Supporting Information

Electrochemical Aminotrifluromethylation of Unactivated Alkenes with Langlois' Reagent as the CF_3 Source

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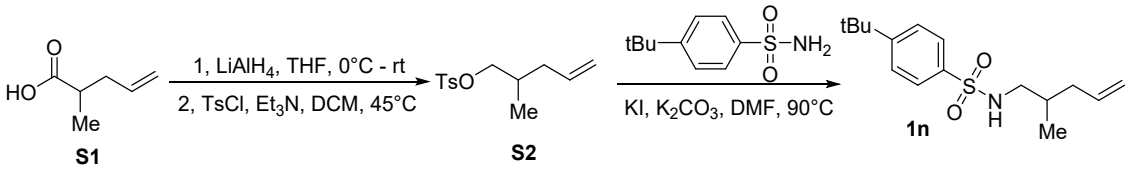
Content

1. General comments

Chemicals were purchased from Adamas, Bidepharm., TCI, or Aladdin and used as such unless stated otherwise. Acetonitrile was purchased from Aladdin (AR, >99% (GC)). The instrument for electrolysis is a domestic dual display DC stabilized power supply (HY3005B). Cyclic voltammograms were obtained on a CHI660E potentiostat. NMR spectra were recorded on Bruker AV 400 spectrometer. Chemical shifts (ppm) are given relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C solvent. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), m (multiplet) and br.s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. High-resolution mass spectra HRMS spectra were recorded on a Thermo Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions preparing sample solution in methanol. The data are given as mass units per charge (m/z). GC yields were calculated using hexadecane as an internal standard. Gas chromatography analysis was performed on an Agilent 6820 instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using nitrogen as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel., 54-74 μm, 200-300 mesh (Yucheng Chemical CO., LTD, Shanghai). Substrates **1a-1p** were prepared according to our previous report.[1]

2. General procedures

2.1.1 General procedures for synthesizing substrates 1n[4]



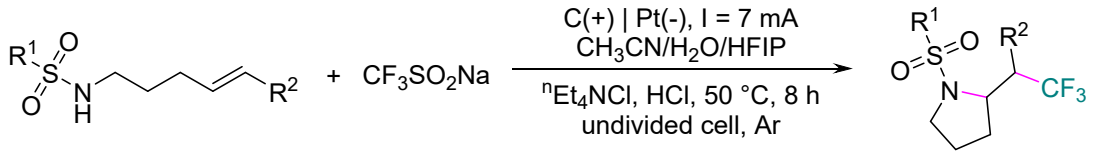
Step 1: To a stirred suspension of $LiAlH_4$ (0.95 g, 25 mmol, 1.0 equiv) in anhydrous THF (50 mL) was slowly added a solution of 2-methylpent-4-enoic acid (2.85 g, 25 mmol, 1.0 equiv) in THF (10 mL). After 16 h at room temperature, the reaction mixture was cooled to 0 °C and cautiously treated with water (1.9 mL), then with a 15% aqueous solution of NaOH (1.9 mL), and then with water (5.7 mL). After 1 h

of stirring at room temperature, the resulting suspension was filtered through Celite. The insoluble salts were washed with diethyl ether (2 x 20 mL) and the filtrate was dried over $MgSO_4$. Filtration and concentration under reduced pressure gave 2.85 g (94%) of 2-methylpent-4-en-1-ol, which was directly engaged in the next step without further purification.

Step 2: To an oven-dried round bottom flask (50 mL) equipped with a stirring bar was added 2-methylpent-4-en-1-ol (5 mmol, 0.5 g, 1.00 eq.), 4-methylbenzenesulfonyl (6 mmol, 1.14g, 1.20 eq.) triethylamine (7 mmol, 0.995 mL, 1.40 eq.) in 25 mL DCM. Then the reaction mixture was stirred at 45° for 24 hours. After the reaction was completed, the reaction mixture was washed with brine, and dried over Na_2SO_4. The crude product was purified by column chromatography after the removal of the solvent to afford product **S2** in 0.71 g, 56% yield.

Step 3: To an oven-dried round bottom flask (50 mL) equipped with a stirring bar was added **S2** (2 mmol, 0.51 1.00 eq.), 4-(tert-butyl)benzenesulfonamide (2 mmol, 0.85g, 2.00 eq.), potassium iodide (0.15 mmol, 25 mg, 0.15 eq.), potassium carbonate (3mmol, 0.415g, 3.00 eq.) in 20 mL DMF. Then the reaction mixture was stirred at 90° for 12 hours. After the reaction was completed, the reaction mixture was washed with brine, dried over Na_2SO_4. The crude product was purified by column chromatography after the removal of the solvent to afford **1n** in 442.5 mg, 75% yield.

2.1.2 General procedures for the electrochemical oxidative trifluoromethylation of unactivated alkenes

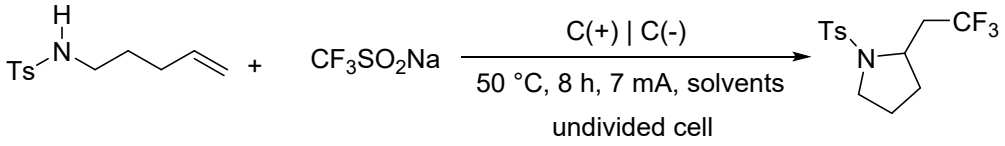


1a-1n **3a-3n**

To an oven-dried tube (10 mL) equipped with a stirring bar was added **1a-1n** (0.4 mmol, 95.6 mg), CF_3SO_2Na (1.0 mmol, 156 mg), nEt_4NCl (0.6 mmol, 99.4 mg) and CH_3CN/H_2O (5/1 mL). The reaction tube was equipped with platinum electrodes (1.0 cm×2.0 cm×0.1 mm) as the cathode and graphite (1.0 cm×2.0 cm×2 mm) as the anode. The tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid solvent HFIP (0.35 mL) and HCl (6 ul) were added through the septum. Then the reaction mixture was stirred and electrolyzed at a constant current of 7 mA under 50 °C and argon atmosphere for 8 hours. After TLC indicated complete conversion of the starting material, the reaction mixture was diluted with sat. NaCl and extracted with EtOAc (3 x 5 mL). The combined organic

phase was concentrated under reduced pressure and crude products were purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give the pure product **3a-3n**.

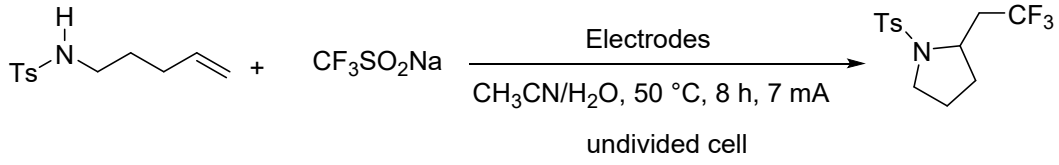
2.1.3 Solvents optimization of electrochemical aminotrifluromethylation of unactivated alkenes.



Entry	Solvents	Yield (%)
1	CH_3CN/H_2O	31.4
2	CH_3CN	7.5
3	MeOH	15.1
4	DCM	7.4
5	THF	10.6
6	DMSO	12.5
7	CH_3CN/H_2O (5:1)	50.8
8	CH_3CN/H_2O (3:1)	39.4
9	CH_3CN/H_2O (2:1)	31.8
10	CH_3CN/H_2O (1:1)	17.3
11	CH_3CN/H_2O/HOAc (10:1:0.2)	43.5

(Reaction conditions: graphite 10 x 20 mm, J = 7 mA/cm^2, platinum electrode surface 10 x 10 mm, J = 7 mA/cm^2, the distance of electrodes = 7 mm, constant current electricity of 7 mA, undivided cell, **1a** 0.4 mmol, **2a** 1.0 mmol, CH_3CN 5 mL , 50 °C, 8 h. GC yield of mixture **3a** was determined by using hexadecane as the internal standard.)

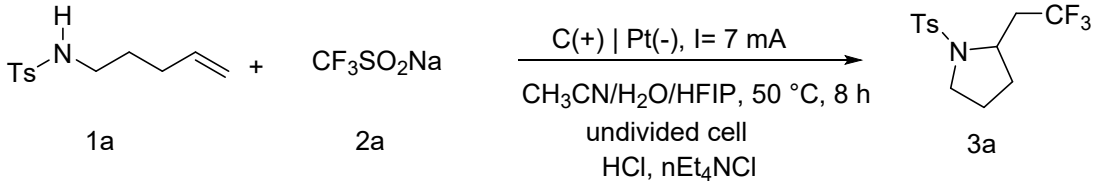
2.1.4 Electrodes optimization of electrochemical aminotrifluromethylation of unactivated alkenes



Entry	Electrode	Yield（%）
1	C (+) | Pt (-)	55
2	C (+) | C (-)	50.8
3	C (+) | Ni (-)	13.2
4	C (+) | SS (-)	47.1
5	Pt (+) | C (-)	17.4

(Reaction conditions: Anode area 10 x 20 mm, J = 7 mA/cm^2, Cathode area 10 x 10 mm, J = 7 mA/cm^2, the distance of electrodes = 7 mm, constant current electricity of 7 mA, undivided cell, **1a** 0.4 mmol, **2a** 1.0 mmol, CH_3CN 5 mL,H_2O 1mL, 50 °C, 8 h. GC yield of mixture **3a** was determined by using hexadecane as the internal standard.)

2.1.5 Additives optimization of electrochemical aminotrifluromethylation of unactivated alkenes

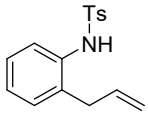


1a 2a 3a

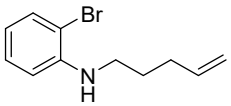
Entry	Other condition	Yield（%）
1[a]	HOAc 0.1 mL	42.2
2[a]	HOAc 0.2 mL	29.0
3[a]	HOAc/HFIP 0.1/0.2 mL	30.3
4[a]	HFIP 0.2 mL	59
5[a]	HFIP 0.35 mL	65
6[a]	HFIP 0.75 mL	63
7[b]	nMe_4NCl 0.3 equiv.	43.9
8[b]	nEt_4NCl 0.3 equiv.	48.8
9[b]	nBuNCl 0.3 equiv.	39.1
10[b]	nEt_4NCl 0.2 equiv.	42.9
11[b]	nEt_4NCl 0.4 equiv.	40.6
12[b]	nEt_4NCl 0.5 equiv.	48.6
13[b]	nEt_4NCl 1.0 equiv.	54.2
14[b]	nEt_4NCl 1.5 equiv.	79.6
15[b]	nEt_4NCl 2 equiv.	70.3
16[c]	HCl	66.0
17[c]	NaOH	0
18[c]	HCl 4.5 μL	56.9
19[c]	HCl 6 μL	83.0 (79) [d]
20[c]	HCl 12 μL	72.5

(Reaction conditions [a]: graphite 10 x 20 mm, J = 7 mA/cm^2, platinum electrode surface 10 x 10 mm, J = 7 mA/cm^2, the distance of electrodes = 10 mm, constant current electricity of 7 mA, undivided cell, **1a** 0.4 mmol, **2a** 1.0 mmol, CH_3CN 5 mL, H_2O 1mL , 50 °C, 8 h. [b]: $CH_3CN/H_2O/HFIP$=5/1.0/0.35 mL [c]: nEt_4NCl 1.5 equiv. [d] GC yield of mixture **3a** was determined by using hexadecane as the internal standard, isolation yield in parentheses.)

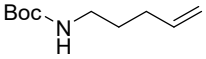
2.2 Failed examples



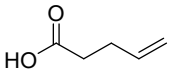
1o



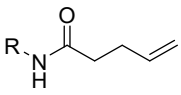
1p



1q

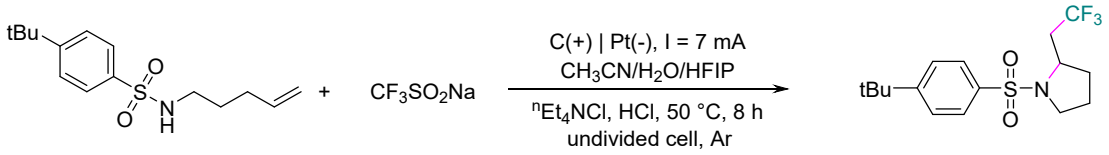


1r



1s, R = Ph
1t, R = Bn

2.3 Large-scale synthesis

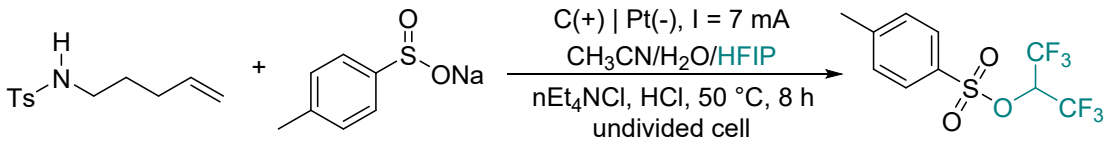


1c, 3.5 mmol, 0.984 g

3c, 0.611 g, 50%

To an oven-dried three-necked flask (50 mL) equipped with a stirring bar was added **1c** (3.5 mmol, 0.984 g), CF_3SO_2Na (7.0 mmol, 1.09 mg), a nEt_4NCl (5.25 mmol, 869.9 mg) and CH_3CN/H_2O (25/5 mL). The reaction tube was equipped with platinum electrodes (1.0 cm×2.0 cm×0.1 mm) as the cathode and graphite (1.0 cm×2.0 cm×2 mm) as the anode. The flask was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid solvent HFIP (1.75 mL) and HCl (30 ul) were added through the septum. Then the reaction mixture was stirred and electrolyzed at a constant current of 7 mA under 50 °C and argon atmosphere for 48 hours. After TLC indicated complete conversion of the starting material, the reaction mixture was diluted with sat. NaCl and extracted with EtOAc (3 x 20 mL). The combined organic phase was concentrated under reduced pressure and crude products were purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give the pure product **3c** in 0.611 g, 50% yield.

2.4 Anodic oxidative coupling of sodium *p*-tolylsulfinate with HFIP



1a

0.4 mmol

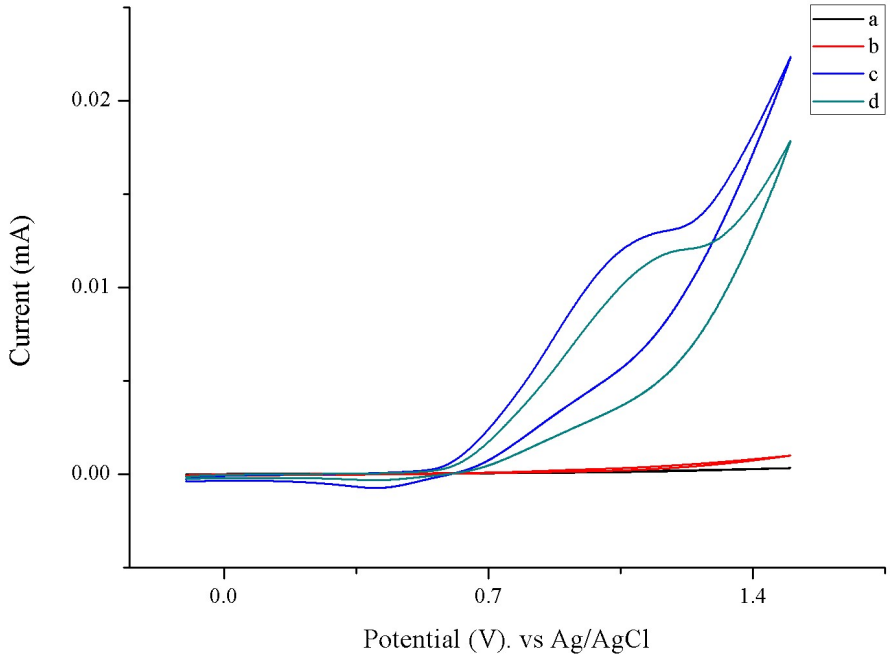
4a, 55% yield

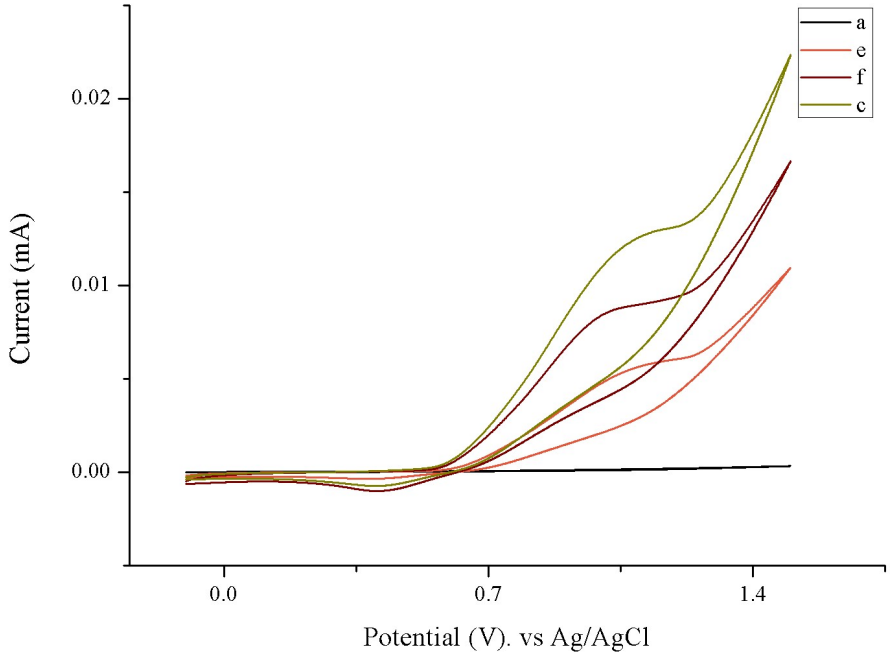
To an oven-dried tube (10 mL) equipped with a stirring bar was added **1a** (0.2 mmol, 47.8 mg), sodium *p*-tolylsulfinate (0.4 mmol, 71.2 mg), nEt_4NCl (0.6 mmol, 99.4 mg) and CH_3CN/H_2O (5/1 mL). The

reaction tube was equipped with platinum electrodes (1.0 cm×2.0 cm×0.1 mm) as the cathode and graphite (1.0 cm×2.0 cm×2 mm) as the anode. The tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid solvent HFIP (0.35 mL) and HCl (6 ul) were added through the septum. Then the reaction mixture was stirred and electrolyzed at a constant current of 7 mA under 50 °C and argon atmosphere for 8 hours. After TLC indicated complete conversion of the starting material, the reaction mixture was diluted with sat. NaCl and extracted with EtOAc (3 x 5 mL). The combined organic phase was concentrated under reduced pressure and crude products were purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give the pure product **4a** in 70.8 mg, 55% yield.

2.5 Cyclic voltammetry measurements

Cyclic voltammetry was obtained using a platinum working electrode (1 x 1 cm), and a graphite counter electrode (1 x 1 cm). The reference was an Ag/AgCl electrode submerged in saturated KCl solution and separated from the reaction by a salt bridge at room temperature. The scan rate was 0.10 V/s, ranging from 0.0 V to 1.5 V. **a)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M); **b)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M) + 0.4 mmol **1c**; **c)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M) + 8 mmol CF_3SO_2Na; **d)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M) + 0.4 mmol **1c** + 8 mmol CF_3SO_2Na; **e)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M) + 2 mmol CF_3SO_2Na; **f)** MeOH (10 mL) + nBu_4NBF_4 (0.01 M) + 4 mmol CF_3SO_2Na.

