Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct copper-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids with $AgSCF_3$

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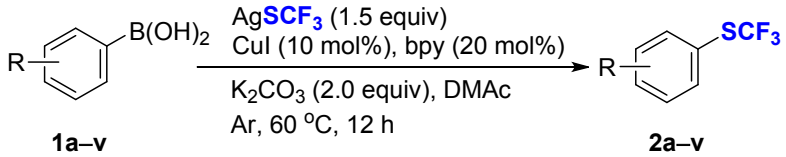
1 General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. The products were purified by column chromatography over silica gel (300–400 mesh size). Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as internal standard. The ^{19}F NMR was obtained using a Bruker AM-400 spectrometer (376 MHz) with $CDCl_3$ as the NMR solvent. Gas chromatography-mass spectra (GC-MS) were recorded on HP 5973 MSD with 6890 GC. High resolution mass spectra (HR MS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. $AgSCF_3$ and $CuSCF_3$ were prepared on a gram scale according to the literature procedure.[1, 2]

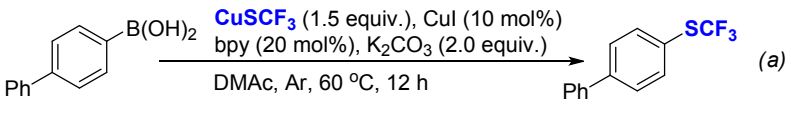
2 General procedure for the synthesis of compounds 2a–v



1a–v **2a–v**

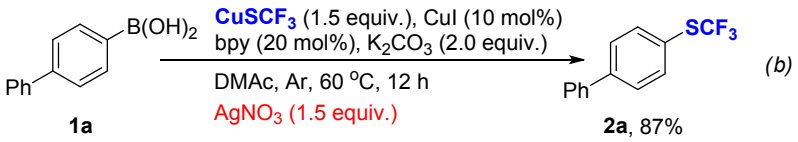
To a mixture of **1a**–**v** (0.2 mmol), $AgSCF_3$ (62.4 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), bpy (6.2 mg, 0.04 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) was added DMAc (2 mL) by syringe at room temperature under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 hours (monitored by TLC). After cooling to ambient temperature, the resulting mixture was filtered through a short pad of Celite and rinsed with EtOAc (5 mL). The filtrate was washed with H_2O (10 mL) and extracted by EtOAc (2 × 10 mL). The organic layer was further washed with H_2O (10 mL), saturated NaCl solution (10 mL), and dried over Na_2SO_4. The organic filtrate was evaporated under reduced pressure. The resultant residue was purified by silica-gel column chromatography using EtOAc/*n*-hexane (V/V = 1/10) as eluent to provide products **2a**–**u**. The yield of compound **2v** was determined by ^{19}F NMR spectroscopy.

3 Control experiments for determination of oxidant

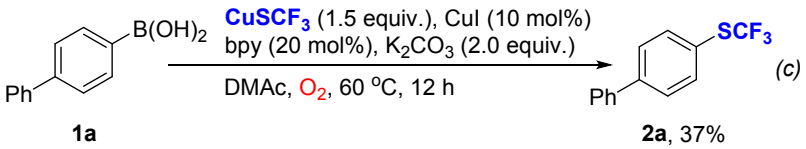


1a **2a**, 2%

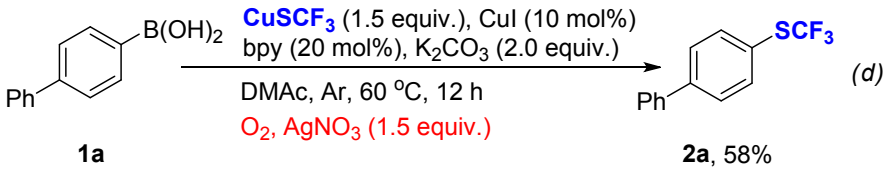
(*a*) To a mixture of **1a** (19.8 mg, 0.1 mmol), $CuSCF_3$ (24.7 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) was added DMAc (1 mL) by syringe at room temperature under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 hours. The yield of **2a** (2%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.



(*b*) To a mixture of **1a** (19.8 mg, 0.1 mmol), $CuSCF_3$ (24.7 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol), $AgNO_3$ (25.5 mg, 0.15 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) was added DMAc (1 mL) by syringe at room temperature under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 hours. The yield of **2a** (87%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.

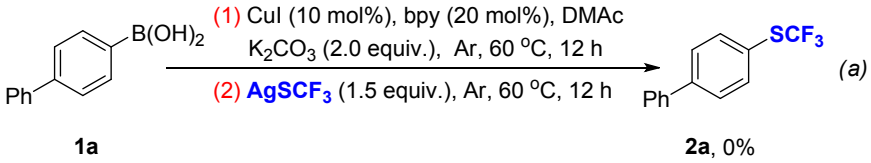


(*c*) To a mixture of **1a** (19.8 mg, 0.1 mmol), $CuSCF_3$ (24.7 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) was added DMAc (1 mL) by syringe at room temperature under oxygen atmosphere. The reaction mixture was stirred at 60 °C for 12 hours. The yield of **2a** (37%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.

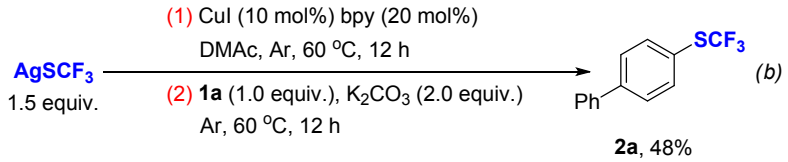


(*d*) To a mixture of **1a** (19.8 mg, 0.1 mmol), $CuSCF_3$ (24.7 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol), $AgNO_3$ (25.5 mg, 0.15 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) was added DMAc (1 mL) by syringe at room temperature under oxygen atmosphere. The reaction mixture was stirred at 60 °C for 12 hours. The yield of **2a** (58%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.

4 Control experiments for mechanistic studies

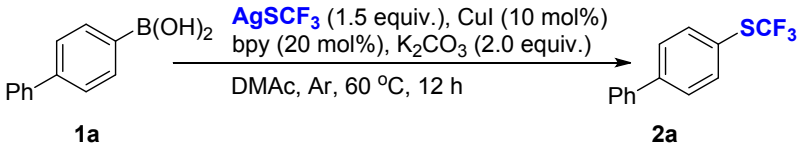


(*a*) Under argon atmosphere, to a dried vessel equipped with a magnetic stir bar was added **1a** (19.8 mg, 0.1 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol), K_2CO_3 (27.6 mg, 0.2 mmol) and DMAc (1 mL). The mixture was then sealed with a septum and stirred at 60 °C for 12 hours. After that, $AgSCF_3$ (31.2 mg, 0.15 mmol) was added to the reaction mixture and stirred at 60 °C for another 12 hours. The yield of **2a** (0%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.



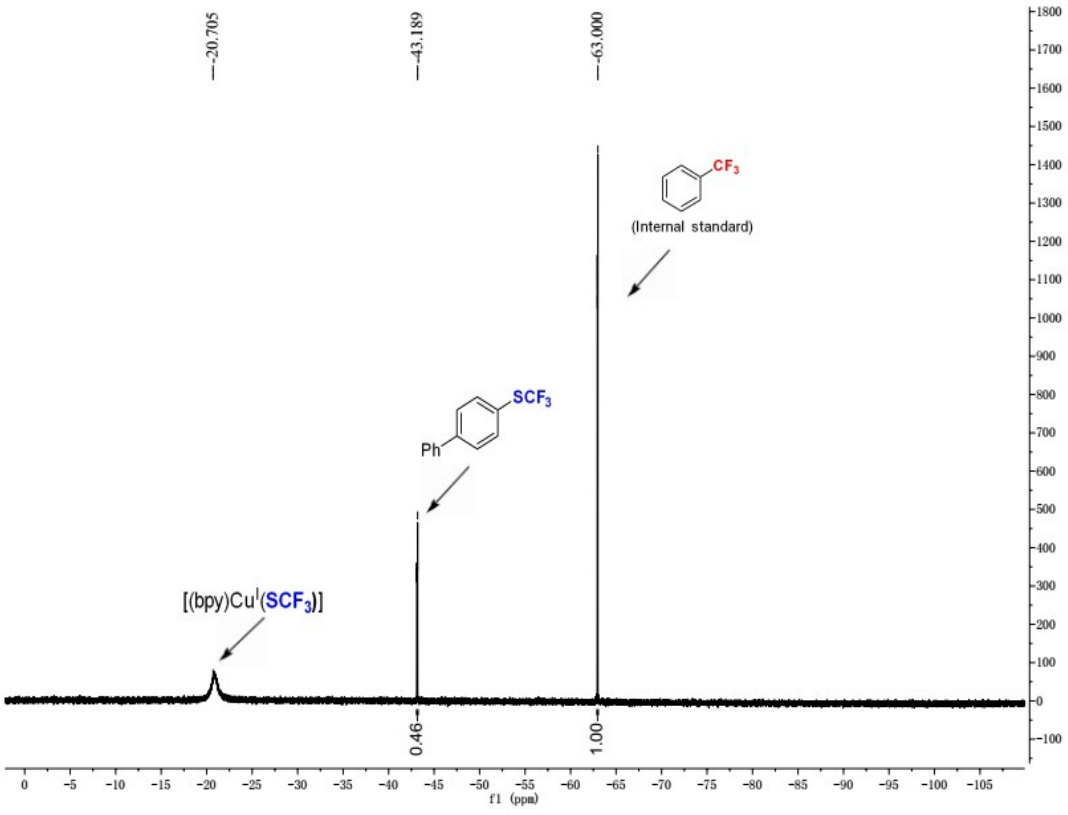
(*b*) Under argon atmosphere, to a dried vessel equipped with a magnetic stir bar was added $AgSCF_3$ (31.2 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol) and DMAc (1 mL). The mixture was then sealed with a septum and stirred at 60 °C for 12 hours. After that, 4-biphenyl boronic acid (**1a**, 19.8 mg, 0.1 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) were added to the reaction mixture and stirred at 60 °C for another 12 hours. The yield of **2a** (48%) was determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard.

5 Control experiments for investigating the intermediate (bpy)Cu^{I}(SCF_3) by ^{19}F NMR

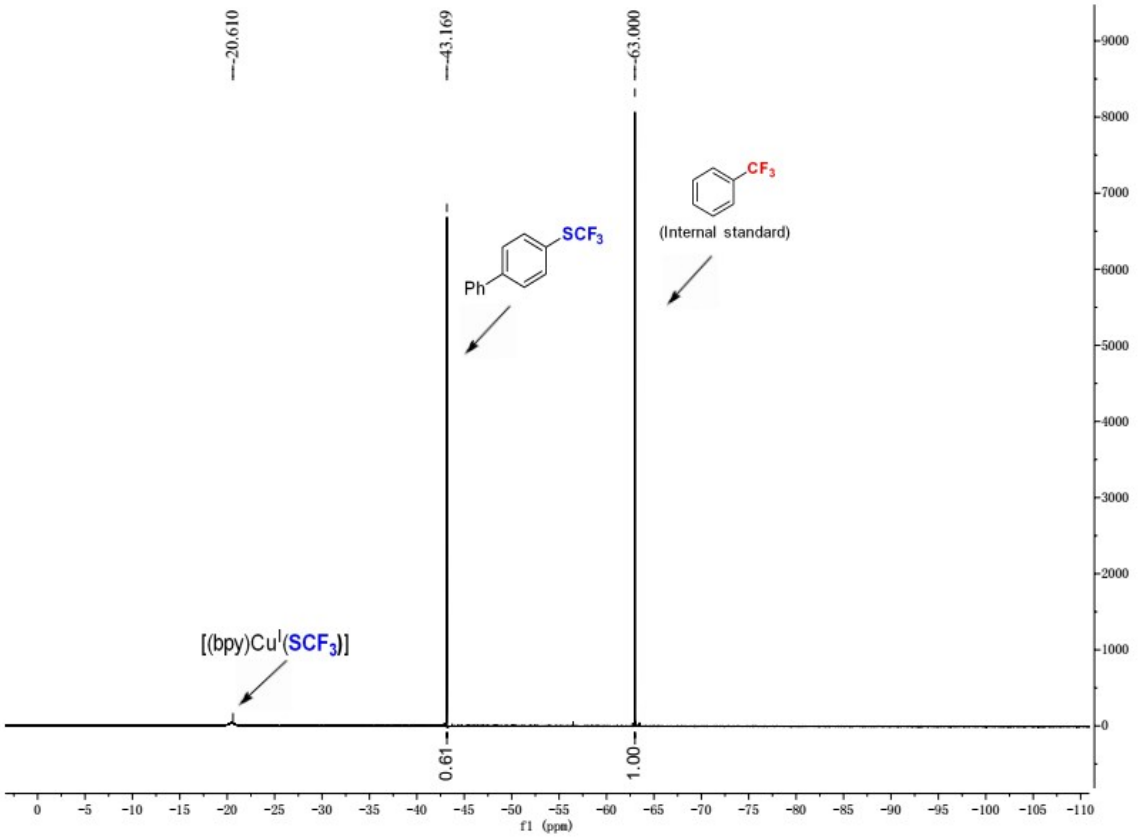


To a mixture of **1a** (19.8 mg, 0.1 mmol), $AgSCF_3$ (31.2 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), bpy (3.1 mg, 0.02 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) was added DMAc (1 mL) by syringe at room temperature under argon atmosphere. The reaction mixture was stirred at 60 °C and the progress of the reaction was monitored by ^{19}F NMR. Four solution samples were taken after the time indicated and analyzed by ^{19}F NMR.

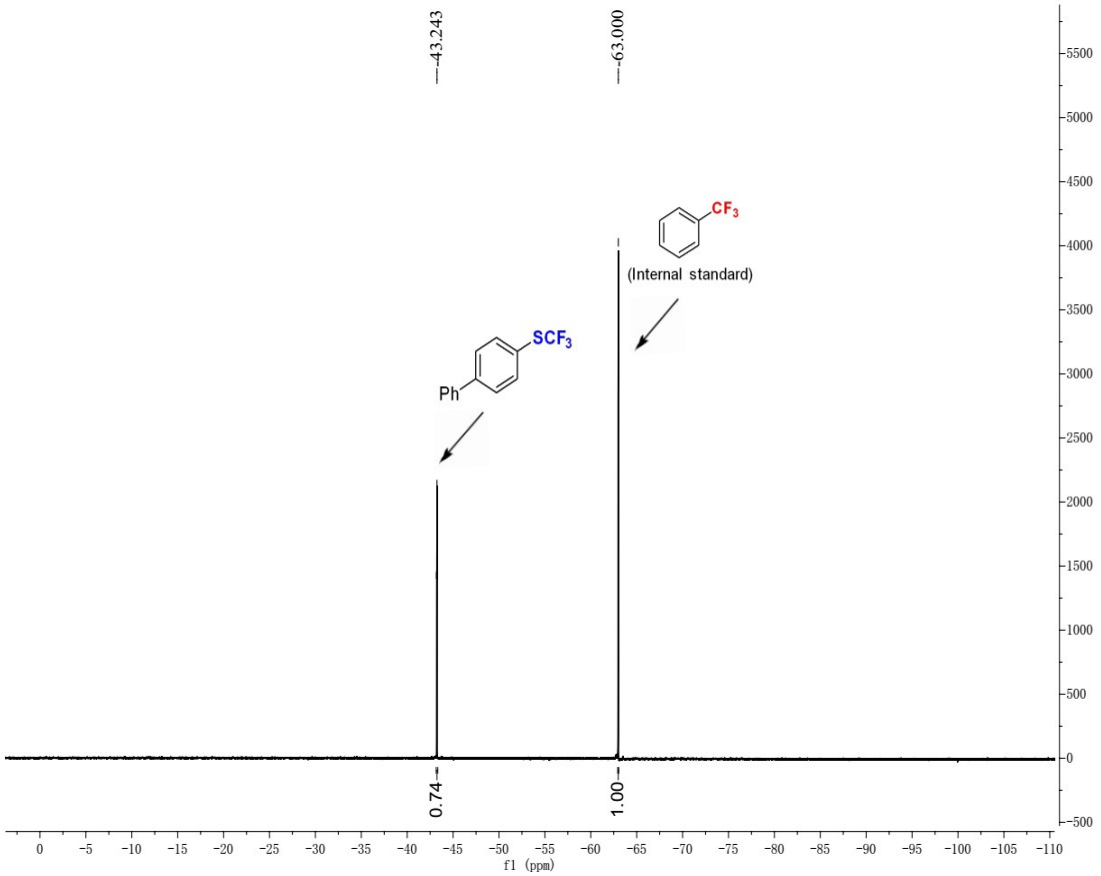
^{19}F NMR spectrum of the reaction (**10 min**)



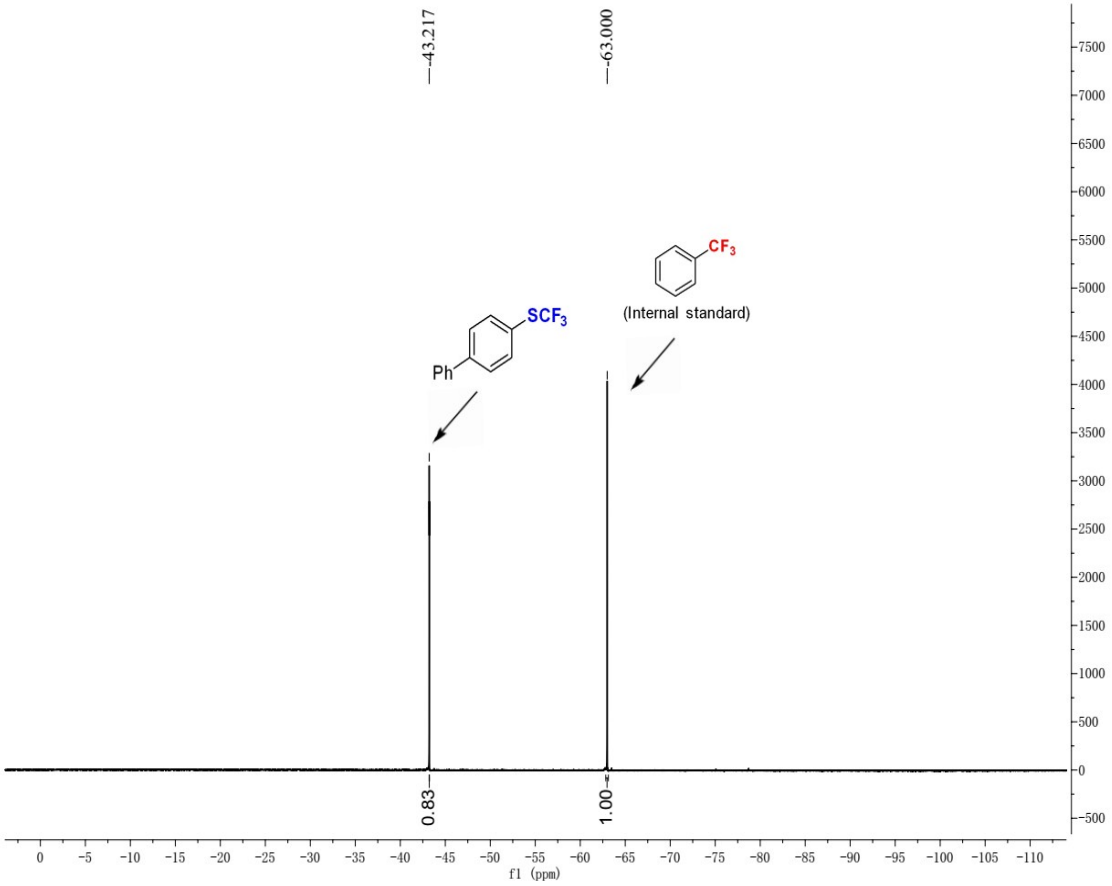
^{19}F NMR spectrum of the reaction (**30 min**)



^{19}F NMR spectrum of the reaction (**1 h**)



^{19}F NMR spectrum of the reaction (**6 h**)



6 References

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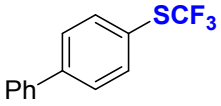
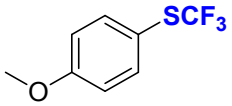
7 Analytical data of target compounds



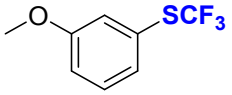
2a

(1, 1'-Biphenyl)-4-yl(trifluoromethyl)sulfane (**2a**, CAS:177551-63-2)[3]. Colorless oil; yield: 85% (43.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.63–7.56 (m, 4H), 7.48–7.43 (m, 2H), 7.41–7.36 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.7 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 139.7, 136.7, 129.7 (q, $^{1}J_{CF}$ = 306.3 Hz), 129.0, 128.2, 127.2, 123.1 (q, $^{3}J_{CF}$ = 2.0 Hz).



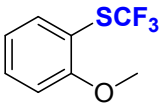
2b

(4-Methoxyphenyl)(trifluoromethyl)sulfane (**2b**, CAS:78914-94-0)[4]. Colorless oil; yield: 70% (29.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –43.9 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 138.3, 129.6 (q, $^{1}J_{CF}$ = 306.2 Hz), 115.0, 114.9 (q, $^{3}J_{CF}$ = 2.2 Hz), 55.4.



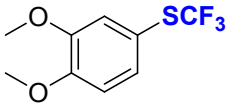
2c

(3-Methoxyphenyl)(trifluoromethyl)sulfane (**2c**, CAS:97675-15-5)[7]. Colorless oil; yield: 45% (18.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 1H), 7.25–7.23 (m, 1H), 7.18–7.17 (m, 1H), 7.04–7.01 (m, 1H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.6 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 130.2, 129.6 (q, $^{1}J_{CF}$ = 306.1 Hz), 128.4, 125.2 (q, $^{3}J_{CF}$ = 2.0 Hz), 121.2, 116.9, 55.5.



2d

(2-Methoxyphenyl)(trifluoromethyl)sulfane (**2d**, CAS:75168-99-9)[7]. Yellow oil; yield: 45% (18.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 1H), 7.46 (dd, J = 8.0, 1.6 Hz 1H), 6.98 (dd, J = 8.0, 1.6 Hz, 2H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 138.5, 132.9, 129.6 (q, $^{1}J_{CF}$ = 306.9 Hz), 121.2, 112.5 (q, $^{3}J_{CF}$ = 1.9 Hz), 111.8, 55.0.



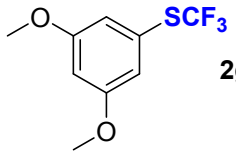
2e

(3,4-Dimethoxyphenyl)(trifluoromethyl)sulfane (**2e**, CAS:1893523-64-2). Light yellow oil; yield: 60% (28.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, J = 8.4, 2.8 Hz, 1H), 7.12 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –43.7 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ

151.5, 149.2, 130.2, 129.6 (q, $^{1}J_{CF}$ = 306.4 Hz), 119.0, 114.9 (q, $^{3}J_{CF}$ = 2.1 Hz), 114.6, 56.1, 56.0. HRMS (EI): calcd. for $C_9H_9F_3O_2S$ $[M]^+$: 238.0275, found: 238.0277.

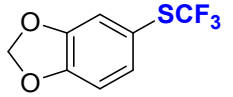
2f

(2,3-Dimethoxyphenyl)(trifluoromethyl)sulfane (**2f**, CAS:2023812-66-8). Colorless oil; yield: 65% (31.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 7.6 Hz, 1H), 7.10–7.06 (m, 1H), 7.02 (dd, *J* = 8.4, 1.6Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.7 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 150.6, 129.6 (q, $^{1}J_{CF}$ = 306.4 Hz), 128.1, 124.4, 119.1 (q, $^{3}J_{CF}$ = 1.9 Hz), 115.1, 61.1, 56.0. HRMS (EI): calcd. for $C_9H_9F_3O_2S$ $[M]^+$: 238.0275, found: 238.0277.



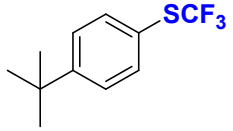
2g

(3,5-Dimethoxyphenyl)(trifluoromethyl)sulfane (**2g**). Colorless oil; yield: 75% (35.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 2.4 Hz, 2H), 6.55 (t, *J* = 2.4 Hz, 1H), 3.79 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 129.6 (q, $^{1}J_{CF}$ = 306.2 Hz), 125.6 (q, $^{3}J_{CF}$ = 2.1 Hz), 113.8, 103.2, 55.5. HRMS (EI): calcd. for $C_9H_9F_3O_2S$ $[M]^+$: 238.0275, found: 238.0277.



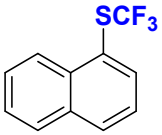
2h

5-((Trifluoromethyl)thio)benzo[d][1,3]dioxole (**2h**, CAS:1677706-17-0)[3]. Colorless oil; yield: 60% (26.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –43.9 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 148.3, 131.6, 129.5 (q, $^{1}J_{CF}$ = 306.5 Hz), 116.2, 115.9 (q, $^{3}J_{CF}$ = 2.2 Hz), 109.0, 101.9.



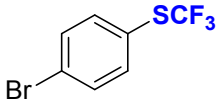
2i

(4-(Tert-butyl)phenyl)(trifluoromethyl)sulfane (**2i**, CAS:80783-57-9)[7]. Colorless oil; yield: 51% (23.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 1.33 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –43.0 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 136.1, 129.7 (q, $^{1}J_{CF}$ = 306.1 Hz), 126.6, 120.9 (q, $^{3}J_{CF}$ = 2.0 Hz), 34.9, 31.1.



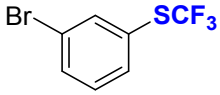
2j

Naphthalen-1-yl(trifluoromethyl)sulfane (**2j**, CAS:1373406-50-8)[5]. Colorless oil; yield: 60% (27.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.4 Hz, 1H), 7.98 (dd, J = 13.6, 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.66–7.62 (m, 1H), 7.58–7.54 (m, 1H), 7.51–7.47 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.2 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 135.4, 134.3, 132.4, 129.7 (q, $^{1}J_{CF}$ = 306.7 Hz), 128.6, 127.7, 126.8, 125.9, 125.6, 121.6 (q, $^{3}J_{CF}$ = 1.7 Hz).



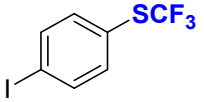
2k

(4-Bromophenyl)(trifluoromethyl)sulfane (**2k**, CAS:333-47-1)[3]. Colorless oil; yield: 60% (30.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.7 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 132.8, 129.2 (q, $^{1}J_{CF}$ = 306.5 Hz), 126.0, 123.5 (q, $^{3}J_{CF}$ = 2.2 Hz).



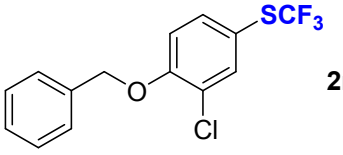
2l

(3-Bromophenyl)(trifluoromethyl)sulfane (**2l**, CAS:2252-45-1)[9]. Colorless oil; yield: 35% (18.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.64–7.59 (m, 2H), 7.33–7.26 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 134.8, 134.0, 130.8, 129.3 (q, $^{1}J_{CF}$ = 306.6 Hz), 126.3 (q, $^{3}J_{CF}$ = 2.1 Hz), 122.9.



2m

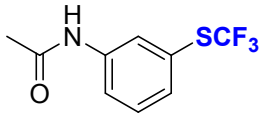
(4-Iodophenyl)(trifluoromethyl)sulfane (**2m**, CAS:372-15-6)[11]. Colorless oil; yield: 65% (39.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.6 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 137.7, 129.2 (q, $^{1}J_{CF}$ = 306.5 Hz), 124.2 (q, $^{3}J_{CF}$ = 2.1 Hz), 98.0.



2n

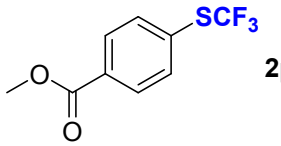
(4-(Benzyloxy)-3-chlorophenyl)(trifluoromethyl)sulfane (**2n**). Yellow oil; yield: 78% (51.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 2.0 Hz, 1H), 7.47–7.42 (m, 3H), 7.40–7.30 (m, 3H), 6.95 (d, J = 8.4 Hz, 1H), 5.15 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –43.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 138.1, 136.5, 135.7, 129.4 (q, $^{1}J_{CF}$ = 306.6 Hz), 128.8, 128.3, 127.1, 123.9, 115.9 (q, $^{3}J_{CF}$ = 2.3 Hz), 114.0, 70.9. HRMS (EI): calcd.

for $C_{14}H_{10}ClF_3OS$ $[M]^+$: 318.0093, found: 318.0096.



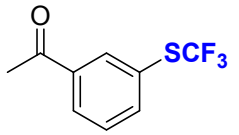
2o

***N*-(3-((Trifluoromethyl)thio)phenyl)acetamide** (**2o**, CAS:351-29-1). White solid; mp: 129.0–130.1 °C; yield: 72% (33.9 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.23 (s, 1H), 8.09 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.49–7.45 (m, 1H), 7.37 (d, J = 7.6 Hz, 1H), 2.09 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6): δ –42.1 (s, 3F). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.7, 140.5, 130.2, 130.1, 129.6 (q, $^1J_{CF}$ = 305.8 Hz), 125.7, 123.1 (q, $^3J_{CF}$ = 1.9 Hz), 121.5, 23.9. HRMS (EI): calcd. for $C_9H_8F_3NOS$ $[M]^+$: 235.0279, found: 235.0280.



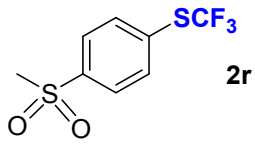
2p

Methyl-4-((trifluoromethyl)thio)benzoate (**2p**, CAS:88489-60-5)[3]. Colorless oil; yield: 71% (33.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 3.9 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.8 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 135.6, 132.2, 130.4, 129.9 (q, $^3J_{CF}$ = 2.0 Hz), 129.3 (q, $^1J_{CF}$ = 306.4 Hz), 52.5.



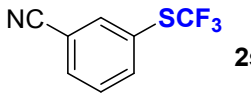
2q

1-(3-((Trifluoromethyl)thio)phenyl)ethan-1-one (**2q**, CAS:56773-33-2)[8]. Colorless oil; yield: 70% (30.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.09–8.06 (m, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.57–7.53 (m, 1H), 2.64 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.5 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 140.4, 138.3, 136.0, 130.5, 129.8, 129.4 (q, $^1J_{CF}$ = 306.4 Hz), 125.4 (q, $^3J_{CF}$ = 2.1 Hz), 26.6.



