Supporting Information *for*

Synthesis of 1,2,2-trifluorovinyl sulphides and selenides from trifluorovinylation of organic thiocyanates and selenocyanates

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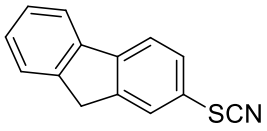
General Information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF at the Shanghai Institute of Organic Chemistry. Reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

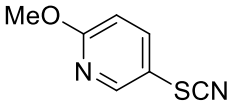
Synthesis of organic thiocyanates and selenocyanates.

Aryl thiocyanates[1] and alkyl thiocyanates,[2] and aryl selenocyanates[3] were prepared according to the published procedures.



2-Thiocyanato-9*H*-fluorene (**2g**)

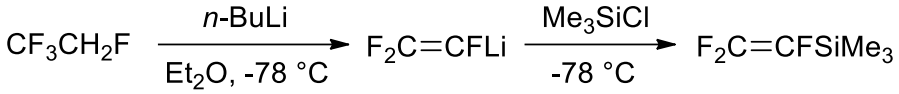
Obtained as a white solid in 88% yield (981 mg). M.p. 85.7-87.2 ℃. R_f (dichloromethane/*n*-pentane 1:5) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.71 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.37 (m, 2H), 3.89 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (s), 143.6 (s), 143.3 (s), 140.0 (s), 129.4 (s), 127.9 (s), 127.4 (s), 127.2 (s), 125.2 (s), 121.3 (s), 121.2 (s), 120.5 (s), 111.2 (s), 36.8 (s). IR (KBr): ν 3065, 2896, 2156, 1478, 1467, 1450, 1414, 1399, 1206, 1278, 1197, 1183, 1004, 953, 905, 870, 823, 765, 725, 648, 580 cm^{-1}. GC-MS m/z 223 (M^+). HRMS (ESI) m/z: calcd. for $C_{14}H_9NS$: 223.0456; found: 223.0450.



2-Methoxy-5-thiocyanatopyridine (**2r**)

Obtained as a yellow oil in 30% yield (249 mg). R_f (dichloromethane/*n*-pentane 1:10) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.6 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (s), 150.8 (s), 142.3 (s), 113.0 (s), 112.3 (s), 110.6 (s), 54.1 (s). IR (KBr): ν 2990, 2944, 2872, 2845, 2158, 1587, 1557, 1475, 1458, 1430, 1368, 1306, 1285, 1254, 1128, 1015, 910, 829, 729, 544, 517 cm^{-1}. GC-MS m/z 166 (M^+). HRMS (ESI) m/z: calcd. for $C_7H_6N_2OS$: 166.0201; found: 166.0202.

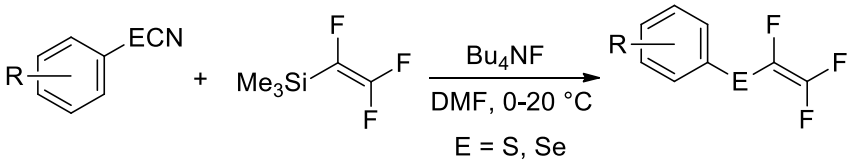
Synthesis of trifluorovinyl trimethylsilane



Under nitrogen atmosphere, a two-neck 100-mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was charged with extra dry diethyl ether (20 mL). The flask was sealed with a rubber septum and CF_3CH_2F was bubbled through the solution via a syringe needle at -50 °C for 5 min. The solution was then cooled down to -78 °C and kept for 5 min. A solution of *n*-BuLi (10 mL, 2.5 mmol/mL in *n*-hexane) was added dropwise (*ca* 10 min). The mixture solution was stirred intensely for 2 h at -78 °C. Trimethyl chlorosilane (4.7 mL, 37.5 mmol) was then added and the reaction mixture was further stirred at -78 °C for 1 h. After warming up to room temperature, the reaction mixture was stirred for additional 24 h.

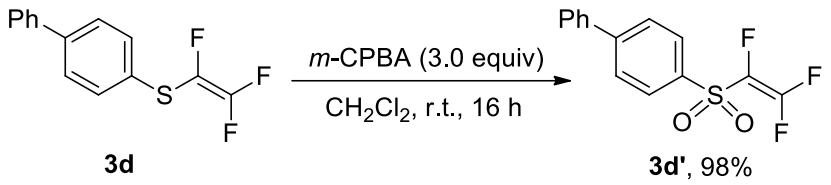
An additional of saturated aqueous NH_4Cl solution was added, and the reaction mixture was stirred for an additional 0.5 h. The resulting mixture was washed with saturated brine (3 × 20 mL) and water (20 mL), dried over $MgSO_4$, and filtered. The crude mixture was further treated with extra dry molecular sieves, and purified by low-temperature vacuum distillation. ^{19}F NMR analysis of the sample indicated that the concentration of $TMSCF=CF_2$ was 0.6 mmol/mL using C_6H_5F (0.5 μL) as internal standard. ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.7 (dd, J = 69.8, 25.3 Hz, 1F), -116.8 (dd, J = 116.3, 69.8 Hz, 1F), -198.9 (dd, J = 116.3, 25.3 Hz, 1F).

Synthesis of 1,2,2-trifluorovinyl sulphides and selenides



Organic thiocyanates or selenocyanates (0.50 mmol), *n*-Bu_4NF (60 μL, 12 mol%, 1 mmol/mL in THF), and DMF (5.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 0 °C for 10 min. A solution of $TMSCF{=}CF_2$ (1 mmol, 2 equiv) in diethyl ether was added dropwise and the resulting solution was stirred at 0 °C for 10 min. After warming up to 20 °C, the reaction mixture was stirred for additional 16 h. The reaction mixture was diluted with diethyl ether (10 mL), washed with saturated brine (30 mL), and water (20 mL), dried over $MgSO_4$, and filtered. The residue obtained was purified by column chromatography over silica gel (*n*-pentane/diethyl ether).

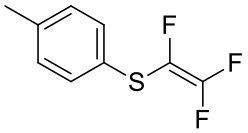
Synthesis of trifluorovinyl sulphoxide 3d′



3d **3d'**, 98%

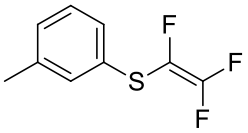
[1,1'-biphenyl]-4-yl(1,2,2-trifluorovinyl)sulfane (**3d**) (80 mg, 0.30 mmol), *m*-chloroperbenzoic acid (155 mg, 0.90 mmol, 3.0 equiv) and CH_2Cl_2 (5.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and concentrated in vacuo. The residue obtained was purified by column chromatography over silica gel (*n*-pentane/CH_2Cl_2 = 5 : 1).

Data for Compounds 3, 5, and 3d′.



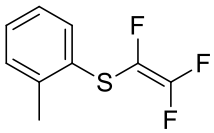
***p*-Tolyl(1,2,2-trifluorovinyl)sulfane (3a)**

Obtained as a colorless oil in 84% yield (86 mg). R_f (*n*-pentane) = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.6 (dd, *J* = 45.6, 34.5 Hz, 1F), -106.7 (dd, *J* = 124.1, 45.6 Hz, 1F), -148.9 (dd, *J* = 124.1, 34.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (ddd, *J* = 302.0, 279.8, 53.9 Hz), 138.7 (s), 130.5 (d, *J* = 1.6 Hz), 130.3 (s), 127.8 (dd, *J* = 6.9, 5.1 Hz), 124.7 (ddd, *J* = 279.4, 50.2, 24.0 Hz), 21.1 (s). IR (ATR): ν 3027, 2926, 2869, 1739, 1493, 1399, 1302, 1130, 1088, 1046, 1017, 905, 804, 729, 581, 523, 509, 478 cm^{-1}. GC-MS m/z 204 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0223.



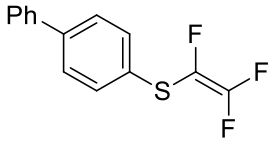
***m*-Tolyl(1,2,2-trifluorovinyl)sulfane (3b)**

Obtained as a colorless oil in 75% yield (77 mg). R_f (*n*-pentane) = 0.86. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 3H), 7.16 (d, *J* = 6.4 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.0 (dd, *J* = 44.5, 34.6 Hz, 1F), -106.2 (dd, *J* = 124.2, 44.5 Hz, 1F), -148.9 (dd, *J* = 124.1, 34.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 302.2, 280.2, 53.7 Hz), 139.6 (s), 131.2 (dt, *J* = 5.1, 3.5 Hz), 130.2 (d, *J* = 1.5 Hz), 129.4 (s), 129.1 (s), 126.7 (d, *J* = 1.6 Hz), 124.4 (ddd, *J* = 279.2, 50.1, 24.3 Hz), 21.3 (s). IR (ATR): ν 3059, 2926, 2858, 1739, 1594, 1576, 1477, 1304, 1195, 1131, 1082, 1046, 997, 905, 852, 773, 732, 687, 650, 587, 515, 471 cm^{-1}. GC-MS m/z 204 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0226.



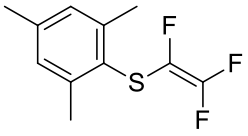
_o_-Tolyl(1,2,2-trifluorovinyl)sulfane (3c)

Obtained as a colorless oil in 80% yield (82 mg). R_f (*n*-pentane) = 0.92. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.20 (m, 3H), 2.47 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.9 (dd, *J* = 45.4, 34.6 Hz, 1F), -106.46 (dd, *J* = 123.7, 45.5 Hz, 1F), -149.45 (dd, *J* = 123.6, 34.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 302.0, 279.9, 53.3 Hz), 138.5 (d, *J* = 1.4 Hz), 130.9 (s), 130.5 (d, *J* = 1.4 Hz), 128.4 (s), 127.0 (s), 123.8 (ddd, *J* = 279.1, 50.7, 24.3 Hz), 20.3 (s). IR (ATR): ν 3066, 3016, 2925, 2854, 1739, 1591, 1472, 1457, 1382, 1305, 1193, 1133, 1060, 1039, 903, 743, 724, 650, 583 cm^{-1}. GC-MS m/z 204 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0224.



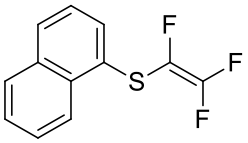
[1,1'-Biphenyl]-4-yl(1,2,2-trifluorovinyl)sulfane (3d)

Obtained as a white solid in 75% yield (100 mg). M.p. 60.2-61.8 ℃. R_f (*n*-pentane) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 4H), 7.56 – 7.45 (m, 4H), 7.41 (t, *J* = 7.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.6 (dd, *J* = 43.9, 34.8 Hz, 1F), -106.0 (dd, *J* = 124.2, 44.0 Hz, 1F), -149.1 (dd, *J* = 124.2, 34.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 302.5, 280.5, 53.5 Hz), 141.4 (s), 139.9 (s), 130.3 (dd, *J* = 3.5, 1.7 Hz), 130.2 (d, *J* = 1.6 Hz), 128.9 (s), 128.2 (s), 127.8 (s), 127.1 (s), 124.2 (ddd, *J* = 279.3, 50.1, 24.4 Hz). IR (ATR): ν 3068, 3030, 2960, 2924, 2854, 1739, 1593, 1556, 1479, 1449, 1397, 1347, 1305, 1260, 1134, 1090, 1048, 1004, 912, 827, 759, 692, 585, 522 cm^{-1}. GC-MS m/z 266 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_9F_3S$: 266.0377; found: 266.0375.



Mesityl(1,2,2-trifluorovinyl)sulfane (3e)

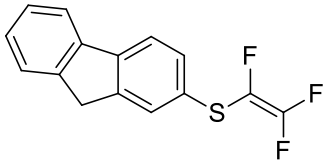
Obtained as a colorless oil in 96% yield (111 mg). R_f (*n*-pentane) = 0.82. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 2H), 2.56 (s, 6H), 2.33 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.9 (dd, *J* = 52.6, 34.9 Hz, 1F), -109.0 (dd, *J* = 121.3, 52.7 Hz, 1F), -149.9 (dd, *J* = 121.3, 34.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (ddd, *J* = 300.6, 278.2, 54.3 Hz), 143.4 (s), 140.0 (s), 129.6 (s), 125.7 (ddd, *J* = 279.8, 51.0, 22.8 Hz), 124.7 (dd, *J* = 6.4, 3.1 Hz), 21.8 (s), 21.0 (s). IR (ATR): ν 3026, 2961, 2927, 2857, 1738, 1602, 1573, 1464, 1438, 1378, 1297, 1196, 1127, 1038, 954, 905, 850, 721, 624, 580, 552, 516 cm^{-1}. GC-MS m/z 232 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_6NF_3S$: 232.0534; found: 232.0530.



Naphthalen-1-yl(1,2,2-trifluorovinyl)sulfane (3f)

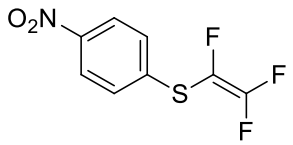
Obtained as a colorless oil in 69% yield (83 mg). R_f (*n*-pentane) = 0.84. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.1 (dd, *J* = 46.1, 35.3 Hz, 1F), -106.3 (dd, *J* = 123.2, 46.1 Hz, 1F), -149.2 (dd, *J* = 123.2, 35.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (ddd, *J* = 302.0, 279.8, 53.5 Hz), 134.3 (s), 132.9 (s), 131.3 (d, *J* = 1.5 Hz), 129.94 (s), 128.7 (s), 127.9 (dt, *J* = 4.9, 3.3 Hz), 127.3 (s), 126.7 (s), 125.7 (s), 124.8 (s), 124.4 (ddd, *J* = 279.4, 50.6, 23.9 Hz). IR (ATR): ν 3058, 1738, 1591, 1566, 1504, 1381, 1302, 1257, 1127, 1043, 967, 906, 796, 766, 733, 663, 583, 535, 475 cm^{-1}.

GC-MS m/z 240 (M^+). HRMS (EI) m/z: calcd. for $C_{12}H_7F_3S$: 240.0221; found: 240.0220.



(9*H*-Fluoren-2-yl)(1,2,2-trifluorovinyl)sulfane (3g)

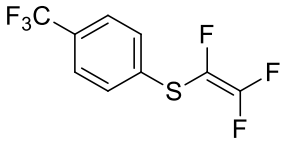
Obtained as a white solid in 76% yield (105.6 mg). M.p. 64.2-65.9 ℃. R_f (*n*-pentane) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 6.9 Hz, 1H), 3.92 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.1 (dd, *J* = 45.0, 34.5 Hz, 1F), -106.4 (dd, *J* = 124.2, 45.0 Hz, 1F), -148.8 (dd, *J* = 124.2, 34.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (ddd, *J* = 302.2, 280.0, 53.7 Hz), 144.6 (s), 143.3 (s), 142.3 (s), 140.6 (s), 129.1 (d, *J* = 1.6 Hz), 127.4 (s), 127.1 (s), 127.0 (s), 126.7 (d, *J* = 2.1 Hz), 125.2 (s), 124.7 (ddd, *J* = 279.4, 50.1, 24.0 Hz), 120.7 (s), 120.2 (s), 36.8 (s). IR (ATR): ν 2926, 1739, 1602, 1568, 1465, 1450, 1410, 1304, 1275, 1132, 1046, 955, 907, 875, 827, 767, 734, 588, 570, 524 cm^{-1}. GC-MS m/z 278 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_9F_3S$: 278.0377; found: 278.0387.



(4-Nitrophenyl)(1,2,2-trifluorovinyl)sulfane (3h)

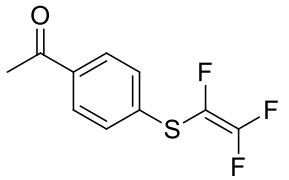
Obtained as a colorless oil in 73% yield (85 mg). R_f (dichloromethane/*n*-pentane 1:10) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.2 (t, *J* = 36.7 Hz, 1F), -103.2 (dd, *J* = 124.2, 37.1 Hz, 1F), -151.3 (dd, *J* = 124.2, 36.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (ddd, *J* = 304.6, 283.3, 51.3 Hz), 147.0 (s), 140.7 (dd, *J* = 7.4, 5.6 Hz), 127.8 (d, *J* = 1.5 Hz), 124.6 (s), 121.8 (ddd, *J* = 279.1, 50.3, 25.6 Hz). IR (ATR): ν 3102, 2923,

2851, 1739, 1600, 1581, 1518, 1480, 1340, 1313, 1183, 1137, 1109, 1088, 1048, 1012, 956, 907, 852, 847, 740, 726, 681, 589, 519, 502, 463 cm^{-1}. GC-MS m/z 235 (M^+). HRMS (EI) m/z: calcd. for $C_8H_4NO_2F_3S$: 234.9915; found: 234.9917.



(4-(Trifluoromethyl)phenyl)(1,2,2-trifluorovinyl)sulfane (3i)

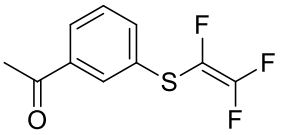
Obtained as a colorless oil in 92% yield (118 mg). R_f (*n*-pentane) = 0.89. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F), -85.7 (dd, *J* = 40.0, 35.8 Hz, 1F), -104.4 (dd, *J* = 124.1, 40.0 Hz, 1F), -150.3 (dd, *J* = 124.1, 35.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4 (ddd, *J* = 303.6, 282.1, 52.3 Hz), 136.9 (s), 130.1 (q, *J* = 33.1 Hz), 128.5 (s), 126.4 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.4 Hz), 122.8 (ddd, *J* = 279.1, 50.1, 25.1 Hz). IR (ATR): ν 2929, 1740, 1608, 1577, 1499, 1403, 1319, 1167, 1124, 1106, 1062, 1048, 1014, 951, 908, 829, 707, 594, 523, 497 cm^{-1}. GC-MS m/z 258 (M^+). HRMS (EI) m/z: calcd. for $C_9H_4F_6S$: 257.9938; found: 257.9935.



1-(4-((1,2,2-Trifluorovinyl)thio)phenyl)ethanone (3j)

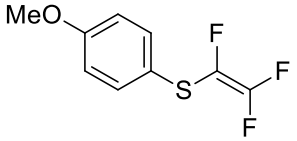
Obtained as a colorless oil in 88% yield (103 mg). R_f (dichloromethane/*n*-pentane 1:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.6 (dd, *J* = 40.0, 35.6 Hz, 1F), -104.4 (dd, *J* = 124.2, 40.0 Hz, 1F), -150.4 (dd, *J* = 124.2, 35.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (s), 156.4 (ddd, *J* = 303.6, 282.1, 52.3 Hz), 138.0 (dt, *J* = 5.5, 3.7 Hz), 136.1 (s), 129.4 (s), 127.7 (s), 122.6 (ddd, *J* = 279.0, 50.2, 25.2 Hz), 26.6

(s). IR (ATR): ν 3007, 2926, 1740, 1683, 1590, 1564, 1397, 1358, 1309, 1259, 1184, 1134, 1092, 1047, 1011, 956, 907, 819, 758, 731, 618, 589, 520, 503 cm^{-1}. GC-MS m/z 232 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_7OF_3S$: 232.0170; found: 232.0173.



1-(3-((1,2,2-Trifluorovinyl)thio)phenyl)ethanone (3k)

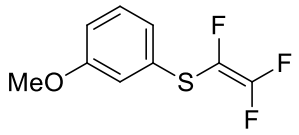
Obtained as a colorless oil in 59% yield (68 mg). R_f (dichloromethane/*n*-pentane 1:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 2.63 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.6 (dd, *J* = 41.9, 35.4 Hz, 1F), -105.2 (dd, *J* = 124.0, 41.8 Hz, 1F), -149.7 (dd, *J* = 124.1, 35.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (s), 156.0 (ddd, *J* = 303.1, 281.3, 52.8 Hz), 138.2 (s), 133.7 (d, *J* = 1.5 Hz), 132.7 (dd, *J* = 7.2, 5.3 Hz), 129.8 (s), 129.1 (d, *J* = 1.6 Hz), 128.0 (s), 123.6 (ddd, *J* = 279.4, 50.2, 24.8 Hz), 26.6 (s). IR (ATR): ν 3063, 3008, 1739, 1687, 1572, 1472, 1418, 1357, 1308, 1283, 1251, 1132, 1075, 1047, 998, 958, 907, 788, 731, 685, 672, 587, 523 cm^{-1}. GC-MS m/z 223 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_7OF_3S$: 232.0170; found: 232.0168.



(4-Methoxyphenyl)(1,2,2-trifluorovinyl)sulfane (3l)

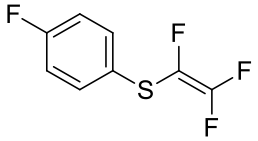
Obtained as a colorless oil in 77% yield (85 mg). R_f (*n*-pentane) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.5 (dd, *J* = 47.3, 34.5 Hz, 1F), -107.4 (dd, *J* = 124.0, 47.4 Hz, 1F), -148.9 (dd, *J* = 124.0, 34.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (s), 155.2 (ddd, *J* = 301.6, 279.1, 53.9 Hz), 133.5 (d, *J* = 1.6 Hz), 125.5 (ddd, *J*

= 279.6, 50.3, 23.5 Hz), 121.6 (dd, *J* = 8.4, 3.5 Hz), 115.1 (s), 55.4 (s). IR (ATR): ν 3008, 2943, 2839, 1739, 1593, 1574, 1494, 1462, 1442, 1299, 1245, 1174, 1129, 1105, 1042, 1031, 1006, 907, 824, 637, 580, 529 cm^{-1}. GC-MS m/z 220 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7OF_3S$: 220.0170; found: 220.0165.



(3-Methoxyphenyl)(1,2,2-trifluorovinyl)sulfane (3m)

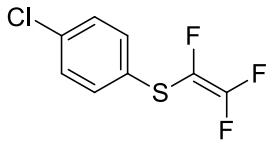
Obtained as a colorless oil in 85% yield (94 mg). R_f (*n*-pentane) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.5 (dd, *J* = 43.5, 34.7 Hz, 1F), -105.8 (dd, *J* = 124.2, 43.4 Hz, 1F), -149.0 (dd, *J* = 124.1, 34.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (s), 156.0 (ddd, *J* = 302.5, 280.5, 53.4 Hz), 132.7 (dt, *J* = 5.2, 3.5 Hz), 130.4 (s), 123.9 (ddd, *J* = 279.1, 50.1, 24.5 Hz), 121.6 (d, *J* = 1.4 Hz), 114.9 (d, *J* = 1.4 Hz), 113.9 (s), 55.4 (s). IR (ATR): ν 3007, 2940, 2837, 1739, 1592, 1577, 1480, 1465, 1427, 1305, 1285, 1248, 1232, 1129, 1038, 992, 906, 857, 844, 770, 729, 684, 566, 518 cm^{-1}. GC-MS m/z 220 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7OF_3S$: 220.0170; found: 220.0162.



(4-Fluorophenyl)(1,2,2-trifluorovinyl)sulfane (3n)

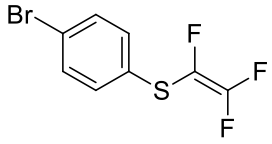
Obtained as a colorless oil in 69% yield (72 mg). R_f (*n*-pentane) = 0.83. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.1 (dd, *J* = 44.5, 35.2 Hz, 1F), -106.4 (dd, *J* = 124.0, 44.5 Hz, 1F), -112.2 – -112.3 (m, 1F), -149.4 (dd, *J* = 124.0, 35.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (s), 161.8 (s), 155.5 (ddd, *J* = 302.5, 280.3, 53.4 Hz), 132.9 (dd, *J* =

8.4, 1.6 Hz), 124.6 (ddd, *J* = 74.3, 48.6, 22.6 Hz), 116.7 (d, *J* = 22.3 Hz). IR (ATR): ν 2926, 2855, 1740, 1591, 1491, 1399, 1309, 1233, 1158, 1136, 1048, 1013, 909, 829, 735, 629, 582, 527 cm^{-1}. GC-MS m/z 208 (M^+). HRMS (EI) m/z: calcd. for $C_8H_4F_4S$: 207.9970; found: 207.9978.



(4-Chlorophenyl)(1,2,2-trifluorovinyl)sulfane (3o)

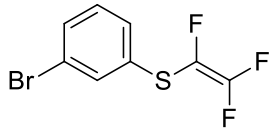
Obtained as a colorless oil in 82% yield (92 mg). R_f (*n*-pentane) = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.2 (dd, *J* = 42.9, 35.3 Hz, 1F), -105.7 (dd, *J* = 124.1, 42.8 Hz, 1F), -149.6 (dd, *J* = 124.1, 35.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 302.9, 280.9, 53.1 Hz), 134.7 (s), 131.2 (d, *J* = 1.6 Hz), 129.9 (dt, *J* = 5.4, 3.6 Hz), 129.7 (s), 123.9 (ddd, *J* = 279.5, 50.2, 24.5 Hz). IR (ATR): ν 2927, 2855, 1739, 1640, 1575, 1477, 1390, 1307, 1191, 1133, 1092, 1045, 1012, 908, 813, 743, 704, 682, 586, 543, 520, 509, 478 cm^{-1}. GC-MS m/z 224 (M^+). HRMS (EI) m/z: calcd. for $C_8H_4ClF_3S$: 223.9674; found: 223.9680.



(4-Bromophenyl)(1,2,2-trifluorovinyl)sulfane (3p)

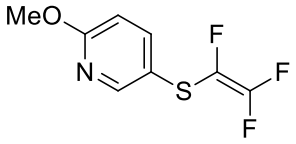
Obtained as a colorless solid in 84% yield (86 mg). M.p. 50.1-50.9 ℃. R_f (*n*-pentane) = 0.93. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.0 (dd, *J* = 42.6, 35.3 Hz, 1F), -105.6 (dd, *J* = 124.1, 42.6 Hz, 1F), -149.6 (dd, *J* = 124.1, 35.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 303.0, 281.1, 53.0 Hz), 132.7 (s), 131.3 (d, *J* = 1.6 Hz), 130.6 (dd, *J* = 7.2, 5.3 Hz), 123.7 (ddd, *J* = 279.5, 50.2, 24.6 Hz), 122.6 (s). IR (ATR): ν 2926,

2854, 1739, 1569, 1744, 1388, 1308, 1192, 1132, 1086, 1069, 1046, 1008, 906, 809, 727, 585, 525, 492, 472 cm^{-1}. GC-MS m/z 269 (M^+). HRMS (EI) m/z: calcd. for $C_8H_4F_3SBr$: 267.9169; found: 267.9176.



(3-Bromophenyl)(1,2,2-trifluorovinyl)sulfane (3q)

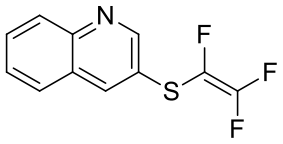
Obtained as a colorless oil in 84% yield (113 mg). R_f (*n*-pentane) = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.4 (dd, *J* = 41.2, 35.4 Hz, 1F), -104.9 (dd, *J* = 124.1, 41.3 Hz, 1F), -149.6 (dd, *J* = 124.1, 35.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (ddd, *J* = 303.3, 281.4, 52.8 Hz), 133.7 (dd, *J* = 9.0, 3.7 Hz), 131.9 (d, *J* = 1.6 Hz), 131.3 (s), 130.8 (s), 127.9 (d, *J* = 1.5 Hz), 123.4 (ddd, *J* = 279.4, 50.1, 24.8 Hz), 123.3 (s). IR (ATR): ν 3058, 2926, 1738, 1574, 1563, 1460, 1404, 1308, 1134, 1068, 1046, 994, 868, 772, 749, 675, 653, 588, 516 cm^{-1}. GC-MS m/z 269 (M^+). HRMS (EI) m/z: calcd. for $C_8H_4F_3SBr$: 267.9169; found: 267.9164.



2-Methoxy-5-((1,2,2-trifluorovinyl)thio)pyridine (3r)

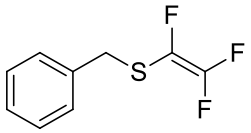
Obtained as a colorless oil in 88% yield (97 mg). R_f (dichloromethane/*n*-pentane 1:10) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.4 Hz, 1H), 7.71 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (dd, *J* = 46.1, 35.6 Hz, 1F), -106.9 (dd, *J* = 123.9, 46.0 Hz, 1F), -149.5 (dd, *J* = 123.9, 35.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (s), 155.1 (ddd, *J* = 302.2, 279.9, 53.1 Hz), 150.6 (d, *J* = 1.9 Hz), 142.6 (d, *J* = 1.4 Hz), 124.9 (ddd, *J* = 280.0, 50.6, 23.6 Hz), 119.3 (dt, *J* = 5.0, 3.6 Hz), 112.1 (s), 53.8 (s). IR (ATR): ν 2946, 1741,

1588, 1558, 1478, 1430, 1366, 1304, 1284, 1252, 1137, 1105, 1046, 1018, 906, 829, 731, 670, 650, 586, 541, 516 cm^{-1}. GC-MS m/z 221 (M^+). HRMS (EI) m/z: calcd. for $C_8H_6NOF_3S$: 221.0122; found: 221.0125.



3-((1,2,2-Trifluorovinyl)thio)quinoline (3s)

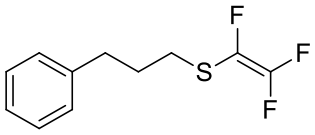
Obtained as a colorless oil in 95% yield (114 mg). R_f (dichloromethane/*n*-pentane 1:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.62 (t, *J* = 7.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.5 (dd, *J* = 42.1, 36.1 Hz, 1F), -105.1 (dd, *J* = 124.0, 42.0 Hz, 1F), -149.6 (dd, *J* = 124.0, 36.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (ddd, *J* = 303.3, 281.4, 52.4 Hz), 150.8 (s), 147.4 (s), 137.8 (s), 130.5 (s), 129.4 (s), 127.9 (dd, *J* = 3.4, 2.3 Hz), 127.8 (s), 127.5 (s), 123.7 (ddd, *J* = 279.9, 50.5, 24.7 Hz), 117.3 (s). IR (ATR): ν 3063, 1739, 1618, 1581, 1565, 1490, 1357, 1309, 1256, 1195, 1132, 1076, 1047, 954, 905, 862, 783, 748, 729, 645, 633, 582, 525, 479 cm^{-1}. GC-MS m/z 241 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_6NF_3S$: 241.0173; found: 241.0175.



Benzyl(1,2,2-trifluorovinyl)sulfane (3t)

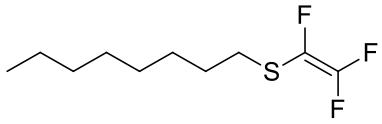
Obtained as a colorless oil in 36% yield (37 mg). R_f (*n*-pentane) = 0.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.31 (d, *J* = 7.2 Hz, 3H), 3.96 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.3 (dd, *J* = 46.3, 33.4 Hz, 1F), -107.6 (dd, *J* = 123.0, 46.5 Hz, 1F), -150.4 (dd, *J* = 123.0, 33.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (ddd, *J* = 301.3, 279.6, 54.5 Hz), 135.9 (s), 129.0 (s), 128.7 (s), 127.8 (s), 124.0 (ddd, *J* =

276.8, 50.5, 24.2 Hz), 38.1 (q, *J* = 3.4 Hz). IR (ATR): ν 3084, 3063, 3025, 2931, 2855, 1739, 1602, 1495, 1453, 1300, 1121, 1043, 905, 742, 698, 564, 515 cm^{-1}. GC-MS m/z 204 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0223.



(3-Phenylpropyl)(1,2,2-trifluorovinyl)sulfane (3u)

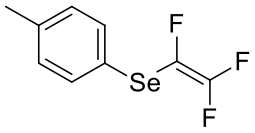
Obtained as a colorless oil in 85% yield (99 mg). R_f (*n*-pentane) = 0.83. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.18 (m, 3H), 2.78 (q, *J* = 7.3 Hz, 4H), 2.02 (p, *J* = 7.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.5 (dd, *J* = 49.6, 33.4 Hz, 1F), -108.1 (dd, *J* = 123.7, 49.6 Hz, 1F), -149.1 (dd, *J* = 123.7, 33.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (ddd, *J* = 300.9, 278.4, 55.0 Hz), 140.8 (s), 128.5 (s), 128.4 (s), 126.2 (s), 124.6 (ddd, *J* = 277.1, 50.6, 23.8 Hz), 34.2 (s), 33.1 (q, *J* = 3.1 Hz), 31.0 (d, *J* = 1.3 Hz). IR (ATR): ν 3087, 3064, 3028, 2934, 2857, 1739, 1604, 1497, 1454, 1301, 1121, 1045, 905, 742, 698, 565, 517 cm^{-1}. GC-MS m/z 232 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_{11}F_3S$: 232.0534; found: 232.0532.



Octyl(1,2,2-trifluorovinyl)sulfane (3v)

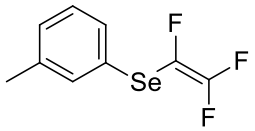
Obtained as a colorless oil in 83% yield (94 mg). R_f (*n*-pentane) = 0.87. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (t, *J* = 7.3 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.46 – 1.38 (m, 2H), 1.37 – 1.22 (m, 8H), 0.91 (t, *J* = 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.5 (dd, *J* = 49.6, 33.4 Hz, 1F), -108.1 (dd, *J* = 123.7, 49.6 Hz, 1F), -149.1 (dd, *J* = 123.7, 33.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (ddd, *J* = 300.5, 278.1, 55.3 Hz), 124.9 (ddd, *J* = 276.8, 50.4, 23.7 Hz), 39.2 (s), 33.9 (q, *J* = 3.0 Hz), 31.8 (s), 29.5 (d, *J* = 1.3 Hz), 29.1 (d, *J* = 7.2 Hz), 28.3 (s), 22.6 (s), 14.1 (s). IR (ATR): ν 2958, 2927, 2856,

1740, 1466, 1379, 1301, 1124, 1045, 905, 724, 575, 517 cm^{-1}. GC-MS m/z 226 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_{17}F_3S$: 226.1003; found: 226.1004.



_p_-Tolyl(1,2,2-trifluorovinyl)selane (5a)

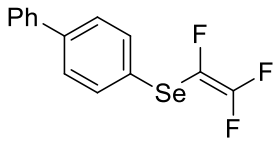
Obtained as a colorless oil in 90% yield (113 mg). R_f (*n*-pentane) = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.7 (dd, *J* = 51.7, 37.3 Hz, 1F), -107.1 (dd, *J* = 129.6, 51.7 Hz, 1F), -151.3 (dd, *J* = 129.6, 37.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (ddd, *J* = 303.7, 276.9, 47.6 Hz), 138.9 (s), 132.8 (s), 130.5 (s), 123.9 (dd, *J* = 2.8, 1.5 Hz), 120.6 (ddd, *J* = 297.5, 56.1, 19.0 Hz), 21.1 (s). IR (ATR): ν 3024, 2925, 2868, 1733, 1490, 1399, 1294, 1210, 1168, 1125, 1011, 907, 800, 732, 651, 567, 511, 491 cm^{-1}. GC-MS m/z 251 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3{}^{74}Se$: 245.9725; found: 245.9717.



_m_-Tolyl(1,2,2-trifluorovinyl)selane (5b)

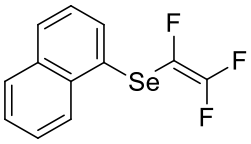
Obtained as a colorless oil in 93% yield (117 mg). R_f (*n*-pentane) = 0.86. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 1H), 7.36 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.2 (dd, *J* = 50.6, 37.3 Hz, 1F), -106.7 (dd, *J* = 129.6, 50.6 Hz, 1F), -151.2 (dd, *J* = 129.6, 37.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (ddd, *J* = 303.9, 277.3, 47.6 Hz), 139.7 (s), 132.7 (s), 129.5 (s), 129.3 (s), 129.2 (d, *J* = 1.3 Hz), 127.4 (dt, *J* = 4.6, 2.8 Hz), 120.2 (ddd, *J* = 75.4, 46.2, 19.8 Hz), 21.3 (s). IR (ATR): ν 3057, 2953, 2911, 1734, 1594, 1571, 1473, 1297, 1167, 1127, 1020, 996, 904, 833, 772, 725, 686, 650, 568, 509 cm^{-1}.

GC-MS m/z 251 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7F_3{}^{74}Se$: 245.9725; found: 245.9719.



[1,1'-Biphenyl]-4-yl(1,2,2-trifluorovinyl)selane (5d)

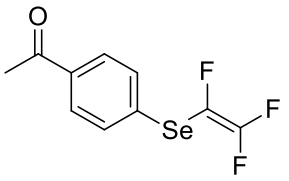
Obtained as a white solid in 95% yield (149 mg). M.p. 50.6-51.6 ℃. R_f (*n*-pentane) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.57 (m, 4H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.40 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.9 (dd, *J* = 50.1, 37.6 Hz, 1F), -106.5 (dd, *J* = 129.7, 50.2 Hz, 1F), -151.3 (dd, *J* = 129.6, 37.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (ddd, *J* = 304.1, 277.4, 47.3 Hz), 141.7 (s), 140.1 (s), 132.7 (d, *J* = 1.2 Hz), 129.0 (s), 128.4 (s), 127.8 (s), 127.1 (s), 126.5 (dt, *J* = 4.4, 2.8 Hz), 120.3 (ddd, *J* = 297.4, 56.1, 19.5 Hz). IR (ATR): ν 3064, 3029, 2963, 1735, 1601, 1478, 1447, 1299, 1261, 1128, 1023, 1005, 904, 827, 759, 727, 697, 650, 546, 511 cm^{-1}. GC-MS m/z 313 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_9F_3{}^{74}Se$: 307.9881; found: 307.9887.



Naphthalen-1-yl(1,2,2-trifluorovinyl)selane (5f)

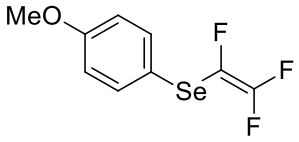
Obtained as a colorless oil in 91% yield (131 mg). R_f (*n*-pentane) = 0.82. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.3, 4.1 Hz, 1H), 8.01 – 7.77 (m, 3H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.9 (ddd, *J* = 51.2, 37.9, 3.3 Hz, 1F), -106.6 (ddd, *J* = 128.7, 51.2, 4.1 Hz, 1F), -151.4 (ddd, *J* = 128.7, 37.9, 11.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (ddd, *J* = 304.0, 277.0, 47.3 Hz), 134.3 (s), 133.8 (s), 133.5 (d, *J* = 1.1 Hz), 130.1 (s), 128.8 (s), 127.3 (s), 127.0 (s), 126.6 (s), 126.4 (dt, *J* = 4.2, 2.7 Hz), 126.0 (s), 120.1

(ddd, J = 297.5, 56.4, 19.2 Hz). IR (ATR): ν 3076, 3056, 3006, 2926, 1732, 1590, 1561, 1502, 1380, 1294, 1254, 1123, 1017, 956, 905, 794, 767, 732, 650, 567, 510 cm^{-1}. GC-MS m/z 287 (M^+). HRMS (EI) m/z: calcd. for $C_{12}H_7F_3{}^{74}Se$: 281.9725; found: 281.9722.



1-(4-((1,2,2-Trifluorovinyl)selanyl)phenyl)ethanone (5j)

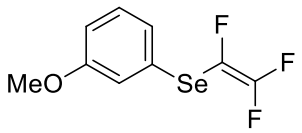
Obtained as a colorless oil in 99% yield (139 mg). R_f (dichloromethane/*n*-pentane 1:1) = 0.60. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 2.60 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.3 (dd, J = 46.6, 38.3 Hz, 1F), -105.2 (dd, J = 129.6, 46.7 Hz, 1F), -152.0 (dd, J = 129.6, 38.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1 (s), 156.2 (ddd, J = 305.0, 278.9, 46.5 Hz), 136.5 (s), 134.6 (dt, J = 4.7, 2.9 Hz), 130.6 (d, J = 1.2 Hz), 129.4 (s), 119.2 (ddd, J = 297.1, 56.0, 20.5 Hz), 26.5 (s). IR (ATR): ν 3007, 2957, 2918, 2849, 1734, 1683, 1588, 1562, 1427, 1394, 1360, 1301, 1264, 1183, 1129, 1081, 1022, 1008, 956, 906, 816, 730, 649, 605, 587, 511, 459 cm^{-1}. GC-MS m/z 279 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_7OF_3{}^{74}Se$: 273.9674; found: 273.9677.



(4-Methoxyphenyl)(1,2,2-trifluorovinyl)selane (5l)

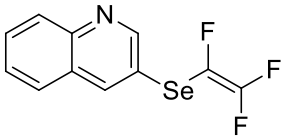
Obtained as a colorless oil in 91% yield (122 mg). R_f (*n*-pentane) = 0.60. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.4 (dd, J = 53.0, 37.2 Hz, 1F), -107.6 (dd, J = 129.4, 53.1 Hz, 1F), -151.6 (dd, J = 129.4, 37.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ

160.4 (s), 155.2 (ddd, *J* = 303.5, 276.3, 47.5 Hz), 135.4 (s), 121.1 (ddd, *J* = 297.7, 56.4, 18.6 Hz), 117.4 (dt, *J* = 4.3, 2.7 Hz), 115.3 (s), 55.4 (s). IR (ATR): ν 3008, 2960, 2939, 2840, 1734, 1589, 1574, 1491, 1462, 1441, 1290, 1247, 1174, 1125, 1074, 1019, 1002, 906, 824, 807, 731, 650, 599, 566, 518 cm^{-1}. GC-MS m/z 267 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7OF_3{}^{74}Se$: 261.9674; found: 261.9684.



