Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Selective *S*-Arylation of Thiols with *o*-OTf-substituted Diaryliodonium Salts Toward Functional Diarylsulfides

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Table of Contents

Part 1. General Information

a. Methods:

NMR spectrum: ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 (with tetramethylsilane as an internal standard) on a Bruker AVANCE 400 spectrometer at ambient temperature, operating at 400 MHz, 101 MHz, and 376 MHz respectively. Data were reported as follows: Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

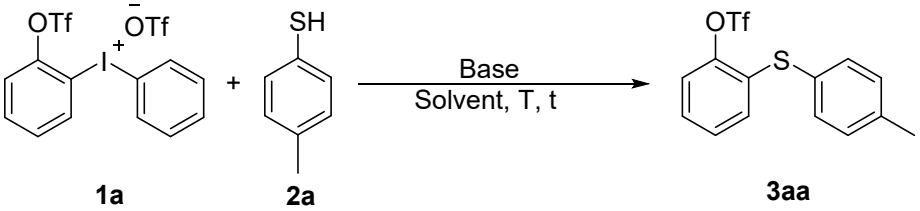
Mass spectroscopy: Mass spectra were in general recorded on a Waters LCT Premier XE spectrometer or EI Mass spectra were measured on HP HP5989A, Aglient HP5873 or Waters Micromass GCT mass spectrometer. ESI-MS analyses were performed in positive ionization mode on an Agilent 1100-MSD or Bruker Daltonics FTMS-7 mass spectrometer.

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

b. Materials:

All solvents were purchased from Adamas-beta and dried and/or distilled by standard methods. All reagents were purchased from commercial sources (Adamas-beta; Sinopharma reagents; TCI; Acros) and used without further purification. Reactions were monitored by TLC (detection with UV light). The preparation of all other materials is described in detail below.

Part 2. Table of Reaction Condition Optimization[a]



1a **2a** **3aa**

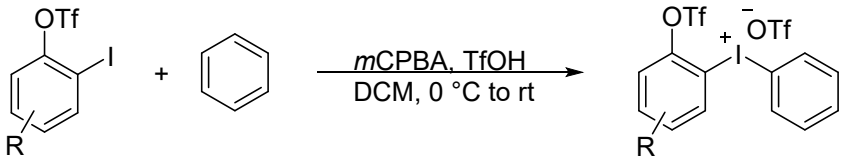
Entry	Base	Solvent	*T* [°C]	t [h]	Yield [%][b]
1[c]	Cs_2CO_3	MeCN	25	12	15
2	/	MeCN	25	12	n.r.
3	Cs_2CO_3	MeCN	50	12	20
4	K_3PO_4	MeCN	50	12	22
5	K_2CO_3	MeCN	50	12	19
6	KOH	MeCN	50	12	n.d.
7	NaOH	MeCN	50	12	n.d.
8	Na_2CO_3	MeCN	50	12	42
9	$NaHCO_3$	MeCN	50	12	10
10	$NaNO_2$	MeCN	50	12	34
11	CH_3COONa	MeCN	50	12	42
12	*t*-BuOK	MeCN	50	12	trace
13	*t*-BuOLi	MeCN	50	12	28
14	$NaOC_2H_5$	MeCN	50	12	40
15	$NaOCH_3$	MeCN	50	12	18
16	Na_2CO_3	DCE	50	12	23
17	Na_2CO_3	DCM	30	12	trace
18	Na_2CO_3	Toluene	50	12	19

19	Na_2CO_3	THF	50	12	21
20	Na_2CO_3	1,4-Dioxane	50	12	trace
21	Na_2CO_3	DMF	50	12	18
22	Na_2CO_3	DMA	50	12	20
23	Na_2CO_3	PhCl	50	12	22
24	Na_2CO_3	DMSO	50	12	28
25	Na_2CO_3	H_2O	50	12	29
26	Na_2CO_3 (6 eq.)	MeCN	50	12	39
27	Na_2CO_3 (4 eq.)	MeCN	50	12	40
28	Na_2CO_3 (3 eq.)	MeCN	50	12	32
29[d]	Na_2CO_3	MeCN	50	12	34
30[e]	Na_2CO_3	MeCN	50	12	40
31[f]	Na_2CO_3	MeCN	50	12	37
32	Na_2CO_3	MeCN	80	12	31
33	Na_2CO_3	MeCN	40	12	45
34	Na_2CO_3	MeCN	30	12	47
35	Na_2CO_3	MeCN	20	12	45
36	Na_2CO_3	MeCN	10	15	46
37	Na_2CO_3	MeCN	0	15	68
38	Na_2CO_3	MeCN	-10	18	48
39	Na_2CO_3	MeCN	-20	18	42
40[g]	Na_2CO_3	MeCN	0	15	66
41[h]	Na_2CO_3	MeCN	0	15	62
42[i]	Na_2CO_3	MeCN	0	15	62

[a] Reaction conditions: **1a** (0.3 mmol, 1 equiv.), **2a** (0.5 mmol, 1.68 equiv.), base (1.5 mmol, 5 equiv.) in 2 mL solvent, temperature (see Table), time (see Table). [b] Yield of isolated product. [c] Cs_2CO_3 (0.33 mmol, 1.1 equiv.). [d] **2a** (0.6 mmol, 2 equiv.). [e] **2a** (0.45 mmol, 1.5equiv.). [f] **2a** (0.36 mmol, 1.2 equiv.). [g] The counteranion BF_4 of **1a** was used. [h] The counteranion NTf_2 of **1a** was used. [i] The counteranion $B(C_6F_5)_4$ of **1a** was used. n. d. = not detected, n. r. = no reaction. DCE = 1,2-dichloroethane, DCM = dichloromethane, THF = tetrahydrofuran, DMSO = dimethylsulfoxide, DMF = *N,N*-dimethylformamide, DMA = *N,N*-dimethylacetamide.

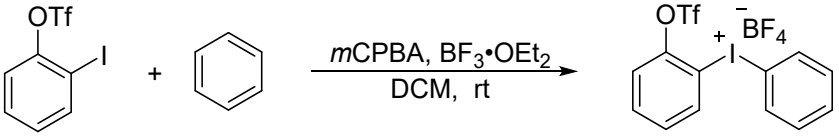
Part 3. Synthesis and Characterization of Diaryliodonium Salts.

General procedure A:[1,4]



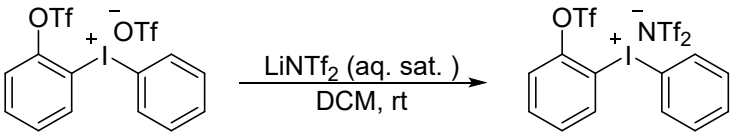
Substituted 2-iodophenyl trifluoromethanesulfonate (5.0 mmol, 1.0 equiv.) and *m*-Chloroperbenzoic acid (75% active oxidant, 1.1 equiv.) were dissolved in CH_2Cl_2 (40 mL) in a round-bottom flask. Then benzene (1.1 equiv.) was added and the solution was cooled to 0 °C followed by dropwise addition of TfOH (3.0 equiv.), resulting in a coloured solution. The reaction mixture was stirred at room temperature for 2 h and subsequently concentrated under vacuum. Et_2O (30 mL) was added and the mixture was stirred at room temperature for 30 min to precipitation out an off-white solid. The solid was filtered off, washed with Et_2O and dried under vacuum to give diaryliodonium salts.

General procedure B:[2,4]



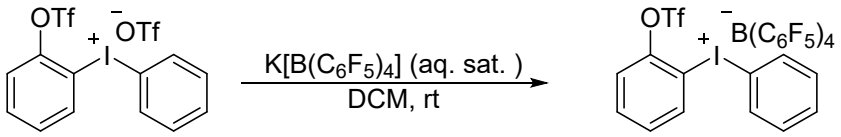
2-Iodophenyl trifluoromethanesulfonate (5.0 mmol, 1.0 equiv.) and *m*-chloroperbenzoic acid (75% active oxidant, 1.1 equiv.) were dissolved in CH_2Cl_2 (40 mL). To the solution was added $BF_3{\cdot}OEt_2$ (2.5 equiv.) at room temperature. The resulting yellow solution was stirred for 1 h and cooled to 0 °C, followed by addition of substituted arylboronic acid (1.1 equiv.). The reaction mixture was stirred at 0 °C for 10 min before it was allowed to warm to room temperature and stirred for further 30 min. Then the solvent was removed under reduced pressure. The resulting crude residue was triturated with diethyl ether and isolated by filtration to give analytically pure diaryliodonium salts.

General procedure C:[3]



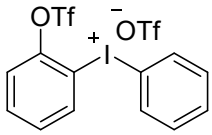
Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium trifluoromethanesulfonate (3.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and mixed with a saturated aqueous solution of $LiNTf_2$ (20 mL), stirred overnight. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel to afford pure diaryliodonium salts.

General procedure D:[3]



Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium trifluoromethanesulfonate (3.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and mixed with a saturated aqueous solution of $K[B(C_6F_5)_4]$ (20 mL), stirred overnight. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel to afford pure diaryliodonium salts.

Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium trifluoromethanesulfonate (1a-OTf)



The preparation was according to the **general procedure A** on 5.0 mmol scale. A white powder (2.33 g, 81%) was obtained through the procedure of trituration of diethyl ether.

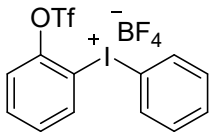
^{1}H NMR (400 MHz, d_6-DMSO) δ 8.64 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 12.4, 6.9 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 2H).

^{19}F NMR (376 MHz, d_6-DMSO) δ -73.36 (s), -77.75 (s).

The ^{1}H NMR is consistent with the reported spectrum.[4]

The preparation of diaryliodonium salts **1b**-**1q** was according to the **general procedure A**, and the spectral data are consistent with previously reported.[4]

Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium tetrafluoroborate (1a-BF_4)



The preparation was according to the **general procedure B** on 5.0 mmol scale. A white powder (2.04 g, 79%) was obtained through the procedure of trituration of diethyl ether.

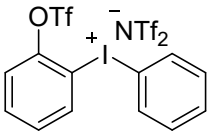
^{1}H NMR (400 MHz, d_6-DMSO) δ 8.65 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.92 – 7.83 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.68 (q, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, d_6-DMSO) δ 147.04, 138.69, 135.68, 134.98, 132.55, 132.13, 131.80, 118.09 (d, $J_{C\text{-}F}$ = 321.2 Hz), 122.67, 117.09, 110.90.

^{19}F NMR (376 MHz, d_6-DMSO) δ -73.61 (s), -148.18 (br), -148.23 (br).

HRMS m/z (ESI): calculated for $C_{13}H_9F_3IO_3S^+[M\text{-}BF_4]^+$ 428.9269, found 428.9257.

Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium bis((trifluoromethyl)sulfonyl)amide (1a-NTf_2)



The preparation was according to the **general procedure C** on 3.0 mmol scale. A white powder (1.79 g, 84%) was obtained through the procedure of column chromatography.

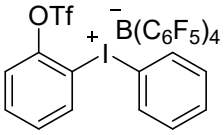
^{1}H NMR (400 MHz, d_6-DMSO) δ 8.64 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, d_6-DMSO) δ 147.13, 138.75, 135.75, 134.89, 132.64, 132.22, 131.87, 118.09 (d, $J_{C\text{-}F}$ = 321.2 Hz), 122.76, 116.39, 111.04.

^{19}F NMR (376 MHz, d_6-DMSO) δ -73.08 (s), -78.76 (s).

HRMS m/z (ESI): calculated for $C_{13}H_9F_3IO_3S^+[M\text{-}NTf_2]^+$ 428.9269, found 428.9263.

Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)iodonium tetrakis(perfluorophenyl)borate (1a-$B(C_6F_5)_4$)



The preparation was according to the **general procedure D** on 3.0 mmol scale. A white viscous solid (1.36 g, 41%) was obtained through the procedure of column chromatography.

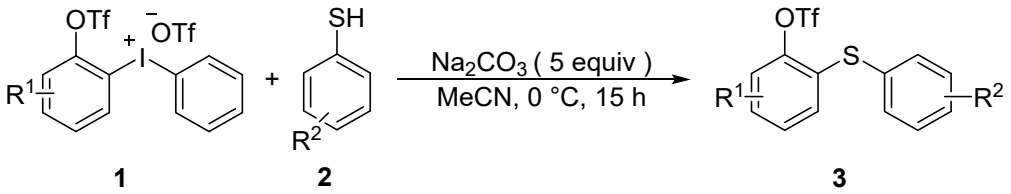
^{1}H NMR (400 MHz, d_6-DMSO) δ 8.65 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.87 (t, *J* = 7.1 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, d_6-DMSO) δ 172.22, 156.07, 147.66 (dm, $J_{C\text{-}F}$ = 239.4 Hz), 147.14, 138.77, 137.29, 135.74 (dm, $J_{C\text{-}F}$ = 249.5 Hz), 135.04, 133.81 (dm, $J_{C\text{-}F}$ = 248.5 Hz), 132.56, 132.16, 131.82, 131.68, 122.69 (d, $J_{C\text{-}F}$ = 14.1 Hz), 118.17 (d, $J_{C\text{-}F}$ = 322.2 Hz), 115.64, 110.99.

^{19}F NMR (376 MHz, d_6-DMSO) δ -73.25 (s), -132.46 (d, *J* = 12.2 Hz), -161.57 (dd, *J* = 27.8, 21.3 Hz), -165.61 – -166.73 (m).

HRMS m/z (ESI): calculated for $C_{13}H_9F_3IO_3S^+[M\text{-}B(C_6F_5)_4]^+$ 428.9269, found 428.9266.

Part 4. Synthesis and Characterization of Products from *S*-arylation Reactions.

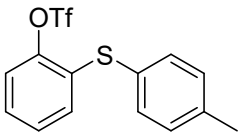


1 **2** **3**

General procedure:

To an oven-dried Schlenk tube was added iodonium salts **1** (0.3 mmol, 1 equiv.), thiophenol **2** (0.5 mmol, 1.68 equiv.) and Na_2CO_3 (1.5 mmol, 5 equiv.). The tube was degassed with argon for three times. Anhydrous acetonitrile (2 mL) was added via syringe, and the mixture was stirred at 0 °C in a cryogenic reactor for 15 h. The solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford the desired products.

2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate (3aa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 68% (71 mg) as a light yellow oil after column chromatography (petroleum ether).

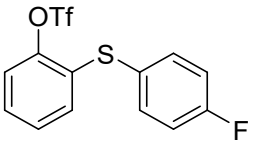
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.18 (m, 2H), 7.18 – 7.16 (m, 1H), 7.09 – 7.05 (m, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.20, 139.25, 134.02, 132.93, 131.48, 130.61, 128.77, 128.06, 127.74, 121.86, 118.76 (q, $J_{C\text{-}F}$ = 321.2 Hz), 21.39.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.58 (s).

The ^{1}H NMR of **3aa** is consistent with the reported spectrum.[5]

2-((4-Fluorophenyl)thio)phenyl trifluoromethanesulfonate (3ab)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 72% (76 mg) as a light yellow oil after column chromatography.

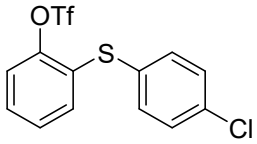
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 (td, *J* = 6.1, 1.9 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.06 – 6.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.25 (d, J_{C-F} = 250.5 Hz), 147.47, 135.88, 135.80, 132.25, 131.92, 128.94, 128.35, 127.25, 127.22, 122.05, 118.76 (q, J_{C-F} = 321.2 Hz), 117.02 (dd, J_{C-F} = 23.2, 7.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.59 (s), -111.85 (s).

HRMS m/z (EI-TOF): calculated for $C_{13}H_8F_4O_3S_2^+$ $[M]^+$ 351.9845, found 351.9854.

2-((4-Chlorophenyl)thio)phenyl trifluoromethanesulfonate (3ac)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 79% (87 mg) as a yellow oil after column chromatography.

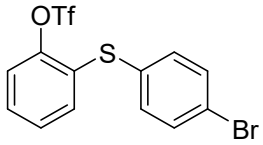
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 3.1 Hz, 4H), 7.22 – 7.18 (m, 2H), 7.18 – 7.15 (m, 1H), 7.15 – 7.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.12, 134.73, 133.92, 133.12, 131.38, 131.02, 129.88, 129.05, 123.52, 122.21, 118.74 (q, J_{C-F} = 321.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56 (s).

HRMS m/z (FI): calculated for $C_{13}H_8ClF_3O_3S_2^+$ $[M]^+$ 367.9550, found 367.9542.

2-((4-Bromophenyl)thio)phenyl trifluoromethanesulfonate (3ad)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 83% (103 mg) as a light yellow oil after column chromatography.

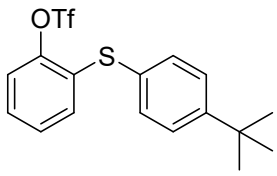
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.29 – 7.22 (m, 2H), 7.22 – 7.19 (m, 1H), 7.19 – 7.18 (m, 1H), 7.18 – 7.17 (m, 1H), 7.17 – 7.16 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.22, 133.98, 133.32, 132.81, 132.18, 130.76, 129.15, 129.07, 122.72, 122.24, 118.74 (q, J_{C-F} = 322.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.55 (s).

HRMS m/z (FI): calculated for $C_{13}H_8BrF_3O_3S_2^+$ $[M]^+$ 411.9045, found 411.9041.

2-(4-(*tert*-Butyl)phenyl)thio)phenyl trifluoromethanesulfonate (3ae)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 46% (54 mg) as a light yellow oil after column chromatography.

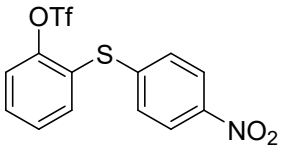
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 3H), 7.10 (ddd, *J* = 7.0, 4.6, 2.0 Hz, 3H), 7.02 – 6.98 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.25, 147.36, 133.49, 132.68, 131.84, 128.78, 128.29, 127.85, 126.87, 121.88, 118.79 (q, $J_{C\text{-}F}$ = 322.2 Hz), 34.85, 31.34.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56 (s).

HRMS m/z (EI-TOF): calculated for $C_{13}H_8F_4O_3S_2^+$ $[M]^+$ 390.0566, found 390.0569.

2-((4-Nitrophenyl)thio)phenyl trifluoromethanesulfonate (3af)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 95% (108 mg) as a bright yellow oil after column chromatography.

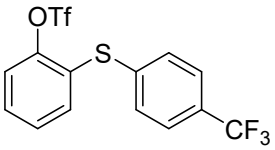
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 2H), 7.64 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.49 – 7.41 (m, 2H), 7.28 – 7.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.22, 146.32, 144.89, 137.15, 131.90, 129.67, 128.29, 126.47, 126.20, 124.54, 124.36, 122.96, 118.64 (q, $J_{C\text{-}F}$ = 321.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.50 (s).

HRMS m/z (EI-TOF): calculated for $C_{13}H_8F_3NO_5S_2^+$ $[M]^+$ 378.9790, found 378.9792.

2-((4-(Trifluoromethyl)phenyl)thio)phenyl trifluoromethanesulfonate (3ag)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 93% (112 mg) as a light yellow oil after column chromatography.

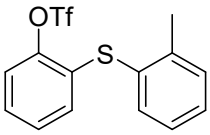
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.40 – 7.34 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.43, 139.48, 135.52, 130.53, 130.26 129.72, 129.56 (q, $J_{C\text{-}F}$ = 99.0 Hz), 129.39, 129.35, 128.57, 126.32 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.03 (q, $J_{C\text{-}F}$ = 273.7 Hz), 122.61, 118.74 (q, $J_{C\text{-}F}$ = 322.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69 (s), -73.50 (s).

HRMS m/z (FI): calculated for $C_{14}H_8F_6O_3S_2^+$ $[M]^+$ 401.9814, found 401.9825.

2-(*o*-Tolylthio)phenyl trifluoromethanesulfonate (3ah)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 66% (69 mg) as a light yellow oil after column chromatography.

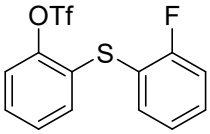
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.14 – 7.09 (m, 2H), 7.09 – 7.04 (m, 1H), 6.75 (dd, *J* = 7.8, 1.9 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.04, 141.92, 135.26, 132.07, 131.22, 130.23, 130.13, 129.60, 128.81, 127.37, 127.30, 121.93, 118.79 (q, $J_{C\text{-}F}$ = 322.2 Hz), 20.66.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.57 (s).

HRMS m/z (FI): calculated for $C_{14}H_{11}F_3O_3S_2^+$ $[M]^+$ 348.0096, found 348.0093.

2-((2-Fluorophenyl)thio)phenyl trifluoromethanesulfonate (3ai)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 58% (61 mg) as a light yellow oil after column chromatography.

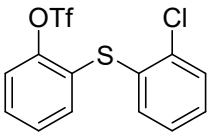
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.21 (m, 2H), 7.20 – 7.16 (m, 1H), 7.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.10 – 7.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07 (d, $J_{C\text{-}F}$ = 250.5 Hz), 147.90, 135.17, 132.37, 131.08 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.77, 128.87, 128.69, 125.13 (d, $J_{C\text{-}F}$ = 4.0 Hz), 122.03, 119.31 (d, $J_{C\text{-}F}$ = 17.2 Hz), 118.69 (q, $J_{C\text{-}F}$ = 322.2 Hz), 116.42 (q, $J_{C\text{-}F}$ = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.50 (s), -107.13 (s).

HRMS m/z (FI): calculated for $C_{13}H_8F_4O_3S_2^+$ $[M]$+ 351.9845, found 351.9834.

2-((2-Chlorophenyl)thio)phenyl trifluoromethanesulfonate (3aj)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 68% (75 mg) as a light yellow oil after column chromatography.

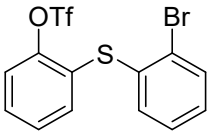
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 1H), 7.31 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 7.17 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72, 135.80, 133.97, 132.87, 132.59, 130.37, 129.54, 129.24, 129.11, 128.90, 127.71, 122.35, 118.74 (q, J_{C-F} = 321.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.47 (s).

HRMS m/z (FI): calculated for $C_{13}H_8ClF_3O_3S_2^+$ $[M]^+$ 367.9550, found 367.9557.

2-((2-Bromophenyl)thio)phenyl trifluoromethanesulfonate (3ak)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 72% (89 mg) as a colorless oil after column chromatography.

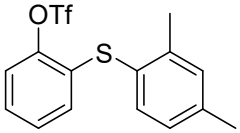
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 7.07 – 7.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.77, 134.90, 134.22, 133.65, 132.43, 129.70, 129.17, 128.98, 128.34, 128.32, 125.73, 122.39, 118.72 (q, J_{C-F} = 321.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.46 (s).

HRMS m/z (FI): calculated for $C_{13}H_8BrF_3O_3S_2^+$ $[M]^+$ 411.9045, found 411.9058.

2-((2,4-Dimethylphenyl)thio)phenyl trifluoromethanesulfonate (3al)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 49% (53 mg) as a light yellow oil after column chromatography.

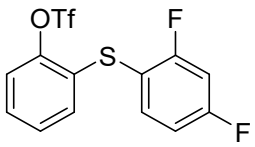
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.19 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 7.6, 1.9 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.55, 142.38, 140.24, 136.20, 132.96, 132.21, 129.22, 128.71, 128.15, 126.77, 125.87, 121.79, 118.79 (q, J_{C-F} = 322.2 Hz), 21.37, 20.64.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.59 (s).

HRMS m/z (FI): calculated for $C_{15}H_{13}F_3O_3S_2^+$ $[M]^+$ 362.0253, found 362.0267.

2-((2,4-Difluorophenyl)thio)phenyl trifluoromethanesulfonate (3am)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 68% (75 mg) as a colorless oil after column chromatography.

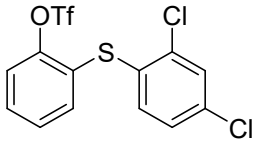
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 1H), 7.23 – 7.17 (m, 2H), 7.17 – 7.12 (m, 1H), 7.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.87 – 6.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.05 (dd, J_{C-F} = 253.5, 11.1 Hz), 162.90 (dd, J_{C-F} = 252.5, 13.1 Hz), 147.72, 137.16 (dd, J_{C-F} = 10.1, 2.0 Hz), 131.82, 130.14, 128.95, 128.70, 122.14, 118.76 (q, J_{C-F} = 321.2 Hz), 114.58 (dd, J_{C-F} = 18.2, 4.0 Hz), 112.75 (dd, J_{C-F} = 22.2, 4.0 Hz), 105.28 (t, J_{C-F} = 26.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.50 (s), -101.51 (d, *J* = 9.6 Hz), -106.48 (d, *J* = 9.6 Hz).

HRMS m/z (FI): calculated for $C_{13}H_7F_5O_3S_2^+$ $[M]^+$ 369.9751, found 369.9754.

2-((2,4-Dichlorophenyl)thio)phenyl trifluoromethanesulfonate (3an)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 75% (90 mg) as a colorless oil after column chromatography.

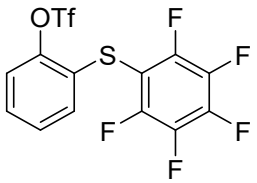
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.2 Hz, 1H), 7.41 (dd, *J* = 6.5, 1.9 Hz, 1H), 7.37 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.17 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.90, 136.28, 134.53, 134.31, 133.28, 131.57, 130.18, 130.03, 129.25, 128.24, 128.04, 122.52, 118.72 (q, J_{C-F} = 321.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.45 (s).

HRMS m/z (FI): calculated for $C_{13}H_7Cl_2F_3O_3S_2^+$ $[M]^+$ 401.9160, found 401.9154.

2-((Perfluorophenyl)thio)phenyl trifluoromethanesulfonate (3ao)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 58% (74 mg) as a light yellow oil after column chromatography.

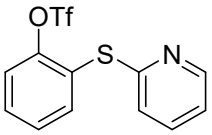
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 1.3 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42, 147.68 (dm, *J* = 244.4 Hz), 142.63 (dm, *J* = 260.6 Hz), 138.09 (dm, *J* = 257.6 Hz), 133.07, 130.14, 129.18, 126.97, 122.47, 118.79 (q, $J_{C\text{-}F}$ = 321.2 Hz), 106.96 (m).

^{19}F NMR (376 MHz, CDCl3) δ -73.24 (s), -130.99 (d, *J* = 4.2 Hz), -149.84 (t, *J* = 20.8 Hz), -159.71 (dd, *J* = 21.0, 15.7 Hz).

HRMS m/z (FI): calculated for $C_{13}H_4F_8O_3S_2^+$ $[M]^+$ 423.9469, found 423.9451.

2-(Pyridin-2-ylthio)phenyl trifluoromethanesulfonate (3ap)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 50% (50 mg) as a yellow oil after column chromatography.

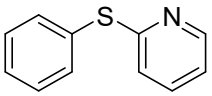
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.55 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.10 – 7.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.96, 150.49, 150.02, 137.71, 137.03, 135.10, 131.25, 129.12, 125.97, 122.48, 120.98, 118.68 (q, $J_{C\text{-}F}$ = 322.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.67 (s).

HRMS m/z (EI-TOF): calculated for $C_{12}H_8NO_3F_3S_2^+$ $[M]^+$ 334.9892, found 334.9896.

2-(Phenylthio)pyridine (3ap')

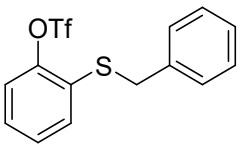


Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 23% (13 mg) as a colorless oil after column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.48 – 7.40 (m, 4H), 6.99 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.89 (dt, *J* = 8.1, 1.0 Hz, 1H).

The ^{1}H NMR is consistent with the reported spectrum.[17]

2-(Benzylthio)phenyl trifluoromethanesulfonate (3aq)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 58% (61 mg) as a colorless oil after column chromatography.

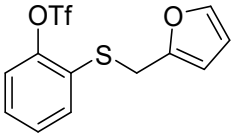
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (ddd, *J* = 7.0, 1.9, 1.0 Hz, 1H), 7.23 (d, *J* = 4.5 Hz, 4H), 7.21 – 7.20 (m, 2H), 7.18 (td, *J* = 6.6, 6.1, 1.9 Hz, 2H), 4.07 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.07, 136.36, 133.20, 130.56, 129.10, 128.72, 128.66, 128.61, 127.66, 121.88, 118.78 (q, $J_{C\text{-}F}$ = 322.2 Hz), 38.77.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.57 (s).

HRMS m/z (FI): calculated for $C_{14}H_{11}F_3O_3S_2^+$ $[M]^+$ 348.0096, found 348.0103.

2-((Furan-2-ylmethyl)thio)phenyl trifluoromethanesulfonate (3ar)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 58% (59 mg) as a colorless oil after column chromatography.

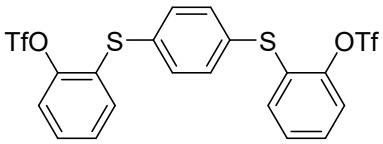
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.26 – 7.17 (m, 3H), 6.18 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.01 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.04 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.05, 149.47, 142.62, 134.24, 129.66, 129.22, 128.69, 121.93, 118.77 (q, $J_{C\text{-}F}$ = 321.2 Hz), 110.65, 108.67, 31.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.65 (s).

HRMS m/z (FI): calculated for $C_{12}H_9F_3O_4S_2^+$ $[M]^+$ 337.9889, found 337.9877.

(1,4-Phenylenebis(sulfanediyl))bis(2,1-phenylene) bis(trifluoromethanesulfonate) (3as)



Prepared according to the general procedure on 0.6 mmol scale and obtained an isolated yield of 33% (58 mg) as a colorless oil after column chromatography.

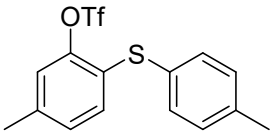
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 (d, *J* = 1.5 Hz, 2H), 7.33 – 7.31 (m, 4H), 7.31 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.52, 133.93, 133.55, 132.64, 130.28, 129.42, 129.11, 122.29, 118.74 (q, $J_{C\text{-}F}$ = 322.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.57 (s).

HRMS m/z (ESI): calculated for $C_{20}H_{12}F_6O_6S_4^+$ $[M]^+$ 589.9415, found 589.9423.

5-Methyl-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ba)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 61% (66 mg) as a yellow oil after column chromatography.

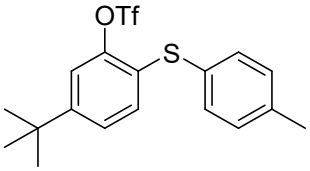
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.03 (m, 1H), 2.36 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.84, 139.34, 138.51, 132.88, 132.75, 130.35, 129.50, 128.33, 122.42, 120.37, 118.78 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.33, 21.13.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.62 (s).

HRMS m/z (FI): calculated for $C_{15}H_{13}F_3O_3S_2^+$ $[M]^+$ 362.0253, found 362.0261

5-(*tert*-Butyl)-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ca)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 47% (57 mg) as a light yellow oil after column chromatography.

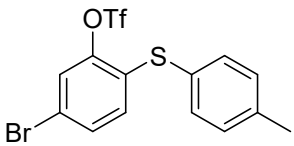
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 2.36 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.62, 147.69, 138.69, 133.27, 132.04, 130.38, 129.13, 128.51, 125.96, 119.08, 118.72 (q, $J_{C\text{-}F}$ = 322.2 Hz), 34.90, 31.16, 21.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56 (s).

HRMS m/z (FI): calculated for $C_{18}H_{19}F_3O_3S_2^+$ $[M]^+$ 404.0722, found 404.0731.

5-Bromo-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3da)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 62% (79 mg) as a light yellow oil after column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 2.38 (s, 3H).

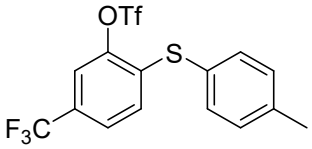
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.71, 139.73, 134.25, 132.71, 132.08, 131.98, 130.79, 127.24, 125.09, 119.84,

118.71 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.37 (s).

HRMS m/z (FI): calculated for $C_{14}H_{10}BrF_3O_3S_2^+$ [M]$^+$ 425.9201, found 425.9213.

2-(*p*-Tolylthio)-5-(trifluoromethyl)phenyl trifluoromethanesulfonate (3ea)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 94% (117 mg) as a light yellow oil after column chromatography.

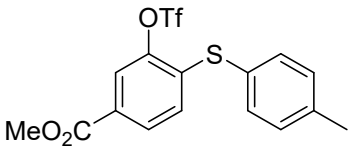
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.41, 140.72, 139.57, 135.46, 131.14 (q, $J_{C\text{-}F}$ = 5.1 Hz), 129.63, 129.52, 129.00 (q, $J_{C\text{-}F}$ = 33.3 Hz), 125.36, 123.11 (q, $J_{C\text{-}F}$ = 273.7 Hz), 118.97, 118.74 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.51.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57 (s), -73.40 (s).

HRMS m/z (FI): calculated for $C_{15}H_{10}F_6O_3S_2^+$ [M]$^+$ 415.9970, found 415.9979.

Methyl 4-(*p*-tolylthio)-3-(((trifluoromethyl)sulfonyl)oxy)benzoate (3fa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 97% (118 mg) as a yellow oil after column chromatography.

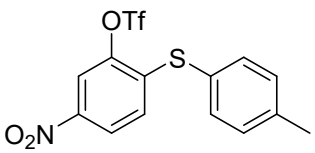
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.7 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.20, 145.37, 140.53, 137.54, 135.39, 131.04, 129.35, 128.72, 128.65, 125.40, 122.59, 118.71 (q, $J_{C\text{-}F}$ = 322.2 Hz), 52.67, 21.44.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.44 (s).

HRMS m/z (FI): calculated for $C_{16}H_{13}F_3O_5S_2^+$ [M]$^+$ 406.0151, found 406.0163.

5-Nitro-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ga)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 92% (108 mg) as a bright yellow oil after column chromatography.

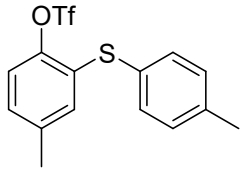
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.98 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.29, 144.41, 144.27, 141.48, 135.79, 131.43, 127.99, 123.84, 123.18, 118.66 (q, $J_{C\text{-}F}$ = 321.2 Hz), 117.26, 21.50.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.19 (s).

HRMS m/z (FI): calculated for $C_{14}H_{10}F_3NO_5S_2^+$ $[M]^+$ 392.9947, found 392.9964.

4-Methyl-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ha)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 53% (58 mg) as a light yellow oil after column chromatography.

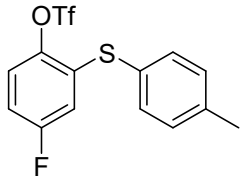
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 1H), 7.15 (d, *J* = 10.1 Hz, 2H), 7.04 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.58, 139.08, 138.88, 133.46, 132.33, 131.83, 130.46, 128.79, 128.65, 121.56, 118.78 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.40, 21.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.60 (s).

HRMS m/z (FI): calculated for $C_{15}H_{13}F_3O_3S_2^+$ $[M]^+$ 362.0253, found 362.0246.

4-Fluoro-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ia)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 63% (69 mg) as a yellow oil after column chromatography.

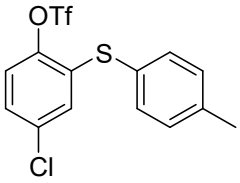
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.21 (m, 3H), 6.90 – 6.84 (m, 1H), 6.62 (dd, *J* = 8.7, 3.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.71 (d, $J_{C\text{-}F}$ = 251.5 Hz), 142.11 (d, $J_{C\text{-}F}$ = 3.0 Hz), 140.35, 136.61 (d, $J_{C\text{-}F}$ = 8.1 Hz), 135.08, 130.99 (d, $J_{C\text{-}F}$ = 4.0 Hz), 126.16, 123.15 (dd, $J_{C\text{-}F}$ = 9.1, 6.1 Hz), 118.75 (q, $J_{C\text{-}F}$ = 322.2 Hz), 116.49 (dd, $J_{C\text{-}F}$ = 26.3, 10.1 Hz), 113.82 (dd, $J_{C\text{-}F}$ = 23.2, 8.1 Hz), 21.46.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.48 (s), -111.47 (s).

HRMS m/z (FI): calculated for $C_{14}H_{10}F_4O_3S_2^+$ $[M]^+$ 366.0002, found 365.9992.

4-Chloro-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ja)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 63% (72 mg) as a light yellow oil after column chromatography.

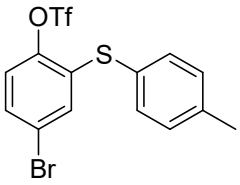
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.17 – 7.14 (m, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.88, 140.20, 135.75, 134.79, 134.60, 131.00, 129.77, 129.67, 127.19, 126.29, 122.85, 118.72 (q, $J_{C\text{-}F}$ = 321.2 Hz), 21.49.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.43 (s).

HRMS m/z (FI): calculated for $C_{14}H_{10}ClF_3O_3S_2^+$ $[M]^+$ 381.9706, found 381.9720.

4-Bromo-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ka)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 51% (65 mg) as a light yellow oil after column chromatography.

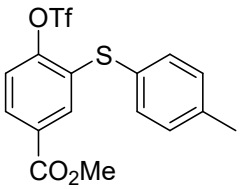
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.52, 140.15, 135.94, 134.67, 132.68, 130.98, 130.23, 126.37, 123.16, 122.38, 118.71 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.49.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.43 (s).

HRMS m/z (FI): calculated for $C_{14}H_{10}BrF_3O_3S_2^+$ $[M]^+$ 425.9201, found 425.9206.

Methyl 3-(*p*-tolylthio)-4-(((trifluoromethyl)sulfonyl)oxy)benzoate (3la)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 82% (100 mg) as a yellow oil after column chromatography.

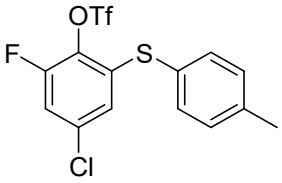
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.34, 149.82, 139.71, 134.13, 133.86, 132.55, 130.85, 130.66, 128.88, 127.08, 121.87, 118.72 (q, $J_{C\text{-}F}$ = 322.2 Hz), 52.78, 21.35.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.43 (s).

HRMS m/z (FI): calculated for $C_{16}H_{13}F_3O_5S_2^+$ $[M]^+$ 406.0151, found 406.0169.

4-Chloro-2-fluoro-6-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3ma)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 64% (77 mg) as a yellow oil after column chromatography.

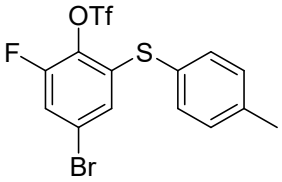
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.69 – 6.63 (m, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.96 (d, $J_{C\text{-}F}$ = 258.6 Hz), 140.65, 138.51, 135.06, 134.57 (d, $J_{C\text{-}F}$ = 10.1 Hz), 132.56 (d, $J_{C\text{-}F}$ = 14.1 Hz), 131.08, 125.66, 124.63 (d, $J_{C\text{-}F}$ = 15.2 Hz), 118.66 (q, $J_{C\text{-}F}$ = 322.2 Hz), 114.87 (dd, $J_{C\text{-}F}$ = 22.2, 12.1 Hz), 21.53.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.74 (d, *J* = 11.3 Hz), -122.70 (d, *J* = 12.7 Hz).

HRMS m/z (FI): calculated for $C_{14}H_9ClF_4O_3S_2^+$ $[M]^+$ 399.9612, found 399.9626.

4-Bromo-2-fluoro-6-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3na)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 50% (67 mg) as a yellow oil after column chromatography.

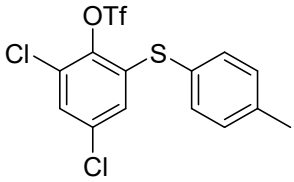
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.82 (t, *J* = 2.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.93 (d, $J_{C\text{-}F}$ = 259.6 Hz), 140.60, 138.71, 134.95, 133.14 (d, $J_{C\text{-}F}$ = 14.1 Hz), 131.11, 127.63 (d, $J_{C\text{-}F}$ = 11.1 Hz), 125.74, 121.84 (d, $J_{C\text{-}F}$ = 9.1 Hz), 118.64 (q, $J_{C\text{-}F}$ = 322.2 Hz), 117.93 (dd, $J_{C\text{-}F}$ = 22.2, 6.1 Hz), 21.52.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.73 (d, *J* = 11.3 Hz), -122.72 (q, *J* = 12.7 Hz).

HRMS m/z (FI): calculated for $C_{14}H_9BrF_4O_3S_2^+$ $[M]^+$ 443.9107, found 443.9097.

2,4-Dichloro-6-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3oa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 66% (82 mg) as a light yellow oil after column chromatography.

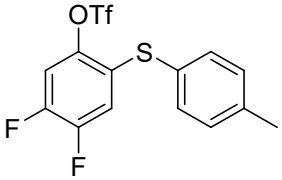
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 2.4 Hz, 2H), 7.24 (s, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.02, 140.57, 138.29, 134.89, 134.46, 131.11, 129.00, 128.16, 127.94, 126.13, 118.65 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.50.

^{19}F NMR (376 MHz, $CDCl_3$) δ -71.74 (s).

HRMS m/z (FI): calculated for $C_{14}H_9Cl_2F_3O_3S_2^+$ $[M]^+$ 415.9317, found 415.9335.

4,5-Difluoro-2-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3pa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 69% (79 mg) as a light yellow oil after column chromatography.

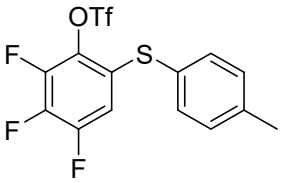
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 9.5, 6.6 Hz, 1H), 6.84 (dd, *J* = 10.2, 8.2 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.41 (dd, $J_{C\text{-}F}$ = 165.6, 12.1 Hz), 147.92 (dd, $J_{C\text{-}F}$ = 166.7, 11.1 Hz), 141.39 (dd, $J_{C\text{-}F}$ = 8.1, 3.0 Hz), 140.19, 134.46, 130.95, 130.54 (d, $J_{C\text{-}F}$ = 11.1 Hz), 126.87, 118.78 (dd, $J_{C\text{-}F}$ = 20.2, 12.1 Hz), 118.72 (q, $J_{C\text{-}F}$ = 322.2 Hz), 112.00 (dd, $J_{C\text{-}F}$ = 22.2, 9.1 Hz), 21.44.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.36 (s), -134.71 (d, *J* = 21.2 Hz), -135.24 (d, *J* = 21.2 Hz).

HRMS m/z (FI): calculated for $C_{14}H_9F_5O_3S_2^+$ $[M]^+$ 383.9908, found 383.9894.

2,3,4-Trifluoro-6-(*p*-tolylthio)phenyl trifluoromethanesulfonate (3qa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 55% (66 mg) as a colorless oil after column chromatography.

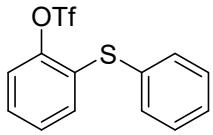
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.59 (ddd, *J* = 10.1, 7.6, 2.5 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.71, 134.90, 131.78, 131.71, 131.14, 125.93, 118.65 (q, $J_{C\text{-}F}$ = 322.2 Hz), 112.20 (d, $J_{C\text{-}F}$ = 3.0 Hz), 111.98 (d, $J_{C\text{-}F}$ = 4.0 Hz), 21.45.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.65 (d, *J* = 13.0 Hz), -131.16 (dd, *J* = 21.1, 6.9 Hz), -142.49 (m), -157.10 – -157.26 (m).

HRMS m/z (FI): calculated for $C_{14}H_8F_6O_3S_2^+$ $[M]^+$ 401.9814, found 401.9802.

2-(Phenylthio)phenyl trifluoromethanesulfonate (3at)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 65% (65 mg) as a colorless oil after column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 (d, *J* = 4.7 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.34 (d, *J* = 3.0 Hz, 1H), 7.29 (dd, *J* = 6.1, 2.0 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 (dd, *J* = 7.5, 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 136.06 (d, $J_{C\text{-}F}$ = 295.9 Hz), 133.06, 132.65, 132.48, 131.95, 131.84, 129.72, 128.89, 128.59, 128.43, 122.04, 118.77 (q, $J_{C\text{-}F}$ = 322.2 Hz).

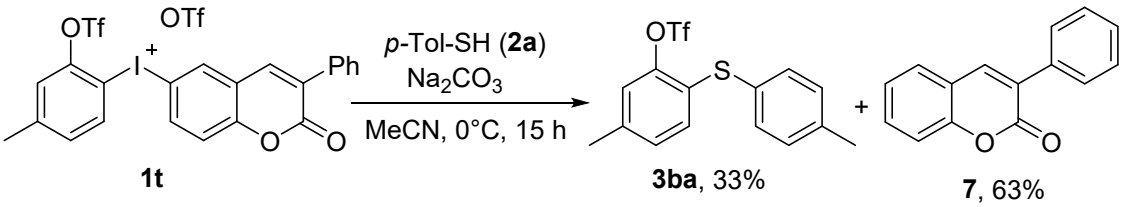
^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56 (s).

HRMS m/z (EI-TOF): calculated for $C_{13}H_9F_3O_3S_2^+$ $[M]^+$ 333.9940, found 333.9946.

Part 5. Mechanism and Derivatization of Thioether 3aa

The preparation and spectral data of diaryliodonium salts **1r** and **1s** were consistent with previously reported.[4]

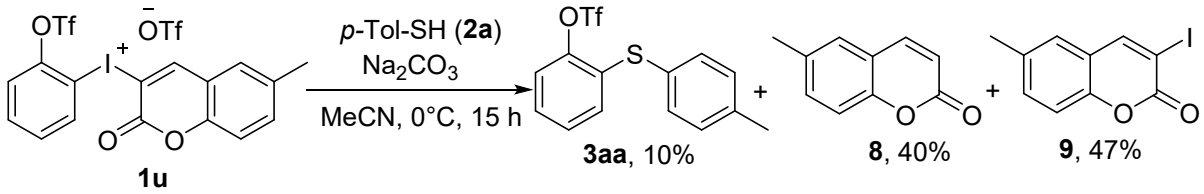
The preparation and spectral data of diaryliodonium salts **1t** and **1u** were consistent with previously reported.[13]



Following the modified procedure described in Part 4 on 0.3 mmol scale and obtained isolated yields of 33% (36 mg, **3ba**) as a yellow oil and 63% (42 mg, **7**) as a white solid after column chromatography.

3-Phenyl-2*H*-chromen-2-one (7): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (s, 1H), 7.80 – 7.69 (m, 2H), 7.63 – 7.53 (m, 2H), 7.49 – 7.31 (m, 4H), 7.31 – 7.25 (m, 1H).

The ^{1}H NMR of **7** is consistent with the reported spectrum.[14]



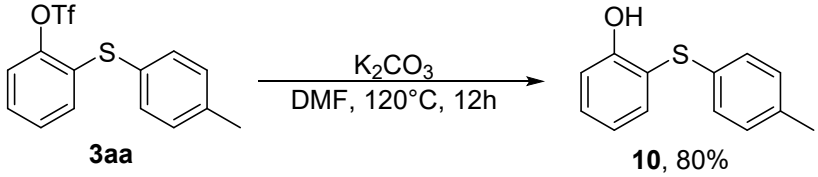
Following the modified procedure described in Part 4 on 0.3 mmol scale and obtained isolated yields of 10% (11 mg, **3aa**) as a light yellow oil, 40% (19 mg, **8**) as a white solid and 47% (40 mg, **9**) as a yellow solid after column chromatography.

6-Methyl-2*H*-chromen-2-one (8): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 9.5 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 9.5 Hz, 1H), 2.34 (s, 3H).

The ^{1}H NMR of **8** is consistent with the reported spectrum.[15]

3-Iodo-6-methyl-2*H*-chromen-2-one (9): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.36 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H).

The ^{1}H NMR of **9** is consistent with the reported spectrum.[16]

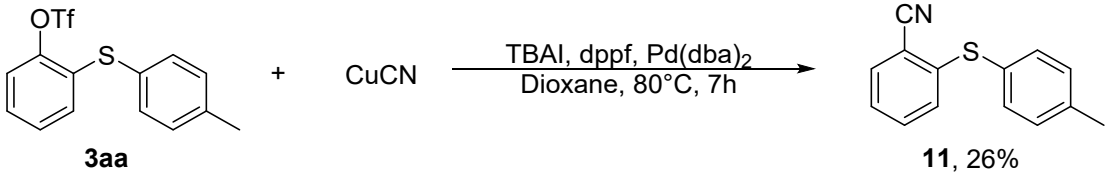


A mixture of 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.) and K_2CO_3 (0.6 mmol, 2 equiv.) in DMF (2 mL) was vigorously stirred at 120 °C under nitrogen atmosphere for 12 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with ethyl acetate and washed with water.

The aqueous phase was extracted with ethyl acetate, and the combined organic phases were dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel. Light yellow oil, 52 mg, 80%.

2-(*p*-Tolylthio)phenol (10): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.09 – 7.02 (m, 5H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 2.30 (s, 3H).

The ^{1}H NMR of **10** is consistent with the reported spectrum.[6]

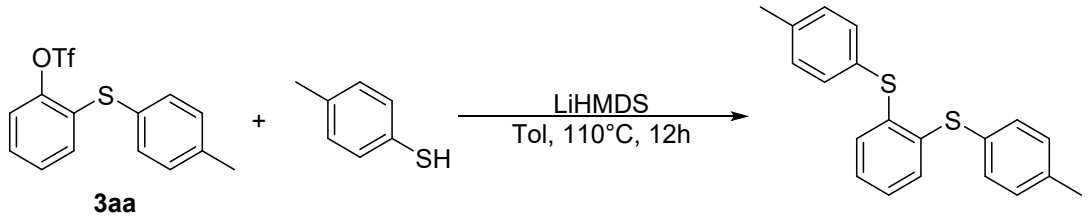


3aa **11**, 26%

Following the modified procedure described by Kazuo et al.[7] A mixture of 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.)， CuCN (1 mmol, 3 equiv.), TBAI (0.3 mmol, 1 equiv.), dppf (0.088 mmol, 3 mol%) and $Pd(dba)_2$ (0.014 mmol, 5 mol%) in Dioxane (2 mL) was vigorously stirred at 80 °C under nitrogen atmosphere for 7 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel. White solid, 18 mg, 26%.

2-(*p*-Tolylthio)benzonitrile (11): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.36 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 1H), 2.39 (s, 3H).

The ^{1}H NMR of **11** is consistent with the reported spectrum.[8]

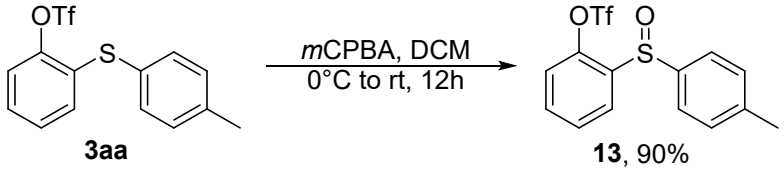


3aa **12**, 52%

Following the modified procedure described by Wang et al.[9] A mixture of 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.) and *p*-methylthiophenol (0.36 mmol, 1.2 equiv.), reduced to 0 °C and LiHMDS (0.3 mmol, 1 equiv.) was added slowly in Toluene (2 mL) , the reaction vigorously stirred at 110 °C under nitrogen atmosphere for 12 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel. White solid, 50 mg, 52%.

1,2-Bis(*p*-tolylthio)benzene (12): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.20 (m, 4H), 7.10 – 6.93 (m, 8H), 2.30 (s, 6H).

The ^{1}H NMR of **12** is consistent with the reported spectrum.[10]

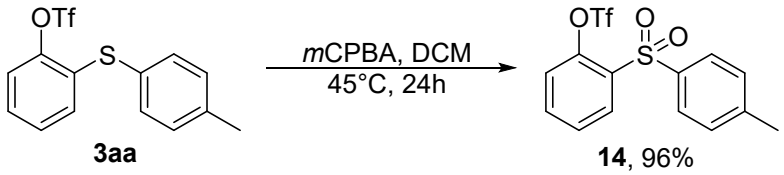


3aa **13**, 90%

Following the modified procedure described by Yoshida et al.[5] 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (2 mL). The solution was stirred and cooled to 0 °C, followed by addition of *m*-chloroperbenzoic acid (85% active oxidant, 1 equiv.) slowly. The reaction was warmed to room temperature and stirred for an additional 12 h. After completion of reaction (monitored by TLC), the mixture was added an aqueous saturated solution of sodium thiosulfate. The mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was washed with an aqueous saturated solution of potassium carbonate (20 mL × 2) and brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The crude compound was purified by column chromatography on silica gel. Light yellow solid, 98 mg, 90%.

2-(*p*-Tolylsulfinyl)phenyl trifluoromethanesulfonate (13): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.42 (td, *J* = 7.8, 1.9 Hz, 1H), 7.20 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.25 (s, 3H).

The ^{1}H NMR of **13** is consistent with the reported spectrum.[5]



3aa **14**, 96%

Following the modified procedure described by Nakajima et al.[11] 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (2 mL). The solution was stirred and followed by addition of *m*-chloroperbenzoic acid (85% active oxidant, 3 equiv.) slowly at room temperature. The reaction was stirred at 45 °C in an oil bath for an additional 24 h. After completion of reaction (monitored by TLC), the mixture was cooled to room temperature and added an aqueous saturated solution of sodium thiosulfate. The mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was washed with an aqueous saturated solution of brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The crude compound was purified by column chromatography on silica gel to afford 2-Tosylphenyl trifluoromethanesulfonate **14** (109 mg, 96%) as a light yellow solid.

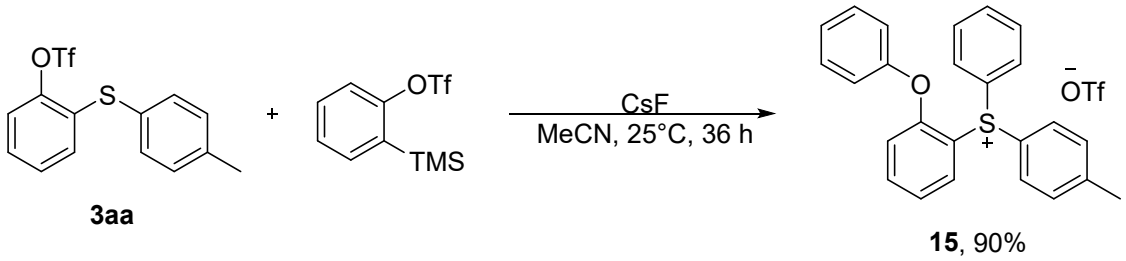
M.p.: 101-103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.67 (td, *J* = 7.9, 1.8 Hz, 1H), 7.55 (td, *J* = 7.7, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.36, 142.75, 140.61, 139.21, 132.79, 130.26, 129.42, 126.10, 125.56, 121.43, 118.58 (q, $J_{C\text{-}F}$ = 322.2 Hz), 21.54.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.32 (s).

HRMS m/z (EI-TOF): calculated for $C_{14}H_{11}F_3O_5S_2^+$ $[M]^+$ 379.9995, found 379.9998.



3aa **15**, 90%

Following the modified procedure described by Peng et al.[12] A mixture of 2-(*p*-Tolylthio)phenyl trifluoromethanesulfonate **3aa** (0.3 mmol, 1 equiv.) , 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (0.6 mmol, 2 equiv.) and CsF (0.9 mmol, 3 equiv., added every 12 h in 3 times) in MeCN (2 mL) was vigorously stirred at 25 °C under nitrogen atmosphere for 36 h. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel to afford (2-Phenoxyphenyl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **15** (140 mg, 90%) as an orange solid.

M.p.: 213-215 °C.

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.91 – 7.78 (m, 8H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, d_6-DMSO) δ 155.90, 153.90, 145.72, 136.39, 134.49, 132.12, 131.58, 131.53, 131.42, 131.37, 131.23, 130.92, 130.55, 128.69, 125.87, 125.35, 123.89, 120.73 (q, $J_{C\text{-}F}$ = 323.2 Hz), 119.74, 119.61, 119.00, 118.10, 115.02, 21.12.

^{19}F NMR (376 MHz, d_6-DMSO) δ -77.74 (s).

HRMS m/z (ESI-TOF): calculated for $C_{25}H_{21}OS^+$ $[M\text{-}OTf]^+$ 369.1308, found 369.1315.

