Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A Facile Approach for the Trifluoromethylthiolation of Methylenecyclopropanes

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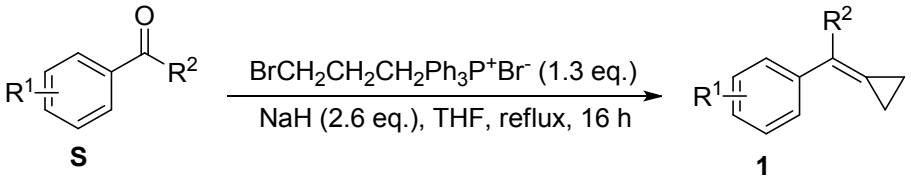
Contents

General Remarks

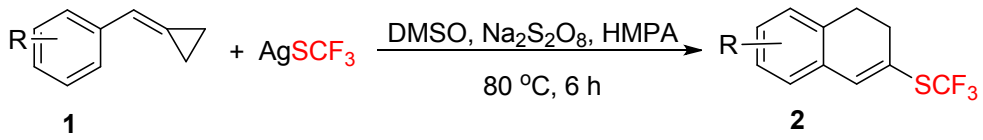
^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates or ^{19}F NMR. Flash column chromatography was carried out using silica gel at increased pressure.

General Procedure for the Synthesis of MCPs



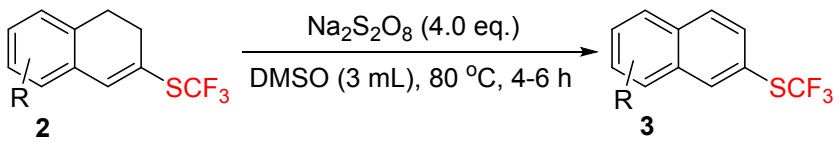
(4-Bromobutyl)triphenylphosphonium bromide (6.03 g, 13 mmol) and NaH (1.04 g, 26 mmol) were placed in a 100 mL flask equipped with a reflux condenser. The reaction set was evacuated and backfilled with Ar for three times. Then 30 mL THF was injected and the reaction mixture was stirred and refluxed at about 75 °C for 10-12 h. Afterwards compound **S** (10 mmol) dissolved in THF (5 mL) was injected slowly into the system and it continued to be refluxed for another 5 h. When the reaction completed, the reaction mixture was cooled to room temperature and quenched with H_2O. The mixture was filtered through a celite. The filtrate was concentrated on a rotary evaporator and the residue was purified by a silica gel flash chromatography to afford the product **1** in moderate yield.

General Procedure for the Trifluoromethylthiolation of MCPs



Compound **1** (0.6 mmol), $AgSCF_3$ (42 mg, 0.2 mmol), and $Na_2S_2O_8$ (142 mg, 0.6 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with Ar for three times and then DMSO (3 mL) and HMPA (0.1 mmol) were injected. Afterwards, the reaction mixture was stirred at 80 °C in an oil bath for 6 h. When the reaction completed, the product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was roughly purified by the silica gel flash chromatography and further purified by the gel permeation chromatography (GPC) to give a pure product.

General Procedure for the Dehydrogenation of 2

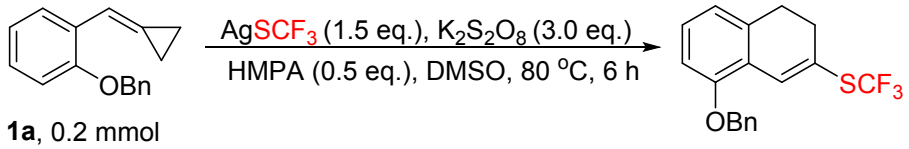


The product **2** (0.2 mmol) and $Na_2S_2O_8$ (191 mg, 0.8 mmol) were placed in a flask and DMSO (3

mL) were added. Then the reaction mixture was stirred at 80 ^{o}C in an oil bath for about 4-6 h. When the reaction completed, the aromatized product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by a silica gel flash chromatography and if necessary, it was further purified by the gel permeation chromatography (GPC) to give a pure product.

Screening of the Reaction Conditions

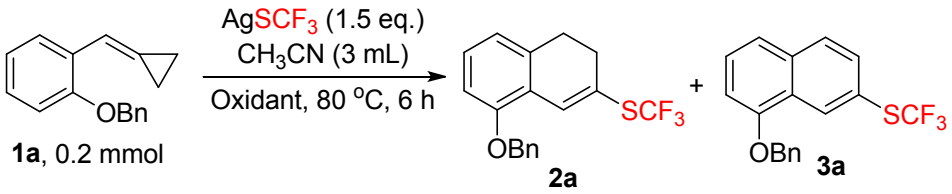
The first attempt



1a, 0.2 mmol

2a, 23%

The effects of oxidants



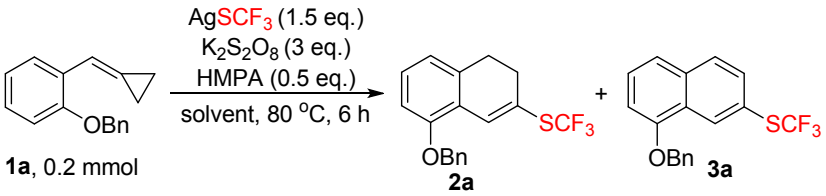
1a, 0.2 mmol

2a **3a**

oxidant (3 eq.)	**2a**:**3a**	yield (%) (**2a**+**3a**)
$K_2S_2O_8$	-:15	15
$Na_2S_2O_8$	-:16	16
$(NH_4)_2S_2O_8$	-:14	14
mCPBA (3 eq.)	n.r.	
$PhI(OAc)_2$	trace	

Compound **1a** (0.2 mmol), $AgSCF_3$ (0.3 mmol, 1.5 eq.) and oxidants (0.6 mmol, 3.0 eq.) were mixed in 3 mL CH_3CN in a Schlenk tube which was filled with Ar. The reaction tube was placed in an oil bath and the reaction mixture was stirred at 80 °C for 6 h. When finished, the yield was determined by ^{19}F NMR with *p*-bromobenzotrifluoride as an internal standard.

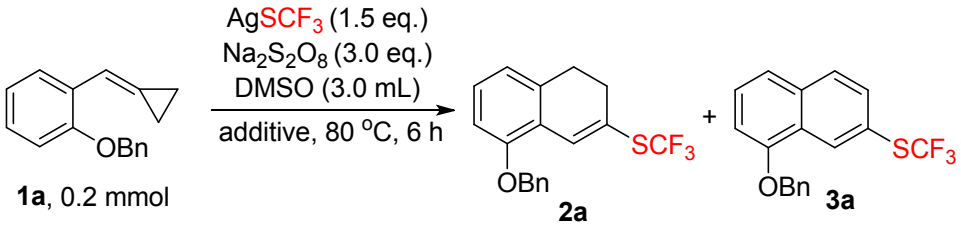
The effects of solvents

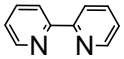


solvent	Vol./mL	**2a**:**3a**	yield (%) (**2a**+**3a**)
MeCN	3	24:0	24
DMSO	3	28:9	37
DMF	3	36:0	36
dioxane	3	n.r.	
Toluene	3	n.r.	
MeCN/DMSO 1:1	3	25:5	30
MeCN/DMF 1:1	3	26:4	30
DMF/DMSO 1:1	3	22:14	36

Compound **1a** (0.2 mmol), $AgSCF_3$ (0.3 mmol, 1.5 eq.) and $K_2S_2O_8$ (0.6 mmol, 3.0 eq.) were mixed in a Schlenk tube which was filled with Ar. Then HMPA (17 μL, 0.5 eq.) and solvent (3 mL) were injected. The reaction tube was placed in an oil bath and the reaction mixture was stirred at 80 °C for 6 h. When finished, the yield was determined by ^{19}F NMR with *p*-bromobenzotrifluoride as an internal standard.

The effects of additives



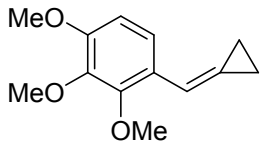
additive (0.5 eq.)	**2a**:**3a**	yield (%) (**2a**+**3a**)
K_2CO_3	10:35	45
K_3PO_4	15:25	40
Cs_2CO_3	4:36	40
AgOAc	trace:17	17
DBU	50:2	52
HMPA	47:7	54
	-:42	42
	-:48	48
HMPA[a]	40:13	53
HMPA[b]	46:6	52

[a]The amount of HMPA was 1.0 eq. [b]The amount of HMPA was 1.5 eq.

Compound **1a** (0.2 mmol), $AgSCF_3$ (0.3 mmol, 1.5 eq.) and $K_2S_2O_8$ (0.6 mmol, 3.0 eq.) were mixed in a Schlenk tube which was filled with Ar. Then different additives (0.5 eq.) and 3 mL DMSO were added. The reaction tube was placed in an oil bath and the reaction mixture was stirred at 80 °C for 6 h. When finished, the yield was determined by ^{19}F NMR with *p*-bromobenzotrifluoride as an internal standard.

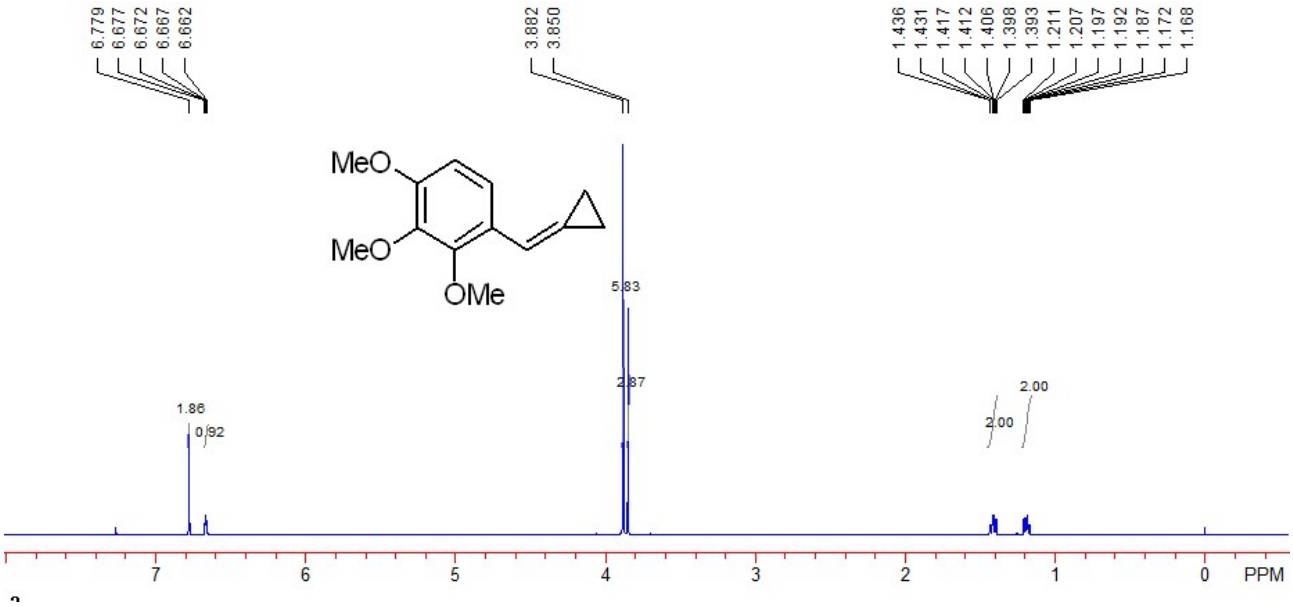
Spectroscopic Data of the Substrates 1a-1p

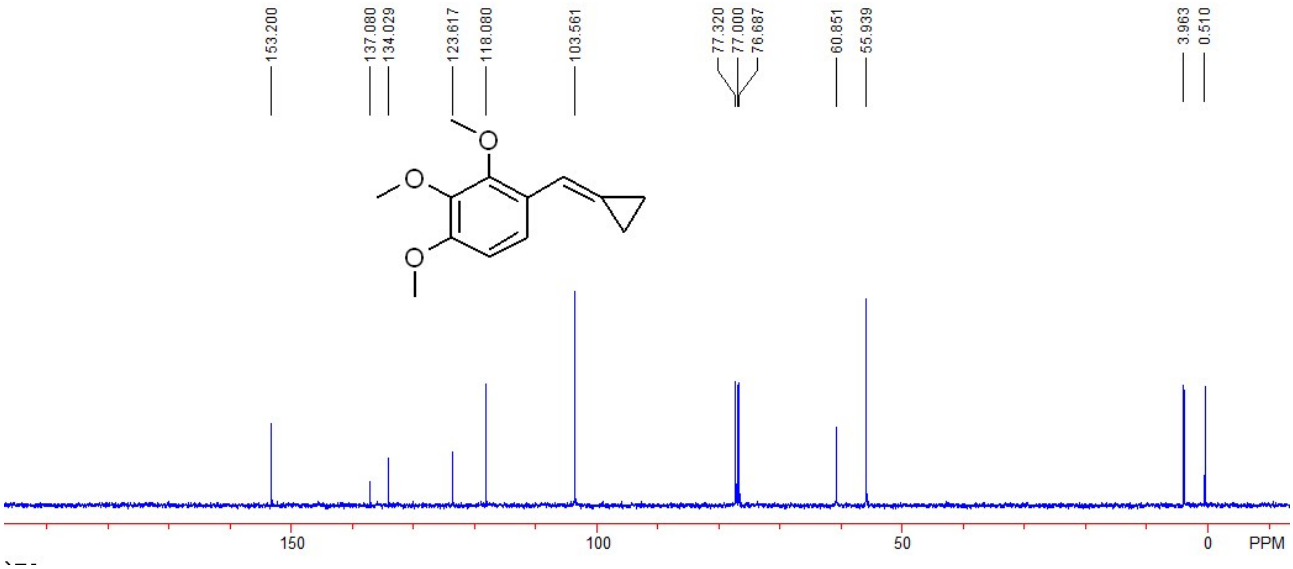
1a-1i, **1k**, and **1m-1p** are all known compounds.[1-5]

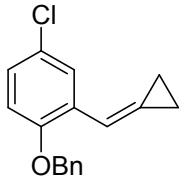


5-(cyclopropylidenemethyl)-1,2,3-trimethoxybenzene (1j).

A white solid, 1.1 g, 50% yield. M.p.: 80-82 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.17-1.21 (m, 2H, CH_2), 1.39-1.44 (m, 2H, CH_2), 3.85 (s, 3H, CH_3), 3.88 (s, 6H, CH_3), 6.66-6.68 (m, 1H, ArH), 6.78 (s, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.5, 4.0, 55.9, 60.8, 103.6, 118.1, 123.6, 134.0, 137.1, 153.2. IR (CH_2Cl_2) ν 3001, 2965, 2937, 2837, 1577, 1505, 1463, 1446, 1413, 1350, 1319, 1234, 1124, 1004, 841, 786, 675 cm^{-1}. MS (%) m/e 220 (20.03), 205 (8.72), 190 (14.34), 189 (M^+, 100.00), 162 (9.87), 145 (11.54), 119 (7.13), 91 (8.68). HRMS (EI) calcd. for $C_{13}H_{16}O_3$: 220.1099, Found: 220.1094.

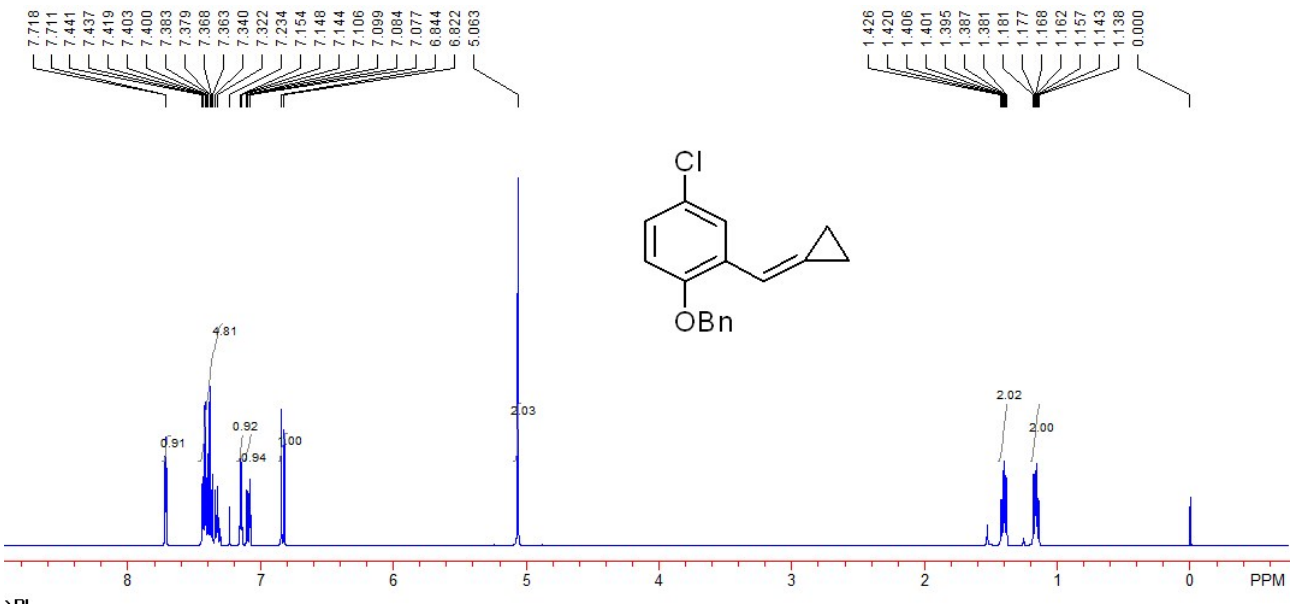






1-(benzyloxy)-4-chloro-2-(cyclopropylidenemethyl)benzene (1l).

A white solid, 1.1 g, 41% yield. M.p.: 72-74 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14-1.18 (m, 2H, CH_2), 1.38-1.43 (m, 2H, CH_2), 5.06 (s, 2H, CH_2), 6.83 (d, J = 8.8 Hz, 1H, ArH), 7.09 (dd, J = 2.8, 8.8 Hz, 1H, ArH), 7.14-7.15 (m, 1H, ArH), 7.30-7.44 (m, 5H, ArH), 7.72 (d, J = 2.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.6, 3.9, 70.6, 111.2, 113.7, 125.9, 126.1, 126.2, 127.1, 127.3, 128.0, 128.6, 129.1, 136.8, 153.7. IR (CH_2Cl_2) ν 3036, 2972, 2936, 2884, 1590, 1482, 1469, 1406, 1378, 1278, 1238, 1128, 1010, 885, 795, 748, 697, 668 cm^{-1}. MS (%) m/e 235 (16.01), 181 (20.94), 179 (58.54), 167 (8.87), 115 (14.51), 92 (7.47), 91 (M^+, 100.00), 65 (8.22). HRMS (EI) calcd. for $C_{17}H_{15}OCl$: 270.0811, Found: 270.0814.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7.144
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7.077
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1.387
1.381
1.181
1.177
1.168
1.162
1.157
1.143
1.138
0.000
Cl
OBn
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0.91
0.92
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2.03
2.02
2.00
8
7
6
5
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3
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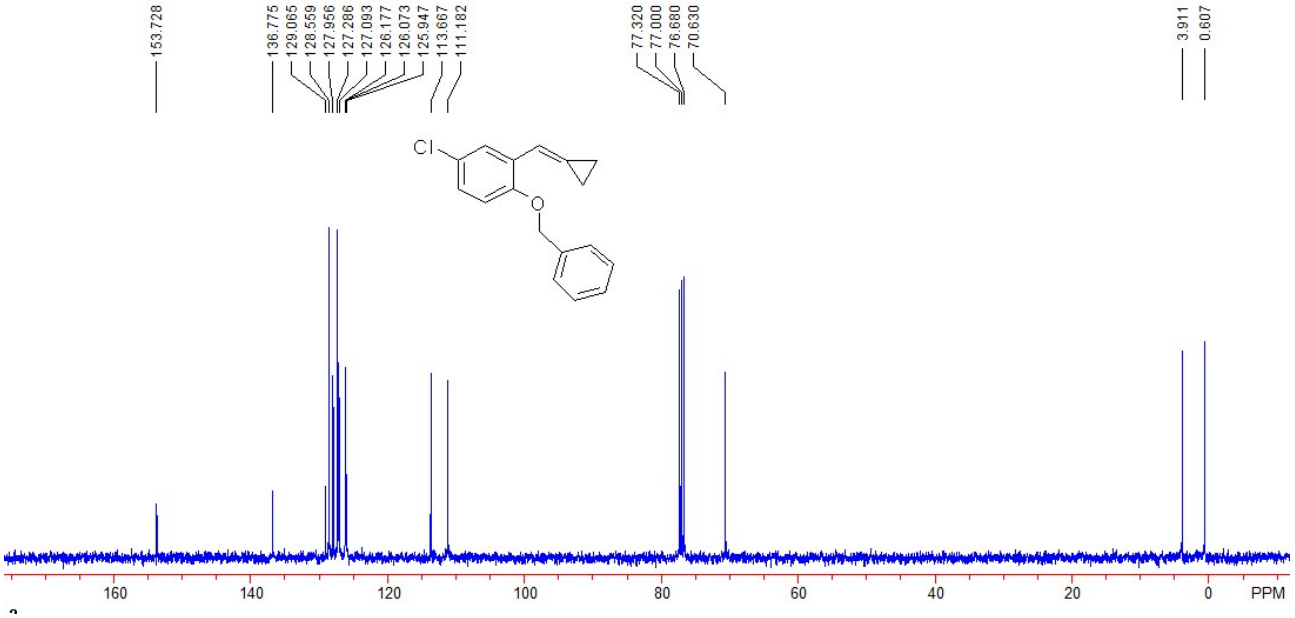
PPM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77.000
76.680
70.630
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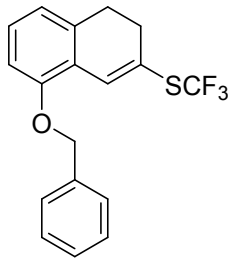
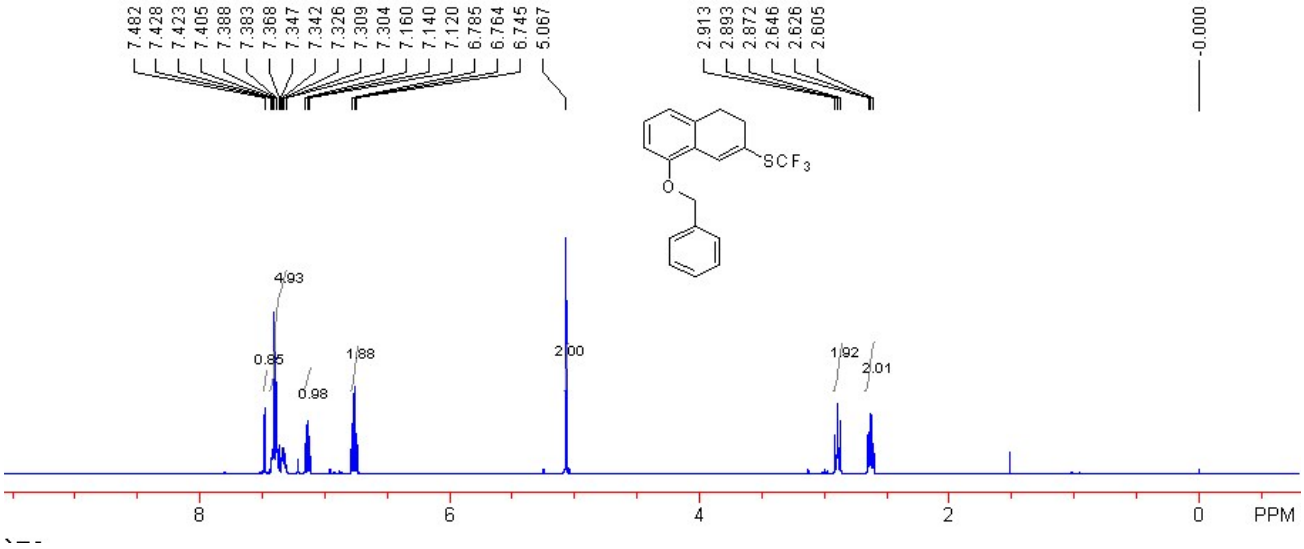
Cl
O
160
140
120
100
80
60
40
20
0
PPM

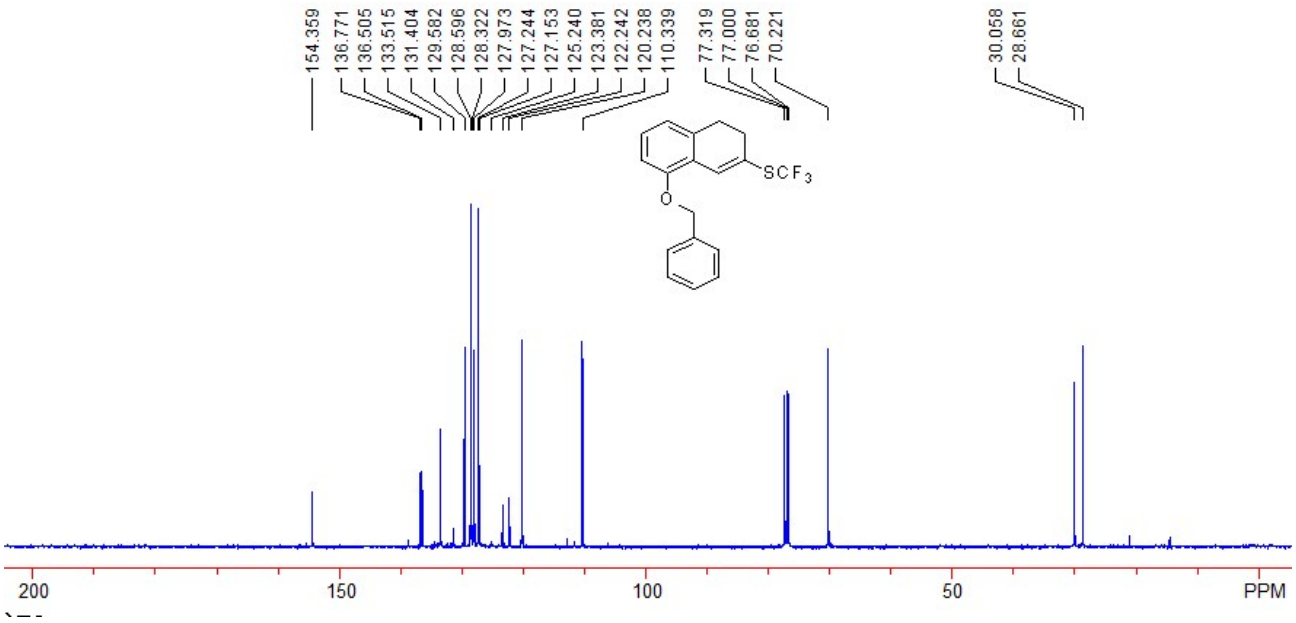
Spectroscopic Data of the Products 2a-2p

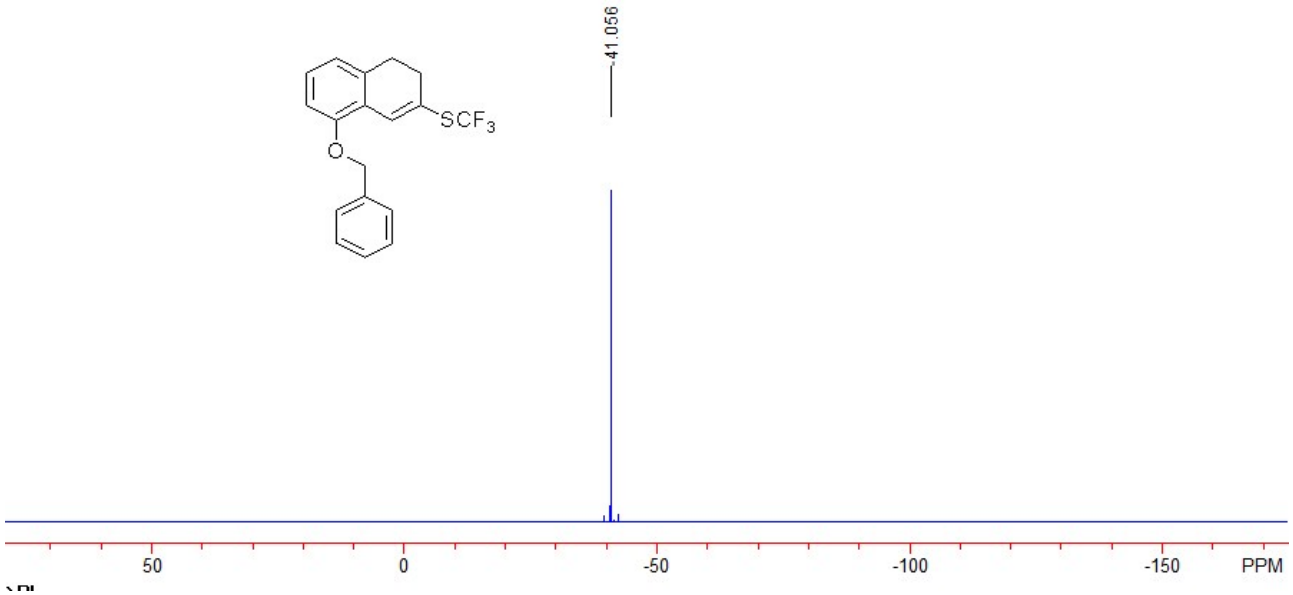


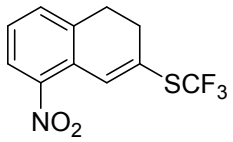
(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2a).

A colorless oil, 41 mg, 61% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.63 (t, J = 8.0 Hz, 2H), 2.89 (t, J = 8.0 Hz, 2H), 5.07 (s, 2H, CH_2), 6.76 (t, J = 8.0 Hz, 2H, ArH), 7.14 (t, J = 8.0 Hz, 1H), 7.30-7.34 (m, 1H, Ar), 7.37-7.43 (m, 4H, ArH), 7.48 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.7, 30.1, 70.2, 110.3, 120.2, 122.2, 123.4, 127.2, 128.0, 128.6, 129.6, 129.9 (q, J = 308.2 Hz), 133.5, 136.5, 136.8, 154.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.06. IR (CH_2Cl_2) ν 3068, 3033, 2939, 2885, 2833, 1570, 1453, 1265, 1105, 1028, 778, 734, 694 cm^{-1}. MS (%) m/e 336 (4.09), 209 (4.71), 147 (2.46), 116 (2.47), 115 (6.84), 92 (8.28), 91 (M^+, 100.00), 65 (6.43). HRMS (EI) calcd. for $C_{18}H_{15}OF_3S$: 336.0796, Found: 336.0792.





