

Supporting Information *for*

One-Pot Synthesis of 3-Difluoromethyl Benzoxazole-2-Thiones

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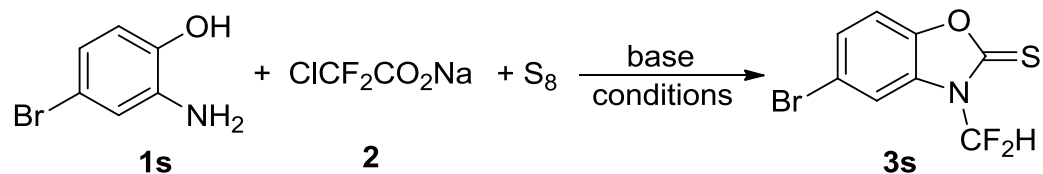
Table of Contents

General information.....	2
The effect of molecular sieves on the reaction.....	3
General procedure of one-pot synthesis of 3-difluoromethyl benzoxazole-2-thiones.....	4
Procedure for gram scale reaction.....	5
Mechanistic Study.....	6
Data for compounds 3 , 5	8
Crystal structure analyses.....	21
The procedure for the insecticidal assay.....	24
References.....	26
Copies of ¹ H NMR, ¹⁹ F NMR and ¹³ C NMR spectra.....	27

General information

^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^1H 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: ^1H 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.

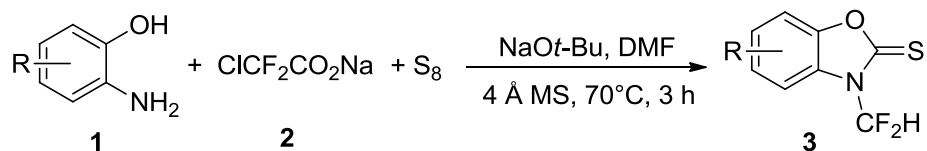
The effect of molecular sieves on the reaction.^a



entry	base	additive	solvent	temp (°C)	time (h)	yield (%) ^b
1	NaO <i>t</i> -Bu	3 Å MS (powder)	DMF	70	3	84
2	NaO <i>t</i> -Bu	3 Å MS (2-3 mm)	DMF	70	3	76
3	NaO <i>t</i> -Bu	4 Å MS (powder)	DMF	70	3	90
4	NaO <i>t</i> -Bu	4 Å MS (2-3 mm)	DMF	70	3	77
5	NaO <i>t</i> -Bu	4 Å MS (3-5 mm)	DMF	70	3	69
6	NaO <i>t</i> -Bu	5 Å MS (2-3 mm)	DMF	70	3	68

^a Reaction conditions: **1s** (0.10 mmol), **2** (0.50 mmol), S_8 (0.50 mmol), base (0.38 mmol), solvent (1.5 mL), under N_2 atmosphere; ^b The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

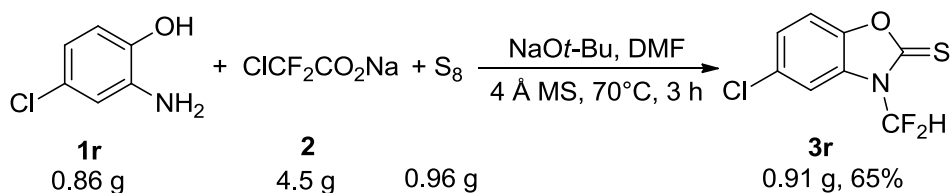
General procedure of one-pot synthesis of 3-difluoromethyl benzoxazole-2-thiones



The 2-aminophenol derivatives (**1**) (0.40 mmol), sodium chlorodifluoroacetate (**2**) (2.00 mmol, 5.0 equiv), S₈ (2.00 mmol, 5.0 equiv), sodium *tert*-butoxide (1.60 mmol, 4.0 equiv), 4 Å molecular sieves (60 mg, dried), and DMF (6.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 70 °C for 3 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting product **3** was purified by column chromatography over silica gel.

Procedure for gram scale reaction for synthesis of

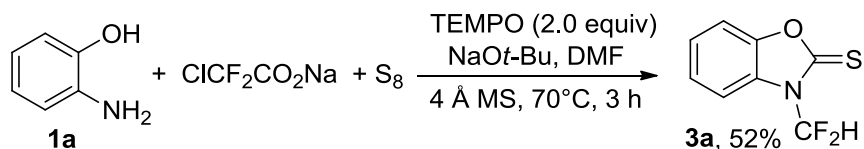
5-chloro-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (**3r**)



The 2-amino-4-chloropheno (**1r**) (0.86 g, 6.0 mmol), sodium chlorodifluoroacetate (**2**) (4.50 g, 30.0 mmol, 5.0 equiv), S_8 (0.96 g, 30.0 mmol, 5.0 equiv), sodium *tert*-butoxide (2.30 g, 24.0 mmol, 4.0 equiv), 4 Å molecular sieves (0.90 g, dried), and DMF (35 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 70 °C for 3 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (150 mL), washed with saturated brine (400 mL), and water (300 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **3r** was purified by column chromatography over silica gel.

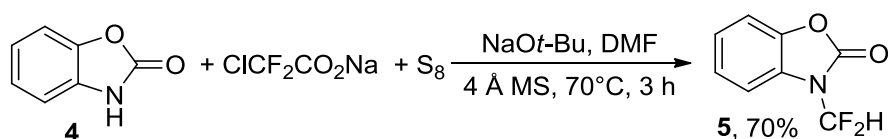
Mechanistic Study

(a).



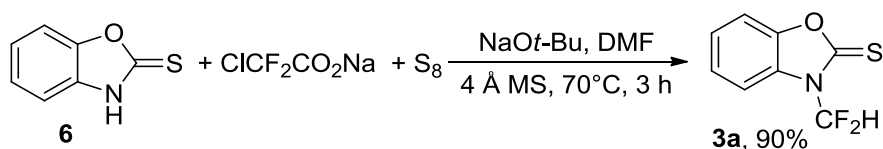
The 2-aminophenol (**1a**) (0.40 mmol), sodium chlorodifluoroacetate (2.00 mmol, 5.0 equiv), S_8 (2.00 mmol, 5.0 equiv), sodium *tert*-butoxide (1.60 mmol, 4.0 equiv), 4 Å molecular sieves (60 mg, dried), TEMPO (0.80 mmol 2.0 equiv) and DMF (6.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 70 °C for 3 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO_4 . The solvent was removed by rotary evaporation and the resulting product **3a** was purified by column chromatography over silica gel.

(b).



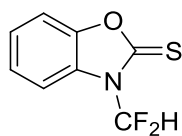
The 2-benzoxazinone (**4**) (0.40 mmol), sodium chlorodifluoroacetate (2.00 mmol, 5.0 equiv), S_8 (2.00 mmol, 5.0 equiv), sodium *tert*-butoxide (1.60 mmol, 4.0 equiv), 4 Å molecular sieves (60 mg, dried), and DMF (6.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 70 °C for 3 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO_4 . The solvent was removed by rotary evaporation and the resulting product **5** was purified by column chromatography over silica gel.

(c)



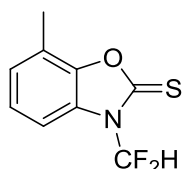
The 2-mercaptobenzoxazole (**6**) (0.40 mmol), sodium chlorodifluoroacetate (2.00 mmol, 5.0 equiv), S₈ (2.00 mmol, 5.0 equiv), sodium *tert*-butoxide (1.60 mmol, 4.0 equiv), 4 Å molecular sieves (60 mg, dried), and DMF (6.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 70 °C for 3 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting product **3a** was purified by column chromatography over silica gel.

Data for compounds 3, 5.



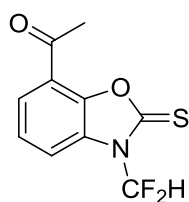
3-(Difluoromethyl)benzo[d]oxazole-2(3H)-thione (3a)¹

Obtained as a light yellow solid in 80% yield (64 mg). M.p. 72.9–74.5 °C. R_f (*n*-pentane) = 0.68. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (t, J = 58.4 Hz, 1H), 7.53 – 7.44 (m, 1H), 7.43 – 7.31 (m, 3H). ¹⁹F NMR (376 MHz, CDCl₃, 2F) δ -104.0 (d, J = 58.4 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 178.9 (t, J = 3.0 Hz), 146.7 (s), 127.1 (s), 125.7 (s), 111.4 (t, J = 2.4 Hz), 110.9 (t, J = 251.5 Hz), 110.7 (s). IR (KBr): ν 1478, 1359, 1349, 1282, 1133, 1069, 1010, 936, 855, 773, 585 cm⁻¹. GC-MS m/z 200 (M⁺).



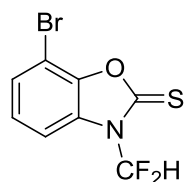
3-(Difluoromethyl)-7-methylbenzo[d]oxazole-2(3H)-thione (3b)

Obtained as a light yellow solid in 44% yield (38 mg). M.p. 70.0–72.5 °C. R_f (*n*-pentane) = 0.52. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (t, J = 58.5 Hz, 1H), 7.35 – 7.21 (m, 2H), 7.17 (d, J = 7.4 Hz, 1H), 2.50 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -104.1 (d, J = 58.5 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 179.0 (t, J = 3.3 Hz), 145.6 (s), 127.0 (s), 126.7 (t, J = 1.4 Hz), 125.5 (s), 121.6 (s), 111.0 (t, J = 251.4 Hz), 108.8 (t, J = 2.5 Hz), 14.6 (s). IR (KBr): ν 1395, 1365, 1343, 1316, 1266, 1137, 1074, 882, 768, 649 cm⁻¹. GC-MS m/z 216 (M⁺). HRMS (EI) m/z : calcd. for C₉H₇NOF₂S: 215.0216; found: 215.0217.



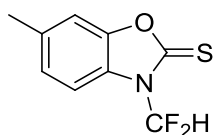
1-(3-(Difluoromethyl)-2-thioxo-2,3-dihydrobenzo[d]oxazol-7-yl)ethanone (3c)

Obtained as a white solid in 72% yield (66 mg). M.p. 117.2–120.8 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 58.3 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 8.1 Hz, 1H), 2.80 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -104.0 (d, J = 58.3 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 193.1 (s), 178.0 (t, J = 3.5 Hz), 145.7 (s), 128.1 (t, J = 1.6 Hz), 125.7 (s), 125.6 (s), 121.3 (s), 115.3 (t, J = 2.7 Hz), 110.9 (t, J = 252.3 Hz), 30.8 (s). IR (KBr): ν 1395, 1366, 1344, 1317, 1266, 1137, 1075, 882, 768, 650 cm^{-1} . GC-MS m/z 243 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_{10}\text{H}_7\text{NO}_2\text{F}_2\text{S}$: 243.0166; found: 243.0171.



7-Bromo-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (3d)

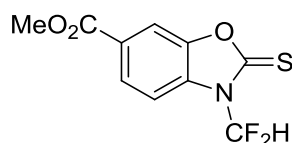
Obtained as a white solid in 84% yield (94 mg). M.p. 92.3–94.8 °C. R_f (*n*-pentane) = 0.55. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (t, J = 58.2 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.25 (t, J = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, J = 58.2 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.0 (t, J = 3.5 Hz), 144.8 (s), 128.8 (s), 128.0 (t, J = 1.5 Hz), 126.8 (s), 110.9 (t, J = 252.4 Hz), 110.2 (t, J = 2.7 Hz), 103.0 (s). IR (KBr): ν 1447, 1386, 1354, 1336, 1316, 1249, 1144, 1118, 1095, 1044, 949 cm^{-1} . GC-MS m/z 281 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{NOF}_2\text{SBr}$: 278.9165; found: 278.9164.



3-(Difluoromethyl)-6-methylbenzo[d]oxazole-2(3H)-thione (3e)

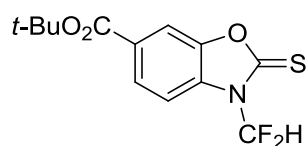
Obtained as a white solid in 81% yield (70 mg). M.p. 95.6–98.5 °C. R_f (*n*-pentane) = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (t, J = 58.5 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.21 (s, 1H), 7.17 (d, J = 8.1 Hz, 1H), 2.48 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ

-104.0 (d, $J = 58.5$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.0 (t, $J = 3.6$ Hz), 147.0 (s), 136.4 (s), 126.4 (s), 124.8 (t, $J = 1.6$ Hz), 111.1 (s), 110.9 (t, $J = 251.2$ Hz), 110.8 (t, $J = 2.5$ Hz), 21.5 (s). IR (KBr): ν 1500, 1397, 1363, 1336, 1276, 1141, 1101, 1083, 1059, 936, 923, 807 cm^{-1} . GC-MS m/z 215 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_7\text{NOF}_2\text{S}$: 215.0216; found: 215.0213.



Methyl 3-(difluoromethyl)-2-thioxo-2,3-dihydrobenzo[d]oxazole-6-carboxylate
(3f)

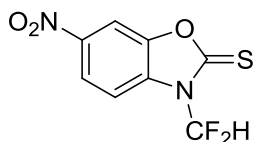
Obtained as a light yellow solid in 75% yield (77 mg). M.p. 117.2–120.8 °C. R_f (n -pentane/ethyl acetate = 25:1) = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.2$ Hz, 1H), 8.01 (s, 1H), 7.72 (t, $J = 58.2$ Hz, 1H), 7.51 (d, $J = 8.2$ Hz, 1H), 3.98 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, $J = 58.2$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.1 (t, $J = 3.2$ Hz), 165.4 (s), 146.4 (s), 130.6 (t, $J = 1.4$ Hz), 128.0 (s), 127.7 (s), 111.8 (s), 110.9 (t, $J = 2.7$ Hz), 110.8 (t, $J = 252.5$ Hz), 52.7 (s). IR (KBr): ν 1719, 1633, 1606, 1496, 1435, 1396, 1359, 1336, 1289, 1209, 1140, 1056 cm^{-1} . GC-MS m/z 259 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_{10}\text{H}_7\text{NO}_3\text{F}_2\text{S}$: 259.0115; found: 259.0121.



3-(Difluoromethyl)-2-thioxo-2,3-dihydrobenzo[d]oxazole-6-carboxylic acid (3g)

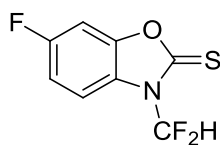
Obtained as a light yellow solid in 67% yield (65 mg). M.p. 69.7–73.0 °C. R_f (n -pentane/ethyl acetate = 25:1) = 0.79. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.0$ Hz, 1H), 7.98 (s, 1H), 7.74 (t, $J = 58.2$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 1.64 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, $J = 58.2$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.2 (t, $J = 3.2$ Hz), 164.0 (s), 146.5 (s), 130.2 (s), 130.0 (s), 127.5 (s),

111.7 (s), 110.8 (t, $J = 252.3$ Hz), 110.6 (t, $J = 2.3$ Hz), 82.2 (s), 28.2 (s). IR (KBr): ν 1715, 1495, 1398, 1363, 1335, 1296, 1158, 1133, 1093, 1076, 933, 761 cm^{-1} . GC-MS m/z 245 ($\text{M}^+ - t\text{-Bu}$). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_5\text{NO}_3\text{F}_2\text{S}$: 244.9958 ($\text{M}^+ - t\text{-Bu}$); found: 244.9959 ($\text{M}^+ - t\text{-Bu}$).



3-(Difluoromethyl)-6-nitrobenzo[d]oxazole-2(3H)-thione (3h)

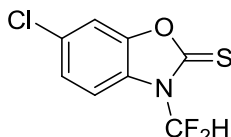
Obtained as a light yellow solid in 69% yield (68 mg). M.p. 134.2–138.1 °C. R_f (n -pentane/ethyl acetate = 25:1) = 0.64. ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 8.7$ Hz, 1H), 8.27 (s, 1H), 7.73 (t, $J = 58.1$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.7 (d, $J = 58.1$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.8 (t, $J = 3.2$ Hz), 146.2 (s), 145.6 (s), 132.1 (t, $J = 1.6$ Hz), 122.0 (s), 111.0 (t, $J = 2.9$ Hz), 110.7 (t, $J = 253.7$ Hz), 106.8 (s). IR (KBr): ν 1521, 1331, 1314, 1264, 1228, 1115, 1076, 1042, 929, 894, 823, 774 cm^{-1} . GC-MS m/z 247 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{N}_2\text{O}_3\text{F}_2\text{S}$: 245.9911; found: 245.9916.



3-(Difluoromethyl)-6-fluorobenzo[d]oxazole-2(3H)-thione (3i)

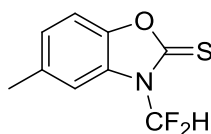
Obtained as a light yellow solid in 86% yield (75 mg). M.p. 172.9–174.6 °C. R_f (n -pentane) = 0.39. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (t, $J = 58.3$ Hz, 1H), 7.48 – 7.36 (m, 1H), 7.22 – 7.02 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, $J = 58.3$ Hz, 2F), -113.6 – -113.8 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.1 (td, $J = 3.5$, 0.9 Hz), 160.6 (d, $J = 247.3$ Hz), 146.9 (d, $J = 13.6$ Hz), 123.5 (dt, $J = 3.3$, 1.5 Hz), 112.8 (d, $J = 24.6$ Hz), 111.7 (dt, $J = 9.5$, 2.7 Hz), 110.9 (t, $J = 251.8$ Hz), 99.7 (d, $J = 28.9$ Hz). IR (KBr): ν 1639, 1494, 1457, 1396, 1366, 1329, 1270, 1120, 1099, 1066,

947, 731 cm^{-1} . GC-MS m/z 219 (M^+). HRMS (EI) m/z : calcd. For $\text{C}_8\text{H}_4\text{NOF}_3\text{S}$: 218.9966; found: 218.9960.



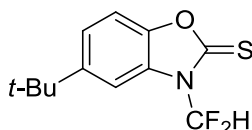
6-Chloro-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (3j)

Obtained as a white solid in 78% yield (73 mg). M.p. 103.8 – 107.7 °C. R_f (*n*-pentane) = 0.54. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (t, $J = 58.3$ Hz, 1H), 7.47 – 7.31 (m, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.8 (d, $J = 58.3$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.6 (t, $J = 3.5$ Hz), 146.9 (s), 131.7 (s), 125.9 (s), 125.8 (t, $J = 1.5$ Hz), 111.8 (t, $J = 2.7$ Hz), 111.5 (s), 110.8 (t, $J = 252.1$ Hz). IR (KBr): ν 1480, 1466, 1449, 1395, 1352, 1330, 1313, 1261, 1227, 1110, 1061, 897 cm^{-1} . GC-MS m/z 235 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{NOF}_2\text{SCl}$: 234.9670; found: 234.9667.



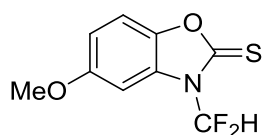
3-(Difluoromethyl)-5-methylbenzo[d]oxazole-2(3H)-thione (3k)

Obtained as a white solid in 65% yield (56 mg). M.p. 100.5–102.1 °C. R_f (*n*-pentane) = 0.54. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (t, $J = 58.4$ Hz, 1H), 7.28 (s, 1H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 1H), 2.47 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -104.1 (d, $J = 58.4$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.1 (t, $J = 3.7$ Hz), 144.9 (s), 136.1 (s), 127.1 (t, $J = 1.6$ Hz), 126.3 (s), 111.7 (t, $J = 2.5$ Hz), 110.9 (t, $J = 251.3$ Hz), 110.2 (s), 21.5 (s). IR (KBr): ν 1474, 1446, 1363, 1345, 1309, 1256, 1235, 1075, 950, 864, 726 cm^{-1} . GC-MS m/z 215 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_7\text{NOF}_2\text{S}$: 215.0216; found: 215.0207.



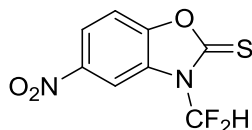
5-(*tert*-Butyl)-3-(difluoromethyl)benzo[*d*]oxazole-2(3*H*)-thione (3l)

Obtained as a light yellow solid in 87% yield (89 mg). M.p. 158.3–162.2 °C. R_f (*n*-pentane) = 0.28. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (t, $J = 58.4$ Hz, 1H), 7.48 (s, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.31 (d, $J = 8.7$ Hz, 1H), 1.39 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -104.0 (d, $J = 58.4$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.4 (t, $J = 3.3$ Hz), 149.8 (s), 144.7 (s), 127.1 (t, $J = 1.9$ Hz), 122.9 (s), 111.1 (t, $J = 251.2$ Hz), 110.0 (s), 108.3 (t, $J = 2.3$ Hz), 35.2 (s), 31.5 (s). IR (KBr): ν 2964, 1491, 1450, 1358, 1312, 1285, 1252, 1158, 1107, 1070, 958 cm^{-1} . GC-MS m/z 258 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_{12}\text{H}_{13}\text{NOF}_2\text{S}$: 257.0686; found: 257.0692.



3-(Difluoromethyl)-5-methoxybenzo[*d*]oxazole-2(3*H*)-thione (3m)

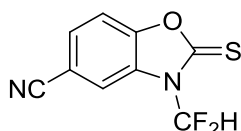
Obtained as a light yellow solid in 50% yield (46 mg). M.p. 105.1–107.5 °C. R_f (*n*-pentane) = 0.25. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (t, $J = 58.4$ Hz, 1H), 7.27 (d, $J = 8.9$ Hz, 1H), 6.99 (s, 1H), 6.88 (d, $J = 8.9$ Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -104.2 (d, $J = 58.4$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.4 (t, $J = 3.6$ Hz), 158.0 (s), 140.9 (s), 127.8 (t, $J = 1.4$ Hz), 111.7 (s), 111.0 (s), 110.9 (t, $J = 251.5$ Hz), 97.1 (t, $J = 2.7$ Hz), 56.2 (s). IR (KBr): ν 1610, 1495, 1459, 1352, 1324, 1274, 1212, 1135, 1102, 1070, 1027, 966 cm^{-1} . GC-MS m/z 231 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_7\text{NO}_2\text{F}_2\text{S}$: 231.0166; found: 231.0165.



3-(Difluoromethyl)-5-nitrobenzo[*d*]oxazole-2(3*H*)-thione (3n)

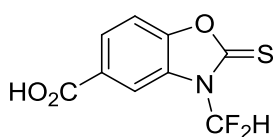
Obtained as a brownish yellow solid in 75% yield (74 mg). M.p. 146.7–149.3 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.46. ^1H NMR (400 MHz, CDCl_3) δ 8.42 – 8.30 (m, 2H), 7.72 (t, $J = 58.1$ Hz, 1H), 7.53 (d, $J = 9.5$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3)

δ -103.6 (d, $J = 58.1$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.6 (t, $J = 3.3$ Hz), 150.1 (s), 145.6 (s), 127.9 (t, $J = 1.4$ Hz), 122.0 (s), 110.8 (s), 110.7 (t, $J = 253.4$ Hz), 107.3 (t, $J = 3.0$ Hz). IR (KBr): ν 3108, 1529, 1456, 1365, 1343, 1258, 1246, 1124, 1101, 1084, 961, 881 cm^{-1} . GC-MS m/z 246 (M^+). HRMS (EI) m/z : calcd. For $\text{C}_8\text{H}_4\text{N}_2\text{O}_3\text{F}_2\text{S}$: 245.9911; found: 245.9907.



3-(Difluoromethyl)-2-thioxo-2,3-dihydrobenzo[*d*]oxazole-5-carbonitrile (3o)

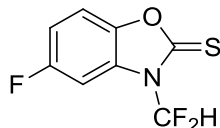
Obtained as a white solid in 78% yield (71 mg). M.p. 148.4–150.8 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.29. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.71 (t, $J = 58.1$ Hz, 1H), 7.69 (s, 1H), 7.50 (d, $J = 8.3$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.7 (d, $J = 58.1$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.2 (t, $J = 3.3$ Hz), 149.0 (s), 130.4 (s), 128.0 (t, $J = 1.7$ Hz), 117.3 (s), 114.8 (t, $J = 2.9$ Hz), 111.6 (s), 110.7 (t, $J = 253.1$ Hz), 109.9 (s). IR (KBr): ν 2228, 1451, 1361, 1313, 1275, 1242, 1179, 1129, 1073, 1052, 964, 875 cm^{-1} . GC-MS m/z 227 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_4\text{N}_2\text{OF}_2\text{S}$: 226.0012; found: 226.0015.



3-(Difluoromethyl)-2-thioxo-2,3-dihydrobenzo[*d*]oxazole-5-carboxylic acid (3p)

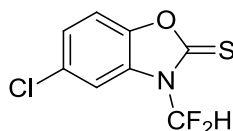
Obtained as a white solid in 50% yield (49 mg). M.p. 190.0–191.5 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.32. ^1H NMR (400 MHz, CD_3OD) δ 8.14 (d, $J = 8.4$ Hz, 1H), 8.10 (s, 1H), 7.93 (t, $J = 58.0$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), the CO_2H was not observed. ^{19}F NMR (376 MHz, CD_3OD) δ -106.1 (d, $J = 58.0$ Hz, 2F). ^{13}C NMR (101 MHz, CD_3OD) δ 179.5 (t, $J = 4.1$ Hz), 166.6 (s), 149.6 (s), 128.7 (s), 127.6 (s), 127.4 (s), 112.0 (t, $J = 2.8$ Hz), 111.4 (t, $J = 250.7$ Hz), 110.1 (s). IR (KBr):

ν 3366, 2473, 2214, 2070, 1454, 1367, 1120, 1100, 973, 819, 768 cm^{-1} . GC-MS m/z 246 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_9\text{H}_5\text{NO}_3\text{F}_2\text{S}$: 244.9958; found: 244.9951.



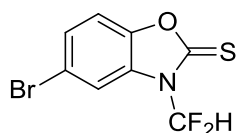
3-(Difluoromethyl)-5-fluorobenzo[d]oxazole-2(3H)-thione (3q)

Obtained as a white solid in 84% yield (73 mg). M.p. 81.8–84.4 °C. R_f (*n*-pentane) = 0.45. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (t, J = 58.3 Hz, 1H), 7.34 (dd, J = 8.9, 4.0 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.07 (t, J = 9.0 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -104.1 (d, J = 58.3 Hz, 2F), -113.7 – -114.5 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.3 (t, J = 3.5 Hz), 160.3 (d, J = 245.8 Hz), 142.7 (d, J = 2.1 Hz), 127.7 (dt, J = 3.0, 1.3 Hz), 112.5 (d, J = 25.3 Hz), 111.3 (d, J = 9.6 Hz), 110.7 (t, J = 252.2 Hz), 99.8 (dt, J = 30.3, 2.7 Hz). IR (KBr): ν 1614, 1490, 1464, 1420, 1347, 1264, 1240, 1128, 1100, 1059, 971, 848 cm^{-1} . GC-MS m/z 219 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{NOF}_3\text{S}$: 218.9966; found: 218.9958.



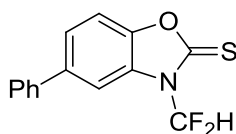
5-Chloro-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (3r)

Obtained as a white solid in 82% yield (77 mg). M.p. 118.6–122.8 °C. R_f (*n*-pentane) = 0.54. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (t, J = 58.2 Hz, 1H), 7.46 (s, 1H), 7.37 – 7.27 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, J = 58.2 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.8 (t, J = 3.5 Hz), 145.2 (s), 131.6 (s), 128.0 (t, J = 1.5 Hz), 125.8 (s), 111.7 (t, J = 2.9 Hz), 111.4 (s), 110.7 (t, J = 252.3 Hz). IR (KBr): ν 1474, 1446, 1363, 1344, 1308, 1255, 1235, 1075, 950, 863, 726 cm^{-1} . GC-MS m/z 235 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{NOF}_2\text{SCl}$: 234.9670; found: 234.9671.



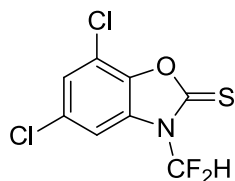
5-Bromo-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (3s)

Obtained as a white solid in 90% yield (101 mg). M.p. 133.1–135.4 °C. R_f (*n*-pentane) = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (t, $J = 58.2$ Hz, 1H), 7.63 (s, 1H), 7.49 (d, $J = 8.6$ Hz, 1H), 7.27 (d, $J = 8.6$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.8 (d, $J = 58.2$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.6 (t, $J = 3.5$ Hz), 145.6 (s), 128.7 (s), 128.3 (t, $J = 1.5$ Hz), 118.6 (s), 114.5 (t, $J = 2.9$ Hz), 111.9 (s), 110.7 (t, $J = 252.4$ Hz). IR (KBr): ν 1602, 1471, 1443, 1345, 1307, 1257, 1144, 1104, 1061, 950, 799, 593 cm^{-1} . GC-MS m/z 279 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_4\text{NOF}_2\text{SBr}$: 278.9165; found: 278.9172.



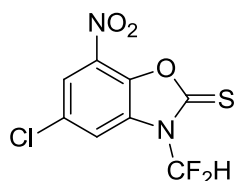
3-(Difluoromethyl)-5-phenylbenzo[d]oxazole-2(3H)-thione (3t)

Obtained as a light yellow solid in 84% yield (93 mg). M.p. 102.7–106.4 °C. R_f (*n*-pentane) = 0.32. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (t, $J = 58.3$ Hz, 1H), 7.66 (s, 1H), 7.62 – 7.54 (m, 3H), 7.52 – 7.48 (m, 2H), 7.45 (d, $J = 7.6$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, $J = 58.3$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 179.1 (t, $J = 3.5$ Hz), 146.1 (s), 139.9 (s), 139.6 (s), 129.1 (s), 128.1 (s), 127.7 (s), 127.4 (s), 124.9 (s), 111.0 (t, $J = 251.6$ Hz), 110.8 (s), 110.0 (t, $J = 2.5$ Hz). IR (KBr): ν 1614, 1478, 1459, 1436, 1350, 1294, 1252, 1134, 1105, 1075, 947, 863 cm^{-1} . GC-MS m/z 277 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_{14}\text{H}_9\text{NOF}_2\text{S}$: 277.0373; found: 277.0368.



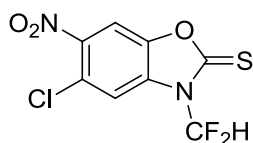
5,7-Dichloro-3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione (3v)

Obtained as a white solid in 52% yield (56 mg). M.p. 104.2–105.8 °C. R_f (*n*-pentane) = 0.72. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (t, J = 58.1 Hz, 1H), 7.37 (s, 1H), 7.36 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9 (d, J = 58.1 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 177.9 (t, J = 3.4 Hz), 142.0 (s), 132.0 (s), 128.8 (t, J = 1.5 Hz), 125.9 (s), 116.7 (s), 110.7 (t, J = 253.2 Hz), 110.1 (t, J = 2.9 Hz). IR (KBr): ν 1625, 1603, 1430, 1360, 1342, 1211, 1144, 1077, 975, 853, 780, 601 cm^{-1} . GC-MS m/z 269 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_3\text{NOF}_2\text{SCl}_2$: 268.9280; found: 268.9285.



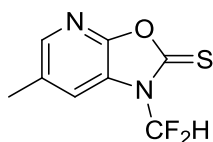
5-Chloro-3-(difluoromethyl)-7-nitrobenzo[d]oxazole-2(3H)-thione (3w)

Obtained as a light yellow solid in 29% yield (32 mg), M.p. 136.5–139.4 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.64. ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 7.74 (s, 1H), 7.69 (t, J = 57.9 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.6 (d, J = 57.9 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 177.4 (t, J = 3.2 Hz), 139.1 (s), 132.0 (s), 131.9 (s), 130.8 (t, J = 1.6 Hz), 120.7 (s), 116.6 (t, J = 3.1 Hz), 110.7 (t, J = 254.2 Hz). IR (KBr): ν 1556, 1472, 1340, 1260, 1125, 1075, 986, 932, 885, 861, 807, 543 cm^{-1} . GC-MS m/z 281 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_3\text{N}_2\text{O}_3\text{F}_2\text{SCl}$: 279.9521; found: 279.9517.



