Supplementary Information (SI) for ChemComm.

Electronic Supplementary Information

Transition metal/photocatalyst-free skeletal editing of indene with iodonium difluorodiazo reagent to access 2-(difluoromethyl)naphthalene

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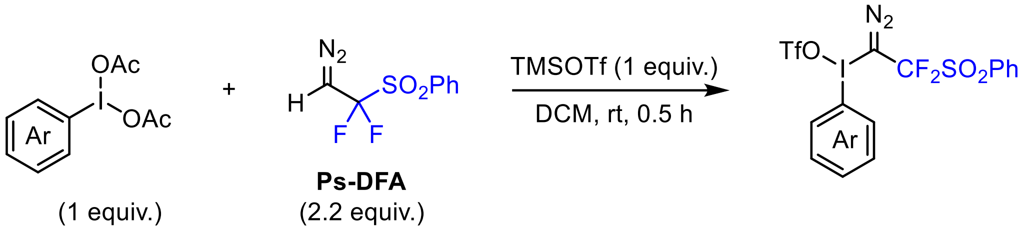
Contents

General Information

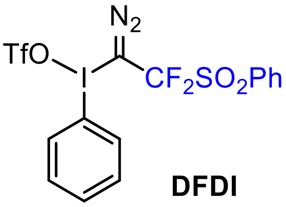
General Analytical Information. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV 500 MHz instrument at 500 MHz (^{1}H NMR), 126 MHz (^{13}C NMR), and 471 MHz (^{19}F NMR, comp. pulse decoupling), or on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR, comp. pulse decoupling). All ^{1}H NMR spectra were measured in parts per million (ppm) downfield from tetramethylsilane (TMS, 0 ppm), or were measured relative to the residual proton signals of d_1-chloroform ($CDCl_3$, 7.26 ppm) or methanol-d_4 (CD_3OD-d_4, 3.31 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual carbon signals of $CDCl_3$ (77.16 ppm) or CD_3OD-d_4 (49.00 ppm) and were obtained with ^{1}H decoupling. All ^{19}F NMR spectra were measured in parts per million (ppm) relative to trichlorofluoromethane ($CFCl_3$, 0 ppm). Coupling constants (*J*) are reported in hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker micrOTOF-QII instrument. Fourier-transform infrared (FT-IR) spectra were collected by using a ThermoFisher Nicolet iS5 instrument. GC-MS analyses were performed on a Shimadzu QP-2010 SE instrument. X-ray structural analysis was conducted on a Bruker APEX-II CCD instrument.

General Reagent Information. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 (DCM) was distilled from calcium hydride. All purchased reagents were used without further purification. Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254 nm. Flash chromatography for purification of compounds were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.). $PhSO_2CF_2CHN_2$ was prepared according to the known procedures[1]. (**Cautions**: $PhSO_2CF_2CHN_2$ are potentially explosive compound! It should be handled with care when synthesizing it or transferring it into the reaction tubes.) Most of the indenes used in this study were purchased from commercial suppliers and used without further purification or were synthesized by ourselves from the reported literature[2,3].

General procedures for the synthesis of hypervalent iodine(III) reagents



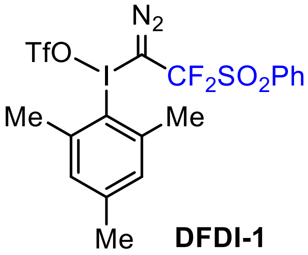
According to the procedures reported previously[4].A solution of phenyliodoso diacetate (5 mmol, 1.0 equiv) in dichloromethane (20 mL, 0.5 M) was treated with trimethylsilyl trifluoromethanesulfonate (0.9 mL, 5 mmol, 1.0 equiv) in one-pot at room temperature under Ar atmosphere. Then the ((2-diazo-1,1-difluoroethyl) sulfonyl) benzene (**Ps-DFA**) (2.55 g, 11 mmol, 2.2 equiv) was added dropwise during 10 minutes. The resulting reaction mixture was stirred at room temperature for 0.5 hours. Solvent was removed under vacuum and the crude was recrystallized from a mixture of diethyl ether/dichloromethane (5/1) during 12 hours at -20 °C. The desired product was collected by filtration washed, with cold diethyl ether, dried under high vacuum and stored a -20 °C.



DFDI

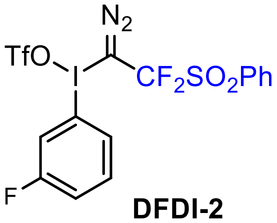
(1-diazo-2,2-difluoro-2-(phenylsulfonyl)ethyl)(phenyl)-iodaneyltrifluoromethanesulfonate (DFDI): orange solid; 2.01 g, 69% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.65 (dt, *J* = 19.9, 7.7 Hz, 3H), 7.50 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.46, 135.39, 133.35, 132.12, 131.23, 130.92, 129.95, 119.73 (q, *J* = 319.0 Hz), 118.72 (t, *J* = 295.9 Hz), 118.50, 29.47 (t, *J* = 42.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$)

δ -78.30, -93.48. **FT-IR (KBr, film):** 3087, 3053, 2110, 1583, 1468, 1360, 1284, 1170, 1018, 806, 737, 636, 588, 514, 451 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{15}H_{11}N_2O_5F_5S_2I^+$ 584.9074; Found 584.9070.



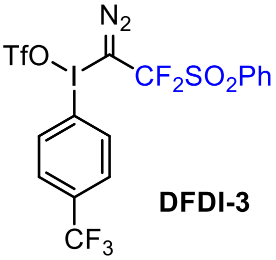
DFDI-1

(1-diazo-2,2-difluoro-2-(phenylsulfonyl)ethyl)(mesityl)-iodaneyl trifluoromethanesulfonate (DFDI-1): orange solid; 2.17 g, 72% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.79 (q, *J* = 6.6 Hz, 1H), 7.62 (q, *J* = 6.4 Hz, 2H), 7.08 (d, *J* = 4.4 Hz, 2H), 2.65 (s, 6H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.85, 142.33, 136.43, 131.20, 130.81, 130.34, 129.95, 125.57, 119.83 (q, *J* = 319.5 Hz), 118.76 (t, *J* = 295.6 Hz), 28.09 (t, *J* = 43.7 Hz), 26.79, 21.27. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.33, -93.94. **FT-IR (KBr, film):** 3083, 2921, 2110, 1583, 1449, 1352, 1249, 1166, 1051, 852, 755, 660, 584, 819, 443 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{17}N_2O_5F_5S_2I^+$ 626.9530; Found 626.9552.



DFDI-2

(1-diazo-2,2-difluoro-2-(phenylsulfonyl)ethyl)(3-fluorophenyl)-l3-iodaneyl trifluoromethanesulfonate (DFDI-2): orange solid; 2.17 g, 72% yield; **^{1}H NMR** (500 MHz, CD_3OD-*d_4*) δ 8.11 (d, *J* = 6.5 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.66 (dt, *J* = 21.3, 6.9 Hz, 3H), 7.54 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3OD-*d_4*) δ 163.78 (d, *J* = 254.8 Hz), 137.84, 134.59 (d, *J* = 7.8 Hz), 132.58 (d, *J* = 3.4 Hz), 132.44, 131.74, 131.16, 123.63 (d, *J* = 25.8 Hz), 121.98 (d, *J* = 21.3 Hz), 121.74 (q, *J* = 318.7 Hz), 120.27 (t, *J* = 293.0 Hz), 118.34 (d, *J* = 7.9 Hz), 32.67 (t, *J* = 43.2 Hz). **^{19}F NMR** (471 MHz, CD_3OD-*d*$_4$) δ -79.97, -93.95, -107.42 (q, *J* = 7.2 Hz). **FT-IR (KBr, film):** 3088, 3069, 2111, 1589, 1469, 1359, 1279, 1211, 1020, 838, 782, 727, 636, 588, 515, 438 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{15}H_9N_2O_5F_6NaS_2I^+$ 624.8786; Found 624.8795.

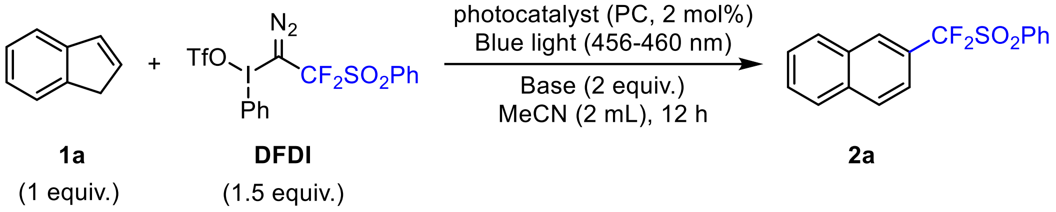


DFDI-3

(1-diazo-2,2-difluoro-2-(phenylsulfonyl)ethyl)(4-(trifluoromethyl)phenyl)-iodaneyl trifluoromethanesulfonate (DFDI-3): orange solid; 2.70 g, 83% yield; **^{1}H NMR** (500 MHz, CD_3OD-*d*$_4$) δ 8.43 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, CD_3OD-*d*$_4$) δ 137.79, 137.19, 135.73 (q, *J* = 33.3 Hz), 132.44, 131.77, 131.15, 129.77 (q, *J* = 3.7 Hz), 124.62 (q, *J* = 272.3 Hz), 123.07, 121.75 (q, *J* = 318.6 Hz), 120.22 (t, *J* = 293.4 Hz). **^{19}F NMR** (471 MHz, CD_3OD-*d*$_4$) δ -64.64, -79.97, -93.93. **FT-IR (KBr, film):** 3103, 2120, 1592, 1400, 1351, 1240, 1173, 1025, 832, 722, 636, 589, 516, 494 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{16}H_{10}N_2O_5F_8S_2I^+$ 652.8948; Found 652.8942.

Optimization of the reaction conditions

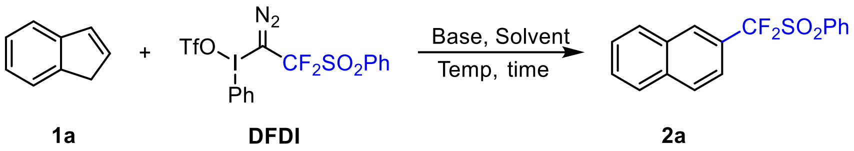
a) Optimization of conditions under light conditions and control experiments



Entry	PC	Base	Yield (%)
1	$Ru(bpz)_3(PF_6)_2$	Na_2CO_3	66
2	$Ru(dtbbpy)_3(PF_6)_2$	Na_2CO_3	61
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)\ PF_6$	Na_2CO_3	38
4	$Ir[dFppy]_2(dtbbpy)PF_6$	Na_2CO_3	55
5	4CzIPN	Na_2CO_3	65
6	Ph_3N	/	tr
7	/	Na_2CO_3	50
8[b]	/	Na_2CO_3	58

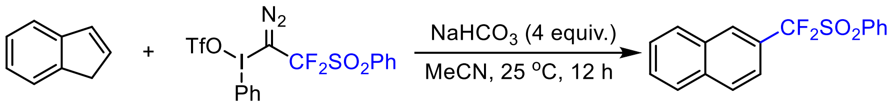
[a] Reaction conditions: **DFDI** (0.15 mmol), **1** (0.1 mmol), PC (2 mol %) and base (0.2 mmol) in MeCN (2 mL), irradiation with blue LEDs (456-460 nm, 30 W) under an Ar atmosphere at room temperature for 12 h. [b] no blue light

b) Optimization of conditions without light



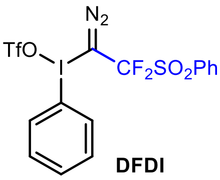
Entry	DFDI:1a (equiv.)	Temp (ºC)	Base (equiv.)	Solvent (2 mL)	Time (h)	Yield (%)
1	1.5:1	0	Na_2CO_3 (2)	MeCN	12	NR
2	1.5:1	25	Na_2CO_3 (2)	MeCN	6	45
3	1.5:1	25	Na_2CO_3 (2)	MeCN	12	58
4	1.5:1	25	Na_2CO_3 (2)	MeCN	24	56
5	1.5:1	50	Na_2CO_3 (2)	MeCN	12	54
6	1.5:1	25	Na_2CO_3 (2)	DCM	12	46
7	1.5:1	25	Na_2CO_3 (2)	Toluene	12	tr
8	1.5:1	25	Na_2CO_3 (2)	n-Hexane	12	NR
9	1.5:1	25	Na_2CO_3 (2)	THF	12	29
10	1.5:1	25	Na_2CO_3 (2)	DMF	12	NR
11	1.5:1	25	Na_2CO_3 (2)	EA	12	39
12	1.5:1	25	Na_2CO_3 (2)	acetone	12	35
13	1.5:1	25	Na_2CO_3 (2)	DCE	12	40
14	1.5:1	25	Cs_2CO_3 (2)	MeCN	12	tr
15	1.5:1	25	K_2CO_3 (2)	MeCN	12	62
16	1.5:1	25	NaOAc (2)	MeCN	12	44
17	1.5:1	25	$NaHCO_3$ (2)	MeCN	12	70

18	1.5:1	25	Et_3N (2)	MeCN	12	tr
19	1.5:1	25	DABCO (2)	MeCN	12	tr
20	1.5:1	25	DBU (2)	MeCN	12	24
21	1.2:1	25	$NaHCO_3$ (2)	MeCN	12	55
22	2:1	25	$NaHCO_3$ (2)	MeCN	12	77
23	2:1	25	$NaHCO_3$ (3)	MeCN	12	92
24	2:1	25	$NaHCO_3$ (4)	MeCN	12	95
25	1.5:1	25	$NaHCO_3$ (4)	MeCN	12	74
26	2:1	25	Na_2CO_3 (4)	MeCN	12	85
27	2:1	25	K_2CO_3 (4)	MeCN	12	74
28	2:1	25	NaOAc (4)	MeCN	12	68
29	2:1	25	DBU (4)	MeCN	12	tr
30	2:1	25	Et_3N(4)	MeCN	12	tr
31	2:1	25	none	MeCN	12	32
32	2:1	25	$NaHCO_3$ (4)	THF	12	31
33	2:1	25	$NaHCO_3$ (4)	DCM	12	55

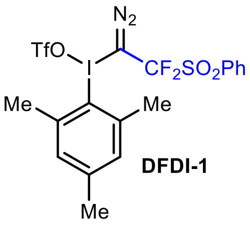


1a (1 equiv.) **DFDI** (2 equiv.) **2a**

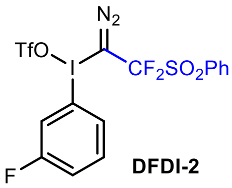
Entry	Variation from the standard conditions	Yield (%)
1	as above	95
2	**DFDI-1** was used	85
3	**DFDI-2** was used	90
4	**DFDI-3** was used	84
5	**Ps-DFA** was used	NR
6	**DDFS** was used	NR



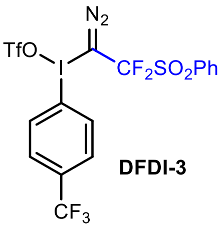
DFDI



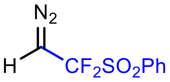
DFDI-1



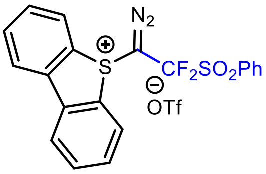
DFDI-2



DFDI-3

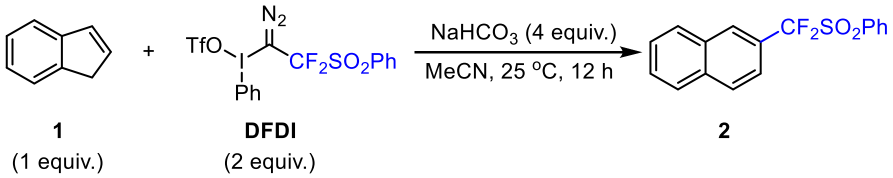


Ps-DFA

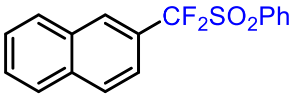


DDFS

General procedure for the reaction of hypervalent iodine reagents with indene

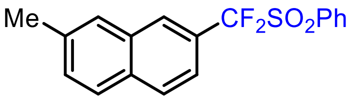


An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.) and $NaHCO_3$ (33.6 mg, 0.4 mmol, 4 equiv.) under Ar atmosphere. Then indene **1** (0.1 mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 °C for 12 hours. The solution mixture was extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product **2**.



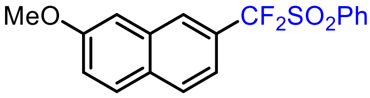
2a

2-(difluoro(phenylsulfonyl)methyl)naphthalene (2a): white solid; 30.2 mg, 95% yield; **M.p.**: 183-184 °C; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.94 (dt, *J* = 14.5, 8.5 Hz, 3H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.56 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.41, 135.02, 132.95, 132.30, 131.05, 129.41, 129.22 (t, *J* = 6.7 Hz), 129.13, 128.69, 128.52, 127.98, 127.22, 123.92 (t, *J* = 22.1 Hz), 123.39 (t, *J* = 5.3 Hz), 122.19 (t, *J* = 286.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.39. **FT-IR (KBr, film):** 3062, 1599, 1581, 1448, 1338, 1288, 1169, 1116, 1063, 758, 720, 686 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{12}O_2F_2NaS^+$ 341.0424; Found 341.0428.



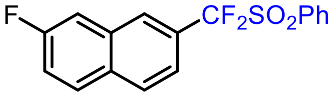
2b

2-(difluoro(phenylsulfonyl)methyl)-7-methylnaphthalene (2b): white solid; 24.2 mg, 73% yield; **M.p.**: 196-198 °C; R*f*=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.70 (s, 1H), 7.66 – 7.57 (m, 3H), 7.46 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.10, 135.37, 133.33, 133.05, 132.57, 131.08, 130.86, 129.40, 128.56 (t, *J* = 6.7 Hz), 128.37, 128.04, 127.76, 123.89 (t, *J* = 21.9 Hz), 122.54 (t, *J* = 5.5 Hz), 122.28 (t, *J* = 286.5 Hz), 21.85. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.38. **FT-IR (KBr, film):** 3060, 2920, 2850, 1582, 1448, 1337, 1280, 1164, 1063, 844, 717, 684 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{14}O_2F_2NaS^+$ 355.0580; Found 355.0583.



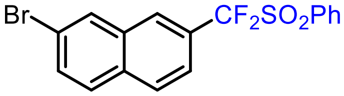
2c

2-(difluoro(phenylsulfonyl)methyl)-7-methoxynaphthalene (2c): white solid; 23.3 mg, 67% yield; **M.p.**: 158-159 °C; R*f*=0.7 (petroleum ether/EtOAc = 5:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.28 (dd, *J* = 9.5, 2.9 Hz, 1H), 7.22 (d, *J* = 2.8 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.57, 135.38, 133.68, 133.05, 131.07, 130.64, 129.44, 129.41, 128.37, 127.85 (t, *J* = 6.6 Hz), 124.38 (t, *J* = 21.9 Hz), 122.30 (t, *J* = 286.5 Hz), 121.63, 121.27 (t, *J* = 5.5 Hz), 106.69, 55.56. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.17. **FT-IR (KBr, film):** 3010, 2962, 2918, 1608, 1580, 1446, 1345, 1238, 1170, 1062, 846, 735 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{14}O_3F_2NaS^+$ 371.0529; Found 371.0533.



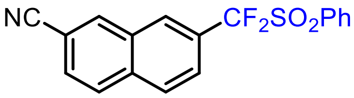
2d

2-(difluoro(phenylsulfonyl)methyl)-7-fluoronaphthalene (2d): white solid; 23.2 mg, 69% yield; **M.p.**: 146-148 ºC; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.91 (dd, *J* = 8.9, 5.7 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.65 (dt, *J* = 15.6, 8.4 Hz, 3H), 7.56 (d, *J* = 9.5 Hz, 1H), 7.41 (td, *J* = 8.7, 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.15 (d, *J* = 248.5 Hz), 135.43, 133.03 (d, *J* = 9.6 Hz), 132.67, 131.90, 130.98, 130.41 (d, *J* = 8.9 Hz), 129.36, 128.60, 128.32 (q, *J* = 6.3 Hz), 125.02 (t, *J* = 21.9 Hz), 122.75 (td, *J* = 5.3, 2.5 Hz), 121.90 (t, *J* = 286.6 Hz), 118.95 (d, *J* = 25.6 Hz), 112.09 (d, *J* = 20.9 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.61, -112.42 (q, *J* = 8.0 Hz). **FT-IR (KBr, film):** 3070, 1610, 1580, 1448, 1342, 1270, 1170, 1115, 1065, 891, 844, 715, 607 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}O_2F_3NaS^+$ 359.0330; Found 359.0329.



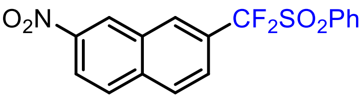
2e

2-bromo-7-(difluoro(phenylsulfonyl)methyl)naphthalene (2e): white solid; 19.4 mg, 49% yield; **M.p.**: 189-190 ºC; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 10.4 Hz, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.79 (dd, *J* = 8.6, 4.0 Hz, 2H), 7.71 (t, *J* = 10.6 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.56, 133.41, 133.36, 132.79, 131.98, 131.11, 129.62, 129.49, 128.72, 128.21 (t, *J* = 6.6 Hz), 125.19 (t, *J* = 22.0 Hz), 123.94 (t, *J* = 5.3 Hz), 121.91 (t, *J* = 286.2 Hz), 121.36. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.69. **FT-IR (KBr, film):** 3056, 1587, 1499, 1447, 1337, 1274, 1163, 1125, 1066, 845, 721, 685, 598 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}O_2F_2NaSBr^+$ 418.9529; Found 418.9523.



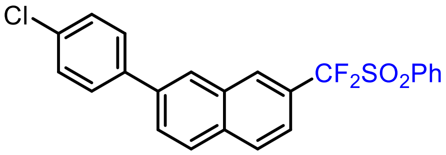
2f

7-(difluoro(phenylsulfonyl)methyl)-2-naphthonitrile (2f): white solid; 18.9 mg, 55% yield; **M.p.**: 204-205 ºC; R*f*=0.4 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.25 (s, 1H), 8.07 – 7.99 (m, 4H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.12, 135.75, 135.16, 132.48, 131.26, 131.13, 129.59 (t, *J* = 6.6 Hz), 129.59, 129.44, 128.96, 128.93, 126.67 (t, *J* = 5.4 Hz), 126.17 (t, *J* = 22.3 Hz), 121.59 (t, *J* = 287.1 Hz), 118.66, 111.06.**^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.94. **FT-IR (KBr, film):** 3074, 2228, 1507, 1450, 1339, 1173, 1116, 1065, 856, 719, 684 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{11}NO_2F_2NaS^+$ 366.0376; Found 366.0377.



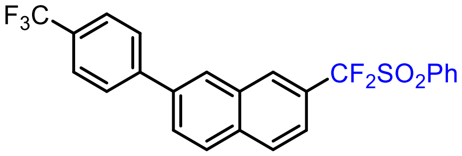
2g

2-(difluoro(phenylsulfonyl)methyl)-7-nitronaphthalene (2g): white solid; 14.5 mg, 40% yield; **M.p.**: 186-188 ºC; R*f*=0.3 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.39 (d, *J* = 5.8 Hz, 2H), 8.12 – 8.04 (m, 4H), 7.97 – 7.91 (m, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.44, 137.26, 135.79, 132.48, 131.14, 131.09, 131.03 (t, *J* = 6.4 Hz), 129.86, 129.61, 128.90, 127.31 (t, *J* = 5.3 Hz), 126.52 (t, *J* = 22.6 Hz), 125.63, 121.88, 121.55 (t, *J* = 286.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -102.00. **FT-IR (KBr, film):** 3085, 1581, 1530, 1347, 1334, 1172, 1126, 1067, 852, 719, 683 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}NO_4F_2NaS^+$ 386.0275; Found 386.0266.



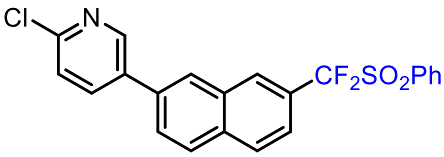
2h

2-(4-chlorophenyl)-7-(difluoro(phenylsulfonyl)methyl)naphthalene (2h): white solid; 38.5 mg, 90% yield; **M.p.**: 153-155 °C; R$_f$=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.25 (s, 1H), 8.09 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.87 – 7.81 (m, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.64 (p, *J* = 3.6 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 138.93, 138.73, 135.47, 134.22, 134.10, 132.92, 132.56, 131.08, 129.45, 129.45 (d, *J* = 6.2 Hz), 129.30, 128.78, 128.70, 128.48, 127.91, 126.81, 124.58 (t, *J* = 21.5 Hz), 123.66 (t, *J* = 5.4 Hz), 122.13 (d, *J* = 286.2 Hz). **^{19}F NMR** (471 MHz, CDCl$_3$) δ -101.47. **FT-IR (KBr, film):** 3060, 1583, 1448, 1339, 1171, 1092, 828, 719, 687 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{23}H_{15}O_2F_2NaSCl^+$ 451.0347; Found 451.0341.



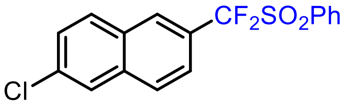
2i

2-(difluoro(phenylsulfonyl)methyl)-7-(4-(trifluoromethyl)phenyl)naphthalene (2i): white solid; 41.1 mg, 89% yield; **M.p.**: 144-146 °C; R$_f$=0.6 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.28 (s, 1H), 8.15 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 2H), 8.00 (t, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.78 (ddd, *J* = 21.2, 14.9, 7.9 Hz, 6H), 7.64 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 144.01, 138.47, 135.51, 134.49, 132.89, 132.51, 131.09, 129.95 (q, *J* = 32.5 Hz), 129.58 (t, *J* = 6.7 Hz), 129.48, 128.88, 128.54, 127.90, 127.85, 127.43, 126.08 (q, *J* = 3.8 Hz), 124.74 (t, *J* = 22.2 Hz), 124.37 (q, *J* = 272.1 Hz), 124.01 (t, *J* = 5.4 Hz), 122.10 (t, *J* = 286.6 Hz). **^{19}F NMR** (471 MHz, CDCl$_3$) δ -62.40, -101.49. **FT-IR (KBr, film):** 3064, 3030, 1606, 1583, 1324, 1195, 1125, 1069, 837, 719, 618, 598 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{24}H_{15}O_2F_5NaS^+$ 485.0611; Found 485.0604.



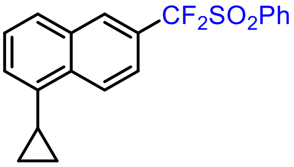
2j

2-chloro-5-(7-(difluoro(phenylsulfonyl)methyl)naphthalen-2-yl)pyridine (2j): white solid; 20.5 mg, 48% yield; **M.p.**: 152-154 °C; R_f=0.5 (petroleum ether/EtOAc = 1:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.2 Hz, 1H), 8.28 (s, 1H), 8.11 (s, 1H), 8.07 – 7.95 (m, 5H), 7.82 – 7.73 (m, 3H), 7.65 (t, *J* = 7.7 Hz, 2H), 7.47 (dd, *J* = 8.1, 2.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.01, 148.34, 137.51, 135.54, 135.26, 135.04, 134.51, 132.83, 132.49, 131.09, 129.51 (t, *J* = 6.6 Hz), 129.49, 129.21, 128.58, 127.40, 127.26, 124.59 (t, *J* = 45.6 Hz), 124.23 (t, *J* = 5.3 Hz), 122.02 (t, *J* = 284.6 Hz).**^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.55. **FT-IR (KBr, film):** 3061, 1582, 1448, 1336, 1170, 1114, 1063, 833, 718, 615 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{15}NO_2F_2SCl^+$ 430.0480; Found 430.0475.



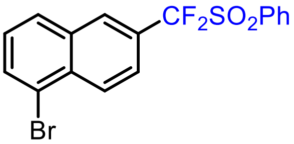
2k

2-chloro-6-(difluoro(phenylsulfonyl)methyl)naphthalene (2k): white solid; 25.0 mg, 71% yield; **M.p.**: 162-163 °C; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.93 – 7.84 (m, 3H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.53 (dd, *J* = 8.6, 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.59, 135.53, 134.56, 132.81, 131.08, 130.68, 130.56, 129.48, 129.09 (t, *J* = 6.7 Hz), 128.32, 127.87, 126.79, 124.60 (t, *J* = 5.4 Hz), 124.34 (t, *J* = 22.1 Hz), 121.97 (t, *J* = 286.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.59. **FT-IR (KBr, film):** 3067, 1581, 1448, 1340, 1280, 1165, 1064, 824, 720 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}O_2F_2NaSCl^+$ 375.0034; Found 375.0034.



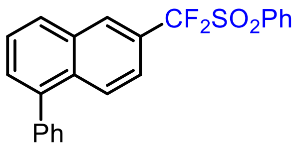
2l

1-cyclopropyl-6-(difluoro(phenylsulfonyl)methyl)naphthalene (2l): white solid; 26.5 mg, 74% yield; **M.p.**: 159-160 ºC; R*f*=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.8 Hz, 1H), 8.18 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 10.3 Hz, 3H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 2.36 (q, *J* = 6.9 Hz, 1H), 1.15 – 1.07 (m, 2H), 0.79 (d, *J* = 5.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.55, 135.40, 135.28, 133.01, 132.51, 131.08, 129.66 (t, *J* = 6.7 Hz), 129.41, 127.65, 126.90, 126.45, 125.40, 123.59 (t, *J* = 22.0 Hz), 123.23 (t, *J* = 5.4 Hz), 122.29 (t, *J* = 286.6 Hz), 13.34, 6.65. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.40. **FT-IR (KBr, film):** 3086, 2920, 1580, 1447, 1336, 1168, 1108, 1065, 794, 716 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{16}O_2F_2NaS^+$ 381.0737; Found 381.0736.



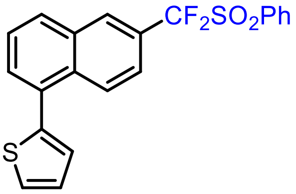
2m

1-bromo-6-(difluoro(phenylsulfonyl)methyl)naphthalene (2m): white solid; 28.5 mg, 72% yield; **M.p.**: 185-186 ºC; R*f*=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 1H), 8.19 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.83 – 7.74 (m, 2H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.57, 133.69, 133.55, 132.75, 132.48, 131.11, 129.56 (t, *J* = 6.5 Hz), 129.50, 129.12, 128.16, 127.65, 125.05 (t, *J* = 22.1 Hz), 124.85 (t, *J* = 5.4 Hz), 122.91, 121.88 (t, *J* = 286.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.69. **FT-IR (KBr, film):** 3059, 1560, 1447, 1338, 1261, 1169, 1112, 1094, 1059, 802, 717, 587 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}O_2F_2NaSBr^+$ 418.9529; Found 418.9527.



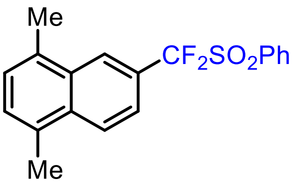
2n

6-(difluoro(phenylsulfonyl)methyl)-1-phenylnaphthalene (2n): white solid; 35.5 mg, 90% yield; **M.p.**: 100-102 ºC; R_f=0.5 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.04 (t, *J* = 9.0 Hz, 3H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 4H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.50 (tq, *J* = 14.7, 7.2 Hz, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.56, 140.03, 135.45, 133.31, 132.92, 132.73, 131.09, 130.14, 129.53 (t, *J* = 6.6 Hz), 129.43, 129.42, 128.80, 128.57, 127.76, 126.99, 126.78, 123.81 (t, *J* = 22.1 Hz), 123.50 (t, *J* = 5.5 Hz), 122.17 (t, *J* = 286.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.45. **FT-IR (KBr, film):** 3054, 1595, 1582, 1448, 1340, 1275, 1169, 1115, 1067, 827, 759, 715, 702, 682 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{16}O_2F_2NaS^+$ 417.0737; Found 417.0732.



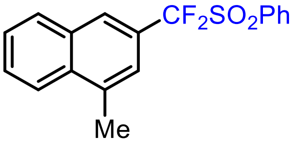
2o

2-(6-(difluoro(phenylsulfonyl)methyl)naphthalen-1-yl)thiophene (2o): white solid; 21.6 mg, 54% yield; **M.p.**: 130-132 ºC; R_f=0.5 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 1H), 8.24 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.66 – 7.58 (m, 3H), 7.47 (d, *J* = 5.0 Hz, 1H), 7.26 (s, 1H), 7.24 – 7.19 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.93, 135.48, 133.59, 132.88, 132.87, 132.83, 131.11, 130.63, 129.55 (t, *J* = 6.4 Hz), 129.50, 129.46, 127.92, 127.61, 126.77, 126.67, 126.29, 124.13 (t, *J* = 22.3 Hz), 123.92 (t, *J* = 5.4 Hz), 122.10 (t, *J* = 286.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.57. **FT-IR (KBr, film):** 3095, 3059, 1595, 1581, 1331, 1263, 1160, 1121, 1092, 1043, 823, 801, 717, 681 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{14}O_2F_2NaS_2^+$ 423.0301; Found 423.0303.



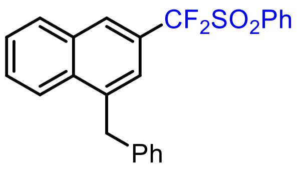
2p

6-(difluoro(phenylsulfonyl)methyl)-1,4-dimethylnaphthalene (2p): white solid; 14.2 mg, 41% yield; **M.p.**: 124-126 ºC; R*f*=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.76 (q, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.28 (m, 2H), 2.68 (d, *J* = 9.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.36, 134.52, 133.66, 133.04, 132.59, 131.85, 131.12, 129.38, 128.89, 127.64, 125.84 (t, *J* = 6.6 Hz), 125.54, 123.24 (t, *J* = 22.0 Hz), 122.94 (t, *J* = 5.4 Hz), 122.41 (t, *J* = 286.5 Hz), 19.47, 19.40. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.48. **FT-IR (KBr, film):** 3063, 2923, 1601, 1583, 1449, 1341, 1280, 1168, 1119, 1073, 880, 833, 717 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{19}H_{16}O_2F_2NaS^+$ 369.0737; Found 369.0741.



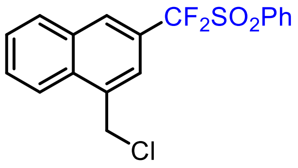
2q

3-(difluoro(phenylsulfonyl)methyl)-1-methylnaphthalene (2q): white solid; 24.6 mg, 74% yield; **M.p.**: 101-103 ºC; R*f*=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 4H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.62 (ddt, *J* = 22.0, 15.1, 7.4 Hz, 4H), 7.54 (s, 1H), 2.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.63, 135.37, 134.36, 133.06, 132.45, 131.08, 129.85, 129.40, 128.39, 127.74 (t, *J* = 6.7 Hz), 126.86, 124.31, 123.74 (t, *J* = 5.3 Hz), 123.47 (t, *J* = 22.1 Hz), 122.22 (t, *J* = 286.1 Hz), 19.66. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.36. **FT-IR (KBr, film):** 3071, 2923, 1582, 1448, 1345, 1296, 1202, 1161, 1094, 1077, 751, 716 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{14}O_2F_2NaS^+$ 355.0580; Found 355.0582.



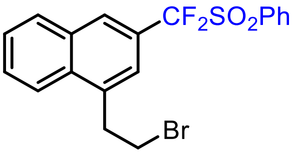
2r

1-benzyl-3-(difluoro(phenylsulfonyl)methyl)naphthalene (2r): white solid; 22.0 mg, 54% yield; **M.p.**: 111-112 ºC; R$_f$=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 3H), 7.95 (d, *J* = 7.3 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 – 7.52 (m, 5H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.19 (q, *J* = 7.5 Hz, 3H), 4.49 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.93, 137.77, 135.38, 133.89, 133.03, 132.96, 131.07, 130.02, 129.41, 128.71, 128.69, 128.63, 128.56 (t, *J* = 6.6 Hz), 126.90, 126.44, 124.70 (t, *J* = 5.5 Hz), 124.67, 123.61 (t, *J* = 21.9 Hz), 122.17 (t, *J* = 286.6 Hz), 39.39. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.57. **FT-IR (KBr, film):** 3063, 3021, 2920, 1602, 1581, 1493, 1448, 1344, 1173, 1112, 888, 746, 684 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{18}O_2F_2NaS^+$ 431.0893; Found 431.0889.



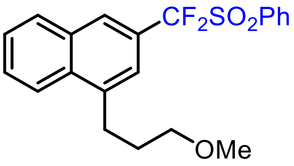
2s

1-(chloromethyl)-3-(difluoro(phenylsulfonyl)methyl)naphthalene (2s): white solid; 20.5 mg, 56% yield; **M.p.**: 100-102 °C; R$_f$=0.4 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.01 (dd, *J* = 13.6, 8.1 Hz, 3H), 7.77 (dt, *J* = 21.8, 7.8 Hz, 2H), 7.71 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 3H), 5.06 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.56, 134.25, 132.99, 132.81, 132.76, 131.10, 130.84 (t, *J* = 6.5 Hz), 130.21, 129.52, 129.37, 127.51, 124.83 (t, *J* = 5.4 Hz), 123.96, 123.55 (t, *J* = 22.4 Hz), 121.81 (t, *J* = 286.6 Hz), 43.95. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.73. **FT-IR (KBr, film):** 3068, 2922, 1583, 1452, 1342, 1167, 1121, 785, 759, 719 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{13}O_2F_2NaSCl^+$ 389.0191; Found 389.0190.



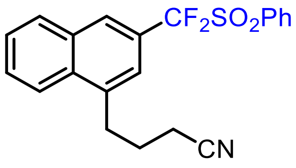
2t

1-(2-bromoethyl)-3-(difluoro(phenylsulfonyl)methyl)naphthalene (2t): white solid; 34.3 mg, 81% yield; **M.p.**: 124-125 ºC; R$_f$=0.4 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.13 (s, 1H), 8.05 (dd, *J* = 13.3, 8.7 Hz, 3H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.63 (q, *J* = 7.7 Hz, 3H), 7.58 (d, *J* = 5.1 Hz, 1H), 3.68 (s, 4H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 136.21, 135.47, 133.31, 132.92, 131.09, 130.33, 129.47, 129.02, 129.00 (t, *J* = 6.7 Hz), 127.14, 124.22 (t, *J* = 5.4 Hz), 123.63 (t, *J* = 22.0 Hz), 123.39, 122.00 (t, *J* = 286.3 Hz), 36.70, 31.42.**^{19}F NMR** (471 MHz, CDCl$_3$) δ -101.58. **FT-IR (KBr, film):** 3071, 2922, 1581, 1447, 1347, 1216, 1169, 1117, 1095, 1077, 746, 684, 592 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{19}H_{15}O_2F_2NaSBr^+$ 446.9842; Found 446.9845.



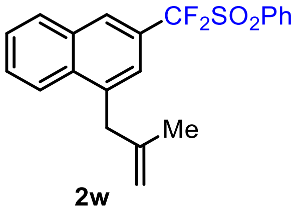
2u

3-(difluoro(phenylsulfonyl)methyl)-1-(3-methoxypropyl)naphthalene (2u): colorless oil; 32.0 mg, 82% yield; R$_f$=0.6 (petroleum ether/EtOAc = 5:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.08 – 8.00 (m, 3H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.63 (q, *J* = 6.0 Hz, 3H), 7.60 – 7.51 (m, 2H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.39 (s, 3H), 3.21 (t, *J* = 7.7 Hz, 2H), 2.03 (t, *J* = 7.3 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 139.42, 135.36, 133.71, 133.08, 132.83, 131.06, 130.06, 129.40, 128.42, 127.88 (t, *J* = 6.8 Hz), 126.77, 124.09, 123.47 (t, *J* = 21.8 Hz), 123.37 (t, *J* = 5.3 Hz), 122.22 (t, *J* = 286.1 Hz), 71.85, 58.82, 30.59, 29.50. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -101.47. **FT-IR (KBr, film):** 3067, 2924, 2872, 1583, 1448, 1343, 1168, 1011, 1024, 752, 719, 685 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{21}H_{20}O_3F_2NaS^+$ 413.0999; Found 413.1002.



2v

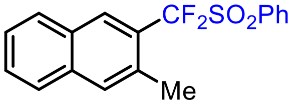
4-(3-(difluoro(phenylsulfonyl)methyl)naphthalen-1-yl)butanenitrile (2v): white solid; 19.2 mg, 50% yield; **M.p.**: 139-140 ºC; R*f*=0.5 (petroleum ether/EtOAc = 5:1); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.06 (t, *J* = 9.5 Hz, 3H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.65 (tt, *J* = 19.4, 7.5 Hz, 4H), 7.55 (s, 1H), 3.30 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.14 (p, *J* = 7.4 Hz, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 137.08, 135.49, 133.31, 132.94, 132.88, 131.07, 130.31, 129.48, 128.92, 128.64 (t, *J* = 6.7 Hz), 127.12, 123.60 (t, *J* = 5.3 Hz), 123.51, 123.42 (t, *J* = 22.1 Hz), 122.05 (t, *J* = 286.6 Hz), 119.53, 31.65, 26.17, 16.97. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -101.69. **FT-IR (KBr, film):** 3065, 2920, 2887, 2247, 1580, 1508, 1452, 1342, 1276, 1167, 1123, 751, 717, 627 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{17}NO_2F_2NaS^+$ 408.0846; Found 408.0849.



2w

3-(difluoro(phenylsulfonyl)methyl)-1-(2-methylallyl)naphthalene (2w): colorless oil; 13.0 mg, 35% yield; R*f*=0.5 (petroleum ether/EtOAc = 20:1); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 3H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 4.90 (s, 1H), 4.62 (s, 1H), 3.82 (s, 2H), 1.79 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 143.92, 137.03, 135.37, 134.18, 133.07, 132.79, 131.07, 129.93, 129.41, 128.38, 128.26 (t, *J* = 6.9 Hz), 126.82, 124.56, 124.45 (t, *J* = 5.2 Hz), 123.50 (t, *J* = 22.1 Hz), 122.20 (t, *J* = 286.6 Hz), 113.07. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -101.61. **FT-IR (KBr, film):** 3069, 2963, 2920, 2849, 1646, 1583, 1448, 1343, 1168, 1096, 991, 895, 748, 719, 685 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{18}O_2F_2NaS^+$ 395.0893; Found

395.0884.

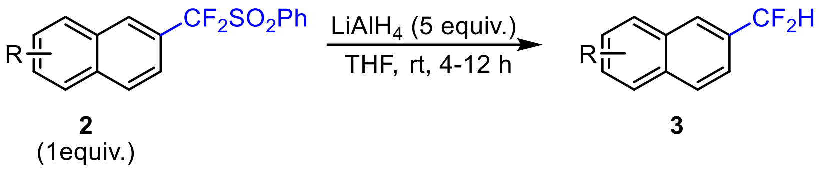


2x

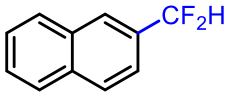
2-(difluoro(phenylsulfonyl)methyl)-3-methylnaphthalene (2x): white solid; 20.6 mg, 62% yield; **M.p.**: 133-135 ºC; R$_f$=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.09 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.73 (s, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 2.74 (t, *J* = 3.4 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 135.35, 135.16, 134.28, 133.22, 131.36 (t, *J* = 8.8 Hz), 131.07, 130.89, 130.77, 129.40, 128.82, 128.66, 127.06, 126.39, 123.72 (t, *J* = 288.3 Hz), 123.40 (t, *J* = 20.1 Hz), 21.28 (t, *J* = 4.7 Hz).**^{19}F NMR** (471 MHz, CDCl$_3$) δ -95.37. **FT-IR (KBr, film):** 3063, 2926, 1596, 1447, 1338, 1165, 1031, 883, 770, 718, 681 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{14}O_2F_2NaS^+$ 355.0580; Found 355.0584.

Synthetic transformations

a) Desulfonation to Access 2-(difluoromethyl)naphthalene

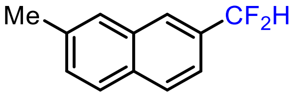


According to the procedures reported previously[5]. To a solution of compound **2** (0.1 mmol, 1.0 equiv.) in 2 mL THF was added dropwise $LiAlH_4$ in THF (0.5 mL, 1.0 M, 0.5 mmol, 5.0 equiv.) at room temperature. The reaction mixture was reacted 4-12 hours until completion indicated by TLC. The obtained solution was subsequently quenched with a saturated ammonium chloride solution, extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4 and concentrated under vacuum to yield the crude expected product **3**, which was purified by column chromatography on silica gel.



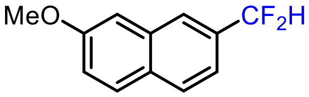
3a

2-(difluoromethyl)naphthalene (3a): white solid; 15.1 mg, 85% yield; **M.p.**: 68-70 °C; R_f=0.6 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.95 – 7.88 (m, 3H), 7.61 (d, J = 8.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 6.81 (t, J = 56.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.45, 132.68, 131.75 (t, J = 22.3 Hz), 129.04, 128.67, 128.02, 127.54, 126.95, 126.03 (t, J = 7.6 Hz), 122.17 (t, J = 4.7 Hz), 115.18 (t, J = 238.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.84 (d, J = 56.4 Hz). **FT-IR (KBr, film):** 3061, 2923, 1558, 1506, 1340, 1083, 1016, 871, 832, 751 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_8F_2Na^+$ 201.0492; Found 201.0489.



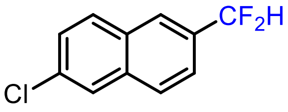
3b

2-(difluoromethyl)-7-methylnaphthalene (3b): white solid; 15.3 mg, 80% yield; **M.p.**: 112-114 °C; R*f*=0.6 (petroleum ether); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.88 (s, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 56.5 Hz, 1H), 2.54 (s, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 136.76, 132.92, 132.70, 131.75 (t, *J* = 22.1 Hz), 129.84, 128.72, 127.79, 127.60, 125.37 (t, *J* = 7.6 Hz), 121.28 (t, *J* = 4.8 Hz), 115.29 (t, *J* = 238.3 Hz), 21.86. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -109.72 (d, *J* = 56.4 Hz). **FT-IR (KBr, film):** 3061, 2921, 1507, 1337, 1022, 916, 847, 807 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{12}H_{10}F_2Na^+$ 215.0648; Found 215.0648.



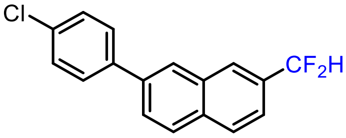
3c

2-(difluoromethyl)-7-methoxynaphthalene (3c): white solid; 16.9 mg, 81% yield; **M.p.**: 68-70 °C; R*f*=0.4 (petroleum ether); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.96 – 7.78 (m, 3H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 9.6 Hz, 1H), 7.23 (s, 1H), 6.82 (t, *J* = 56.5 Hz, 1H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 158.42, 134.01, 132.28 (t, *J* = 22.2 Hz), 129.95, 129.48, 128.71, 124.73 (t, *J* = 7.4 Hz), 120.45, 119.98 (t, *J* = 4.9 Hz), 115.26 (t, *J* = 238.5 Hz), 106.43, 55.51. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -109.93 (d, *J* = 56.6 Hz). **FT-IR (KBr, film):** 3022, 2962, 1515, 1265, 1017, 848, 813, 724 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{12}H_{10}OF_2Na^+$ 231.0597; Found 231.0591.



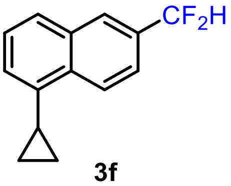
3d

2-chloro-6-(difluoromethyl)naphthalene (3d): white solid; 14.8 mg, 70% yield; **M.p.**: 80-82 ºC; R*f*=0.6 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.86 (dd, *J* = 10.1, 6.6 Hz, 3H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 6.79 (t, *J* = 56.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.00, 133.45, 132.08 (t, *J* = 22.4 Hz), 130.92, 130.21, 128.20, 127.97, 125.87 (t, *J* = 7.5 Hz), 123.36 (t, *J* = 4.9 Hz), 114.86 (t, *J* = 238.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.28 (d, *J* = 56.2 Hz). **FT-IR (KBr, film):** 3059, 2923, 1558, 1507, 1456, 1340, 1016, 870, 787, 751 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_7F_2NaCl^+$ 235.0102; Found 235.0098.



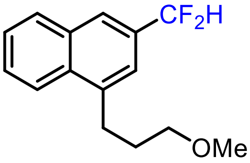
3e

2-(4-chlorophenyl)-7-(difluoromethyl)naphthalene (3e): white solid; 26.2 mg, 91% yield; **M.p.**: 97-98 ºC; R*f*=0.5 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 13.9 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 9.6 Hz, 3H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.82 (t, *J* = 56.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.14, 138.43, 133.97, 133.63, 132.91, 132.36 (t, *J* = 22.3 Hz), 129.26, 128.81, 128.77, 128.72, 126.92, 126.39, 126.23 (t, *J* = 7.5 Hz), 122.46 (t, *J* = 4.9 Hz), 115.06 (t, *J* = 238.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.06 (d, *J* = 56.4 Hz). **FT-IR (KBr, film):** 3052, 2922, 1495, 1059, 911, 815, 735 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{11}F_2NaCl^+$ 311.0415; Found 311.0420.



3f

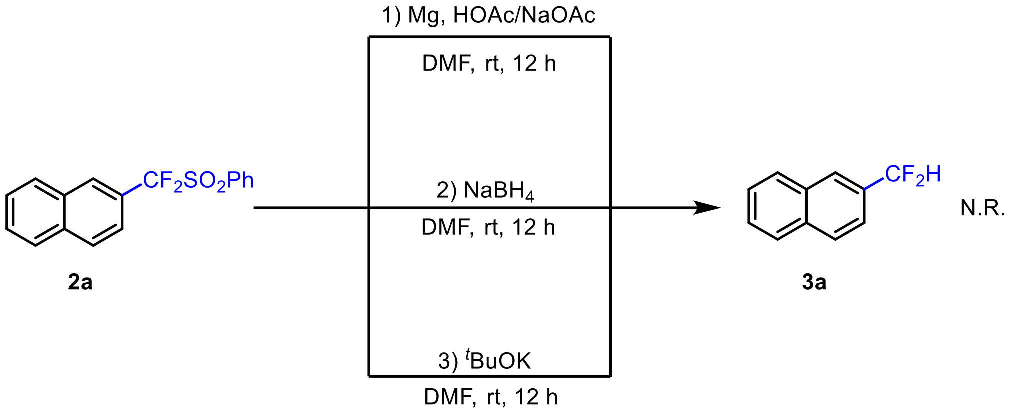
1-cyclopropyl-6-(difluoromethyl)naphthalene (3f): colorless oil; 15.5 mg, 71% yield; R$_f$=0.5 (petroleum ether); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.51 (d, *J* = 8.7 Hz, 1H), 7.98 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 56.4 Hz, 1H), 2.36 (dt, *J* = 9.9, 5.9 Hz, 1H), 1.10 (ddt, *J* = 8.5, 6.3, 3.0 Hz, 2H), 0.79 (dd, *J* = 5.8, 3.3 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 139.51, 134.61, 132.84, 131.45 (t, *J* = 22.5 Hz), 127.20, 126.62, 126.51 (t, *J* = 7.5 Hz), 125.67, 125.47, 121.97 (t, *J* = 4.8 Hz), 115.25 (t, *J* = 238.3 Hz), 13.38, 6.63. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -109.83 (d, *J* = 56.5 Hz). **FT-IR (KBr, film):** 3080, 2961, 2919, 1506, 1260, 1020, 800 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{14}H_{12}F_2Na^+$ 241.0805; Found 241.0803.



3g

3-(difluoromethyl)-1-(3-methoxypropyl)naphthalene (3g): yellow oil; 19.3 mg, 77% yield; R$_f$=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (s, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 (s, 1H), 6.78 (t, *J* = 56.4 Hz, 1H), 3.48 – 3.43 (m, 2H), 3.39 (t, *J* = 1.8 Hz, 3H), 3.21 (t, *J* = 7.9 Hz, 2H), 2.08 – 2.01 (m, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 139.72, 133.17, 133.06, 131.30 (t, *J* = 22.0 Hz), 129.53, 127.44, 126.52, 124.67 (t, *J* = 7.6 Hz), 124.10, 122.11 (t, *J* = 4.7 Hz), 115.28 (t, *J* = 238.3 Hz), 72.00, 58.81, 30.64, 29.60. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -109.90 (d, *J* = 56.4 Hz). **FT-IR (KBr, film):** 3056, 2920, 2850, 1507, 1457, 1261, 1180, 1020, 888, 784, 750 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{15}H_{16}OF_2Na^+$ 273.1067; Found 273.1066.

Failed methods



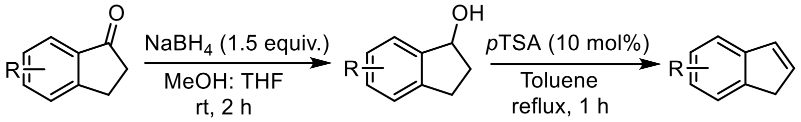
1) Into a 50 mL flask containing compound **2a** (31.8 mg, 0.1 mmol, 1 equiv.) in DMF(1.5 mL) at room temperature was added HOAc/NaOAc (1:1) buffer solution (8 mol/L, 4 mL). Magnesium turnings (36.0 mg, 3 mmol, 15 equiv.) were added in portions. The reaction mixture was stirred at room temperature for 12 hours. The reaction process was monitored by TLC, and the desulfonylation product **3a** was not found.

2) To a solution of compound **2a** (31.8 mg, 0.1 mmol, 1 equiv.) in DMF (1.5 mL) was added $NaBH_4$(7.6 mg, 0.2 mmol, 2 equiv.) slowly at room temperature. The reaction mixture was stirred 12 hours and monitored by TLC, but the desulfonylation product **3a** was not found.

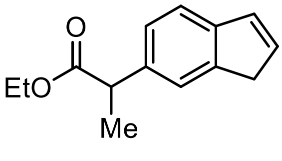
3) To a solution of compound **2a** (31.8 mg, 0.1 mmol, 1 equiv.) in DMF (1.5 mL) was added dropwise ^{t}BuOK (22.5 mg, 0.2 mmol, 2 equiv.) at room temperature. The reaction mixture was stirred 12 hours and monitored by TLC, but the desulfonylation product **3a** was not found.

b) Application in synthesis of drug derivatives

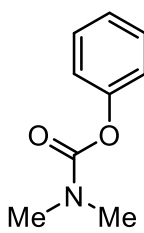
General procedure for the substrates 4a-4c



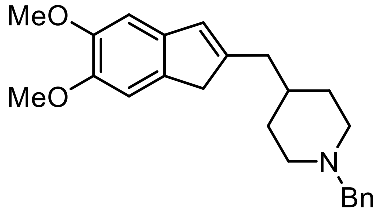
According to the procedures reported previously[2], to a stirred solution of 1-indanone (3 mmol) in MeOH (3 mL) and THF (1.5 mL) was added $NaBH_4$ (4.5 mmol, 170.2 mg, 1.5 equiv.) at 0 °C. After stirring at room temperature for 2 h, the reaction was quenched with water (3 mL). The resulting mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product of alcohol was used directly for the next step without further purification. To a stirred solution of crude product of alcohol in toluene (22 mL) was added $TsOH{\cdot}H_2O$ (*p*TSA, 0.3 mmol, 57.1 mg, 10 mol%). The reaction mixture was heated at reflux for 1 h. After cooling down to ambient temperature, K_2CO_3 (10% aq., 15 ml) was added. The organic phase was further washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product indene.



ethyl 2-(1*H*-inden-6-yl)propanoate (4a): colorless oil; 434.4 mg, 67% yield; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.90 – 6.83 (m, 1H), 6.55 (dt, *J* = 5.6, 2.0 Hz, 1H), 4.23 – 4.03 (m, 2H), 3.76 (q, *J* = 7.1 Hz, 1H), 3.40 (d, *J* = 2.1 Hz, 2H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.01, 144.26, 143.96, 137.24, 134.36, 131.81, 125.76, 122.93, 120.96, 60.78, 45.64, 39.10, 19.03, 14.25. **FT-IR (KBr, film):** 3054, 2982, 2928, 1728, 1501, 1375, 1265, 1179, 1093, 946, 875, 799, 739, 704 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{14}H_{16}O_2Na^+$ 239.1048; Found 239.1051.