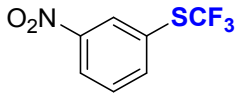
2r

(4-(Methylsulfonyl)phenyl)(trifluoromethyl)sulfane (**2r**, CAS:1373406-51-9)[3]. White solid; mp: 83.5–84.7 °C; yield: 55% (28.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 3.10 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 136.2, 131.5 (q, $^3J_{CF}$ = 2.2 Hz), 129.1 (q, $^1J_{CF}$ = 306.8 Hz), 128.4, 44.4.



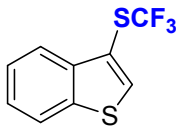
2s

3-((Trifluoromethyl)thio)benzonitrile (**2s**, CAS:660-44-6)[10]. Colorless oil; yield: 65% (26.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.81–7.78 (m, 1H), 7.60–7.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.1 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 139.3, 134.3, 130.4, 129.0 (q, $^{1}J_{CF}$ = 306.8 Hz), 126.5 (q, $^{3}J_{CF}$ = 2.3 Hz), 117.3, 114.1.



2t

(3-Nitrophenyl)(trifluoromethyl)sulfane (**2t**, CAS:370-47-8)[4]. Light yellow oil; yield: 55% (24.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54–8.53 (m, 1H), 8.39–8.36 (m, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.69–7.65 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.1 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 141.8, 130.8, 130.5, 129.0 (q, $^{1}J_{CF}$ = 306.9 Hz), 126.7 (q, $^{3}J_{CF}$ = 2.3 Hz), 125.7.

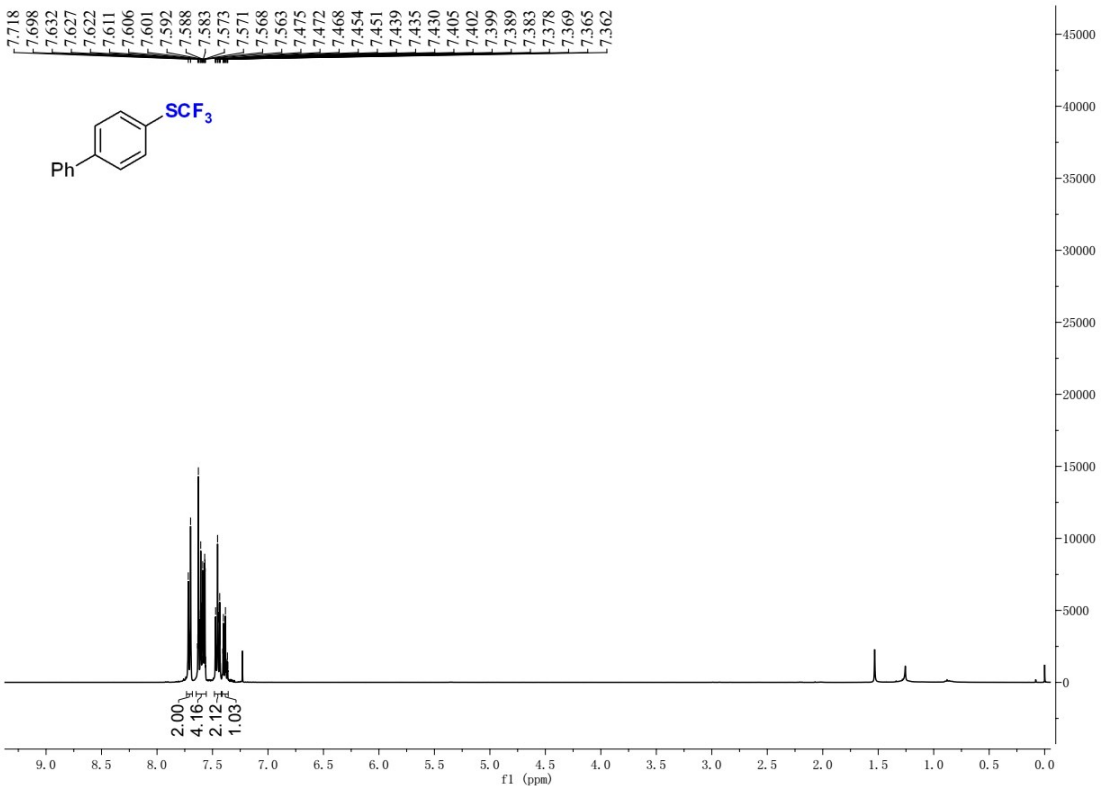


2u

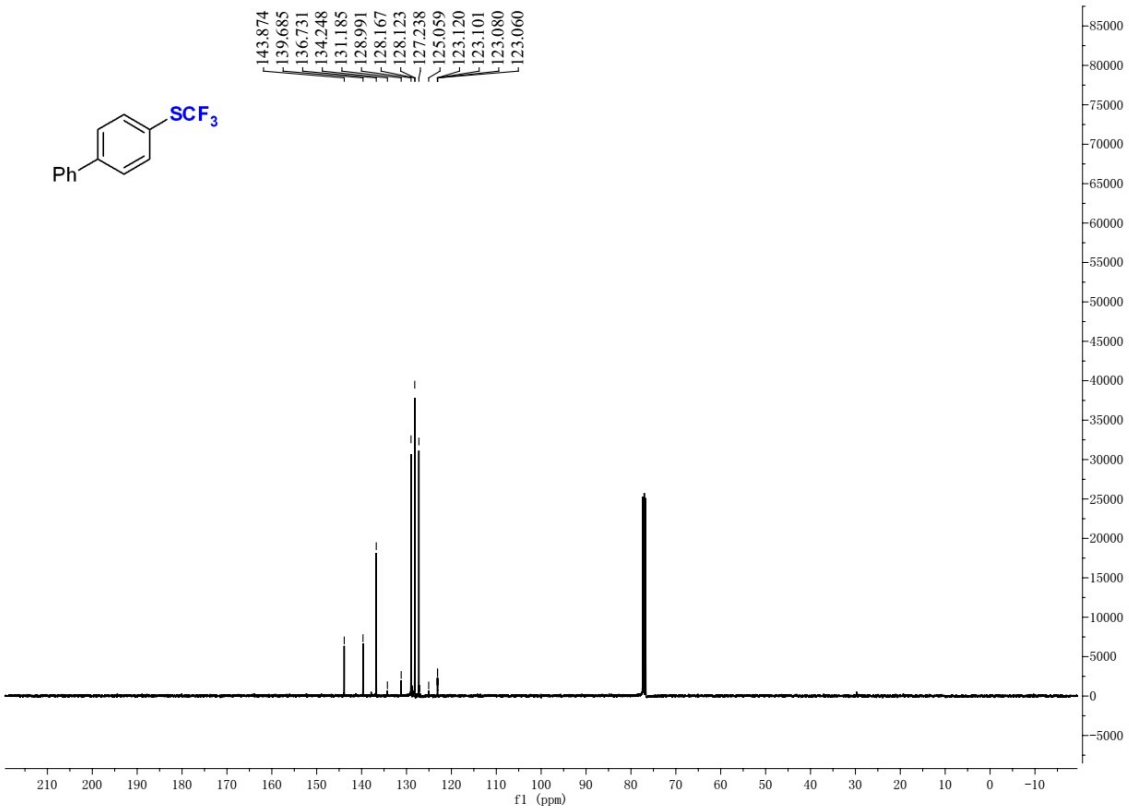
3-((Trifluoromethyl)thio)benzo[b]thiophene (**2u**, CAS:1333415-87-4)[7]. Colorless oil; yield: 50% (23.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 1H), 7.97 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.53–7.49 (m, 1H), 7.46–7.42 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –42.6 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 139.4, 137.9, 129.0 (q, $^{1}J_{CF}$ = 308.1 Hz), 125.4, 125.3, 122.9, 122.8, 115.2 (q, $^{3}J_{CF}$ = 2.0 Hz).

