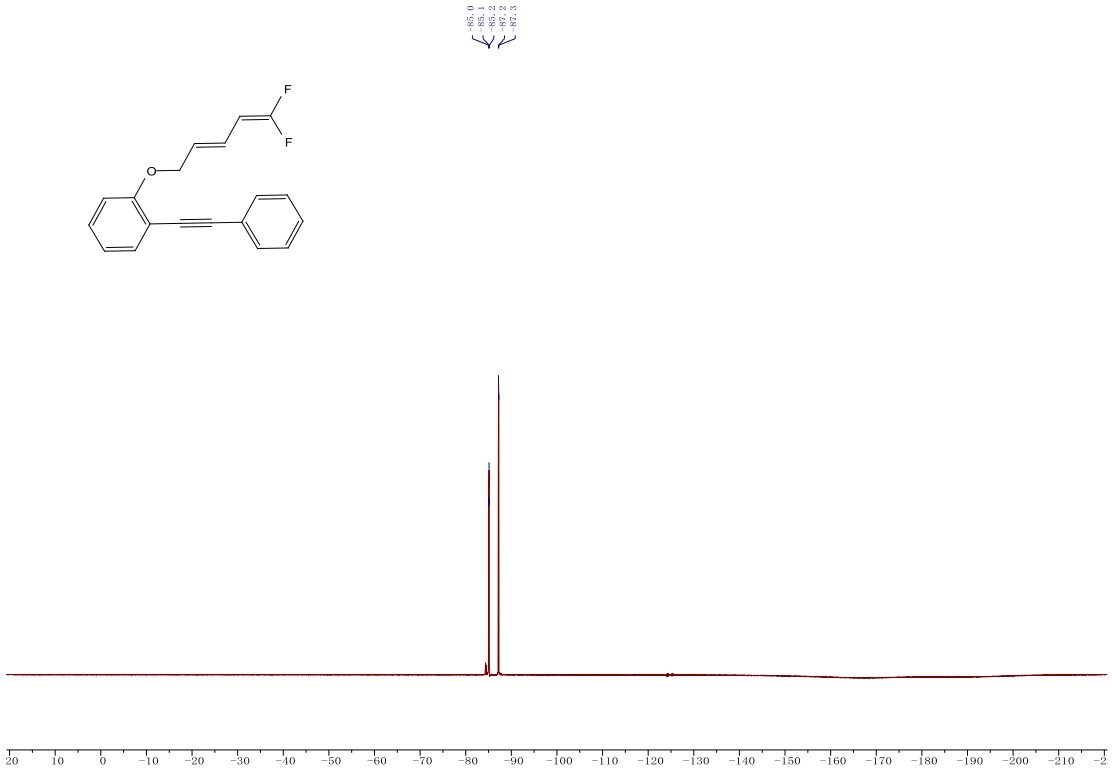
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x**



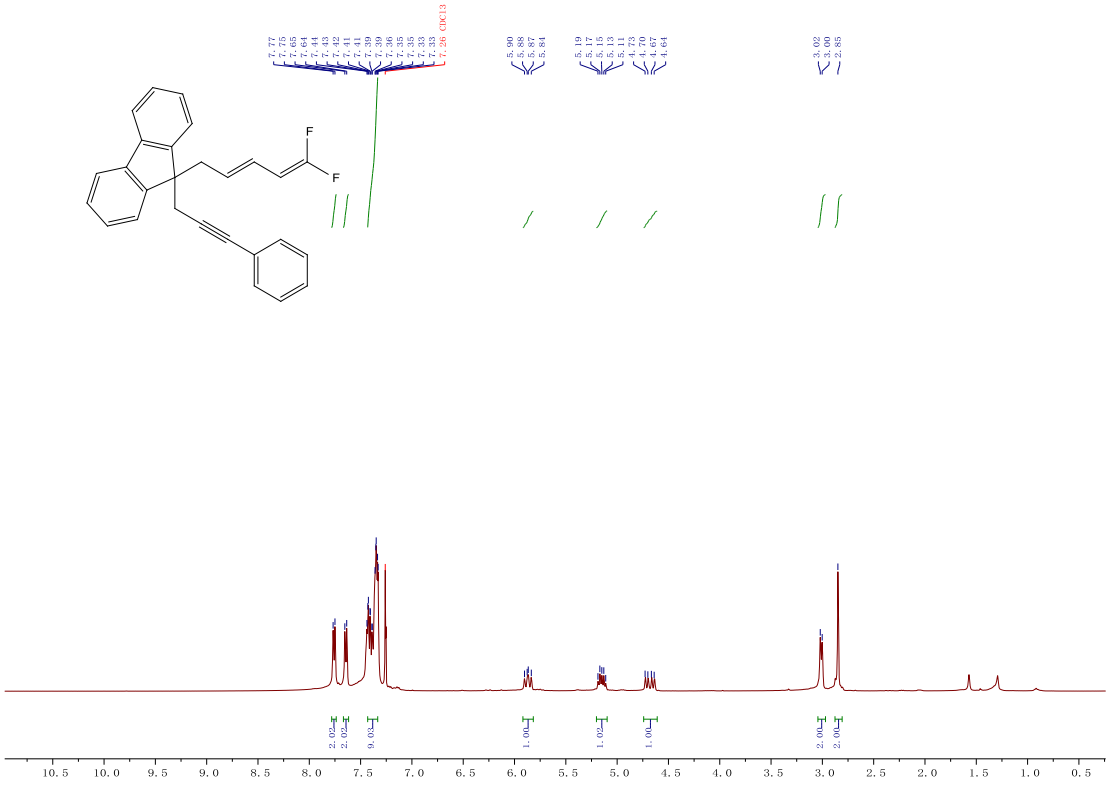
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3x**



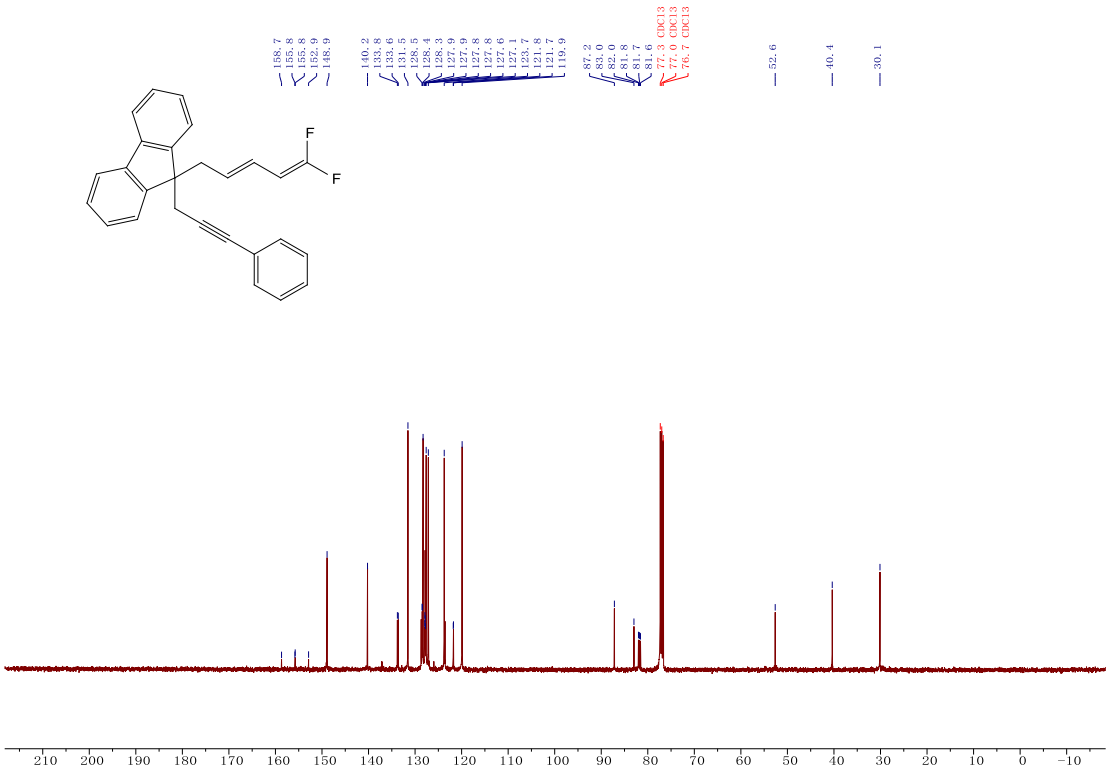
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3x**



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

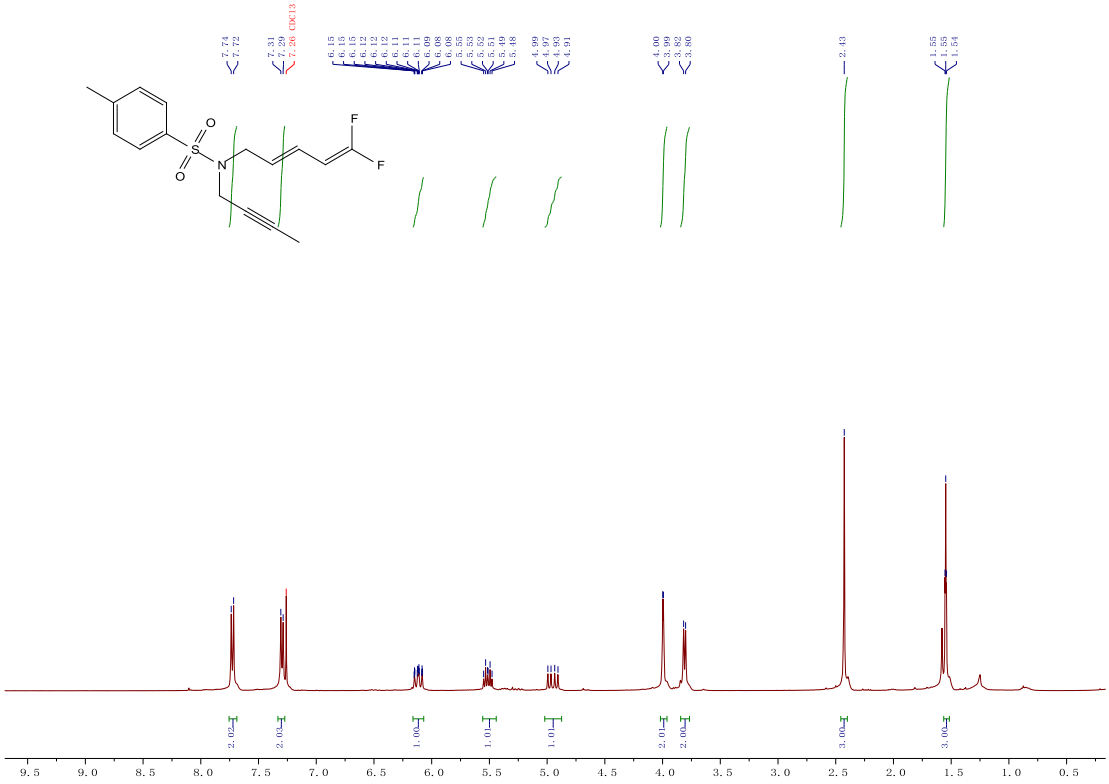


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ag**

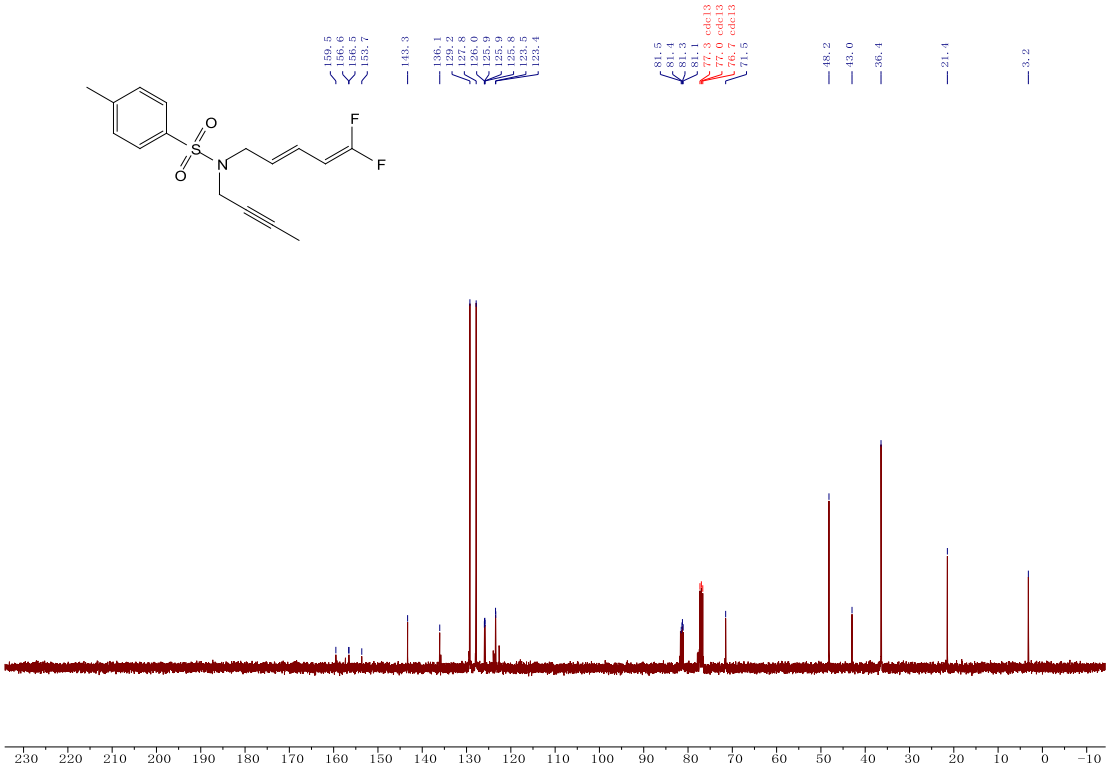


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ag**

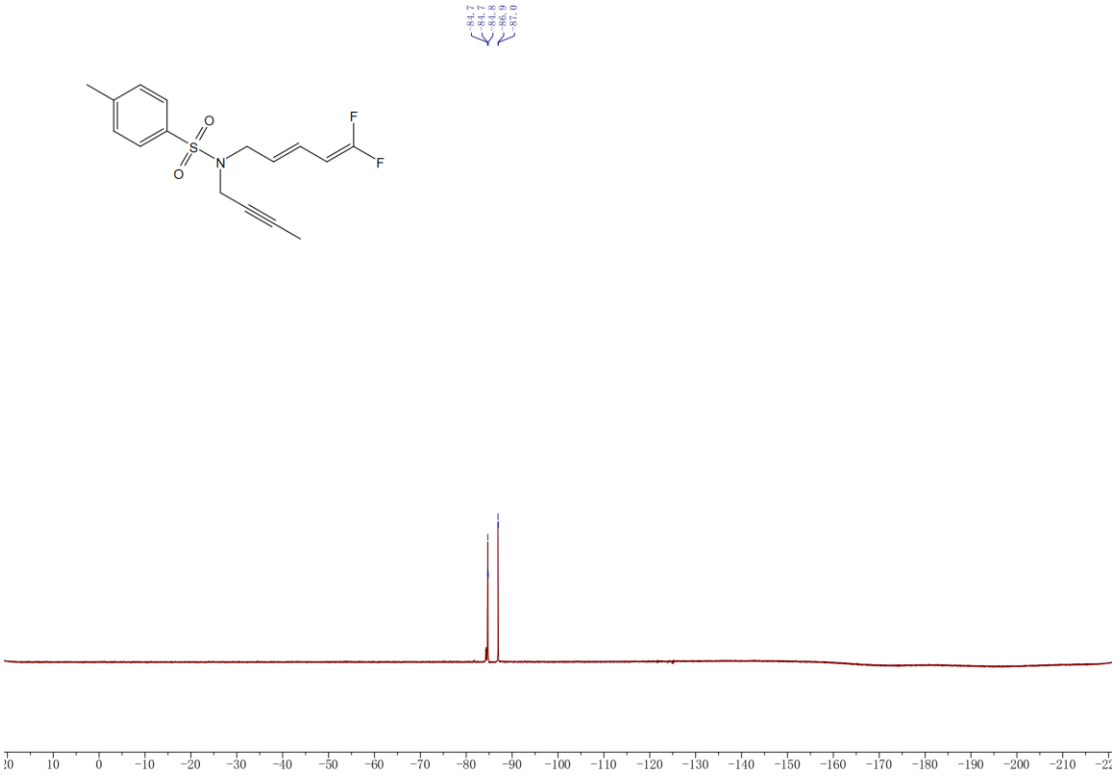
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



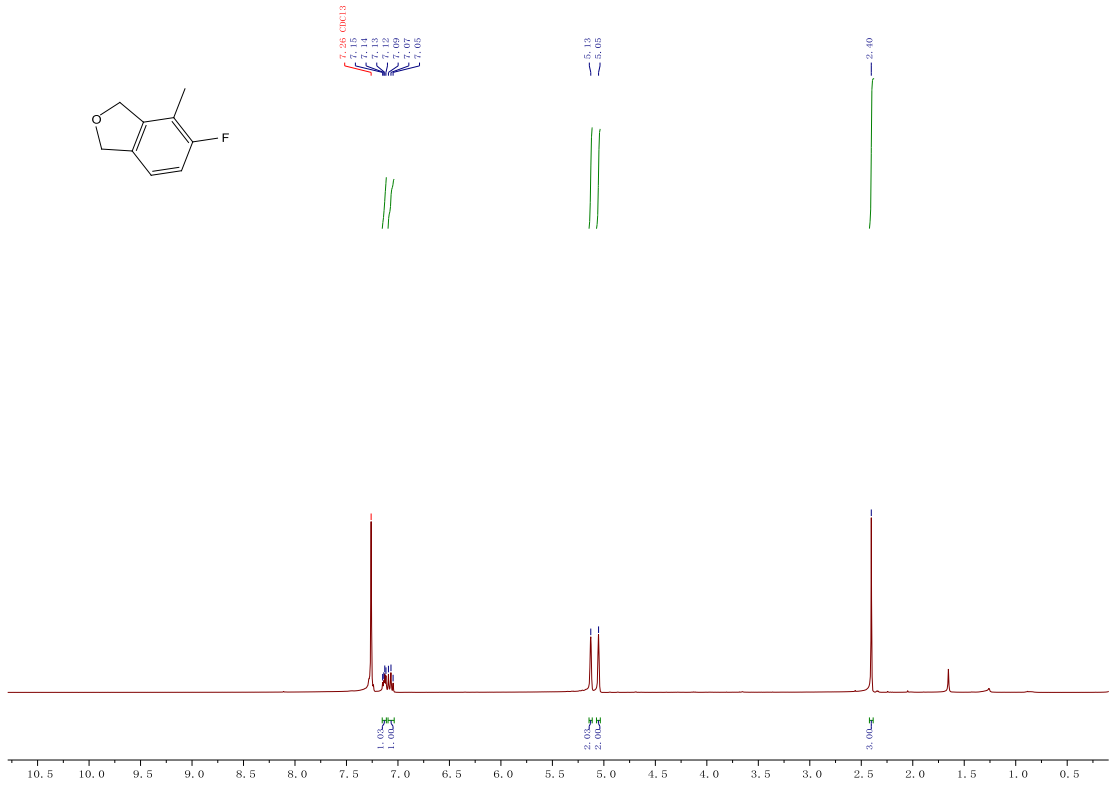
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ah**



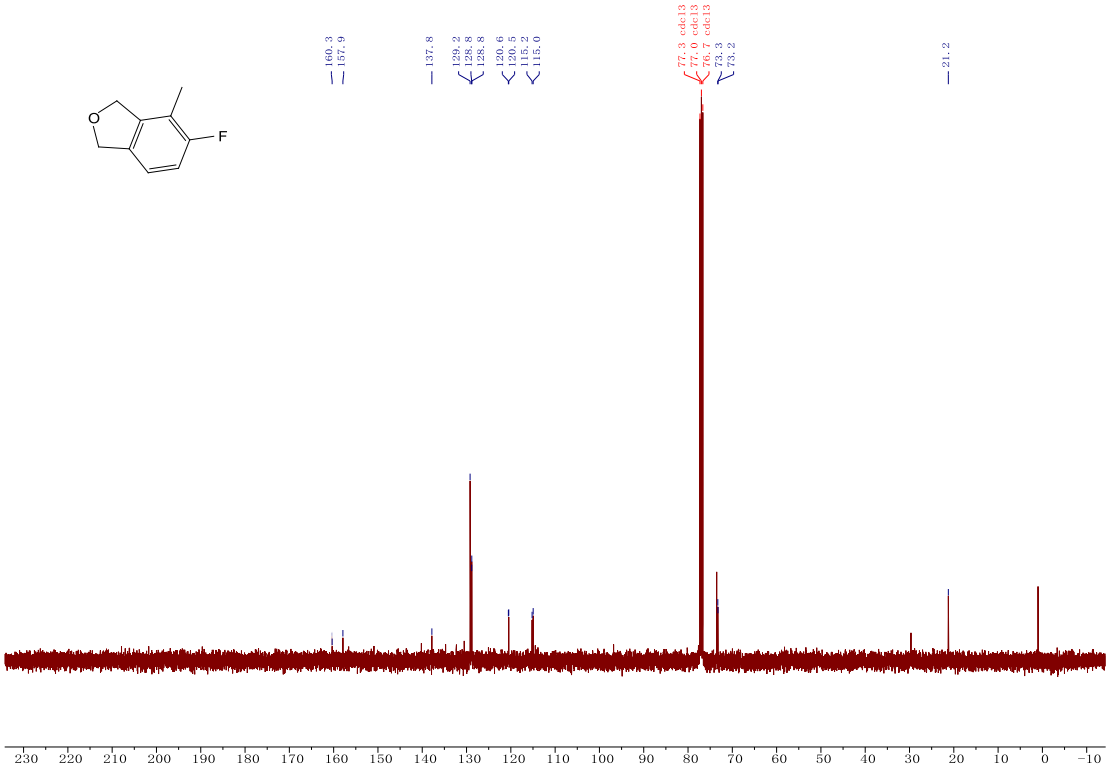
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ah**



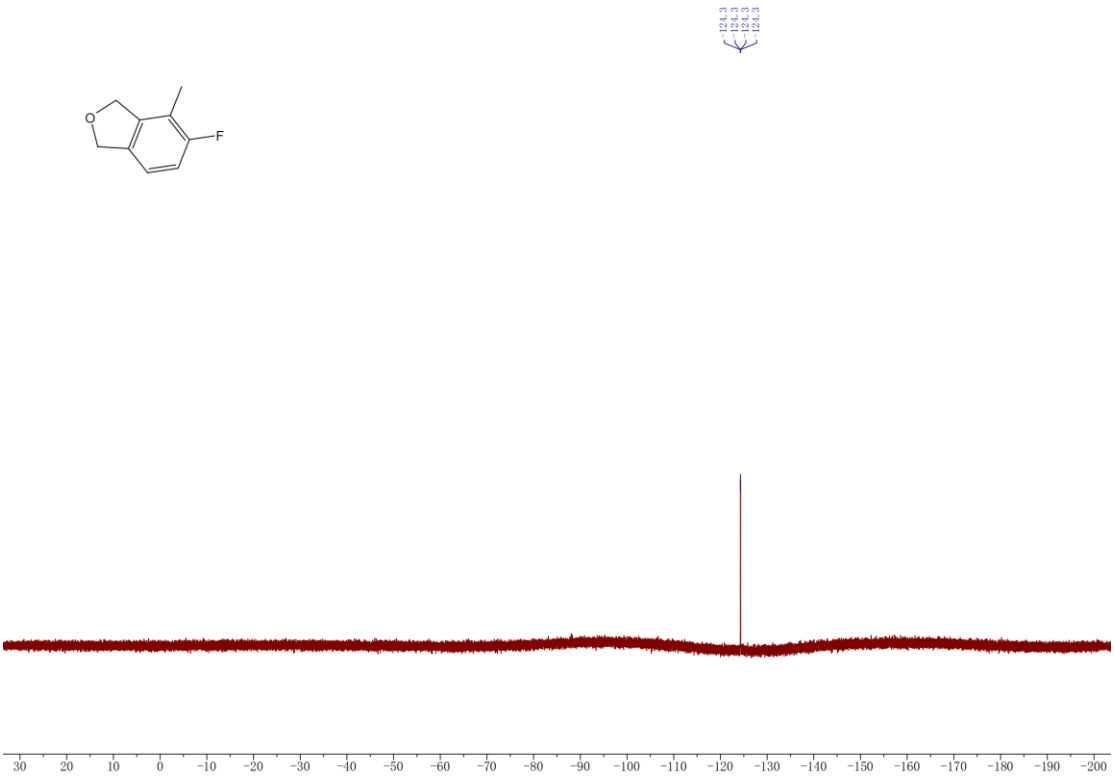
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



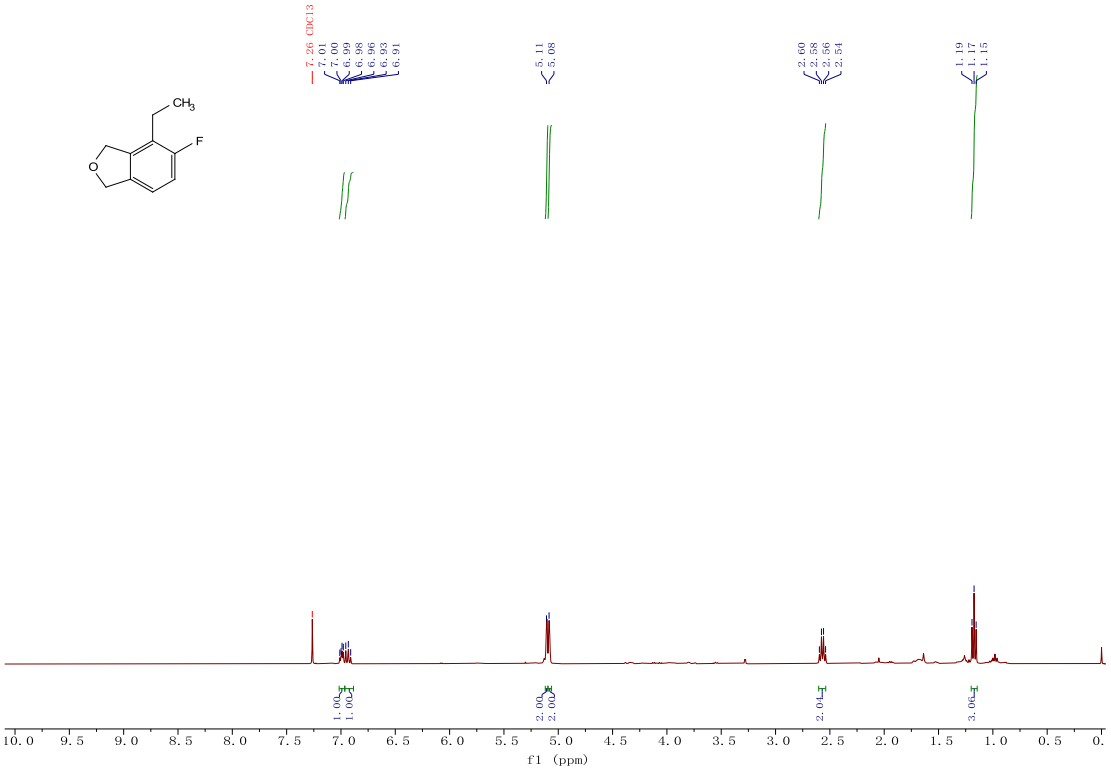
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**



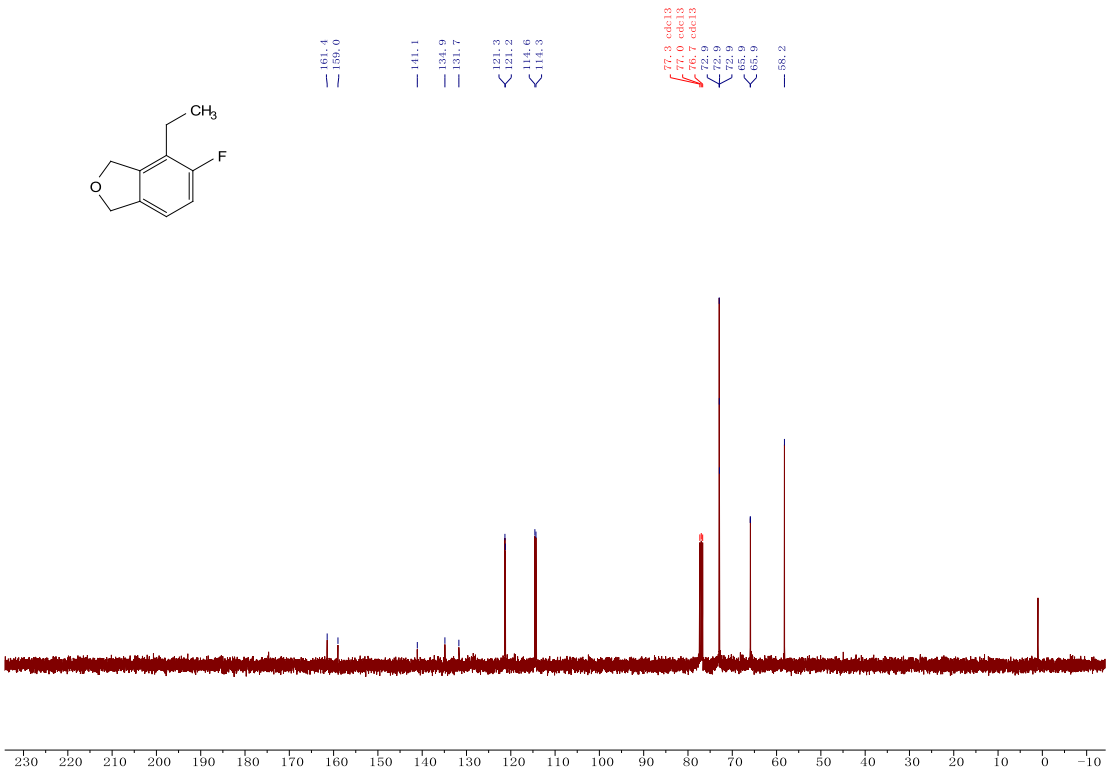
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4a**



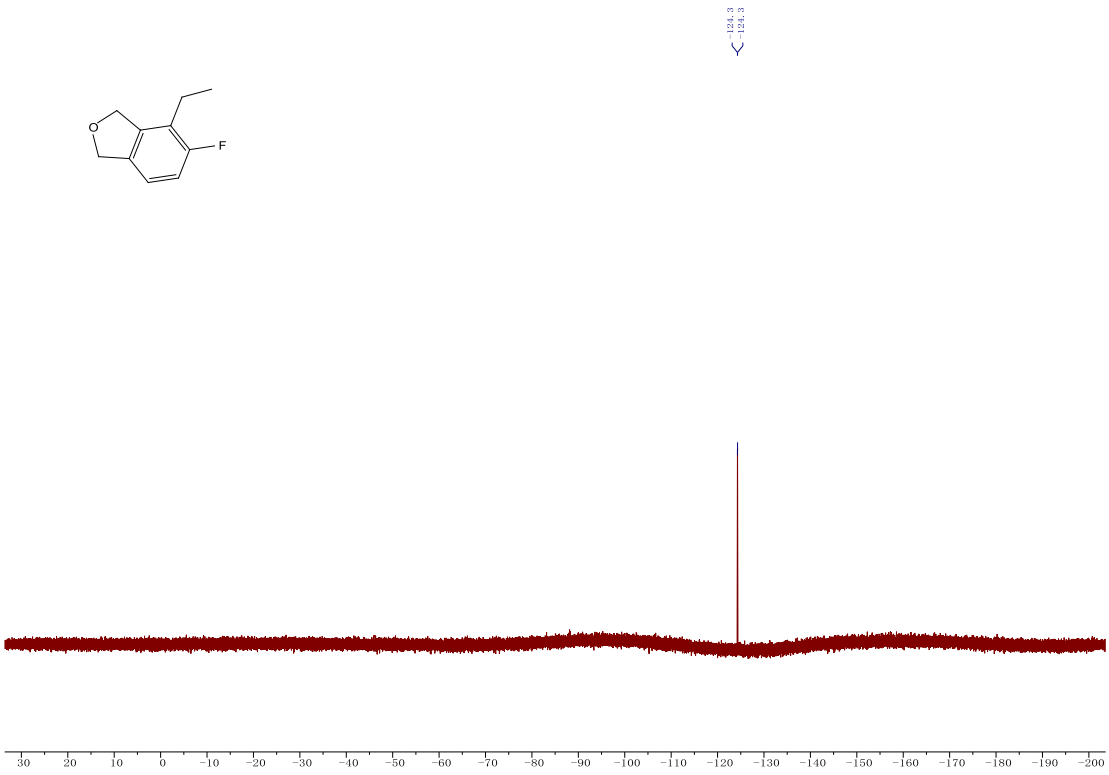
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



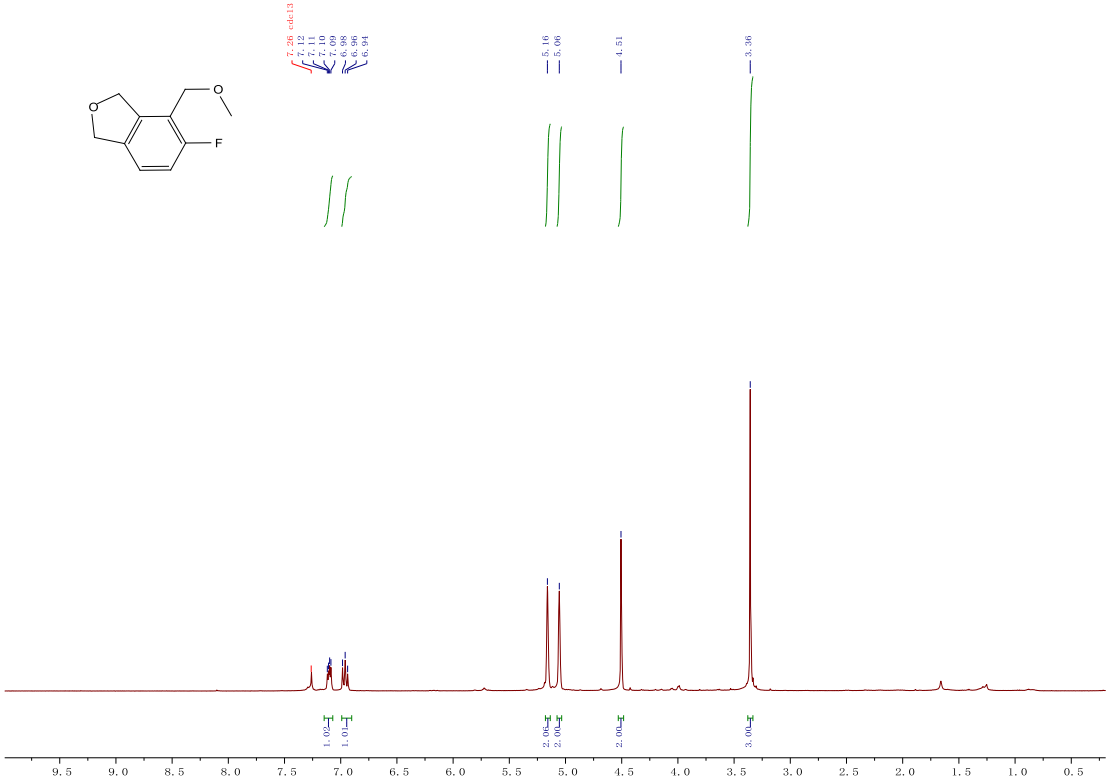
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**



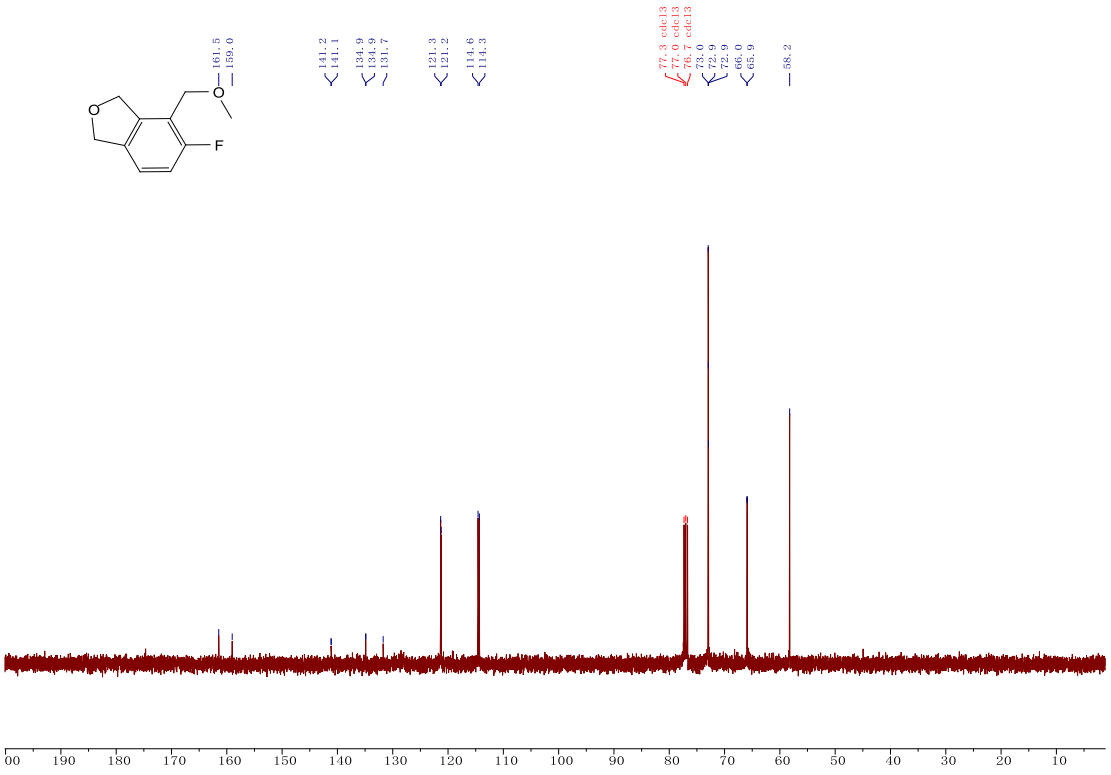
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4b**