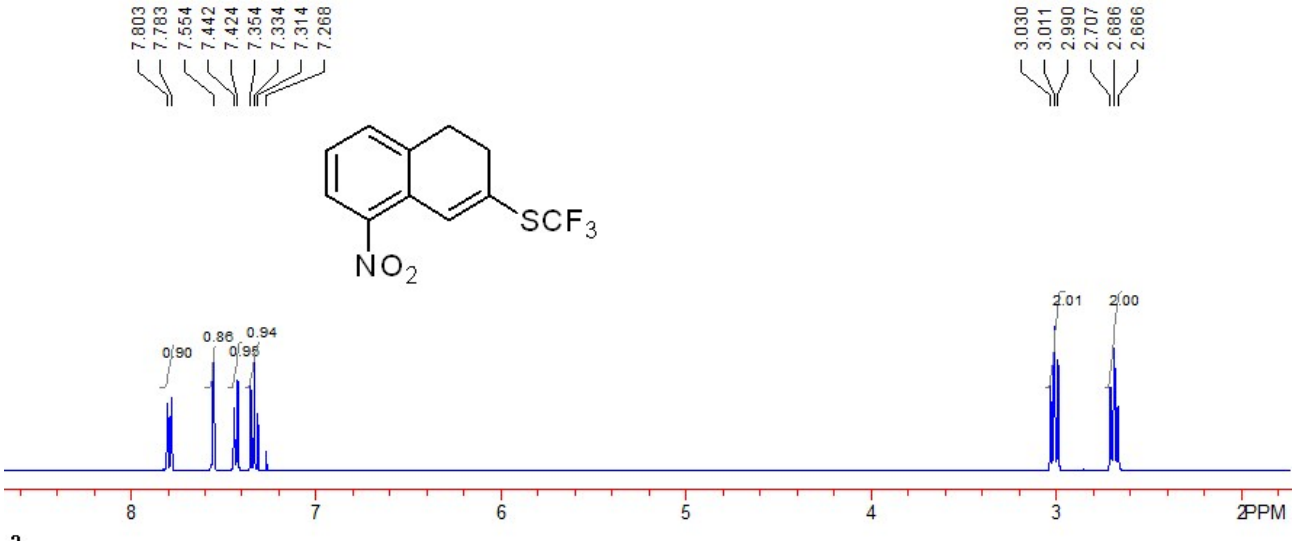


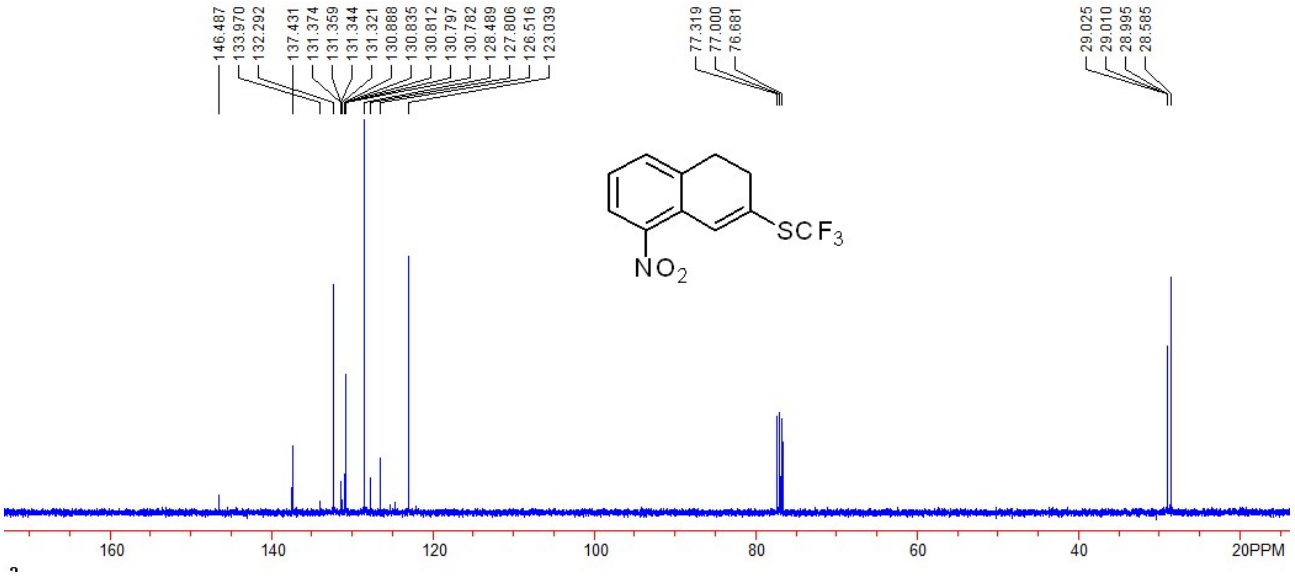


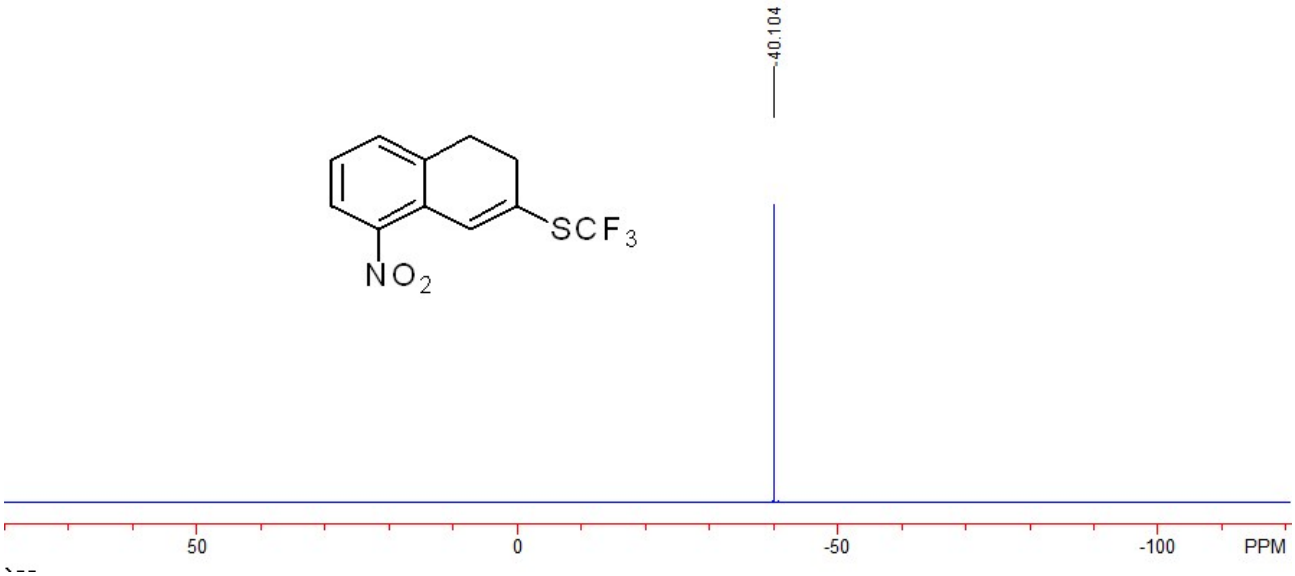
(8-nitro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2b).

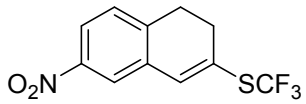
A black oil, 14 mg, 25% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.69 (t, J = 8.0 Hz, 2H, CH_2), 3.01 (t, J = 8.0 Hz, 2H, CH_2), 7.33 (t, J = 8.0, 1H, ArH), 7.43 (d, J = 7.2 Hz, 1H, ArH), 7.55 (s, 1H, ArH), 7.79 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.6, 29.0, 123.0, 126.5, 128.5, 129.4 (q, J = 308.2 Hz), 130.8, 131.4, 132.3, 137.4, 146.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.10. IR (CH_2Cl_2) ν 3091, 2946, 2894, 2835, 1523, 1346, 1099, 1051, 874, 804, 778, 752, 737 cm^{-1}. MS (%) m/e 275 (66.67), 128 (68.7), 127 (34.69), 116 (37.11), 115 (M^+, 100.00),

103 (26.99), 102 (36.23), 89 (27.44). HRMS (EI) calcd. for $C_{11}H_8NO_2F_3S$: 275.0228, Found: 275.0226.



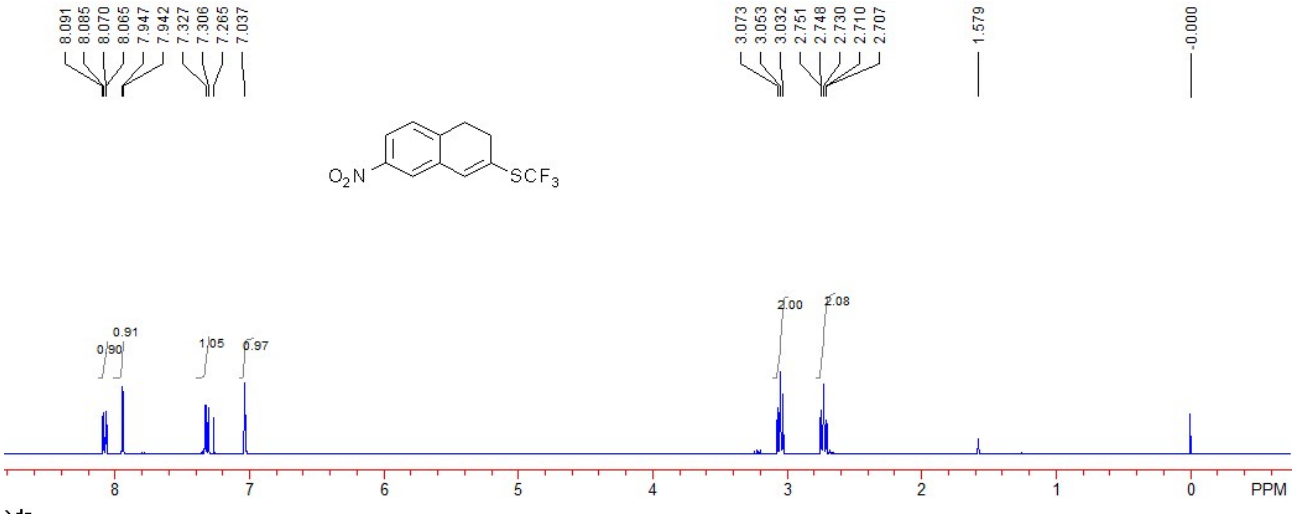


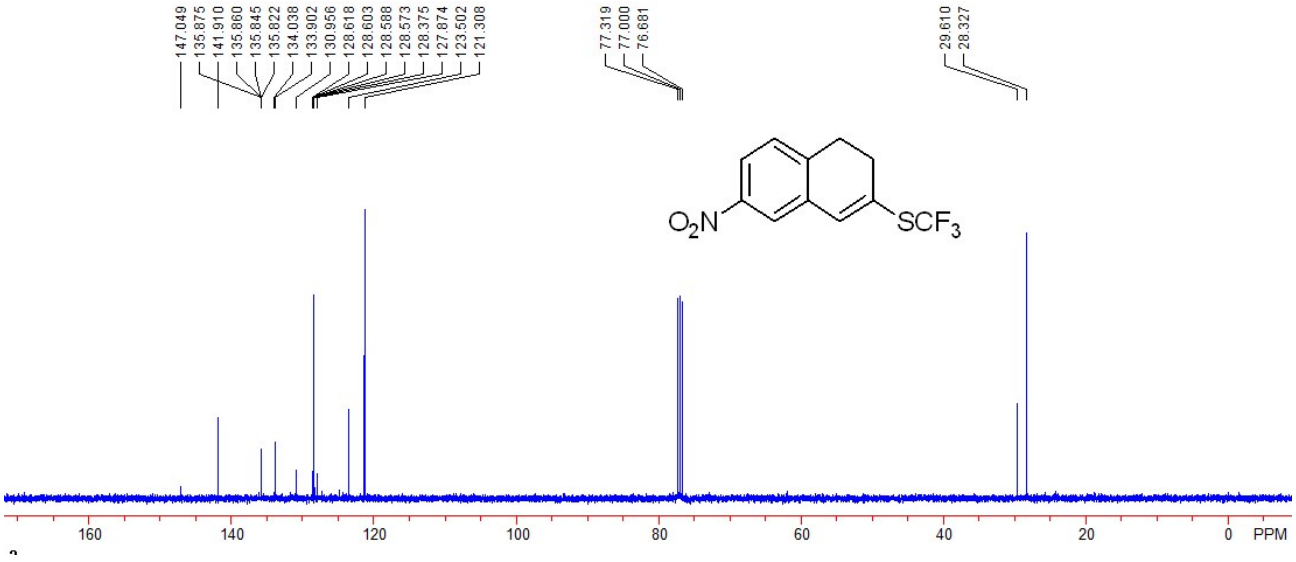


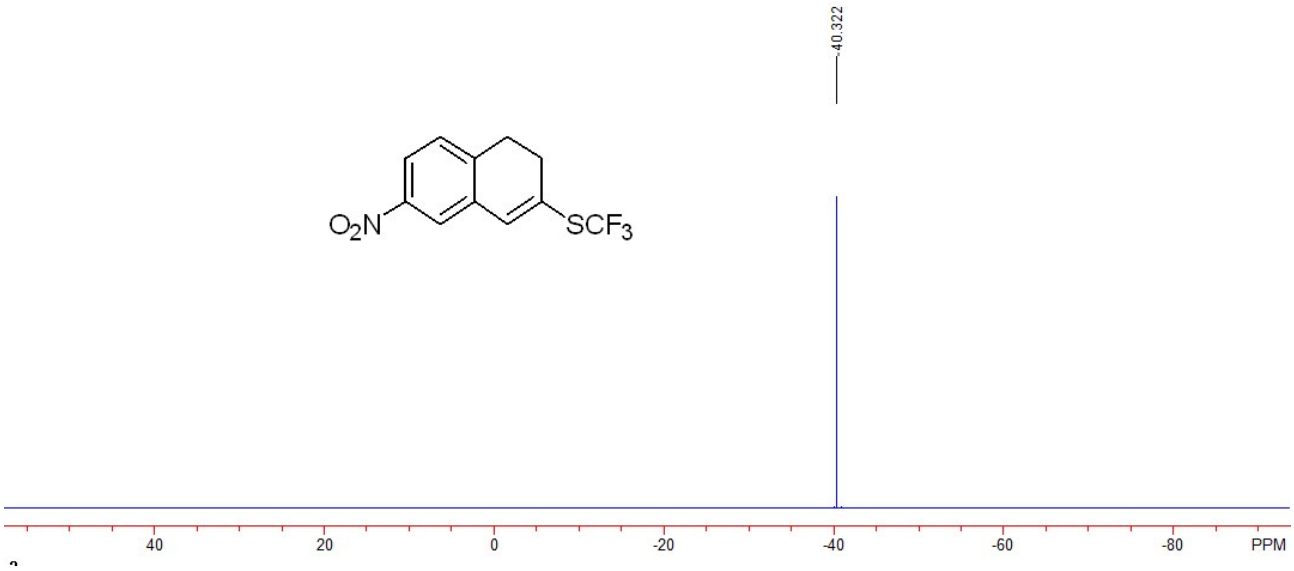


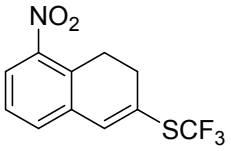
(7-nitro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2c) (can be separated with **2c'**)

A yellow oil, 11 mg, 20% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.73 (t, J = 8.0 Hz, 2H, CH_2), 3.05 (t, J = 8.0 Hz, 2H, CH_2), 7.04 (s, 1H, CH), 7.32 (d, J = 8.4 Hz, 1H, ArH), 7.94 (d, J = 2.4 Hz, 1H, ArH), 8.08 (dd, J = 2.4, 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.3, 29.6, 121.3, 123.5, 128.4, 128.6, 129.4 (q, J = 308.2 Hz), 133.9, 135.8, 141.9, 147.1. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.32. IR (CH_2Cl_2) ν 3078, 2951, 2894, 2835, 1520, 1344, 1099, 1036, 910, 835, 817, 755, 736 cm^{-1}. MS (%) m/e 275 (M^+, 100.00), 162 (18.17), 160 (27.43), 159 (18.27), 128 (88.96), 127 (29.32), 116 (32.75), 115 (59.95). HRMS (EI) calcd. for $C_{11}H_8NO_2F_3S$: 275.0228, Found: 275.0236.



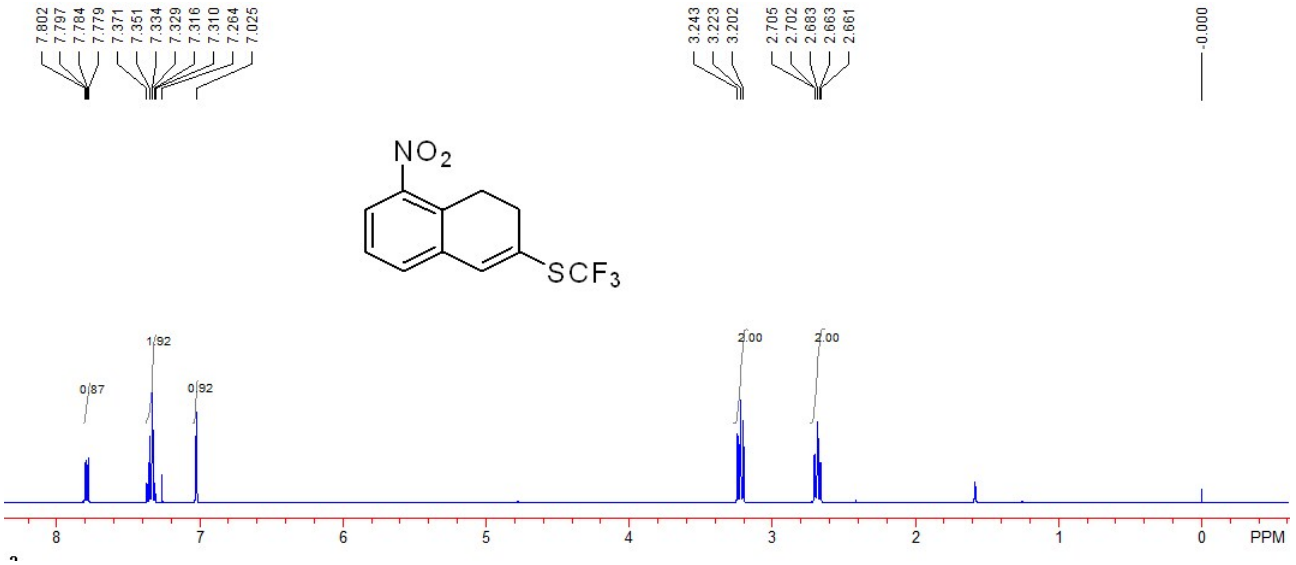






(5-nitro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2c') (can be separated from **2c**)

A yellow oil, 22 mg, 40% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.68 (t, J = 8.0 Hz, 2H, CH_2), 3.22 (t, J = 8.0 Hz, 2H, CH_2), 7.03 (s, 1H, CH), 7.31-7.37 (m, 2H, ArH), 7.79 (dd, J = 2.0, 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.3, 29.2, 124.3, 127.3, 127.8 (q, J = 1.5 Hz), 129.4 (q, J = 308.2 Hz), 129.5, 131.2, 135.2, 136.2 (q, J = 1.6 Hz), 149.0. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.35. IR (CH_2Cl_2) ν 3083, 2897, 2835, 1525, 1346, 1100, 1044, 892, 806, 772, 755, 733, 704 cm^{-1}. MS (%) m/e 258 (M^+, 100.00), 275 (30.37), 228 (15.91), 159 (28.49), 158 (14.49), 128 (42.29), 127 (33.26), 115 (55.78). HRMS (EI) calcd. for $C_{11}H_8NO_2F_3S$: 275.0228, Found: 275.0224.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7.025
3.243
3.223
3.202
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2.702
2.683
2.663
2.661
0.000
NO2
SCF3
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2.00
8
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6
5
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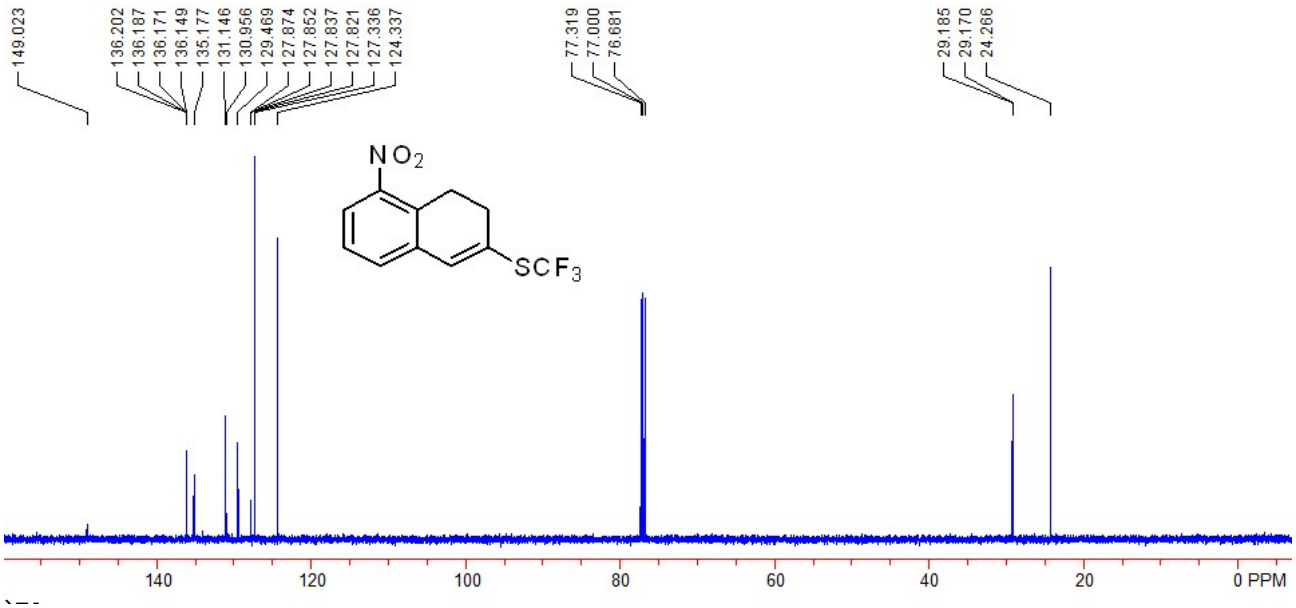
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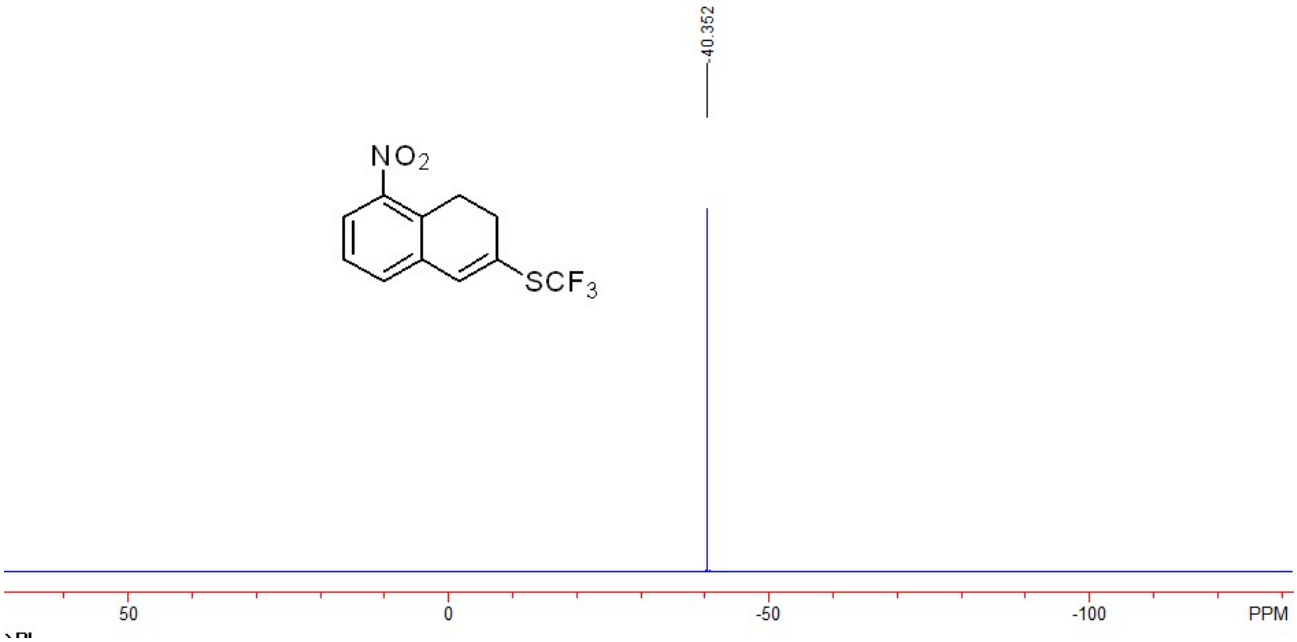
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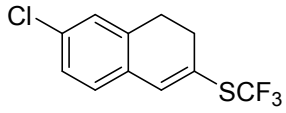
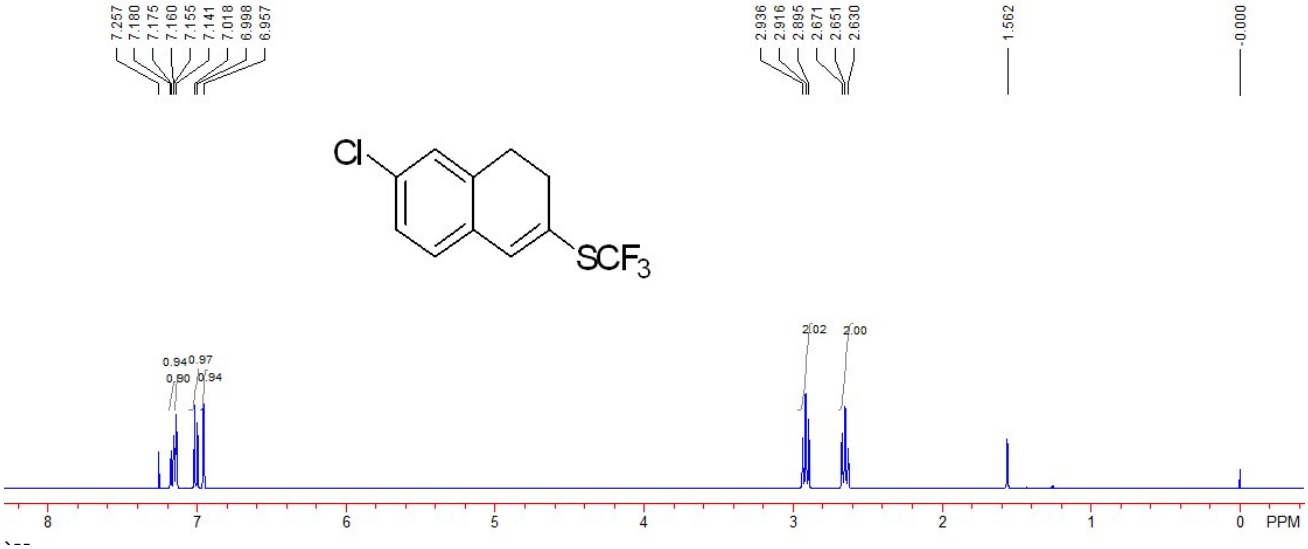
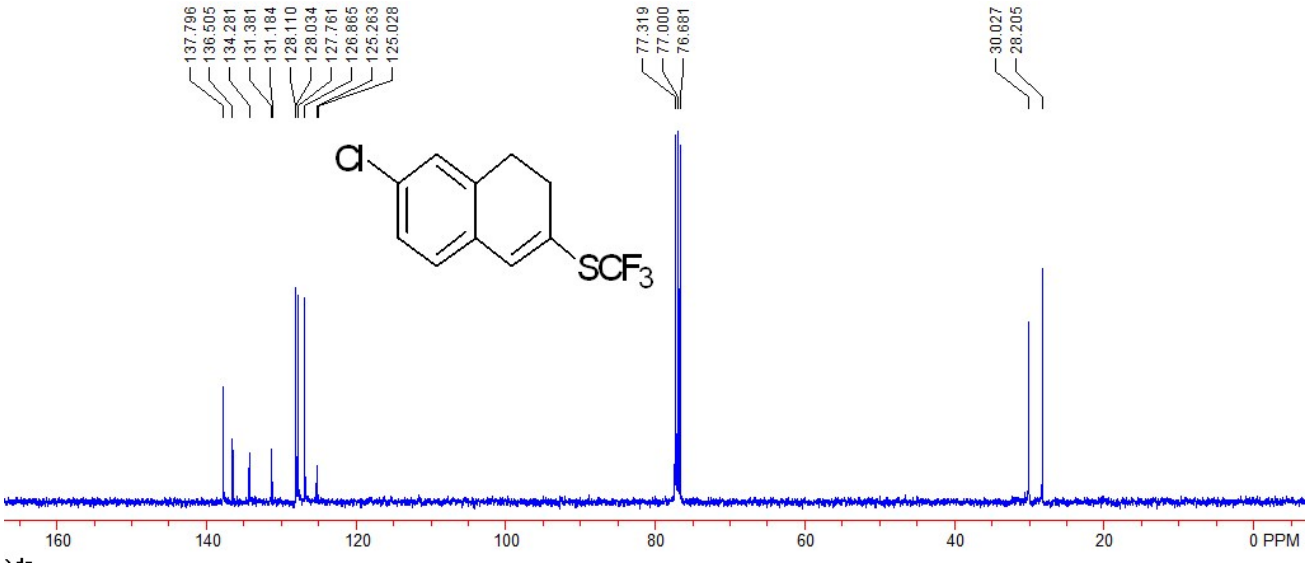
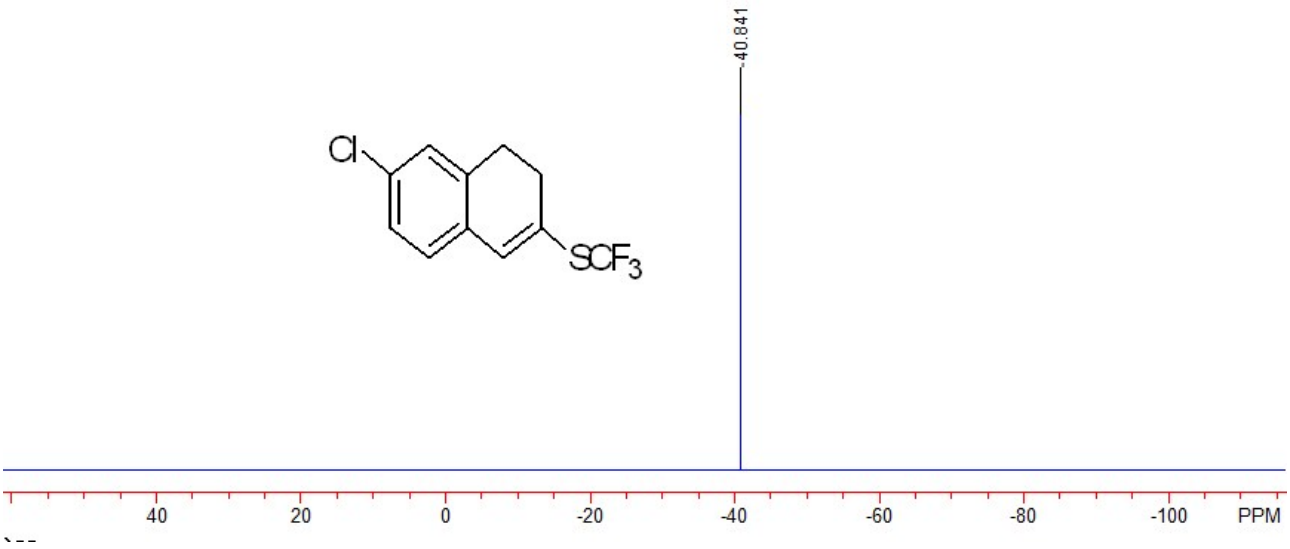


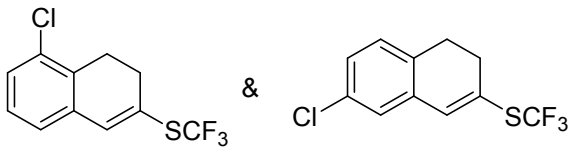
(6-chloro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2d).