8 ^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of target compounds

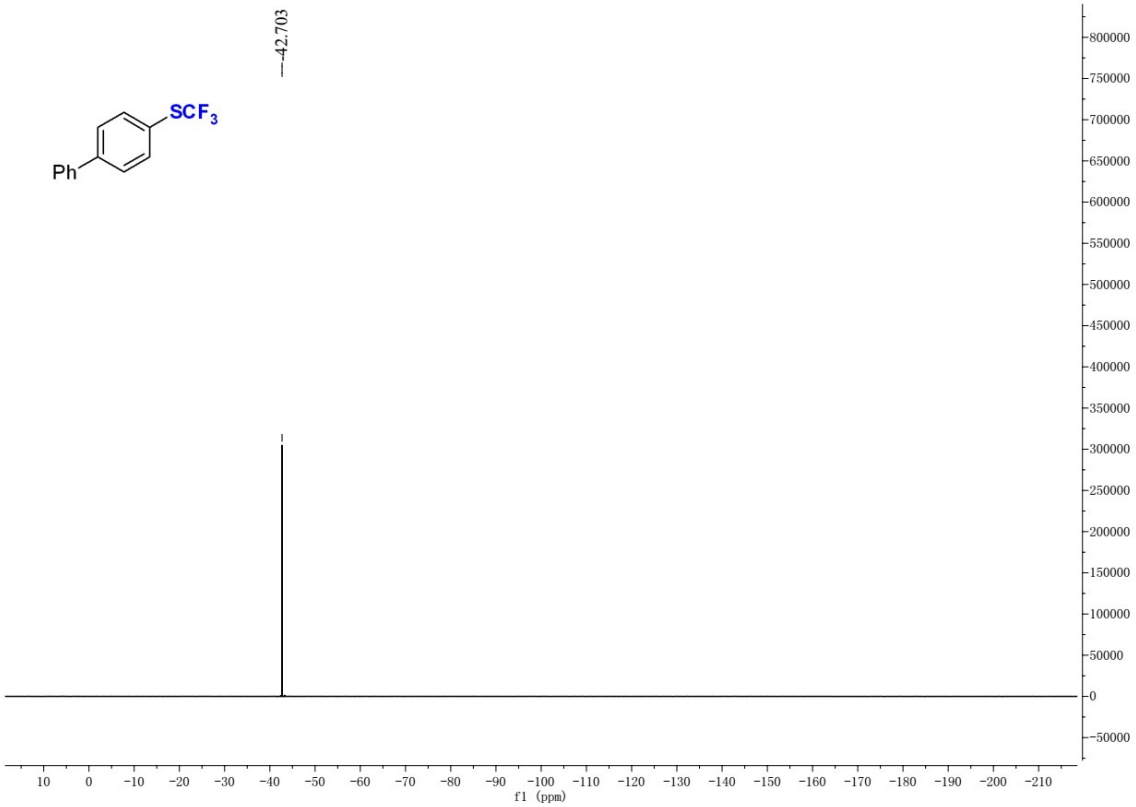
^{1}H NMR spectrum of **2a**



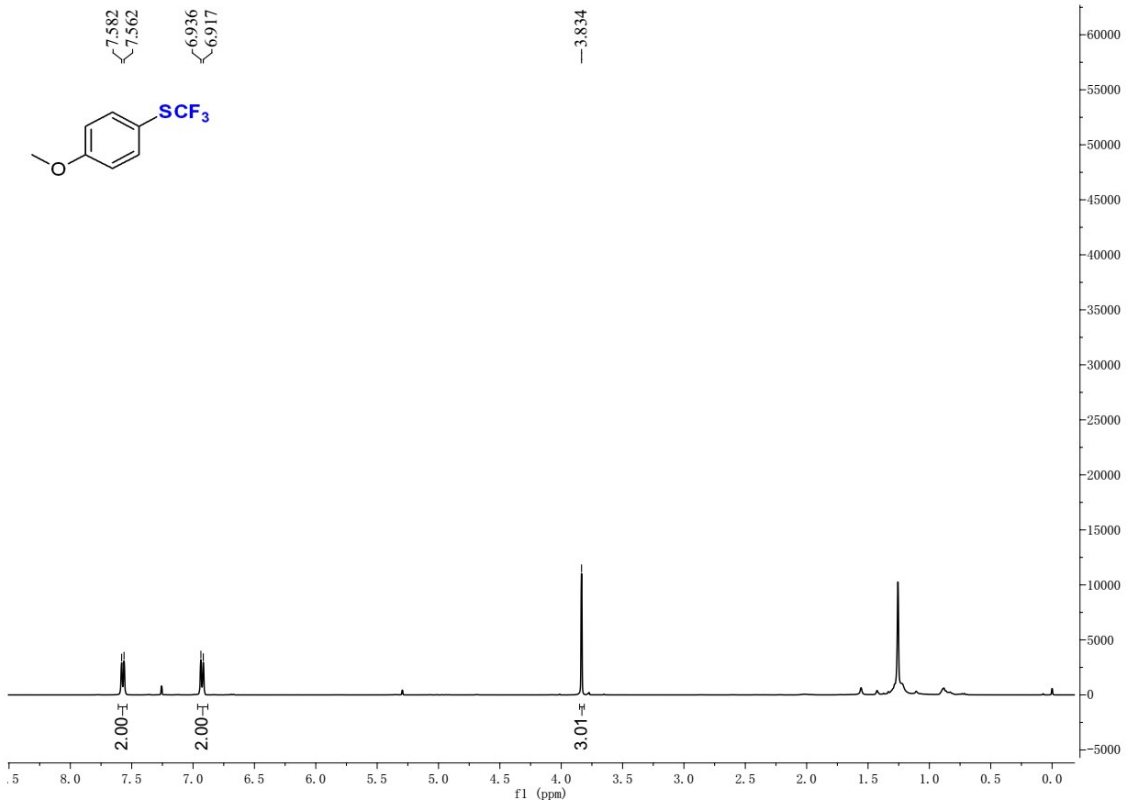
^{13}C NMR spectrum of **2a**



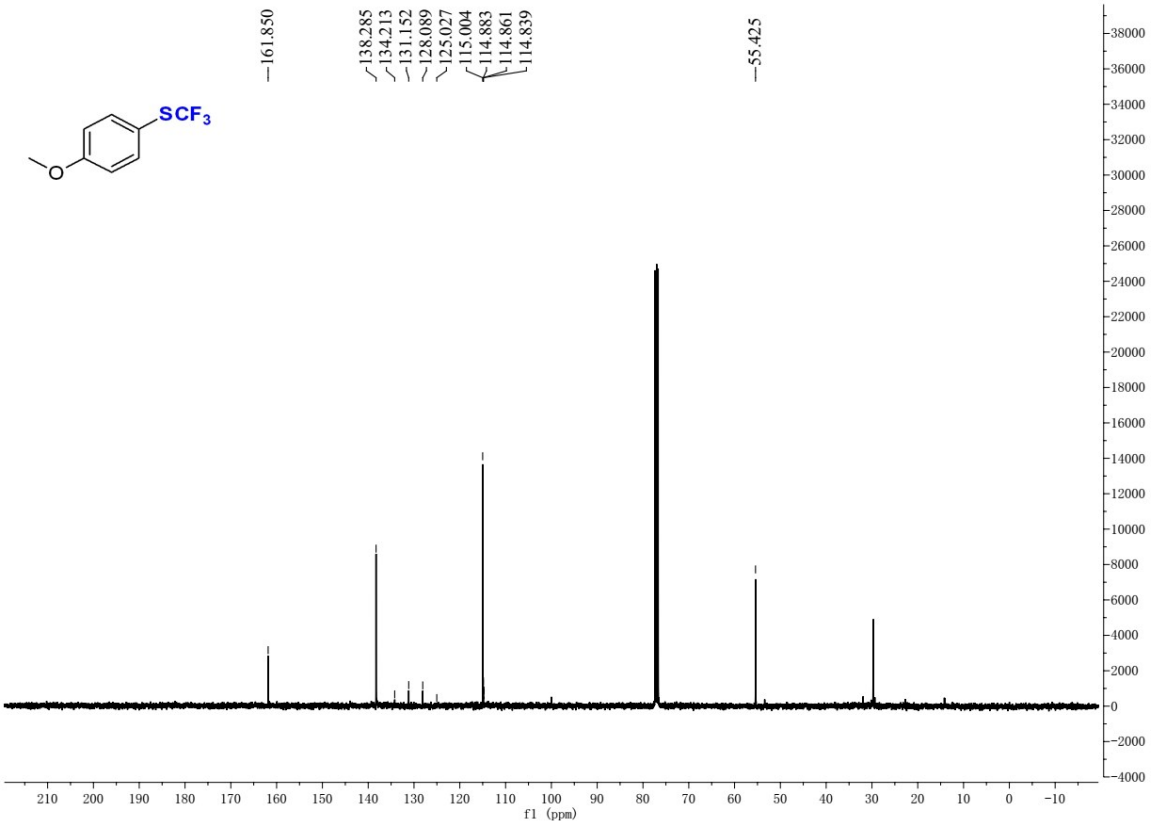
^{19}F NMR spectrum of **2a**



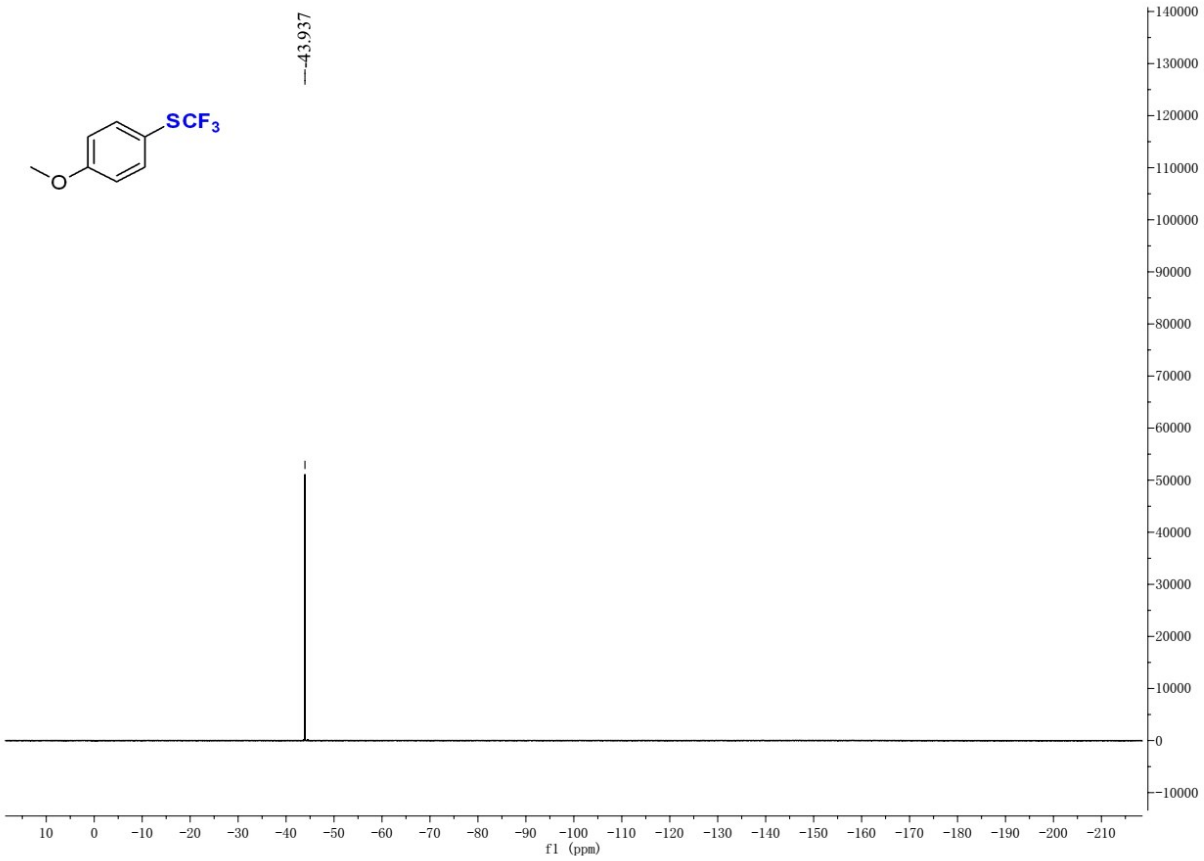
^{1}H NMR spectrum of **2b**



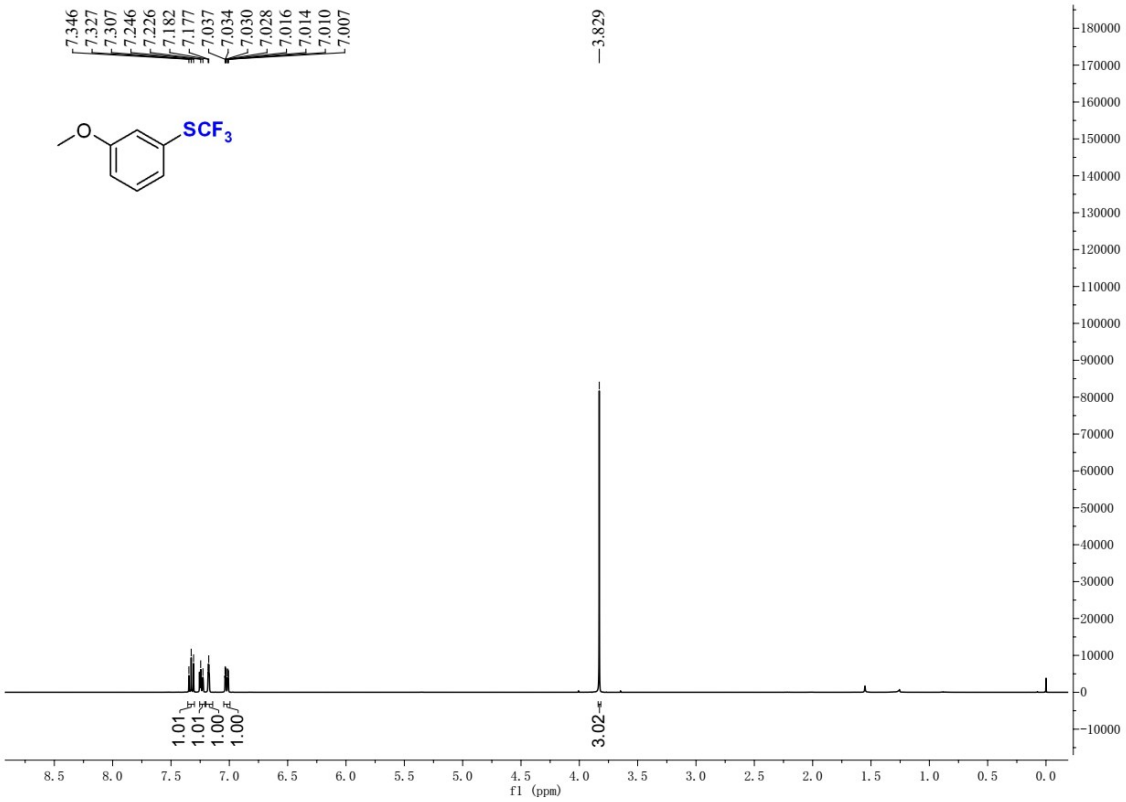
^{13}C NMR spectrum of **2b**



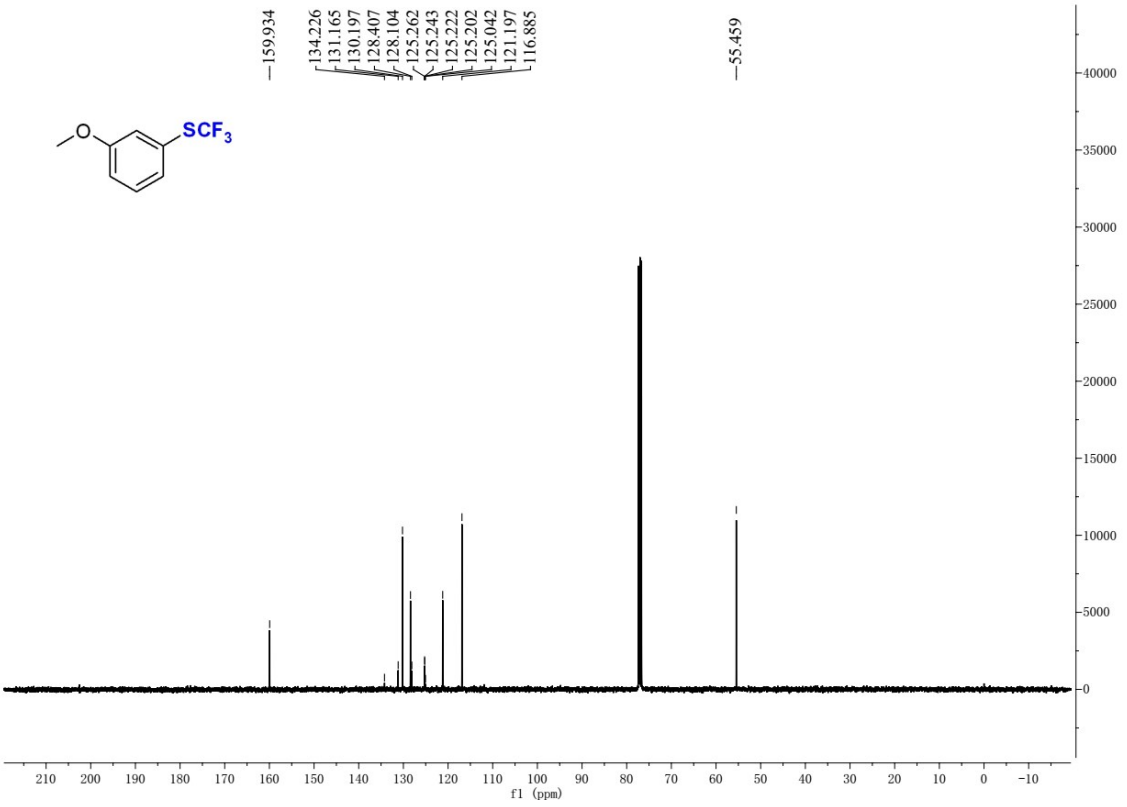
^{19}F NMR spectrum of **2b**



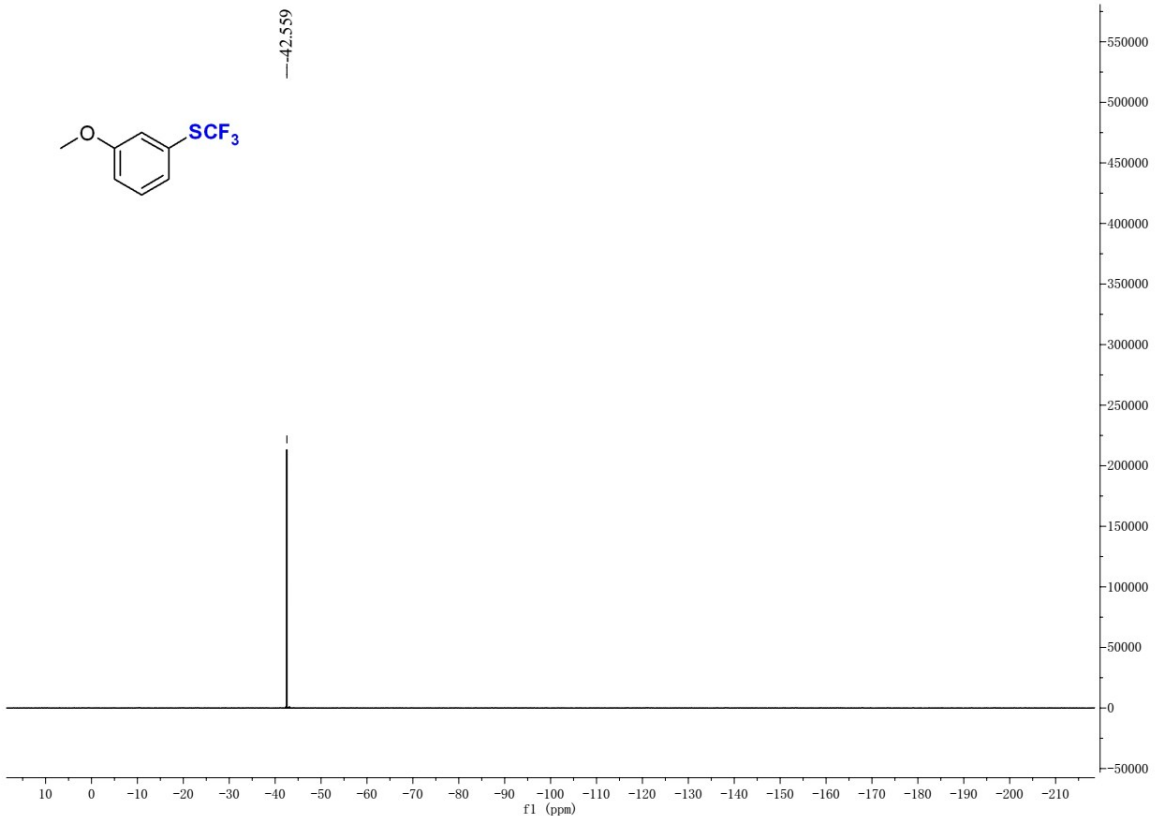
^{1}H NMR spectrum of **2c**



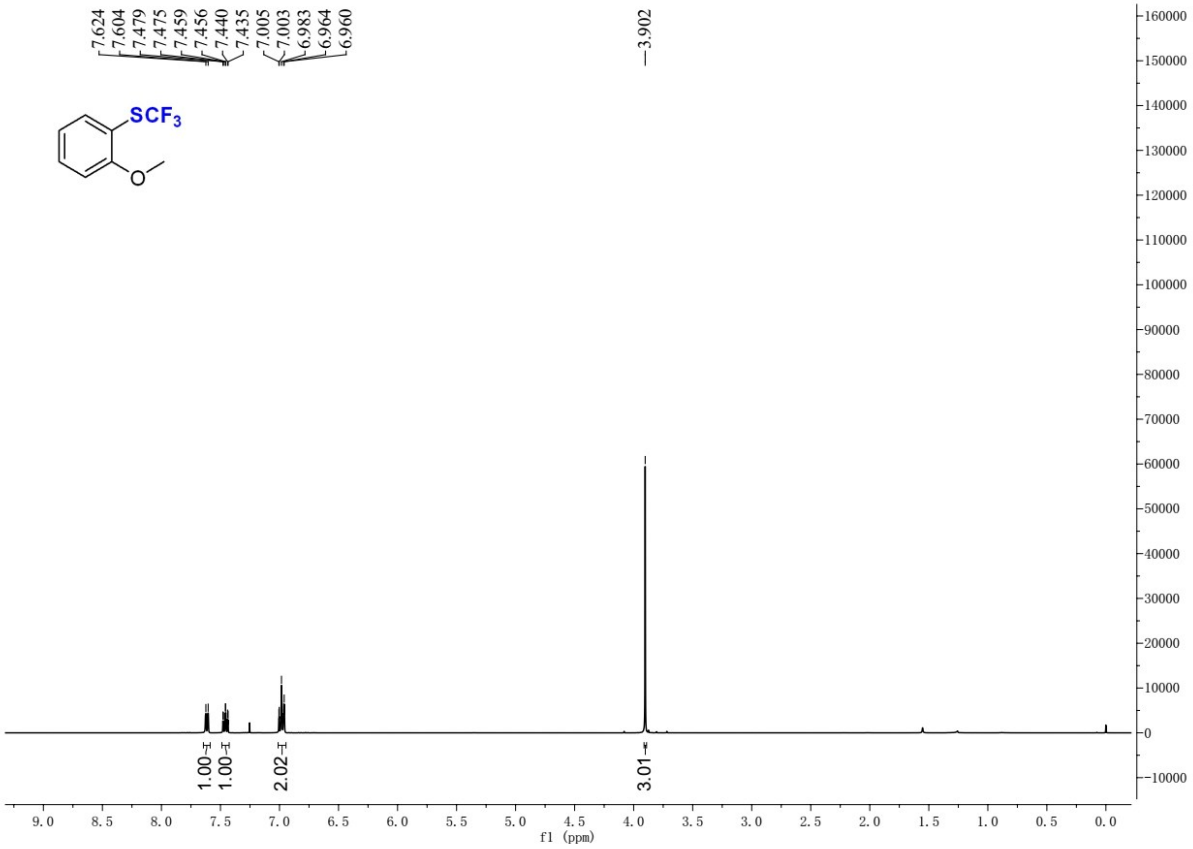
^{13}C NMR spectrum of **2c**



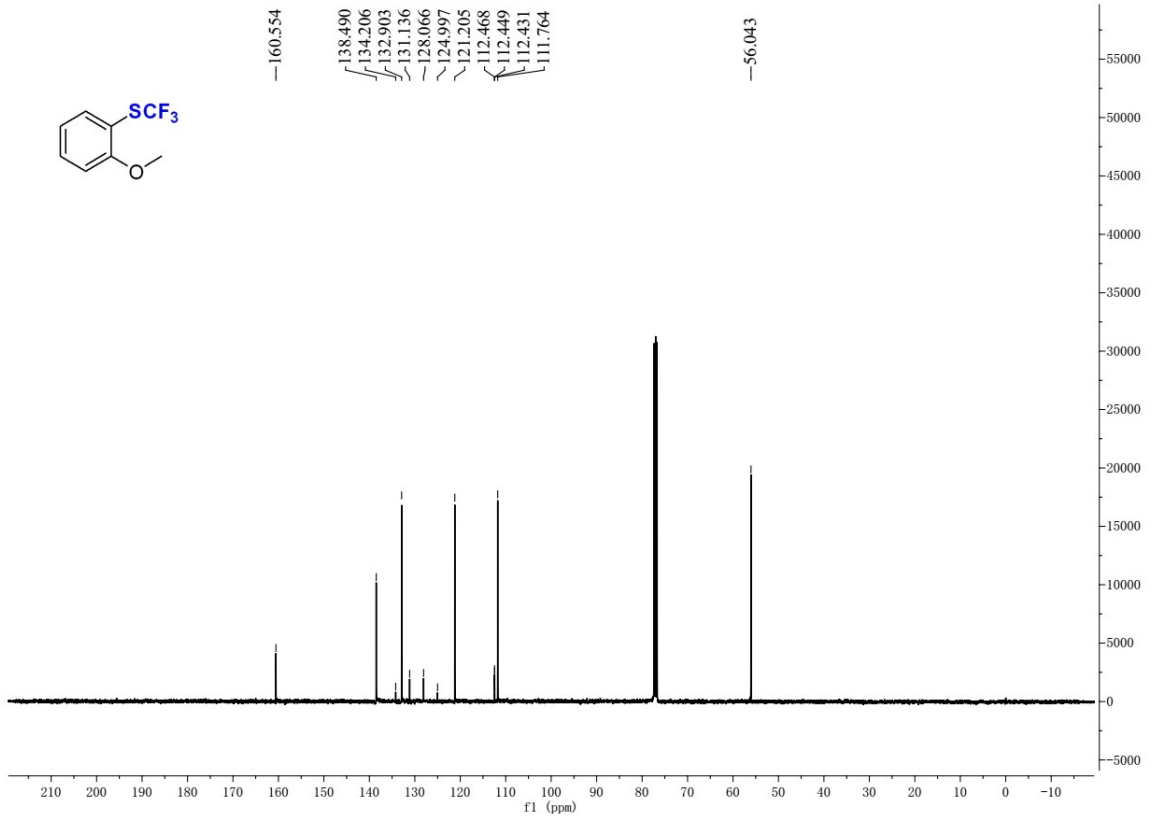
^{19}F NMR spectrum of **2c**



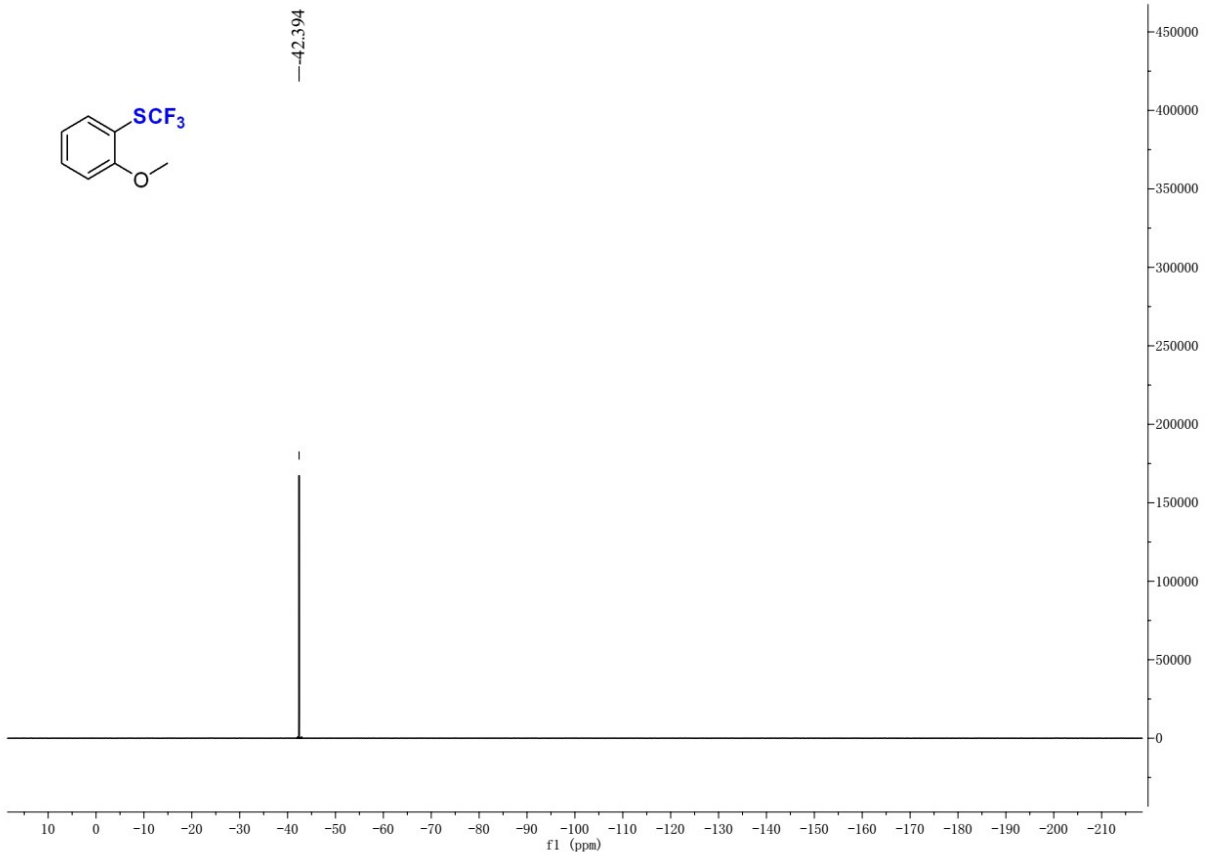
^{1}H NMR spectrum of **2d**



