Supporting Information *for*

Copper-catalyzed one-pot synthesis of 2-(2,2,2-trifluoroethyl)-substituted benzofused heterocycles

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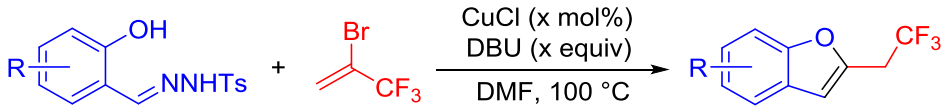
General information

^{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 ($CDCl_3$ δ 7.26) and ^{13}C NMR ($CDCl_3$ δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Salicylaldehyde *p*-tosylhydrazones **2**[1] and 2-aminobenzaldehyde *p*-tosylhydrazones **4**[2,3] were prepared according to the published procedures. Other 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.

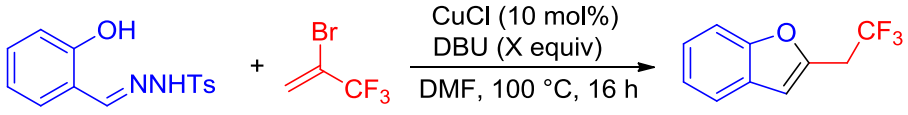
General procedure of copper-catalyzed one-pot synthesis of 2-(2,2,2-trifluoroethyl)-substituted benzofused heterocycles



2 **1** **3**

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added CuCl (10 mg, 0.10 mmol, 0.10 equiv), **2a** (1.0 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoro-1-propene **1** (0.26 g, 1.5 mmol, 1.5 equiv), DBU (0.53 g, 3.5 mmol, 3.5 equiv) and DMF (4.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (60 mL). The solution was washed with saturated NH_4Cl (3 × 100 mL) and saturated brine (3 × 100 mL) in turn. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with *n*-pentane/dichloromethane or *n*-pentane/ethyl acetate.

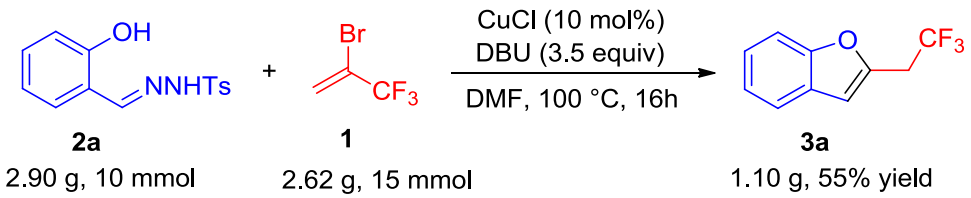
The effect of the amount of base DBU for the reaction



2a **1** **3a**

Entry	X equiv of DBU	Yield of **3a** (%)
1	1.0	21
2	2.0	36
3	3.0	51
4	3.5	73
5	4.0	53
6	5.0	45

Procedure for gram scale reaction for synthesis of 2-(2,2,2-trifluoroethyl)benzofuran (3a)



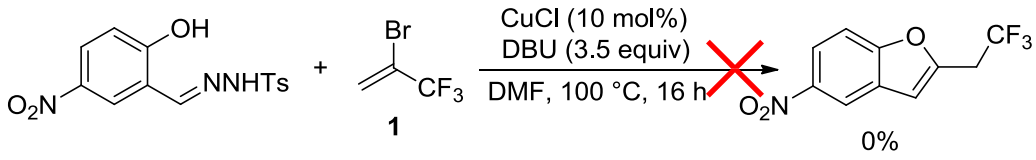
2a
2.90 g, 10 mmol

1
2.62 g, 15 mmol

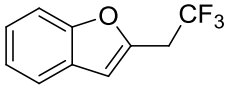
3a
1.10 g, 55% yield

In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added CuCl (0.10 g, 1.0 mmol, 0.10 equiv), *N*'-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (2.90 g, 10 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoro-1-propene **1** (2.62 g, 15 mmol, 1.5 equiv), DBU (5.31 g, 35 mmol, 3.5 equiv) and DMF (40 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (200 mL). The solution was washed with saturated NH_4Cl (3 × 300 mL) and saturated brine (3 × 200 mL) in turn. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with *n*-pentane to give 1.10 g of product **3a** (55% yield).

Unsuccessful reaction with other salicylaldehyde *p*-tosylhydrazone substrate

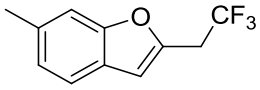


Data for compounds



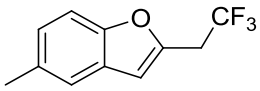
2-(2,2,2-trifluoroethyl)benzofuran (3a)

Obtained as a colorless liquid in 66% yield (132 mg). R_f (*n*-pentane) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.76 (s, 1H), 3.65 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (s), 147.1 (q, *J* = 3.6 Hz), 128.1 (s), 124.6 (s), 124.5 (q, *J* = 277.1 Hz), 123.0 (s), 121.0 (s), 111.3 (s), 106.8 (s), 34.0 (q, *J* = 32.3 Hz). IR (KBr): ν 2928, 1607, 1588, 1454, 1366, 1288, 1264, 1133, 1080, 1009, 956, 915, 833, 806, 738, 663, 555 cm^{-1}. GC-MS m/z 200 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_7F_3O$: 200.0449; found: 200.0452.



6-methyl-2-(2,2,2-trifluoroethyl)benzofuran (3b)

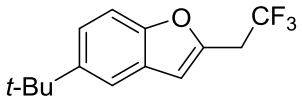
Obtained as a white solid in 70% yield (149 mg). M.p. 45–46 °C. R_f (*n*-pentane) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 3.62 (q, *J* = 10.1 Hz, 2H), 2.50 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 9.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5 (s), 146.4 (q, *J* = 3.7 Hz), 134.9 (s), 125.6 (s), 124.6 (q, *J* = 277.1 Hz), 124.4 (s), 120.4 (s), 111.4 (s), 106.6 (s), 34.0 (q, *J* = 32.2 Hz), 21.7 (s). IR (KBr): ν 2189, 1364, 1265, 1247, 1199, 1138, 1119, 1083, 963, 904, 820, 727, 648, 508, 458, 432 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_9F_3O$: 214.0605; found: 214.0610.



5-methyl-2-(2,2,2-trifluoroethyl)benzofuran (3c)

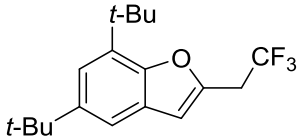
Obtained as a colorless liquid in 85% yield (181 mg). R_f (*n*-pentane) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H),

6.67 (s, 1H), 3.63 (q, J = 10.1 Hz, 2H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, J = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5 (s), 147.1 (q, J = 3.6 Hz), 132.5 (s), 128.2 (s), 125.8 (s), 124.6 (q, J = 277.1 Hz), 120.8 (s), 110.7 (s), 106.6 (s), 34.1 (q, J = 32.2 Hz), 21.3 (s). IR (KBr): ν 2925, 1603, 1475, 1420, 1363, 1323, 1243, 1161, 1081, 958, 873, 838, 799, 740, 665, 585, 476 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_9F_3O$: 214.0605; found: 214.0612.



5-(*tert*-butyl)-2-(2,2,2-trifluoroethyl)benzofuran (3d)

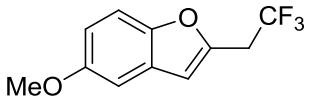
Obtained as a white solid in 80% yield (204 mg). M.p. 44–45 °C. R_f (*n*-pentane) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 – 7.37 (m, 2H), 6.72 (s, 1H), 3.63 (q, J = 10.1 Hz, 2H), 1.41 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, J = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3 (s), 147.1 (q, J = 3.7 Hz), 146.2 (s), 127.8 (s), 124.6 (q, J = 277.3 Hz), 122.6 (s), 117.2 (s), 110.5 (s), 107.0 (q, J = 0.9 Hz), 34.7 (s), 34.1 (q, J = 32.2 Hz), 31.8 (s). IR (KBr): ν 2964, 1603, 1478, 1364, 1258, 1189, 1136, 1085, 958, 881, 731, 664, 538, 455 cm^{-1}. GC-MS m/z 256 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_{15}F_3O$: 256.1075; found: 256.1077.



5,7-di-*tert*-butyl-2-(2,2,2-trifluoroethyl)benzofuran (3e)

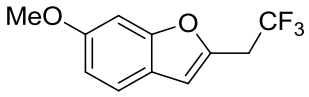
Obtained as a white solid in 50% yield (156 mg). M.p. 66–67 °C. R_f (*n*-pentane) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.29 (s, 1H), 6.68 (s, 1H), 3.64 (q, J = 10.1 Hz, 2H), 1.53 (s, 9H), 1.40 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, J = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7 (s), 146.1 (q, J = 3.7 Hz), 145.8 (s), 133.9 (s), 128.2 (s), 124.6 (q, J = 277.5 Hz), 119.2 (s), 114.9 (s), 106.9 (q, J = 0.6 Hz), 34.9 (s), 34.5 (s), 34.2 (q, J = 32.1 Hz), 31.9 (s), 29.8 (s). IR (KBr): ν 2960, 1481,

1364, 1262, 1149, 1084, 963, 904, 871, 839, 728, 672, 650 cm^{-1}. GC-MS m/z 312 (M^+). HRMS (EI) m/z: calcd. for $C_{18}H_{23}F_3O$: 312.1701; found: 312.1707.



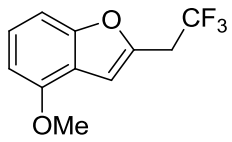
5-methoxy-2-(2,2,2-trifluoroethyl)benzofuran (3f)

Obtained as a colorless liquid in 93% yield (213 mg). R_f (*n*-pentane/ethyl acetate = 15:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.68 (s, 1H), 3.87 (s, 3H), 3.62 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (s), 150.1 (s), 147.8 (q, *J* = 3.7 Hz), 128.7 (s), 124.7 (q, *J* = 277.5 Hz), 113.4 (s), 111.7 (s), 106.9 (q, *J* = 0.8 Hz), 103.4 (s), 55.9 (s), 34.1 (q, *J* = 32.2 Hz). IR (KBr): ν 2939, 1607, 1478, 1439, 1322, 1246, 1205, 1168, 1128, 1082, 961, 838, 731, 650, 536 cm^{-1}. GC-MS m/z 230 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_9F_3O_2$: 230.0555; found: 230.0566.



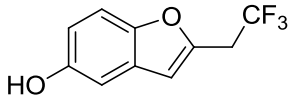
6-methoxy-2-(2,2,2-trifluoroethyl)benzofuran (3g)

Obtained as a colorless liquid in 60% yield (138 mg). R_f (*n*-pentane/ethyl acetate = 15:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 1H), 7.04 (s, 1H), 6.91 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.66 (s, 1H), 3.88 (s, 3H), 3.60 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.4 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (s), 156.1 (s), 145.9 (q, *J* = 3.5 Hz), 130.3 (s), 124.6 (q, *J* = 277.2 Hz), 121.1 (s), 112.2 (s), 106.6 (s), 95.8 (s), 55.7 (s), 33.9 (q, *J* = 32.2 Hz). IR (KBr): ν 2943, 1630, 1589, 1493, 1439, 1294, 1273, 1245, 1191, 1108, 966, 821, 665, 535, 439 cm^{-1}. GC-MS m/z 230 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_9F_3O_2$: 230.0555; found: 230.0550.



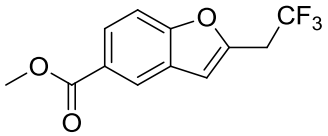
4-methoxy-2-(2,2,2-trifluoroethyl)benzofuran (3h)

Obtained as a colorless liquid in 45% yield (103 mg). R_f (*n*-pentane/ethyl acetate = 15:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.62 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (s), 153.4 (s), 145.6 (q, *J* = 3.4 Hz), 126.9 (q, *J* = 277.2 Hz), 125.3 (s), 118.4 (s), 104.4 (s), 104.3 (s), 103.4 (s), 55.6 (s), 33.9 (q, *J* = 32.3 Hz). IR (KBr): ν 2946, 2841, 2323, 2168, 1979, 1609, 1592, 1499, 1361, 1258, 1215, 1088, 957, 815, 770, 701, 645, 487 cm^{-1}. GC-MS m/z 230 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_9F_3O_2$: 230.0555; found: 230.0563.



2-(2,2,2-trifluoroethyl)benzofuran-5-ol (3i)

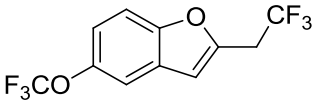
Obtained as a colorless liquid in 60% yield (129 mg). R_f (*n*-pentane) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (s, 1H), 5.11 (br s, 1H), 3.60 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6 (s), 150.2 (s), 148.1 (q, *J* = 3.7 Hz), 128.9 (s), 124.5 (q, *J* = 277.1 Hz), 113.3 (s), 111.7 (s), 106.7 (q, *J* = 0.9 Hz), 105.9 (s), 34.1 (q, *J* = 32.3 Hz). IR (KBr): ν 2189, 1474, 1261, 1167, 1147, 1084, 903, 789, 725, 649, 432 cm^{-1}. GC-MS m/z 216 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_7F_3O_2$: 216.0398; found: 216.0400.



Methyl 2-(2,2,2-trifluoroethyl)benzofuran-5-carboxylate (3j)

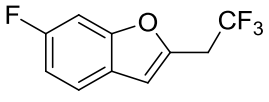
Obtained as a white solid in 58% yield (140 mg). M.p. 67–68 °C. R_f (*n*-pentane/ethyl

acetate = 15:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 6.80 (s, 1H), 3.96 (s, 3H), 3.65 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (s), 157.6 (s), 148.6 (q, *J* = 3.7 Hz), 128.1 (s), 126.4 (s), 125.5 (s), 124.4 (q, *J* = 277.2 Hz), 123.5 (s), 111.1 (s), 107.3 (s), 52.1 (s), 33.9 (q, *J* = 32.4 Hz). IR (KBr): ν 2889, 2256, 1715, 1606, 1455, 1366, 1289, 1193, 1116, 1089, 984, 905, 839, 808, 769, 649, 579, 434 cm^{-1}. GC-MS m/z 258 (M^+). HRMS (EI) m/z: calcd. for $C_{12}H_9F_3O_3$: 258.0504; found: 258.0503.



2-(2,2,2-trifluoroethyl)-5-(trifluoromethoxy)benzofuran (3k)

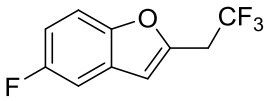
Obtained as a colorless liquid in 56% yield (159 mg). R_f (*n*-pentane) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 9.0 Hz, 1H), 7.45 (s, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 6.76 (s, 1H), 3.65 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.3 (s, 3F), -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1 (s), 149.2 (q, *J* = 3.5 Hz), 145.1 (q, *J* = 2.1 Hz), 128.8 (s), 124.3 (q, *J* = 277.1 Hz), 120.6 (q, *J* = 256.3 Hz), 118.3 (s), 113.7 (s), 112.0 (s), 107.0 (s), 34.1 (q, *J* = 32.4 Hz). IR (KBr): ν 2212, 1606, 1469, 1420, 1366, 1249, 1189, 1144, 1083, 960, 906, 873, 804, 787, 664, 612, 434 cm^{-1}. GC-MS m/z 284 (M^+). HRMS (EI) m/z: calcd. for $C_{11}H_6F_6O_2$: 284.0272; found: 284.0266.



6-fluoro-2-(2,2,2-trifluoroethyl)benzofuran (3l)

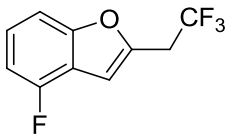
Obtained as a colorless liquid in 60% yield (130 mg). R_f (*n*-pentane) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.10 – 6.98 (m, 1H), 6.72 (s, 1H), 3.63 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.0 Hz, 3F), -116.9 (td, *J* = 9.2, 5.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 243.6 Hz), 154.9 (d, *J* = 13.6 Hz), 147.8 (q, *J* = 3.7 Hz), 129.8 (s),

124.4 (q, *J* = 277.0 Hz), 121.3 (d, *J* = 10.0 Hz), 111.5 (d, *J* = 24.1 Hz), 106.6 (s), 99.1 (d, *J* = 26.8 Hz), 33.9 (q, *J* = 32.3 Hz). IR (KBr): ν 2919, 1621, 1599, 1487, 1435, 1366, 1255, 1191, 1101, 1081, 969, 896, 819, 776, 665, 595, 481, 437 cm^{-1}. GC-MS m/z 218 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6F_4O$: 218.0355; found: 218.0361.



5-fluoro-2-(2,2,2-trifluoroethyl)benzofuran (3m)

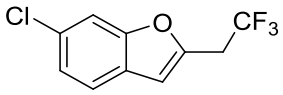
Obtained as a colorless liquid in 60% yield (130 mg). R_f (*n*-pentane) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 9.1 Hz, 1H), 6.72 (s, 1H), 3.64 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F), -120.7 (td, *J* = 8.8, 4.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 239.4 Hz), 151.3 (d, *J* = 0.6 Hz), 148.9 (q, *J* = 3.7 Hz), 128.9 (d, *J* = 10.9 Hz), 124.4 (q, *J* = 277.1 Hz), 112.3 (d, *J* = 26.6 Hz), 111.8 (d, *J* = 9.6 Hz), 107.0 (m), 106.5 (d, *J* = 25.1 Hz), 34.1 (q, *J* = 32.4 Hz). IR (KBr): ν 1626, 1607, 1471, 1449, 1419, 1365, 1283, 1188, 1168, 1117, 1081, 953, 905, 839, 797, 734, 616, 534, 478 cm^{-1}. GC-MS m/z 218 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6F_4O$: 218.0355; found: 218.0358.



4-fluoro-2-(2,2,2-trifluoroethyl)benzofuran (3n)

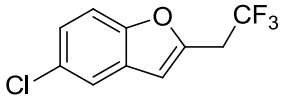
Obtained as a colorless liquid in 50% yield (109 mg). R_f (*n*-pentane) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 2H), 6.96 (t, *J* = 8.2 Hz, 1H), 6.84 (s, 1H), 3.65 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.0 Hz, 3F), -119.6 (dd, *J* = 9.4, 5.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (s), 155.7 (d, *J* = 250.9 Hz), 147.7 (q, *J* = 3.7 Hz), 125.2 (d, *J* = 7.6 Hz), 124.4 (q, *J* = 277.2 Hz), 117.3 (d, *J* = 21.9 Hz), 108.6 (d, *J* = 18.8 Hz), 107.5 (d, *J* = 4.2 Hz), 103.1 (s), 33.9 (q, *J* = 32.5 Hz). IR (KBr): ν 2926, 1593, 1496, 1437, 1366, 1259, 1213, 1148, 1086, 1027, 904, 776, 727, 650 cm^{-1}. GC-MS m/z 218 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6F_4O$:

218.0355; found: 218.0351.



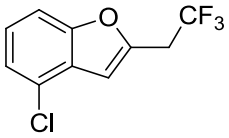
6-chloro-2-(2,2,2-trifluoroethyl)benzofuran (3o)

Obtained as a white solid in 60% yield (140 mg). M.p. 66–67 °C. R_f (*n*-pentane) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 6.72 (s, 1H), 3.63 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (s), 147.9 (q, *J* = 3.7 Hz), 130.5 (s), 126.7 (s), 124.4 (q, *J* = 277.2 Hz), 123.8 (s), 121.5 (s), 111.9 (s), 106.7 (q, *J* = 0.9 Hz), 33.9 (q, *J* = 32.4 Hz). IR (KBr): ν 1606, 1468, 1424, 1312, 1246, 1189, 1150, 1081, 959, 927, 905, 845, 728, 650, 577, 469 cm^{-1}. GC-MS m/z 234 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6ClF_3O$: 234.0059; found: 234.0057.



5-chloro-2-(2,2,2-trifluoroethyl)benzofuran (3p)

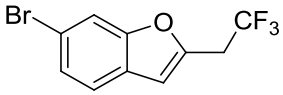
Obtained as a white solid in 62% yield (145 mg). M.p. 34–35 °C. R_f (*n*-pentane) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 6.70 (s, 1H), 3.64 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4 (s), 148.7 (q, *J* = 3.6 Hz), 129.4 (s), 128.7 (s), 124.9 (s), 124.6 (q, *J* = 275.1 Hz), 120.6 (s), 112.2 (s), 106.5 (s), 34.1 (q, *J* = 32.4 Hz). IR (KBr): ν 2208, 1447, 1255, 1186, 1151, 1085, 903, 803, 726, 653, 649, 429 cm^{-1}. GC-MS m/z 234 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6ClF_3O$: 234.0059; found: 234.0056.



4-chloro-2-(2,2,2-trifluoroethyl)benzofuran (3q)

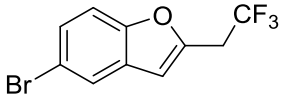
Obtained as a colorless liquid in 53% yield (124 mg). R_f (*n*-pentane) = 0.70. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.28 – 7.22 (m, 2H), 6.85 (s, 1H), 3.66 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 147.8 (q, *J* = 3.7 Hz), 127.6 (s), 125.9 (s), 125.2 (s), 124.3 (q, *J* = 277.2 Hz), 123.1 (s), 109.9 (s), 105.5 (s), 34.0 (q, *J* = 32.4 Hz). IR (KBr): ν 2928, 1602, 1584, 1477, 1365, 1321, 1253, 1173, 1082, 957, 942, 897, 860, 767, 731, 681, 575, 488 cm^{-1}. GC-MS m/z 234 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6ClF_3O$: 234.0059; found: 234.0063.



6-bromo-2-(2,2,2-trifluoroethyl)benzofuran (3r)

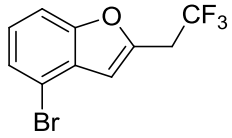
Obtained as a white solid in 67% yield (185 mg). M.p. 54–55 °C. R_f (*n*-pentane) = 0.70. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 6.72 (s, 1H), 3.63 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 147.8 (q, *J* = 3.7 Hz), 127.1 (s), 126.5 (s), 124.3 (q, *J* = 277.2 Hz), 121.9 (s), 117.9 (s), 114.8 (s), 106.7 (q, *J* = 0.8 Hz), 33.9 (q, *J* = 32.4 Hz). IR (KBr): ν 2156, 1606, 1463, 1450, 1362, 1311, 1246, 1149, 1077, 1047, 955, 879, 822, 728, 664, 591, 570, 431 cm^{-1}. GC-MS m/z 277 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6BrF_3O$: 277.9554; found: 277.9559.



5-bromo-2-(2,2,2-trifluoroethyl)benzofuran (3s)

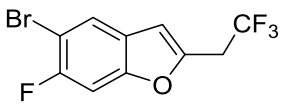
Obtained as a white solid in 66% yield (182 mg). M.p. 46–47 °C. R_f (*n*-pentane) = 0.70. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 6.69 (s, 1H), 3.64 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 (s), 148.5 (q, *J* = 3.6 Hz), 130.0 (s), 127.6 (s), 124.4 (q, *J* = 277.2 Hz), 123.7 (s), 116.1 (s), 112.7 (s), 106.3 (q, *J* = 0.9 Hz), 34.0 (q, *J* = 32.4 Hz). IR (KBr): ν 3094, 2930, 1876, 1743, 1605, 1461, 1416, 1361, 1263, 1183, 1084, 952, 917, 881, 807, 739, 607, 534, 464 cm^{-1}.

GC-MS m/z 277 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6BrF_3O$: 277.9554; found: 277.9561.



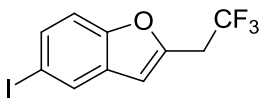
4-bromo-2-(2,2,2-trifluoroethyl)benzofuran (3t)

Obtained as a white solid in 55% yield (152 mg). M.p. 62–63 °C. R_f (*n*-pentane) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 8.9 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 3.65 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (s), 147.7 (q, *J* = 3.7 Hz), 129.7 (s), 126.1 (s), 125.6 (s), 124.3 (q, *J* = 277.3 Hz), 113.9 (s), 110.4 (s), 107.1 (q, *J* = 0.9 Hz), 34.1 (q, *J* = 32.4 Hz). IR (KBr): ν 2154, 1578, 1473, 1422, 1365, 1255, 1152, 1084, 904, 812, 773, 676, 623, 569, 482 cm^{-1}. GC-MS m/z 277 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6BrF_3O$: 277.9554; found: 277.9557.



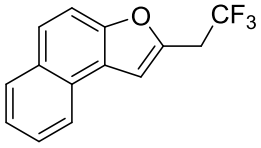
5-bromo-6-fluoro-2-(2,2,2-trifluoroethyl)benzofuran (3u)

Obtained as a white solid in 55% yield (163 mg). M.p. 42–43 °C. R_f (*n*-pentane) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.68 (s, 1H), 3.63 (q, *J* = 9.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.0 Hz, 3F), -109.6 (t, *J* = 7.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (d, *J* = 201.2 Hz), 153.9 (d, *J* = 12.1 Hz), 148.9 (q, *J* = 3.7 Hz), 125.6 (s), 124.4 (s), 124.3 (q, *J* = 277.2 Hz), 106.0 (s), 104.4 (d, *J* = 23.0 Hz), 100.1 (d, *J* = 27.9 Hz), 33.9 (q, *J* = 32.5 Hz). IR (KBr): ν 2918, 1607, 1463, 1423, 1364, 1312, 1246, 1184, 1132, 1080, 1006, 952, 871, 840, 740, 674, 559 cm^{-1}. GC-MS m/z 296 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_6BrF_4O$ $[M+H]^+$: 296.9533; found:296.9526.



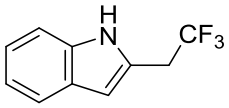
5-iodo-2-(2,2,2-trifluoroethyl)benzofuran (3v)

Obtained as a white solid in 61% yield (198 mg). M.p. 52–53 °C. R_f (*n*-pentane) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.67 (s, 1H), 3.64 (q, *J* = 9.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 9.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4 (s), 148.1 (q, *J* = 3.6 Hz), 133.2 (s), 130.8 (s), 129.9 (s), 124.4 (q, *J* = 277.2 Hz), 113.3 (s), 106.0 (s), 86.6 (s), 33.9 (q, *J* = 32.4 Hz). IR (KBr): ν 2232, 1602, 1441, 1419, 1364, 1249, 1183, 1079, 957, 914, 872, 797, 665, 607, 569, 518, 425 cm^{-1}. GC-MS m/z 325 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_6IF_3O$: 325.9416; found: 325.9421.



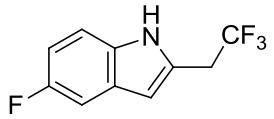
2-(2,2,2-trifluoroethyl)naphtho[1,2-*b*]furan (3w)

Obtained as a white solid in 70% yield (175 mg). M.p. 80–81 °C. R_f (*n*-pentane) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 3.74 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (s), 146.2 (q, *J* = 3.7 Hz), 130.4 (s), 128.8 (s), 127.5 (s), 126.5 (s), 125.6 (s), 124.7 (s), 124.6 (q, *J* = 277.1 Hz), 123.3 (s), 112.2 (s), 112.2 (s), 105.9 (q, *J* = 0.7 Hz), 34.2 (q, *J* = 32.3 Hz). IR (KBr): ν 3059, 1631, 1578, 1526, 1448, 1386, 1363, 1319, 1255, 1185, 1134, 1078, 959, 800, 774, 699, 651, 516, 483 cm^{-1}. GC-MS m/z 250 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_9F_3O$: 250.0605; found: 250.0604.



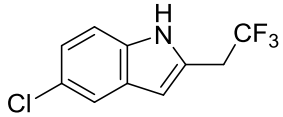
2-(2,2,2-trifluoroethyl)-1*H*-indole (5a)[4]

Obtained as a white solid in 42% yield (84 mg). M.p. 65–66 °C. R_f(*n*-pentane/ethyl acetate = 20:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 3.62 (q, *J* = 10.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6 (s), 128.0 (s), 126.5 (q, *J* = 3.3 Hz), 125.2 (q, *J* = 277.0 Hz), 122.6 (s), 120.5 (s), 120.2 (s), 110.8 (s), 104.5 (s), 33.8 (q, *J* = 31.4 Hz). IR (KBr): ν 3403, 2983, 1737, 1456, 1427, 1372, 1291, 1253, 1135, 1078, 1044, 915, 736, 662, 555 cm^{-1}. GC-MS m/z 199 (M^+).



5-fluoro-2-(2,2,2-trifluoroethyl)-1*H*-indole (5b)[4]

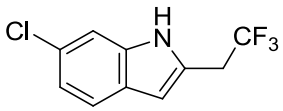
Obtained as a colorless liquid in 40% yield (86 mg). R_f(*n*-pentane/ethyl acetate = 20:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.27 (d, *J* = 9.4 Hz, 2H), 7.00 (t, *J* = 9.0 Hz, 1H), 6.50 (s, 1H), 3.60 (q, *J* = 10.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.4 Hz, 3F), -124.1 – -124.3 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (d, *J* = 234.8 Hz), 133.1 (s), 128.4 (q, *J* = 3.1 Hz), 125.4 (s), 125.1 (q, *J* = 276.9 Hz), 111.5 (d, *J* = 9.7 Hz), 110.9 (d, *J* = 26.4 Hz), 105.4 (d, *J* = 23.7 Hz), 104.5 (d, *J* = 4.6 Hz), 33.8 (q, *J* = 31.5 Hz). GC-MS m/z 217 (M^+).



5-chloro-2-(2,2,2-trifluoroethyl)-1*H*-indole (5c)[4]

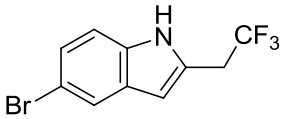
Obtained as a white solid in 45% yield (105 mg). M.p. 72–73 °C. R_f(*n*-pentane/ethyl acetate = 20:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.58 (s, 1H), 7.29 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.47 (s, 1H), 3.61 (q, *J* = 10.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ

134.9 (s), 129.1 (s), 128.1 (q, J = 3.3 Hz), 125.9 (s), 125.0 (q, J = 277.1 Hz), 122.9 (s), 119.9 (s), 111.9 (s), 104.1 (s), 33.8 (q, J = 31.6 Hz). IR (KBr): ν 3416, 2926, 1985, 1656, 1583, 1550, 1468, 1448, 1369, 1311, 1267, 1253, 1149, 1079, 923, 869, 792, 664 cm^{-1}. GC-MS m/z 233 (M^+).



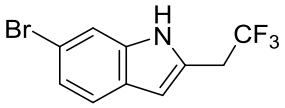
6-chloro-2-(2,2,2-trifluoroethyl)-1*H*-indole (5d)

Obtained as a white solidin 43% yield (101 mg). M.p. 48–49 °C. R_f(*n*-pentane/ethyl acetate = 20:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (br s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.13 (d, J = 8.1 Hz, 1H), 6.50 (s, 1H), 3.60 (q, J = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, J = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (s), 128.4 (s), 127.3 (q, J = 2.7 Hz), 126.6 (s), 125.0 (q, J = 276.9 Hz), 121.4 (s), 121.0 (s), 110.8 (s), 104.5 (s), 33.8 (q, J = 31.6 Hz). IR (KBr): ν 3398, 2951, 1709, 1612, 1545, 1410, 1363, 1290, 1255, 1137, 1076, 996, 925, 895, 819, 741, 660, 490 cm^{-1}. GC-MS m/z 233 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_8ClF_3N$ $[M+H]^+$: 234.0292; found: 234.0286.



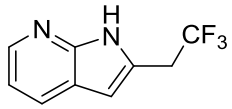
5-bromo-2-(2,2,2-trifluoroethyl)-1*H*-indole (5e)[4]

Obtained as a white solid in 50% yield (138 mg). M.p. 87–88 °C. R_f(*n*-pentane/ethyl acetate = 20:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.74 (s, 1H), 7.35 – 7.22 (m, 2H), 6.47 (s, 1H), 3.61 (q, J = 10.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, J = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1 (s), 129.7 (s), 128.0 (q, J = 3.3 Hz), 125.5 (s), 125.1 (q, J = 277.1 Hz), 123.1 (s), 113.4 (s), 112.3 (s), 104.0 (s), 33.8 (q, J = 31.6 Hz). IR (KBr): ν 3416, 2957, 2858, 1668, 1586, 1545, 1465, 1377, 1254, 1213, 1146, 1078, 1051, 917, 869, 792, 663 cm^{-1}. GC-MS m/z 277 (M^+).



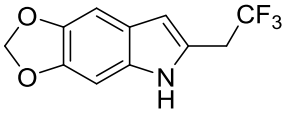
6-bromo-2-(2,2,2-trifluoroethyl)-1*H*-indole (5f)

Obtained as a white solid in 48% yield (133 mg). M.p. 81–82°C. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.54 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.50 (s, 1H), 3.60 (q, *J* = 10.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3 (s), 127.3 (q, *J* = 3.1 Hz), 126.9 (s), 125.1 (q, *J* = 274.0 Hz), 123.6 (s), 121.8 (s), 116.0 (s), 113.8 (s), 104.6 (s), 33.7 (q, *J* = 31.5 Hz). IR (KBr): ν 3413, 2923, 1654, 1612, 1540, 1454, 1364, 1287, 1252, 1140, 1077, 994, 904, 812, 732, 664, 553 cm^{-1}. GC-MS m/z 279 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_7BrF_3N$ $[M]^+$: 278.9693; found: 278.9691.



2-(2,2,2-trifluoroethyl)-1*H*-pyrrolo[2,3-*b*]pyridine (5g)

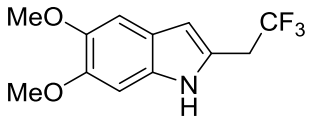
Obtained as a white solid in 15% yield (30 mg). M.p. 126.8–128.0 °C. R_f (*n*-pentane/ethyl acetate = 1:1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (br s, 1H), 8.32 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.06 (m, 1H), 6.48 (s, 1H), 3.69 (q, *J* = 10.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (s), 142.2 (s), 129.0 (s), 128.1 (q, *J* = 3.2 Hz), 125.0 (q, *J* = 277.2 Hz), 121.1 (s), 116.1 (s), 102.0 (s), 34.2 (q, *J* = 31.7 Hz). IR (KBr): ν 3136, 2922, 2851, 1420, 1248, 1143, 1115, 1074, 807, 769 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_8F_3N_2$ $[M+H]^+$: 201.0634; found: 201.0628.



6-(2,2,2-trifluoroethyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (5h)

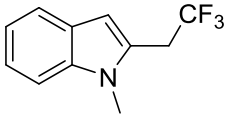
Obtained as a colorless liquid in *ca*. 5% yield (12 mg). R_f (*n*-pentane/ethyl acetate =

3:1) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 6.95 (s, 1H), 6.84 – 6.79 (m, 1H), 6.40 – 6.31 (m, 1H), 5.93 (s, 2H), 3.52 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 (t, *J* = 10.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (s), 143.2 (s), 131.4 (s), 125.1 (q, *J* = 277.1 Hz), 125.0 (q, *J* = 3.4 Hz), 121.8 (s), 104.6 (s), 100.6 (s), 99.0 (s), 91.8 (s), 33.8 (q, *J* = 31.5 Hz). IR (KBr): ν 3403, 2926, 1363, 1328, 1294, 1254, 1176, 1141, 1080, 1040, 947 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_7F_3NO_2$ $[M-H]^-$: 242.0423; found: 242.0425.



5,6-dimethoxy-2-(2,2,2-trifluoroethyl)-1*H*-indole (5i)

Obtained as a colorless liquid in *ca*. 5% yield (13 mg). R_f (*n*-pentane/ethyl acetate = 1:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.03 (s, 1H), 6.87 (s, 1H), 6.37 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.55 (q, *J* = 10.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 (t, *J* = 10.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4 (s), 145.4 (s), 130.9 (s), 125.2 (q, *J* = 277.0 Hz), 124.9 (q, *J* = 3.3 Hz), 120.7 (s), 104.2 (s), 102.2 (s), 94.3 (s), 56.3 (s), 56.2 (s), 33.8 (q, *J* = 31.4 Hz). IR (KBr): ν 3365, 2937, 1486, 1364, 1258, 1204, 1140, 1125, 1081, 1010, 723 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{12}H_{13}F_3NO_2$ $[M+H]^+$: 260.0893; found: 260.0887.



1-methyl-2-(2,2,2-trifluoroethyl)-1*H*-indole (5j)

Obtained as a white solid in 25% yield (53 mg). M.p. 65.5–66.9 °C. R_f (*n*-pentane/CH_2Cl_2) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.18 – 7.12 (m, 1H), 6.57 (s, 1H), 3.73 (s, 3H), 3.62 (q, *J* = 10.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 10.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (s), 128.3 (q, *J* = 3.2 Hz), 127.3 (s), 125.0 (q, *J* = 277.0 Hz), 122.0 (s), 120.5 (s), 119.9 (s), 109.4 (s), 103.8 (s), 32.0 (q, *J* = 31.8

Hz), 29.8 (s). IR (ATR): ν 3060, 2951, 2866, 1548, 1469, 1350, 1318, 1251, 1235, 1147, 1073, 903, 787, 753, 656 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{11}H_{10}F_3N$ $[M]^+$: 213.0765; found: 213.0766.

Crystal structure analyses

The crystal samples of **3j** were prepared by slow volatilization in a *n*-hexane/$CDCl_3$ (1:1) solvent mixture. The suitable crystals of **3j** (CCDC 2055439) 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.[5] Structure solution and refinement were carried out with the SHELXTL suite of programs.[5] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

ORTEP diagrams

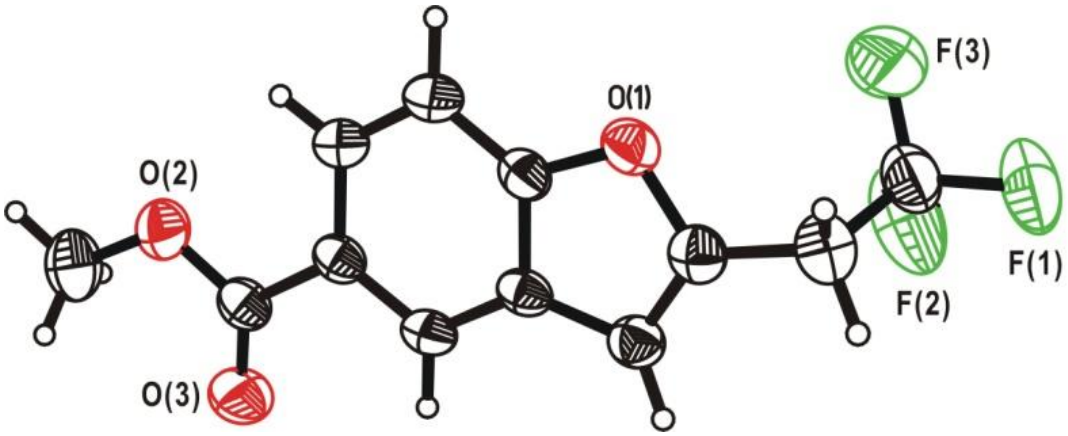


Figure S1. ORTEP diagram of compound 3j. Thermal ellipsoids are drawn at 40% probability

References:

(1) Ragupathi, A.; Sagadevan, A.; Charpe, V. P.; Lin, C.-C.; Hwu, J.-R.; Hwang, K. C. *Chem. Commun.* **2019**, *55*, 5151.