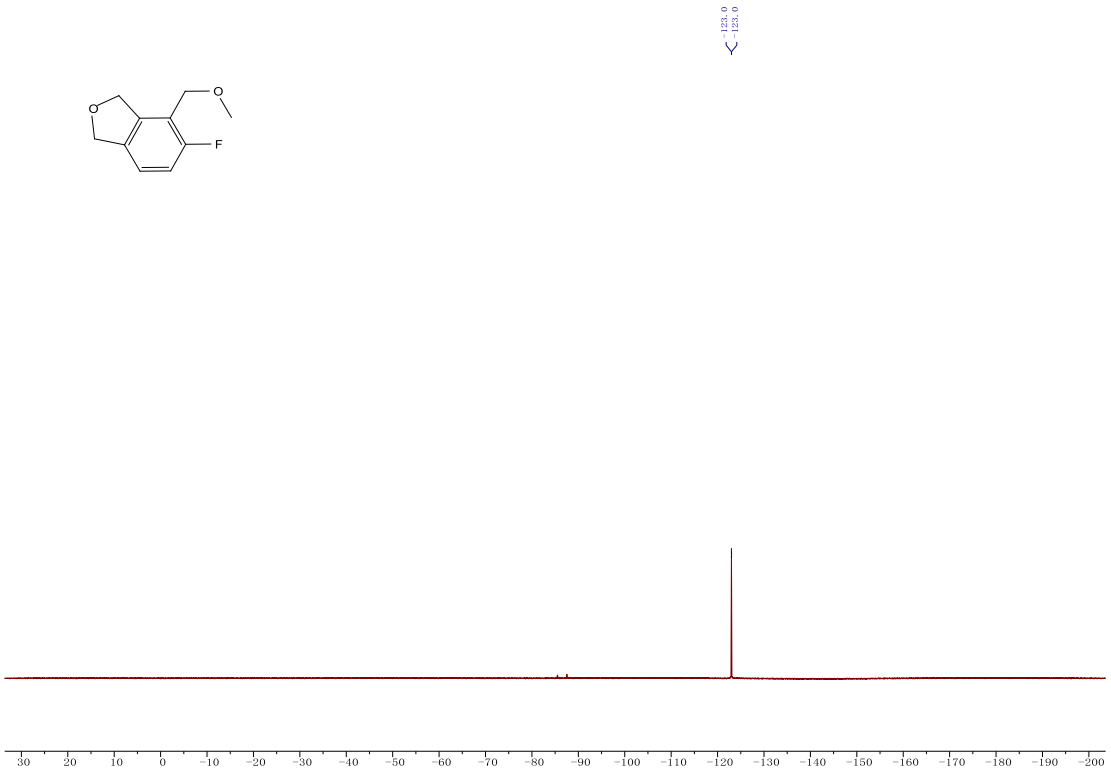
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



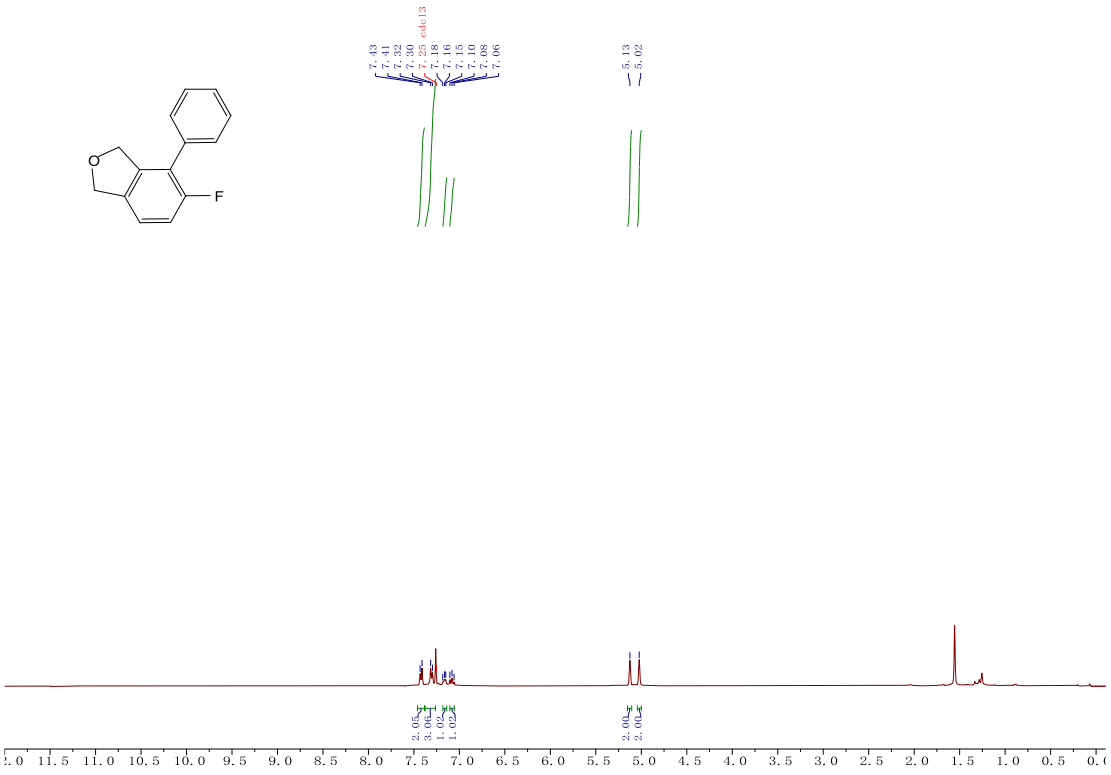
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4c**



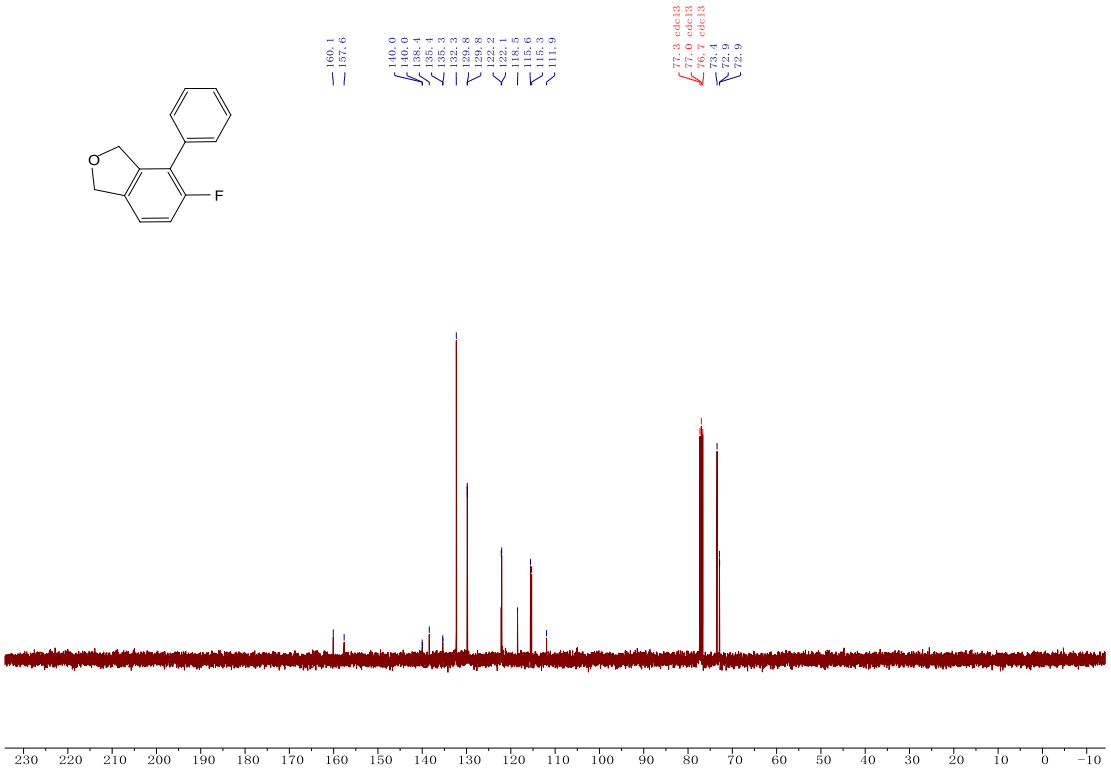
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4c**



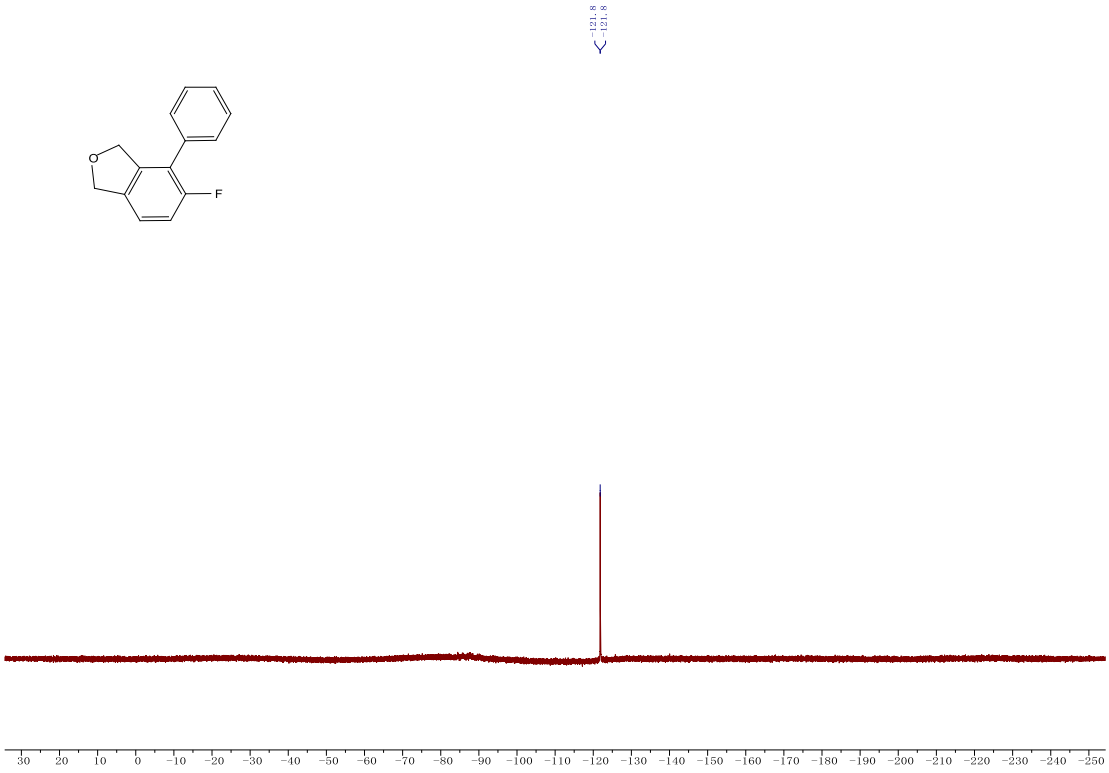
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



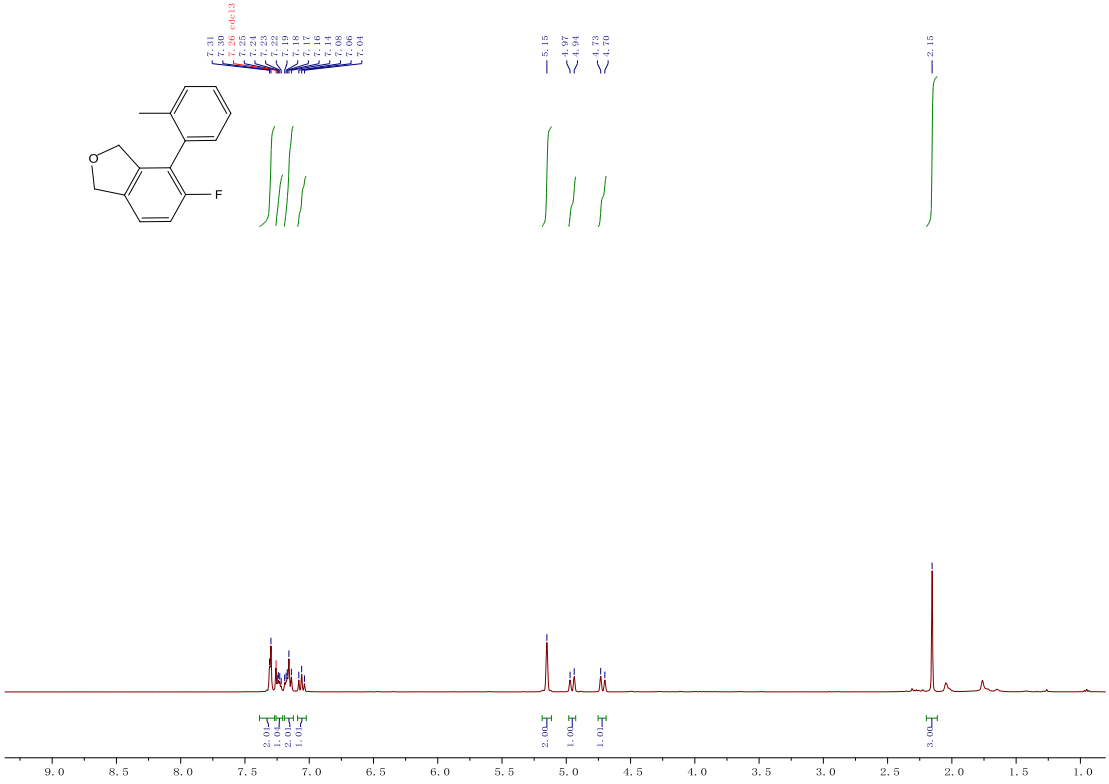
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4d**



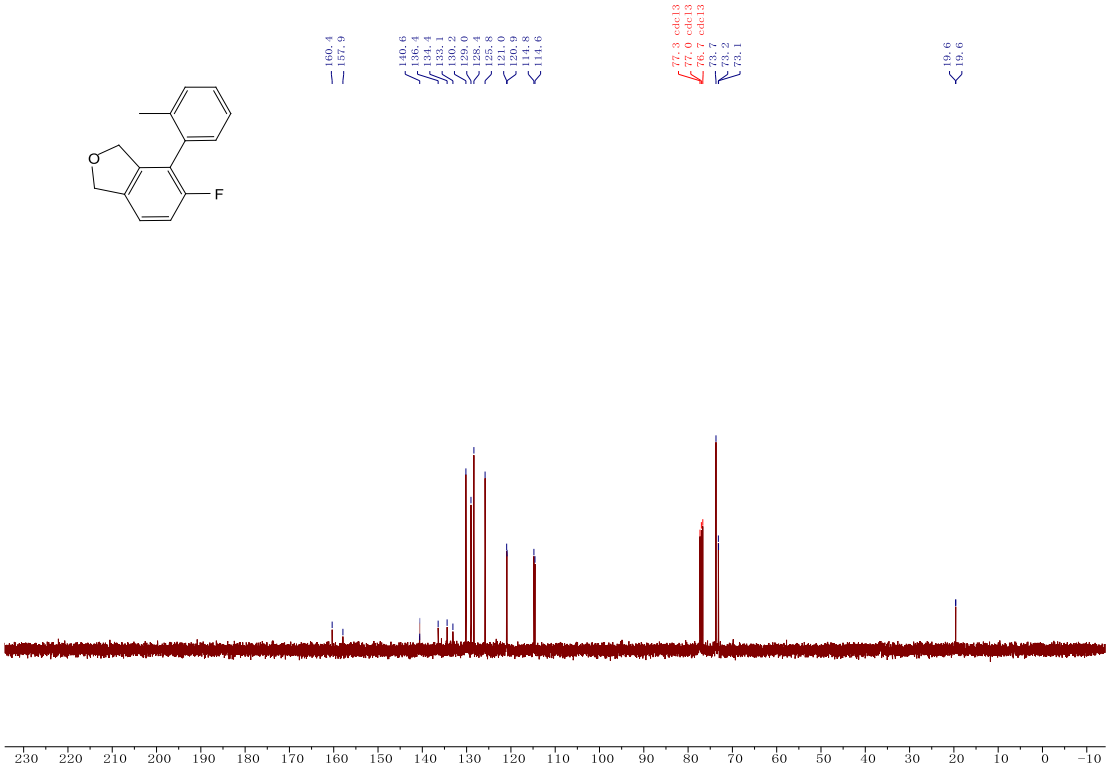
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4d**



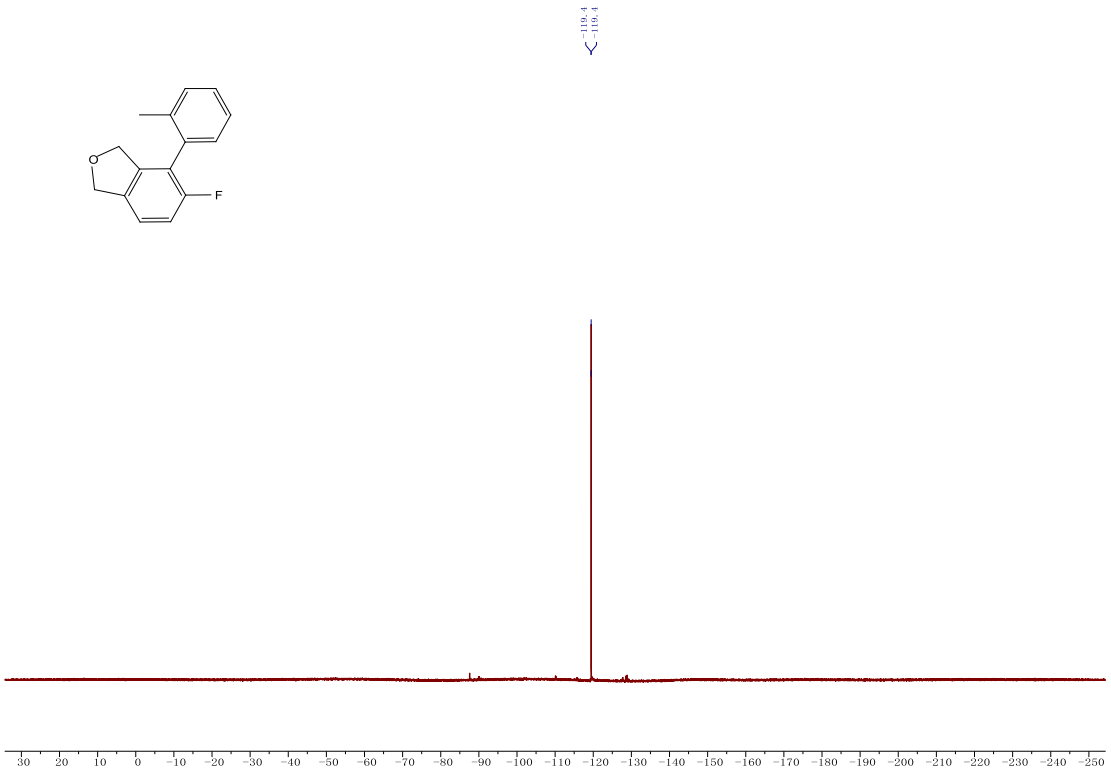
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



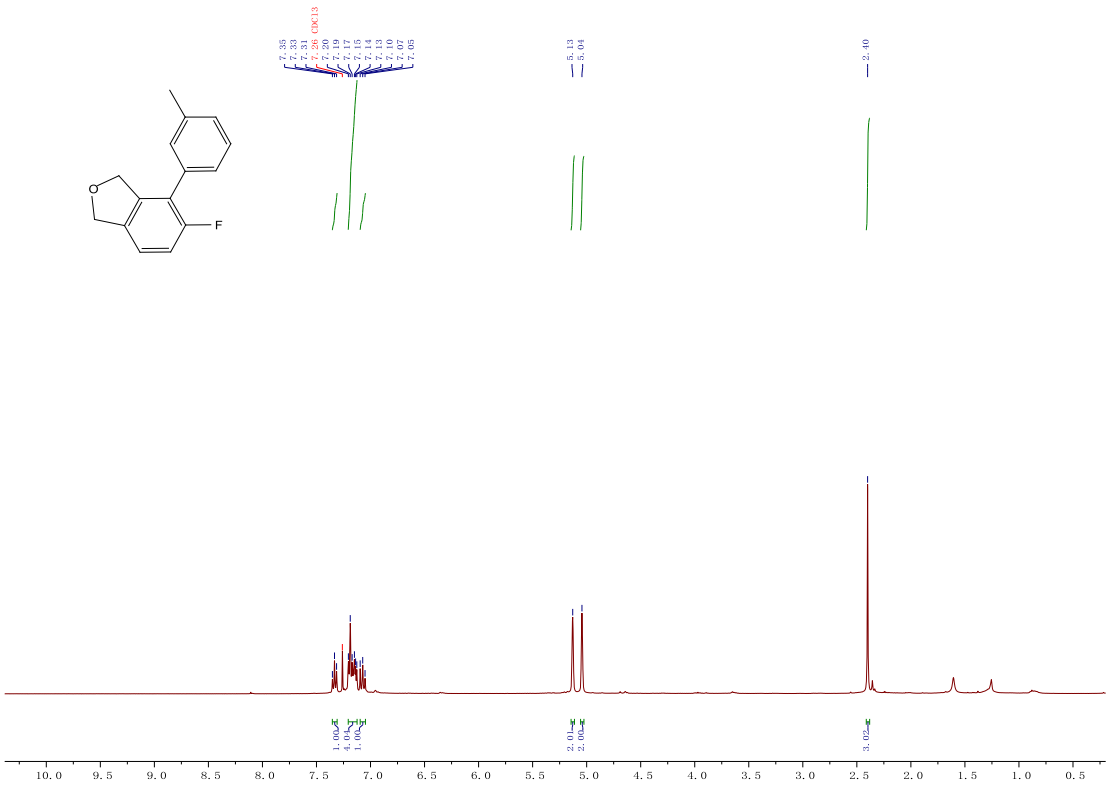
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4e**



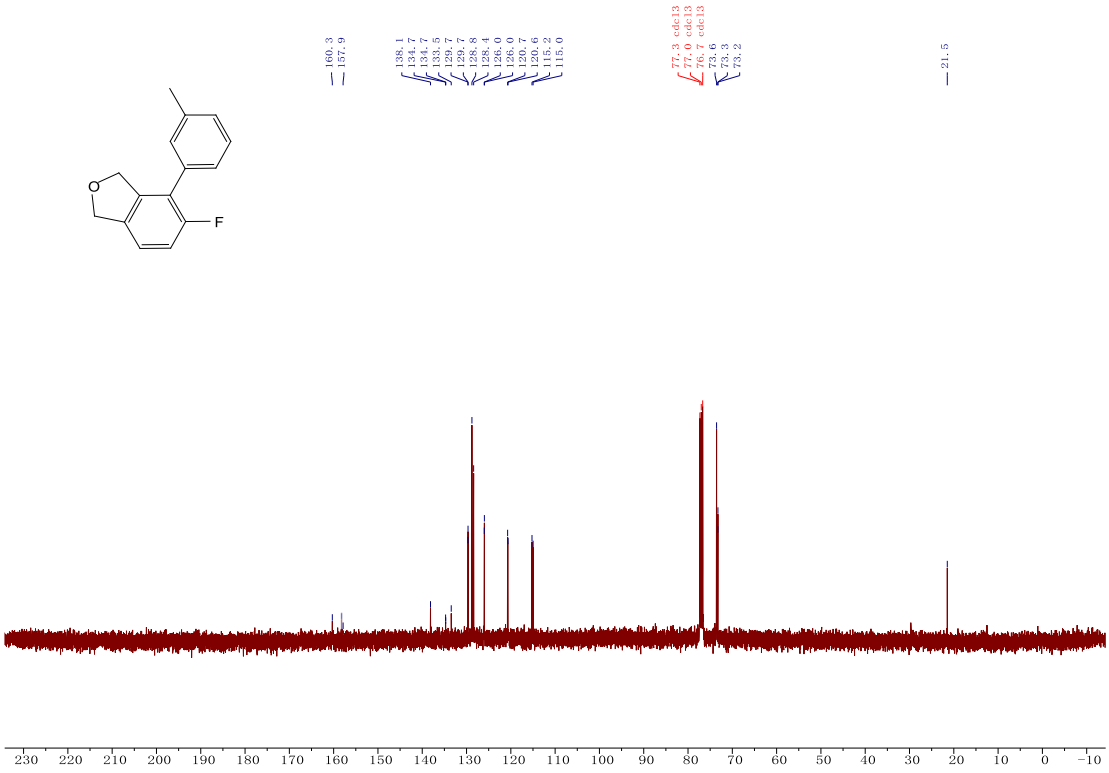
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4e**



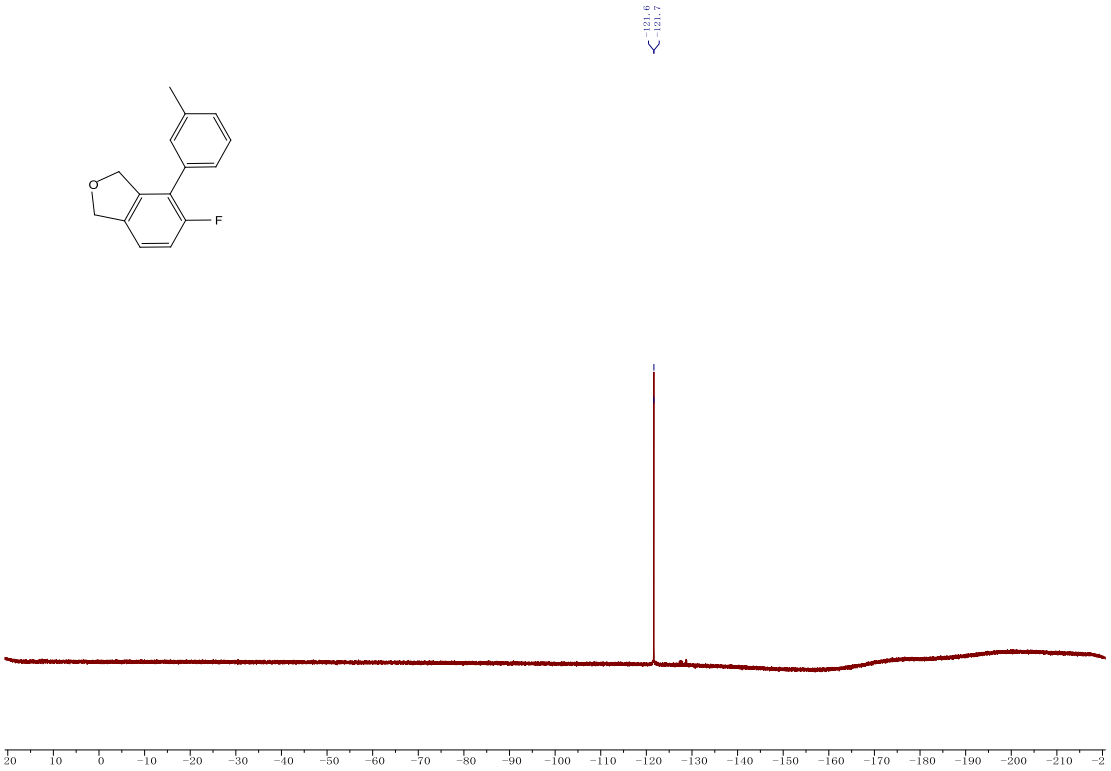
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**



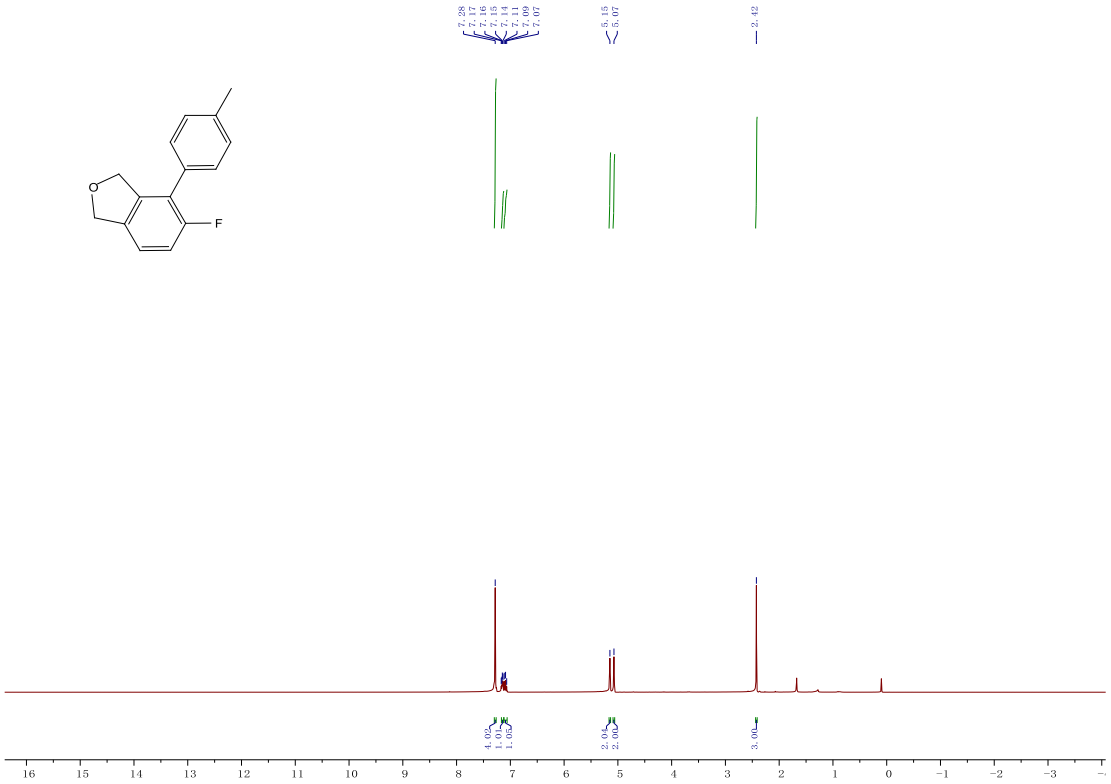
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4f**



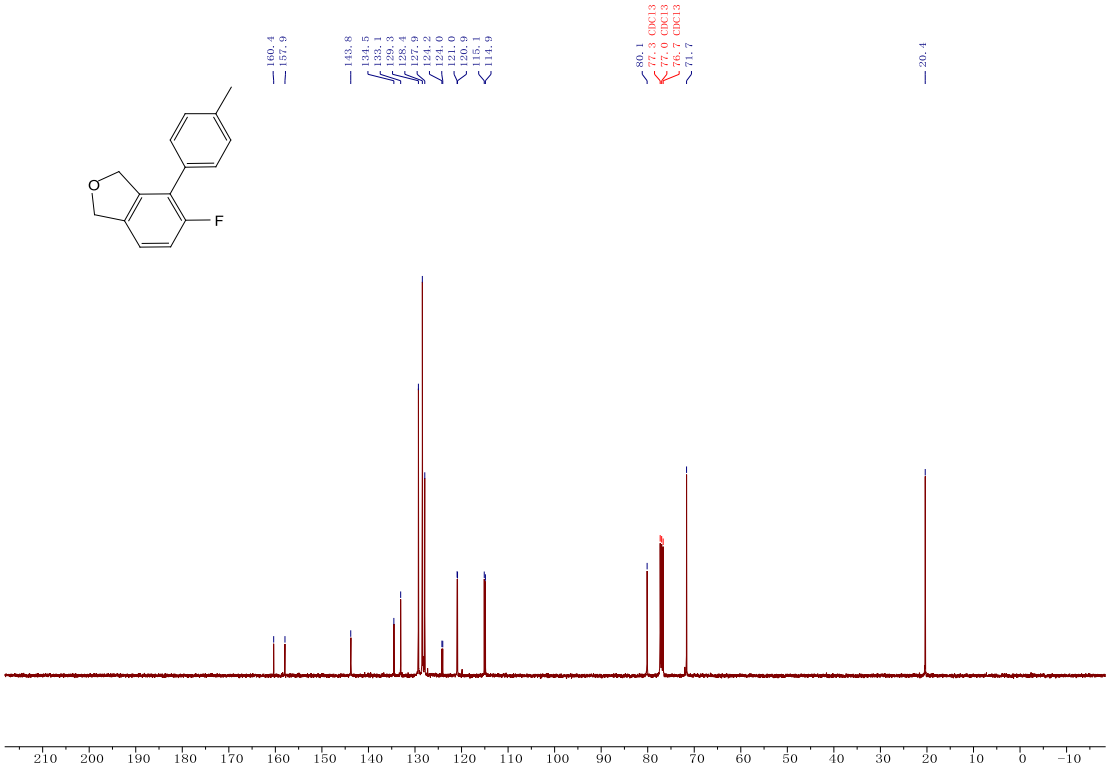
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4f**



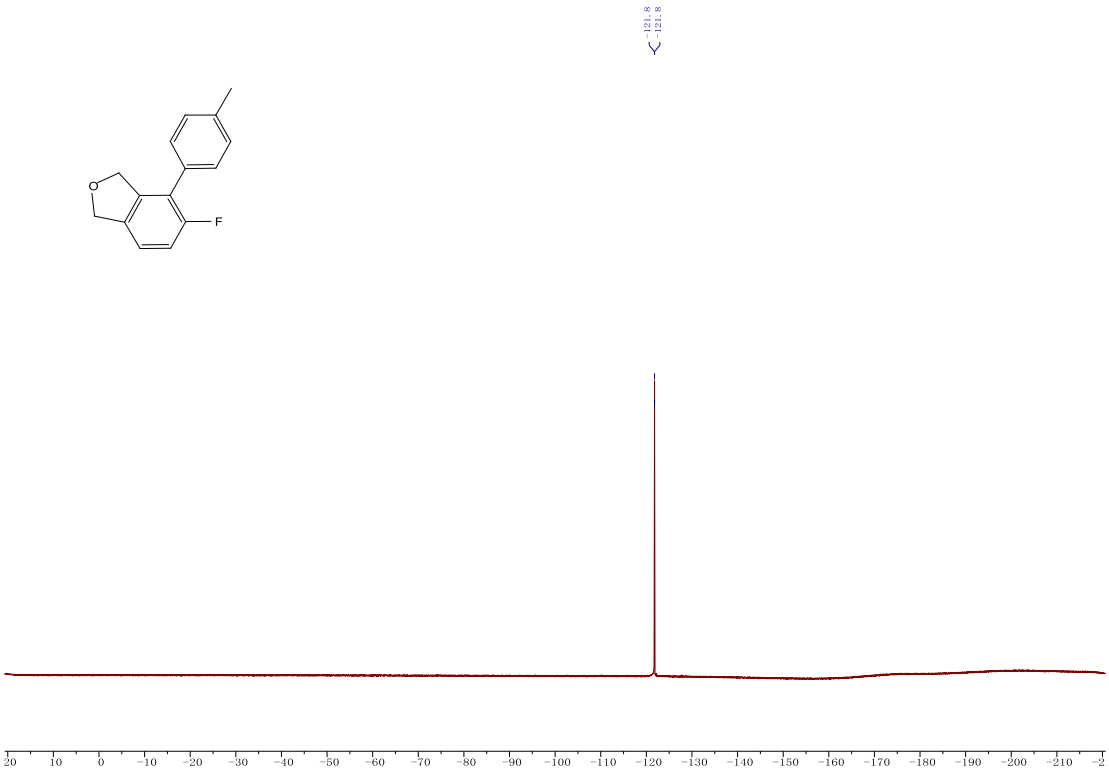
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**



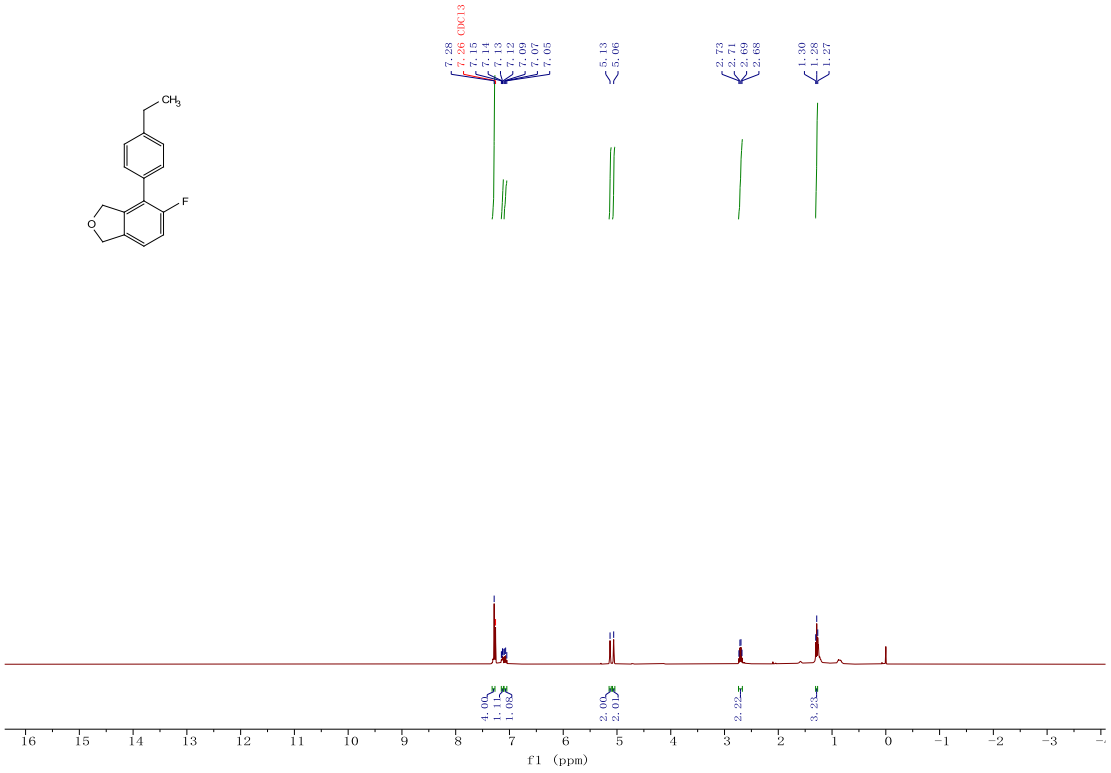
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4g**



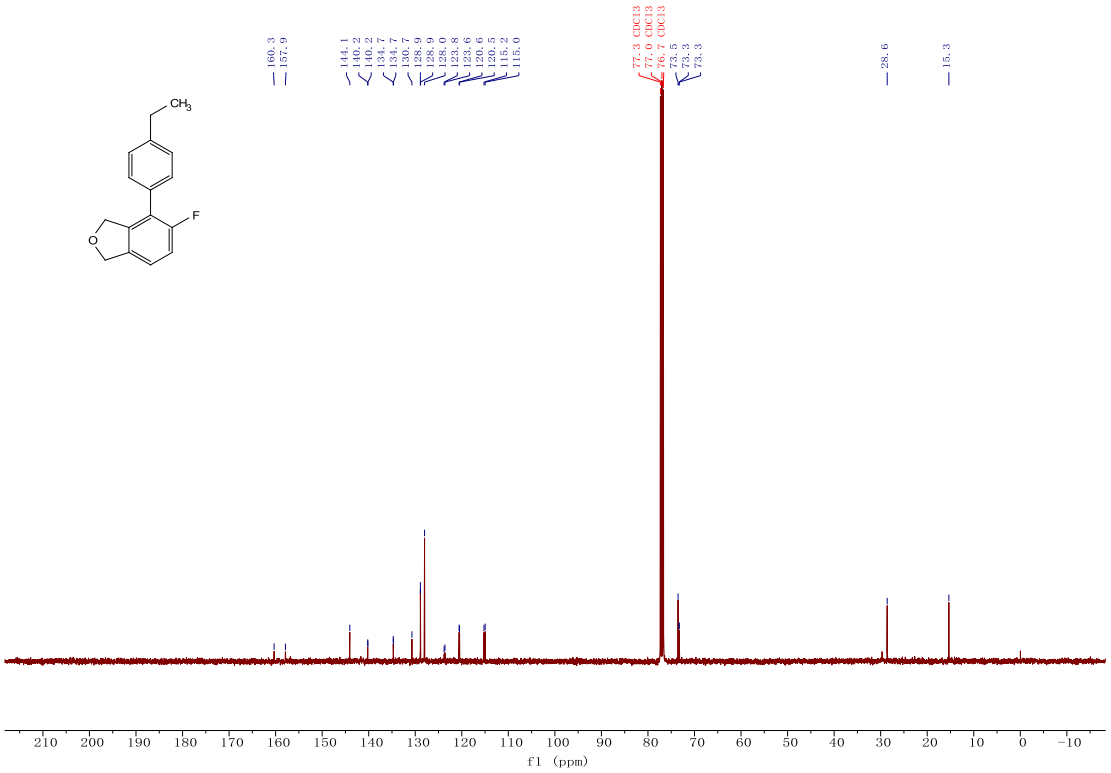
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4g**