Part 6. References

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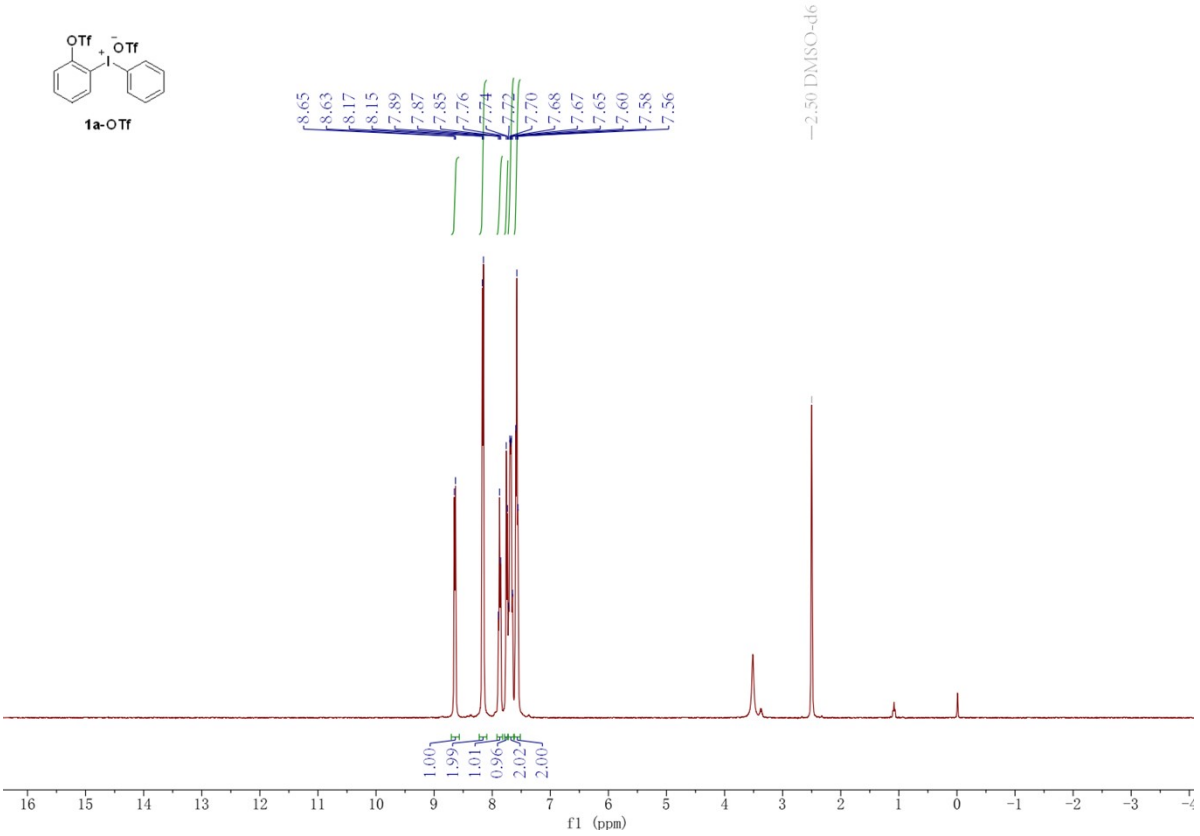
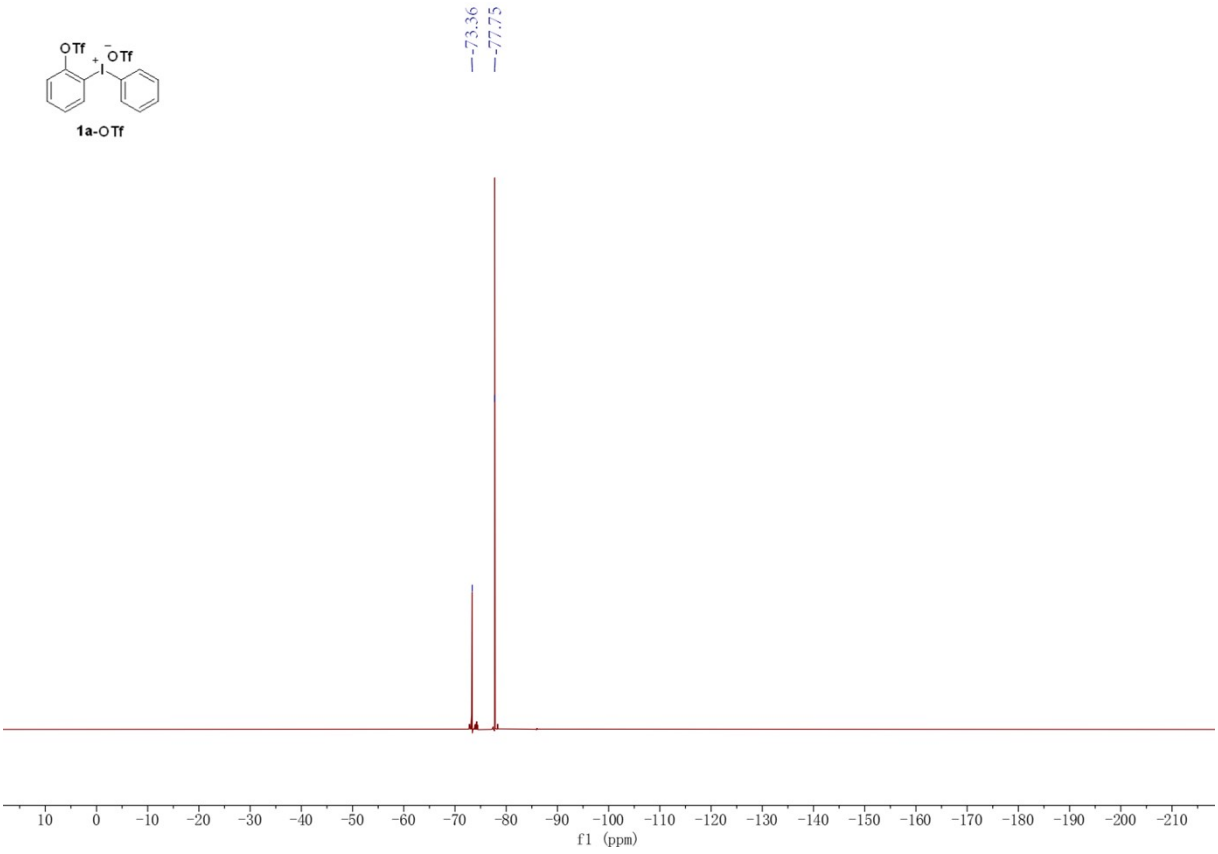
Part 7. ^{1}H, ^{13}C, and ^{19}F NMR spectra of Diaryliodonium Salts

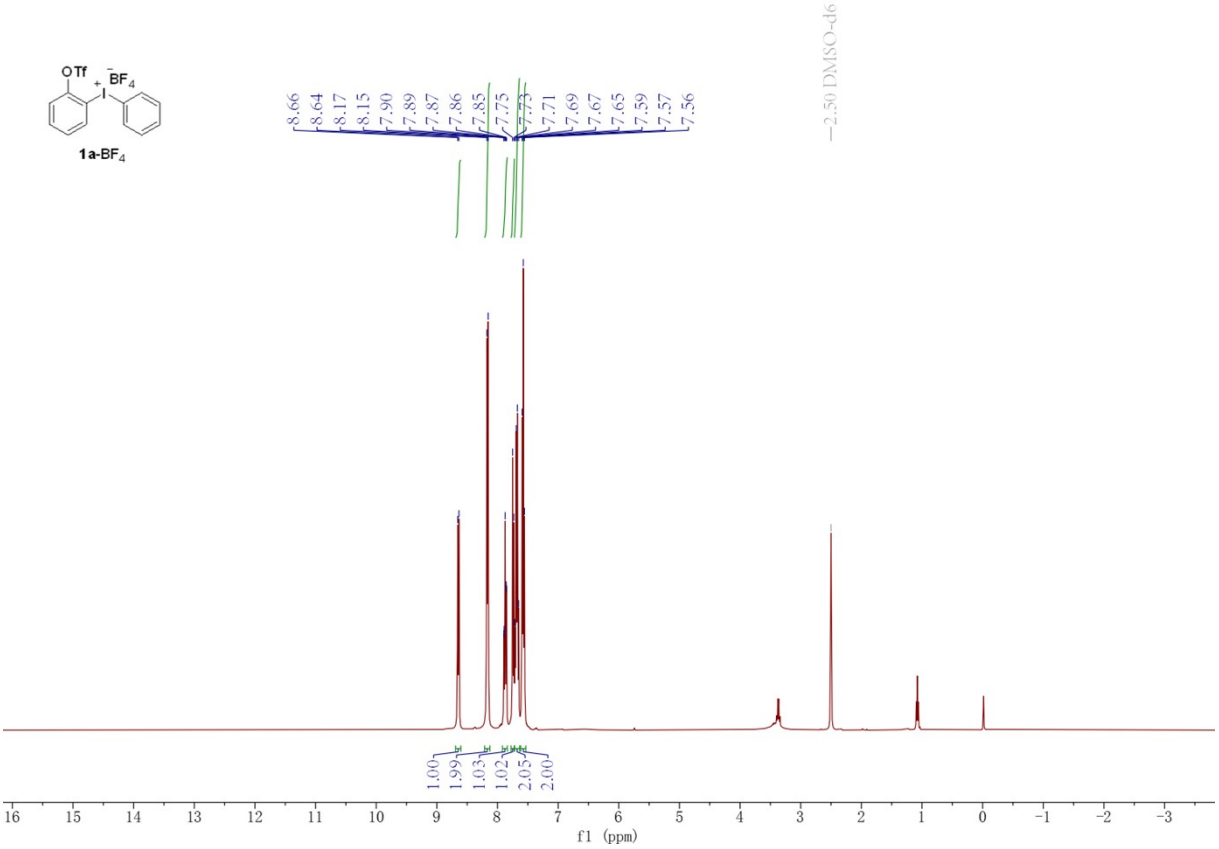
^{1}H NMR spectrum of 1a-OTf (400 MHz, d_6-DMSO)



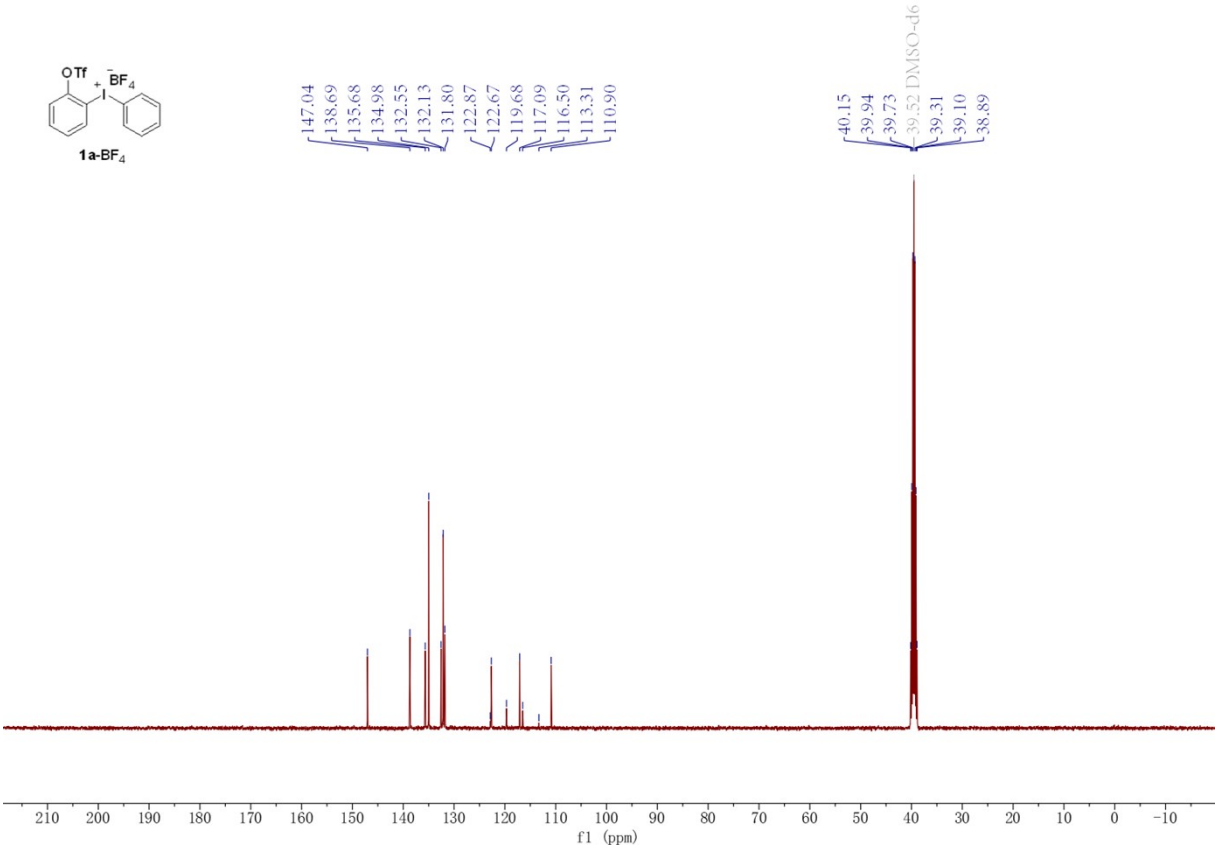
^{19}F NMR spectrum of 1a-OTf (376 MHz, d_6-DMSO)



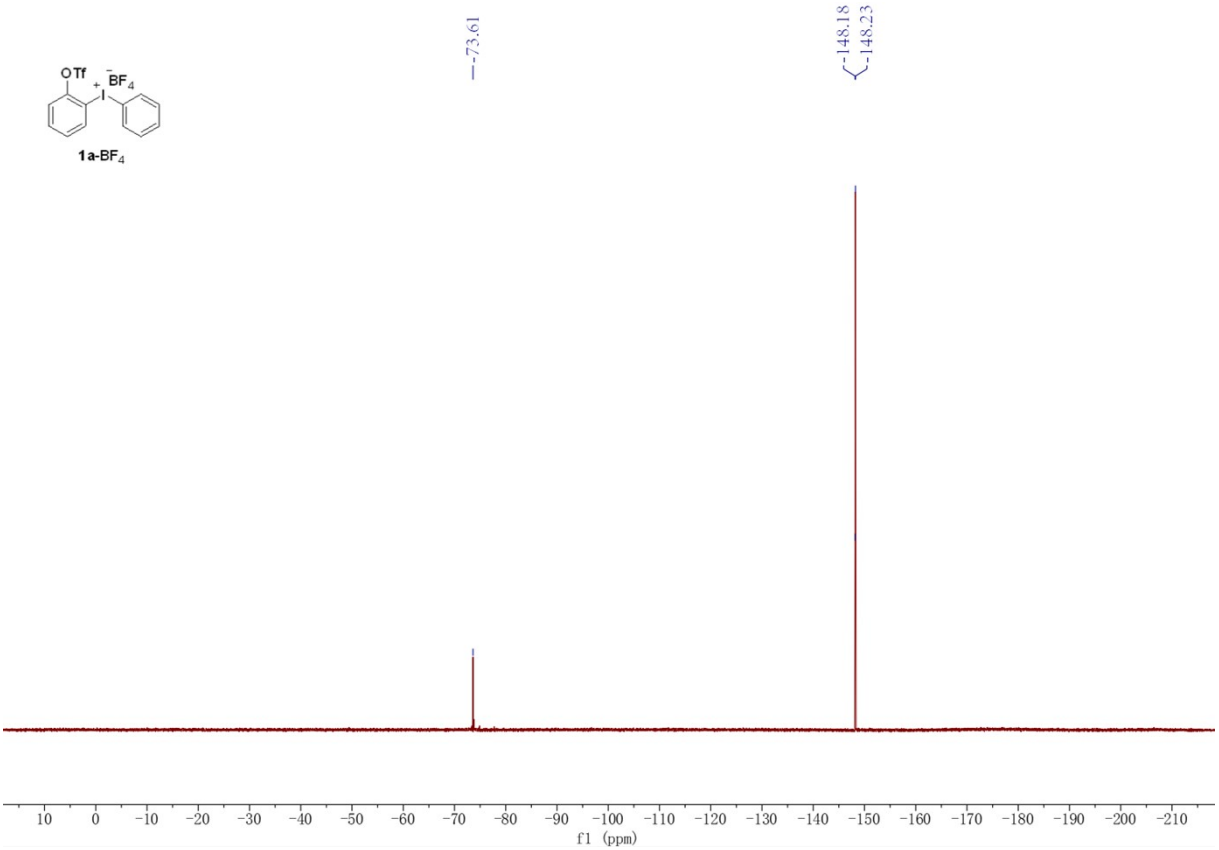
^{1}H NMR spectrum of 1a-BF_4 (400 MHz, d_6-DMSO)



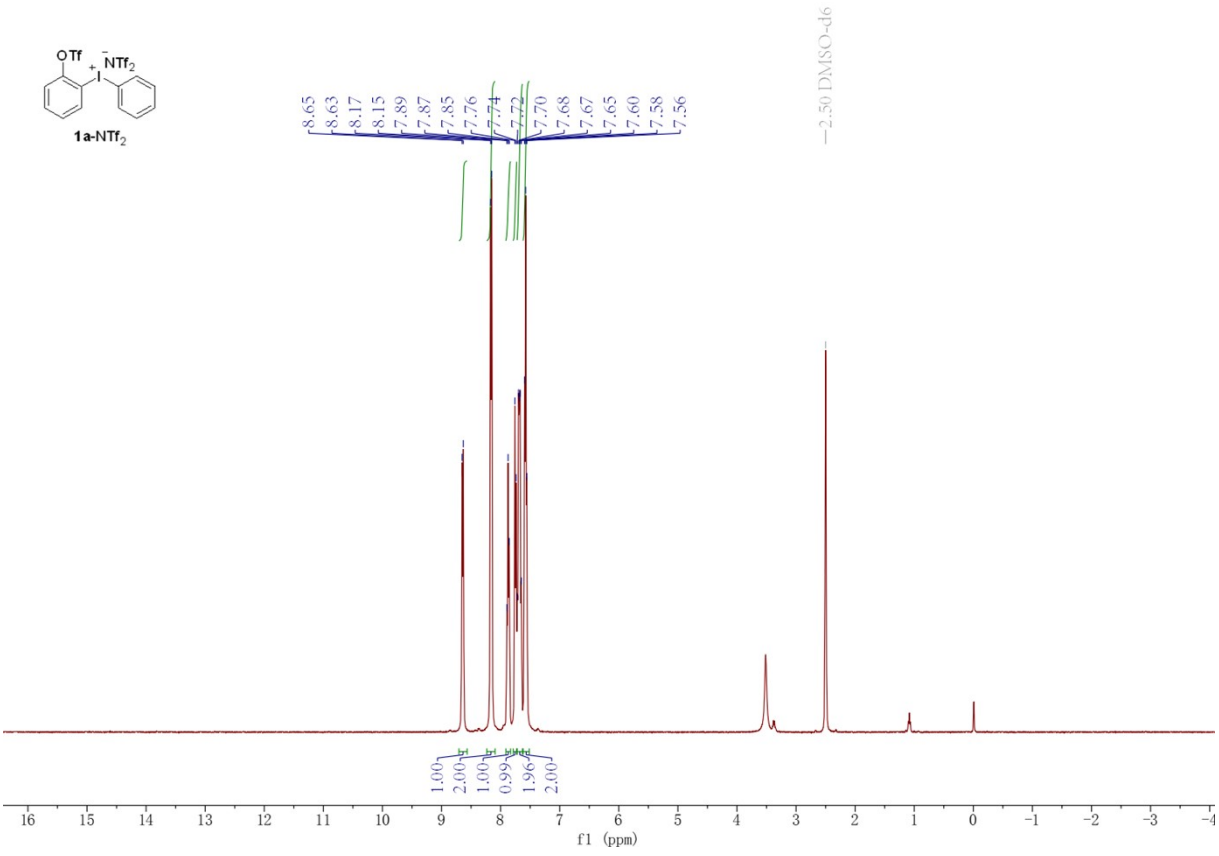
^{13}C NMR spectrum of 1a-BF_4 (101 MHz, d_6-DMSO)



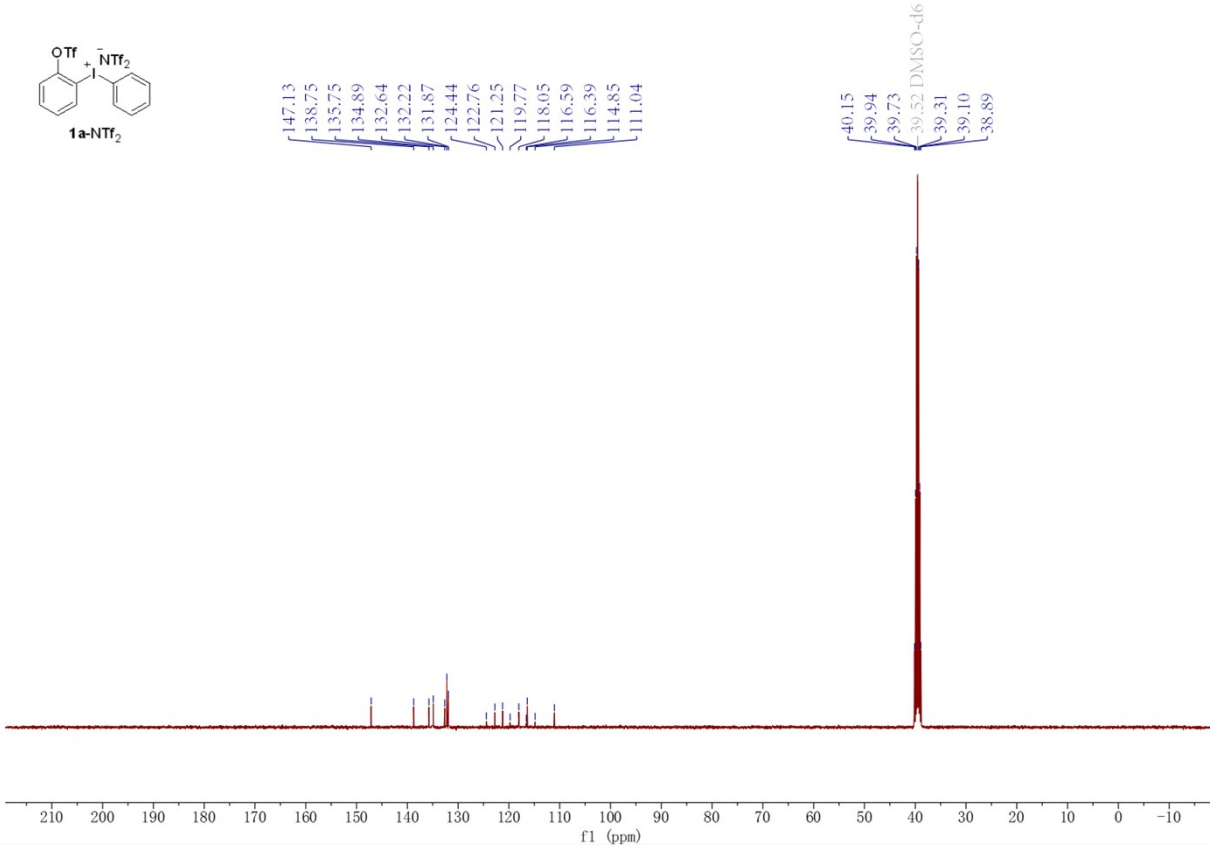
^{19}F NMR spectrum of 1a-BF_4 (376 MHz, d_6-DMSO)



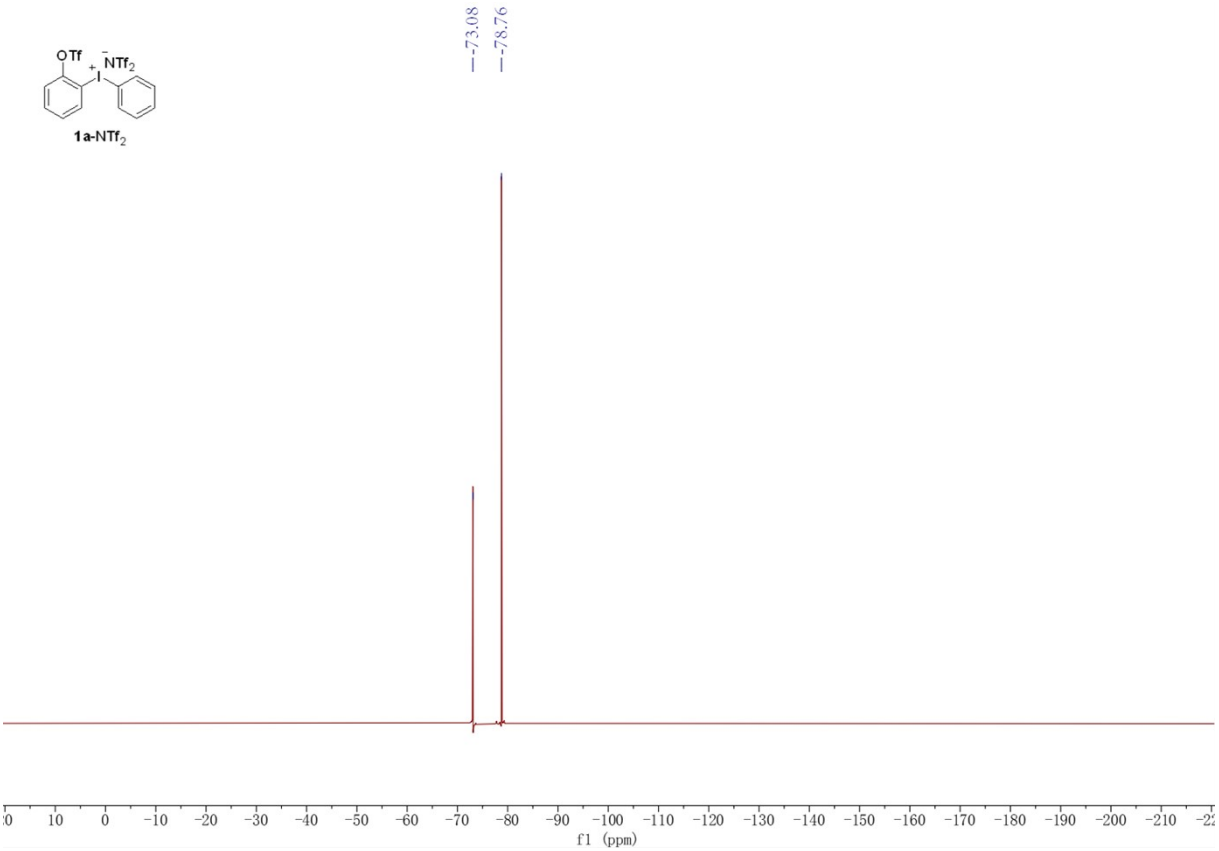
^{1}H NMR spectrum of 1a-NTf_2 (400 MHz, d_6-DMSO)



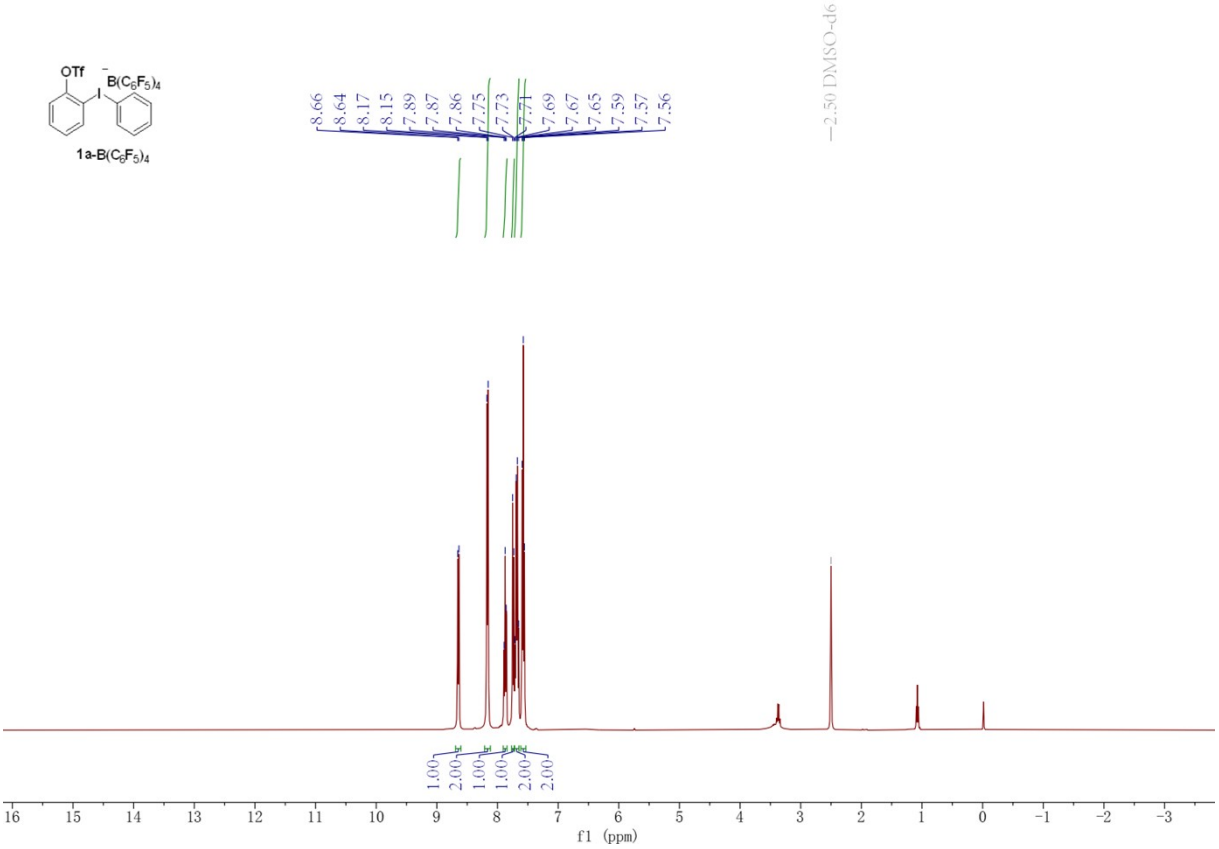
^{13}C NMR spectrum of 1a-NTf$_2$ (101 MHz, d_6-DMSO)



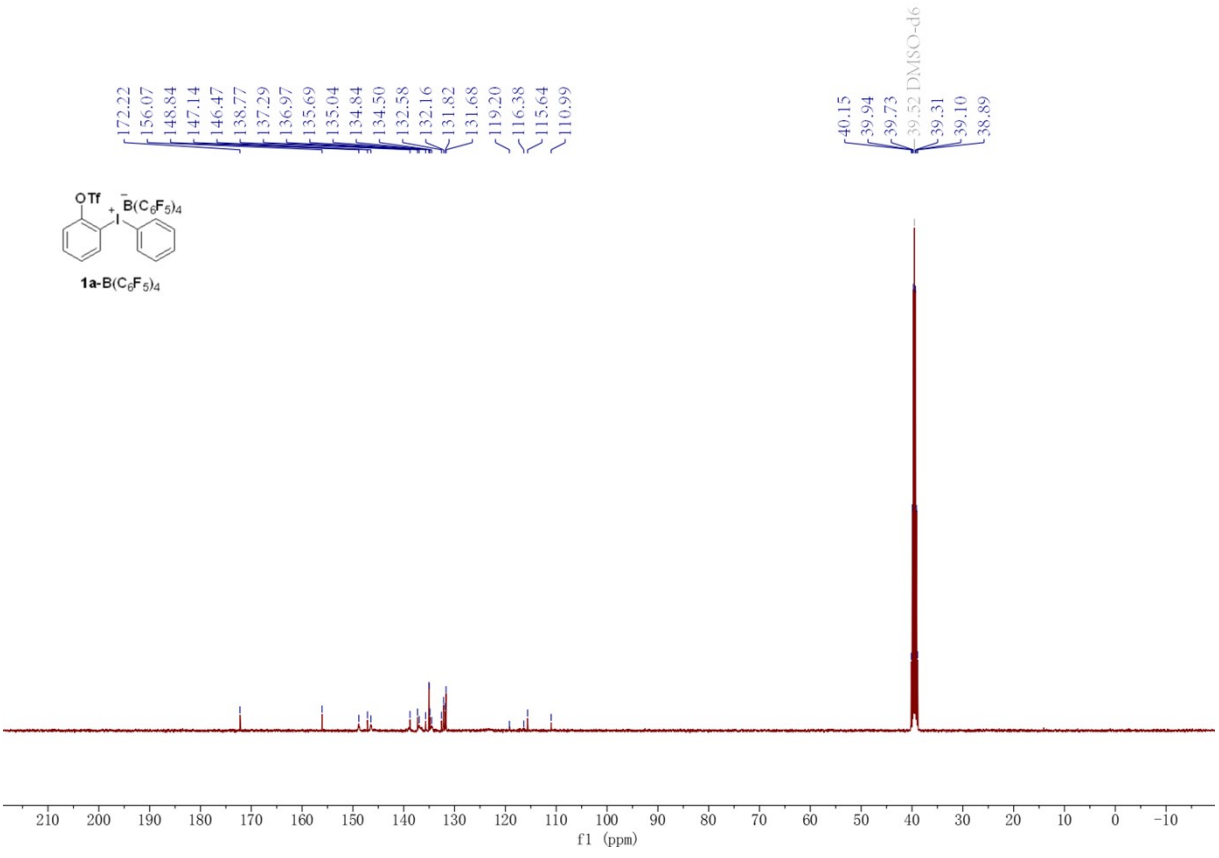
^{19}F NMR spectrum of 1a-NTf$_2$ (376 MHz, d_6-DMSO)



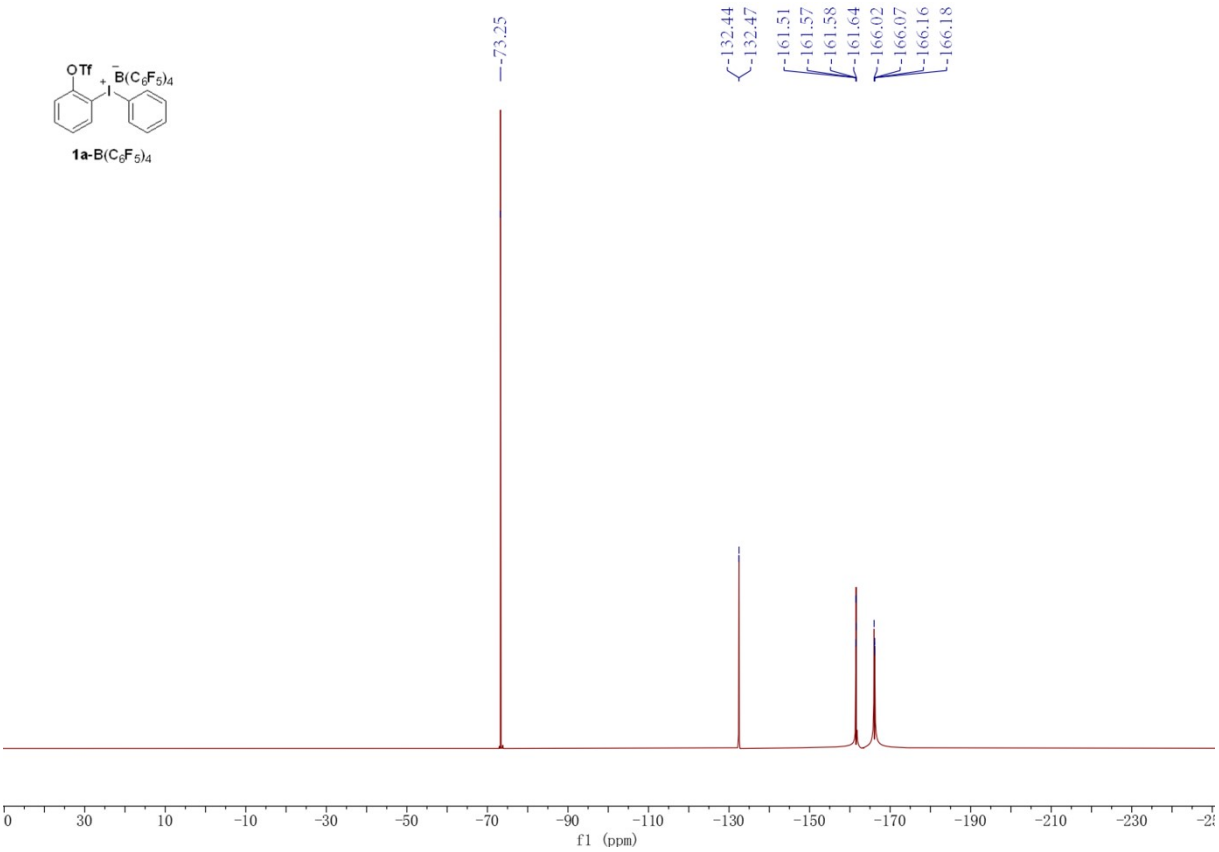
^{1}H NMR spectrum of 1a- $B(C_6F_5)_4$ (400 MHz, d_6-DMSO)



^{13}C NMR spectrum of 1a- $B(C_6F_5)_4$ (101 MHz, d_6-DMSO)

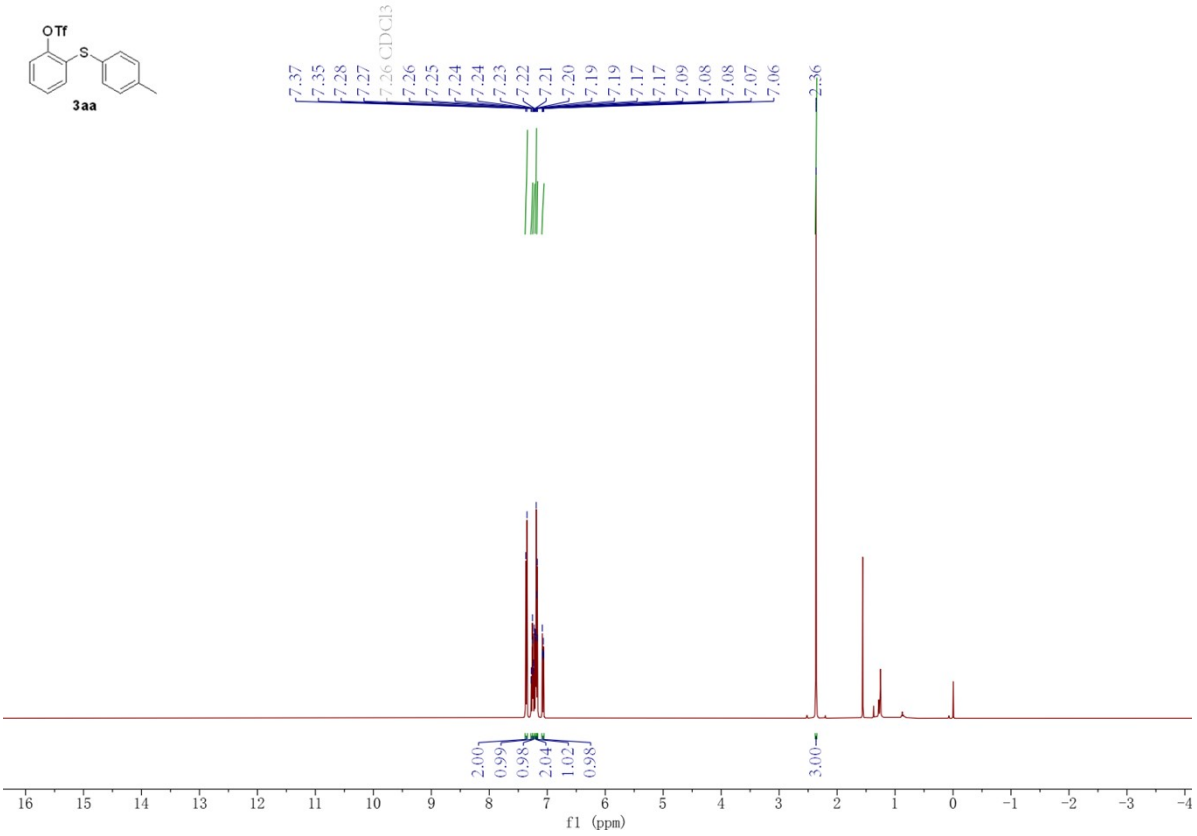


^{19}F NMR spectrum of 1a-B(C_6F_5)$_4$ (376 MHz, d_6-DMSO)

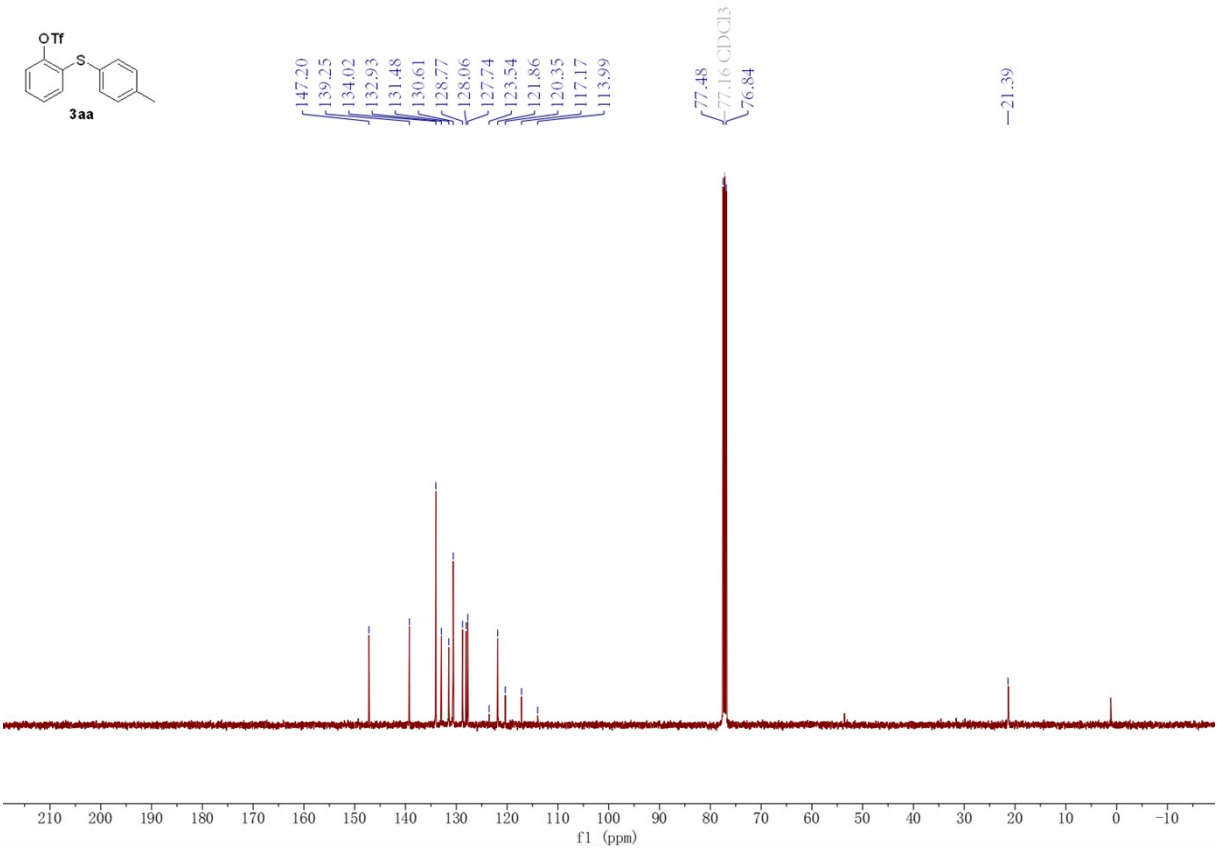


Part 8. ^{1}H, ^{13}C, and ^{19}F NMR spectra of Products

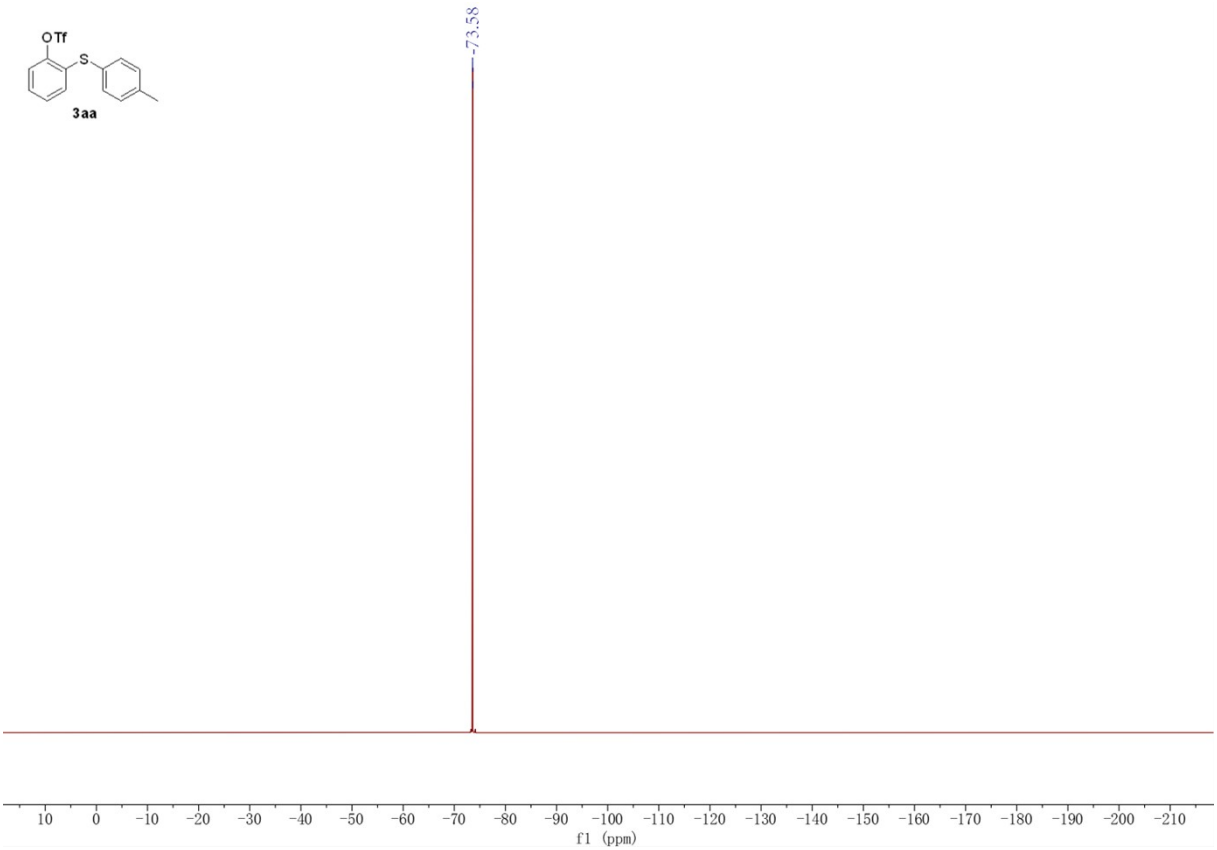
^{1}H NMR spectrum of 3aa (400 MHz, $CDCl_3$)



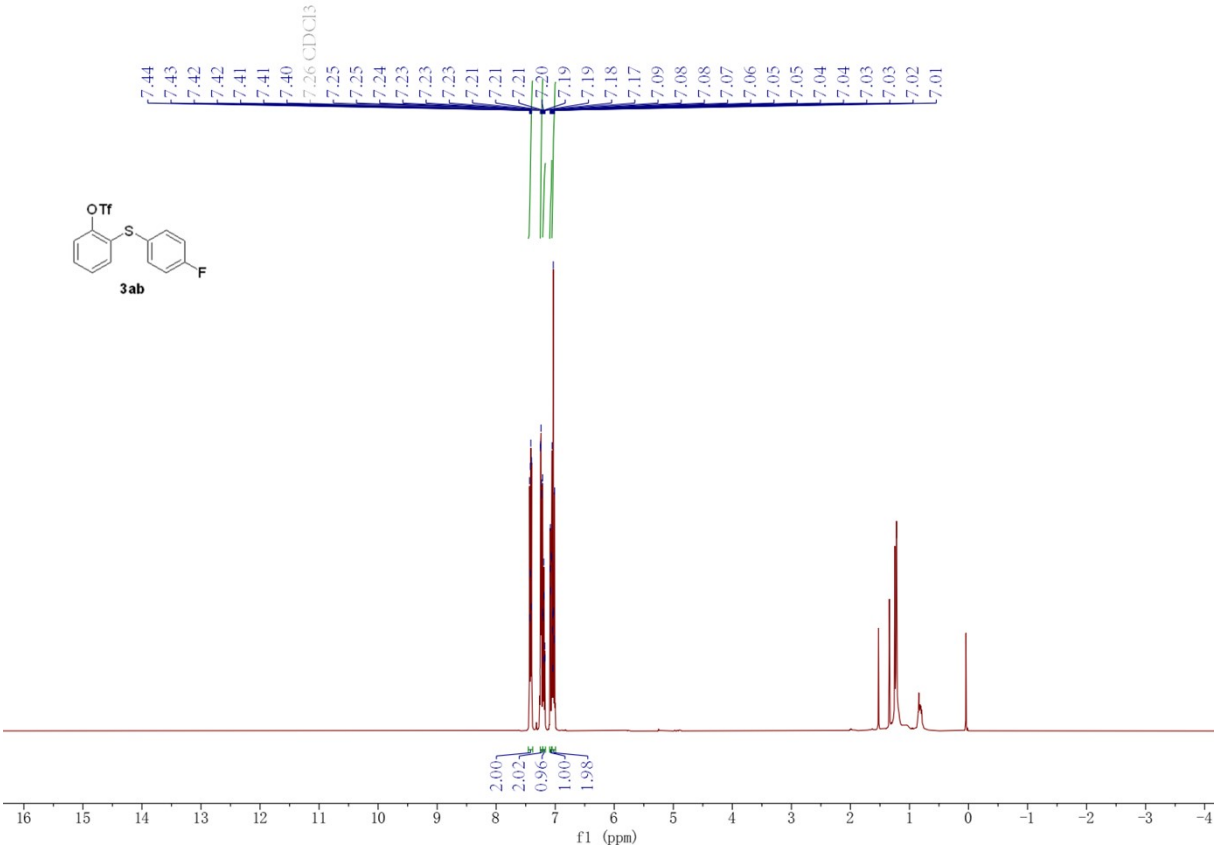
^{13}C NMR spectrum of 3aa (101 MHz, $CDCl_3$)



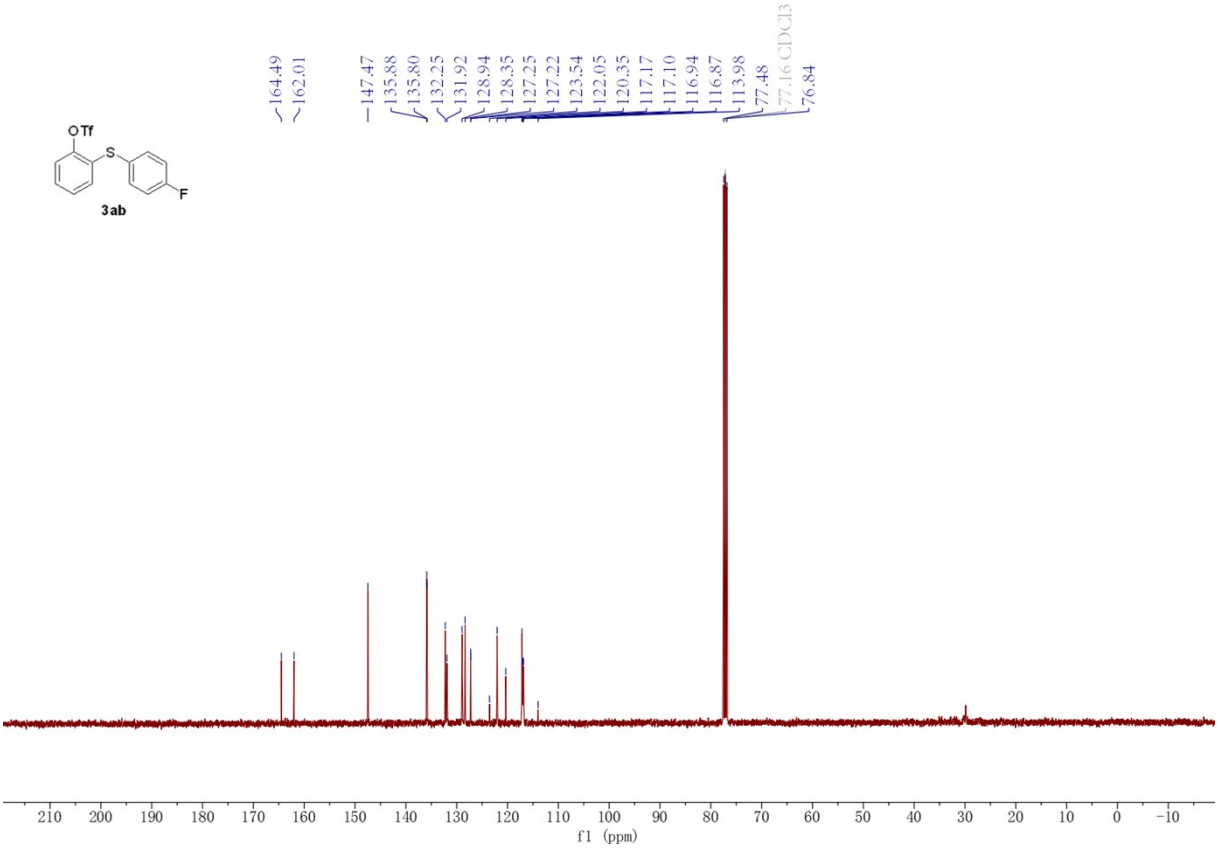
^{19}F NMR spectrum of 3aa (376 MHz, $CDCl_3$)



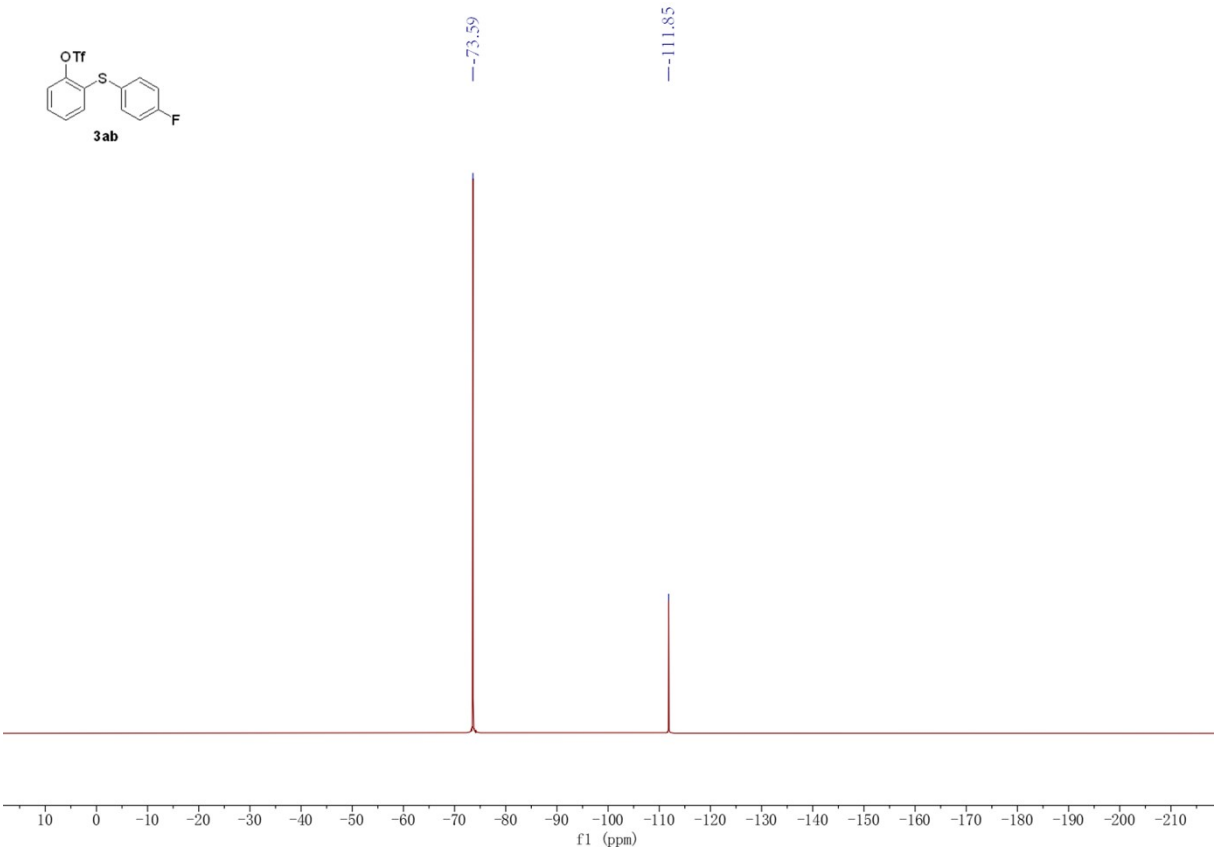
^{1}H NMR spectrum of 3ab (400 MHz, $CDCl_3$)



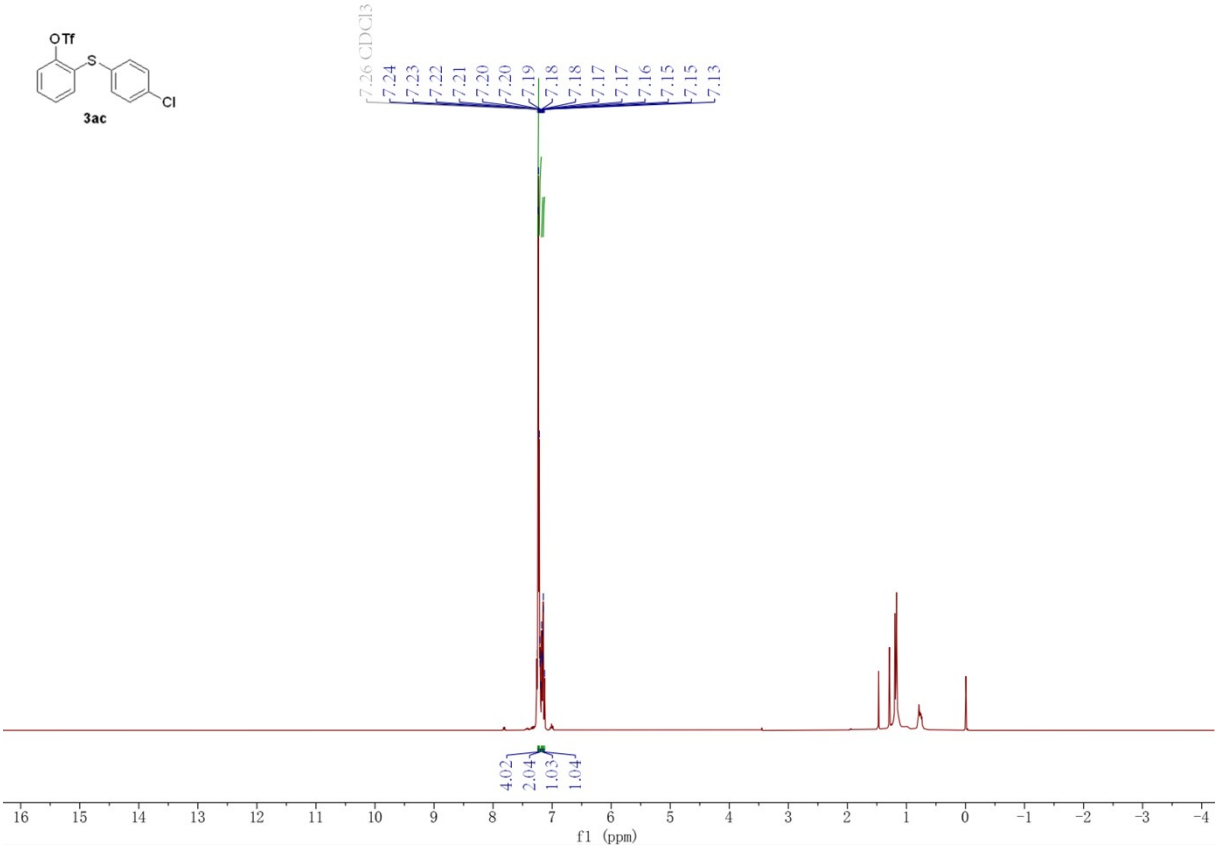
^{13}C NMR spectrum of 3ab (101 MHz, $CDCl_3$)



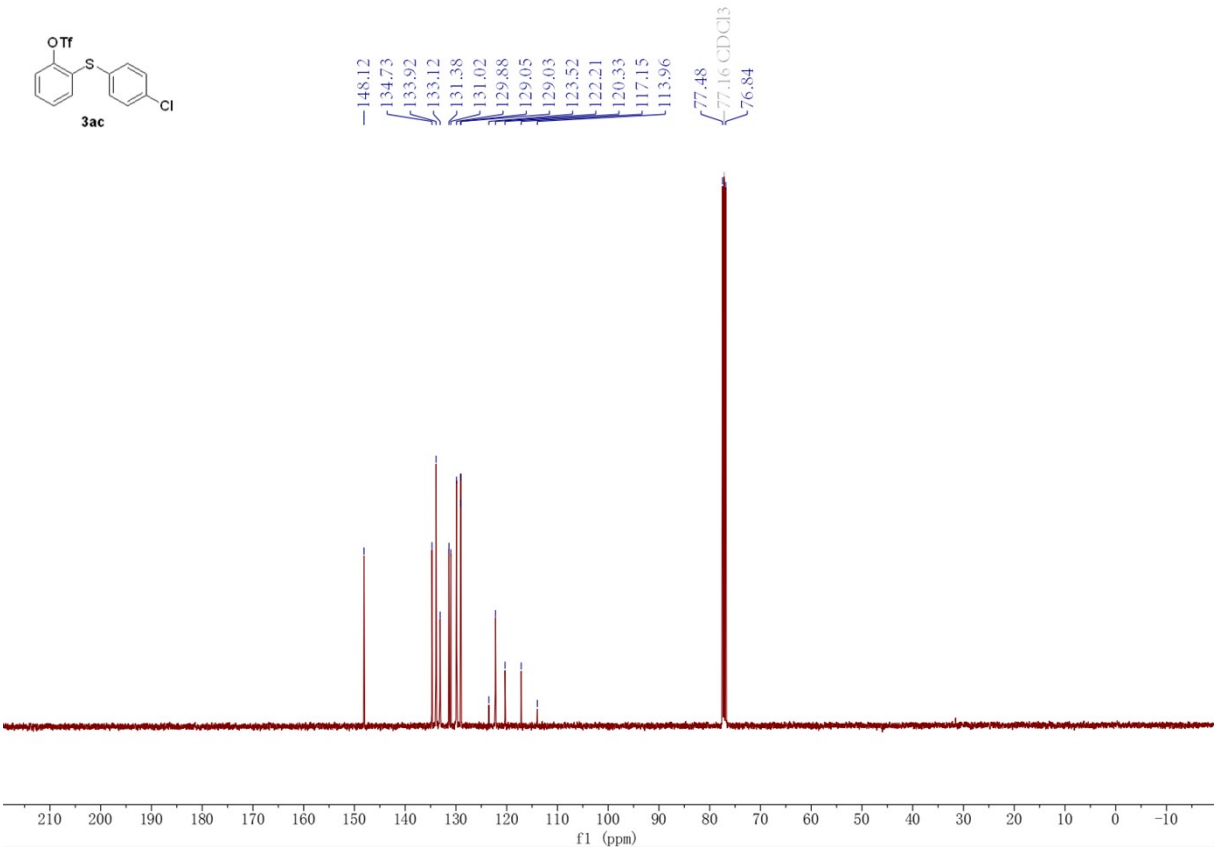
^{19}F NMR spectrum of 3ab (376 MHz, $CDCl_3$)



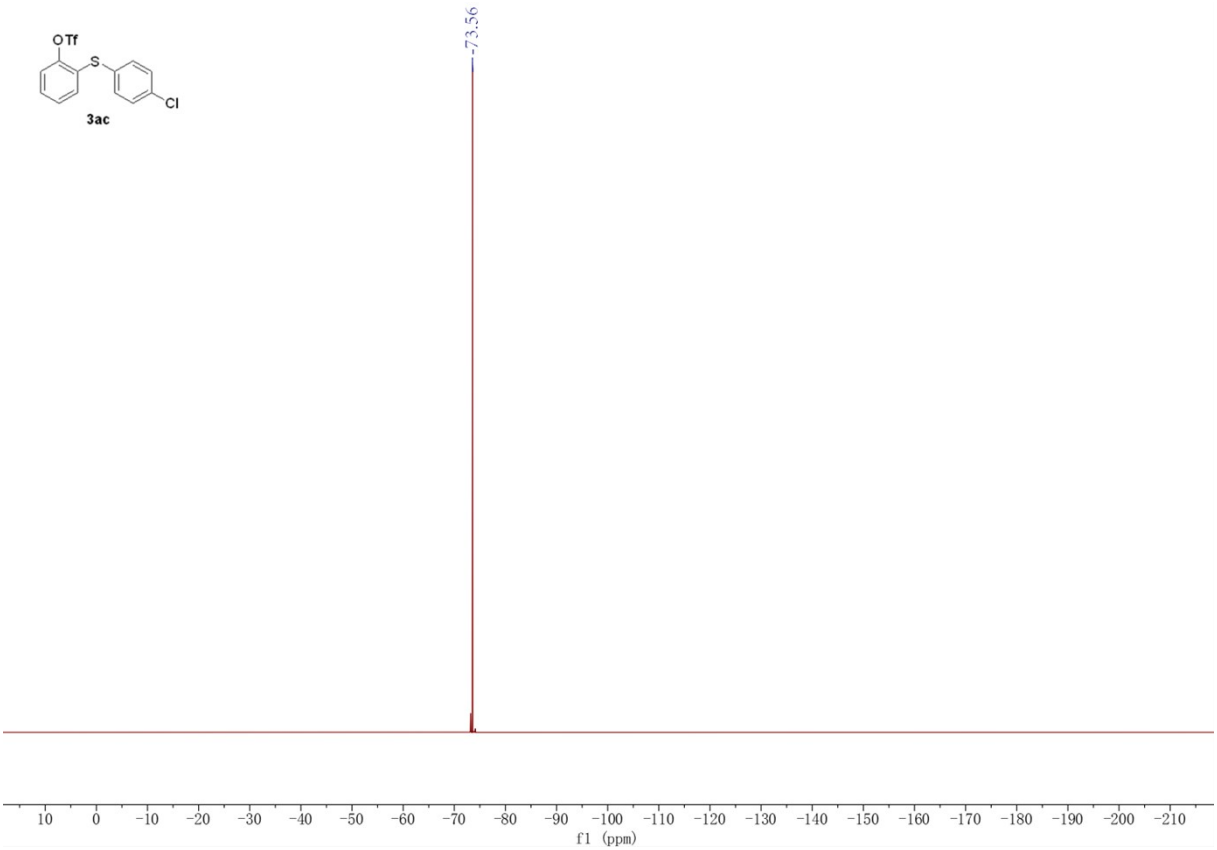
^{1}H NMR spectrum of 3ac (400 MHz, $CDCl_3$)



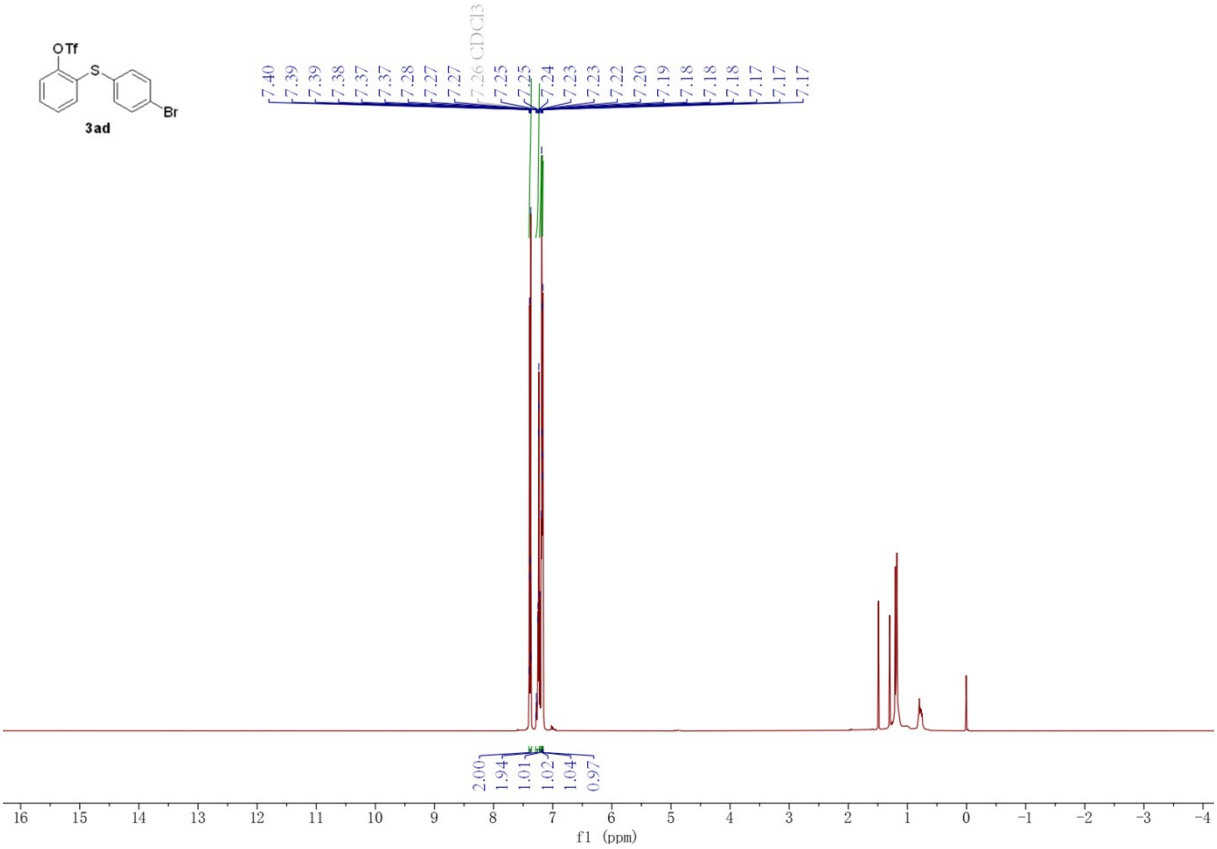
^{13}C NMR spectrum of 3ac (101 MHz, $CDCl_3$)