(2) Patil, V. S.; Pal, S. S.; Pathare, R. S.; Reddy, L. K. K.; Pathak, A. *Tetrahedron Lett.* **2015**, *56*, 6370.

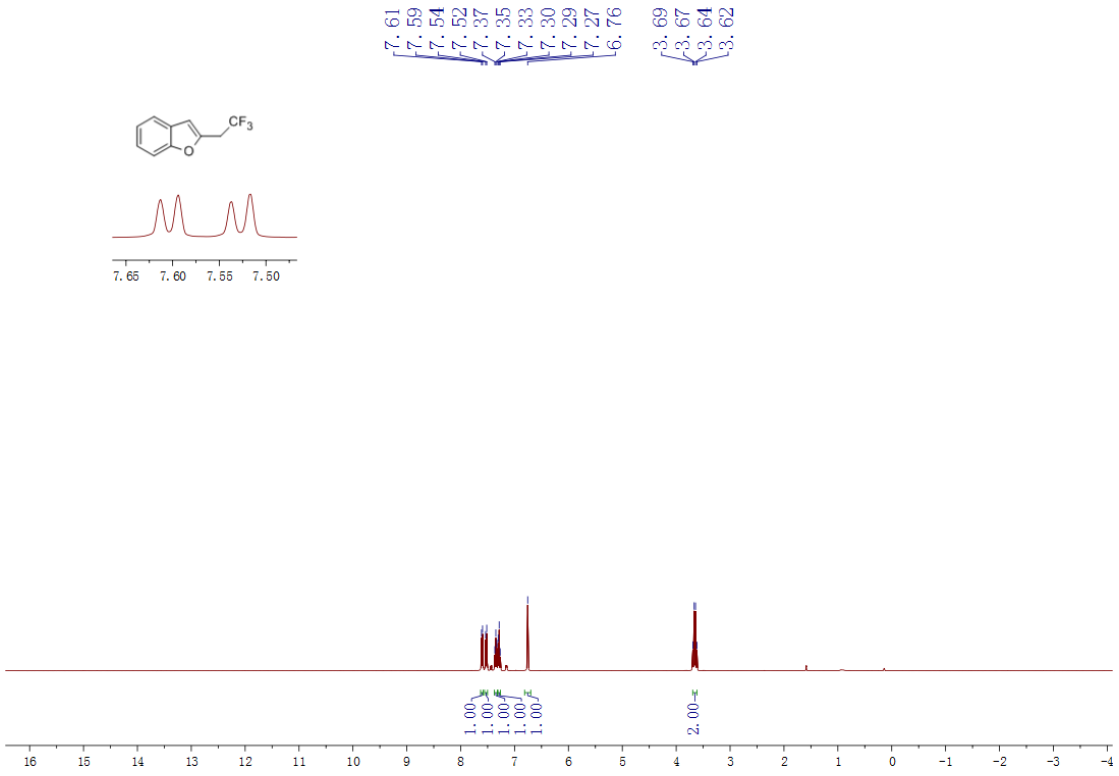
(3) Zhang, X.; Yuan, C.; Zhang, C.; Gao, X.; Wang, B.; Sun, Z.; Xiao, Y.; Guo, H. *Tetrahedron* **2016**, *72*, 8274.

(4) Zhang, H.; Wang, H.-Y.; Luo, Y.; Chen, C.; Cao, Y.; Chen, P.; Guo, Y.-L.; Lan, Y.; Liu, G. *ACS Catalysis* **2018**, *8*, 2173.

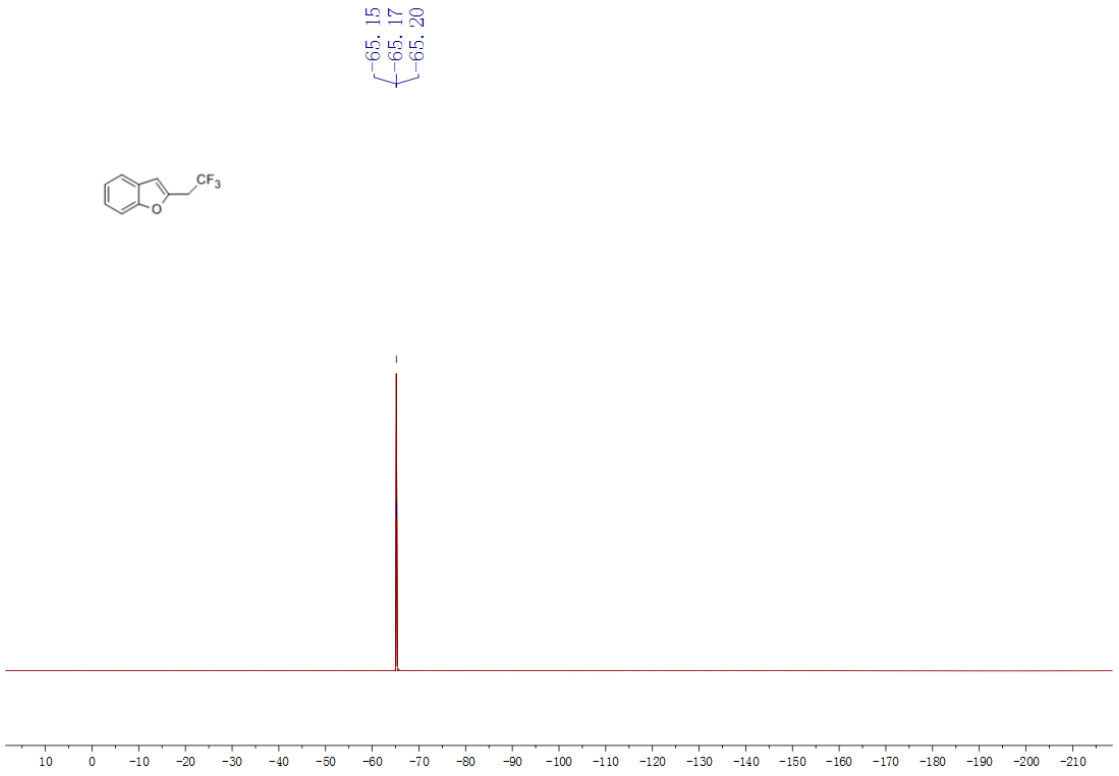
(5) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, **1997**.

Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

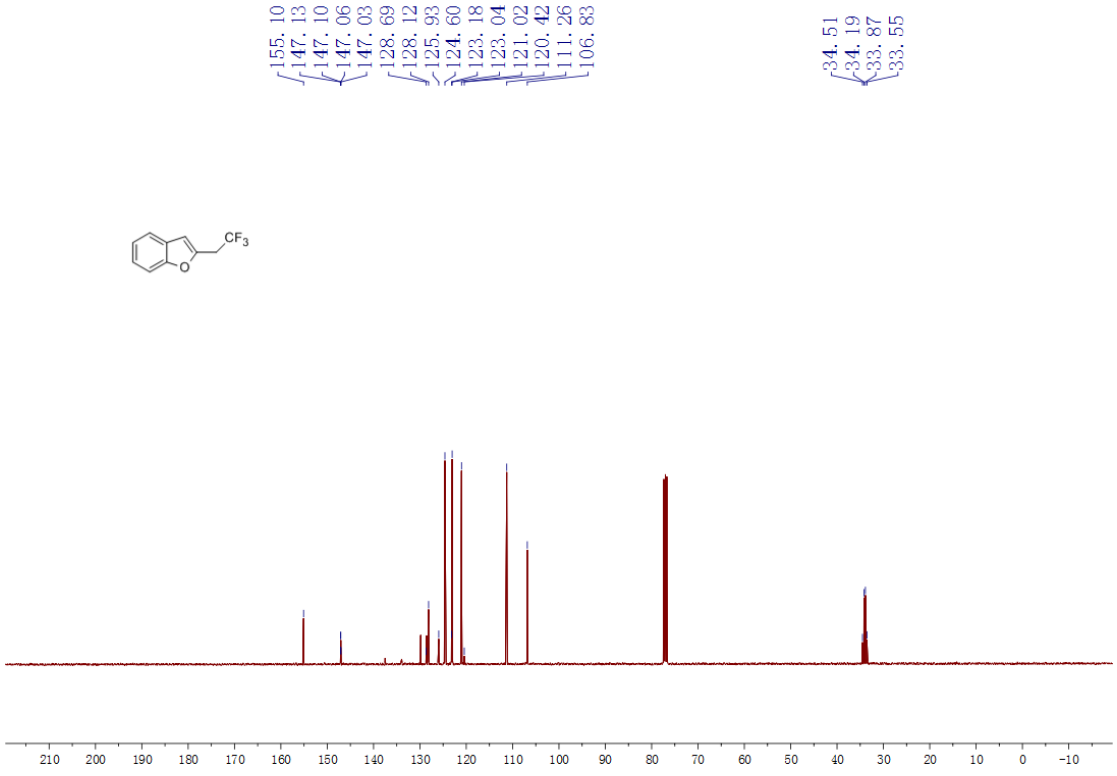
^{1}H NMR spectrum of **3a** in $CDCl_3$



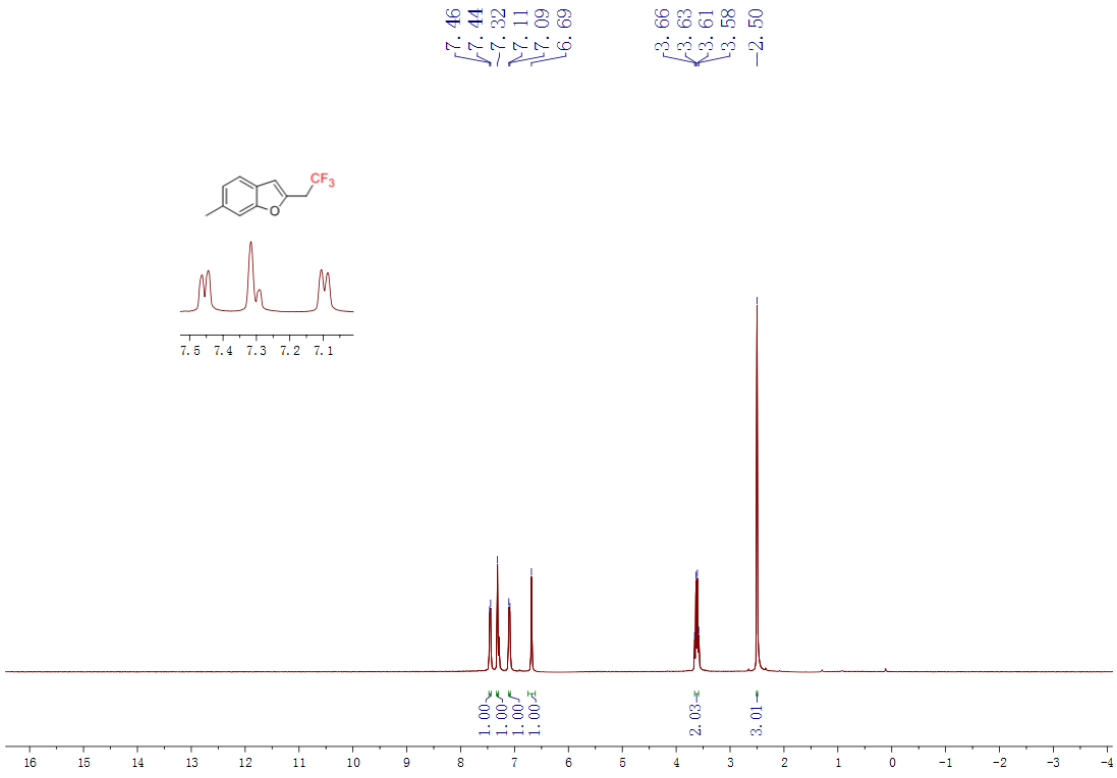
^{19}F NMR spectrum of **3a** in $CDCl_3$



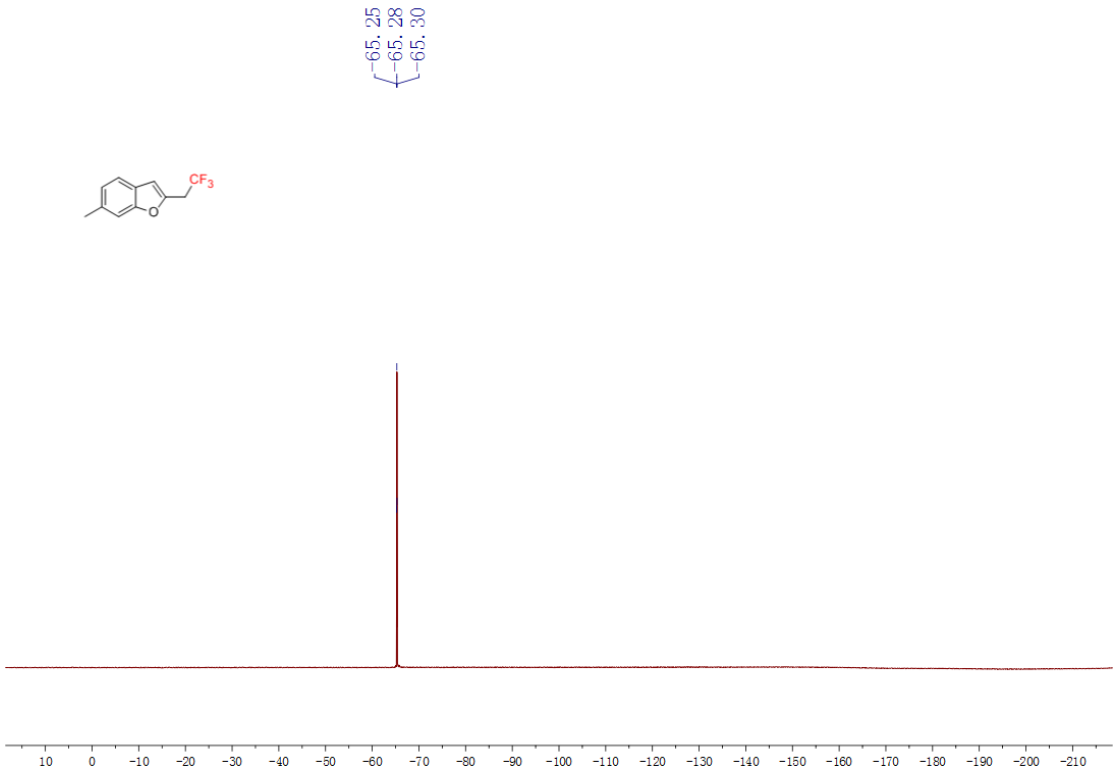
^{13}C NMR spectrum of **3a** in $CDCl_3$



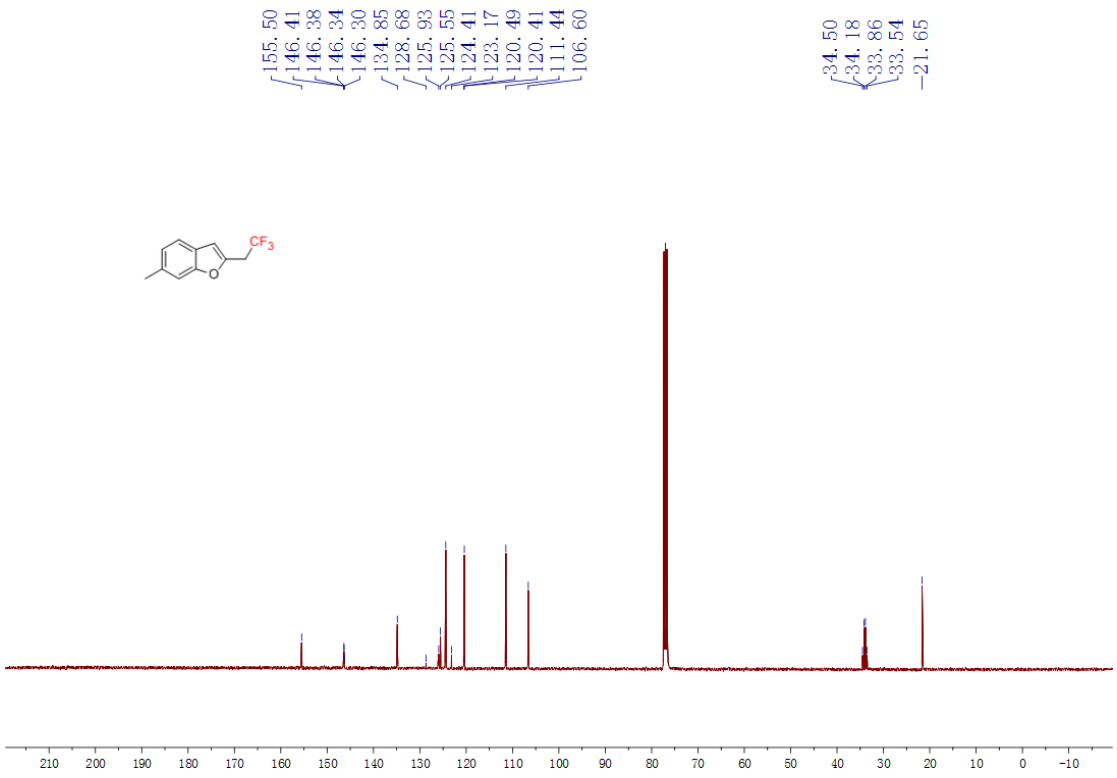
^{1}H NMR spectrum of **3b** in $CDCl_3$



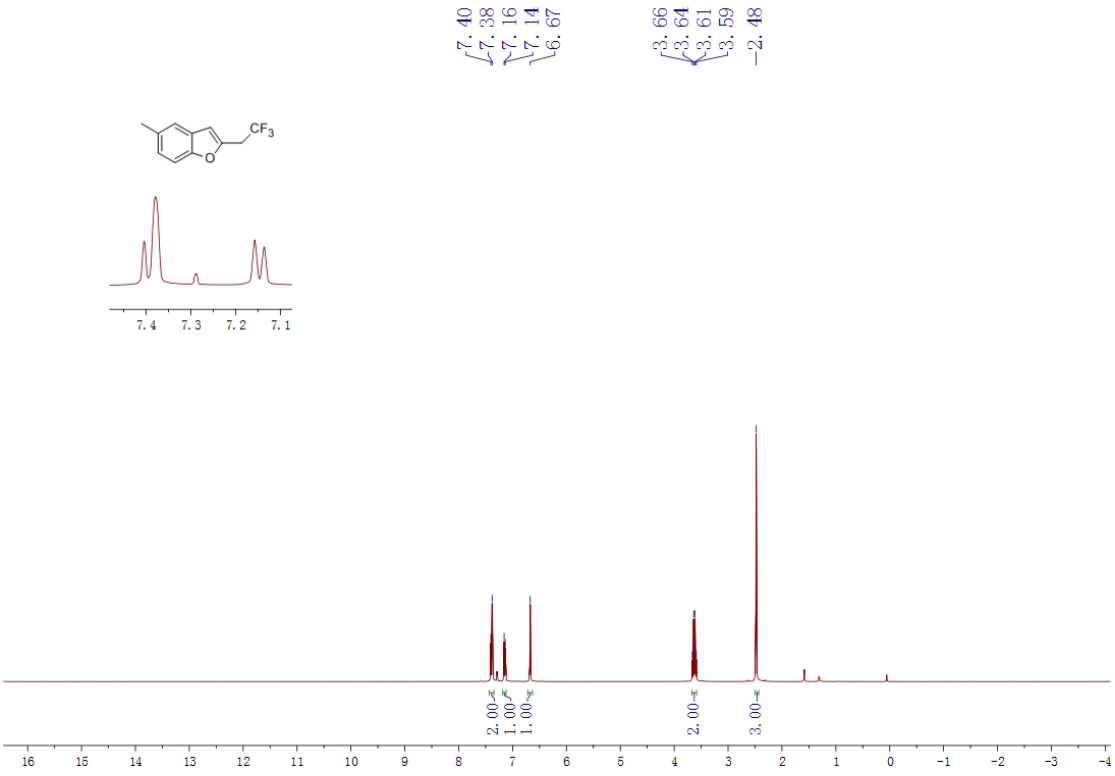
^{19}F NMR spectrum of **3b** in $CDCl_3$



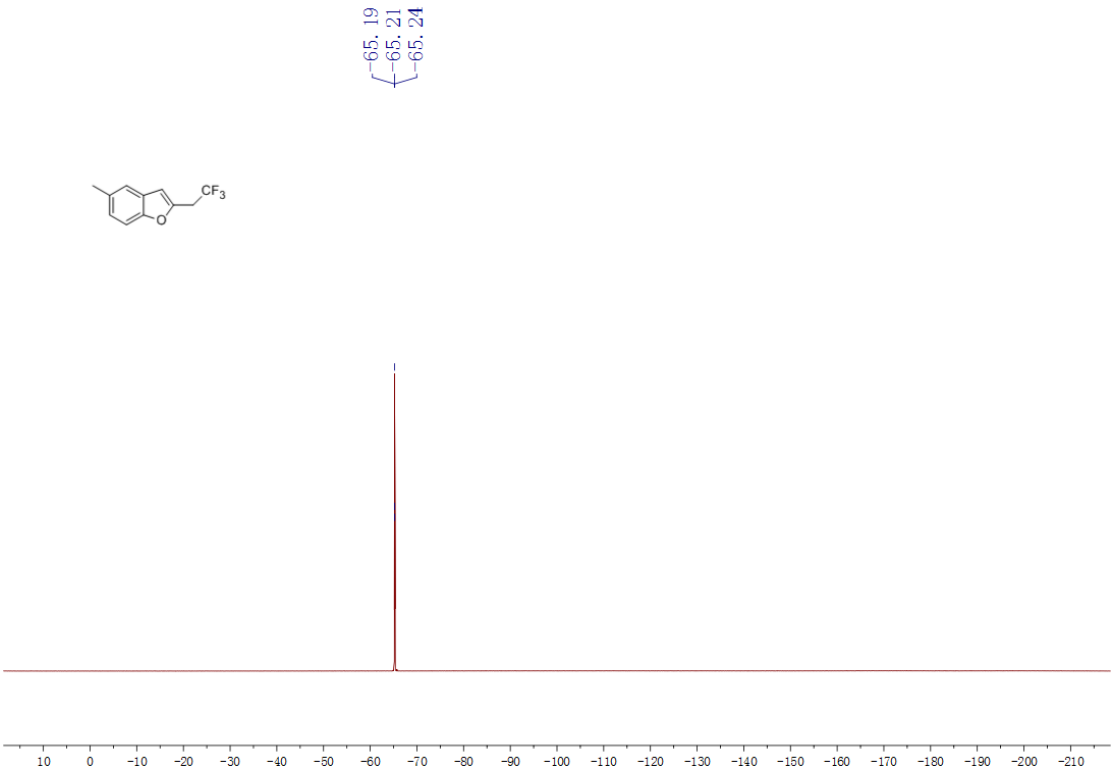
^{13}C NMR spectrum of **3b** in $CDCl_3$



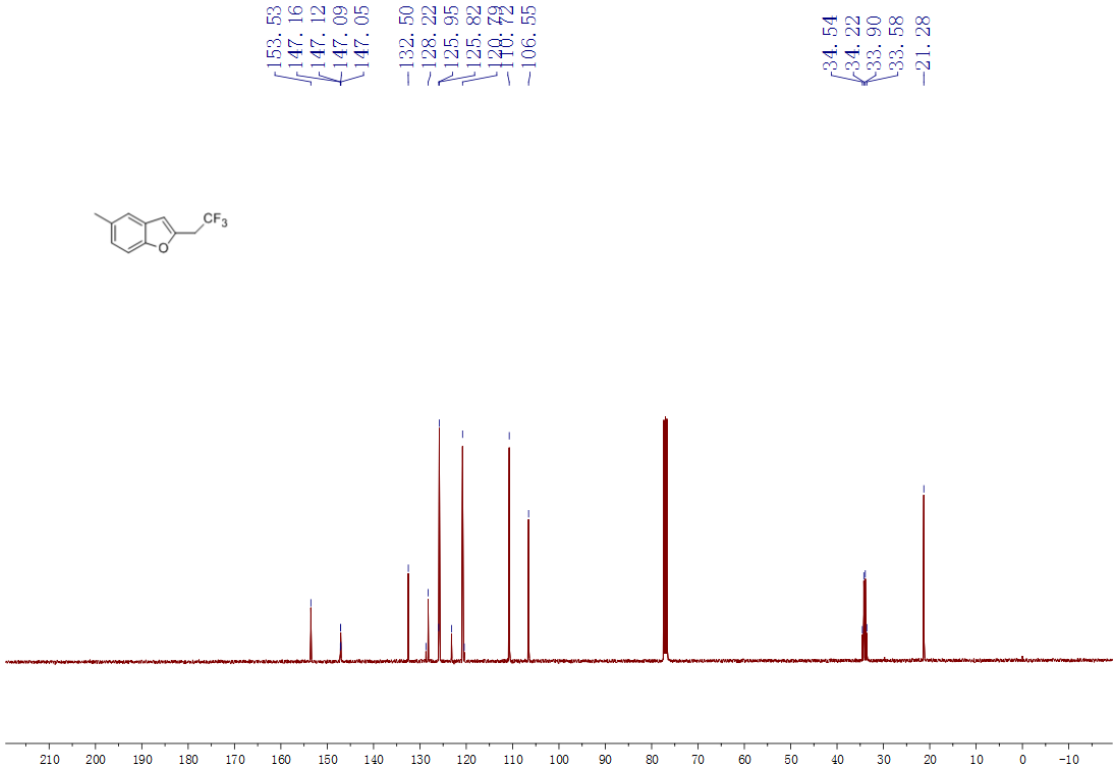
^{1}H NMR spectrum of **3c** in $CDCl_3$



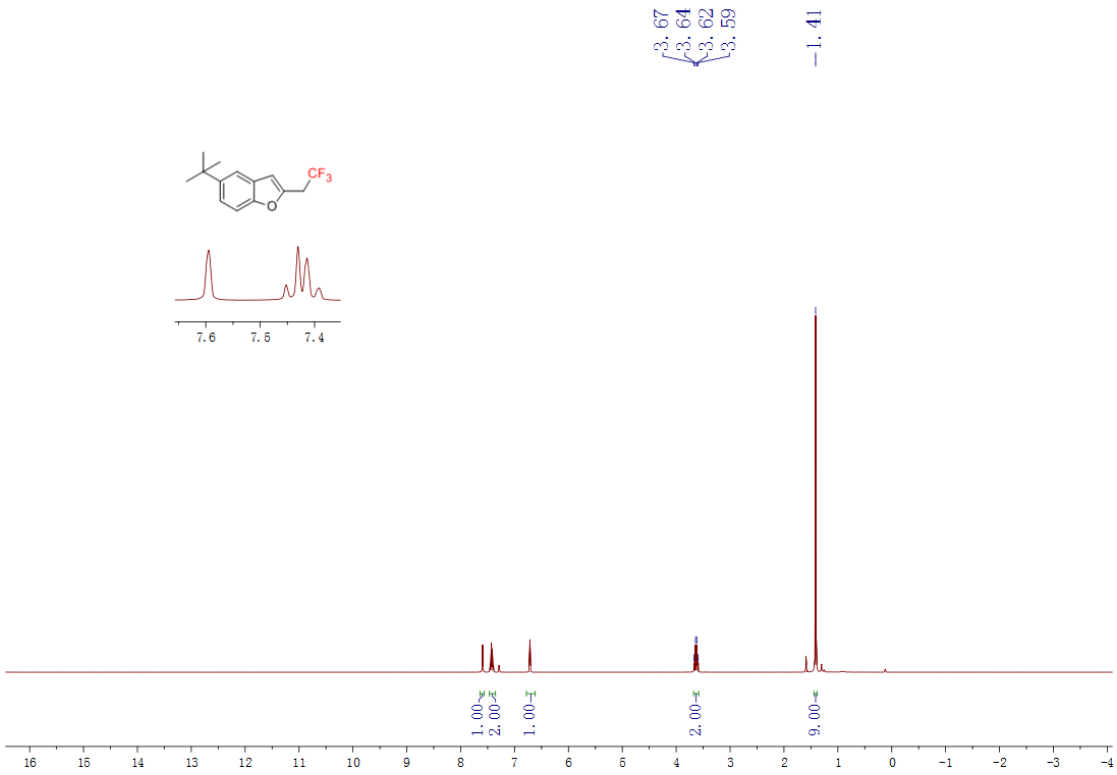
^{19}F NMR spectrum of **3c** in $CDCl_3$



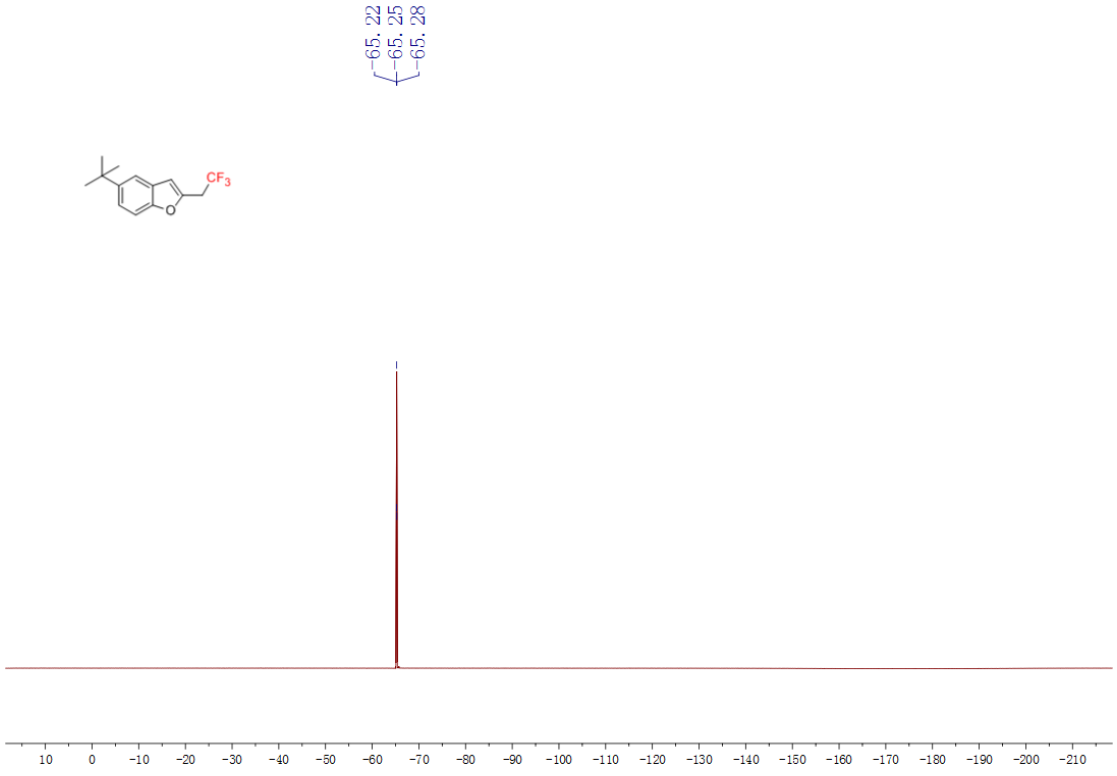
^{13}C NMR spectrum of **3c** in $CDCl_3$



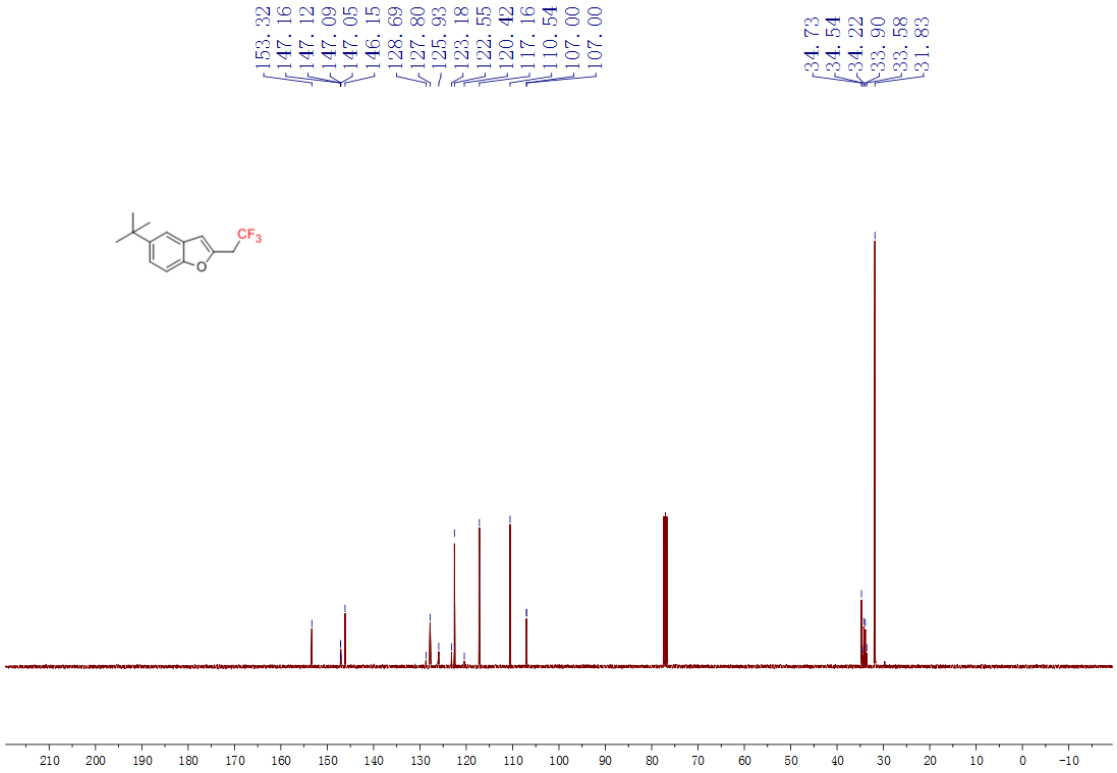
^{1}H NMR spectrum of **3d** in $CDCl_3$



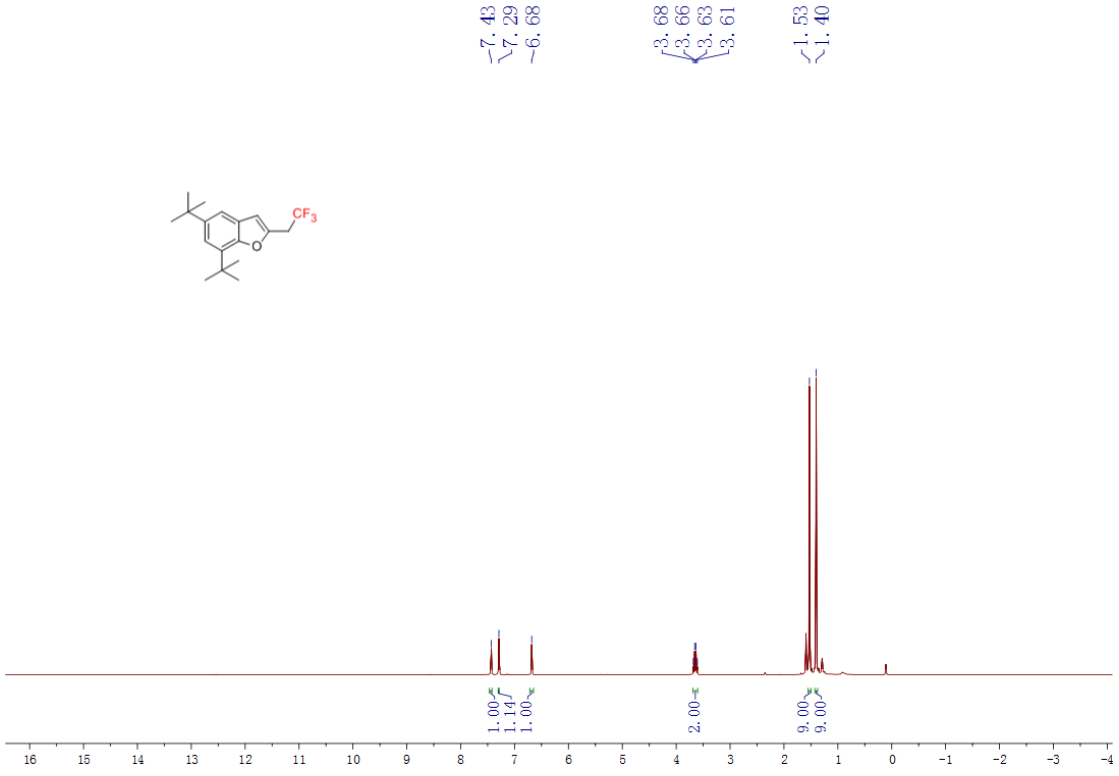
^{19}F NMR spectrum of **3d** in $CDCl_3$