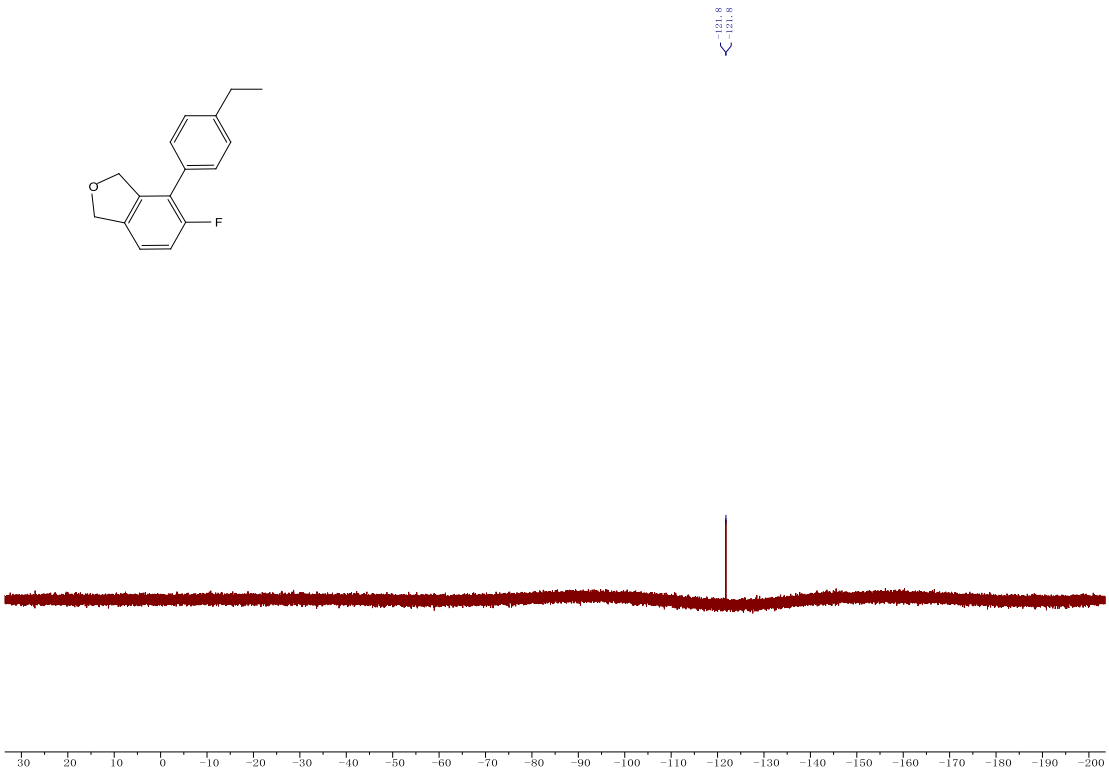
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



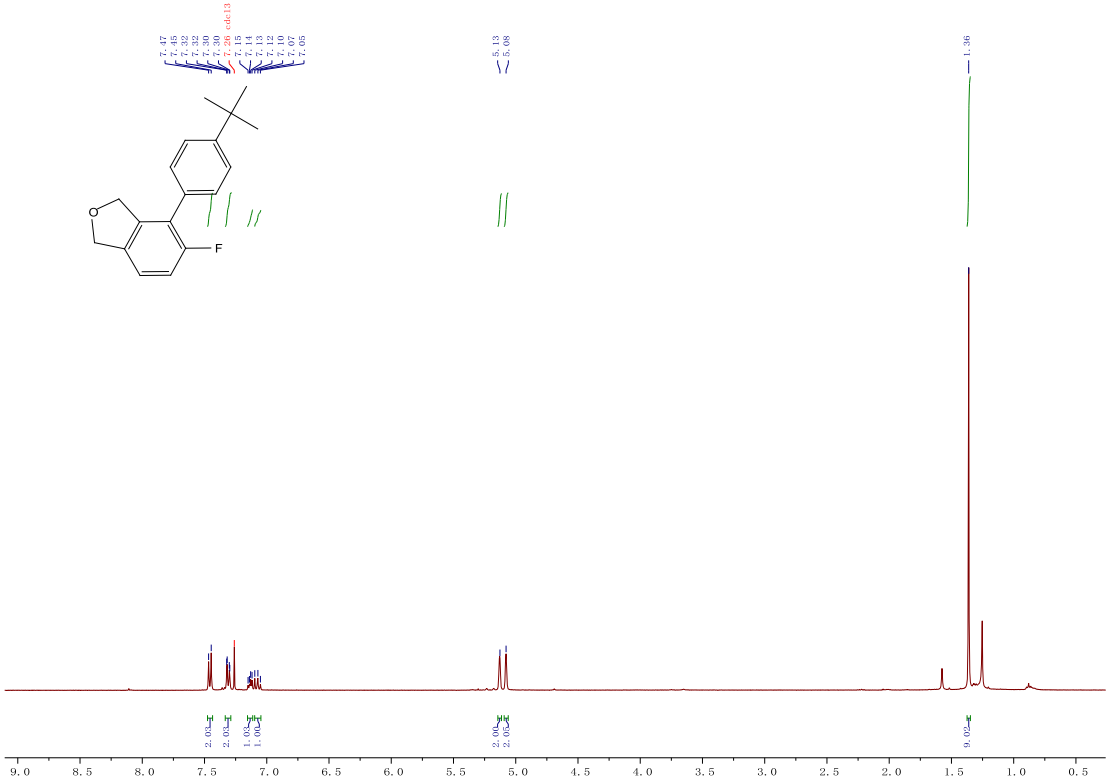
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4h**



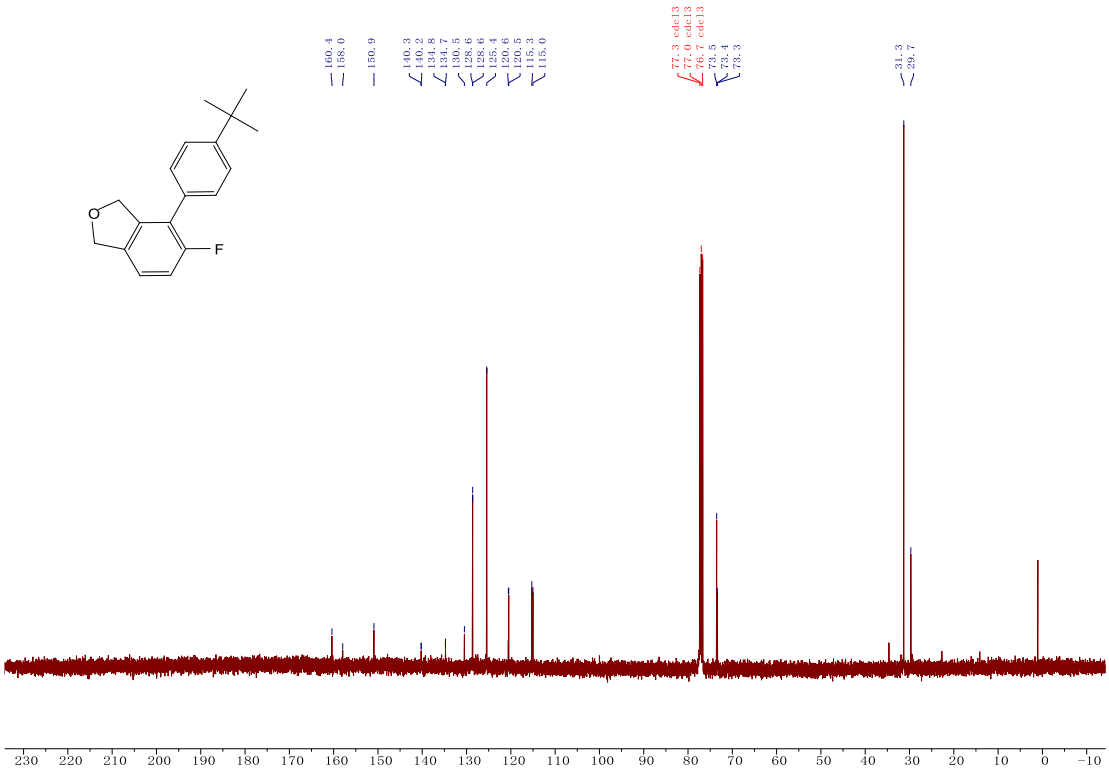
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4h**



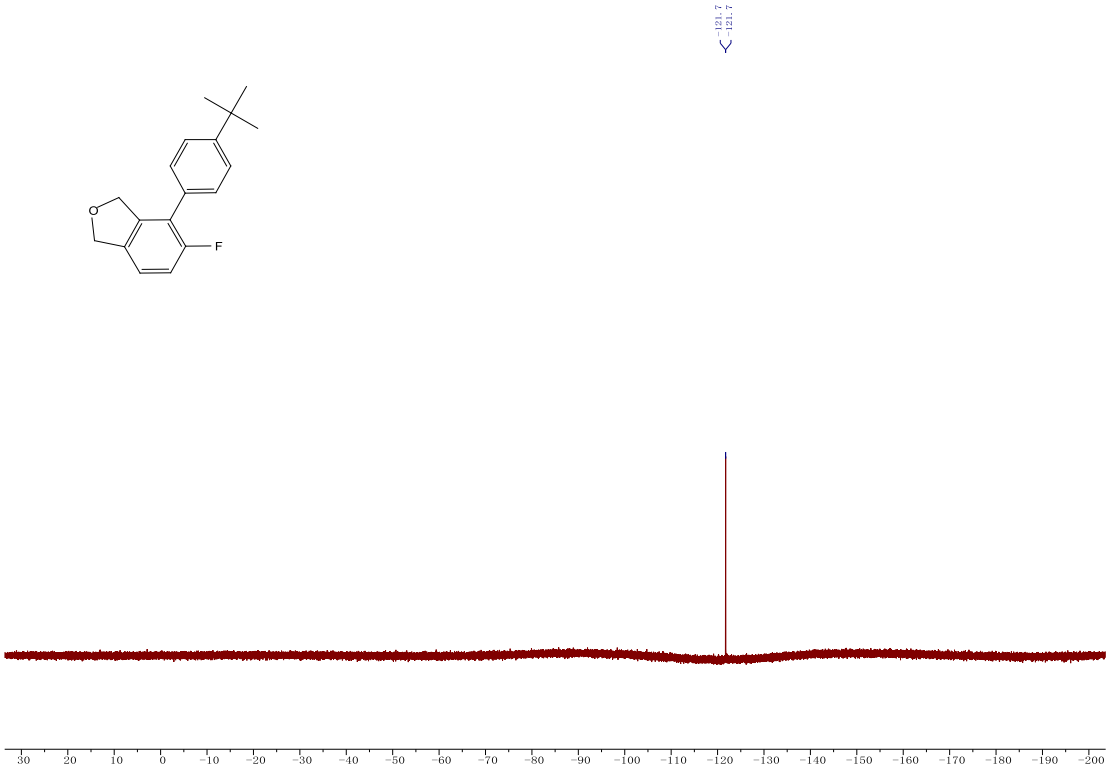
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



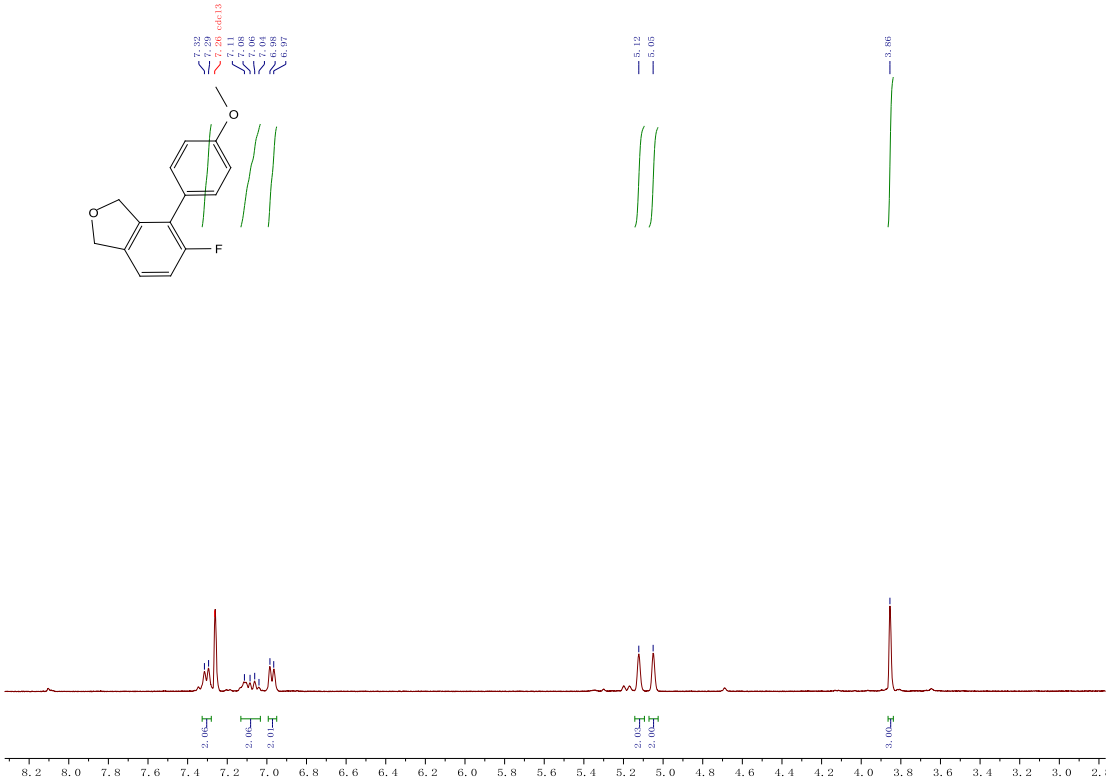
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4i**



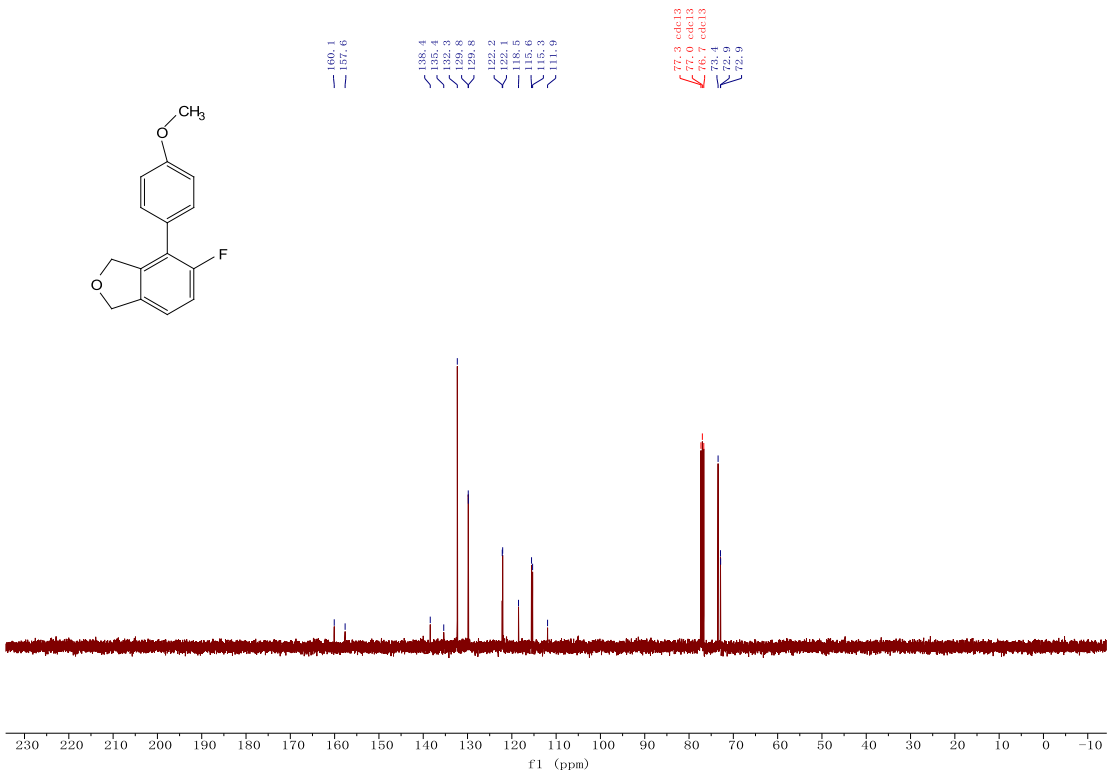
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4i**



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

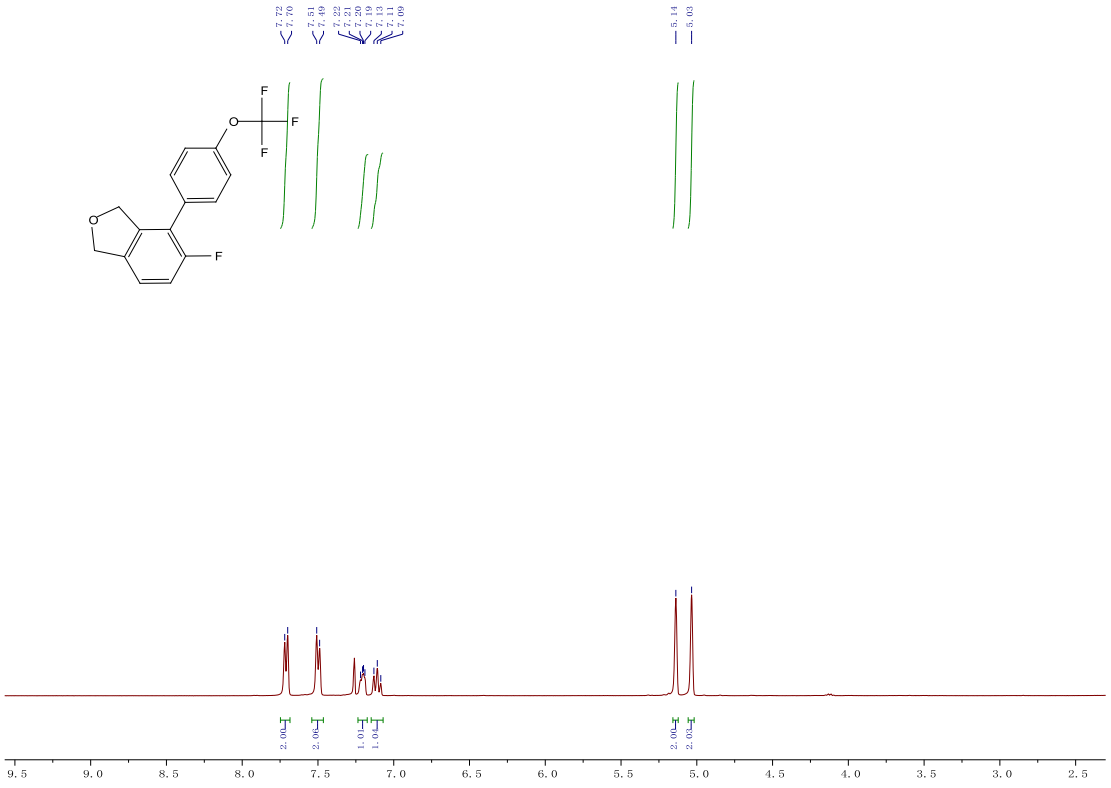


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4j**

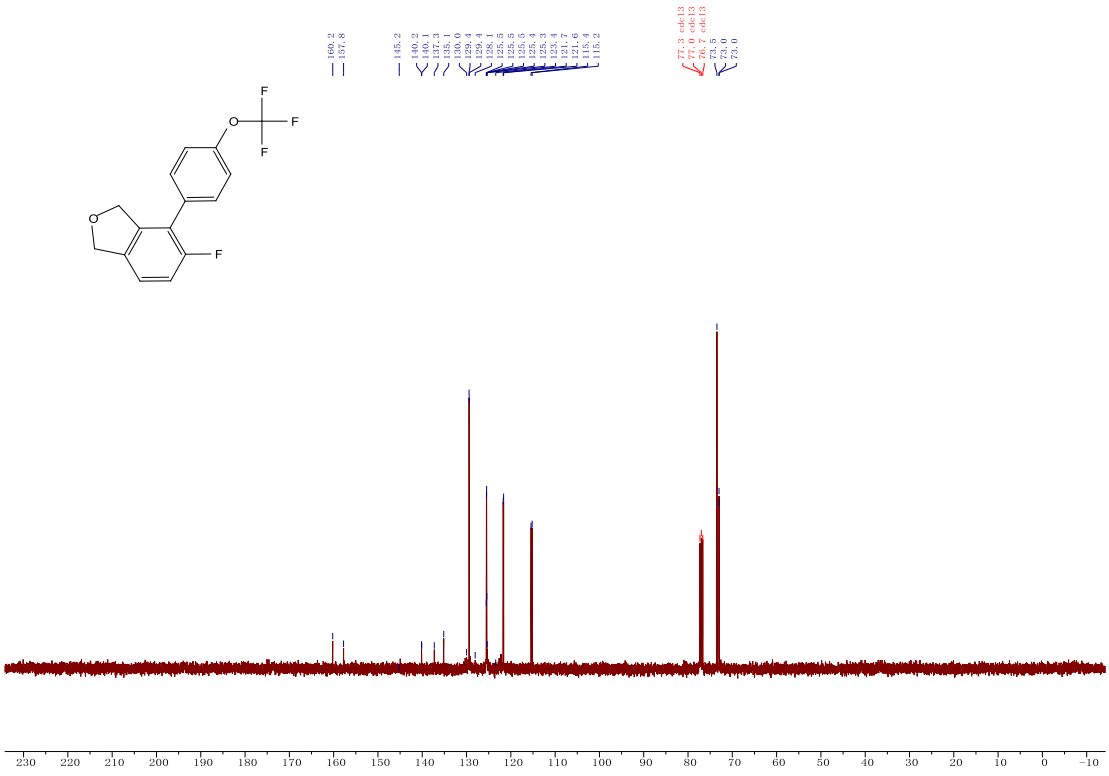


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4j**

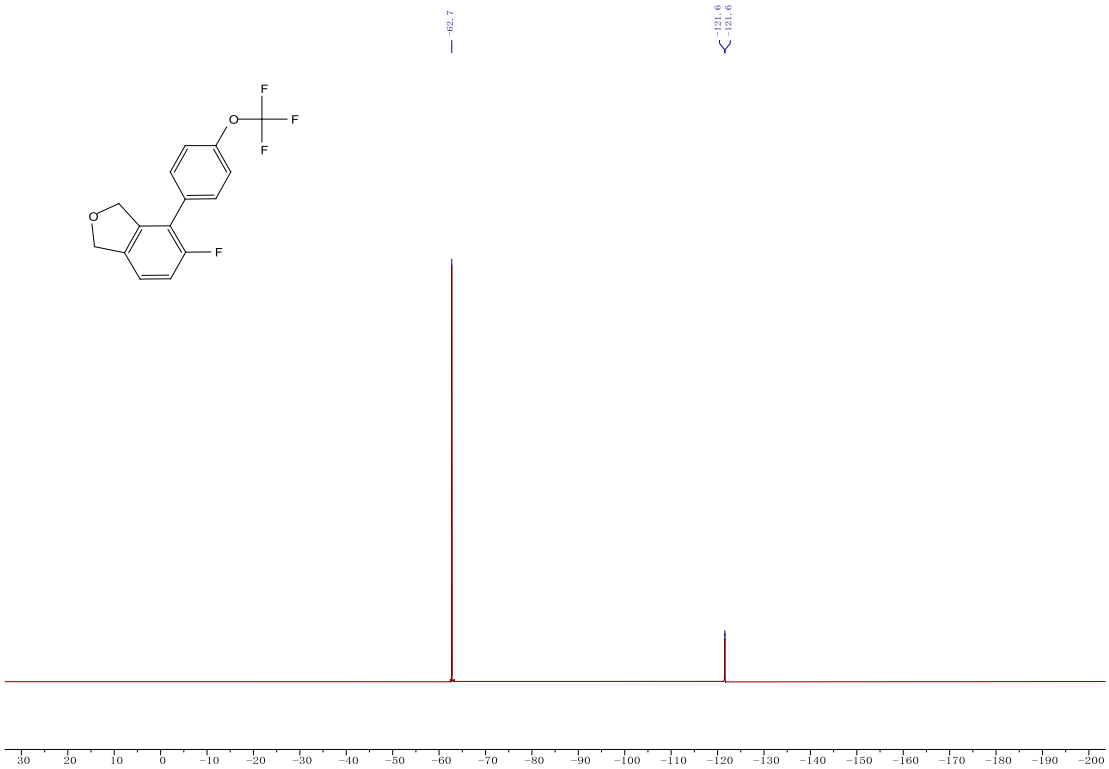
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**



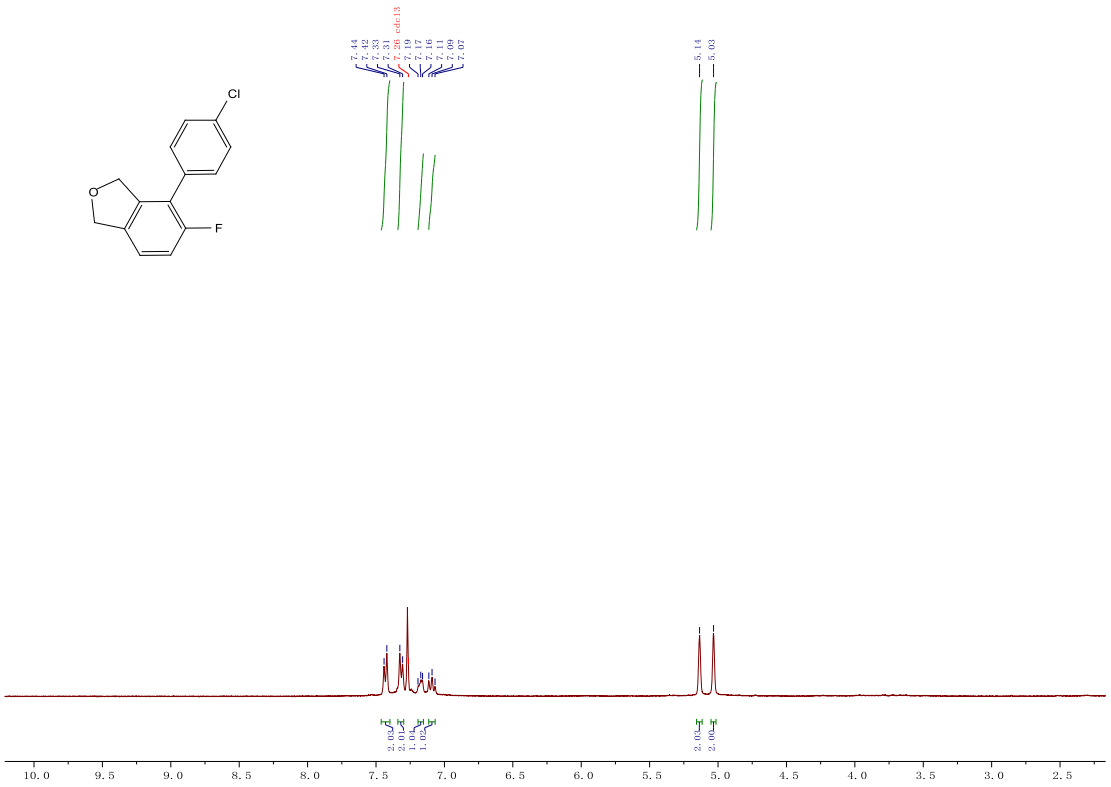
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4k**



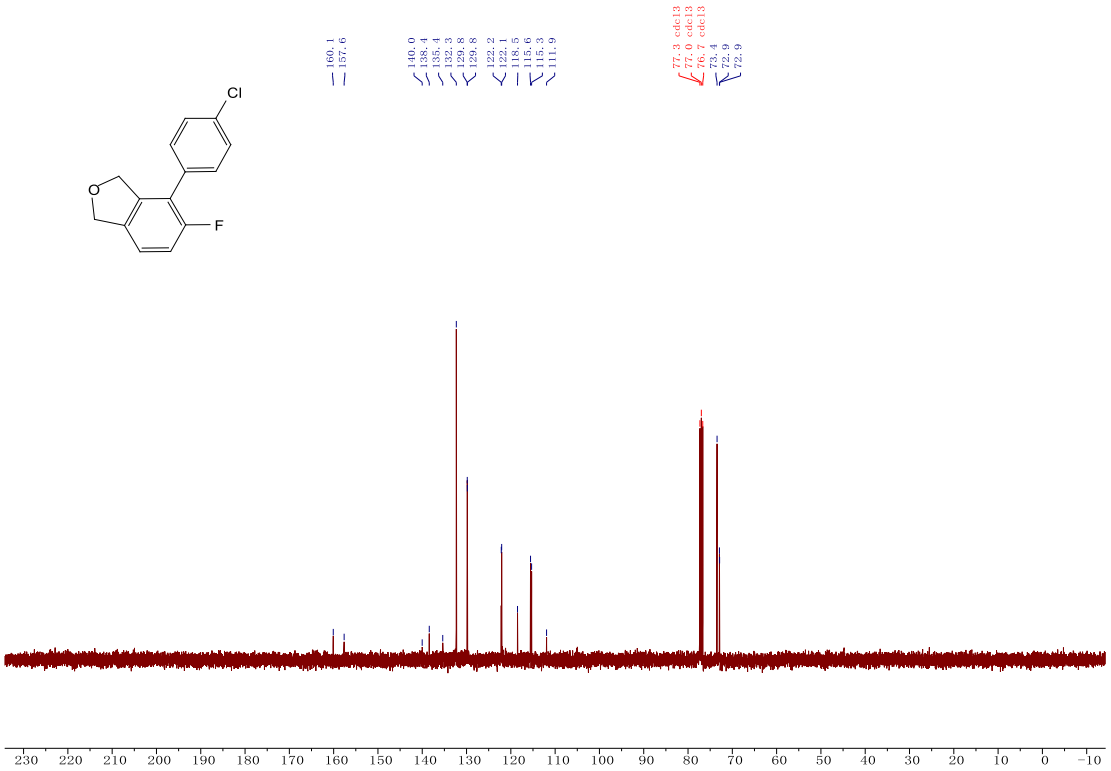
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4k**



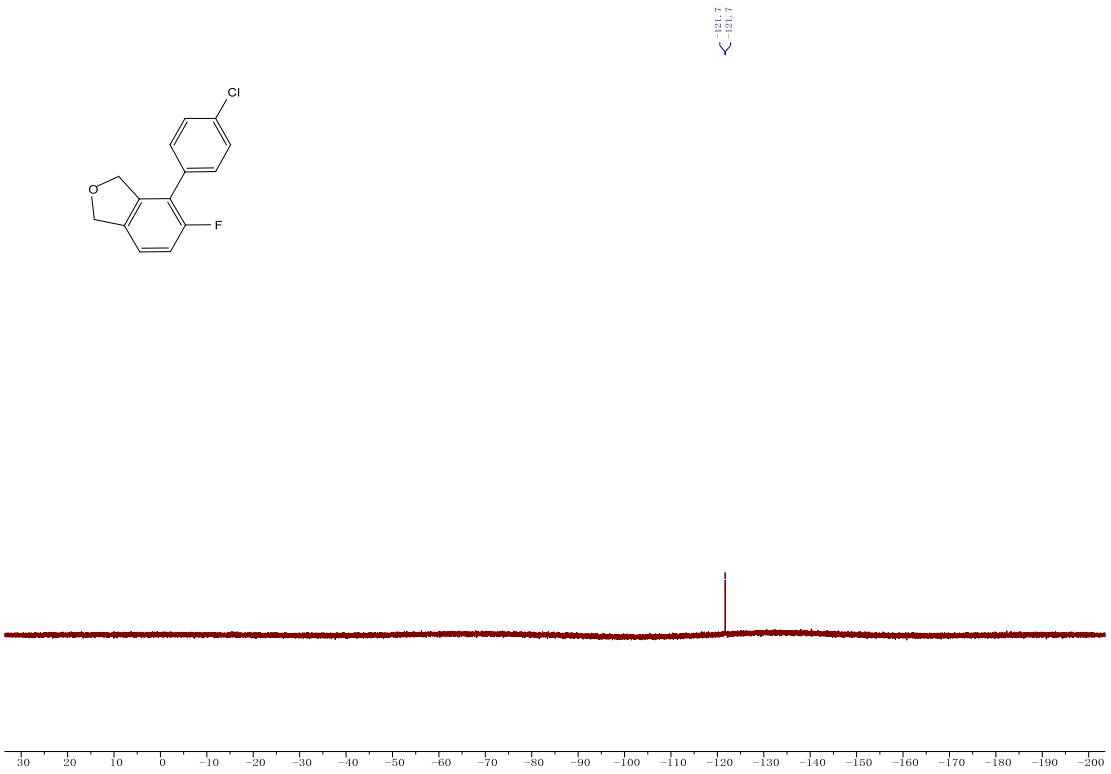
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l**



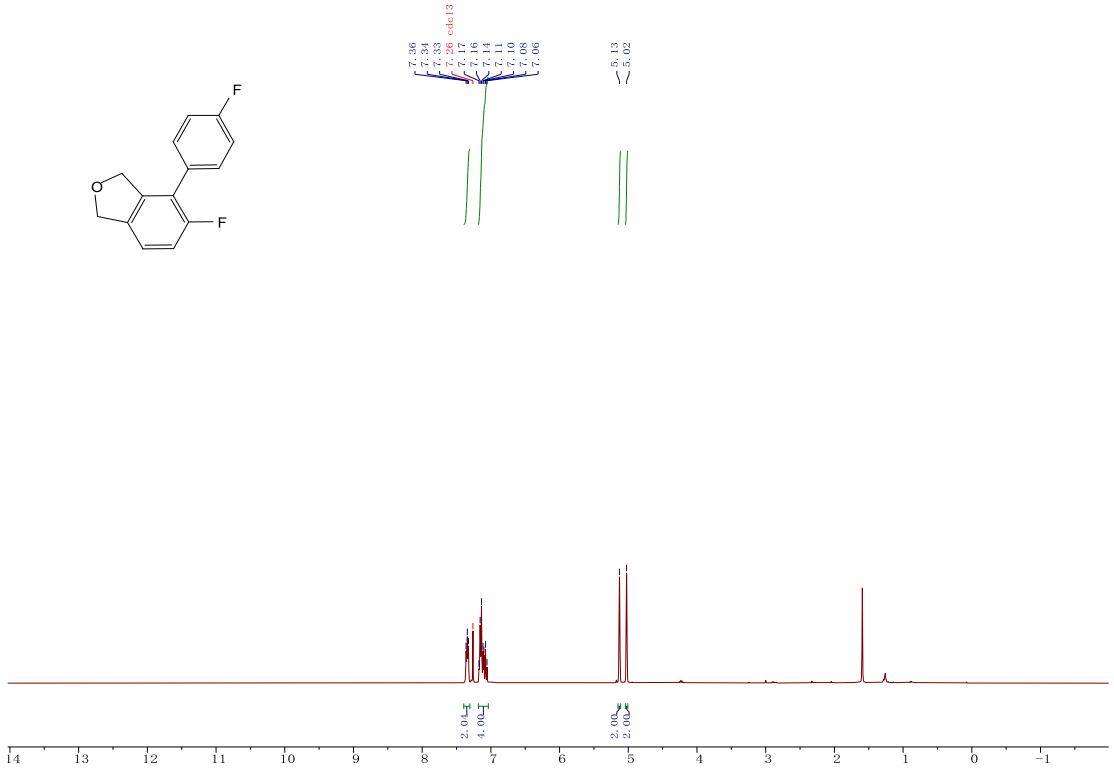
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4l**



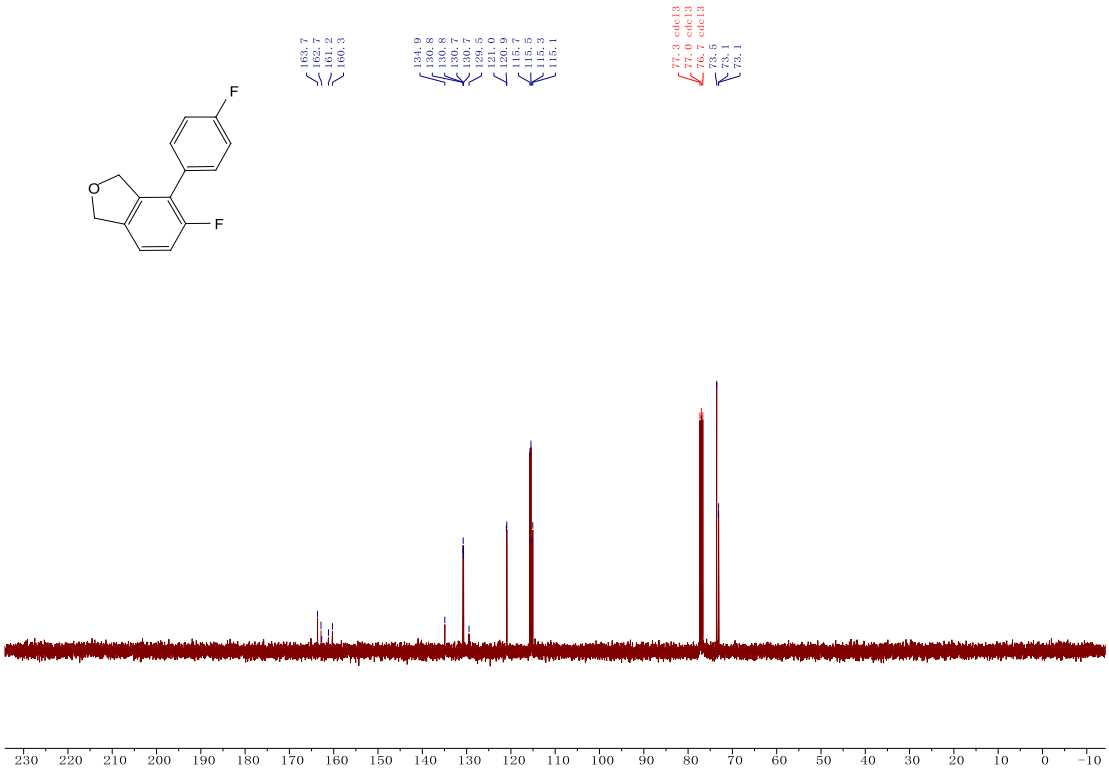
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4l**