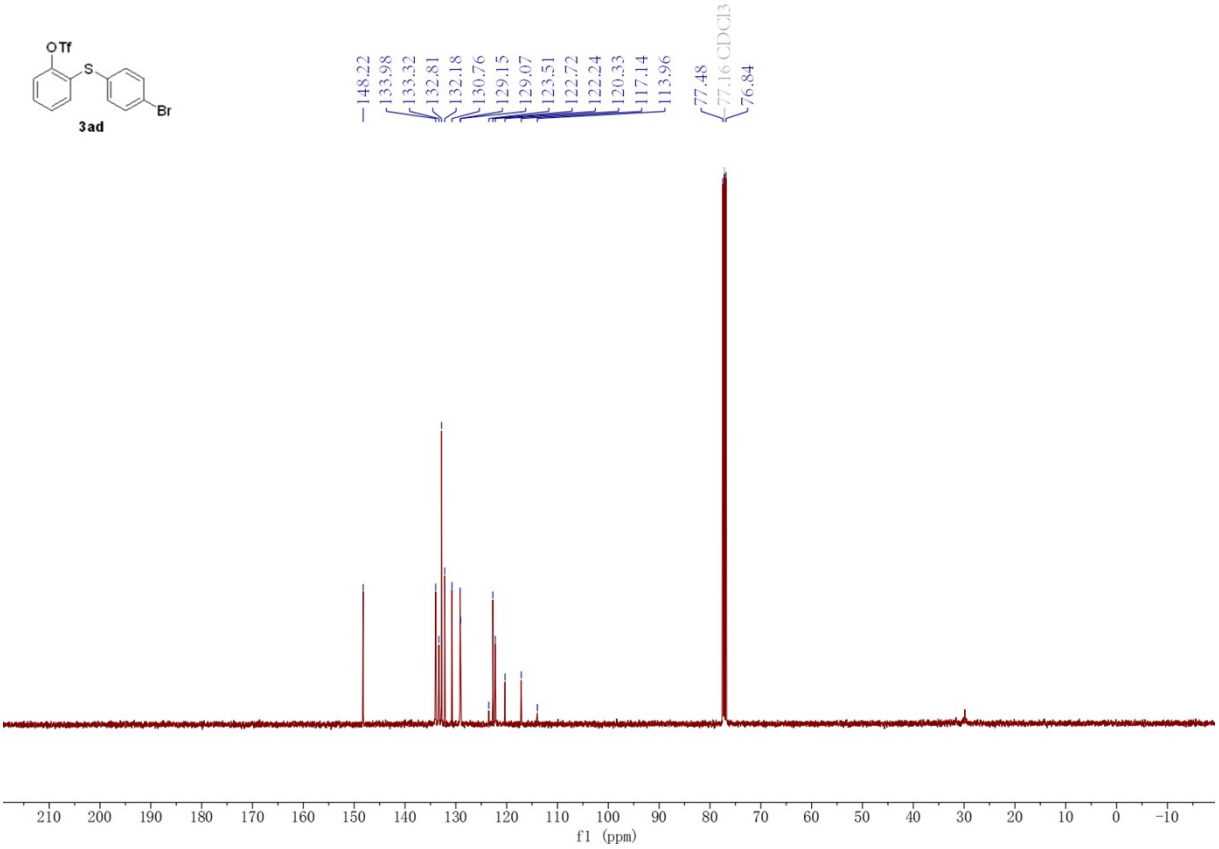
^{19}F NMR spectrum of 3ac (376 MHz, $CDCl_3$)



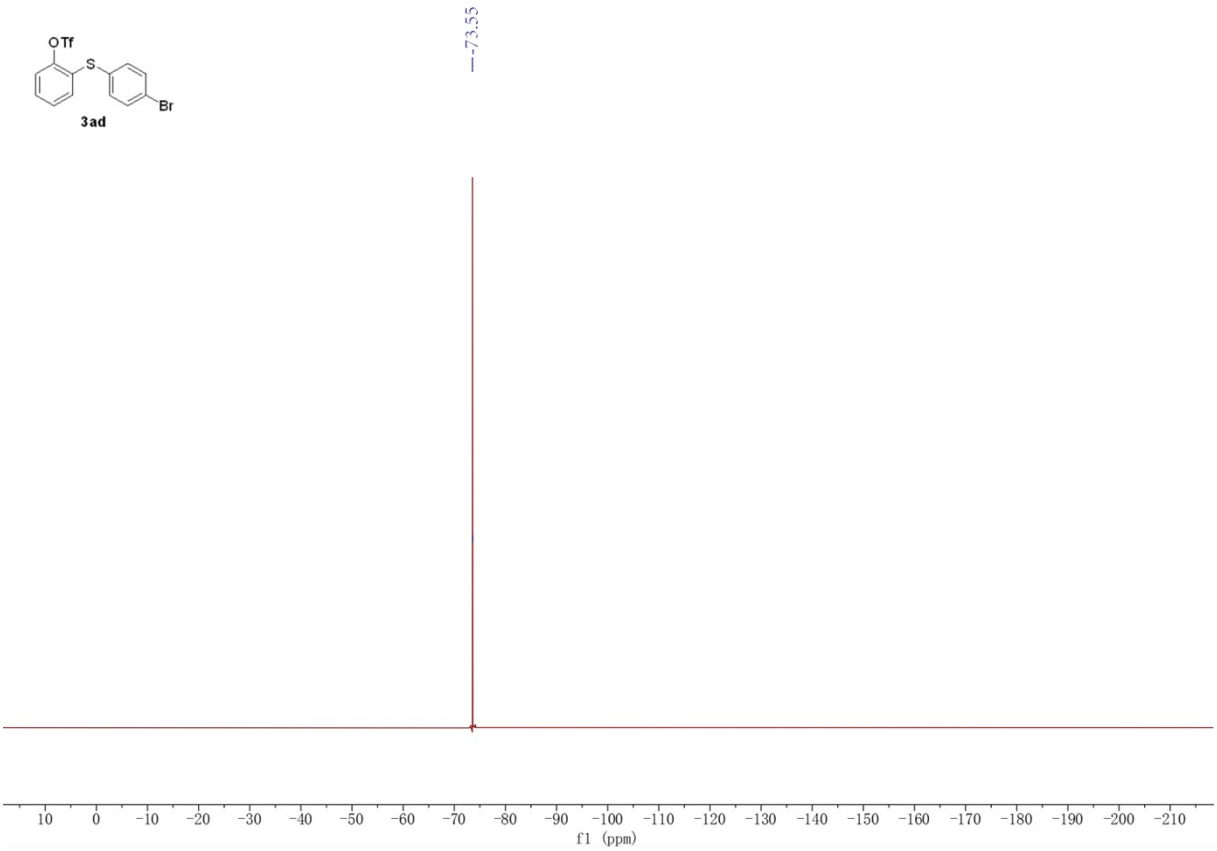
^{1}H NMR spectrum of 3ad (400 MHz, $CDCl_3$)



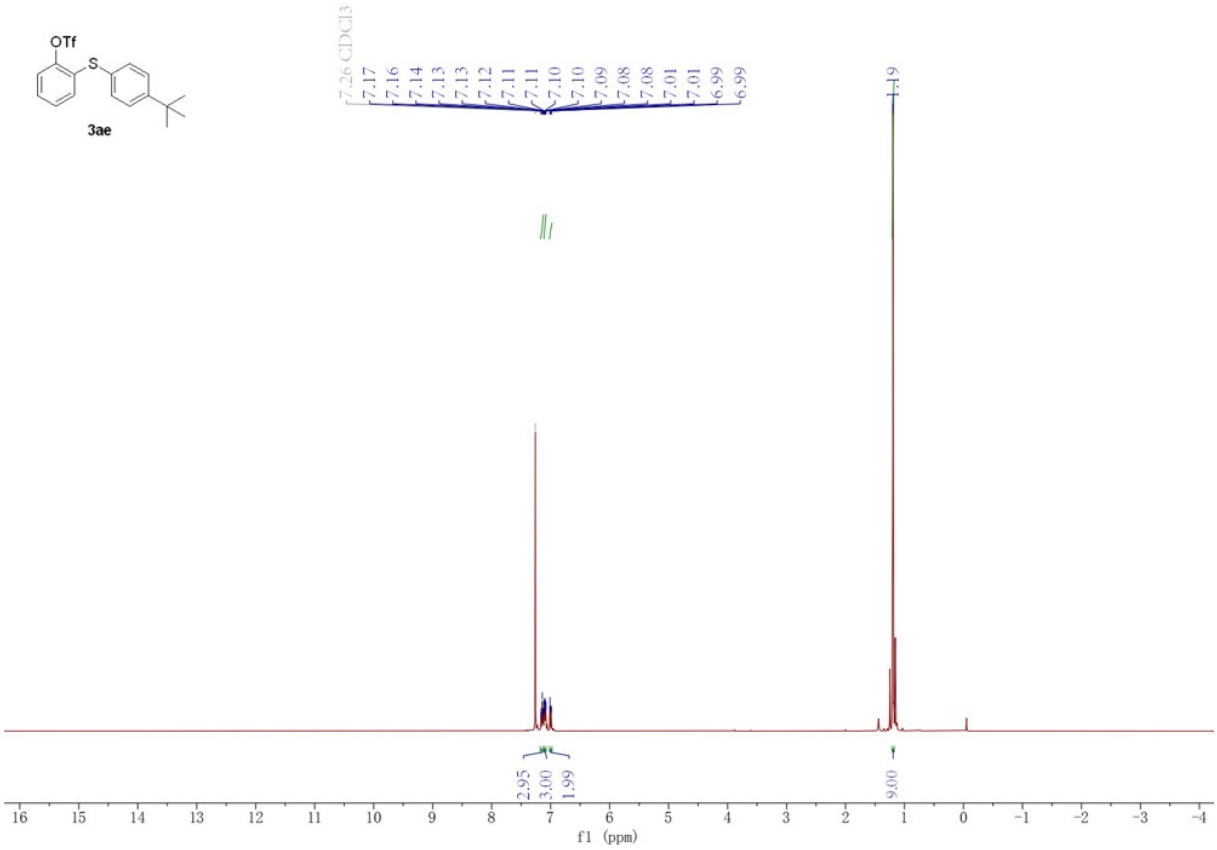
^{13}C NMR spectrum of 3ad (101 MHz, $CDCl_3$)



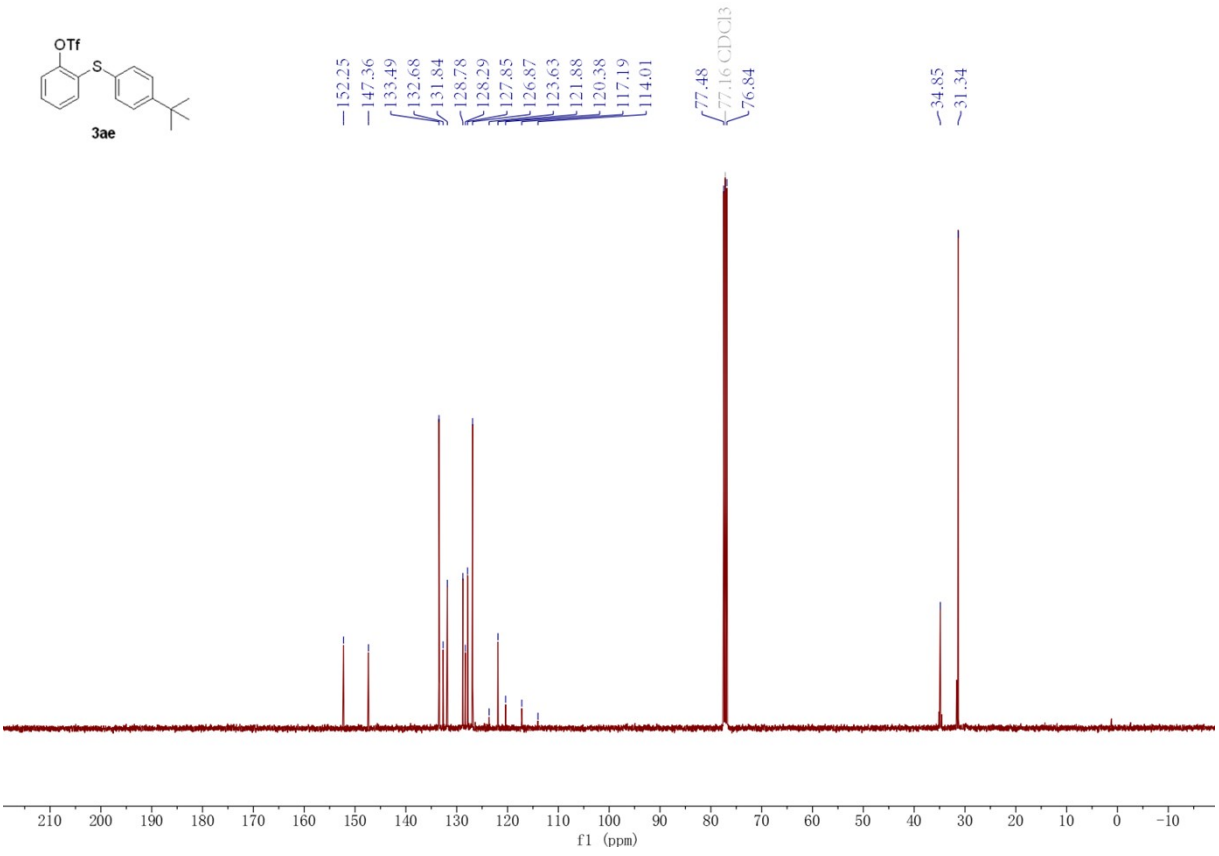
^{19}F NMR spectrum of 3ad (376 MHz, $CDCl_3$)



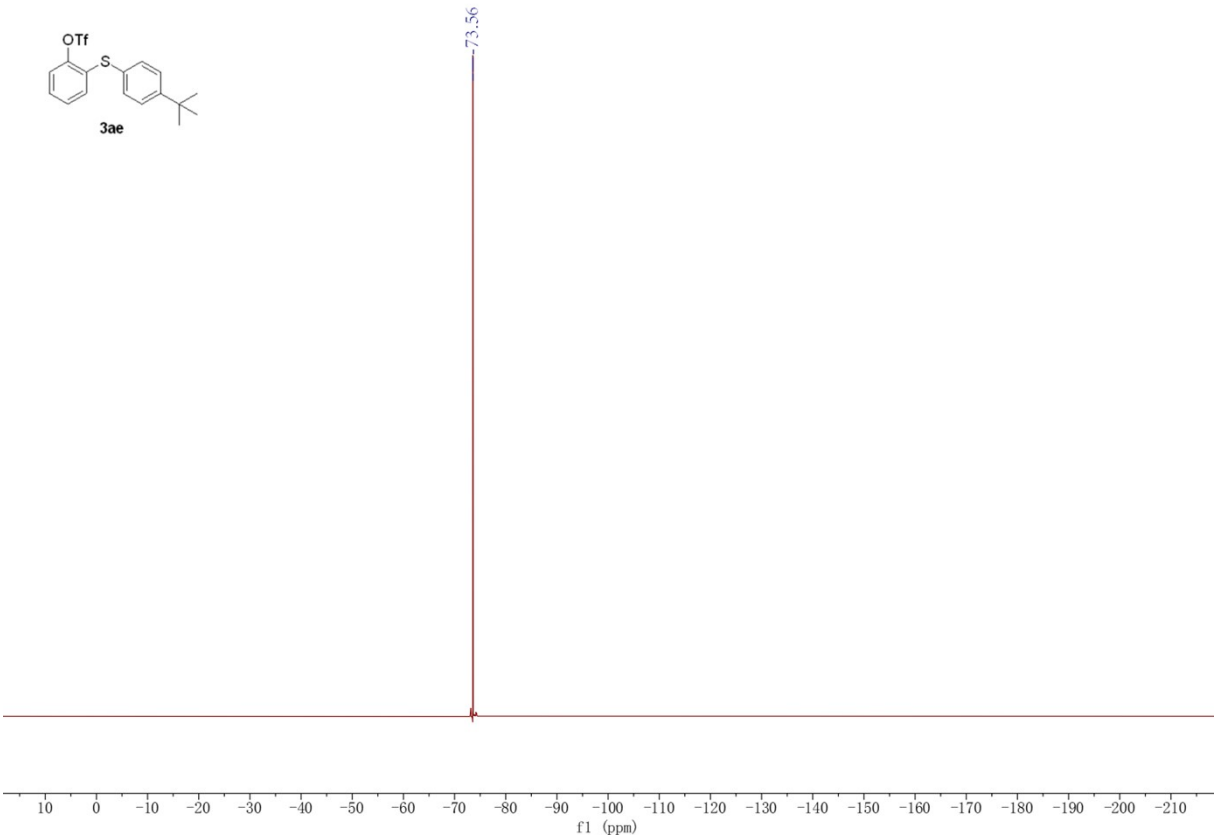
^{1}H NMR spectrum of 3ae (400 MHz, $CDCl_3$)



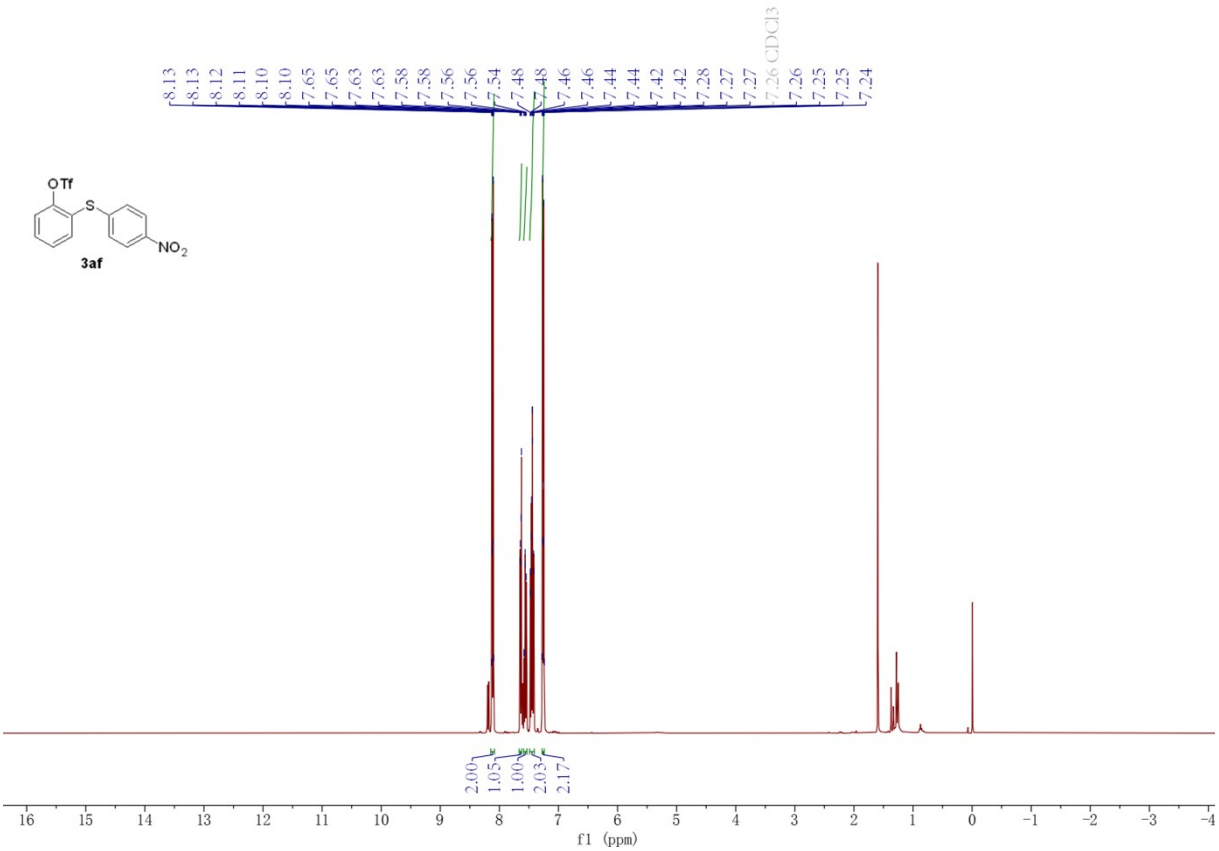
^{13}C NMR spectrum of 3ae (101 MHz, $CDCl_3$)



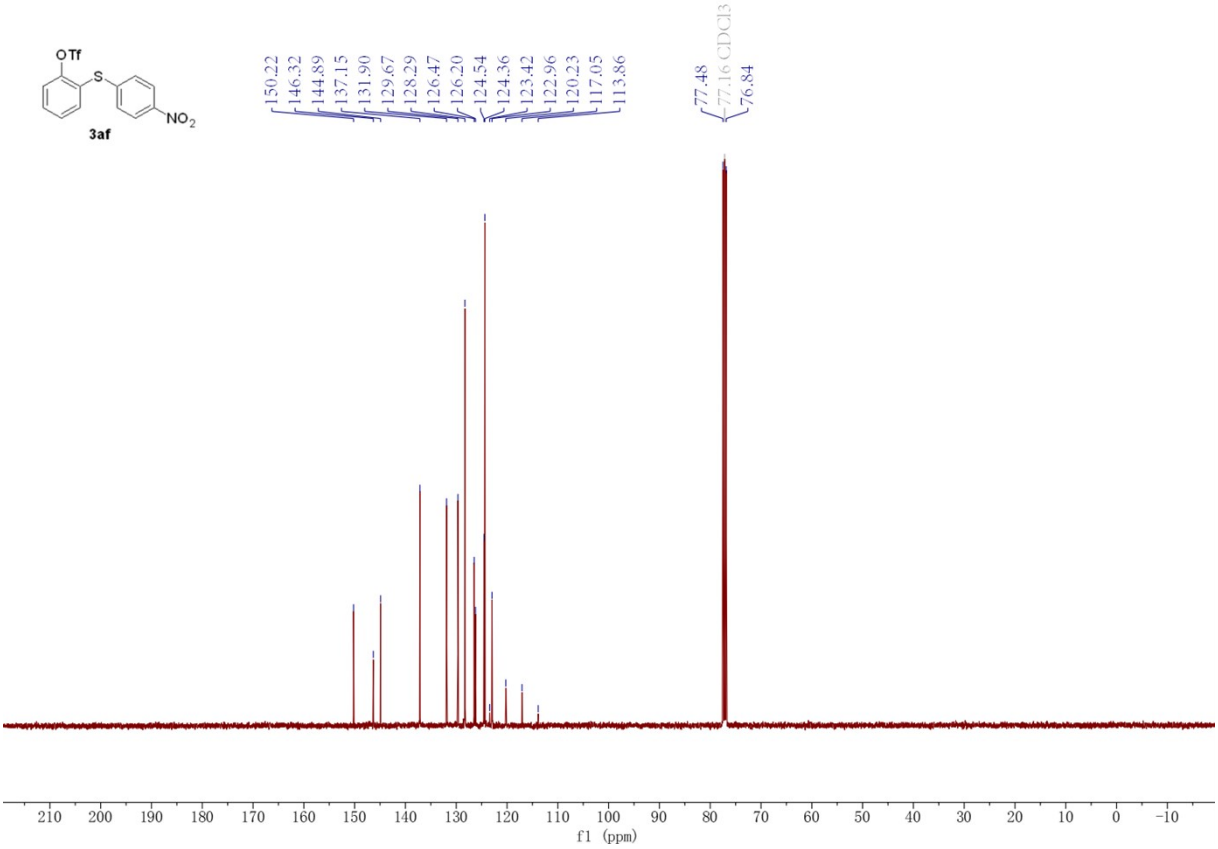
^{19}F NMR spectrum of 3ae (376 MHz, $CDCl_3$)



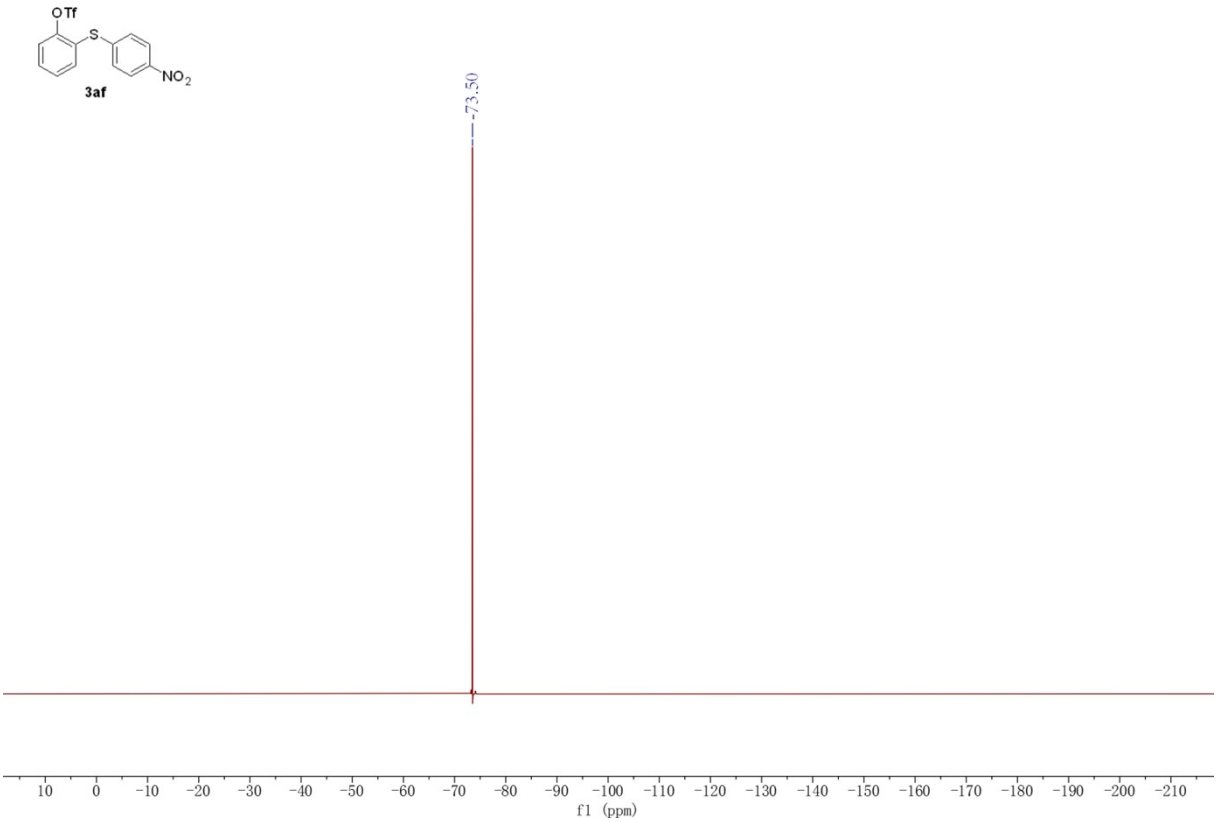
^{1}H NMR spectrum of 3af (400 MHz, $CDCl_3$)



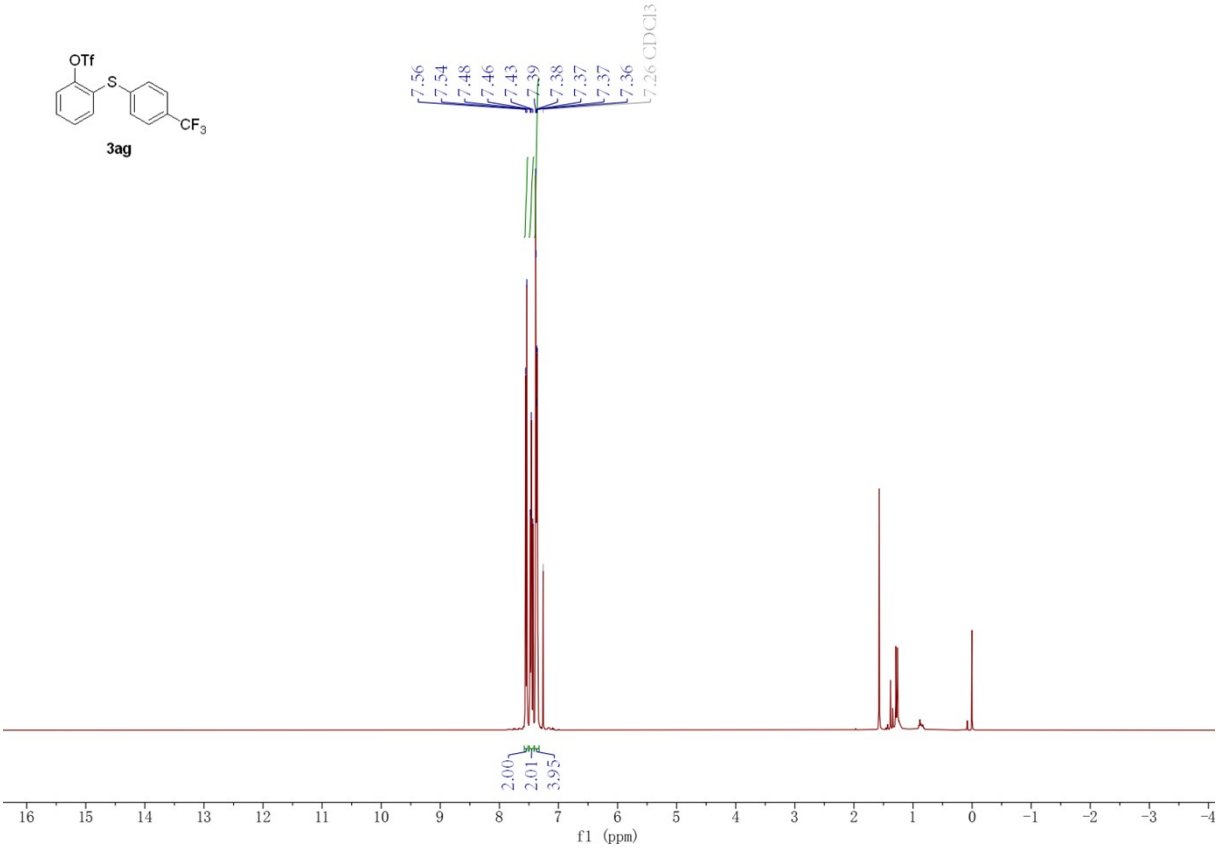
^{13}C NMR spectrum of 3af (101 MHz, $CDCl_3$)



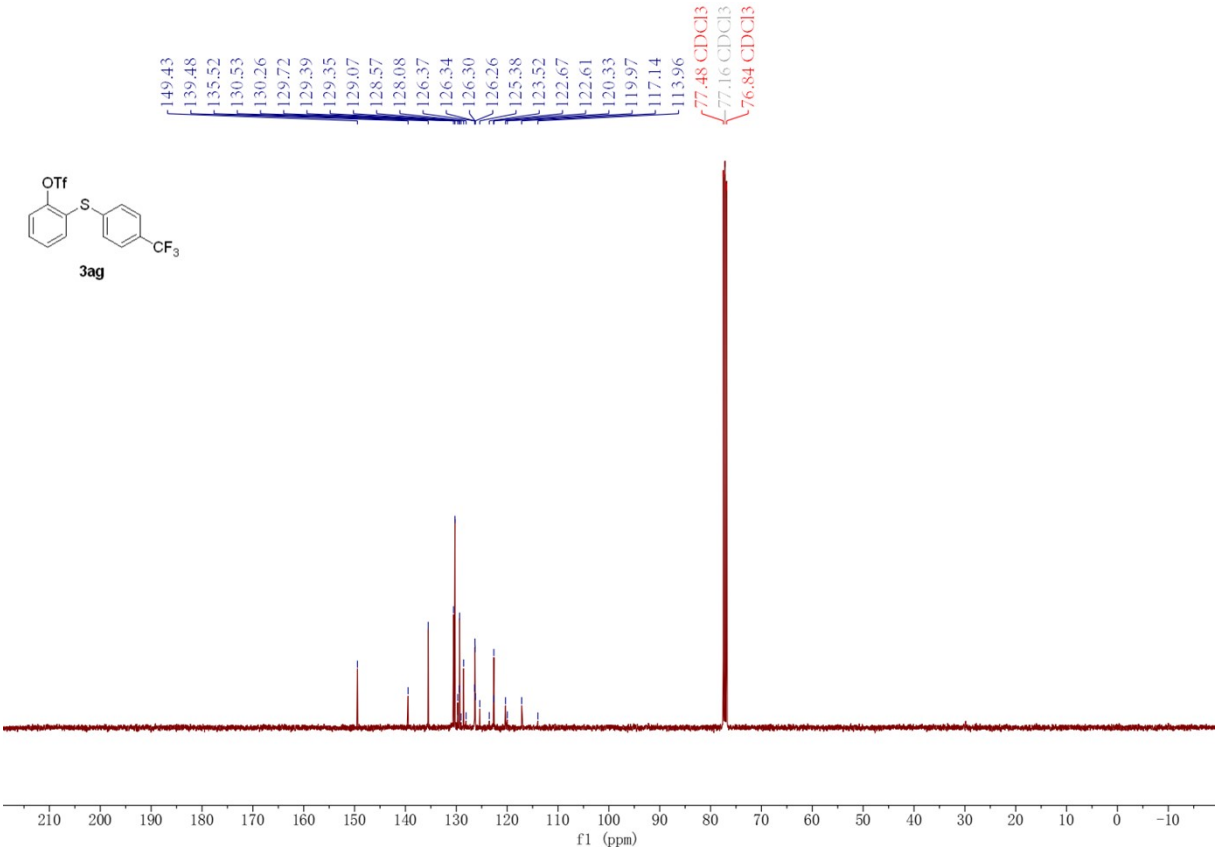
^{19}F NMR spectrum of 3af (376 MHz, $CDCl_3$)



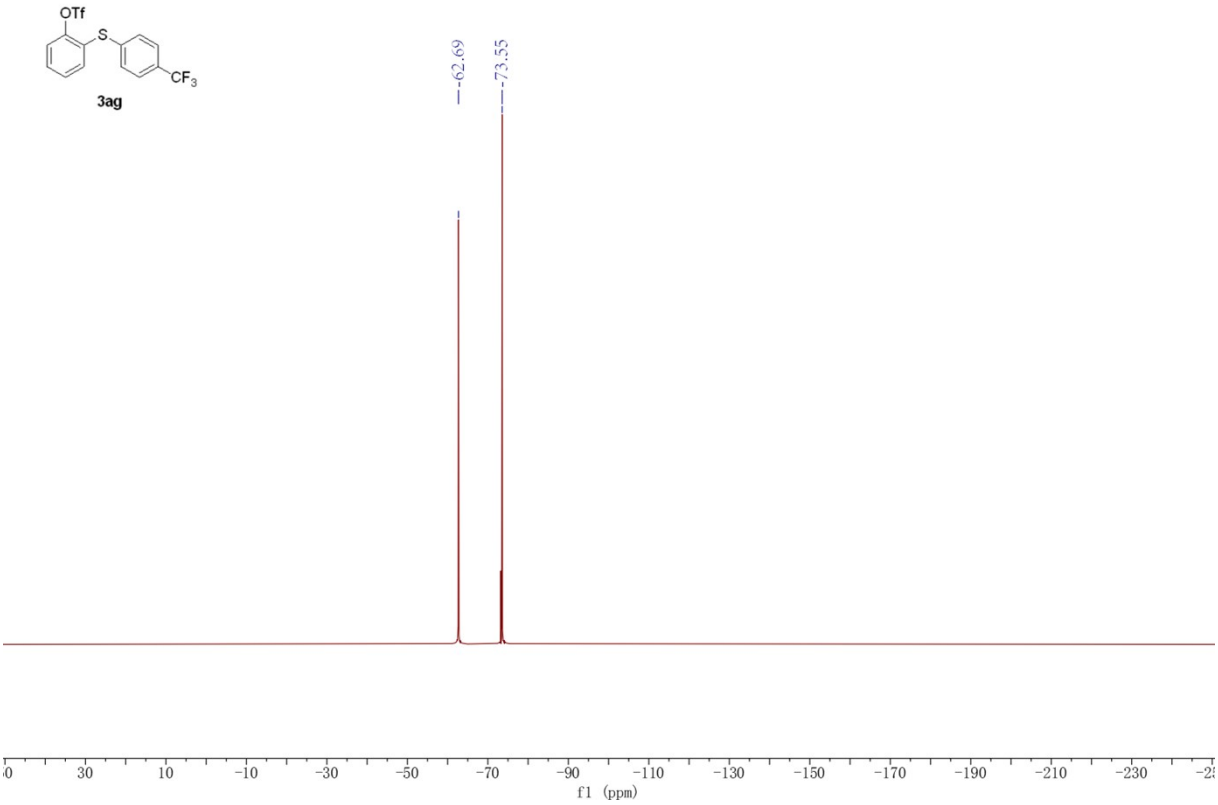
^{1}H NMR spectrum of 3ag (400 MHz, $CDCl_3$)



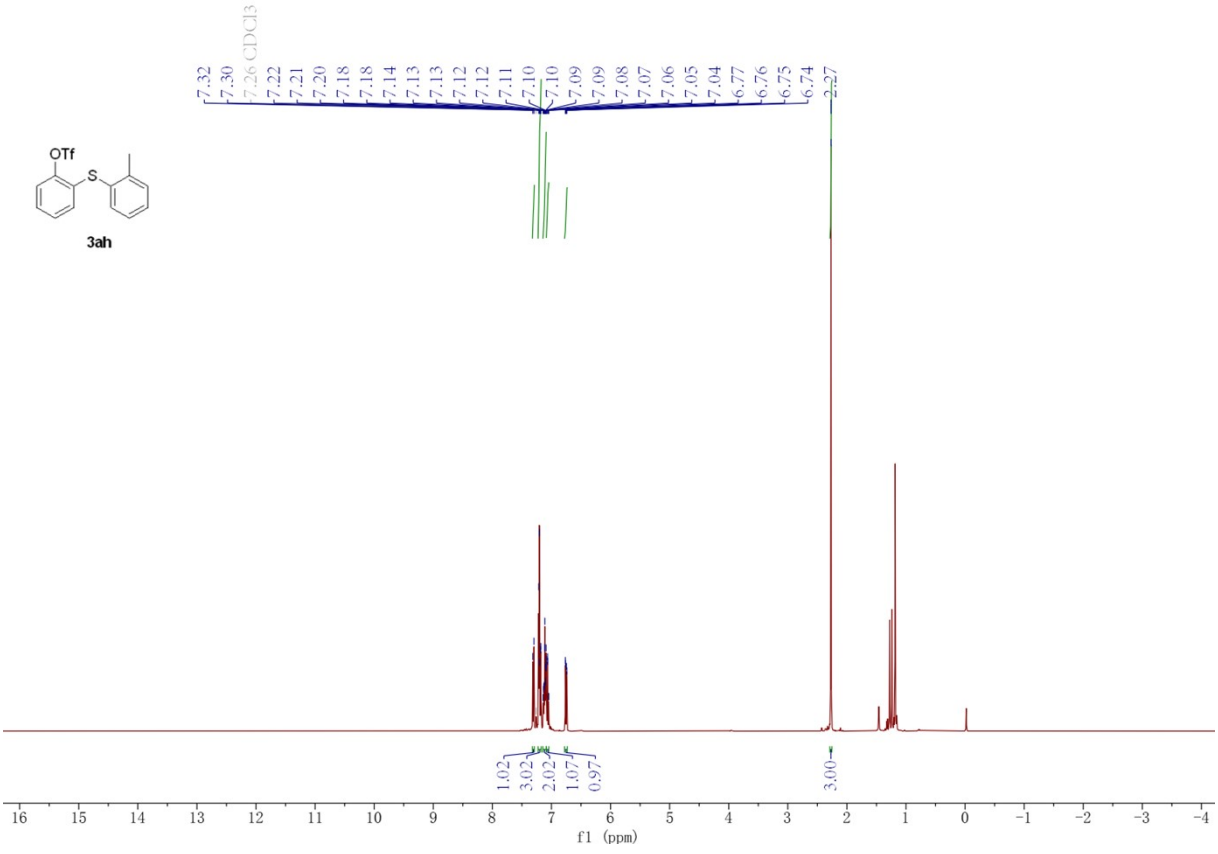
^{13}C NMR spectrum of 3ag (101 MHz, $CDCl_3$)



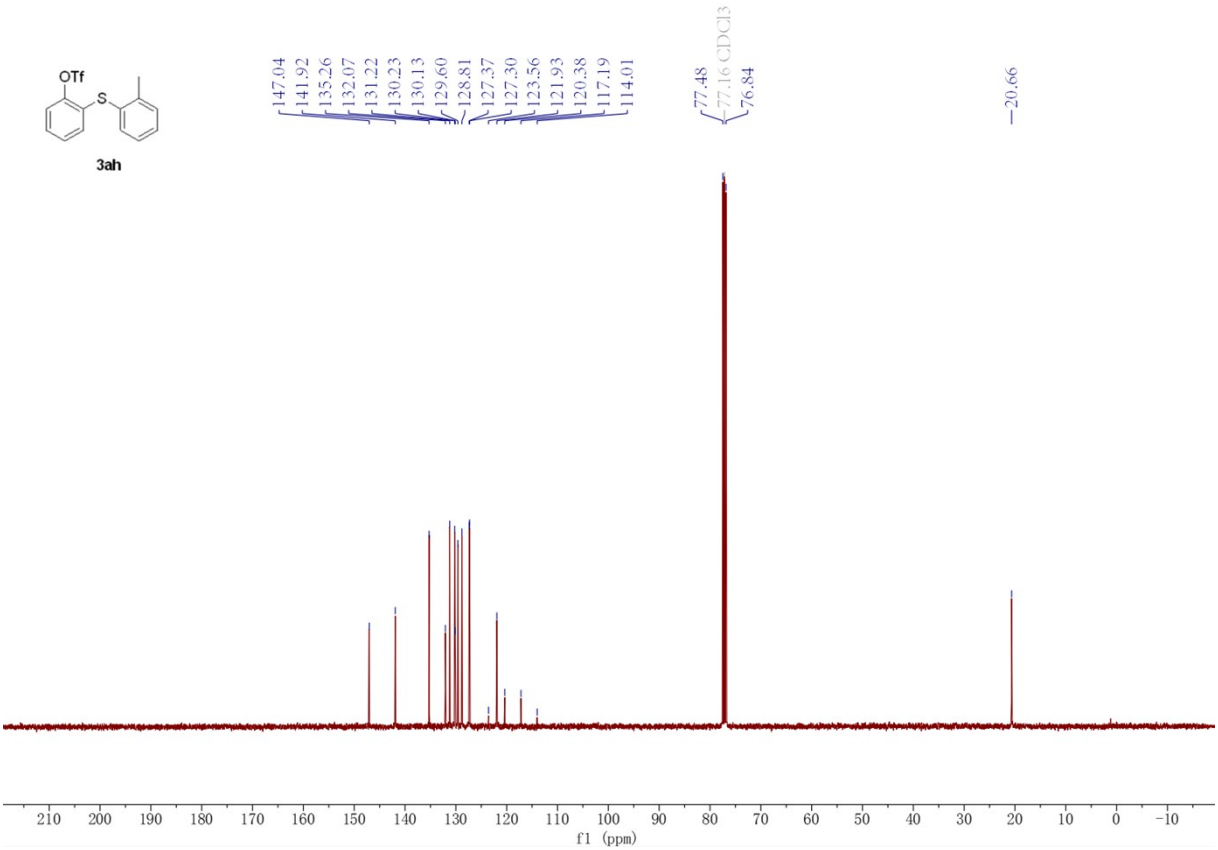
^{19}F NMR spectrum of 3ag (376 MHz, $CDCl_3$)



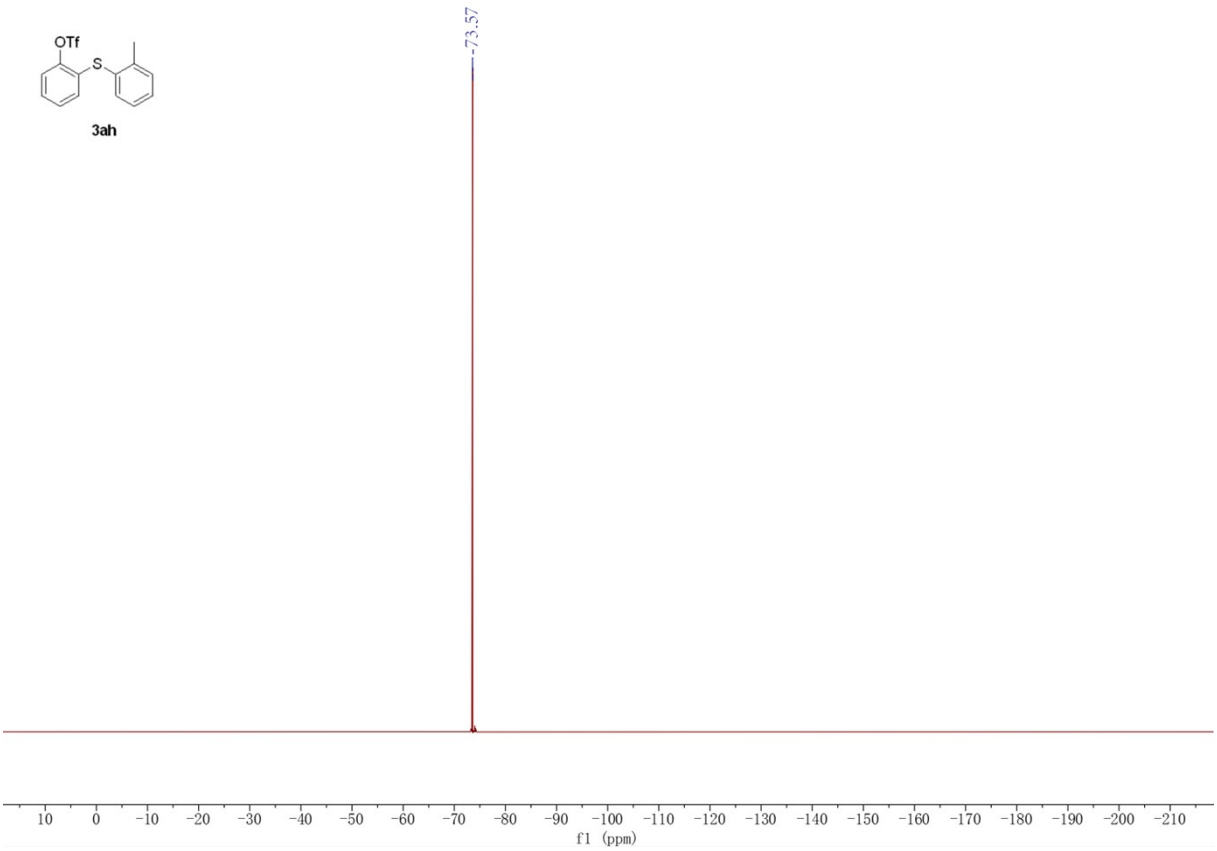
^{1}H NMR spectrum of 3ah (400 MHz, $CDCl_3$)



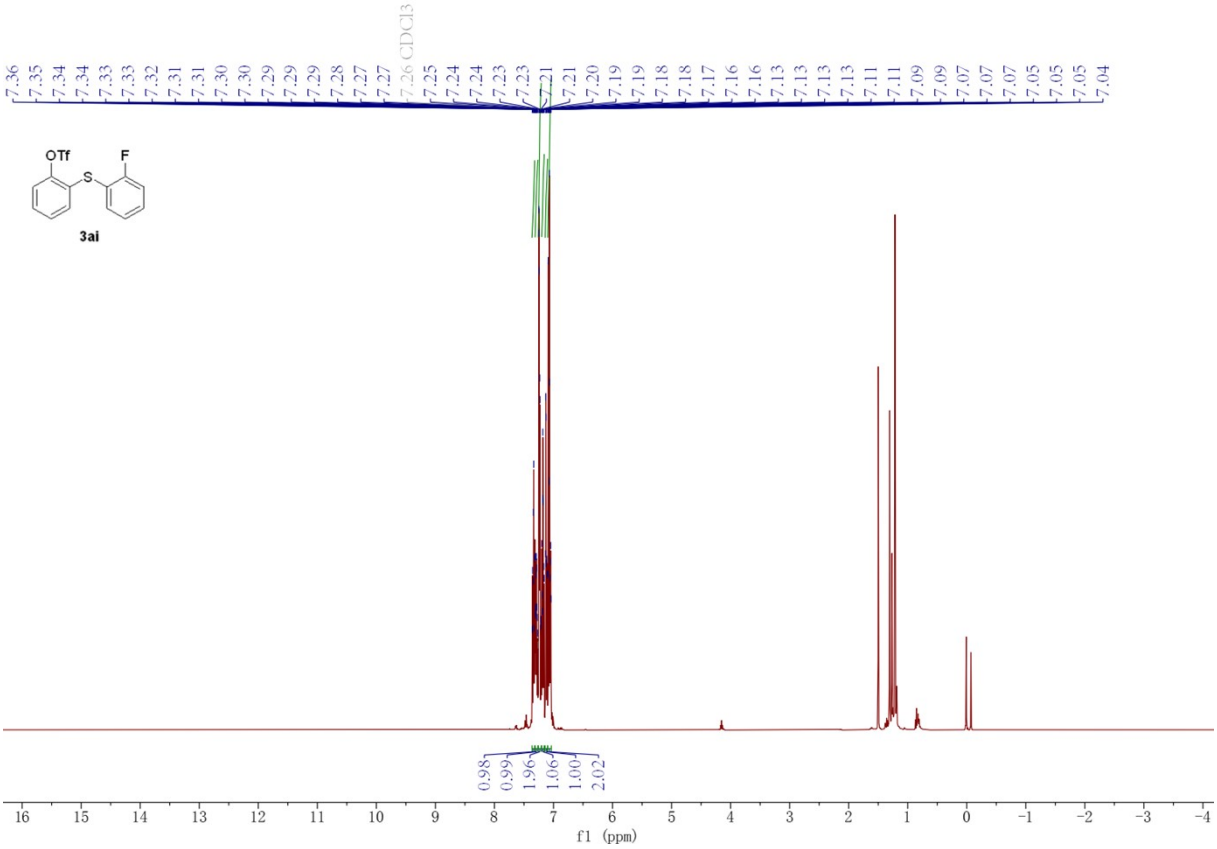
^{13}C NMR spectrum of 3ah (101 MHz, $CDCl_3$)



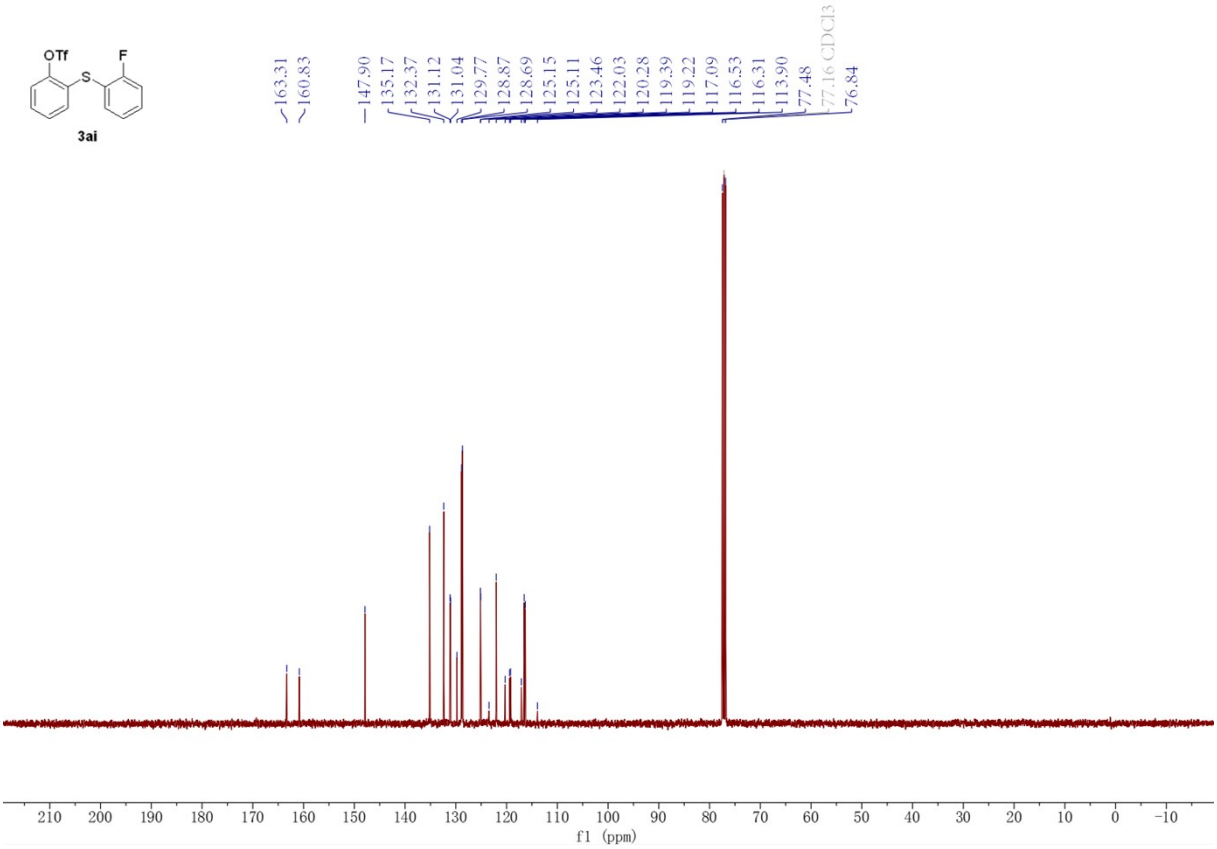
^{19}F NMR spectrum of 3ah (376 MHz, $CDCl_3$)



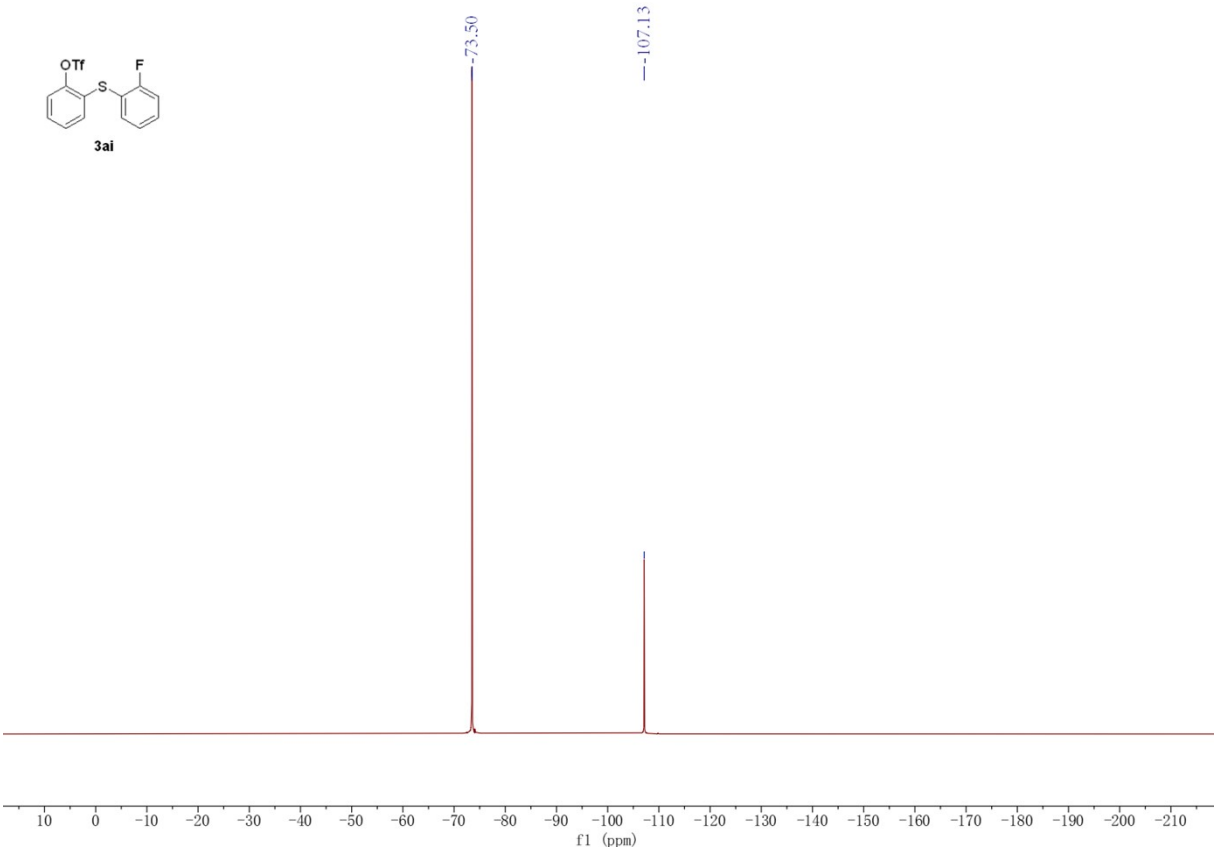
^{1}H NMR spectrum of 3ai (400 MHz, $CDCl_3$)



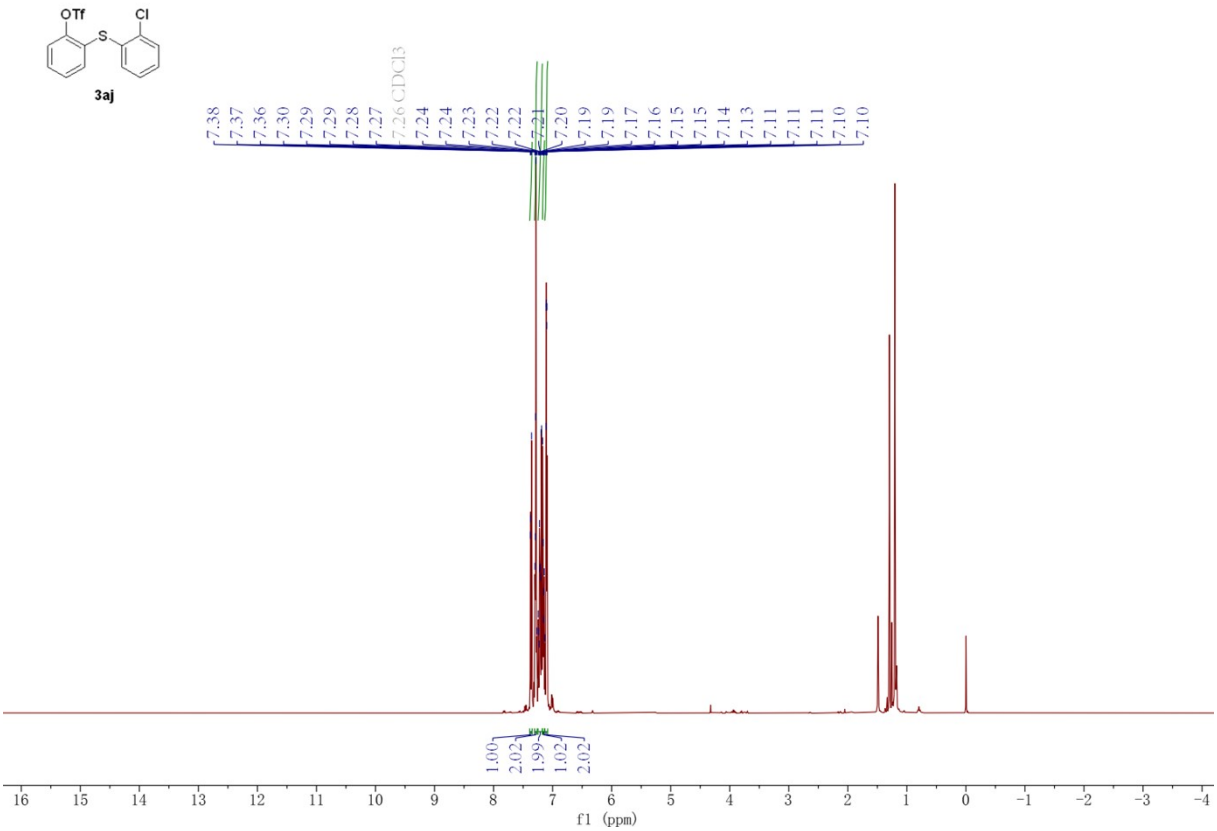
^{13}C NMR spectrum of 3ai (101 MHz, $CDCl_3$)