A colorless oil, 24 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.65 (t, J = 8.4 Hz, 2H, CH_2), 2.92 (t, J = 8.4 Hz, 2H, CH_2), 6.96 (s, 1H, ArH), 7.01 (d, J = 8.0 Hz, 1H, ArH), 7.14-7.18 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.2, 30.0, 125.3, 126.9, 127.8, 128.0, 129.6 (q, J = 307.4 Hz), 131.4, 134.3, 136.5, 137.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.84. IR (CH_2Cl_2) ν 2946, 2894, 2832, 1593, 1483, 1097, 1039, 959, 877, 862, 814, 755, 673 cm^{-1}. MS (%) m/e 266 (37.56), 264 (M^+, 100), 195 (50.68), 162 (31.02), 151 (57.33), 128 (27.82), 127 (23.43), 115 (27.49). HRMS (EI) calcd. for $C_{11}H_8F_3SCl$: 263.9987, Found: 263.9976.



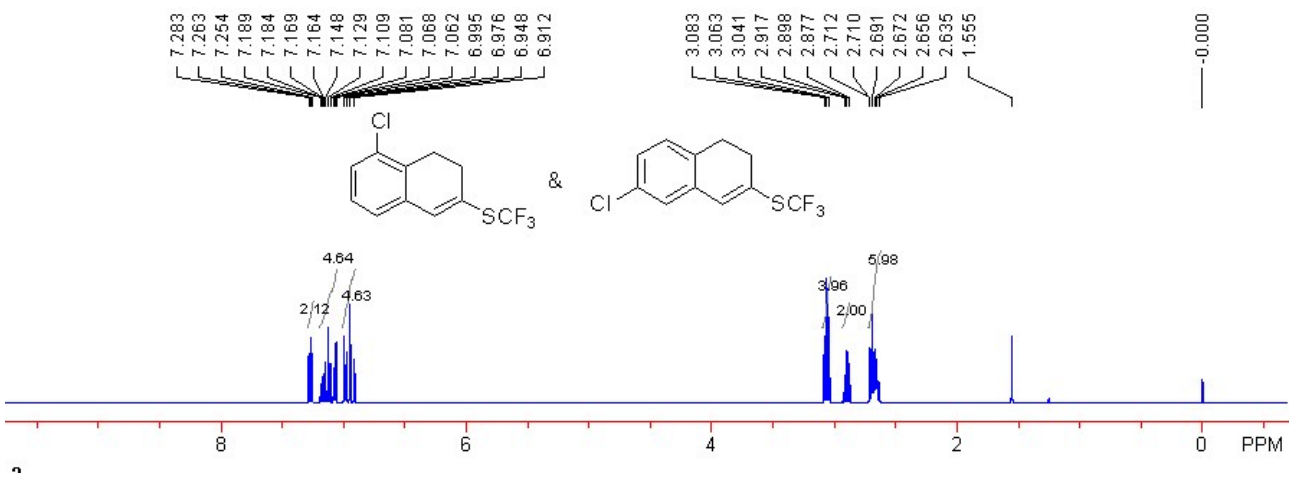


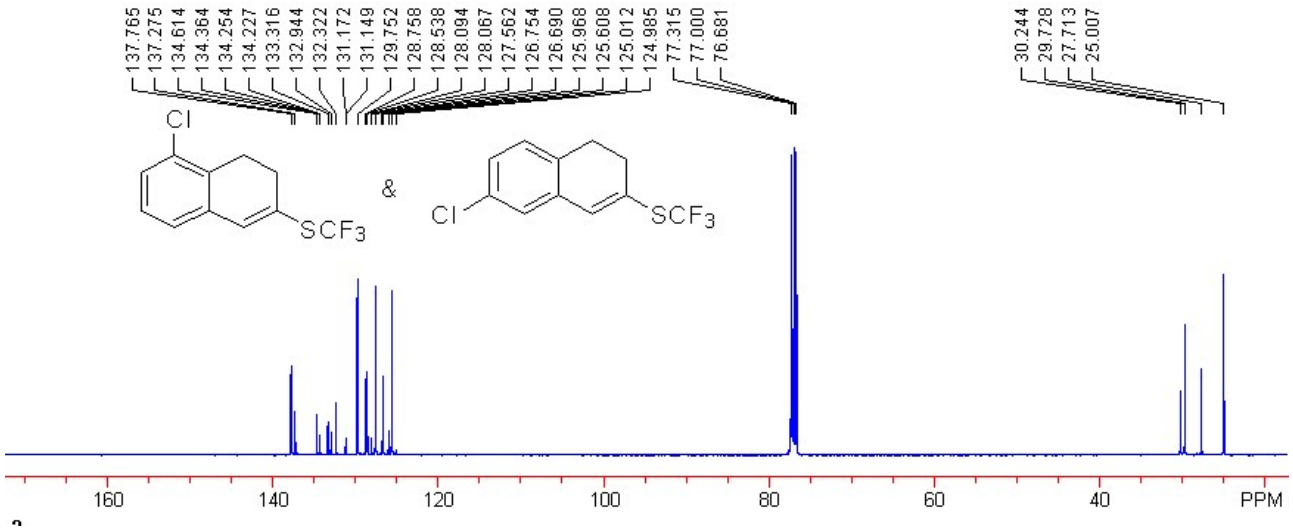


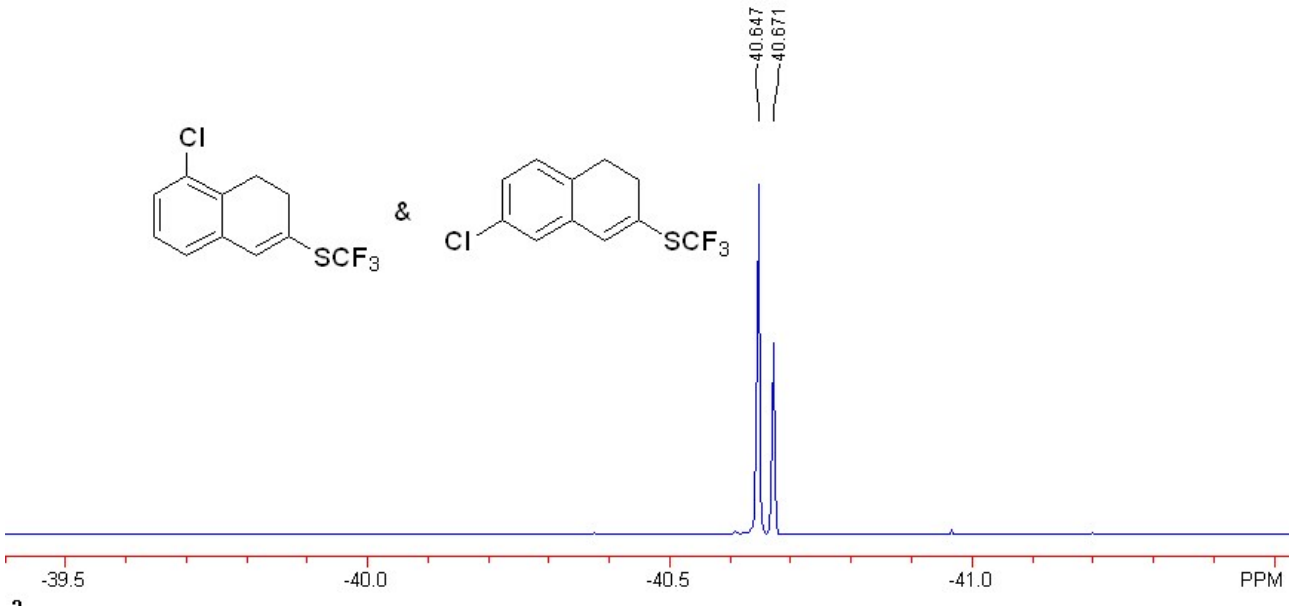


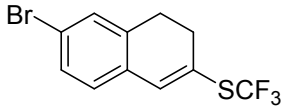
(5-chloro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane& (7-chloro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2e) (The two regioisomers can not be separated).

A colorless oil, 26.4 mg, 50% yield (2:1). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.64-2.71 (m, 6H, CH_2), 2.90 (t, *J* = 7.6 Hz, 2H, CH_2), 3.06 (t, *J* = 8.0 Hz, 4H, CH_2), 6.91-7.00 (m, 5H, ArH), 7.06-7.19 (m, 5H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 25.0, 27.7, 29.7, 30.2, 125.6, 126.0, 126.7, 126.8, 127.6, 128.5, 128.8, 129.61 (q, *J* = 308.2 Hz), 129.63 (q, *J* = 307.8 Hz), 129.8, 132.3, 132.9, 133.3, 134.4, 134.6, 137.3, 137.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.67, -40.65. IR (CH_2Cl_2) ν 3062, 2954, 2892, 2838, 1556, 1435, 1100, 972, 781, 755, 706 cm^{-1}. MS (%) m/e 266 (36.10), 264 (M^+, 100.00), 163 (34.57), 162 (32.96), 151 (38.80), 128 (41.92), 127 (30.01), 115 (27.46). HRMS (EI) calcd. for $C_{11}H_8F_3SCl$: 263.9987, Found: 263.9984.



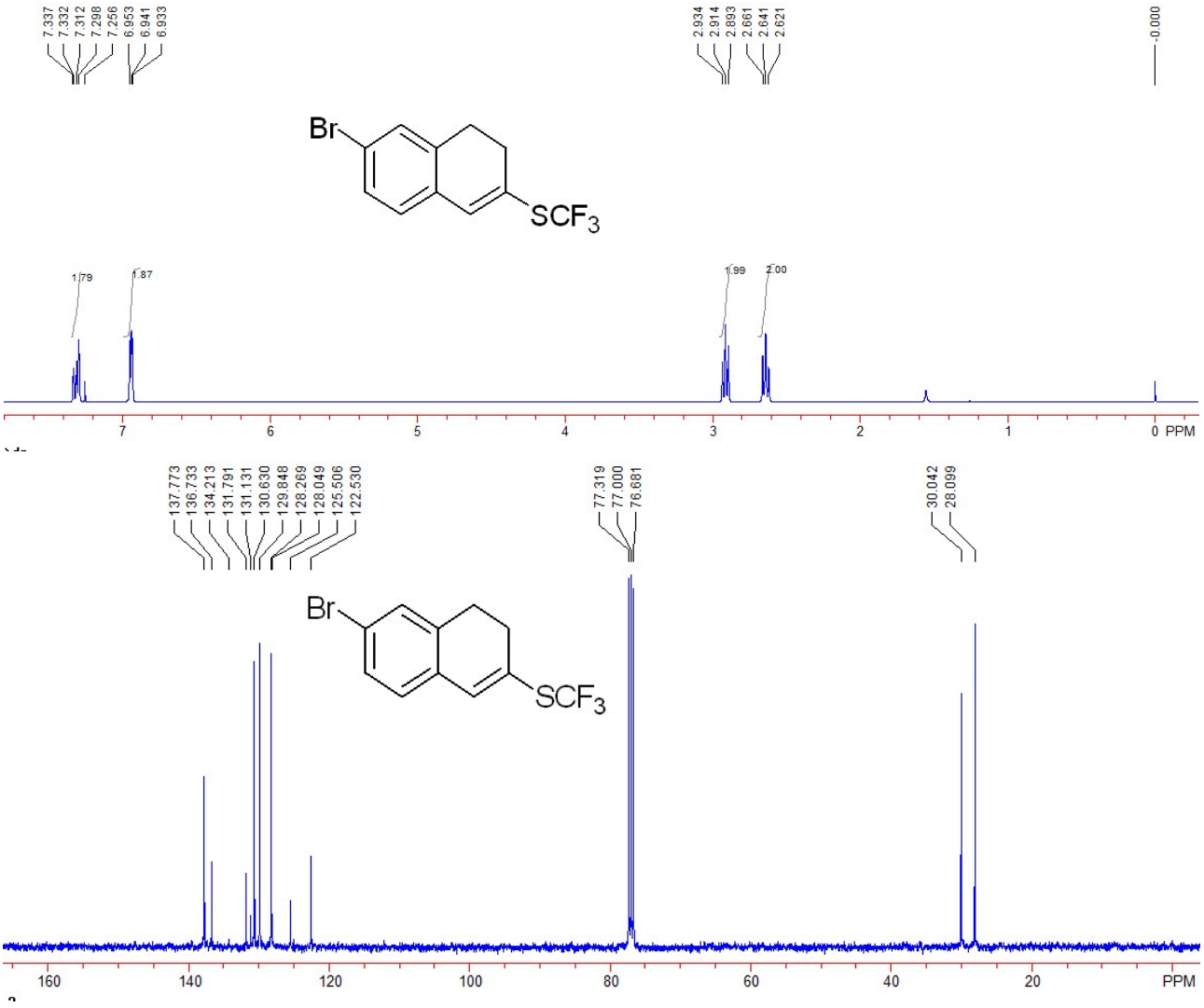


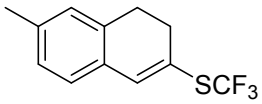




(6-bromo-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2f).

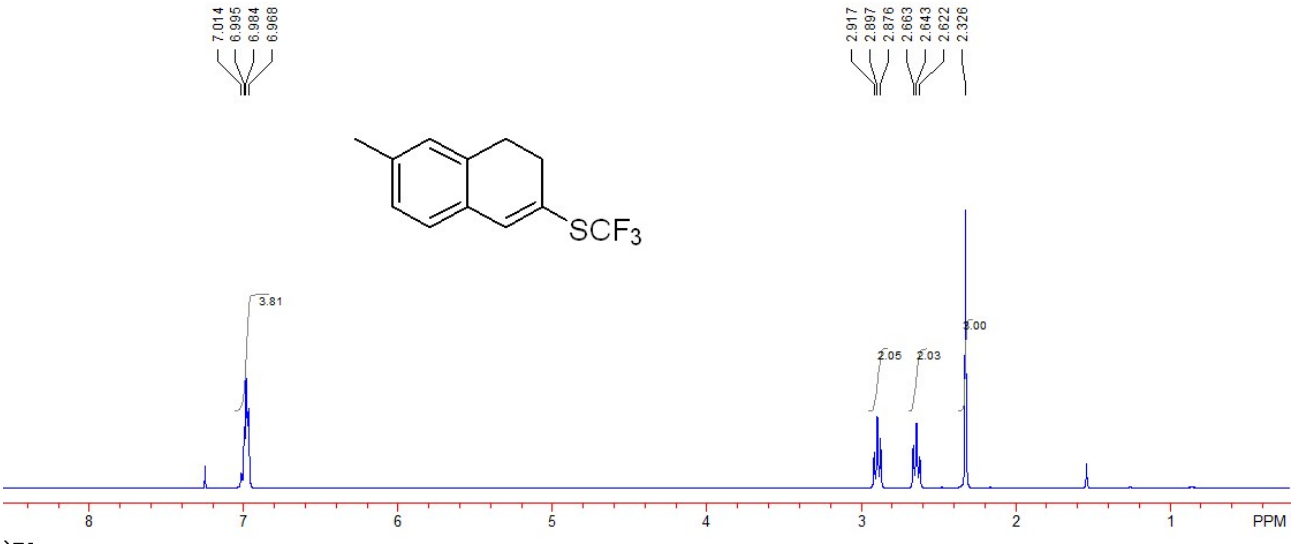
A white solid, 24.6 mg, 40% yield. M.p.: 55-57 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.64 (t, J = 8.0 Hz, 2H, CH_2), 2.91 (t, J = 8.0 Hz, 2H, CH_2), 6.93-6.95 (m, 2H, ArH), 7.30-7.34 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.1, 30.0, 122.5, 125.5, 128.3, 129.6 (q, J = 308.2 Hz), 129.8, 130.6, 131.8, 136.7, 137.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.80. IR (CH_2Cl_2) ν 2954, 2918, 2845, 1585, 1478, 1437, 1423, 1403, 1117, 1072, 882, 850, 814, 755 cm^{-1}. MS (%) m/e 310 (83.15), 308 (82.29), 241 (32.63), 239 (33.96), 128 (M^+, 100.00), 160 (78.16), 116 (70.77), 115 (61.49). HRMS (EI) calcd. for $C_{11}H_8F_3SBr$: 307.9482, Found: 307.9486.

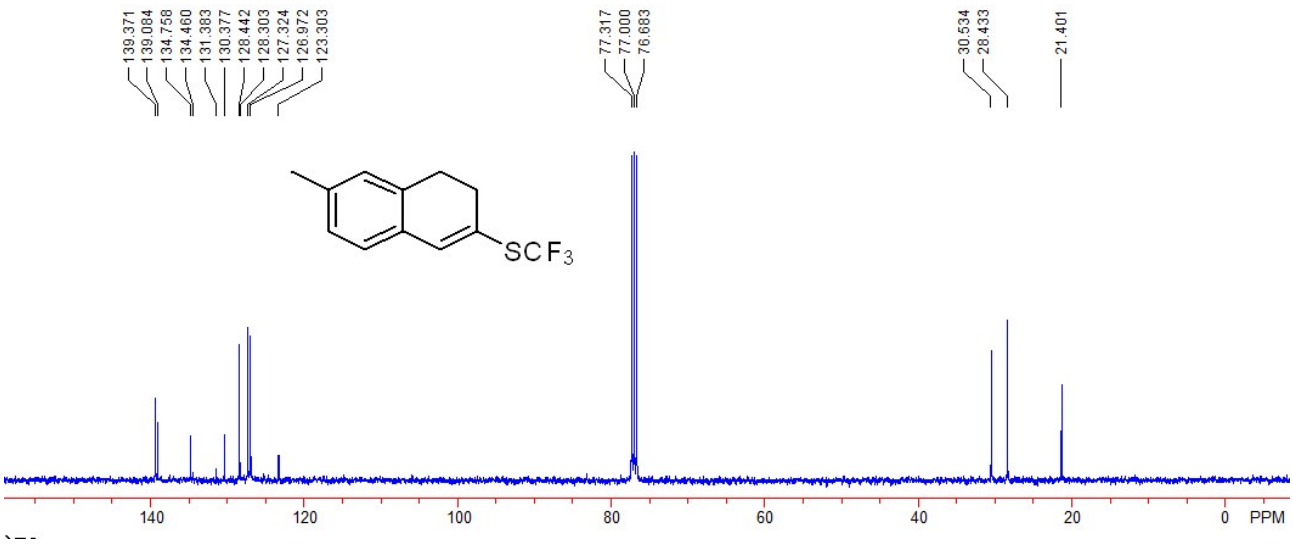


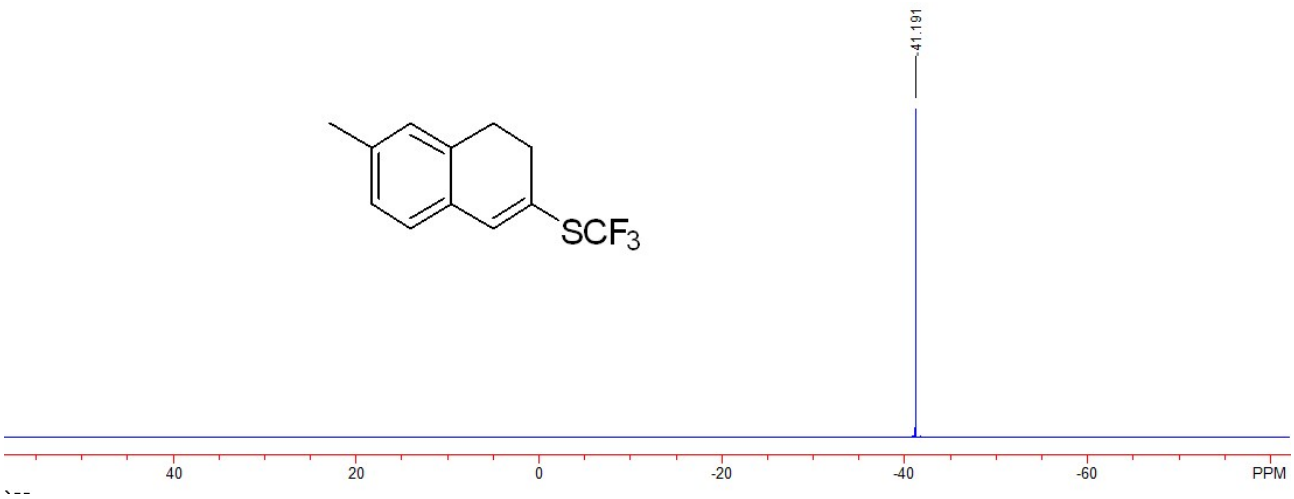


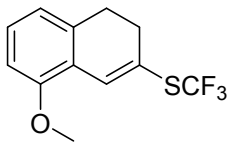
(6-methyl-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2g).

A colorless oil, 14.6 mg, 30% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H, CH_3), 2.64 (t, J = 8.4 Hz, 2H, CH_2), 2.90 (t, J = 8.4 Hz, 2H, CH_2), 6.97-7.01 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.4, 30.5, 123.3, 127.0, 127.3, 128.4, 129.8 (q, J = 308.0 Hz), 130.4, 134.8, 139.1, 139.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.19. IR (CH_2Cl_2) ν 3011, 2941, 2889, 2832, 1613, 1492, 1440, 1149, 1102, 882, 813, 754 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 175 (50.77), 143 (22.42), 142 (32.1), 141 (22.61), 131 (60.4), 128 (22.16), 115 (18.86). HRMS (EI) calcd. for $C_{12}H_{11}SF_3$: 244.0534, Found: 244.0530.



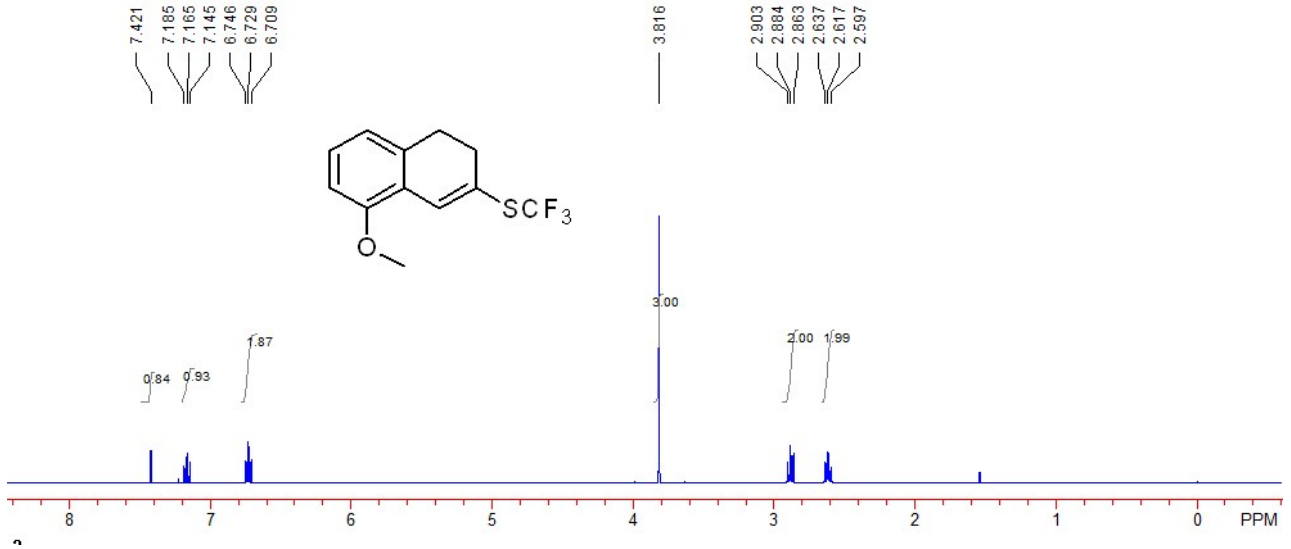






(8-methoxy-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2h).