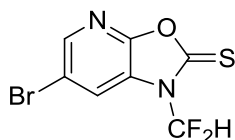
5-Chloro-3-(difluoromethyl)-6-nitrobenzo[d]oxazole-2(3H)-thione (3x)

Obtained as a light yellow solid in 50% yield (56 mg), M.p. 156.0–157.8 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.68. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.68 (t, J = 58.0 Hz, 1H), 7.63 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.6 (d, J = 58.0 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.3 (t, J = 2.9 Hz), 144.9 (t, J = 4.7 Hz), 144.4 (s), 130.7 (s), 125.9 (s), 113.6 (t, J = 3.0 Hz), 110.5 (t, J = 254.2 Hz), 108.4 (s). IR (KBr): ν 1538, 1472, 1340, 1260, 1125, 1075, 986, 932, 885, 862, 807, 543 cm^{-1} . GC-MS m/z 280 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_3\text{N}_2\text{O}_3\text{F}_2\text{S}$: 279.9521; found:279.9531.



1-(Difluoromethyl)-6-methyloxazolo[5,4-*b*]pyridine-2(1*H*)-thione (3z)

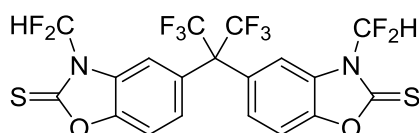
Obtained as a light yellow solid in 36% yield (31 mg), M.p. 98.0–102.8 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.59. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.80 (t, J = 58.5 Hz, 1H), 7.57 (s, 1H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.6 (d, J = 58.5 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 177.3 (t, J = 3.5 Hz), 153.4 (s), 144.4 (s), 131.8 (s), 120.1 (t, J = 1.5 Hz), 119.8 (t, J = 2.4 Hz), 110.4 (t, J = 252.1 Hz), 18.4 (s). IR (KBr): ν 1625 1415, 1356, 1339, 1310, 1277, 1228, 1112, 1069, 889, 828, 598 cm^{-1} . GC-MS m/z 217 (M^+). HRMS (EI) m/z : calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{OF}_2\text{S}$: 216.0169; found: 216.0173.



6-Bromo-1-(difluoromethyl)oxazolo[5,4-*b*]pyridine-2(1*H*)-thione (3aa)

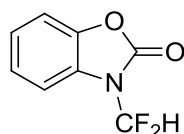
Obtained as a white solid in 37% yield (42 mg). M.p. 106.8–109.7 °C. R_f (*n*-pentane/ethyl acetate = 25:1) = 0.71. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 7.87 (s, 1H), 7.70 (t, J = 58.3 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -103.4 (d, J = 58.3 Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 176.7 (t, J = 3.1 Hz), 153.7 (s), 145.1 (s),

121.7 (t, $J = 2.7$ Hz), 121.5 (t, $J = 1.3$ Hz), 117.0 (s), 110.3 (t, $J = 253.2$ Hz). IR (KBr): ν 1616, 1596, 1416, 1357, 1343, 1320, 1299, 1224, 1110, 1069, 944, 876 cm^{-1} . GC-MS m/z 281 (M^+). HRMS (EI) m/z : calcd. for $C_7H_3N_2OF_2SBr$: 279.9118; found: 279.9121.



5,5'-(Perfluoropropane-2,2-diyl)bis(3-(difluoromethyl)benzo[d]oxazole-2(3H)-thione) (3ab)

Obtained as a light yellow solid in 98% yield (215 mg), M.p. 135.6–1136.7 °C. R_f (n -pentane/ethyl acetate = 25:1) = 0.68. ^1H NMR (400 MHz, CDCl_3) δ 7.71 (t, $J = 58.2$ Hz, 2H), 7.53 (s, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -63.7 (s, 6F), -103.9 (d, $J = 58.2$ Hz, 4F). ^{13}C NMR (101 MHz, CDCl_3) δ 178.8 (t, $J = 3.3$ Hz), 147.0 (s), 130.6 (s), 127.9 (s), 127.7 (s), 123.6 (q, $J = 286.1$ Hz), 113.0 (s), 110.8 (t, $J = 252.4$ Hz), 110.6 (s), 65.7 – 63.9 (m). IR (KBr): ν 1498, 1457, 1362, 1314, 1297, 1179, 1108, 964, 814, 790, 719, 597 cm^{-1} . GC-MS m/z 550 (M^+). HRMS (EI) m/z : calcd. for $C_{19}H_8N_2O_2F_{10}S_2$: 549.9868; found: 549.9877.



3-(Difluoromethyl)benzo[d]oxazol-2(3H)-one (5)

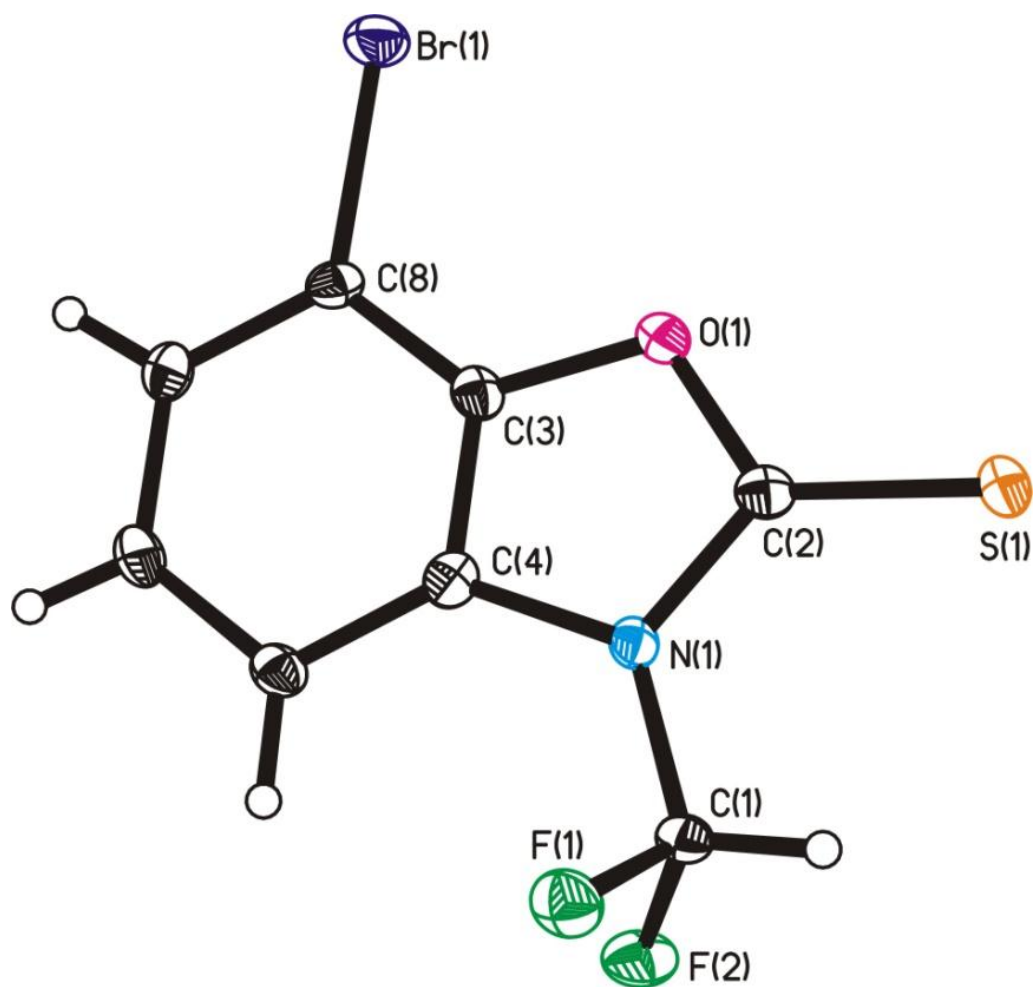
Obtained as a light yellow liquid in 70% yield (52 mg). R_f (n -pentane) = 0.75. ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.35 (m, 1H), 7.28 – 7.24 (m, 3H), 7.23 (t, $J = 58.1$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -102.4 (d, $J = 58.1$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 151.2 (t, $J = 3.5$ Hz), 142.4 (s), 125.6 (s), 124.7 (s), 124.6 (s), 111.4 (t, $J = 1.8$ Hz), 110.6 (s), 108.8 (t, $J = 247.1$ Hz). IR (KBr): ν 1792, 1483, 1408, 1370,

1328, 1253, 1140, 1112, 1052, 1015, 989 cm^{-1} . GC-MS m/z 186 (M^+). HRMS (EI)
 m/z : calcd. for $\text{C}_8\text{H}_5\text{NO}_2\text{F}_2$: 185.0288; found: 185.0286.

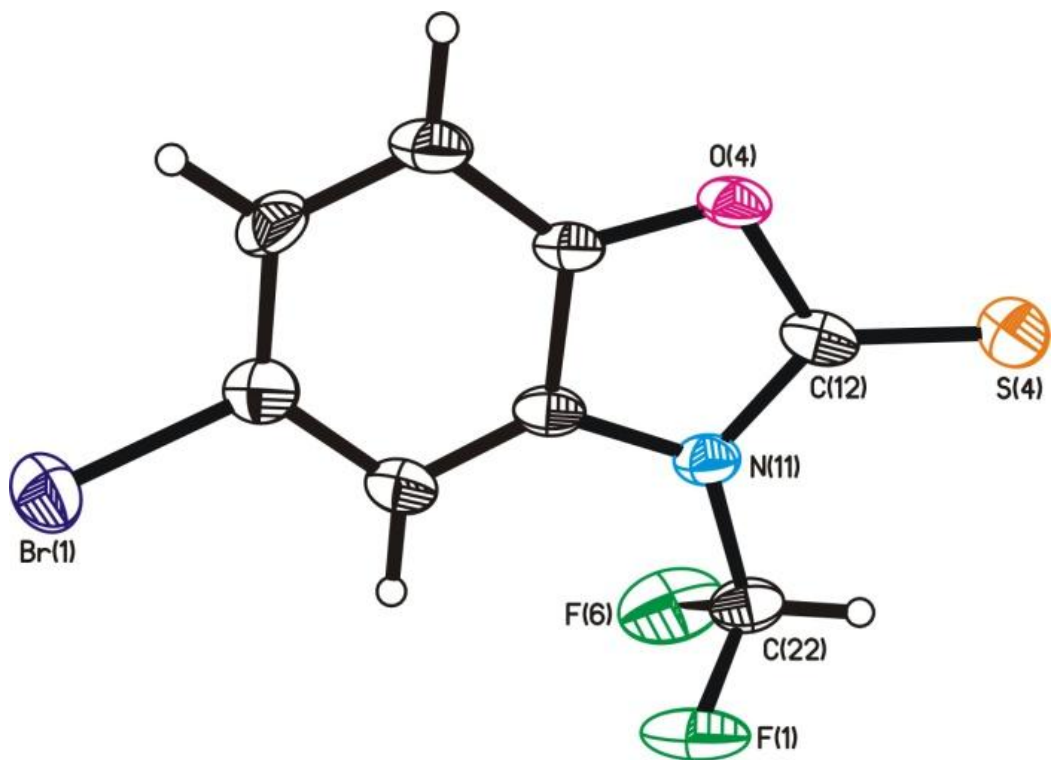
Crystal structure analyses

The suitable crystals of **3d** (CCDC 1843392), and **3s** (CCDC 1852585) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoK α 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.² Structure solution and refinement were carried out with the SHELXTL suite of programs.² The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

ORTEP diagrams



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



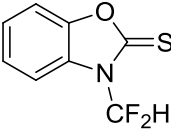
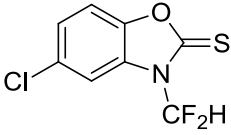
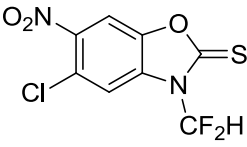
ORTEP diagram of compound 3s. Thermal ellipsoids are drawn at 40% probability

The procedure for the insecticidal assay

Each of the test compounds was first dissolved in 5 mL of mixture of acetone and methanol (1:1 by volume), and then 5 mL of water containing 0.1% Tween 80 was added to generate a 10 mL stock solution of 600 mg/L concentration.

The cabbage leaves were cut into small circular pieces ($\phi = 30$ mm), and placed on the glass Petri dishes ($\phi = 60$ mm) layered with filter papers that had been wet with sterilized distilled water. The cabbage leaves were sprayed with the aforementioned solutions using an Airbrush sprayer (dosage 0.5 mL). After they were air dried, the third-instar insects were introduced to the cabbage leaves. They were kept in a special room for normal cultivation (temperature: 23-25 °C; RH: 40-60%, L/D: 13 h/11 h). Assessments were made after 48 h by the number of killed and size of live insects relative to that in the negative control, and evaluations were based on a percentage scale of 0-100, in which 100 was total kill and 0 was no activity.

The general screening of the title compounds on insecticidal activities

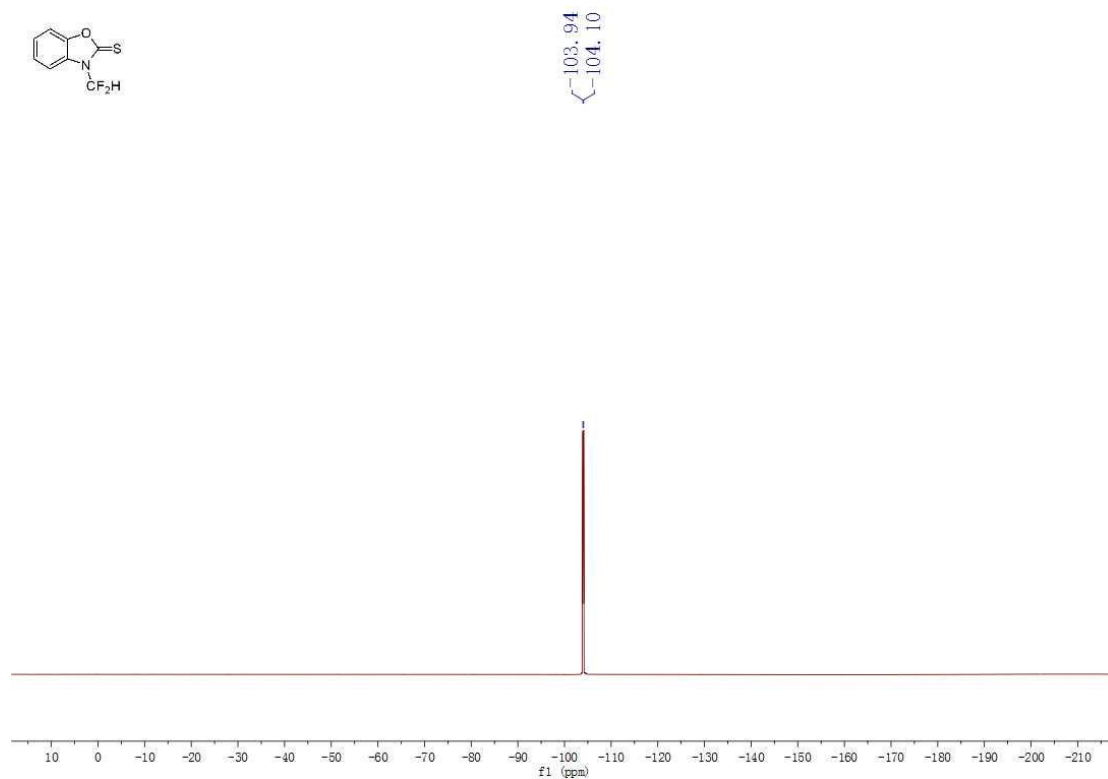
Compound	Mortality (%) at the concentration of 600 mg/L		
	Plutella xylostella	Myzus persicae	Two-spotted spider mite
 3a	12	0	0
 3r	0	0	0
 3x	42	0	0

References:

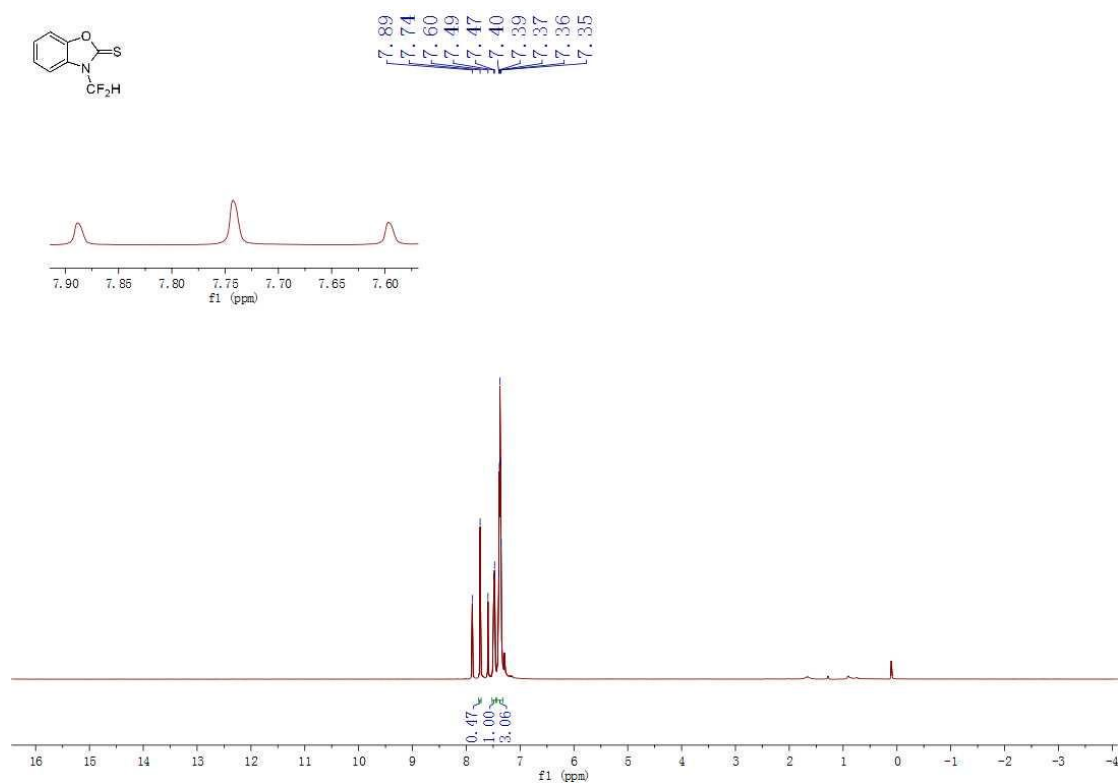
- (1) (a) Mehta, V. P.; Greaney, M. F. *Org. Lett.* **2013**, *15*, 5036; (b) Heine, N. B.; Studer, A. *Org. Lett.* **2017**, *19*, 4150.
- (2) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

