

Supporting Information

Copper-promoted indirect trifluoromethylthiolation of sulfonyl chloride with TMSCF₃: a facile access to trifluoromethyl thioethers

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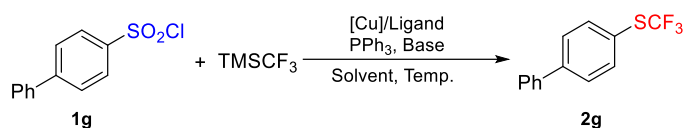
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1. General Information

Unless otherwise noted, all commercially available materials were purchased from Energy Chemical and used without further purification. Column chromatography was carried out on silica gel 60 (200–300 mesh). Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates and visualized with short-wavelength UV light (254 nm). ¹H NMR, ¹³C NMR, ¹⁹F NMR were all recorded using CDCl₃ as a solvent on a Bruker 400 MHz spectrometer at 298 K (400 MHz for ¹H, 100 MHz for ¹³C, and 376 MHz for ¹⁹F). Chemical shifts (δ) were measured in ppm relative to TMS $\delta = 0$ for ¹H or to chloroform $\delta = 77.0$ for ¹³C as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, m = multiplet). Coupling constant *J* was reported in hertz (Hz).

2. General procedure for synthesis of trifluoromethyl thioethers

Table SI. Optimization of the reaction conditions^a



Entry	[Cu]	Ligand	PPh ₃ (eq.)	additive	Solvent	Temp. (°C)	time (h)	Yield (%) ^b
1	-	-	2.0	KF	CH ₃ CN	25	14	0
2	CuI	bpy	2.0	KF	CH ₃ CN	25	14	8
3	CuI	bpy	1.0	KF	CH ₃ CN	25	14	6
4	CuI	bpy	1.5	KF	CH ₃ CN	25	14	18
5	CuI	bpy	1.5	KF	DMSO	25	14	5
6	CuI	bpy	1.5	KF	DMF	25	14	71
7	CuI	bpy	1.5	KF	DMAc	25	14	12
8	CuI	bpy	1.5	KF	H ₂ O	25	14	0
9	CuI	bpy	1.5	K ₂ CO ₃	DMF	25	14	35
10	CuI	bpy	1.5	<i>t</i> -BuOK	DMF	25	14	2
11	CuI	bpy	1.5	Cs ₂ CO ₃	DMF	25	14	37
12	CuI	bpy	1.5	NaOAc	DMF	25	14	29
13	CuI	bpy	1.5	CsF	DMF	25	14	82
14	CuBr	bpy	1.5	CsF	DMF	25	14	61
15	CuBr ₂	bpy	1.5	CsF	DMF	25	14	67
16	CuCl	bpy	1.5	CsF	DMF	25	14	49
17	CuCl ₂	bpy	1.5	CsF	DMF	25	14	48
18	CuI	1,10-Phen	1.5	CsF	DMF	25	14	23
19	CuI	4,4'-bpy	1.5	CsF	DMF	25	14	0
20	CuI	bpy	1.5	CsF	DMF	60	14	73
21	CuI	bpy	1.5	CsF	DMF	90	14	80
22	CuI (1.0 eq)	bpy (1.0 eq)	1.5	CsF	DMF	25	14	78
23	CuI (0.1 eq)	bpy (0.1 eq)	1.5	CsF	DMF	25	14	65
24	CuI	bpy	1.5	CsF	DMF	25	6	71
25	CuI	bpy	1.5	CsF	DMF	25	24	82
26 ^c	CuI	bpy	1.5	CsF	DMF	25	14	65

^aReaction conditions: **1a** (0.10 mmol, 1.0 equiv), TMSCF₃ (0.40 mmol, 4.0 equiv), PPh₃ (0.15 mmol, 1.5 equiv), Cu salts (0.02 mmol, 20 mol%), ligand (0.02 mmol, 20 mol%), base (0.40 mmol, 4.0 equiv), 4,4-

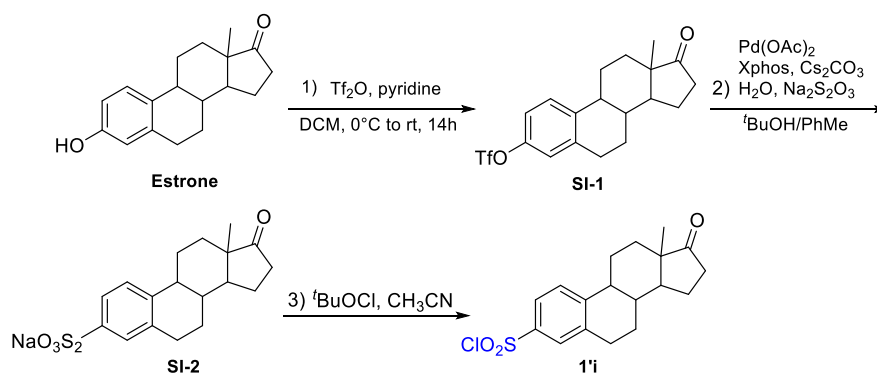
Difluorobiphenyl (0.1 mmol, 1.0 equiv, internal standard), solvent (1.5 ml). ^bYields determined by ¹⁹F NMR spectroscopy based on **1a**. ^cTMSCF₃ 2.0 equiv; CsF 2.0 equiv.

To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added sulfonyl chloride **1a** (0.5 mmol), TMSCF₃ (4.0 equiv), CuI (0.2 equiv), bpy (0.2 equiv), PPh₃ (1.5 equiv), CsF (4.0 equiv). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). DMF (5 mL) was then added to the tube by syringe. The reaction mixture was required to stir for 14 hours at room temperature in a nitrogen atmosphere. After the reaction finished, the reaction mixture was diluted with dichloromethane, filtered through a plug of celite and washed with dichloromethane. The filtrate was washed with H₂O (3×10 mL). The organic layer was washed with brine (30 mL) and dried over anhydrous Na₂SO₄, then concentrated under vacuum. The residue was purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent.

3. Modification of complex natural product and pharmaceutical molecules

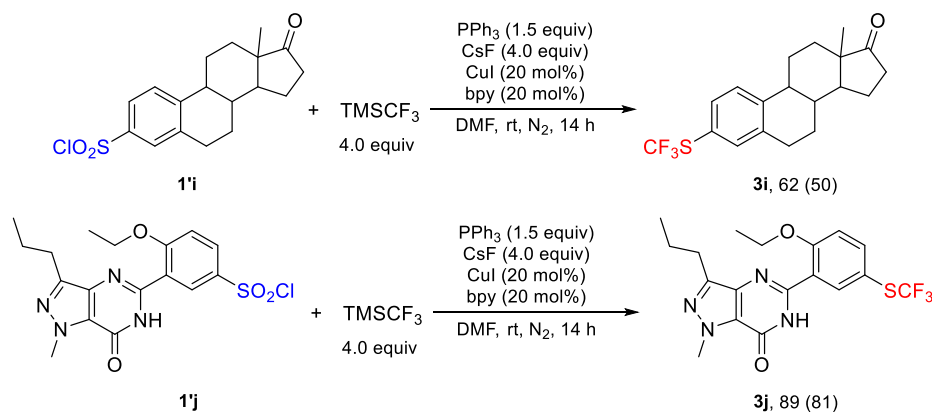
The arylsulfonyl chloride **1'i** corresponding to product **3i** was prepared according to the literature procedures.¹

1) Synthesis of estrone derivative^a

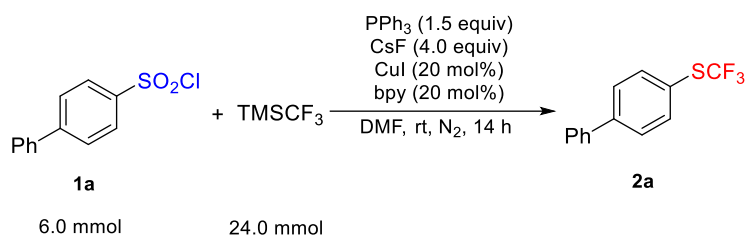


^aReagents and conditions: 1) estrone (4.056 g, 15.0 mmol, 1 equiv.), pyridine (3.640 mL, 3 equiv.), DCM (90 mL), 0 °C, trifluoromethanesulfonic anhydride (3.028 mL, 18 mmol, 1.2 equiv.) was added dropwise. Then the mixture was stirred at room temperature for 14 h. 2) **SI-1** (2.415 g, 6.0 mmol, 1.0 equiv.), Pd(OAc)₂ (0.135 g, 0.6 mmol, 10 mol%), xphos (0.858 g, 1.8 mmol, 30 mol%), Cs₂CO₃ (3.91g, 12.0 mmol, 2.0 equiv.), H₂O (0.216g, 12.0 mmol, 2.0 equiv.), Na₂S₂O₃ (2.367g, 15.0 mmol, 2.5 equiv.), ^tBuOH/PhMe (36.0/54.0 mL), N₂, 80 °C, 8 h. 3) **SI-2** (1.095g, 2.0 mmol, 1.0 equiv.), H₂O (0.18 mg, 10.0 mmol, 5.0 equiv.), ^tBuOCl (1.086 g, 10.0 mmol, 5.0 equiv.), CH₃CN (30 mL), 0 °C, 30 min.

2) Target product of complex substrates were prepared according to the general procedure.

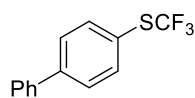


4. Synthesis of aryl trifluoromethyl thioethers in 6 mmol scale

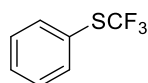


To an oven-dried 100 mL Schlenk tube equipped with a stir bar were added arylsulfonyl chloride **1a** (6 mmol, 1.516g, 1 equiv), TMSCF₃ (24 mmol, 3.408g, 4.0 equiv), CuI (1.2 mmol, 0.229g, 0.2 equiv), bpy (1.2 mmol, 0.187g, 0.2 equiv), PPh₃ (9 mmol, 2.361g, 1.5 equiv), CsF (24 mmol, 3.648g, 4.0 equiv). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). DMF (60 mL) was then added to the tube by syringe. The reaction mixture was required to stirred for 14 hours at room temperature in a nitrogen atmosphere. After the reaction finished, the reaction mixture was diluted with dichloromethane, filtered through a plug of celite and washed with dichloromethane. The filtrate was washed with H₂O (3×60 mL). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄, then concentrated under vacuum and the residue was purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent to afford pure compound **2a** (1.099 g, 72%).

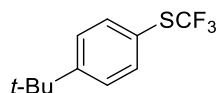
5. Characterization data of the products



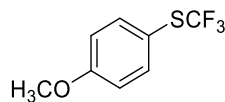
(1,1'-biphenyl)-4-yl(trifluoromethyl)sulfane (2a)² Following the general procedure, compound **2a** was synthesized and isolated as white solid (0.095 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.50 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.70 (s). ¹³C NMR (101 MHz, CDCl₃) δ 143.8 (s), 139.7 (s), 136.7 (s), 129.6 (q, *J* = 308.3 Hz), 129.0 (s), 128.2 (s), 127.2 (s), 123.1 (dd, *J* = 3.9, 1.9 Hz).



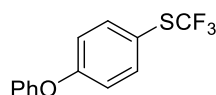
phenyl(trifluoromethyl)sulfane (2b)³ Following the general procedure, compound **2b** was synthesized and isolated as a colorless liquid (0.026 g, 29%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.77 (s). ¹³C NMR (101 MHz, CDCl₃) δ 136.4 (s), 130.8 (s), 129.7 (q, *J* = 307.9 Hz), 129.5 (s), 124.4 (dd, *J* = 4.1, 2.0 Hz).



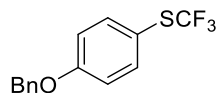
(4-(tert-butyl)phenyl)(trifluoromethyl)sulfane (2c)³ Following the general procedure, compound **2c** was synthesized and isolated as yellow oil (0.081 g, 69%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.39 (m, 2H), 1.33 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.98 (s). ¹³C NMR (101 MHz, CDCl₃) δ 154.4 (s), 136.2 (s), 129.7 (q, *J* = 307.9 Hz), 126.6 (s), 120.9 (dd, *J* = 4.1, 2.0 Hz).



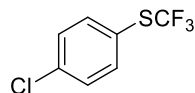
(4-methoxyphenyl)(trifluoromethyl)sulfane (2d)³ Following the general procedure, compound **2d** was synthesized and isolated as colorless oil (0.036g, 35%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.8 Hz, 2H), 6.99 – 6.87 (m, 2H), 3.83 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.94 (s). ¹³C NMR (101 MHz, CDCl₃) δ 161.9 (s), 138.3 (s), 129.6 (q, J = 308.1 Hz), 115.0 (s), 114.8 (d, J = 2.2 Hz), 55.4 (s).



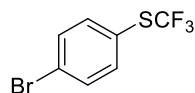
(4-phenoxyphenyl)(trifluoromethyl)sulfane (2e)⁴ Following the general procedure, compound **2e** was synthesized and isolated as colorless oil (0.077g, 57%). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 8.7 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.10 (dd, J = 8.5, 0.9 Hz, 2H), 7.06 – 6.99 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.52 (s). ¹³C NMR (101 MHz, CDCl₃) δ 160.42 (s), 155.6 (s), 138.4 (s), 130.1 (s), 129.6 (q, J = 308.2 Hz), 124.6 (s), 120.1 (s), 118.6 (s), 117.3 (dd, J = 4.1, 2.0 Hz).



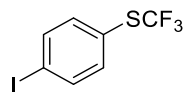
(4-benzyloxyphenyl)(trifluoromethyl)sulfane (2f)⁴ Following the general procedure, compound **2f** was synthesized and isolated as colorless oil (0.078 g, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.8 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.02 – 6.97 (m, 2H), 5.08 (s, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.82 (s). ¹³C NMR (101 MHz, CDCl₃) δ 161.0 (s), 138.3 (s), 136.2 (s), 129.6 (q, J = 308.1 Hz), 128.7 (s), 128.3 (s), 127.5 (s), 115.8 (s), 115.1 (q, J = 2.0 Hz), 70.2 (s).



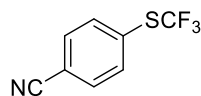
(4-chlorophenyl)(trifluoromethyl)sulfane (2g)³ Following the general procedure, compound **2g** was synthesized and isolated as colorless oil (0.021 g, 20%). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.5 Hz, 2H), 7.38 – 7.33 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.95 (s). ¹³C NMR (101 MHz, CDCl₃) δ 137.7 (s), 137.6 (s), 129.77 (s), 129.4 (q, J = 308.2 Hz), 122.8 (q, J = 2.1 Hz).



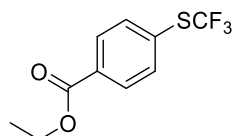
(4-bromophenyl)(trifluoromethyl)sulfane (2h)⁴ Following the general procedure, compound **2h** was synthesized and isolated as colorless oil (0.039 g, 30%). ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.55 (m, 2H), 7.52 (d, J = 8.5 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.52 (s). ¹³C NMR (101 MHz, CDCl₃) δ 140.2 (s), 134.8 (s), 131.3 (s), 129.6 (q, J = 308.6 Hz), 121.8 (d, J = 2.1 Hz).



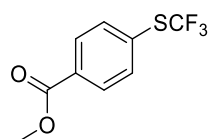
(4-iodophenyl)(trifluoromethyl)sulfane (2i)³ Following the general procedure, compound **2i** was synthesized and isolated as colorless oil (0.058 g, 38%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.74 (m, 2H), 7.40 – 7.34 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.29 (s). ¹³C NMR (101 MHz, CDCl₃) δ 138.8 (s), 137.7 (s), 129.2 (q, J = 308.4 Hz), 124.2 (dd, J = 4.3, 2.2 Hz), 98.0 (s).



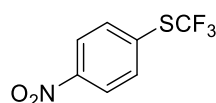
4-((trifluoromethyl)thio)benzotrile (2j)⁴ Following the general procedure, compound **2j** was synthesized and isolated as colorless oil (0.04 g, 39%). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.3 Hz, 2H), 7.75 – 7.69 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.53 (s). ¹³C NMR (101 MHz, CDCl₃) δ 136.0 (s), 133.0 (s), 130.6 (q, J = 2.1 Hz), 129.1 (q, J = 308.8 Hz), 117.6 (s), 114.7 (s).



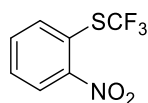
ethyl 4-((trifluoromethyl)thio)benzoate (2k)⁴ Following the general procedure, compound **2k** was synthesized and isolated as colorless oil (0.065 g, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.06 (m, 2H), 7.72 (d, J = 8.3 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.82 (s). ¹³C NMR (101 MHz, CDCl₃) δ 165.6 (s), 135.6 (s), 132.6 (s), 130.4 (s), 129.7 (dd, J = 4.1, 2.0 Hz), 129.3 (q, J = 308.4 Hz), 61.5 (s), 14.3 (s).



1-(4-((trifluoromethyl)thio)phenyl)ethan-1-one (2l)³ Following the general procedure, compound **2l** was synthesized and isolated as colorless oil (0.059 g, 50%). ¹H NMR (400 MHz, CDCl₃) δ 8.27 – 7.97 (m, 2H), 7.72 (d, J = 8.3 Hz, 2H), 3.94 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.83 (s). ¹³C NMR (101 MHz, CDCl₃) δ 166.1 (s), 135.6 (s), 132.2 (s), 130.4 (s), 129.9 (dd, J = 4.1, 2.1 Hz), 129.3 (q, J = 308.3 Hz), 52.5 (s).

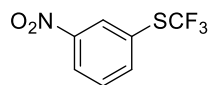


(4-nitrophenyl)(trifluoromethyl)sulfane (2m)⁵ Following the general procedure, compound **2m** was synthesized and isolated as yellow oil (0.035 g, 31%). ¹H NMR (400 MHz, CDCl₃) δ 8.31 – 8.24 (m, 2H), 7.85 (t, J = 7.4 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.31 (s). ¹³C NMR (101 MHz, CDCl₃) δ 136.1 (d, J = 0.4 Hz), 129.1 (q, J = 310.1 Hz), 126.8 (dd, J = 7.1, 3.0 Hz), 124.4 (s), 124.1 (s).

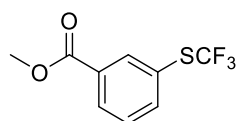


(2-nitrophenyl)(trifluoromethyl)sulfane (2n)⁵ Following the general procedure, compound **2n** was synthesized and isolated as yellow oil (0.019 g, 17%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (dd, J = 8.2, 1.4 Hz,

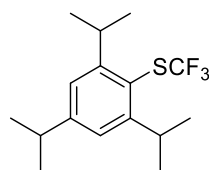
1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.68 (td, $J = 7.8, 1.5$ Hz, 1H), 7.58 – 7.53 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -43.14 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 149.4 (d, $J = 1.6$ Hz), 133.7 (s), 132.4 (d, $J = 2.1$ Hz), 129.5 (s), 128.9 (q, $J = 310.4$ Hz), 125.7 (s), 124.1 (d, $J = 2.2$ Hz).



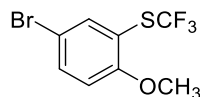
(3-nitrophenyl)(trifluoromethyl)sulfane (2o)⁶ Following the general procedure, compound **2o** was synthesized and isolated as yellow oil (0.030 g, 27%). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 1.7$ Hz, 1H), 8.37 (ddd, $J = 8.3, 2.1, 0.9$ Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.66 (t, $J = 8.0$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.05 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 148.6 (s), 141.8 (s), 130.8 (s), 130.5 (s), 129.1 (q, $J = 308.8$ Hz), 126.7 (dd, $J = 4.0, 2.0$ Hz), 125.8 (s).



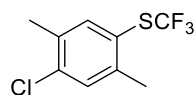
1-(3-((trifluoromethyl)thio)phenyl)ethan-1-one (2p)⁷ Following the general procedure, compound **2p** was synthesized and isolated as colorless oil (0.041 g, 35%). ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 8.22 – 8.12 (m, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 3.95 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.48 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 165.80 (s), 140.4 (s), 137.3 (s), 131.9 (s), 131.7 (s), 129.6 (s), 129.4 (q, $J = 308.3$ Hz), 125.1 (dd, $J = 4.0, 2.0$ Hz), 52.5 (s).



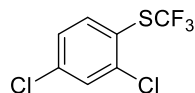
(trifluoromethyl)(2,4,6-triisopropylphenyl)sulfane (2q)⁸ Following the general procedure, compound **2q** was synthesized and isolated as colorless liquid (0.090 g, 59%). ^1H NMR (400 MHz, CDCl_3) δ 7.09 (s, 2H), 3.90 (dt, $J = 13.7, 6.9$ Hz, 2H), 2.90 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.26 (d, $J = 6.9$ Hz, 8H), 1.22 (d, $J = 8.2$ Hz, 12H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.70 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 155.1 (s), 152.5 (s), 129.6 (q, $J = 309.2$ Hz), 122.6 (s), 121.8 (s), 117.8 (d, $J = 1.6$ Hz), 34.4 (s), 31.6 (s), 23.8 (s).



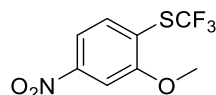
(5-bromo-2-methoxyphenyl)(trifluoromethyl)sulfane (2r)² Following the general procedure, compound **2r** was synthesized and isolated as colorless oil (0.065 g, 45%). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 2.4$ Hz, 1H), 7.55 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.86 (d, $J = 8.9$ Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.04 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 158.6 (s), 139.2 (s), 134.5 (s), 128.3 (q, $J = 309.3$ Hz), 113.4 (dd, $J = 3.9, 2.0$ Hz), 112.2 (s), 111.6 (s), 55.3 (s).



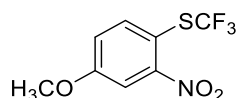
(4-chloro-2,5-dimethylphenyl)(trifluoromethyl)sulfane (2s) Following the general procedure, compound **2s** was synthesized and isolated as colorless oil (0.058 g, 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 1H), 7.32 (s, 1H), 2.47 (s, 3H), 2.35 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.52 (s). ¹³C NMR (101 MHz, CDCl₃) δ 142.9 (s), 140.2 (s), 137.8 (s), 134.8 (s), 131.3 (s), 129.6 (q, *J* = 308.6 Hz), 121.8 (d, *J* = 2.1 Hz), 20.6 (s), 19.4 (s). HRMS *m/z* (EI): calcd. for C₉H₈ClF₃S, [M]⁺: 239.9987; found: 239.9988.



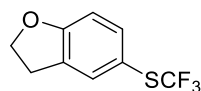
(2,4-Dichlorophenyl)(trifluoromethyl)sulfane (2t) Following the general procedure, compound **2t** was synthesized and isolated as colorless oil (0.025 g, 20%). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.2 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.05 (s). ¹³C NMR (101 MHz, CDCl₃) δ 141.1 (s), 139.2 (s), 138.3 (s), 130.6 (s), 129.0 (q, *J* = 309.7 Hz), 128.1 (s), 122.5 (dd, *J* = 4.3, 2.2 Hz). HRMS *m/z* (EI): calcd. for C₇H₃Cl₂F₃S, [M]⁺: 245.9285; found: 245.9283.



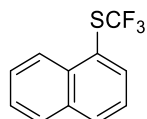
(2-methoxy-4-nitrophenyl)(trifluoromethyl)sulfane (2u) Following the general procedure, compound **2u** was synthesized and isolated as a yellow oil (0.049 g, 39%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 4.02 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.32 (s). ¹³C NMR (101 MHz, CDCl₃) δ 159.7 (s), 150.2 (s), 136.0 (d, *J* = 1.1 Hz), 129.0 (q, *J* = 309.4 Hz), 121.8 (dd, *J* = 4.0, 2.0 Hz), 116.0 (s), 106.3 (s), 56.8 (s). HRMS *m/z* (EI): calcd. for C₈H₆O₃NF₃S, [M]⁺: 253.0020; found: 253.0012.



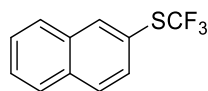
(4-methoxy-2-nitrophenyl)(trifluoromethyl)sulfane (2v)⁹ Following the general procedure, compound **2v** was synthesized and isolated as yellow oil (0.038 g, 30%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.92 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.05 (s). ¹³C NMR (101 MHz, CDCl₃) δ 161.3 (s), 153.1 (dd, *J* = 2.8, 1.3 Hz), 137.1 (d, *J* = 1.1 Hz), 128.9 (q, *J* = 310.1 Hz), 119.4 (s), 111.0 (dd, *J* = 4.8, 2.5 Hz), 110.5 (s), 56.2 (s).



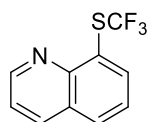
5-((trifluoromethyl)thio)-2,3-dihydrobenzofuran (2w)¹⁰ Following the general procedure, compound **2w** was synthesized and isolated as colorless oil (0.087 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 4.64 (t, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 8.8 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -44.18 (s). ¹³C NMR (101 MHz, CDCl₃) δ 156.0 (s), 137.3 (s), 135.1 (s), 128.6 (q, *J* = 308.1 Hz), 127.7 (s), 127.2 (s), 126.5 (s), 114.1 (dd, *J* = 4.0, 2.0 Hz), 69.1 (s).



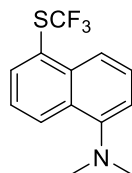
naphthalen-1-yl(trifluoromethyl)sulfane (3a)² Following the general procedure, compound **3a** was synthesized and isolated as colorless oil (0.067 g, 59%). ¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 8.5 Hz, 1H), 7.95 (t, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.46 (dd, *J* = 8.1, 7.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.14 (s). ¹³C NMR (101 MHz, CDCl₃) δ 136.7 (s), 136.7 (s), 134.34 (s), 133.2 (s), 131.3 (s), 128.7 (q, *J* = 309.2 Hz), 127.5 (s), 126.6 (s), 125.7 (s), 124.8 (s), 124.5 (s), 120.6 (dd, *J* = 3.6, 1.8 Hz).



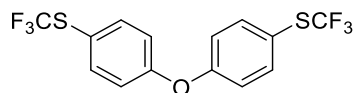
naphthalen-2-yl(trifluoromethyl)sulfane (3b)⁴ Following the general procedure, compound **3b** was synthesized and isolated as colorless oil (0.071 g, 62%). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 3H), 7.66 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.60 – 7.51 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.47 (s). ¹³C NMR (101 MHz, CDCl₃) δ 137.0 (s), 133.9 (s), 133.4 (s), 131.8 (s), 129.8 (q, *J* = 309.1 Hz), 129.2 (s), 128.2 (s), 128.0 (s), 127.8 (s), 127.0 (s), 121.5 (dd, *J* = 3.9, 1.9 Hz).



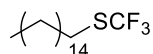
8-((trifluoromethyl)thio)quinolone (3c)¹¹ Following the general procedure, compound **3c** was synthesized and isolated as colorless liquid (0.069 g, 60%). ¹H NMR (400 MHz, CDCl₃) δ 9.04 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 4.2 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.10 (s). ¹³C NMR (101 MHz, CDCl₃) δ 150.7 (s), 146.6 (s), 136.8 (s), 134.3 (d, *J* = 1.1 Hz), 129.9 (q, *J* = 308.5 Hz), 129.7 (s), 128.8 (s), 126.7 (s), 122.1 (s).



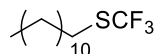
N,N-dimethyl-5-((trifluoromethyl)thio)naphthalen-1-amine (3d)¹² Following the general procedure, compound **3d** was synthesized and isolated as yellow oil (0.079 g, 58%). ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 1H), 7.60 – 7.43 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 2.88 (s, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.24 (s). ¹³C NMR (101 MHz, CDCl₃) δ 151.4 (s), 137.8 (s), 136.8 (s), 129.8 (s), 129.7 (q, *J* = 309.2 Hz), 128.6 (s), 127.5 (s), 124.6 (s), 121.8 (d, *J* = 1.8 Hz), 120.6 (s), 115.0 (s), 45.4 (s).



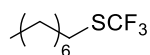
Bis[4-((trifluoromethyl)sulfonyl)phenyl] ether (3e) Following the general procedure, compound **3e** was synthesized and isolated as colorless oil (0.137 g, 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.63 (m, 4H), 7.09 – 7.04 (m, 4H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.29 (s). ¹³C NMR (101 MHz, CDCl₃) δ 157.7 (s), 137.5 (s), 128.4 (q, *J* = 308.2 Hz), 118.9 (s), 118.0 (q, *J* = 2.1 Hz). HRMS *m/z* (EI): calcd. for C₁₄H₈OF₆S₂, [M]⁺: 369.9921; found: 369.9912.



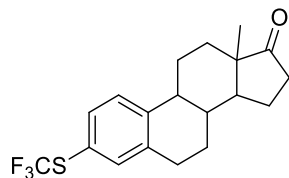
1-[(trifluoromethyl)thio]hexadecane (3f)¹³ Following the general procedure, compound **3f** was synthesized and isolated as colorless oil (0.052 g, 32%). ¹H NMR (400 MHz, CDCl₃) δ 2.92 – 2.81 (m, 2H), 1.74 – 1.63 (m, 2H), 1.44 – 1.35 (m, 2H), 1.26 (s, 24H), 0.88 (t, J = 6.8 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.29 (s). ¹³C NMR (101 MHz, CDCl₃) δ 131.2 (q, J = 305.6 Hz), 32.0 (s), 29.9 (d, J = 1.9 Hz), 29.7 (br s), 29.7 (s), 29.7 (s), 29.7 (s), 29.6 (s), 29.6 (s), 29.4 (br s), 29.4 (s), 29.0 (s), 28.5 (s), 22.7 (s), 14.1 (s).



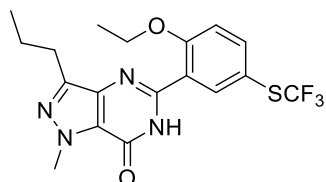
1-[(Trifluoromethyl)thio]dodecane (3g)¹⁴ Following the general procedure, compound **3g** was synthesized and isolated as colorless oil (0.047g 35%). ¹H NMR (400 MHz, CDCl₃) δ 2.87 (t, J = 7.5 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.46 – 1.35 (m, 2H), 1.27 (s, 16H), 0.88 (t, J = 6.6 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.38 (s). ¹³C NMR (101 MHz, CDCl₃) δ 130.3 (q, J = 305.6 Hz), 31.0 (s), 28.9 (d, J = 1.7 Hz), 28.7 (br s), 28.6 (s), 28.4 (br s), 28.4 (s), 28.0 (s), 27.6 (s), 21.7 (s), 13.1 (s).



1-[(trifluoromethyl)thio]octane (3h)¹⁵ Following the general procedure, compound **3h** was synthesized and isolated as colorless oil (0.029 g, 27%). ¹H NMR (400 MHz, CDCl₃) δ 2.92 – 2.82 (m, 2H), 1.73 – 1.64 (m, 2H), 1.39 (dd, J = 14.2, 7.1 Hz, 2H), 1.28 (s, 8H), 0.89 (t, J = 6.9 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.31 (s). ¹³C NMR (101 MHz, CDCl₃) δ 131.2 (q, J = 305.6 Hz), 31.7 (s), 29.9 (dd, J = 3.8, 1.8 Hz), 29.4 (s), 29.1 (s), 28.9 (s), 28.5 (s), 22.6 (s), 14.1 (s).

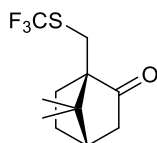


13-methyl-3-(trifluoro(thioxo)-16-methyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3i)¹² Following the general procedure, compound **3i** was synthesized and isolated as colorless oil (0.089 g, 50%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.29 (m, 3H), 2.94 (dd, J = 9.5, 4.8 Hz, 2H), 2.61 – 2.26 (m, 3H), 2.24 – 1.93 (m, 4H), 1.74 – 1.41 (m, 6H), 0.92 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.86 (s). ¹³C NMR (101 MHz, CDCl₃) δ 220.6 (s), 143.0 (s), 138.2 (s), 136.8 (s), 133.5 (s), 129.7 (q, J = 308.0 Hz), 126.6 (s), 121.2 (d, J = 1.9 Hz), 50.5 (s), 47.9 (s), 44.4 (s), 37.8 (s), 35.8 (s), 31.5 (s), 29.1 (s), 26.2 (s), 25.5 (s), 21.6 (s), 13.8 (s).



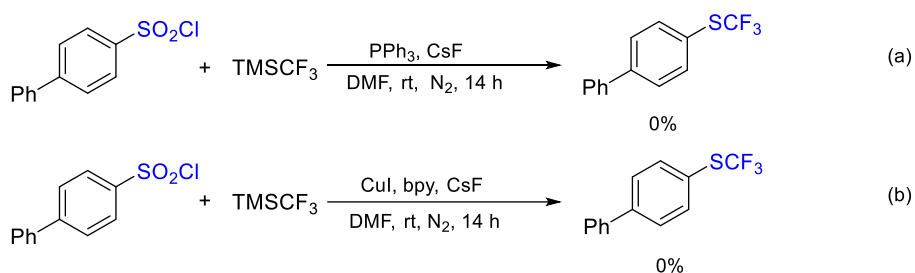
5-(2-ethoxy-5-((trifluoromethyl)thio)phenyl)-1-methyl-3-propyl-1,6-dihydro-7H-pyrazolo[4,3-d]pyrimidin-7-one (3j)¹² Following the general procedure, compound **3j** was synthesized and isolated as white solid (0.167 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 10.95 (s, 1H), 8.70 (d, J = 2.4 Hz, 1H), 7.72 (dd, J = 8.7, 2.4 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 4.33 (q, J = 7.0 Hz, 2H), 4.26 (s, 3H), 2.99 – 2.90 (m, 2H), 1.93 – 1.81

(m, 2H), 1.62 (t, $J = 7.0$ Hz, 3H), 1.04 (t, $J = 7.4$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.68 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 158.4 (s), 153.7 (d, $J = 9.4$ Hz), 146.9 (d, $J = 5.8$ Hz), 140.2 (s), 139.4 (s), 138.4 (s), 129.5 (q, $J = 308.4$ Hz), 124.5 (s), 121.6 (s), 116.9 (dd, $J = 4.3, 2.1$ Hz), 113.8 (s), 65.8 (s), 38.2 (s), 27.7 (s), 22.4 (s), 14.6 (s), 14.0 (s).



(1S,4R)-7,7-dimethyl-1-(((trifluoromethyl)thio)methyl)bicyclo[2.2.1]heptan-2-one (3k) Following the general procedure, compound **3k** was synthesized and isolated as white solid (0.025 g, 20%). ^1H NMR (400 MHz, CDCl_3) δ 2.96 (dd, $J = 144.8, 13.0$ Hz, 2H), 2.40 (ddd, $J = 18.5, 4.7, 2.8$ Hz, 1H), 2.14 (t, $J = 4.5$ Hz, 1H), 2.10 – 1.86 (m, 3H), 1.66 (ddd, $J = 13.6, 9.3, 4.0$ Hz, 1H), 1.48 – 1.38 (m, 1H), 1.06 (s, 3H), 0.93 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -42.99 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 216.6 (s), 131.3 (q, $J = 305.5$ Hz), 60.2 (s), 47.9 (s), 43.7 (s), 42.9 (s), 26.8 (s), 26.6 (s), 26.4 (q, $J = 2.5$ Hz), 20.0 (s), 19.7 (s). HRMS m/z (EI): calcd. for $\text{C}_{11}\text{H}_{15}\text{OF}_3\text{S}$, $[\text{M}]^+$: 252.0796; found: 252.0794.

6. Mechanism study

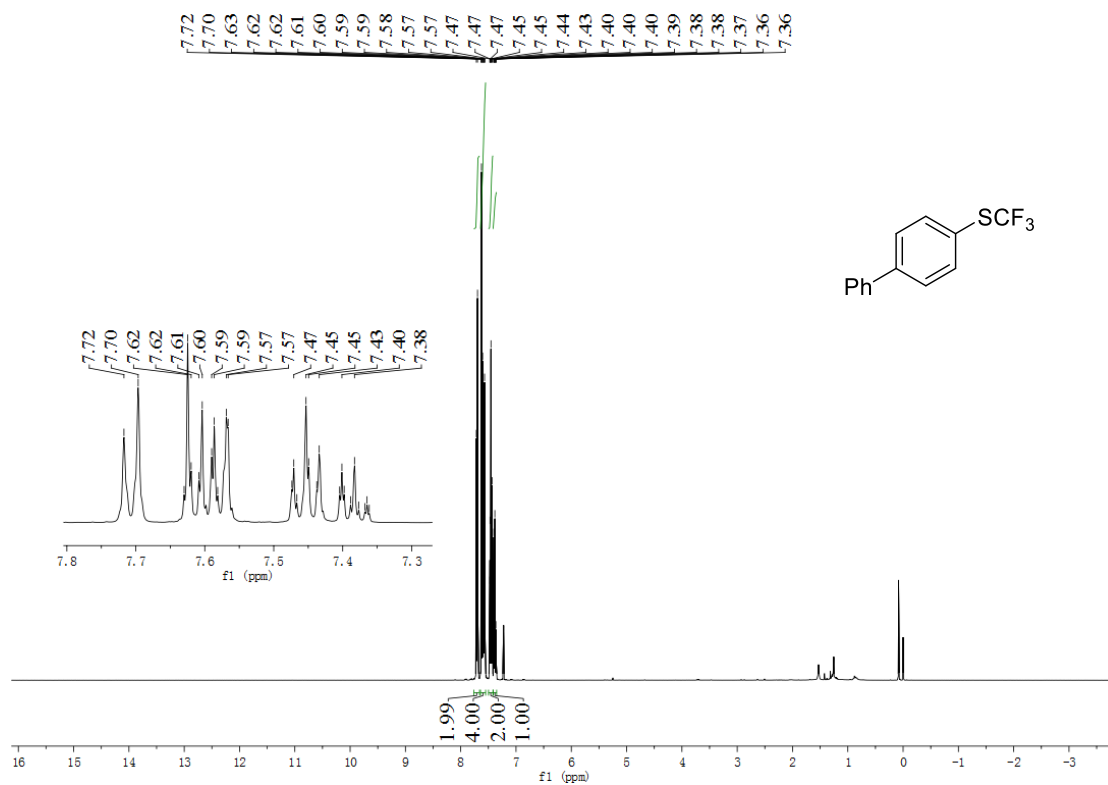


(a) To an oven-dried 25 mL Schlenk tube equipped with a stir bar was added arylsulfonyl chloride **1a** (0.5 mmol), TMSCF_3 (4.0 equiv), PPh_3 (1.5 equiv), CsF (4.0 equiv). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). DMF (5 mL) was then added to the tube by syringe. The reaction mixture was required to stirred for 14 hours at room temperature in a nitrogen atmosphere. After the reaction finished, the reaction mixture was diluted with dichloromethane, filtered through a plug of celite and washed with dichloromethane. The filtrate was washed with H_2O (3×10 mL). The organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4 , then filtered and concentrated under vacuum. The raw product was analyzed by ^{19}F NMR using 4,4'-difluorobiphenyl (-115.0 ppm) as internal standard.

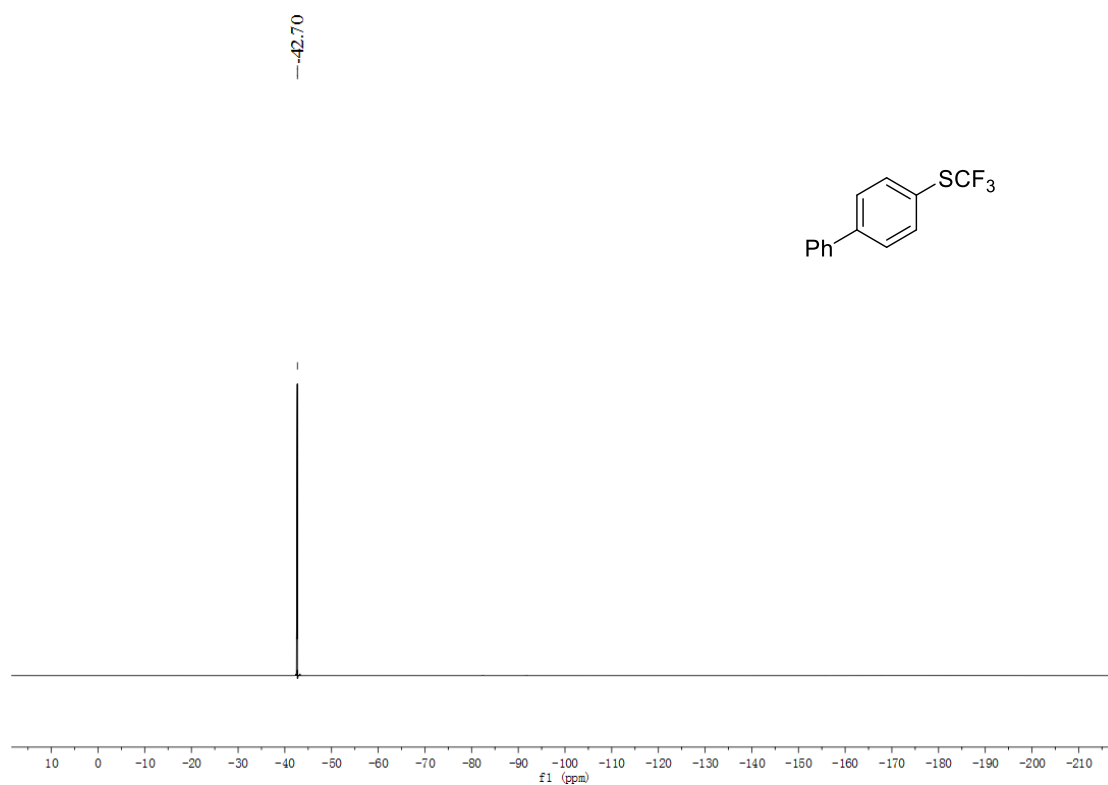
(b) To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added arylsulfonyl chloride **1a** (0.5 mmol), TMSCF_3 (4.0 equiv), CuI (0.2 equiv), bpy (0.2 equiv), CsF (4.0 equiv). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). DMF (5 mL) was then added to the tube by syringe. The reaction mixture was required to stirred for 14 hours at room temperature in a nitrogen atmosphere. After the reaction finished, the reaction mixture was diluted with dichloromethane, filtered through a plug of celite and washed with dichloromethane. The filtrate was washed with H_2O (3×10 mL). The organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4 , then filtered and concentrated under vacuum. The raw product was analyzed by ^{19}F NMR using 4,4'-difluorobiphenyl (-115.0 ppm) as internal standard.

7. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products

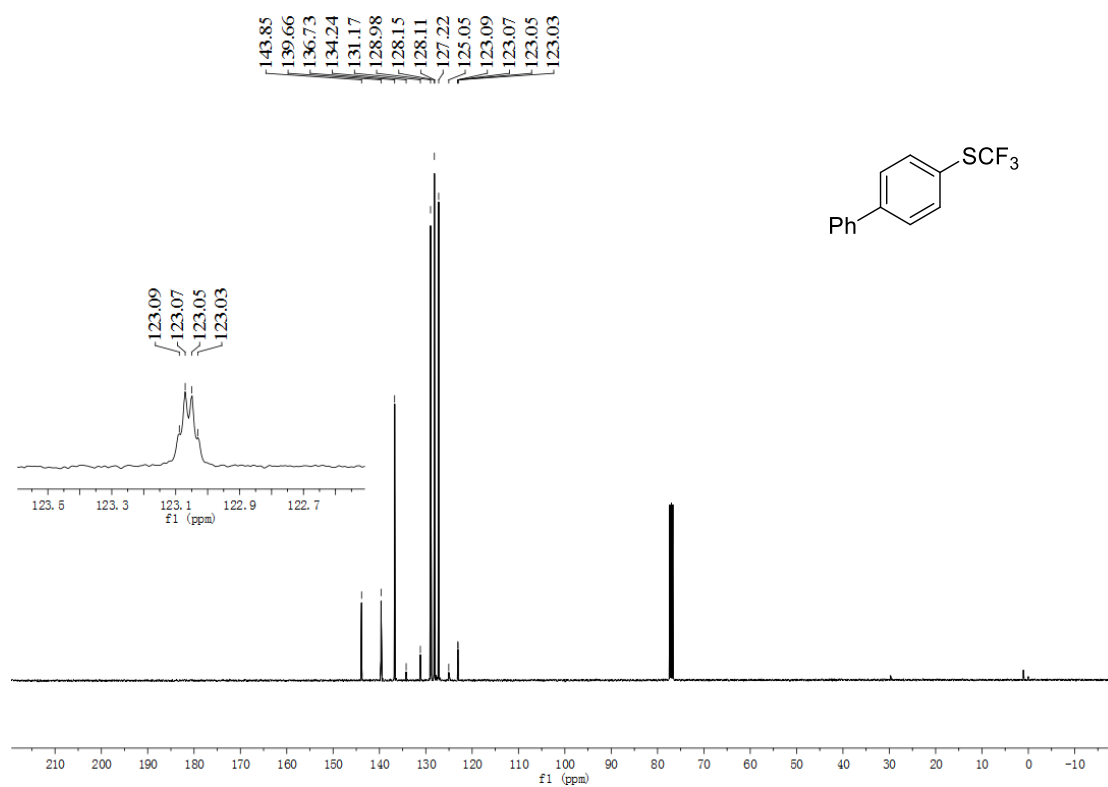
^1H NMR spectrum of **2a** (400 MHz, CDCl_3)



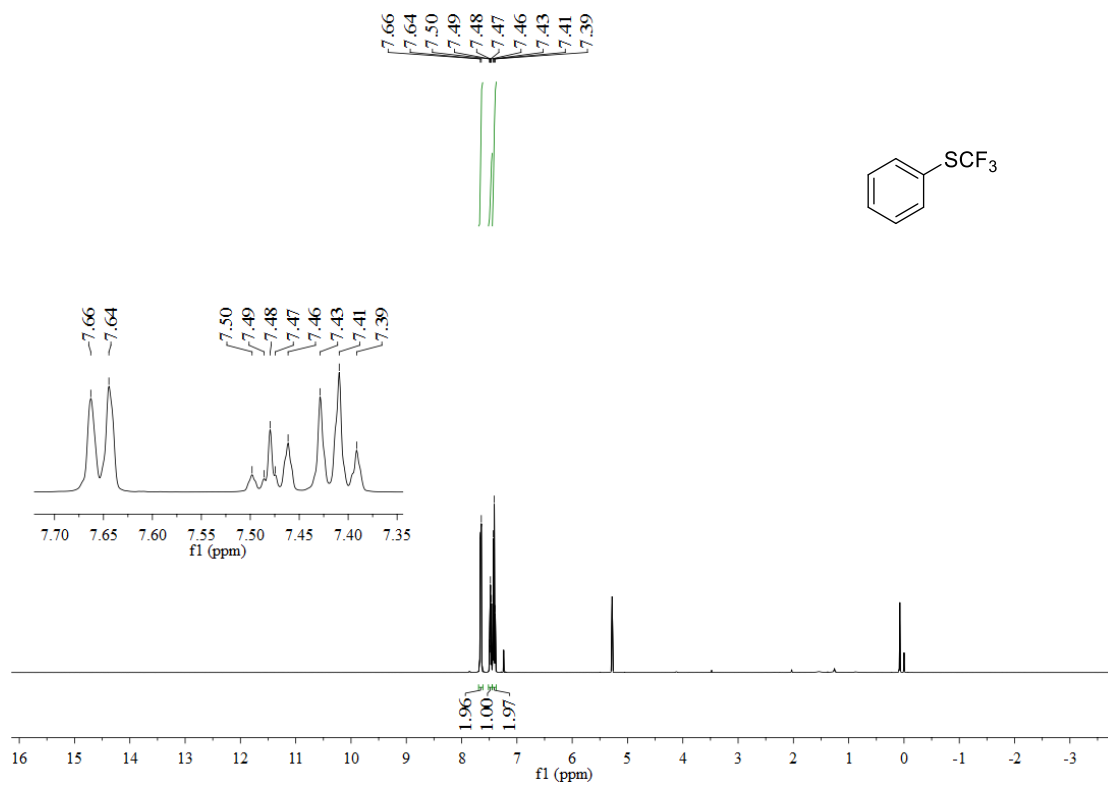
^{19}F NMR spectrum of **2a** (376 MHz, CDCl_3)



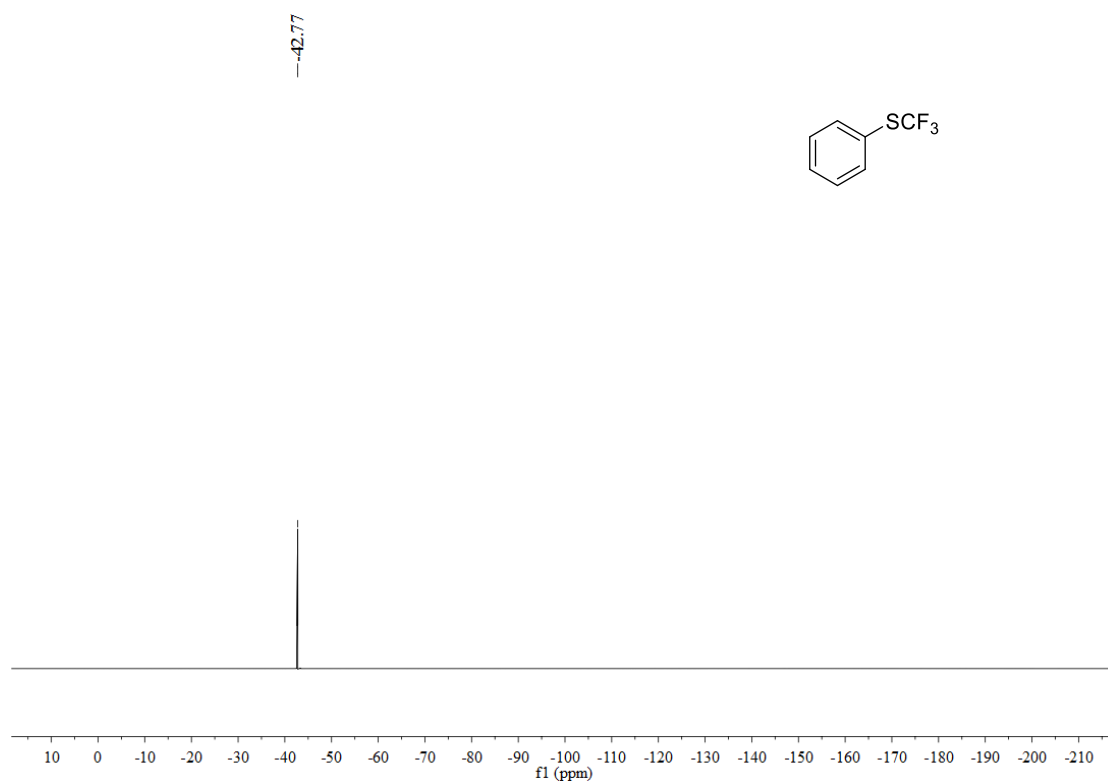
^{13}C NMR spectrum of **2a** (101 MHz, CDCl_3)



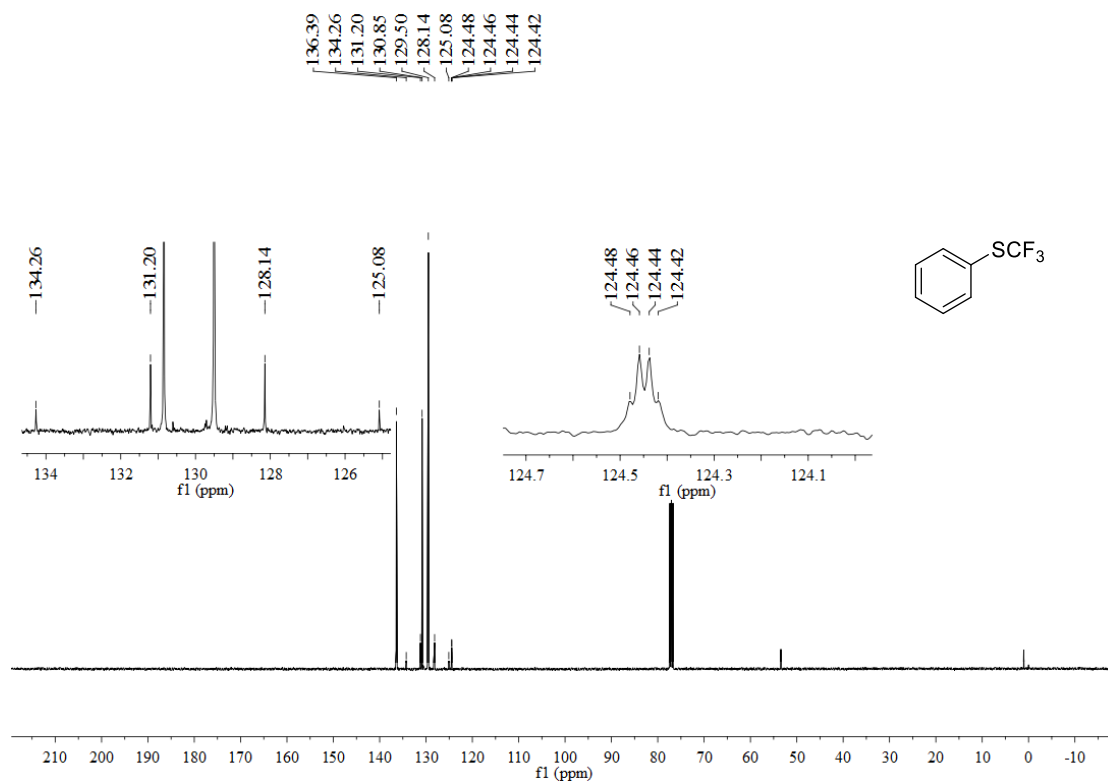
^1H NMR spectrum of **2b** (400 MHz, CDCl_3)



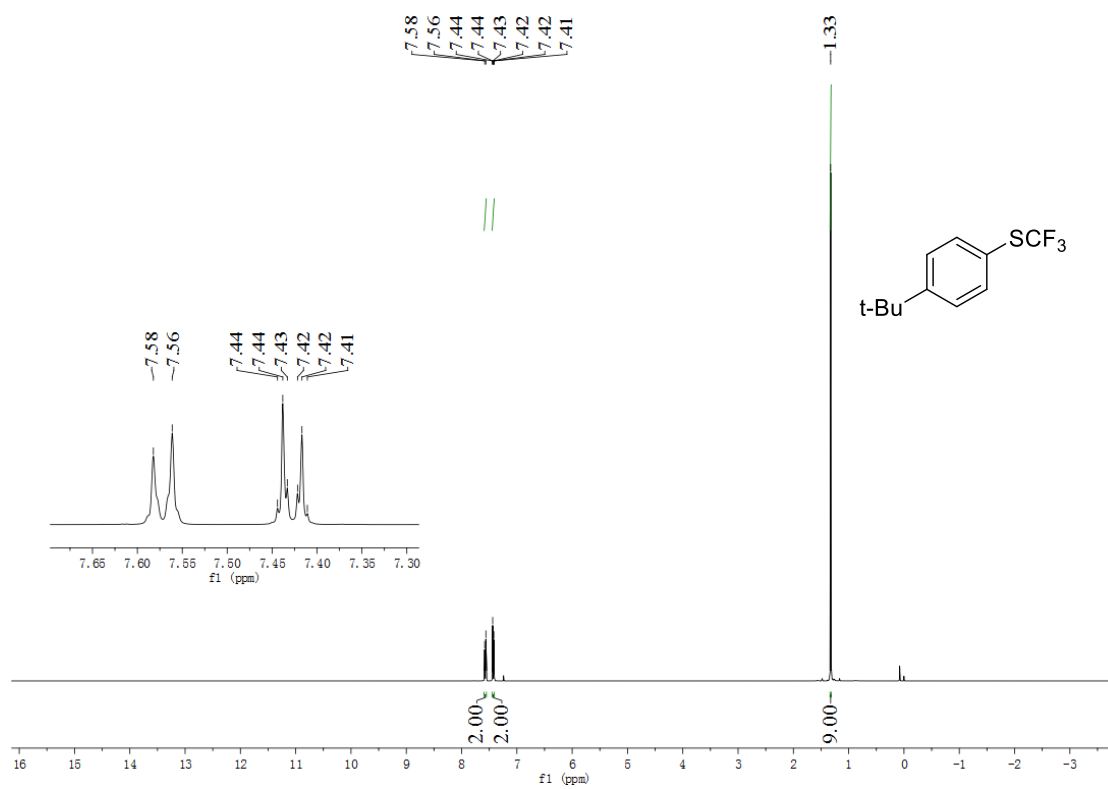
^{19}F NMR spectrum of **2b** (376 MHz, CDCl_3)



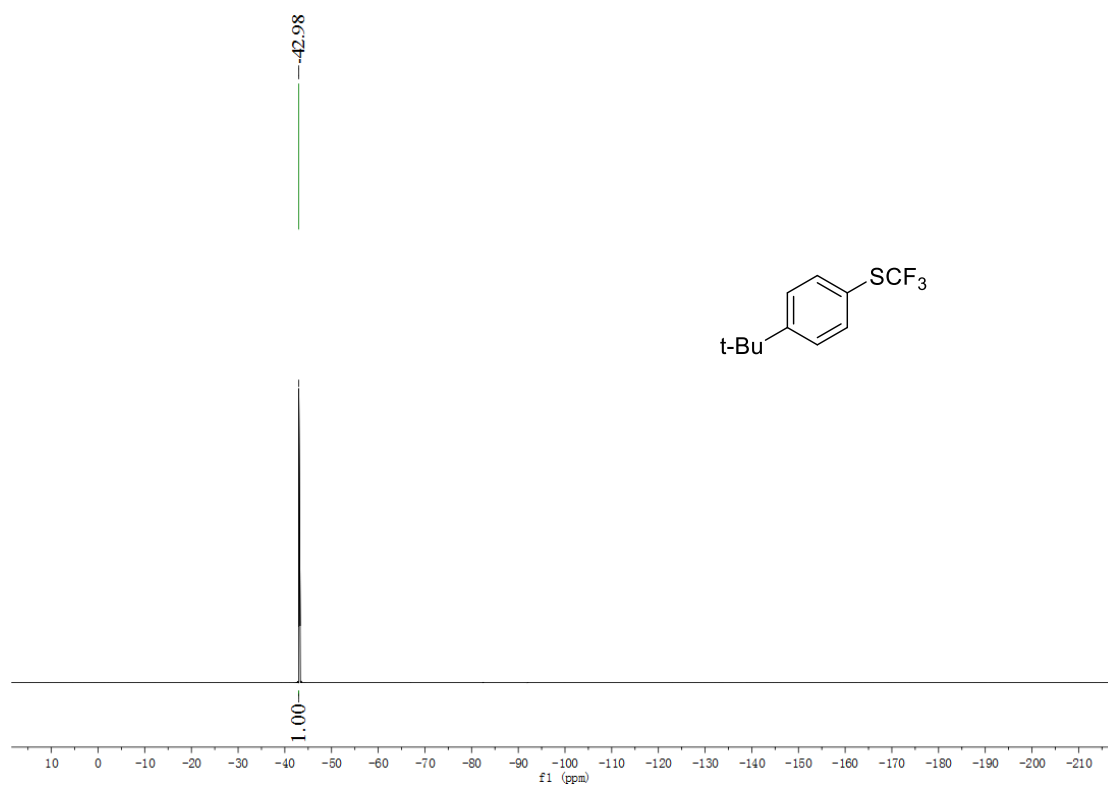
^{13}C NMR spectrum of **2b** (101 MHz, CDCl_3)



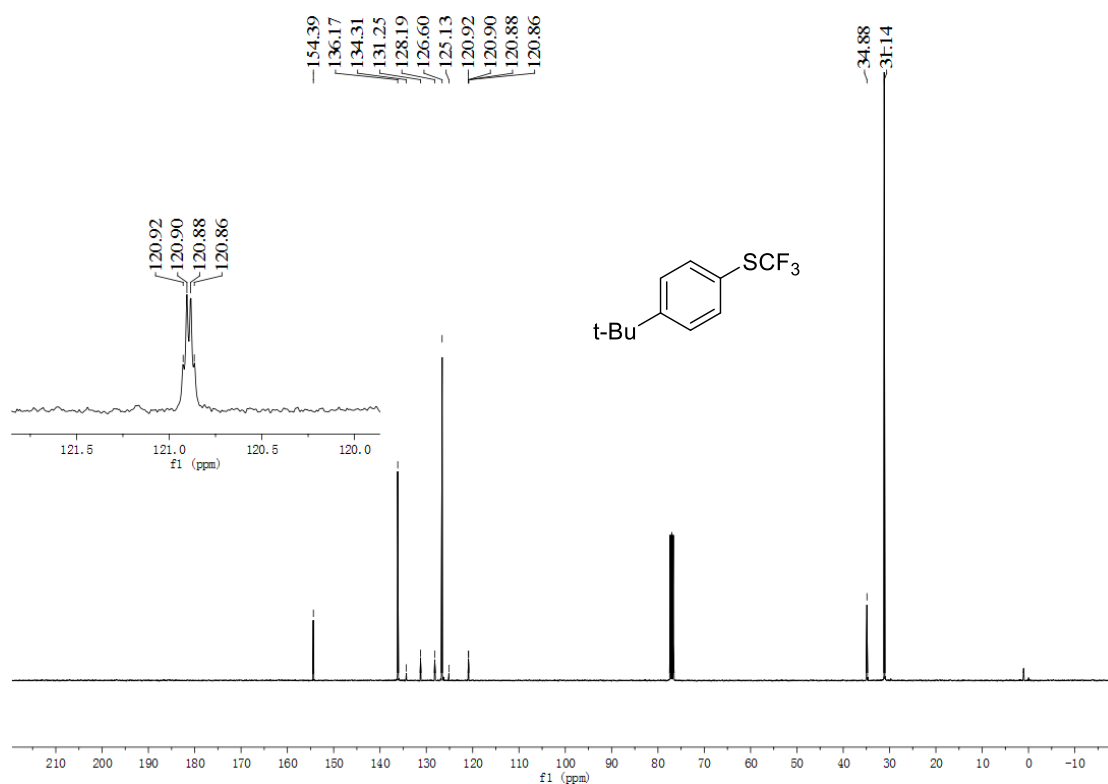
^1H NMR spectrum of **2c** (400 MHz, CDCl_3)



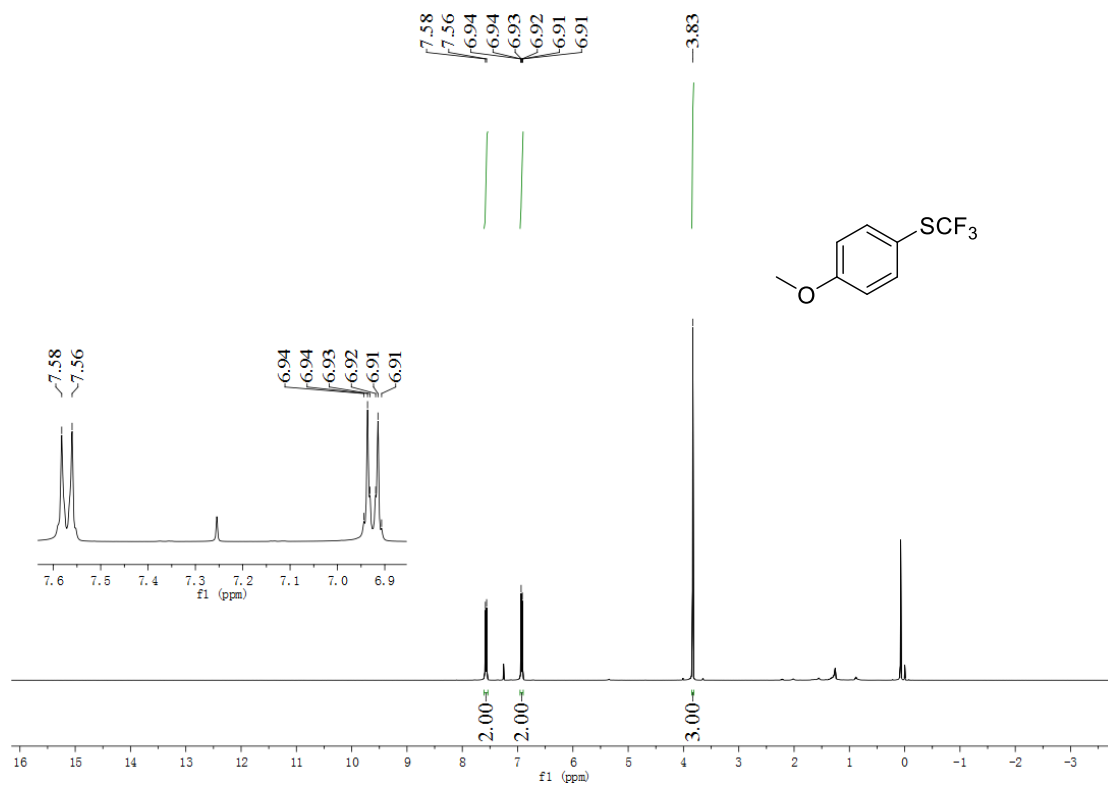
^{19}F NMR spectrum of **2c** (376 MHz, CDCl_3)



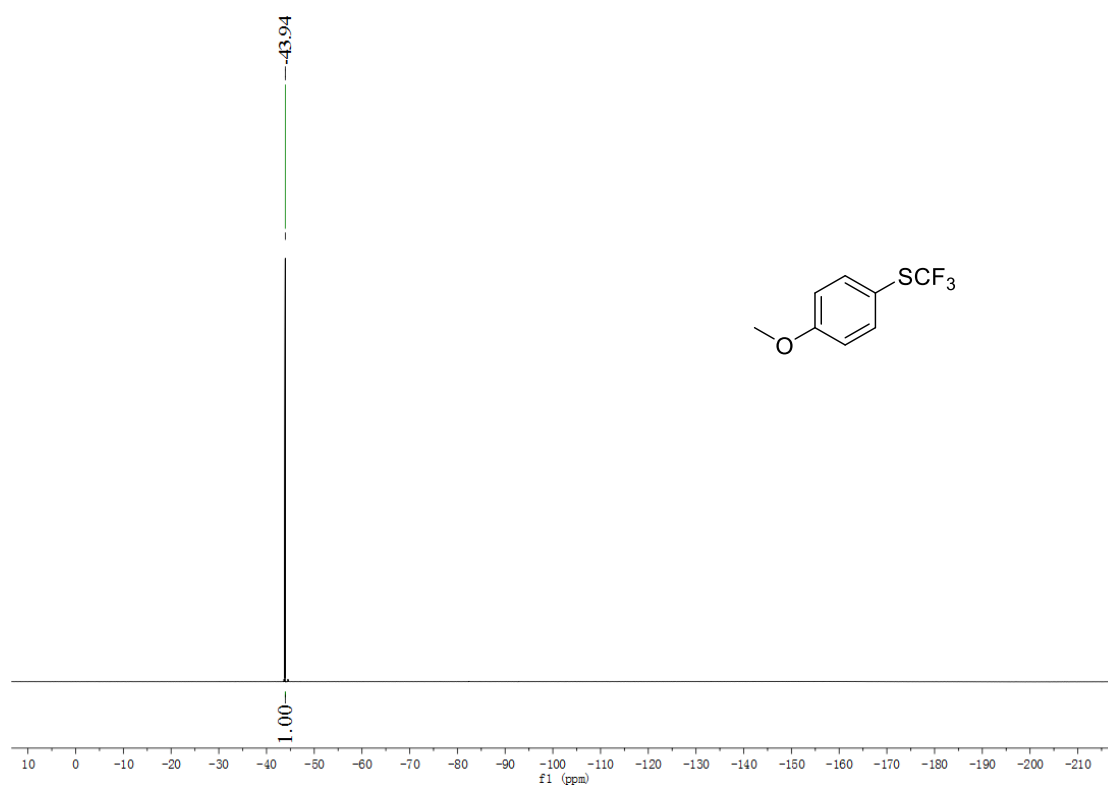
^{13}C NMR spectrum of **2c** (101 MHz, CDCl_3)



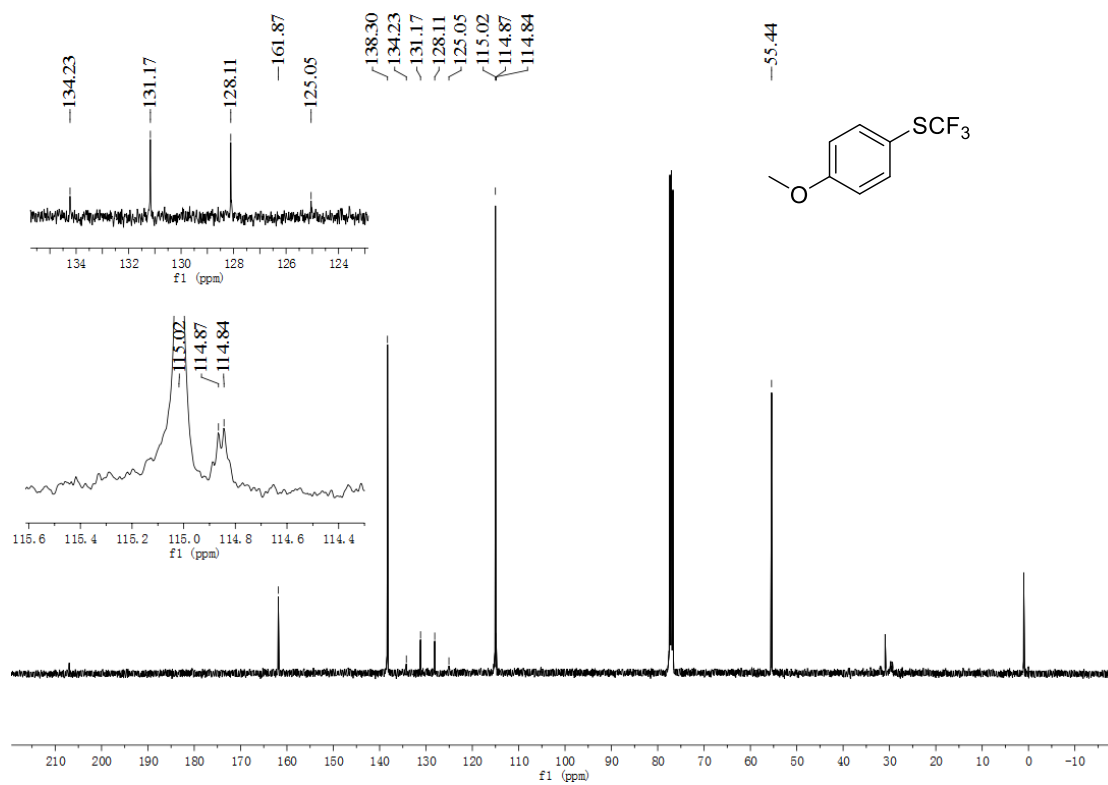
^1H NMR spectrum of **2d** (400 MHz, CDCl_3)



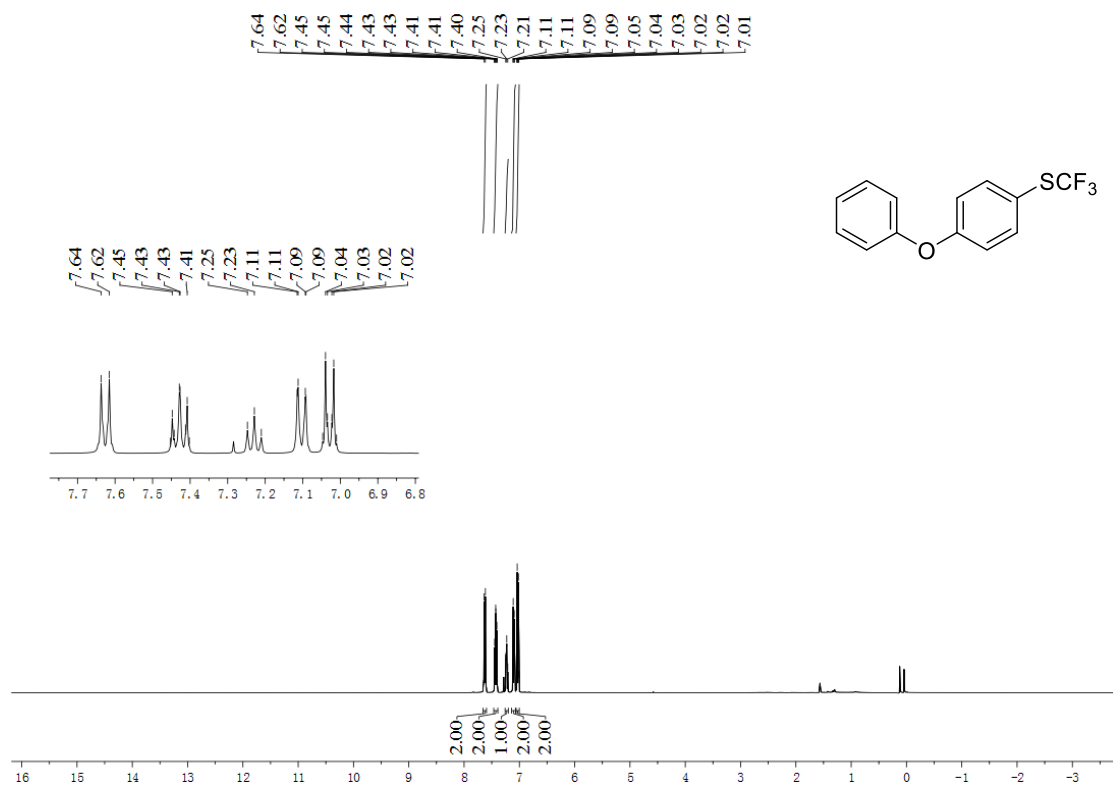
^{19}F NMR spectrum of **2d** (376 MHz, CDCl_3)



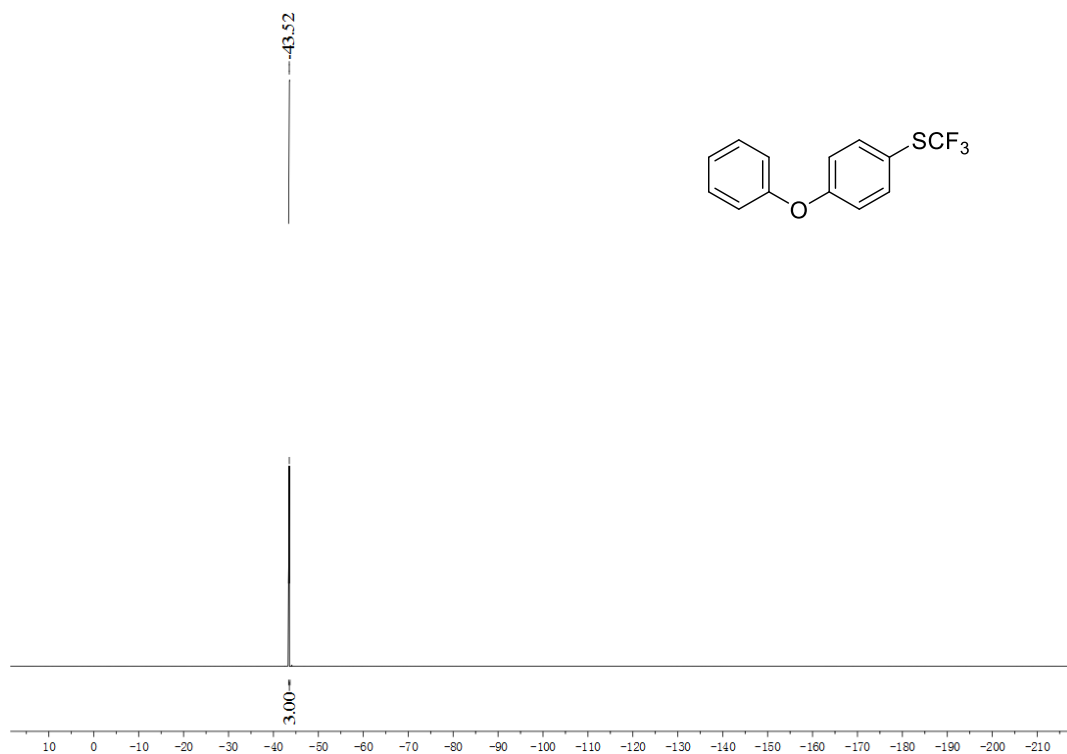
^{13}C NMR spectrum of **2d** (101 MHz, CDCl_3)



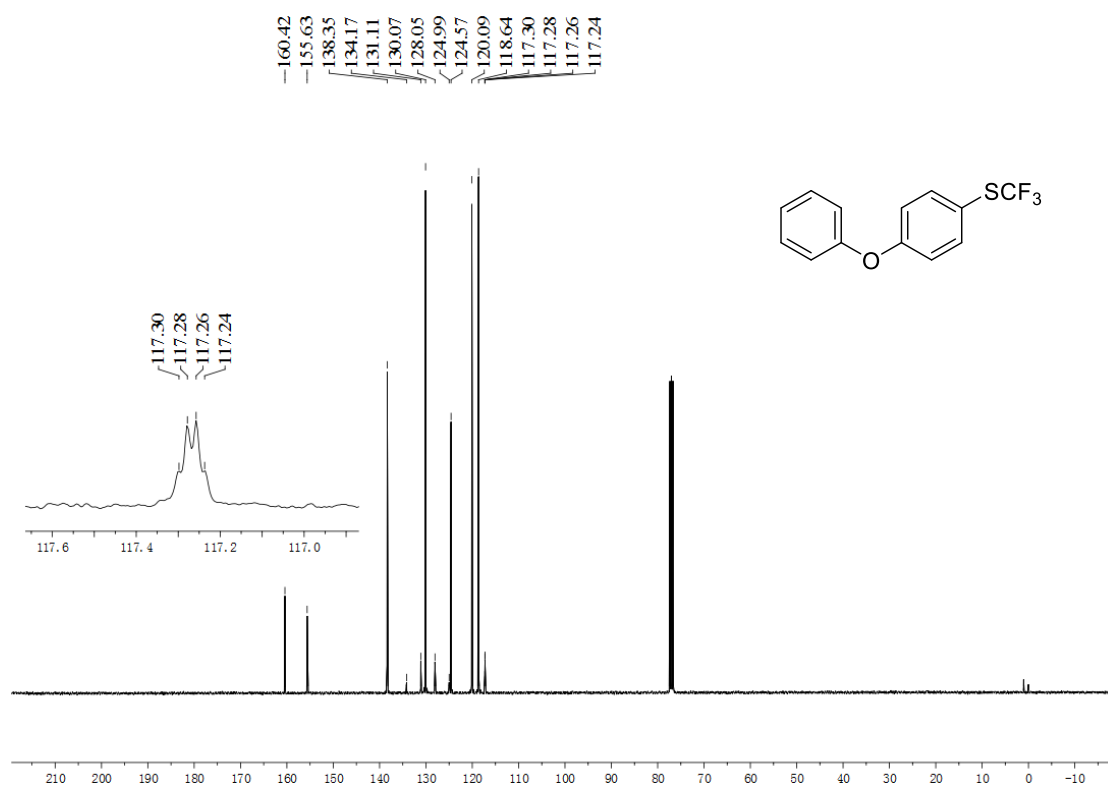
^1H NMR spectrum of **2e** (400 MHz, CDCl_3)



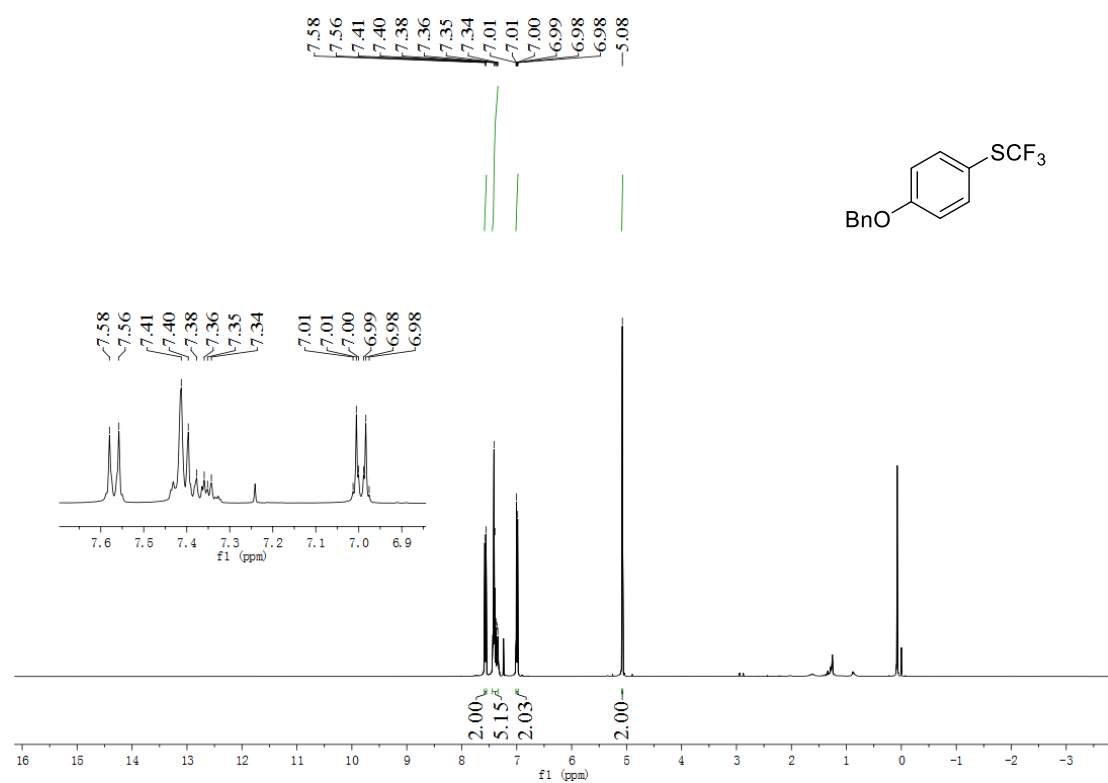
^{19}F NMR spectrum of **2e** (376 MHz, CDCl_3)



