Supporting information

Se–S dynamic exchange reaction: a strategy of highly efficient S–S bond cleavage for synthesizing benzothiazole derivatives

Tian-Xing Zhang,*‡ Er-Wei Zhang,‡ Wen-Yue Zhang, Zihao Zhao, Qingxiang Guo and Ning Zhu*

College of Chemical Engineering, Inner Mongolia University of Technology
Inner Mongolia Engineering Research Center for CO_2 Capture and Utilization
Key Laboratory of CO_2 Resource Utilization at Universities of Inner Mongolia Autonomous Region
Hohhot 010051, China

E-mail: txzhang@imut.edu.cn
E-mail: zhuning@imut.edu.cn

‡These authors contributed equally to this work.

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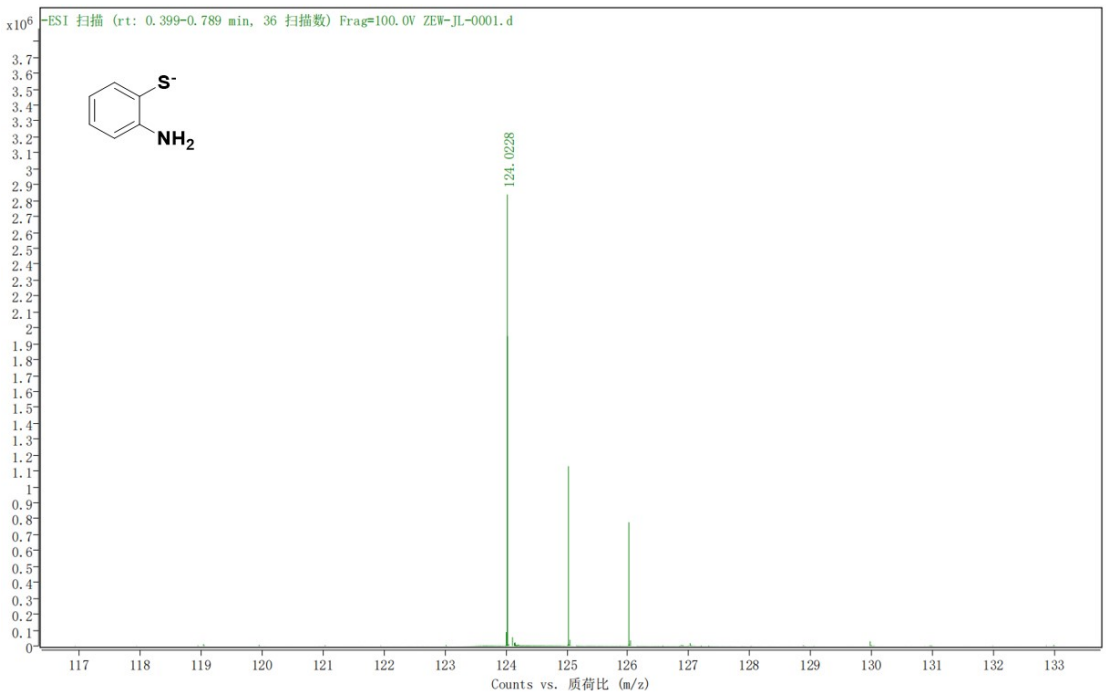
1. General remarks

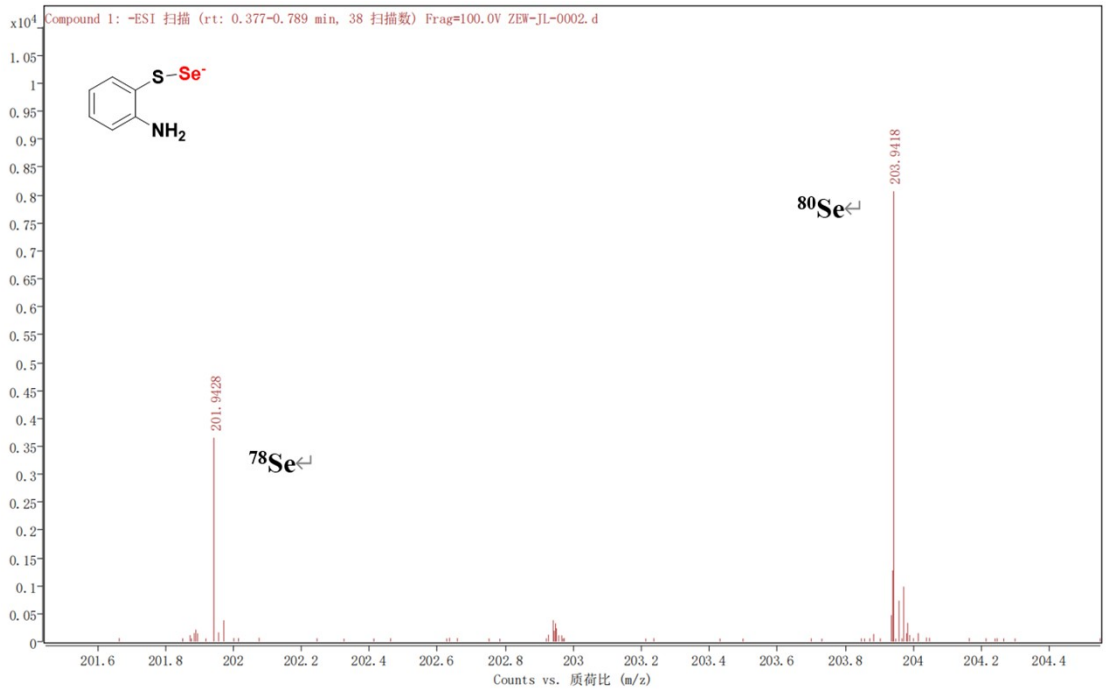
All reagents were used without further purification, which were purchased from Aladdin and Energy Chemical. All reactions were performed in clean glassware with magnetic stirring. Chromatographic purification was carried out on silica gel (200 ~ 300 mesh) and analytical thin layer chromatography (TLC). Melting points were measured with an SGC X-4 microscopic melting point meter. The ^{1}H, ^{13}C, and ^{19}F-NMR spectra were obtained on an Agilent 500 MHz DD2 spectrometer. The NMR results were processed using MestReNova software. All ESI-MS experiments were carried out on a 6545 QTOF mass spectrometer (Agilent Technologies).

2. MS spectrometry of metal Na_2Se-disulfide interchange reaction

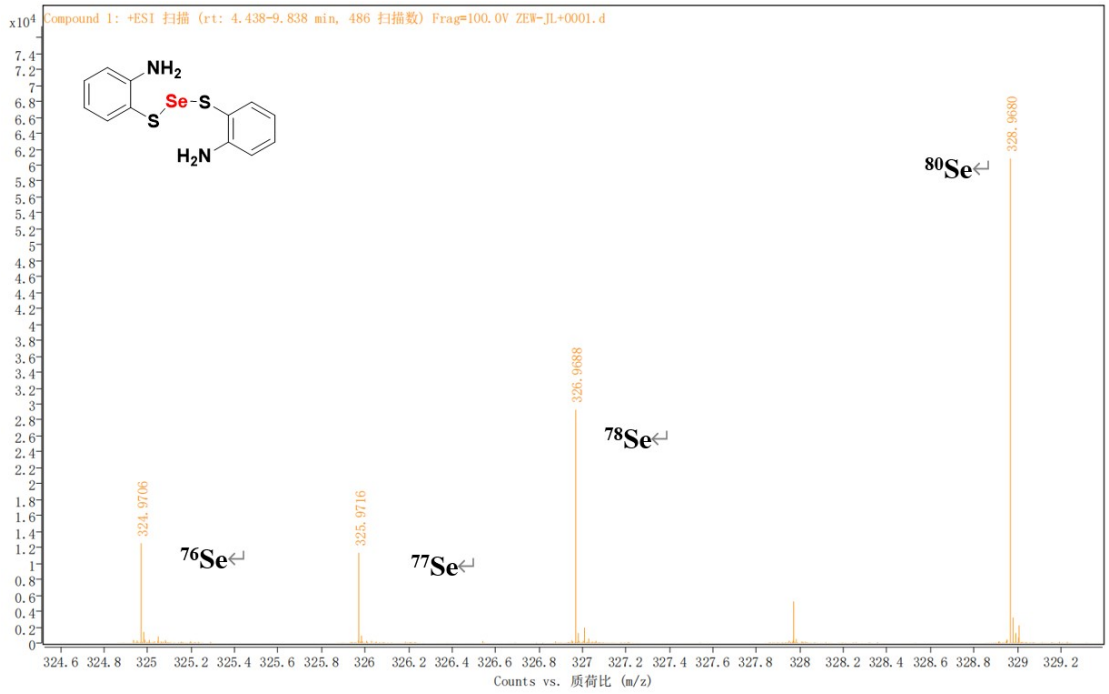
(a)



(b)



(c)



(d)

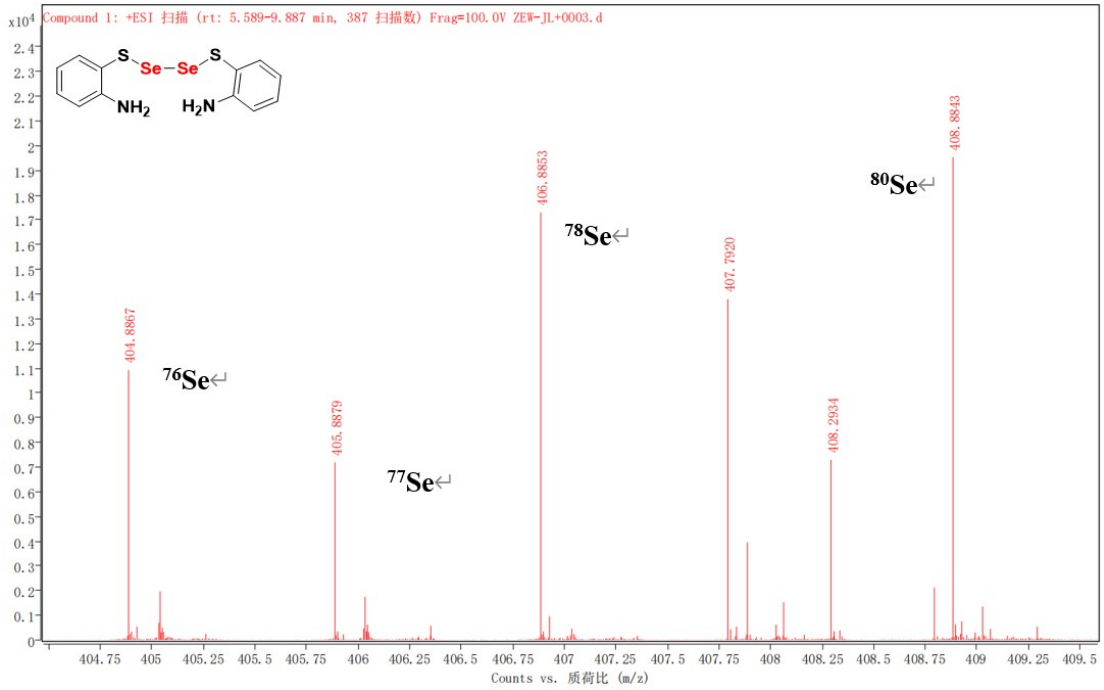


Fig. S1 (a) MS spectra of a) intermediate **A** (2-aminobenzenethiolate), b) intermediate **B**, c) intermediate **C**, d) intermediate **E**. Reaction conditions: 2,2'-disulfanediyldianiline **1a** (0.2 mmol), Na_2Se (0.2 mmol) were added in EtOH (2.5 ml), stirred under an Ar atmosphere at room temperature for 20 min and the reaction mixture was analyzed by ESI-MS.

3. The exchange efficiency of selenium or sulfur to facilitate the cleavage of S–S bonds

The ^{1}H NMR spectrum of a mixture containing 2,2'-disulfanediyldianiline (**1a**, 0.1 mmol, 25 mg) and sodium selenite (Na_2Se, 0.05 mmol, 6.3 mg) in deuterated methanol (0.5 mL) was recorded after the mixture was introduced into the NMR tube, as depicted in **Fig. S2a**. Similarly, the ^{1}H NMR spectrum of a mixture solution composed of **1a** (0.1 mmol, 25 mg) and potassium sulfide (K_2S, 0.05 mmol, 5.5 mg) in deuterated methanol (0.5 mL) was also acquired and was illustrated in **Fig. S2b**. **1a,** 2-aminobenzenethiolate and several intermediates were found in the dynamic interchange reaction between disulfide and Na_2Se or K_2S. Notably, the total aromatic hydrogen on the benzene ring remained unchange during the dynamic interchange reaction between disulfide and Na_2Se or K_2S. Given that all the hydrogens on the benzene ring originate from disulfides, the total count of benzene ring hydrogens can be correlated with the molar amount of disulfides involved in the reaction. According to Scheme 2, it is clear that the peak labeled "**a**" corresponds to one hydrogen of 2-aminobenzenethiolate. To determine the relative amount of 2-aminobenzenethiolate, we set the integral area of the "**a**" peak to 1.00 and then multiplied this value by 4 to represent the equivalent molar amount of 2-aminobenzenethiolate. Therefore, the relative amount of 2-aminobenzenethiolate can be calculated as four divided by the total integral area of all aromatic hydrogen signals.

According to this calculation method, we could calculate the relative amount of 2-aminobenzenethiolate in the reaction solution of **1a** and Na_2Se from **Fig. S2a**.

(1.00*4)/(2.13+1.14+2.04+2.32+1.00)*100%=46.3%

According to this calculation method, we could calculate the relative amount of 2-aminobenzenethiolate in the reaction solution of **1a** and K_2S from **Fig. S2b**.