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

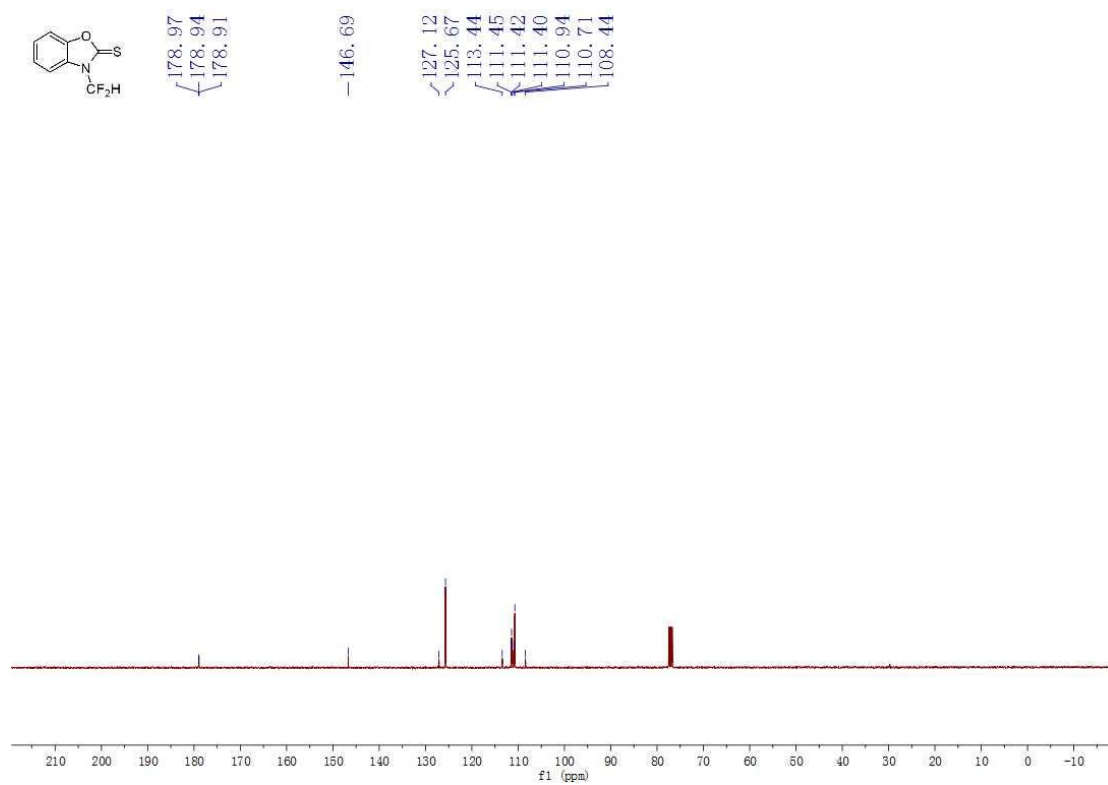
^{19}F NMR spectrum of **3a** in CDCl_3



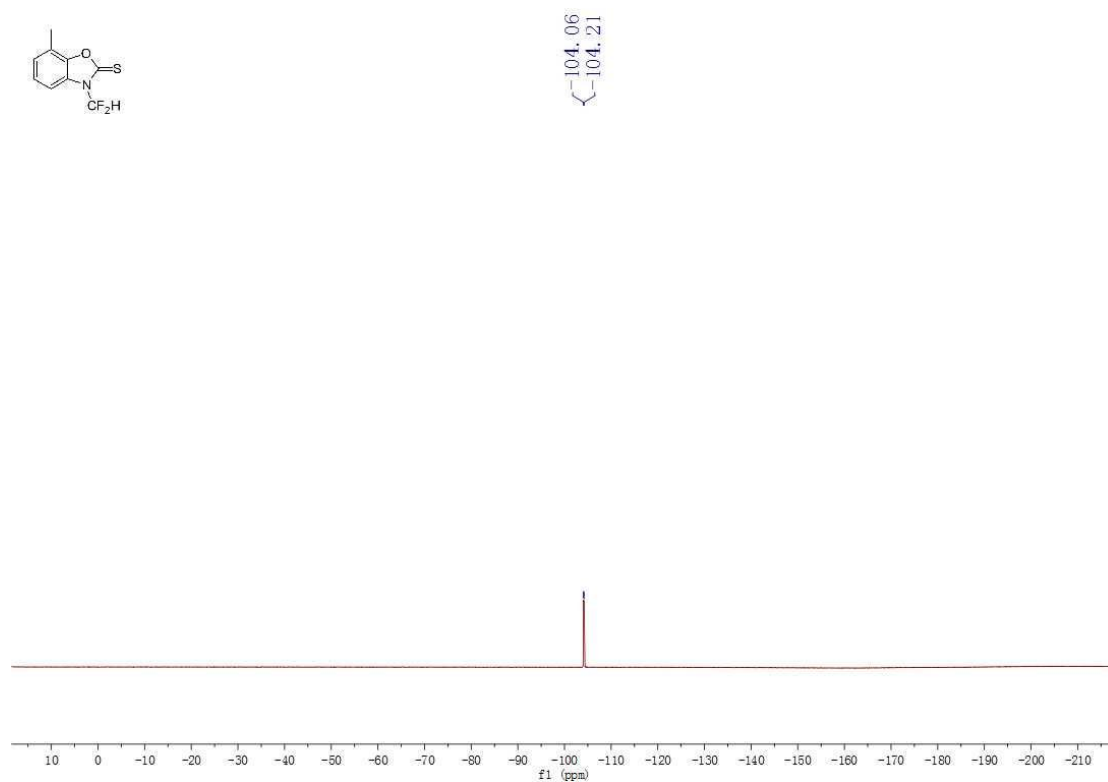
^1H NMR spectrum of **3a** in CDCl_3



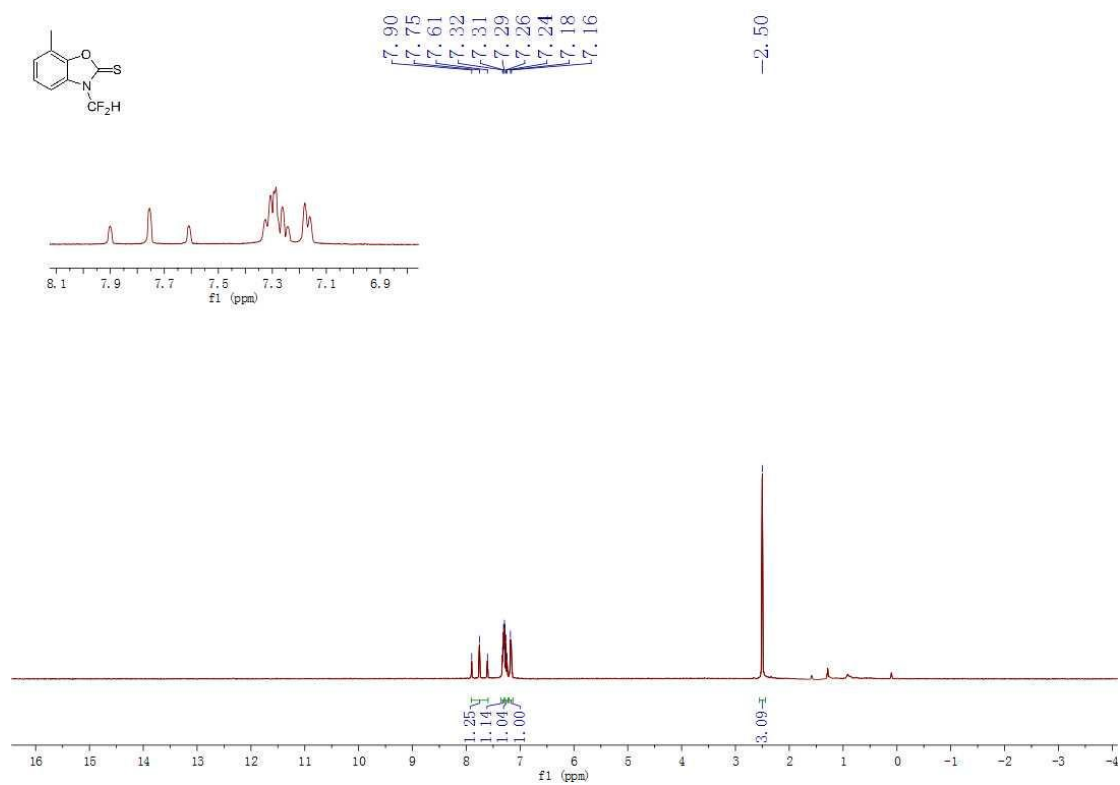
¹³C NMR spectrum of 3a in CDCl₃



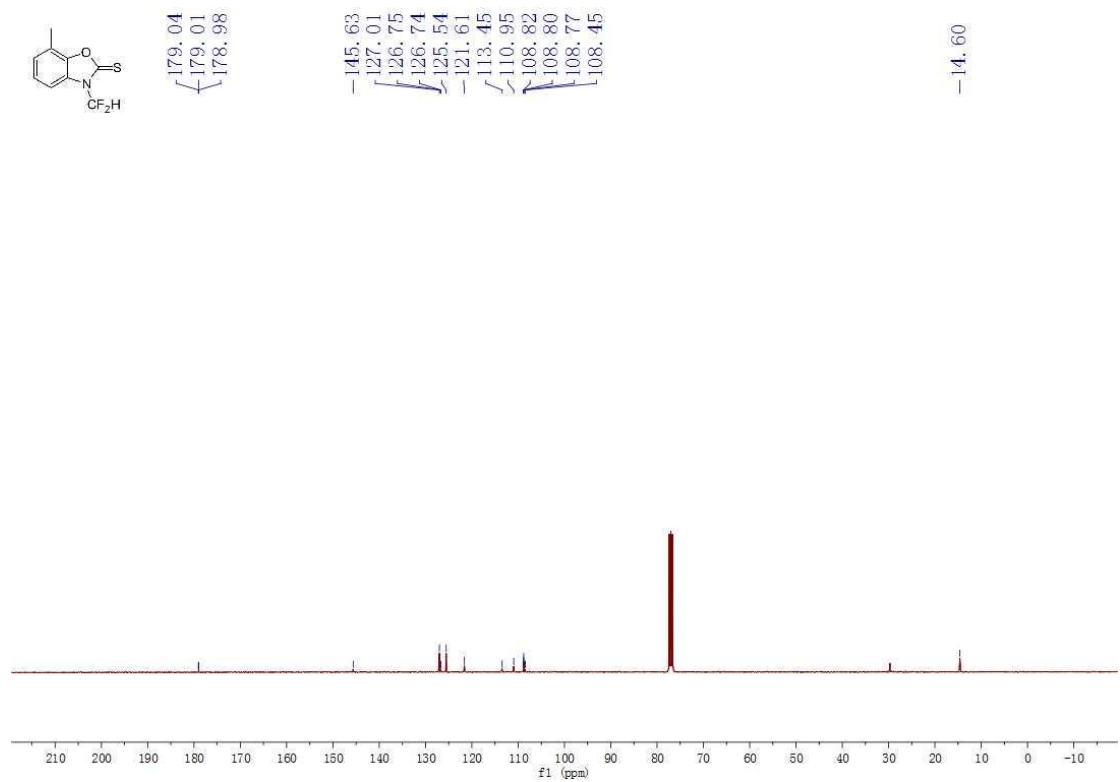
¹⁹F NMR spectrum of 3b in CDCl₃



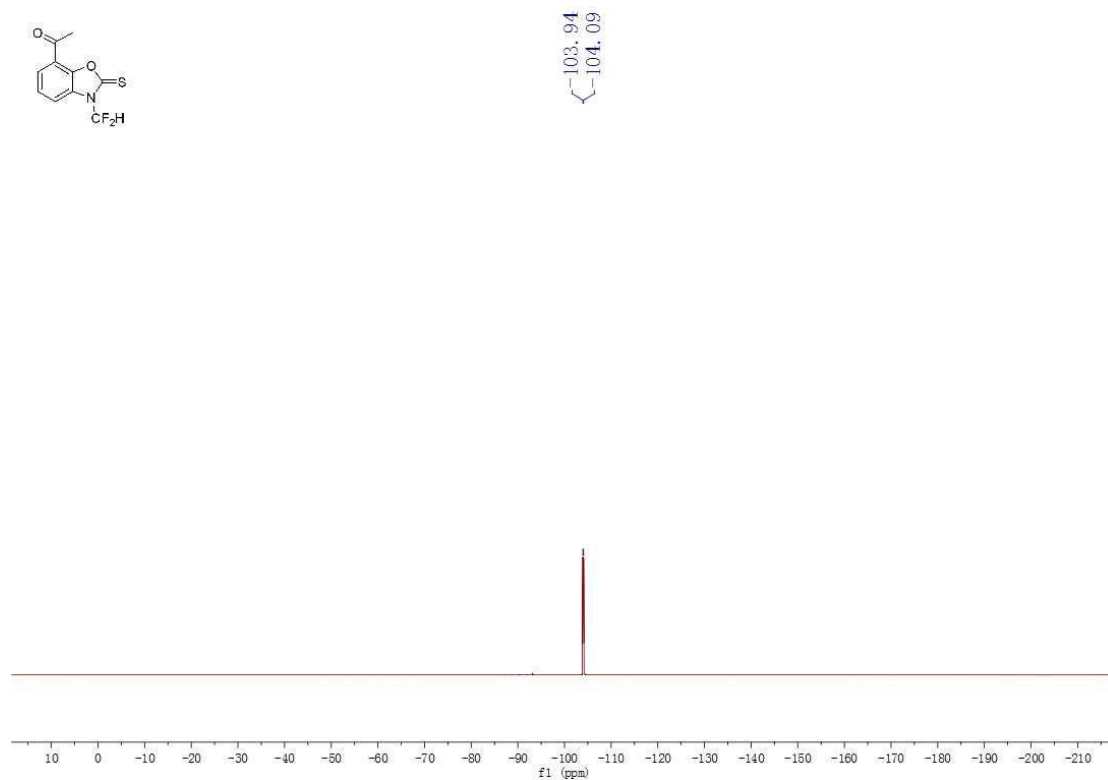
¹H NMR spectrum of 3b in CDCl₃



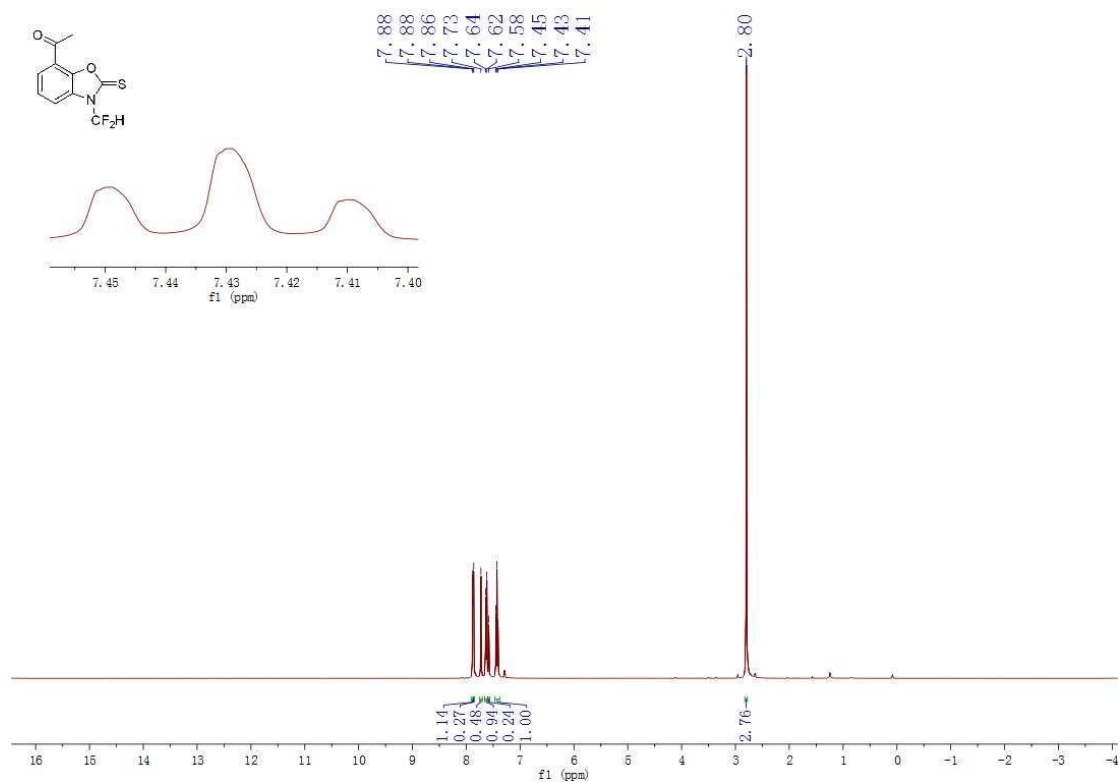
¹³C NMR spectrum of 3b in CDCl₃



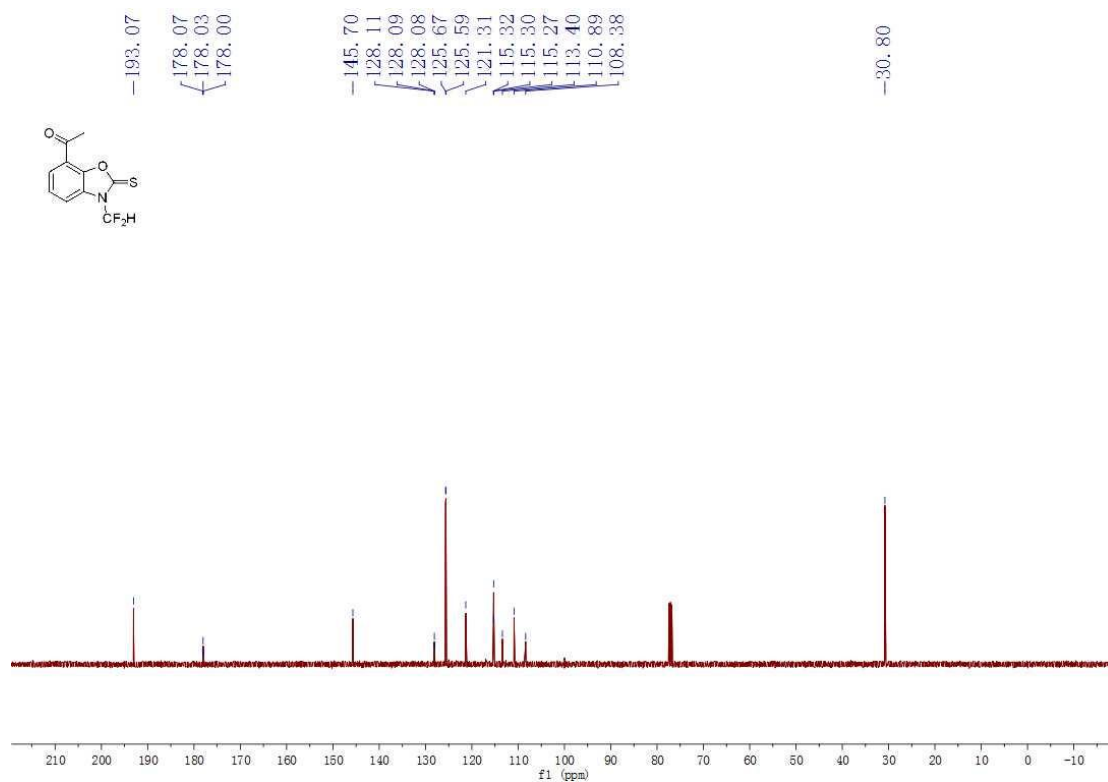
¹⁹F NMR spectrum of 3c in CDCl₃



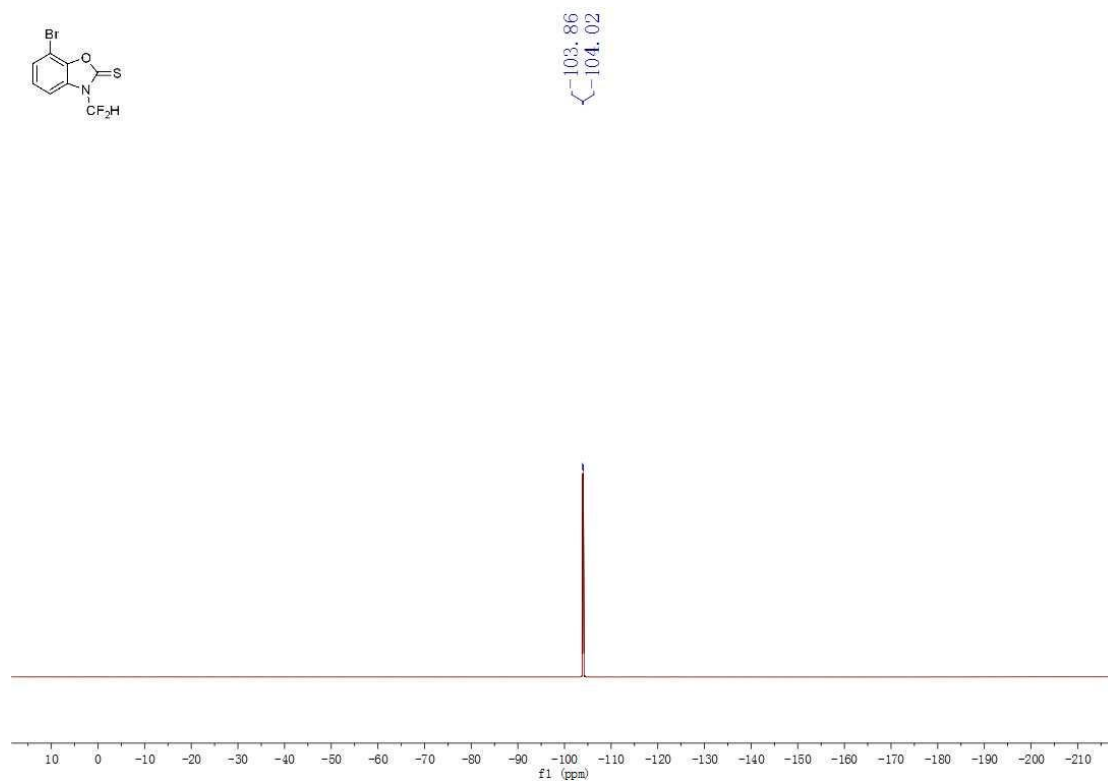
¹H NMR spectrum of 3c in CDCl₃



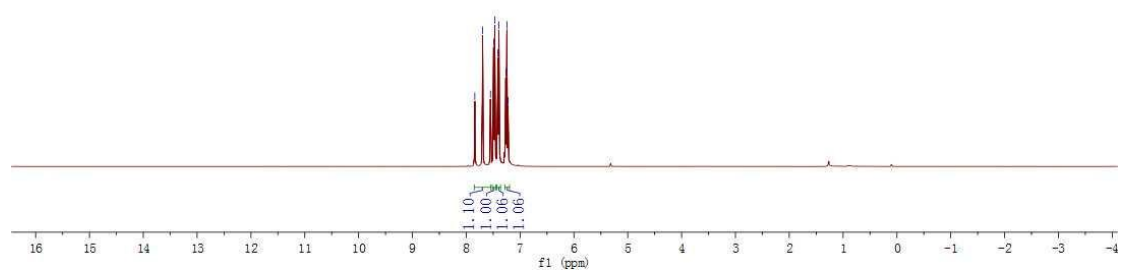
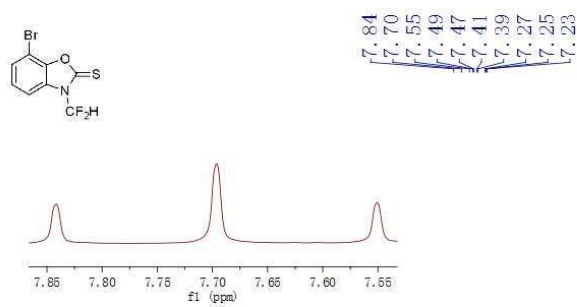
^{13}C NMR spectrum of **3c** in CDCl_3