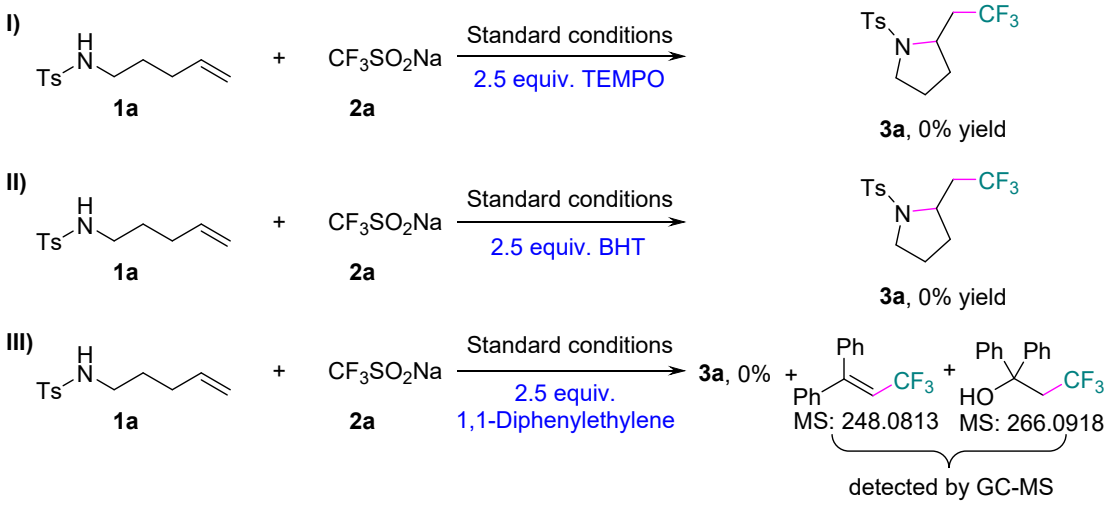


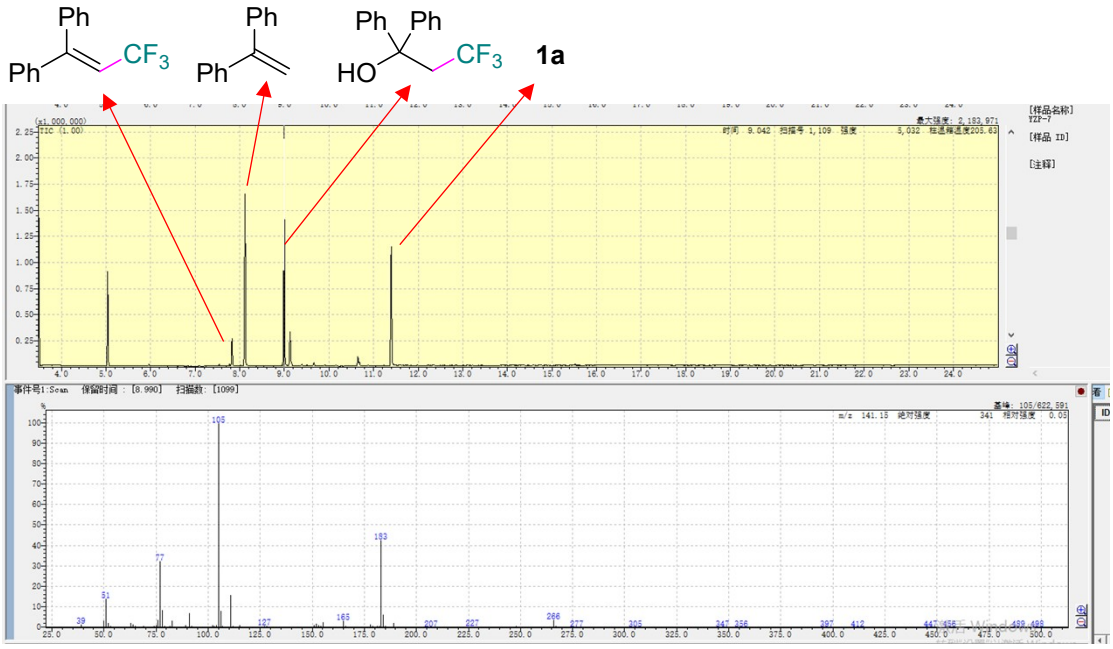


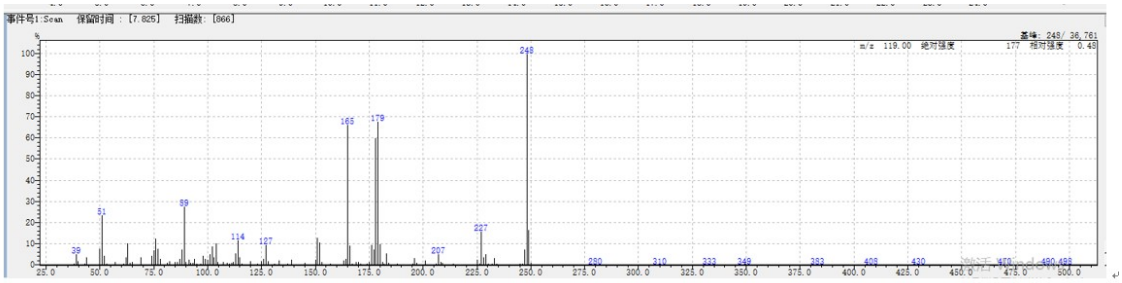
2.6 Control experiments

To an oven-dried tube (10 mL) equipped with a stirring bar was added **1a** (0.4 mmol, 95.6 mg), radical scavengers (TEMPO or THP or 1,1-Diphenylethylene, 2.5 eq.), CF_3SO_2Na (1.0 mmol, 156 mg), nEt_4NCl (0.6 mmol, 99.4 mg) and CH_3CN/H_2O (5/1 mL). The reaction tube was equipped with platinum

electrodes (1.0 cm×2.0 cm×0.1 mm) as the cathode and graphite (1.0 cm×2.0 cm×2 mm) as the anode. The tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid solvent HFIP (0.35 mL) and HCl (6 ul) were added through the septum. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under 50 °C and argon atmosphere for 8 hours, and then those reaction mixtures were detected by GC-MS.



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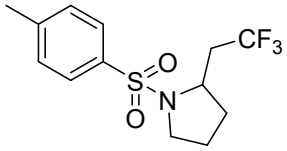
m/z 119.00 绝对强度 177 相对强度 0.48
%
248
165
179
89
51
227
114
127
39
207

3. Characterization data of products



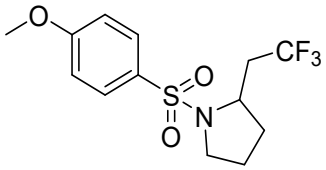
Tosyl-2-(2,2,2-trifluoroethyl)pyrrolidine (3a): (97 mg, white solid, yield: 79%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 3.79 – 3.63 (m, 1H), 3.51 – 3.38 (m, 1H), 3.16 (dt, J = 10.2, 6.9 Hz, 1H), 3.01 (dqd, J = 14.6, 11.7, 2.8 Hz, 1H), 2.44 (s, 3H), 2.36 – 2.17 (m, 1H), 1.89 – 1.68 (m, 3H), 1.56 – 1.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.86, 133.56, 129.84, 127.56, 125.69 (q, J_{C-F} = 278.76 Hz), 54.58 (d, J_{C-F} = 3.03 Hz), 48.97, 40.45 (q, J_{C-F} = 26.26 Hz), 31.56, 23.87, 21.50.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.77.

The analytical data are consistent with those reported in the literature.[2]



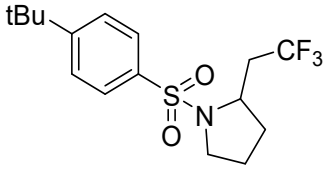
1-((4-Methoxyphenyl)sulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3b): (77 mg, white solid, yield: 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.71 (ddd, *J* = 8.3, 6.1, 3.3 Hz, 1H), 3.42 (ddd, *J* = 9.8, 6.1, 5.0 Hz, 1H), 3.15 (dt, *J* = 10.8, 6.3 Hz, 1H), 3.00 (ddd, *J* = 14.7, 11.7, 2.9 Hz, 1H), 2.25 (dt, *J* = 14.8, 10.5 Hz, 1H), 1.84 – 1.72 (m, 3H), 1.59 – 1.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14,, 129.63, 128.21,125.70 (q, J_{C-F}=278.76 Hz), 114.35, 55.58, 54.55 (d, J_{C-F} =3.03 Hz), 48.97, 40.45 (q, J_{C-F} = 26.26 Hz), 31.58, 23.89.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.78.

HRMS (ESI-TOF) Calc. for $C_{13}H_{16}F_3NNaO_3S^+$ $[M+Na]^+$: 346.0695; found: 346.0698.



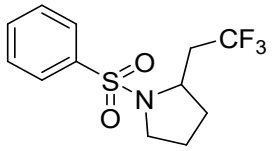
1-((4-(tert-Butyl)phenyl)sulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3c): (117.2 mg, white solid, yield: 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 3.85 – 3.68 (m, 1H), 3.44 (ddd, *J* = 9.7, 6.1, 4.9 Hz, 1H), 3.18 (dt, *J* = 10.7, 6.5 Hz, 1H), 3.02 (ddd, *J* = 14.7, 11.7, 2.9 Hz, 1H), 2.26 (dt, *J* = 14.9, 10.5 Hz, 1H), 1.80 (dd, *J* = 4.6, 1.8 Hz, 3H), 1.55 – 1.45 (m, 1H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.77, 133.54, 127.45, 126.19, 125.71 (q, J_{C-F} = 277.75 Hz), 54.54 (d, J_{C-F} = 4.04 Hz), 48.96, 40.47 (q, J_{C-F}=26.26 Hz), 35.16, 31.58, 31.04, 23.90.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.74.

HRMS (ESI-TOF) Calc. for $C_{16}H_{23}F_3NO_2S^+$ $[M+H]^+$: 350.1396; found: 350.1400.



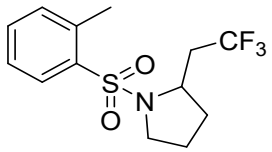
1-(Phenylsulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3d): (78 mg, white solid, yield: 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 3.75 (dtd, *J* = 11.4, 5.7, 2.7 Hz, 1H), 3.45 (ddd, *J* = 10.4, 6.4, 5.4 Hz, 1H), 3.18 (dt, *J* = 10.4, 6.9 Hz, 1H), 3.06 – 2.89 (m, 1H), 2.26 (dq, *J* = 14.8, 10.5 Hz, 1H), 1.86 – 1.71 (m, 3H), 1.58 – 1.43 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.54, 133.01, 129.24, 127.51 (q, J_{C-F} = 277.75 Hz), 127.50, 54.64 (d, J_{C-F} = 3.03 Hz), 48.96, 40.42 (q, J_{C-F} = 26.26 Hz), 31.55, 23.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.77.

HRMS (ESI-TOF) Calc. for $C_{12}H_{14}F_3NNaO_2S^+$ $[M+Na]^+$: 316.0590; found: 316.0595.



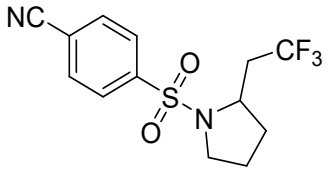
1-(O-tolylsulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3e): (74 mg, white solid, yield: 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 (ddd, *J* = 8.0, 5.9, 1.7 Hz, 2H), 4.05 (ddt, *J* = 10.8, 6.8, 3.2 Hz, 1H), 3.39 – 3.21 (m, 2H), 2.86 – 2.70 (m, 1H), 2.66 (s, 3H), 2.18 (dt, *J* = 14.7, 10.4 Hz, 1H), 2.04 (dq, *J* = 7.9, 3.2 Hz, 1H), 1.96 – 1.74 (m, 3H), 1.47 – 1.14 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.98, 136.54, 133.06, 132.89, 129.73, 126.34, 125.53(q,J_{C-F} = 278.76 Hz), 53.93 (d, J_{C-F} = 3.03 Hz), 48.34, 39.54 (q, J_{C-F} = 26.26 Hz), 31.64, 24.13, 20.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.67.

HRMS (ESI-TOF) Calc. for $C_{13}H_{16}F_3NNaO_2S^+$ $[M+Na]^+$: 330.0746; found: 330.0749.



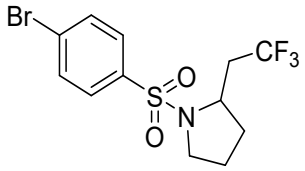
4-((2-(2,2,2-Trifluoroethyl)pyrrolidin-1-yl)sulfonyl)benzonitrile (3f): (62 mg, white solid, yield: 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 3.74 (ddt, *J* = 11.0, 7.3, 3.7 Hz, 1H), 3.49 (dt, *J* = 10.3, 5.8 Hz, 1H), 3.14 (dt, *J* = 10.3, 6.9 Hz, 1H), 2.95 (ddd, *J* = 14.6, 11.5, 2.9 Hz, 1H), 2.29 (dt, *J* = 14.8, 10.4 Hz, 1H), 1.91 – 1.74 (m, 3H), 1.59 (ddd, *J* = 11.9, 6.1, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.83, 133.07, 128.04, 125.43 (q, J_{C-F} = 278.76 Hz), 117.13, 116.75, 54.87 (d, J_{C-F} = 4.04 Hz), 48.99, 40.23 (q, J_{C-F} = 27.27 Hz), 31.50, 23.83.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.75.

HRMS (ESI-TOF) Calc. for $C_{13}H_{13}F_3N_2NaO_2S^+$ $[M+Na]^+$: 341.0542; found: 341.0551.



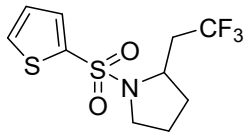
1-((4-Bromophenyl)sulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3g): (105 mg, white solid, yield: 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 3.79 – 3.60 (m, 1H), 3.45 (ddd, *J* = 10.3, 6.5, 5.4 Hz, 1H), 3.13 (dt, *J* = 10.3, 7.0 Hz, 1H), 2.96 (dtd, *J* = 14.5, 11.6, 2.9 Hz, 1H), 2.27 (dp, *J* = 14.8, 10.4 Hz, 1H), 1.89 – 1.71 (m, 3H), 1.59 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.49, 132.55, 128.97, 128.12, 125.55 (q, J_{C-F} = 278.76 Hz), 54.71 (d, J_{C-F} = 3.03 Hz), 49.01, 40.35 (q, J_{C-F} = 27.27 Hz), 31.53, 23.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.76.

HRMS (ESI-TOF) Calc. for $C_{12}H_{13}Br^{79}F_3NNaO2S^+$ $[M+Na]^+$: 393.9695; found: 393.9702. Calc. for $C_{12}H_{13}Br^{81}F_3N\ NaO_2S^+$ $[M+Na]^+$: 393.9674; found: 393.9681.



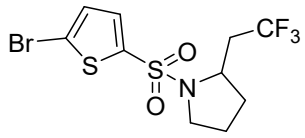
1-(Thiophen-2-ylsulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3h): (64 mg, white solid, yield: 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.49 (dd, *J* = 3.9, 1.1 Hz, 1H), 3.79 (td, *J* = 5.0, 4.4, 2.6 Hz, 1H), 3.53 (ddd, *J* = 9.9, 6.2, 4.9 Hz, 1H), 3.25 (dt, *J* = 10.9, 6.6 Hz, 1H), 2.97 (dqd, *J* = 14.4, 11.5, 2.9 Hz, 1H), 2.32 (dt, *J* = 14.8, 10.4 Hz, 1H), 2.03 – 1.79 (m, 3H), 1.64 (m, 1H), 1.27 – 1.24 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.34, 132.62, 132.16, 127.62,125.60 (q, J_{C-F} = 278.76 Hz), 55.06 (q, J_{C-F} = 4.04 Hz), 49.20, 40.23 (q, J_{C-F} = 26.26 Hz), 31.53, 23.97.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.71.

HRMS (ESI-TOF) Calc. for $C_{10}H_{13}F_3NO_2S_2^+$ $[M+H]^+$:300.0334; found: 300.0341.



1-((5-Bromothiophen-2-yl)sulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3i):

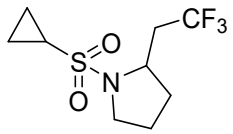
(70mg,white solid,yield:47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 3.9 Hz, 1H), 3.84 – 3.68 (m, 1H), 3.49 (ddd, *J* = 9.9, 6.3, 5.1 Hz, 1H), 3.28 – 3.10 (m, 1H), 2.95 (dqd, *J* = 14.5, 11.6, 2.9 Hz, 1H), 2.29 (dp, *J* = 14.8, 10.4 Hz, 1H), 1.97 – 1.74 (m, 3H), 1.63 (td, *J* = 6.6, 5.6, 1.7 Hz, 1H).

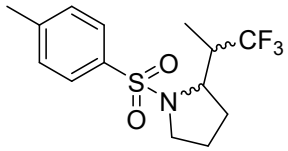
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.27, 132.70, 130.67, 125.53 (q, J_{C-F} = 278.76 Hz), 120.12, 55.16 (d, J_{C-F} = 4.04 Hz), 49.23, 40.29 (q, J_{C-F} = 27.27 Hz), 31.54, 23.98.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.71.

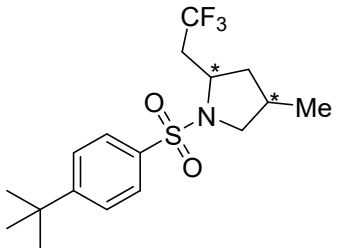
HRMS (ESI-TOF) Calc. for $C_{10}H_{11}Br^{79}F_3NNaO_2S_2^+$ $[M+Na]^+$: 399.9259; found: 399.9259. Calc. for $C_{10}H_{11}Br^{81}F_3NNaO_2S_2^+$ $[M+Na]^+$: 399.9238; found: 399.9238



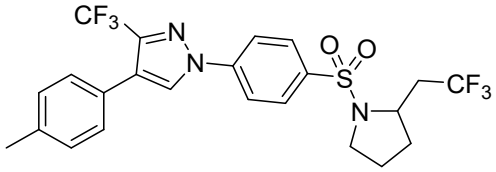
1-(Cyclopropylsulfonyl)-2-(2,2,2-trifluoroethyl)pyrrolidine (3j): (55 mg, white solid, yield: 54%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 – 3.99 (m, 1H), 3.51 – 3.31 (m, 2H), 2.86 (ddd, *J* = 14.8, 11.7, 3.1 Hz, 1H), 2.43 – 2.29 (m, 1H), 2.26 – 2.09 (m, 2H), 2.00 – 1.83 (m, 3H), 1.24 – 1.18 (m, 2H), 1.03 – 0.98 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 125.59 (q, J_{C-F} = 278.76 Hz), 54.42 (d, J_{C-F} = 3.03 Hz), 48.73, 40.16 (q, J_{C-F} = 27.27 Hz), 31.76, 26.40, 24.52, 4.72, 4.42.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.70.
HRMS (ESI-TOF) Calc. for $C_9H_{15}F_3NO_2S^+$ $[M+H]^+$: 258.0770; found: 258.0769.



1-Tosyl-2-(1,1,1-trifluoropropan-2-yl)pyrrolidine (3l-m): (63 mg, white solid, yield: 49%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.4, 2.5 Hz, 2H), 7.33 (t, *J* = 8.2 Hz, 2H), 3.87 – 3.71 (m, 1H), 3.32 (dt, *J* = 5.1, 1.9 Hz, 2H), 3.25 (dt, *J* = 10.4, 7.3 Hz, 1H), 2.70 – 2.55 (m, 1H), 2.43 (d, *J* = 3.3 Hz, 3H), 1.95 – 1.37 (m, 4H), 1.25 (d, *J* = 7.3 Hz, 2H), 1.16 (d, *J* = 7.1 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.86, 143.70, 134.61, 133.43, 129.84, 129.77, 129.04, 128.81, 127.65, 127.55, 126.25, 126.02, 60.46, 60.44, 58.02, 57.99, 49.96, 48.45, 42.16, 41.92, 41.70, 41.46, 28.55, 26.54, 24.67, 23.83, 21.50, 12.05, 6.61.
^{19}F NMR (376 MHz, $CDCl_3$) δ -67.78, -70.24.
HRMS (ESI-TOF) Calc. for $C_{14}H_{18}F_3NNaO_2S^+$ $[M+Na]^+$: 344.0903; found: 344.0907.