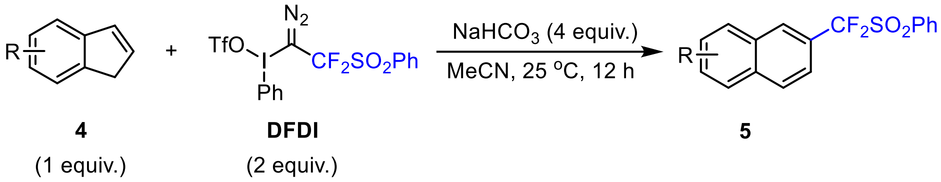


1*H*-inden-7-yl dimethylcarbamate (4b): colorless oil; 377.8 mg, 62% yield; R$_f$=0.7(petroleum ether/EtOAc = 5:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.84 (s, 1H), 6.52 (s, 1H), 3.34 (s, 2H), 3.09 (s, 3H), 2.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.35, 147.38, 147.10, 134.96, 134.12, 131.83, 127.71, 118.33, 118.24, 36.69, 36.52, 36.46. **FT-IR (KBr, film):** 3066, 2931, 1722, 1617, 1591, 1554, 1466, 1314, 1234, 1162, 1032, 943, 848, 782, 705 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{12}H_{14}NO_2^+$ 204.1025; Found 204.1030.

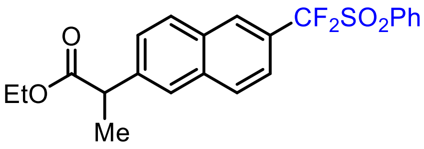


1-benzyl-4-((5,6-dimethoxy-1*H*-inden-2-yl)methyl)piperidine (4c): white solid; 991.6 mg, 91% yield; **M.p.**: 110-112 ºC; R$_f$=0.5 (petroleum ether/EtOAc = 1:5); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.4 Hz, 4H), 7.26 (s, 1H), 7.00 (s, 1H), 6.86 (s, 1H), 6.41 (s, 1H), 3.89 (d, *J* = 3.0 Hz, 6H), 3.50 (s, 2H), 3.24 (s, 2H), 2.88 (d, *J* = 11.7 Hz, 2H), 2.39 (d, *J* = 7.3 Hz, 2H), 1.95 (t, *J* = 11.7 Hz, 2H), 1.69 (d, *J* = 13.3 Hz, 2H), 1.54 (s, 1H), 1.31 (q, *J* = 10.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.21, 147.59, 146.37, 138.63, 138.40, 135.40, 129.27, 128.20, 127.21, 126.96, 108.17, 103.92, 63.55, 56.41, 56.18, 53.93, 41.34, 38.44, 36.17, 32.58. **FT-IR (KBr, film):** 3037, 2941, 2918, 2789, 1608, 1575, 1490, 1464, 1299, 1220, 1101, 995, 865, 738, 695 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{24}H_{30}NO_2^+$ 364.2277; Found 364.2278.

General procedure for the substrates 5a-5c

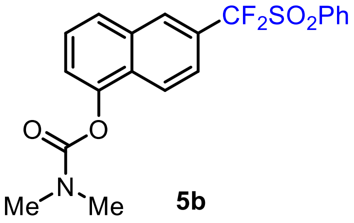


An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.) and $NaHCO_3$ (33.6 mg, 0.4 mmol, 4 equiv.) under Ar atmosphere. Then indene **4** (0.1 mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 °C for 12 hours. The solution mixture was extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product **5**.



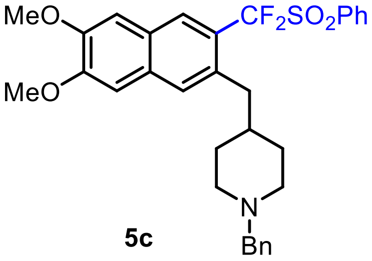
5a

ethyl 2-(6-(difluoro(phenylsulfonyl)methyl)naphthalen-2-yl)propanoate (5a): white solid; 36.4 mg, 87% yield; **M.p.**: 86-88 °C; R_f=0.3 (petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.91 (t, J = 8.2 Hz, 2H), 7.82 (s, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.56 (d, J = 8.5 Hz, 1H), 4.22 – 4.08 (m, 2H), 3.92 (q, J = 6.9 Hz, 1H), 1.61 (dd, J = 7.1, 2.6 Hz, 3H), 1.21 (td, J = 7.2, 4.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.21, 141.09, 135.40, 135.11, 132.92, 131.42, 131.03, 129.48, 129.40, 128.91 (t, J = 6.6 Hz), 128.55, 127.23, 126.19, 123.80 (t, J = 22.2 Hz), 123.68 (t, J = 5.5 Hz), 122.16 (t, J = 286.4 Hz), 61.09, 45.87, 18.60, 14.23. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.43. **FT-IR (KBr, film):** 3060, 2962, 2931, 1716, 1581, 1450, 1345, 1254, 1174, 1108, 1096, 1062, 824, 717, 684 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{20}O_4F_2NaS^+$ 441.0948; Found 441.0953.



5b

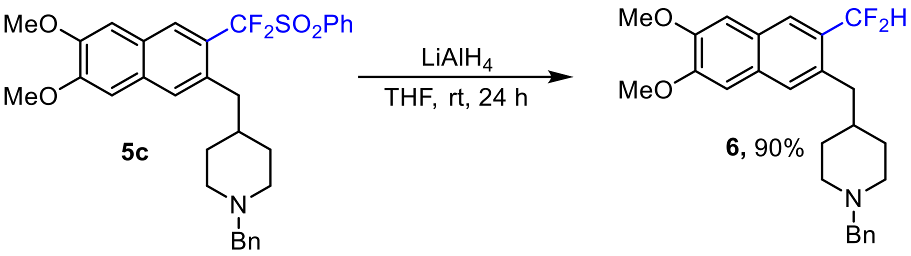
6-(difluoro(phenylsulfonyl)methyl)naphthalen-1-yl dimethylcarbamate (5b): yellow oil; 34.4 mg, 85% yield; R_f=0.7 (petroleum ether/EtOAc = 1:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.75 (q, *J* = 8.1 Hz, 2H), 7.59 (dt, *J* = 20.9, 7.8 Hz, 3H), 7.44 (d, *J* = 7.6 Hz, 1H), 3.27 (s, 3H), 3.08 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.60, 147.30, 135.45, 133.35, 132.70, 130.99, 129.40, 129.13 (t, *J* = 6.7 Hz), 129.01, 127.05, 126.42, 124.45 (t, *J* = 22.1 Hz), 123.72 (t, *J* = 5.4 Hz), 122.38, 121.97 (t, *J* = 286.5 Hz), 120.82, 37.00, 36.70. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.73. **FT-IR (KBr, film):** 3068, 2921, 1725, 1646, 1606, 1582, 1448, 1366, 1339, 1276, 1166, 1065, 977, 814, 752, 717, 686 cm^{-1} **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{17}NO_4F_2NaS^+$ 428.0744; Found 428.0746.



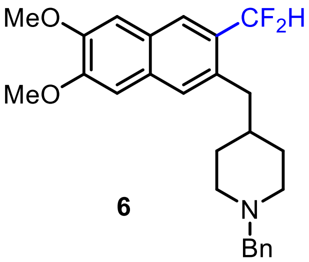
5c

1-benzyl-4-((3-(difluoro(phenylsulfonyl)methyl)-6,7-dimethoxynaphthalen-2-yl)methyl)-piperidine (5c): white solid; 26.6 mg, 47% yield; **M.p.**: 93-94 °C; R_f=0.4 (petroleum ether/EtOAc = 1:5); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.96 (s, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.54 (s, 1H), 7.30 (d, *J* = 4.3 Hz, 4H), 7.25 (s, 1H), 7.13 (s, 1H), 7.07 (s, 1H), 4.00 (d, *J* = 15.7 Hz, 6H), 3.48 (s, 2H), 2.88 (d, *J* = 7.3 Hz, 4H), 1.88 (t, *J* = 11.8 Hz, 2H), 1.67 (d, *J* = 12.9 Hz, 2H), 1.58 (s, 1H), 1.49 – 1.39 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.72, 149.97, 135.27, 135.21, 133.27, 131.15, 130.95, 129.69, 129.59 (t, *J* = 8.9 Hz), 129.40, 129.36, 128.24, 127.06, 126.62, 123.90 (t, *J* = 288.4 Hz), 120.71 (t, *J* = 19.9 Hz), 106.74, 105.39, 63.48, 56.10, 56.06, 53.96, 41.10, 38.42, 32.37. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -93.75. **FT-IR (KBr, film):** 3062, 2934, 2800, 1628, 1583, 1508, 1485, 1448, 1340, 1234, 1163, 1150, 1038, 900, 722, 686 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{32}H_{34}NO_4F_2S^+$ 566.2177; Found 566.2175.

General procedure for the substrate 6



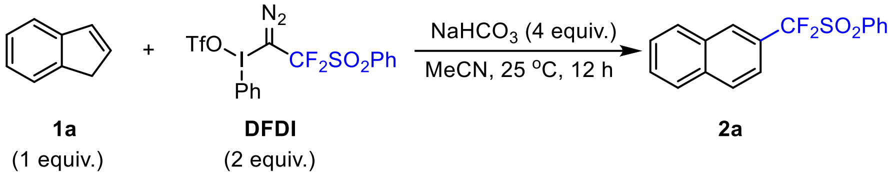
To a solution of compound **5c** (56.5 mg, 0.1 mmol, 1.0 equiv.) in 2 mL THF was added dropwise LiAlH$_4$ in THF (0.5 mL, 1.0 M, 0.5 mmol, 5.0 equiv.) at room temperature. The reaction mixture was reacted 24 hours until completion indicated by TLC. The obtained solution was subsequently quenched with a saturated ammonium chloride solution, extracted with EtOAc, and the organic phase was washed with brine, dried over Na$_2$SO$_4$ and concentrated under vacuum to yield the crude expected product **6**, which was purified by column chromatography on silica gel.



6

1-benzyl-4-((3-(difluoromethyl)-6,7-dimethoxynaphthalen-2-yl)methyl)piperidine (6): white solid; 38.3 mg, 90% yield; **M.p.**: 129-131 °C; R$_f$ =0.5 (petroleum ether/EtOAc = 1:5); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.89 (s, 1H), 7.48 (s, 1H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.25 (s, 1H), 7.14 (s, 1H), 7.07 (s, 1H), 6.89 (t, *J* = 55.4 Hz, 1H), 4.00 (d, *J* = 5.8 Hz, 6H), 3.48 (s, 2H), 2.88 (d, *J* = 11.0 Hz, 2H), 2.77 (d, *J* = 6.8 Hz, 2H), 1.91 (t, *J* = 11.7 Hz, 2H), 1.67 (d, *J* = 13.5 Hz, 2H), 1.61 (s, 1H), 1.40 (q, *J* = 12.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.84, 149.76, 138.60, 133.73 (t, *J* = 3.7 Hz), 130.24, 129.32, 128.97 (t, *J* = 20.4 Hz), 128.24, 128.21, 127.01, 124.92 (t, *J* = 8.1 Hz), 114.69 (t, *J* = 237.6 Hz), 106.61, 105.63, 63.53, 56.03, 56.01, 53.90, 39.27, 37.74, 32.50. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.05 (d, *J* = 55.4 Hz). **FT-IR (KBr, film):** 3060, 2920, 2849, 2759, 1633, 1611, 1489, 1437, 1256, 1218, 1157, 1013, 902, 800, 739, 699 cm^{-1} **HRMS** (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{26}H_{30}NO_2F_2^+$ 426.2245; Found 426.2244.

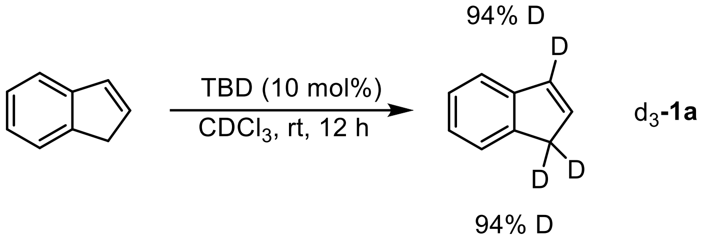
Scale-up Synthesis



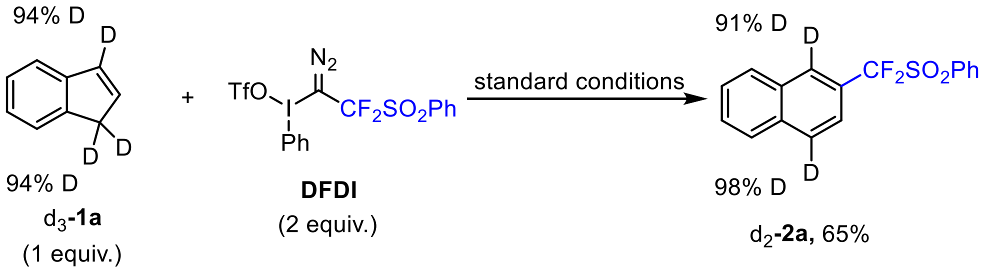
An oven dried 50 mL Schlenk tube equipped with a magnetic stir bar was charged with $NaHCO_3$ (336.0 mg, 4.0 mmol, 4 equiv.), indene **1a** (116.2 mg, 1 mmol, 1 equiv.) and MeCN (10 mL) under Ar. The solution of **DFDI** (583.9 mg, 1 mmol, 1 equiv.) in 5 mL of MeCN was added dropwise into the Schlenk tube. After the mixture was stirred at 25 °C for 12 hours, a second solution of **DFDI** (583.9 mg, 1 mmol, 1 equiv.) in 5 mL of MeCN was also slowly introduced. The solution mixture was extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product **2a** (201.0 mg, 63%). Additionally, we also conducted the model reaction on a 1.0 mmol scale under standard conditions, but the desired product **2a** was obtained in only 37% isolated yield after 48 hours. We observed a significant release of bubbles initially, indicating rapid decomposition of the iodonium diazo reagent.

Control Experiments and Proposed Mechanism

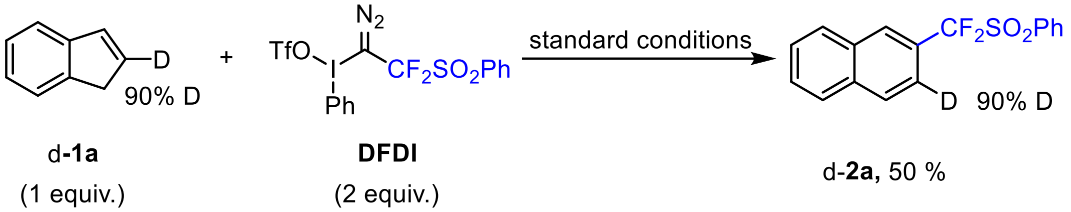
a) Deuterated labeling experiments



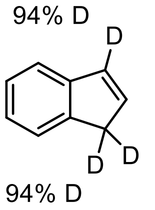
The 1*H*-indene-1,1,3-d*3* (d3-**1a**) was prepared according to literature[6]. To a solution of 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD) (CAS: 5807-14-7, 41.7 mg, 0.3mmol, 10 mol%) in 10 mL of $CDCl_3$ was added indene (348.5 mg, 3.0 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 12 h and quenched with 1 N HCl (1 mL). The organic layer was washed with water (2 × 2 mL) and brine (1 mL), dried over anhydrous Na_2SO_4, and filtered. Filtrate was concentrated to afford d3-**1a**.



An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.) and $NaHCO_3$ (33.6 mg, 0.4 mmol, 4 equiv.) under Ar atmosphere. Then 1*H*-indene-1,1,3-d*3* (d3-**1a**) (0.1 mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 °C for 12 hours. The solution mixture was extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product d2-**2a**.

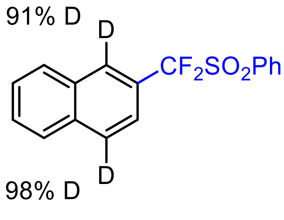


An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.) and $NaHCO_3$ (33.6 mg, 0.4 mmol, 4 equiv.) under Ar atmosphere. Then 1*H*-Indene-2-*d* (d-**1a**) (0.1 mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 ºC for 12 hours. The solution mixture was extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product d-**2a**.



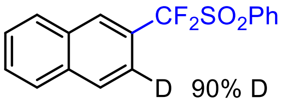
d_3-**1a**

1*H*-indene-1,1,3-d*3* (d3-1a): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.97, 143.77, 134.15, 126.37, 124.65, 123.86, 121.04.



d_2**-2a**

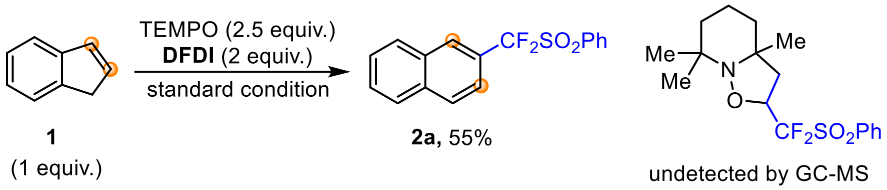
2-(difluoro(phenylsulfonyl)methyl)naphthalene-1,4-*d2* (d2-2a): white solid; 20.7 mg, 65% yield; **M.p.**: 183-184 ºC; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.99 – 7.88 (m, 2H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.61 (dt, J = 13.0, 7.3 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.42, 134.95, 132.95, 132.22, 131.08, 129.42, 129.09, 128.52, 127.94, 127.22, 123.82 (t, J = 22.0 Hz), 123.27 (t, J = 5.5 Hz), 122.20 (t, J = 286.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.41. **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{10}D_2O_2F_2NaS^+$ 343.0549 Found 343.0552.



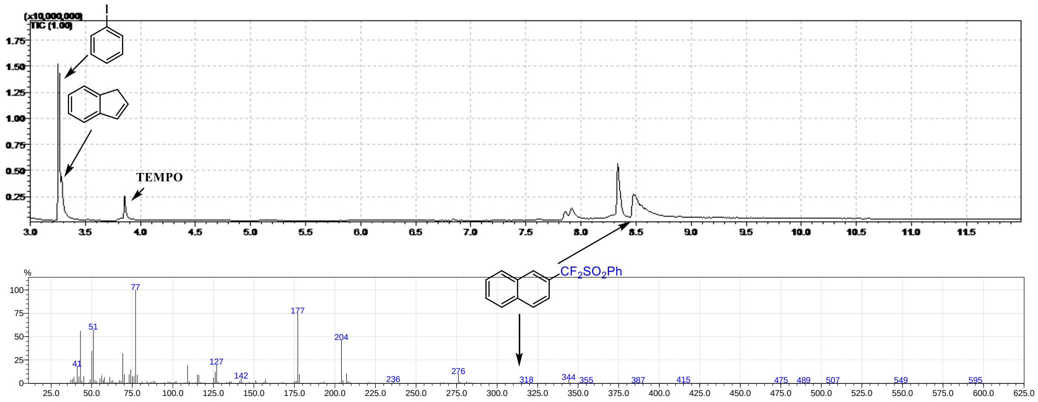
d-**2a**

2-(difluoro(phenylsulfonyl)methyl)naphthalene-3-*d* (d-2a): white solid; 16.0 mg, 50% yield; **M.p.**: 183-184 °C; R_f=0.5 (petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.99 – 7.88 (m, 3H), 7.77 (t, J = 7.6 Hz, 1H), 7.61 (dt, J = 20.3, 7.5 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.43, 135.01, 132.92, 132.30, 131.06, 129.42, 129.22 (t, J = 6.7 Hz), 129.14, 128.57, 128.52, 127.98, 127.22, 123.82 (t, J = 22.2 Hz), 122.18 (t, J = 286.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.40. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{12}DO_2F_2S^+$ 320.0667; Found 320.0670.

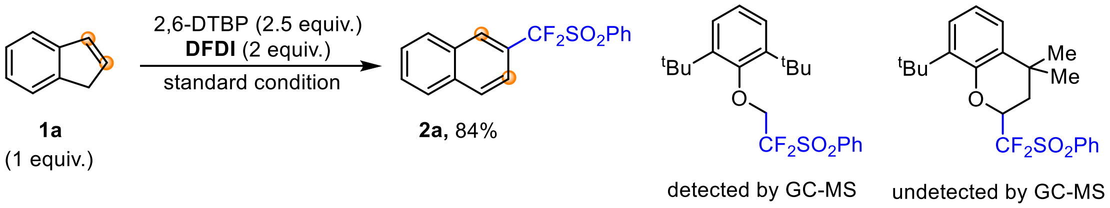
b) Radical probe experiments



An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.), NaHCO$_3$ (33.6 mg, 0.4 mmol, 4 equiv.) and TEMPO (39.1 mg, 0.25 mmol, 2.5 equiv.) under Ar atmosphere. Then indene **1a** (11.6 mg, 0.1 mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 °C for 12 hours. After irradiation, the resulting solution was analysis by GC-MS. The analysis showed that 55% desired product was detected. The expected TEMPO-adduct was not observed in the **Supplementary Figure S1.**

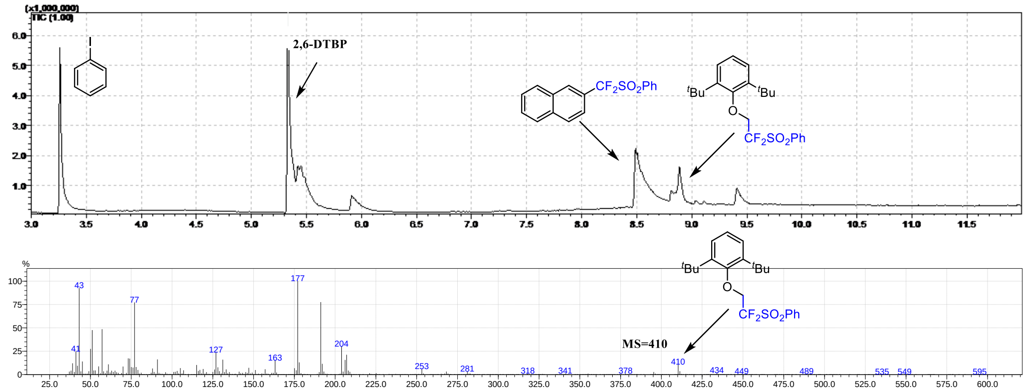


Supplementary Figure S1. GC-MS Spectra for the crude reaction with TEMPO.



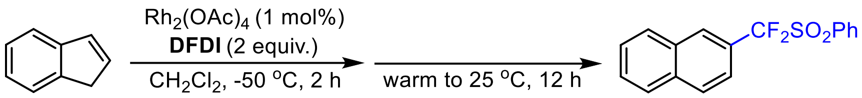
An oven dried 4 mL vial equipped with a magnetic stir bar was charged with **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.), NaHCO$_3$ (33.6 mg, 0.4 mmol, 4 equiv.) and 2,6-DTBP (51.6 mg, 0.25 mmol, 2.5 equiv.) under Ar atmosphere. Then indene **1a** (11.6 mg, 0.1

mmol, 1 equiv.) and MeCN (2 mL) were added, the mixture was stirred at 25 °C for 12 hours. After irradiation, the resulting solution was analysis by GC-MS. The analysis showed that 84% desired product was detected. The expected 2,6-DTBP-adduct was observed in the **Supplementary Figure S2**.



Supplementary Figure S2. GC-MS Spectra for the crude reaction with 2,6-DTBP.

c) Rhodium catalysis experiment



1a
(1 equiv.)

2a, 56%

An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with $Rh_2(OAc)_4$ (0.4 mg, 1 mol%). Then the vessel was evacuated and re-filled with Ar for four times. After the indene **1a** (11.6 mg, 0.1 mmol, 1 equiv.) and dry DCM (1 mL) were added, the solution of **DFDI** (116.8 mg, 0.2 mmol, 2 equiv.) in 1 mL of DCM was added dropwise into the Schlenk tube at -50 °C and stirred for 2 hours. Then the mixture was warmed to 25 °C and stirred for 12 hours. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the product **2a**.

References

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[3] M. Umeda, H. Noguchi and T. Nishimura, *Org. Lett.*, 2020, **22**, 9597–9602.

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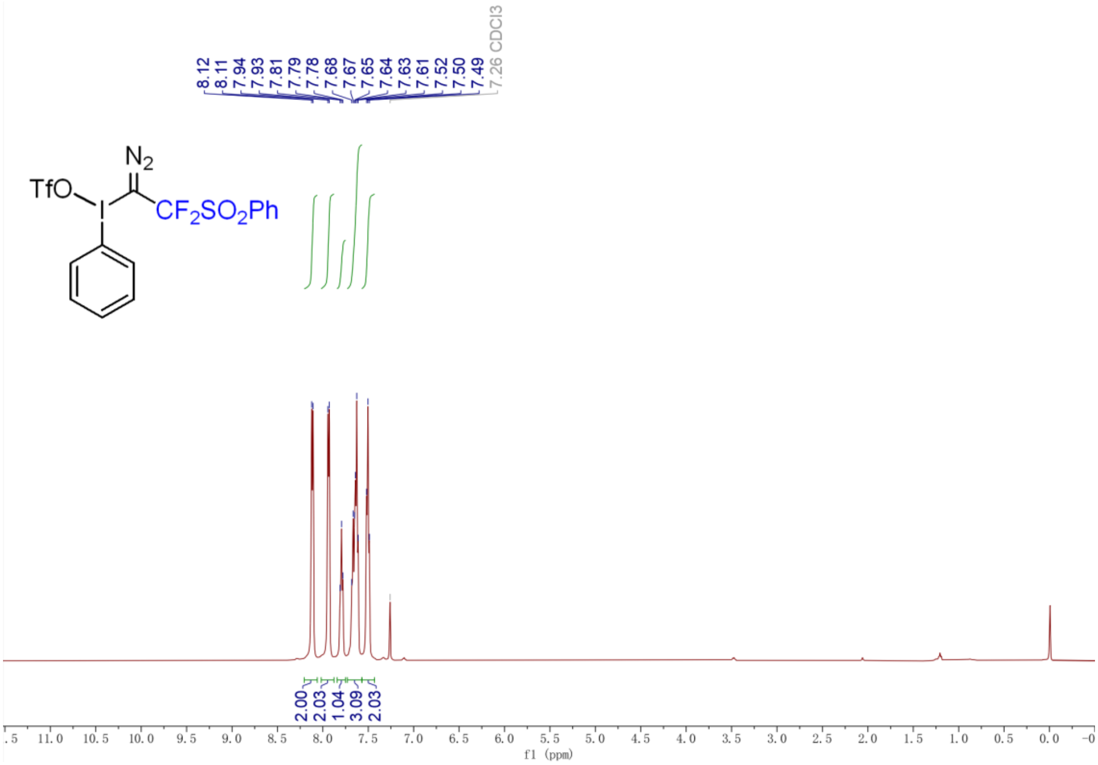
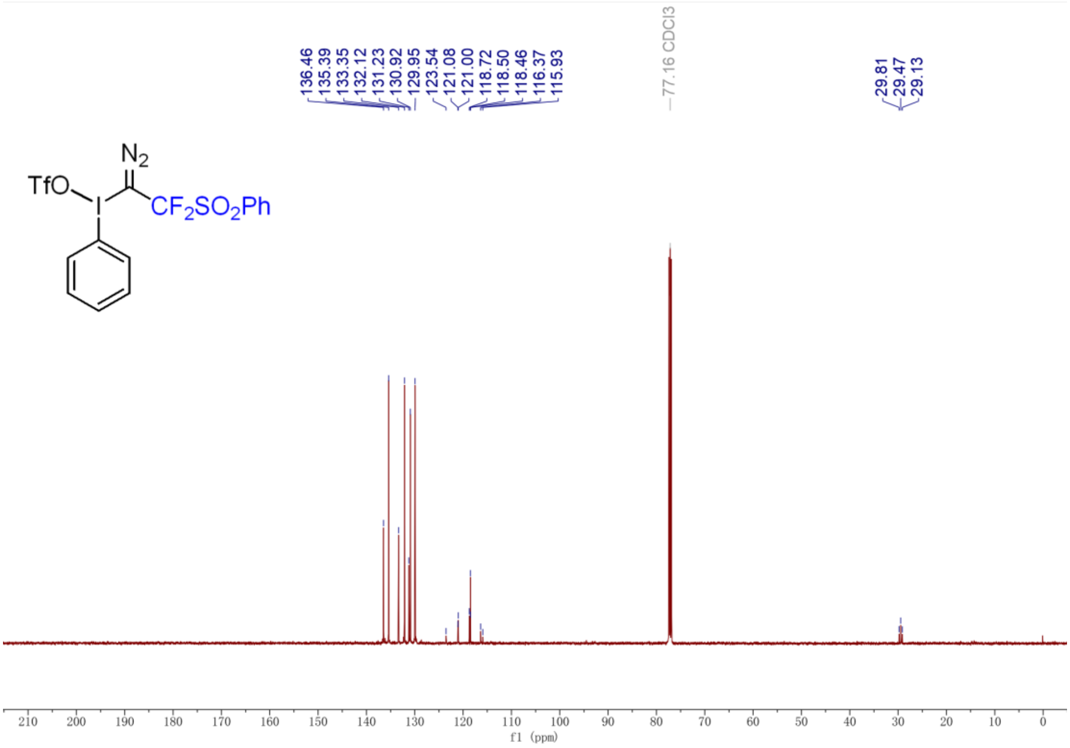
[6] C. Sabot, K. A. Kumar, C. Antheaume and C. Mioskowski, *J. Org. Chem.*, 2007, **72**, 5001–5004.

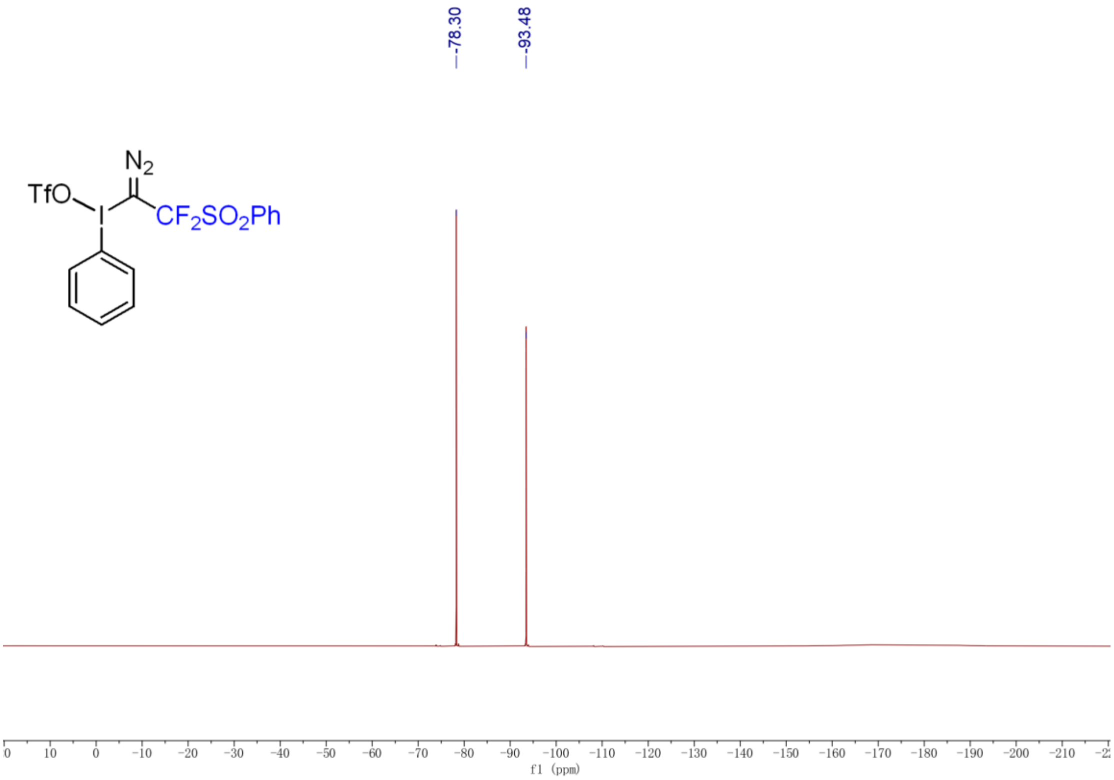
NMR spectra of the related compounds



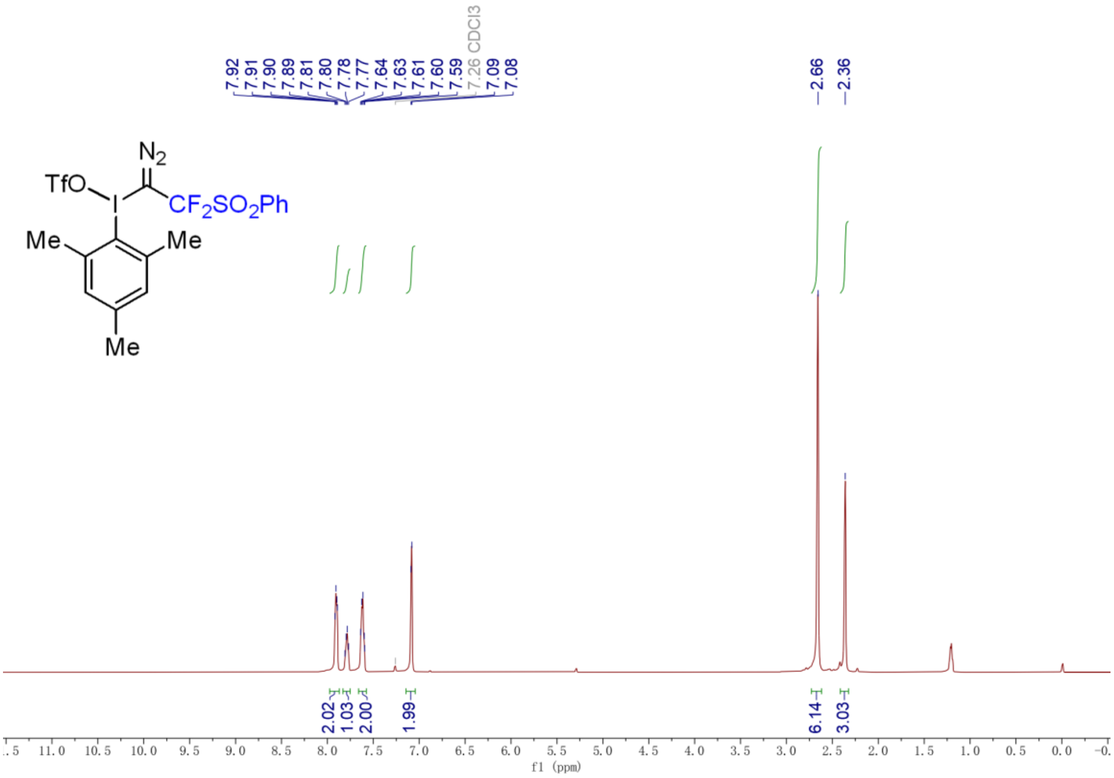
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **DFDI**



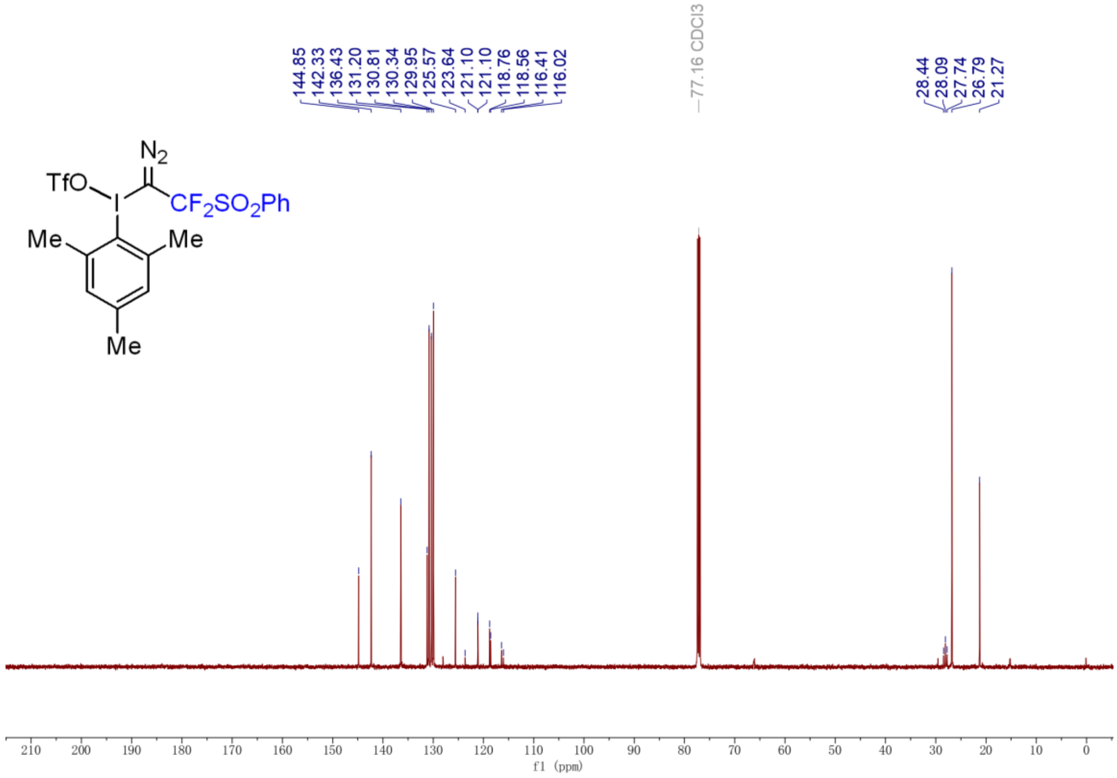
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **DFDI**



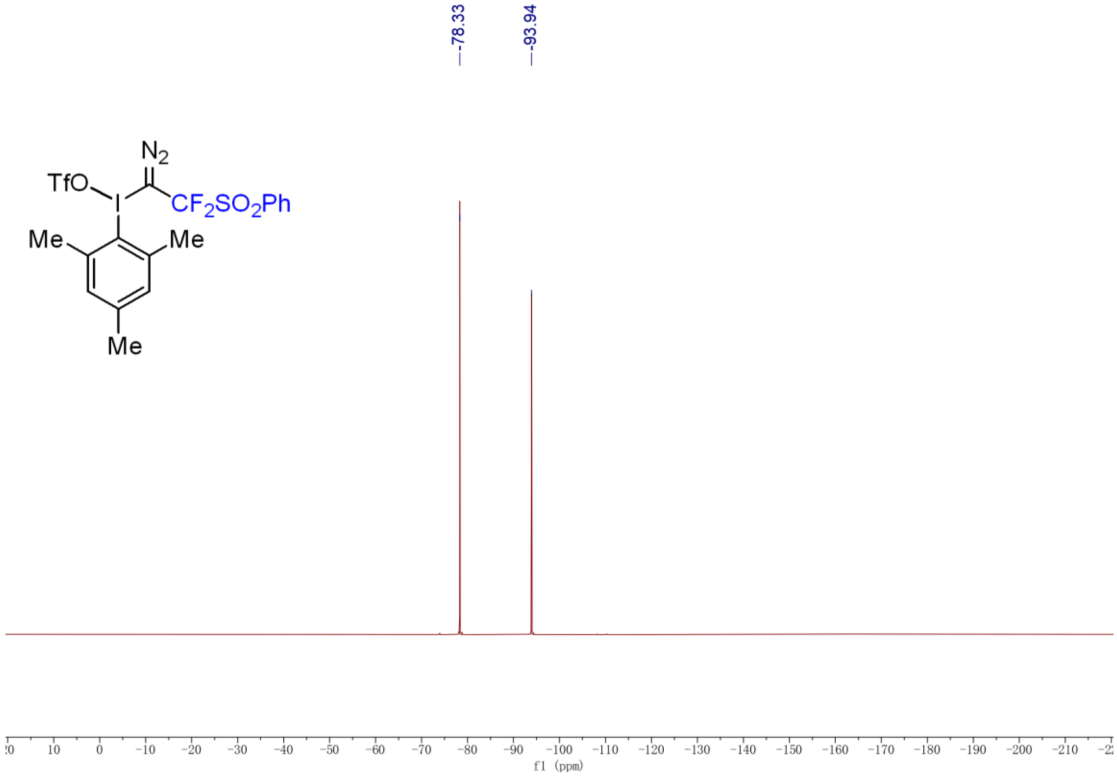
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **DFDI**



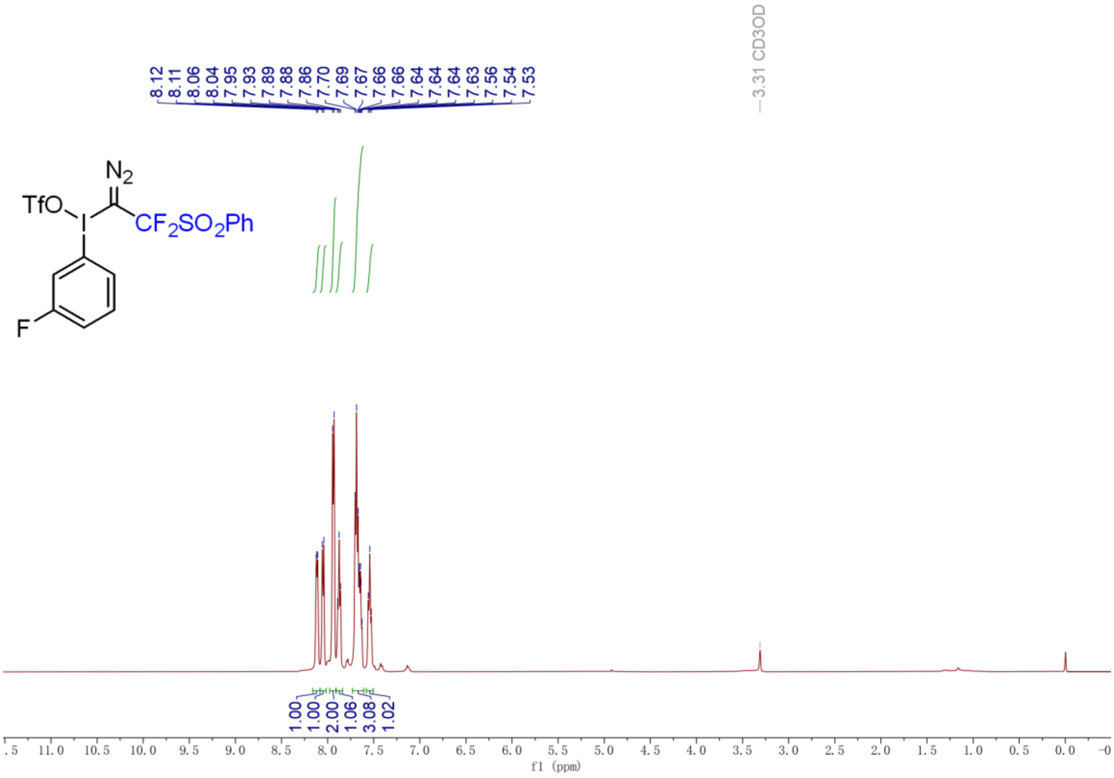
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **DFDI-1**



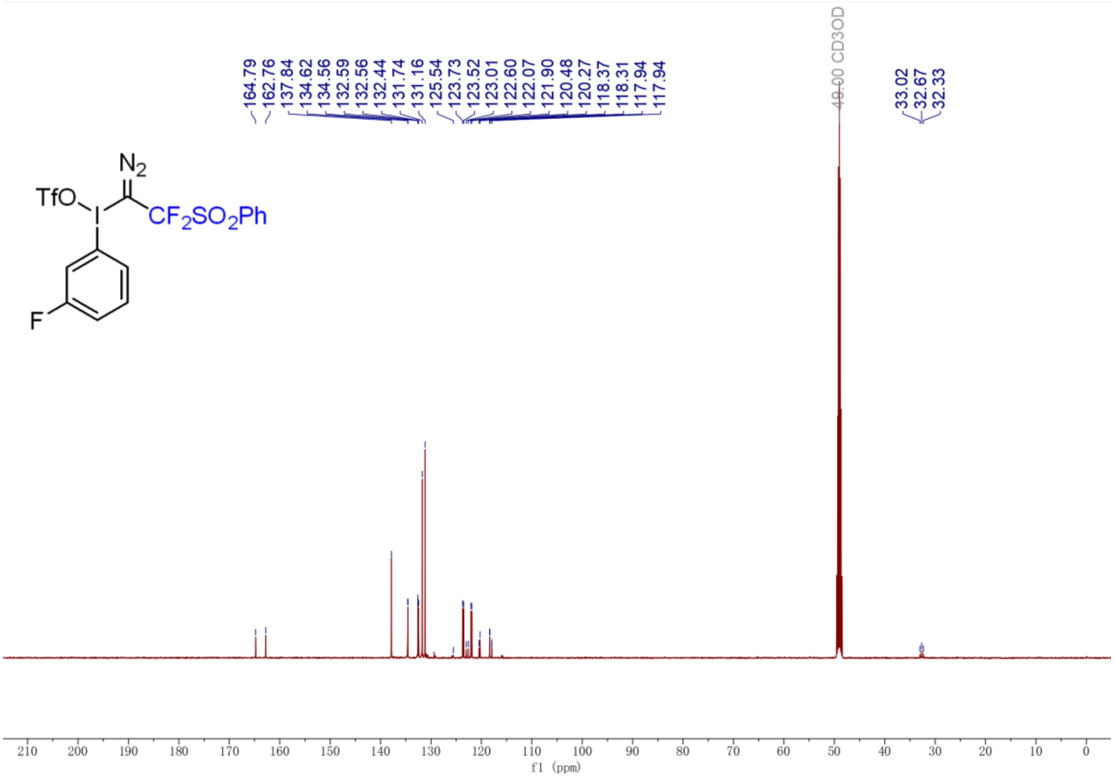
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **DFDI-1**



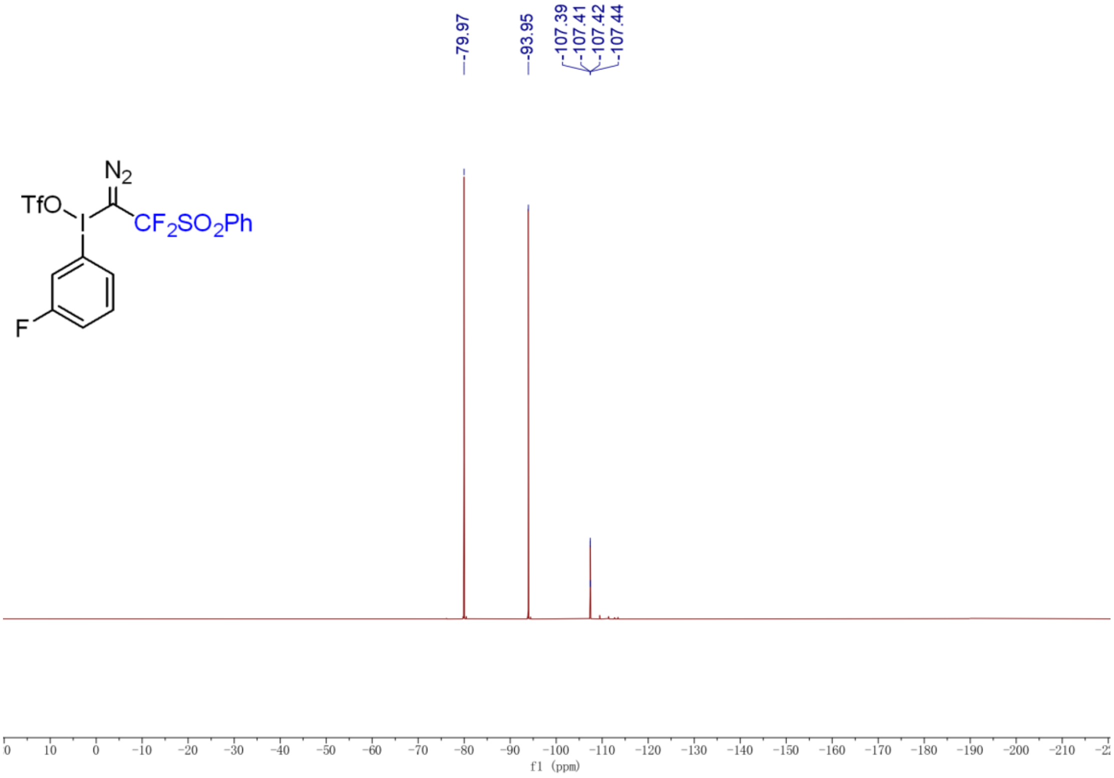
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **DFDI-1**



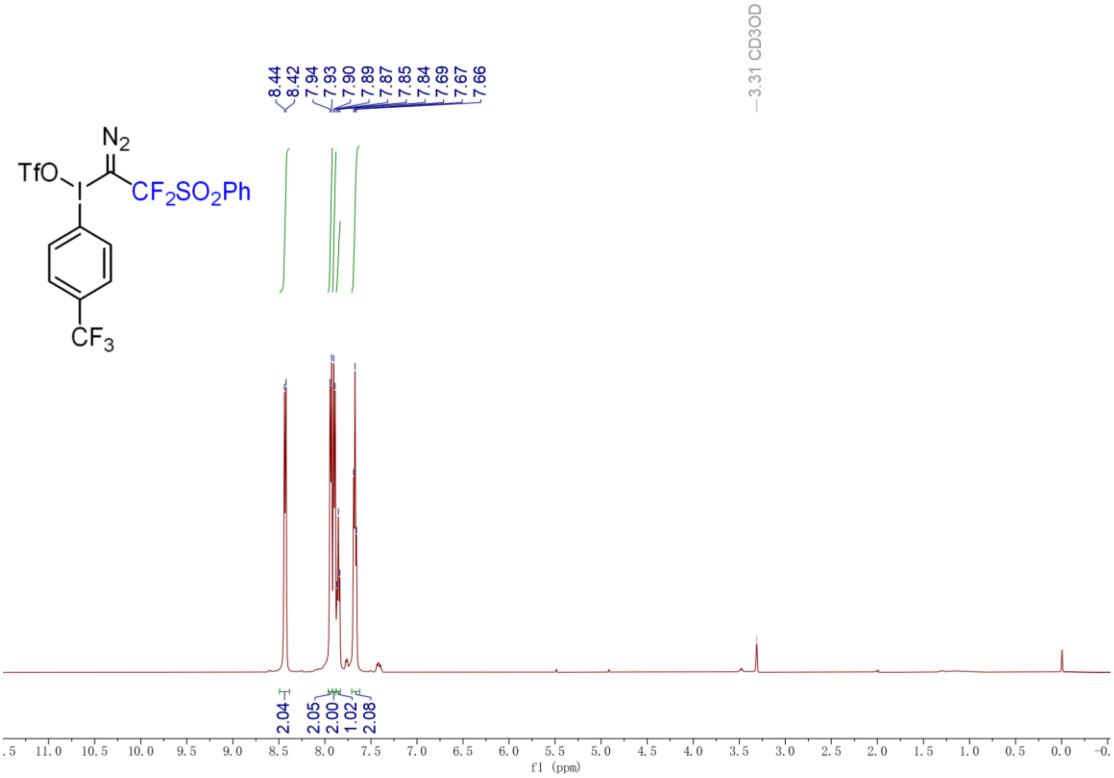
^{1}H NMR spectrum (500 MHz, Methanol-*d$_4$*) of **DFDI-2**



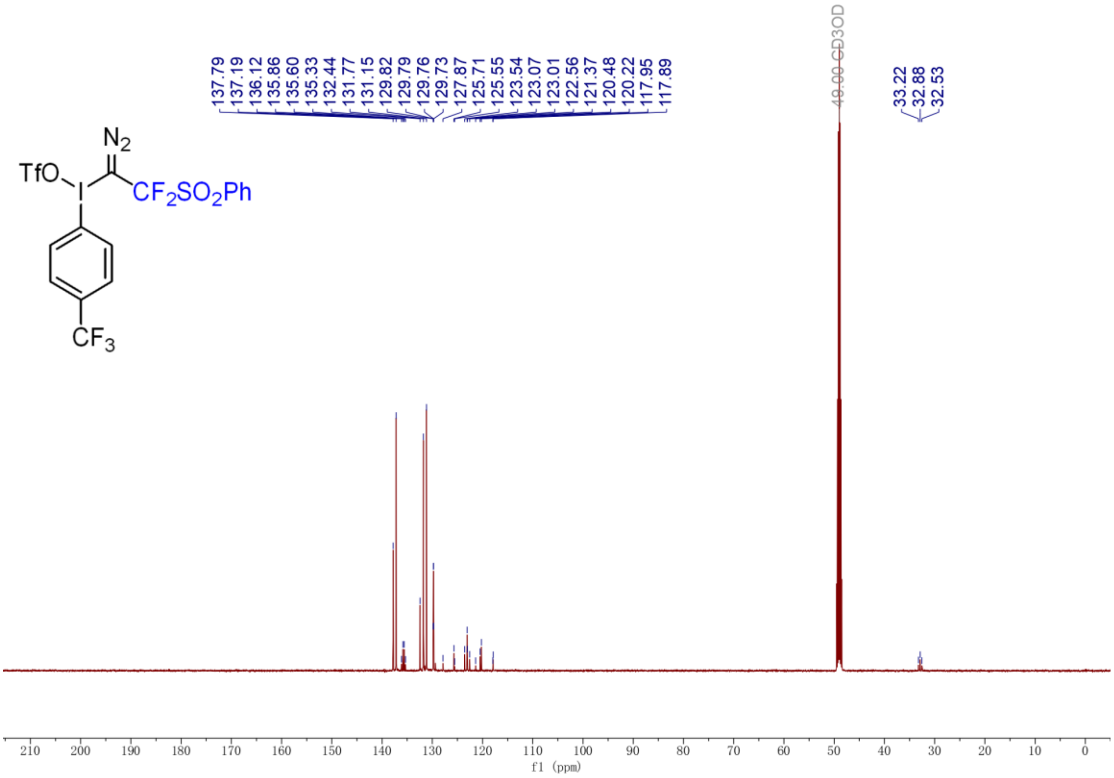
^{13}C NMR spectrum (126 MHz, Methanol-*d$_4$*) of **DFDI-2**