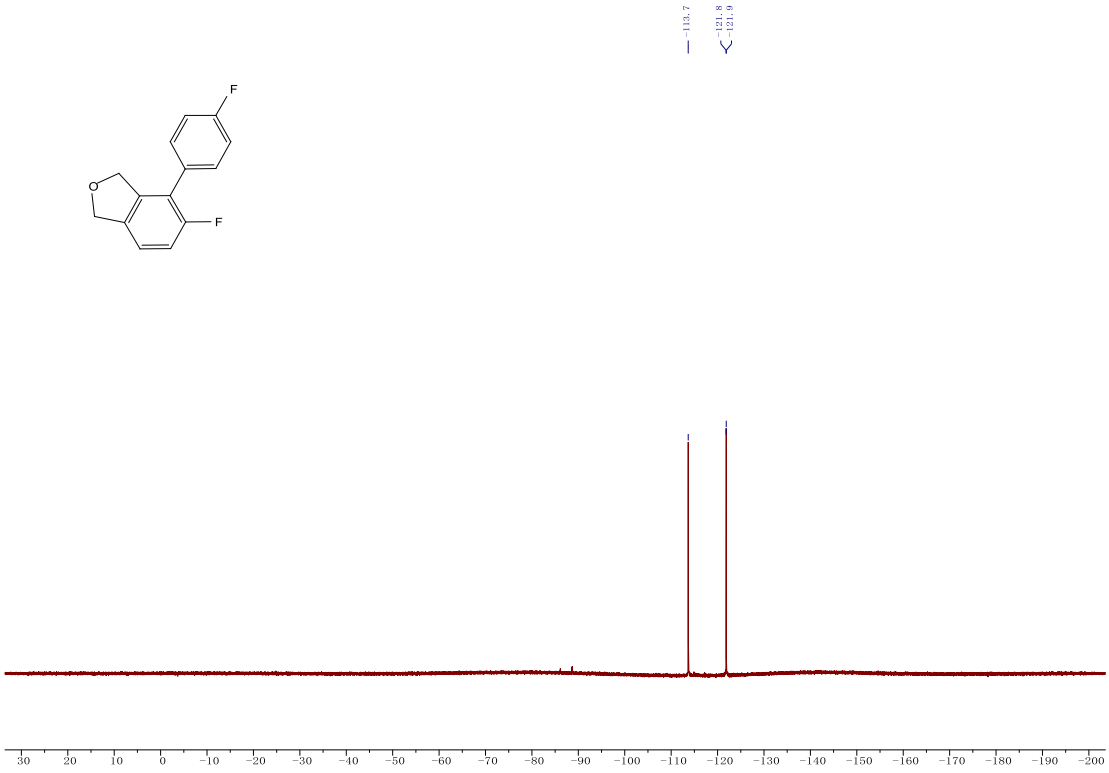
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**



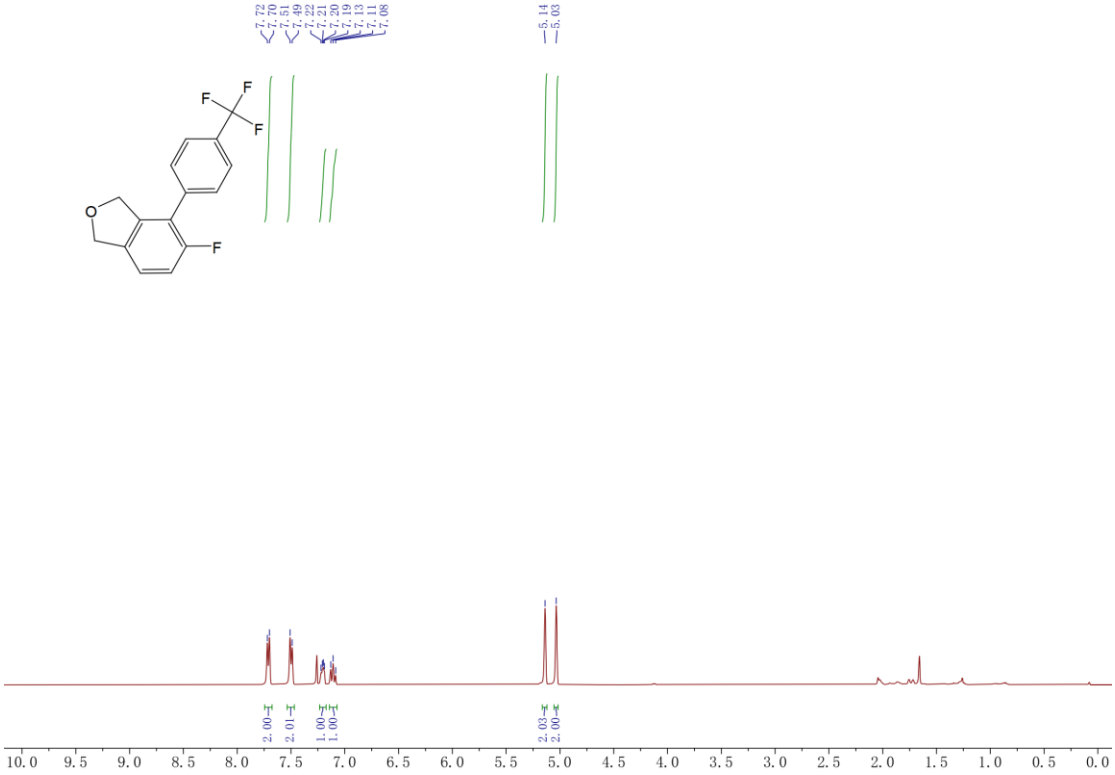
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4m**



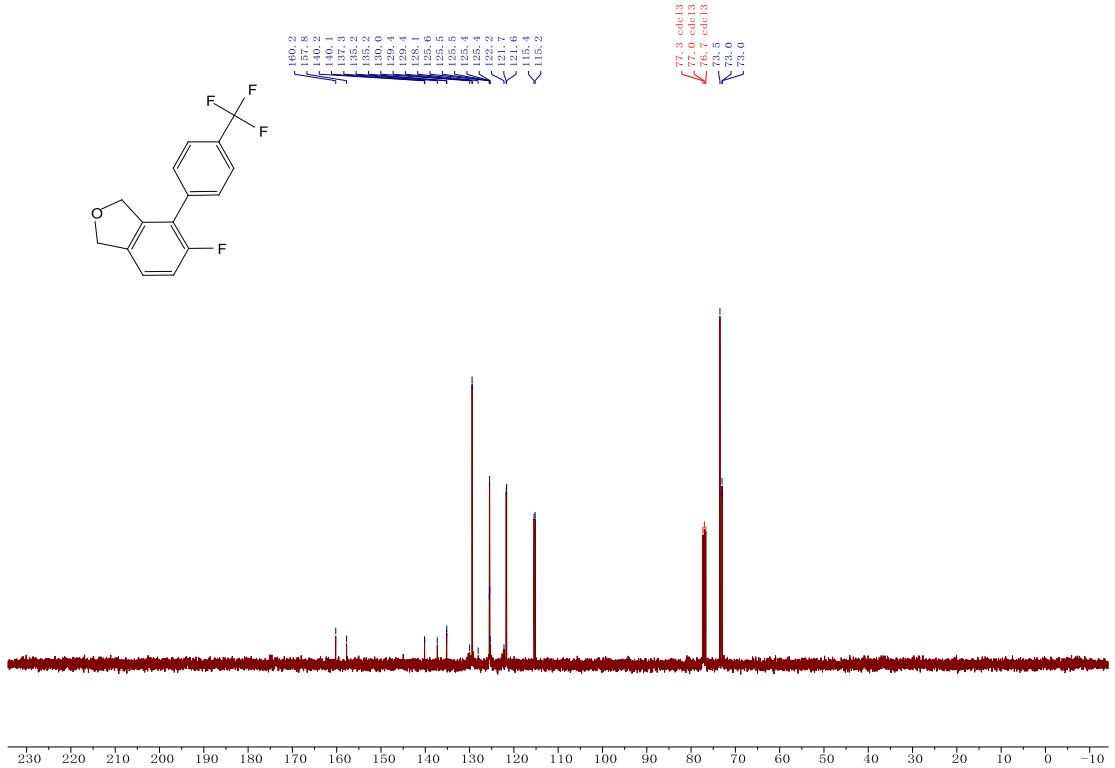
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4m**



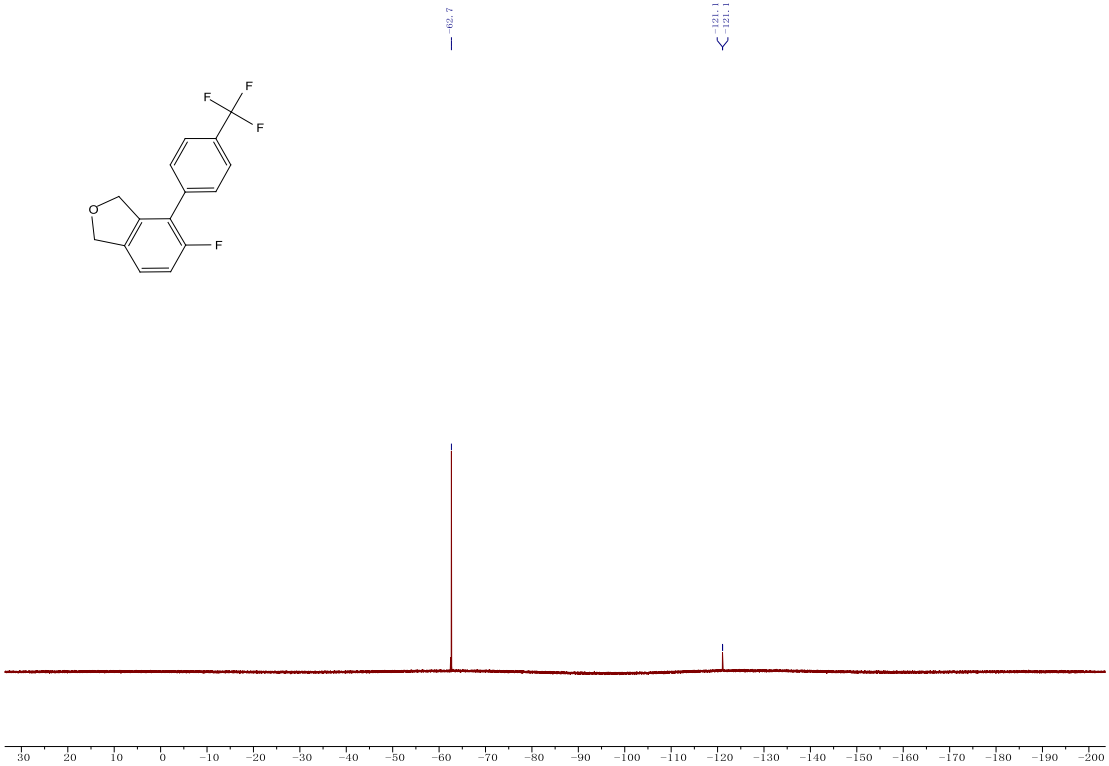
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**



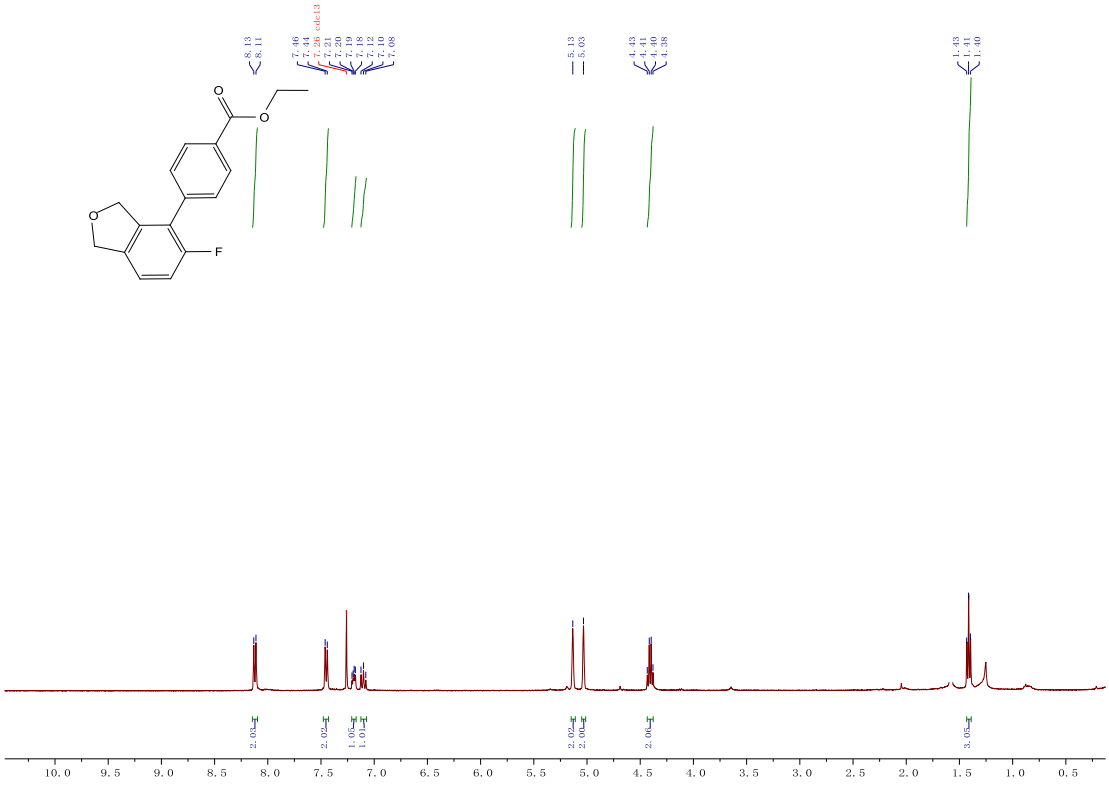
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4n**



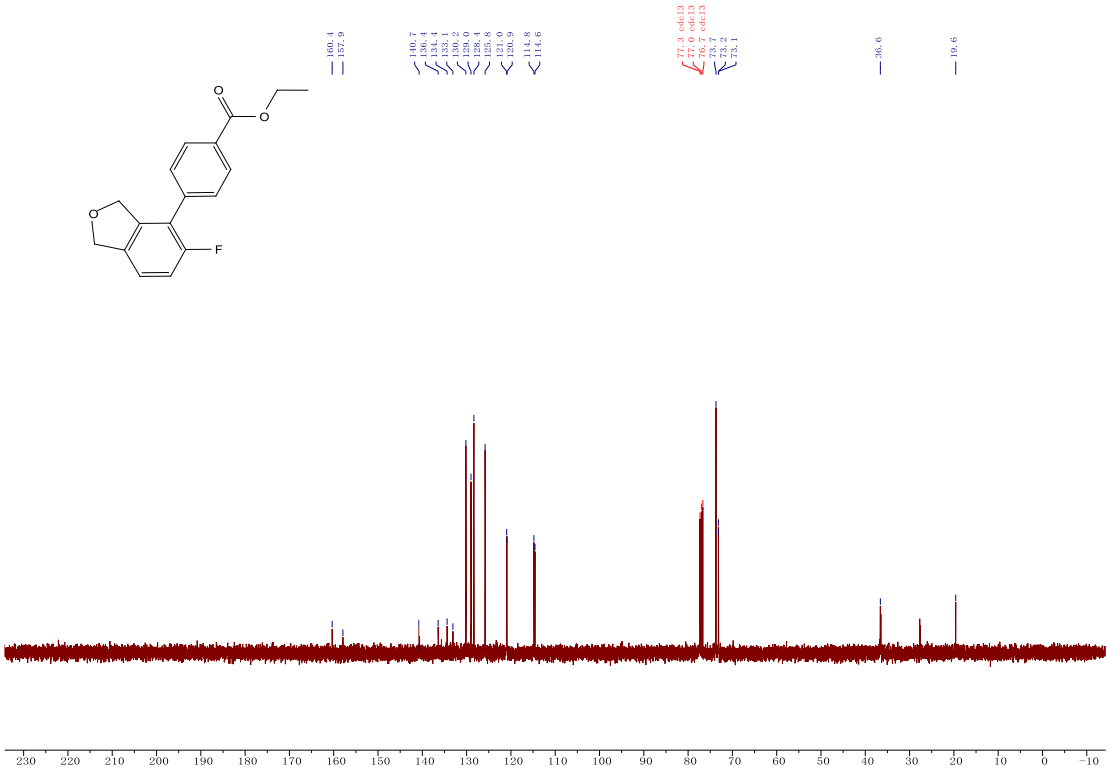
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4n**



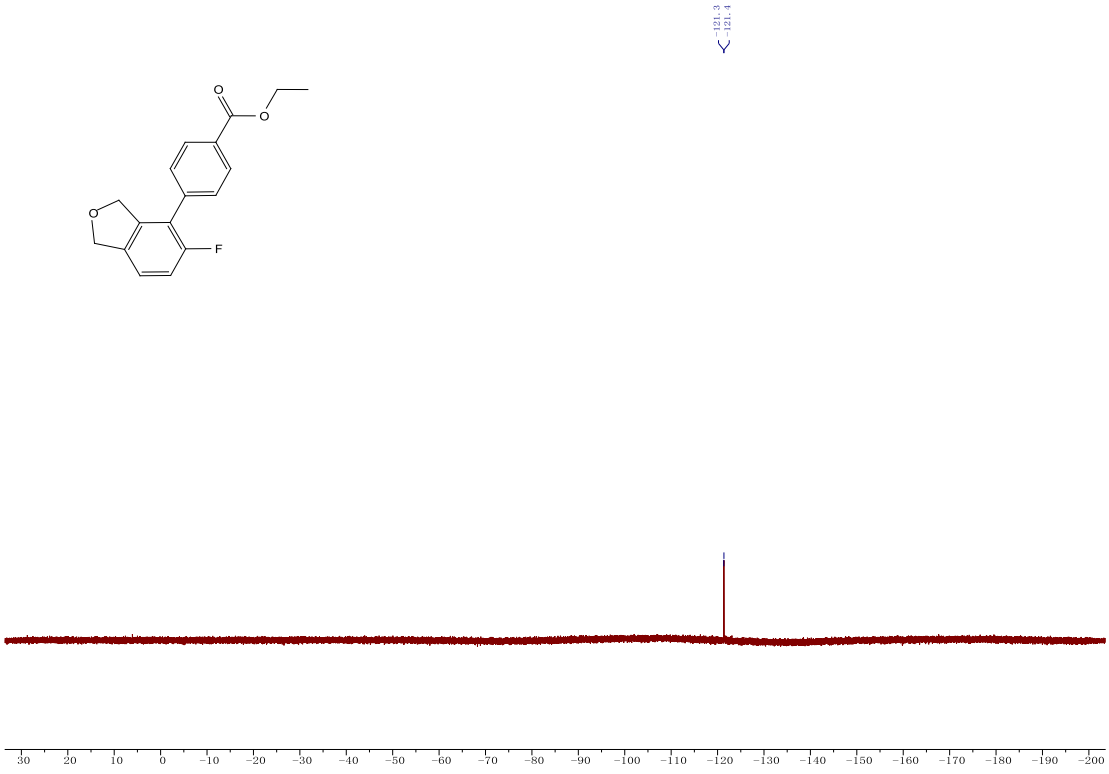
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**



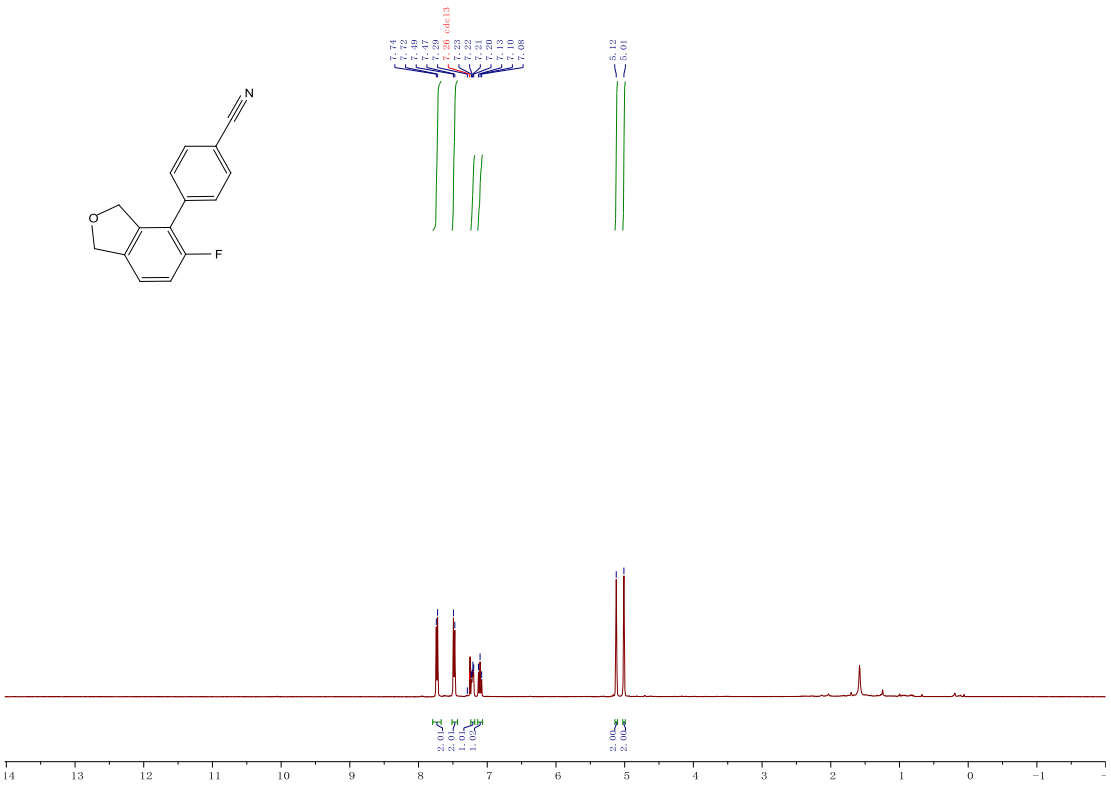
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4o**



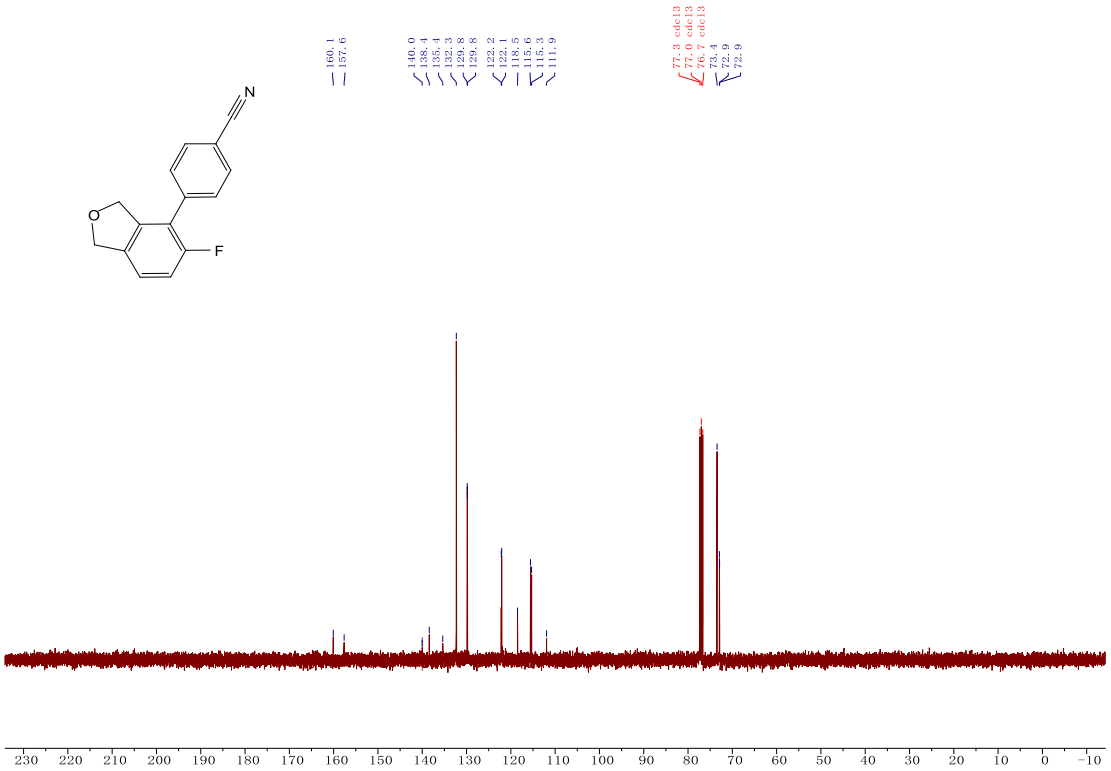
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4o**



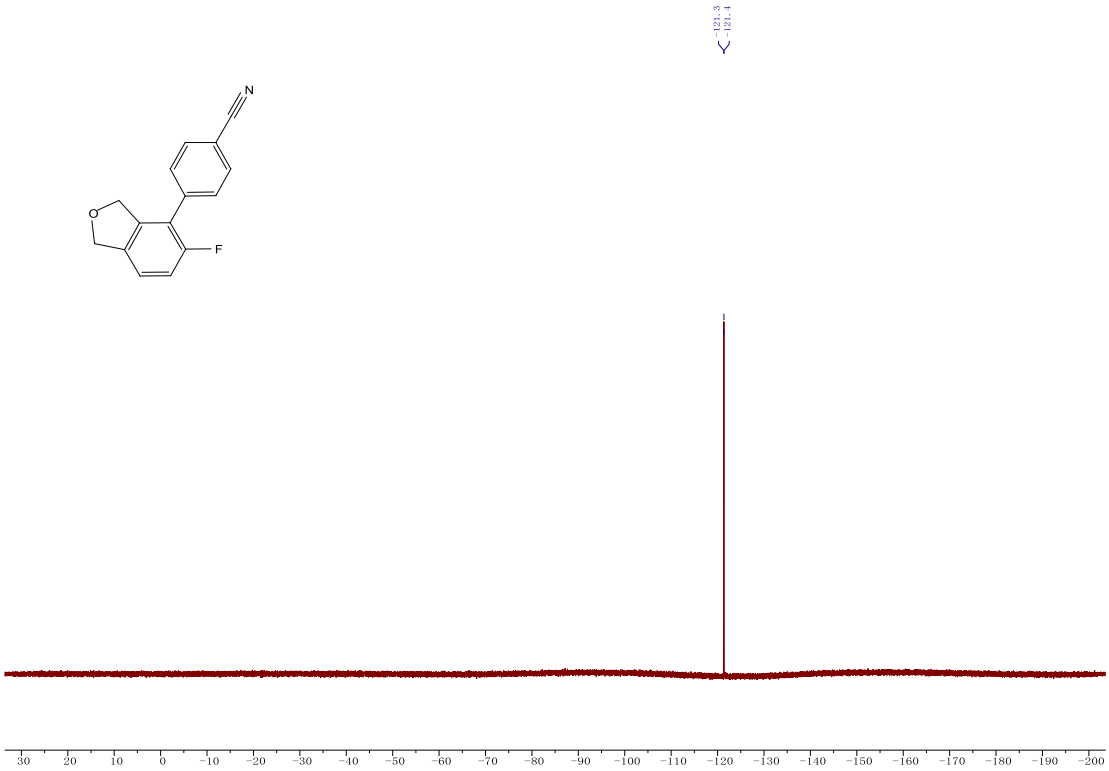
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p**



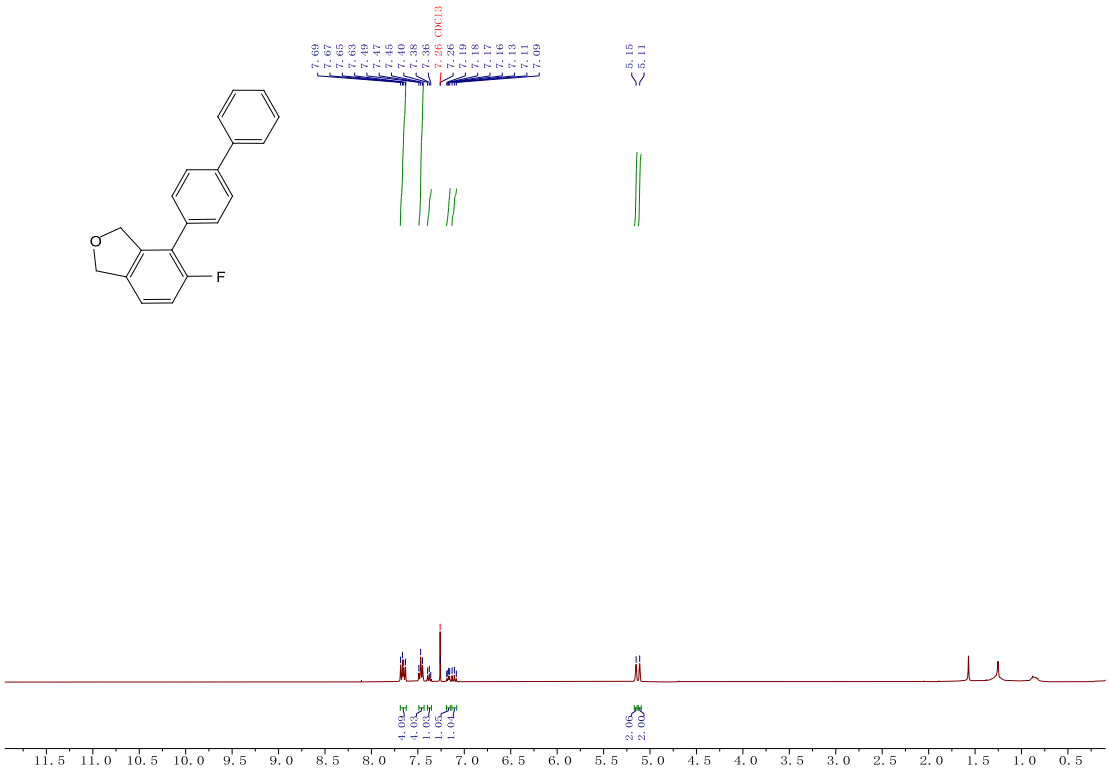
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4p**



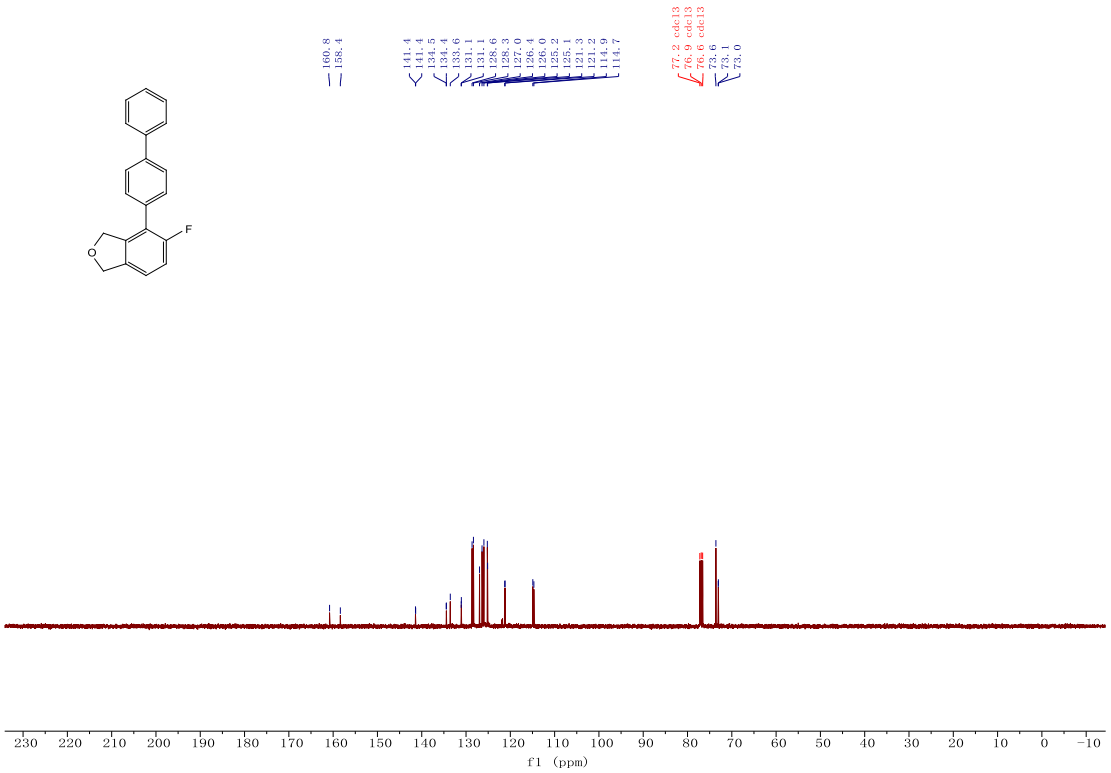
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4p**



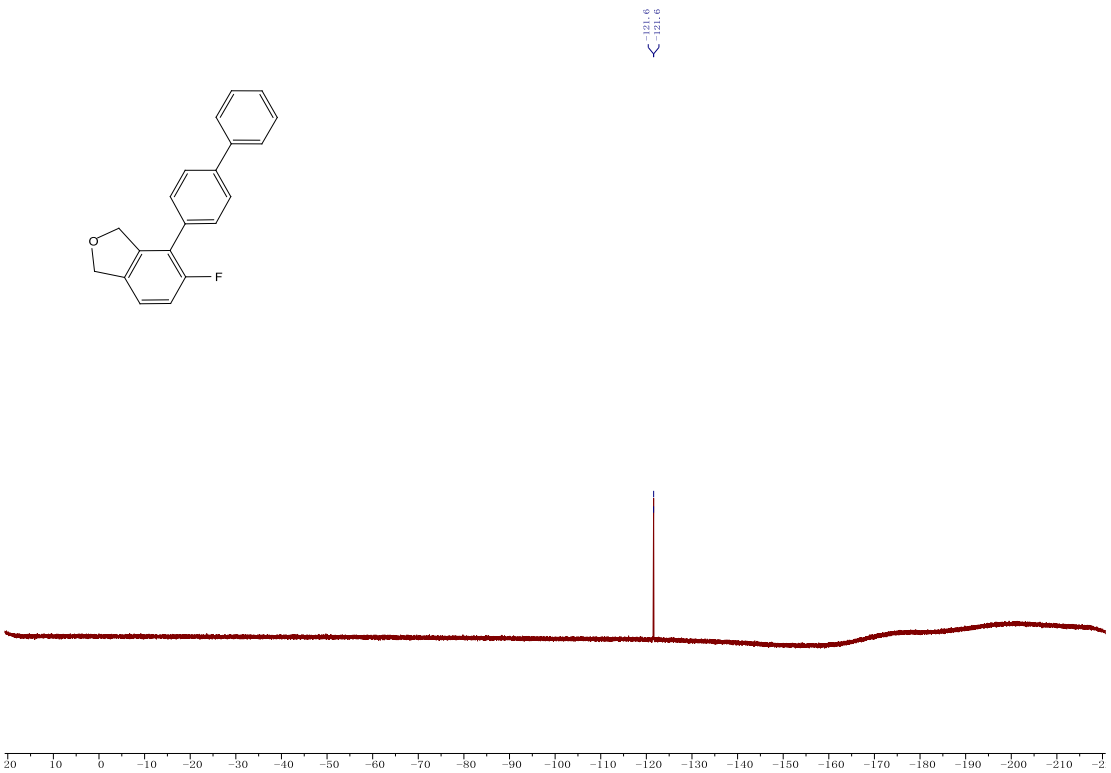
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**



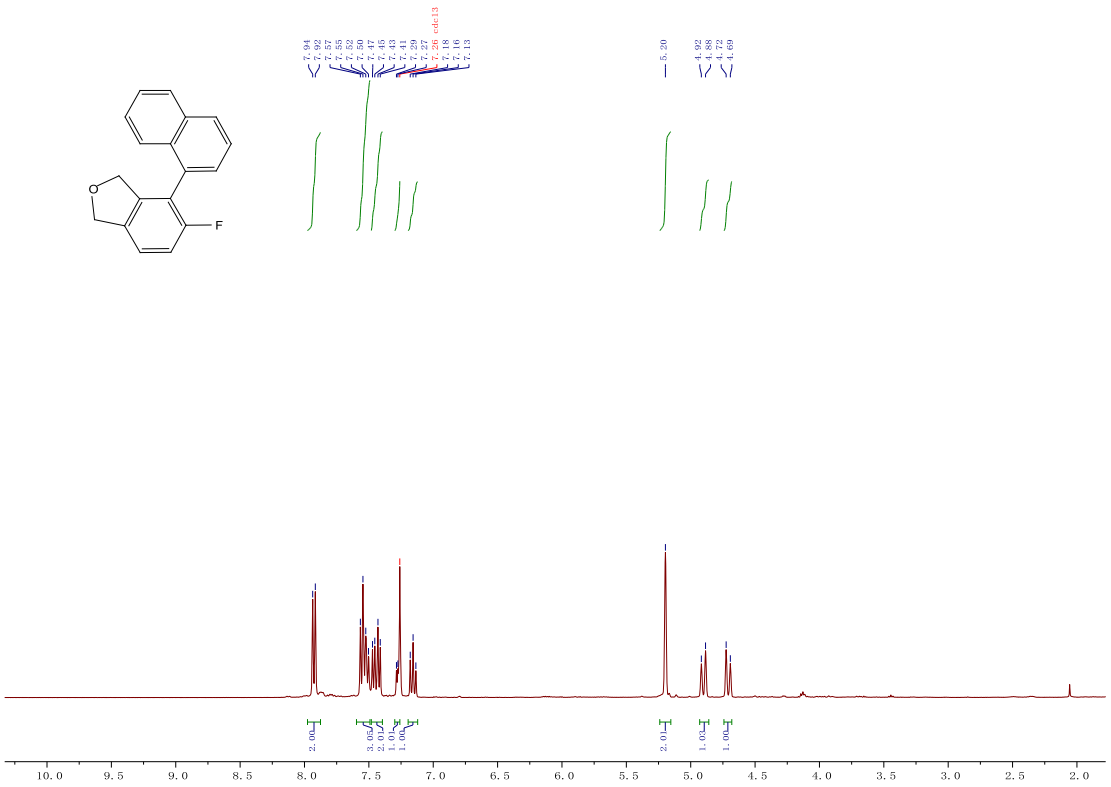
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4q**



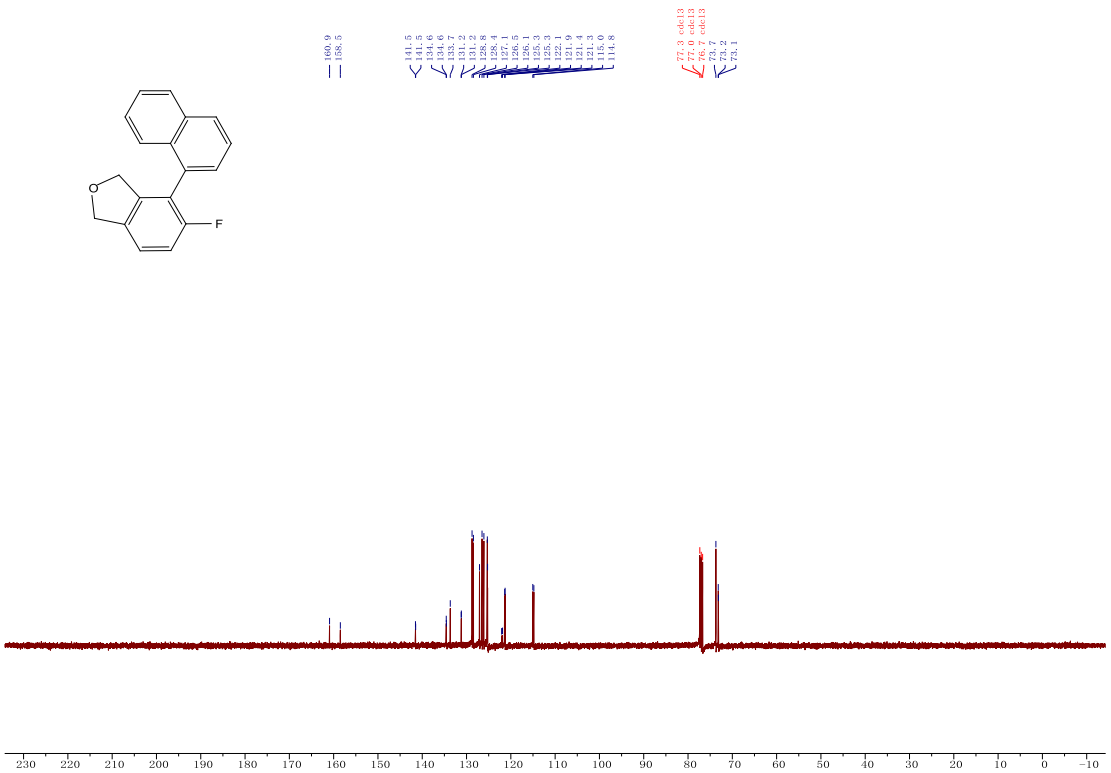
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4q**