1-((4-(tert-butyl)phenyl)sulfonyl)-4-methyl-2-(2,2,2-trifluoroethyl)pyrrolidine (3n): (84 mg, white solid, yield: 77%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 3.74 – 3.44 (m, 2H), 3.41 – 3.14 (m, 1H), 2.91 (t, *J* = 10.9 Hz, 1H), 2.41 – 2.15 (m, 2H), 1.63 – 1.38 (m, 2H), 1.35 (s, 9H), 0.93 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.81, 133.87, 127.47, 126.29, 125.92 (q, J_{C-F} = 278.80 Hz), 55.82, 55.57 (d, J_{C-F} = 3.03 Hz), 41.31, 41.07 (q, J_{C-F} = 27.27 Hz), 35.21, 32.71, 31.09, 16.40.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.75, -63.78.



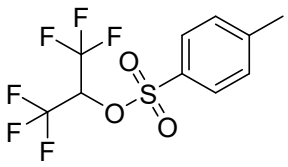
4-(p-Tolyl)-1-(4-((2-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)sulfonyl)phenyl)-3-(trifluoromethyl)-1H-pyrazole (3o): (88 mg, white solid, yield: 43%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 3.70 (dtd, *J* = 11.2, 5.7, 5.0, 2.7 Hz, 1H), 3.53 – 3.40 (m, 1H), 3.13 (dt, *J* = 10.4, 6.9 Hz, 1H), 2.96 (ddd, *J* = 14.6, 11.6, 2.9 Hz, 1H), 2.38 (s, 3H), 2.27 (dt, *J* = 14.8, 10.4 Hz, 1H), 1.91 – 1.72 (m, 3H), 1.61 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.32, 144.18 (d, J_{C-F} = 38.38 Hz), 142.80, 139.88, 136.08, 129.72, 128.68, 128.49, 125.70, 125.56, 123.25 (q, J_{C-F} = 269.67 Hz), 106.27, 54.78 (d, J_{C-F} = 3.03 Hz), 49.02, 40.34 (q, J_{C-F} = 27.27 Hz), 31.54, 23.83, 21.25.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.46, -63.82.

HRMS (ESI-TOF) Calc. for $C_{23}H_{21}F_6NNa_3O_2S^+$ $[M+Na]^+$: 540.1151; found: 540.1152.



1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzenesulfonate (4a): (70.8 mg, colorless oil, yield: 55%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 5.27 (hept, *J* = 5.6 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.64, 131.83, 128.15, 119.86 (q, J_{C-F} = 282 Hz), 71.82 (p, J_{C-F} = 35 Hz), 21.75

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.14.

The analytical data are consistent with those reported in the literature.[3]

3. Reference

1. Y. He, X. Qin, X. He, X.-F. Wu and Z. Yin, *Eur. J. Org. Chem.* , **2021**, 5831-5834.

2. J.-S. Lin, Y.-P. Xiong, C.-L. Ma, L.-J. Zhao, B. Tan and X.-Y. Liu, *Chem. Eur. J.*, 2014, **20**, 1332-1340.

3. E. Deruer, V. Hamel, S. Blais and S. Canesi, *Beilstein J. Org. Chem.* , 2018, **14**, 1203-1207.

4. (a) A. Archambeau, T. Rovis, *Angew. Chem. Int. Ed.* **2015**, *54*, 13337-13340; (b) C. Taillier, B. Gille, V. Bellosta, J. Cossy, *J. Org. Chem.* **2005**, *70*, 2097-2108.