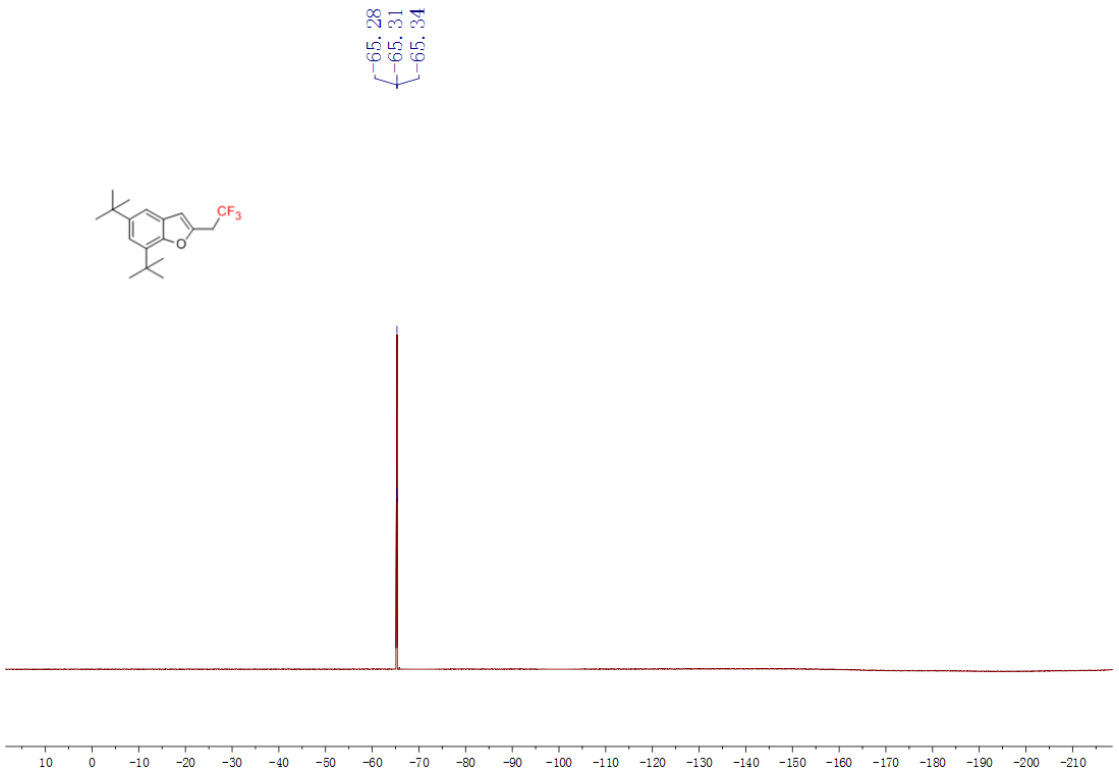
^{13}C NMR spectrum of **3d** in $CDCl_3$



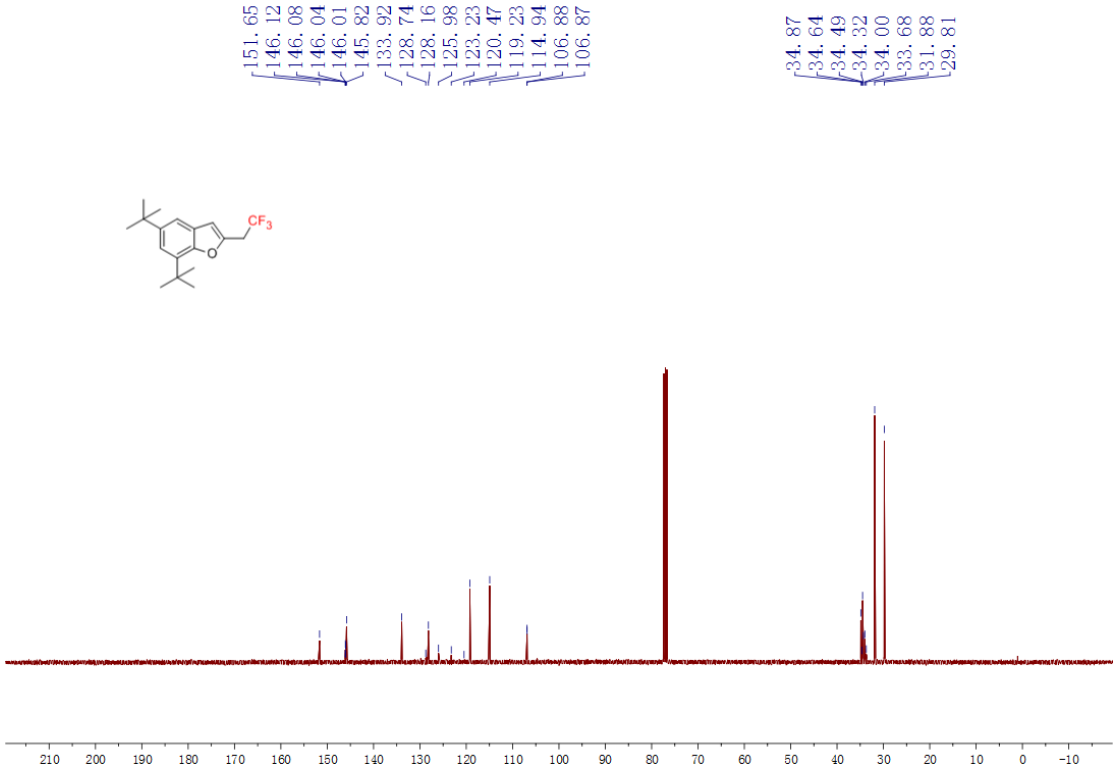
^{1}H NMR spectrum of **3e** in $CDCl_3$



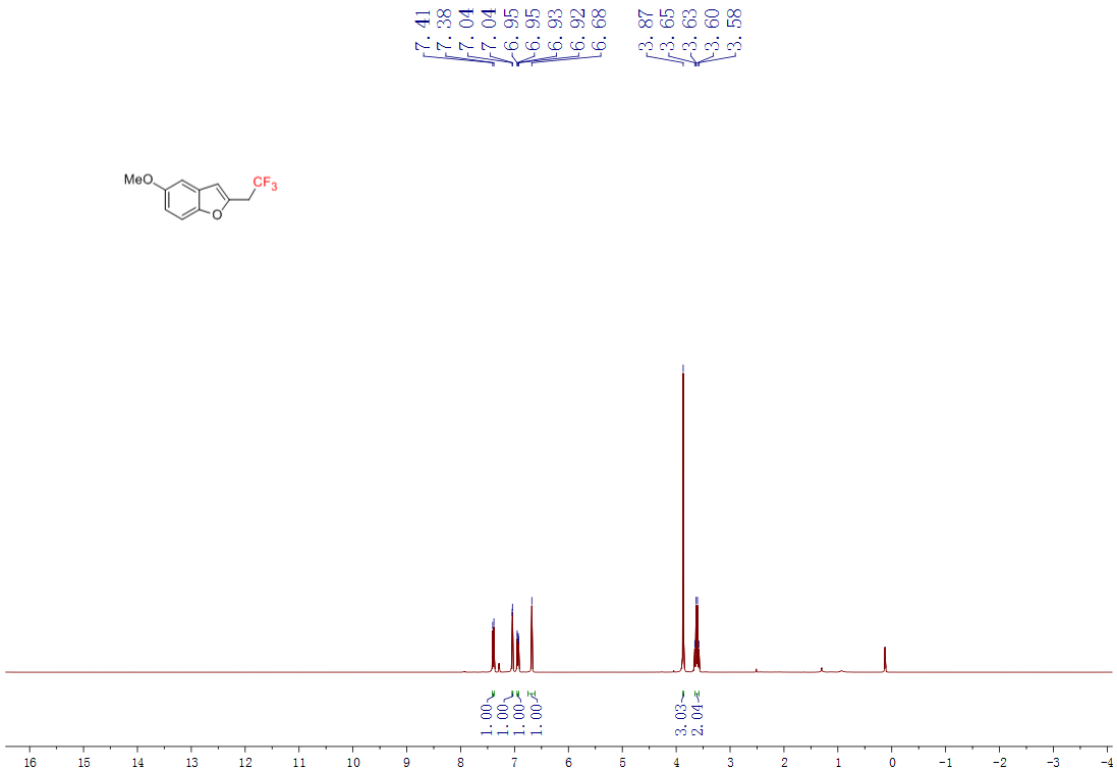
^{19}F NMR spectrum of **3e** in $CDCl_3$



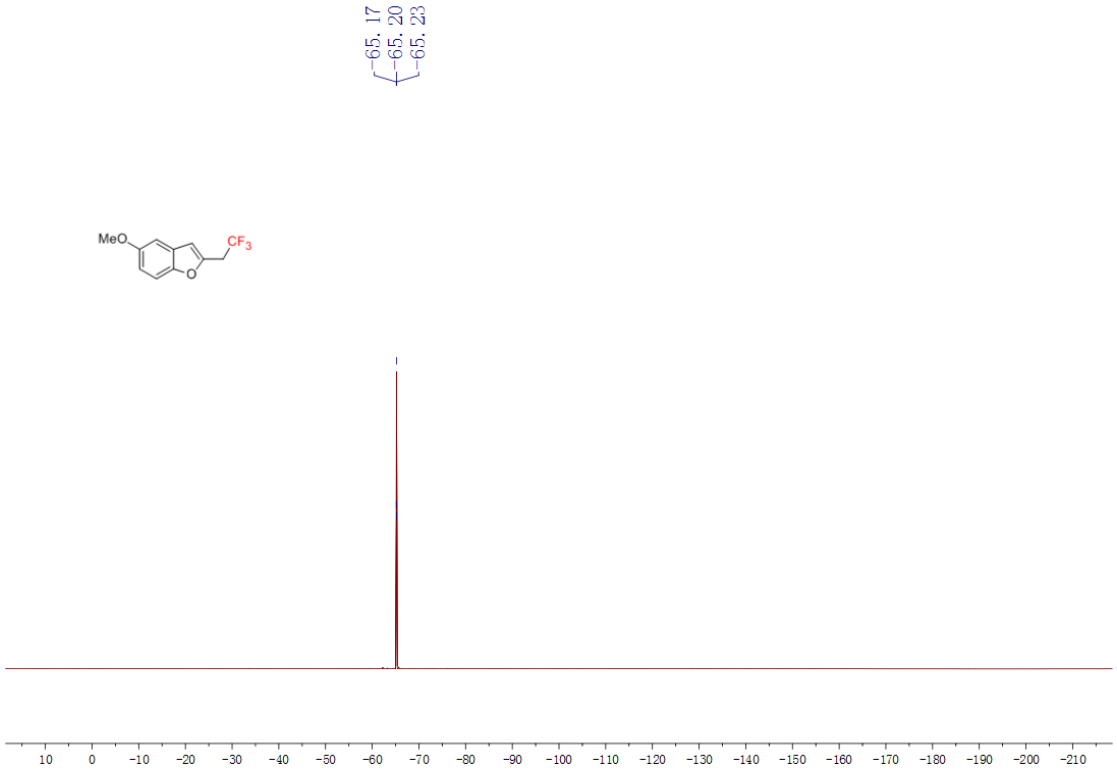
^{13}C NMR spectrum of **3e** in $CDCl_3$



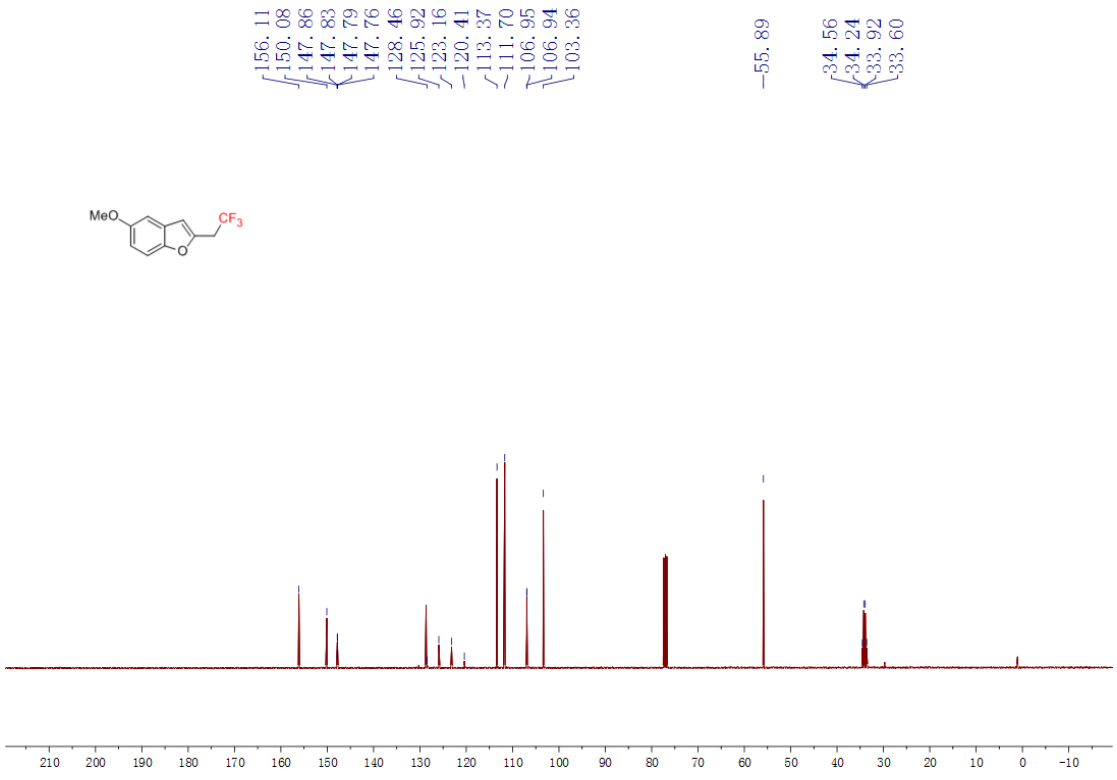
^{1}H NMR spectrum of **3f** in $CDCl_3$



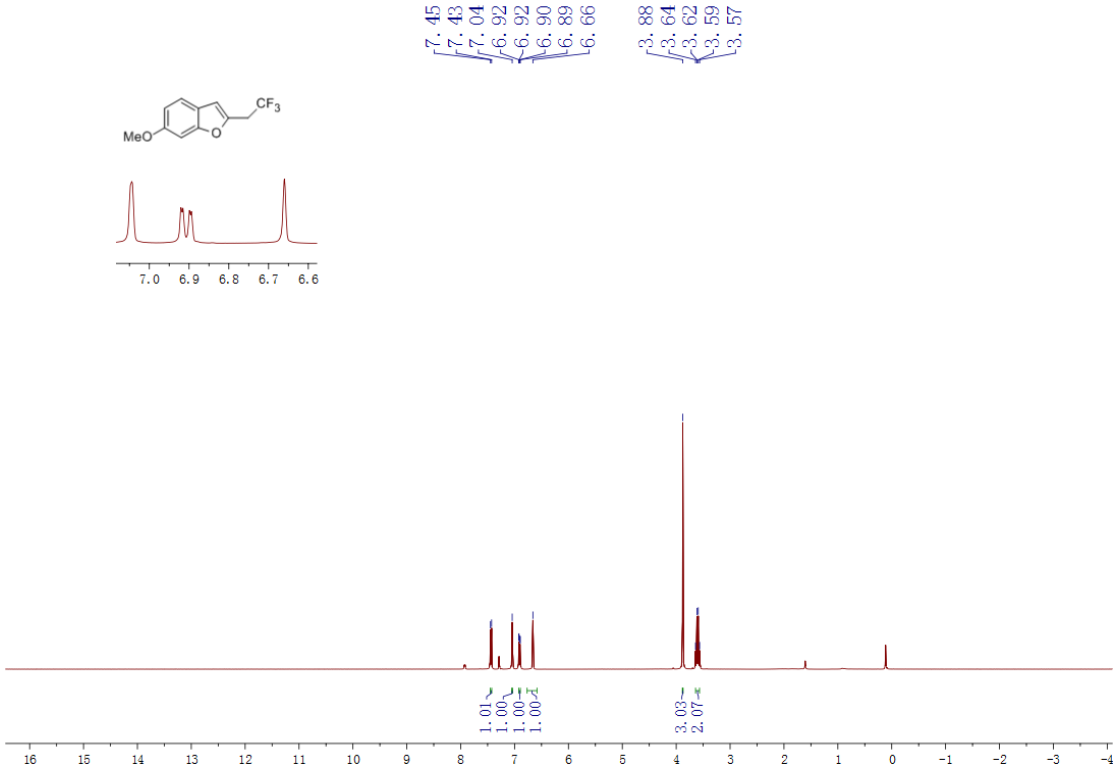
^{19}F NMR spectrum of **3f** in $CDCl_3$



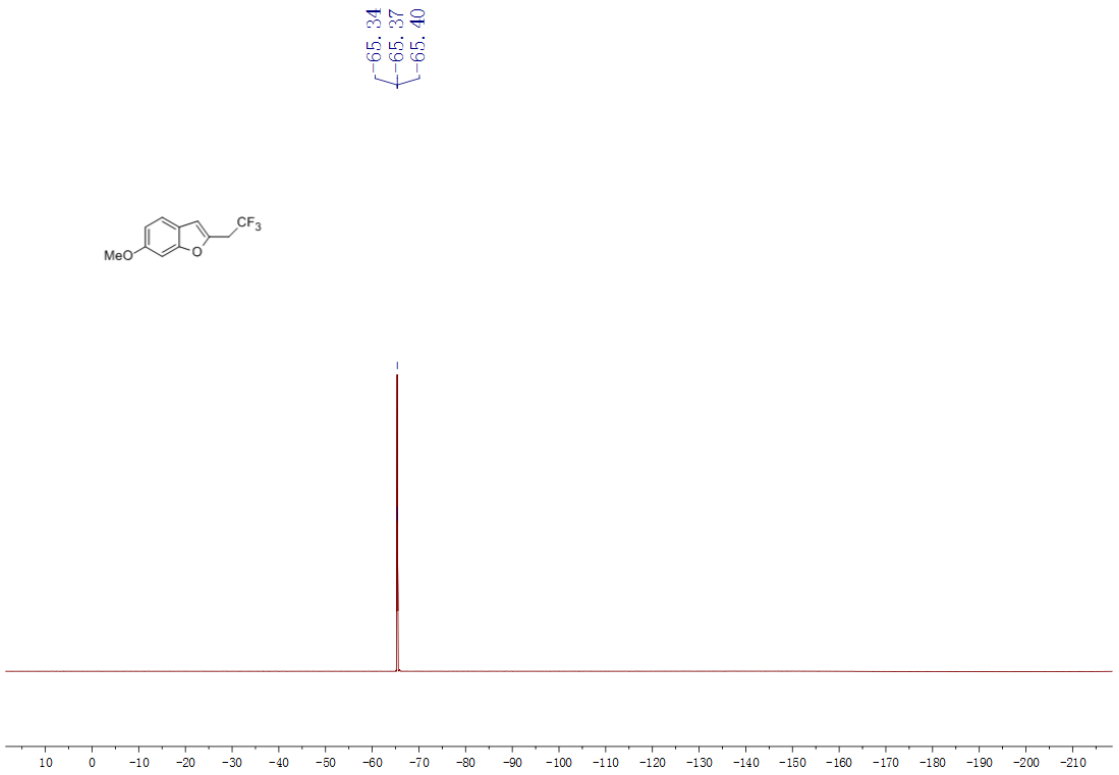
^{13}C NMR spectrum of **3f** in $CDCl_3$



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



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



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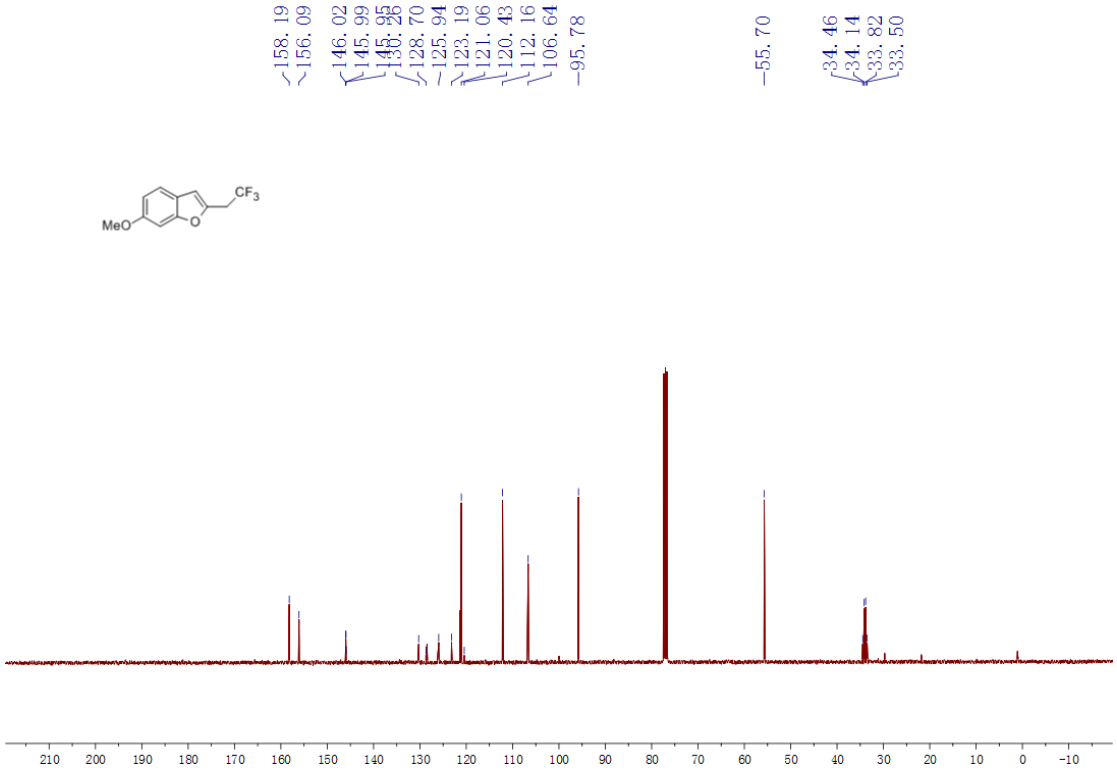
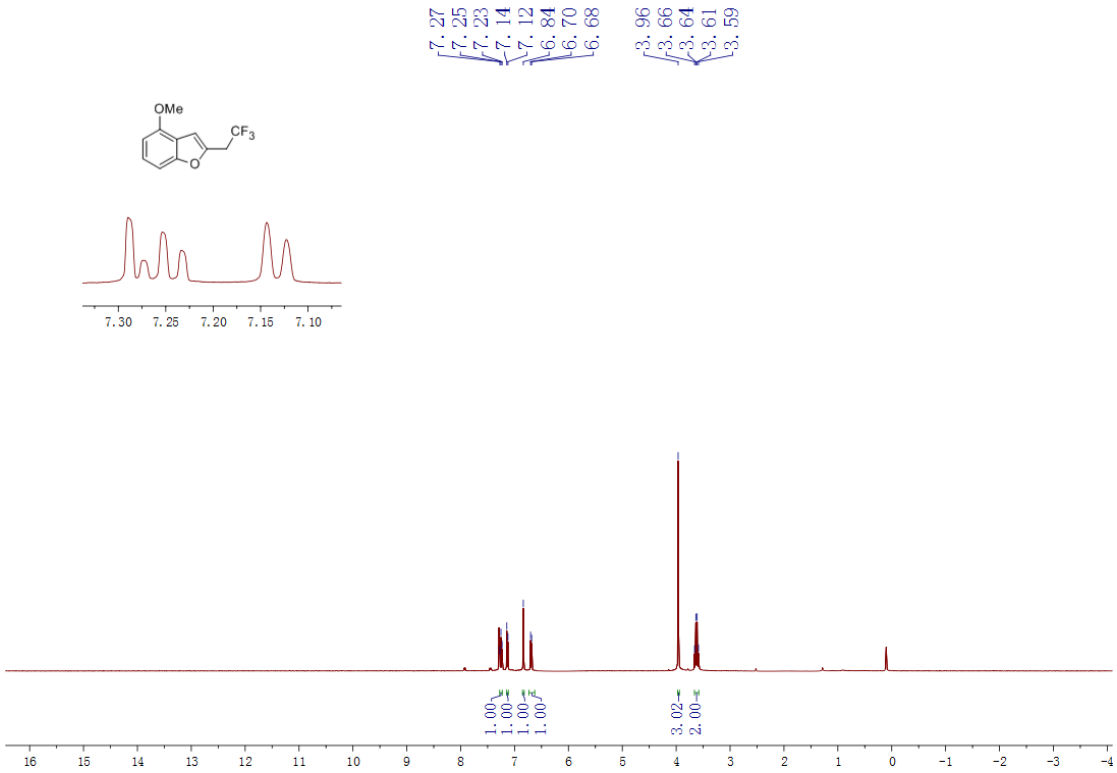
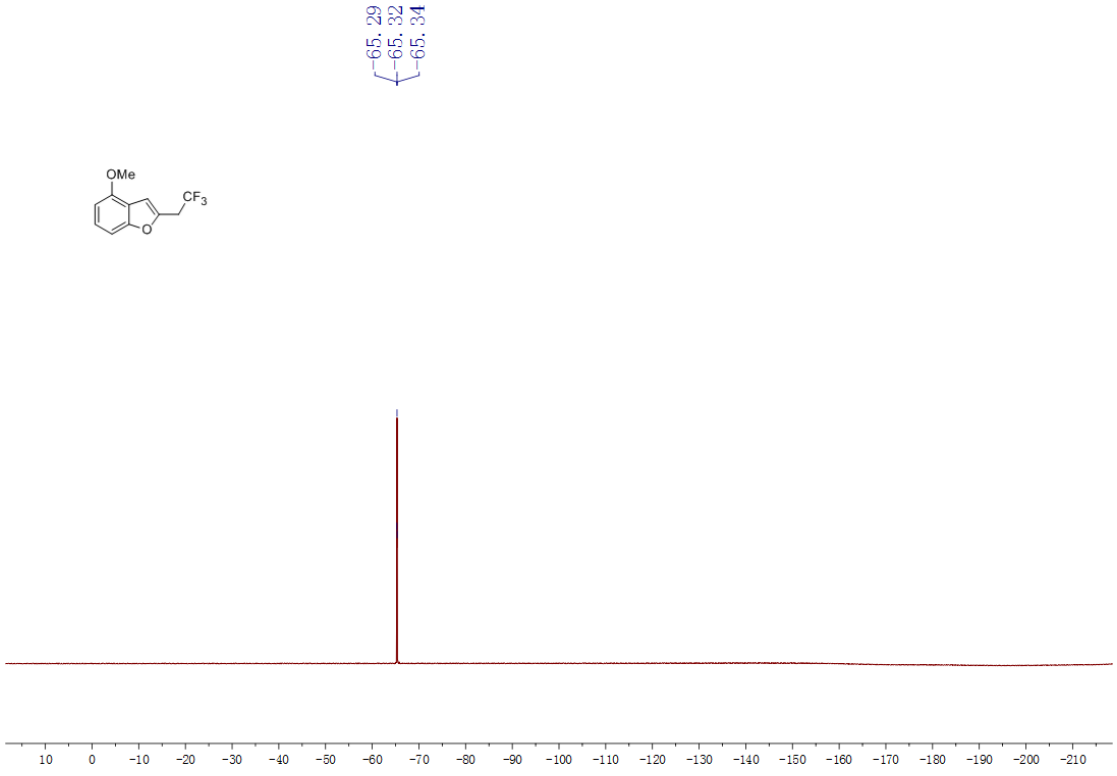


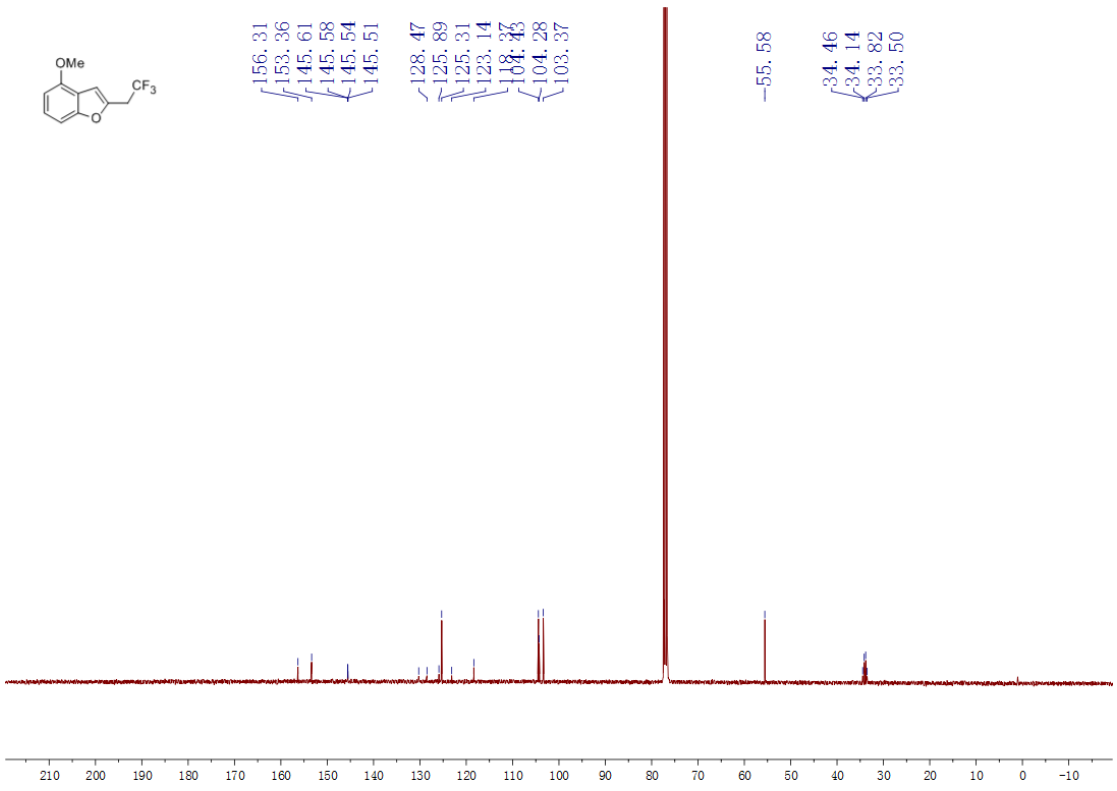
^{1}H NMR spectrum of **3h** in $CDCl_3$



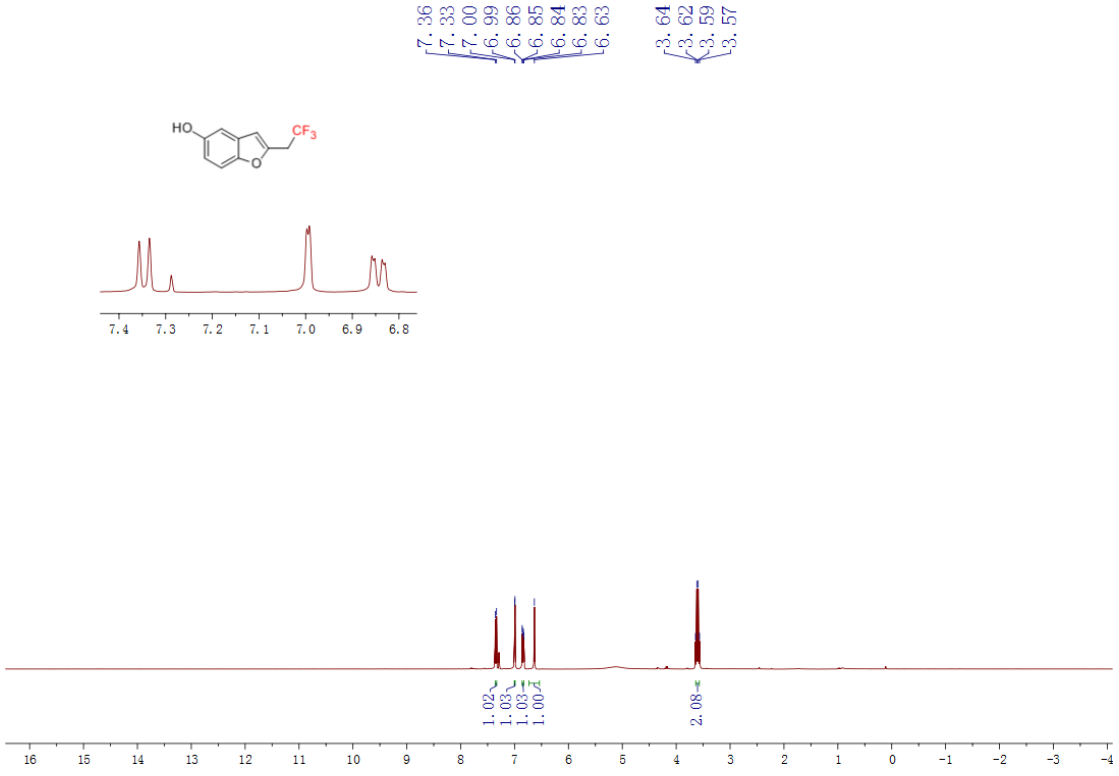
^{19}F NMR spectrum of **3h** in $CDCl_3$



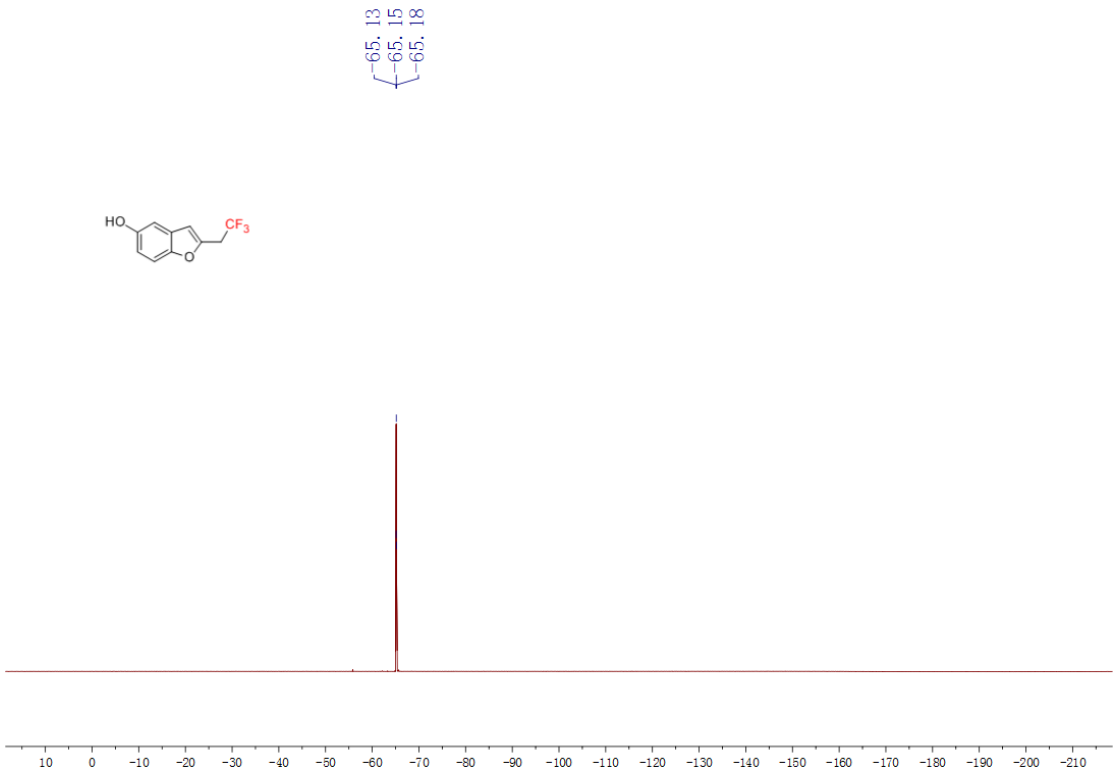
^{13}C NMR spectrum of **3h** in $CDCl_3$



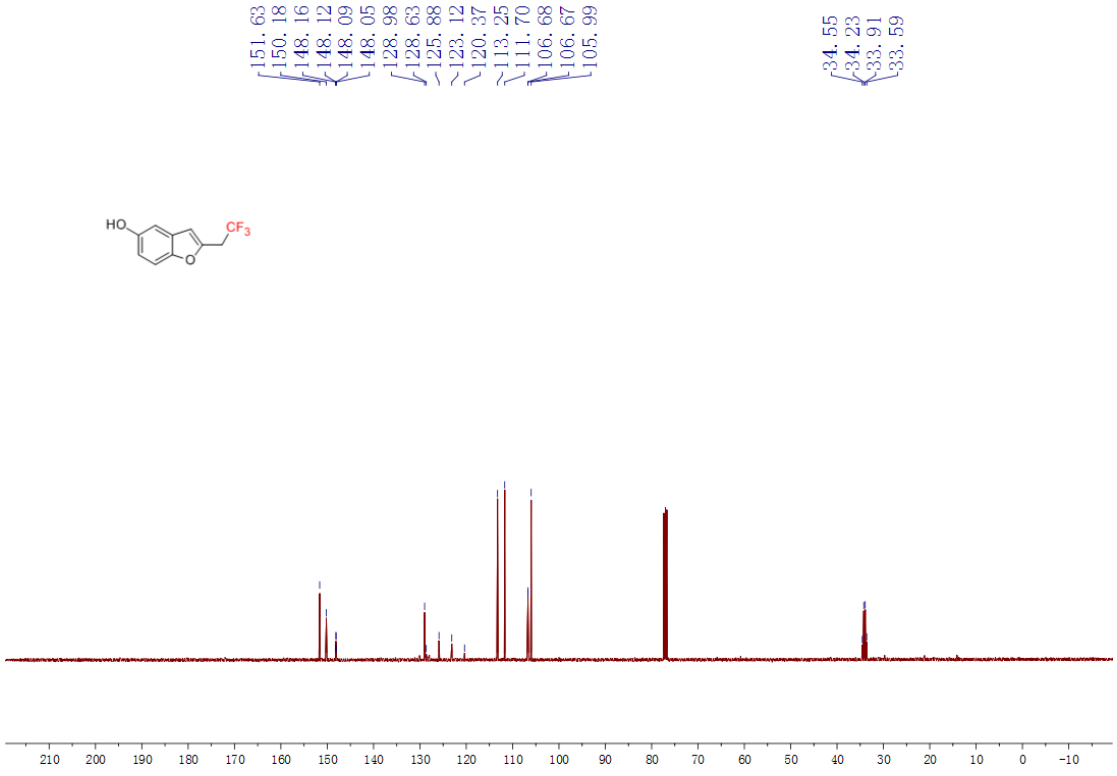
^{1}H NMR spectrum of **3i** in $CDCl_3$