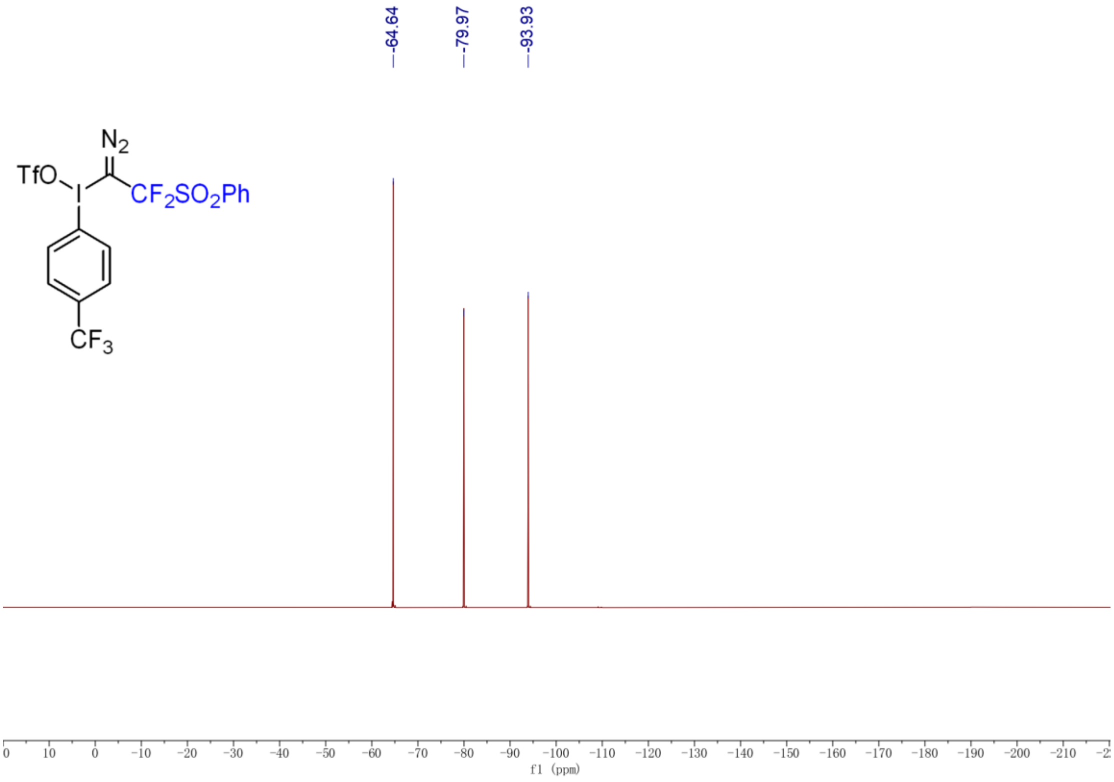
^{19}F NMR spectrum (471 MHz, Methanol-d_4) of **DFDI-2**



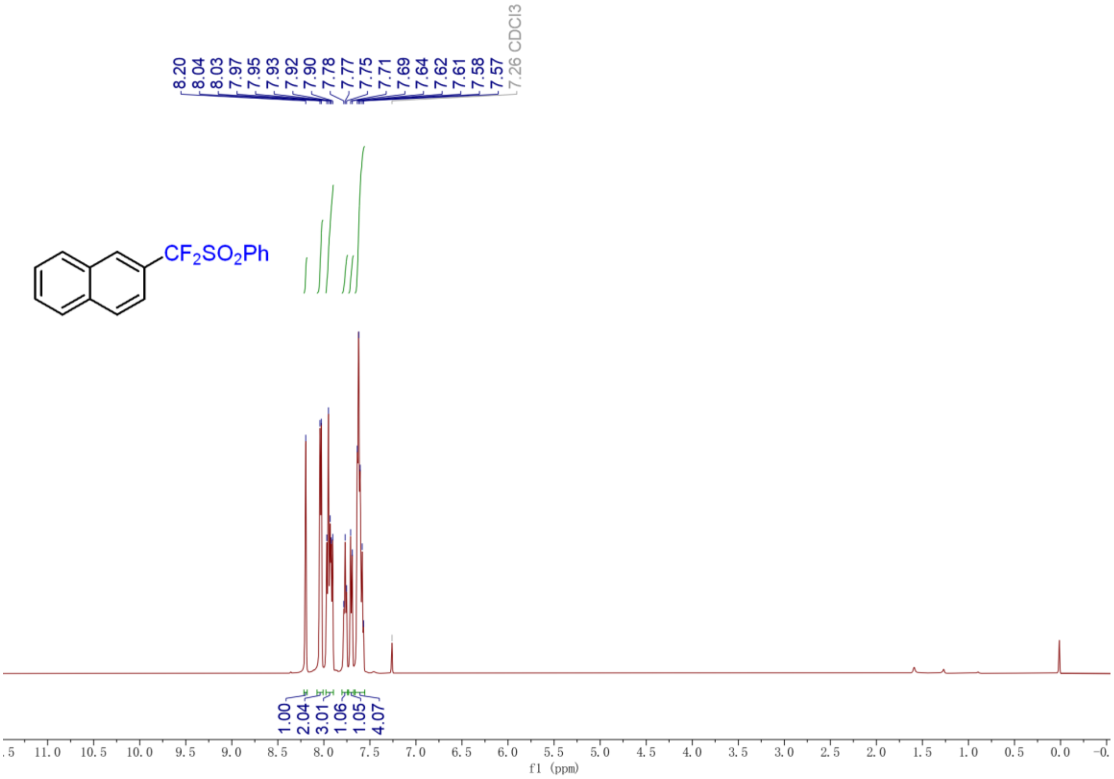
^{1}H NMR spectrum (500 MHz, Methanol-d_4) of **DFDI-3**



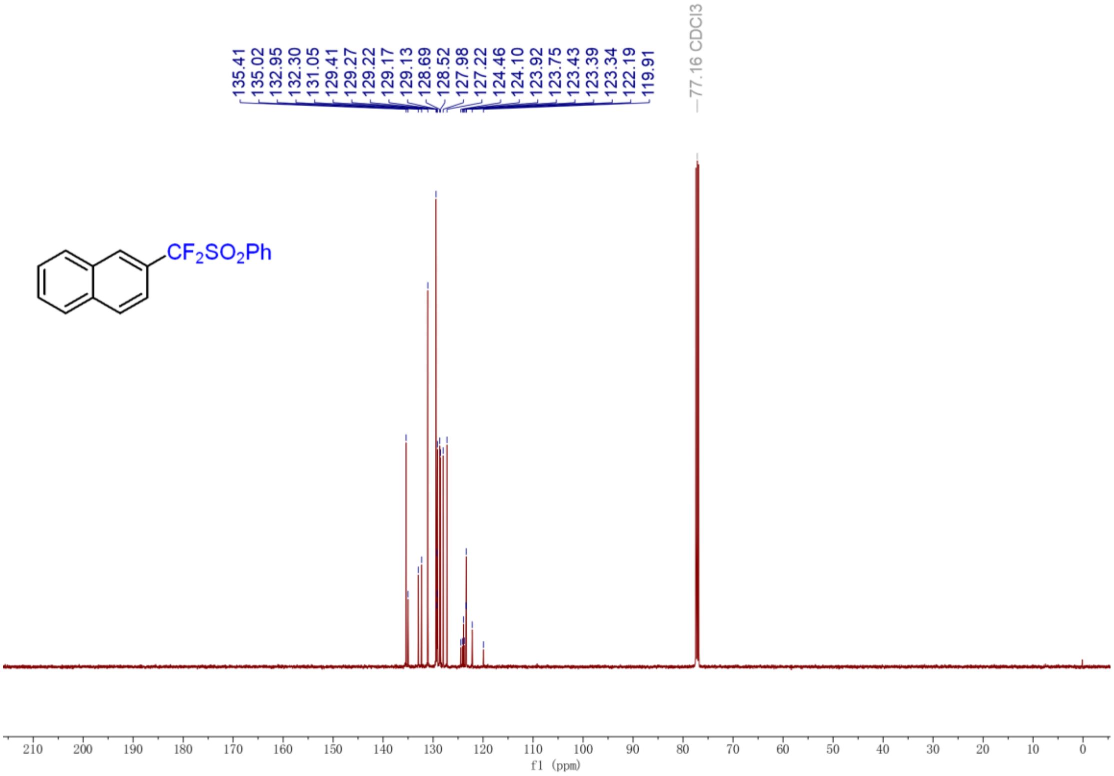
^{13}C NMR spectrum (126 MHz, Methanol-*d$_4$*) of **DFDI-3**



^{19}F NMR spectrum (471 MHz, Methanol-*d$_4$*) of **DFDI-3**



^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2a**



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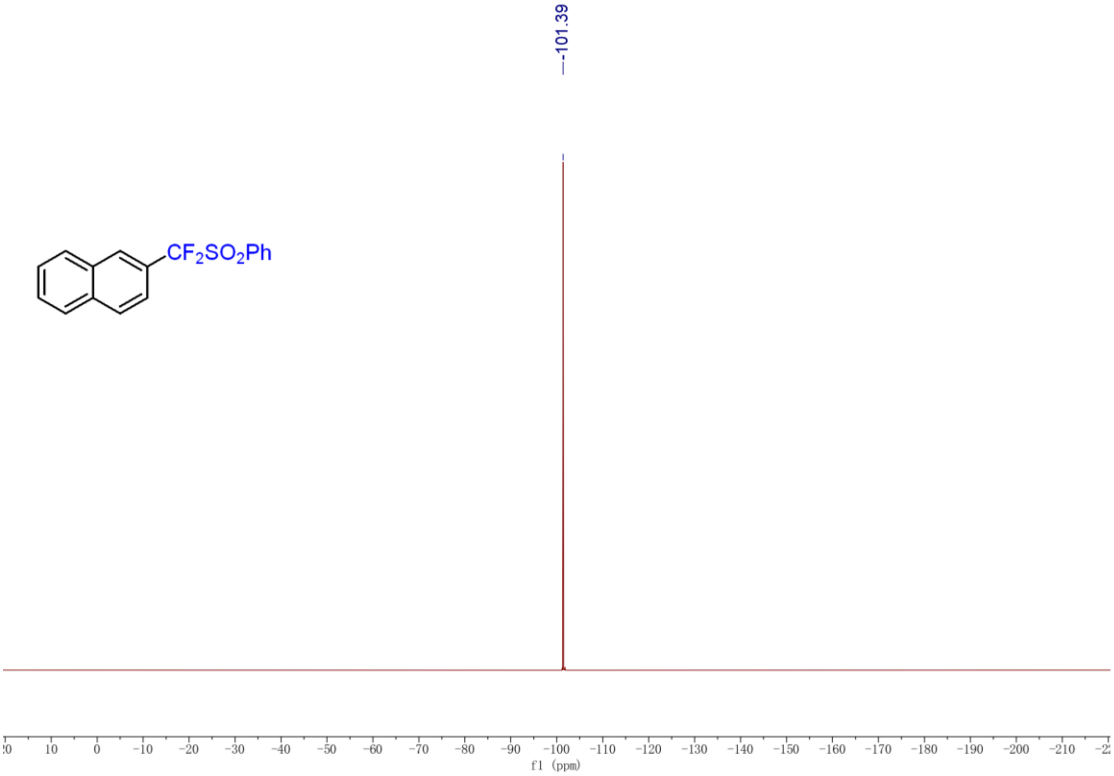
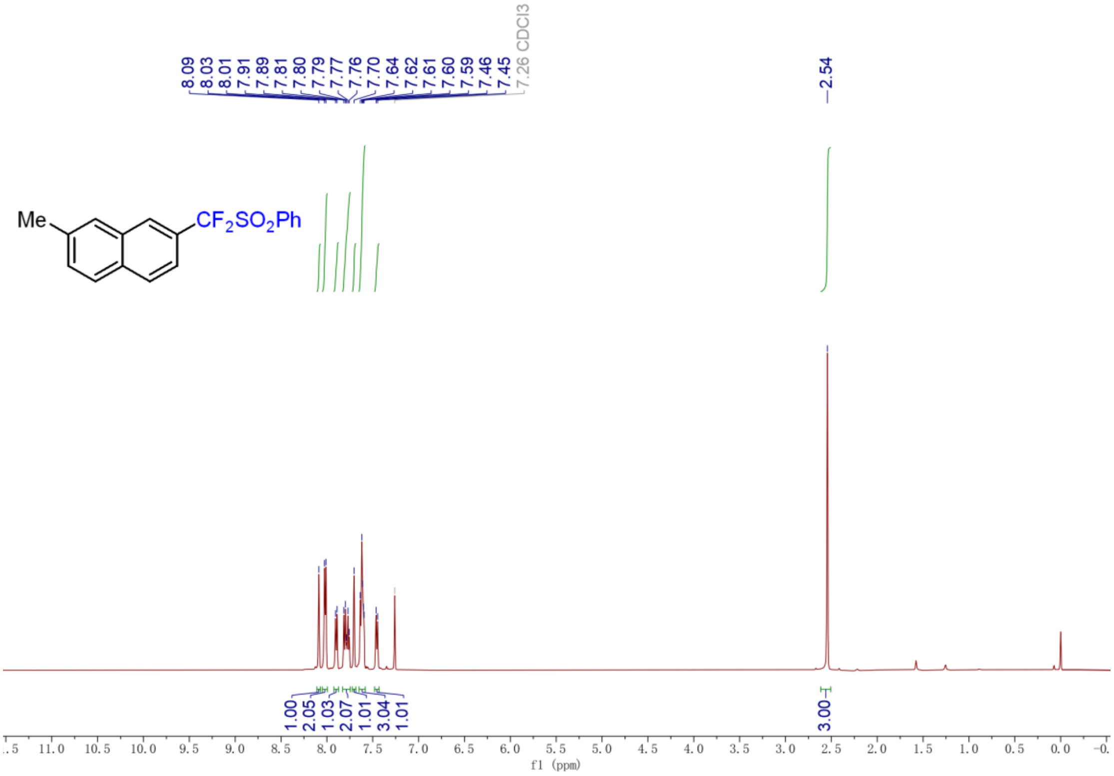
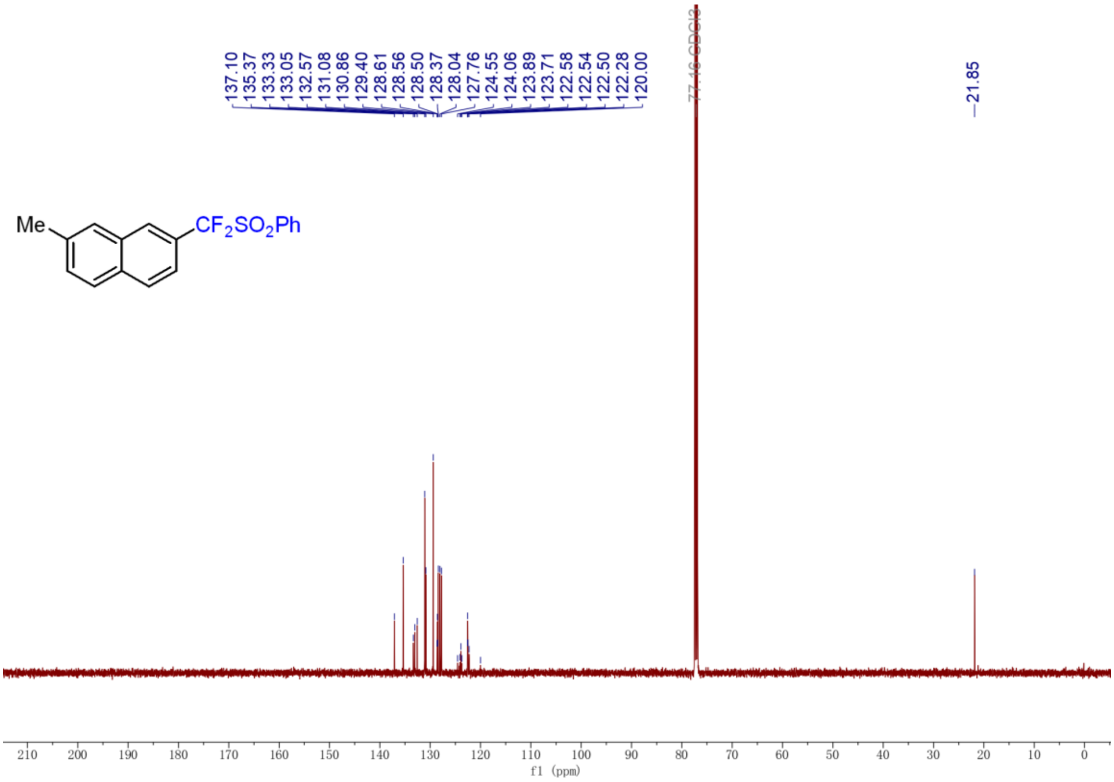


^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2a**



^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2b**



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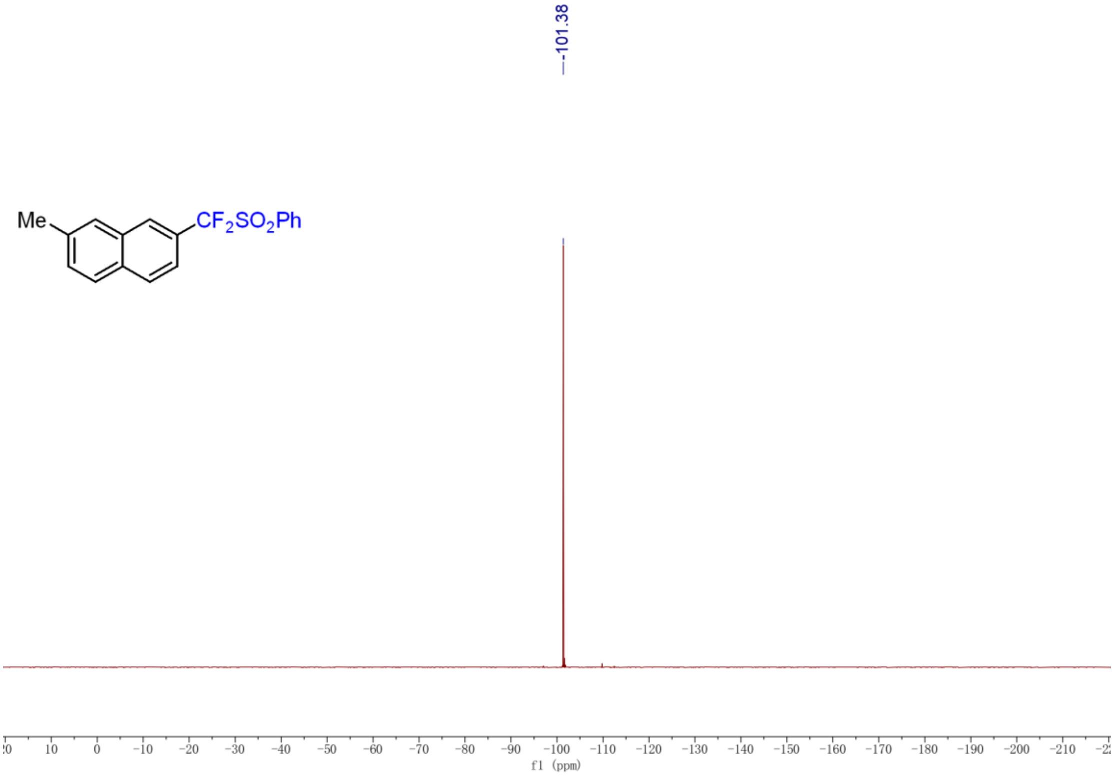
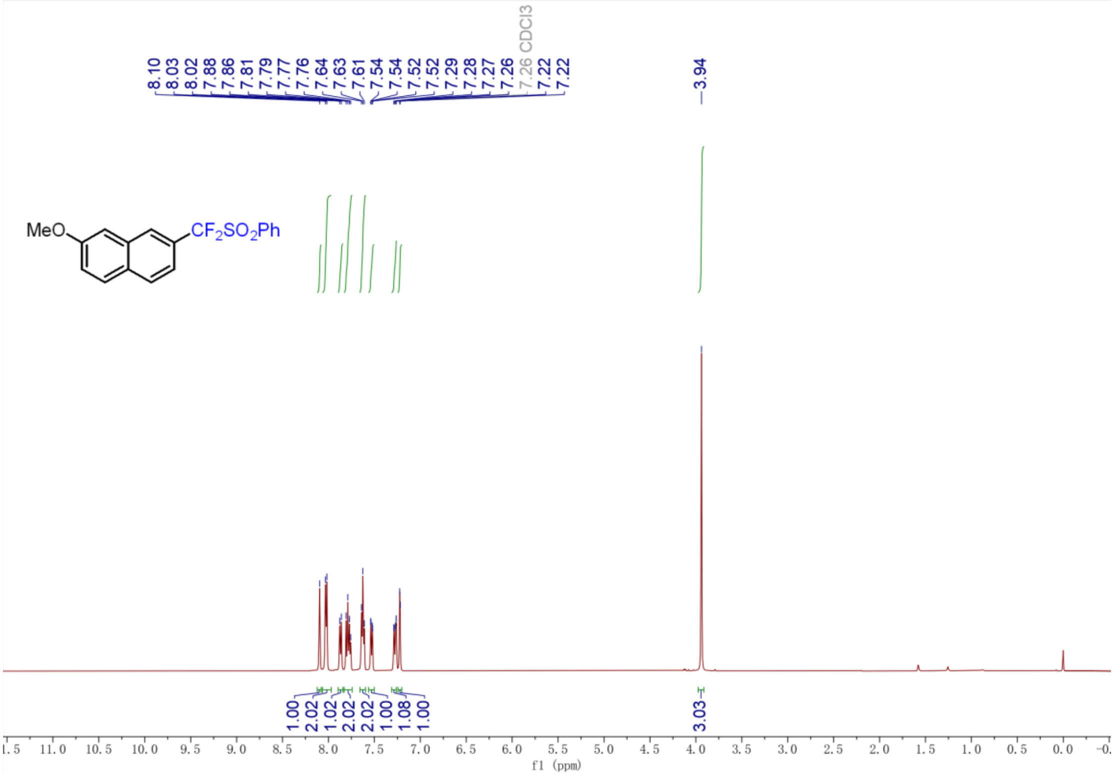
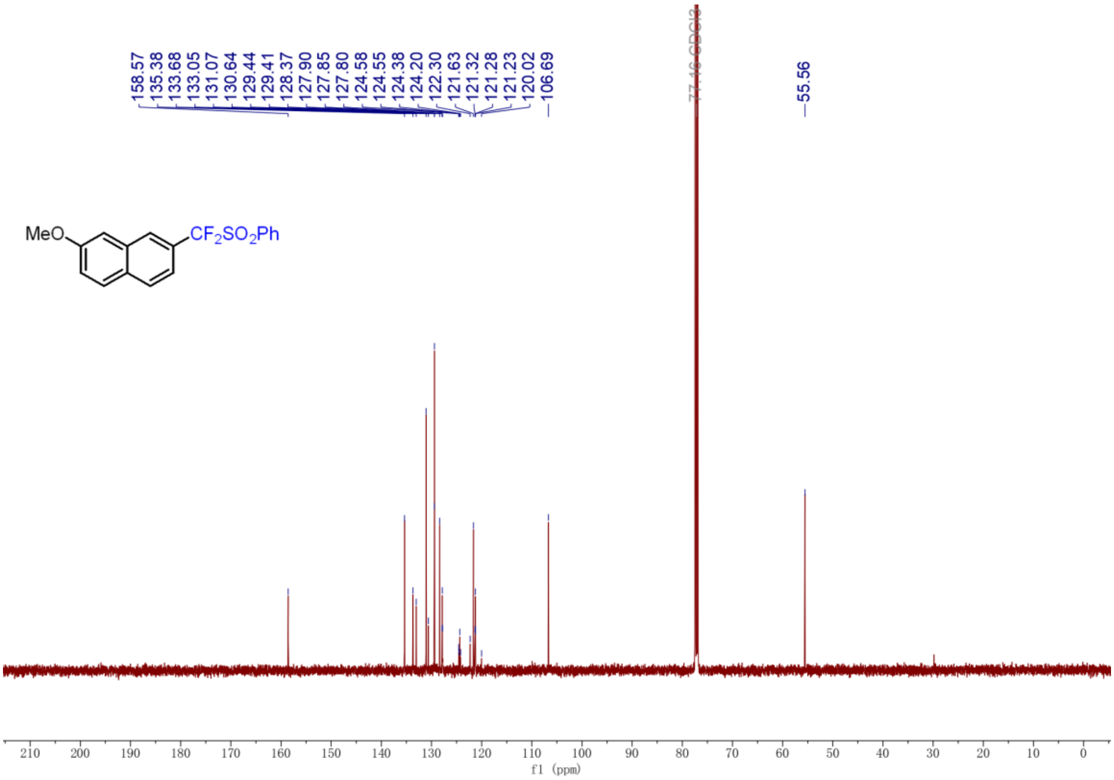


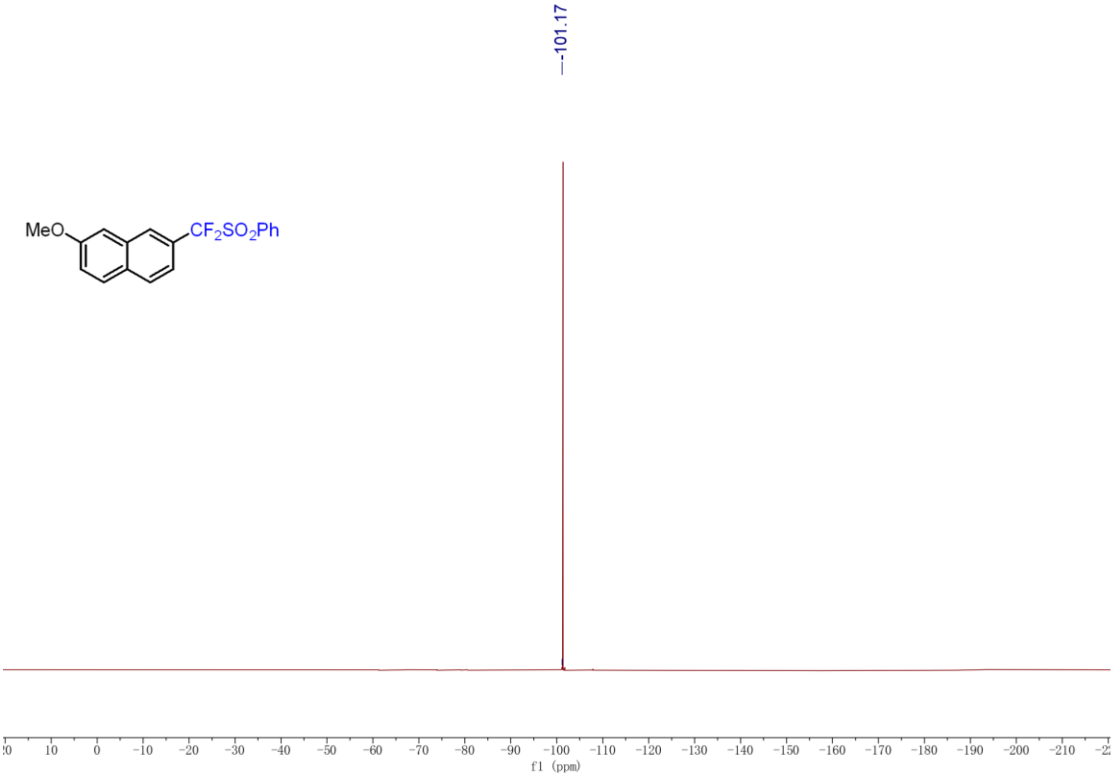
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2b**



^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2c**



^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2c**



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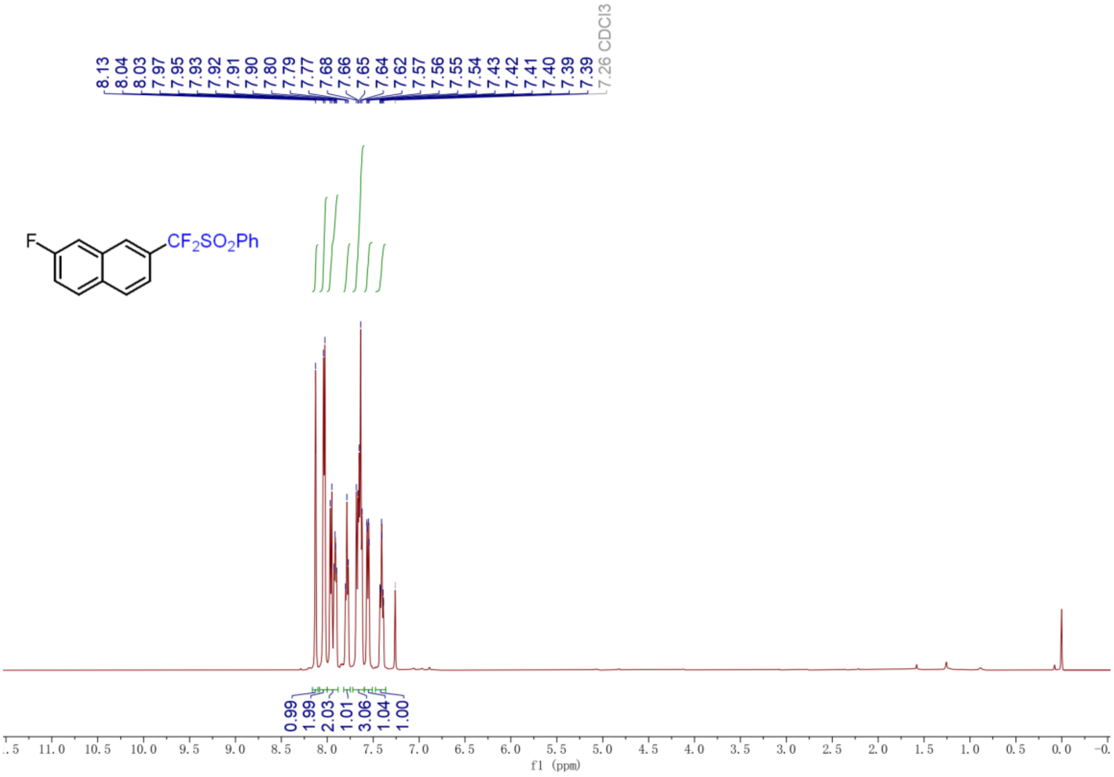

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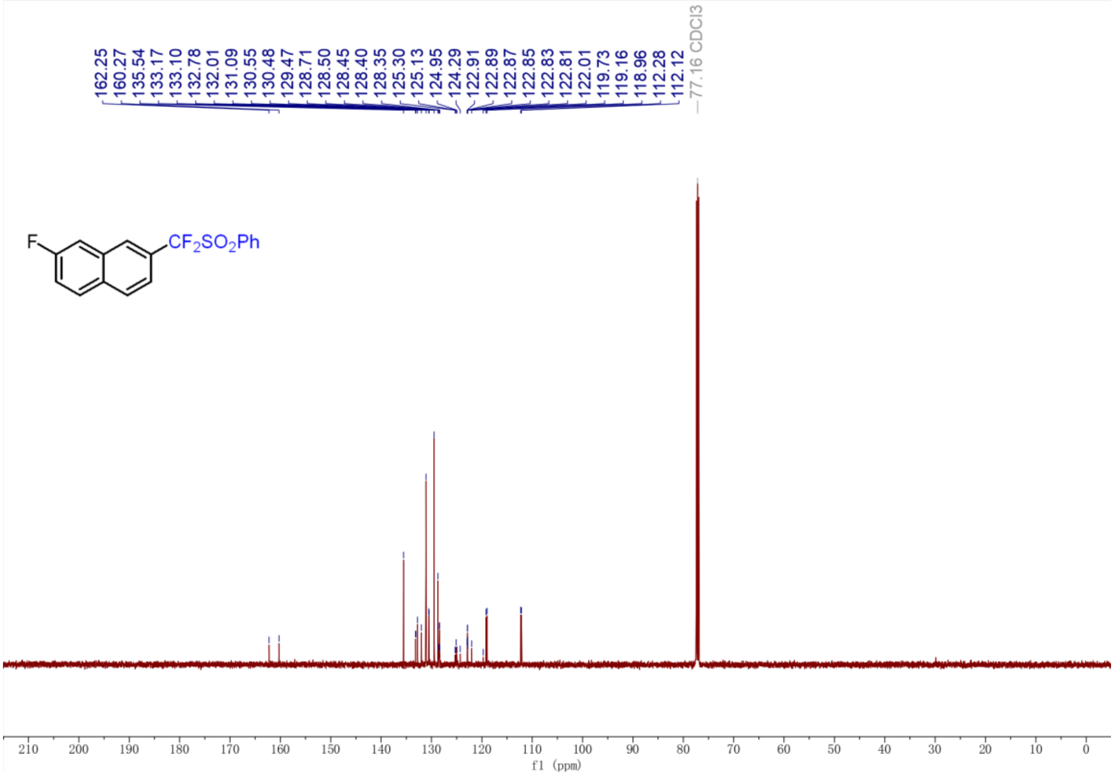

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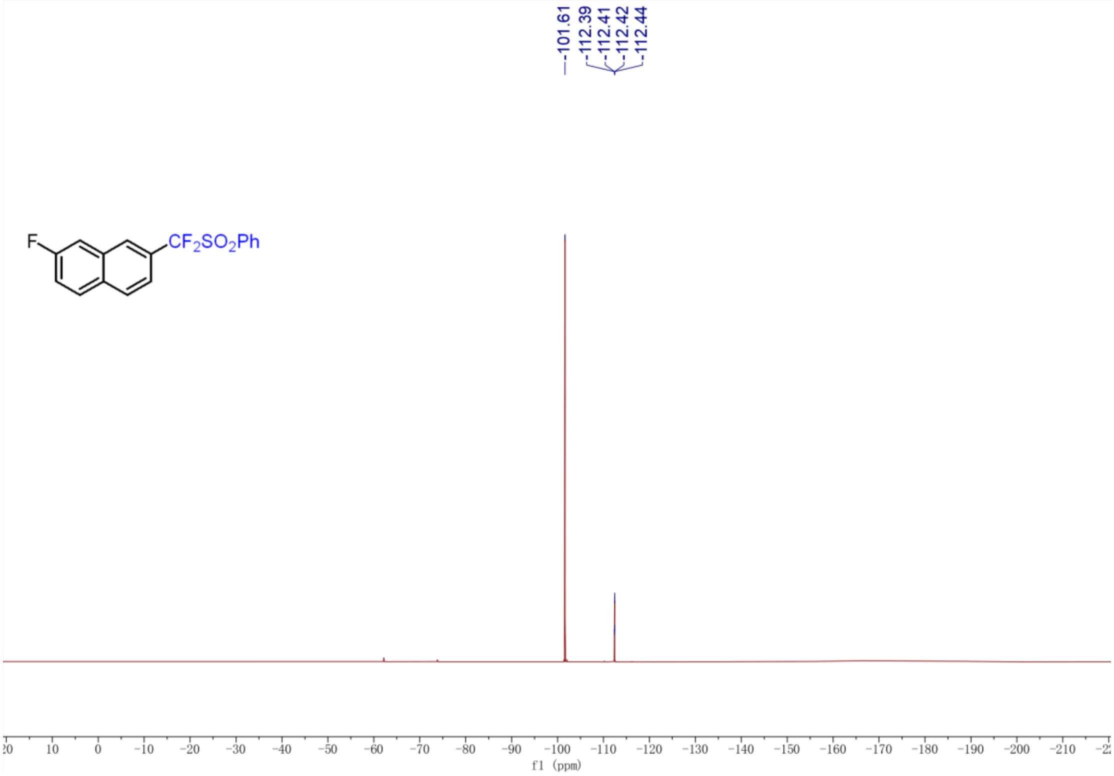

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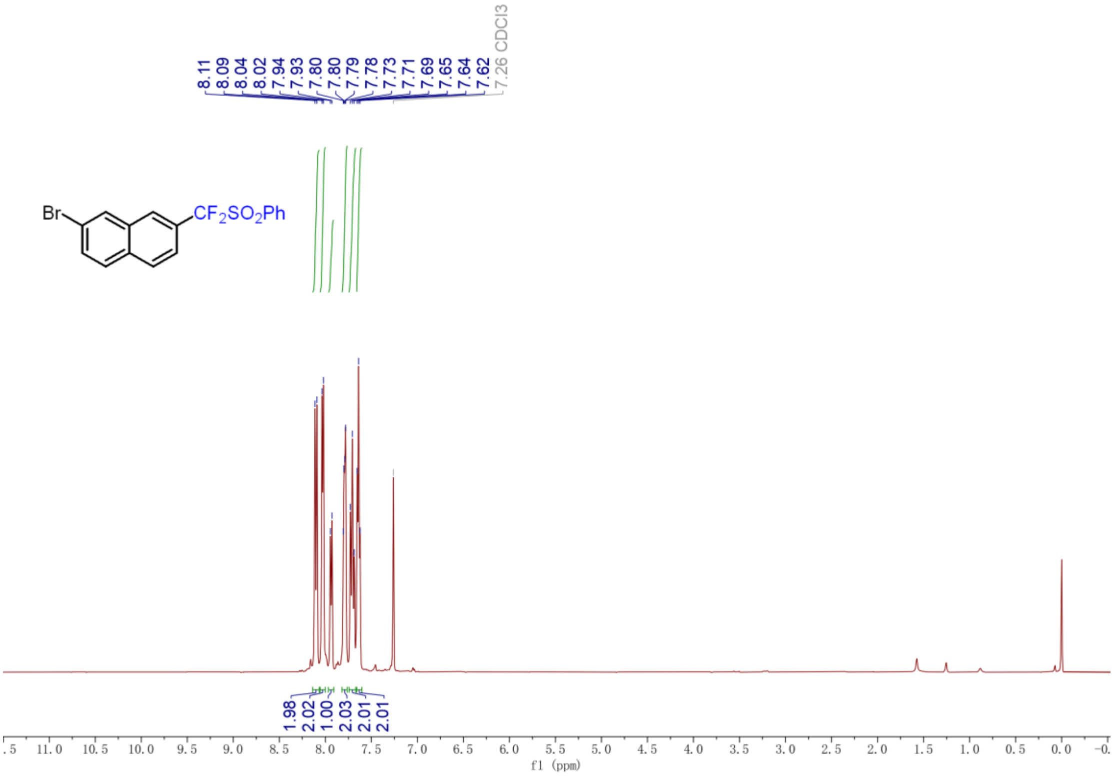

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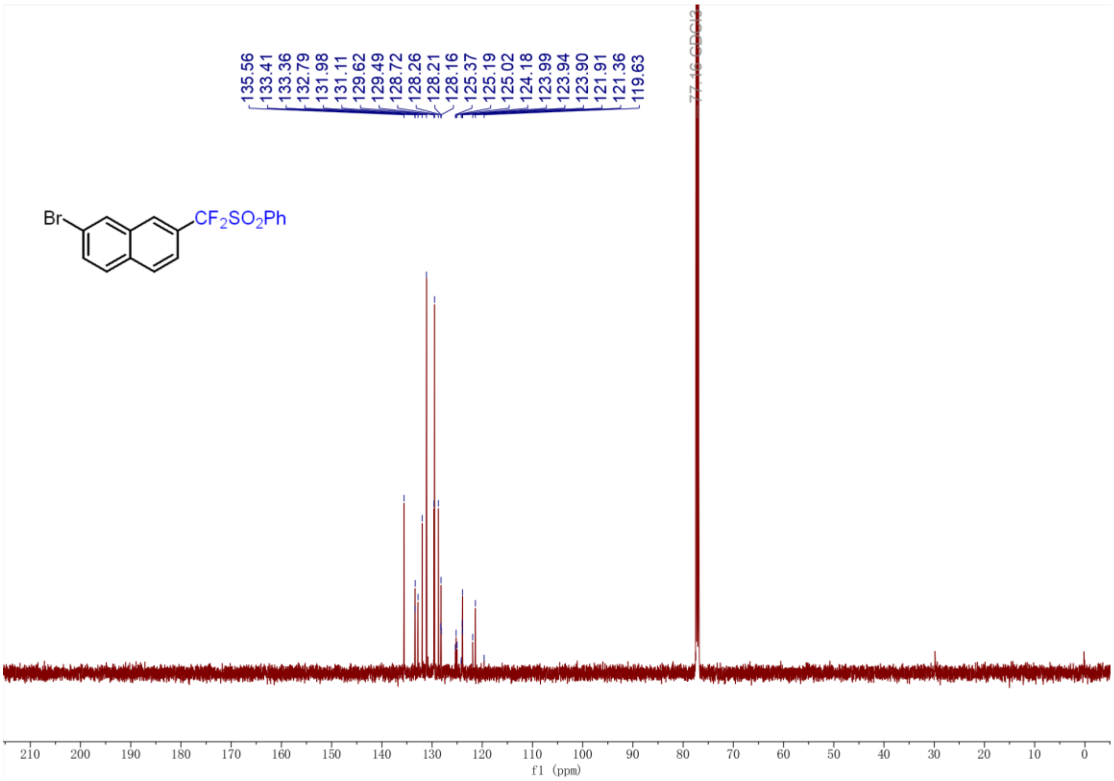

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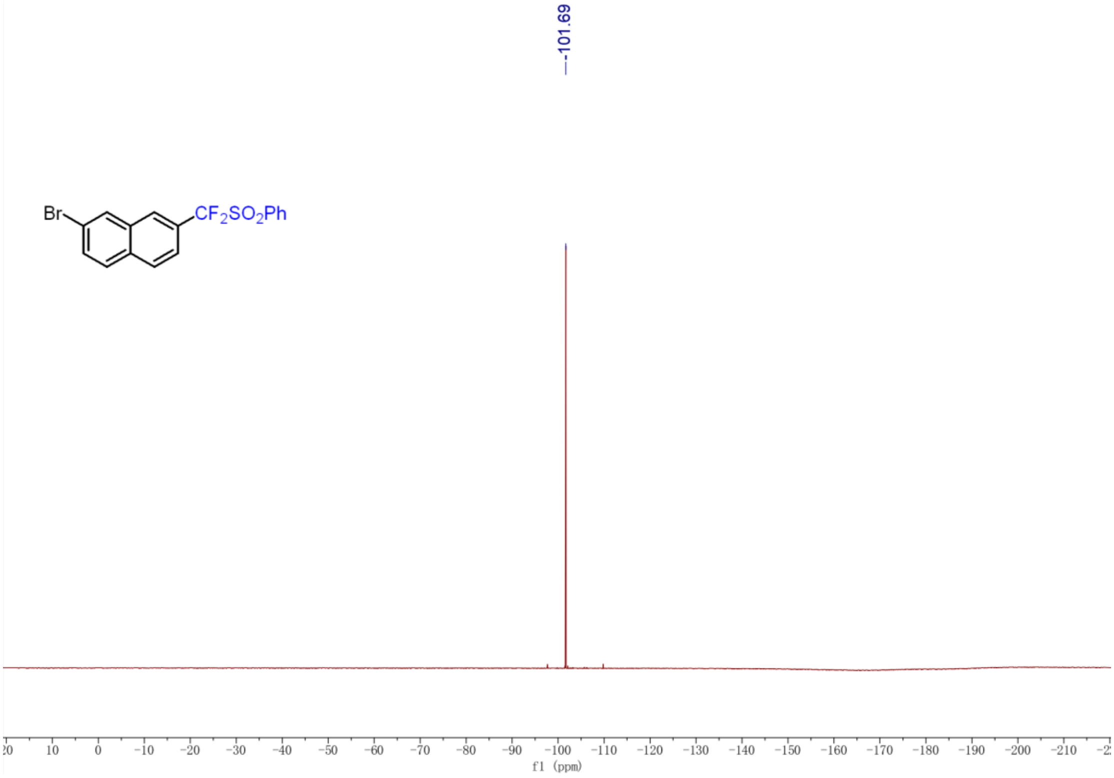

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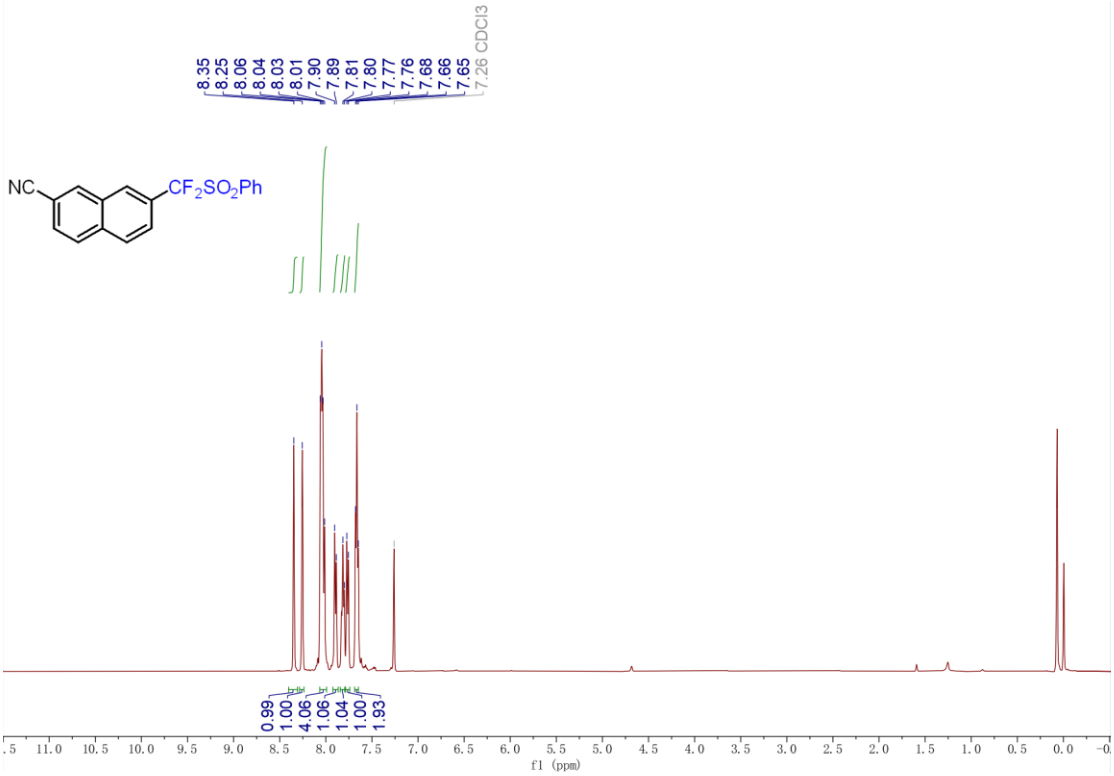

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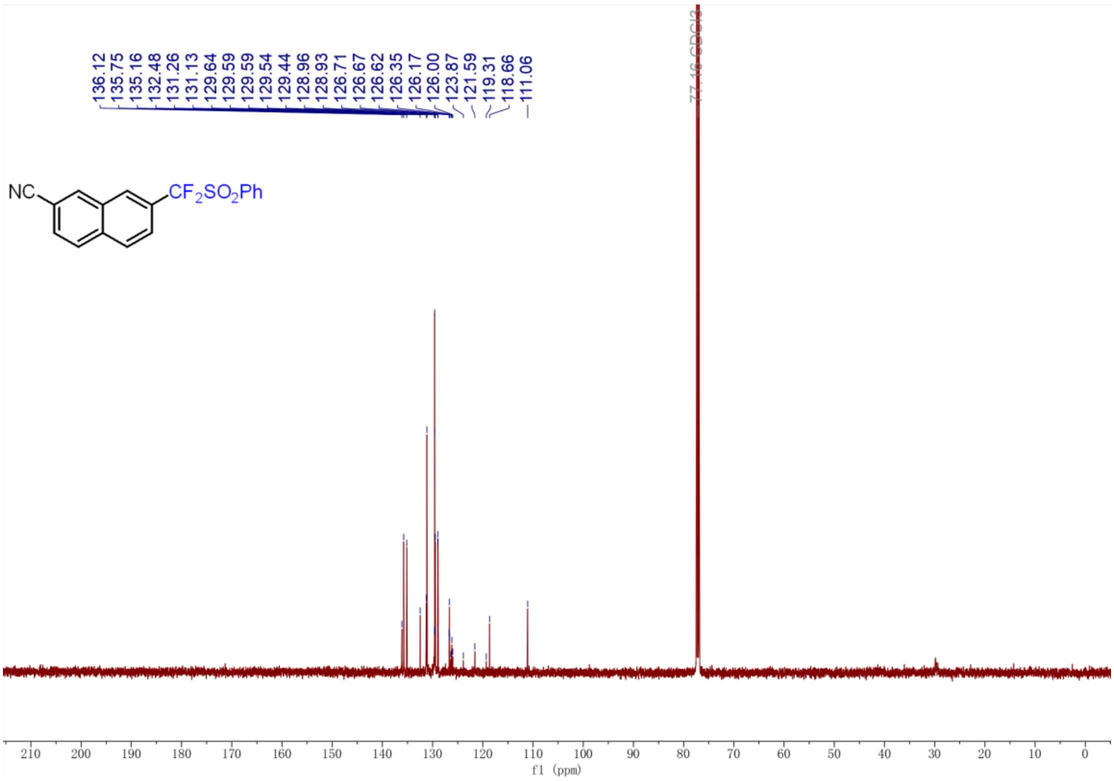
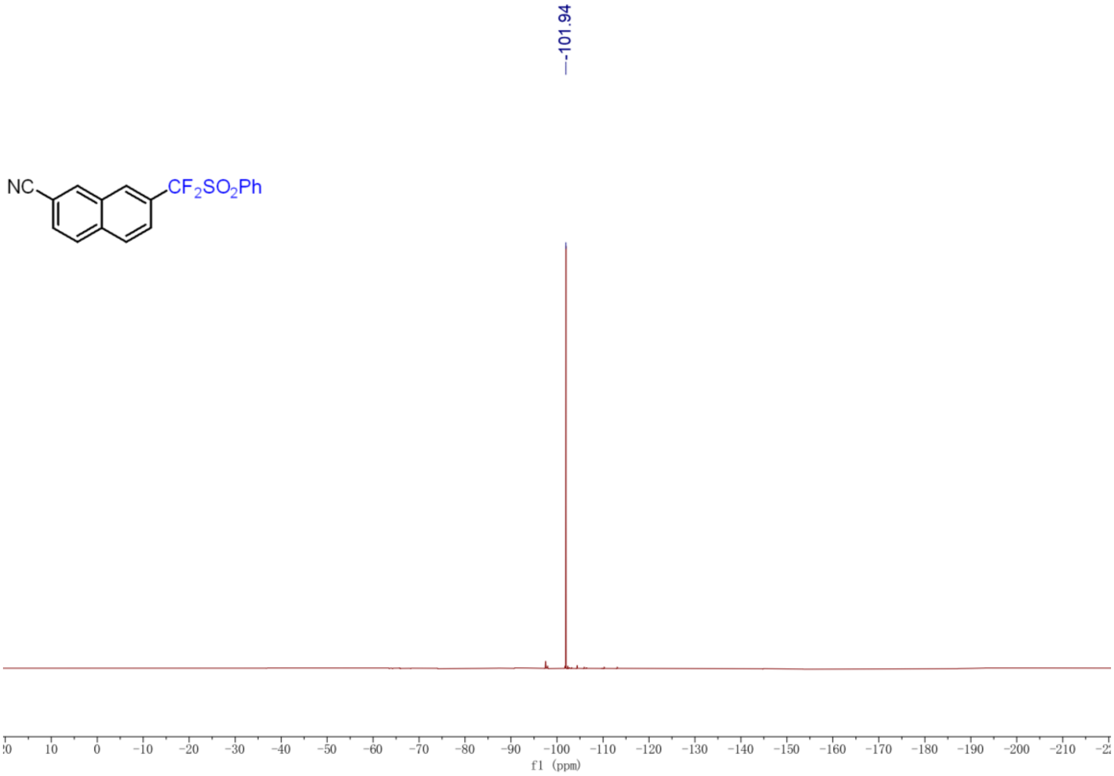


^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2f**



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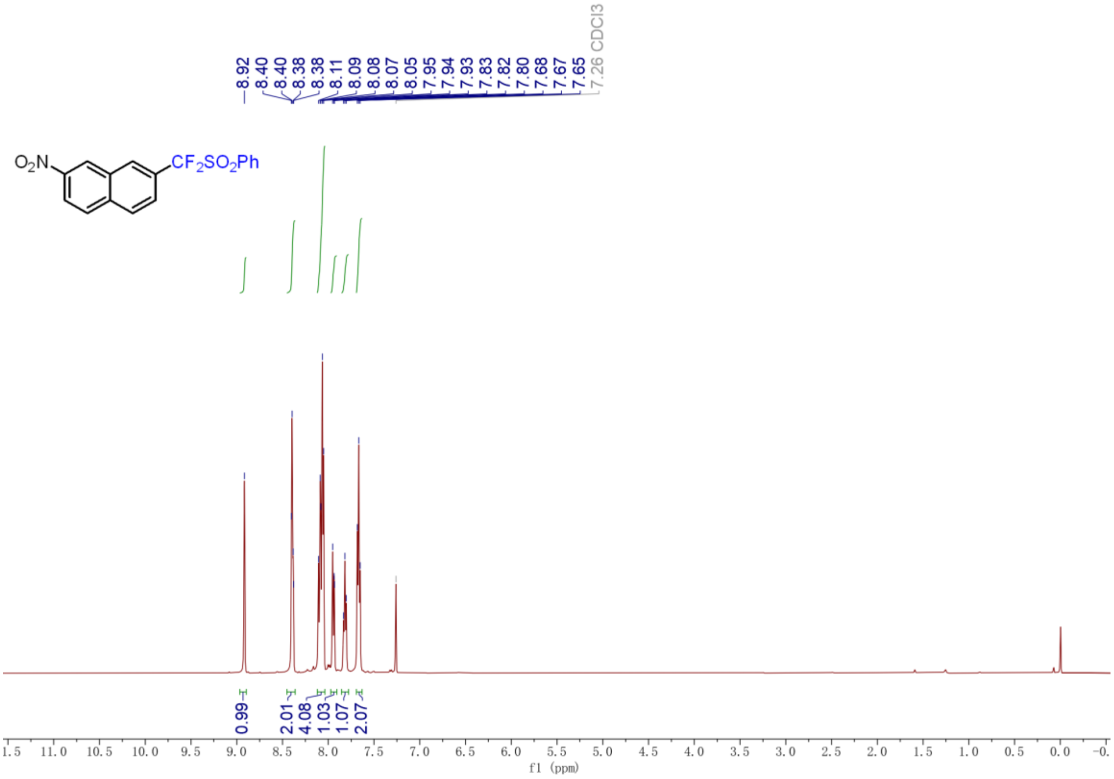