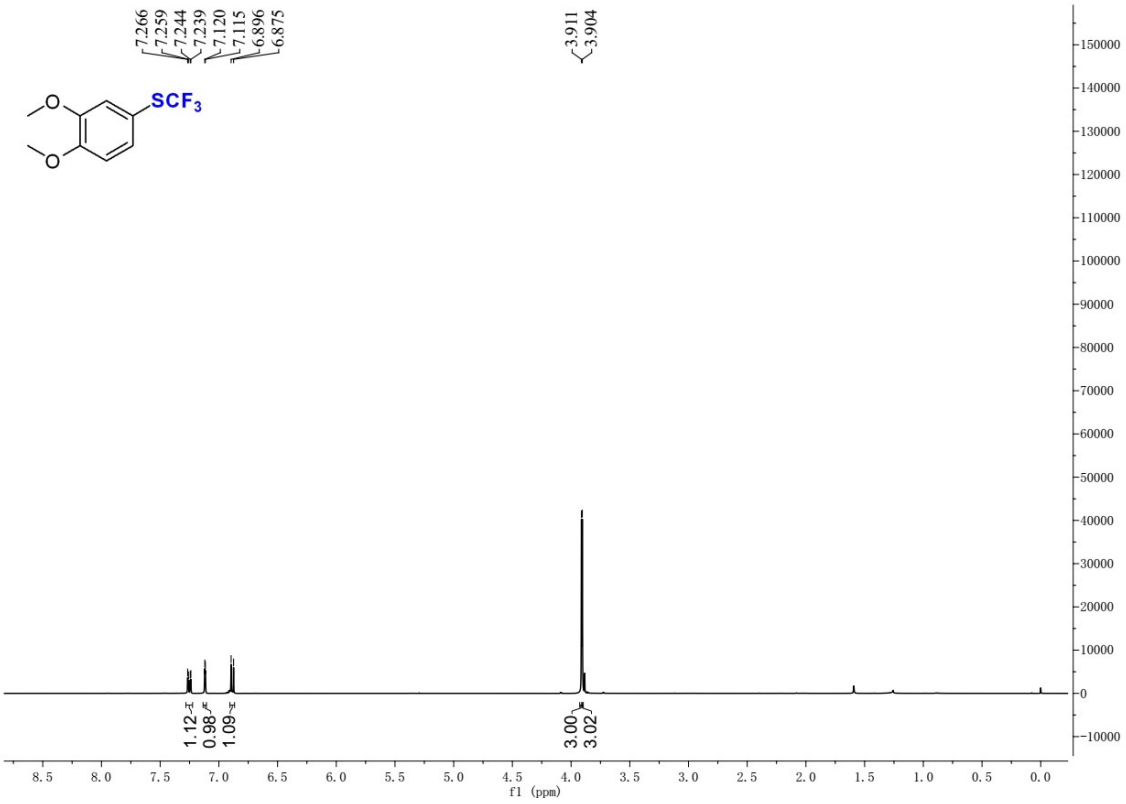
^{13}C NMR spectrum of **2d**



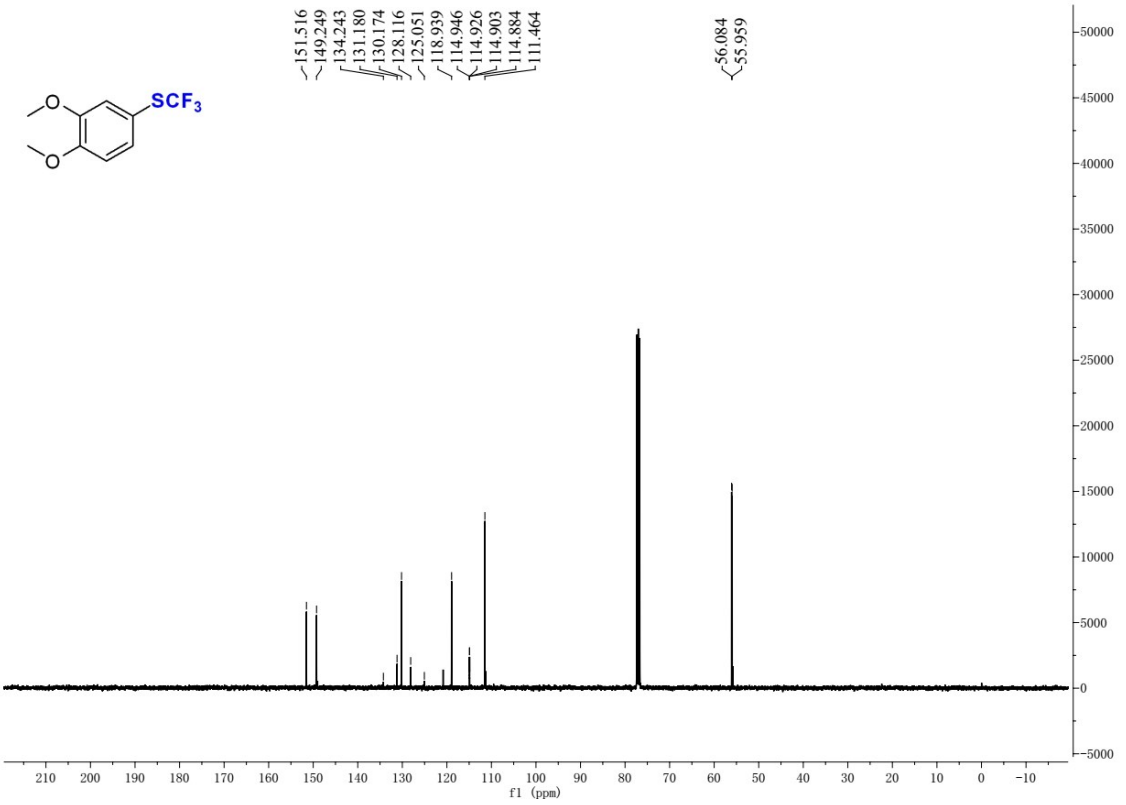
^{19}F NMR spectrum of **2d**



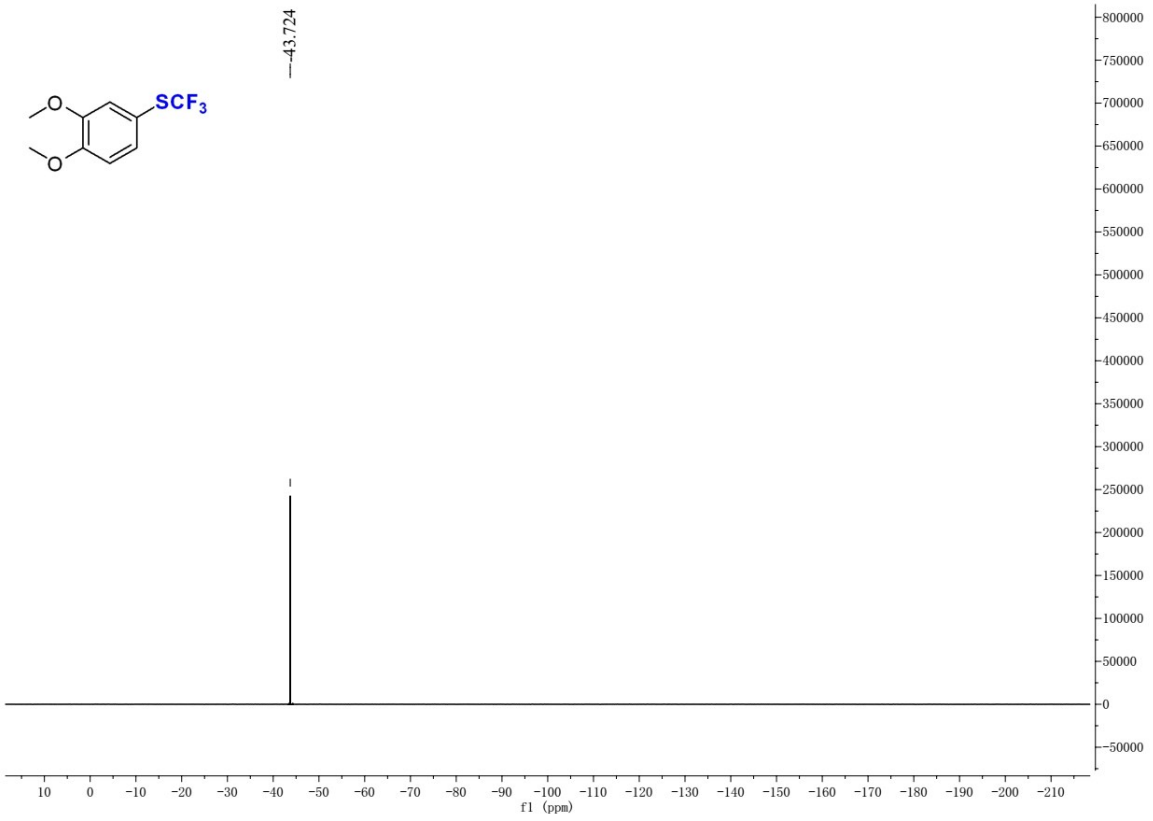
^{1}H NMR spectrum of **2e**



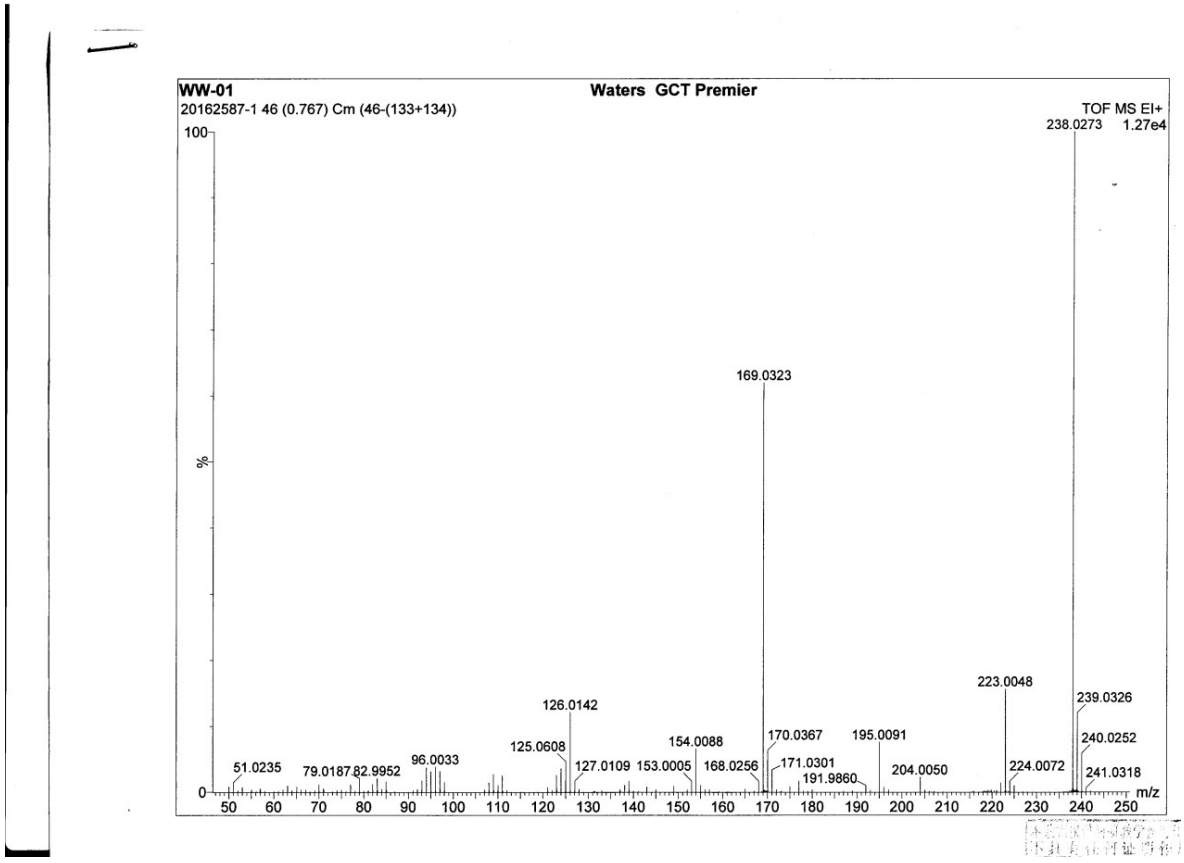
^{13}C NMR spectrum of **2e**



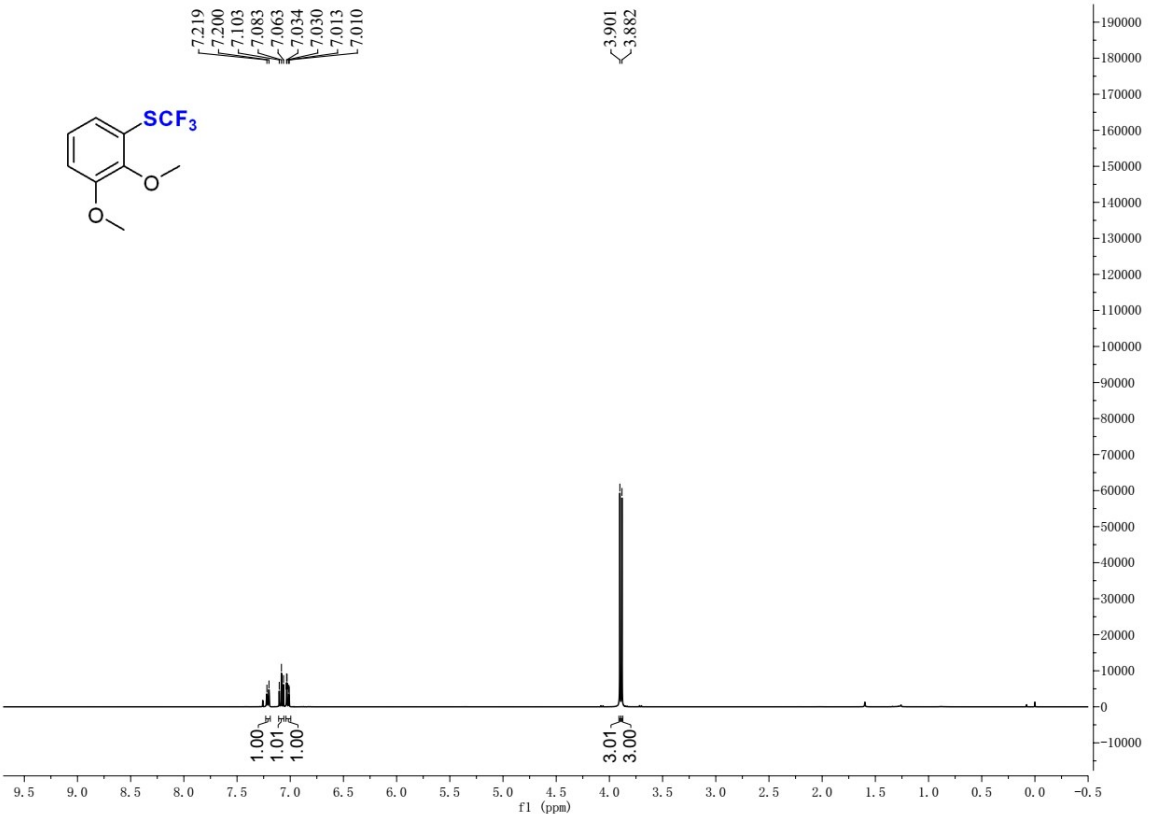
^{19}F NMR spectrum of **2e**



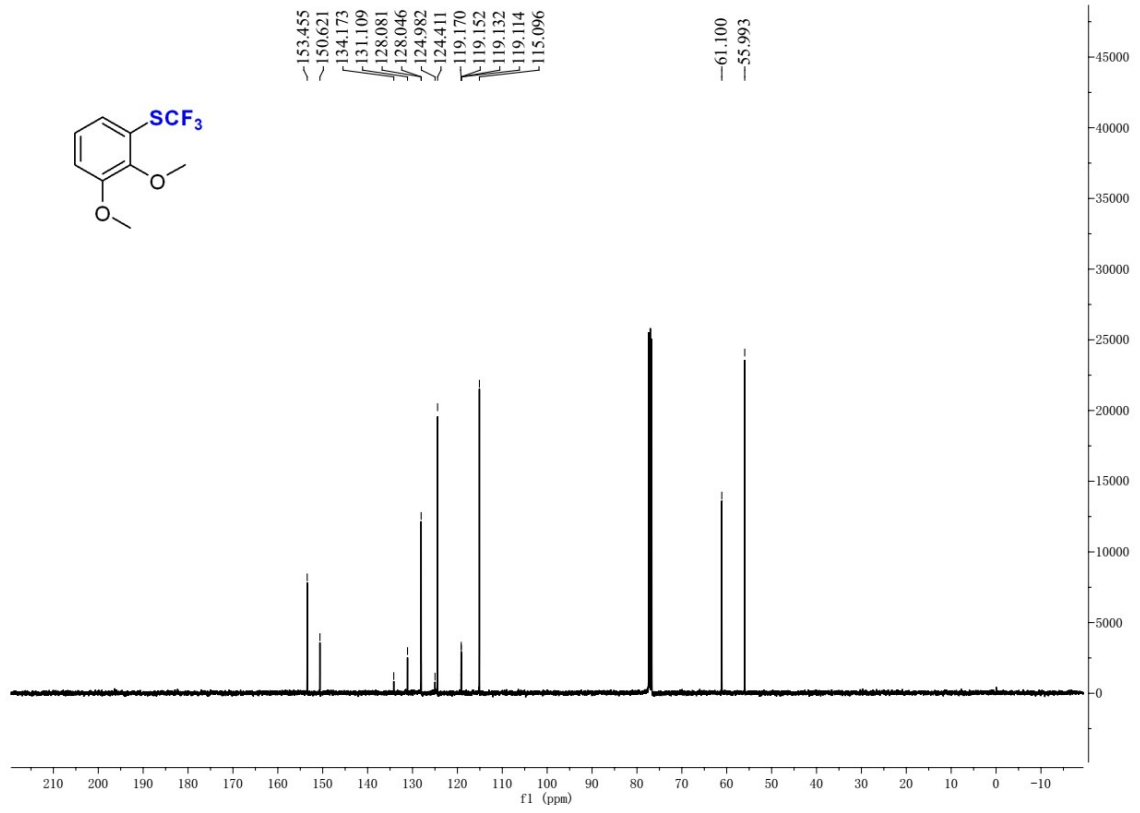
HRMS (EI) of **2e**



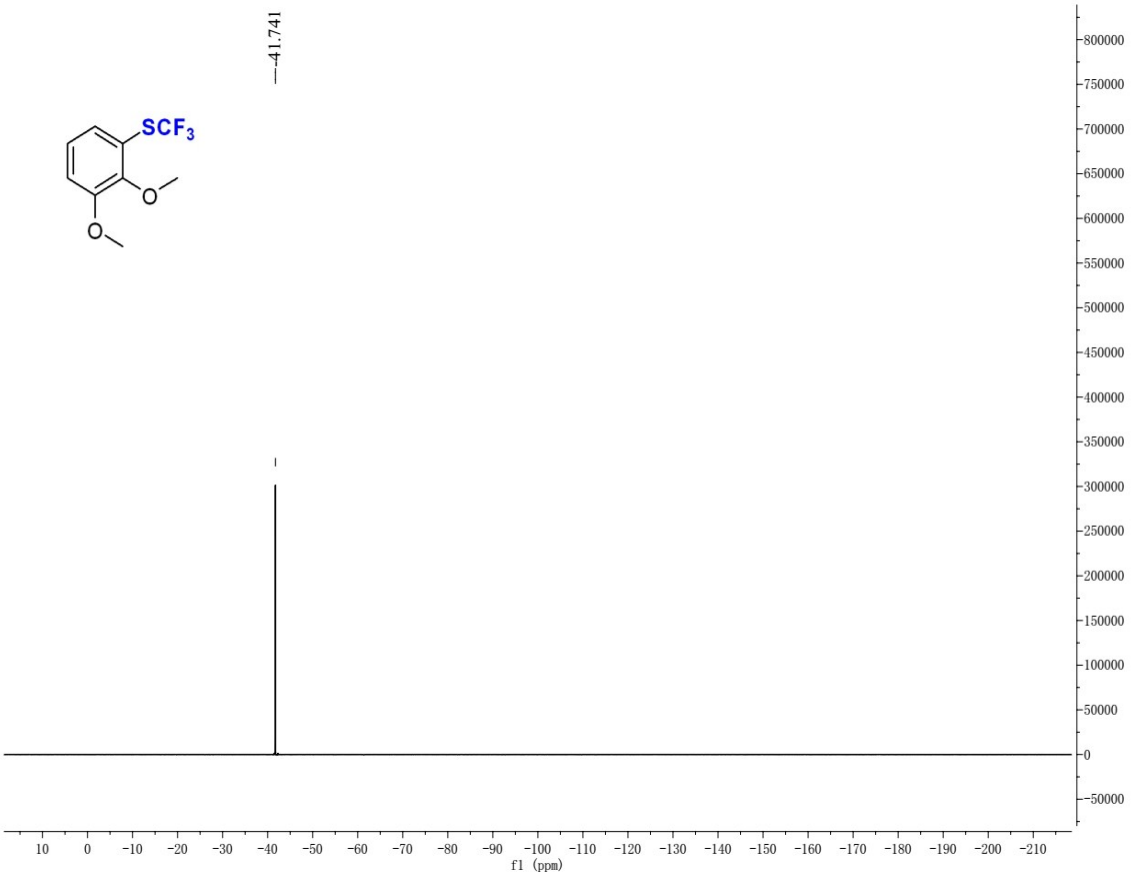
^{1}H NMR spectrum of **2f**



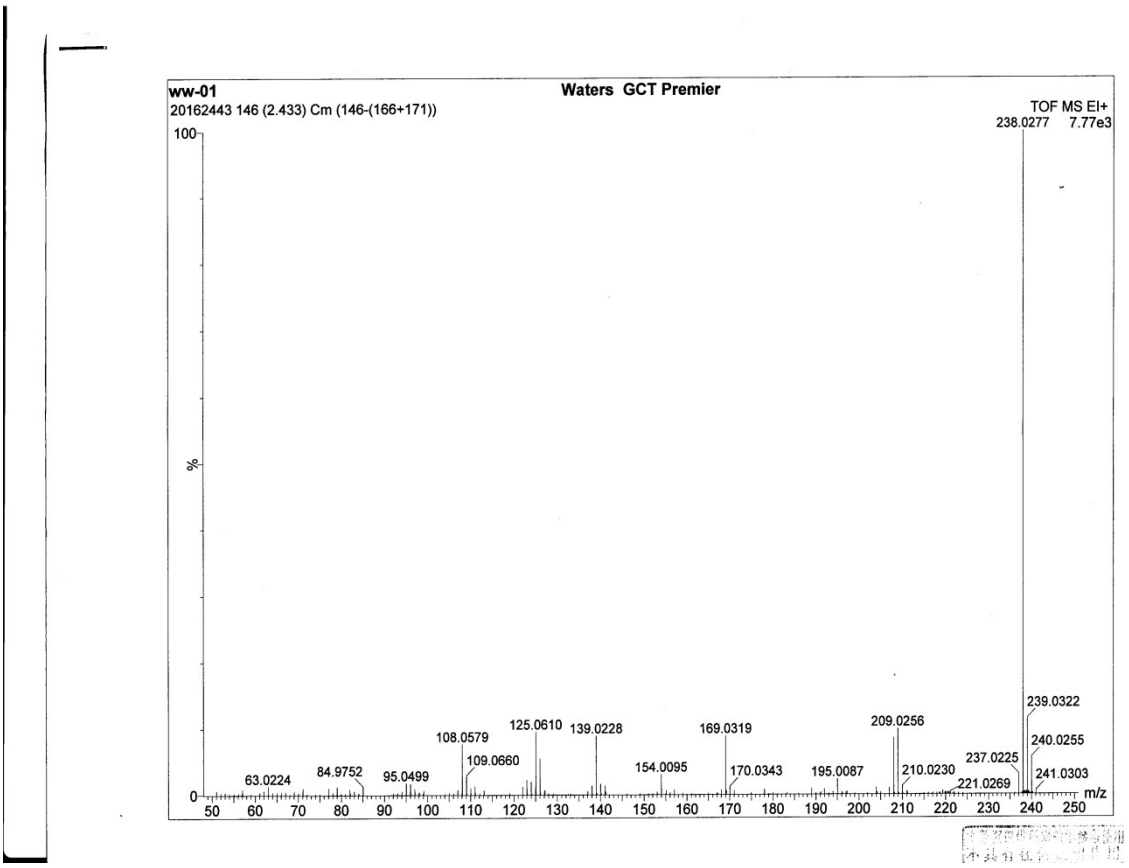
^{13}C NMR spectrum of **2f**



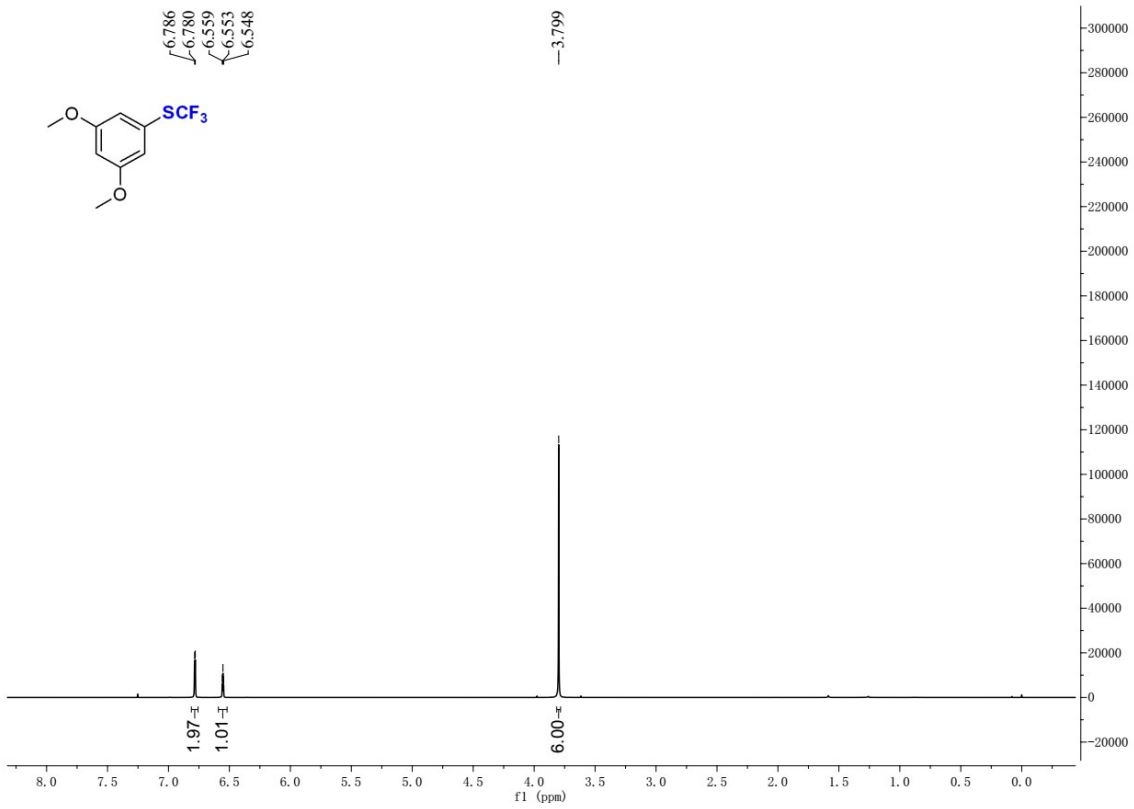
^{19}F NMR spectrum of **2f**



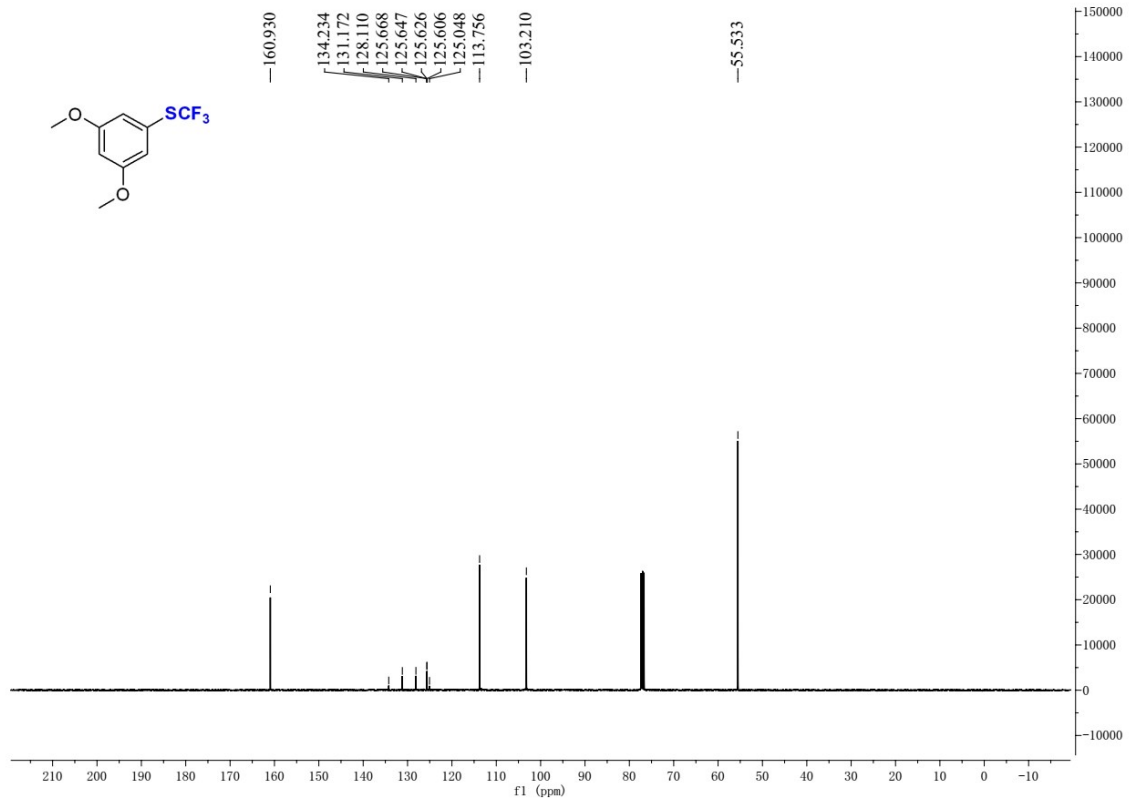
HRMS (EI) of **2f**



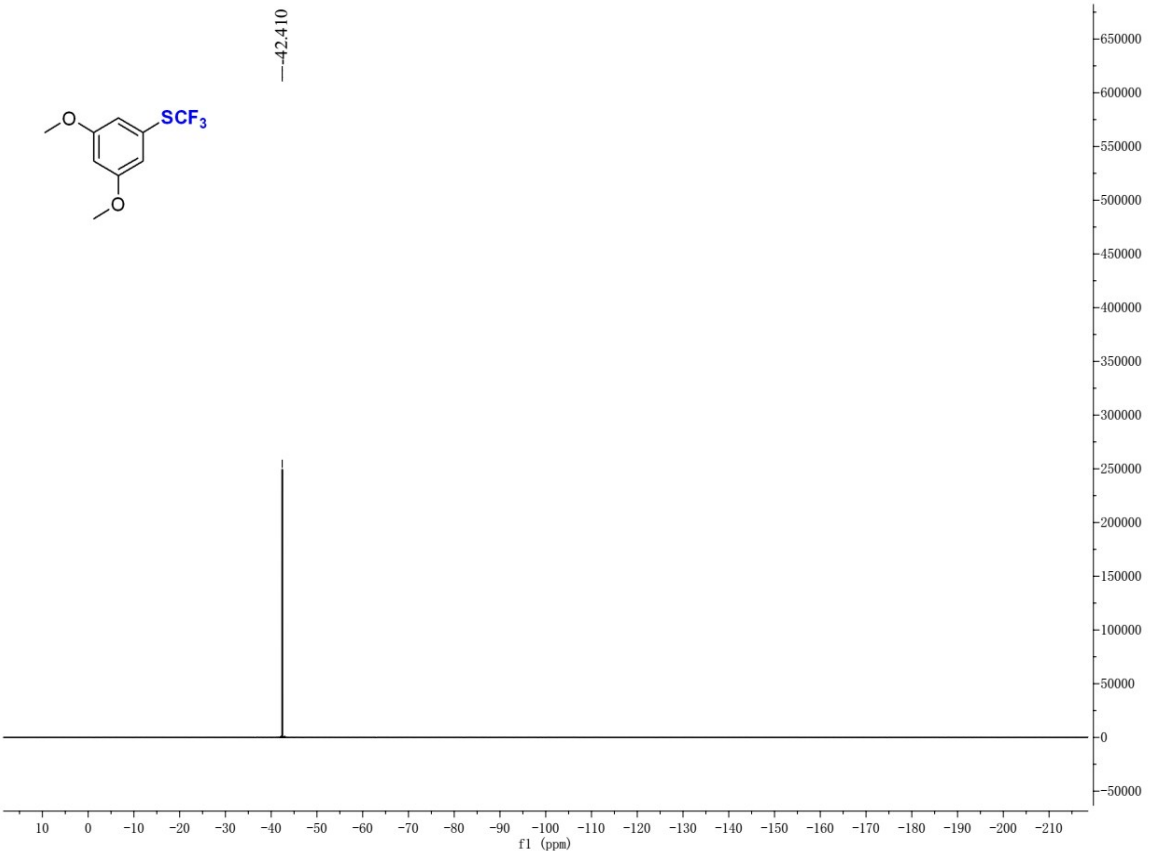
^{1}H NMR spectrum of **2g**



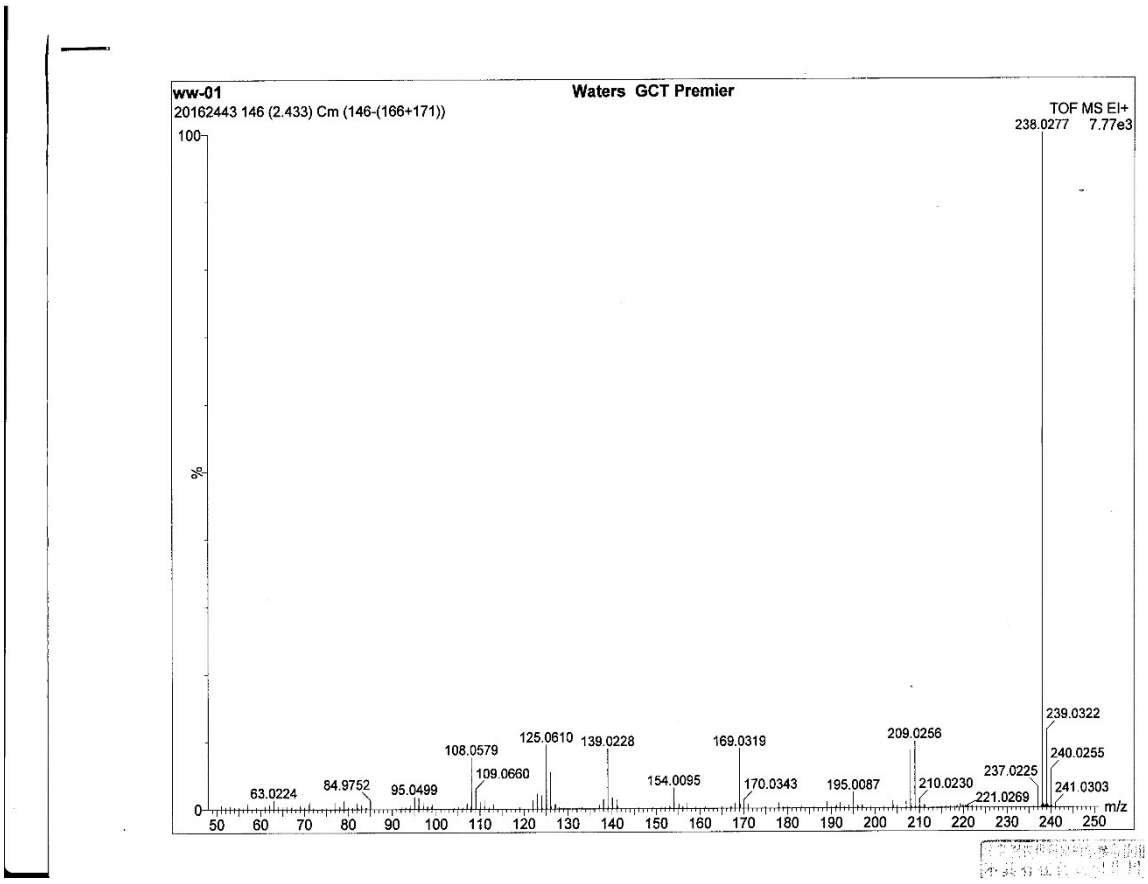