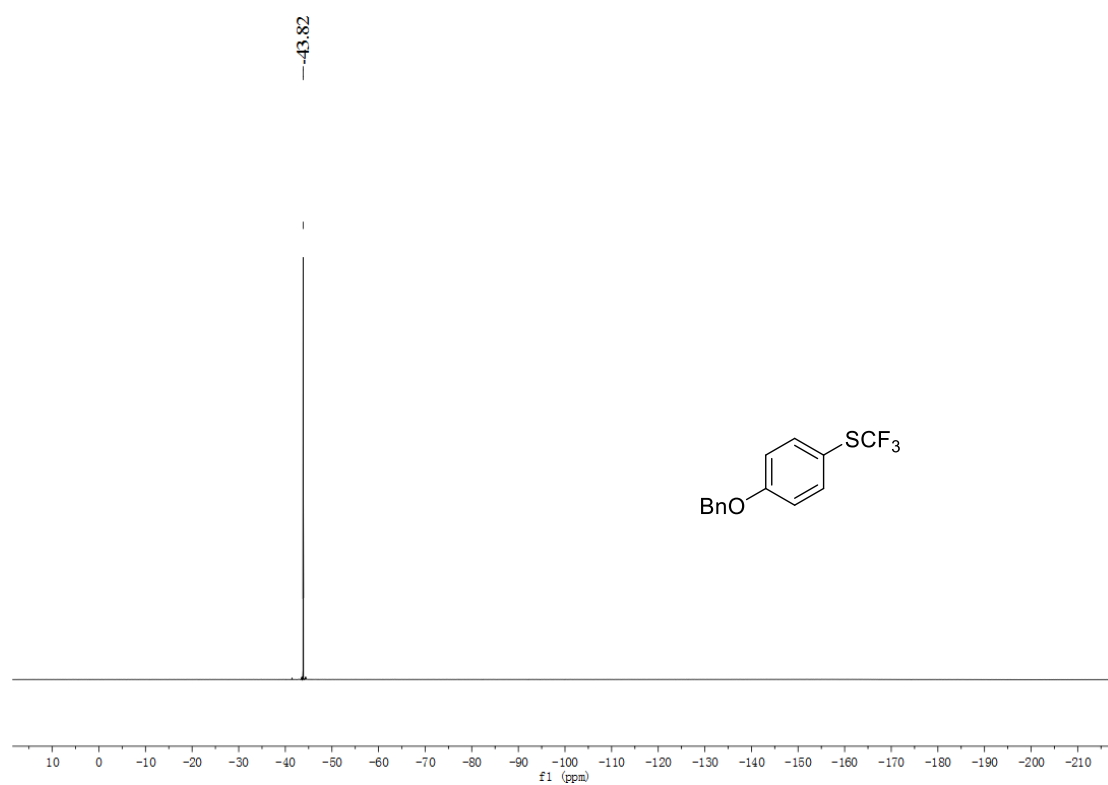
^{13}C NMR spectrum of **2e** (101 MHz, CDCl_3)



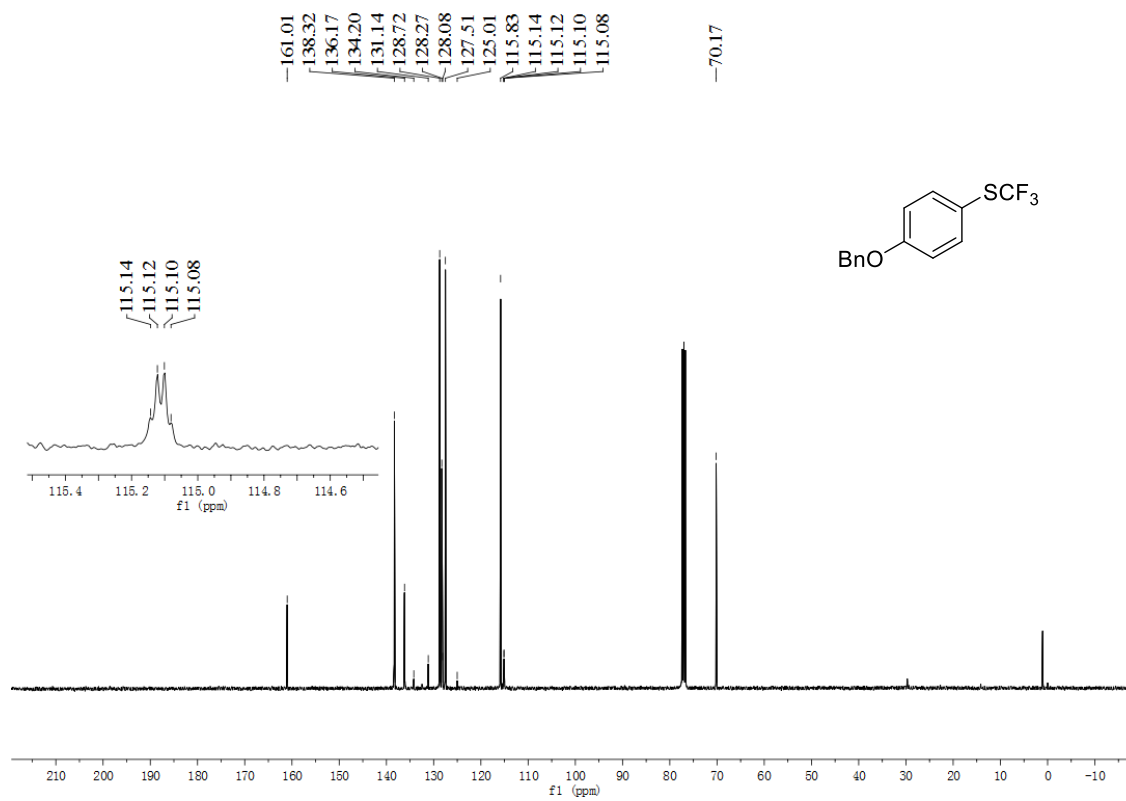
^1H NMR spectrum of **2f** (400 MHz, CDCl_3)



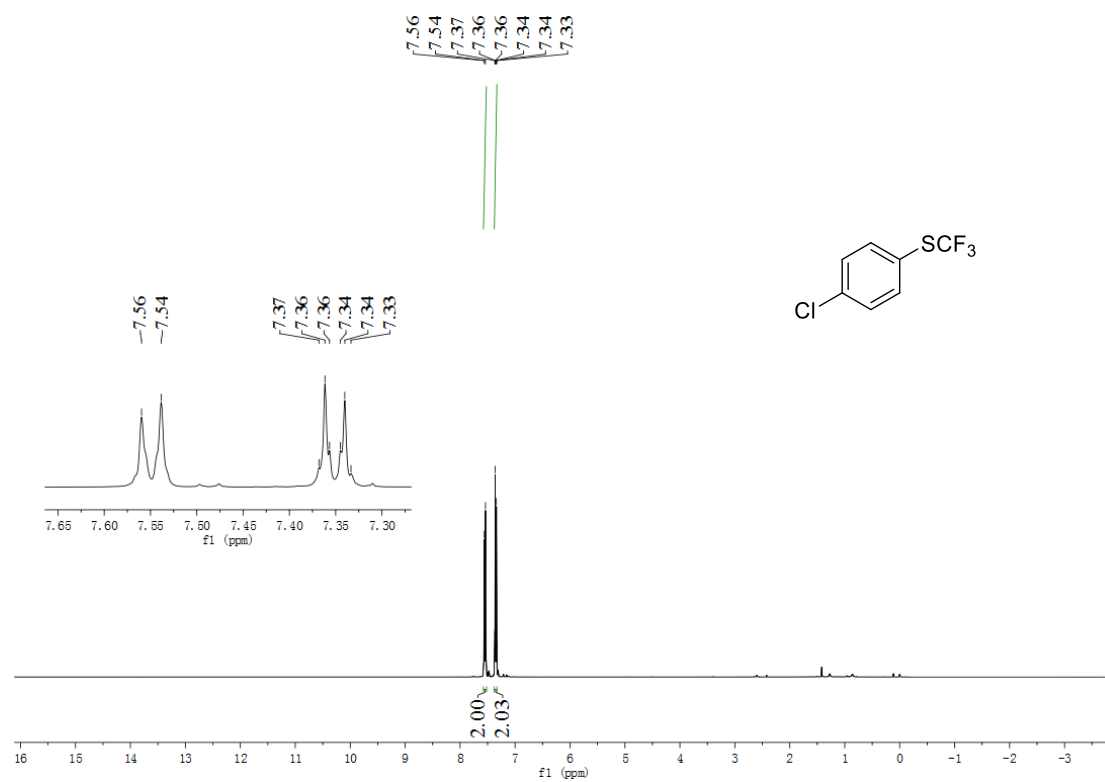
^{19}F NMR spectrum of **2f** (376 MHz, CDCl_3)



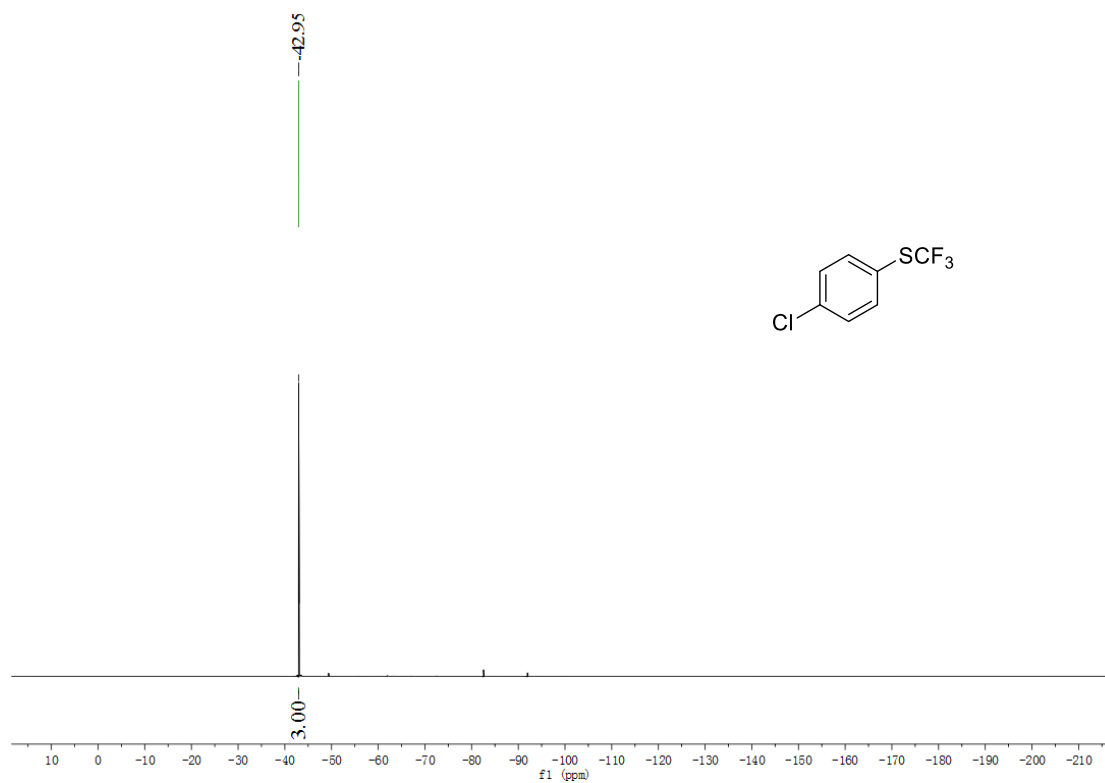
^{13}C NMR spectrum of **2f** (101 MHz, CDCl_3)



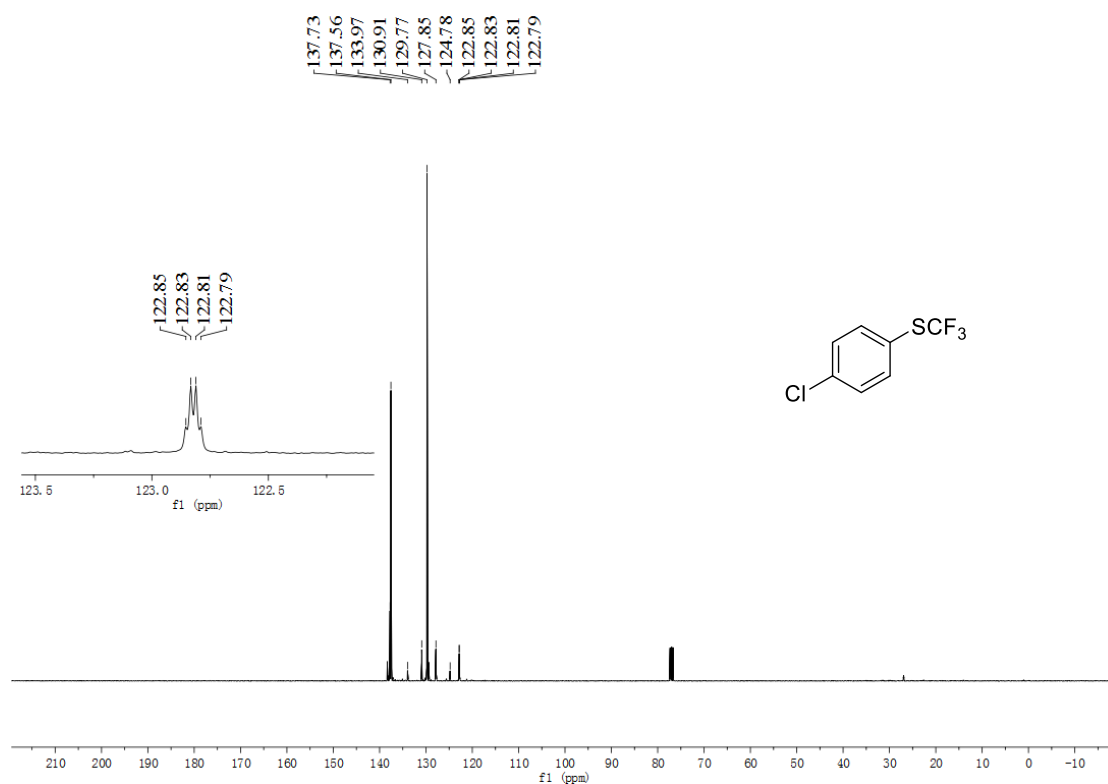
^1H NMR spectrum of **2g** (400 MHz, CDCl_3)



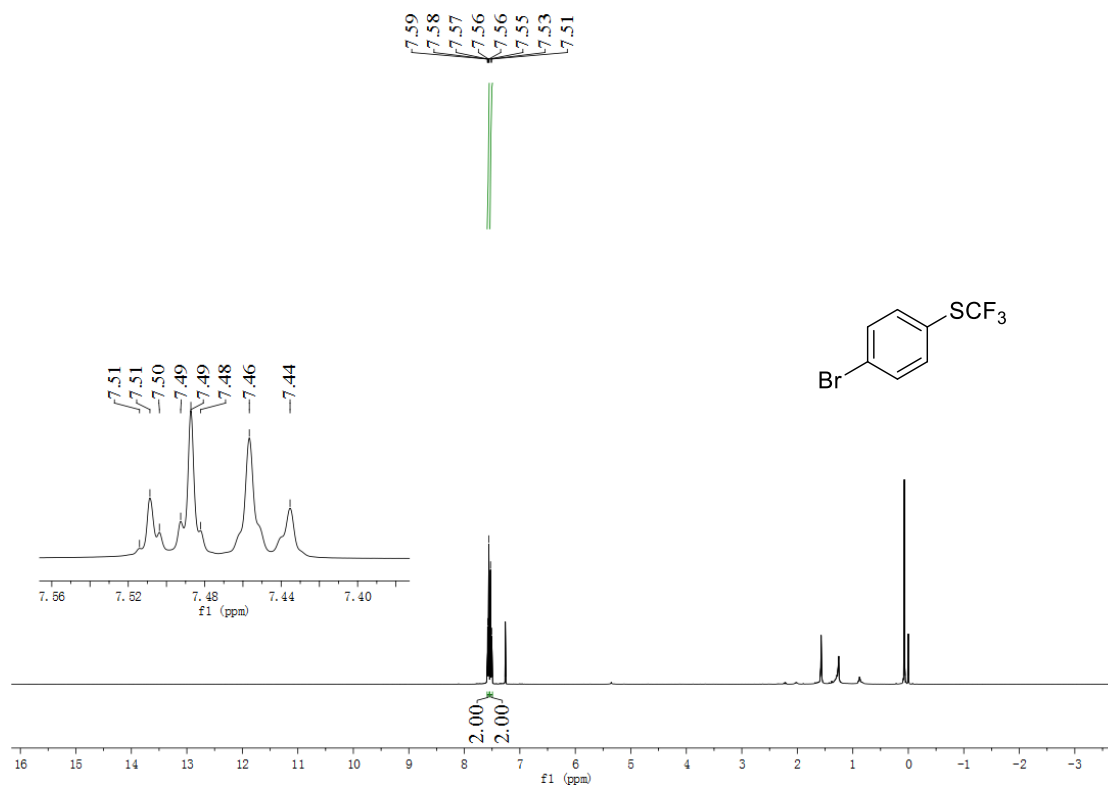
^{19}F NMR spectrum of **2g** (376 MHz, CDCl_3)



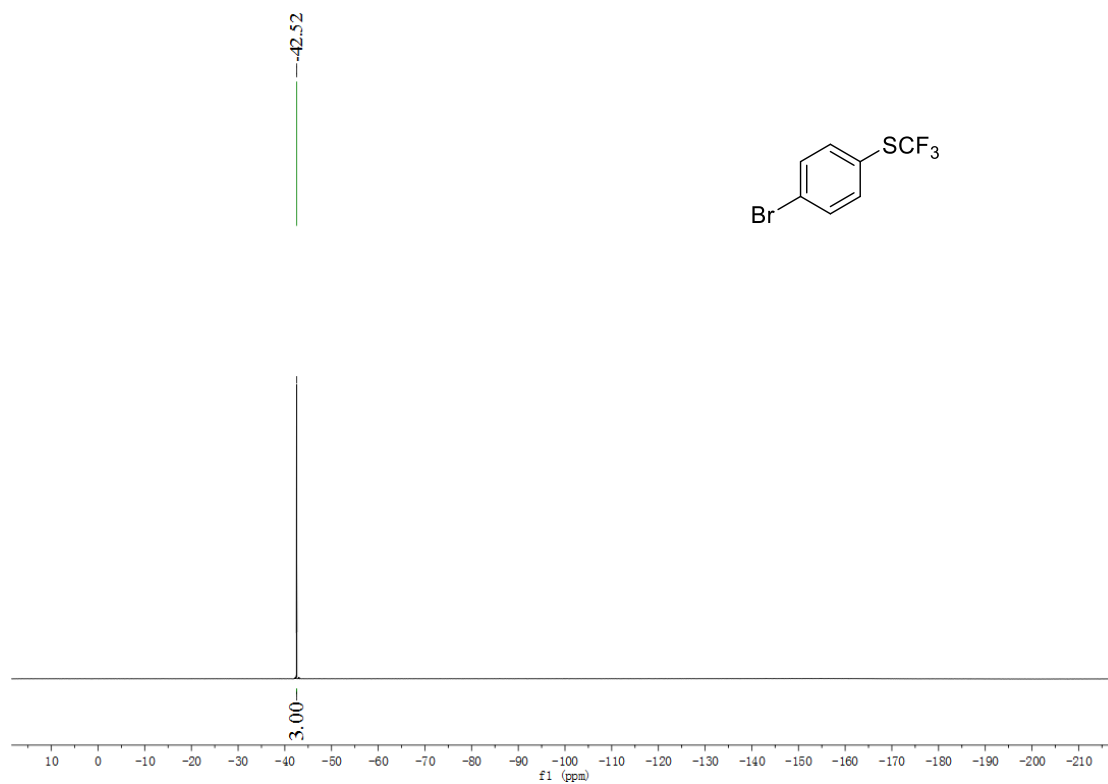
^{13}C NMR spectrum of **2g** (101 MHz, CDCl_3)



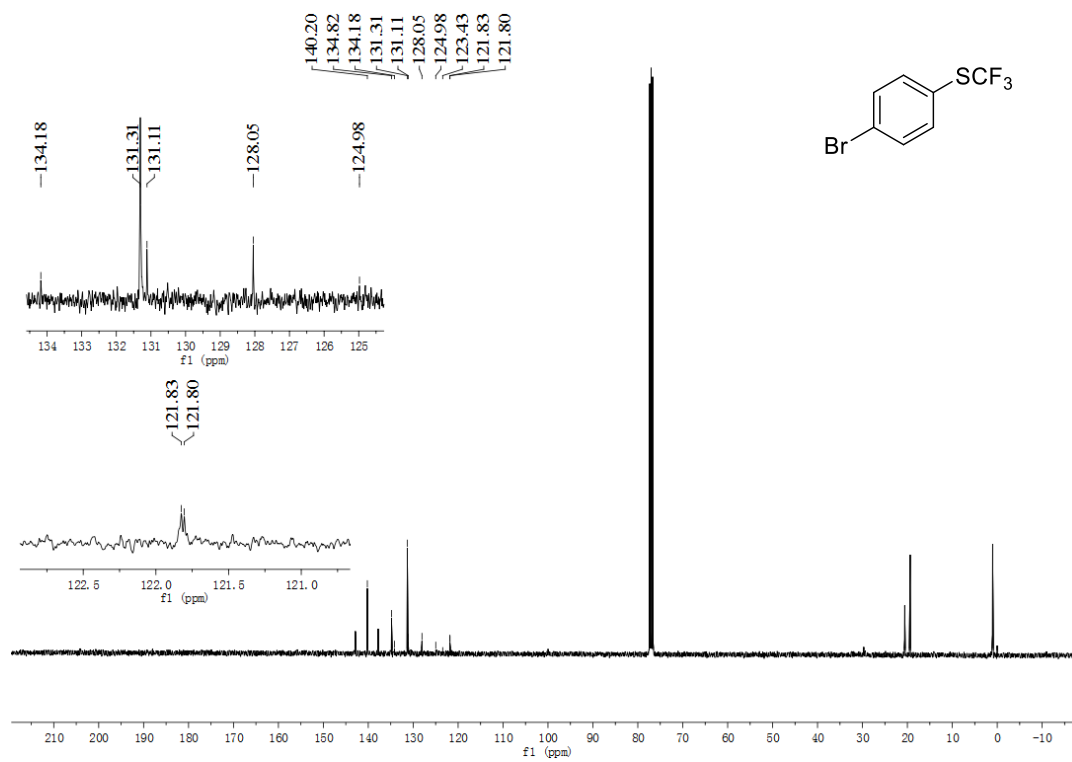
^1H NMR spectrum of **2h** (400 MHz, CDCl_3)



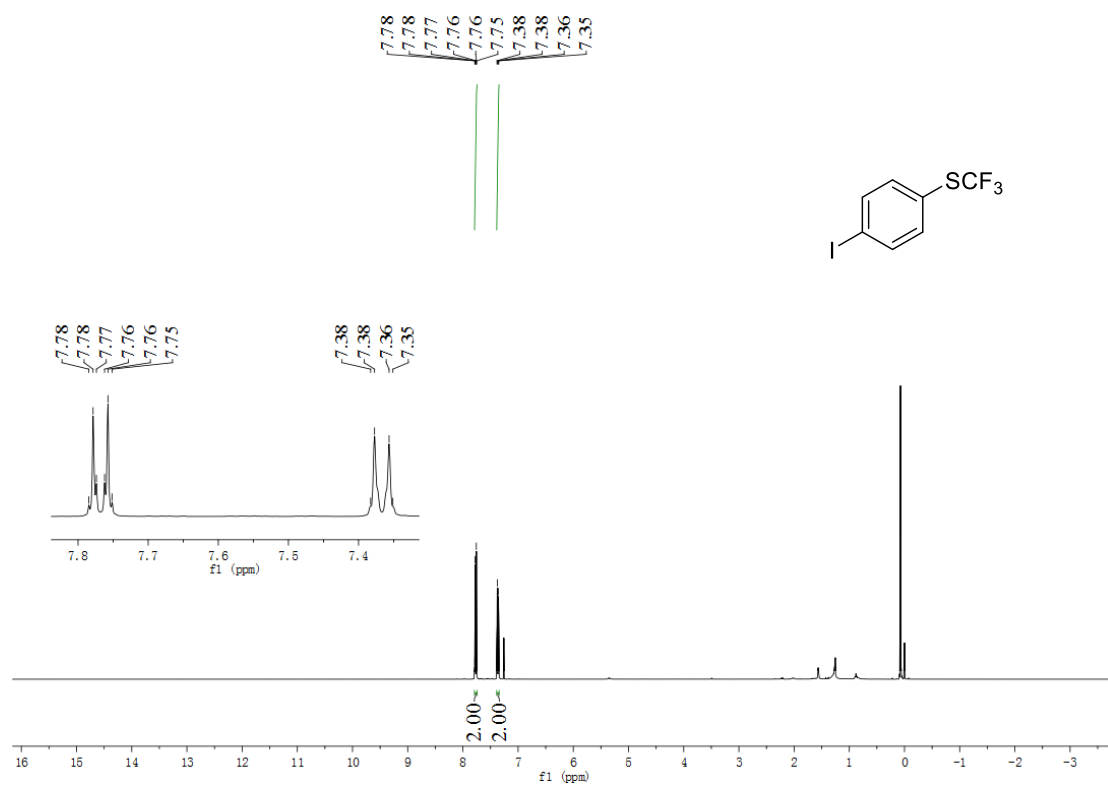
^{19}F NMR spectrum of **2h** (376 MHz, CDCl_3)



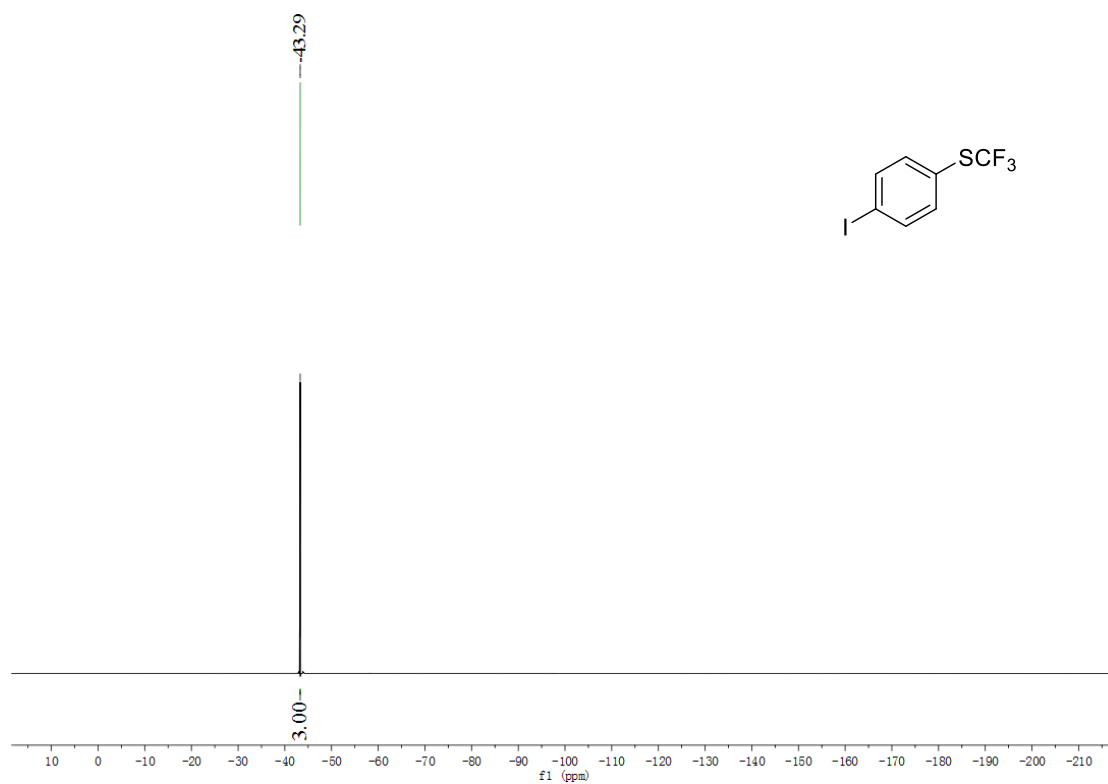
^{13}C NMR spectrum of **2h** (101 MHz, CDCl_3)



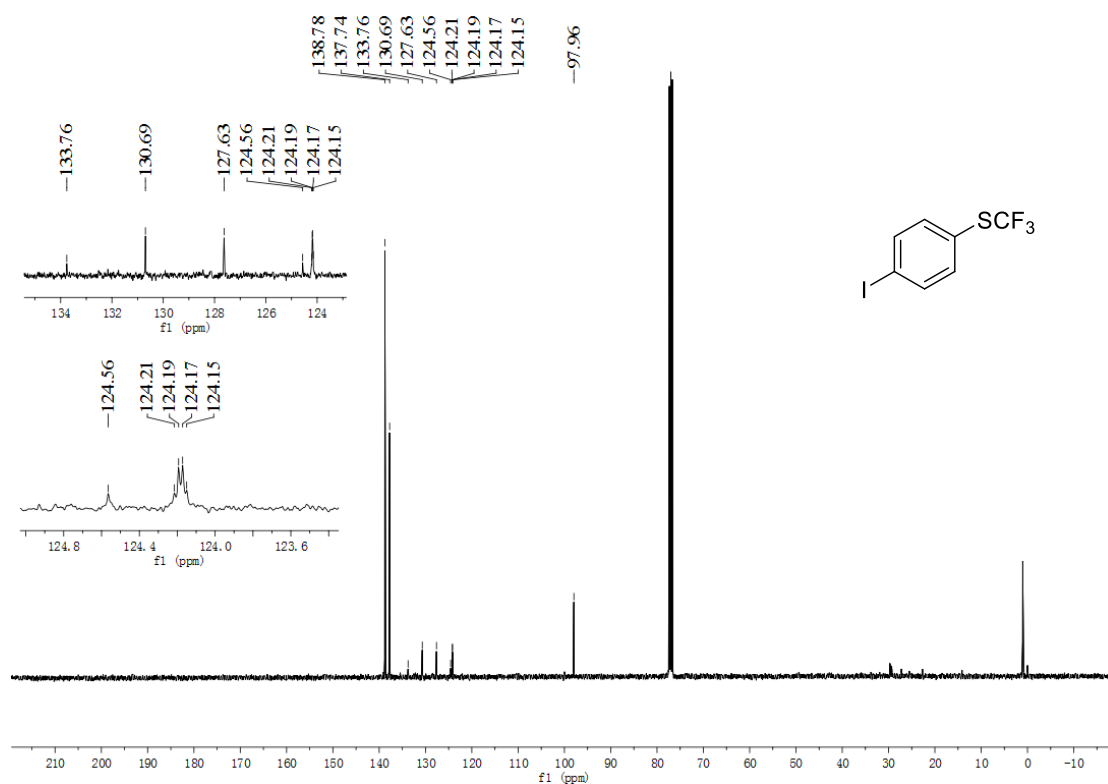
^1H NMR spectrum of **2i** (400 MHz, CDCl_3)



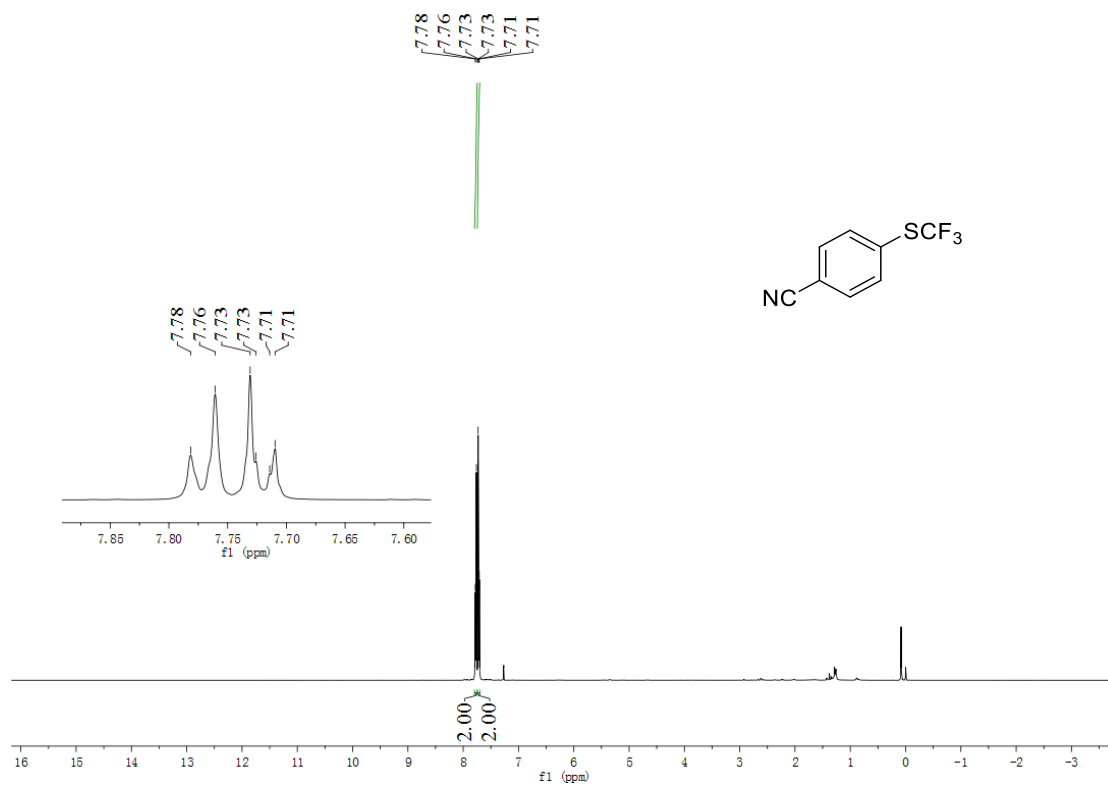
^{19}F NMR spectrum of **2i** (376 MHz, CDCl_3)



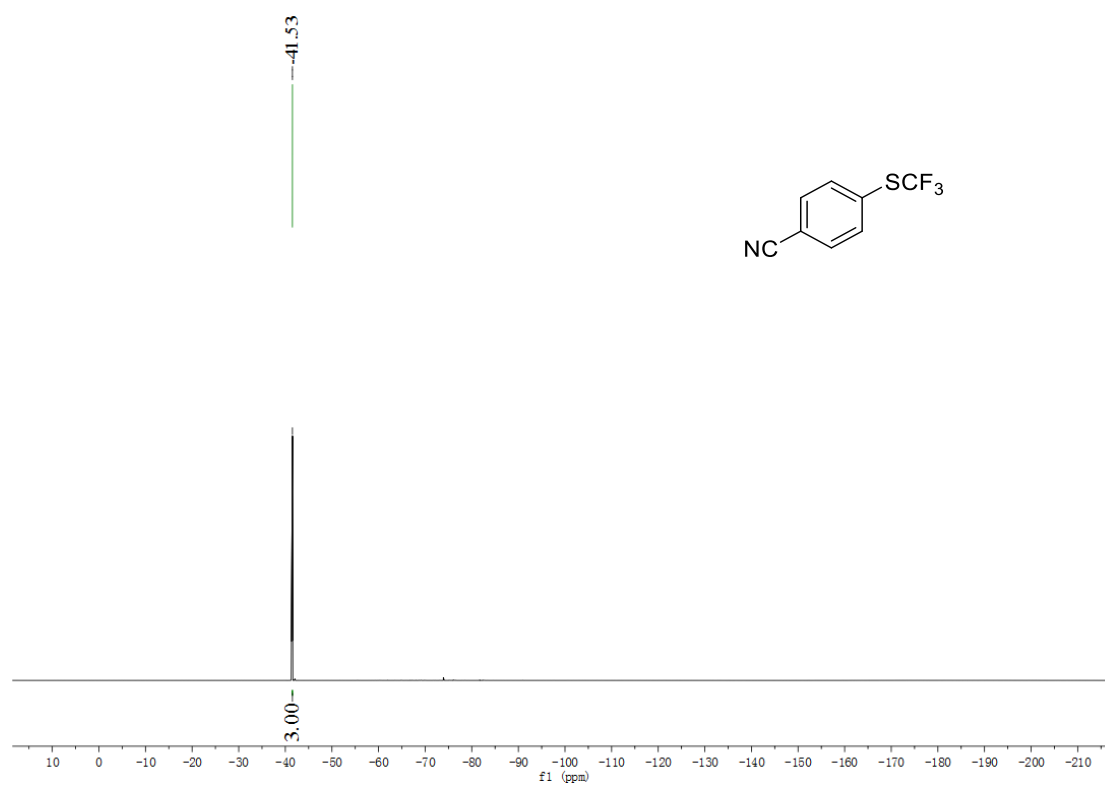
^{13}C NMR spectrum of **2i** (101 MHz, CDCl_3)



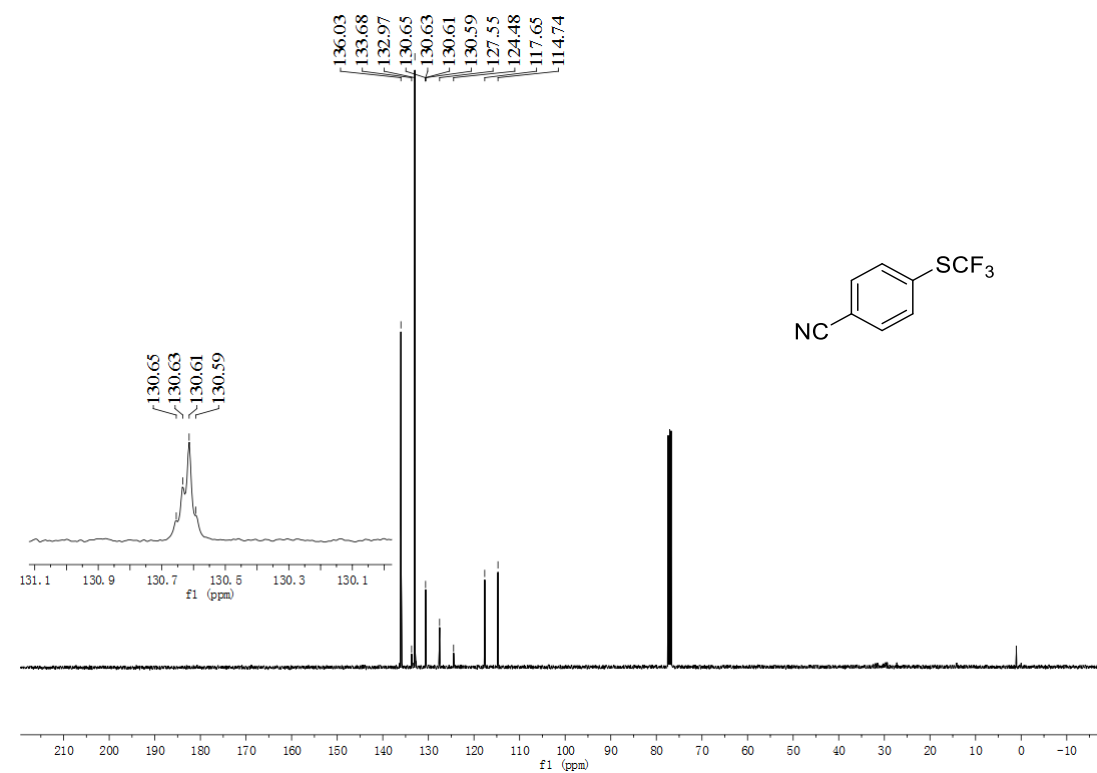
^1H NMR spectrum of **2j** (400 MHz, CDCl_3)



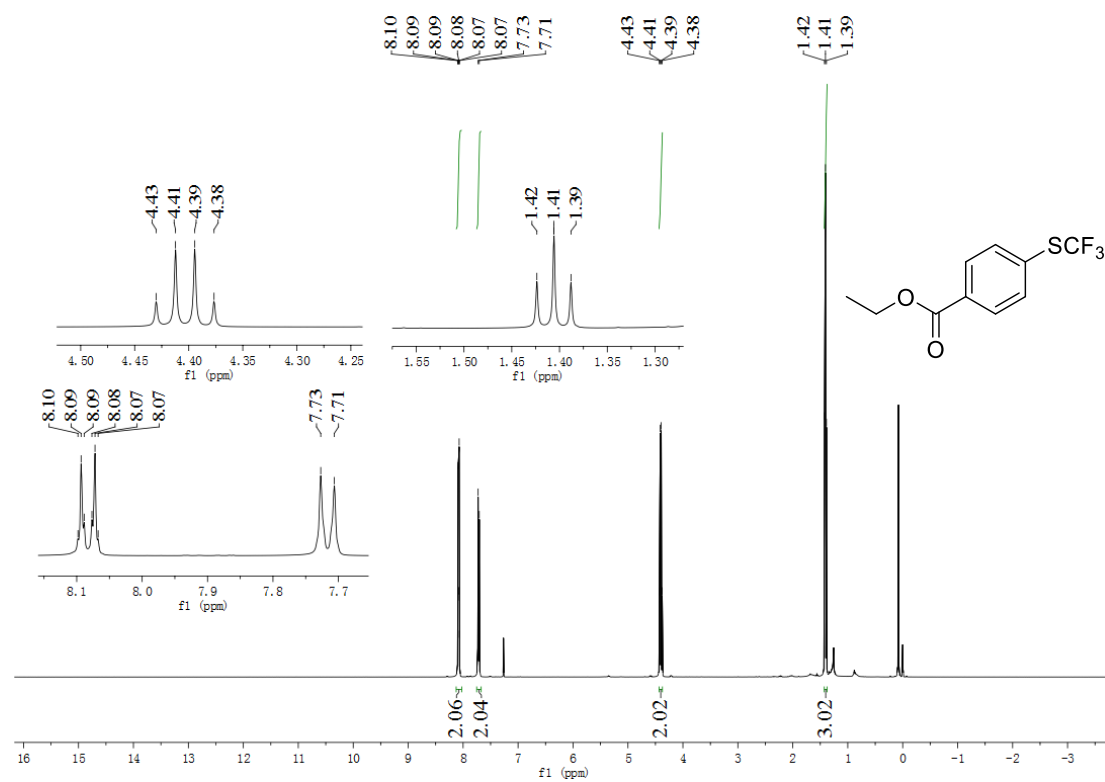
^{19}F NMR spectrum of **2j** (376 MHz, CDCl_3)