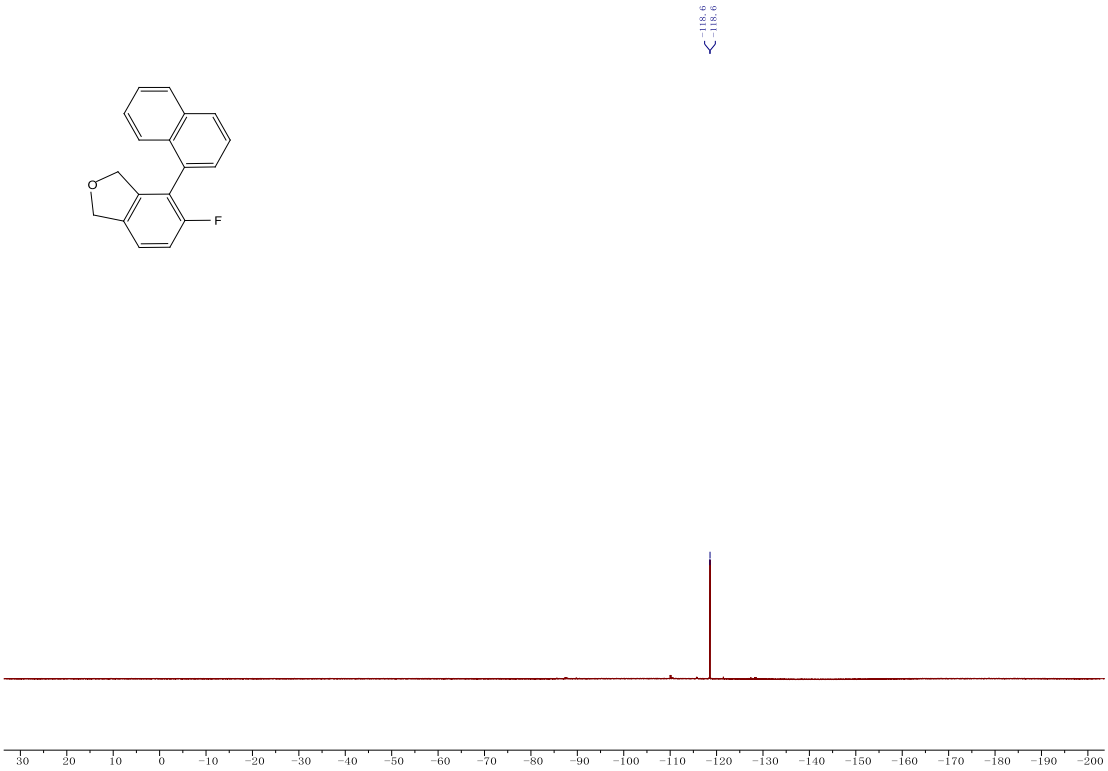
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**



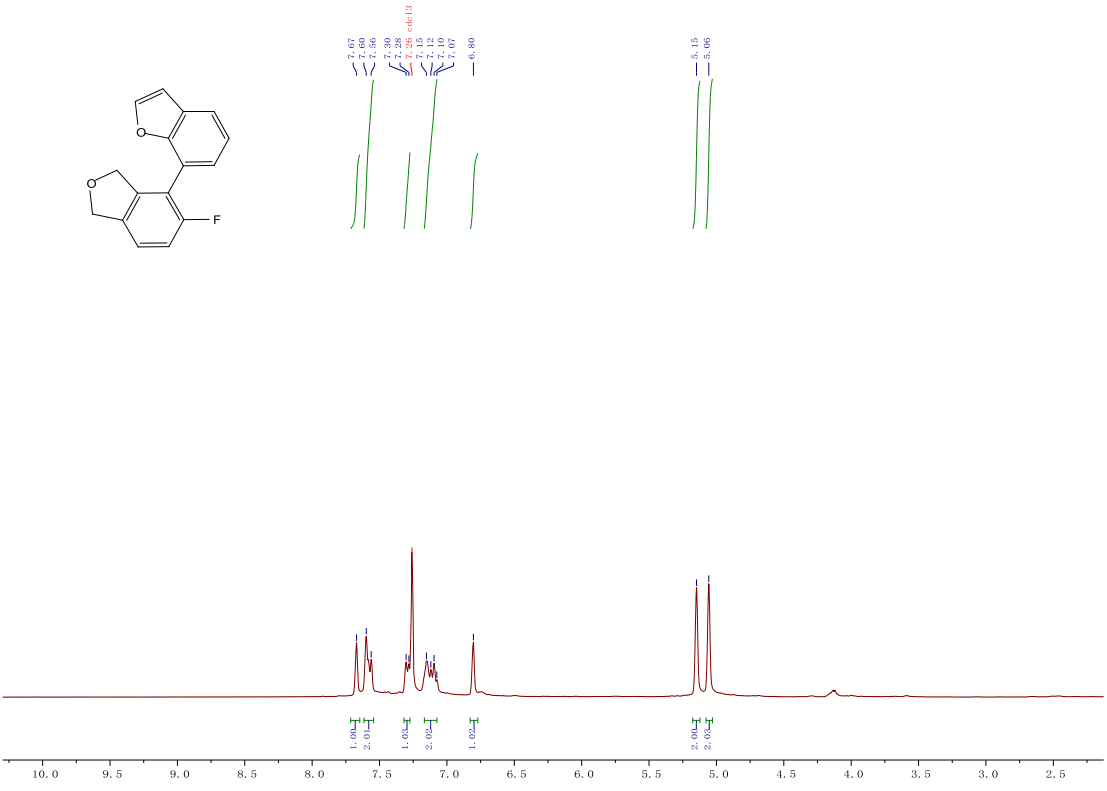
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4r**



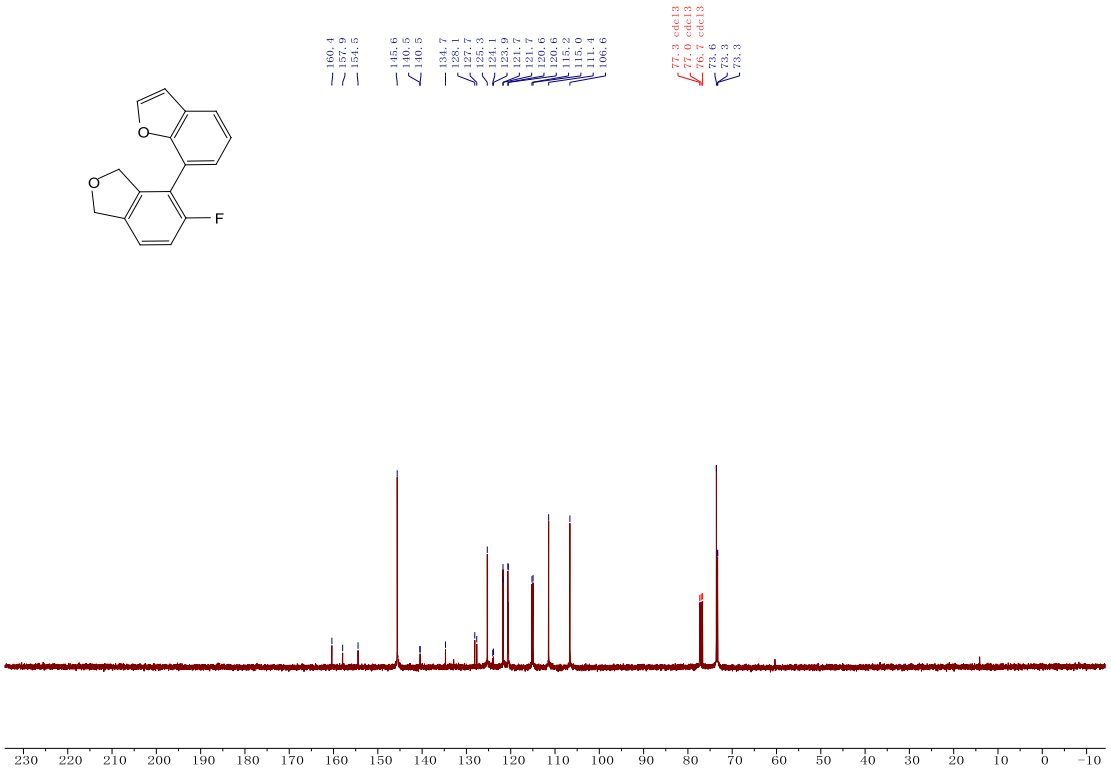
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4r**



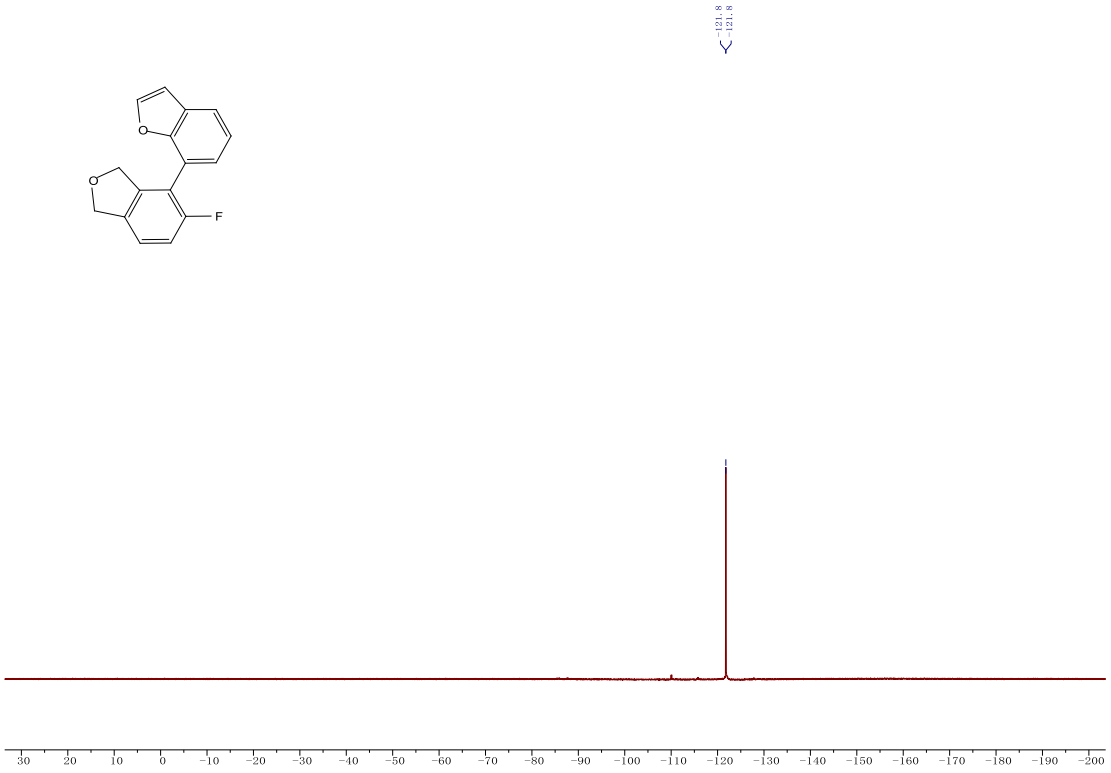
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**



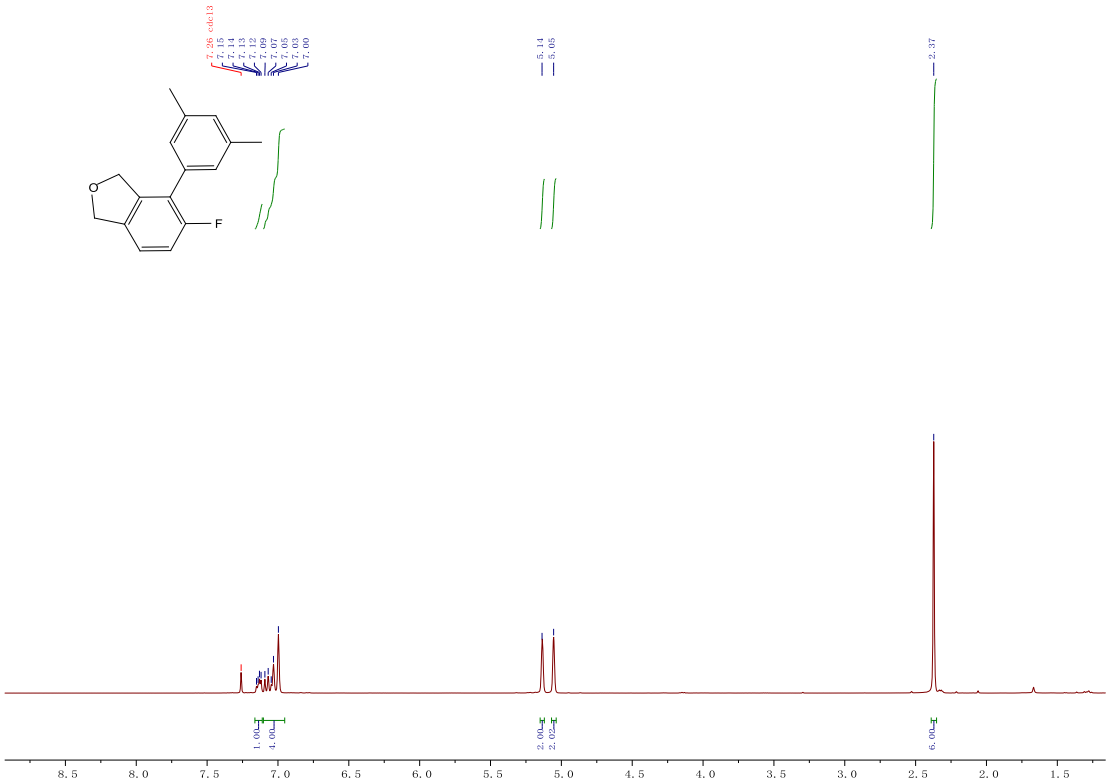
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4s**



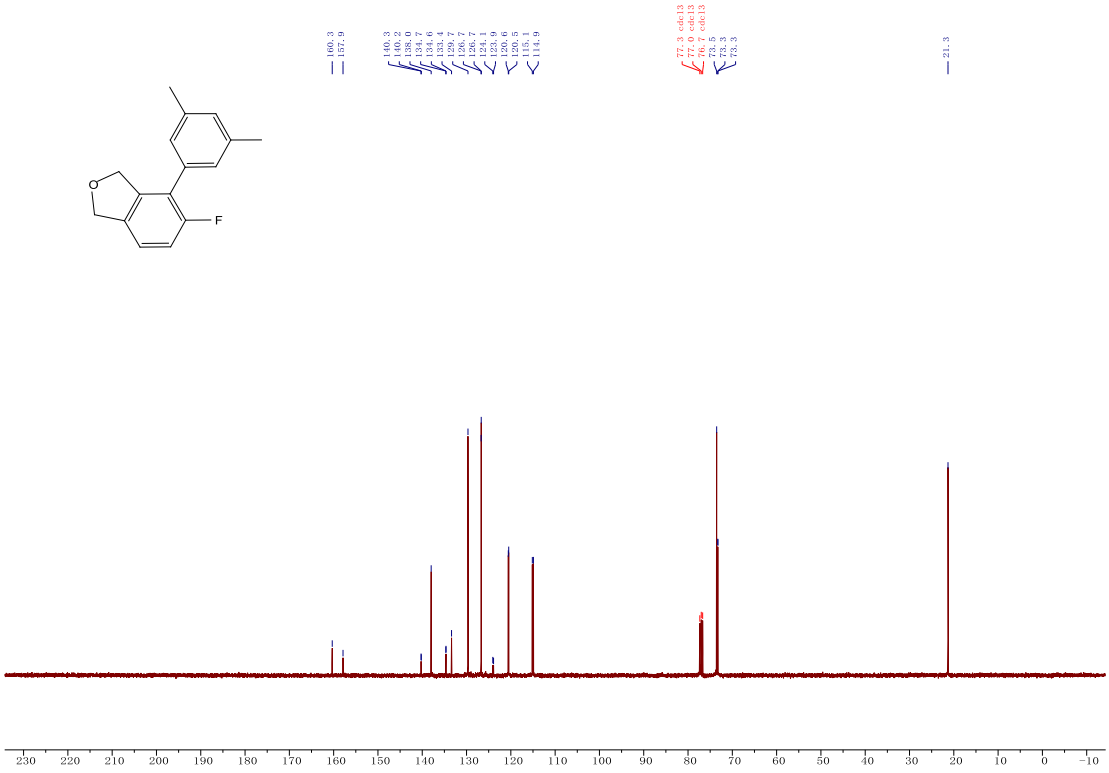
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4s**



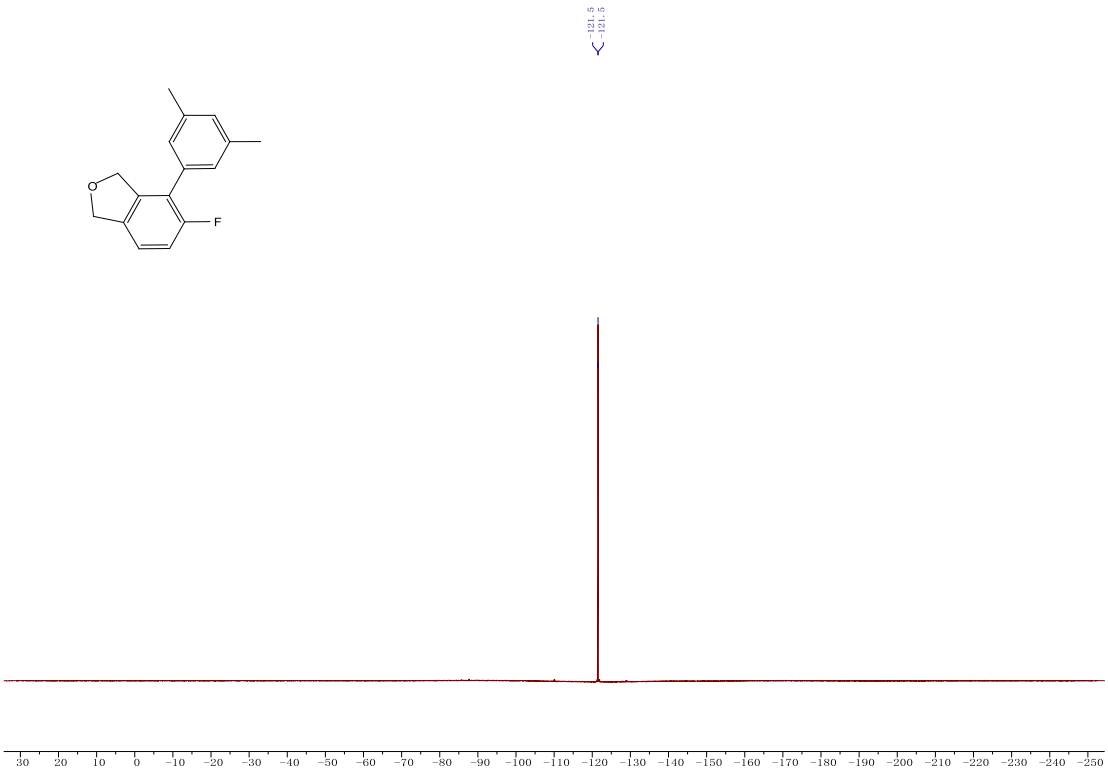
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4t**



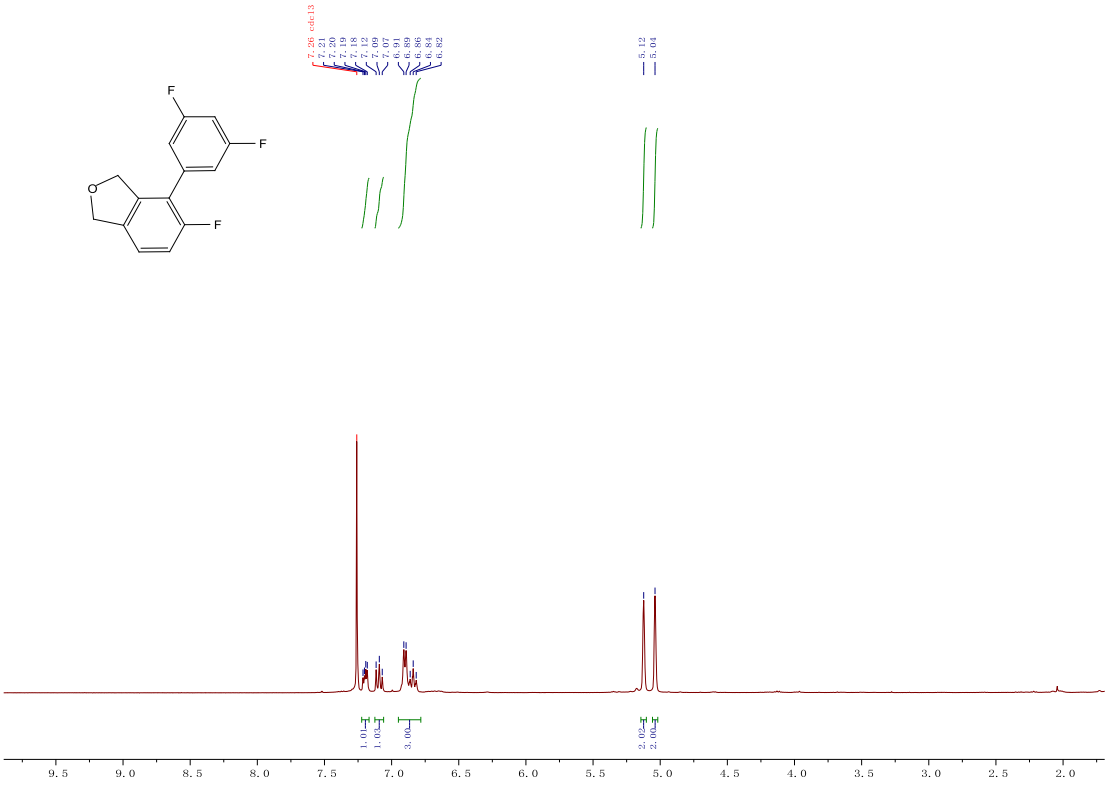
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4t**



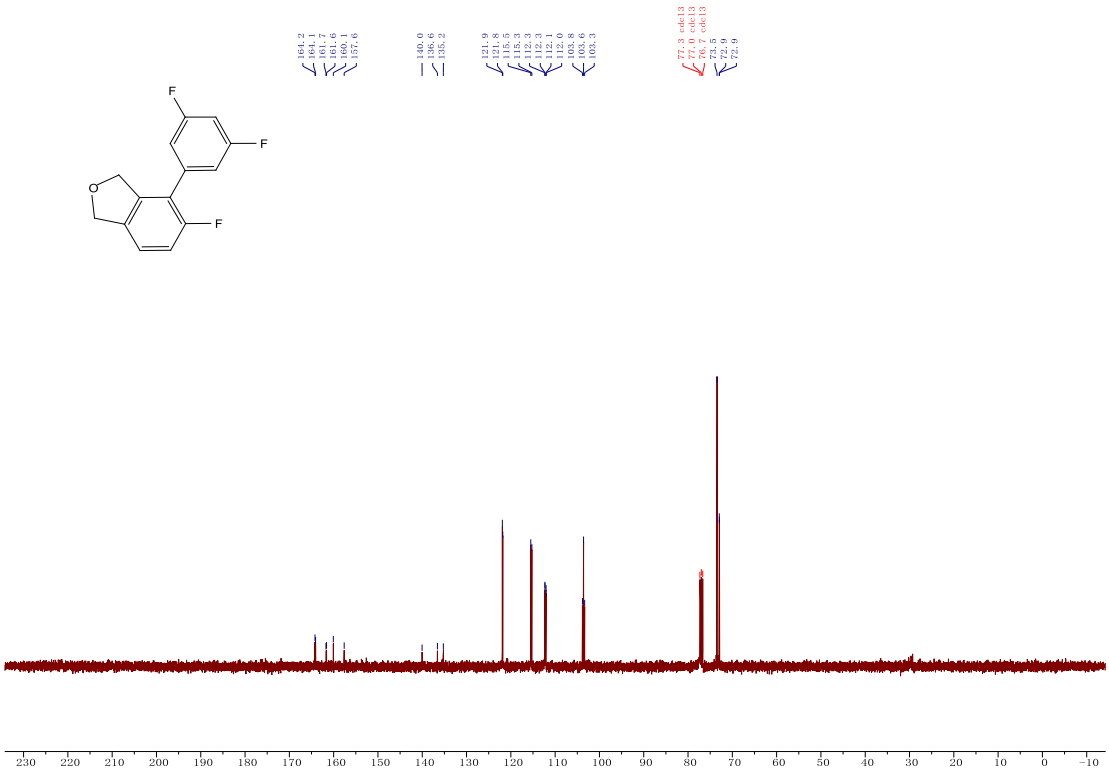
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4t**



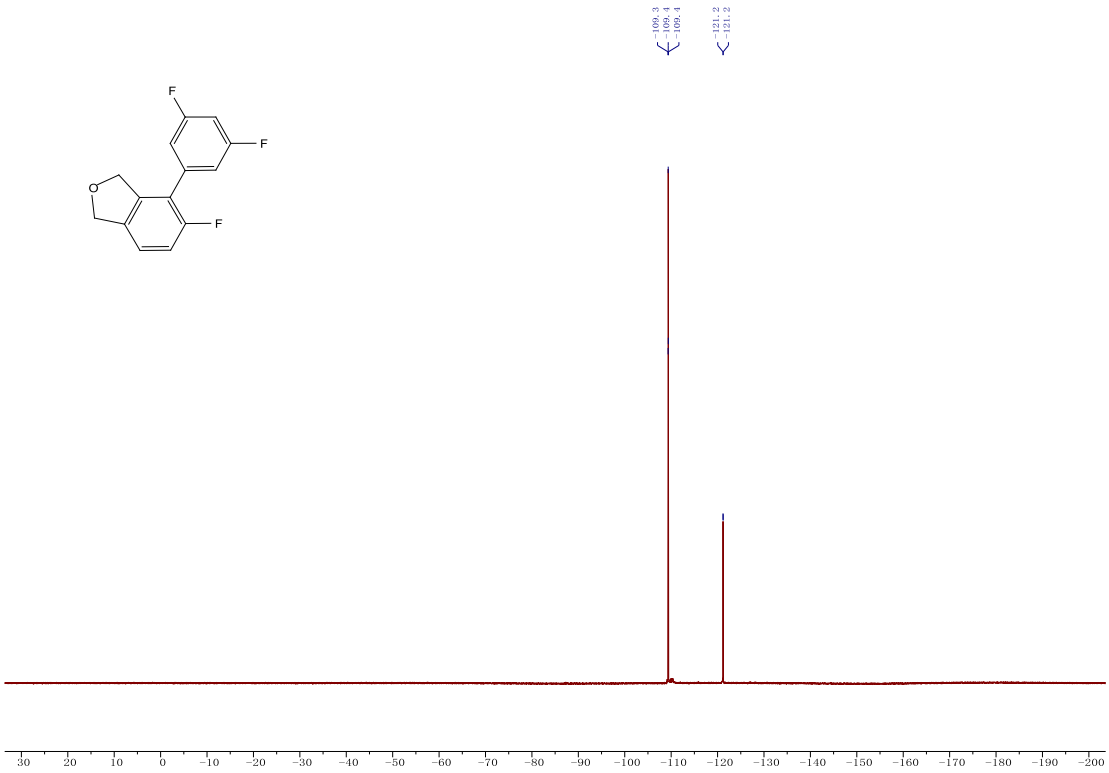
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4u**



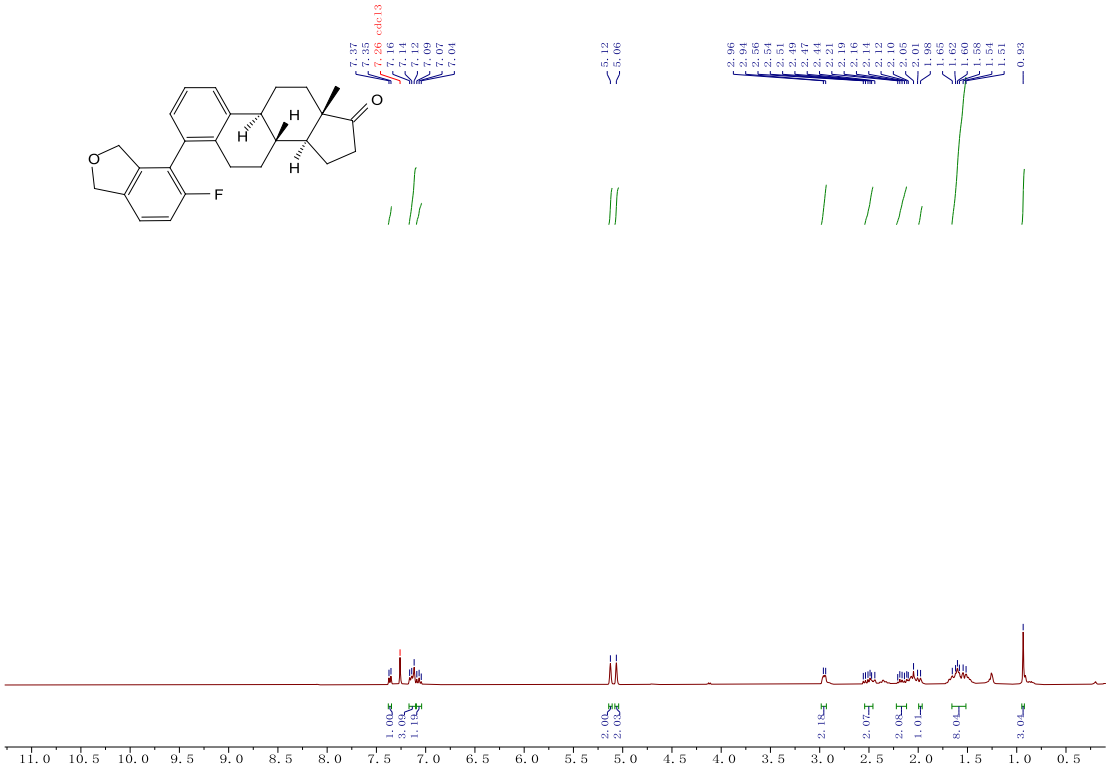
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4u**



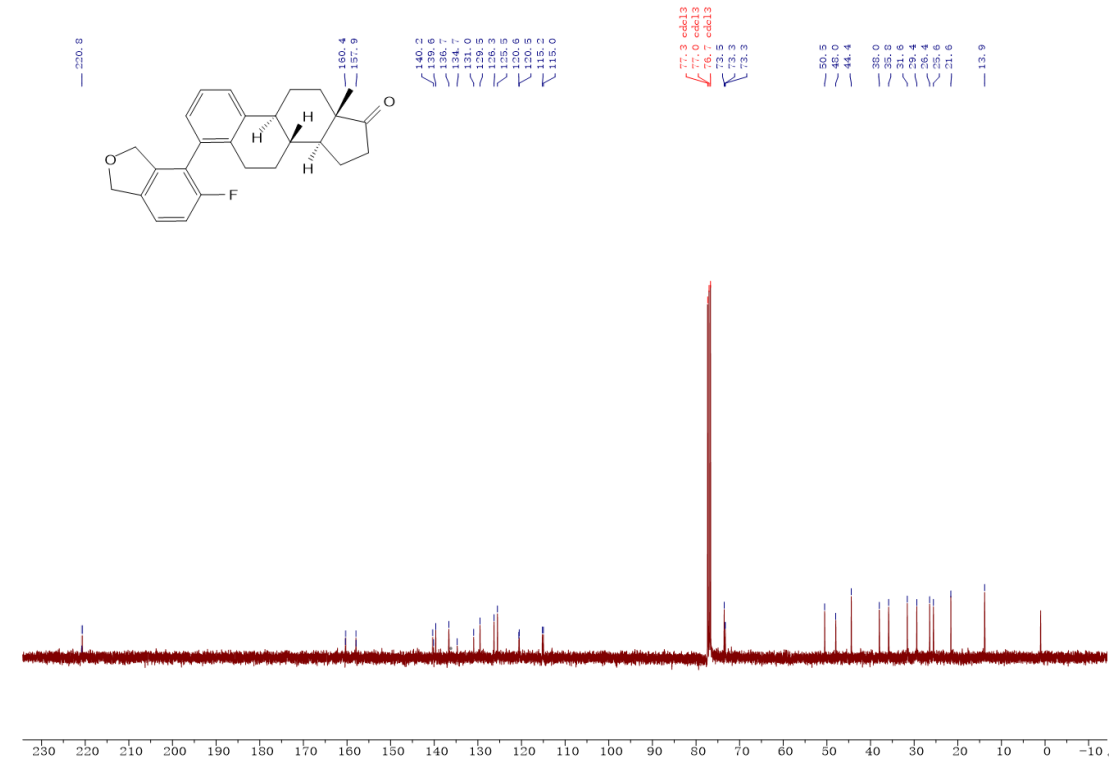
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4u**



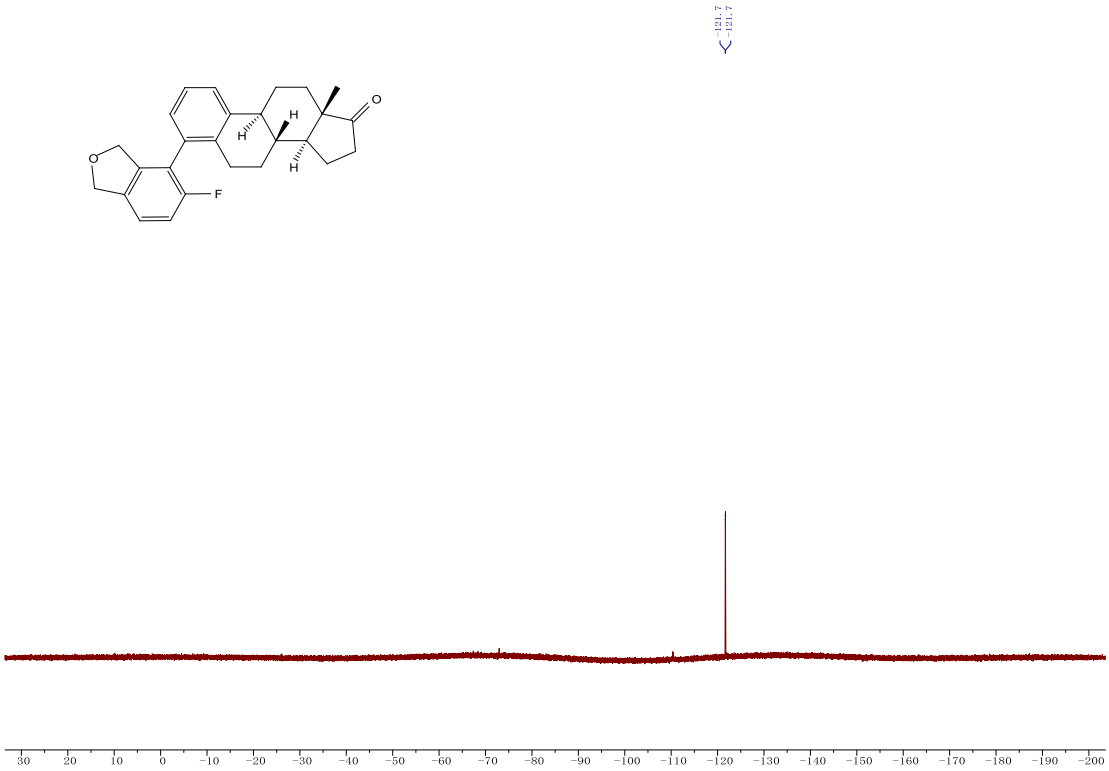
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4v**



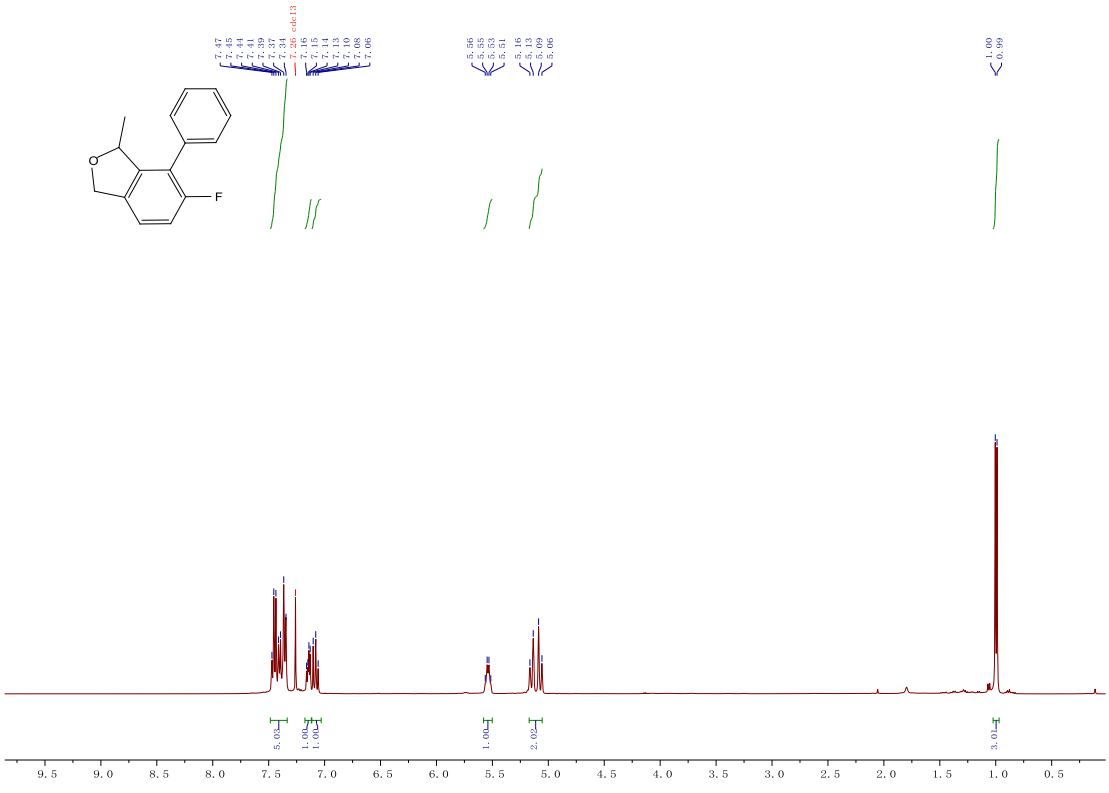
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4v**