A colorless oil, 31.2 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.62 (t, J = 8.0 Hz, 2H, CH_2), 2.88 (t, J = 8.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 6.73 (t, J = 8.0, 2H, ArH), 7.17 (t, J = 8.0 Hz, 1H, ArH), 7.42 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.6, 30.1, 55.5, 108.9, 119.9, 121.8, 123.1, 129.6, 129.9 (q, J = 308.2 Hz), 133.6, 136.3, 155.2. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.18. IR (CH_2Cl_2) ν 3067, 2943, 2889, 2838, 1472, 1438, 1265, 1093, 1038, 778, 747 cm^{-1}. MS (%) m/e 261 (14.44), 260 (M^+, 100.00), 191 (61.01), 159 (12.73), 158 (19.2), 147 (56.65), 144 (12.38), 115 (31.95). HRMS (EI) calcd. for $C_{12}H_{11}OF_3S$: 260.0483, Found: 260.0474.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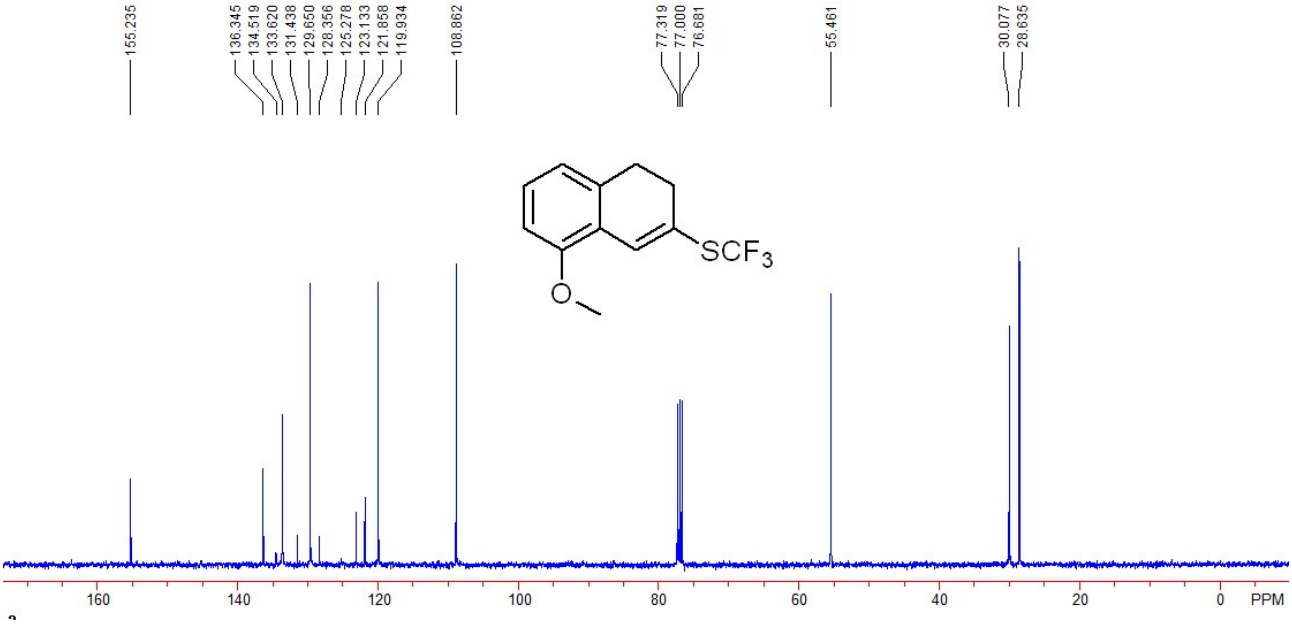
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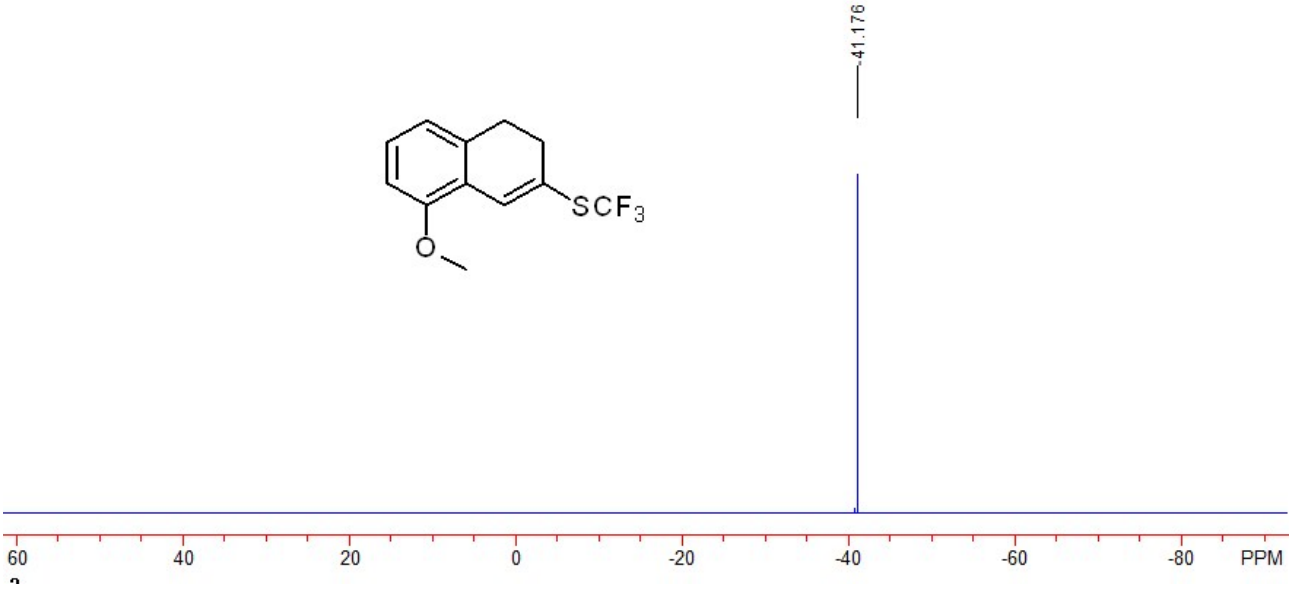
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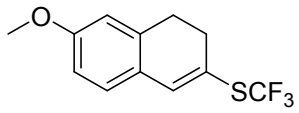
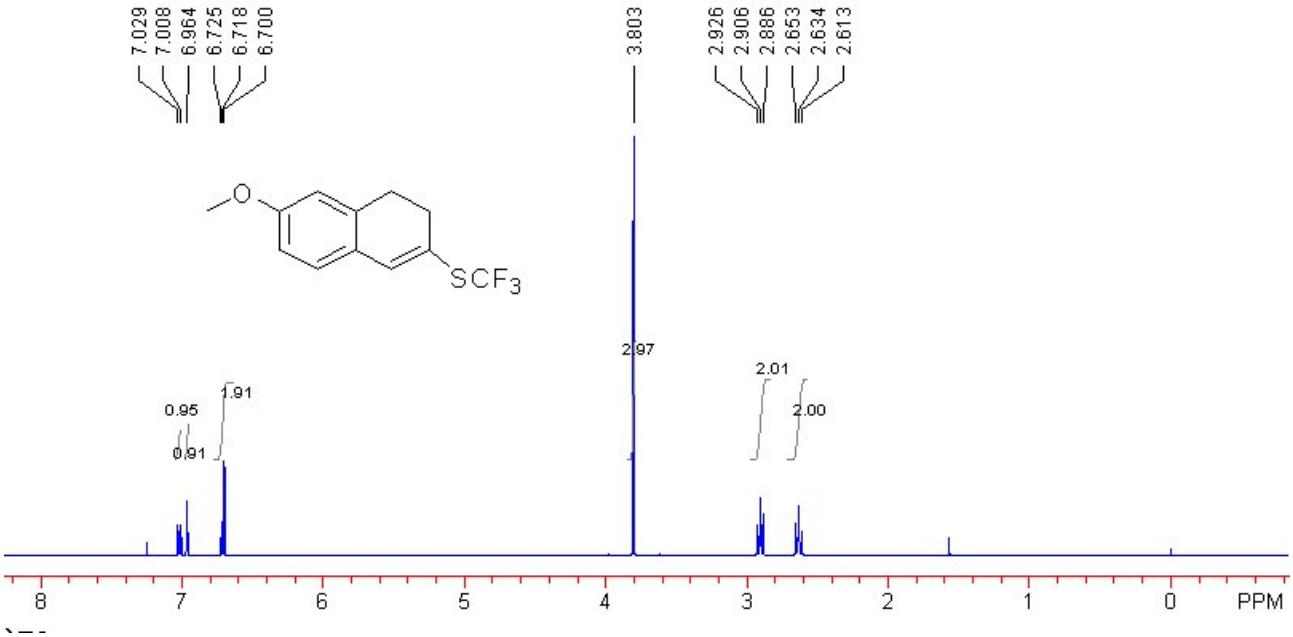
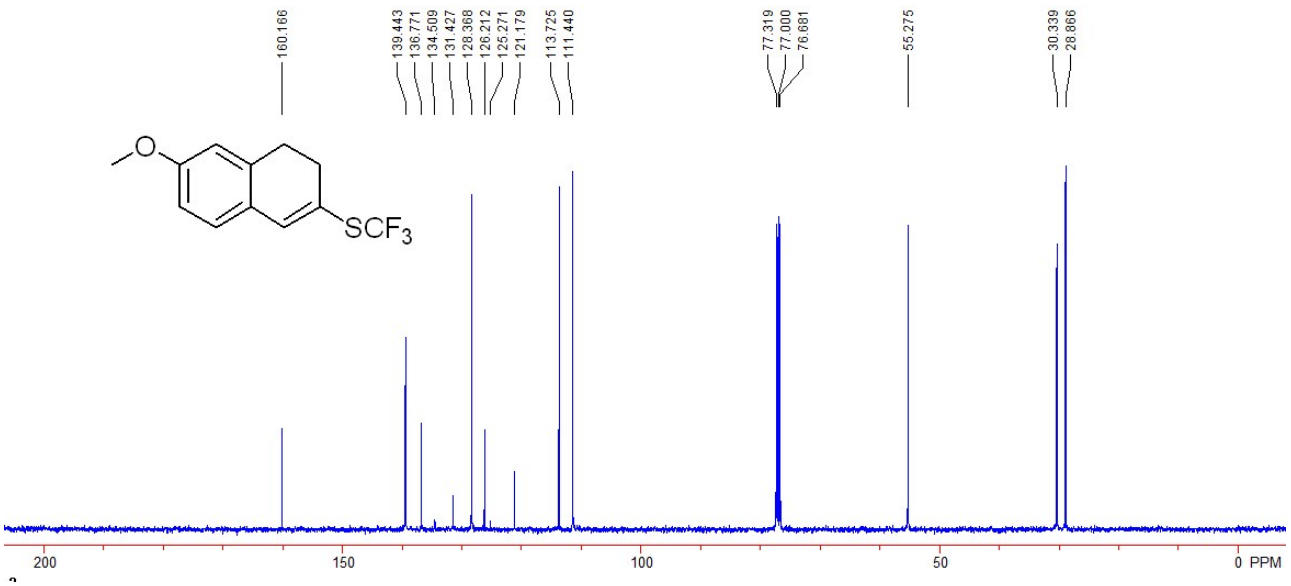
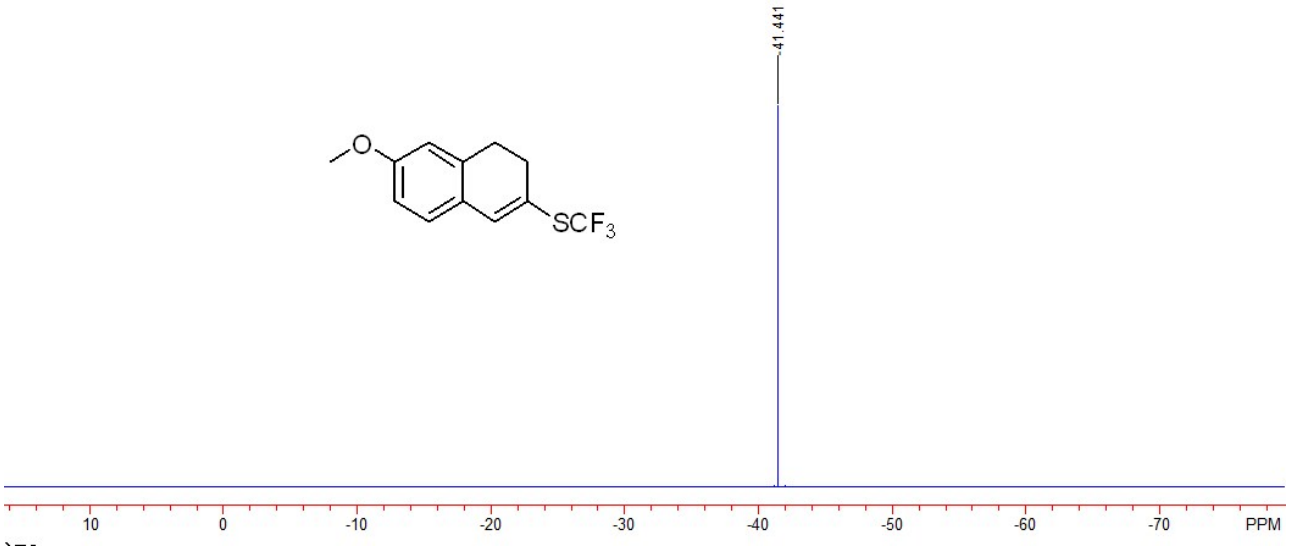


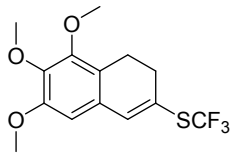
(6-methoxy-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2i).

A colorless oil, 20.8 mg, 40% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.63 (t, *J* = 8.0 Hz, 2H, CH_2), 2.91 (t, *J* = 8.0 Hz, 2H, CH_2), 3.80 (s, 3H, CH_3), 6.70-6.73 (m, 2H, ArH), 6.96 (s, 1H, ArH), 7.02 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.9, 30.3, 55.3, 111.4, 113.7, 121.2, 126.2, 128.4, 129.9 (q, *J* = 308.2 Hz), 136.8, 139.4, 160.2. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.44. IR (CH_2Cl_2) ν 3000, 2938, 2894, 2835, 1606, 1500, 1267, 1250, 1150, 1102, 1038 cm^{-1}. MS (%) m/e 261 (13.83), 260 (97.35), 192 (12.93), 191 (M^+, 100.00), 158 (20.91),147 (64.12), 115 (37.83), 40 (12.47). HRMS (EI) calcd. for $C_{12}H_{11}OF_3S$: 260.0483, Found: 260.0487.



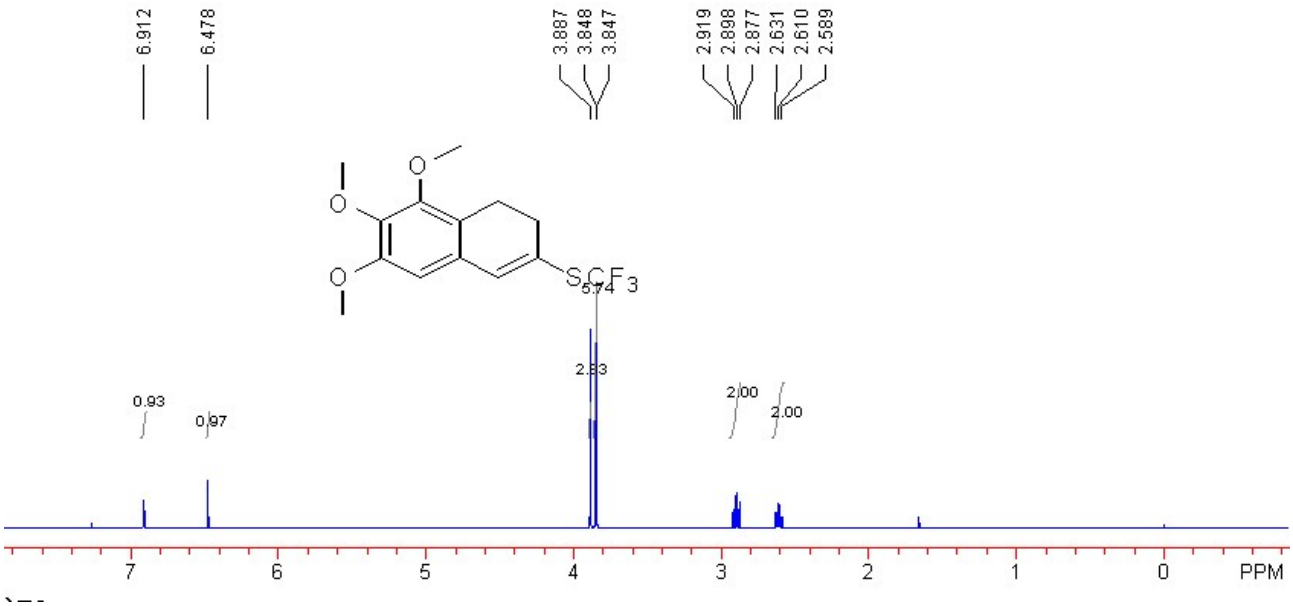






(trifluoromethyl)(5,6,7-trimethoxy-3,4-dihydronaphthalen-2-yl)sulfane (2j).

A colorless oil, 41.6 mg, 65% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.61 (t, J = 8.4 Hz, 2H, CH_2), 2.90 (t, J = 8.4 Hz, 2H, CH_2), 3.847 (s, 3H, CH_3), 3.848 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 6.48 (s, 1H, ArH), 6.91 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.2, 30.0, 56.1, 60.8, 60.9, 106.9, 120.7, 124.0, 128.6, 129.8 (q, J = 308.2 Hz), 138.8, 143.0, 150.7, 151.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.12. IR (CH_2Cl_2) ν 2996, 2936, 2836, 1562, 1489, 1458, 1410, 1342, 1321, 1277, 1106, 1028, 993, 754 cm^{-1}. MS (%) m/e 321.78 (16.78), 320 (M^+, 100.00), 305 (45.5), 251 (49.88), 207 (15.68), 161 (19.76), 118 (12.03), 115 (12.31). HRMS (EI) calcd. for $C_{14}H_{15}O_3F_3S$: 320.0694, Found: 320.0700.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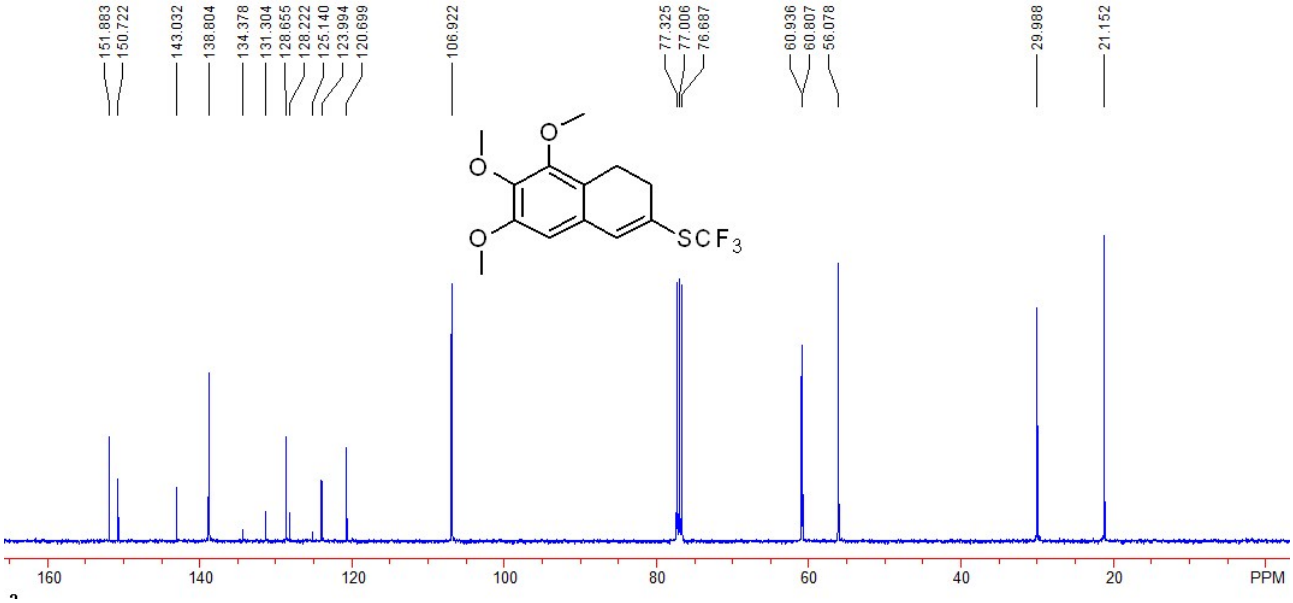
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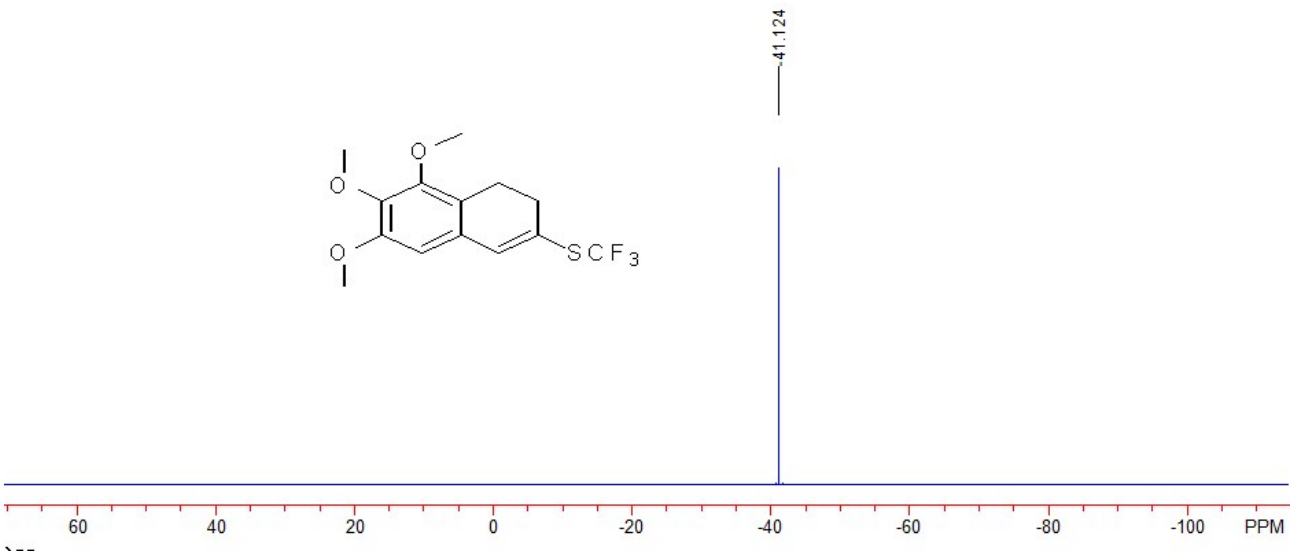
O
O
SCF3
160
140
120
100
80
60
40
20
PPM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-80
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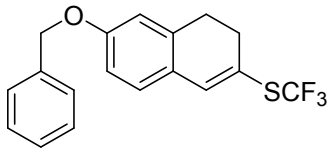
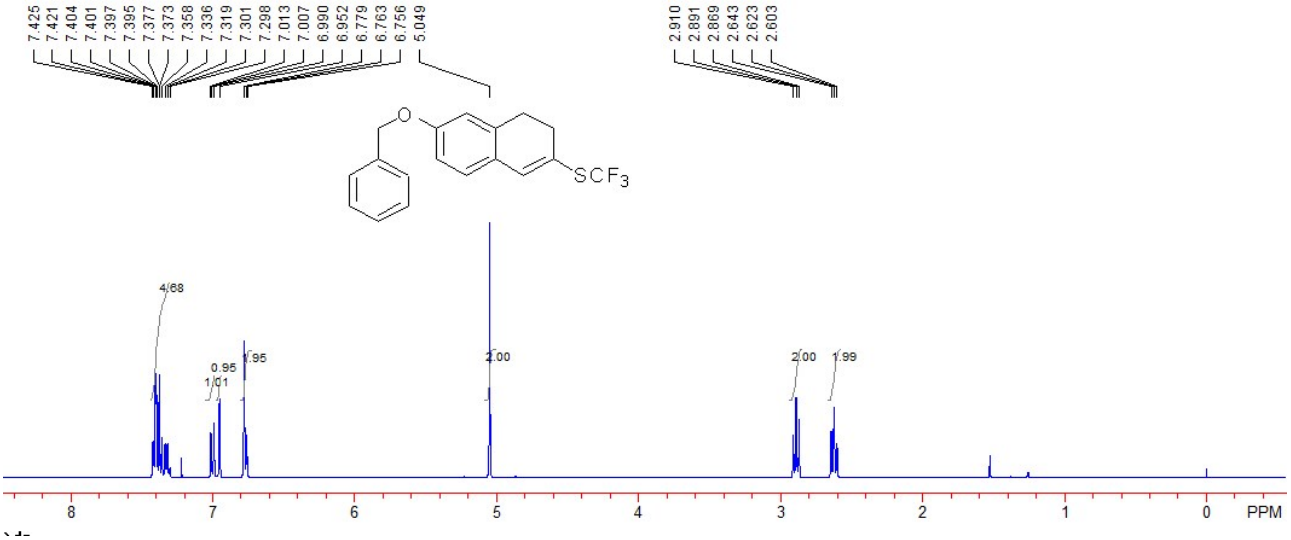
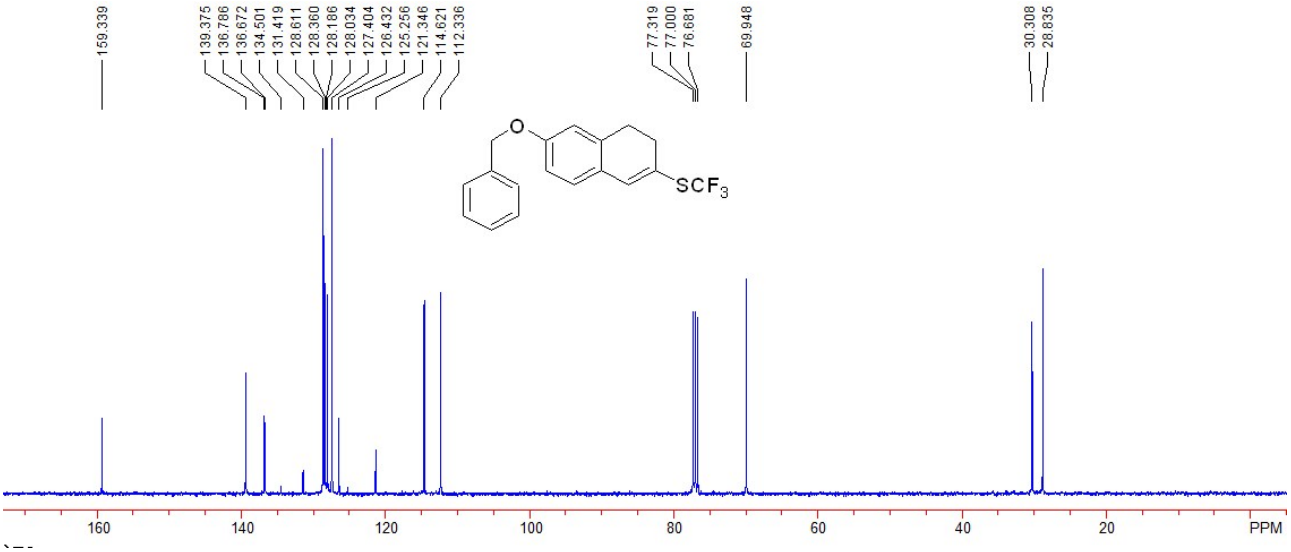
PPM

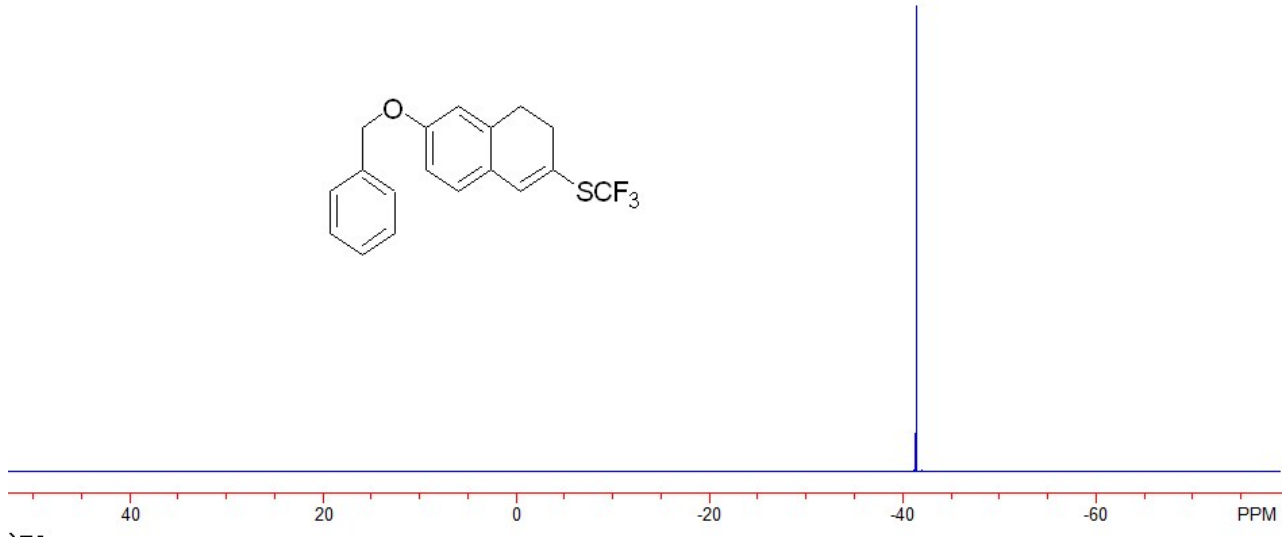


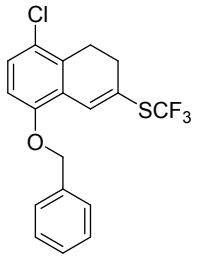
(6-(benzyloxy)-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2k).

A light yellow solid, 37.6 mg, 56% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.62 (t, *J* = 8.0 Hz, 2H, CH_2), 2.90 (t, *J* = 8.0 Hz, 2H, CH_2), 5.05 (s, 2H, CH_2), 6.76-6.78 (m, 2H, ArH), 6.95 (s, 1H, ArH), 7.00 (d, *J* = 9.2 Hz, 1H, ArH), 7.30-7.42 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.8, 30.3, 69.9, 112.3, 114.6, 121.4, 126.4, 127.4, 128.0, 128.4, 128.6, 129.9 (q, *J* = 308.2 Hz), 136.7, 136.8, 139.4, 159.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -41.36. IR (CH_2Cl_2) ν 3034, 2956, 2892, 2832, 1604, 1498, 1270, 1160, 1111, 1040, 873, 810, 735, 695 cm^{-1}. MS (%) m/e 336 (23.5), 260 (14.14), 191 (10.78), 147 (11.04), 116 (6.32), 115 (16.37), 92 (8.12), 91 (M^+, 100.00). HRMS (EI) calcd. for $C_{18}H_{15}OF_3S$: 336.0796, Found: 336.0794.



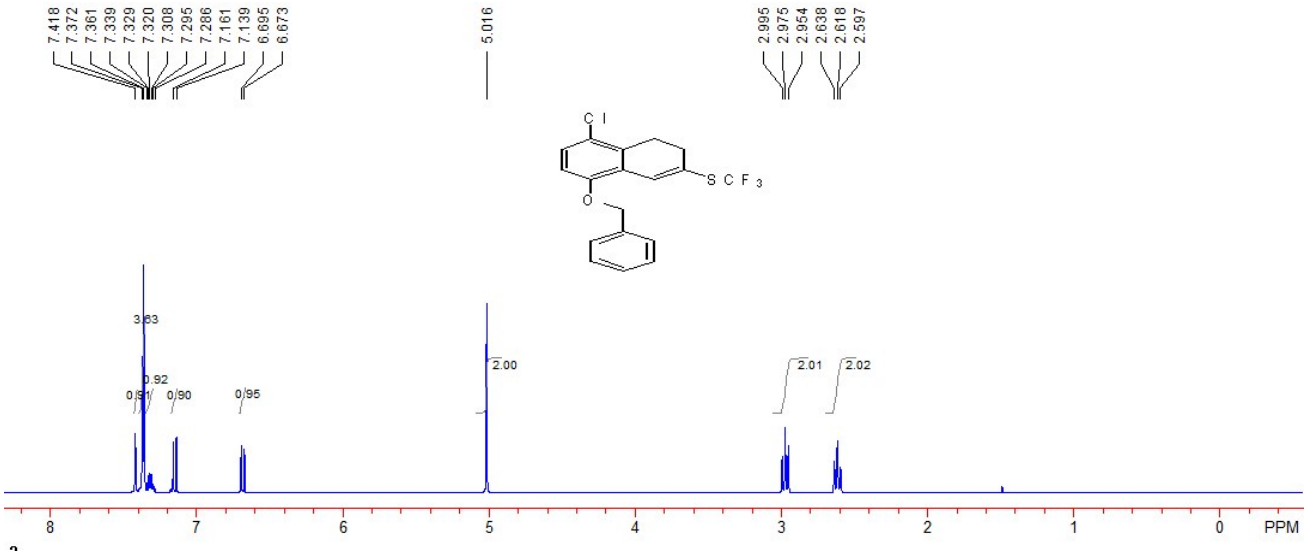






(8-(benzyloxy)-5-chloro-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2l).