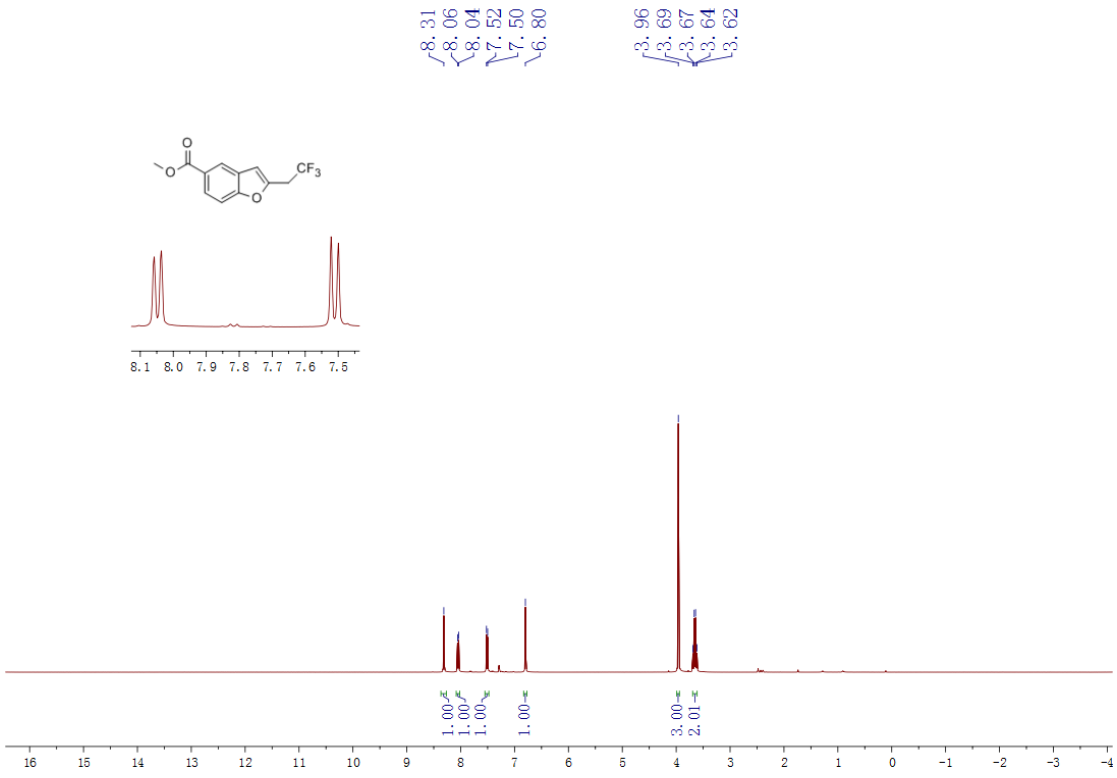
^{19}F NMR spectrum of **3i** in $CDCl_3$



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

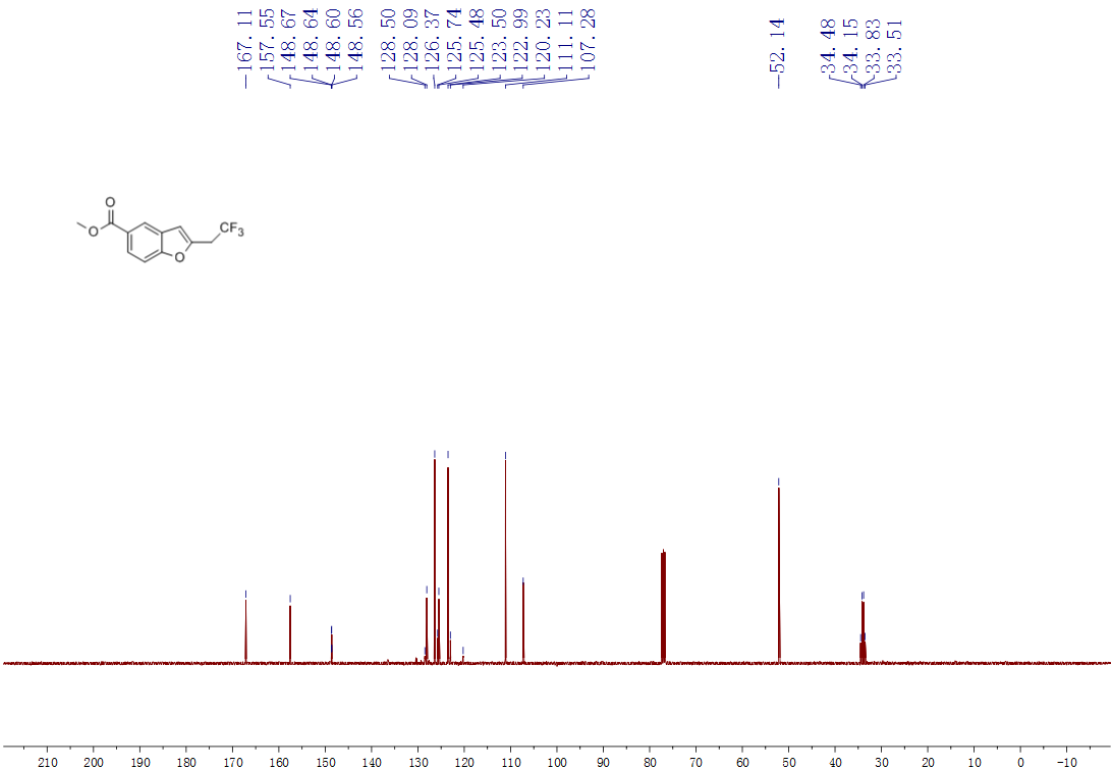


^{1}H NMR spectrum of **3j** in $CDCl_3$

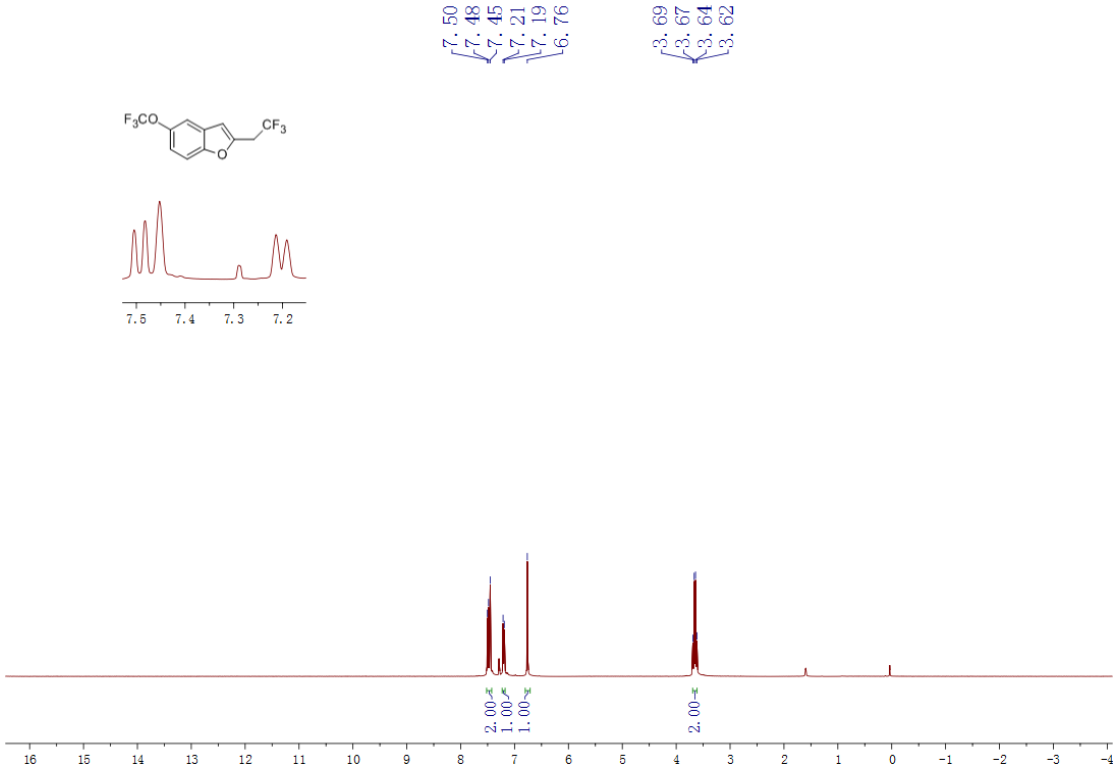


^{19}F NMR spectrum of **3j** in $CDCl_3$

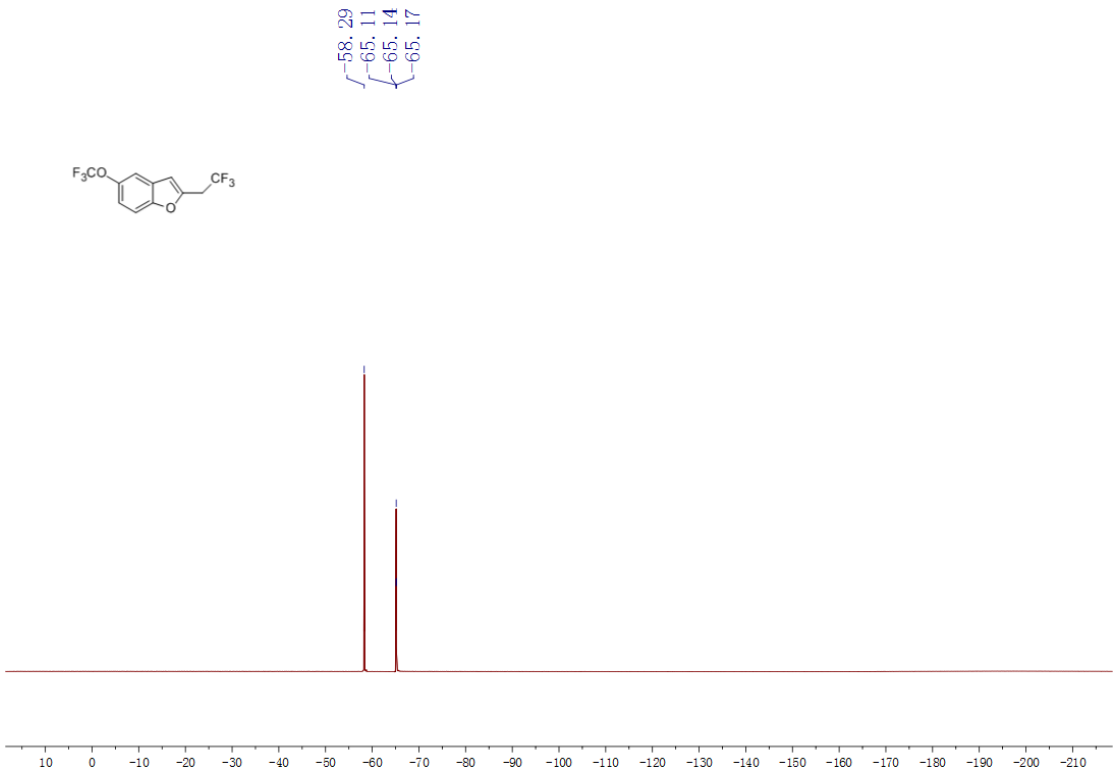
^{13}C NMR spectrum of **3j** in $CDCl_3$



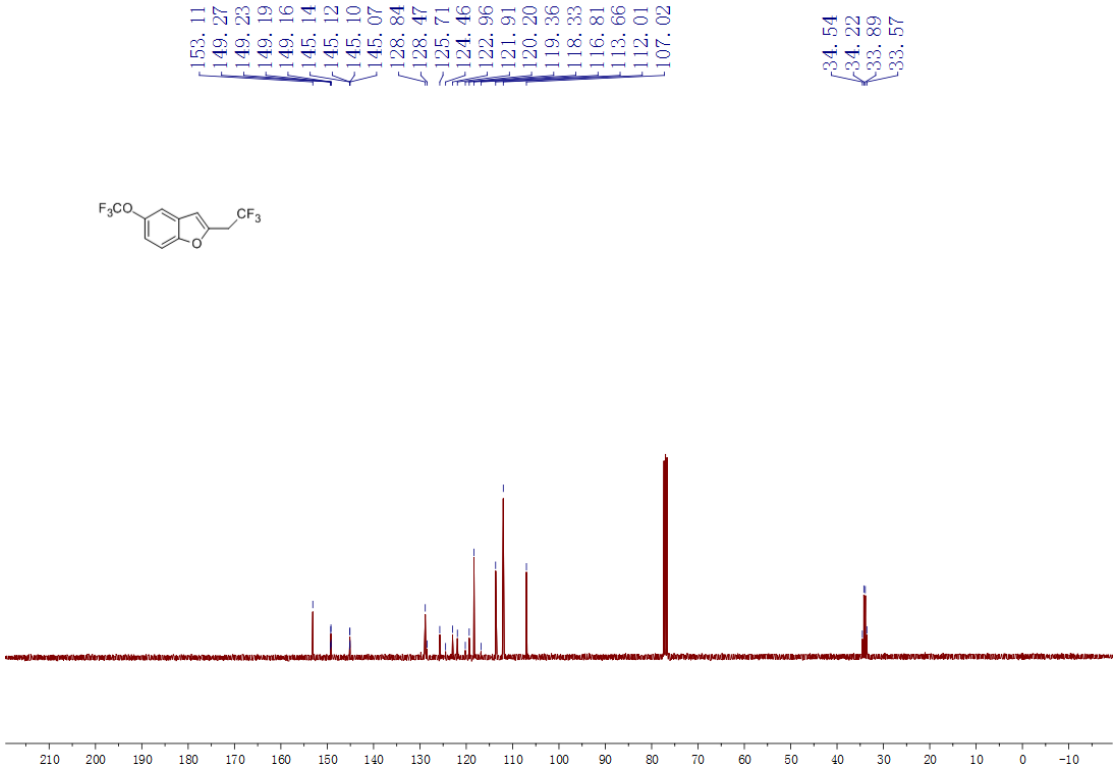
^{1}H NMR spectrum of **3k** in $CDCl_3$



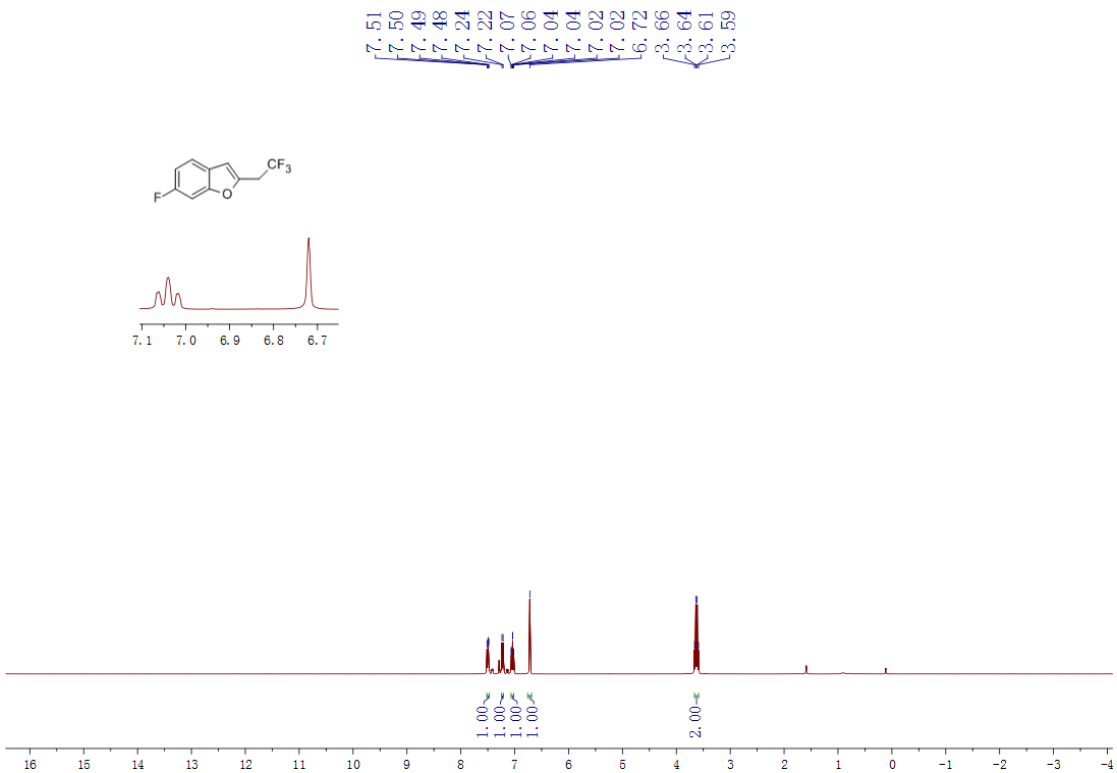
^{19}F NMR spectrum of **3k** in $CDCl_3$



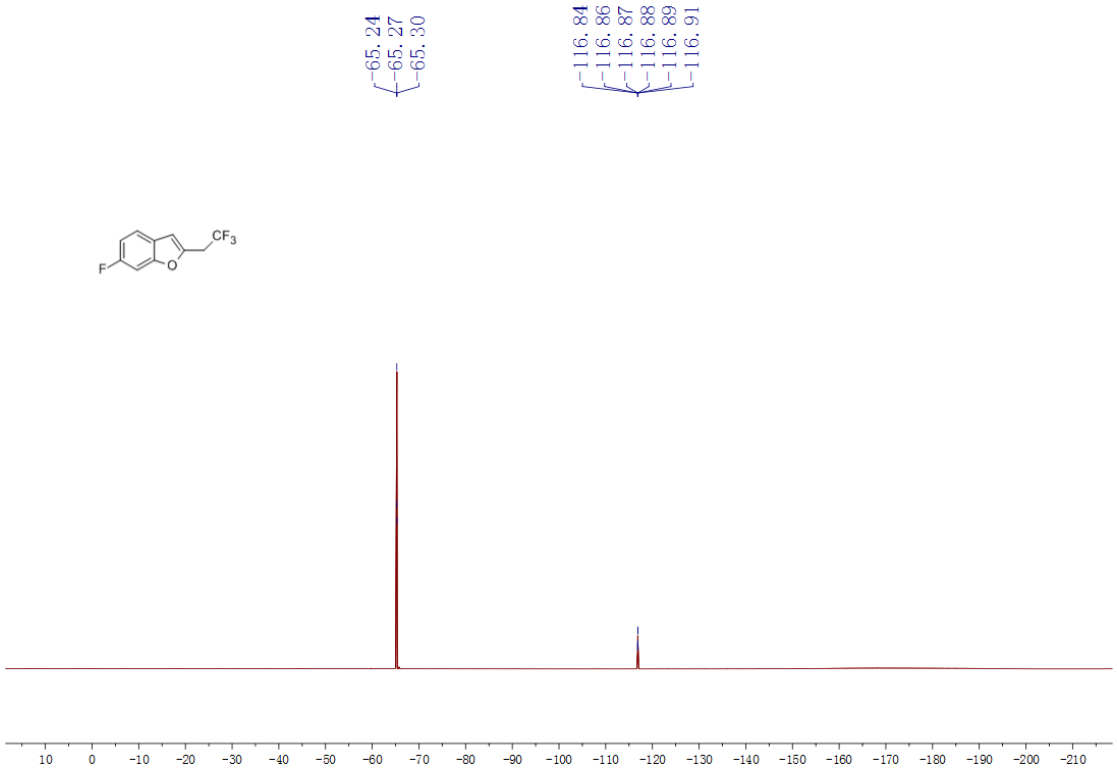
^{13}C NMR spectrum of **3k** in $CDCl_3$



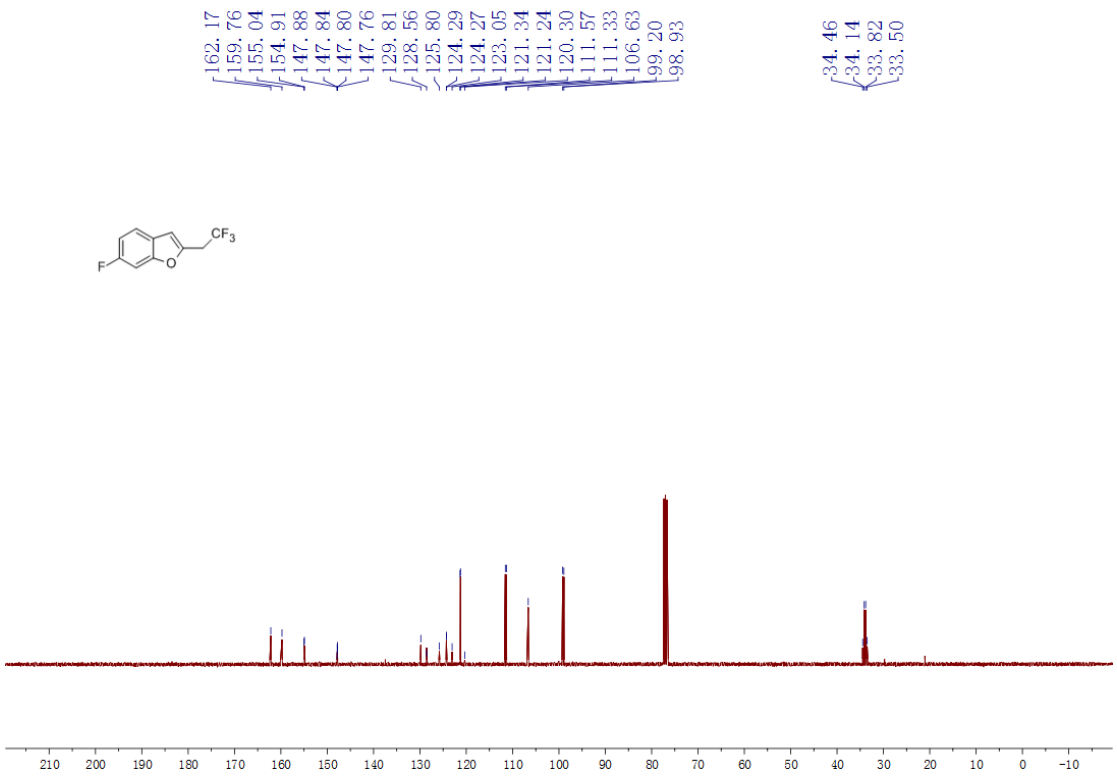
^{1}H NMR spectrum of **3l** in $CDCl_3$



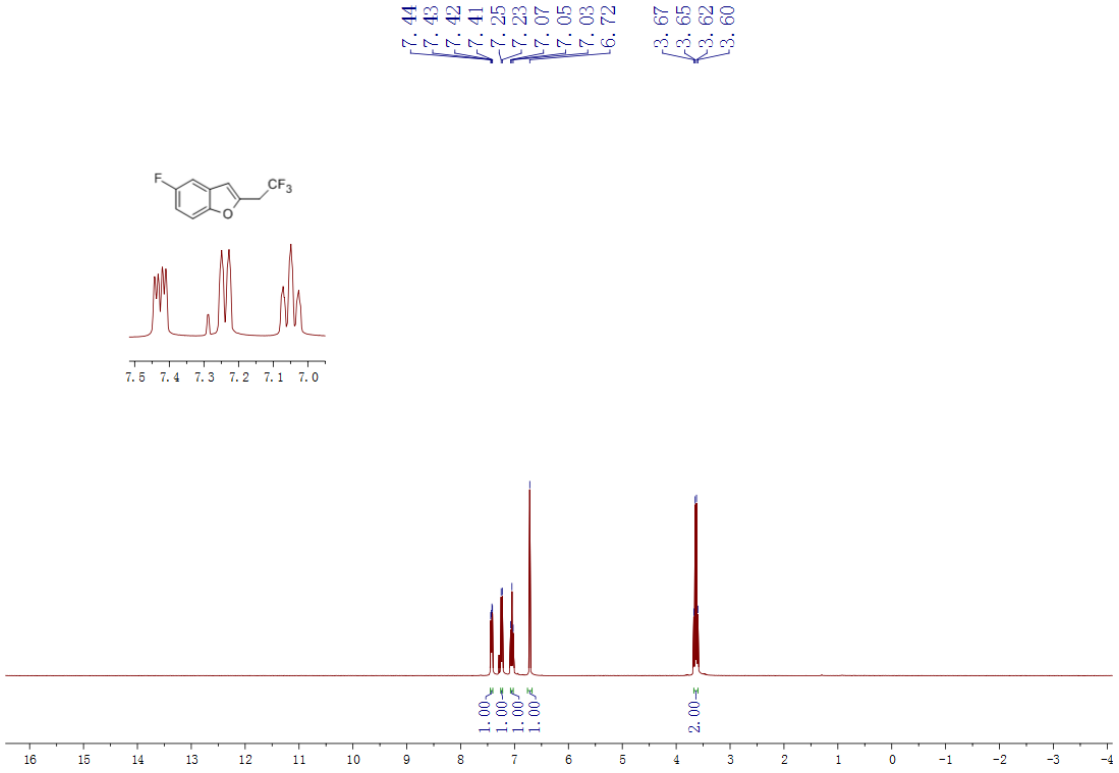
^{19}F NMR spectrum of **3l** in $CDCl_3$



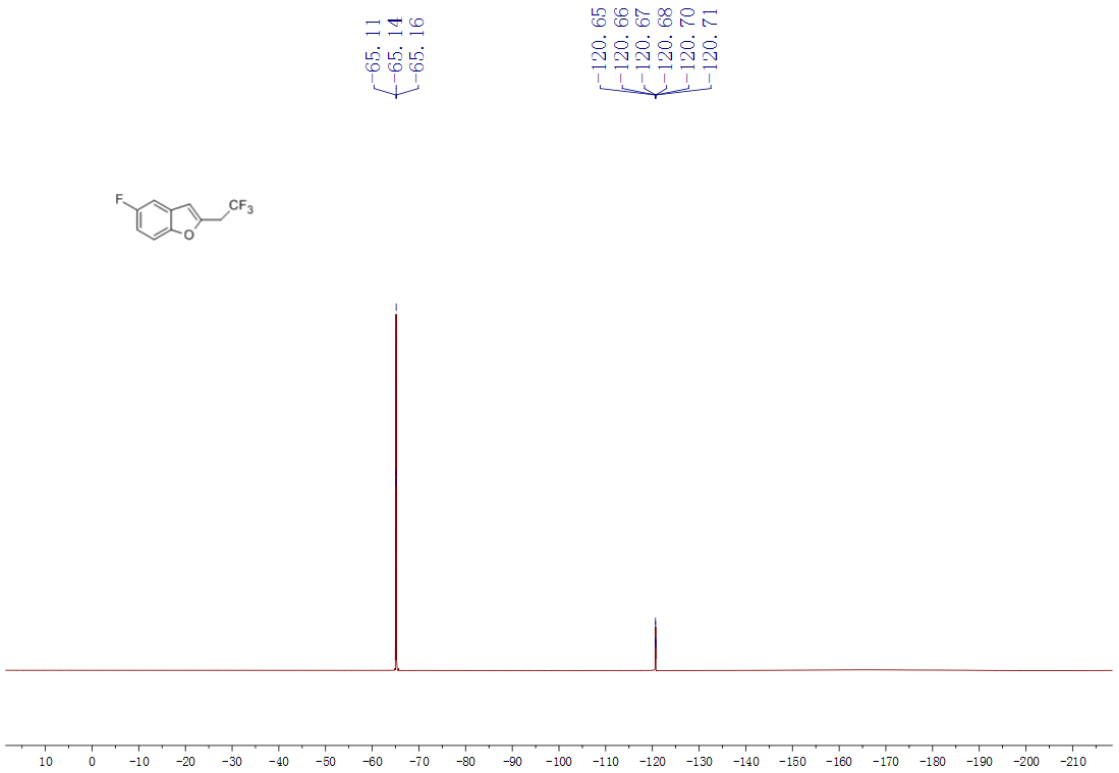
^{13}C NMR spectrum of **3l** in $CDCl_3$



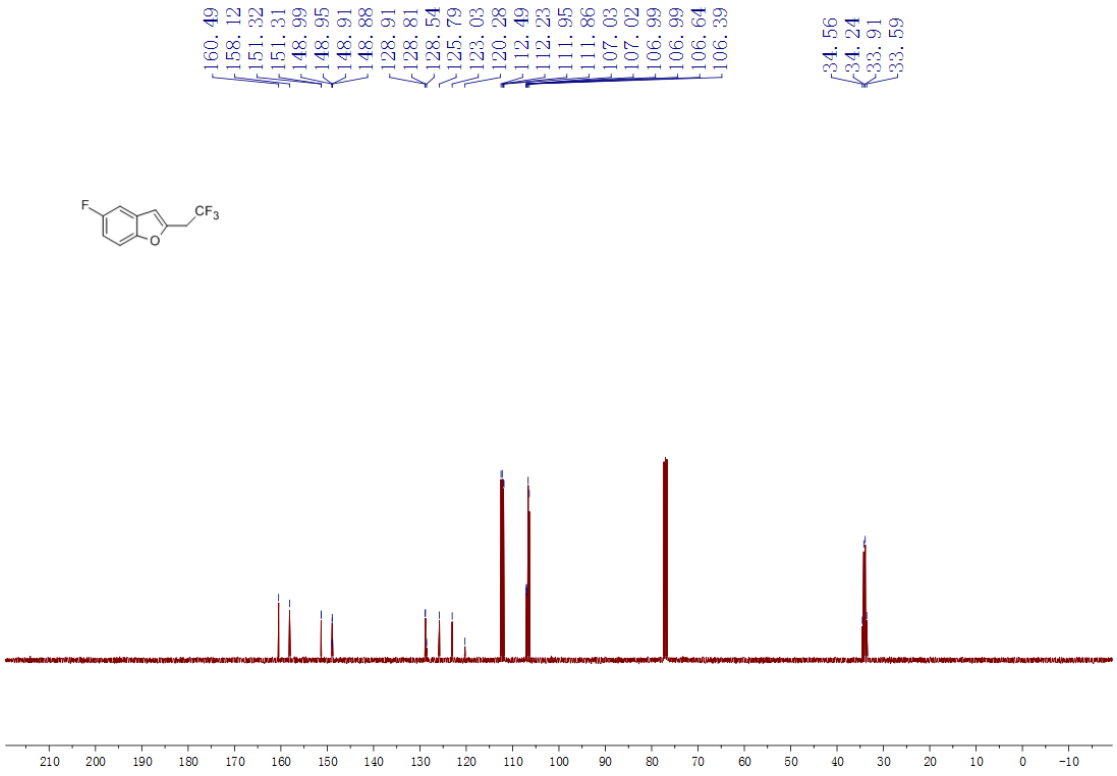
^{1}H NMR spectrum of **3m** in $CDCl_3$



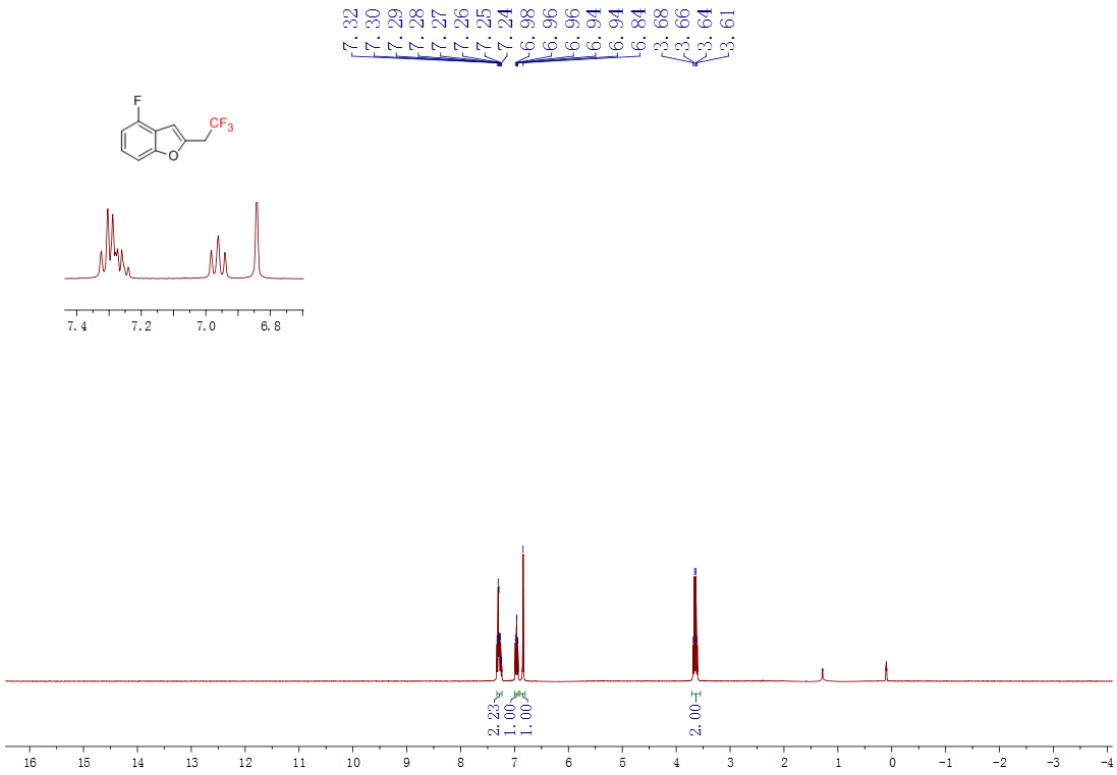
^{19}F NMR spectrum of **3m** in $CDCl_3$



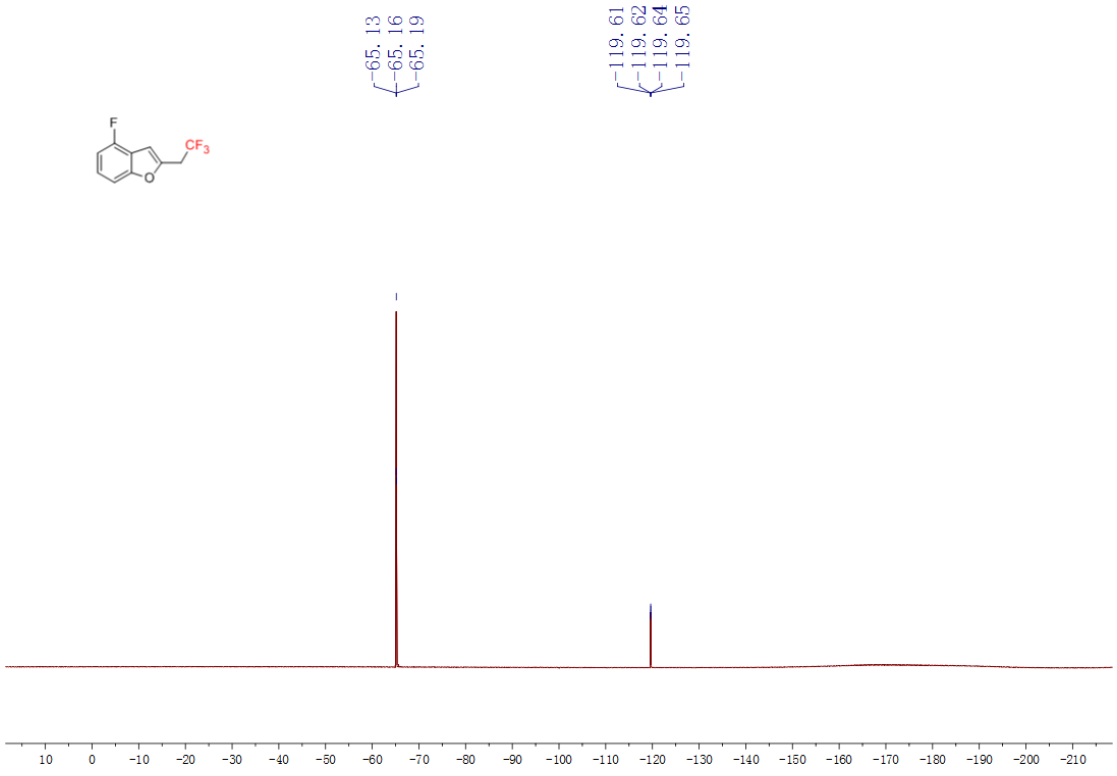
^{13}C NMR spectrum of **3m** in $CDCl_3$



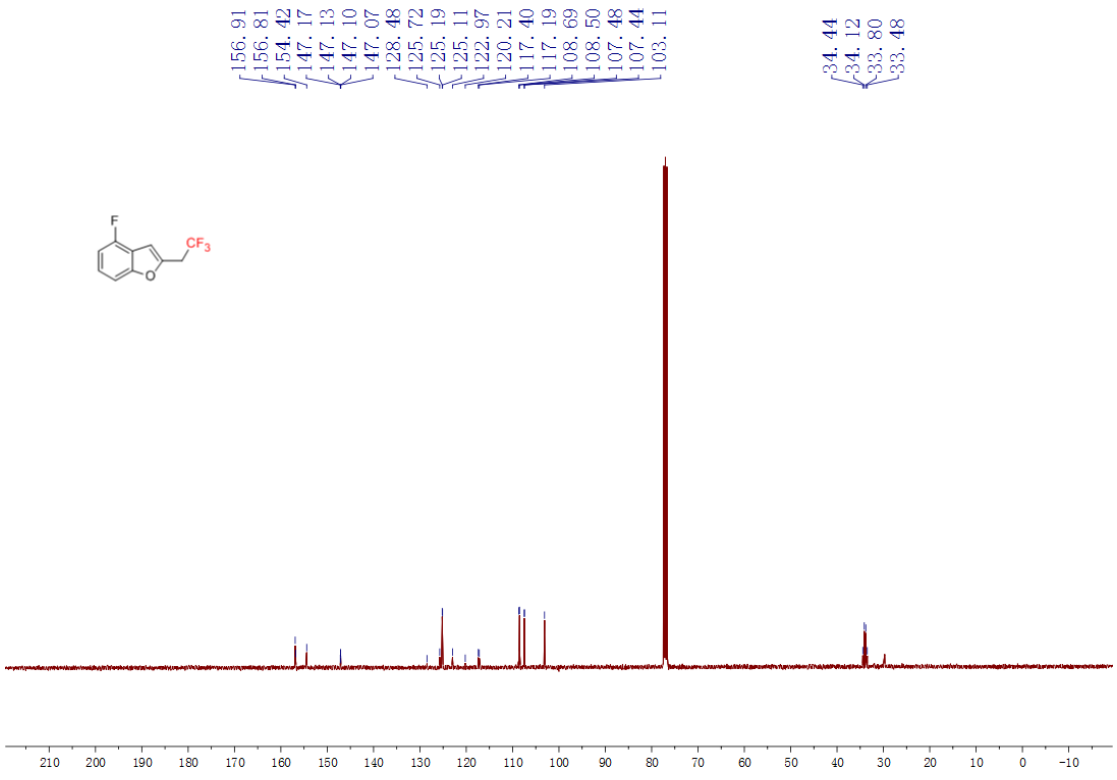
^{1}H NMR spectrum of **3n** in $CDCl_3$