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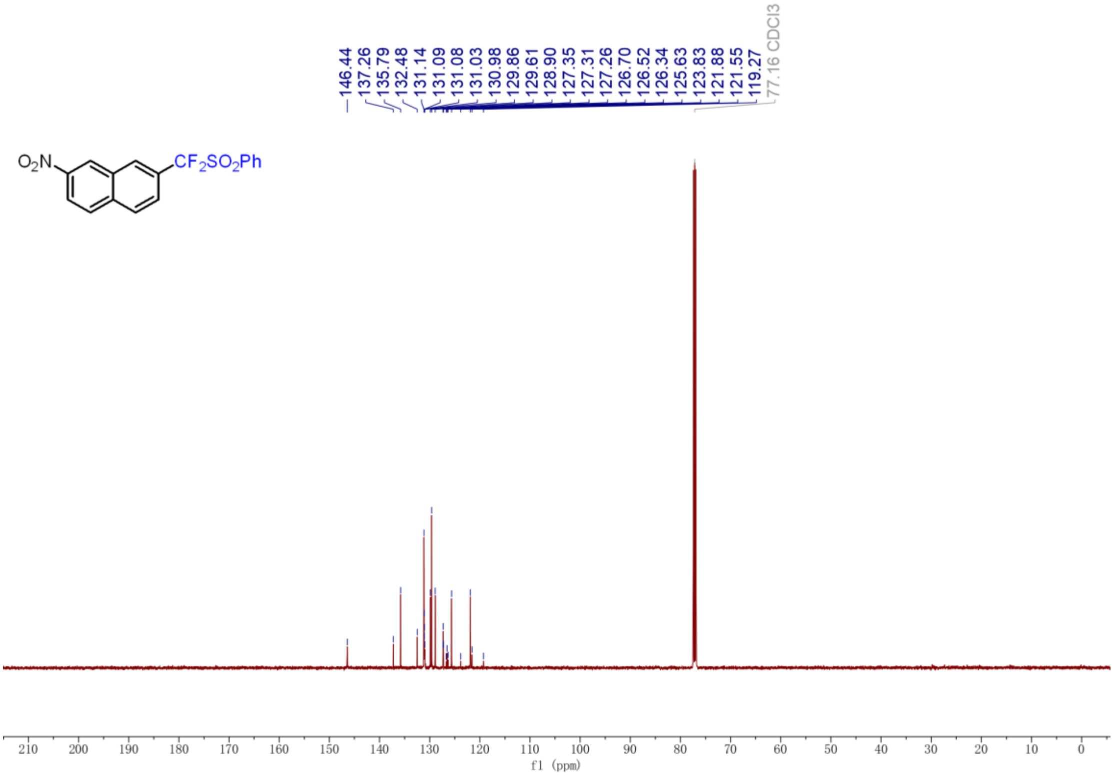

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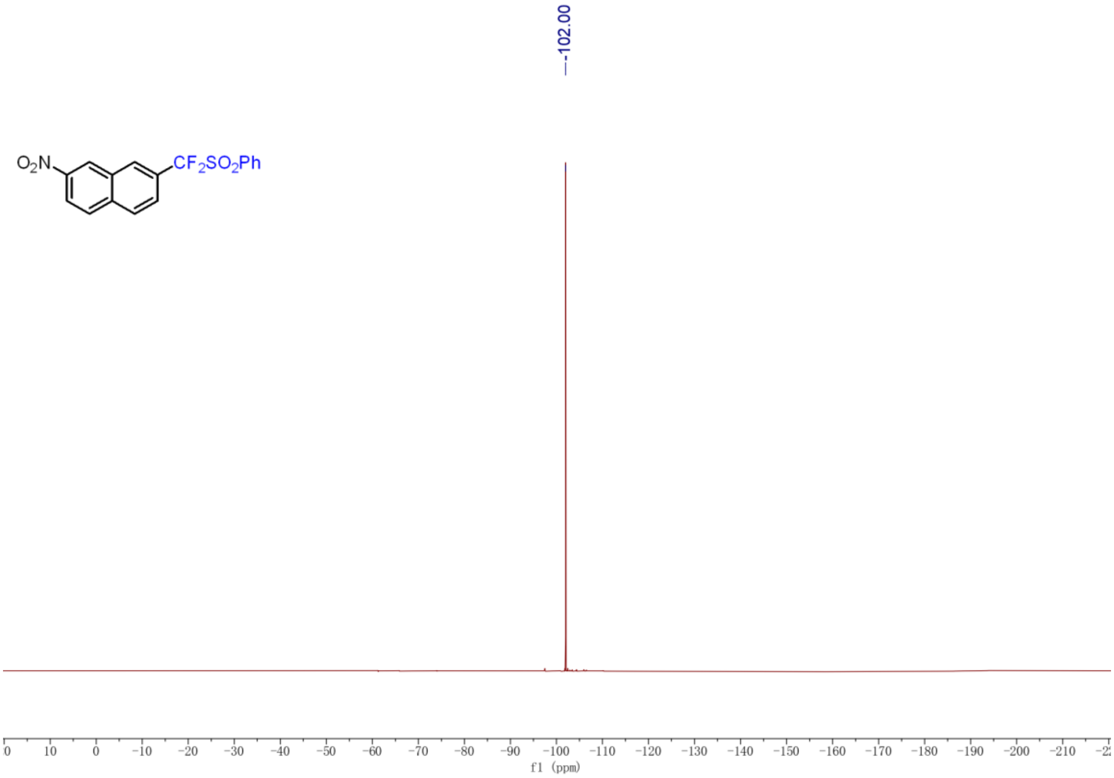

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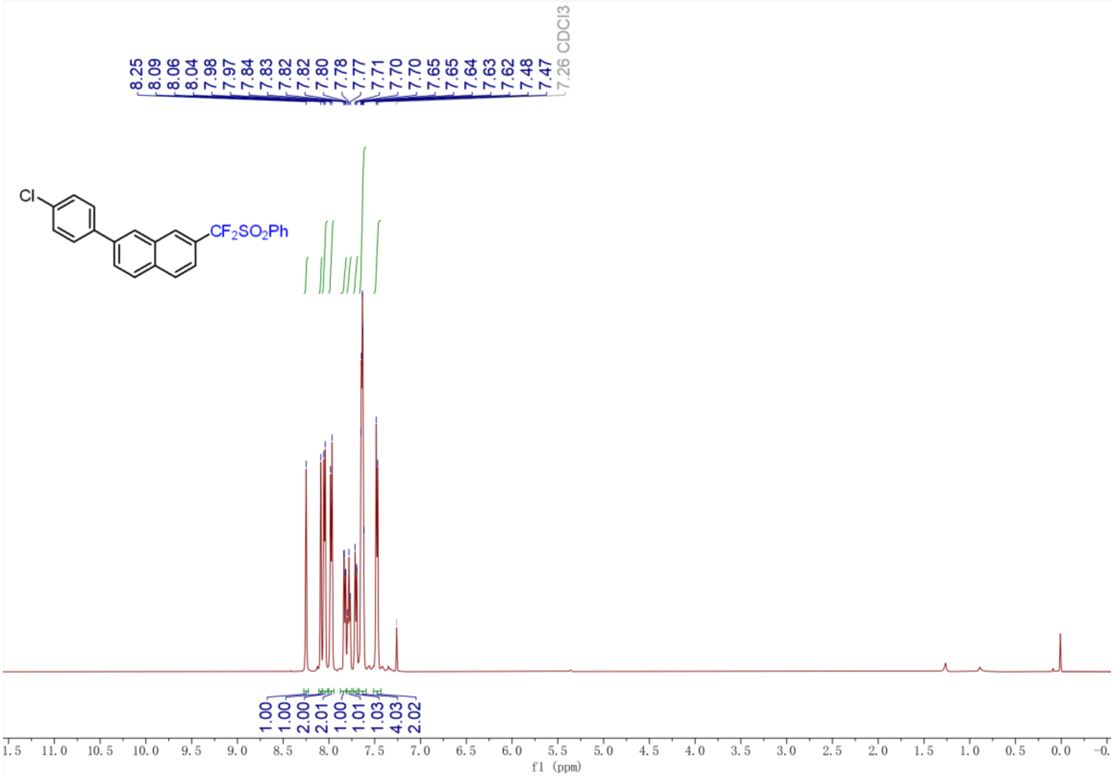

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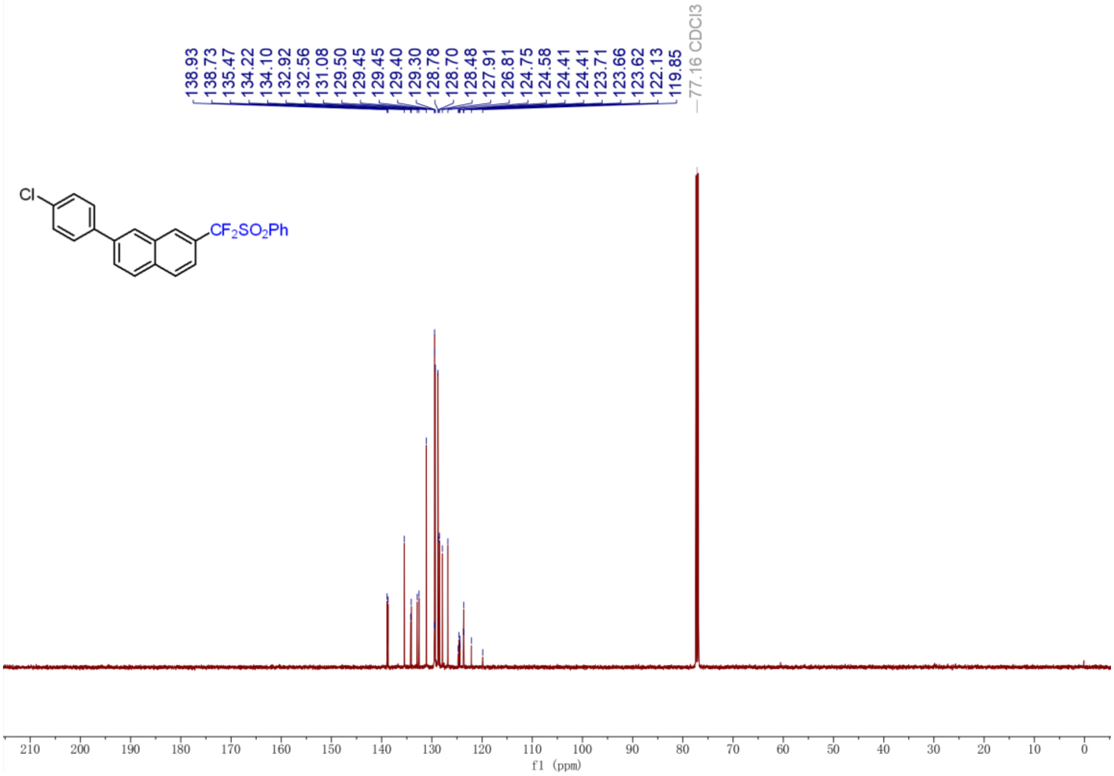

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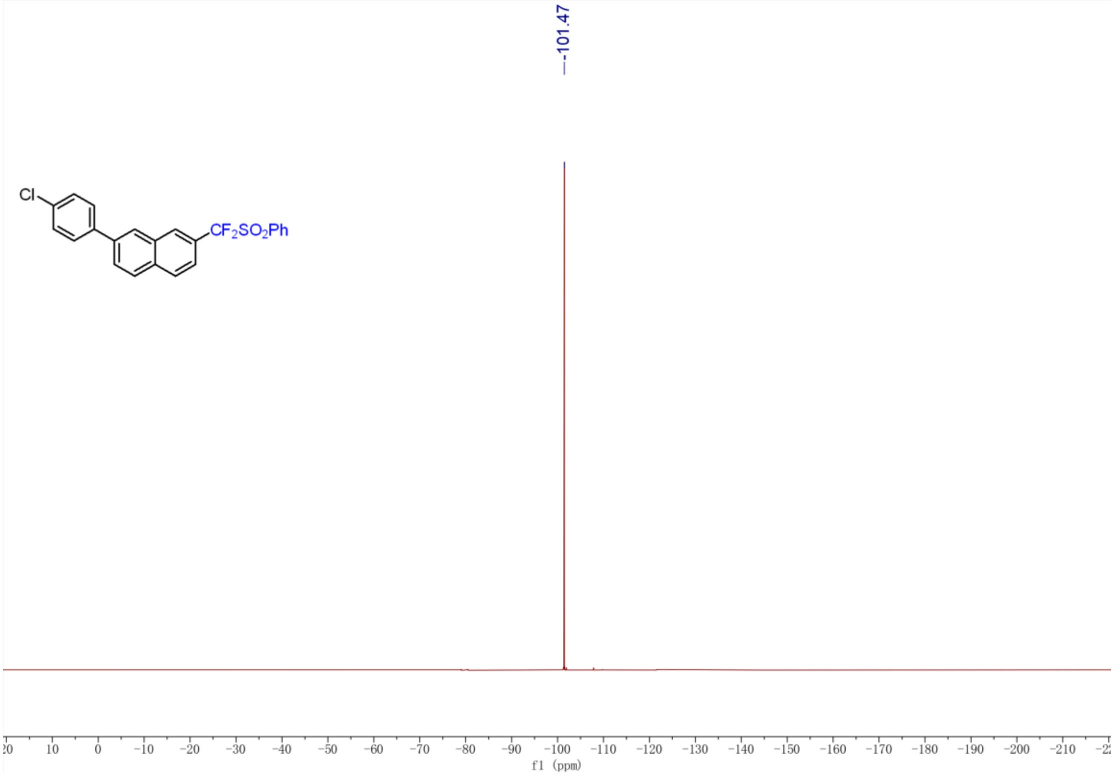

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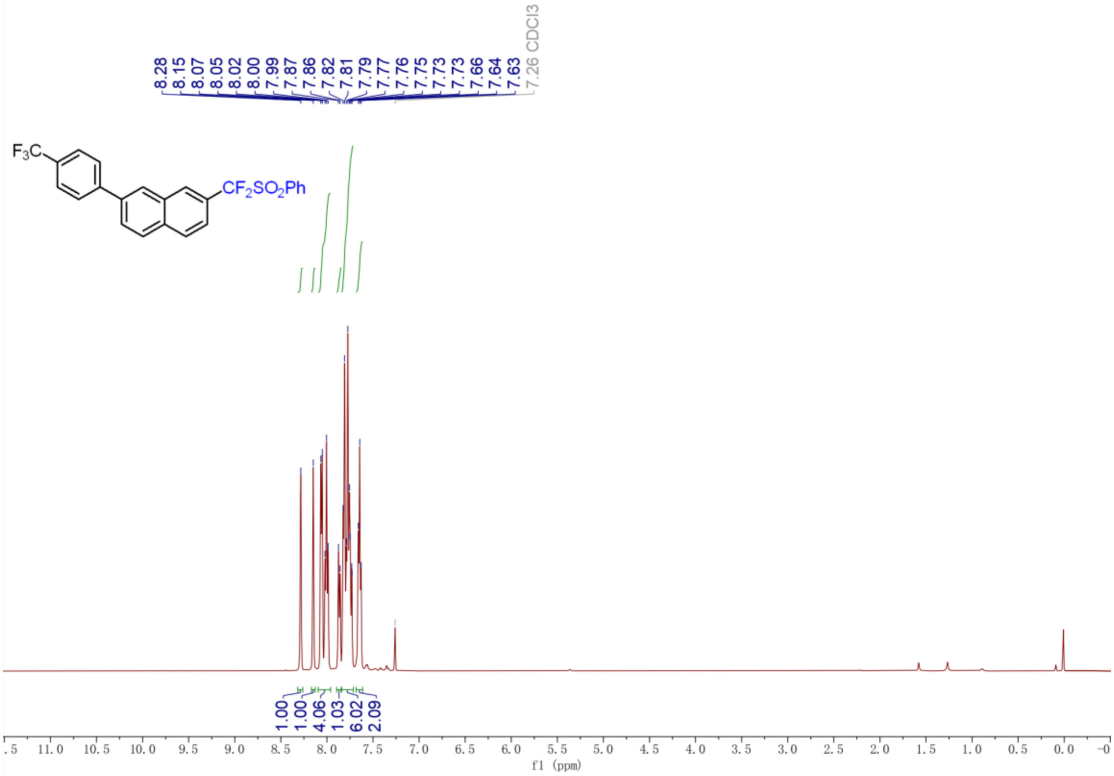

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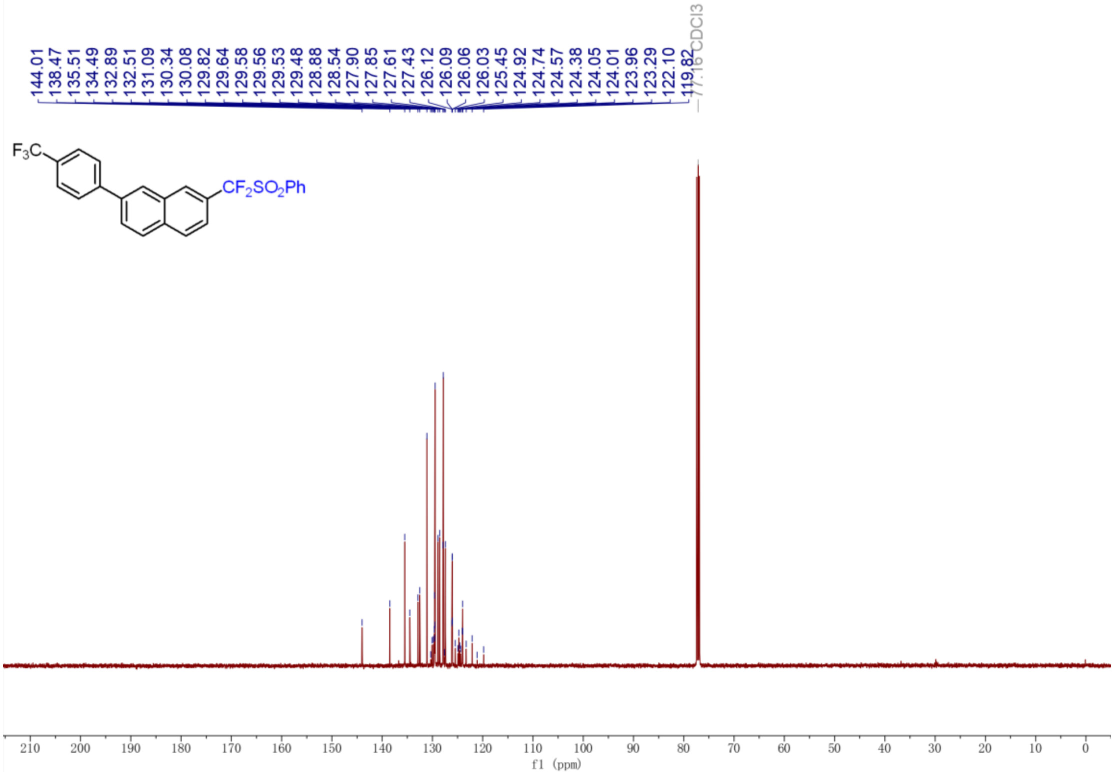

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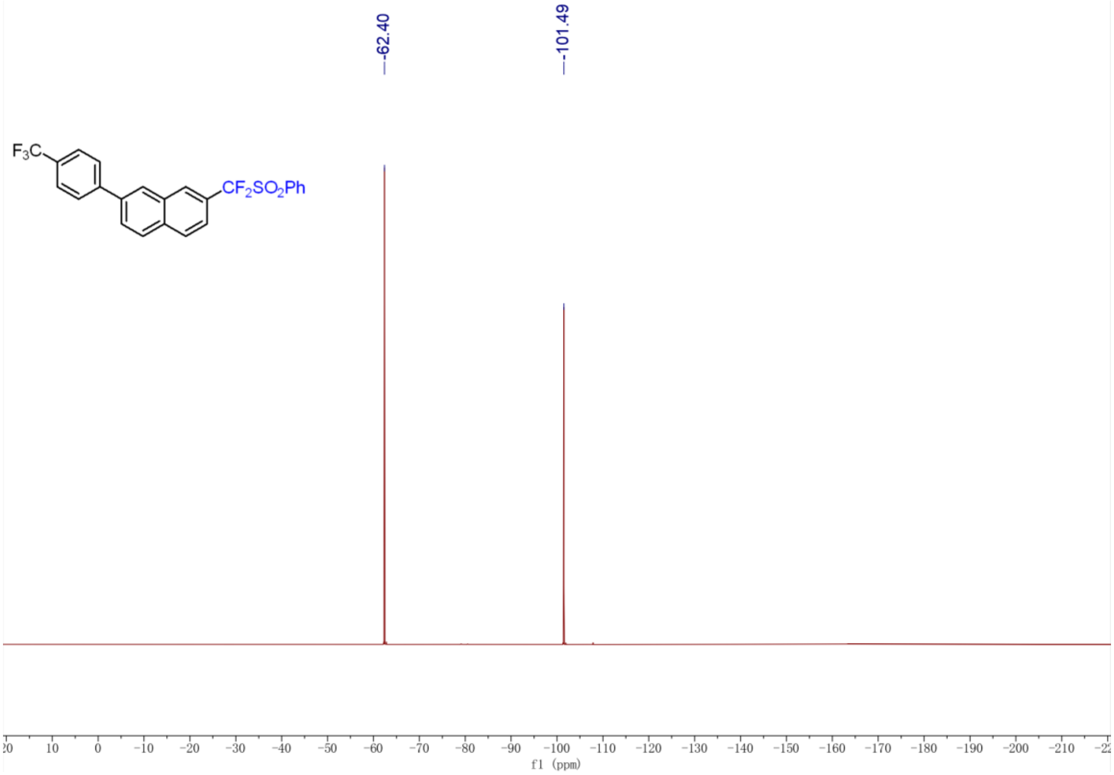

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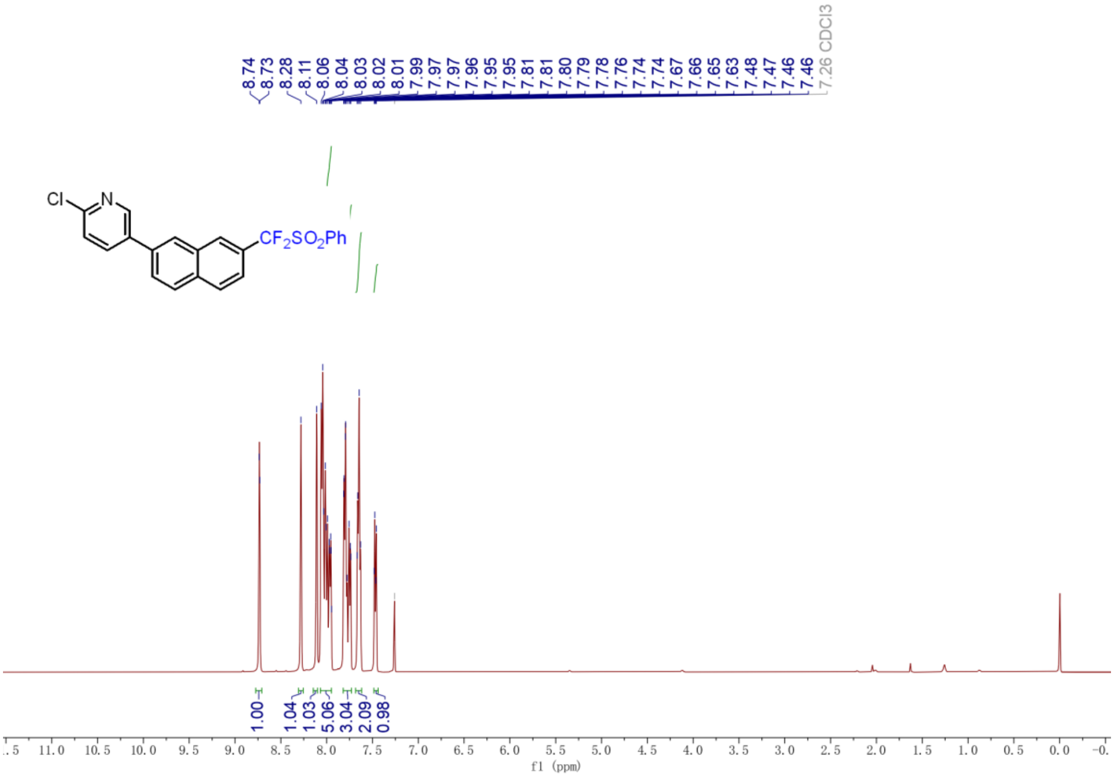

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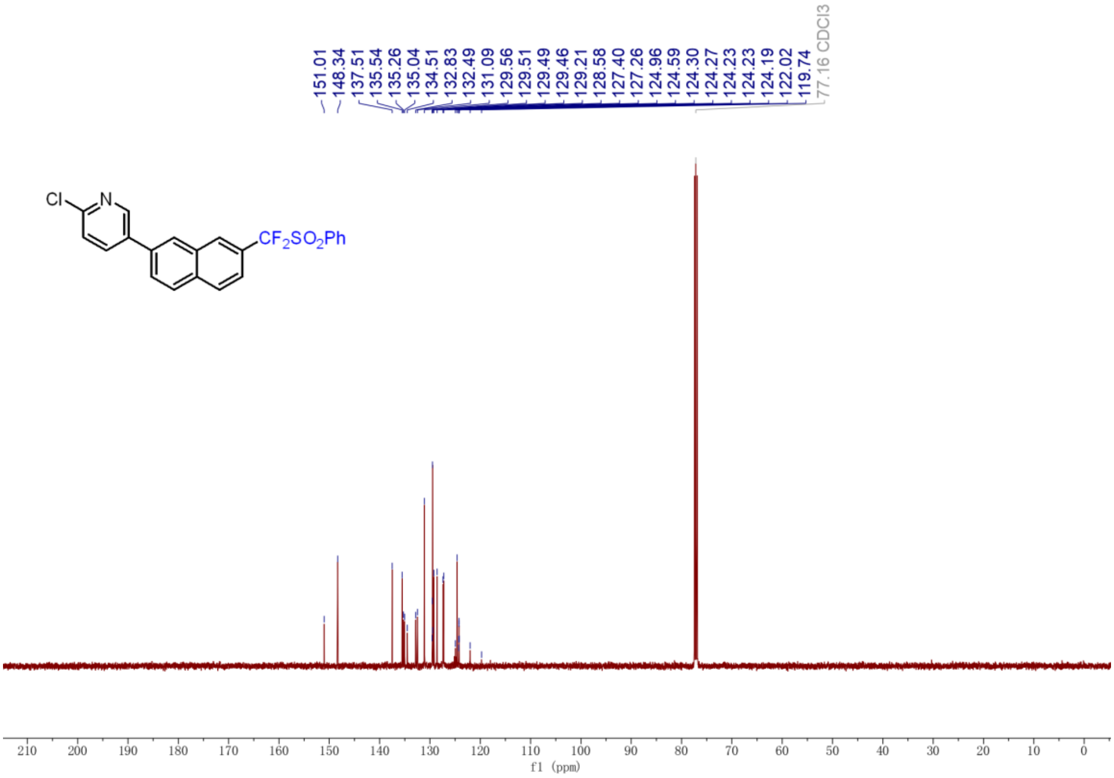

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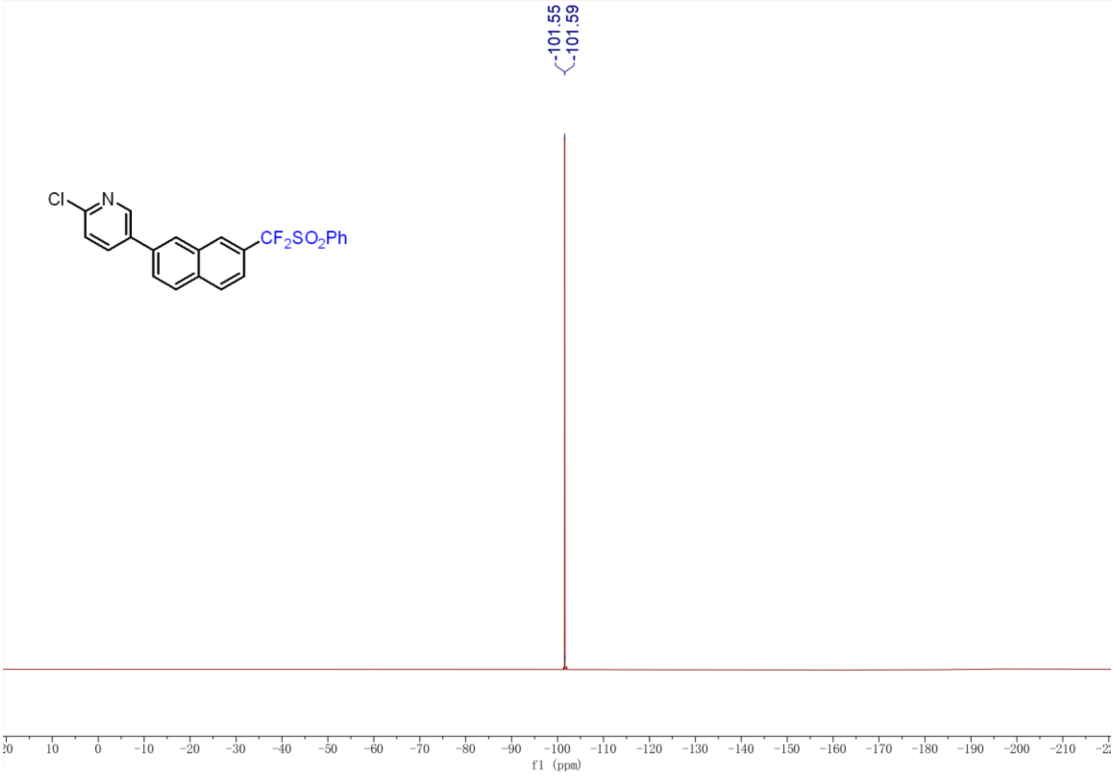

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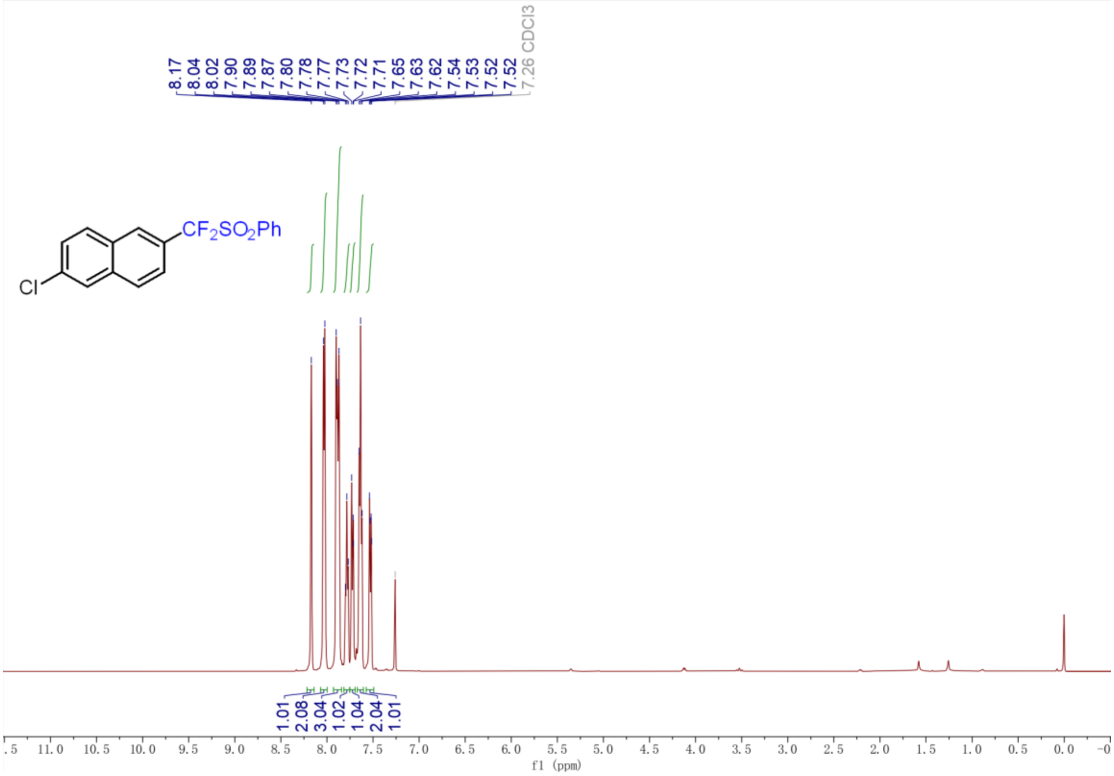

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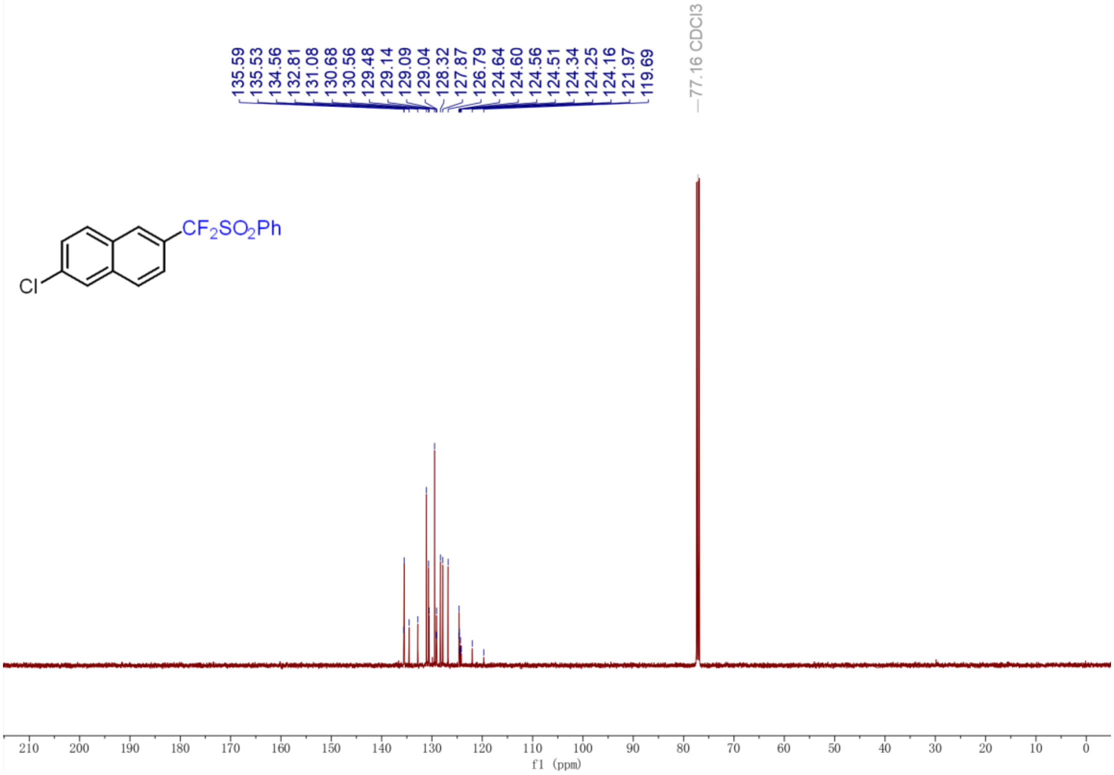
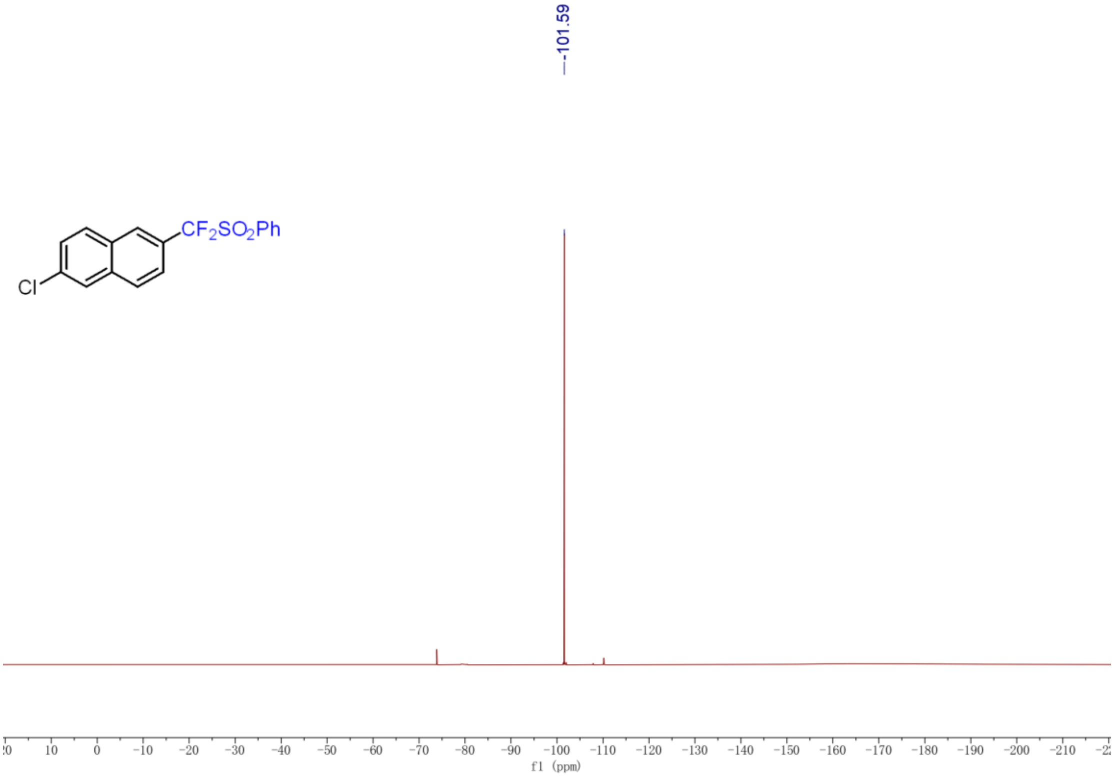
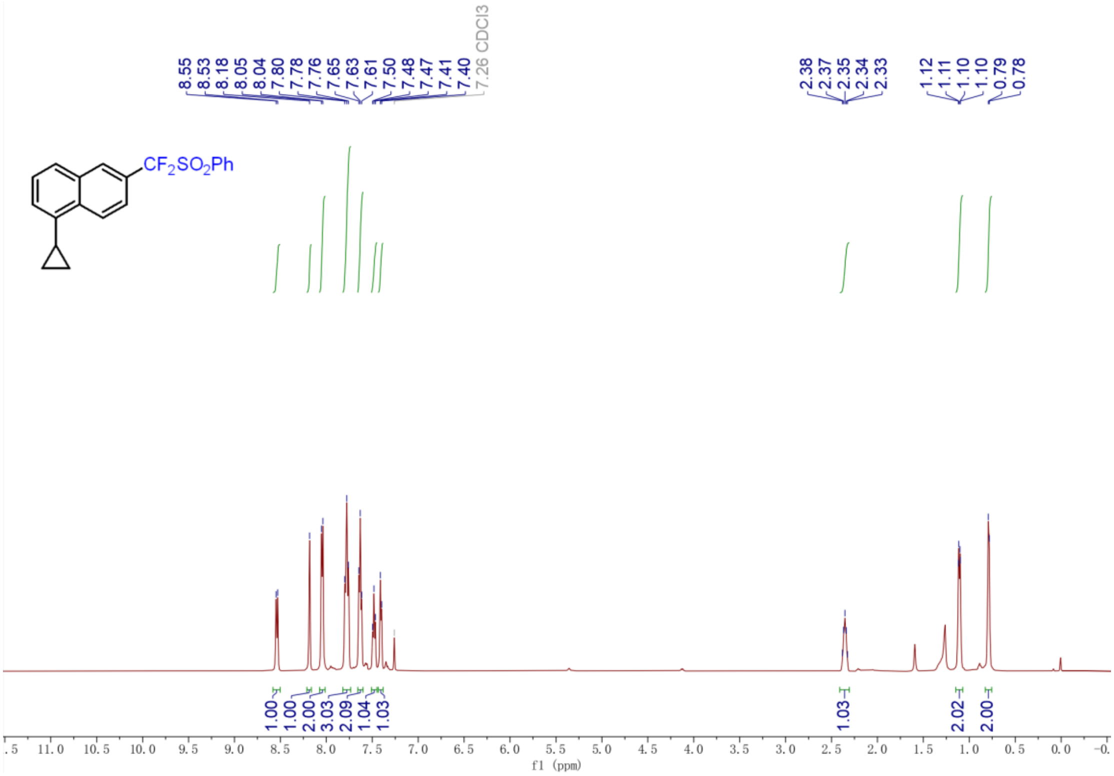


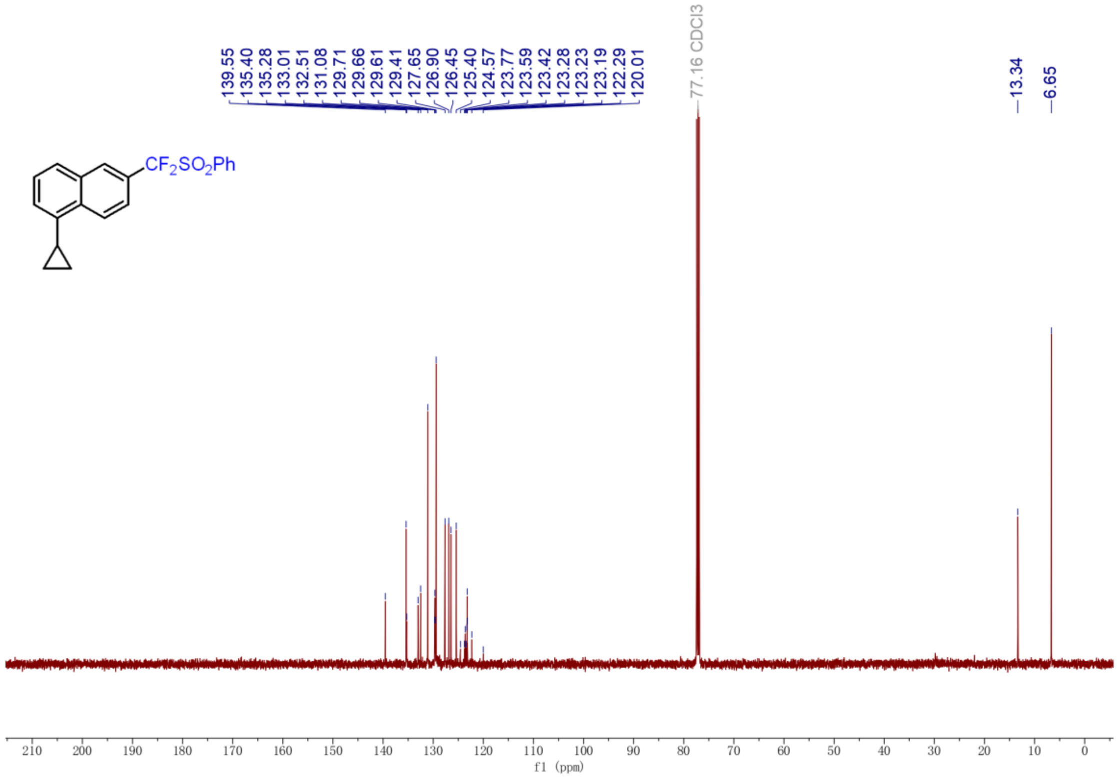
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2k**



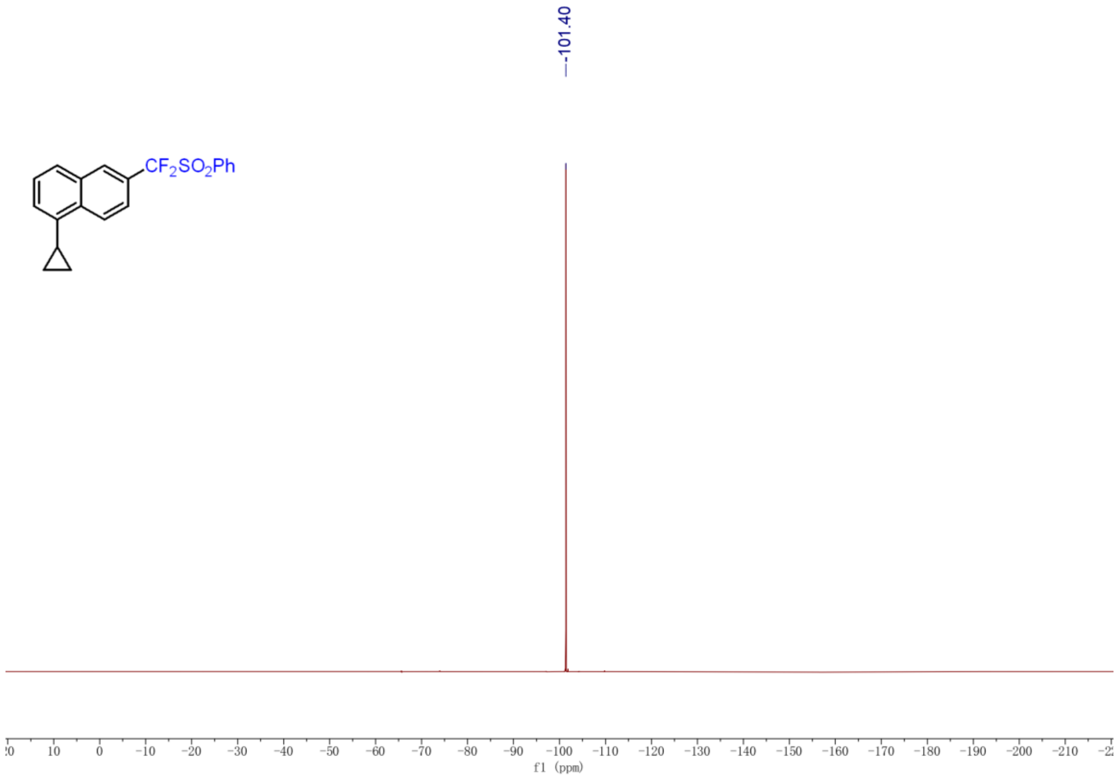
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2k**



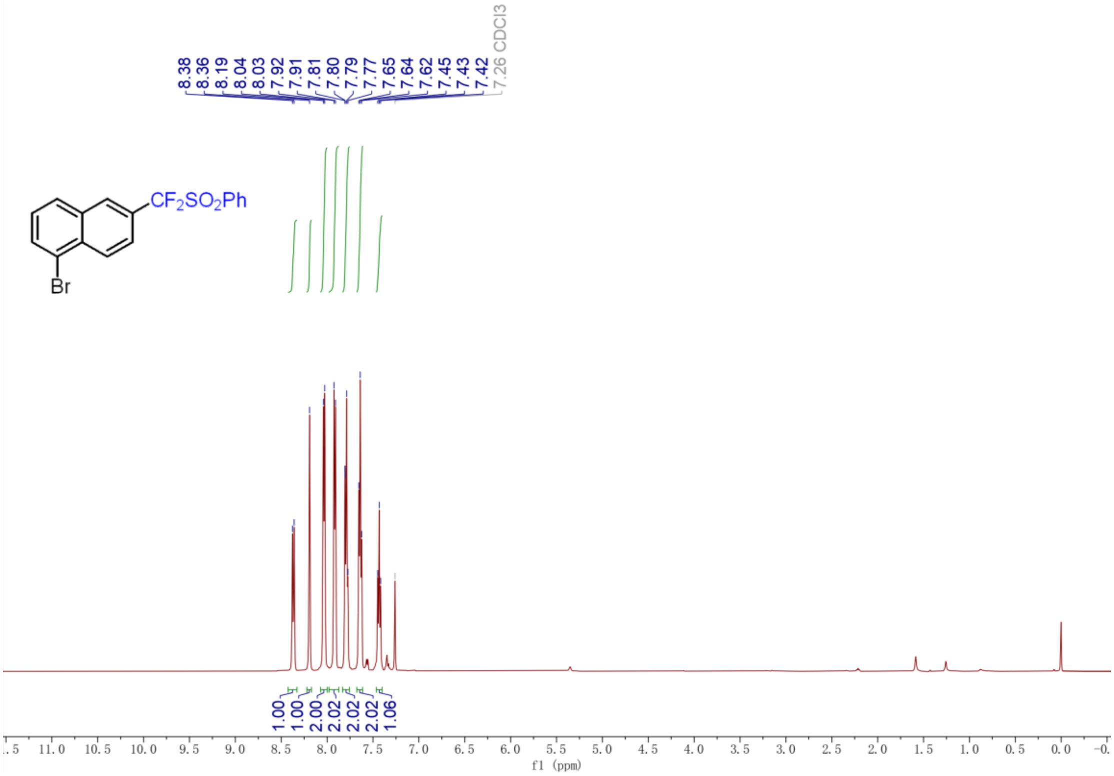
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2l**



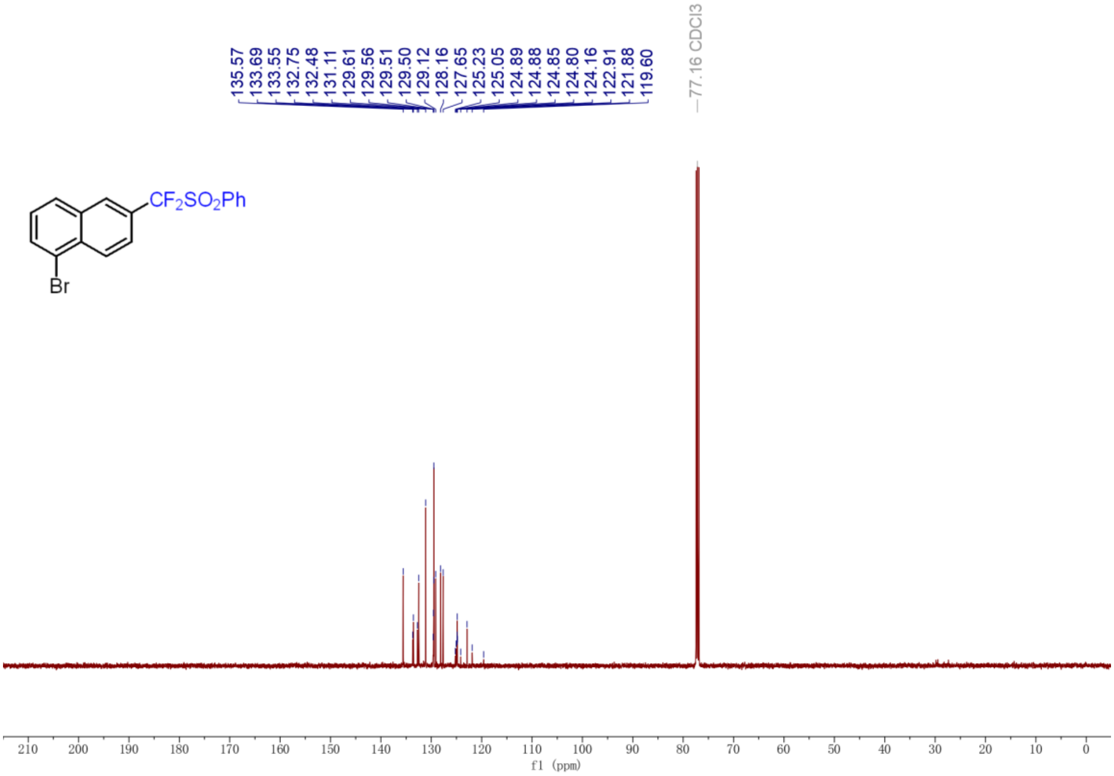
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2l**



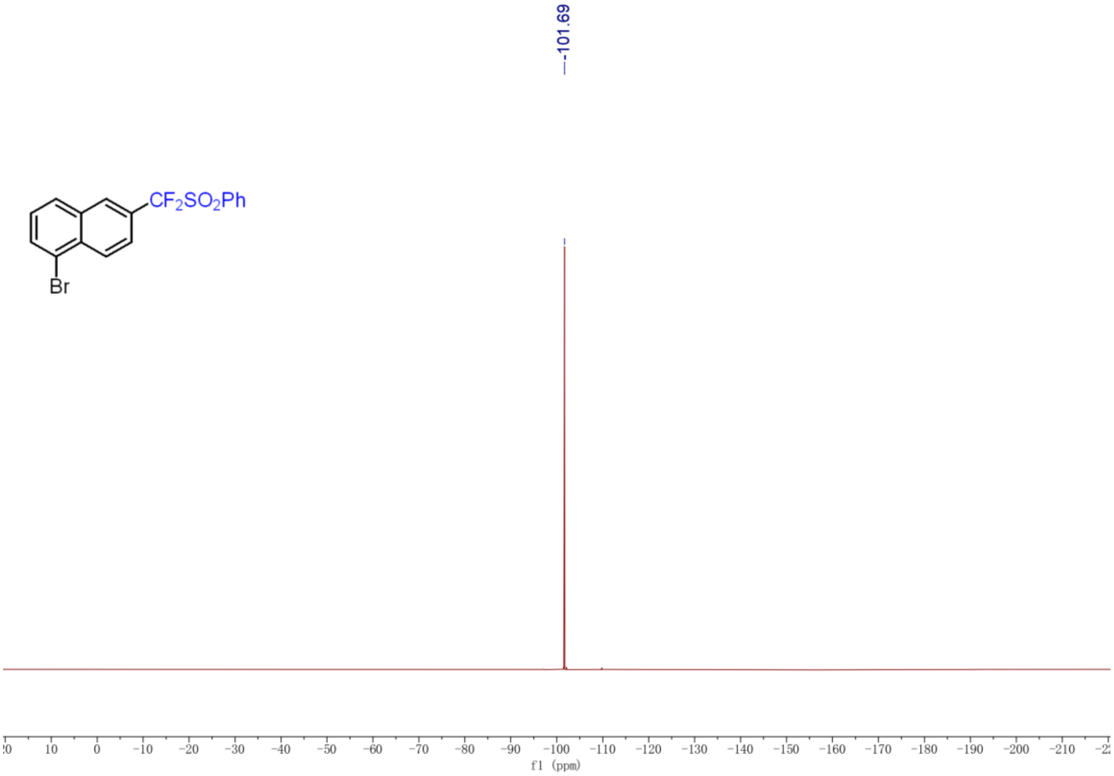
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2l**



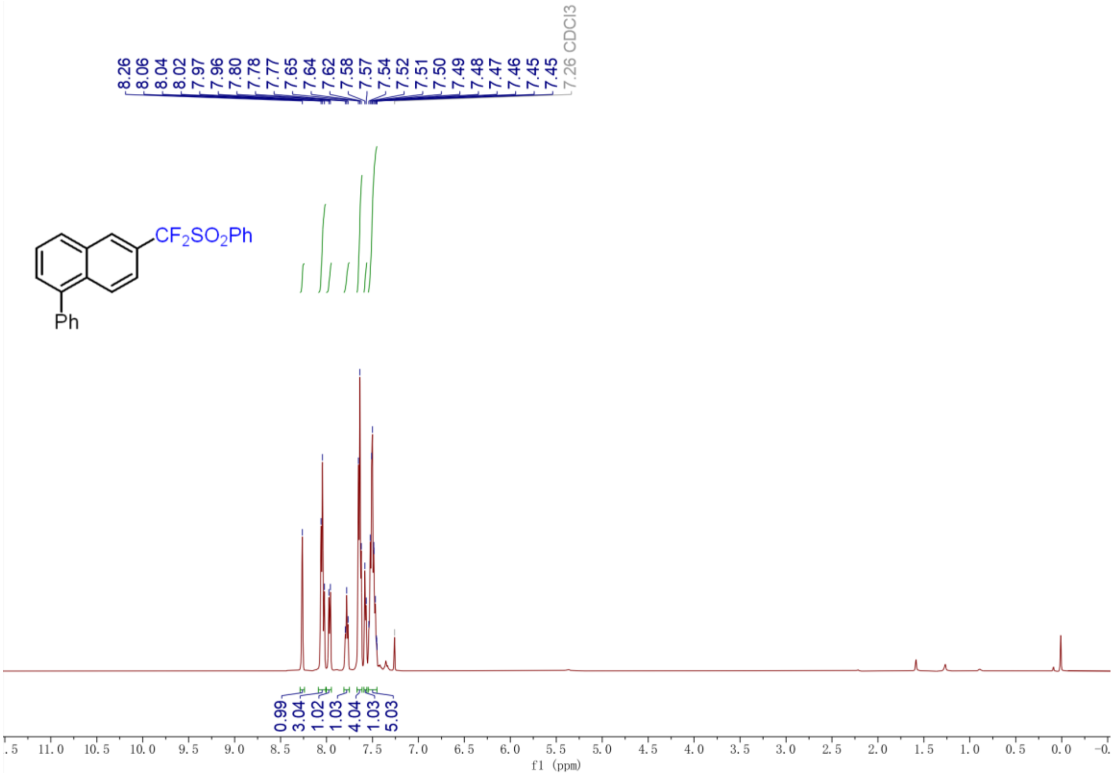
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2m**