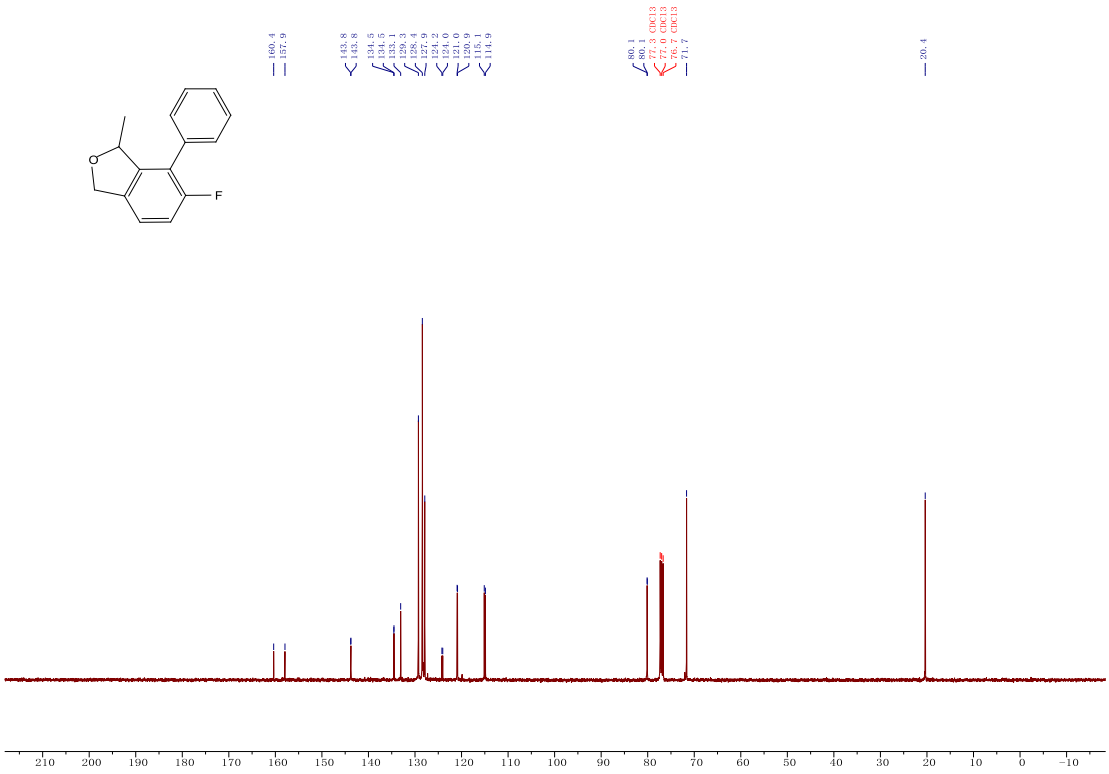
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4v**



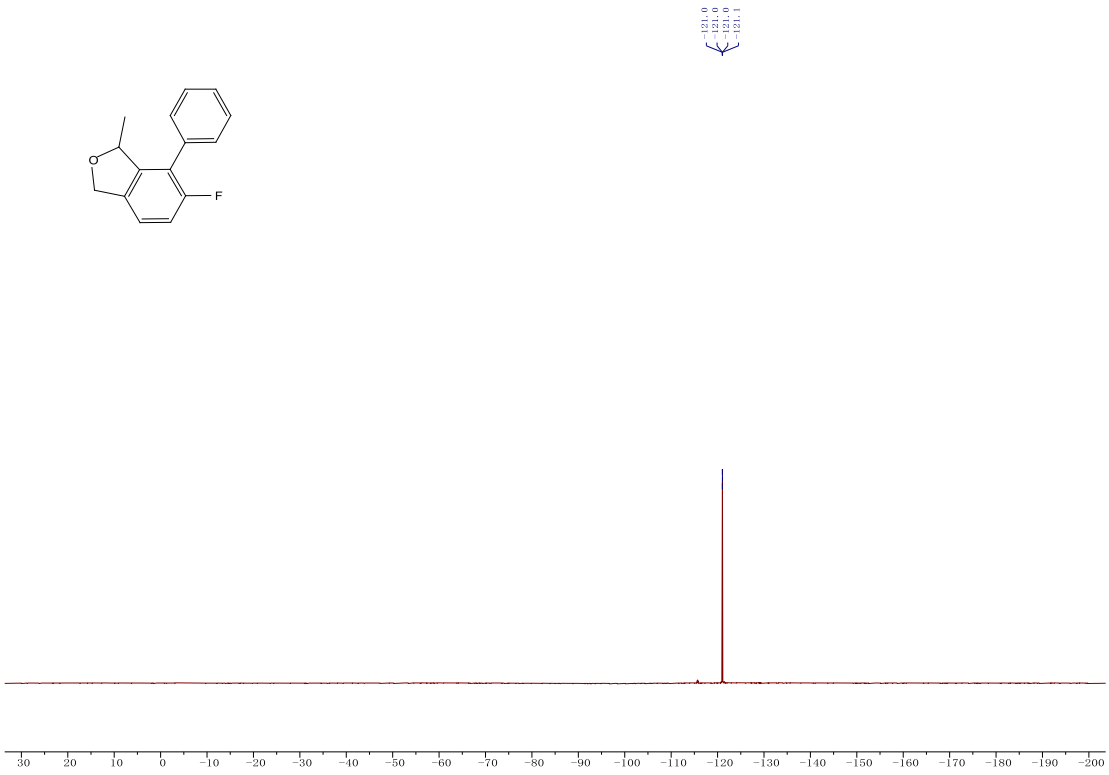
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4w**



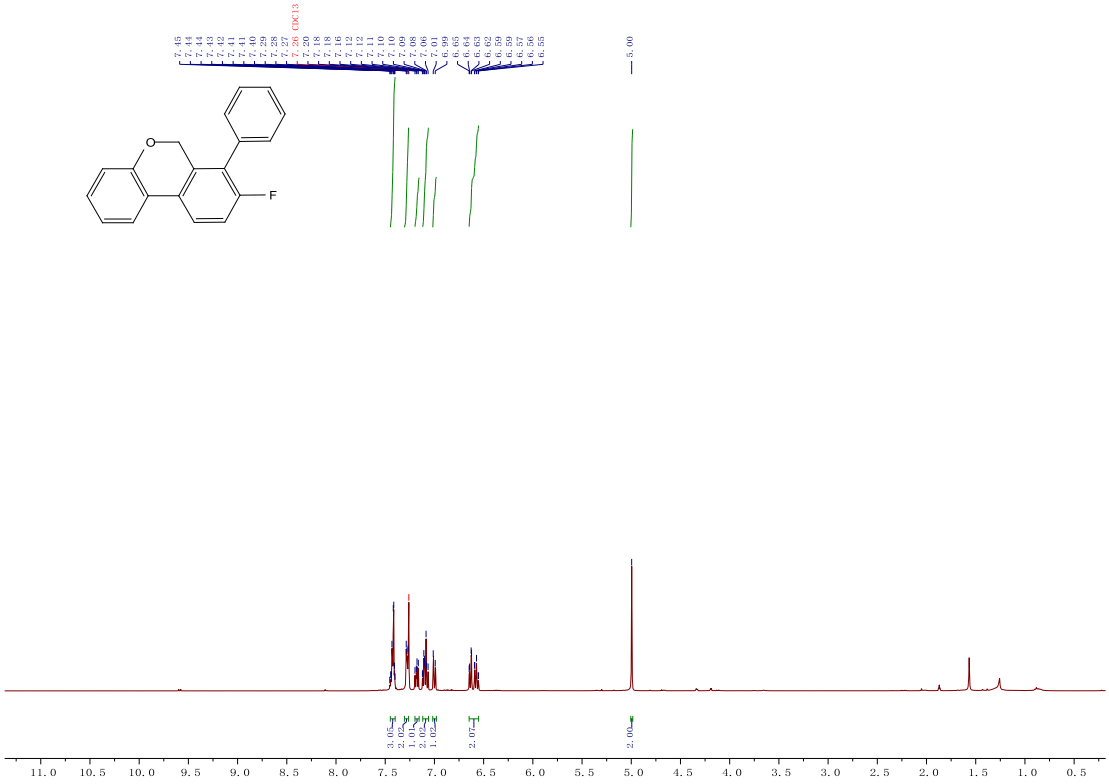
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4w**



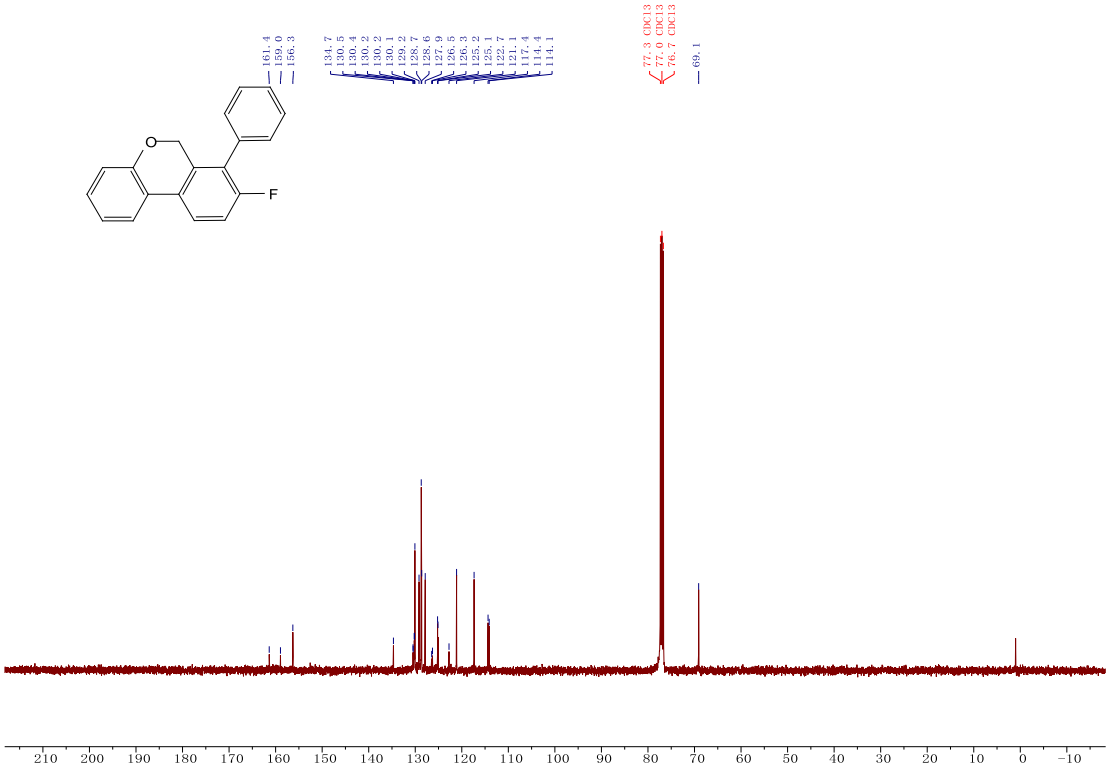
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4w**



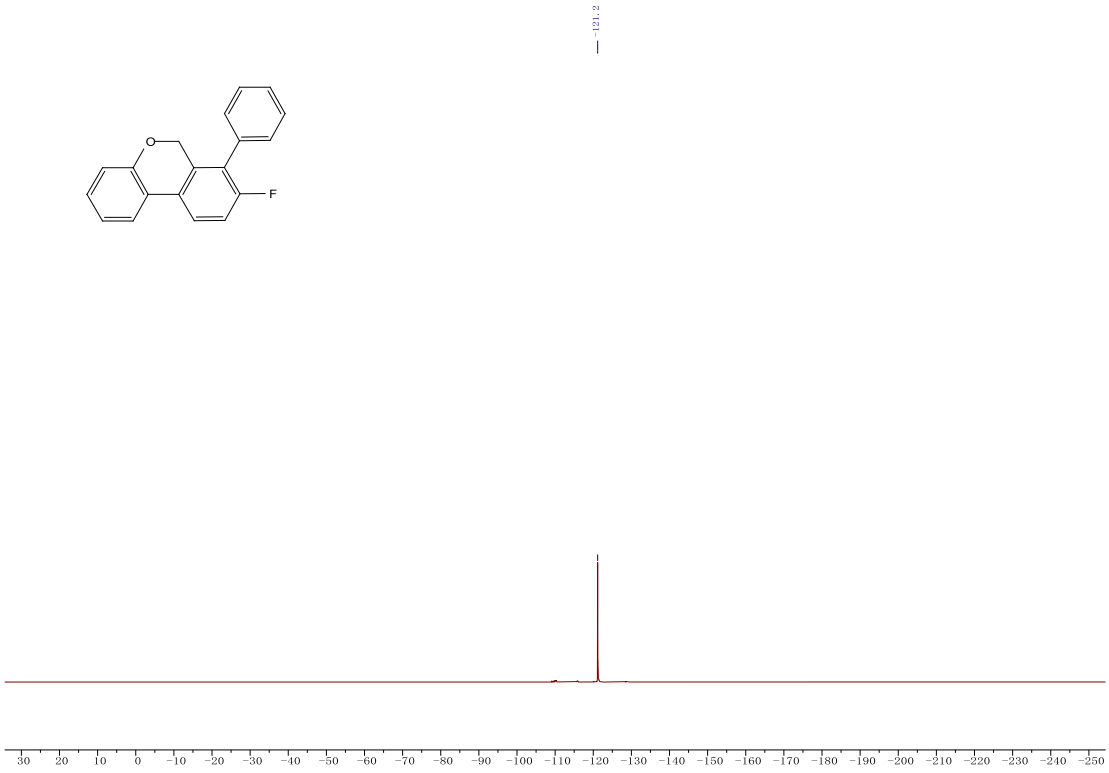
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4x**



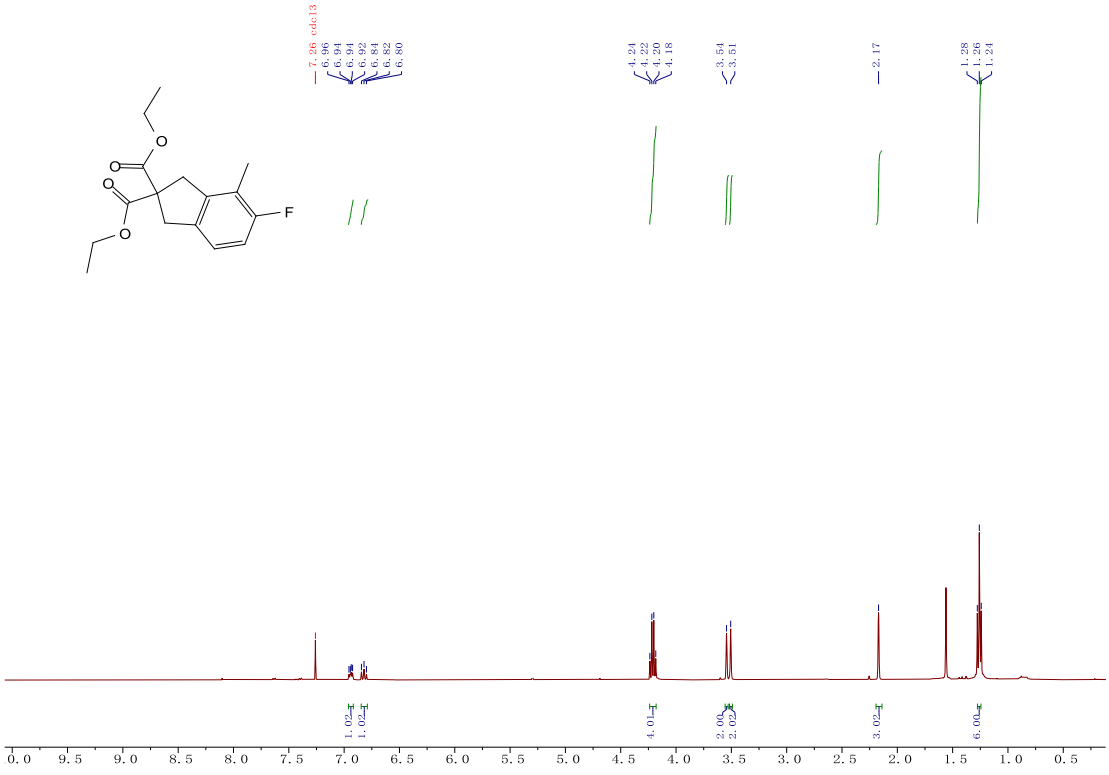
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4x**



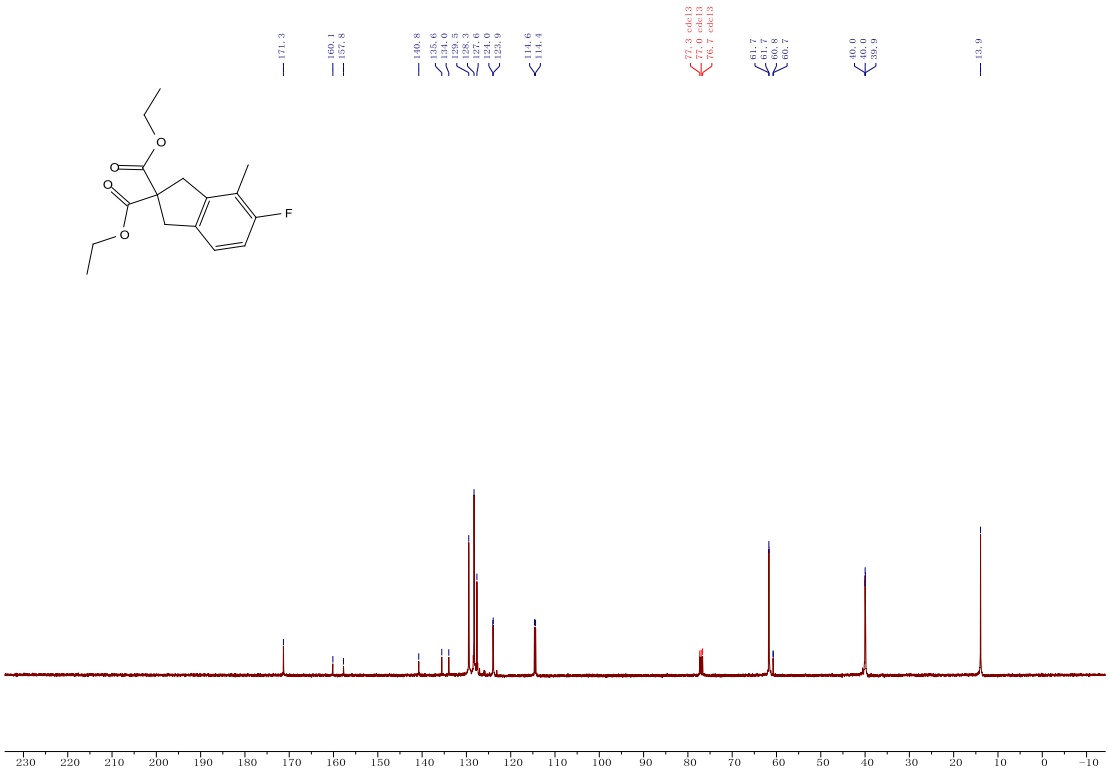
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4x**



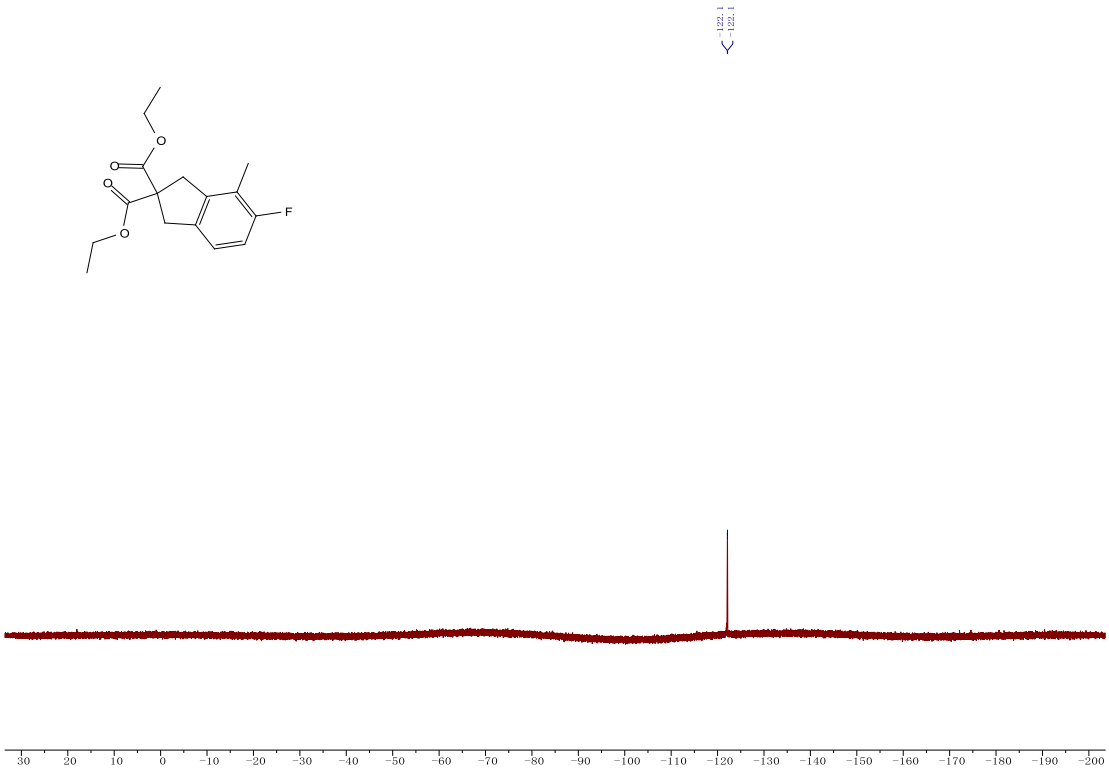
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**



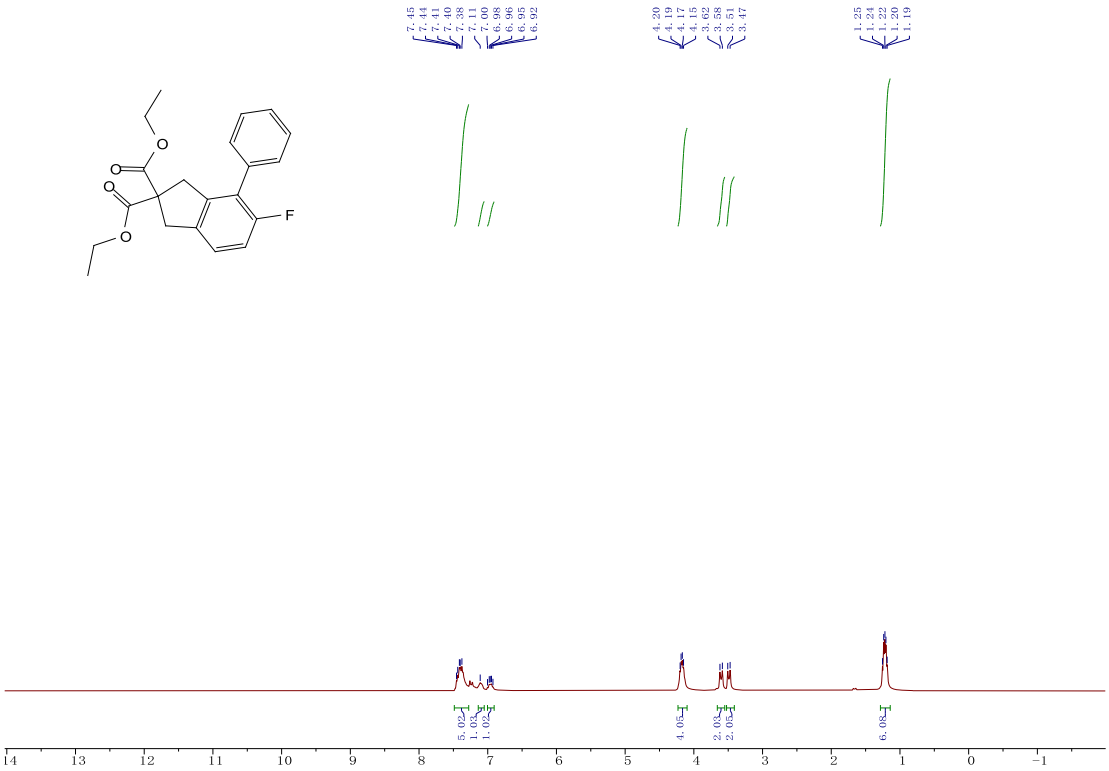
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**



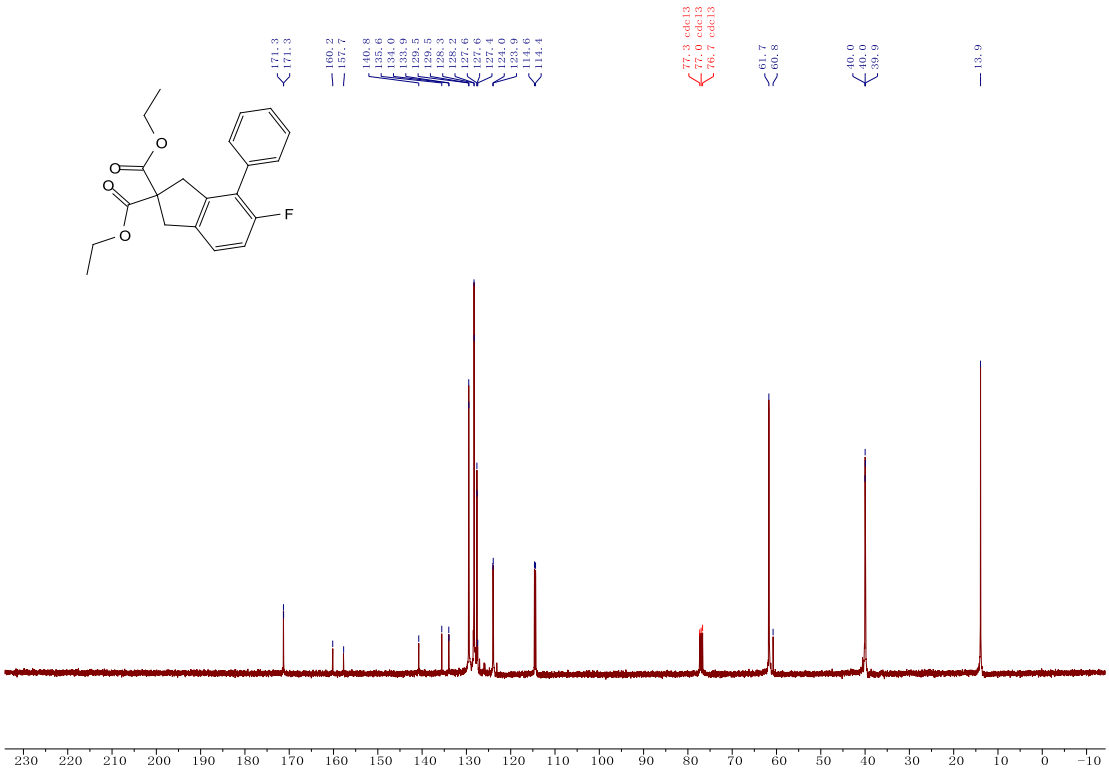
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2**



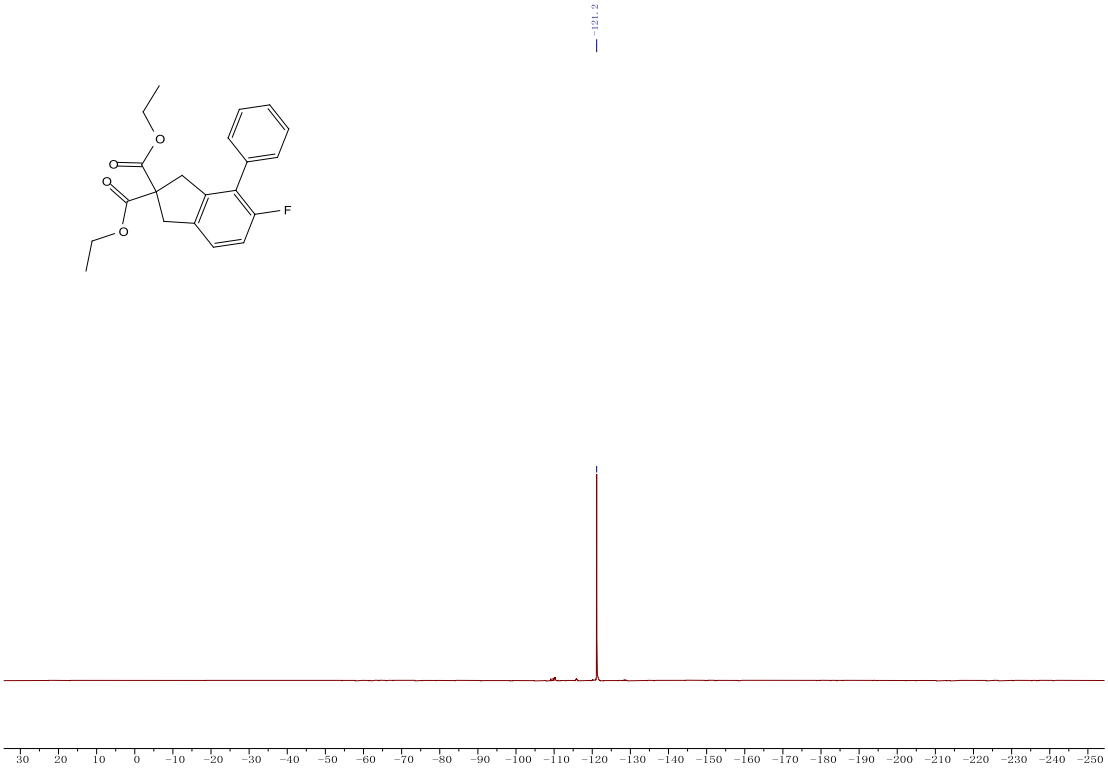
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4aa**



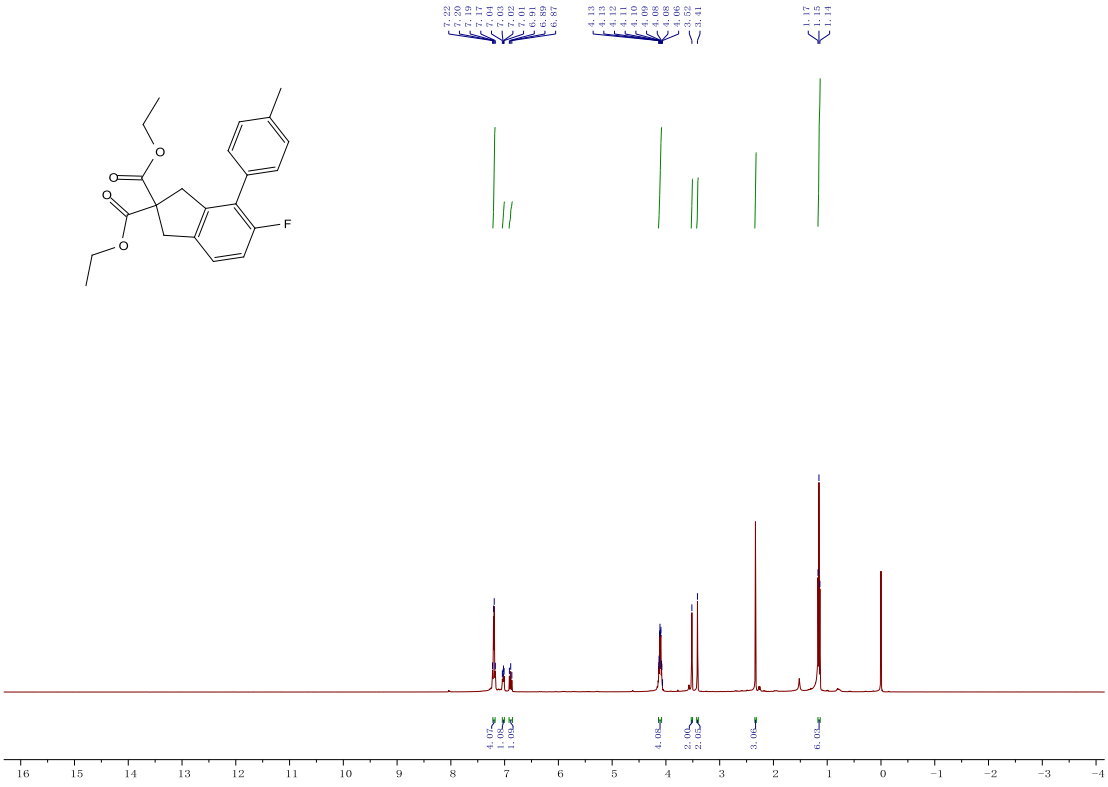
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4aa**



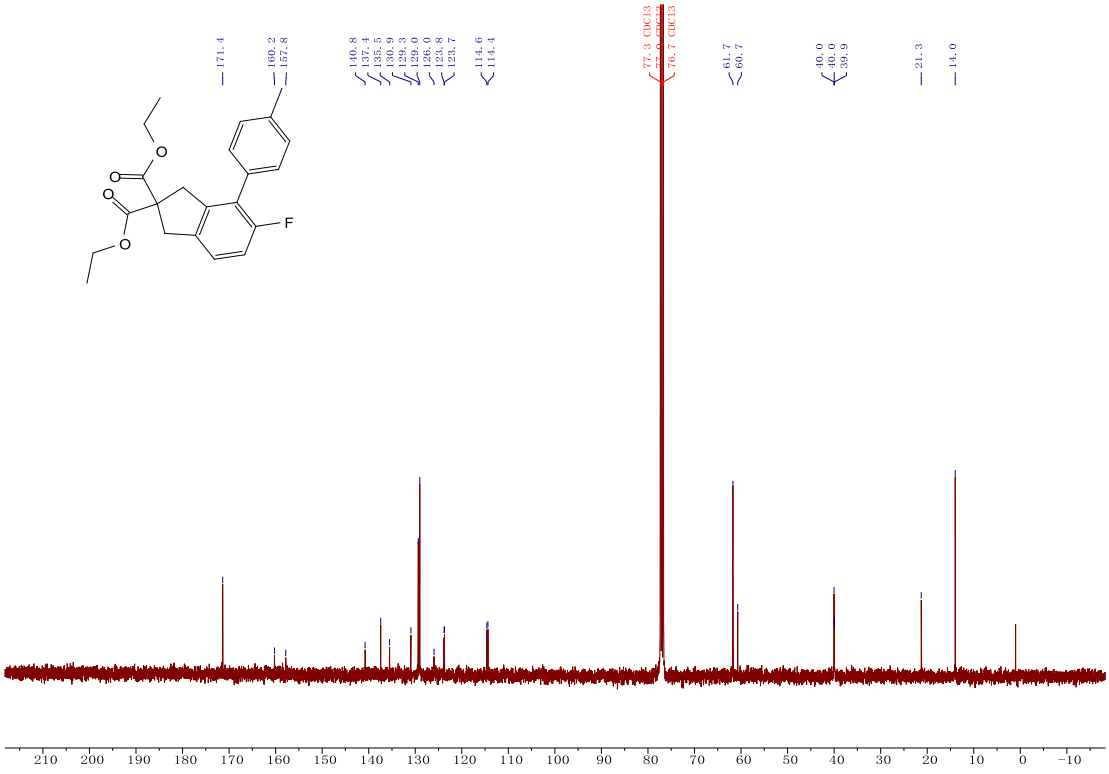
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4aa**



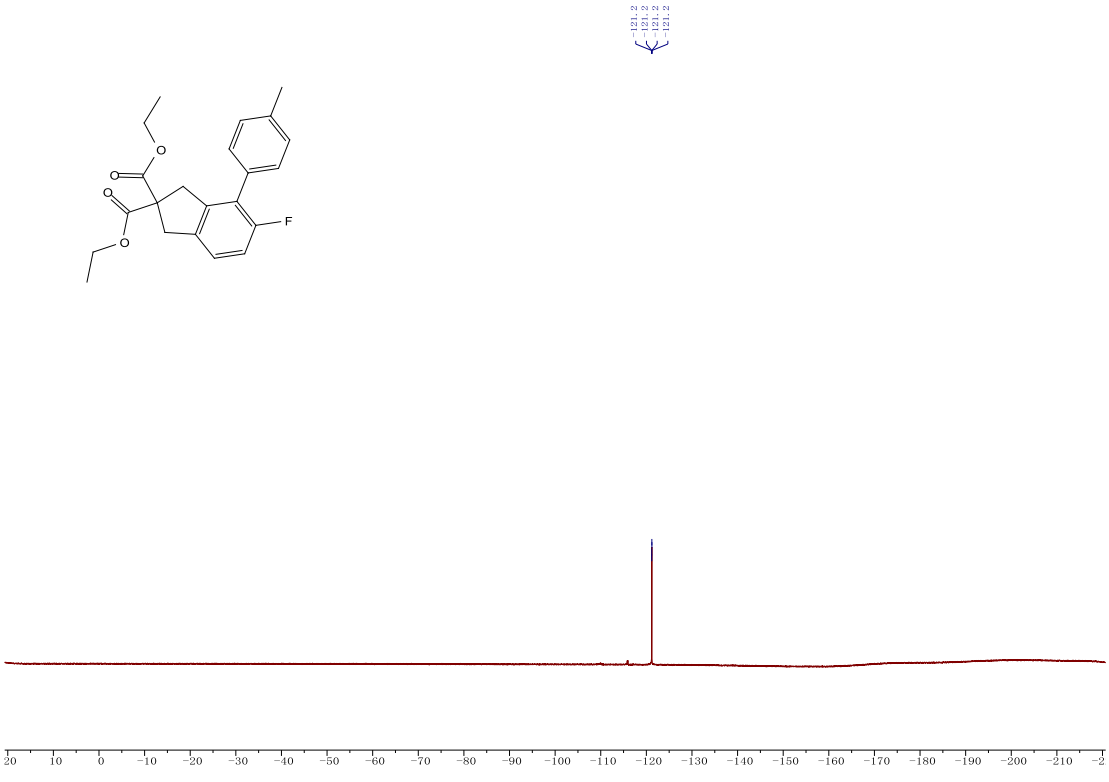
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ab**