(3-Methoxyphenyl)(1,2,2-trifluorovinyl)selane (5m)

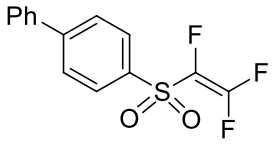
Obtained as a colorless oil in 88% yield (118 mg). R_f (*n*-pentane) = 0.55. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.1 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.12 – 7.09 (m, 1H), 6.91 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.9 (dd, *J* = 49.8, 37.5 Hz, 1F), -106.3 (dd, *J* = 129.6, 49.8 Hz, 1F), -151.2 (dd, *J* = 129.6, 37.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (s), 155.9 (ddd, *J* = 304.1, 277.6, 47.4 Hz), 130.4 (s), 128.6 (dt, *J* = 4.4, 2.7 Hz), 124.1 (d, *J* = 1.2 Hz), 120.2 (ddd, *J* = 297.2, 56.0, 19.7 Hz), 117.5 (d, *J* = 1.3 Hz), 114.2 (s), 55.4 (s). IR (ATR): ν 3007, 2961, 2939, 2838, 1734, 1589, 1574, 1477, 1464, 1426, 1299, 1246, 1232, 1128, 1038, 1019, 991, 905, 837, 771, 729, 684, 650, 564, 511 cm^{-1}. GC-MS m/z 267 (M^+). HRMS (EI) m/z: calcd. for $C_9H_7OF_3{}^{74}Se$: 261.9674; found: 261.9680.



3-((1,2,2-Trifluorovinyl)selanyl)quinoline (5s)

Obtained as a colorless oil in 83% yield (120 mg). R_f (dichloromethane/*n*-pentane 1:1) = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.41 (d, *J* = 1.9 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.61 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.9 (dd, *J* = 48.4, 38.8 Hz, 1F), -105.8 (dd, *J* = 129.3, 48.5 Hz, 1F), -151.5

(dd, *J* = 129.4, 38.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (ddd, *J* = 300.9, 276.4, 44.5 Hz), 152.5 (d, *J* = 0.7 Hz), 147.5 (s), 140.3 (s), 130.5 (s), 129.5 (s), 128.4 (s), 127.6 (s), 127.5 (s), 121.4 (dt, *J* = 4.3, 2.7 Hz), 119.7 (ddd, *J* = 298.0, 56.4, 20.0 Hz). IR (ATR): ν 3063, 2927, 2854, 1734, 1617, 1590, 1583, 1492, 1355, 1300, 1127, 1021, 947, 904, 851, 727, 648, 623, 568, 477 cm^{-1}. GC-MS m/z 288 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_6NF_3{}^{74}Se$: 282.9677; found: 282.9678.



4-((1,2,2-Trifluorovinyl)sulfonyl)-1,1'-biphenyl (3d′)

Obtained as a white solid in 98% yield (89 mg). M.p. 73.5-74.4 ℃. R_f (dichloromethane/*n*-pentane 1:5) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.42 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8 (dd, *J* = 39.4, 30.0 Hz, 1F), -94.6 (dd, *J* = 120.0, 30.0 Hz, 1F), -174.9 (dd, *J* = 120.1, 39.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (ddd, *J* = 307.6, 298.4, 37.5 Hz), 148.3 (s), 138.8 (s), 136.3 (d, *J* = 2.0 Hz), 130.1 (ddd, *J* = 277.5, 41.8, 17.2 Hz), 129.2 (s), 129.1 (s), 128.9 (s), 128.3 (s), 127.5 (s). IR (ATR): ν 3069, 3034, 2956, 2921, 2850, 1741, 1601, 1593, 1478, 1447, 1299, 1261, 1128, 1023, 1005, 904, 827, 759, 697, 650, 546, 511 cm^{-1}. GC-MS m/z 298 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_9O_2F_3S$: 298.0275; found: 298.0273.

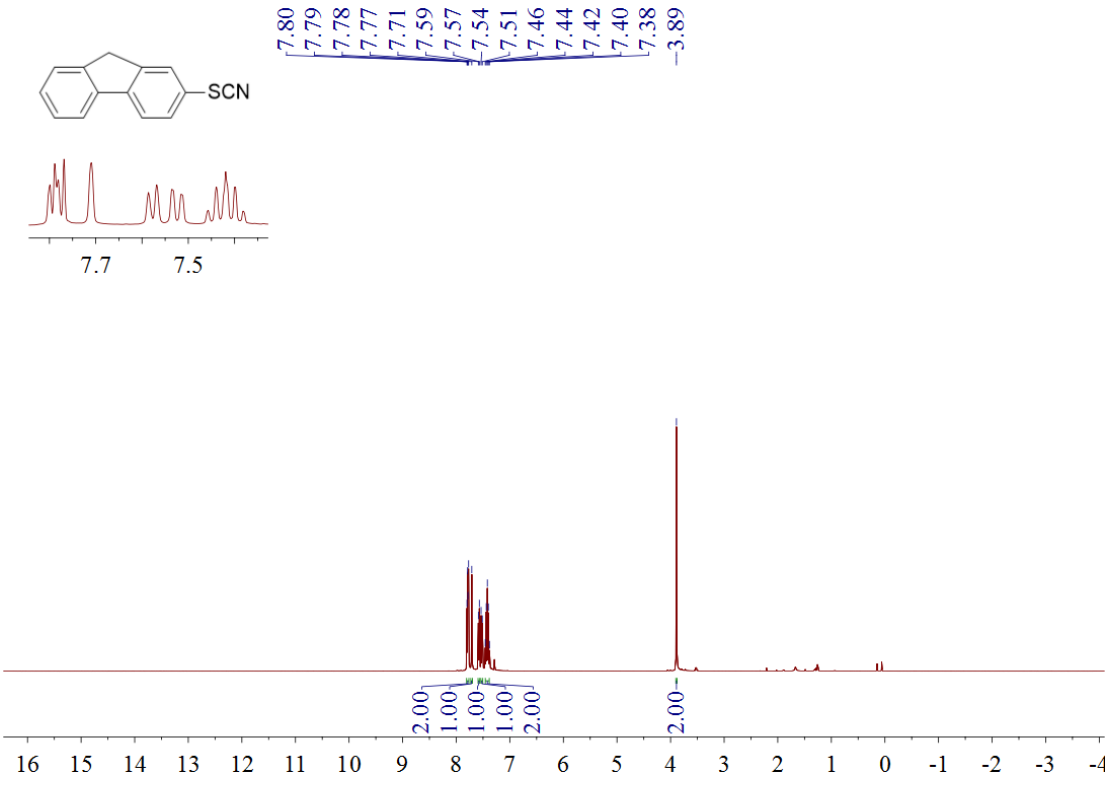
Crystal structure analyses.

The suitable crystals of **3p** (CCDC 1555080) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[4] Structure solution and refinement were carried out with the SHELXTL suite of programs.[4] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

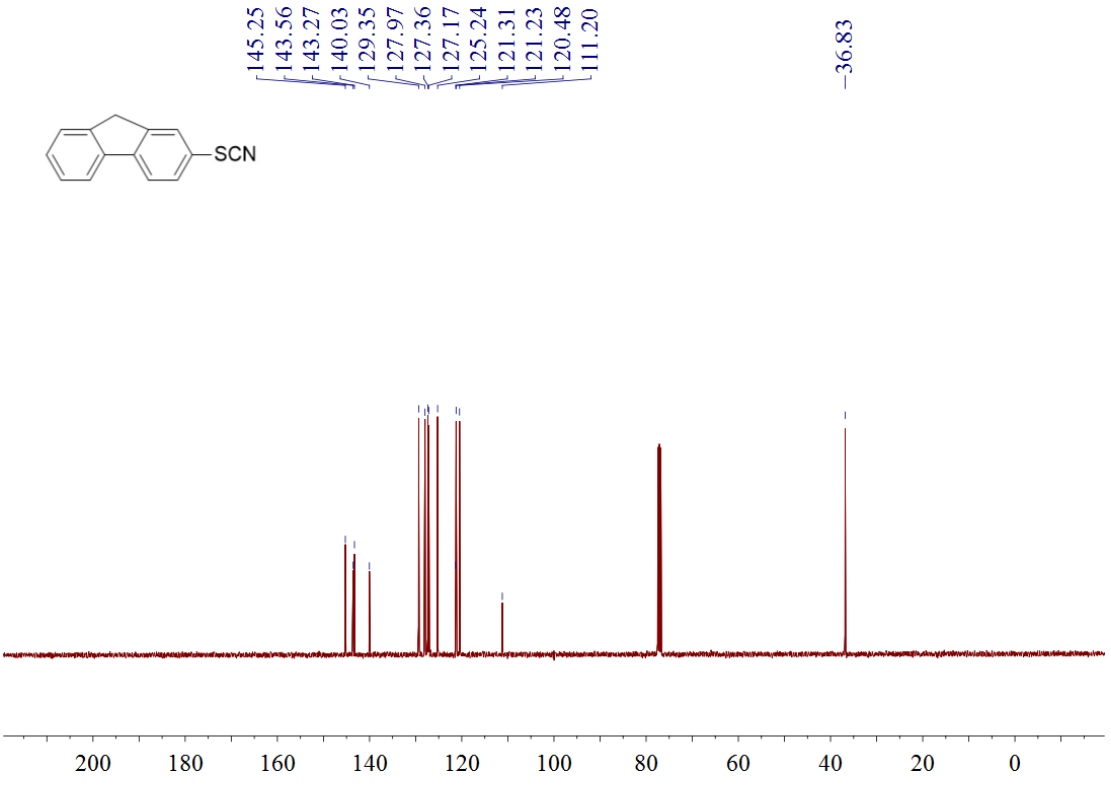
References:

1. B. Exner, B. Bayarmagnai, F. Jia and L. J. Goossen, *Chem.-Eur. J*., 2015, **21**, 17220-17223.
2. Z. Benfodda, F. Guillen, H. Arnion, A. Dahmani and H. Blancou, *Heteroatom Chem.*, 2009, **20**, 355-361.
3. P. Nikolaienko and M. Rueping, *Chem.-Eur. J*., 2016, **22**, 2620-2623.
4. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

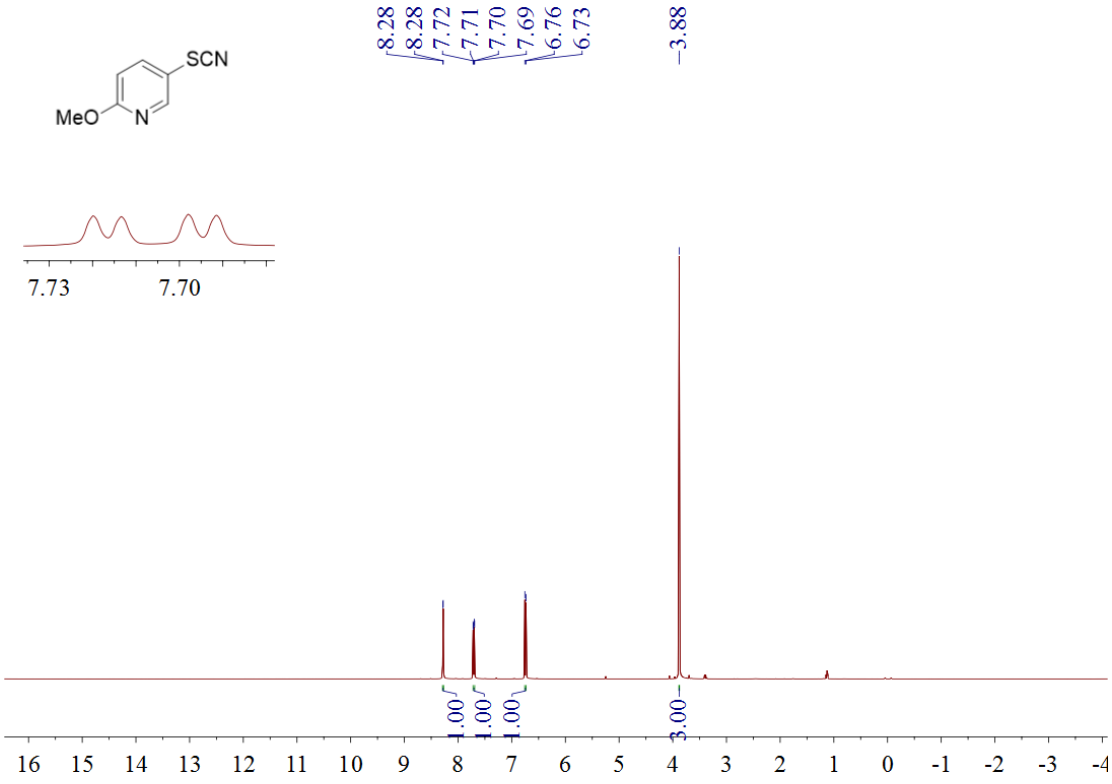
^{1}H NMR spectrum of **2g** in $CDCl_3$



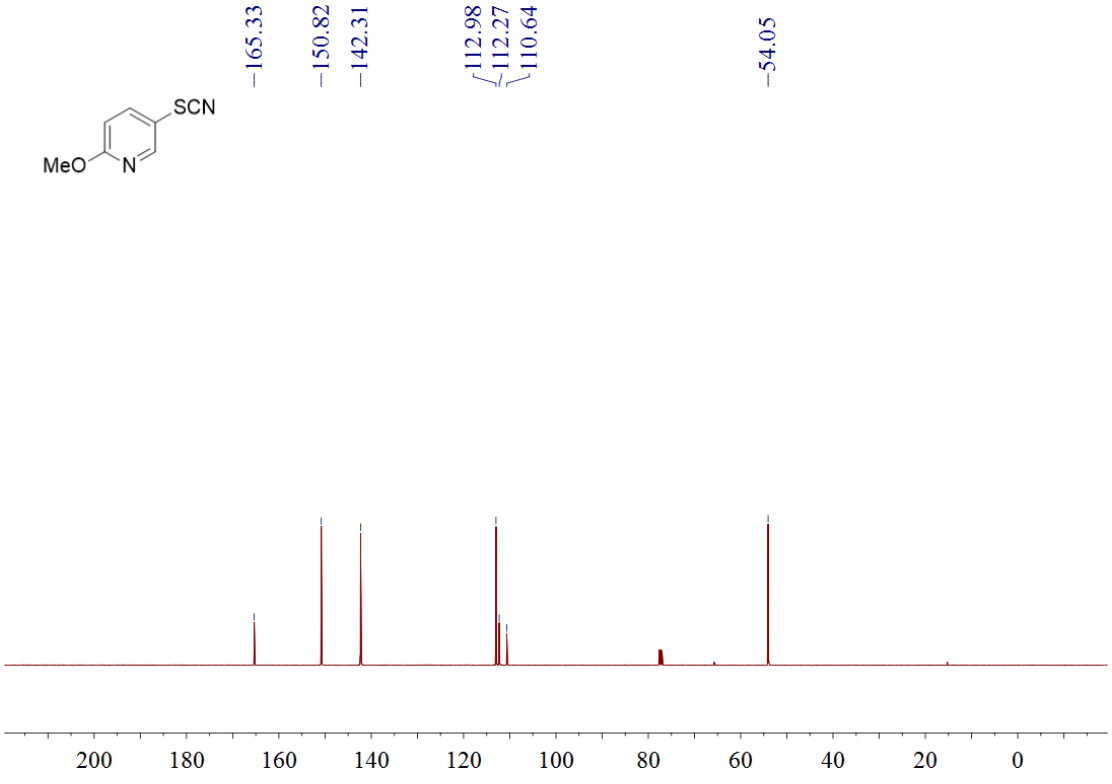
^{13}C NMR spectrum of **2g** in $CDCl_3$



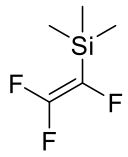
^{1}H NMR spectrum of **2r** in $CDCl_3$



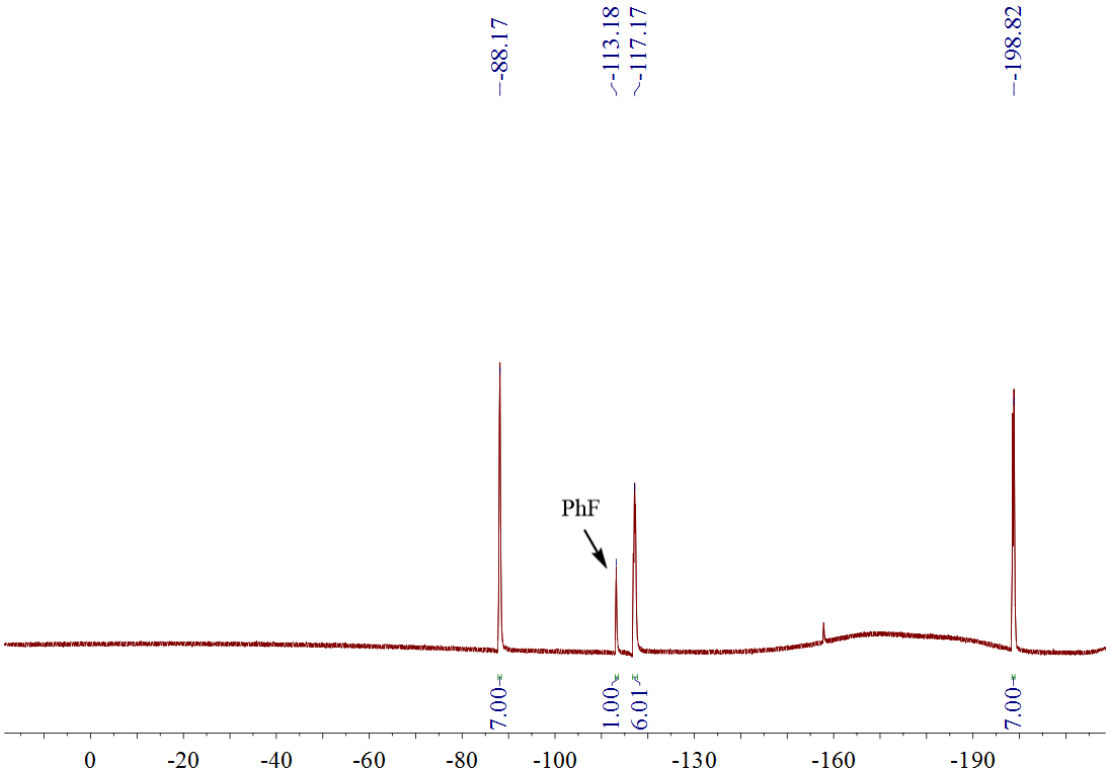
^{13}C NMR spectrum of **2r** in $CDCl_3$



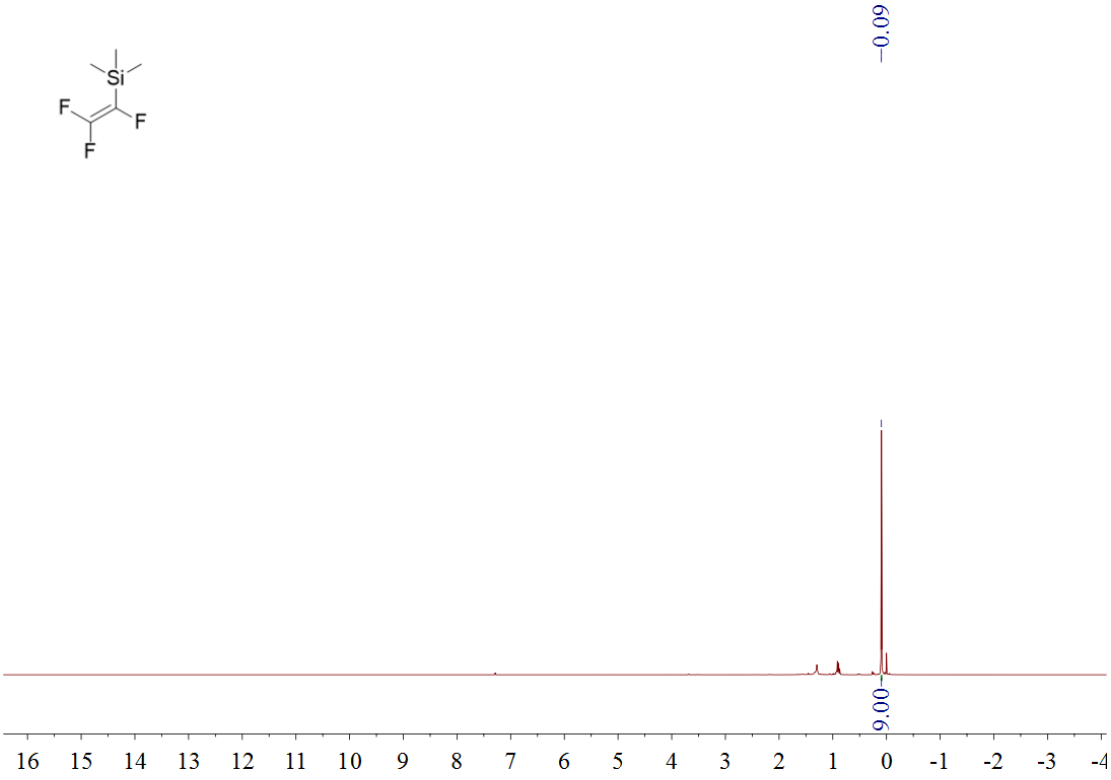
^{19}F NMR spectrum of $TMSCF=CF_2$ (unlocked)



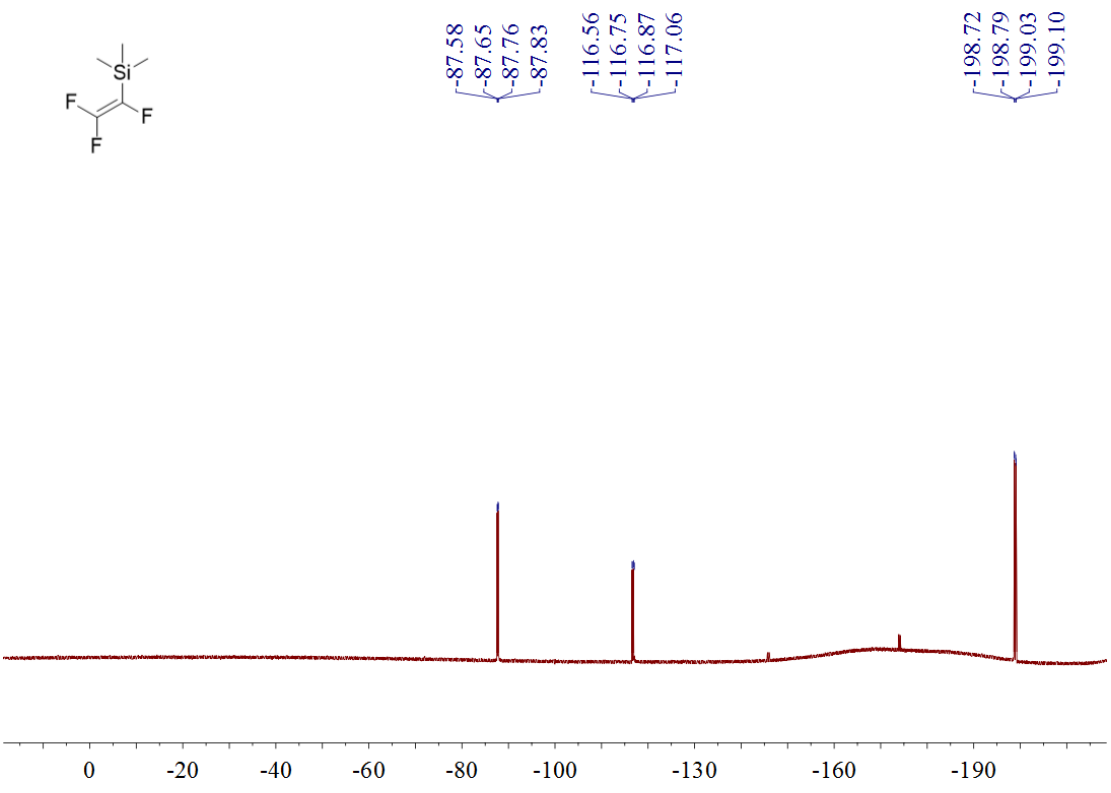
trimethyl(1,2,2-trifluorovinyl)silane



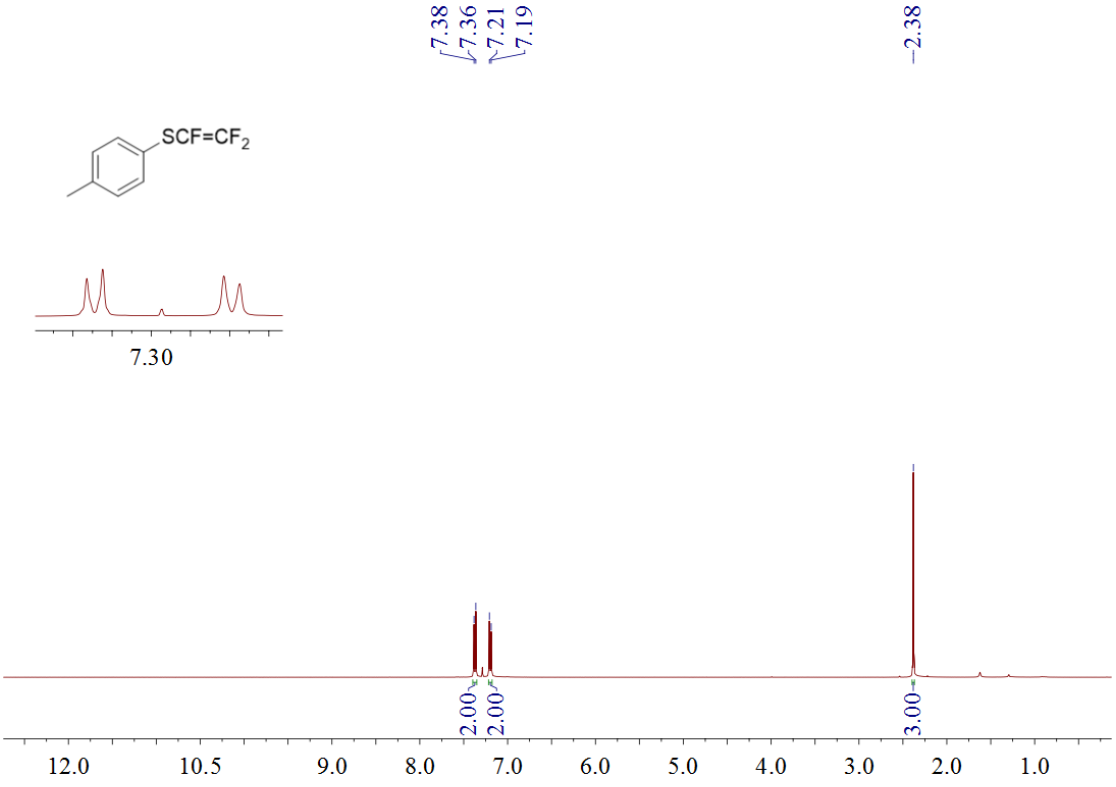
^{1}H NMR spectrum of $TMSCF=CF_2$ in $CDCl_3$



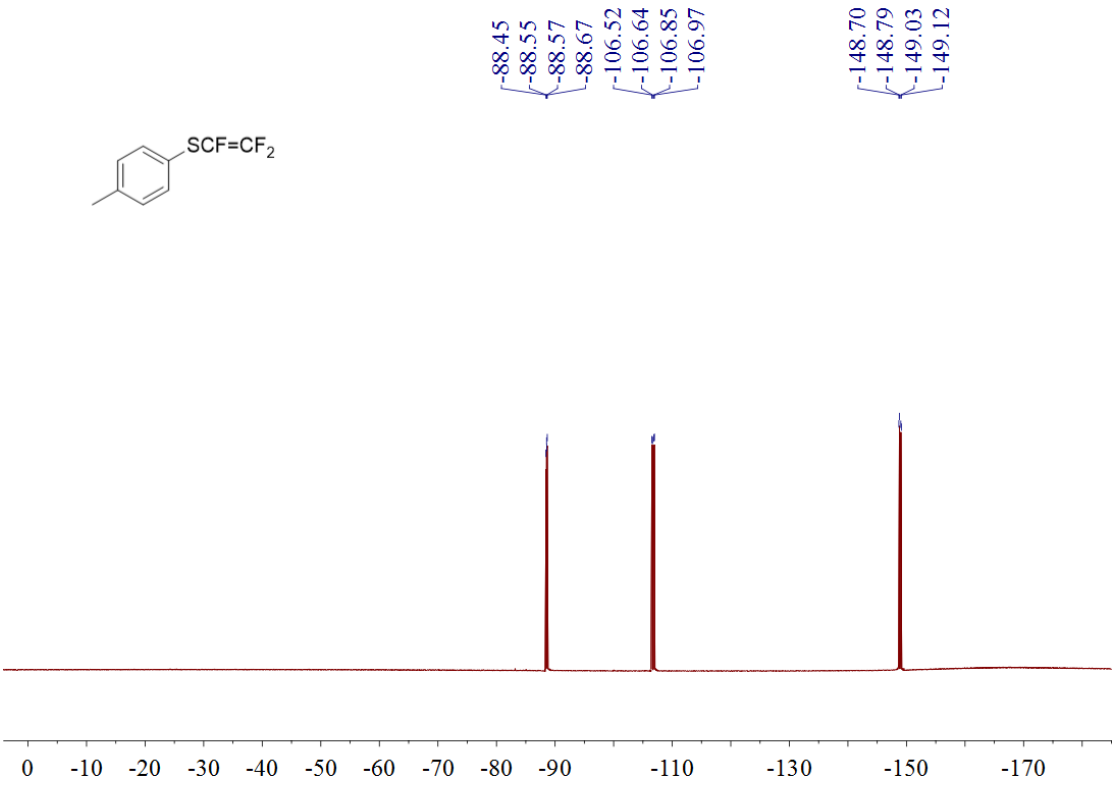
^{19}F NMR spectrum of $TMSCF=CF_2$ in $CDCl_3$



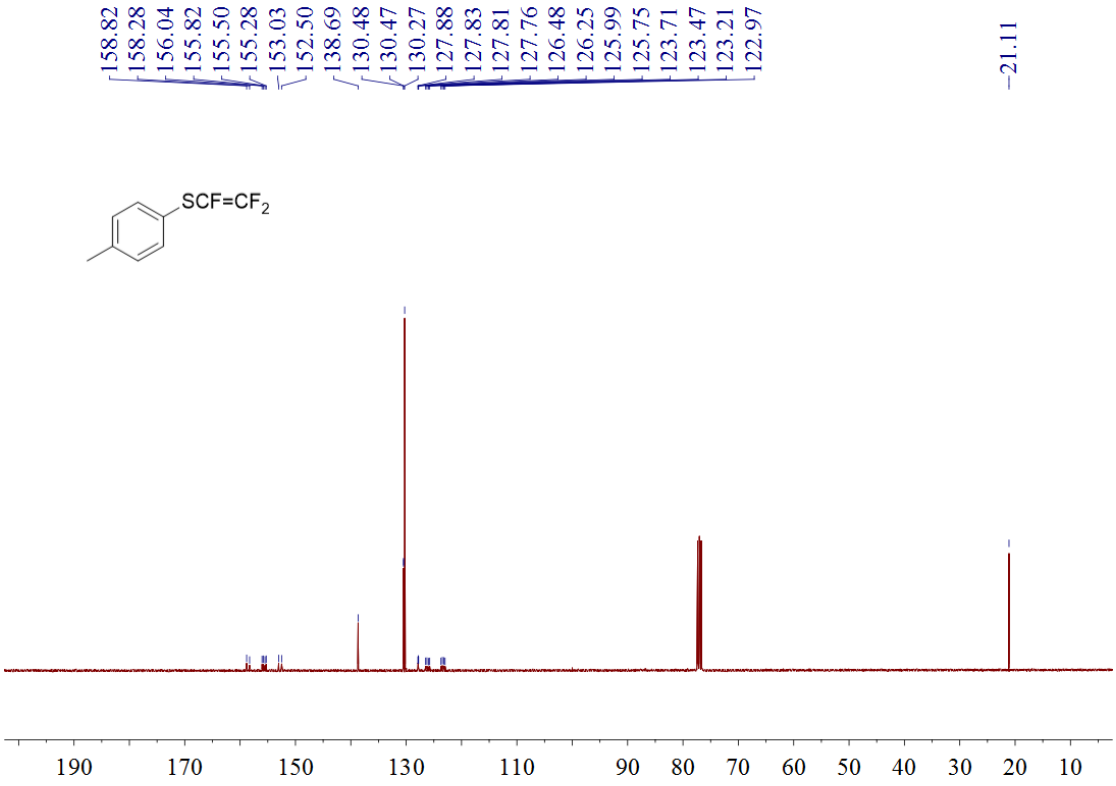
^{1}H NMR spectrum of **3a** in $CDCl_3$



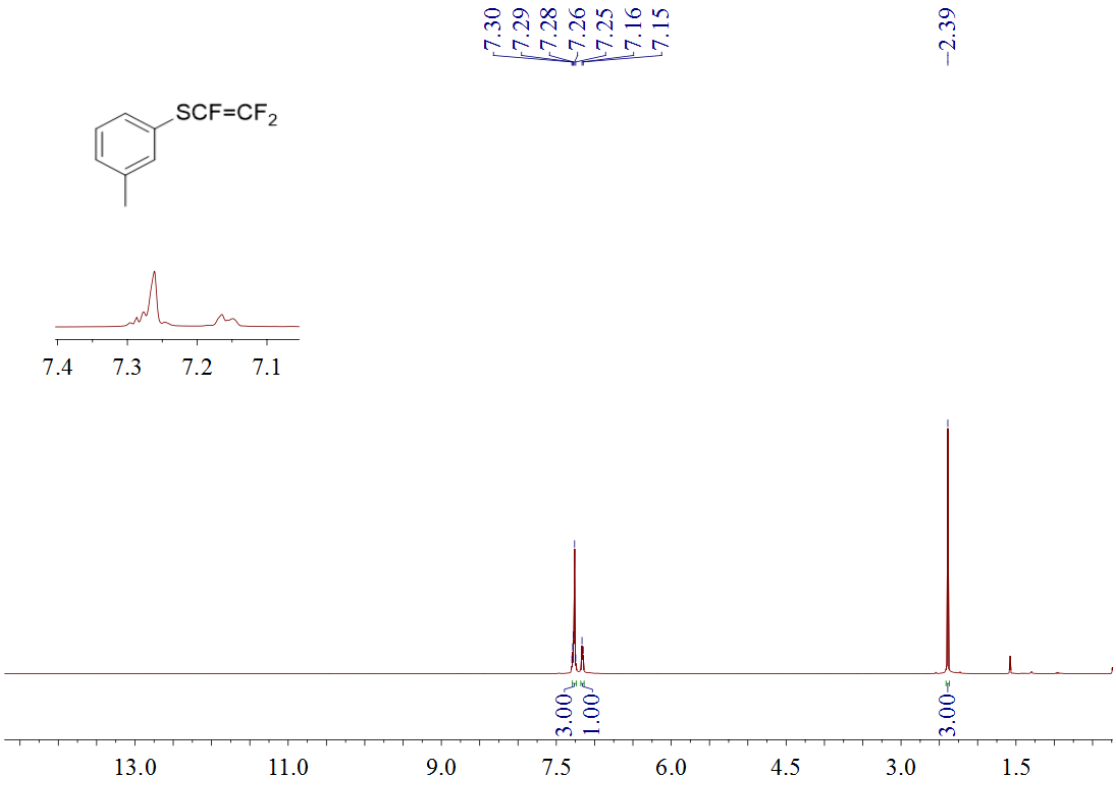
^{19}F NMR spectrum of **3a** in $CDCl_3$



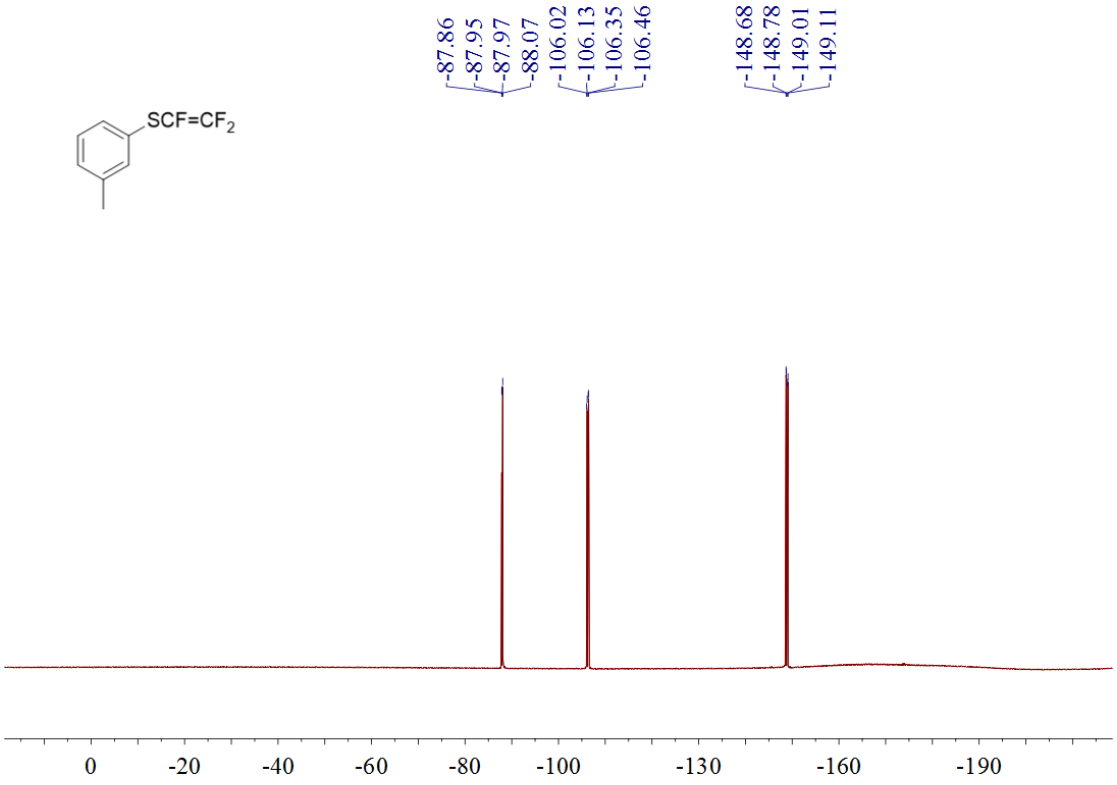
^{13}C NMR spectrum of **3a** in $CDCl_3$



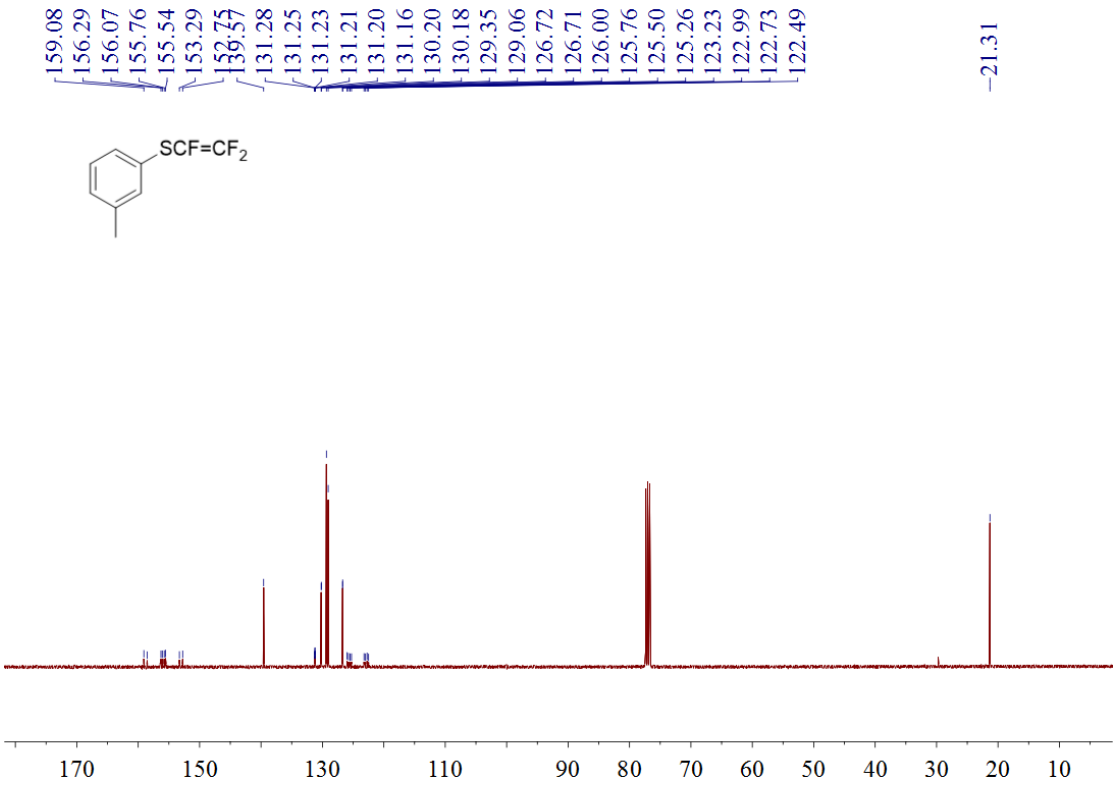
^{1}H NMR spectrum of **3b** in $CDCl_3$



