Supporting Information *for*

Elemental Sulfur-Promoted One-Pot Synthesis of 2-(2,2,2-Trifluoroethyl)benzoxazoles and their derivatives

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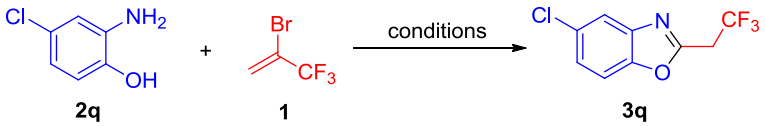
Table of Contents

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. 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.

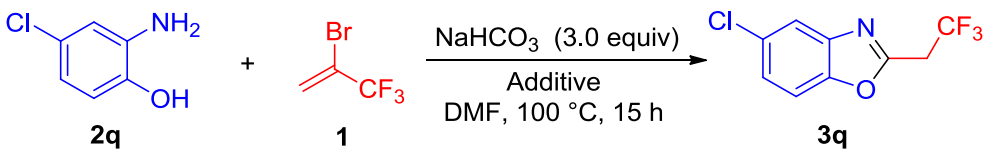
Table 1. The effect of the reaction temperature and time, and the addition of water for the synthesis of **3q**[a]



Entry	Promoter (equiv)	Base (3.0 equiv)	Additive	Solvent	Temp (°C)	Time (h)	Yield (%) [b]
1	S_8 (8)	$NaHCO_3$	ADVN/B_2Pin_2	DMF	100	15	87
2	S_8 (8)	$NaHCO_3$	ADVN/B_2Pin_2	DMF	80	15	42
3	S_8 (8)	$NaHCO_3$	ADVN/B_2Pin_2	DMF	100	6	56
4	S_8 (8)	$NaHCO_3$	H_2O [c]	DMF	100	15	56
5	S_8 (8)	$NaHCO_3$	ADVN/B_2Pin_2/H_2O [d]	DMF	100	15	76
6	S_8 (5)	K_2CO_3	-	DMF	100	15	0
7	S_8 (5)	K_3PO_4	-	DMF	100	15	0
8	S_8 (5)	NEt_3	-	DMF	100	15	0

[a] Reaction conditions: **1** (0.70 mmol), **2q** (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N_2 atmosphere; [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard; [c] 1.0 equiv.; [d] ADVN : B_2Pin_2 : H_2O = 0.9 : 0.7 : 1.0.

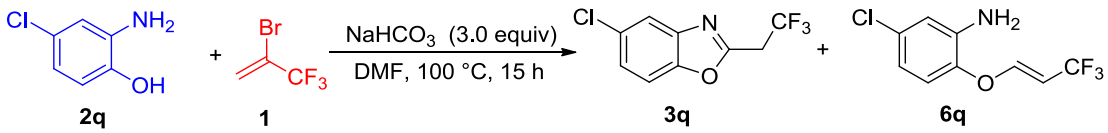
Table 2. The effect of relative amounts of elemental sulfur and 2-bromo-3,3,3-trifluoropropene (**1**) for the cyclization[a]



Entry	equiv of S_8	equiv of **1**	Additive	Yield (%) [b]
1	8.0	1.0	-	7
2	8.0	2.0	-	22
3	8.0	3.0	-	31
4	8.0	4.0	-	35
5	8.0	5.0	-	40
6	8.0	6.0	-	46
7	8.0	7.0	-	54
8	8.0	1.0	ADVN/B_2Pin_2 [c]	8
9	8.0	2.0	ADVN/B_2Pin_2 [c]	40
10	8.0	3.0	ADVN/B_2Pin_2 [c]	55
11	8.0	4.0	ADVN/B_2Pin_2 [c]	61
12	8.0	5.0	ADVN/B_2Pin_2 [c]	67
13	8.0	6.0	ADVN/B_2Pin_2 [c]	83
14	8.0	7.0	ADVN/B_2Pin_2 [c]	87
15	2.0	7.0	ADVN/B_2Pin_2 [c]	14
16	3.0	7.0	ADVN/B_2Pin_2 [c]	25
17	4.0	7.0	ADVN/B_2Pin_2 [c]	49
18	5.0	7.0	ADVN/B_2Pin_2 [c]	64
19	6.0	7.0	ADVN/B_2Pin_2 [c]	70
20	7.0	7.0	ADVN/B_2Pin_2 [c]	79

[a] Reaction conditions: **1** (0.70 mmol), **2q** (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N_2 atmosphere; [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard; [c] ADVN (0.9 equiv), B_2Pin_2 (0.7 equiv).

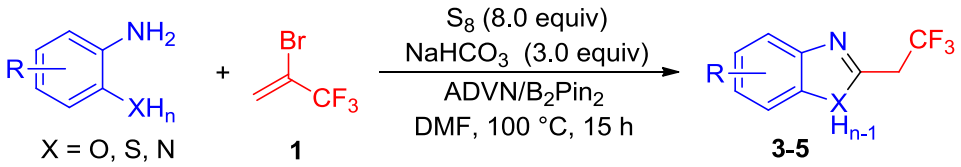
Table 3. The reaction of **2q** with **1** mediated by other promoters



Entry	Promoter (equiv)	Yield (%) [b]	
		3q	**6q**
1	I_2 (5)	0	0
2	KI (5)	0	46
3	O_2	0	15

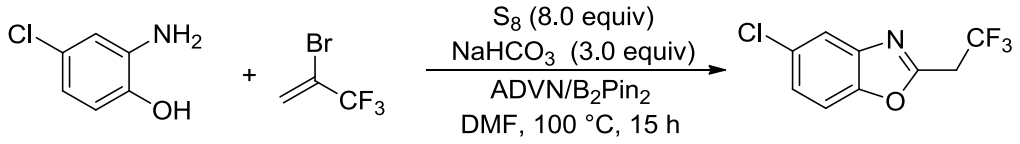
[a] Reaction conditions: **1** (0.70 mmol), **2q** (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N_2 atmosphere; [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

General procedure of one-pot synthesis of 2-(2,2,2-trifluoroethyl)benzoxazoles, benzothiazoles, and benzoimidazoles



The 2-aminophenol derivatives (**2**), *o*-aminobenzenethiols, or benzene-1,2-diamines (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (**1**) (2.10 mmol, 7.0 equiv), S_8 (2.40 mmol, 8.0 equiv), $NaHCO_3$ (0.90 mmol, 3.0 equiv), 2,2'-azobis-(2,4-dimethylvaleronitrile) (ADVN) (0.27 mmol, 0.90 equiv), bis(pinacolato)diboron (B_2Pin_2) (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. After cooled down to room temperature, the reaction system was quenched with water (10 mL) and ethyl acetate (10 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **3** was purified by column chromatography over silica gel.

Scalability of the reaction of 2q with 1



2q
0.868 g

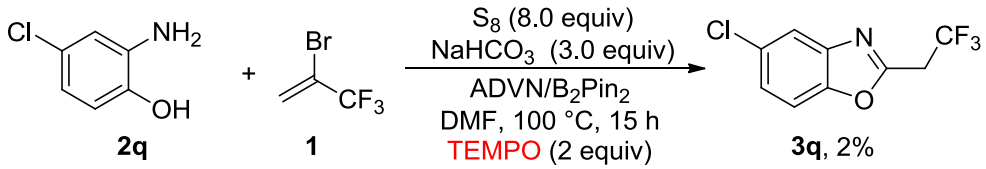
1
4.2 mL

3q
0.51 g, 36%

The 2-amino-4-chlorophenol (**2q**) (6.0 mmol, 0.868 g, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (**1**) (42.0 mmol, 4.2 mL, 7.0 equiv), S_8 (48.0 mmol, 1.74 g, 8.0 equiv), $NaHCO_3$ (18.0 mmol, 1.50 g, 3.0 equiv), ADVN (5.4 mmol, 1.32 g, 0.90 equiv), B_2Pin_2 (4.2 mmol, 0.96 g, 0.70 equiv), and DMF (40 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. After cooled down to room temperature, the reaction system was quenched with water (150 mL) and ethyl acetate (100 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 70 mL). The combined organic layers were washed with saturated brine (3 ×300 mL), and water (3 × 300 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **3q** (0.51 g, 36% yield) was purified by column chromatography over silica gel.

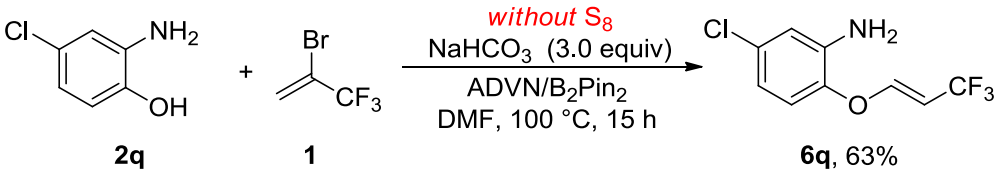
Mechanistic Study

(a).



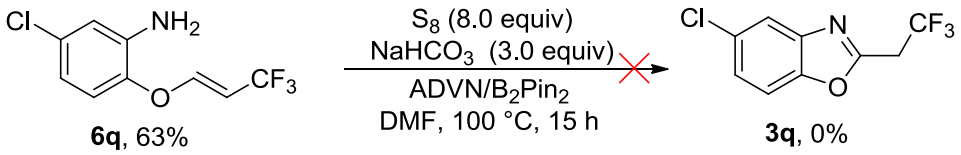
The 2-amino-4-chlorophenol (**2q**) (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (**1**) (2.10 mmol, 7.0 equiv), S_8 (2.40 mmol, 8.0 equiv), $NaHCO_3$ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B_2Pin_2 (0.21 mmol, 0.70 equiv), TEMPO (0.60 mmol, 2.0 equiv) and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard. The yield of the product **3q** was calculated to be 2%.

(b).



The 2-amino-4-chlorophenol (**2q**) (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (**1**) (2.10 mmol, 7.0 equiv), $NaHCO_3$ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B_2Pin_2 (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (3 × 10 mL), washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **6q** was purified by column chromatography over silica gel.

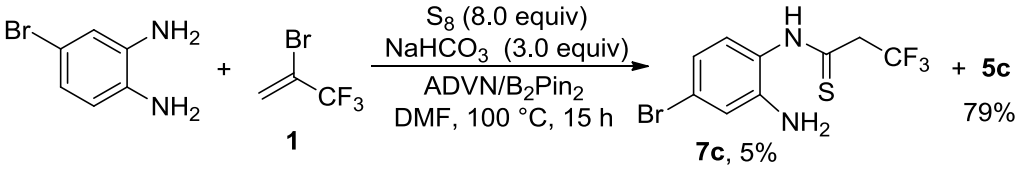
(c).



6q, 63% **3q**, 0%

The 5-chloro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)aniline (**6q**) (0.15 mmol, 1.0 equiv), S_8 (1.20 mmol, 8.0 equiv), $NaHCO_3$ (0.45 mmol, 3.0 equiv), ADVN (0.14 mmol, 0.90 equiv), B_2Pin_2 (0.11 mmol, 0.70 equiv), and DMF (1.5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. A ^{19}F-NMR spectrum was acquired, and no trace of **3q** was detectable.

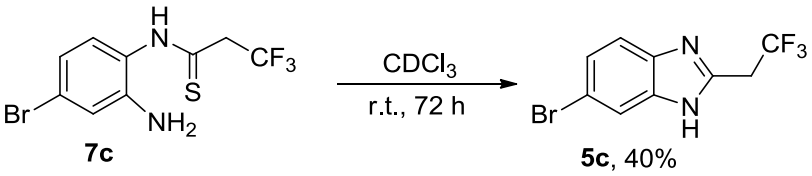
(d).



7c, 5%

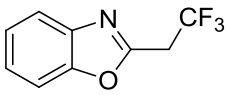
The 4-bromobenzene-1,2-diamine (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (**1**) (2.10 mmol, 7.0 equiv), S_8 (2.40 mmol, 8.0 equiv), $NaHCO_3$ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B_2Pin_2 (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 ℃ for 15 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (3 × 10 mL), washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **5c** and **7c** was purified by column chromatography over silica gel.

(e).



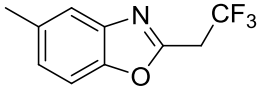
The solution of *N*-(2-amino-4-bromophenyl)-3,3,3-trifluoropropanethioamide (**7c**) (10 mg, 0.030 mmol), in 1.5 mL $CDCl_3$ was added into a NMR tube. A ^{19}F-NMR spectrum was acquired. The tube was kept at r.t. for 72 hours, a second ^{19}F-NMR spectrum was acquired, and the yield of product **5c** was determined to be 40%. The solution was analyzed by GC-MS.

Data for compounds



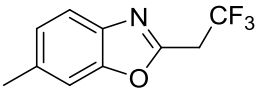
2-(2,2,2-Trifluoroethyl)benzoxazole (3a)

Purification by column chromatography (silica gel, *n*-pentane) gave final product **3a** as a light yellow liquid in 70% yield (42 mg). R_f (*n*-pentane) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.36 (m, 2H), 3.85 (q, *J* = 9.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 9.8 Hz，3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (q, *J* = 4.1 Hz), 151.1 (s), 140.8 (s), 125.8 (s), 124.8 (s), 123.7 (q, *J* = 278.6 Hz), 120.4 (s), 110.8 (s), 34.7 (q, *J* = 32.9 Hz). IR (ATR): ν 2248, 1616, 1498, 1454, 1261, 1153, 813, 728, 497, 458, 428 cm^{-1}. GC-MS m/z 200 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_7NOF_3$ $[M+H]^+$: 202.0474; found: 202.0472.



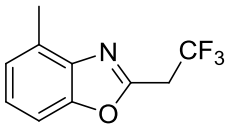
5-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3b)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product **3b** as a brownish yellow liquid in 65% yield (42 mg). R_f (*n*-pentane/ethyl acetate = 25:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 3.82 (q, *J* = 9.8 Hz, 2H), 2.50 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (q, *J* = 4.0 Hz), 149.4 (s), 141.0 (s), 134.7 (s), 126.9 (s), 123.7 (q, *J* = 277.5 Hz), 120.2 (s), 110.2 (s), 34.7 (q, *J* = 32.9 Hz), 21.4 (s). IR (ATR): ν 2927, 1617, 1578, 1542, 1500, 1484, 1419, 1368, 1334, 1259, 1244, 1147, 1094, 800, 594 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3NO$ $[M+H]^+$: 216.0631; found: 216.0627.



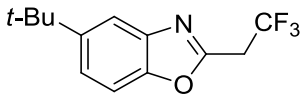
6-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3c)

Purification by column chromatography (silica gel, *n*-pentane) gave final product **3c** as a light yellow liquid in 66% yield (43 mg). R_f (*n*-pentane) = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.38 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 3.81 (q, *J* = 9.8 Hz, 2H), 2.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (q, *J* = 4.2 Hz), 151.5 (s), 138.7 (s), 136.3 (s), 126.1 (s), 123.8 (q, *J* = 277.6 Hz), 119.7 (s), 110.9 (s), 34.7 (q, *J* = 32.9 Hz), 21.8 (s). IR (ATR): ν 3252, 2252, 1593, 1498, 1270, 1151, 813, 688, 421 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3NO$ $[M+H]^+$: 216.0631; found: 216.0628.



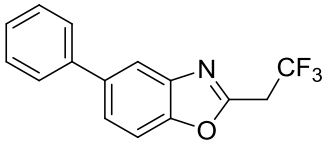
4-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3d)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3d** as a brown solid in 83% yield (54 mg). M.p. 38.4–40.1 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.82. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 3.84 (q, *J* = 9.8 Hz, 2H), 2.65 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5 (q, *J* = 4.1 Hz), 151.0 (s), 140.1 (s), 130.9 (s), 125.4 (s), 125.3 (s), 123.8 (q, *J* = 277.6 Hz), 108.1 (s), 34.7 (q, *J* = 33.0 Hz), 16.4 (s). IR (ATR): ν 3328, 2973, 2881, 1379, 1274, 1087, 1046, 880, 807, 609, 474, 421 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3NO$ $[M+H]^+$: 216.0631; found: 216.0628.



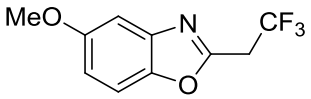
5-(*tert*-Butyl)-2-(2,2,2-trifluoroethyl)benzoxazole (3e)

Purification by column chromatography (silica gel, *n*-pentane) gave final product **3e** as a light yellow liquid in 57% yield (44 mg). R_f (*n*-pentane) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.55 – 7.42 (m, 2H), 3.83 (q, *J* = 9.8 Hz, 2H), 1.40 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4 (q, *J* = 4.1 Hz), 149.2 (s), 148.5 (s), 140.7 (s), 123.8 (q, *J* = 277.5 Hz), 123.6 (s), 116.8 (s), 110.0 (s), 35.0 (s), 34.7 (q, *J* = 32.9 Hz), 31.7 (s). IR (ATR): ν 2963, 1670, 1579, 1482, 1425, 1365, 1259, 1245, 1146, 1124, 1092, 963, 863, 810, 623 cm^{-1}. GC-MS m/z 256 (M^+). HRMS (ESI) m/z: calcd. for $C_{13}H_{15}F_3NO$ $[M+H]^+$: 258.1100; found: 258.1096.



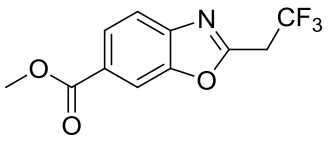
5-Phenyl-2-(2,2,2-trifluoroethyl)benzoxazole (3f)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3f** as a light yellow solid in 50% yield (42 mg). M.p. 47.6–49.3 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 – 7.57 (m, 4H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 1H), 3.87 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (q, *J* = 4.3 Hz), 150.7 (s), 141.5 (s), 140.8 (s), 138.9 (s), 128.9 (s), 127.5 (s), 127.4 (s), 125.4 (s), 123.7 (q, *J* = 277.5 Hz), 118.8 (s), 110.8 (s), 34.7 (q, *J* = 32.9 Hz). IR (ATR): ν 2928, 1620, 1577, 1468, 1452, 1420, 1367, 1259, 1201, 1148, 960, 925, 894, 859, 839, 817, 761, 698, 649, 632, 520 cm^{-1}. GC-MS m/z 276 (M^+). HRMS (ESI) m/z: calcd. for $C_{15}H_{11}F_3NO$ $[M+H]^+$: 278.0787; found: 278.0786.



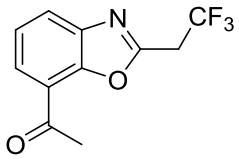
5-Methoxy-2-(2,2,2-trifluoroethyl)benzoxazole (3g)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product **3g** as a brown solid in 71% yield (49 mg). M.p. 33.2–34.5 ℃. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.87 (s, 3H), 3.81 (q, *J* = 9.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (s), 157.0 (q, *J* = 4.1 Hz), 145.8 (s), 141.6 (s), 123.7 (q, *J* = 277.5 Hz), 114.6 (s), 111.0 (s), 103.0 (s), 56.0 (s), 34.7 (q, *J* = 32.9 Hz). IR (ATR): ν 2943, 1614, 1577, 1533, 1483, 1439, 1369, 1343, 1260, 1243, 1148, 1093, 1026, 806, 640 cm^{-1}. GC-MS m/z 230 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3NO_2$ $[M+H]^+$: 232.0580; found: 232.0576.



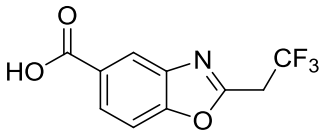
Methyl 2-(2,2,2-trifluoroethyl)benzoxazole-6-carboxylate (3h)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3h** as a light yellow solid in 68% yield (53 mg). M.p. 63.6–65.8 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.88 (q, *J* = 9.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (t, *J* = 9.7 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (s), 159.0 (q, *J* = 4.1 Hz), 150.8 (s), 144.5 (s), 128.0 (s), 126.5 (s), 123.5 (q, *J* = 277.6 Hz), 120.1 (s), 112.6 (s), 52.5 (s), 34.8 (q, *J* = 33.1 Hz). IR (ATR): ν 2955, 1718, 1610, 1574, 1497, 1436, 1319, 1284, 1261, 1240, 1220, 1148, 1077, 981, 513, 423 cm^{-1}. GC-MS m/z 258 (M^+). HRMS (ESI) m/z: calcd. for $C_{11}H_9F_3NO_3$ $[M+H]^+$: 260.0529; found: 260.0524.



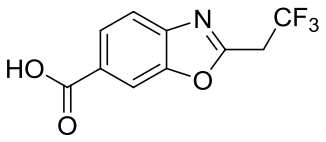
1-(2-(2,2,2-Trifluoroethyl)benzoxazol-7-yl)ethanone (3i)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3i** as a light yellow solid in 63% yield (47 mg). M.p. 61.7–63.6 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 1H), 3.94 (q, *J* = 9.6 Hz, 2H), 2.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5 (s), 156.9 (q, *J* = 4.1 Hz), 149.6 (s), 142.1 (s), 126.5 (s), 125.5 (s), 124.9 (s), 123.6 (q, *J* = 281.1 Hz), 122.1 (s), 34.7 (q, *J* = 33.2 Hz), 30.2 (s). IR (ATR): ν 2254, 1618, 1498, 1279, 1155, 814, 543, 504, 478, 443, 421 cm^{-1}. GC-MS m/z 242 (M^+). HRMS (ESI) m/z: calcd. for $C_{11}H_9F_3NO_2$ $[M+H]^+$: 244.0580; found: 244.0576.



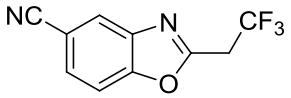
2-(2,2,2-Trifluoroethyl)benzoxazole-5-carboxylic acid (3j)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 2:1) gave final product **3j** as a light yellow solid in 62% yield (46 mg). M.p. 148.1–150.2 ℃. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.32. ^{1}H NMR (400 MHz, CD_3OD) δ 8.40 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 4.13 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -65.4 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, CD_3OD) δ 167.6 (s), 158.9 (q, *J* = 4.5 Hz), 153.8 (s), 140.7 (s), 128.0 (s), 127.5 (s), 124.1 (q, *J* = 276.2 Hz), 121.6 (s), 110.4 (s), 33.4 (q, *J* = 32.8 Hz). IR (ATR): ν 3371, 2489, 2077, 1691, 1626, 1578, 1439, 1367, 1261, 1237, 1171, 1114, 1086, 967, 900, 836, 774 cm^{-1}. GC-MS m/z 244 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_7F_3NO_3$ $[M+H]^+$: 246.0373; found: 246.0372.



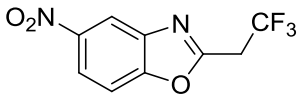
2-(2,2,2-Trifluoroethyl)benzoxazole-6-carboxylic acid (3k)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **3k** as a light yellow solid in 58% yield (43 mg). M.p. 145.0–147.0 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.30. ^{1}H NMR (400 MHz, CD_3OD) δ 8.28 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 4.14 (q, *J* = 10.1 Hz, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -65.3 (t, *J* = 10.2 Hz, 3F). ^{13}C NMR (101 MHz, CD_3OD) δ 167.5 (s), 160.1 (q, *J* = 4.2 Hz), 150.7 (s), 144.2 (s), 128.6 (s), 126.3 (s), 124.1 (q, *J* = 276.4 Hz), 119.3 (s), 112.1 (s), 33.5 (q, *J* = 32.7 Hz). IR (ATR): ν 3372, 2924, 2495, 2077, 1679, 1609, 1572, 1435, 1360, 1274, 1238, 1189, 1115, 1044, 1021, 971, 895, 848, 778, 750, 551, 430 cm^{-1}. GC-MS m/z 244 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_7F_3NO_3$ $[M+H]^+$: 246.0373; found: 246.0372.



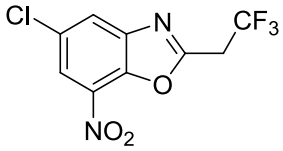
2-(2,2,2-Trifluoroethyl)benzoxazole-5-carbonitrile (3l)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3l** as a light yellow solid in 72% yield (49 mg). M.p. 51.2–52.8 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.77 – 7.61 (m, 2H), 3.89 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (q, *J* = 4.1 Hz), 153.3 (s), 141.2 (s), 129.8 (s), 125.2 (s), 123.4 (q, *J* = 277.7 Hz), 118.3 (s), 112.3 (s), 109.1 (s), 34.6 (q, *J* = 33.3 Hz). IR (ATR): ν 2960, 2231, 1626, 1577, 1471, 1417, 1368, 1336, 1258, 1242, 1183, 1095, 963, 861, 818, 741, 618, 527, 487, 430 cm^{-1}. GC-MS m/z 225 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_6F_3N_2O$ $[M+H]^+$: 227.0427; found: 227.0425.



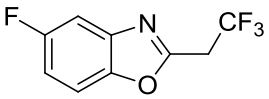
5-Nitro-2-(2,2,2-trifluoroethyl)benzoxazole (3m)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3m** as a brownish yellow solid in 42% yield (31 mg). M.p. 69.3-70.8 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 3.92 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (q, *J* = 4.1 Hz), 154.5 (s), 145.6 (s), 141.2 (s), 123.4 (q, *J* = 277.9 Hz), 121.9 (s), 117.0 (s), 111.2 (s), 34.8 (q, *J* = 33.4 Hz). IR (ATR): ν 3110, 1623, 1578, 1533, 1500, 1438, 1348, 1260, 1240, 1149, 1096, 1063, 963, 829, 737, 690 cm^{-1}. GC-MS m/z 245 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3N_2O_3$ $[M+H]^+$: 247.0325; found: 247.0320.



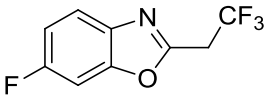
5-Chloro-7-nitro-2-(2,2,2-trifluoroethyl)benzoxazole (3n)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3n** as a brownish yellow solid in 38% yield (32 mg). M.p. 68.6–70.0 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.10 (s, 1H), 3.98 (q, *J* = 9.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (t, *J* = 9.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (q, *J* = 4.1 Hz), 144.9 (s), 142.6 (s), 133.2 (s), 130.7 (s), 127.0 (s), 123.2 (q, *J* = 277.7 Hz), 122.1 (s), 34.6 (q, *J* = 33.6 Hz). IR (ATR): ν 3094, 1612, 1540, 1519, 1452, 1415, 1351, 1327, 1299, 1252, 1206, 1153, 1023, 949, 910, 877, 851, 762, 629, 588 cm^{-1}. GC-MS m/z 279 (M^+). HRMS (EI) m/z: calcd. for $C_9H_4F_3N_2O_3Cl$: 279.9863; found: 279.9868.



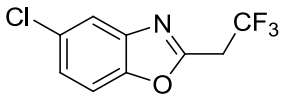
5-Fluoro-2-(2,2,2-trifluoroethyl)benzoxazole (3o)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product **3o** as a light yellow liquid in 78% yield (51 mg). R_f (*n*-pentane/ethyl acetate = 25:1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 9.0 Hz, 1H), 3.84 (q, *J* = 9.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 9.7 Hz, 3F), -117.1 (td, *J* = 8.7, 4.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 241.6 Hz), 158.1 (q, *J* = 4.0 Hz), 147.5 (d, *J* = 1.2 Hz), 141.6 (d, *J* = 13.2 Hz), 123.6 (q, *J* = 277.5 Hz), 113.7 (d, *J* = 26.4 Hz), 111.2 (d, *J* = 10.0 Hz), 106.9 (d, *J* = 25.8 Hz), 34.7 (q, *J* = 33.2 Hz). IR (ATR): ν 3027, 2161, 1578, 1479, 1261, 1244, 1151, 1133, 1095, 970, 857, 807, 635, 607, 536, 434 cm^{-1}. GC-MS m/z 218 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_4NO$ $[M+H]^+$: 220.0380; found: 220.0377.



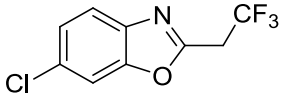
6-Fluoro-2-(2,2,2-trifluoroethyl)benzoxazole (3p)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product **3p** as a light yellow liquid in 67% yield (44 mg). R_f (*n*-pentane/ethyl acetate = 25:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.7, 4.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 9.1 Hz, 1H), 3.83 (q, *J* = 9.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9 (t, *J* = 9.7 Hz, 3F), -114.0 (td, *J* = 8.7, 5.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 245.4 Hz), 156.9 (q, *J* = 4.1 Hz), 151.1 (d, *J* = 14.7 Hz), 137.1 (d, *J* = 1.6 Hz), 123.6 (q, *J* = 277.6 Hz), 120.8 (d, *J* = 10.2 Hz), 113.0 (d, *J* = 24.8 Hz), 98.9 (d, *J* = 28.3 Hz), 34.6 (q, *J* = 33.1 Hz). IR (ATR): ν 3350, 2963, 1723, 1622, 1587, 1485, 1440, 1369, 1341, 1277, 1258, 1125, 1101, 958, 839, 629 cm^{-1}. GC-MS m/z 218 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_4NO$ $[M+H]^+$: 220.0380; found: 220.0377.



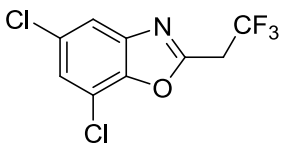
5-Chloro-2-(2,2,2-trifluoroethyl)benzoxazole (3q)

Purification by column chromatography (silica gel, *n*-pentanep) gave final product **3q** as a brown solid in 85% yield (60 mg). M.p. 32.7–34.1 ℃. R_f (*n*-pentane) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 3.83 (q, *J* = 9.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.7 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (q, *J* = 4.1 Hz), 149.7 (s), 141.9 (s), 130.4 (s), 126.2 (s), 123.6 (q, *J* = 277.5 Hz), 120.4 (s), 111.6 (s), 34.6 (q, *J* = 33.1 Hz). IR (ATR): ν 2958, 1605, 1573, 1453, 1419, 1365, 1331, 1299, 1243, 1145, 1118, 1054, 800, 732, 631, 424 cm^{-1}. GC-MS m/z 234 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3NOCl$ $[M+H]^+$: 236.0085; found: 236.0081.



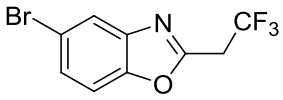
6-Chloro-2-(2,2,2-trifluoroethyl)benzoxazole (3r)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3r** as a light yellow solid in 75% yield (52 mg). M.p. 41.7–42.9 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.61 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 3.83 (q, *J* = 9.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.7 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (q, *J* = 3.5 Hz), 151.3 (s), 139.6 (s), 131.7 (s), 125.7 (s), 123.5 (q, *J* = 275.7 Hz), 121.0 (s), 111.5 (s), 34.6 (q, *J* = 33.2 Hz). IR (ATR): ν 3352, 2966, 1615, 1578, 1497, 1464, 1429, 1367, 1261, 1243, 1148, 1095, 1053, 928, 814, 688 cm^{-1}. GC-MS m/z 234 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3NOCl$ $[M+H]^+$: 236.0085; found: 236.0081.



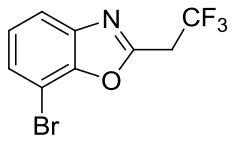
5,7-Dichloro-2-(2,2,2-trifluoroethyl)benzoxazole (3s)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3s** as a light yellow solid in 52% yield (42 mg). M.p. 103.4–105.1 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.45 (s, 1H), 3.87 (q, *J* = 9.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (t, *J* = 9.5 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (q, *J* = 4.1 Hz), 146.6 (s), 142.6 (s), 130.8 (s), 126.4 (s), 123.4 (q, *J* = 277.8 Hz), 119.1 (s), 116.8 (s), 34.6 (q, *J* = 33.2 Hz). IR (ATR): ν 2962, 1693, 1591, 1574, 1528, 1459, 1422, 1258, 1153, 1074, 992, 948, 853, 816, 632 cm^{-1}. GC-MS m/z 268 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_5F_3NOCl_2$ $[M+H]^+$: 269.9695; found: 269.9691.



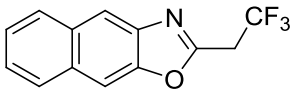
5-Bromo-2-(2,2,2-trifluoroethyl)benzoxazole (3t)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3t** as a light yellow solid in 39% yield (33 mg). M.p. 54.2–56.1 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 3.84 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (q, *J* = 3.9 Hz), 150.1 (s), 142.4 (s), 129.0 (s), 123.6 (q, *J* = 277.6 Hz), 123.5 (s), 117.7 (s), 112.1 (s), 34.7 (q, *J* = 33.1 Hz). IR (ATR): ν 2928, 2101, 2062, 2028, 1997, 1964, 1570, 1449, 1421, 1368, 1329, 1259, 1150, 1096, 1044, 961, 921, 890, 866, 840, 803, 683, 631, 588, 465, 426 cm^{-1}. GC-MS m/z 278 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3NOBr$ $[M+H]^+$: 279.9579; found: 279.9583.



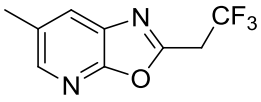
7-Bromo-2-(2,2,2-trifluoroethyl)benzoxazole (3u)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3u** as a light yellow solid in 68% yield (57 mg). M.p. 318.9–320.0 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 3.88 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, *J* = 3.9 Hz), 149.4 (s), 141.5 (s), 129.0 (s), 126.1 (s), 123.5 (q, *J* = 277.6 Hz), 119.5 (s), 102.7 (s), 34.6 (q, *J* = 33.2 Hz). IR (ATR): ν 3328, 2973, 2881, 1593, 1379, 1274, 1087, 1046, 880, 807, 609, 474, 421 cm^{-1}. GC-MS m/z 278 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3NOBr$ $[M+H]^+$: 279.9579; found: 279.9576.



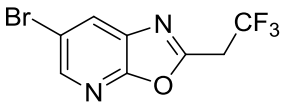
2-(2,2,2-Trifluoroethyl)naphtho[2,3-*d*]oxazole (3v)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3v** as a light yellow solid in 36% yield (27 mg). M.p. 116.4–117.3 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.77. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.65 – 7.46 (m, 2H), 3.90 (q, *J* = 9.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (t, *J* = 9.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (q, *J* = 3.7 Hz), 149.7 (s), 140.5 (s), 131.9 (s), 131.4 (s), 128.7 (s), 128.0 (s), 126.0 (s), 125.0 (s), 124.0 (q, *J* = 347.7 Hz), 118.1 (s), 106.8 (s), 34.9 (q, *J* = 33.0 Hz). IR (ATR): ν 2940, 2288, 2165, 2050, 1982, 1617, 1579, 1505 ,1443, 1421, 1367, 1308, 1270, 1257, 1241, 1202, 1162, 1142, 1089, 956, 920, 898, 875, 858, 843, 749, 623, 473 cm^{-1}. GC-MS m/z 250 (M^+). HRMS (ESI) m/z: calcd. for $C_{13}H_9F_3NO$ $[M+H]^+$: 252.0631; found: 252.0631.



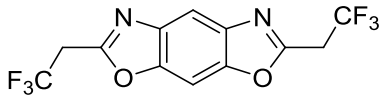
6-Methyl-2-(2,2,2-trifluoroethyl)oxazolo[5,4-b]pyridine (3w)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3w** as a light yellow liquid in 39% yield (25 mg). R_f (*n*-pentane/ethyl acetate = 10:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.90 (s, 1H), 3.85 (q, *J* = 9.5 Hz, 2H), 2.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (t, *J* = 9.5 Hz,3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (s), 156.9 (q, *J* = 4.5 Hz), 146.0 (s), 132.4 (s), 131.3 (s), 129.2 (s), 123.5 (q, *J* = 277.6 Hz), 35.0 (q, *J* = 33.1 Hz), 18.4 (s). IR (ATR): ν 2931, 2283, 2202, 2160, 2049, 2034, 1996, 1979, 1620, 1570, 1419, 1366, 1264, 1231, 1151, 946, 880, 842, 779, 635, 596, 460, 445 cm^{-1}. GC-MS m/z 215 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_8F_3N_2O$ $[M+H]^+$: 217.0583; found: 217.0584.



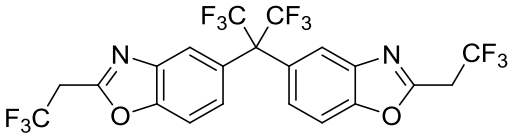
6-Bromo-2-(2,2,2-trifluoroethyl)oxazolo[5,4-*b*]pyridine (3x)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **3x** as a light yellow solid in 28% yield (23 mg). M.p. 90.7–91.2 ℃. R_f (*n*-pentane/ethyl acetate = 20:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.25 (s, 1H), 3.88 (q, *J* = 9.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (t, *J* = 9.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (q, *J* = 4.7 Hz), 146.6 (s), 133.9 (s), 131.7 (s), 123.3 (q, *J* = 277.9 Hz), 116.8 (s), 107.4 (s), 35.0 (q, *J* = 32.2 Hz). GC-MS m/z 279 (M^+). HRMS (ESI) m/z: calcd. for $C_8H_5F_3N_2OBr$ $[M+H]^+$: 280.9532; found: 280.9533.



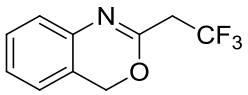
2,6-Bis(2,2,2-trifluoroethyl)benzo[1,2-*d*:5,4-*d'*]bis(oxazole) (3y)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3y** as a light yellow solid in 61% yield (59 mg). M.p. 87.3–88.6 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.77 (s, 1H), 3.88 (q, *J* = 9.6 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 9.6 Hz, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (q, *J* = 5.1 Hz), 149.3 (s), 138.7 (s), 123.6 (q, *J* = 277.7 Hz), 111.1 (s), 93.8 (s), 34.8 (q, *J* = 33.2 Hz). IR (ATR): ν 2926, 1621, 1590, 1431, 1375, 1255, 1106, 954, 877, 837, 673, 627, 529 cm^{-1}. GC-MS m/z 323 (M^+). HRMS (ESI) m/z: calcd. for $C_{12}H_7F_6N_2O_2$ $[M+H]^+$: 325.0406; found: 325.0405.



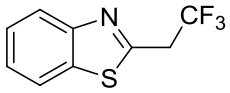
5,5'-(Perfluoropropane-2,2-diyl)bis(2-(2,2,2-trifluoroethyl)benzoxazole) (3z)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **3z** as a light yellow solid in 70% yield (116 mg). M.p. 67.8–69.2 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 3.86 (q, *J* = 9.6 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (s, 6F), -63.7 (t, *J* = 9.6 Hz, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (q, *J* = 4.0 Hz), 151.1 (s), 140.9 (s), 130.5 (s), 128.0 (s), 124.1 (q, *J* = 287.4 Hz), 122.9 (s), 120.8 (q, *J* = 277.6 Hz), 110.7 (s), 65.4 – 64.1 (m), 34.6 (q, *J* = 33.2 Hz). IR (ATR): ν 2960, 1624, 1580, 1482, 1421, 1368, 1337, 1244, 1203, 1187, 1126, 964, 858, 811, 679, 637, 535, 484, 435 cm^{-1}. GC-MS m/z 479 (M^+). HRMS (ESI) m/z: calcd. for $C_{21}H_{11}F_{12}N_2O_2$ $[M+H]^+$: 551.0623; found: 551.0630.



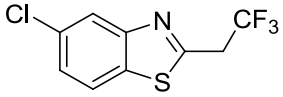
2-(2,2,2-Trifluoroethyl)-4*H*-benzo[*d*][1,3]oxazine (3aa)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **3aa** as a brownish yellow solid in 53% yield (34 mg). M.p. 107.0-108.5 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.55. ^{1}H NMR (400 MHz, CD_3OD) δ 7.59 (d, *J* = 7.1 Hz, 1H), 7.45 – 7.27 (m, 3H), 4.62 (s, 2H), 3.79 (q, *J* = 10.2 Hz, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -65.6 (t, *J* = 10.2 Hz, 3F). ^{13}C NMR (101 MHz, CD_3OD) δ 192.0 (q, *J* = 3.4 Hz), 137.4 (s), 136.6 (s), 127.7 (s), 127.5 (s), 127.4 (s), 126.2 (s), 124.2 (q, *J* = 277.4 Hz), 60.1 (s), 49.5 (q, *J* = 28.6 Hz). IR (ATR): ν 3326, 2483, 2084, 1657, 1493, 1432, 1344, 1255, 1189, 1140, 1043, 754 cm^{-1}. GC-MS m/z 214 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_9F_3NO$ $[M+H]^+$: 216.0631; found: 216.0631.



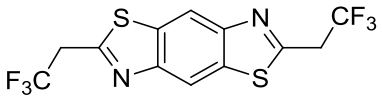
2-(2,2,2-Trifluoroethyl)benzo[*d*]thiazole (4a)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 20:1) gave final product **4a** as a light yellow liquid in 80% yield (52 mg). R_f (*n*-pentane/ethyl acetate = 20:1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.99 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.5 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (q, *J* = 3.4 Hz), 152.7 (s), 135.7 (s), 126.5 (s), 125.9 (s), 124.2 (q, *J* = 277.5 Hz), 123.5 (s), 121.6 (s), 39.1 (q, *J* = 31.7 Hz). IR (ATR): ν 2930, 1518, 1458, 1434, 1356, 1314, 1285, 1251, 1180, 1141, 1079, 1013, 929, 866, 836, 760, 555, 430 cm^{-1}. GC-MS m/z 216 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_7F_3NS$ $[M+H]^+$: 218.0246; found: 218.0246.



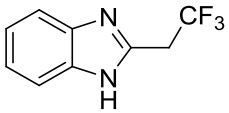
5-Chloro-2-(2,2,2-trifluoroethyl)benzo[*d*]thiazole (4b)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **4b** as a brownish yellow solid in 85% yield (64 mg). M.p. 75.6–77.0 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 3.97 (q, *J* = 9.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (q, *J* = 3.5 Hz), 153.6 (s), 134.0 (s), 132.6 (s), 126.4 (s), 124.1 (q, *J* = 277.6 Hz), 123.3 (s), 122.3 (s), 39.1 (q, *J* = 31.7 Hz). IR (ATR): ν 3052, 1595, 1562, 1509, 1435, 1357, 1282, 1250, 1177, 1144, 1069, 941, 838, 806, 688, 613, 581, 560, 542, 433 cm^{-1}. GC-MS m/z 250 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_6F_3NSCl$ $[M+H]^+$: 251.9856; found: 251.9857.



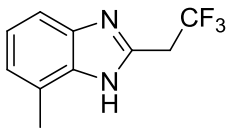
2,6-Bis(2,2,2-trifluoroethyl)benzo[1,2-*d*:4,5-*d'*]bis(thiazole) (4c)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 10:1) gave final product **4c** as a light yellow solid in 87% yield (93 mg). M.p. 169.6–170.8 ℃. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 2H), 4.03 (q, *J* = 9.9 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.2 (t, *J* = 9.9 Hz, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (q, *J* = 3.3 Hz), 151.0 (s), 135.1 (s), 124.1 (q, *J* = 277.6 Hz), 116.0 (s), 39.4 (q, *J* = 31.9 Hz). IR (ATR): ν 3070, 2924, 2257, 1597, 1528, 1455, 1420, 1376, 1278, 1249, 1161, 1119, 1086, 1049, 923, 883, 835, 685, 639 cm^{-1}. GC-MS m/z 355 (M^+). HRMS (ESI) m/z: calcd. for $C_{12}H_7F_6N_2S_2$ $[M+H]^+$: 356.9949; found: 356.9948.