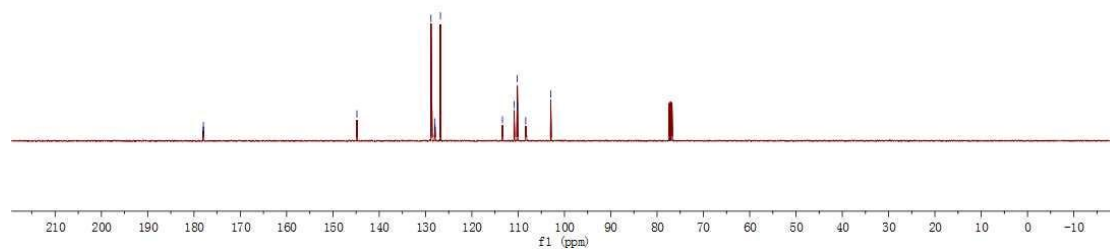
^{19}F NMR spectrum of **3d** in CDCl_3



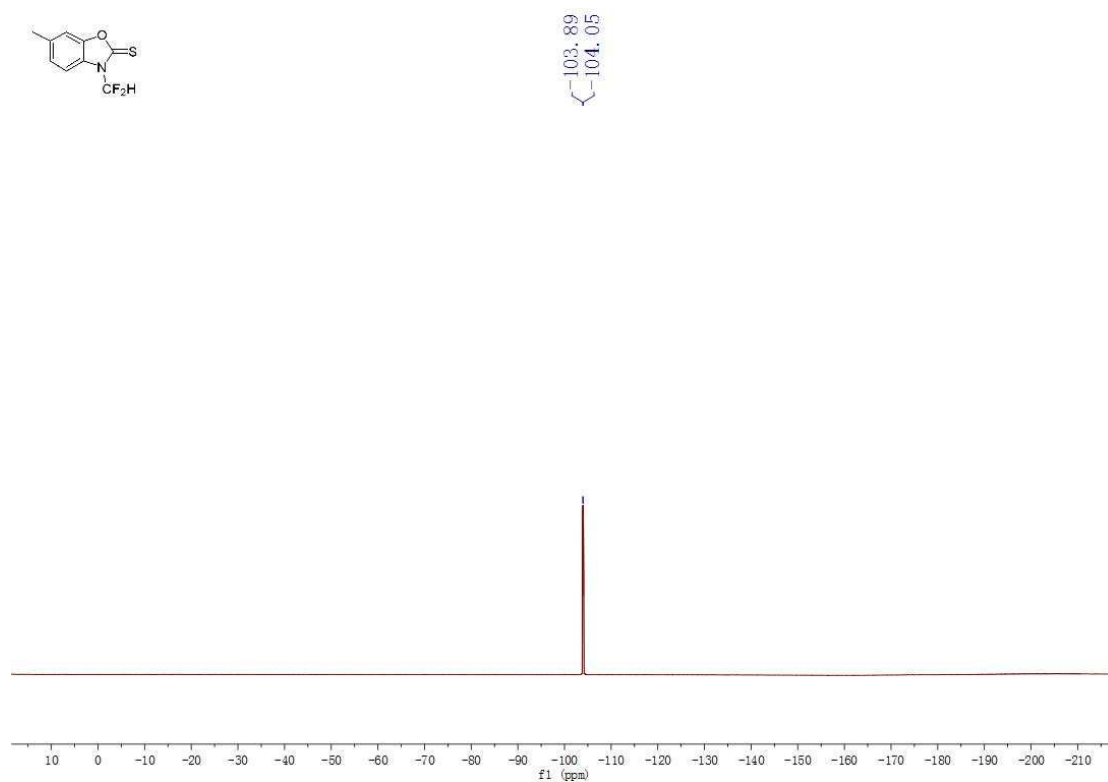
¹H NMR spectrum of **3d** in CDCl₃



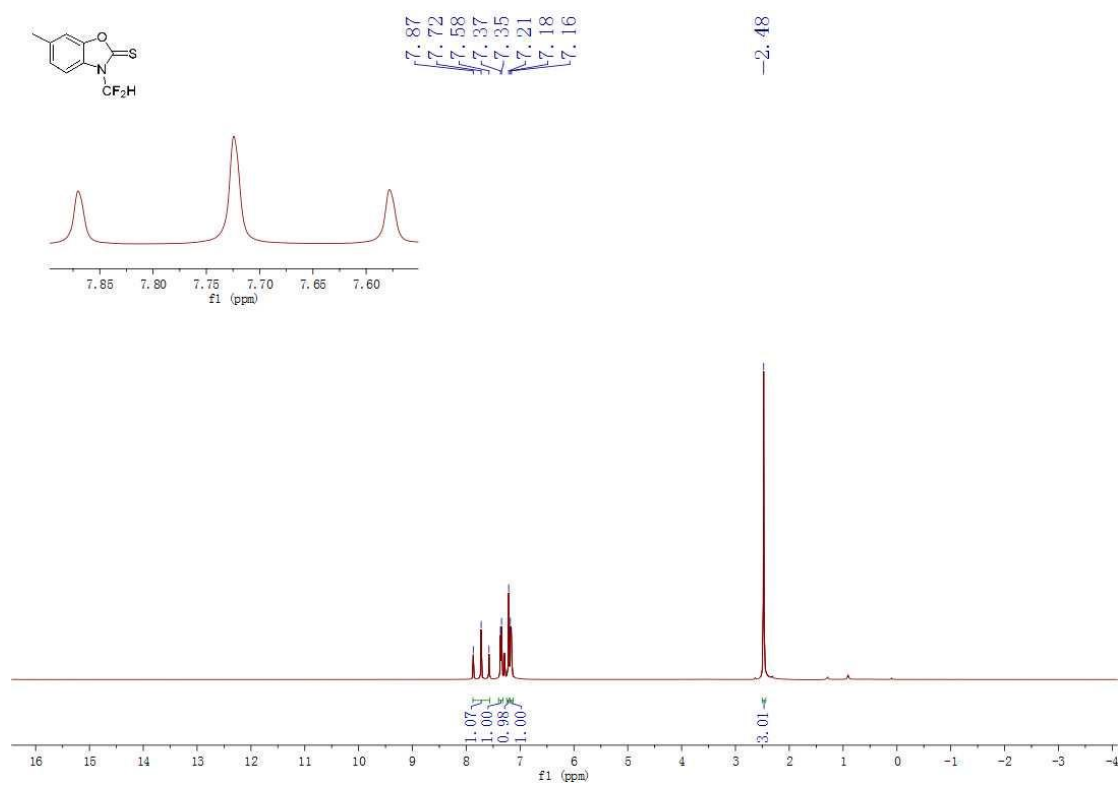
¹³C NMR spectrum of **3d** in CDCl₃



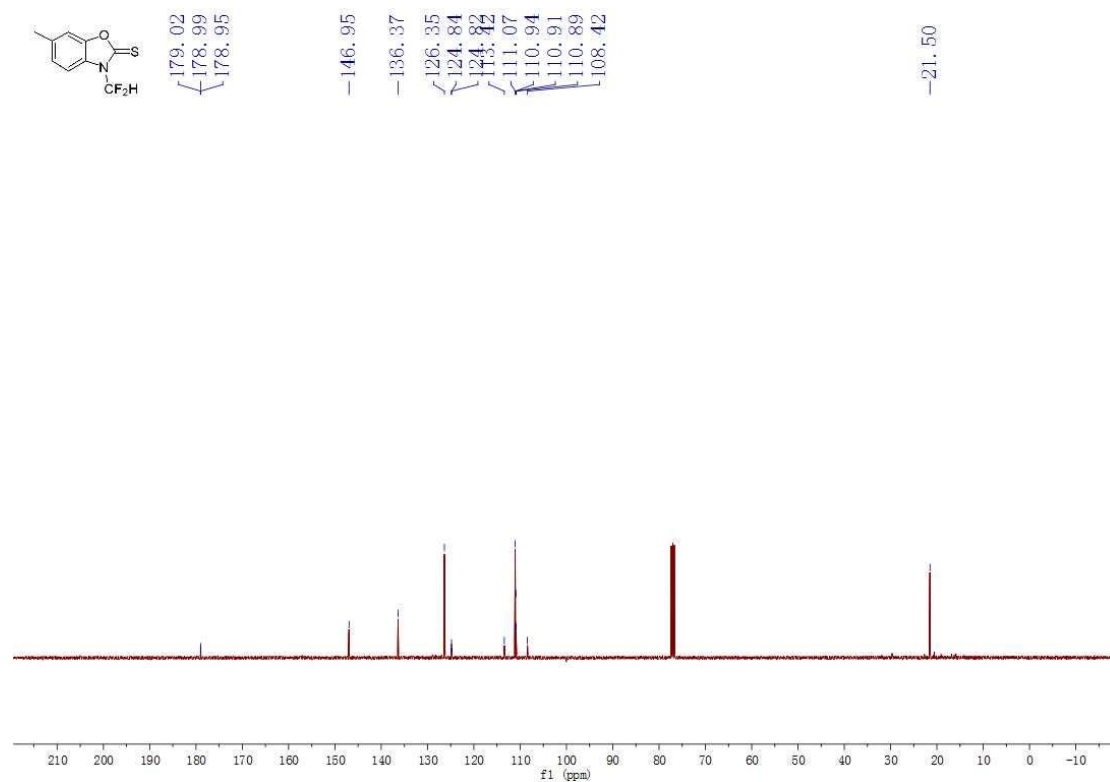
¹⁹F NMR spectrum of 3e in CDCl₃



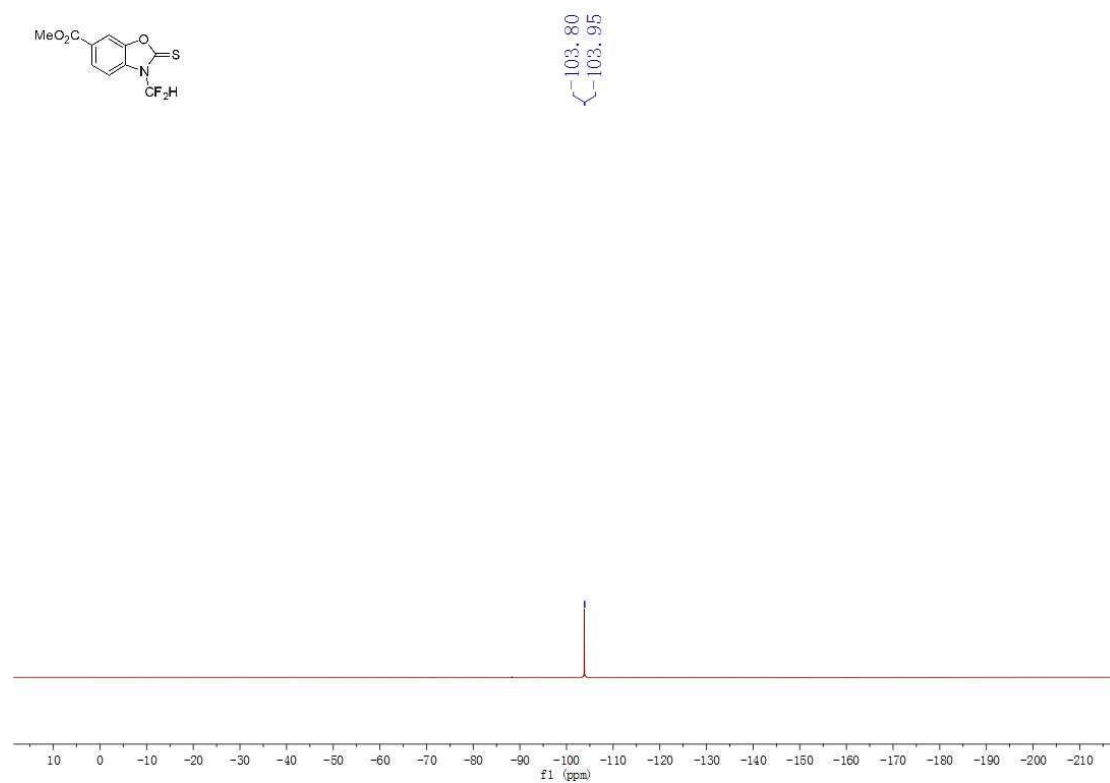
¹H NMR spectrum of 3e in CDCl₃



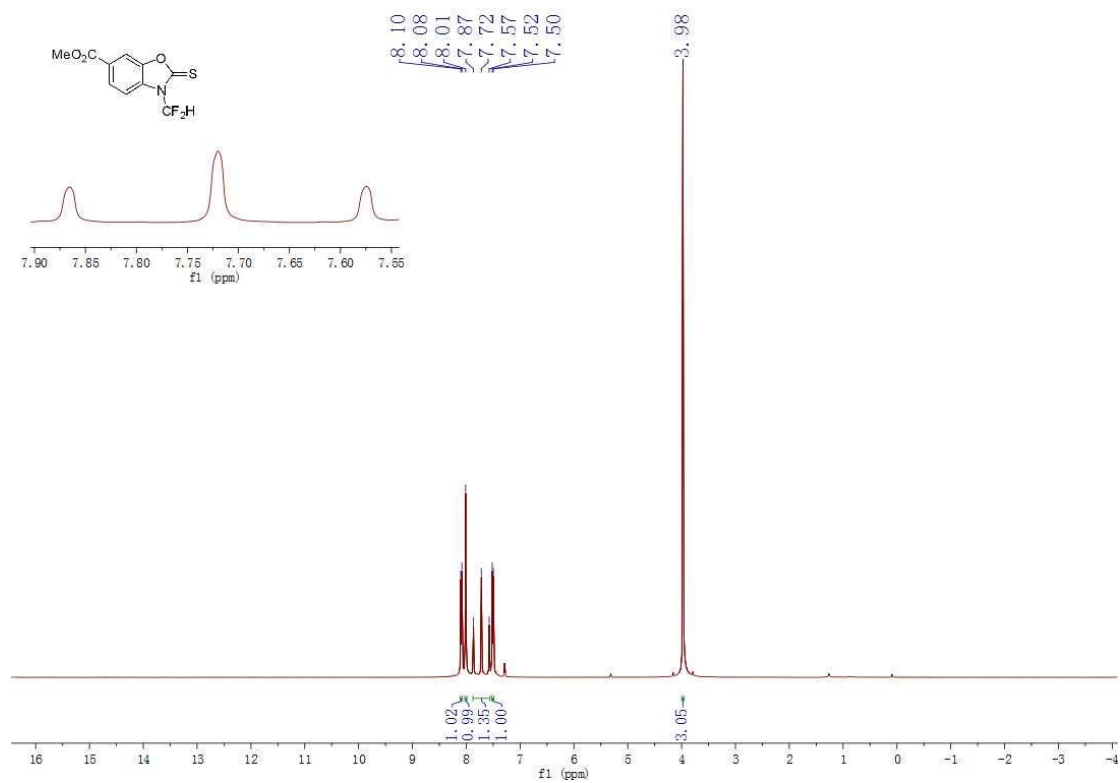
¹³C NMR spectrum of **3e** in CDCl₃



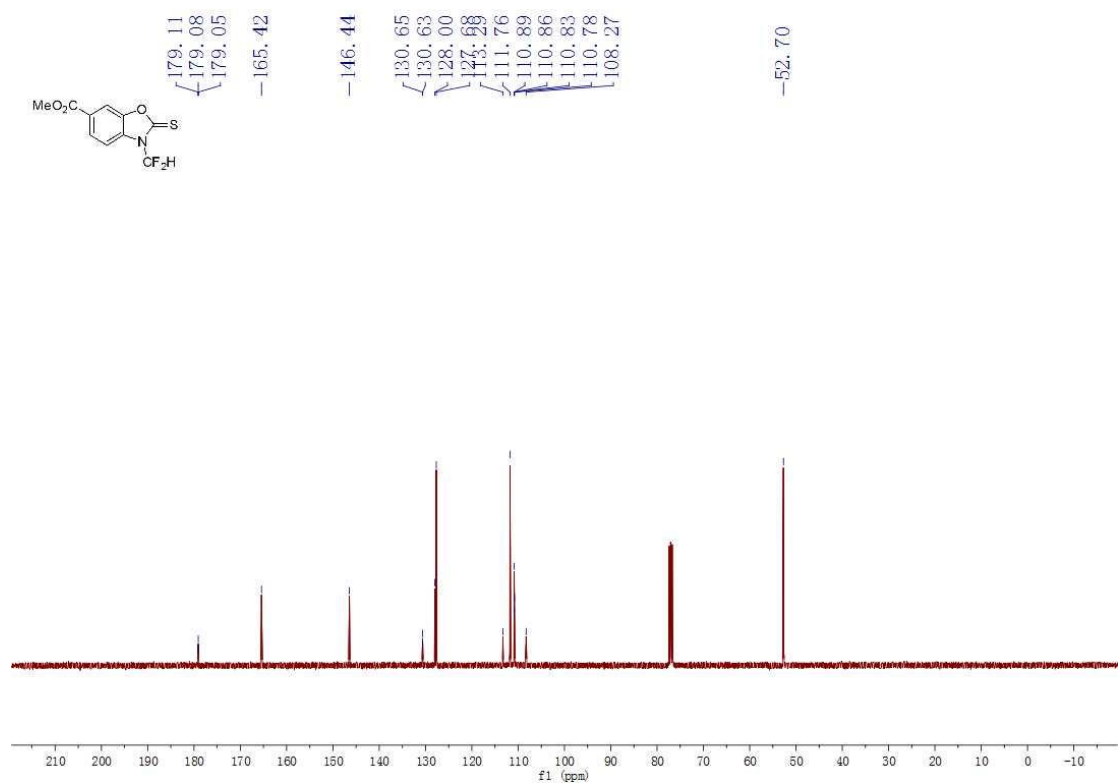
¹⁹F NMR spectrum of **3f** in CDCl₃



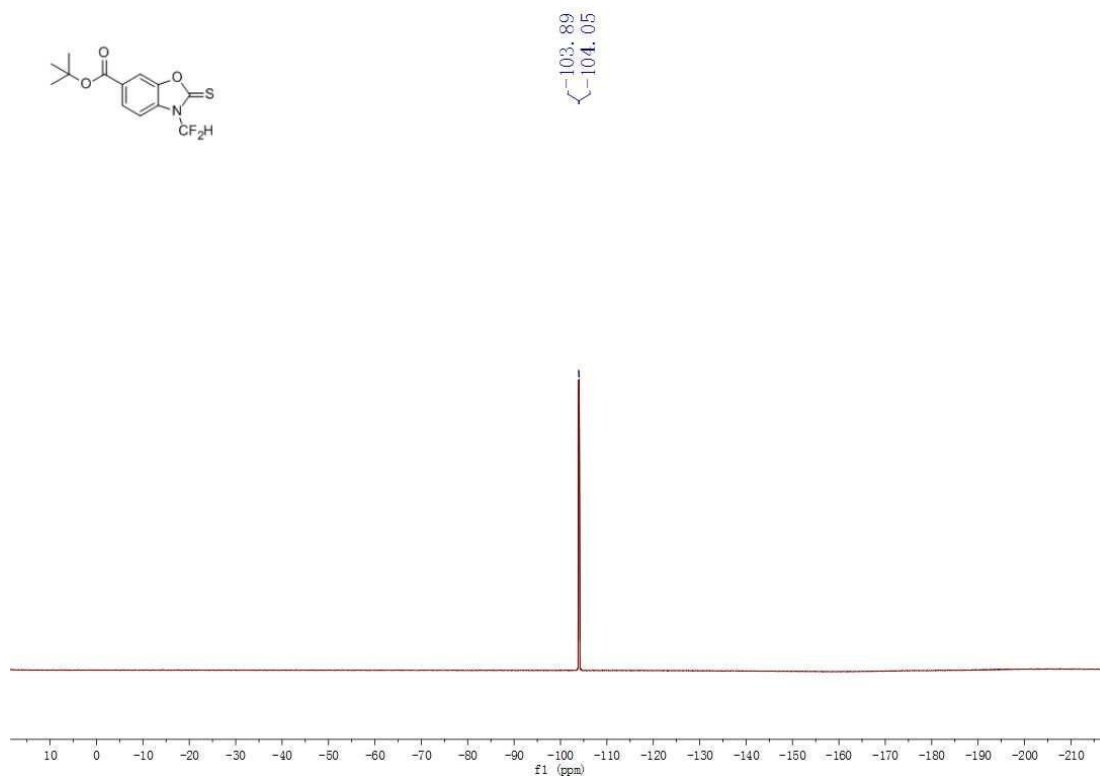
^1H NMR spectrum of **3f** in CDCl_3



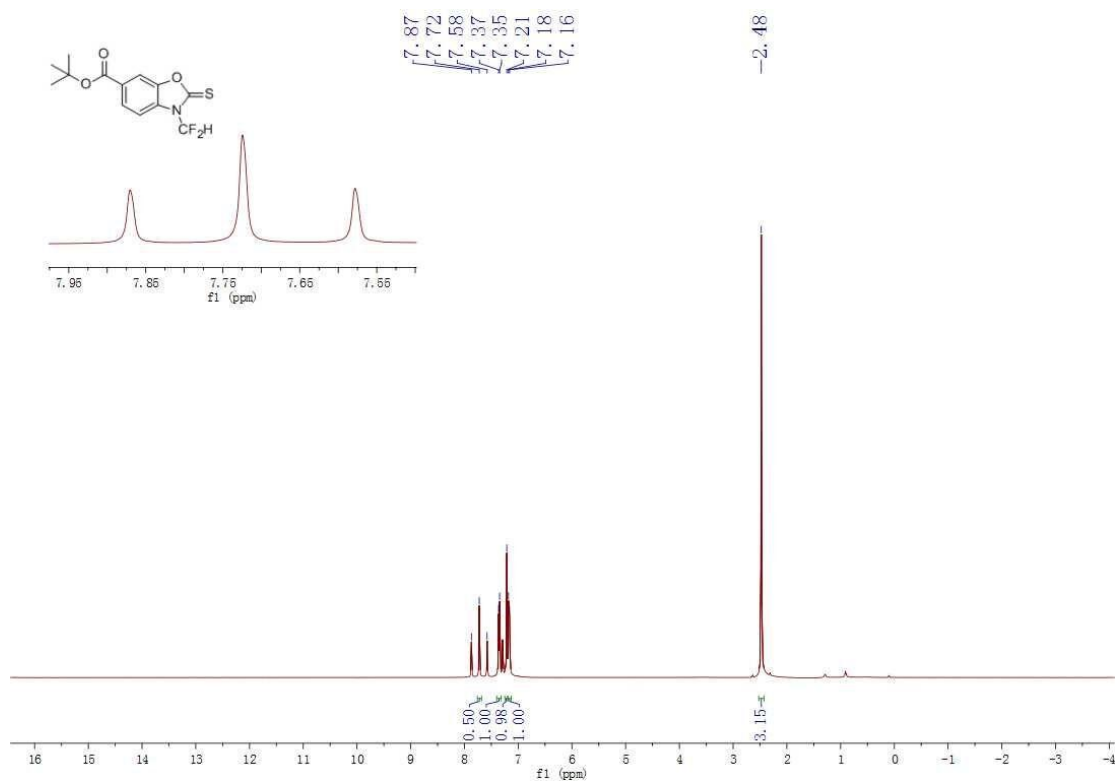
^{13}C NMR spectrum of **3f** in CDCl_3



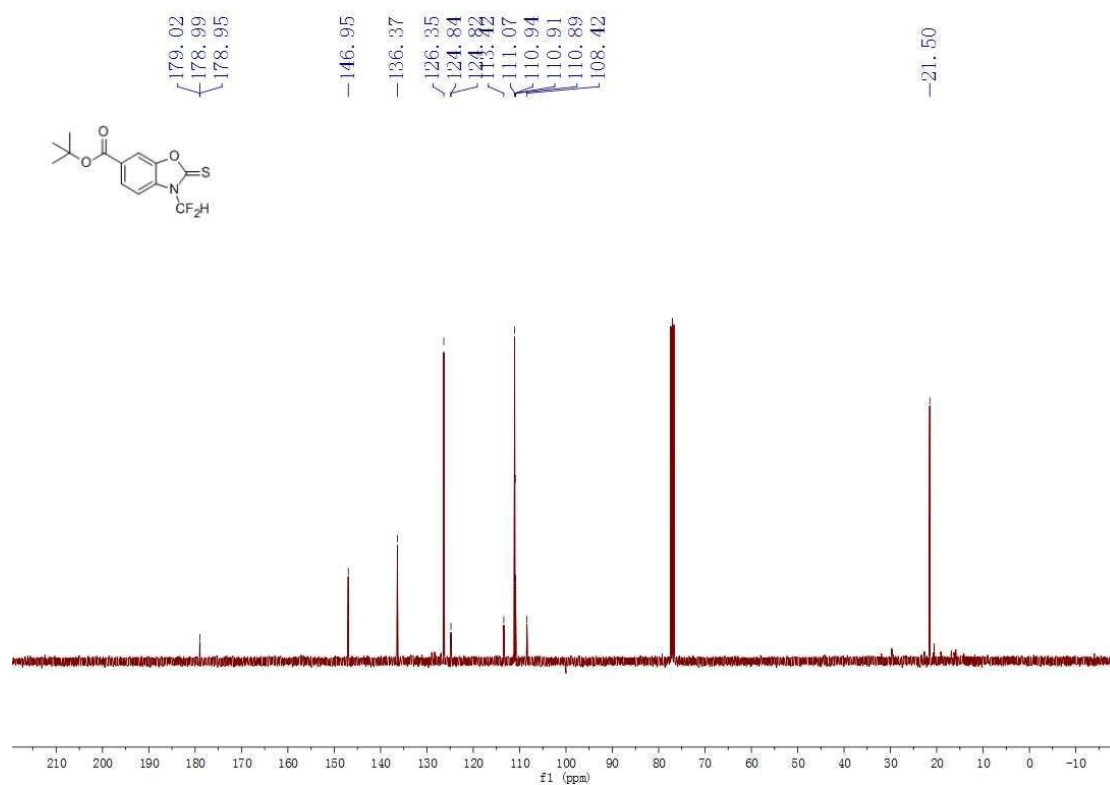
¹⁹F NMR spectrum of 3g in CDCl₃



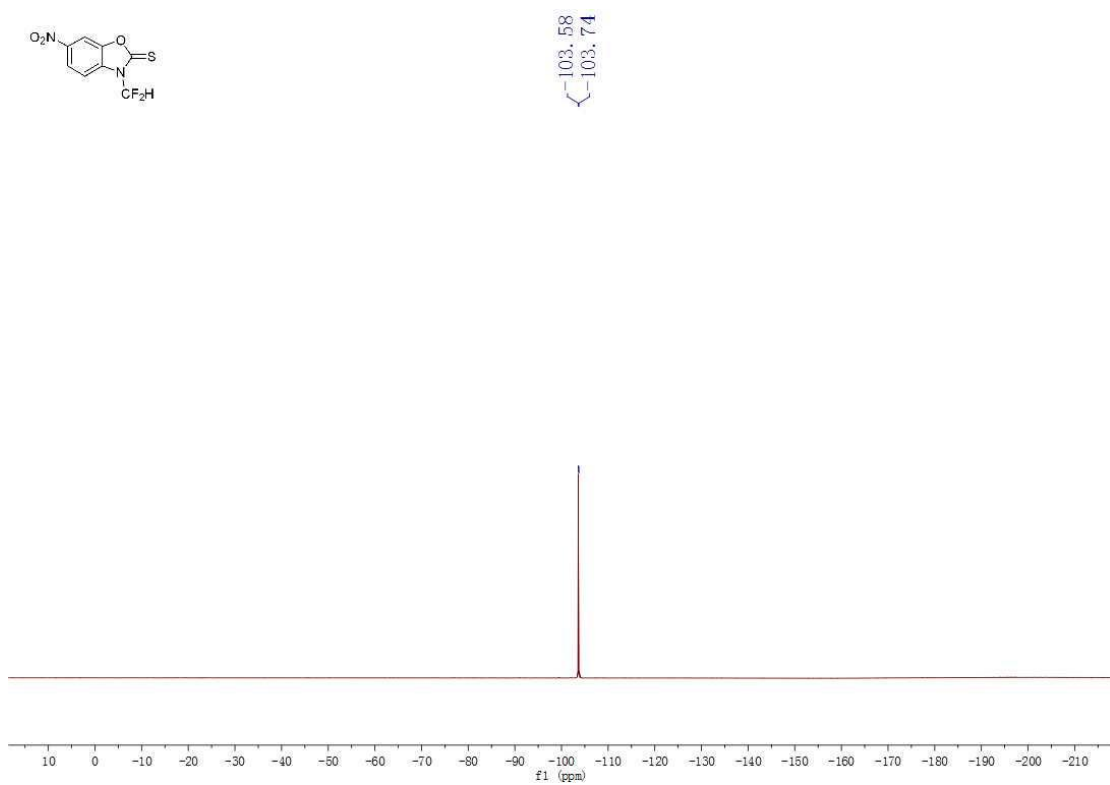
¹H NMR spectrum of 3g in CDCl₃



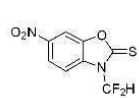
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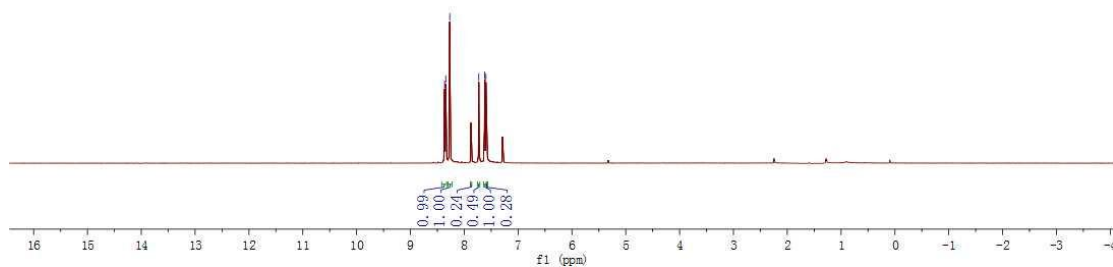
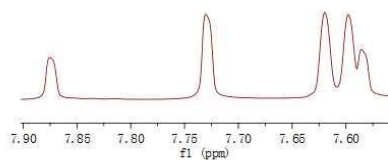
¹⁹F NMR spectrum of **3h** in CDCl₃



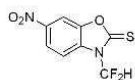
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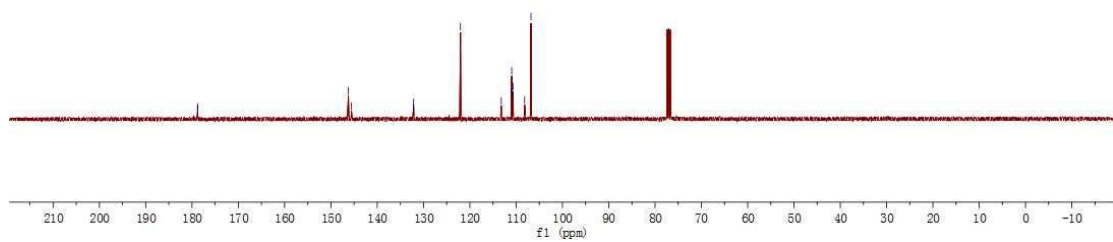
8.37
8.34
8.27
7.73
7.62
7.60



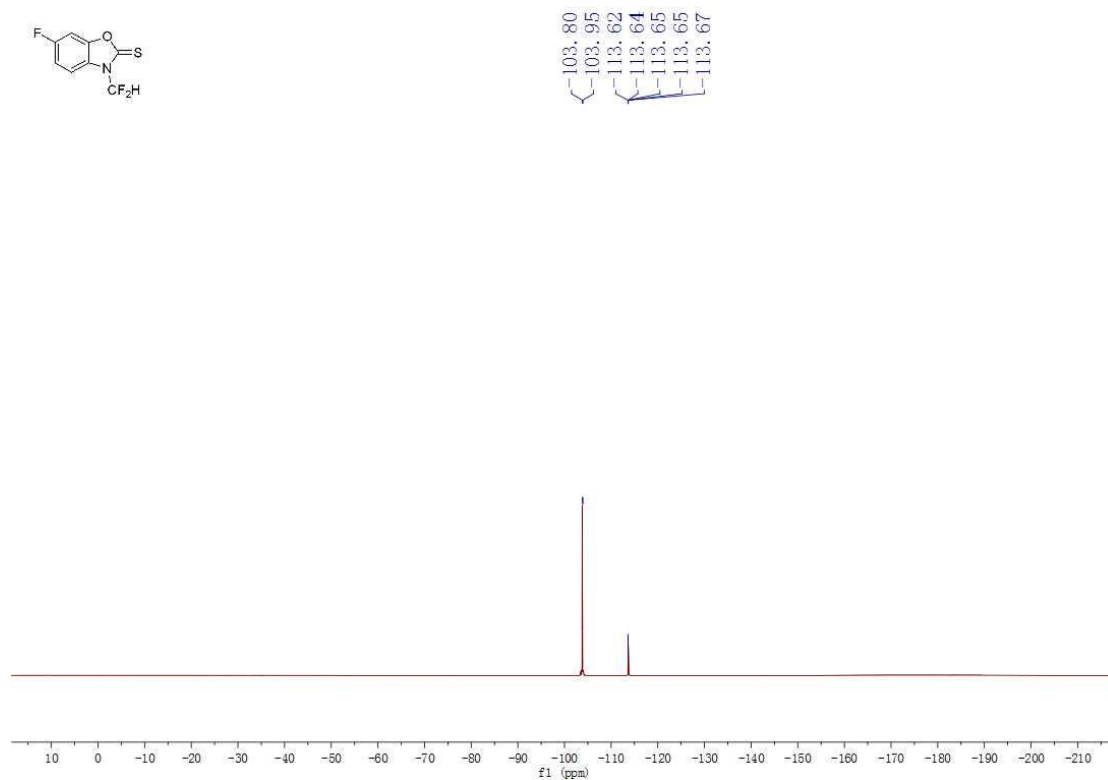
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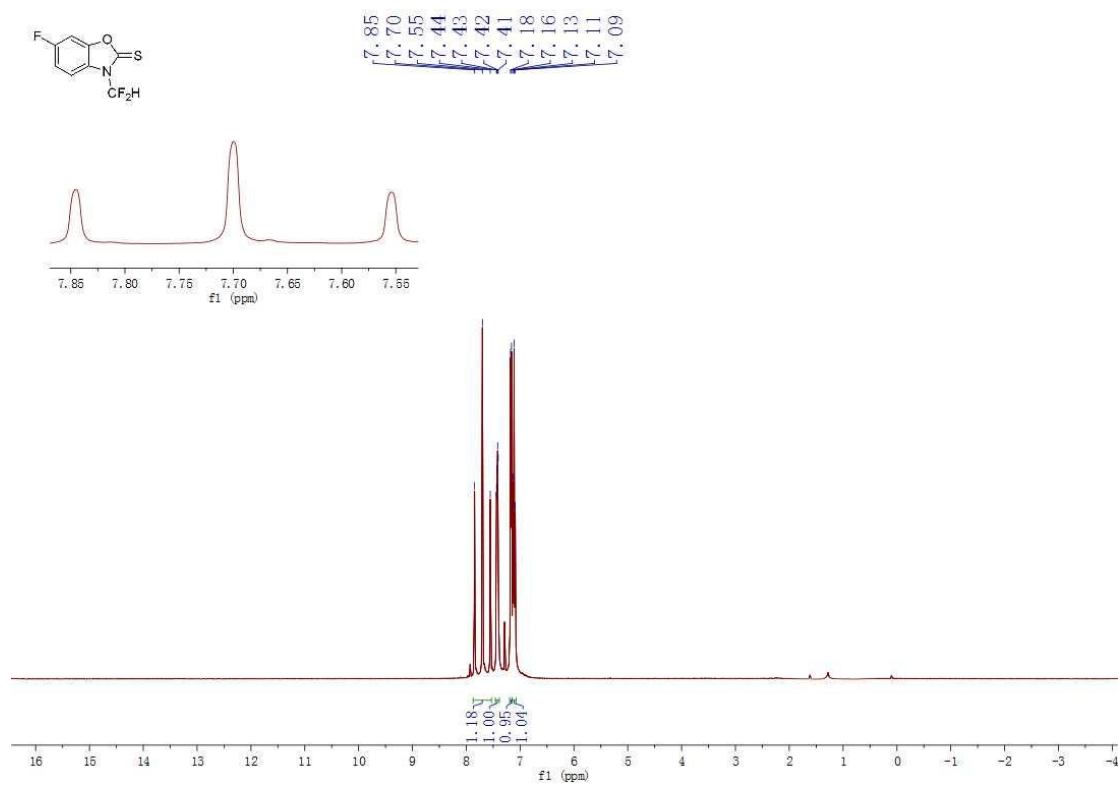
178.82
178.79
178.76
146.22
145.56
132.16
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113.21
110.98
110.96
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110.69
108.17
106.80