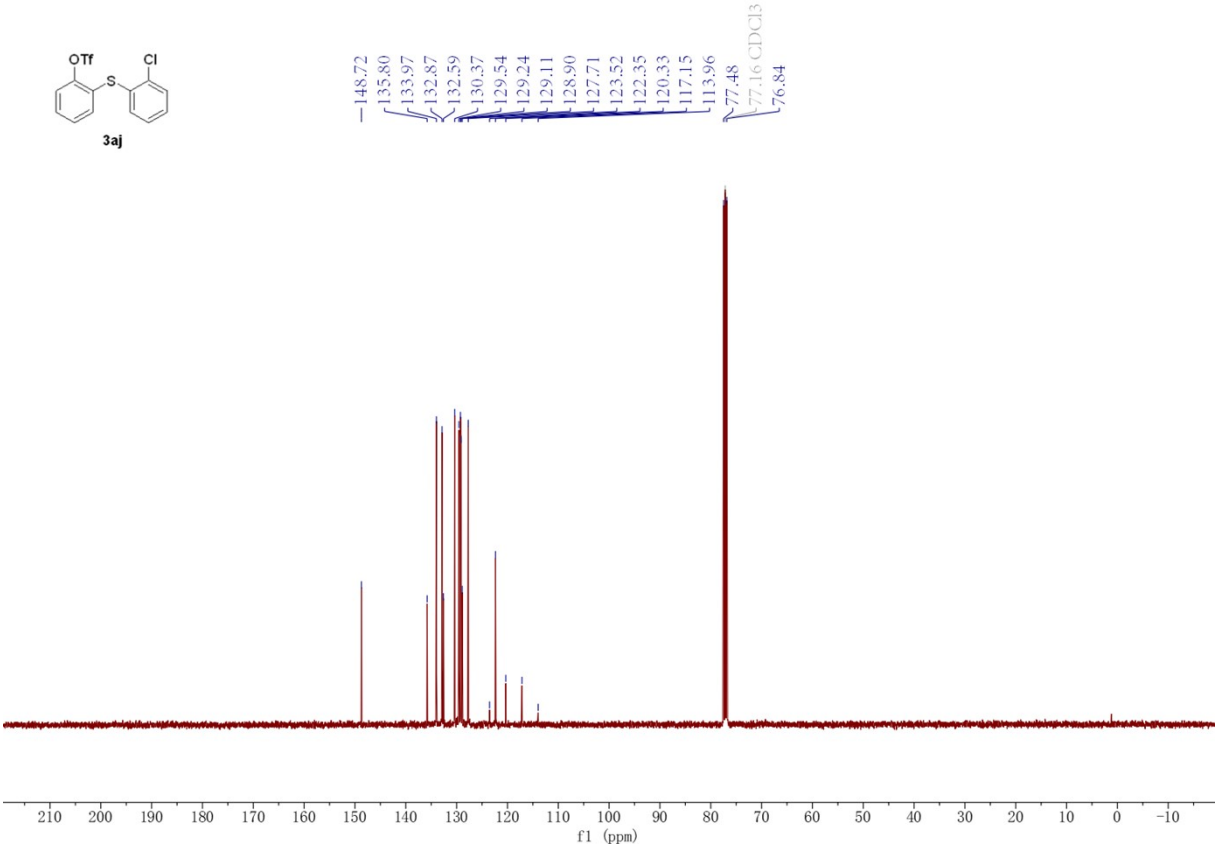
^{19}F NMR spectrum of 3ai (376 MHz, $CDCl_3$)



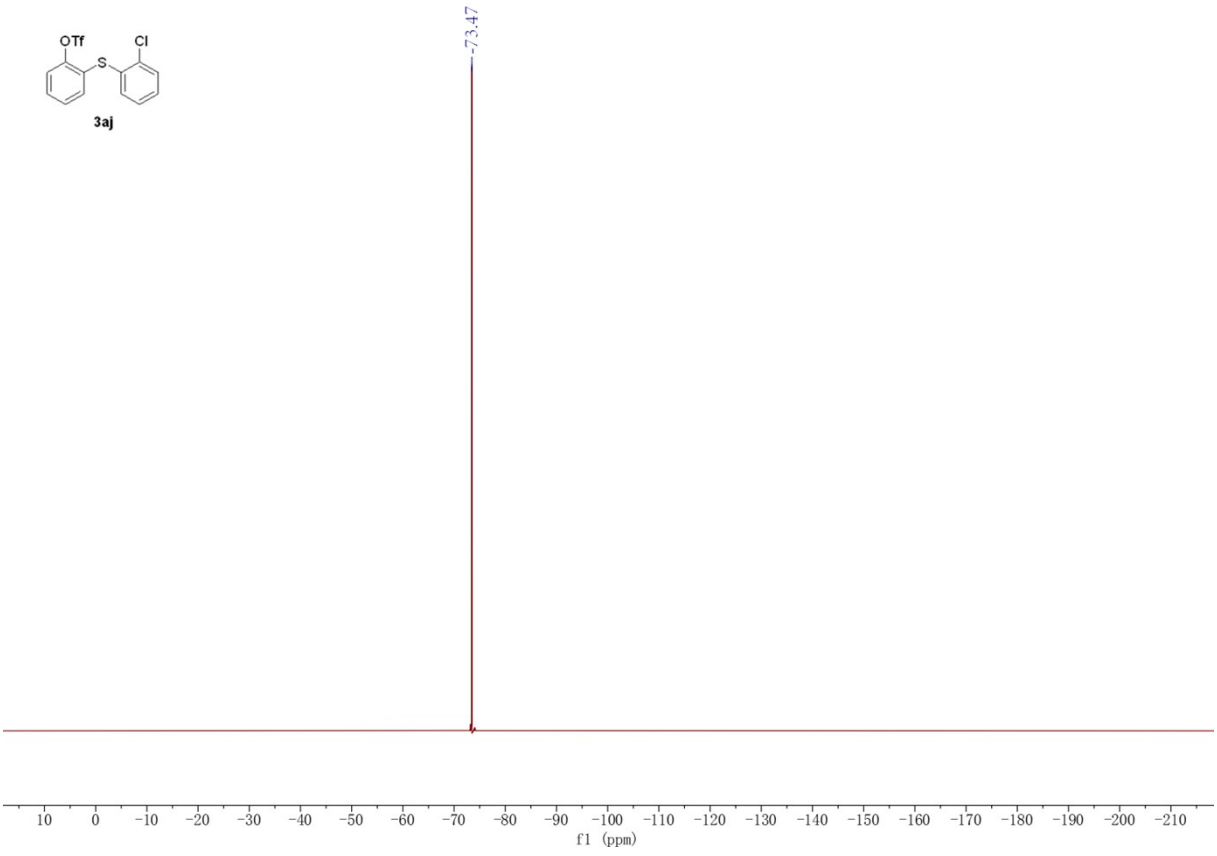
^{1}H NMR spectrum of 3aj (400 MHz, $CDCl_3$)



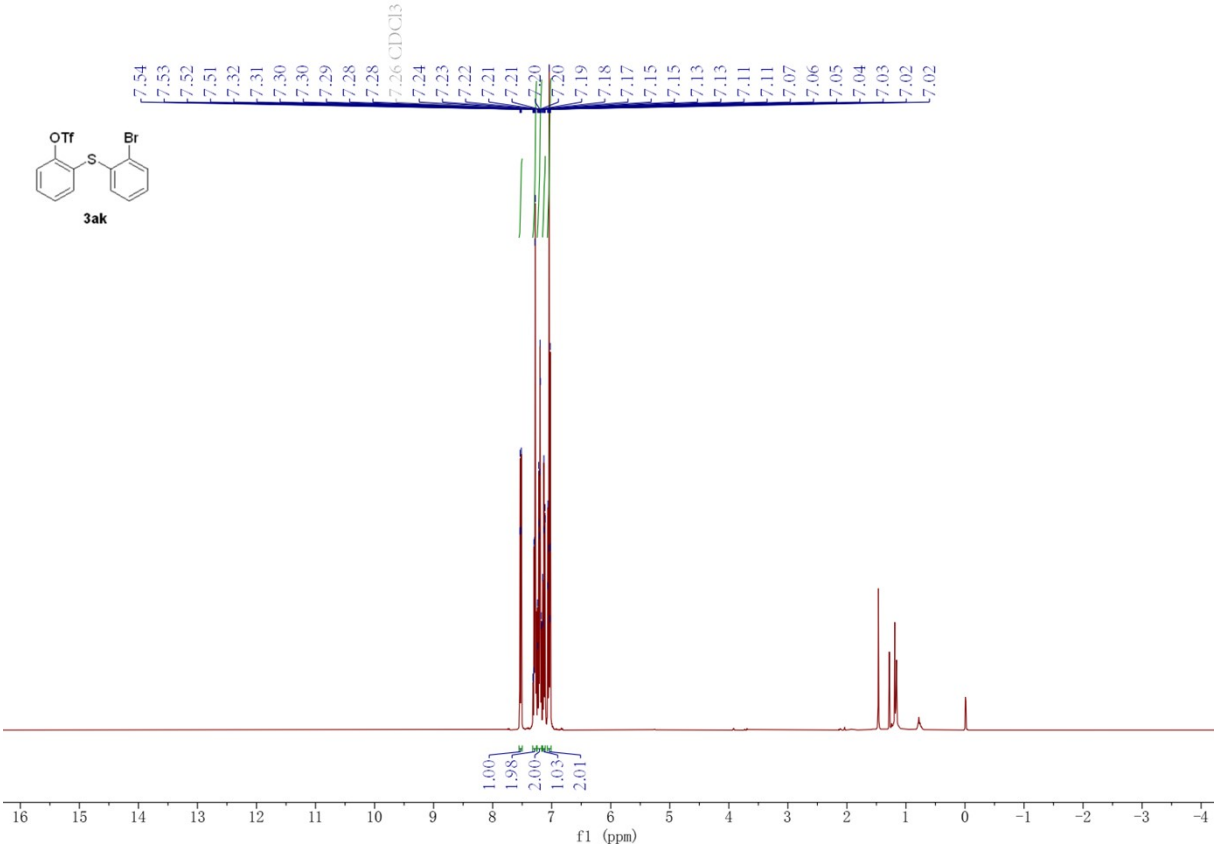
^{13}C NMR spectrum of 3aj (101 MHz, $CDCl_3$)



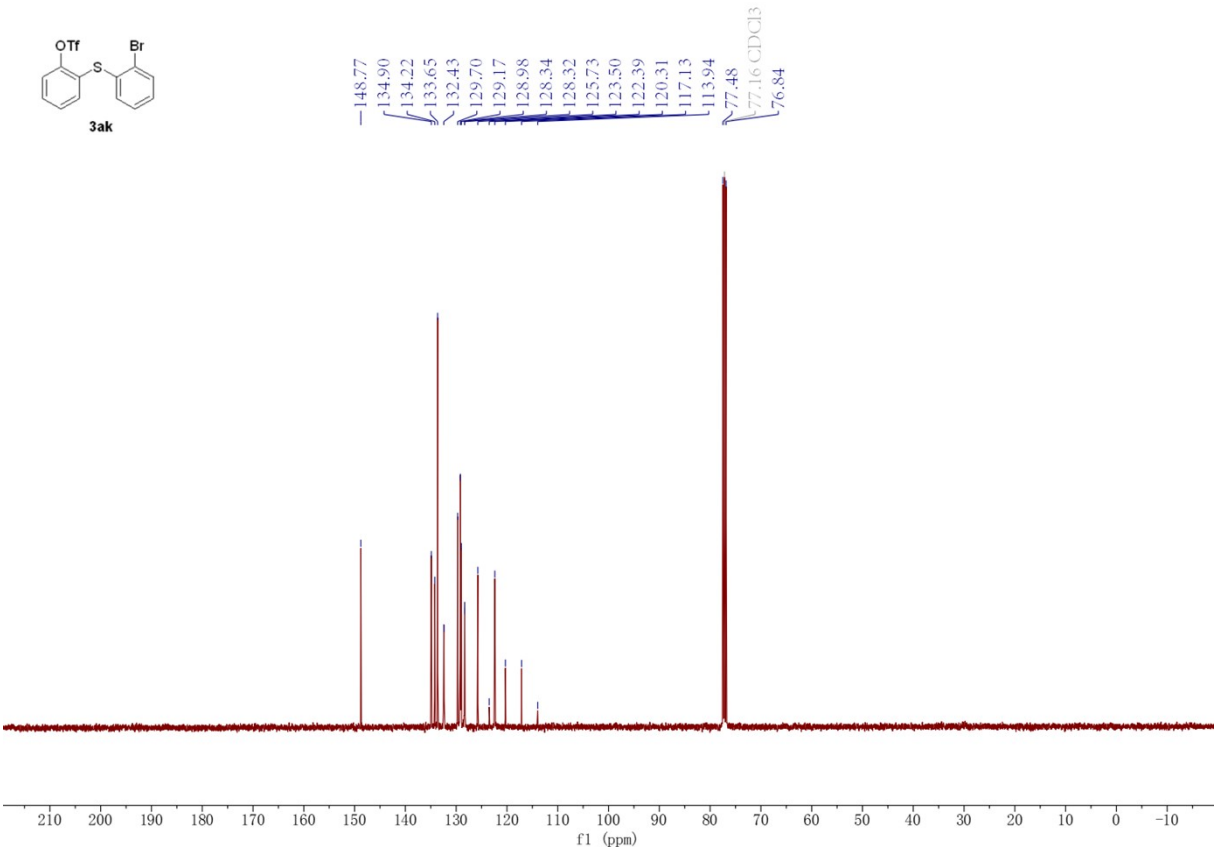
^{19}F NMR spectrum of 3aj (376 MHz, $CDCl_3$)



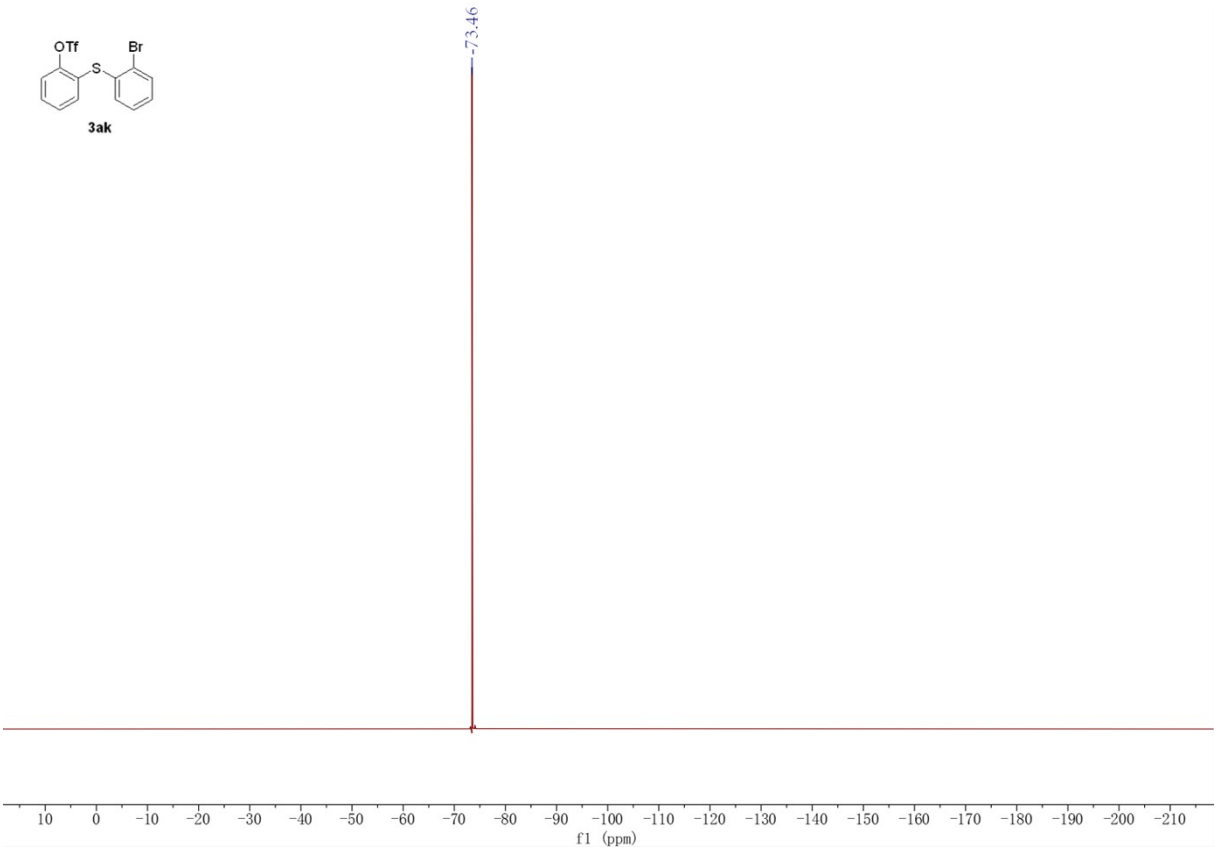
^{1}H NMR spectrum of 3ak (400 MHz, $CDCl_3$)



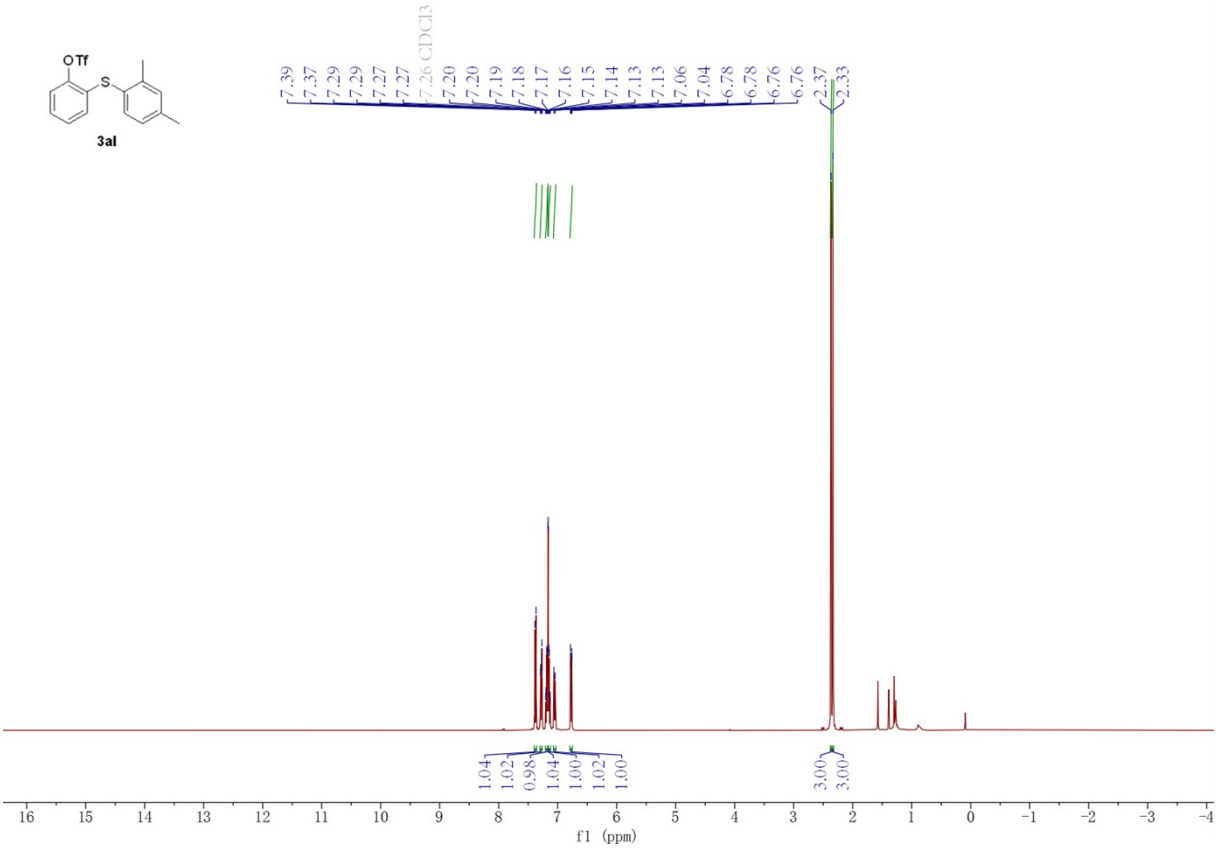
^{13}C NMR spectrum of 3ak (101 MHz, $CDCl_3$)



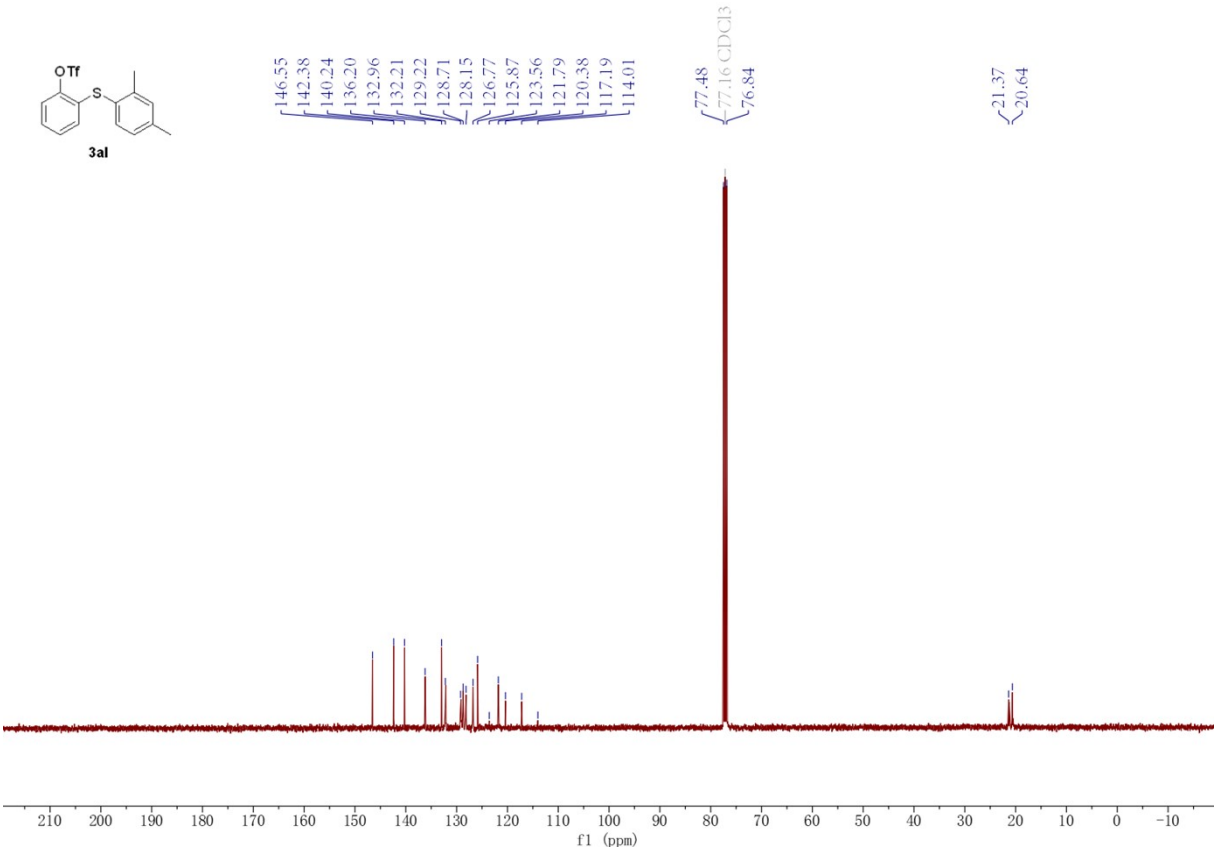
^{19}F NMR spectrum of 3ak (376 MHz, $CDCl_3$)



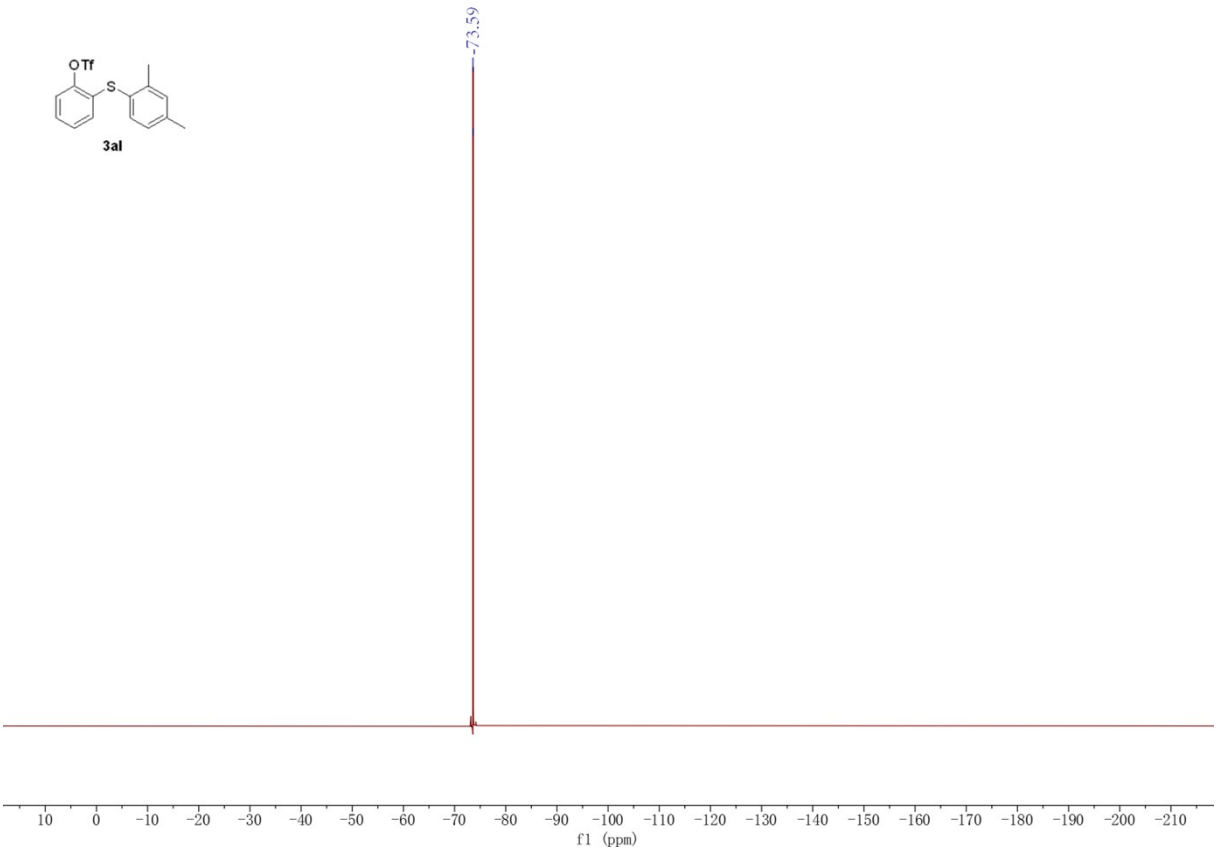
^{1}H NMR spectrum of 3al (400 MHz, $CDCl_3$)



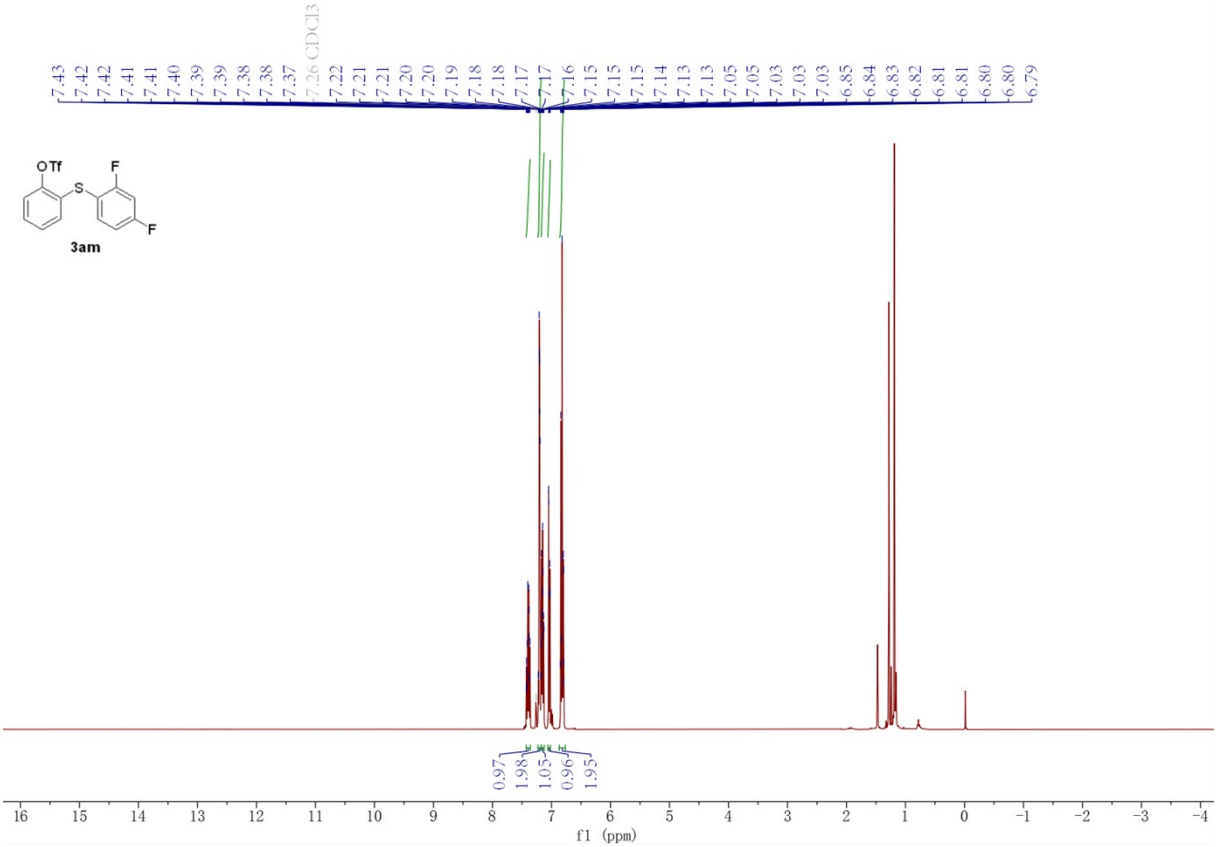
^{13}C NMR spectrum of 3al (101 MHz, $CDCl_3$)



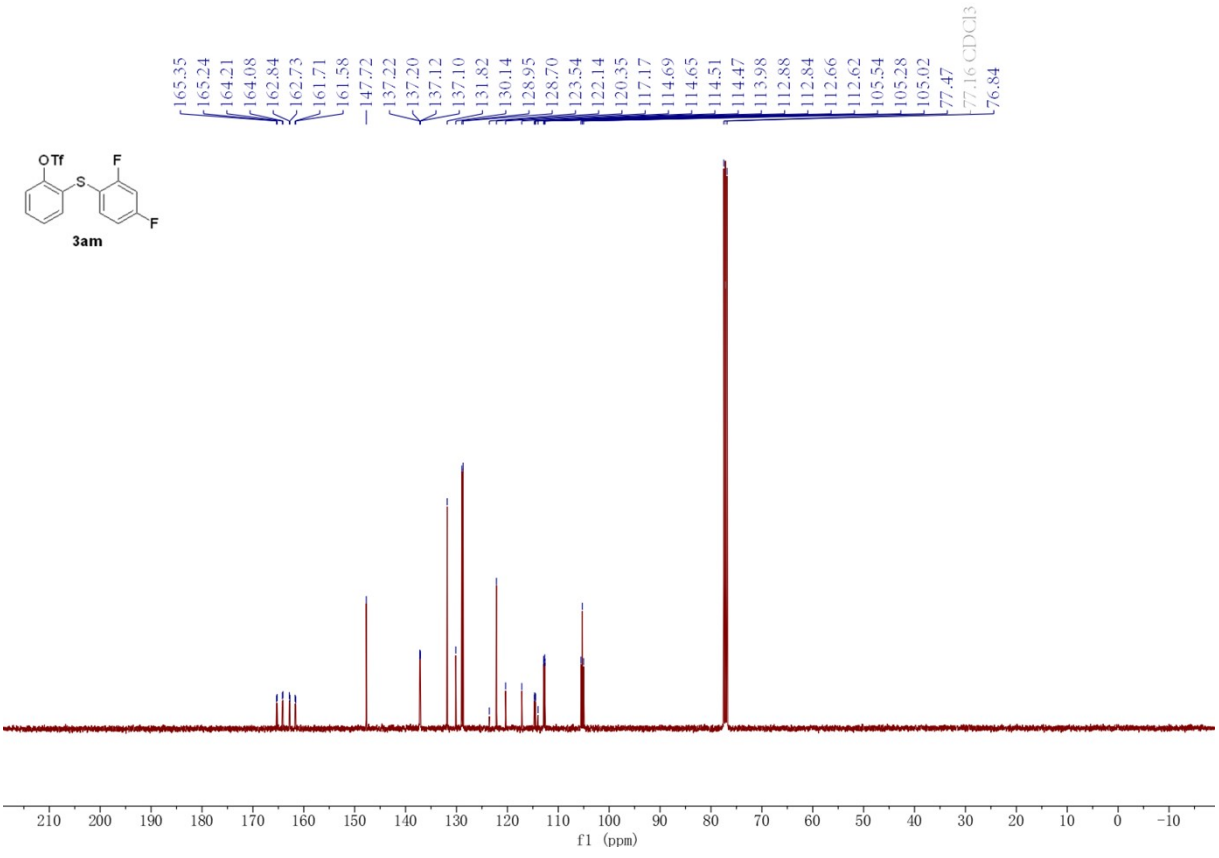
^{19}F NMR spectrum of 3al (376 MHz, $CDCl_3$)



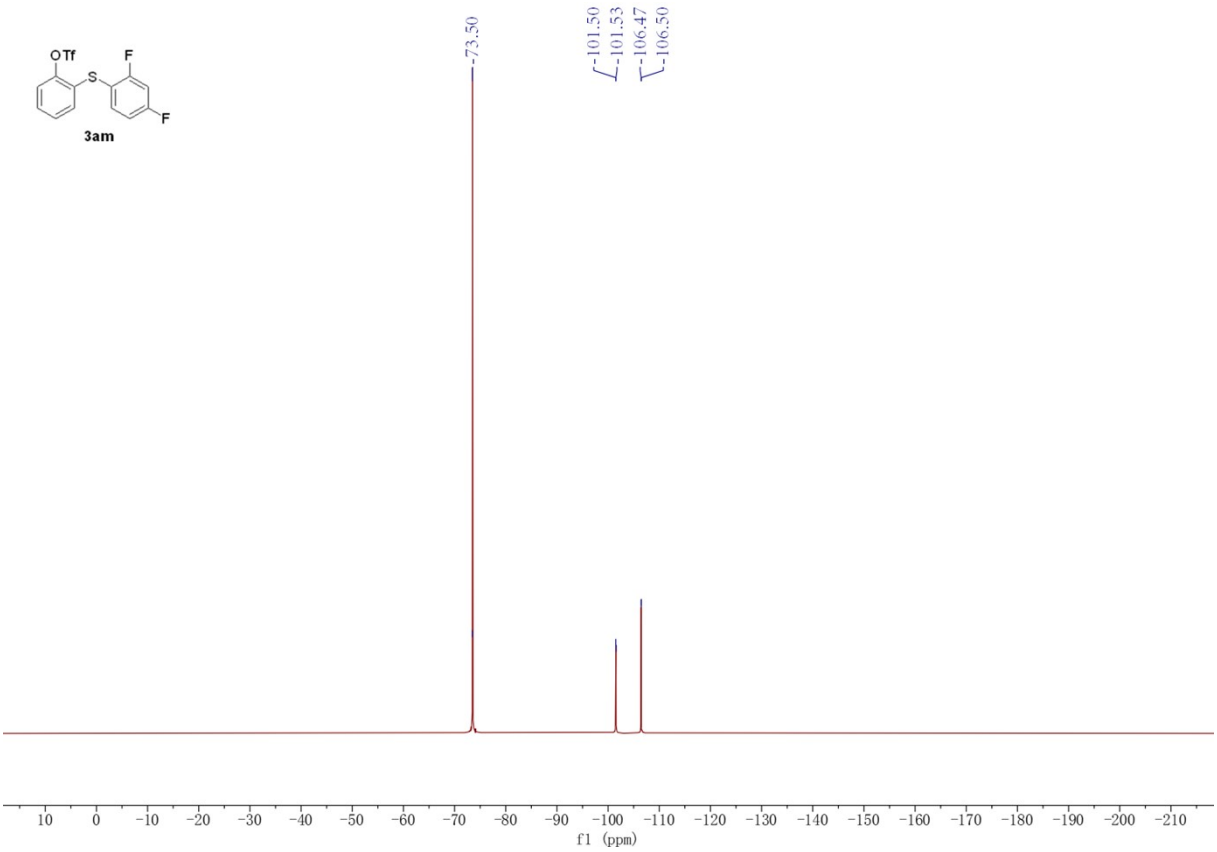
^{1}H NMR spectrum of 3am (400 MHz, $CDCl_3$)



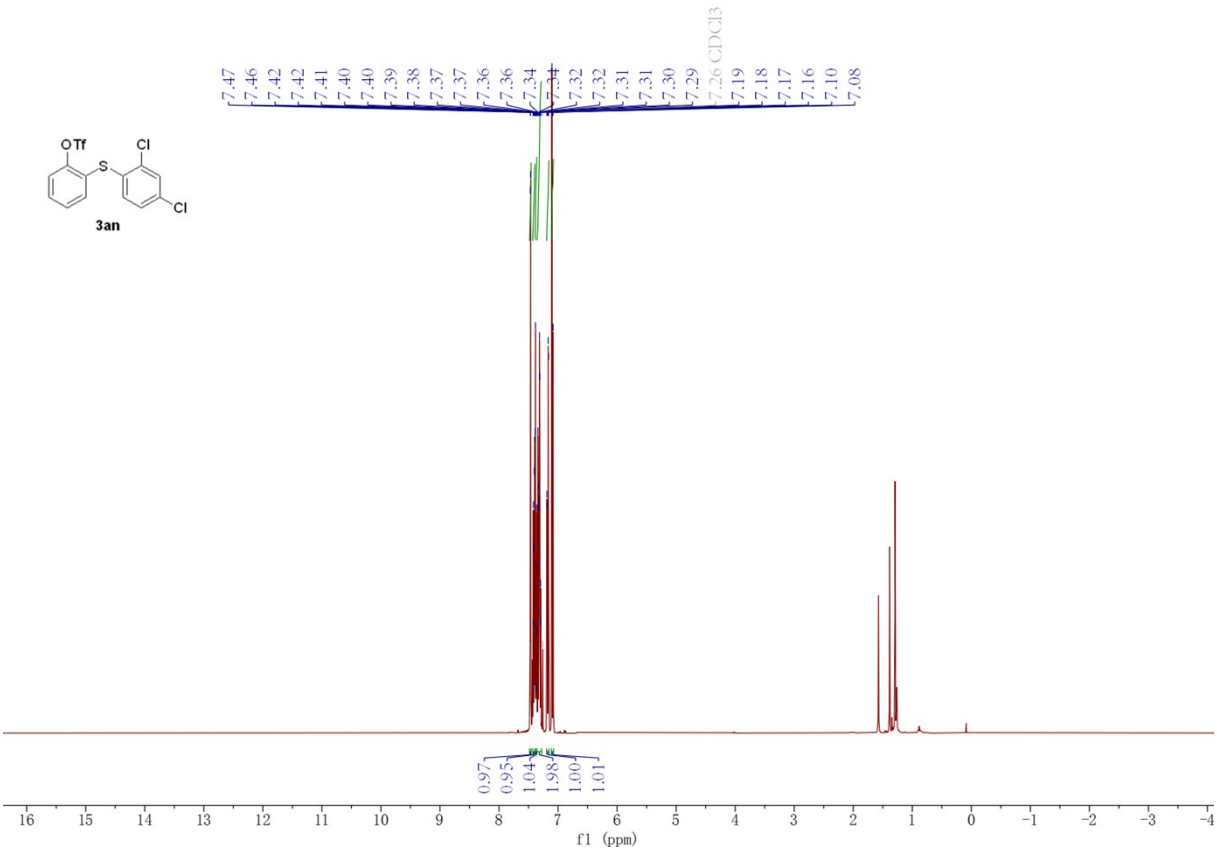
^{13}C NMR spectrum of 3am (101 MHz, $CDCl_3$)



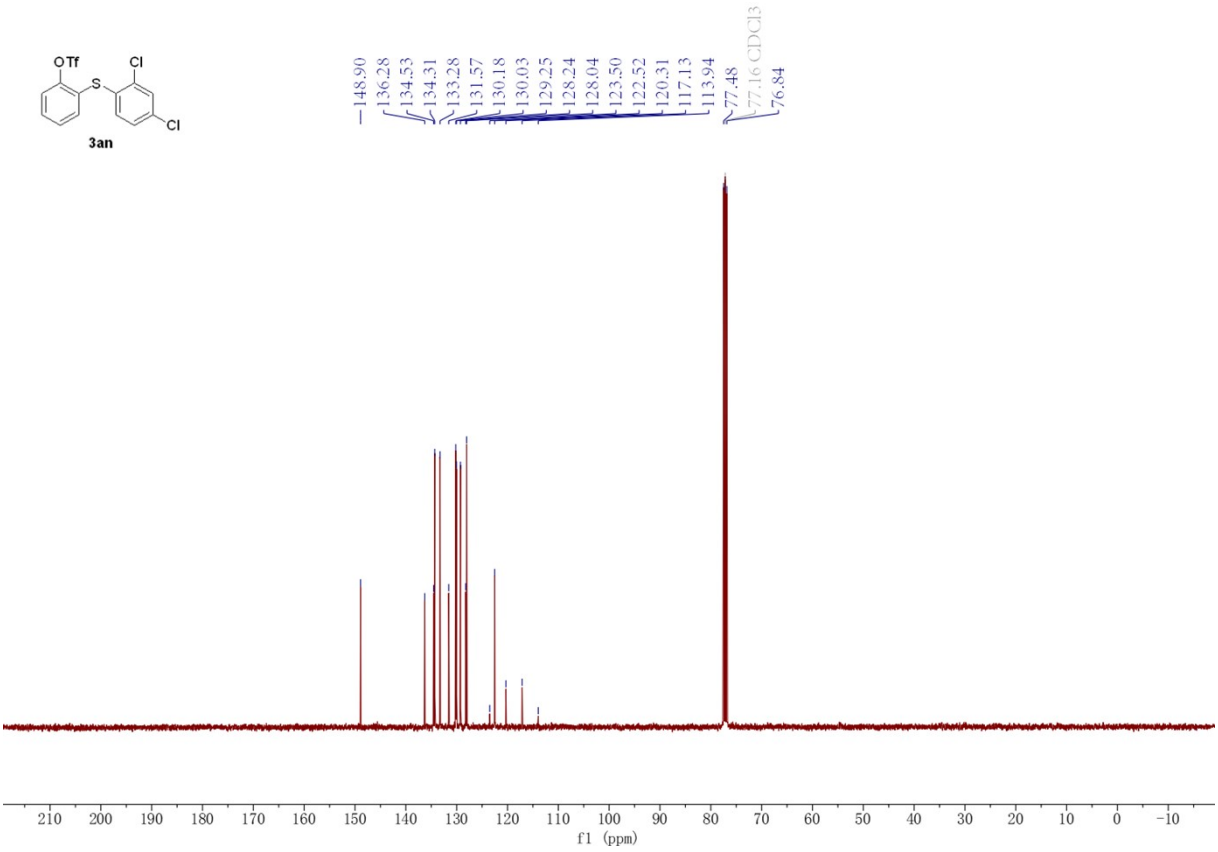
^{19}F NMR spectrum of 3am (376 MHz, $CDCl_3$)



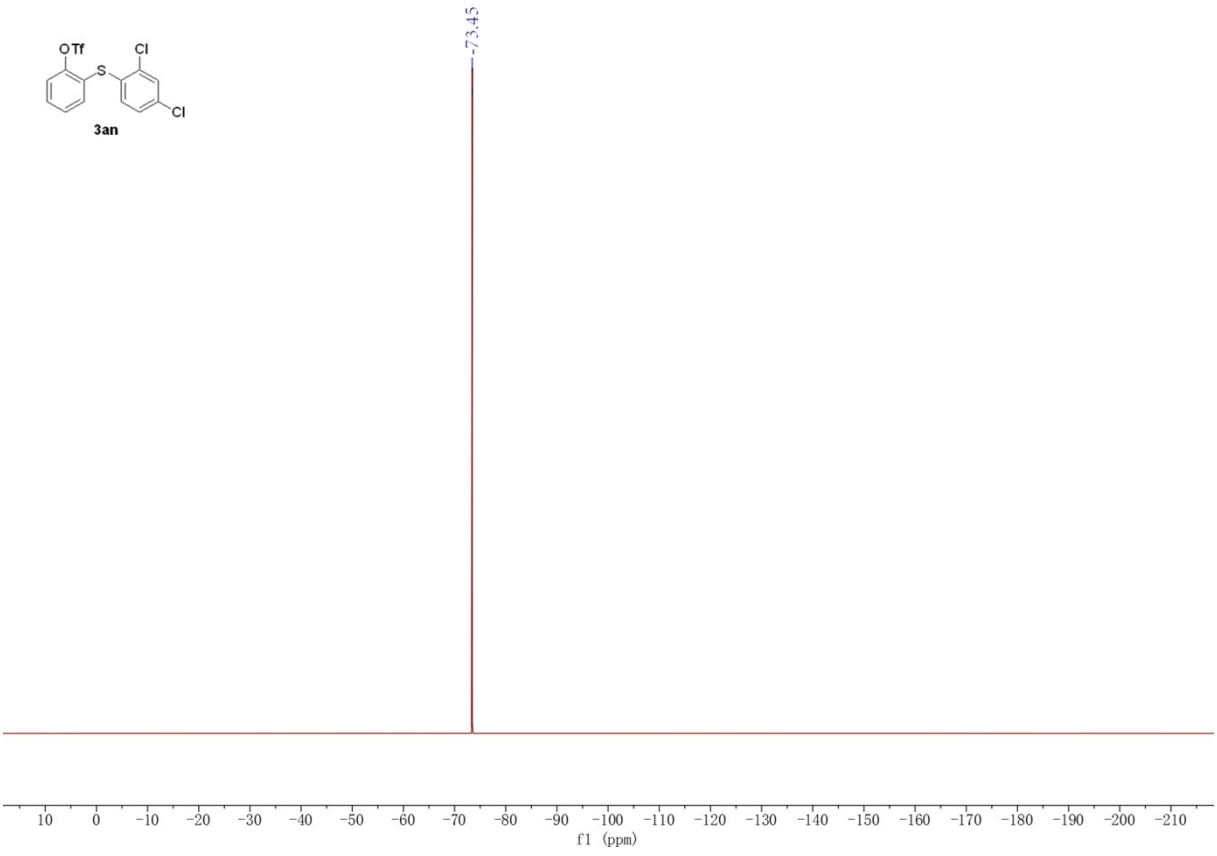
^{1}H NMR spectrum of 3an (400 MHz, $CDCl_3$)



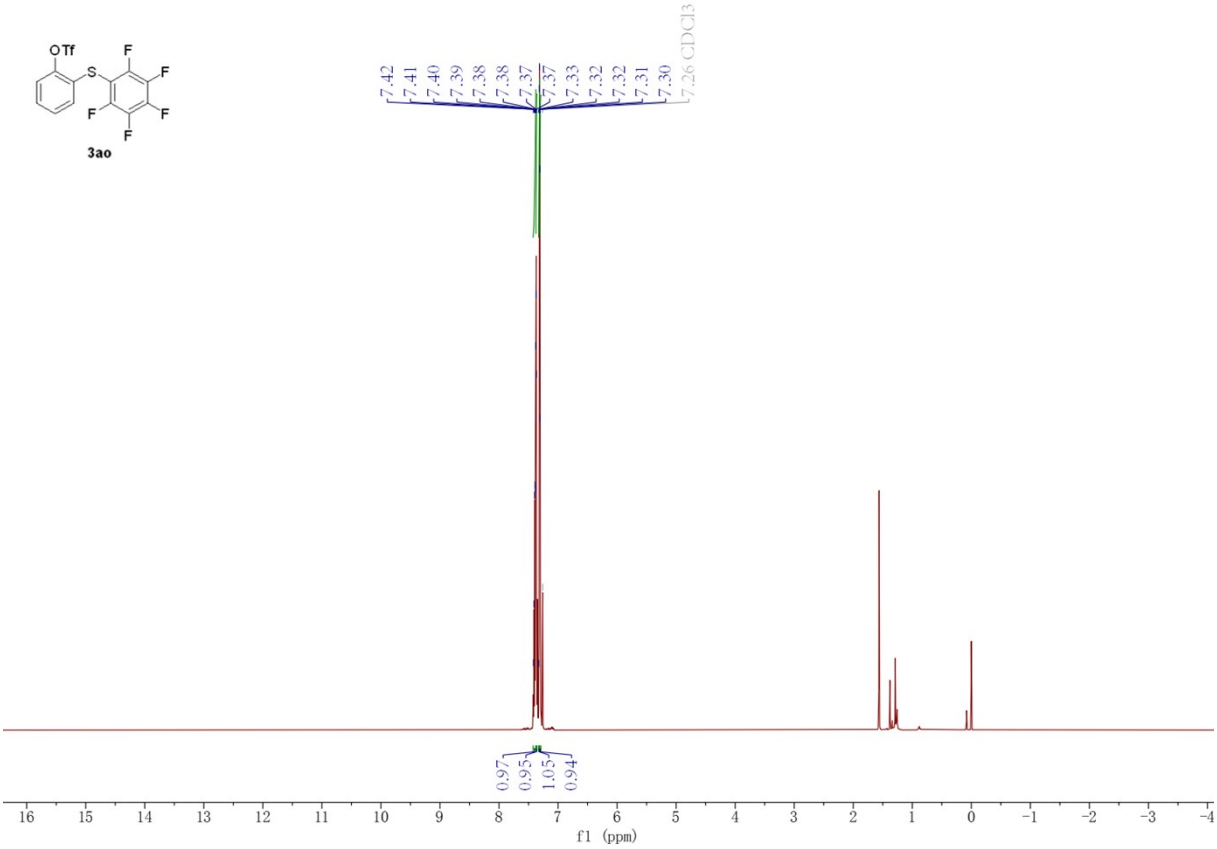
^{13}C NMR spectrum of 3an (101 MHz, $CDCl_3$)



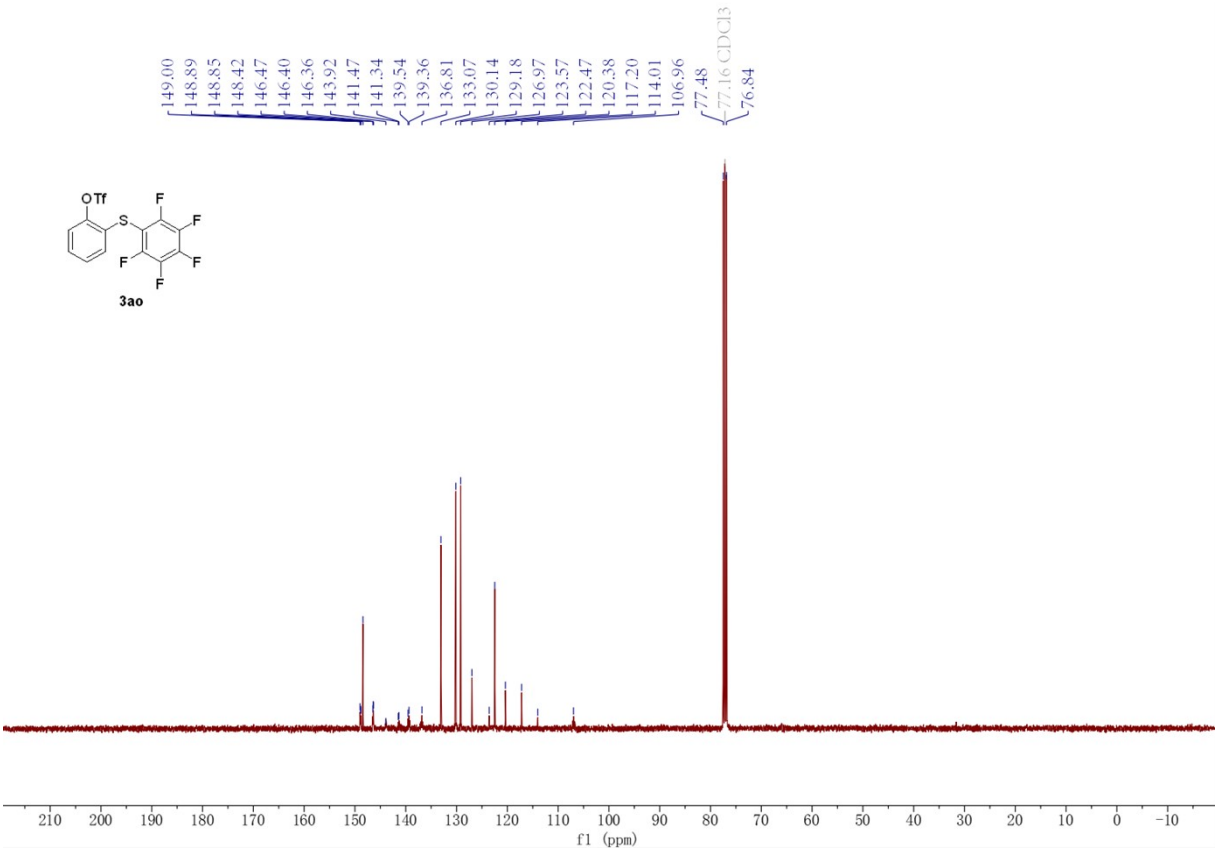
^{19}F NMR spectrum of 3an (376 MHz, $CDCl_3$)



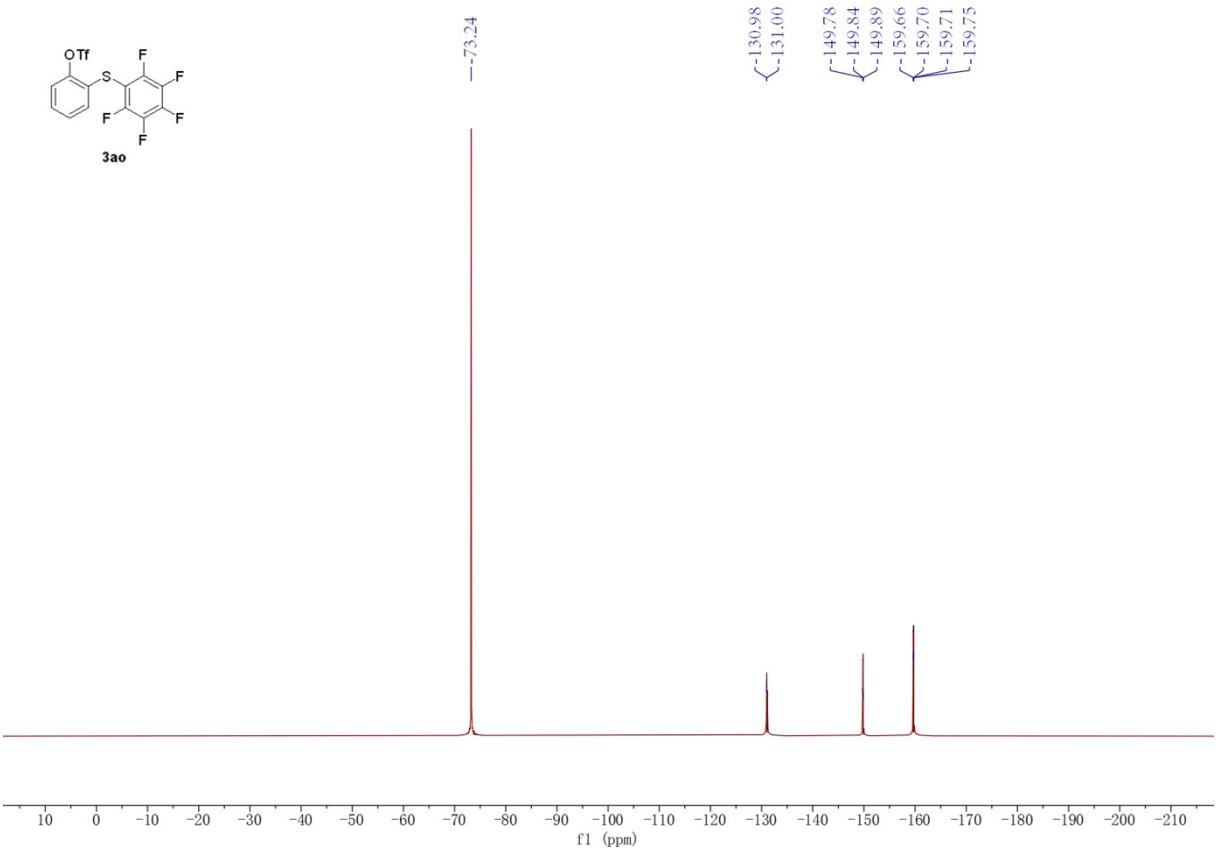
^{1}H NMR spectrum of 3ao (400 MHz, $CDCl_3$)



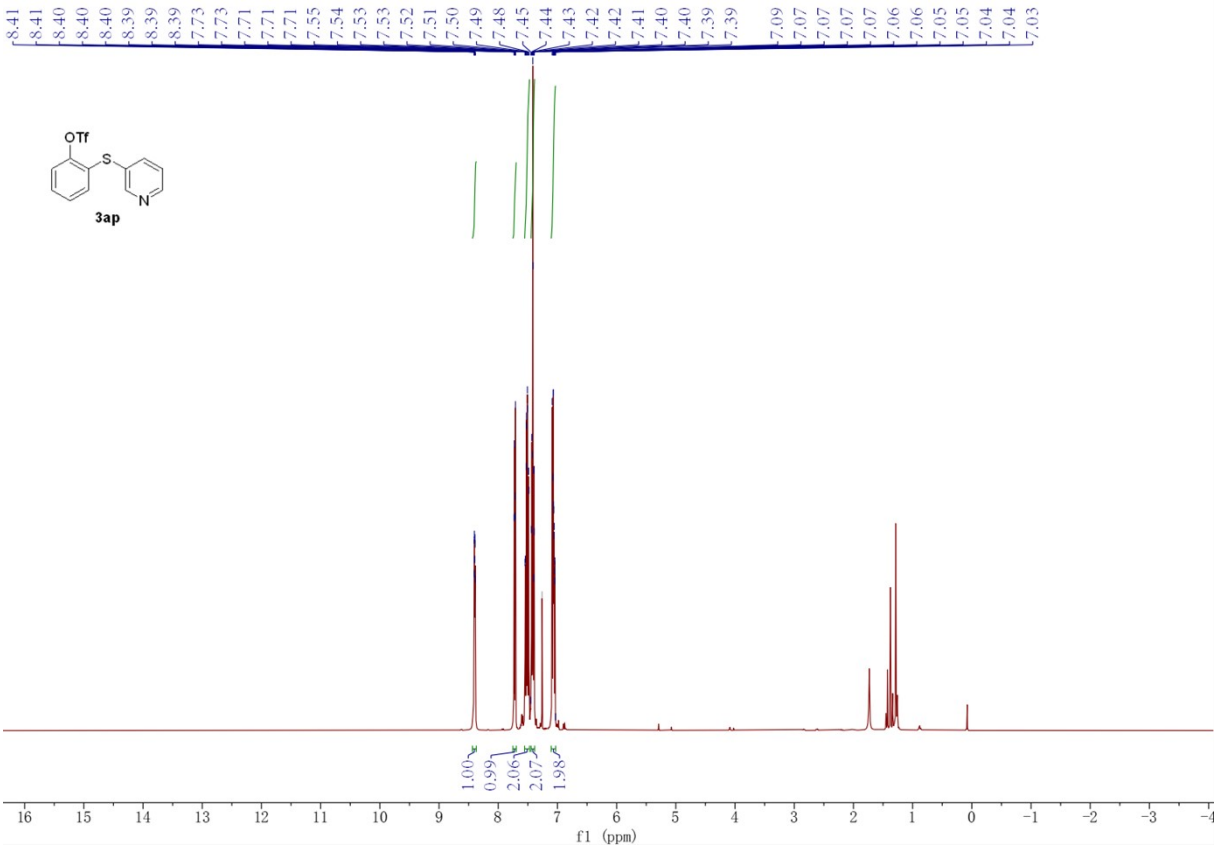
^{13}C NMR spectrum of 3ao (101 MHz, $CDCl_3$)



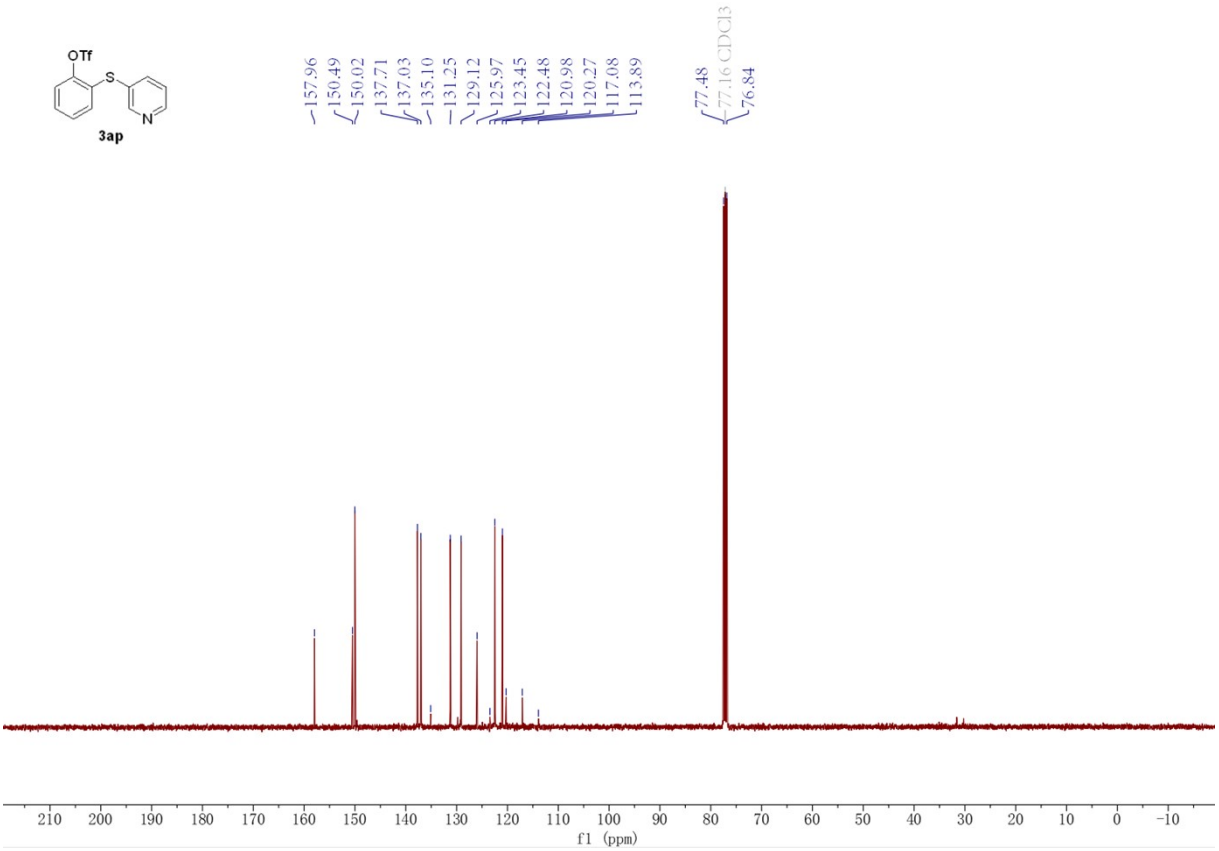
^{19}F NMR spectrum of 3ao (376 MHz, $CDCl_3$)