(1.00*4)/(2.74+11.23+6.75+10.78+5.04+7.82+1)*100%=8.8%

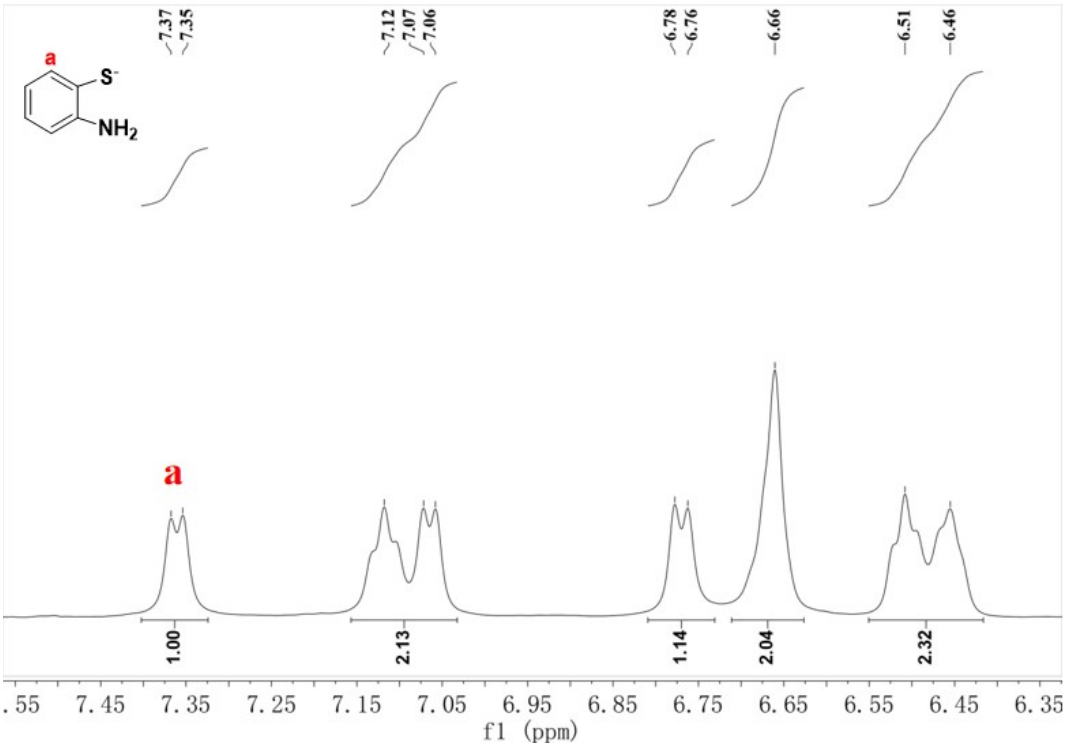


Fig. S2a The integral area of the aromatic hydrogen signals in ^{1}H NMR spectra about the reaction solution of **1a** and Na_2Se in deuterated methanol.

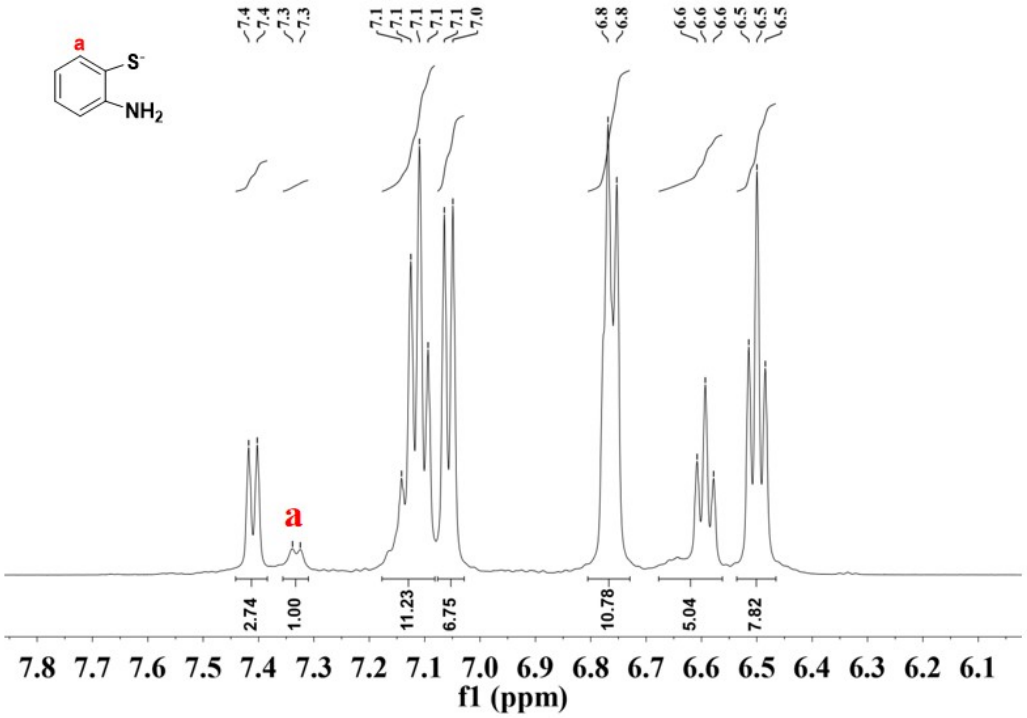
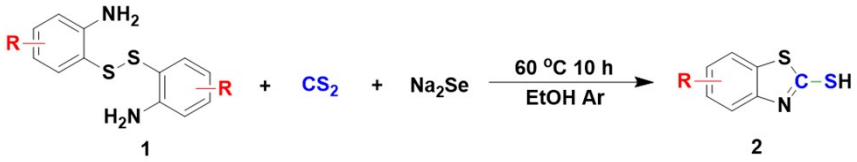
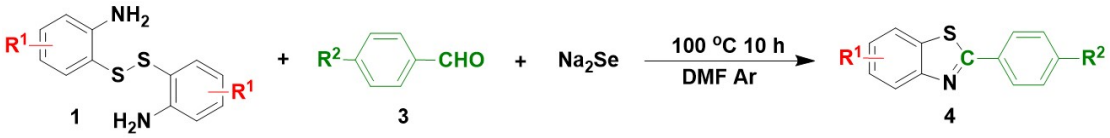


Fig. S2b The integral area of the aromatic hydrogen signals in ^{1}H NMR spectra about the reaction solution of **1a** and K_2S in deuterated methanol.

4. General procedure for the synthesis of benzothiazole derivatives



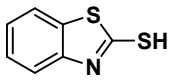
2,2'-Disulfanediyldianiline or its corresponding derivatives **1** (0.4 mmol), CS_2 (1.6 mmol), and Na_2Se (0.04 mmol) were added in EtOH (2.5 mL), and stirred under an Ar atmosphere at 60 °C for 10 h. The reaction mixture was acidified by dilute hydrochloric acid (3 mol L^{-1}) and extracted with CH_2Cl_2, or EtOAc. The organic layers were dried over anhydrous $MgSO_4$. After filtering to remove the $MgSO_4$, the solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the pure products **2**.



2,2'-Disulfanediyldianiline or its corresponding derivatives **1** (0.4 mmol), **3** (0.8 mmol), and Na_2Se (0.04 mmol) were added in DMF (2.5 mL), and stirred under an Ar atmosphere at 100 °C for 10 h. The reaction mixture was then washed with aqueous sodium bisulfite solution to remove the excess aldehyde and extracted with CH_2Cl_2. The organic layers were dried over anhydrous $MgSO_4$. After filtering to remove the $MgSO_4$, the solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the pure products **4**.

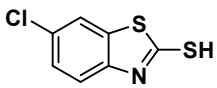
5. Characterization data for all products

2-Mercaptobenzothiazole 2a[1]



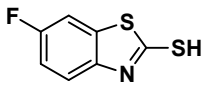
Isolated as a white solid (132 mg, 99% yield). Mp: 182–183 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.74 (brs, 1H), 7.77 (d, 1H, J = 10.0 Hz), 7.38 (t, 1H, J = 5.0 Hz), 7.31-7.24 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 190.3, 141.7, 129.8, 127.6, 124.6, 122.2, 112.9.

6-Chlorobenzo[*d*]thiazole-2-thiol 2b[1]



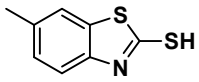
Isolated as a white solid (147 mg, 91% yield). Mp: 239–241 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.04 (brs, 1H), 7.46-7.40 (m, 2H), 7.28 (d, 1H, J = 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 190.6, 140.7, 131.5, 129.0, 127.7, 121.9, 114.0.

6-Fluorobenzo[*d*]thiazole-2-thiol 2c[2]



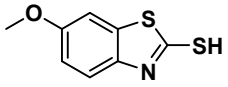
Isolated as a white solid (144 mg, 97% yield). Mp: 205–209 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.80 (brs, 1H), 7.67 (dd, 1H, J_1 = 10.0 Hz, J_2 = 5.0 Hz), 7.31–7.24 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 190.4, 159.6 (d, 1C, J = 239.4 Hz), 138.5, 131.3 (d, 1C, J = 12.6 Hz), 115.2 (d, 1C, J = 25.2 Hz), 113.9 (d, 1C, J = 12.6 Hz), 109.4, (d, 1C, J = 37.8 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -116.34 ~ -116.38 (m, 1F).

6-Methylbenzo[*d*]thiazole-2-thiol 2d[1]



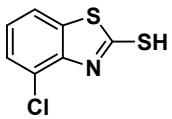
Isolated as a white solid (139 mg, 96% yield). Mp: 179–181 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.67 (brs, 1H), 7.49 (s, 1H), 7.20 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 189.6, 139.7, 134.2, 129.9, 128.5, 122.0, 112.6, 21.2.

6-Methoxybenzo[*d*]thiazole-2-thiol 2e[1]



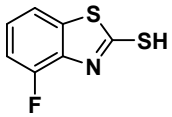
Isolated as a white solid (153 mg, 97% yield). Mp:193–196 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.63 (brs, 1H), 7.34 (s, 1H), 7.21 (d, 1H, J = 5.0 Hz), 7.00 (dd, 1H, J_1 = 5.0 Hz, J_2 = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 188.8, 157.1, 135.7, 131.2, 115.2, 113.5, 106.4, 56.2.

4-Chlorobenzo[*d*]thiazole-2-thiol 2f[2]



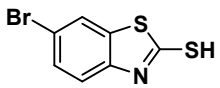
Isolated as a white solid (157 mg, 97% yield). Mp: 207 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.97 (brs, 1H), 7.66 (d, 1H, *J* = 5.0 Hz), 7.46 (d, 1H, *J* = 10.0 Hz), 7.28 (t, 1H, *J* = 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 188.3, 157.2, 127.5, 125.5, 125.4, 113.5, 120.8.

4-Fluorobenzo[*d*]thiazole-2-thiol 2g[1]



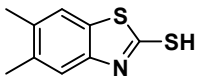
Isolated as a white solid (145 mg, 98% yield). Mp: 205–209 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.75 (brs, 1H),7.66 (d, 1H, *J* = 5.0 Hz), 7.31-7.23 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 190.3, 159.6 (d, 1C, *J* = 239.4 Hz), 138.8, 131.4 (d, 1C, *J* = 12.6 Hz), 115.1 (d, 1C, *J* = 25.2 Hz), 114.0 (d, 1C, *J* = 12.6 Hz), 109.3 (d, 1C, *J* = 37.8 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ (ppm) -118.25 (s, 1F).

6-Bromobenzo[*d*]thiazole-2-thiol 2h[1]



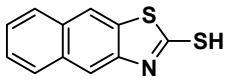
Isolated as a white solid (177 mg, 90% yield). Mp: 265–266 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.85 (brs, 1H), 7.98 (s, 1H), 7.56 (d, 1H, *J* = 5.0 Hz), 7.22 (d, 1H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 190.5, 141.1, 131.9, 130.4, 124.6, 116.8, 114.3.

5,6-Dimethylbenzo[*d*]thiazole-2-thiol 2i



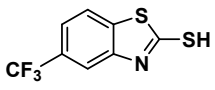
Isolated as a primrose yellow solid (141 mg, 90% yield). Mp: 109–110 °C. HRMS (ESI): m/z, Calcd for $C_9H_9NS_2$ $[M-H]^-$ 194.0104, Found 194.0104. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.61 (brs, 1H), 7.44 (s, 1H), 7.10 (s, 1H), 2.26 (d, 6H, *J* = 15.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 189.6, 140.0, 136.4, 133.5, 126.9, 122.2, 113.3, 20.0, 19.8.

Naphtho[2,3-*d*] thiazole-2-thiol 2j[3]



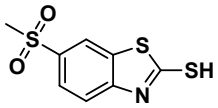
Isolated as a primrose yellow solid (147 mg, 92% yield). Mp: 240 °C. HRMS (ESI): m/z, Calcd for $C_{11}H_7NS_2$ $[M-H]^-$ 215.9947, Found 215.9949. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.40 (brs, 1H), 8.59 (d, 2H, *J* = 10.0 Hz), 8.05 (d, 1H, *J* = 10.0 Hz), 7.69-7.62 (m, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 174.7, 153.4, 140.9, 132.2, 130.1, 128.9, 127.9 (2C), 127.1 (2C), 110.0.

5-(Trifluoromethyl) benzo[d]thiazole-2-thiol 2k[1]



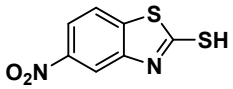
Isolated as a white solid (173mg, 92% yield). Mp: 248–250 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.05 (brs, 1H), 7.95 (d, 1H, *J* = 5.0 Hz), 7.64 (d, 1H, *J*= 5.0 Hz), 7.49 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 191.5, 142.0, 134.6, 128.1 (d, 1C, *J*=37.8 Hz), 124.4 (d, 1C, *J*=277.2 Hz), 121.0 (d, 1C, *J*=12.6 Hz), 109.1 (dd, 1C, J_1=8.8 Hz, J_2=5.0 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ (ppm) -60.68 (s, 3F).

6-(Methylsulfonyl) benzo[d]thiazole-2-thiol 2l[1]



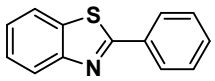
Isolated as a white solid (177 mg, 90% yield). Mp: 243–244 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.12 (brs, 1H), 8.32 (s, 1H), 7.91 (d, 1H, *J*= 10.0 Hz), 7.46 (d, 1H, *J*= 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 192.6, 136.7, 136.6, 130.7, 126.8, 121.9, 113.1, 44.4.

5-(Nitro) benzo[d]thiazole-2-thiol 2m



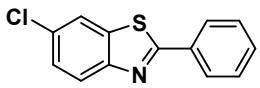
Isolated as a white solid (246 mg, 91% yield). Mp: 155–157 °C. MS (ESI): m/z, Calcd for $C_7H_3N_2S_2O_2$ $[M-H]^-$ 210.9641, Found 210.9645 ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.16 (brs, 1H), 8.13 (d, 1H, *J*= 10.0 Hz), 7.97 (d, 2H, *J*= 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 192.0, 147.0, 142.1, 137.7, 123.2, 119.2, 107.3.

2-Phenylbenzo[*d*]thiazole 4a[4]



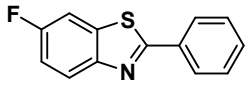
Isolated as a primrose yellow solid (160 mg, 95% yield). Mp: 107-108 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.16 (d, 1H, *J* = 5.0 Hz), 8.11-8.07 (m, 3H), 7.59-7.54 (m, 4H), 7.48 (t, 1H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.8, 154.0, 134.9, 133.3, 131.9, 129.9(2C), 127.7(2C), 127.1, 126.0, 123.4, 122.8.

6-Chloro-2-phenylbenzo[*d*]thiazole 4b[5]



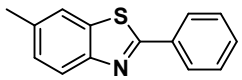
Isolated as a primrose yellow solid (153 mg, 78% yield). Mp: 160–161 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.16-8.1 (m, 3H), 7.67-7.65 (m, 1H), 7.62-7.59 (m, 3H), 7.47 (t, 1H, *J* = 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 169.0, 150.7, 136.6, 132.9, 132.3, 130.0(2C), 127.9 (2C), 127.2, 127.0, 126.9, 122.0.