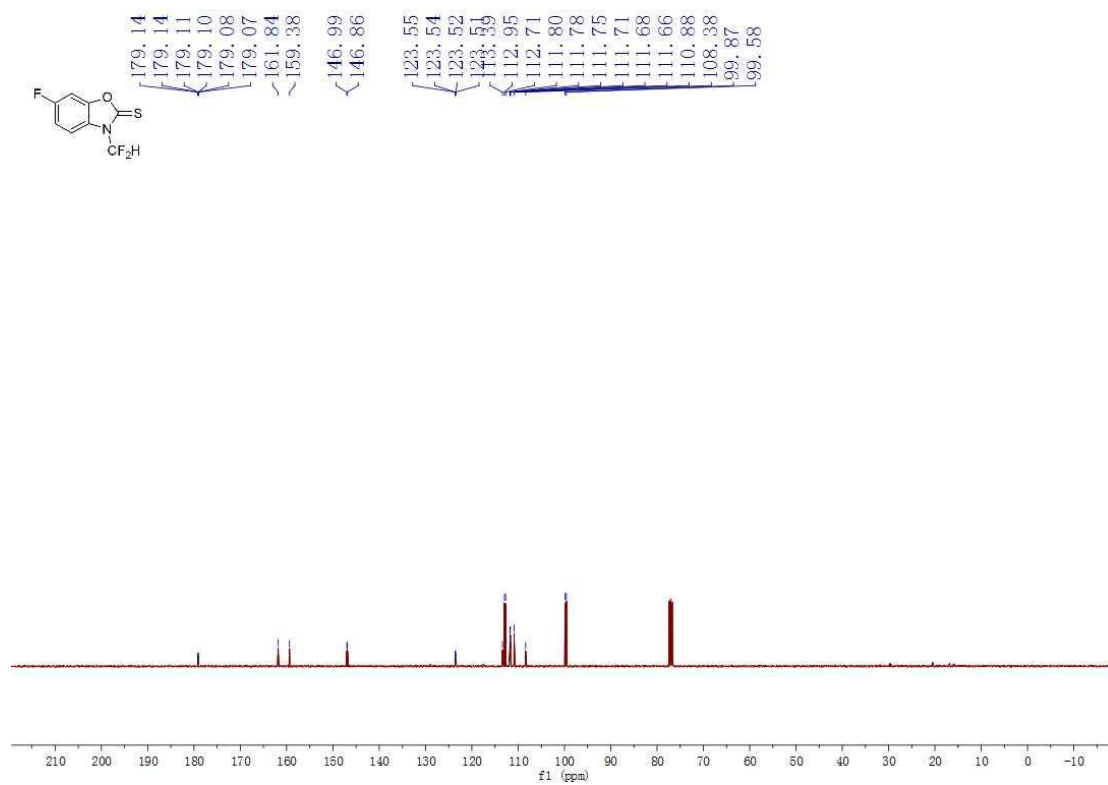
¹⁹F NMR spectrum of **3i** in CDCl₃



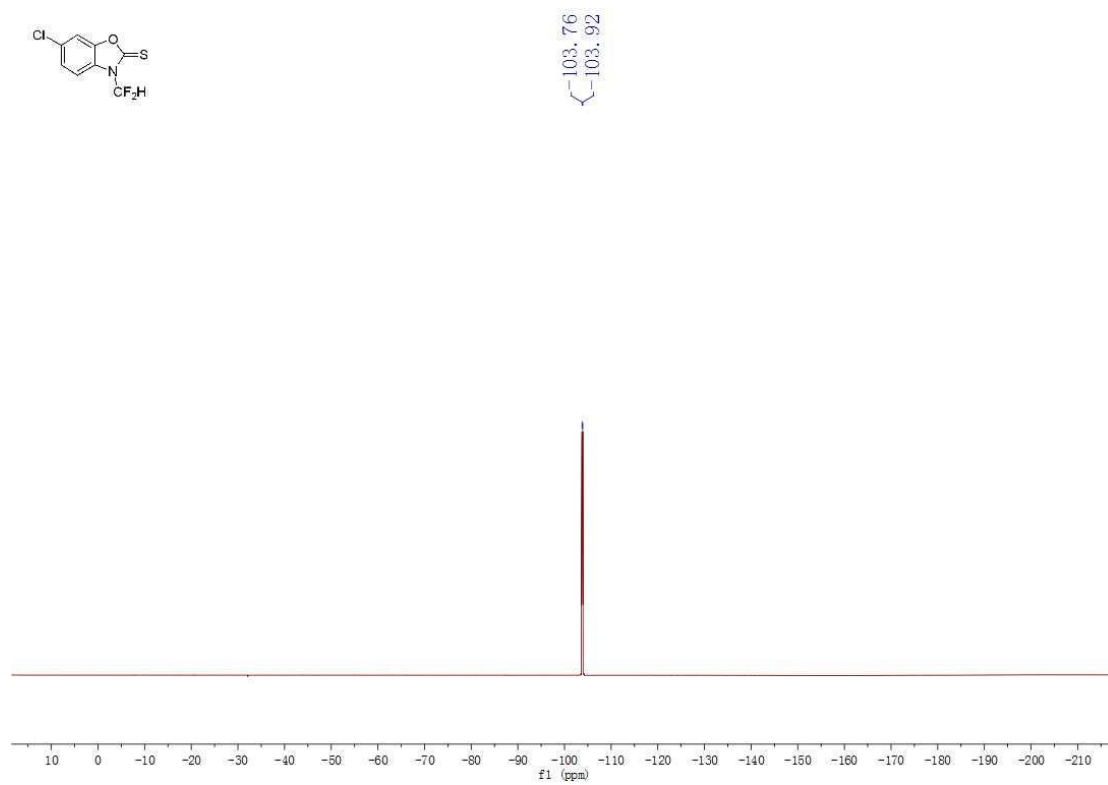
¹H NMR spectrum of **3i** in CDCl₃



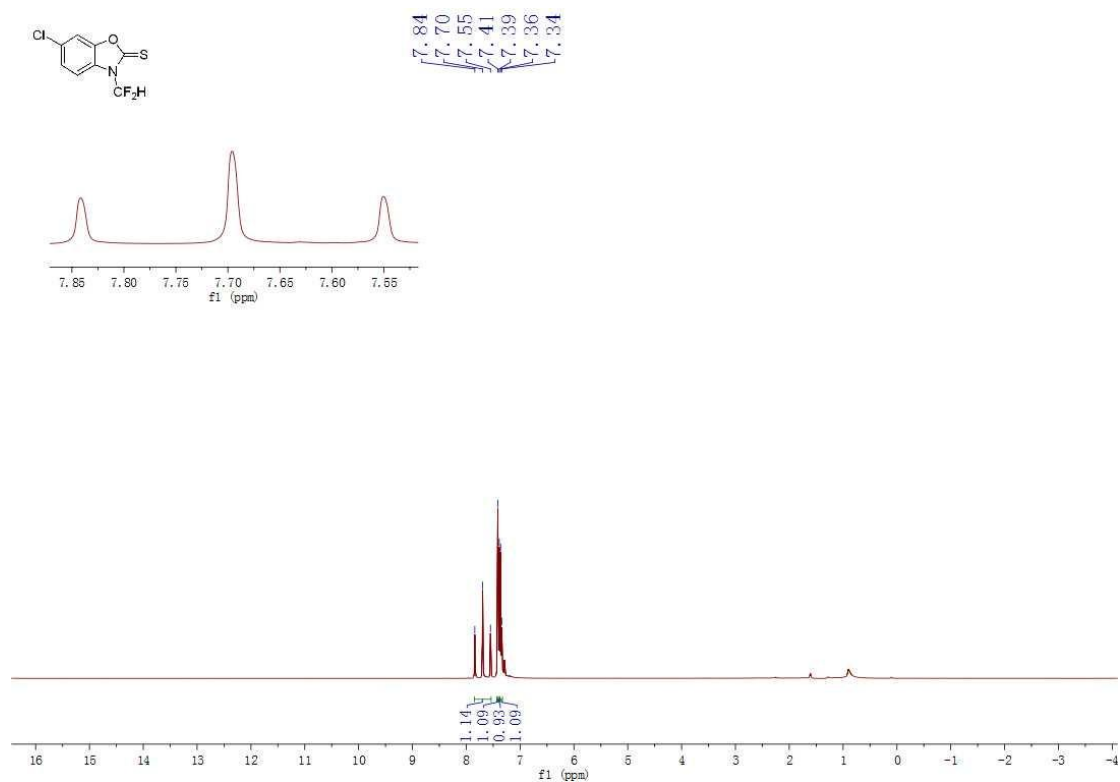
¹³C NMR spectrum of 3i in CDCl₃



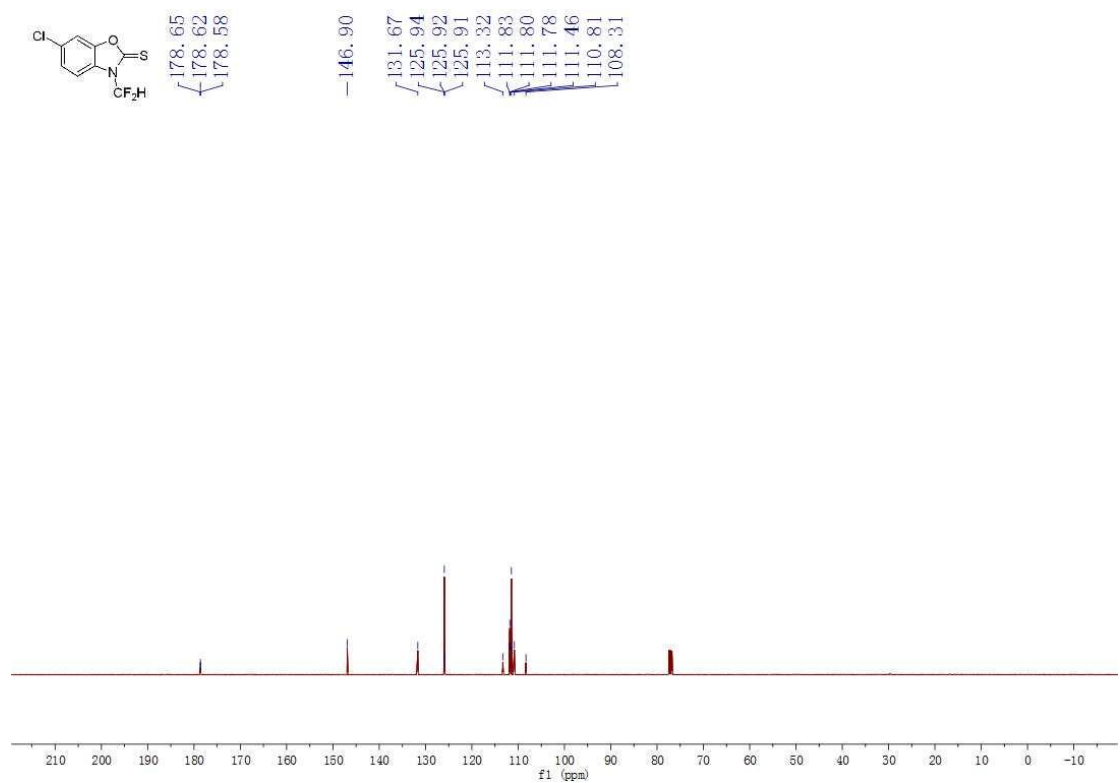
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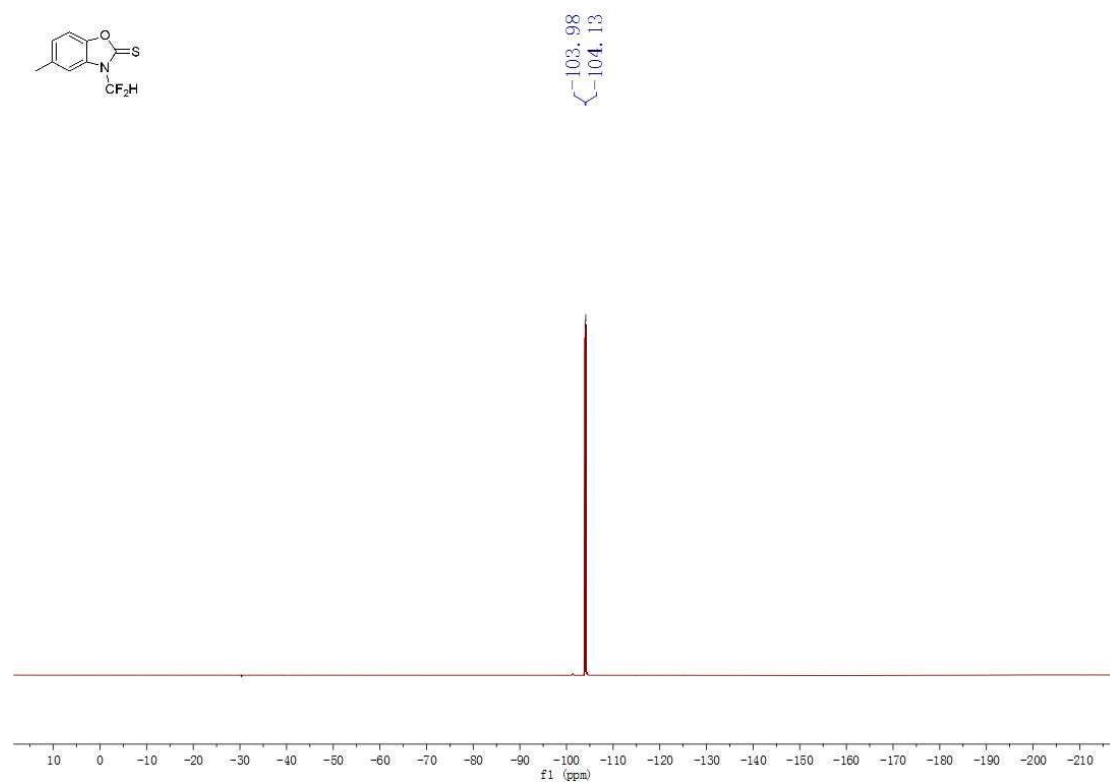
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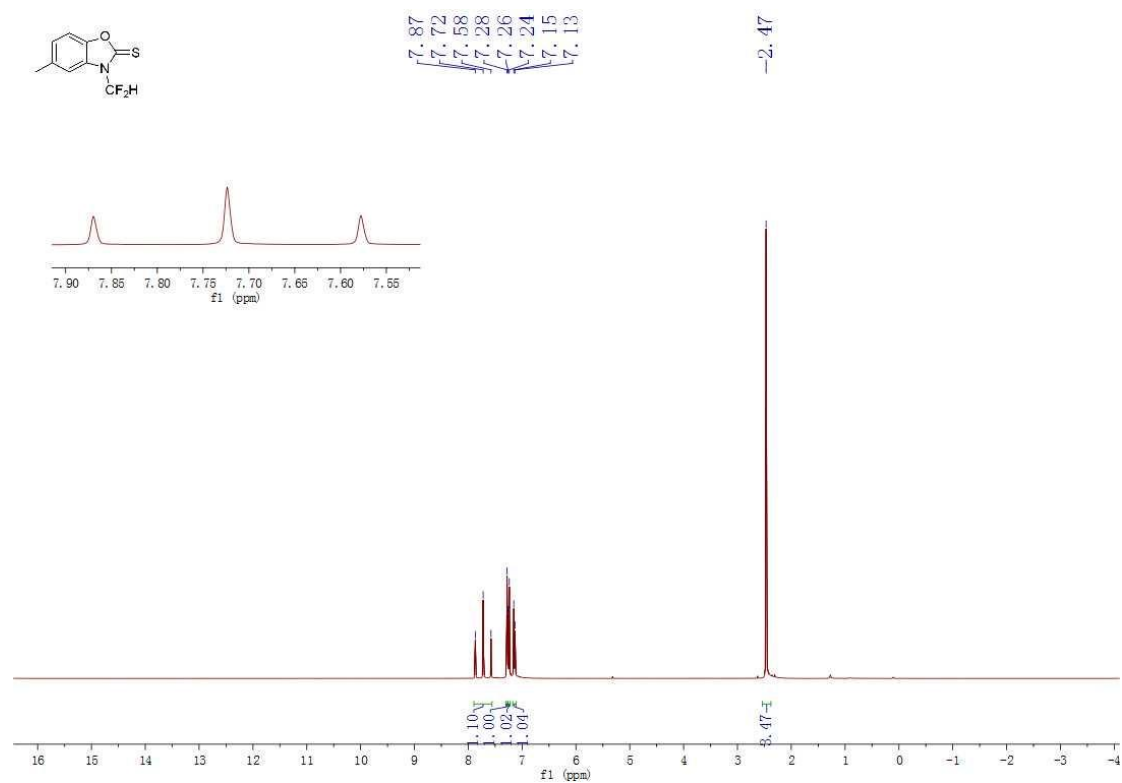
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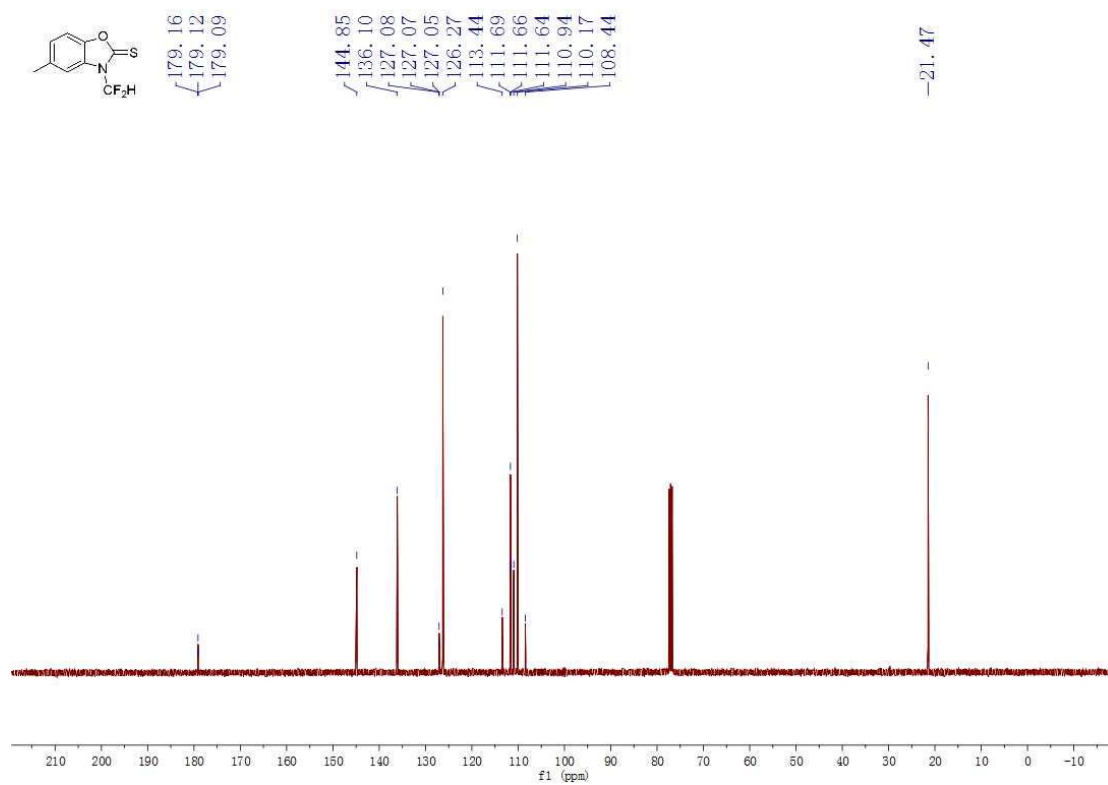
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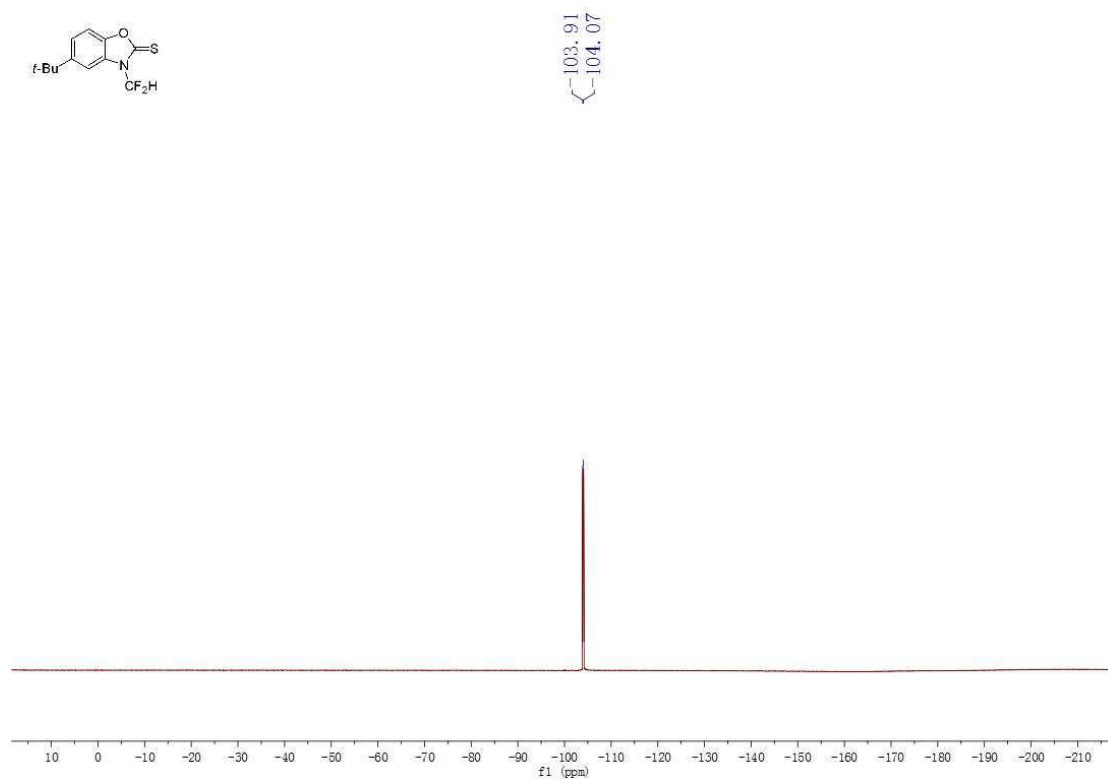
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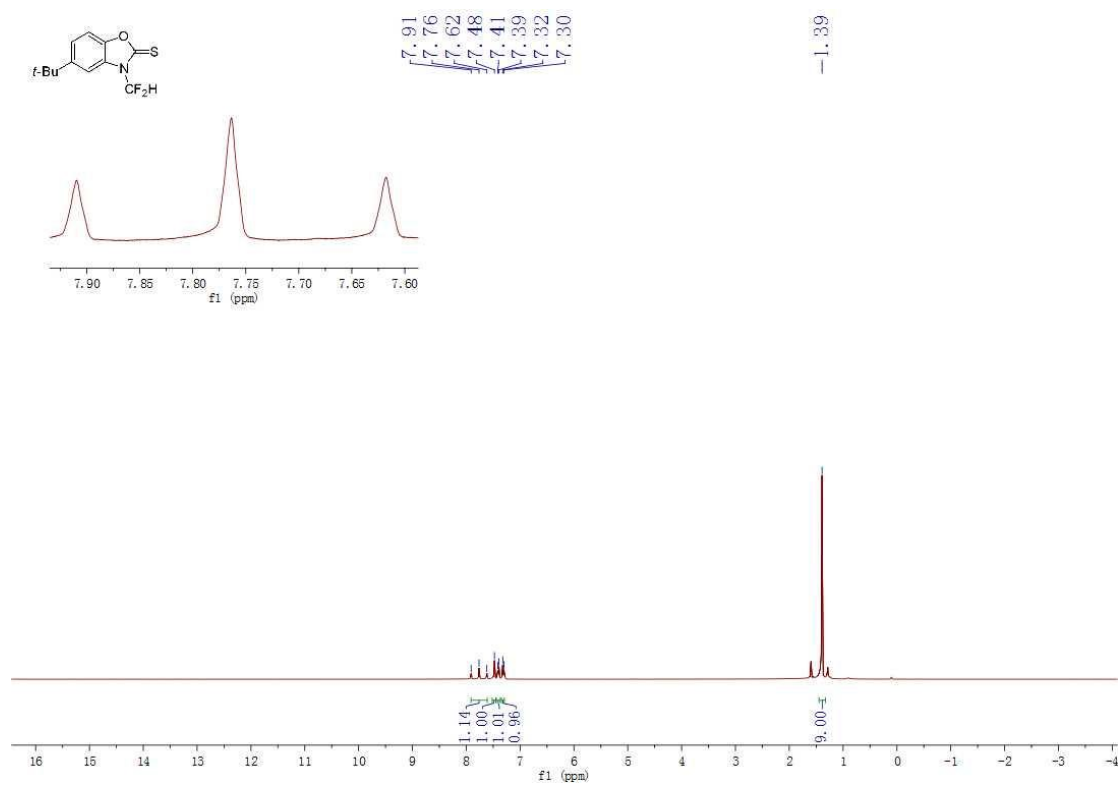
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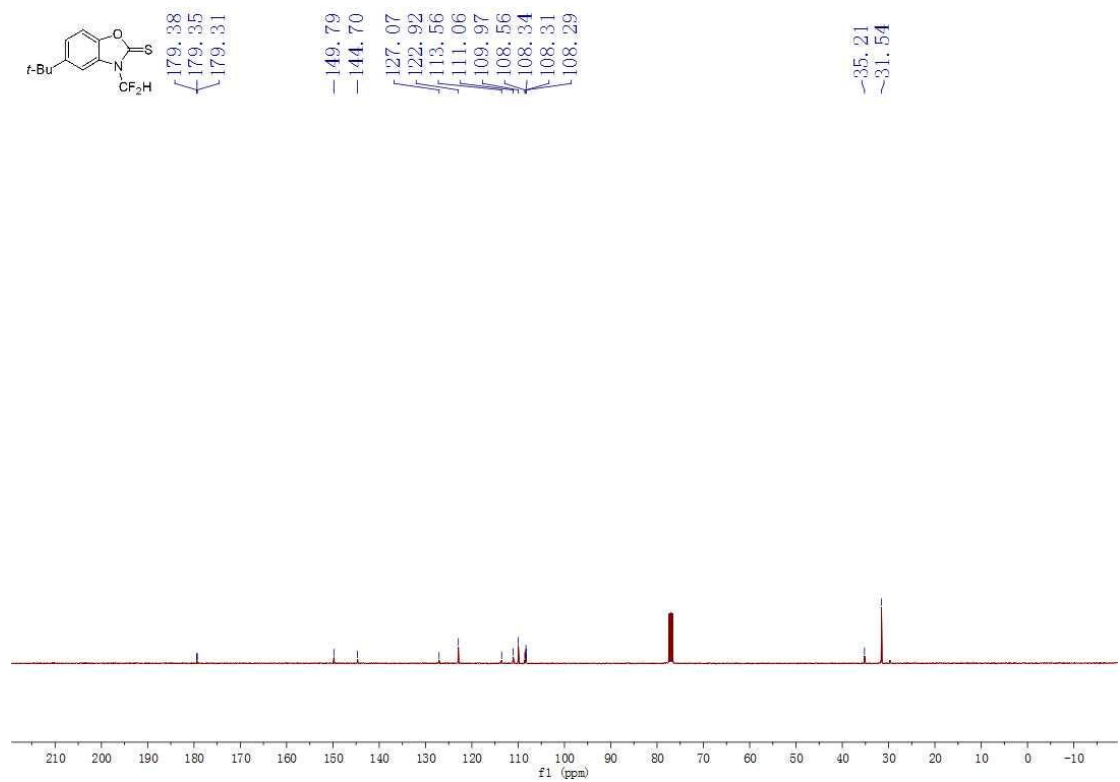
¹⁹F NMR spectrum of **3l** in CDCl₃



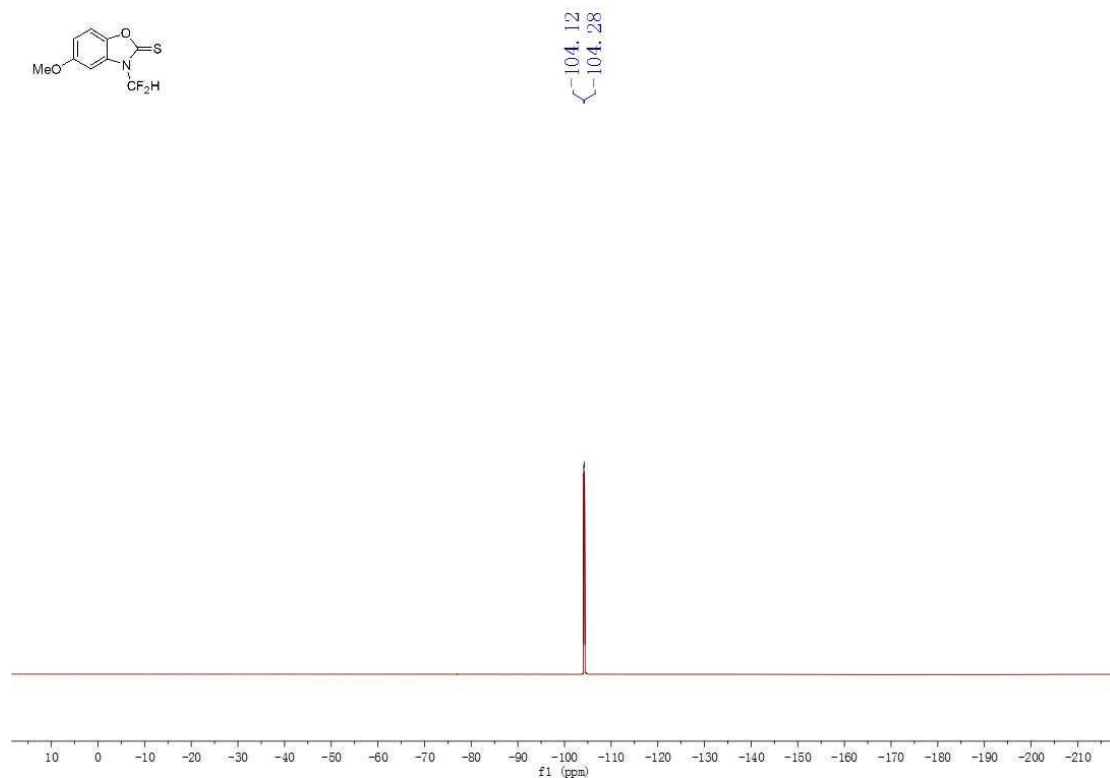
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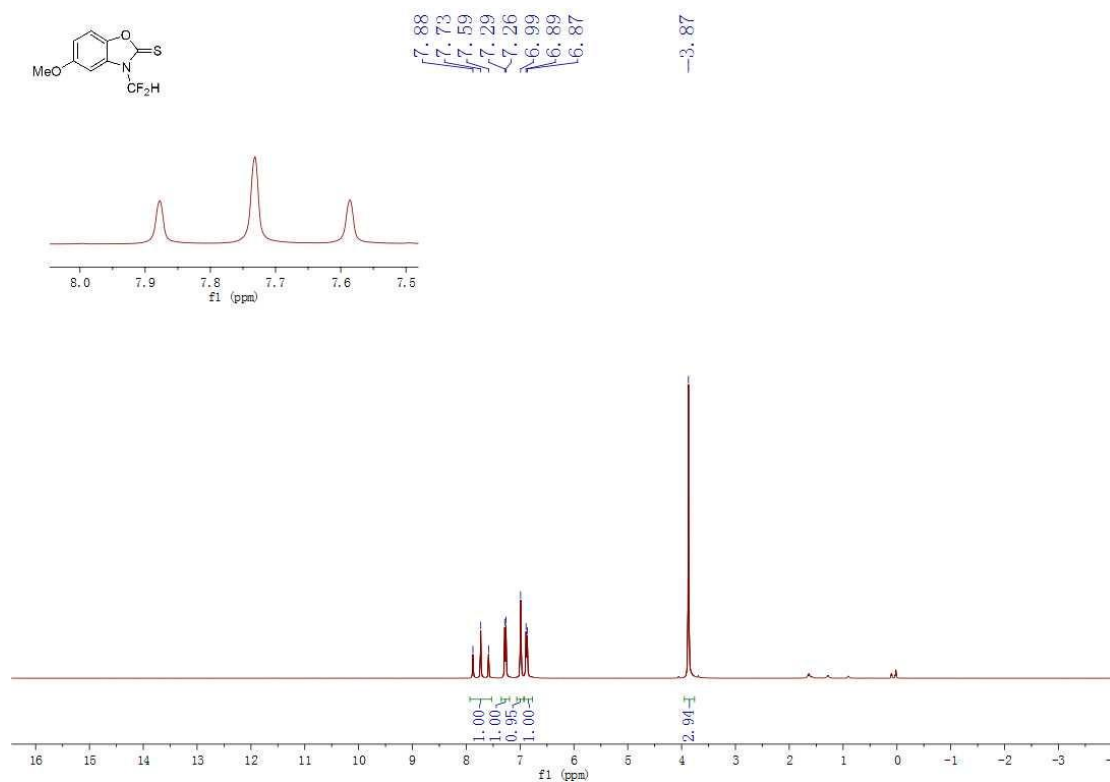
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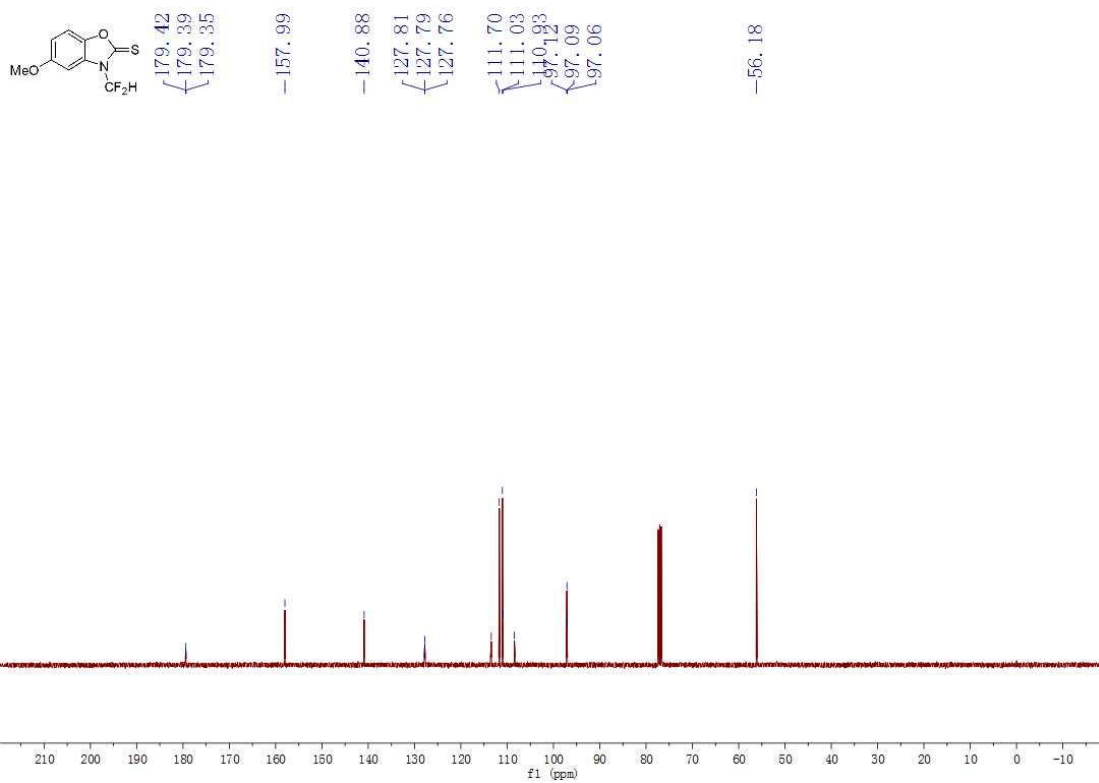
¹⁹F NMR spectrum of 3m in CDCl₃



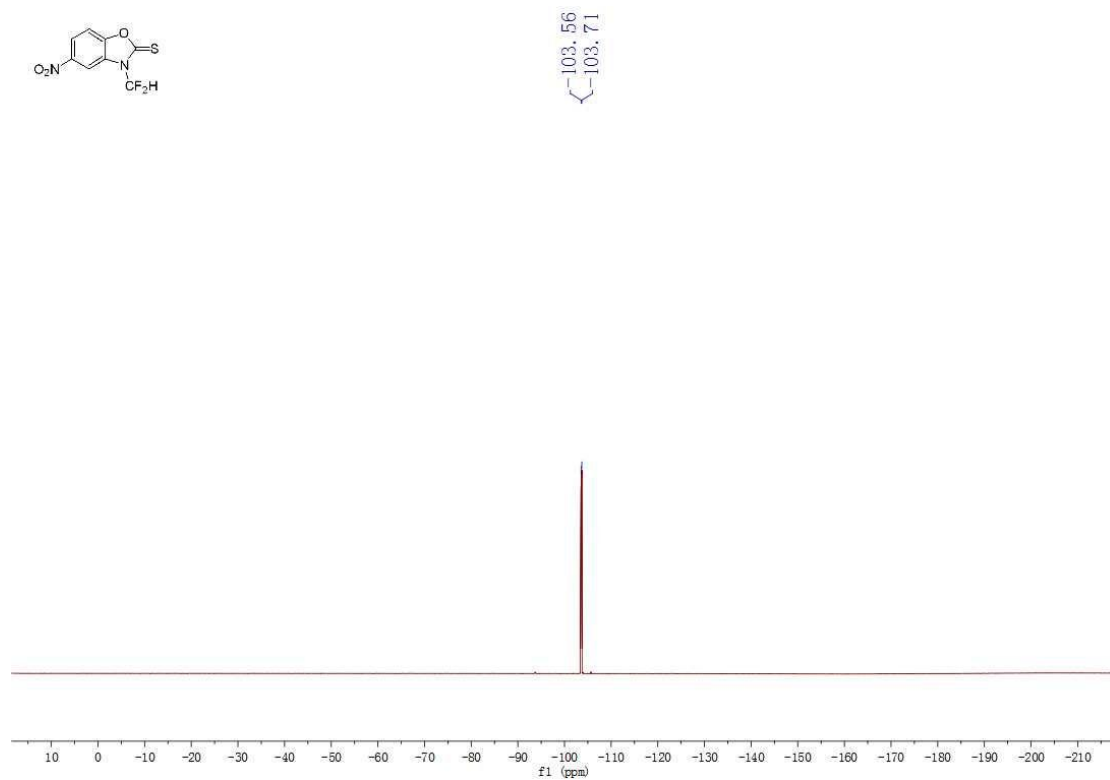
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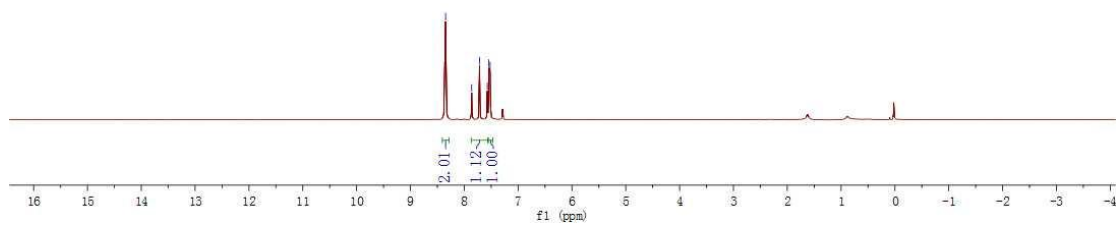
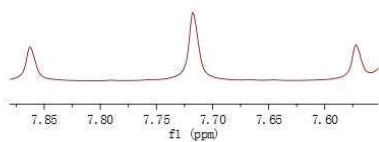
¹³C NMR spectrum of 3m in CDCl₃



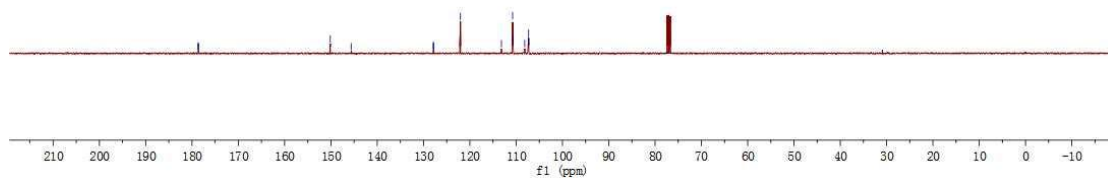
¹⁹F NMR spectrum of 3n in CDCl₃



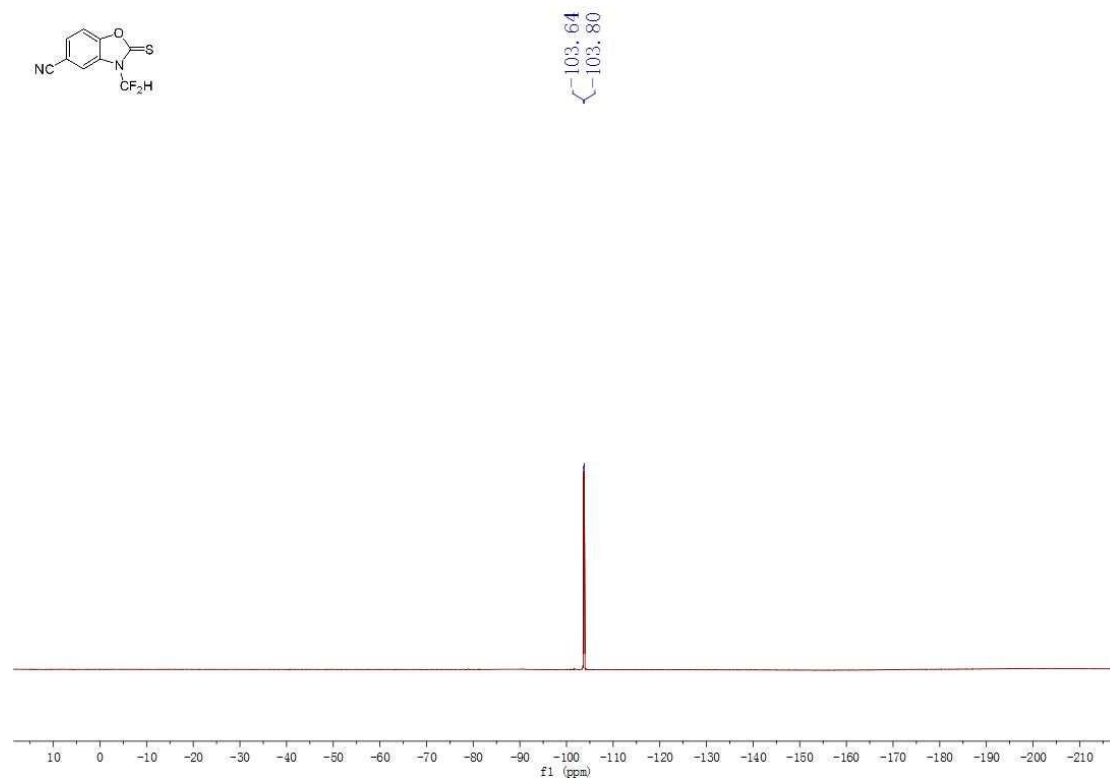
¹H NMR spectrum of 3n in CDCl₃



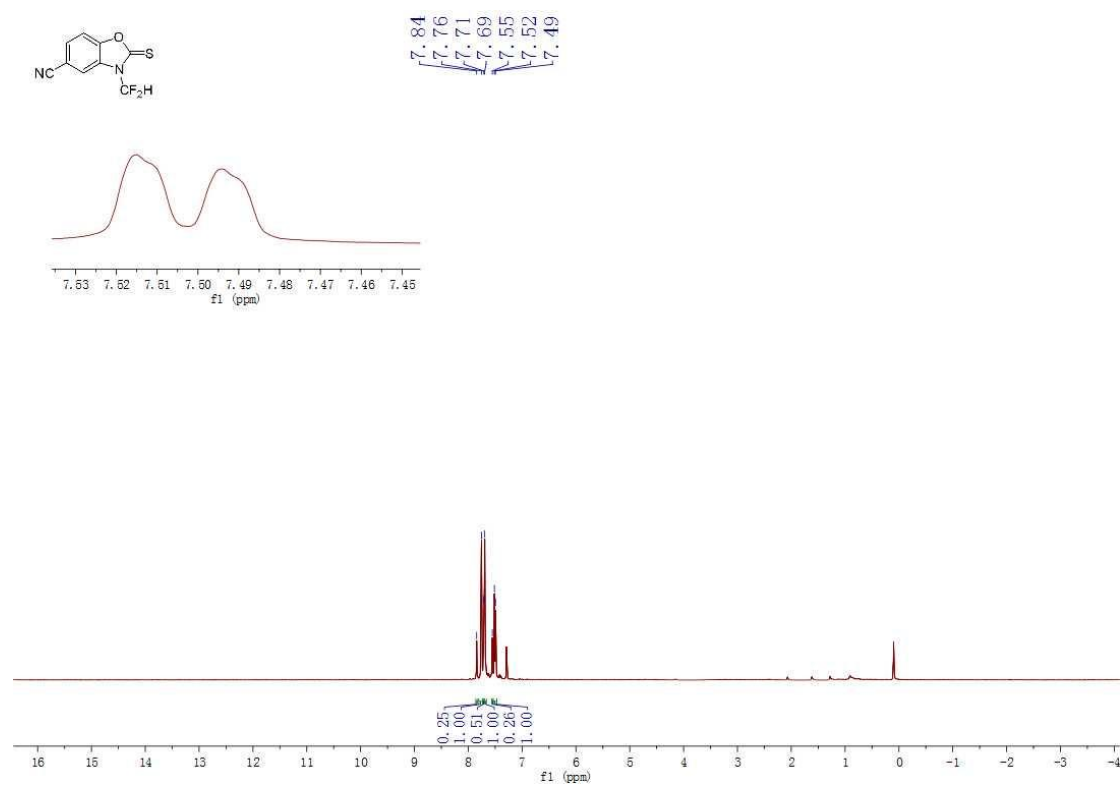
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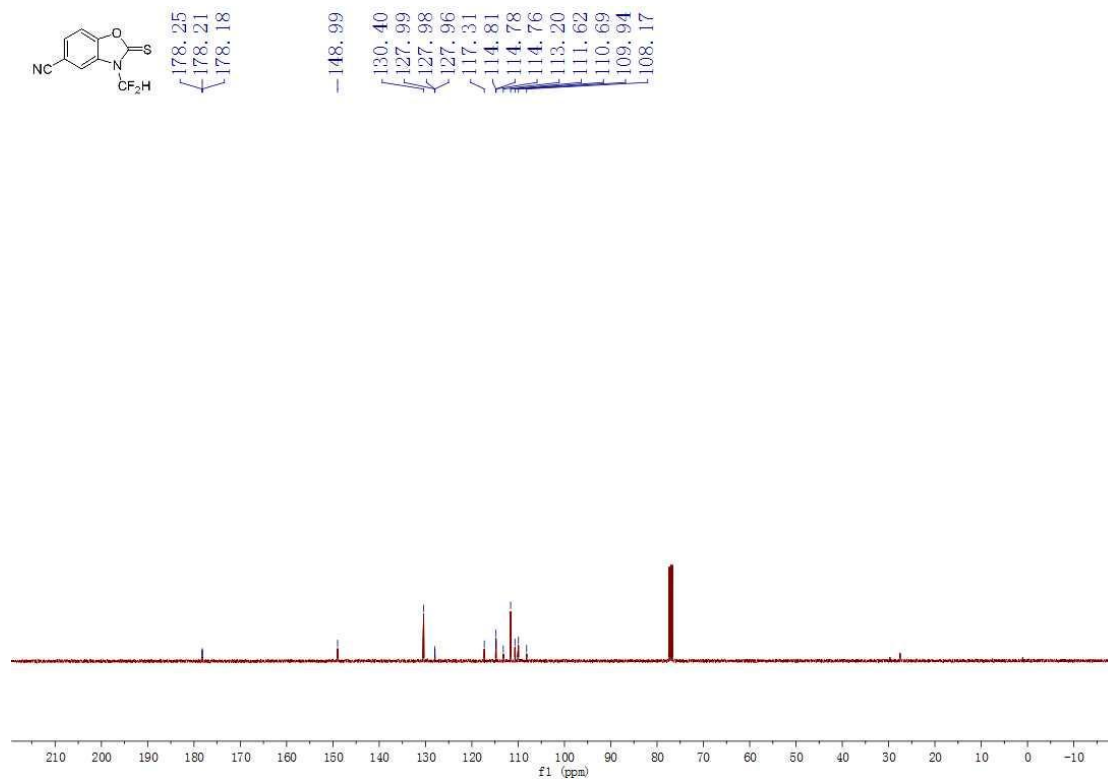
¹⁹F NMR spectrum of 3o in CDCl₃