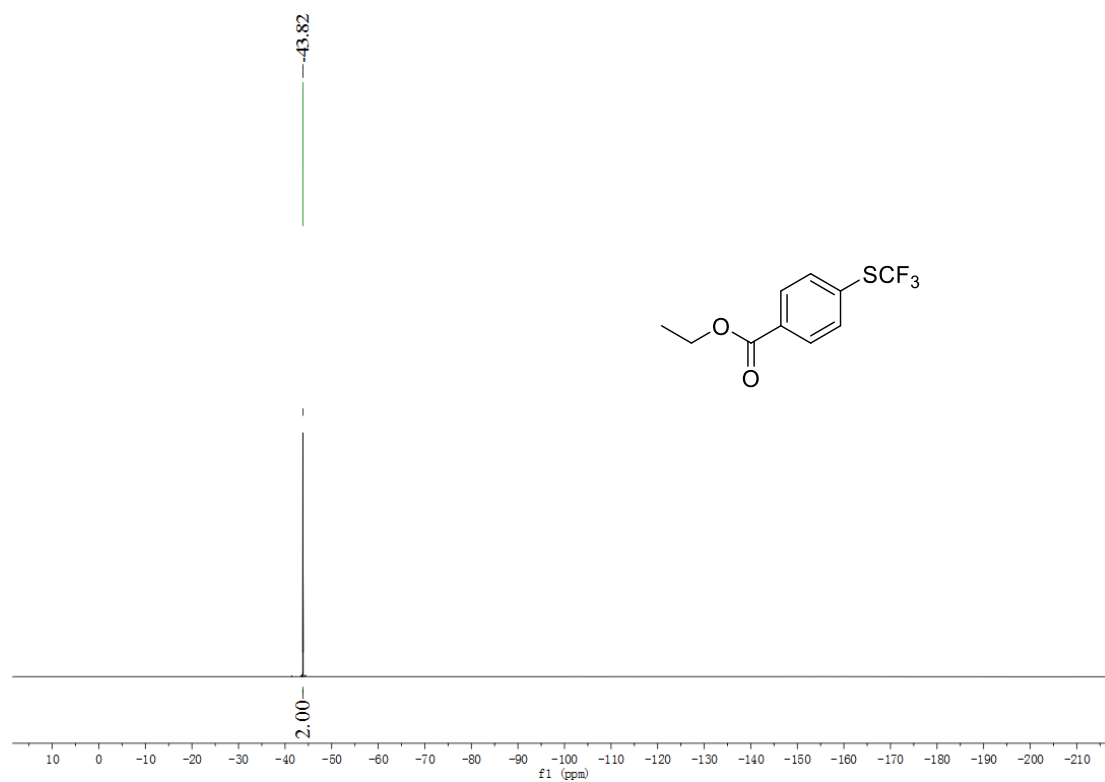
^{13}C NMR spectrum of **2j** (101 MHz, CDCl_3)



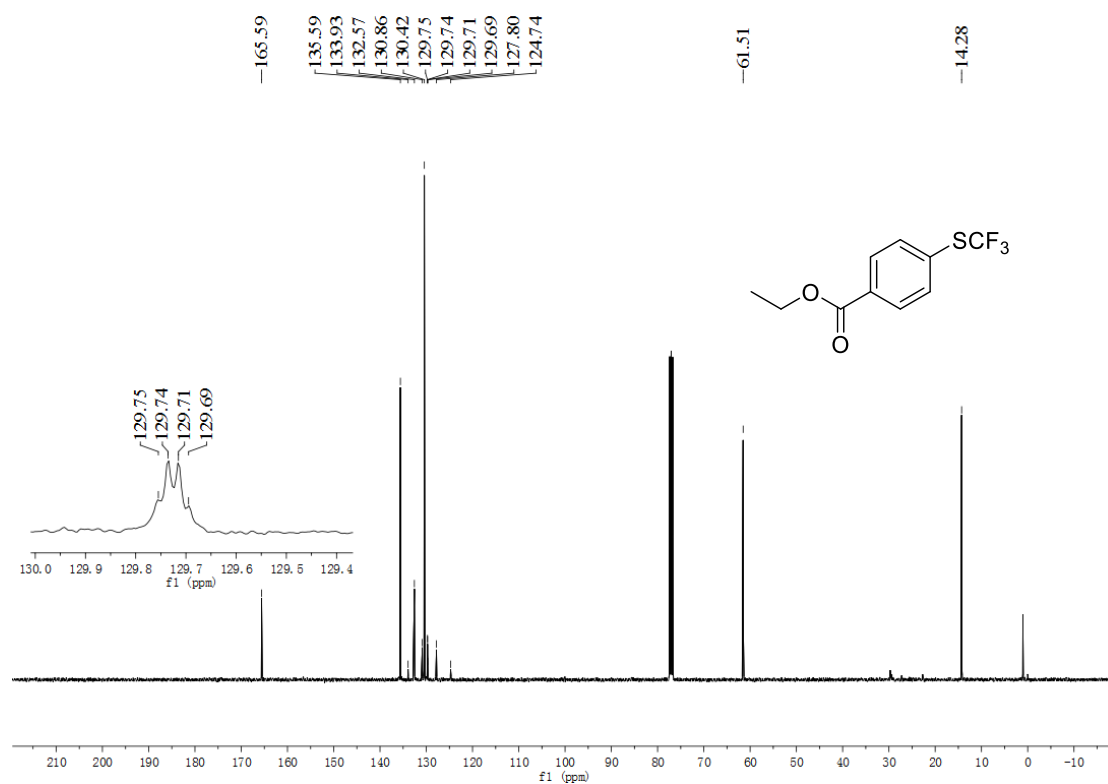
^1H NMR spectrum of **2k** (400 MHz, CDCl_3)



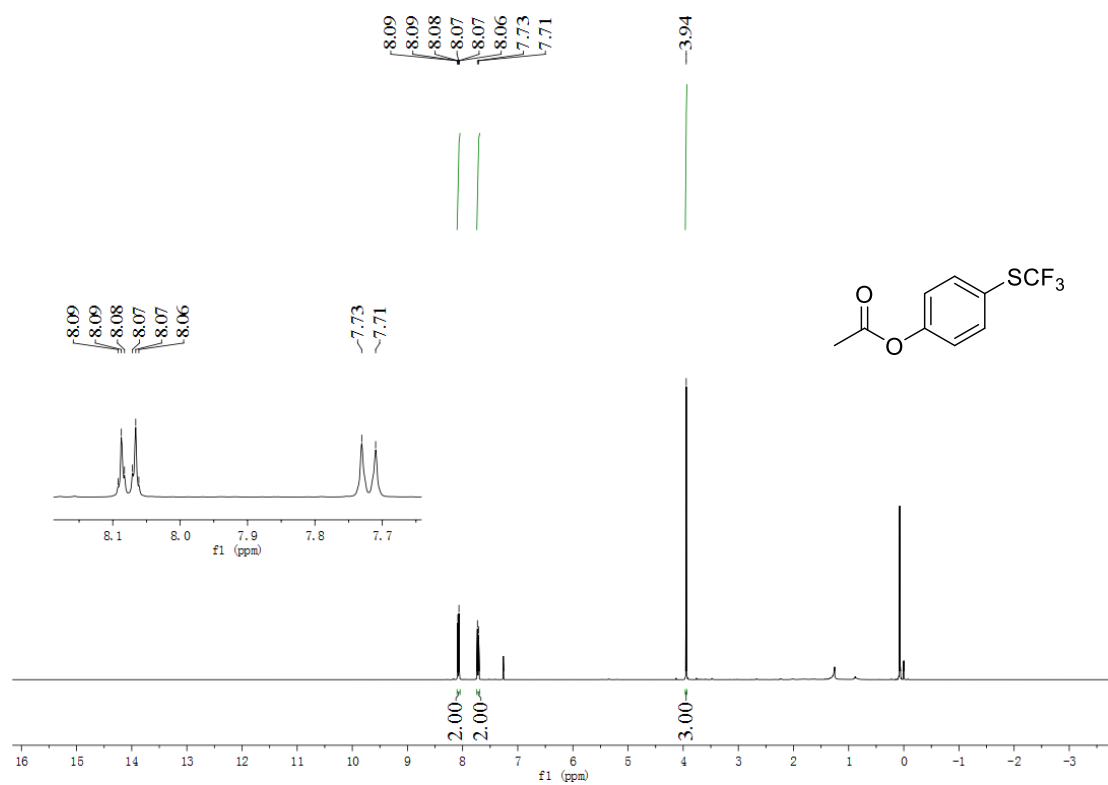
^{19}F NMR spectrum of **2k** (376 MHz, CDCl_3)



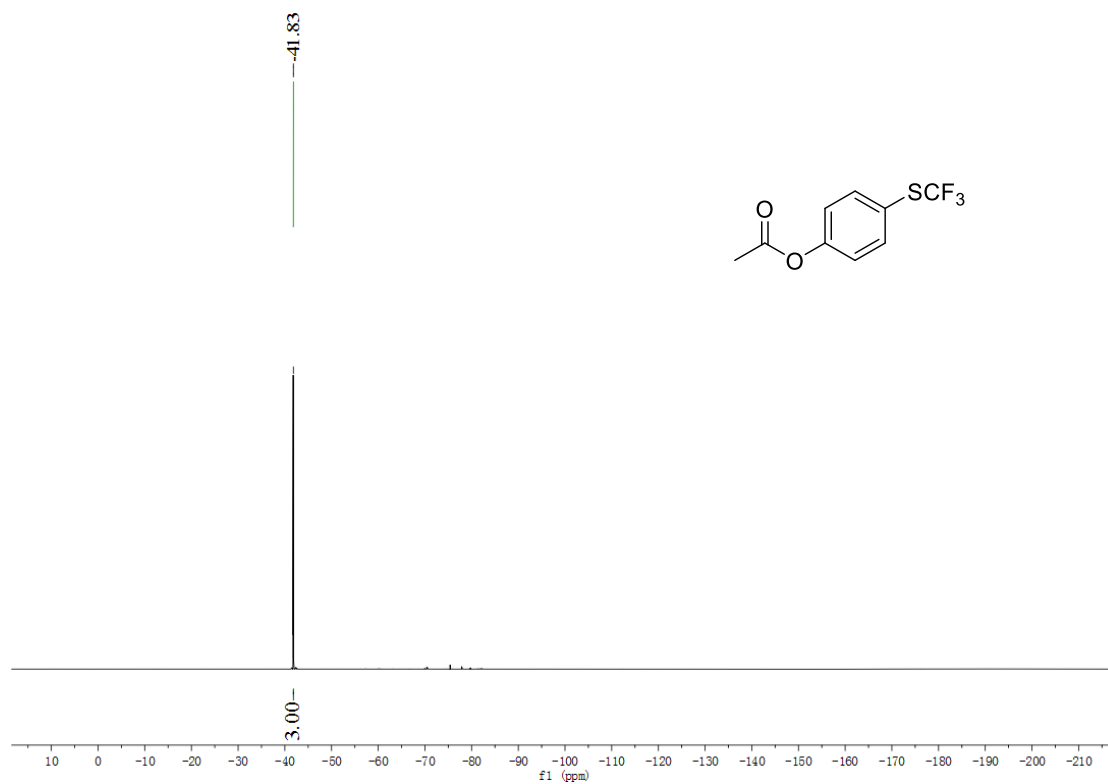
^{13}C NMR spectrum of **2k** (101 MHz, CDCl_3)



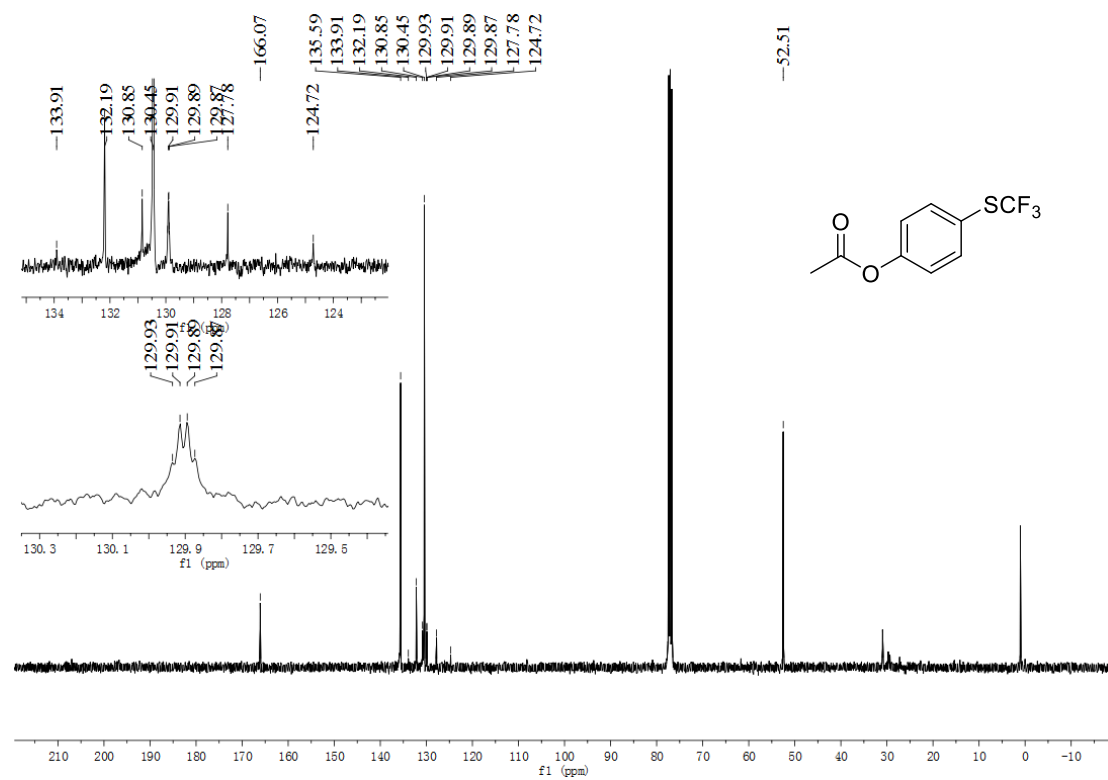
^1H NMR spectrum of **2l** (400 MHz, CDCl_3)



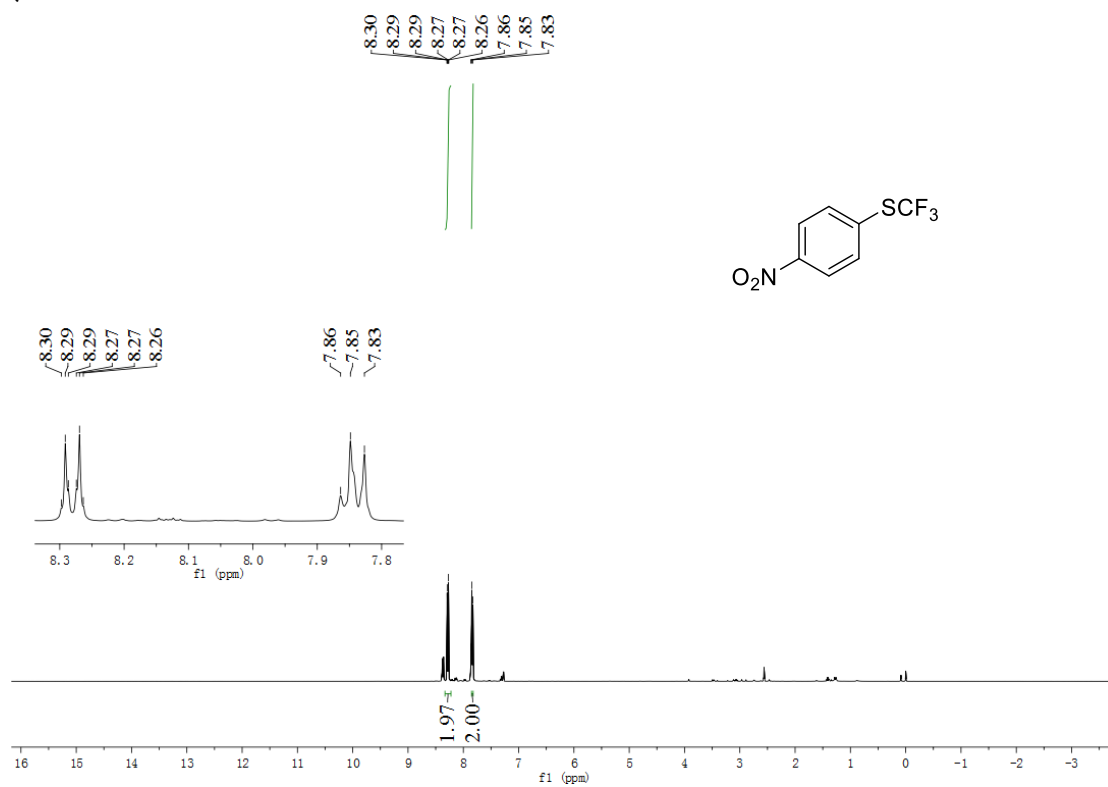
^{19}F NMR spectrum of **2l** (376 MHz, CDCl_3)



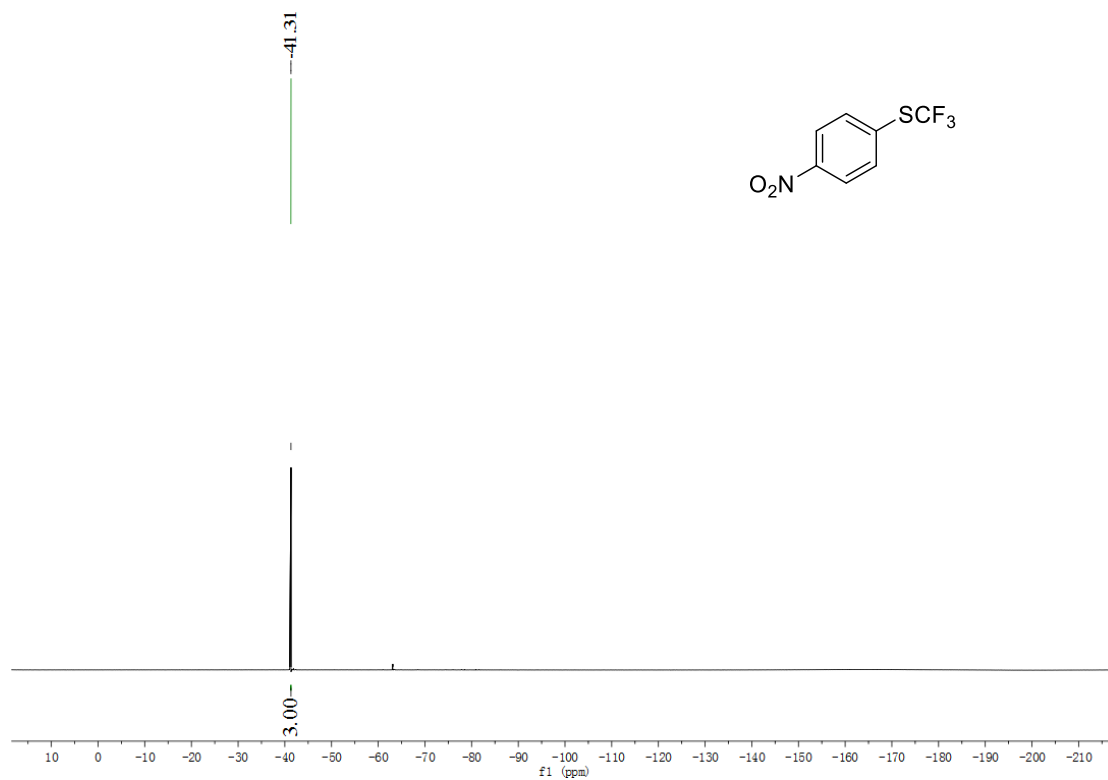
^{13}C NMR spectrum of **2l** (101 MHz, CDCl_3)



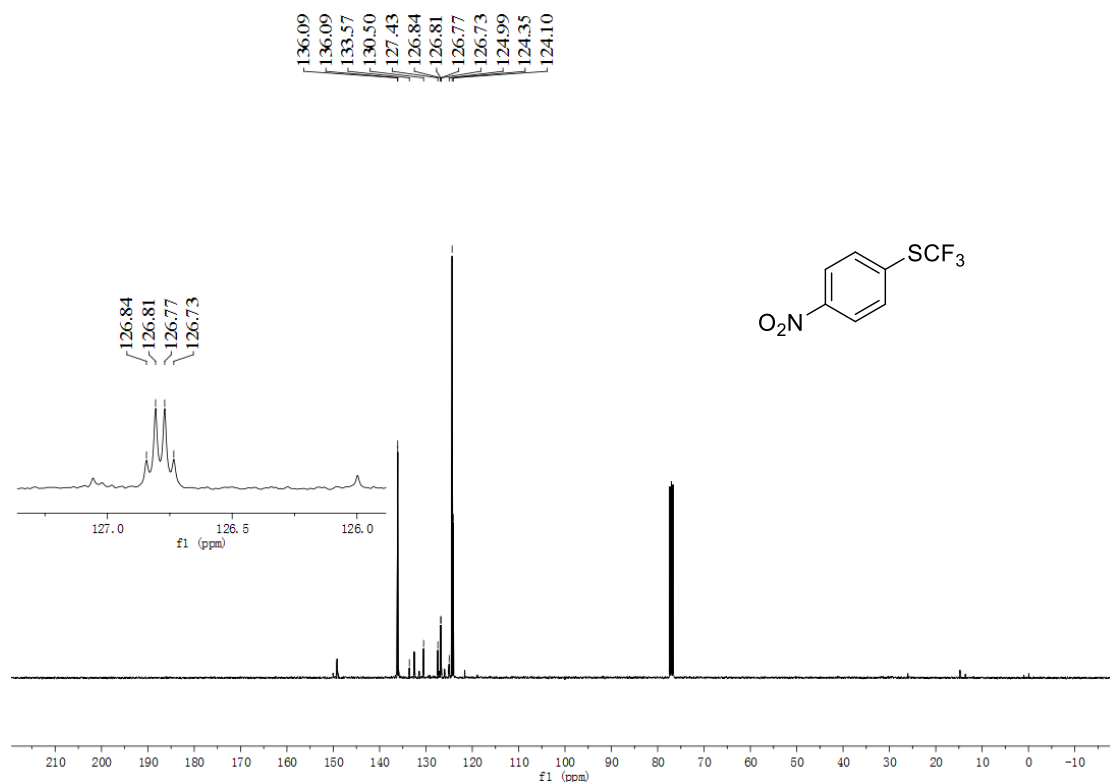
^1H NMR spectrum of **2m** (400 MHz, CDCl_3)



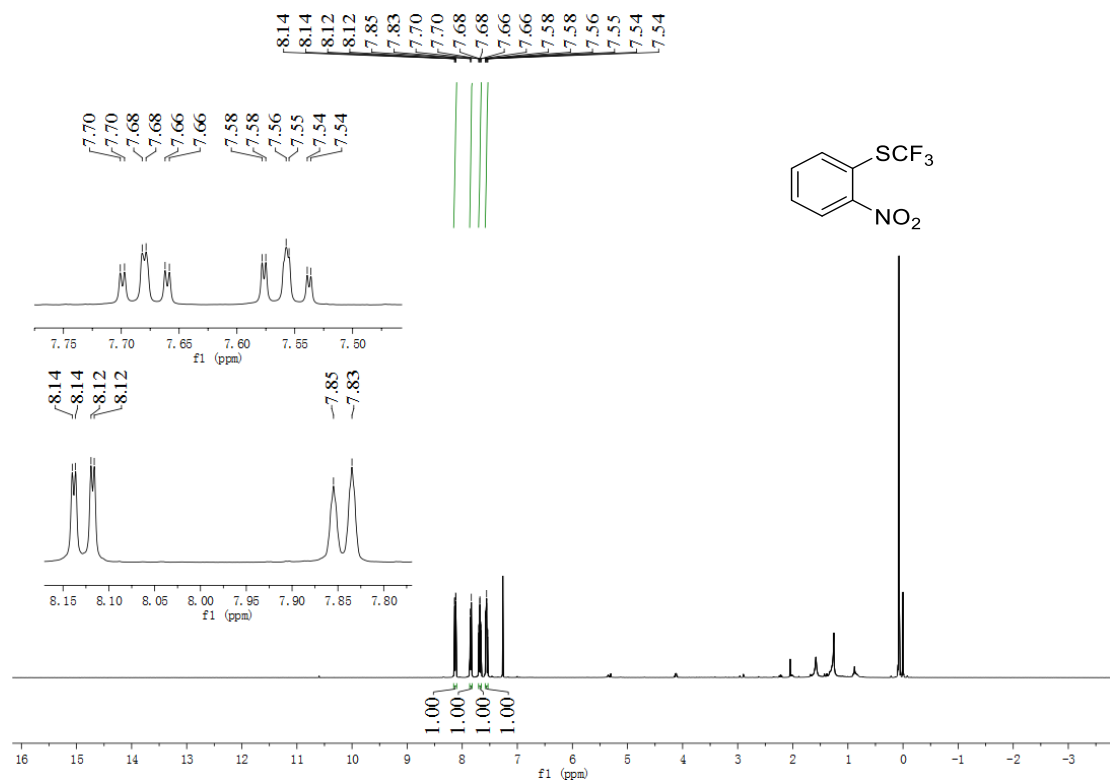
^{19}F NMR spectrum of **2m** (376 MHz, CDCl_3)



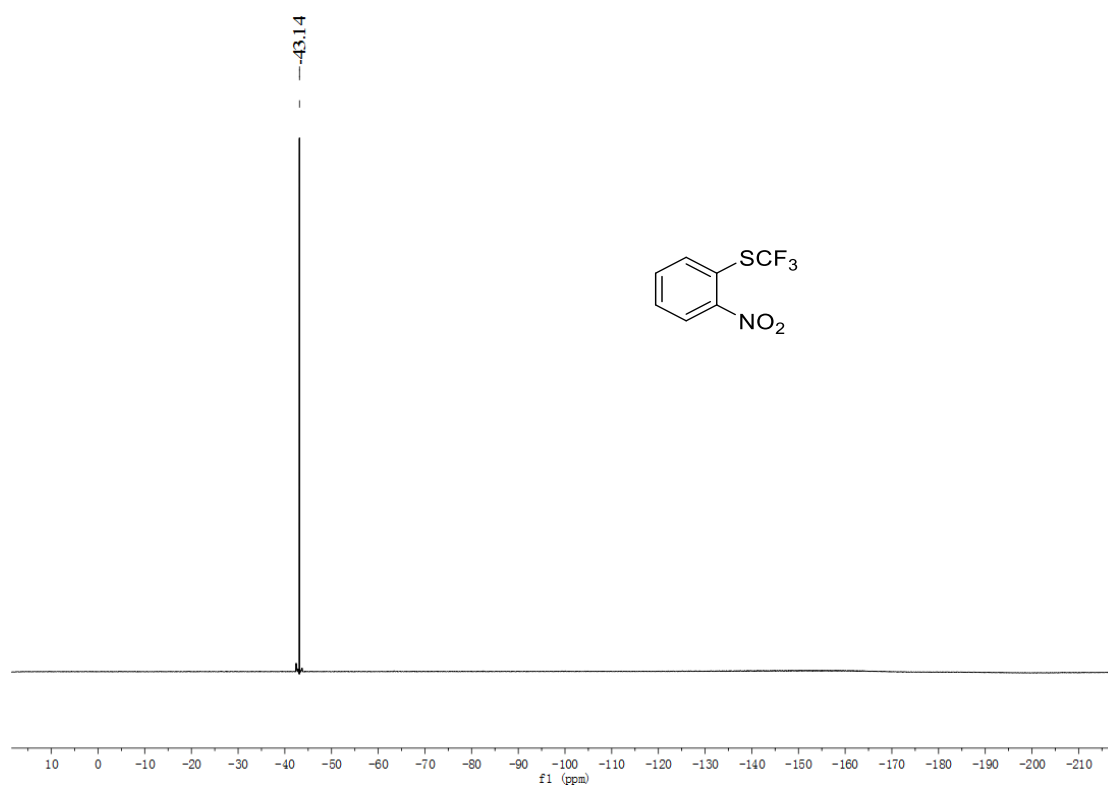
^{13}C NMR spectrum of **2m** (101 MHz, CDCl_3)



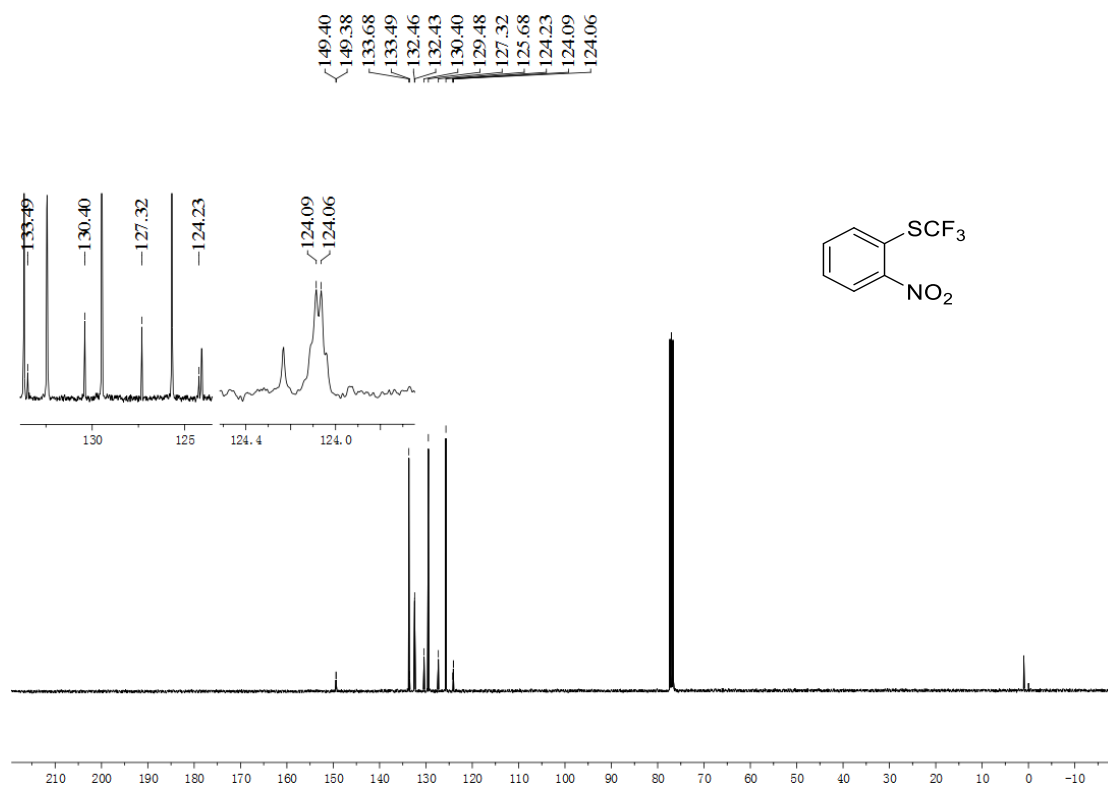
^1H NMR spectrum of **2n** (400 MHz, CDCl_3)



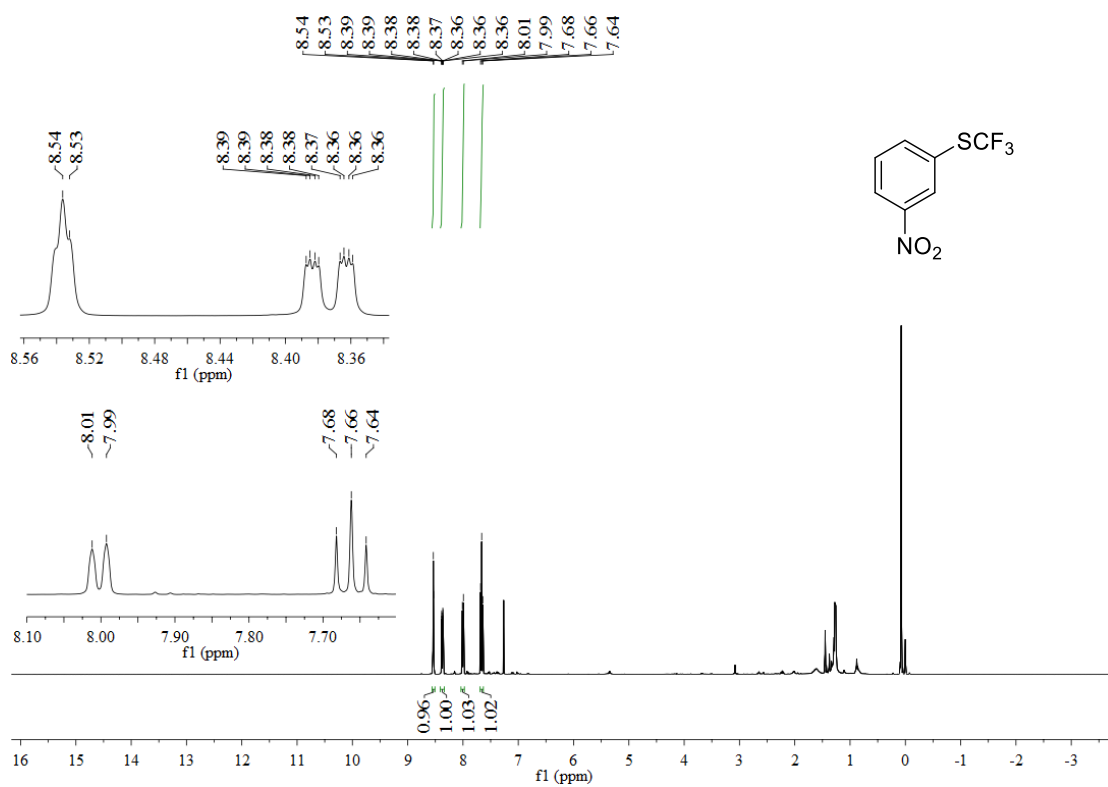
^{19}F NMR spectrum of **2n** (376 MHz, CDCl_3)



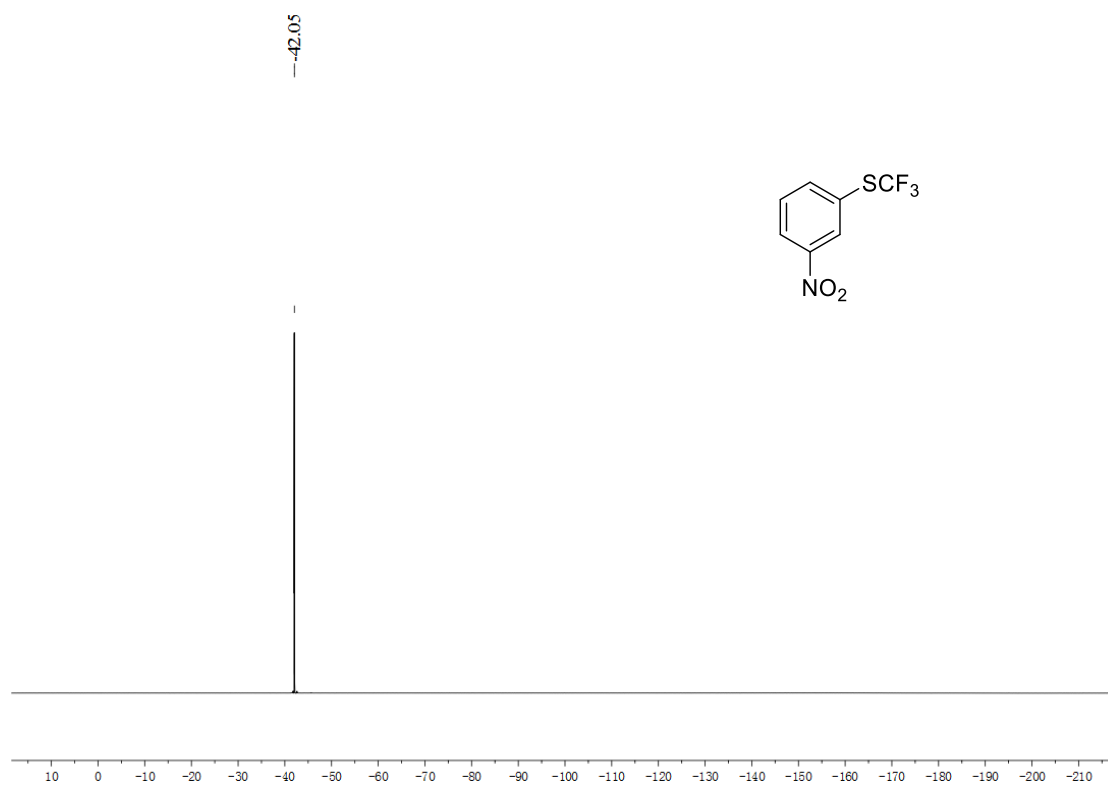
^{13}C NMR spectrum of **2n** (101 MHz, CDCl_3)



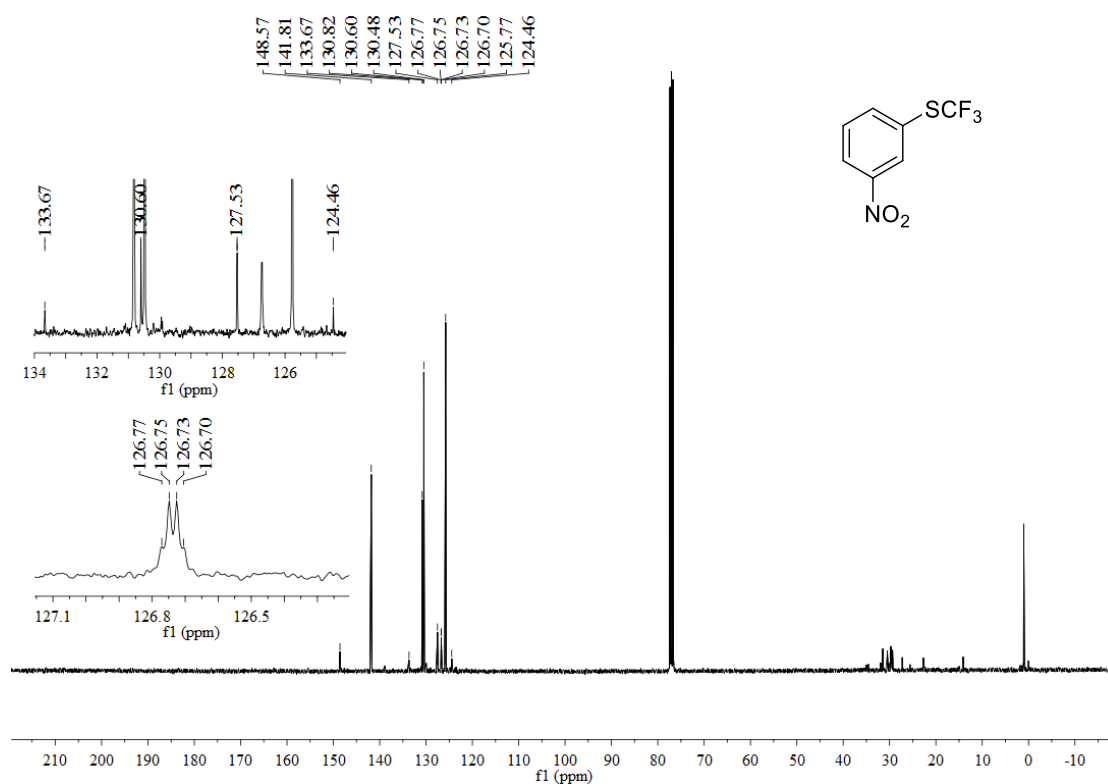
^1H NMR spectrum of **2o** (400 MHz, CDCl_3)