4. Copies of NMR Spectra of products

Figure S1 ^{1}H NMR spectrum for compound 3a

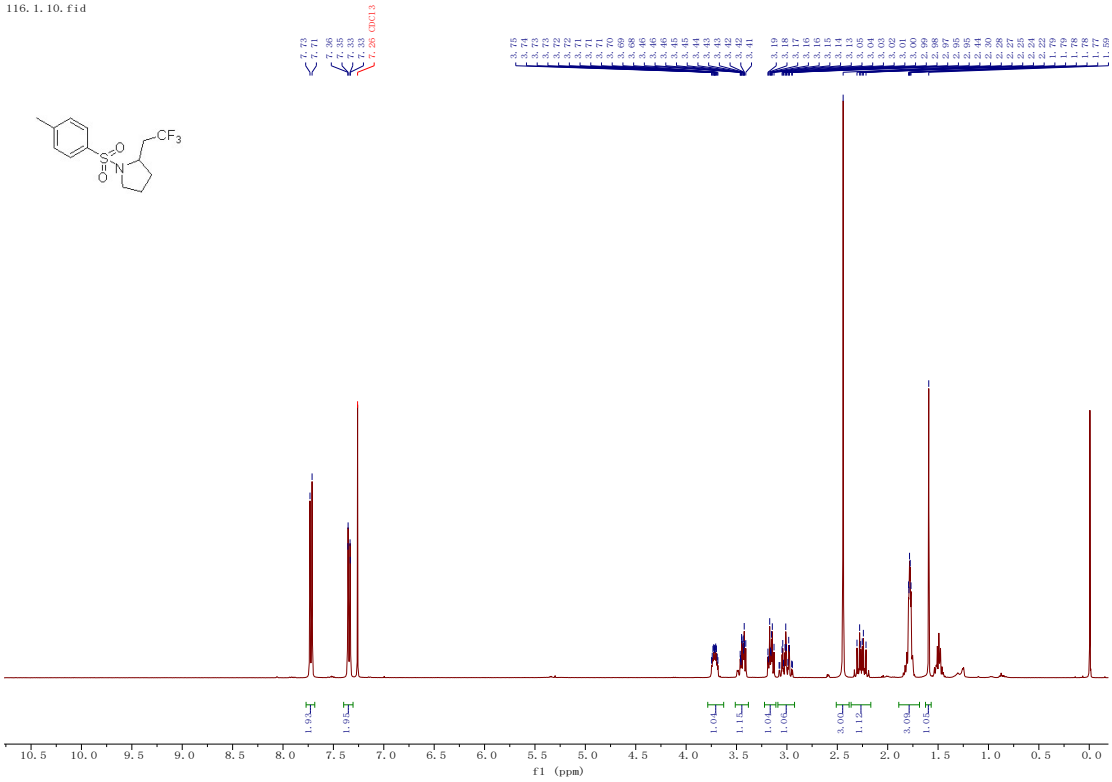


Figure S2 ^{13}C NMR spectrum for compound 3a

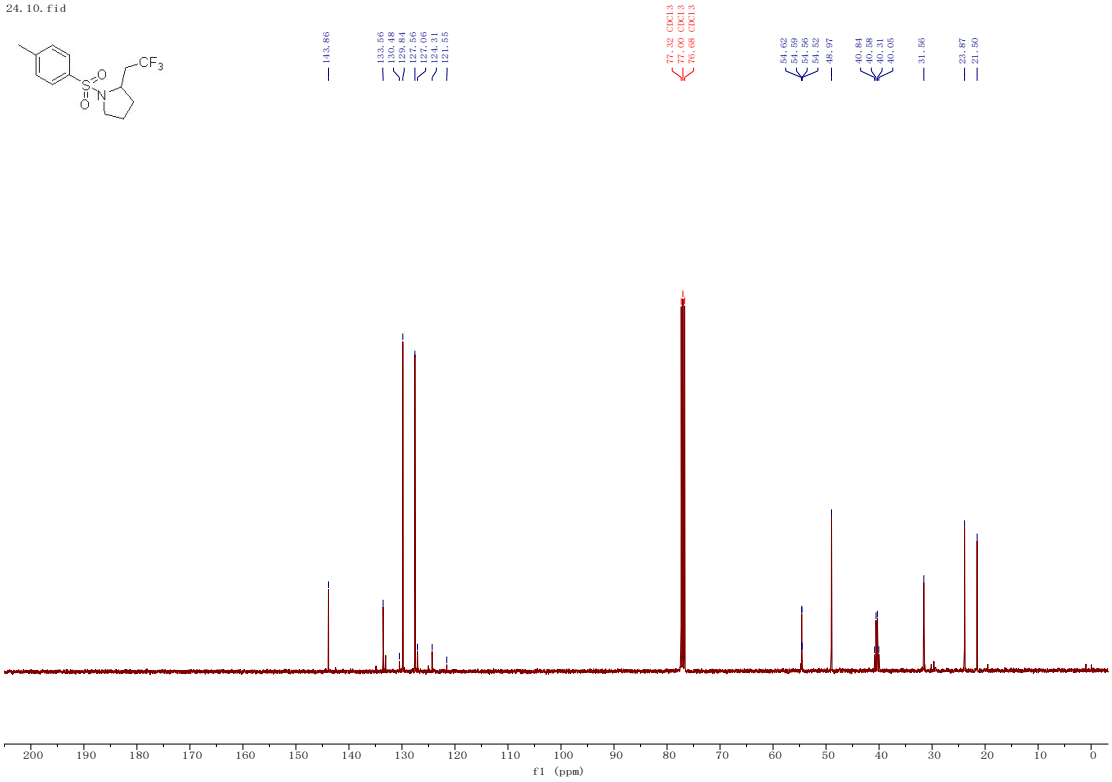


Figure S3 ^{19}F NMR spectrum for compound 3a

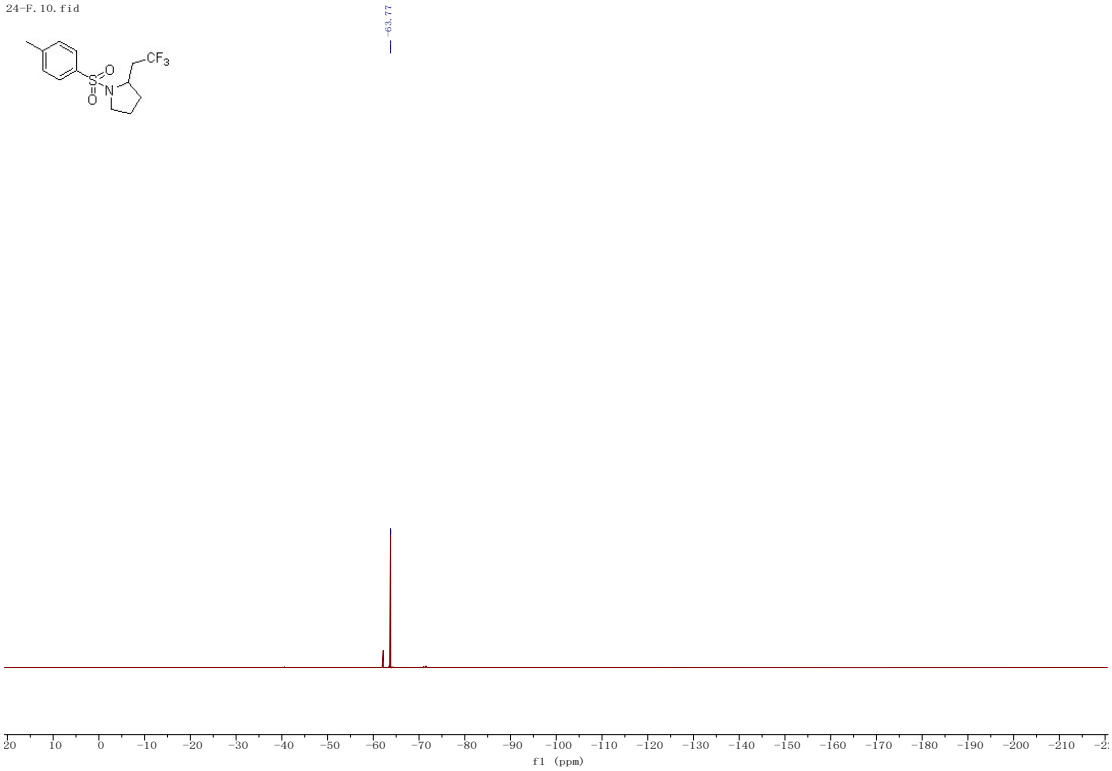


Figure S4 ^{1}H NMR spectrum for compound 3b

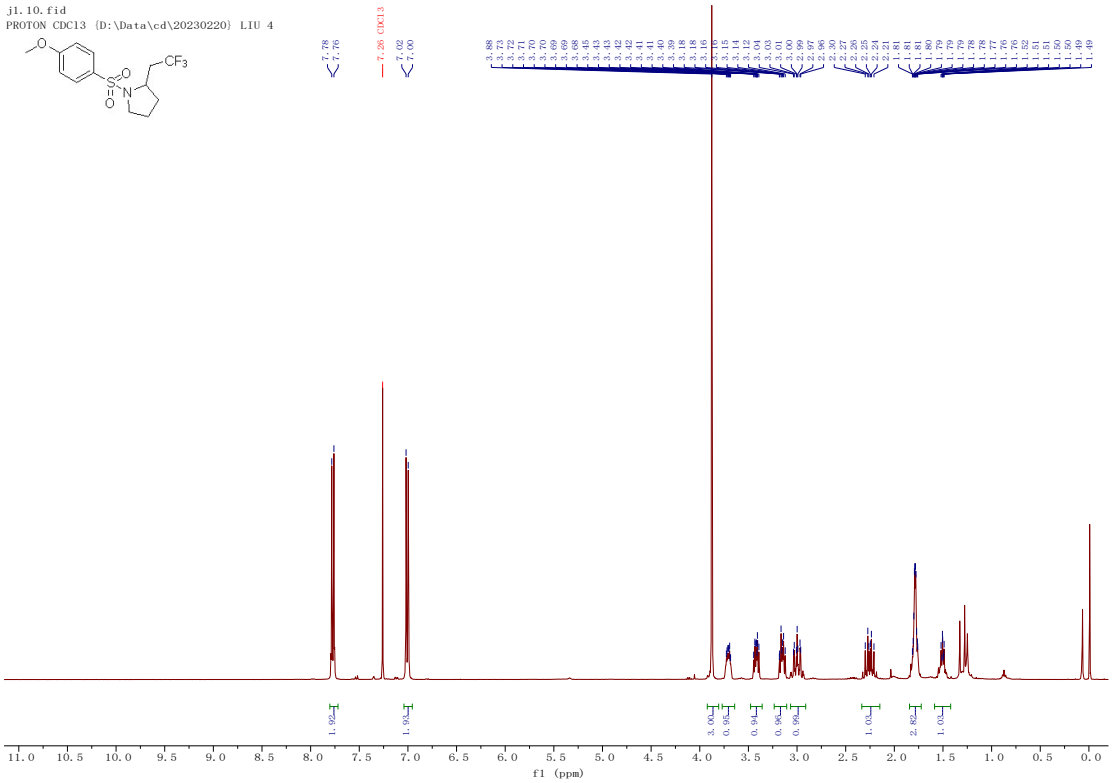


Figure S5 ^{13}C NMR spectrum for compound 3b

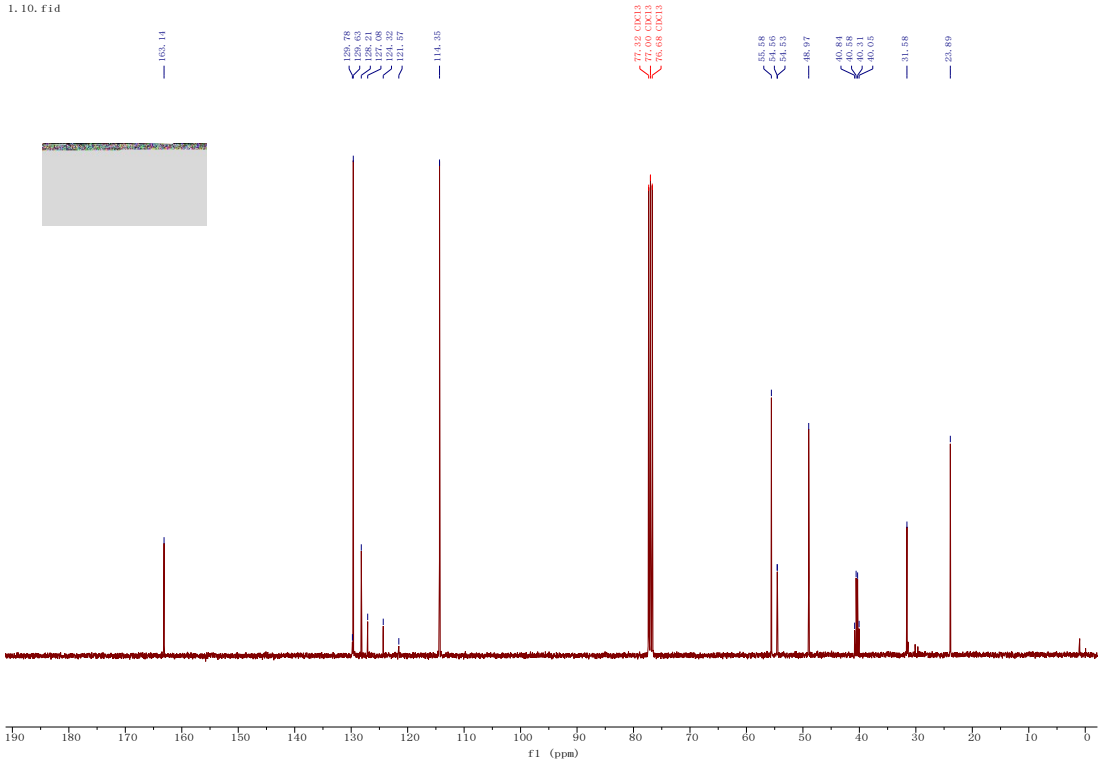


Figure S6 ^{19}F NMR spectrum for compound 3b

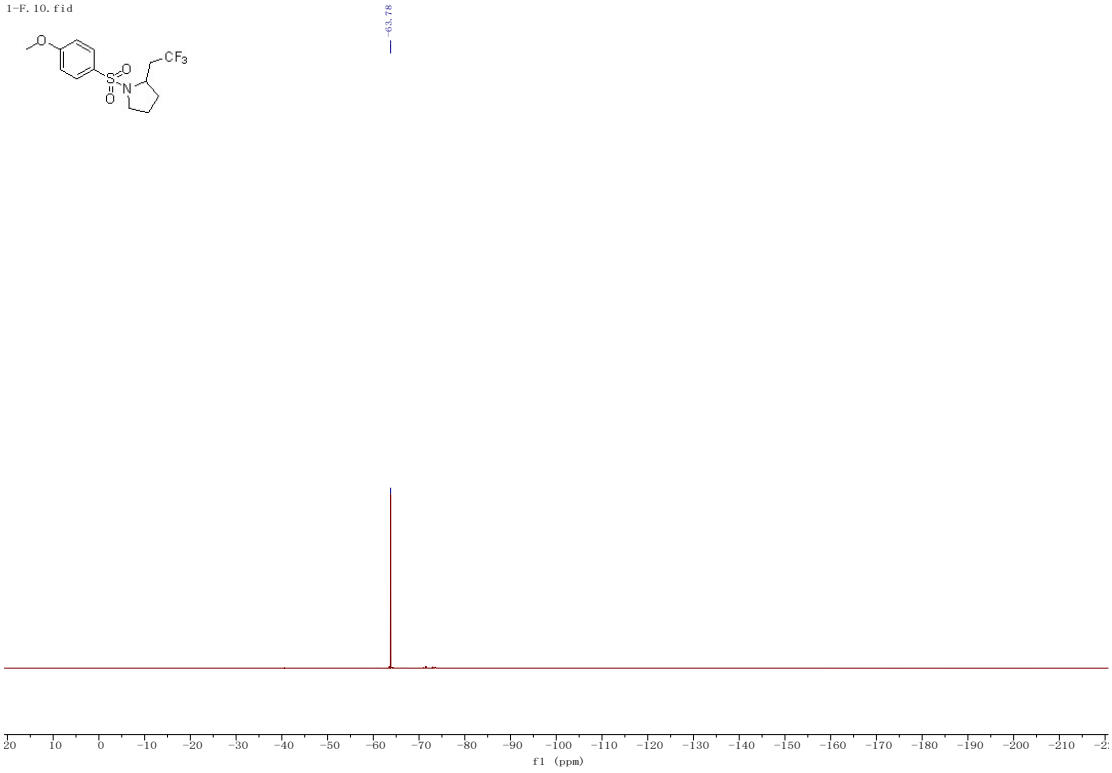


Figure S7 ^{1}H NMR spectrum for compound 3c

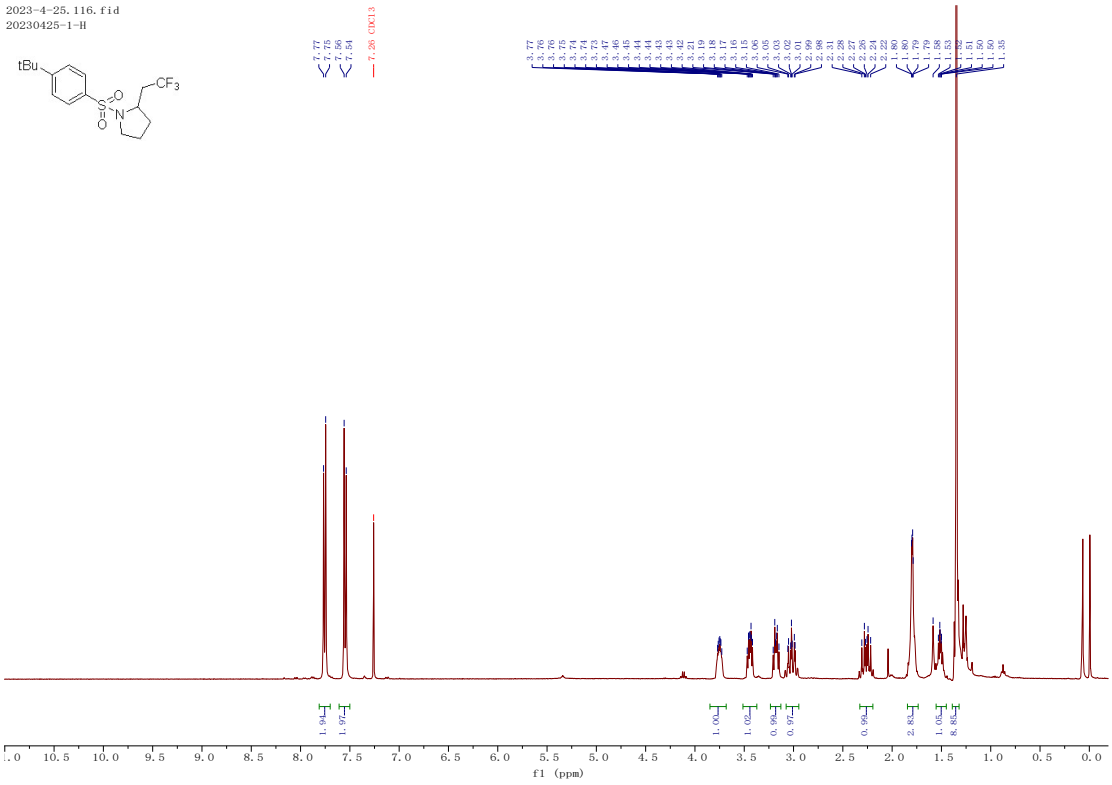


Figure S8 ^{13}C NMR spectrum for compound 3c

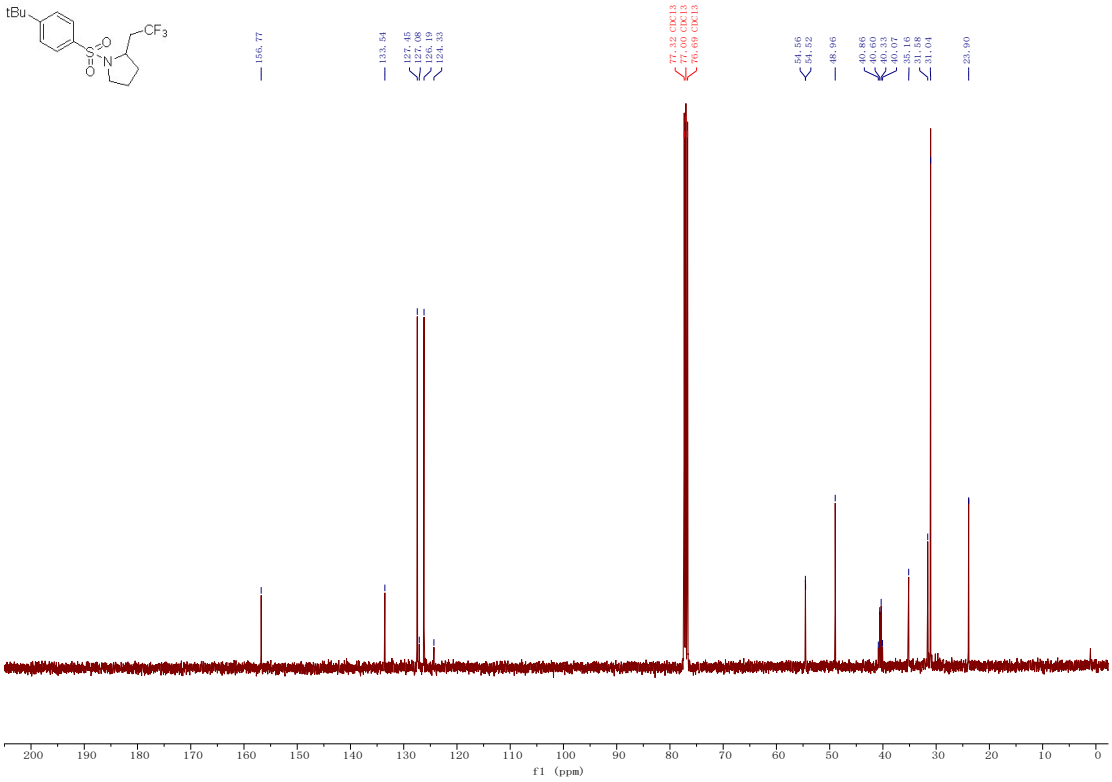