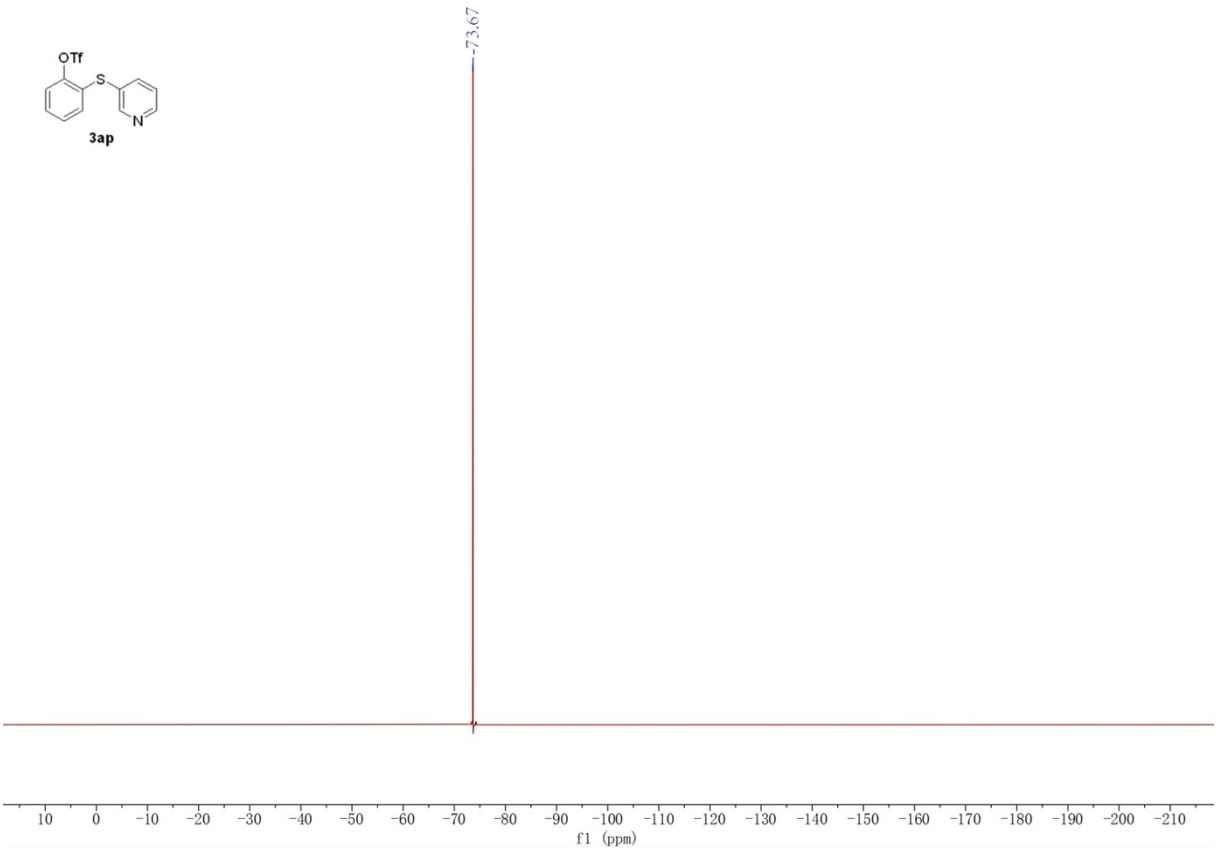
^{1}H NMR spectrum of 3ap (400 MHz, $CDCl_3$)



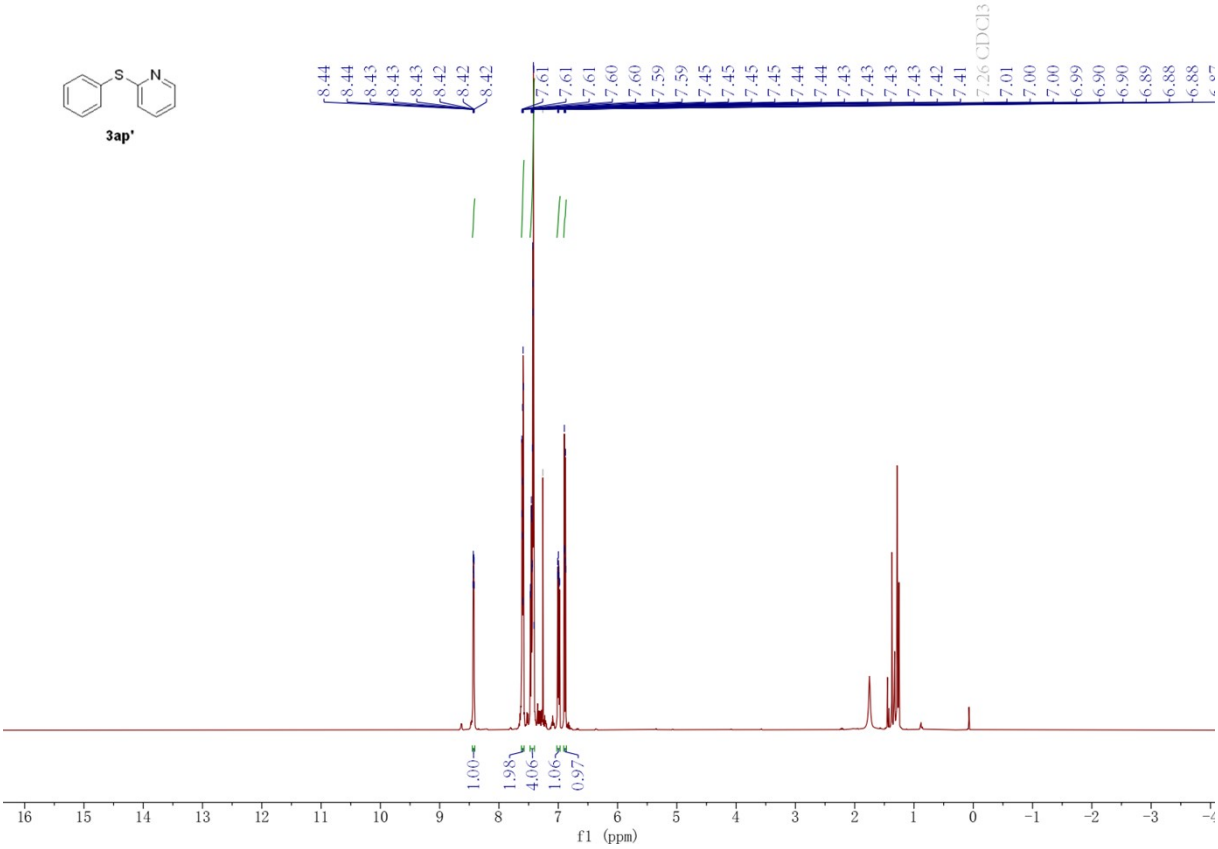
^{13}C NMR spectrum of 3ap (101 MHz, $CDCl_3$)



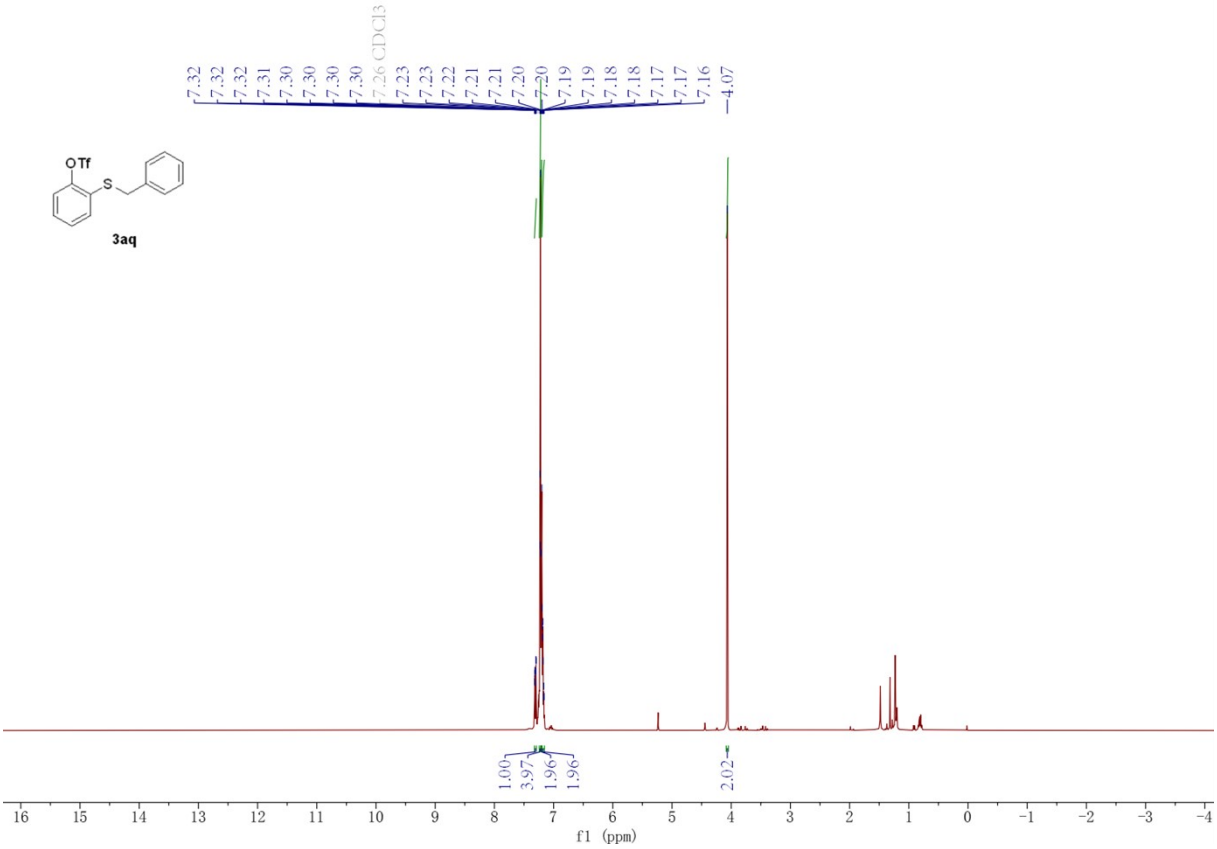
^{19}F NMR spectrum of 3ap (376 MHz, $CDCl_3$)



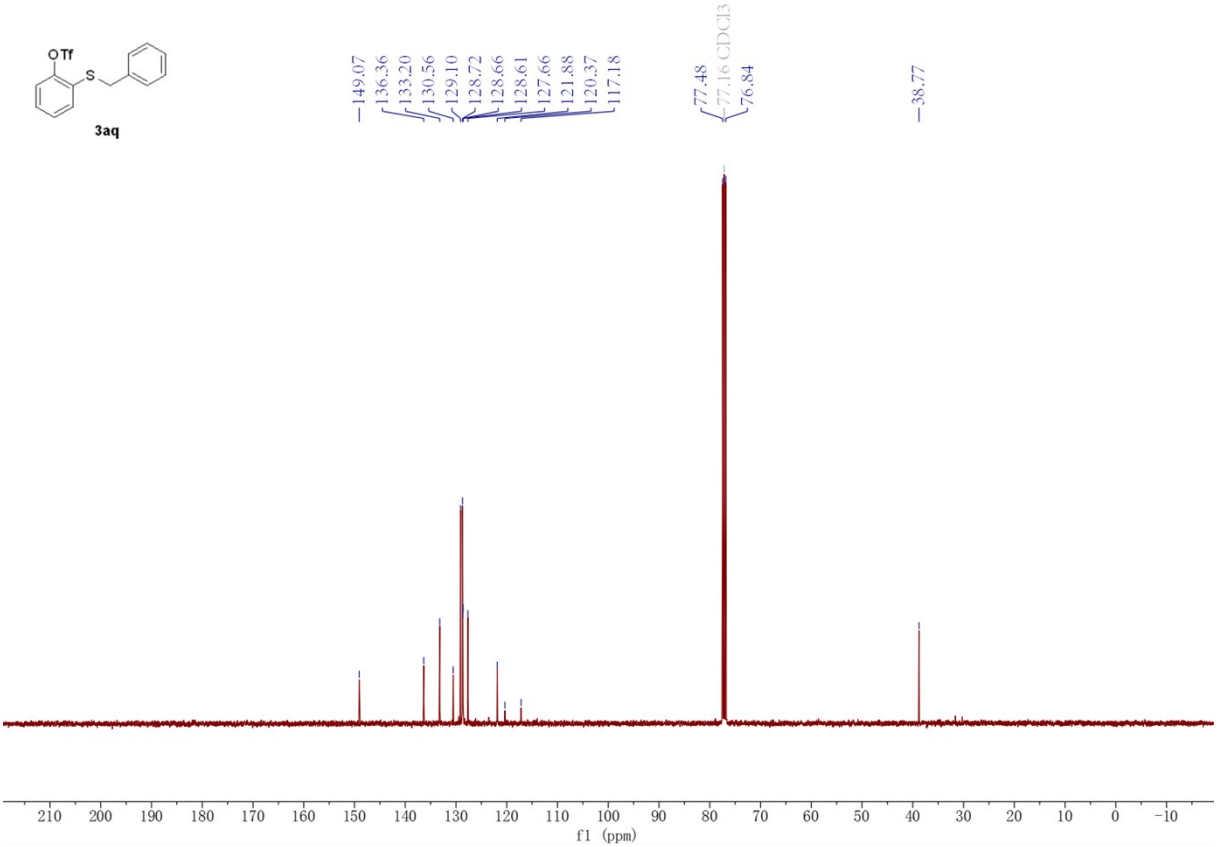
^{1}H NMR spectrum of 3ap' (400 MHz, $CDCl_3$)



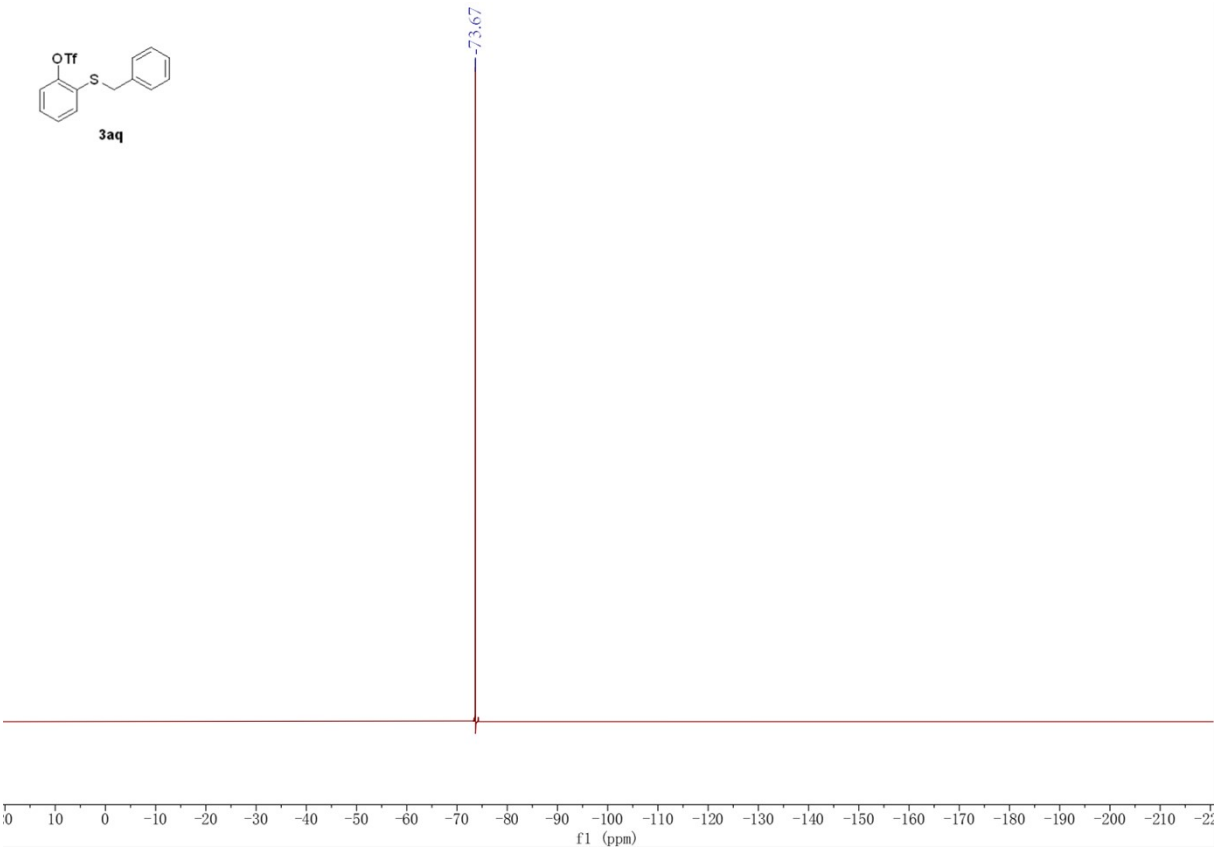
^{1}H NMR spectrum of 3aq (400 MHz, $CDCl_3$)



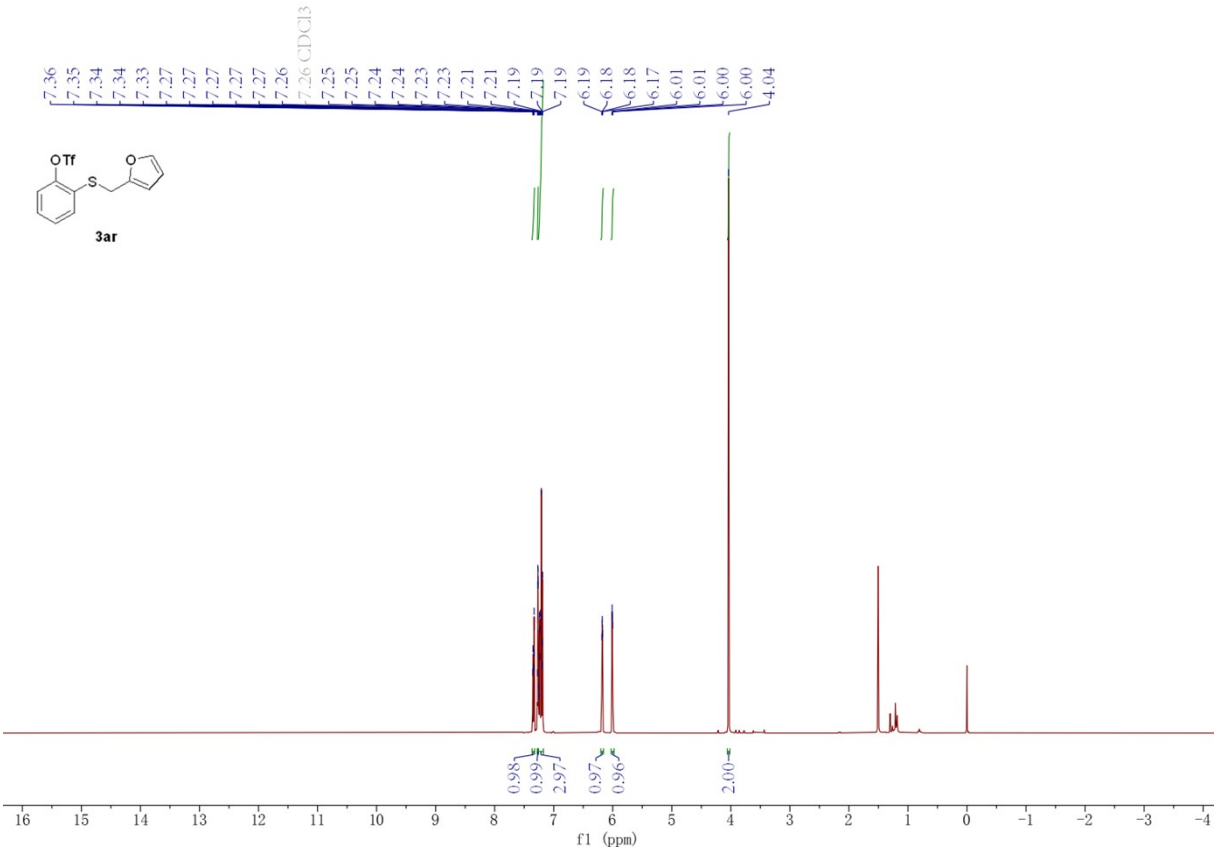
^{13}C NMR spectrum of 3aq (101 MHz, $CDCl_3$)



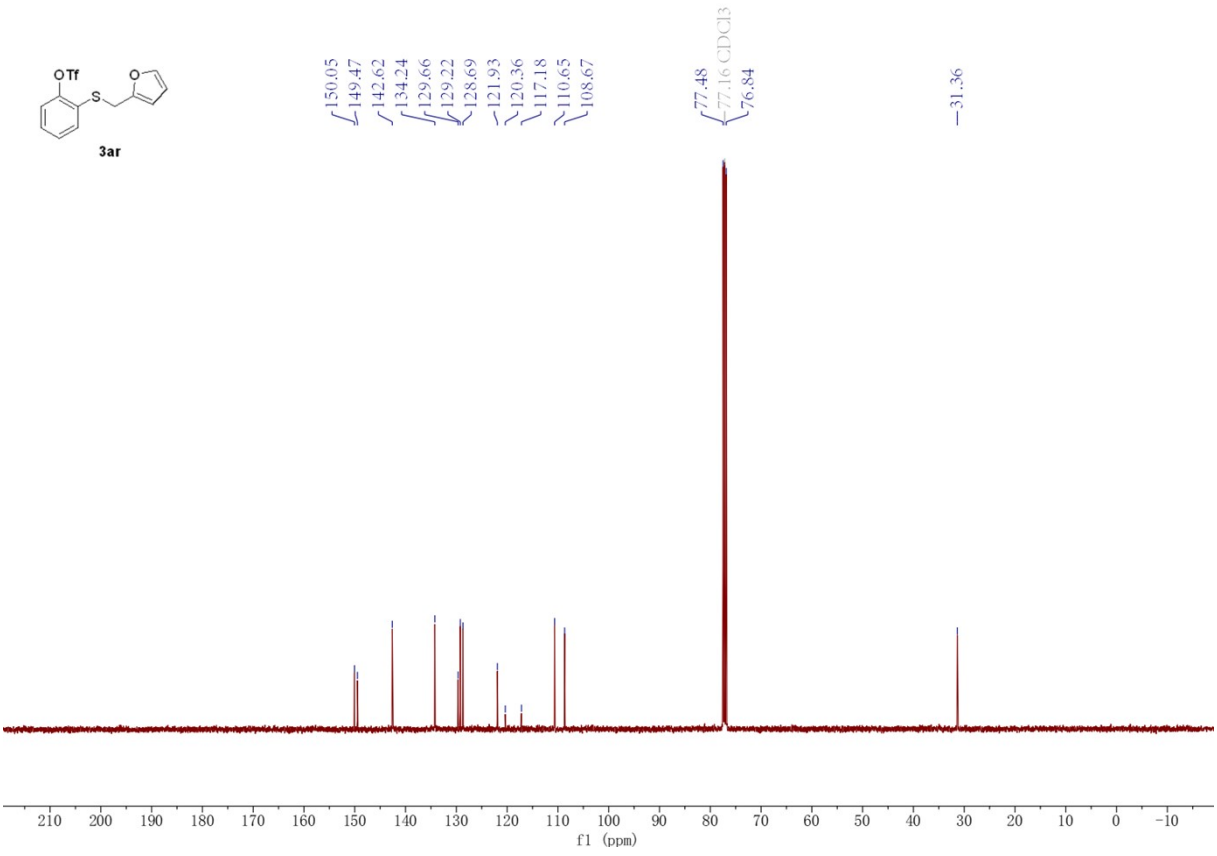
^{19}F NMR spectrum of 3aq (376 MHz, $CDCl_3$)



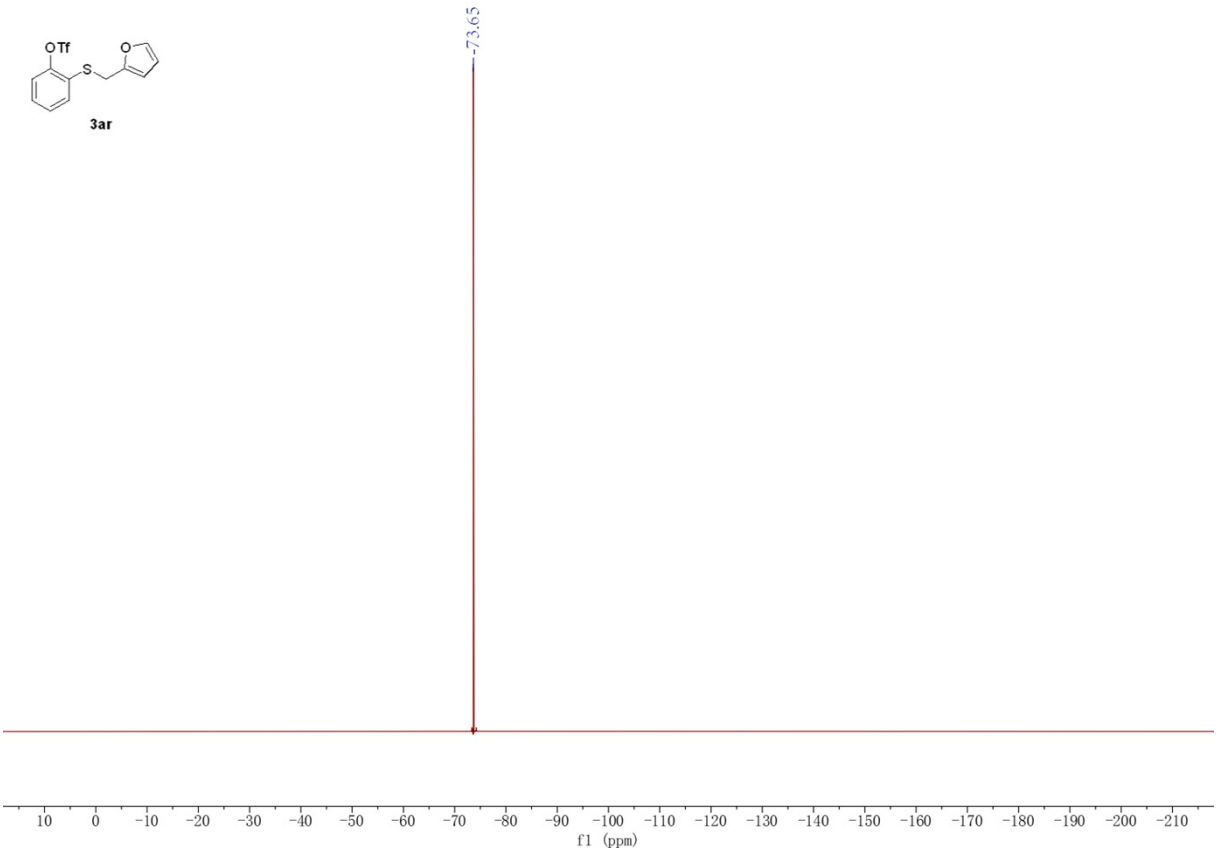
^{1}H NMR spectrum of 3ar (400 MHz, $CDCl_3$)



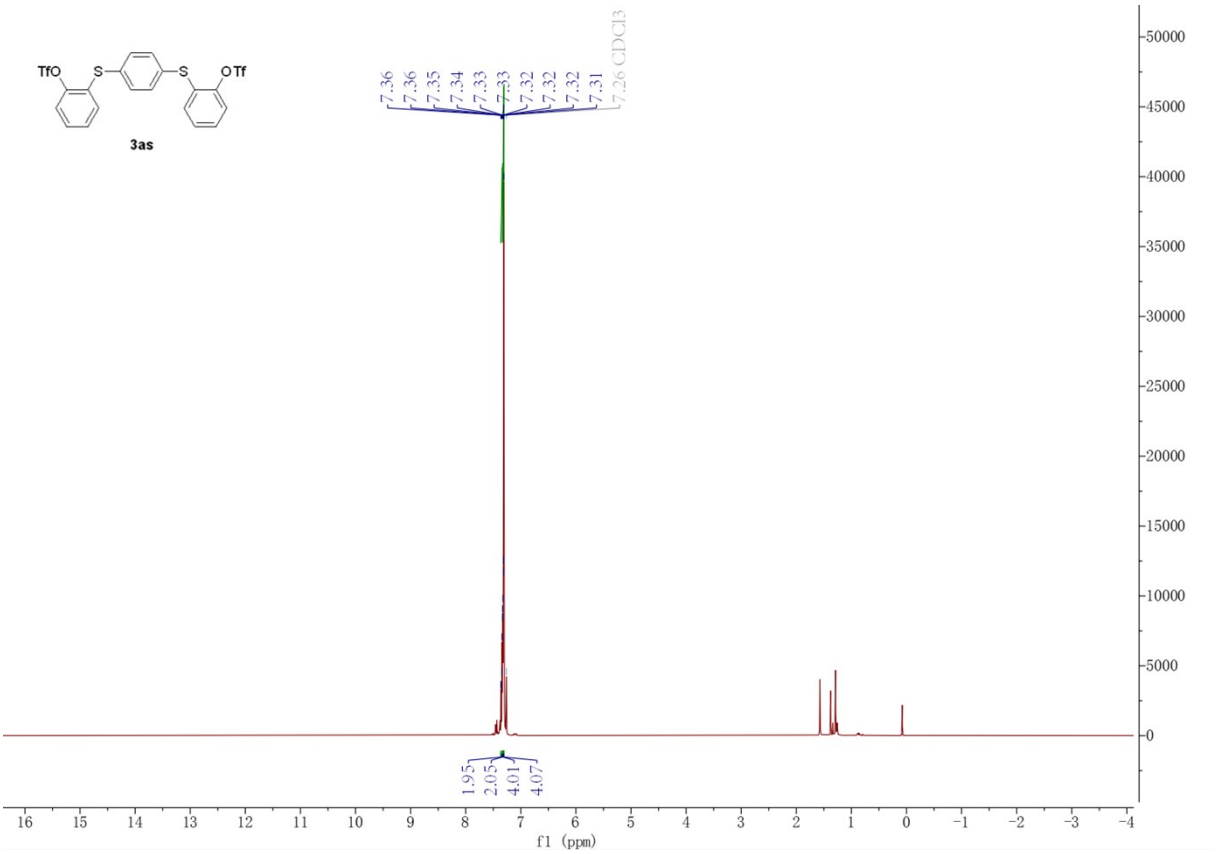
^{13}C NMR spectrum of 3ap (101 MHz, $CDCl_3$)



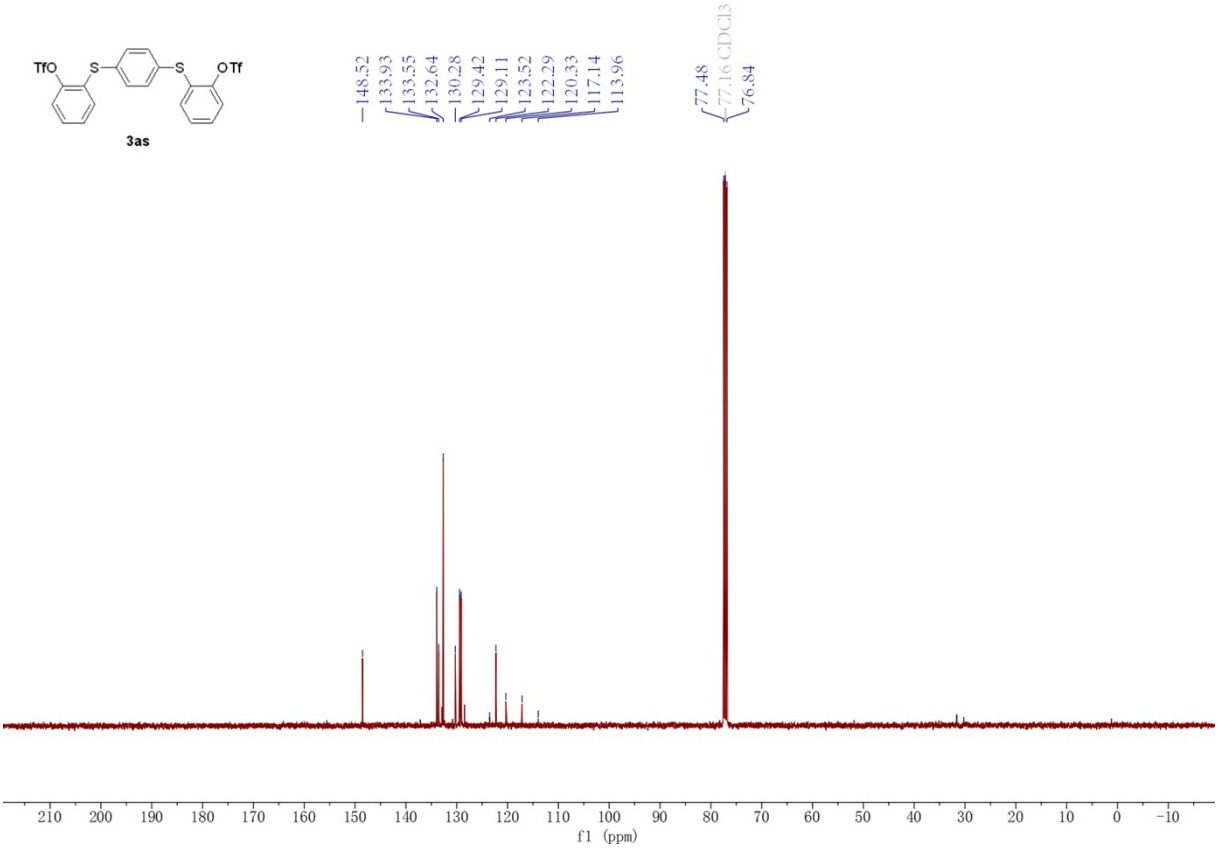
^{19}F NMR spectrum of 3ap (376 MHz, $CDCl_3$)



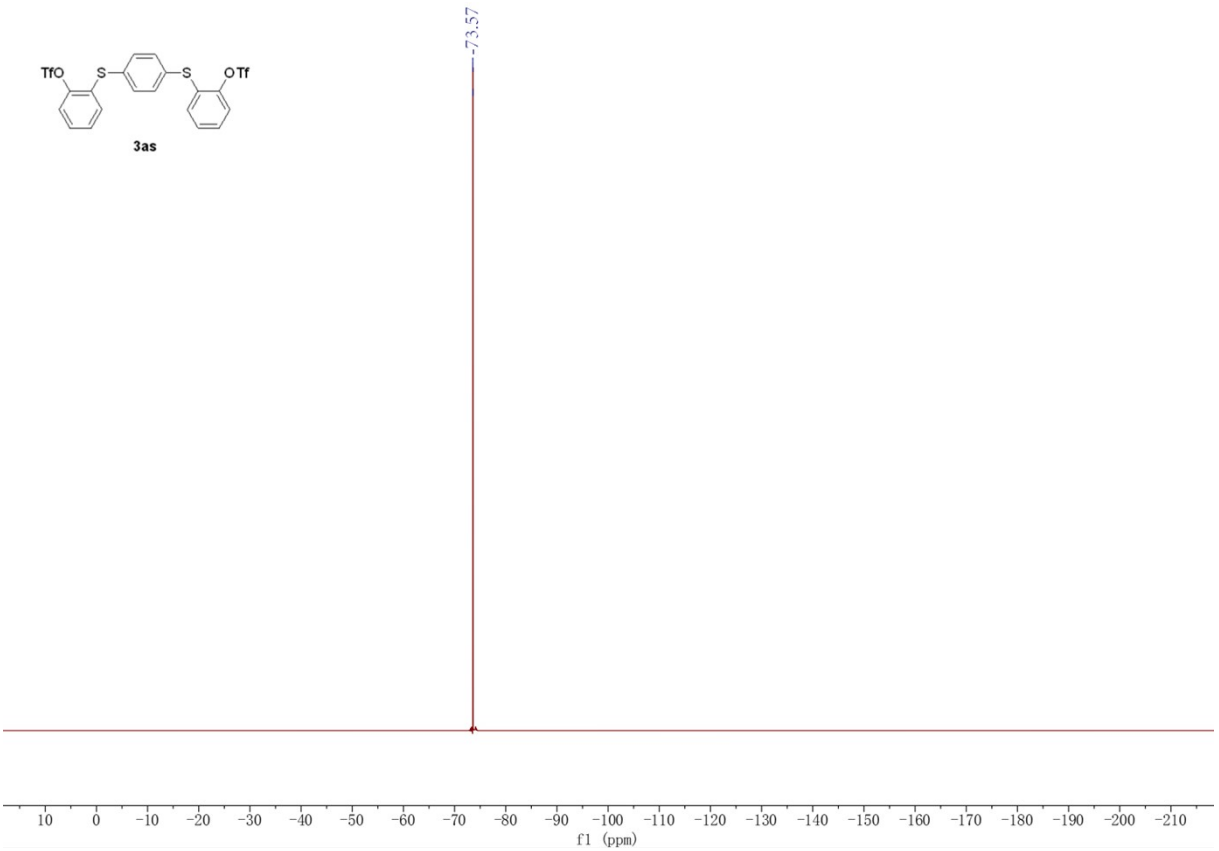
^{1}H NMR spectrum of 3as (400 MHz, $CDCl_3$)



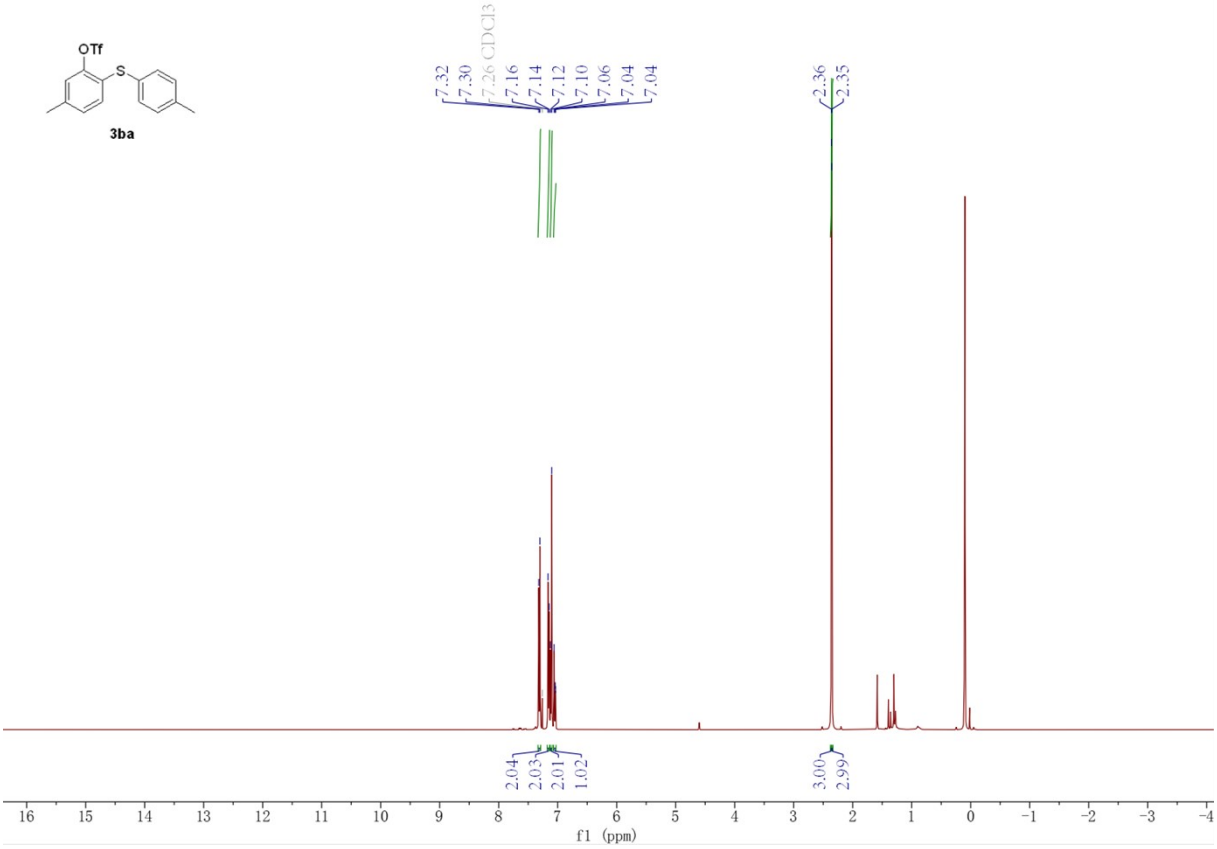
^{13}C NMR spectrum of 3as (101 MHz, $CDCl_3$)



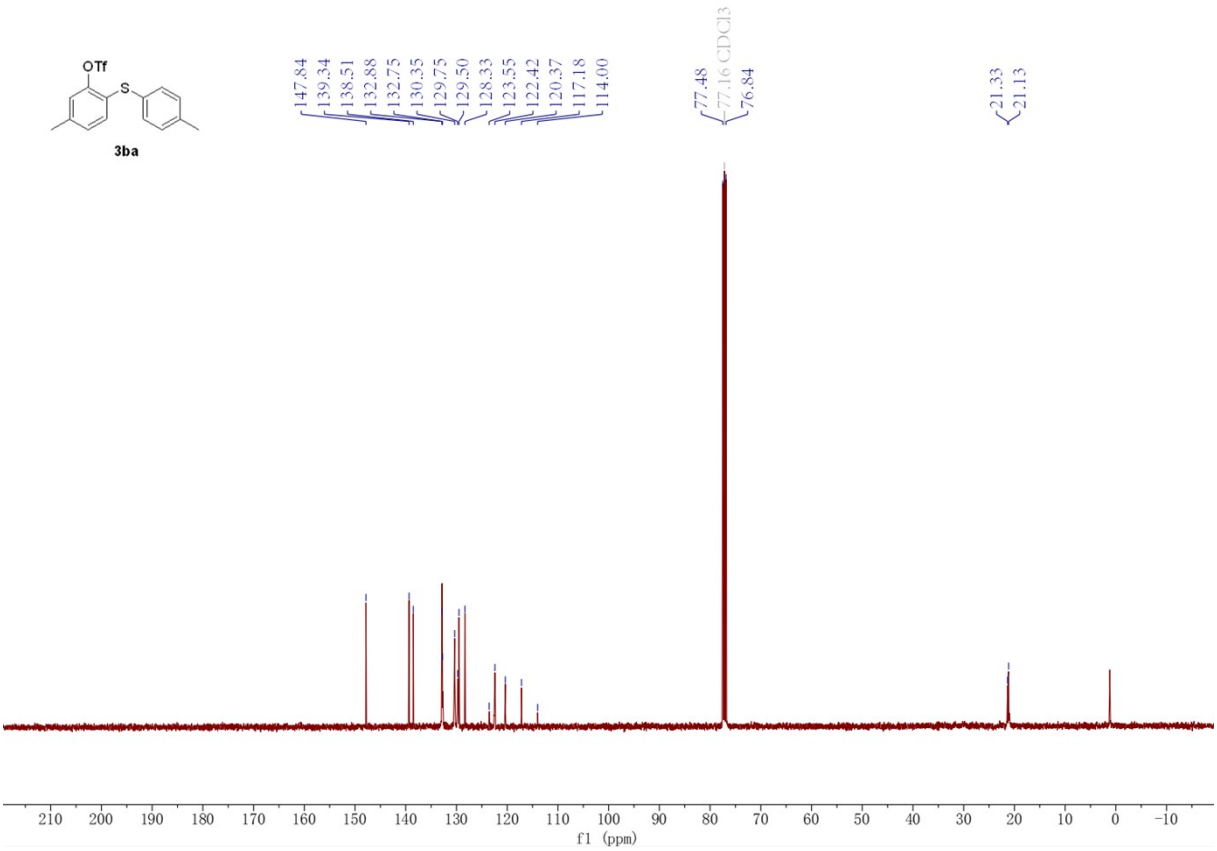
^{19}F NMR spectrum of 3as (376 MHz, $CDCl_3$)



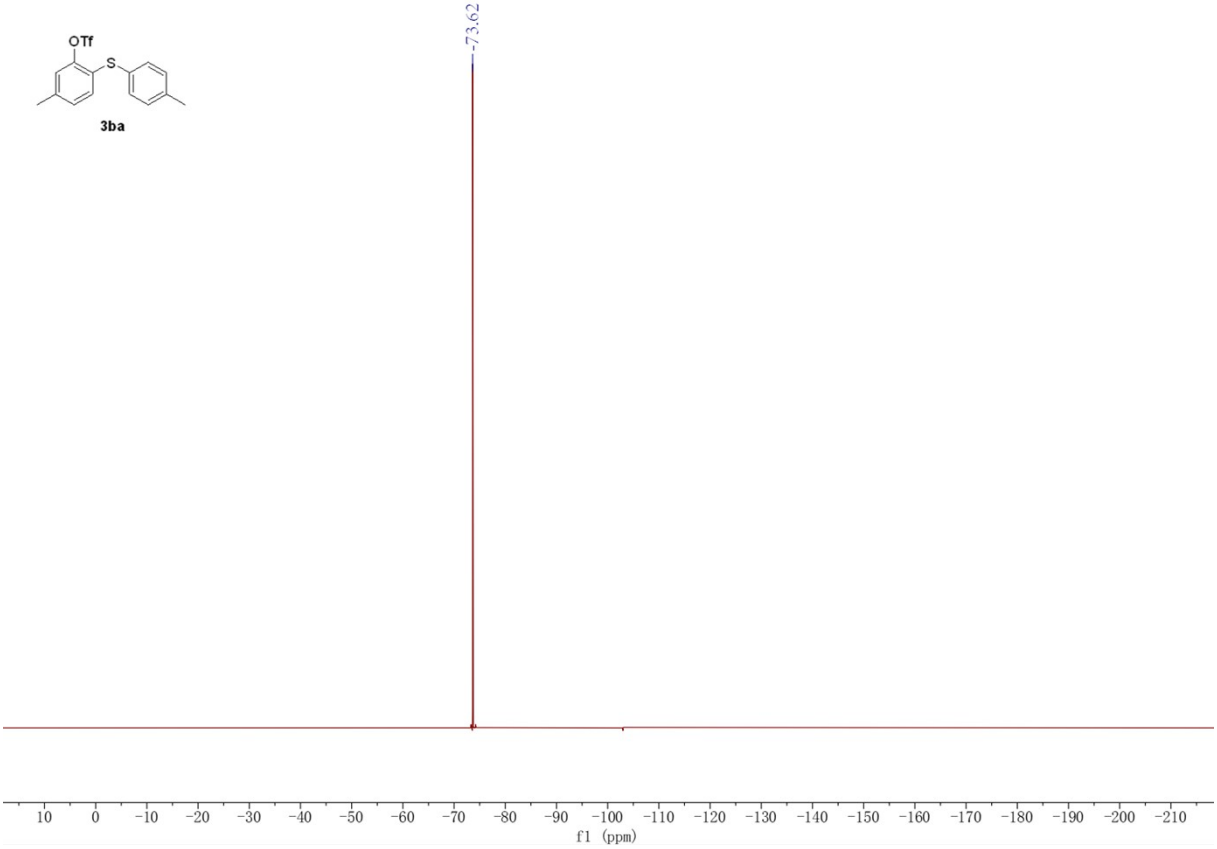
^{1}H NMR spectrum of 3ba (400 MHz, $CDCl_3$)



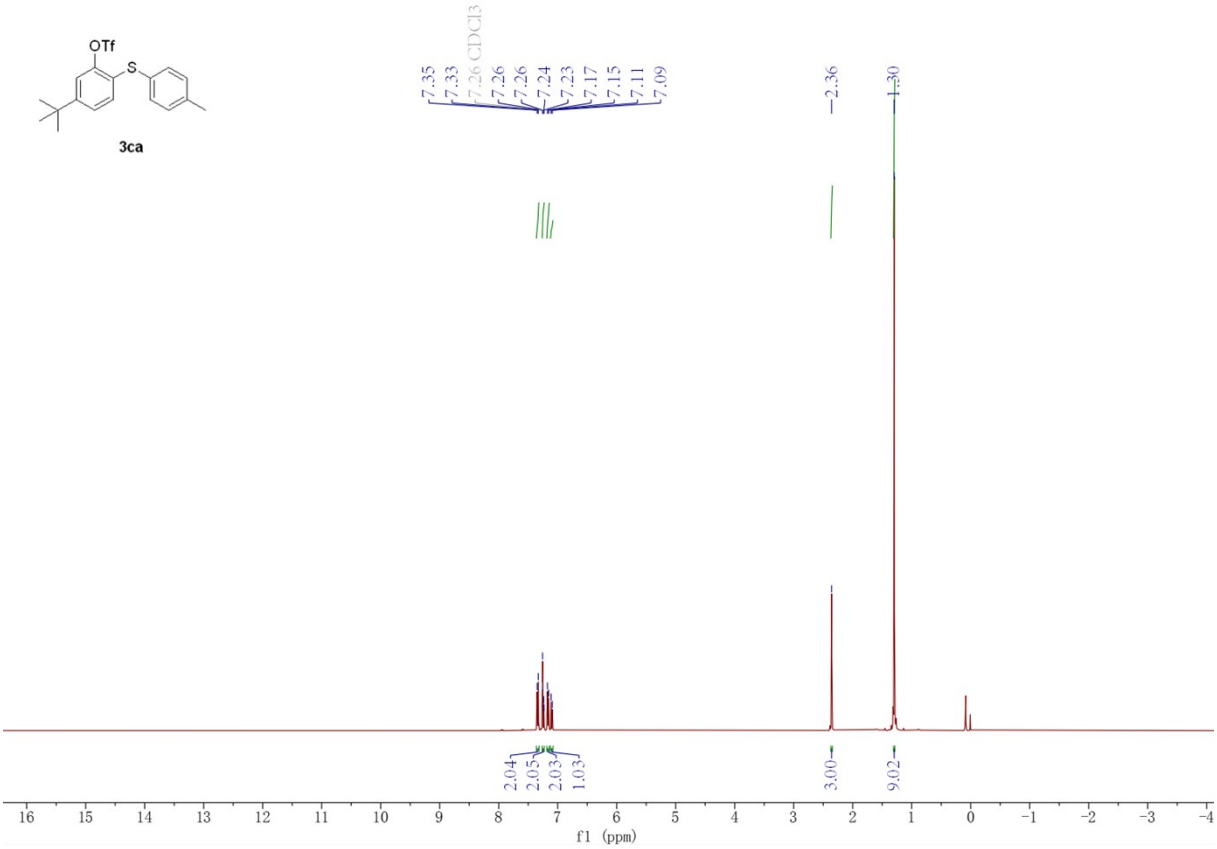
^{13}C NMR spectrum of 3ba (101 MHz, $CDCl_3$)



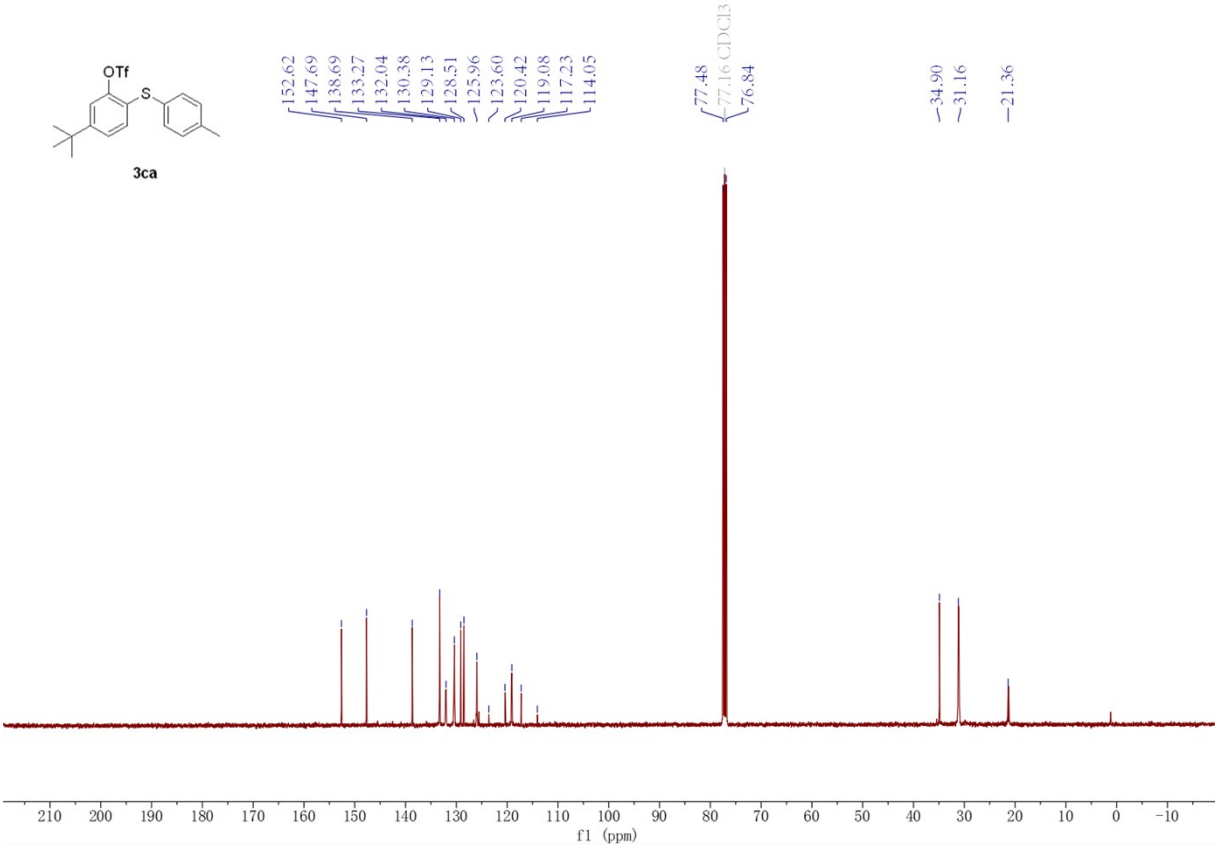
^{19}F NMR spectrum of 3ba (376 MHz, $CDCl_3$)



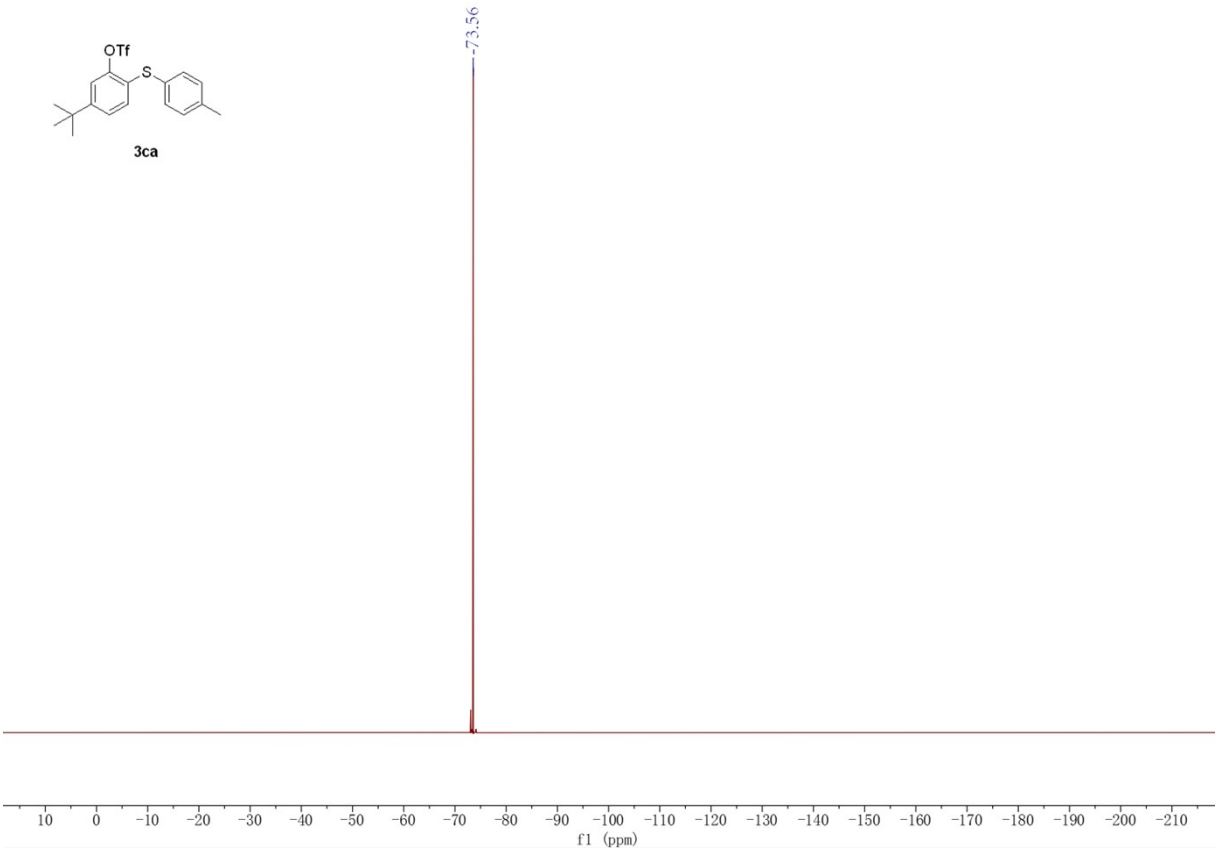
^{1}H NMR spectrum of 3ca (400 MHz, $CDCl_3$)



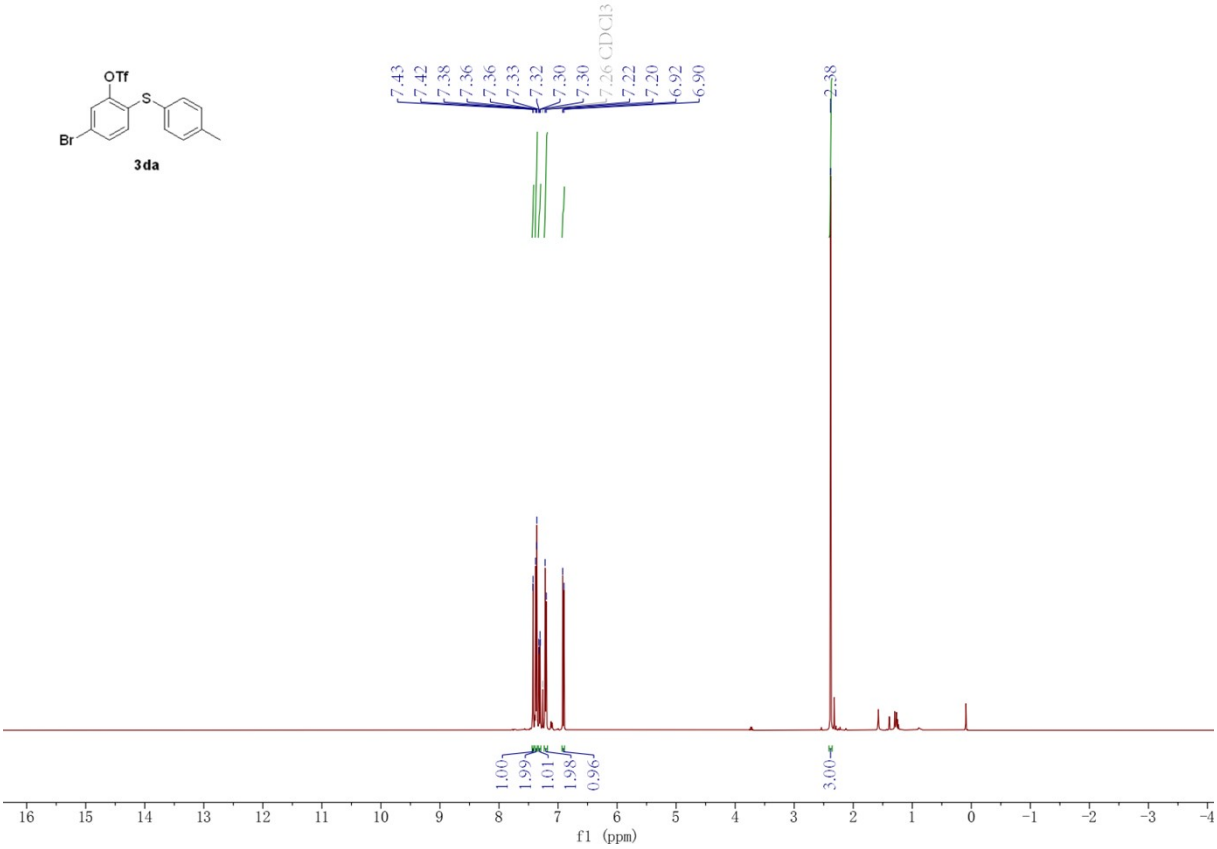
^{13}C NMR spectrum of 3ca (101 MHz, $CDCl_3$)