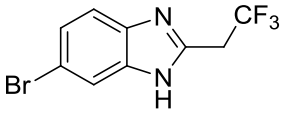
2-(2,2,2-Trifluoroethyl)-1*H*-benzo[*d*]imidazole (5a)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **5a** as a brownish yellow solid in 81% yield (49 mg). M.p. 173.9-175.4 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.40. ^{1}H NMR (400 MHz, CD_3OD) δ 7.59 (dd, *J* = 5.9, 3.0 Hz, 2H), 7.28 (dd, *J* = 5.9, 3.0 Hz, 2H), 3.89 (q, *J* = 10.4 Hz, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -66.1 (t, *J* = 10.4 Hz, 3F). ^{13}C NMR (101 MHz, CD_3OD) δ 144.0 (q, *J* = 3.9 Hz), 138.2 (s), 124.7 (q, *J* = 276.6 Hz), 122.7 (s), 114.6 (s), 33.7 (q, *J* = 31.8 Hz). IR (ATR): ν 3367, 2914, 2749, 2524, 2227, 1624, 1542, 1513, 1438, 1424, 1294, 1271, 1197, 1178, 1148, 1132, 1104, 1083, 1045, 1006, 980, 805, 744, 616, 434 cm^{-1}. GC-MS m/z 199 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_8F_3N_2$ $[M+H]^+$: 201.0634; found: 201.0609.



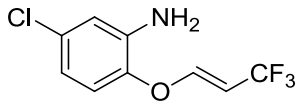
7-Methyl-2-(2,2,2-trifluoroethyl)-1*H*-benzo[*d*]imidazole (5b)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **5b** as a brown solid in 83% yield (53 mg). M.p. 264.2-266.4 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 3.96 (q, *J* = 10.0 Hz, 2H), 2.62 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7 (q, *J* = 4.2 Hz), 136.8 (s), 136.6 (s), 125.5 (s), 124.5 (s), 124.2 (q, *J* = 277.4 Hz), 124.1 (s), 112.3 (s), 34.2 (q, *J* = 32.4 Hz), 17.0 (s). IR (ATR): ν 2923, 2855, 1622, 1537, 1453, 1381, 1351, 1305, 1254, 1148, 1091, 1022, 914, 841, 785, 750, 631, 596, 517 cm^{-1}. GC-MS m/z 213 (M^+). HRMS (ESI) m/z: calcd. for $C_{10}H_{10}F_3N_2$ $[M+H]^+$: 215.0791; found: 215.0788.



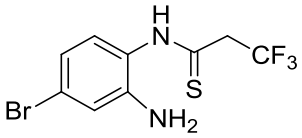
6-Bromo-2-(2,2,2-trifluoroethyl)-1*H*-benzo[*d*]imidazole (5c)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **5c** as a light brown solid in 79% yield (66 mg). M.p. 152.2–153.4 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.48. ^{1}H NMR (400 MHz, CD_3OD) δ 7.03 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.77 (q, *J* = 10.2 Hz, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -65.6 (t, *J* = 10.2 Hz, 3F). ^{13}C NMR (101 MHz, CD_3OD) δ 191.6 (q, *J* = 3.2 Hz), 144.5 (s), 128.4 (s), 124.2 (q, *J* = 277.2 Hz), 123.7 (s), 121.6 (s), 119.9 (s), 118.9 (s), 49.3 (q, *J* = 28.7 Hz). IR (ATR): ν 3881, 3703, 3596, 3536, 2685, 2604, 2559, 2396, 2291, 2171, 2109, 2066, 1971, 1929, 1886, 1719, 1055, 970, 922, 894, 726, 590, 555, 494, 454, 429 cm^{-1}. GC-MS m/z 277 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_7F_3N_2Br$ $[M+H]^+$: 278.9739; found: 278.9740.



5-Chloro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)aniline (6q)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 50:1) gave final product **6q** as a brownish yellow liquid in 63% yield (44 mg). R_f (*n*-pentane) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.5 Hz, 1H), 6.77 (s, 1H), 6.69 (t, *J* = 8.1 Hz, 2H), 5.07 (p, *J* = 7.6 Hz, 1H), 3.93 (br, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (d, *J* = 7.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 (q, *J* = 5.3 Hz), 142.6 (s), 138.6 (s), 130.6 (s), 122.8 (q, *J* = 269.3 Hz), 118.0 (s), 117.5 (s), 115.8 (s), 99.5 (q, *J* = 35.3 Hz). IR (ATR): ν 1676, 1619, 1499, 1419, 1265, 1199, 1154, 1123, 1039, 850, 813, 726, 449 cm^{-1}.GC-MS m/z 236 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_8ClF_3NO$ $[M+H]^+$: 238.0241; found: 238.0236.



***N*-(2-Amino-4-bromophenyl)-3,3,3-trifluoropropanethioamide (7c)**

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 5:1) gave final product **7c** as a light brown solid in 5% yield (5 mg). M.p. 145.0-146.8 ℃. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.06 – 6.91 (m, 2H), 3.80 (q, 10.1 Hz, 2H), NH_2 was not observed. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (t, *J* = 10.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8 (q, *J* = 3.1 Hz), 143.1 (s), 128.4 (s), 125.0 (s), 123.2 (q, *J* = 46.6 Hz), 122.3 (s), 122.0 (s), 120.3 (s), 50.9 (q, *J* = 28.8 Hz). IR (ATR): ν 3149, 2923, 1697, 1621, 1494, 1401, 1344, 1252, 1144, 896, 806, 756, 682, 624 cm^{-1}. GC-MS m/z 311 (M^+). HRMS (ESI) m/z: calcd. for $C_9H_9BrF_3N_2S$ $[M+H]^+$: 312.9616; found: 312.9615.

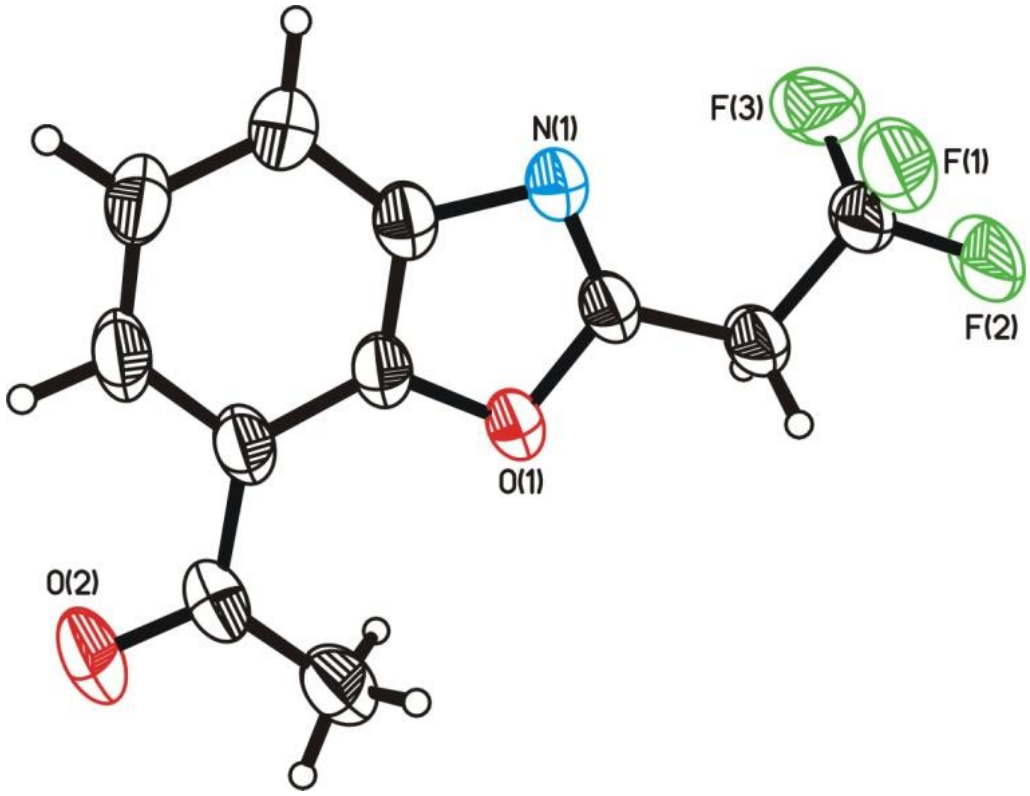
Crystal structure analyses

The suitable crystals of **3i** (CCDC 1921974) and **7c** (CCDC 1922077) 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.[1] Structure solution and refinement were carried out with the SHELXTL suite of programs.[1] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

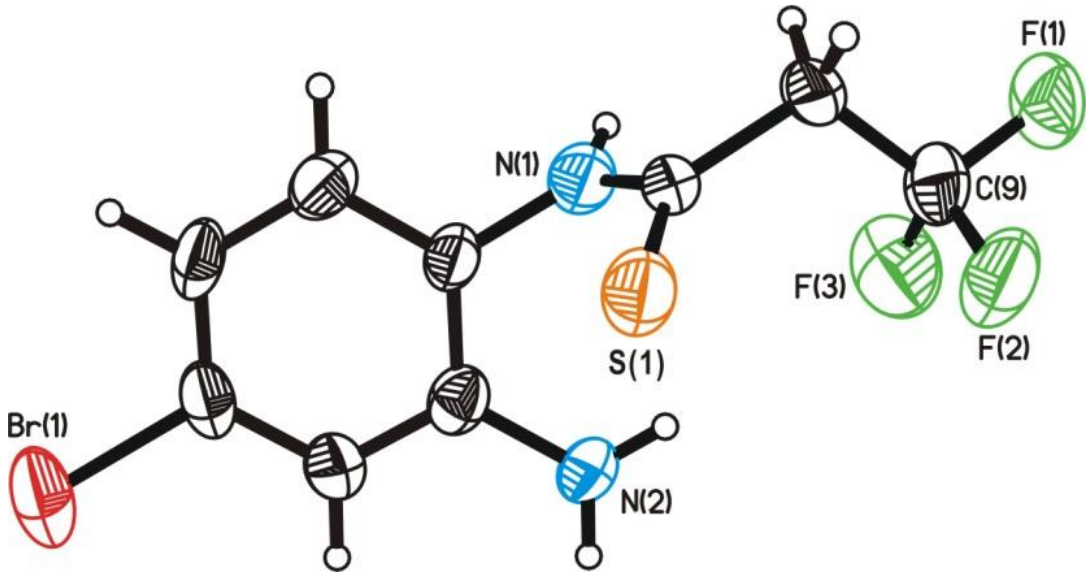
References:

1. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

ORTEP diagrams



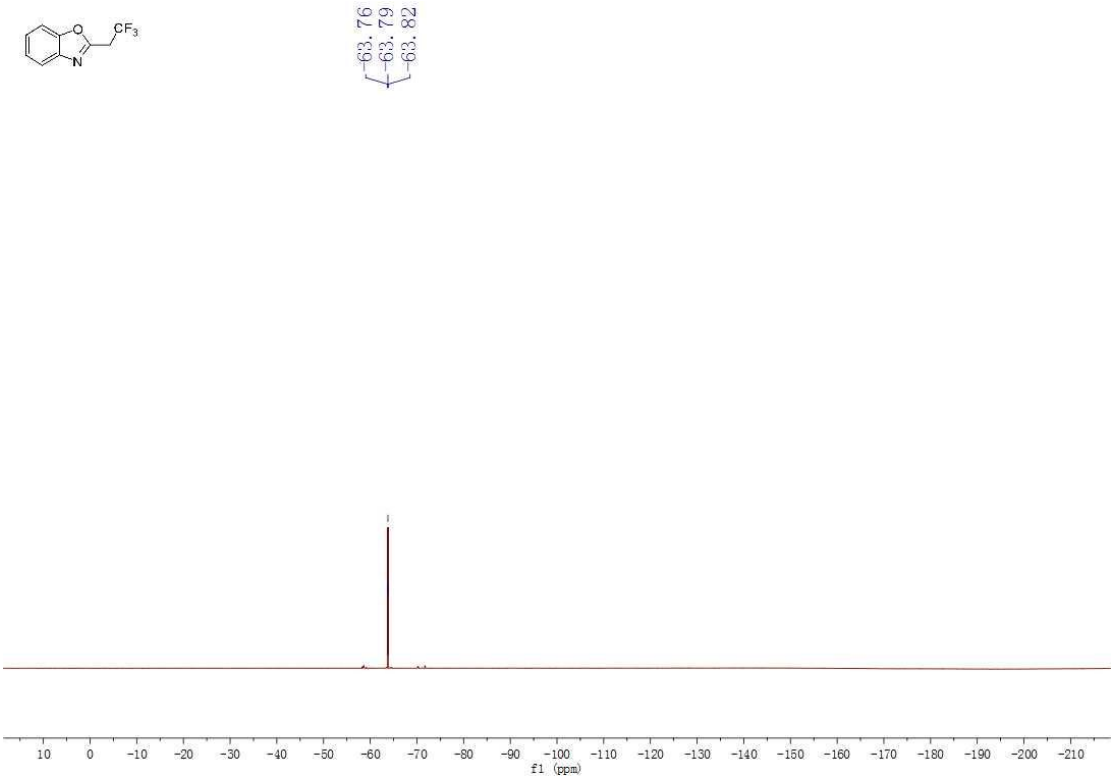
ORTEP diagram of compound 3i. Thermal ellipsoids are drawn at 40% probability



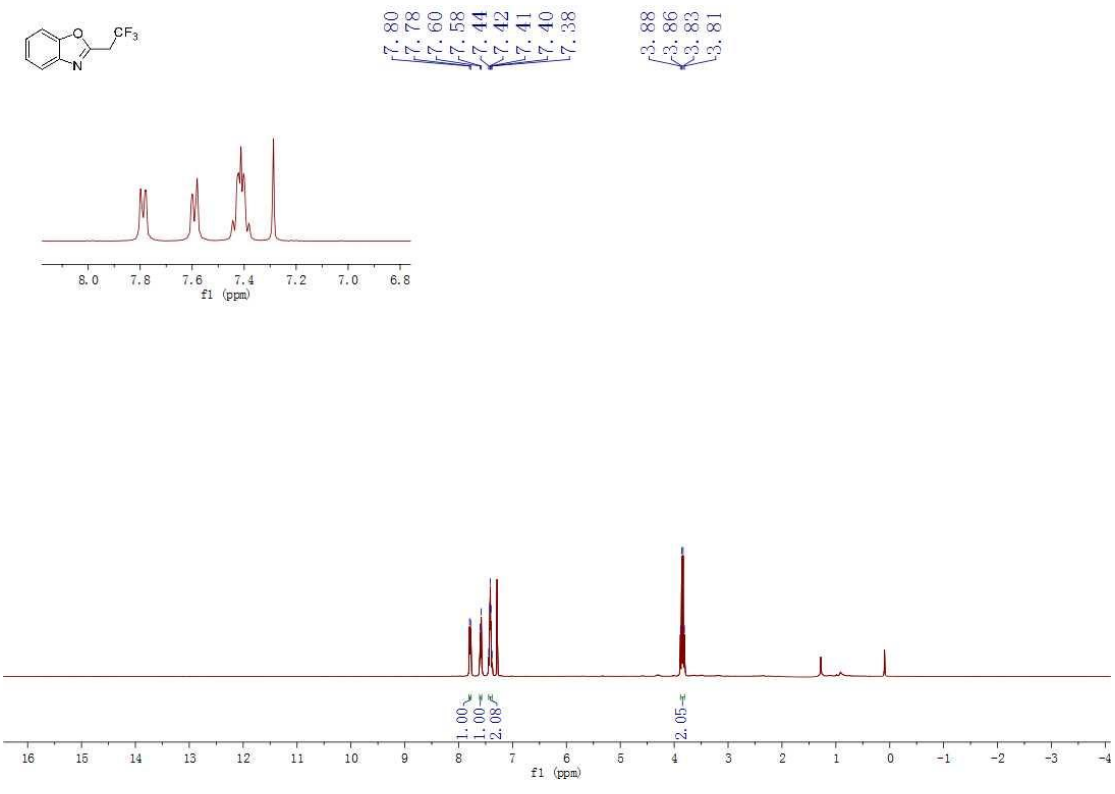
ORTEP diagram of compound 7c. Thermal ellipsoids are drawn at 40% probability

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

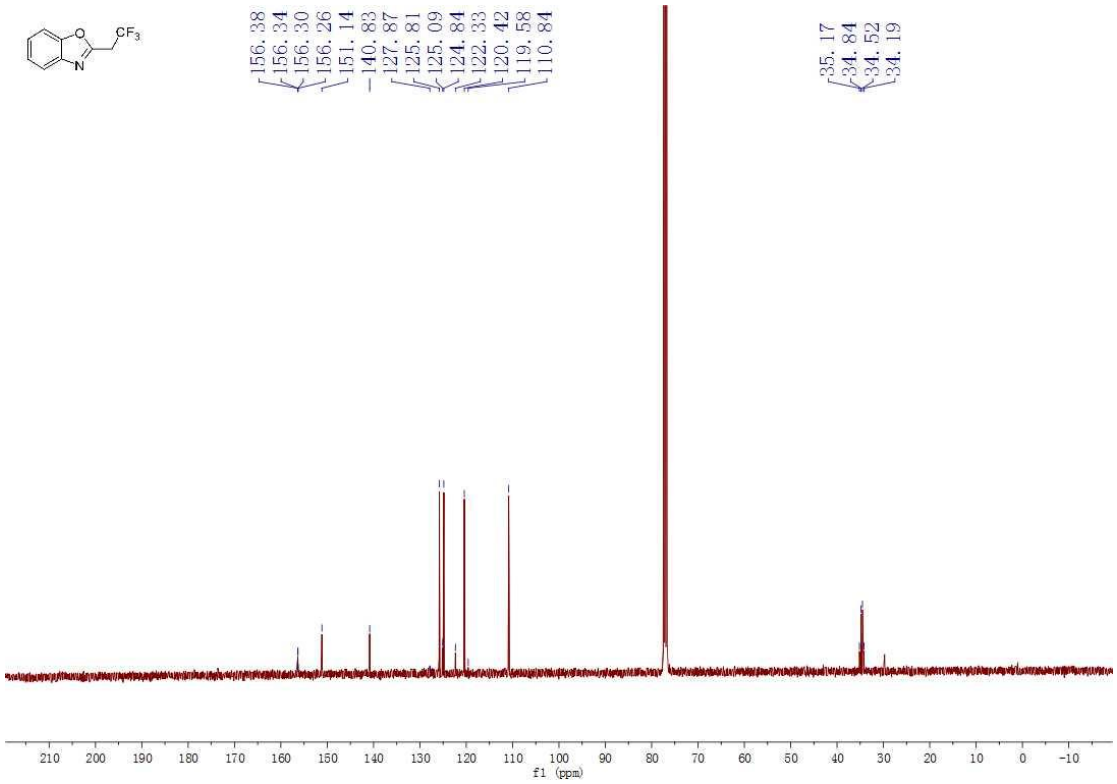
^{19}F NMR spectrum of **3a** in $CDCl_3$



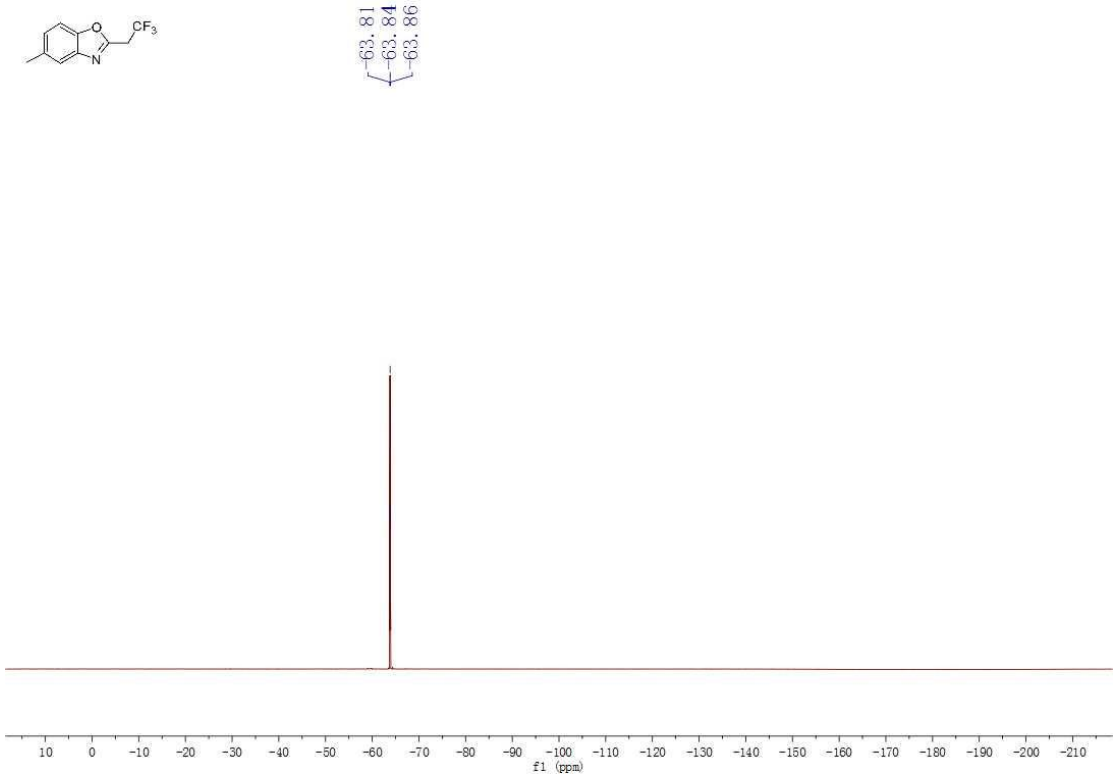
^{1}H NMR spectrum of **3a** in $CDCl_3$



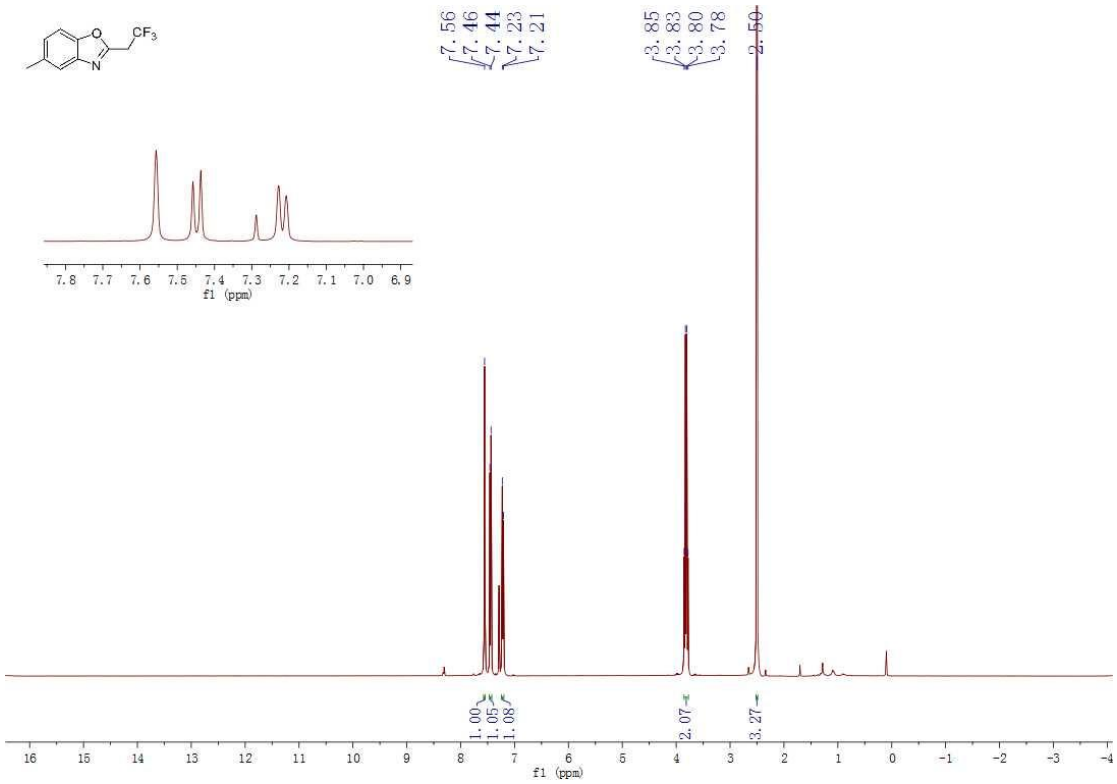
^{13}C NMR spectrum of **3a** in $CDCl_3$



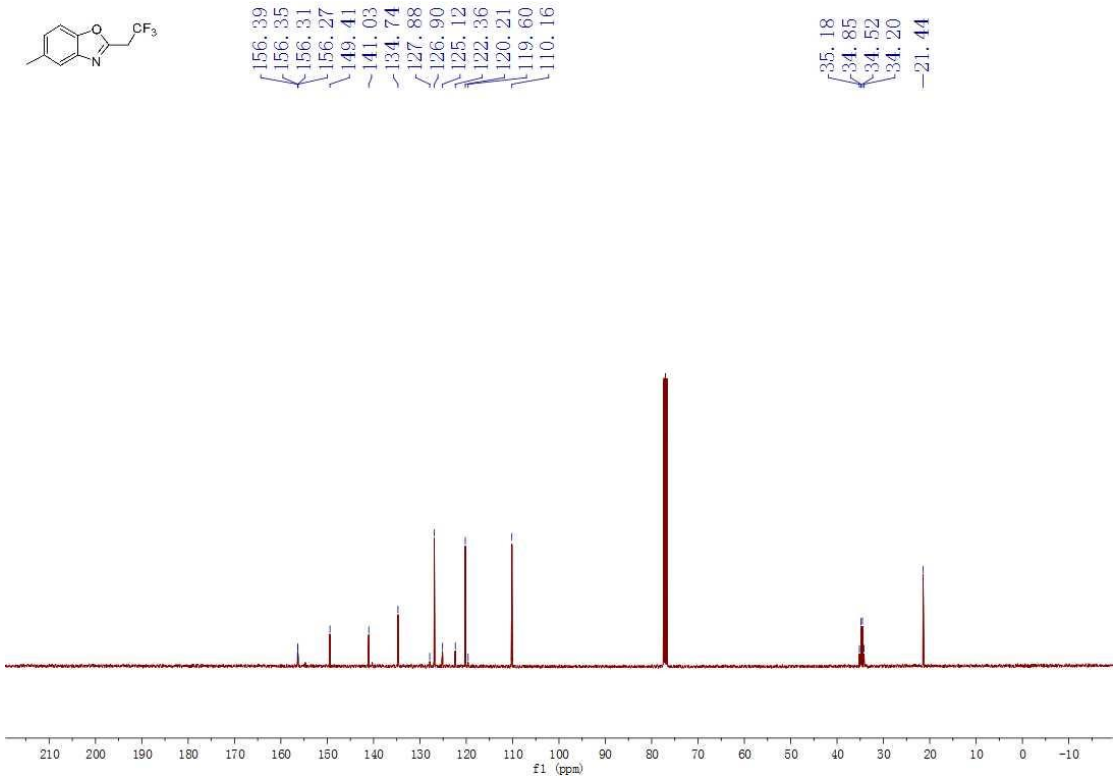
^{19}F NMR spectrum of **3b** in $CDCl_3$



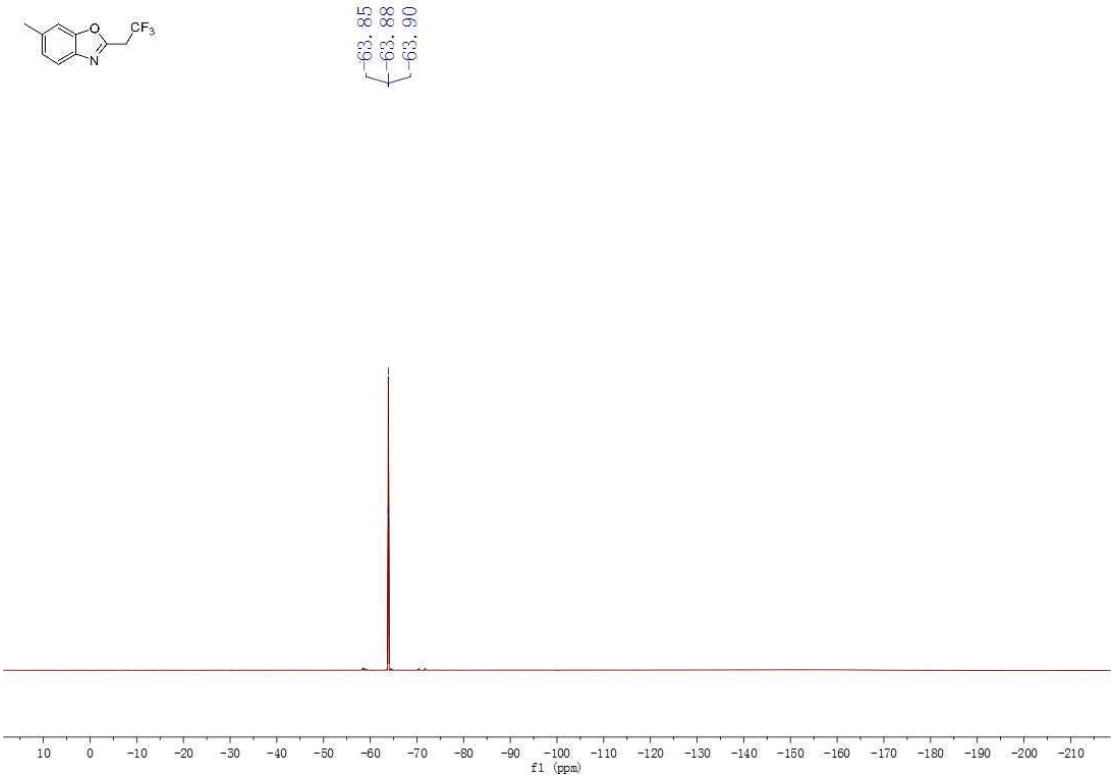
^{1}H NMR spectrum of **3b** in $CDCl_3$



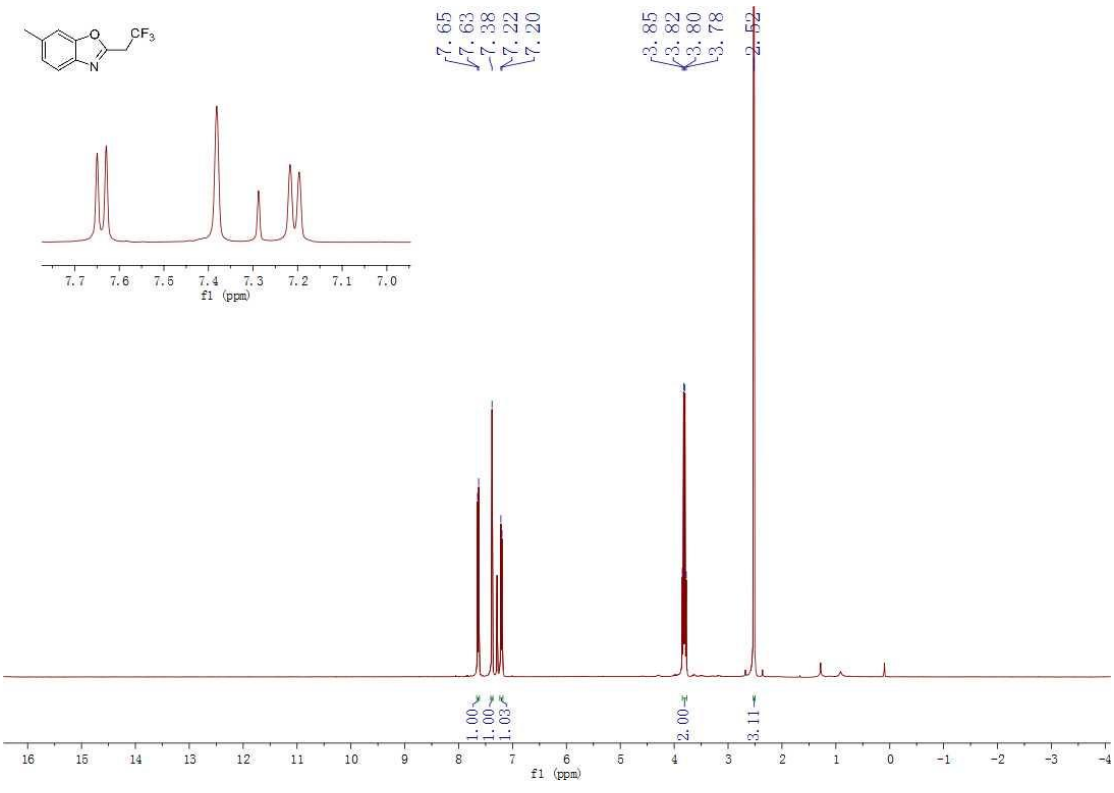
^{13}C NMR spectrum of **3b** in $CDCl_3$



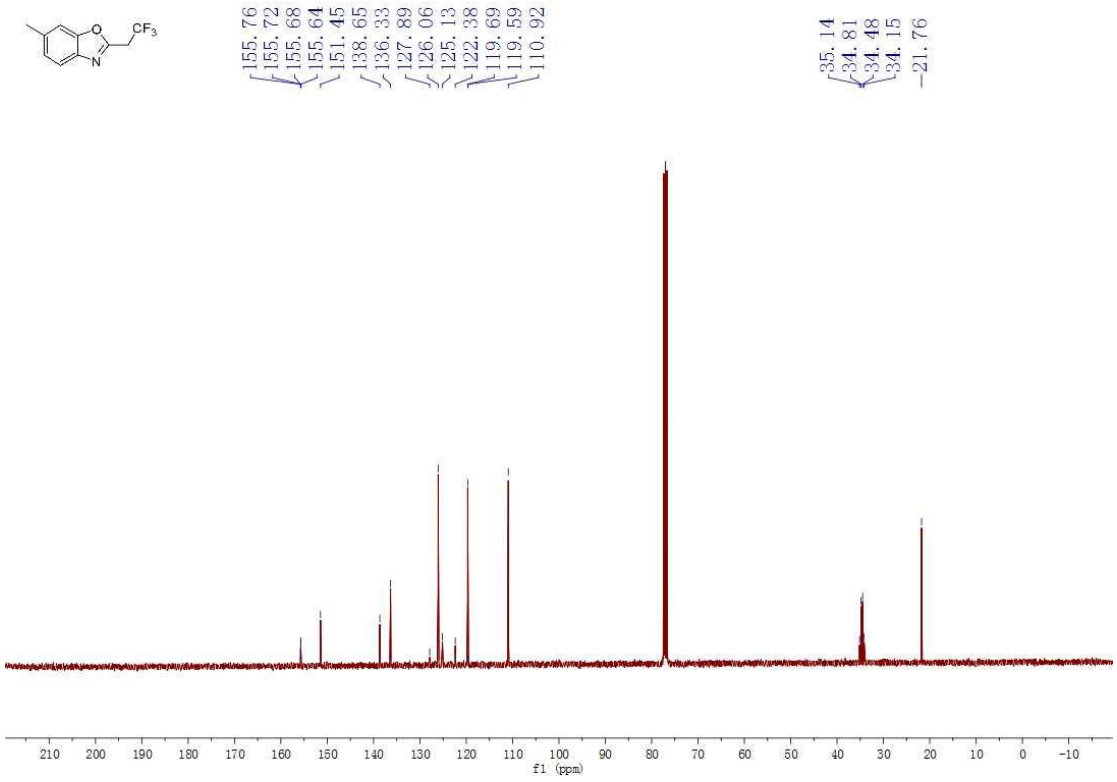
^{19}F NMR spectrum of **3c** in $CDCl_3$



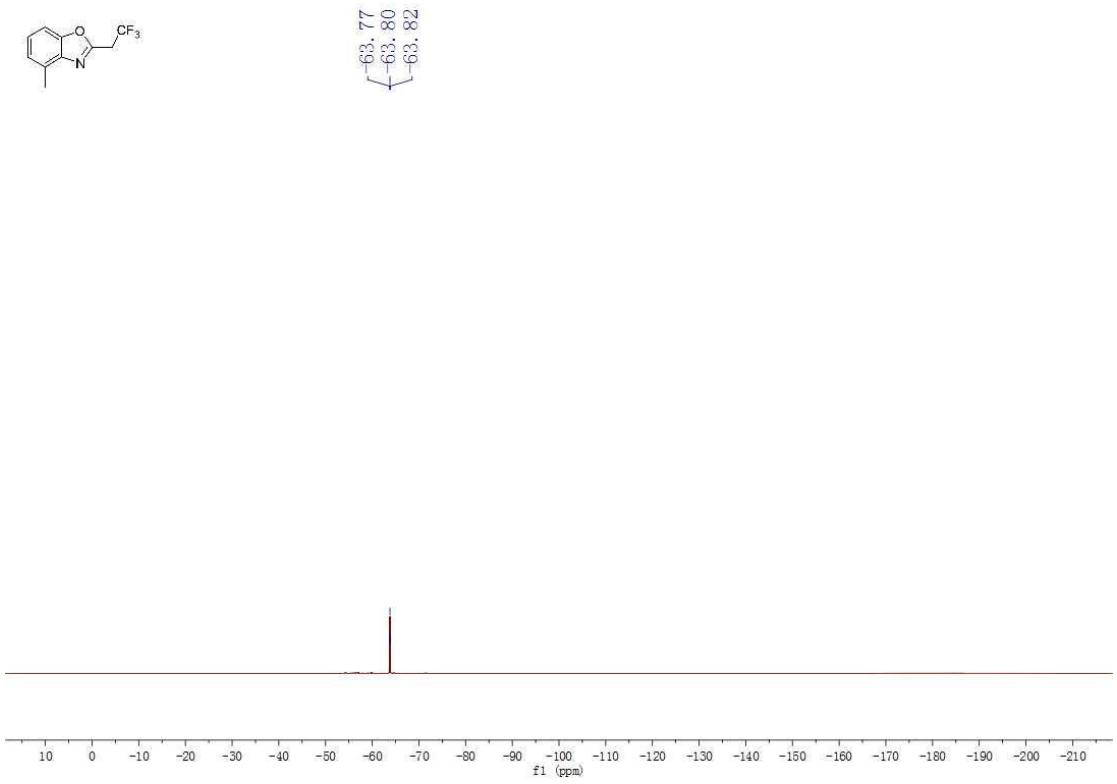
^{1}H NMR spectrum of **3c** in $CDCl_3$



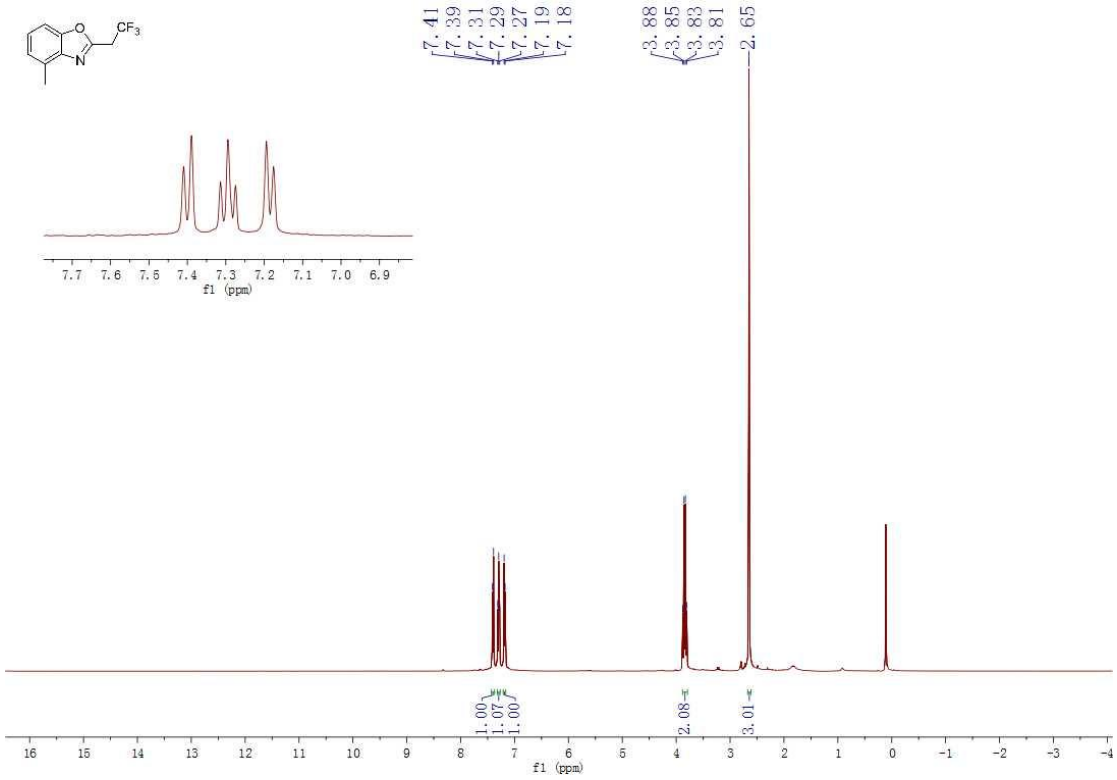
^{13}C NMR spectrum of **3c** in $CDCl_3$



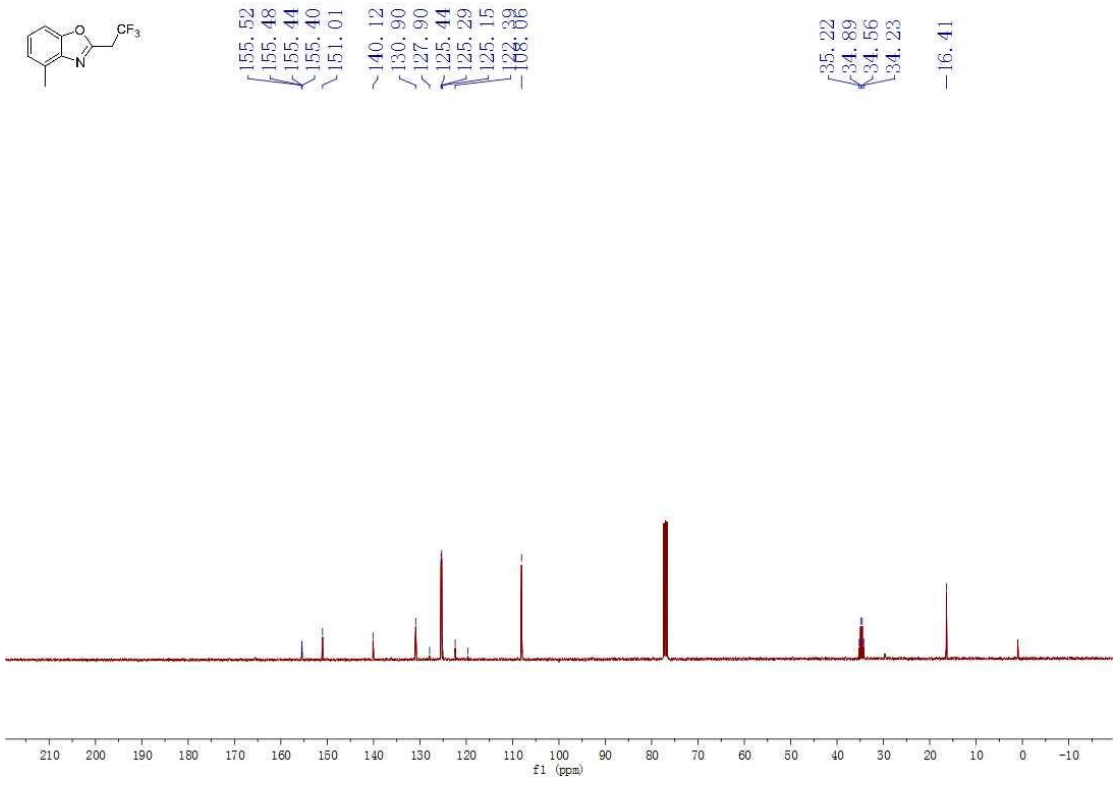
^{19}F NMR spectrum of **3d** in $CDCl_3$