^{13}C NMR spectrum of **2g**



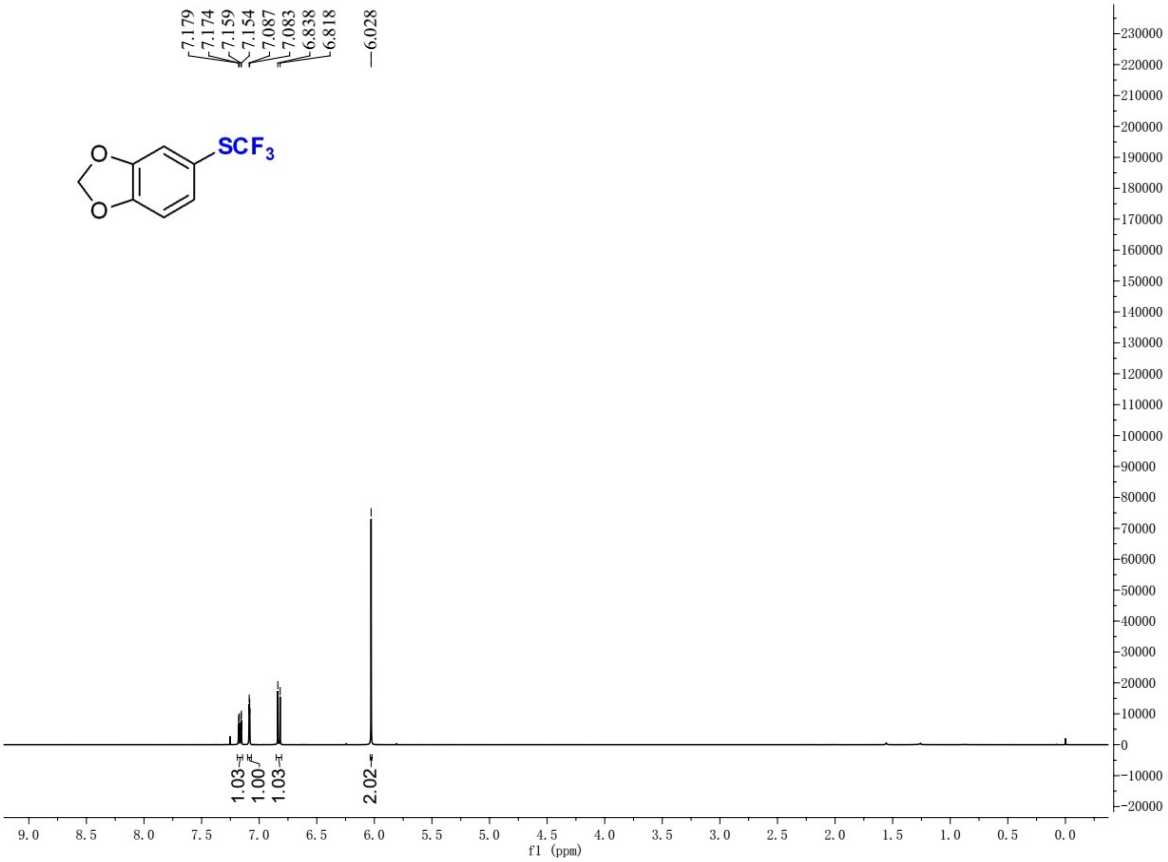
^{19}F NMR spectrum of **2g**



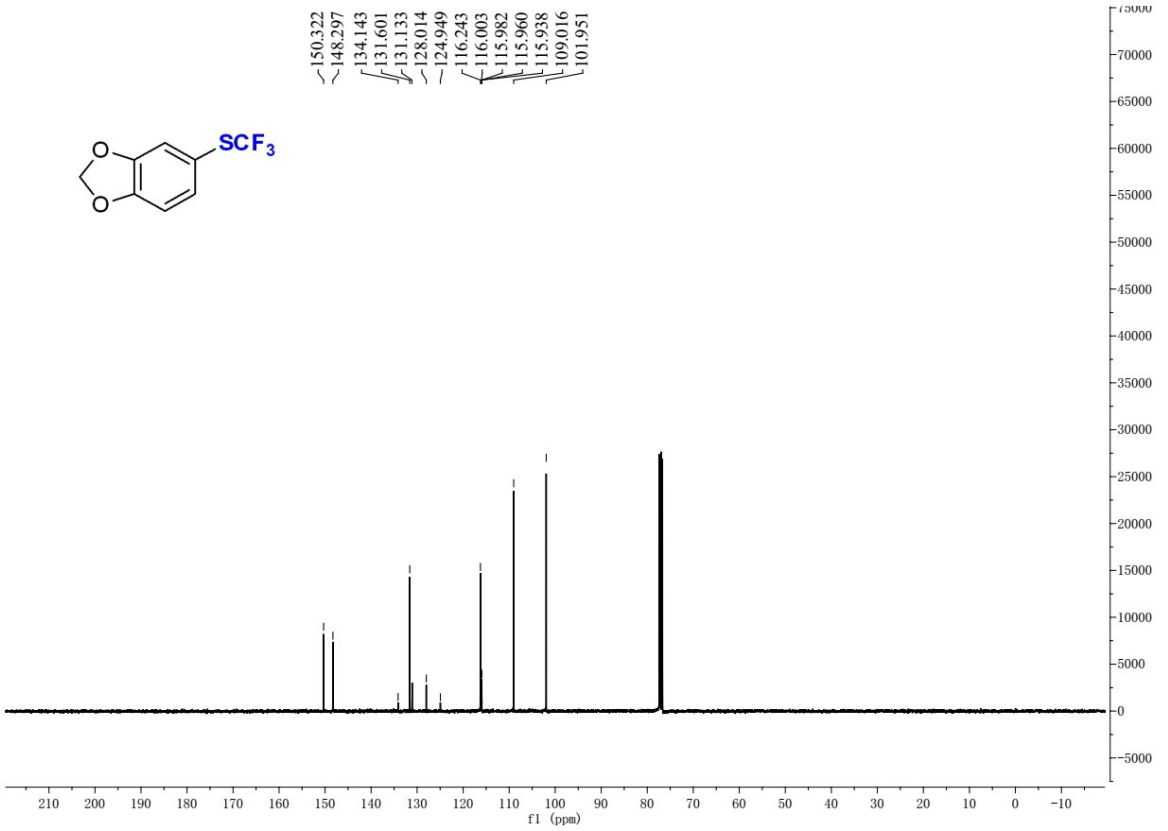
HRMS (EI) of **2g**



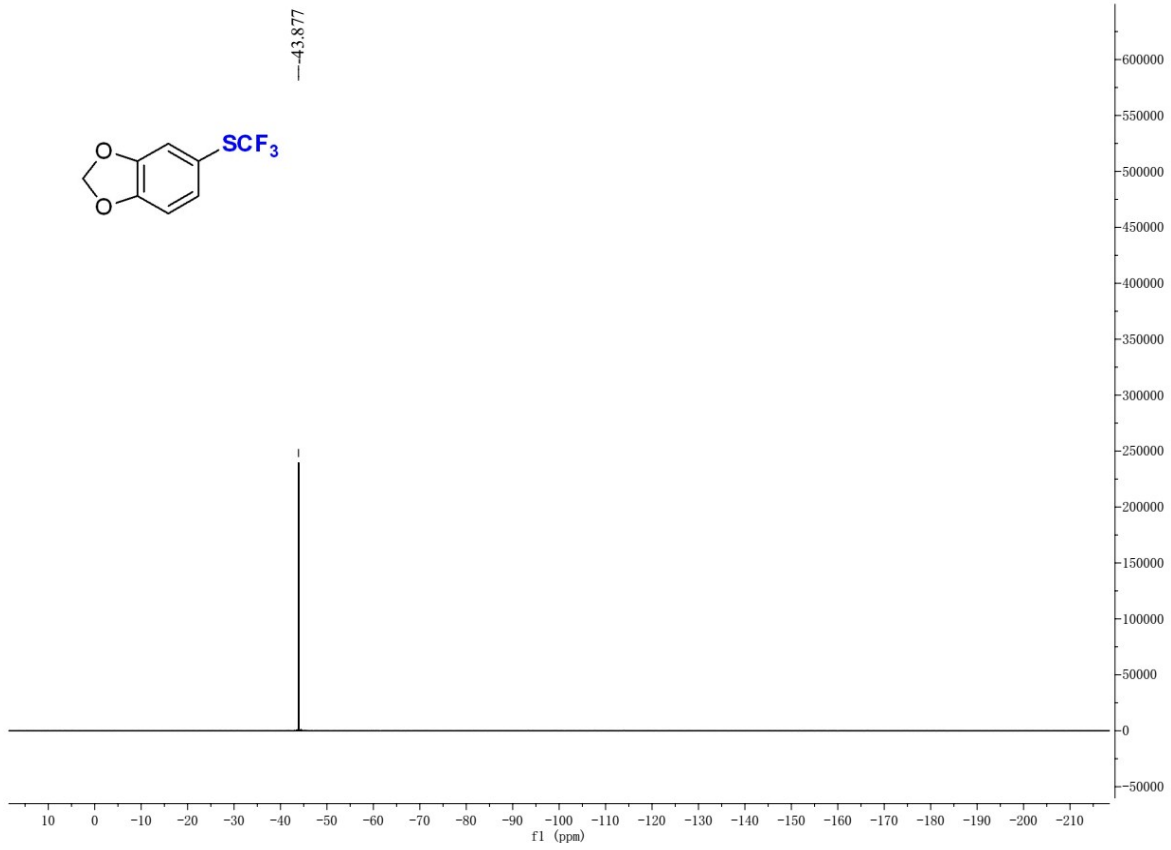
^{1}H NMR spectrum of **2h**



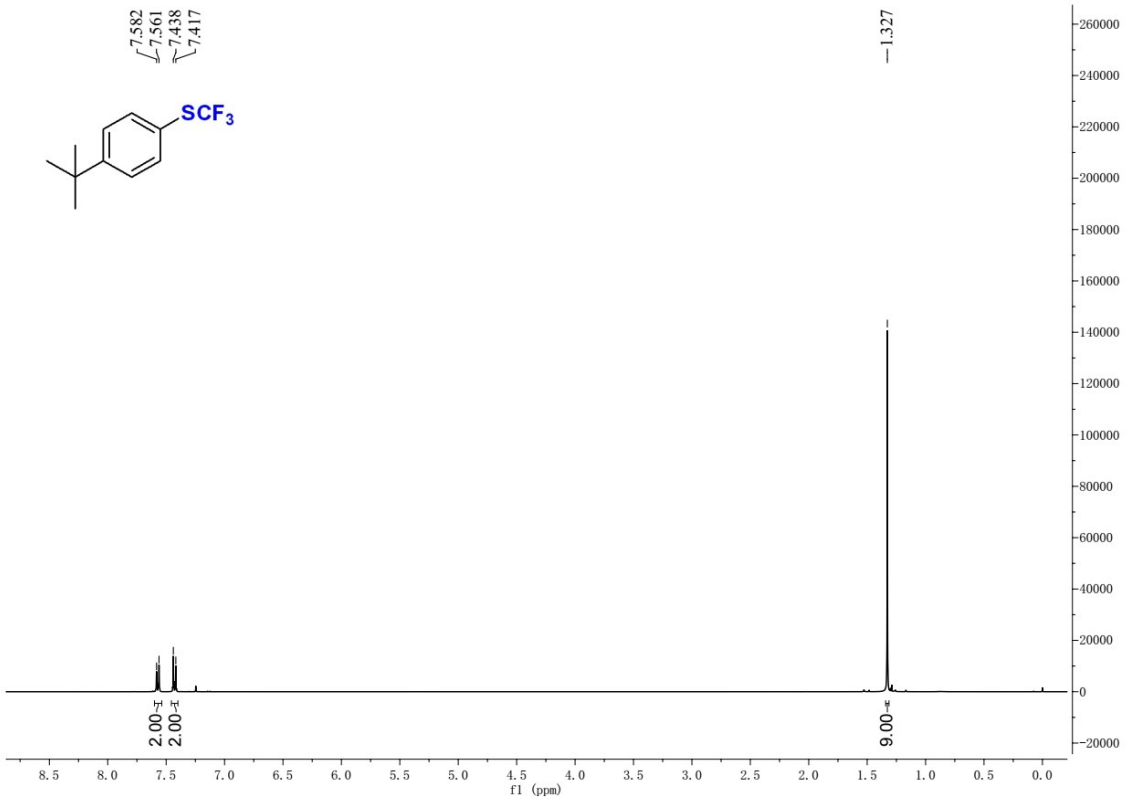
^{13}C NMR spectrum of **2h**



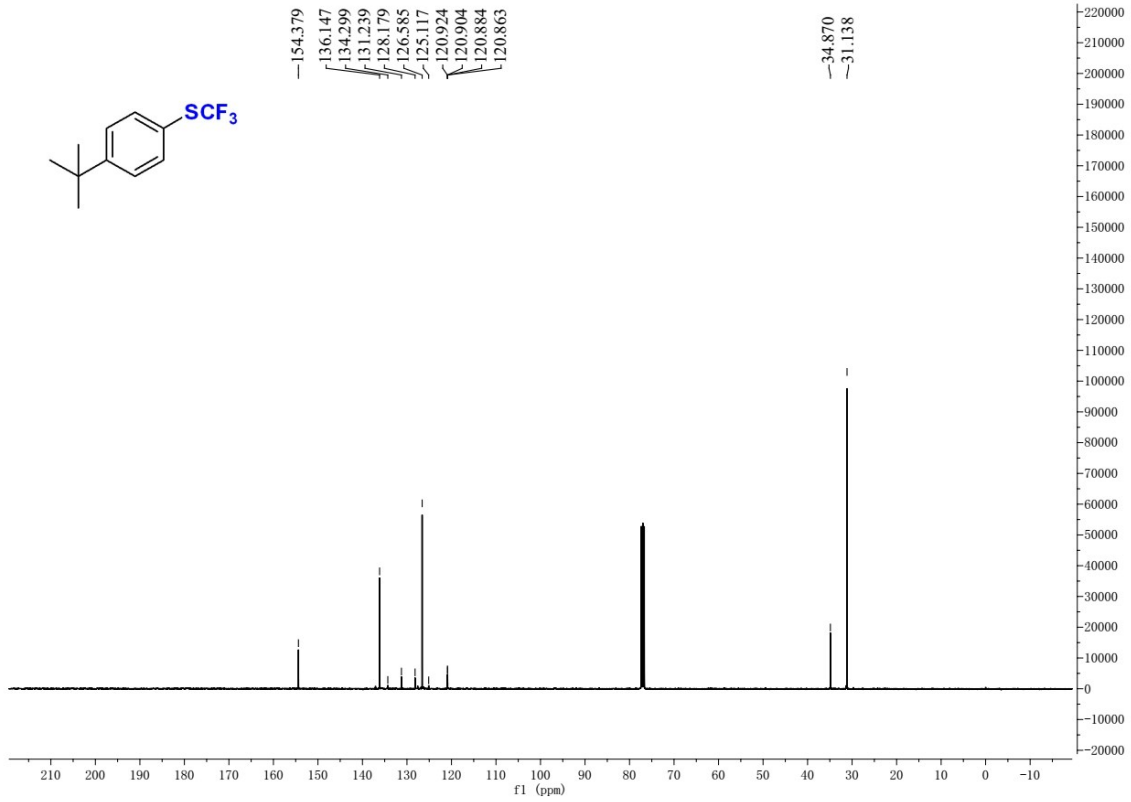
^{19}F NMR spectrum of **2h**



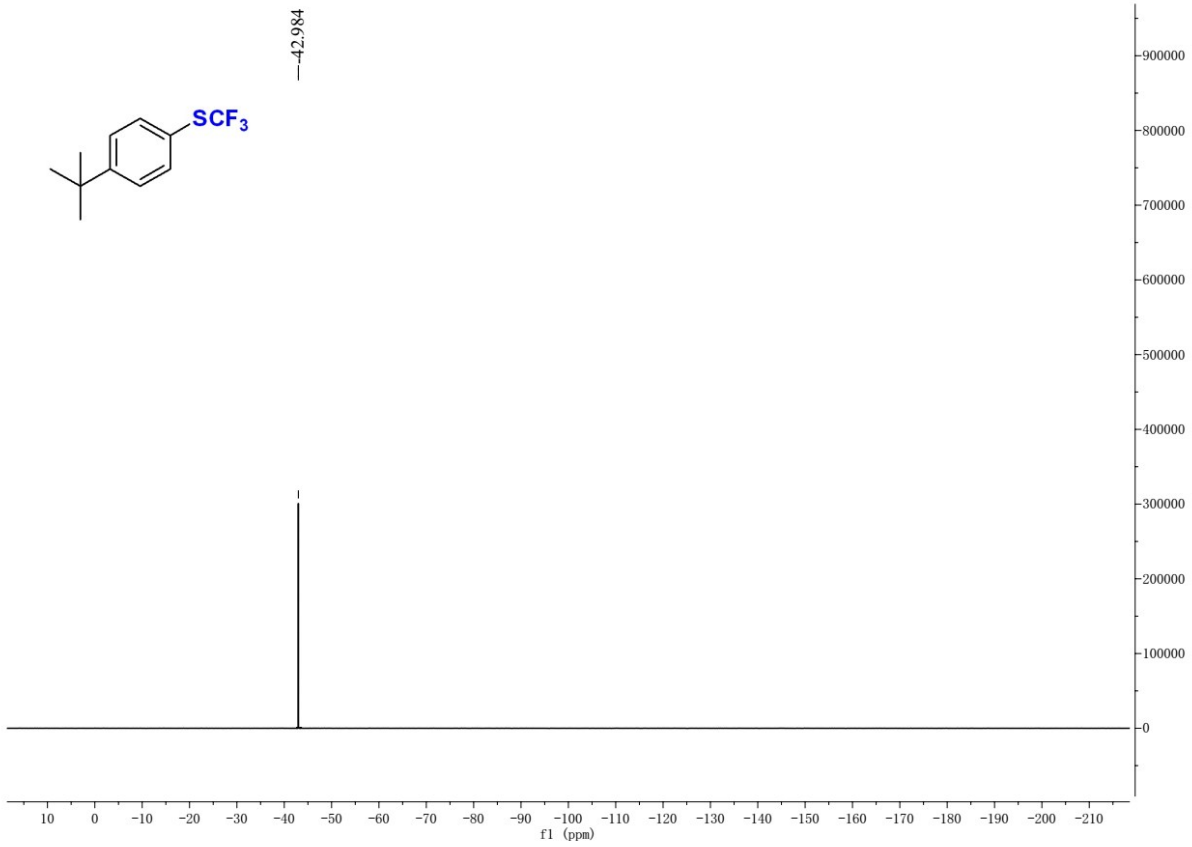
^{1}H NMR spectrum of **2i**



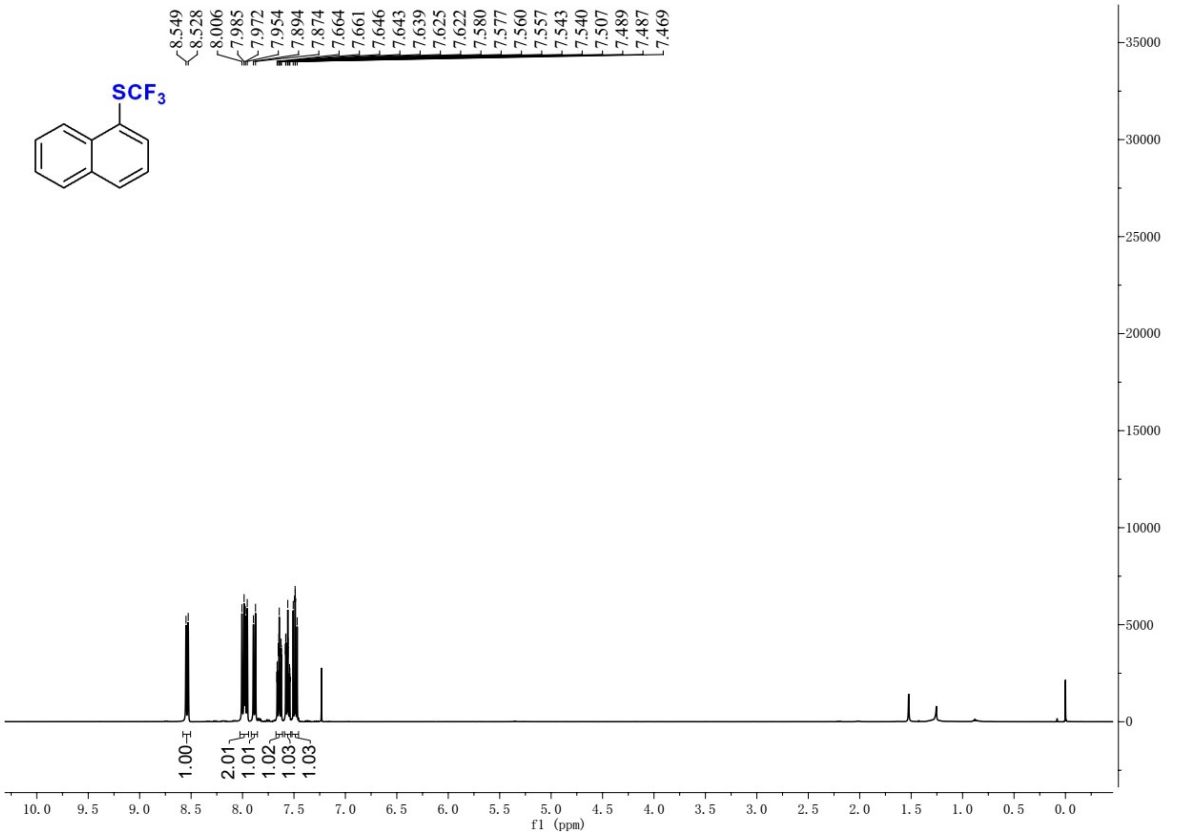
^{13}C NMR spectrum of **2i**



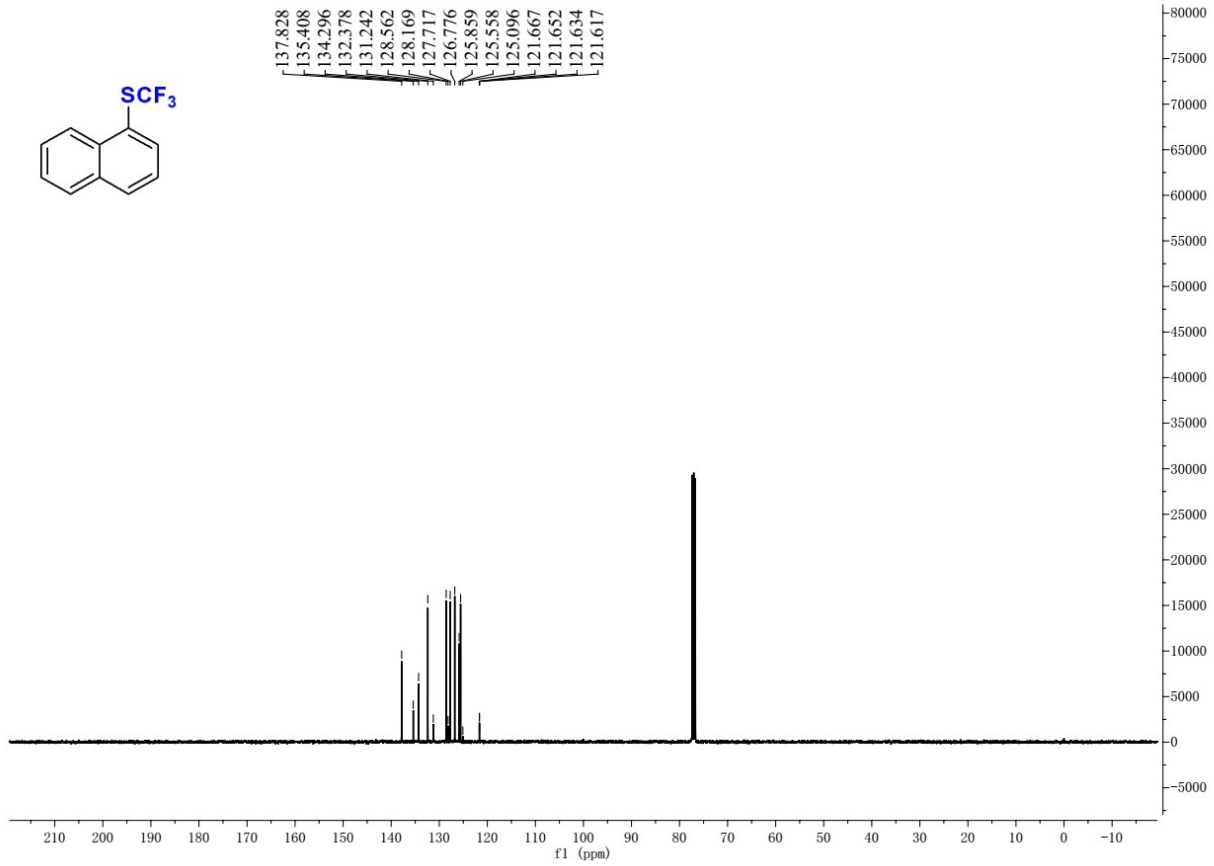
^{19}F NMR spectrum of **2i**



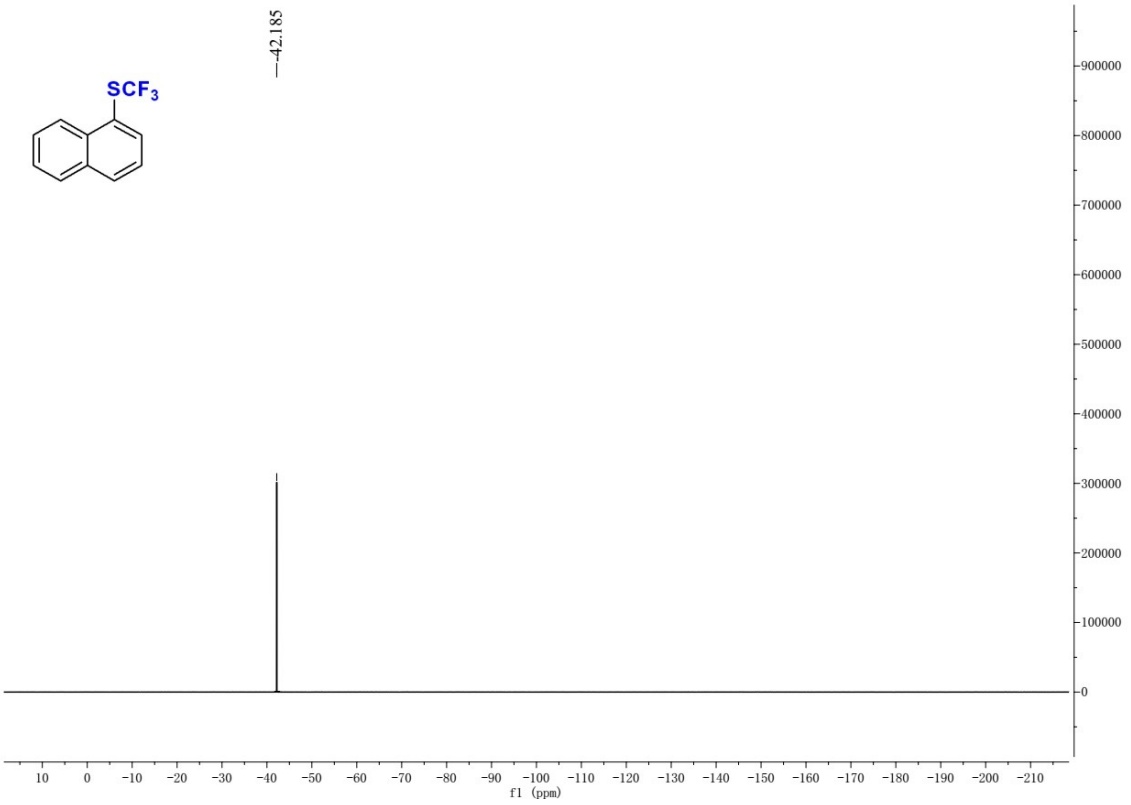
^{1}H NMR spectrum of **2j**



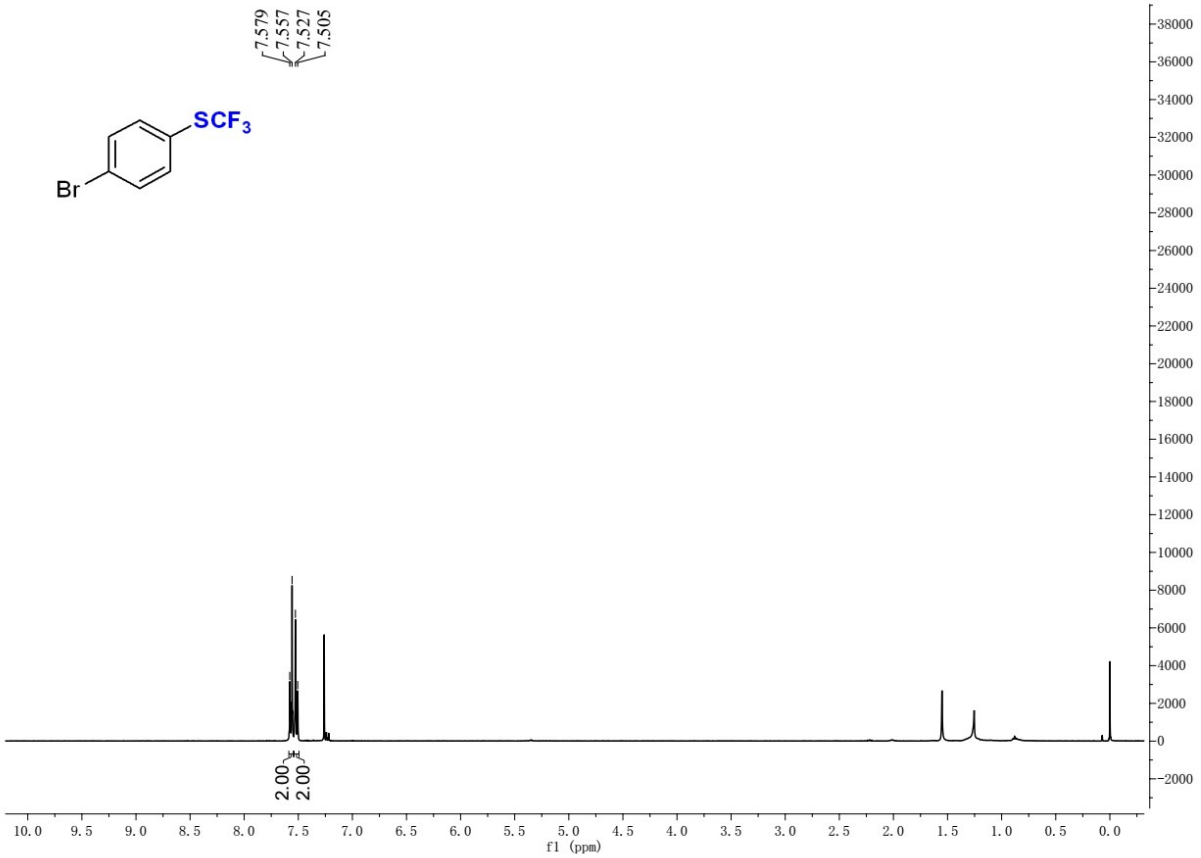
^{13}C NMR spectrum of **2j**



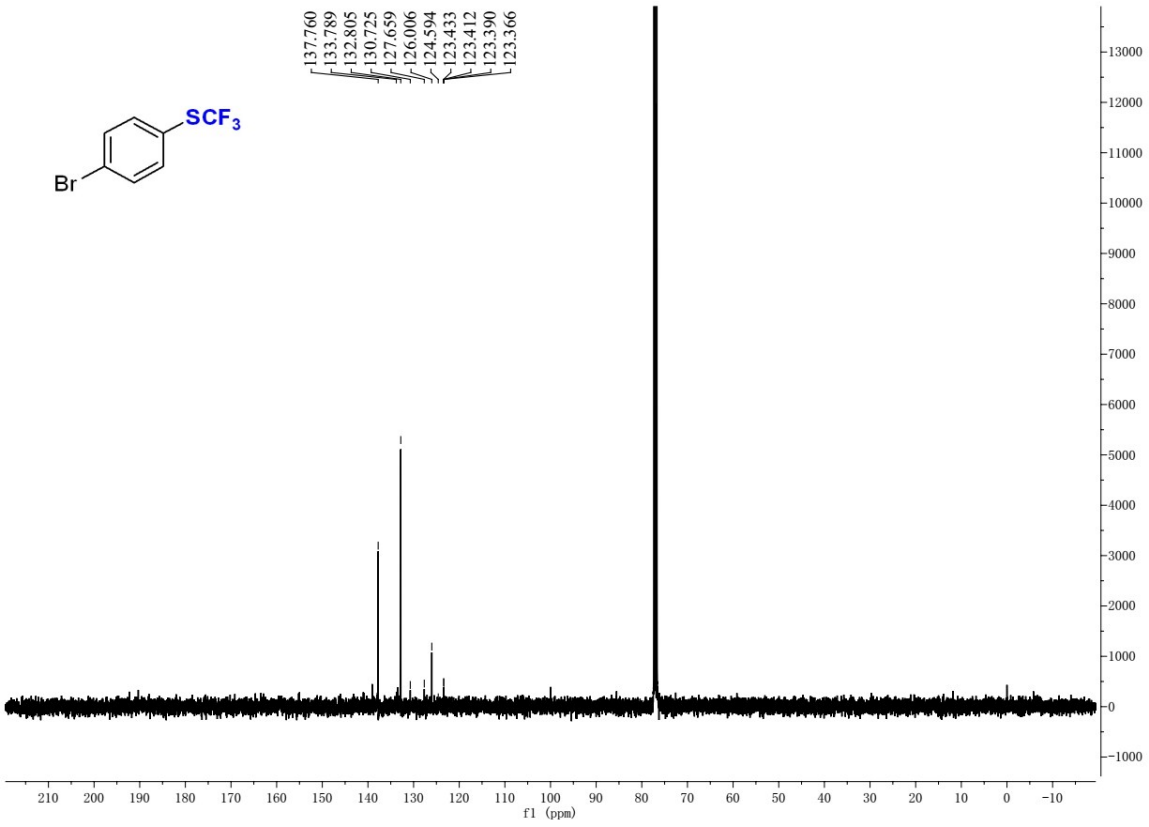