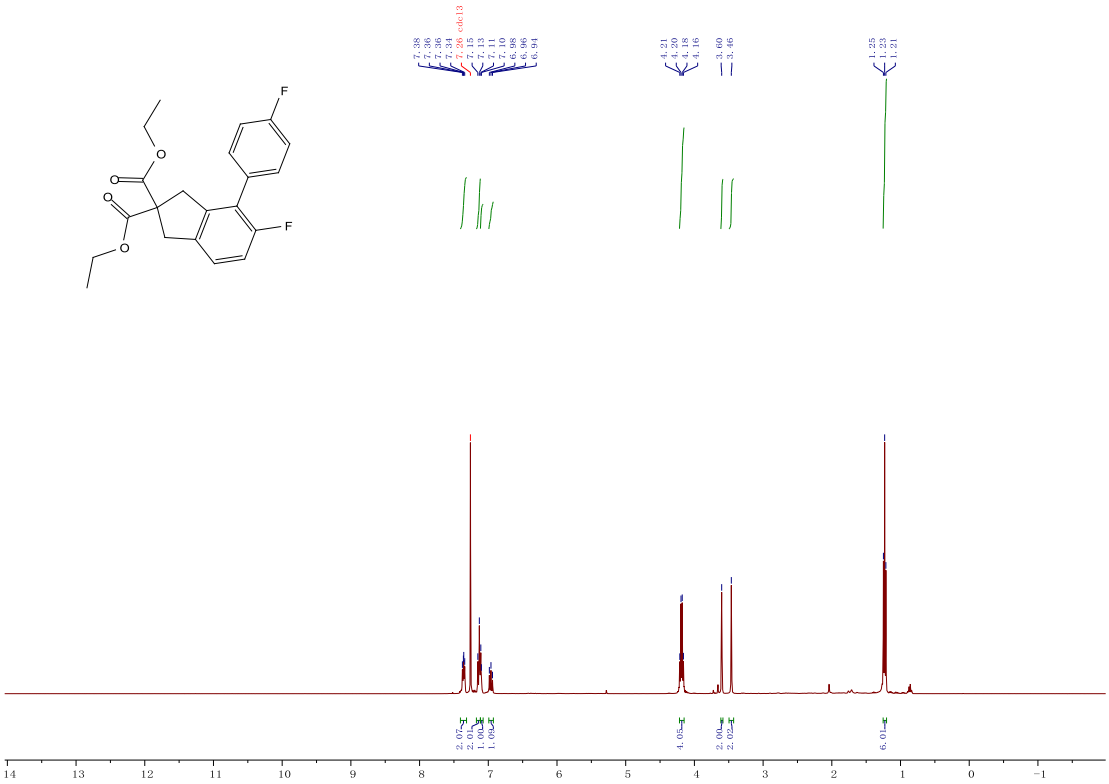
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ab**



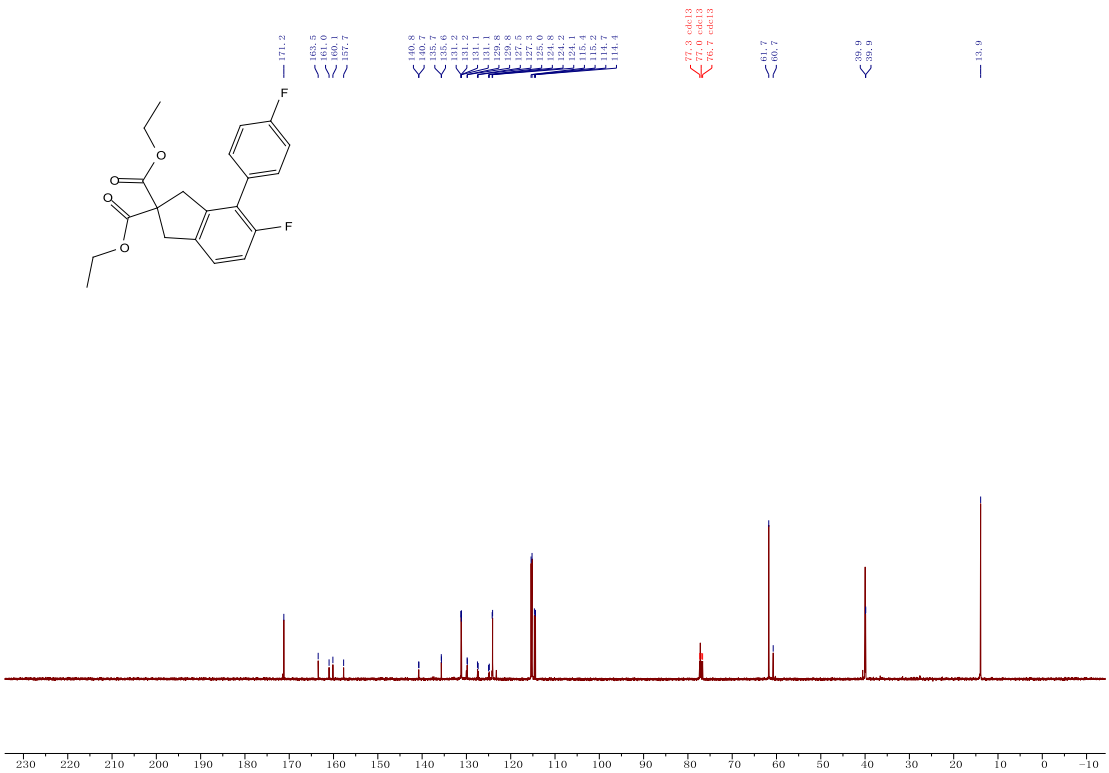
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ab**



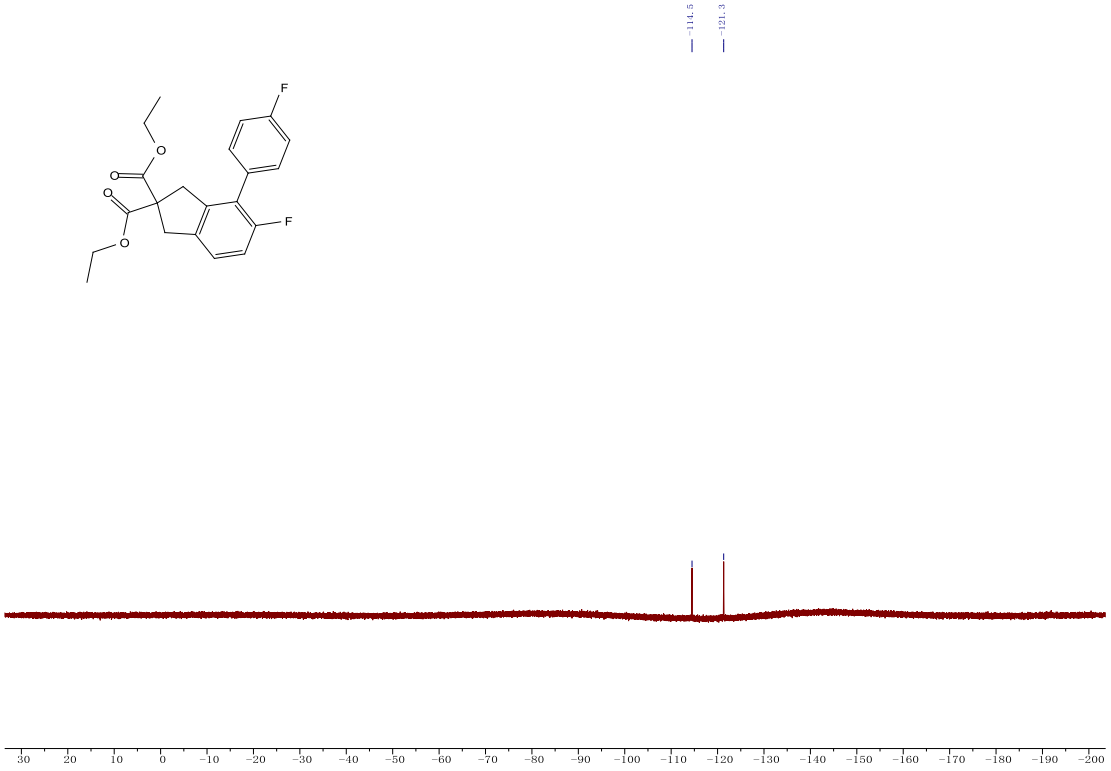
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ac**



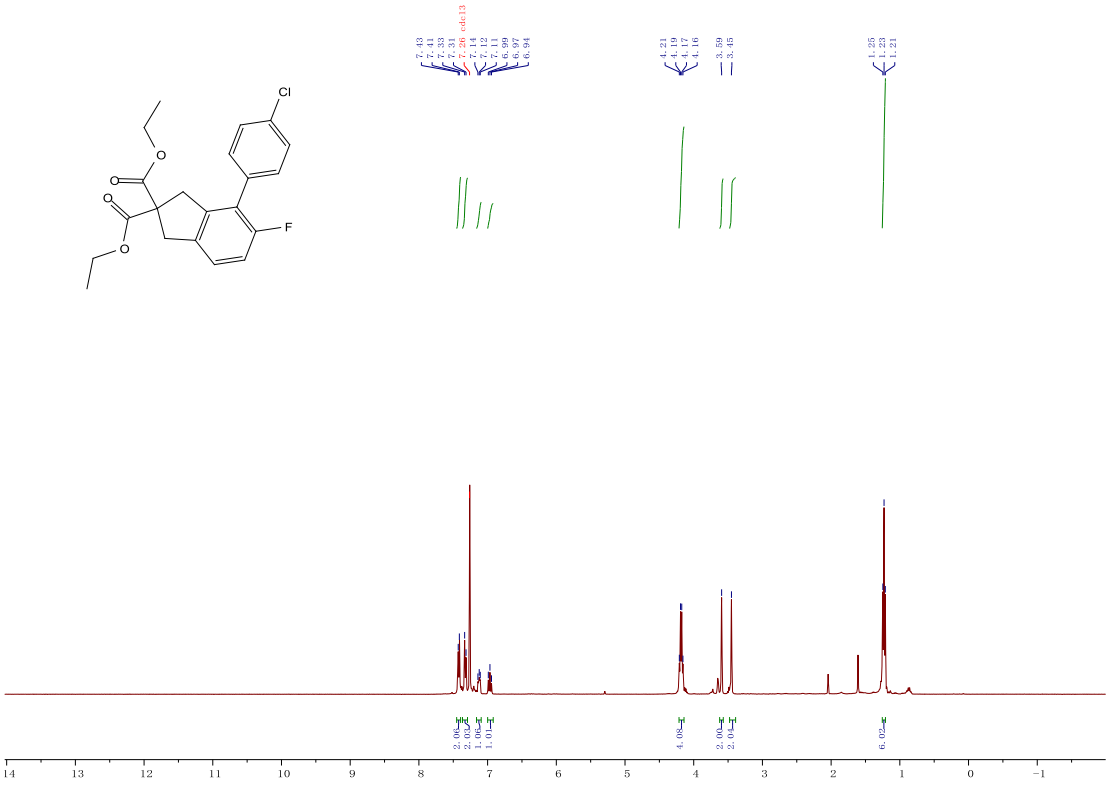
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ac**



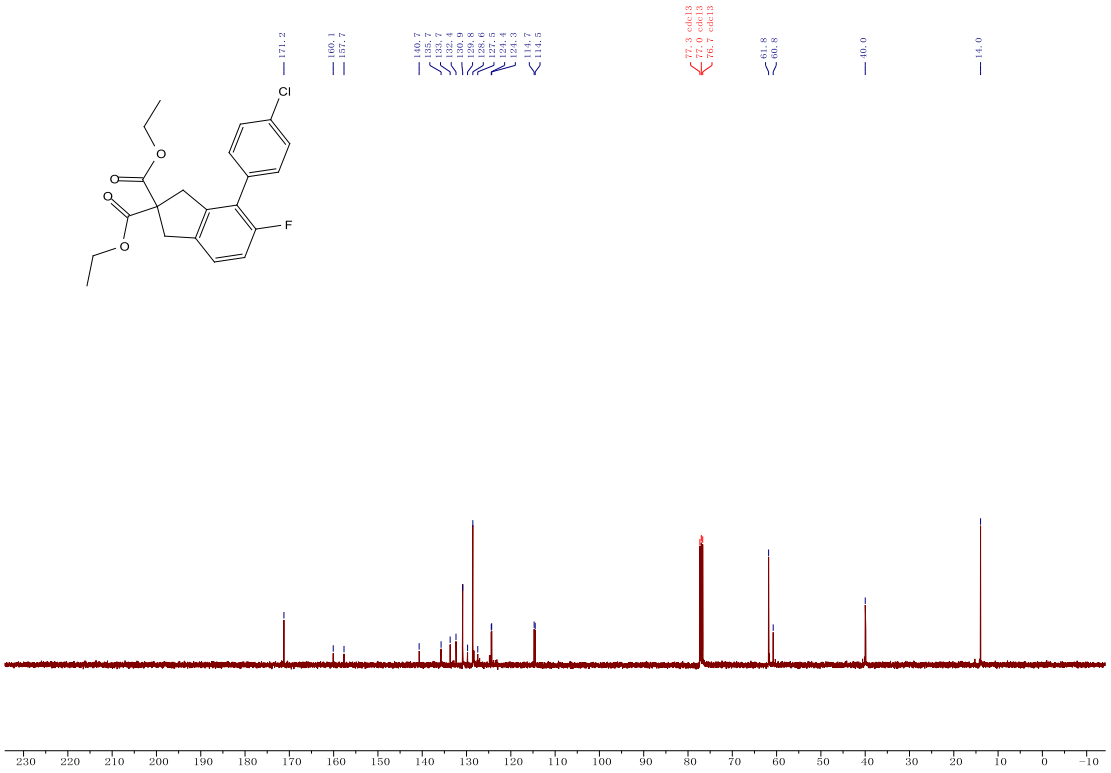
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ac**



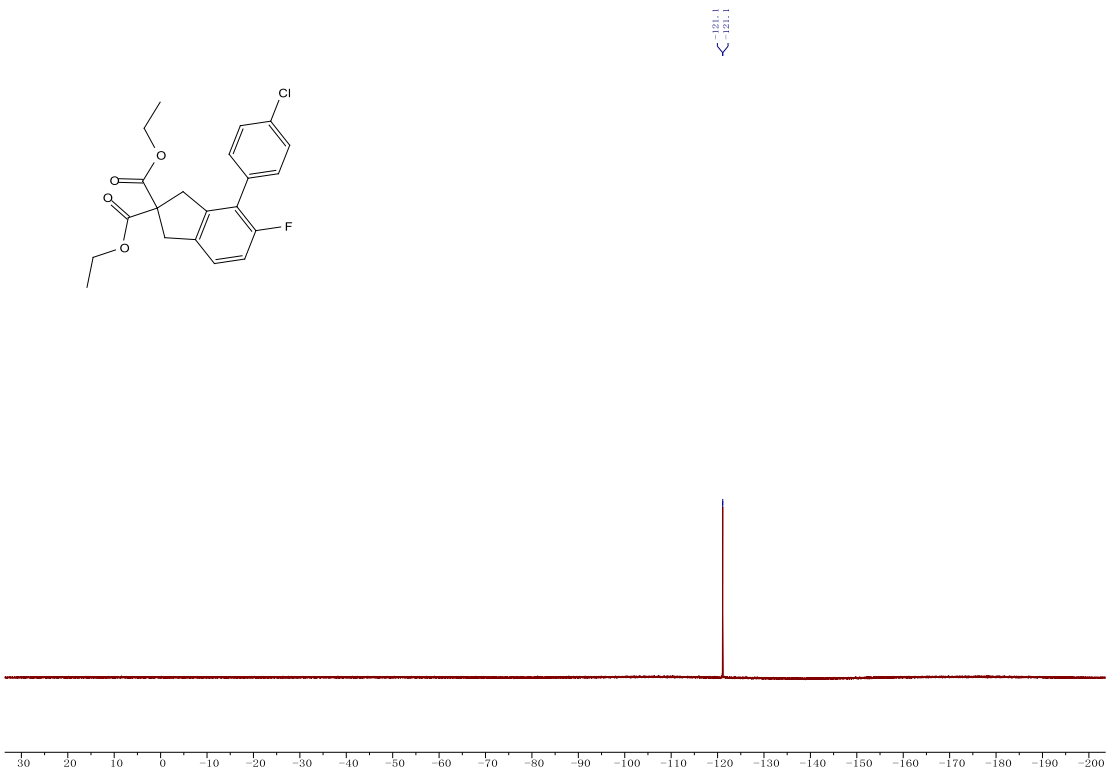
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ad**



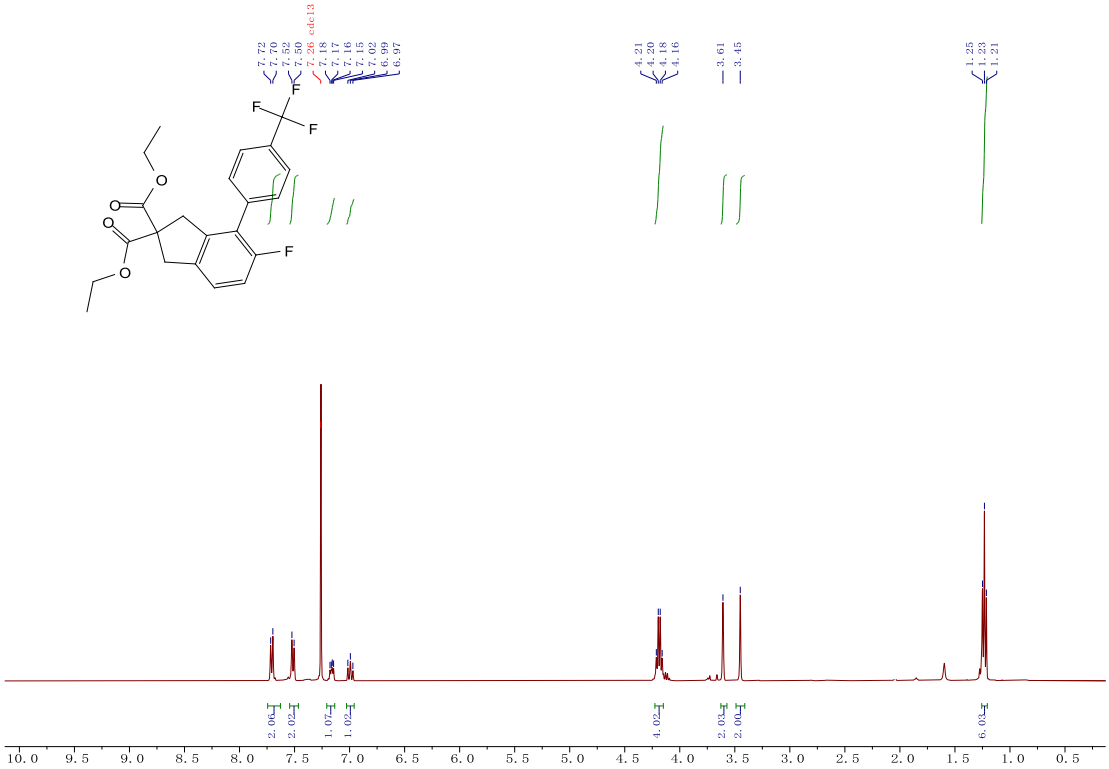
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ad**



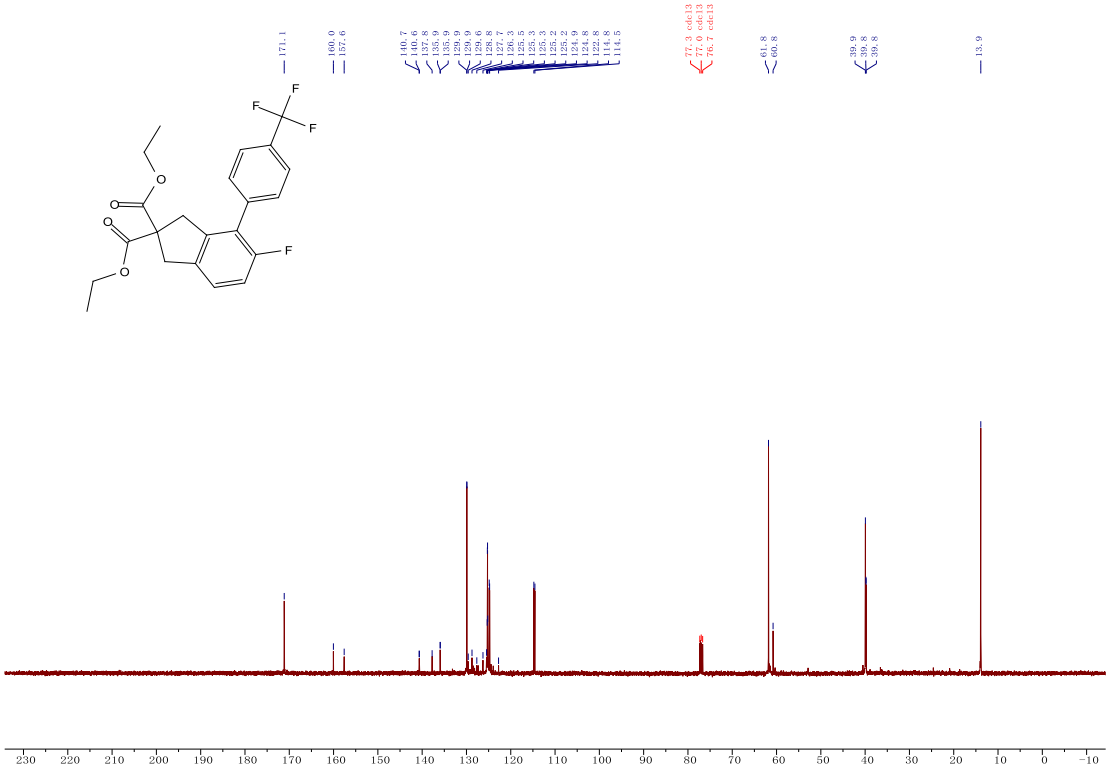
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ad**



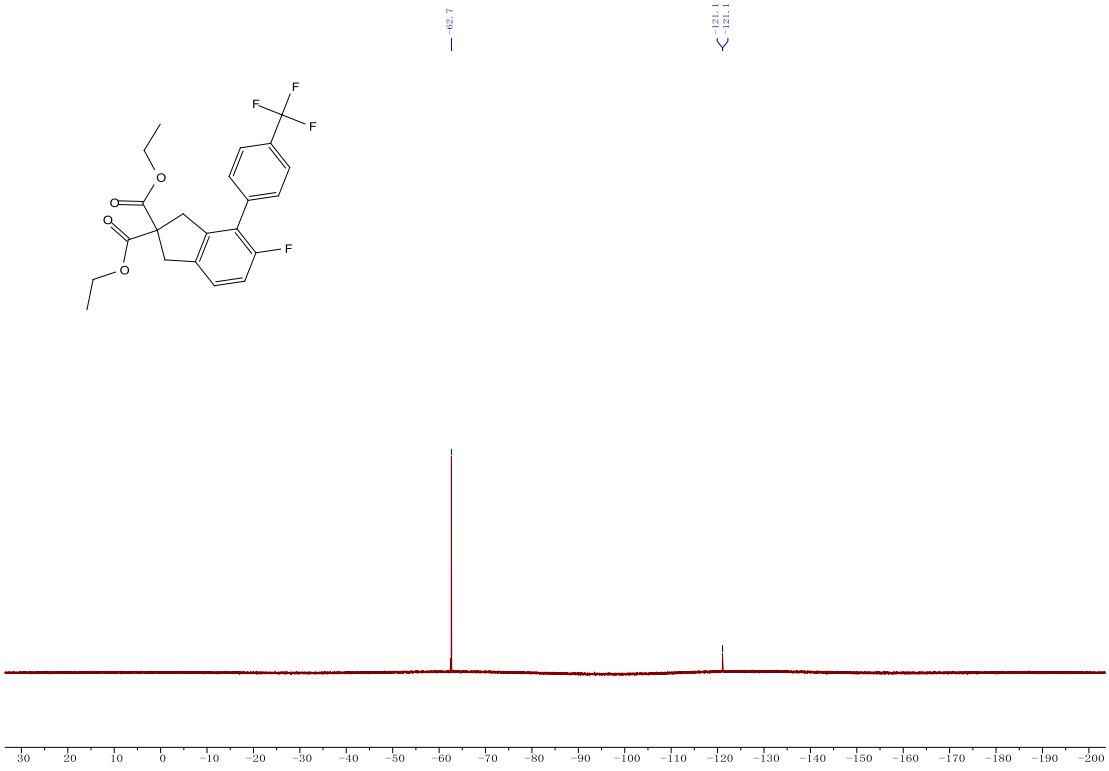
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ae**



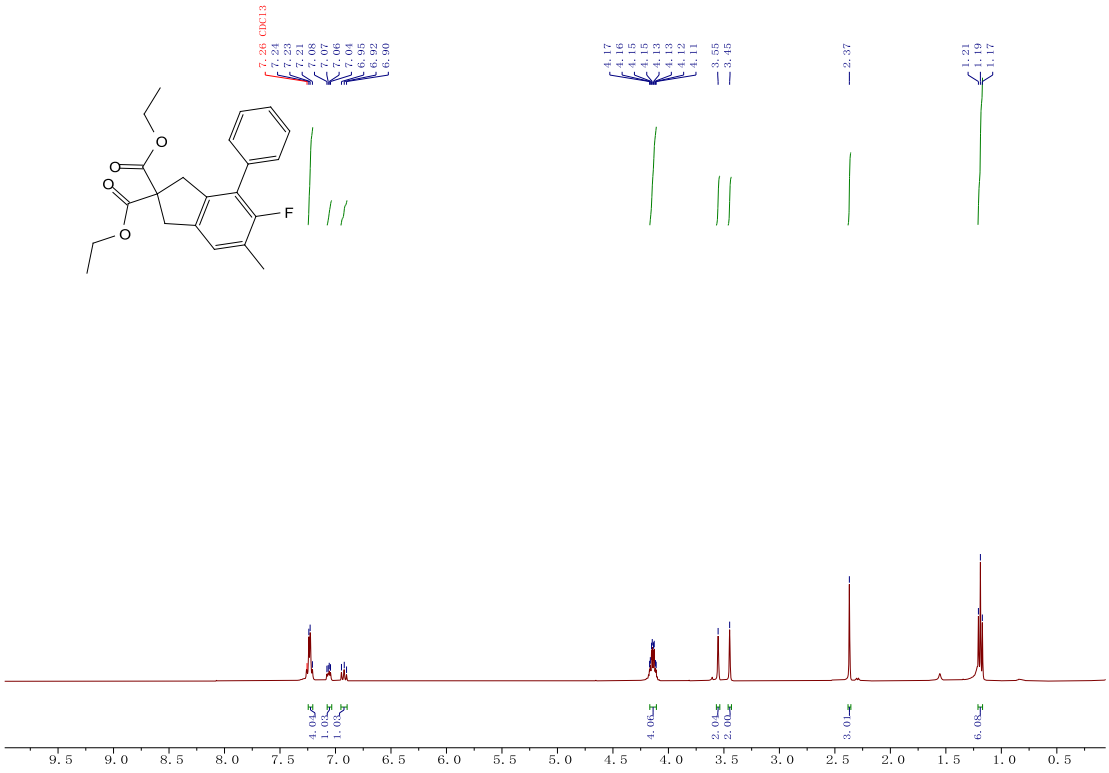
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ae**



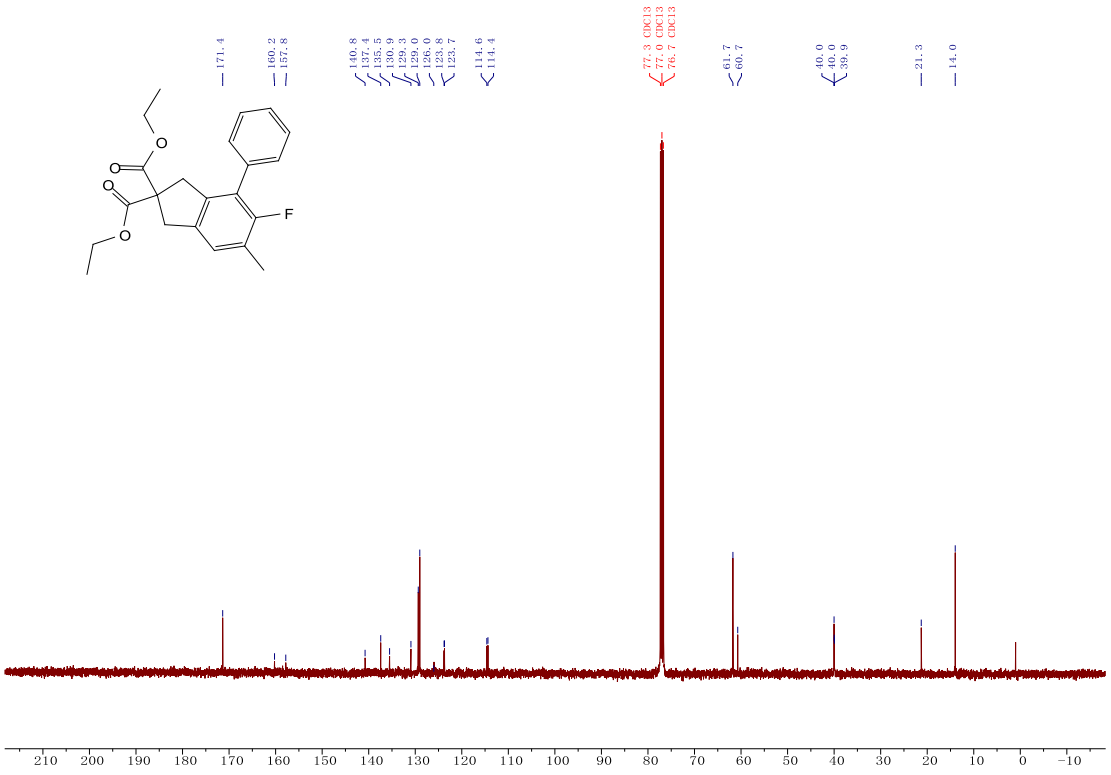
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ae**



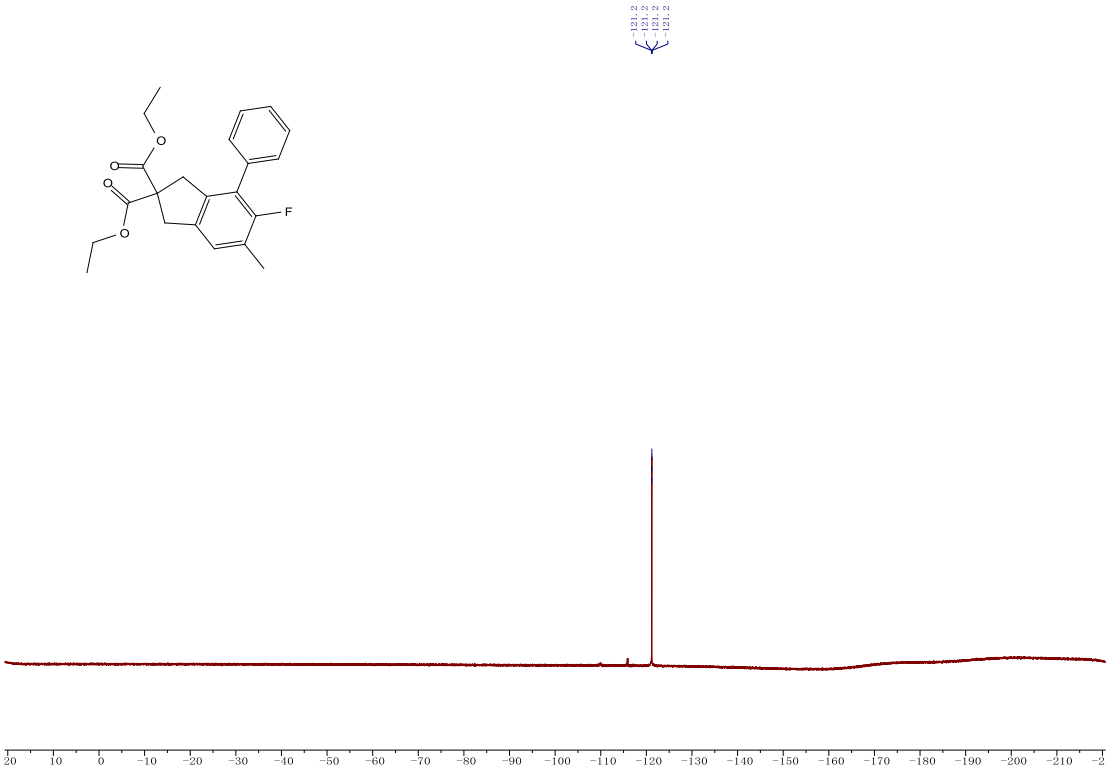
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4af**



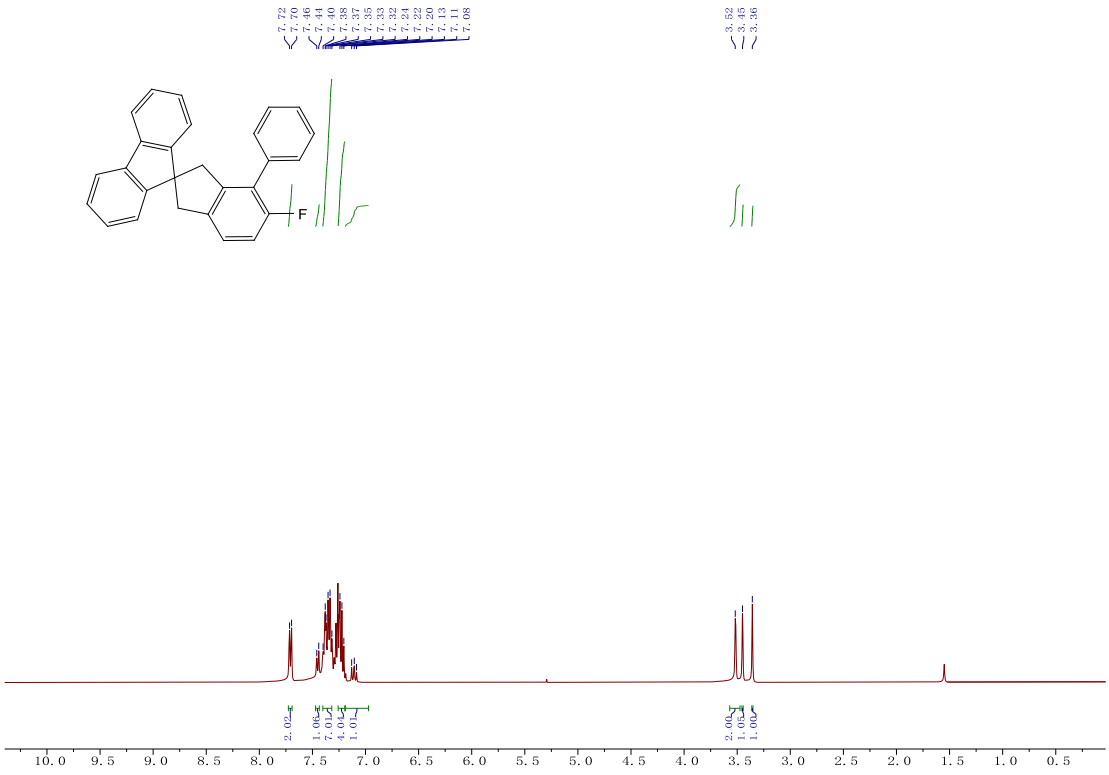
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4af**



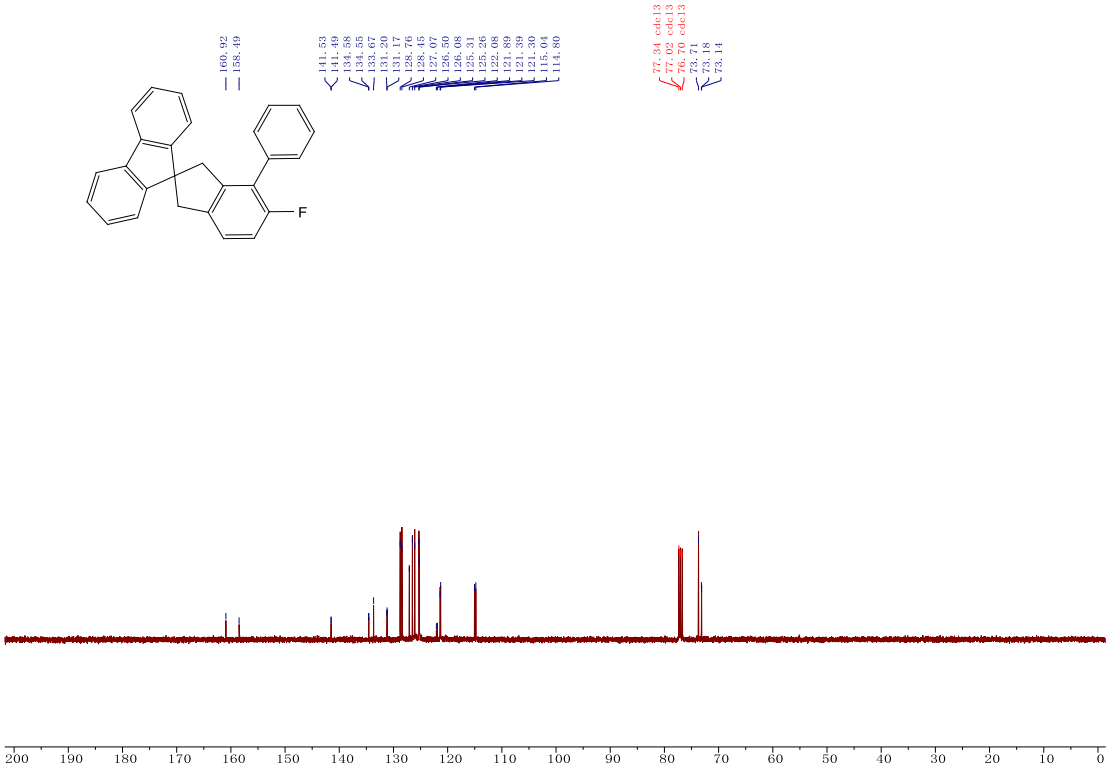
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4af**



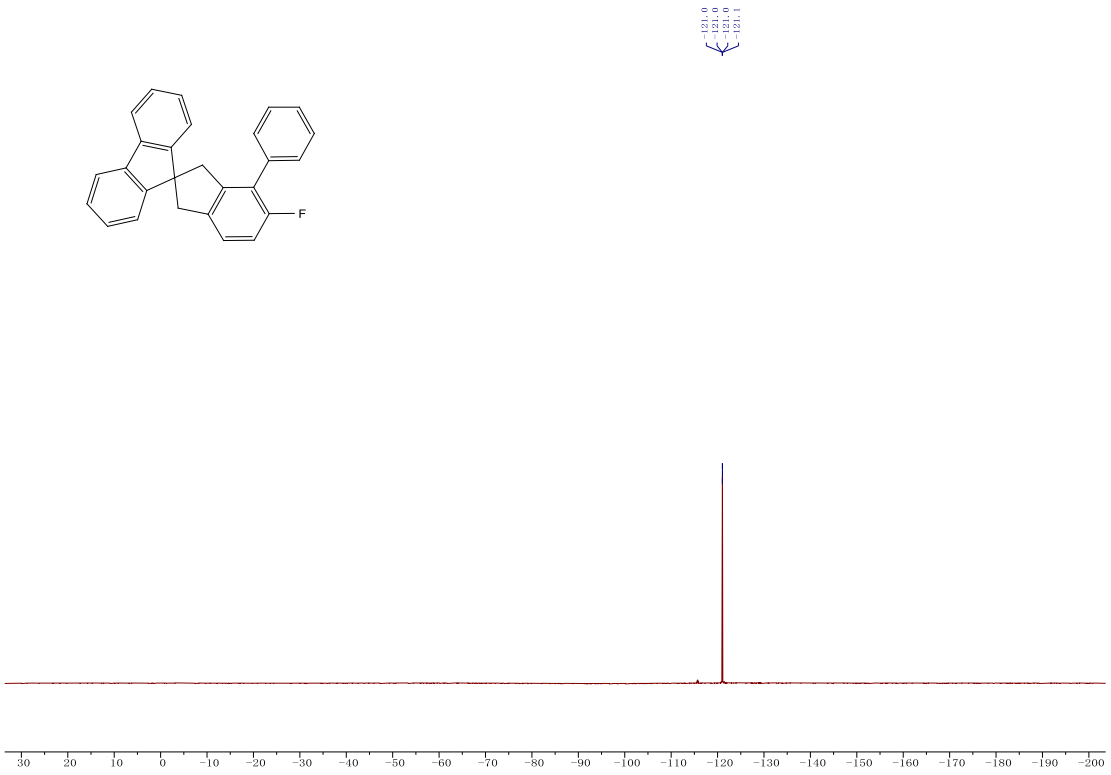
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ag**