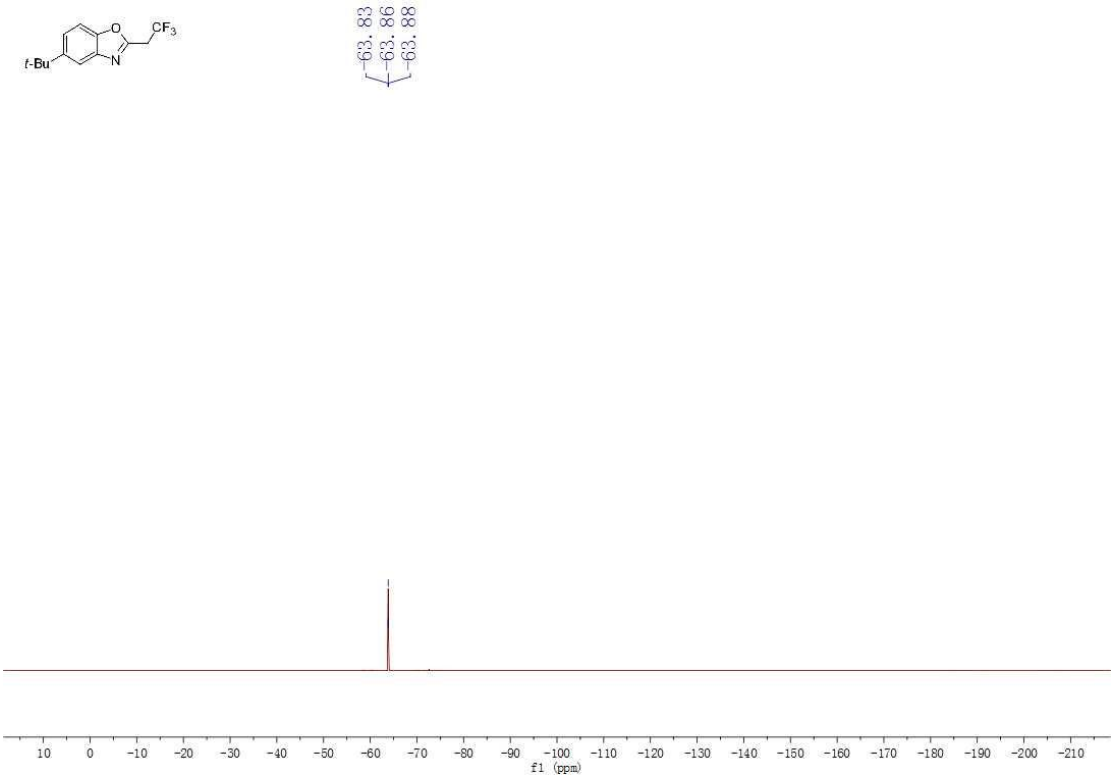
^{1}H NMR spectrum of **3d** in $CDCl_3$



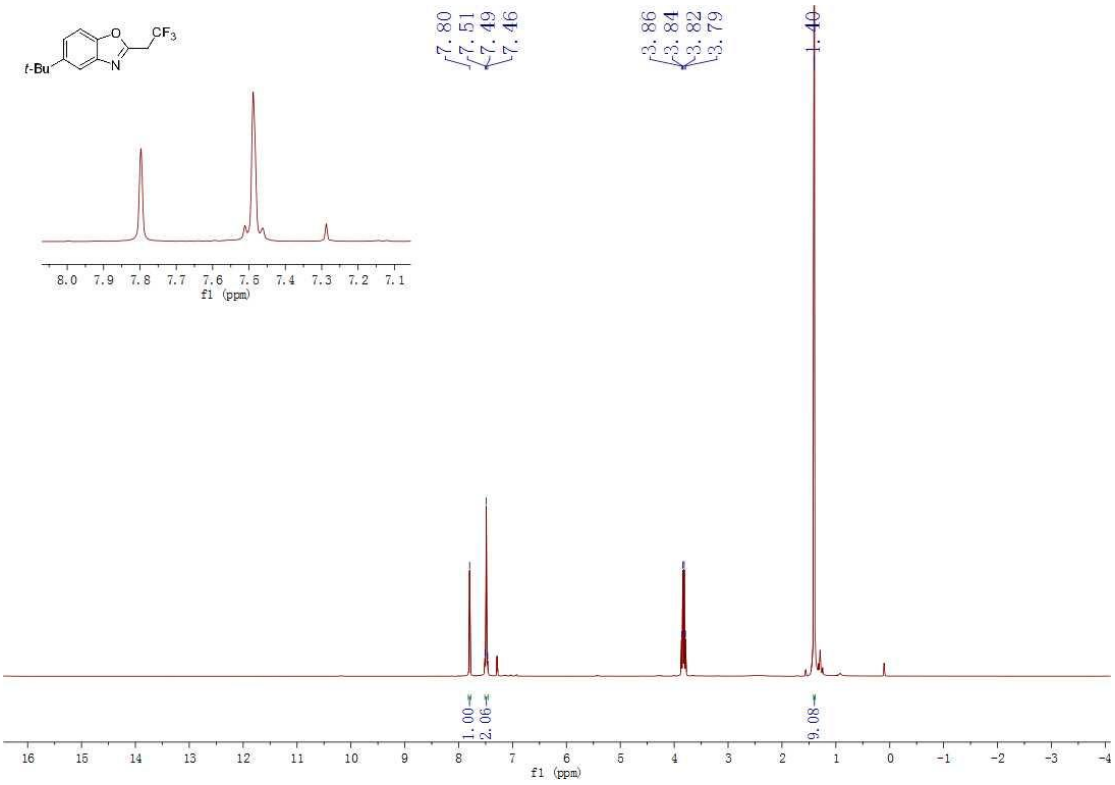
^{13}C NMR spectrum of **3d** in $CDCl_3$



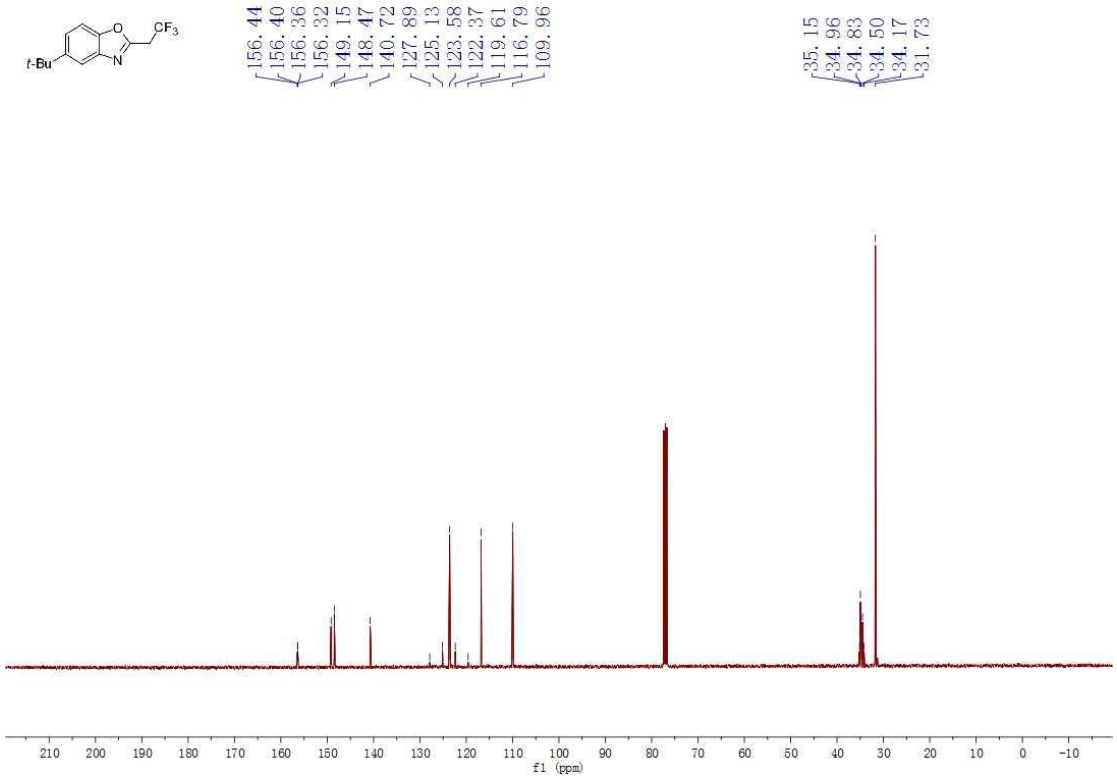
^{19}F NMR spectrum of **3e** in $CDCl_3$



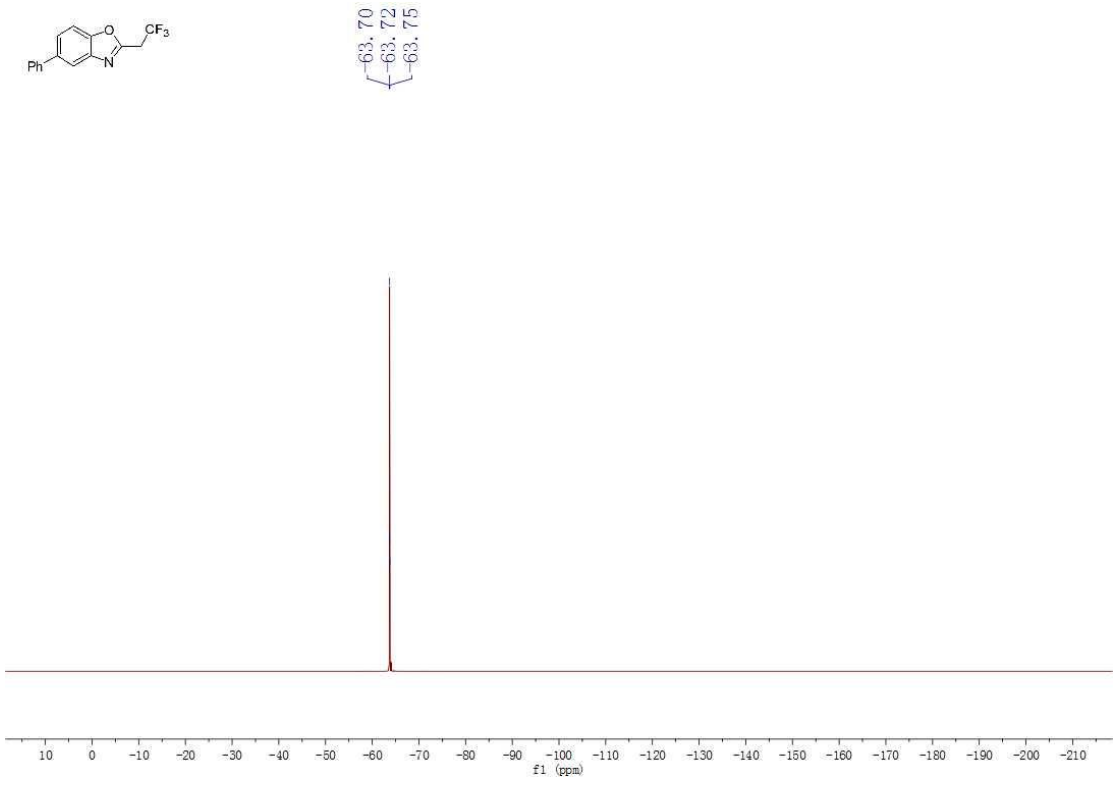
^{1}H NMR spectrum of **3e** in $CDCl_3$



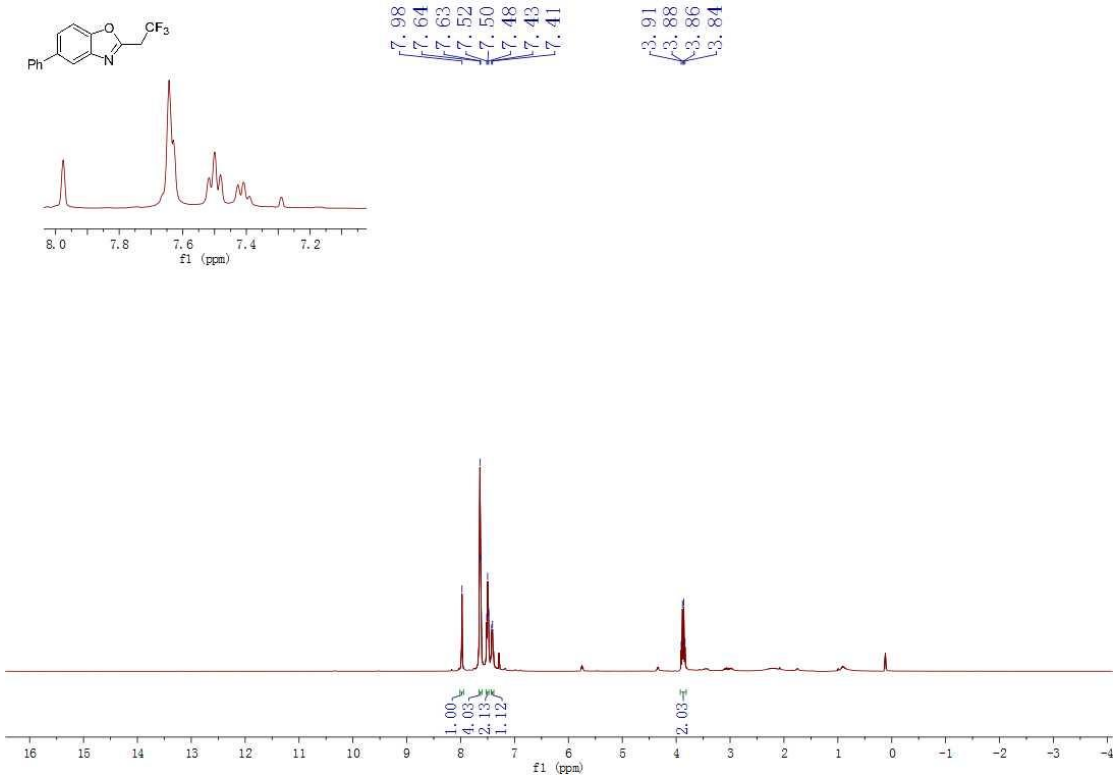
^{13}C NMR spectrum of **3e** in $CDCl_3$



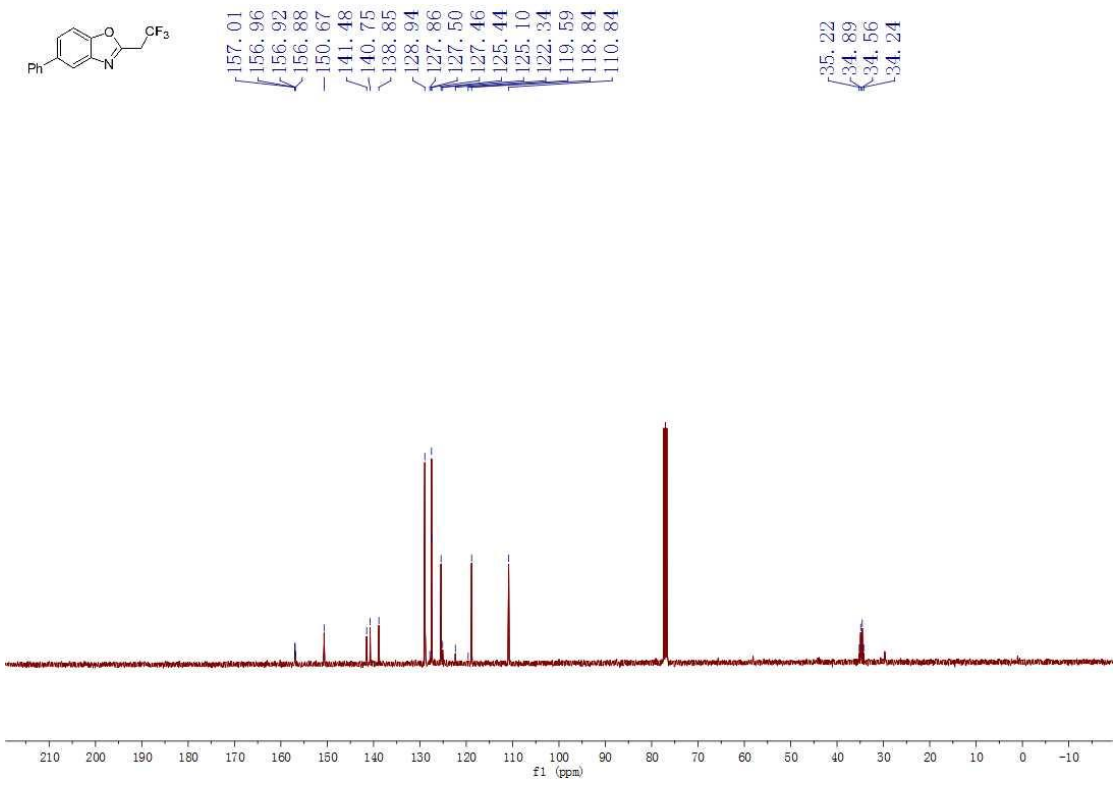
^{19}F NMR spectrum of **3f** in $CDCl_3$



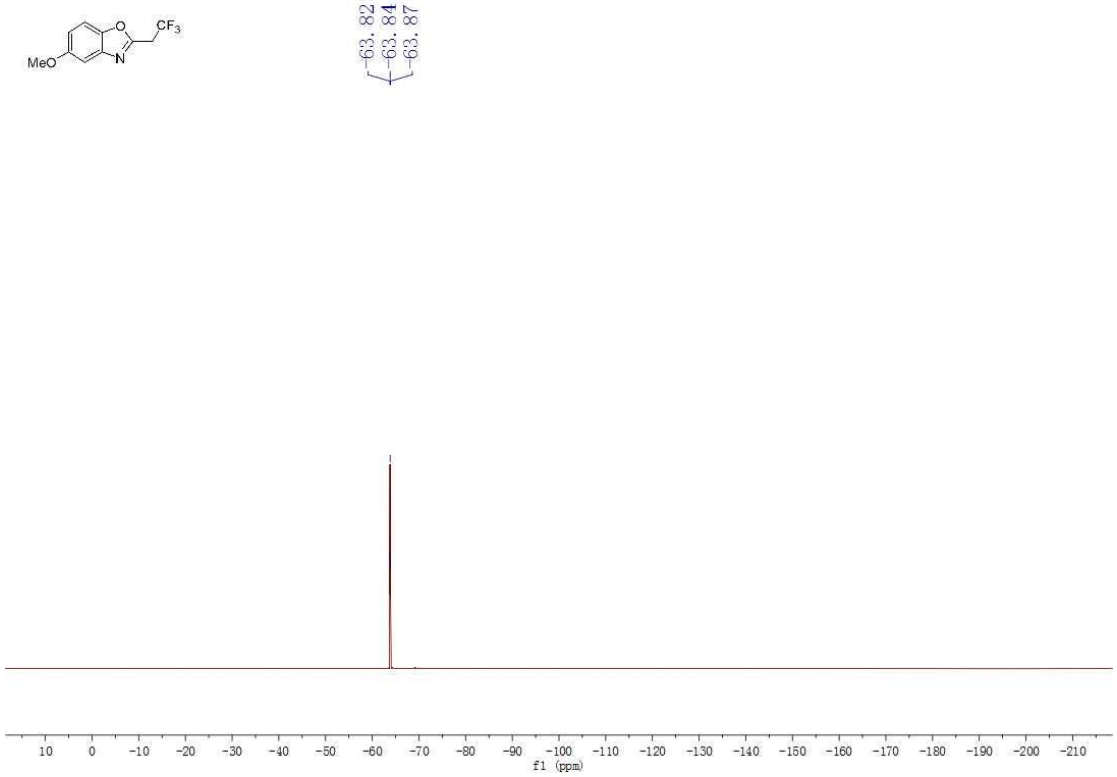
^{1}H NMR spectrum of **3f** in $CDCl_3$



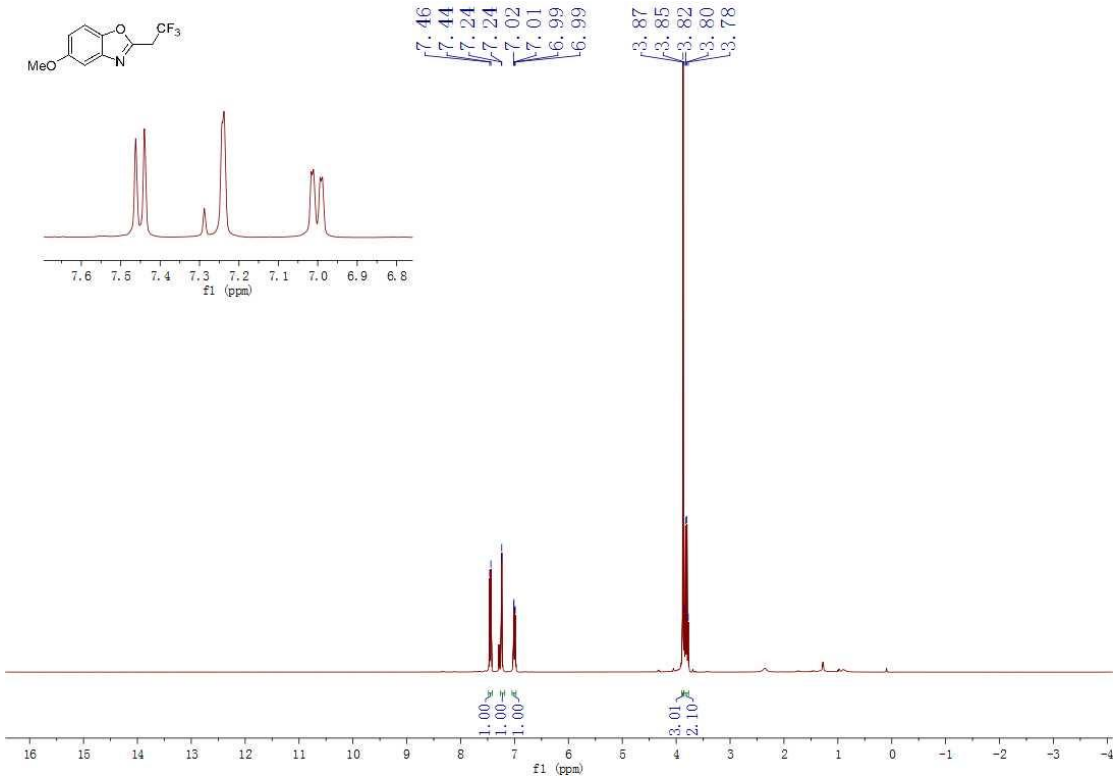
^{13}C NMR spectrum of **3f** in $CDCl_3$



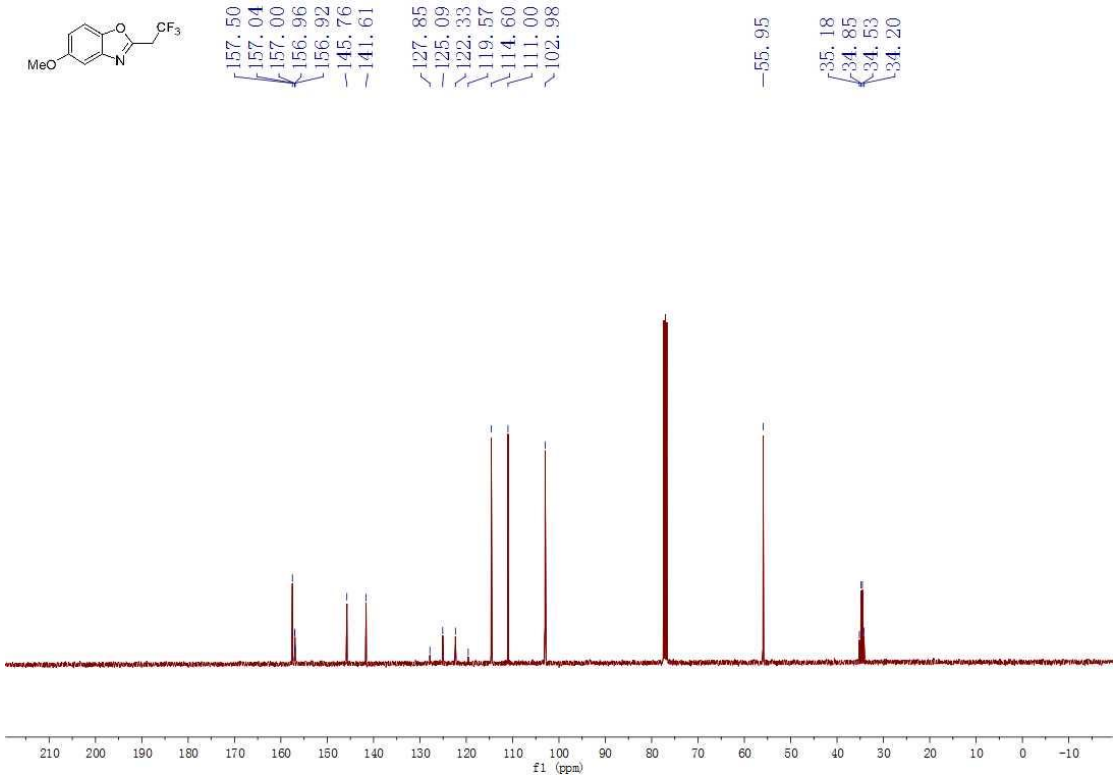
^{19}F NMR spectrum of **3g** in $CDCl_3$



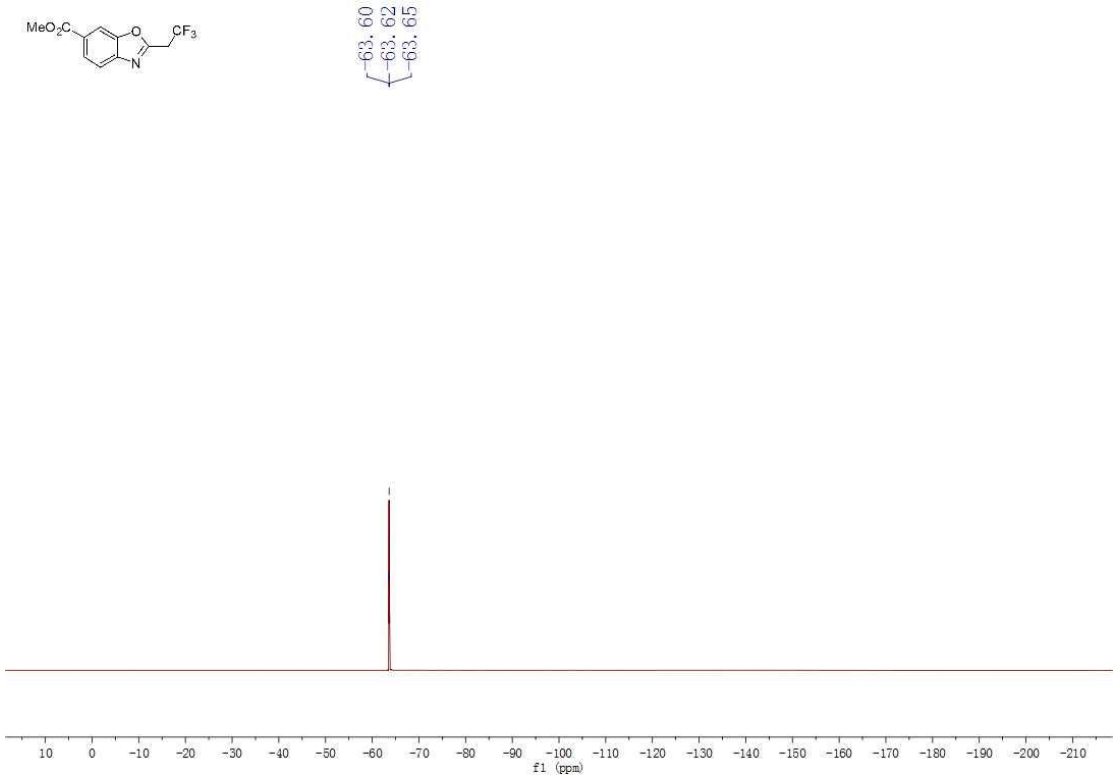
^{1}H NMR spectrum of **3g** in $CDCl_3$



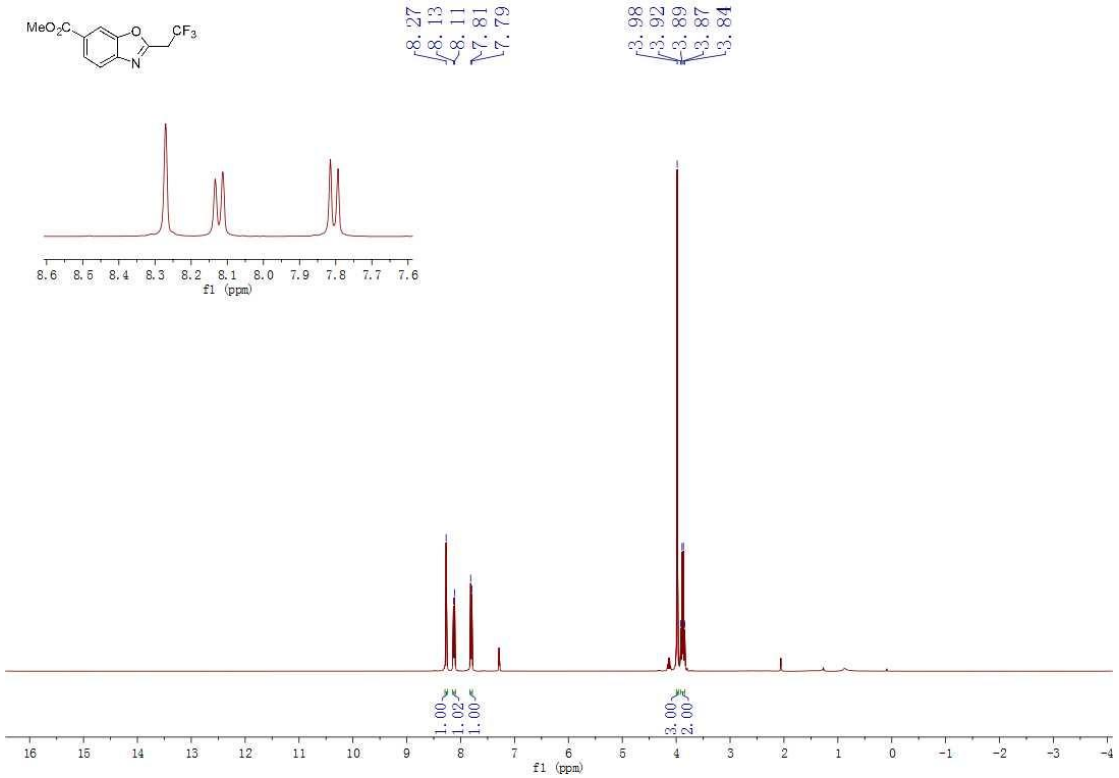
^{13}C NMR spectrum of **3g** in $CDCl_3$



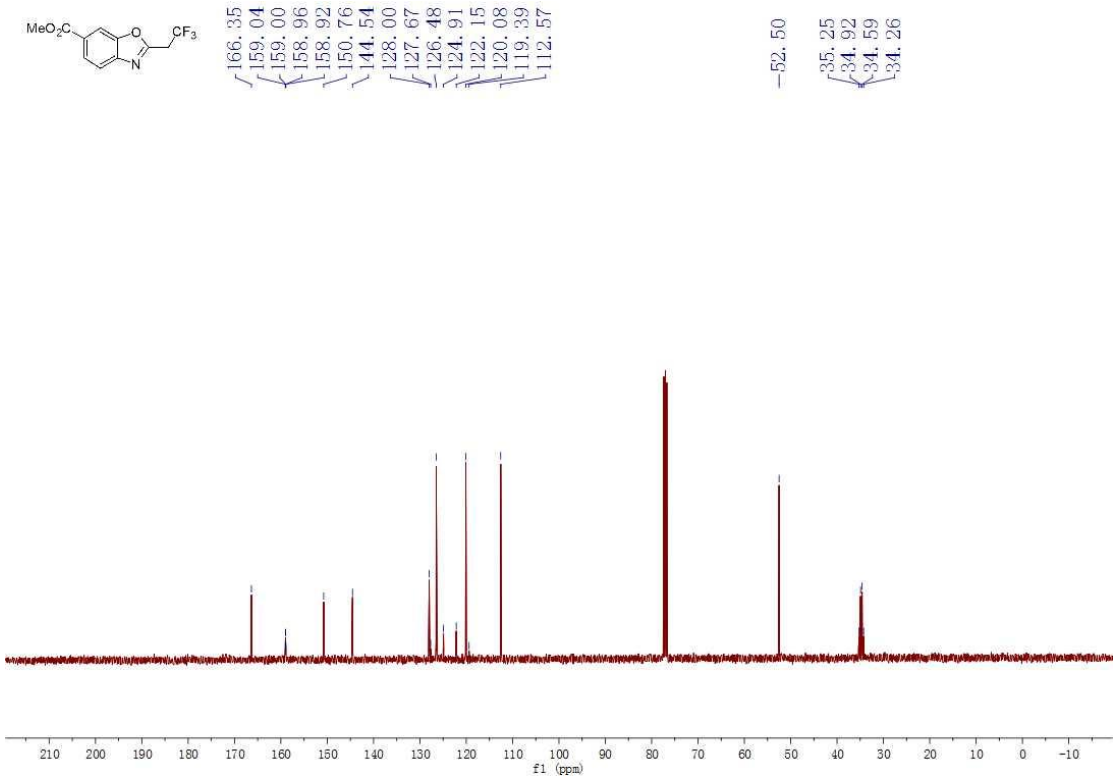
^{19}F NMR spectrum of **3h** in $CDCl_3$



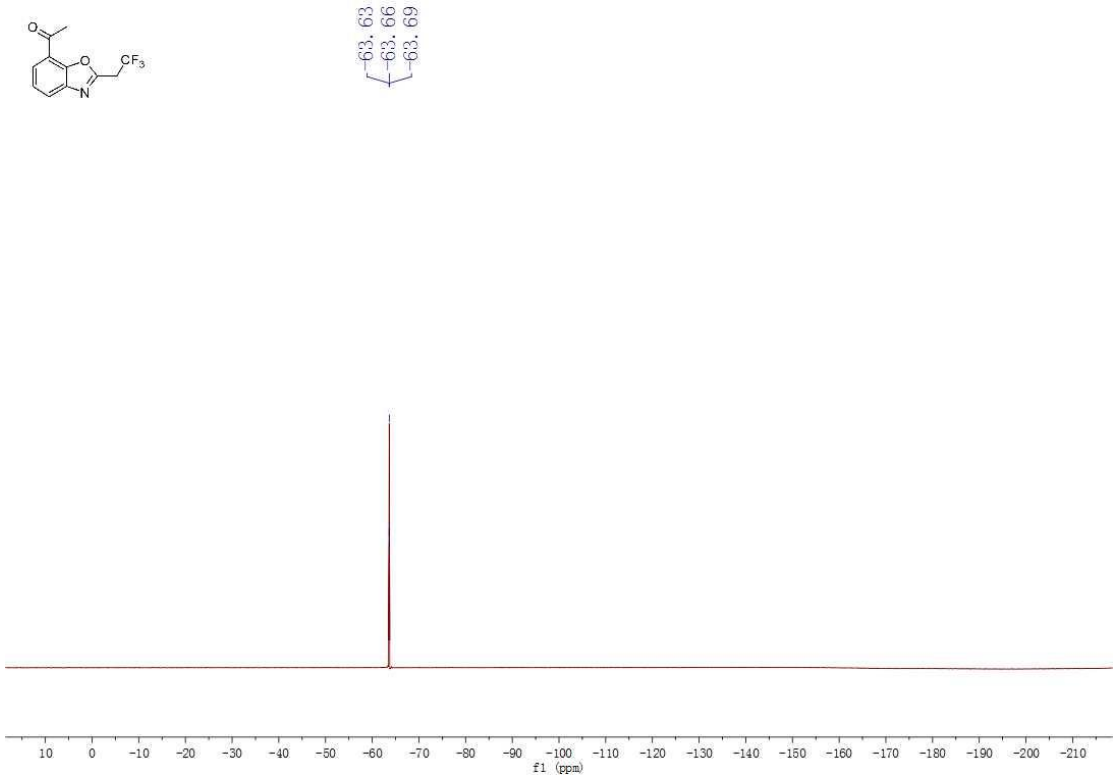
^{1}H NMR spectrum of **3h** in $CDCl_3$



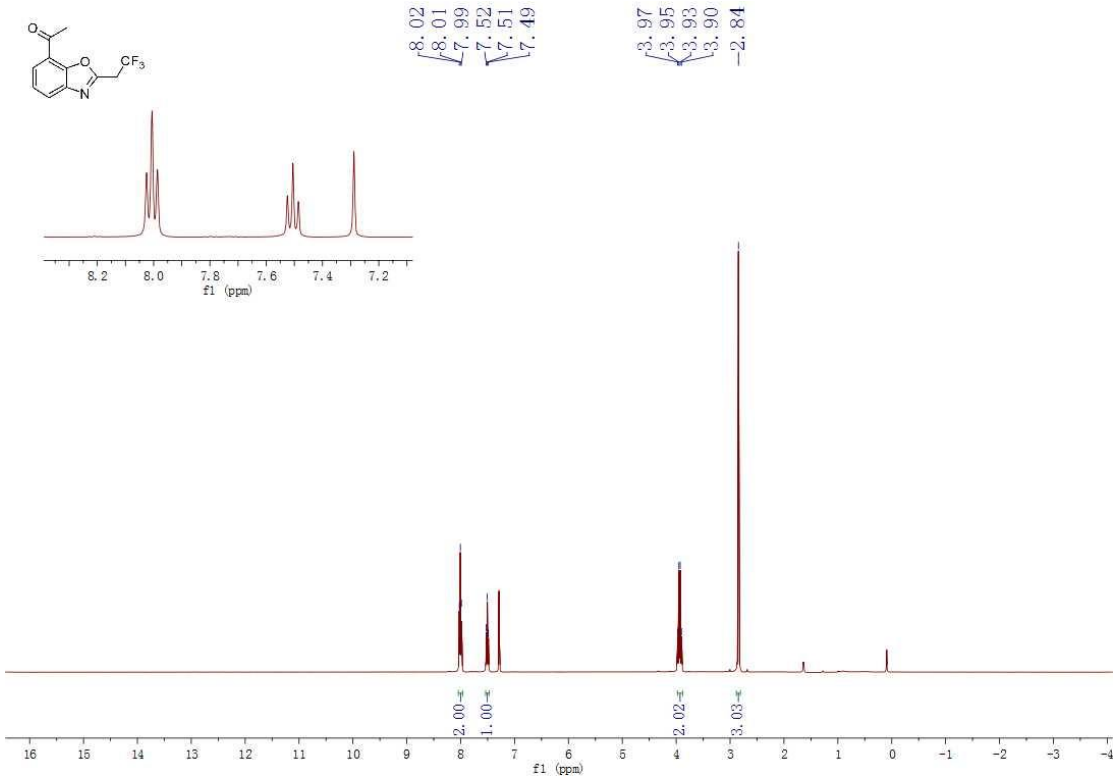
^{13}C NMR spectrum of **3h** in $CDCl_3$



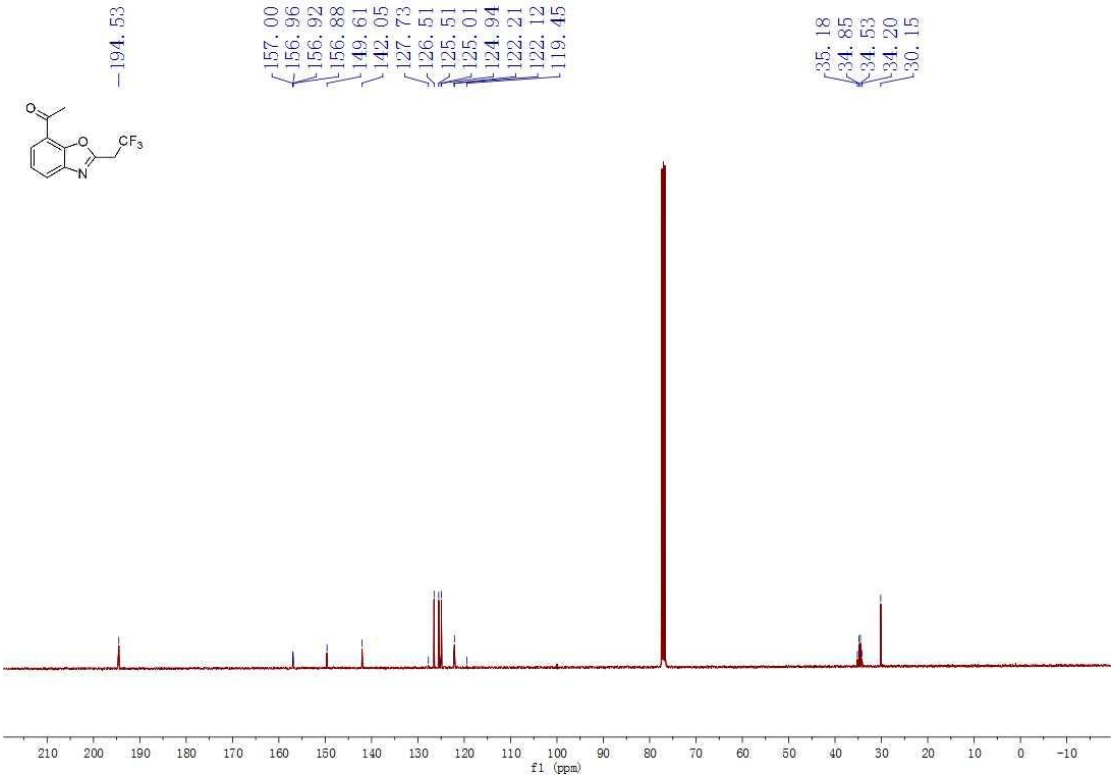
^{19}F NMR spectrum of **3i** in $CDCl_3$