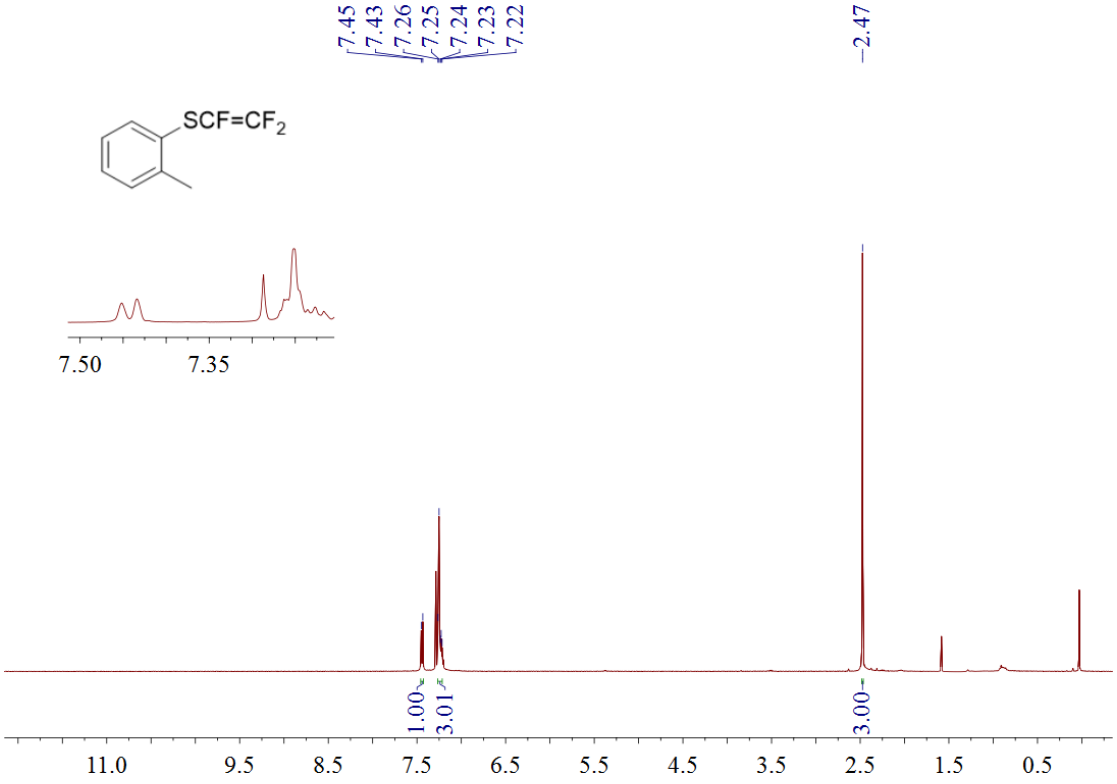
^{19}F NMR spectrum of **3b** in $CDCl_3$



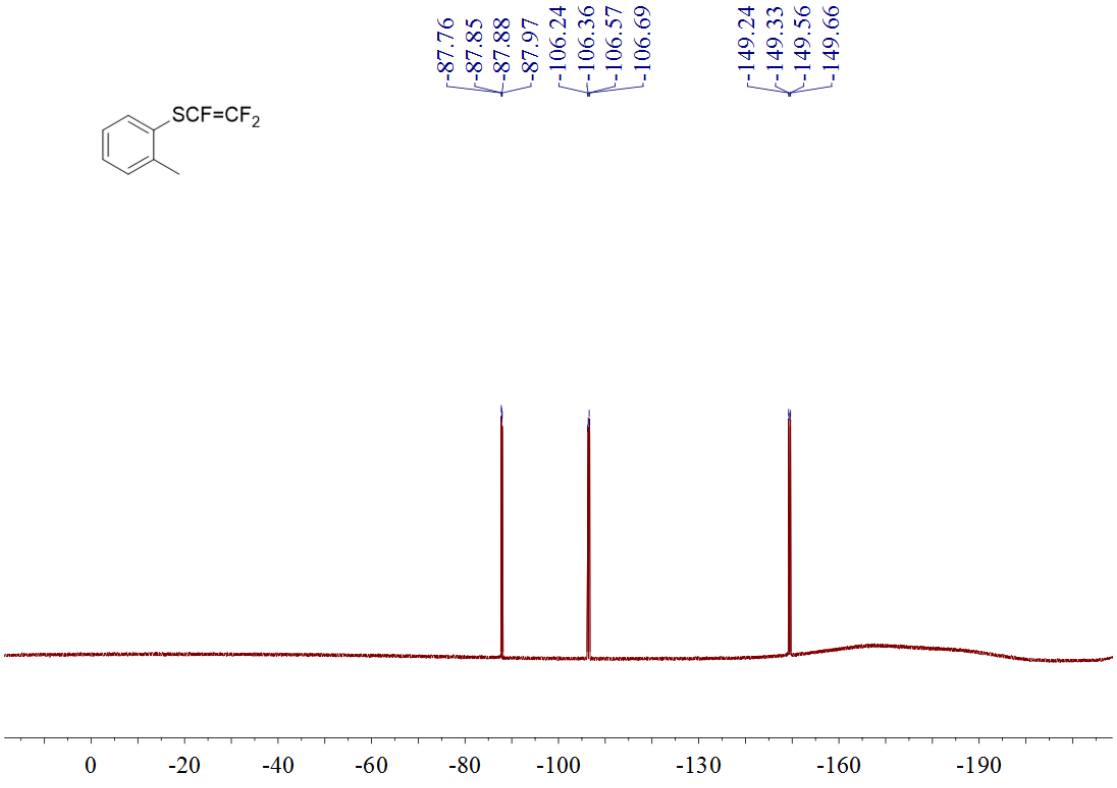
^{13}C NMR spectrum of **3b** in $CDCl_3$



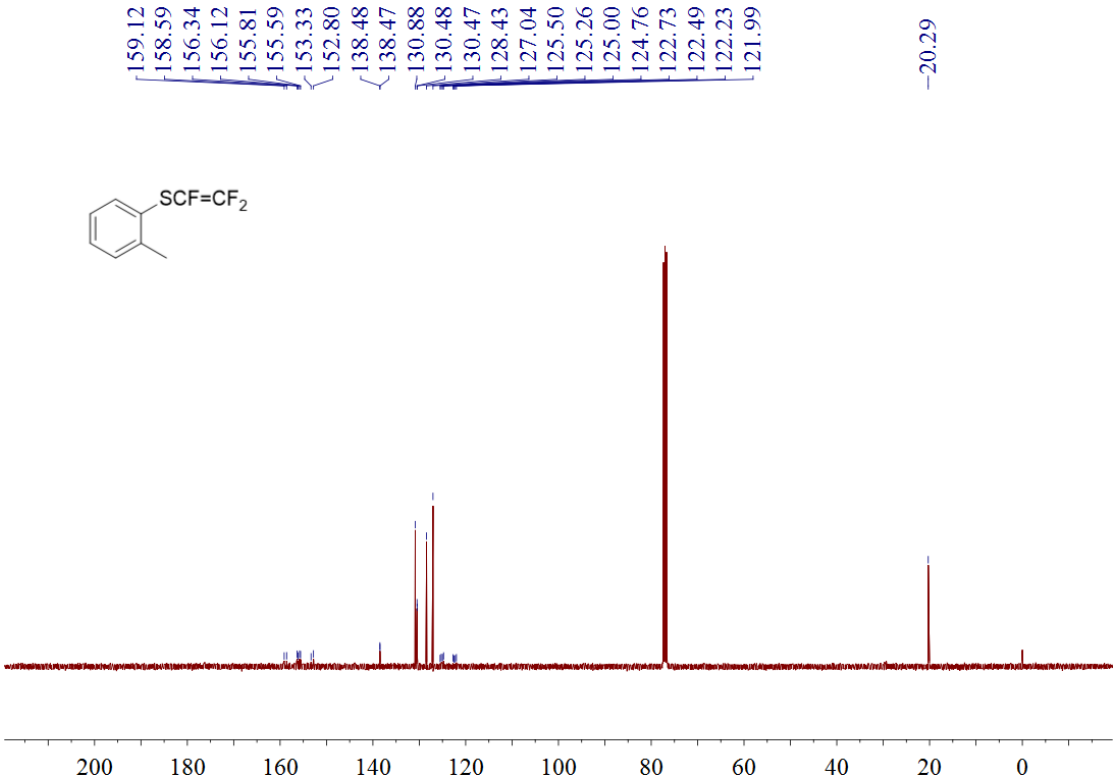
^{1}H NMR spectrum of **3c** in $CDCl_3$



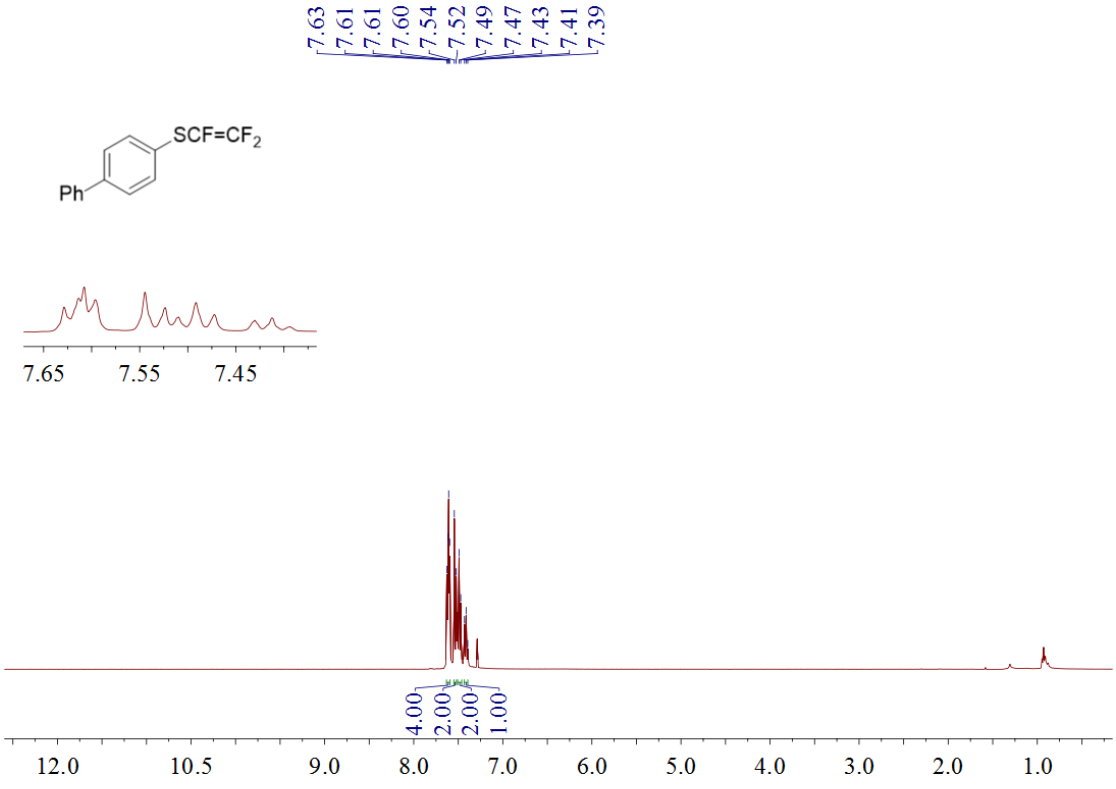
^{19}F NMR spectrum of **3c** in $CDCl_3$



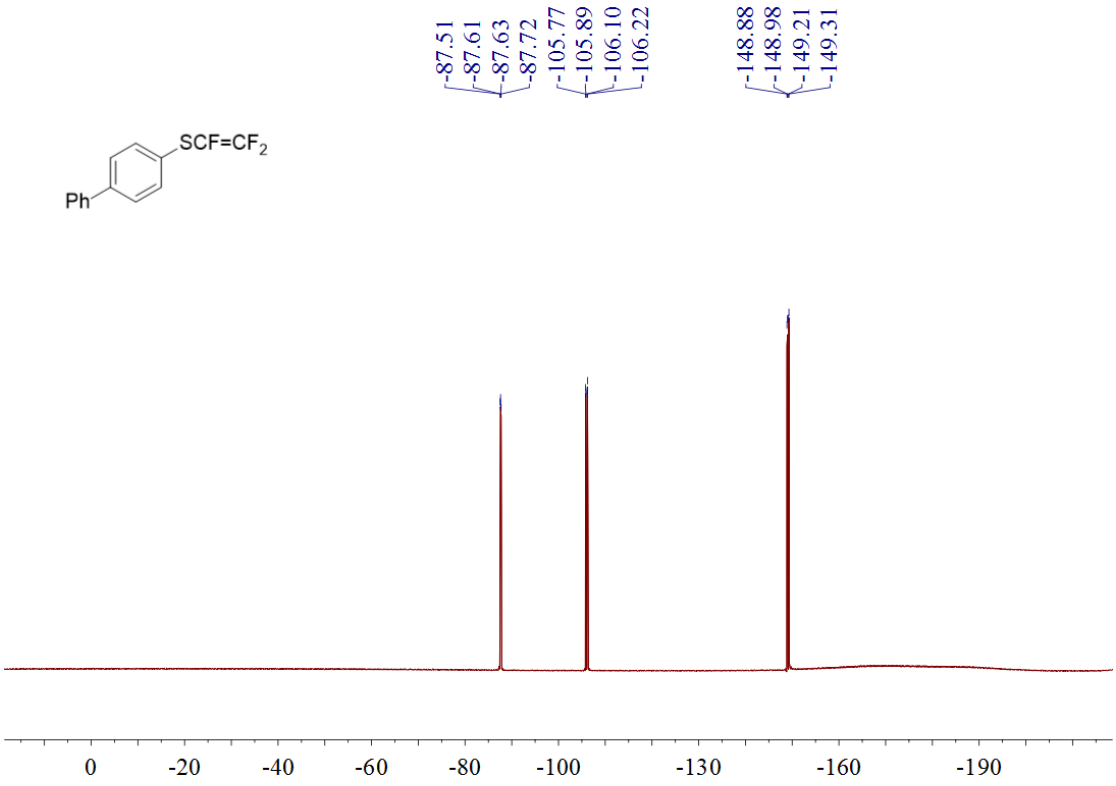
^{13}C NMR spectrum of **3c** in $CDCl_3$



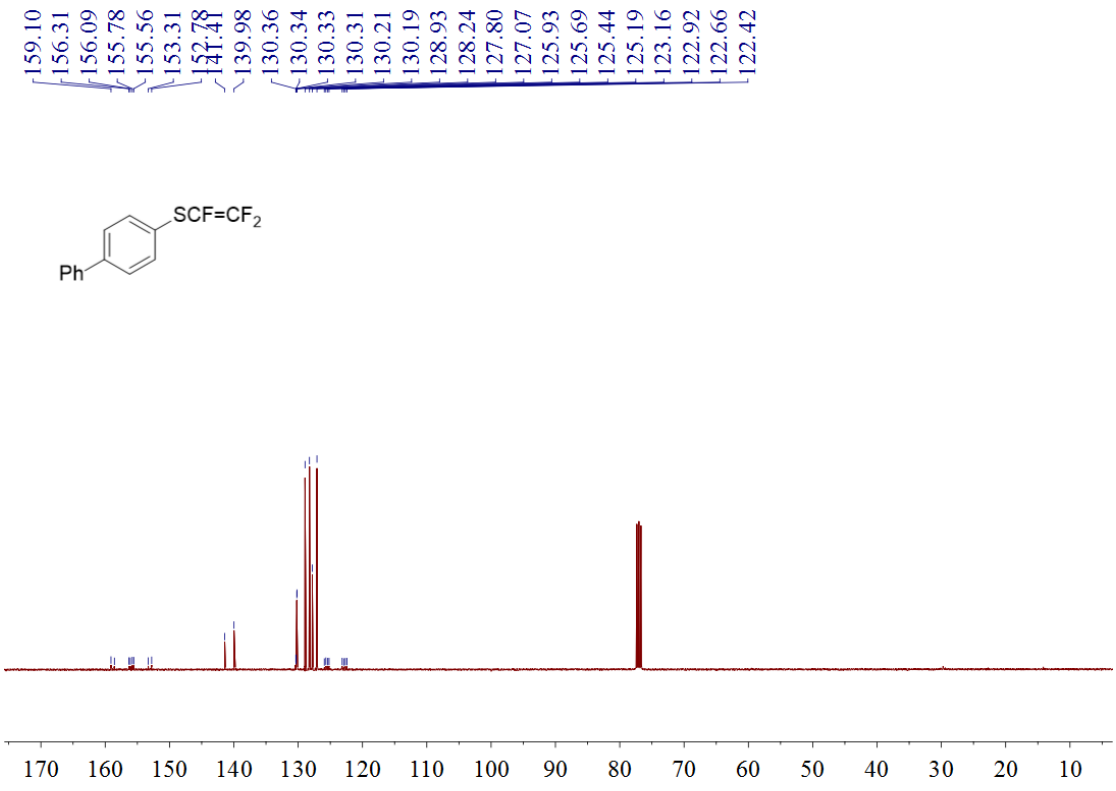
^{1}H NMR spectrum of **3d** in $CDCl_3$



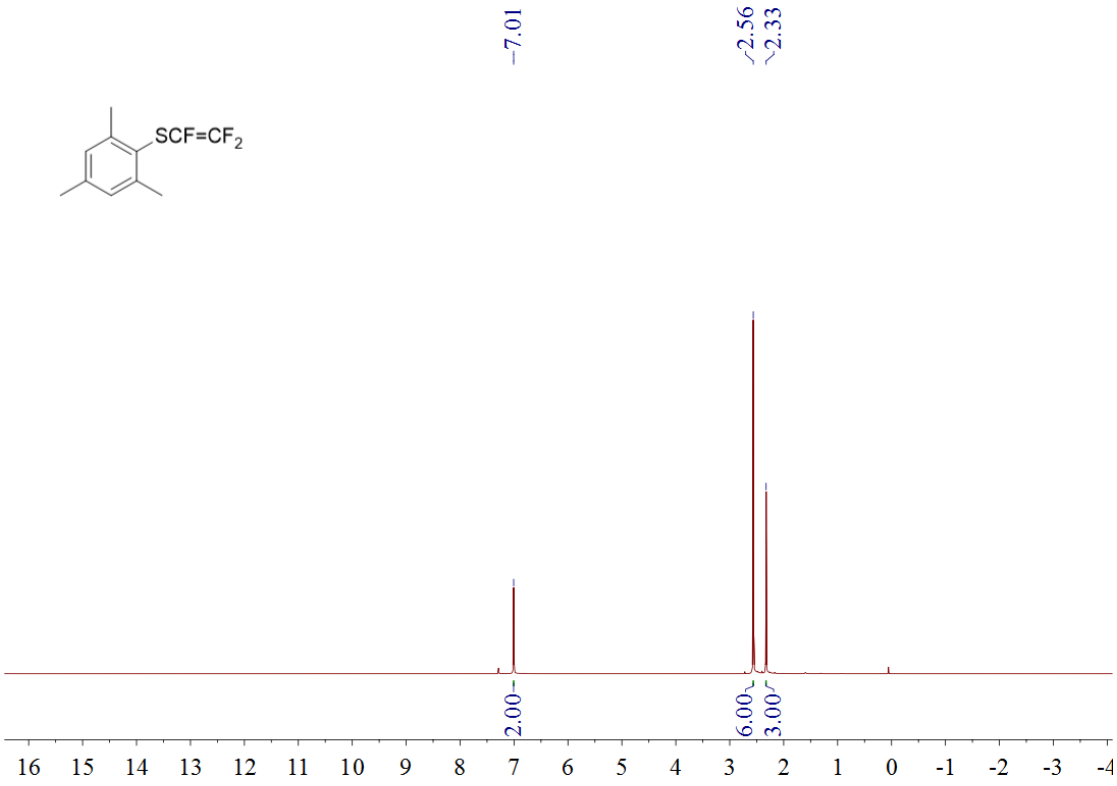
^{19}F NMR spectrum of **3d** in $CDCl_3$



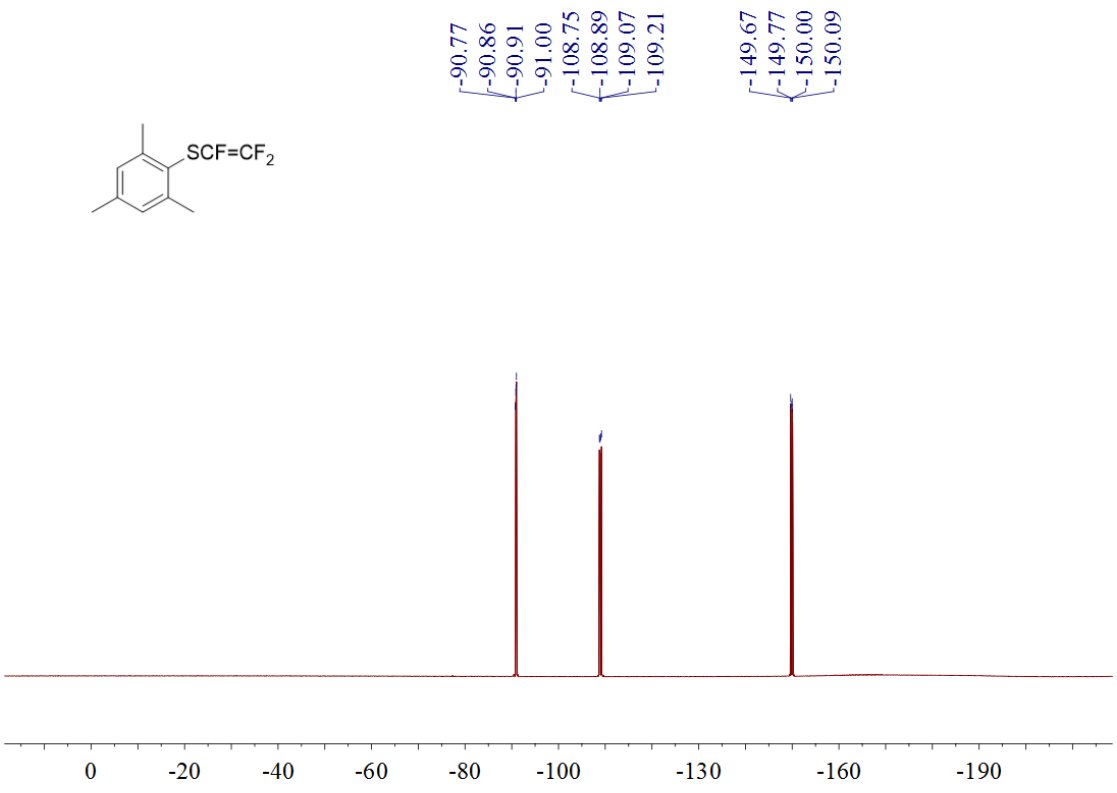
^{13}C NMR spectrum of **3d** in $CDCl_3$



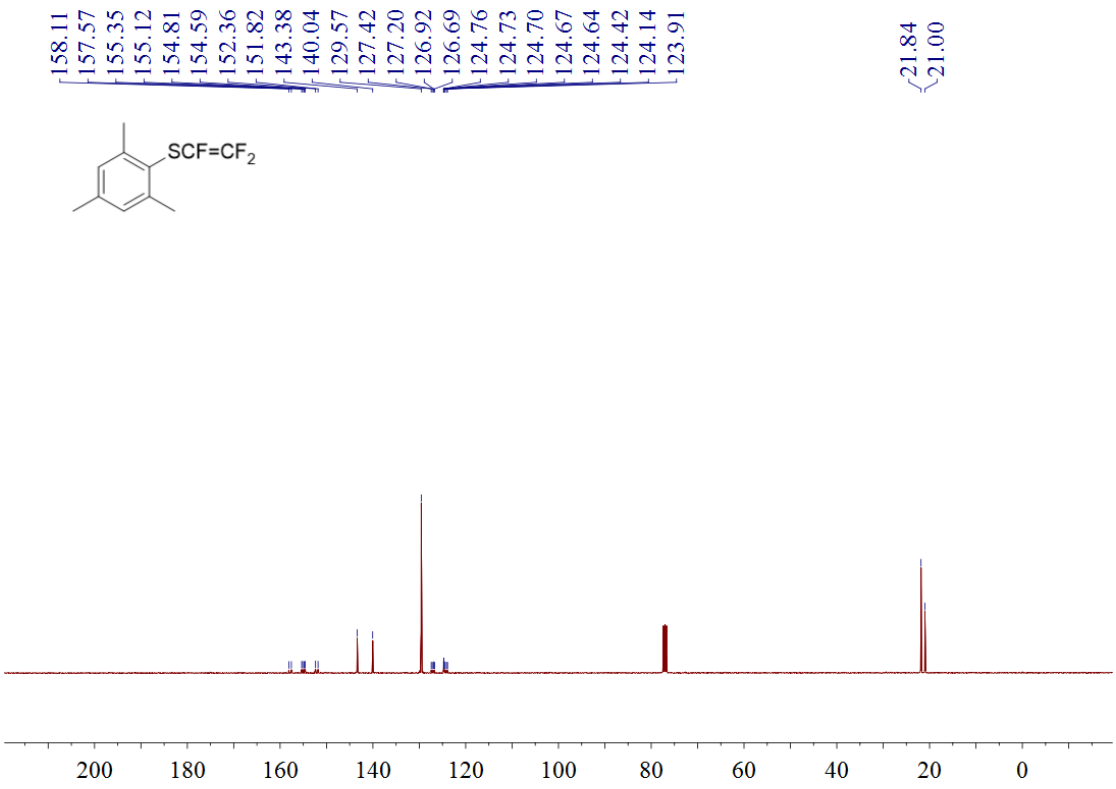
^{1}H NMR spectrum of **3e** in $CDCl_3$



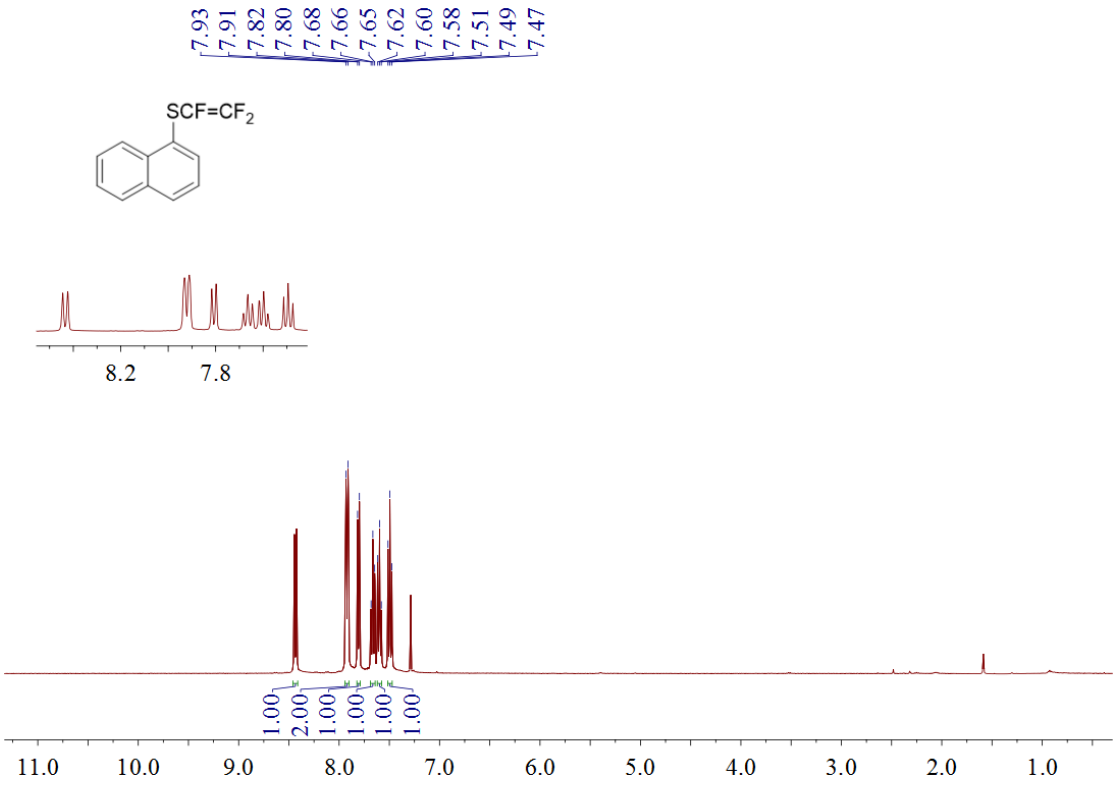
^{19}F NMR spectrum of **3e** in $CDCl_3$



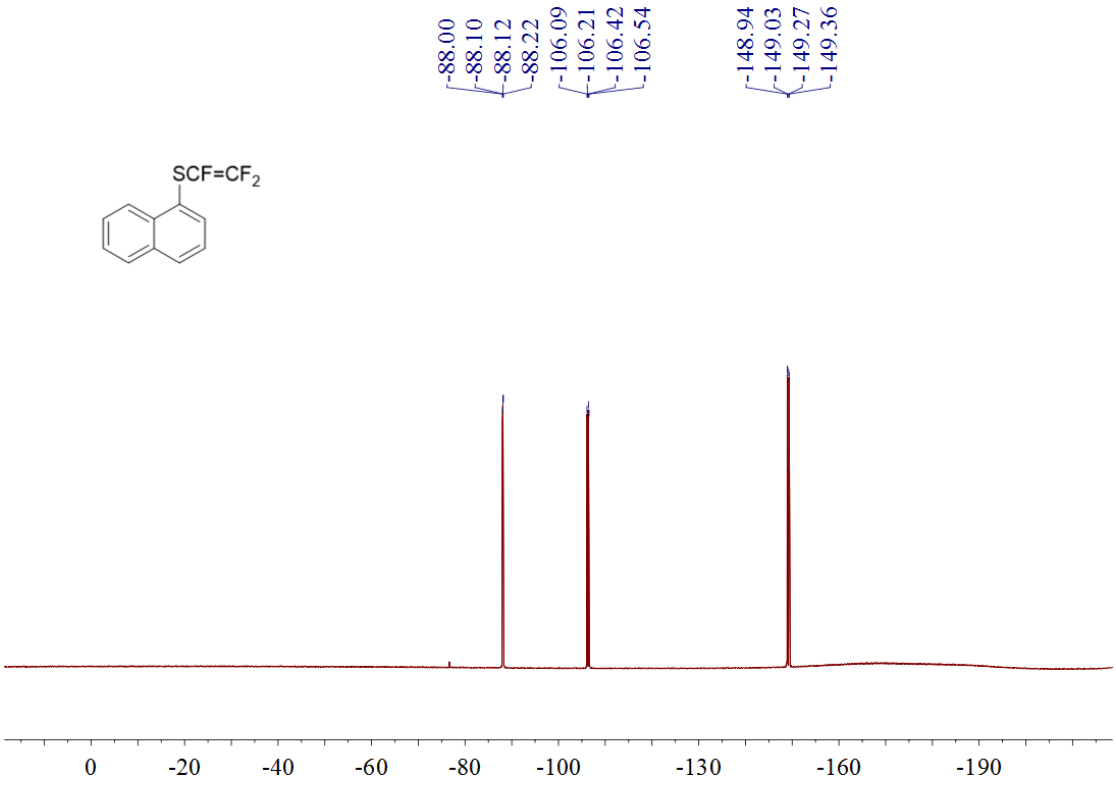
^{13}C NMR spectrum of **3e** in $CDCl_3$



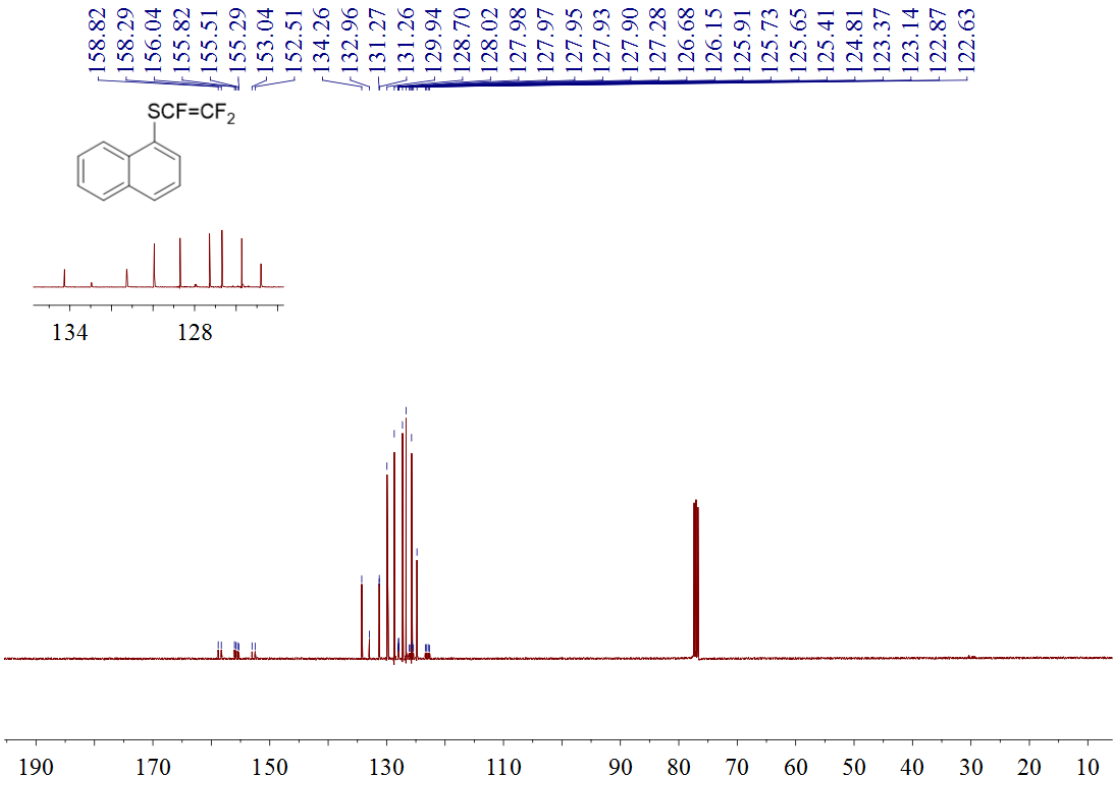
^{1}H NMR spectrum of **3f**



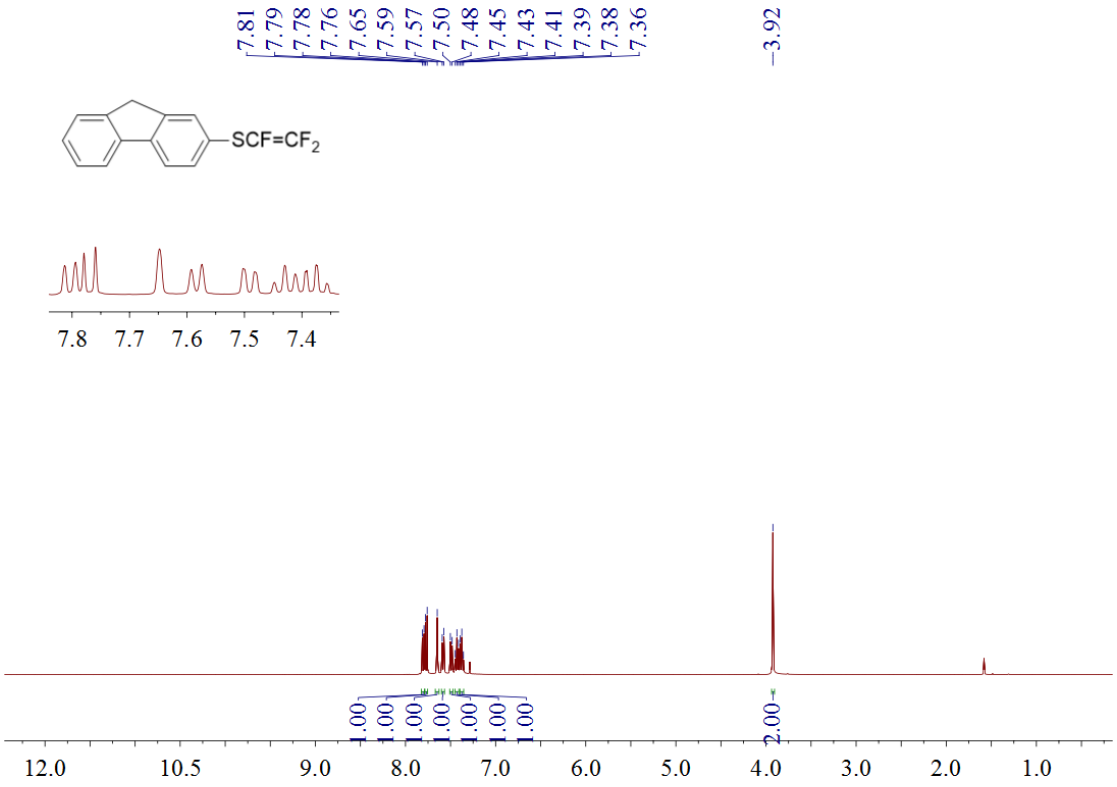
^{19}F NMR spectrum of **3f**



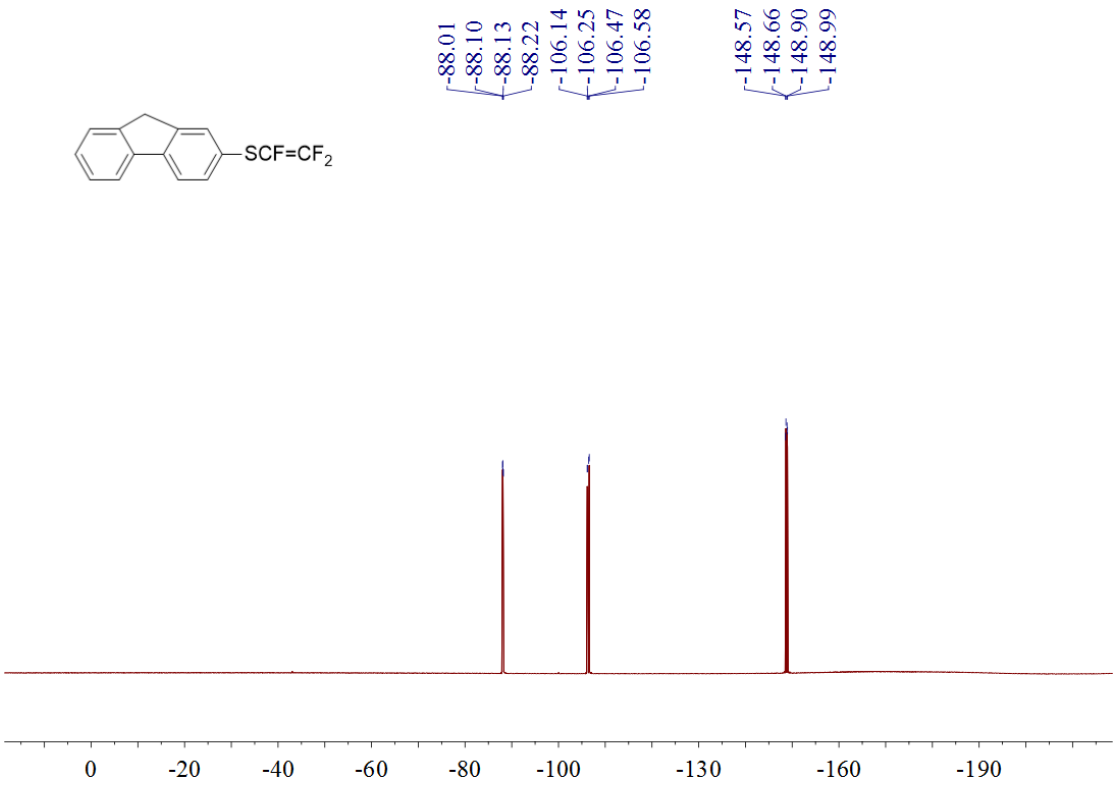
^{13}C NMR spectrum of **3f**



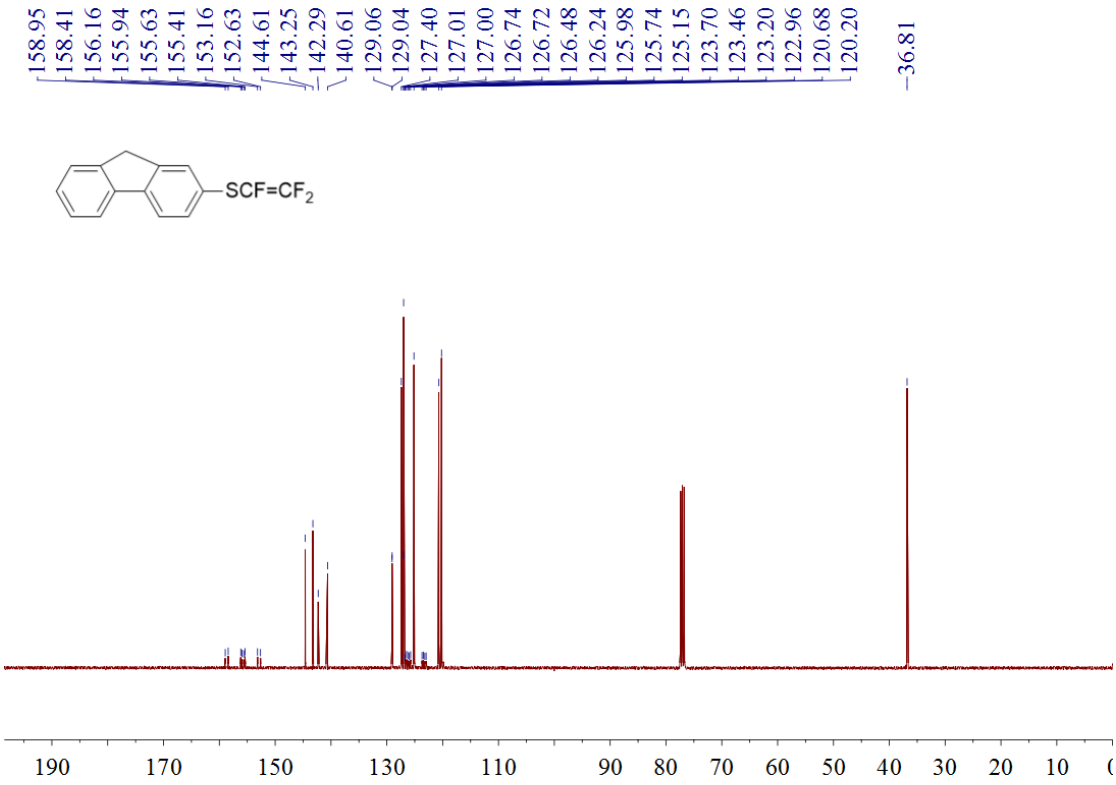
^{1}H NMR spectrum of **3g** in $CDCl_3$