6-Fluoro-2-phenylbenzo[*d*]thiazole 4c[6]



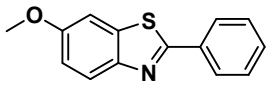
Isolated as a white solid (147 mg, 80% yield). Mp: 137–138 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.10-8.05 (m, 4H), 7.59 (d, 3H, *J* = 5.0 Hz), 7.42 (t, 1H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.9, 160.3 (d, 1C, *J* = 252.0 Hz), 150.9, 136.1 (d, 1C, *J* = 12.6 Hz), 133.1, 131.9, 129.9, 127.6, 124.7 (d, 1C, *J* = 12.6 Hz), 115.6 (d, 1C, *J* = 25.2 Hz), 109.3 (d, 1C, *J* = 37.8 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ (ppm) -115.63 ~ -115.68 (m, 1F).

6-Methyl-2-phenylbenzo[*d*]thiazole 4d[6]



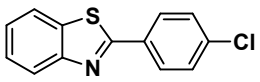
Isolated as a white solid (155 mg, 86% yield). Mp: 126–127 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.08-8.07 (m, 2H), 7.95-7.94 (m, 3H), 7.58-7.56 (m, 2H), 7.37 (d, 1H, *J* = 10.0 Hz), 2.47 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 166.6, 152.2, 135.8, 135.1, 133.4, 131.7, 129.8 (2C), 128.6, 127.5 (2C), 122.9, 122.3, 21.5.

6-Methoxy-2-phenylbenzo[*d*]thiazole 4e[5]



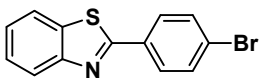
Isolated as a primrose yellow solid (158 mg, 82% yield). Mp: 116–117 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.05-8.03 (m, 2H), 7.95 (d, 1H), 7.72 (d, 1H), 7.57-7.55 (m, 3H), 7.14 (d, 1H, *J* = 10.0 Hz), 3.85 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 165.1, 158.0, 148.5, 136.5, 133.5, 131.4, 129.8 (2C), 127.3 (2C), 123.9, 116.4, 105.3, 56.2.

2-(4-Clorophenyl)benzo[*d*]thiazole 4f[4]



Isolated as a white solid (153mg, 78% yield). Mp: 112–113 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.18 (d, 1H, *J* = 5.0 Hz), 8.13-8.07 (m, 3H), 7.66-7.64 (m, 2H), 7.57 (t, 1H, *J* = 5.0 Hz), 7.49 (t, 1H, *J*= 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-d): δ (ppm) 166.4, 153.9, 136.5, 135.0, 132.2, 130.0 (2C), 129.4 (2C), 127.3, 126.2, 123.4, 122.9.

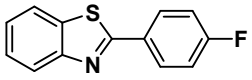
2-(4-Bromophenyl)benzo[*d*]thiazole 4g[4]



Isolated as a white solid (186 mg, 80% yield). Mp: 126–128 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.17 (d, 1H, *J* = 5.0 Hz), 8.09-8.04 (m, 3H), 7.80-7.78 (m, 2H), 7.57 (t, 1H, *J* = 5.0 Hz), 7.50 (t, 1H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 166.6, 153.9, 135.0, 132.9 (2C),

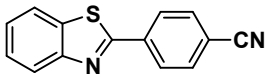
132.5, 129.5 (2C), 127.3, 126.2, 125.3, 123.4, 122.9.

2-(4-Fluorophenyl)benzo[*d*]thiazole 4h[4]



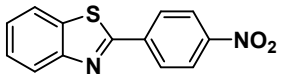
Isolated as a white solid (158mg, 86% yield). Mp: 102–105 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.18-8.15 (m, 3H), 8.07 (d, 1H, J = 5.0 Hz), 7.56 (t, 1H, J = 5.0 Hz), 7.49-7.41 (m, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 166.5, 164.3 (d, 1C, J = 252.0 Hz), 154.0, 135.0, 130.1 (d, 2C, J = 12.6 Hz), 130.0 (d, 1C, J = 3.3 Hz), 127.2, 126.0, 123.3, 122.9, 117.0 (d, 2C, J = 12.6 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ (ppm) -108.84 ~ -108.90 (m, 1F).

4-(Benzo[*d*]thiazol-2-yl)benzonitrile 4i[4]



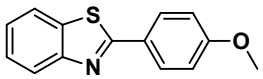
Isolated as a white solid (174 mg, 92% yield). Mp: 169–171 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.29 (d, 2H, J = 5.0 Hz), 8.22 (d, 1H, J = 10.0 Hz), 8.14 (d, 1H, J = 5.0 Hz), 8.05 (d, 2H, J = 10.0 Hz), 7.50 (t, 1H, J = 10.0 Hz), 7.53 (t, 1H, J = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 165.8, 153.9, 137.9, 135.4, 133.8 (2C), 128.3 (2C), 127.5, 126.7, 123.1, 118.8, 113.8.

2-(4-Nitrophenyl)benzo[*d*]thiazole 4j[7]



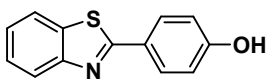
Isolated as a yellow solid (166 mg, 81% yield). Mp: 228–230 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.38 (dd, 4H, J_1 = 10.0 Hz, J_2 = 20.0 Hz), 8.23 (d, 1H, J = 10.0 Hz), 8.15 (d, 1H, J = 10.0 Hz), 7.61 (t, 1H, J = 5.0 Hz), 7.54 (t, 1H, J = 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 165.3, 153.9, 149.2, 138.8, 135.5, 128.8, 127.6, 126.8, 125.1 (2C), 123.9, 123.2.

3-(4-Methoxyphenyl)benzo[*d*]thiazole 4k[4]



Isolated as a white solid (174 mg, 90% yield). Mp: 121–122 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.10 (d, 1H, J = 5.0 Hz), 8.04-7.99 (m, 3H), 7.51 (t, 1H, J = 5.0 Hz), 7.42 (t, 1H, J = 5.0 Hz), 7.11 (d, 2H, J = 10.0 Hz), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.5, 162.2, 154.1, 134.7, 129.3 (2C), 127.0, 126.0, 125.6, 122.9, 122.7, 115.2 (2C), 56.0.

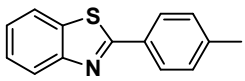
4-(Benzo[*d*]thiazol-2-yl)phenol 4l[4]



Isolated as a white solid (156 mg, 86% yield). Mp: 224–226 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 10.22 (s, 1H), 8.09 (d, 1H, J = 5.0 Hz), 7.98 (d, 1H, J = 5.0 Hz), 7.94 (d, 2H, J = 5.0 Hz), 7.50 (t, 1H, J = 10.0

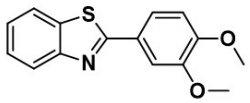
Hz), 7.40 (t, 1H, *J* = 10.0 Hz), 6.93 (d, 2H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.9, 161.0, 154.2, 134.5, 129.5 (2C), 126.9, 125.4, 124.5, 122.7, 122.6, 116.5 (2C).

2-(p-Tolyl)benzo[*d*]thiazole 4m[4]



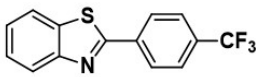
Isolated as a white solid (175 mg, 97% yield). Mp: 84–86 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.13 (d, 1H, *J* = 5.0 Hz), 8.03 (d, 1H, *J* = 10.0 Hz), 7.98 (d, 2H, *J* = 10.0 Hz), 7.53 (t, 1H, *J* = 10.0 Hz), 7.44 (t, 1H, *J* = 10.0 Hz), 7.39 (d, 2H, *J* = 5.0 Hz), 2.39 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.8, 154.0, 142.0, 134.8, 130.7, 130.4 (2C), 127.6 (2C), 127.1, 125.8, 123.2, 122.8, 21.5.

3-(3,4-Dimethoxyphenyl)benzo[*d*]thiazole 4n[4]



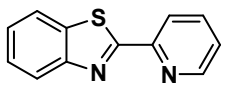
Isolated as a white solid (193 mg, 89% yield). Mp: 130–131 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.09 (t, 1H, *J* = 5.0 Hz), 8.02 (d, 1H, *J* = 5.0 Hz), 7.62 (t, 2H, *J* = 10.0 Hz), 7.51 (t, 1H, *J* = 10.0 Hz), 7.42 (t, 1H, *J* = 5.0 Hz), 7.12 (d, 1H, *J* = 10.0 Hz), 3.88 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 167.7, 154.0, 152.1, 149.6, 134.7, 129.9, 127.0, 125.6, 122.9, 122.6, 121.4, 112.4, 109.9, 56.2, 56.1.

2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole 4o[8]



Isolated as a yellow solid (190 mg, 85% yield). Mp: 156–158 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.30 (d, 2H, *J* = 10.0 Hz), 8.20 (d, 1H, *J* = 5.0 Hz), 8.12 (d, 1H, *J* = 5.0 Hz), 7.93 (d, 2H, *J* = 5.0 Hz), 7.58 (t, 1H, *J* = 10.0 Hz), 7.51 (d, 1H, *J* = 10.0 Hz). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 166.0, 153.9, 136.9, 135.2, 131.4 (q, 1C, *J* = 37.8 Hz), 128.4 (2C), 127.4, 126.8 (q, 2C, *J* = 2.52 Hz), 126.6, 124.5 (q, 1C, *J* = 277.2 Hz), 123.7, 123.0. ^{19}F NMR (470 MHz, DMSO-d_6): δ (ppm) -61.41 (s, 3F).

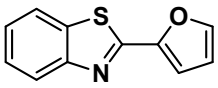
2-(Pyridin-2-yl)-1,3-benzothiazole 4p[9]



Isolated as a white solid (138 mg, 81% yield). Mp: 136–137 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.73 (d, 1H, *J* = 5.0 Hz), 8.32 (d, 1H, *J* = 10.0 Hz), 8.16 (d, 1H, *J* = 10.0 Hz), 8.10 (d, 1H, *J* = 5.0 Hz), 8.03 (t, 1H, *J* = 10.0 Hz), 7.60-7.54 (m, 2H), 7.49 (t, 1H, *J* = 5.0 Hz). ^{13}C NMR (126 MHz, DMSO-

d_6): δ (ppm) 169.5, 154.2, 150.8, 150.4, 138.3, 135.8, 127.1, 126.6, 126.4, 123.8, 123.0, 120.8.

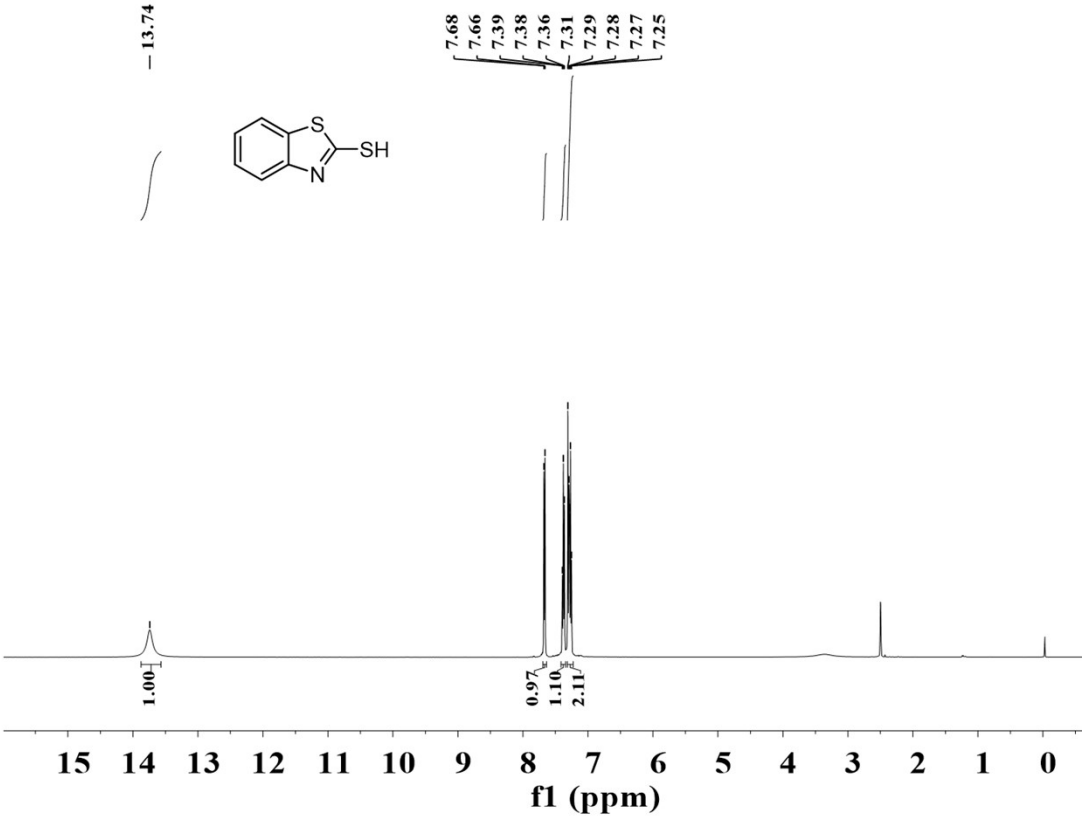
2-(Furan-2-yl)-1,3-benzothiazole 4q[9]



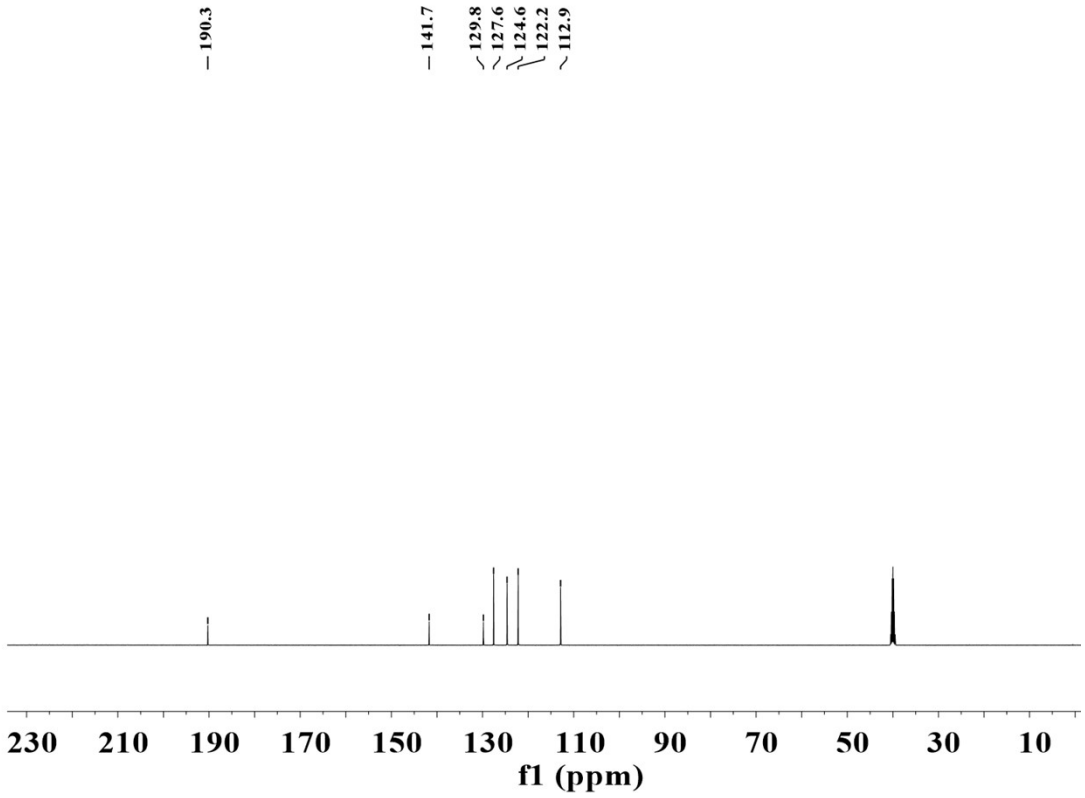
Isolated as a pale brown solid (132 mg, 82% yield). Mp: 100–101 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.13 (d, 1H, *J* = 5.0 Hz), 8.01 (d, 2H, *J* = 10.0 Hz), 7.54 (t, 1H, *J* = 5.0 Hz), 7.44 (t, 1H, *J* = 10.0 Hz), 7.36 (d, 1H, *J* = 5.0 Hz), 6.79-6.78 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 157.3, 153.8, 148.4, 146.6., 134.1, 127.2, 125.9, 123.1, 122.8, 113.5, 112.4.