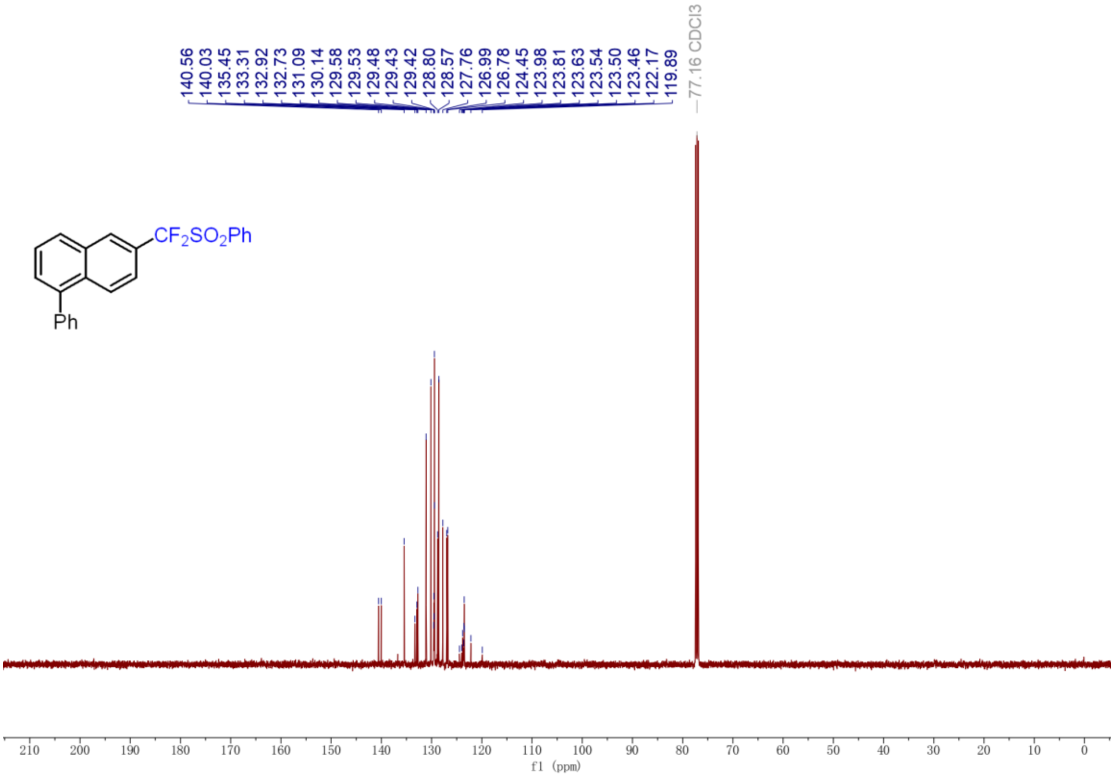
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2m**



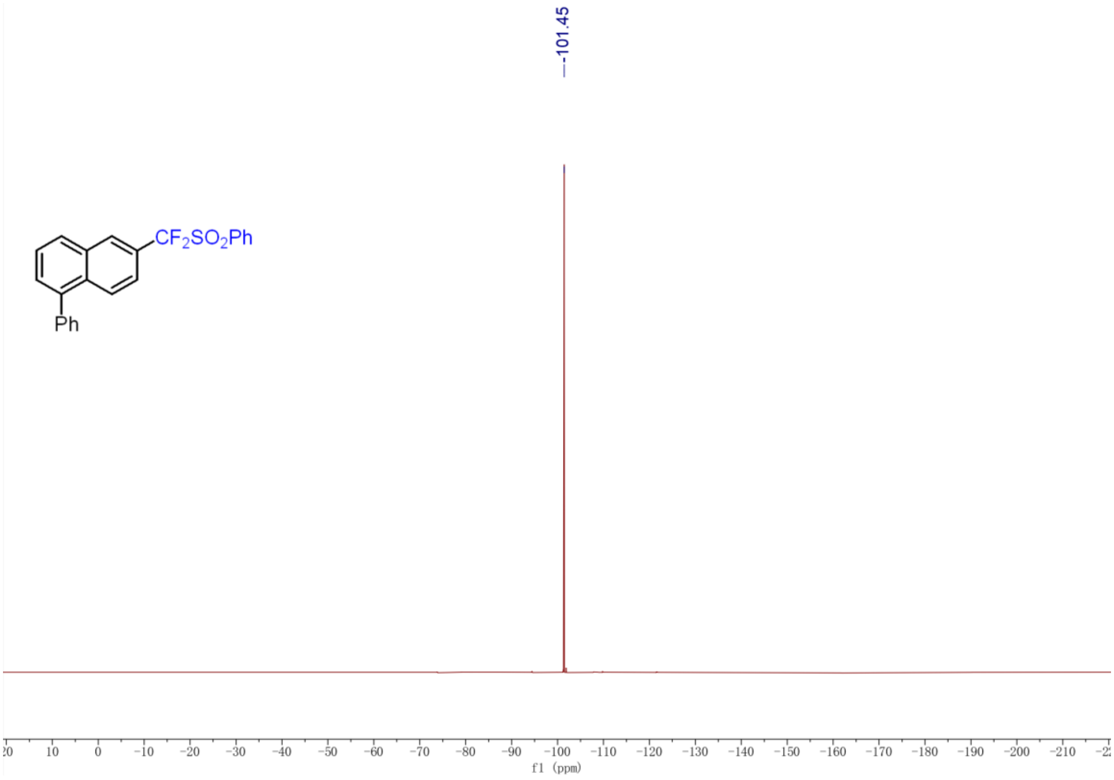
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2m**



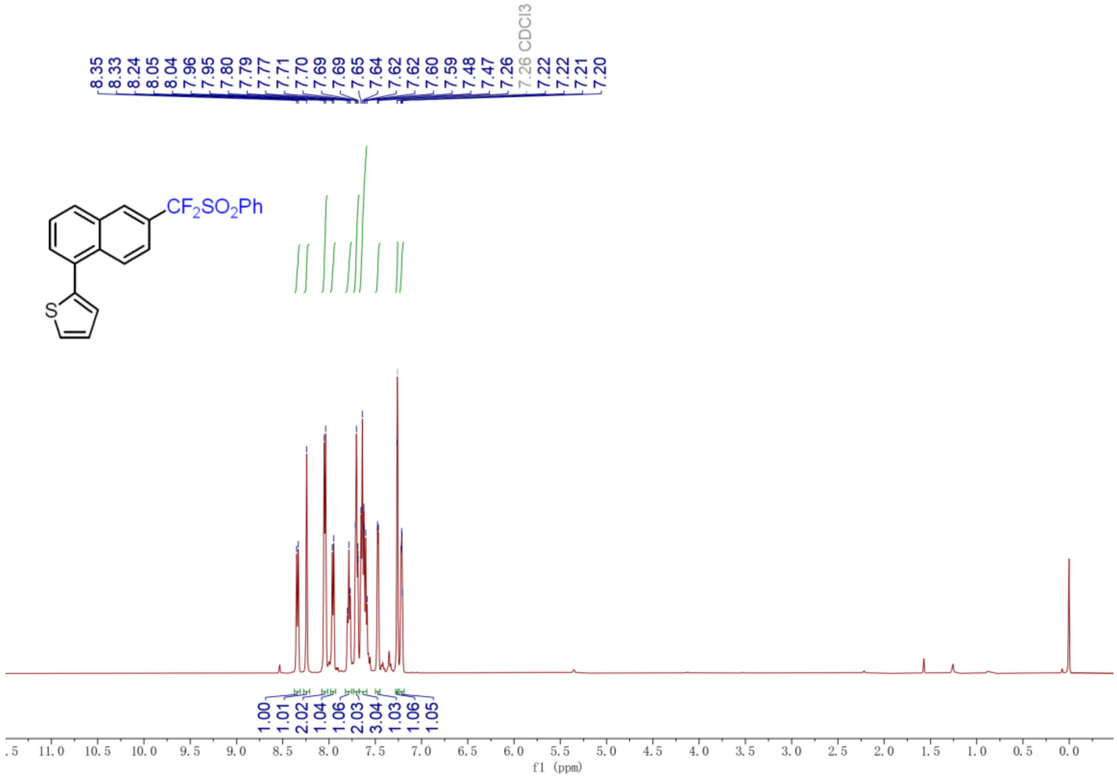
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2n**



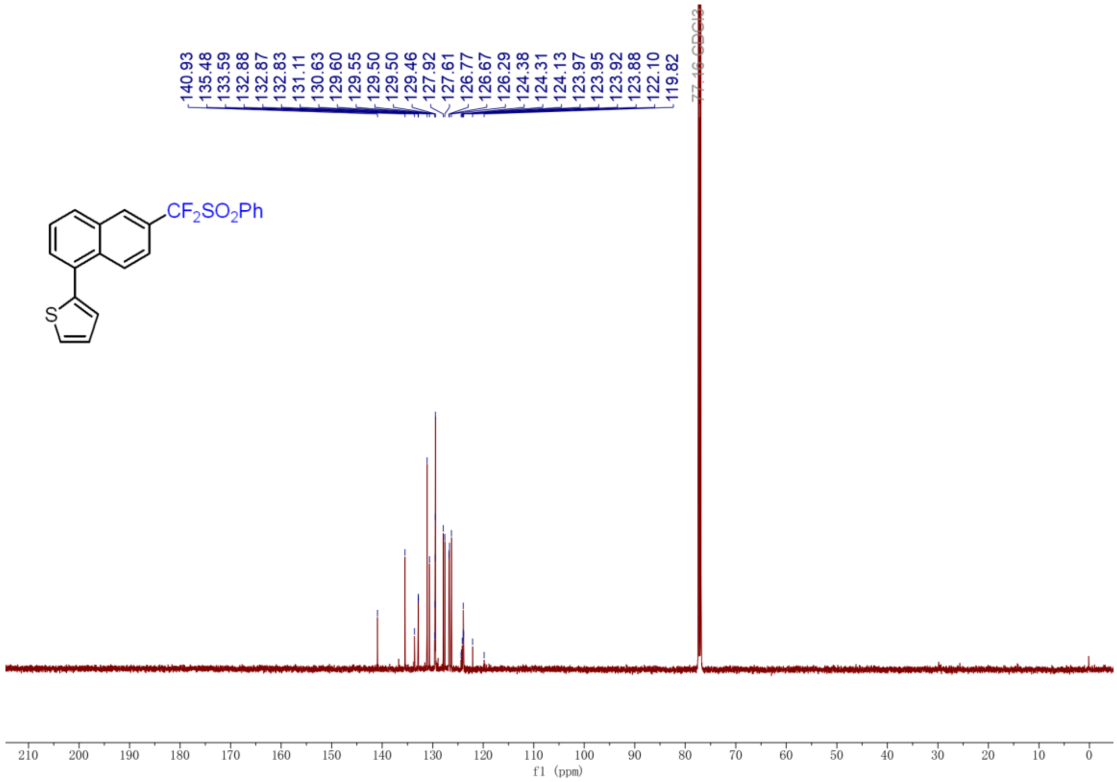
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2n**



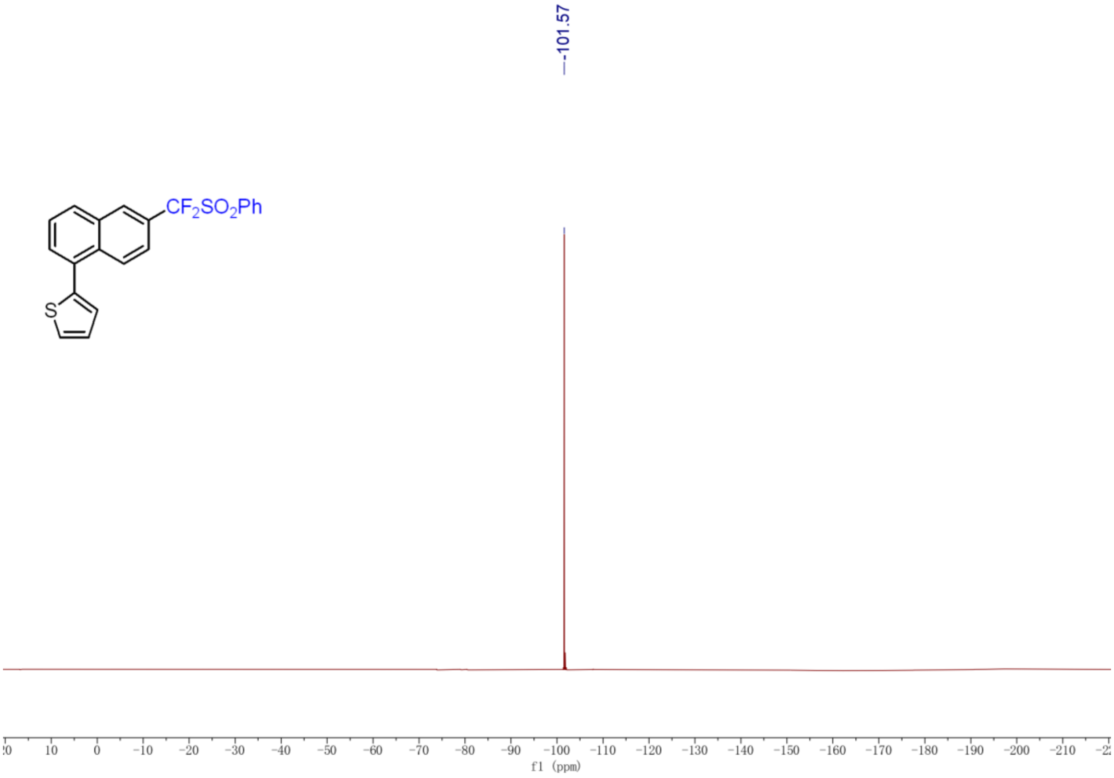
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2n**



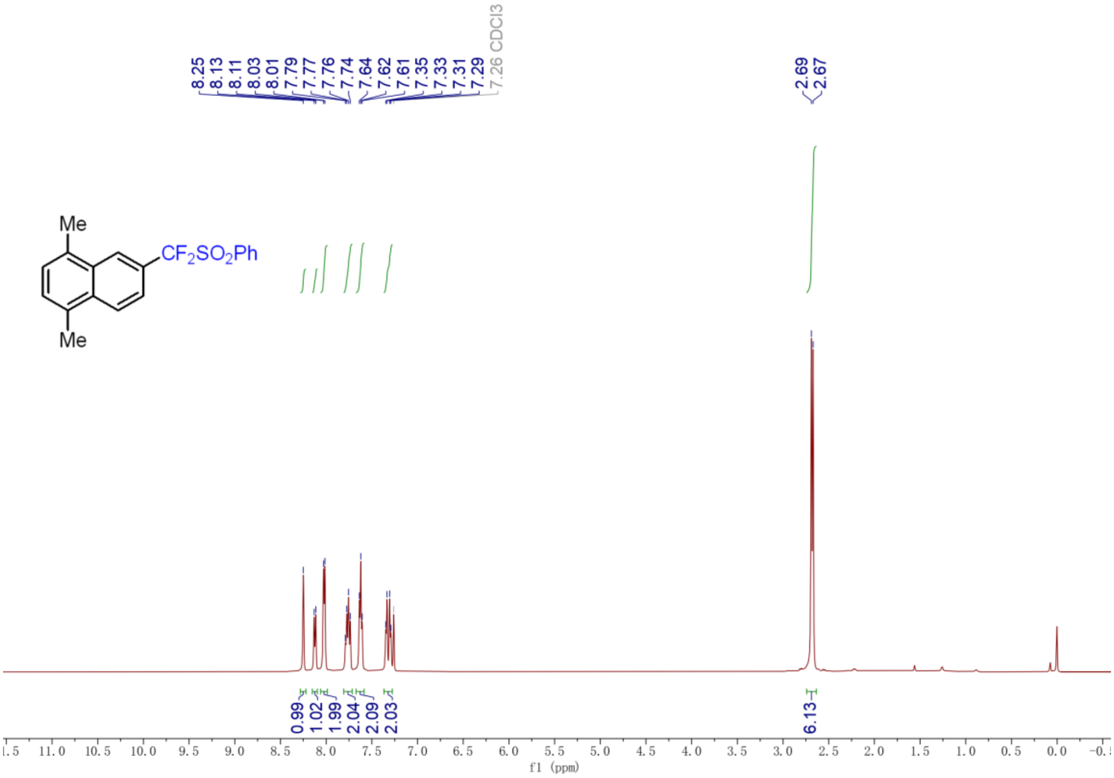
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2o**



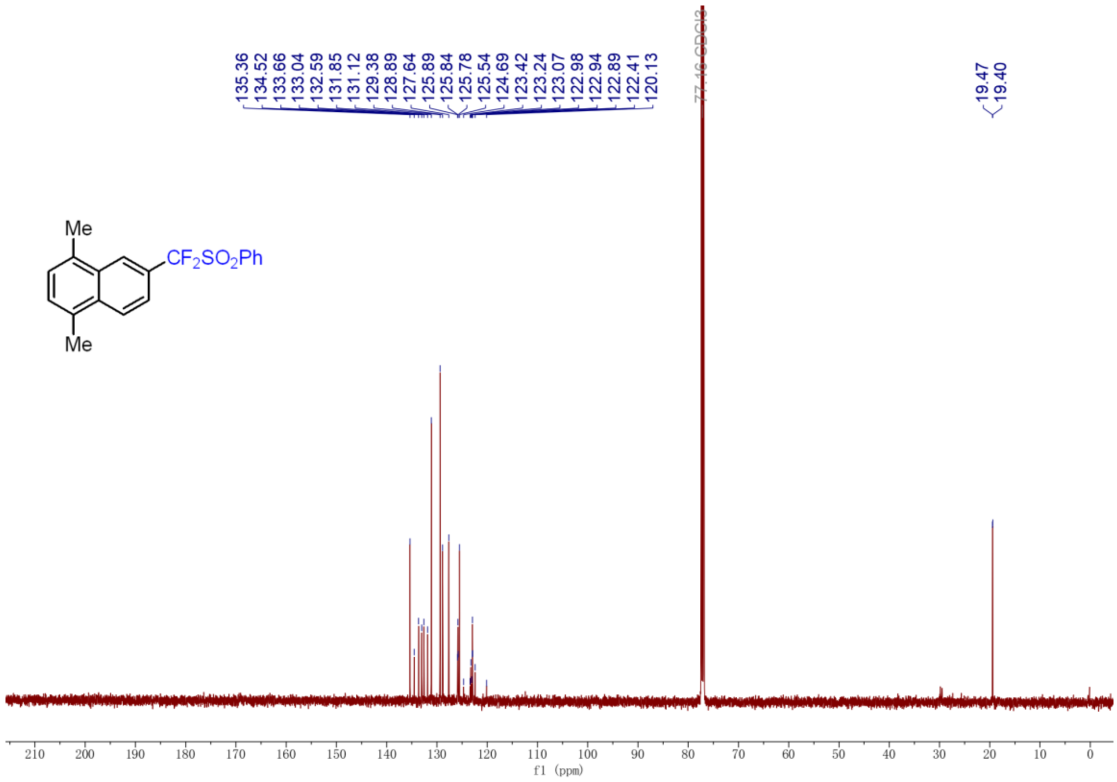
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2o**



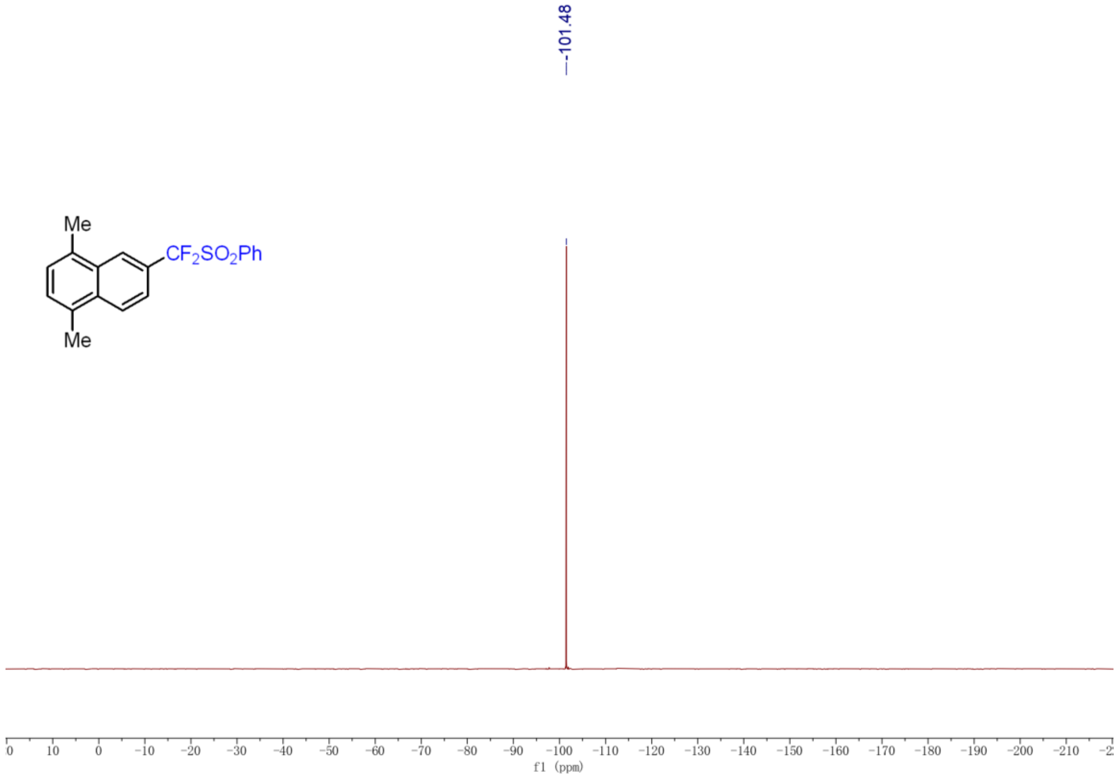
^{19}F NMR spectrum (471 MHz, Chloroform-d) of **2o**



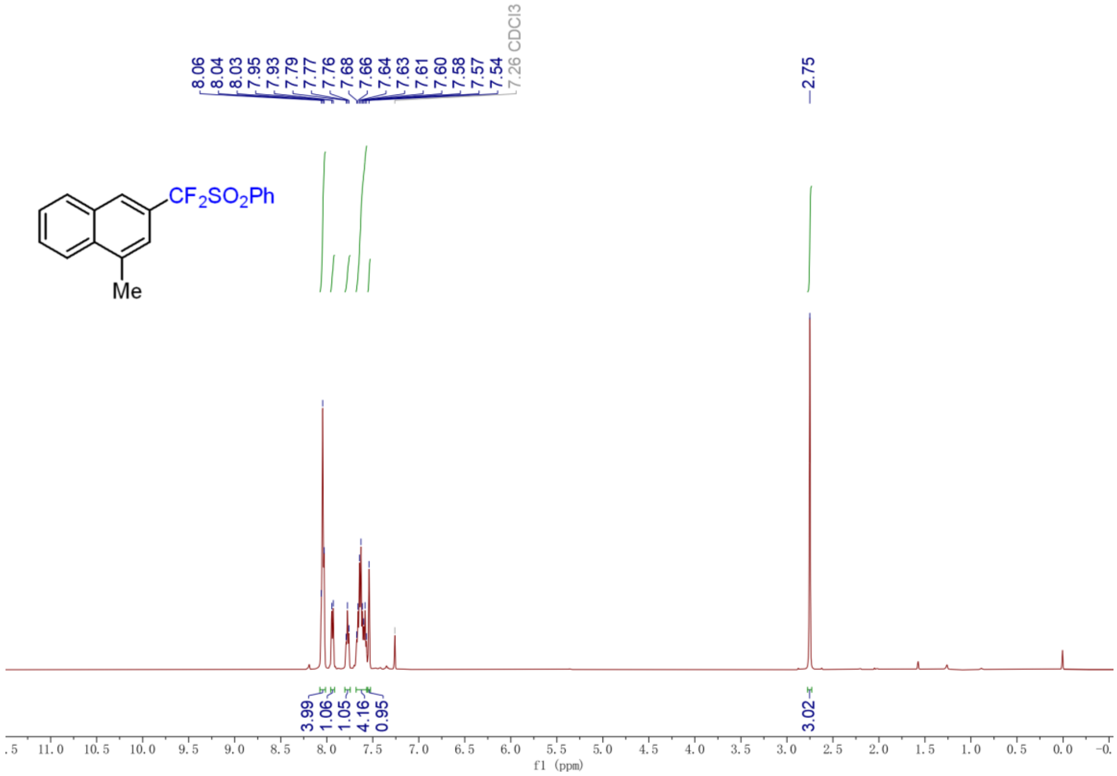
^{1}H NMR spectrum (500 MHz, Chloroform-d) of **2p**



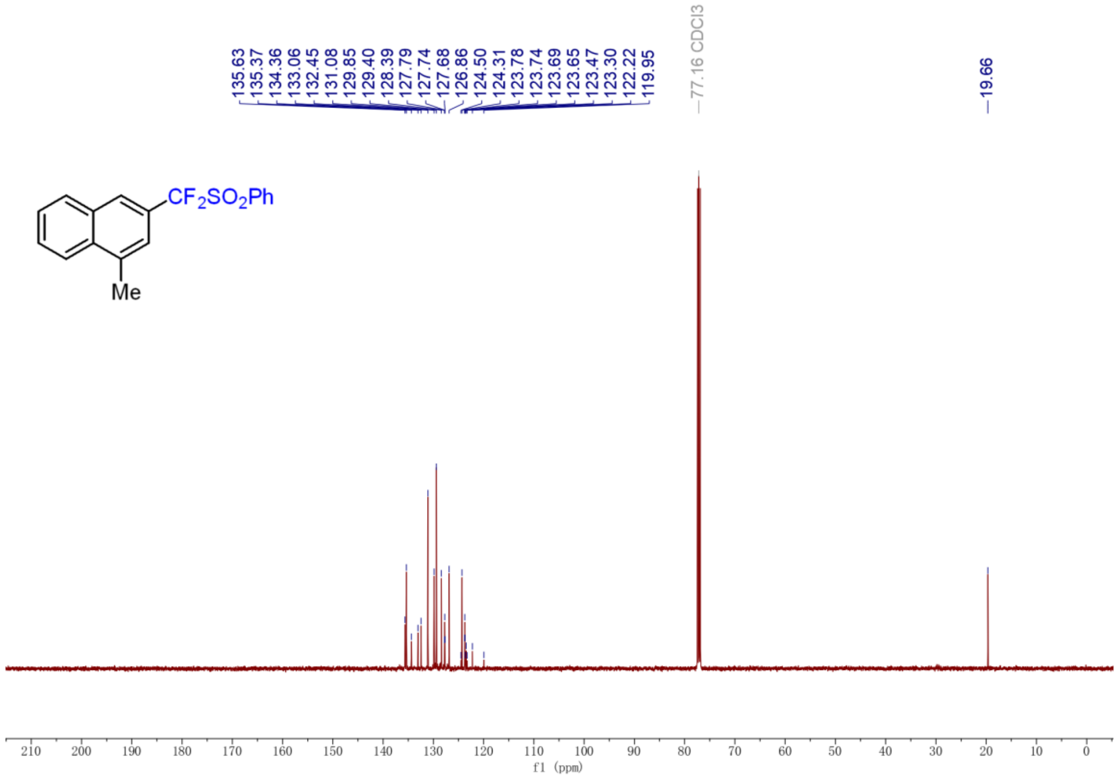
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2p**



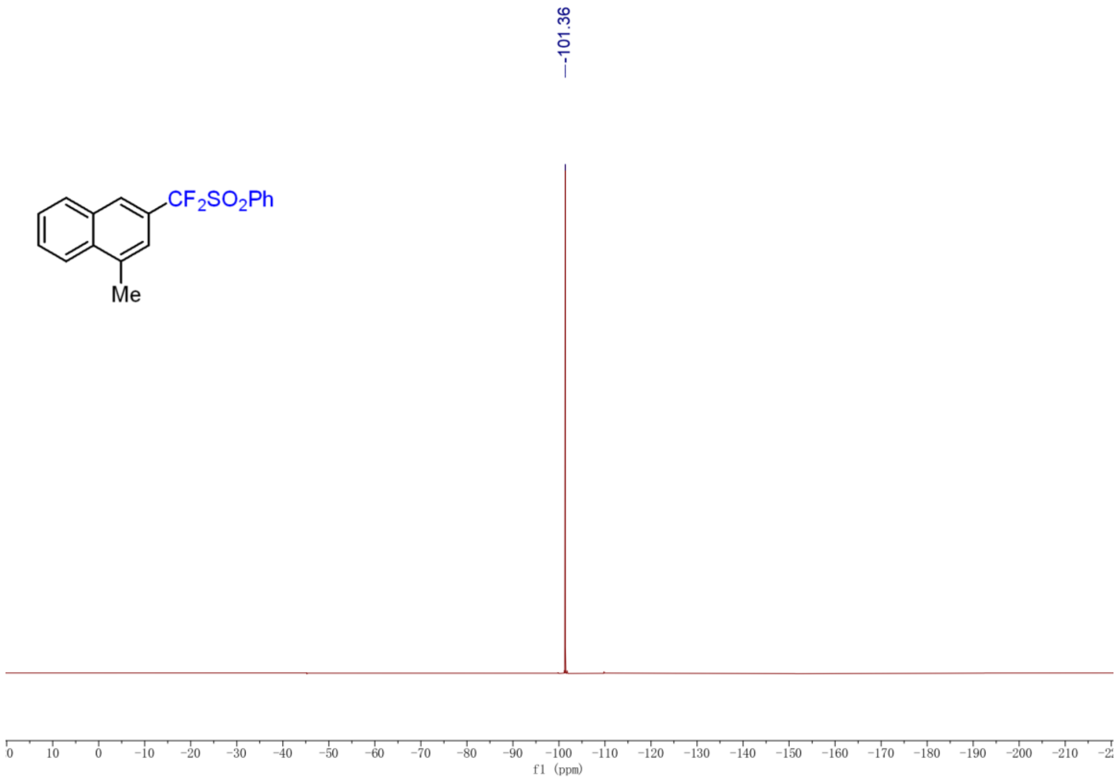
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2p**



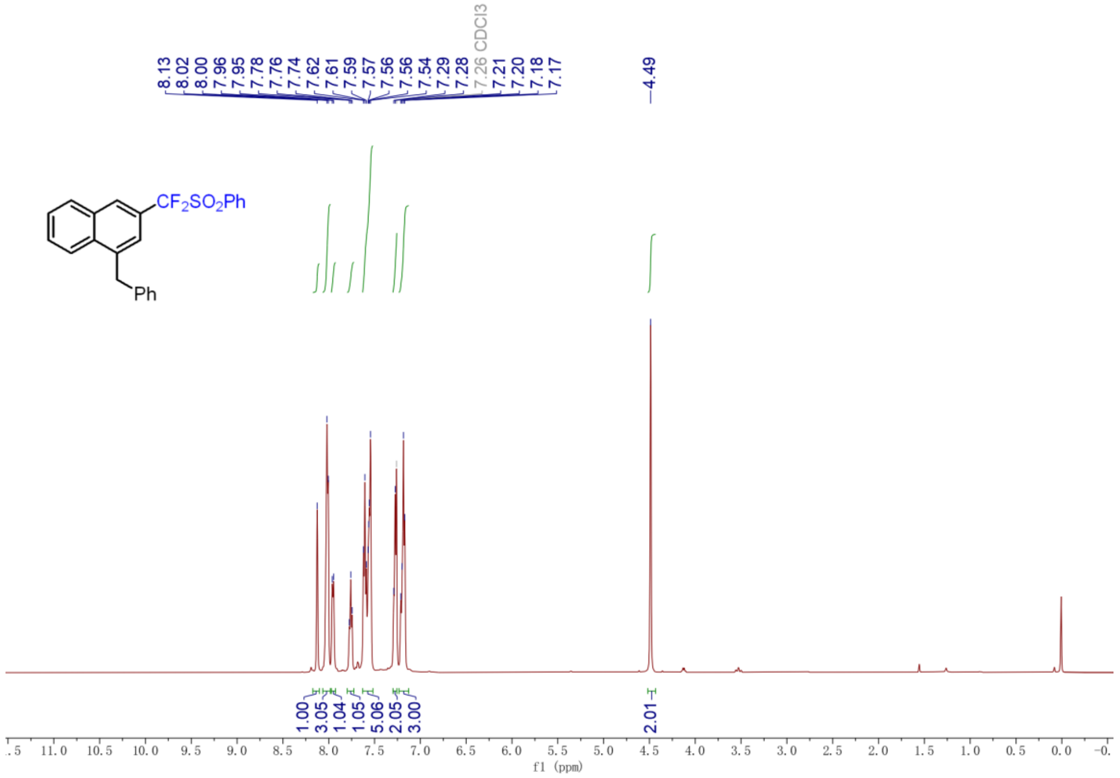
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2q**



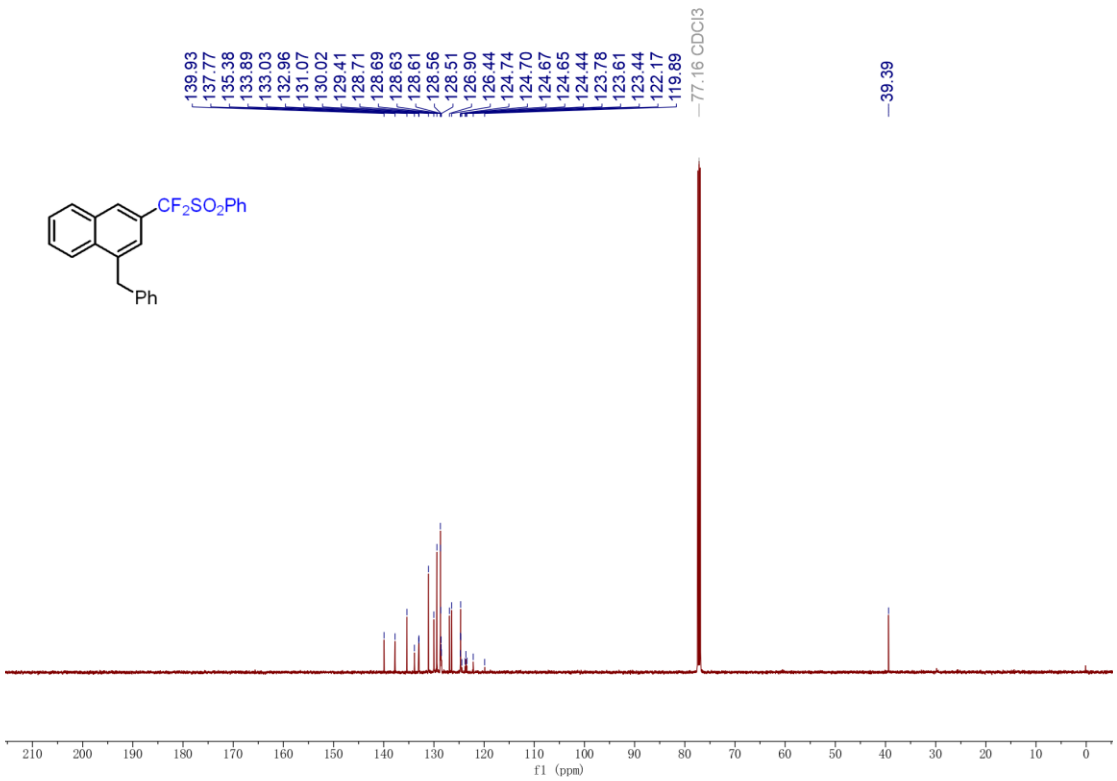
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2q**



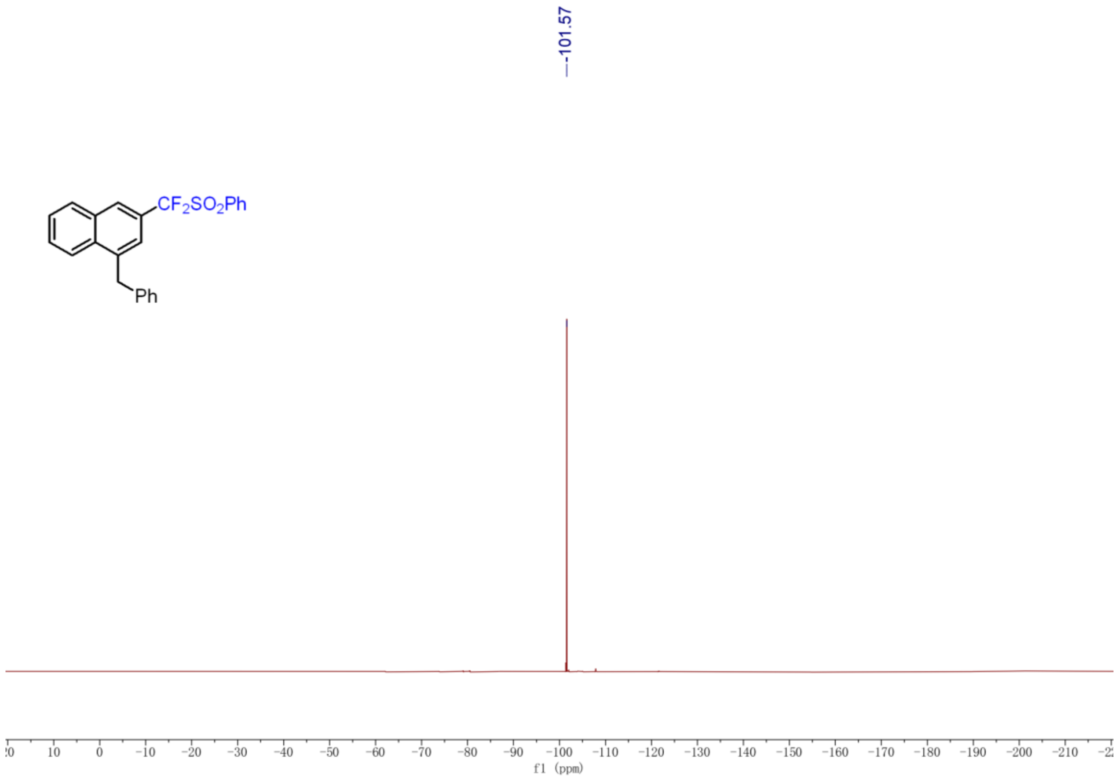
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2q**



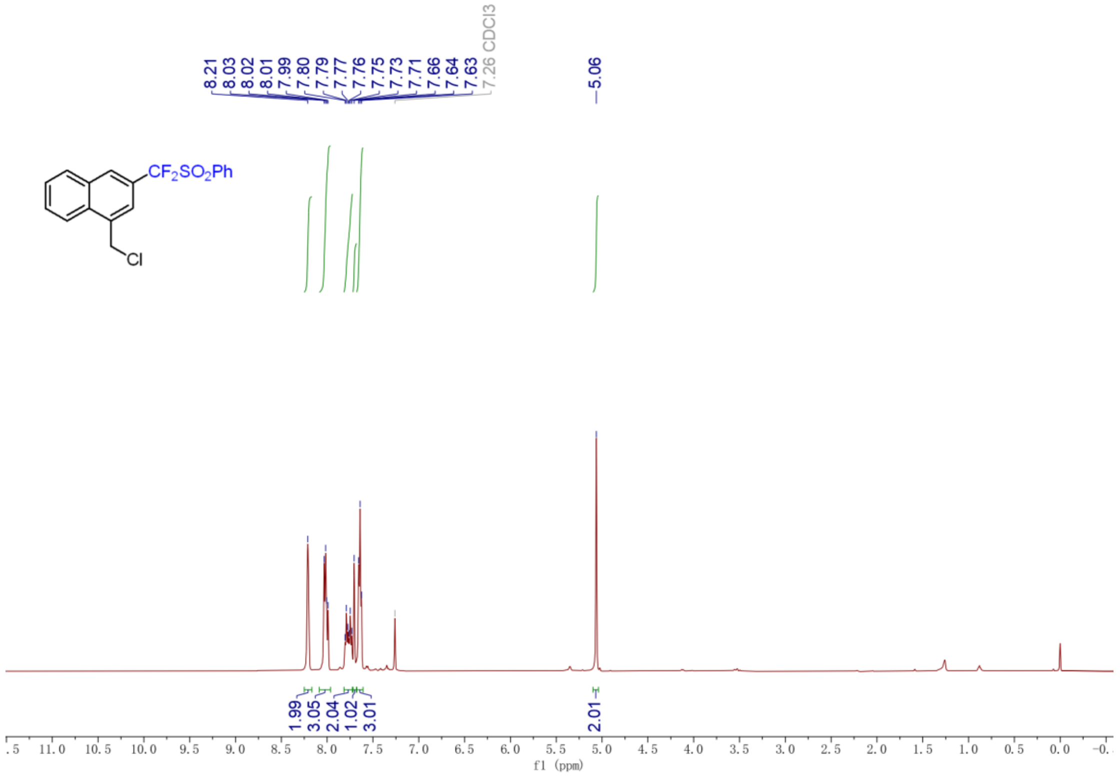
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2r**



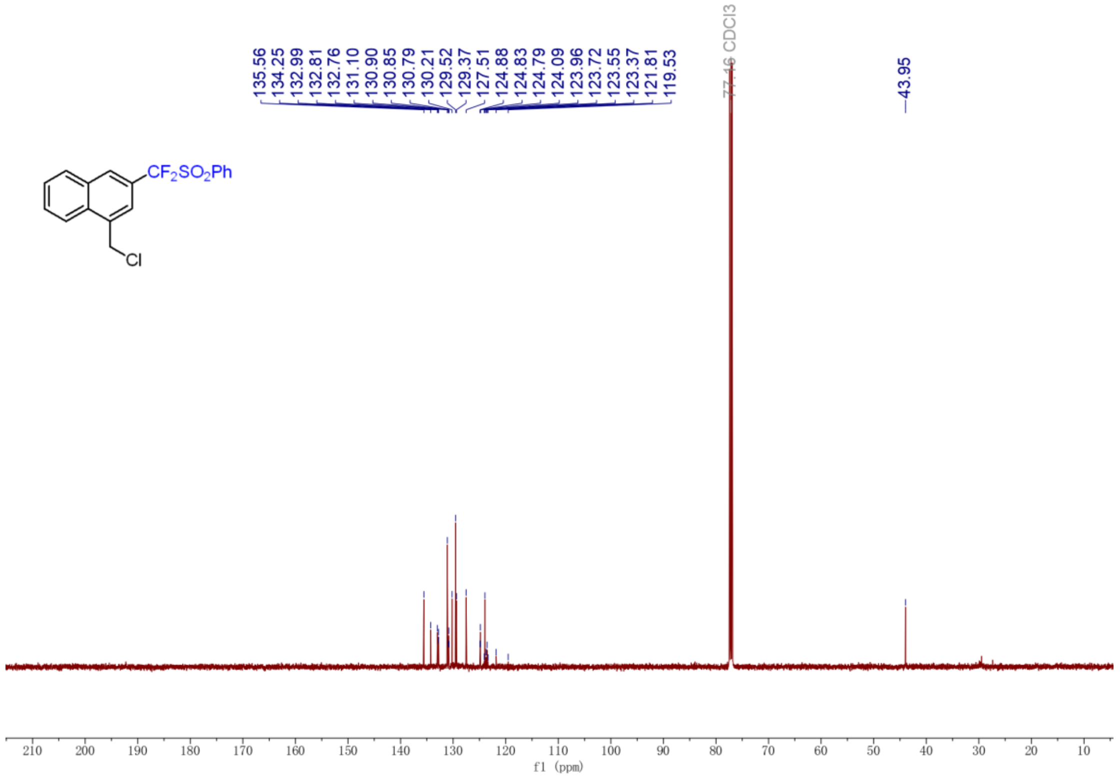
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2r**



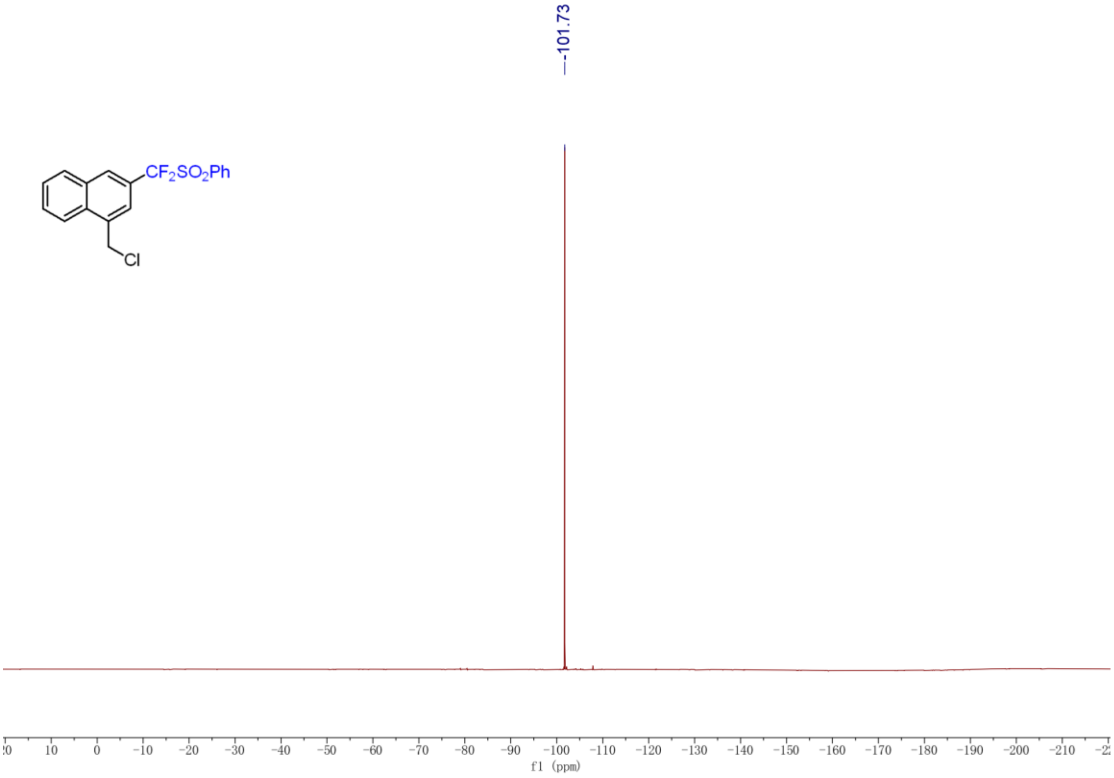
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2r**



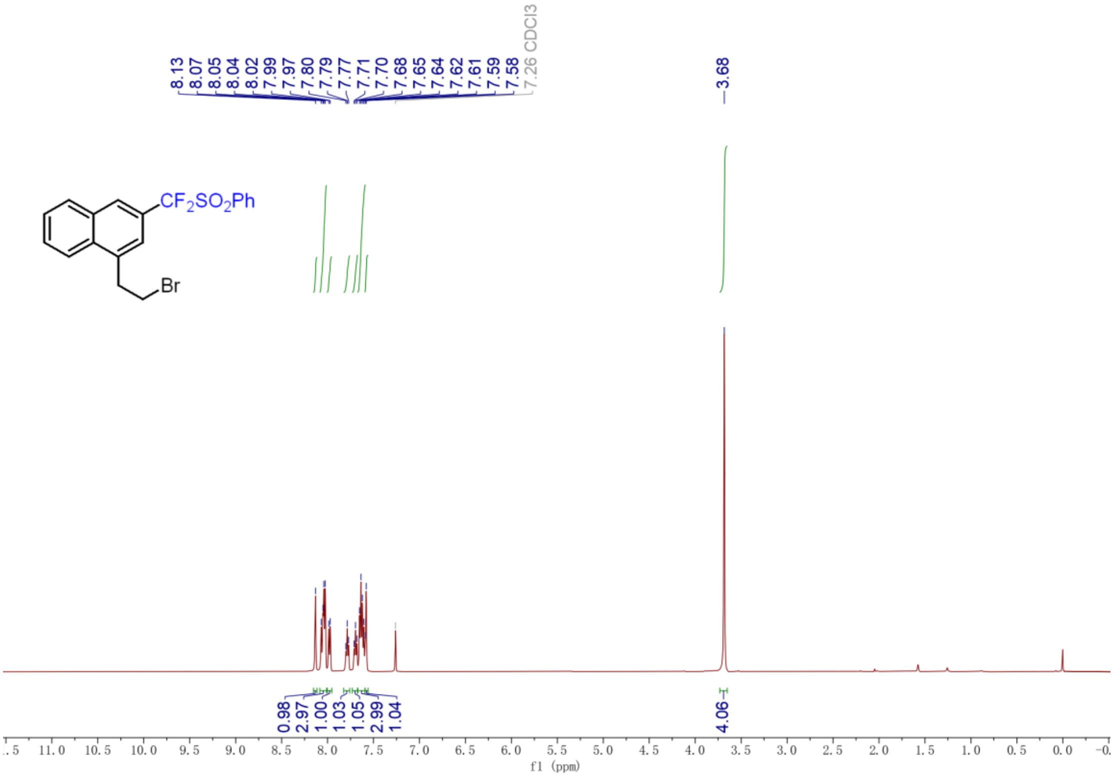
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2s**



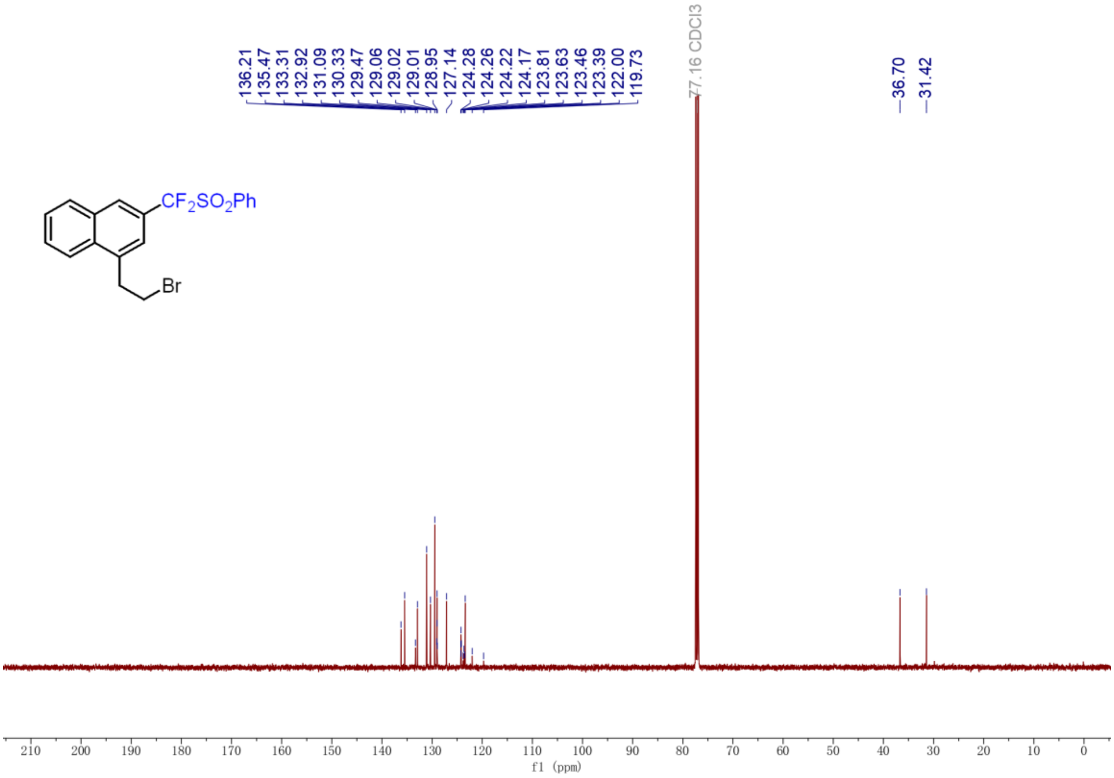
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2s**



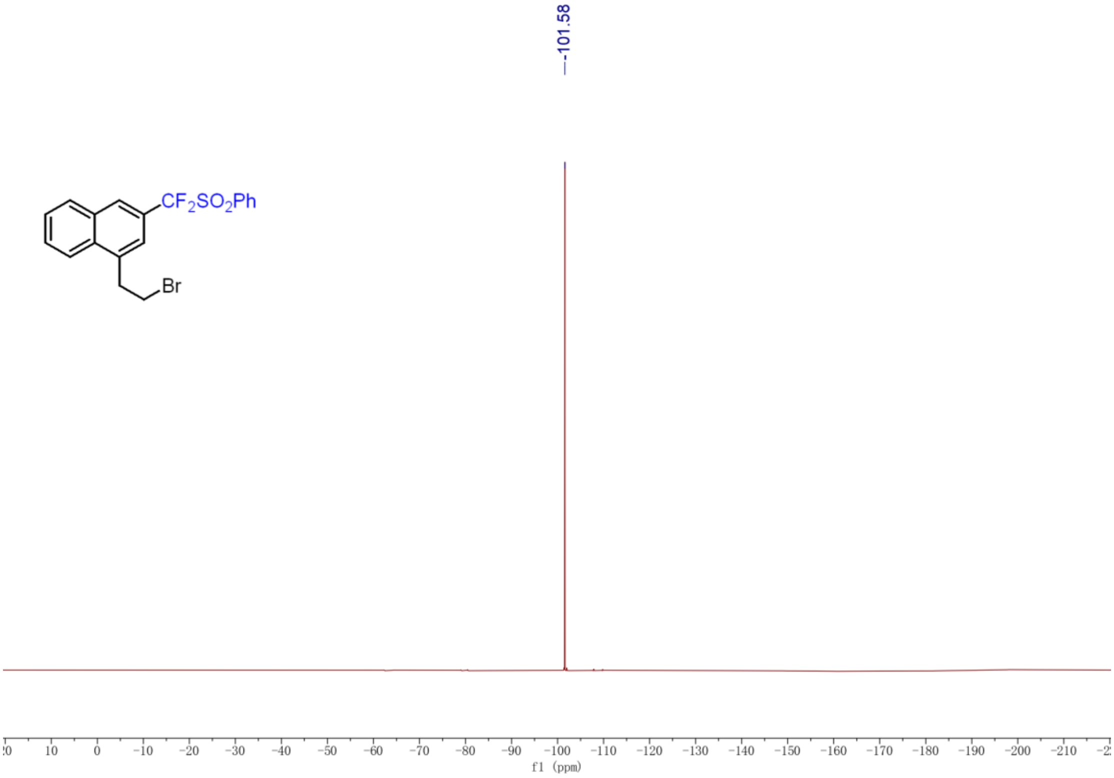
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2s**