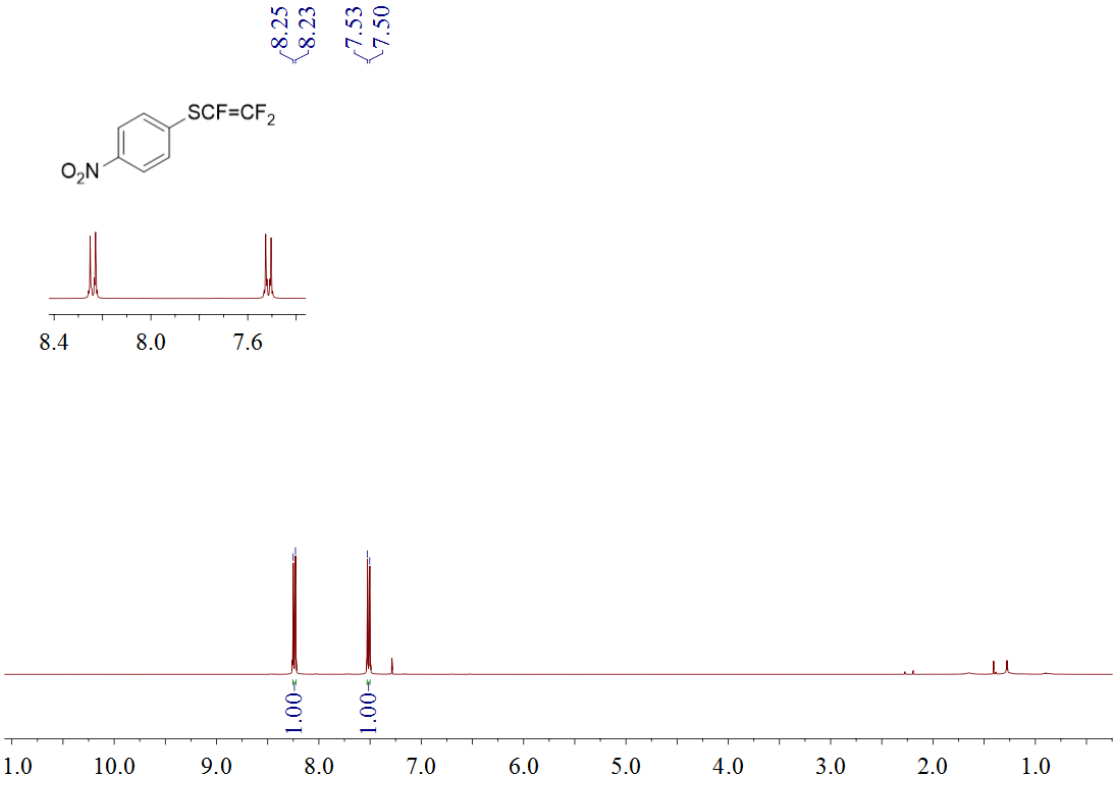
^{19}F NMR spectrum of **3g** in $CDCl_3$



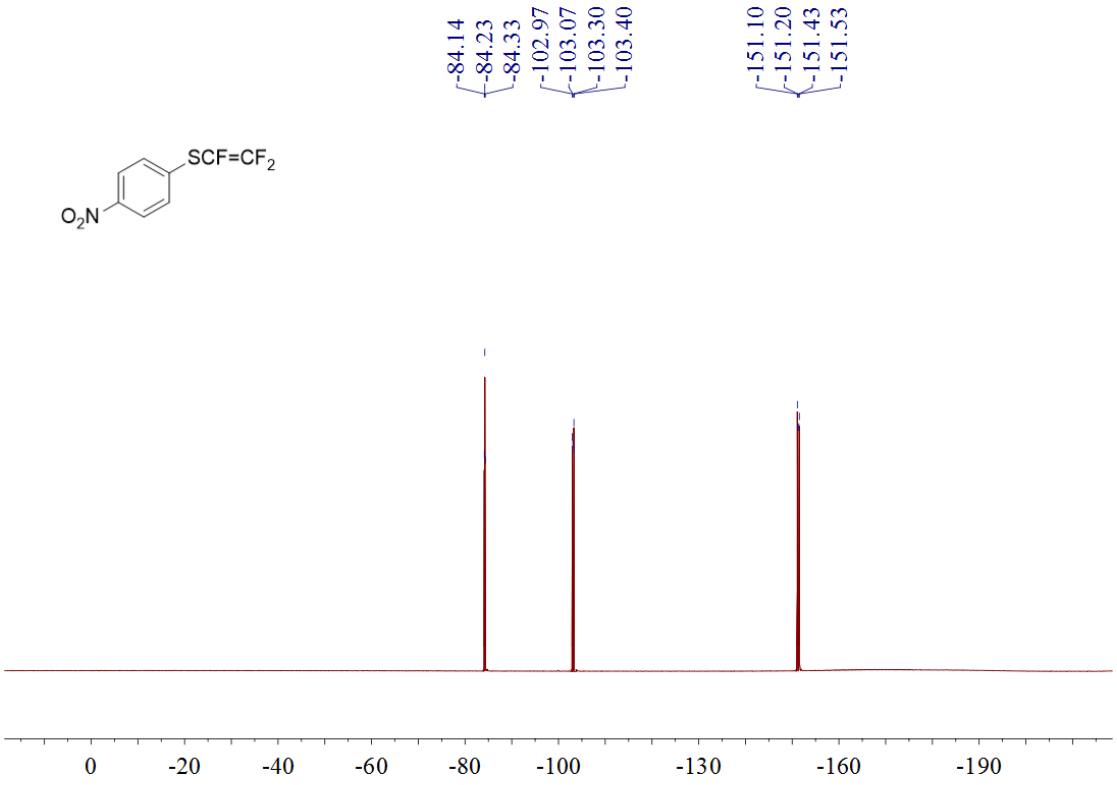
^{13}C NMR spectrum of **3g** in $CDCl_3$



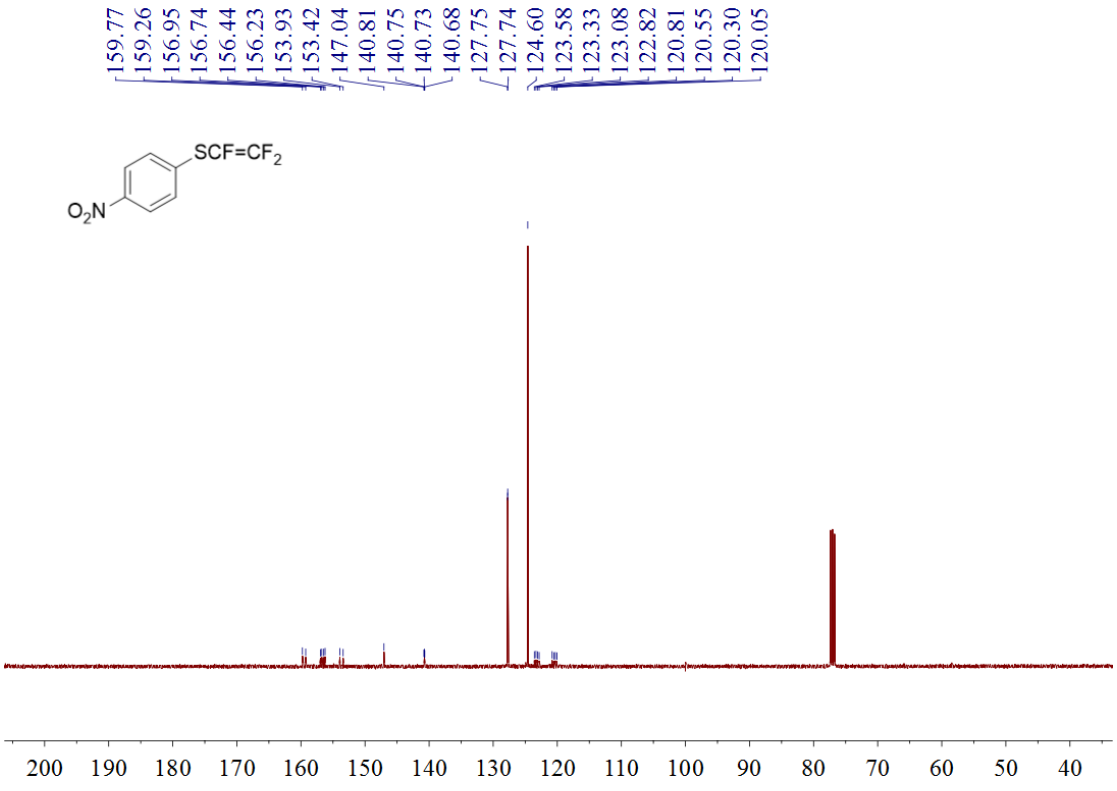
^{1}H NMR spectrum of **3h** in $CDCl_3$



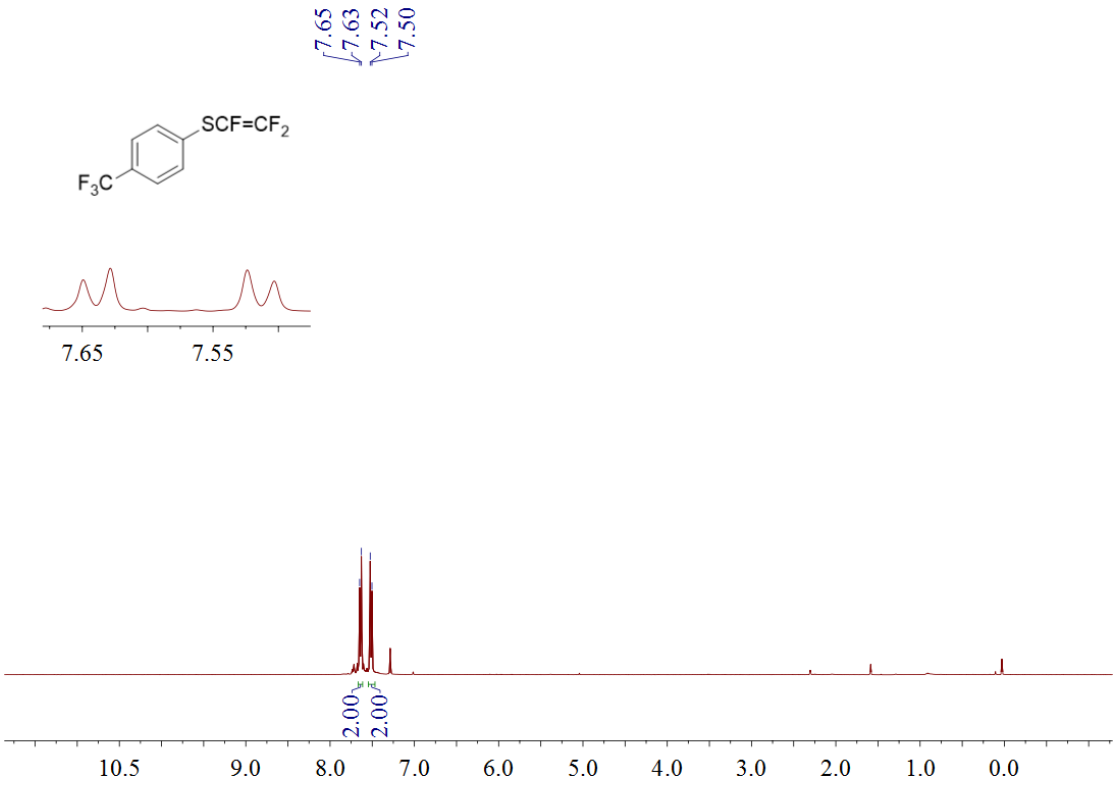
^{19}F NMR spectrum of **3h** in $CDCl_3$



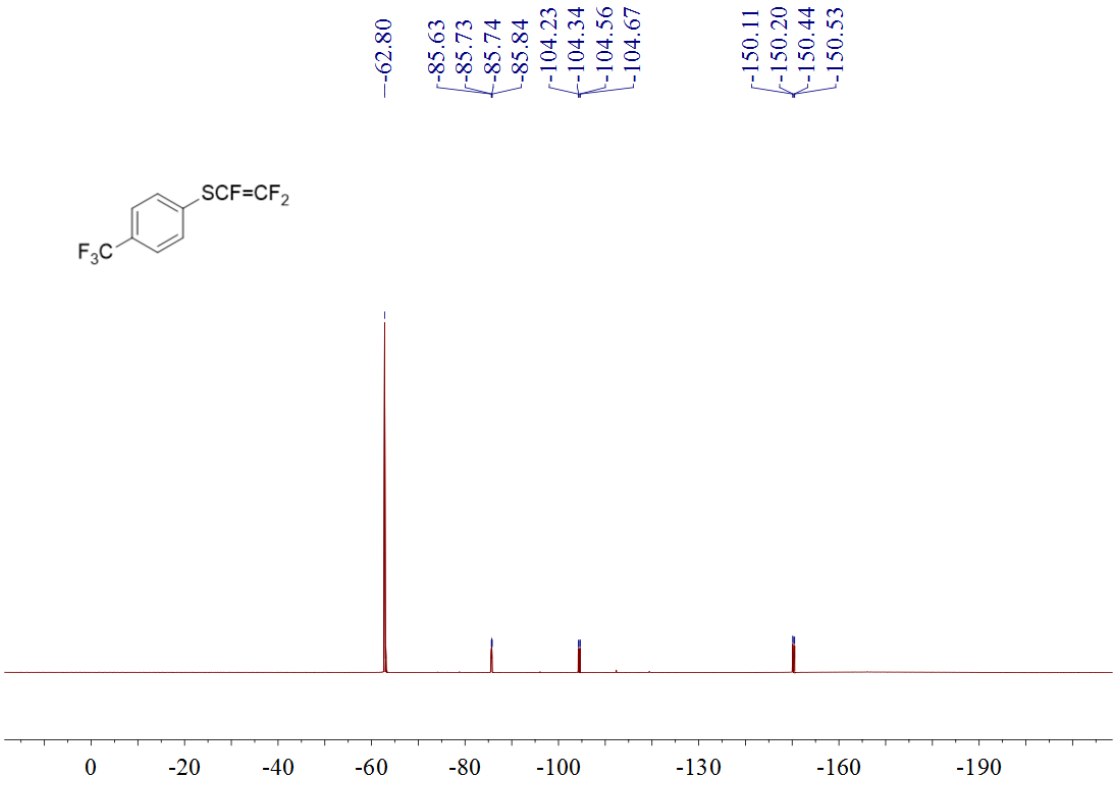
^{13}C NMR spectrum of **3h** in $CDCl_3$



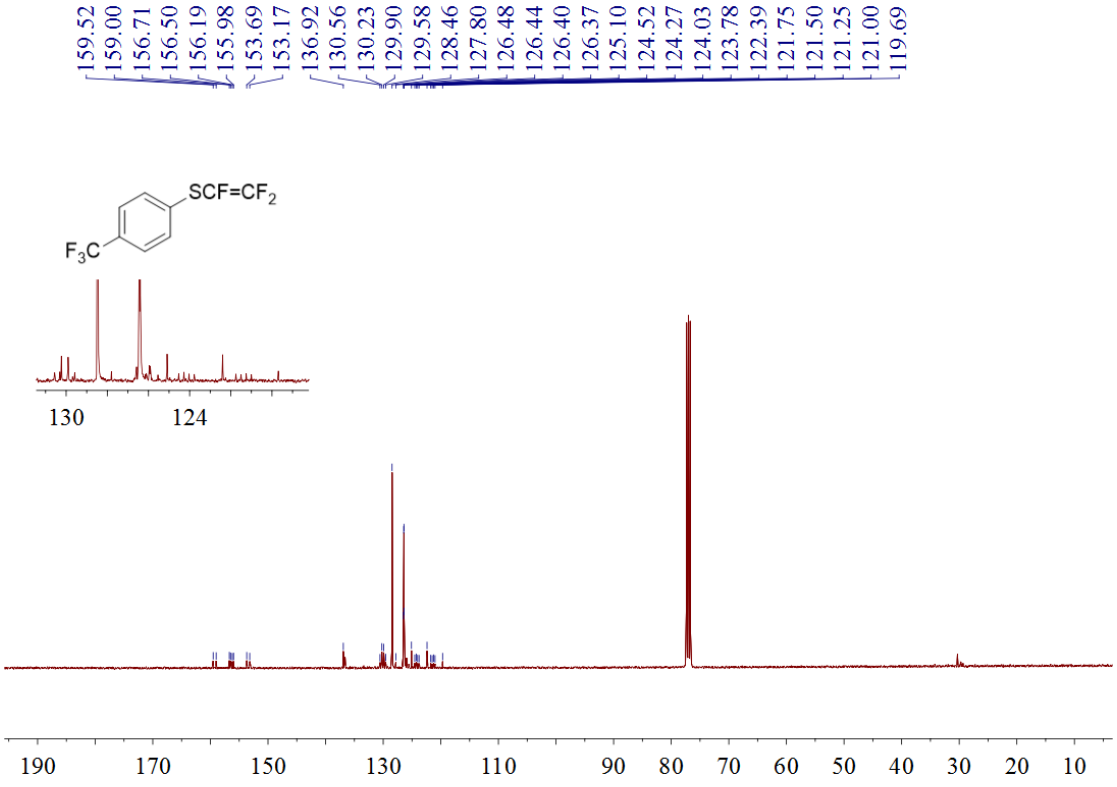
^{1}H NMR spectrum of **3i** in $CDCl_3$



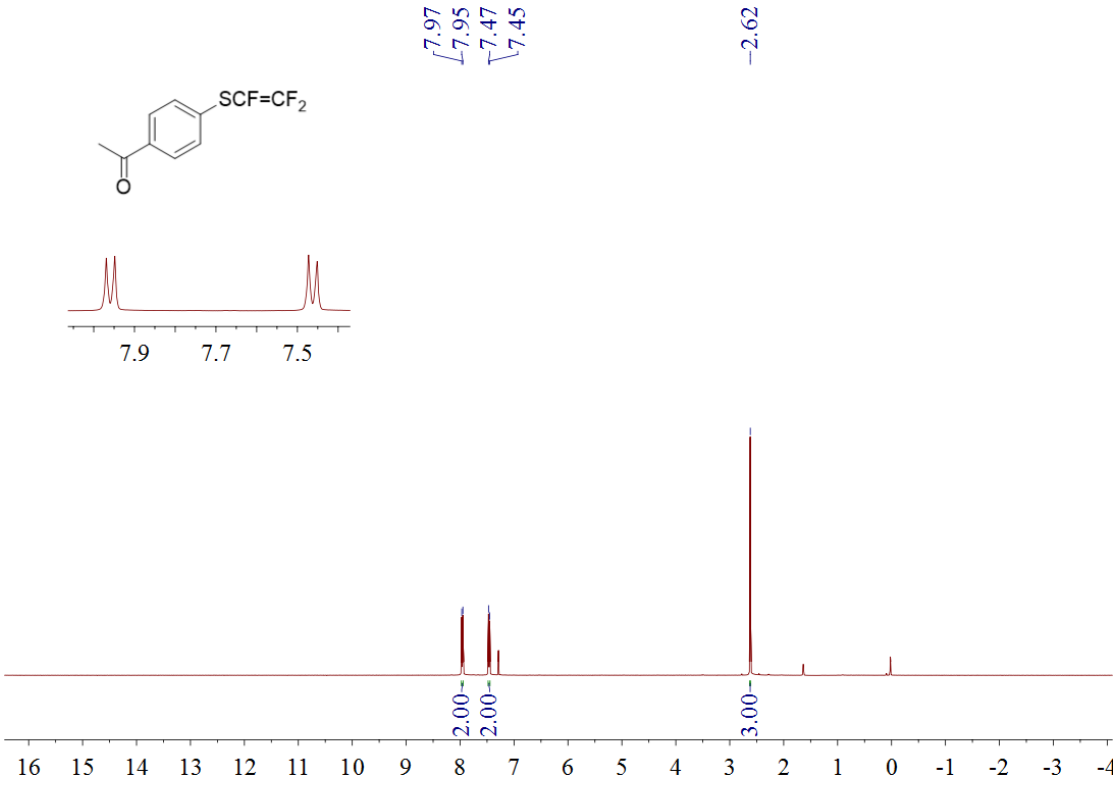
^{19}F NMR spectrum of **3i** in $CDCl_3$



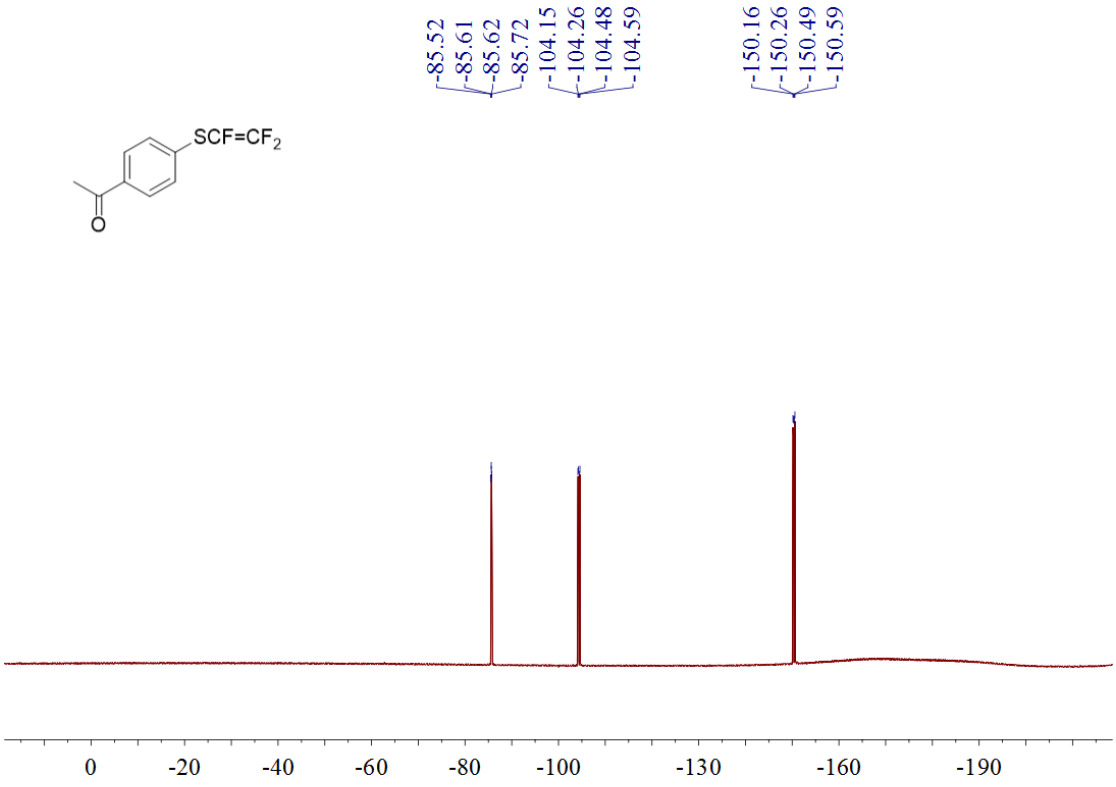
^{13}C NMR spectrum of **3i** in $CDCl_3$



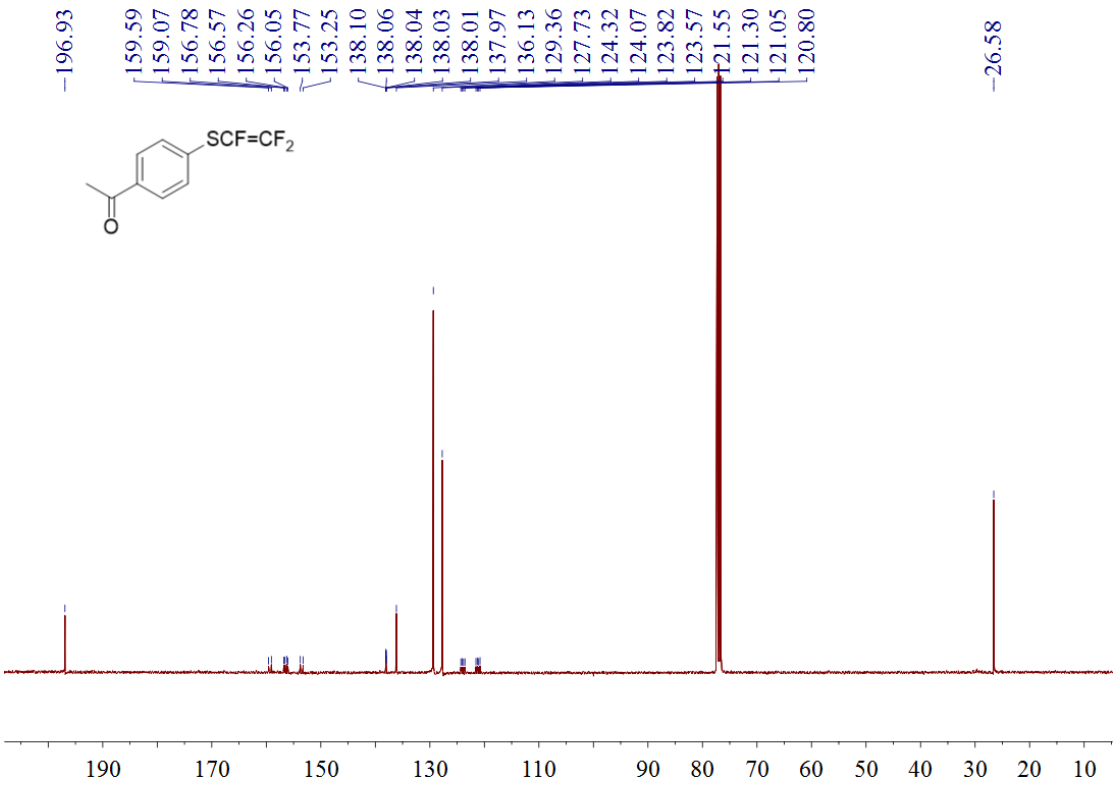
^{1}H NMR spectrum of **3j** in $CDCl_3$



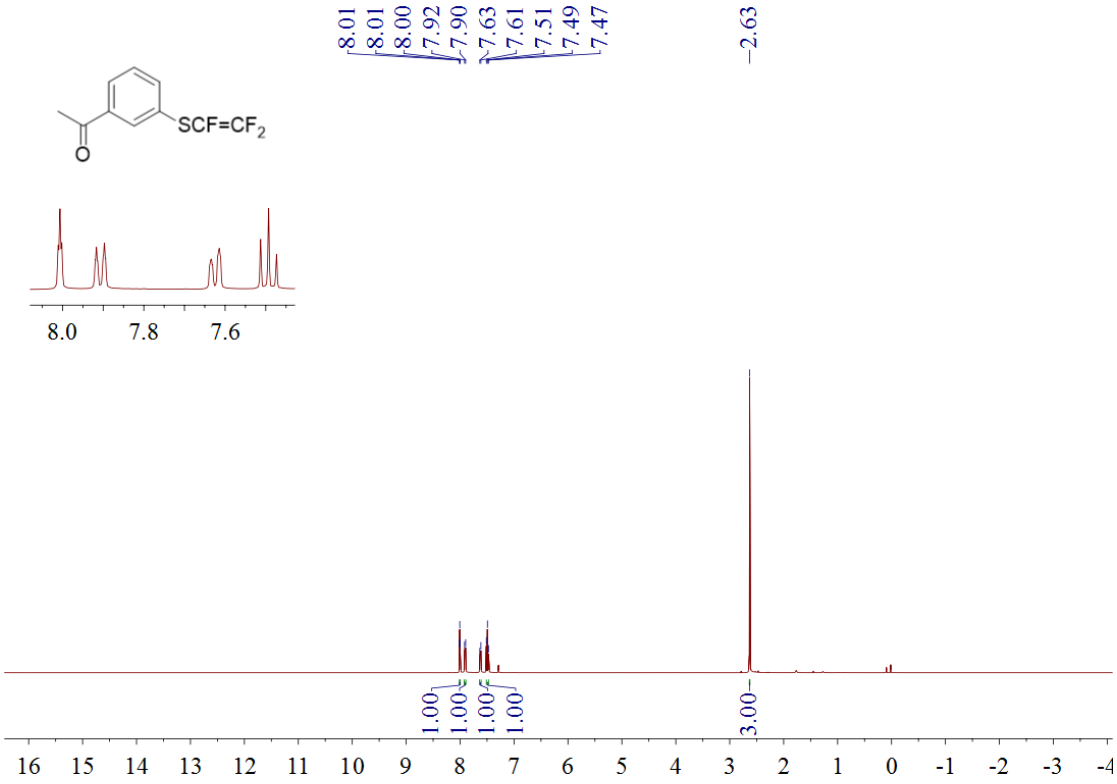
^{19}F NMR spectrum of **3j** in $CDCl_3$



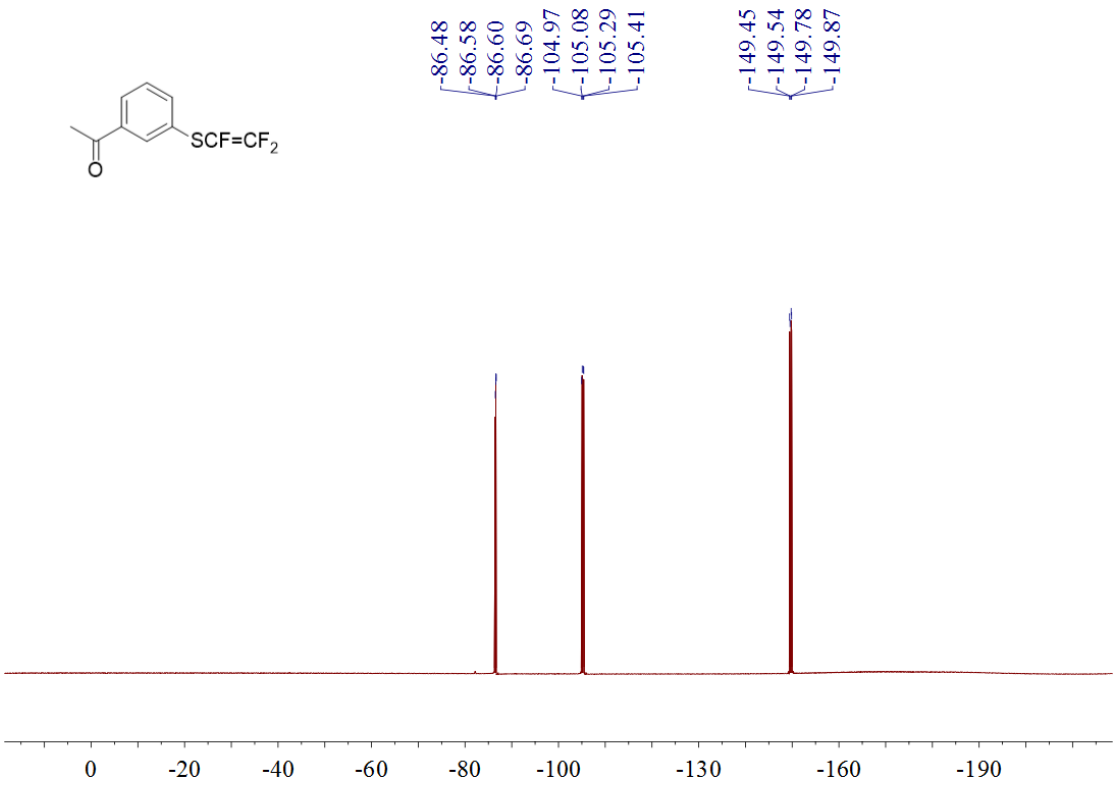
^{13}C NMR spectrum of **3j** in $CDCl_3$



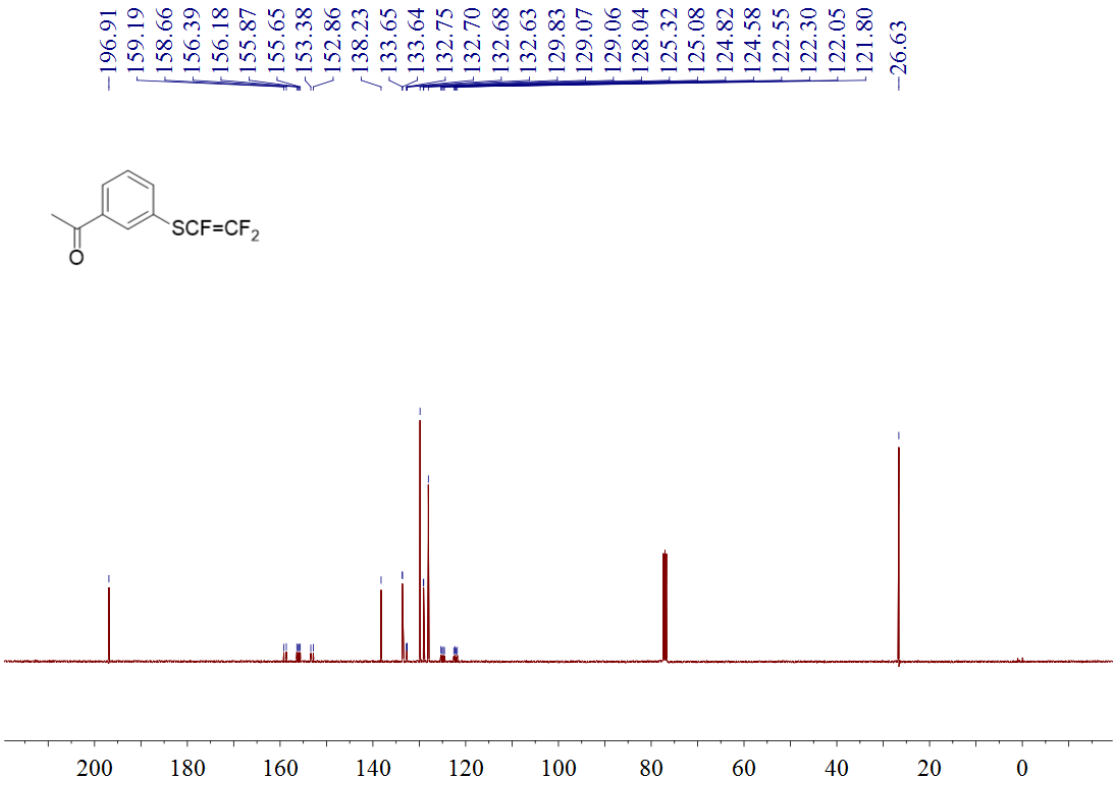
^{19}F NMR spectrum of **3k** in $CDCl_3$



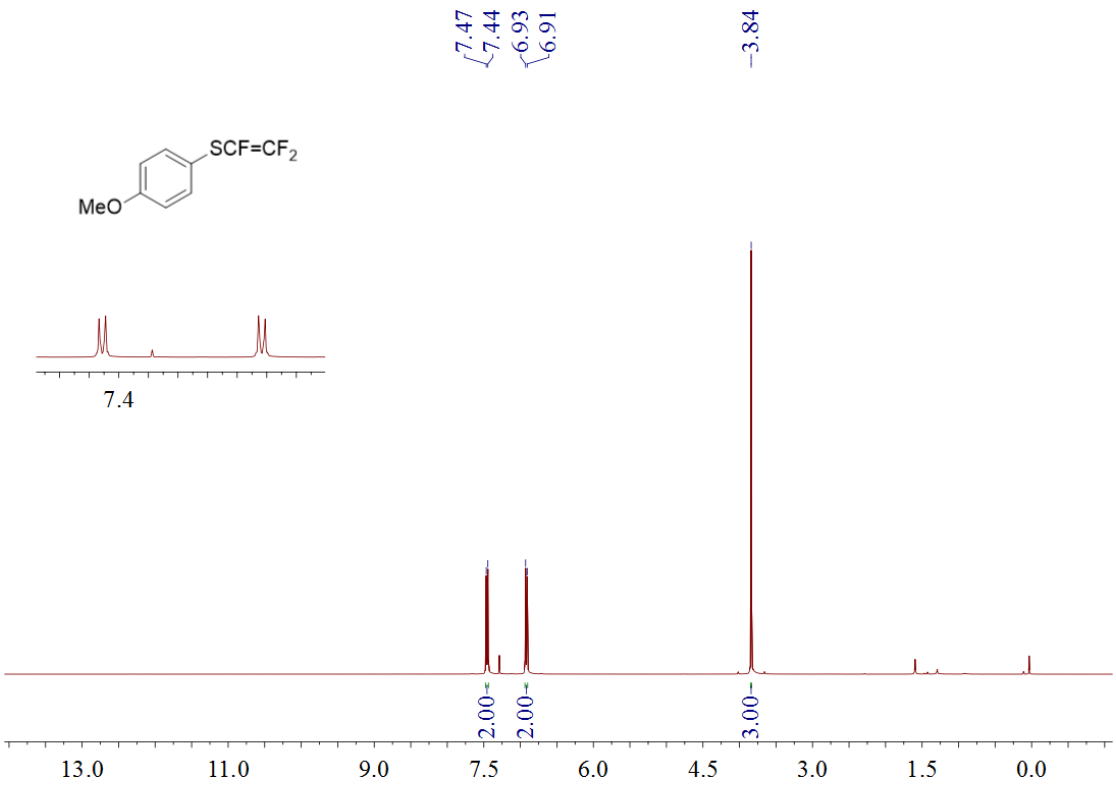
^{1}H NMR spectrum of **3k** in $CDCl_3$