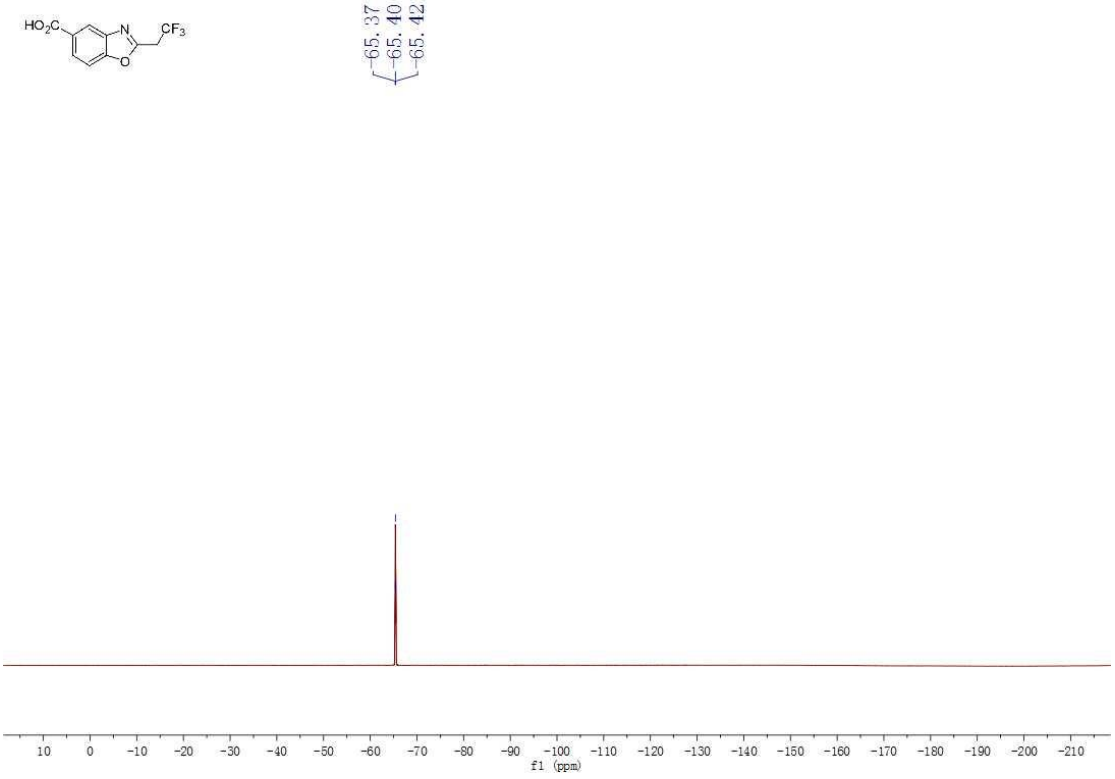
^{1}H NMR spectrum of **3i** in $CDCl_3$



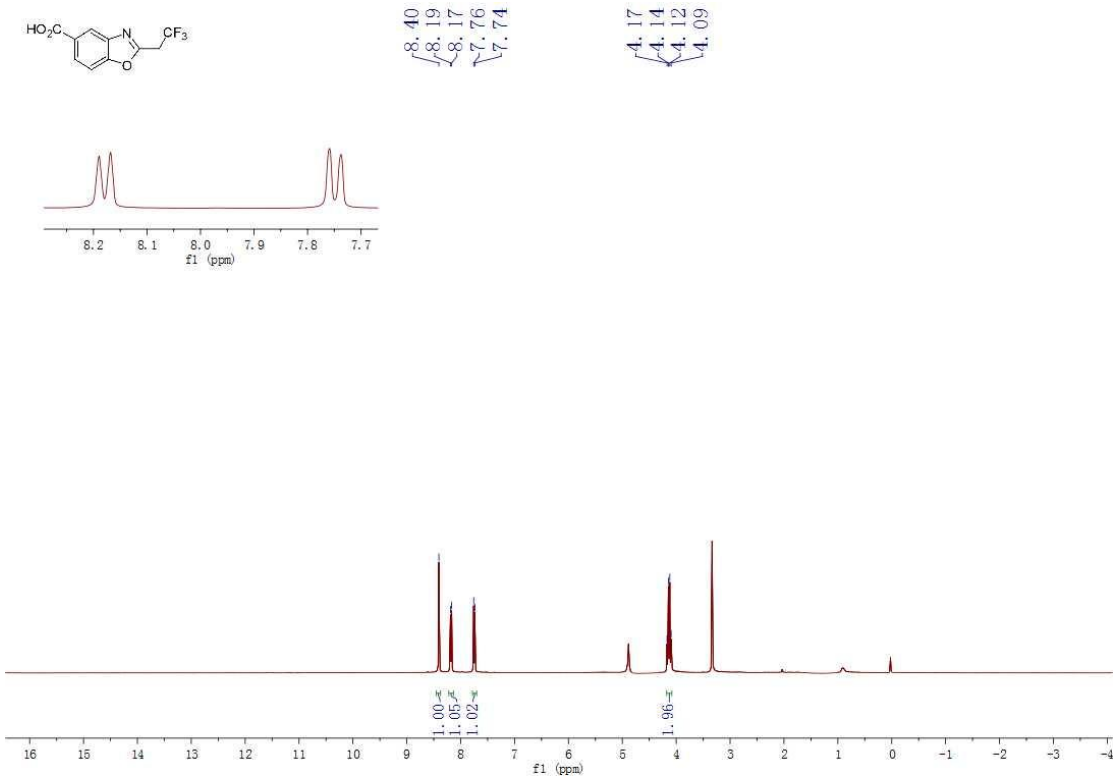
^{13}C NMR spectrum of **3i** in $CDCl_3$



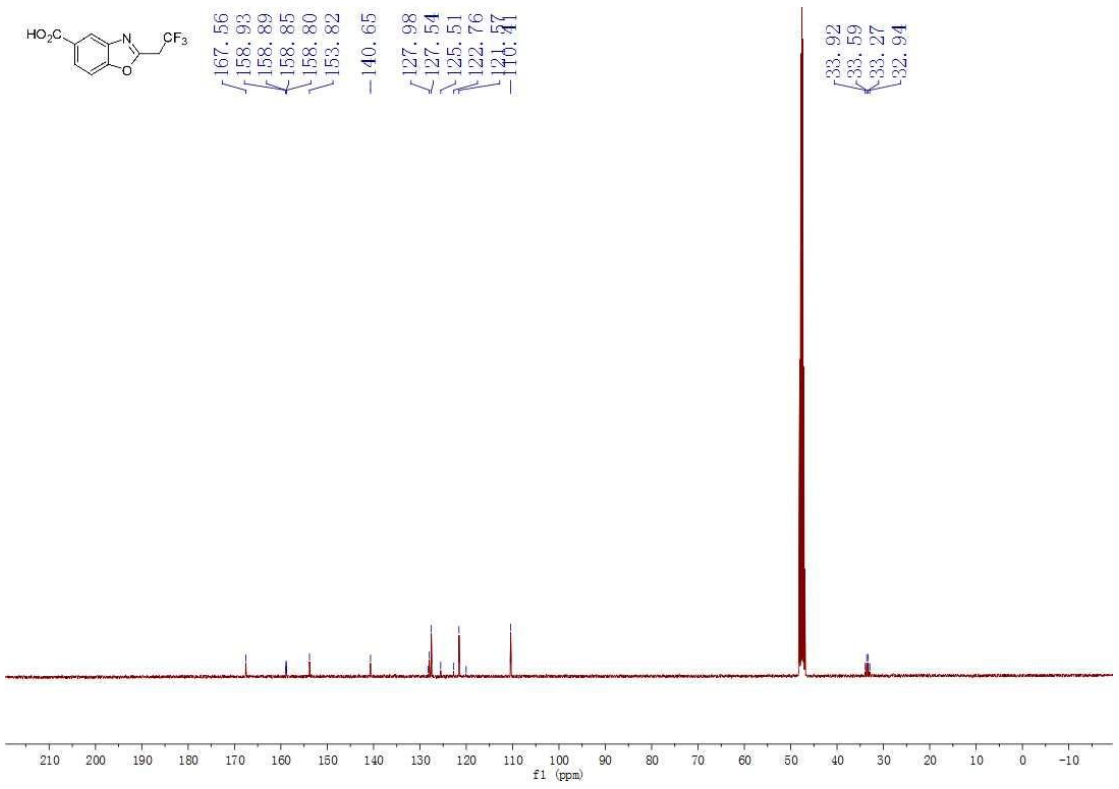
^{19}F NMR spectrum of **3j** in CD_3OD



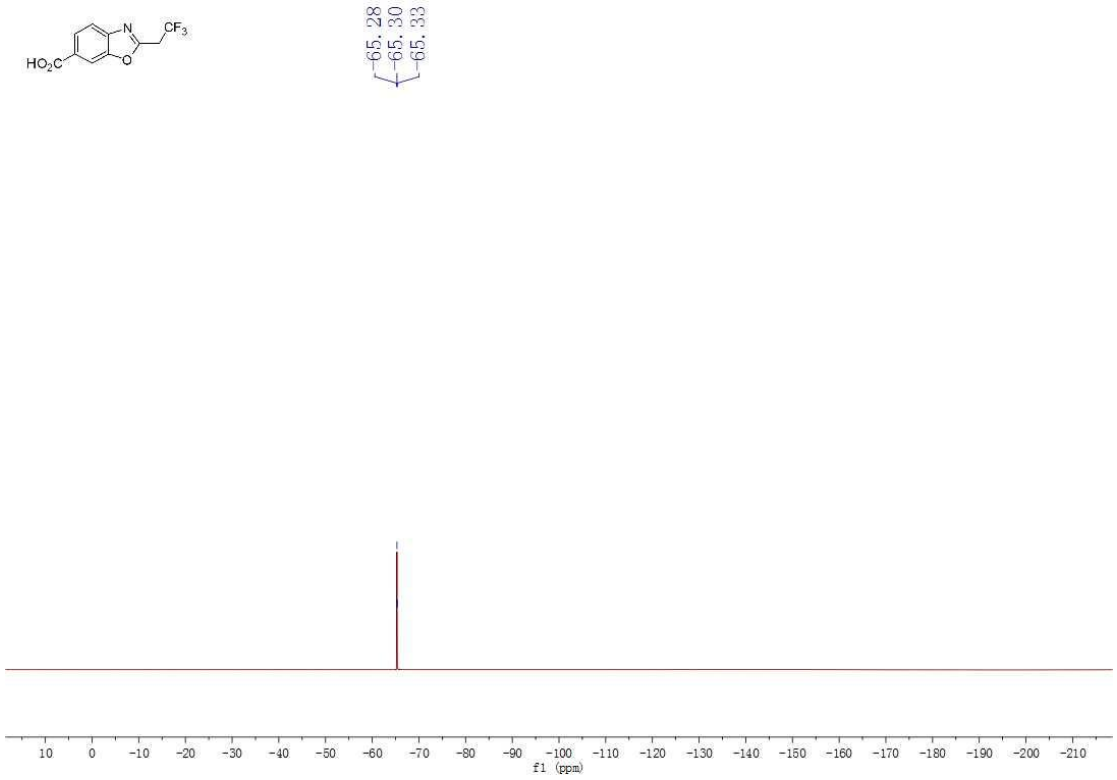
^{1}H NMR spectrum of **3j** in CD_3OD



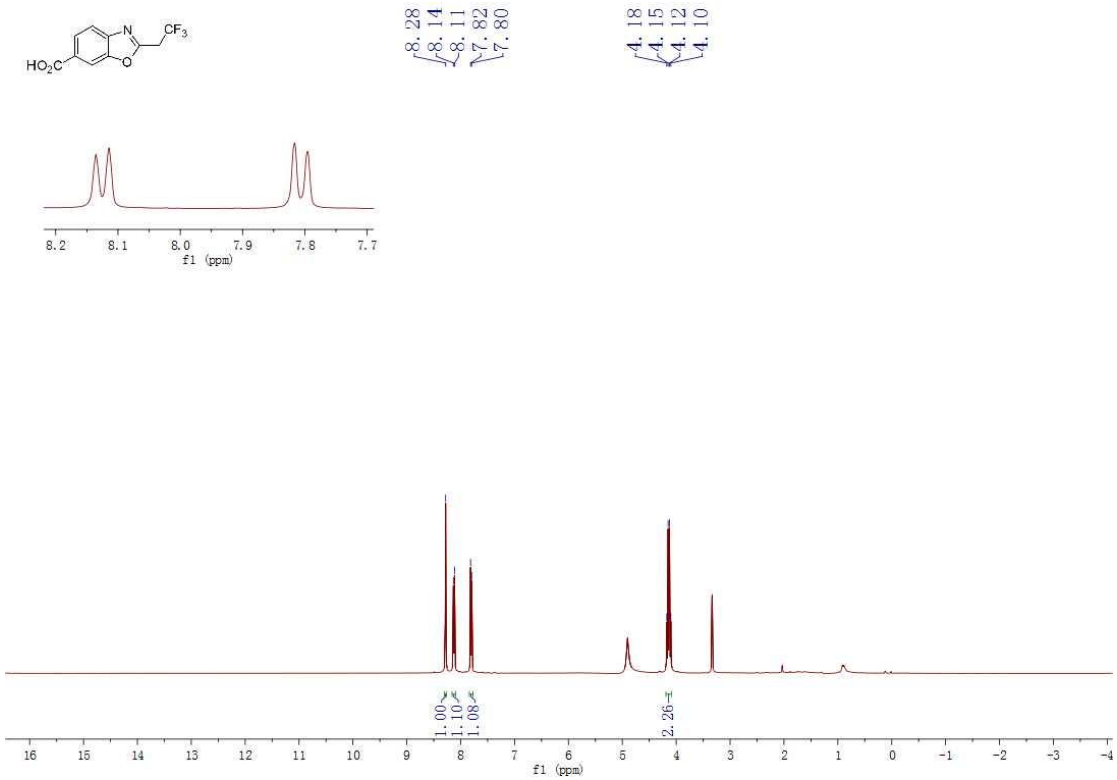
^{13}C NMR spectrum of **3j** in CD_3OD



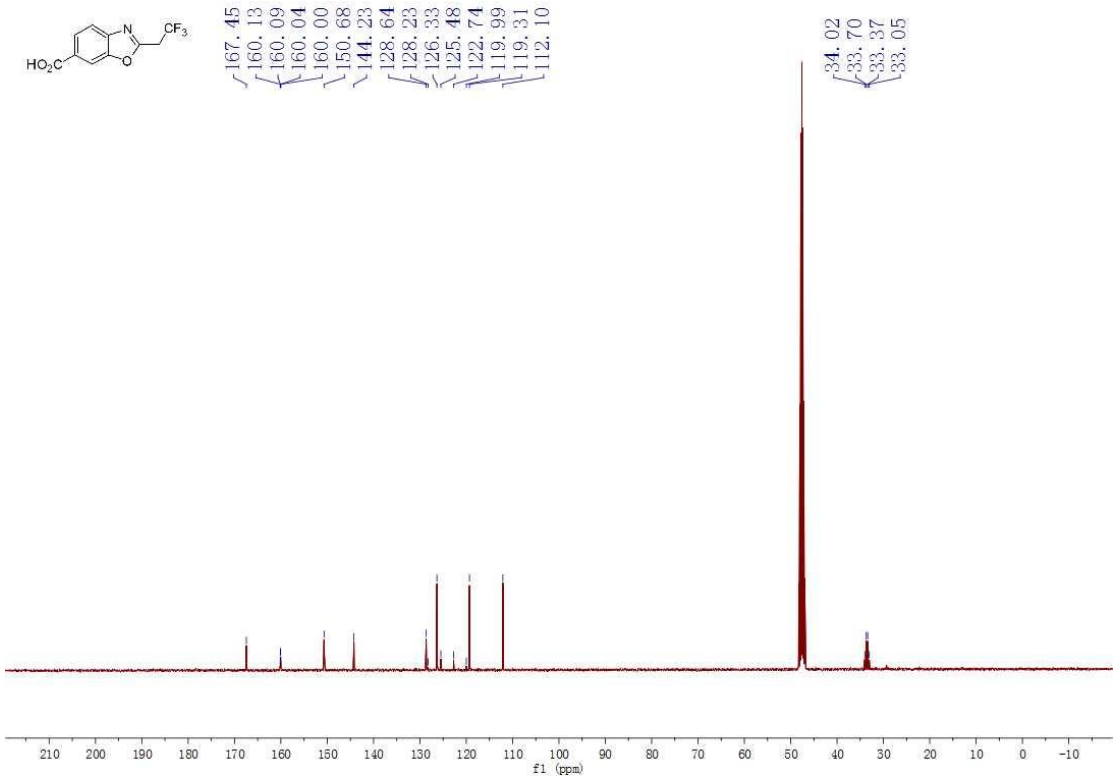
^{19}F NMR spectrum of **3k** in CD_3OD



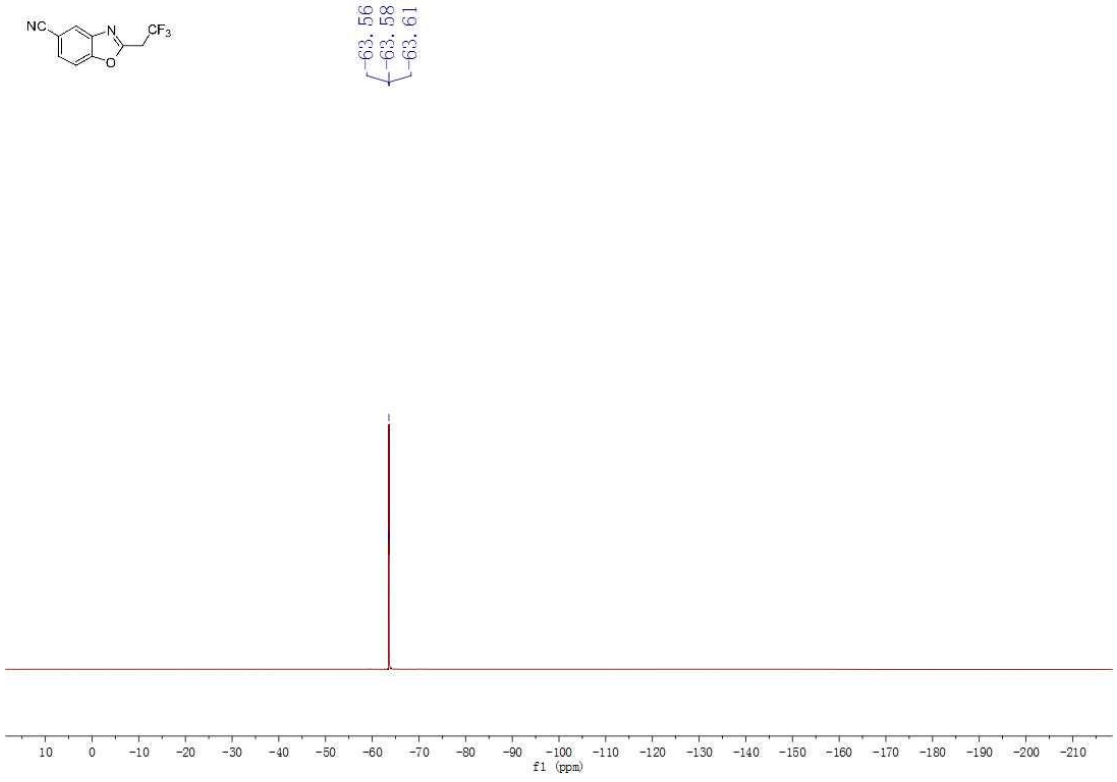
^{1}H NMR spectrum of **3k** in CD_3OD



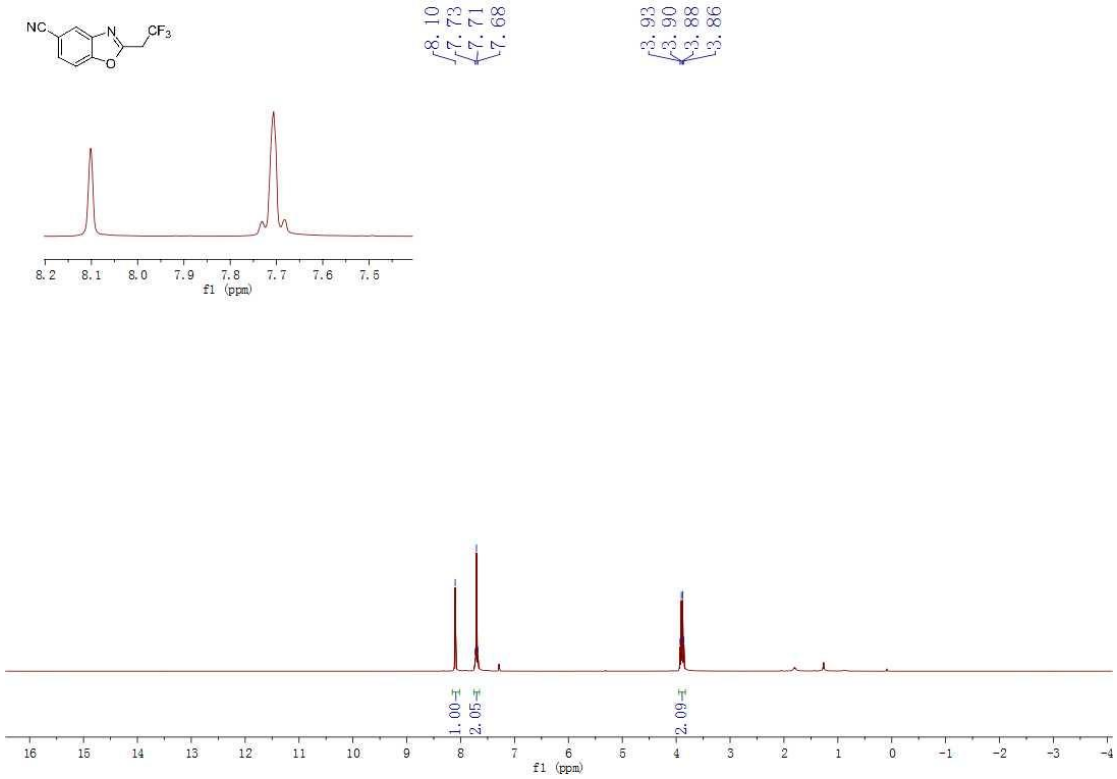
^{13}C NMR spectrum of **3k** in CD_3OD



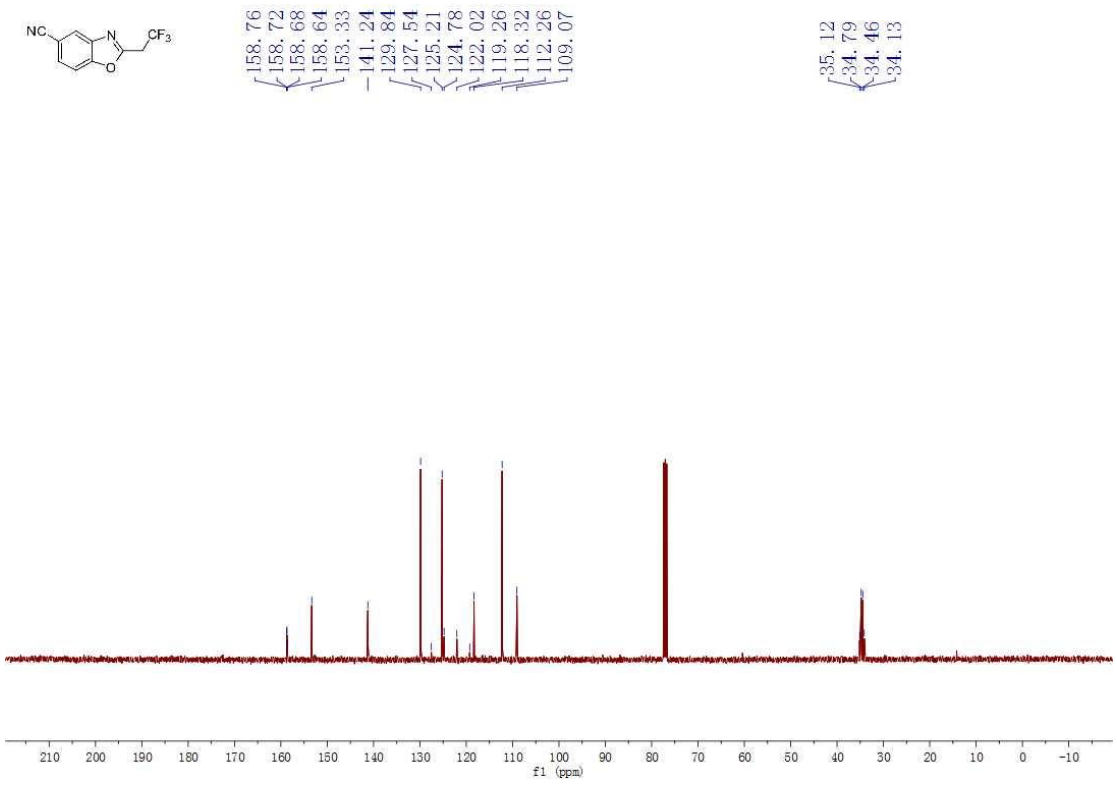
^{19}F NMR spectrum of **3l** in $CDCl_3$



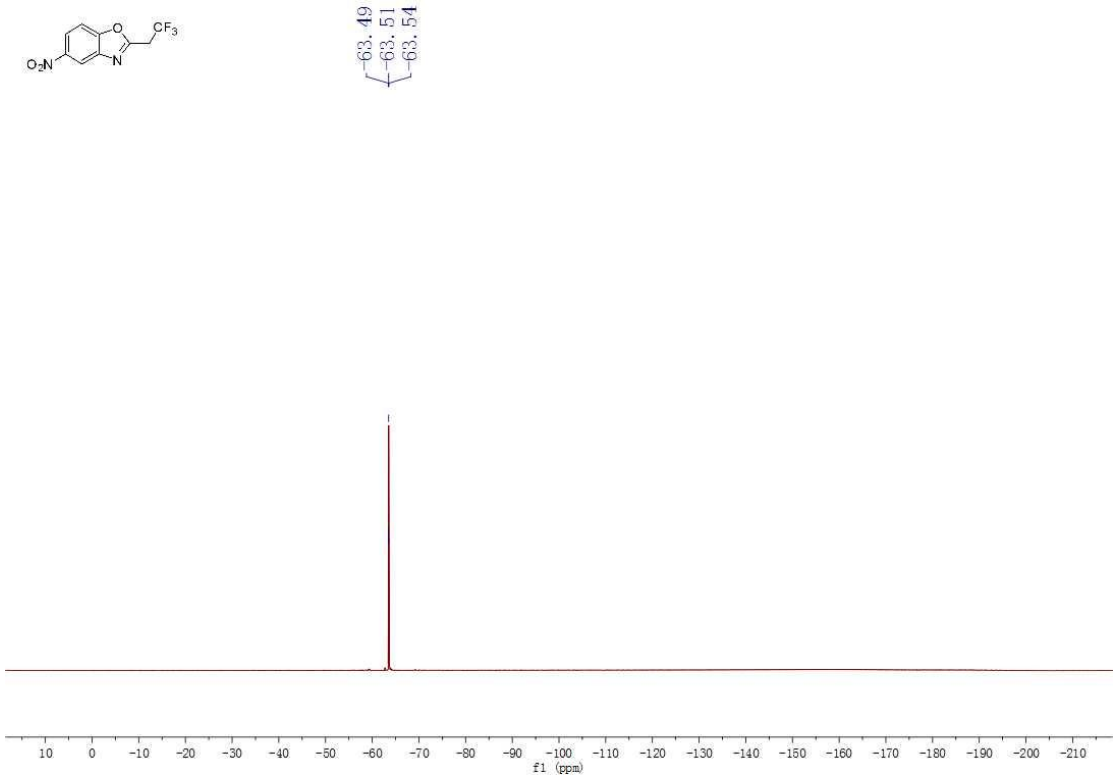
^{1}H NMR spectrum of **3l** in $CDCl_3$



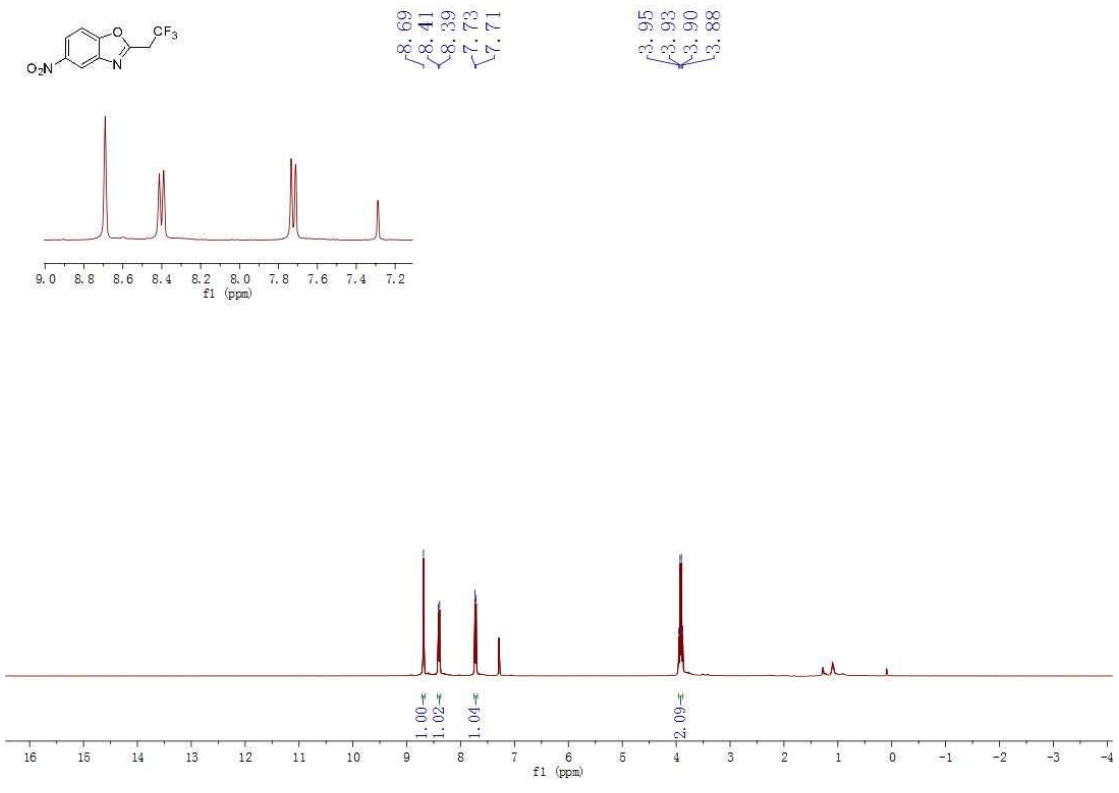
^{13}C NMR spectrum of **3l** in $CDCl_3$



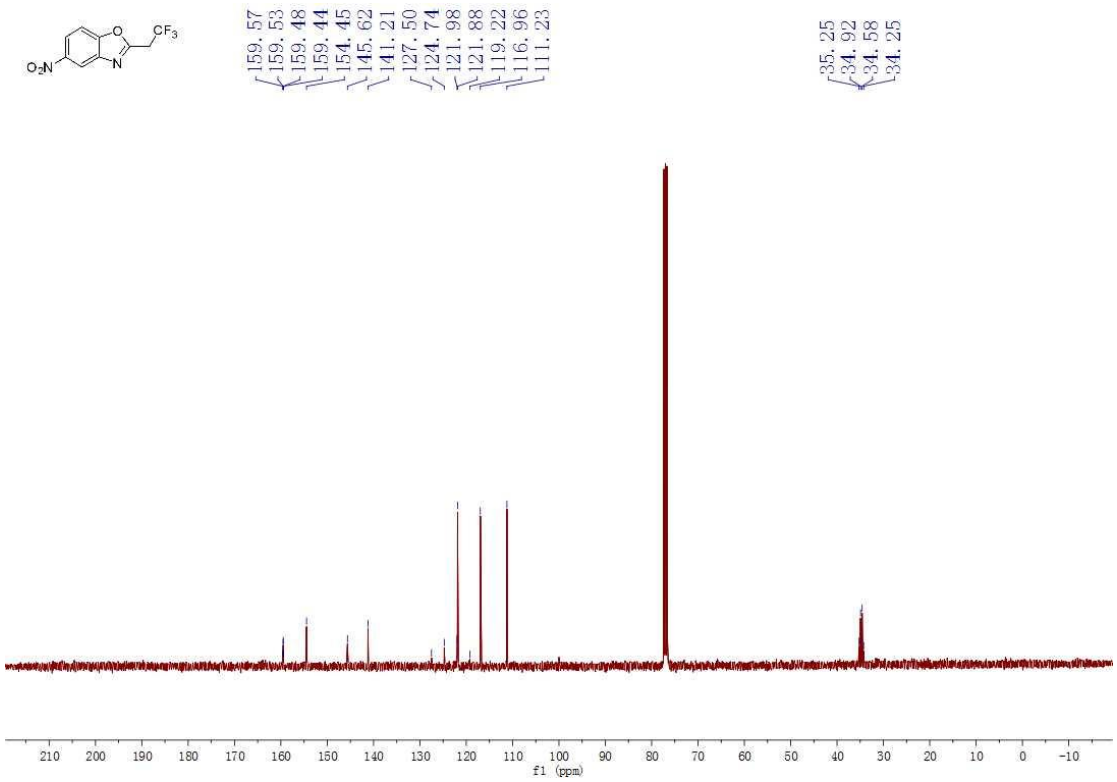
^{19}F NMR spectrum of **3m** in $CDCl_3$



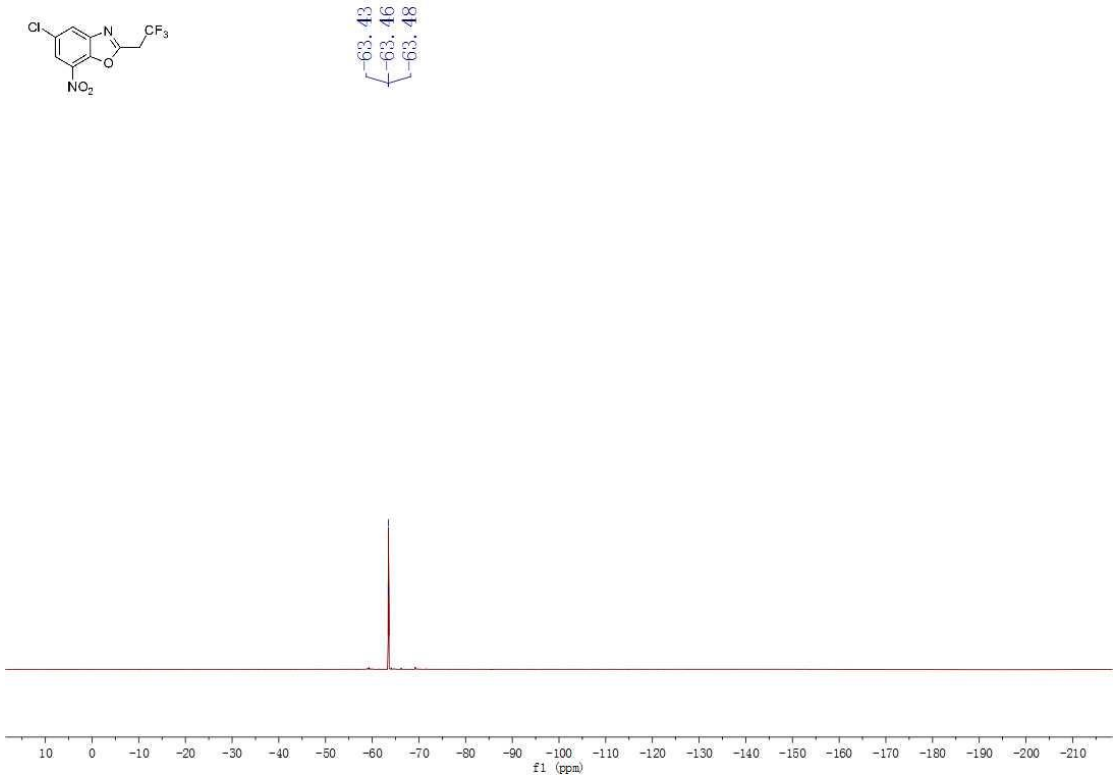
^{1}H NMR spectrum of **3m** in $CDCl_3$



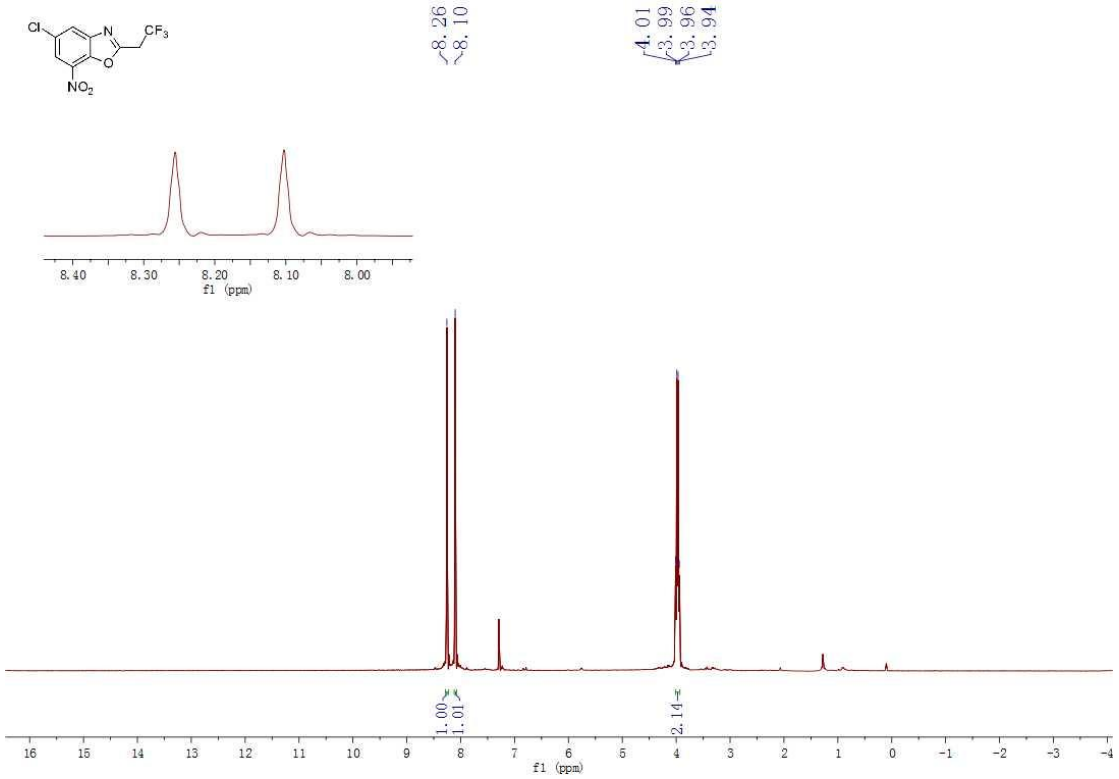
^{13}C NMR spectrum of **3m** in $CDCl_3$



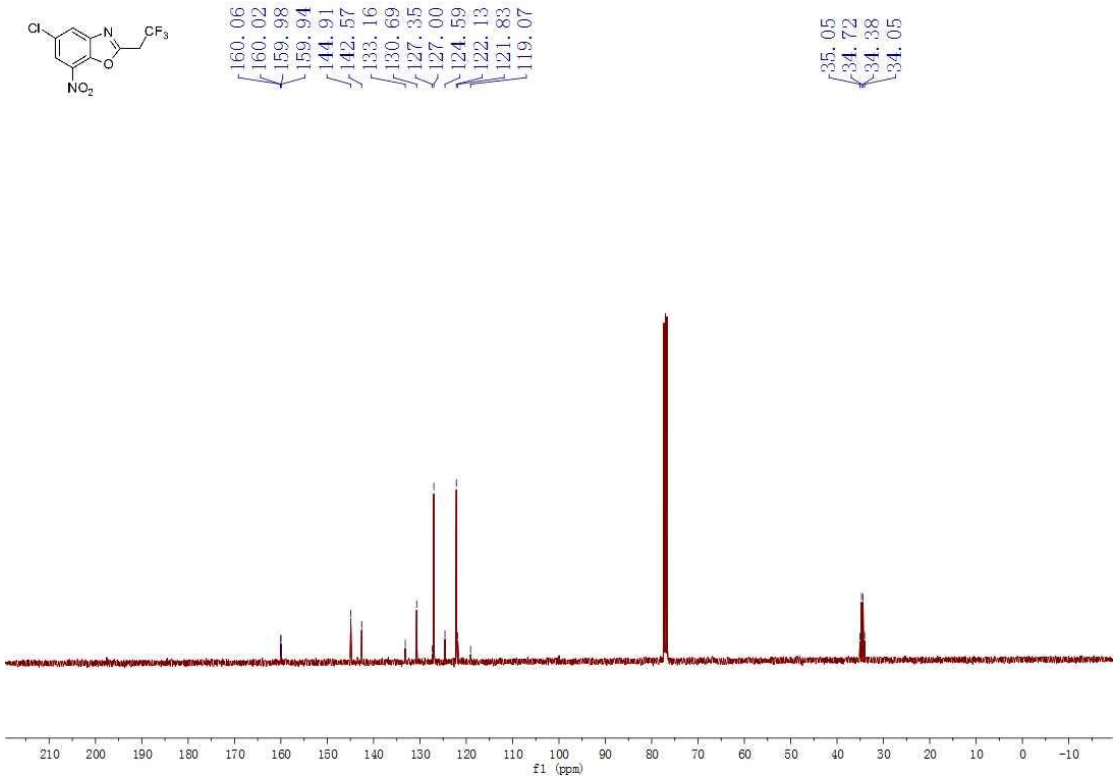
^{19}F NMR spectrum of **3n** in $CDCl_3$



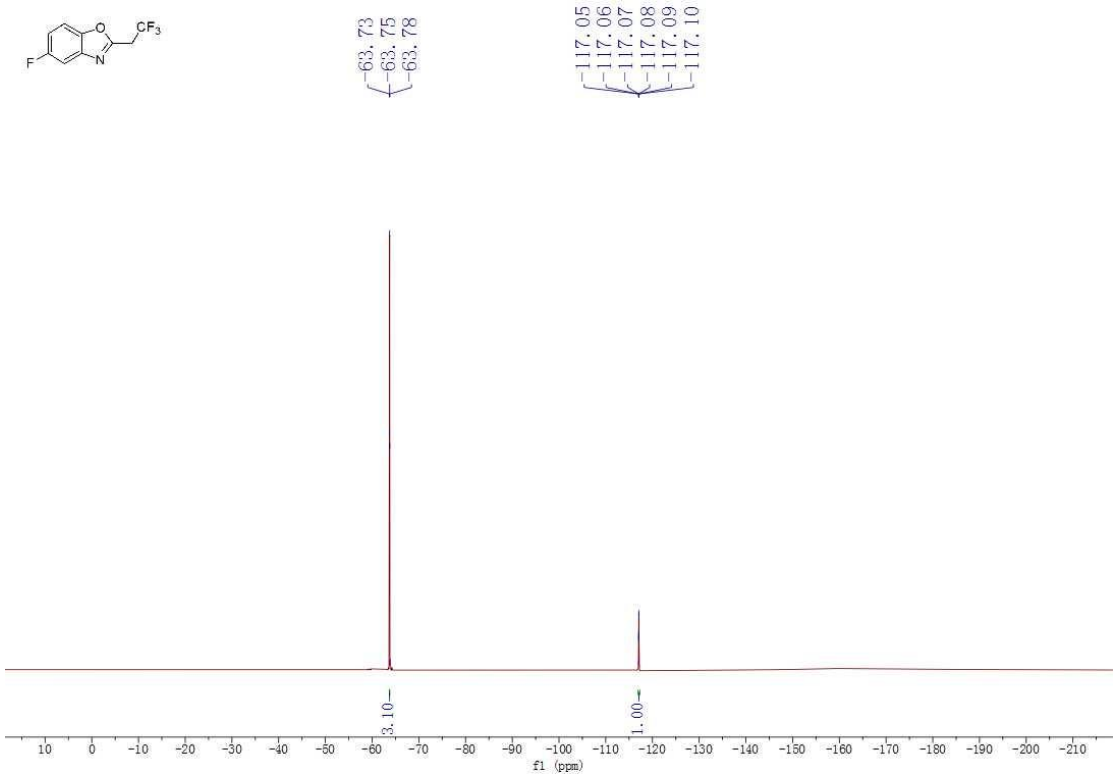
^{1}H NMR spectrum of **3n** in $CDCl_3$