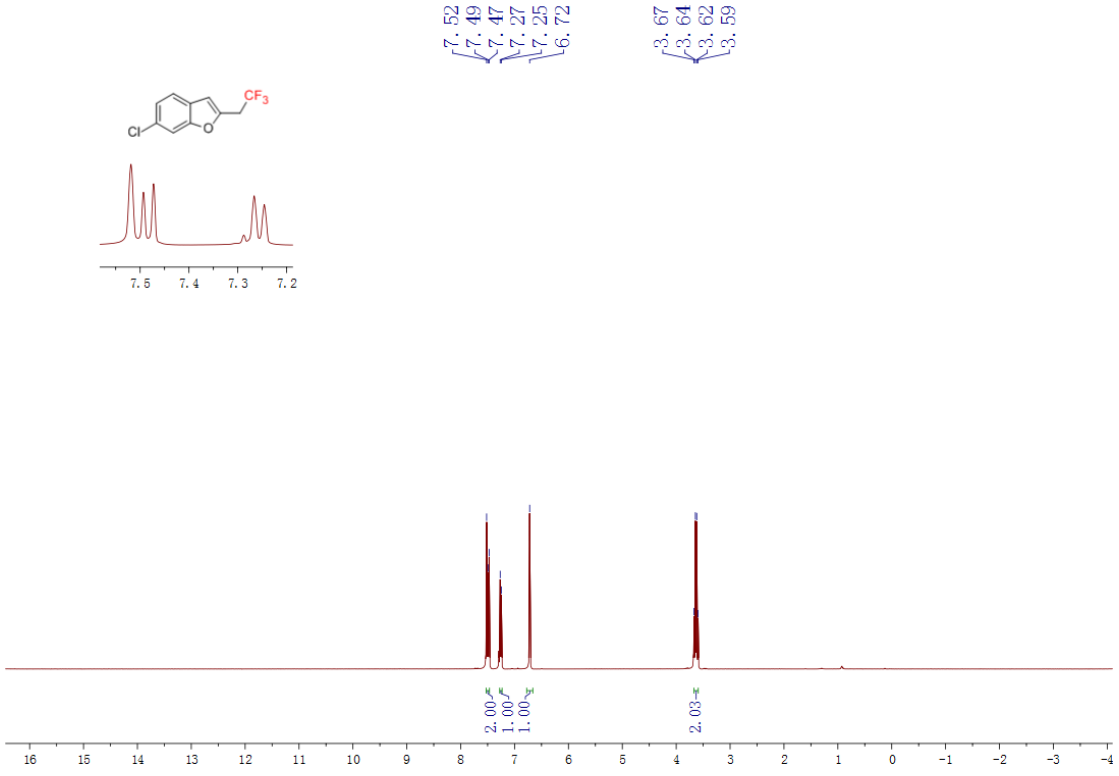
^{19}F NMR spectrum of **3n** in $CDCl_3$



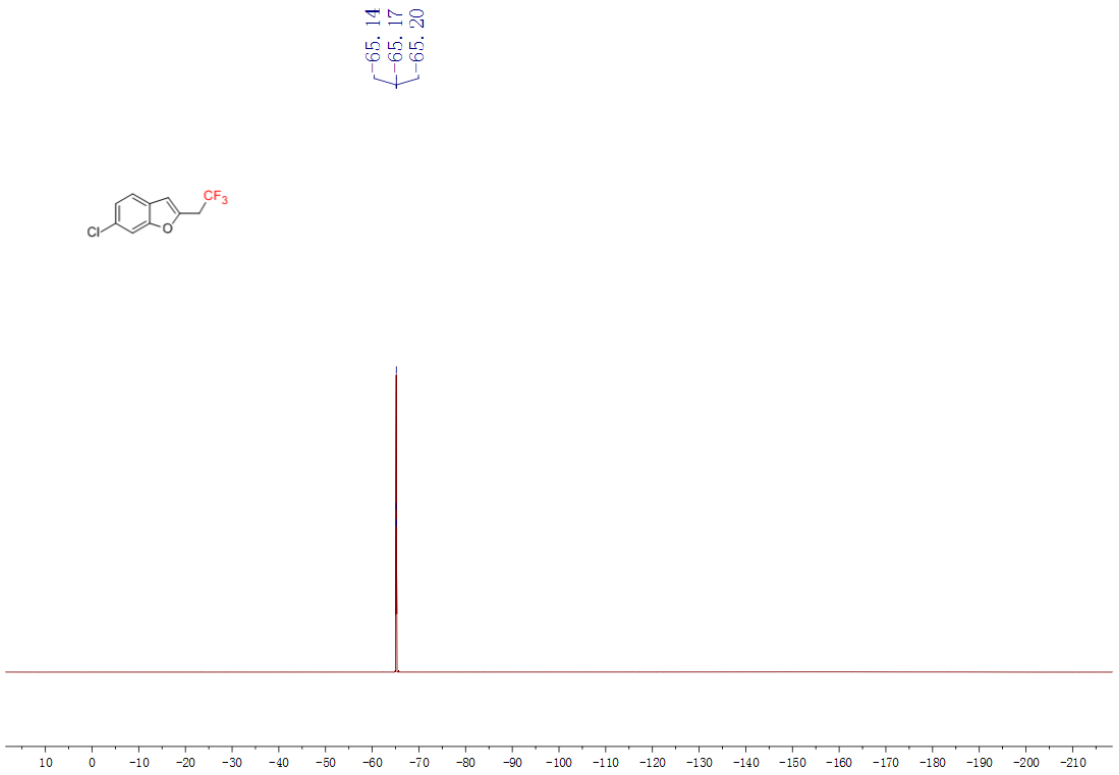
^{13}C NMR spectrum of **3n** in $CDCl_3$



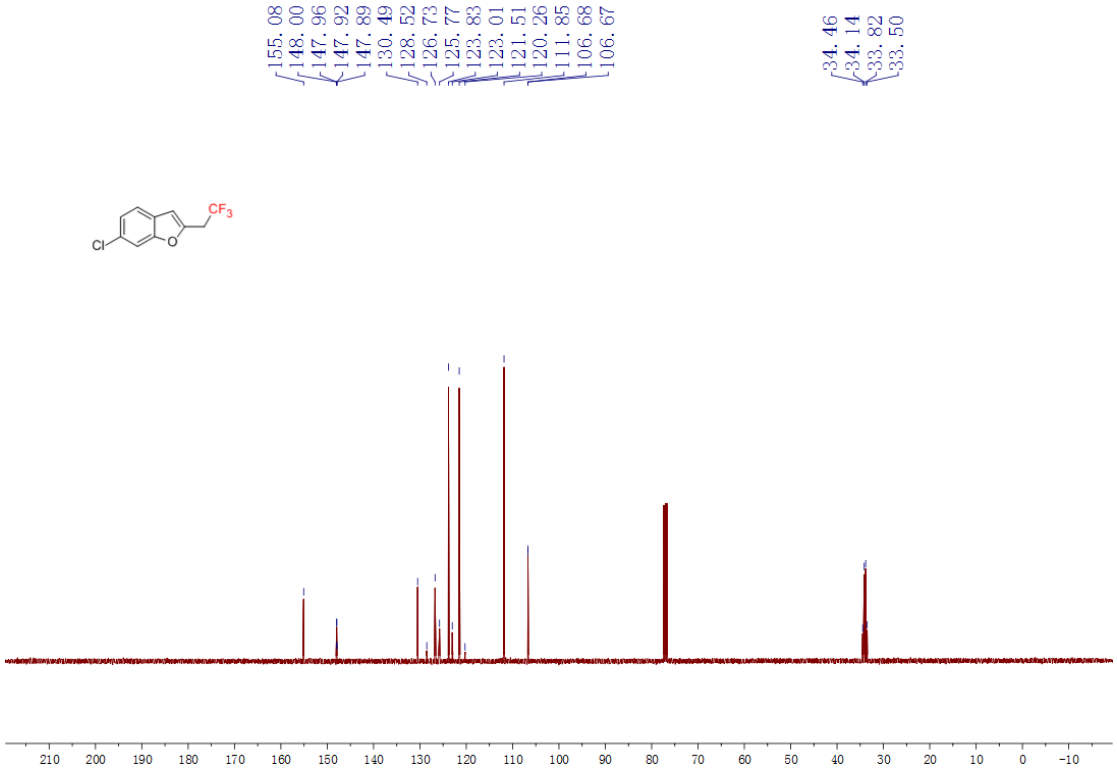
^{1}H NMR spectrum of **3o** in $CDCl_3$



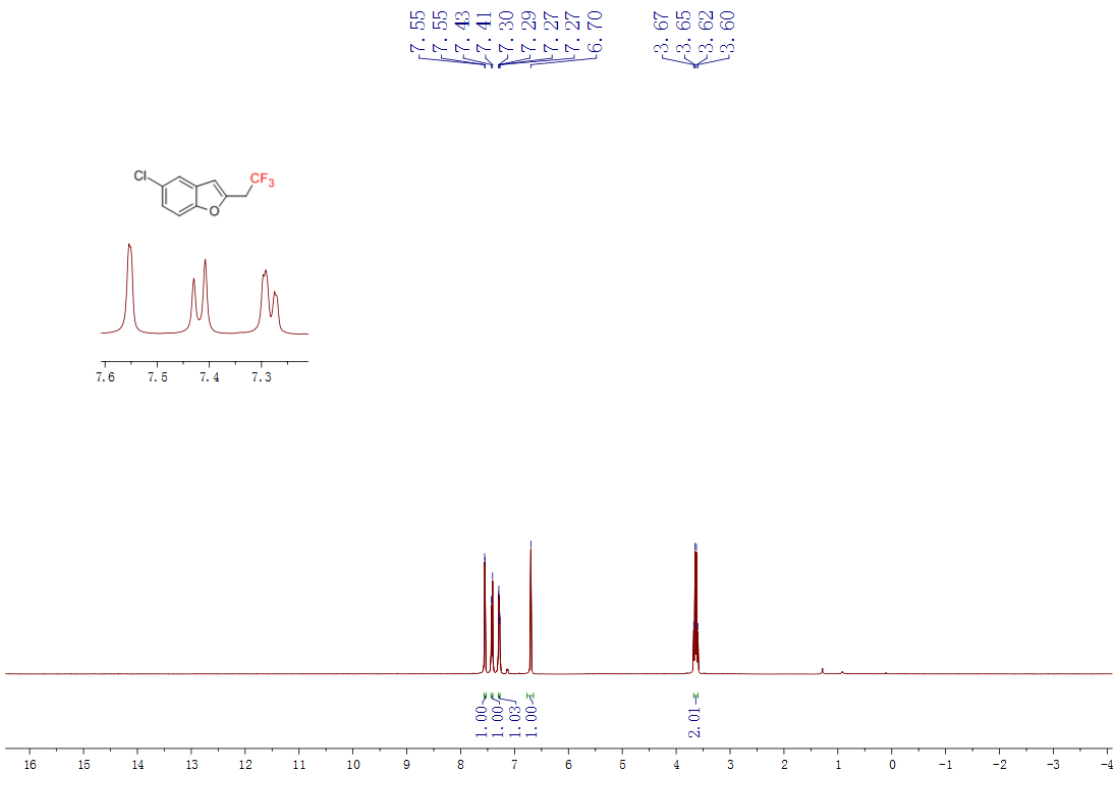
^{19}F NMR spectrum of **3o** in $CDCl_3$



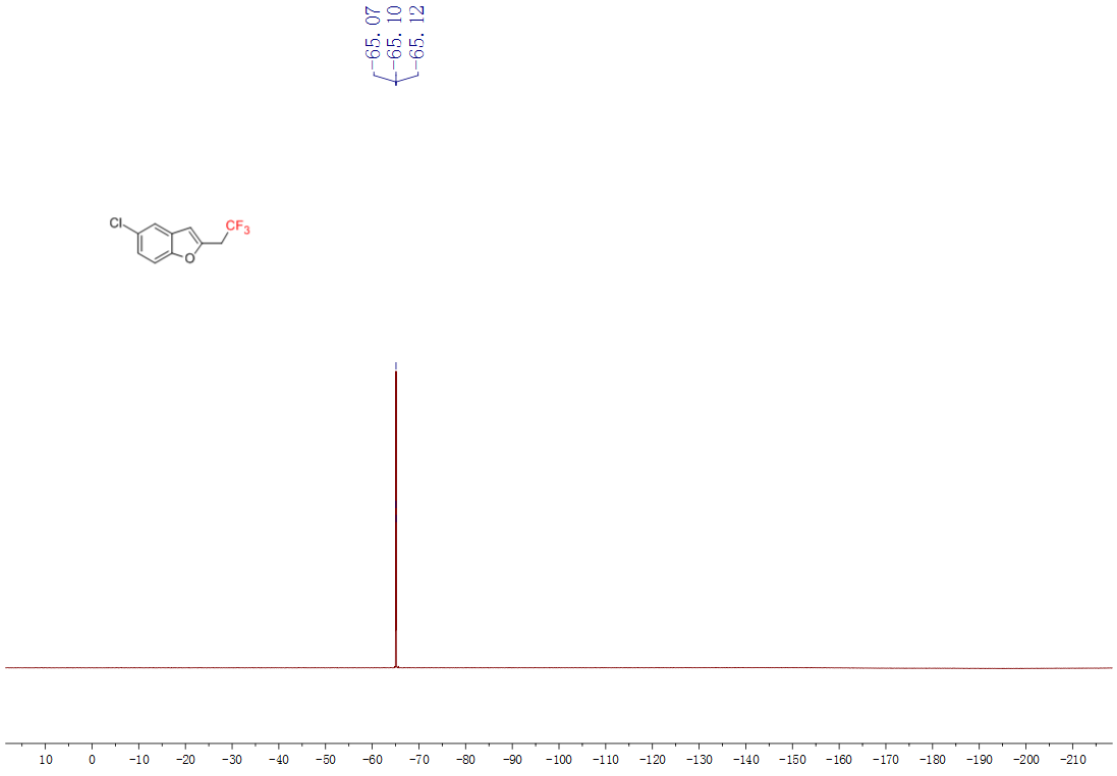
^{13}C NMR spectrum of **3o** in $CDCl_3$



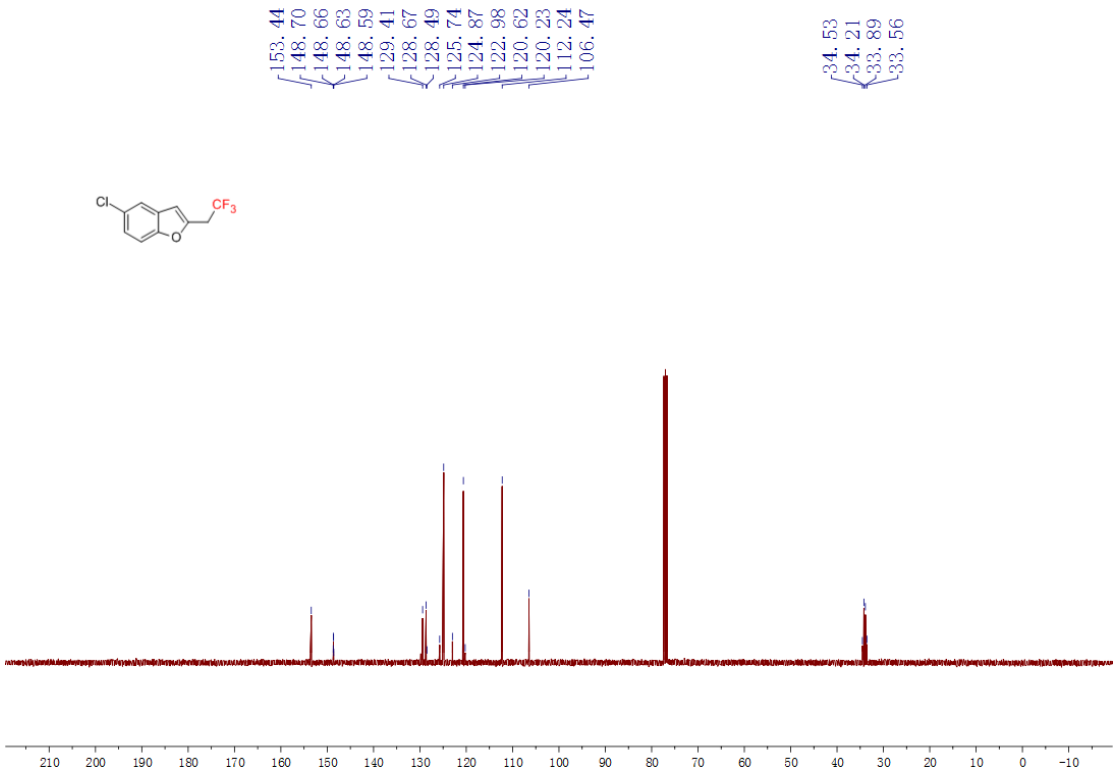
^{1}H NMR spectrum of **3p** in $CDCl_3$



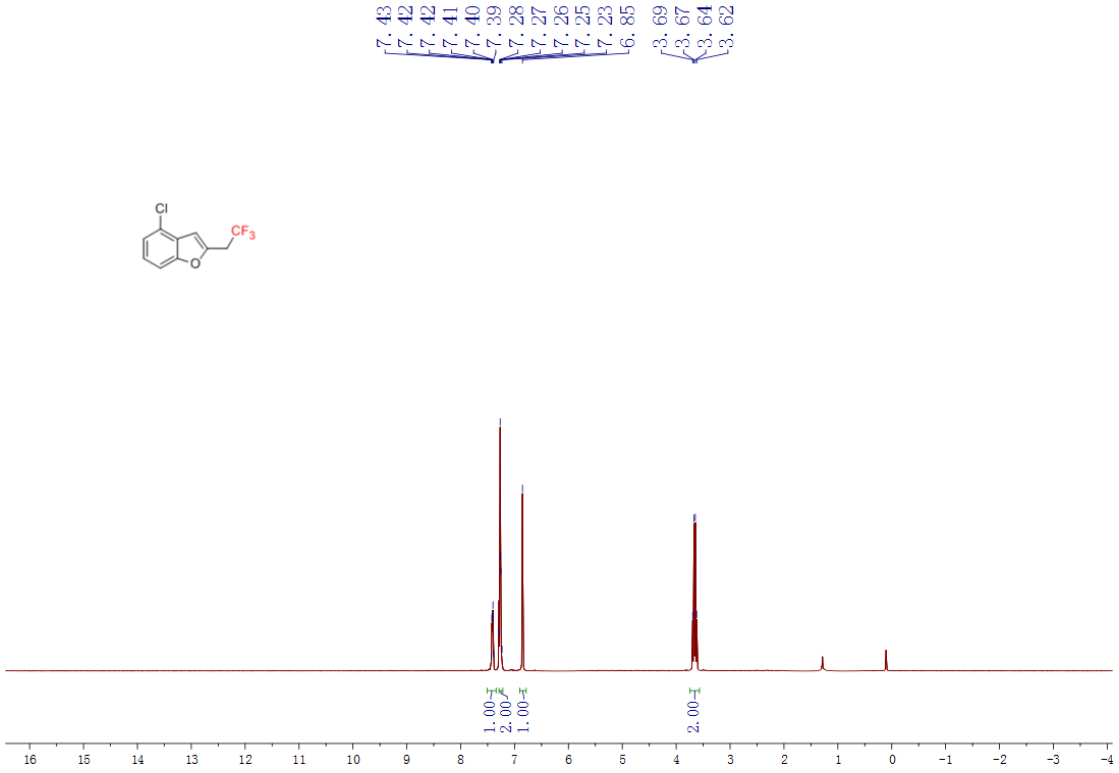
^{19}F NMR spectrum of **3p** in $CDCl_3$



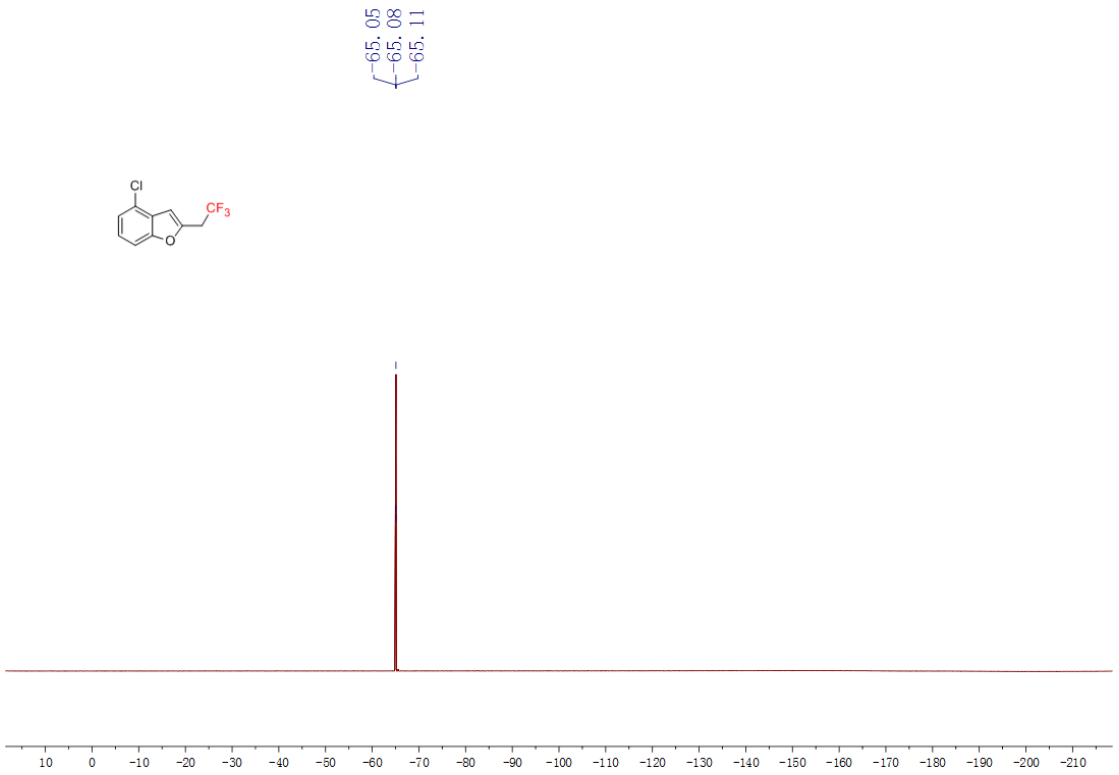
^{13}C NMR spectrum of **3p** in $CDCl_3$



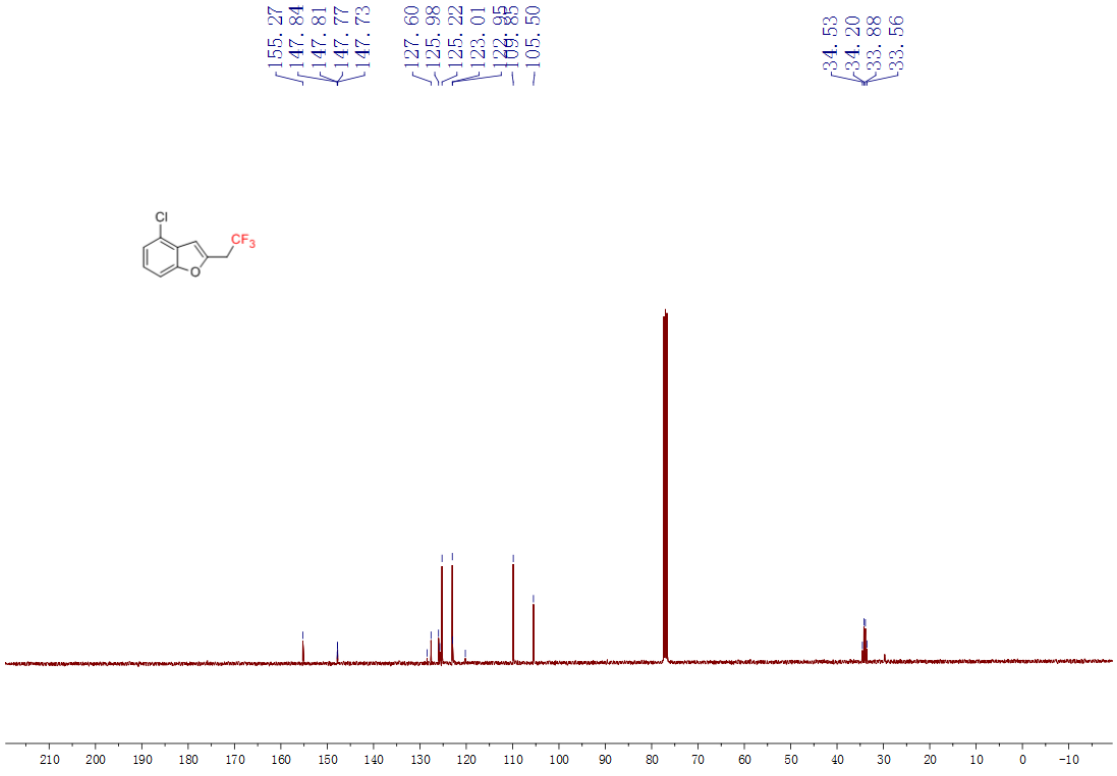
^{1}H NMR spectrum of **3q** in $CDCl_3$



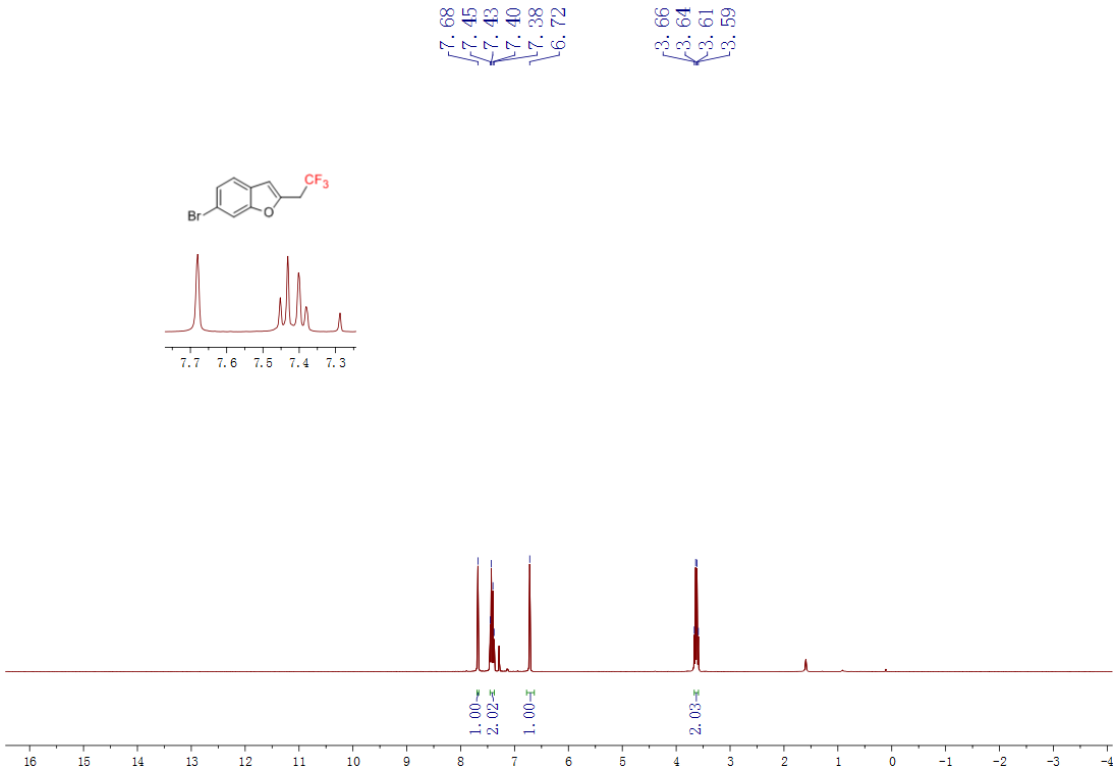
^{19}F NMR spectrum of **3q** in $CDCl_3$



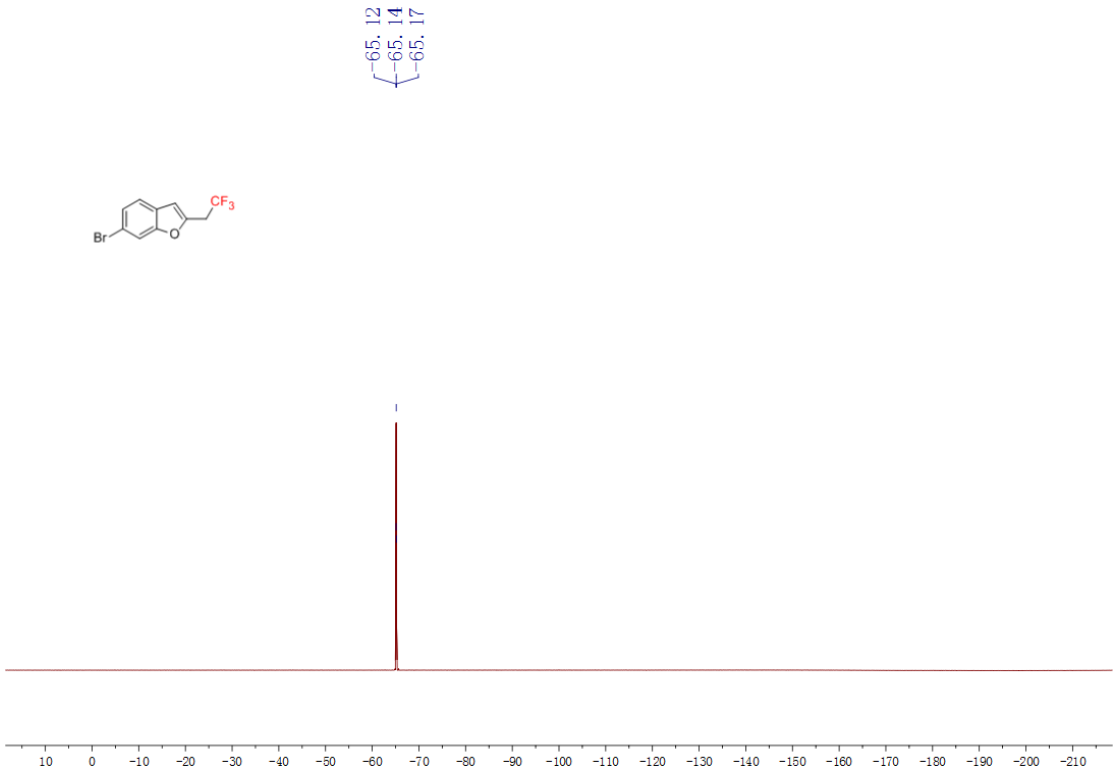
^{13}C NMR spectrum of **3q** in $CDCl_3$



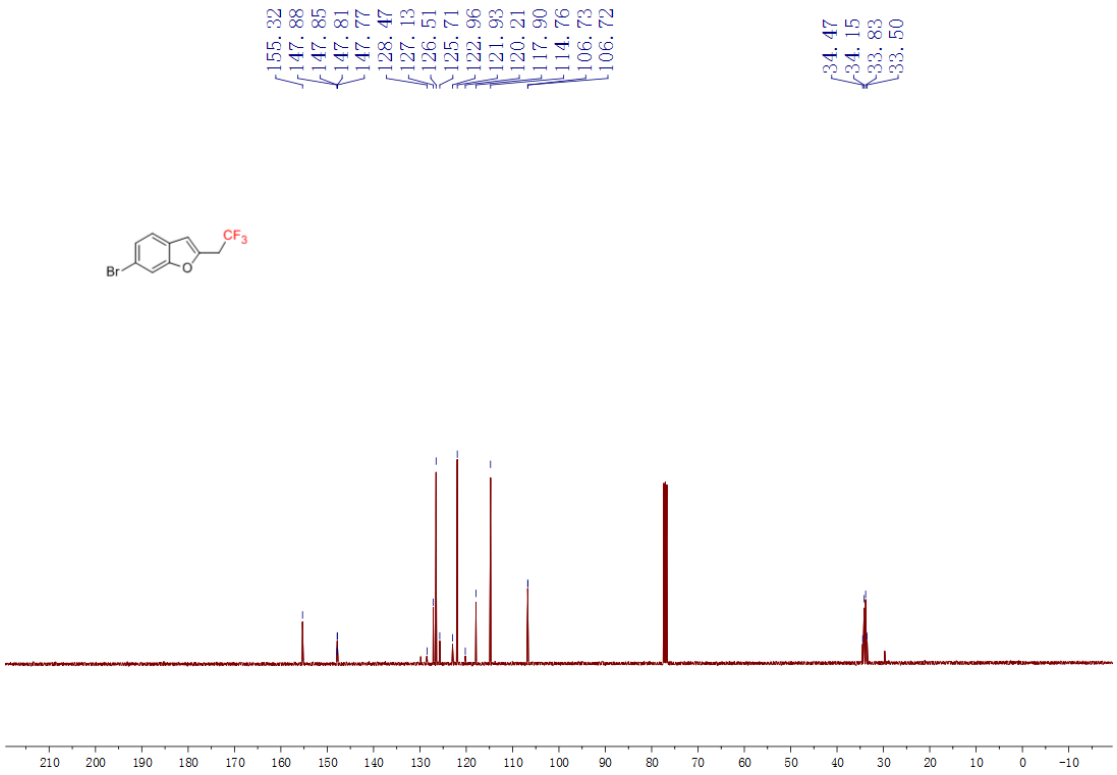
^{1}H NMR spectrum of **3r** in $CDCl_3$



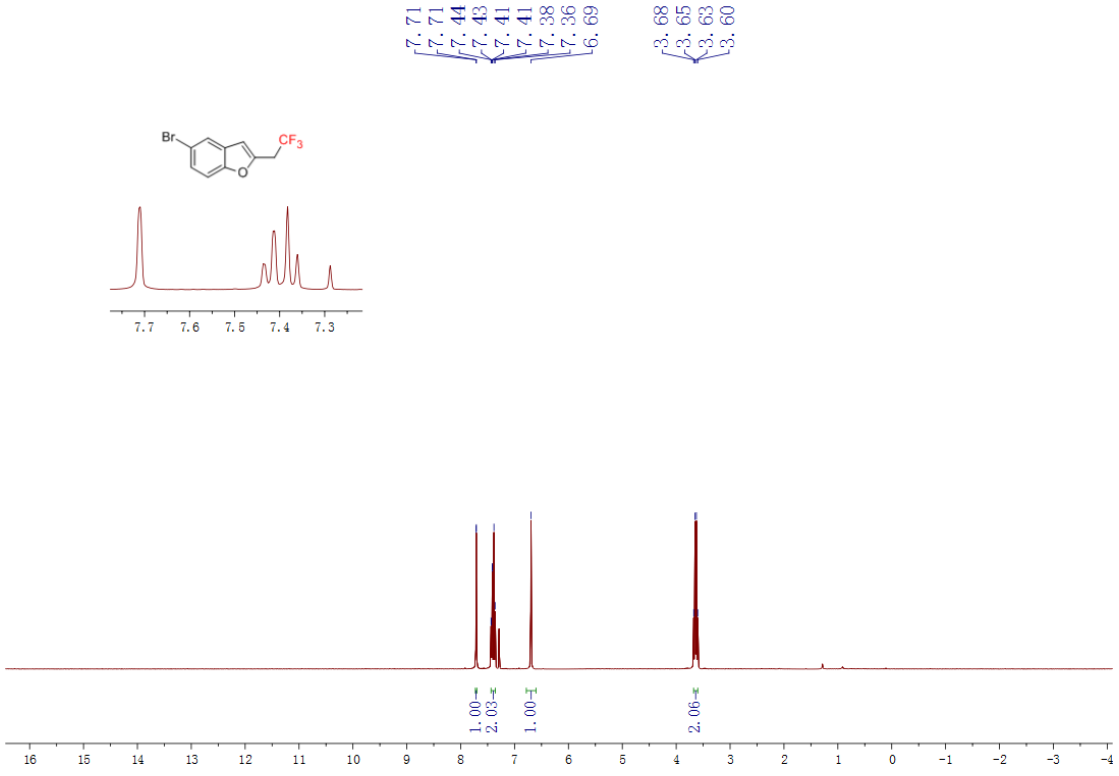
^{19}F NMR spectrum of **3r** in $CDCl_3$



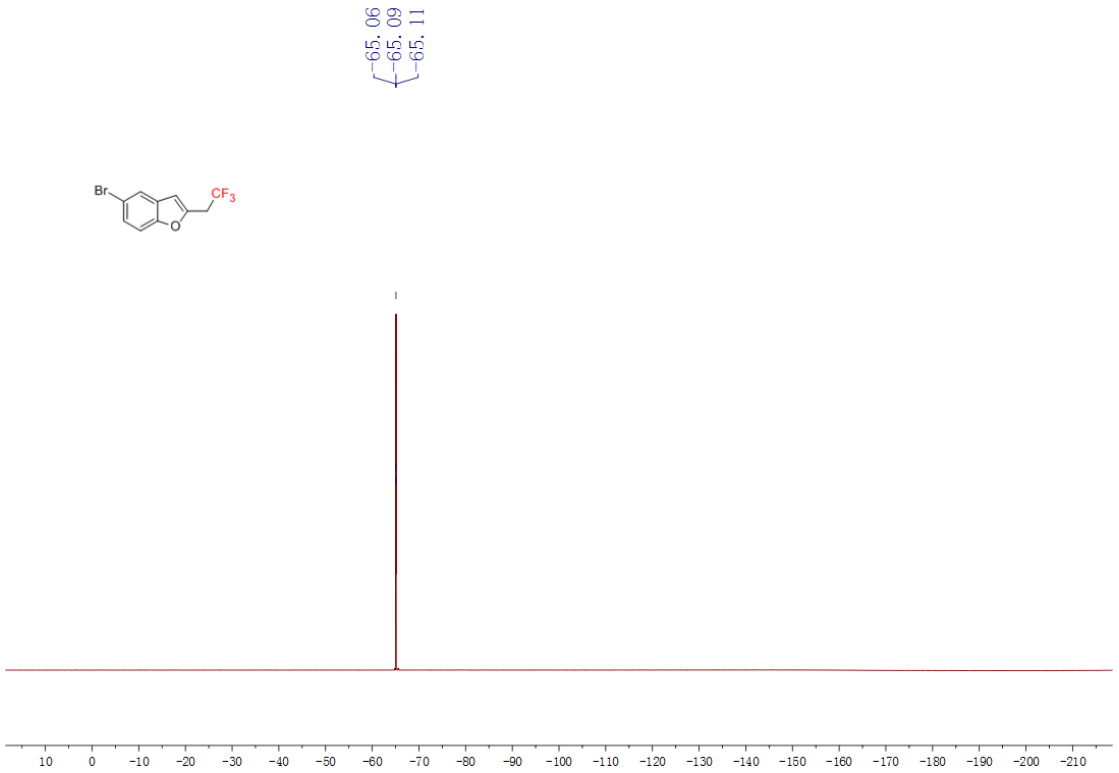
^{13}C NMR spectrum of **3r** in $CDCl_3$