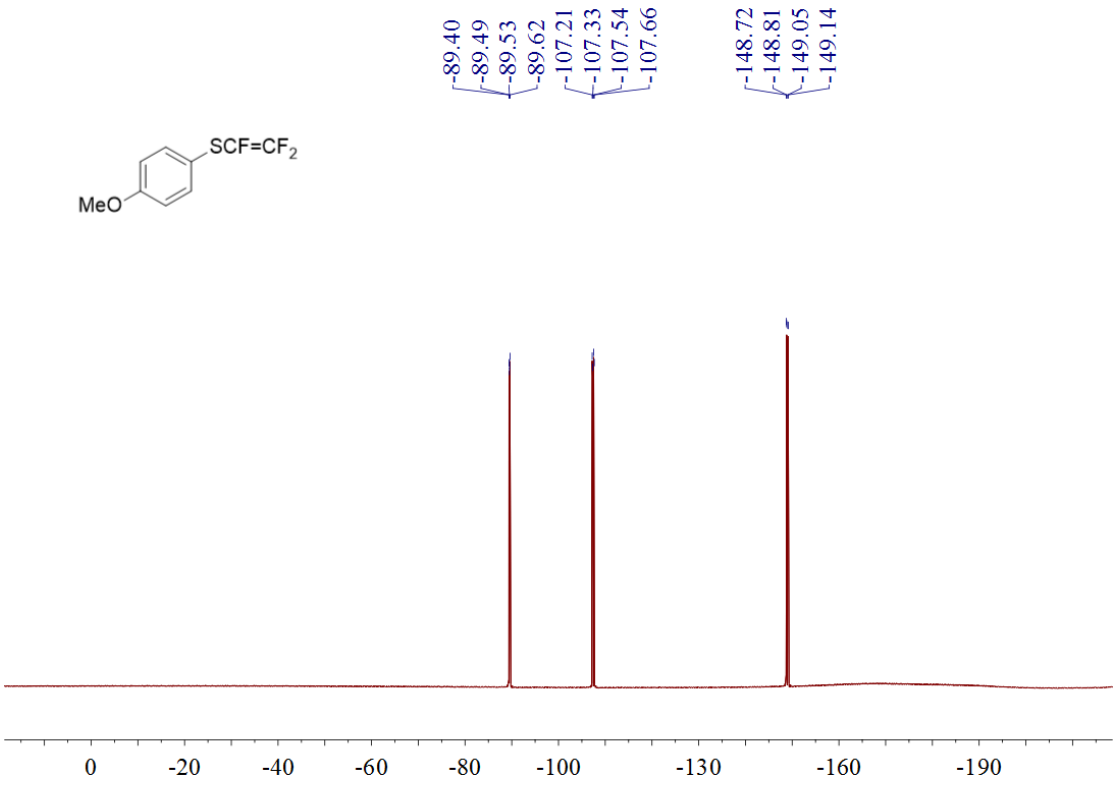
^{13}C NMR spectrum of **3k** in $CDCl_3$



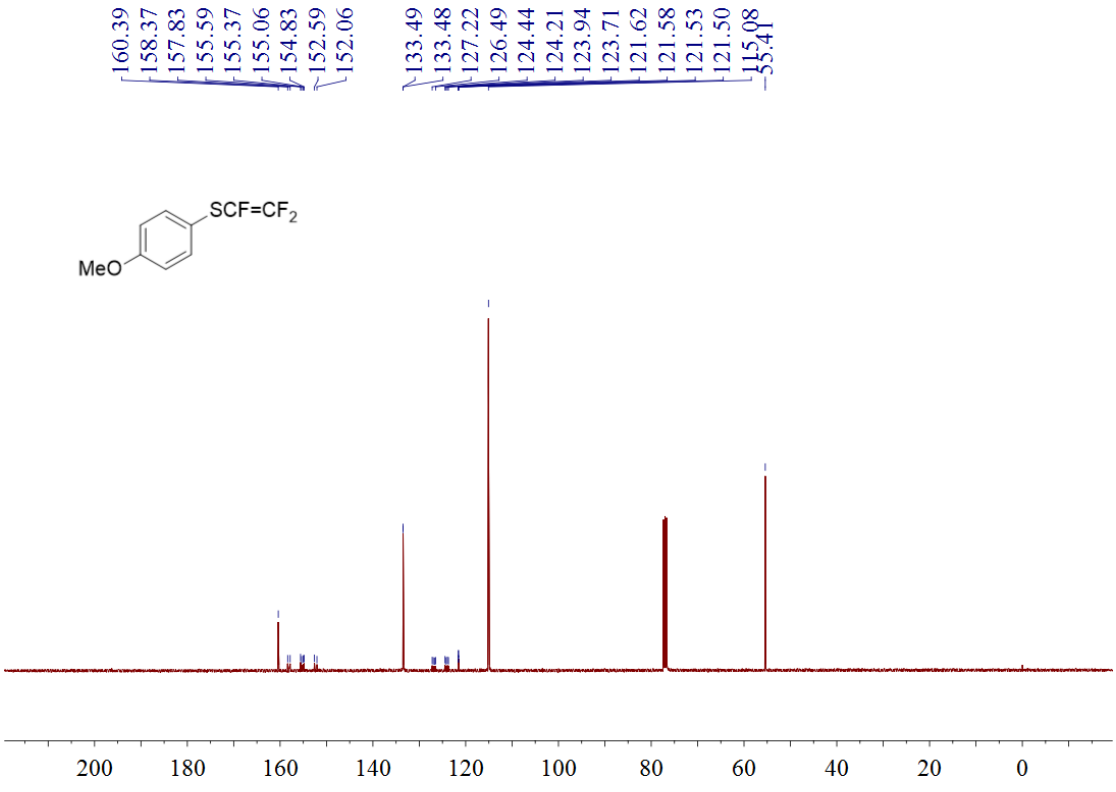
^{1}H NMR spectrum of **3l** in $CDCl_3$



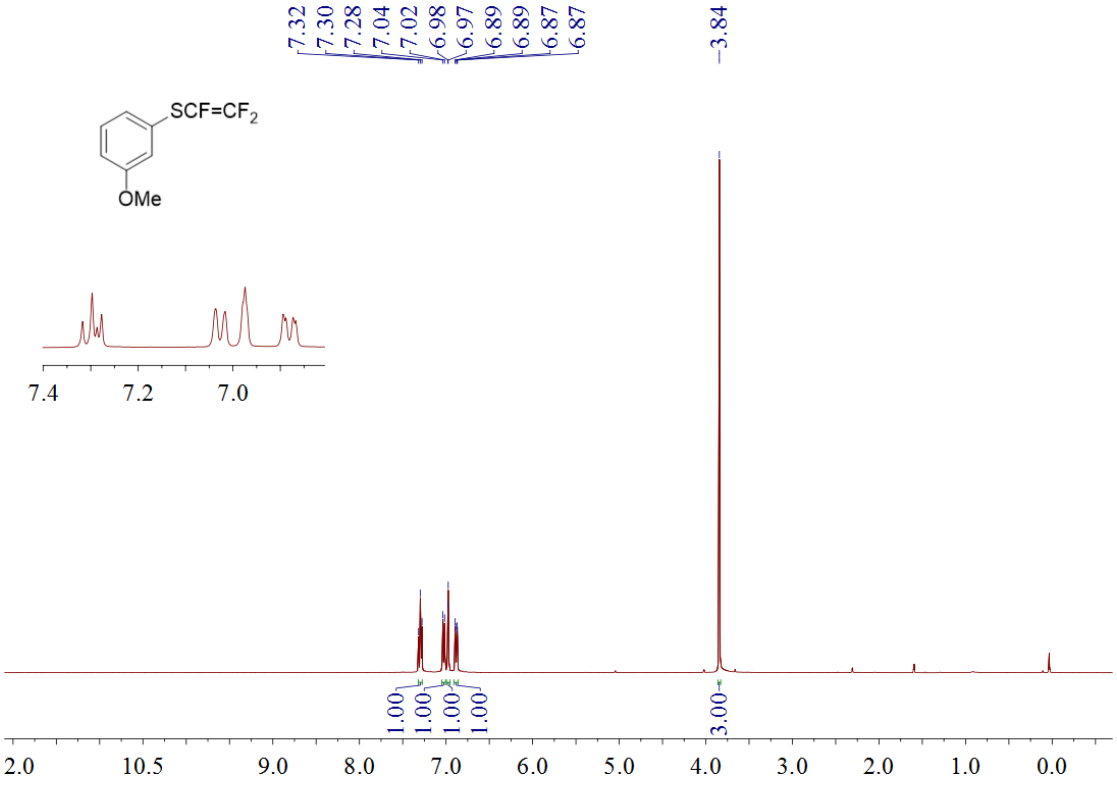
^{19}F NMR spectrum of **3l** in $CDCl_3$



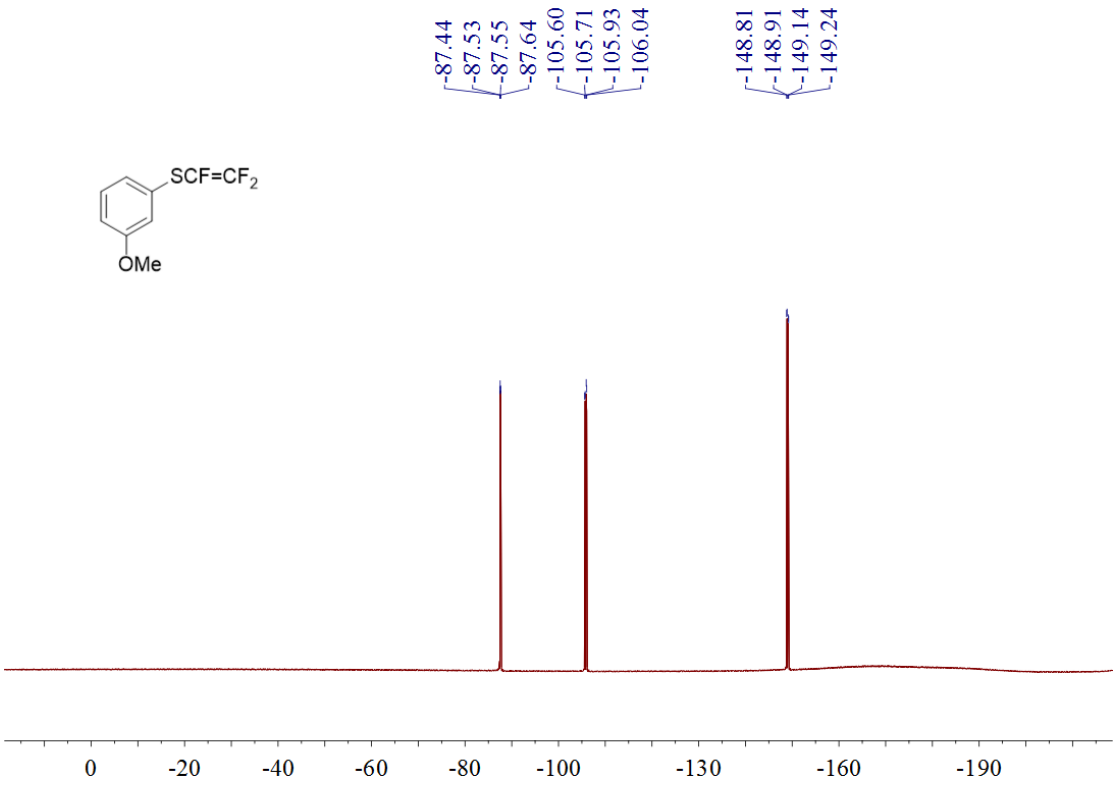
^{13}C NMR spectrum of **3l** in $CDCl_3$



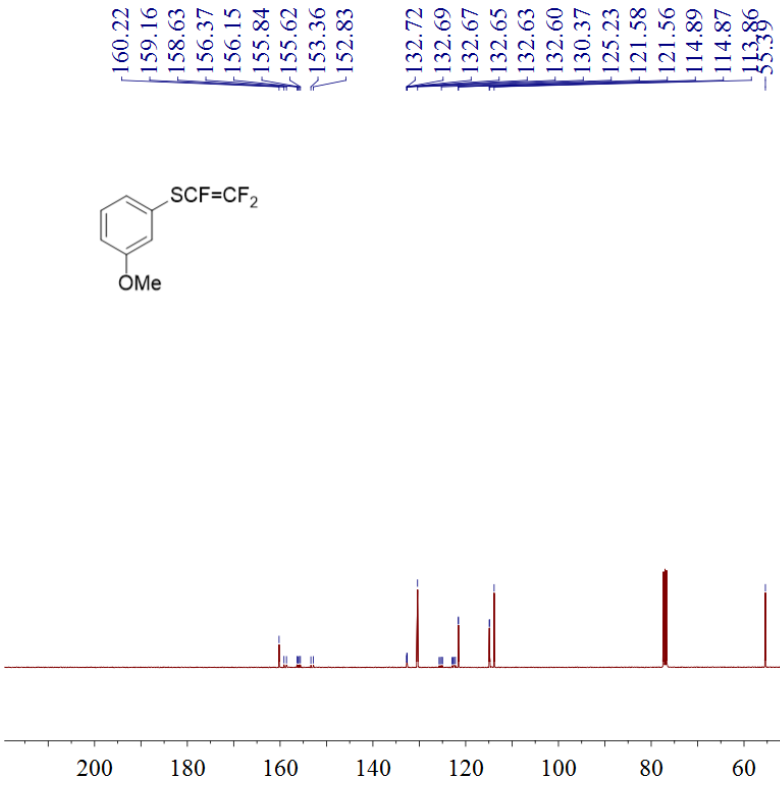
^{1}H NMR spectrum of **3m** in $CDCl_3$



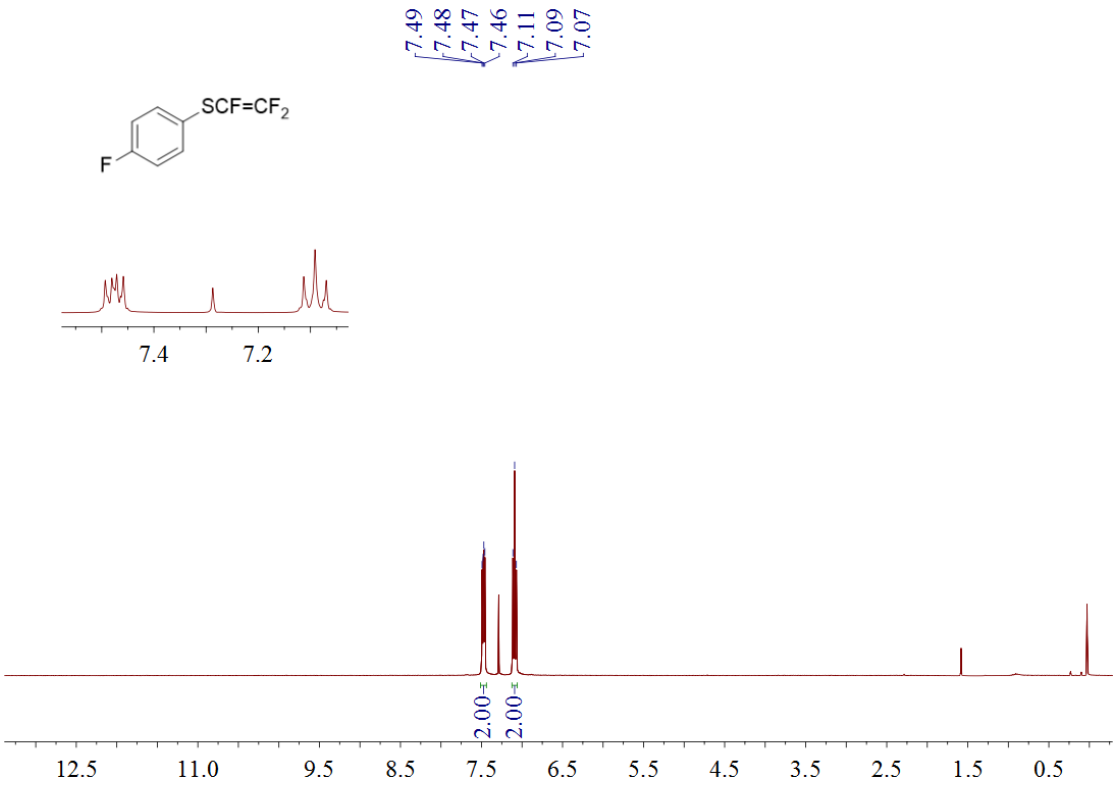
^{19}F NMR spectrum of **3m** in $CDCl_3$



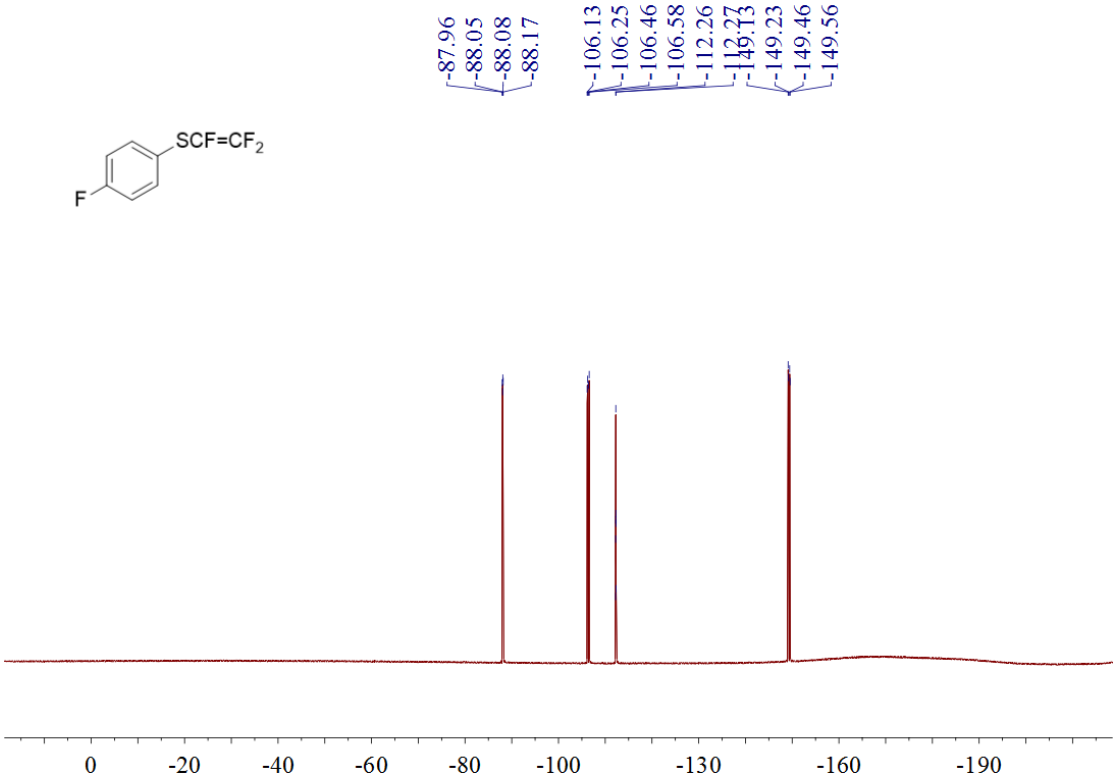
^{13}C NMR spectrum of **3m** in $CDCl_3$



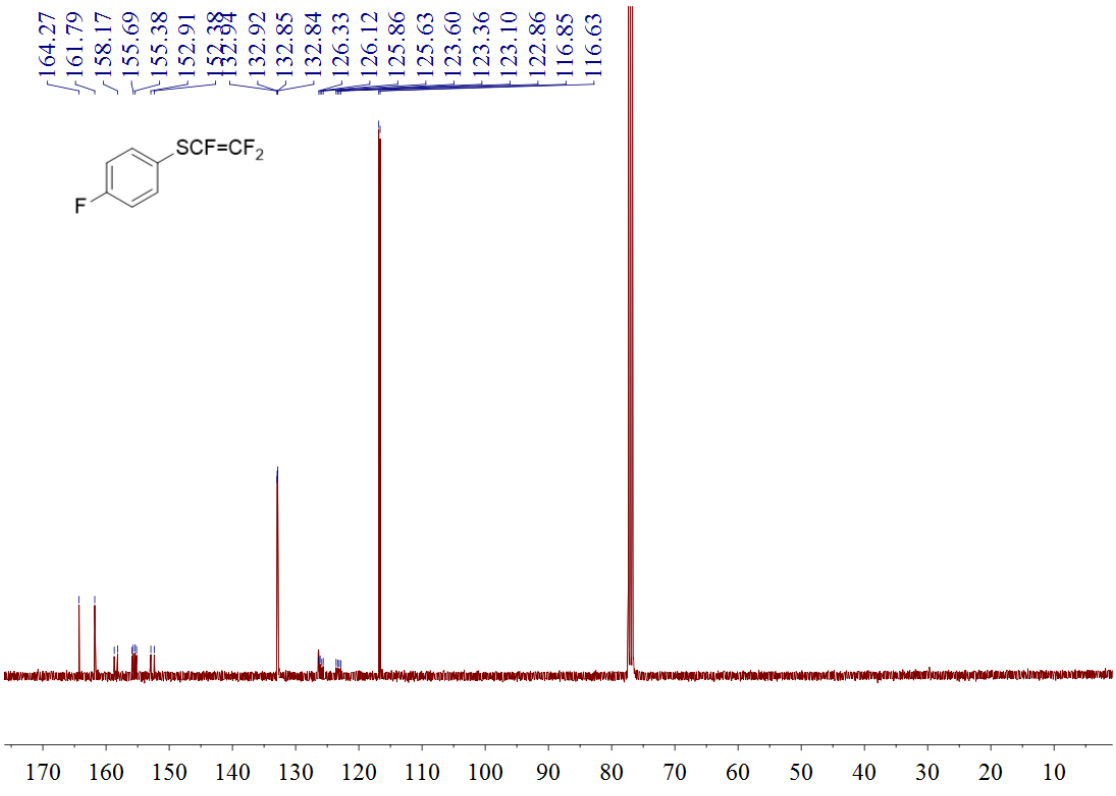
^{1}H NMR spectrum of **3n** in $CDCl_3$



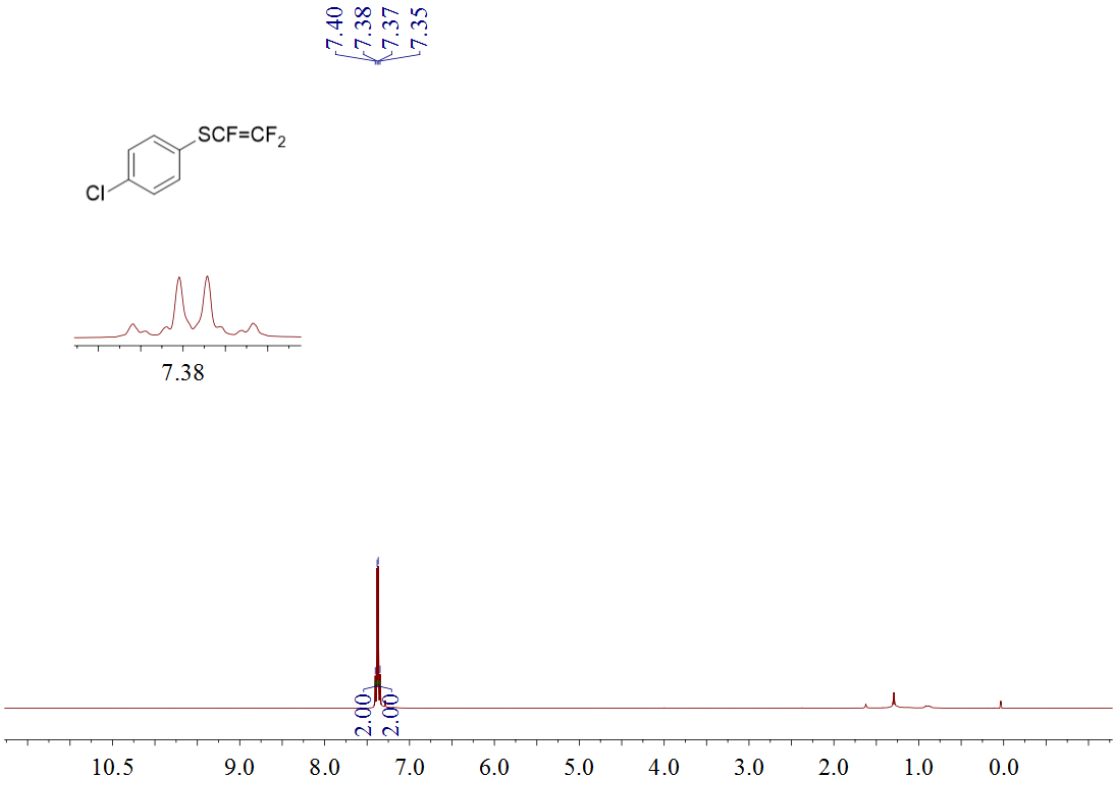
^{19}F NMR spectrum of **3n** in $CDCl_3$



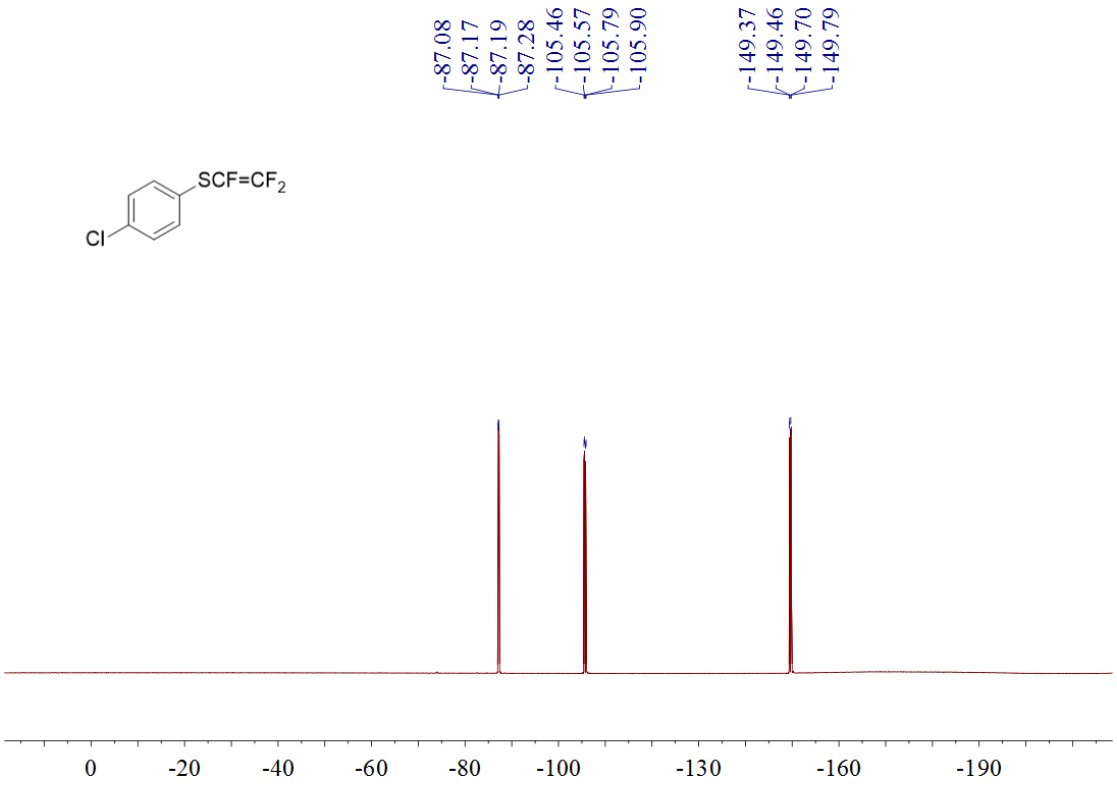
^{13}C NMR spectrum of **3n** in $CDCl_3$



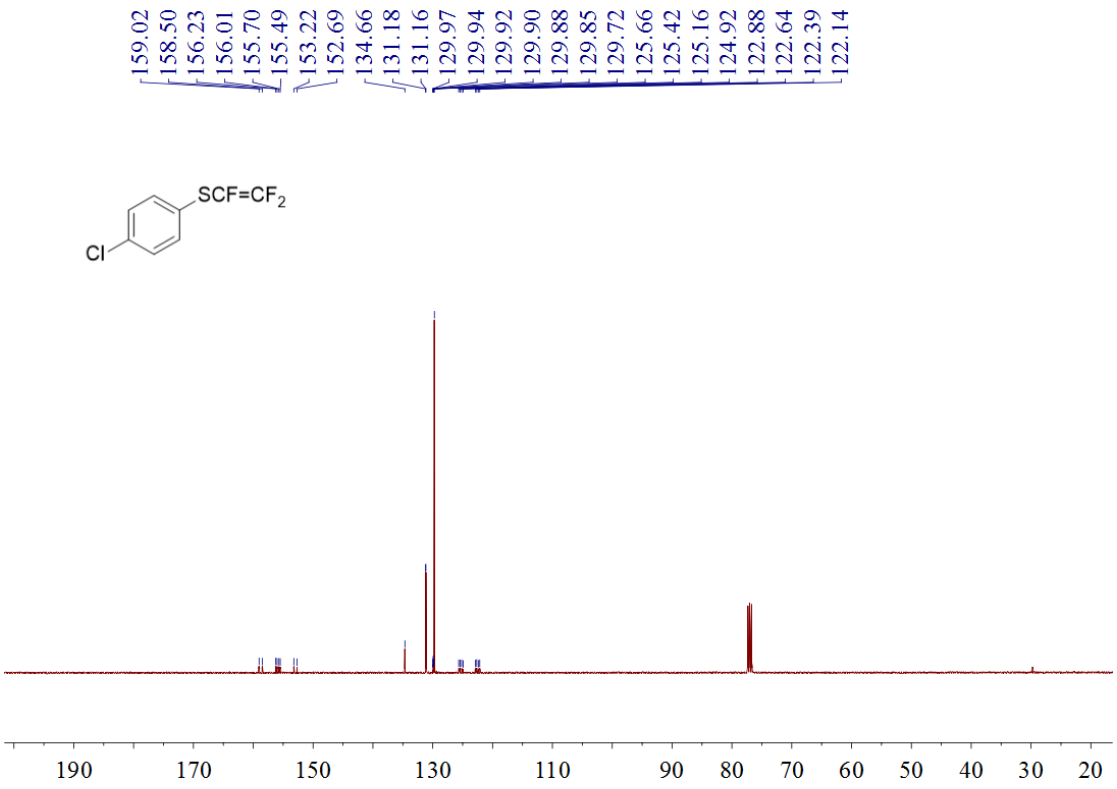
^{1}H NMR spectrum of **3o** in $CDCl_3$



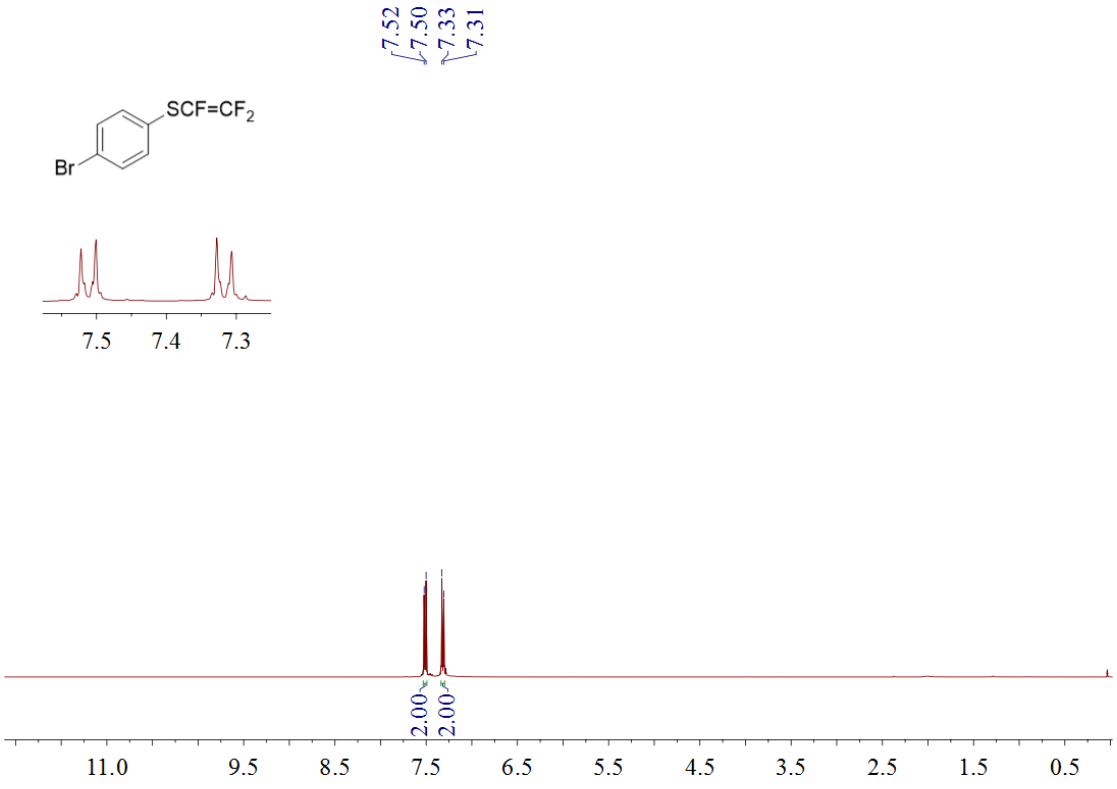
^{19}F NMR spectrum of **3o** in $CDCl_3$



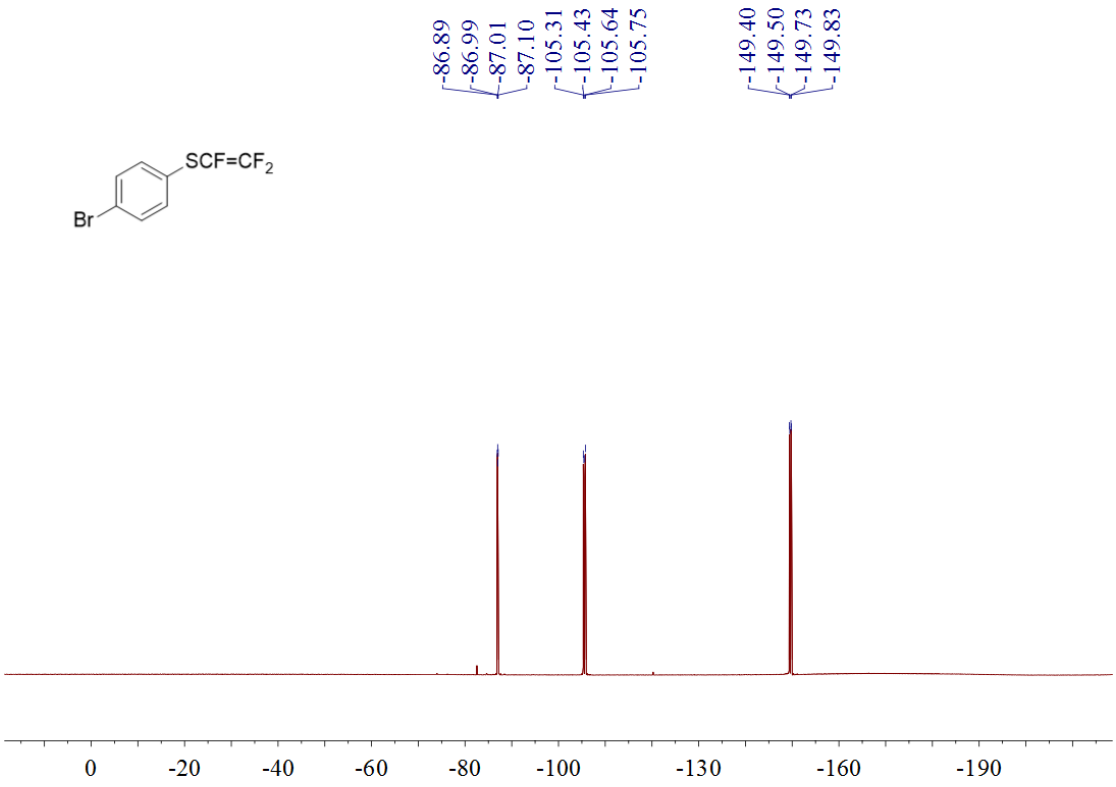
^{13}C NMR spectrum of **3o** in $CDCl_3$



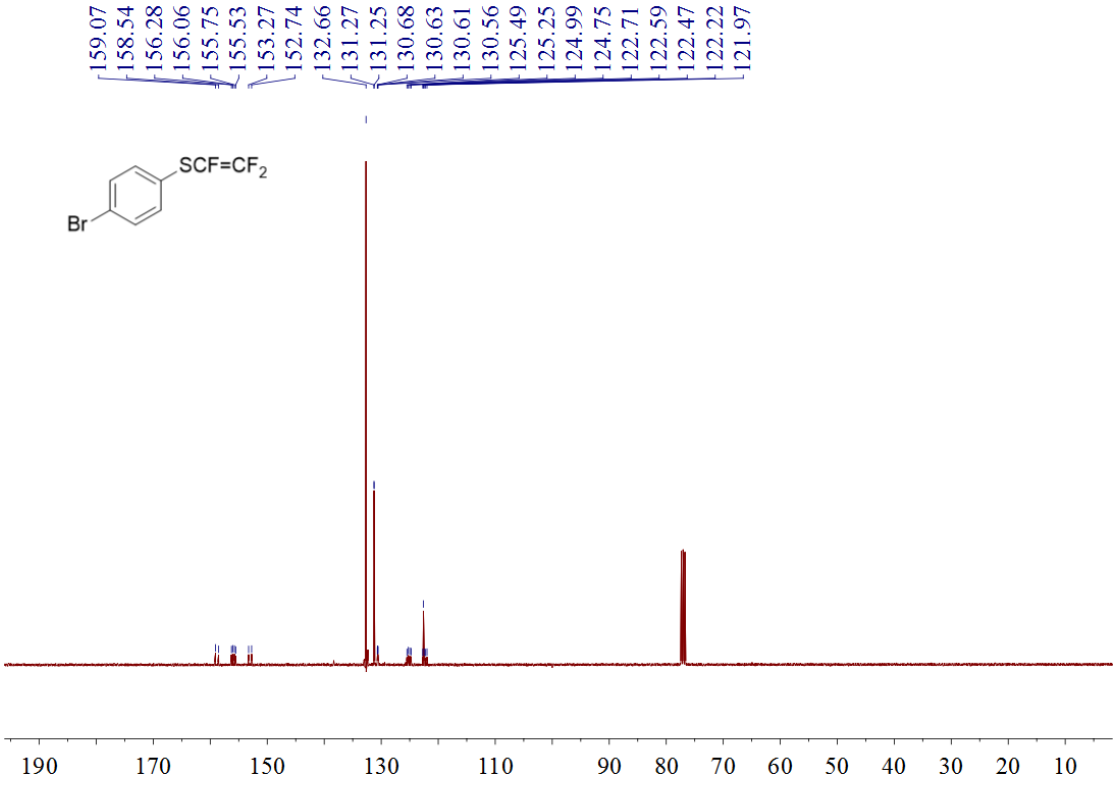
^{1}H NMR spectrum of **3p** in $CDCl_3$



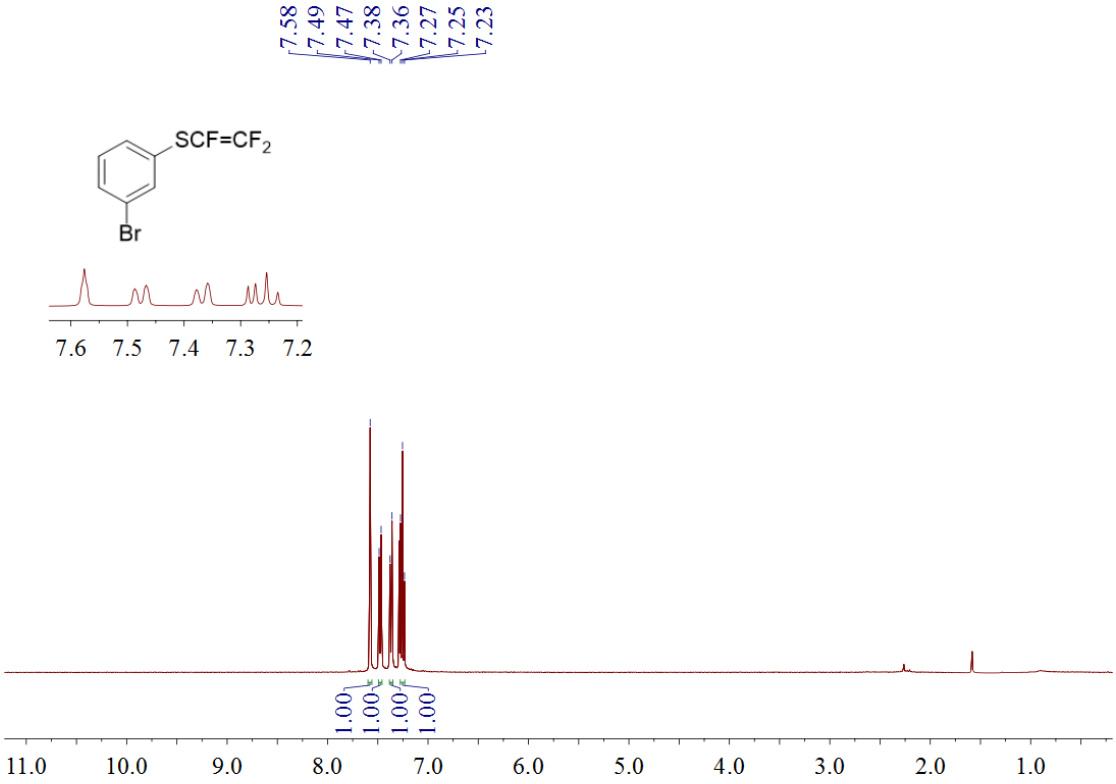
^{19}F NMR spectrum of **3p** in $CDCl_3$