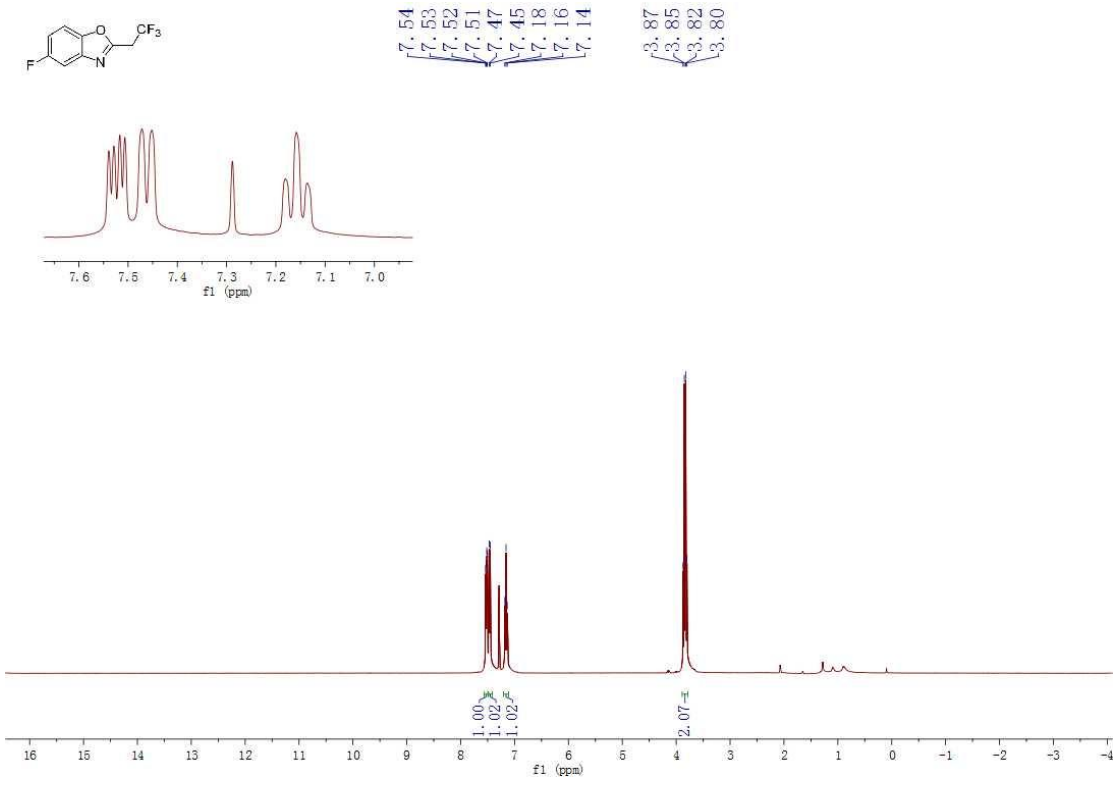
^{13}C NMR spectrum of **3n** in $CDCl_3$



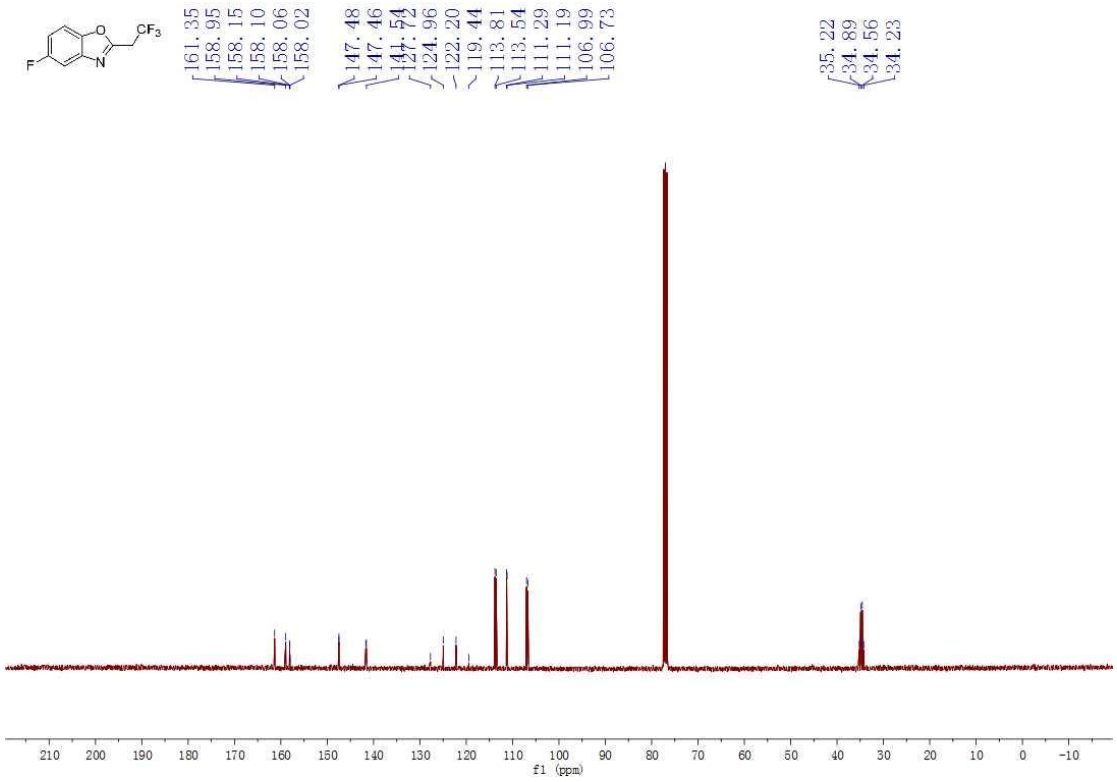
^{19}F NMR spectrum of **3o** in $CDCl_3$



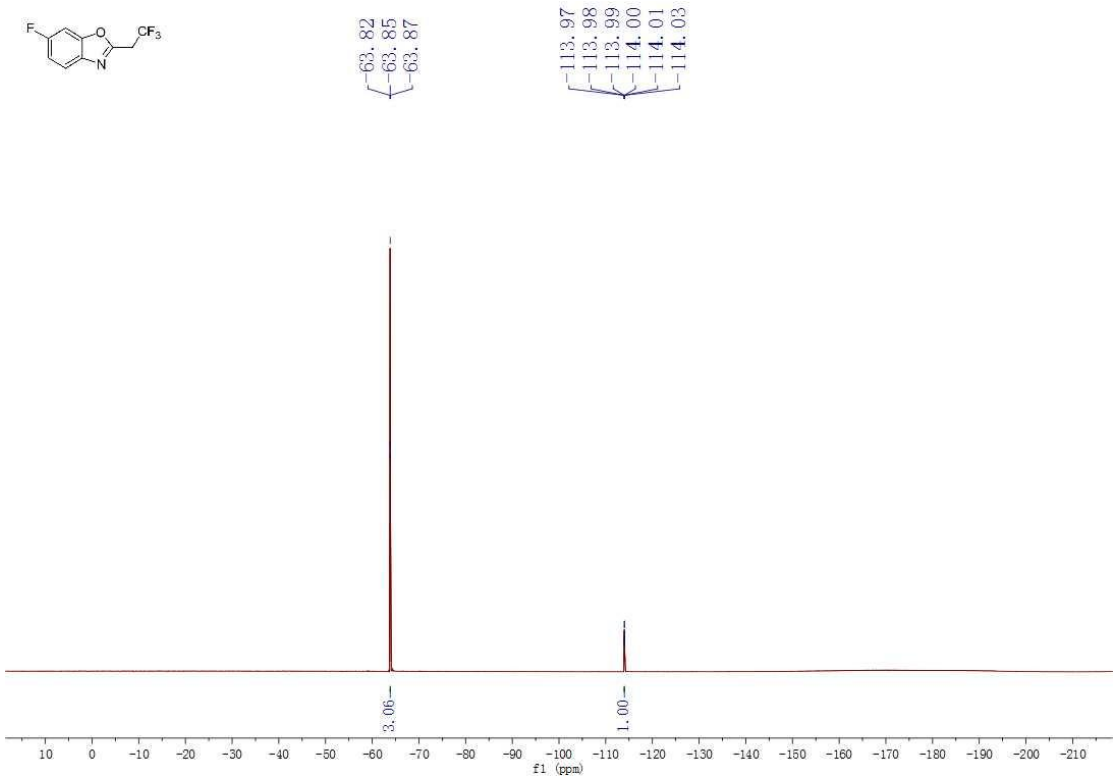
^{1}H NMR spectrum of **3o** in $CDCl_3$



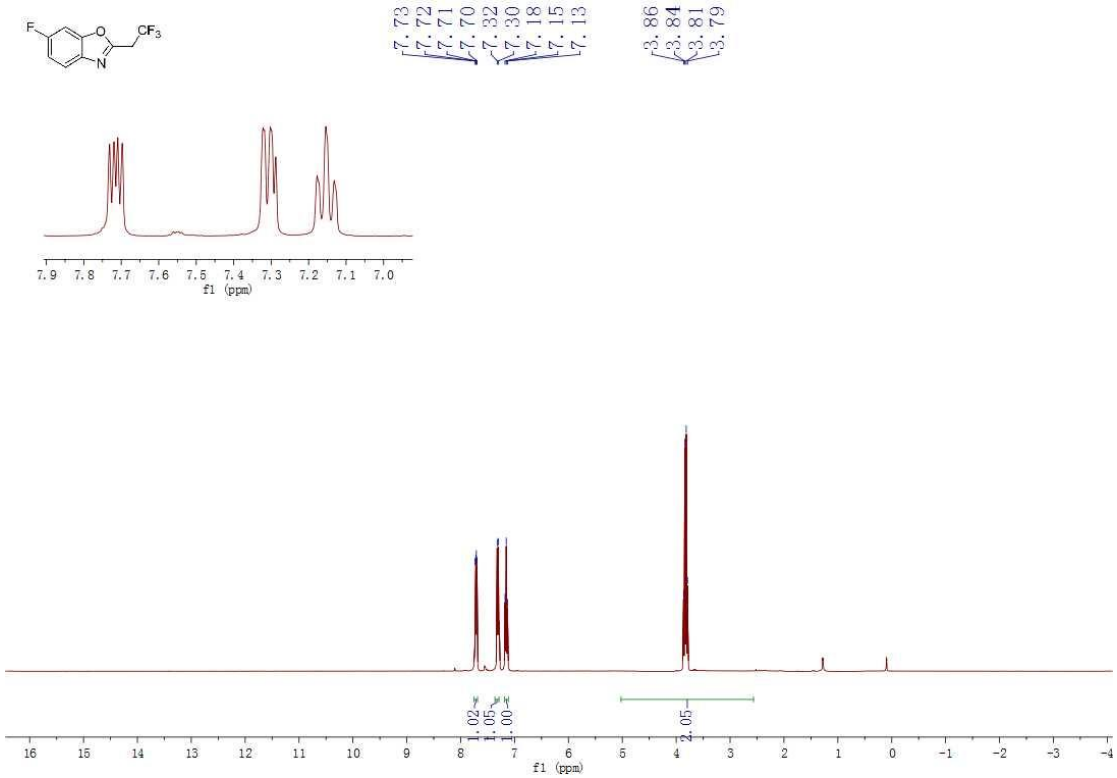
^{13}C NMR spectrum of **3o** in $CDCl_3$



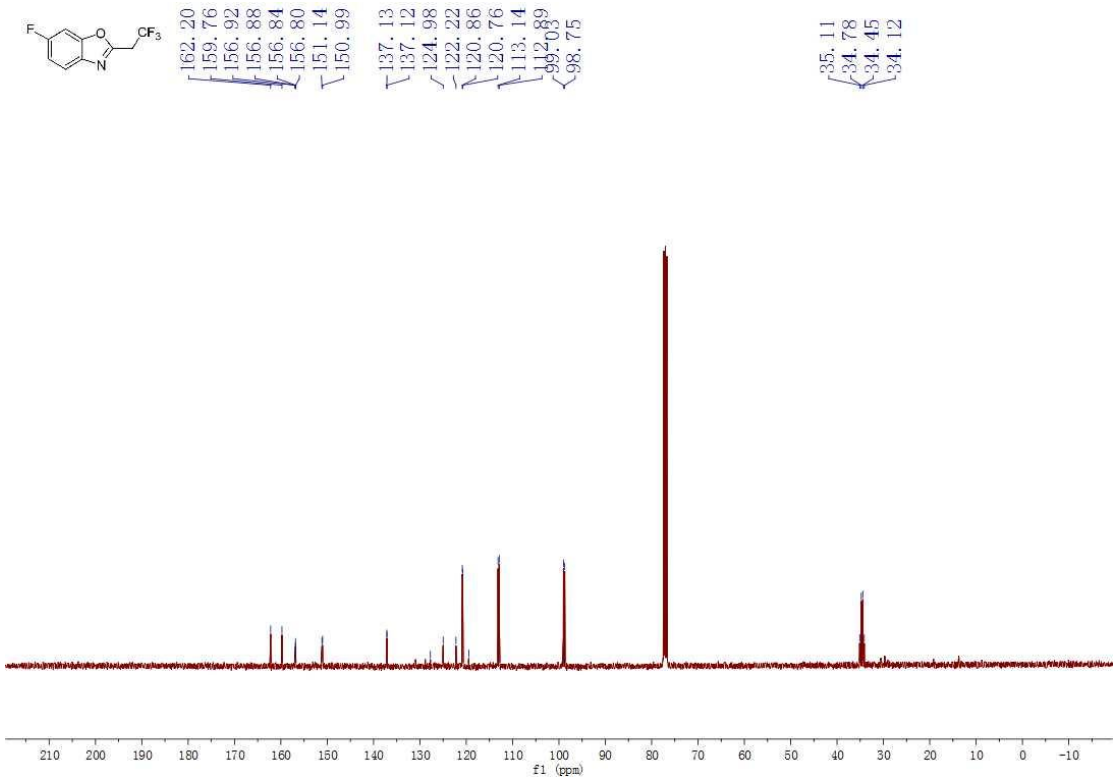
^{19}F NMR spectrum of **3p** in $CDCl_3$



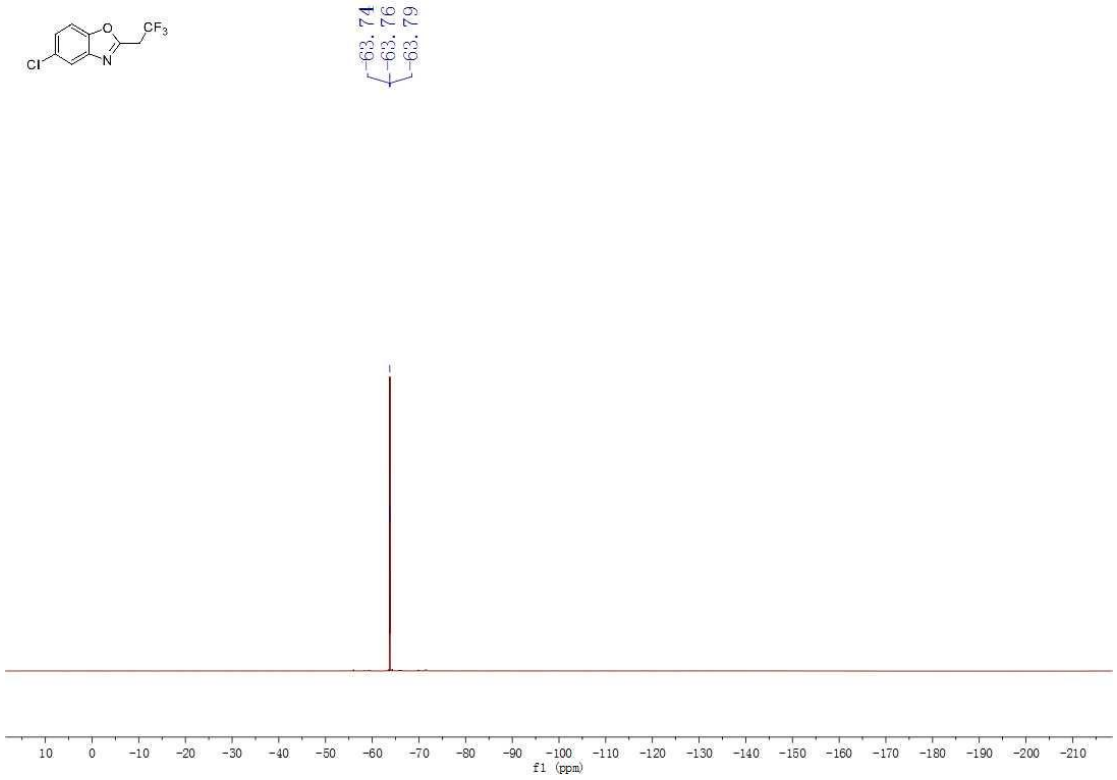
^{1}H NMR spectrum of **3p** in $CDCl_3$



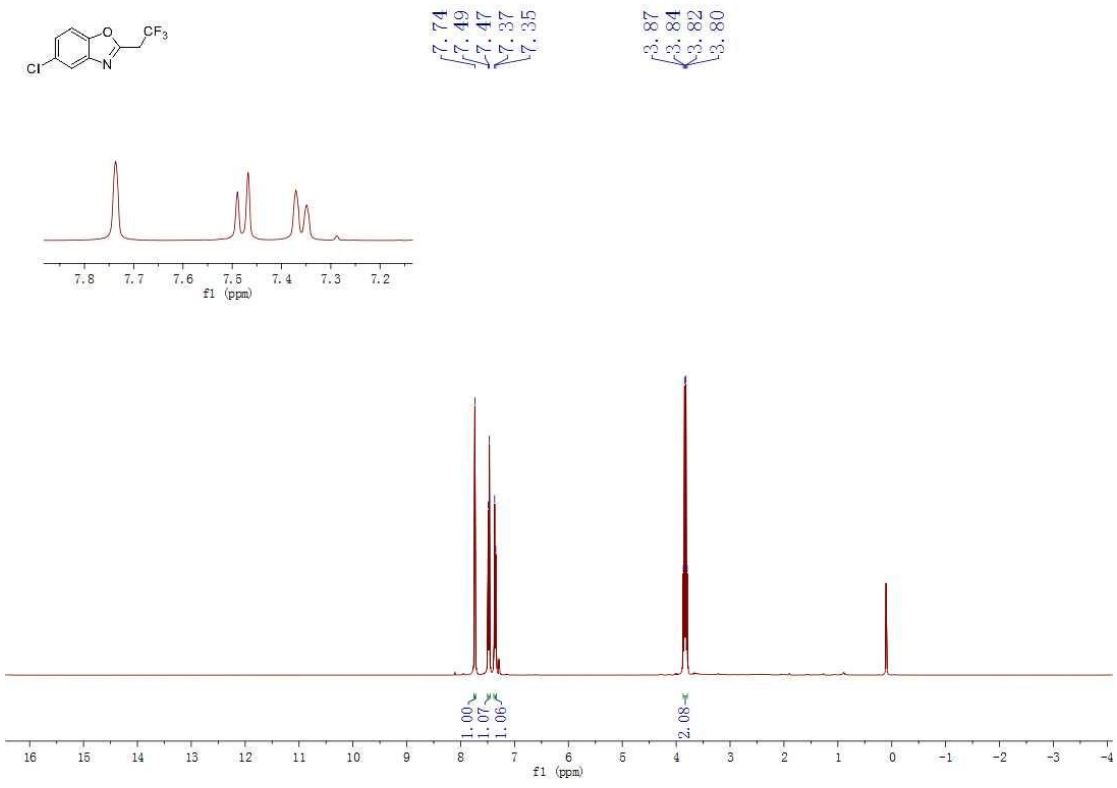
^{13}C NMR spectrum of **3p** in $CDCl_3$



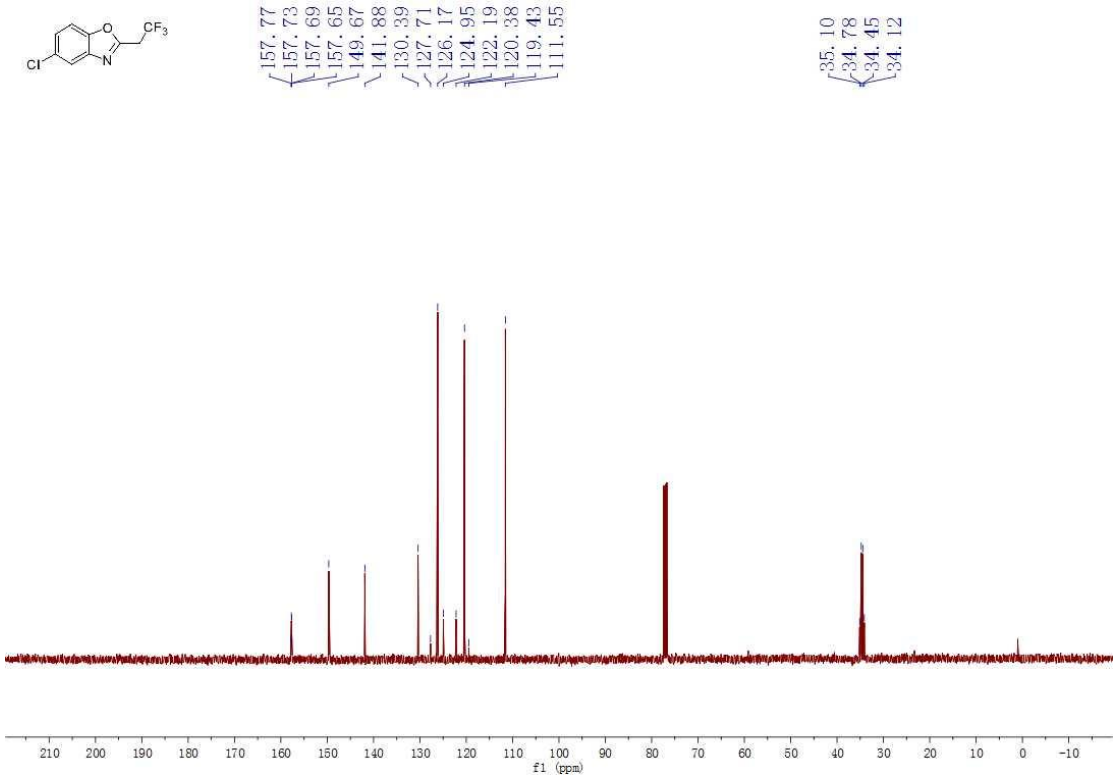
^{19}F NMR spectrum of **3q** in $CDCl_3$



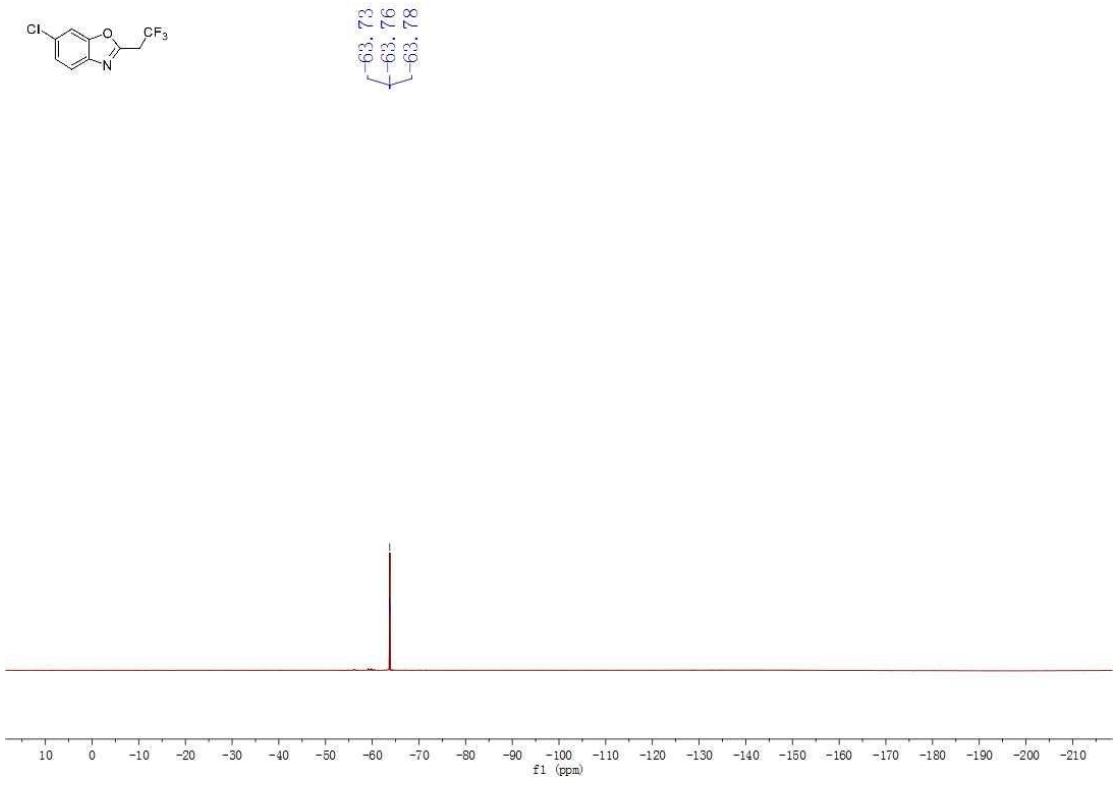
^{1}H NMR spectrum of **3q** in $CDCl_3$



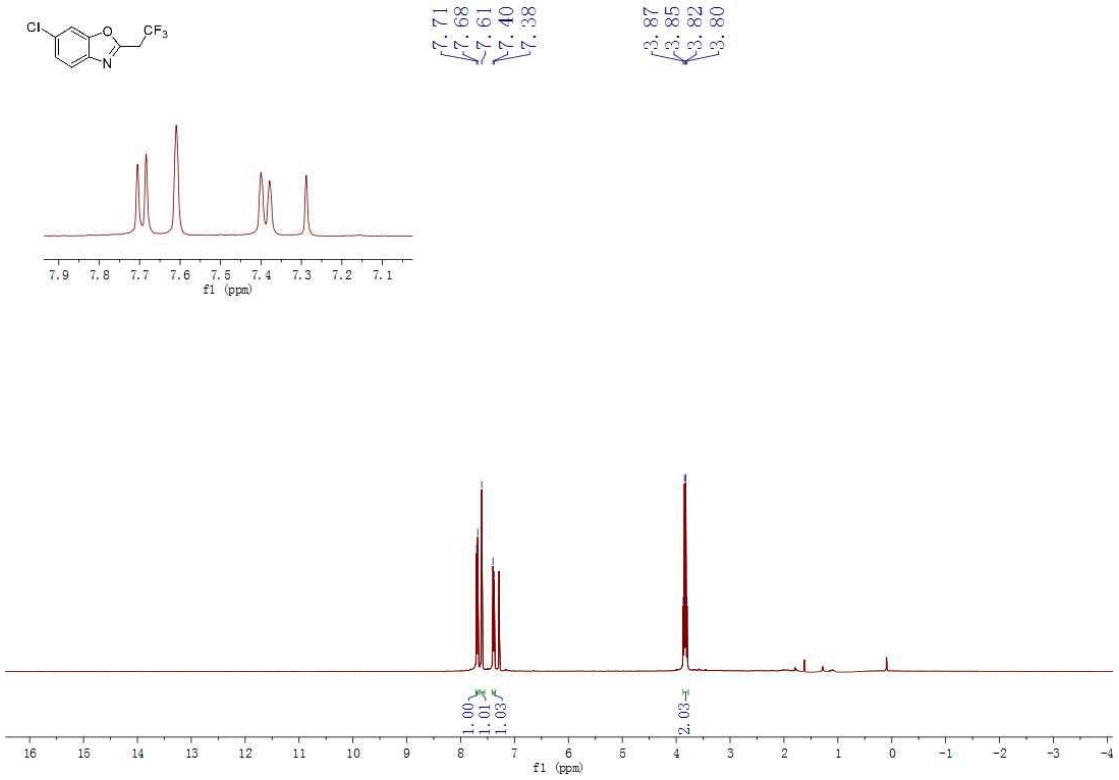
^{13}C NMR spectrum of **3q** in $CDCl_3$



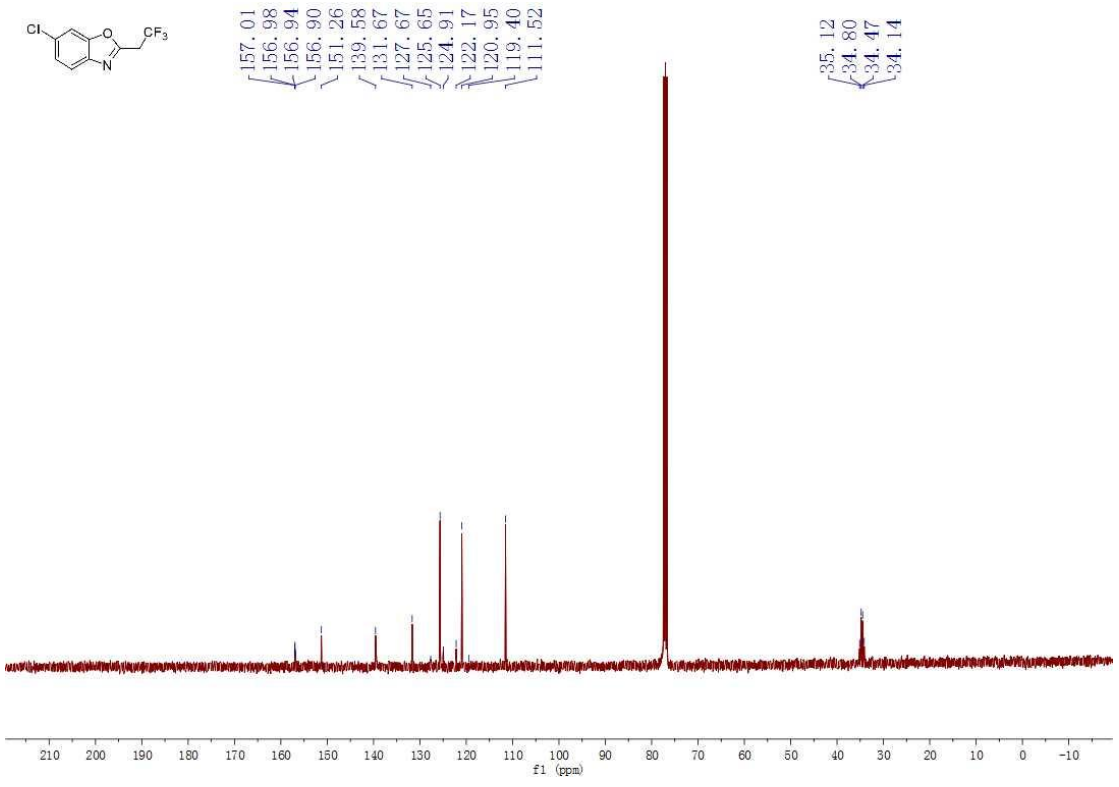
^{19}F NMR spectrum of **3r** in $CDCl_3$



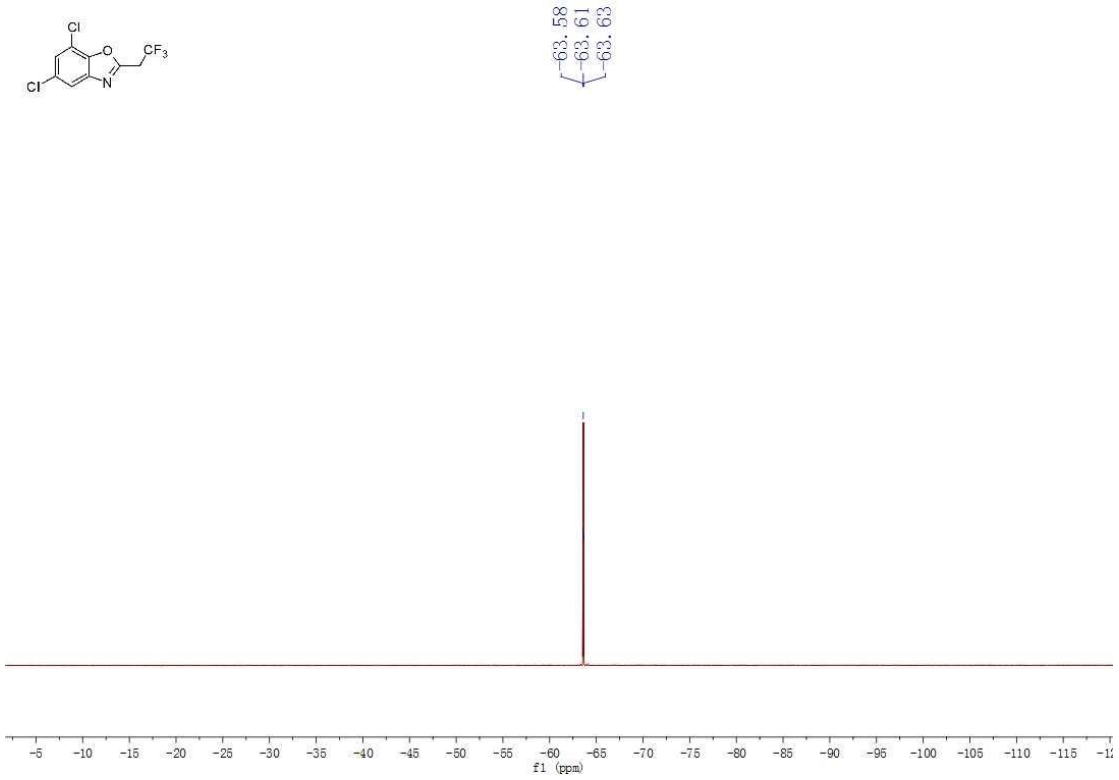
^{1}H NMR spectrum of **3r** in $CDCl_3$



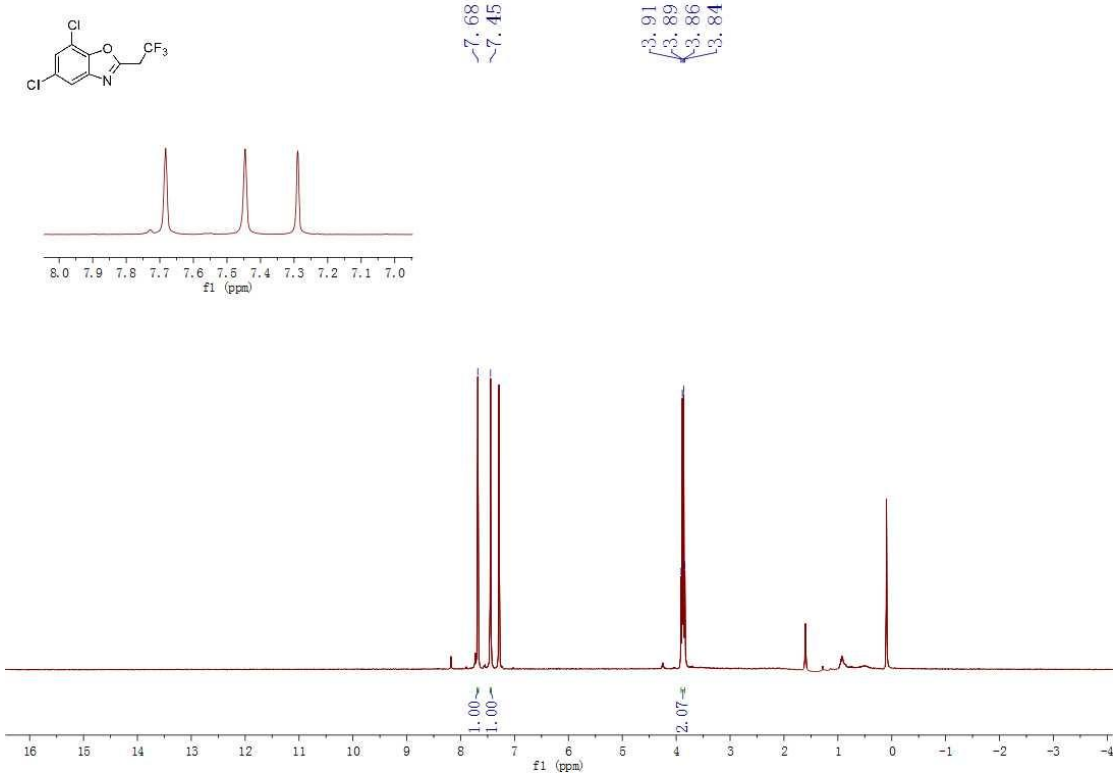
^{13}C NMR spectrum of **3r** in $CDCl_3$



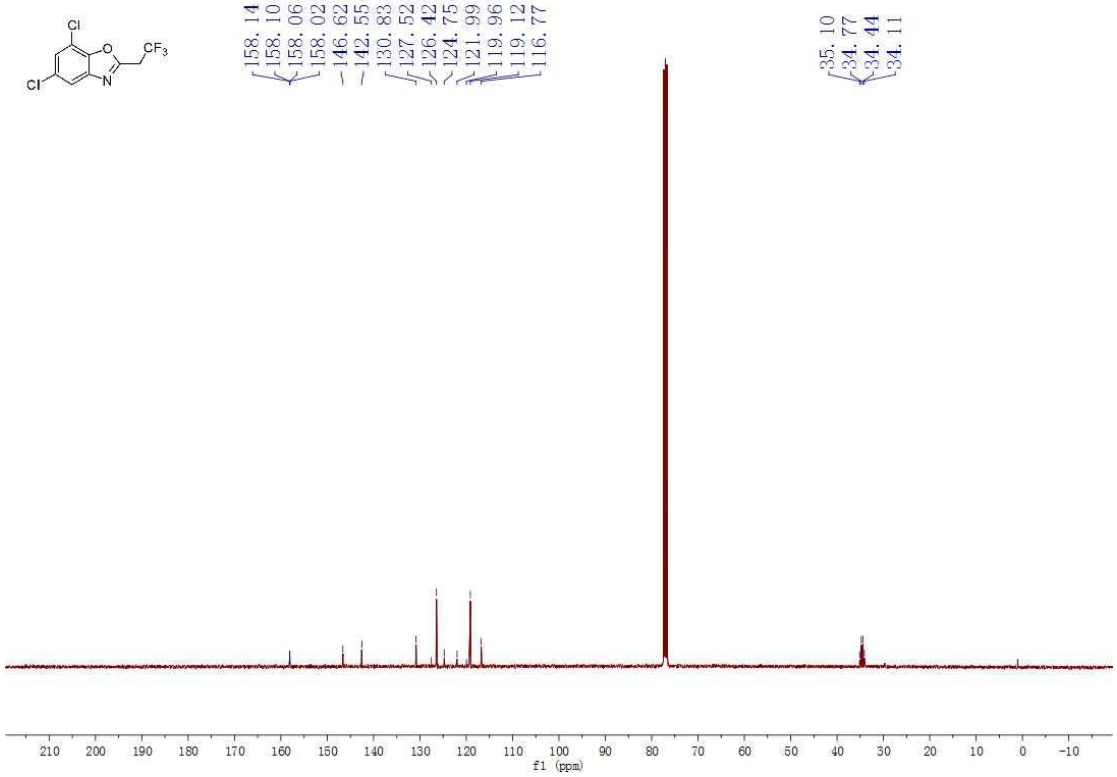
^{19}F NMR spectrum of **3s** in $CDCl_3$



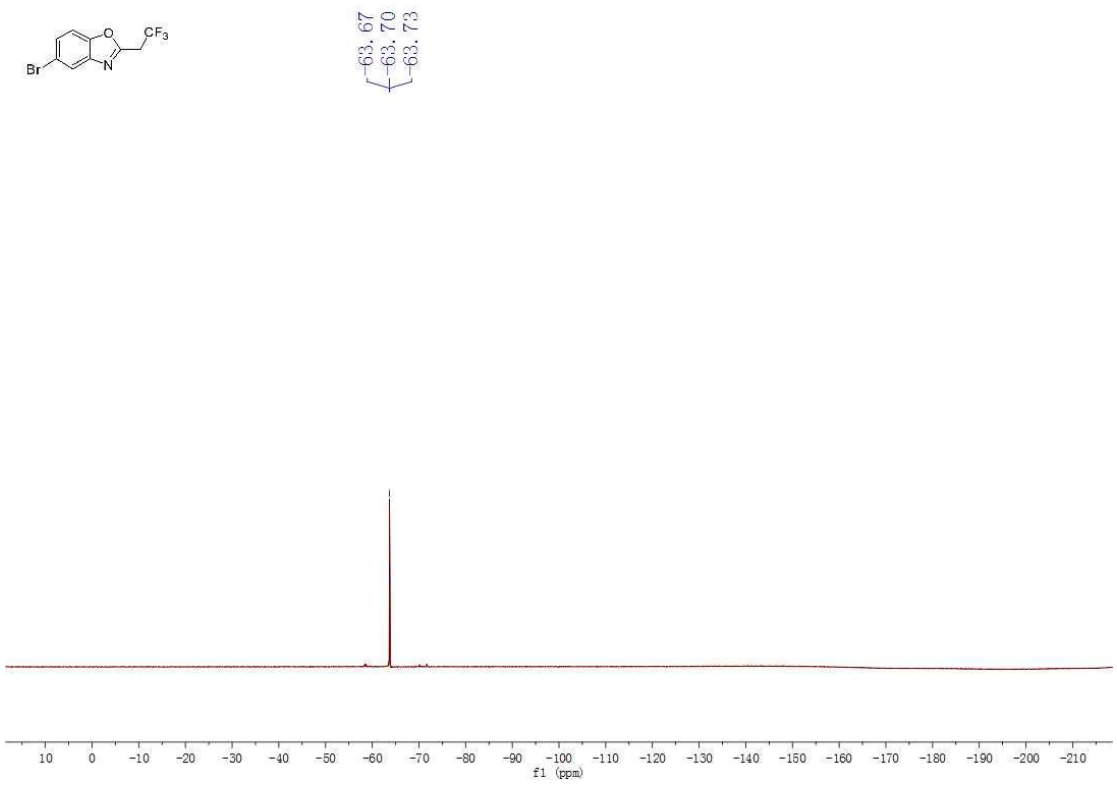
^{1}H NMR spectrum of **3s** in $CDCl_3$