Figure S9 ^{19}F NMR spectrum for compound 3c

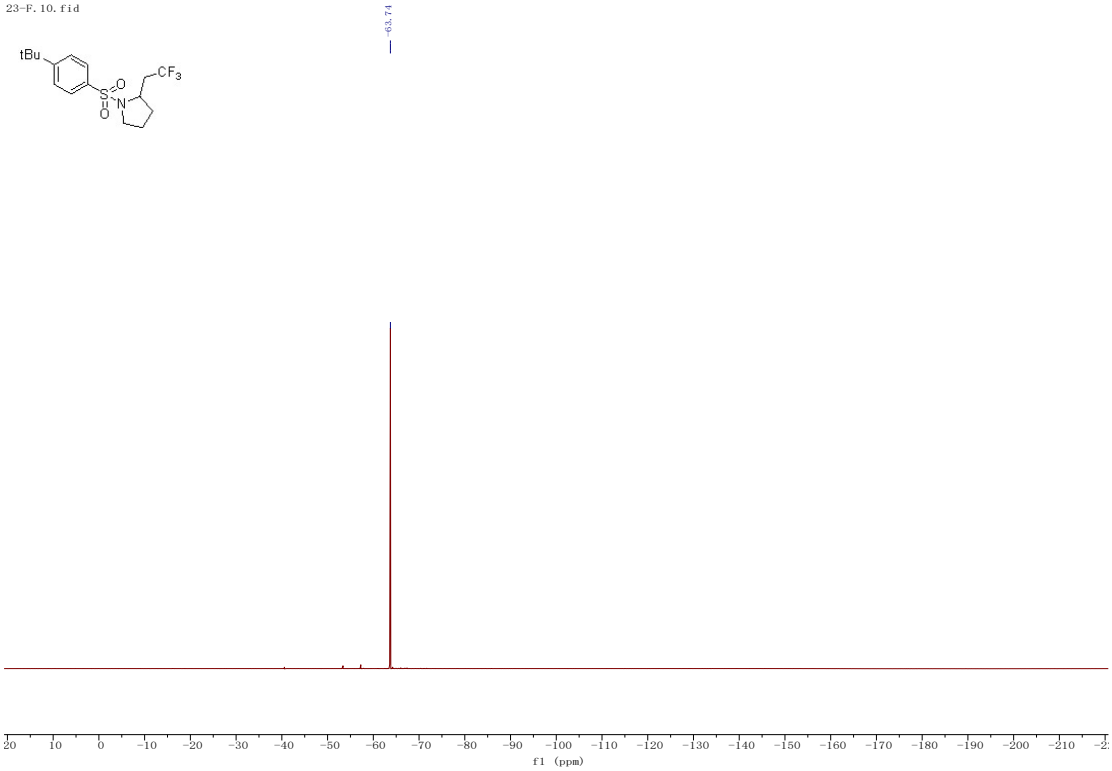


Figure S10 ^{1}H NMR spectrum for compound 3d

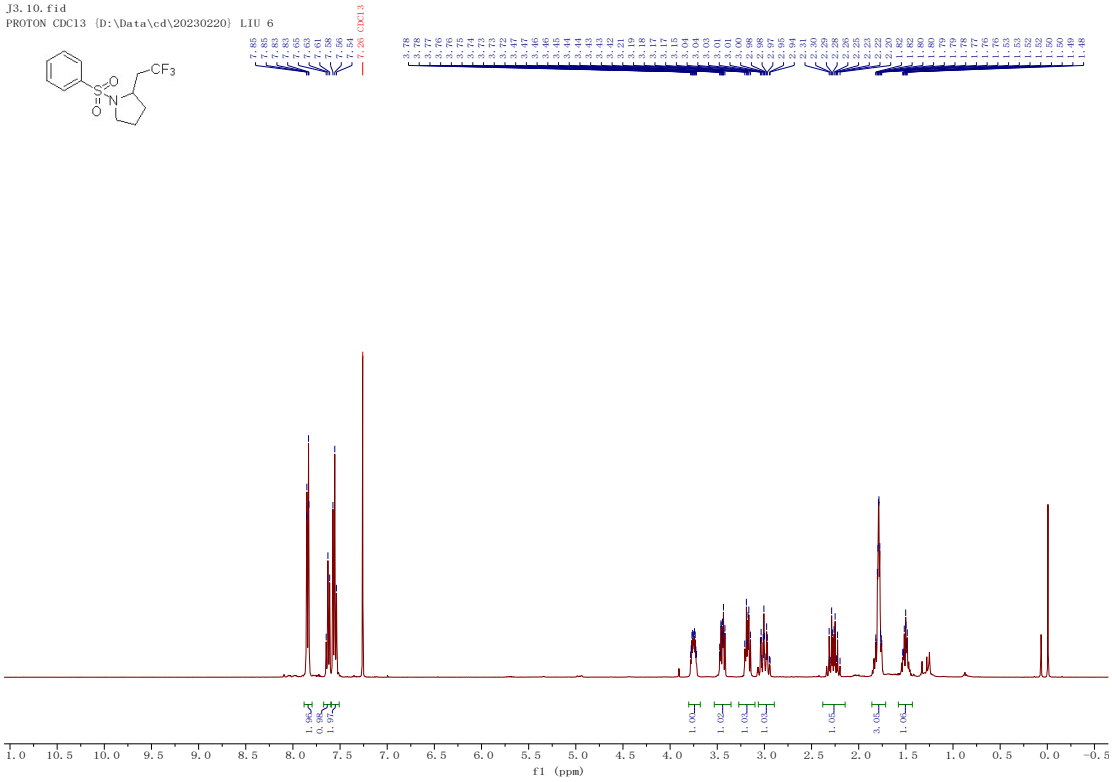


Figure S11 ^{13}C NMR spectrum for compound 3d

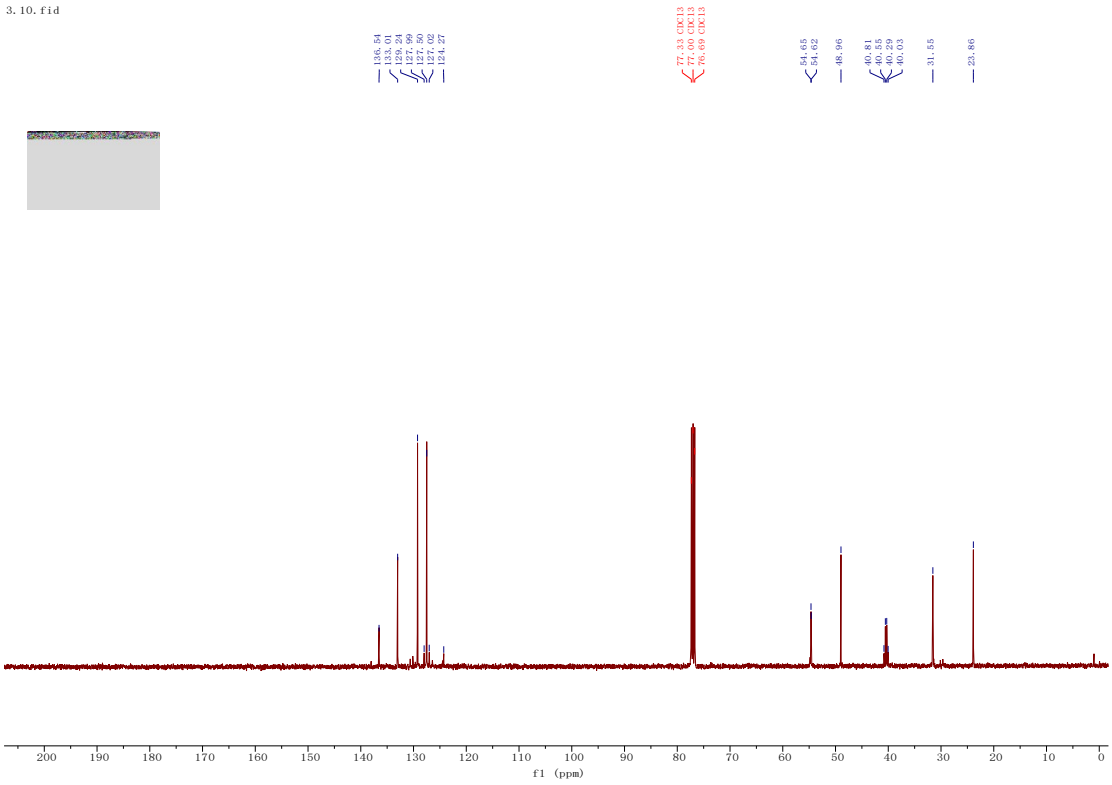


Figure S12 ^{19}F NMR spectrum for compound 3d

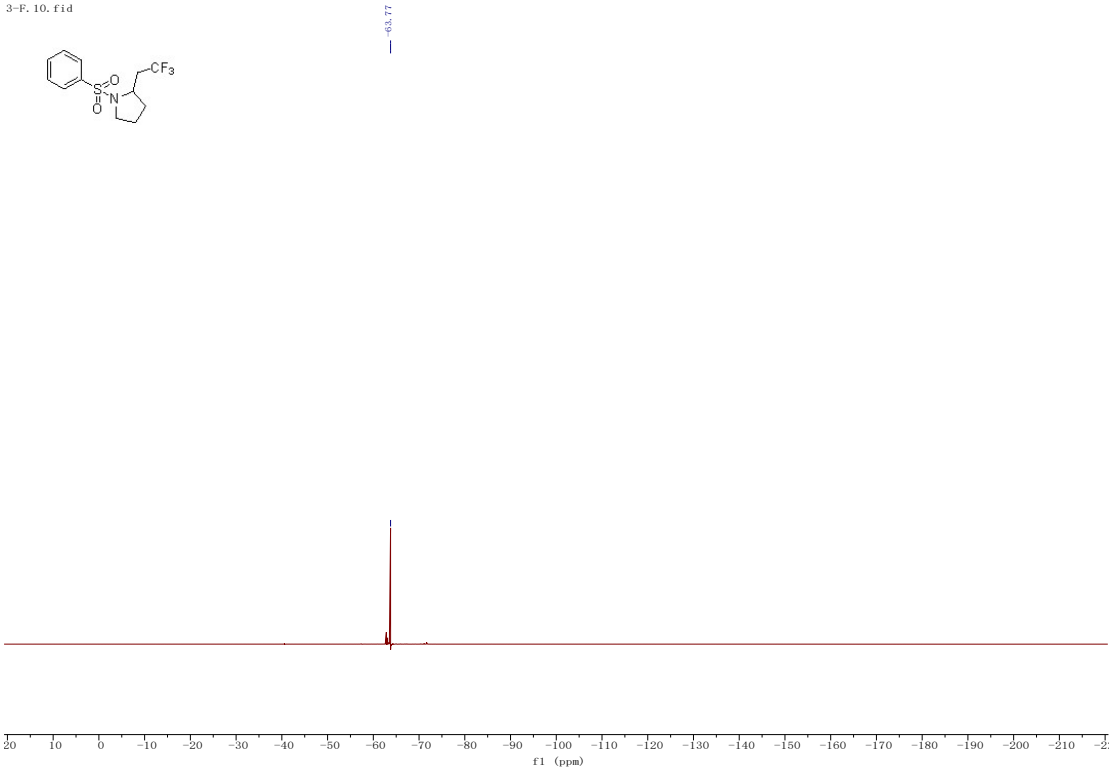


Figure S13 ^{1}H NMR spectrum for compound 3e

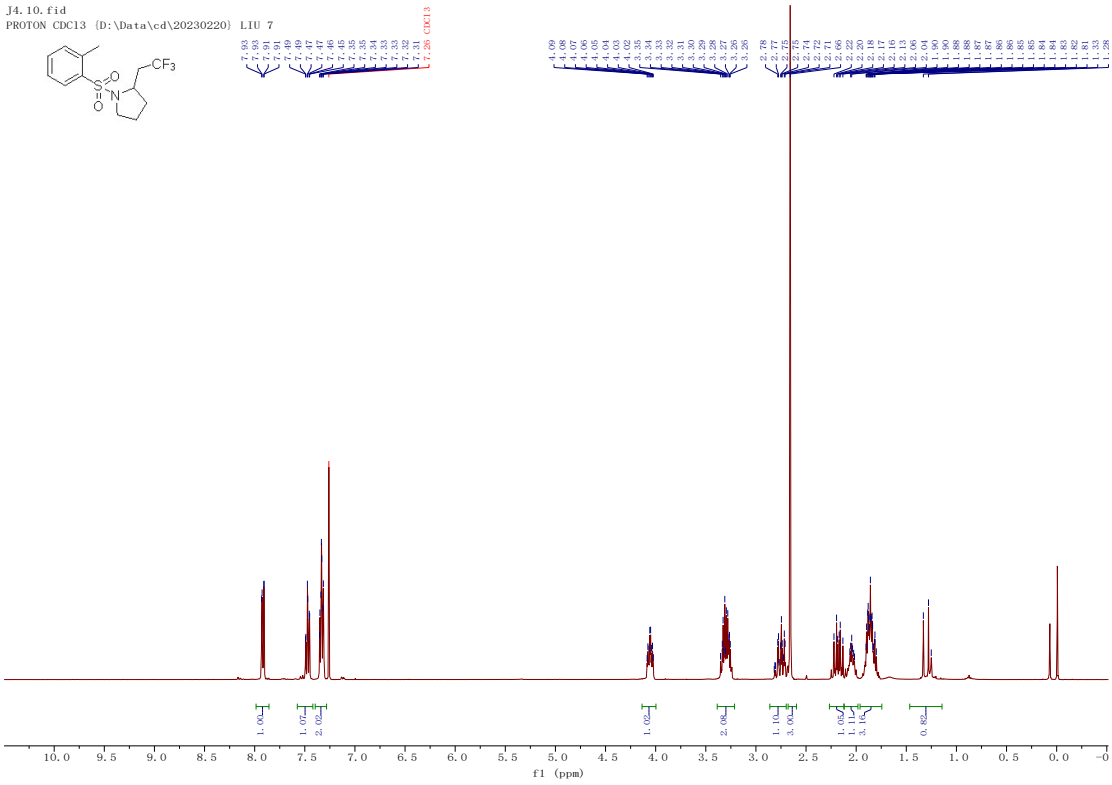


Figure S14 ^{13}C NMR spectrum for compound 3e

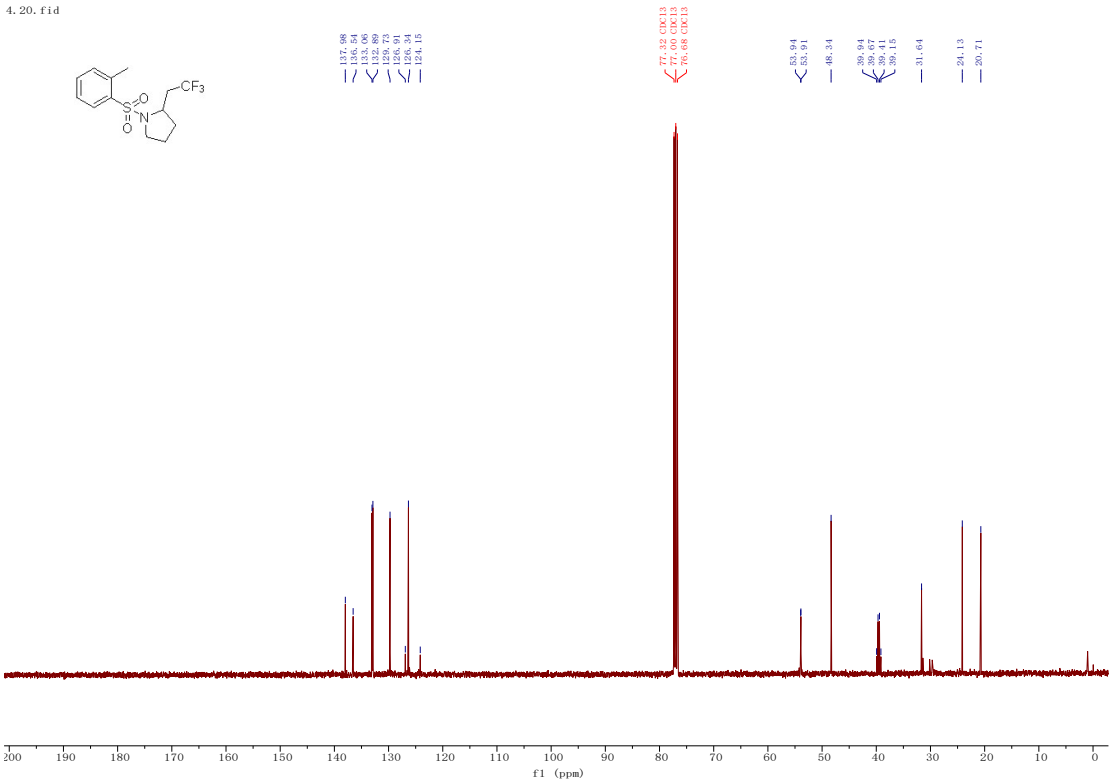


Figure S15 ^{19}F NMR spectrum for compound 3e

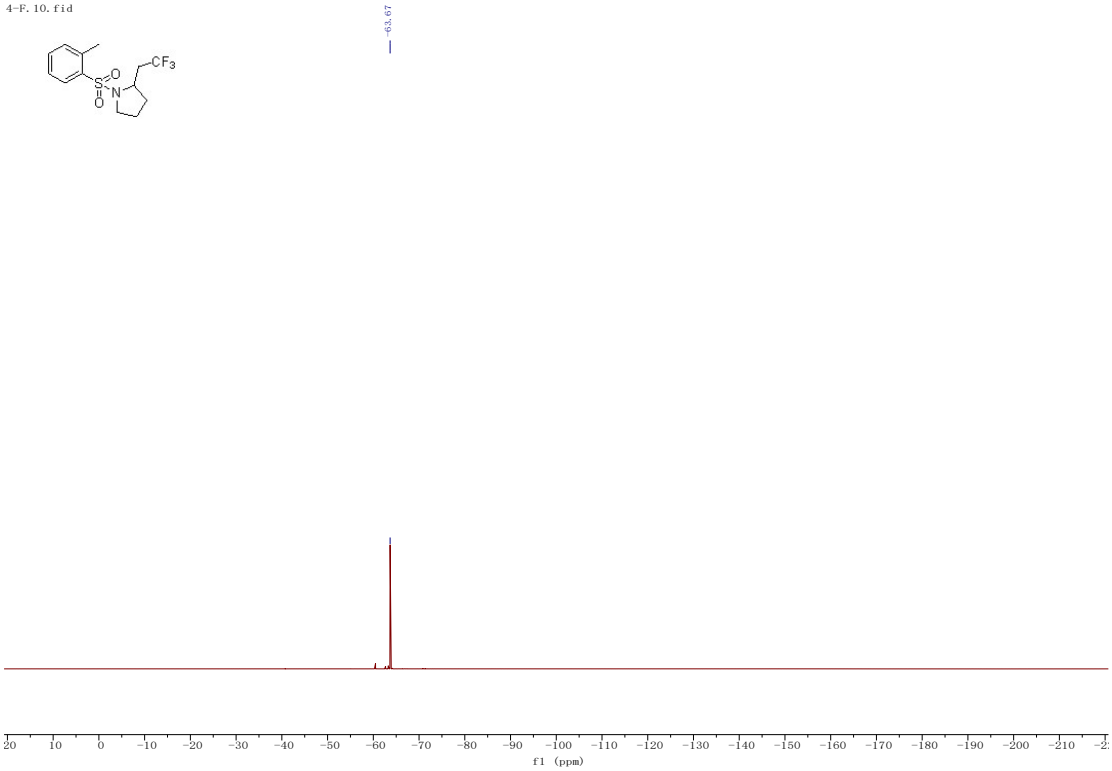


Figure S16 ^{1}H NMR spectrum for compound 3f

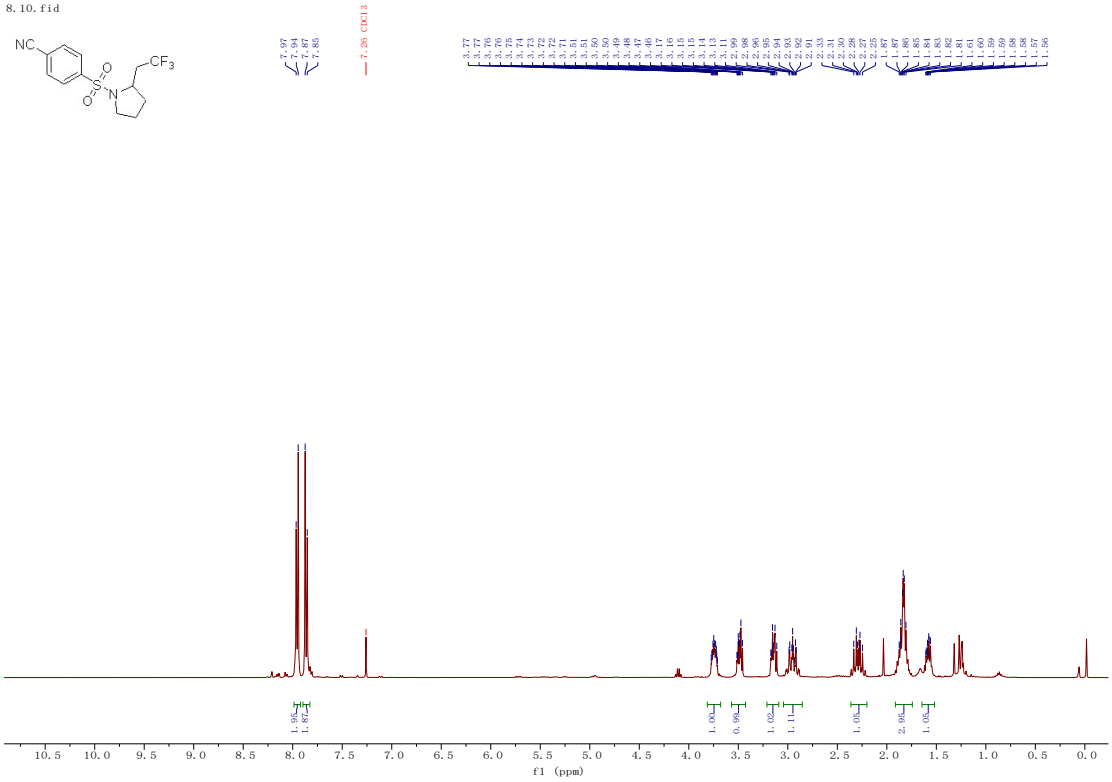


Figure S17 ^{13}C NMR spectrum for compound 3f