6. ^{1}H, ^{13}C, and ^{19}F-NMR spectra of compounds 2a-m, 4a-4q

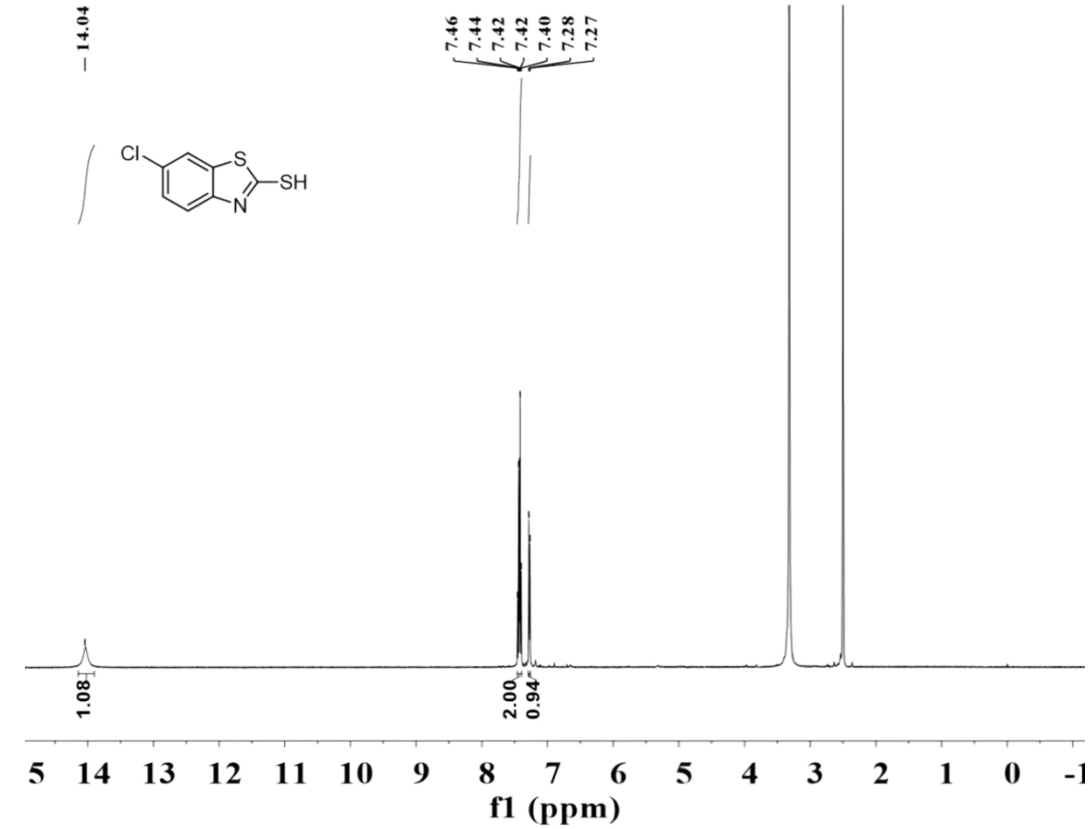
^{1}H NMR spectrum of compound **2a**



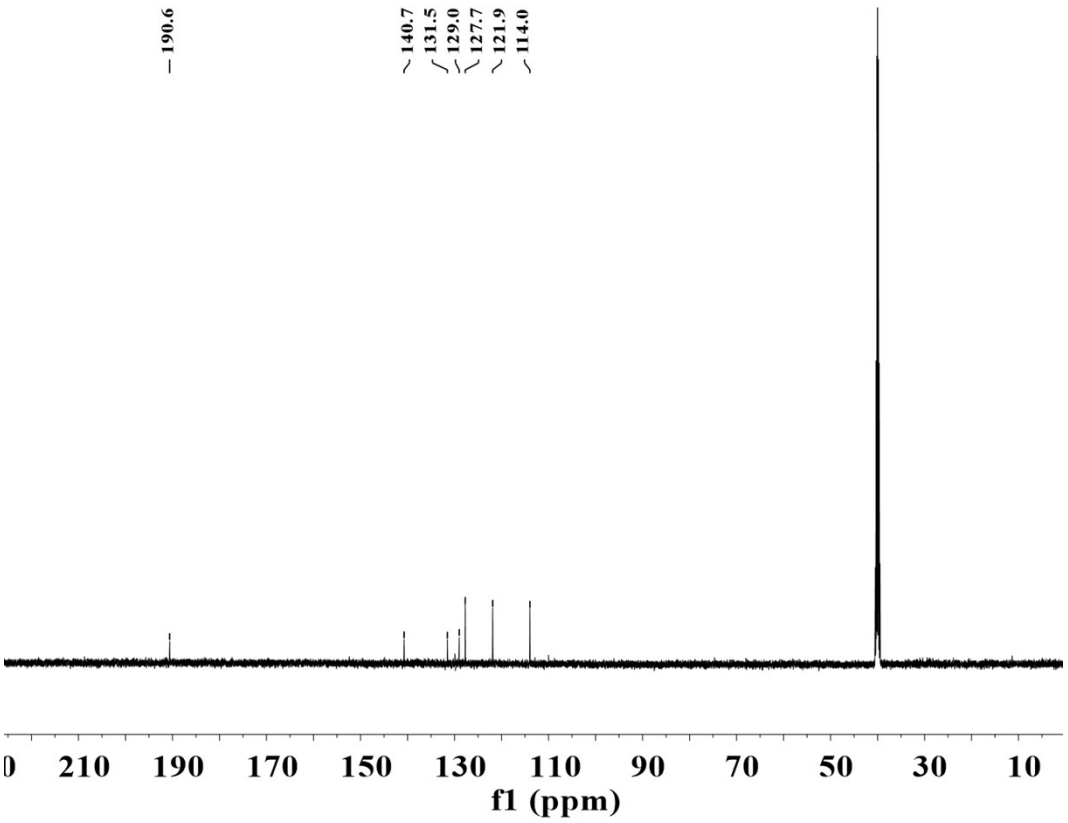
^{13}C NMR spectrum of compound **2a**



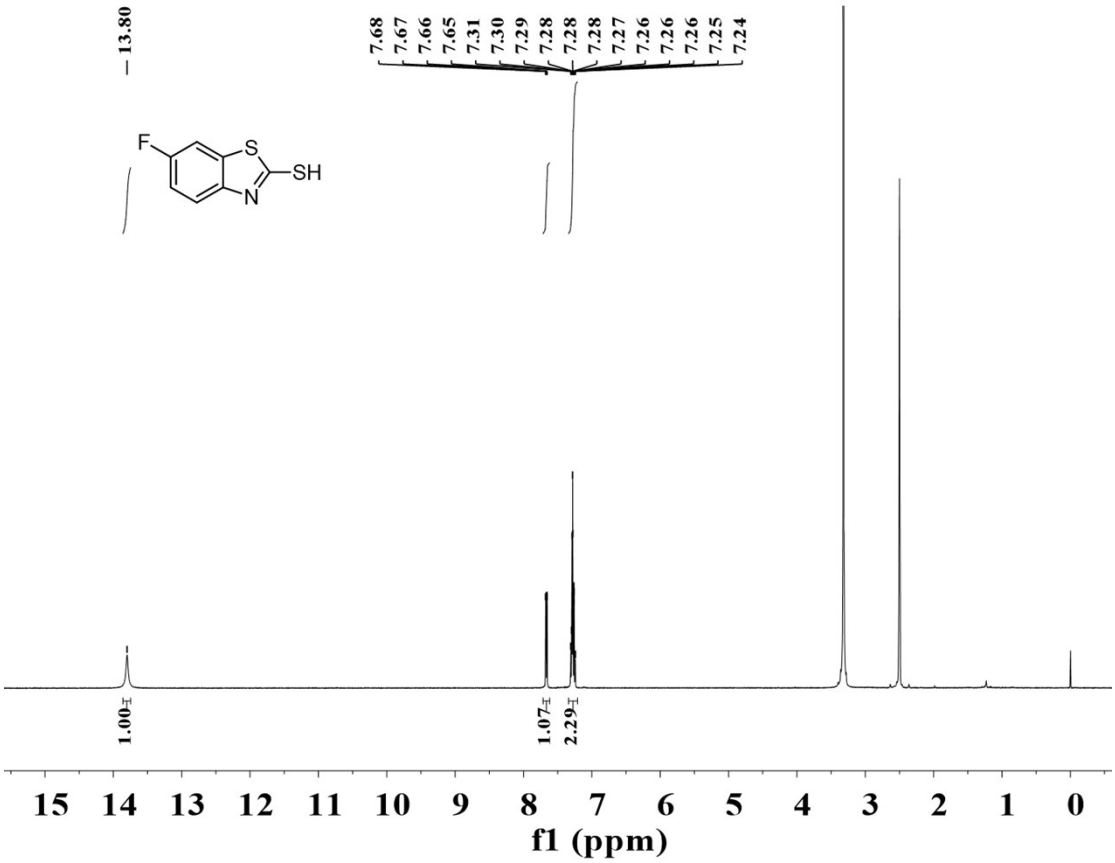
^{1}H NMR spectrum of compound **2b**



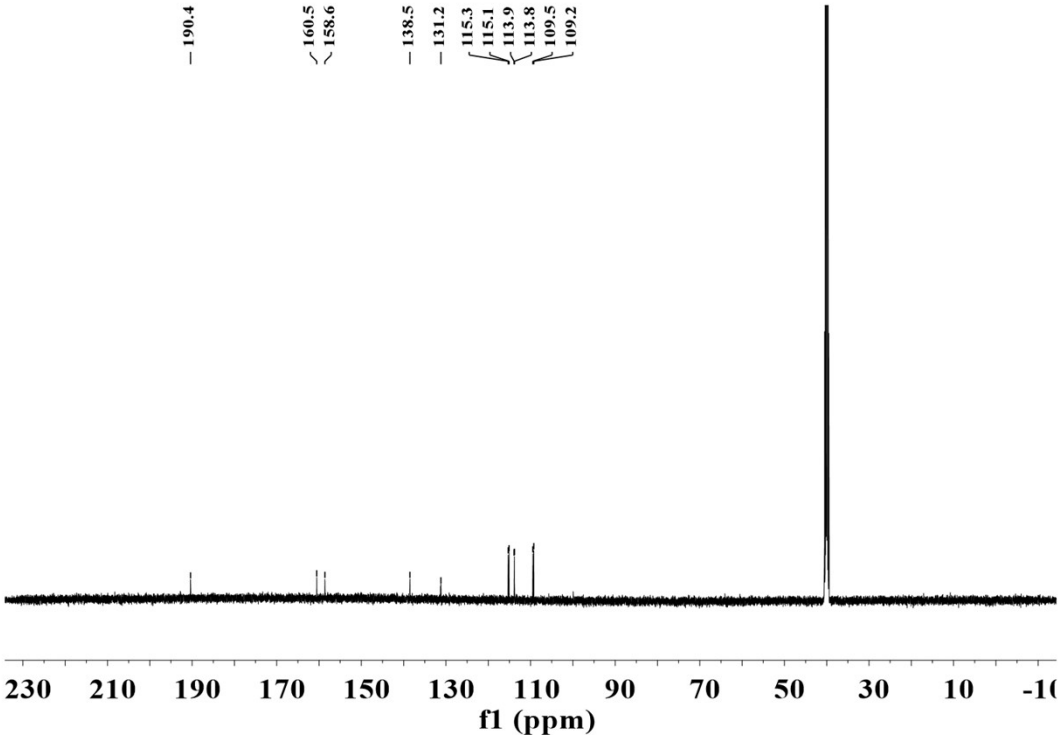
^{13}C NMR spectrum of compound **2b**



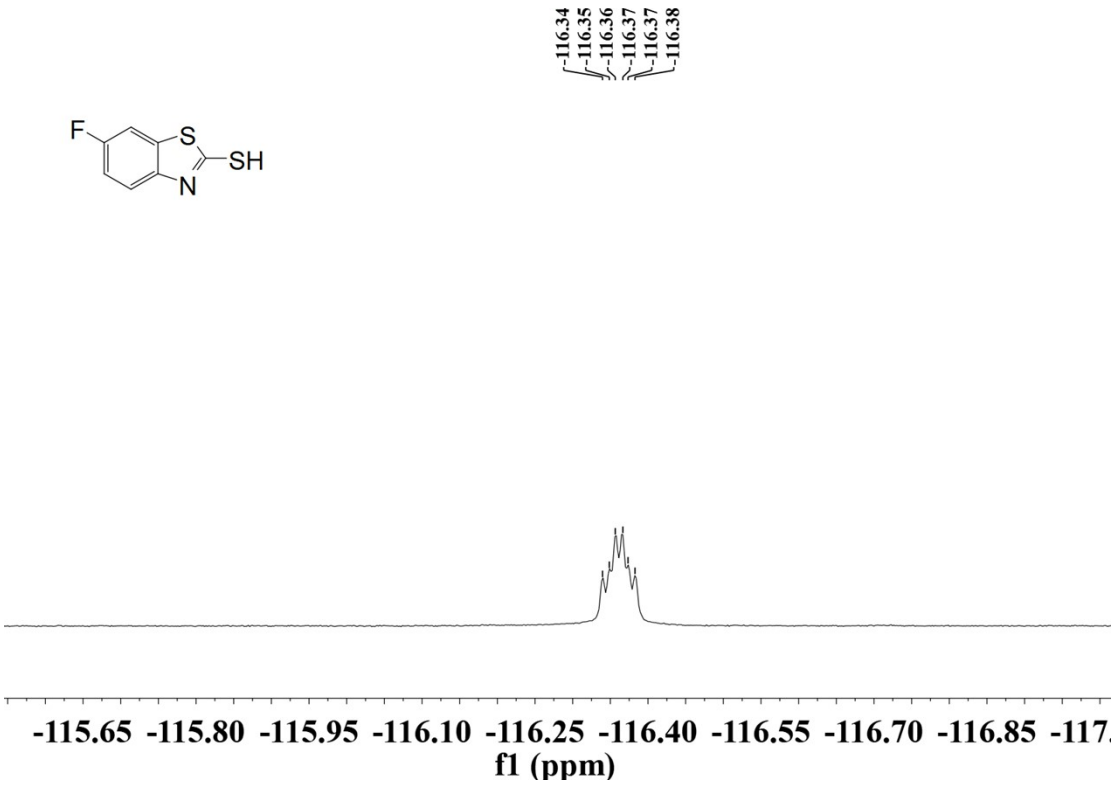