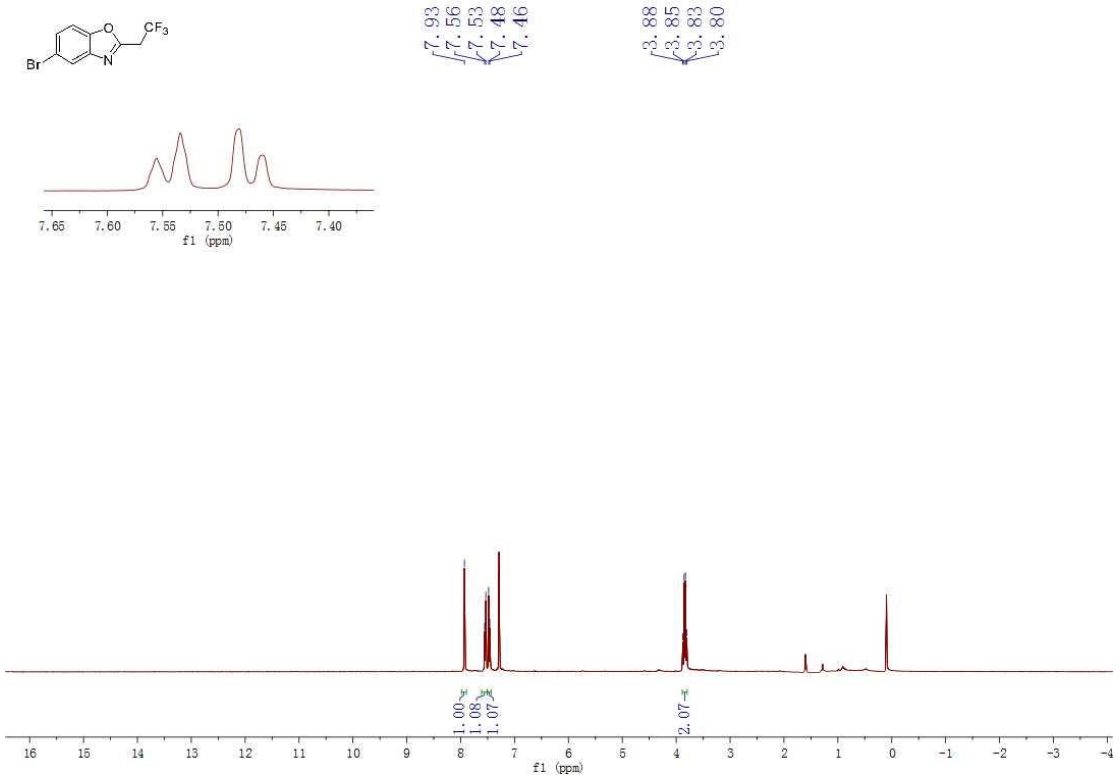
^{13}C NMR spectrum of **3s** in $CDCl_3$



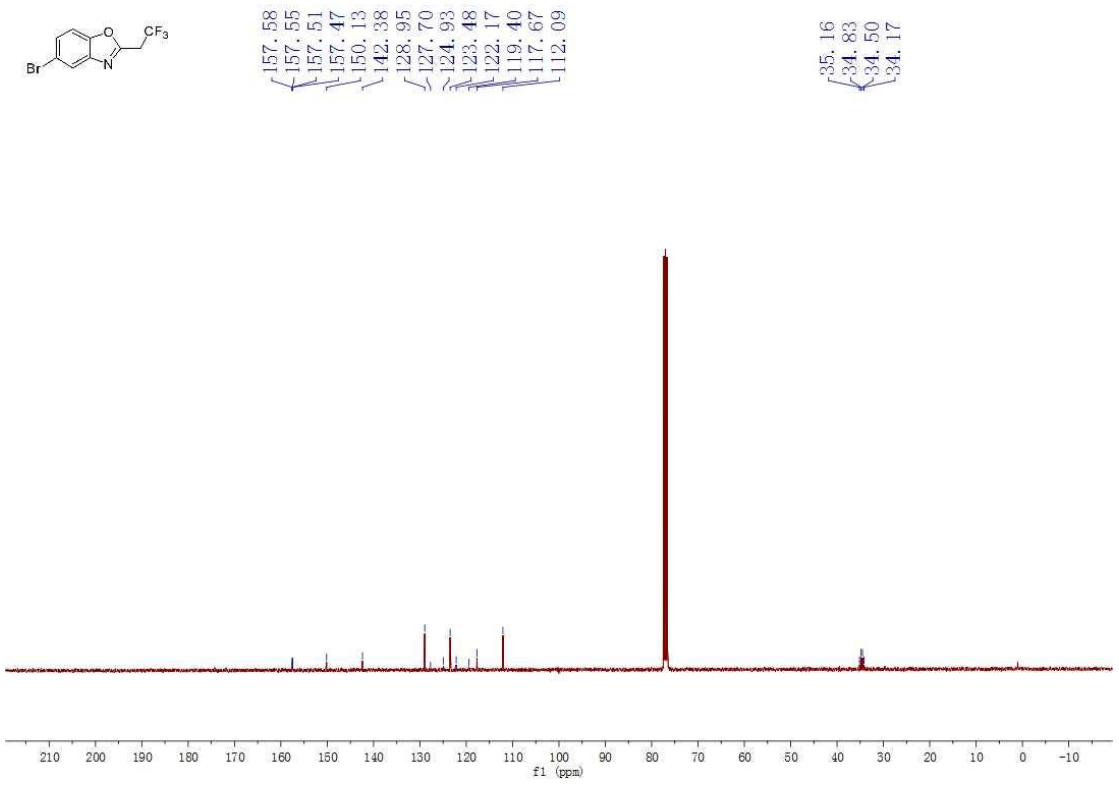
^{19}F NMR spectrum of **3t** in $CDCl_3$



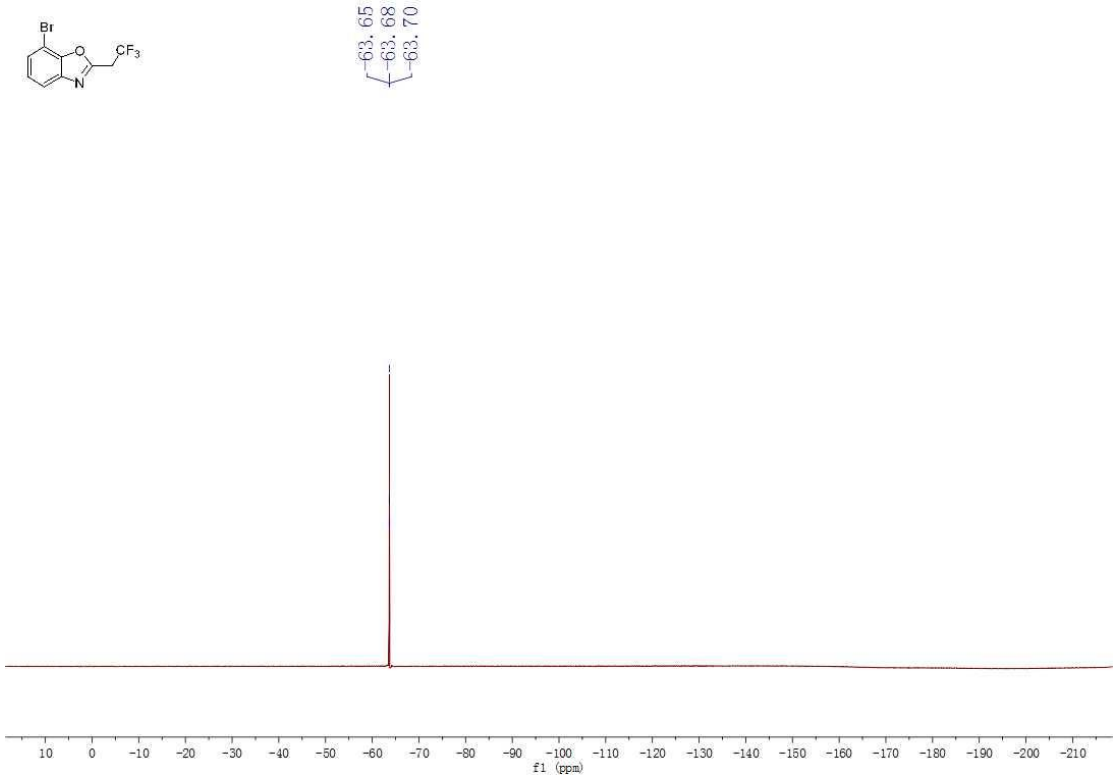
^{1}H NMR spectrum of **3t** in $CDCl_3$



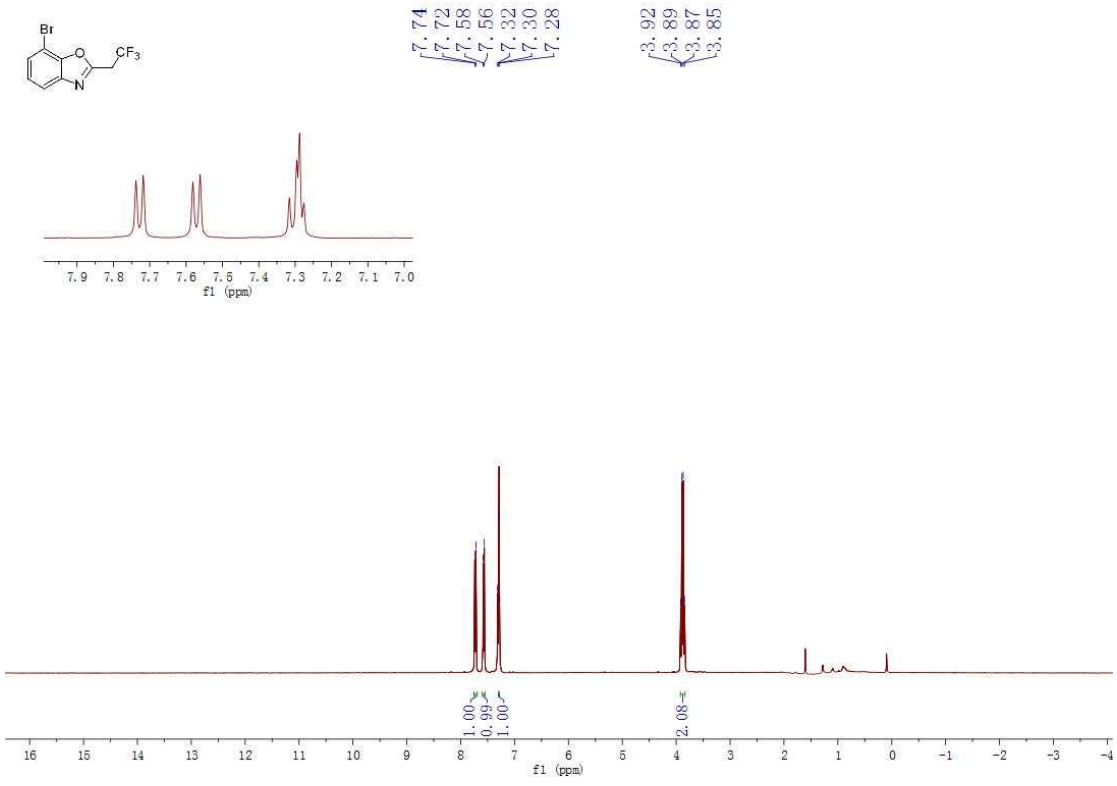
^{13}C NMR spectrum of **3t** in $CDCl_3$



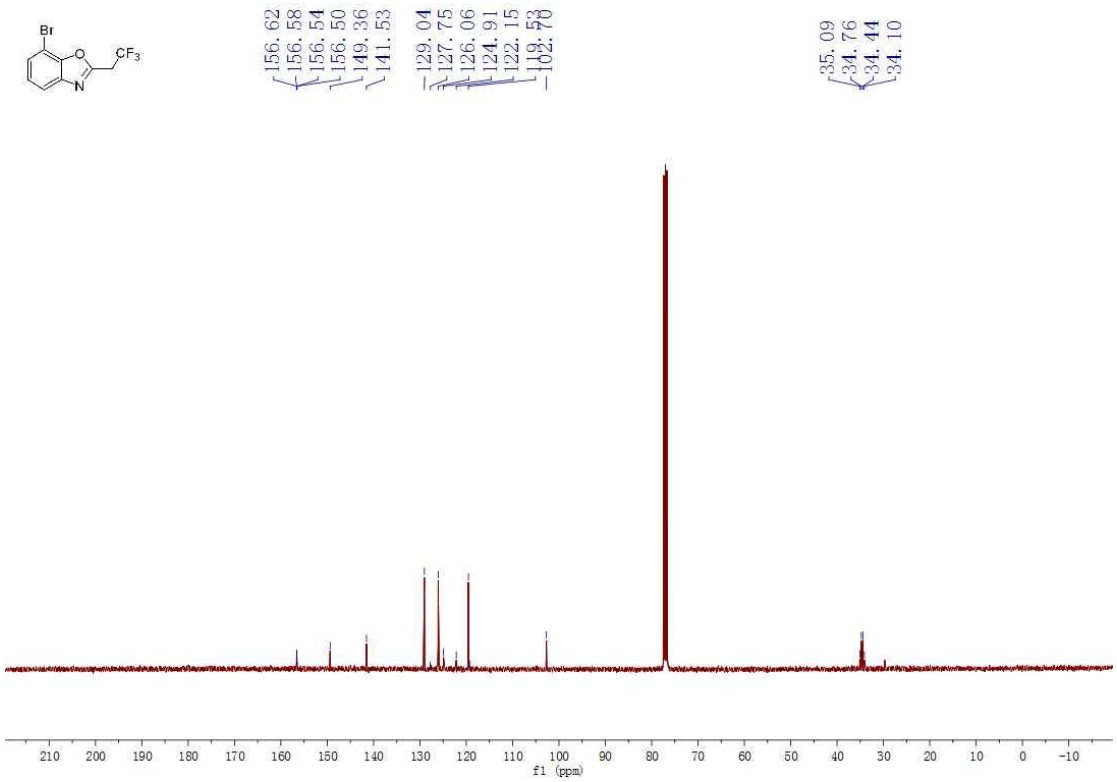
^{19}F NMR spectrum of **3u** in $CDCl_3$



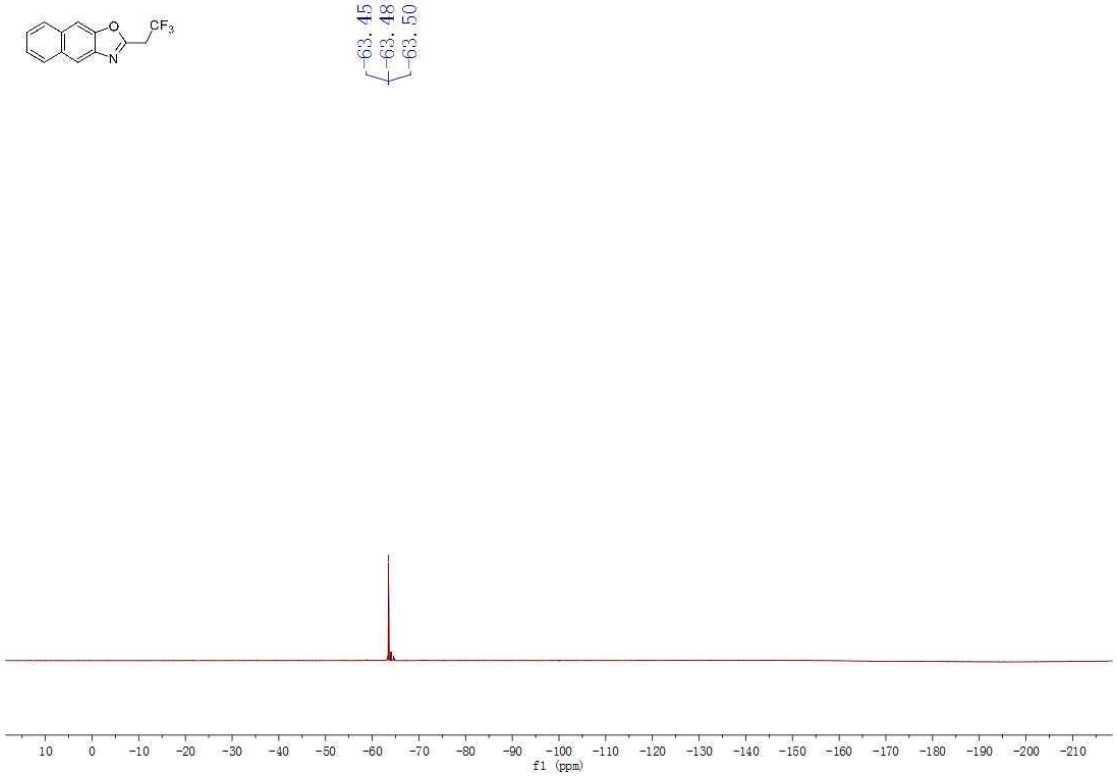
^{1}H NMR spectrum of **3u** in $CDCl_3$



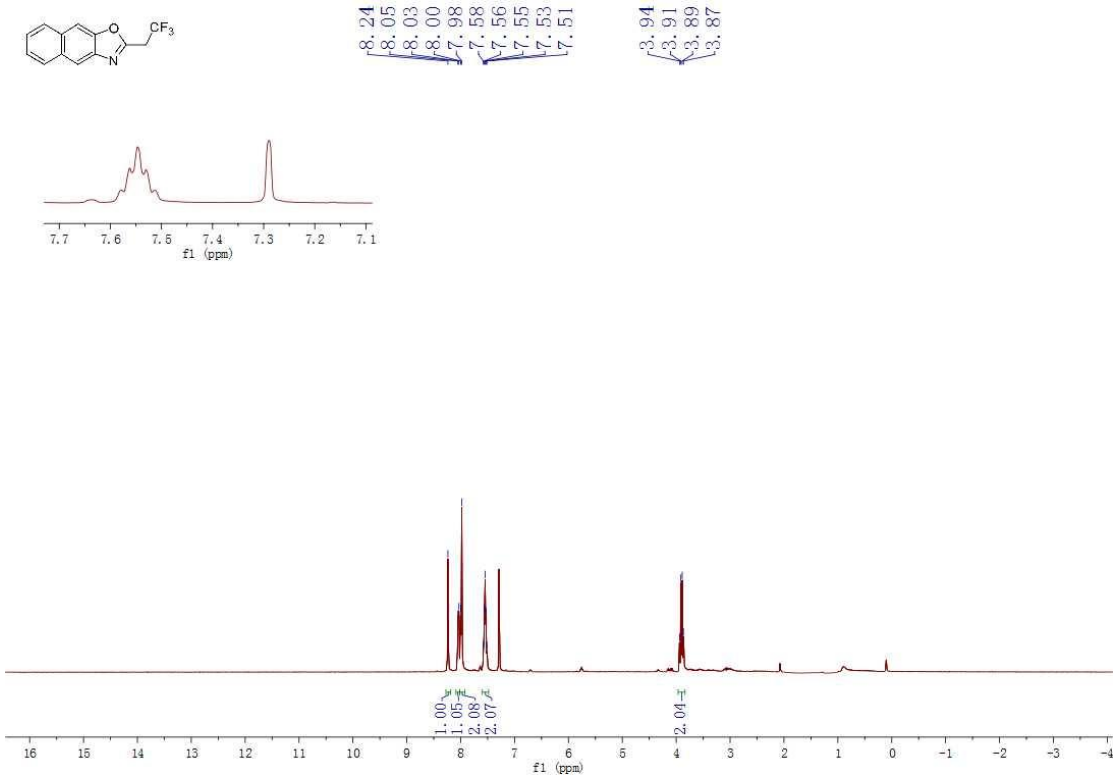
^{13}C NMR spectrum of **3u** in $CDCl_3$



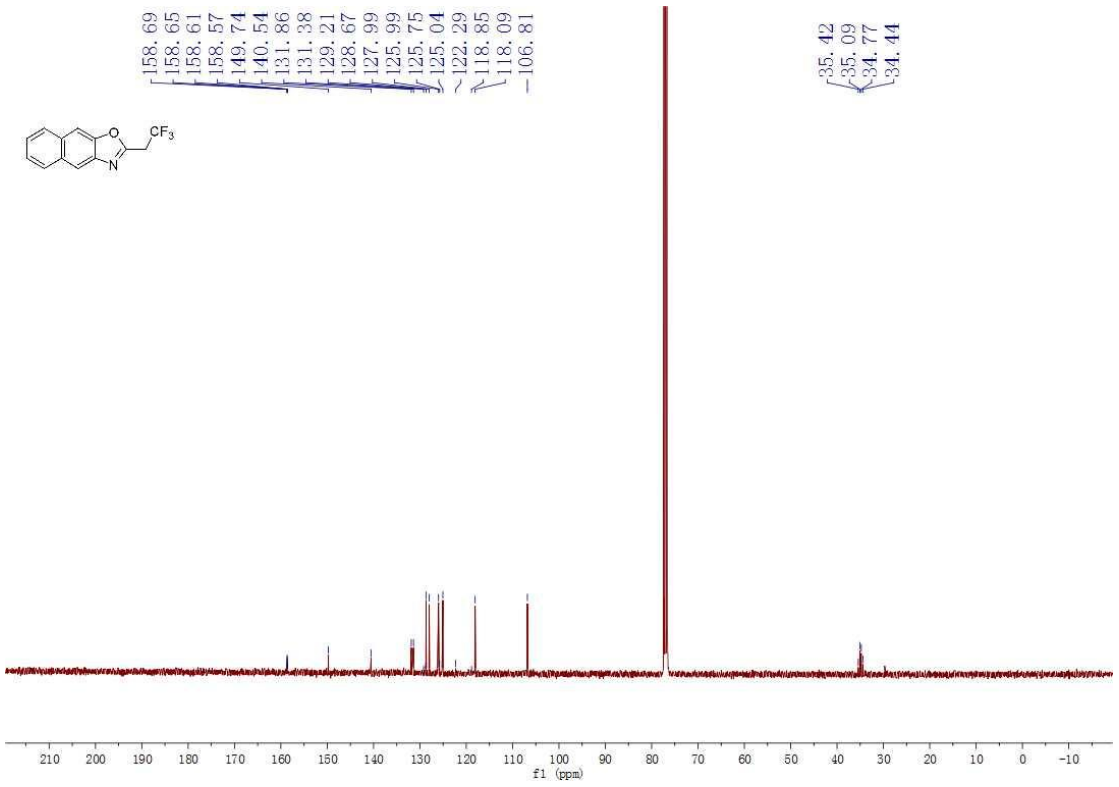
^{19}F NMR spectrum of **3v** in $CDCl_3$



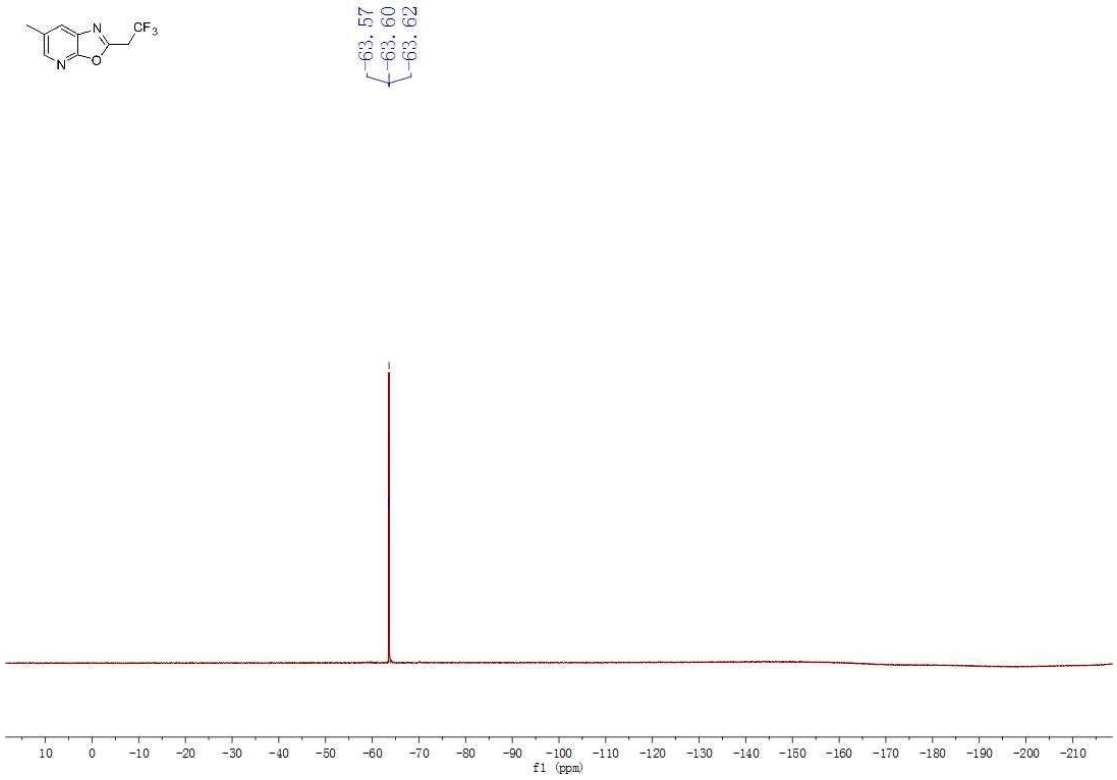
^{1}H NMR spectrum of **3v** in $CDCl_3$



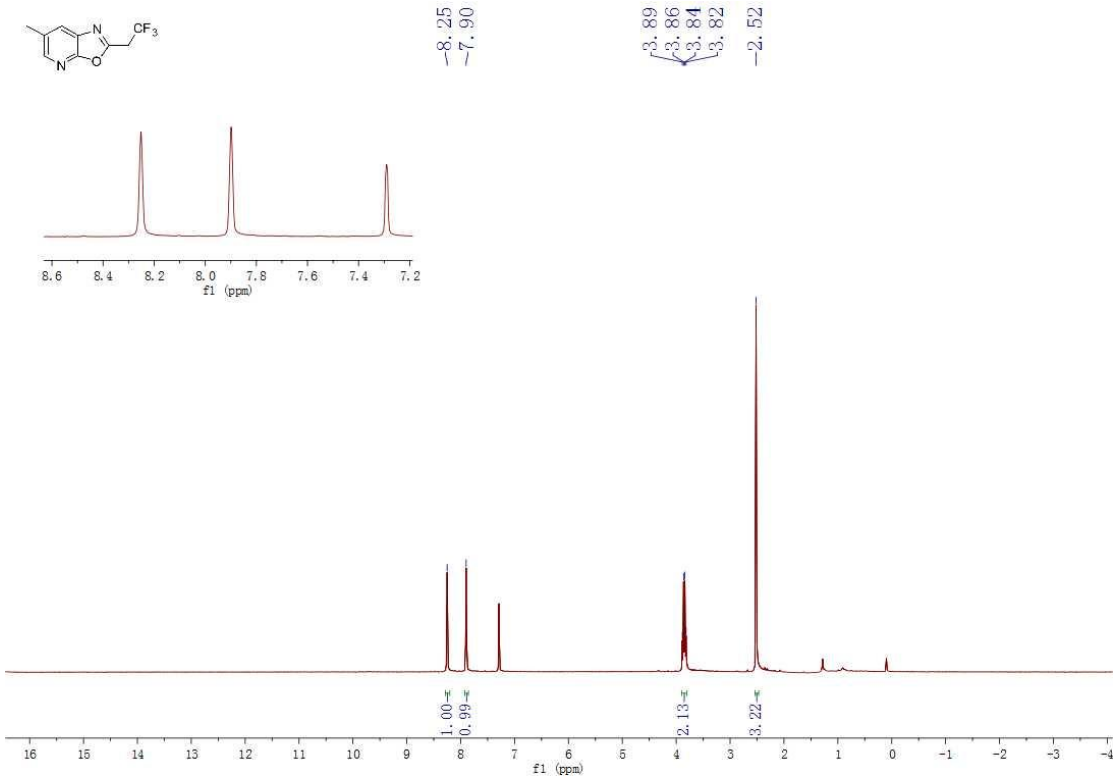
^{13}C NMR spectrum of **3v** in $CDCl_3$



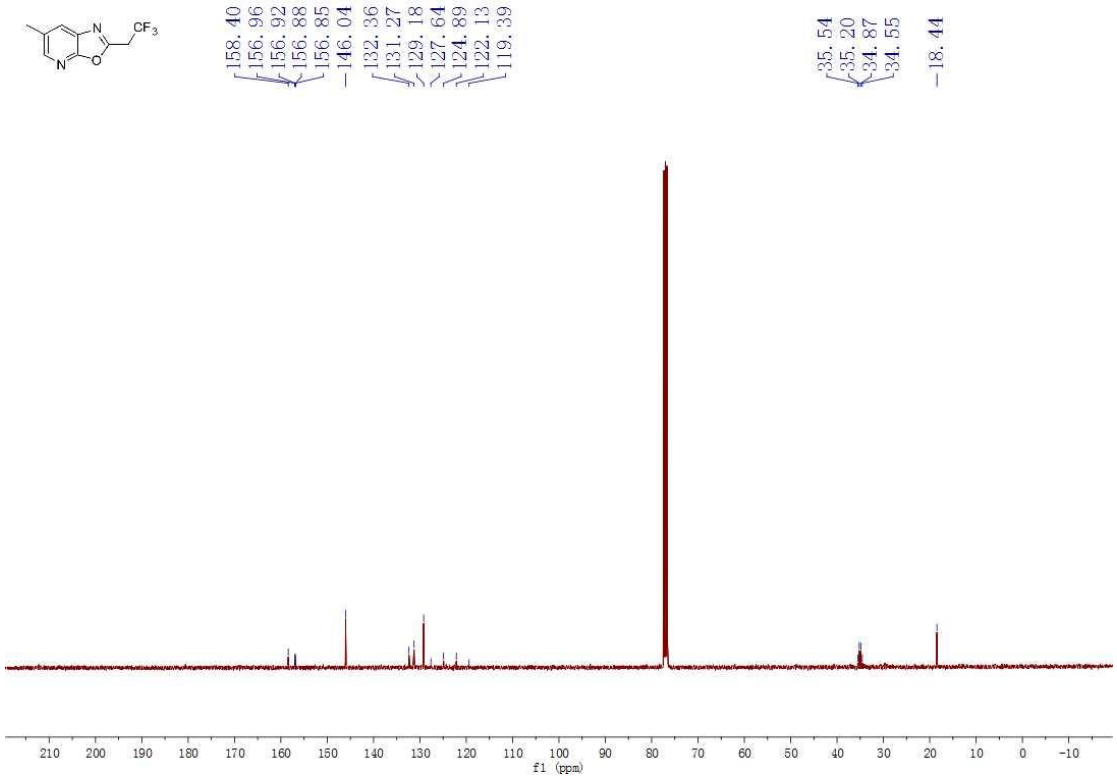
^{19}F NMR spectrum of **3w** in $CDCl_3$



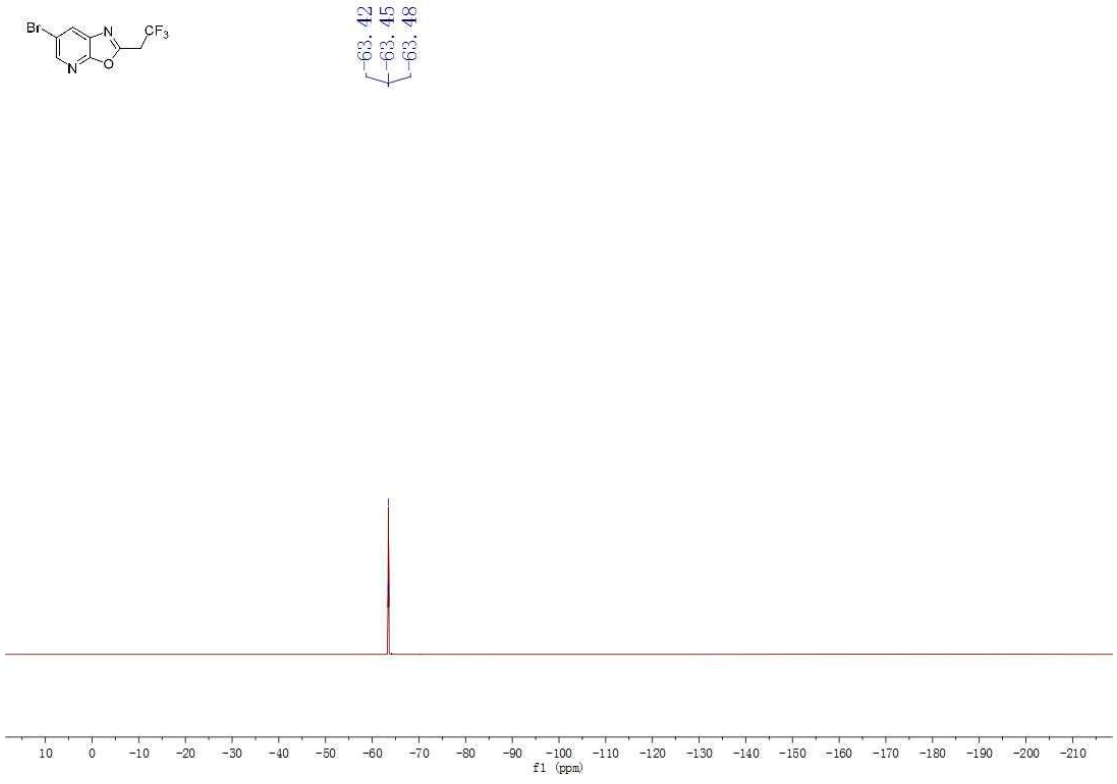
^{1}H NMR spectrum of **3w** in $CDCl_3$



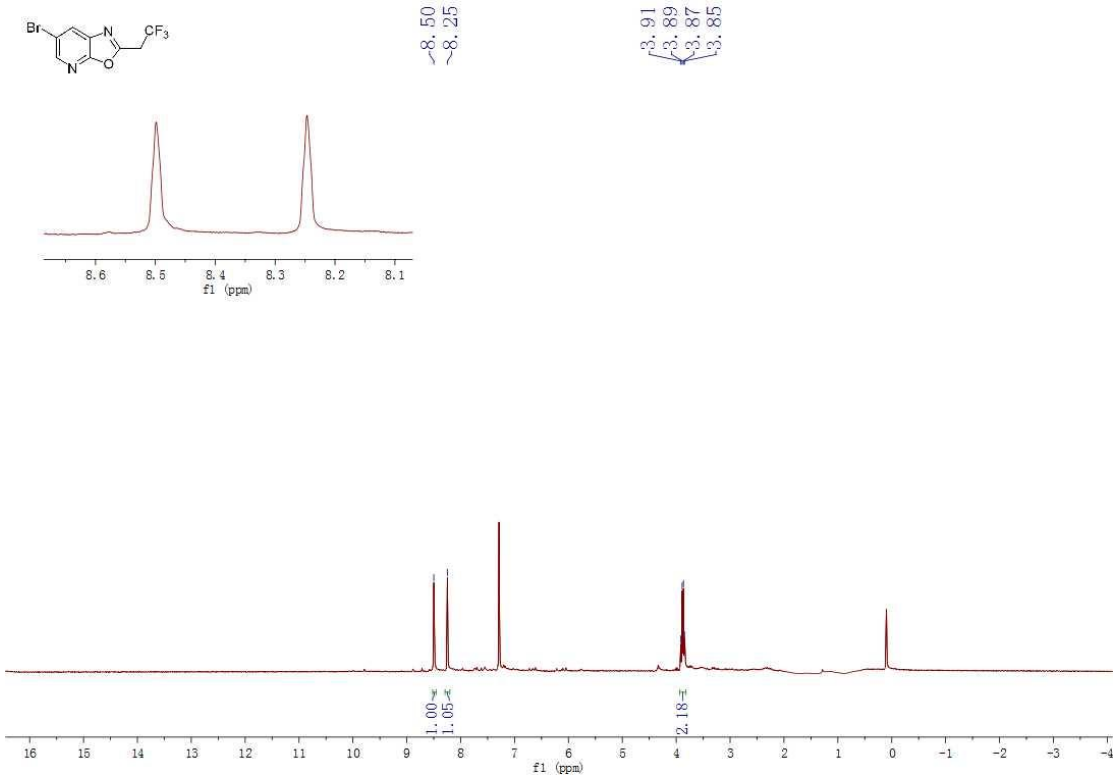
^{13}C NMR spectrum of **3w** in $CDCl_3$



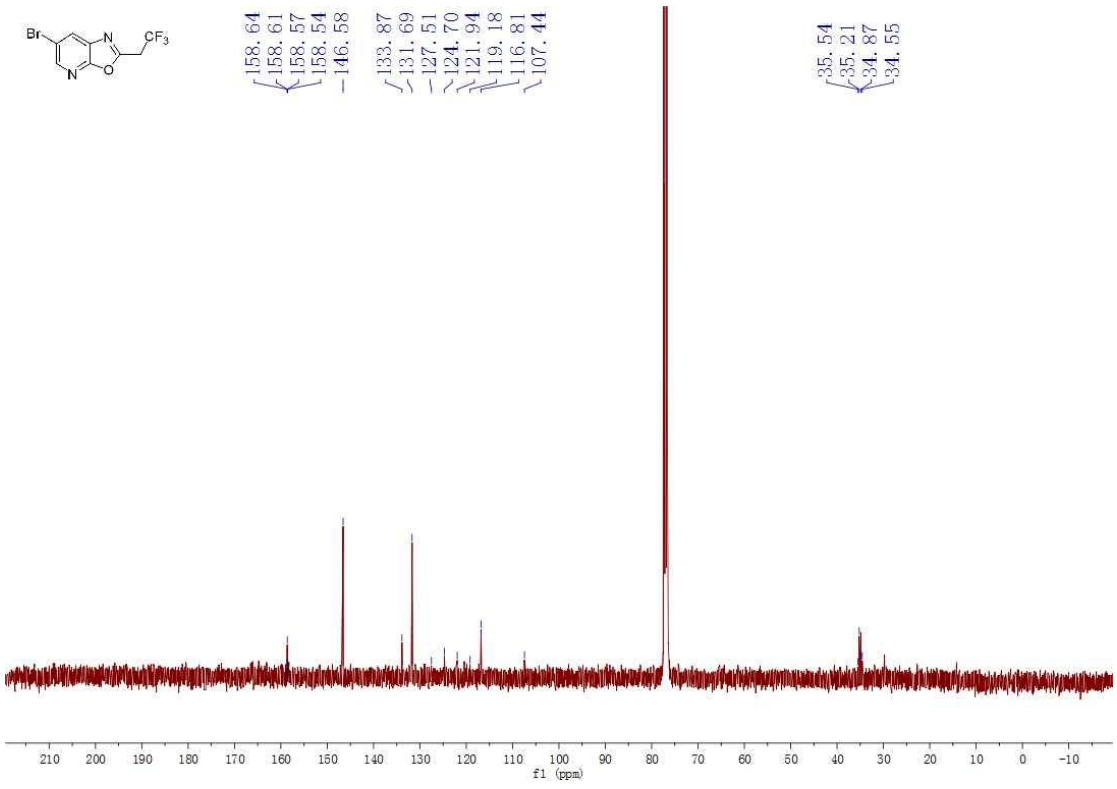
^{19}F NMR spectrum of **3x** in $CDCl_3$



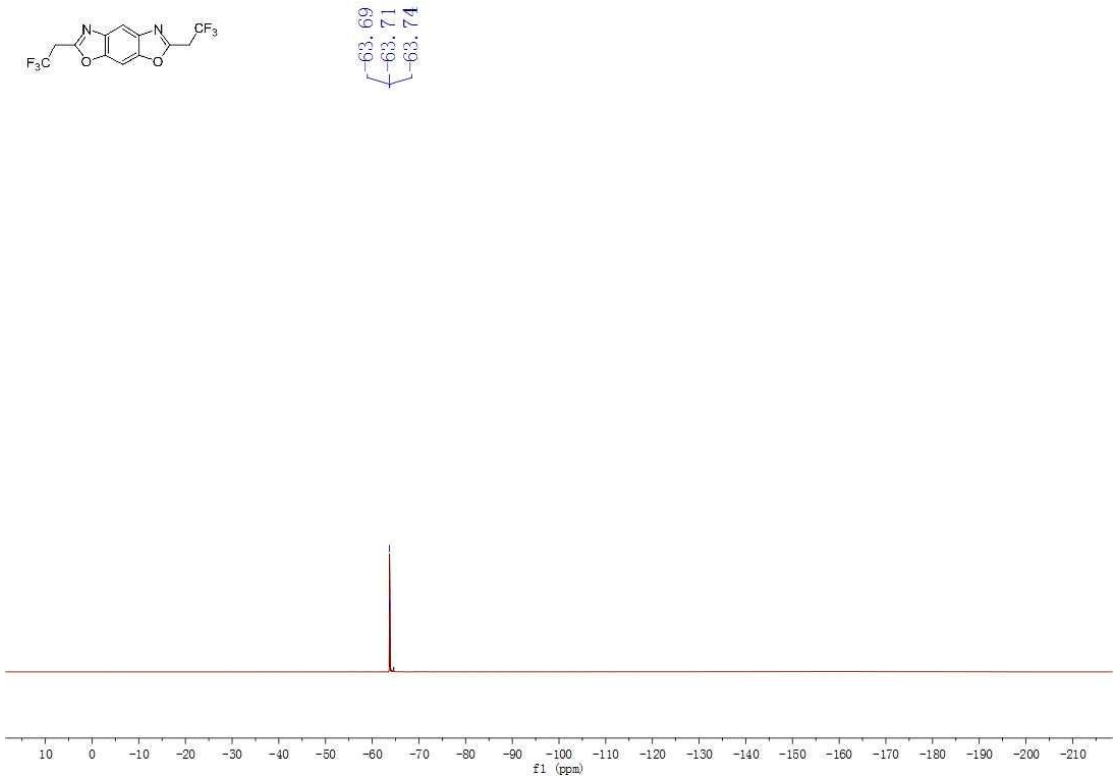
^{1}H NMR spectrum of **3x** in $CDCl_3$