^{19}F NMR spectrum of **2j**



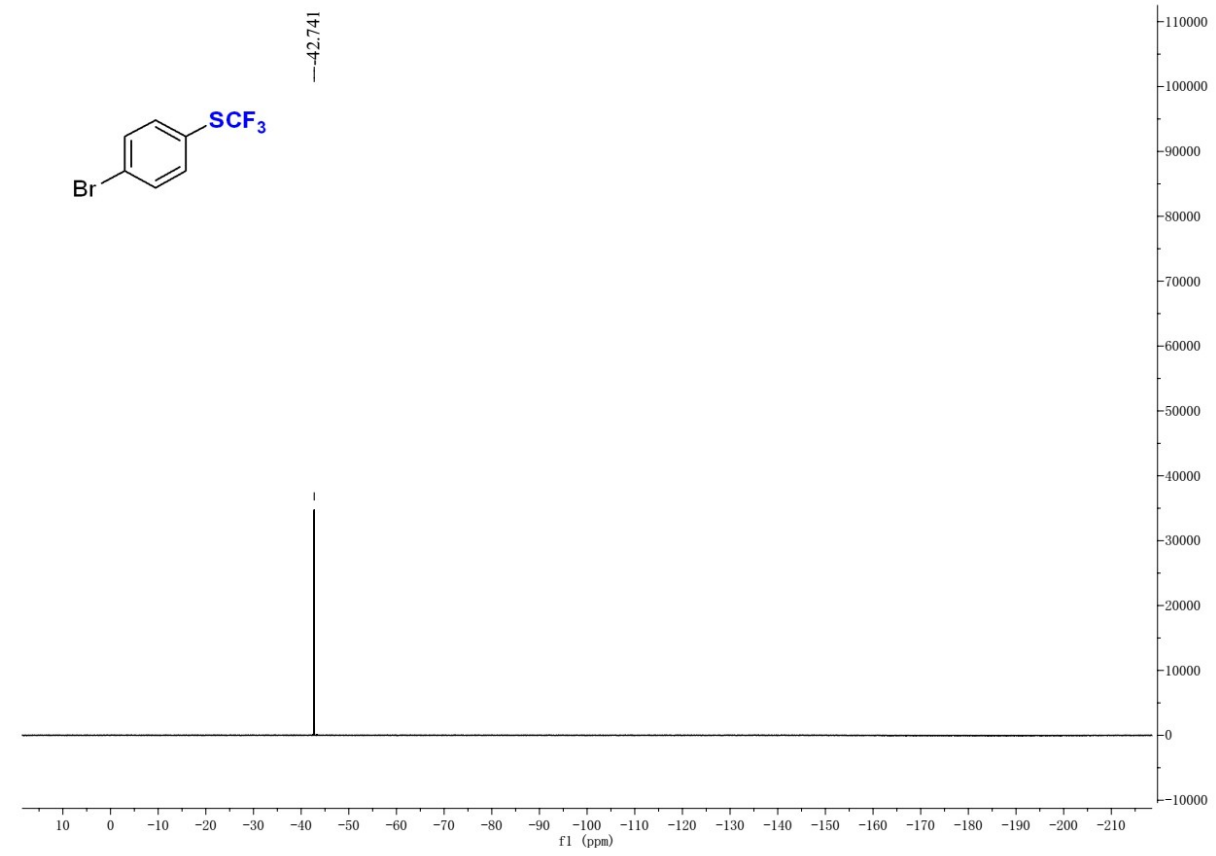
^{1}H NMR spectrum of **2k**



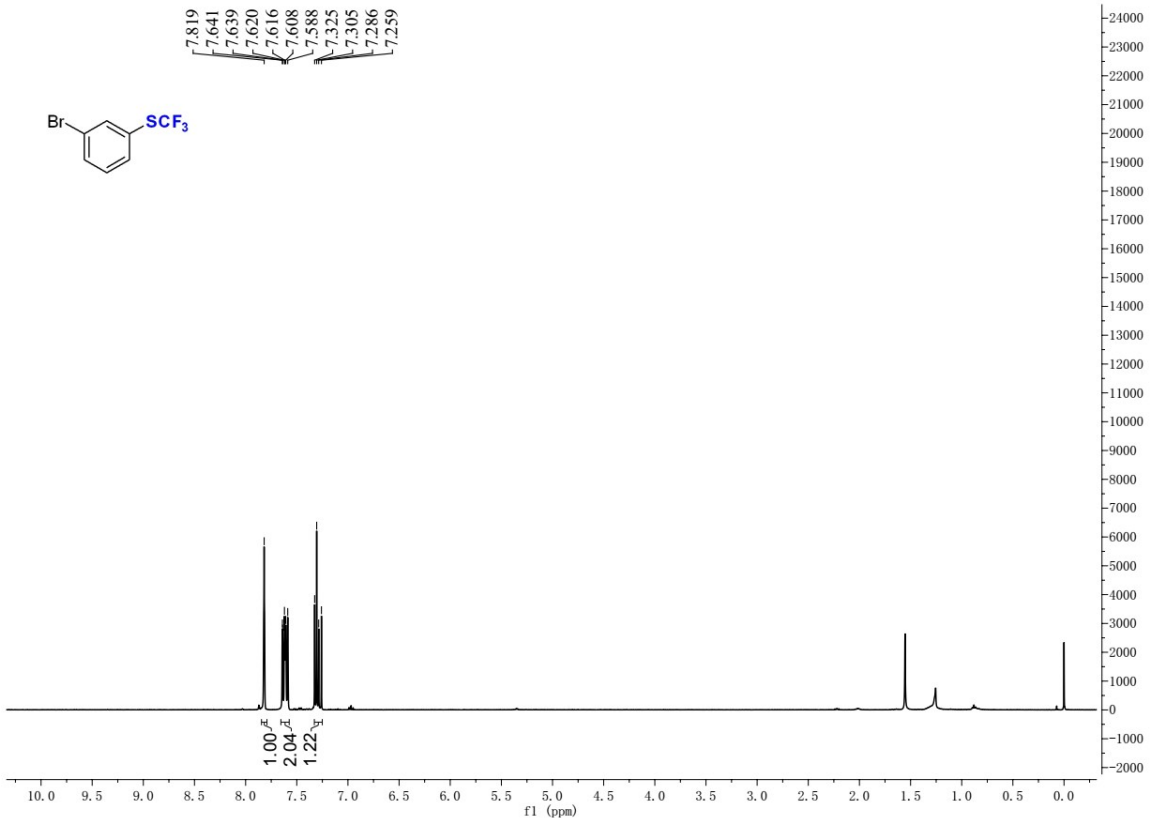
^{13}C NMR spectrum of **2k**



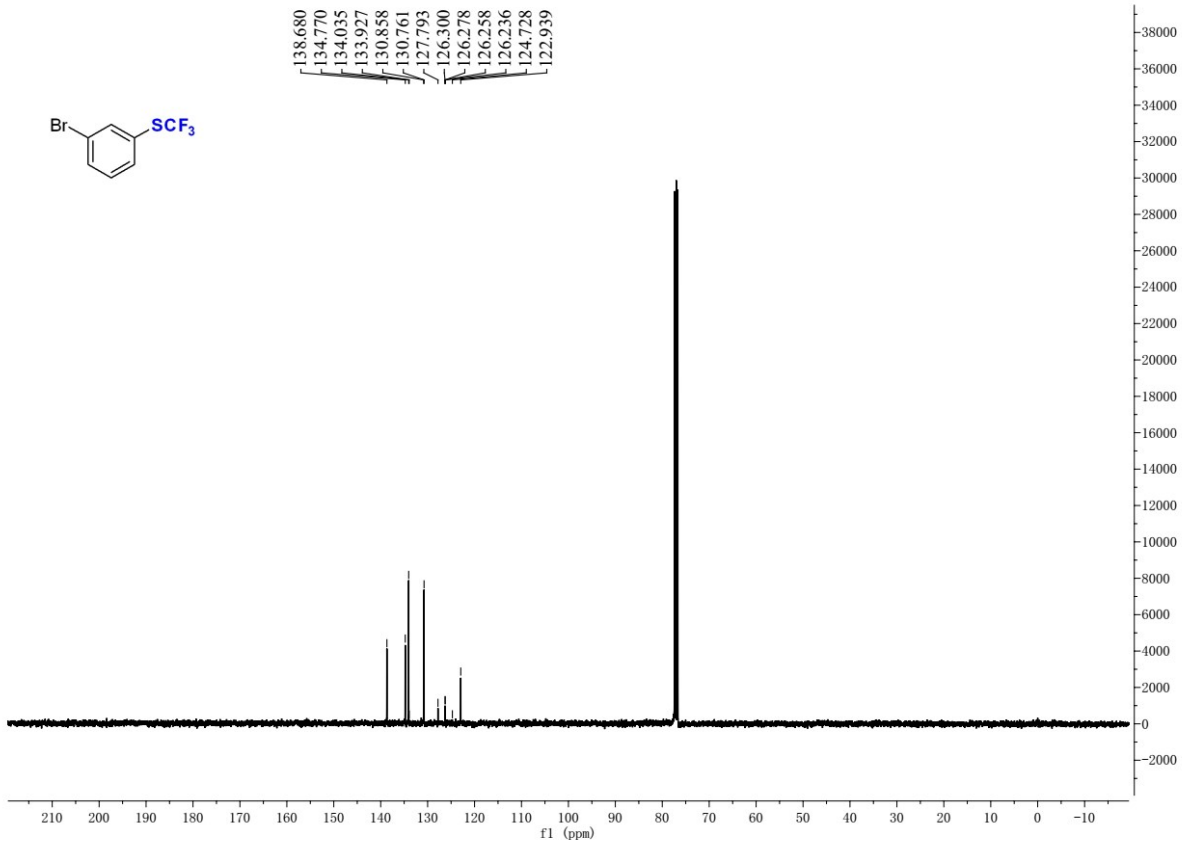
^{19}F NMR spectrum of **2k**



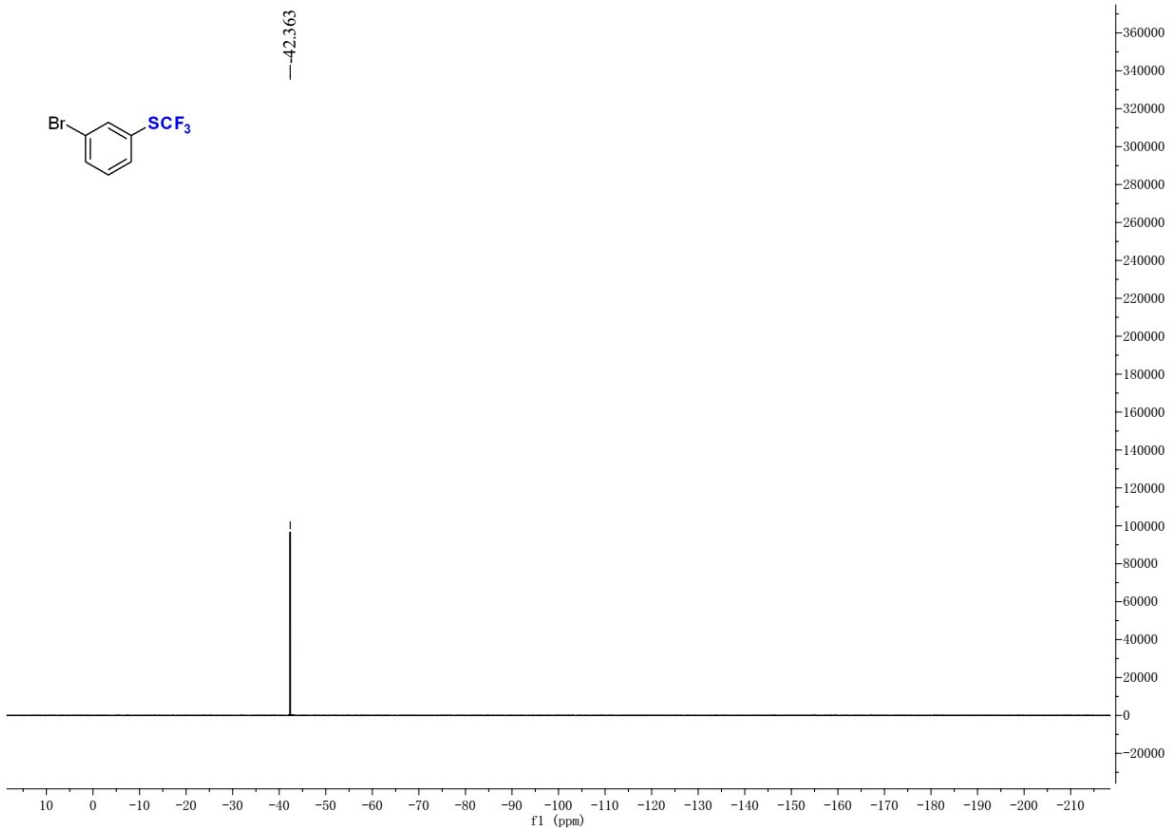
^{1}H NMR spectrum of **2l**



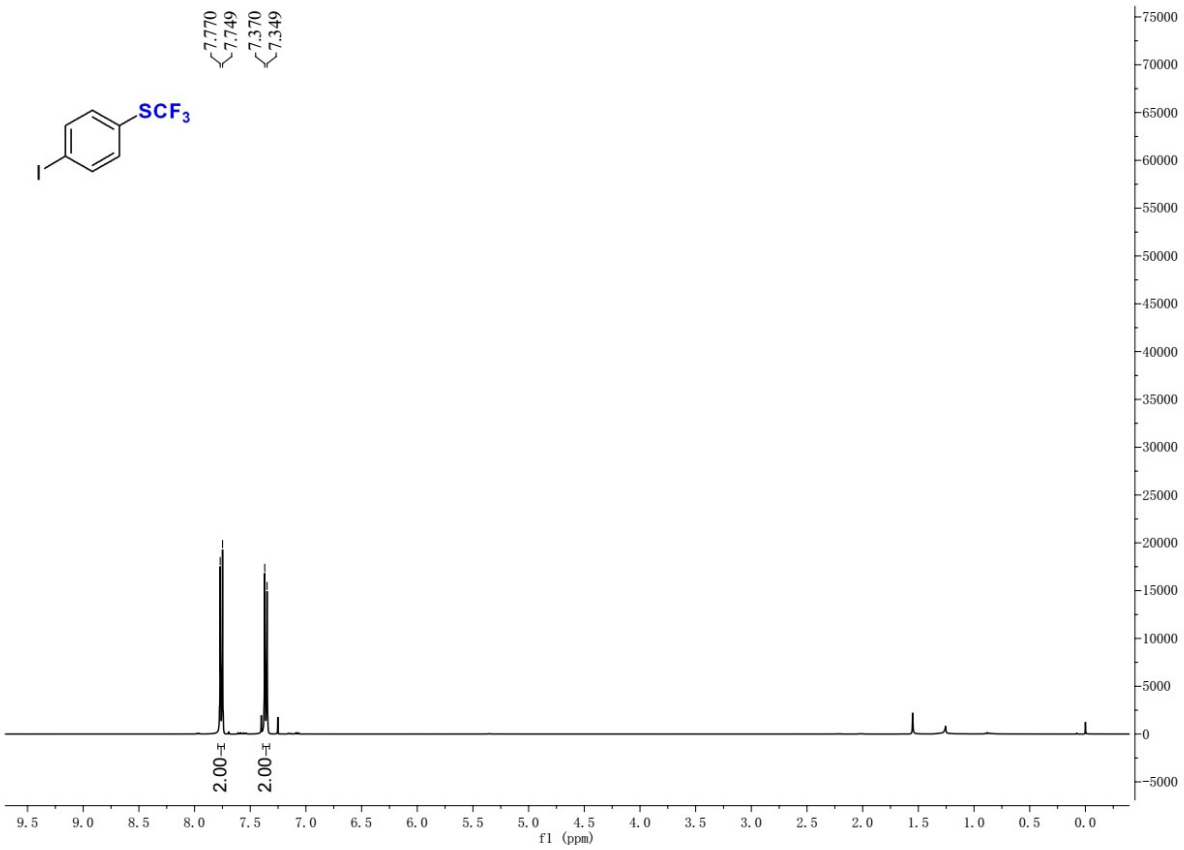
^{13}C NMR spectrum of **2l**



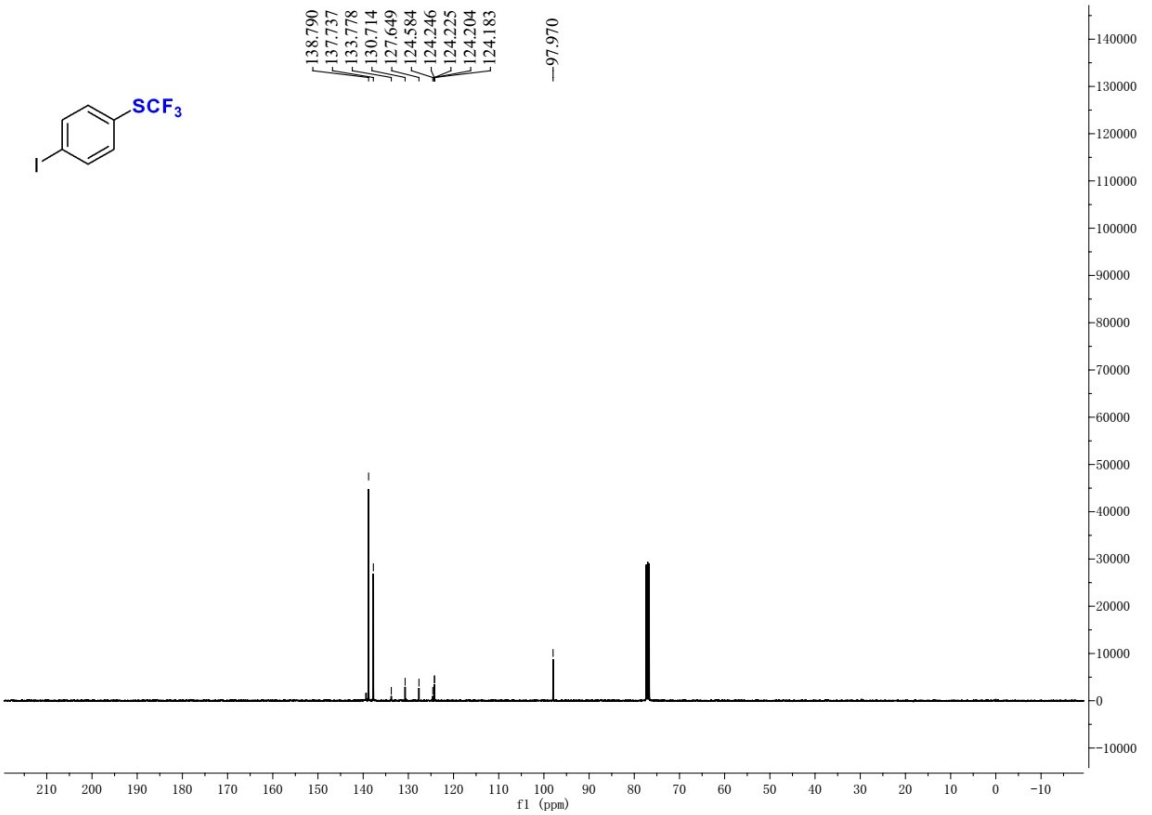
^{19}F NMR spectrum of **2l**



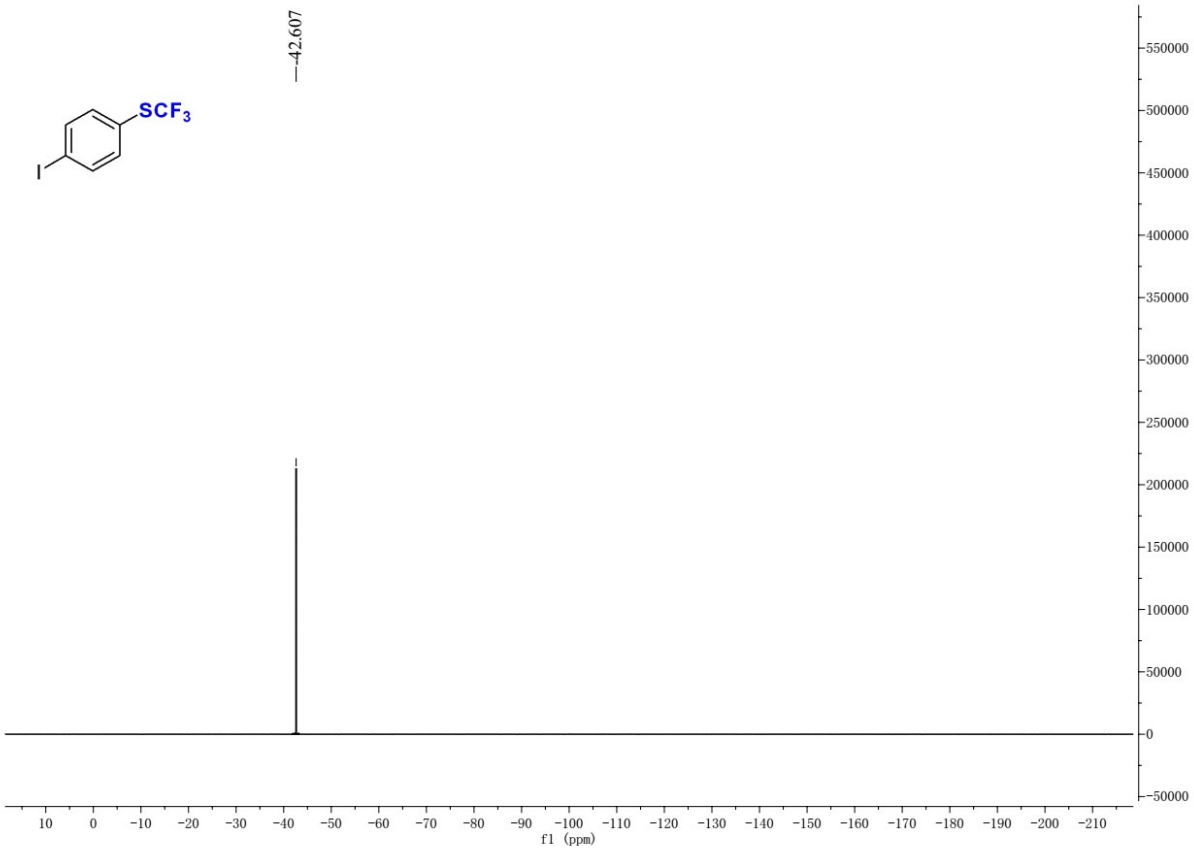
^{1}H NMR spectrum of **2m**



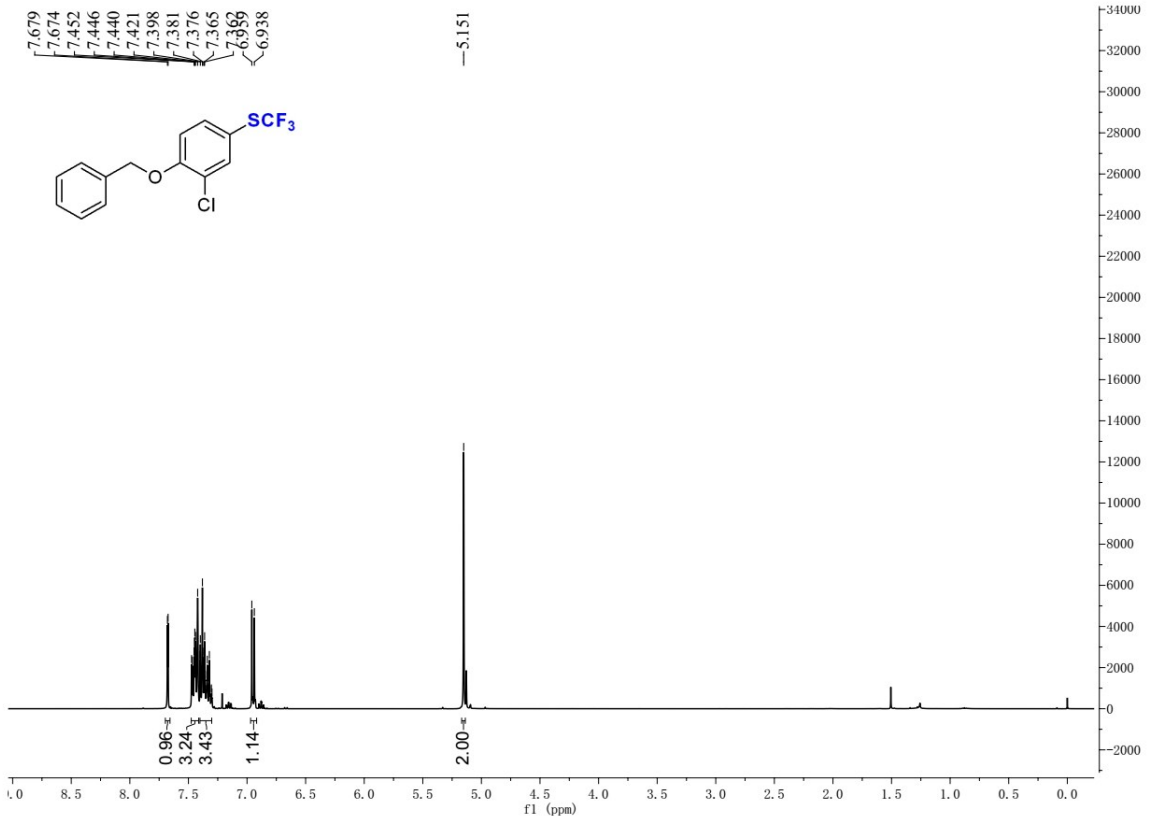
^{13}C NMR spectrum of **2m**



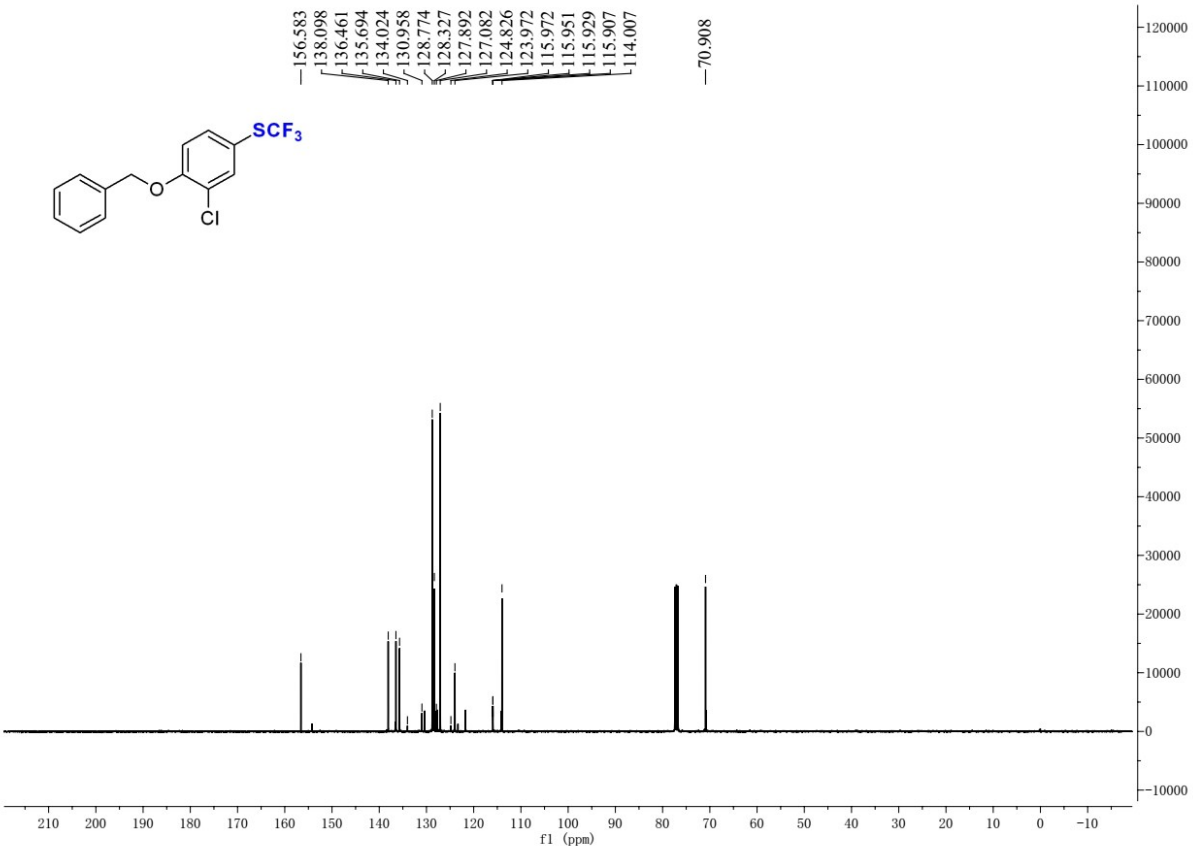
^{19}F NMR spectrum of **2m**



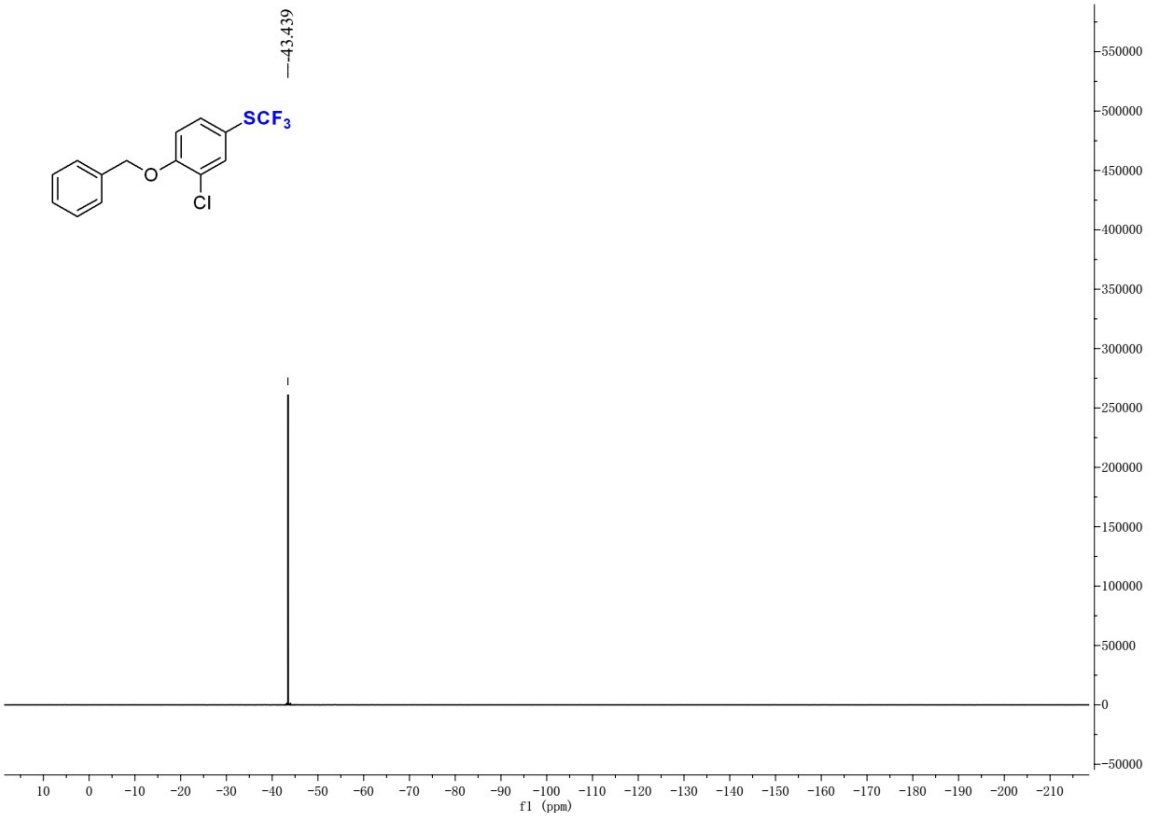
^{1}H NMR spectrum of **2n**



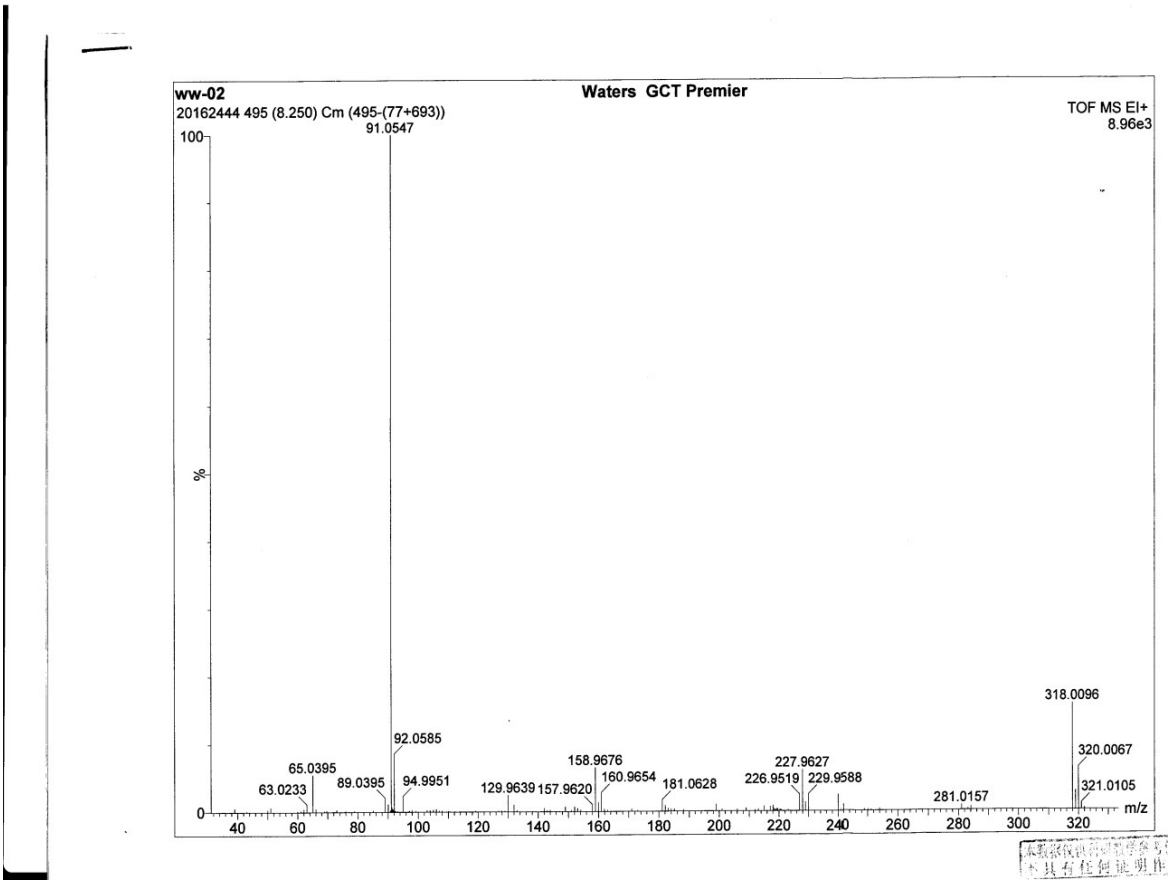
^{13}C NMR spectrum of **2n**