A white solid, 48.1 mg, 65% yield. M.p.: 54-55 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.62 (t, *J* = 8.4 Hz, 2H, CH_2), 2.98 (t, *J* = 8.4 Hz, 2H, CH_2), 5.02 (s, 2H, CH_2), 6.68 (d, *J* = 8.8 Hz, 1H, ArH), 7.15 (d, *J* = 8.8 Hz, 1H, ArH), 7.29-7.34 (m, 1H, ArH), 7.36-7.37 (m, 4H, ArH), 7.42 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 25.5, 29.3, 70.5, 111.5, 123.8, 124.5, 125.0, 127.2, 128.1, 128.6, 129.7 (q, *J* = 308.2 Hz), 129.8, 132.3, 133.6, 136.3, 152.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.69. IR (CH_2Cl_2) ν 3065, 3034, 2951, 2890, 2827, 1587, 1452, 1316, 1266, 1149, 1103, 1028, 798, 753, 734, 694 cm^{-1}. MS (%) m/e 370 (7.95), 264 (7.18), 195 (3.99), 151 (5.53), 115 (7.47), 92 (7.51), 91 (M^+, 100.00), 65 (5.37). HRMS (EI) calcd. for $C_{18}H_{14}OF_3SCl$: 370.0406, Found: 370.0399.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2.975
2.954
2.638
2.618
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Cl
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0.90
0.95
2.00
2.01
2.02
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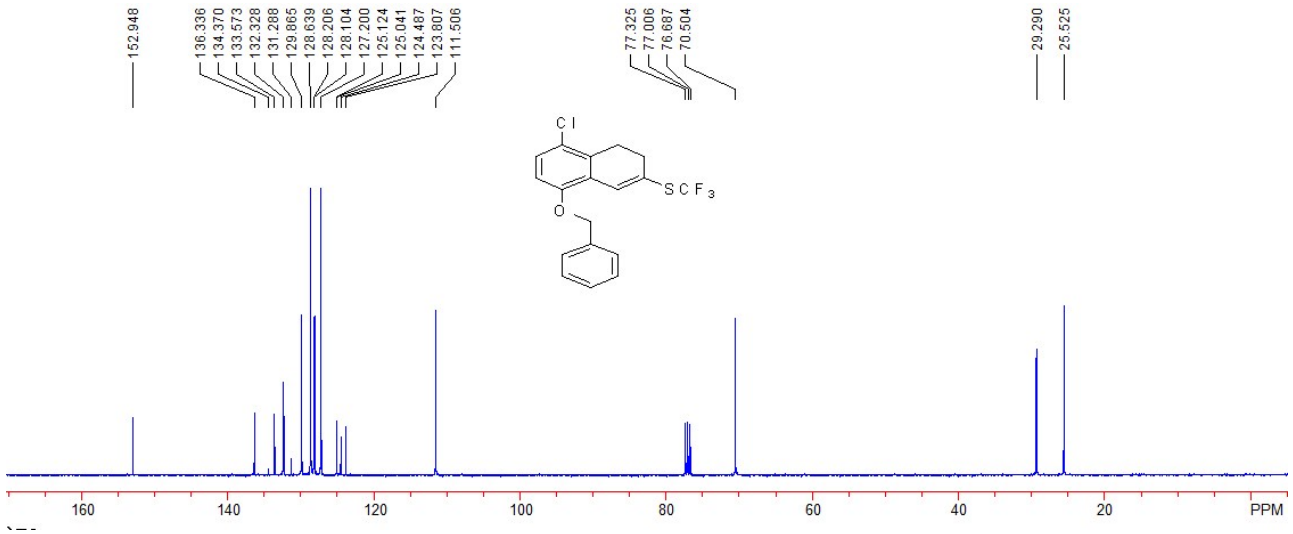
6
5
4
3
2
1
0
PPM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129.865
128.639
128.206
128.104
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111.506
77.325
77.006
76.687
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29.290
25.525
Cl
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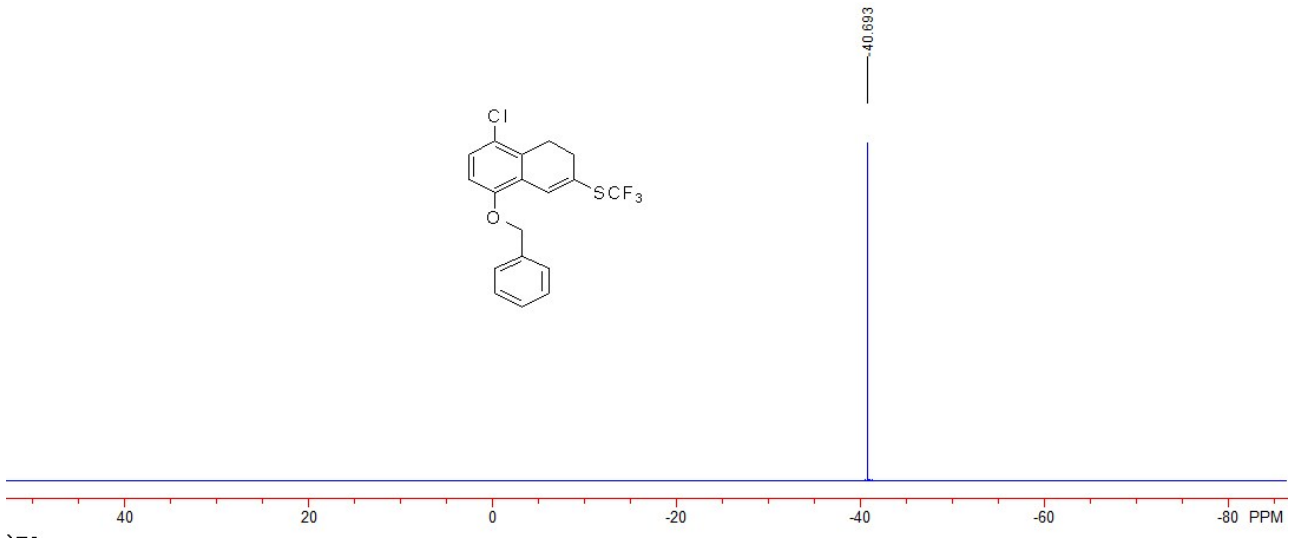
160
140
120
100
80
60
40
20
PPM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0
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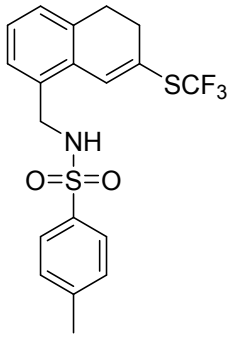
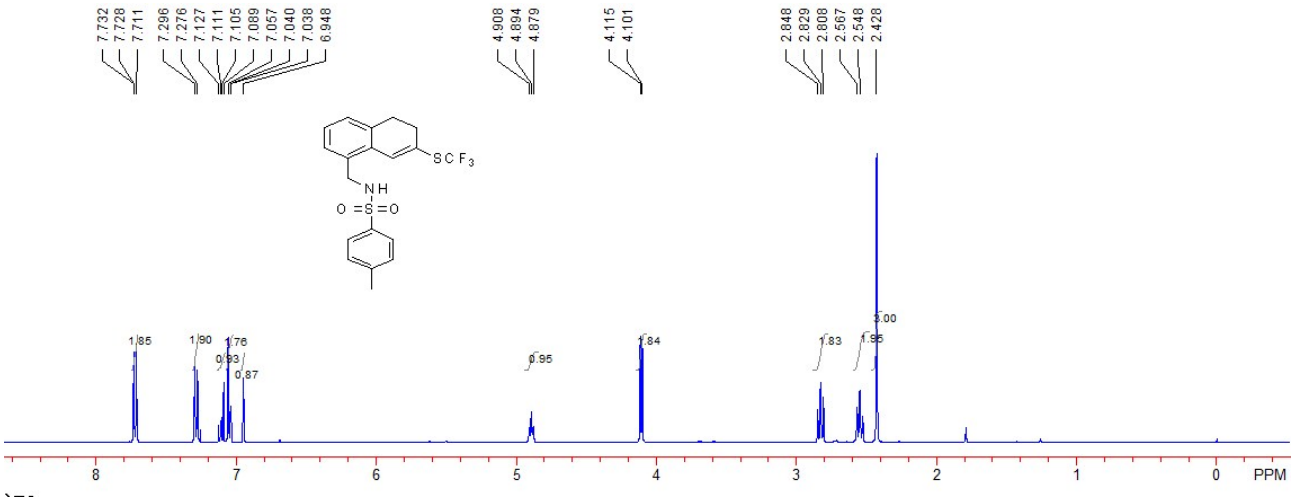
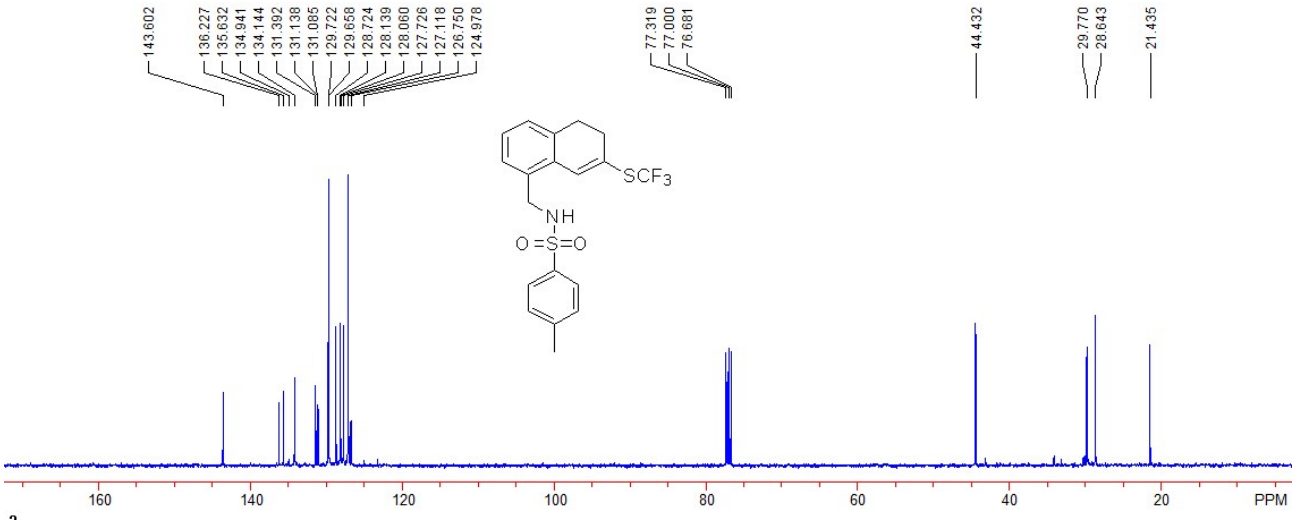
-60
-80
PPM

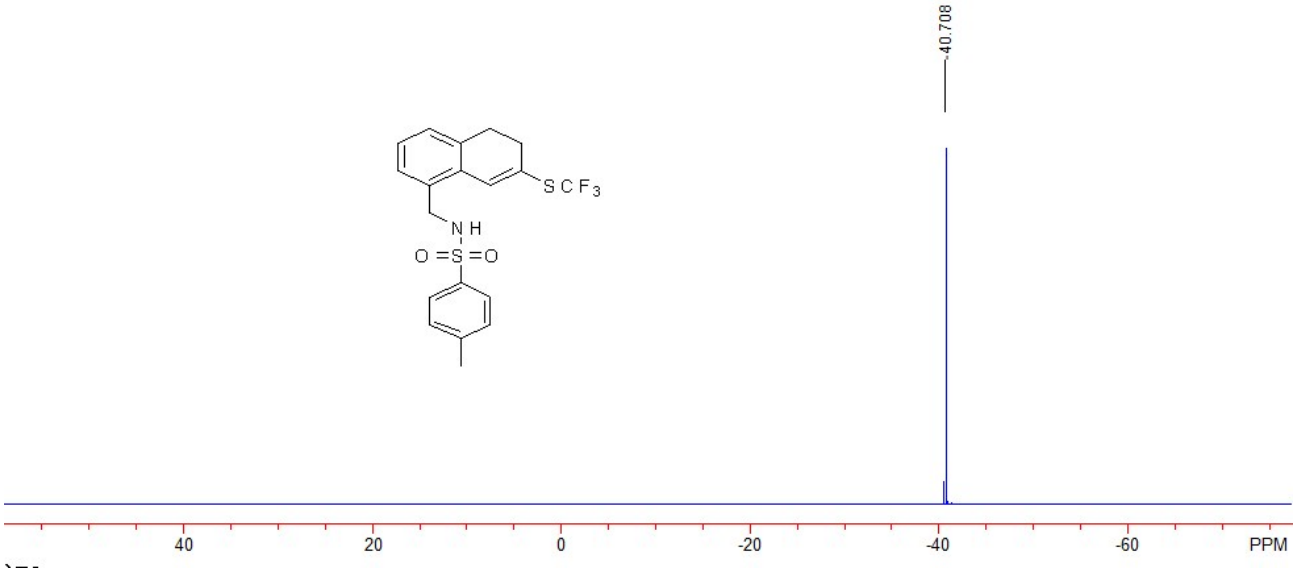


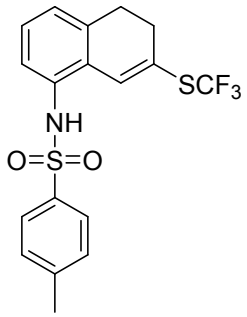
4-methyl-N-((7-((trifluoromethyl)thio)-5,6-dihydronaphthalen-1-yl)methyl)benzenesulfonamide (2m).

A white solid, 42.1 mg, 51% yield. M.p.: 107-109 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 2.55 (t, *J* = 8.0 Hz, 2H, CH_2), 2.83 (t, *J* = 8.0 Hz, 2H, CH_2), 4.11 (d, *J* = 5.6 Hz, 2H, CH_2), 4.89 (t, *J* = 5.6 Hz, 1H, NH), 6.95 (s, 1H, ArH), 7.04-7.11 (m, 3H, ArH), 7.29 (d, *J* = 8.0 Hz, 2H, ArH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.6, 29.8, 44.4, 126.8, 127.1, 127.7, 128.1, 128.7, 129.6 (q, *J* = 307.8 Hz), 129.7, 131.1, 131.4, 134.1, 135.6, 136.2, 143.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.71. IR (CH_2Cl_2) ν 3271, 3067, 2943, 2884, 2830, 1325, 1154, 1108, 1048, 814, 662 cm^{-1}. MS (%) m/e 413 (32.8), 258 (36.81), 188 (M^+, 100.00), 156 (76.15), 130 (35.05), 129 (22.21), 128 (25.08), 91 (37.69). HRMS (EI) calcd. for $C_{19}H_{18}NO_2F_3S_2$: 413.0731, Found: 413.0739.





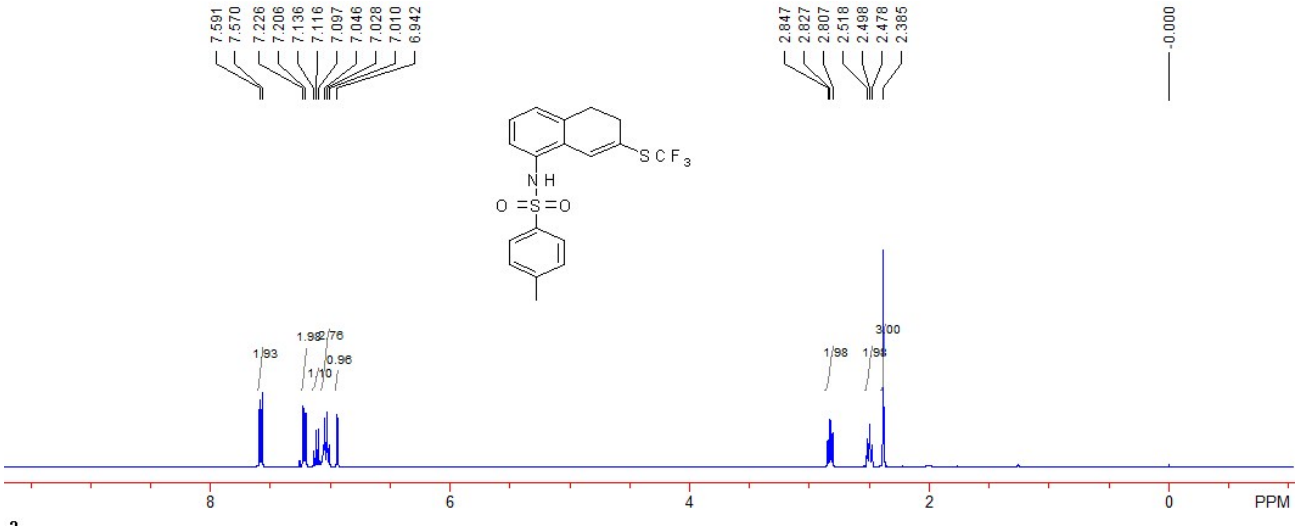


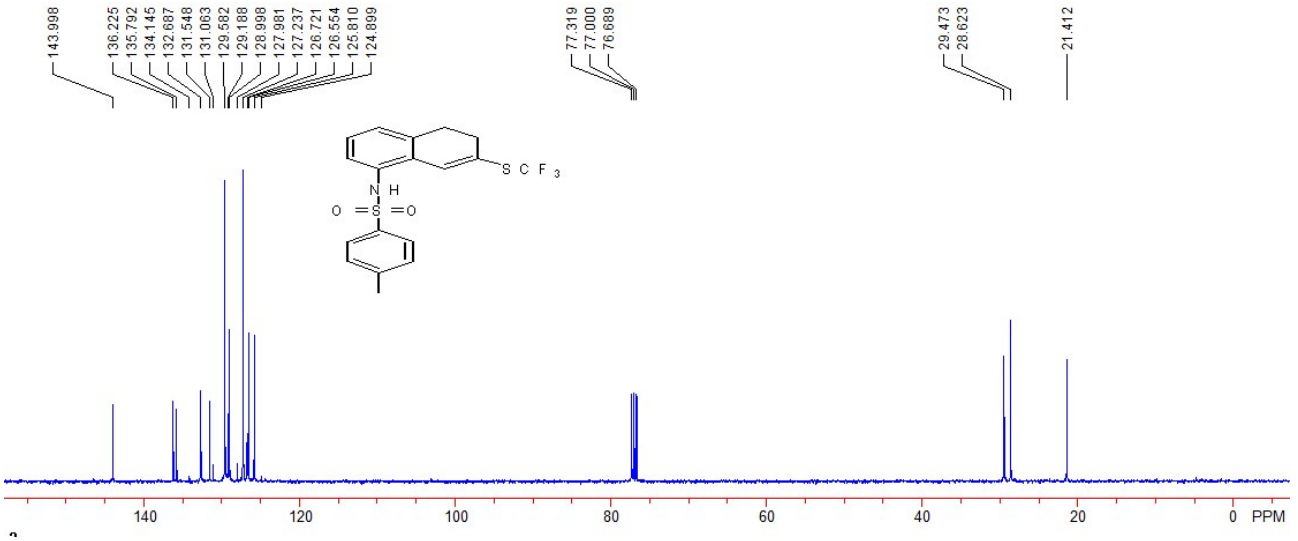


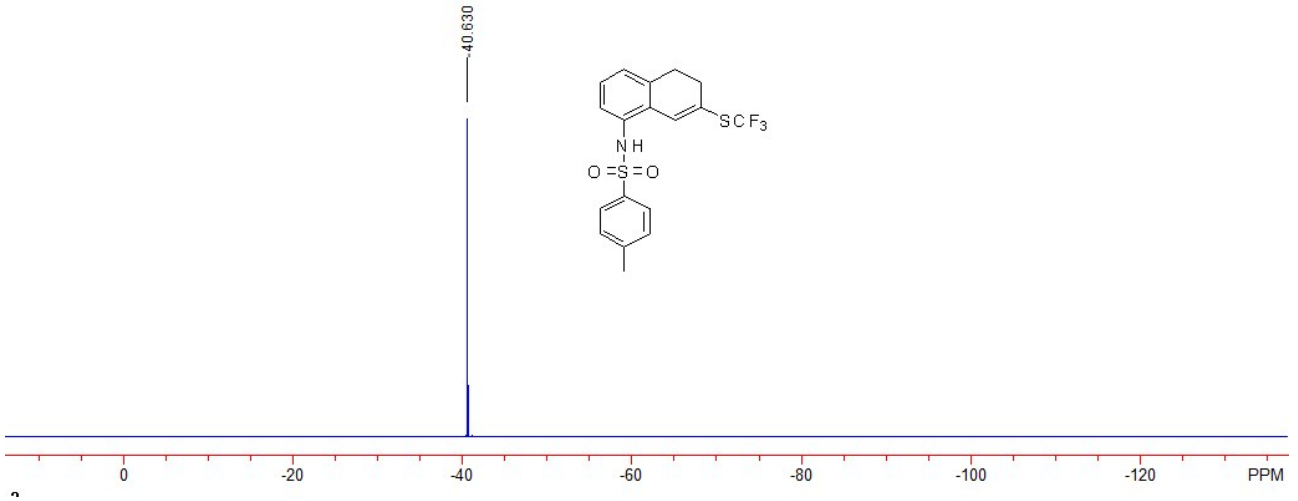
4-methyl-N-(7-((trifluoromethyl)thio)-5,6-dihydronaphthalen-1-yl)benzenesulfonamide (2n).

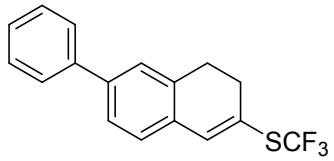
A white solid, 39.9 mg, 50% yield. M.p.: 135-137 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H, CH_3), 2.50 (t, J = 8.0 Hz, 2H, CH_2), 2.83 (t, J = 8.0 Hz, 2H, CH_2), 6.94 (s, 1H, ArH), 7.01-7.05 (m, 3H, ArH&NH), 7.11 (t, J = 7.6 Hz, 1H, ArH), 7.22 (d, J = 8.0 Hz, 2H, ArH), 7.58 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.6, 29.5, 125.8, 126.6, 126.7, 127.2, 129.0, 129.2, 129.5 (q, J = 308.2 Hz), 129.6, 131.5, 132.7, 135.8, 136.2, 144.0. ^{19}F NMR (376 MHz,

$CDCl_3$, $CFCl_3$) δ -40.63. IR (CH_2Cl_2) ν 3256, 3065, 2942, 2895, 2831, 1594, 1463, 1399, 1325, 1156, 1106, 1086, 916, 813, 752, 665 cm^{-1}. MS (%) m/e 399 (61.77), 244 (99.53), 175 (M^+, 100.00), 174 (31.21), 143 (81.98), 130 (23.61), 115 (46.07), 91 (39.05). HRMS (EI) calcd. for $C_{18}H_{16}NO_2F_3S_2$: 399.0575, Found: 399.0569.



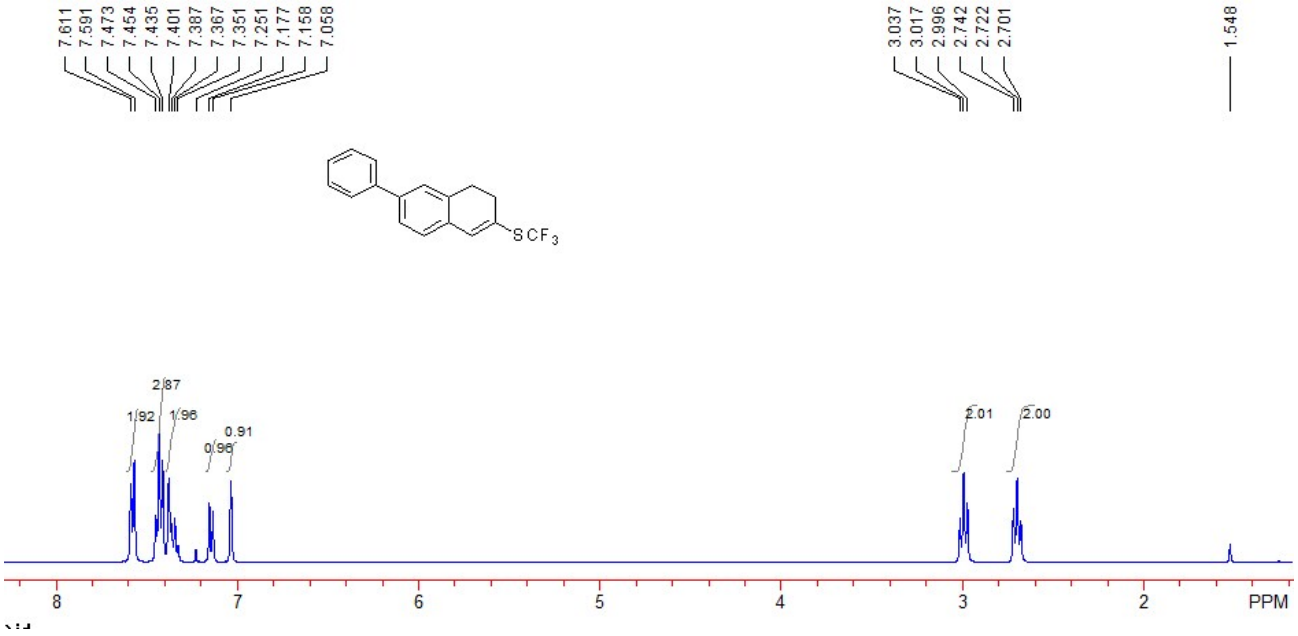


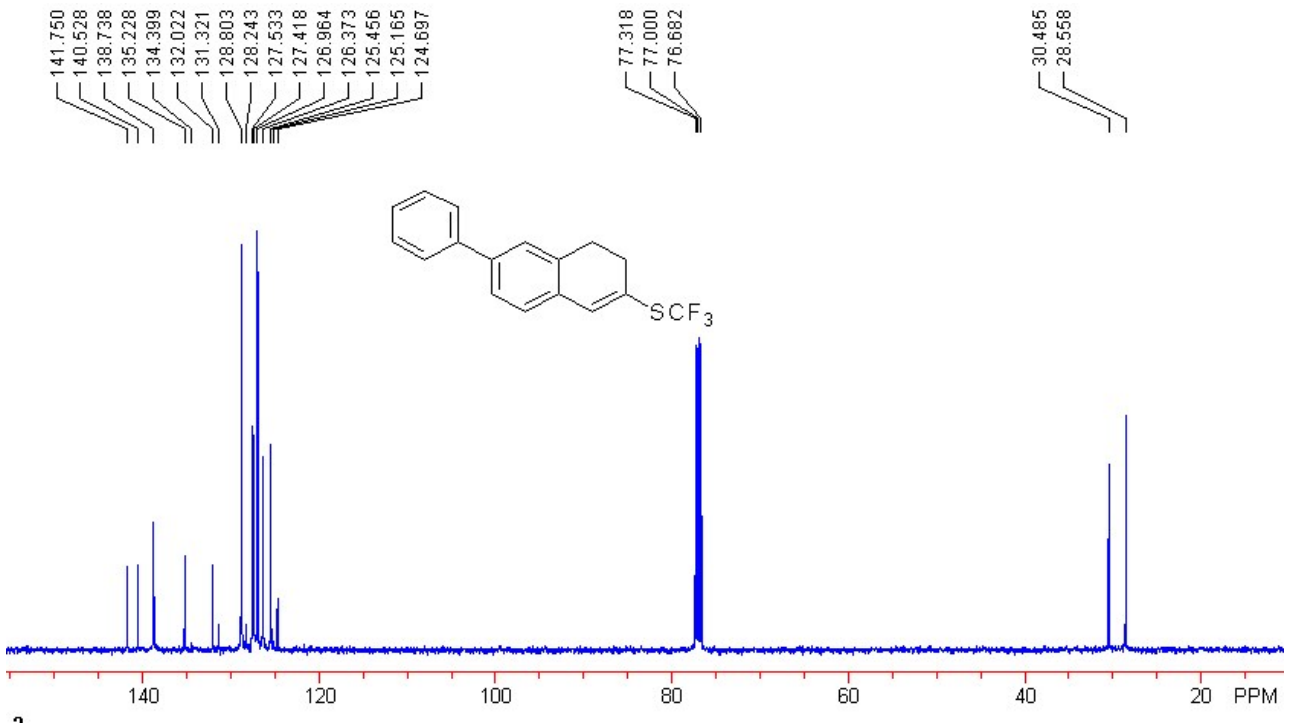


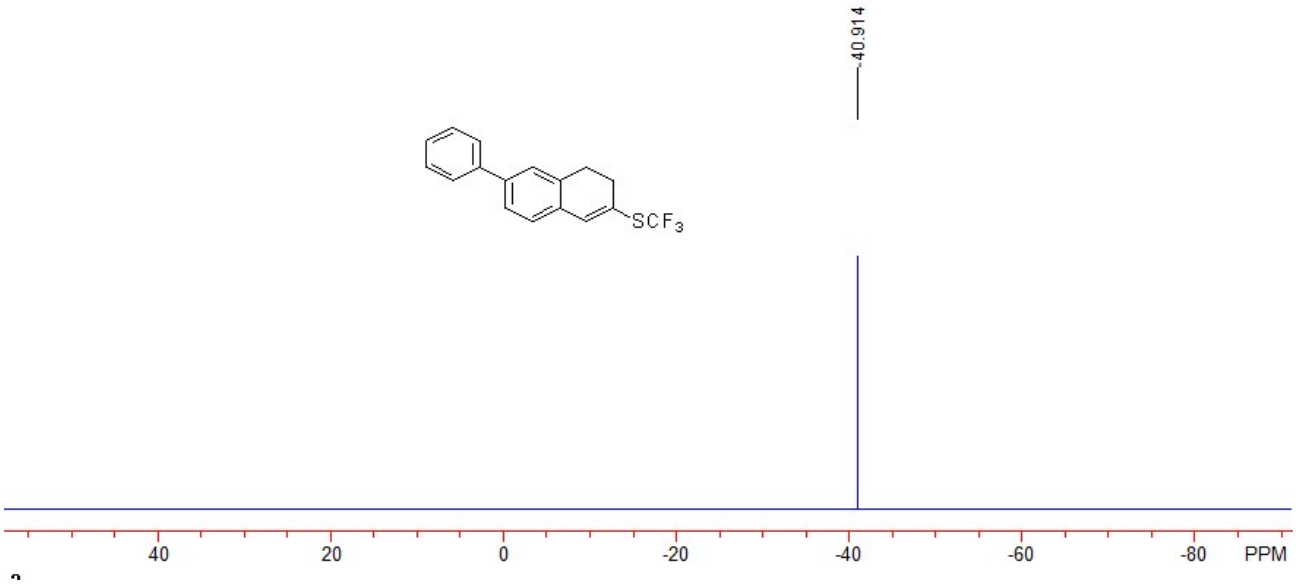


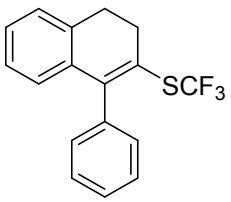
(6-phenyl-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2o).