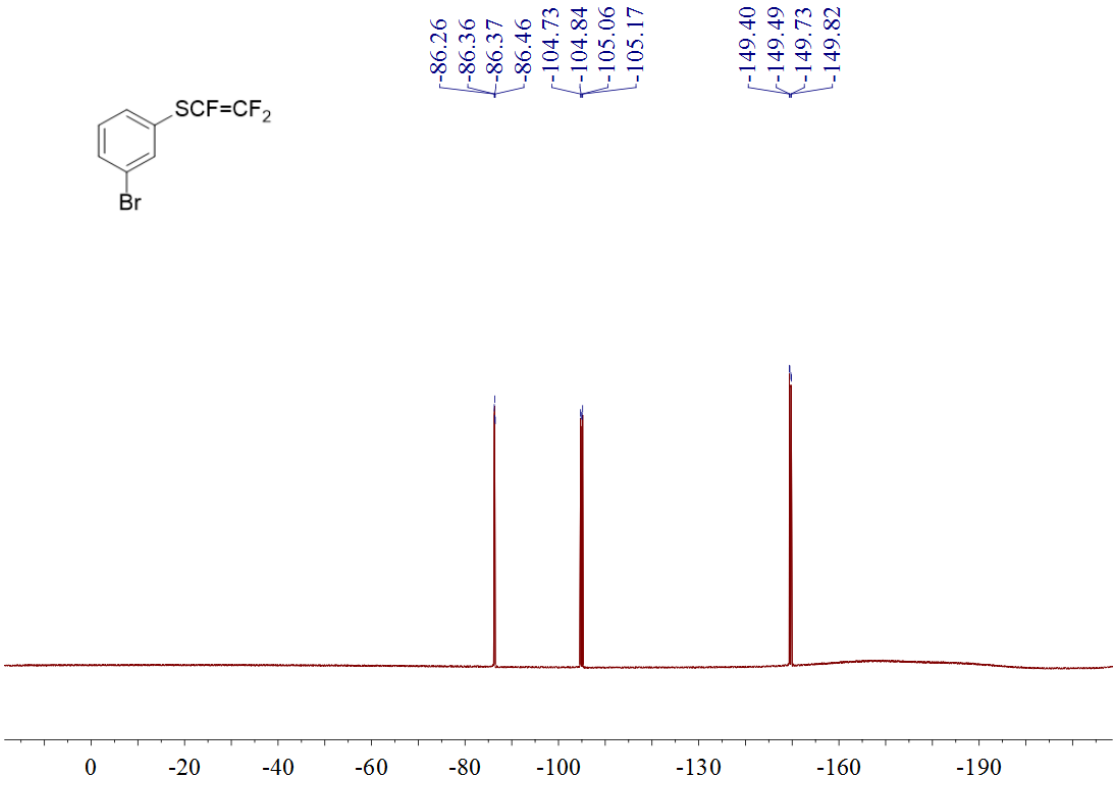
^{13}C NMR spectrum of **3p** in $CDCl_3$



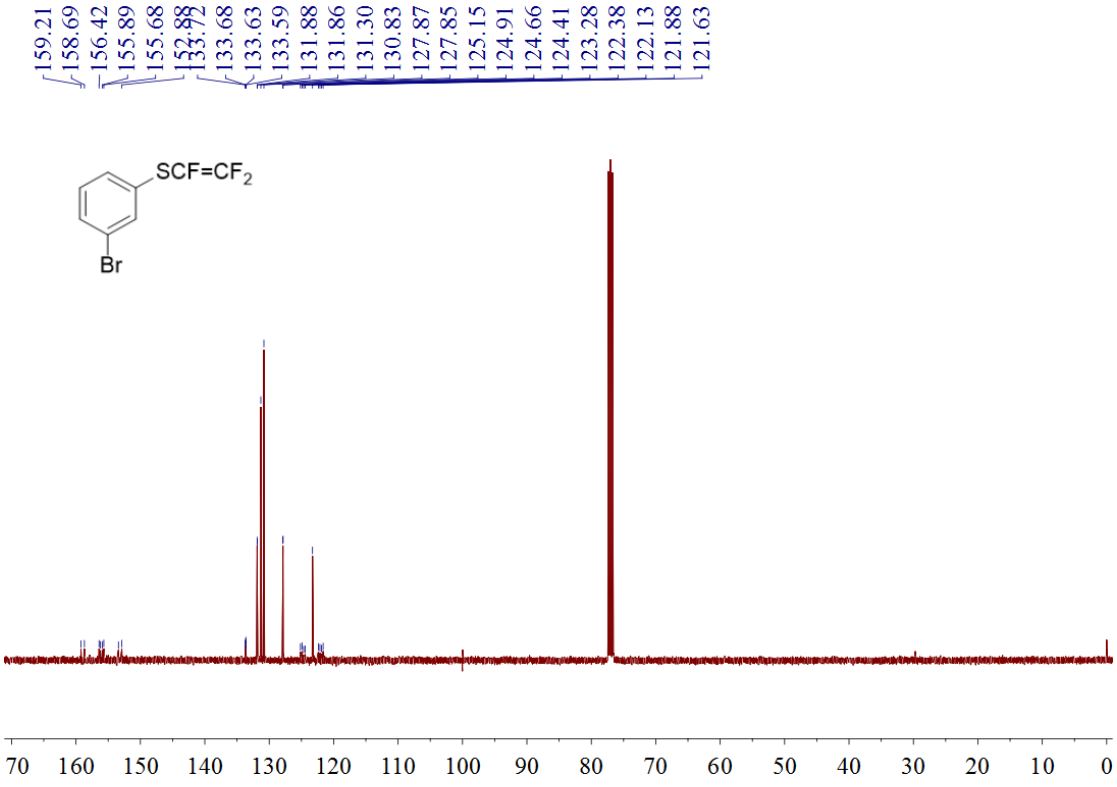
^{1}H NMR spectrum of **3q** in $CDCl_3$



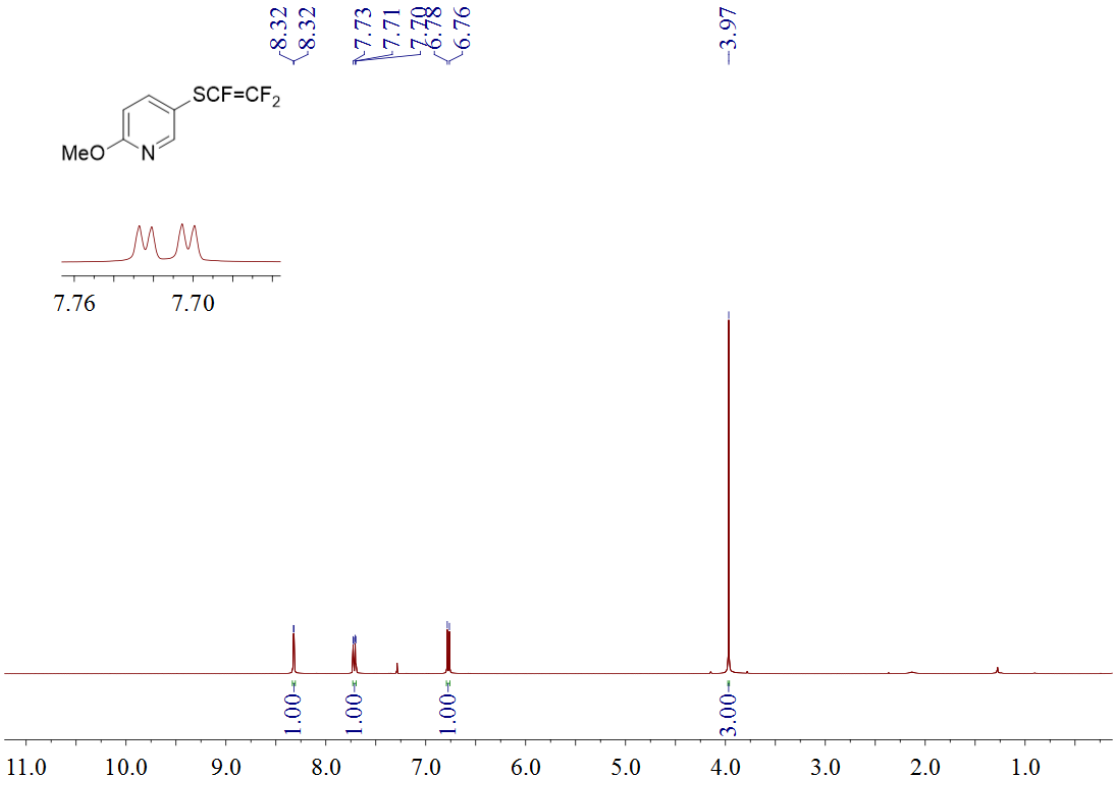
^{19}F NMR spectrum of **3q** in $CDCl_3$



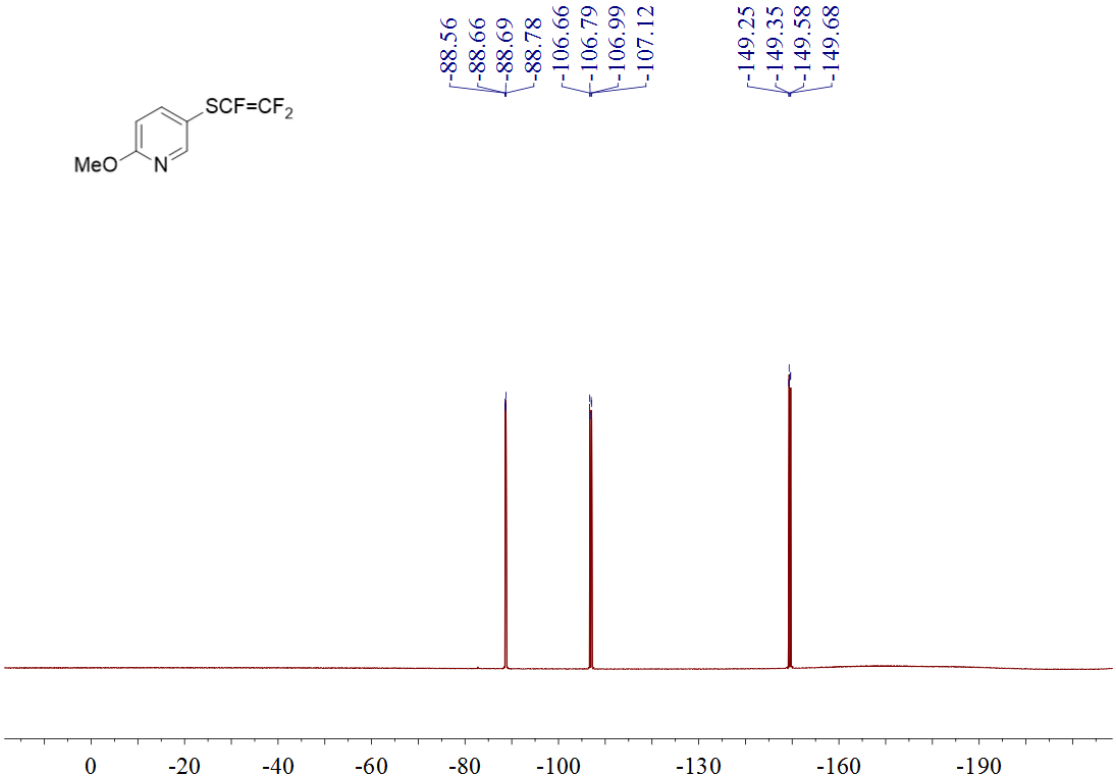
^{13}C NMR spectrum of **3q** in $CDCl_3$



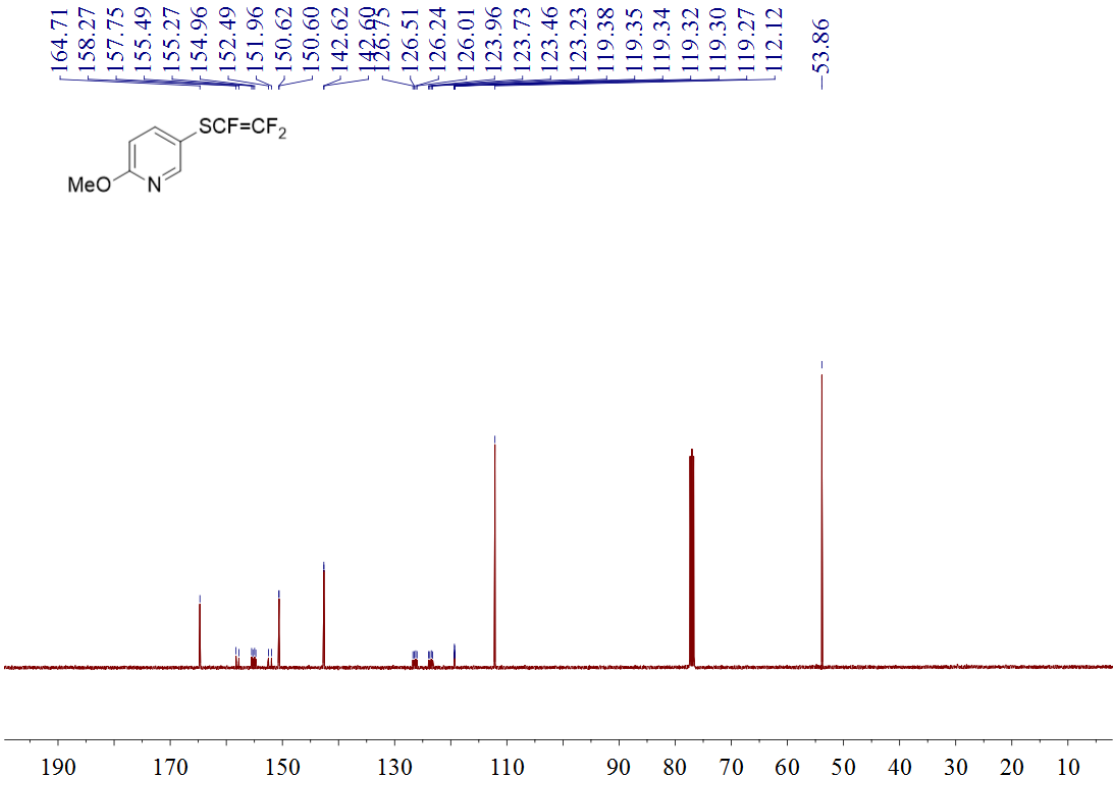
^{1}H NMR spectrum of **3r** in $CDCl_3$



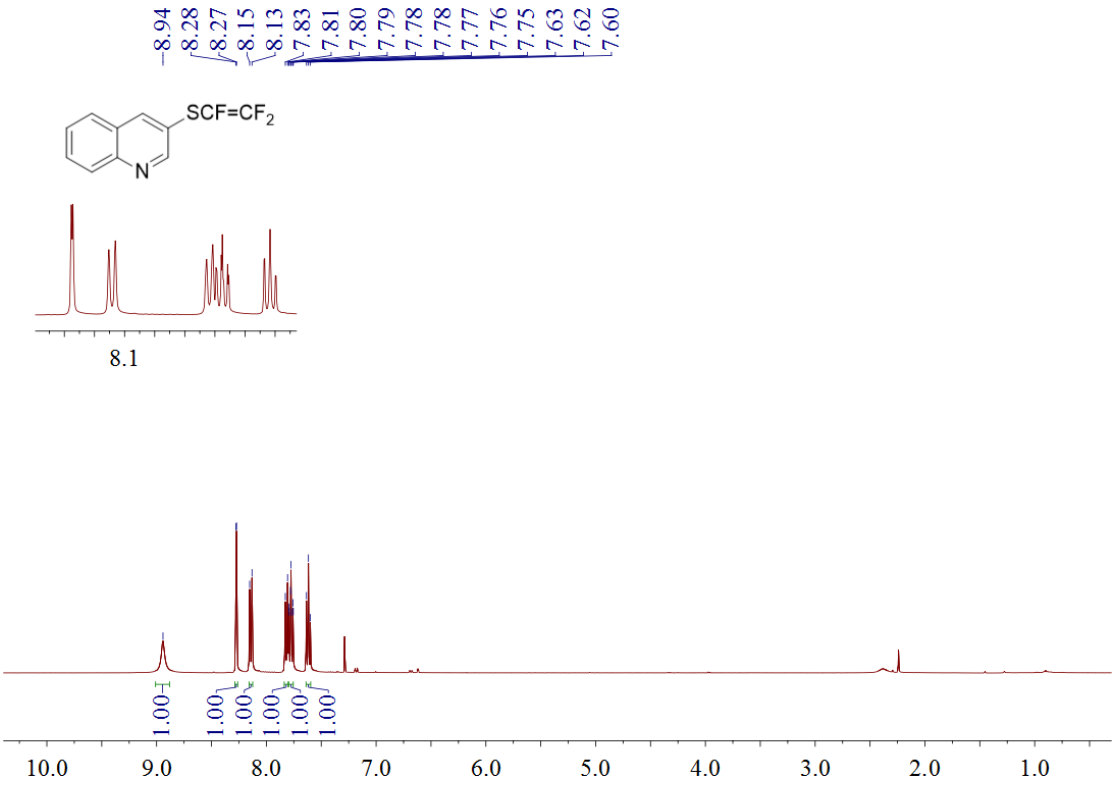
^{19}F NMR spectrum of **3r** in $CDCl_3$



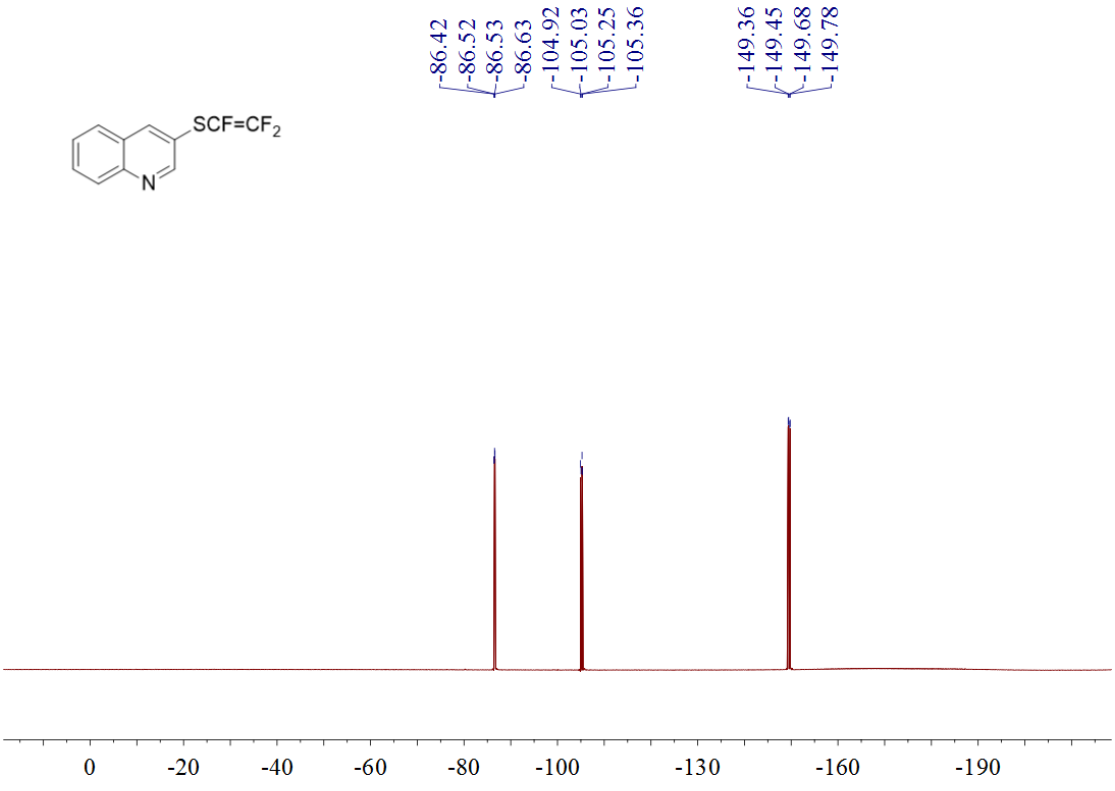
^{13}C NMR spectrum of **3r** in $CDCl_3$



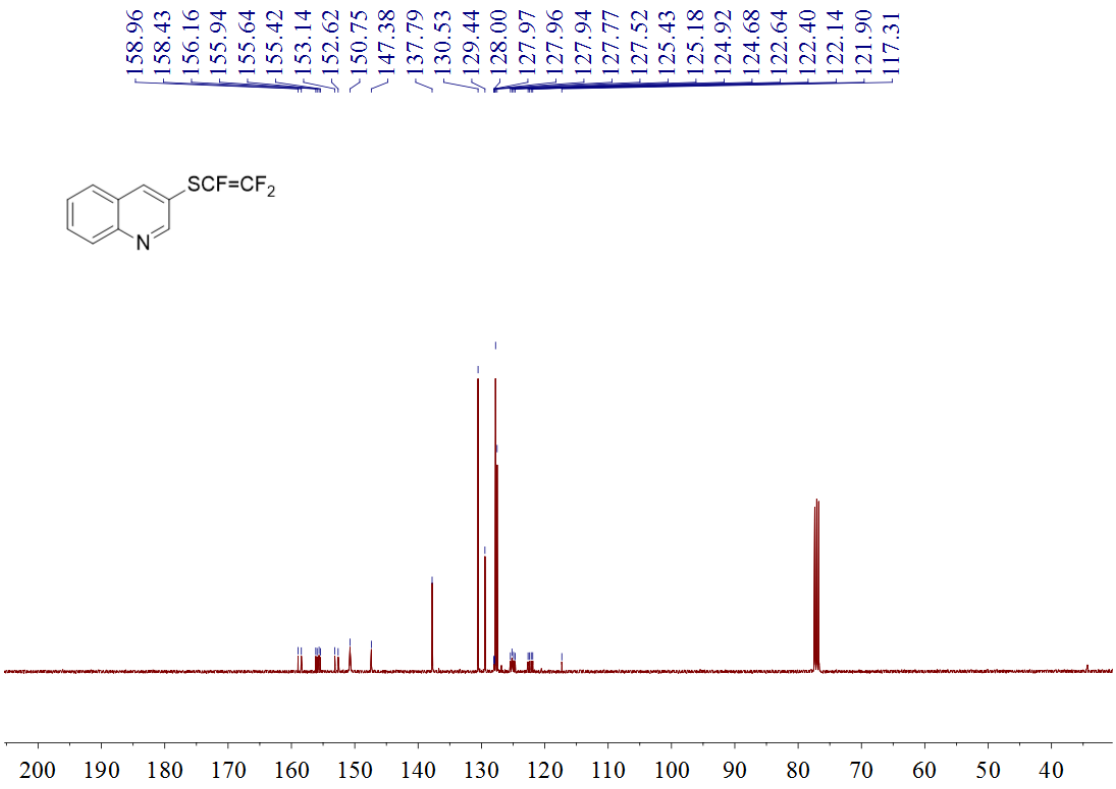
^{1}H NMR spectrum of **3s** in $CDCl_3$



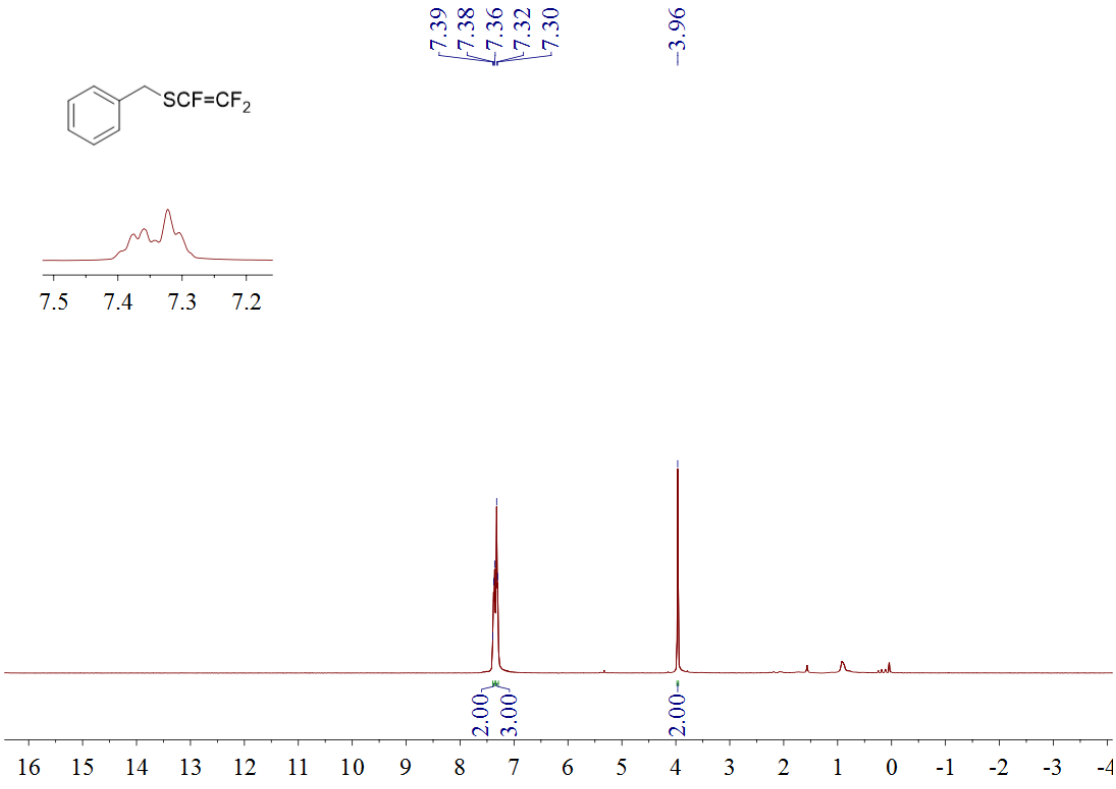
^{19}F NMR spectrum of **3s** in $CDCl_3$



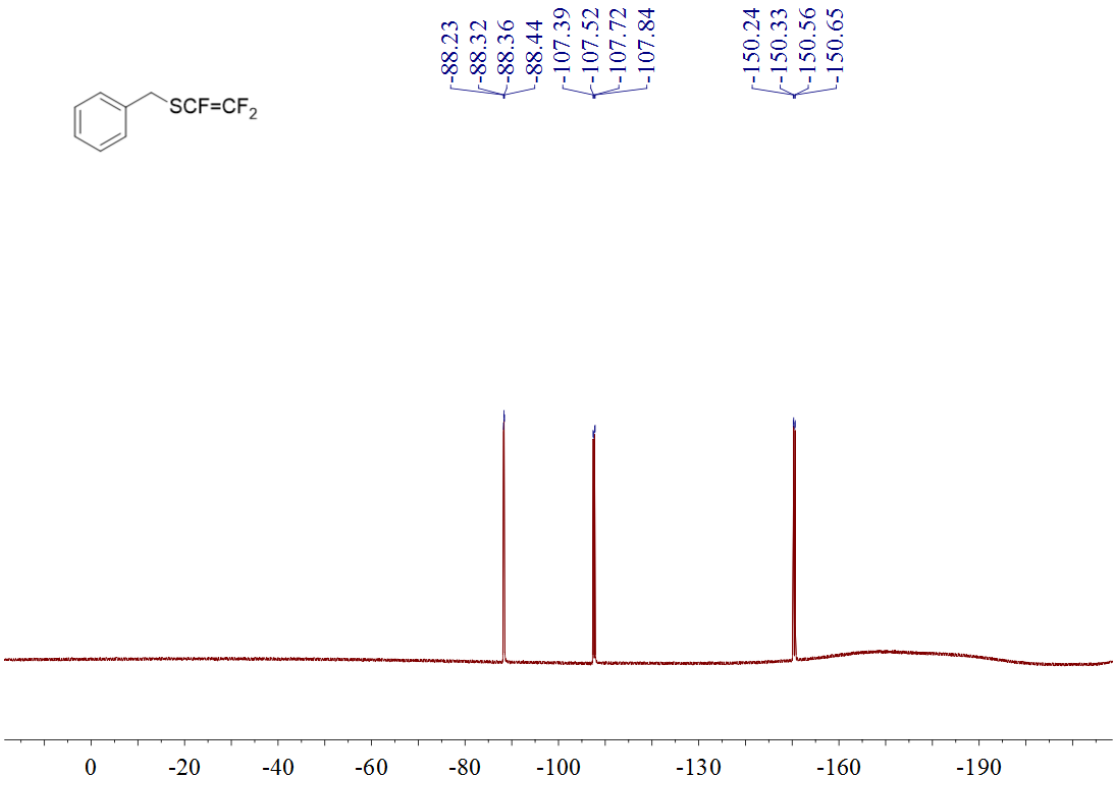
^{13}C NMR spectrum of **3s** in $CDCl_3$



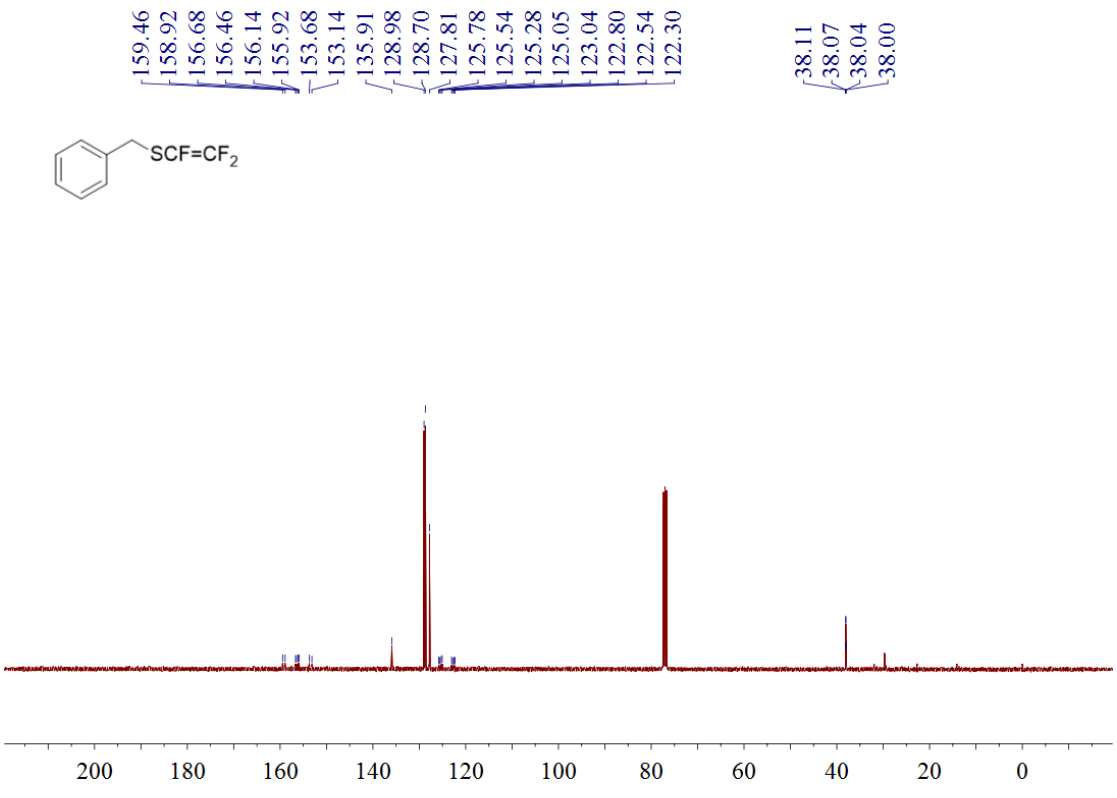
^{1}H NMR spectrum of **3t** in $CDCl_3$



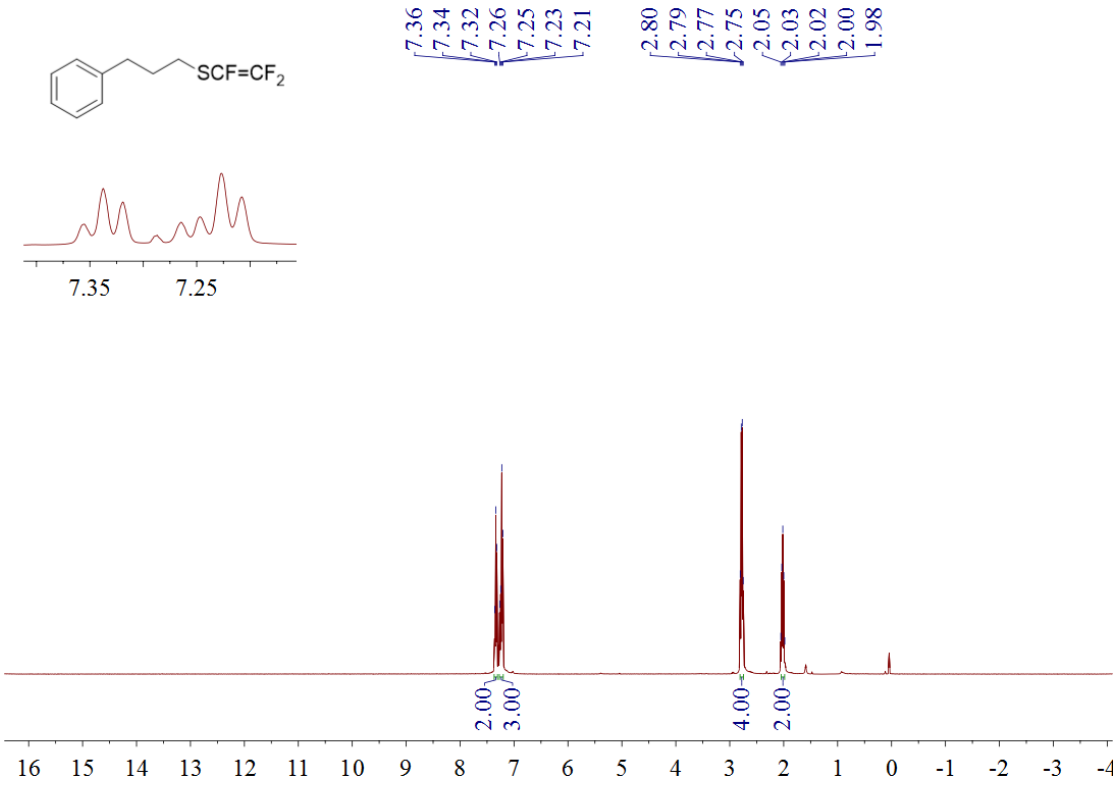
^{19}F NMR spectrum of **3t** in $CDCl_3$



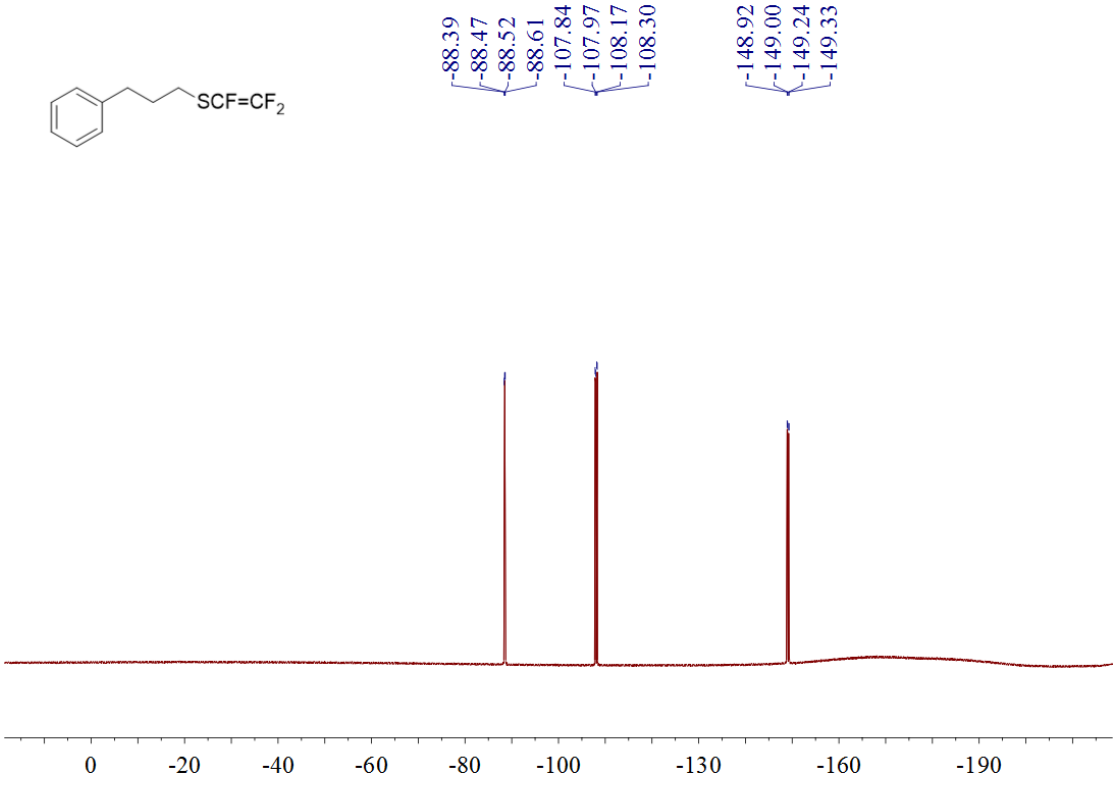
^{13}C NMR spectrum of **3t** in $CDCl_3$



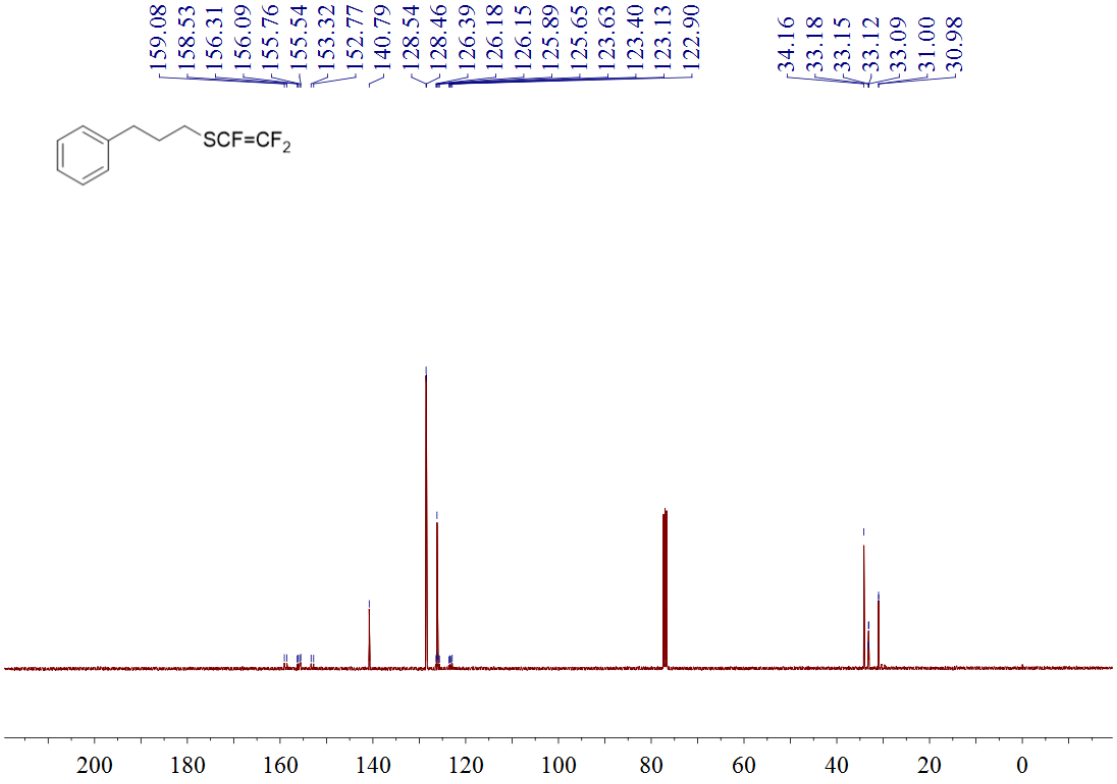
^{1}H NMR spectrum of **3u** in $CDCl_3$