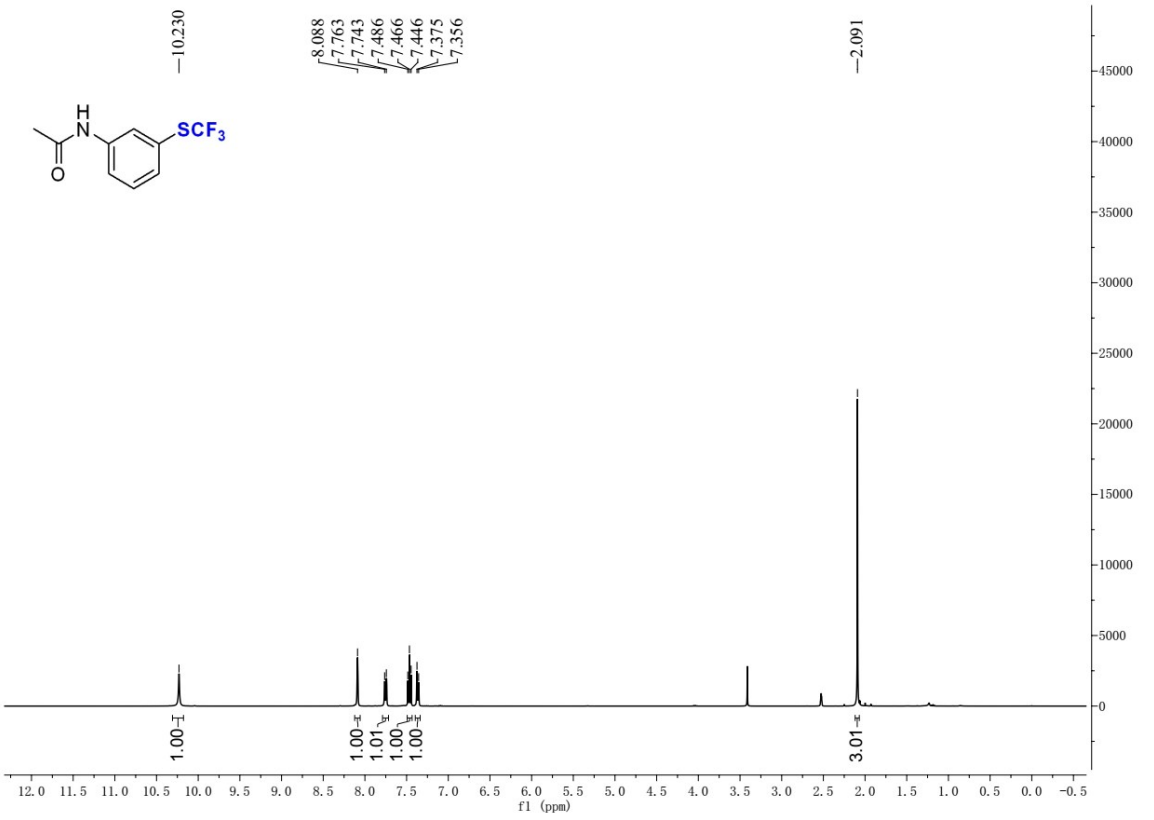
^{19}F NMR spectrum of **2n**



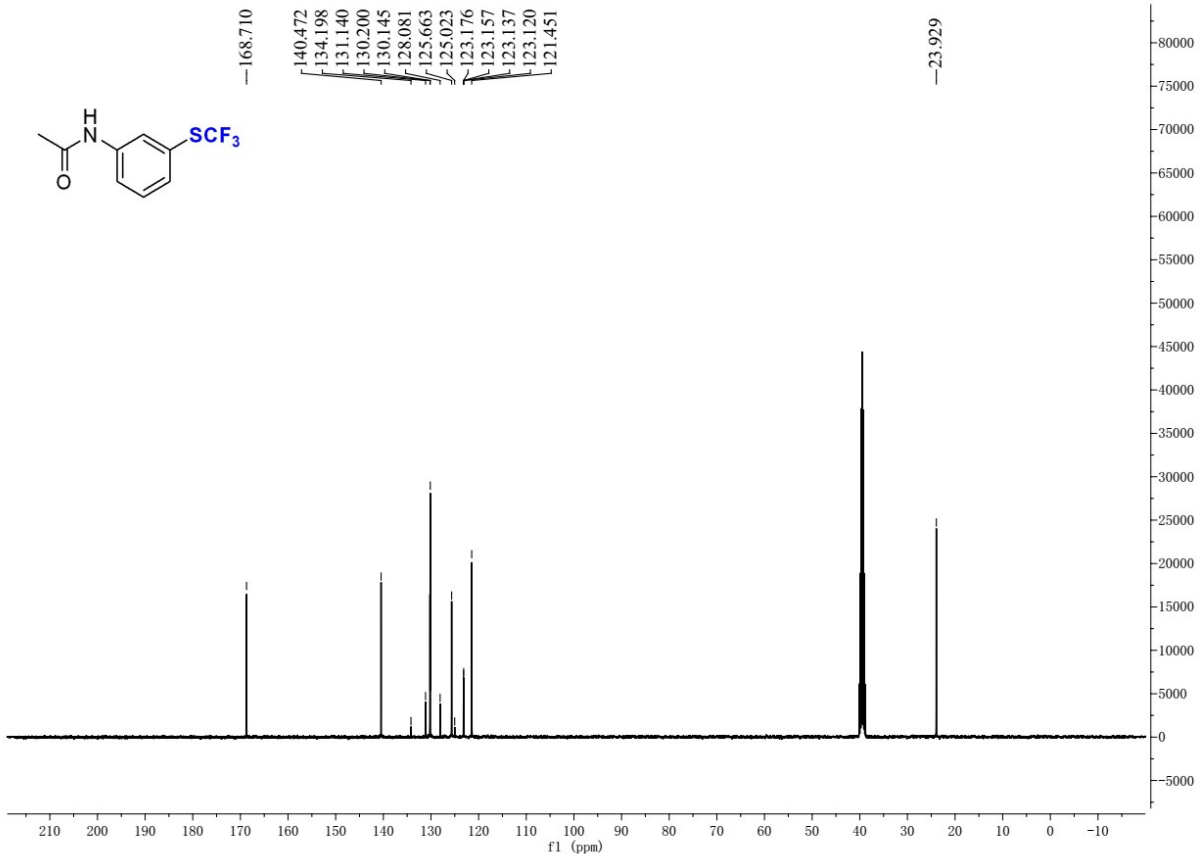
HRMS (EI) of **2n**



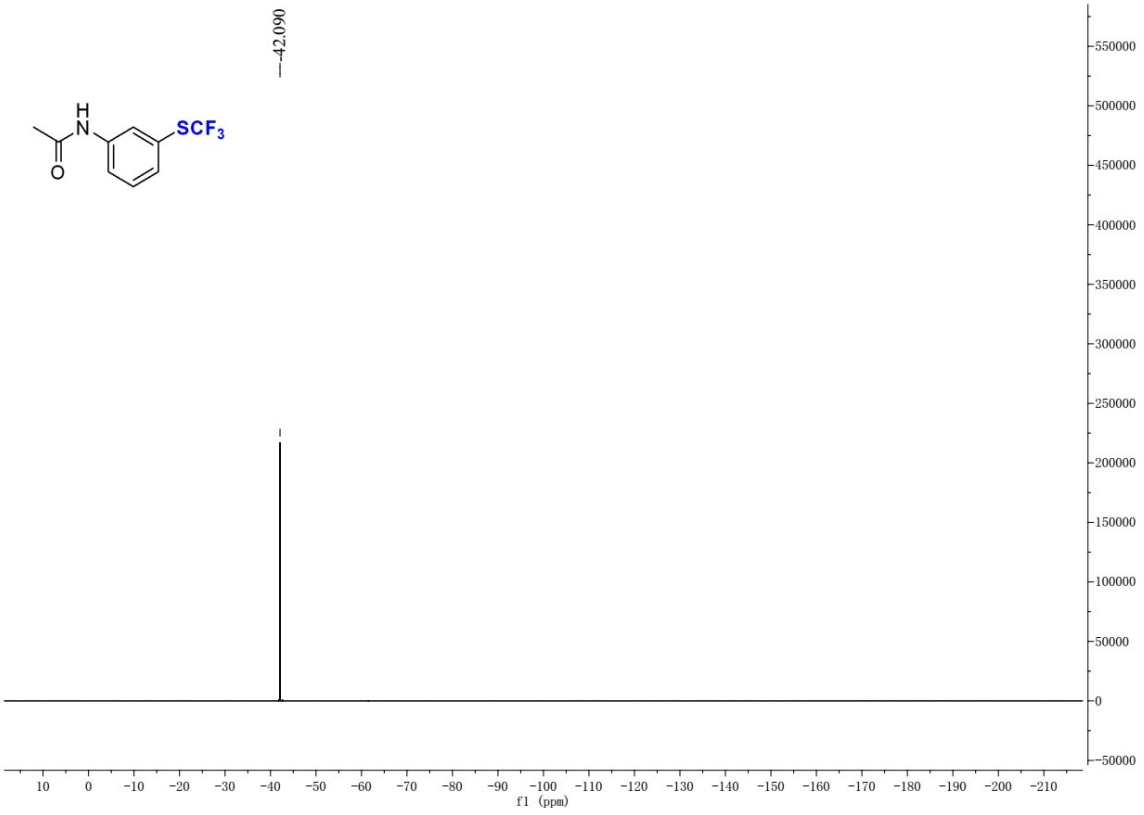
^{1}H NMR spectrum of **2o**



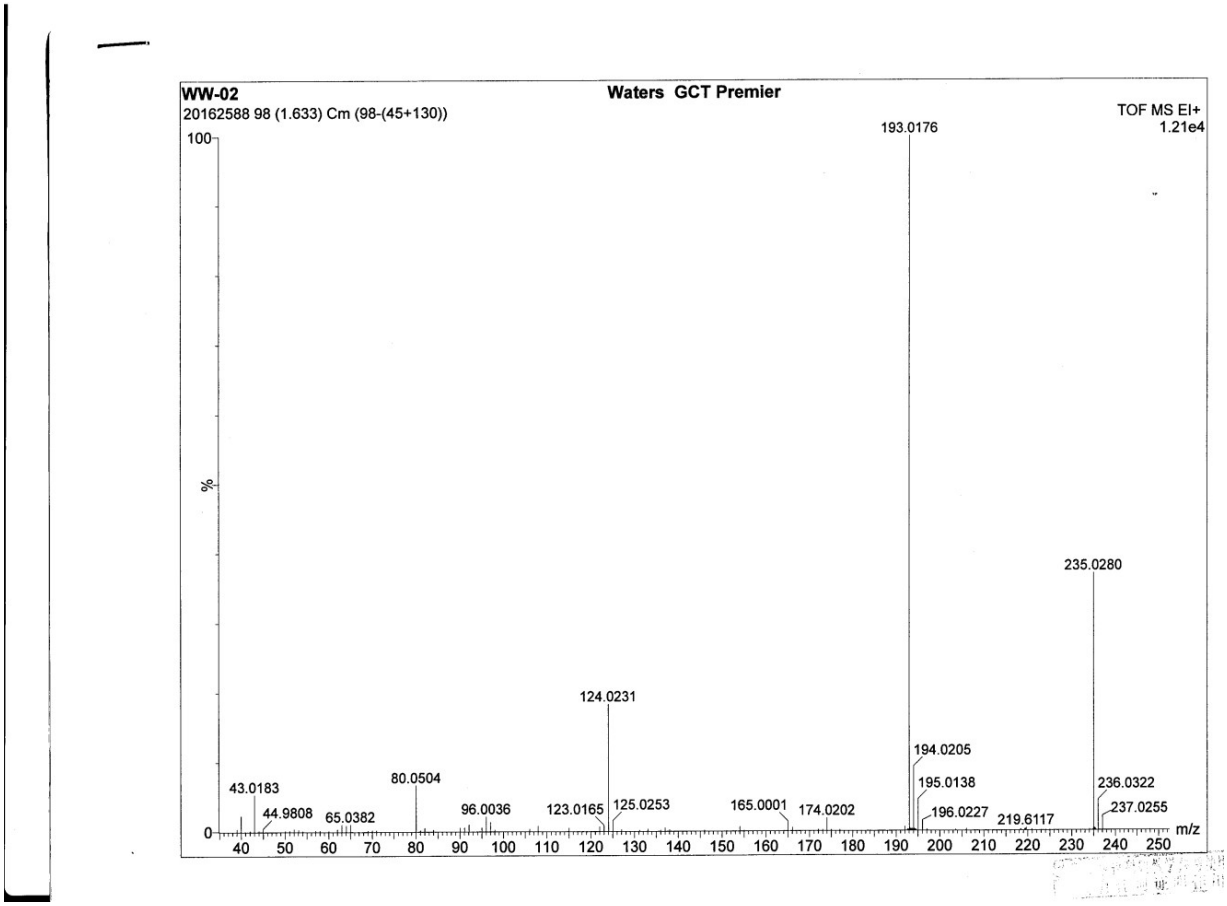
^{13}C NMR spectrum of **2o**



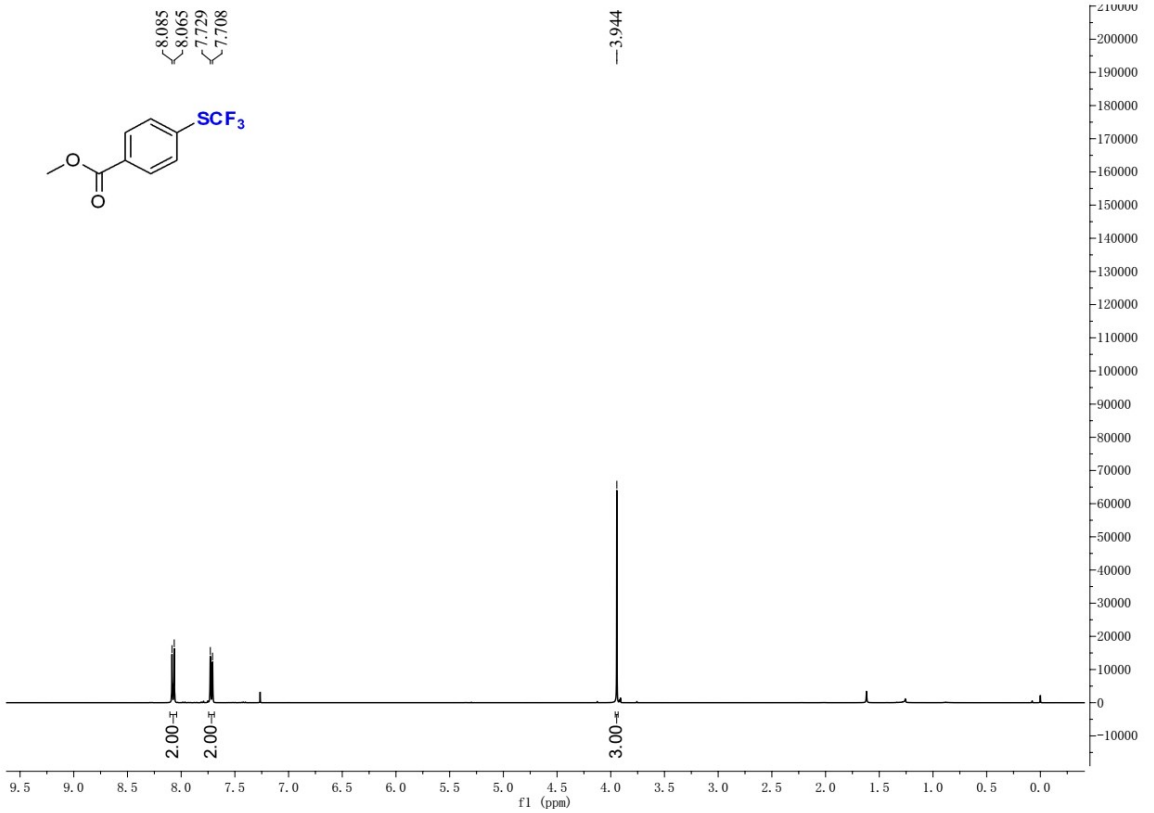
^{19}F NMR spectrum of **2o**



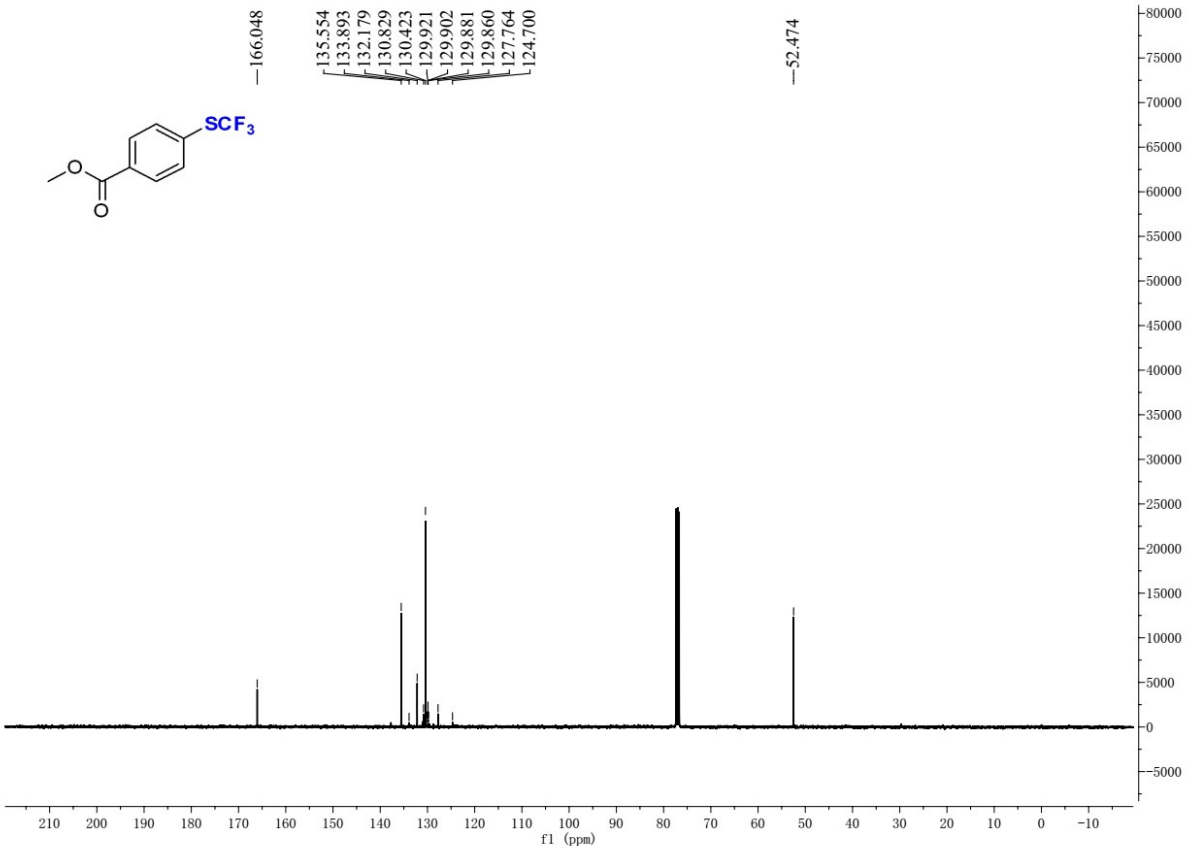
HRMS (EI) of **2o**



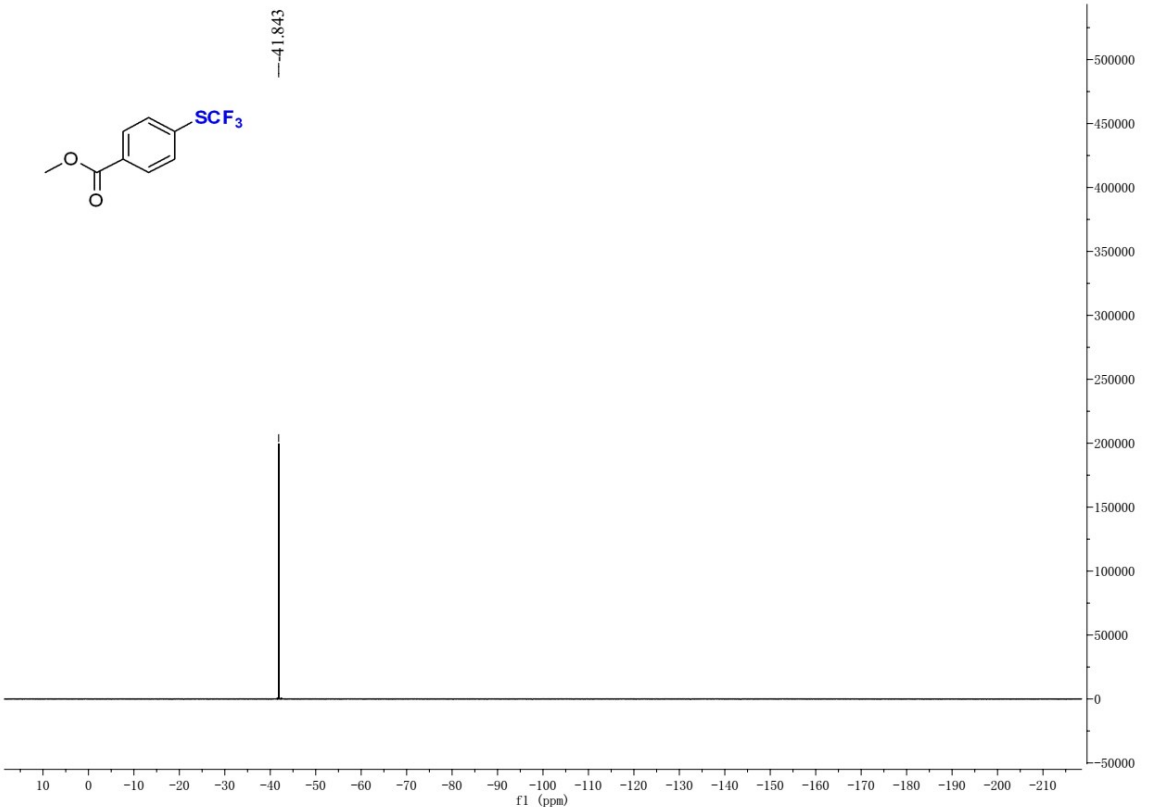
^{1}H NMR spectrum of **2p**



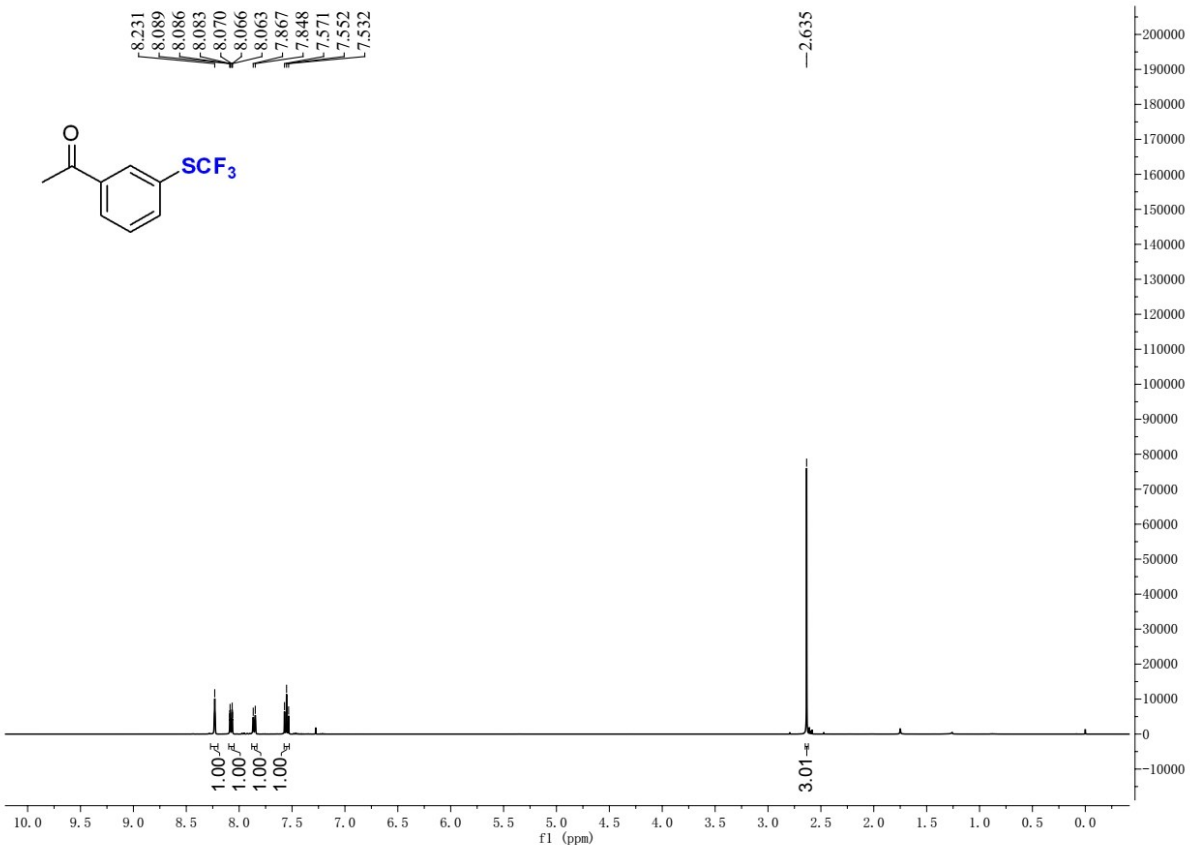
^{13}C NMR spectrum of **2p**



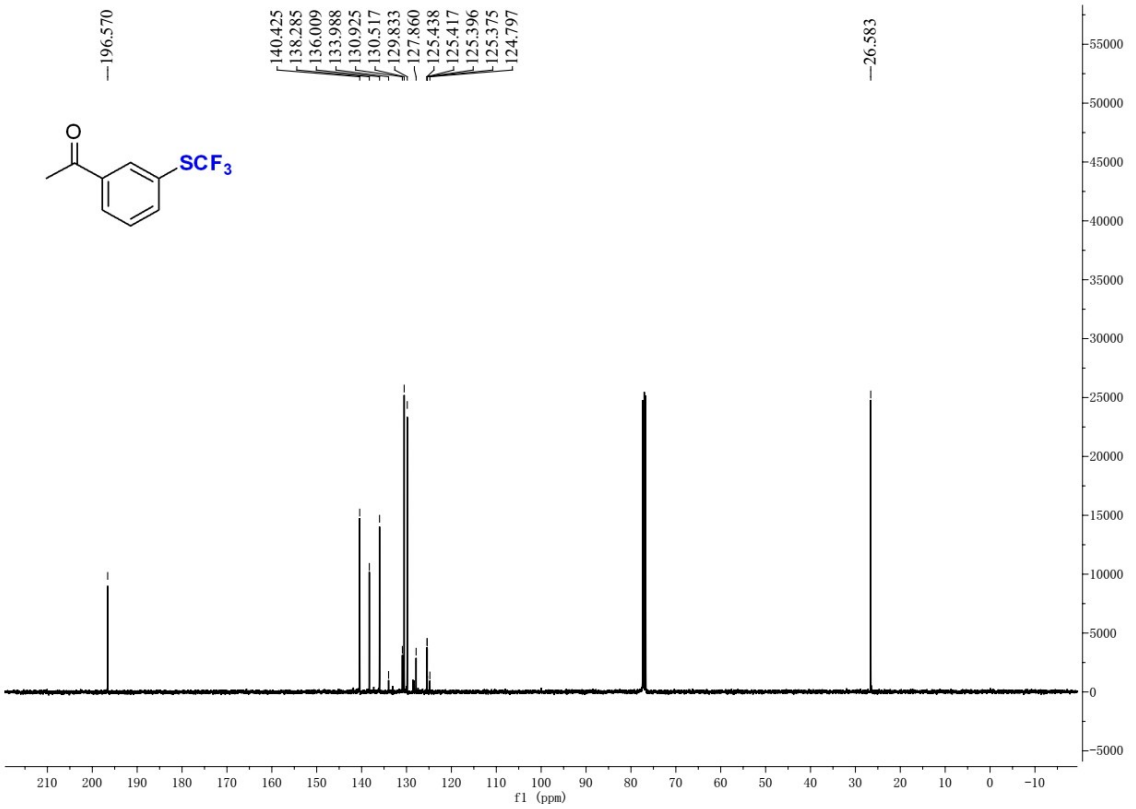
^{19}F NMR spectrum of **2p**



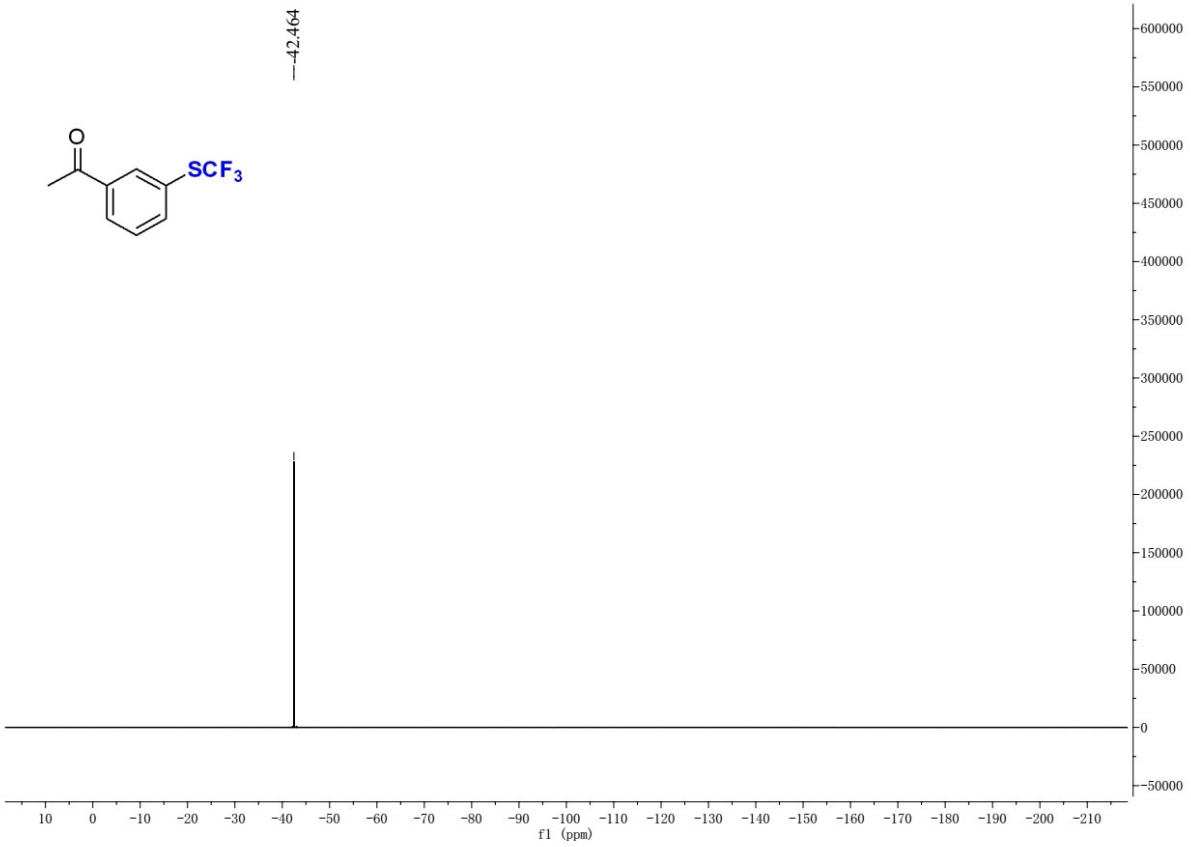
^{1}H NMR spectrum of **2q**



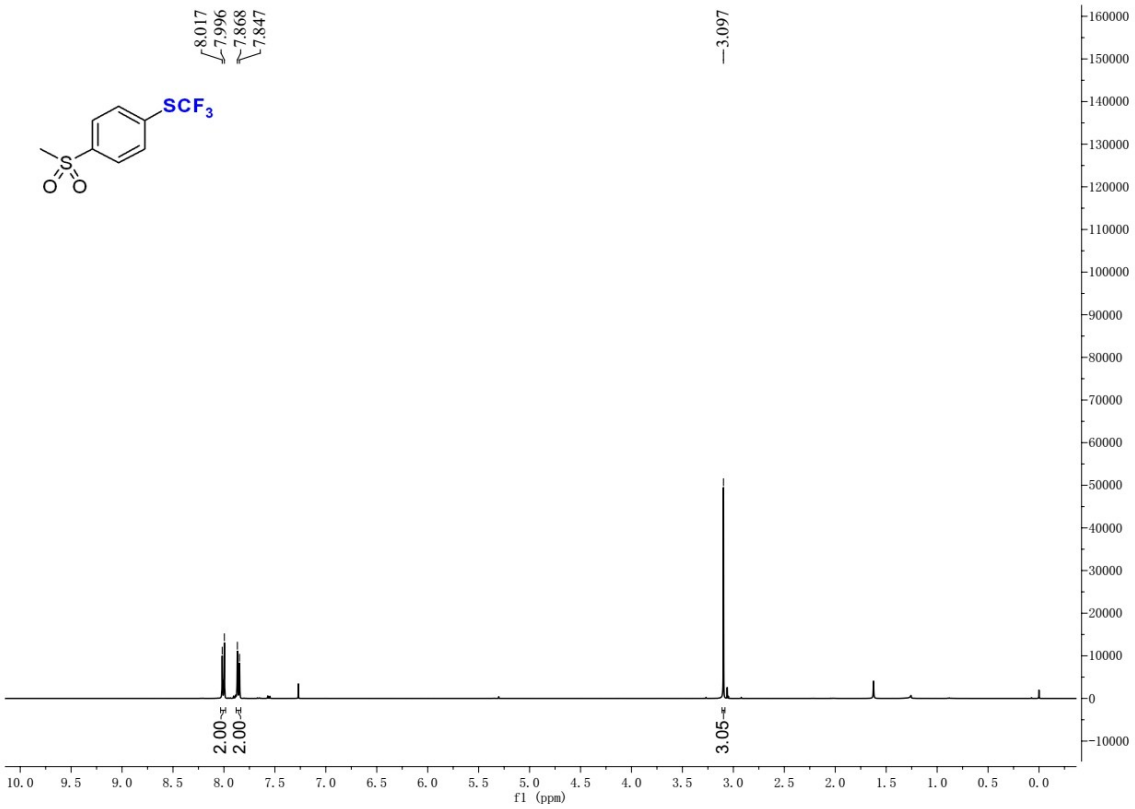
^{13}C NMR spectrum of **2q**