A light yellow solid, 33.7 mg, 55% yield. M.p.: 61-63°C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.72 (t, *J* = 8.0 Hz, 2H, CH_2), 3.02 (t, *J* = 8.0 Hz, 2H, CH_2), 7.06 (s, 1H, ArH), 7.17 (d, *J* = 7.6 Hz, 1H, ArH), 7.35-7.47 (m, 5H, ArH), 7.60 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.6, 30.5, 124.7, 125.4, 126.4, 127.0, 127.4, 127.5, 128.8, 129.8 (q, *J* = 307.8 Hz), 132.0, 135.2, 138.7, 140.5, 141.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -40.91. IR (CH_2Cl_2) ν 3024, 2920, 2850, 1479, 1153, 1135, 1099, 890, 828, 762, 696 cm^{-1}. MS (%) m/e 307 (19.32), 306 (M^+, 100.00), 237 (52.88), 204 (27.69), 203 (28.25), 202 (31.37), 193 (39.46), 178 (27.18). HRMS (EI) calcd. for $C_{17}H_{13}F_3S$: 306.0690, Found: 306.0697.





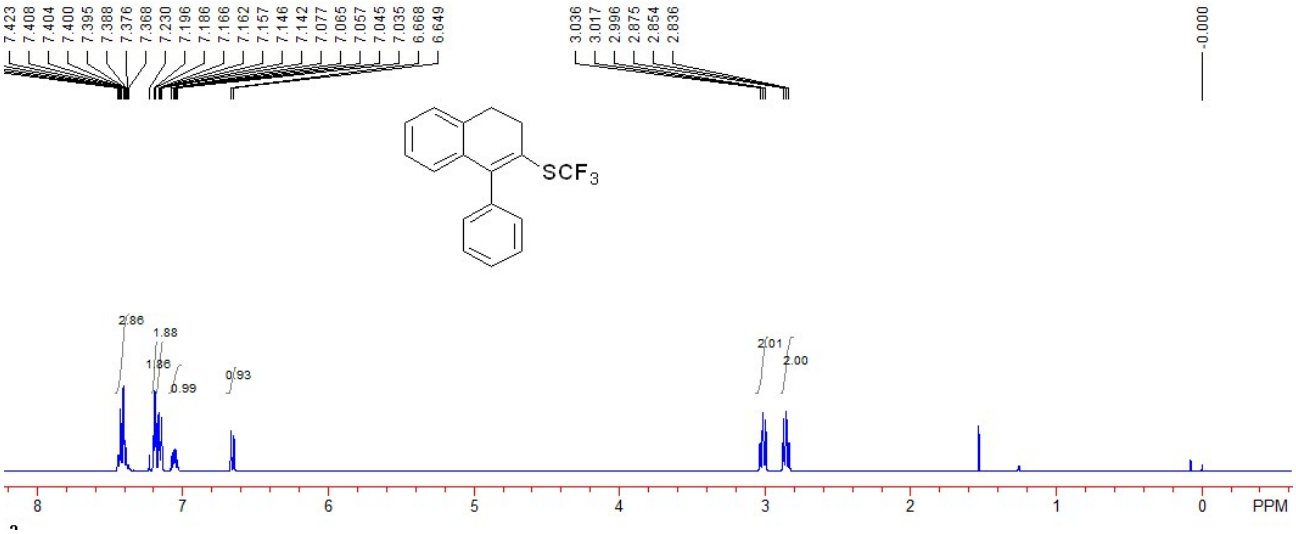


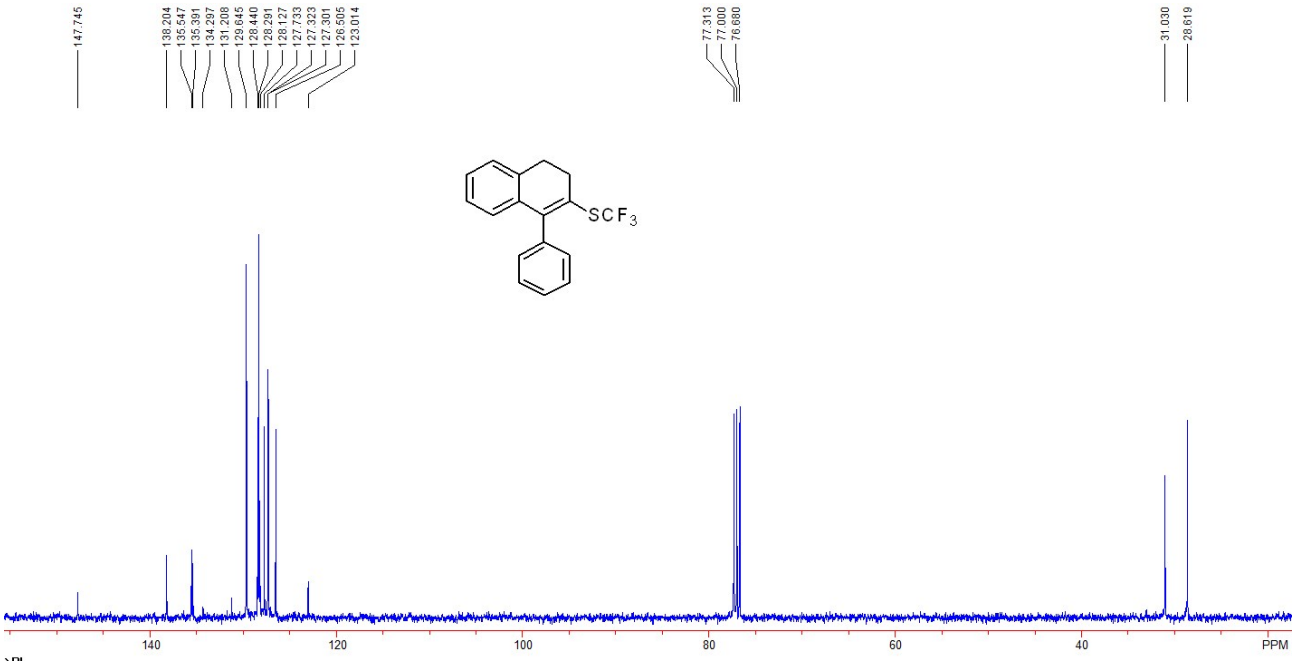


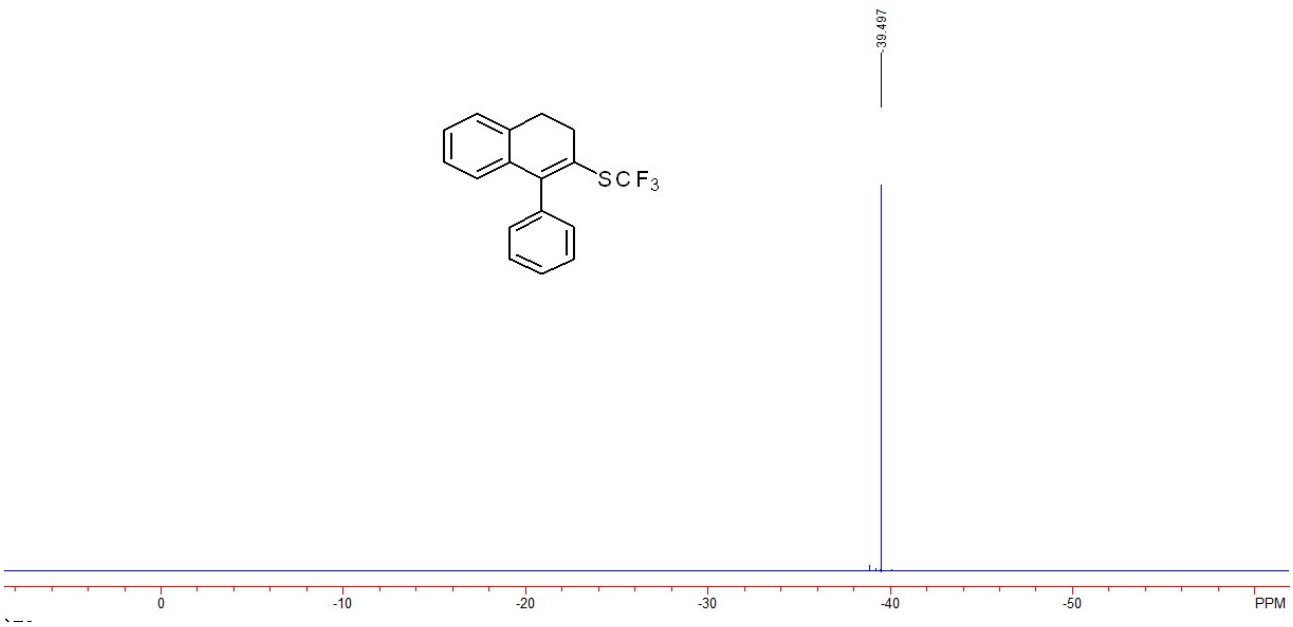
(1-phenyl-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (2p).

A colorless oil, 27.5 mg, 36 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.85 (t, J = 8.4 Hz, 2H, CH_2), 3.02 (t, J = 8.4 Hz, 2H, CH_2), 6.66 (d, J = 7.6 Hz, 1H, ArH), 7.04-7.08 (m, 1H, ArH), 7.14-7.20 (m, 4H, ArH), 7.37-7.45 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.6, 31.0, 123.0, 126.5, 127.30, 127.32, 127.7, 128.3, 128.4, 129.6, 129.7 (q, J = 308.1 Hz), 135.4, 135.5,

138.2, 147.7. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -39.50. IR (CH_2Cl_2) ν 3062, 3018, 2936, 2889, 2832, 1593, 1479, 1440, 1148, 1118, 1098, 1070, 768, 699 cm^{-1}. MS (%) m/e 306 (M^+, 100.00), 237 (61.54), 235 (23.16), 222 (34.43), 221 (32.79), 204 (45.65), 203 (38.41), 202 (34.39). HRMS (EI) calcd. for $C_{17}H_{13}SF_3$: 306.0690, Found: 306.0694.



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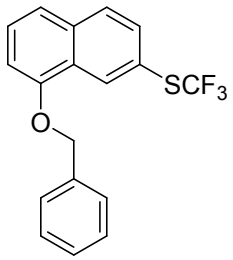
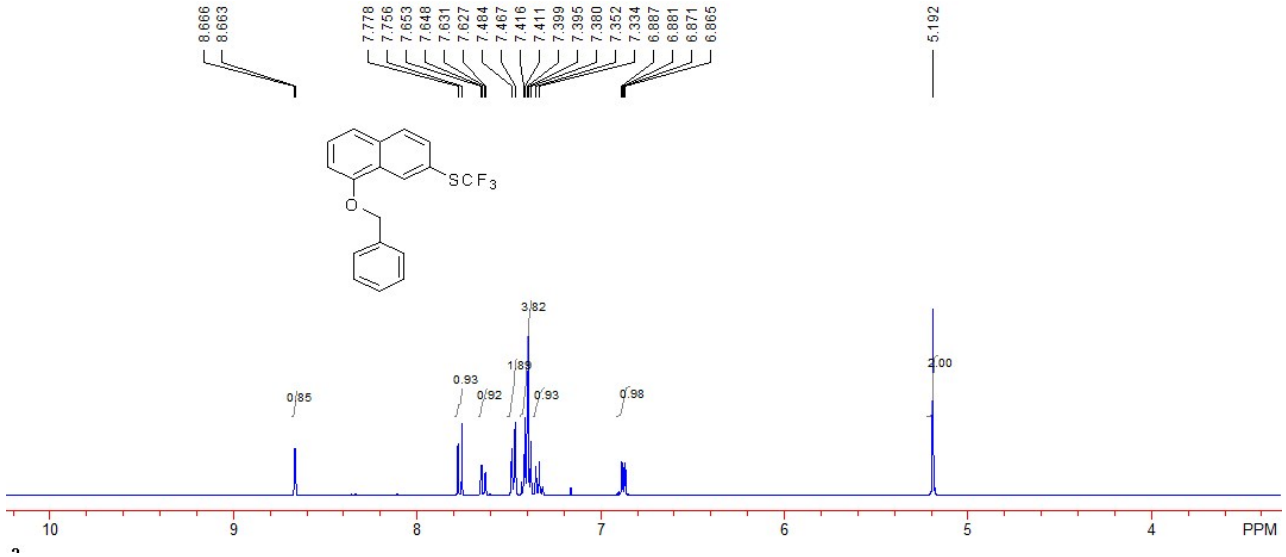
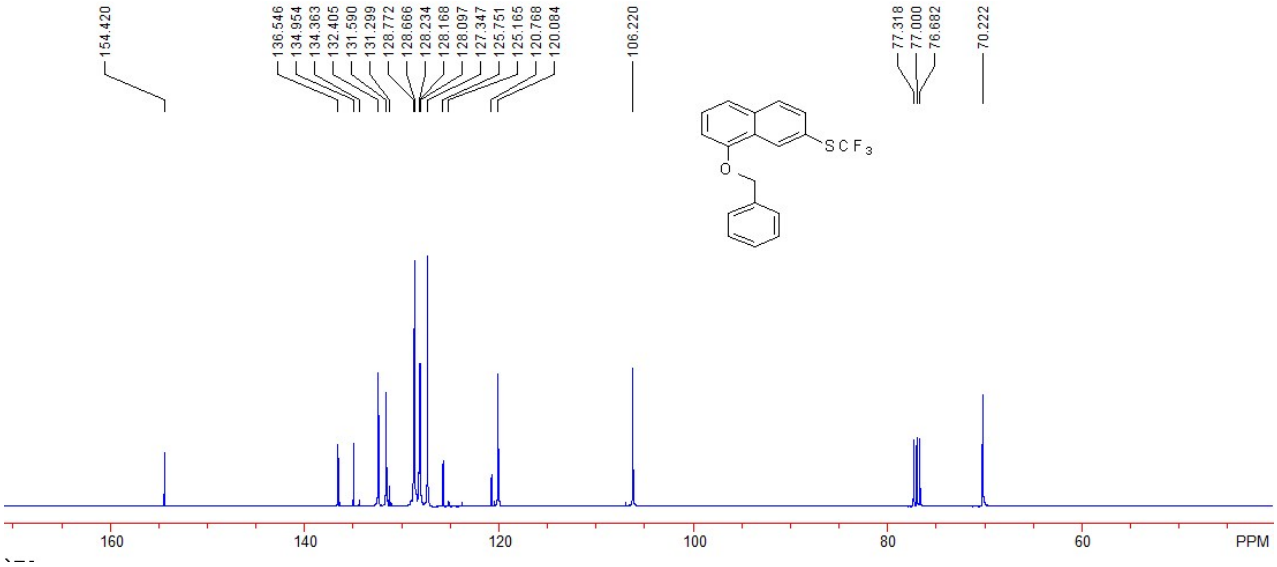
Spectroscopic Data of the Products 3

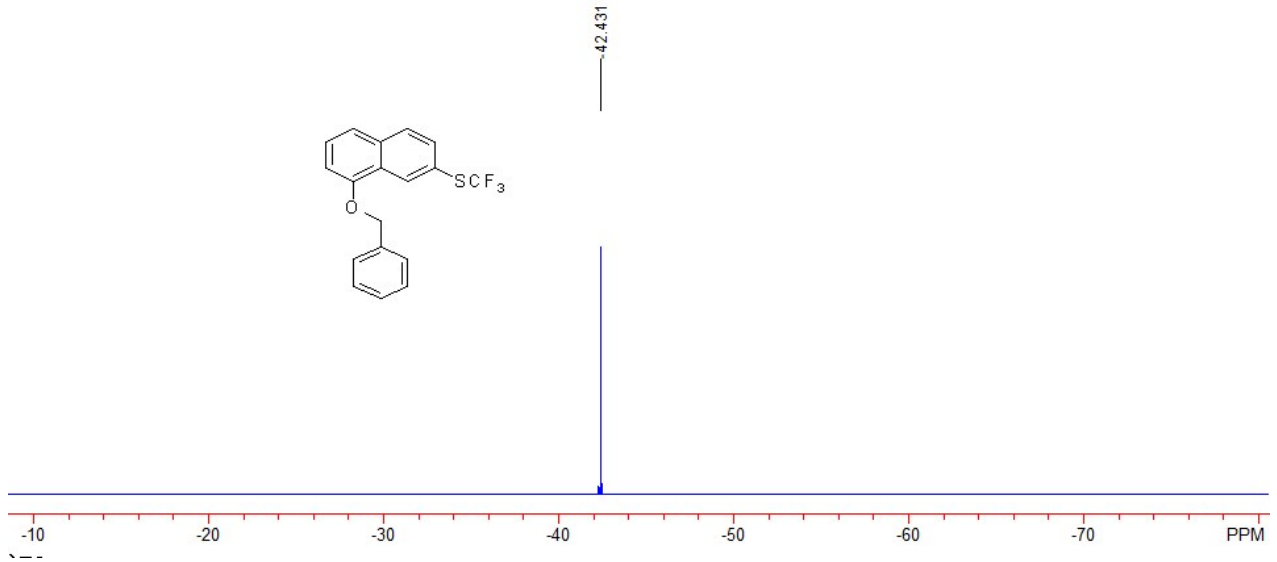


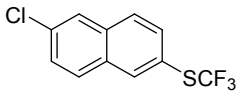
(8-(benzyloxy)naphthalen-2-yl)(trifluoromethyl)sulfane (3a).

A colorless oil, 36 mg, 54% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.19 (s, 2H, CH_2), 6.88 (dd, *J* = 2.4, 6.4 Hz, 1H, ArH), 7.35 (d, *J* = 7.2 Hz, 1H, ArH), 7.38-7.42 (m, 4H, ArH), 7.48 (d, *J* = 6.8 Hz, 2H, ArH), 7.64 (dd, *J* = 1.6, 8.4 Hz, 1H, ArH), 7.77 (d, *J* = 8.8 Hz, 1H, ArH), 8.66 (d, *J* = 1.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 70.2, 106.2, 120.1, 120.7 (q, *J* = 8.0 Hz), 125.7, 127.3, 128.1, 128.2, 128.7, 128.8, 129.8 (q, *J* = 306.5 Hz), 131.6 (q, *J* = 4.2 Hz), 132.4, 135.0, 136.5, 154.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.43. IR (CH_2Cl_2) ν 3065, 3026, 2925, 2856, 1571, 1445, 1362, 1270, 1150, 1097, 823, 732, 694 cm^{-1}. MS (%) m/e 334 (9.30), 146 (4.34), 145 (2.08), 131 (6.56), 102 (4.31), 92 (8.18), 91 (M^+, 100.00), 65 (6.07). HRMS (EI) calcd. for $C_{18}H_{13}OF_3S$: 334.0639, Found:334.0641.



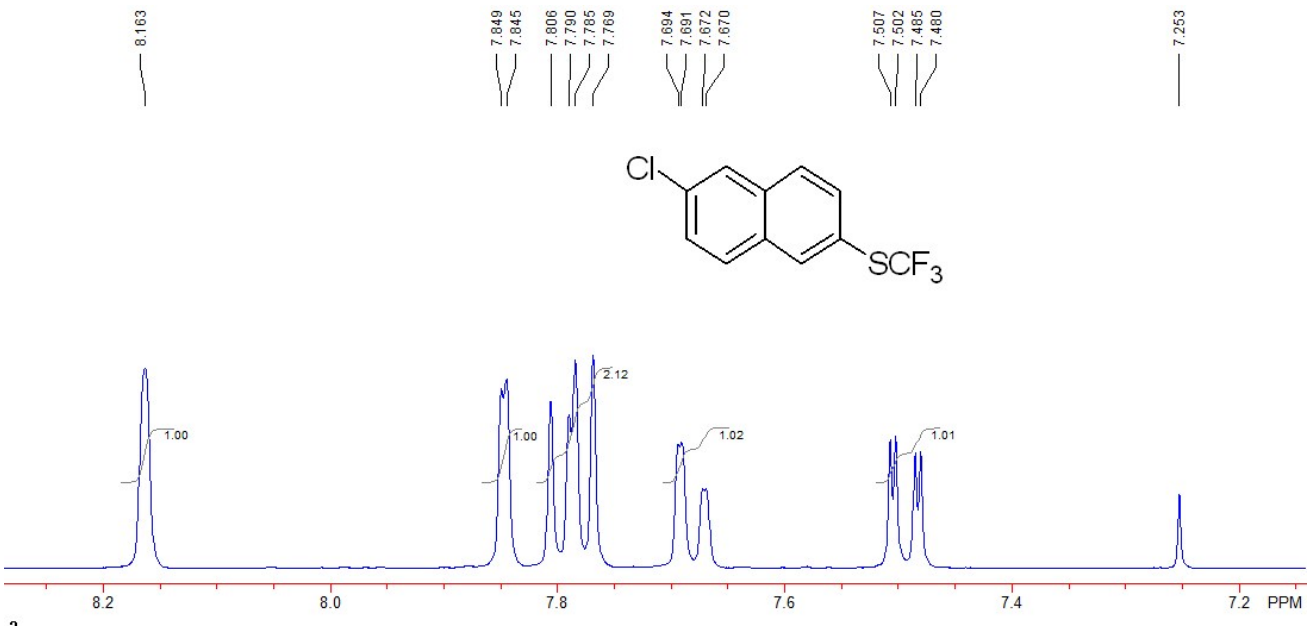






(6-chloronaphthalen-2-yl)(trifluoromethyl)sulfane (3d).

A white solid, 21 mg, 40% yield. M.p.: 74-76 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.49 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 7.68 (dd, J = 0.8, 8.4 Hz, 1H, ArH), 7.77-7.81 (m, 2H, ArH), 7.85 (d, J = 1.6 Hz, 1H, ArH), 8.16 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 122.0, 126.6, 128.0, 128.3, 129.6 (q, J = 307.3 Hz), 129.7, 131.6, 132.9, 133.9, 134.4, 136.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.41. IR (CH_2Cl_2) ν 3057, 2925, 2853, 1621, 1577, 1489, 1154, 1106, 1074, 877, 807 cm^{-1}. MS (%) m/e 264 (36.33), 262 (M^+, 100), 195 (28.46), 193 (76.05), 158 (41.55), 151 (23.56), 149 (71.23), 114 (16.77). HRMS (EI) calcd. for $C_{11}H_6F_3SCl$: 261.9831, Found: 261.9828.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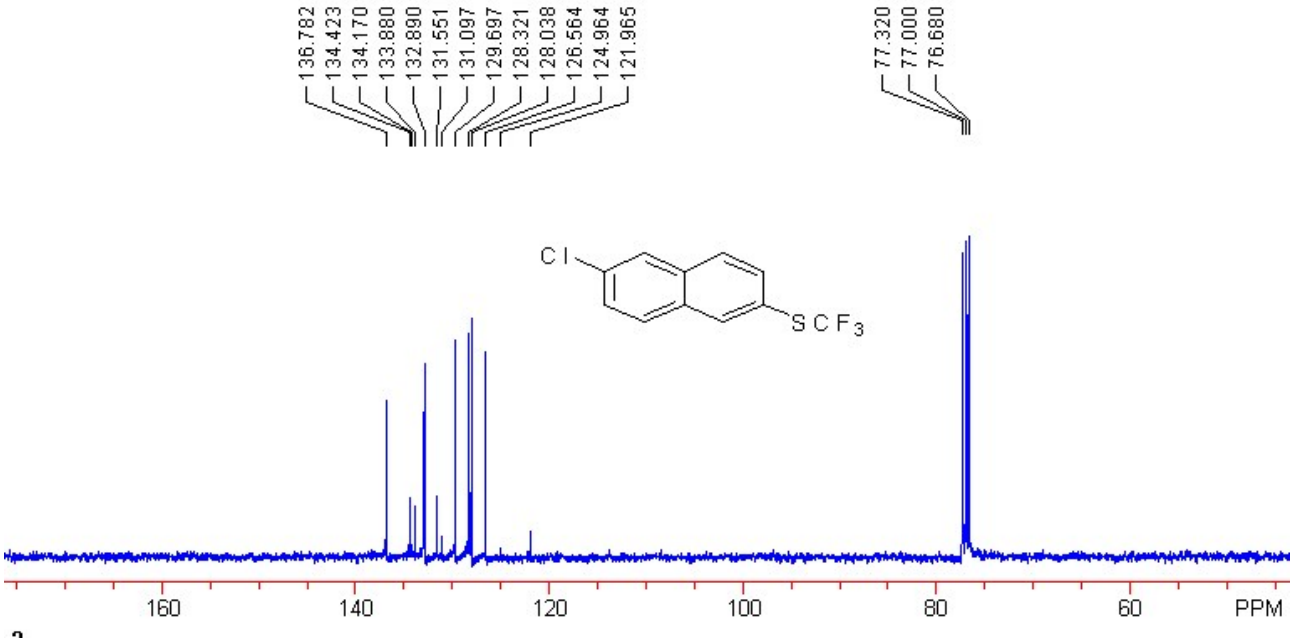
7.845
7.806
7.790
7.785
7.769
7.694
7.691
7.672
7.670
7.507
7.502
7.485
7.480
7.253
Cl
SCF3
1.00
1.00
2.12
1.02
1.01
8.2
8.0
7.8
7.6
7.4
7.2
PPM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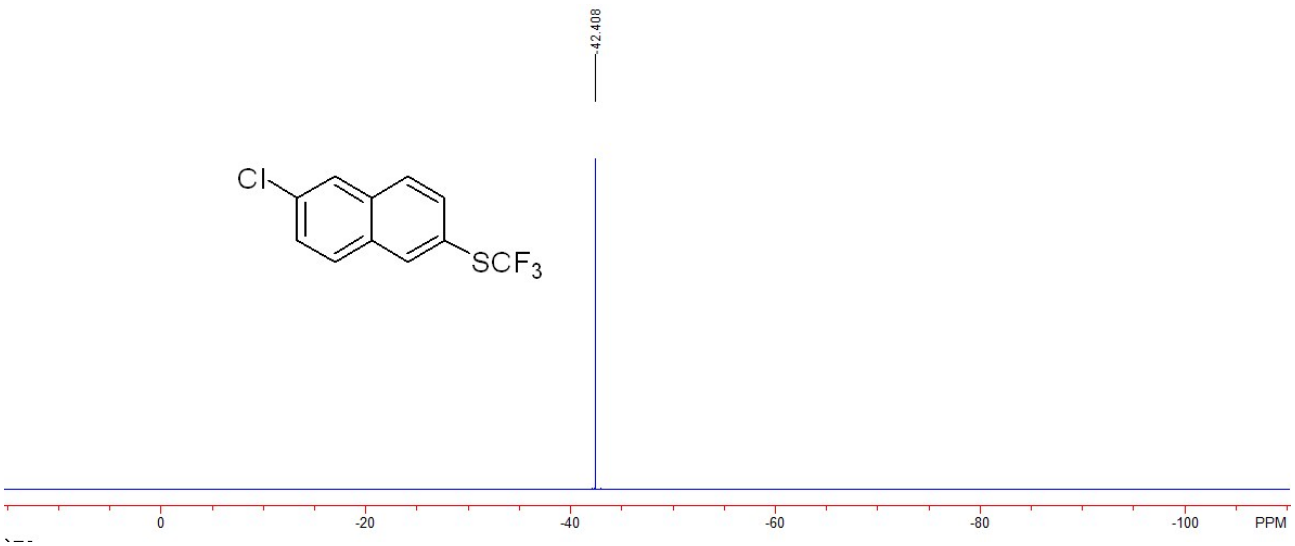
134.170
133.880
132.890
131.551
131.097
129.697
128.321
128.038
126.564
124.964
121.965
77.320
77.000
76.680
Cl
SCF3
160
140
120
100
80
60
PPM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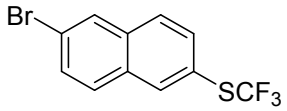
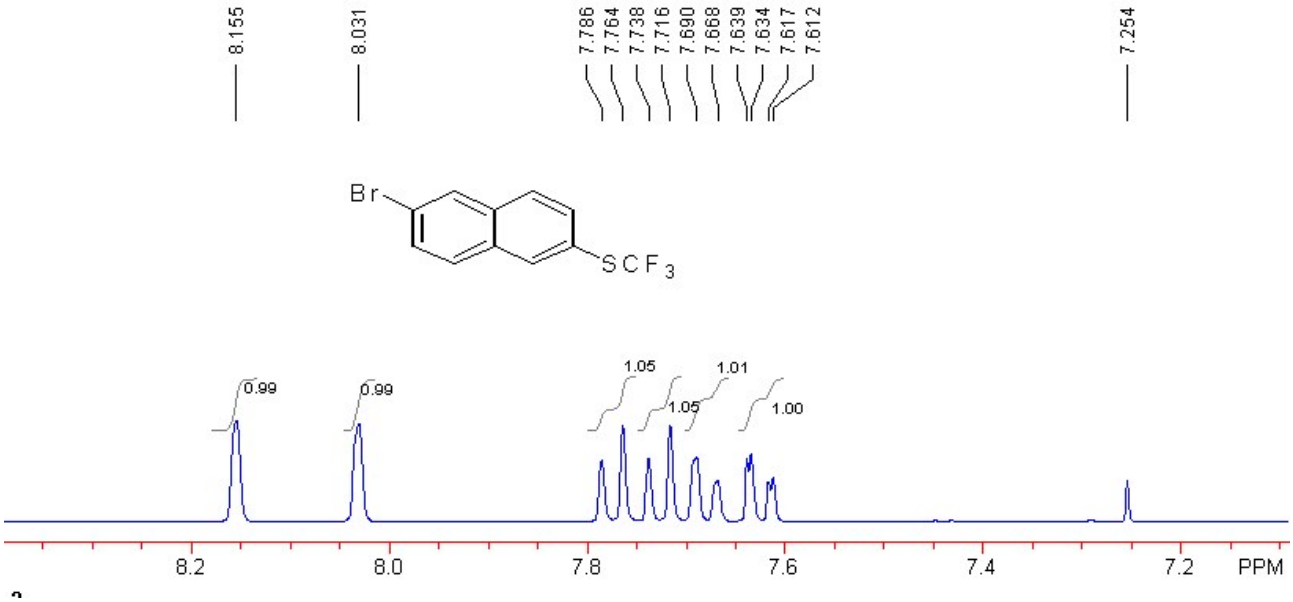
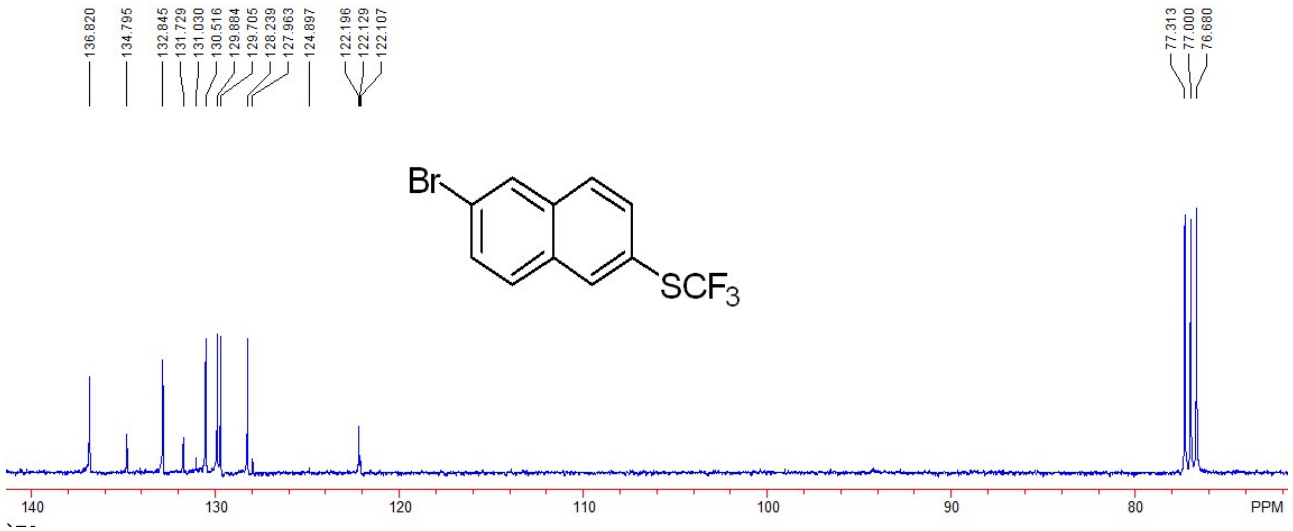
PPM