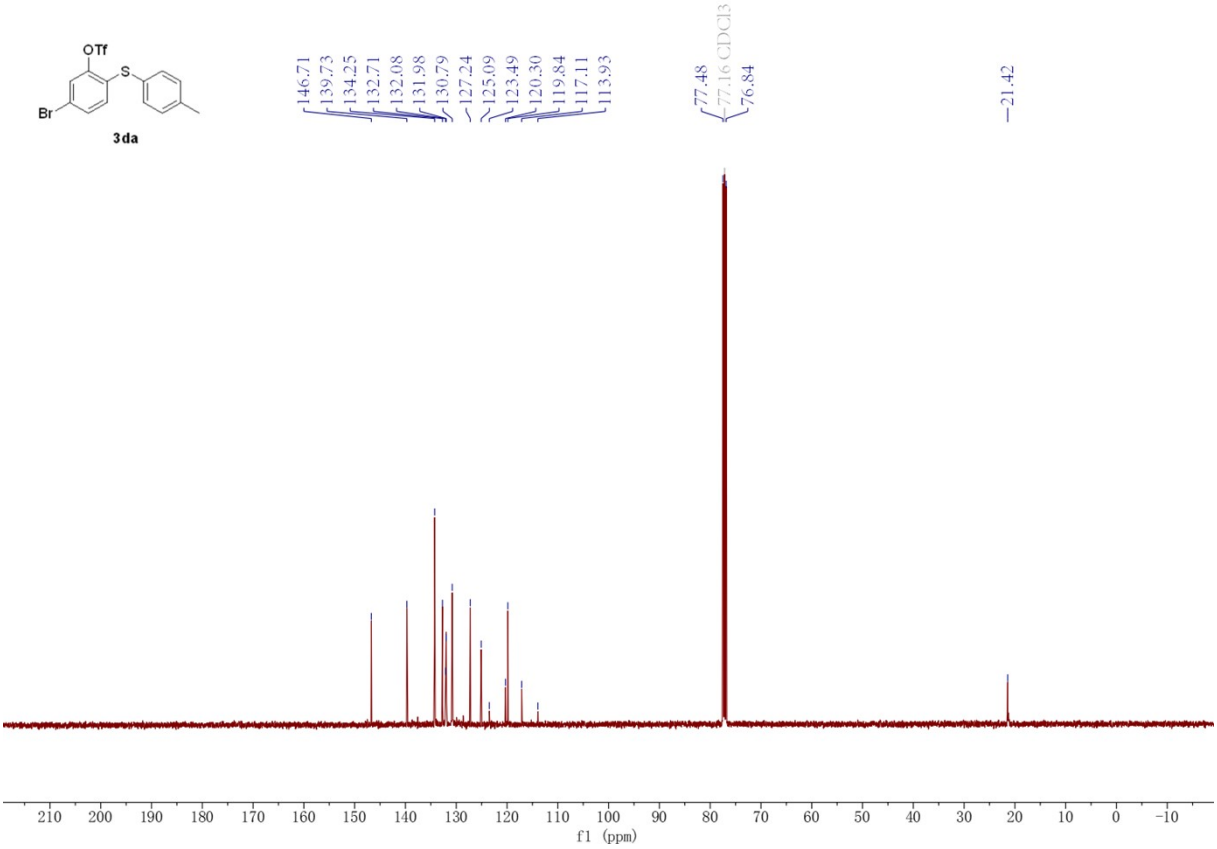
^{19}F NMR spectrum of 3ca (376 MHz, $CDCl_3$)



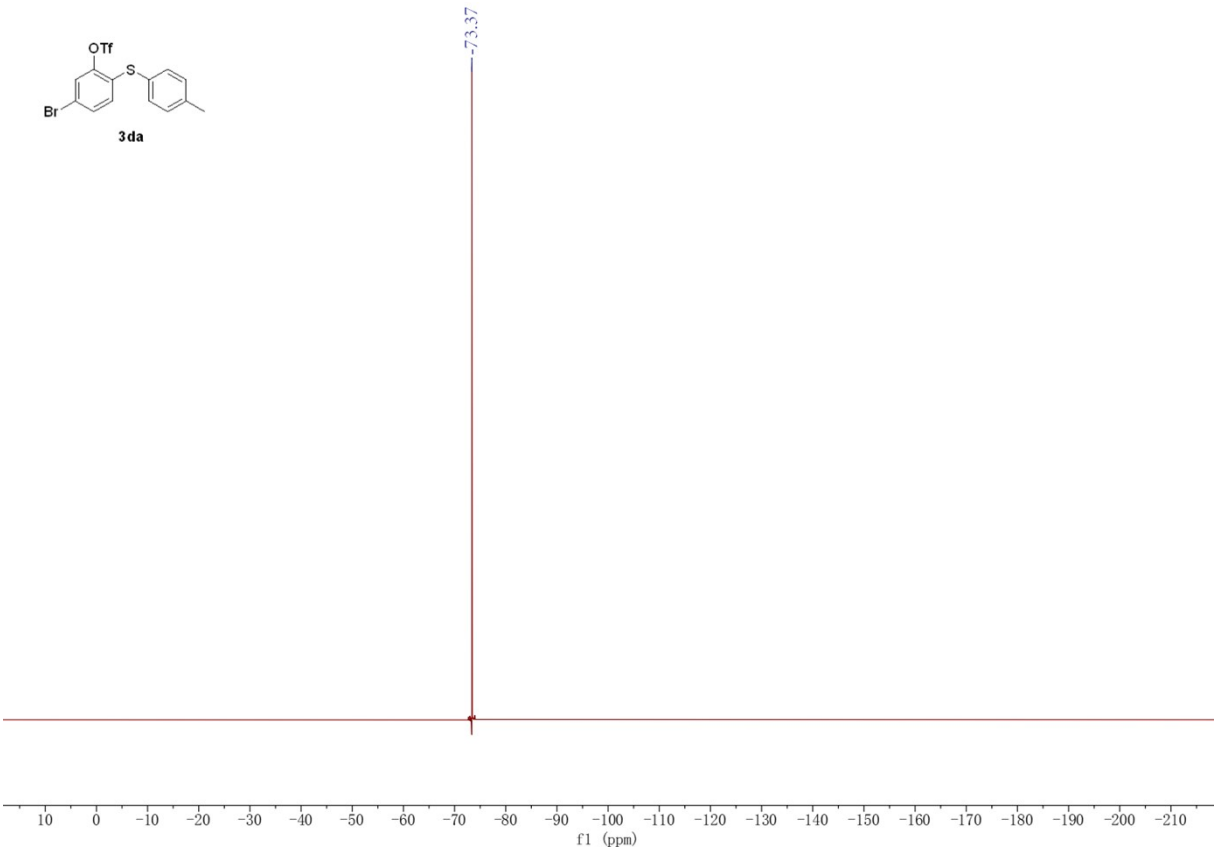
^{1}H NMR spectrum of 3da (400 MHz, $CDCl_3$)



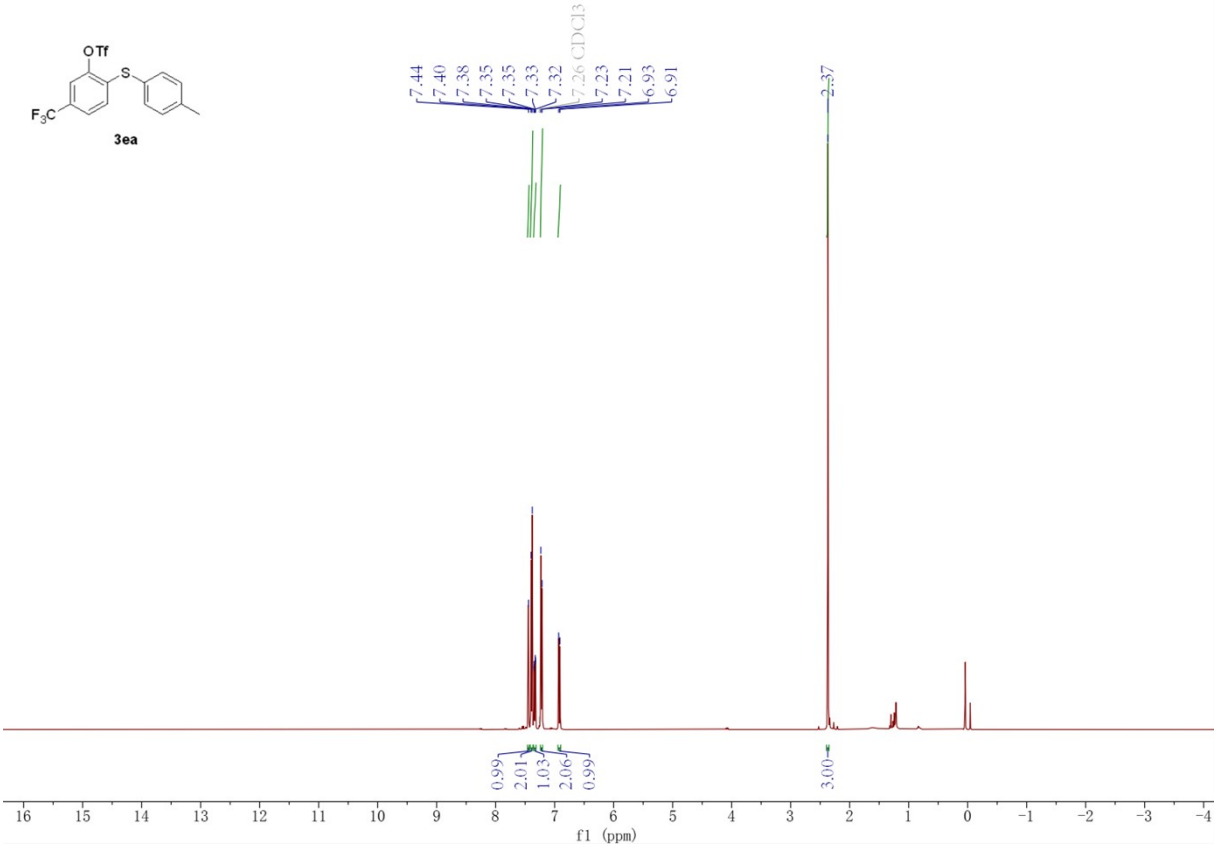
^{13}C NMR spectrum of 3da (101 MHz, $CDCl_3$)



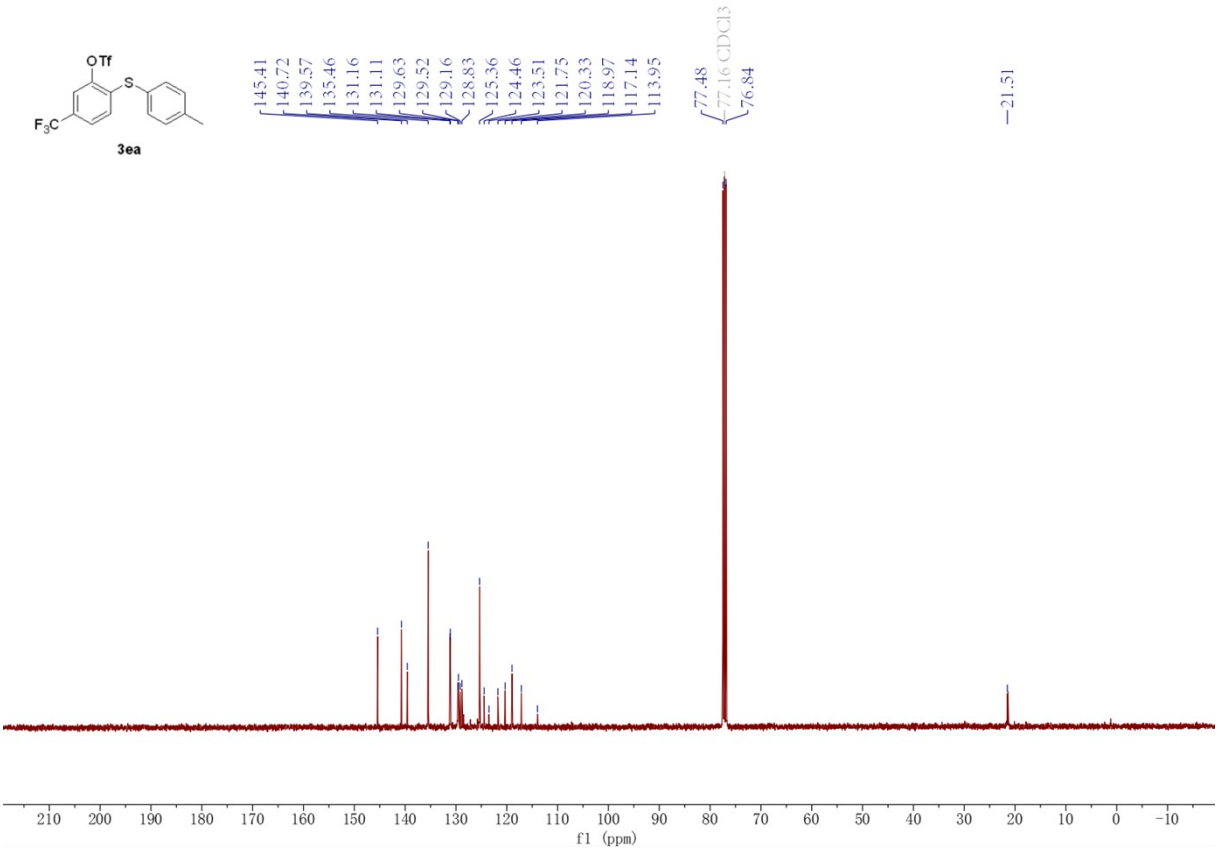
^{19}F NMR spectrum of 3da (376 MHz, $CDCl_3$)



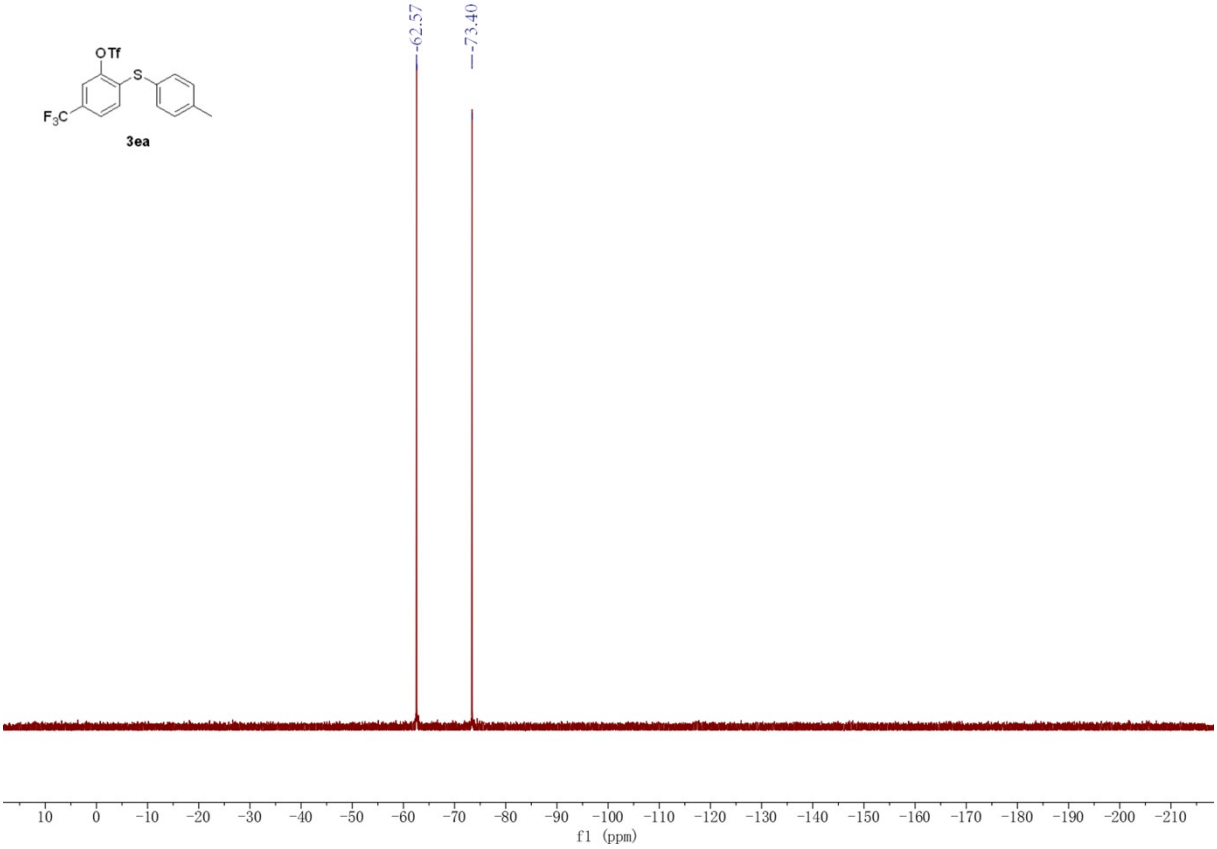
^{1}H NMR spectrum of 3ea (400 MHz, $CDCl_3$)



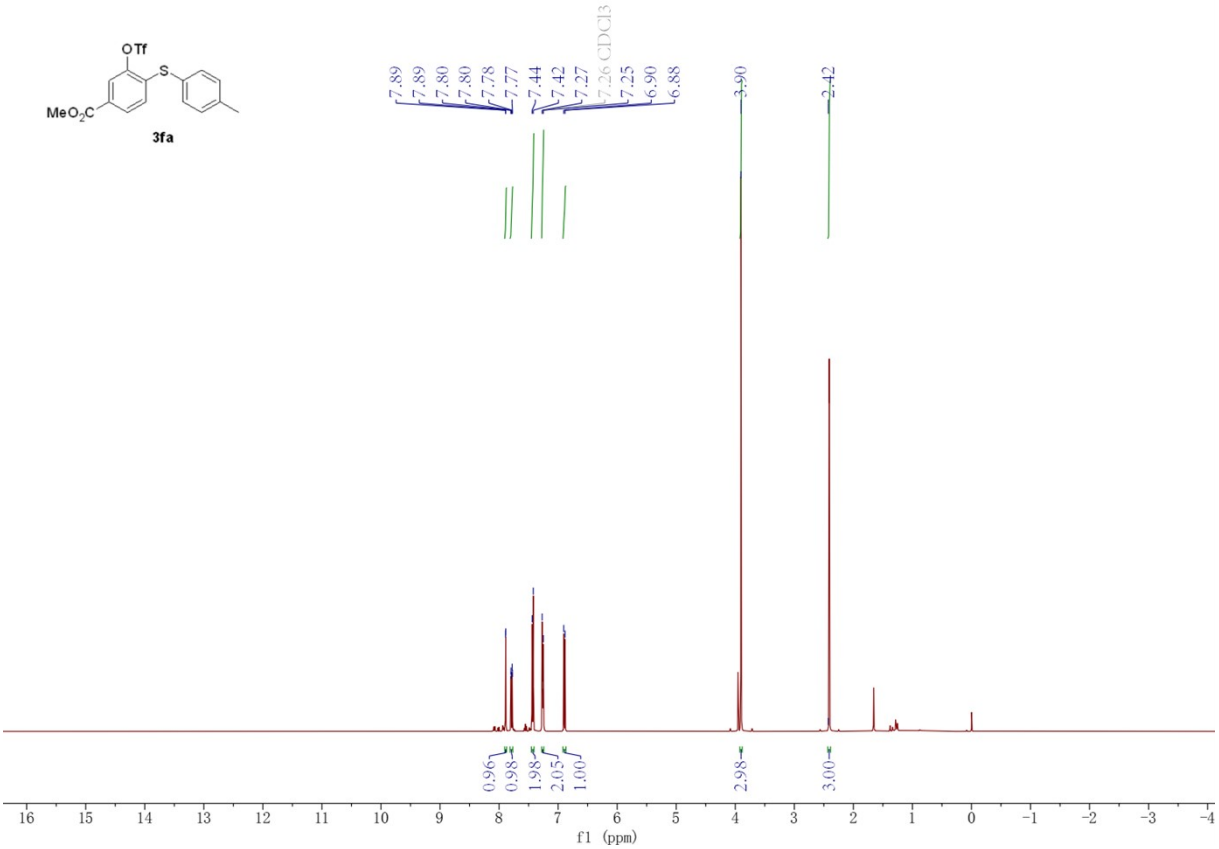
^{13}C NMR spectrum of 3ea (101 MHz, $CDCl_3$)



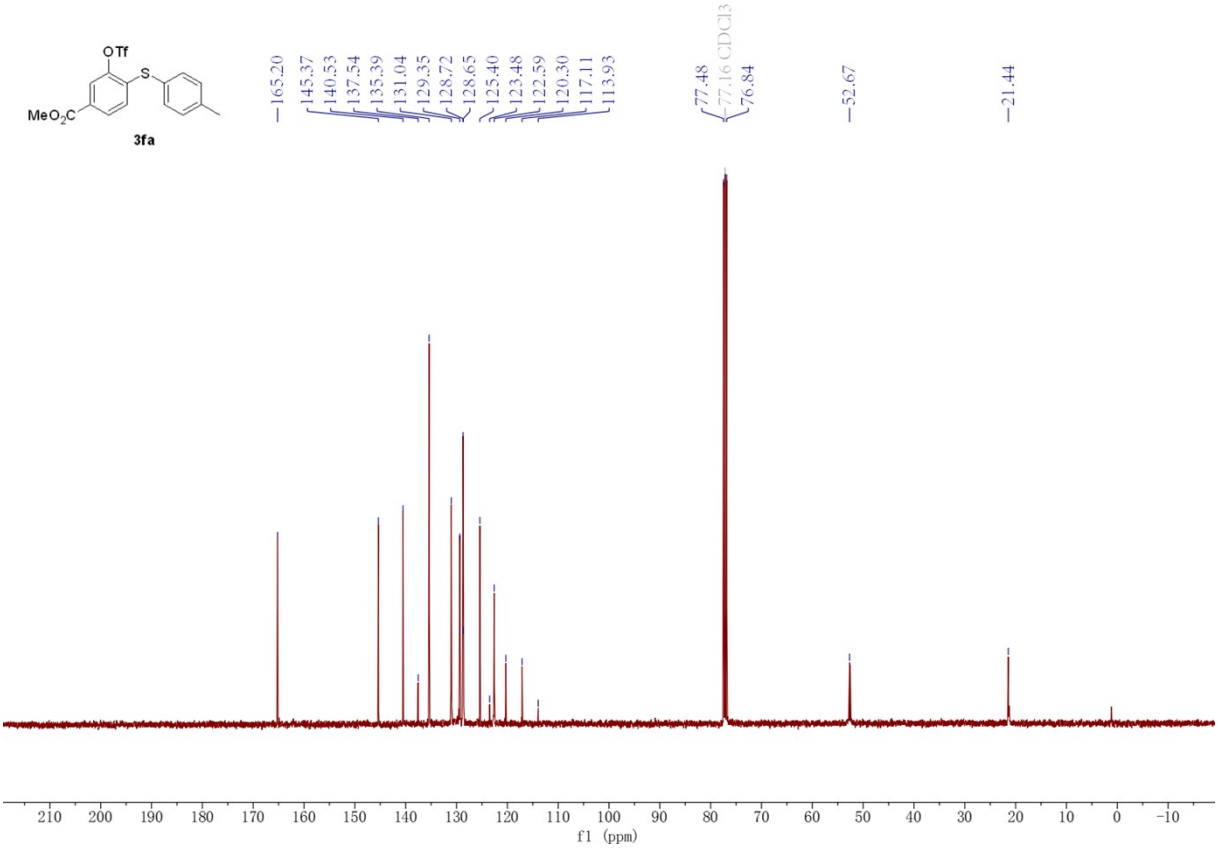
^{19}F NMR spectrum of 3ea (376 MHz, $CDCl_3$)



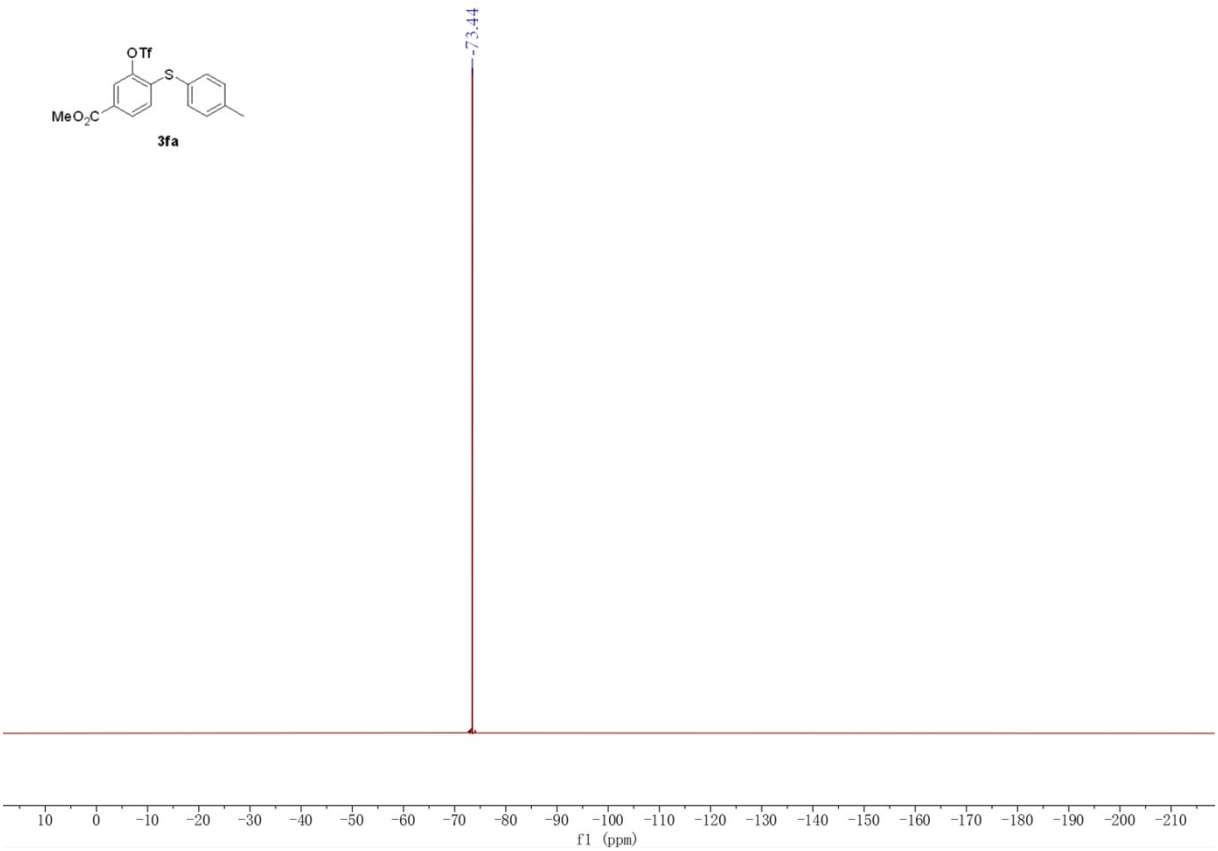
^{1}H NMR spectrum of 3fa (400 MHz, $CDCl_3$)



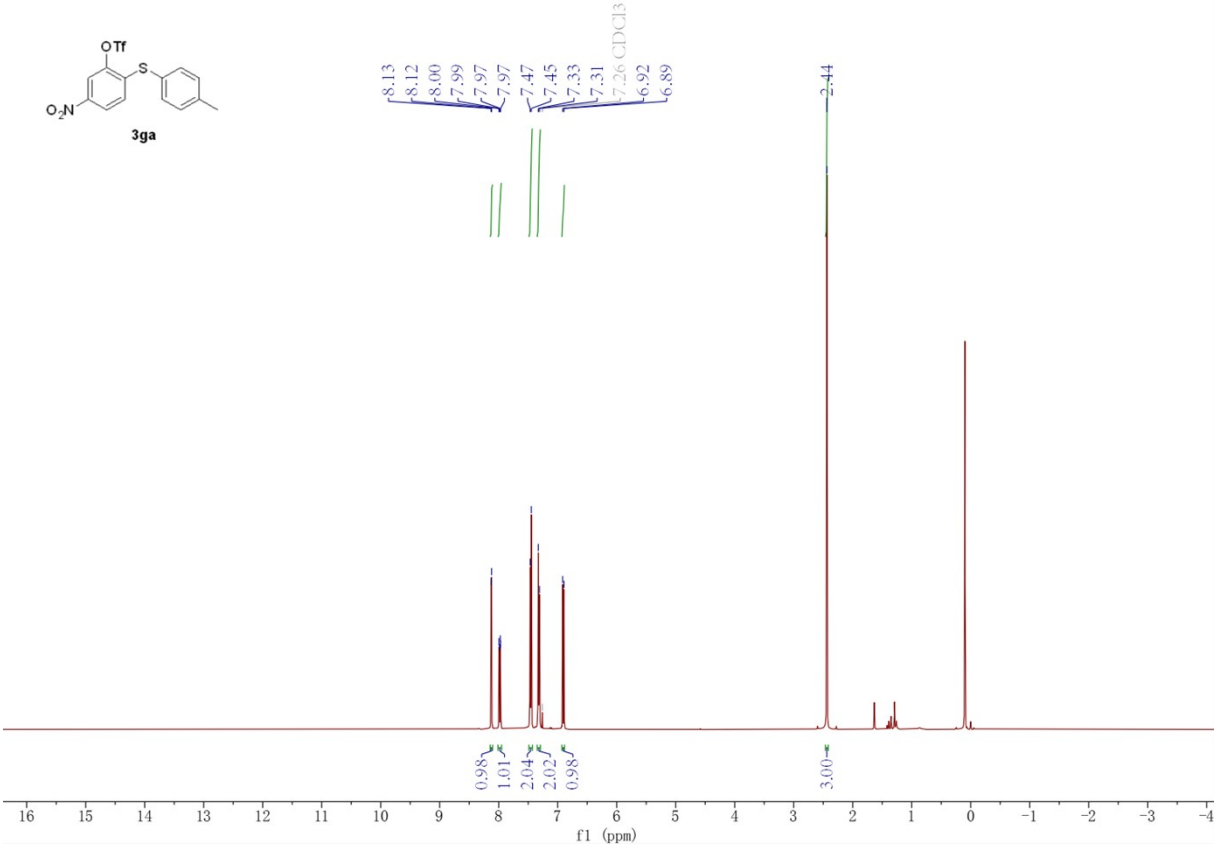
^{13}C NMR spectrum of 3fa (101 MHz, $CDCl_3$)



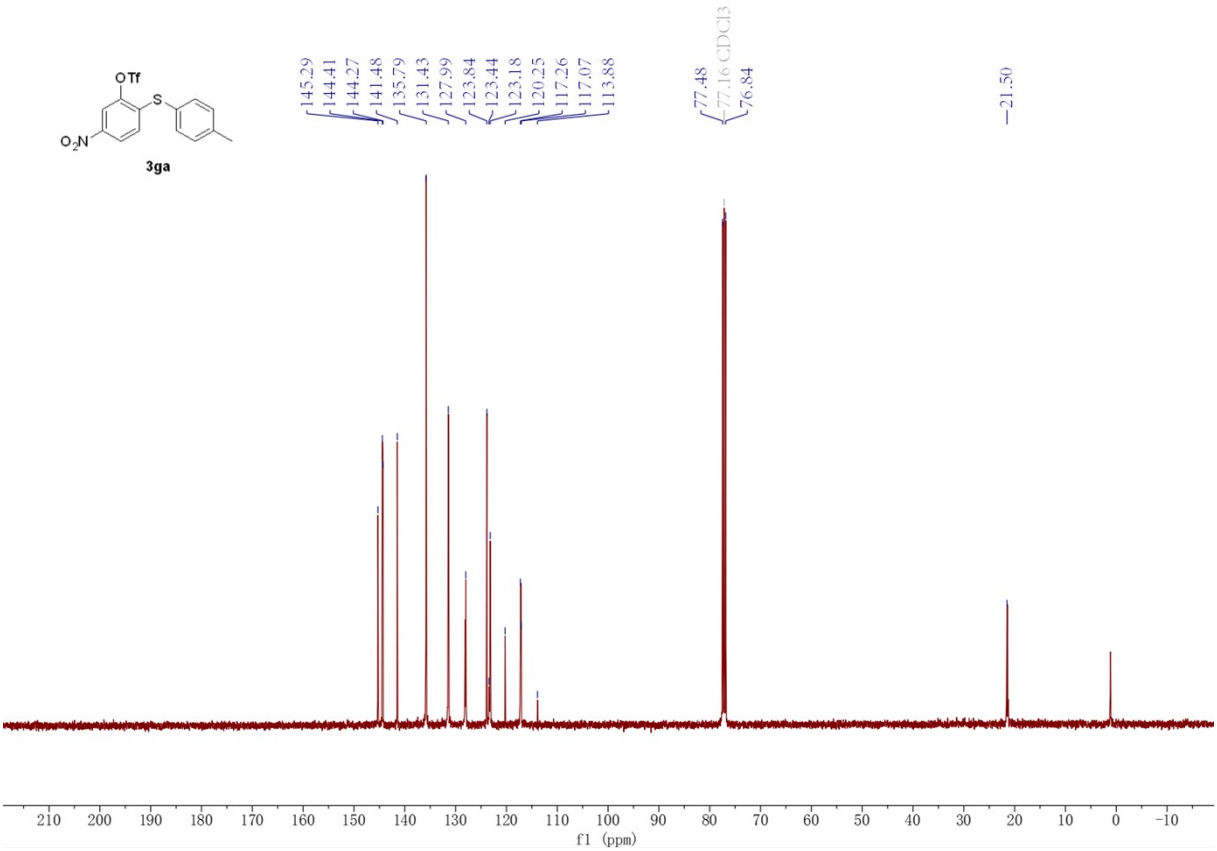
^{19}F NMR spectrum of 3fa (376 MHz, $CDCl_3$)



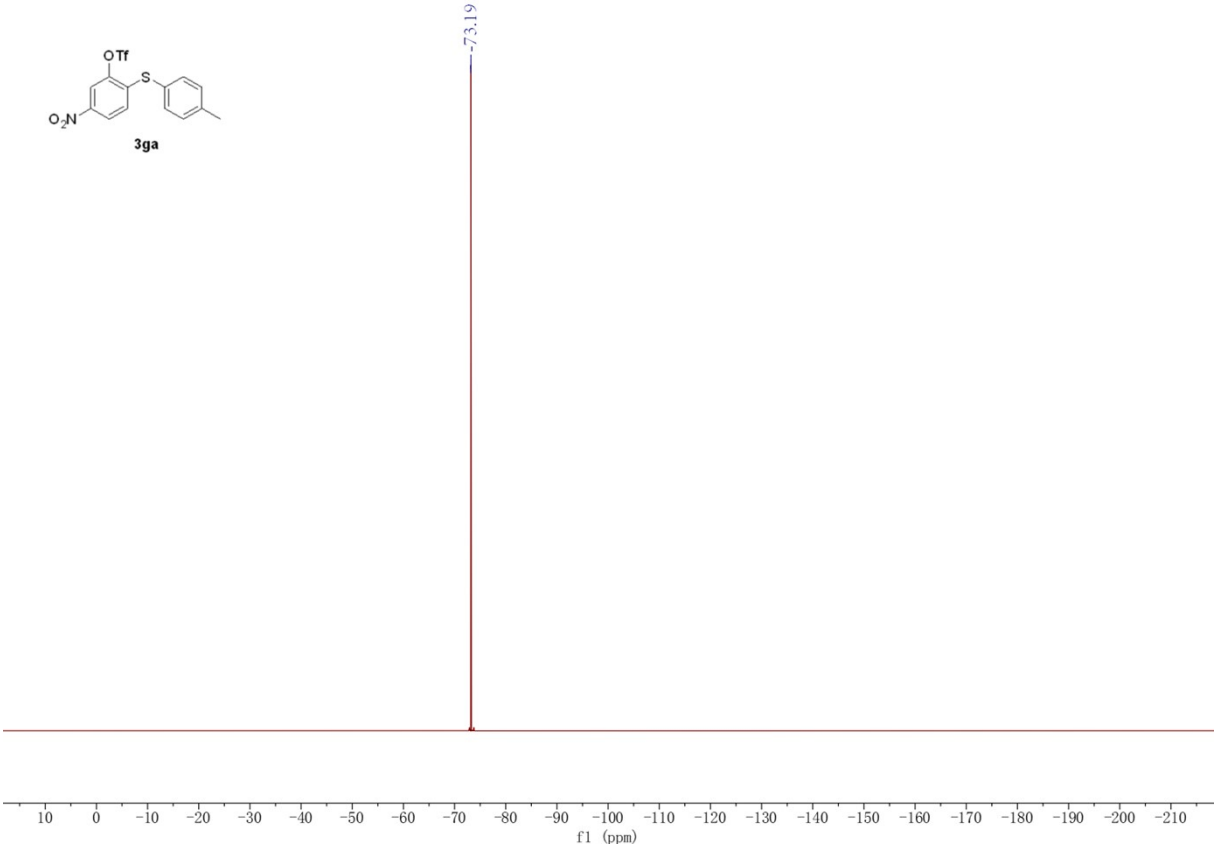
^{1}H NMR spectrum of 3ga (400 MHz, $CDCl_3$)



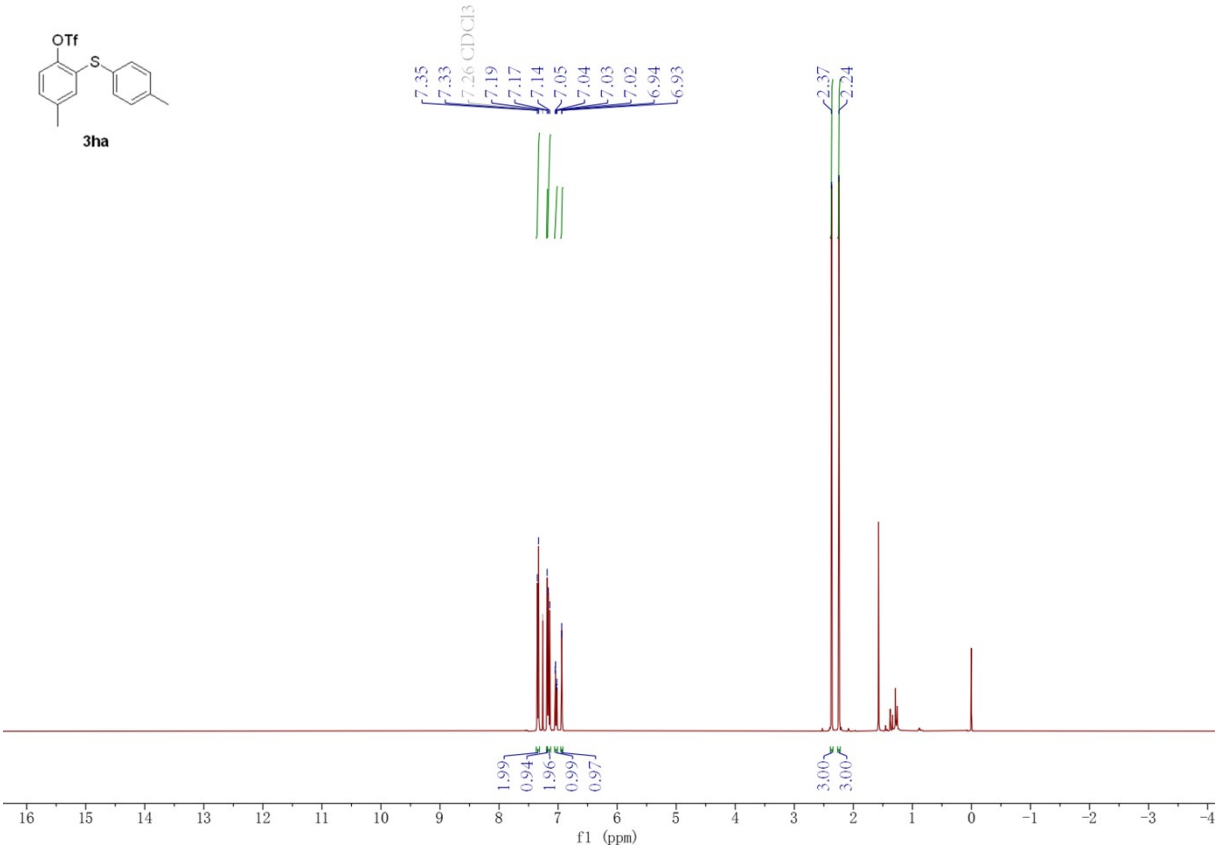
^{13}C NMR spectrum of 3ga (101 MHz, $CDCl_3$)



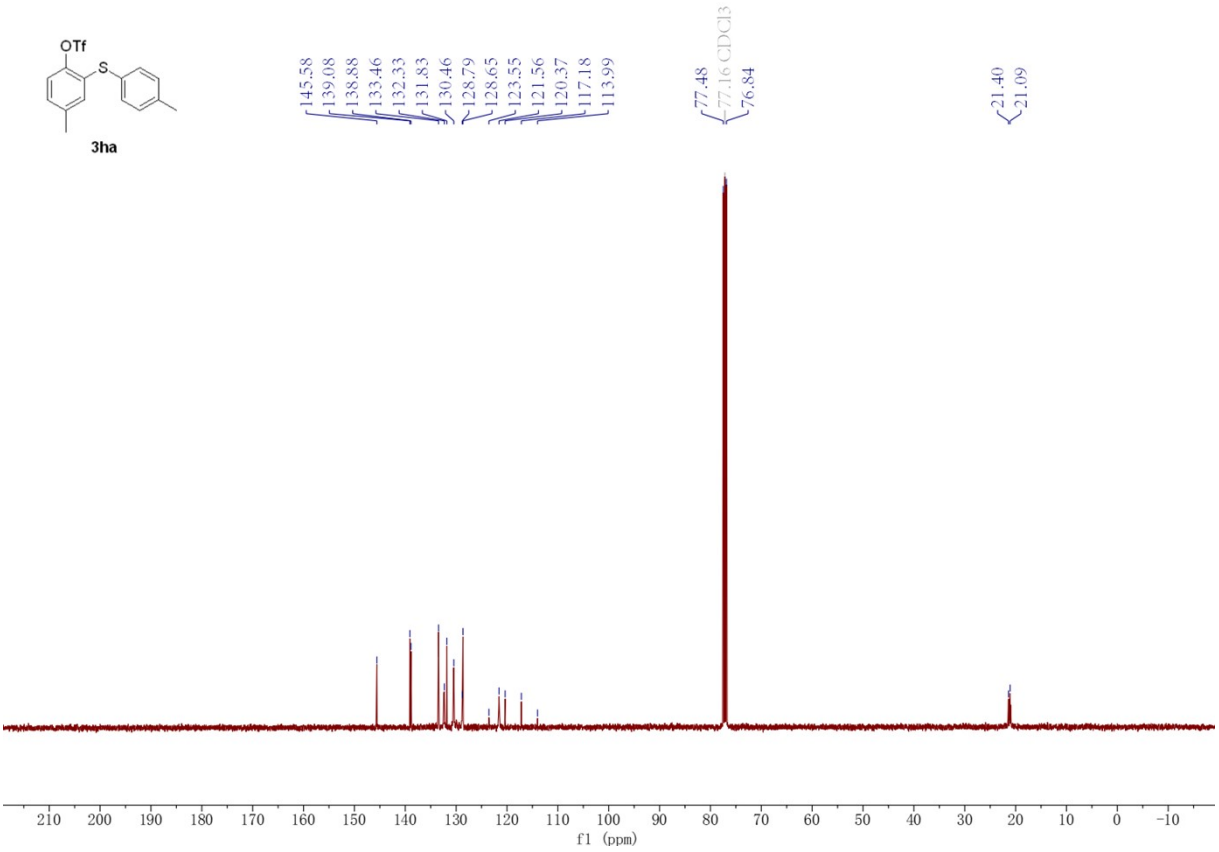
^{19}F NMR spectrum of 3ga (376 MHz, $CDCl_3$)



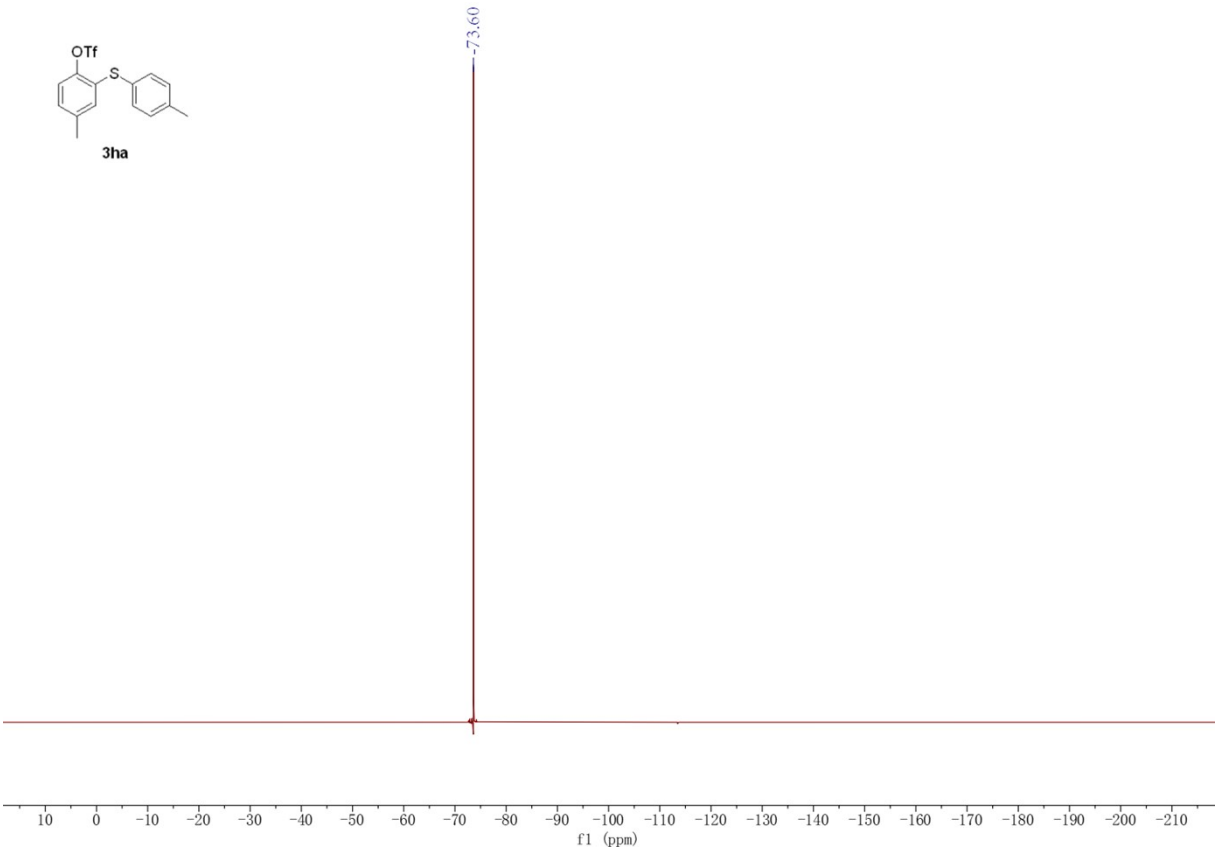
^{1}H NMR spectrum of 3ha (400 MHz, $CDCl_3$)



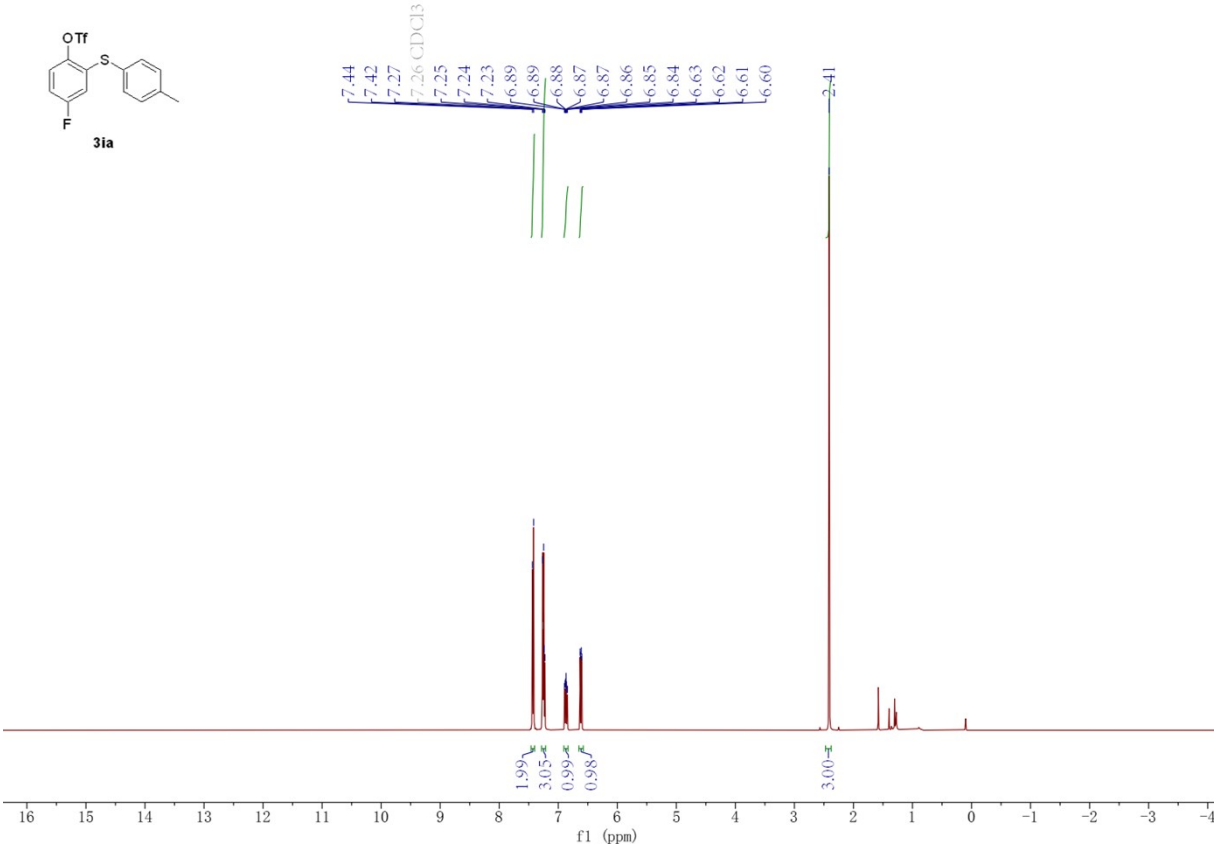
^{13}C NMR spectrum of 3ha (101 MHz, $CDCl_3$)



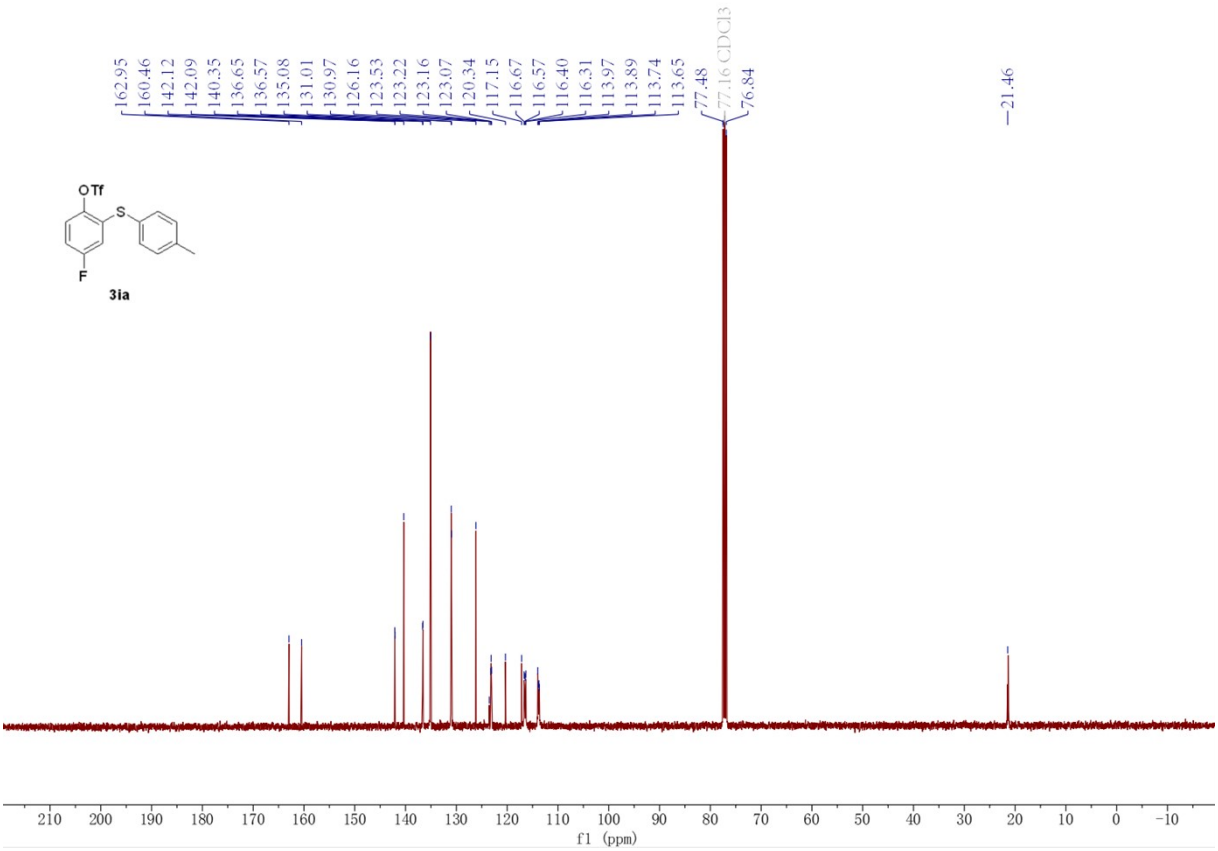
^{19}F NMR spectrum of 3ha (376 MHz, $CDCl_3$)



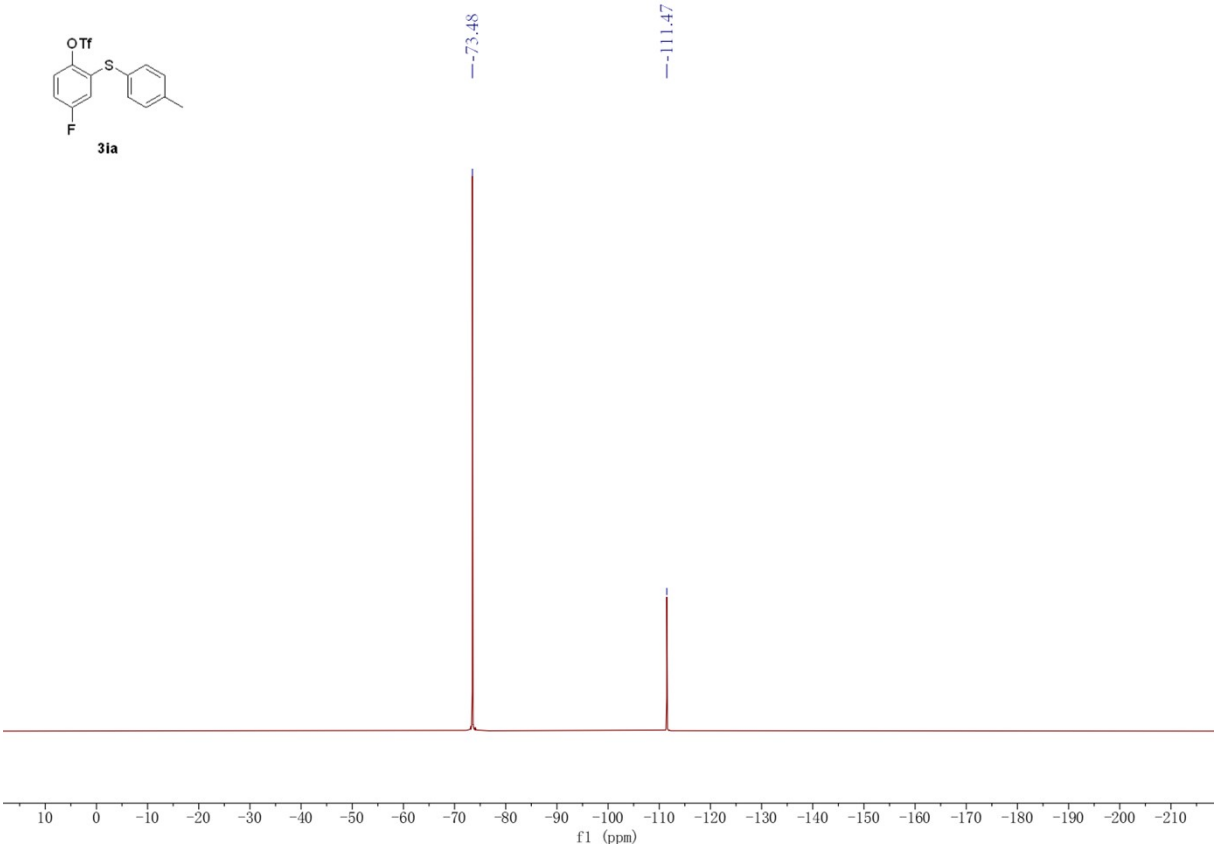
^{1}H NMR spectrum of 3ia (400 MHz, $CDCl_3$)



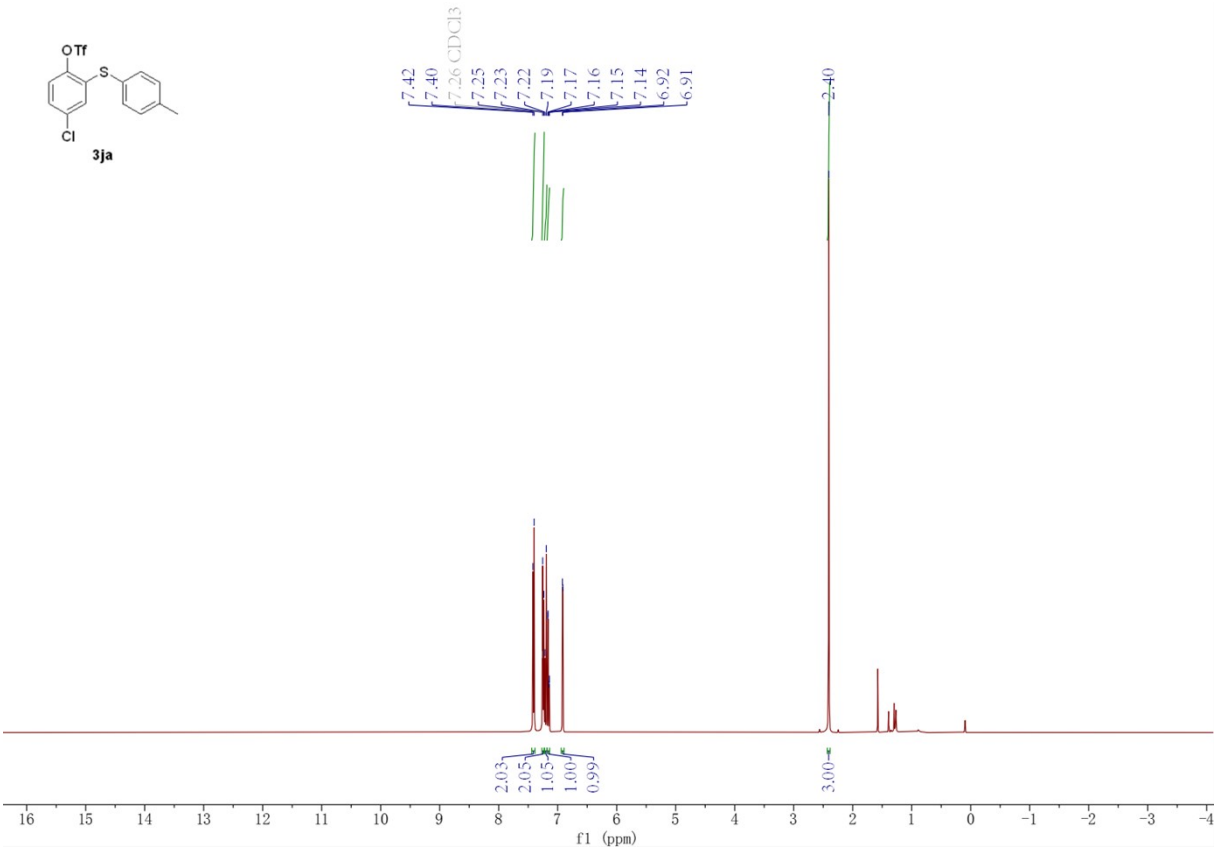
^{13}C NMR spectrum of 3ia (101 MHz, $CDCl_3$)



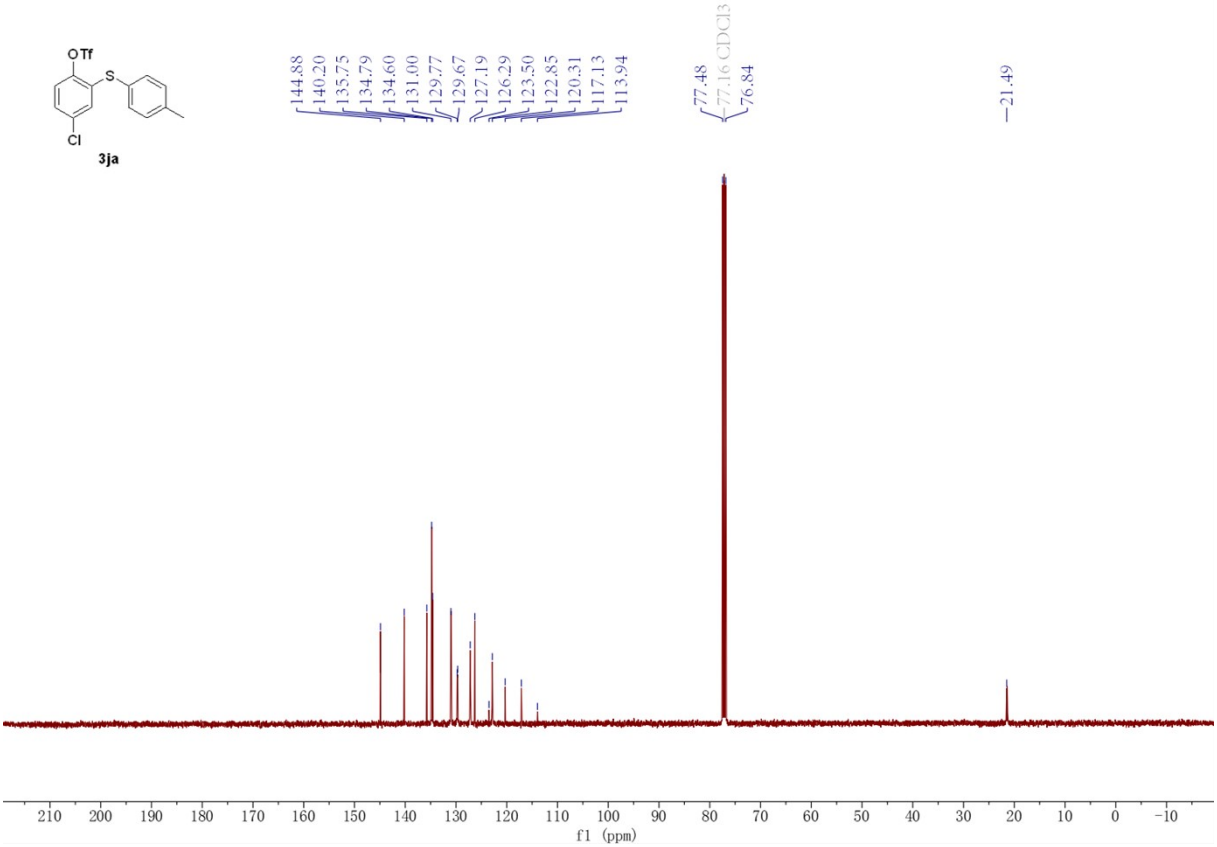
^{19}F NMR spectrum of 3ia (376 MHz, $CDCl_3$)