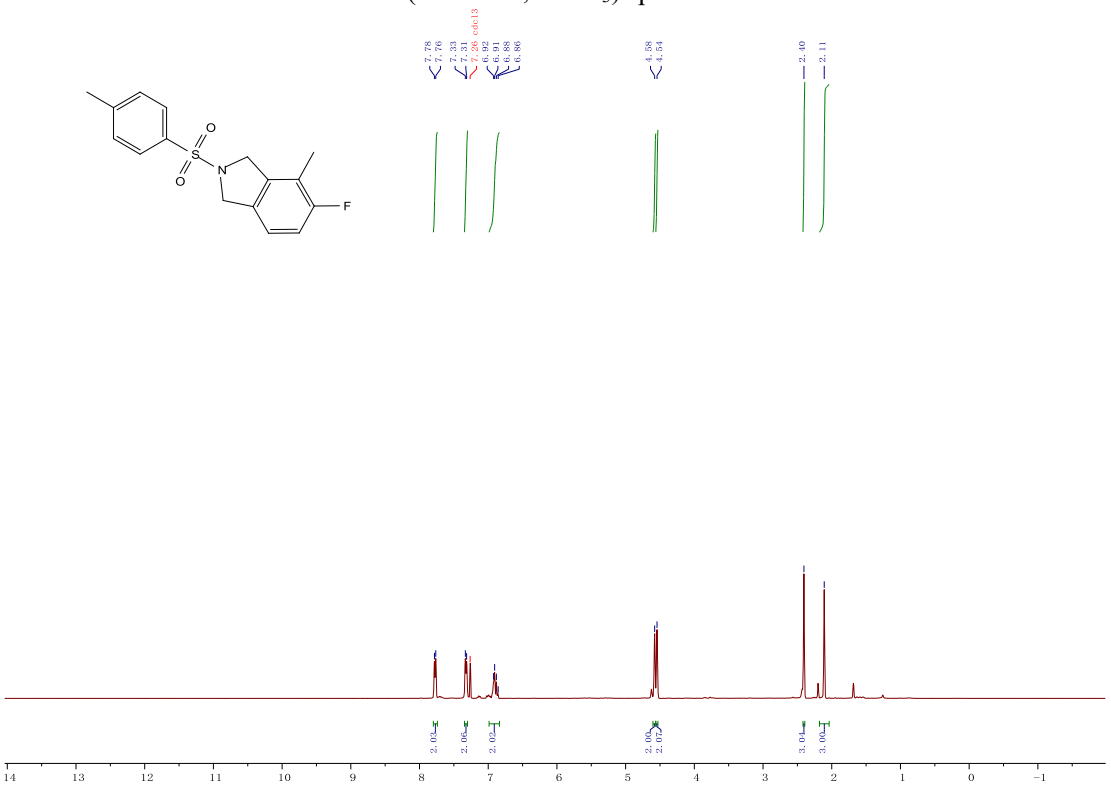
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ag**



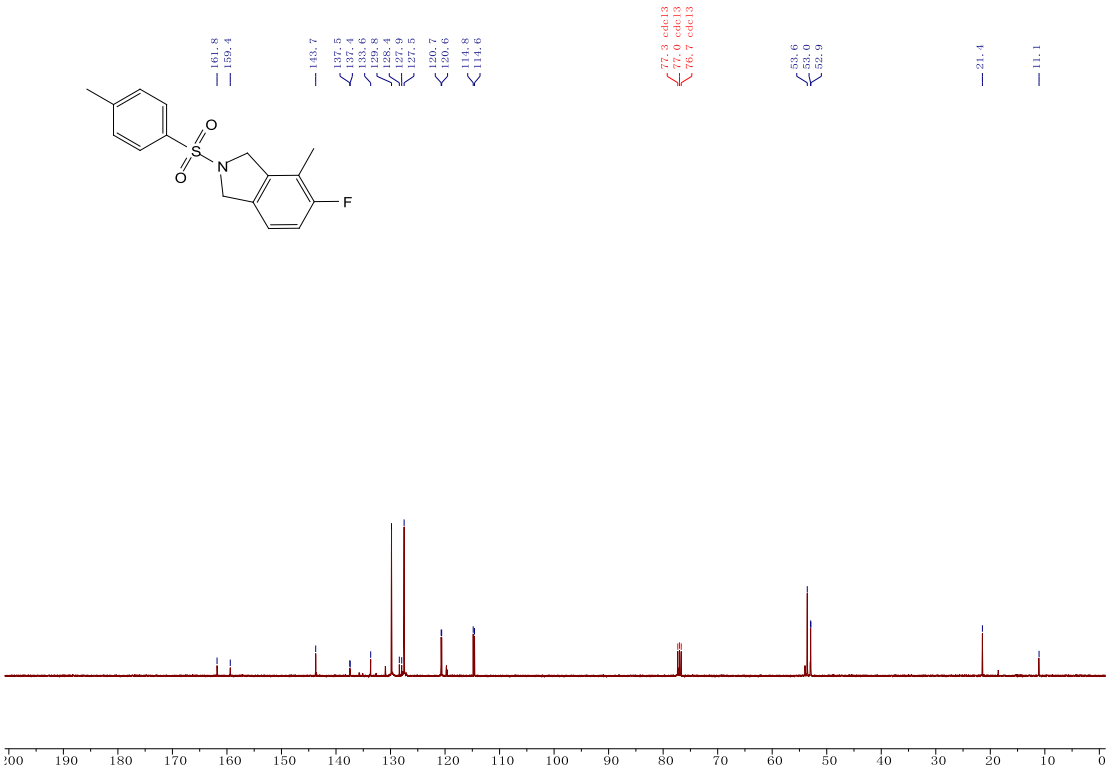
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ag**



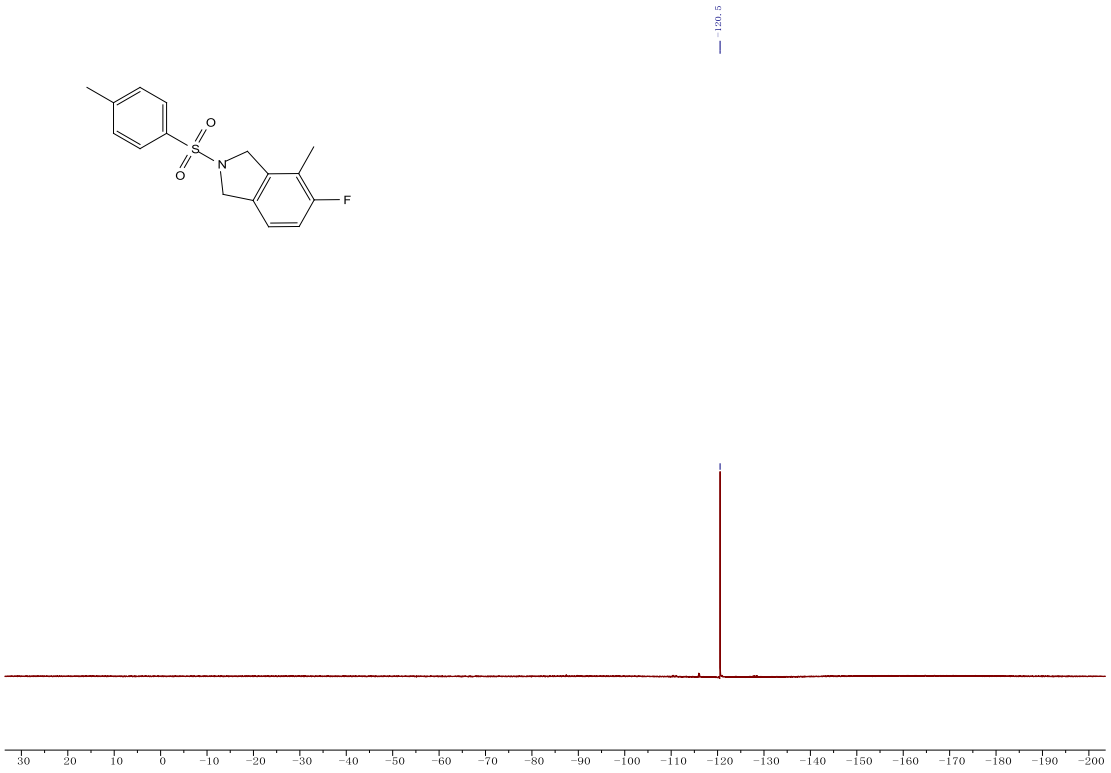
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ah**



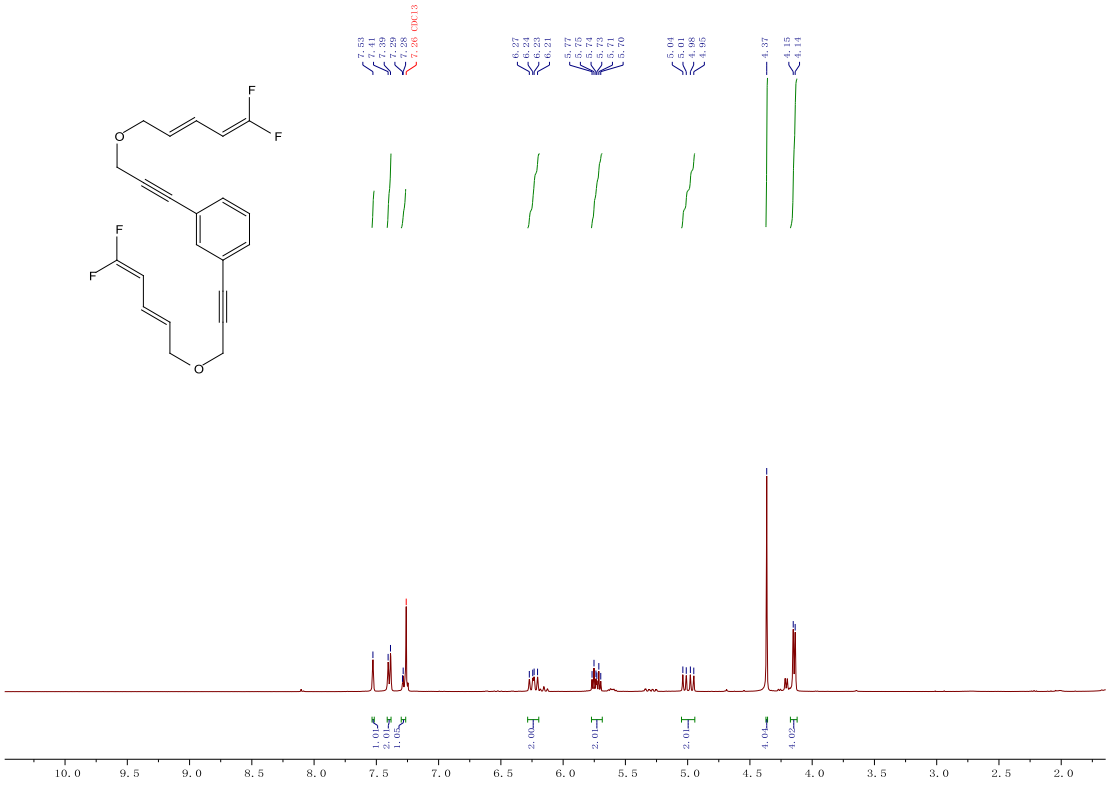
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ah**



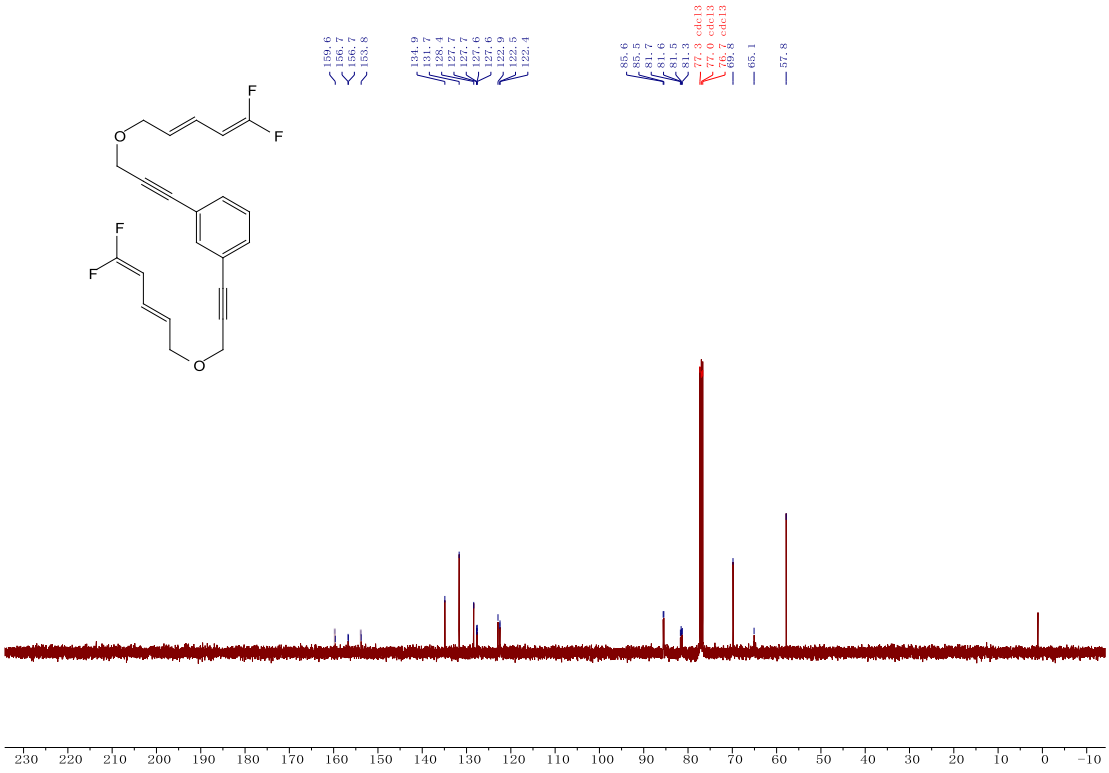
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ah**



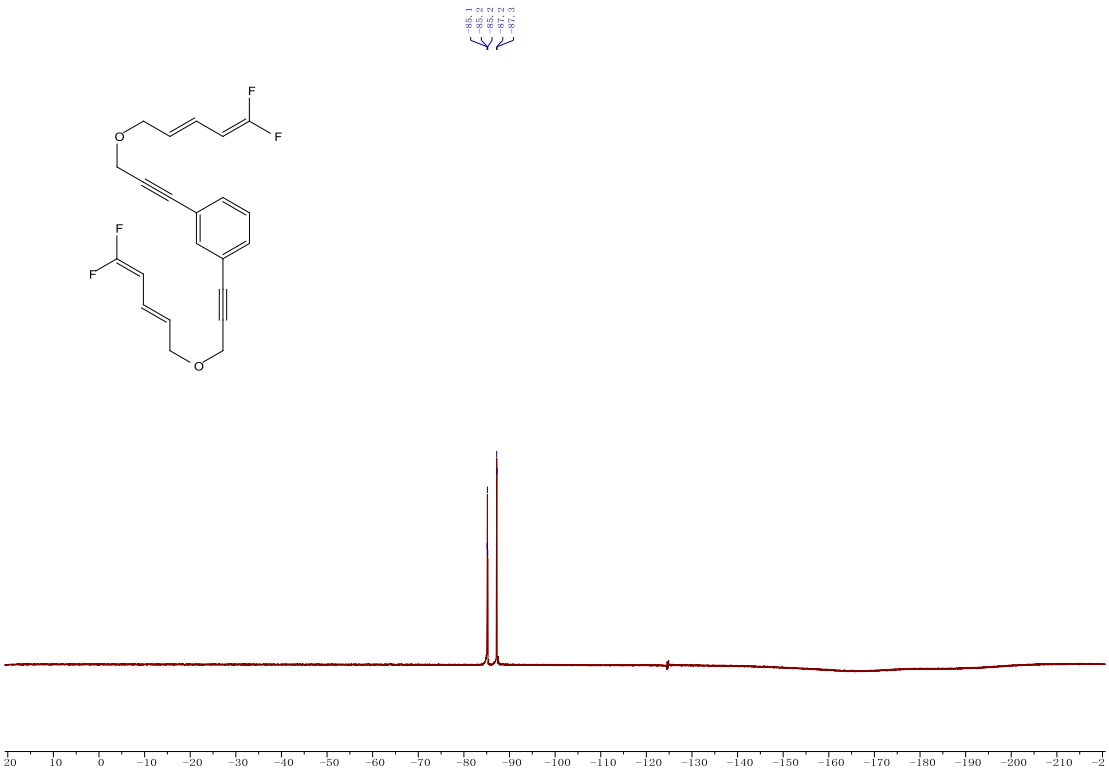
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**



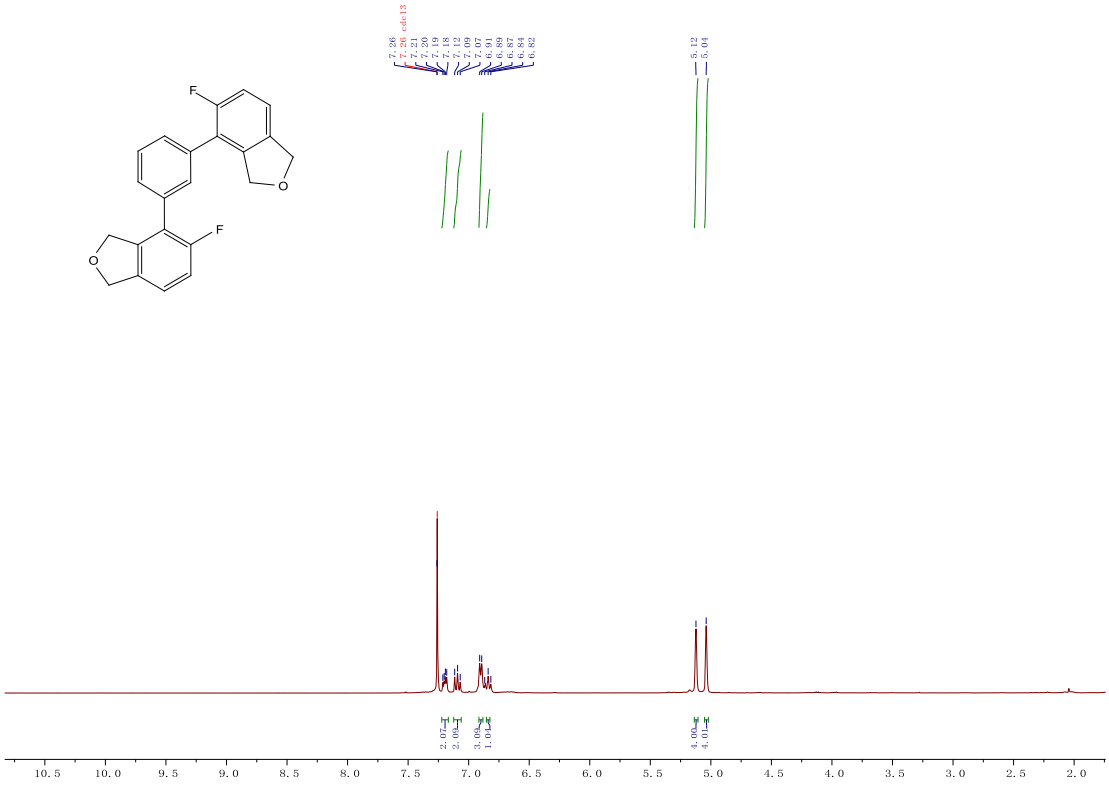
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**



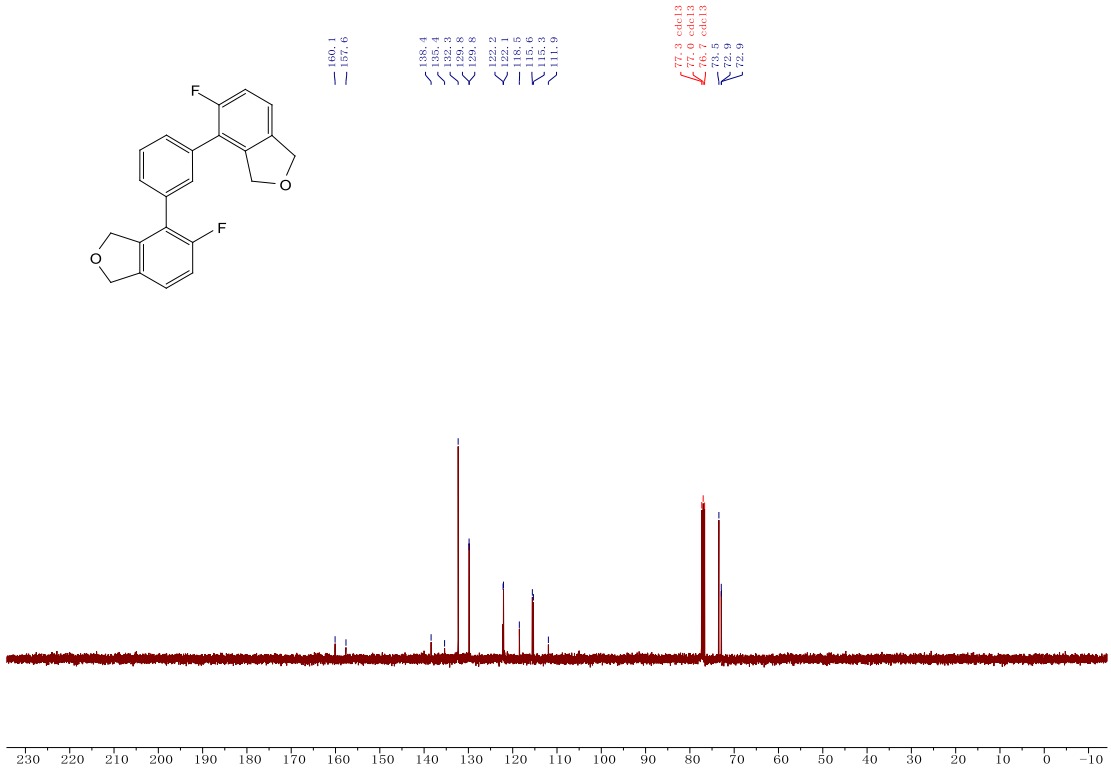
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5**



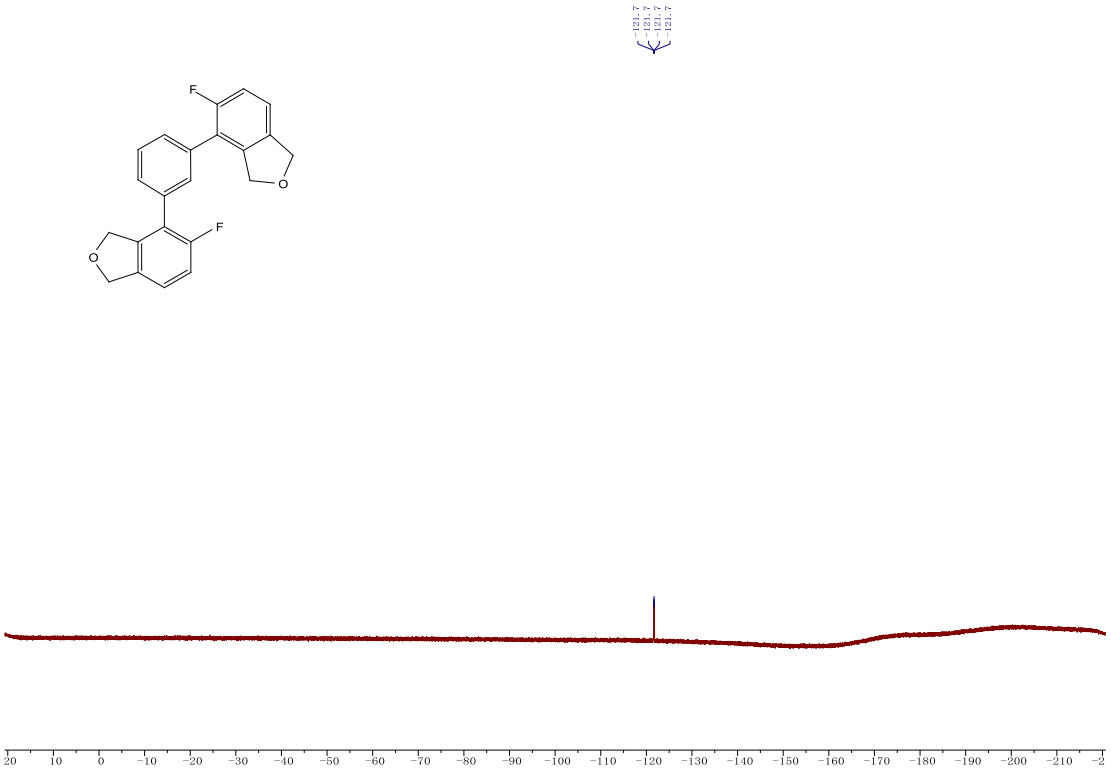
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



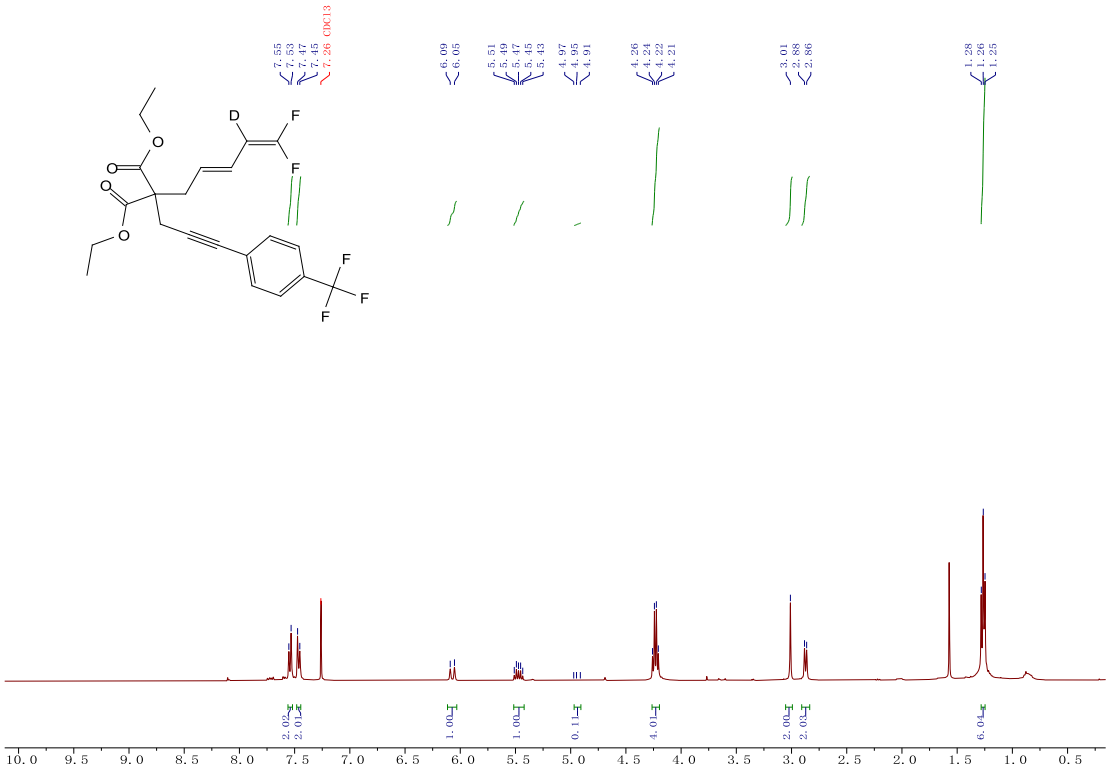
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**



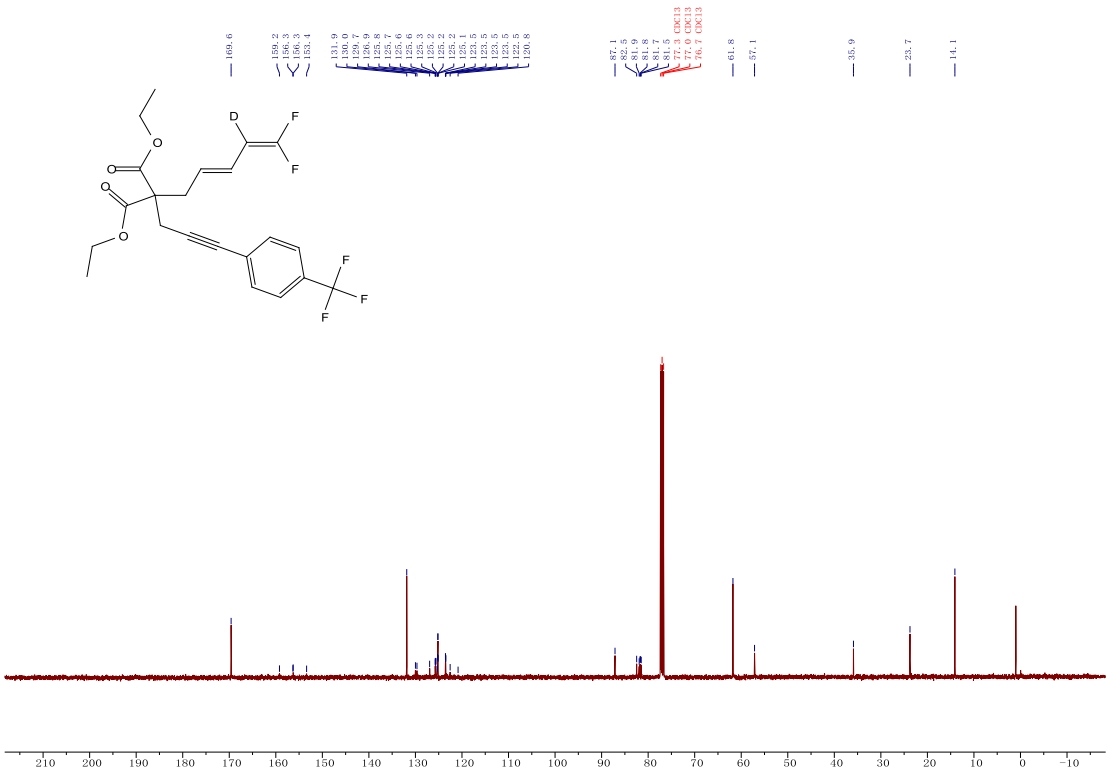
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **6**



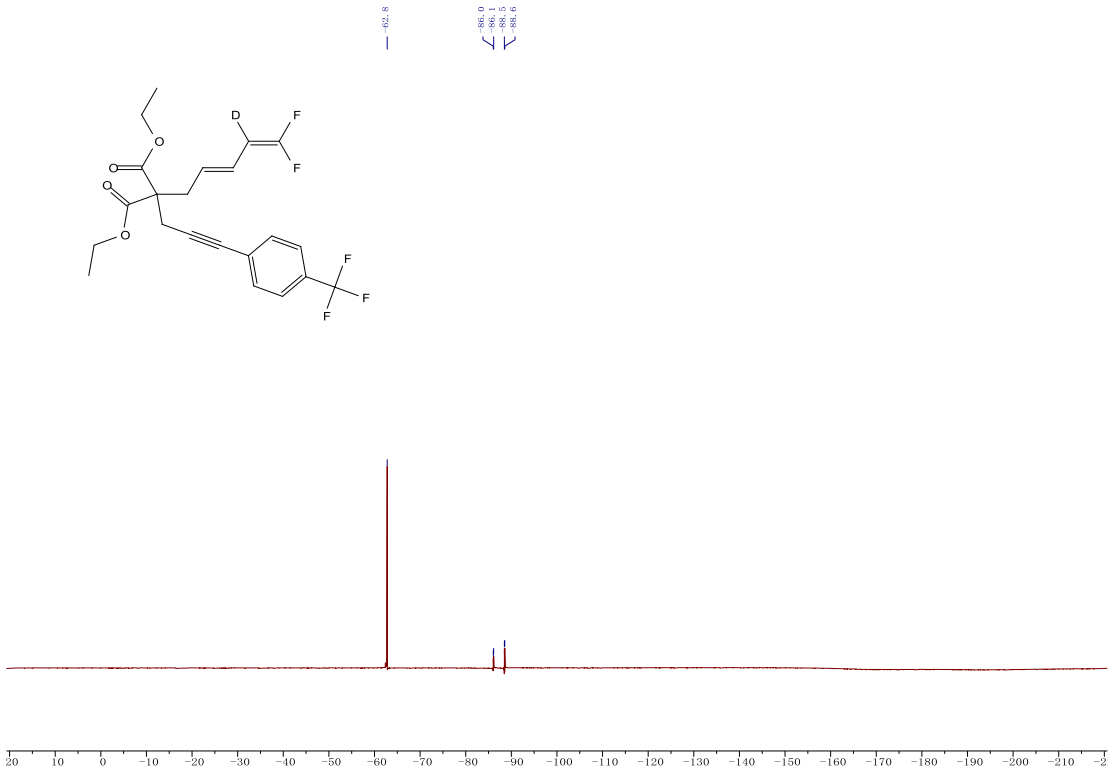
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **D-3n**



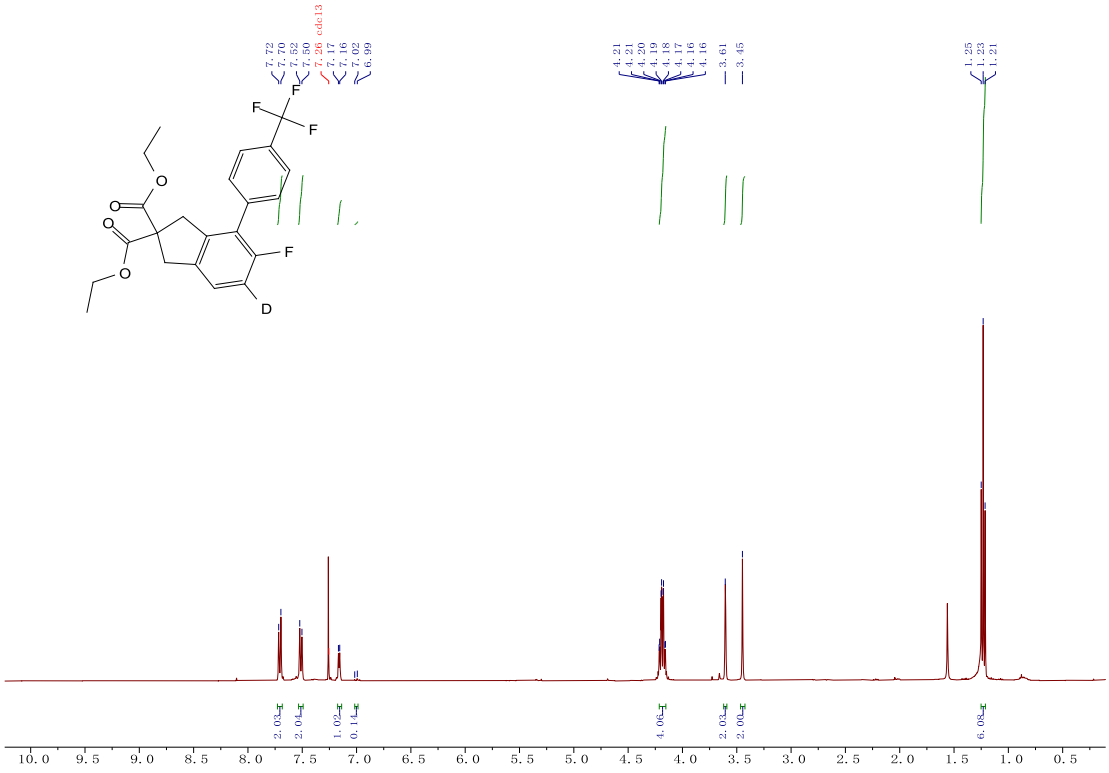
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **D-3n**



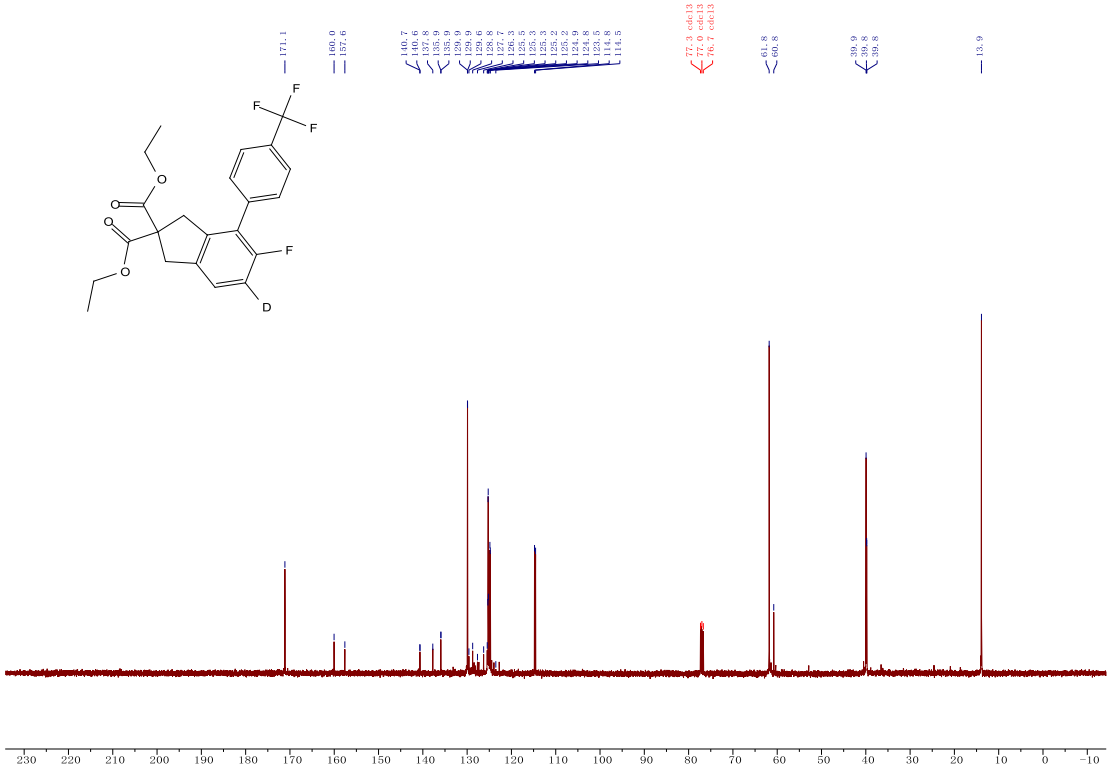
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **D-3n**



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



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



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