^{1}H NMR spectrum of compound **2c**



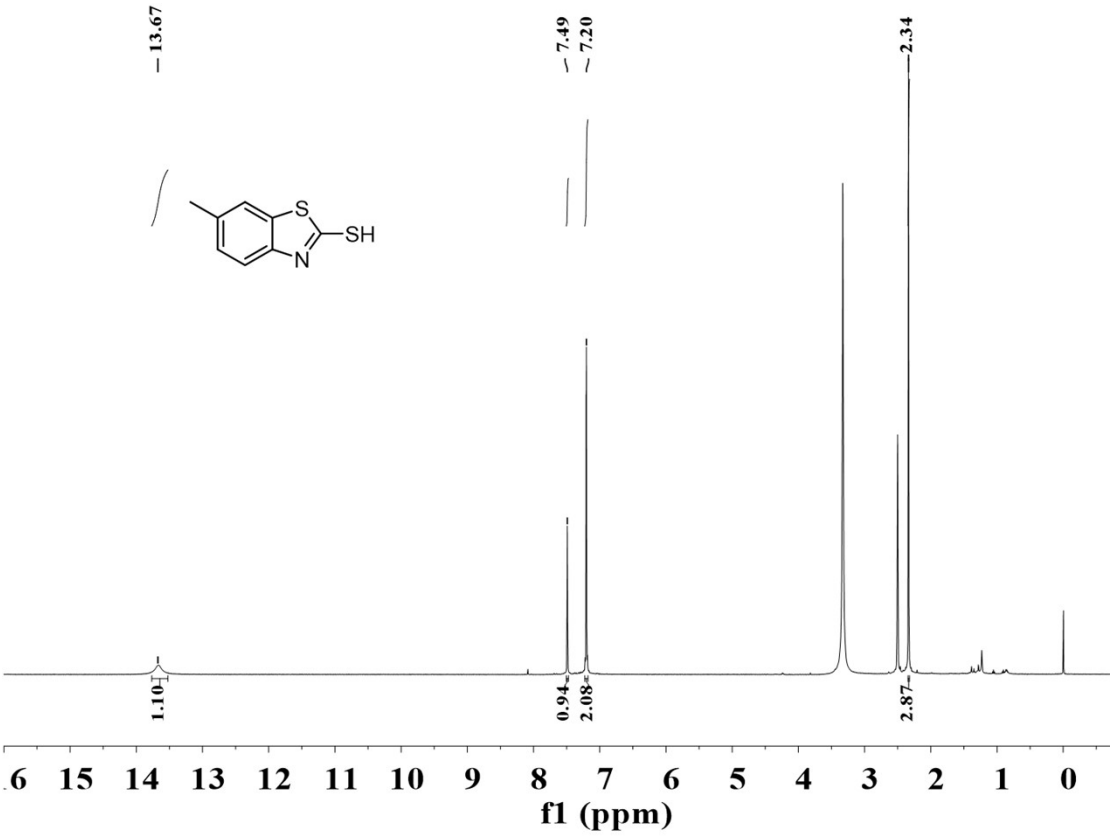
^{13}C NMR spectrum of compound **2c**



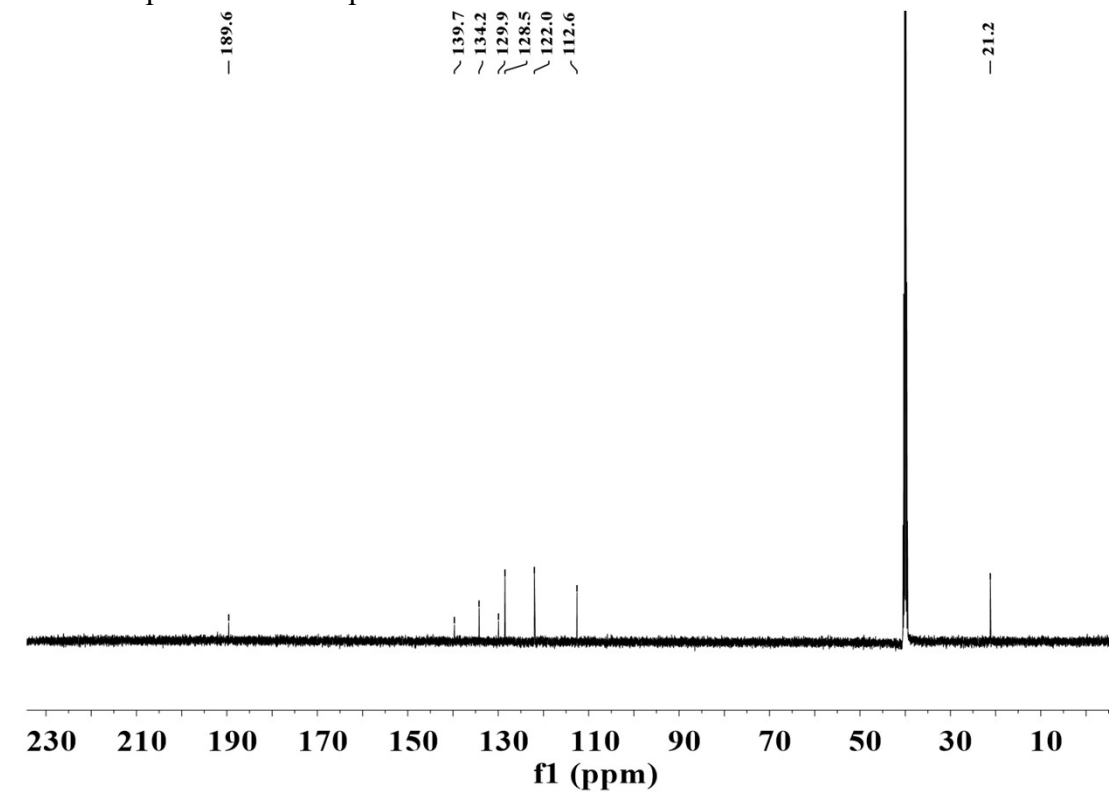
^{19}F NMR spectrum of compound **2c**



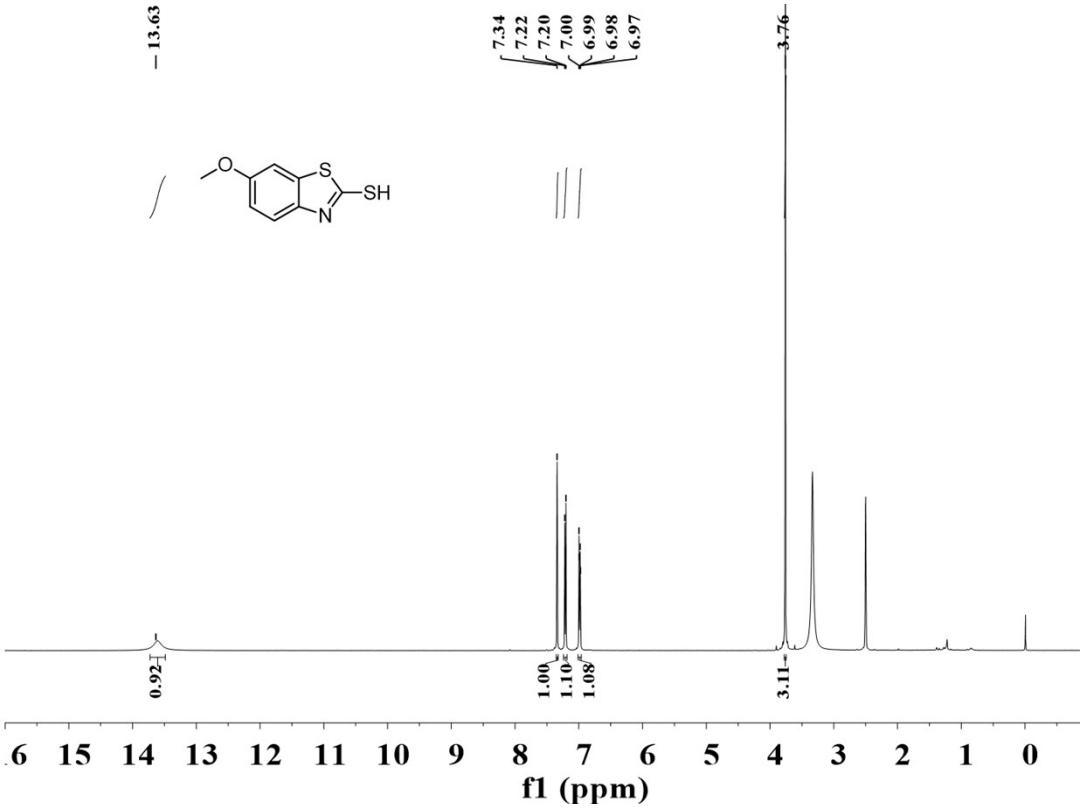
^{1}H NMR spectrum of compound **2d**



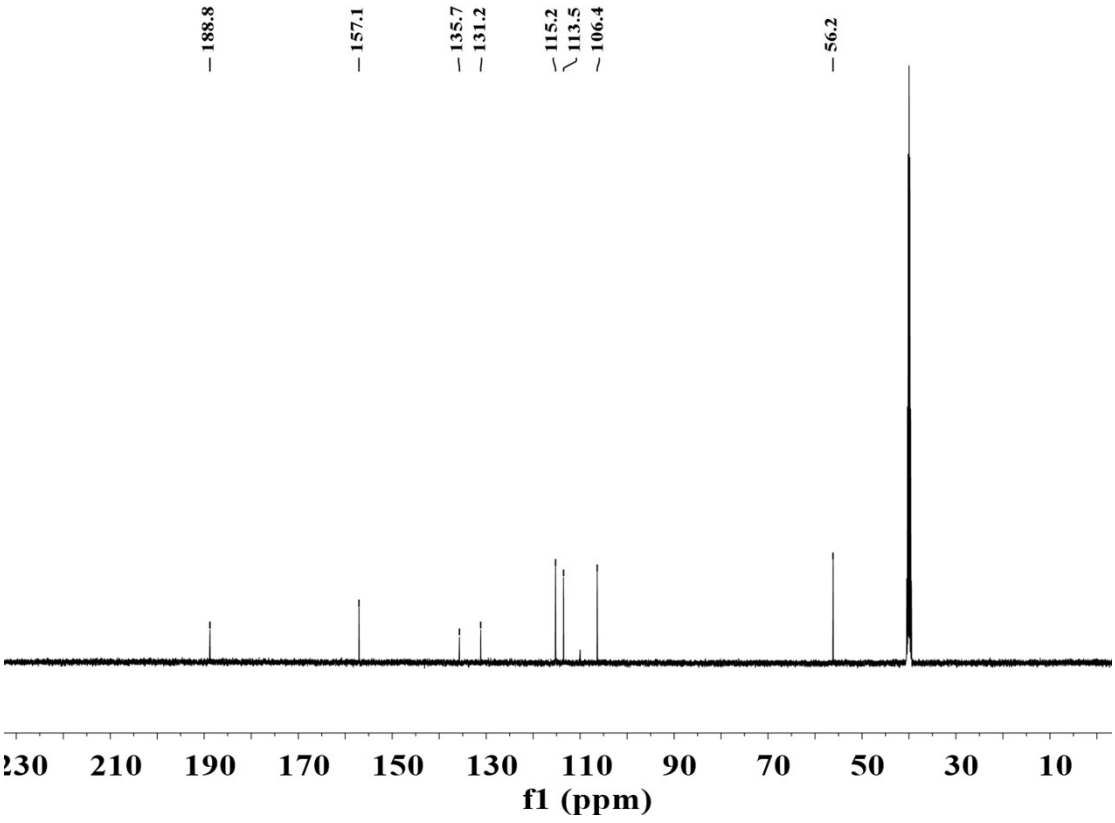
^{13}C NMR spectrum of compound **2d**



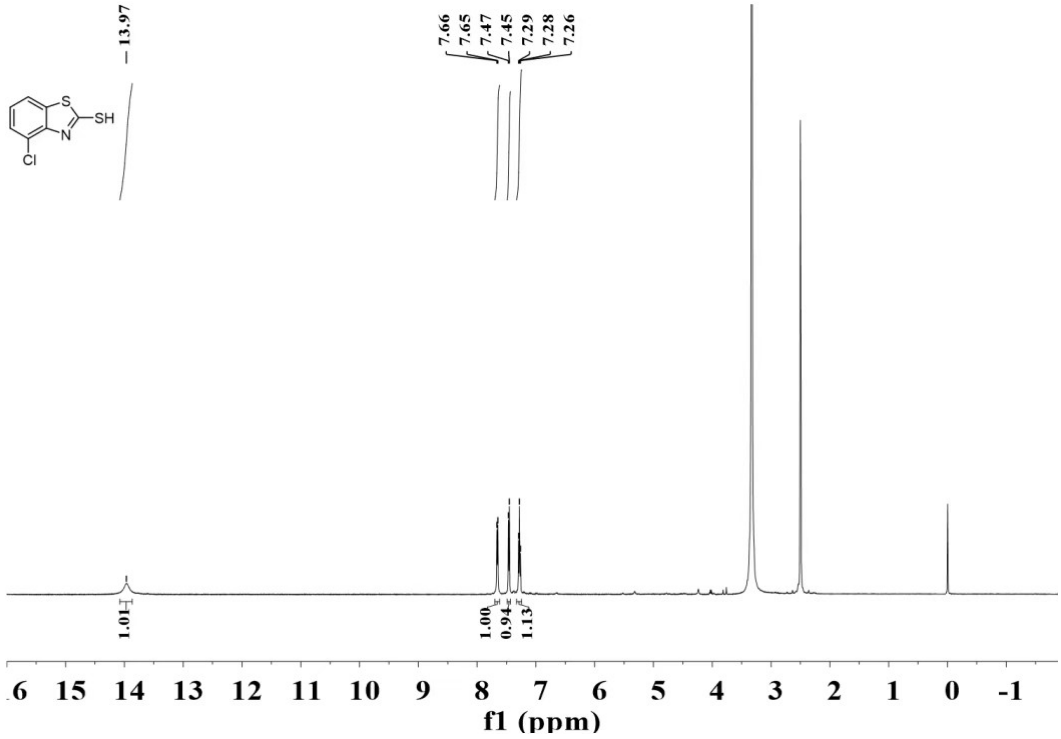