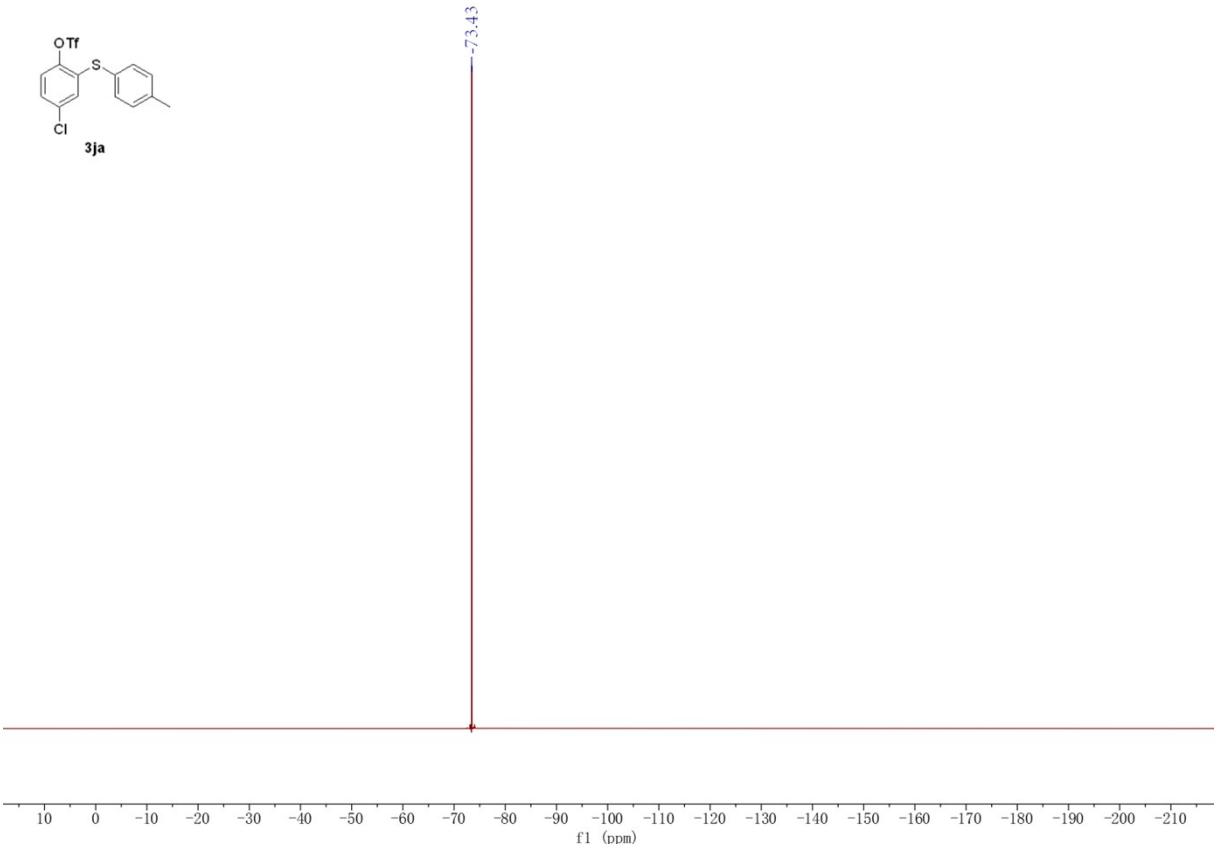
^{1}H NMR spectrum of 3ja (400 MHz, $CDCl_3$)



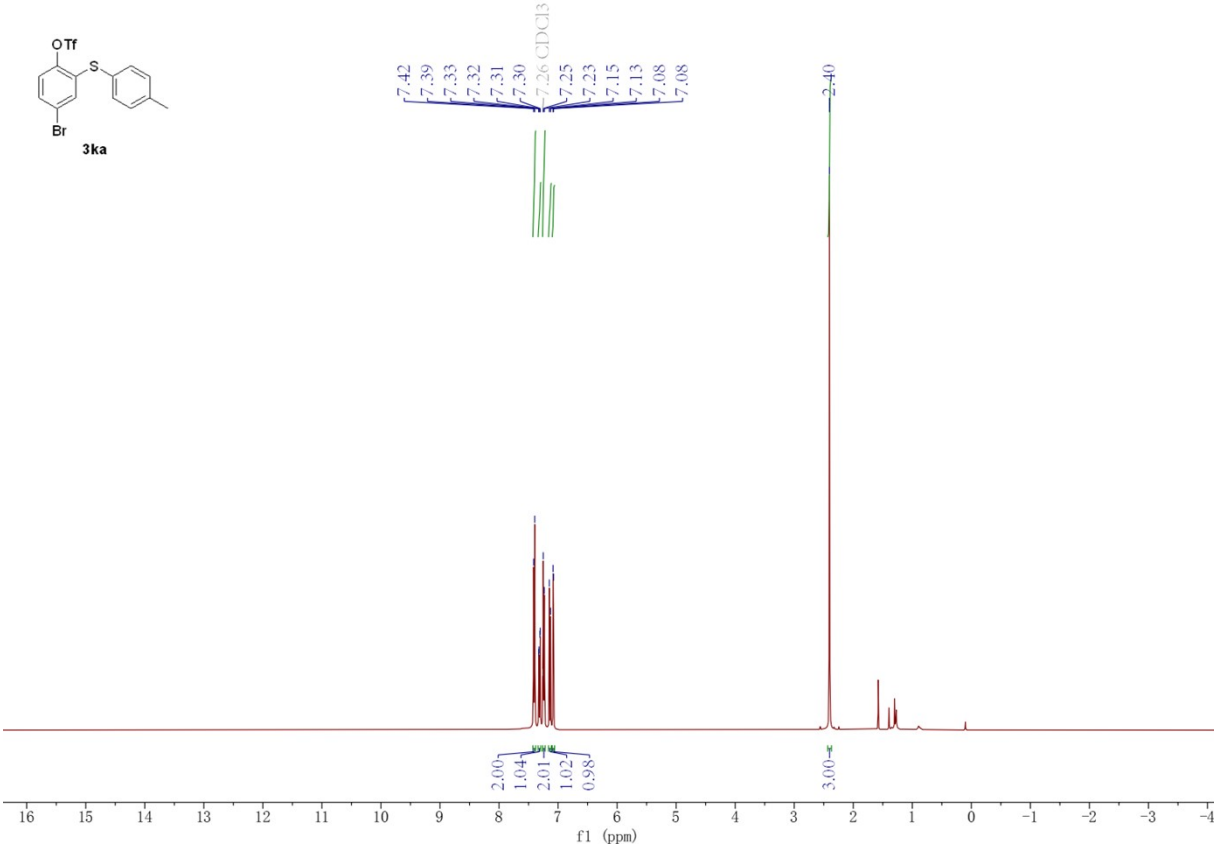
^{13}C NMR spectrum of 3ja (101 MHz, $CDCl_3$)



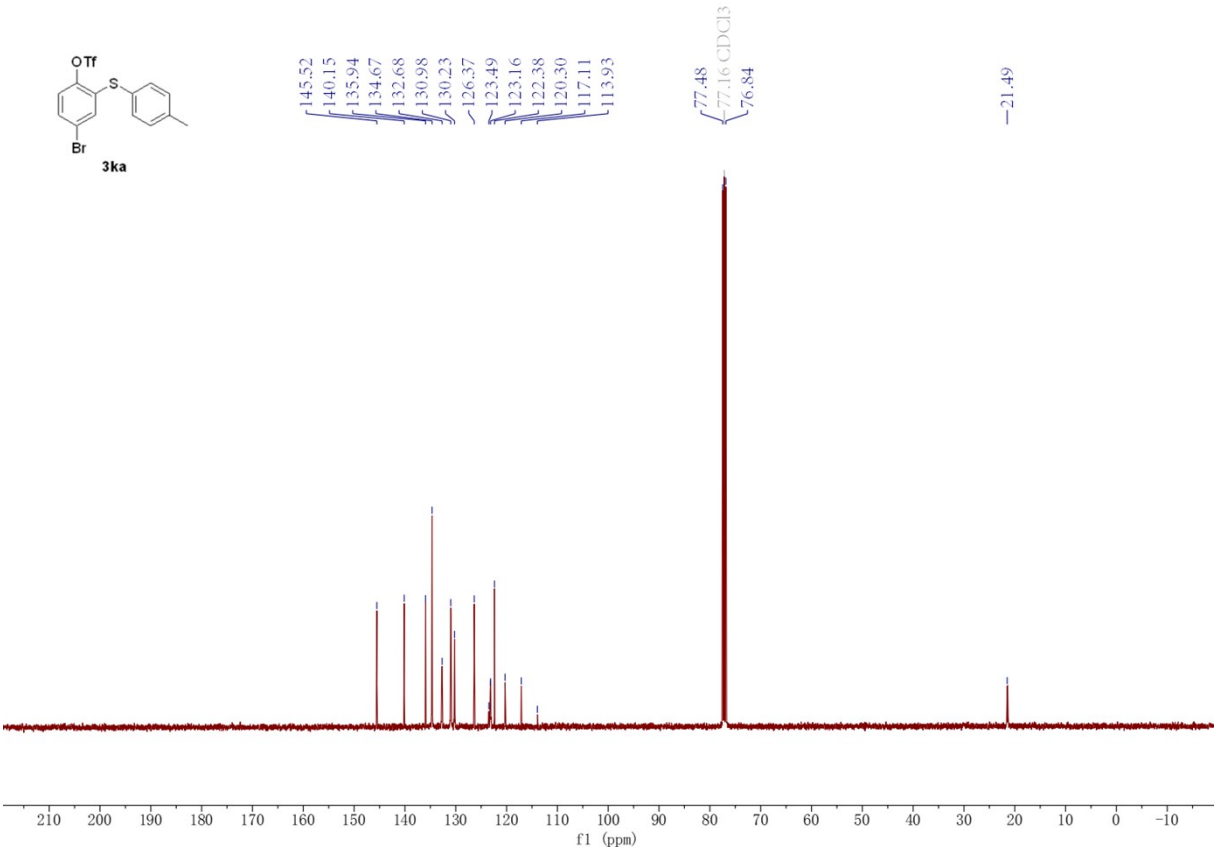
^{19}F NMR spectrum of 3ja (376 MHz, $CDCl_3$)



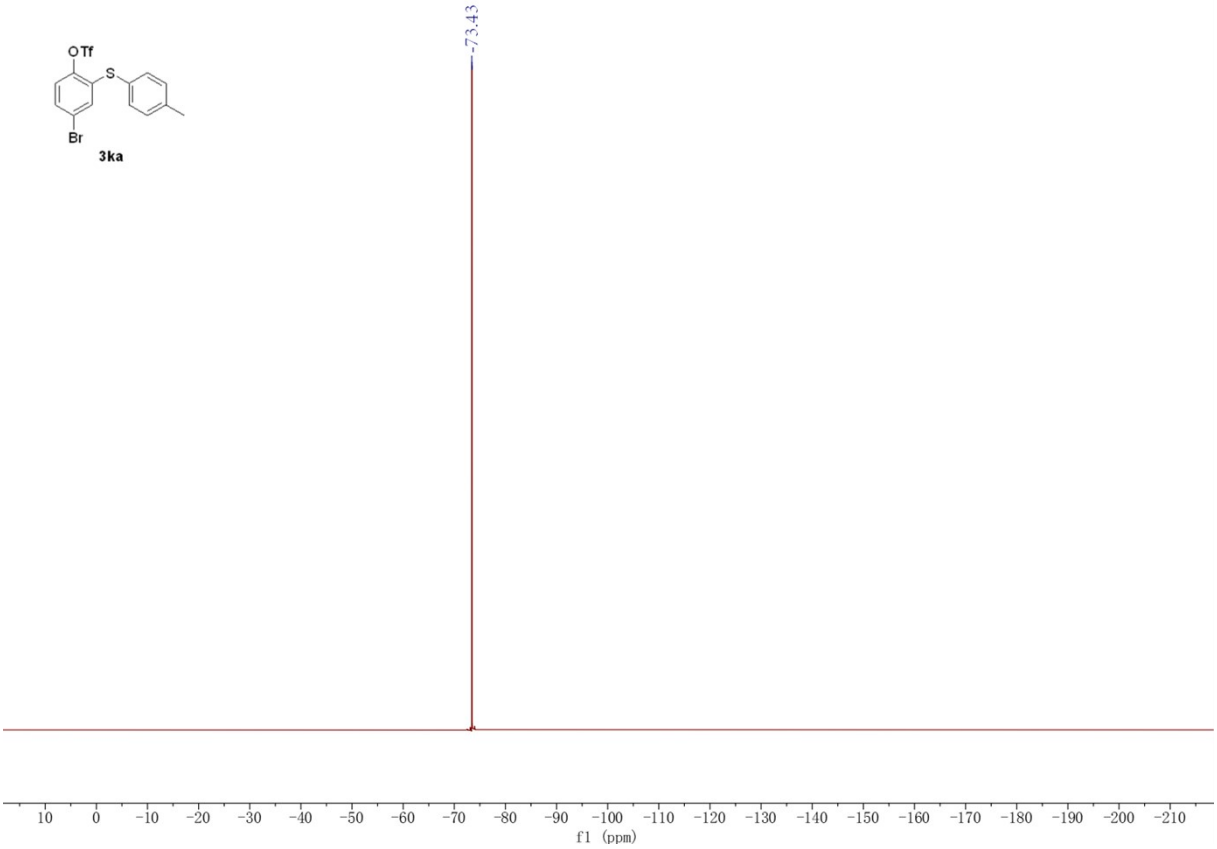
^{1}H NMR spectrum of 3ka (400 MHz, $CDCl_3$)



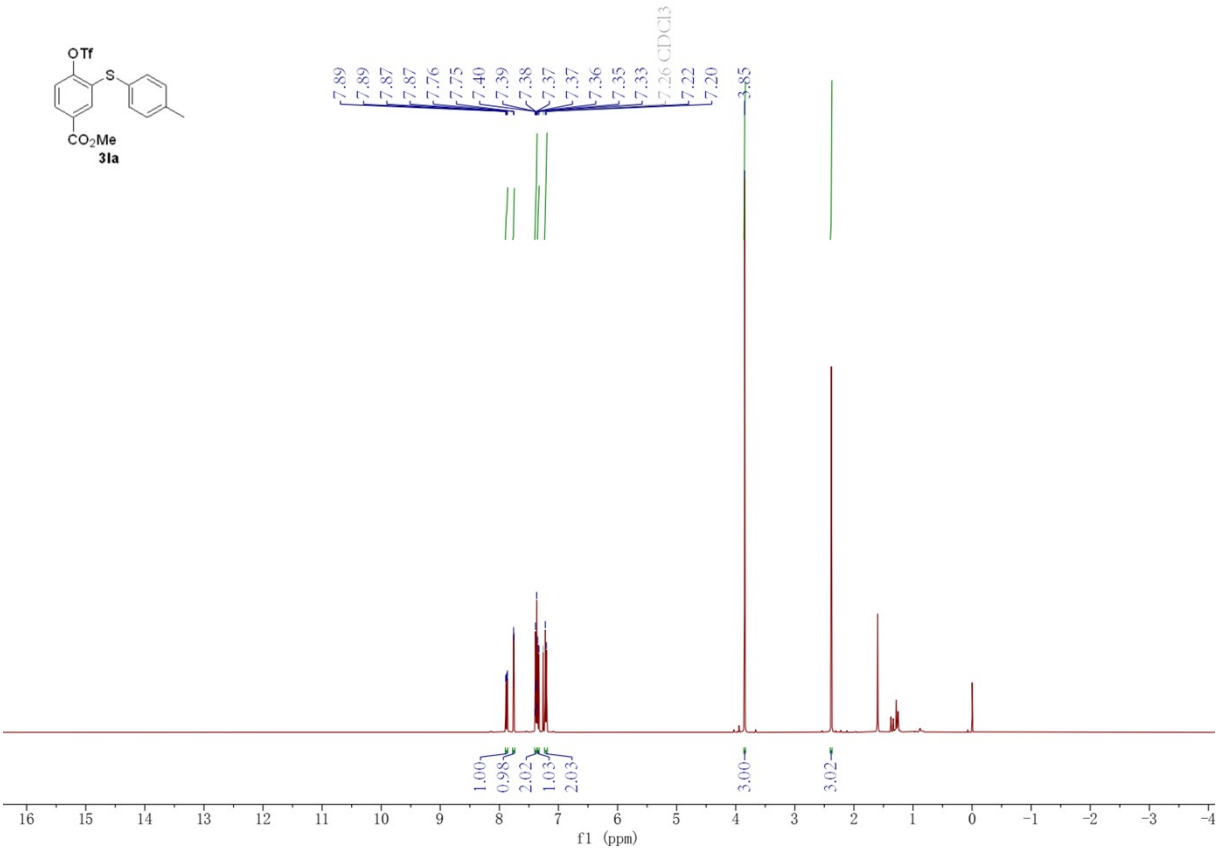
^{13}C NMR spectrum of 3ka (101 MHz, $CDCl_3$)



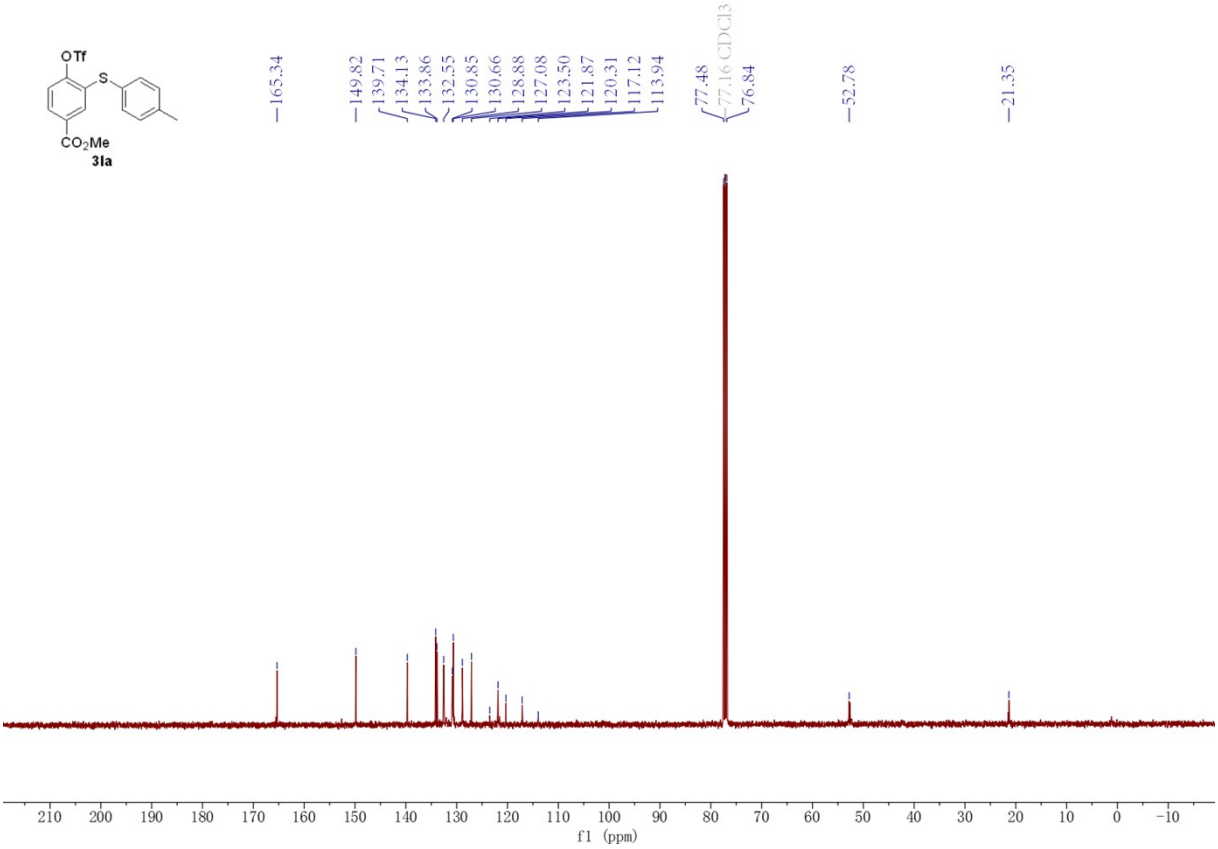
^{19}F NMR spectrum of 3ka (376 MHz, $CDCl_3$)



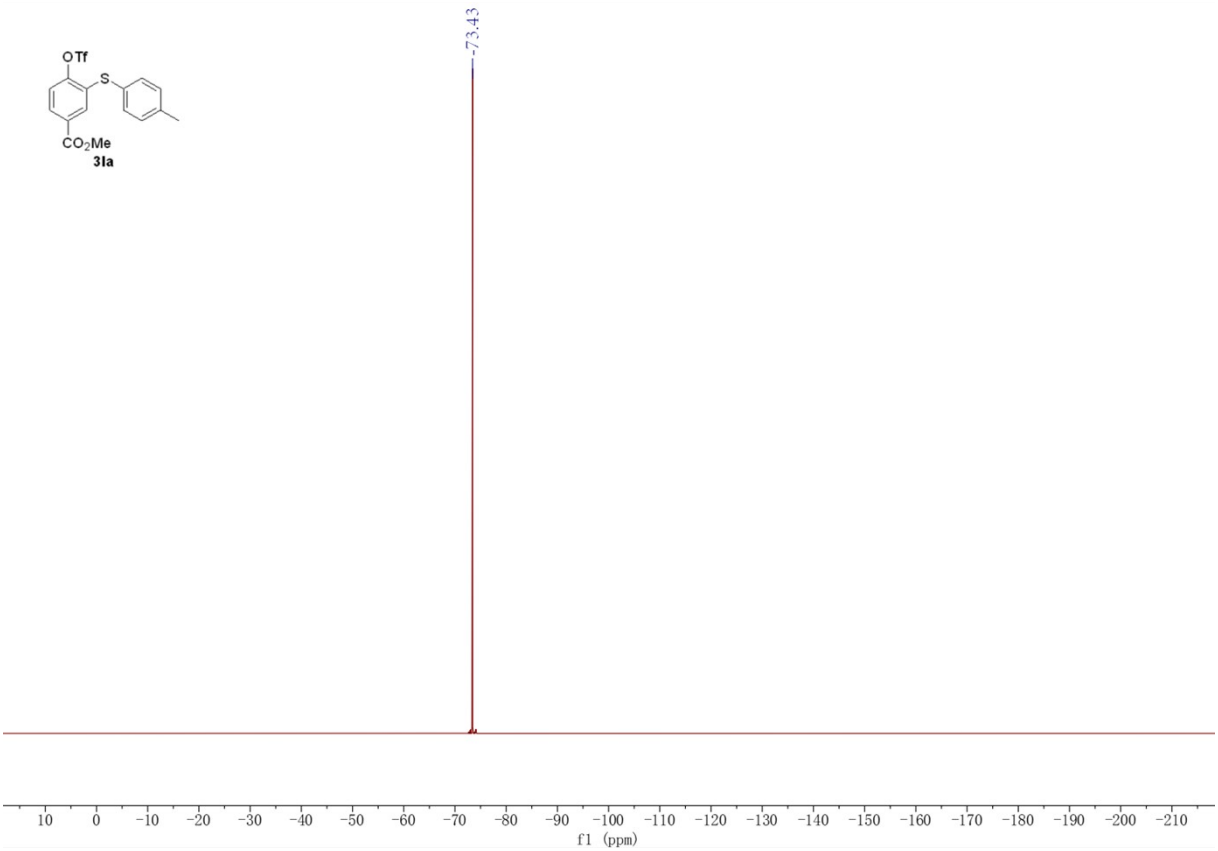
^{1}H NMR spectrum of 3la (400 MHz, $CDCl_3$)



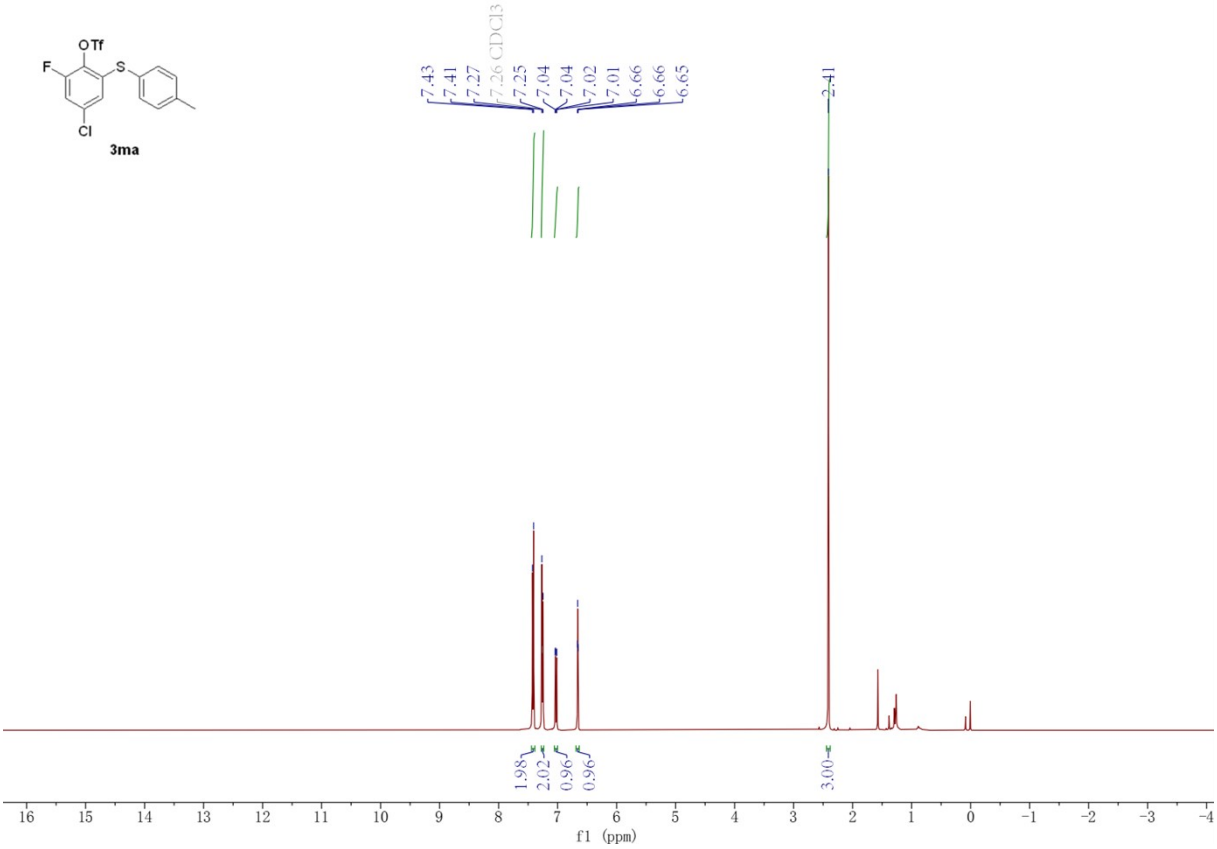
^{13}C NMR spectrum of 3la (101 MHz, $CDCl_3$)



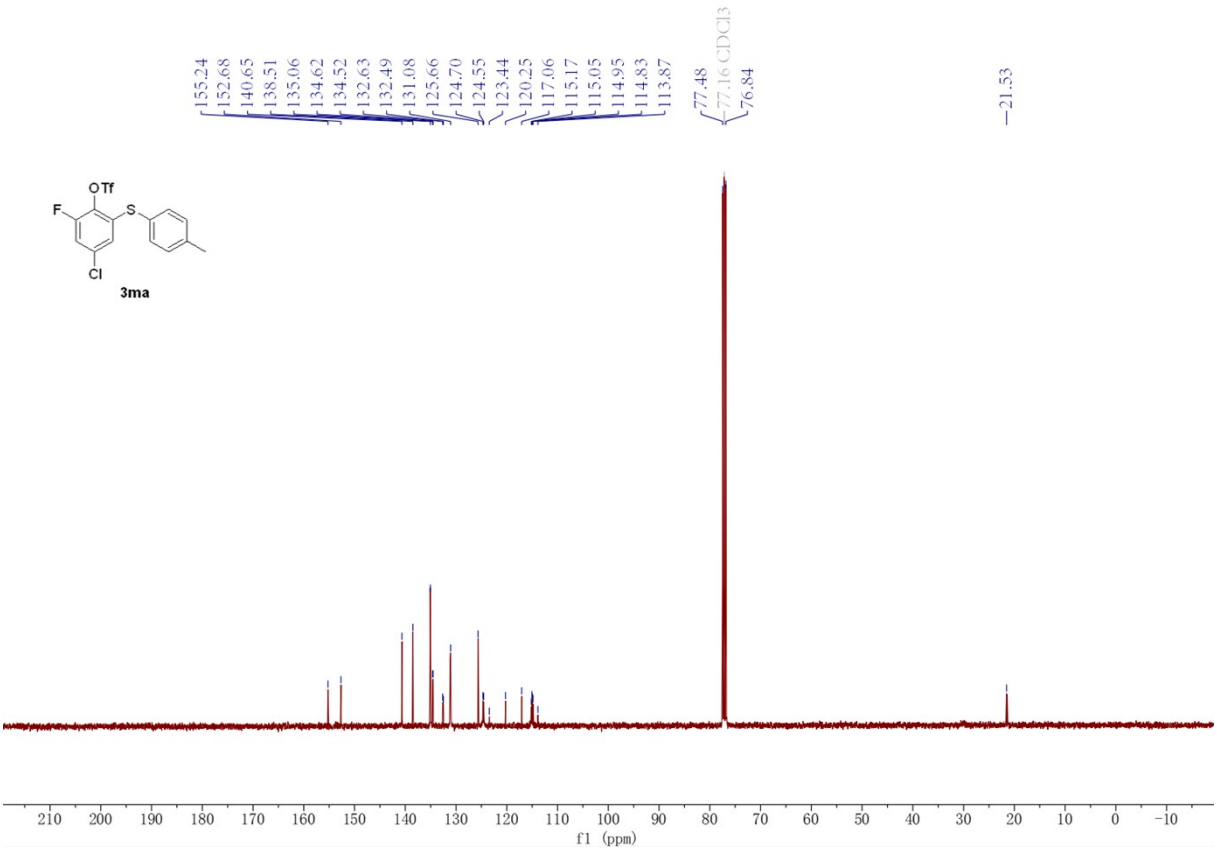
^{19}F NMR spectrum of 3la (376 MHz, $CDCl_3$)



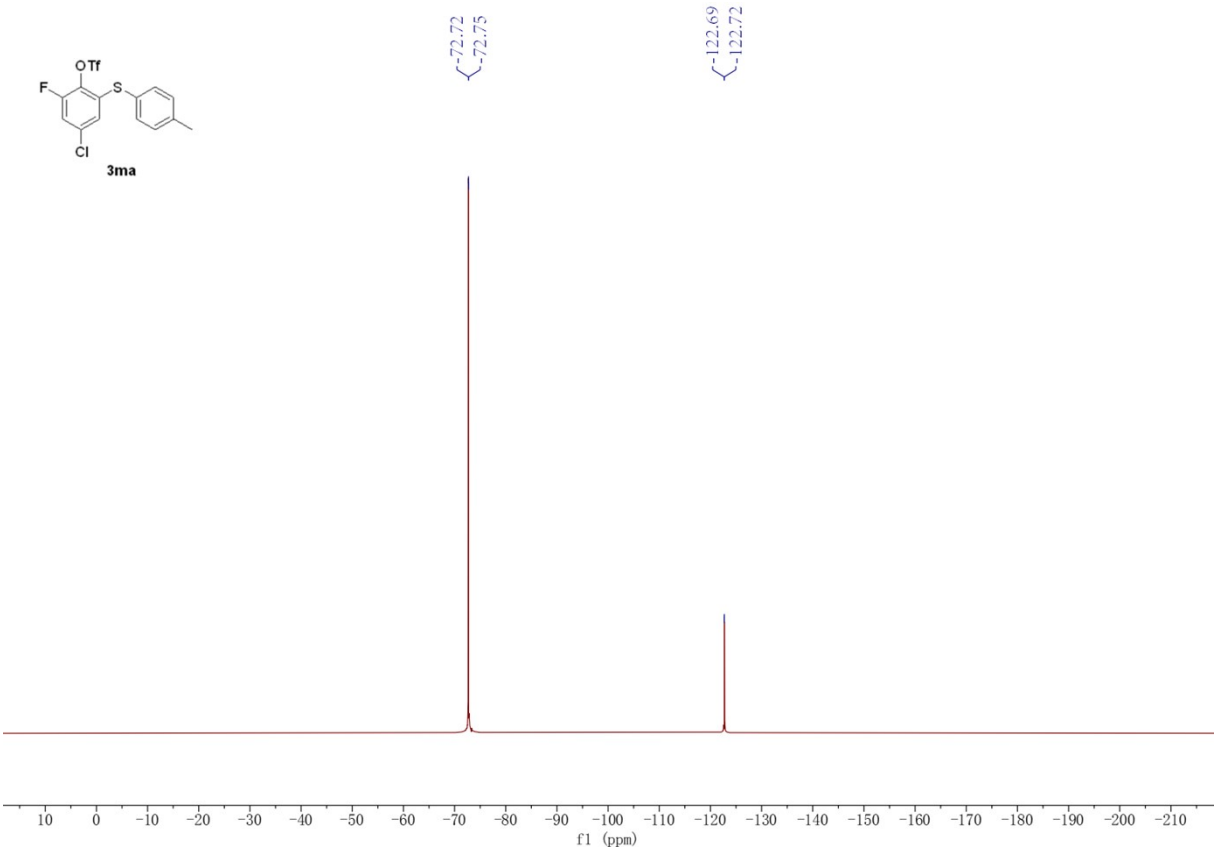
^{1}H NMR spectrum of 3ma (400 MHz, $CDCl_3$)



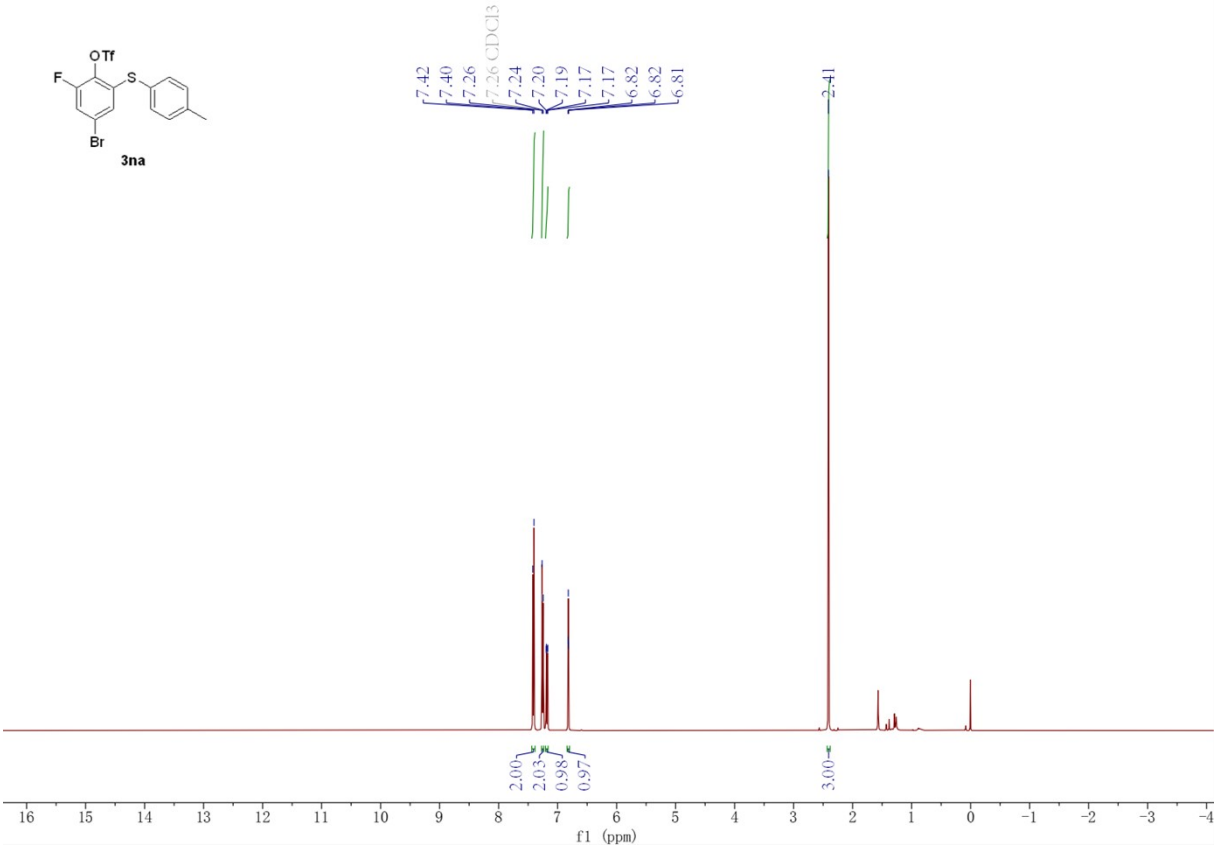
^{13}C NMR spectrum of 3ma (101 MHz, $CDCl_3$)



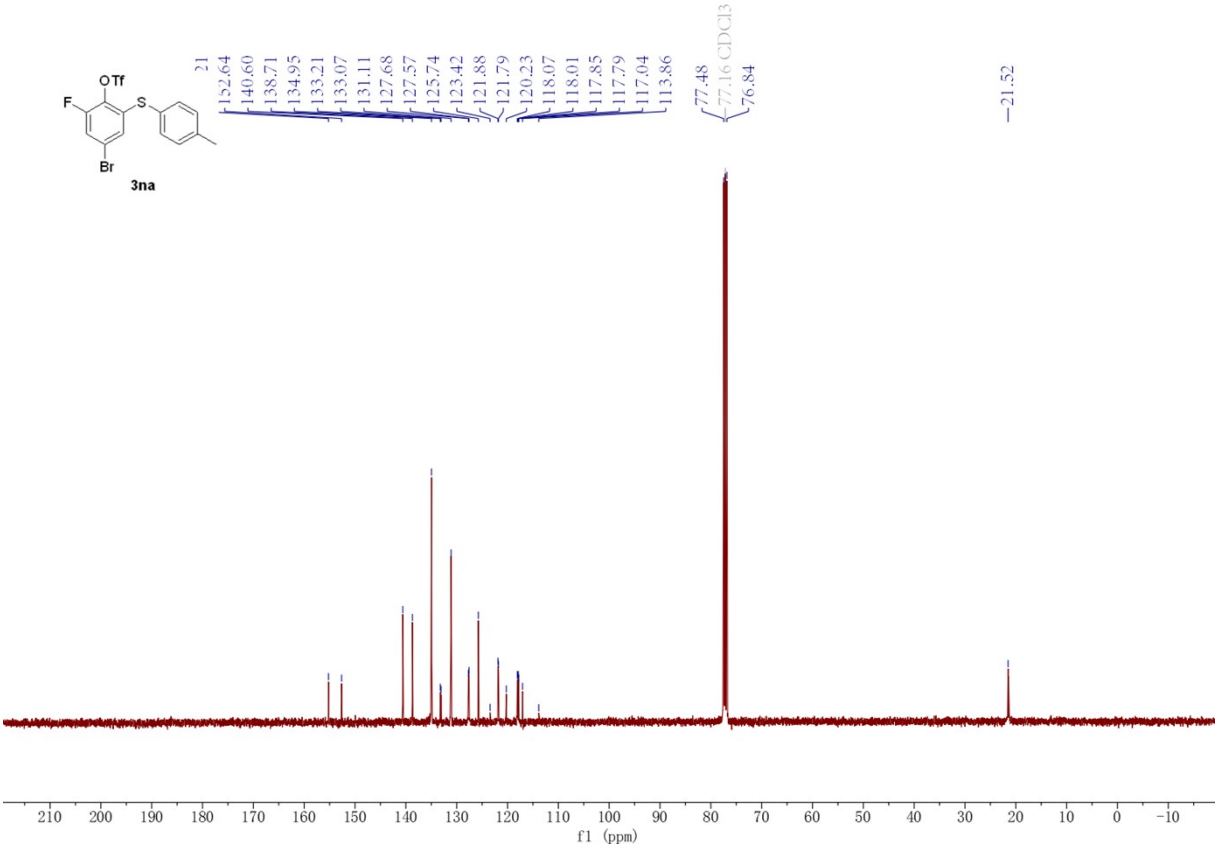
^{19}F NMR spectrum of 3ma (376 MHz, $CDCl_3$)



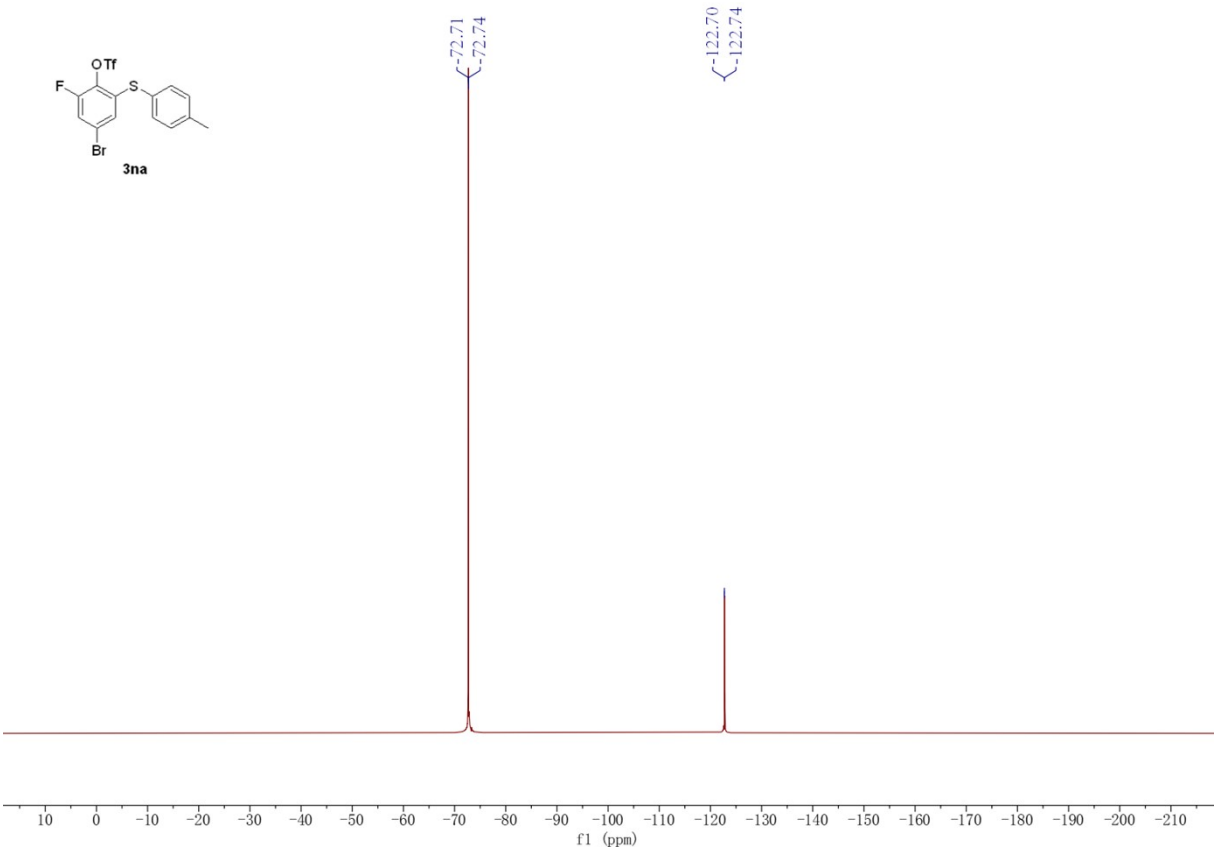
^{1}H NMR spectrum of 3na (400 MHz, $CDCl_3$)



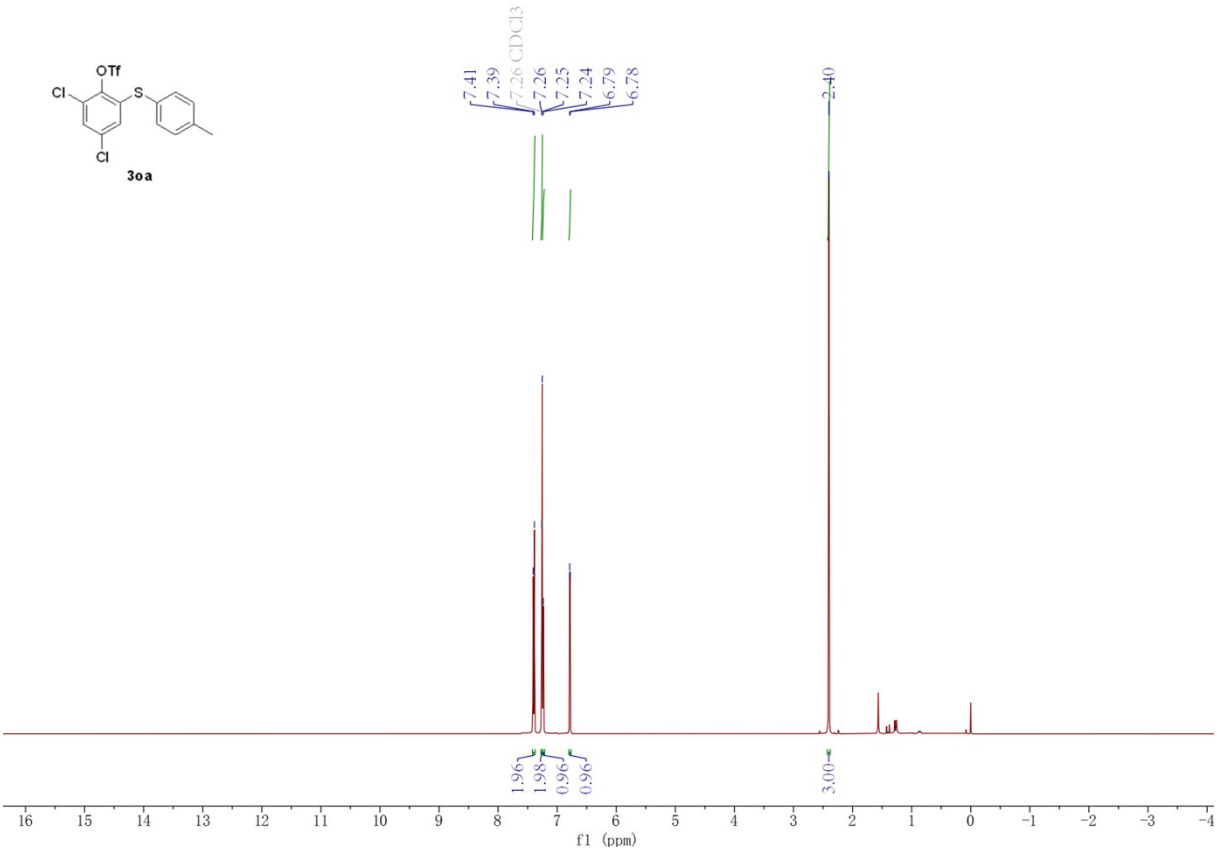
^{13}C NMR spectrum of 3na (101 MHz, $CDCl_3$)



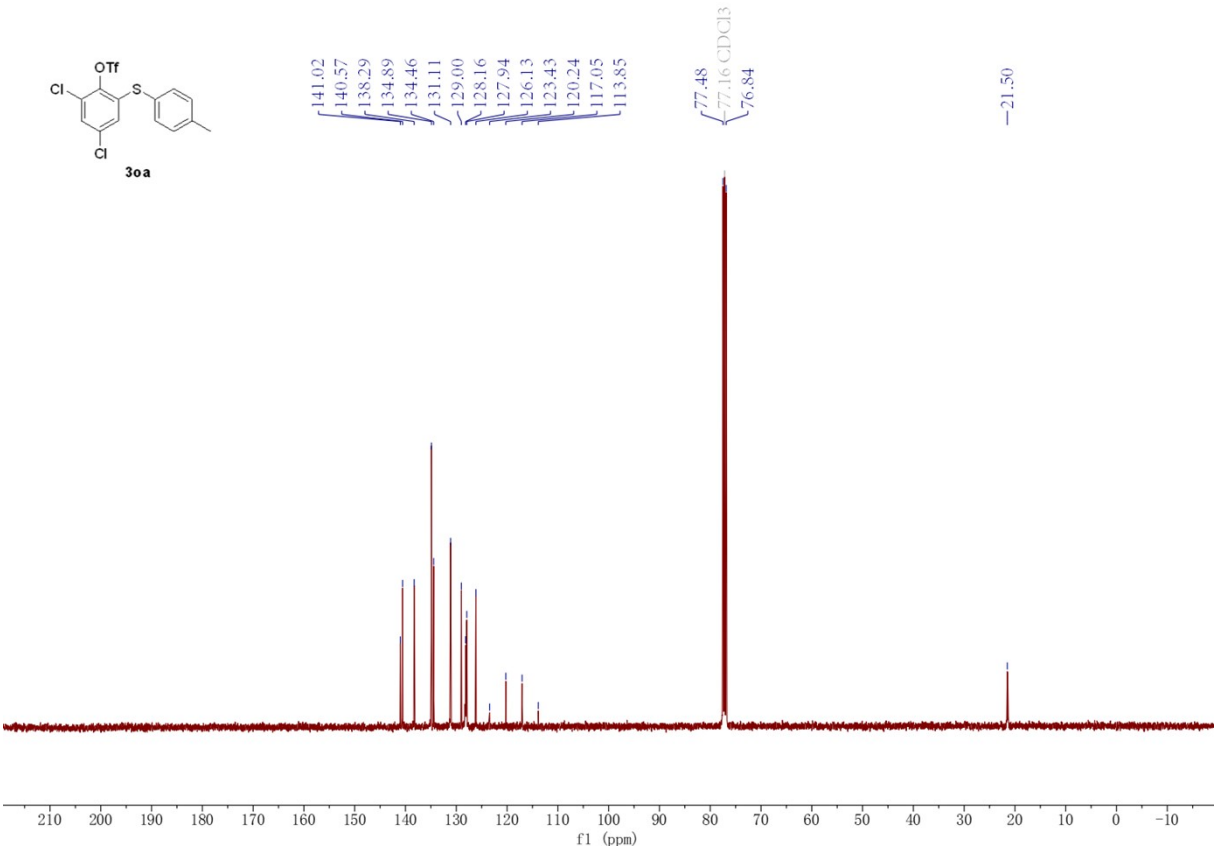
^{19}F NMR spectrum of 3na (376 MHz, $CDCl_3$)



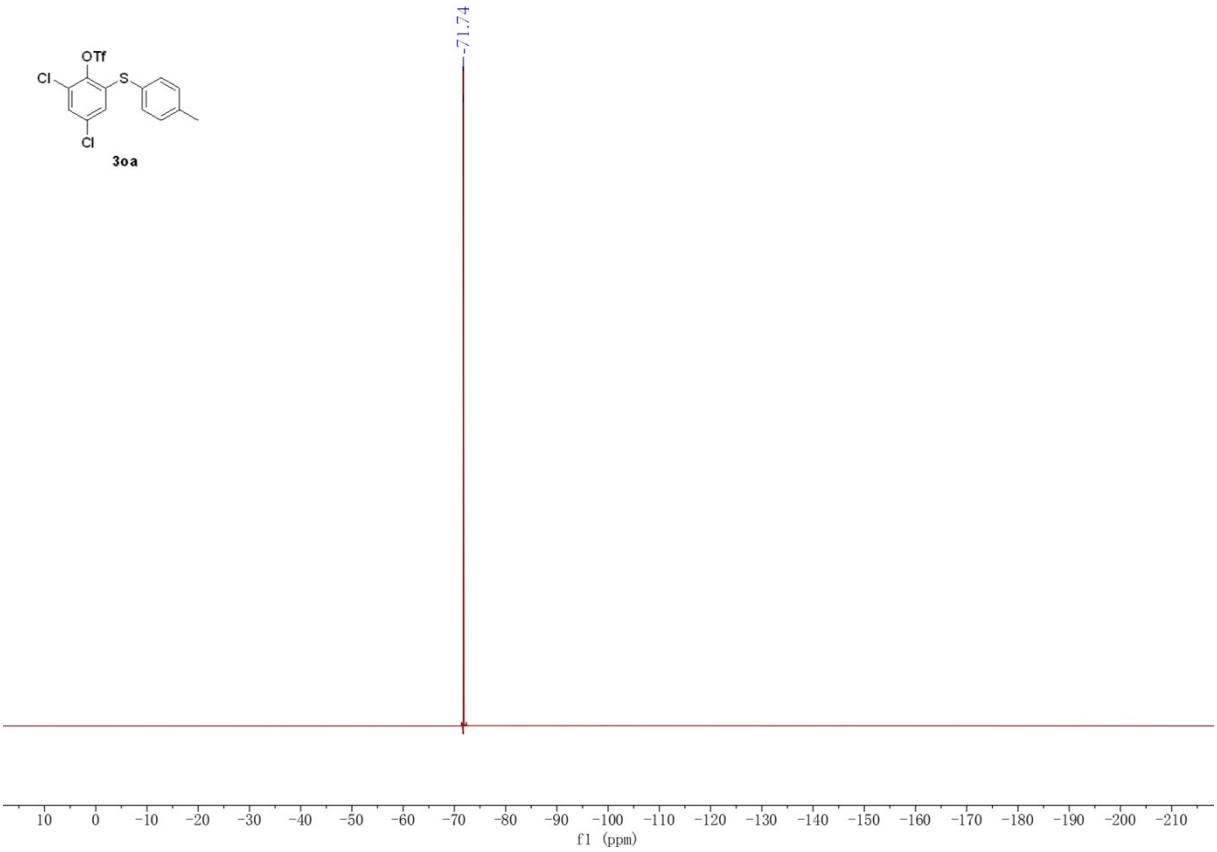
^{1}H NMR spectrum of 3oa (400 MHz, $CDCl_3$)



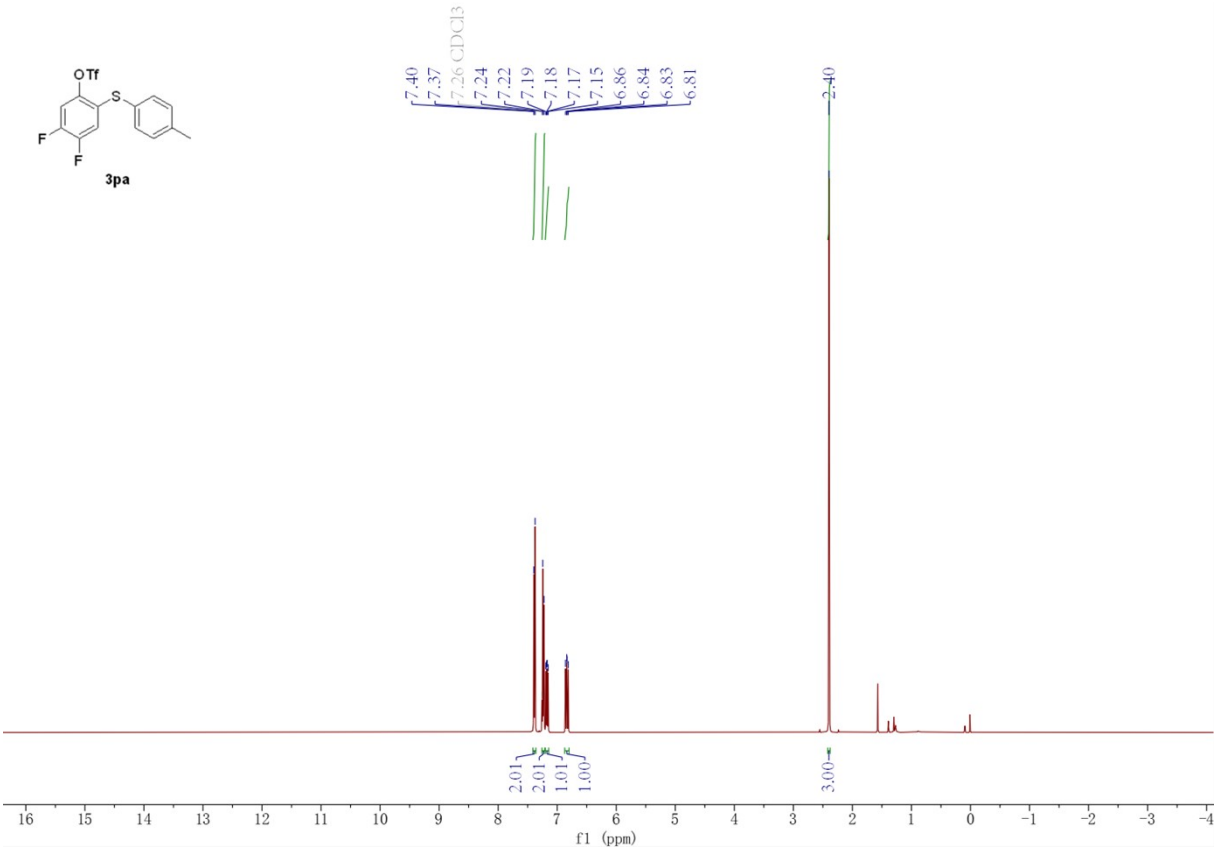
^{13}C NMR spectrum of 3oa (101 MHz, $CDCl_3$)



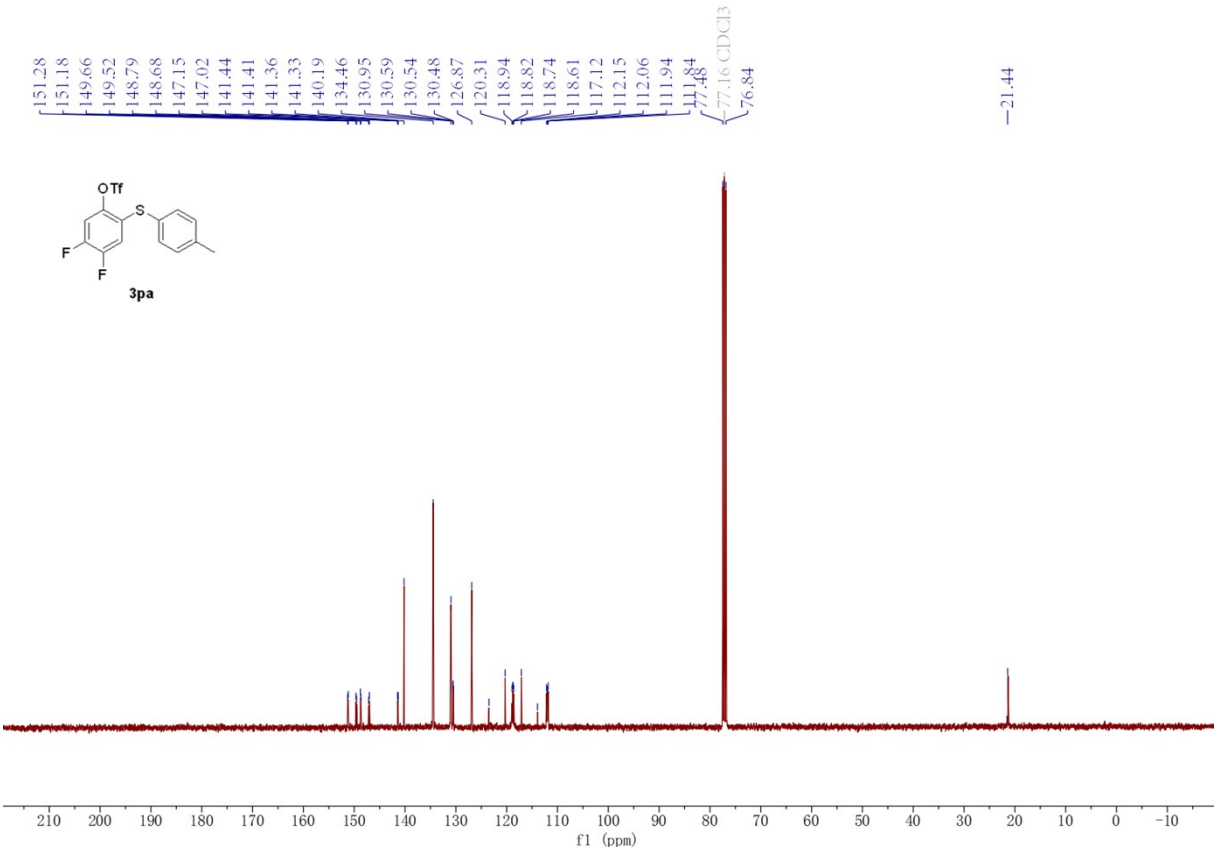
^{19}F NMR spectrum of 3oa (376 MHz, $CDCl_3$)