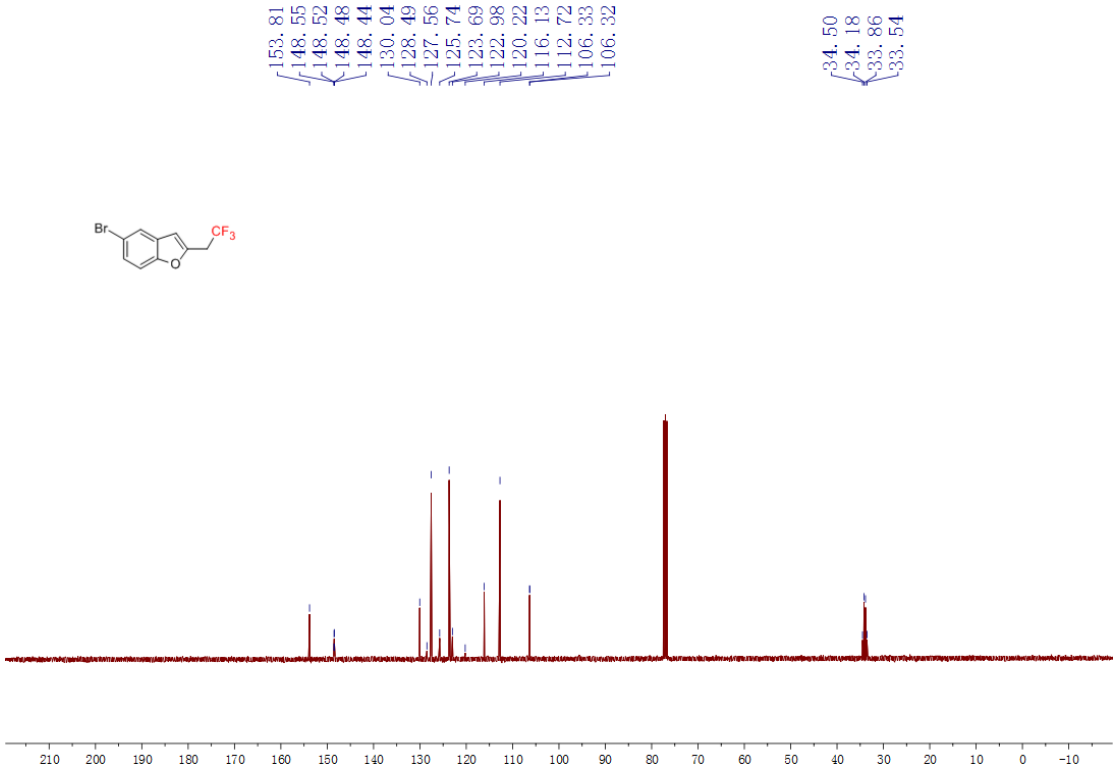
^{1}H NMR spectrum of **3s** in $CDCl_3$



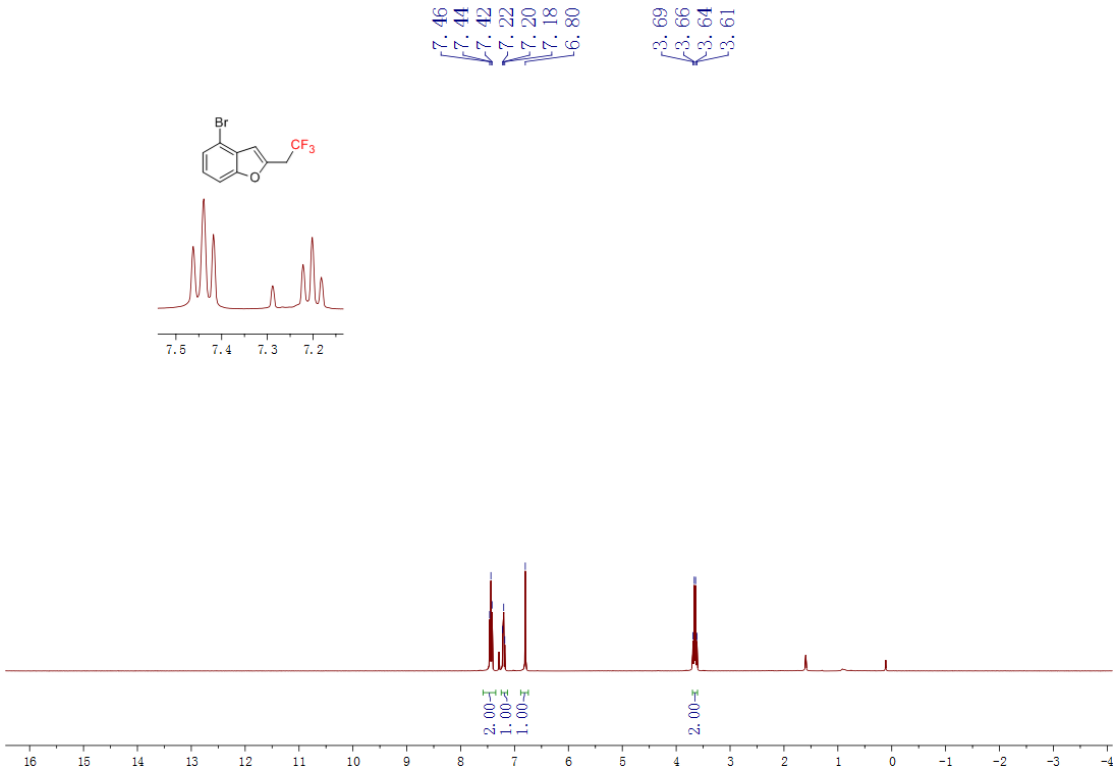
^{19}F NMR spectrum of **3s** in $CDCl_3$



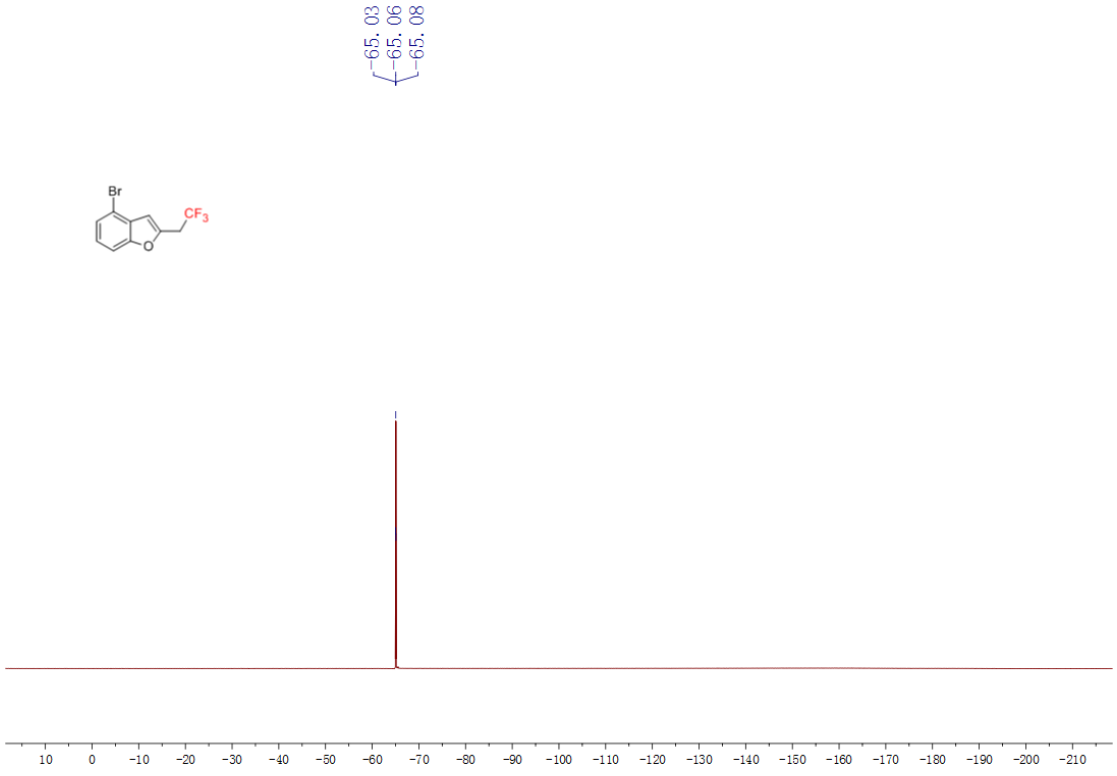
^{13}C NMR spectrum of **3s** in $CDCl_3$



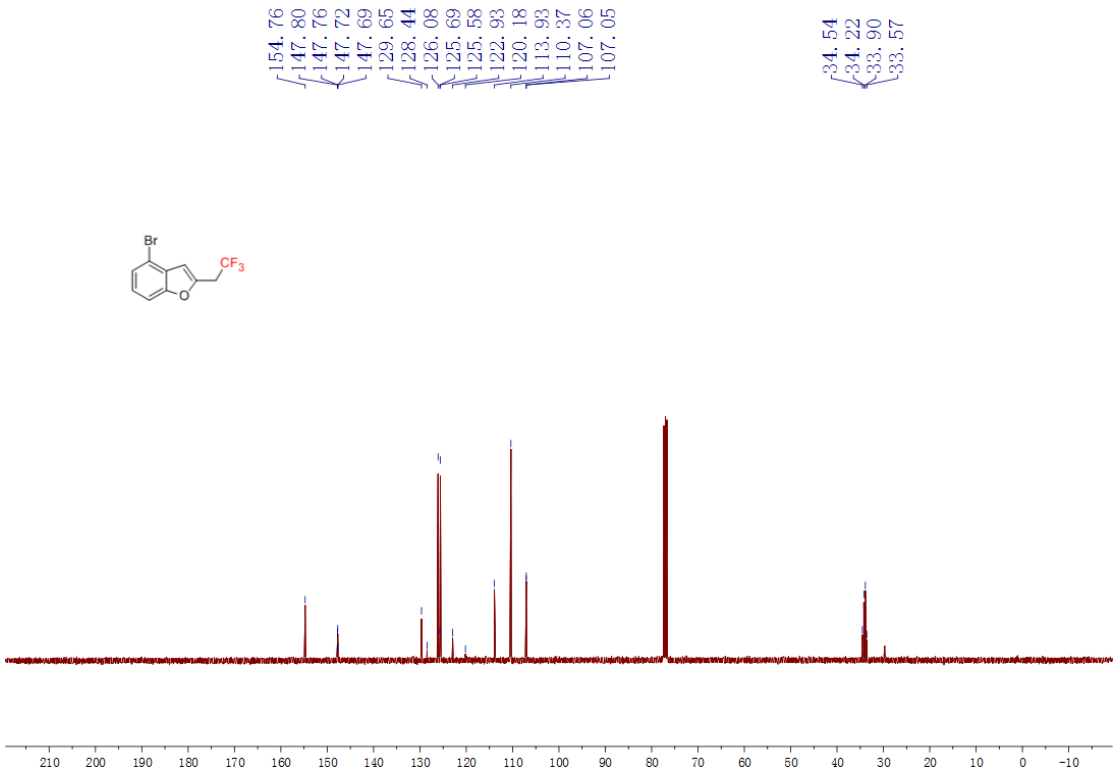
^{1}H NMR spectrum of **3t** in $CDCl_3$



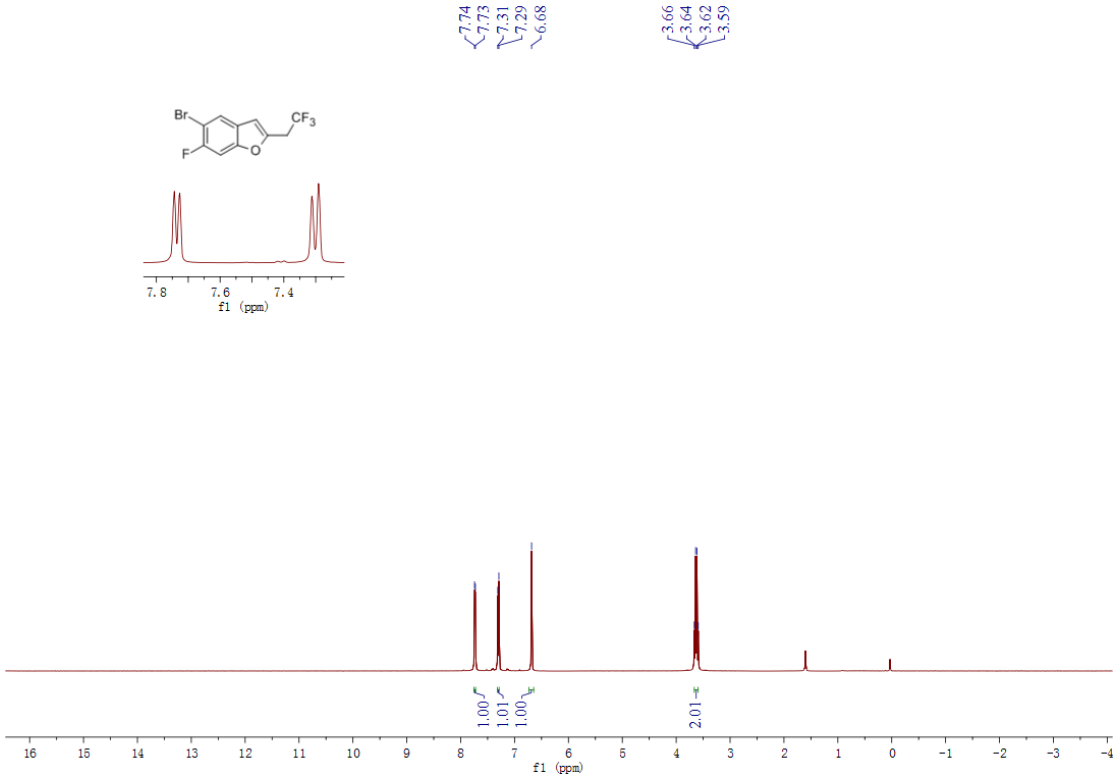
^{19}F NMR spectrum of **3t** in $CDCl_3$



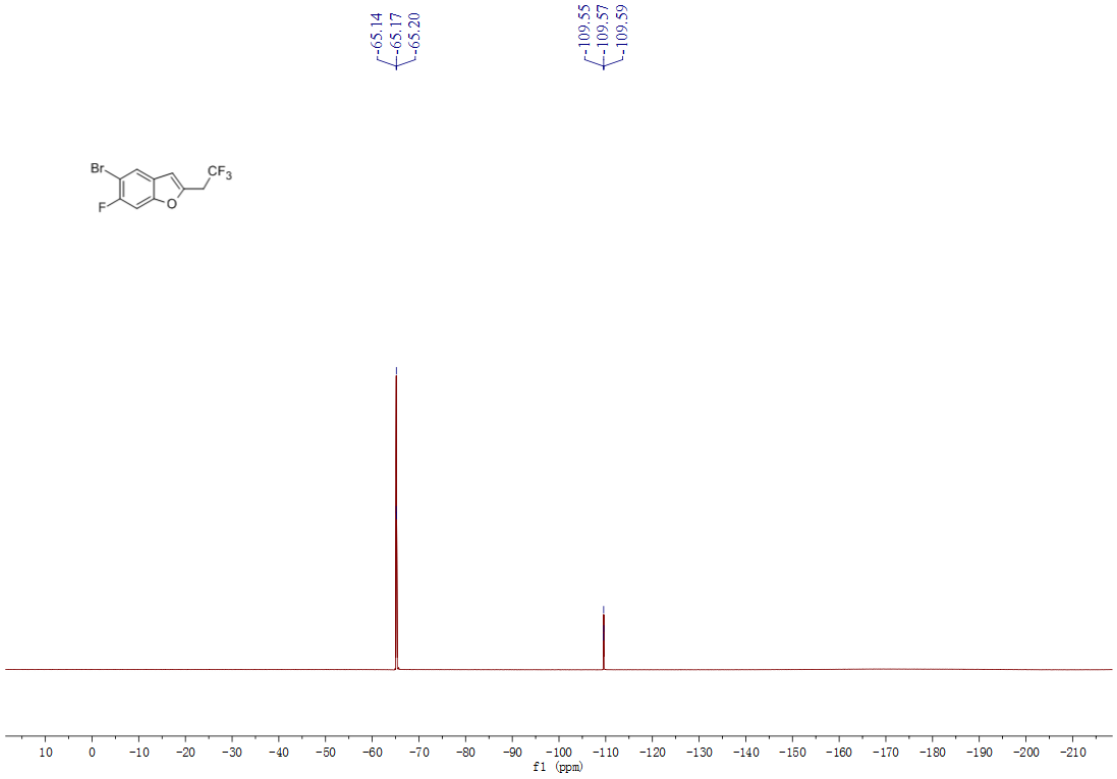
^{13}C NMR spectrum of **3t** in $CDCl_3$



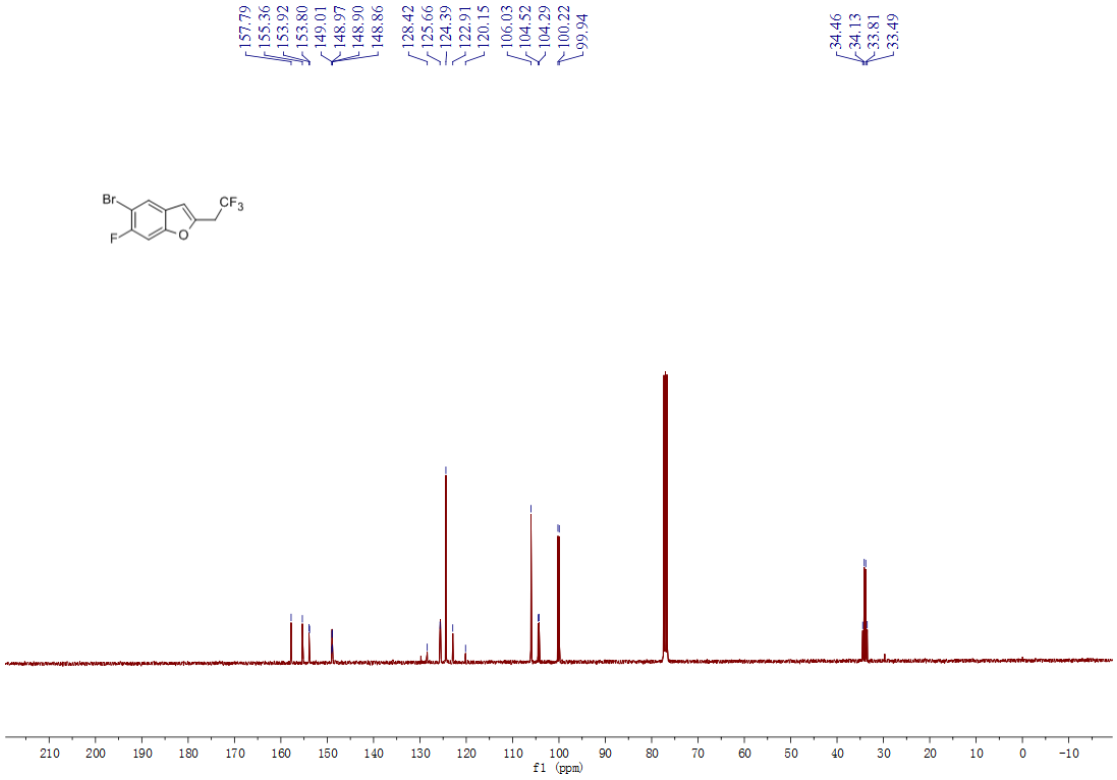
^{1}H NMR spectrum of **3u** in $CDCl_3$



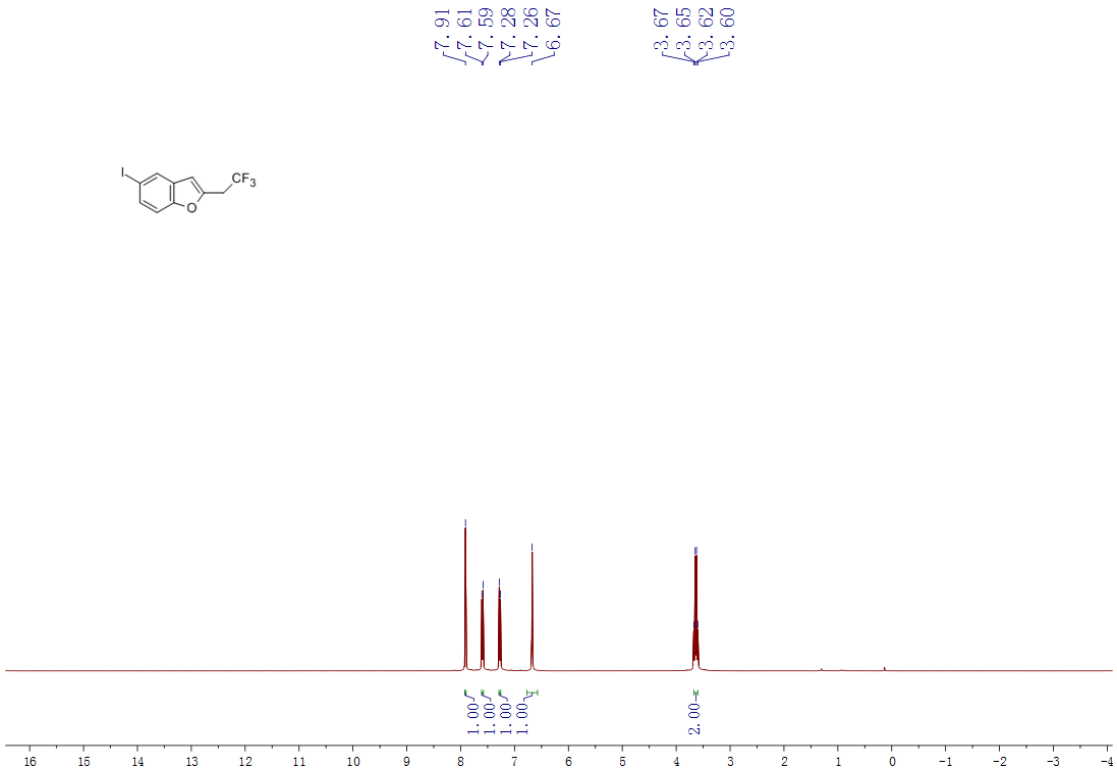
^{19}F NMR spectrum of **3u** in $CDCl_3$



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

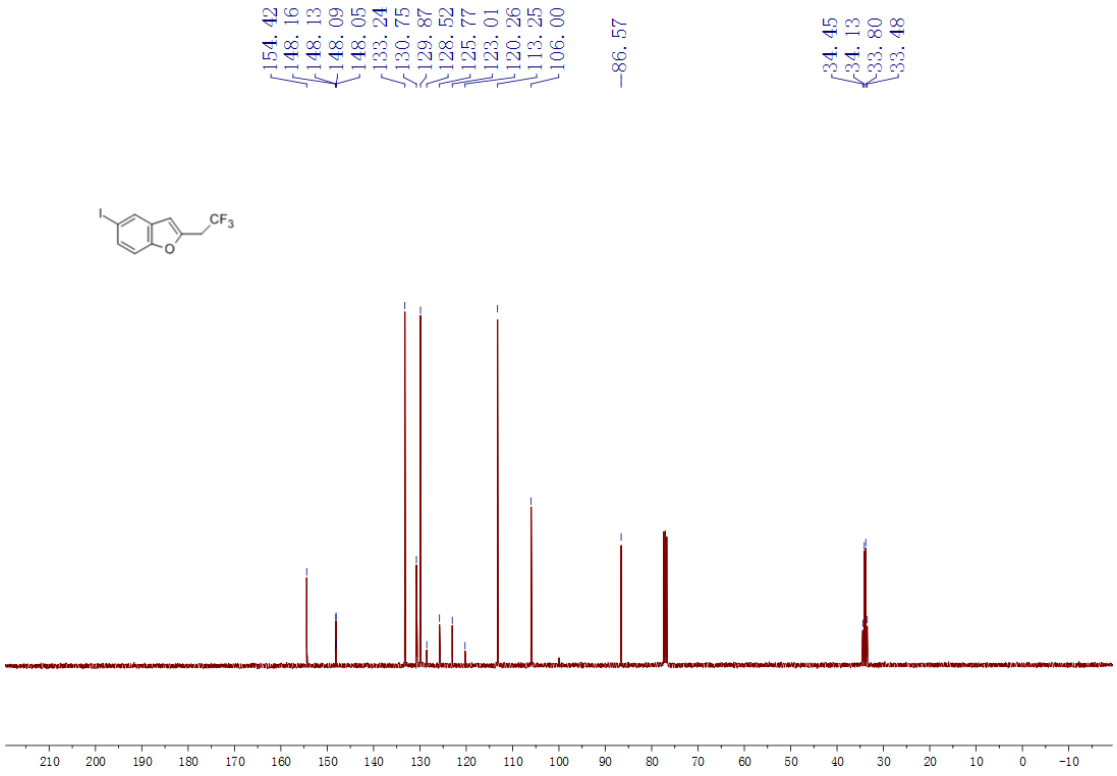


^{1}H NMR spectrum of **3v** in $CDCl_3$

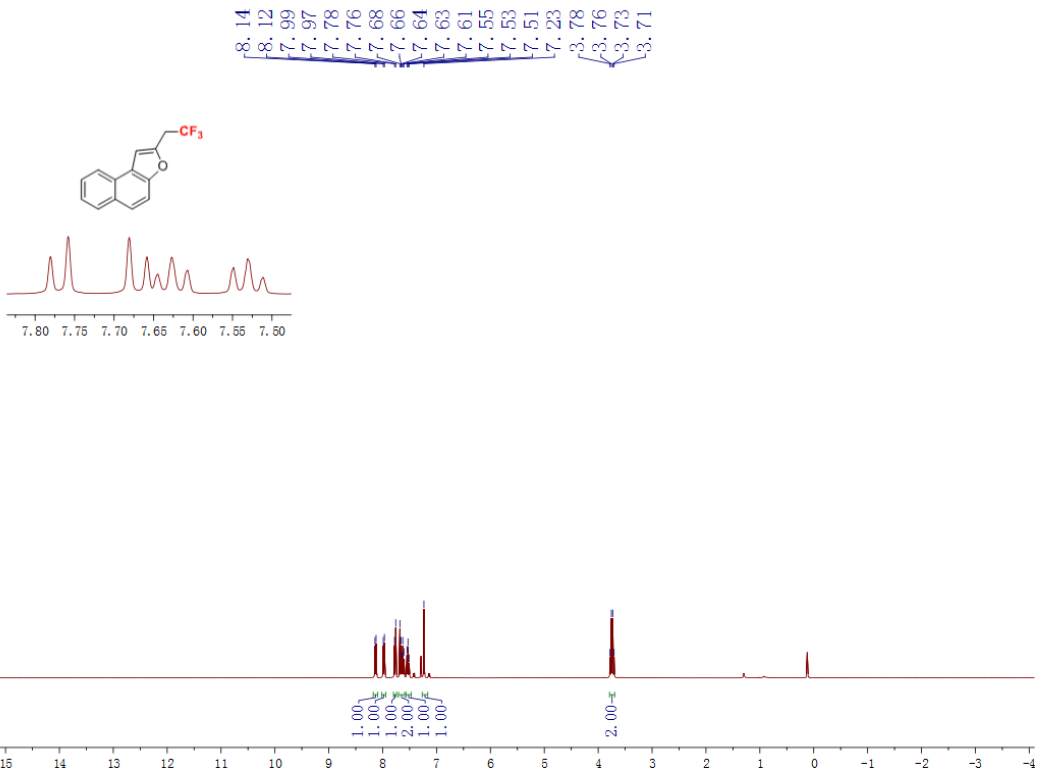


^{19}F NMR spectrum of **3v** in $CDCl_3$

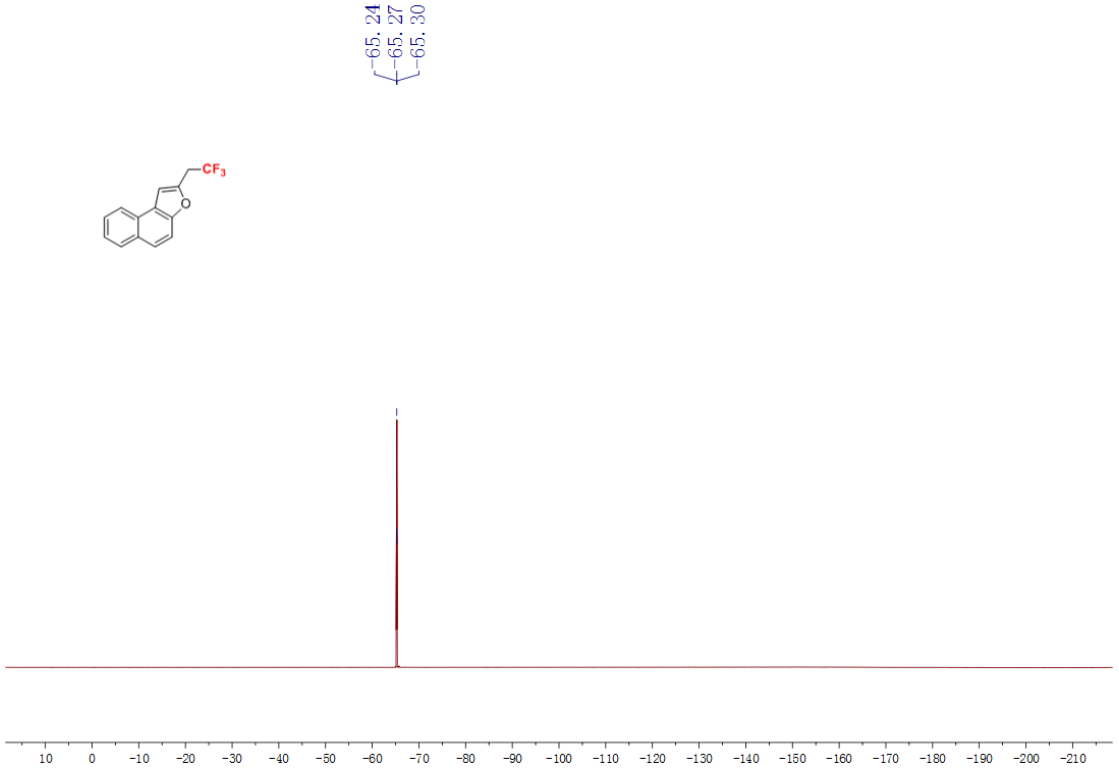
^{13}C NMR spectrum of **3v** in $CDCl_3$



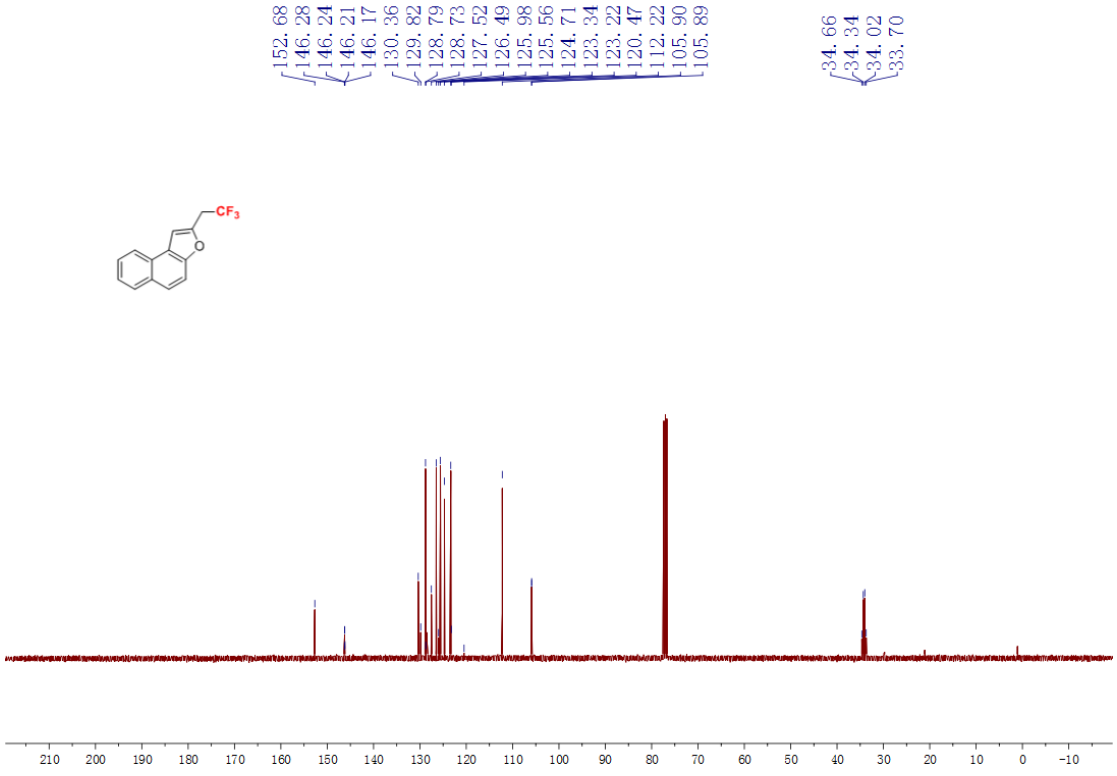
^{1}H NMR spectrum of **3w** in $CDCl_3$



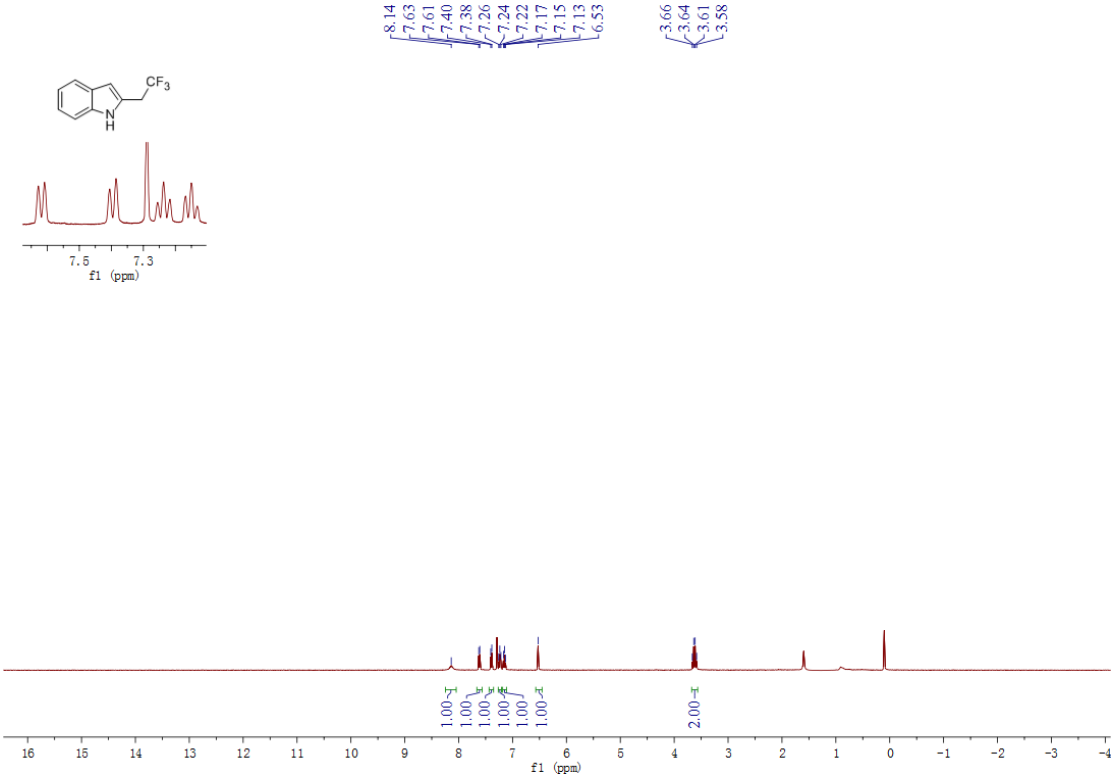
^{19}F NMR spectrum of **3w** in $CDCl_3$