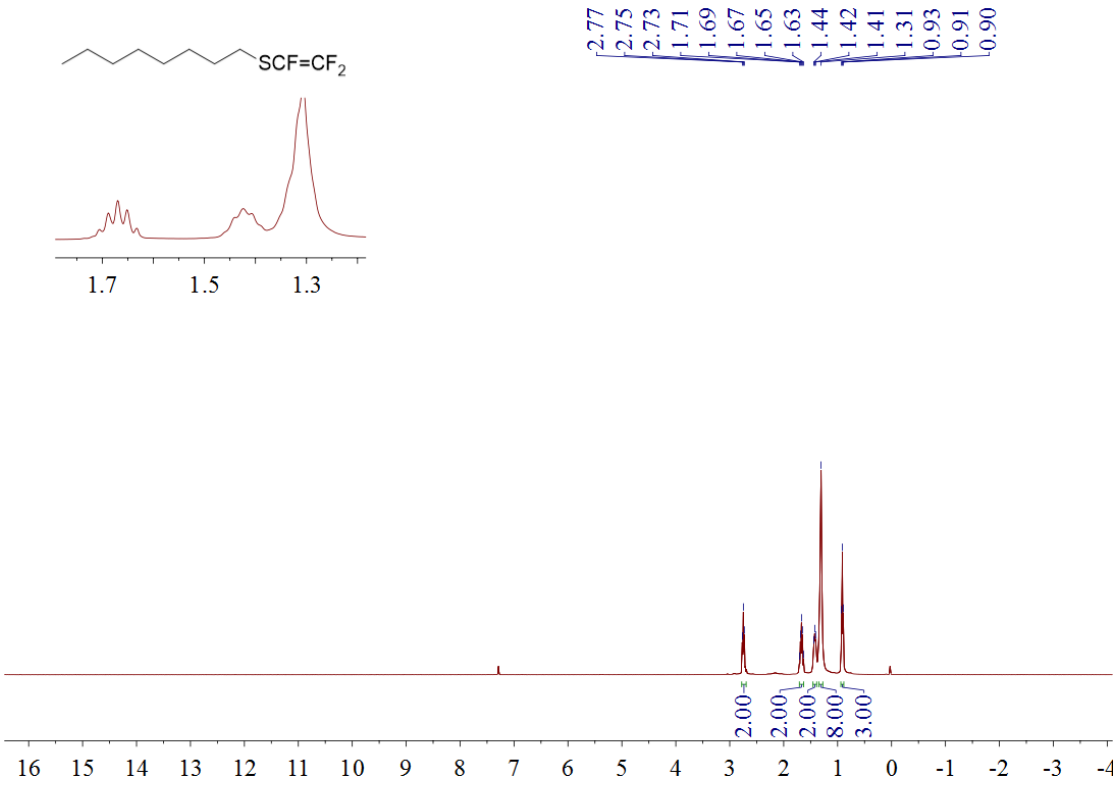
^{19}F NMR spectrum of **3u** in $CDCl_3$



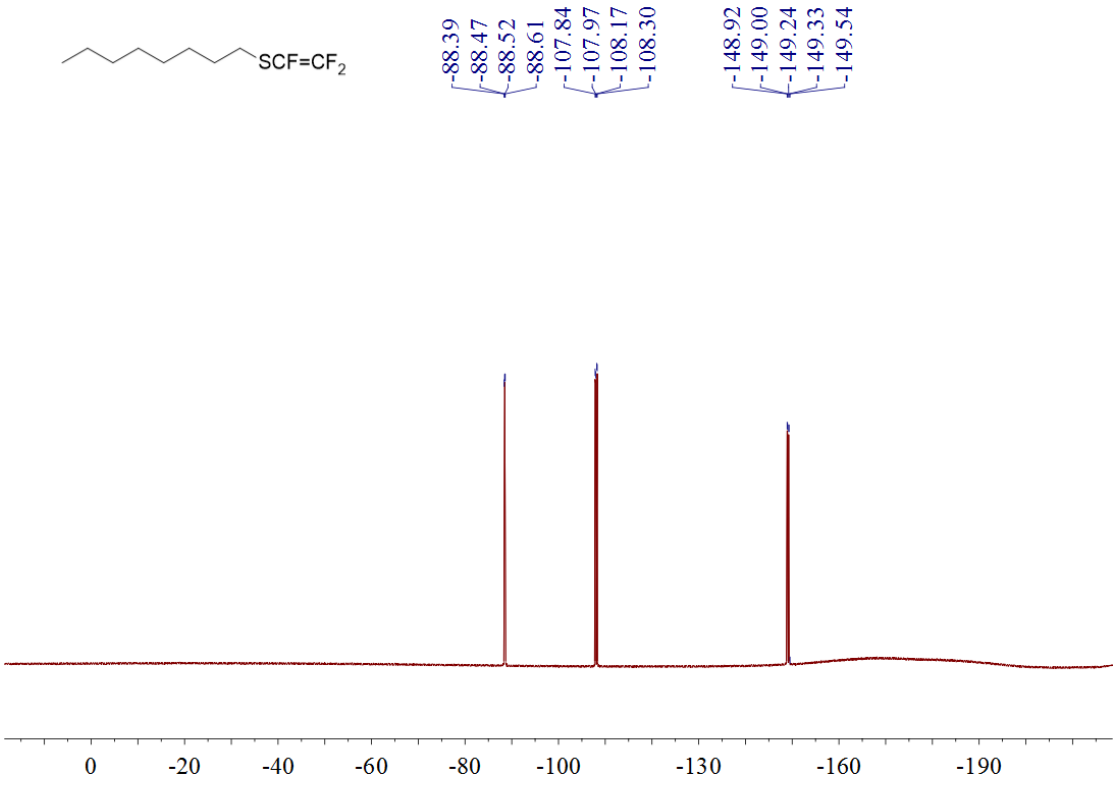
^{13}C NMR spectrum of **3u** in $CDCl_3$



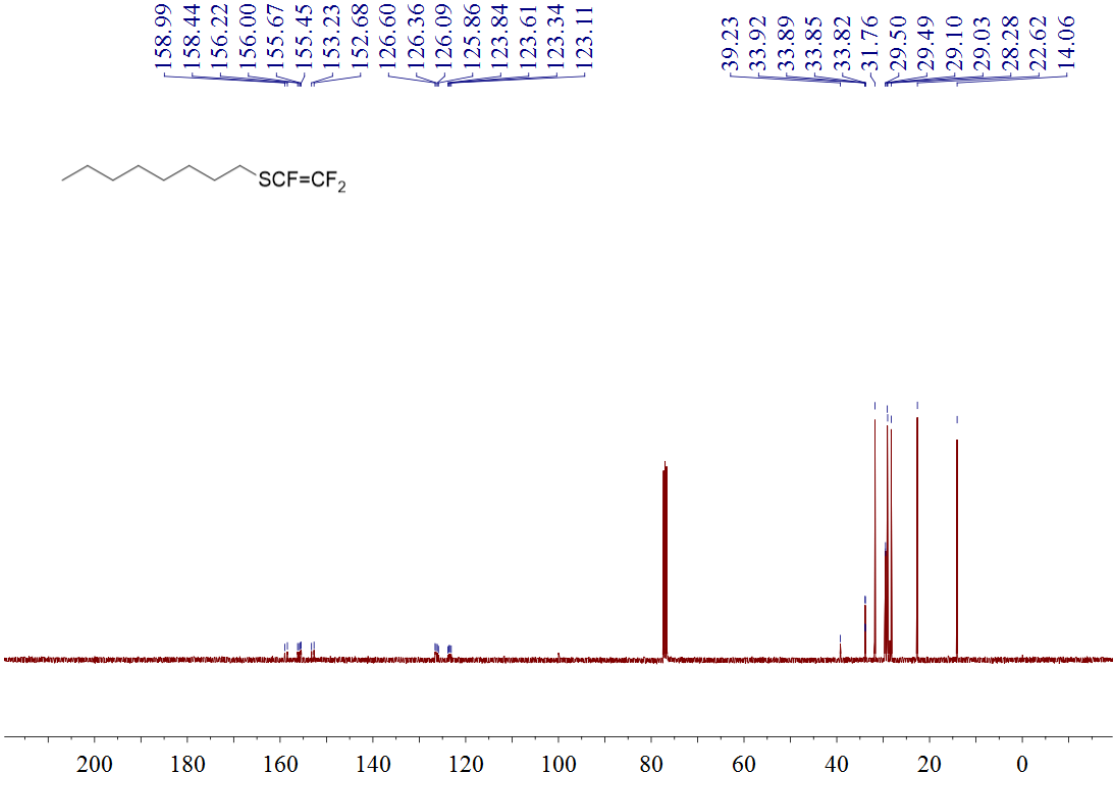
^{1}H NMR spectrum of **3v** in $CDCl_3$



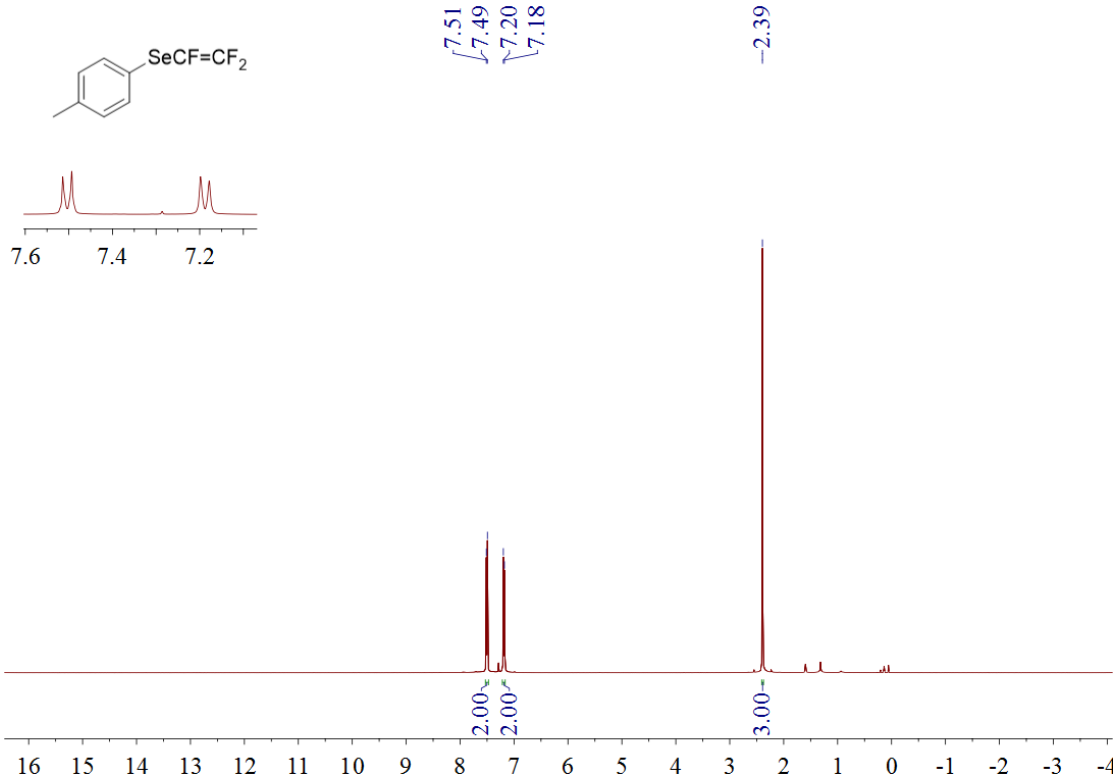
^{19}F NMR spectrum of **3v** in $CDCl_3$



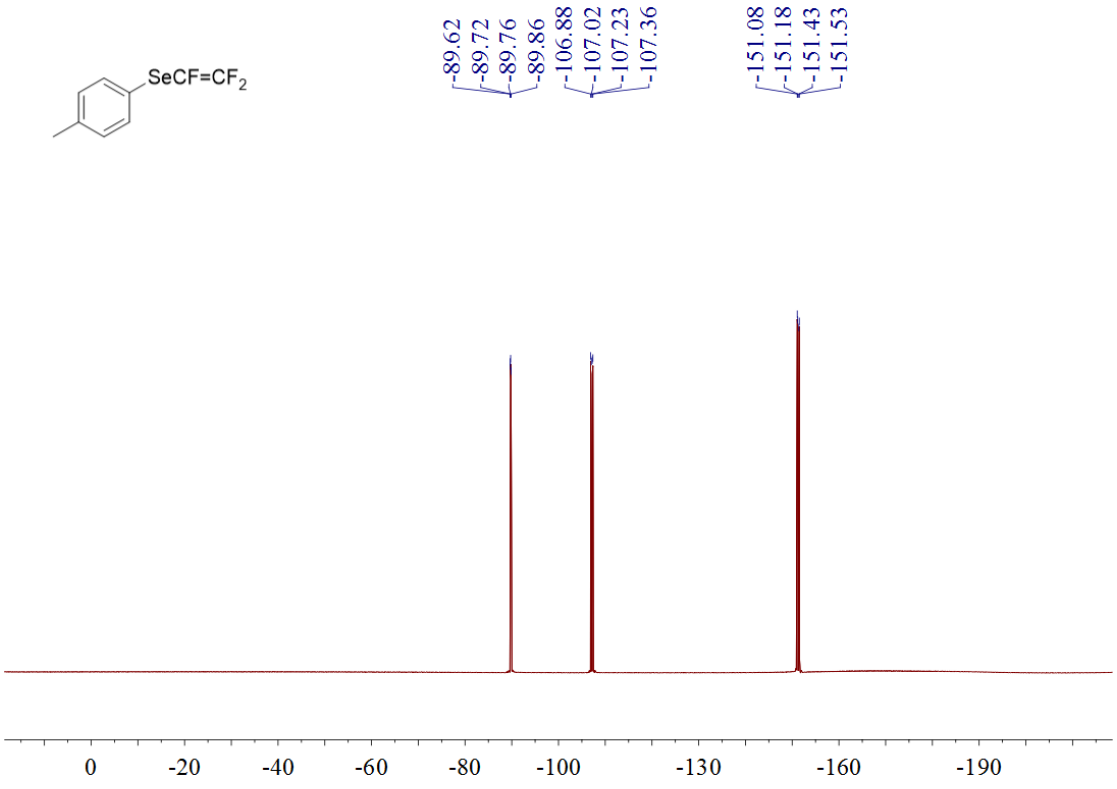
^{13}C NMR spectrum of **3v** in $CDCl_3$



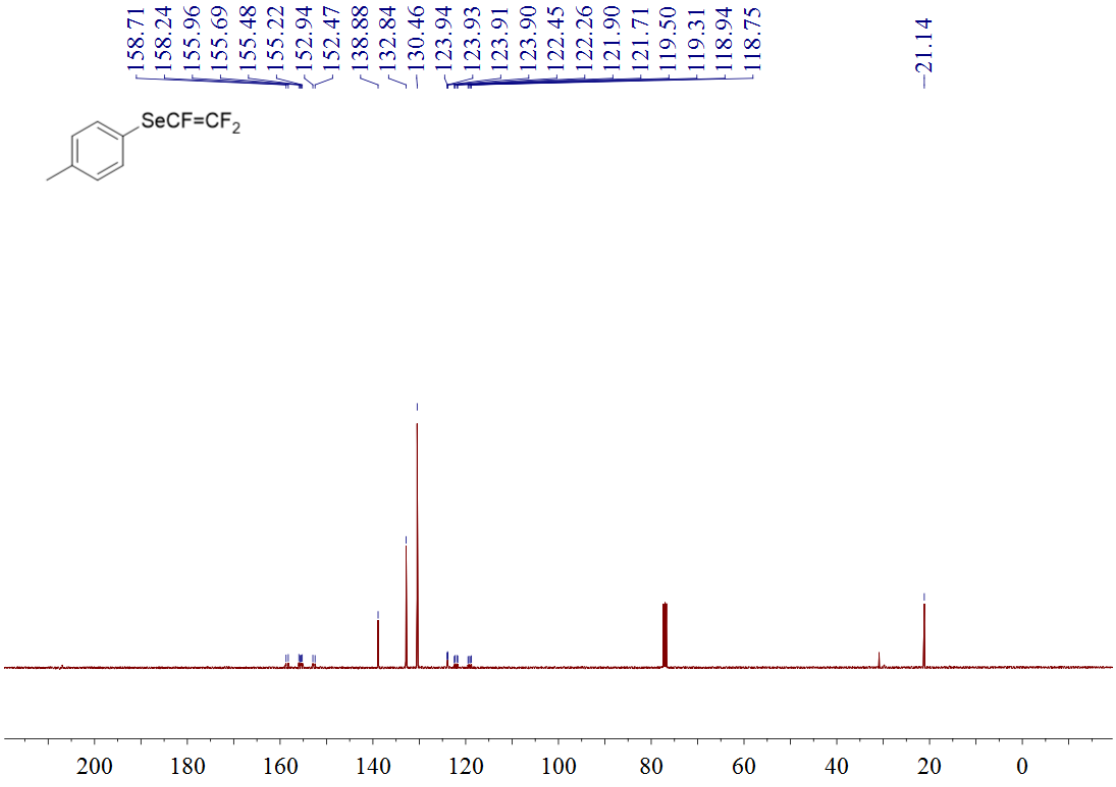
^{1}H NMR spectrum of **5a** in $CDCl_3$



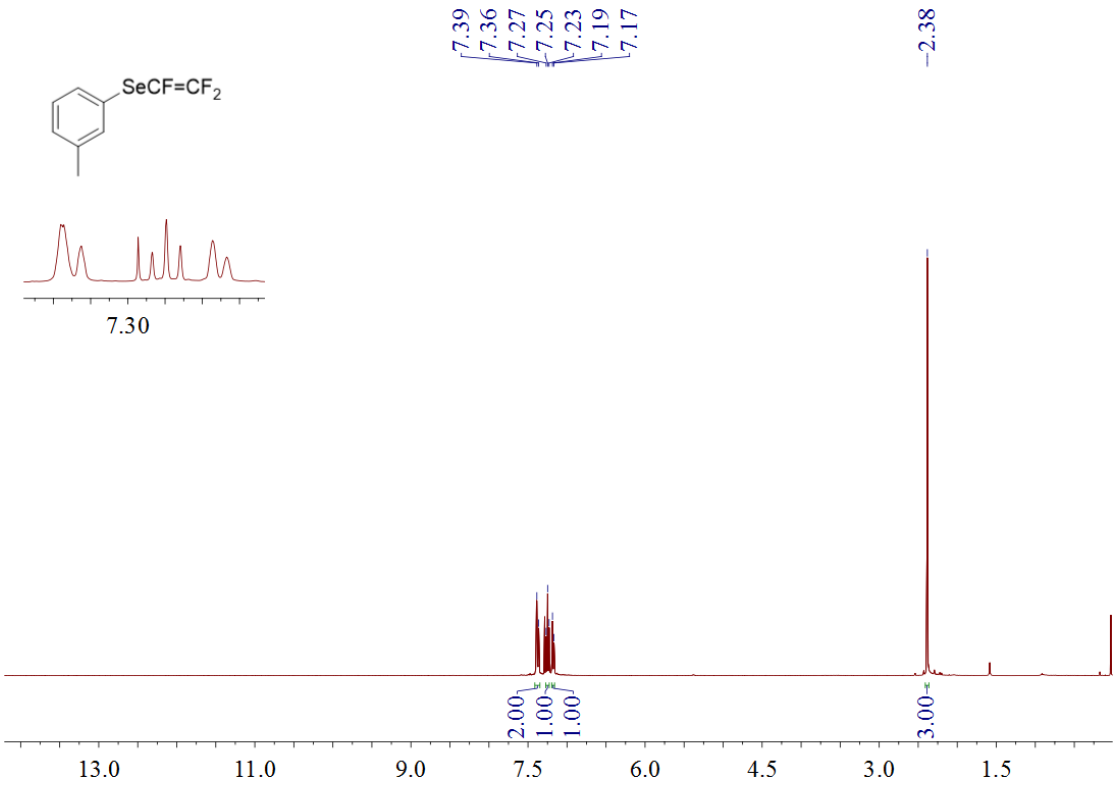
^{19}F NMR spectrum of **5a** in $CDCl_3$



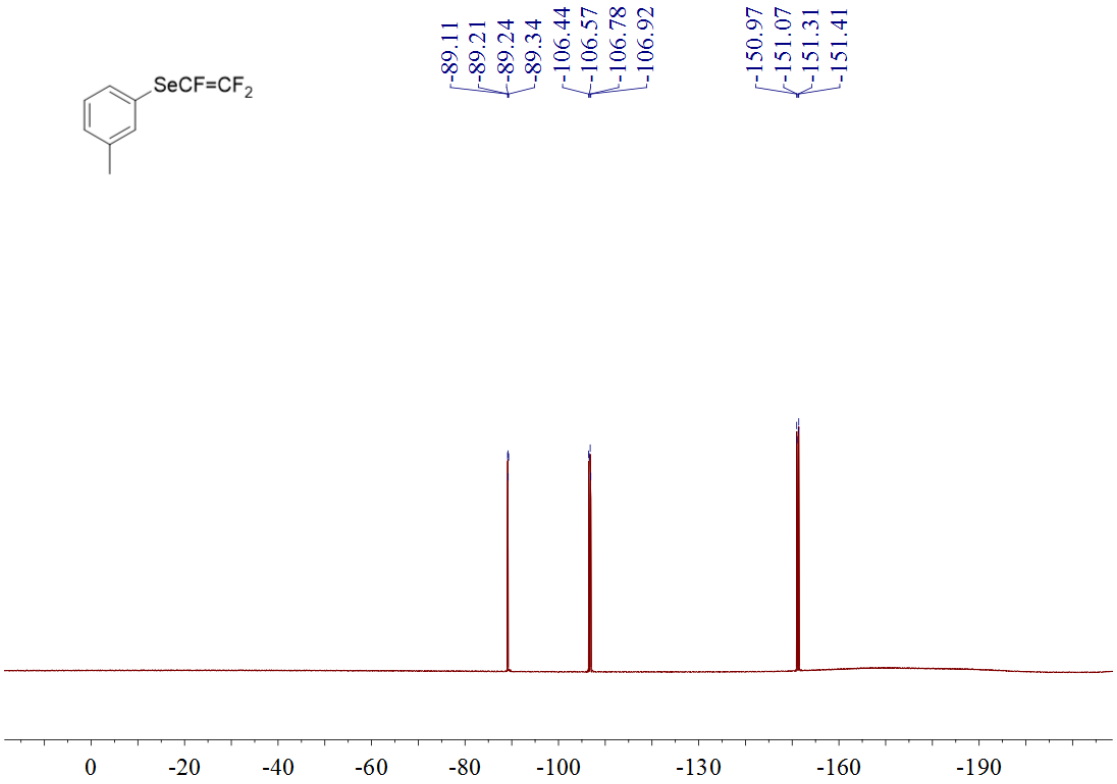
^{13}C NMR spectrum of **5a** in $CDCl_3$



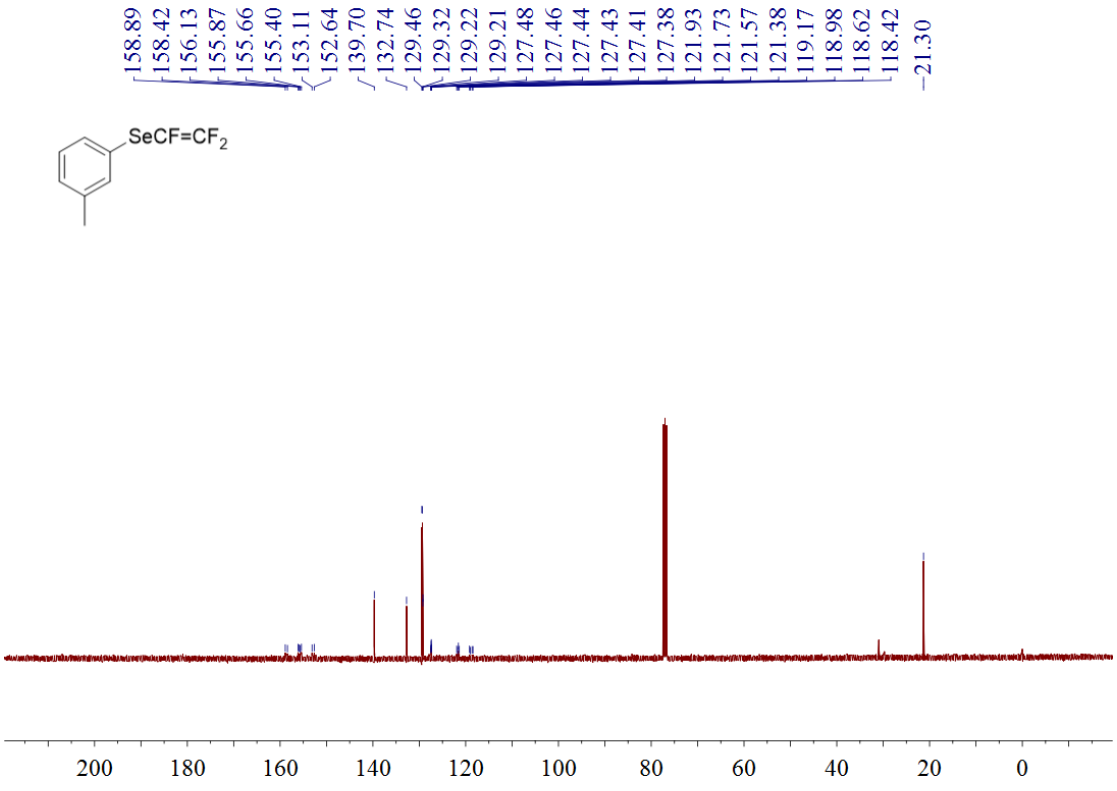
^{1}H NMR spectrum of **5b** in $CDCl_3$



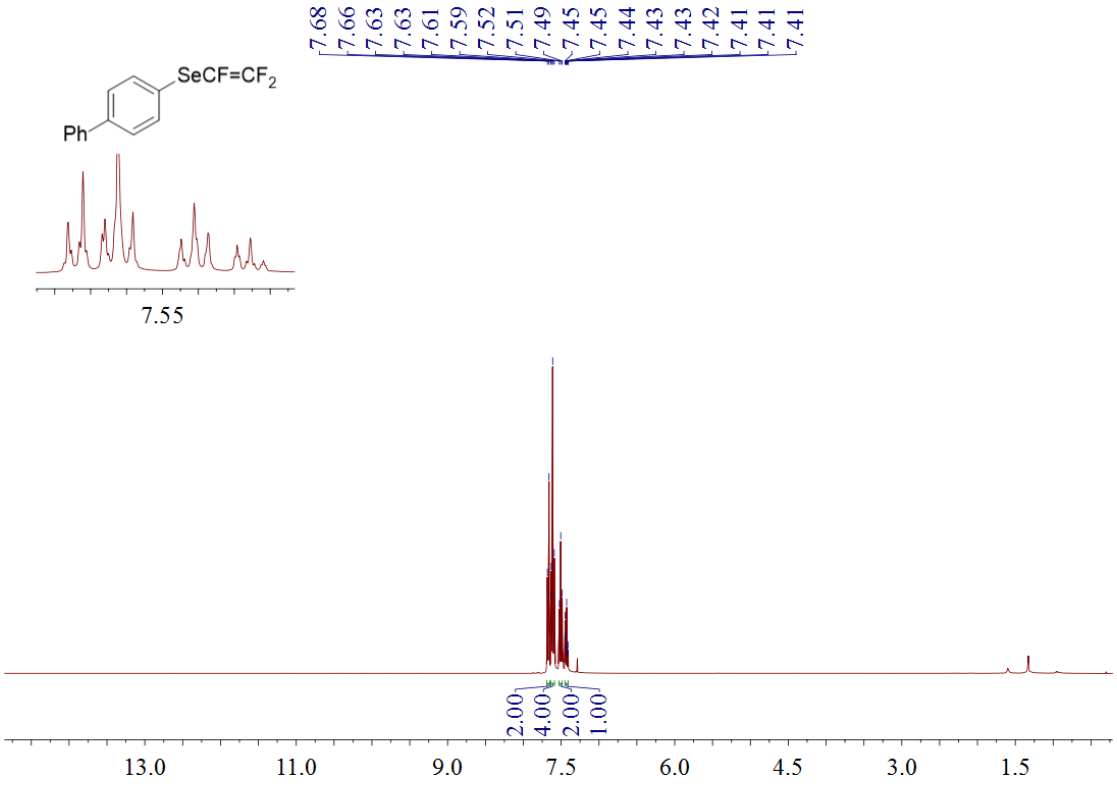
^{19}F NMR spectrum of **5b** in $CDCl_3$



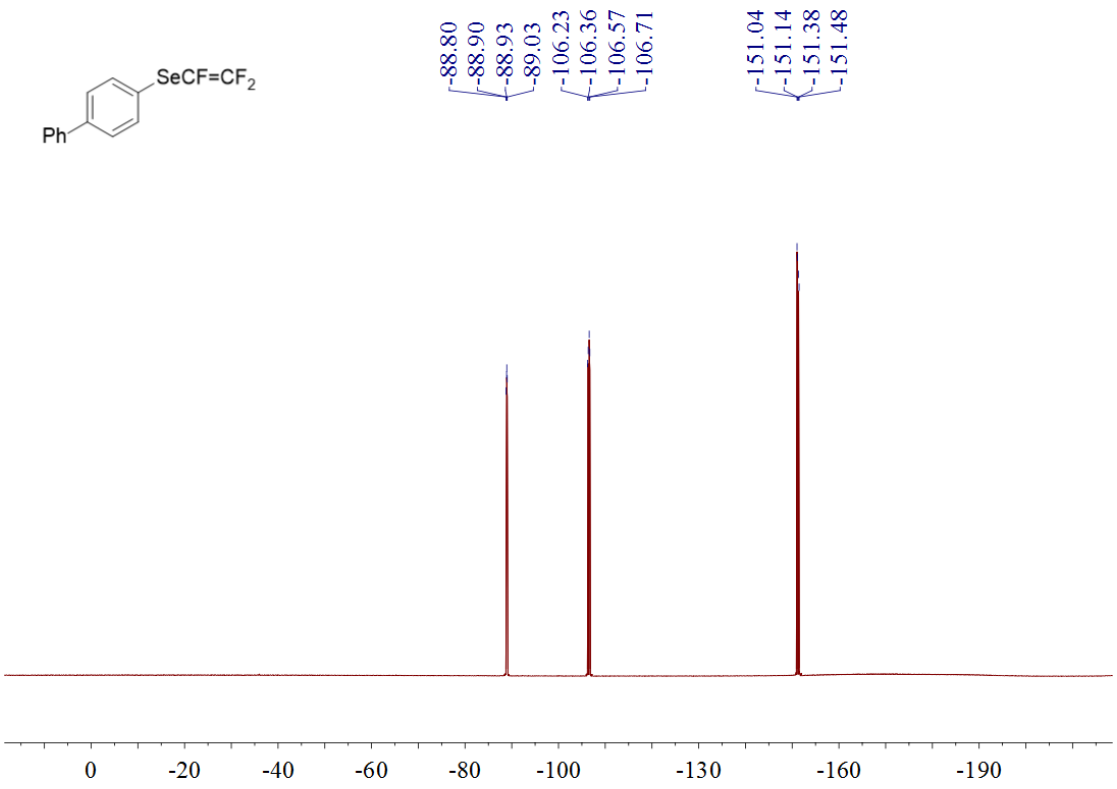
^{13}C NMR spectrum of **5b** in $CDCl_3$



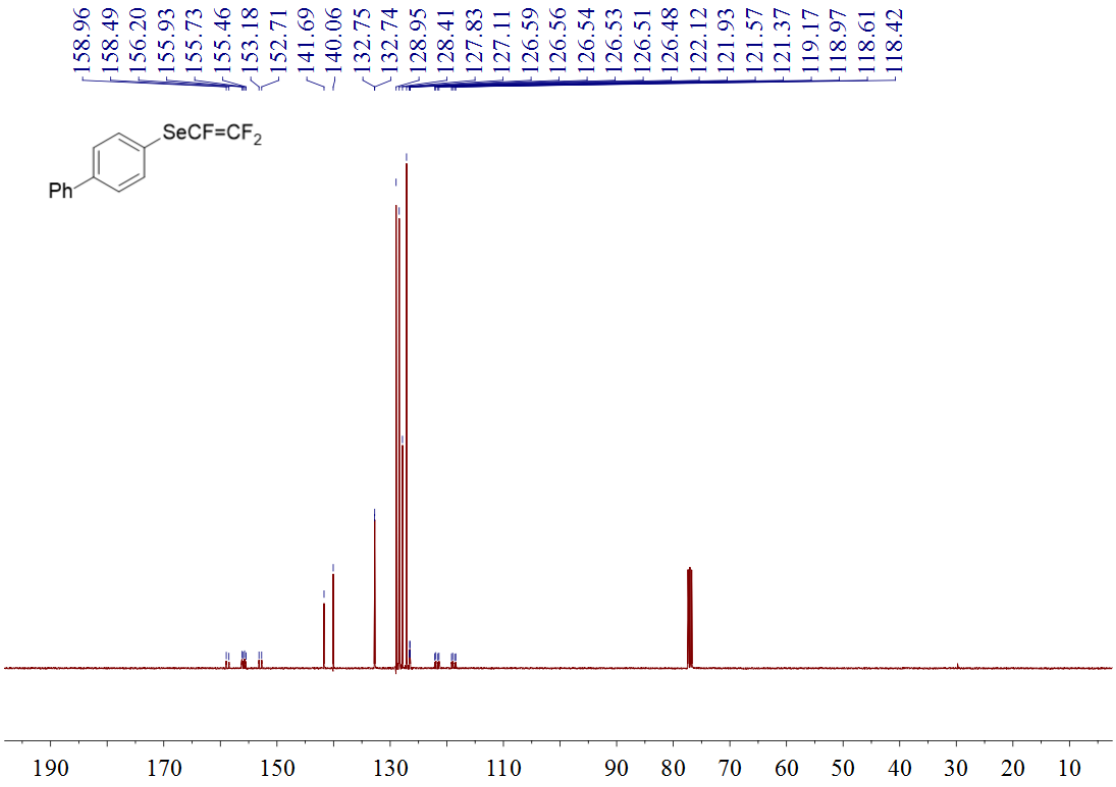
^{1}H NMR spectrum of **5d** in $CDCl_3$



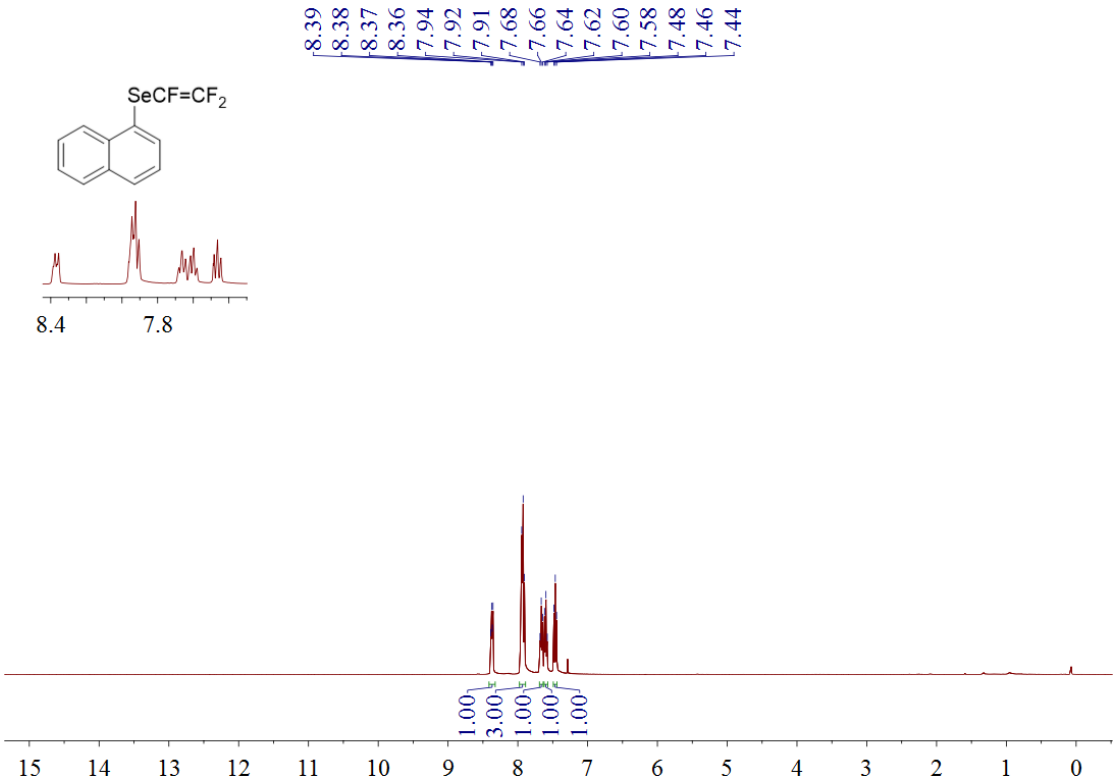
^{19}F NMR spectrum of **5d** in $CDCl_3$



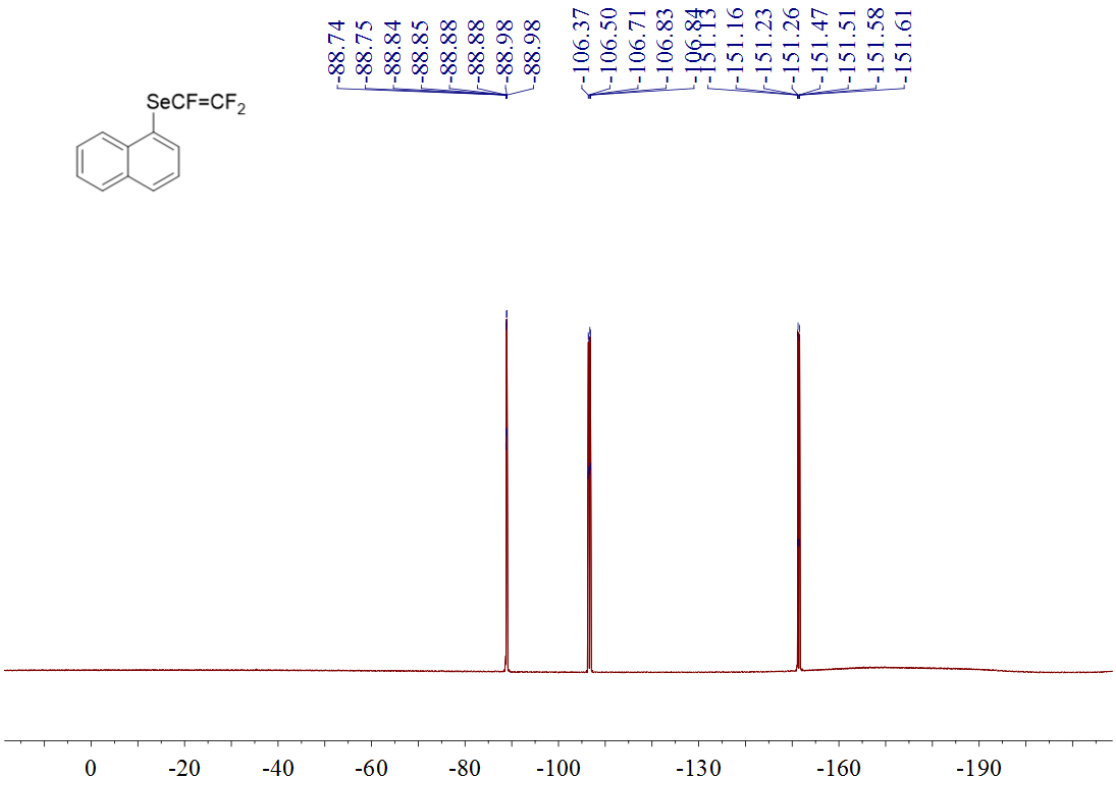
^{13}C NMR spectrum of **5d** in $CDCl_3$



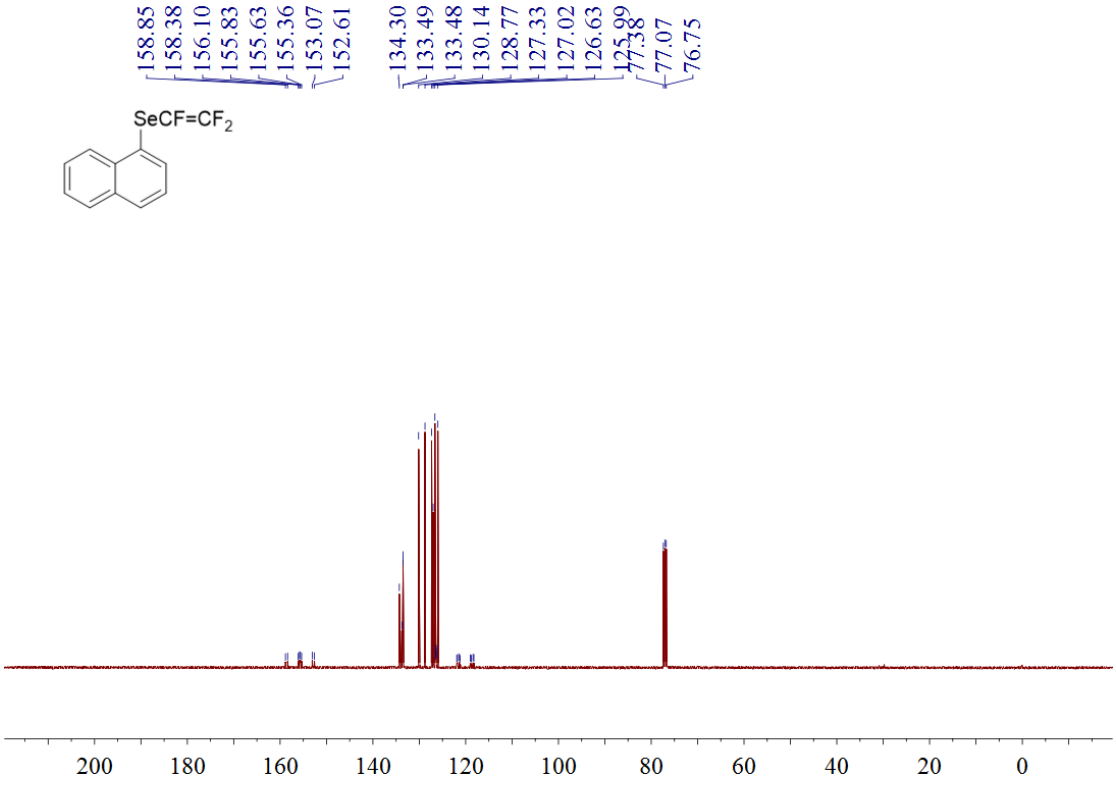
^{1}H NMR spectrum of **5f** in $CDCl_3$