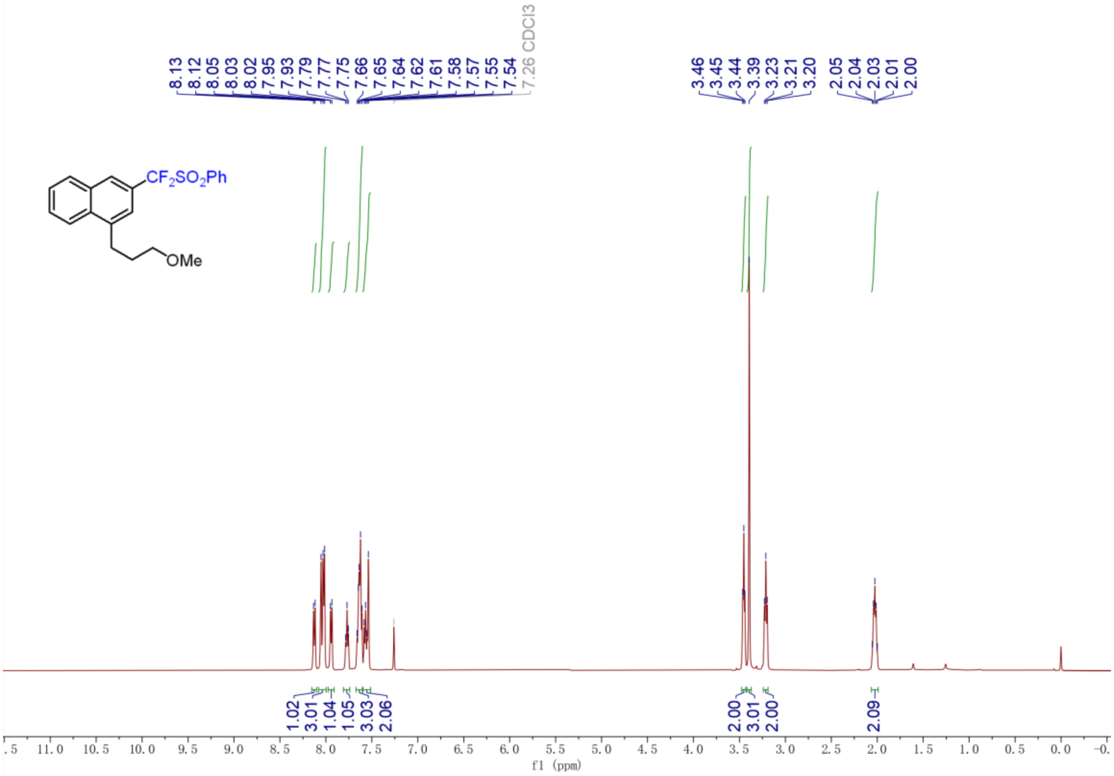
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2t**



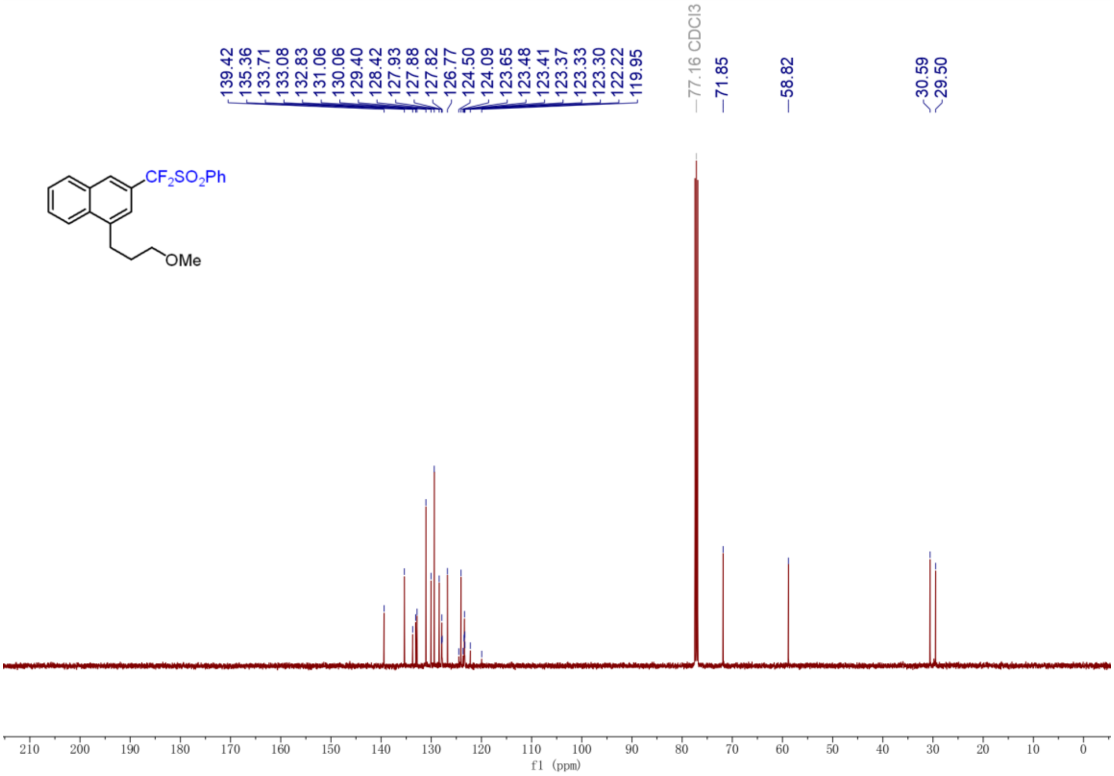
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2t**



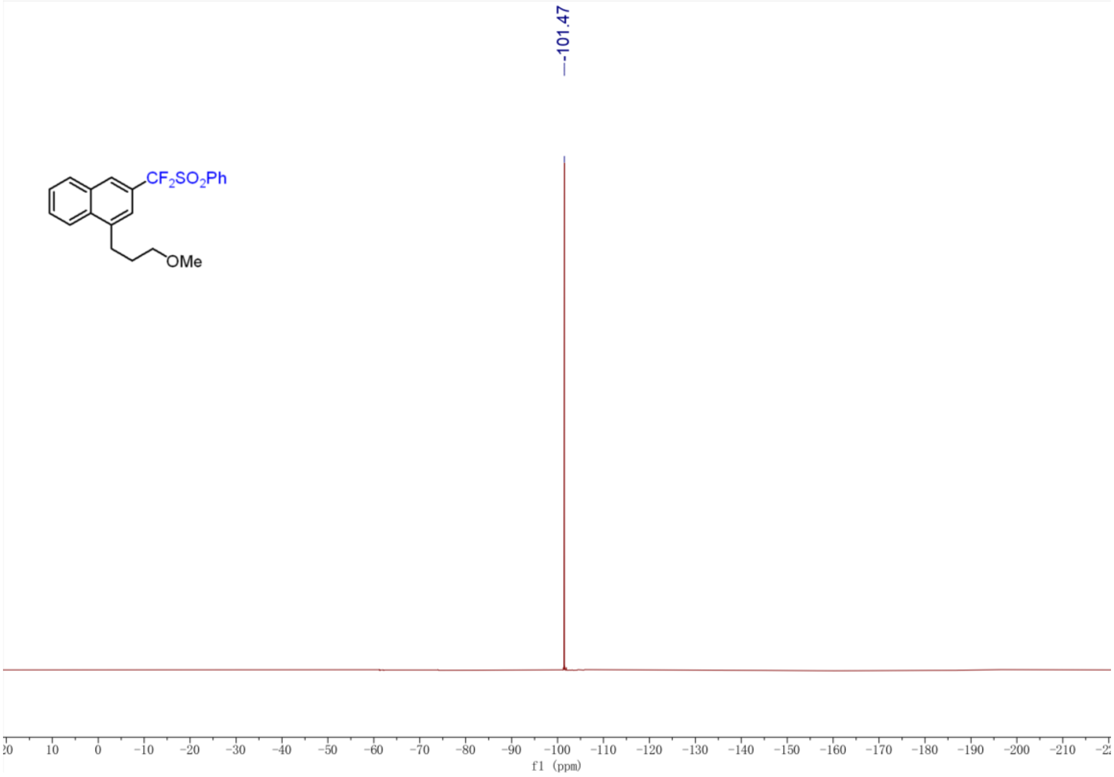
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2t**



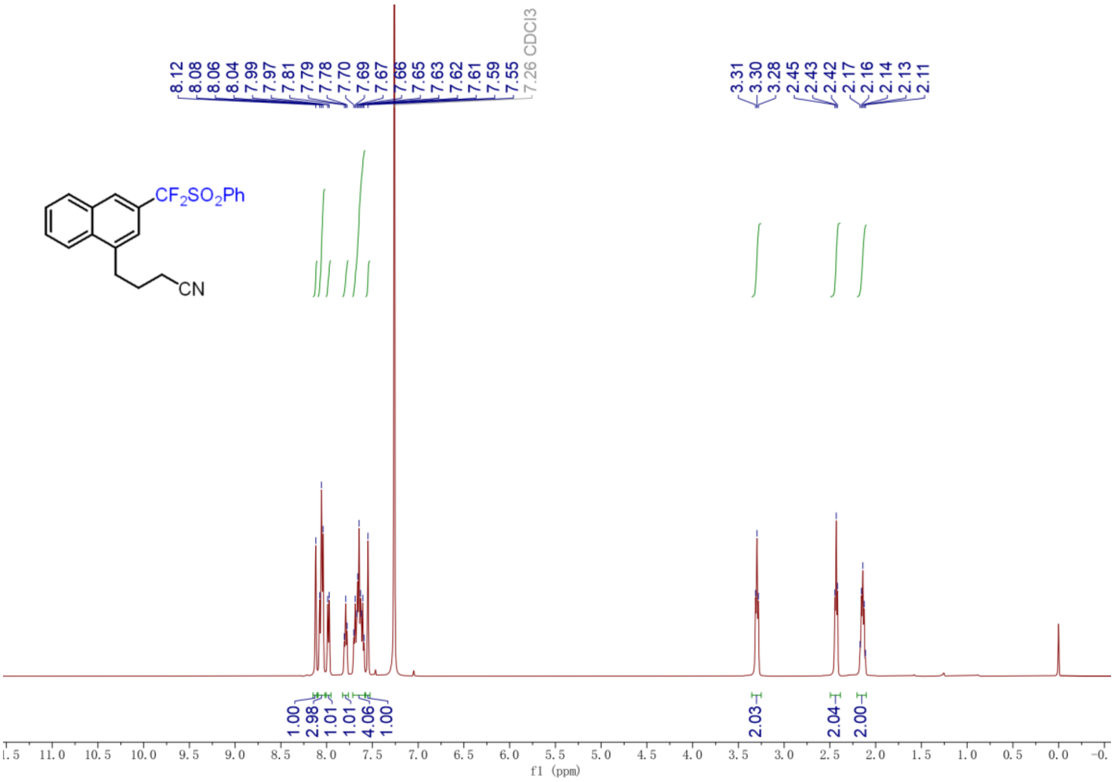
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2u**



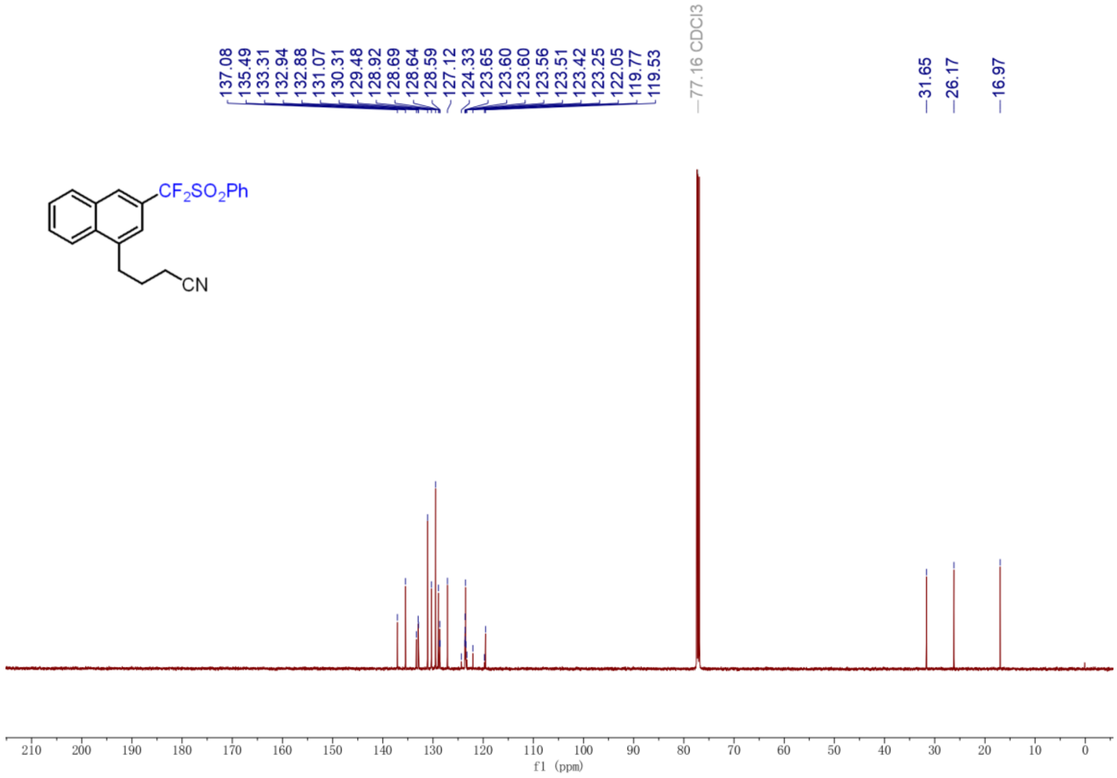
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2u**



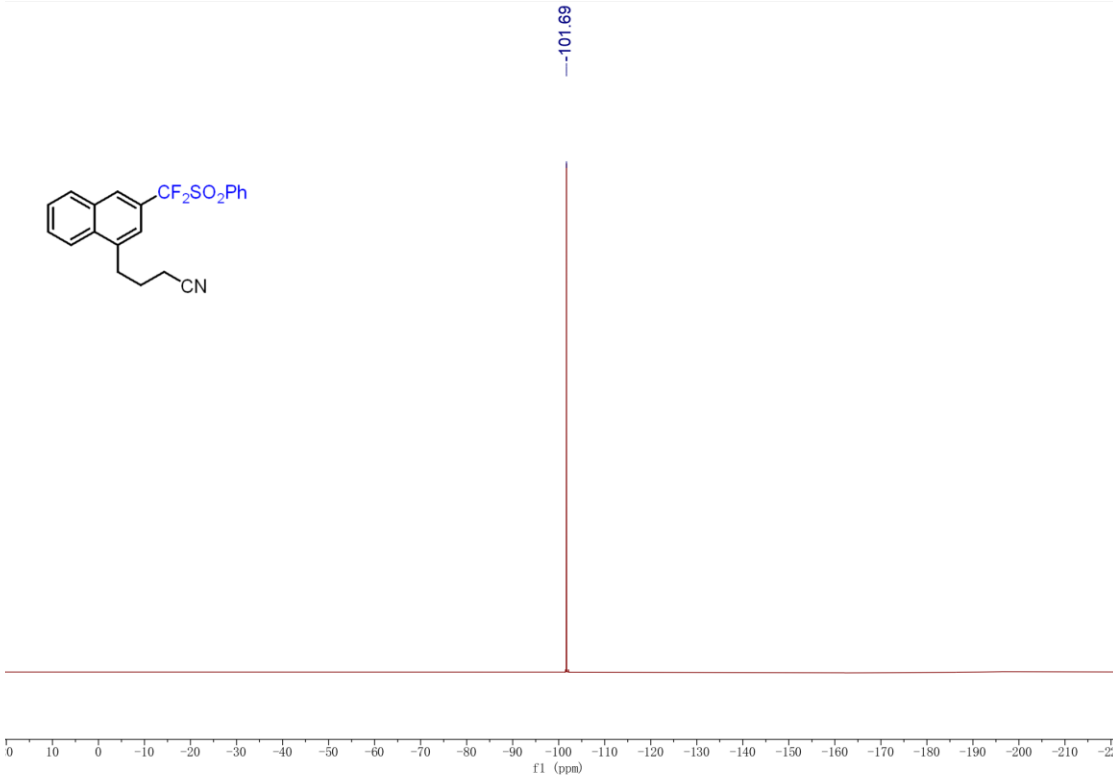
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2u**



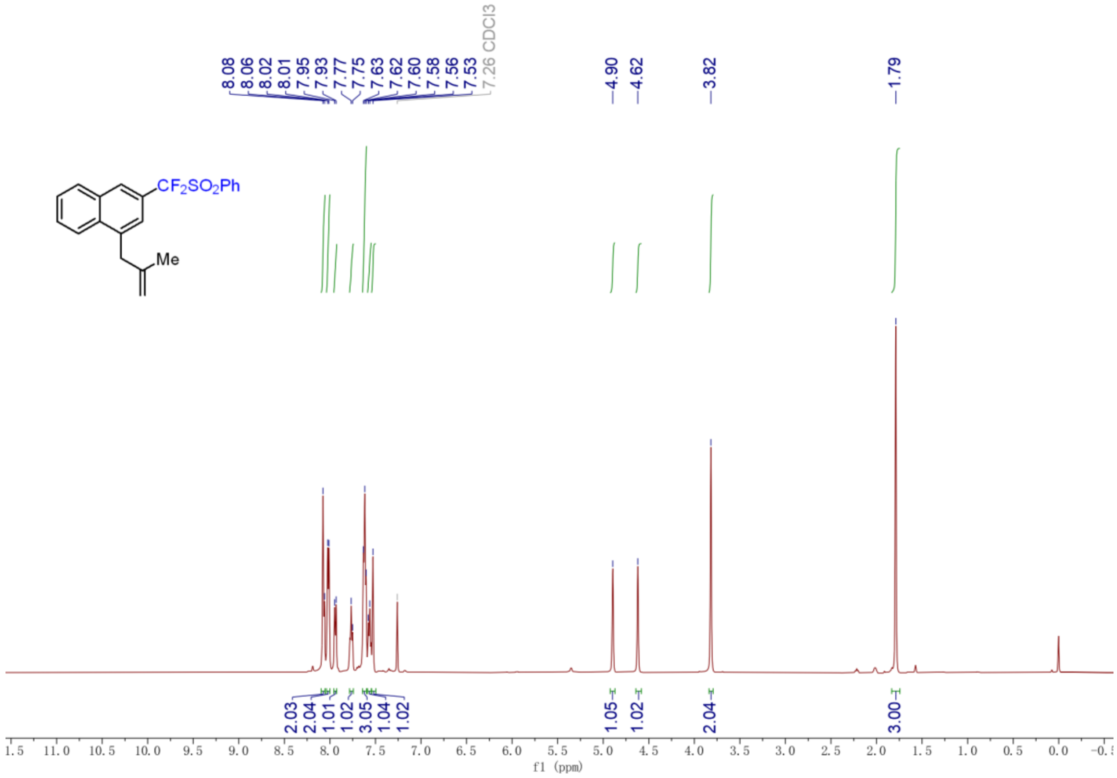
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2v**



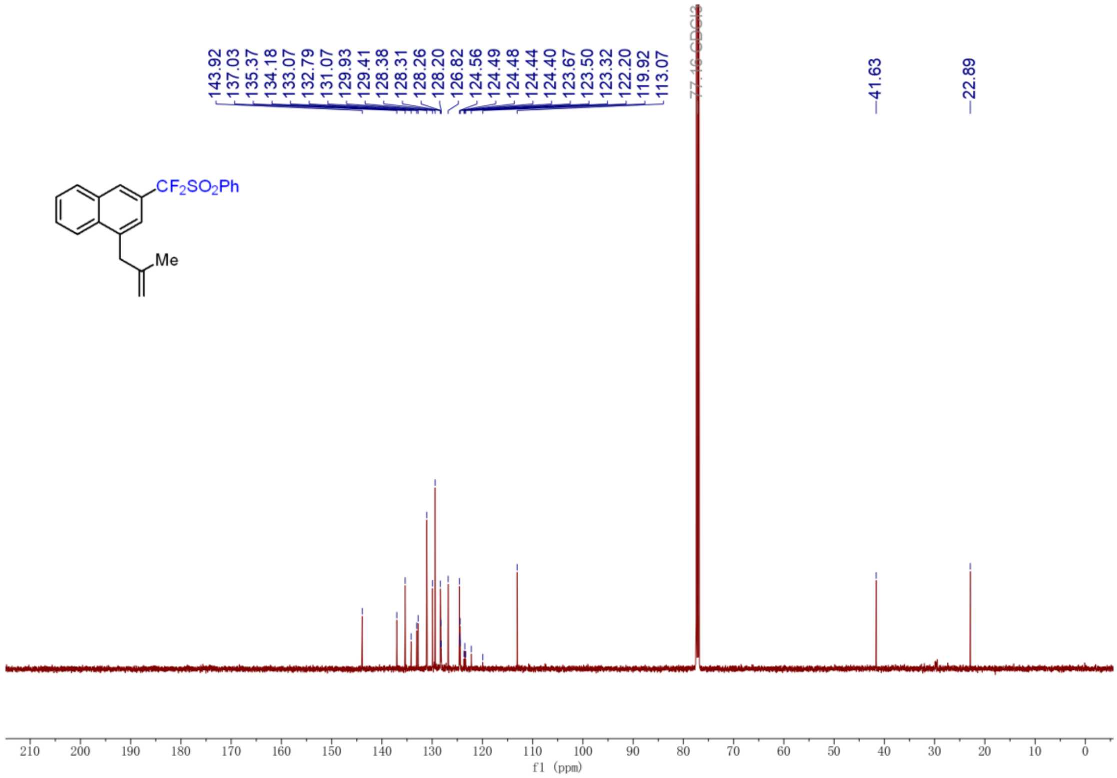
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2v**



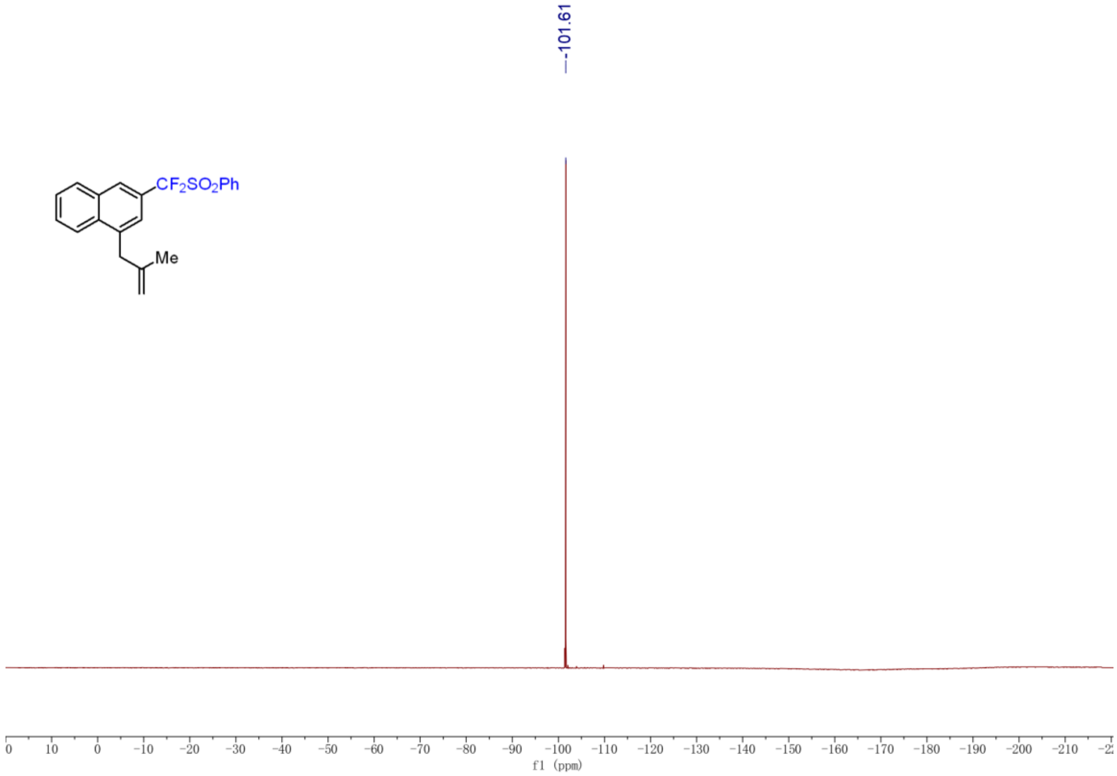
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2v**



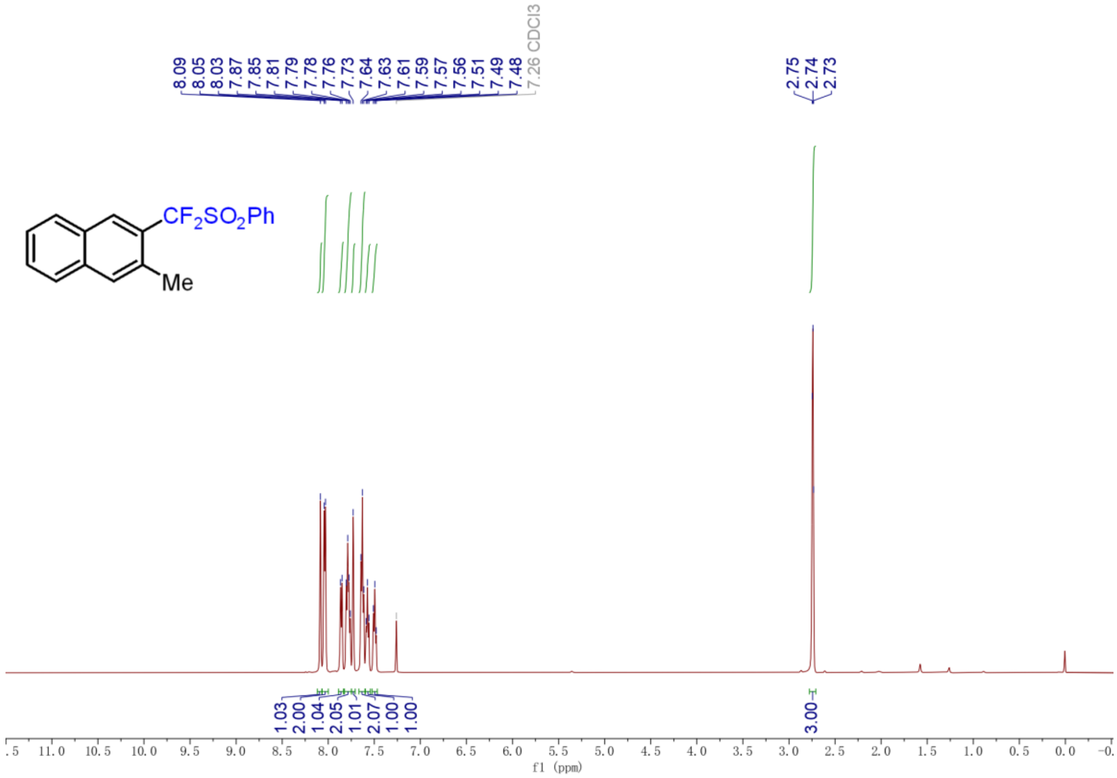
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2w**



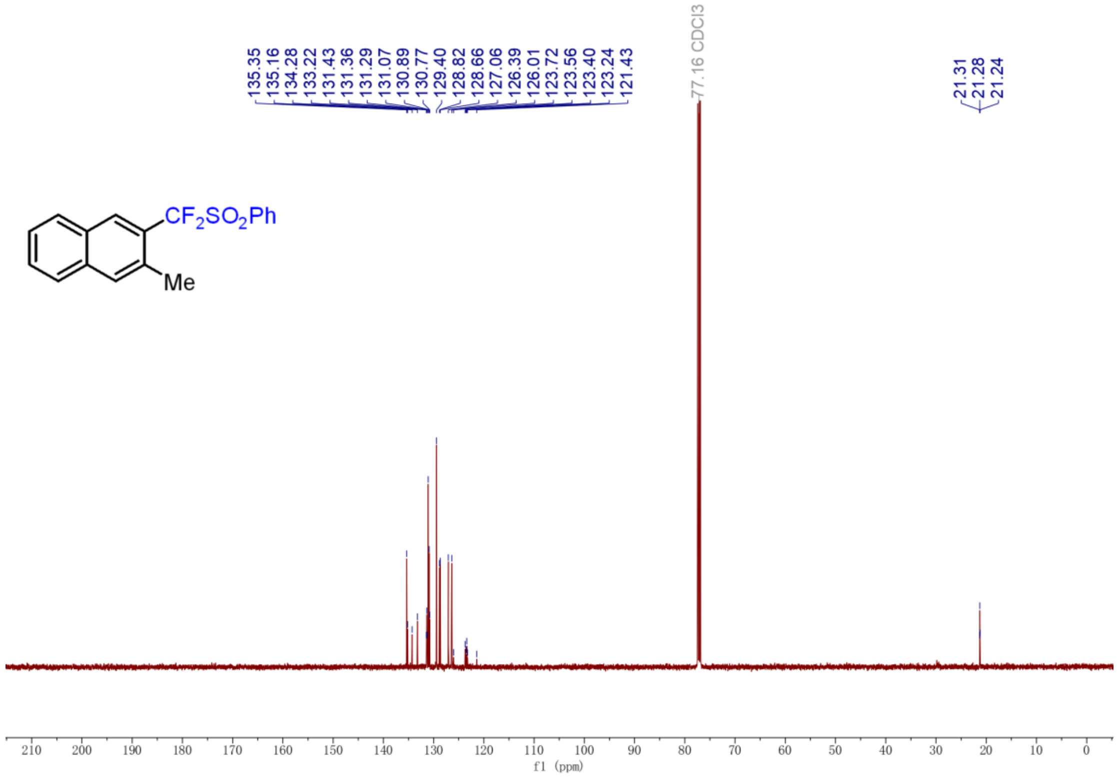
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2w**



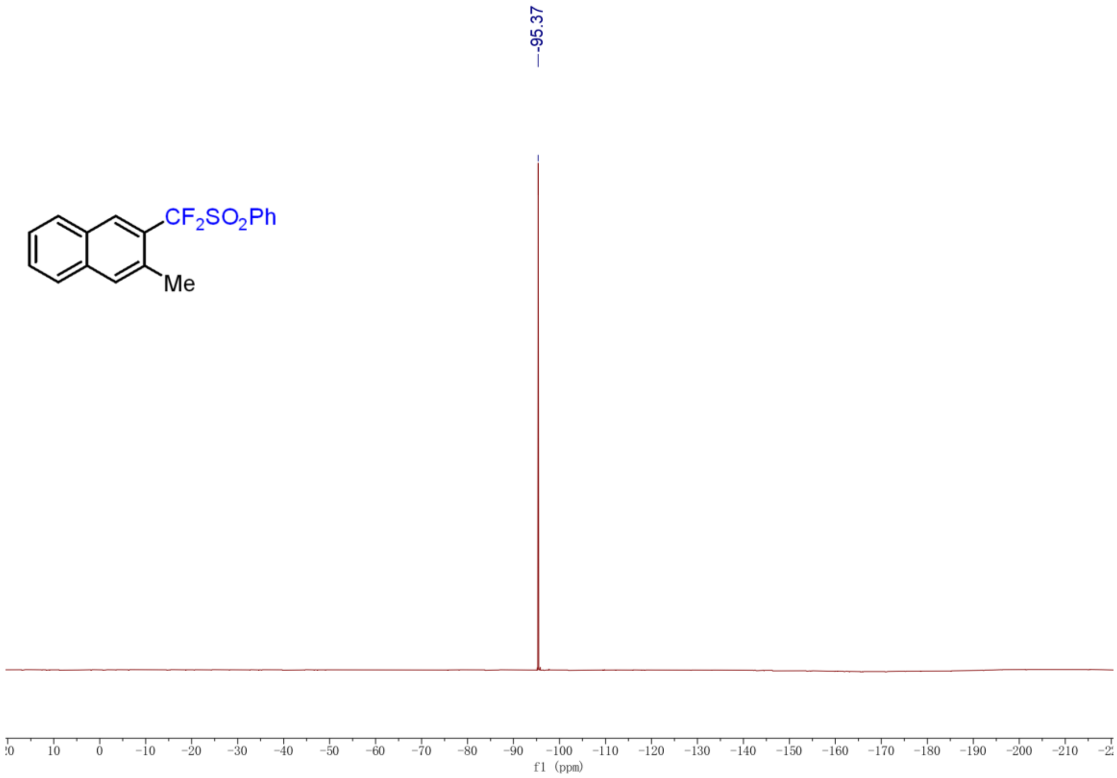
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2w**



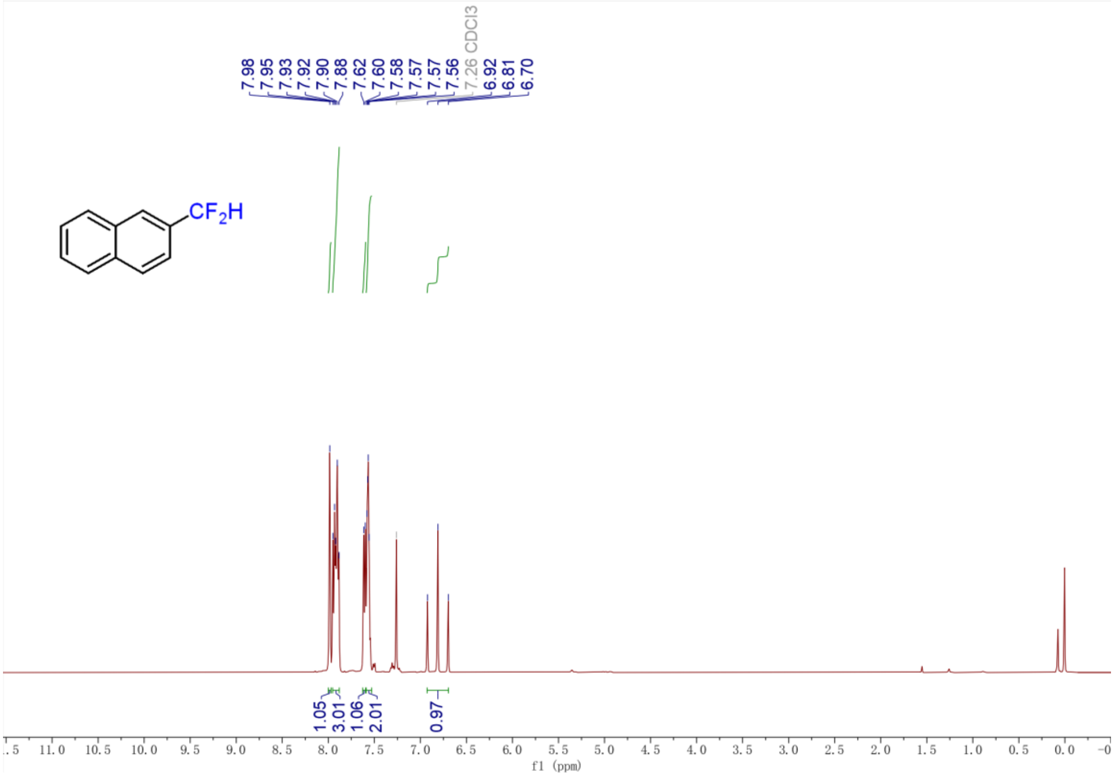
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **2x**



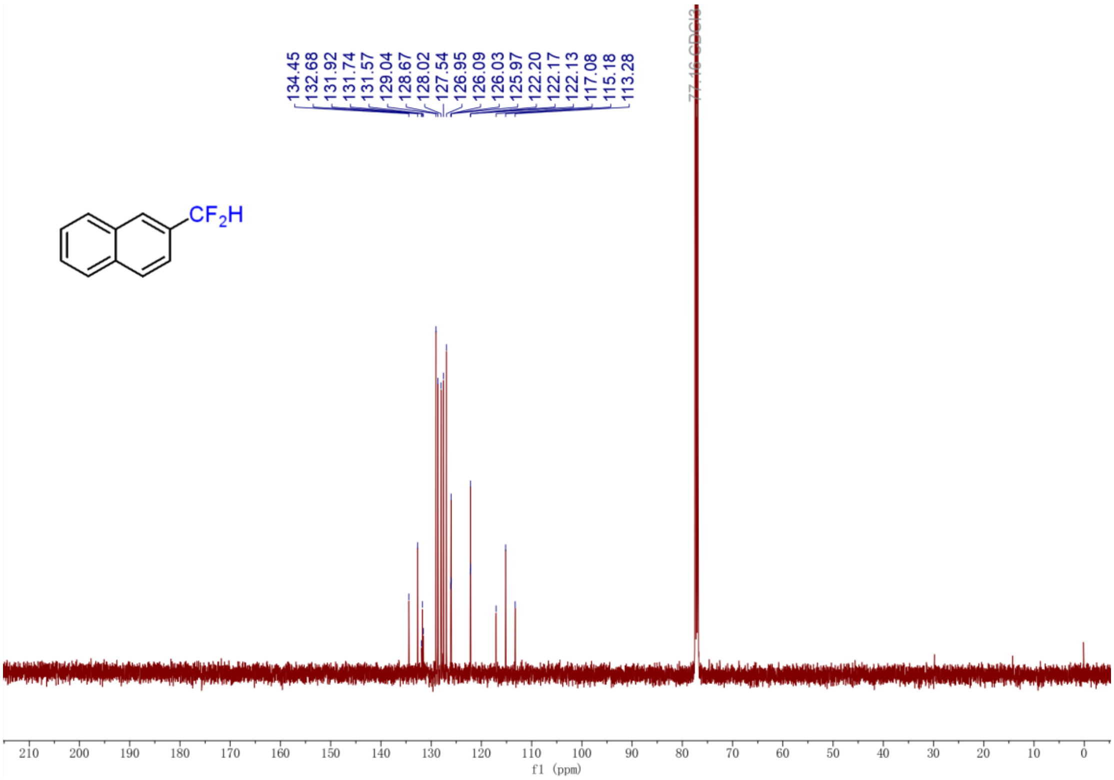
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **2x**



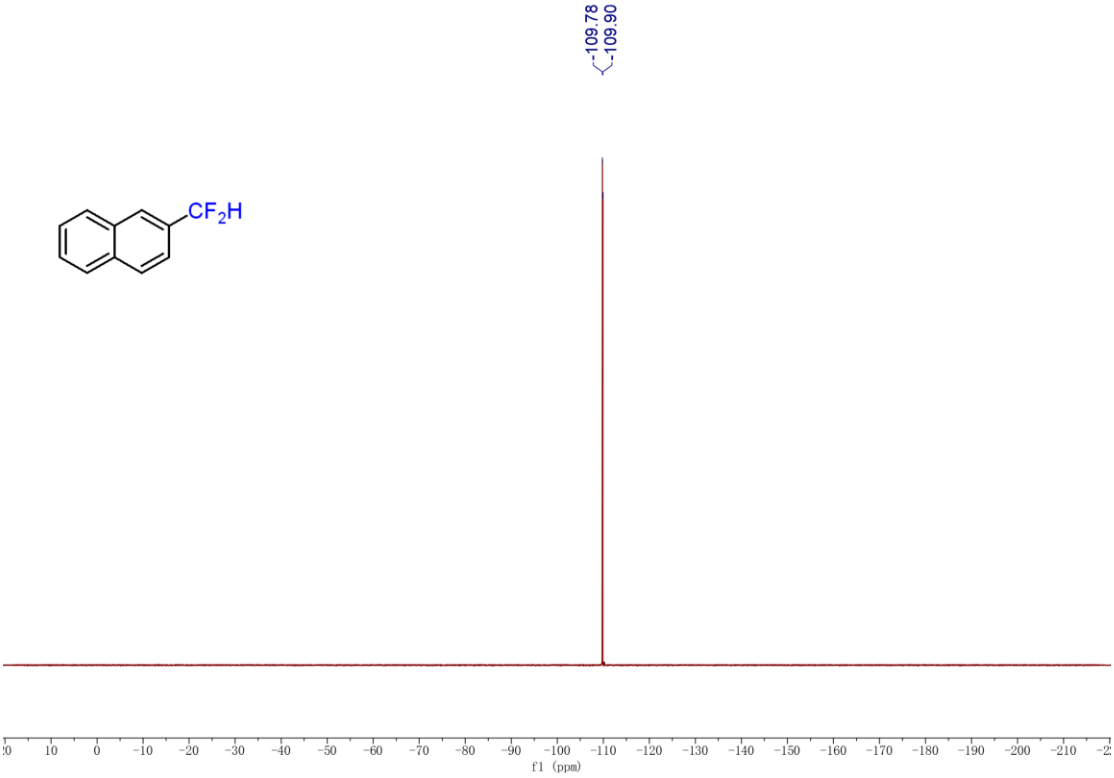
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **2x**



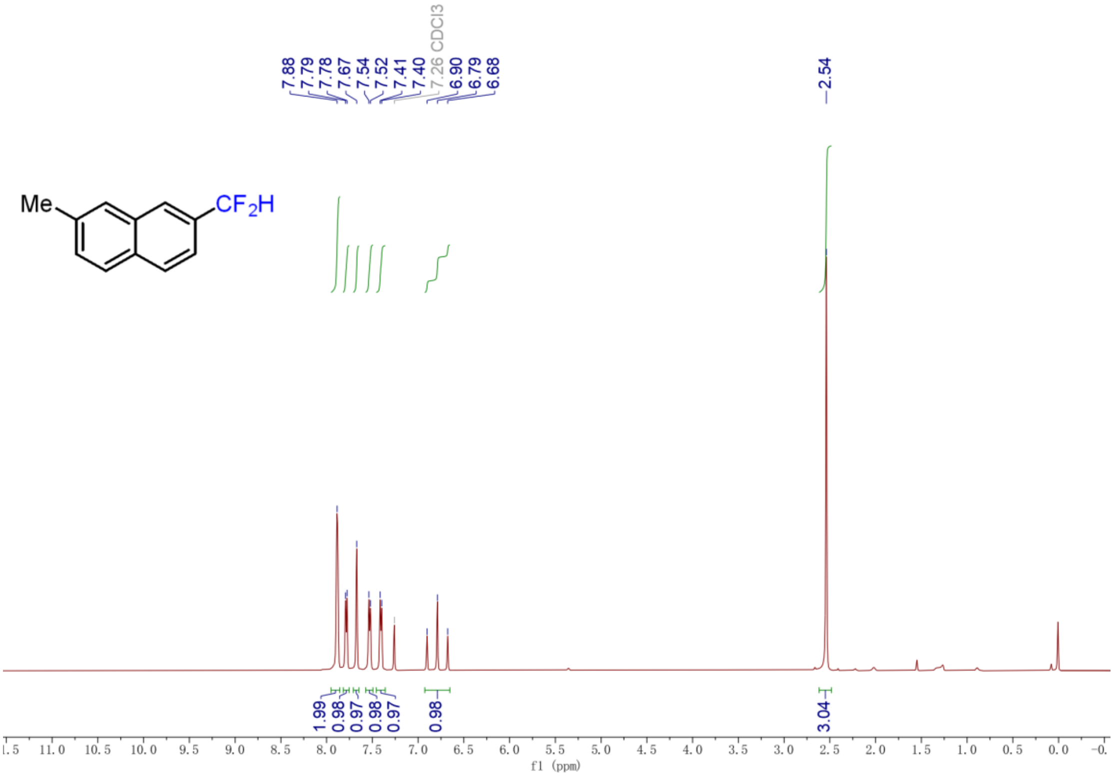
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3a**



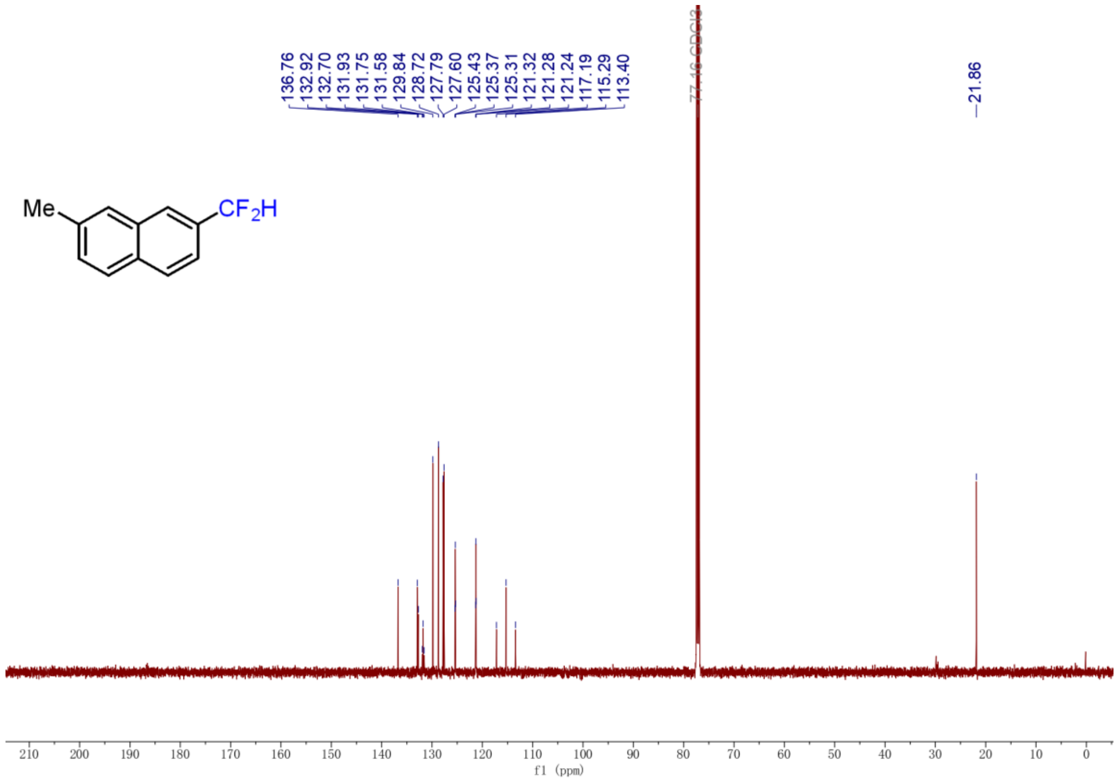
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3a**



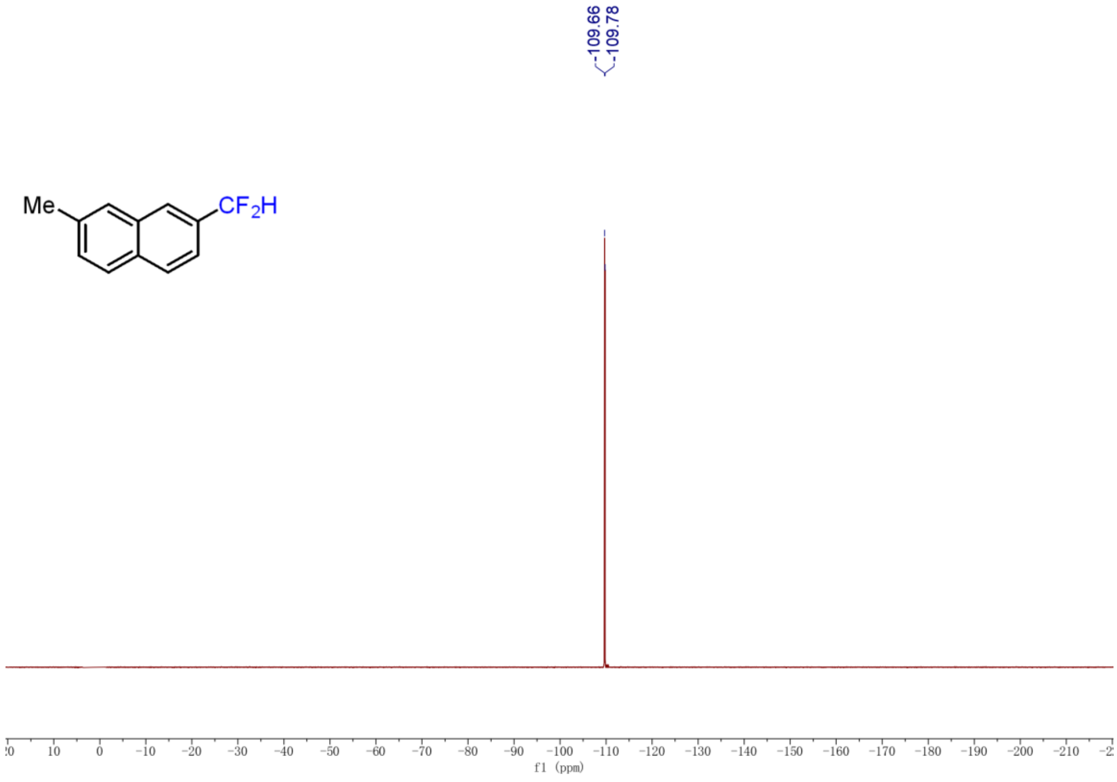
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3a**



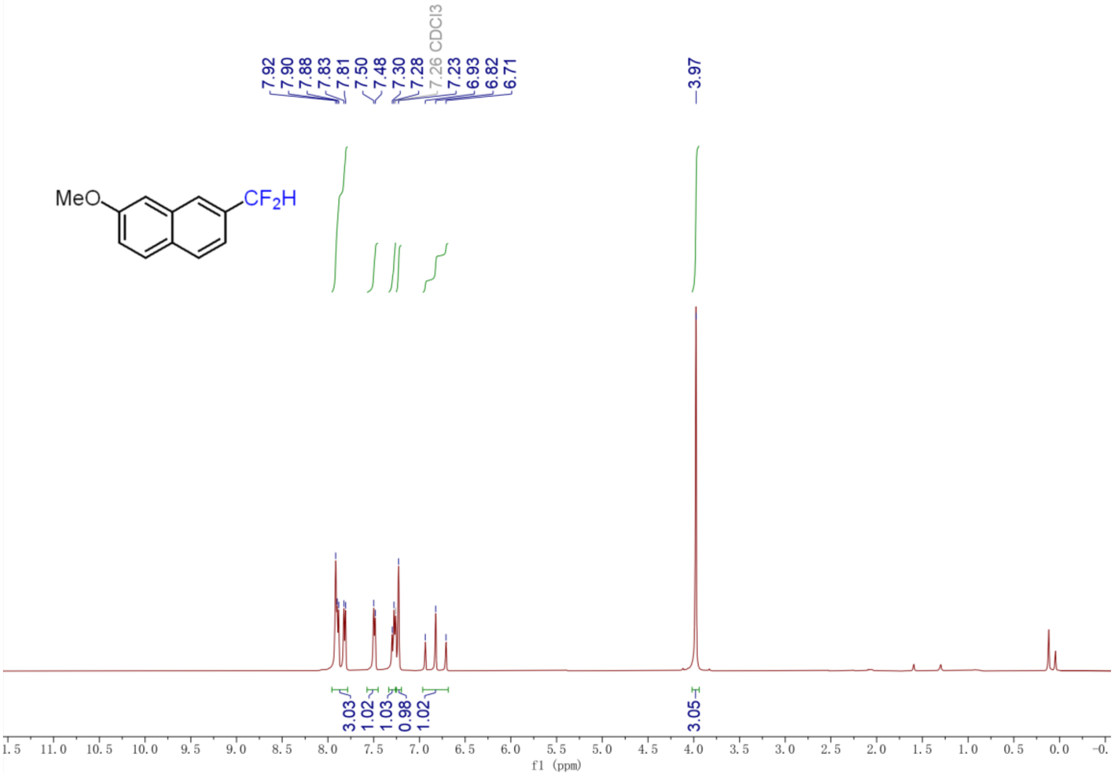
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3b**



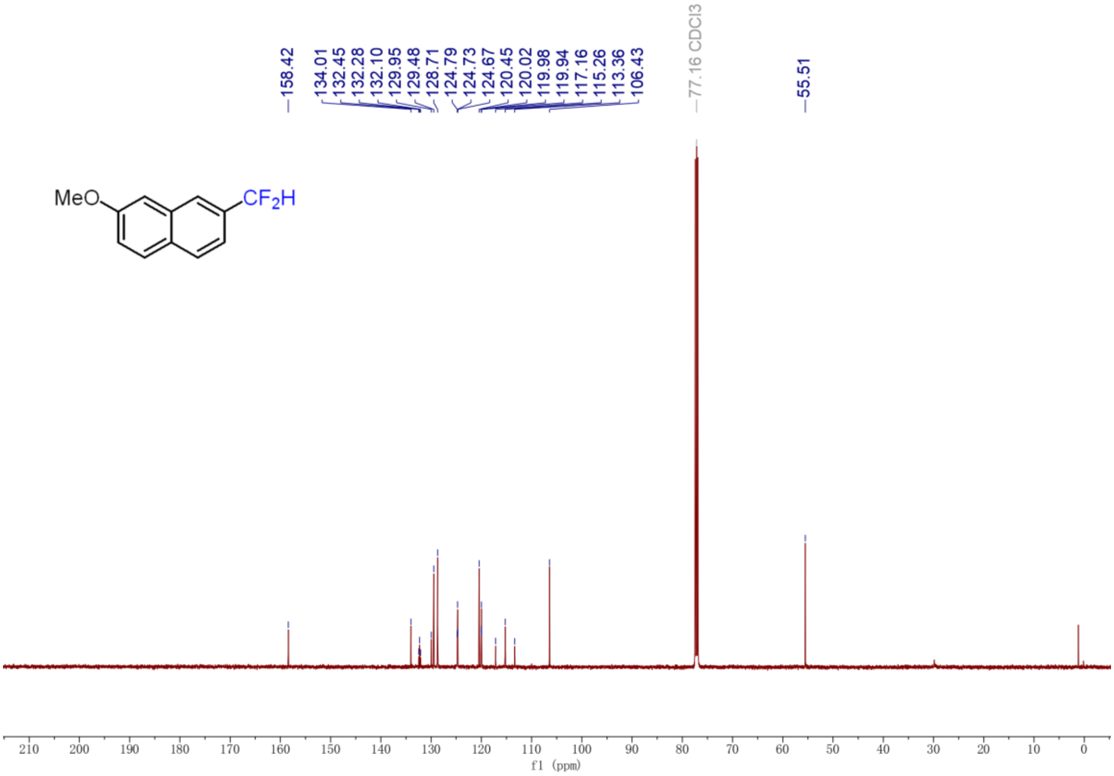
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3b**