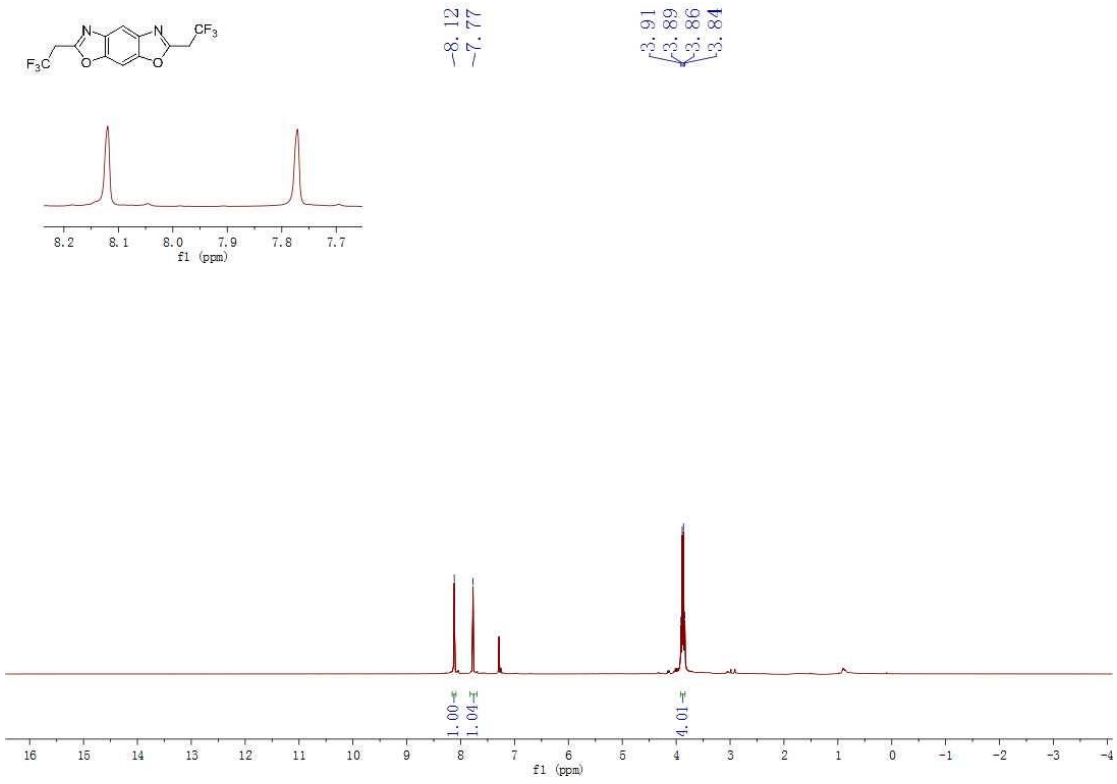
^{13}C NMR spectrum of **3x** in $CDCl_3$



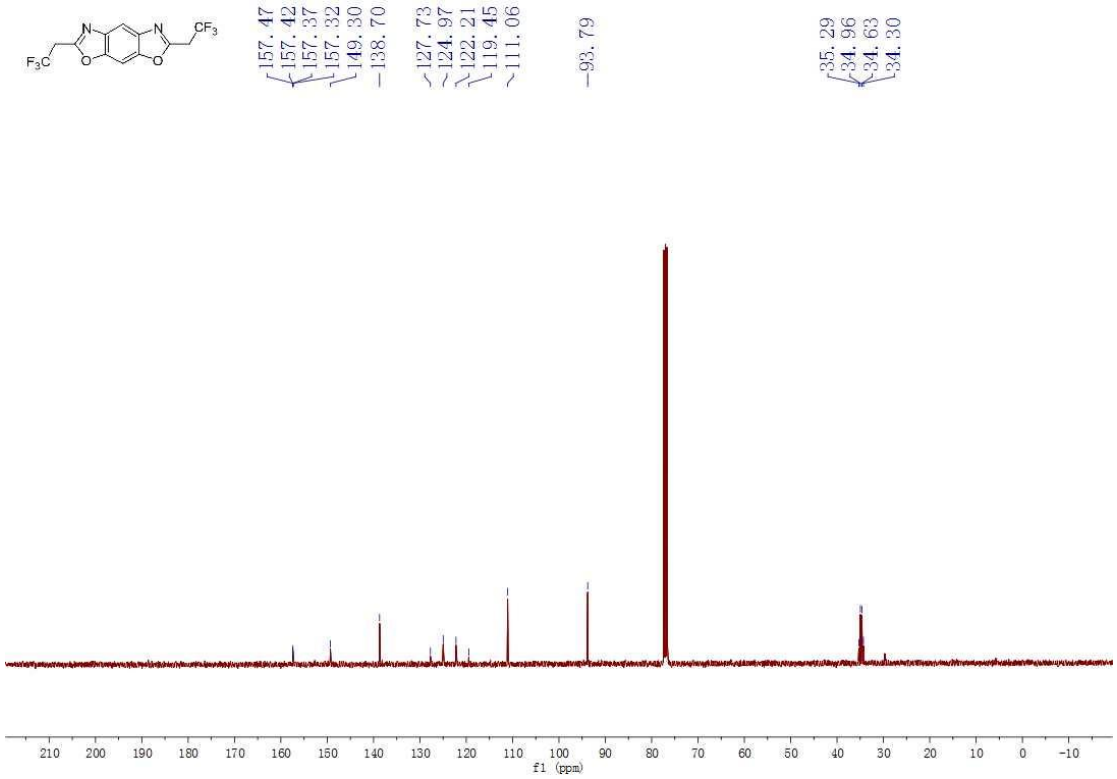
^{19}F NMR spectrum of **3y** in $CDCl_3$



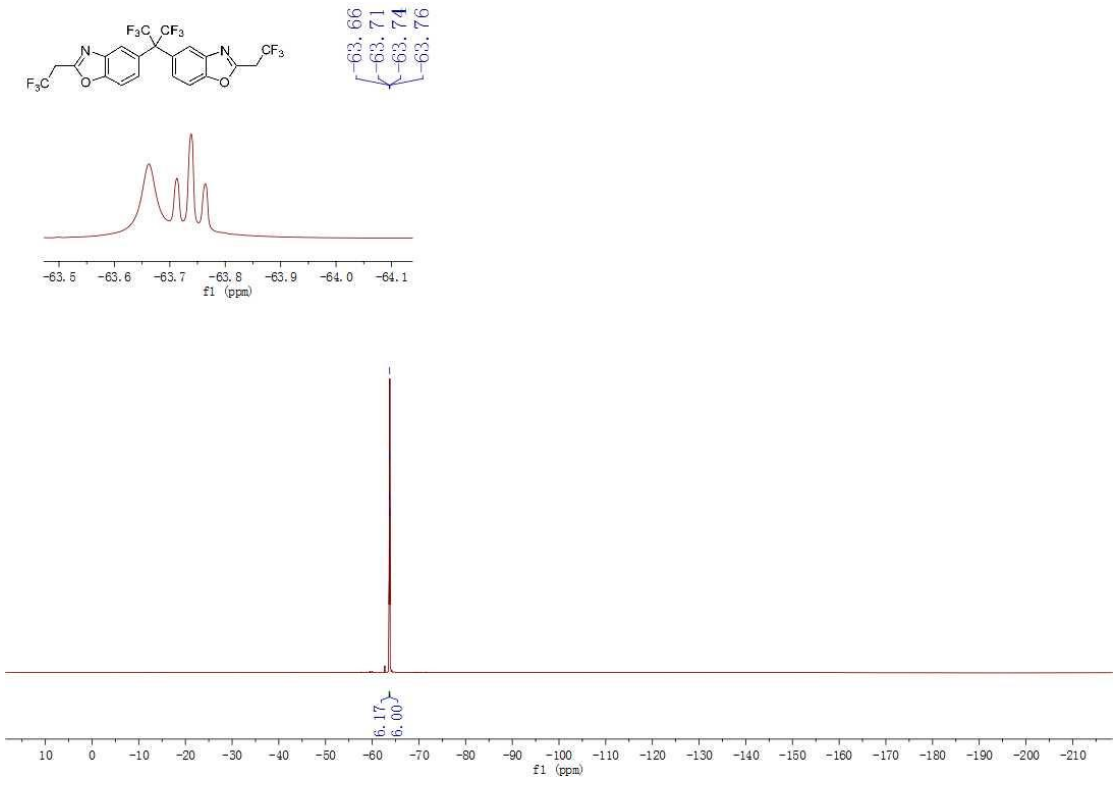
^{1}H NMR spectrum of **3y** in $CDCl_3$



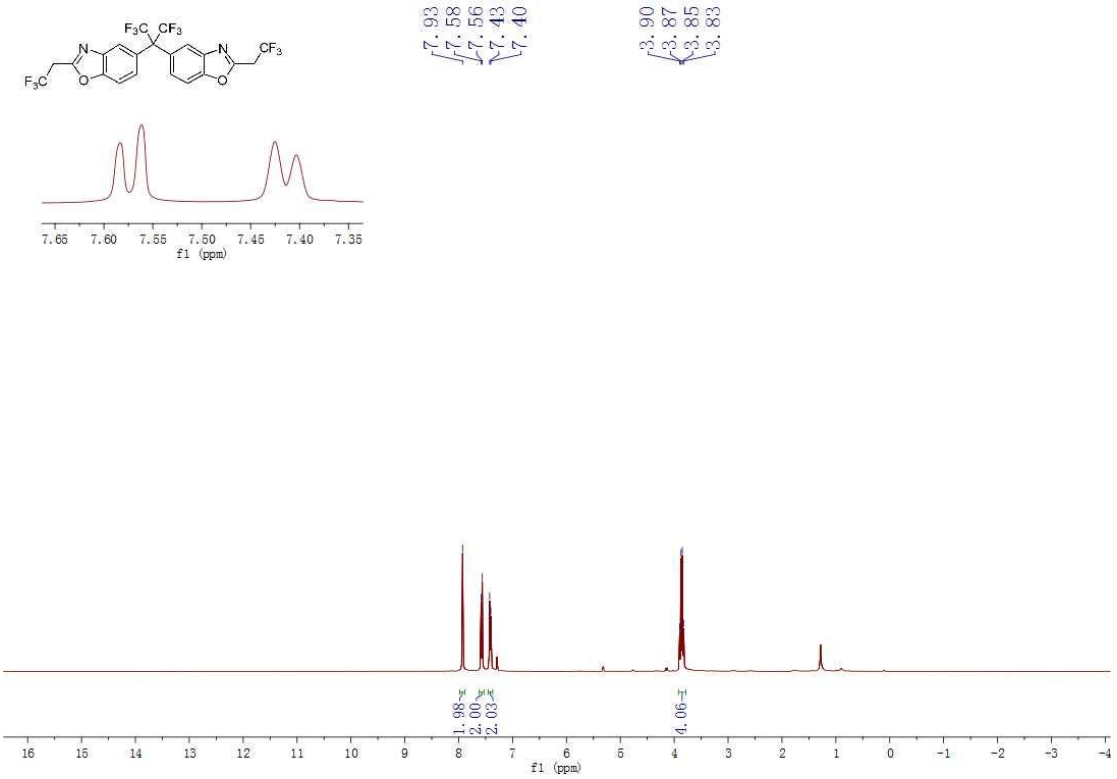
^{13}C NMR spectrum of **3y** in $CDCl_3$



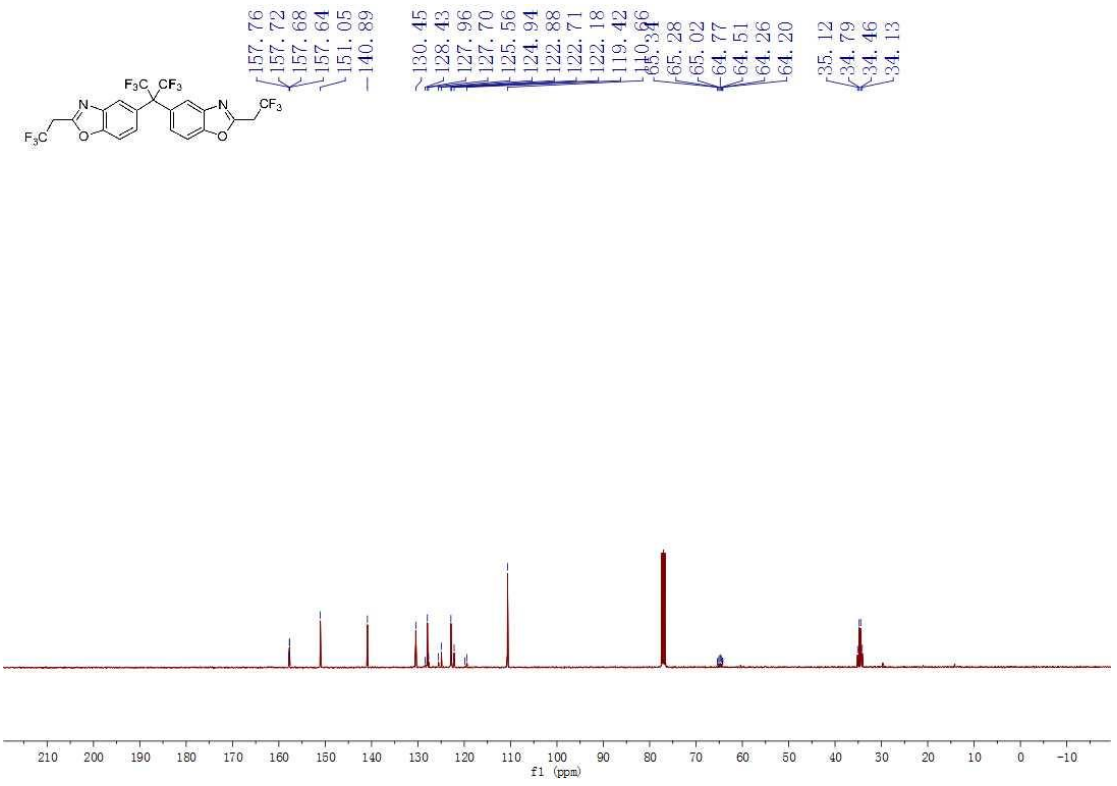
^{19}F NMR spectrum of **3z** in $CDCl_3$



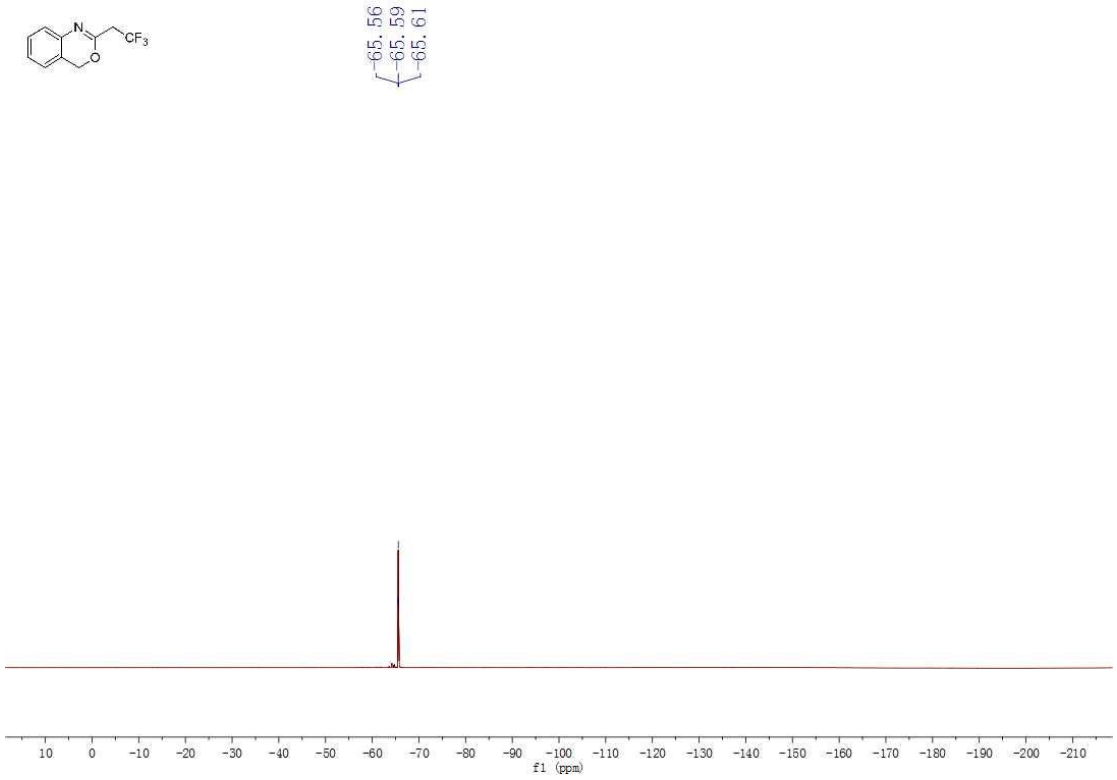
^{1}H NMR spectrum of **3z** in $CDCl_3$



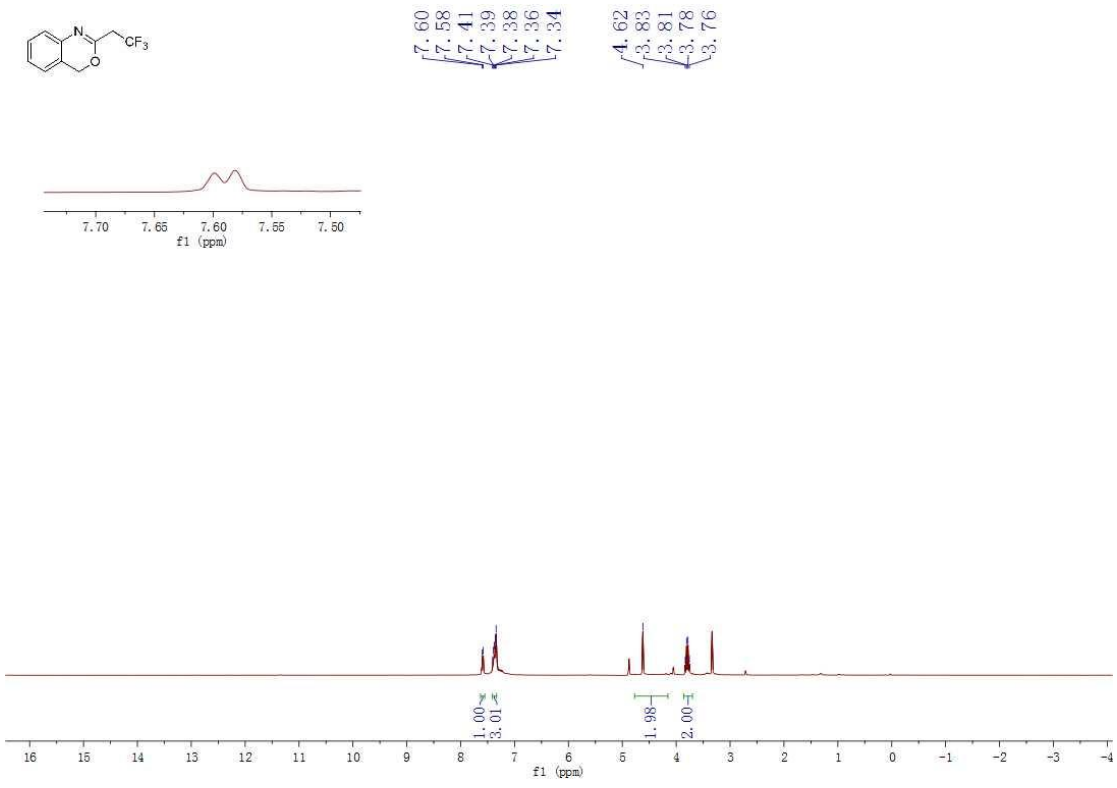
^{13}C NMR spectrum of **3z** in $CDCl_3$



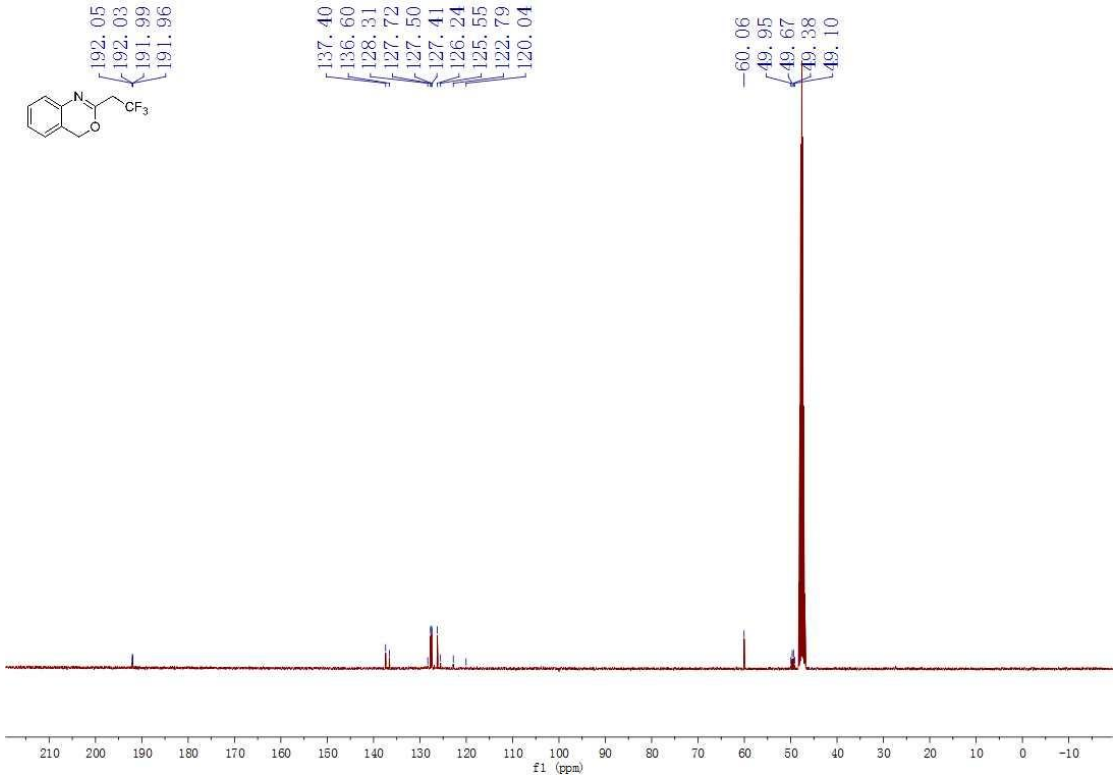
^{19}F NMR spectrum of **3aa** in CD_3OD



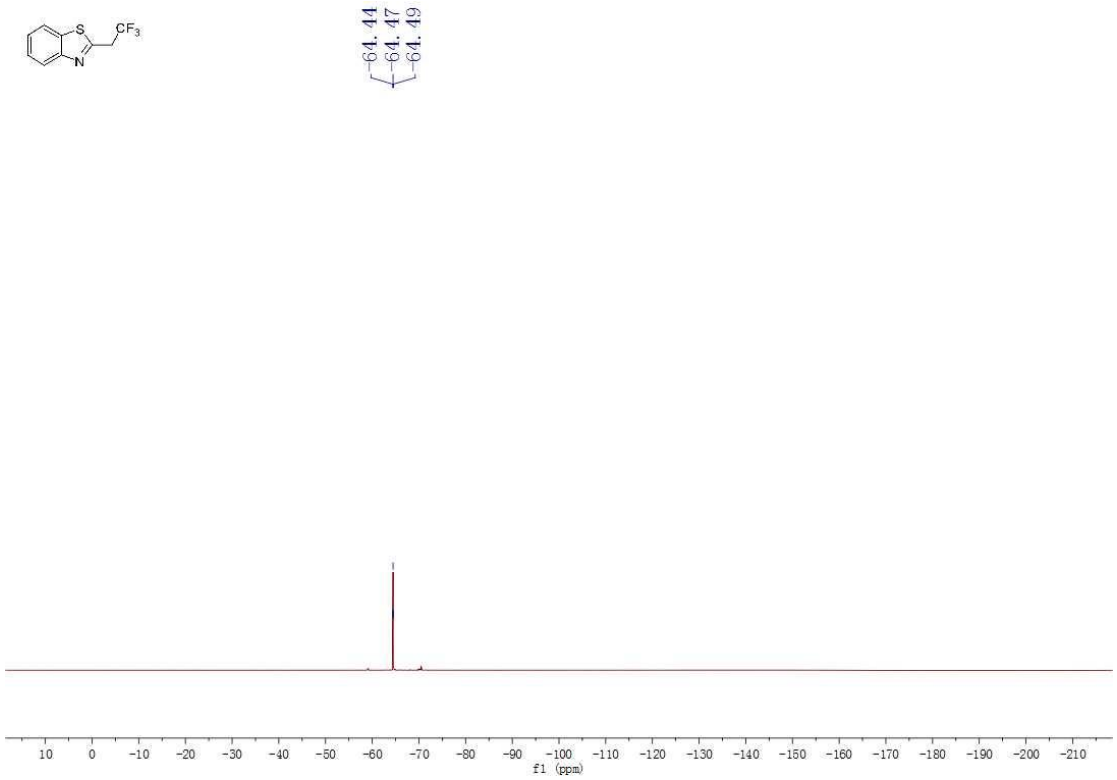
^{1}H NMR spectrum of **3aa** in CD_3OD



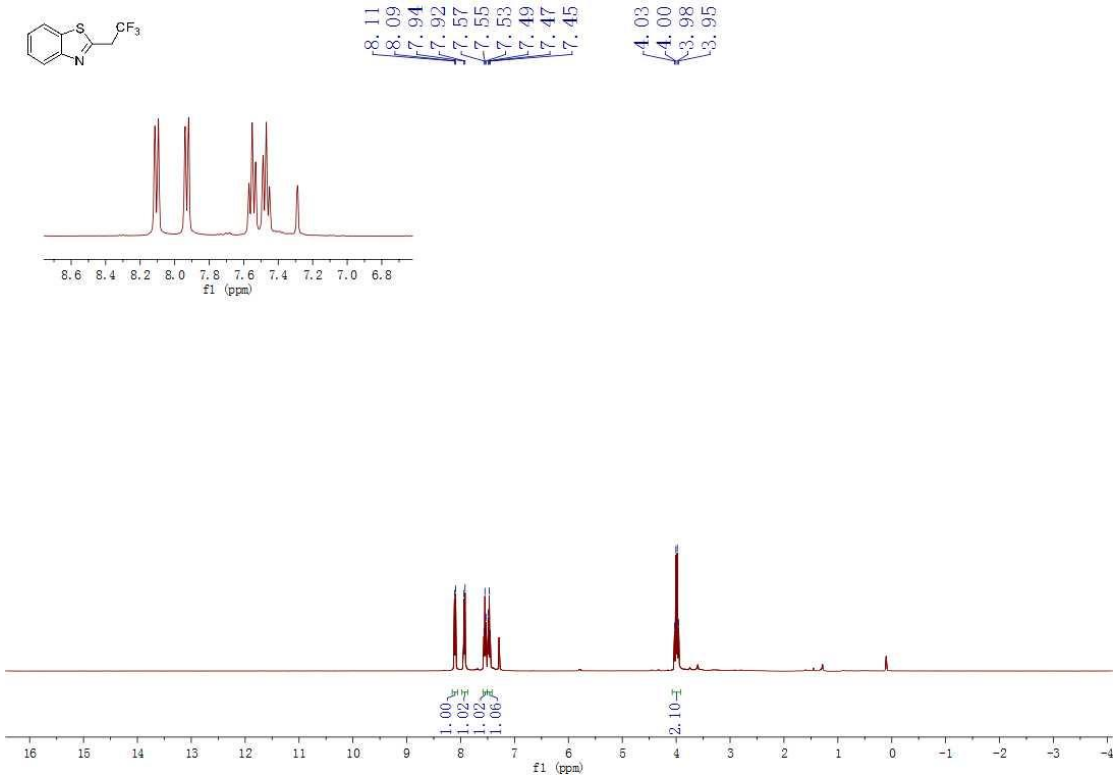
^{13}C NMR spectrum of **3aa** in CD_3OD



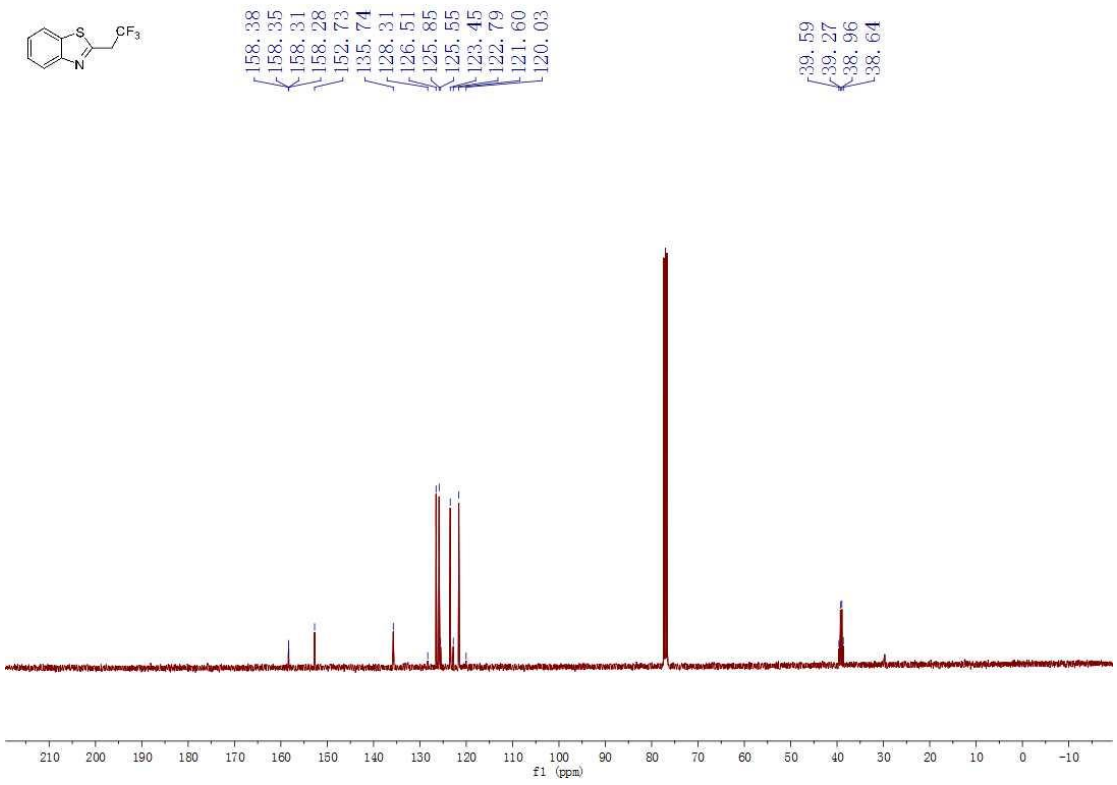
^{19}F NMR spectrum of **4a** in $CDCl_3$



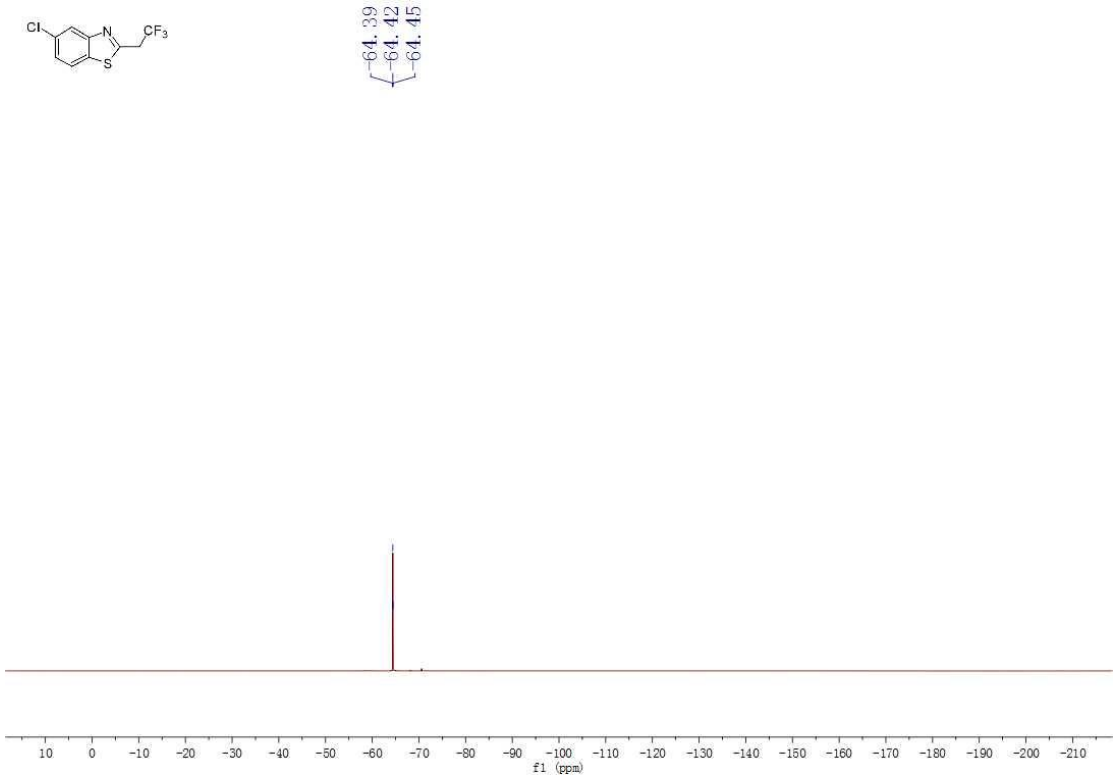
^{1}H NMR spectrum of **4a** in $CDCl_3$



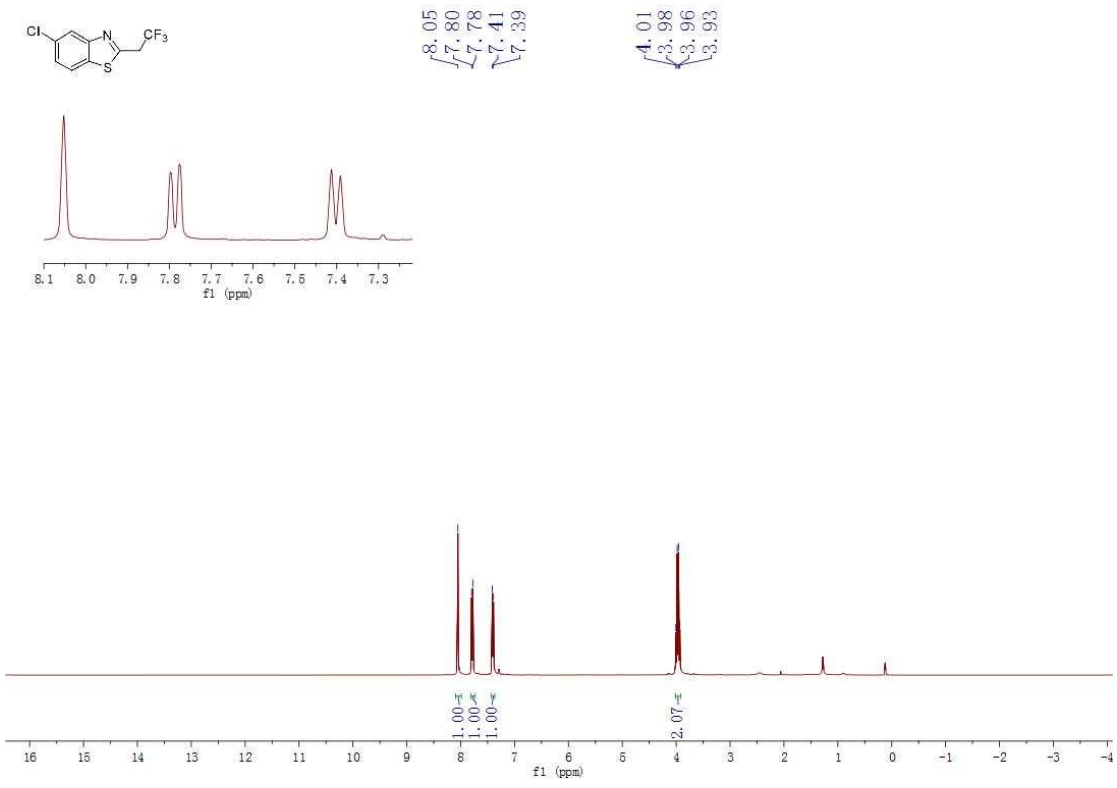
^{13}C NMR spectrum of **4a** in $CDCl_3$



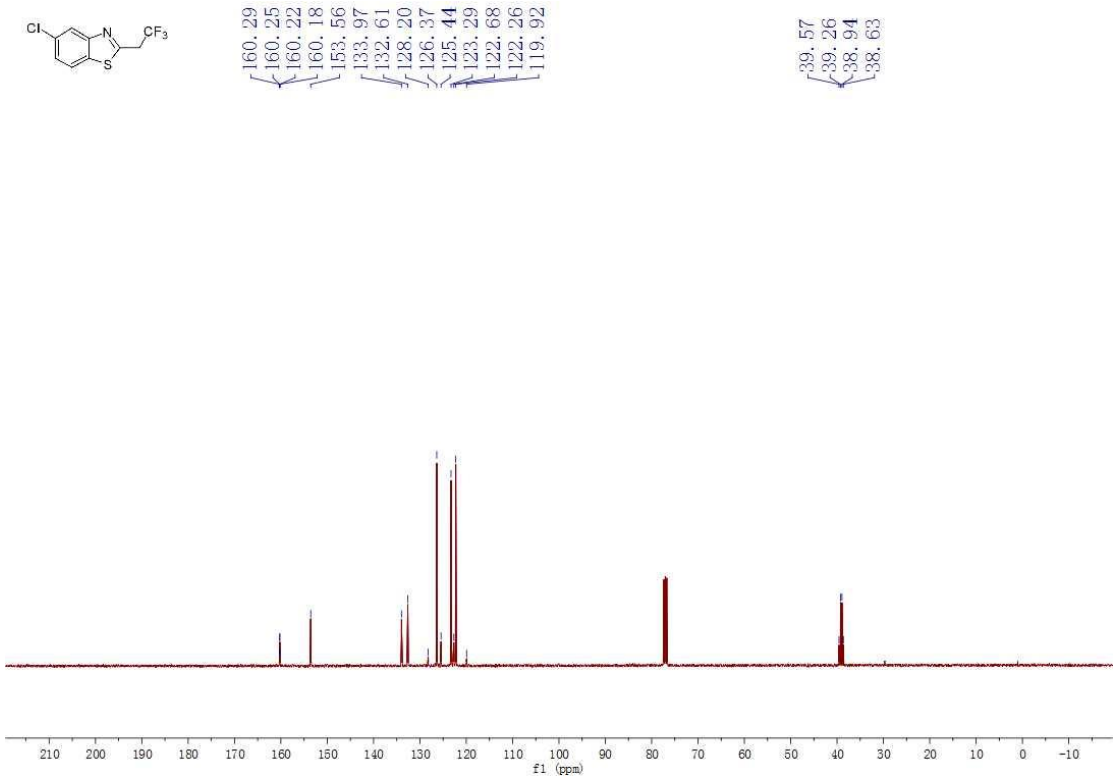
^{19}F NMR spectrum of **4b** in $CDCl_3$



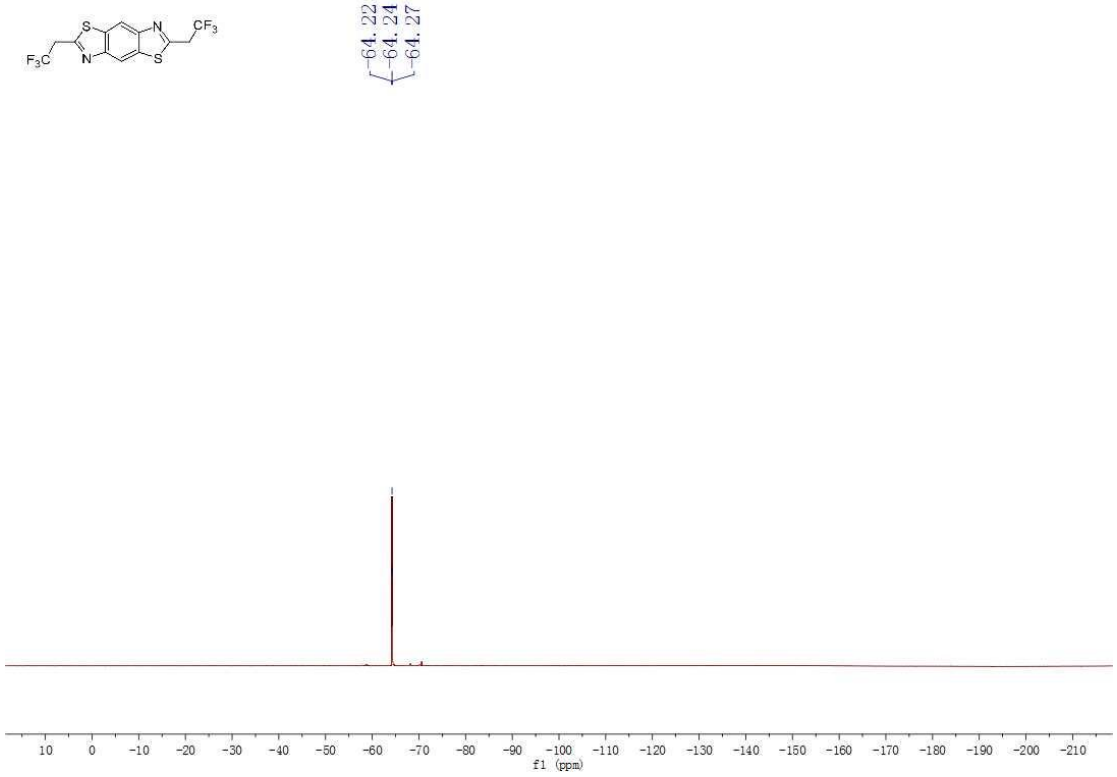
^{1}H NMR spectrum of **4b** in $CDCl_3$



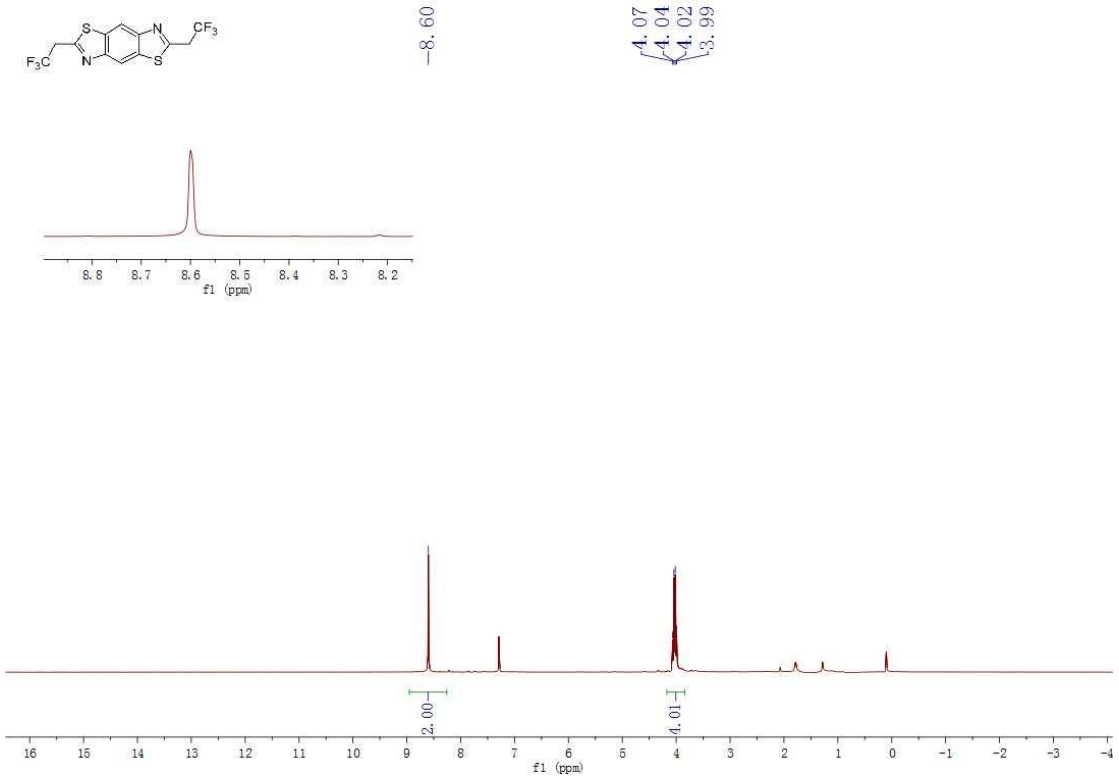
^{13}C NMR spectrum of **4b** in $CDCl_3$