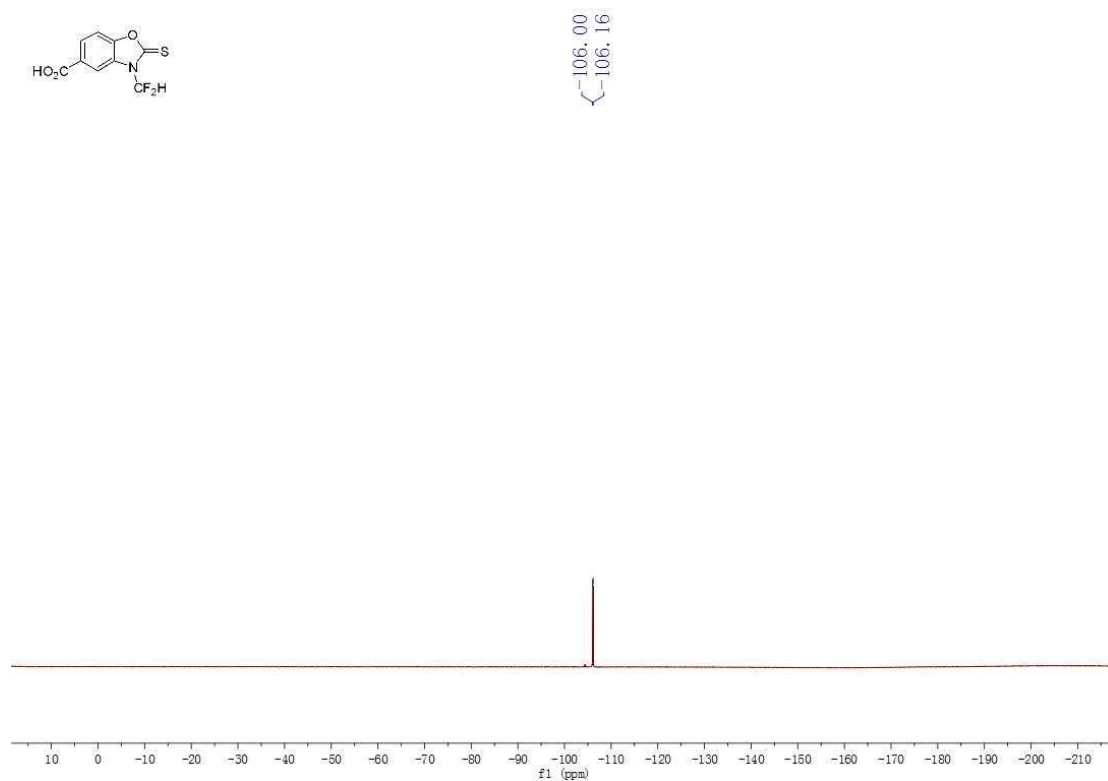
¹H NMR spectrum of 3o in CDCl₃



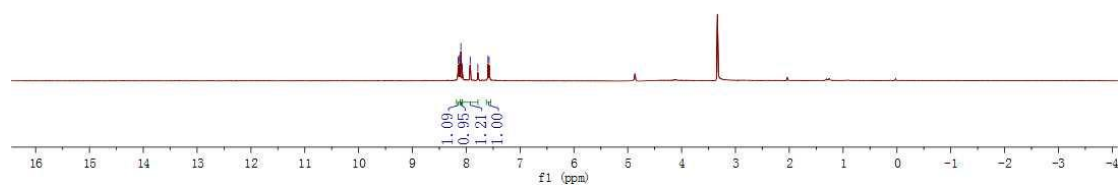
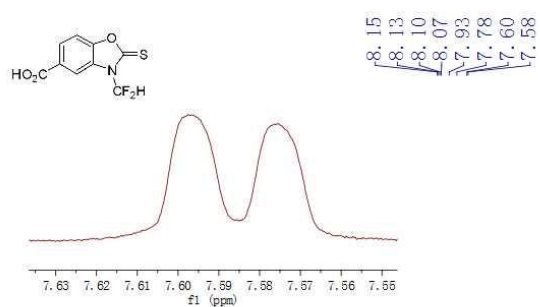
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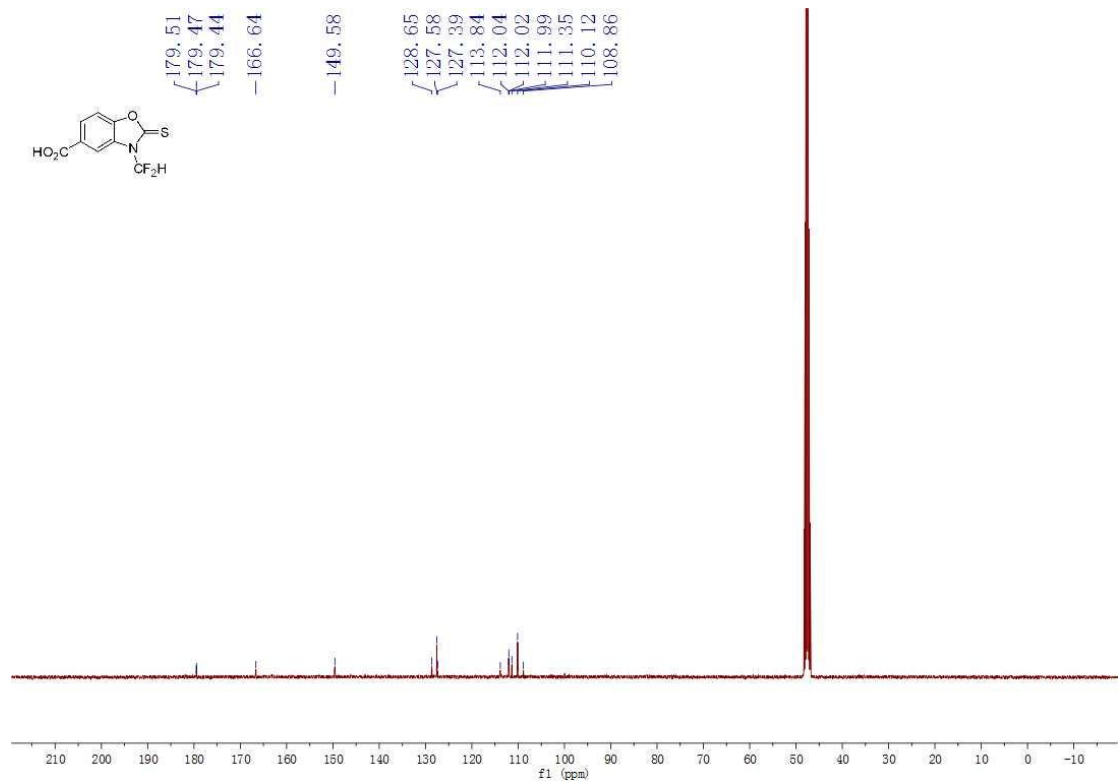
¹⁹F NMR spectrum of **3p** in CD₃OD



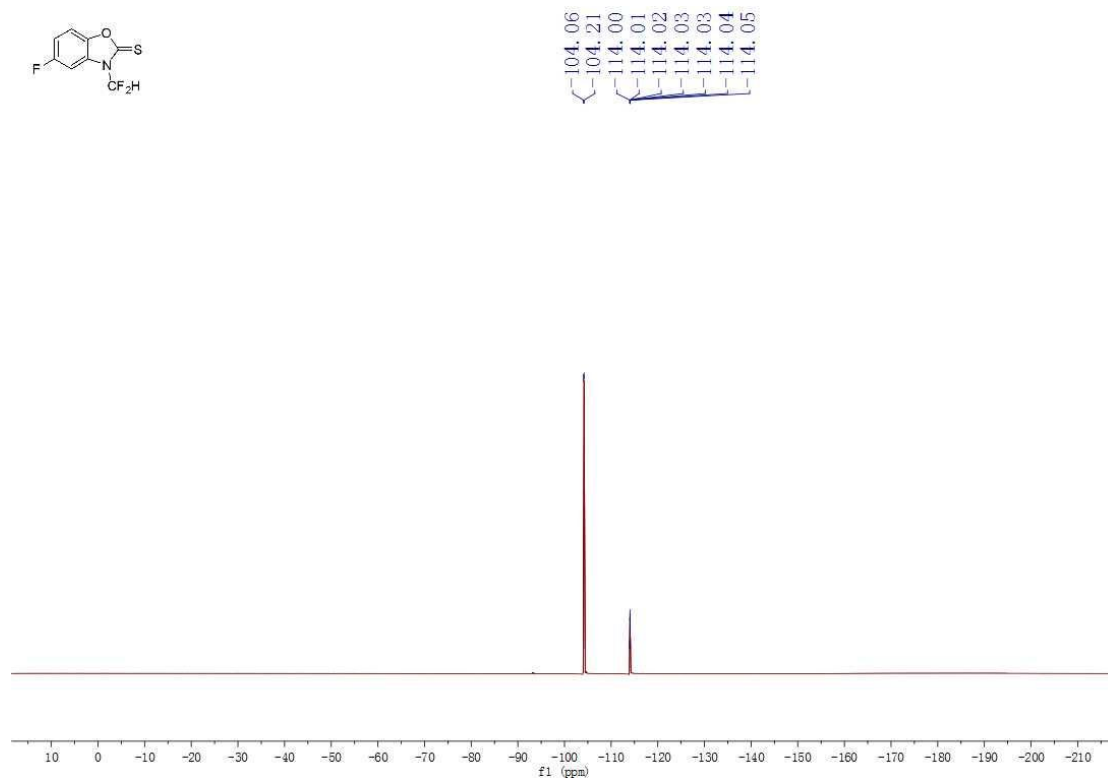
¹H NMR spectrum of 3p in CD₃OD



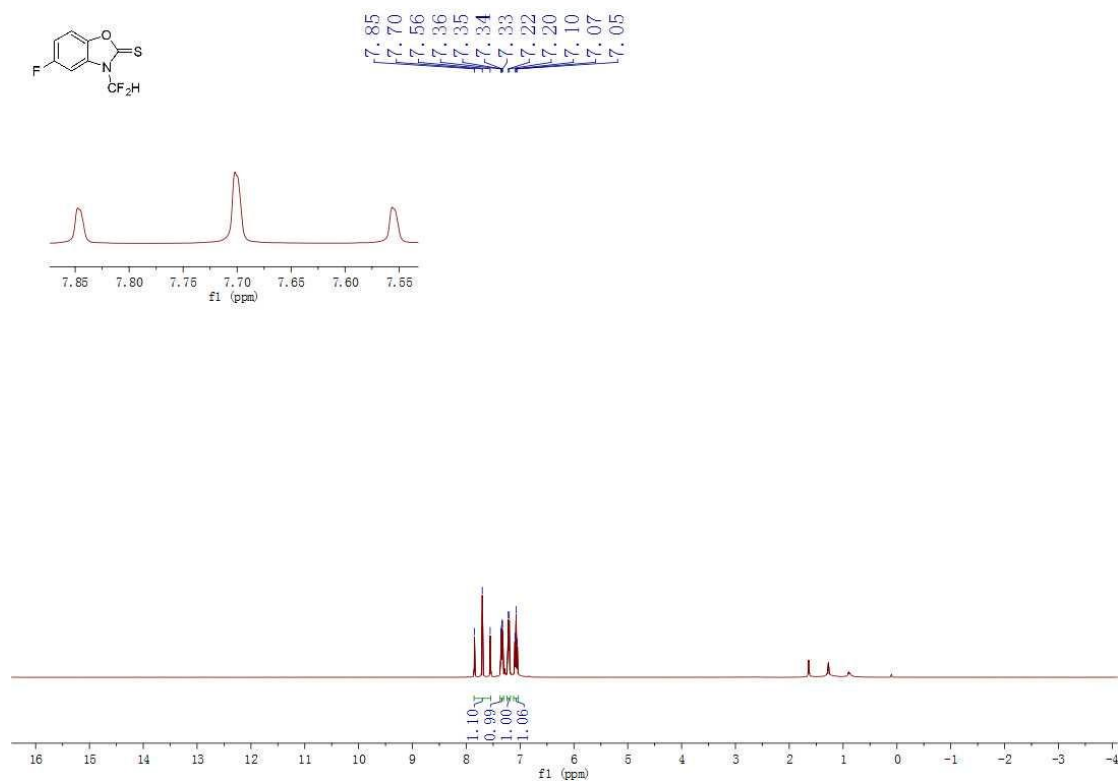
¹³C NMR spectrum of 3p in CD₃OD



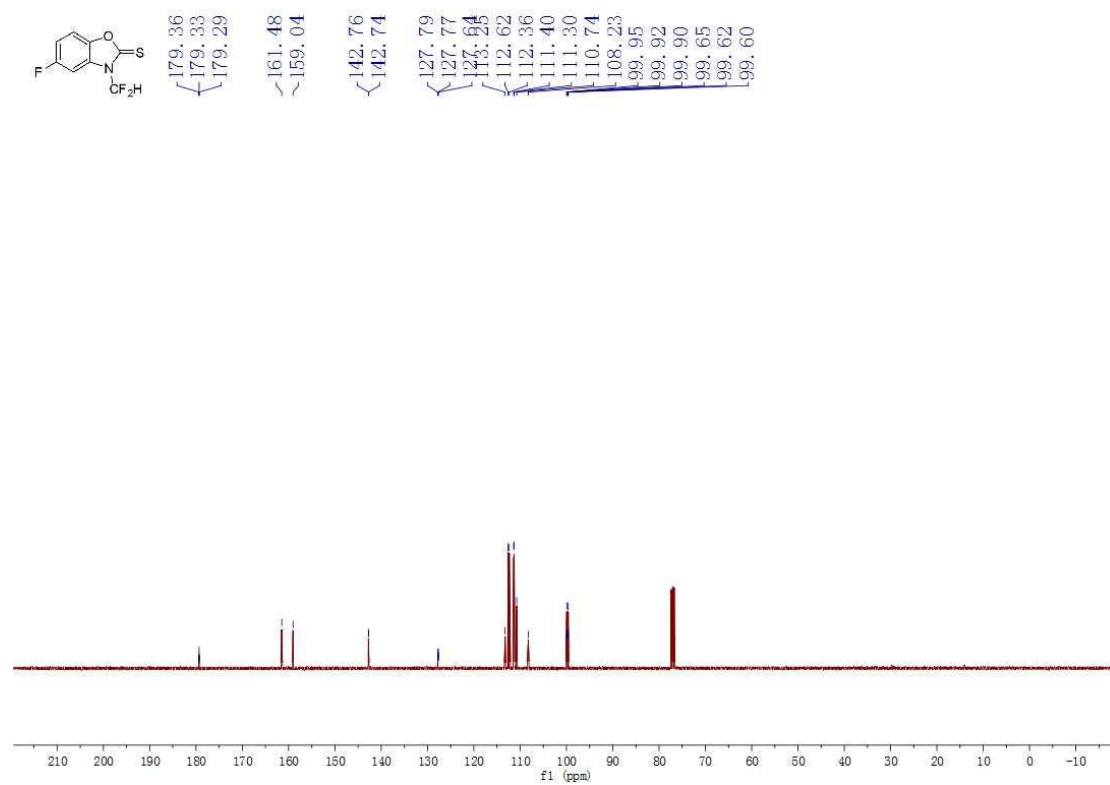
¹⁹F NMR spectrum of 3q in CDCl₃



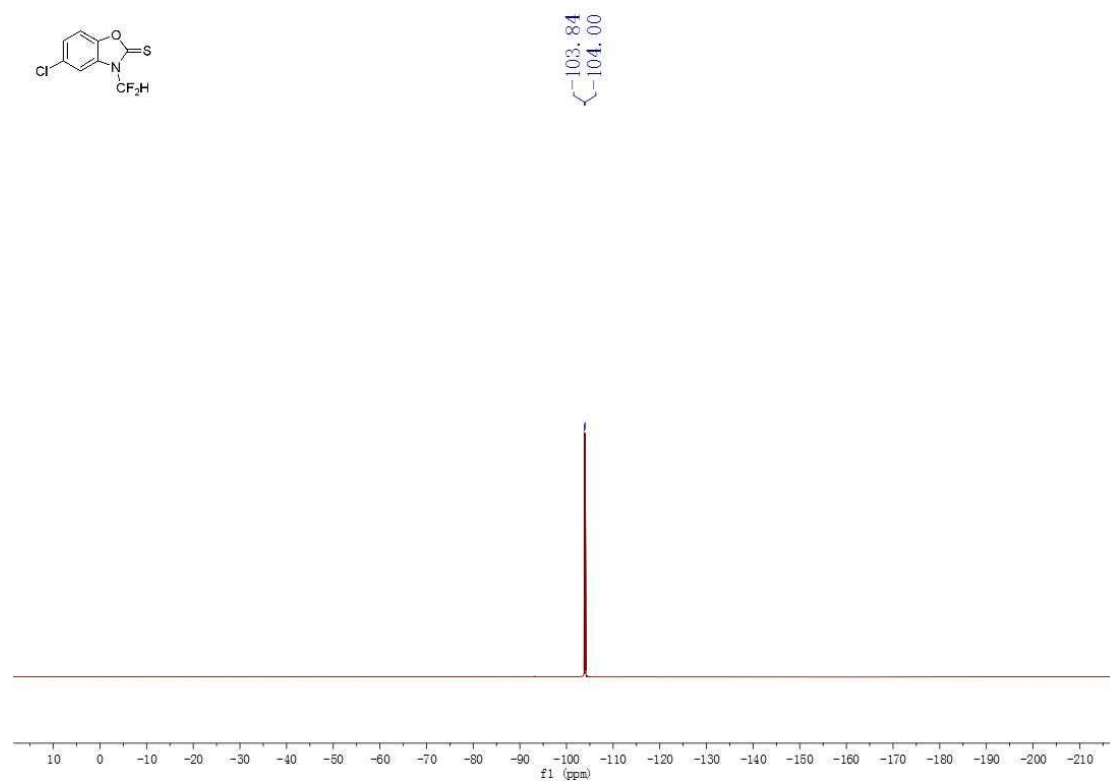
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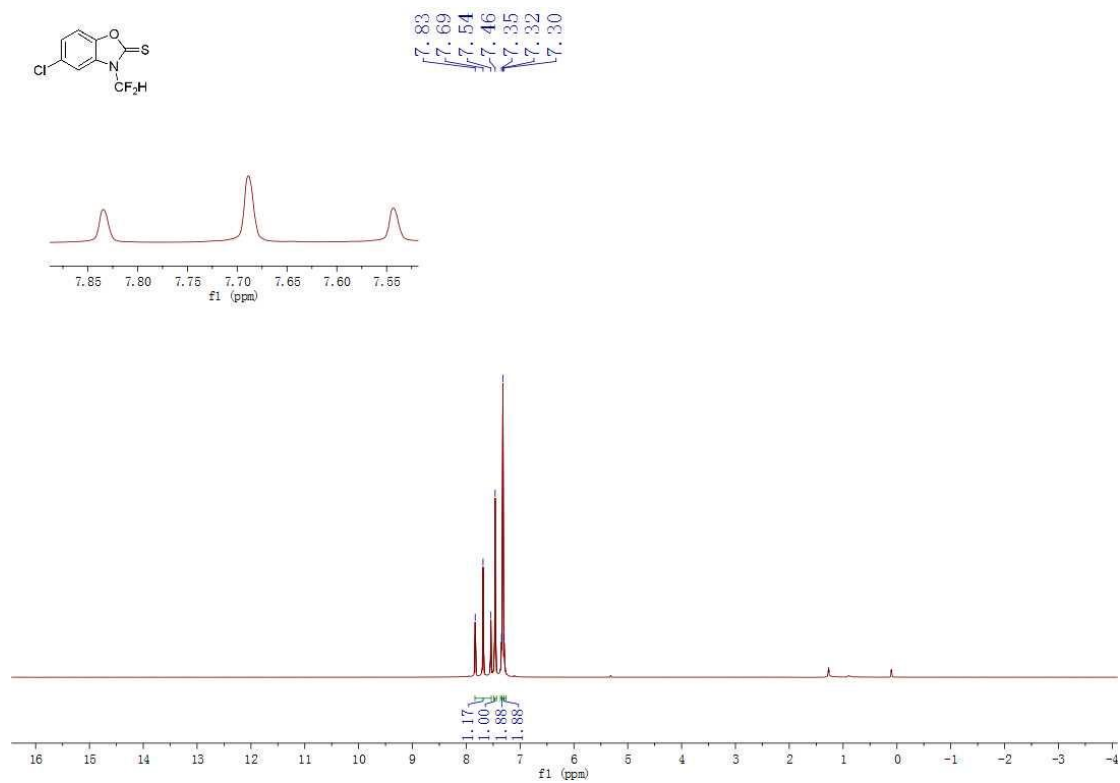
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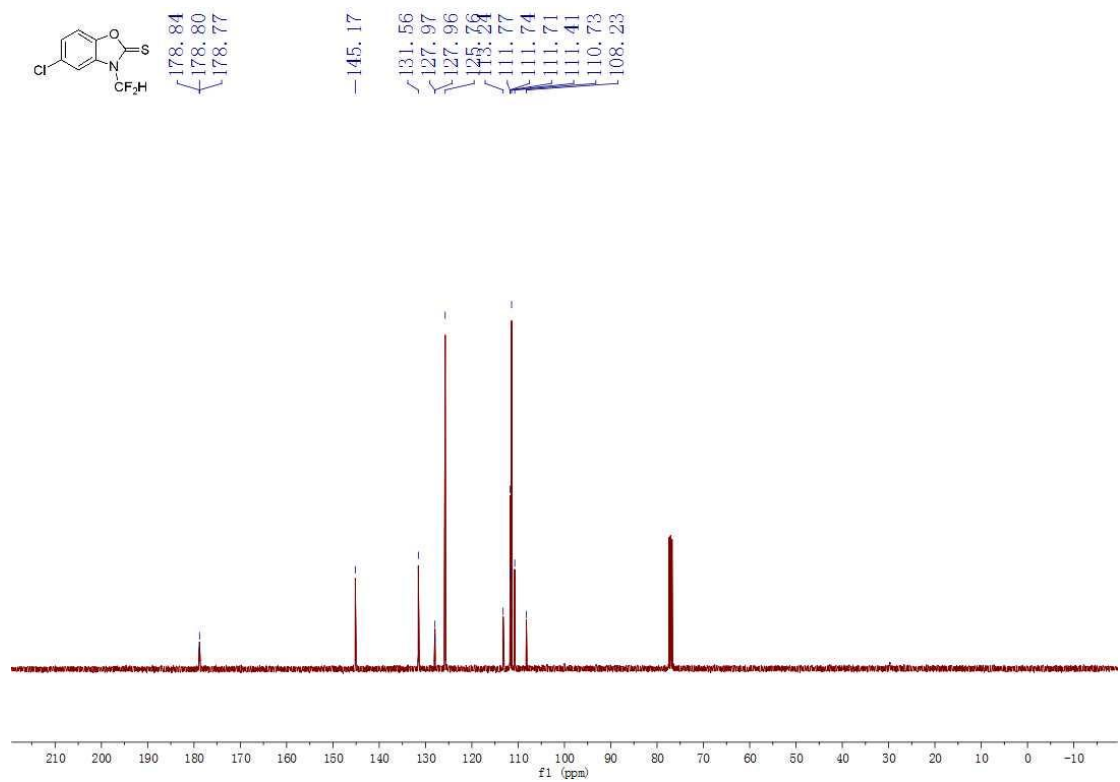
¹⁹F NMR spectrum of **3r** in CDCl₃