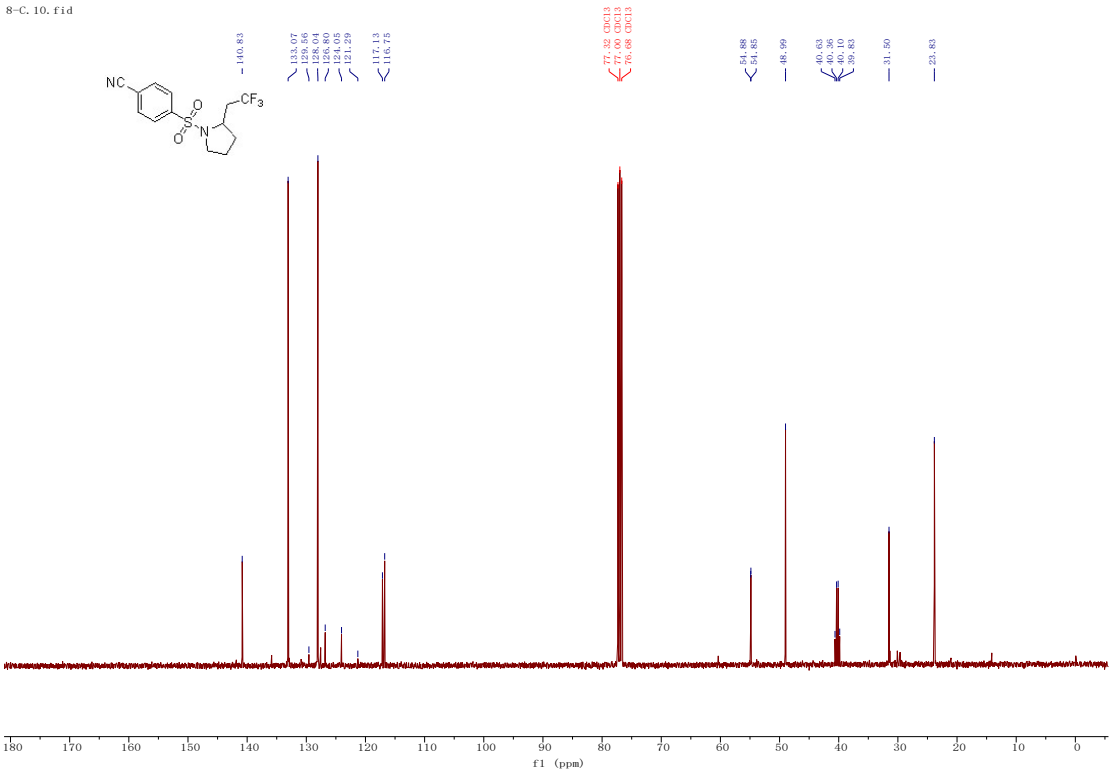


Figure S18 ^{19}F NMR spectrum for compound 3f

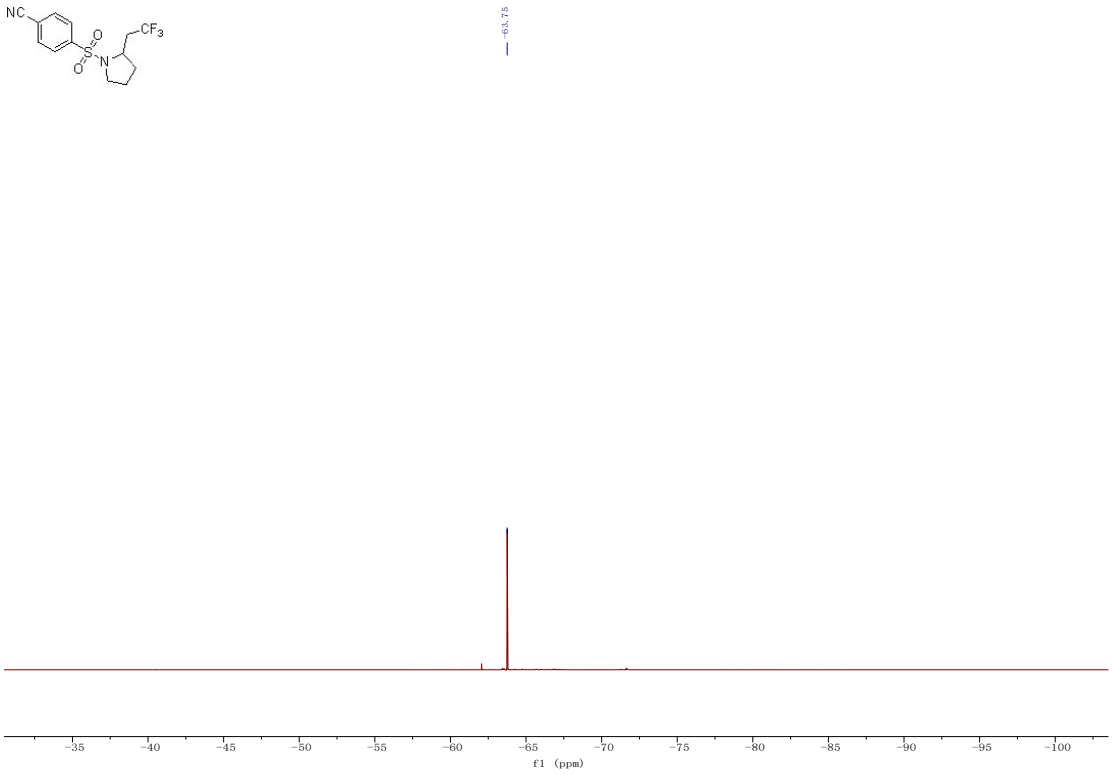


Figure S19 ^{1}H NMR spectrum for compound 3g

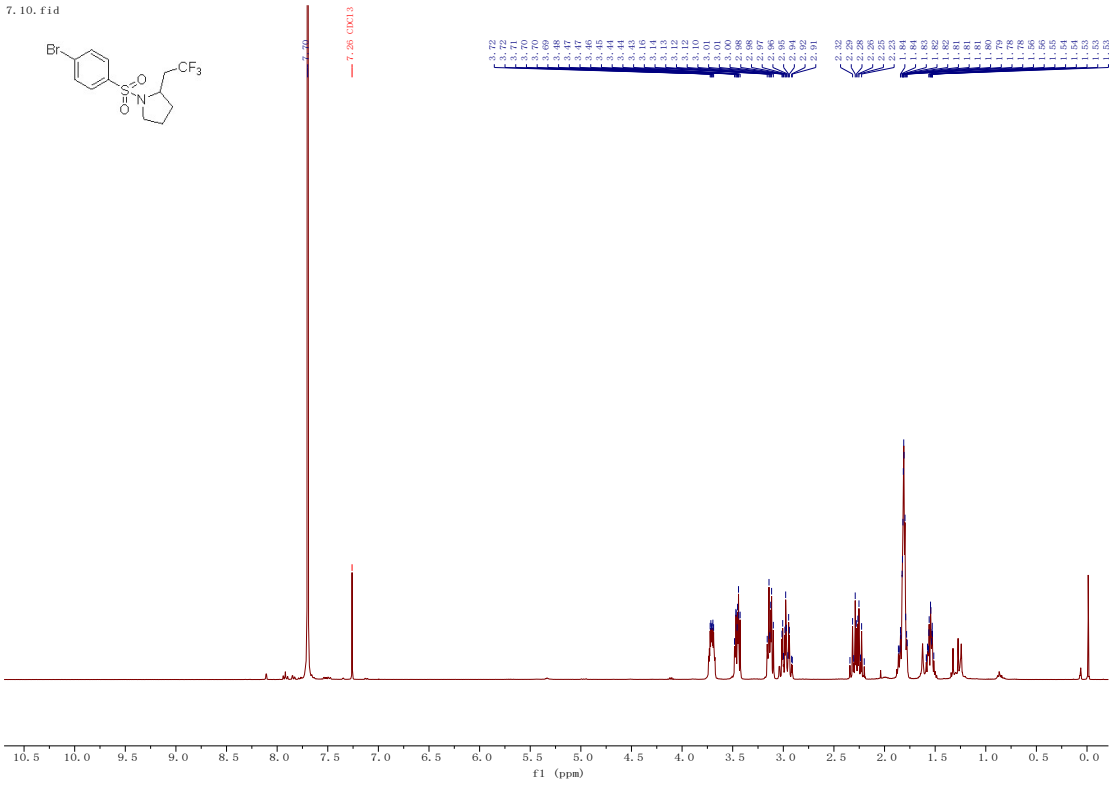


Figure S20 ^{13}C NMR spectrum for compound 3g

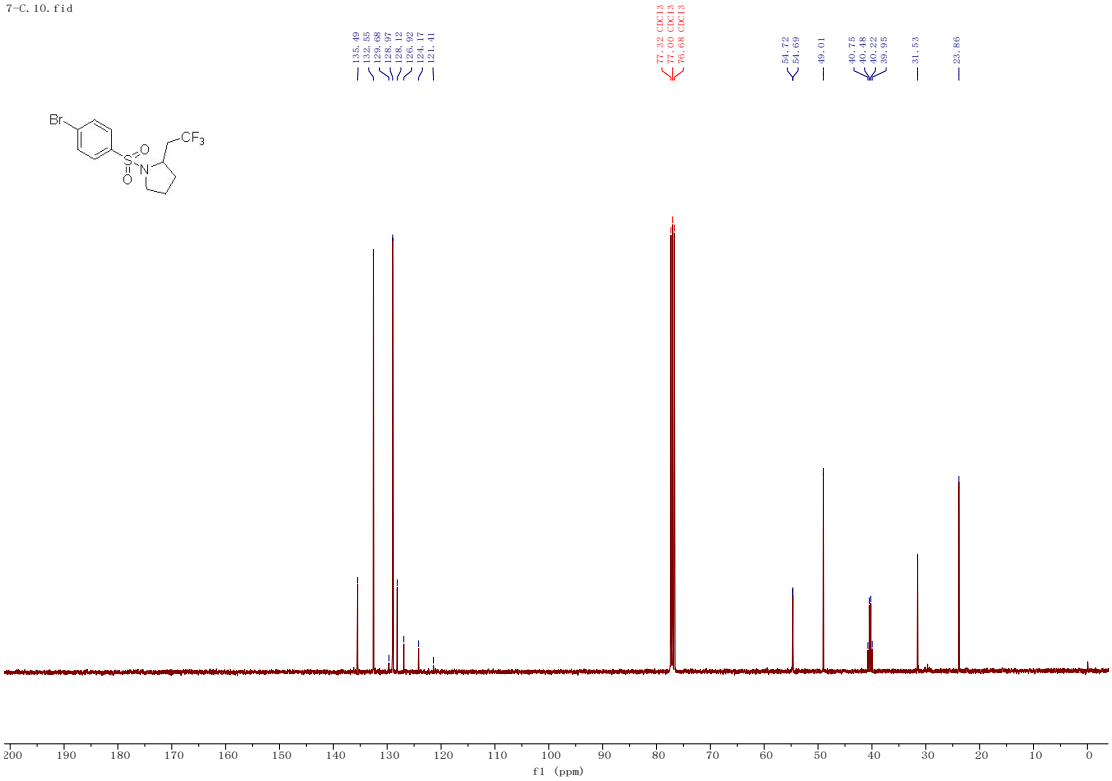


Figure S21 ^{19}F NMR spectrum for compound 3g

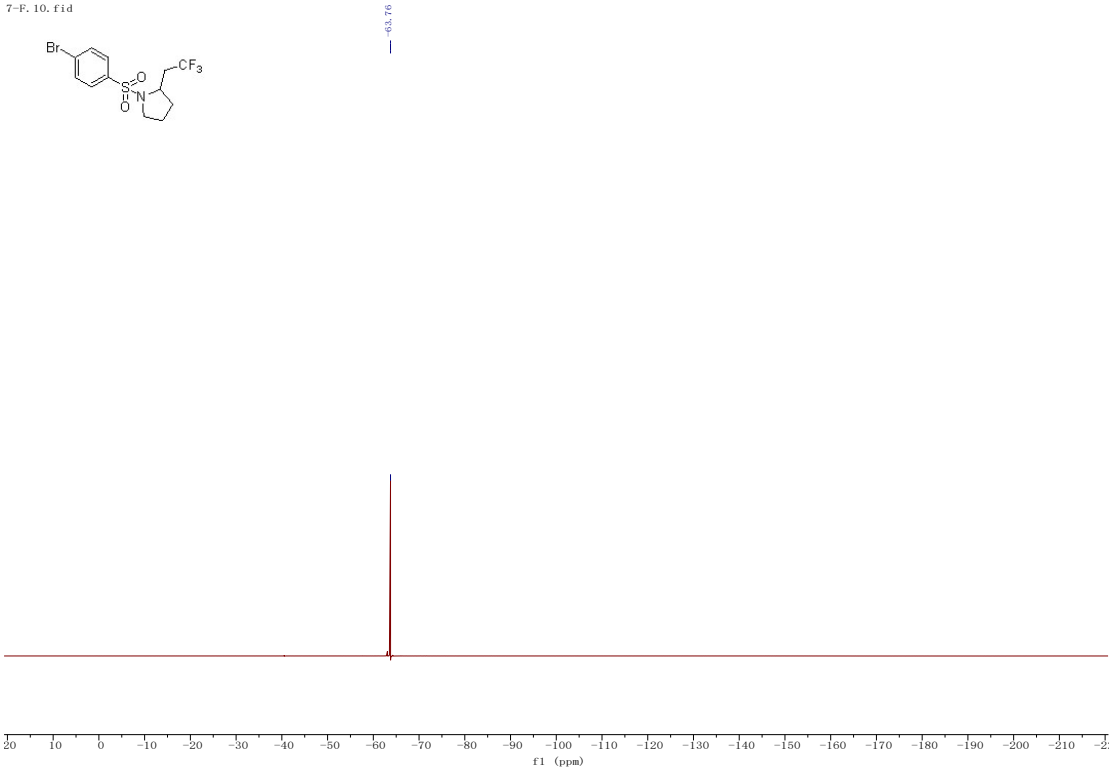


Figure S22 ^{1}H NMR spectrum for compound 3h

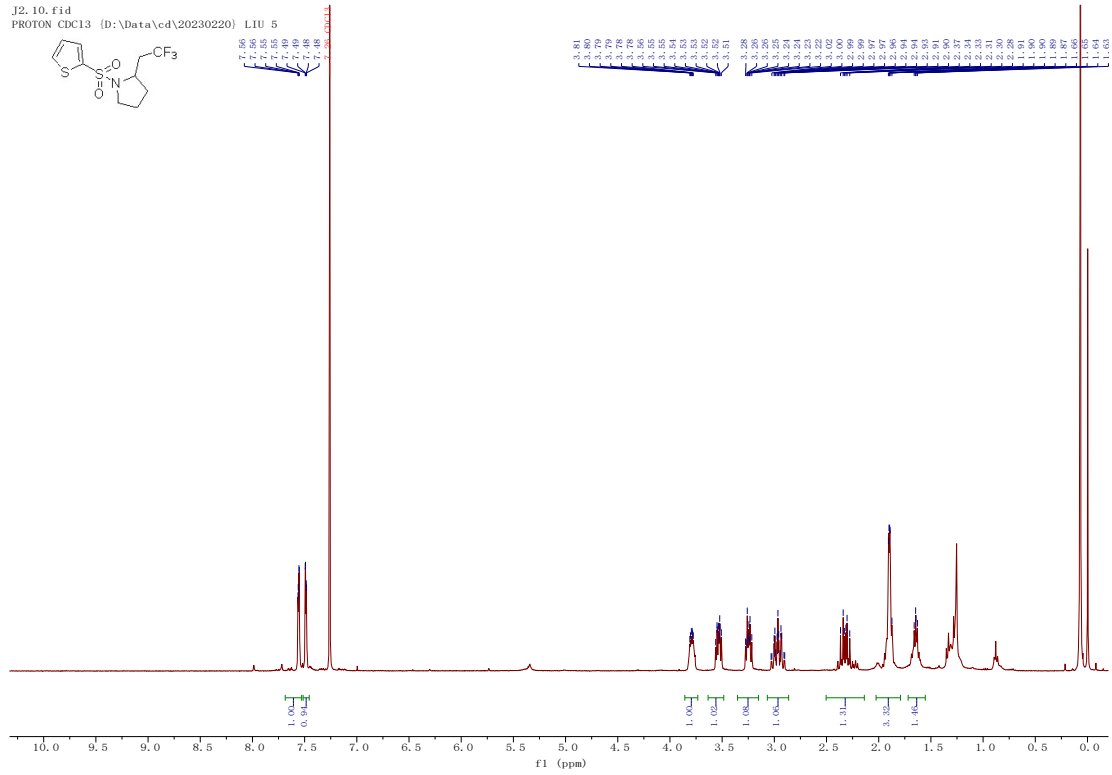


Figure S23 ^{13}C NMR spectrum for compound 3h

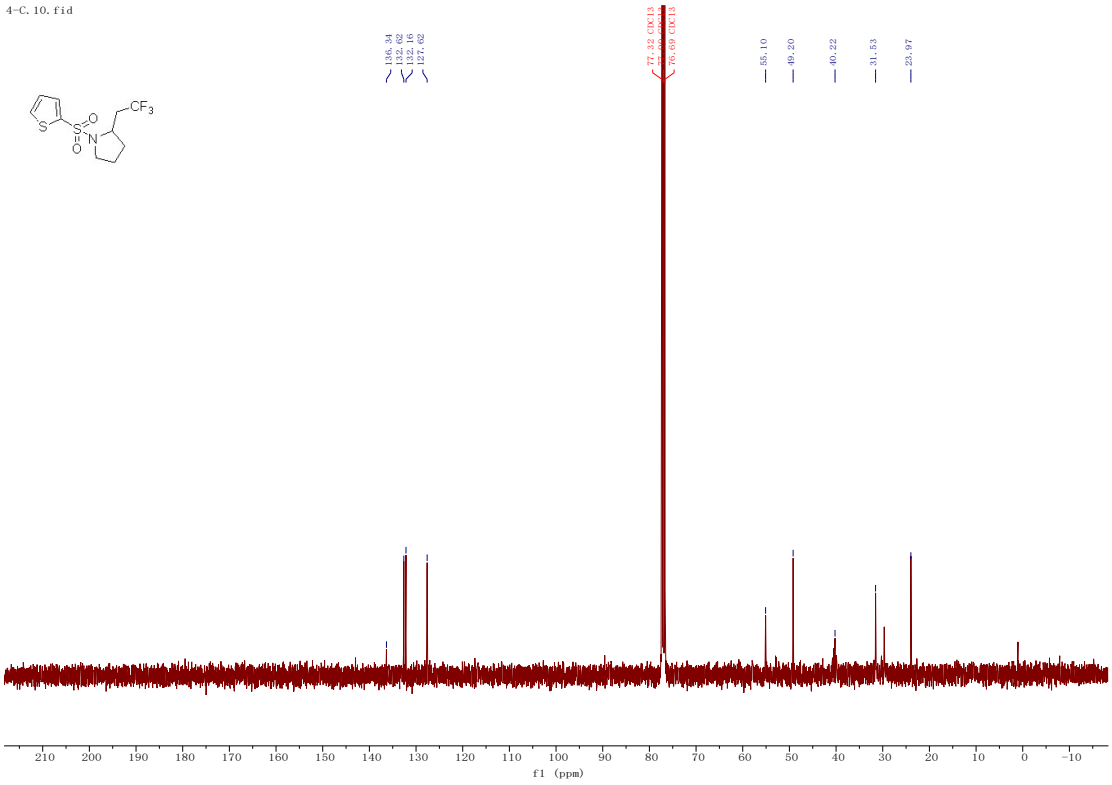


Figure S24 ^{19}F NMR spectrum for compound 3h

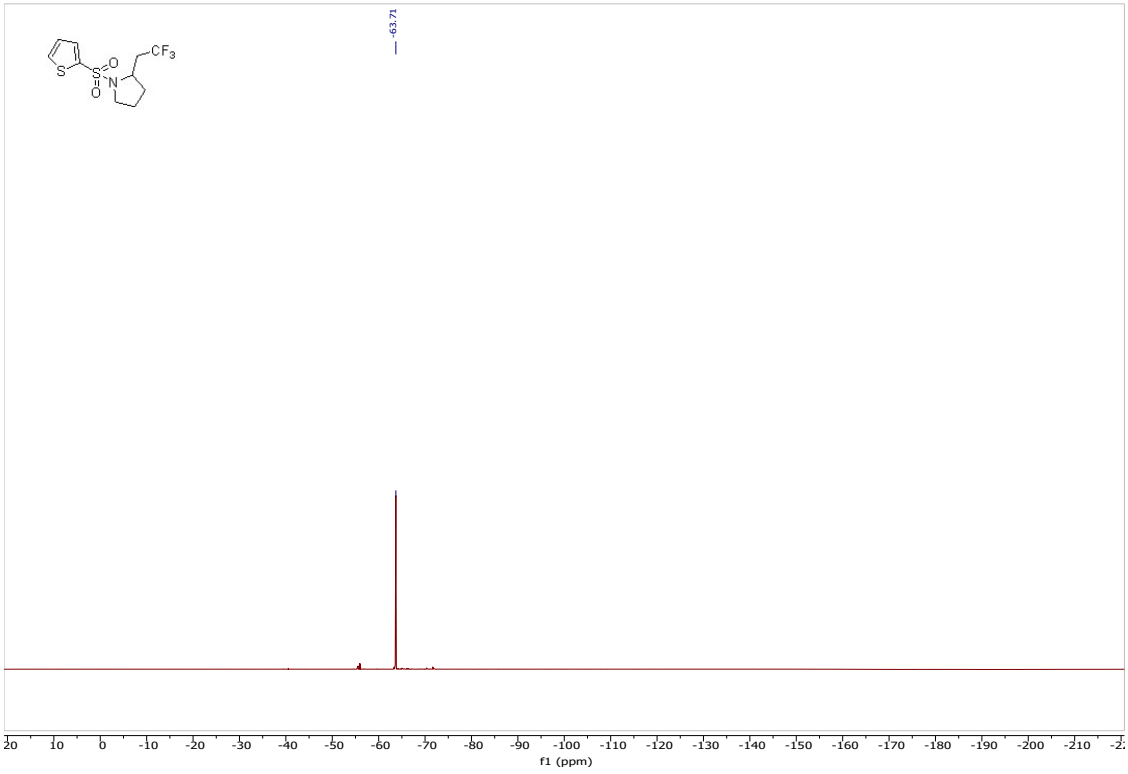


Figure S25 ^{1}H NMR spectrum for compound 3i

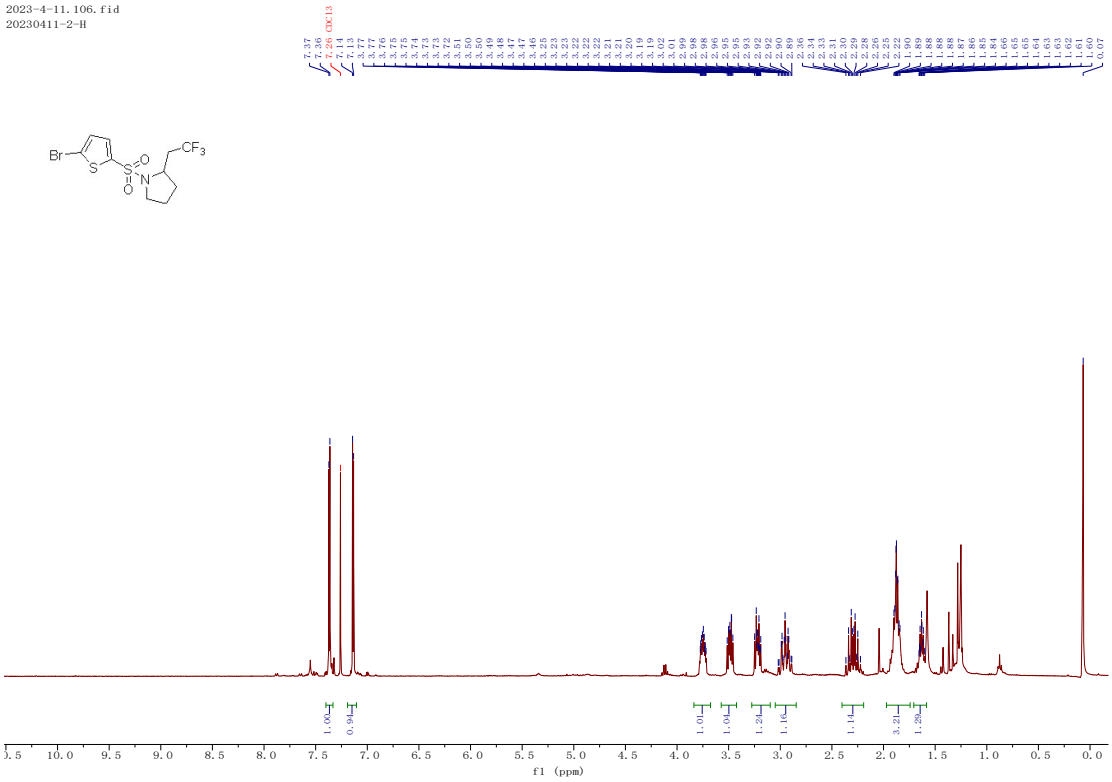