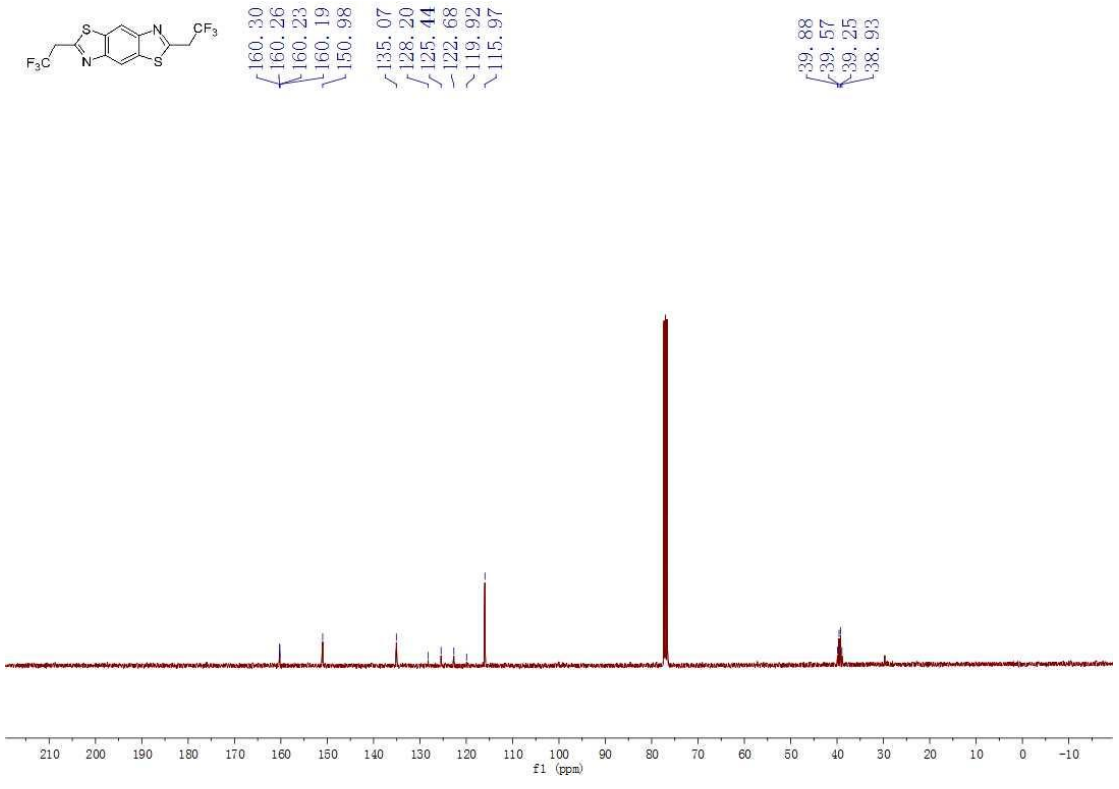
^{19}F NMR spectrum of **4c** in $CDCl_3$



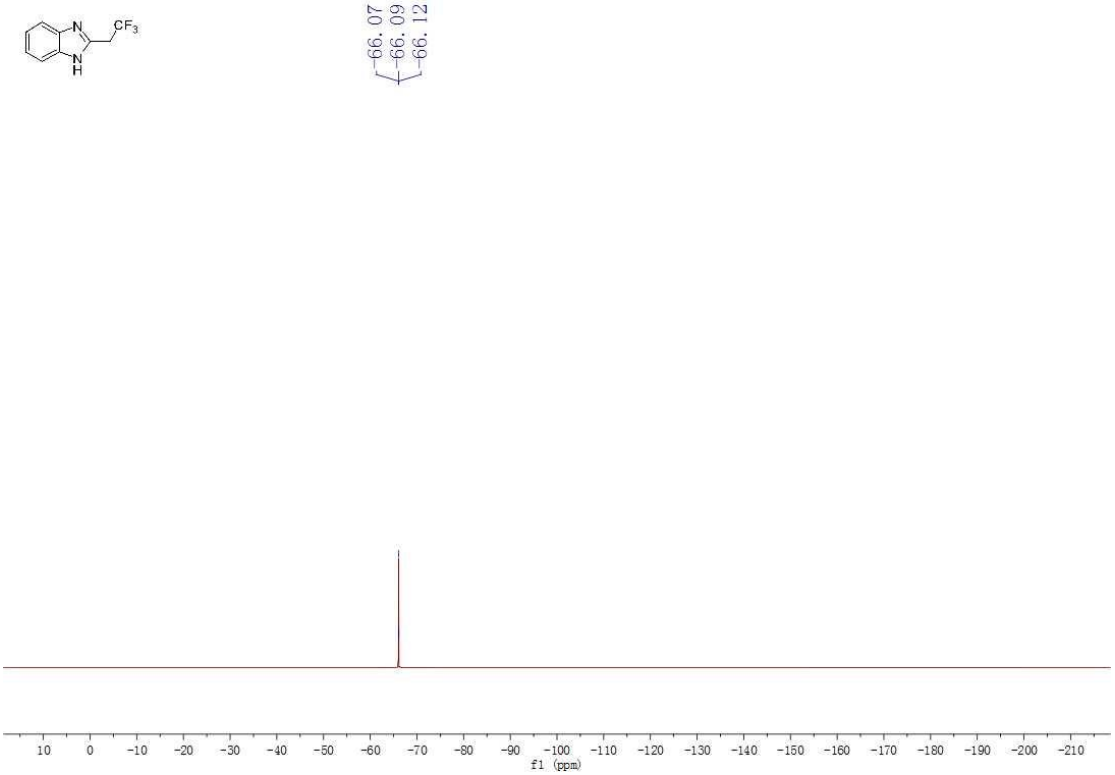
^{1}H NMR spectrum of **4c** in $CDCl_3$



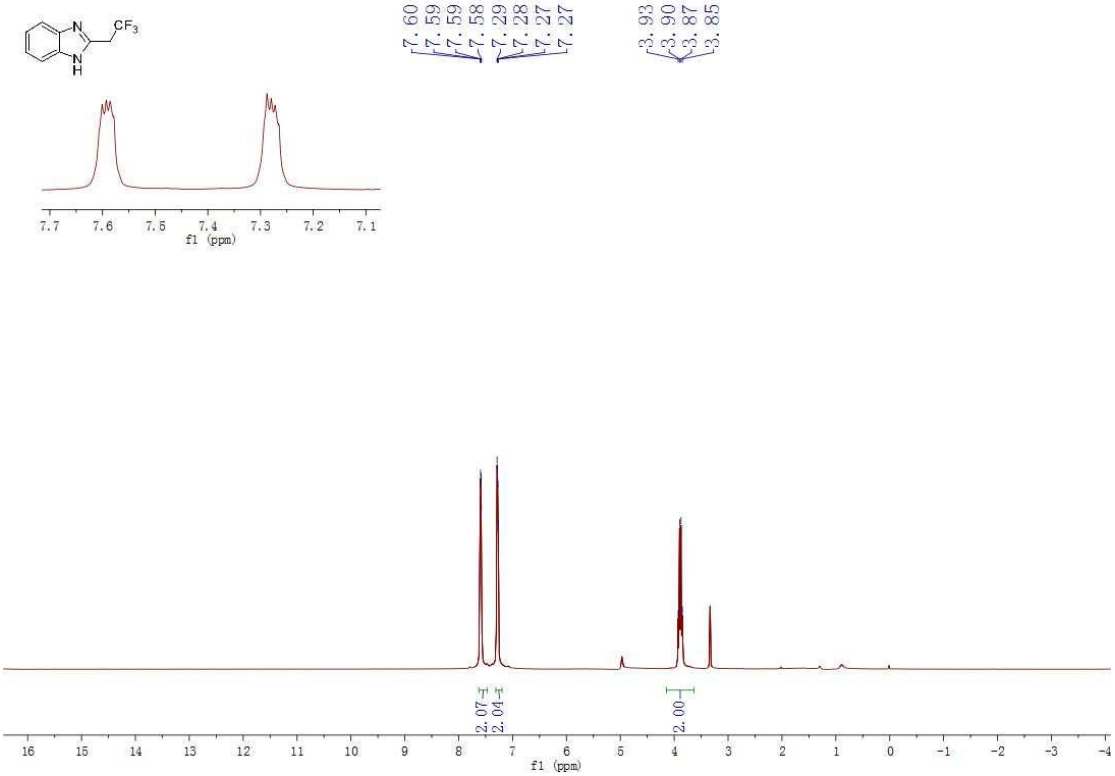
^{13}C NMR spectrum of **4c** in $CDCl_3$



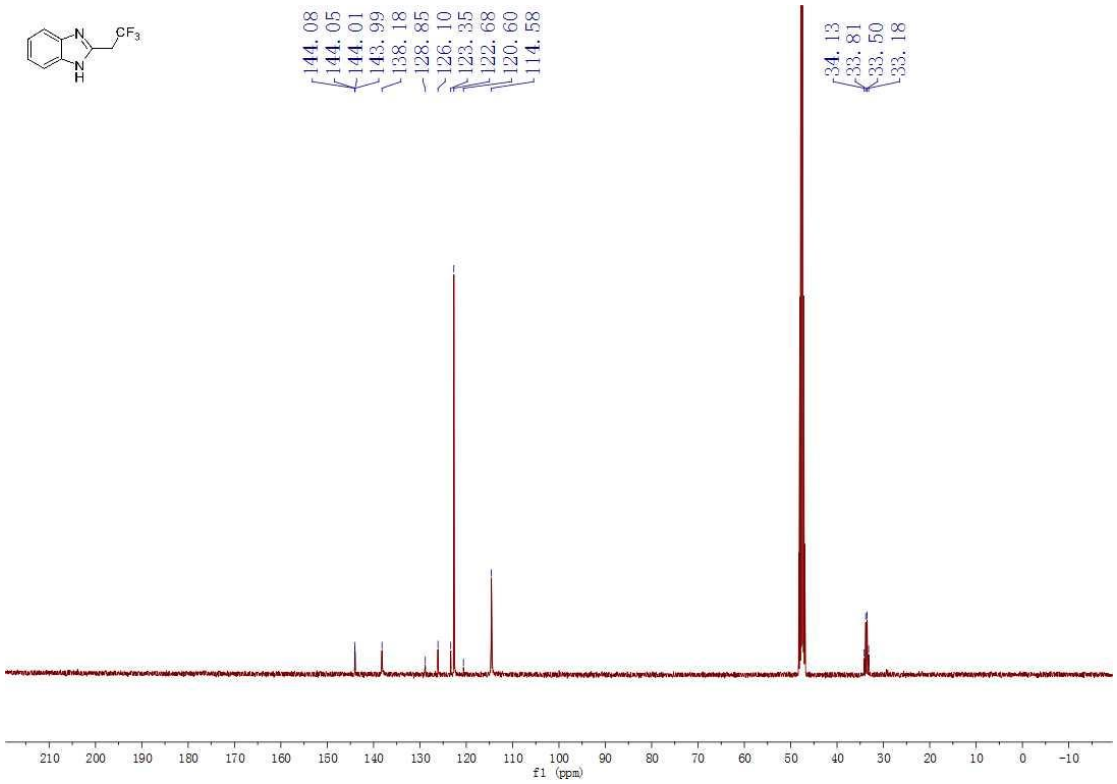
^{19}F NMR spectrum of **5a** in CD_3OD



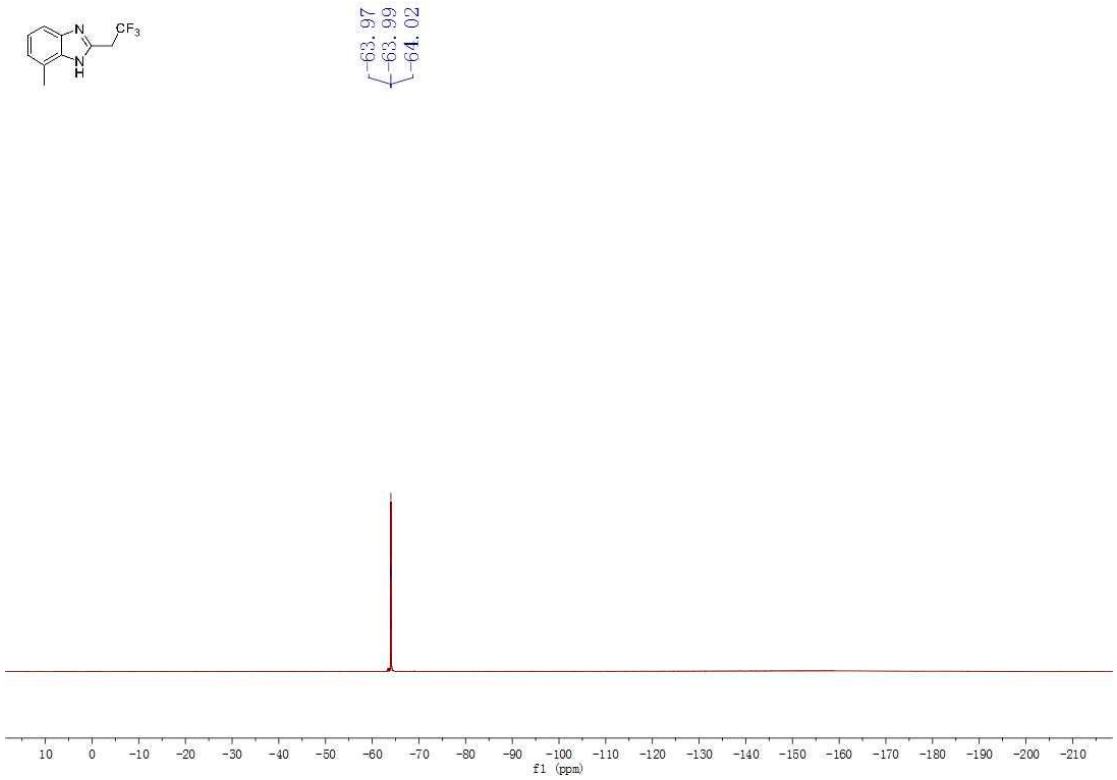
^{1}H NMR spectrum of **5a** in CD_3OD



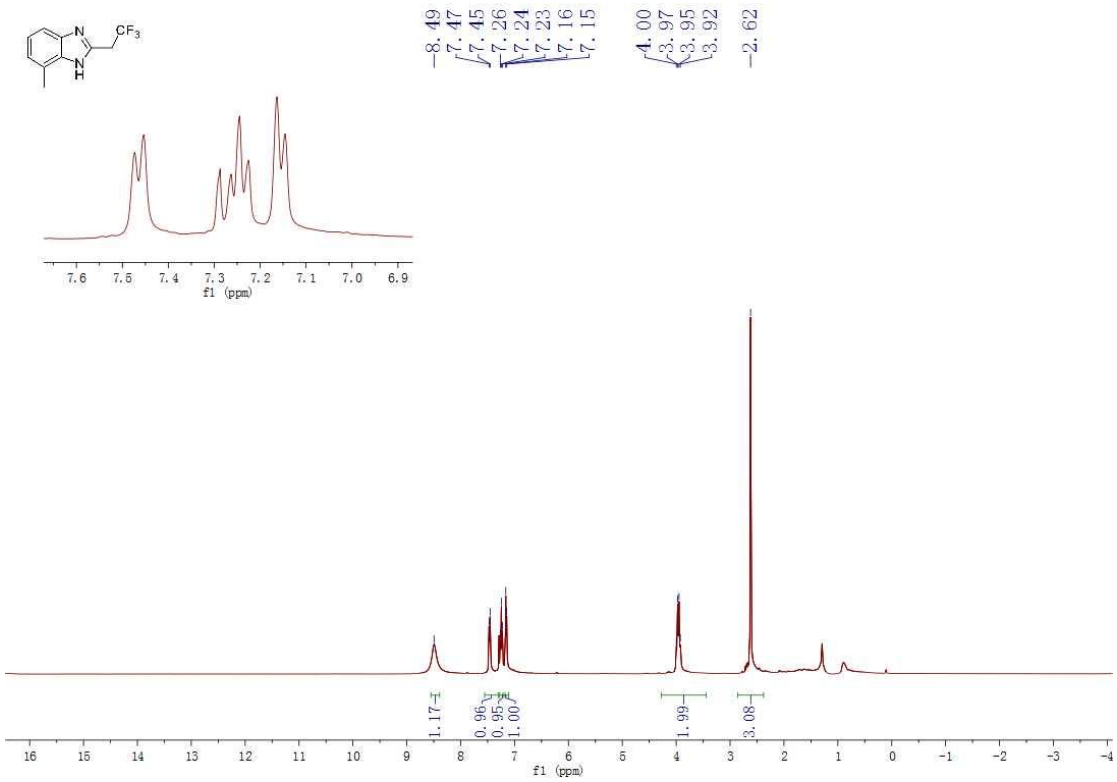
^{13}C NMR spectrum of **5a** in CD_3OD



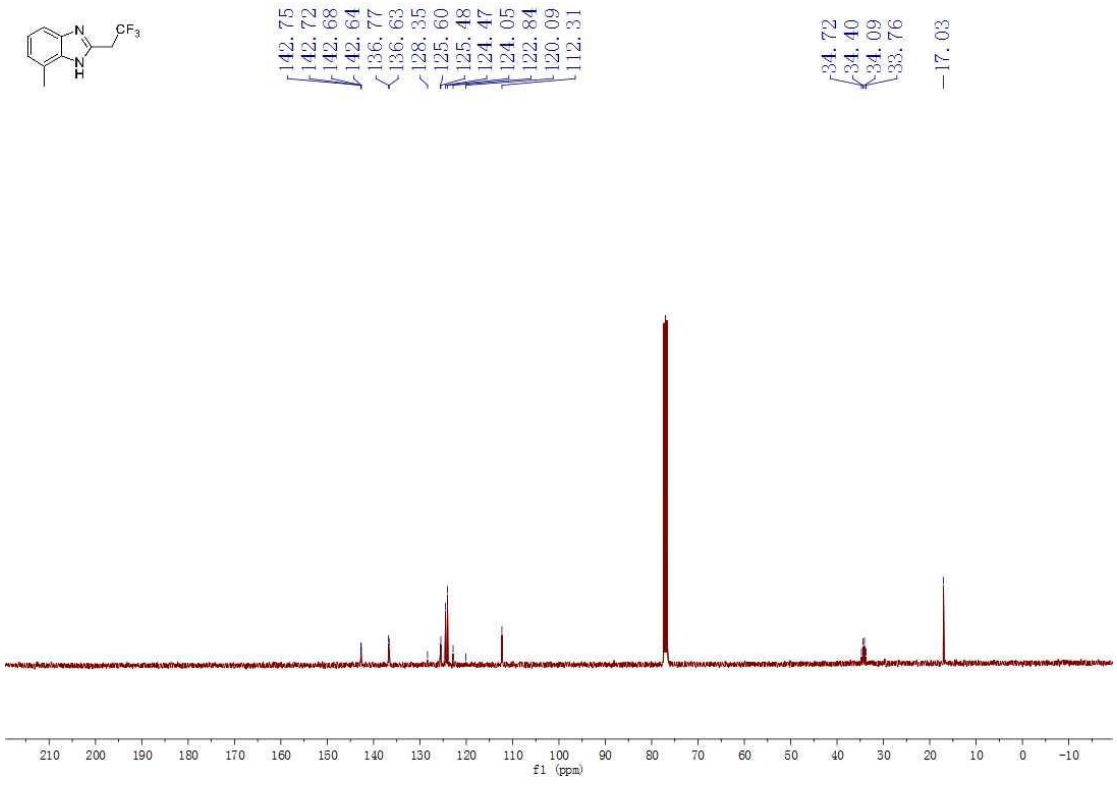
^{19}F NMR spectrum of **5b** in $CDCl_3$



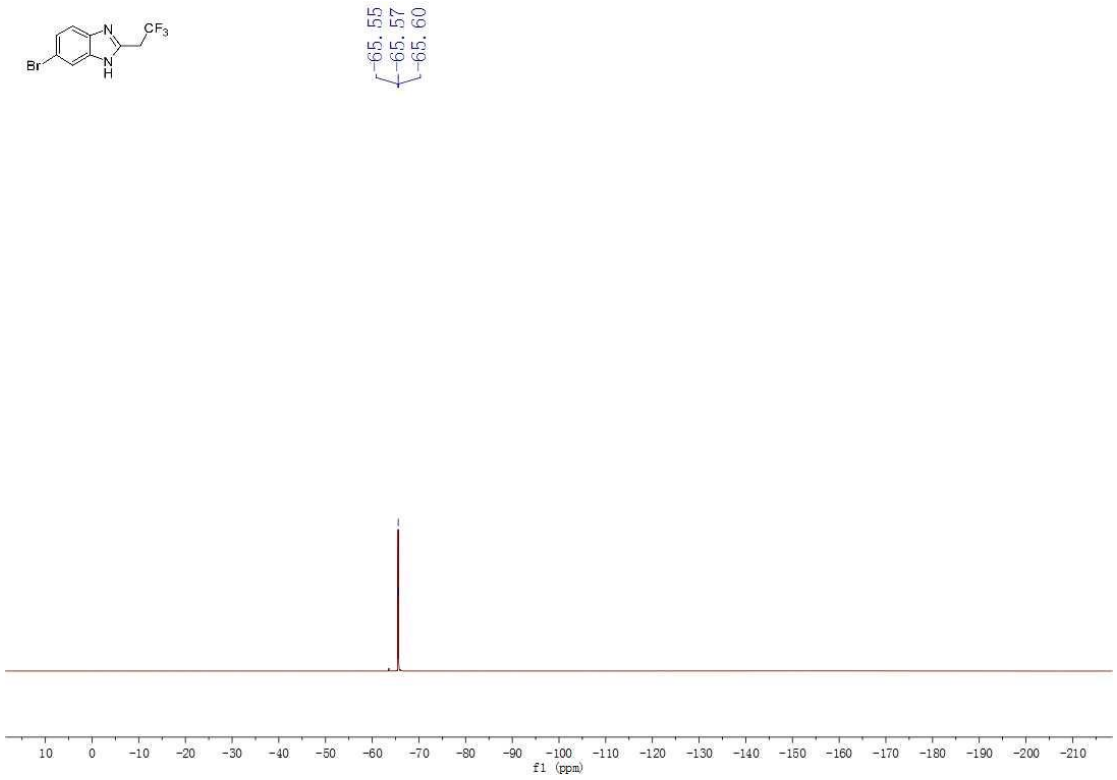
^{1}H NMR spectrum of **5b** in $CDCl_3$



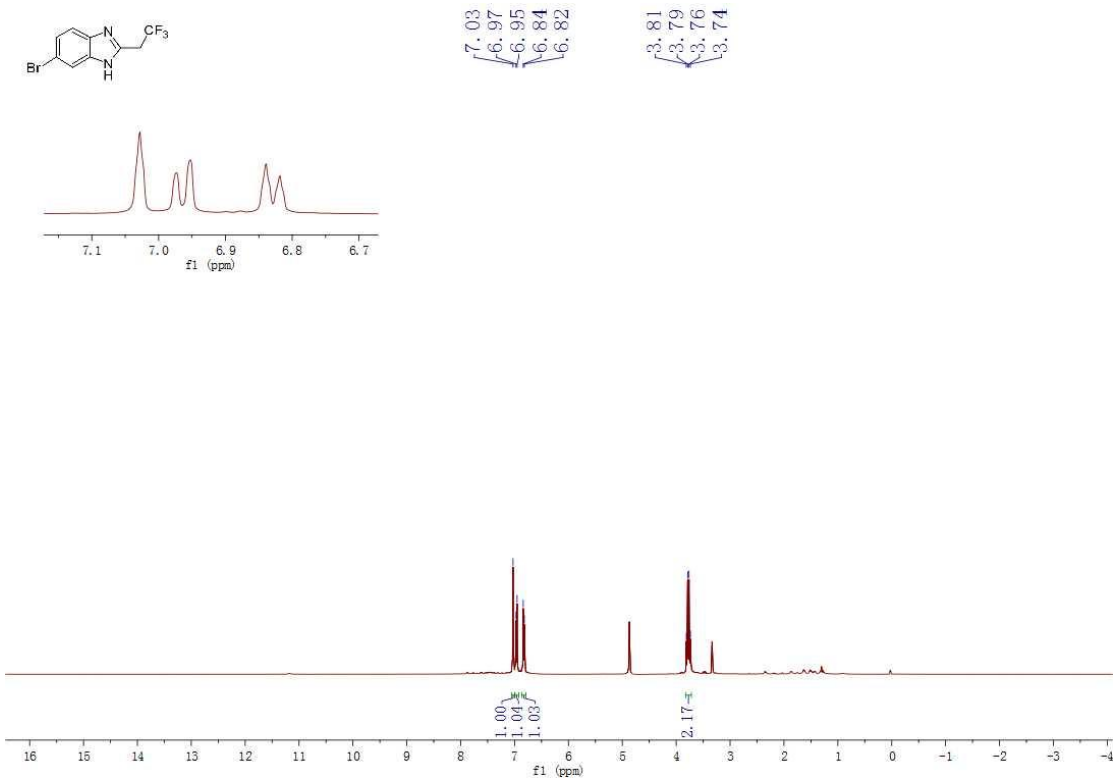
^{13}C NMR spectrum of **5b** in $CDCl_3$



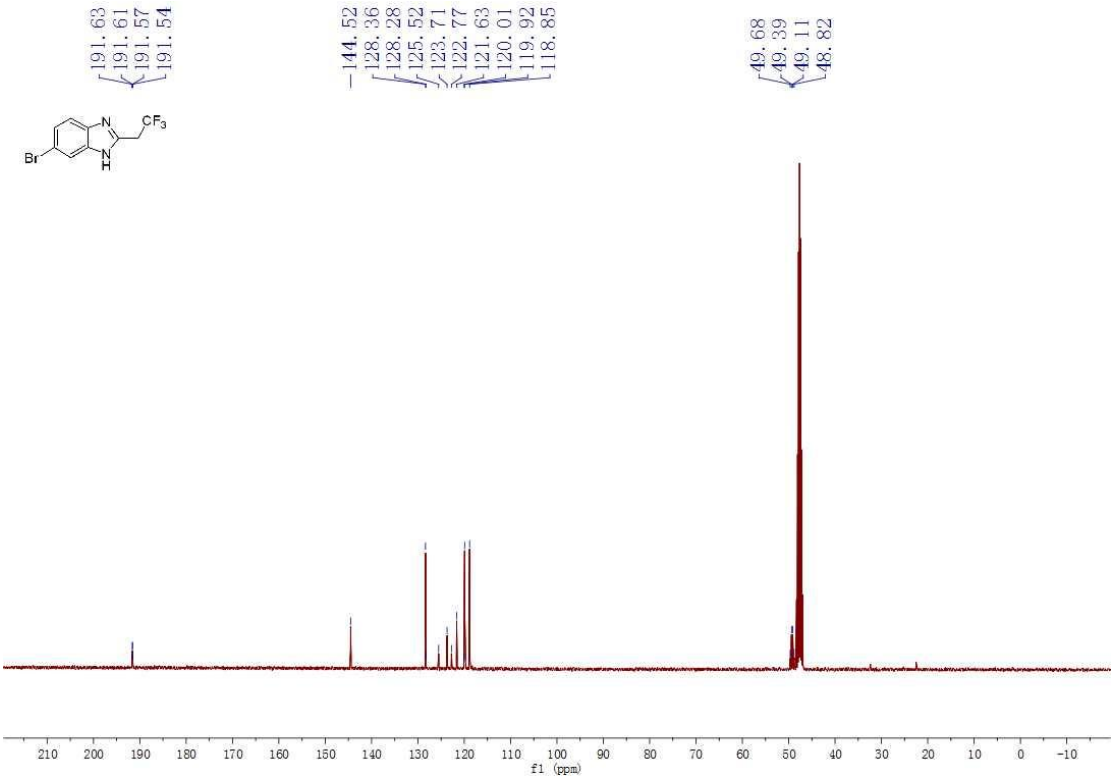
^{19}F NMR spectrum of **5c** in CD_3OD



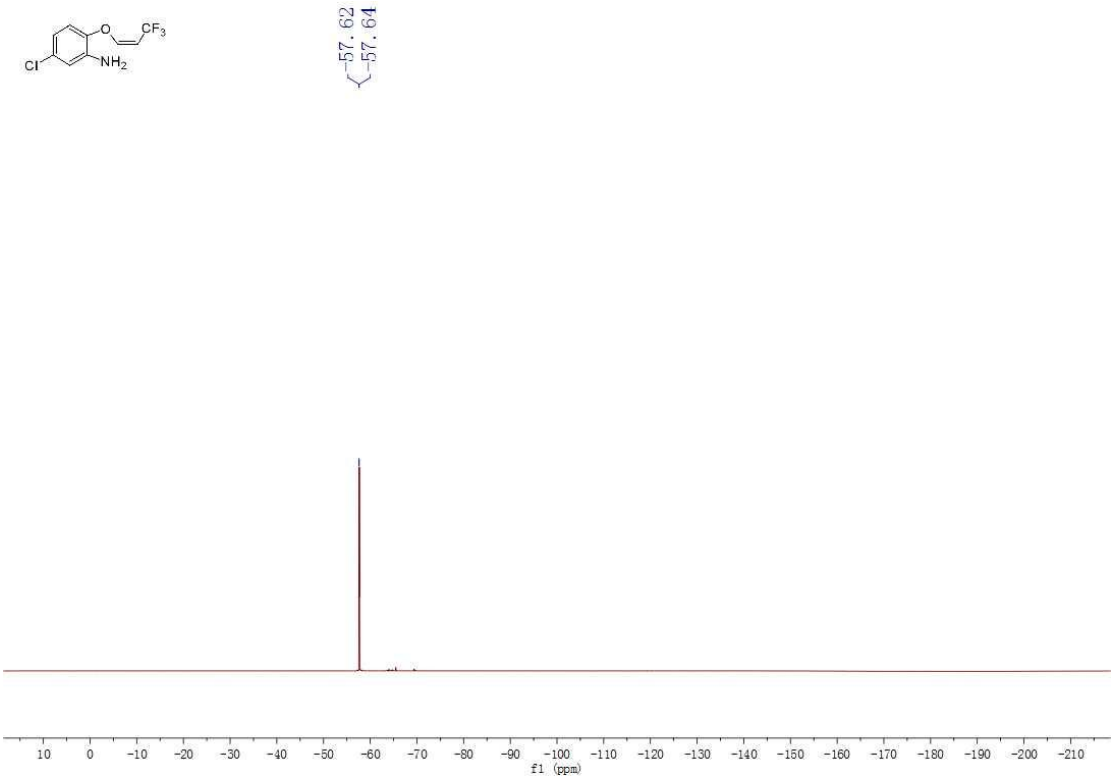
^{1}H NMR spectrum of **5c** in CD_3OD



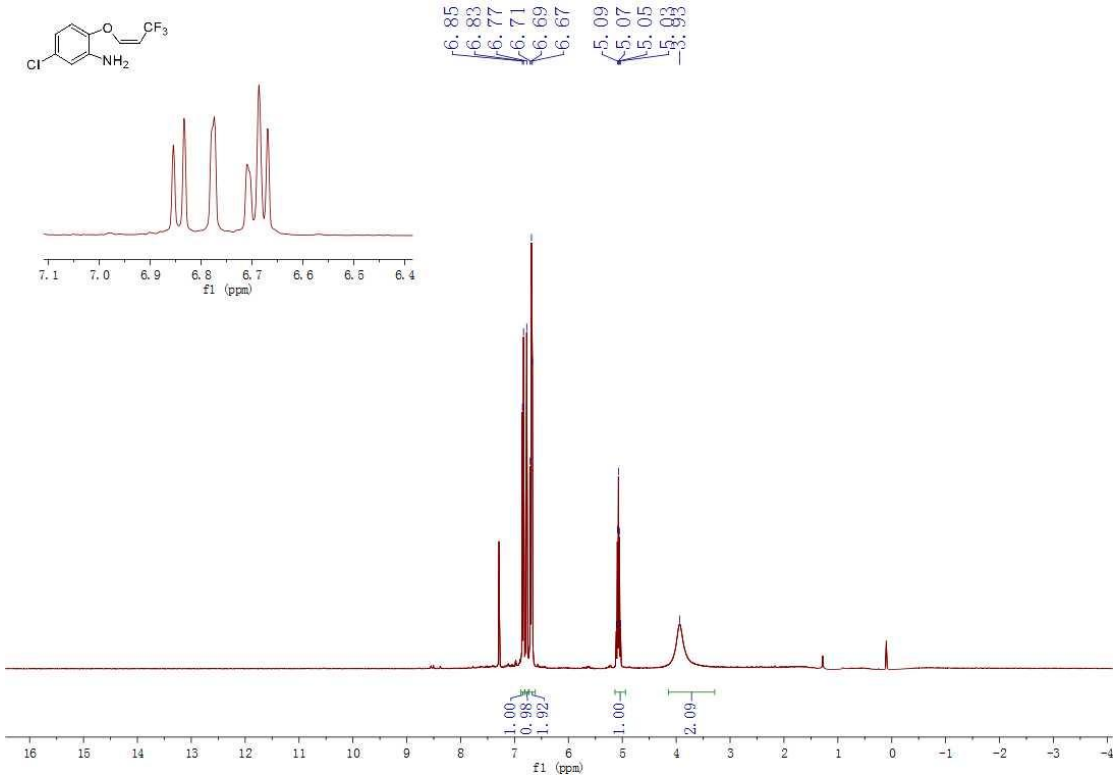
^{13}C NMR spectrum of **5c** in CD_3OD



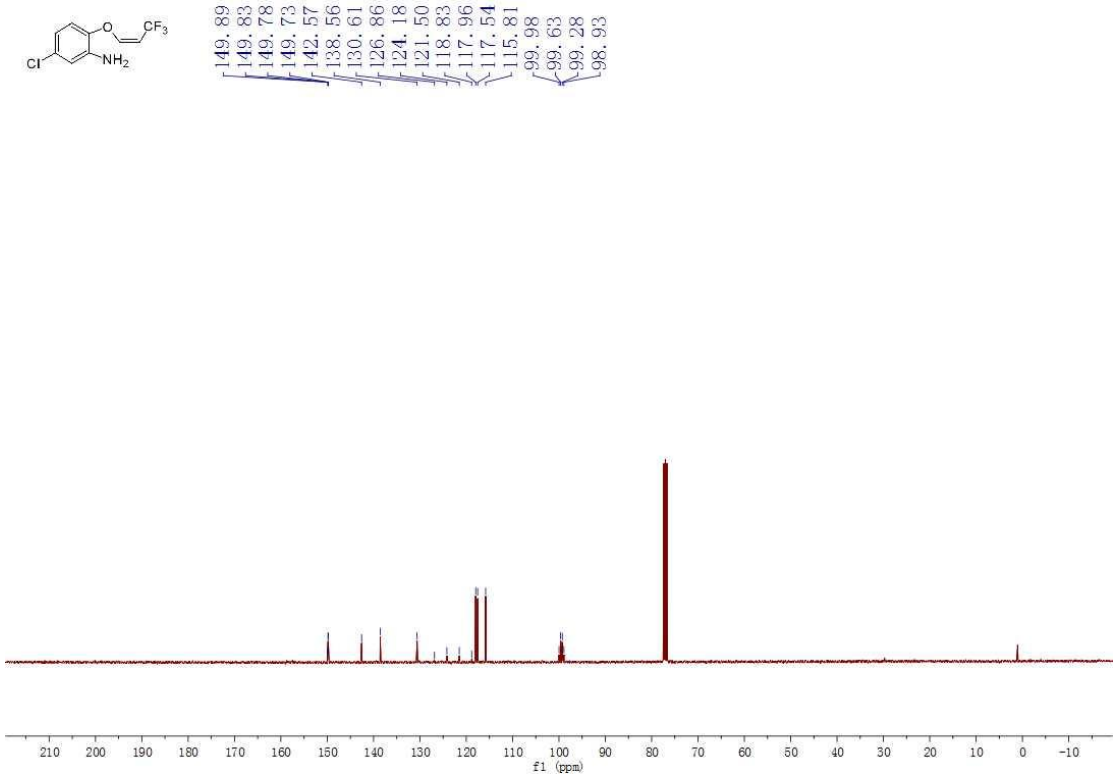
^{19}F NMR spectrum of **6q** in $CDCl_3$



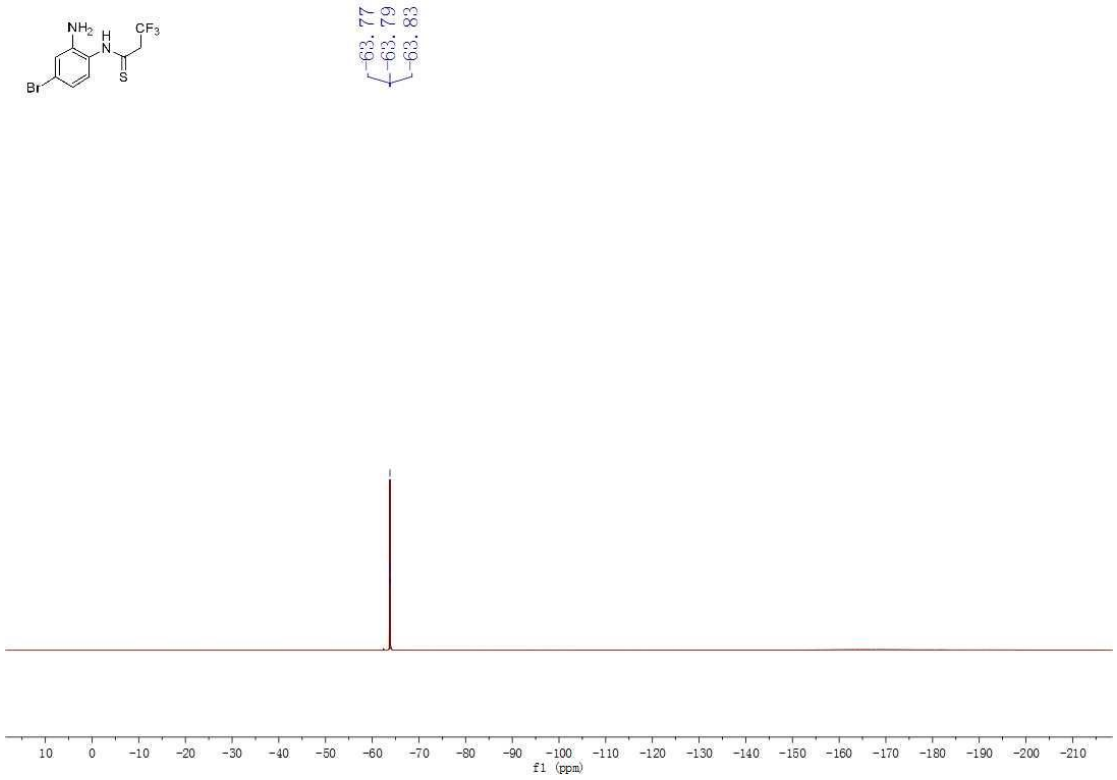
^{1}H NMR spectrum of **6q** in $CDCl_3$



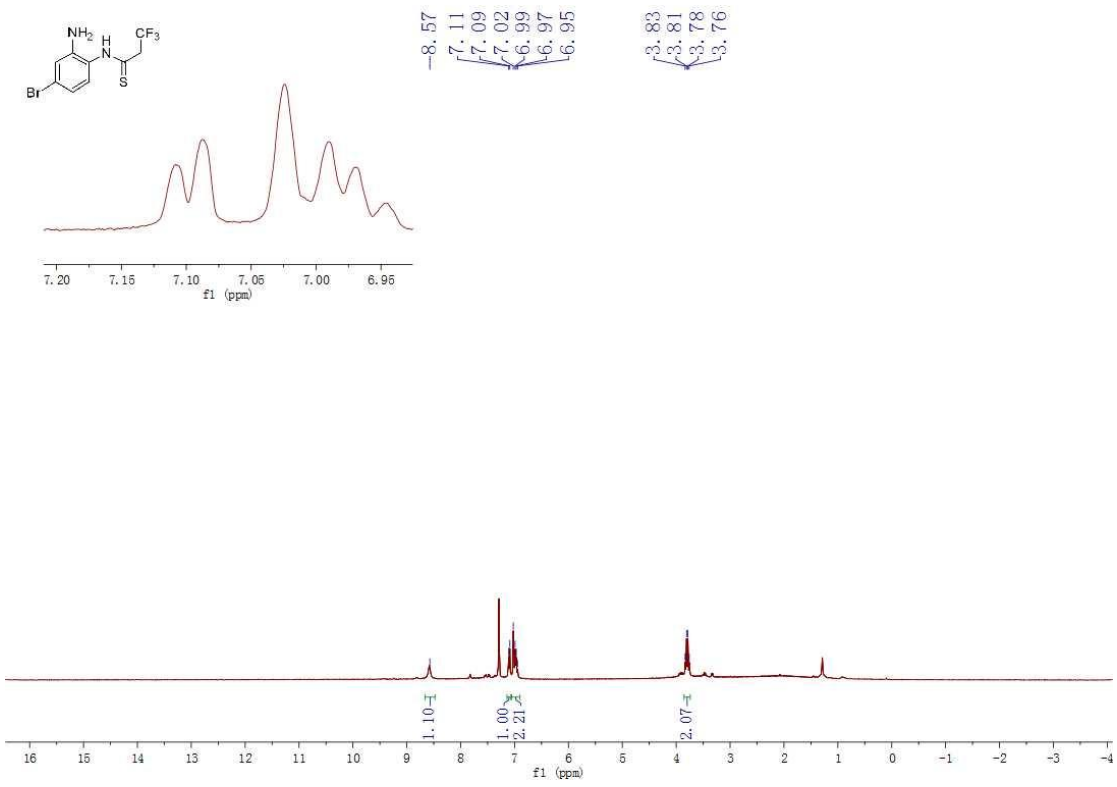
^{13}C NMR spectrum of **6q** in $CDCl_3$



^{19}F NMR spectrum of **7c** in $CDCl_3$



^{1}H NMR spectrum of **7c** in $CDCl_3$



^{13}C NMR spectrum of **7c** in $CDCl_3$