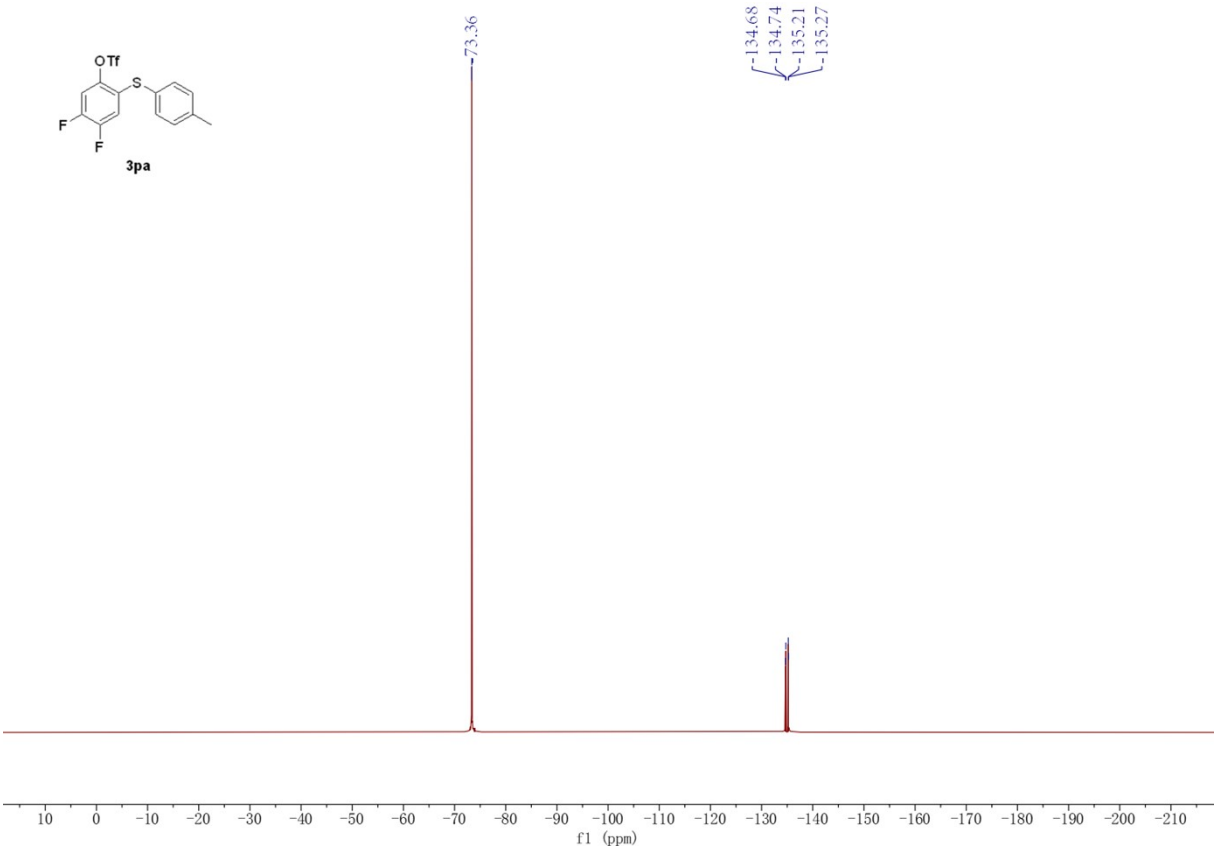
^{1}H NMR spectrum of 3pa (400 MHz, $CDCl_3$)



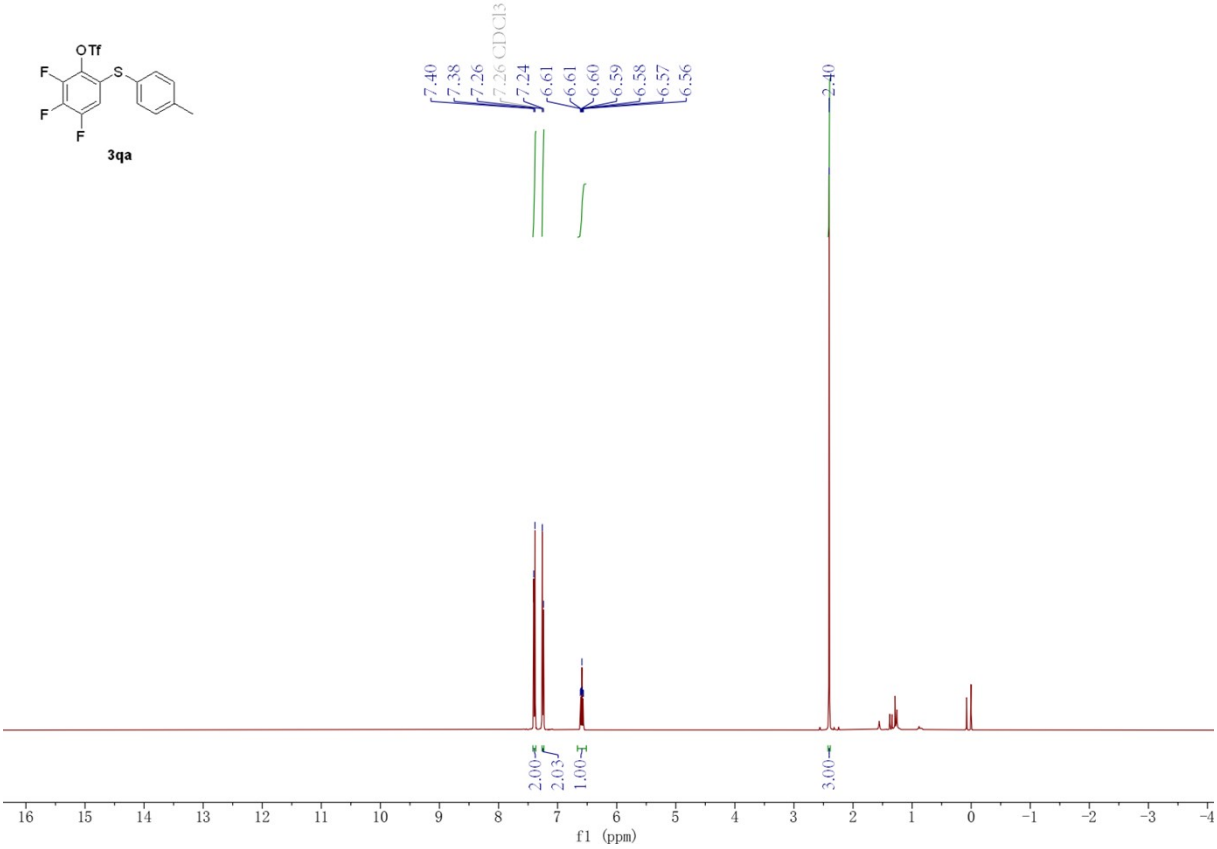
^{13}C NMR spectrum of 3pa (101 MHz, $CDCl_3$)



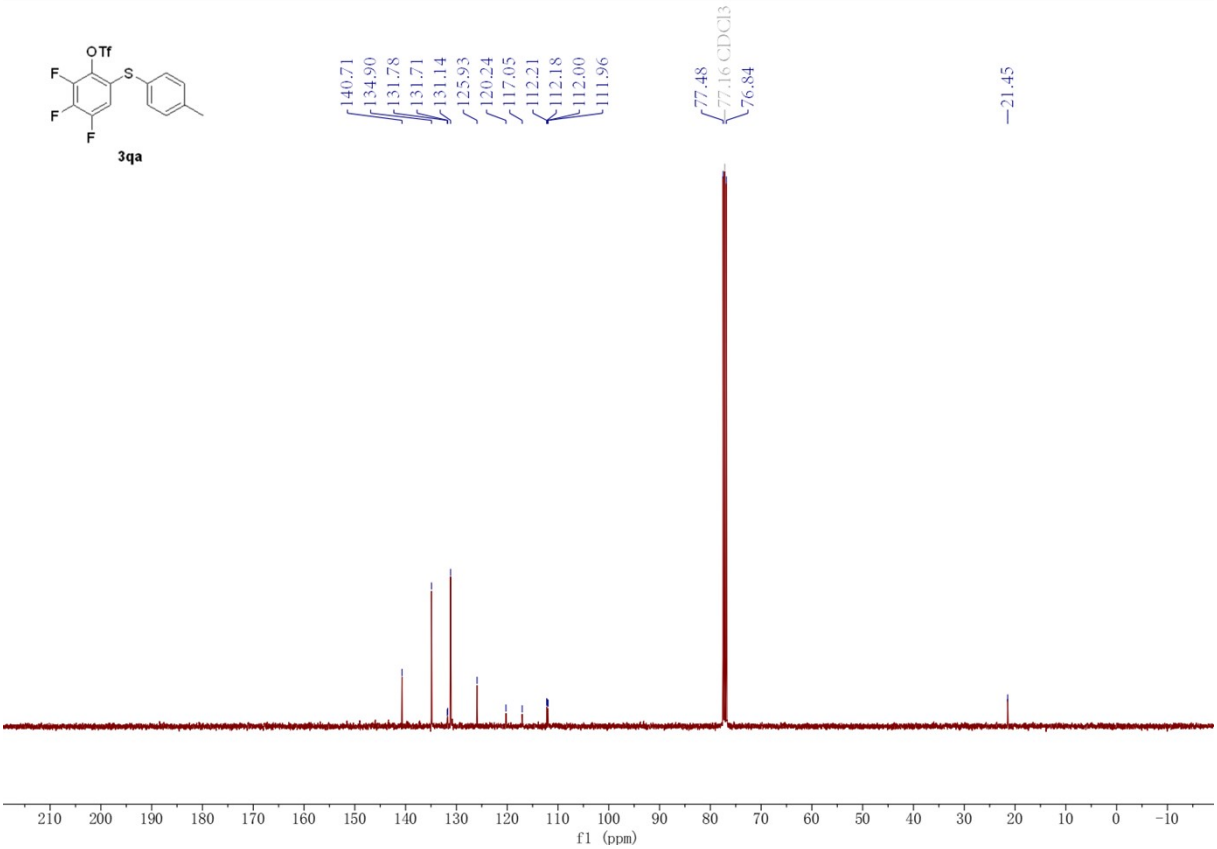
^{19}F NMR spectrum of 3pa (376 MHz, $CDCl_3$)



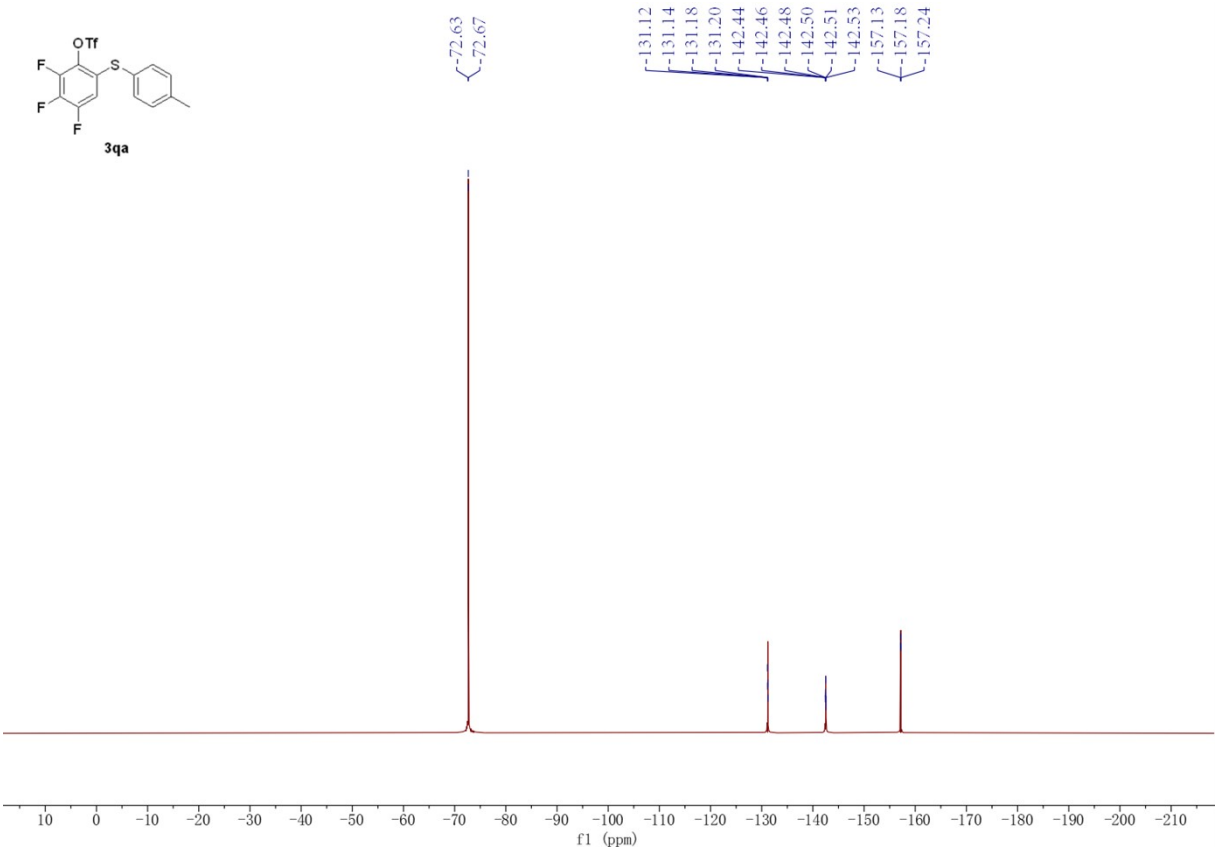
^{1}H NMR spectrum of 3pa (400 MHz, $CDCl_3$)



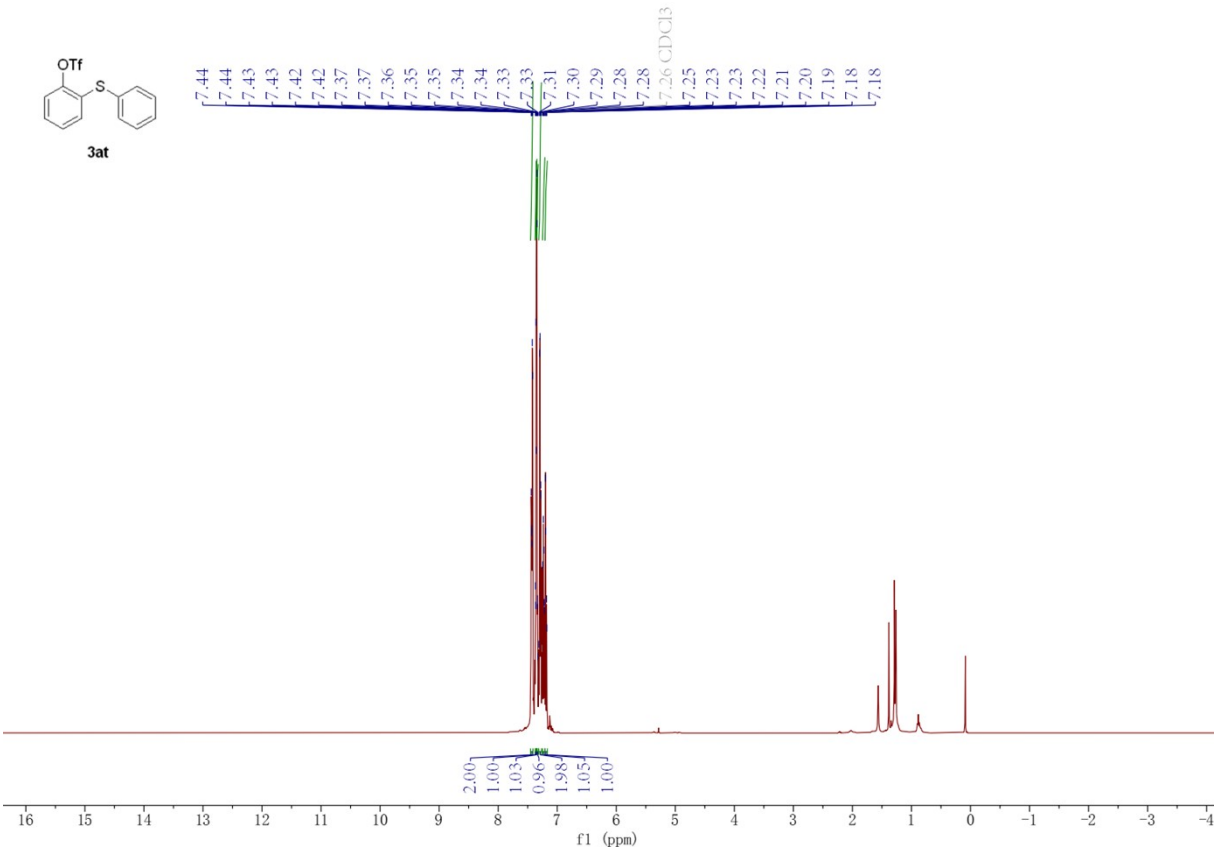
^{13}C NMR spectrum of 3pa (101 MHz, $CDCl_3$)



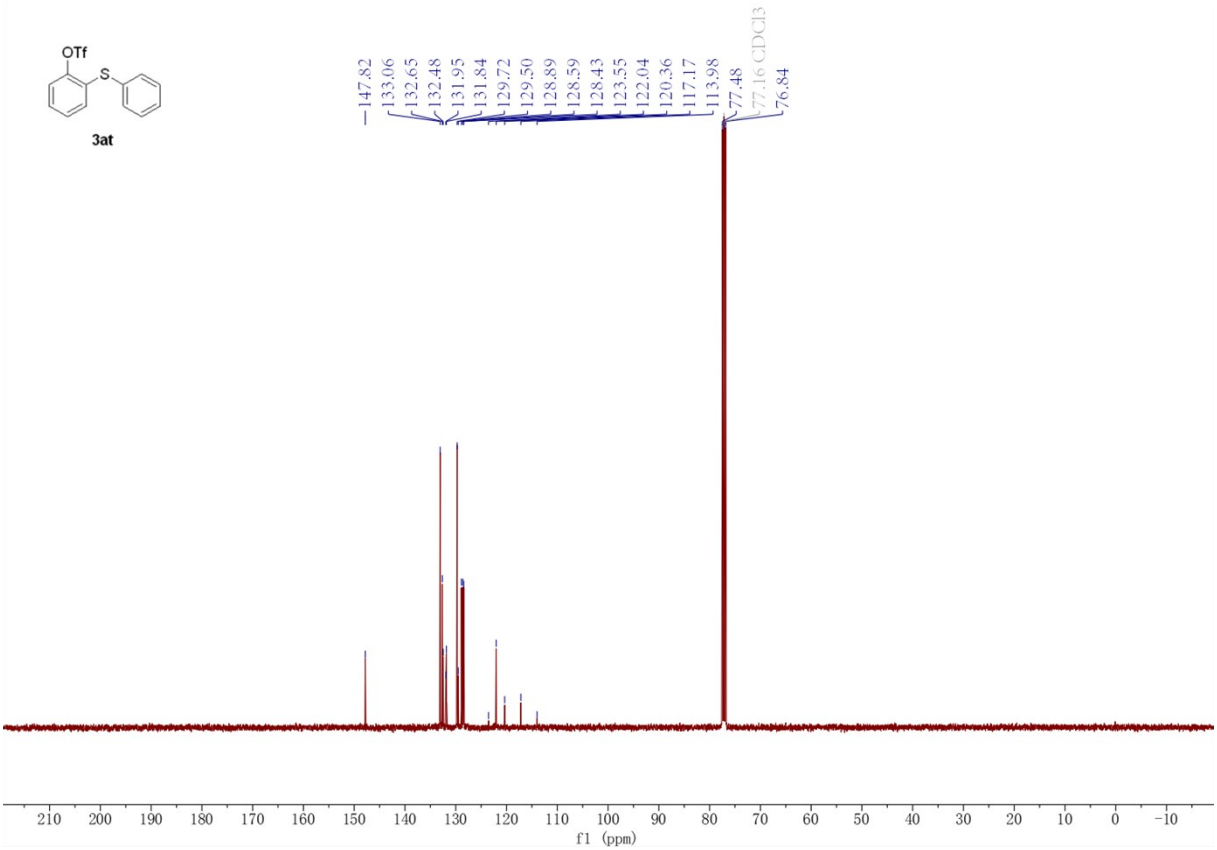
^{19}F NMR spectrum of 3pa (376 MHz, $CDCl_3$)



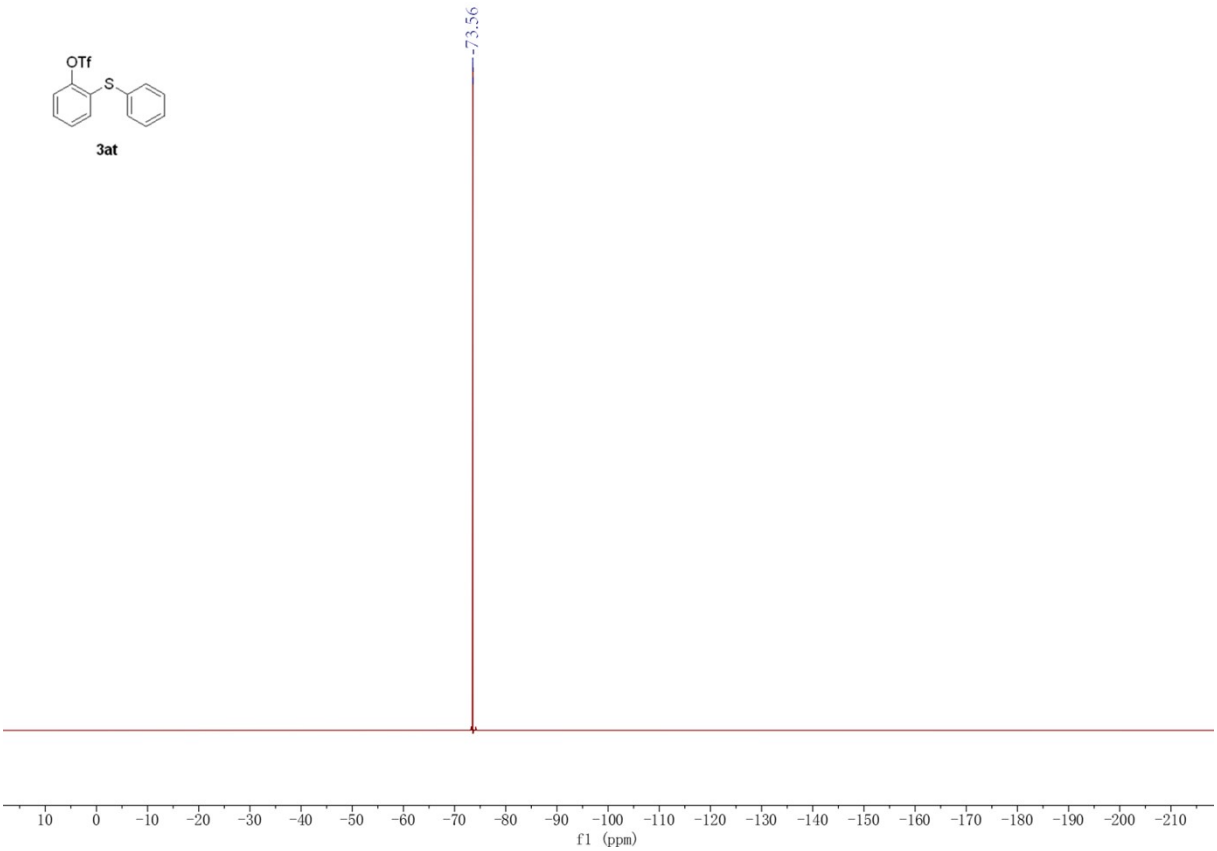
^{1}H NMR spectrum of 3at (400 MHz, $CDCl_3$)



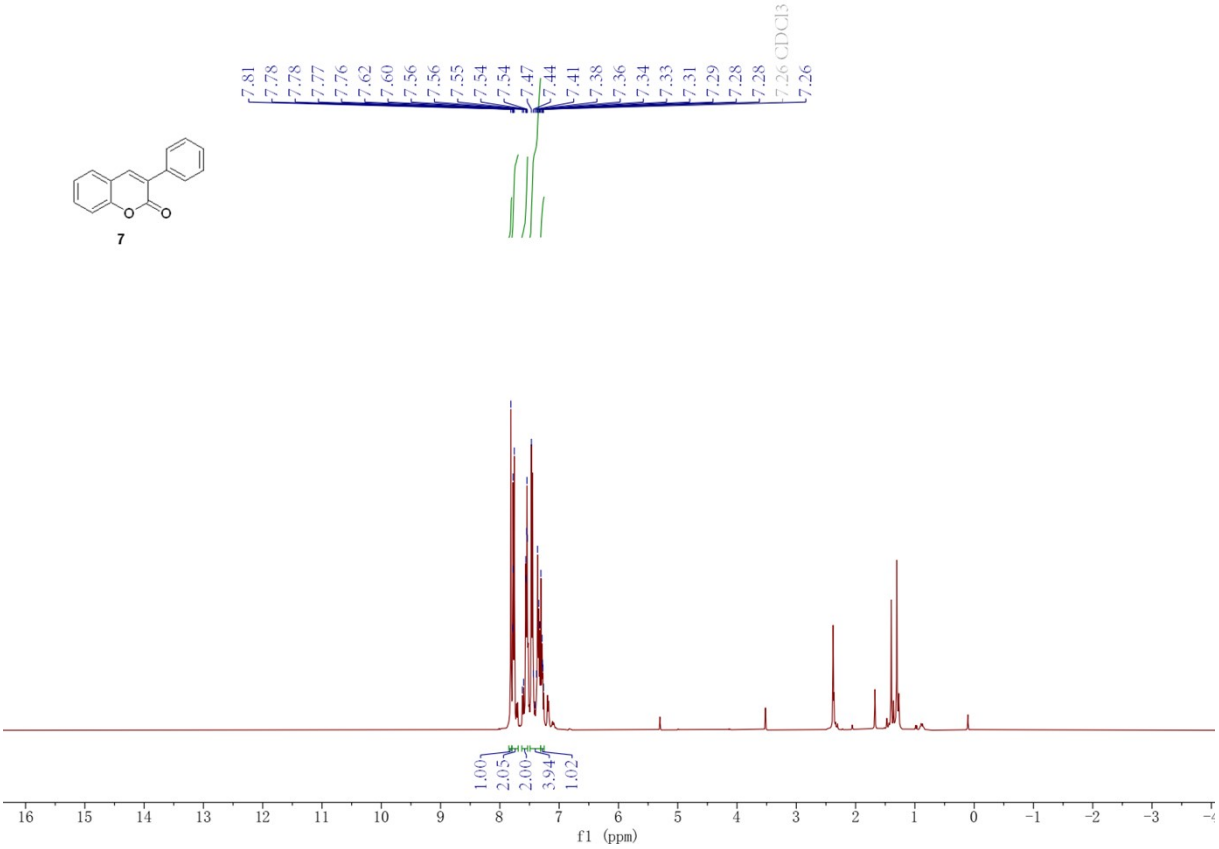
^{13}C NMR spectrum of 3at (101 MHz, $CDCl_3$)



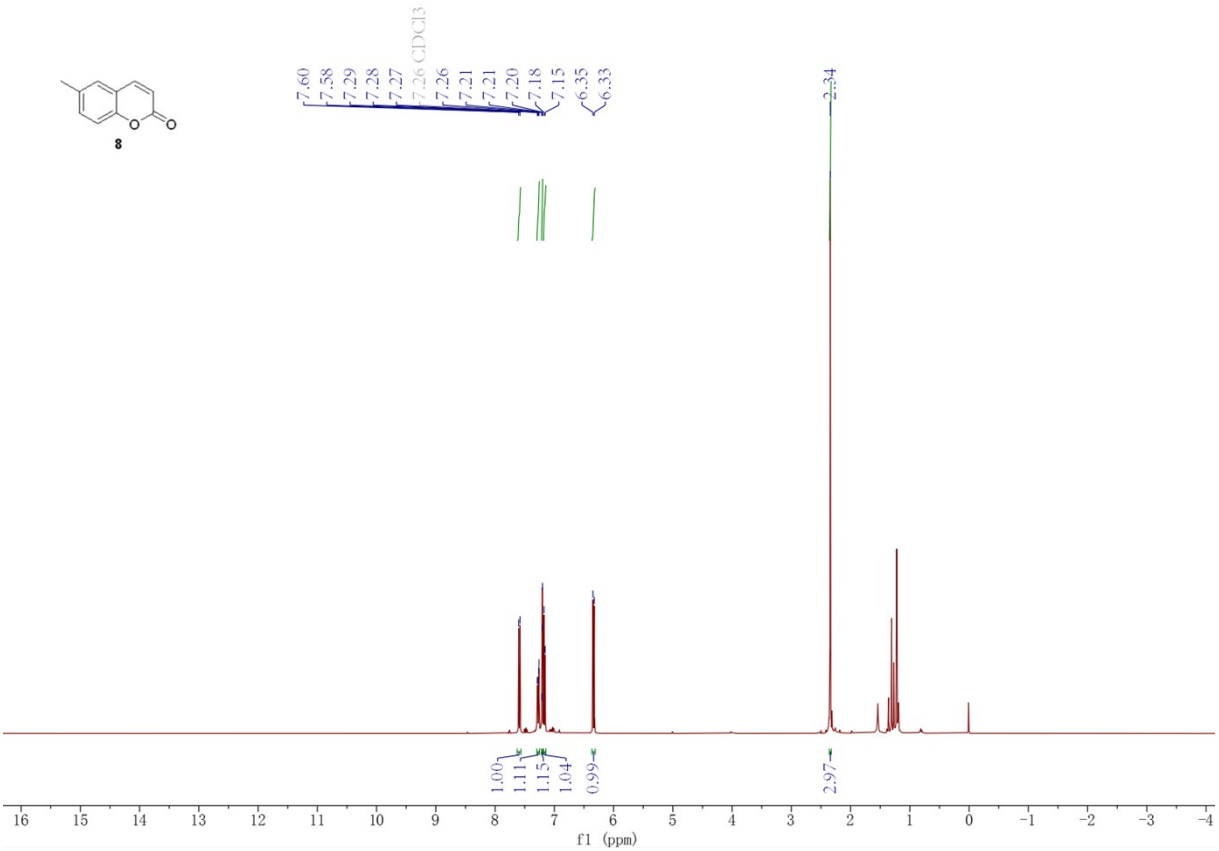
^{19}F NMR spectrum of 3at (376 MHz, $CDCl_3$)



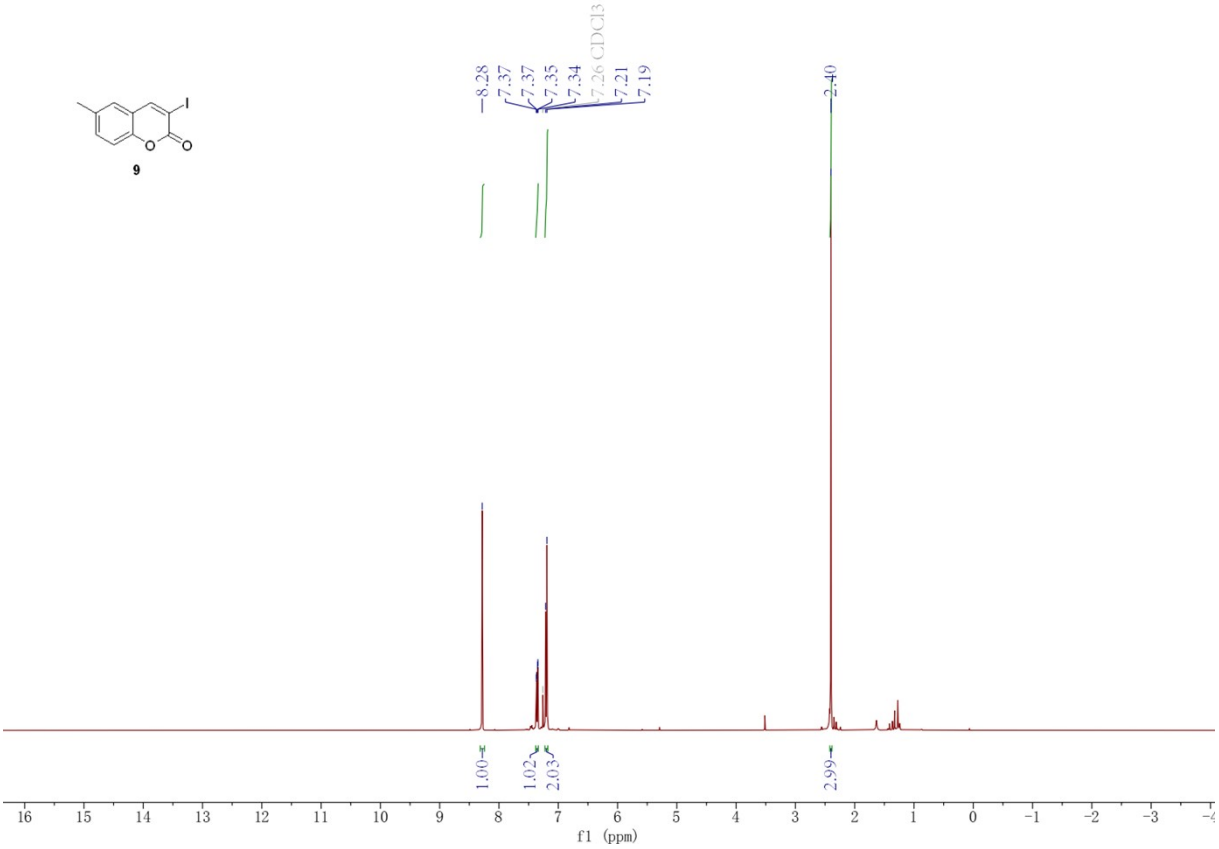
^{1}H NMR spectrum of 7 (400 MHz, $CDCl_3$)



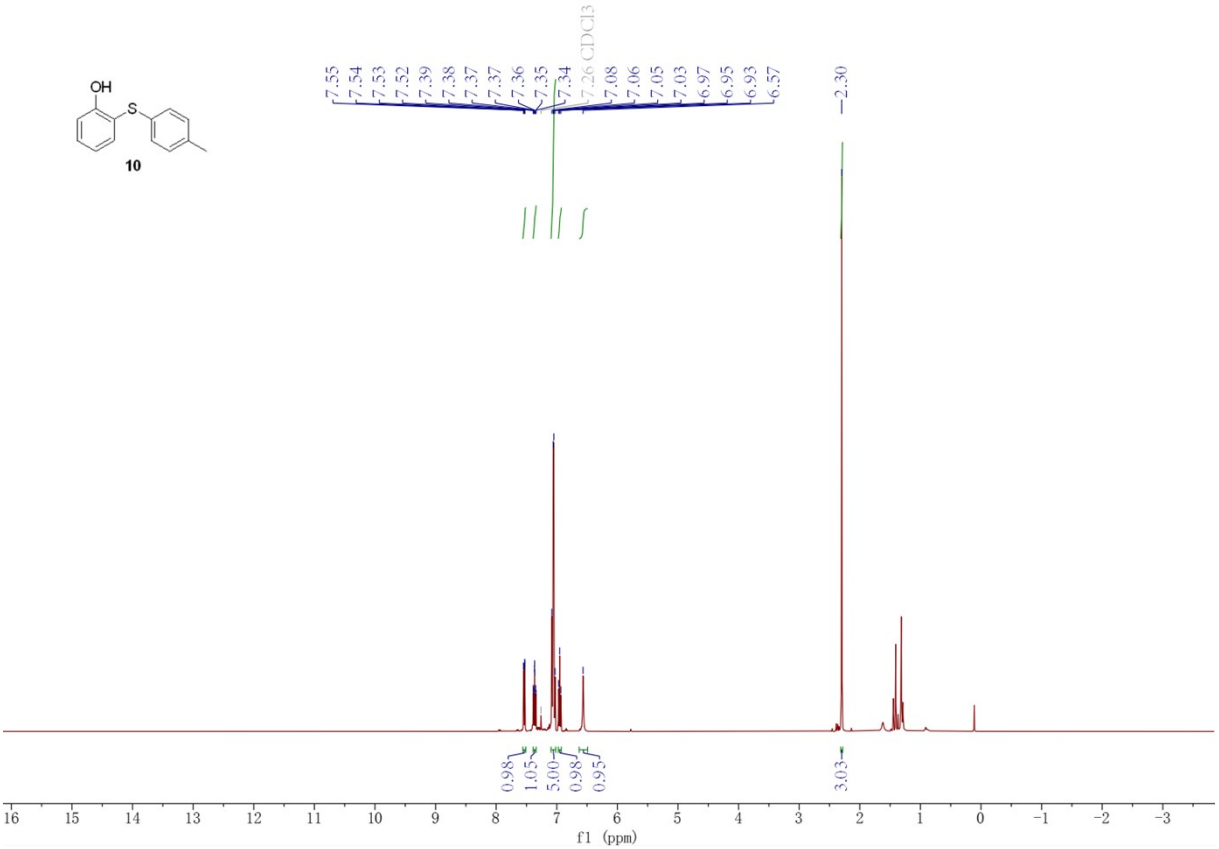
^{1}H NMR spectrum of 8 (400 MHz, $CDCl_3$)



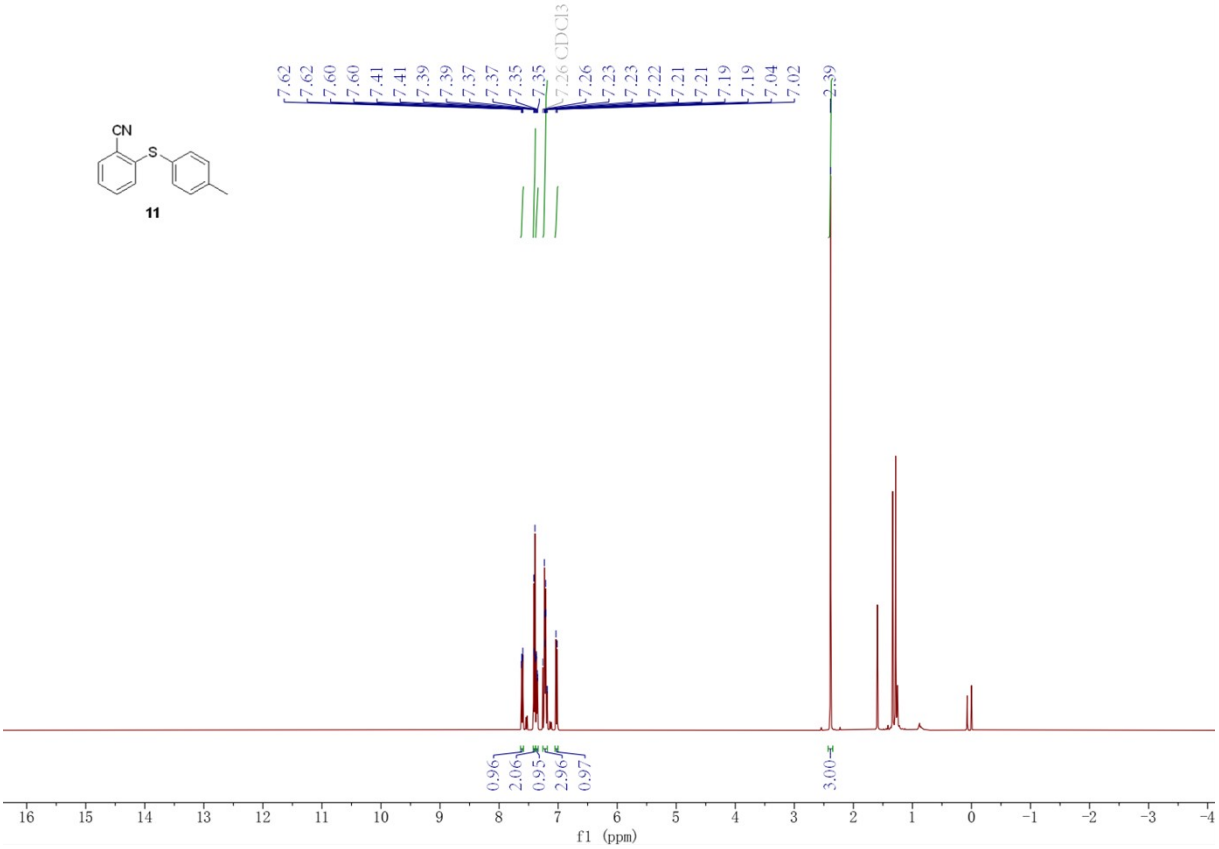
^{1}H NMR spectrum of 9 (400 MHz, $CDCl_3$)



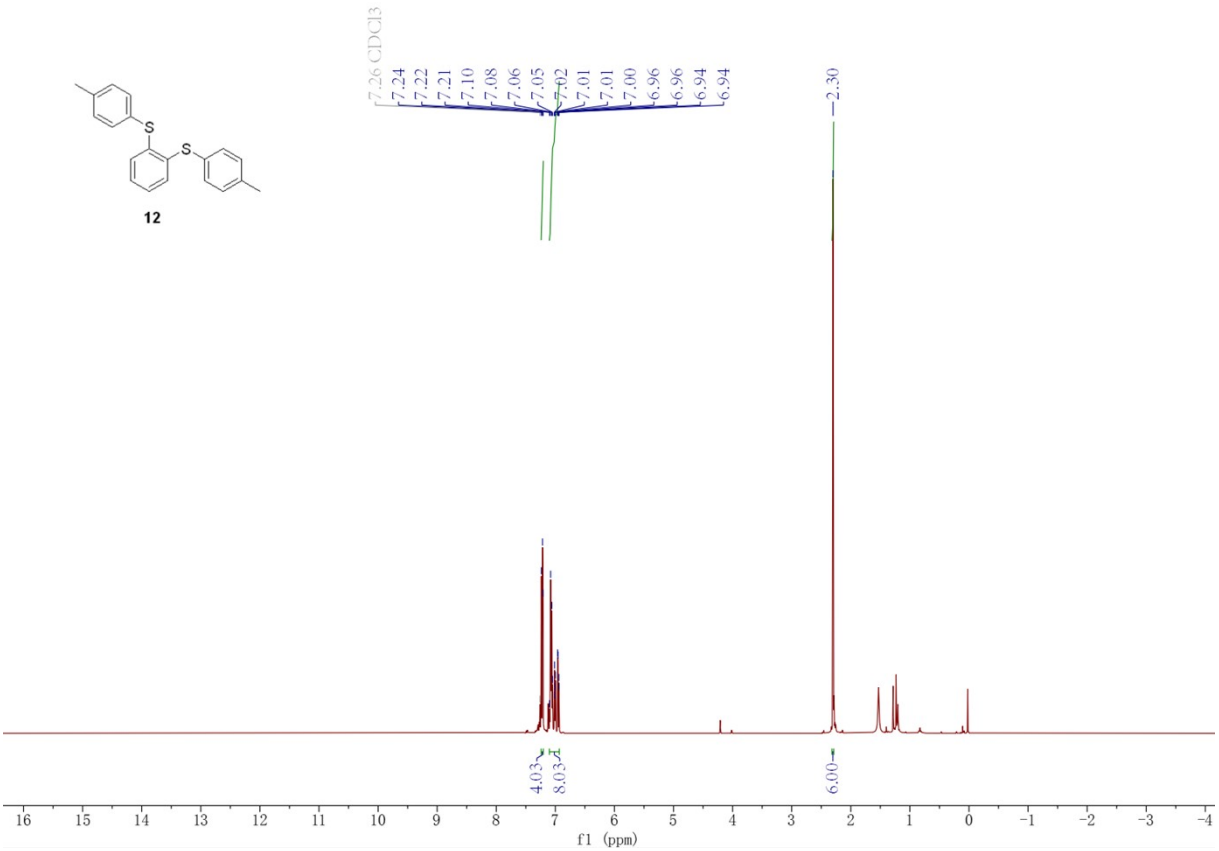
^{1}H NMR spectrum of 10 (400 MHz, $CDCl_3$)



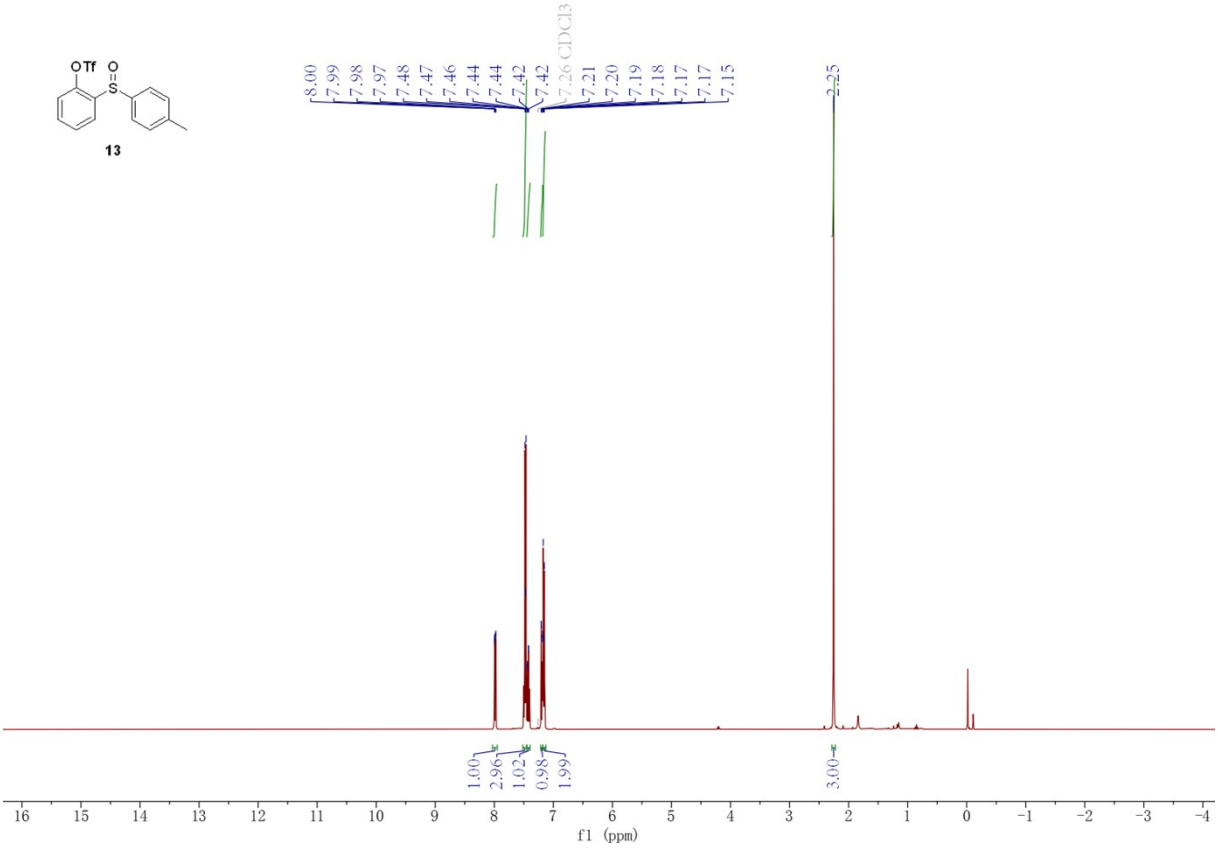
^{1}H NMR spectrum of 11 (400 MHz, $CDCl_3$)



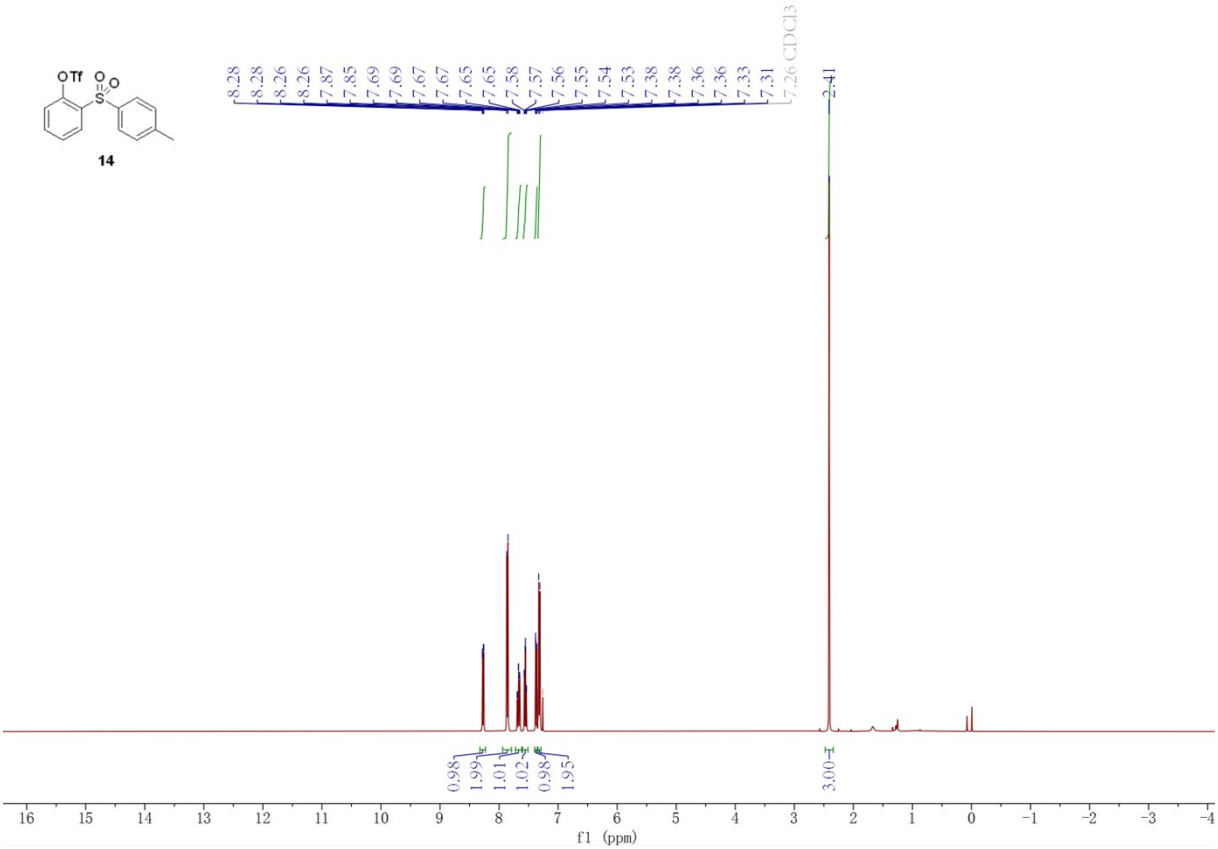
^{1}H NMR spectrum of 12 (400 MHz, $CDCl_3$)



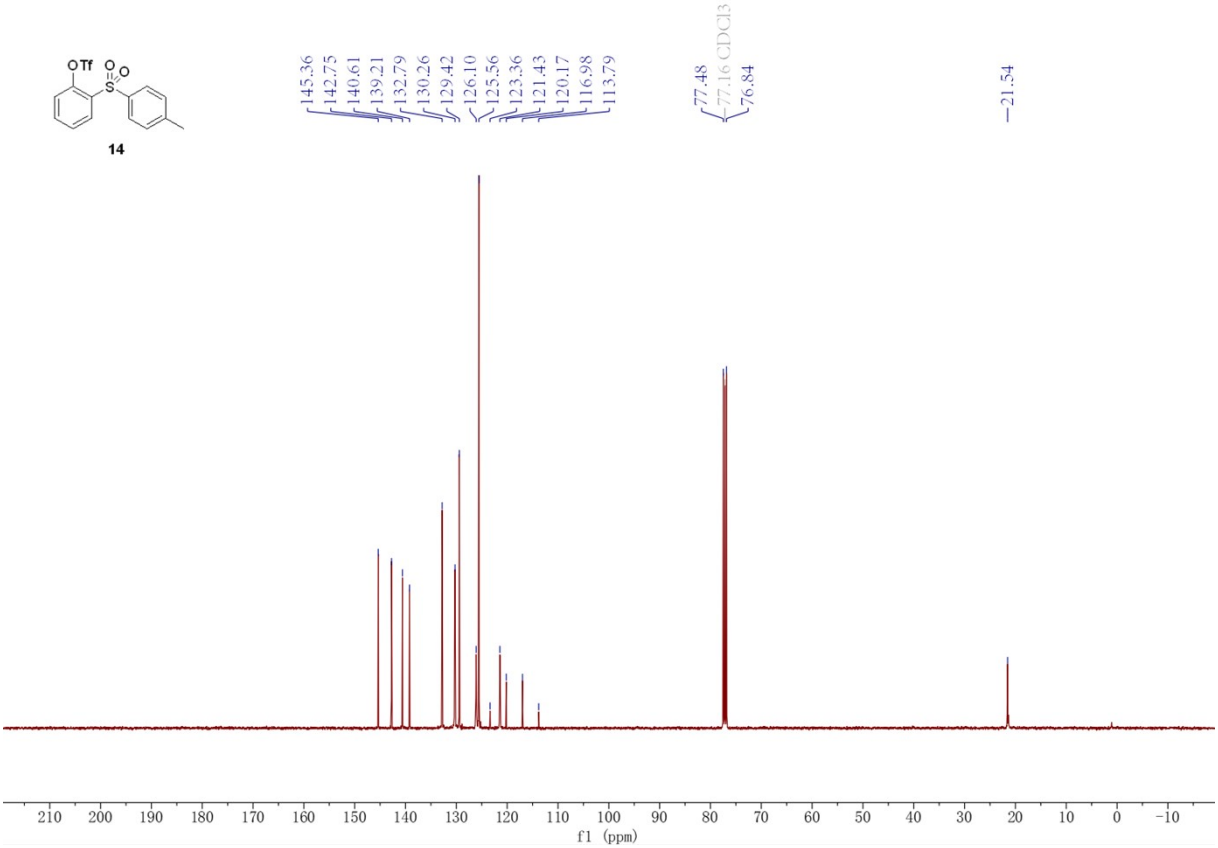
^{1}H NMR spectrum of 13 (400 MHz, $CDCl_3$)



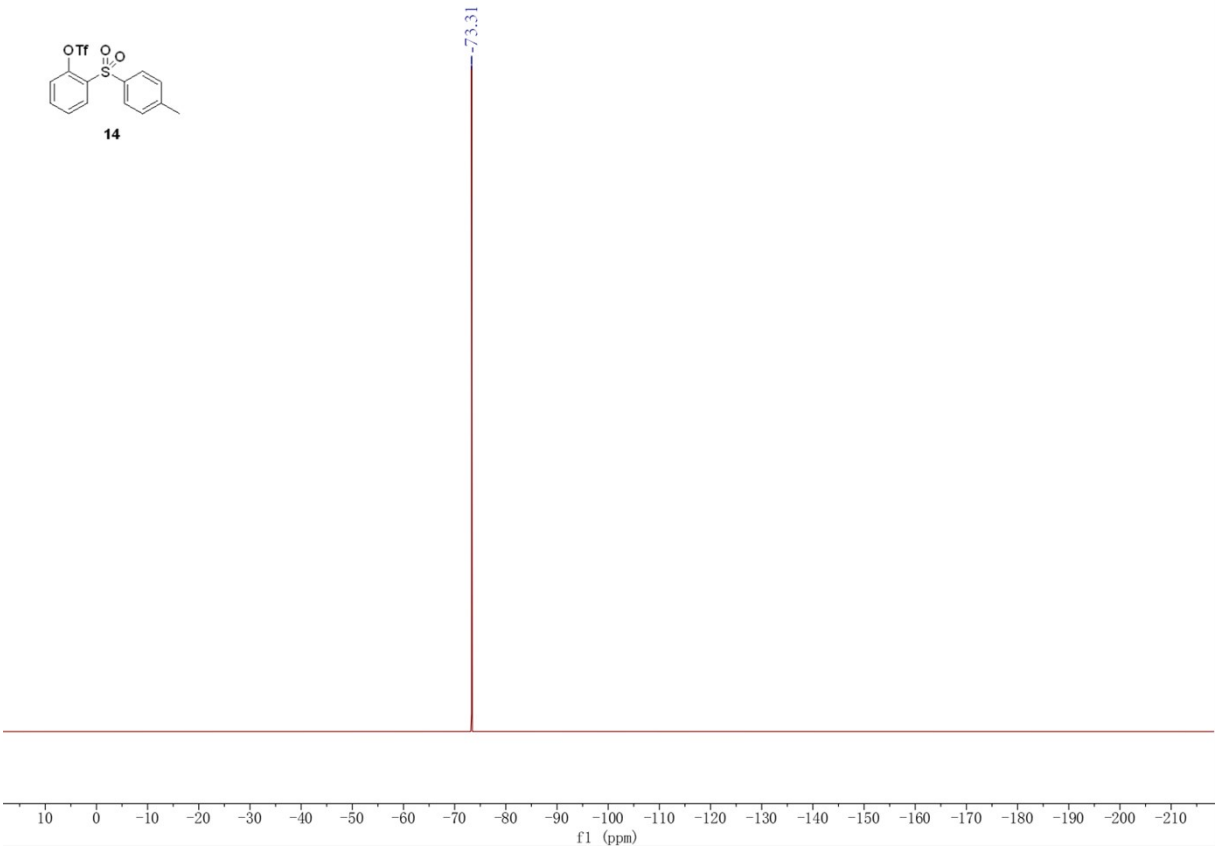
^{1}H NMR spectrum of 14 (400 MHz, $CDCl_3$)



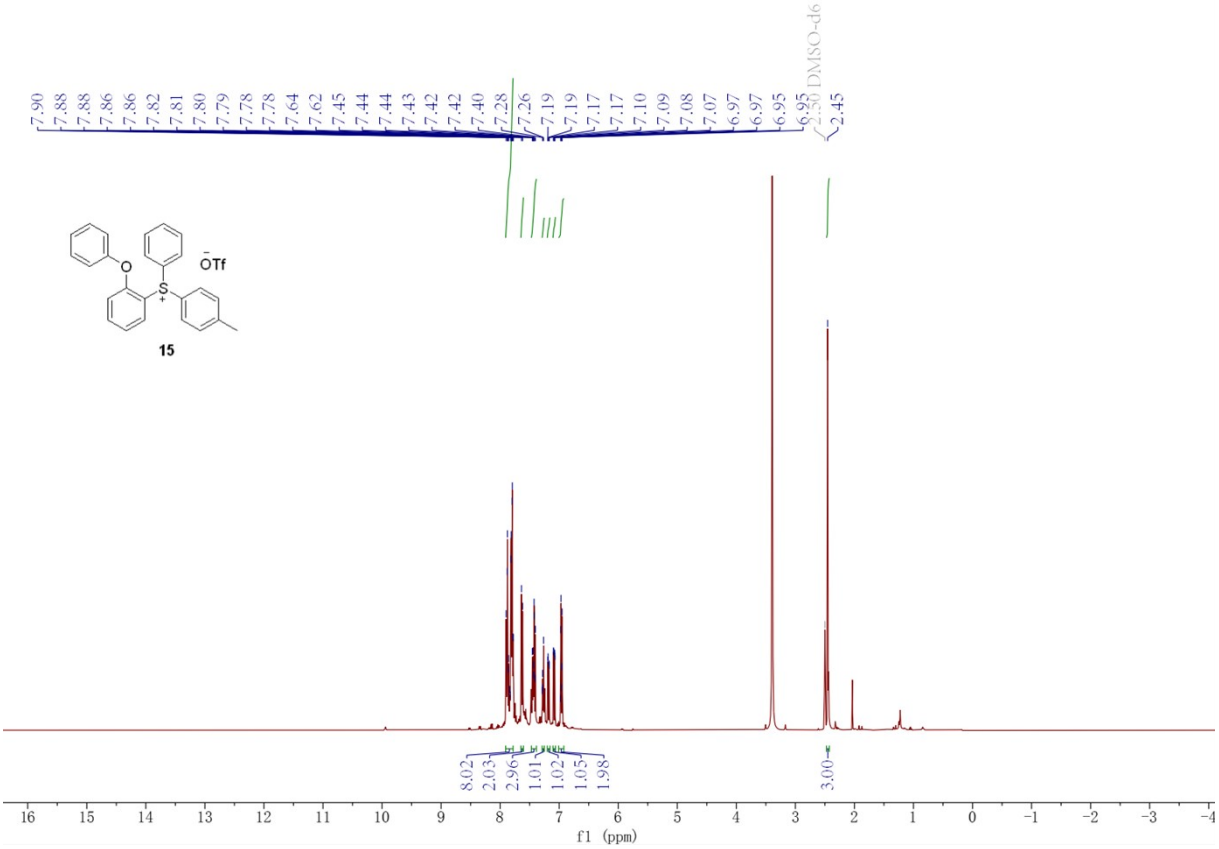
^{13}C NMR spectrum of 14 (101 MHz, $CDCl_3$)



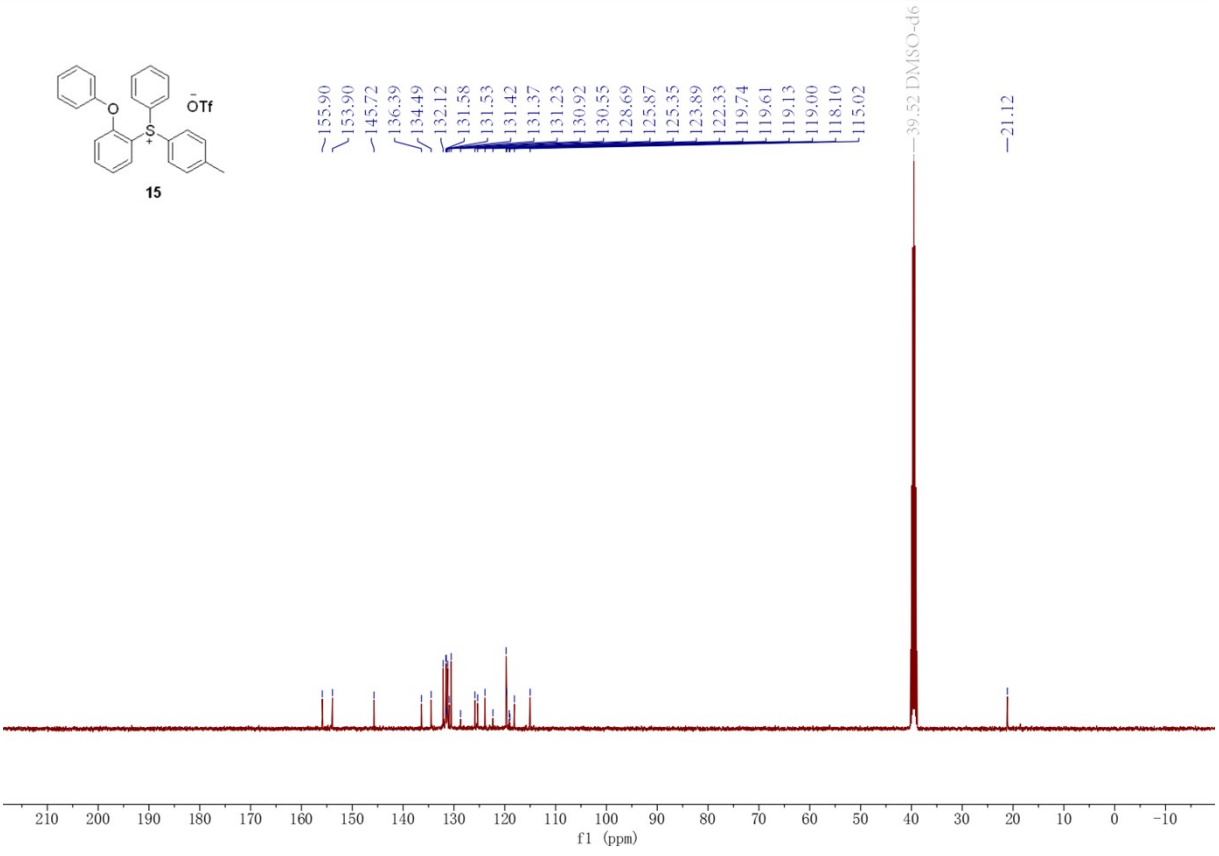
^{19}F NMR spectrum of 14 (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of 15 (400 MHz, d_6-DMSO)



^{13}C NMR spectrum of 15 (101 MHz, d_6-DMSO)



^{19}F NMR spectrum of 15 (376 MHz, d_6-DMSO)