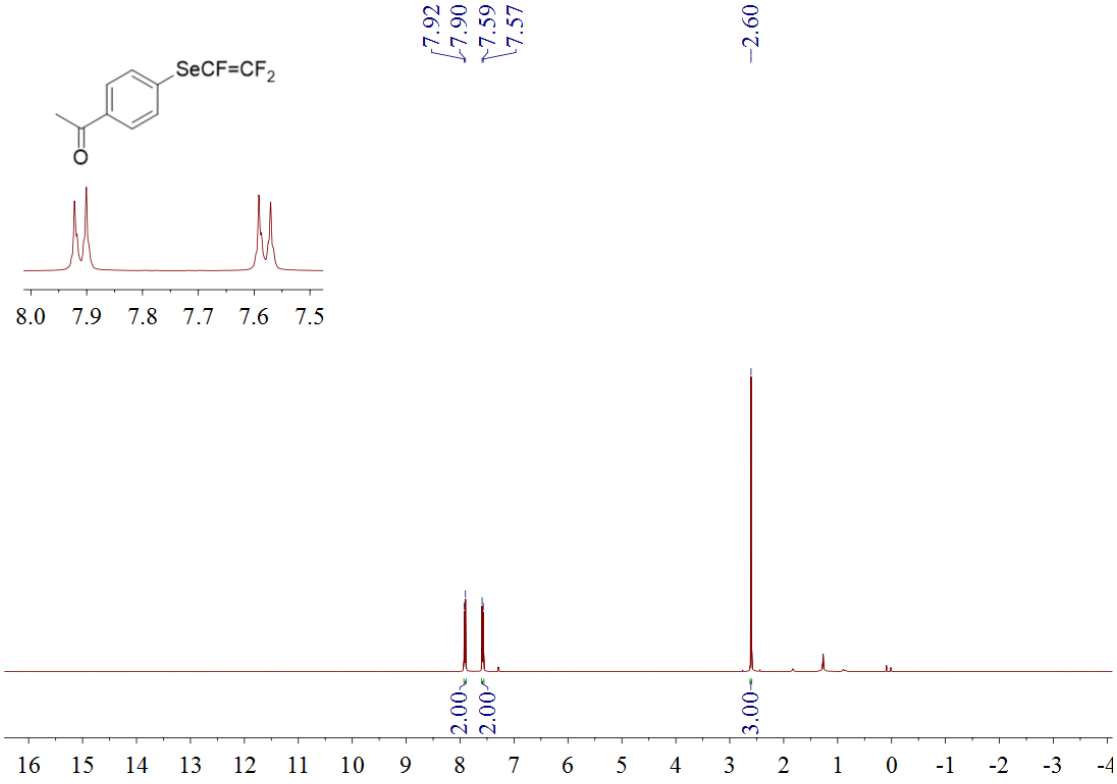
^{19}F NMR spectrum of **5f** in $CDCl_3$



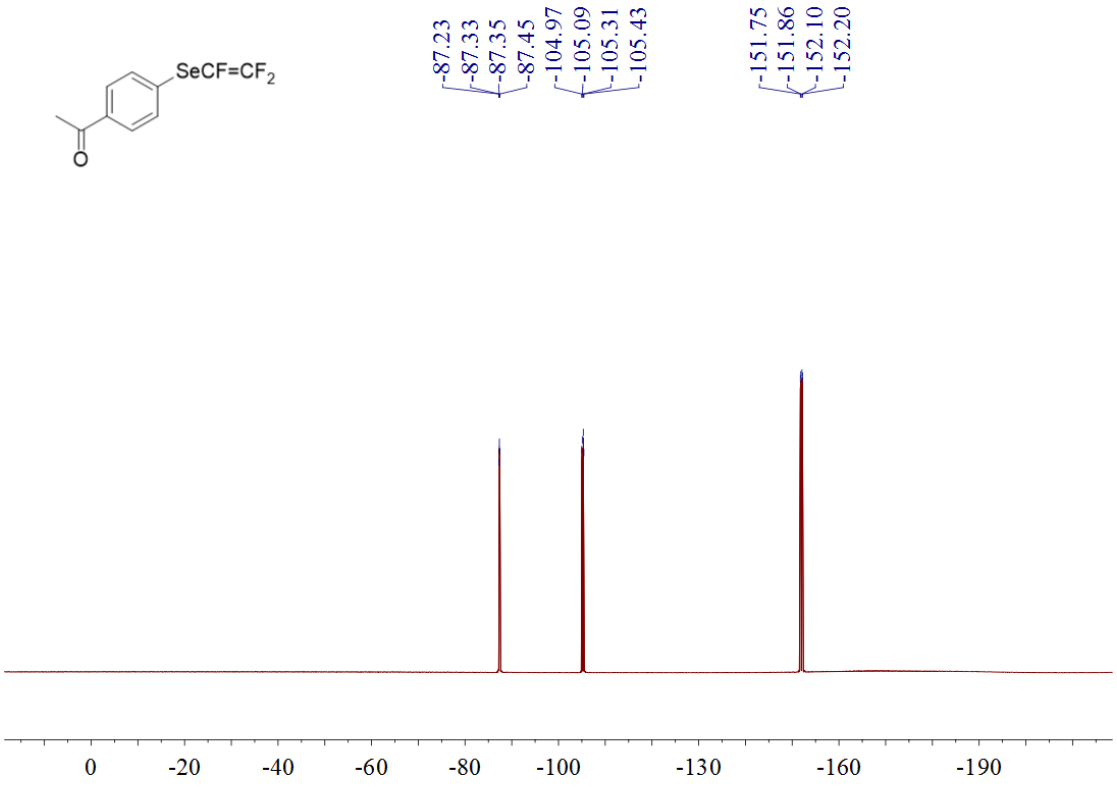
^{13}C NMR spectrum of **5f** in $CDCl_3$



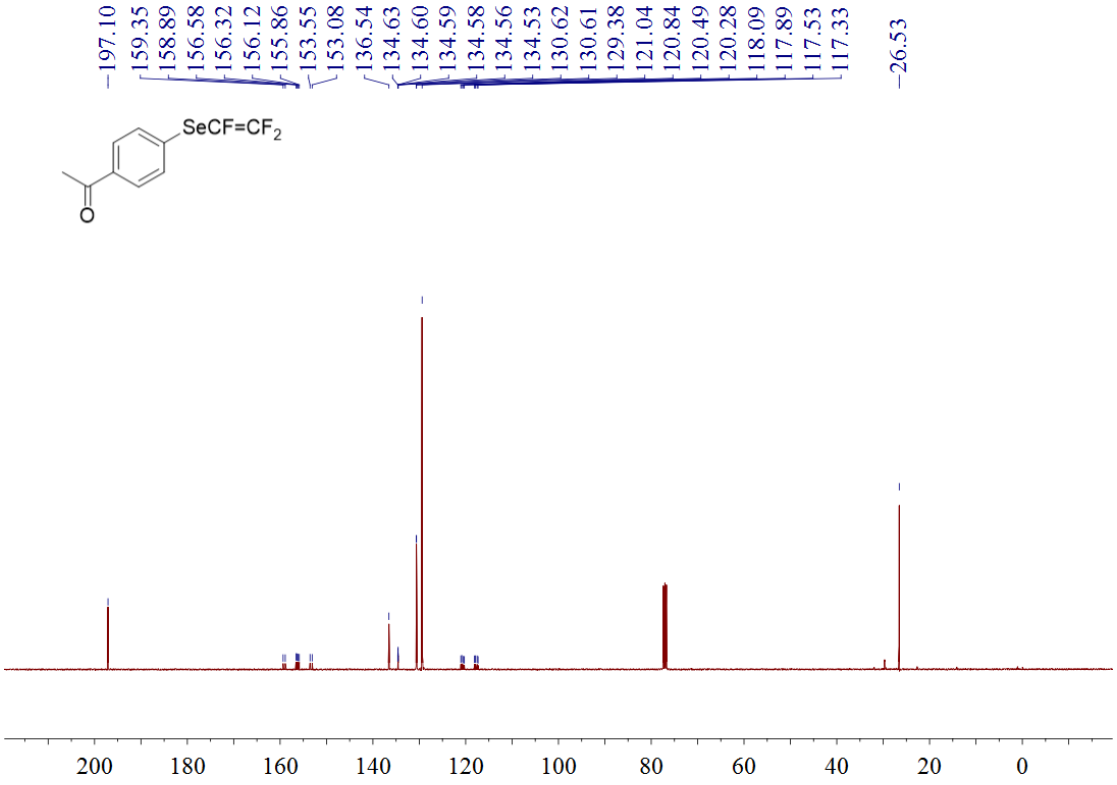
^{1}H NMR spectrum of **5j** in $CDCl_3$



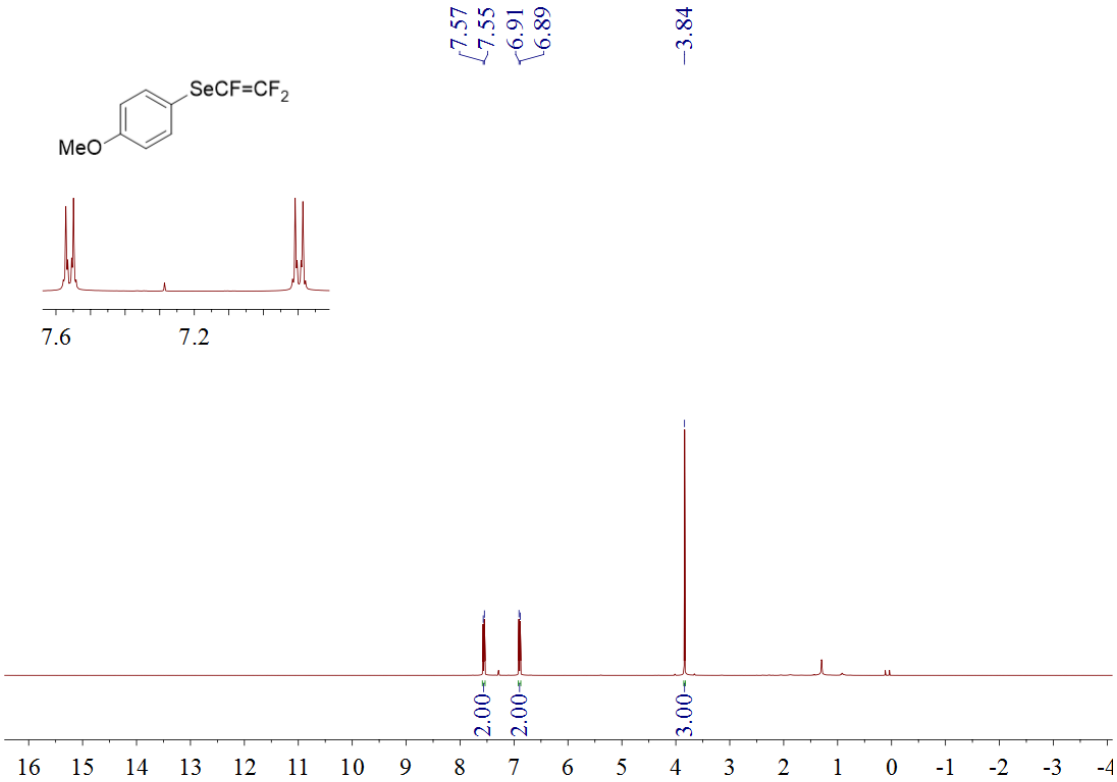
^{19}F NMR spectrum of **5j** in $CDCl_3$



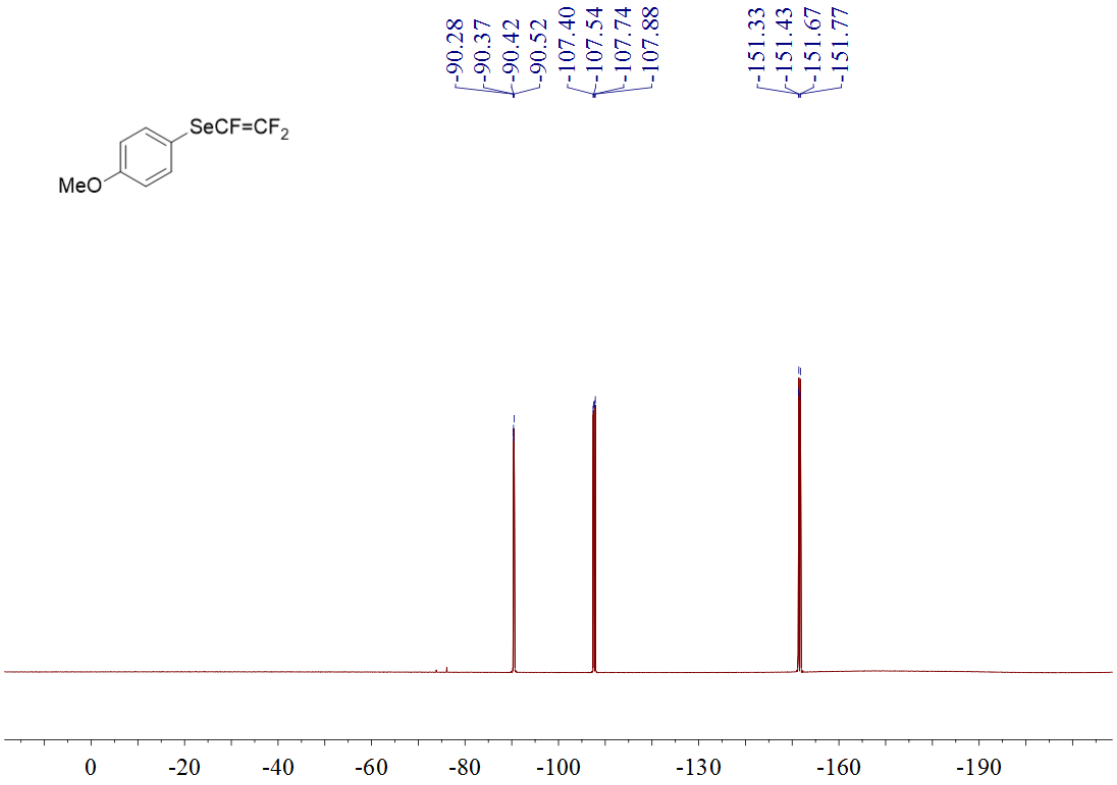
^{13}C NMR spectrum of **5j** in $CDCl_3$



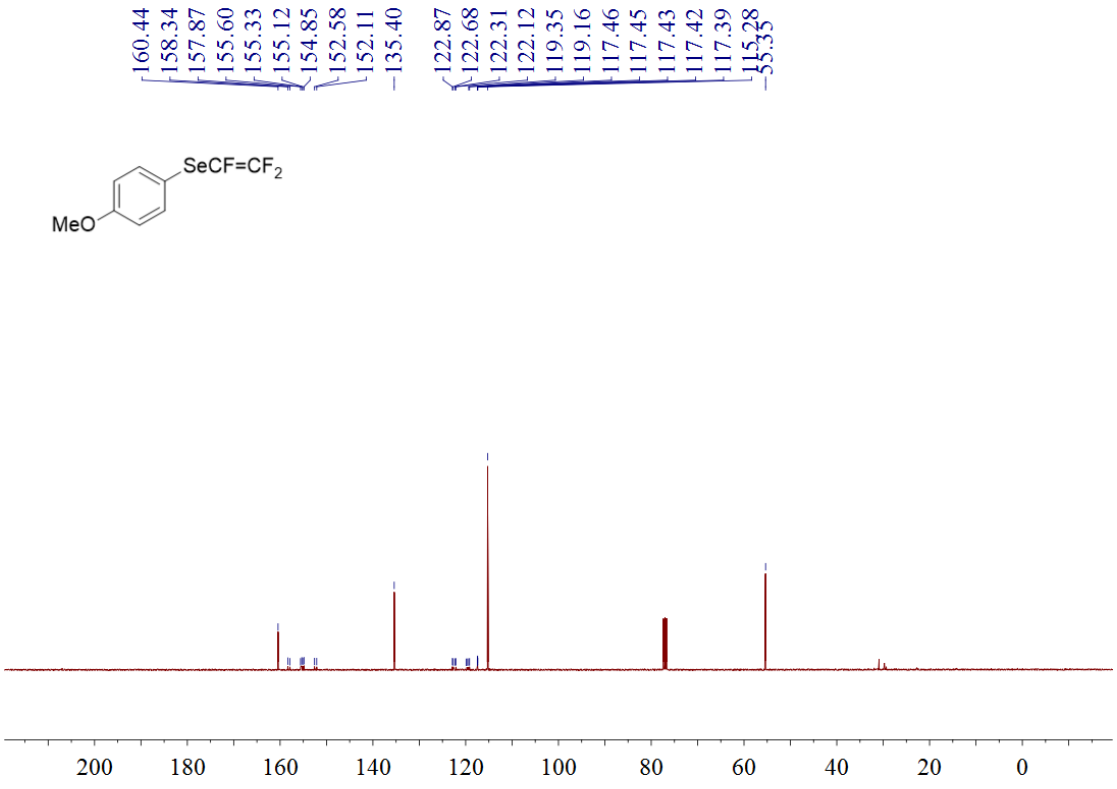
^{1}H NMR spectrum of **5l** in $CDCl_3$



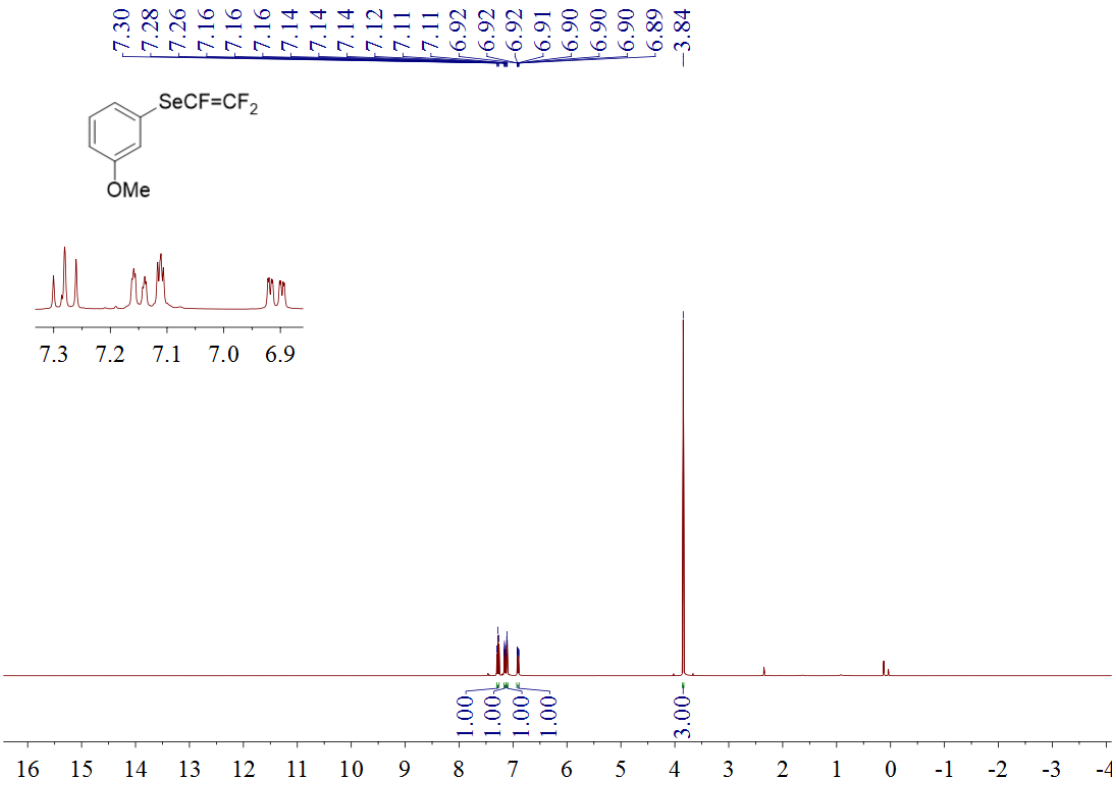
^{19}F NMR spectrum of **5l** in $CDCl_3$



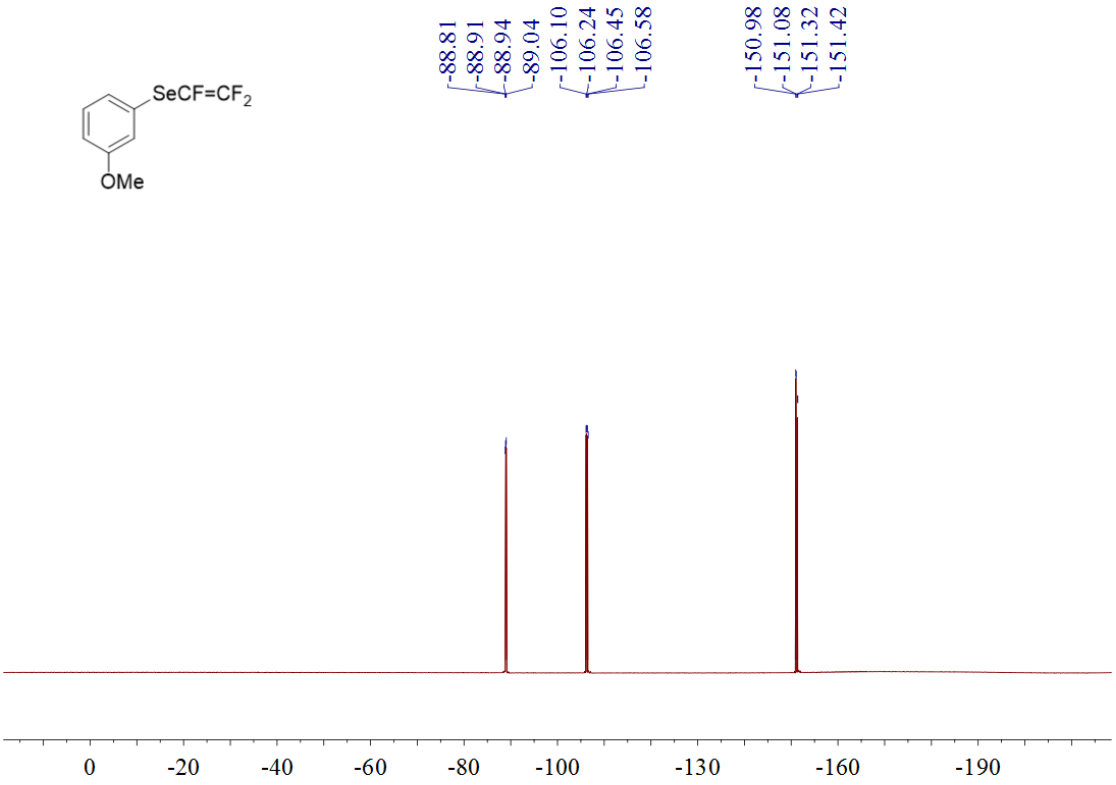
^{13}C NMR spectrum of **5l** in $CDCl_3$



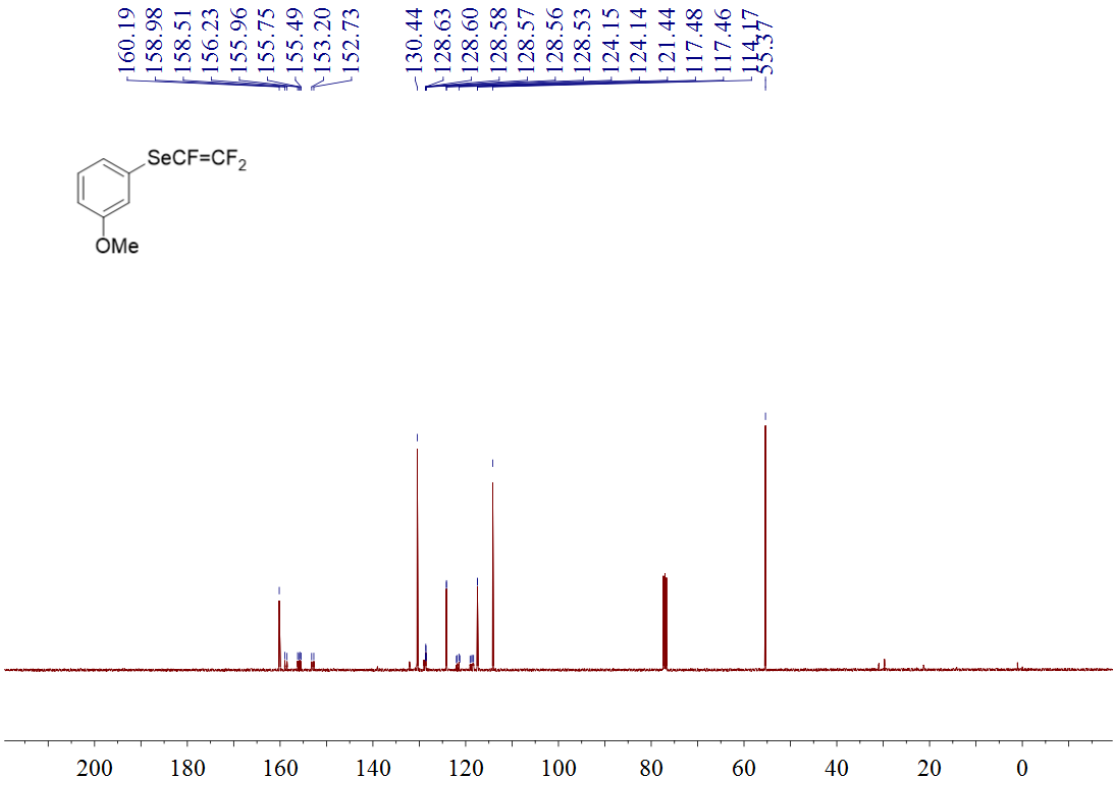
^{1}H NMR spectrum of **5m** in $CDCl_3$



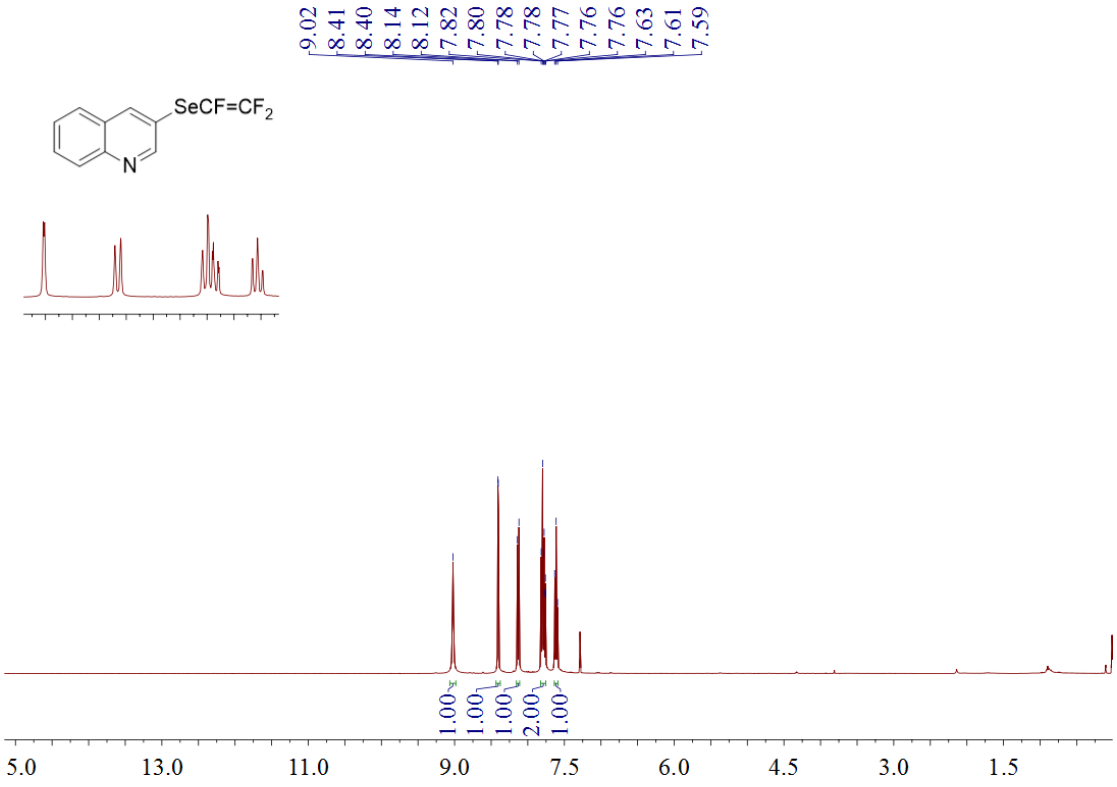
^{19}F NMR spectrum of **5m** in $CDCl_3$



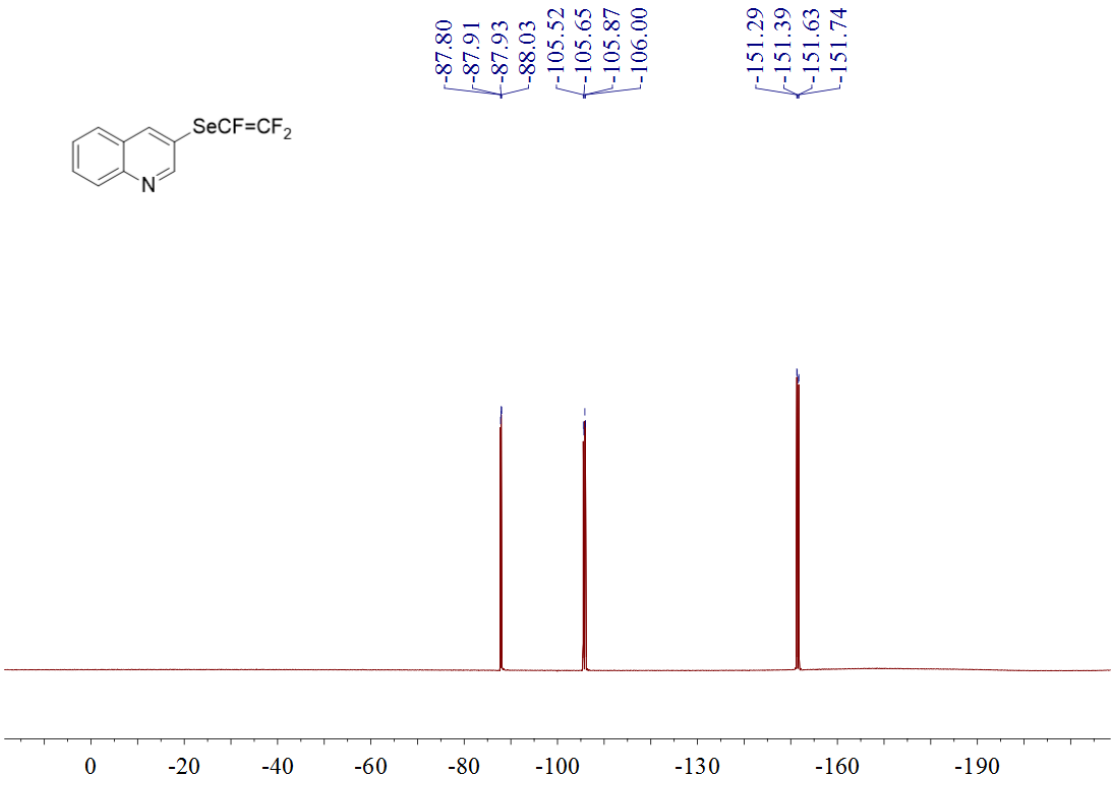
^{13}C NMR spectrum of **5m** in $CDCl_3$



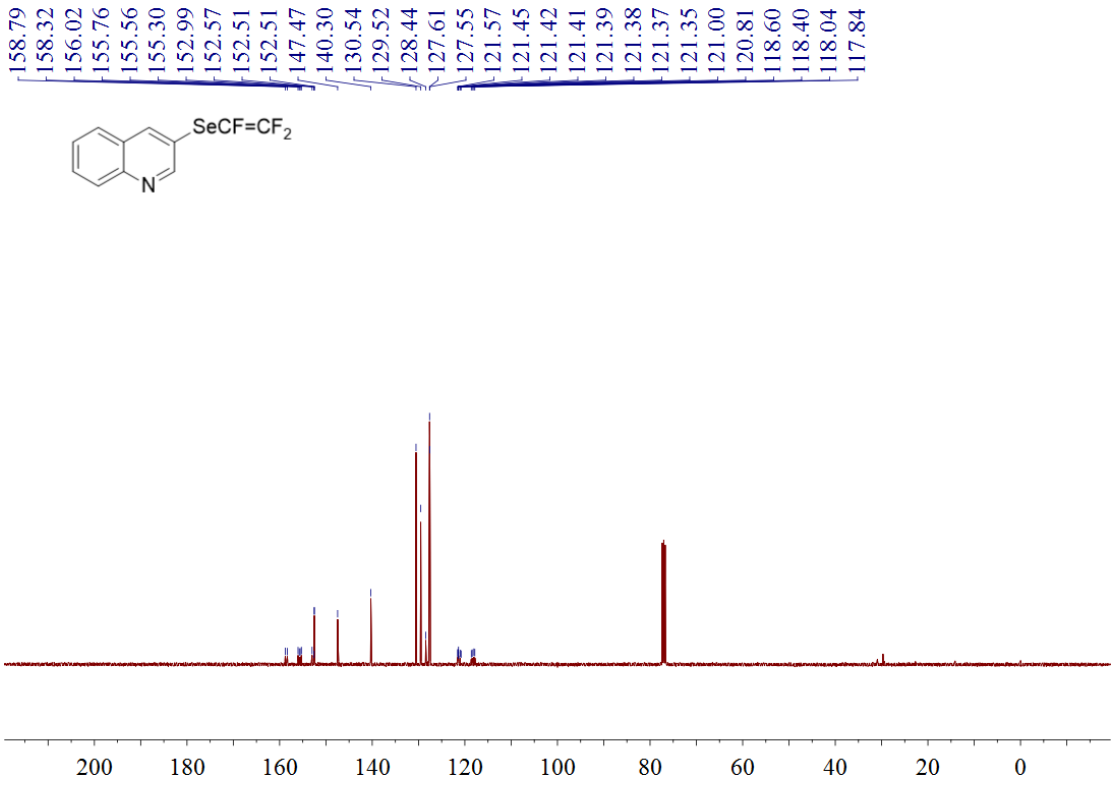
^{1}H NMR spectrum of **5s** in $CDCl_3$



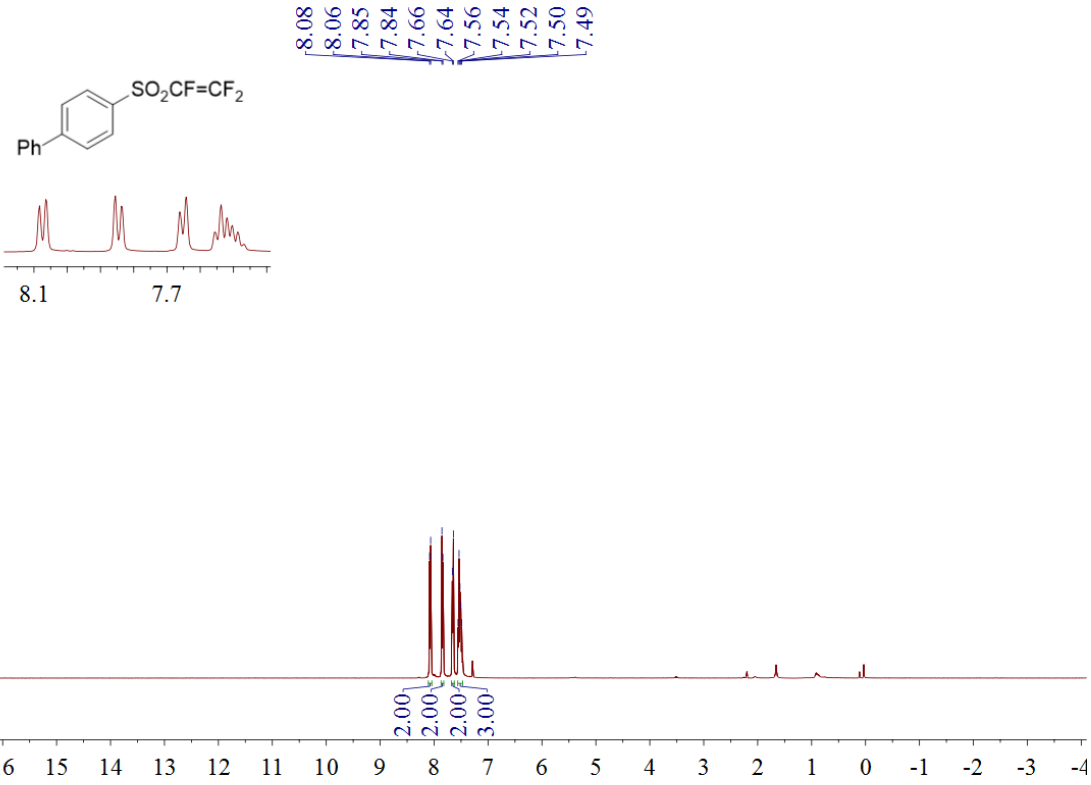
^{19}F NMR spectrum of **5s** in $CDCl_3$



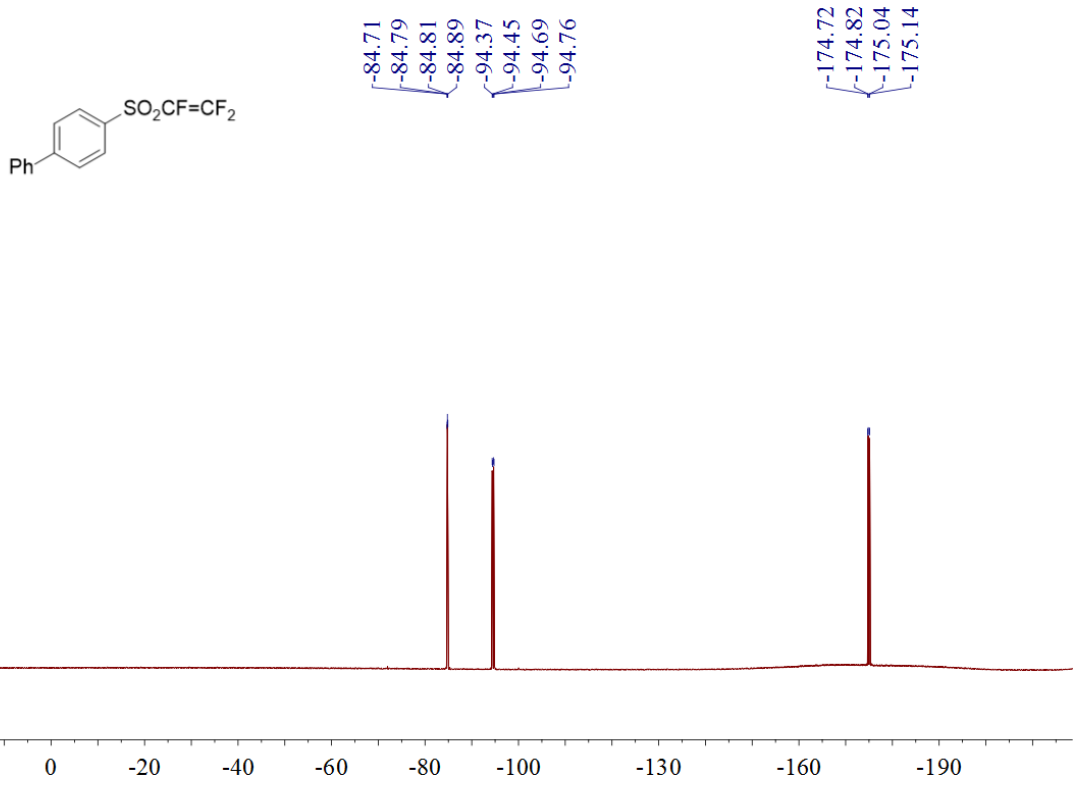
^{13}C NMR spectrum of **5s** in $CDCl_3$



^{1}H NMR spectrum of **3d′** in $CDCl_3$



^{19}F NMR spectrum of **3d′** in $CDCl_3$



^{13}C NMR spectrum of **3d′** in $CDCl_3$