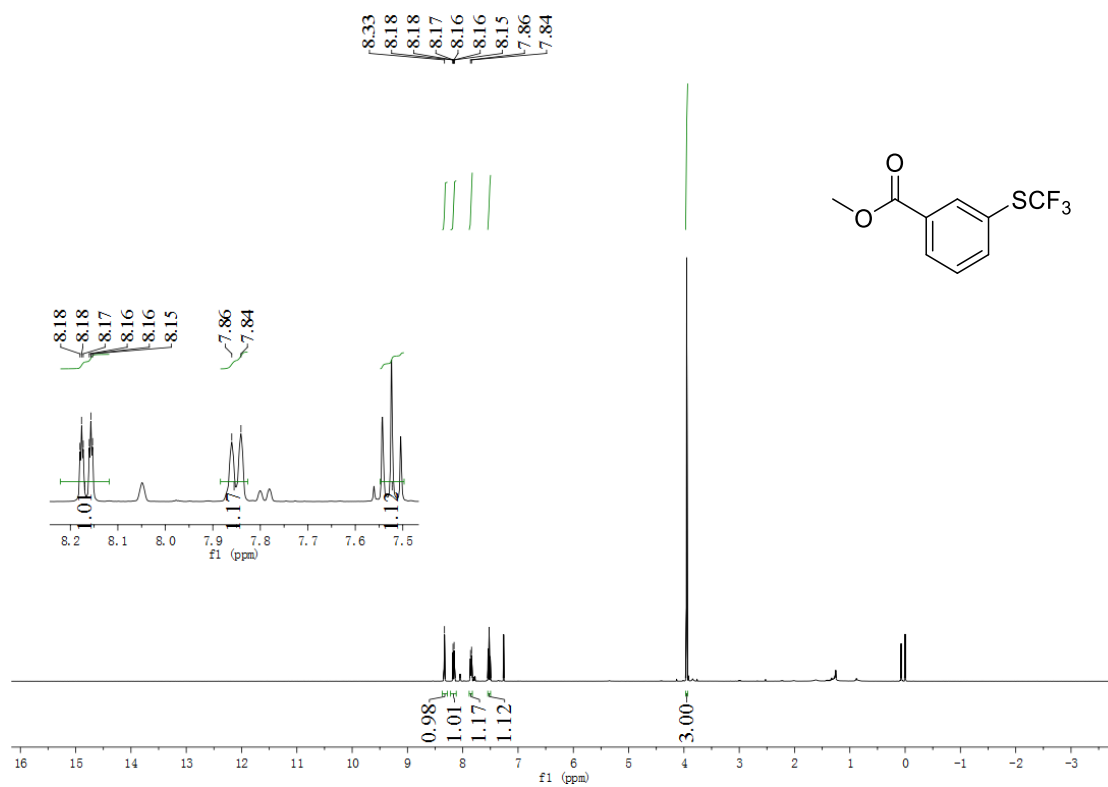
^{19}F NMR spectrum of **2o** (376 MHz, CDCl_3)



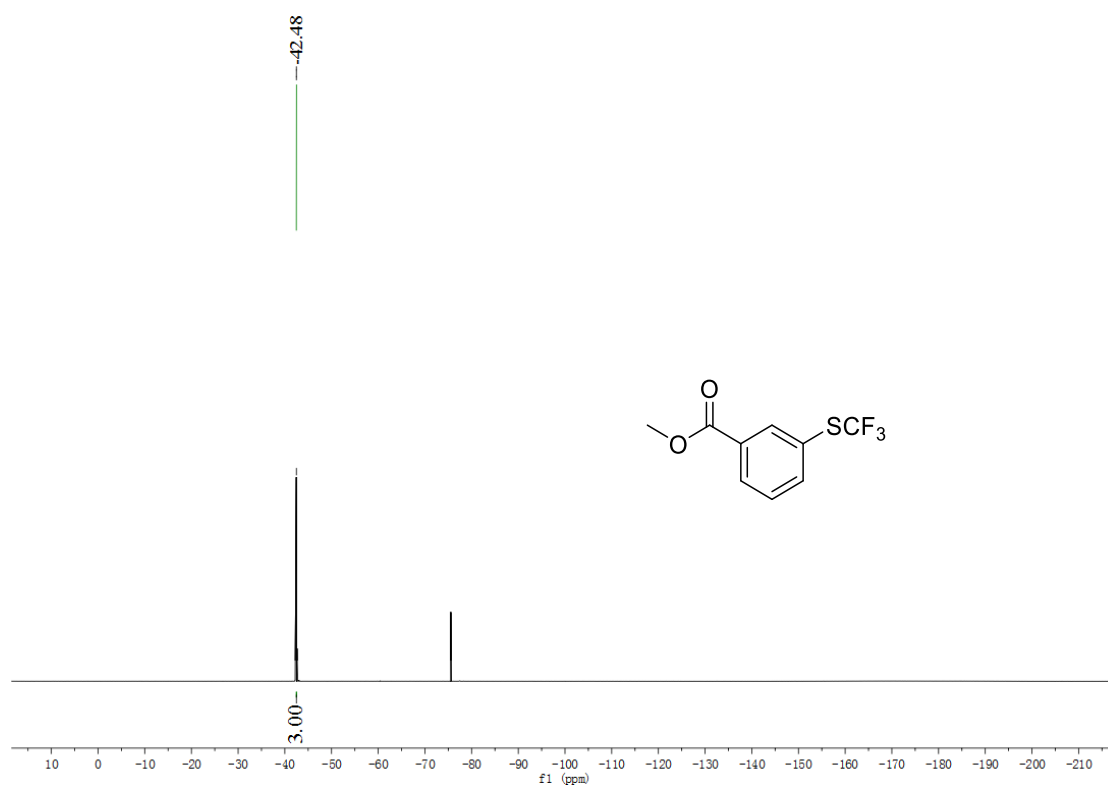
^{13}C NMR spectrum of **2o** (101 MHz, CDCl_3)



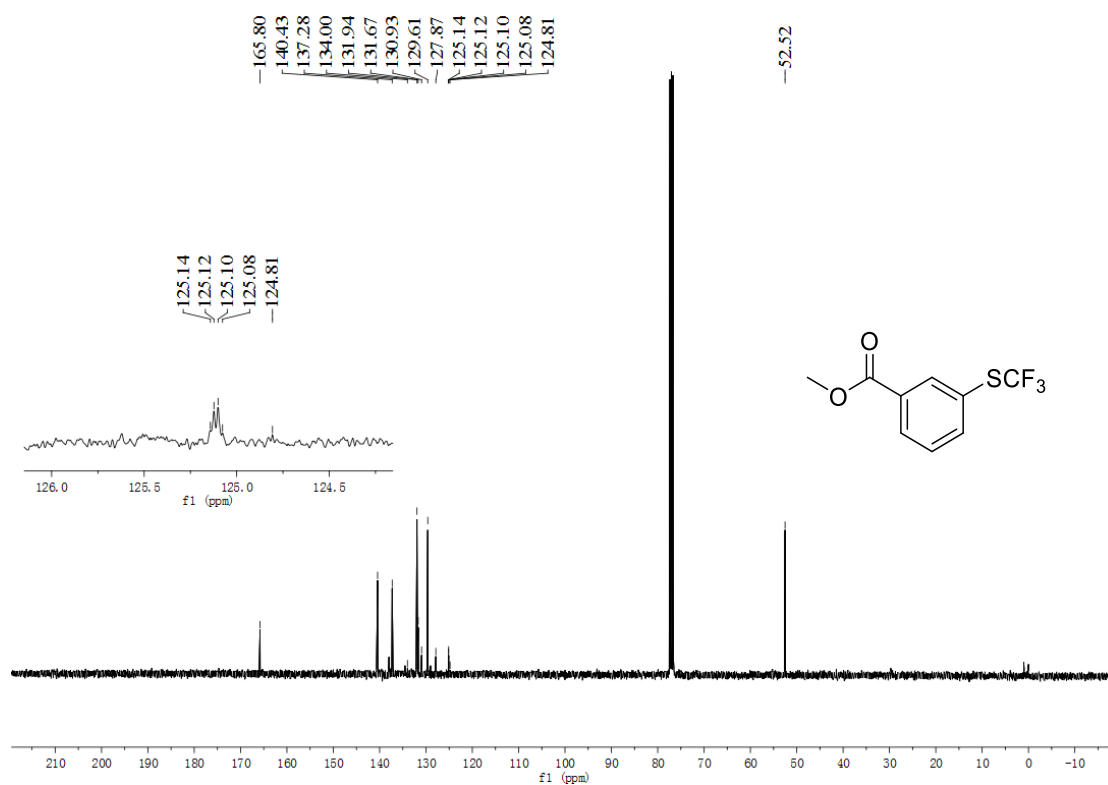
^1H NMR spectrum of **2p** (400 MHz, CDCl_3)



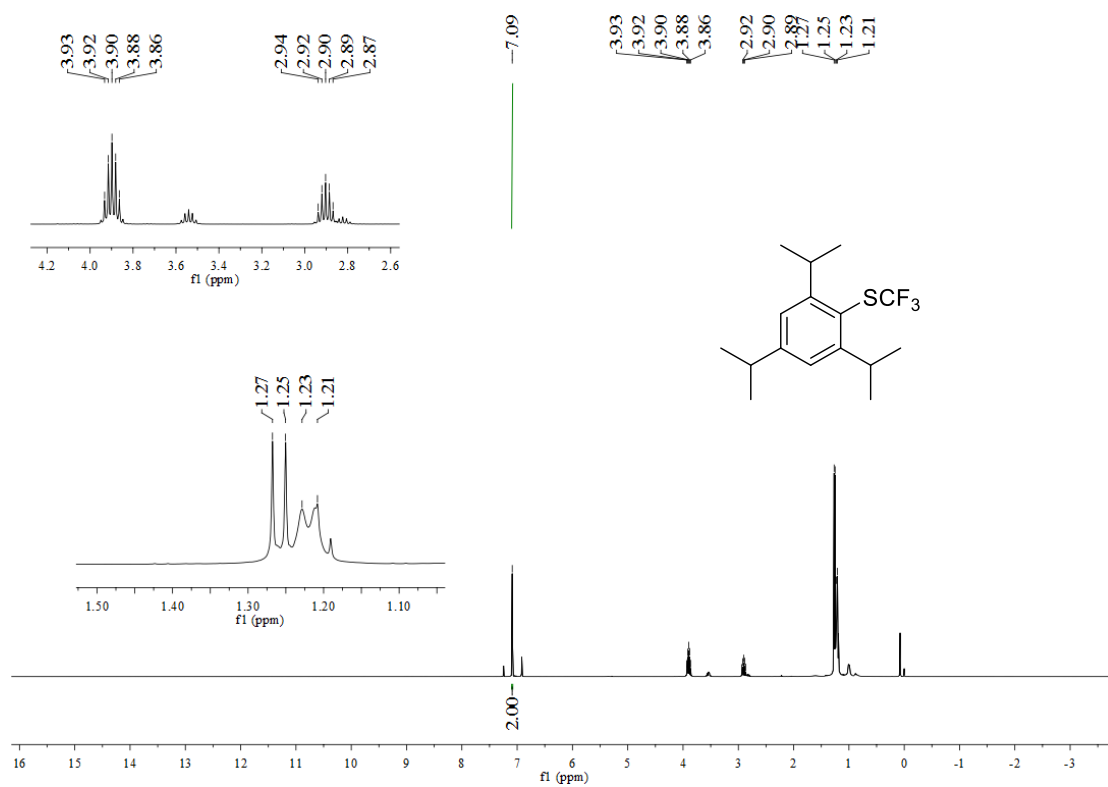
^{19}F NMR spectrum of **2p** (376 MHz, CDCl_3)



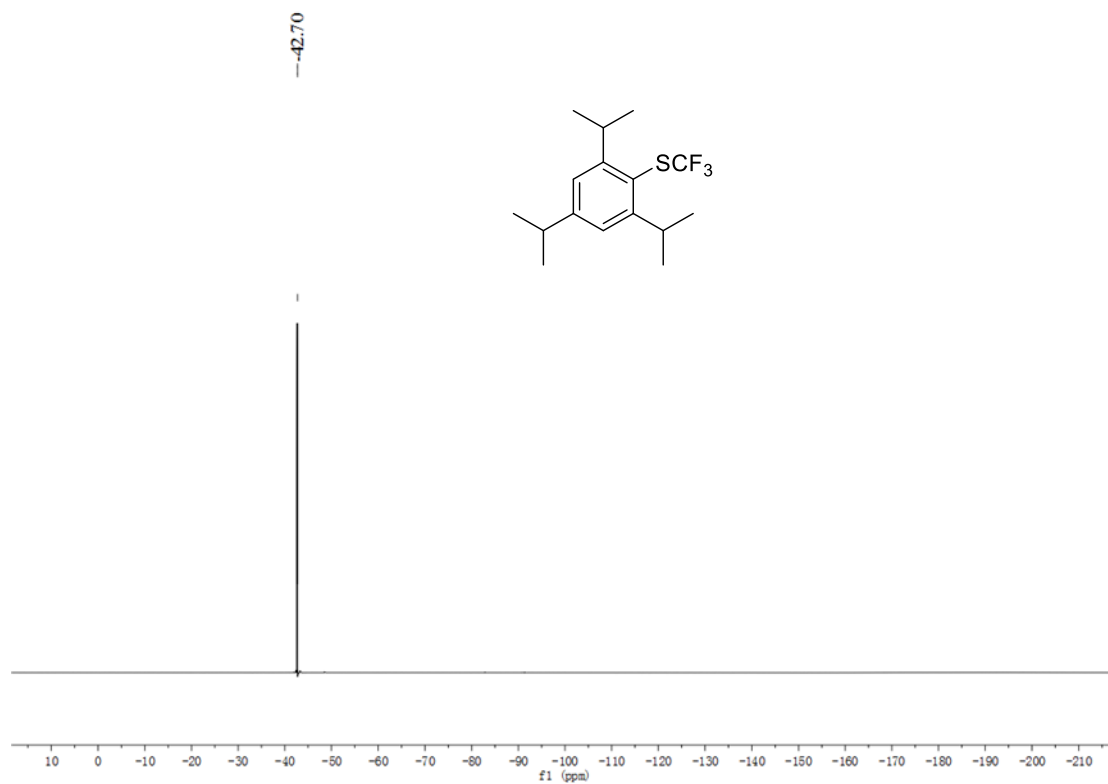
^{13}C NMR spectrum of **2p** (101 MHz, CDCl_3)



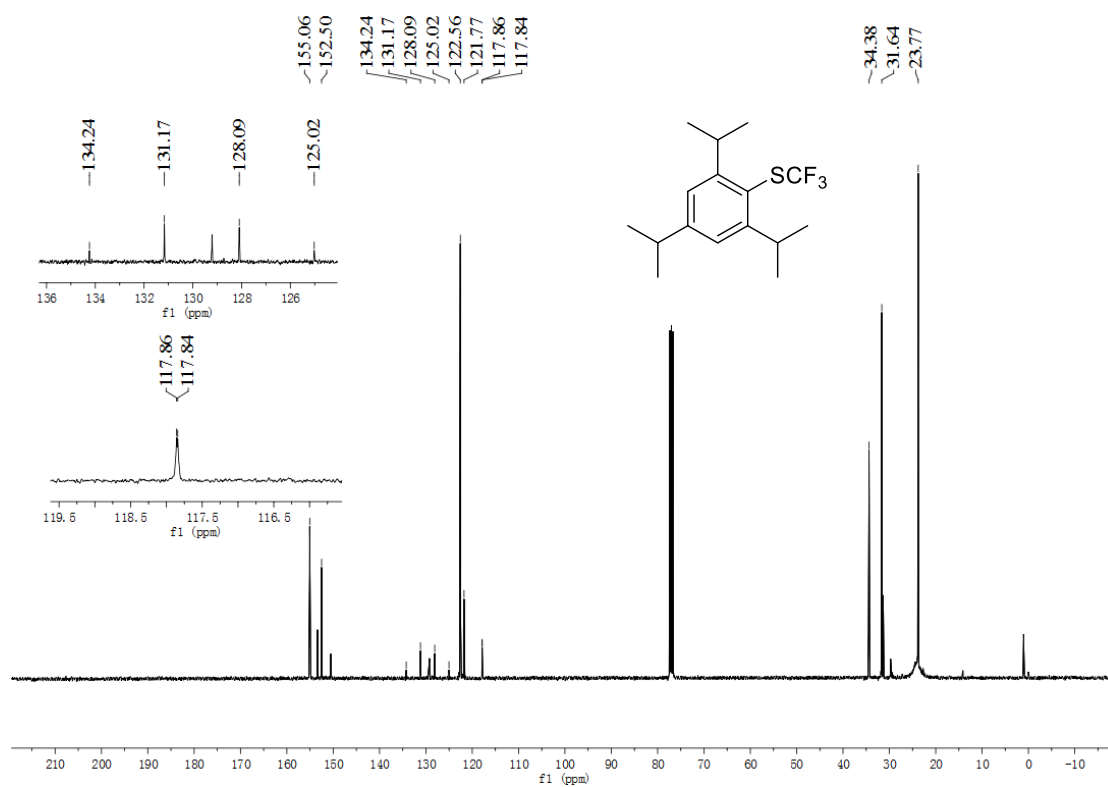
^1H NMR spectrum of **2q** (400 MHz, CDCl_3)



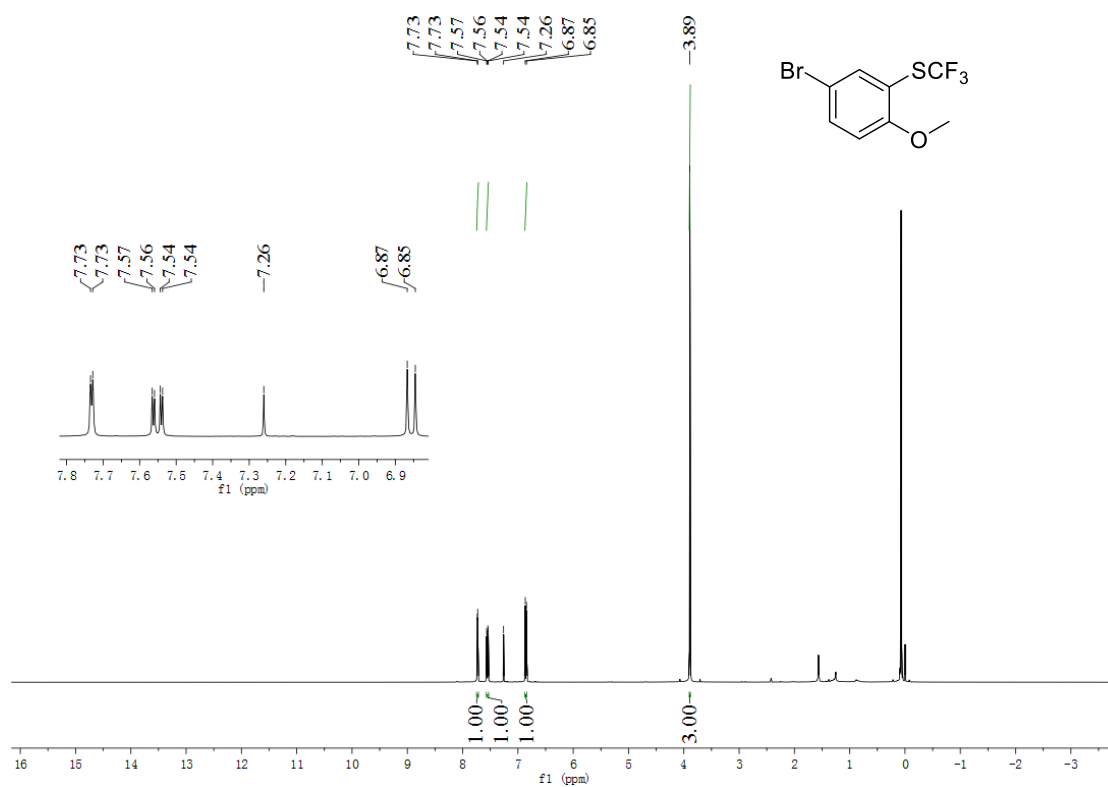
^{19}F NMR spectrum of **2q** (376 MHz, CDCl_3)



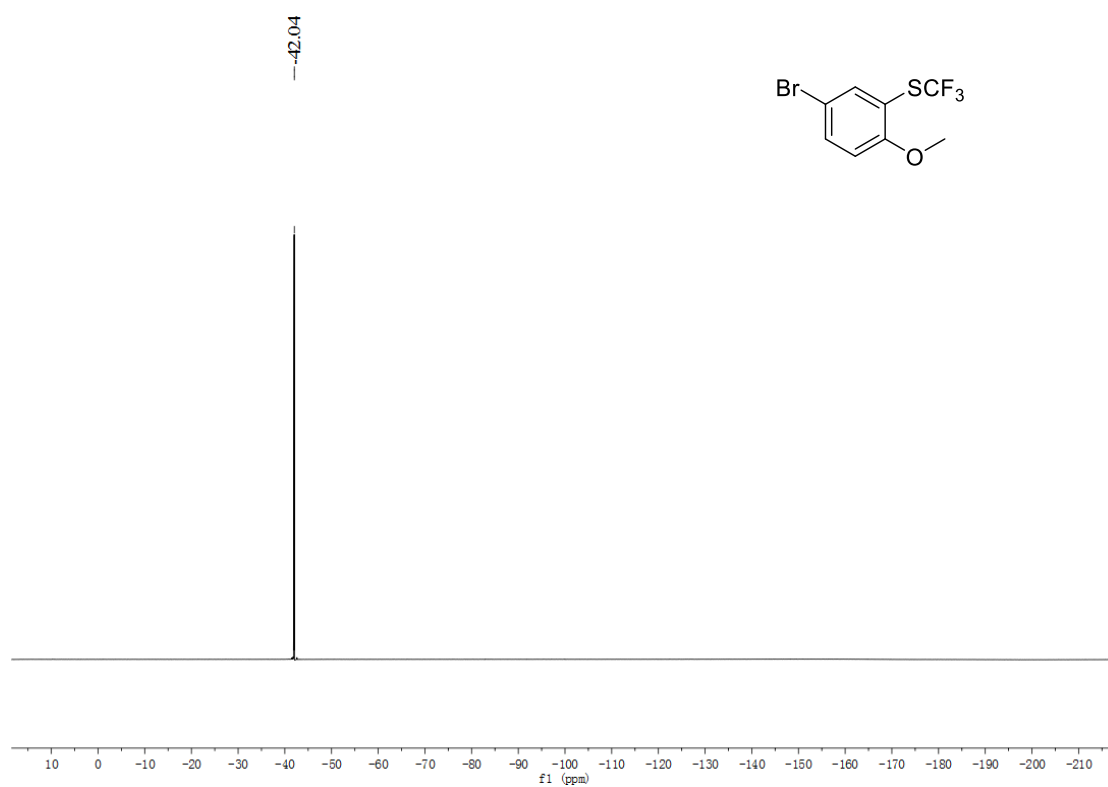
^{13}C NMR spectrum of **2q** (101 MHz, CDCl_3)



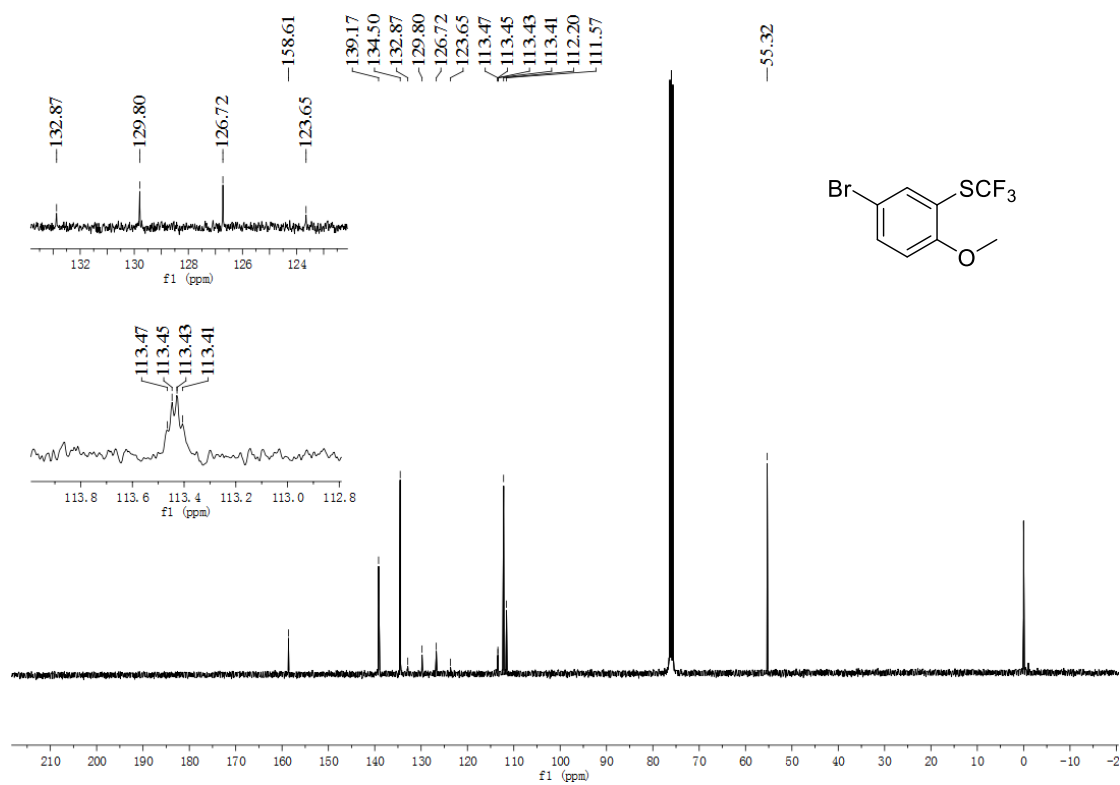
^1H NMR spectrum of **2r** (400 MHz, CDCl_3)



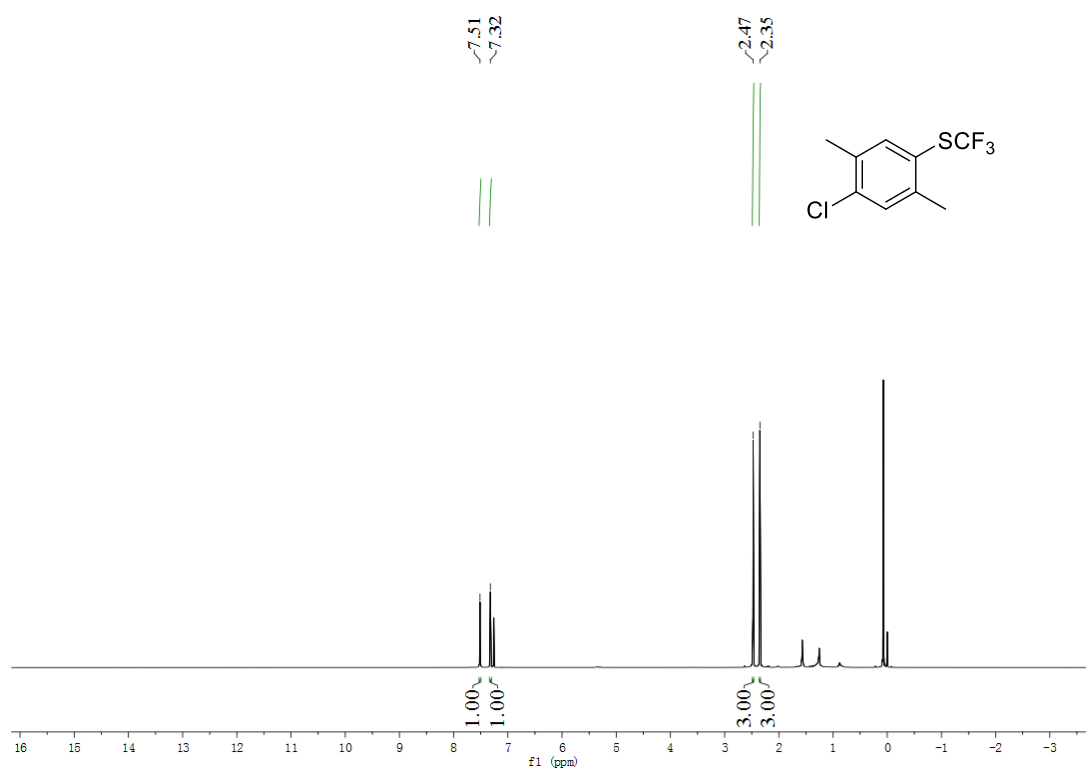
^{19}F NMR spectrum of **2r** (376 MHz, CDCl_3)



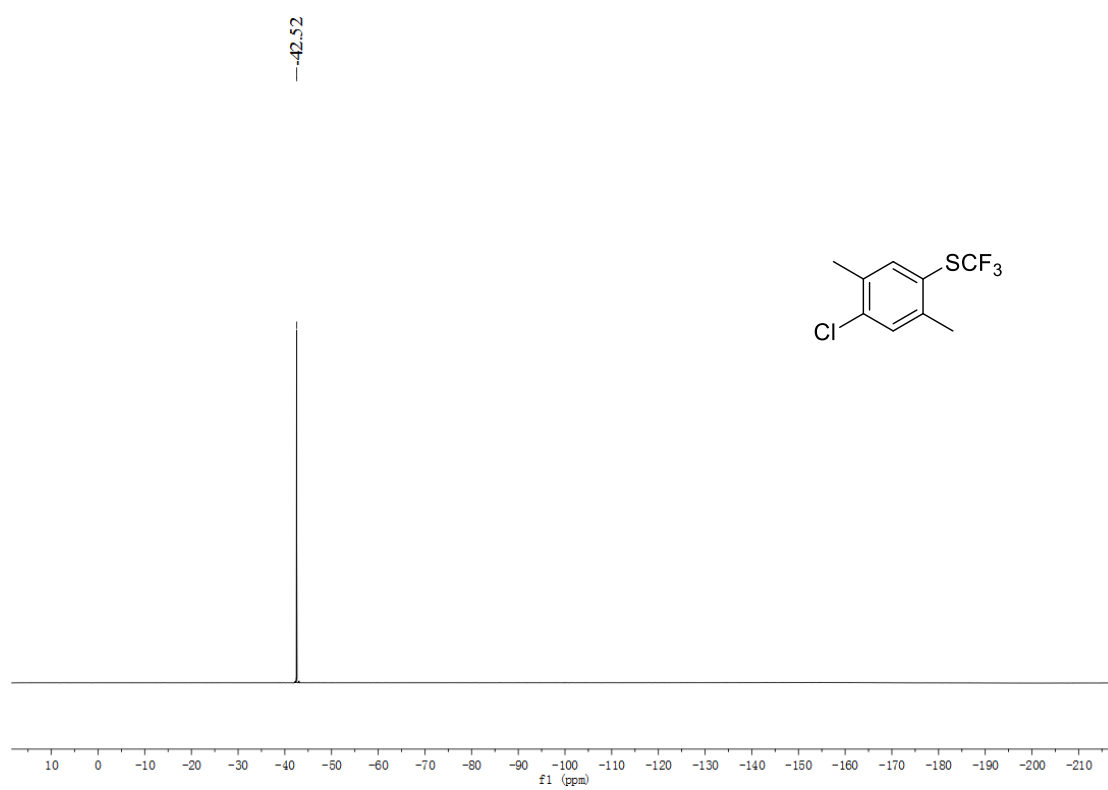
^{13}C NMR spectrum of **2r** (101 MHz, CDCl_3)



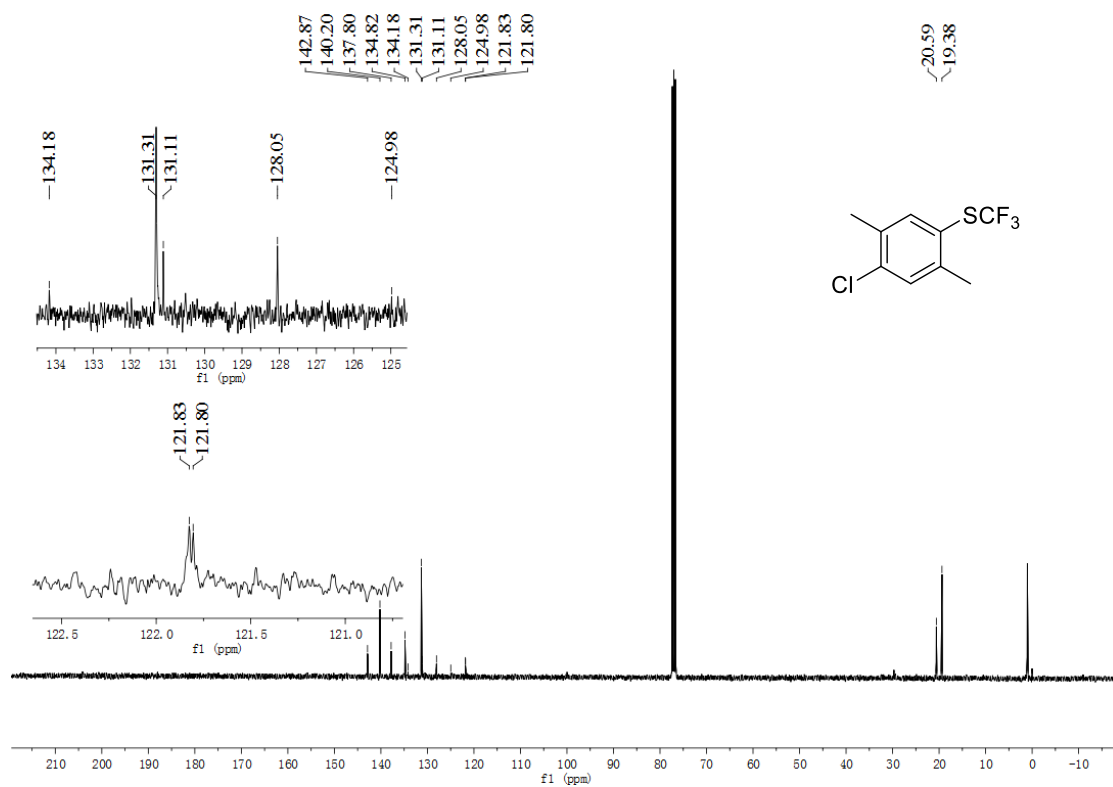
^1H NMR spectrum of **2s** (400 MHz, CDCl_3)



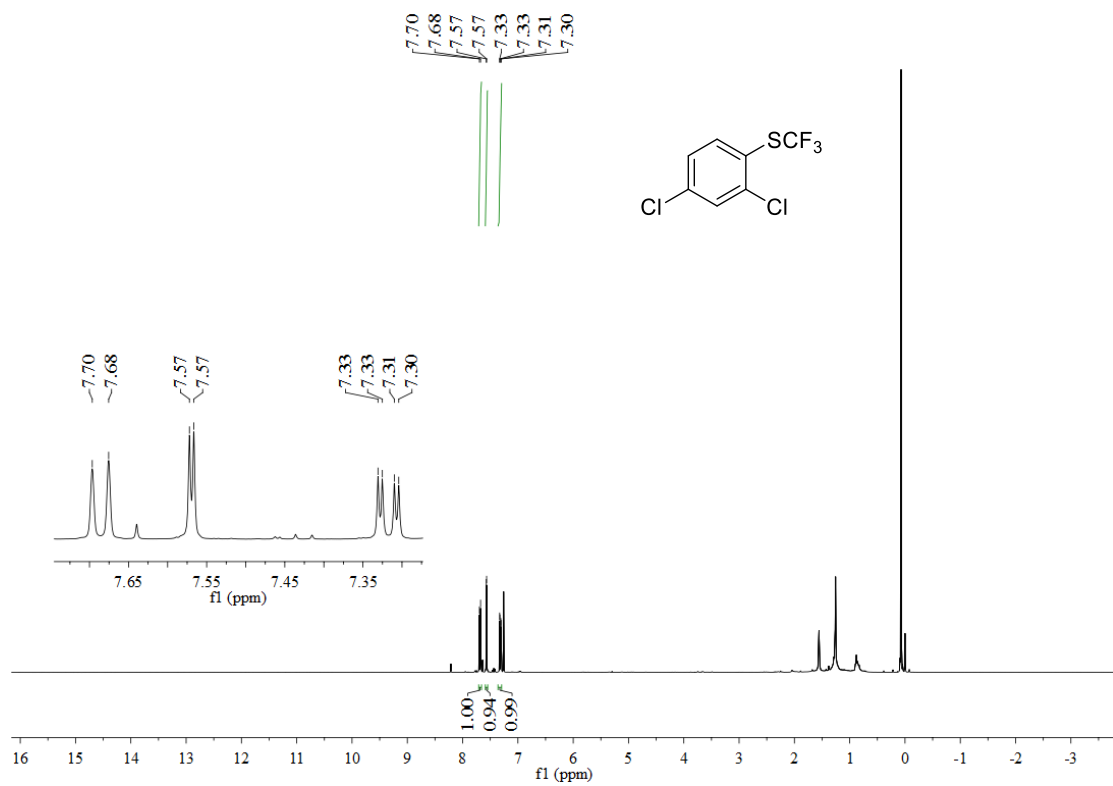
^{19}F NMR spectrum of **2s** (376 MHz, CDCl_3)



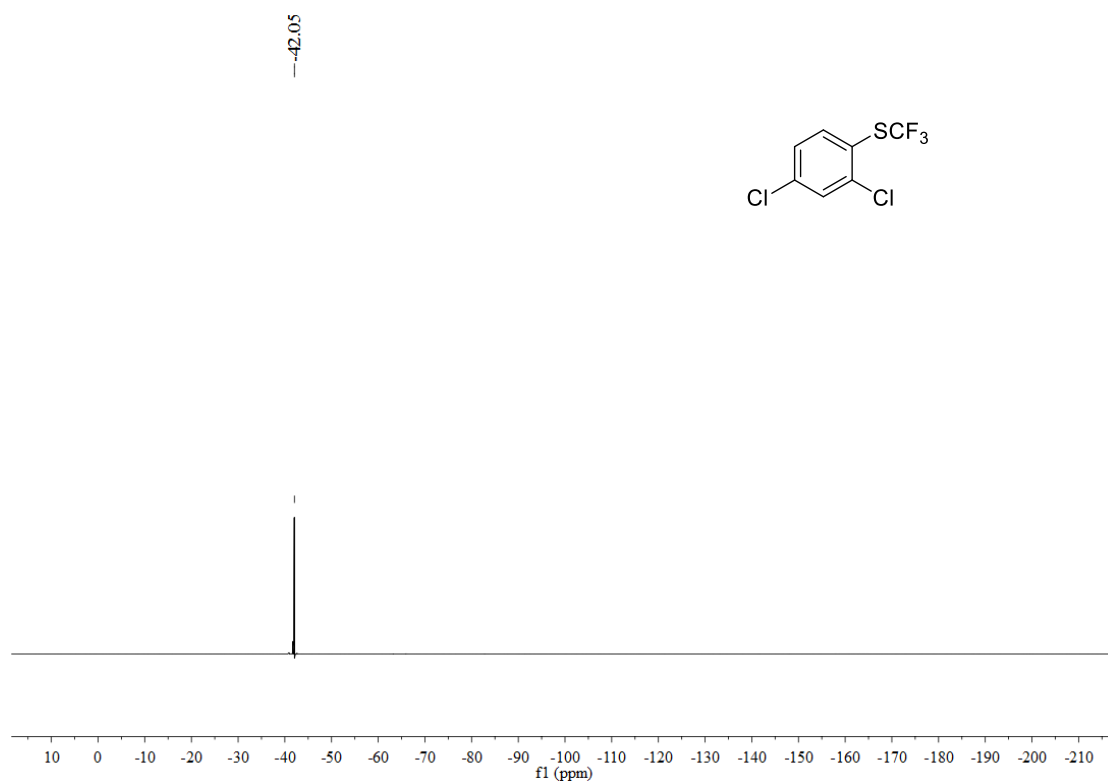
^{13}C NMR spectrum of **2s** (101 MHz, CDCl_3)