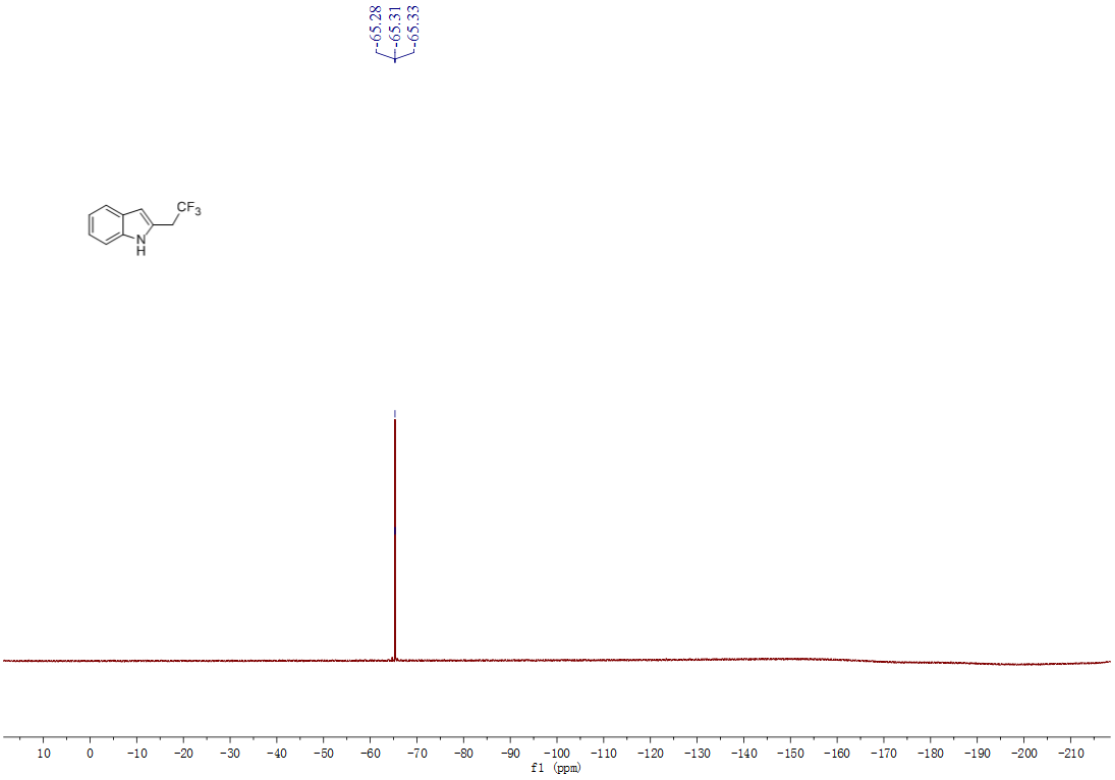
^{13}C NMR spectrum of **3w** in $CDCl_3$



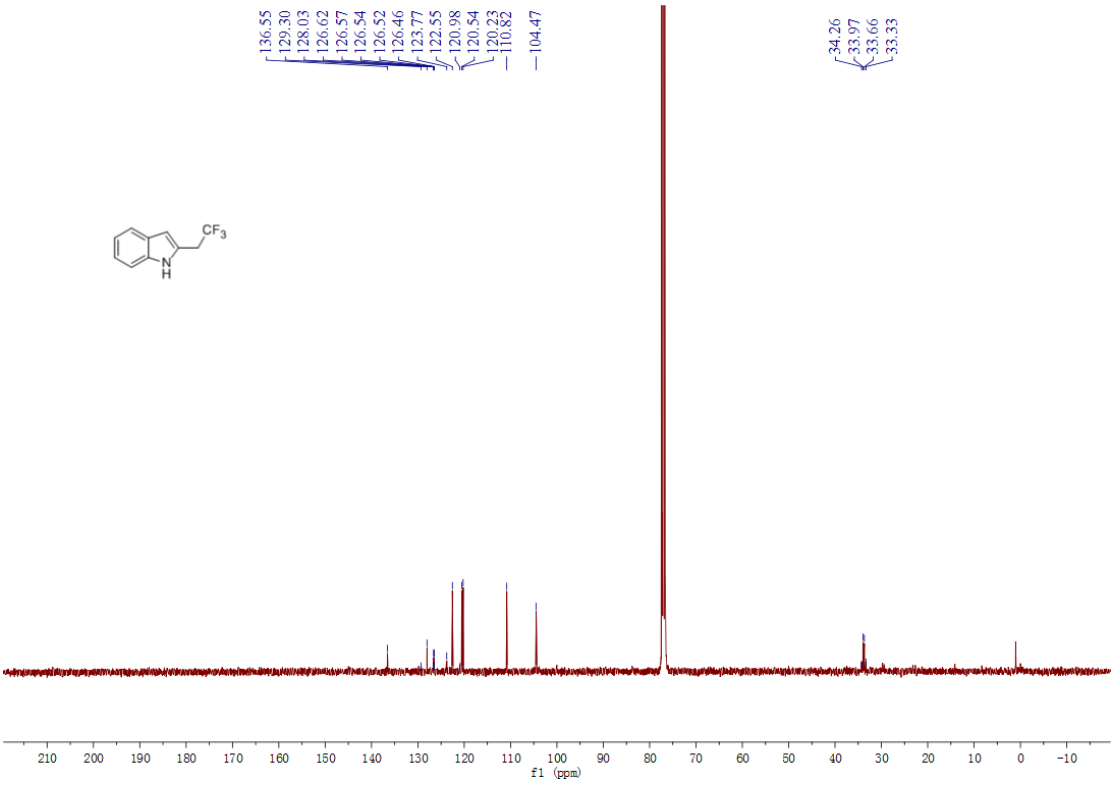
^{1}H NMR spectrum of **5a** in $CDCl_3$



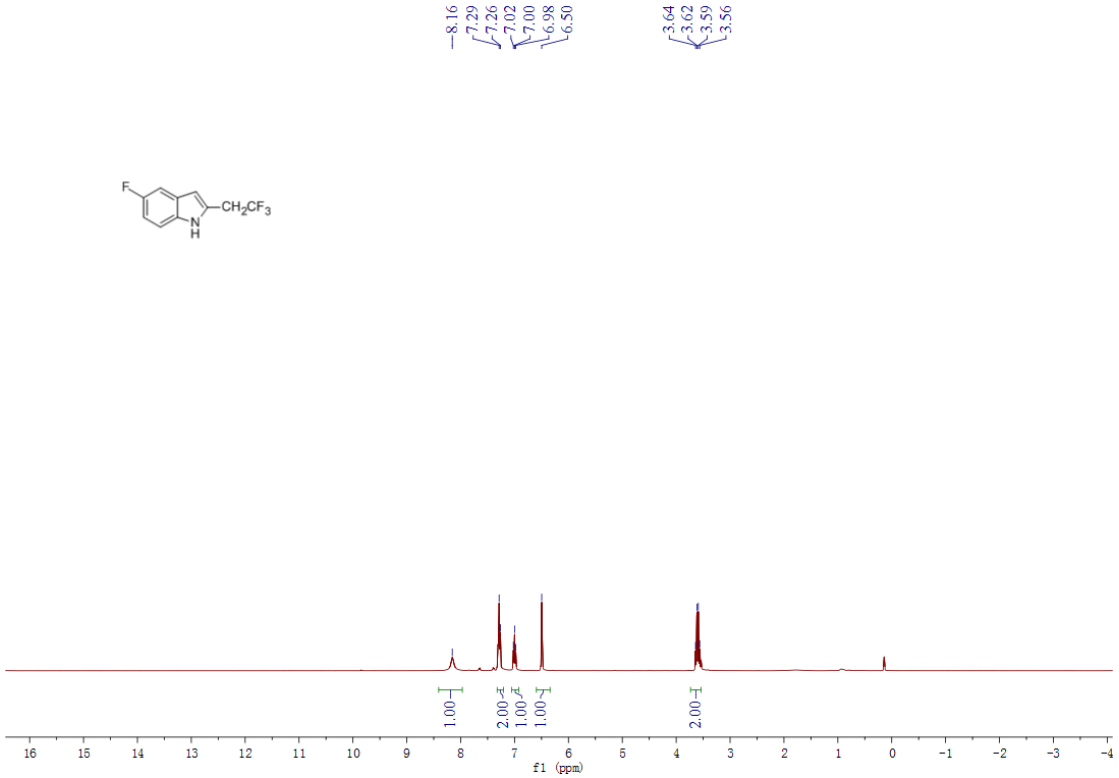
^{19}F NMR spectrum of **5a** in $CDCl_3$



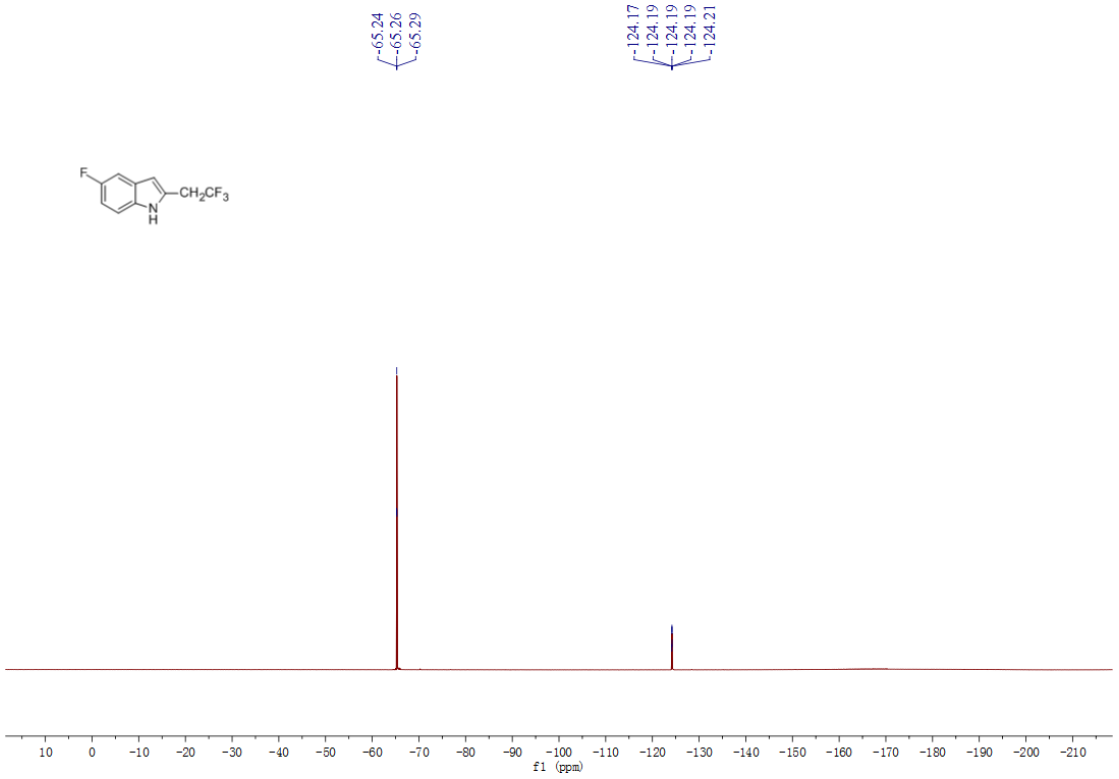
^{13}C NMR spectrum of **5a** in $CDCl_3$



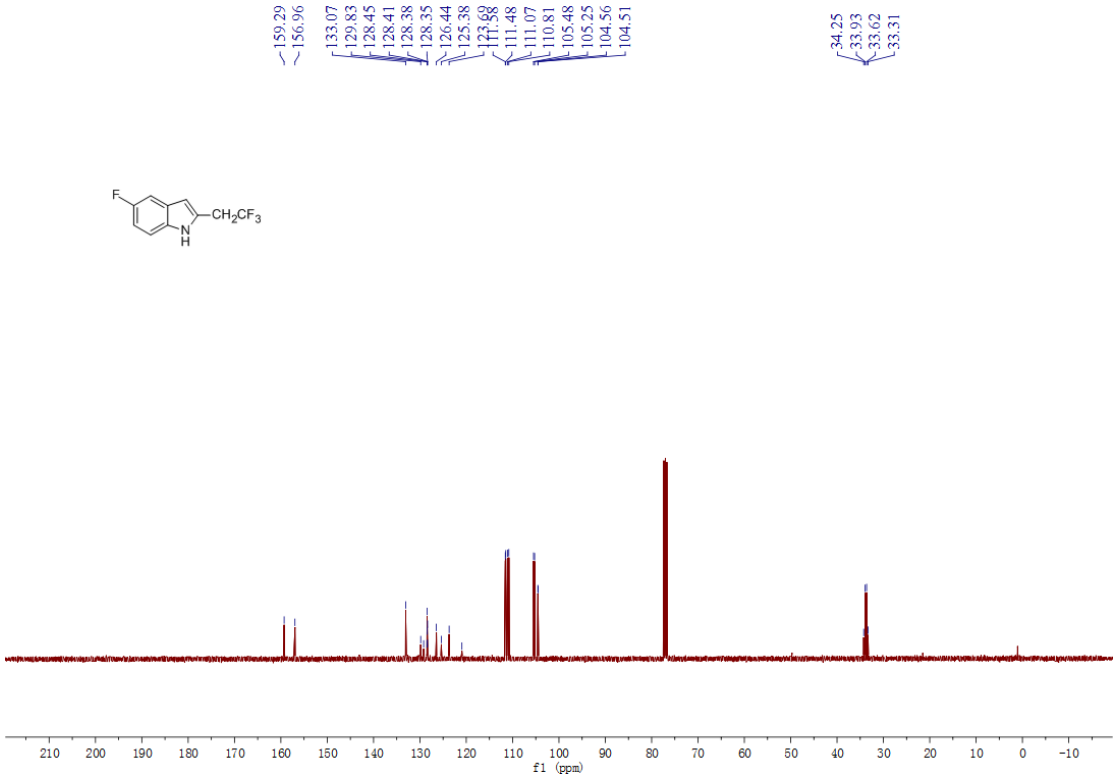
^{1}H NMR spectrum of **5b** in $CDCl_3$



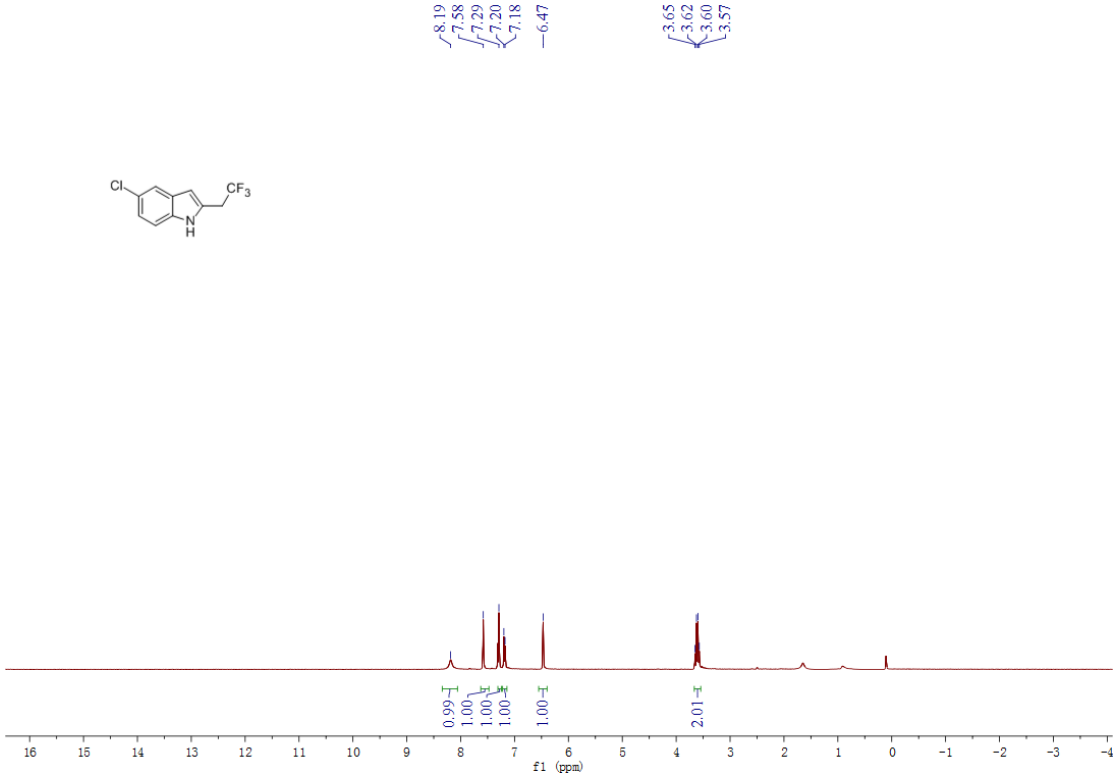
^{19}F NMR spectrum of **5b** in $CDCl_3$



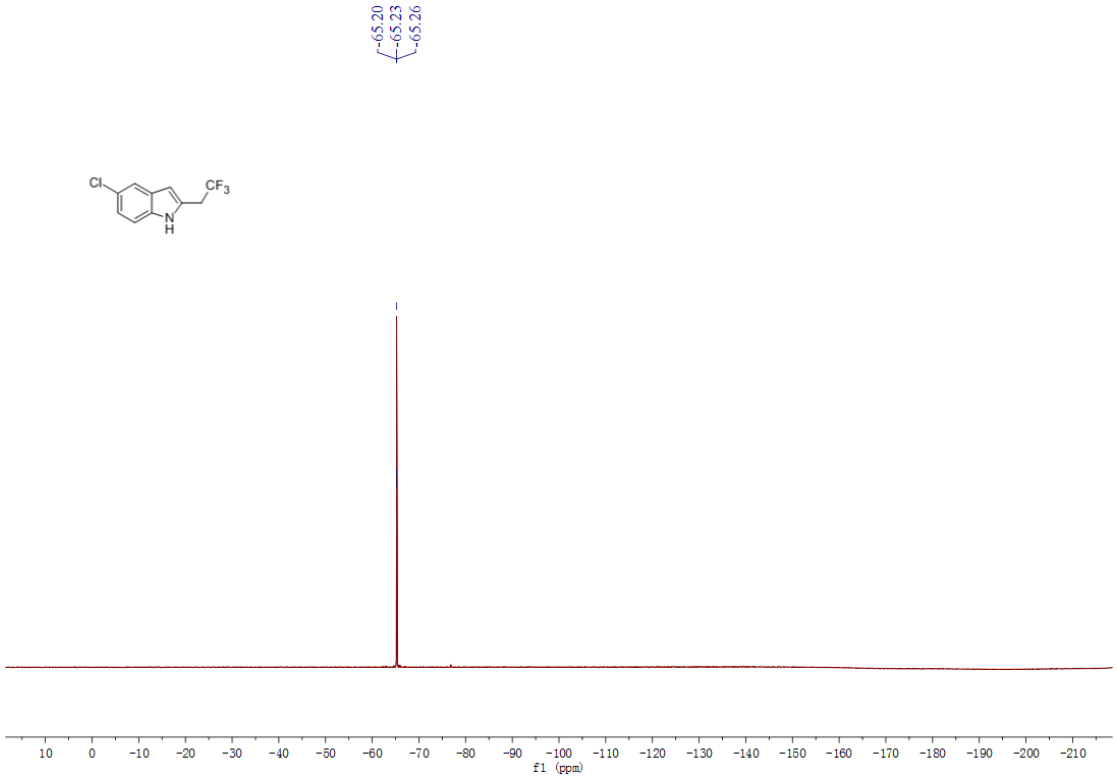
^{13}C NMR spectrum of **5b** in $CDCl_3$



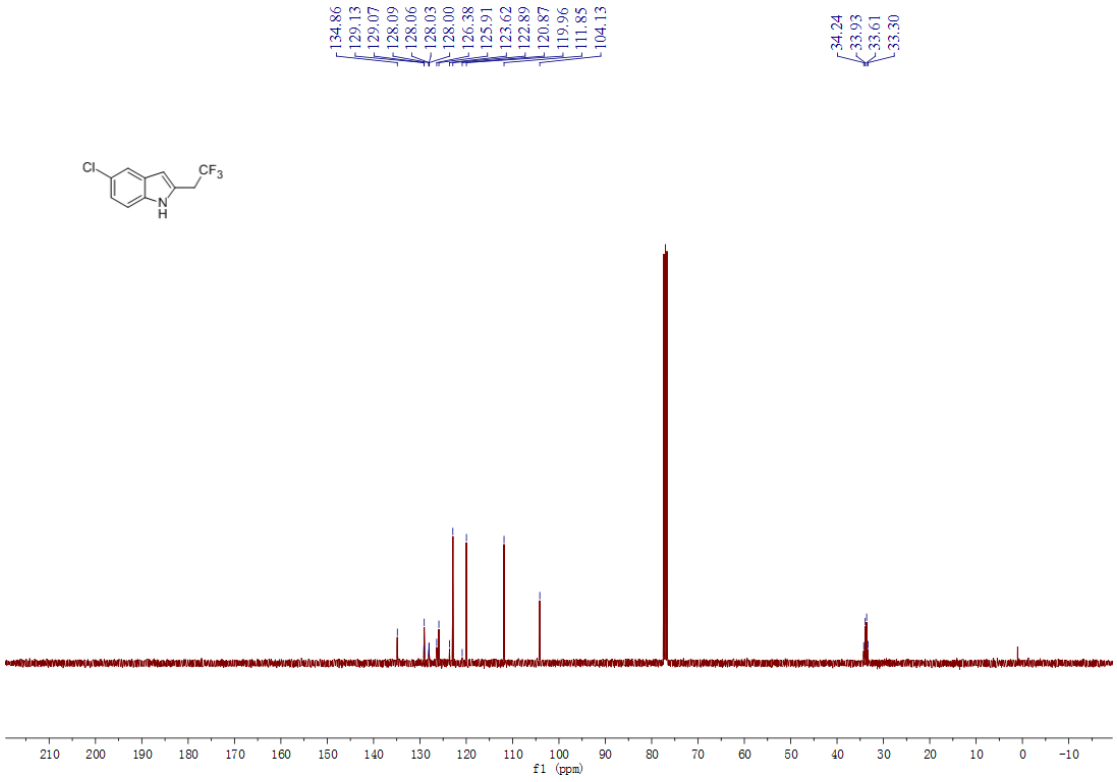
^{1}H NMR spectrum of **5c** in $CDCl_3$



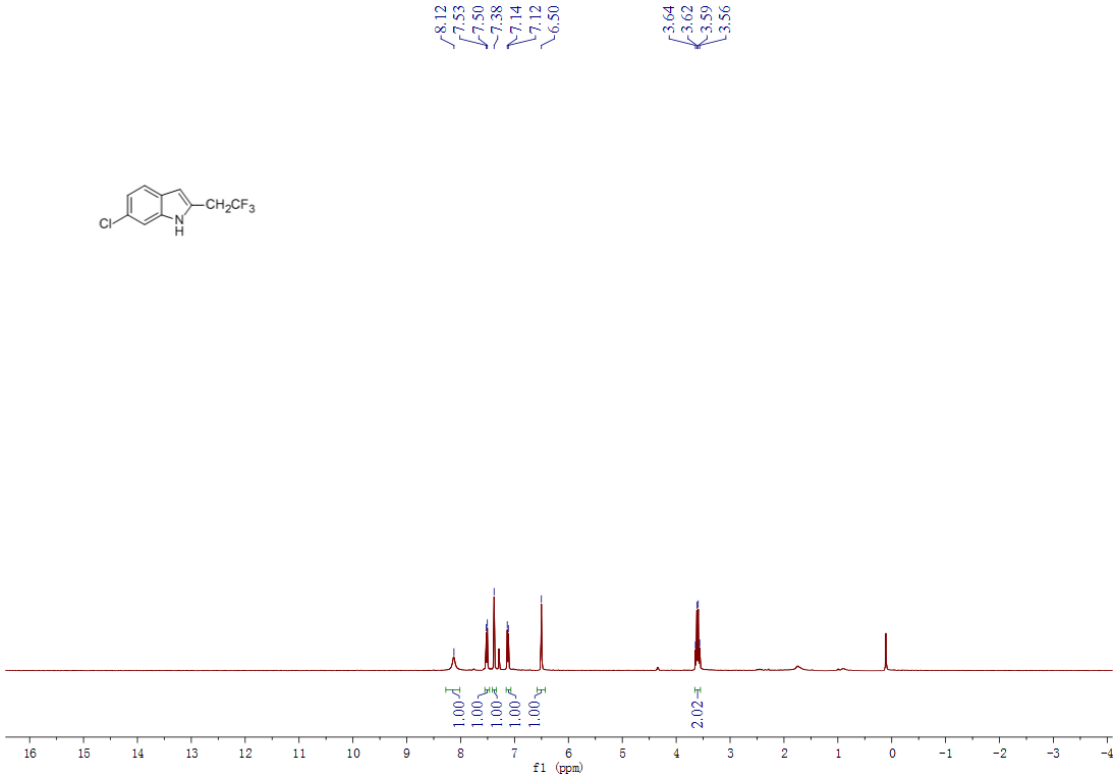
^{19}F NMR spectrum of **5c** in $CDCl_3$



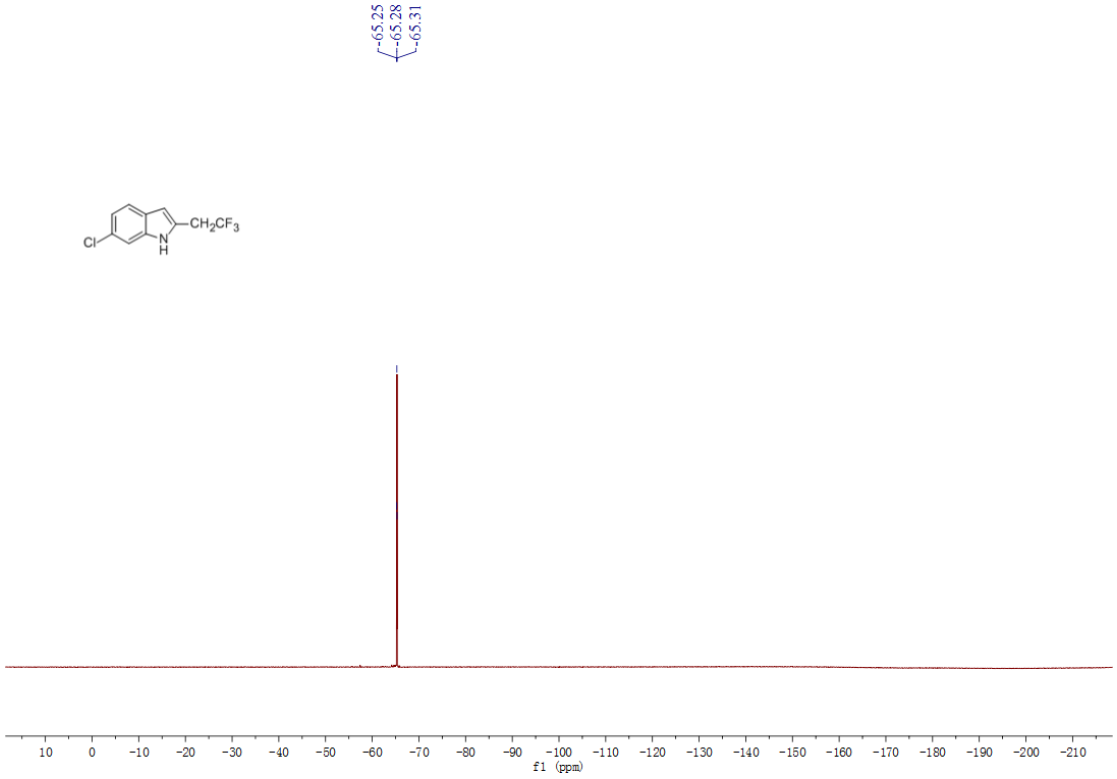
^{13}C NMR spectrum of **5c** in $CDCl_3$



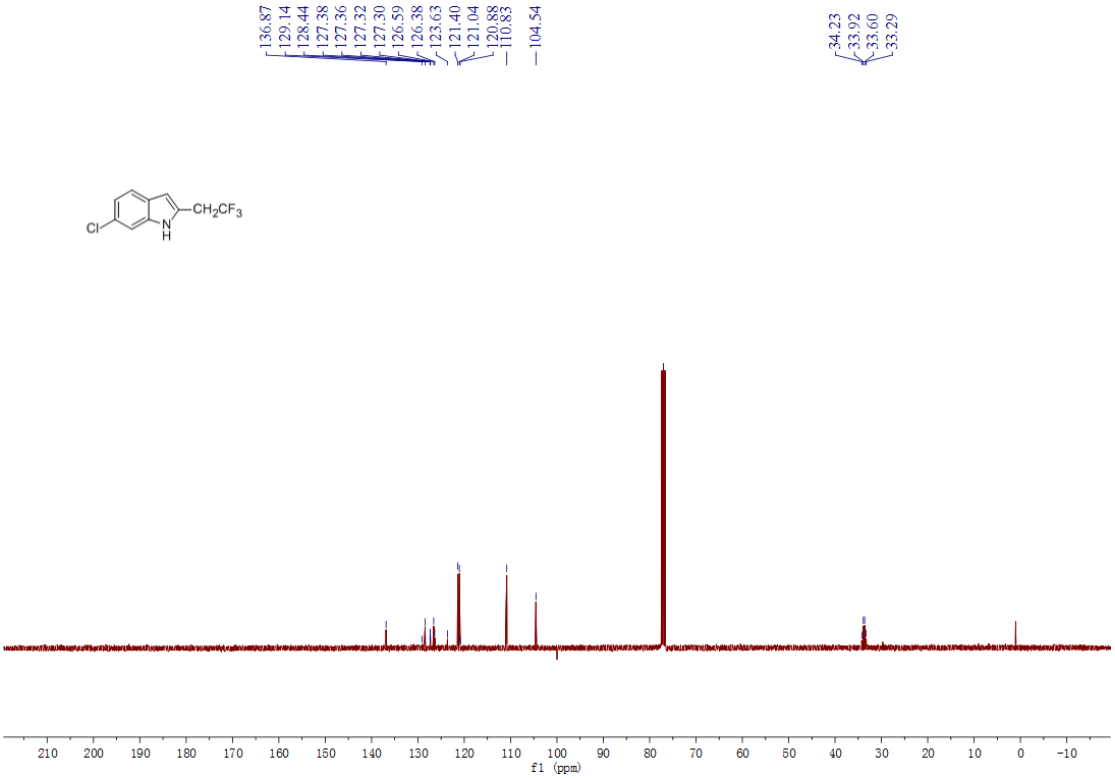
^{1}H NMR spectrum of **5d** in $CDCl_3$



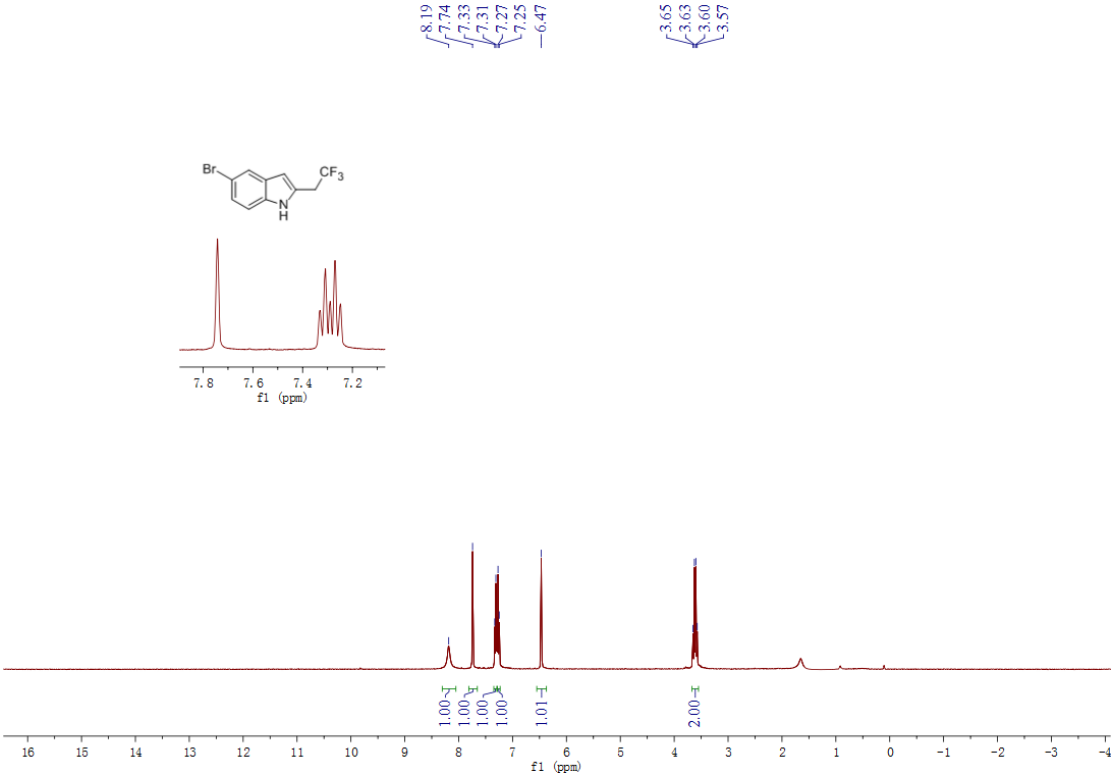
^{19}F NMR spectrum of **5d** in $CDCl_3$



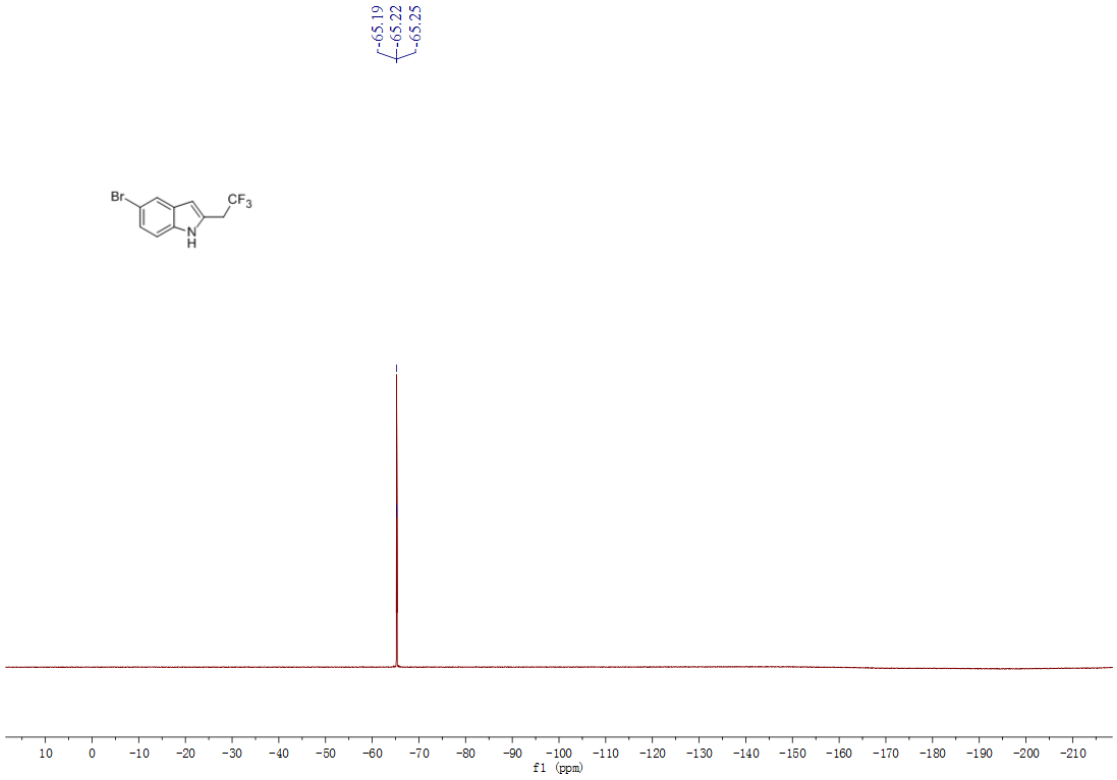
^{13}C NMR spectrum of **5d** in $CDCl_3$



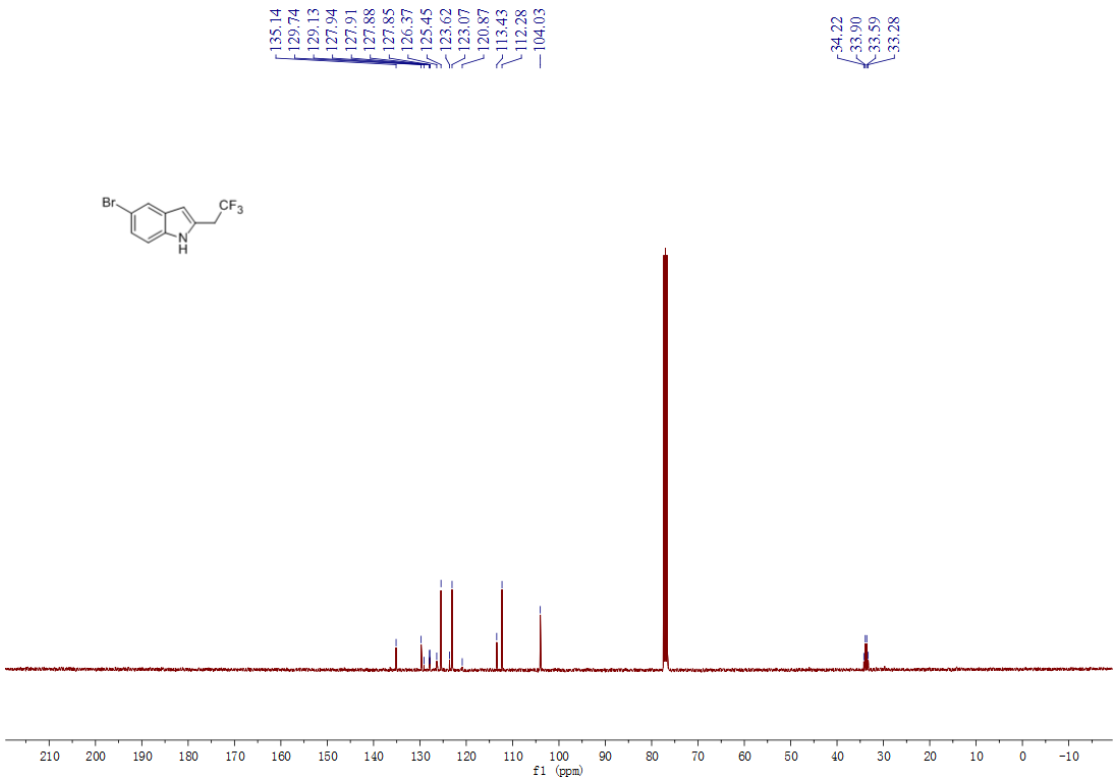
^{1}H NMR spectrum of **5e** in $CDCl_3$