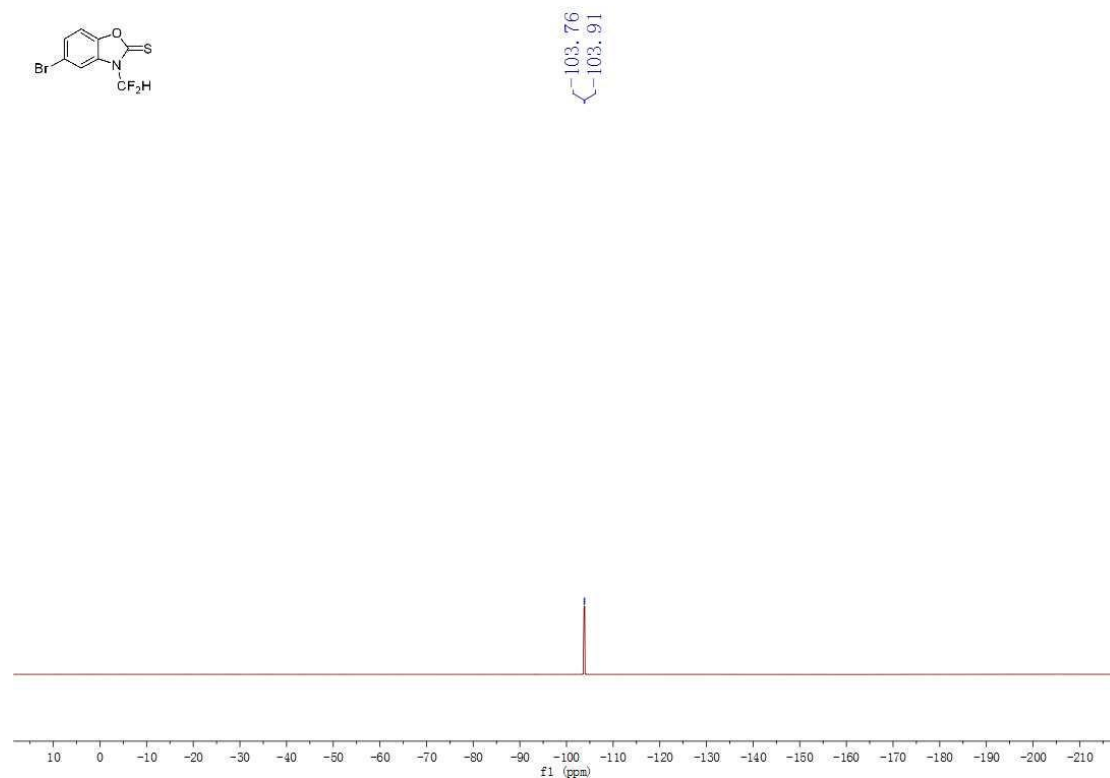
¹H NMR spectrum of 3r in CDCl₃



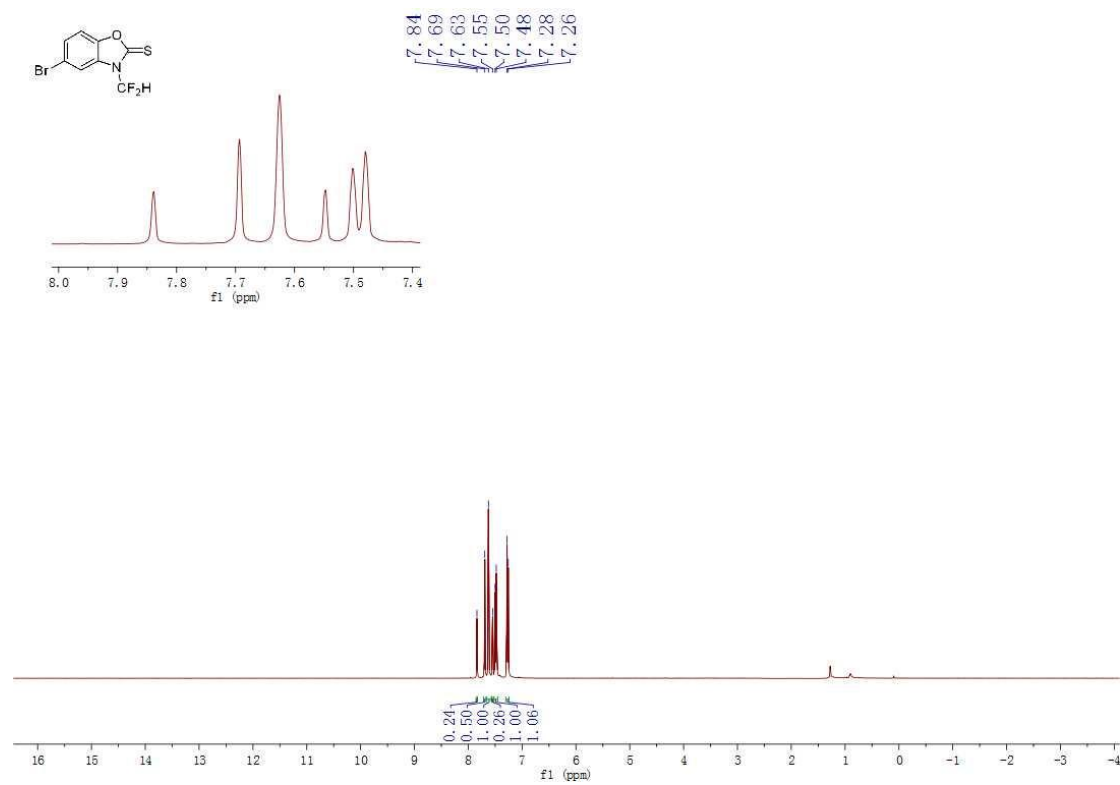
¹³C NMR spectrum of 3r in CDCl₃



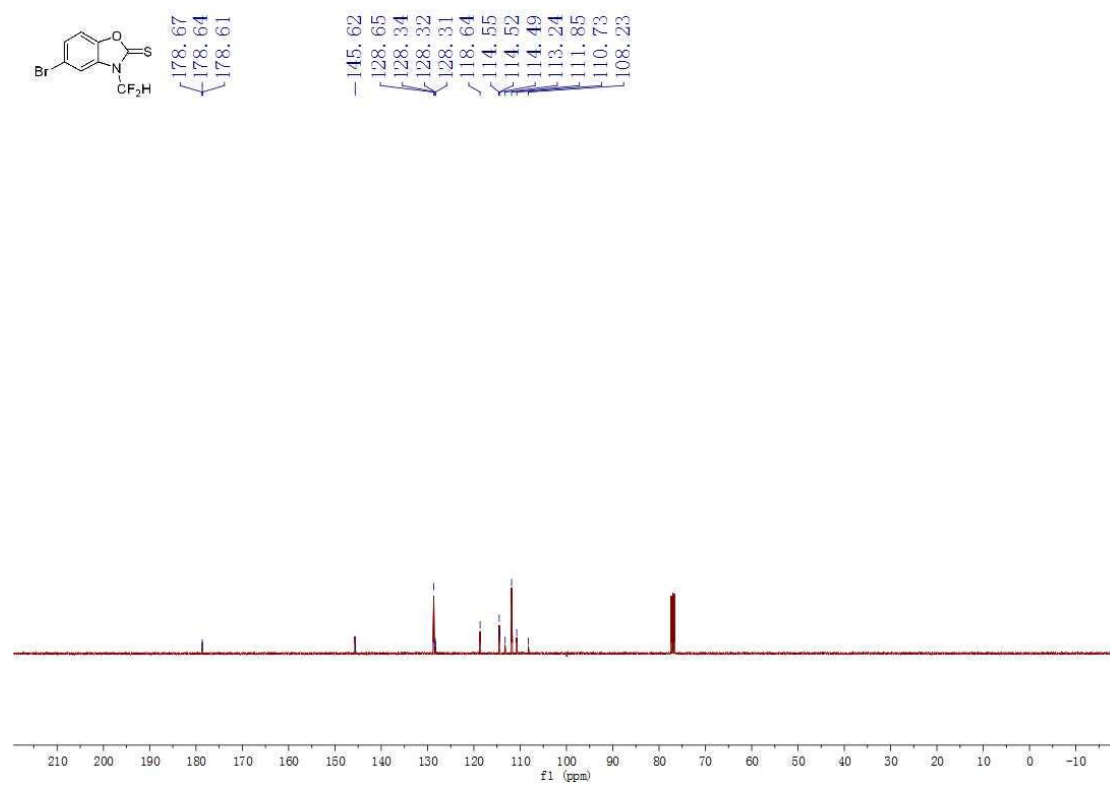
¹⁹F NMR spectrum of 3s in CDCl₃



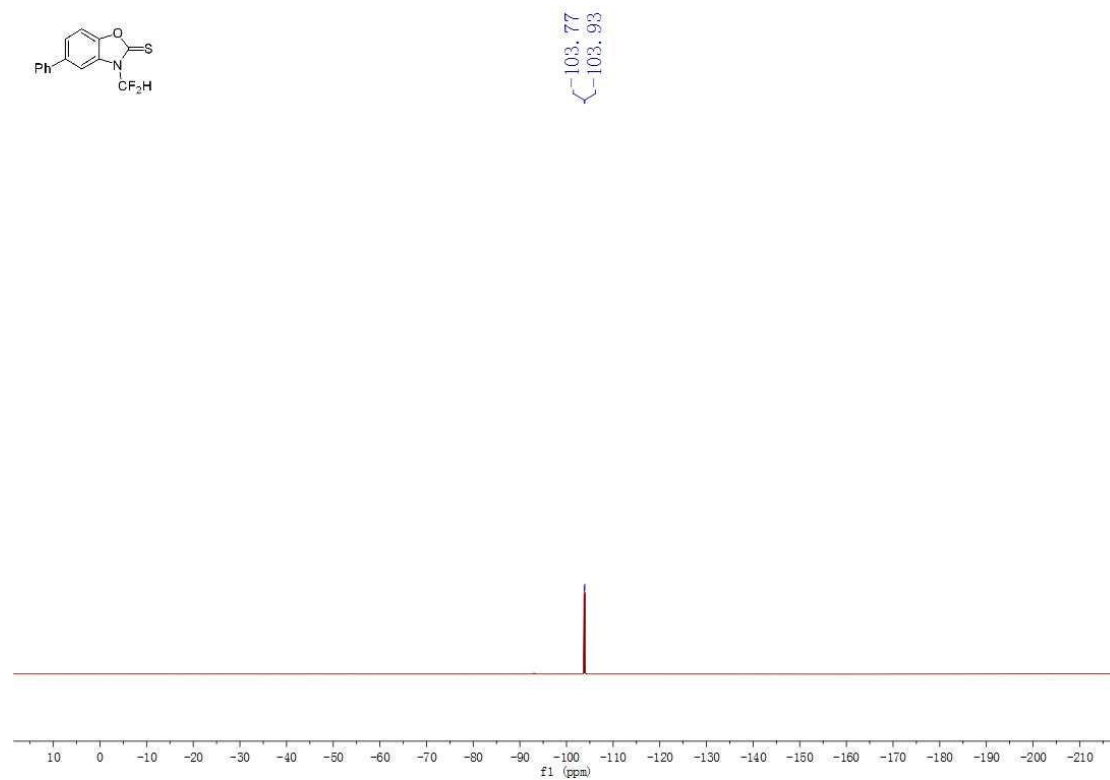
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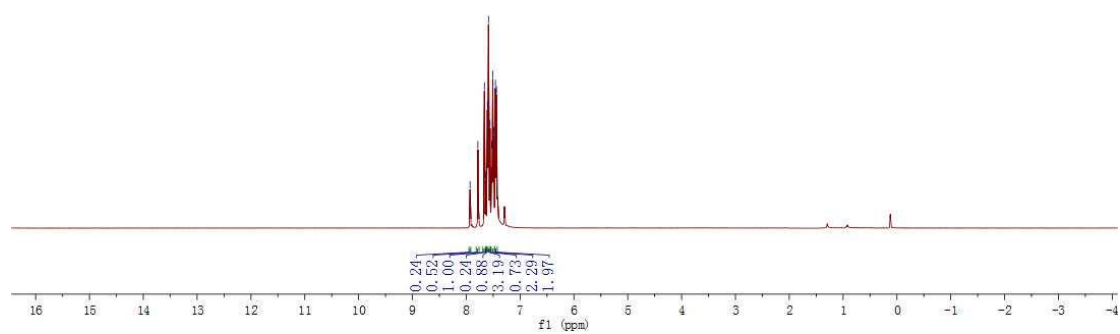
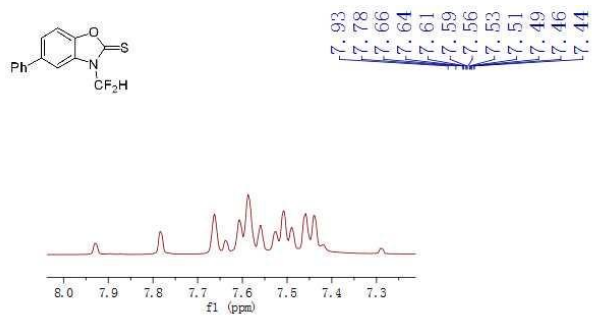
¹³C NMR spectrum of **3s** in CDCl₃