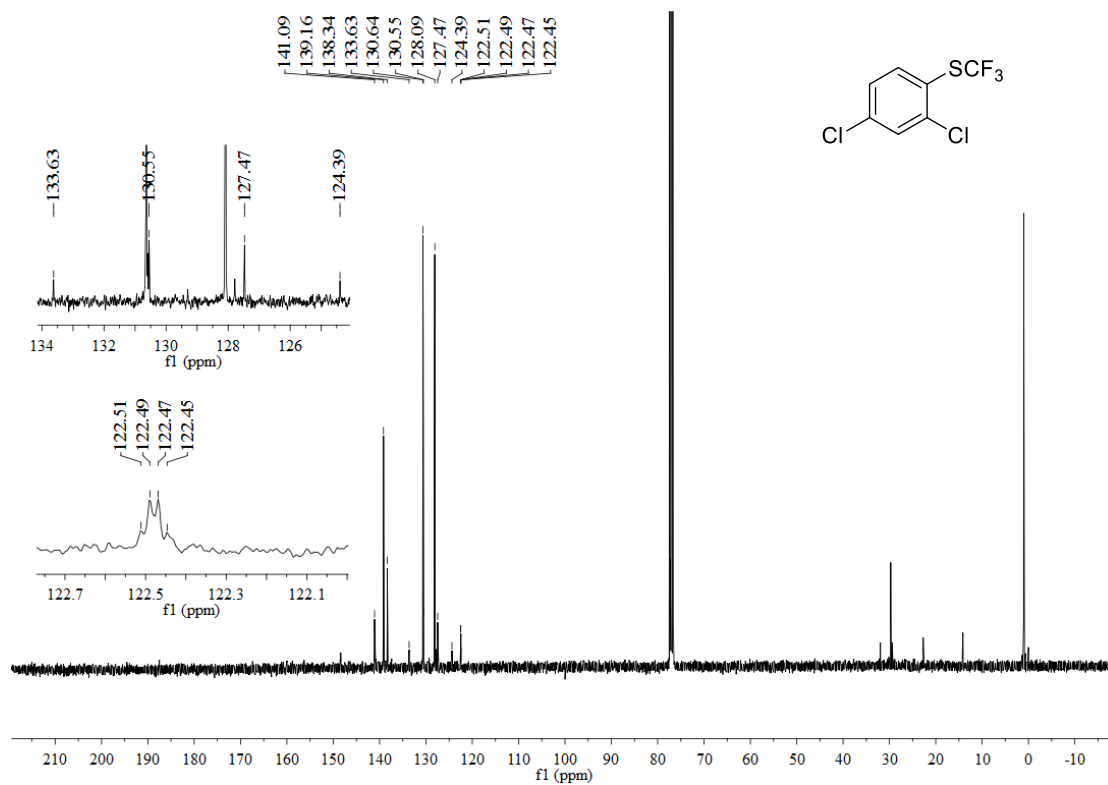
^1H NMR spectrum of **2t** (400 MHz, CDCl_3)



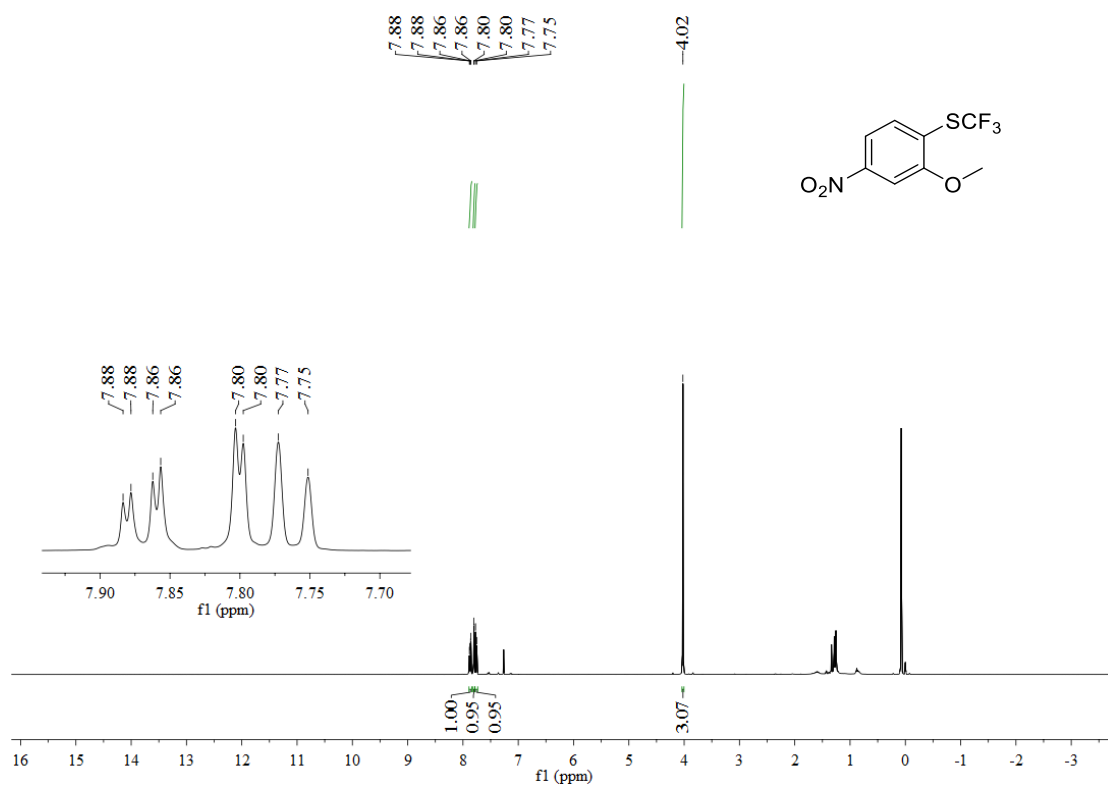
^{19}F NMR spectrum of **2t** (376 MHz, CDCl_3)



^{13}C NMR spectrum of **2t** (101 MHz, CDCl_3)



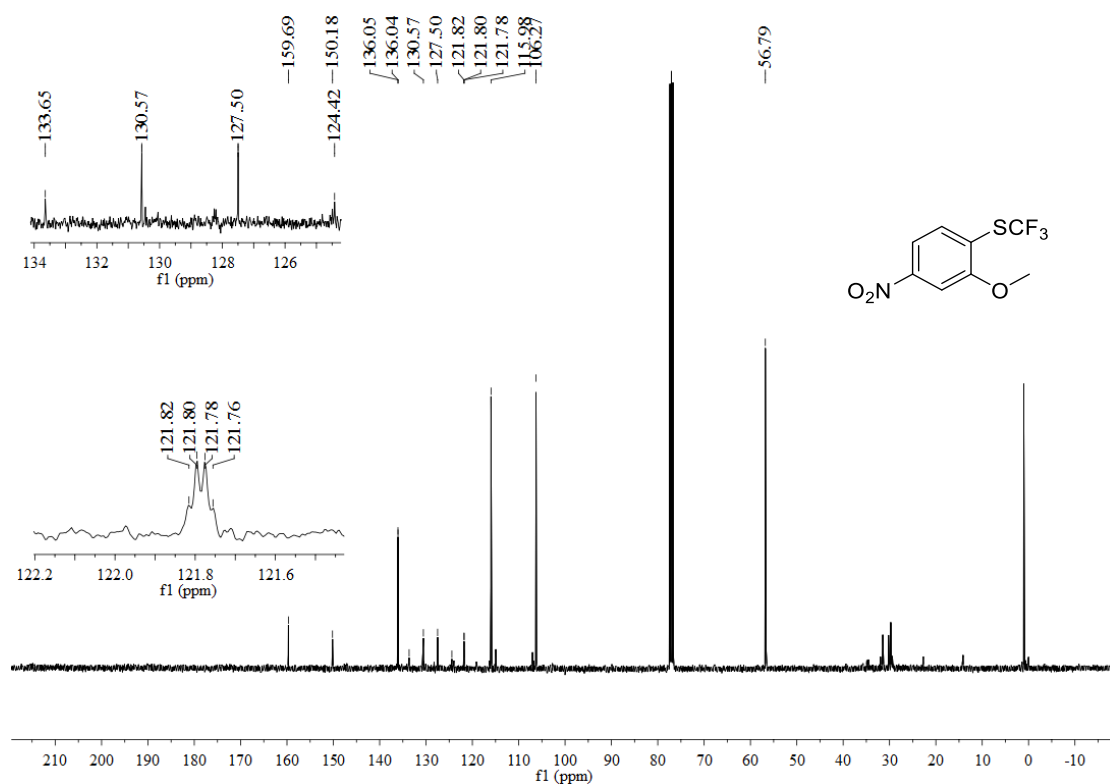
^1H NMR spectrum of **2u** (400 MHz, CDCl_3)



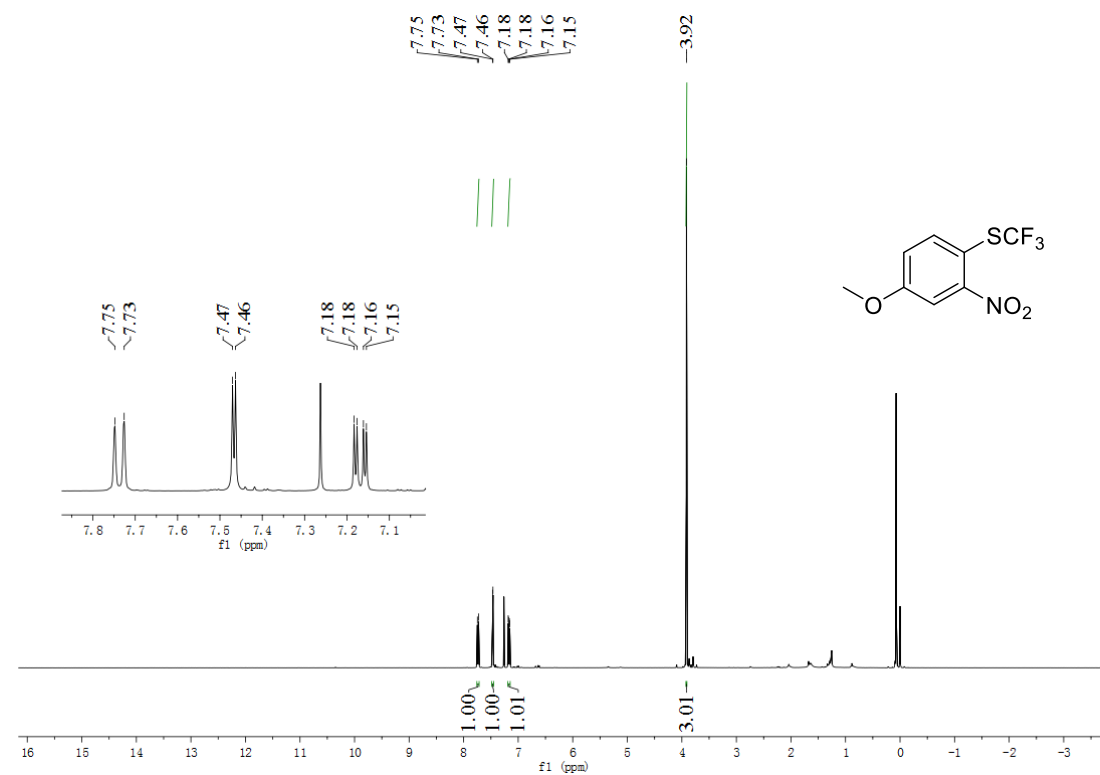
^{19}F NMR spectrum of **2u** (376 MHz, CDCl_3)



^{13}C NMR spectrum of **2u** (101 MHz, CDCl_3)



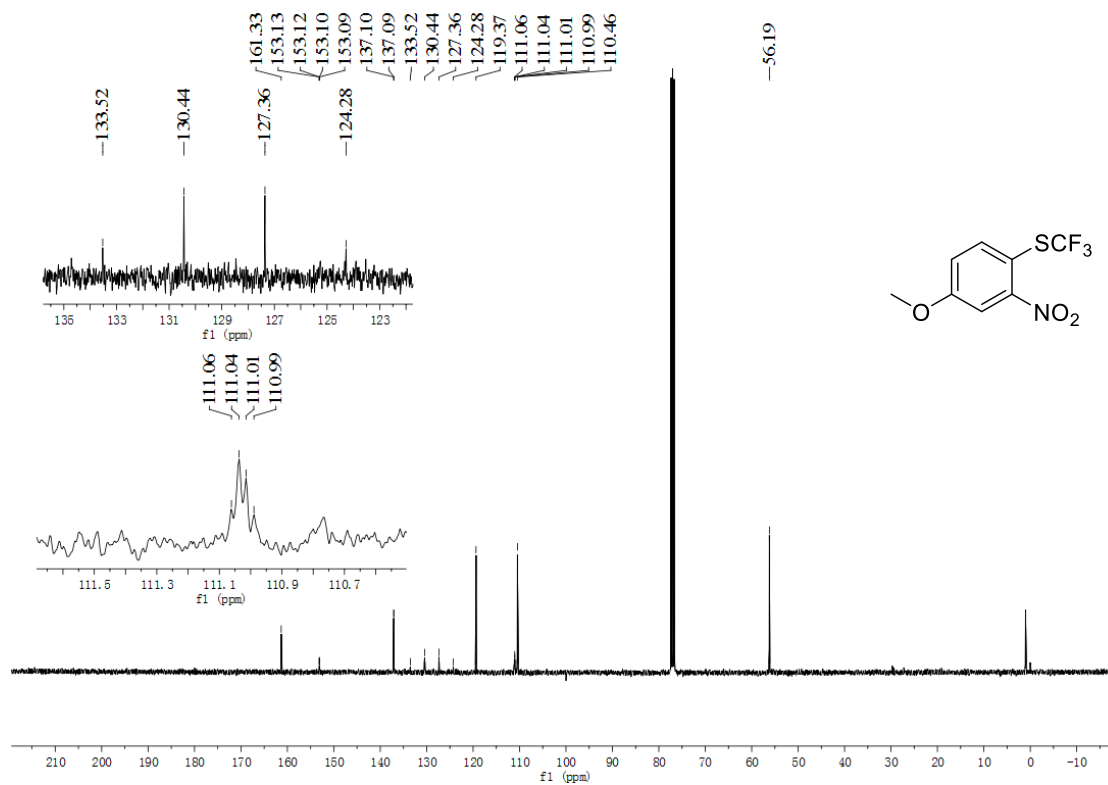
^1H NMR spectrum of **2v** (400 MHz, CDCl_3)



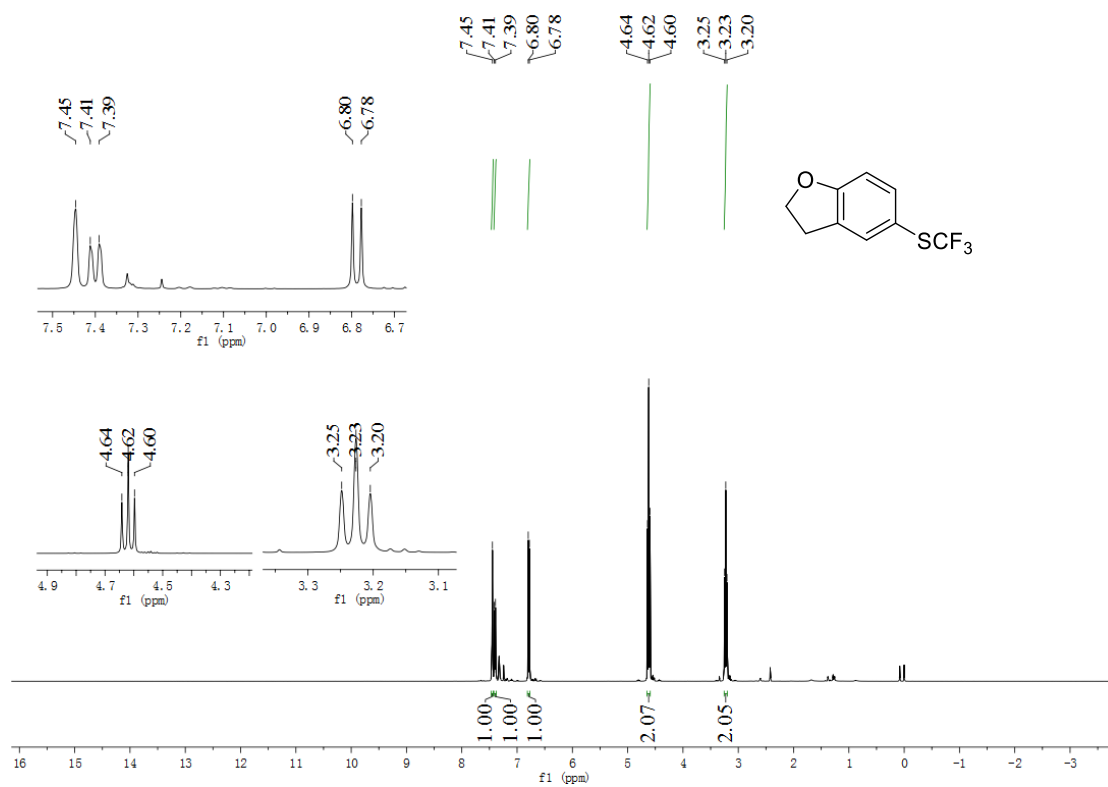
^{19}F NMR spectrum of **2v** (376 MHz, CDCl_3)



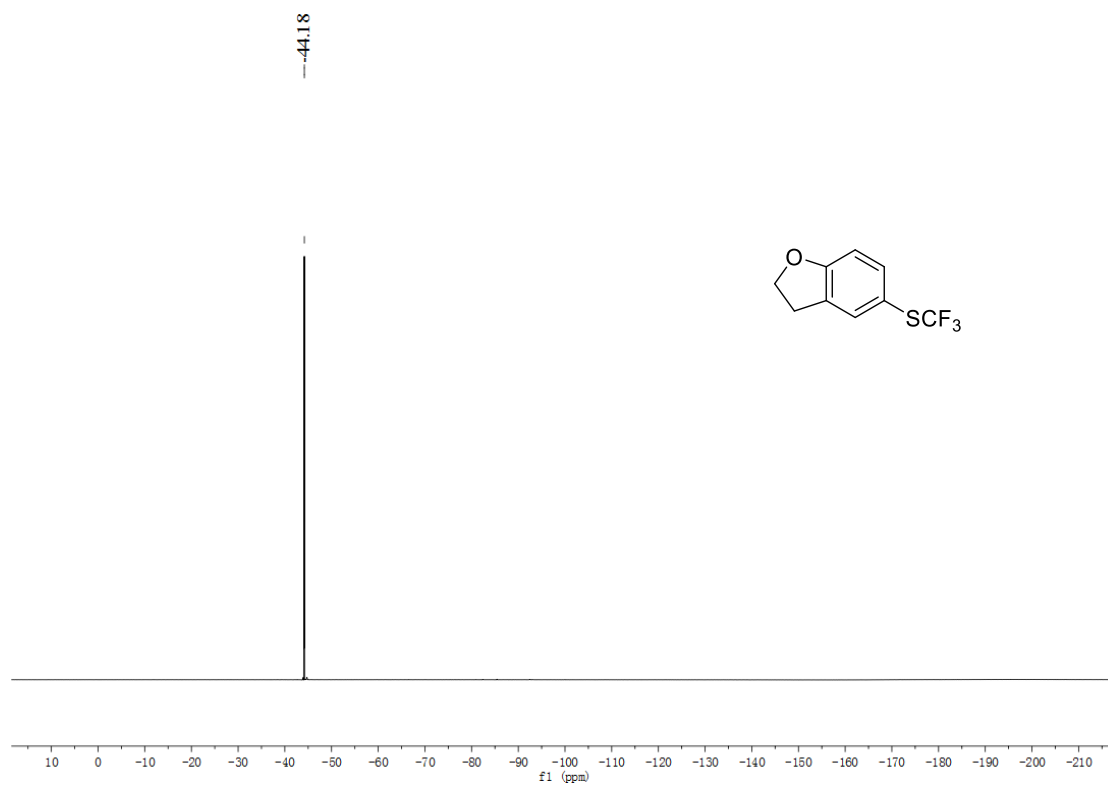
^{13}C NMR spectrum of **2v** (101 MHz, CDCl_3)



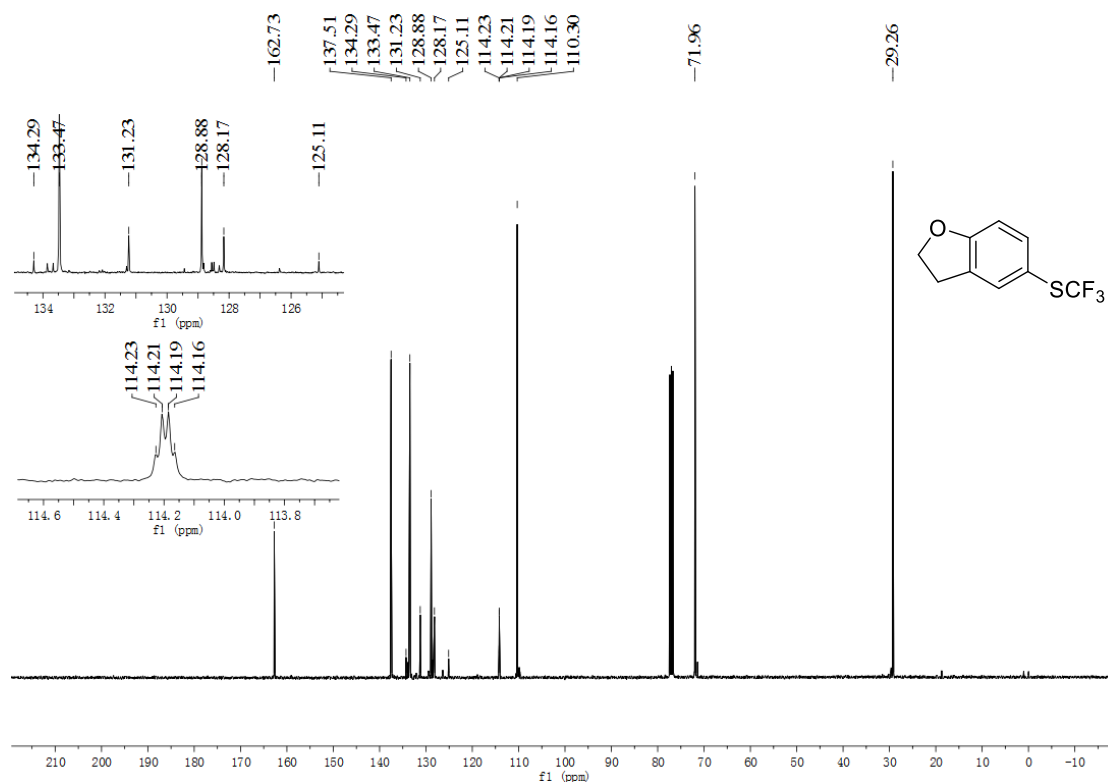
^1H NMR spectrum of **2w** (400 MHz, CDCl_3)



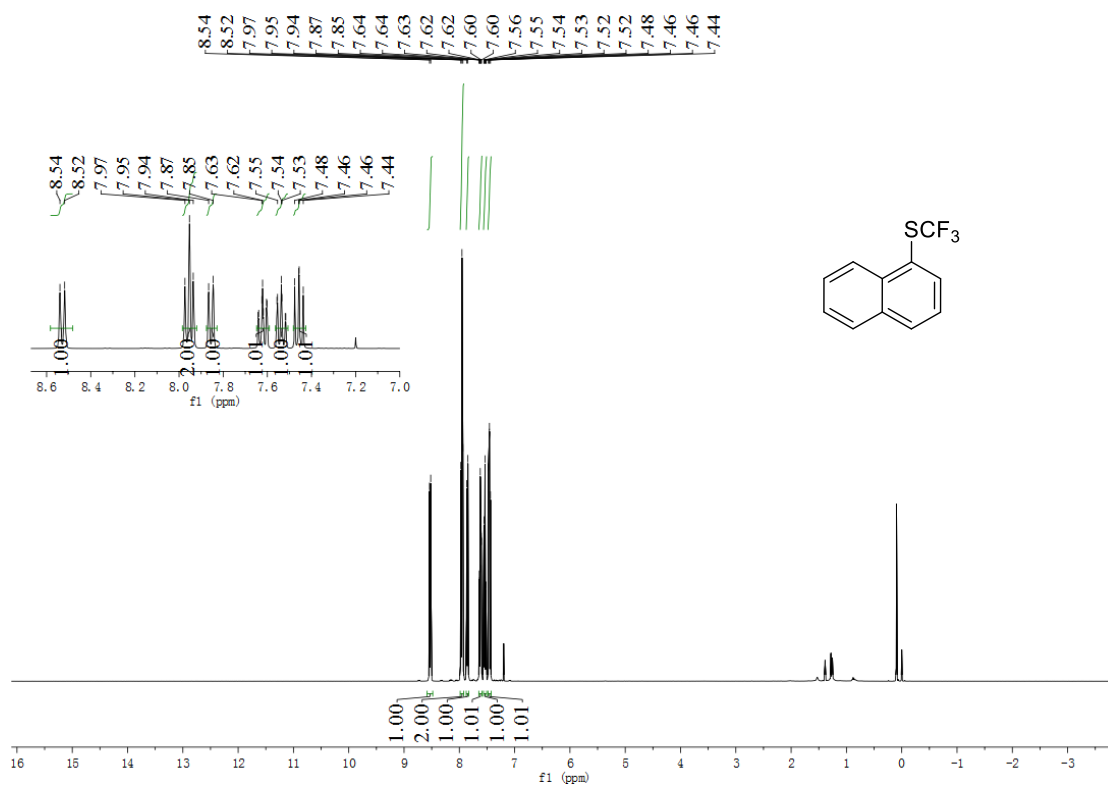
^{19}F NMR spectrum of **2w** (376 MHz, CDCl_3)



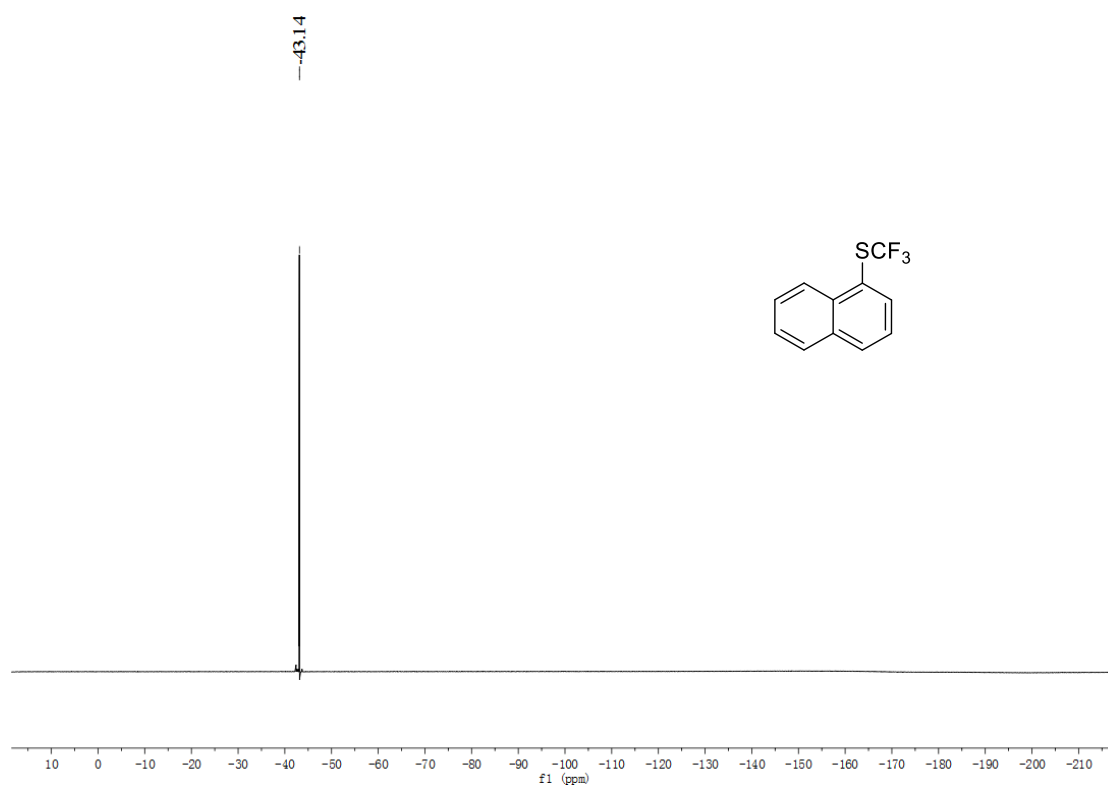
^{13}C NMR spectrum of **2w** (101 MHz, CDCl_3)



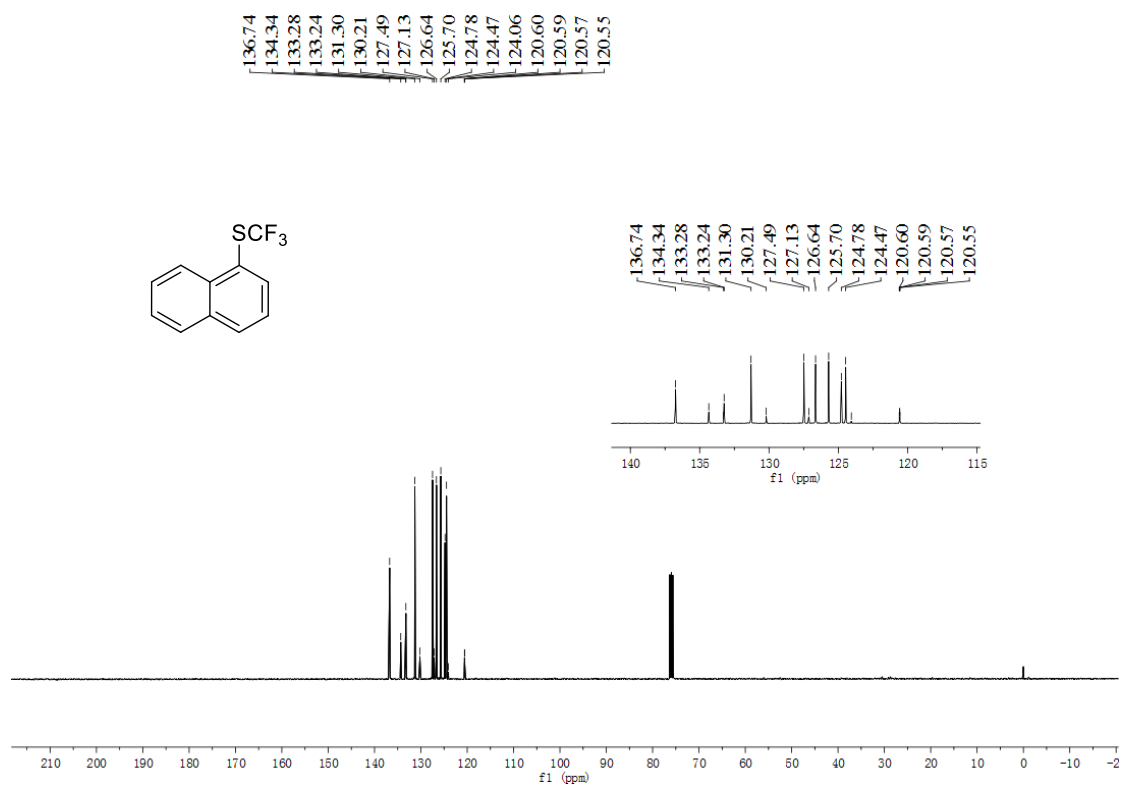
^1H NMR spectrum of **3a** (400 MHz, CDCl_3)



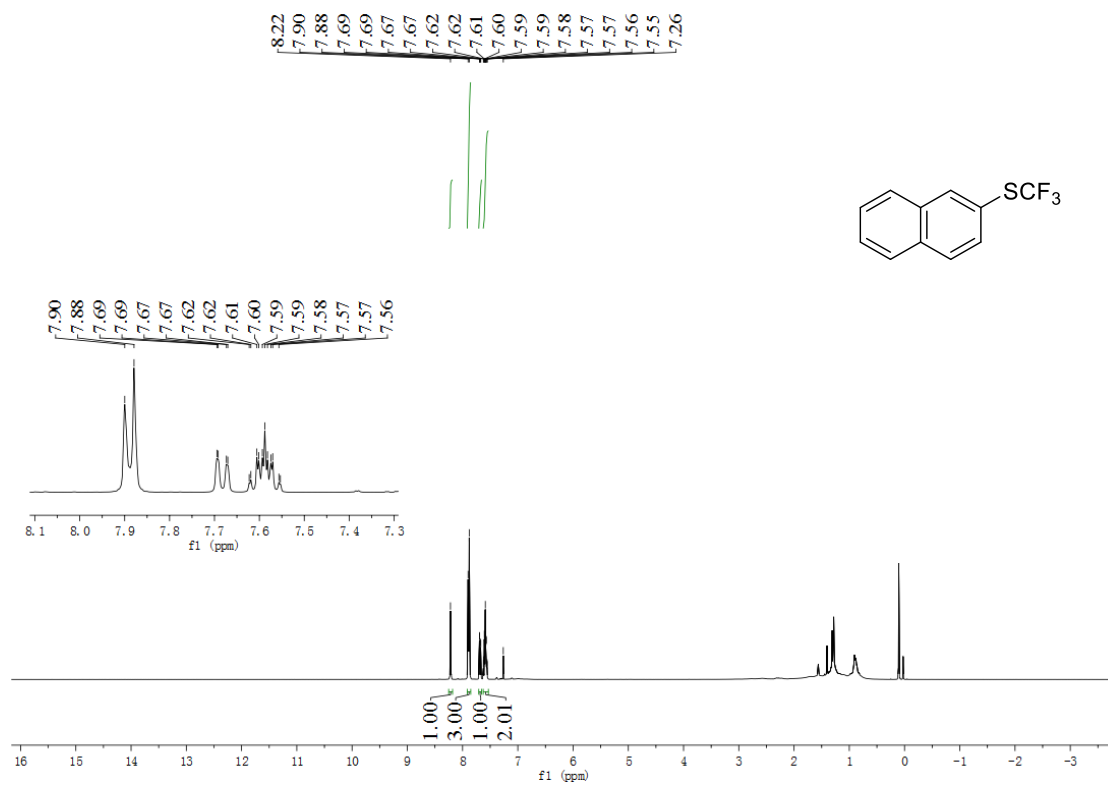
^{19}F NMR spectrum of **3a** (376 MHz, CDCl_3)



^{13}C NMR spectrum of **3a** (101 MHz, CDCl_3)



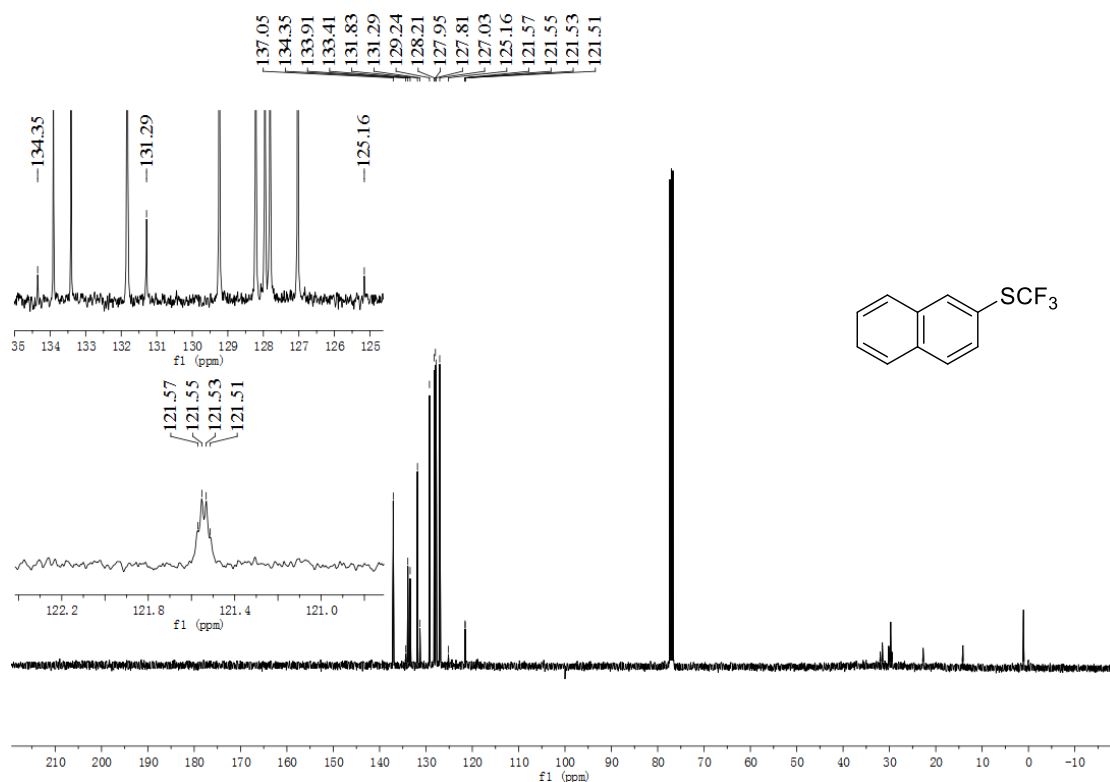
^1H NMR spectrum of **3b** (400 MHz, CDCl_3)



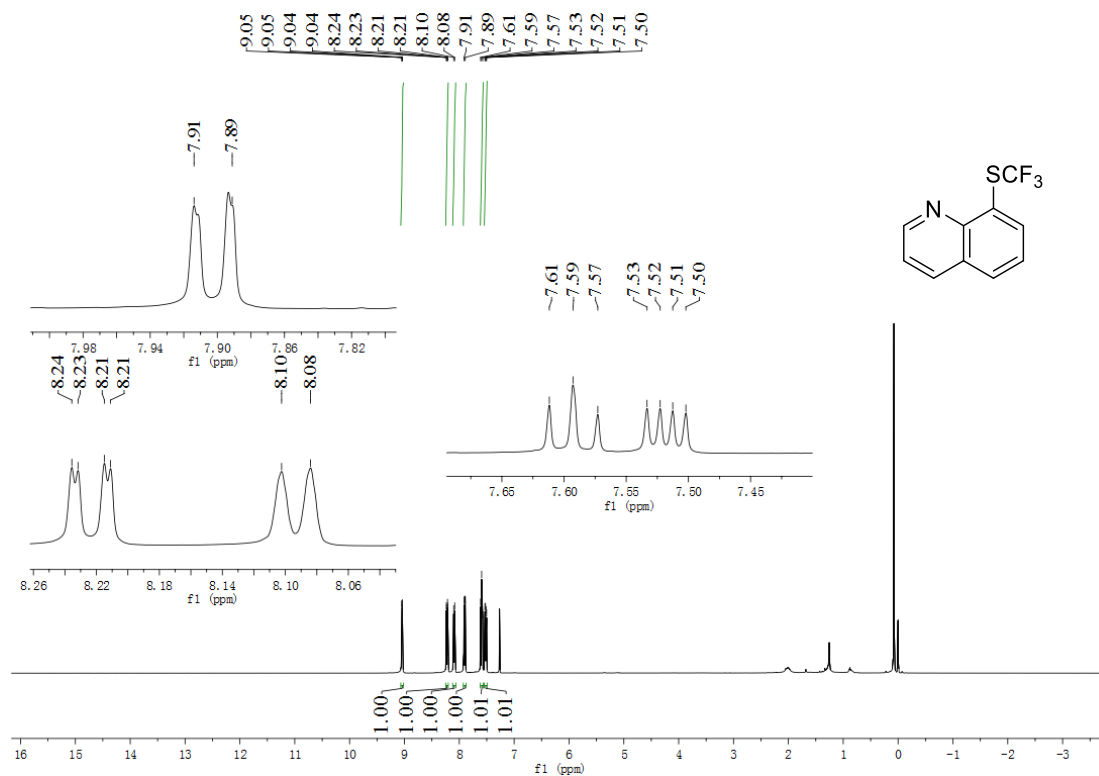
^{19}F NMR spectrum of **3b** (376 MHz, CDCl_3)



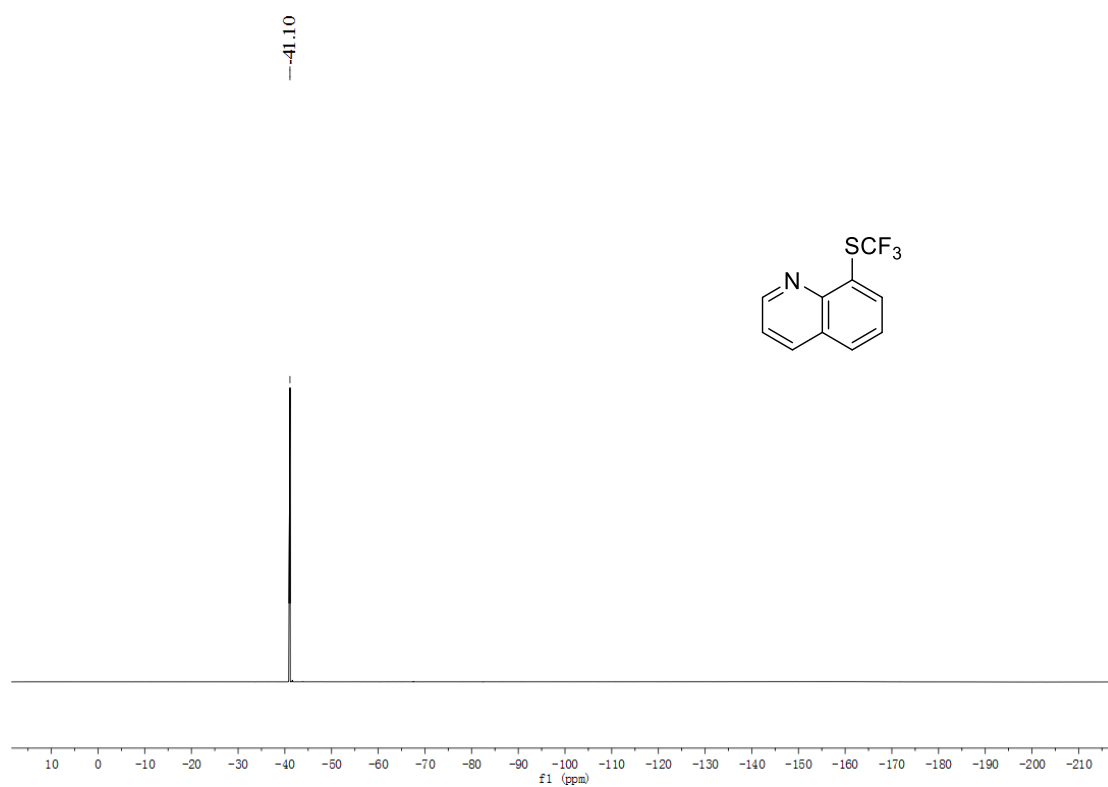
^{13}C NMR spectrum of **3b** (101 MHz, CDCl_3)