^{1}H NMR spectrum of compound **2e**



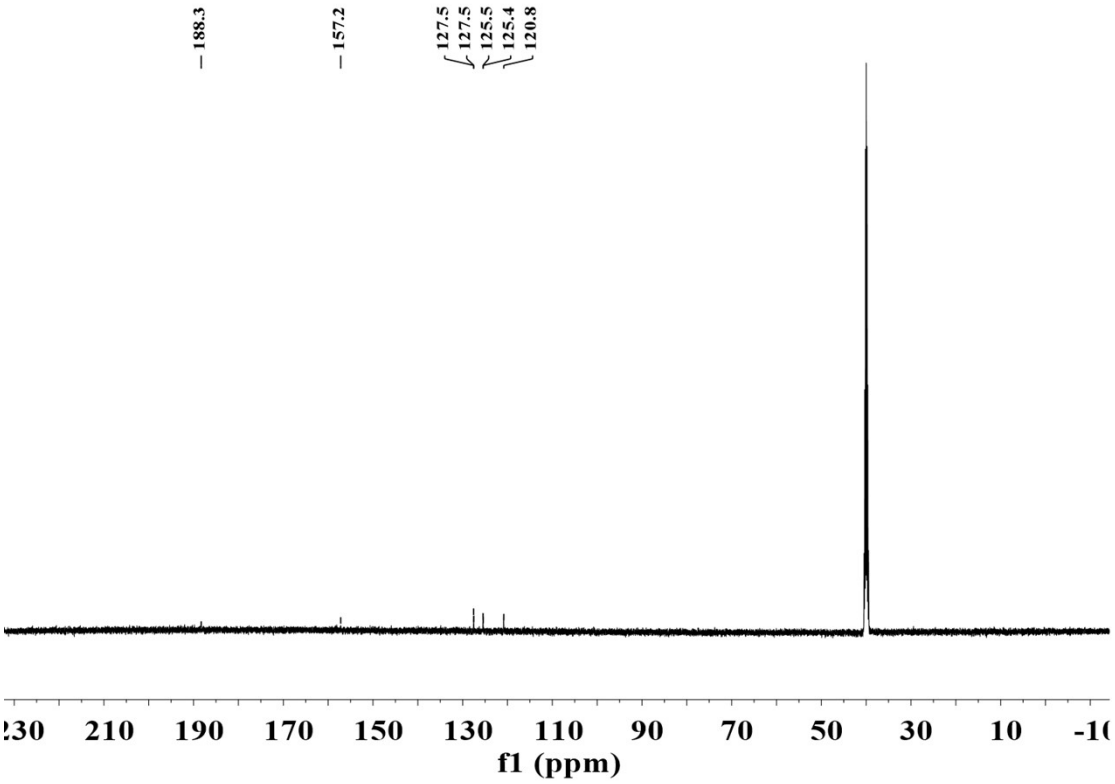
^{13}C NMR spectrum of compound **2e**



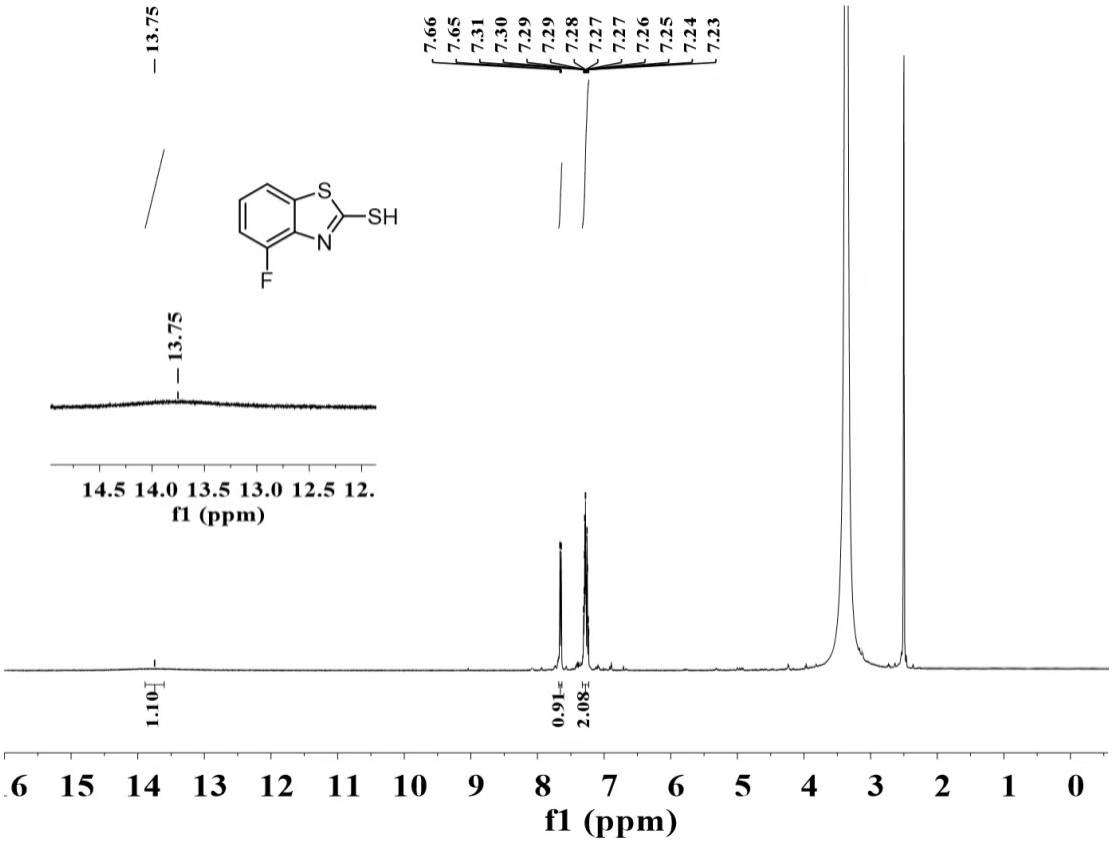
^{1}H NMR spectrum of compound **2f**



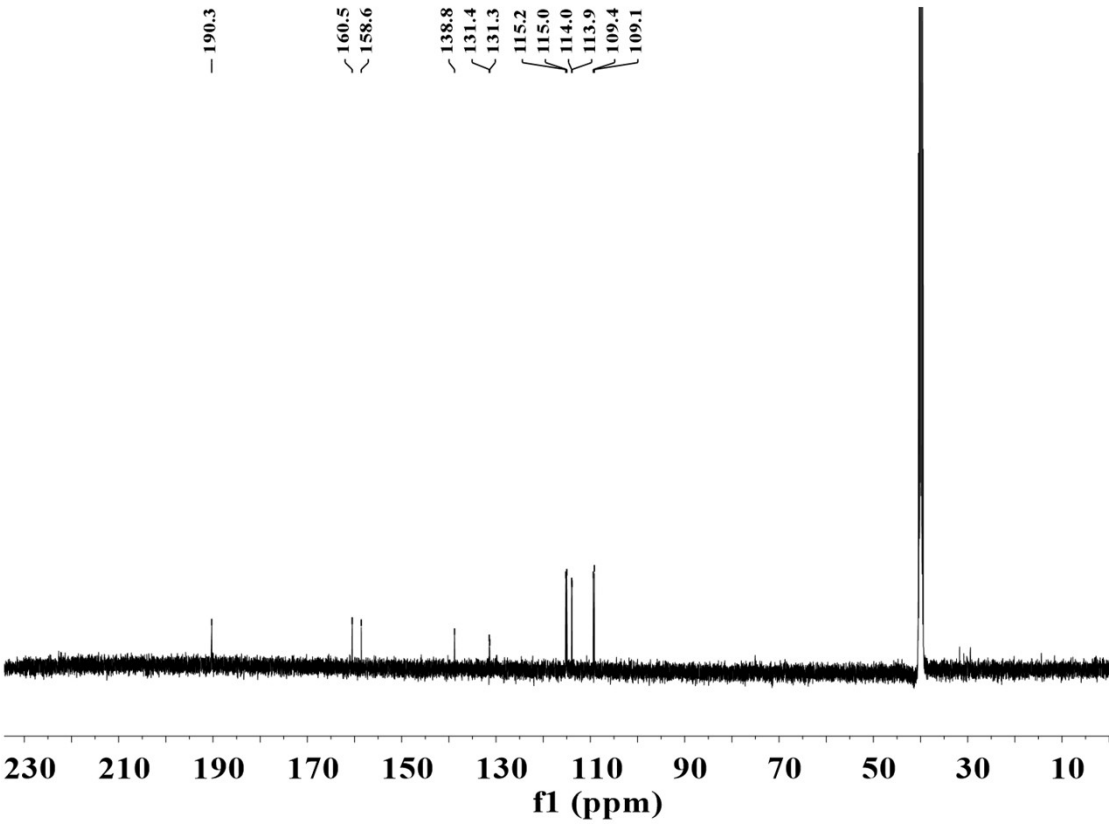
^{13}C NMR spectrum of compound **2f**



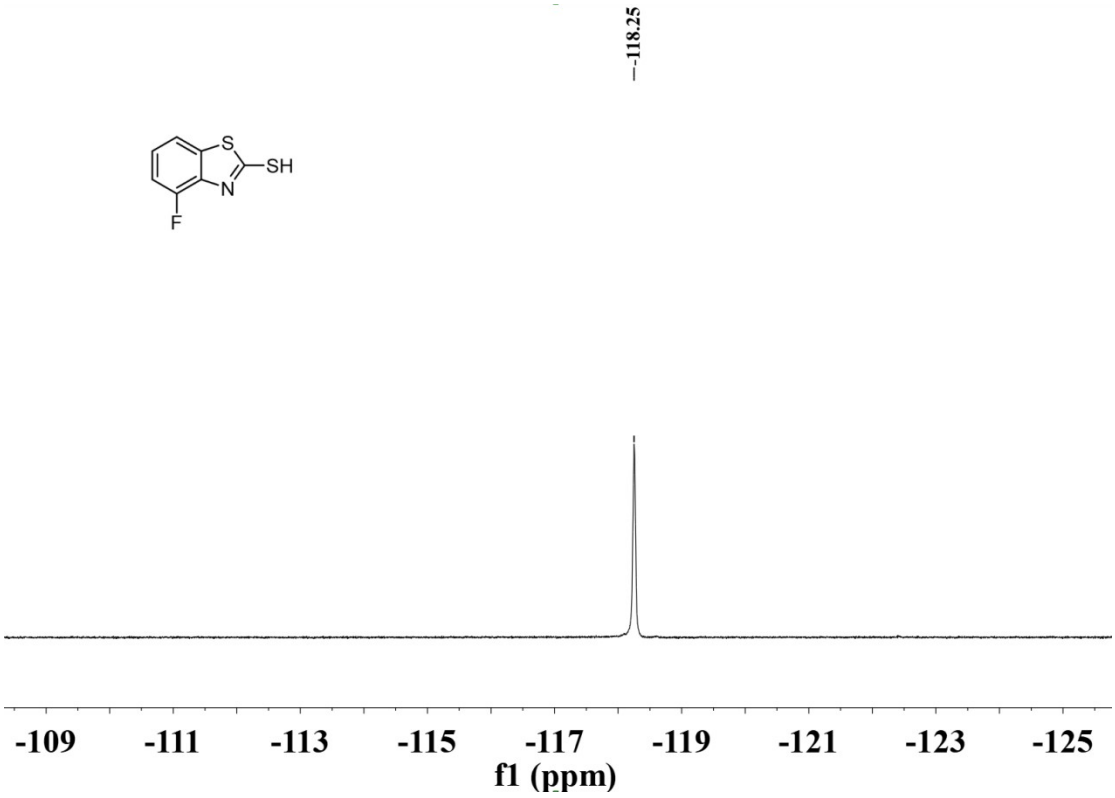
^{1}H NMR spectrum of compound **2g**



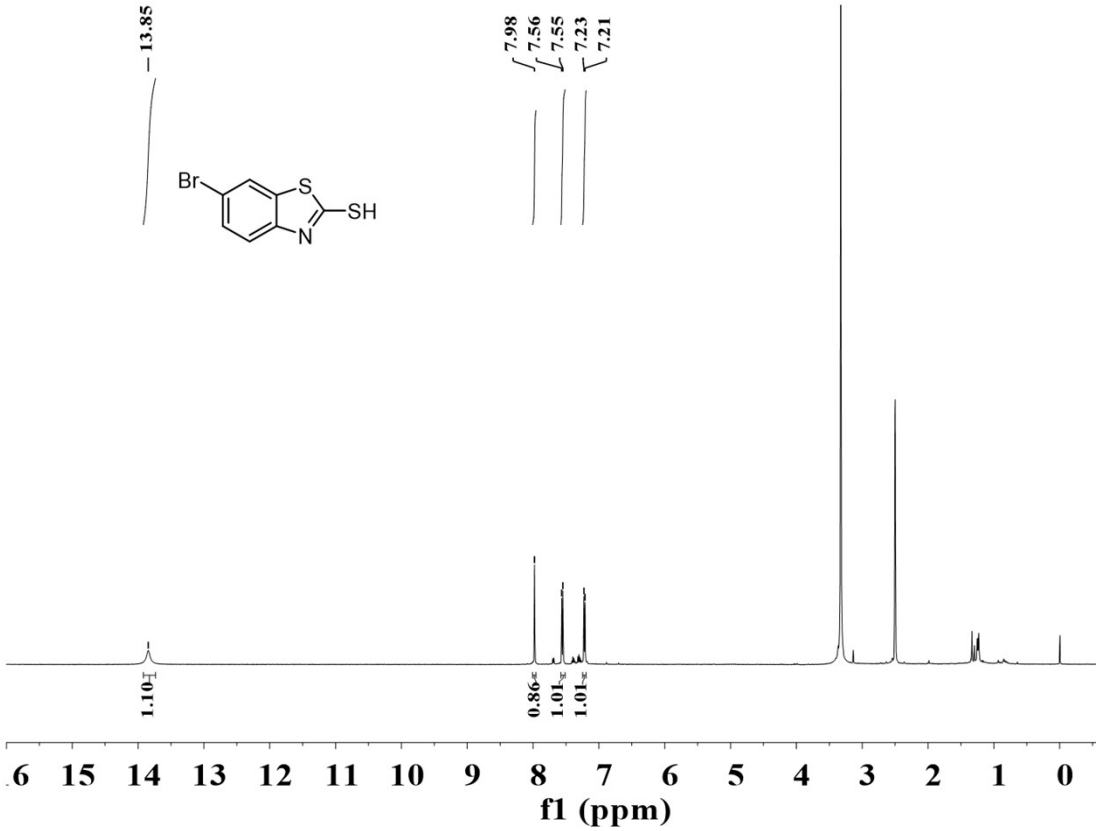