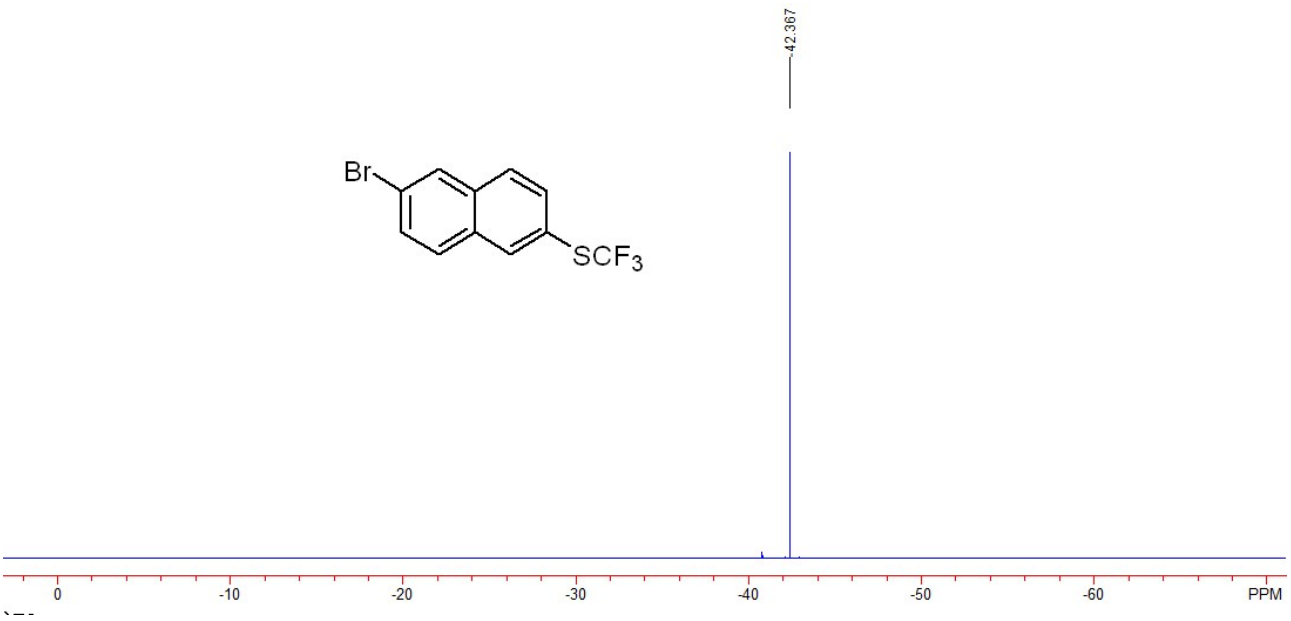


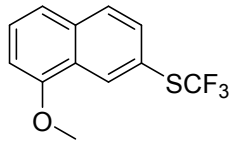
(6-bromonaphthalen-2-yl)(trifluoromethyl)sulfane (3f).

A white solid, 30.6 mg, 50% yield. M.p.: 74-76 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.62 (dd, *J* = 2.0, 8.8 Hz, 1H, ArH), 7.68 (d, *J* = 8.8 Hz, 1H, ArH), 7.73 (d, *J* = 8.8 Hz, 1H, ArH), 7.78 (d, *J* = 8.8 Hz, 1H, ArH), 8.03 (s, 1H, ArH), 8.16 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 122.1, 122.2, 128.2, 129.5 (q, *J* = 306.7 Hz), 129.7, 129.9, 130.5, 131.7, 132.8, 134.8, 136.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.37. IR (CH_2Cl_2) ν 2954, 2923, 2848, 1484, 1155, 1133, 1106, 903, 872, 862, 810, 800 cm^{-1}. MS (%) m/e 308 (59.01), 306 (59.12), 239 (28.09), 237 (27.81), 159 (12.99), 158 (M^+, 100.00), 114 (25.83), 113 (13.27). HRMS (EI) calcd. for $C_{11}H_6F_3SBr$: 305.9326, Found: 305.9320.



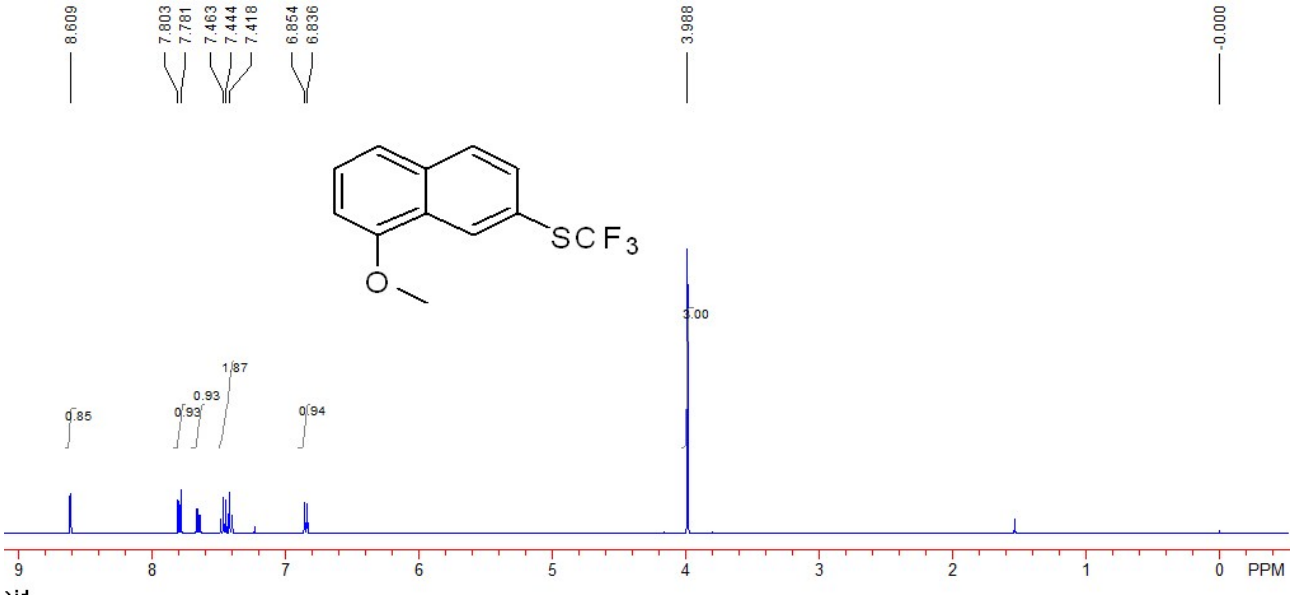






(8-methoxynaphthalen-2-yl)(trifluoromethyl)sulfane (3h).

A light yellow oil, 41.3 mg, 80% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.99 (s, 3H, CH_3), 6.84 (d, J = 7.2 Hz, 1H, ArH), 7.40-7.48 (m, 2H, ArH), 7.65 (d, J = 9.2 Hz, 1H, ArH), 7.79 (d, J = 8.8 Hz, 1H, ArH), 8.61 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 55.6, 104.8, 119.8, 120.6, 125.6, 128.2, 128.7, 129.8 (q, J = 306.7 Hz), 131.6, 132.4, 134.9, 155.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.64. IR (CH_2Cl_2) ν 3054, 3008, 2964, 2936, 2843, 1626, 1569, 1456, 1365, 1271, 1154, 1098, 1075, 999, 823, 741 cm^{-1}. MS (%) m/e 259 (14.43), 258 (M^+, 100.00), 243 (19.04), 189 (39.33), 146 (23.71), 145 (21.88), 115 (23.35), 102 (22.27). HRMS (EI) calcd. for $C_{12}H_9OF_3S$: 258.0326, Found: 258.0321.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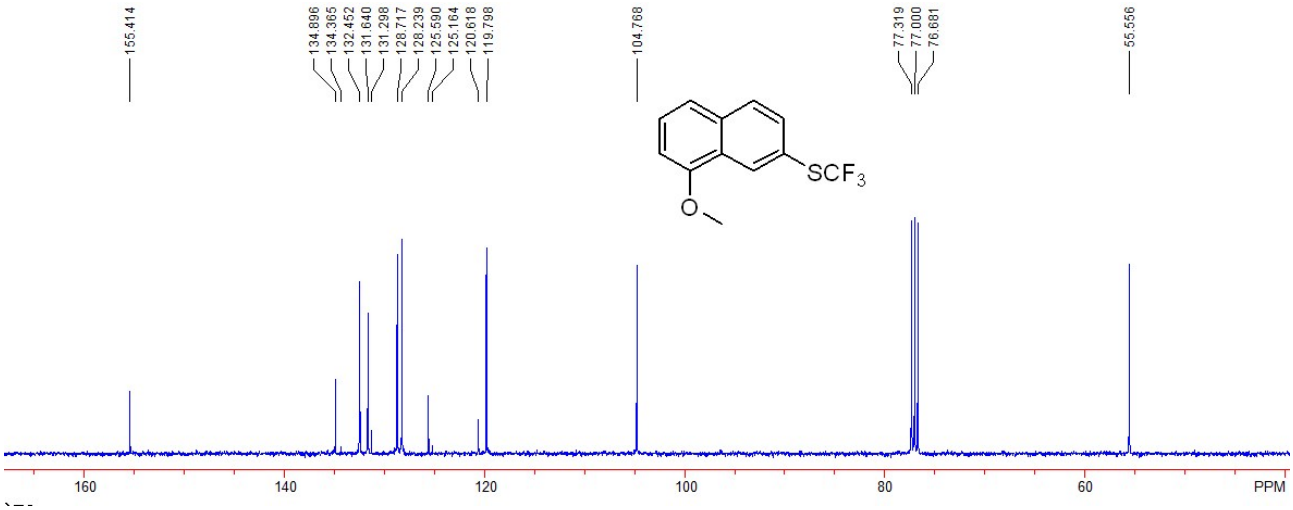
7.418
6.854
6.836
3.988
-0.000
SCF3
O
3.00
1.87
0.93
0.93
0.85
0.94
9
8
7
6
5
4
3
2
1
0
PPM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128.239
125.590
125.164
120.618
119.798
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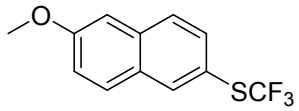
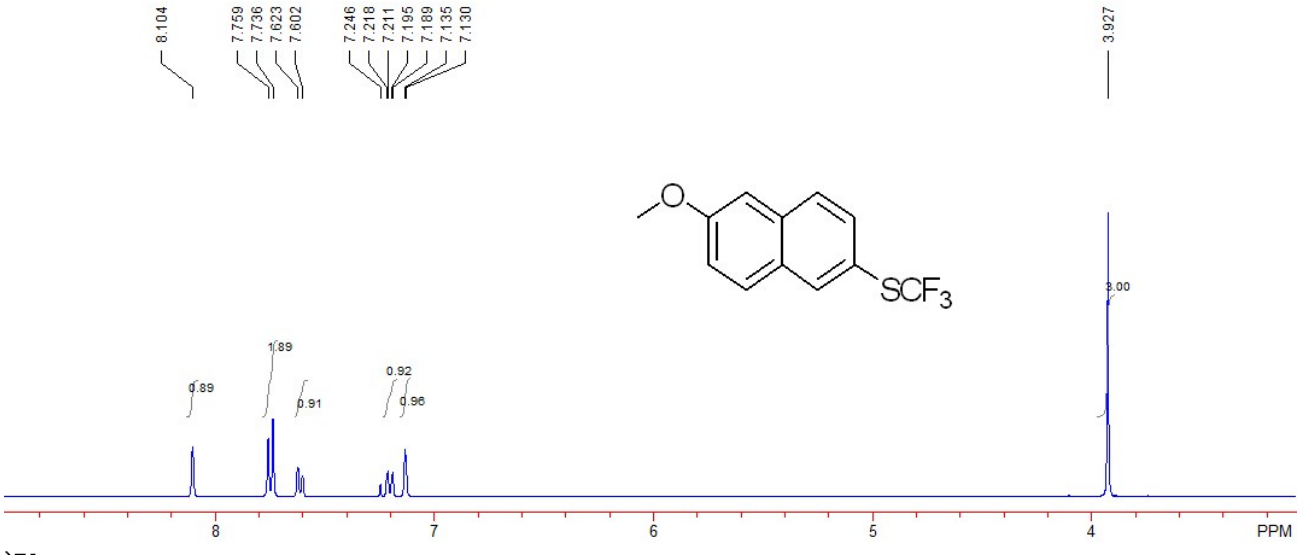
77.319
77.000
76.681
55.556
SCF3
O
160
140
120
100
80
60
PPM

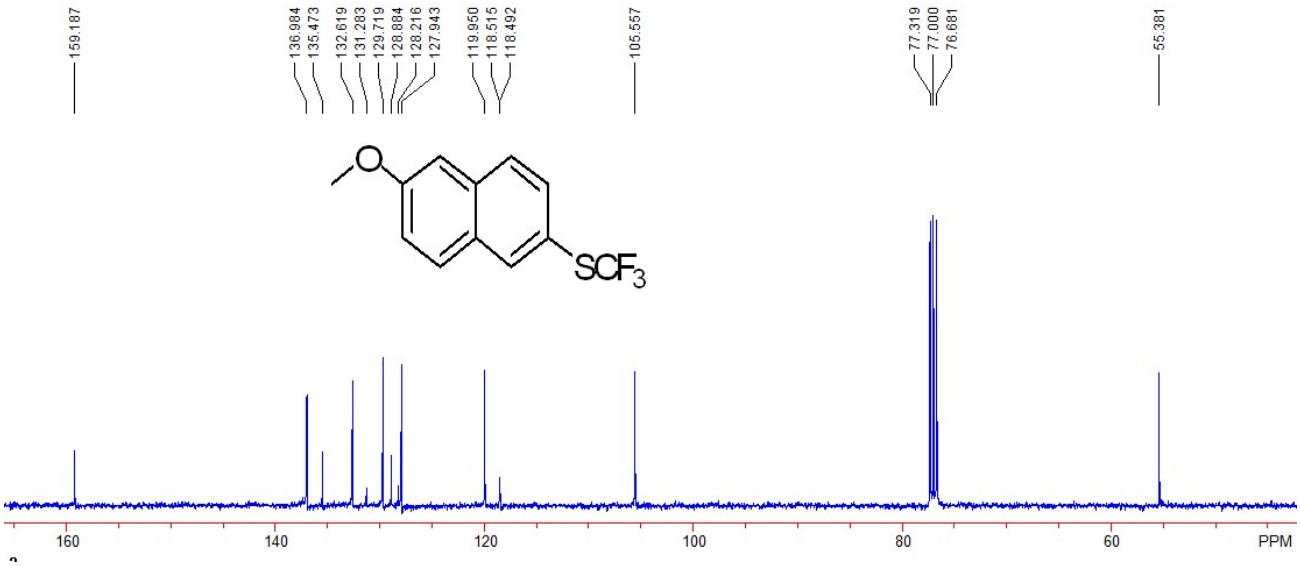

-42.635
SCF3
O
60
40
20
0
-20
-40
-60
-80
-100
PPM

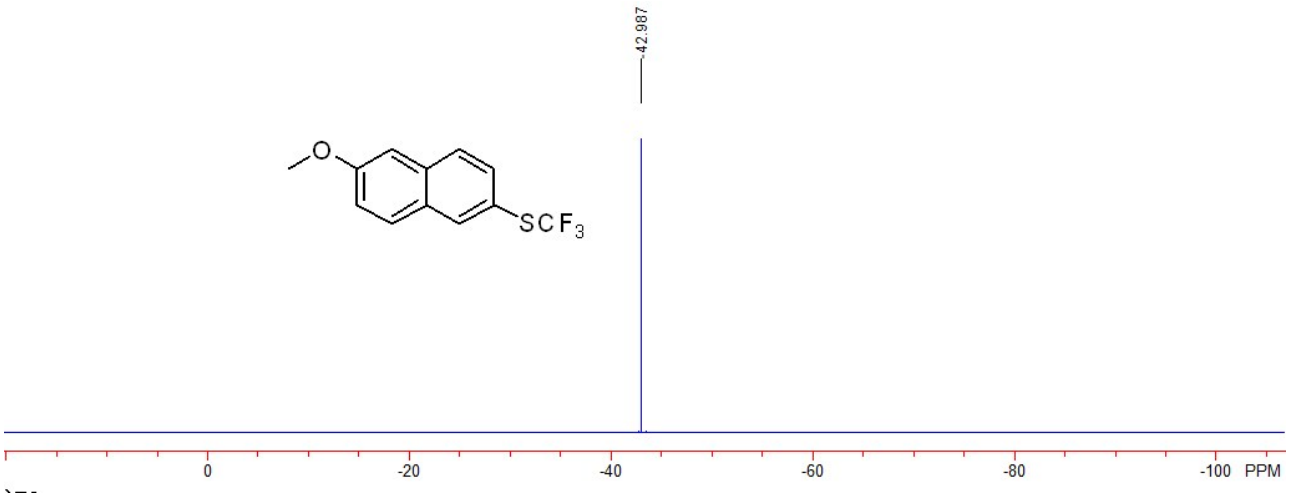


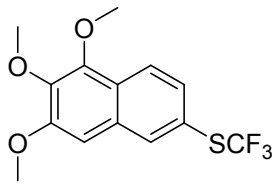
(6-methoxynaphthalen-2-yl)(trifluoromethyl)sulfane (3i).

A light yellow oil, 31 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.93 (s, 3H, CH_3), 7.13 (d, *J* = 2.0 Hz, 1H, ArH), 7.20 (dd, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.61 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 (d, *J* = 9.2 Hz, 2H, ArH), 8.10 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 55.4, 105.6, 118.5, 120.0, 127.9, 128.9, 129.72, 129.75 (q, *J* = 306.7 Hz), 132.6, 135.5, 137.0, 159.2. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.99. IR (CH_2Cl_2) ν 3057, 3011, 2967, 2930, 2840, 1626, 1587, 1494, 1389, 1264, 1213, 1152, 1101, 1075, 1030, 851, 659 cm^{-1}. MS (%) m/e 259 (13.70), 258 (96.41), 190 (13.23), 189 (M^+, 100.00), 158 (8.04), 146 (23.35), 145 (54.51), 102 (27.81). HRMS (EI) calcd. for $C_{12}H_9OF_3S$: 258.0326, Found: 258.0325.



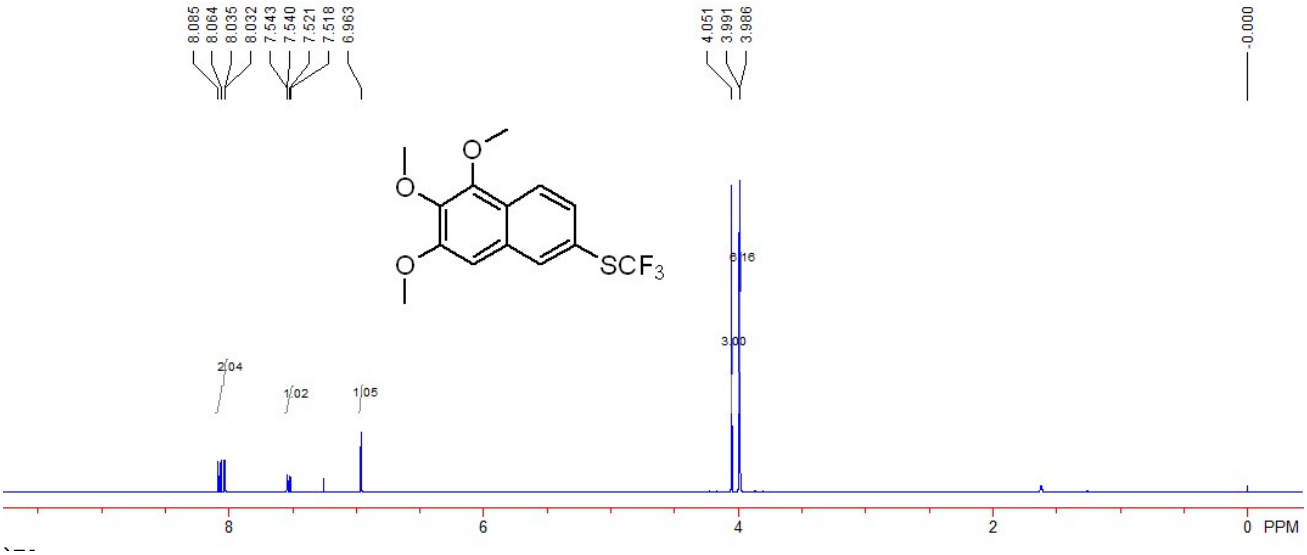


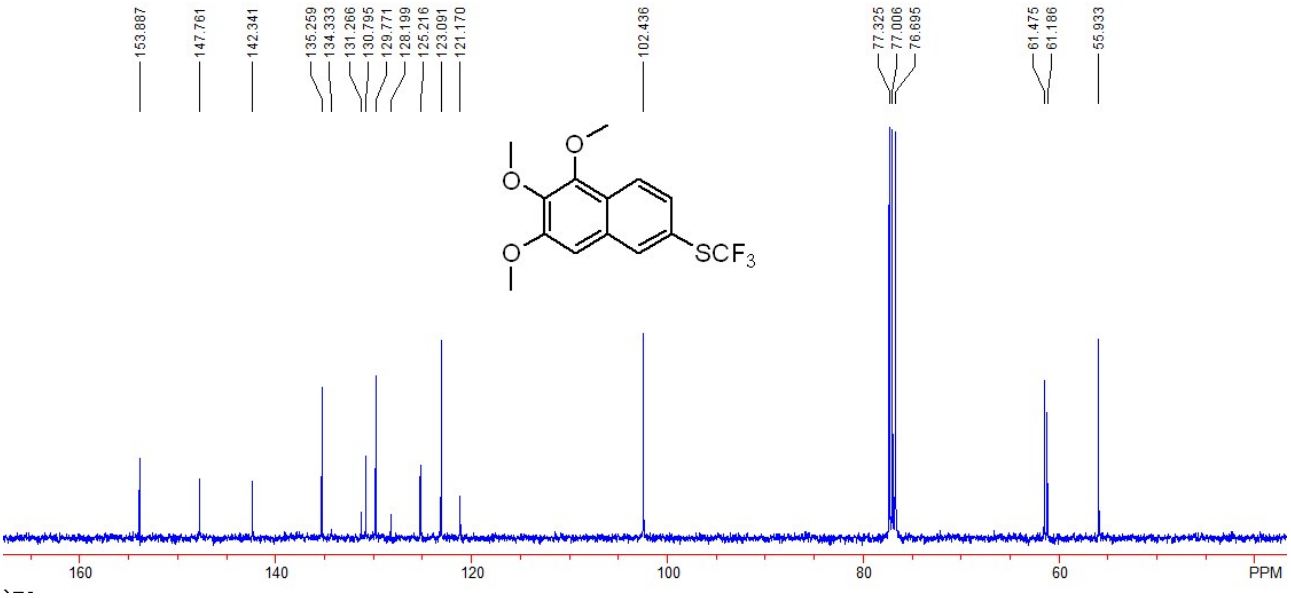


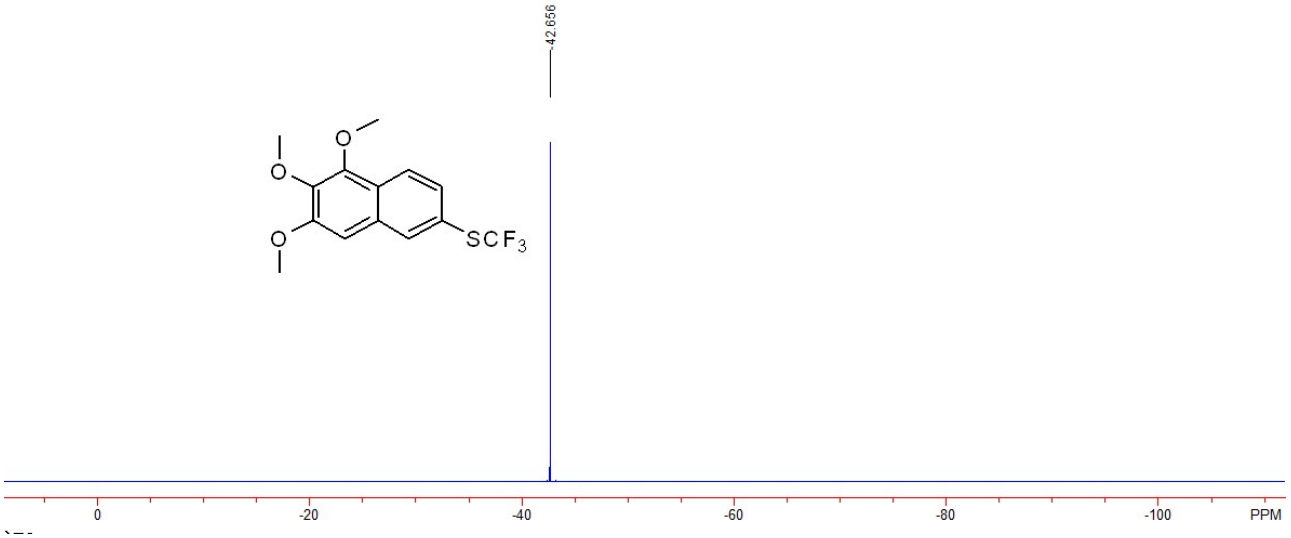


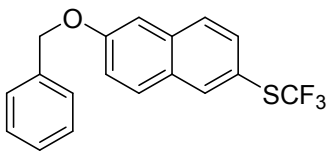
(trifluoromethyl)(5,6,7-trimethoxynaphthalen-2-yl)sulfane (3j).

A white solid, 41.3 mg, 65% yield. M.p.: 83-85 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.986 (s, 3H, CH_3), 3.991 (s, 3H, CH_3), 4.05 (s, 3H, CH_3), 6.96 (s, 1H, ArH), 7.53 (dd, *J* = 1.2, 8.8 Hz, 1H, ArH), 8.03 (d, *J* = 1.2 Hz, 1H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 55.9, 61.2, 61.5, 102.4, 121.2, 123.1, 125.2, 129.7 (q, *J* = 306.7 Hz), 129.8, 130.8, 135.2, 142.3, 147.8, 153.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.66. IR (CH_2Cl_2) ν 2987, 2936, 2856, 2830, 1616, 1585, 1572, 1474, 1401, 1391, 1319, 1252, 1110, 1099, 1079, 1034, 996, 818 cm^{-1}. MS (%) m/e 319 (17.16), 318 (M^+, 100.00), 303 (37.81), 275 (17.38), 260 (17.45), 189 (21.95), 174 (29.86), 120 (13.62). HRMS (EI) calcd. for $C_{14}H_{13}O_3F_3S$: 318.0538, Found: 318.0539.