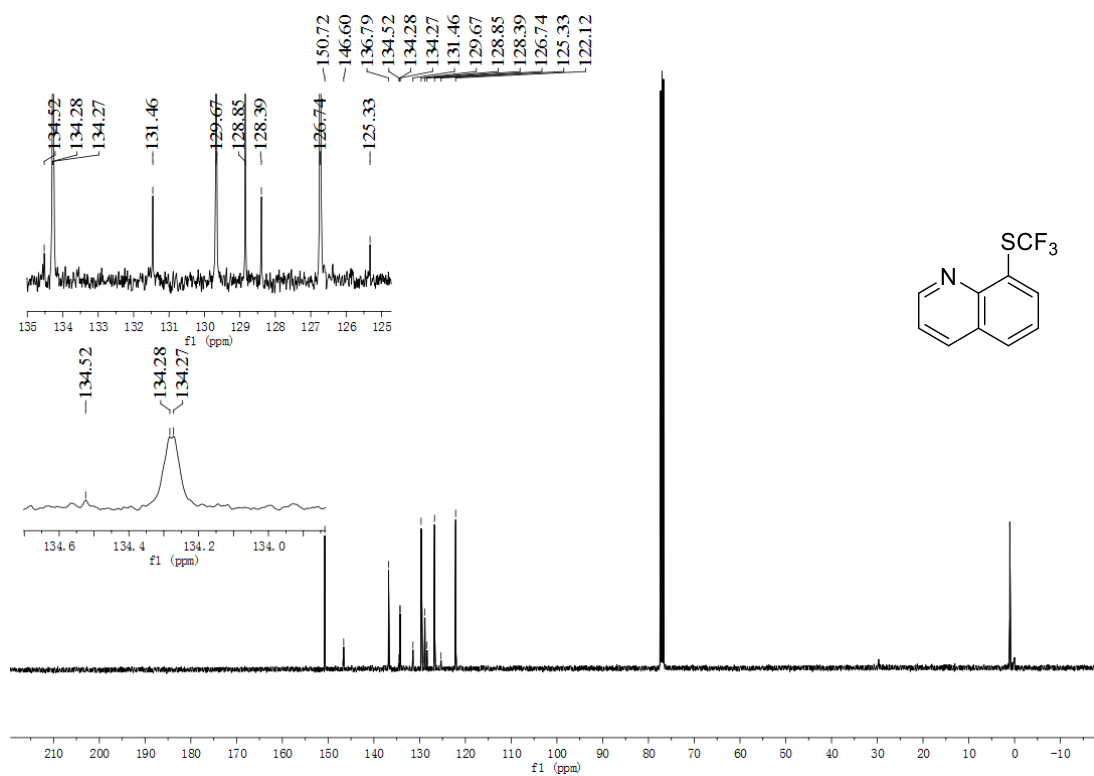
^1H NMR spectrum of **3c** (400 MHz, CDCl_3)



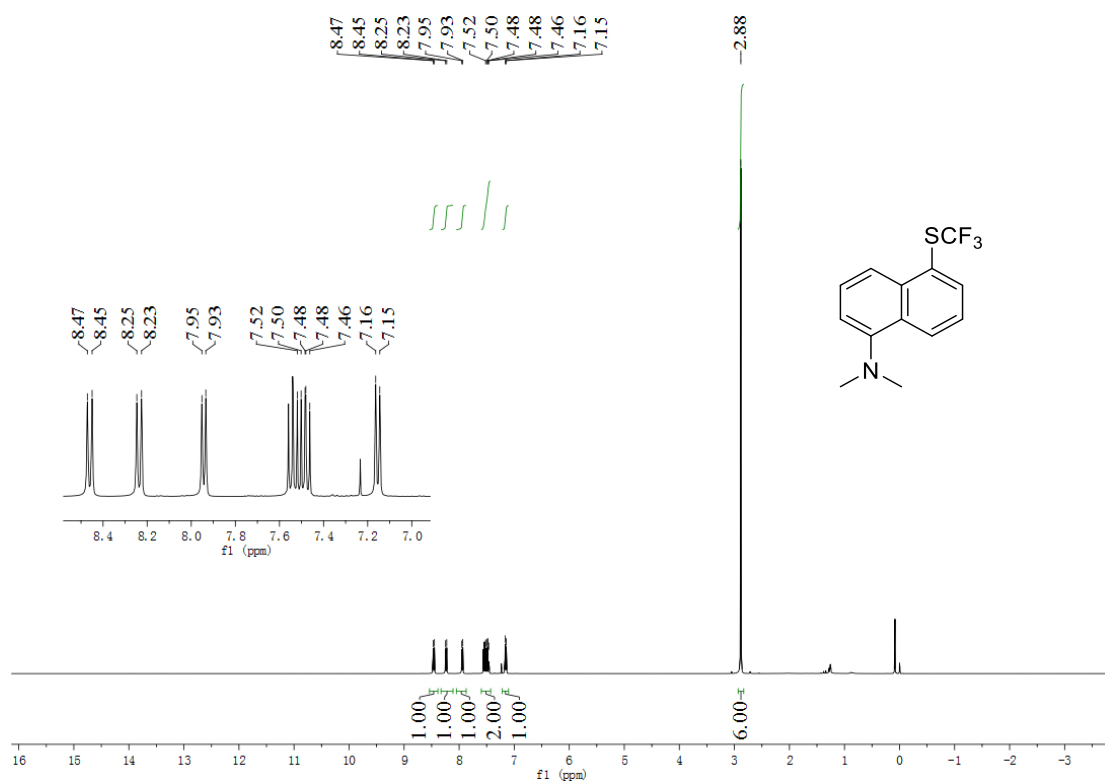
^{19}F NMR spectrum of **3c** (376 MHz, CDCl_3)



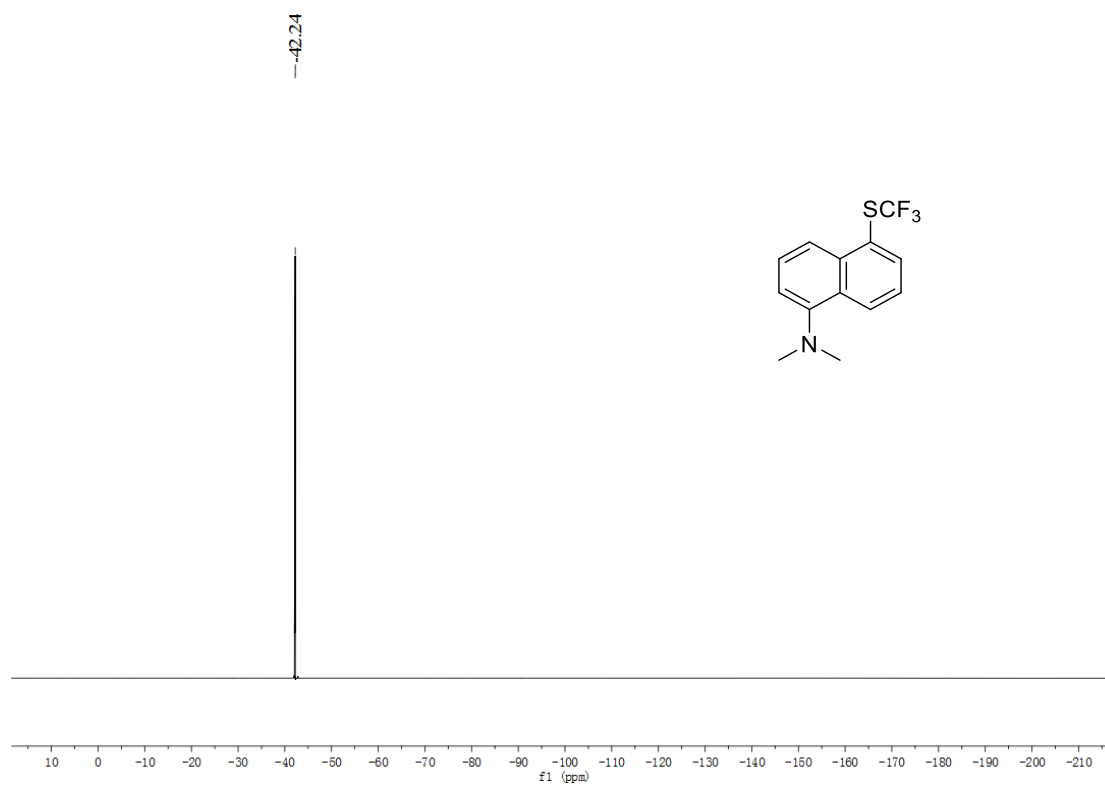
^{13}C NMR spectrum of **3c** (101 MHz, CDCl_3)



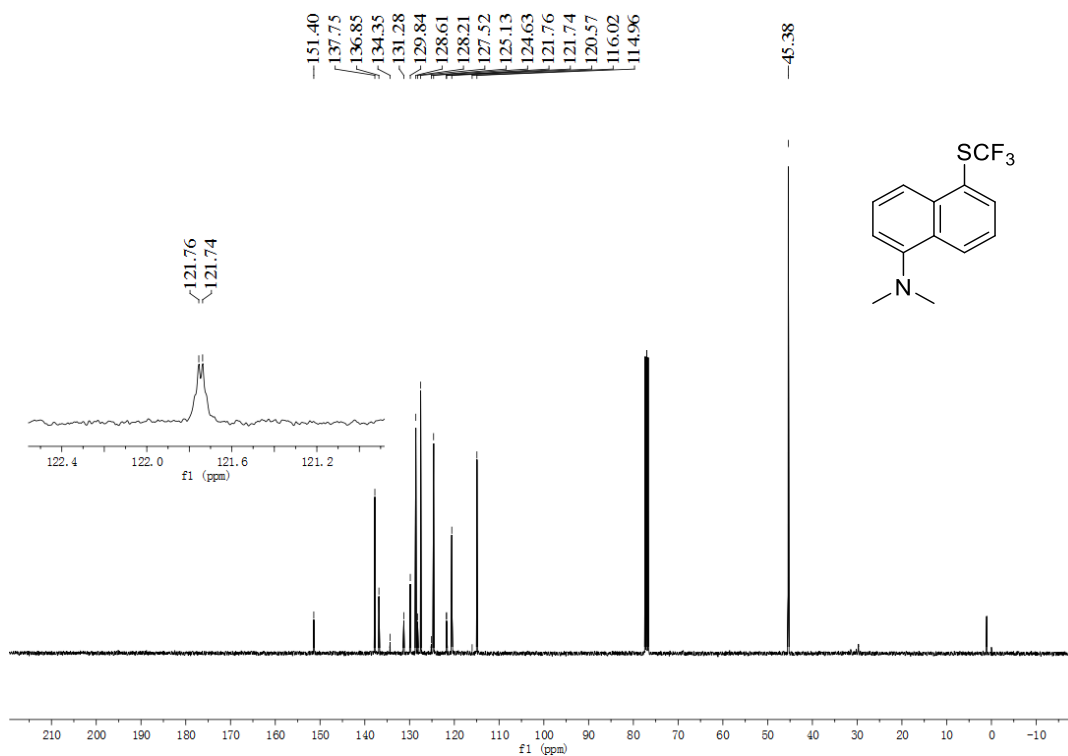
^1H NMR spectrum of **3d** (400 MHz, CDCl_3)



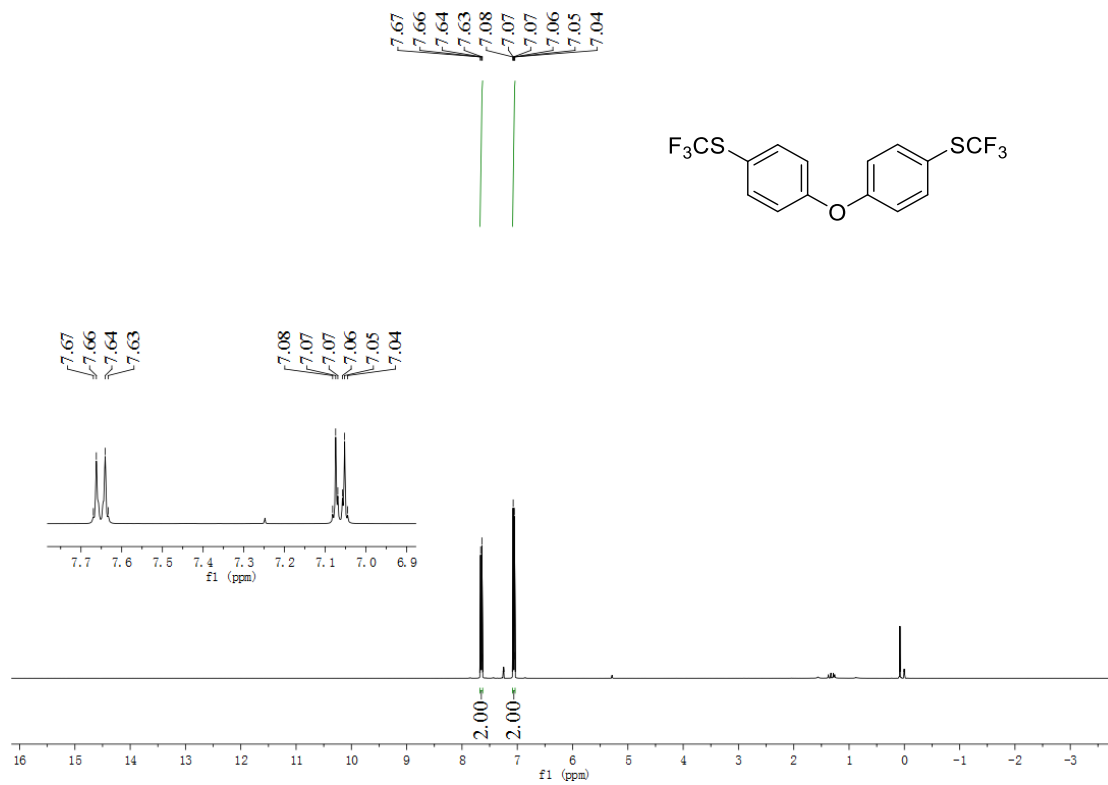
^{19}F NMR spectrum of **3d** (376 MHz, CDCl_3)



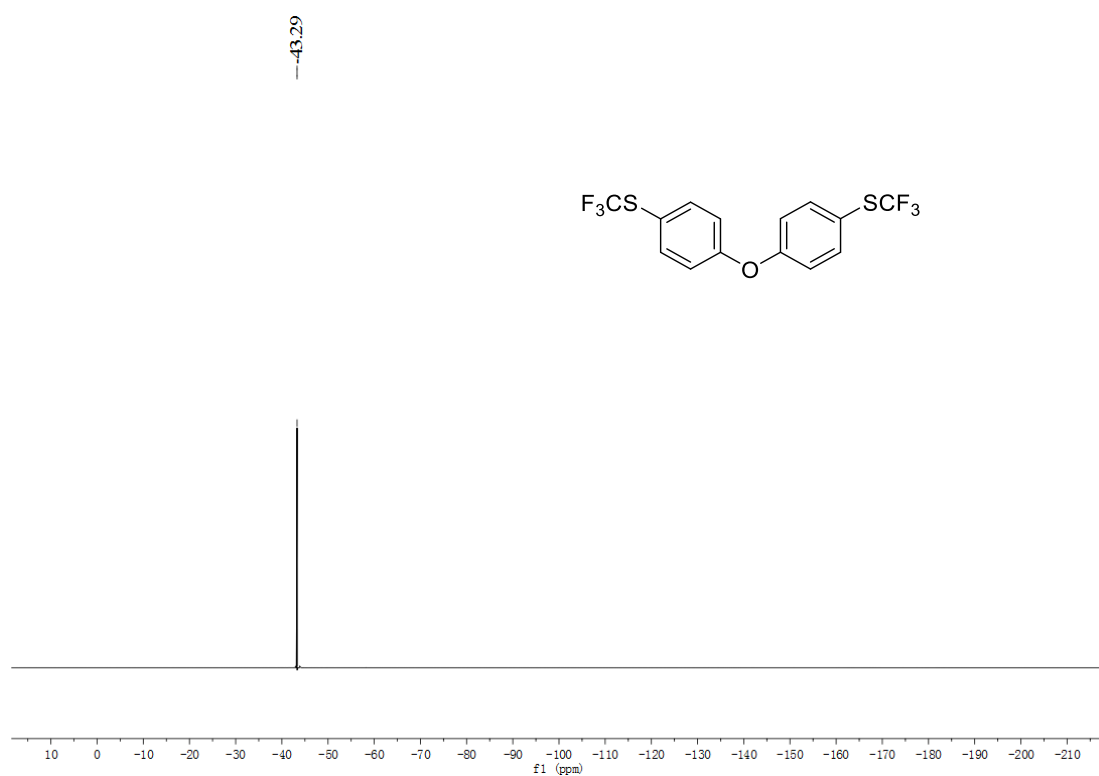
^{13}C NMR spectrum of **3d** (101 MHz, CDCl_3)



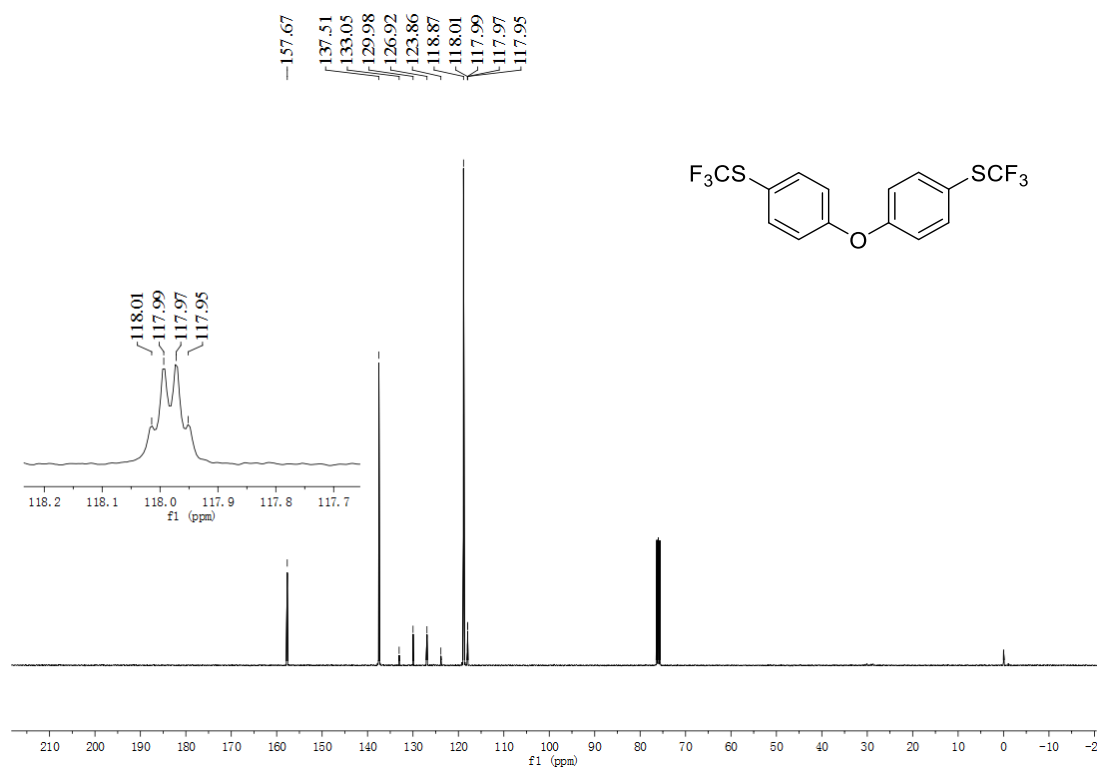
^1H NMR spectrum of **3e** (400 MHz, CDCl_3)



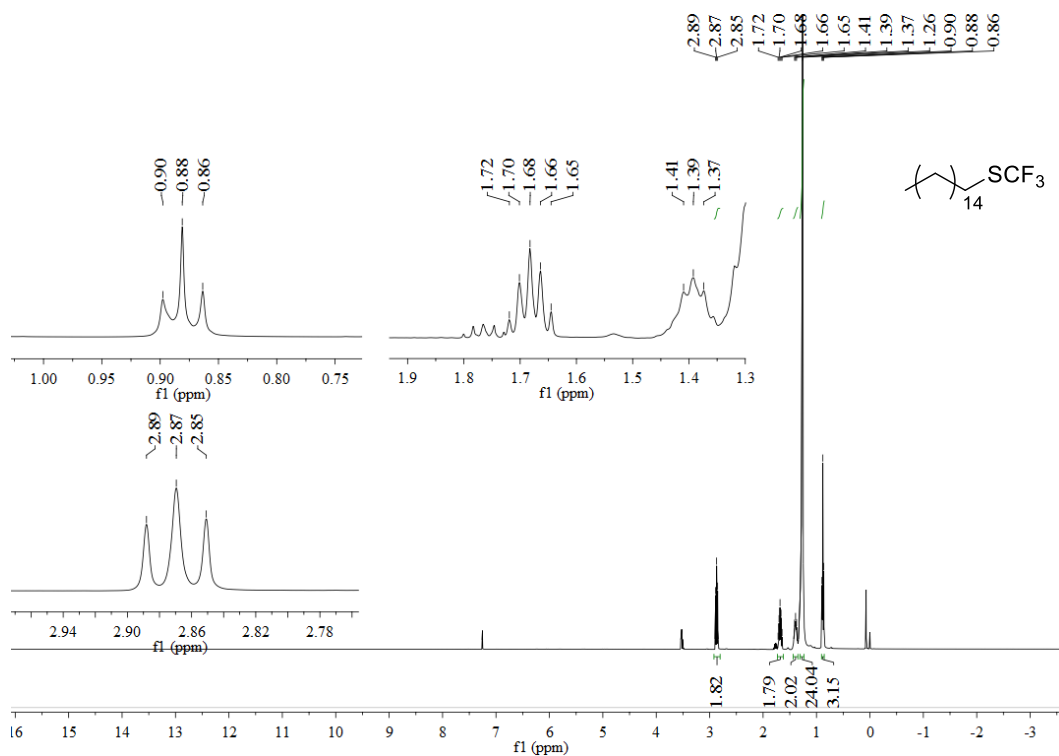
^{19}F NMR spectrum of **3e** (376 MHz, CDCl_3)



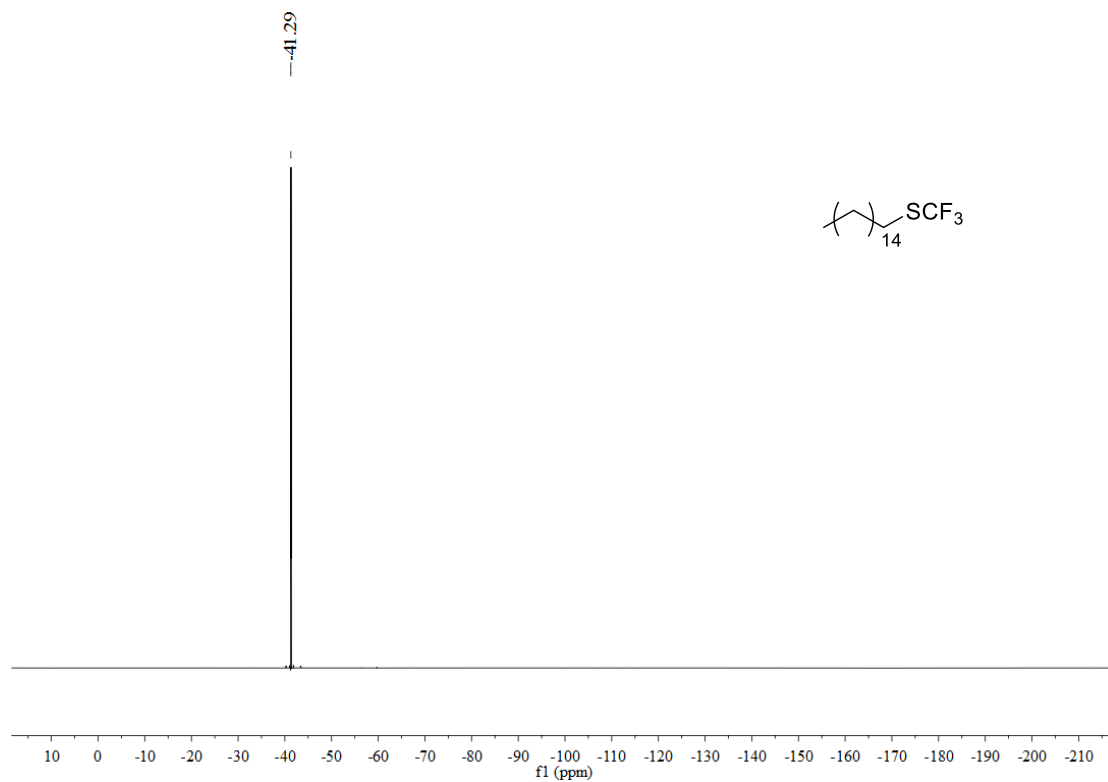
^{13}C NMR spectrum of **3e** (101 MHz, CDCl_3)



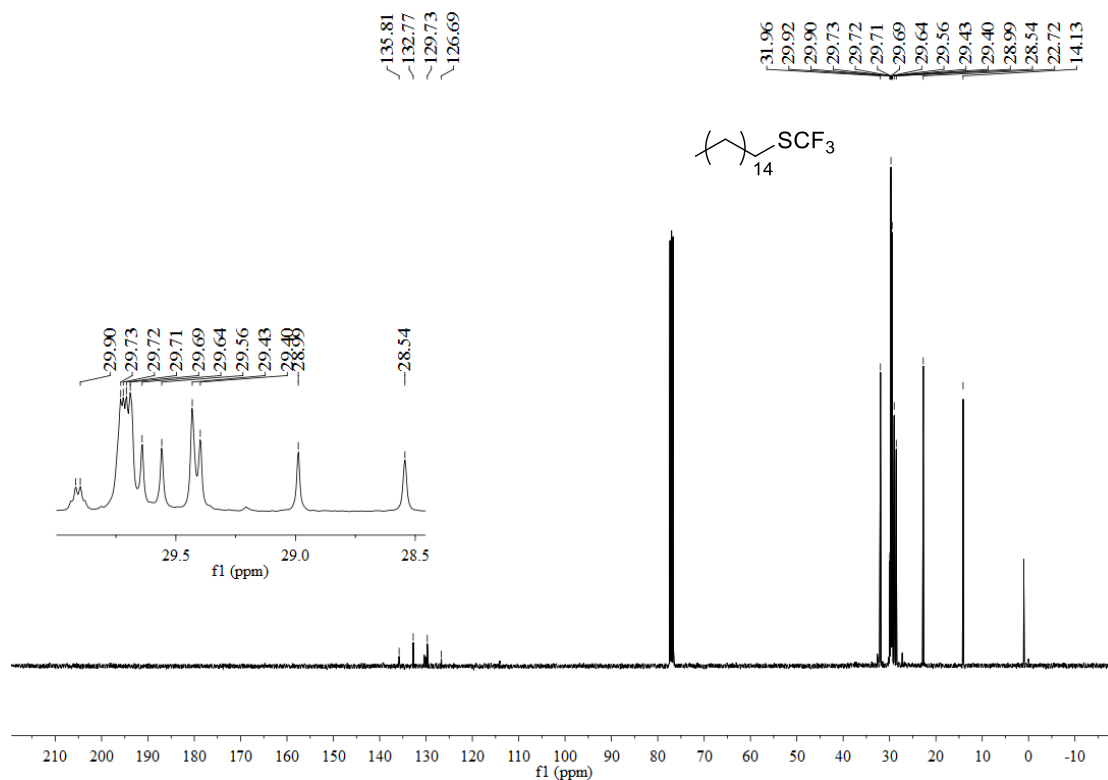
^1H NMR spectrum of **3f** (400 MHz, CDCl_3)



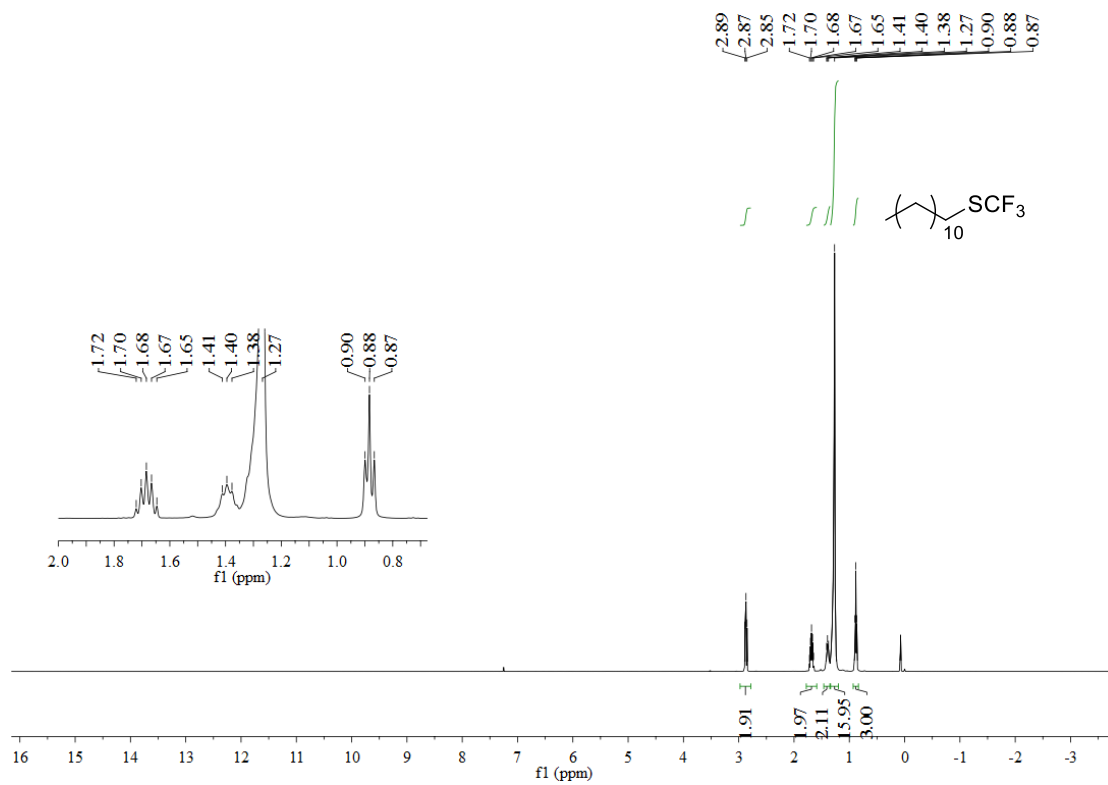
^{19}F NMR spectrum of **3f** (376 MHz, CDCl_3)



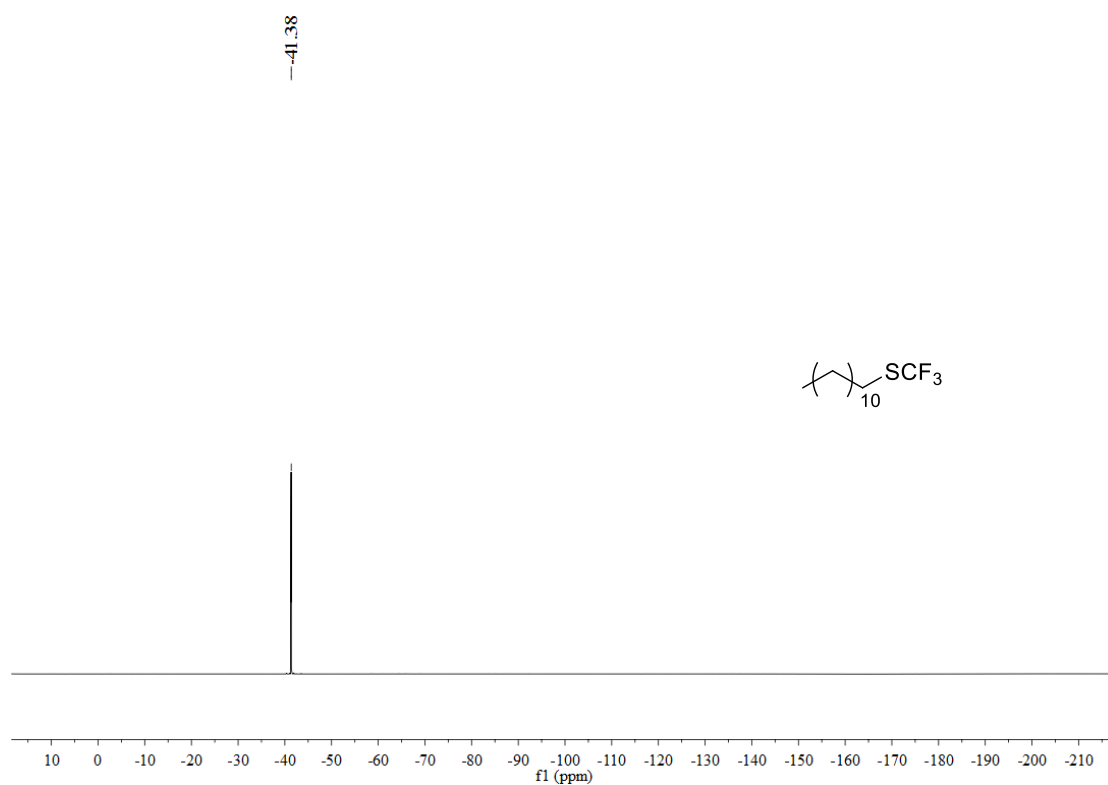
^{13}C NMR spectrum of **3f** (101 MHz, CDCl_3)



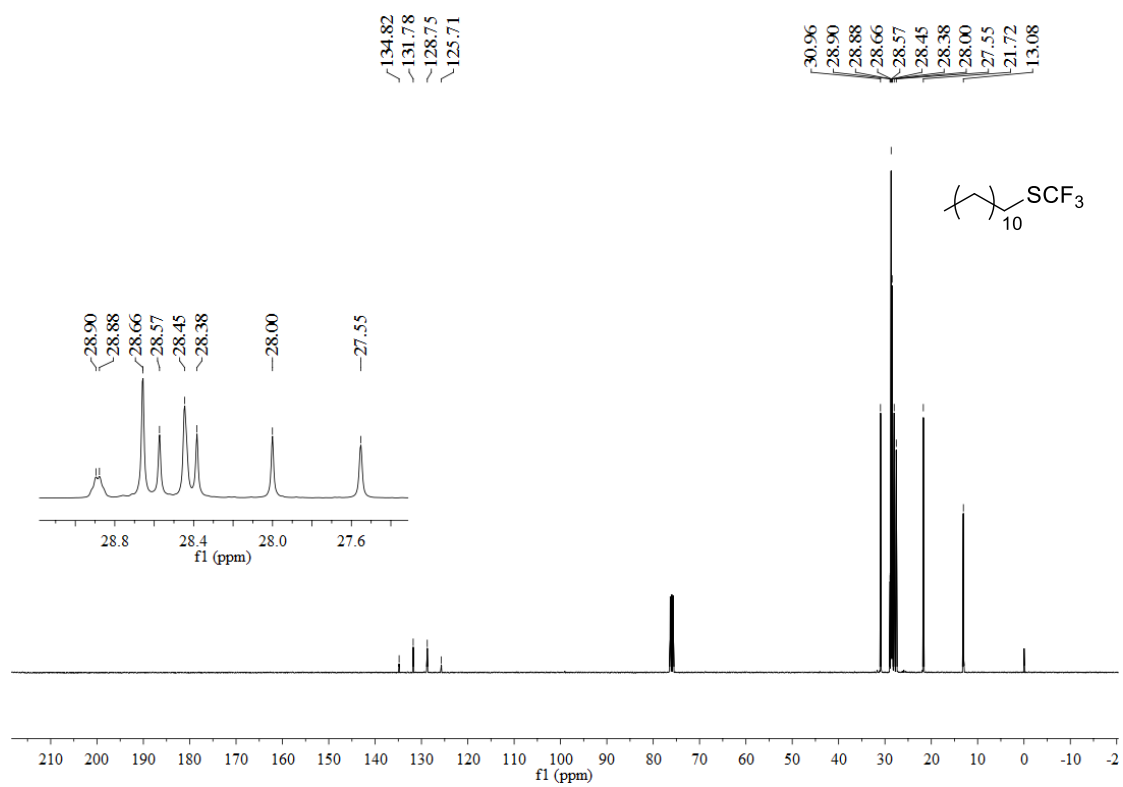
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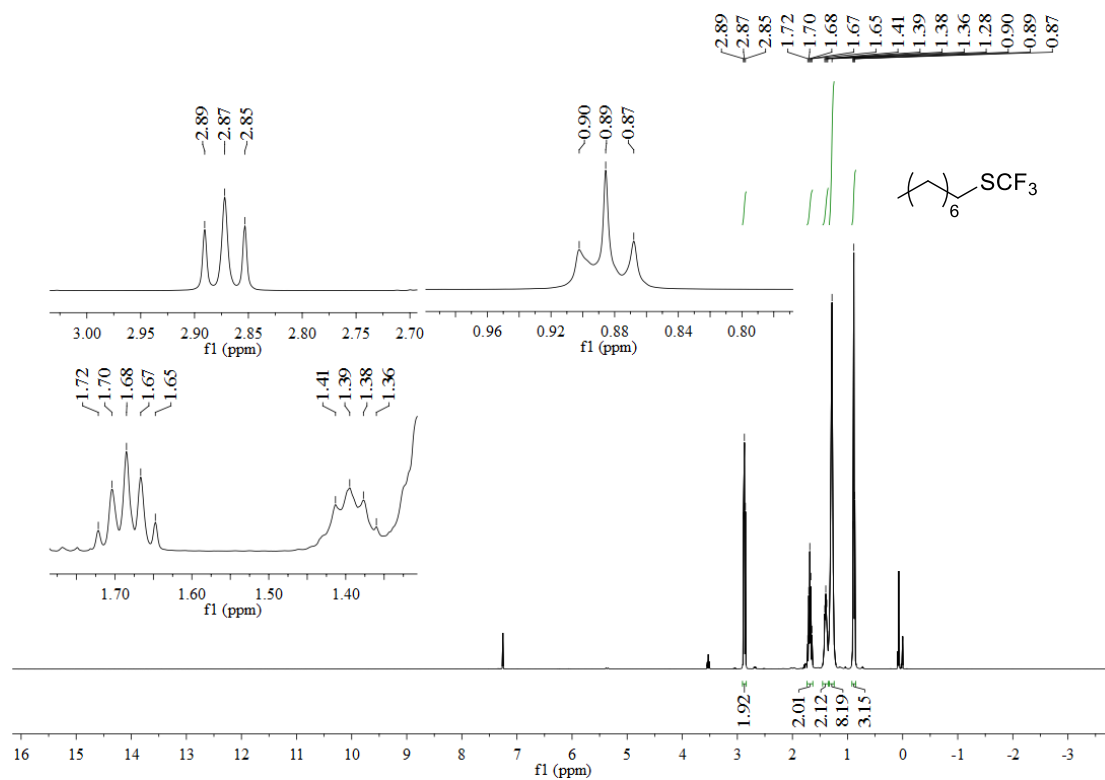
^{19}F NMR spectrum of **3g** (376 MHz, CDCl_3)



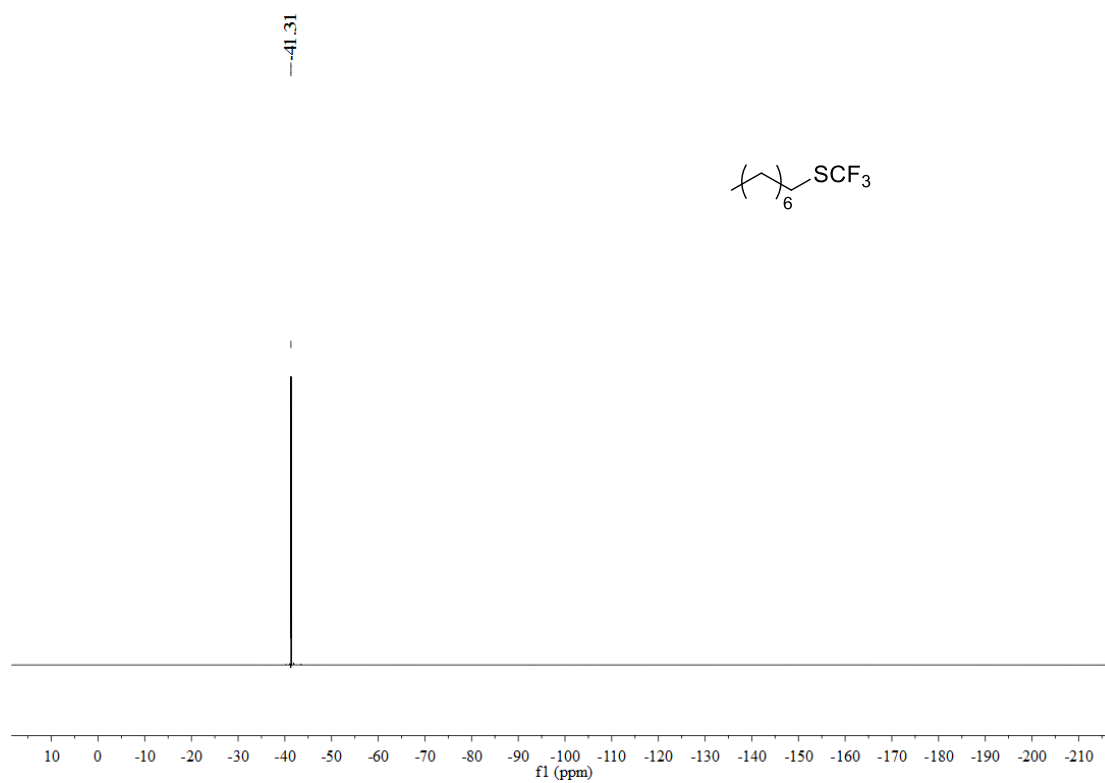
^{13}C NMR spectrum of **3g** (101 MHz, CDCl_3)