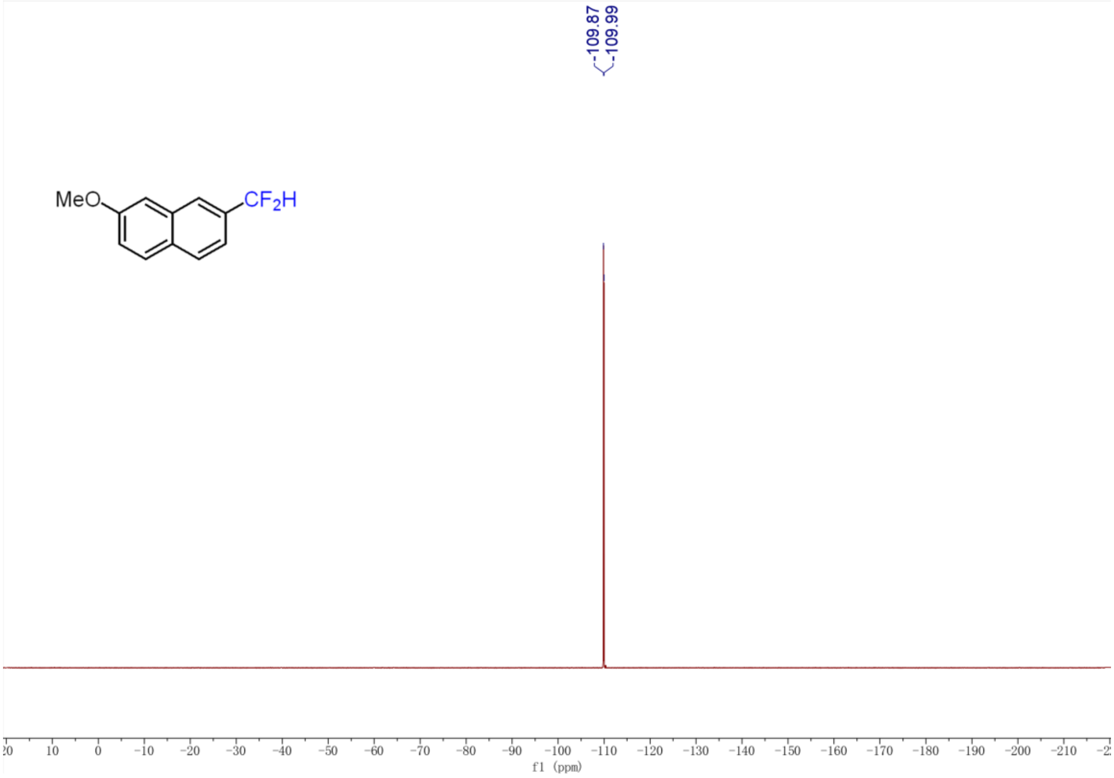
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3b**



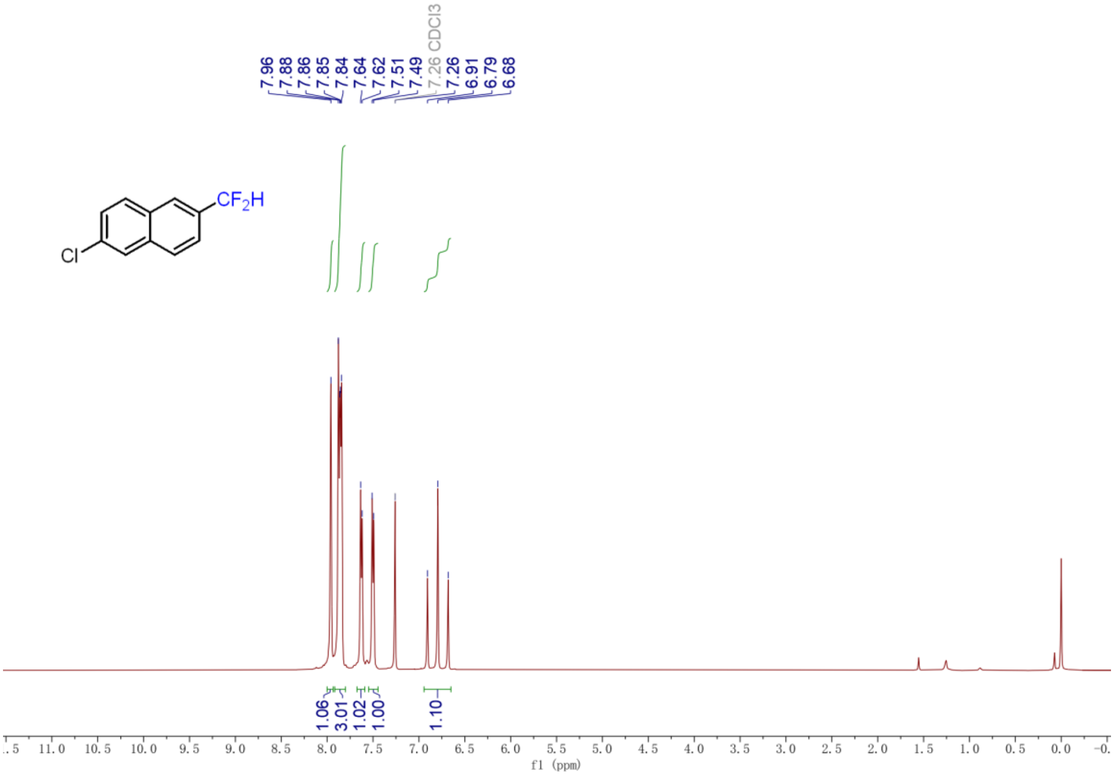
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3c**



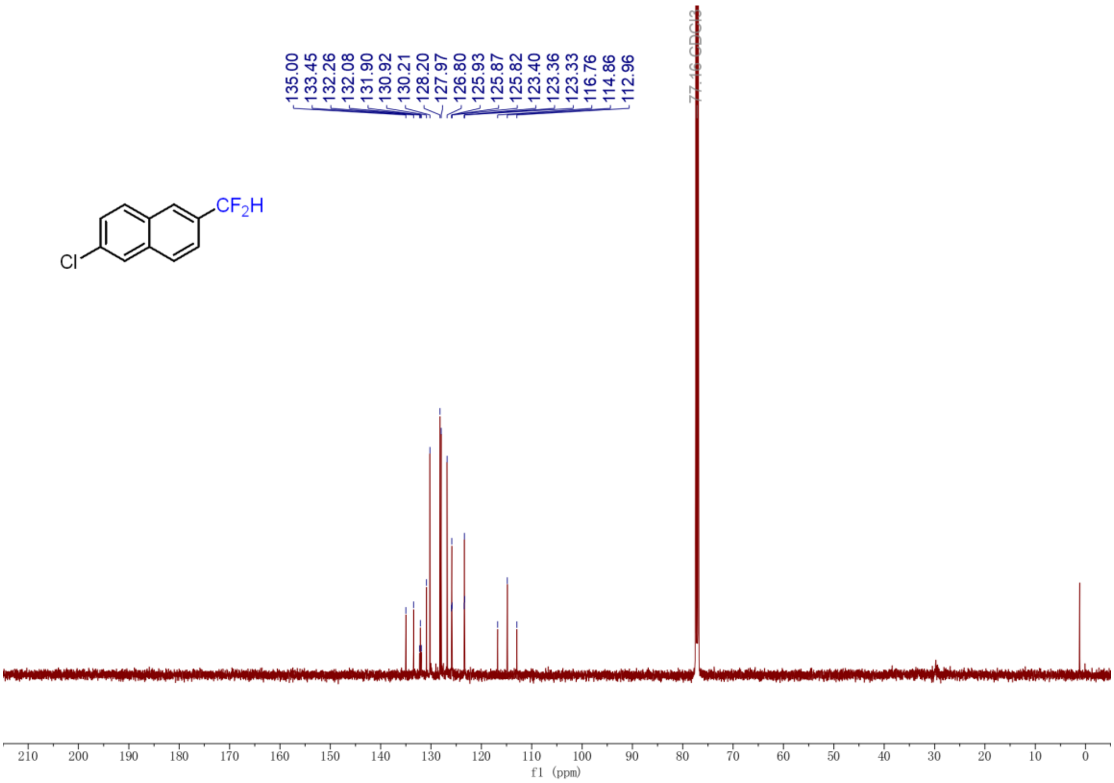
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3c**



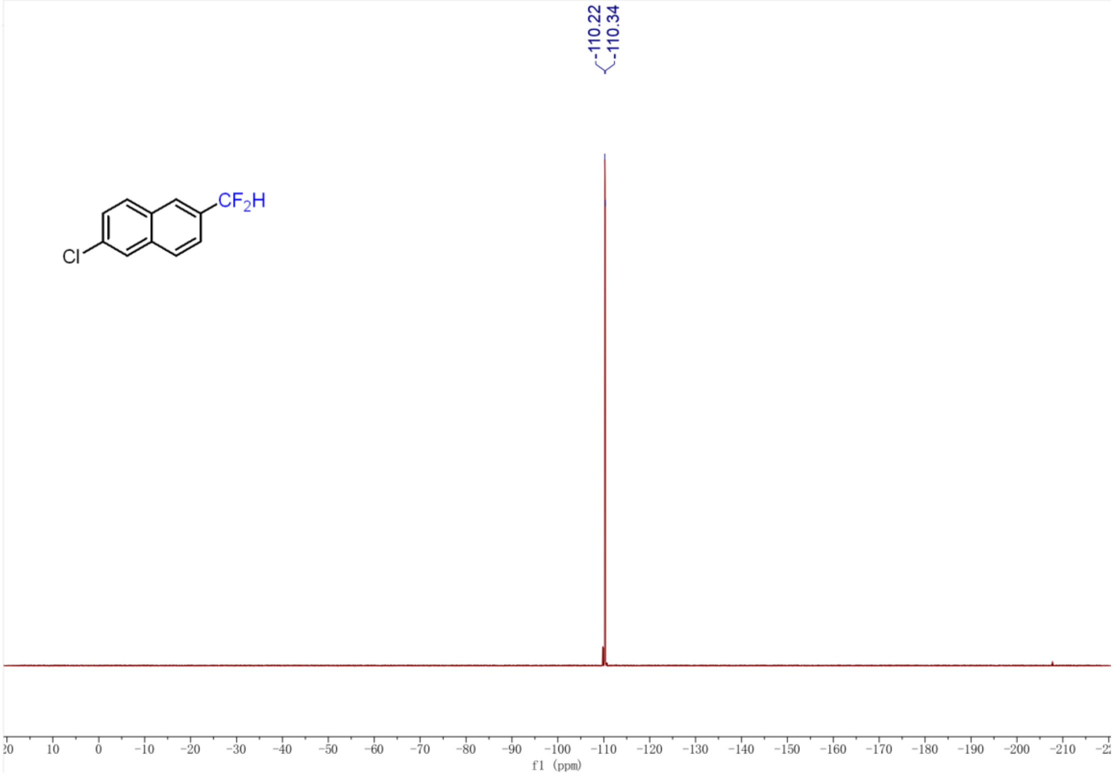
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3c**



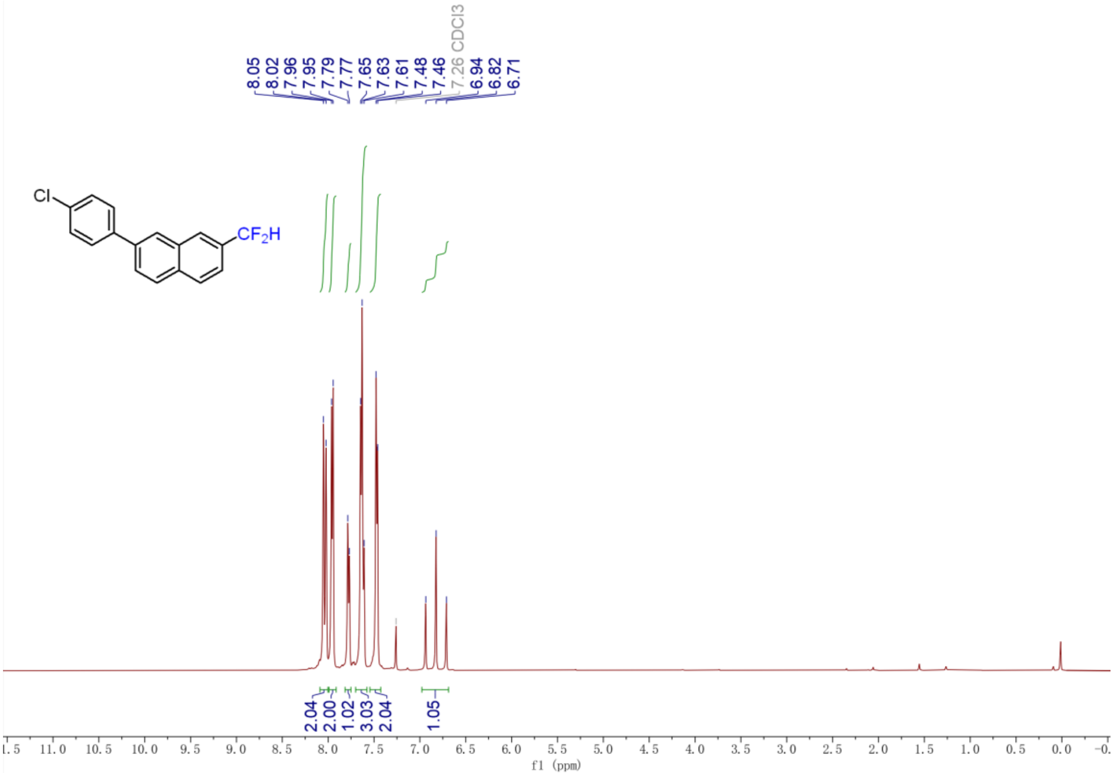
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3d**



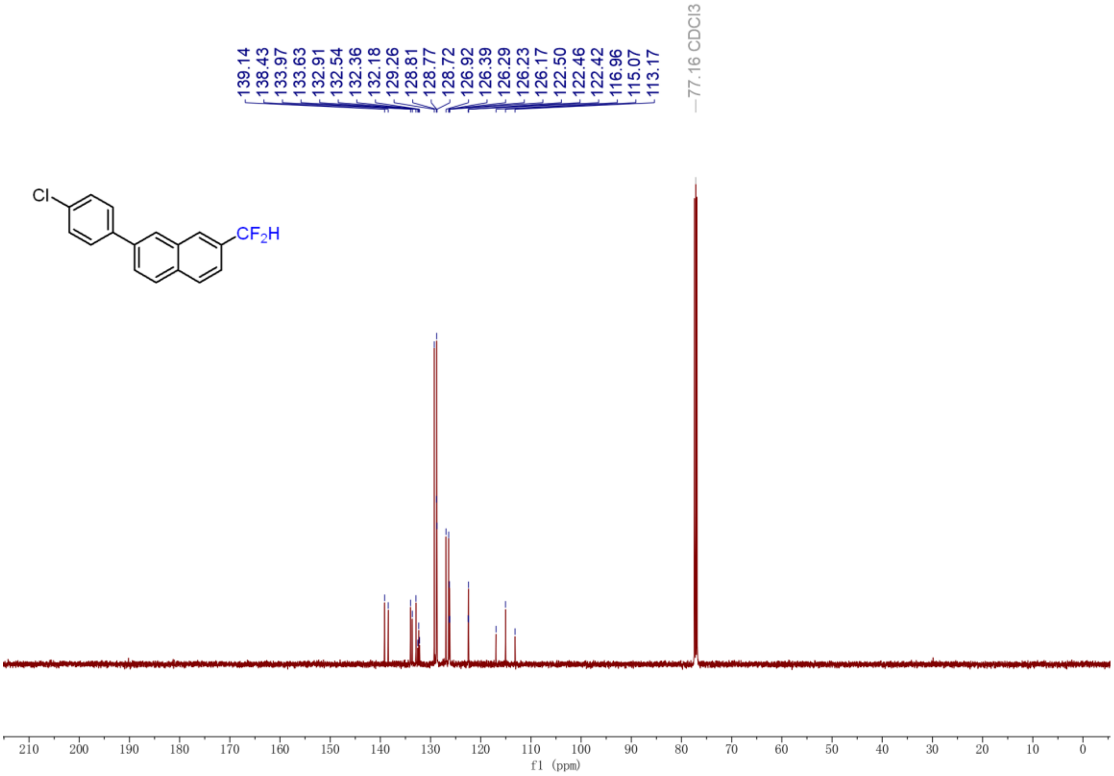
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3d**



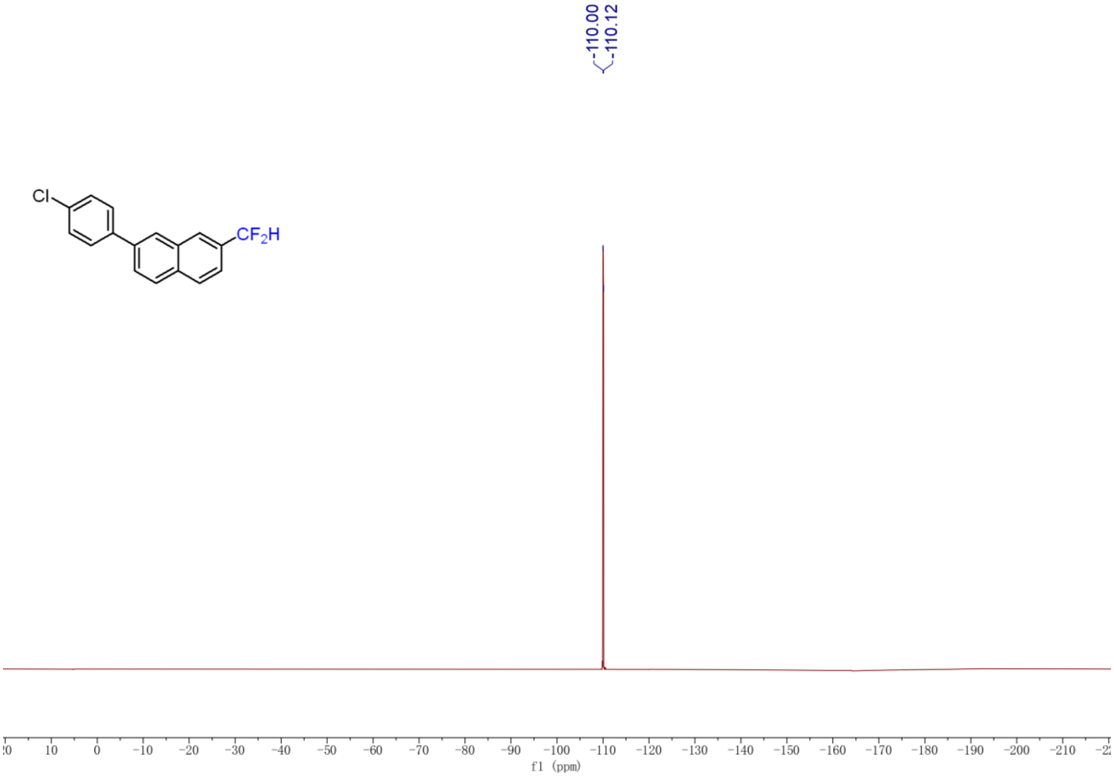
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3d**



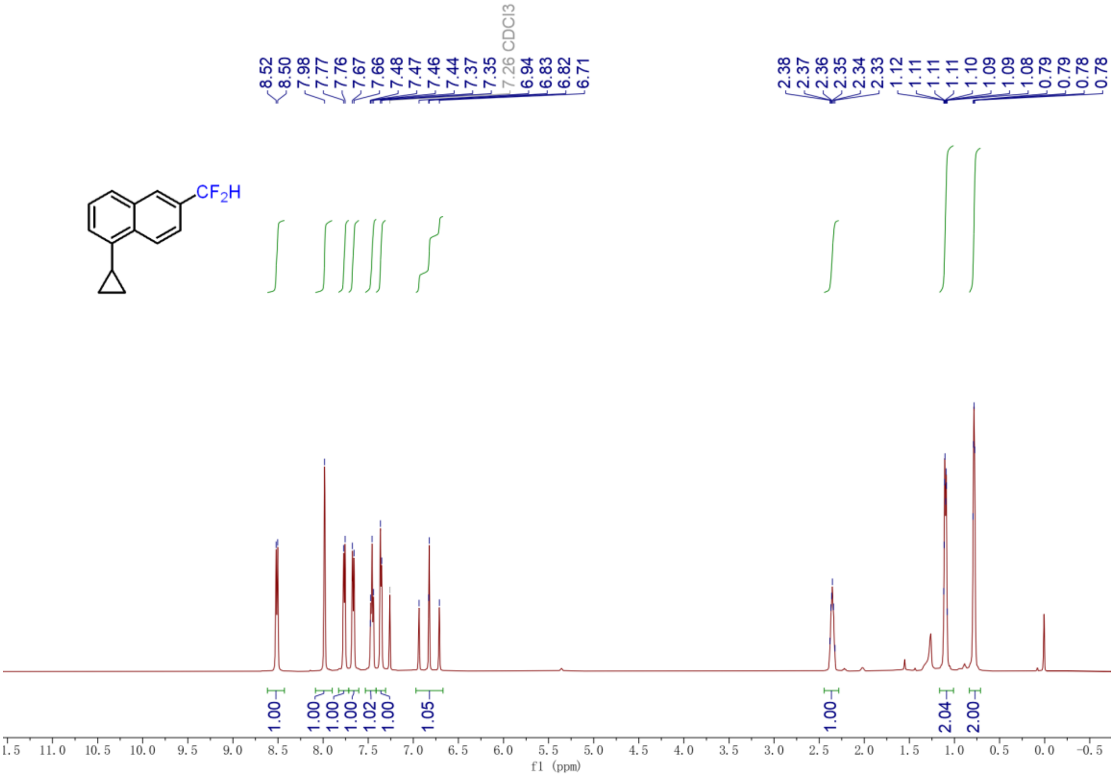
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3e**



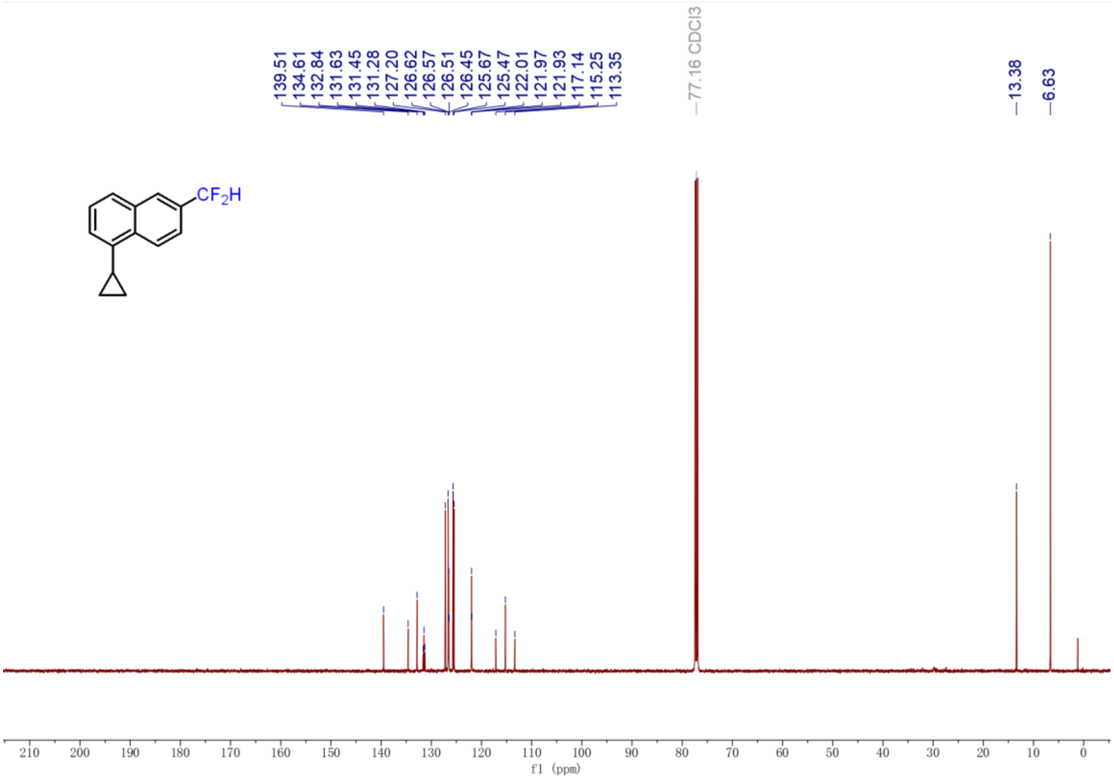
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3e**



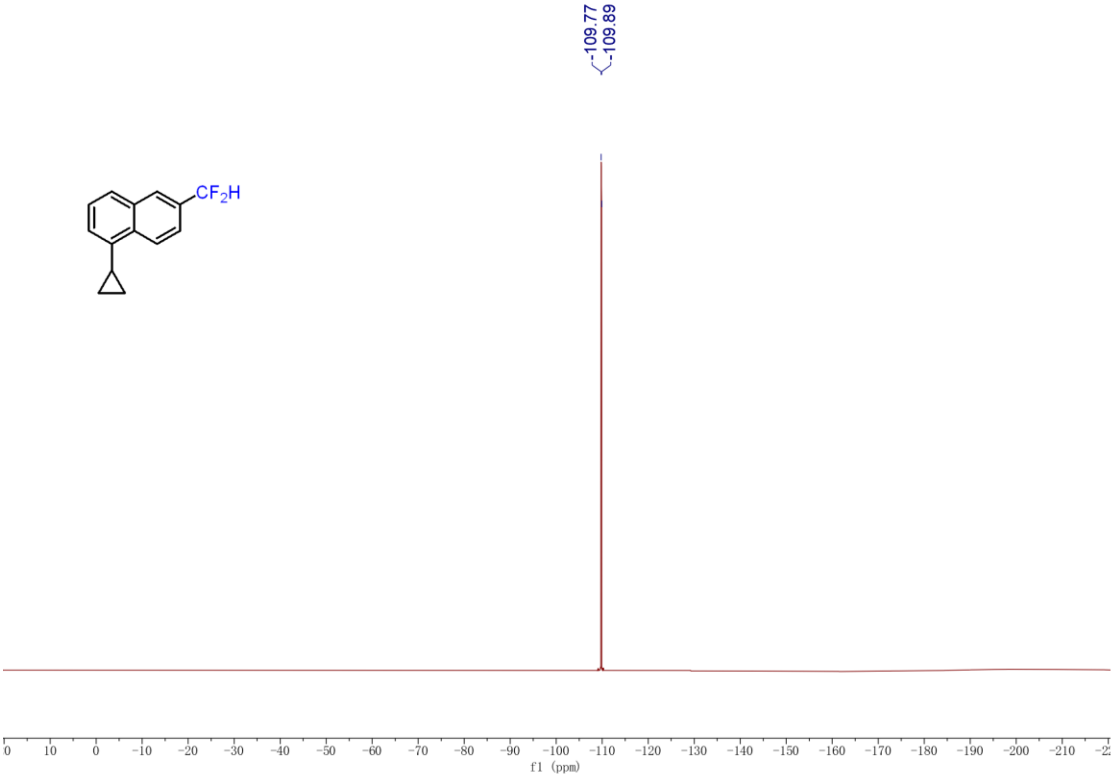
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) **3e**



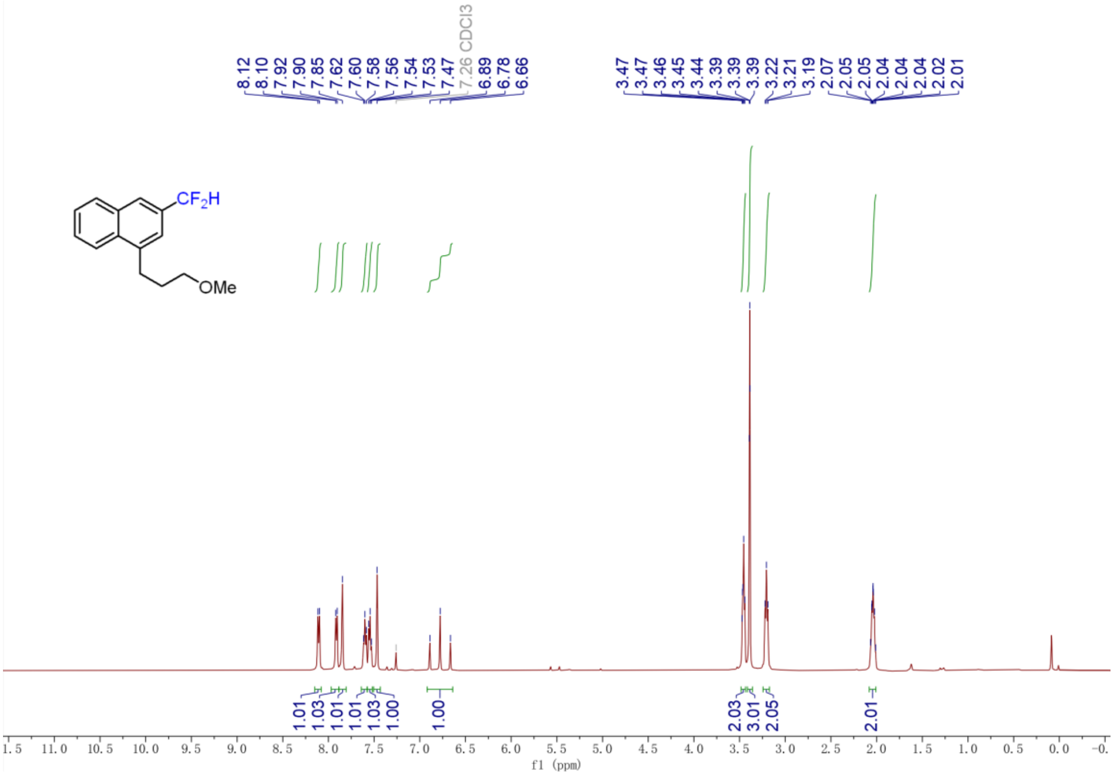
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3f**



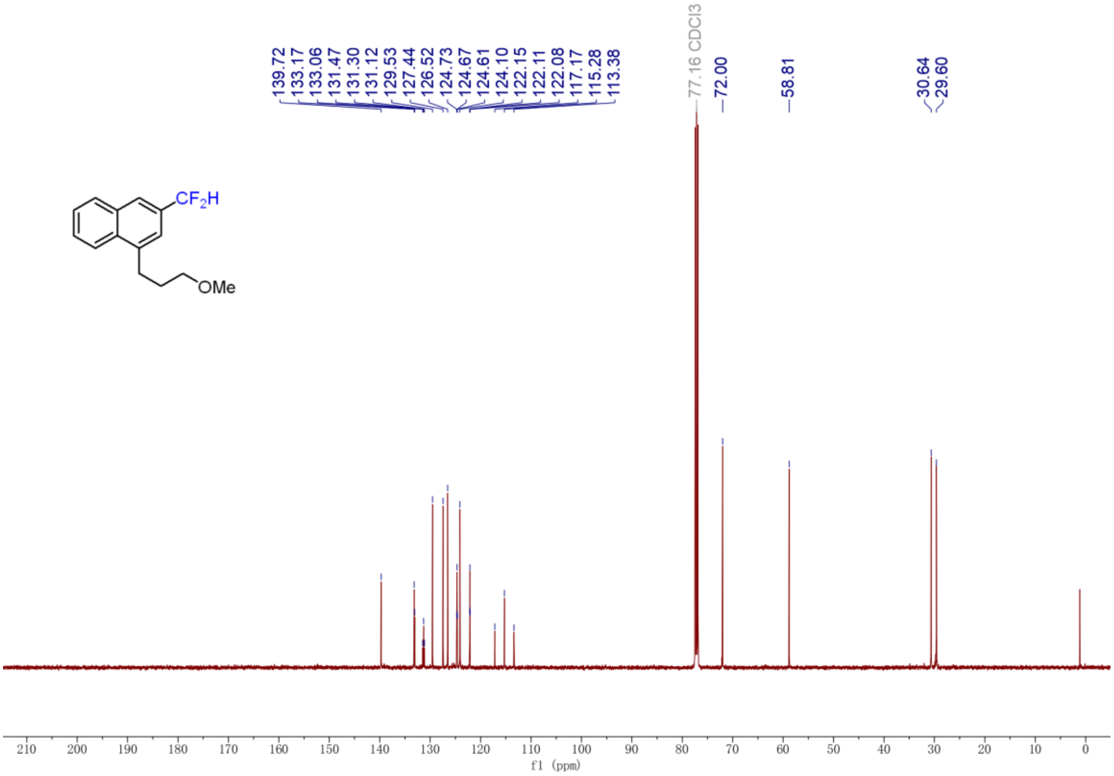
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3f**



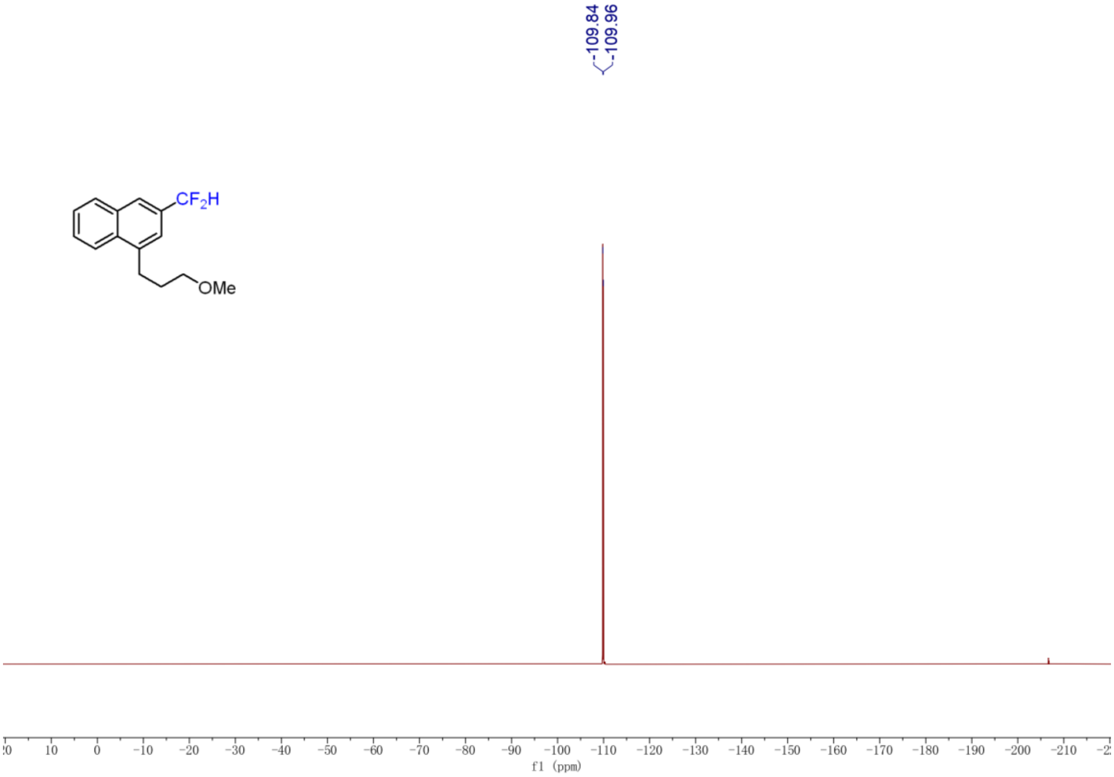
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3f**



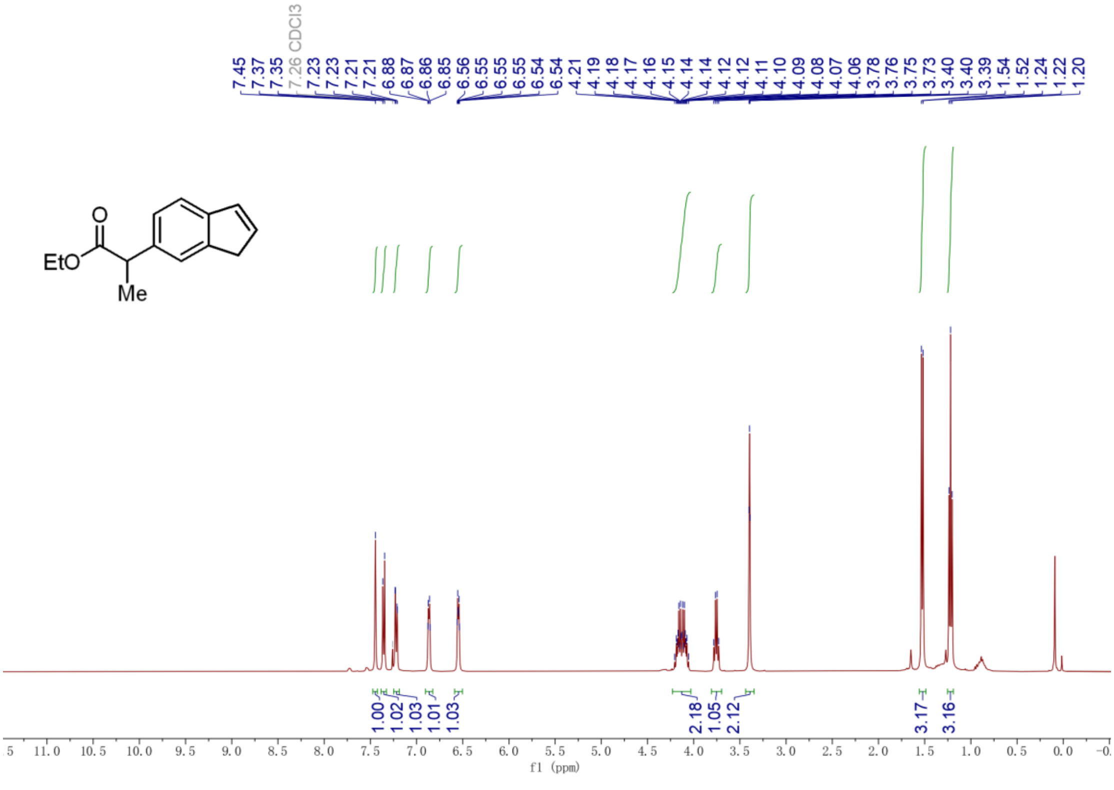
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **3g**



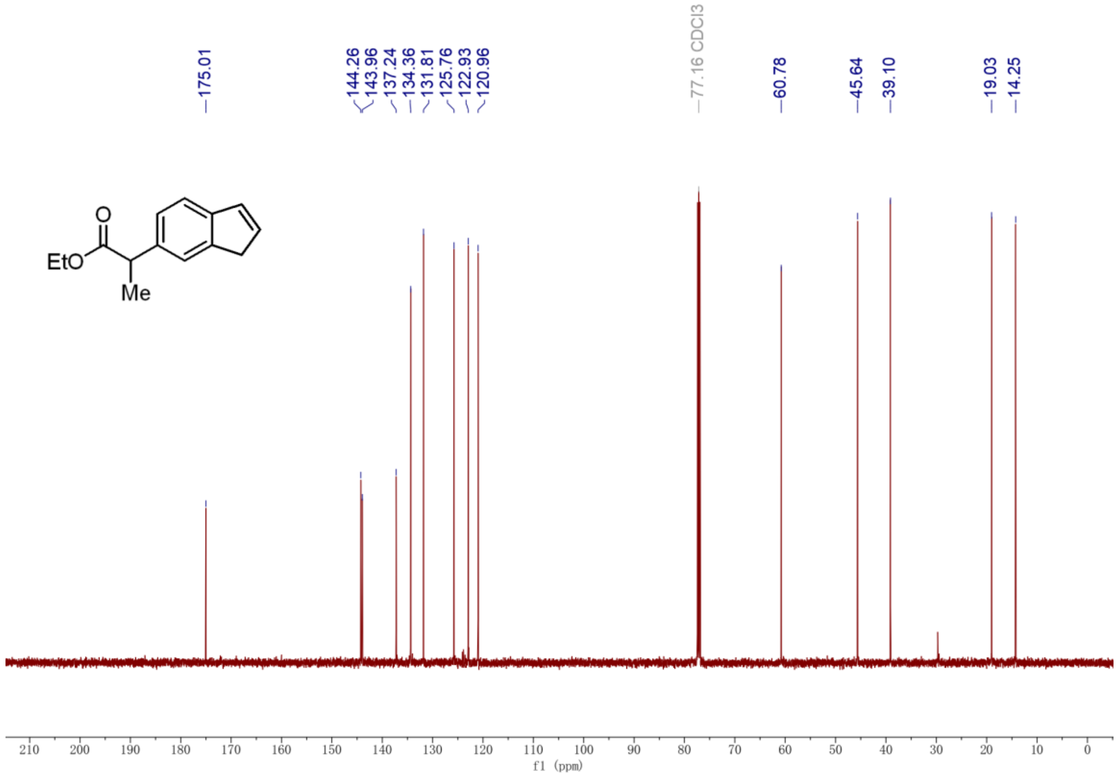
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **3g**



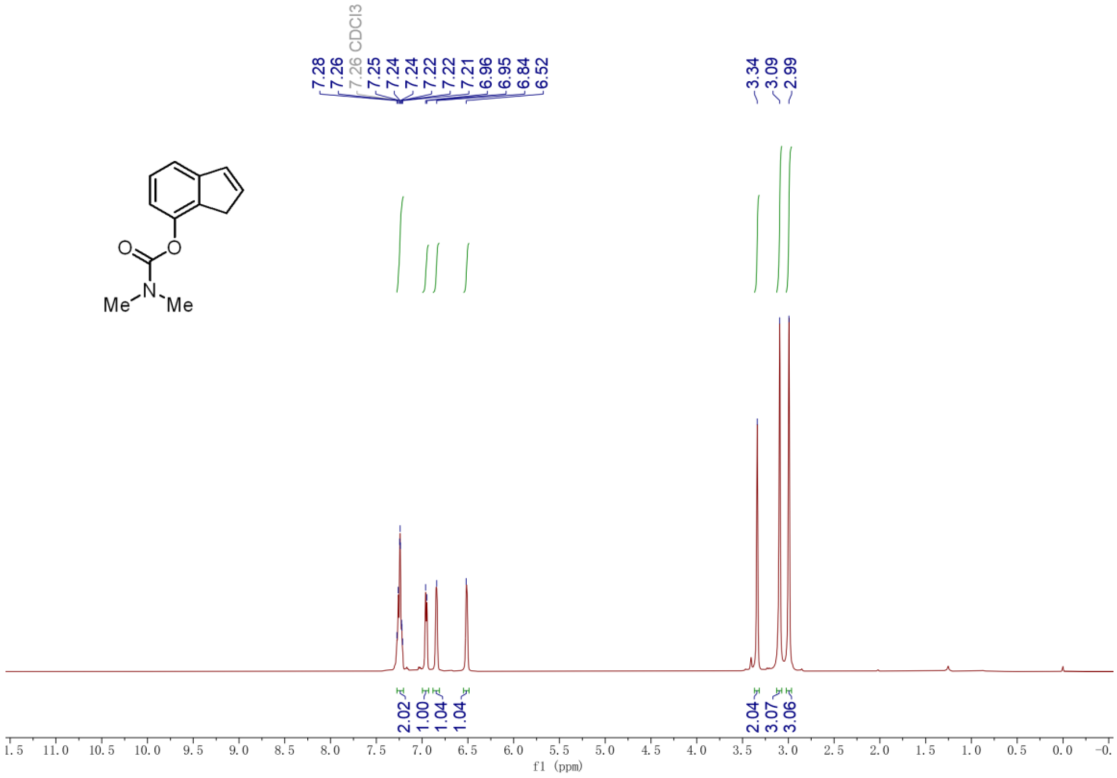
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **3g**



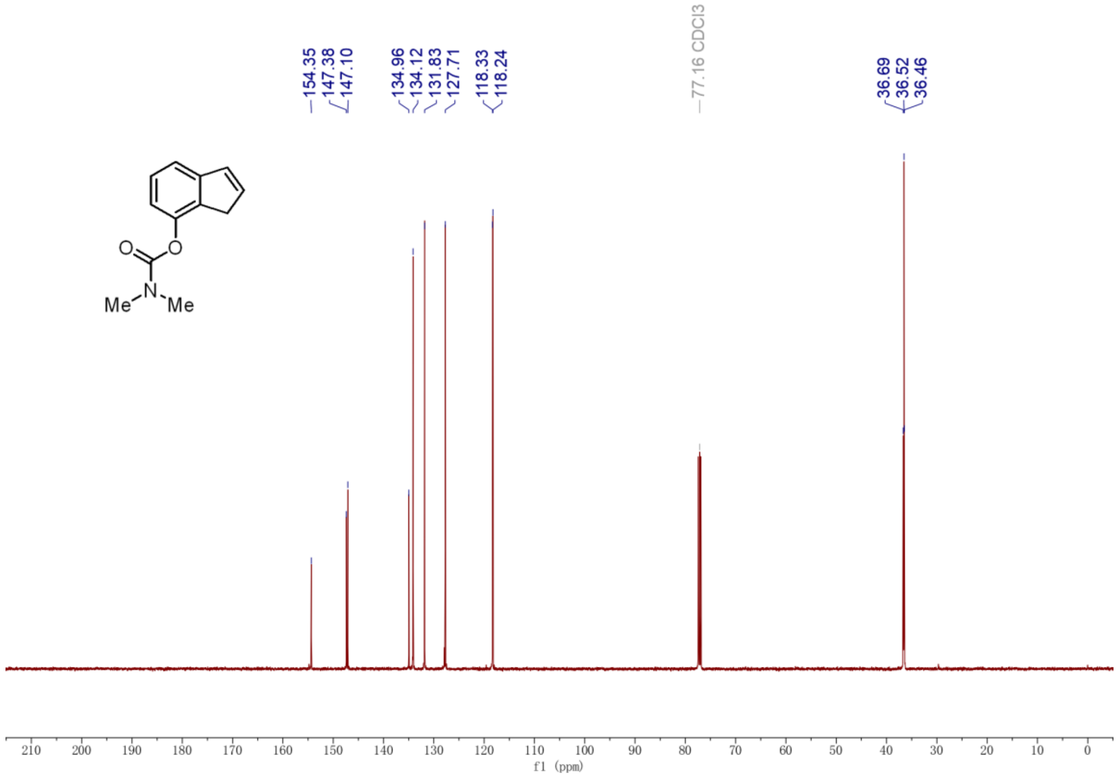
^{1}H NMR spectrum (400 MHz, Chloroform-*d*) of **4a**



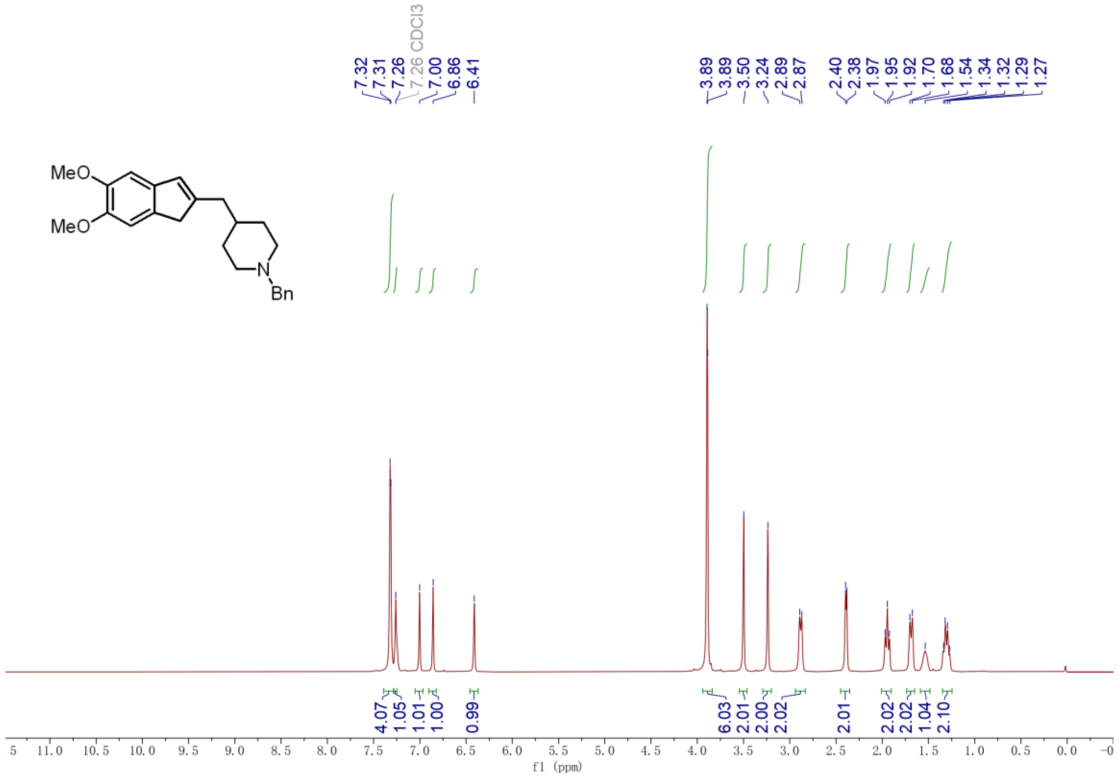
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **4a**



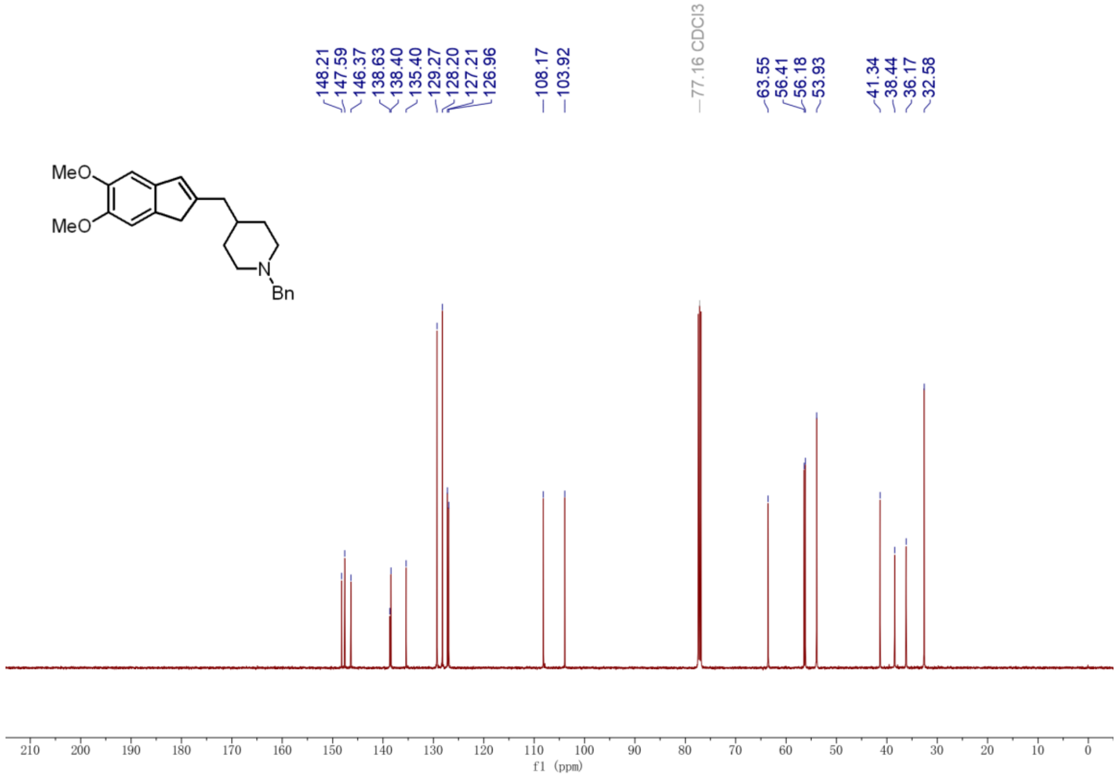
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **4b**



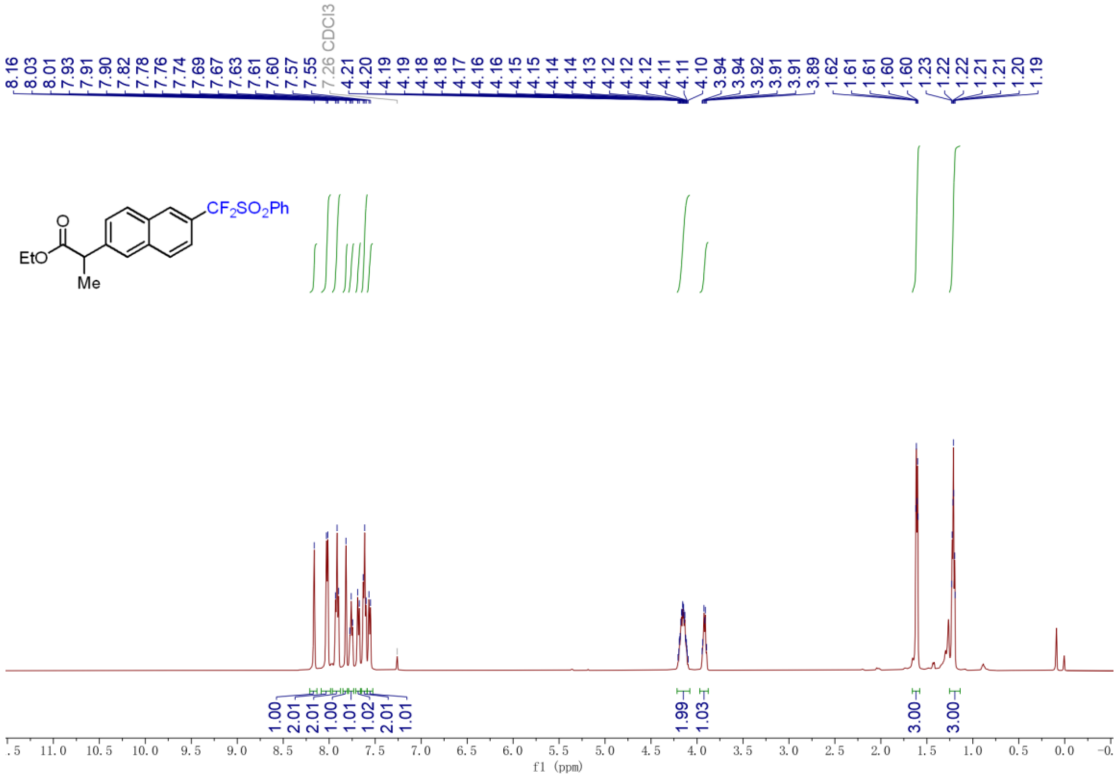
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **4b**



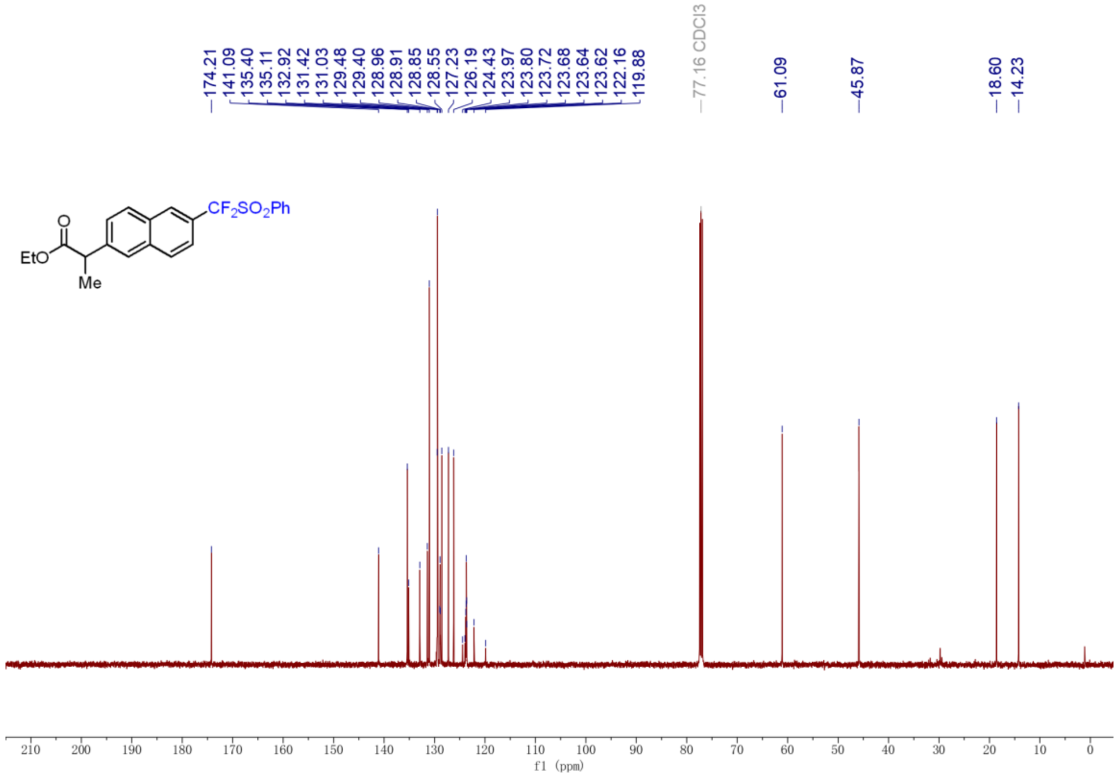
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **4c**