Figure S26 ^{13}C NMR spectrum for compound 3i

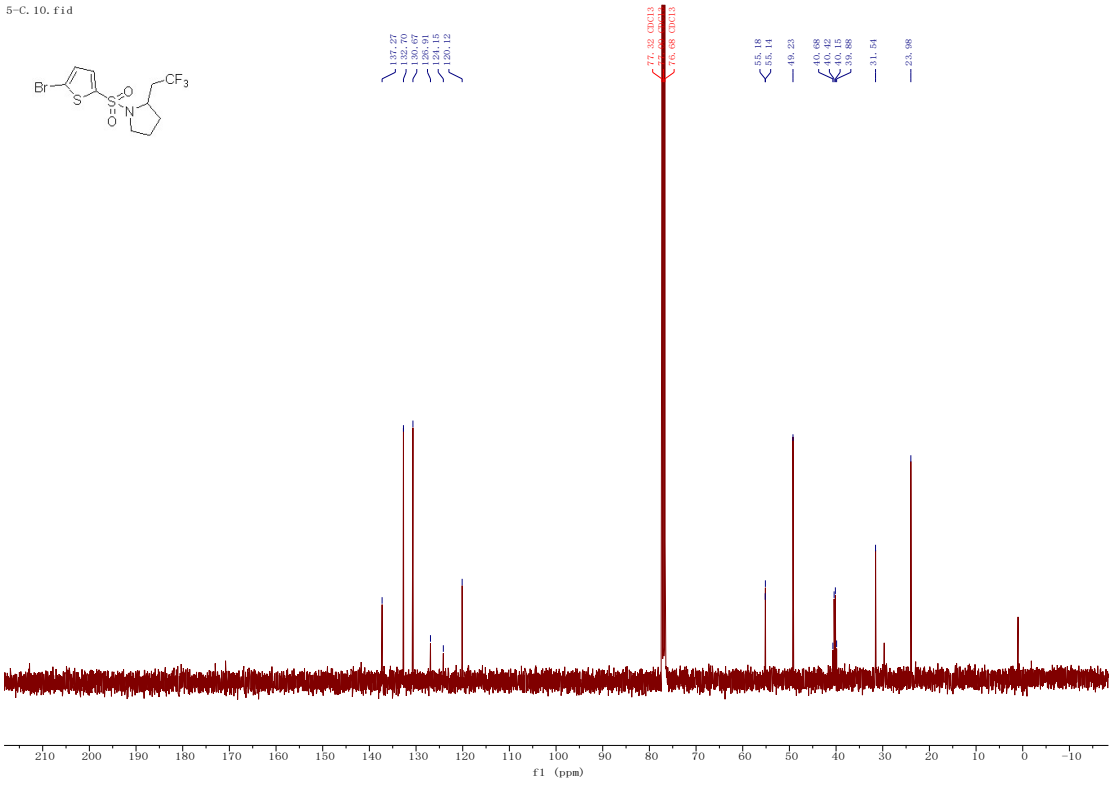


Figure S27 ^{19}F NMR spectrum for compound 3i

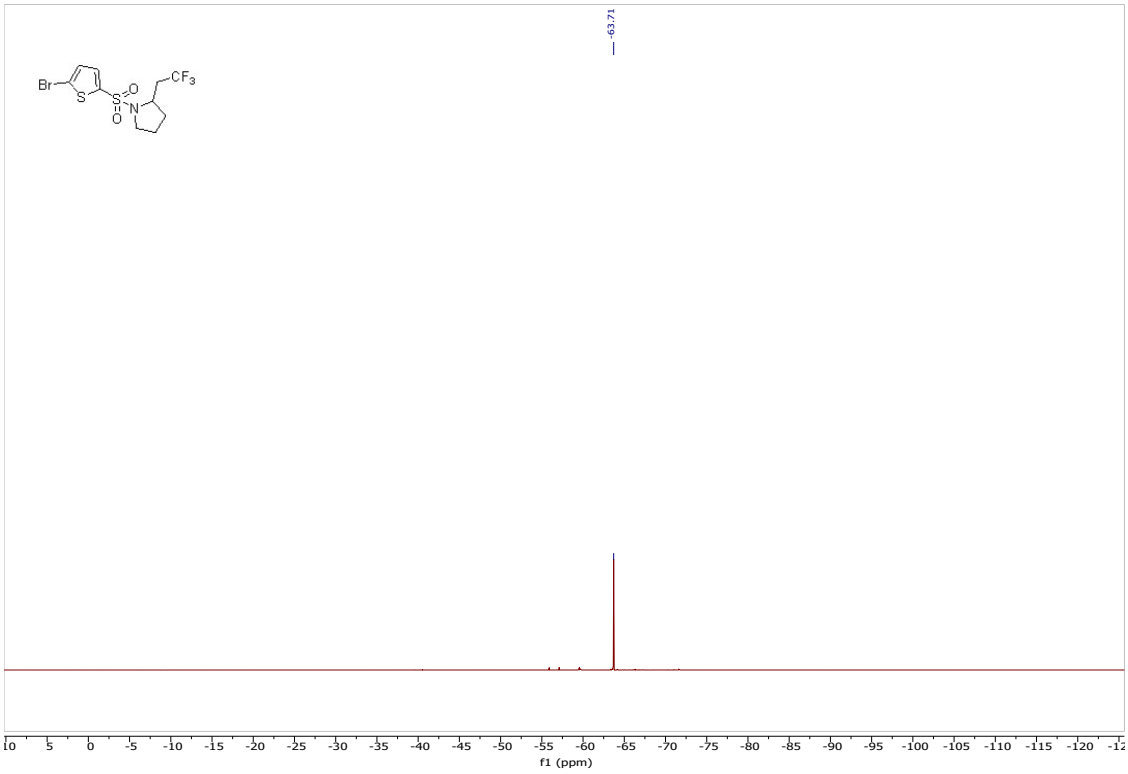


Figure S28 ^{1}H NMR spectrum for compound 3j

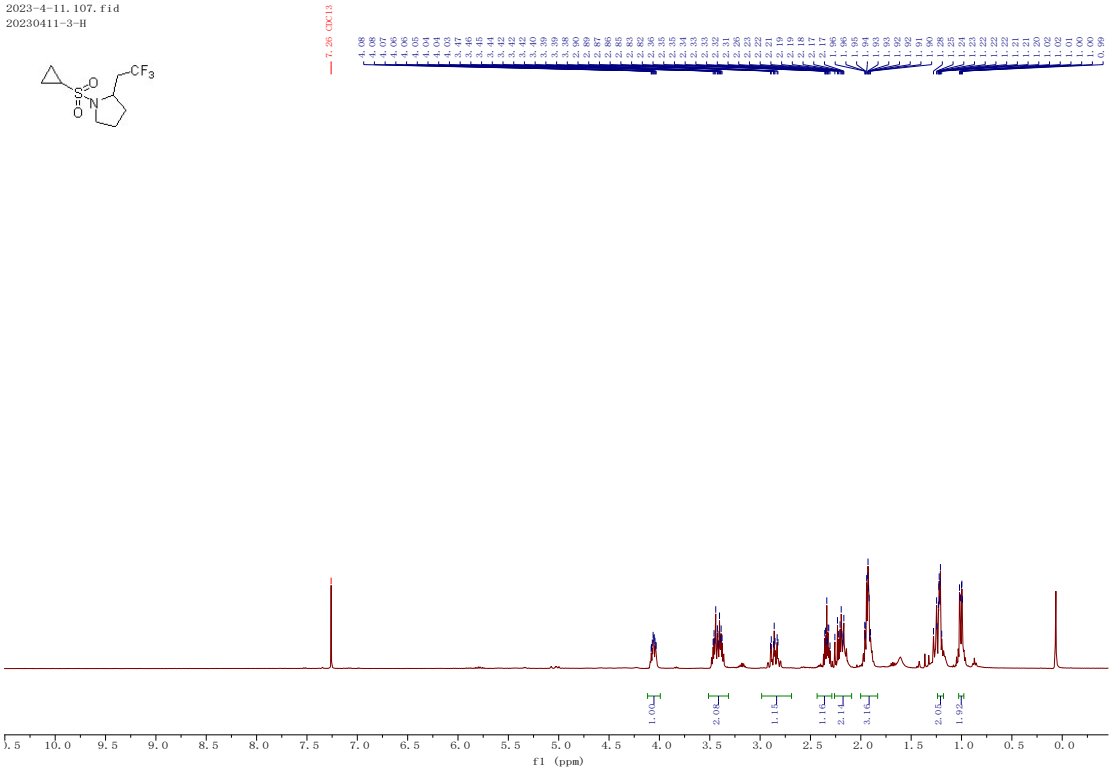


Figure S29 ^{13}C NMR spectrum for compound 3j

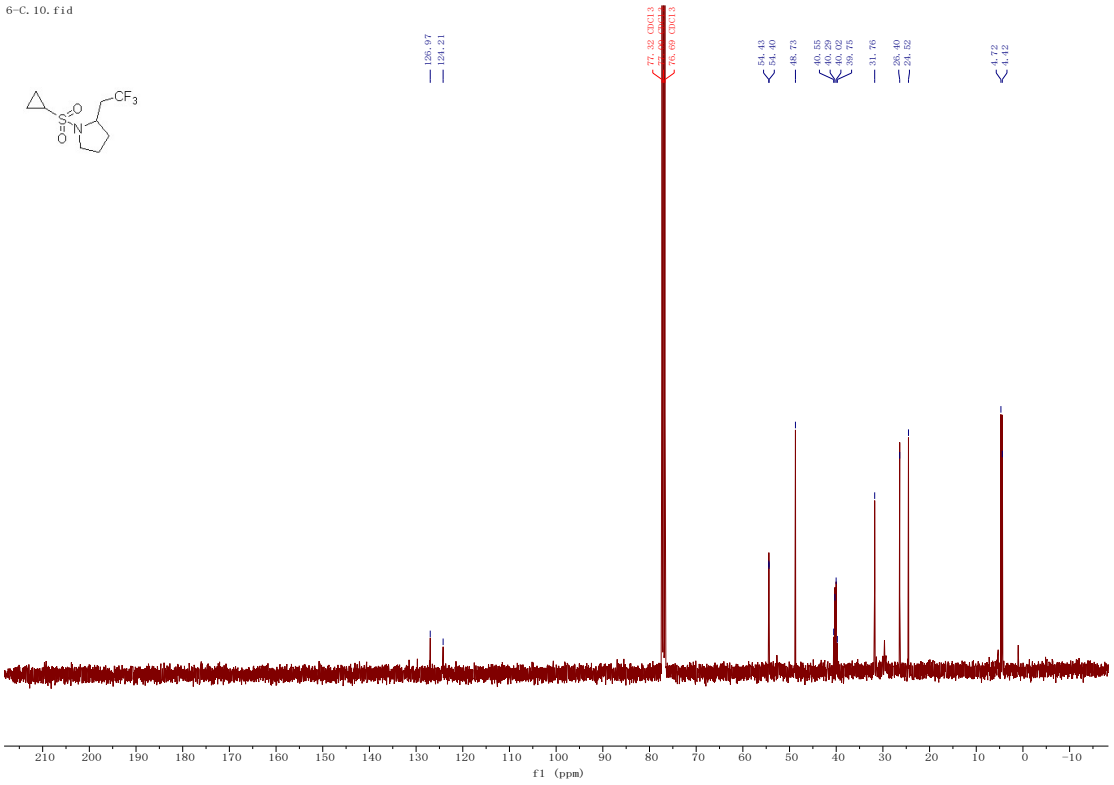


Figure S30 ^{19}F NMR spectrum for compound 3j

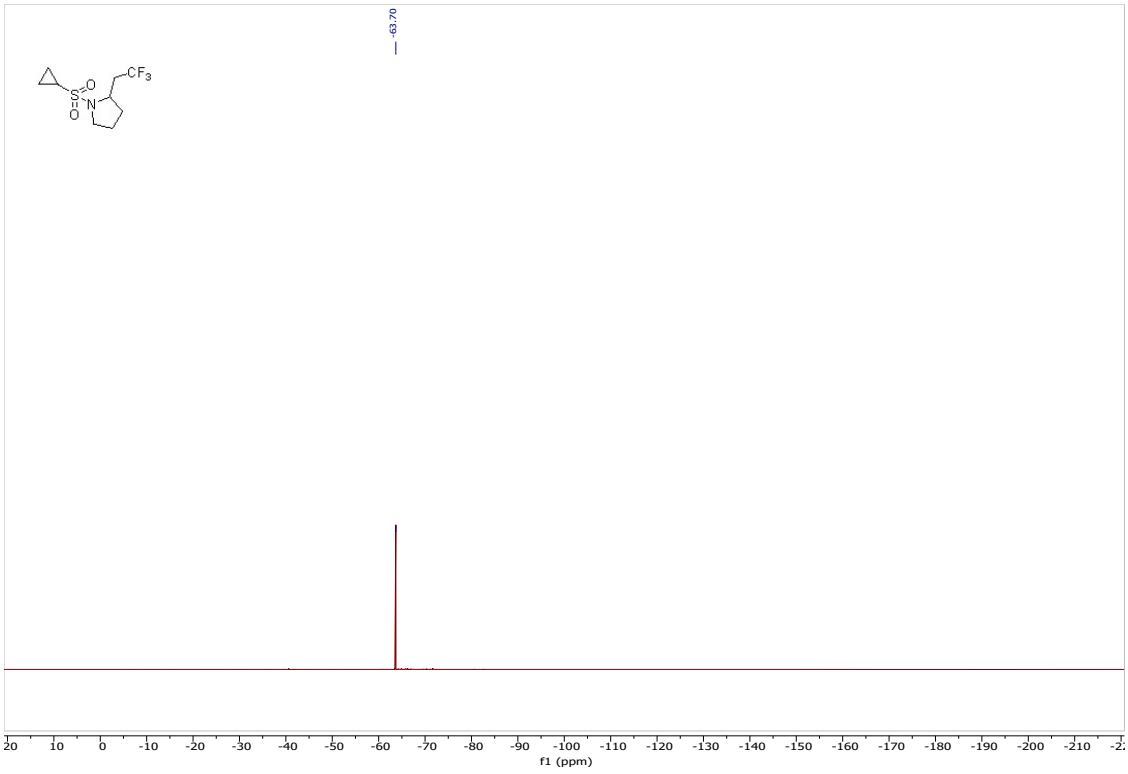


Figure S31 ^{1}H NMR spectrum for compound 3l-m

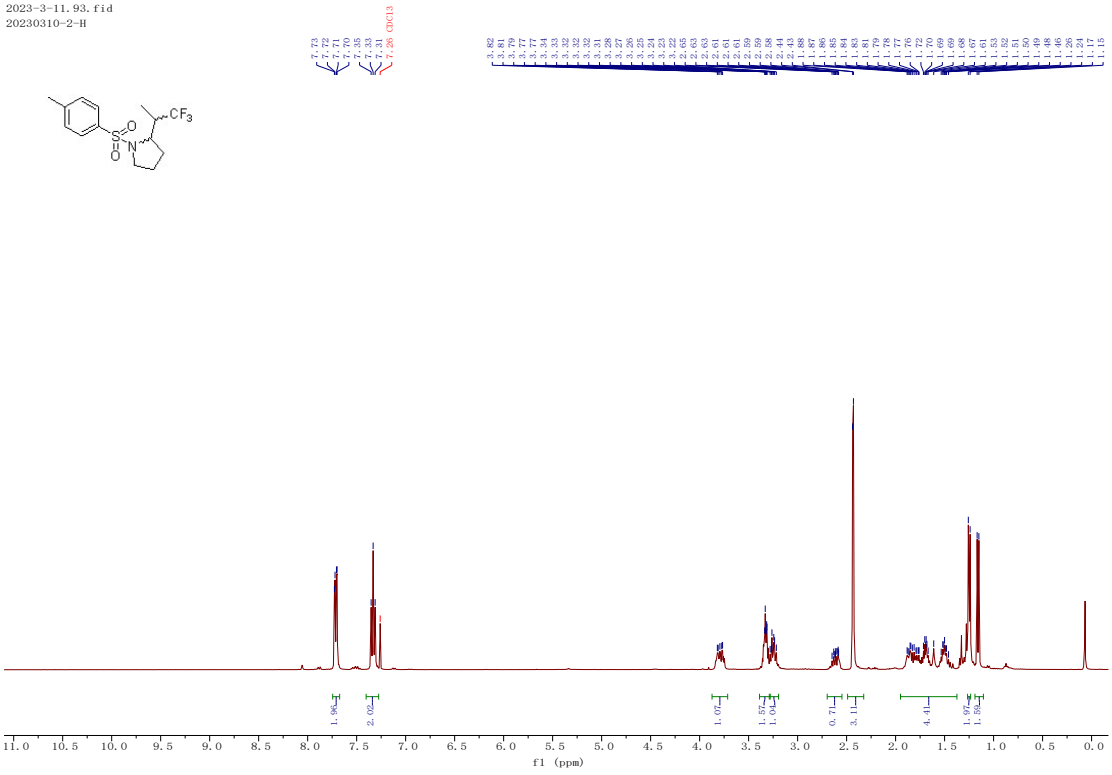


Figure S32 ^{13}C NMR spectrum for compound 3 l-m

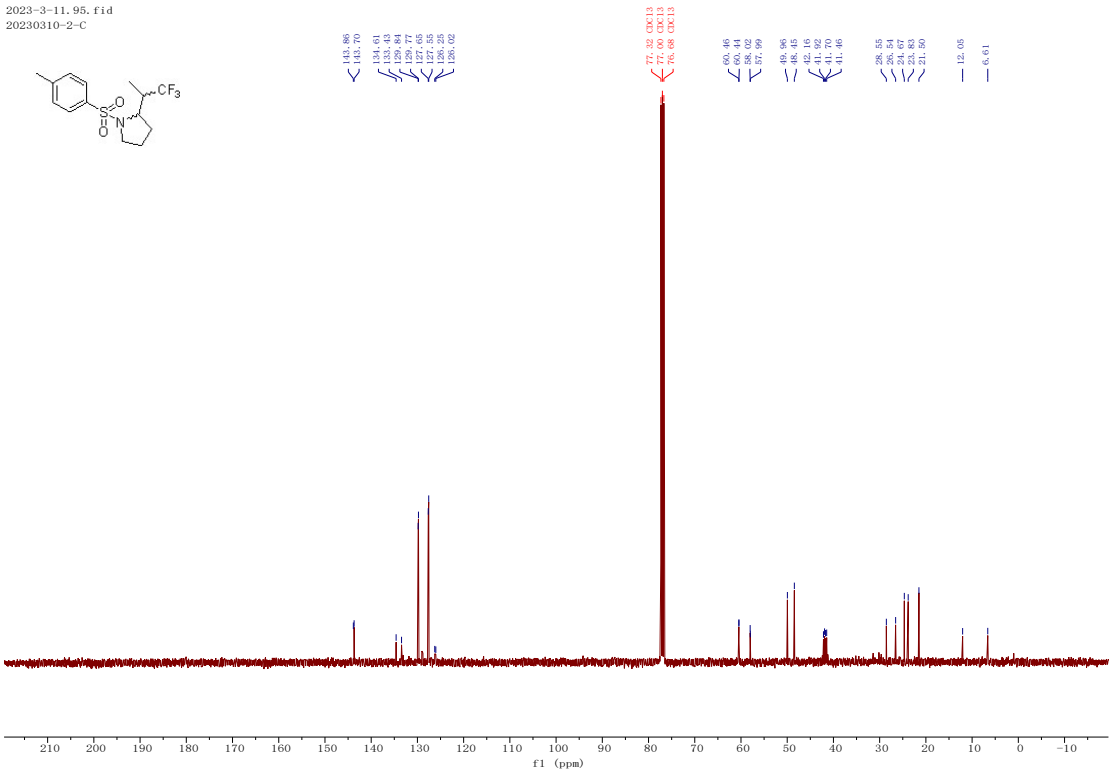


Figure S33 ^{19}F NMR spectrum for compound 3 l-m

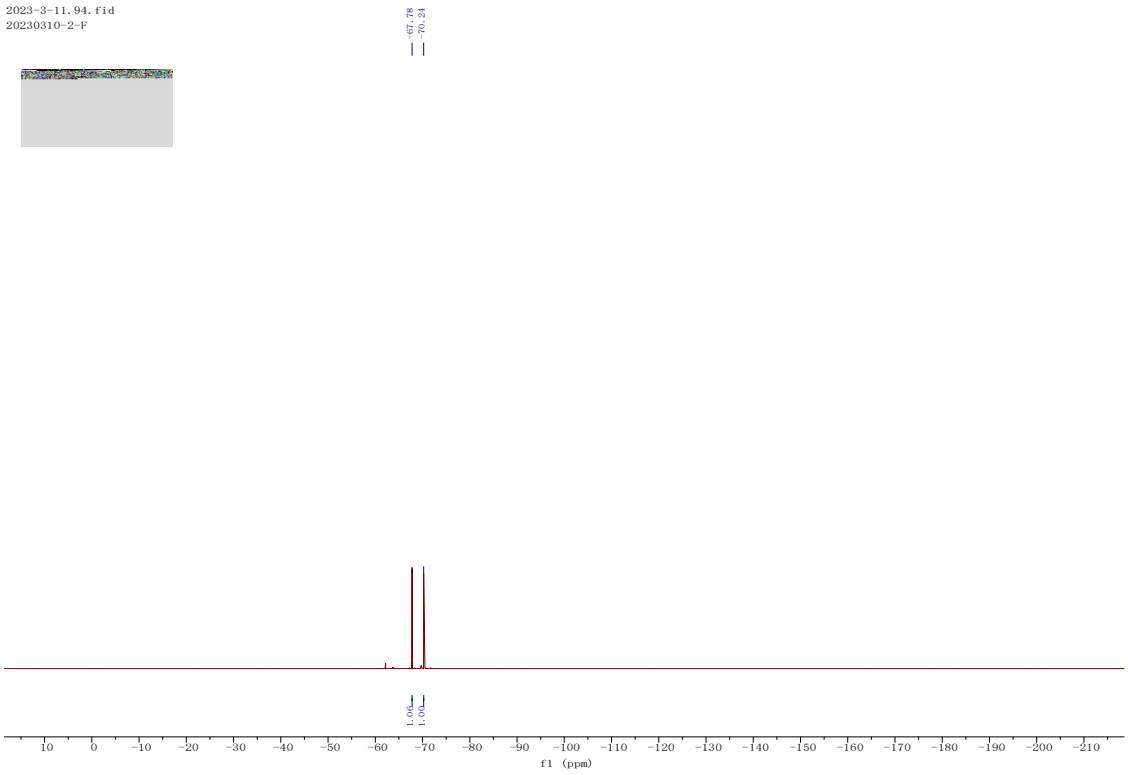


Figure S34 ^{1}H NMR spectrum for compound 3n