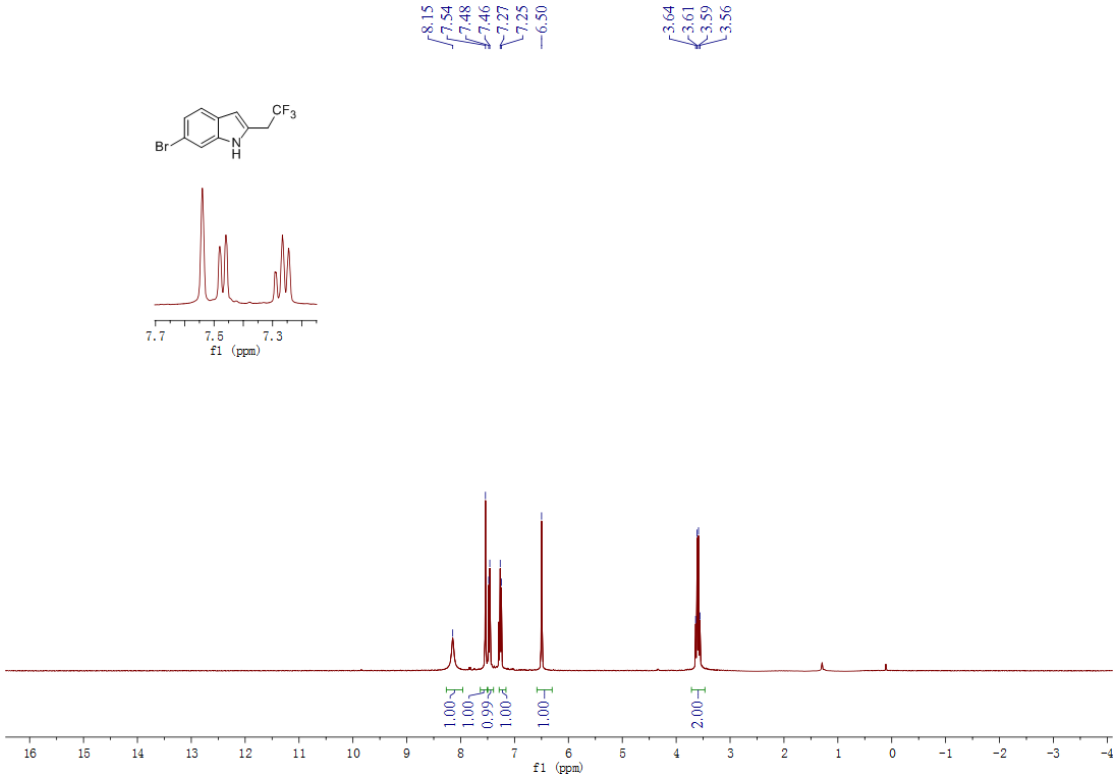
^{19}F NMR spectrum of **5e** in $CDCl_3$



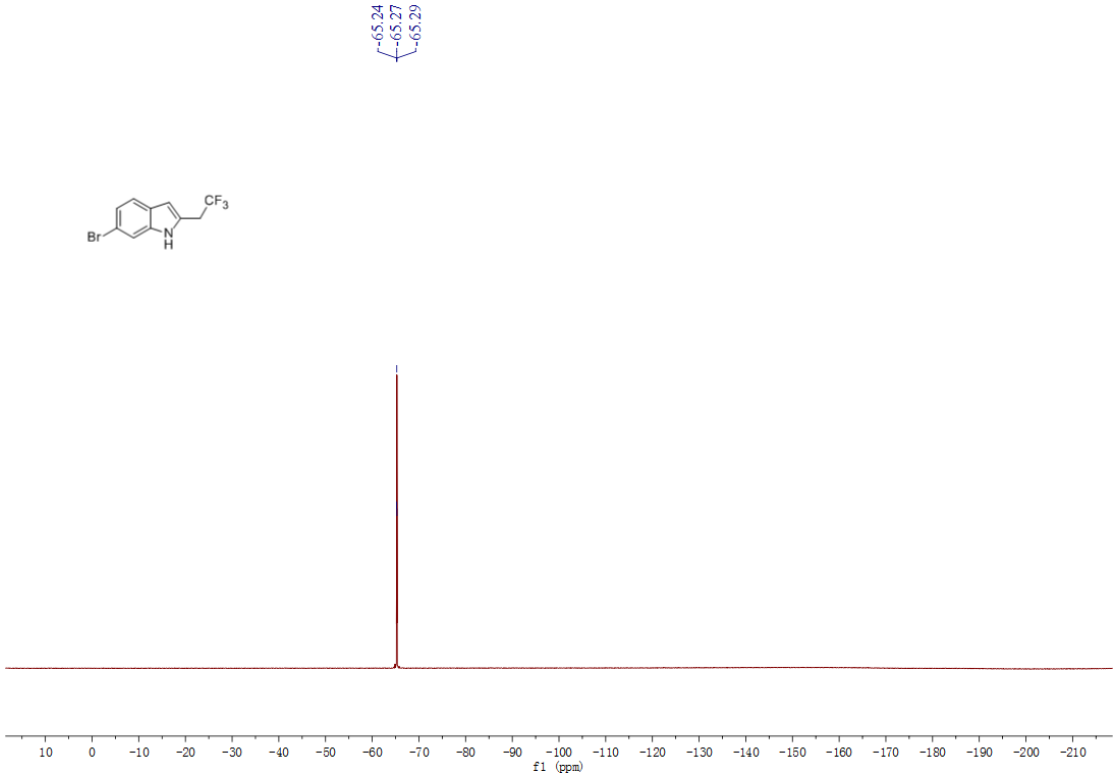
^{13}C NMR spectrum of **5e** in $CDCl_3$



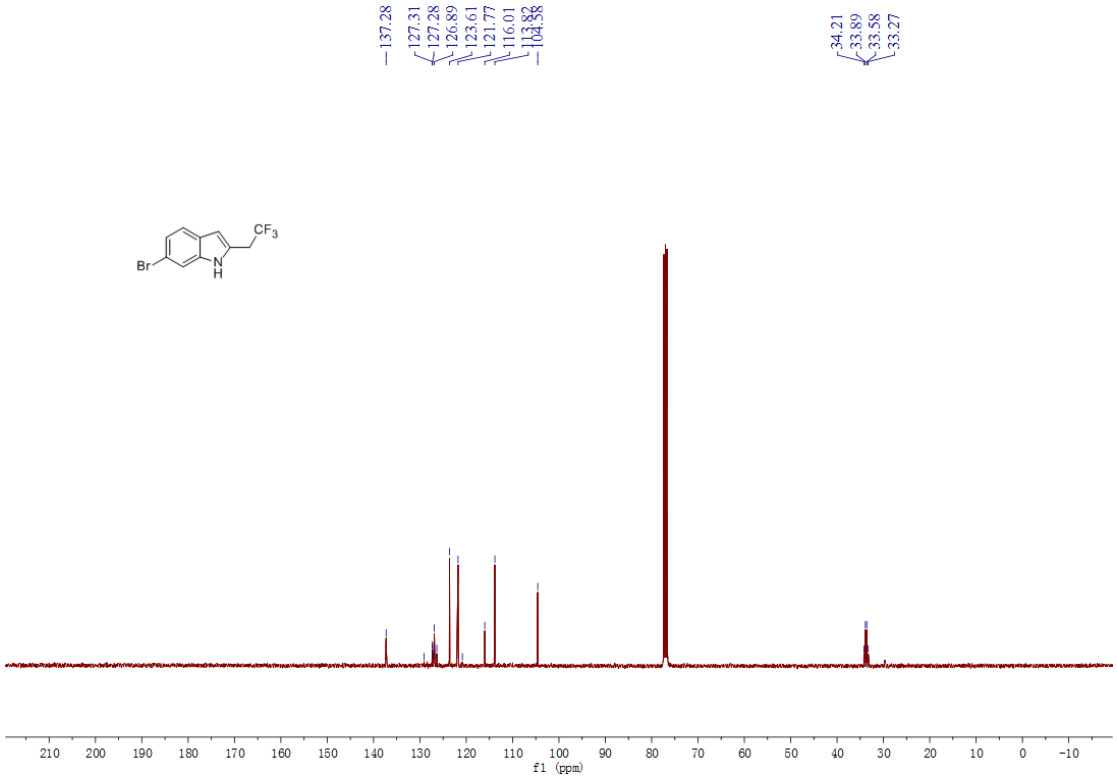
^{1}H NMR spectrum of **5f** in $CDCl_3$



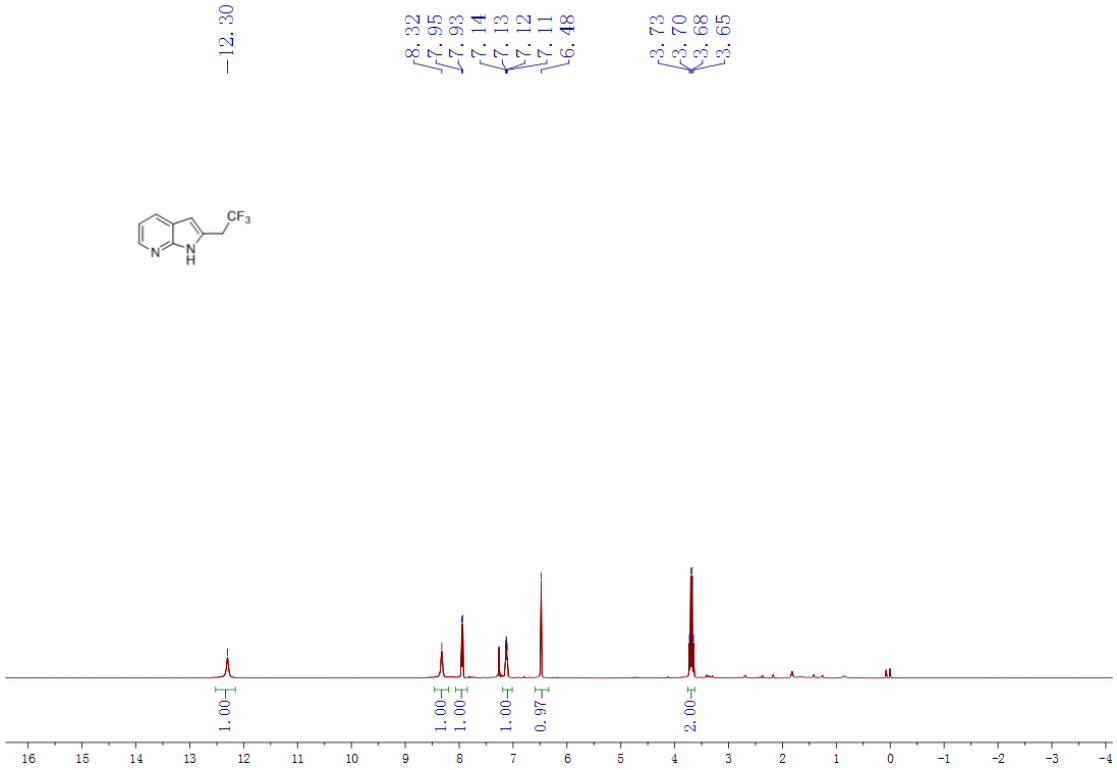
^{19}F NMR spectrum of **5f** in $CDCl_3$



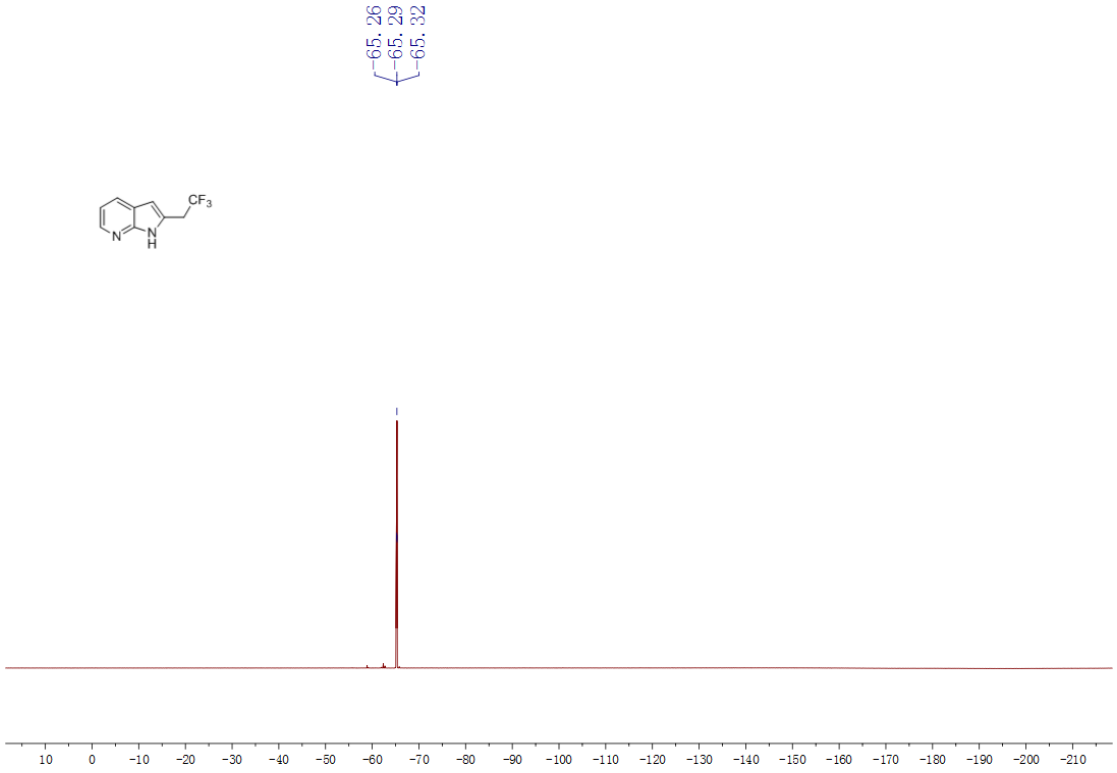
^{13}C NMR spectrum of **5f** in $CDCl_3$



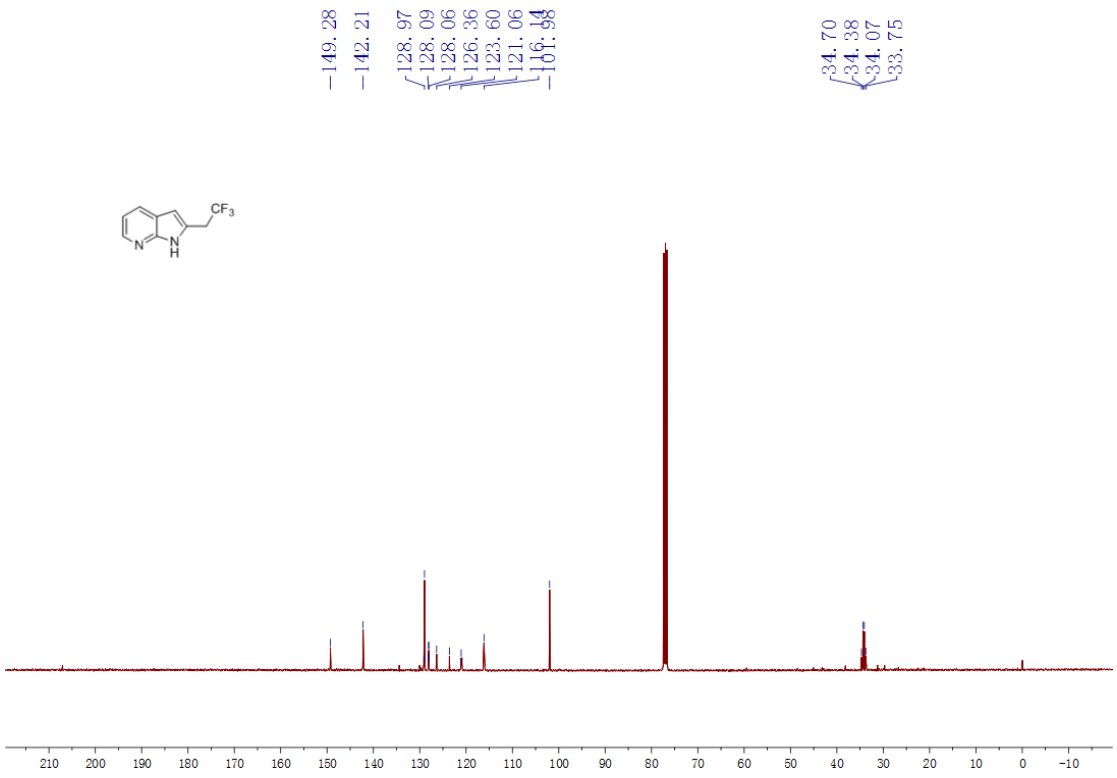
^{1}H NMR spectrum of **5g** in $CDCl_3$



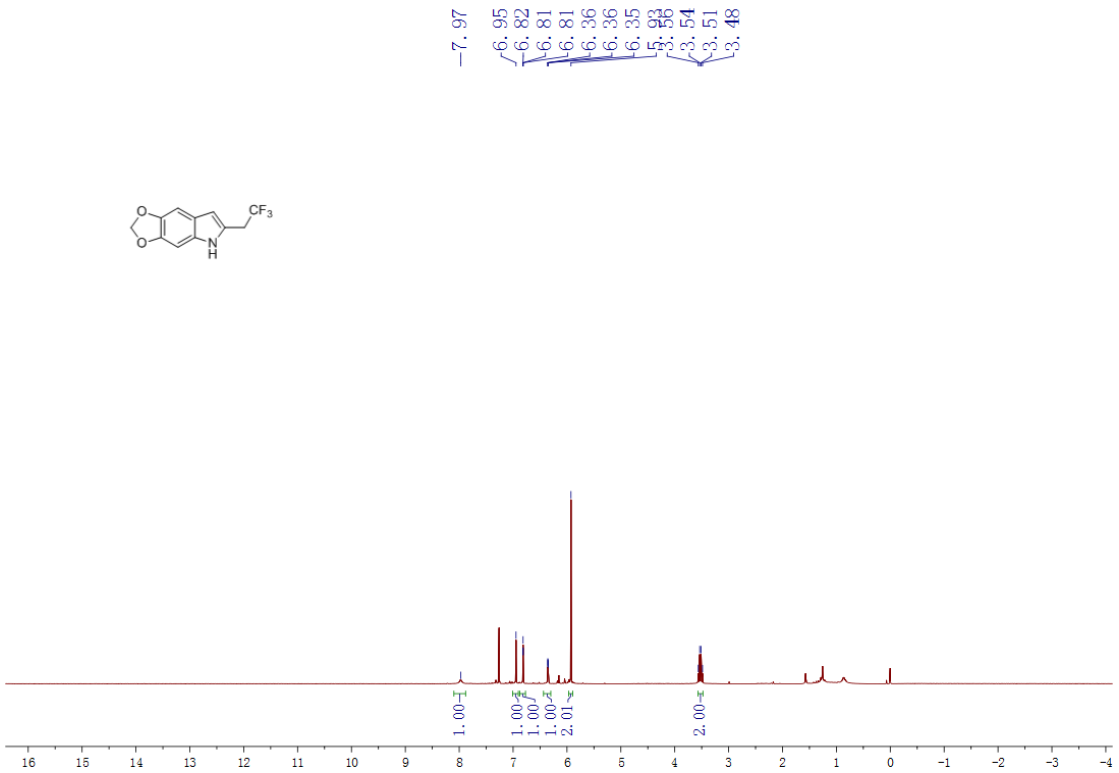
^{19}F NMR spectrum of **5g** in $CDCl_3$



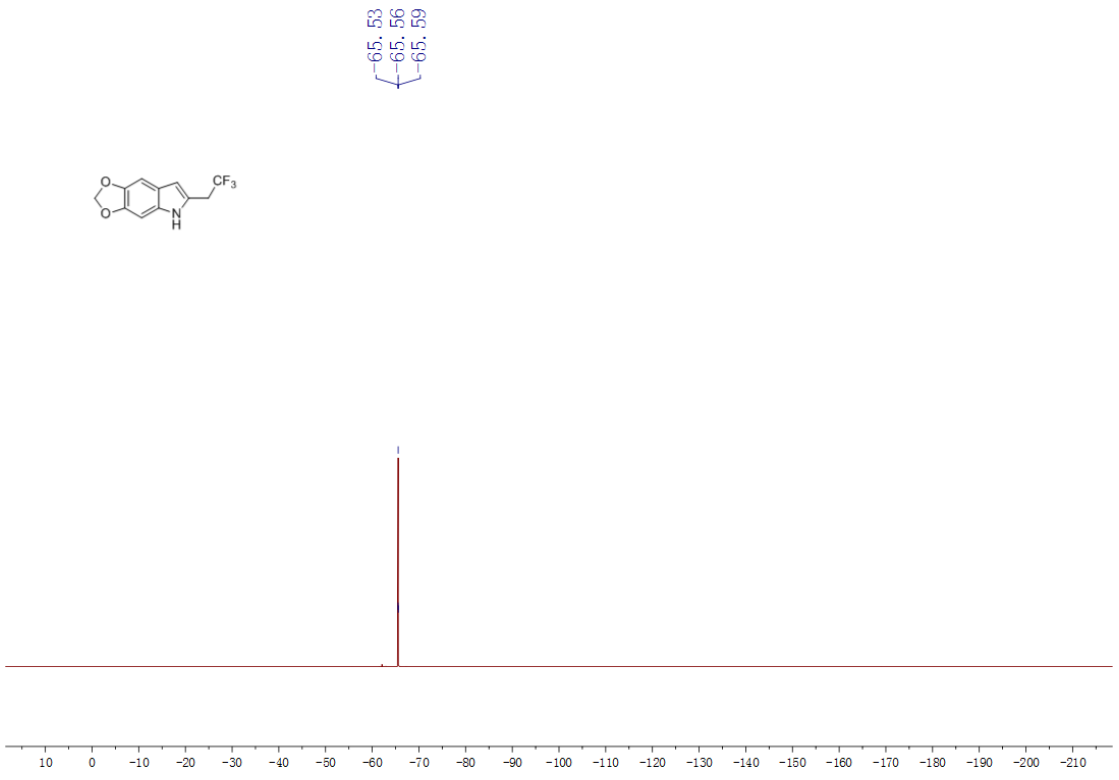
^{13}C NMR spectrum of **5g** in $CDCl_3$



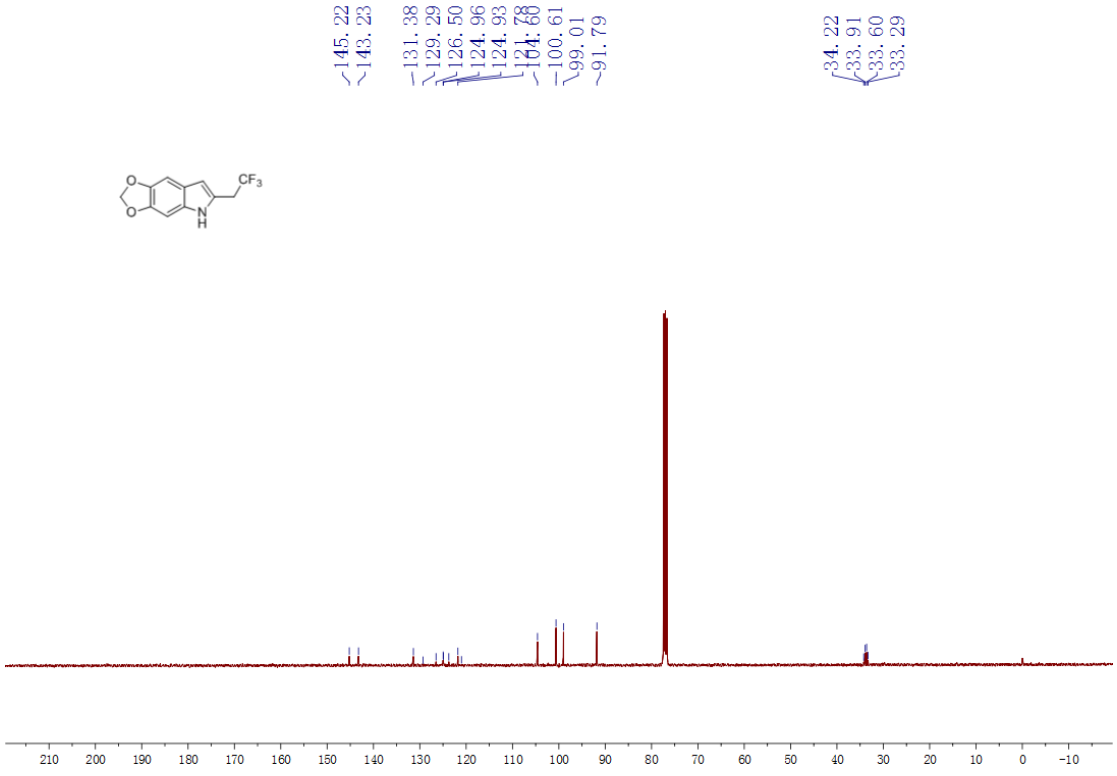
^{1}H NMR spectrum of **5h** in $CDCl_3$



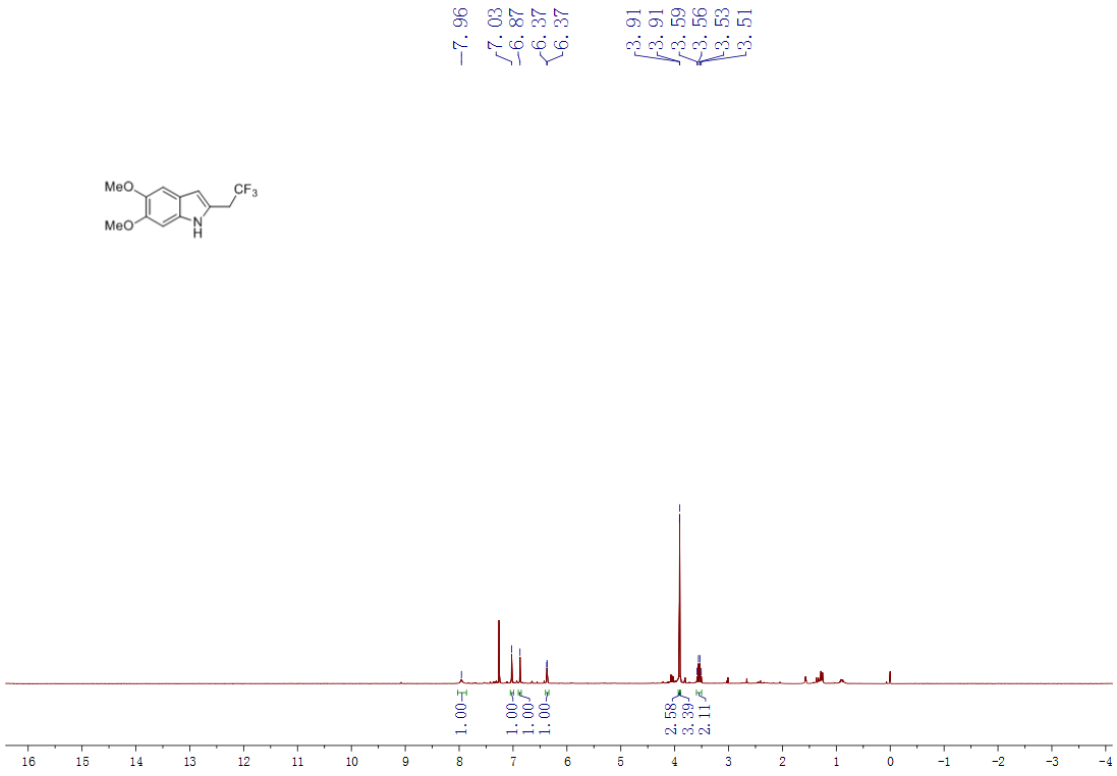
^{19}F NMR spectrum of **5h** in $CDCl_3$



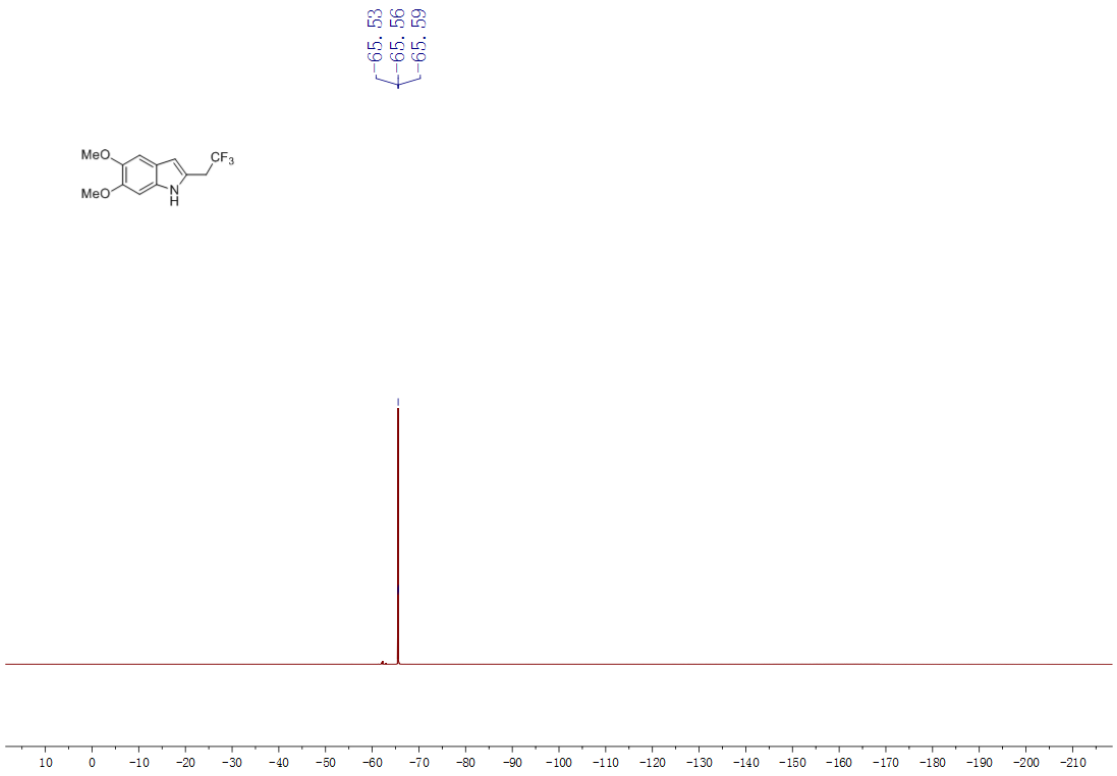
^{13}C NMR spectrum of **5h** in $CDCl_3$



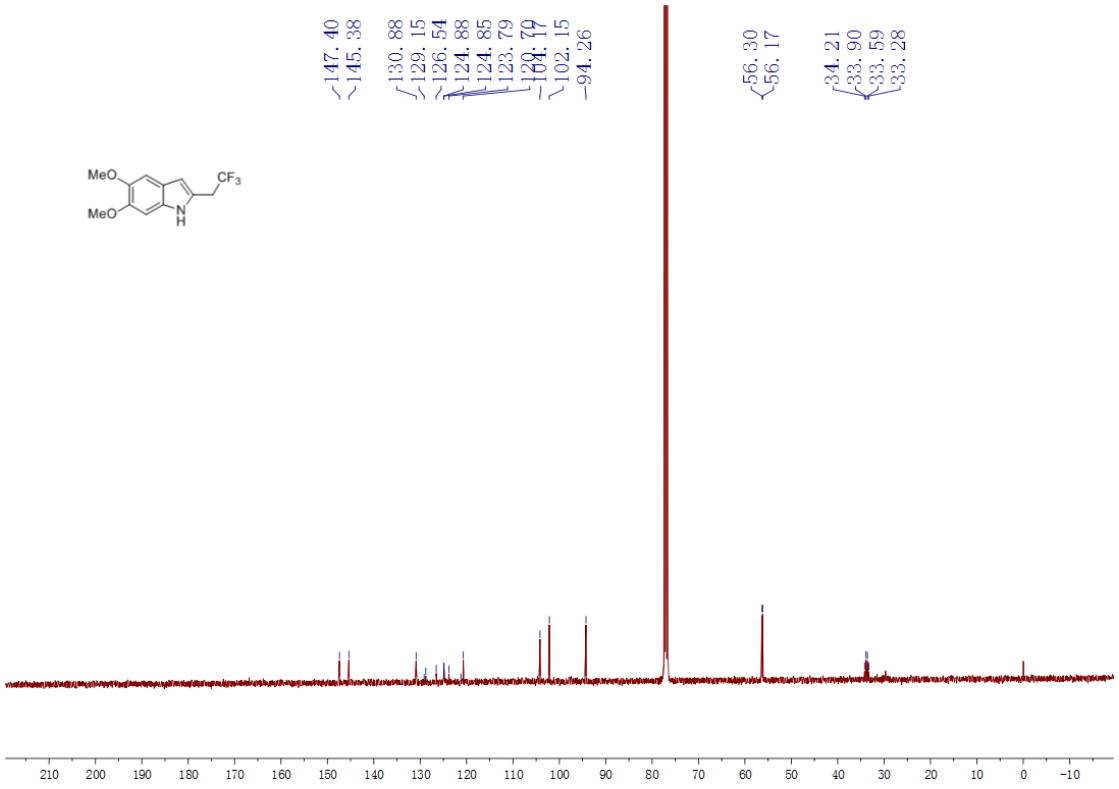
^{1}H NMR spectrum of **5i** in $CDCl_3$



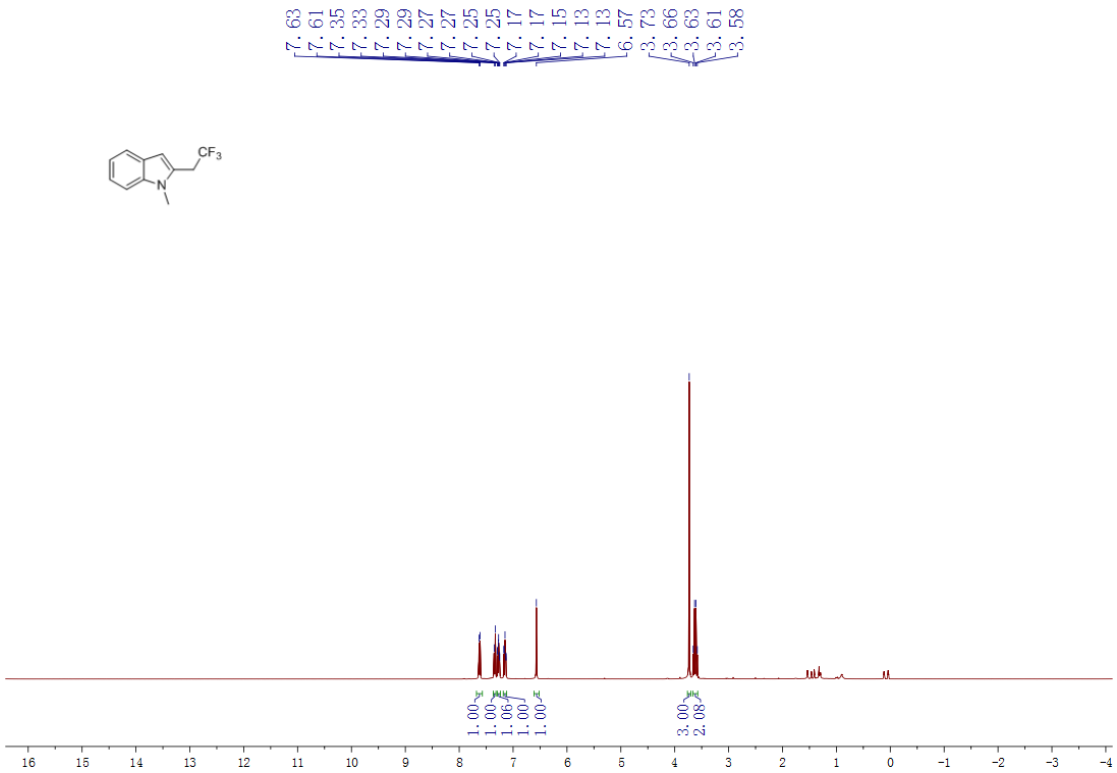
^{19}F NMR spectrum of **5i** in $CDCl_3$



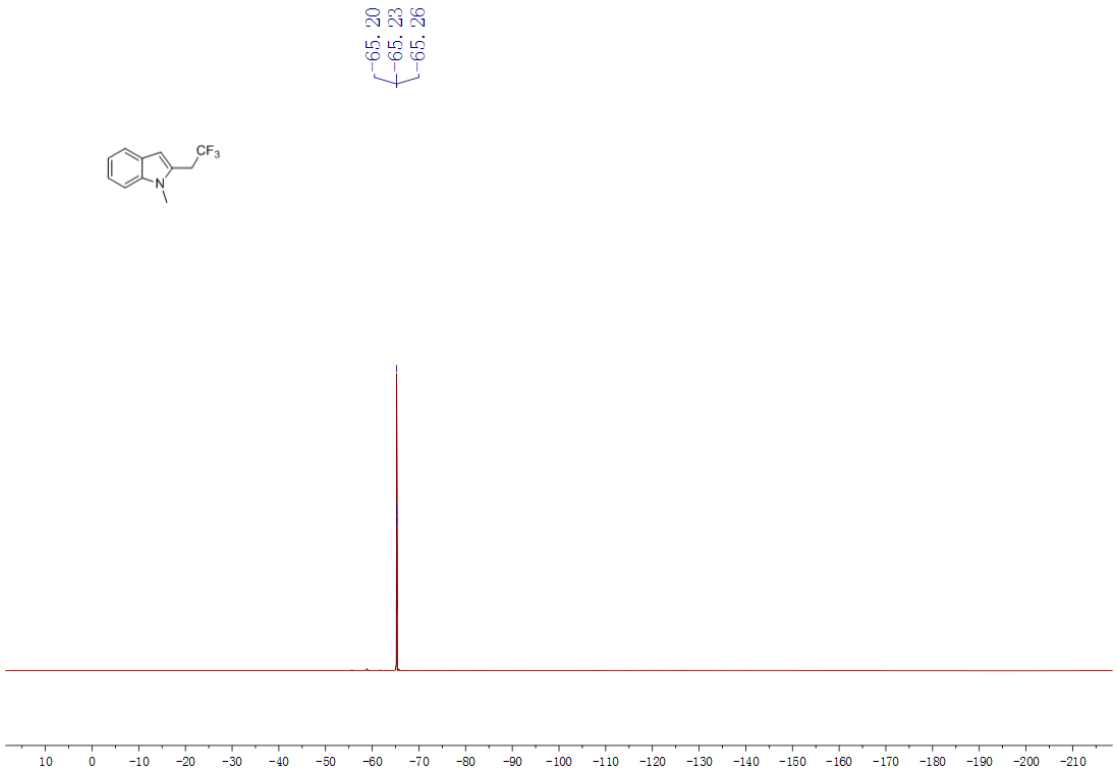
^{13}C NMR spectrum of **5i** in $CDCl_3$



^{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 $CDCl_3$