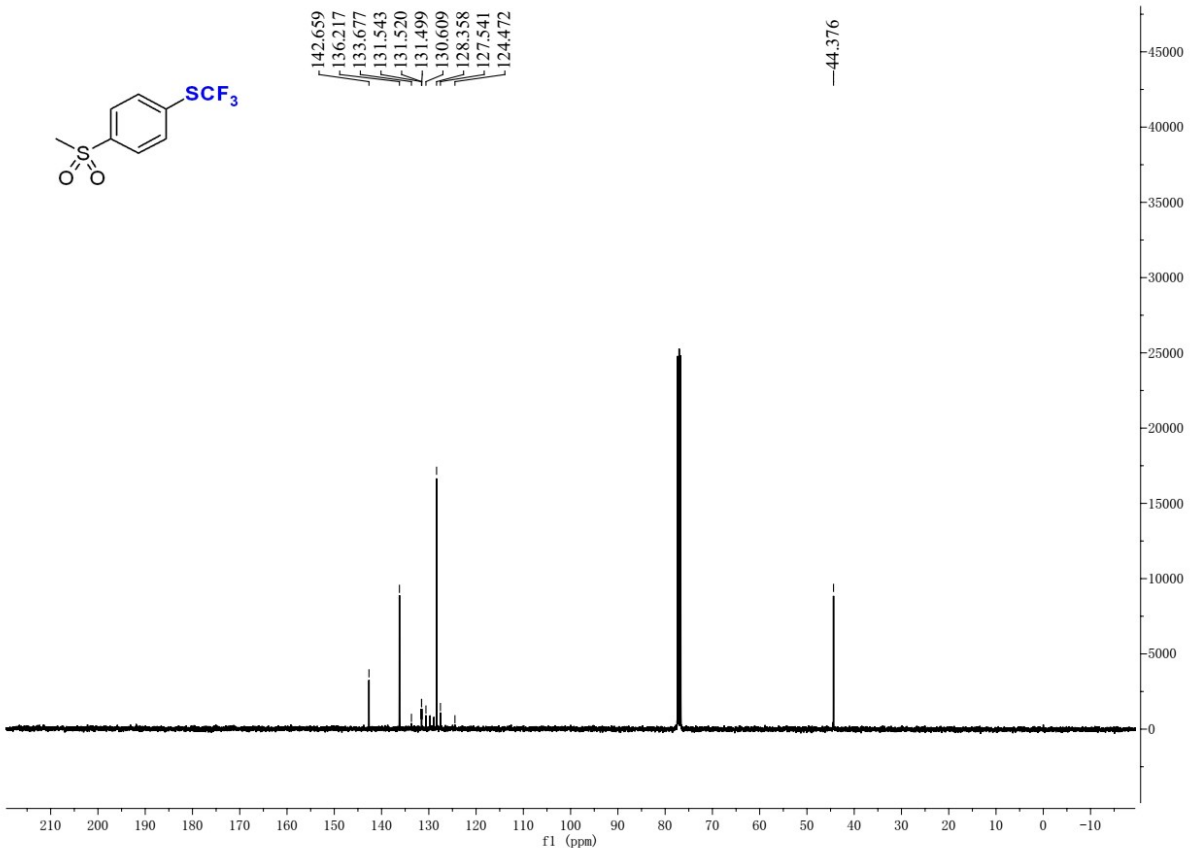
^{19}F NMR spectrum of **2q**



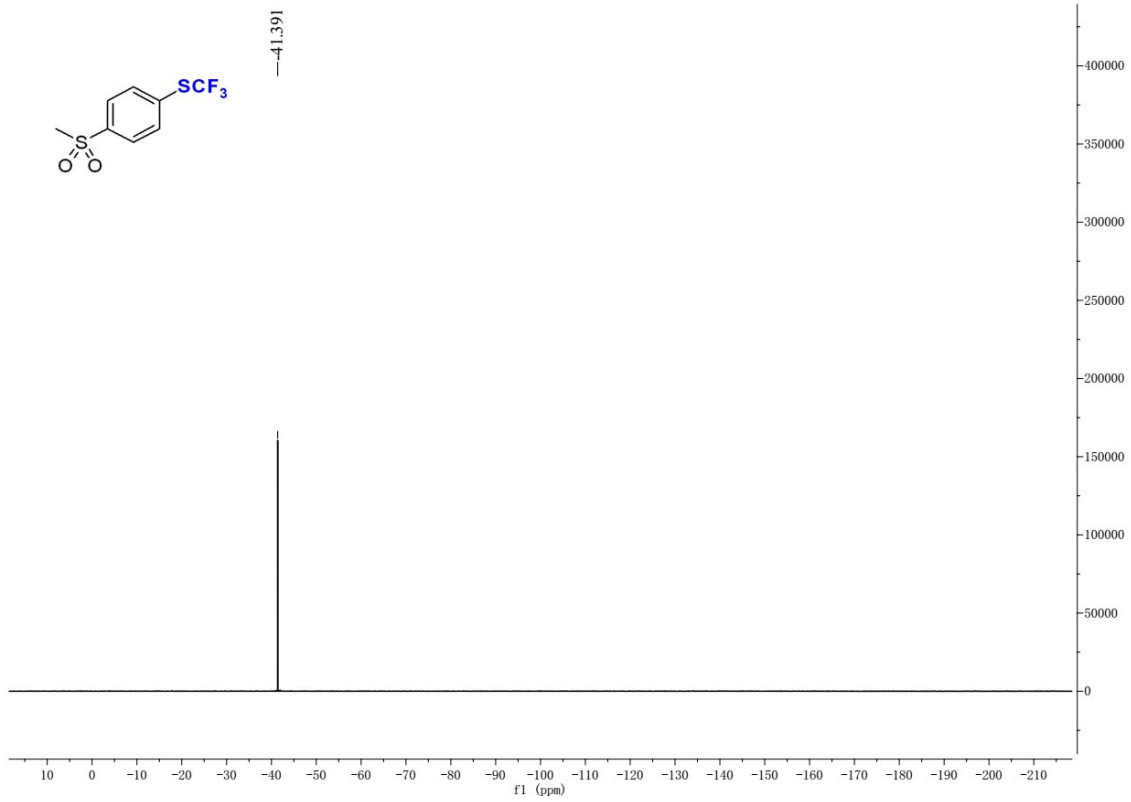
^{1}H NMR spectrum of **2r**



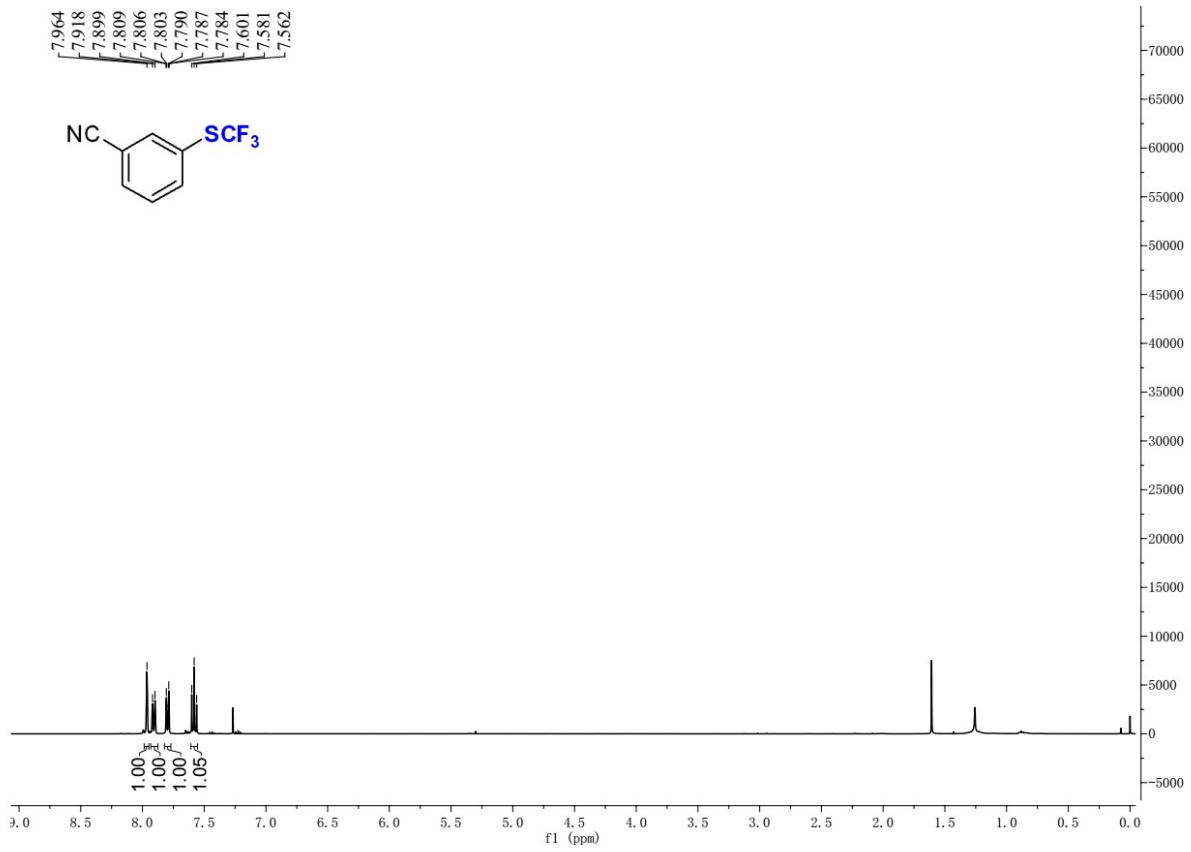
^{13}C NMR spectrum of **2r**



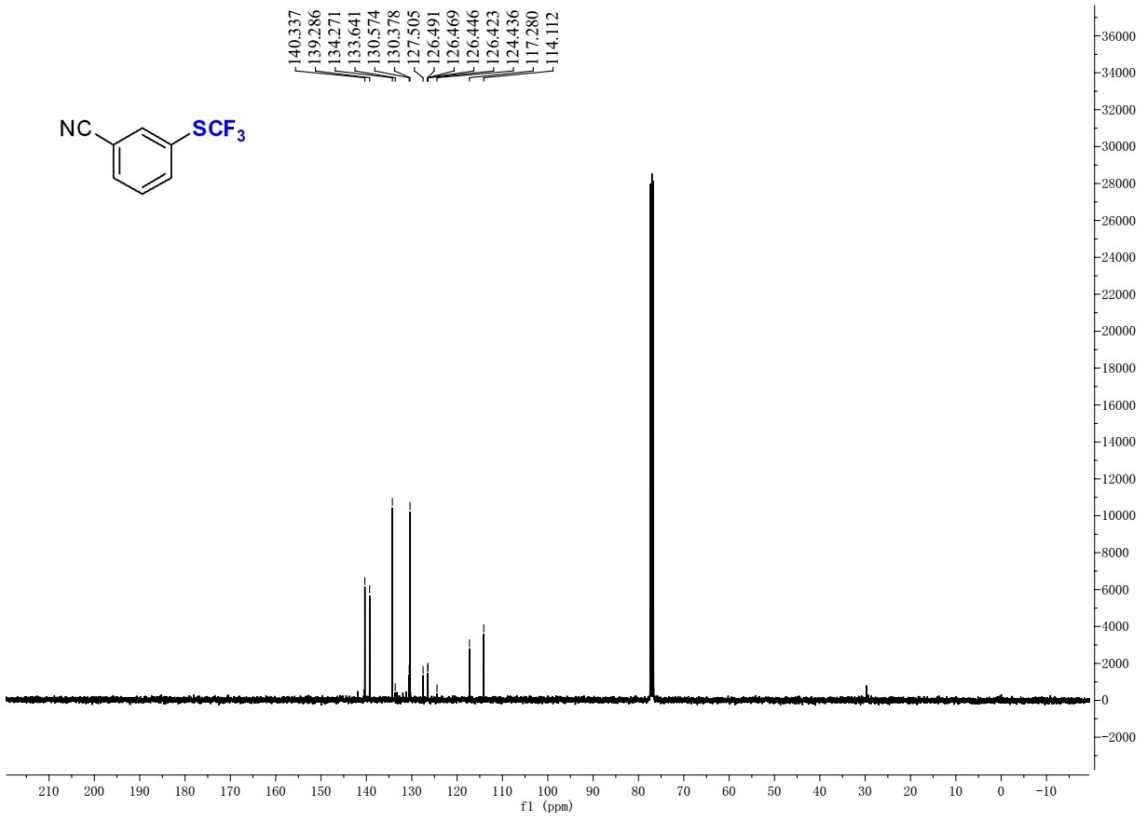
^{19}F NMR spectrum of **2r**



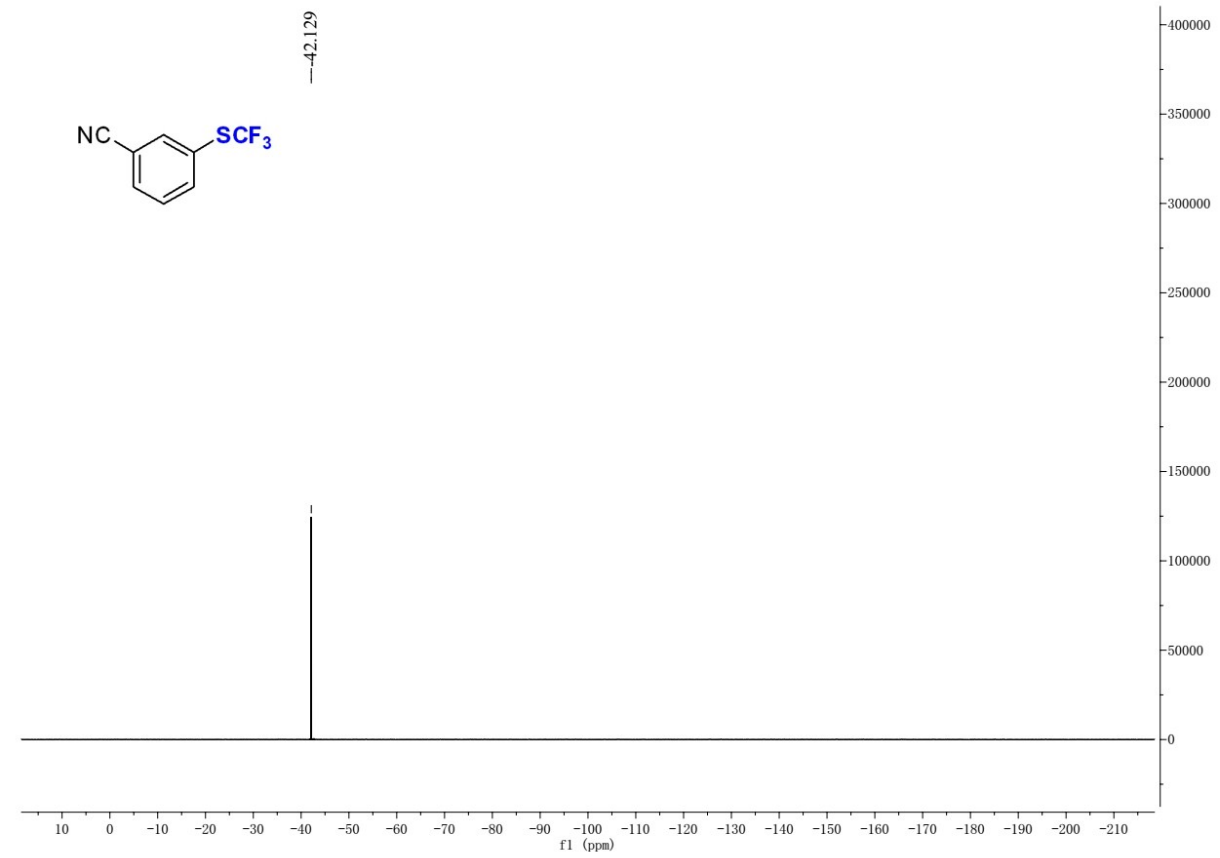
^{1}H NMR spectrum of **2s**



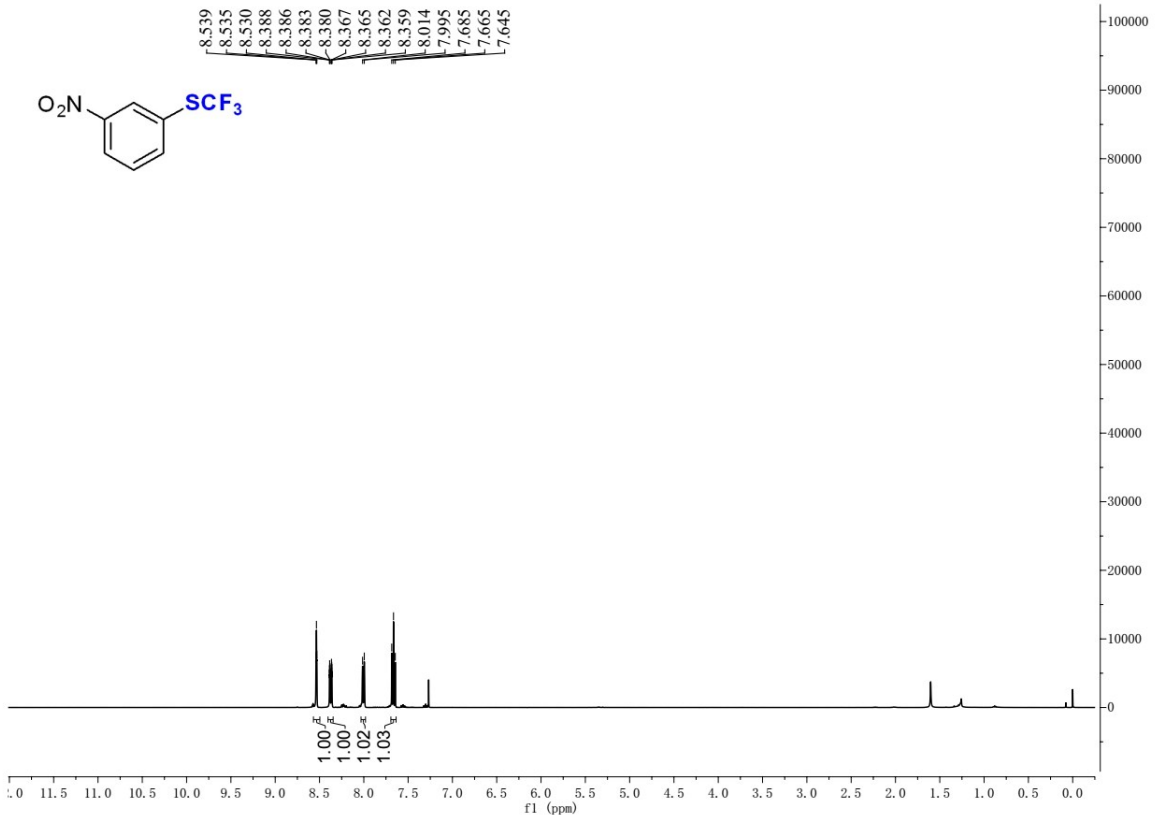
^{13}C NMR spectrum of **2s**



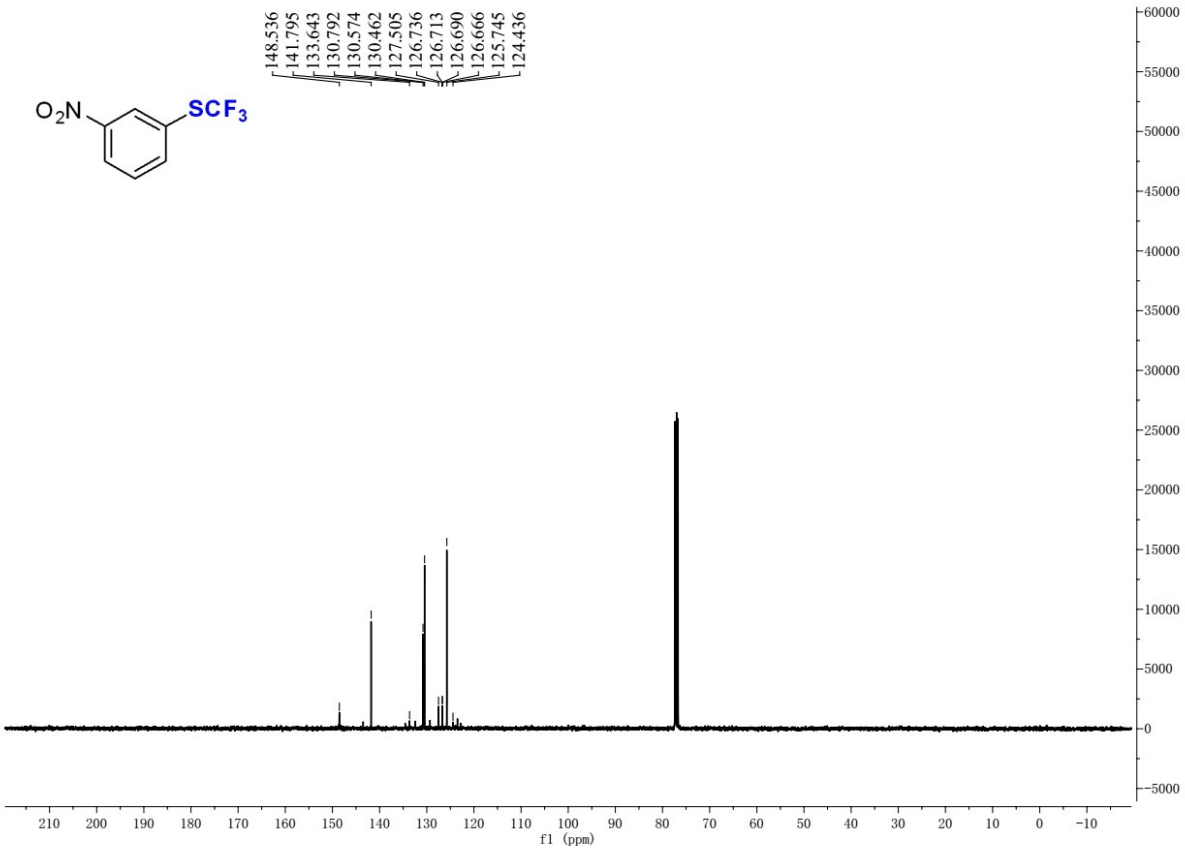
^{19}F NMR spectrum of **2s**



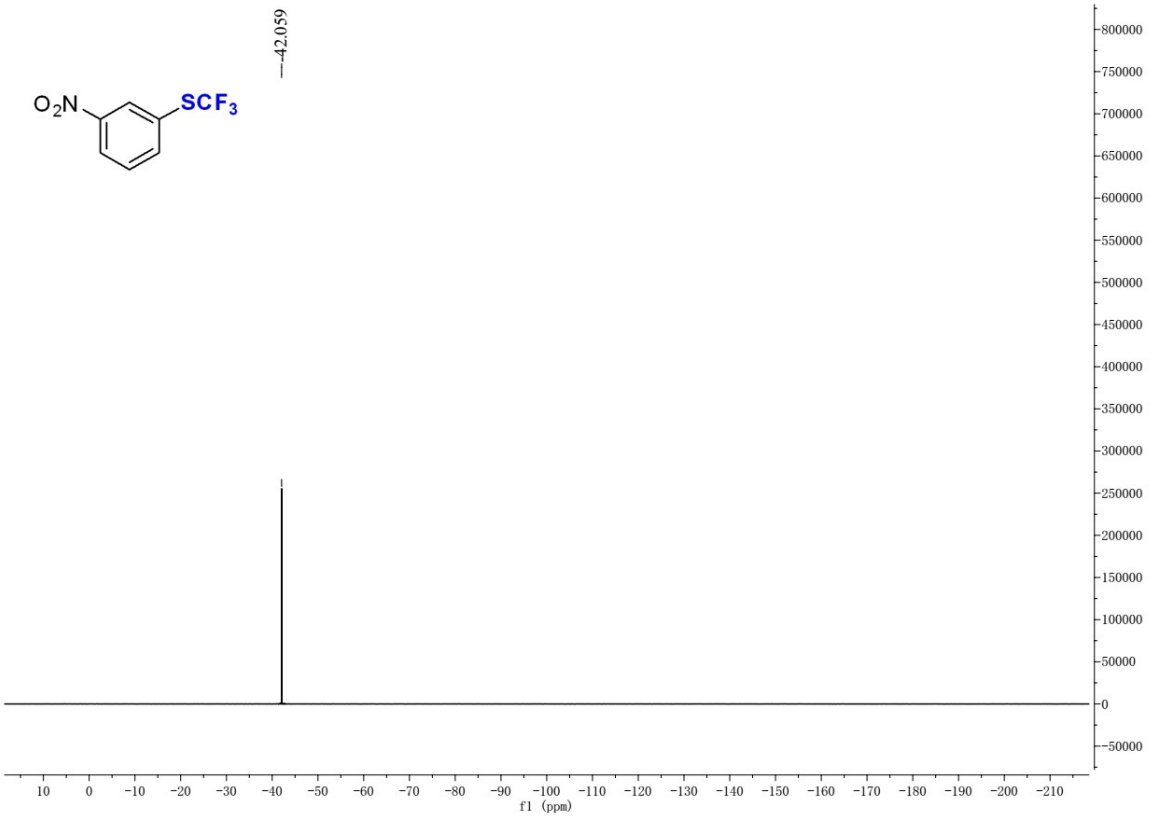
^{1}H NMR spectrum of **2t**



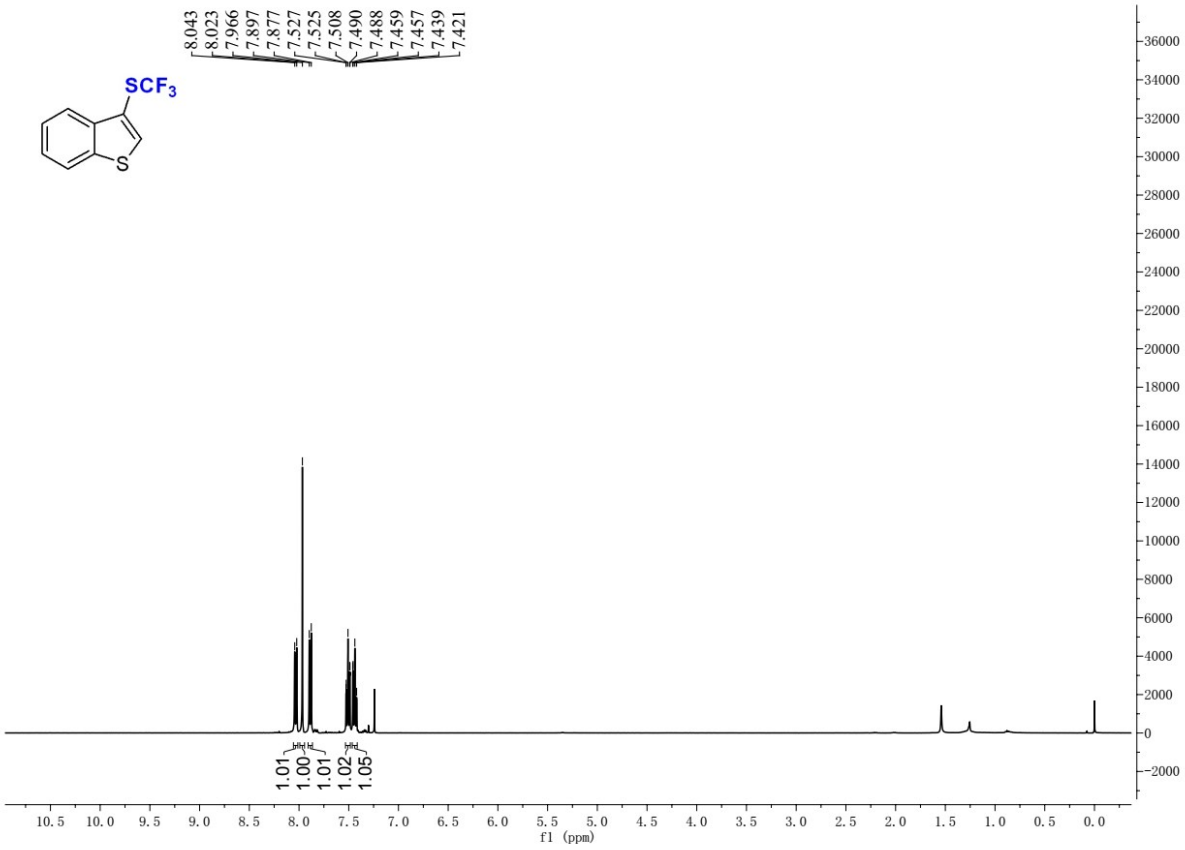
^{13}C NMR spectrum of **2t**



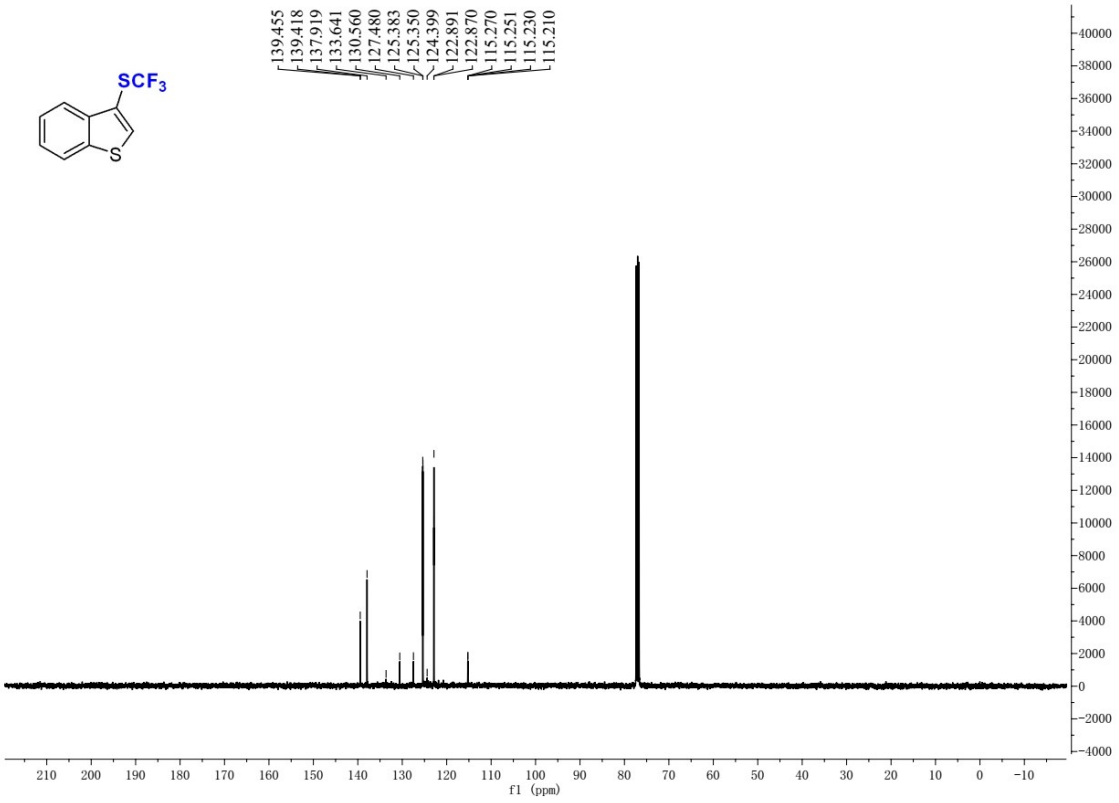
^{19}F NMR spectrum of **2t**



^{1}H NMR spectrum of **2u**



^{13}C NMR spectrum of **2u**



^{19}F NMR spectrum of **2u**