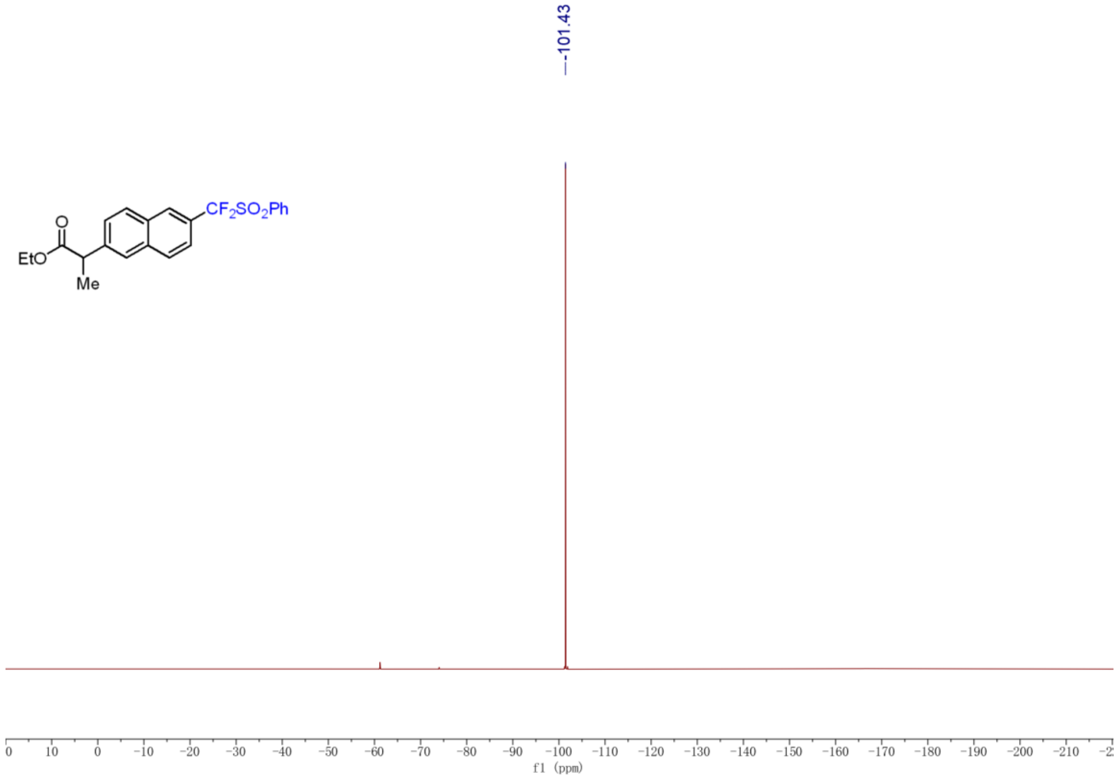
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **4c**



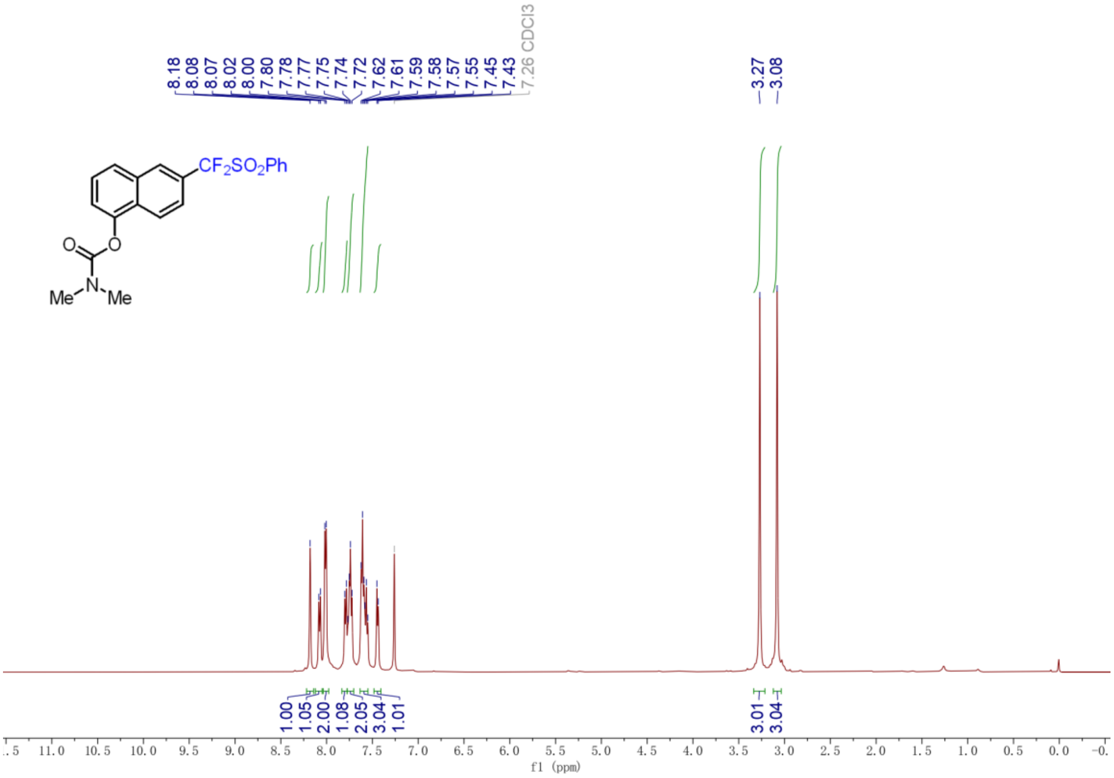
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **5a**



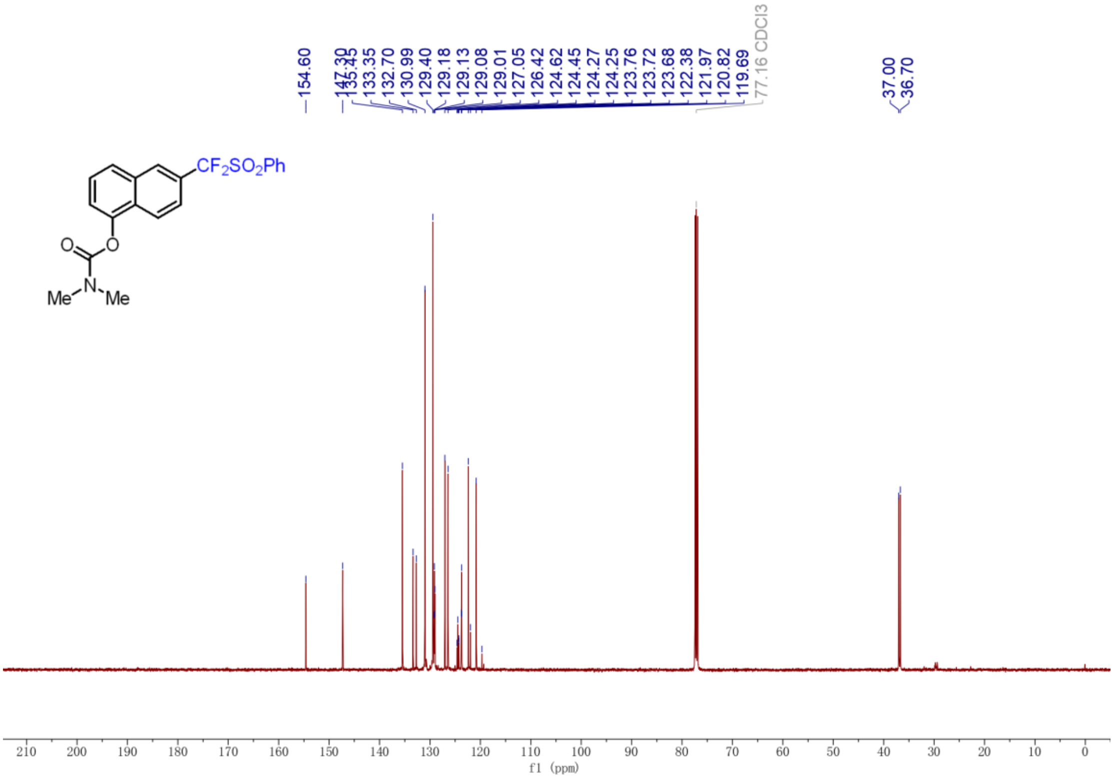
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **5a**



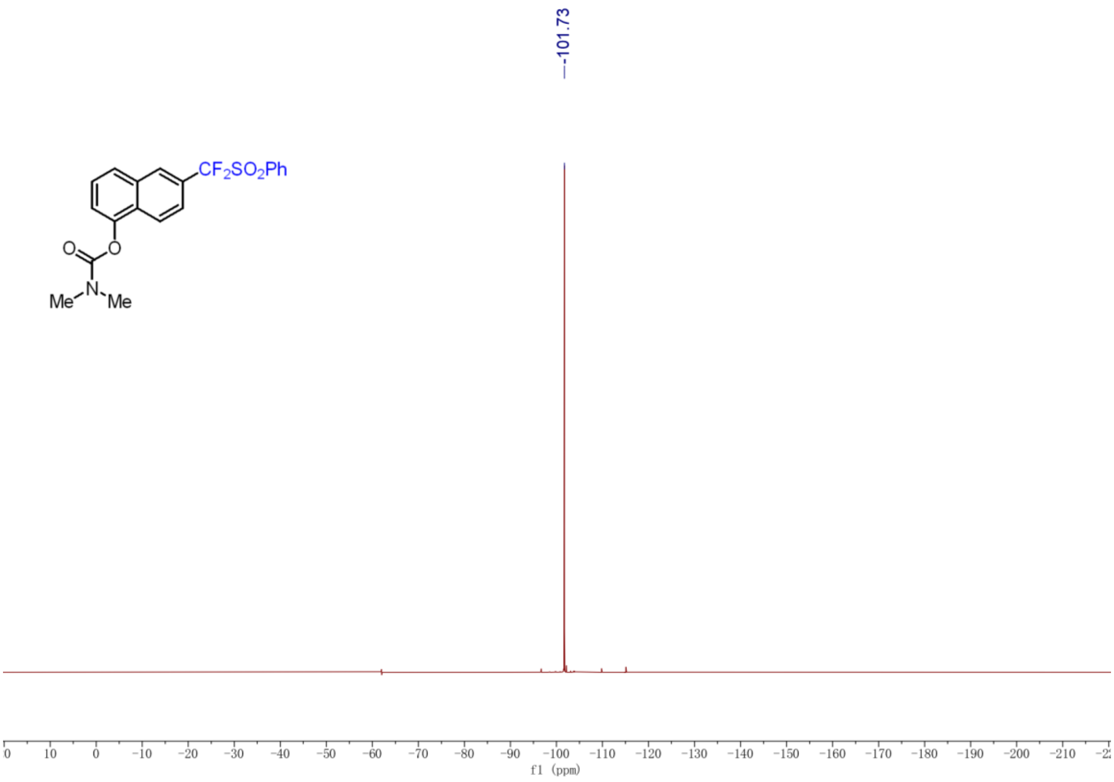
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **5a**



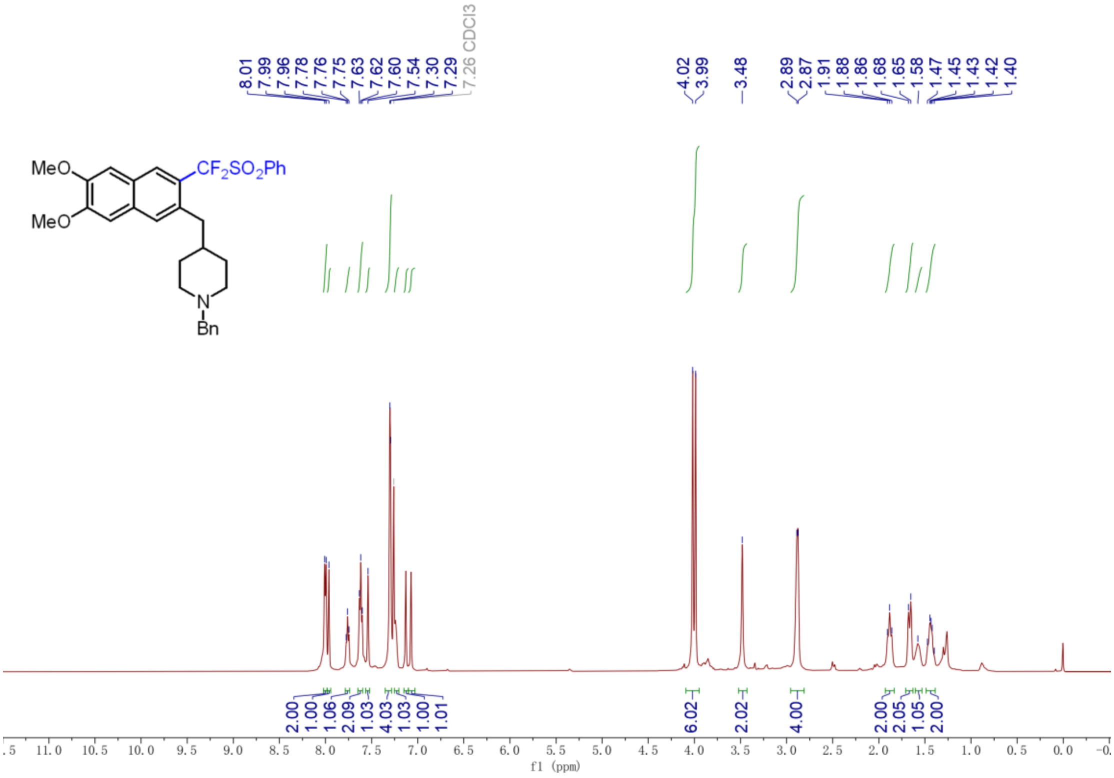
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **5b**



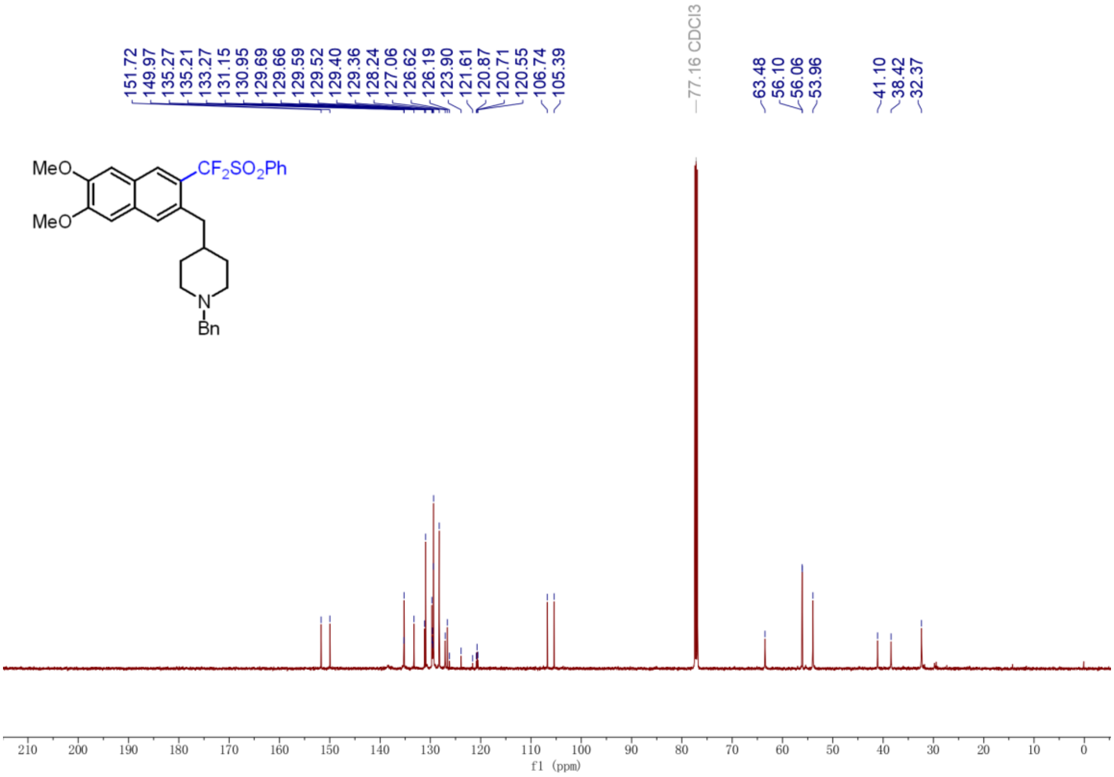
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **5b**



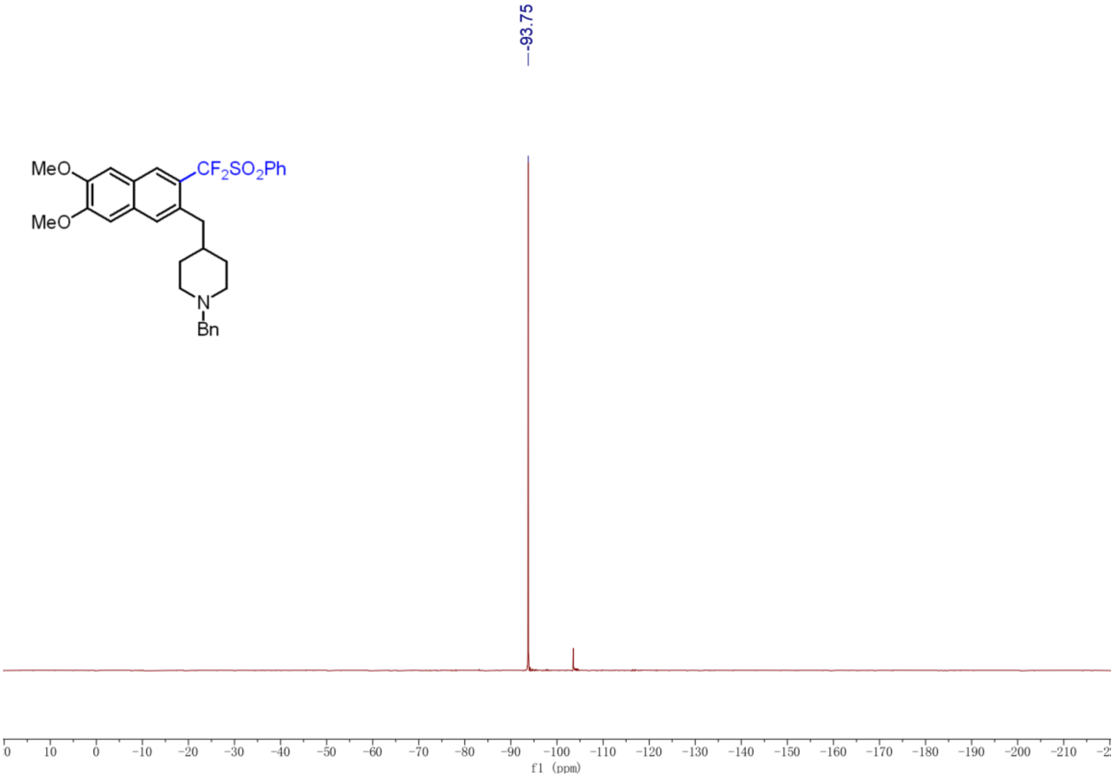
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **5b**



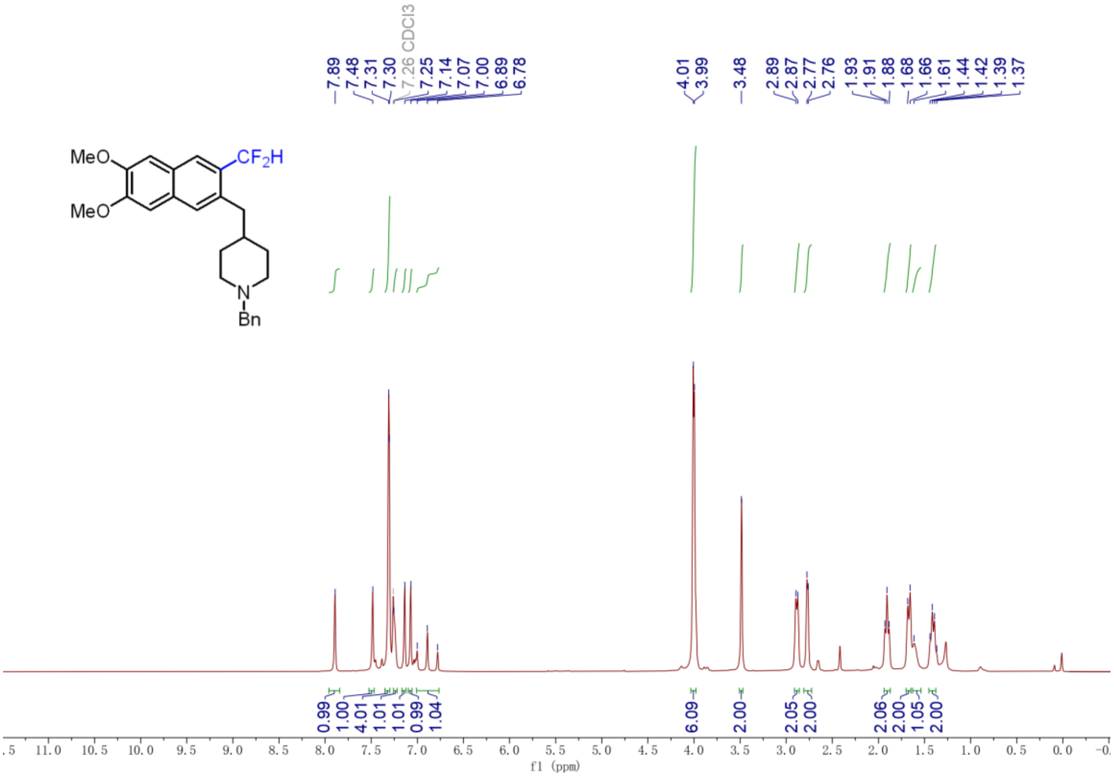
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **5c**



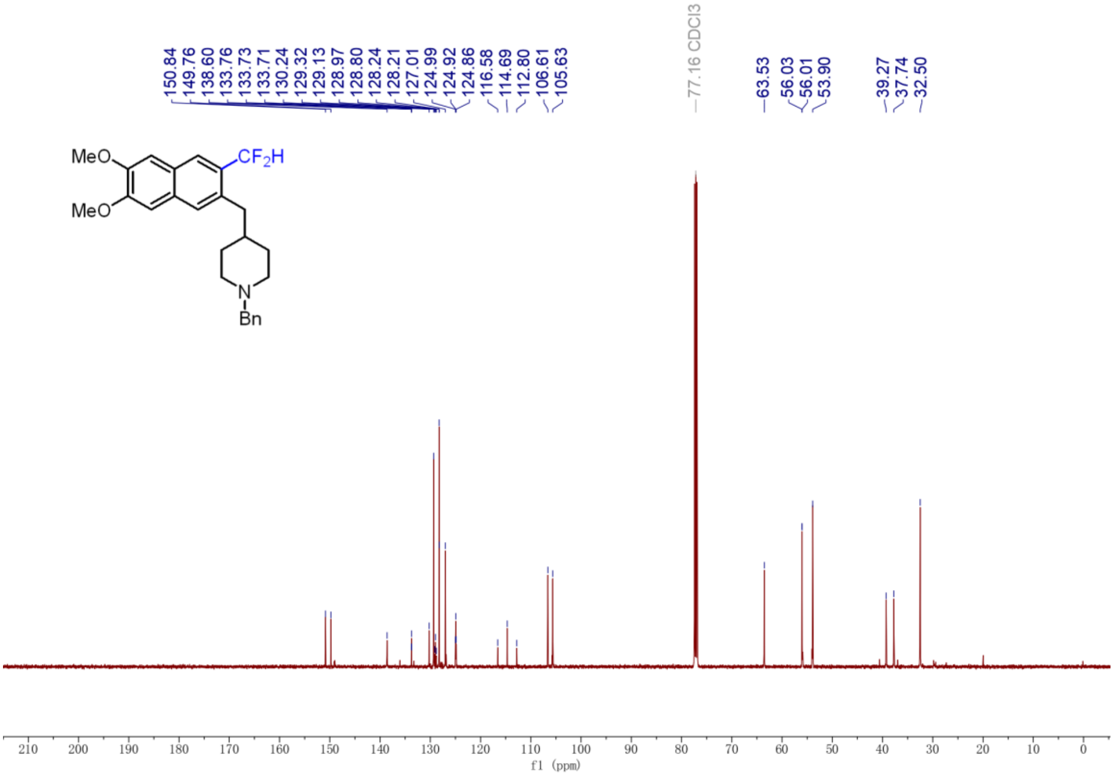
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **5c**



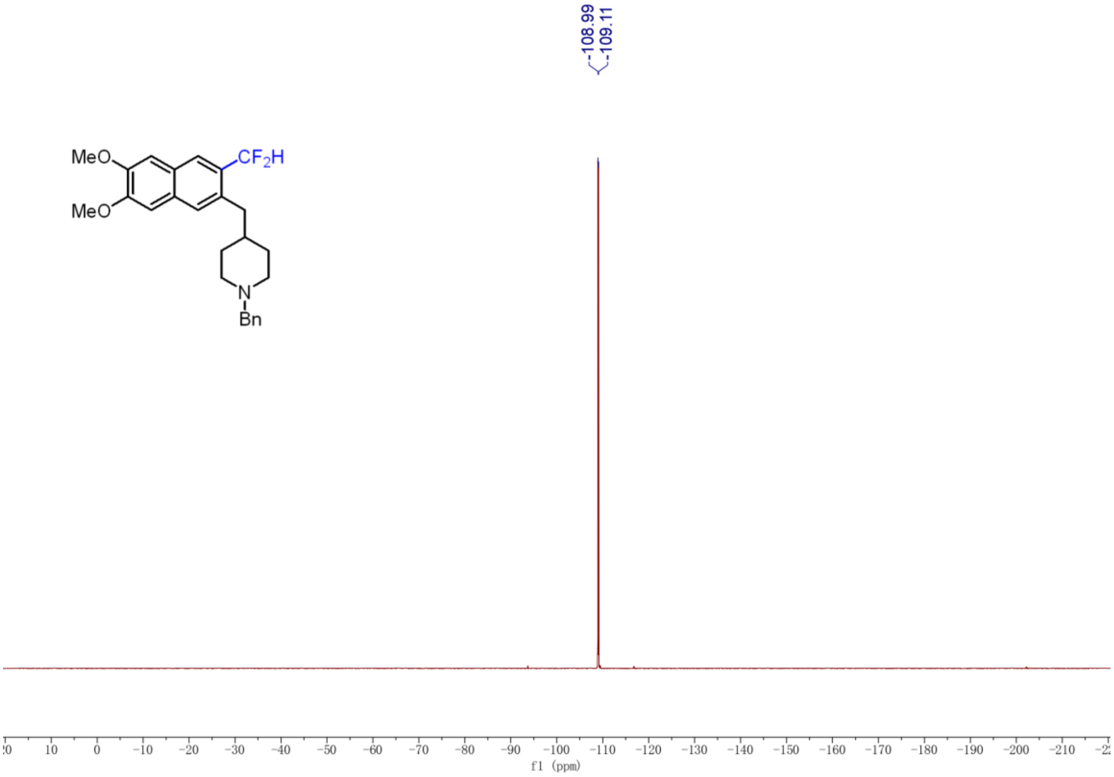
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **5c**



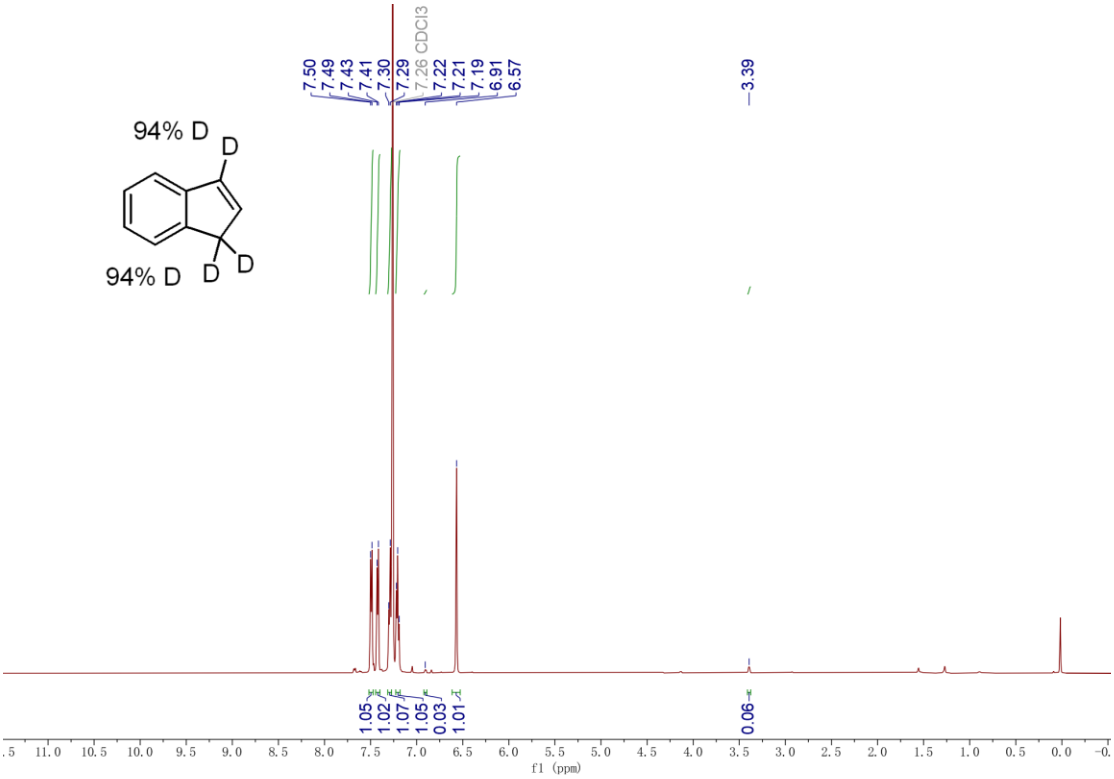
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of **6**



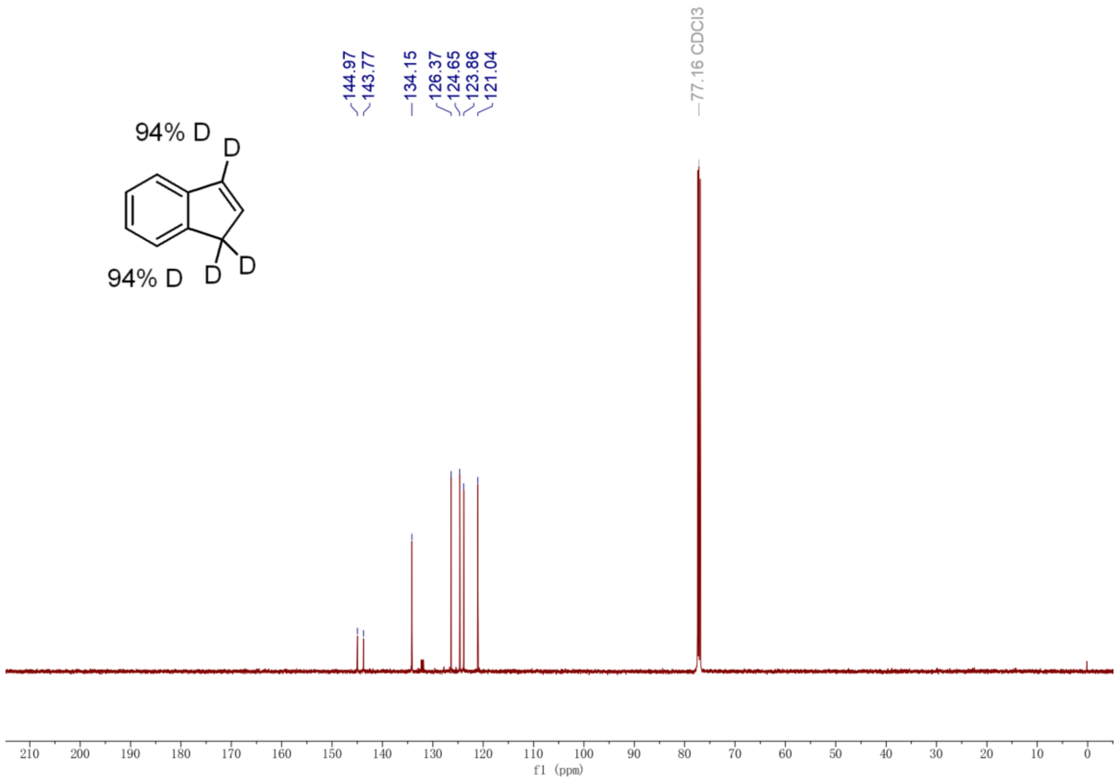
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of **6**



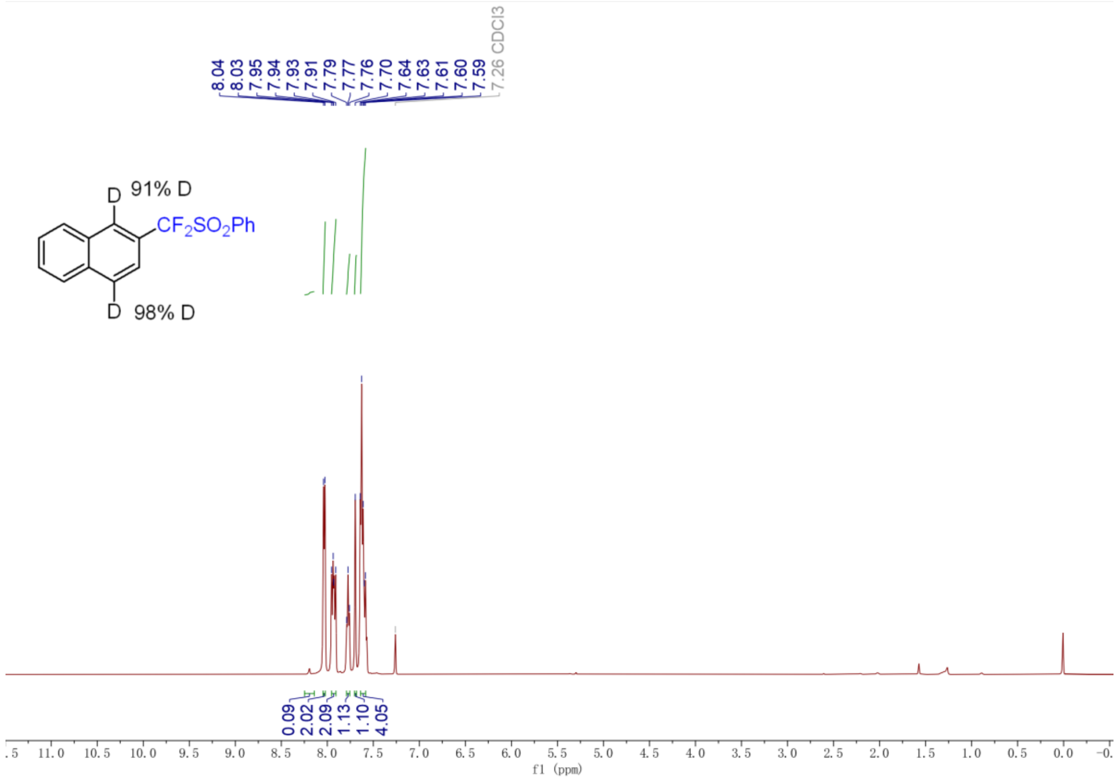
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of **6**



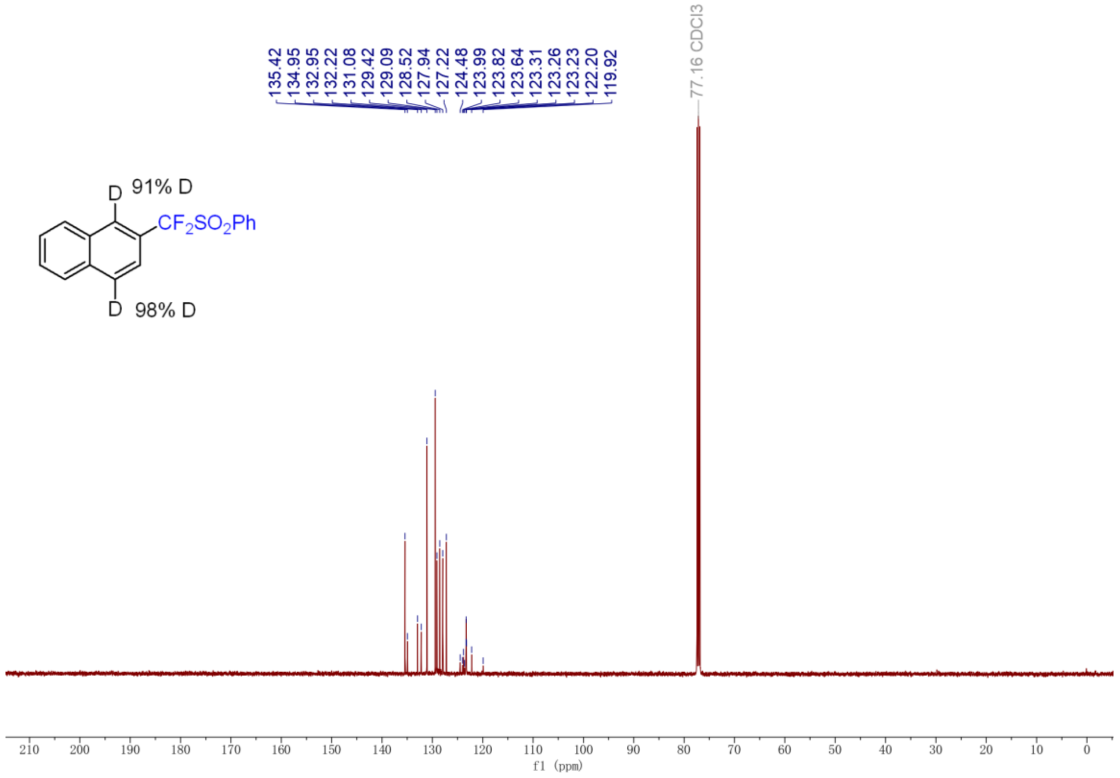
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of d$_3$-**1a**



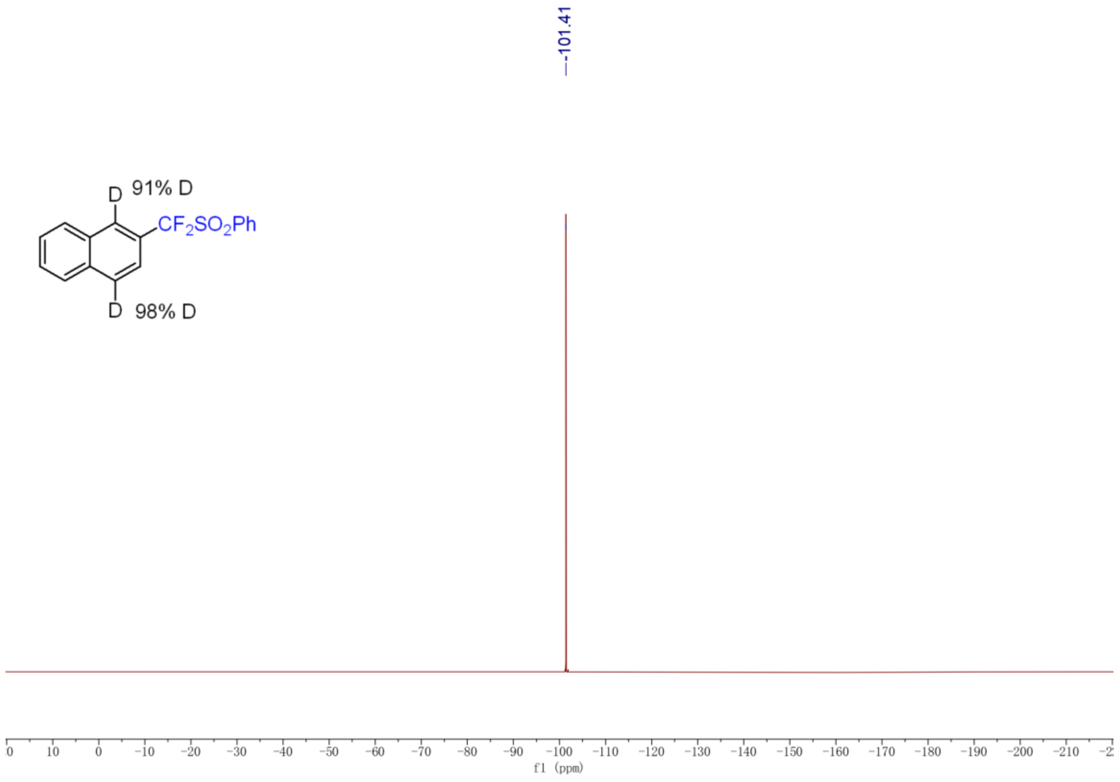
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of d$_3$-**1a**



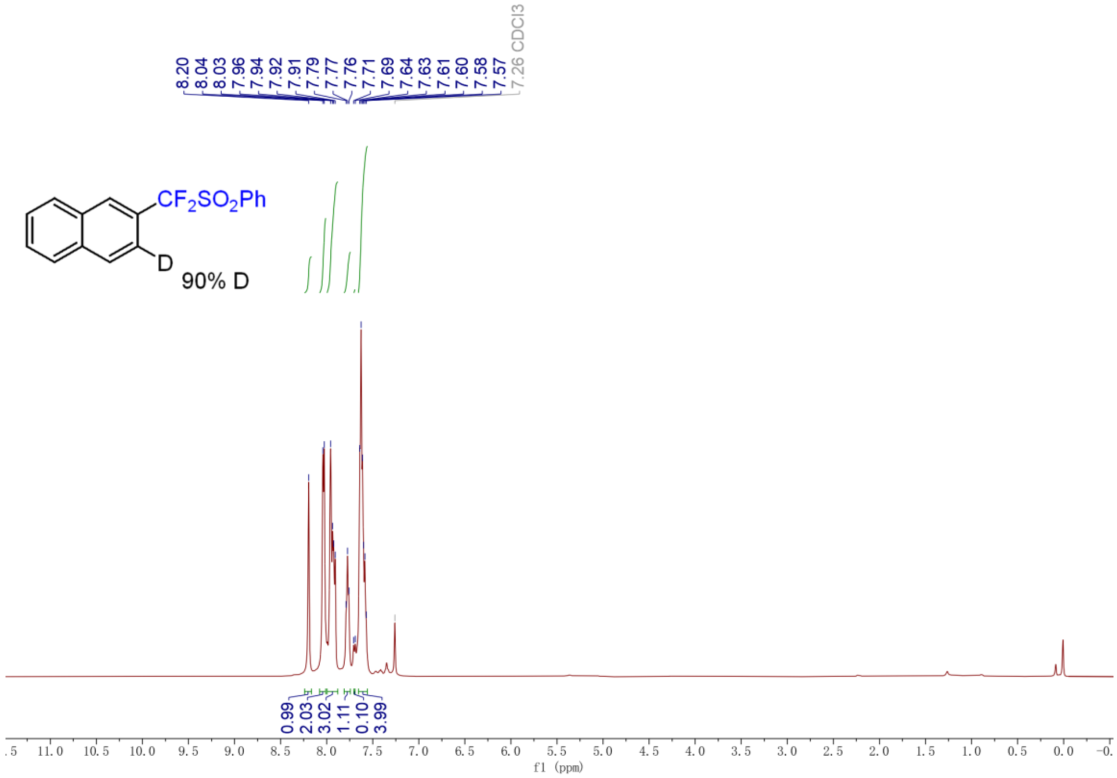
^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of d$_2$-**2a**



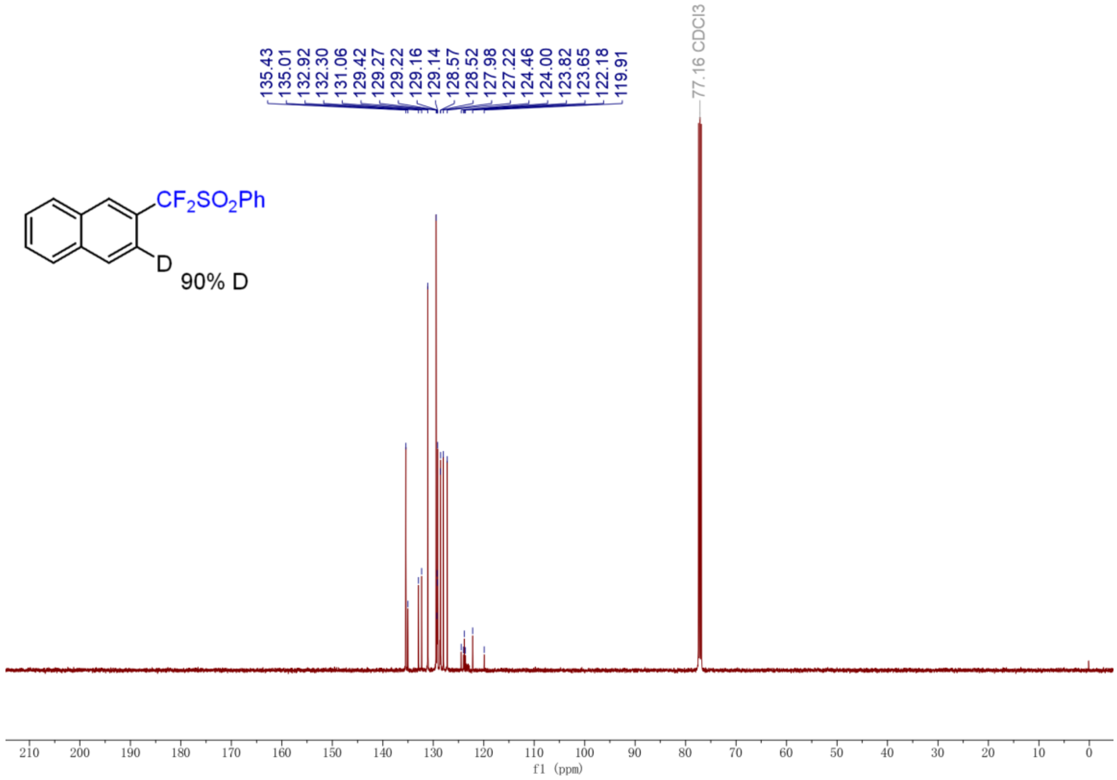
^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of d$_2$-**2a**



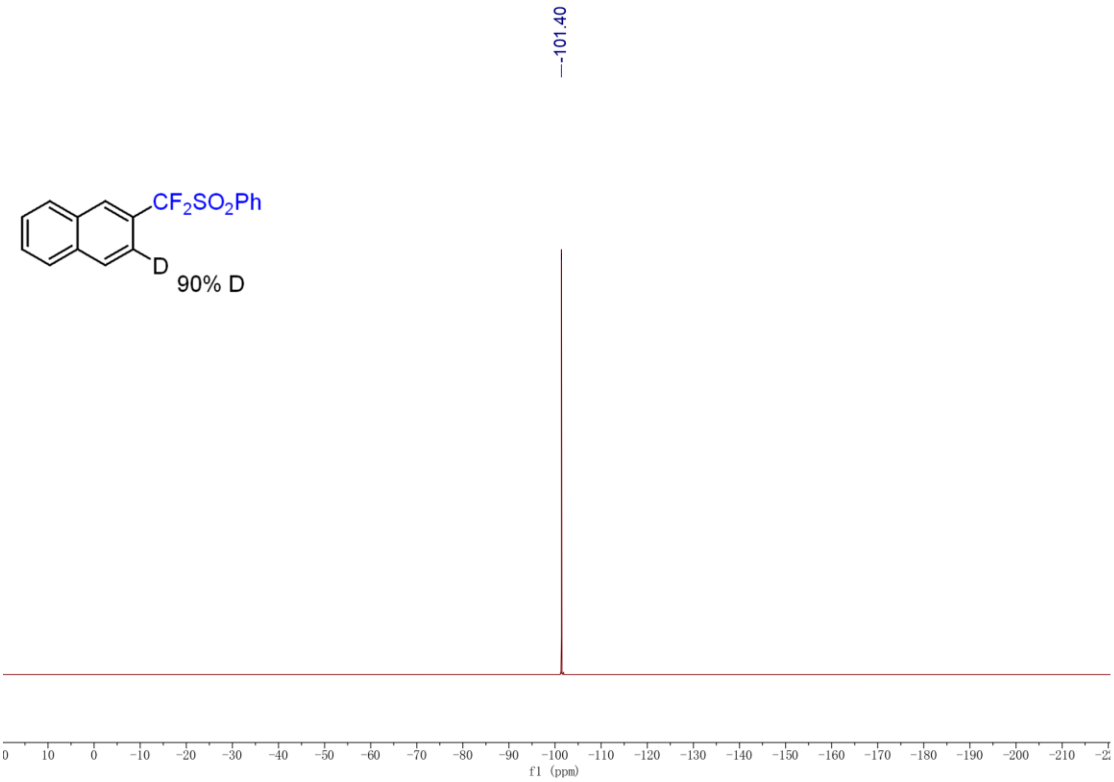
^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of d$_2$-**2a**



^{1}H NMR spectrum (500 MHz, Chloroform-*d*) of d-**2a**



^{13}C NMR spectrum (126 MHz, Chloroform-*d*) of d-**2a**

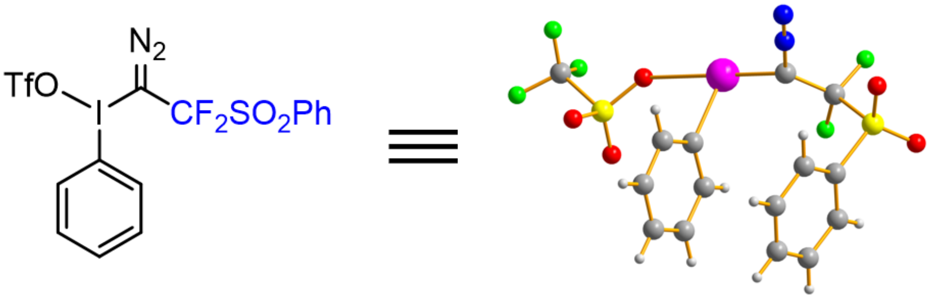


^{19}F NMR spectrum (471 MHz, Chloroform-*d*) of d-**2a**

X-ray crystallographic analysis

The X-ray crystallographic structure for **DFDI**. Crystal data has been deposited to CCDC, number 2421062.

Vacuum-dried pure sample **DFDI** (around 50-80 mg) was transferred into a vial and dissolved in 1 mL of DCM followed by the layering of 5 mL Diethyl ether. The vial was kept at room temperature to allow for slow evaporation. Orange yellow, blocky crystals were formed after 1-2 days. The crystals were subjected to the single crystal X-ray crystallographic analysis.

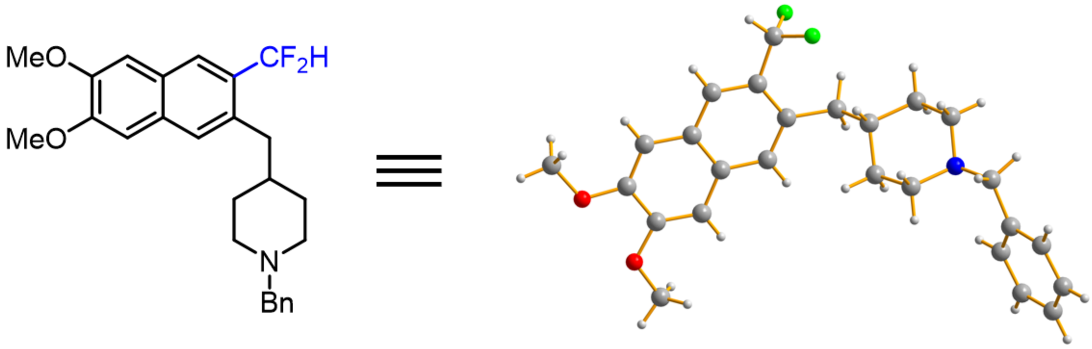


Empirical formula	$C_{15}H_{10}F_5IN_2O_5S_2$
Formula weight	584.27
Temperature/K	296.15
Crystal system	monoclinic
Space group	P21/c
a/Å	13.9965(4)
b/Å	9.6084(3)
c/Å	15.2172(5)
α/°	90
β/°	90.1610(10)

γ/°	90
Volume/Å3	2046.46(11)
Z	4
ρcalcg/cm3	1.896
μ/mm-1	1.844
F(000)	1136.0
Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.014 to 50.068
Index ranges	-16 ≤ h ≤ 14, -11 ≤ k ≤ 10, -18 ≤ l ≤ 18
Reflections collected	22518
Independent reflections	3592 [Rint = 0.0480, Rsigma = 0.0383]
Data/restraints/parameters	3592/1/271
Goodness-of-fit on F2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0446, wR2 = 0.0886
Final R indexes [all data]	R1 = 0.0696, wR2 = 0.1018
Largest diff. peak/hole / e Å-3	1.02/-0.71

The X-ray crystallographic structure for **6**. Crystal data has been deposited to CCDC, number 2426298.

Vacuum-dried pure sample **6** (around 30-50 mg) was transferred into a vial and dissolved in 1 mL of DCM followed by the layering of 2 mL n-Hexane. The vial was kept at room temperature to allow for slow evaporation. Colorless, blocky crystals were formed after 3-4 days. The crystals were subjected to the single crystal X-ray crystallographic analysis.



Empirical formula	$C_{26}H_{29}F_2NO_2$
Formula weight	425.50
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.04360(10)
b/Å	64.4922(10)
c/Å	8.45790(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4387.53(10)
Z	8
ρ_{calc}g/cm^3	1.288
μ/mm^{-1}	0.754

F(000)	1808.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα ($\lambda = 1.54184$)
2Θ range for data collection/°	5.482 to 145.6
Index ranges	$-9 \leq h \leq 8$, $-79 \leq k \leq 77$, $-9 \leq l \leq 10$
Reflections collected	16726
Independent reflections	4231 [$R_{int} = 0.0353$, $R_{sigma} = 0.0218$]
Data/restraints/parameters	4231/0/282
Goodness-of-fit on F^2	1.154
Final R indexes [I>=2σ (I)]	$R_1 = 0.0742$, $wR_2 = 0.1928$
Final R indexes [all data]	$R_1 = 0.0764$, $wR_2 = 0.1939$
Largest diff. peak/hole / e Å^{-3}	0.34/-0.50