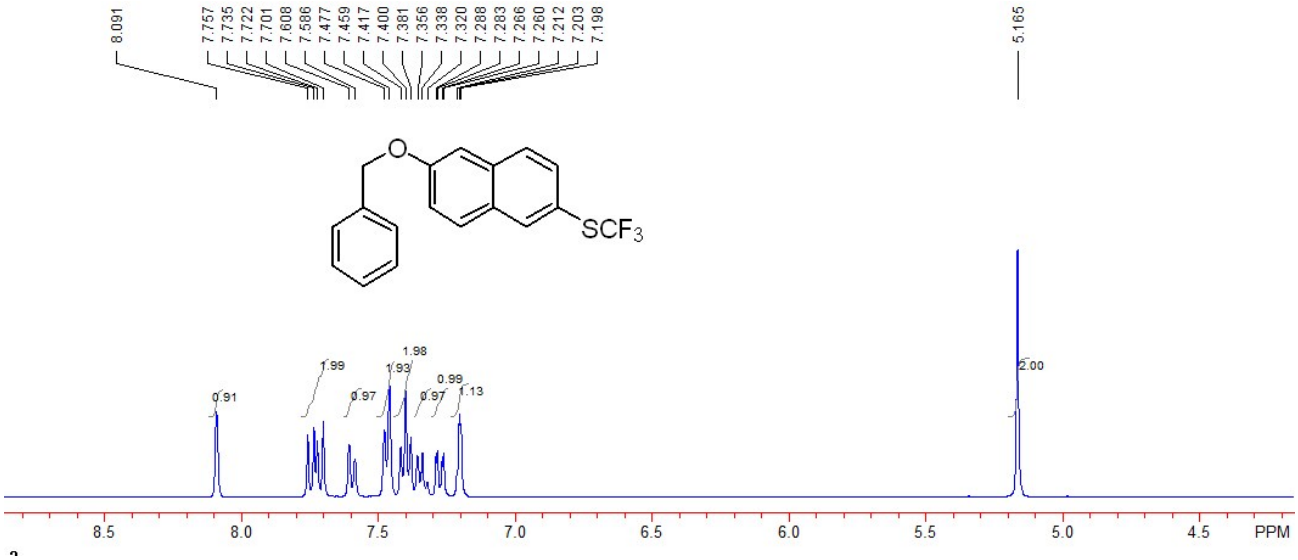


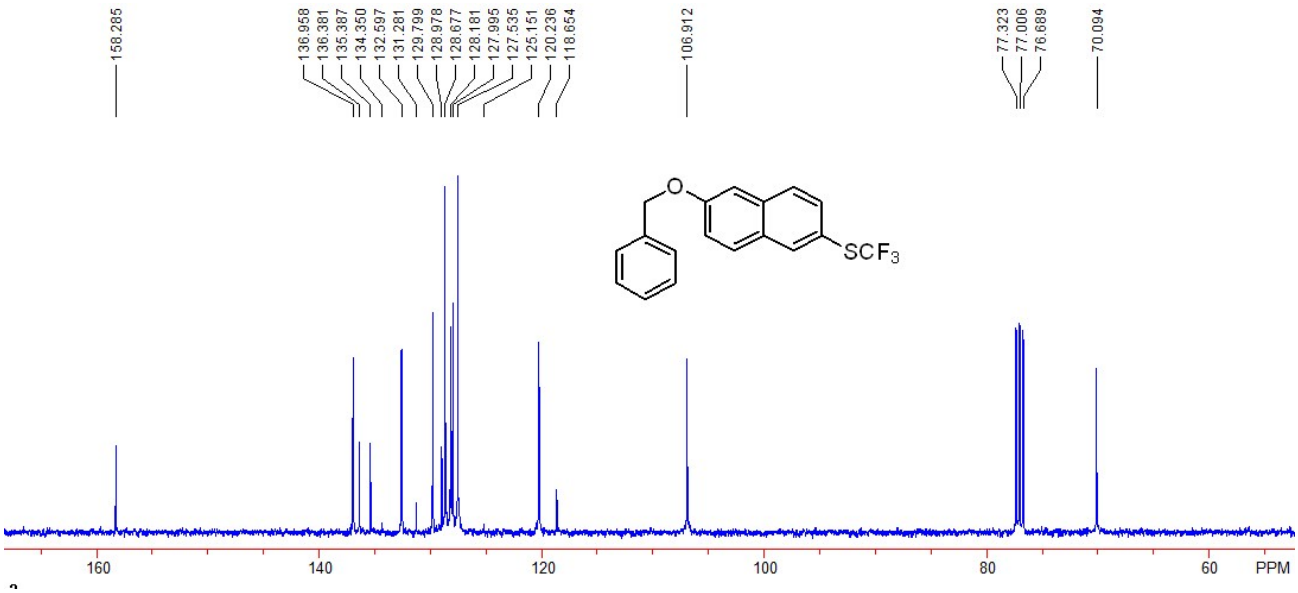


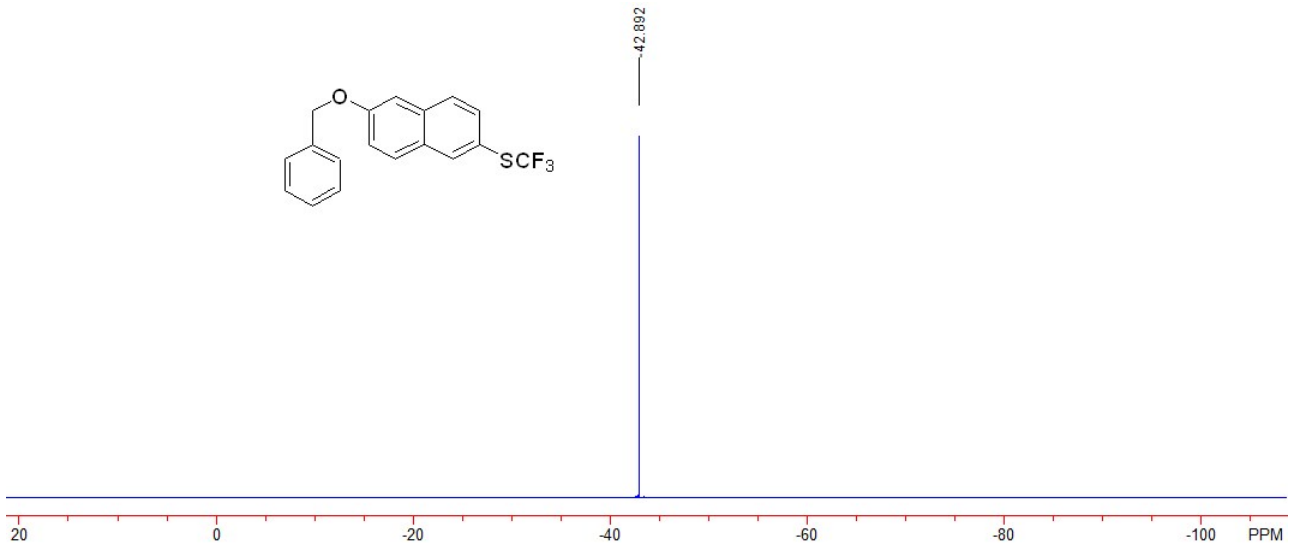
(6-(benzyloxy)naphthalen-2-yl)(trifluoromethyl)sulfane (3k).

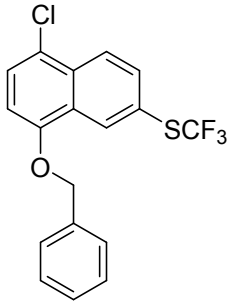
A white solid, 40 mg, 51.5 mg, 60% yield. M.p.: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.16 (s, 2H, CH_2), 7.20-7.21 (m, 1H, ArH), 7.27 (dd, *J* = 2.4, 9.2 Hz, 1H, ArH), 7.34 (t, *J* = 7.2 Hz, 1H, ArH), 7.40 (t, *J* = 6.8 Hz, 2H, ArH), 7.47 (d, *J* = 7.2 Hz, 2H, ArH), 7.60 (d, *J* = 8.8 Hz, 1H, ArH), 7.70-7.76 (m, 2H, ArH), 8.09 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 70.1, 106.9, 118.6, 120.2, 127.5, 128.0, 128.2, 128.7, 129.0, 129.7 (q, *J* = 309.6 Hz), 129.8, 132.6, 135.4, 136.4, 137.0, 158.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.89. IR (CH_2Cl_2) ν 3062, 3034, 2923, 2853, 2347, 1621, 1497, 1461, 1387, 1261, 1220, 1208, 1142, 1129, 1104, 1010, 850, 738, 696, 660 cm^{-1}.

MS (%) m/e 335 (2.87), 334 (14.38), 146 (5.08), 145 (2.21), 102 (5.52), 92 (8.32), 91 (M^+, 100.00), 65 (7.24). HRMS (EI) calcd. for $C_{18}H_{13}OF_3S$: 334.0639, Found: 334.0634.



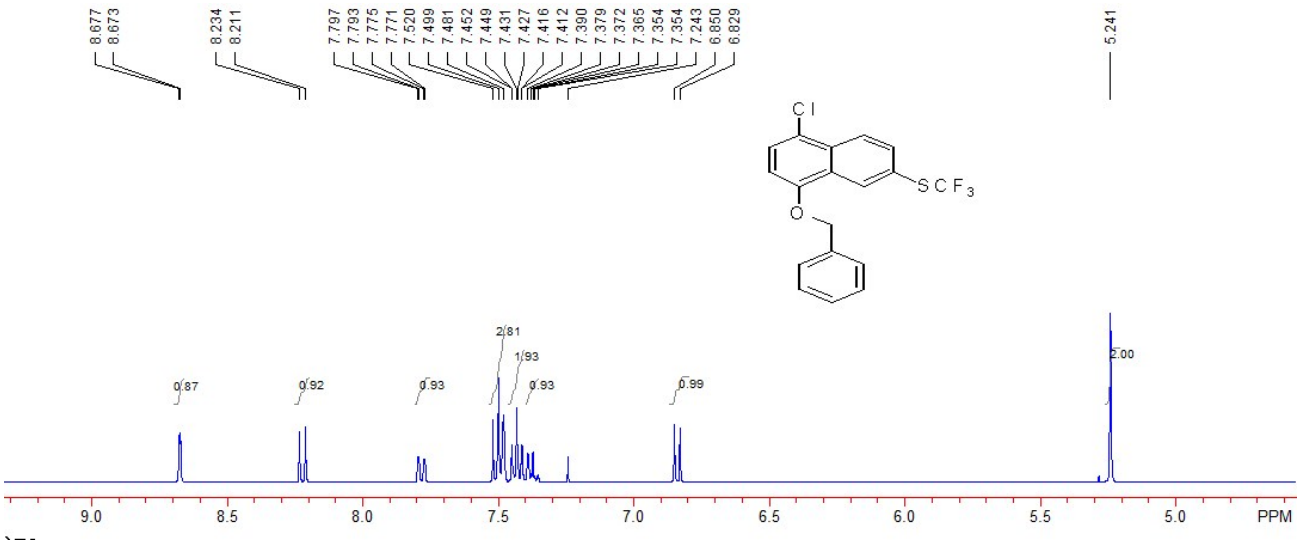


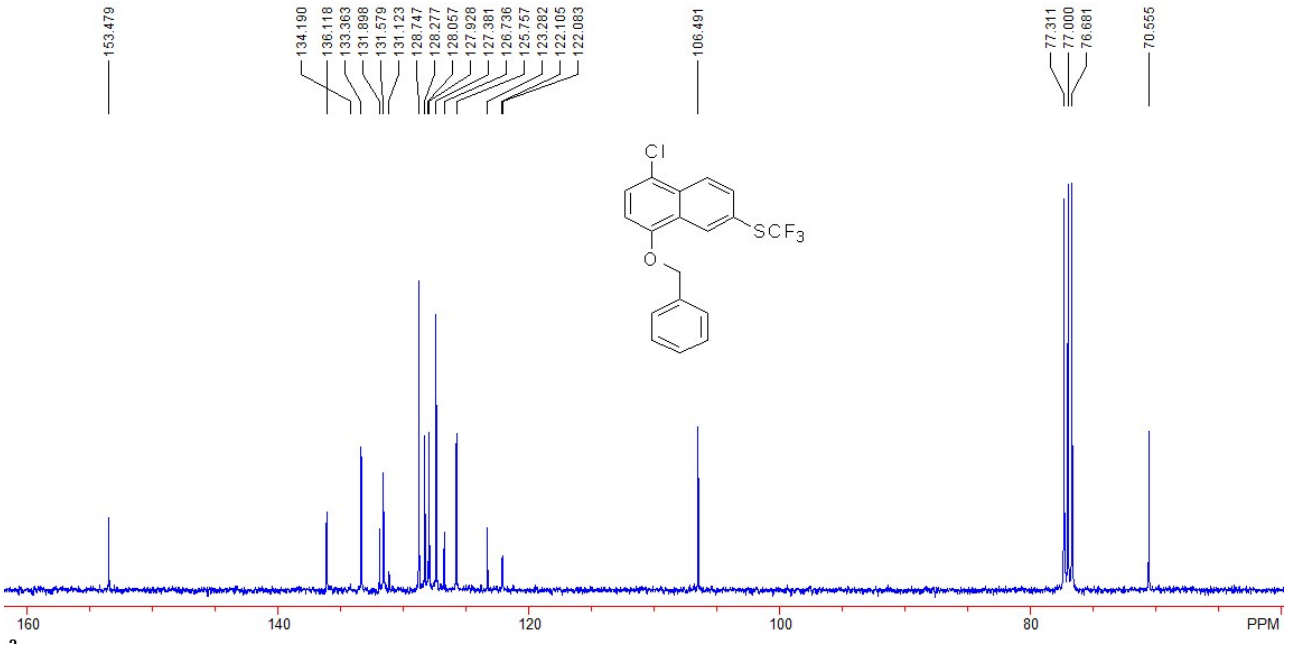


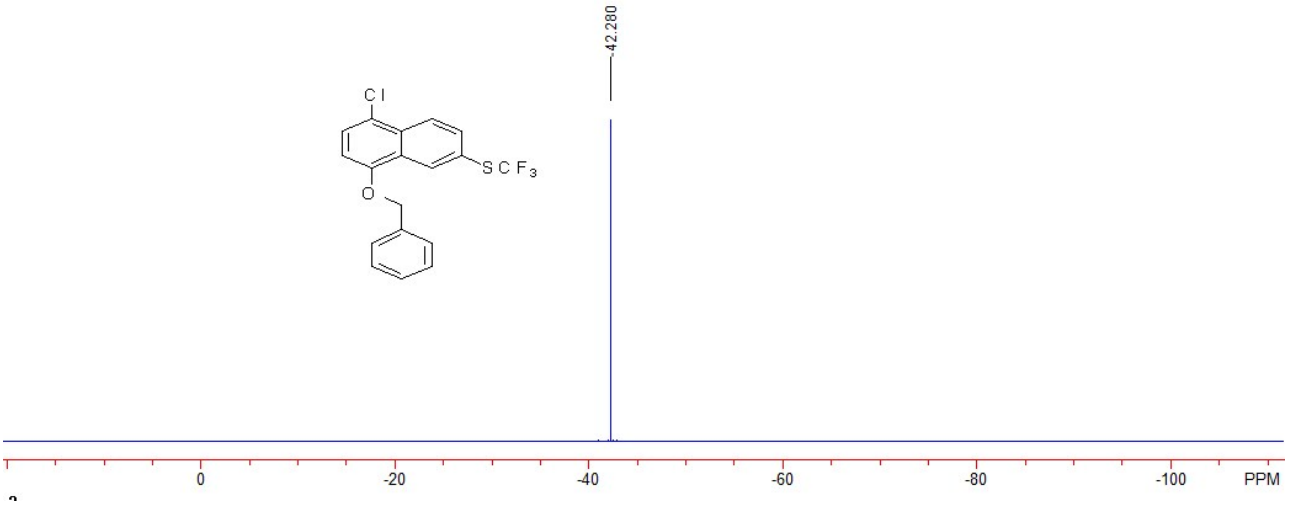


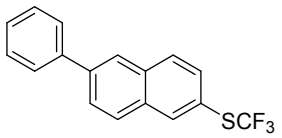
(8-(benzyloxy)-5-chloronaphthalen-2-yl)(trifluoromethyl)sulfane (3l).

A white solid, 51.5 mg, 70% yield. M.p.: 59-61 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.24 (s, 2H, CH_2), 6.84 (d, J = 8.4 Hz, 1H, ArH), 7.35-7.39 (m, 1H, ArH), 7.41-7.45 (m, 2H, ArH), 7.50 (t, J = 7.2 Hz, 3H), 7.78 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 8.22 (d, J = 9.2 Hz, 1H, ArH), 8.68 (d, J = 2.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 70.6, 106.5, 122.1, 123.3, 125.8, 126.7, 127.4, 127.9, 128.3, 128.7, 129.6 (q, J = 306.6 Hz), 131.6, 131.9, 133.4, 136.1, 153.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.28. IR (CH_2Cl_2) ν 3088, 3062, 3034, 2928, 2868, 1624, 1590, 1443, 1346, 1262, 1154, 1110, 1089, 820, 802 cm^{-1}. MS (%) m/e 368 (4.06), 258 (5.77), 189 (6.41), 146 (2.47), 145 (6.20), 92 (7.54), 91 (M^+, 100.00), 65 (5.77). HRMS (EI) calcd. for $C_{18}H_{12}OF_3SCl$: 368.0249, Found: 368.0251.





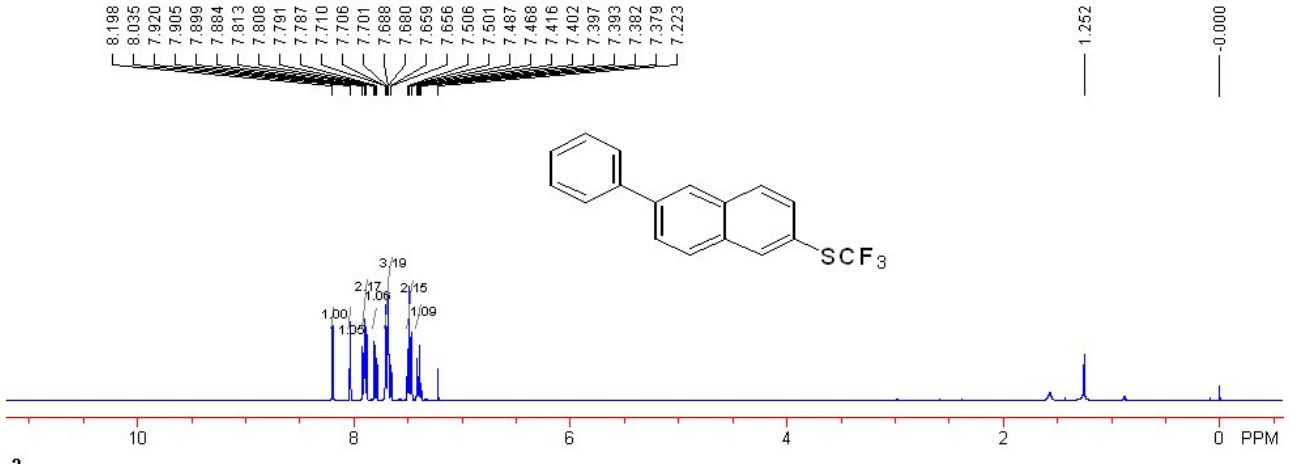


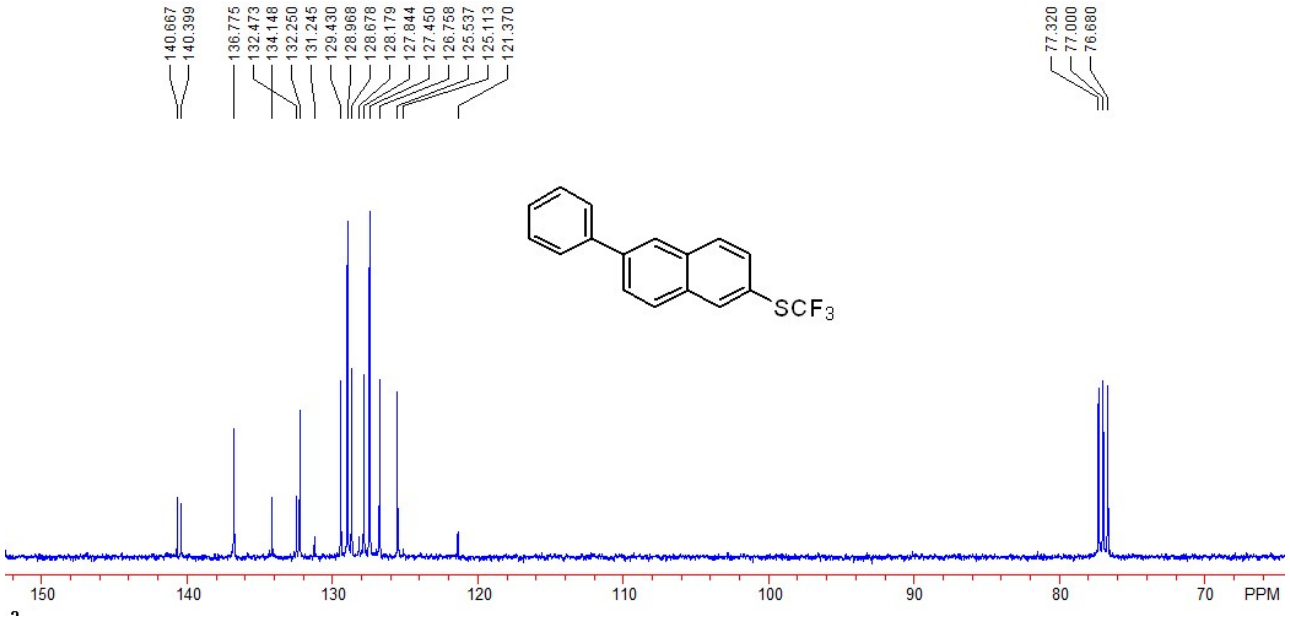


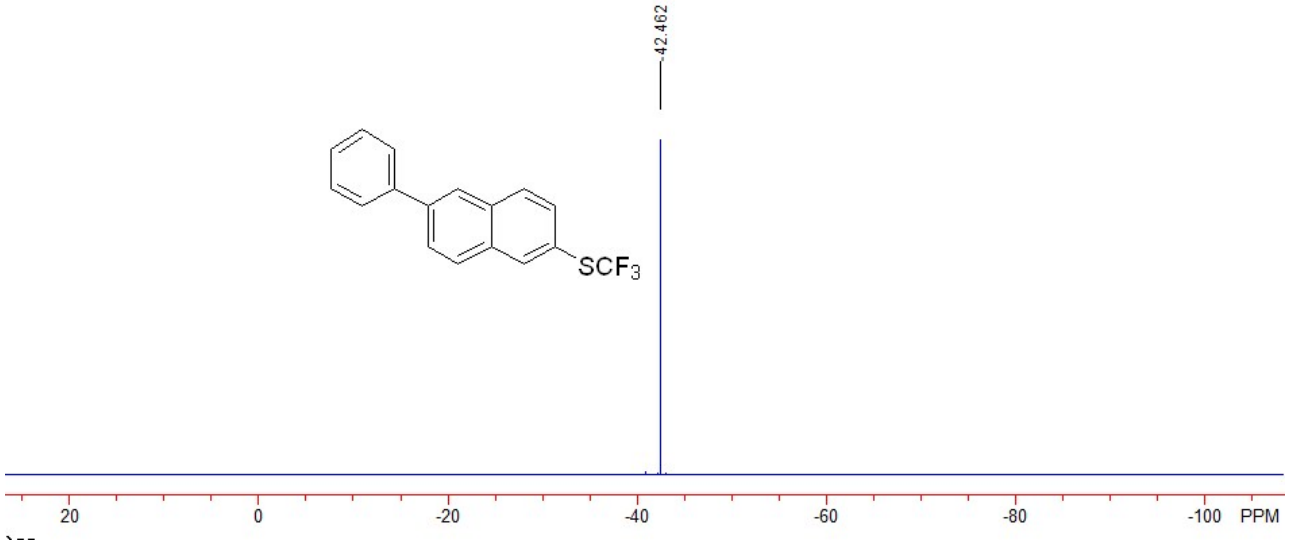
(6-phenylnaphthalen-2-yl)(trifluoromethyl)sulfane (3o).

A white solid, 28.6 mg, 47% yield. M.p.: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.40 (t, *J* = 8.0 Hz, 1H, ArH), 7.49 (t, *J* = 7.6 Hz, 2H, ArH), 7.66-7.71 (m, 3H, ArH), 7.80 (dd, *J* = 1.6, 8.4 Hz, 1H, ArH), 7.88-7.92 (m, 2H, ArH), 8.04 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 121.4, 125.5, 126.8, 127.4, 127.8, 128.7, 129.0, 129.4, 129.7 (q, *J* = 306.6 Hz), 132.2, 132.5, 134.1, 136.8, 140.4, 140.7. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -42.46. IR (CH_2Cl_2) ν 3065, 2929, 2854, 2360, 1175, 1106, 1074, 892, 811, 767, 756 cm^{-1}. MS (%) m/e 305 (20.07), 304

(M$^+$, 100.00), 235 (57.94), 234 (18.83), 202 (52.74), 191 (25.15), 189 (23.15), 91 (13.59). HRMS (EI) calcd. for $C_{17}H_{11}SF_3$: 304.0534, Found: 304.0532.

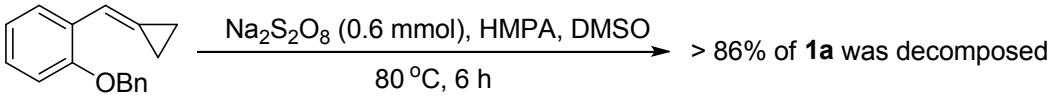






Mechanistic Study of the Reaction

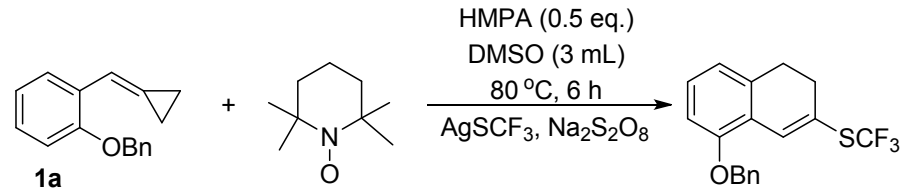
1) Difficulty on the Improvement of the Yield.



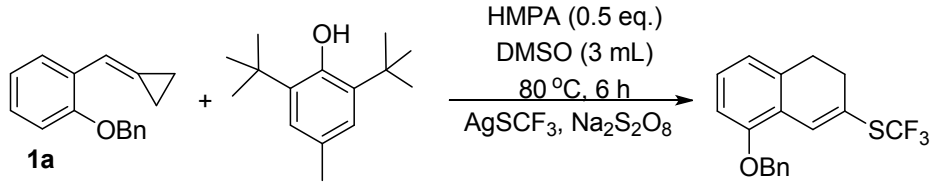
1a, 0.6 mmol

When $AgSCF_3$ was not added, at least 86% of the starting material **1a** was decomposed, which may be the major hamper for the improvement of the yield.

2) Radical Inhibition Experiments



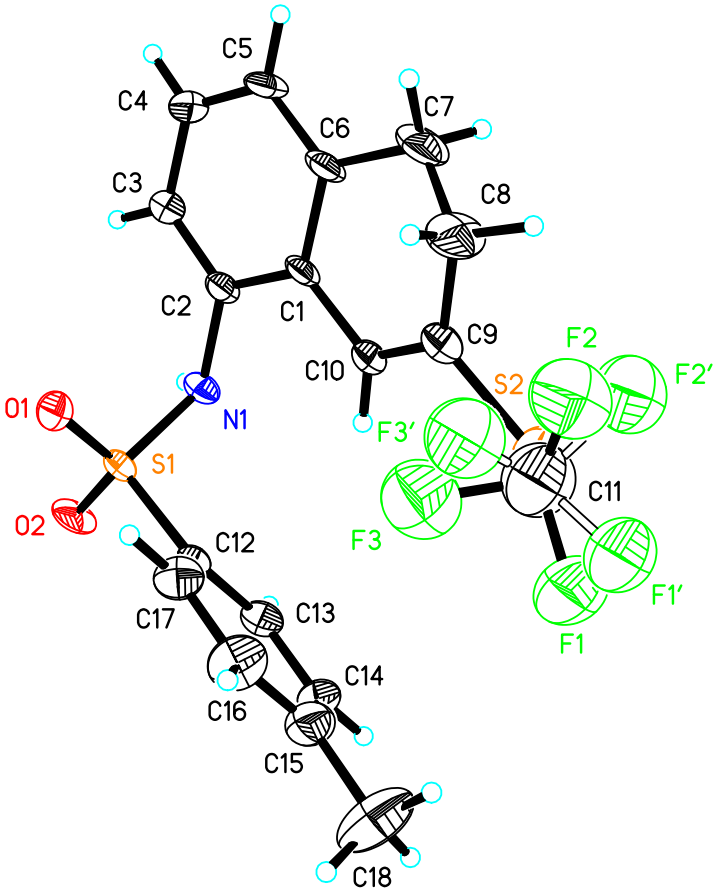
0.2 mmol	3.0 eq.	1.5 eq.	3.0 eq.	<5%
0.2 mmol	4.0 eq.	1.5 eq.	3.0 eq.	0%
0.2 mmol	8.0 eq.	1.5 eq.	3.0 eq.	0%



0.2 mmol	3.0 eq.	1.5 eq.	3.0 eq.	25%
0.2 mmol	4.0 eq.	1.5 eq.	3.0 eq.	16%
0.2 mmol	8.0 eq.	1.5 eq.	3.0 eq.	10%

Compound **1a** (0.2 mmol), $AgSCF_3$ (0.3 mmol, 1.5 eq.), $Na_2S_2O_8$ (0.6 mmol, 3.0 eq.) and TEMPO or BHT were mixed in 3 mL DMSO in a Schlenk tube which was filled with Ar. The reaction tube was placed in an oil bath and the reaction mixture was stirred at 80 °C for 6 h. When finished, the yield was determined by ^{19}F NMR with *p*-Bromobenzotrifluoride as an internal standard.

The Crystal Data of 2n



The crystal data of **2n** have been deposited in CCDC with number 1493132. Empirical formula: $C_{18}H_{16}F_3NO_2S_2$, Formula weight: 399.44, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 6.520(6) Å, α = 102.278(14)°; b = 8.149(7) Å, β = 95.210(15)°; c = 18.175(15) Å, γ = 97.731(16)°. Volume: 927.9(13) $Å^3$, Z = 2, Density (calculated): 1.430 Mg/m^3, F(000) = 412, Crystal size: 0.200 x 0.140 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0942, wR2 = 0.2386.

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