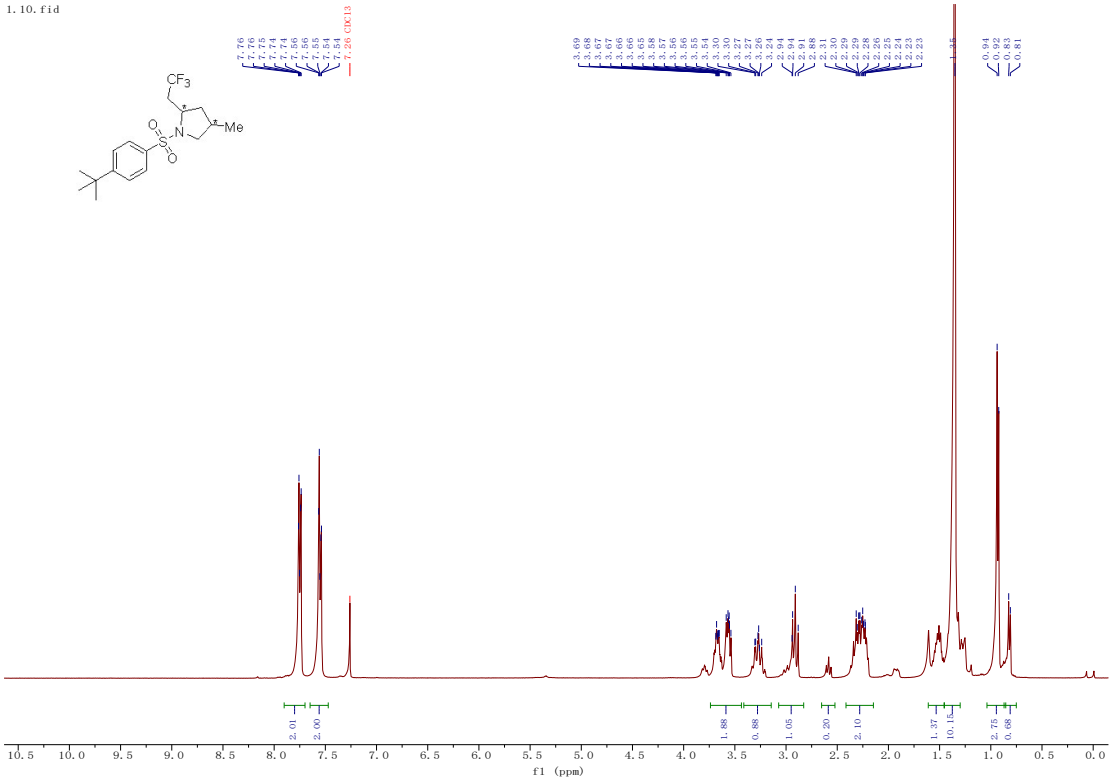


Figure S35 ^{13}C NMR spectrum for compound 3n

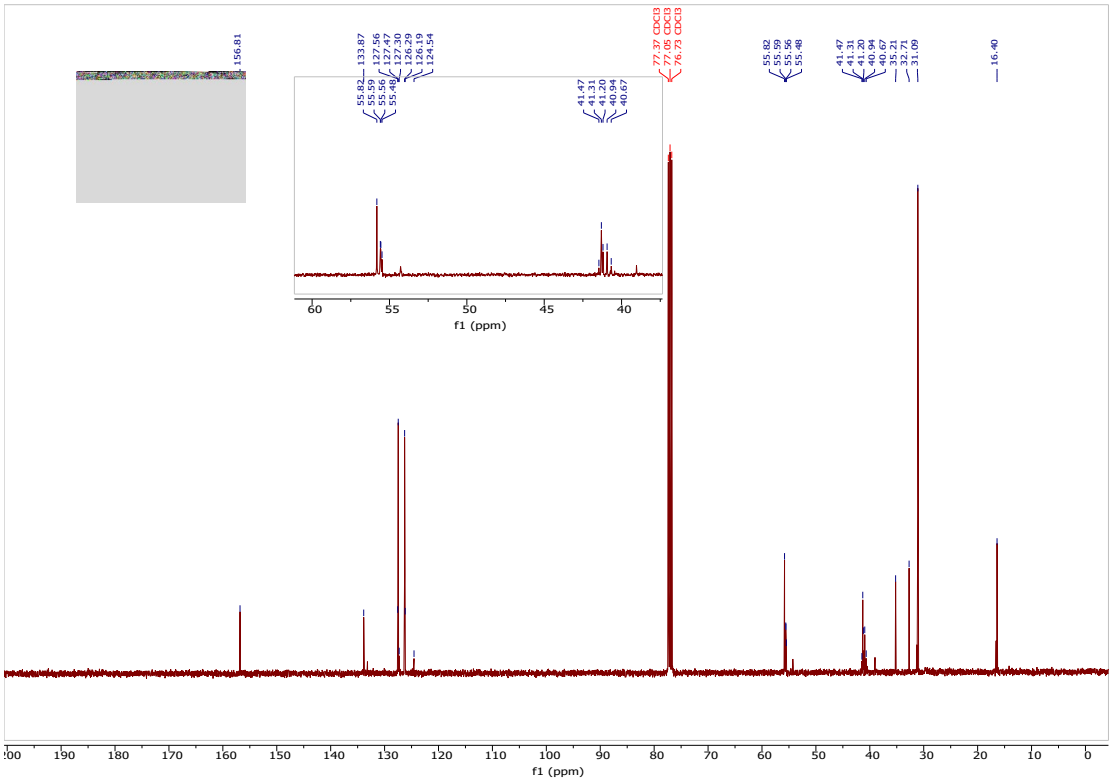


Figure S36^{19}F NMR spectrum for compound 3n

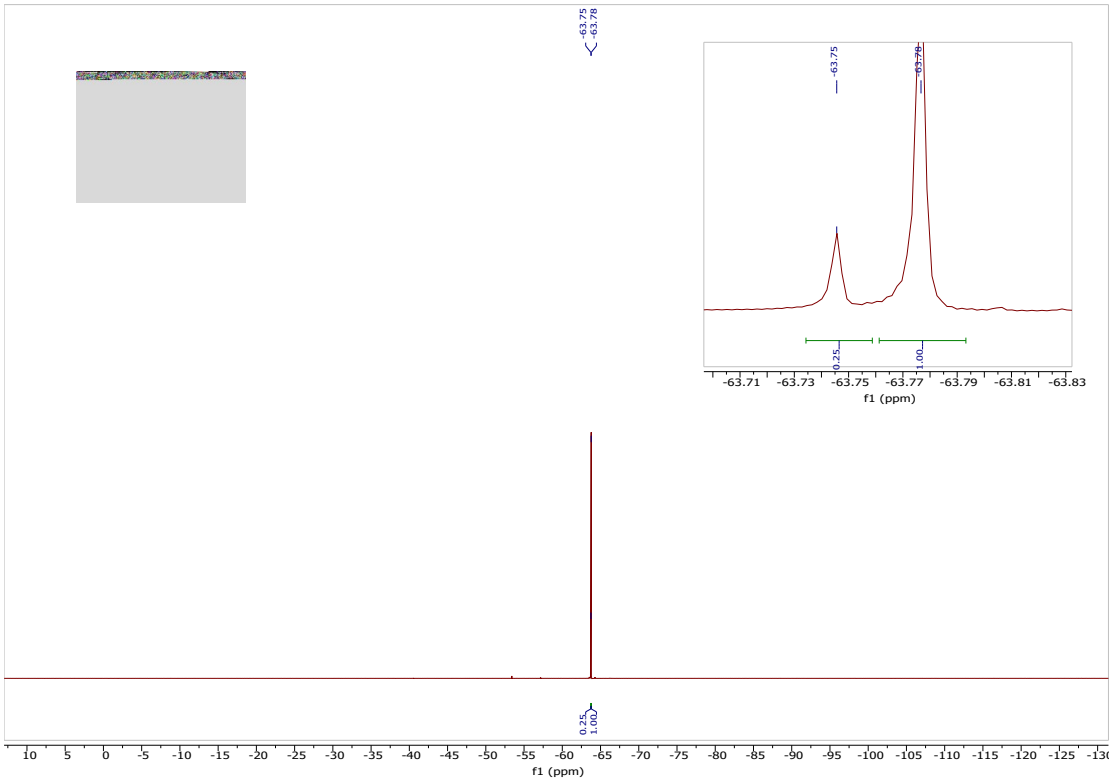


Figure S37 ^{1}H NMR spectrum for compound 3o

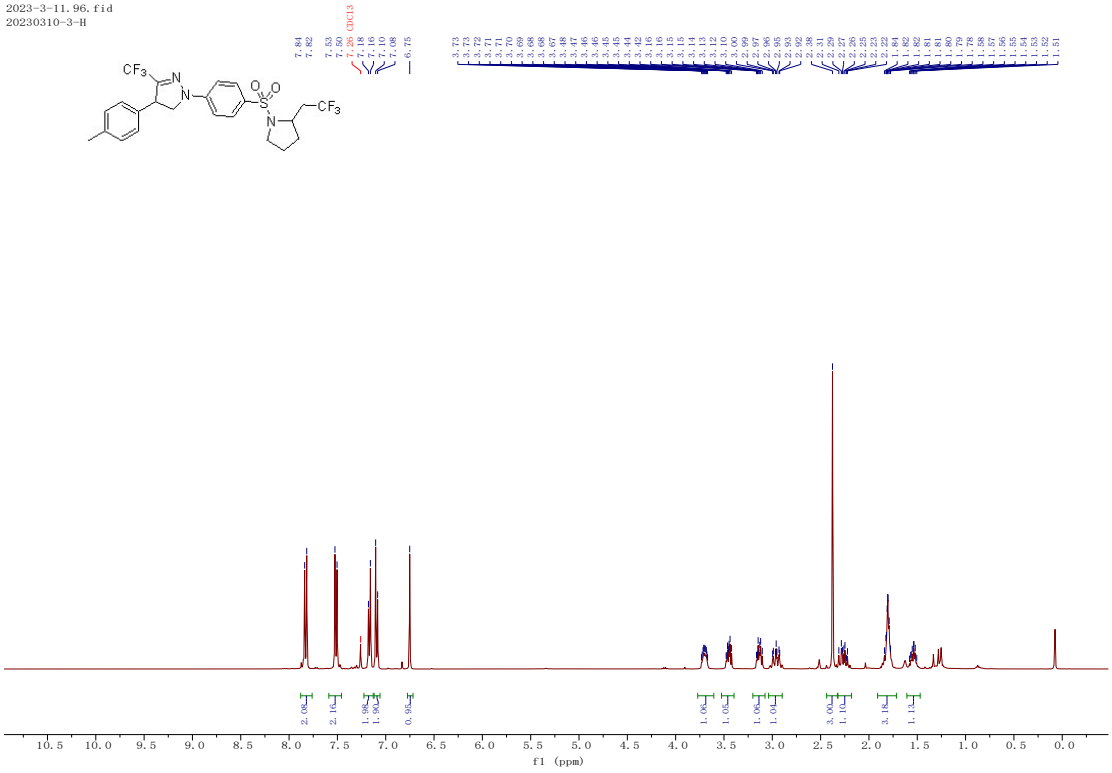


Figure S38 ^{13}C NMR spectrum for compound 3o

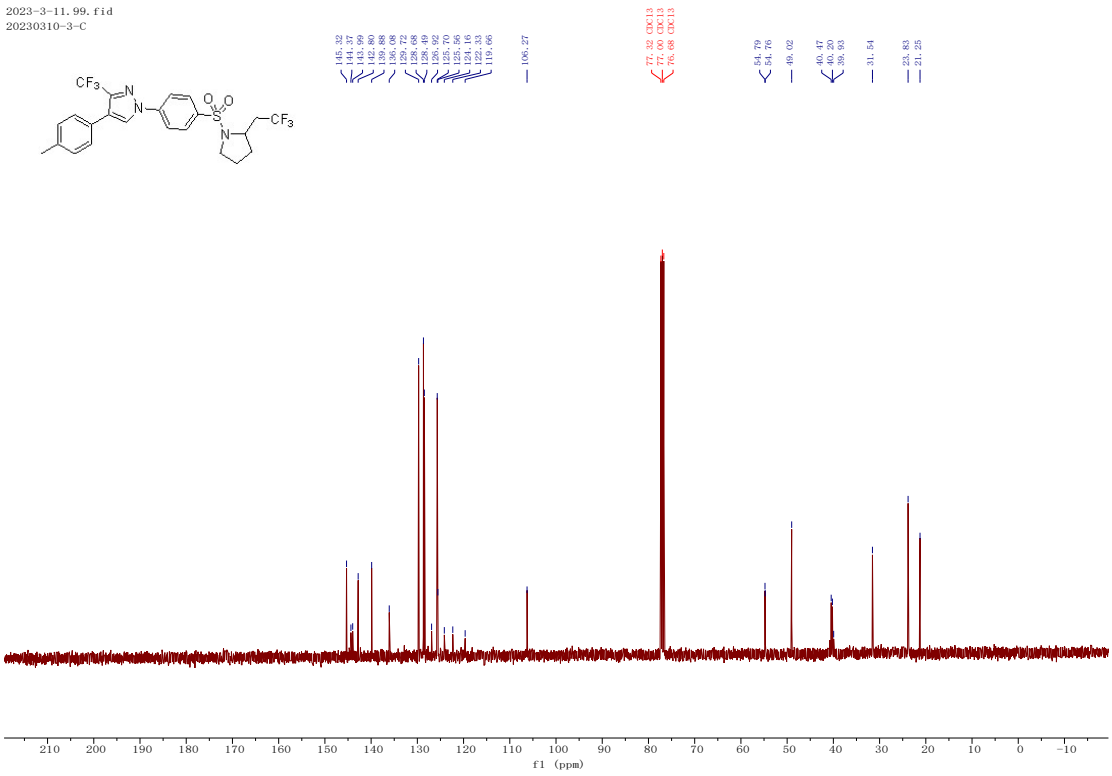


Figure S39 ^{19}F NMR spectrum for compound 3O

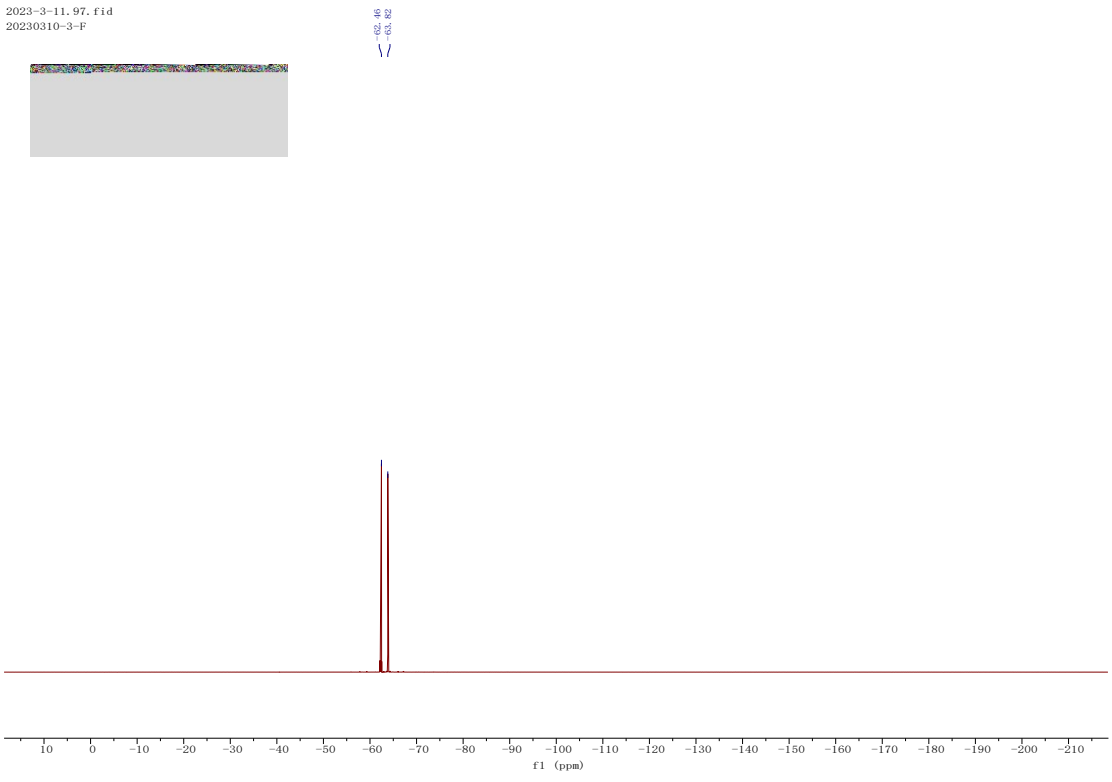


Figure S40 ^{1}H NMR spectrum for compound 4a

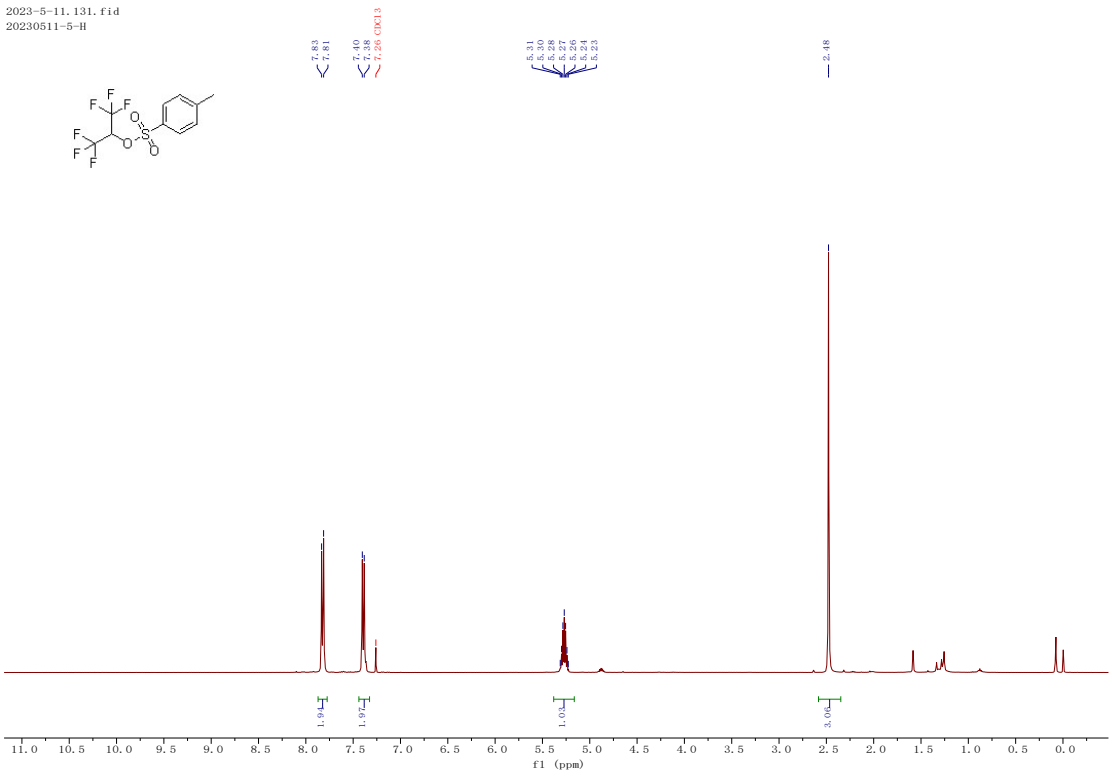


Figure S41 ^{13}C NMR spectrum for compound 4a

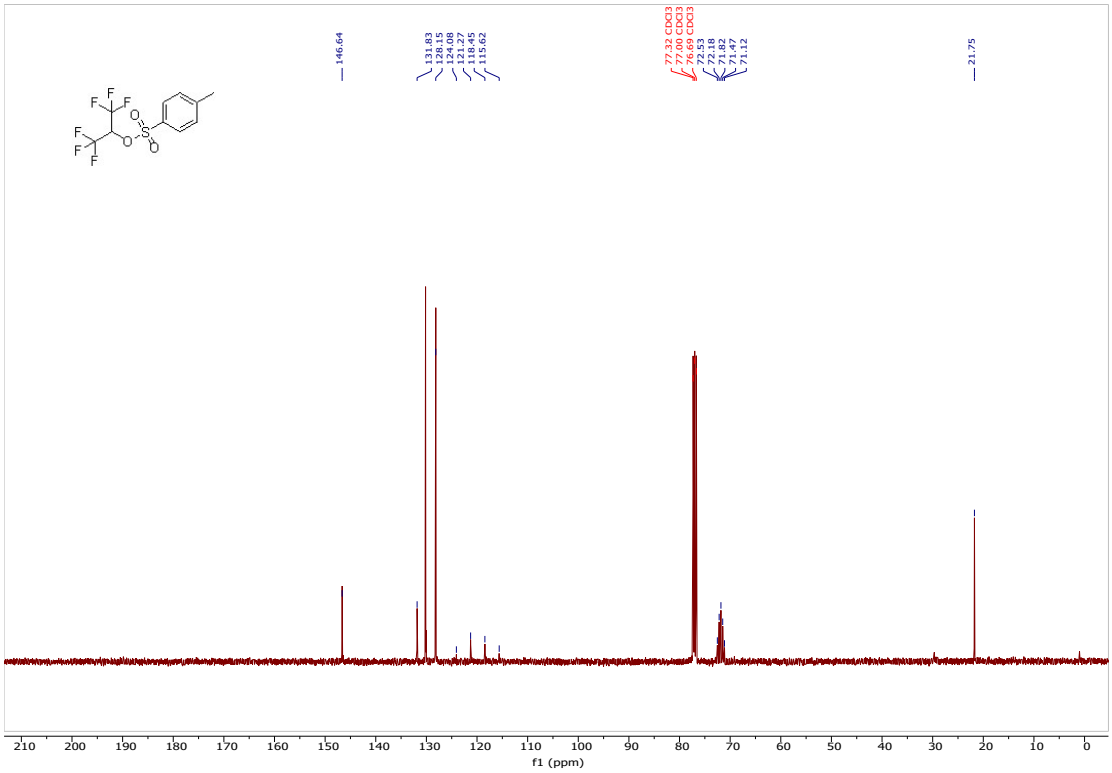


Figure S42 ^{19}F NMR spectrum for compound 4a

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