^{13}C NMR spectrum of compound **2g**



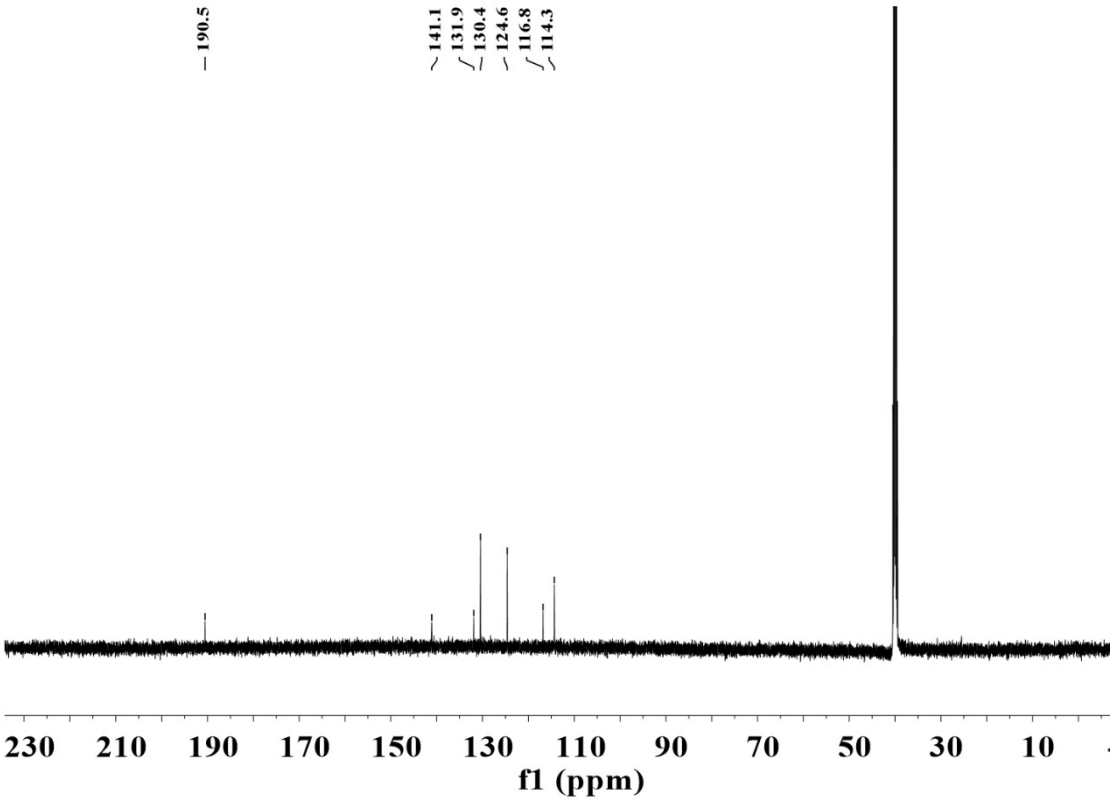
^{19}F NMR spectrum of compound **2g**



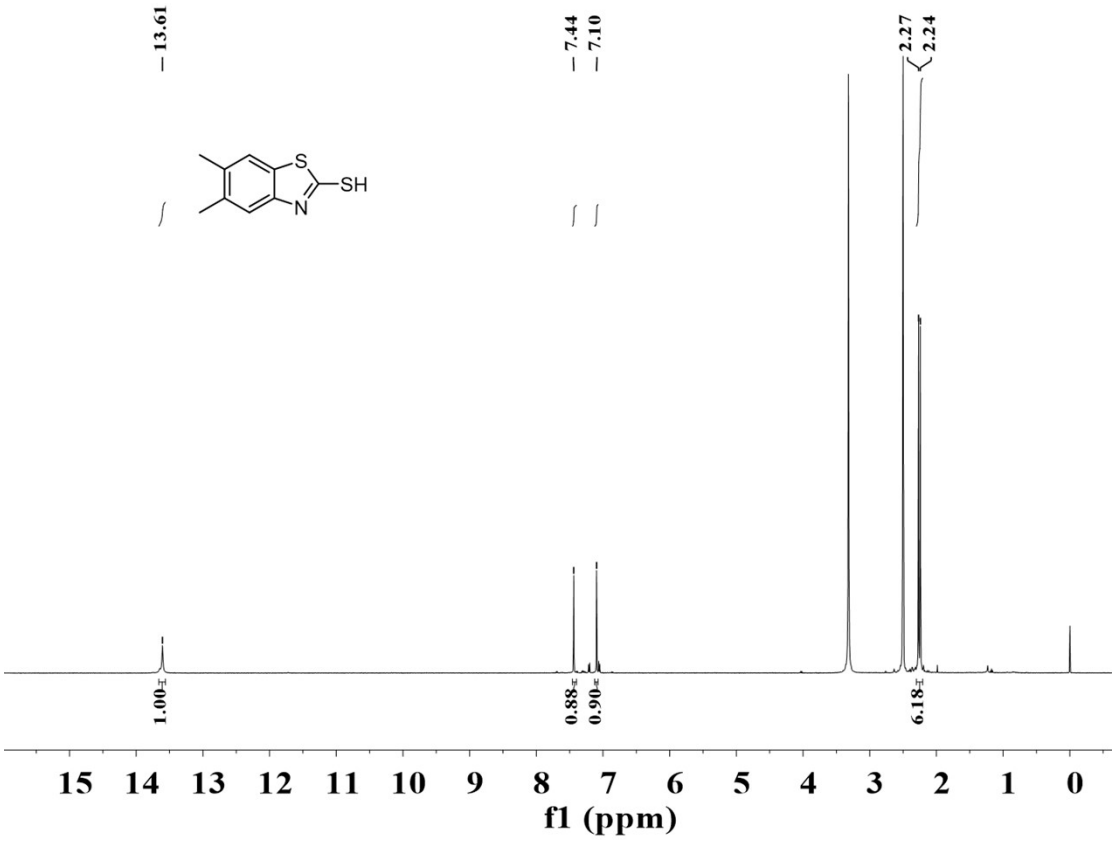
^{1}H NMR spectrum of compound **2h**



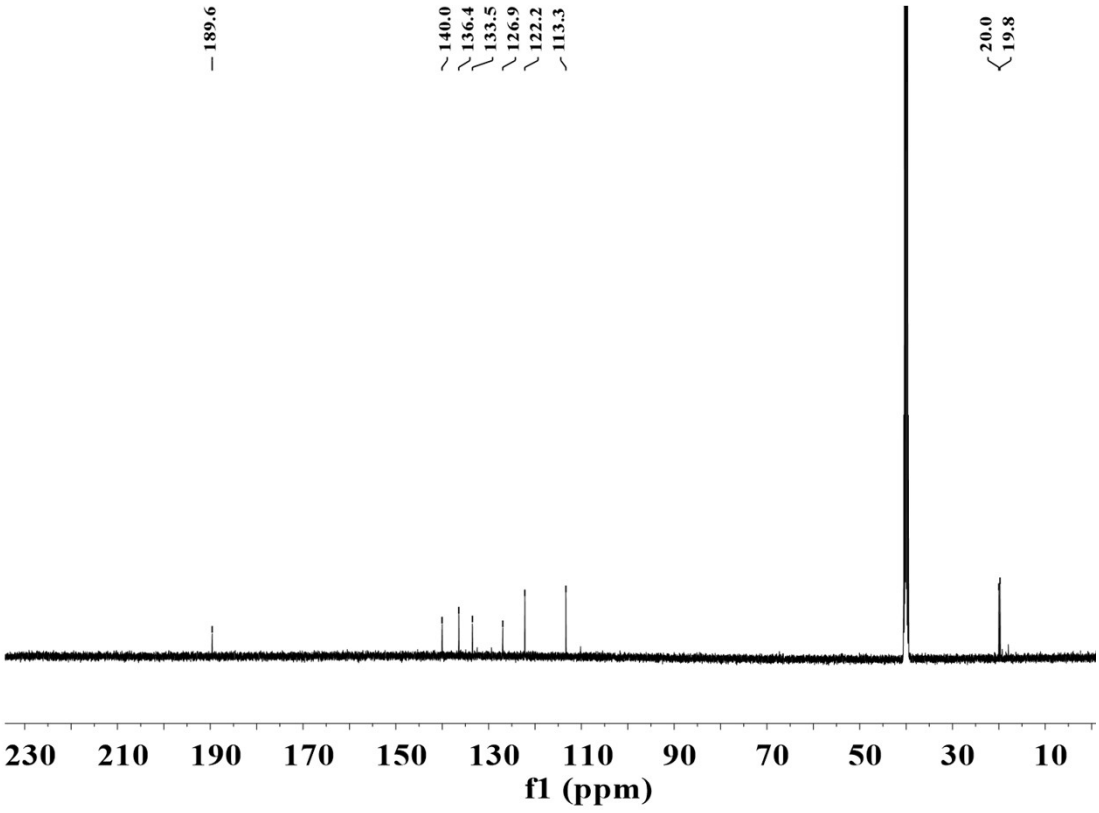
^{13}C NMR spectrum of compound **2h**



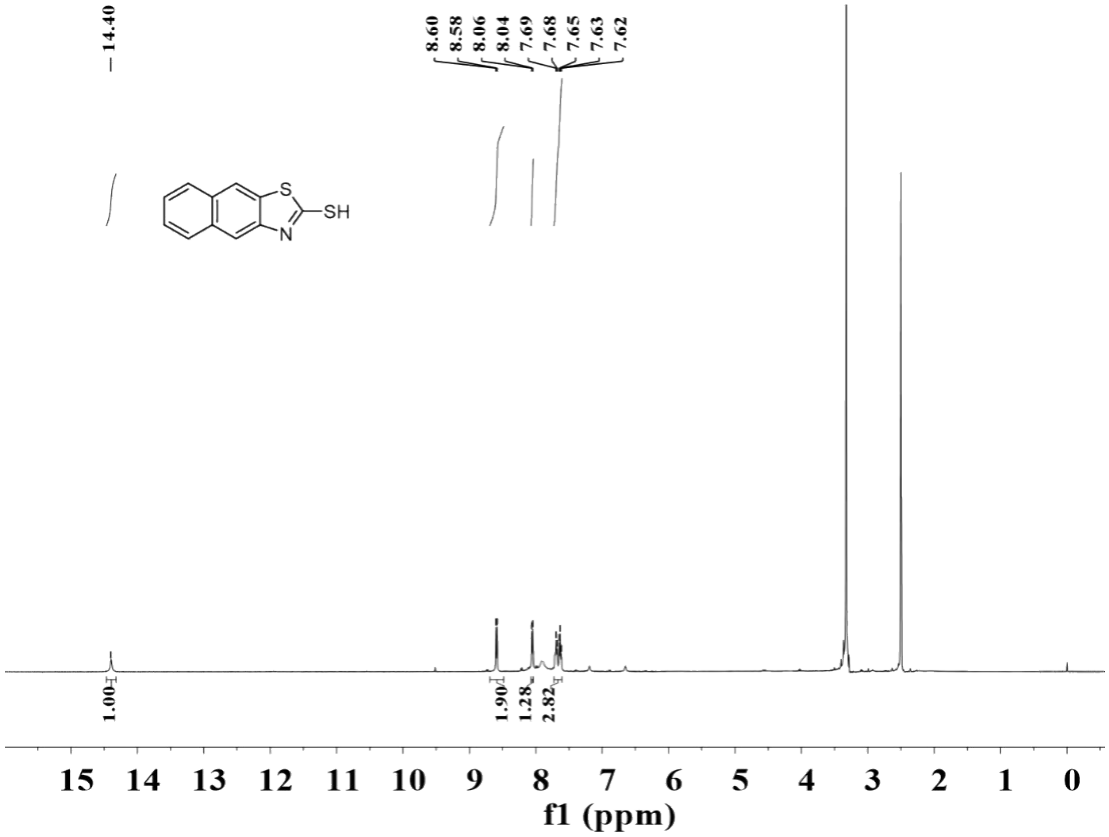
^{1}H NMR spectrum of compound **2i**



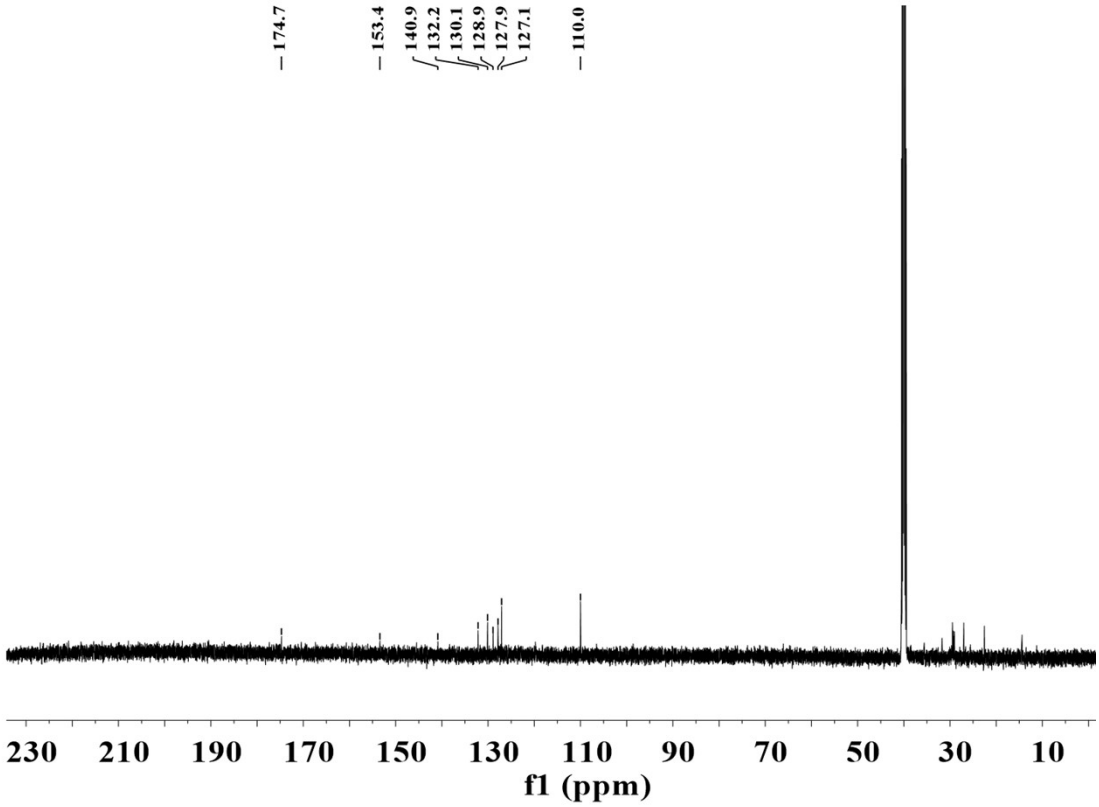
^{13}C NMR spectrum of compound **2i**