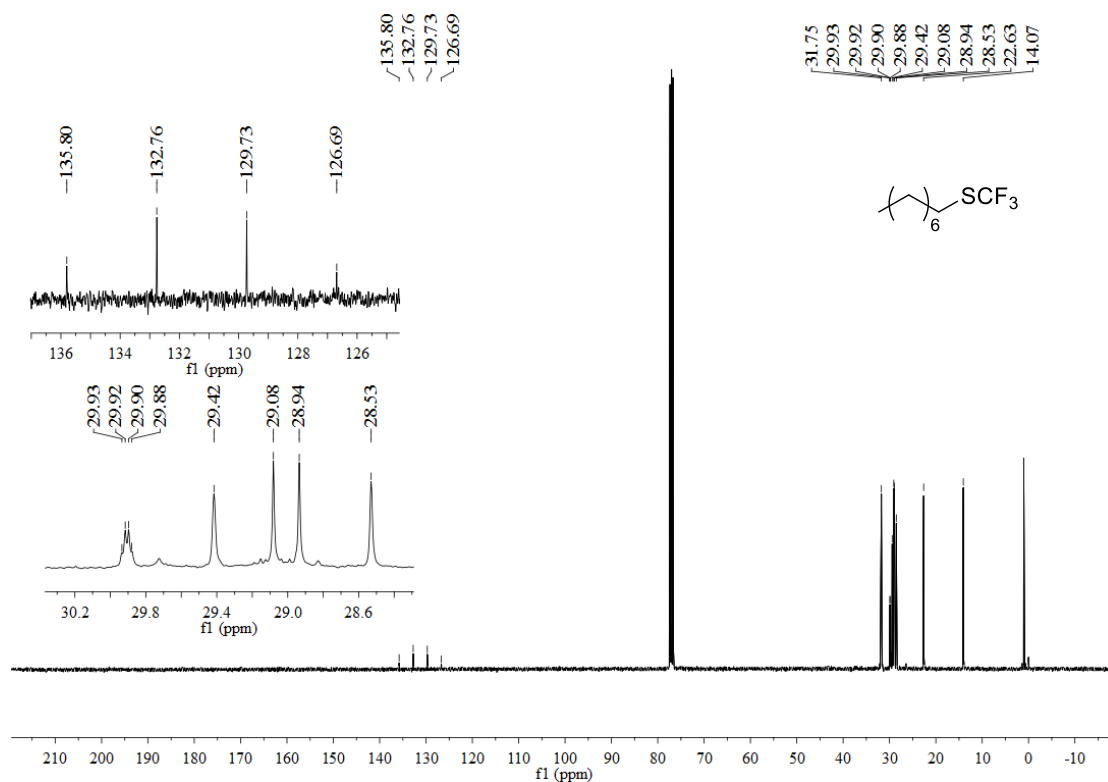
^1H NMR spectrum of **3h** (400 MHz, CDCl_3)



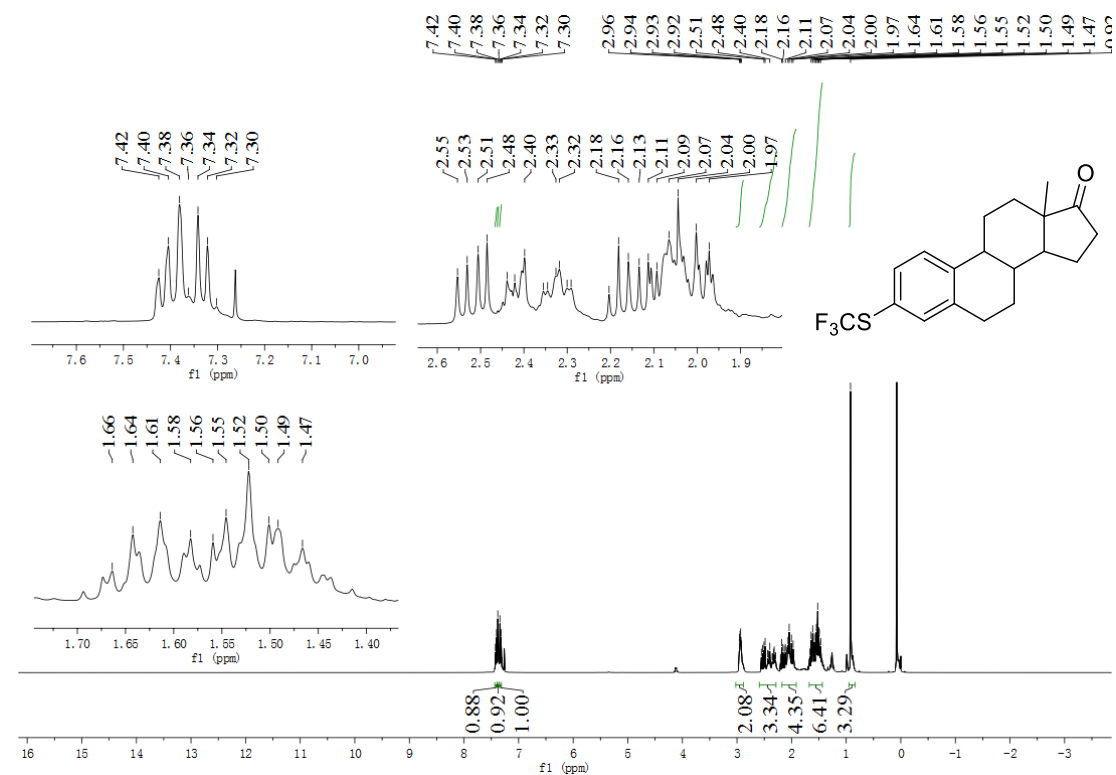
^{19}F NMR spectrum of **3h** (376 MHz, CDCl_3)



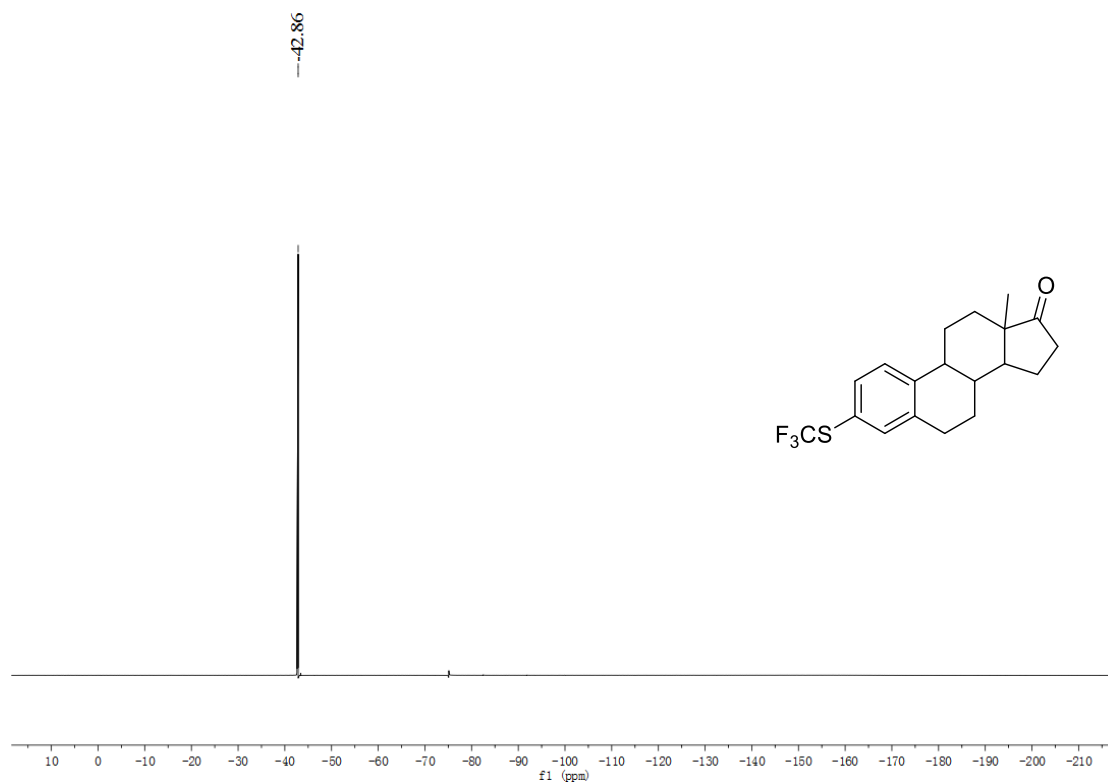
^{13}C NMR spectrum of **3h** (101 MHz, CDCl_3)



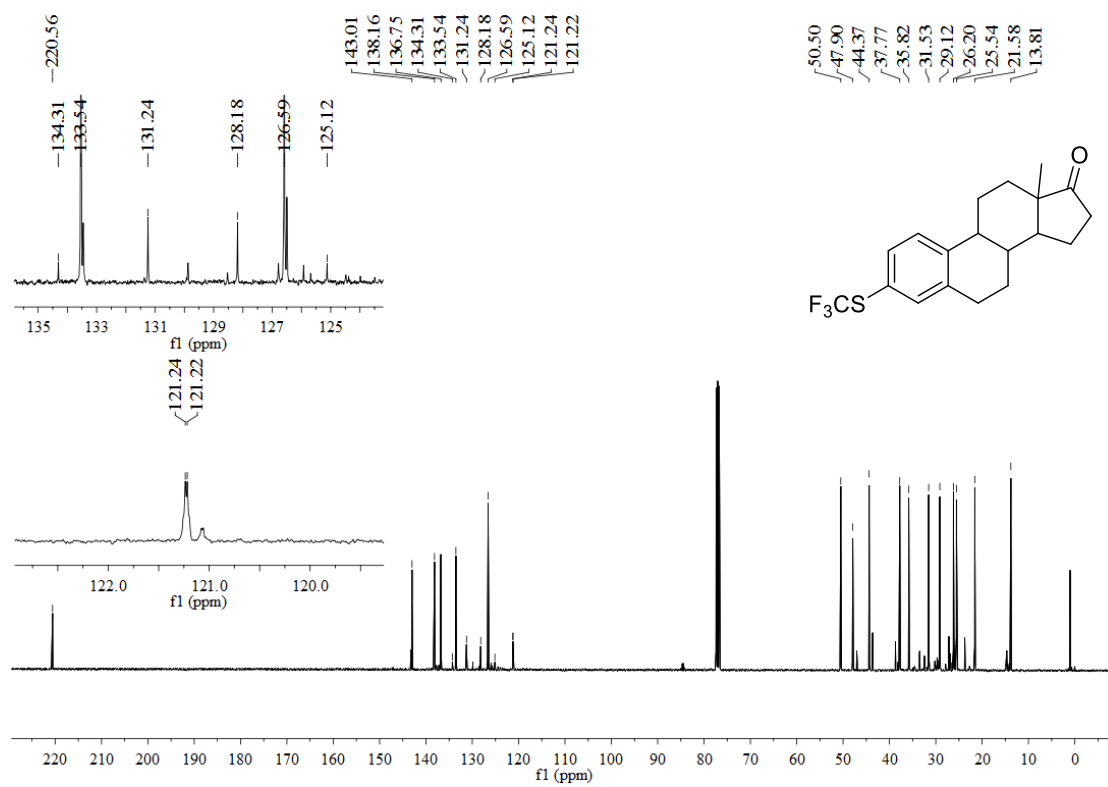
^1H NMR spectrum of **3i** (400 MHz, CDCl_3)



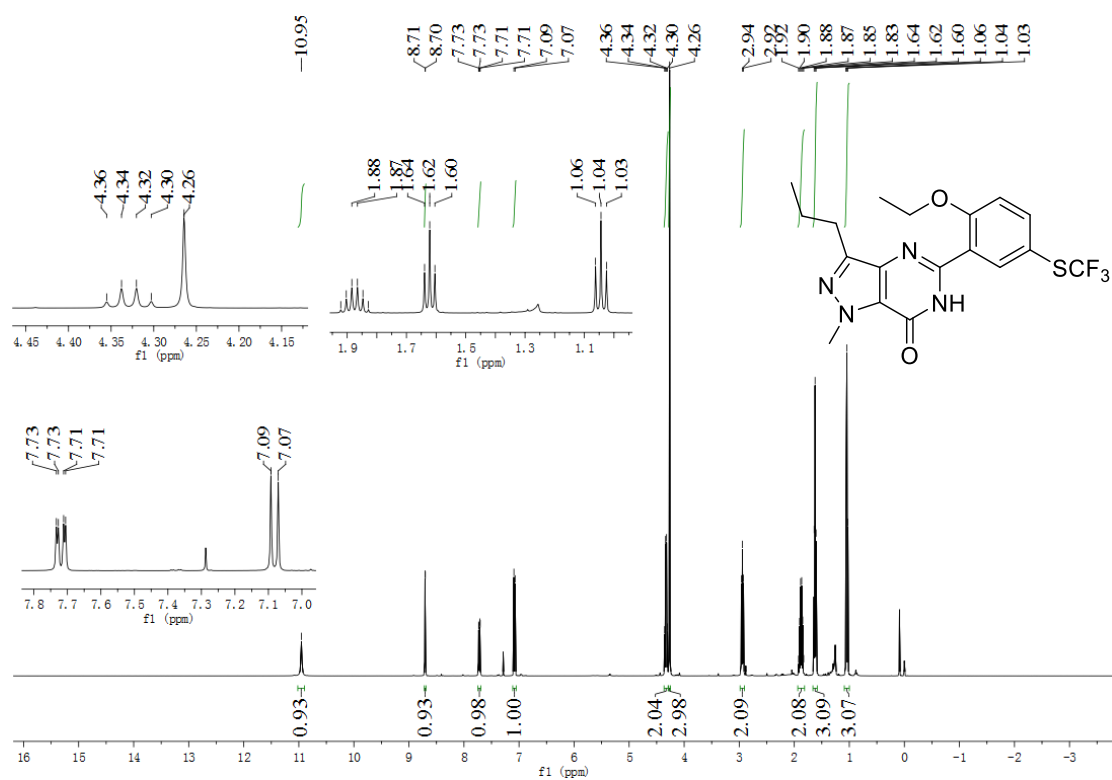
^{19}F NMR spectrum of **3i** (376 MHz, CDCl_3)



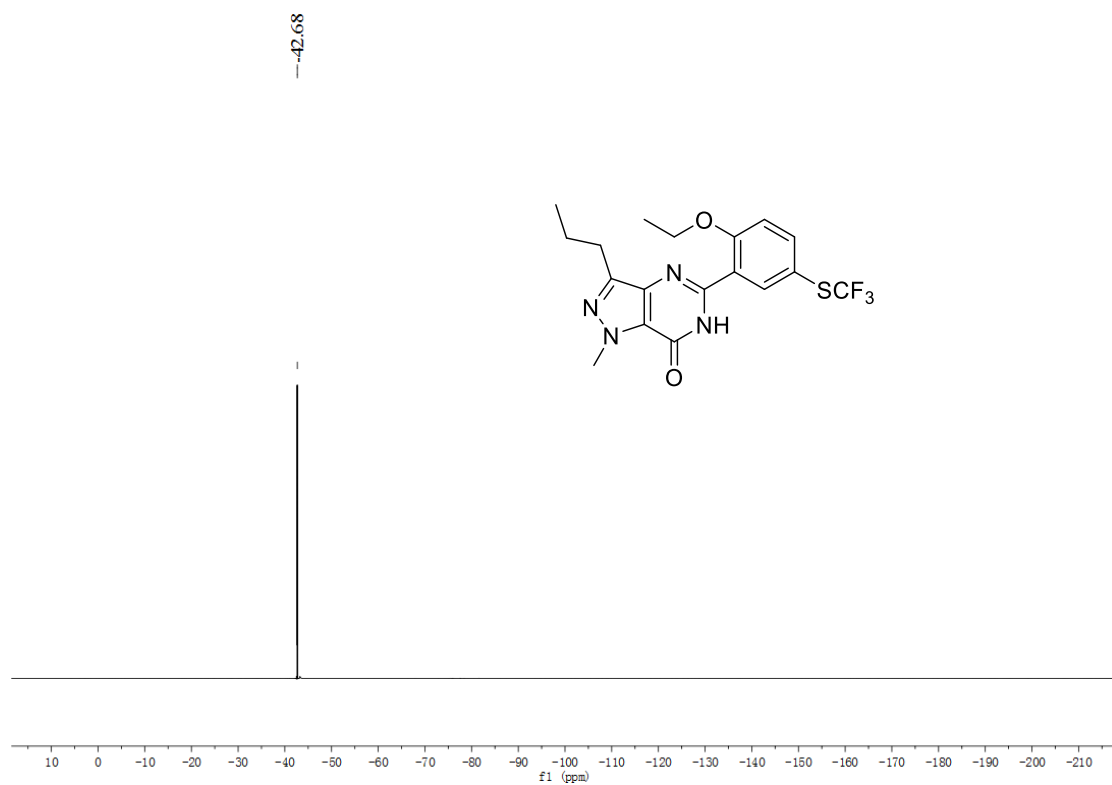
^{13}C NMR spectrum of **3i** (101 MHz, CDCl_3)



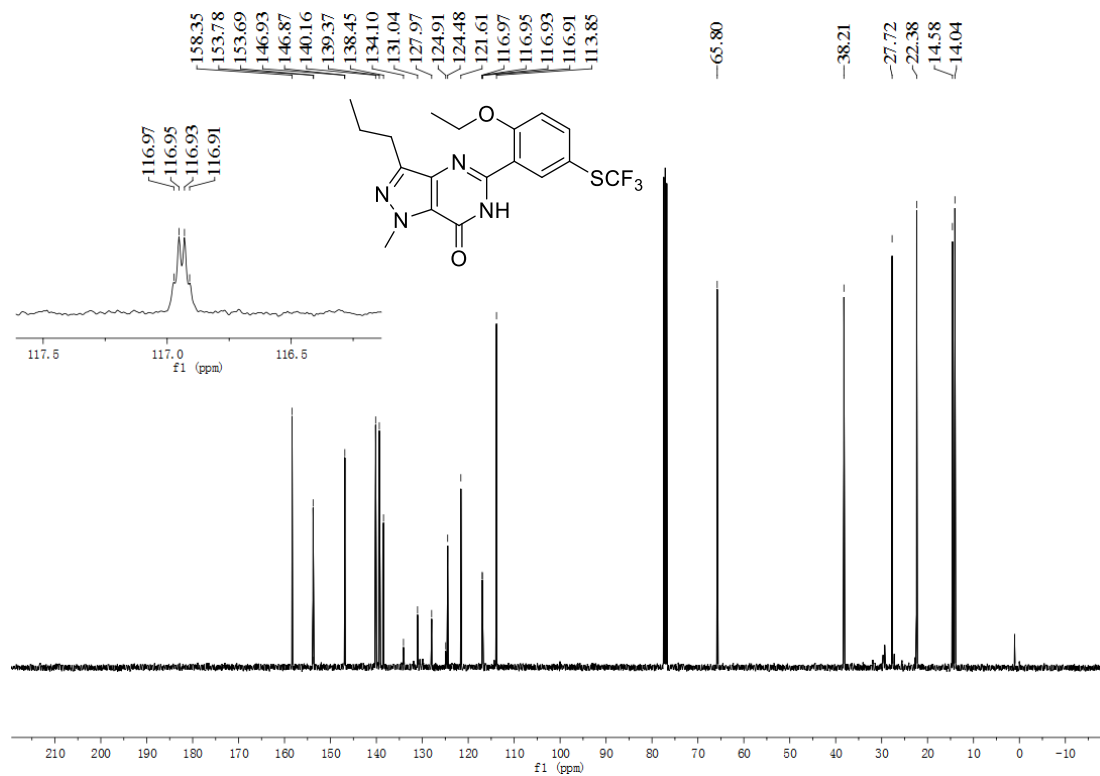
^1H NMR spectrum of **3j** (400 MHz, CDCl_3)



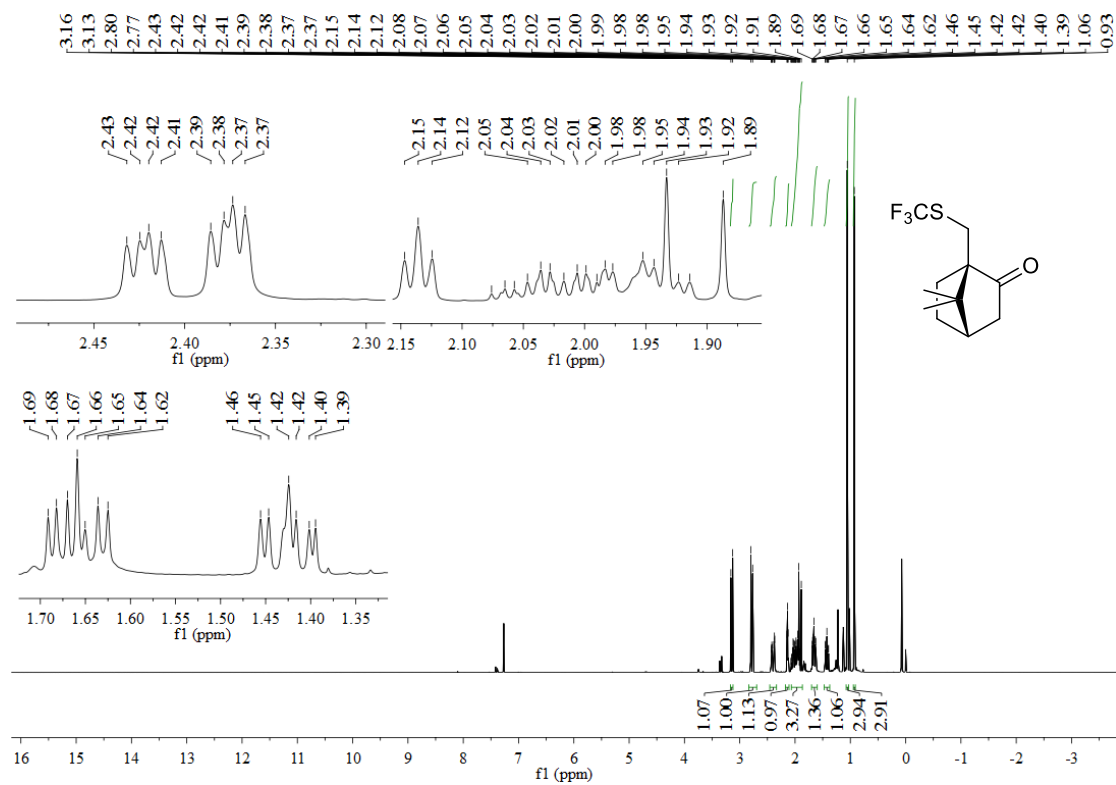
^{19}F NMR spectrum of **3j** (376 MHz, CDCl_3)



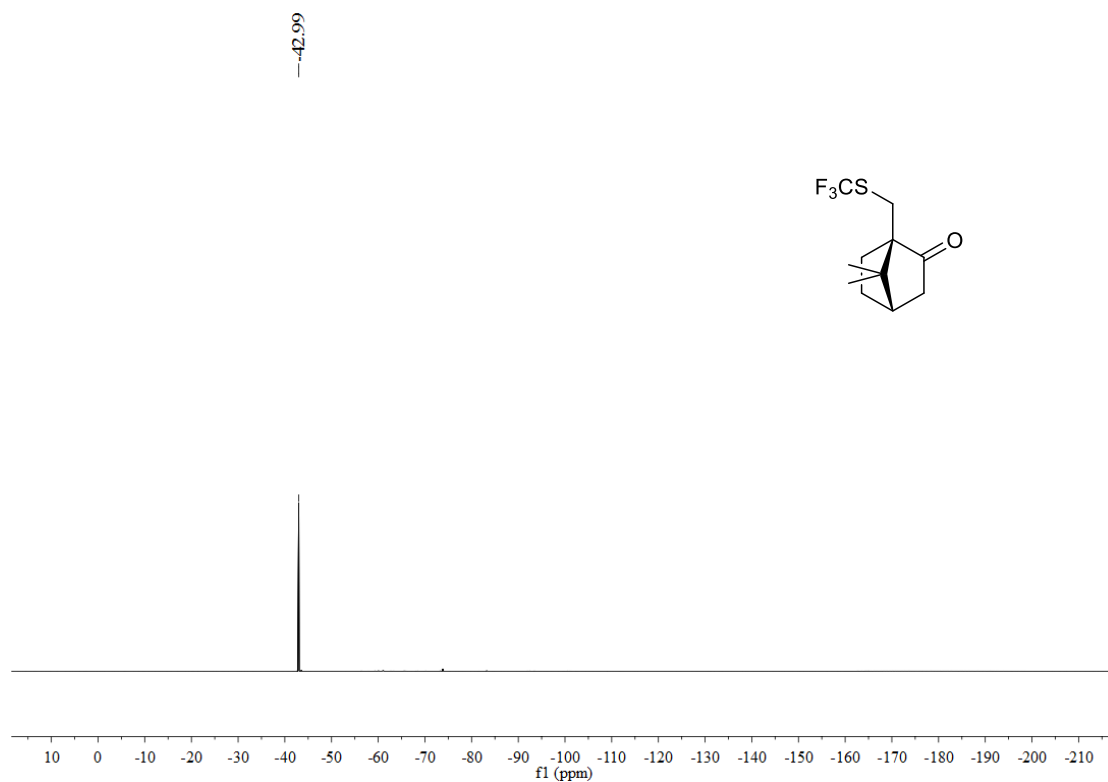
^{13}C NMR spectrum of **3j** (101 MHz, CDCl_3)



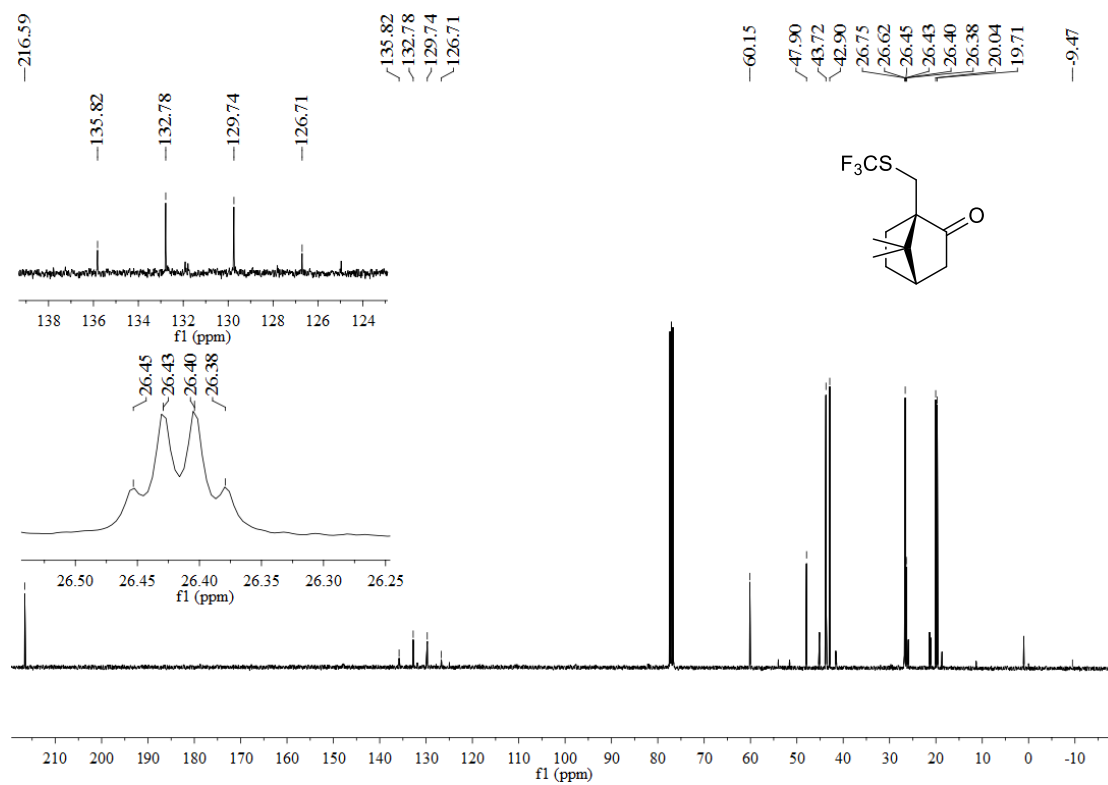
^1H NMR spectrum of **3k** (400 MHz, CDCl_3)



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



^{13}C NMR spectrum of **3k** (101 MHz, CDCl_3)



8. HRMS analysis reports for the new compounds

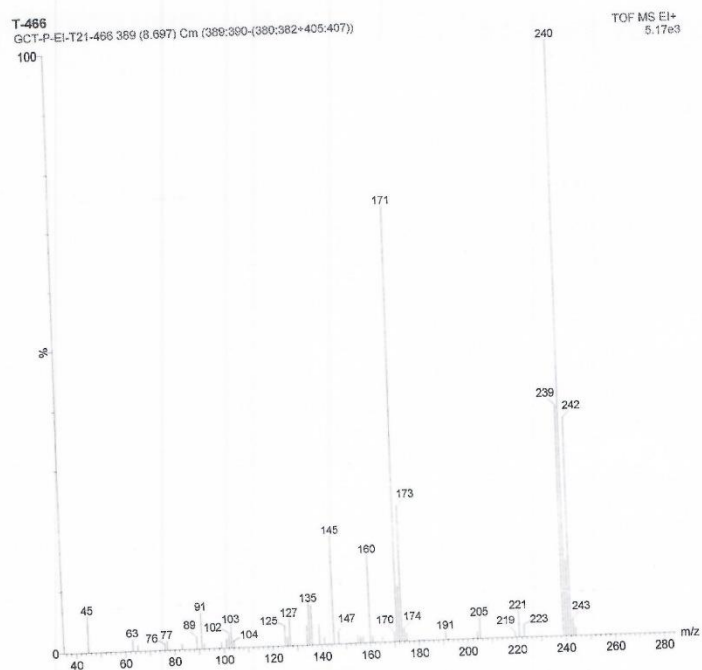
HRMS (EI) spectra of **2s**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution EI-MS Report
Low Resolution EI-MS Report



Instrument: Waters Premier GC-TOF MS
Operation Mode: EI Positive Ion Mode (Electron Energy: 70eV)
Card Serial Number: GCT-P-EI-T21-2738
Sample Serial Number: 2019551-ZK-1
Operator: Li Date: 2021/11/01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
239.9988	239.9988	0.00	12.0	C ₁₂ H ₄ O ₂ N ₂ S
239.9984	239.9984	1.66	8.0	C ₁₁ H ₆ O ₃ ClF
239.9982	239.9982	2.56	4.0	C ₉ H ₈ ClF ₃ S
239.9995	239.9995	-2.72	21.0	C ₂₀
239.9995	239.9995	-3.10	4.0	C ₈ H ₇ O ₄ ClF ₂



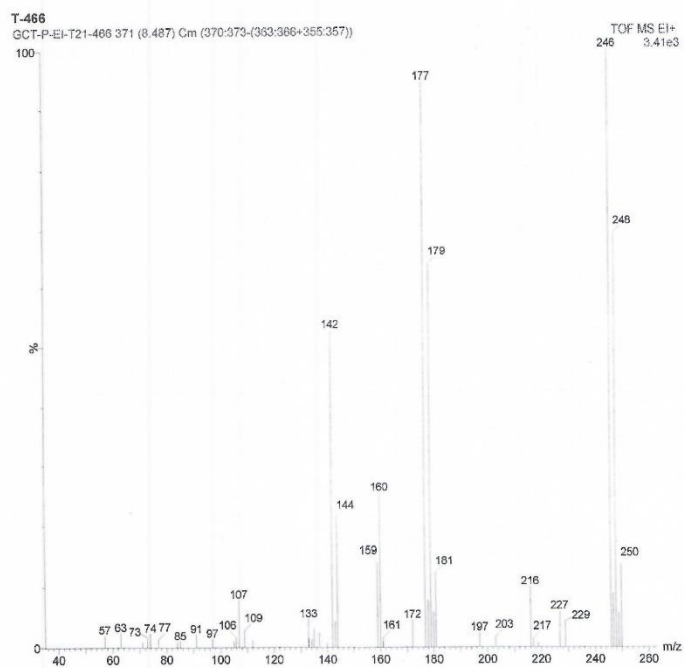
HRMS (EI) spectra of **2t**

National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution EI-MS Report
 Low Resolution EI-MS Report



Instrument: Waters Premier GC-TOF MS
 Operation Mode: EI Positive Ion Mode (Electron Energy: 70eV)
 Card Serial Number: GCT-P-EI-T21-2739
 Sample Serial Number: 2019551-ZK-2
 Operator: Li Date: 2021/11/01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
245.9283	245.9281	0.70	8.0	C ₉ H ₃ O ₃ Cl ₂ F
	245.9279	1.58	4.0	C ₇ H ₃ Cl ₂ F ₃ S
	245.9293	-3.95	4.0	C ₆ H ₂ O ₄ Cl ₂ F ₂

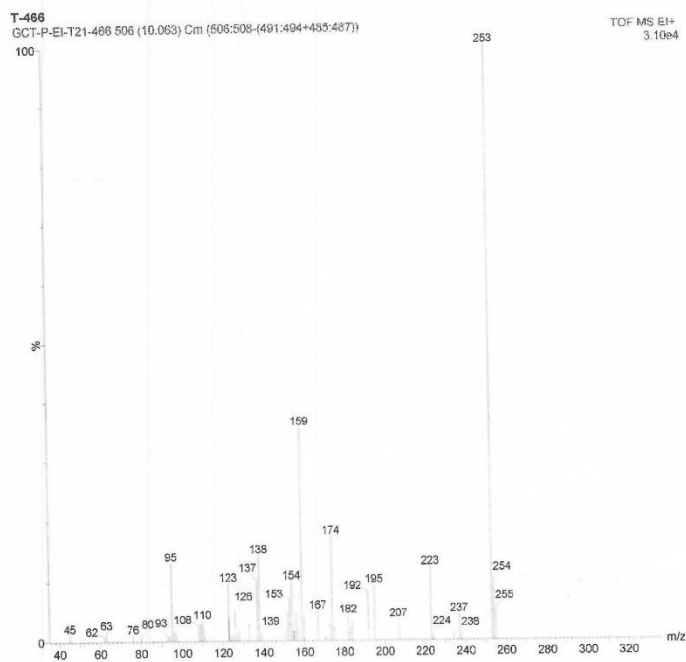


National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution EI-MS Report
 Low Resolution EI-MS Report



Instrument: Waters Premier GC-TOF MS
 Operation Mode: EI Positive Ion Mode (Electron Energy: 70eV)
 Card Serial Number: GCT-P-EI-T21-2740
 Sample Serial Number: 2019551-ZK-3
 Operator: Li Date: 2021/11/01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
253.0012	253.0011	0.55	8.5	C ₁₀ H ₆ O ₄ N ₂ Cl
	253.0015	-1.19	5.0	C ₈ H ₆ O ₃ NF ₃ S
	253.0015	-1.31	3.5	C ₁₀ H ₁₂ Cl ₂ F ₃ S
	253.0008	1.41	4.5	C ₈ H ₈ ON ₂ ClF ₂ S
	253.0008	1.54	14.5	C ₁₄ N ₂ F ₃



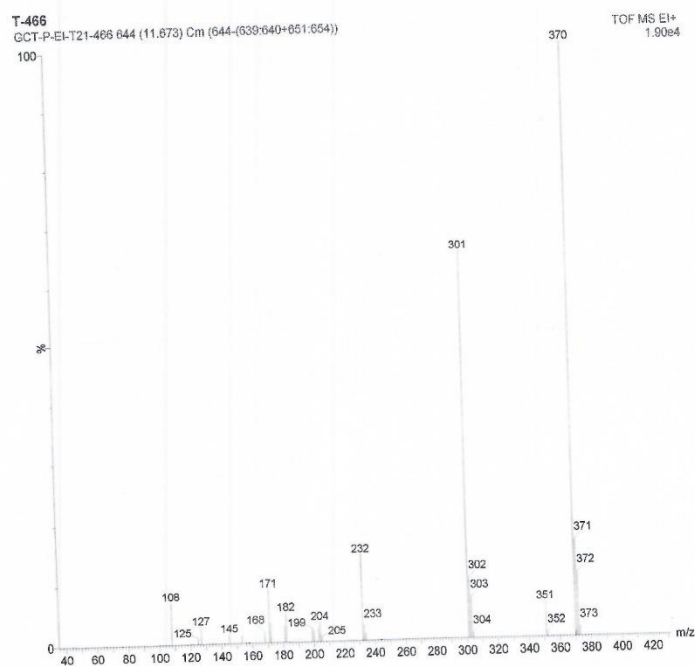
HRMS (EI) spectra of **3e**

National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution EI-MS Report
 Low Resolution EI-MS Report



Instrument: Waters Premier GC-TOF MS
 Operation Mode: EI Positive Ion Mode (Electron Energy: 70eV)
 Card Serial Number: GCT-P-EI-T21-2741
 Sample Serial Number: 2019551-ZK-4
 Operator: Li Date: 2021/11/01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
369.9912	369.9911	0.40	21.5	C ₂₂ O N F ₄
	369.9915	-0.88	8.0	C ₁₄ H ₈ O F ₆ S ₂
	369.9917	-1.31	19.0	C ₂₂ H ₇ O F S ₂
	369.9917	-1.47	12.0	C ₁₆ H ₆ O ₄ F ₄ S
	369.9906	1.62	16.0	C ₁₉ H ₅ O ₃ F ₃ S

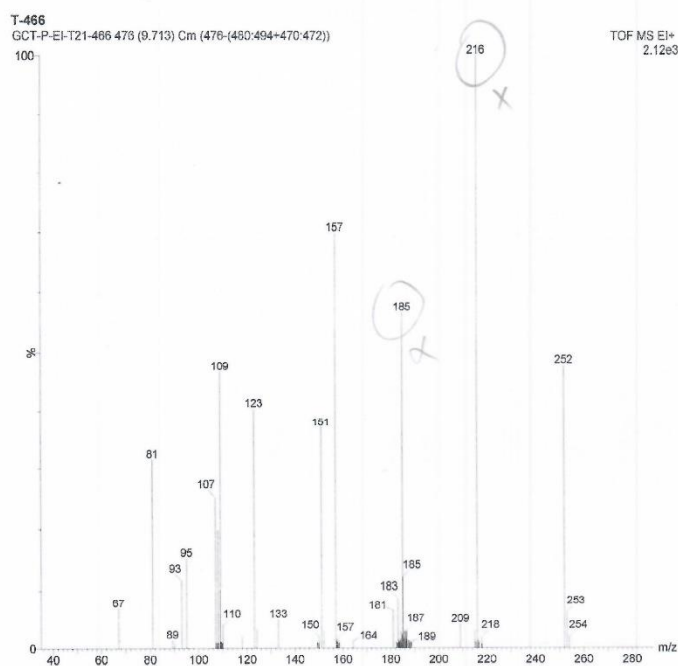


National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution EI-MS Report
 Low Resolution EI-MS Report



Instrument:	Waters Premier GC-TOF MS		
Operation Mode:	EI Positive Ion Mode	(Electron Energy: 70eV)	
Card Serial Number:	GCT-P-EI-T21-2743		
Sample Serial Number:	2019551-ZK-6		
Operator:	Li	Date:	2021/11/01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
252.0794	252.0795	-0.45	-10.0	H ₂₀ O ₄ N ₂ F ₄ S ₂
	252.0792	0.64	7.0	C ₁₃ H ₁₃ O ₄ F
	252.0791	1.27	-4.0	C ₅ H ₁₄ O ₄ F ₆
	252.0790	1.50	3.0	C ₁₁ H ₁₅ O ₄ F ₃ S
	252.0802	-3.03	-1.0	C ₈ H ₁₆ O ₂ F ₄ S



9. References

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