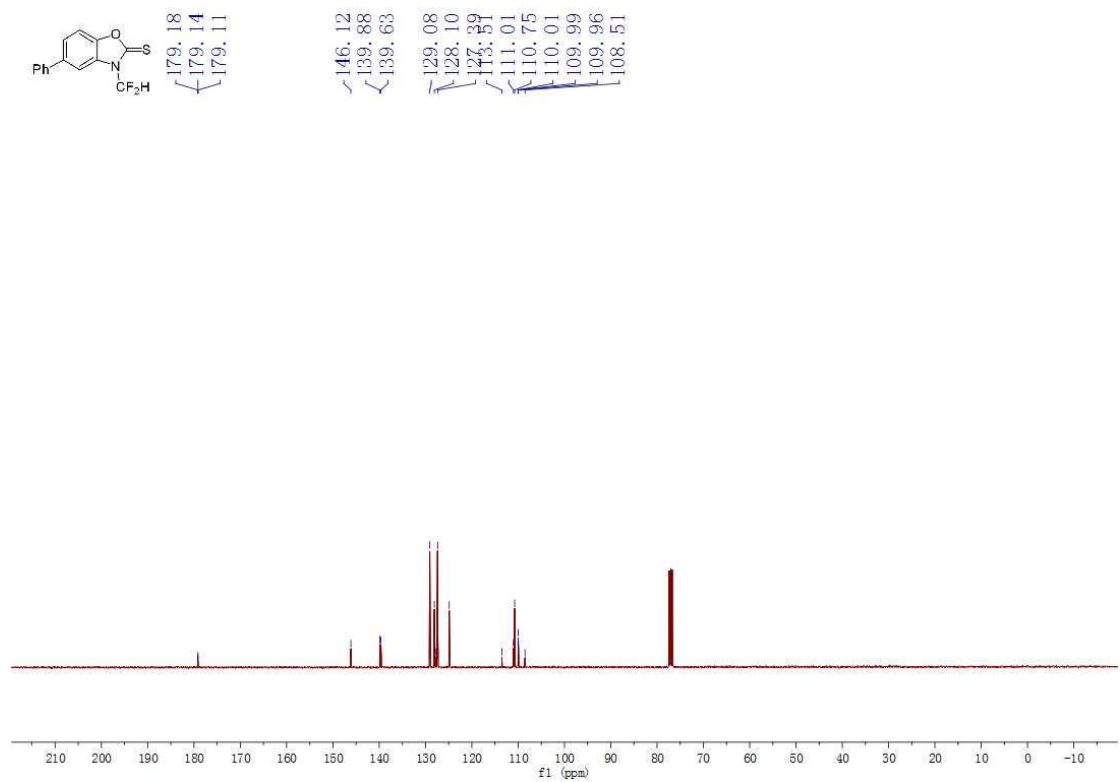
¹⁹F NMR spectrum of **3t** in CDCl₃



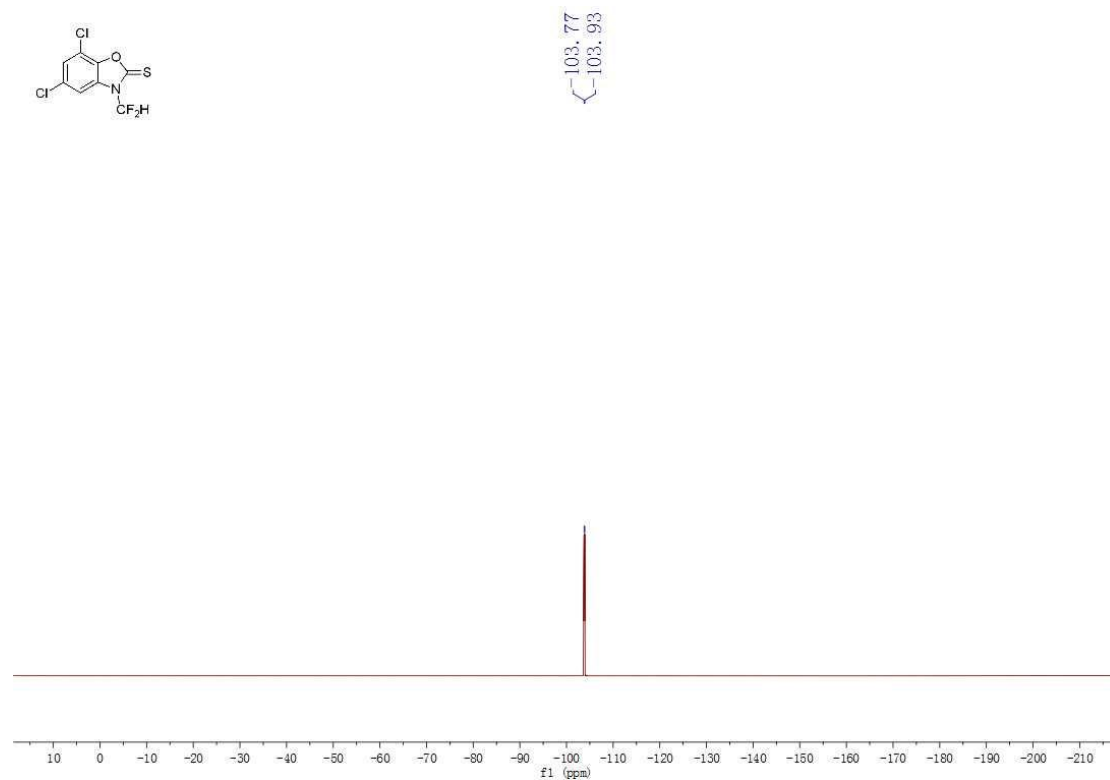
^1H NMR spectrum of **3t** in CDCl_3



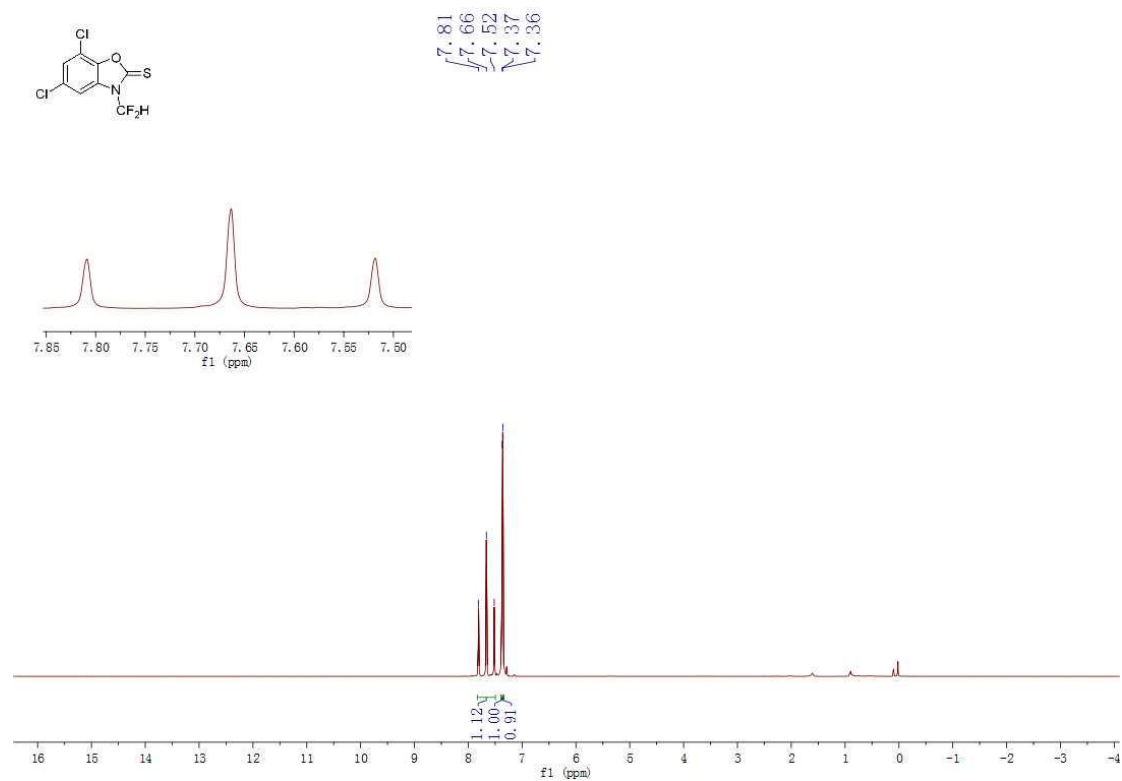
^{13}C NMR spectrum of **3t** in CDCl_3



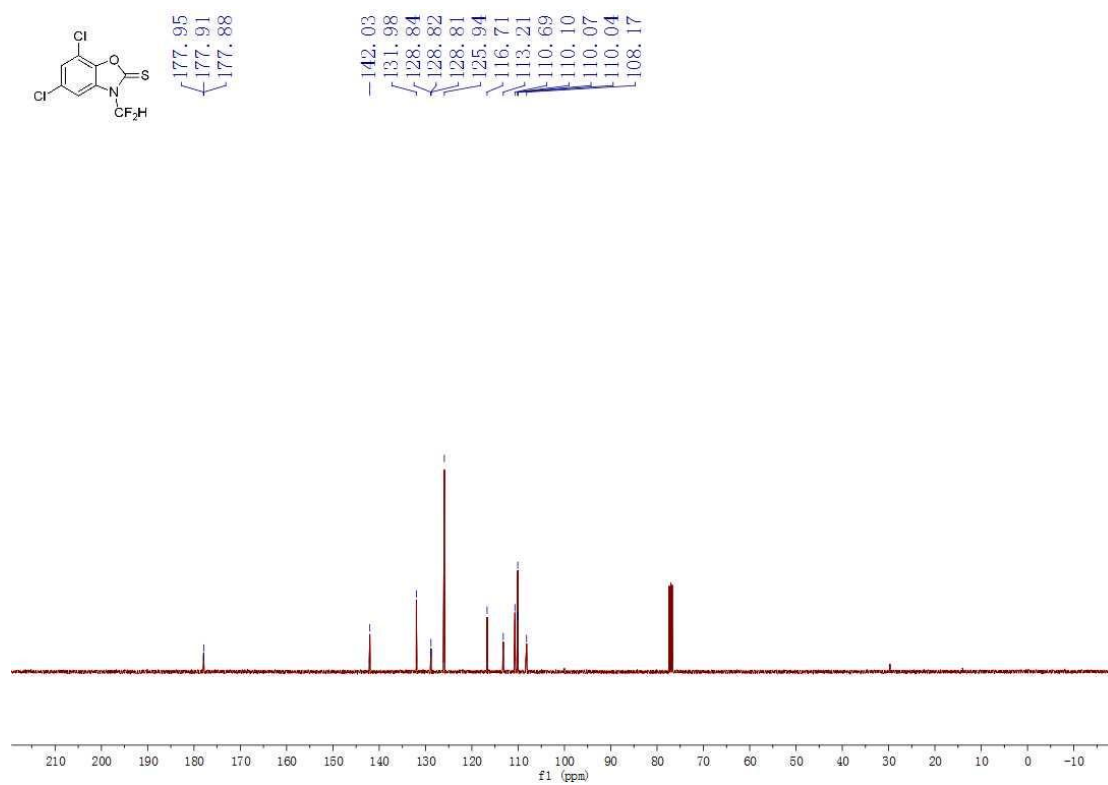
¹⁹F NMR spectrum of 3v in CDCl₃



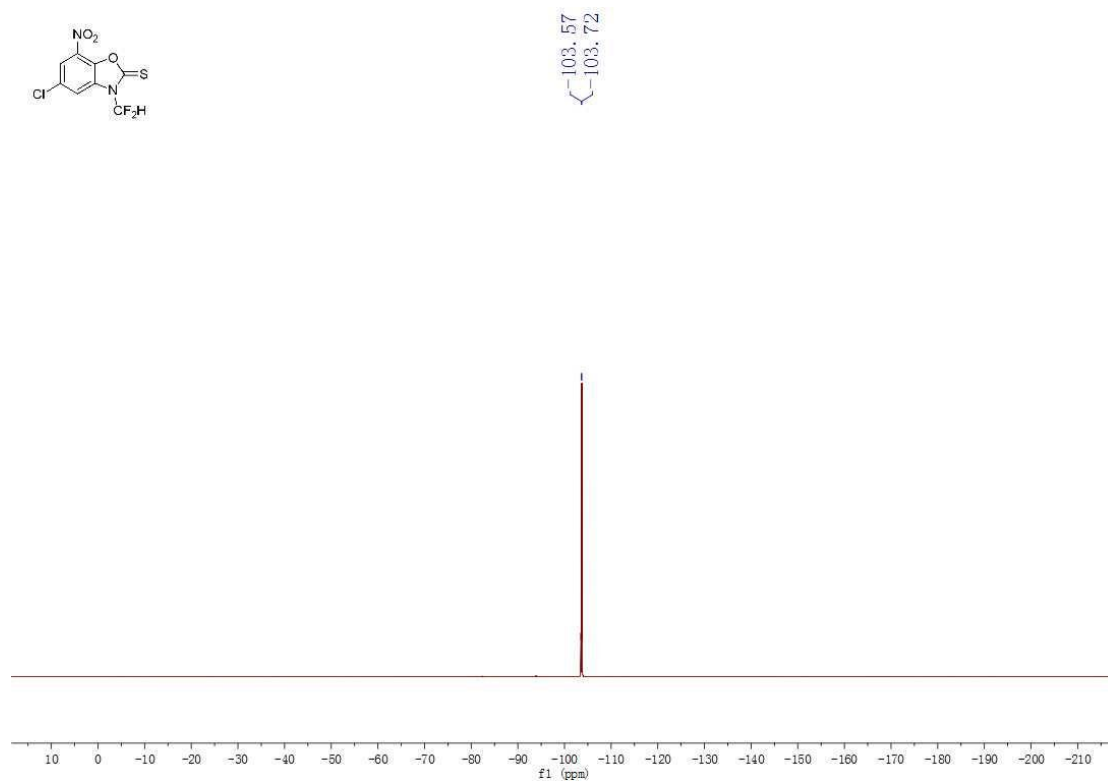
¹H NMR spectrum of 3v in CDCl₃



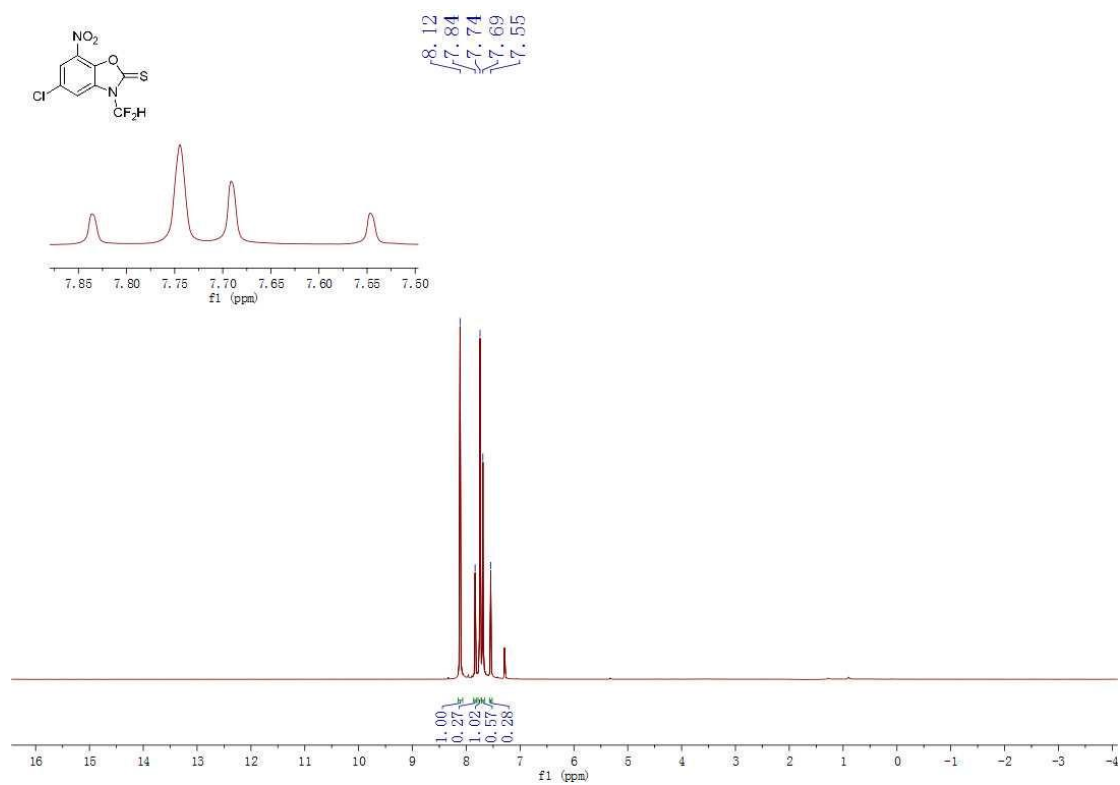
¹³C NMR spectrum of 3v in CDCl₃



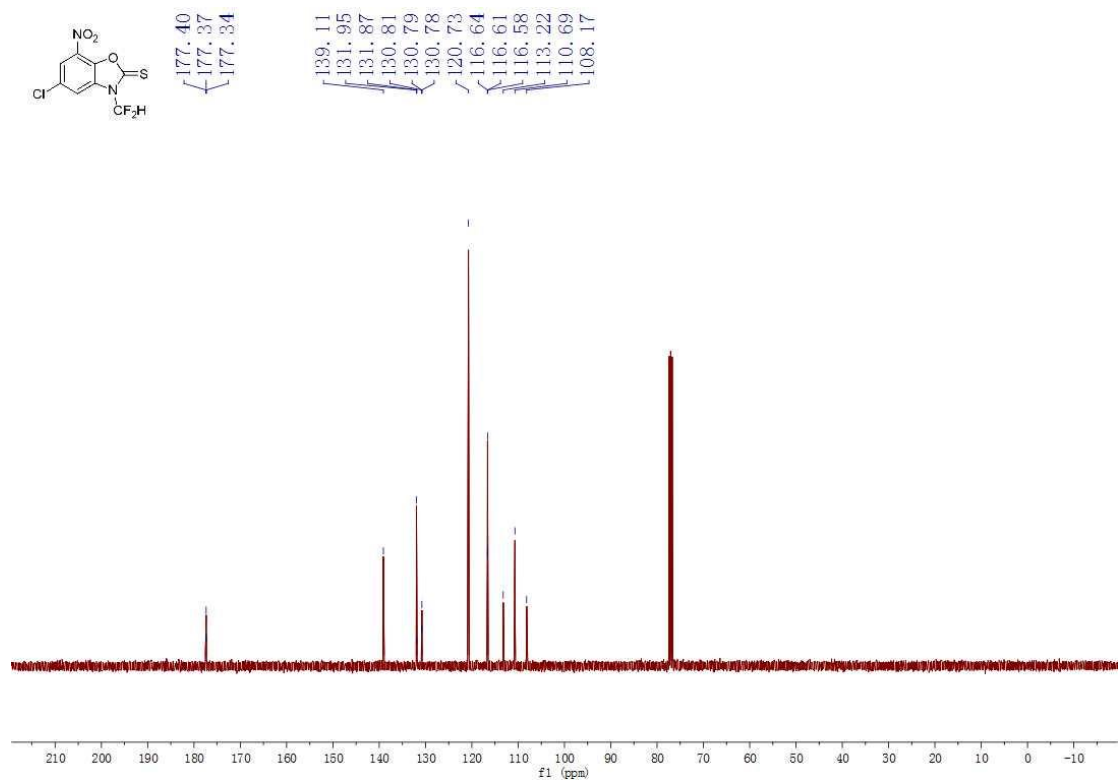
¹⁹F NMR spectrum of 3w in CDCl₃



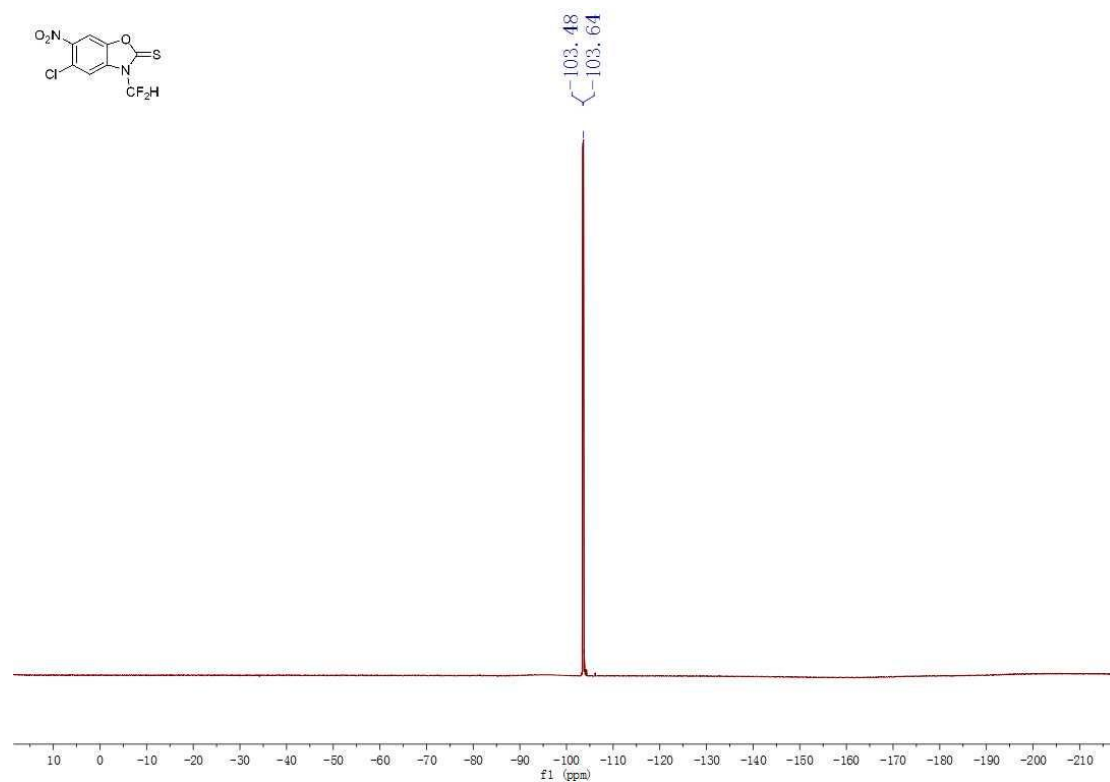
^1H NMR spectrum of **3w** in CDCl_3



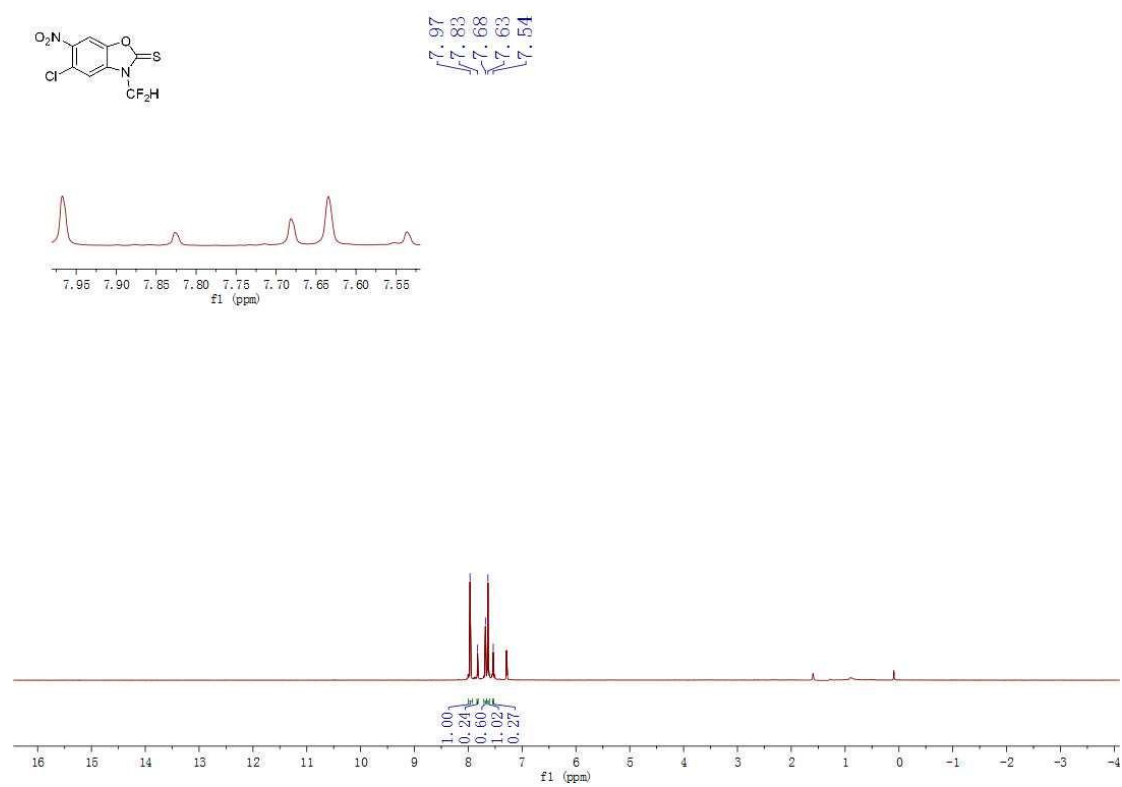
^{13}C NMR spectrum of **3w** in CDCl_3



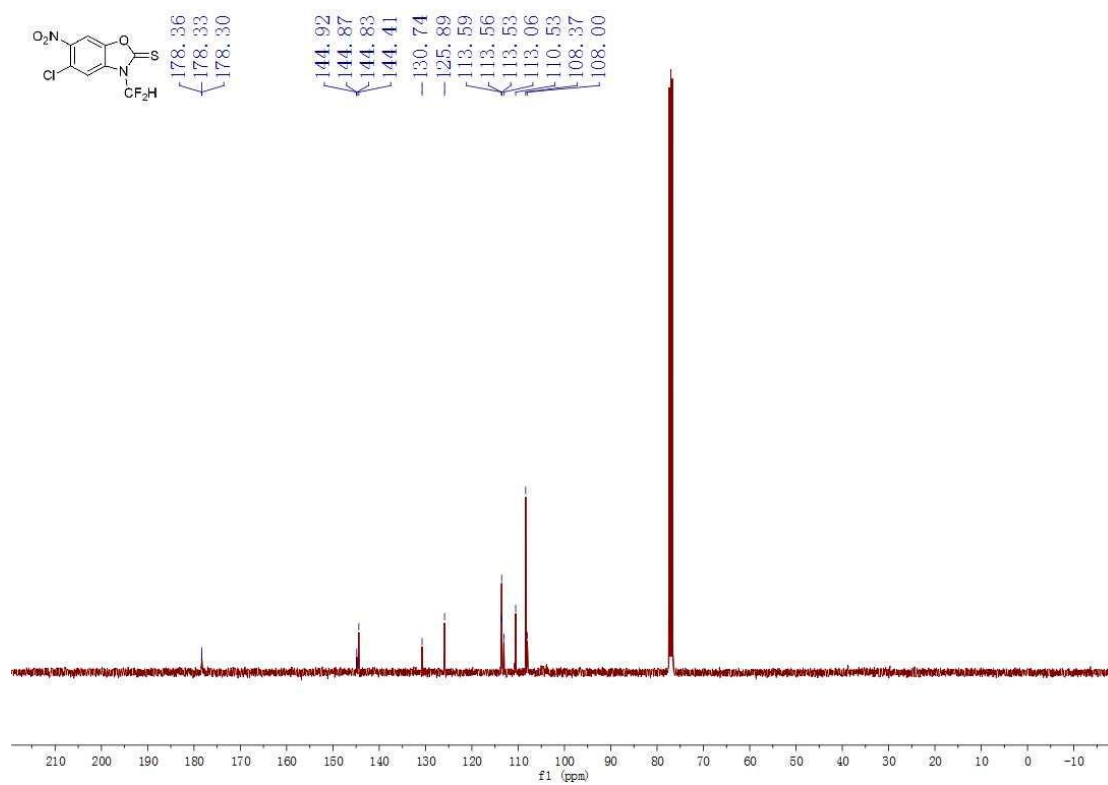
¹⁹F NMR spectrum of 3x in CDCl₃



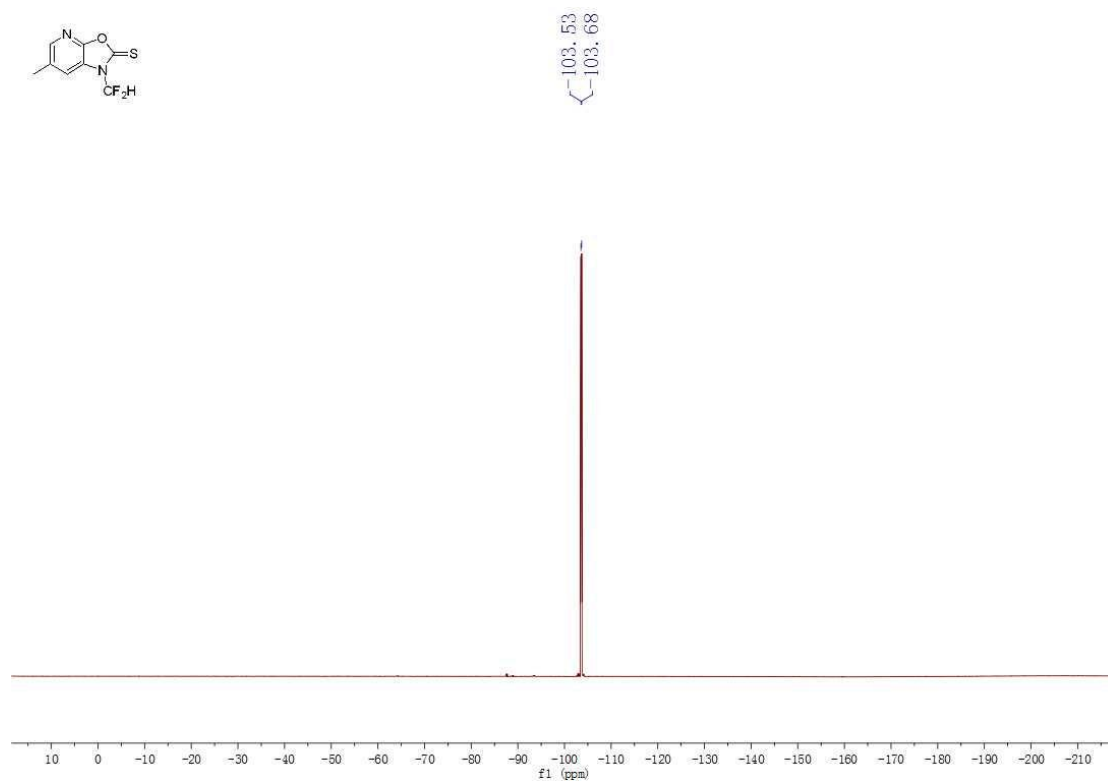
¹H NMR spectrum of 3x in CDCl₃



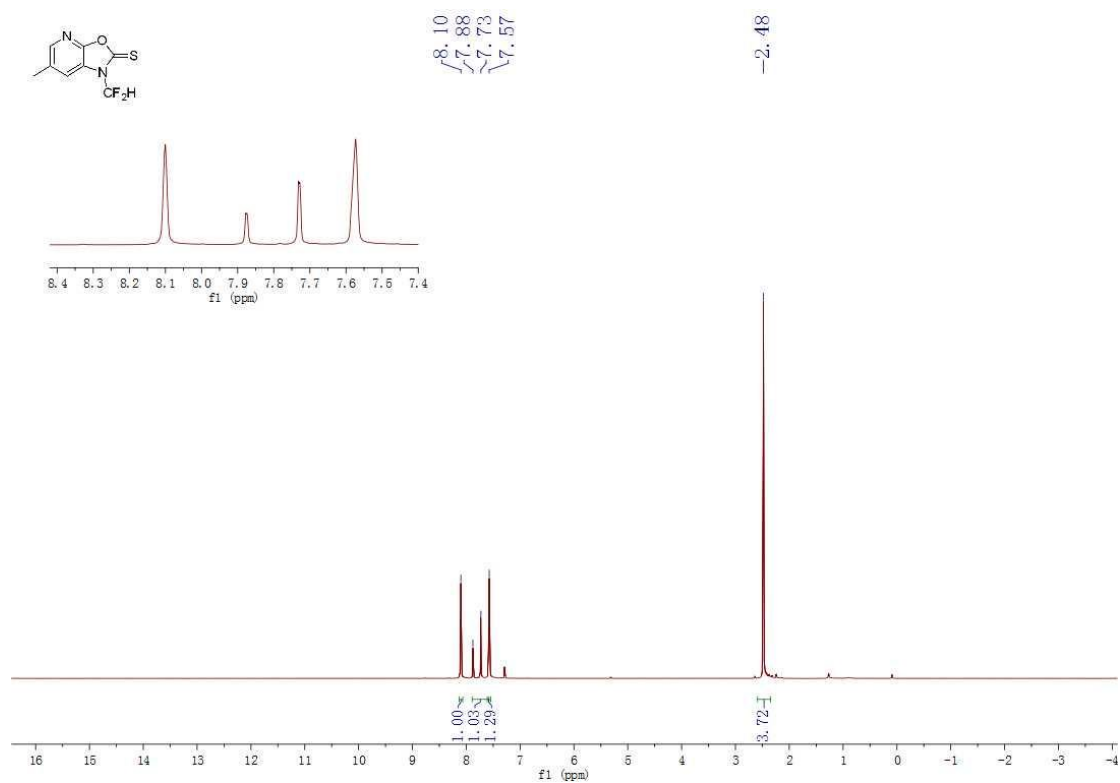
¹³C NMR spectrum of 3x in CDCl₃



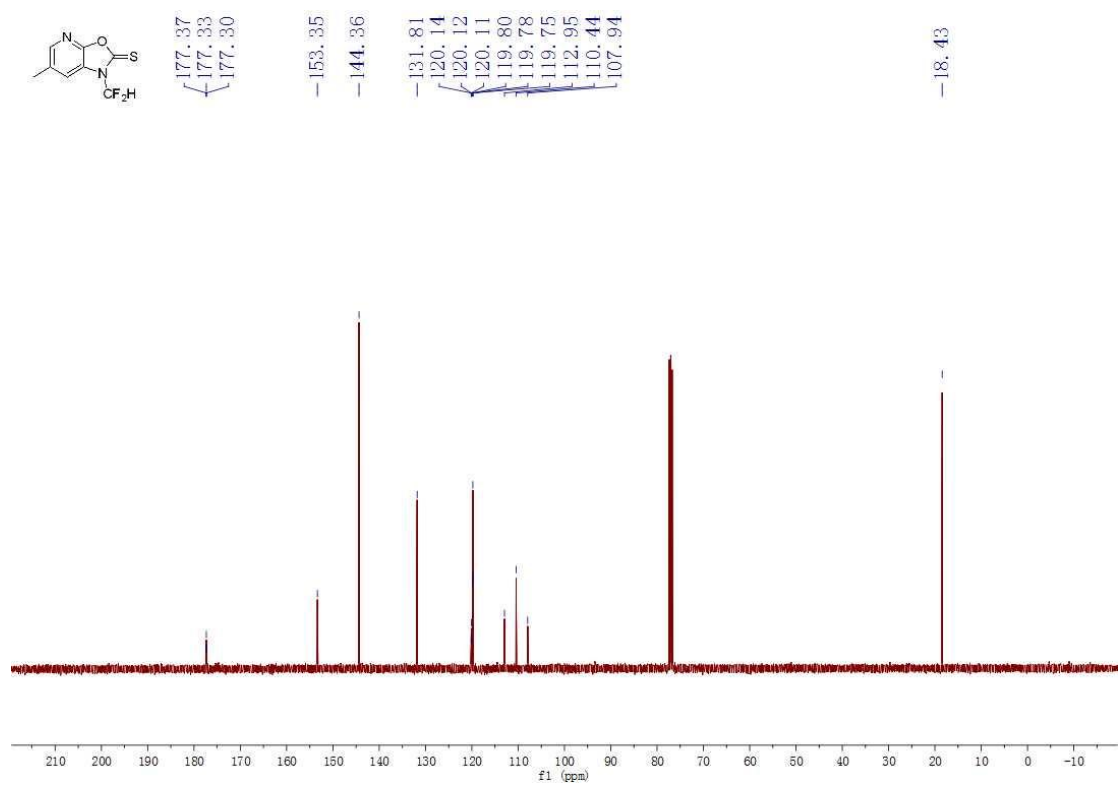
¹⁹F NMR spectrum of 3z in CDCl₃



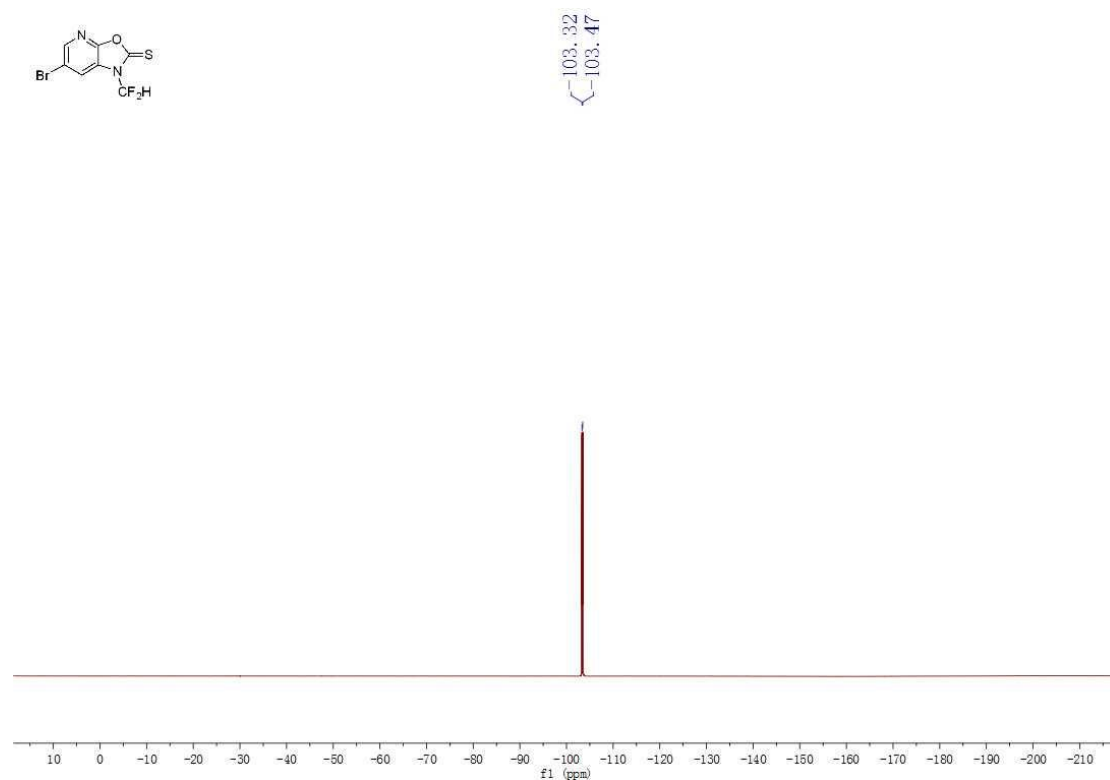
¹H NMR spectrum of 3z in CDCl₃



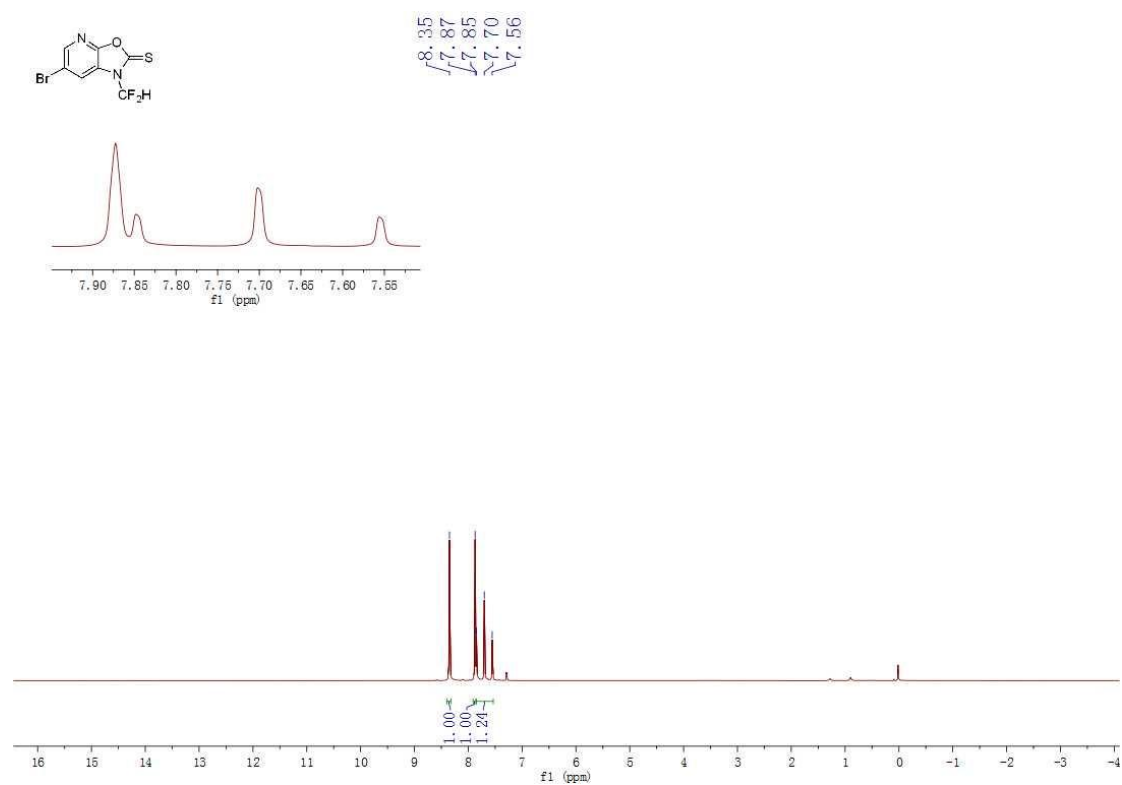
¹³C NMR spectrum of 3z in CDCl₃



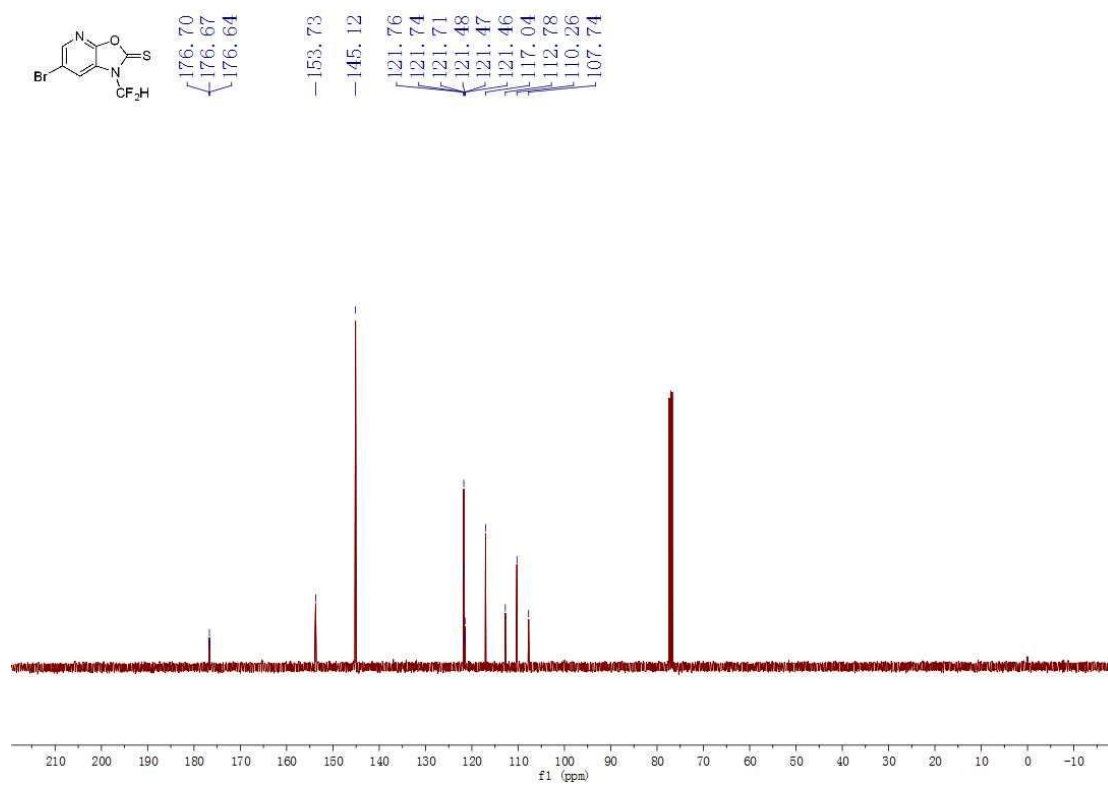
¹⁹F NMR spectrum of 3aa in CDCl₃



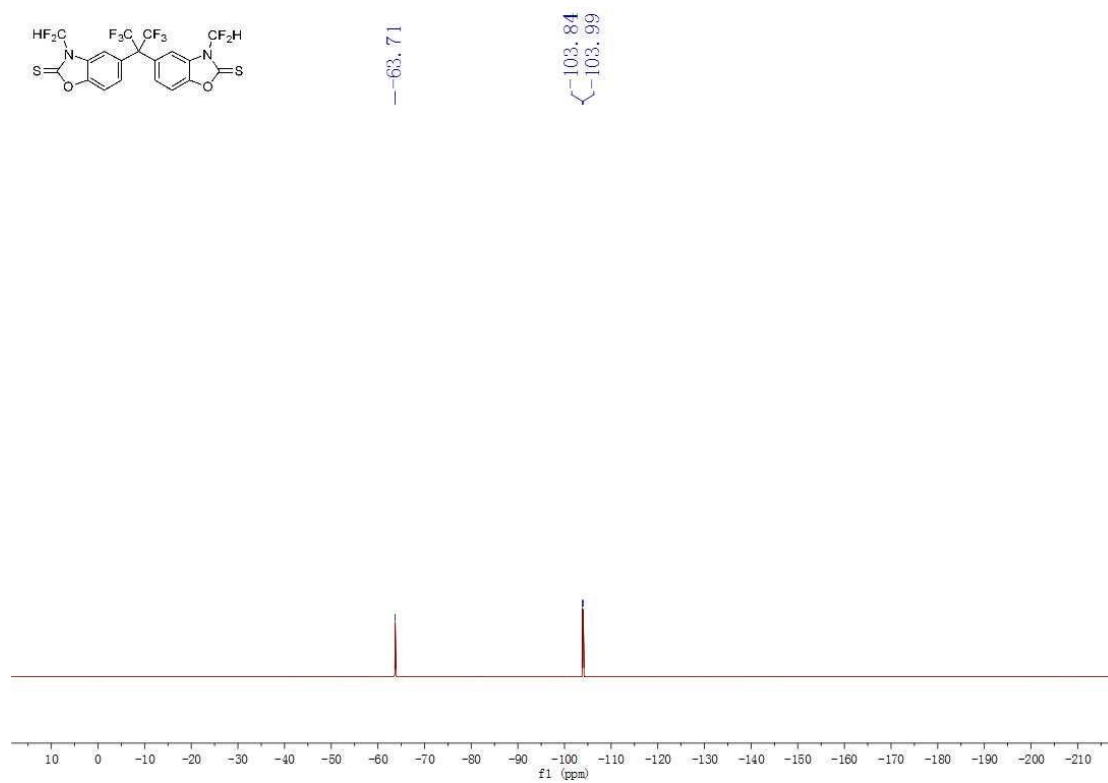
¹H NMR spectrum of 3aa in CDCl₃



¹³C NMR spectrum of 3aa in CDCl₃



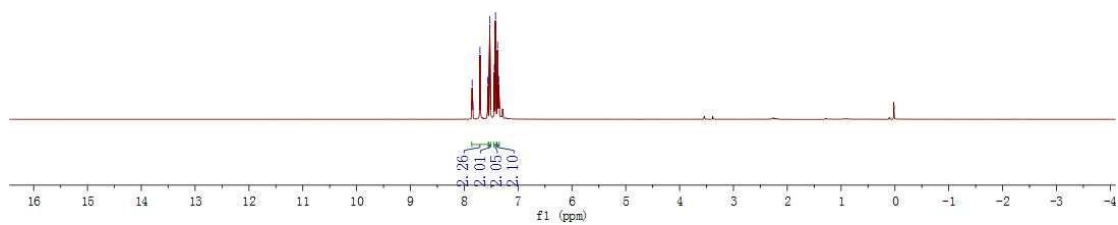
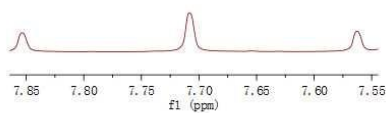
¹⁹F NMR spectrum of 3ab in CDCl₃



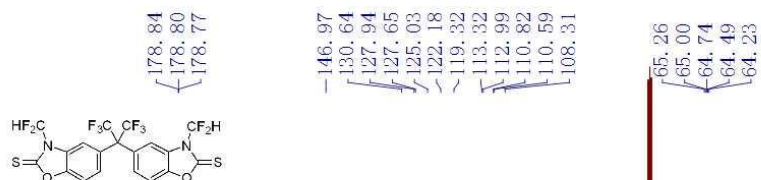
^1H NMR spectrum of **3ab** in CDCl_3



7.85
7.71
7.56
7.53
7.44
7.42
7.38
7.36



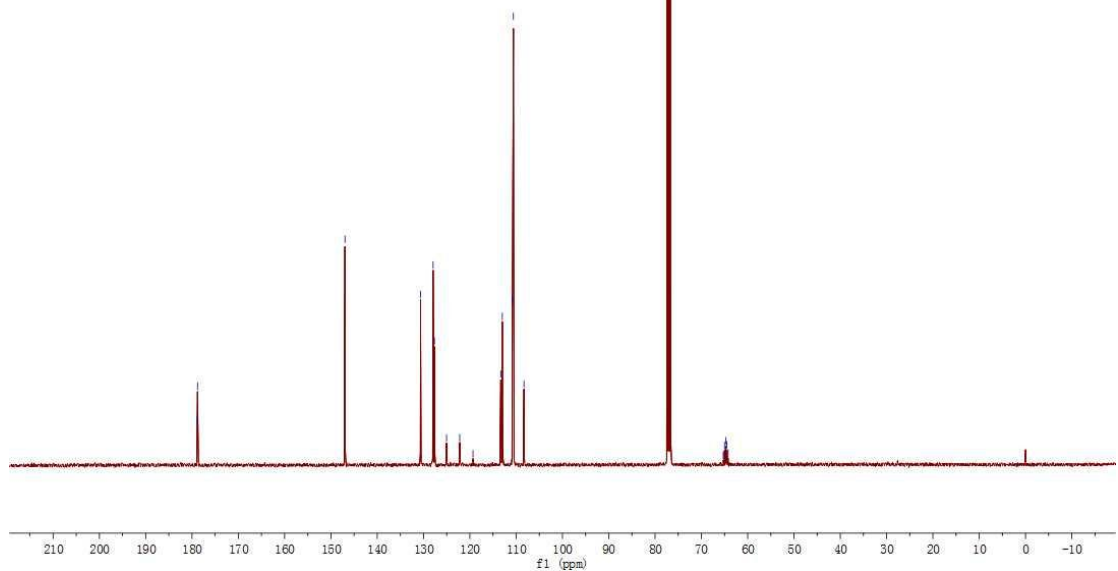
^{13}C NMR spectrum of **3ab** in CDCl_3



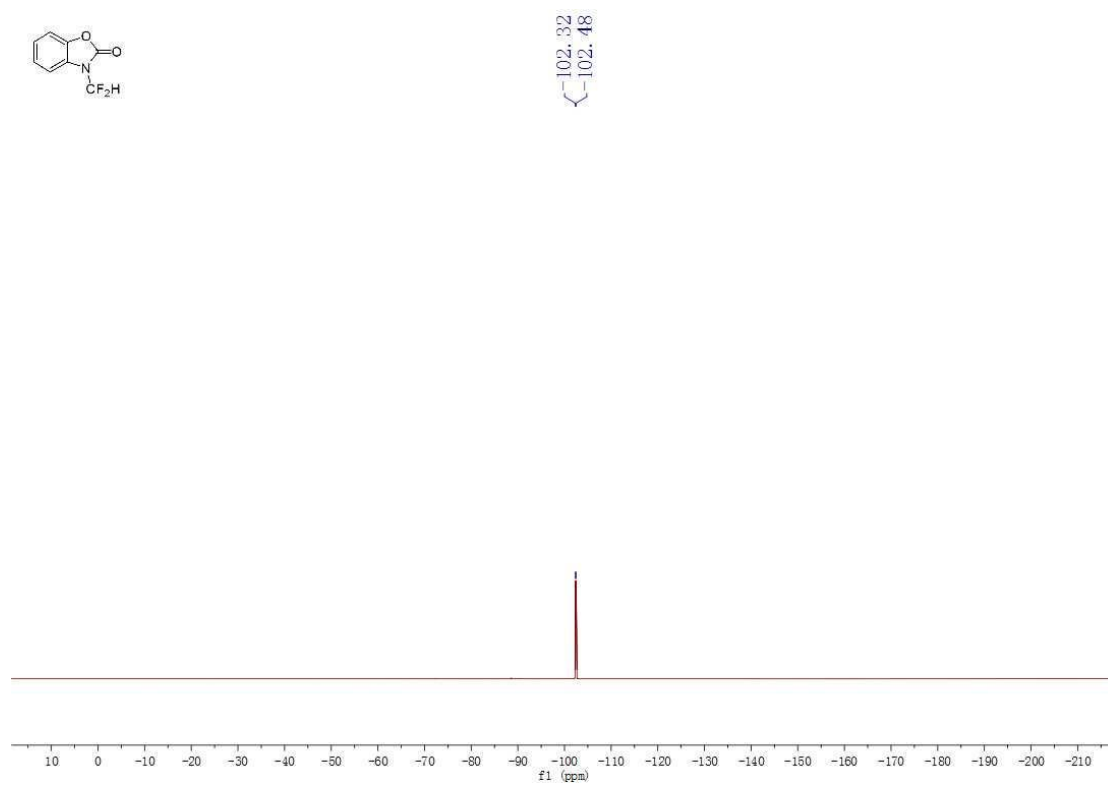
178.84
178.80
178.77

146.97
130.64
127.94
127.65
125.03
122.18
119.32
113.32
112.99
110.82
110.59
108.31

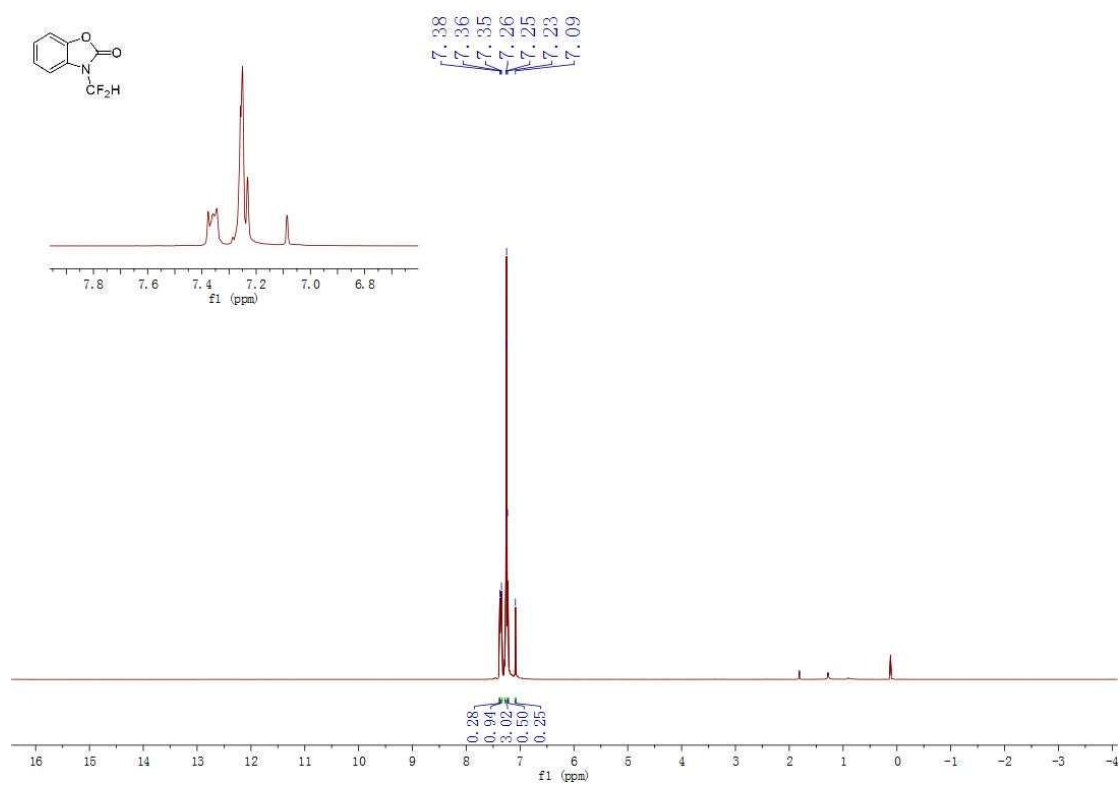
65.26
65.00
64.74
64.49
64.23



¹⁹F NMR spectrum of compound **5 in CDCl₃**



¹H NMR spectrum of compound **5 in CDCl₃**



¹³C NMR spectrum of compound **5** in CDCl₃