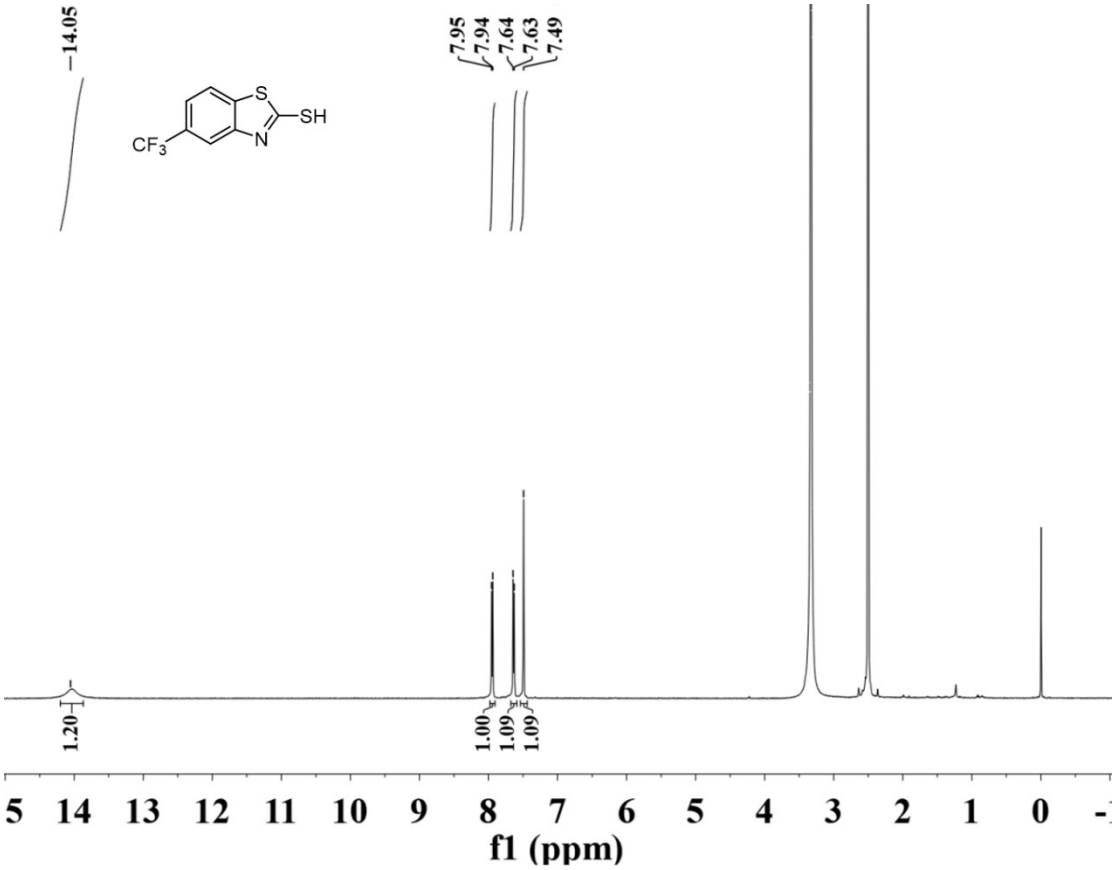
^{1}H NMR spectrum of compound **2j**



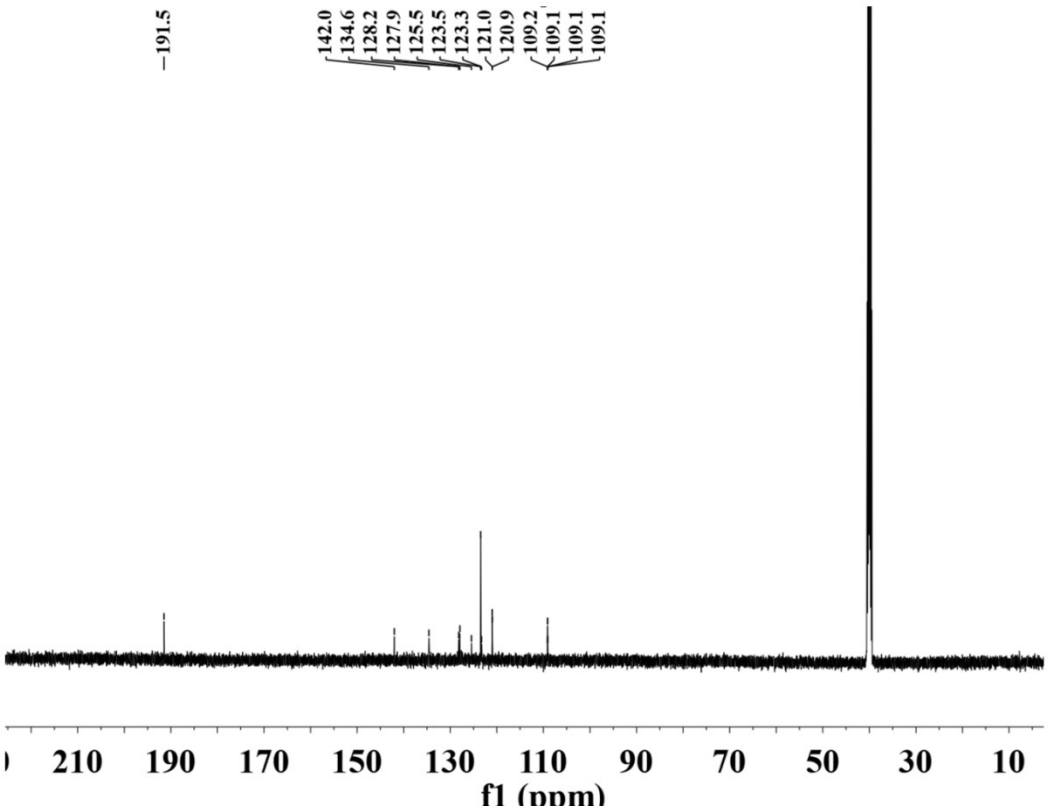
^{13}C NMR spectrum of compound **2j**



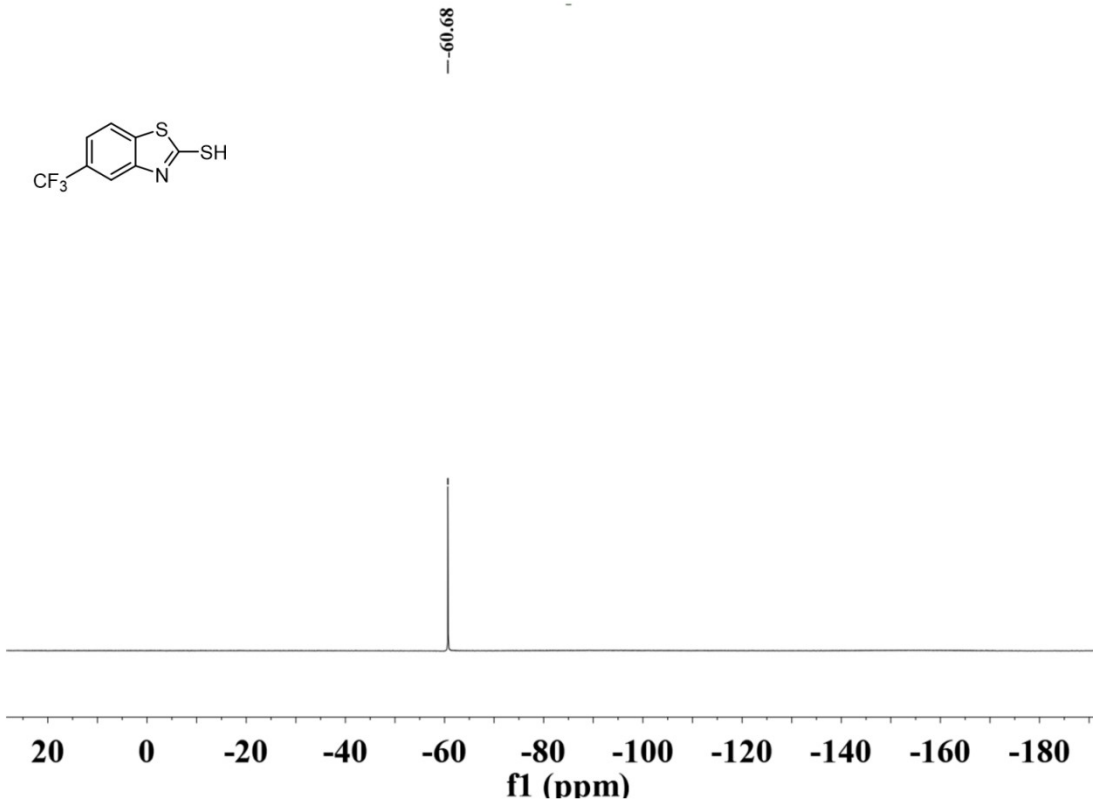
^{1}H NMR spectrum of compound **2k**



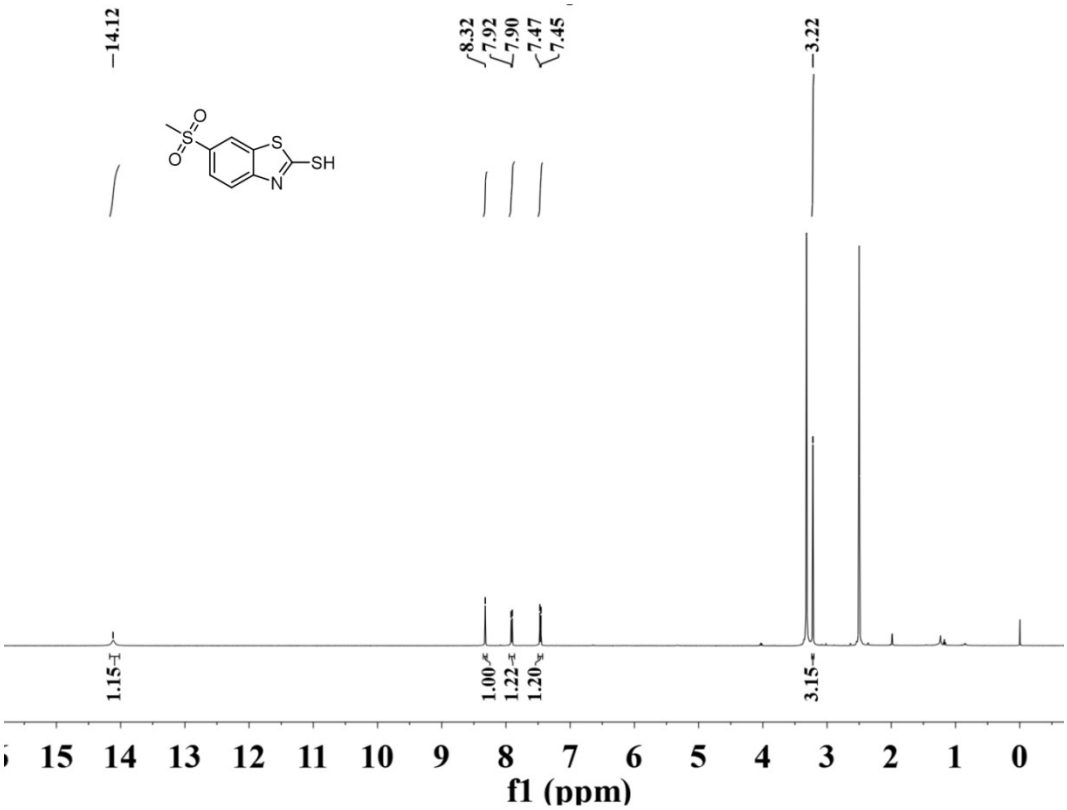
^{13}C NMR spectrum of compound **2k**



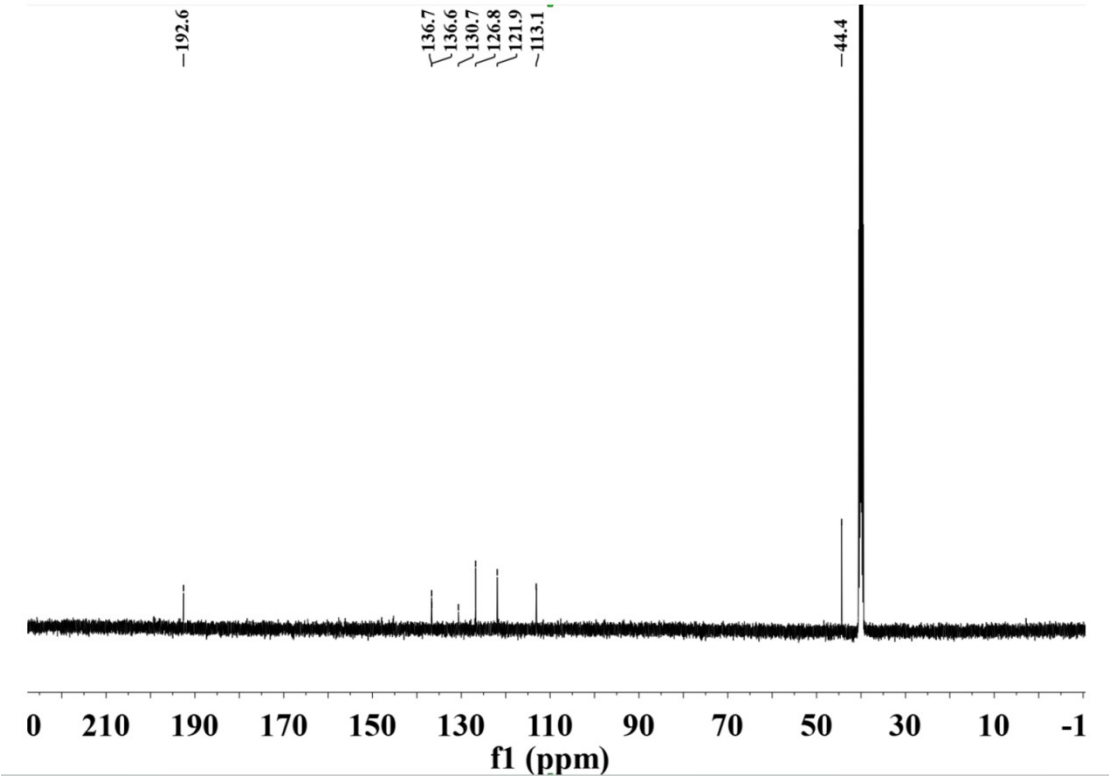
^{19}F NMR spectrum of compound **2k**



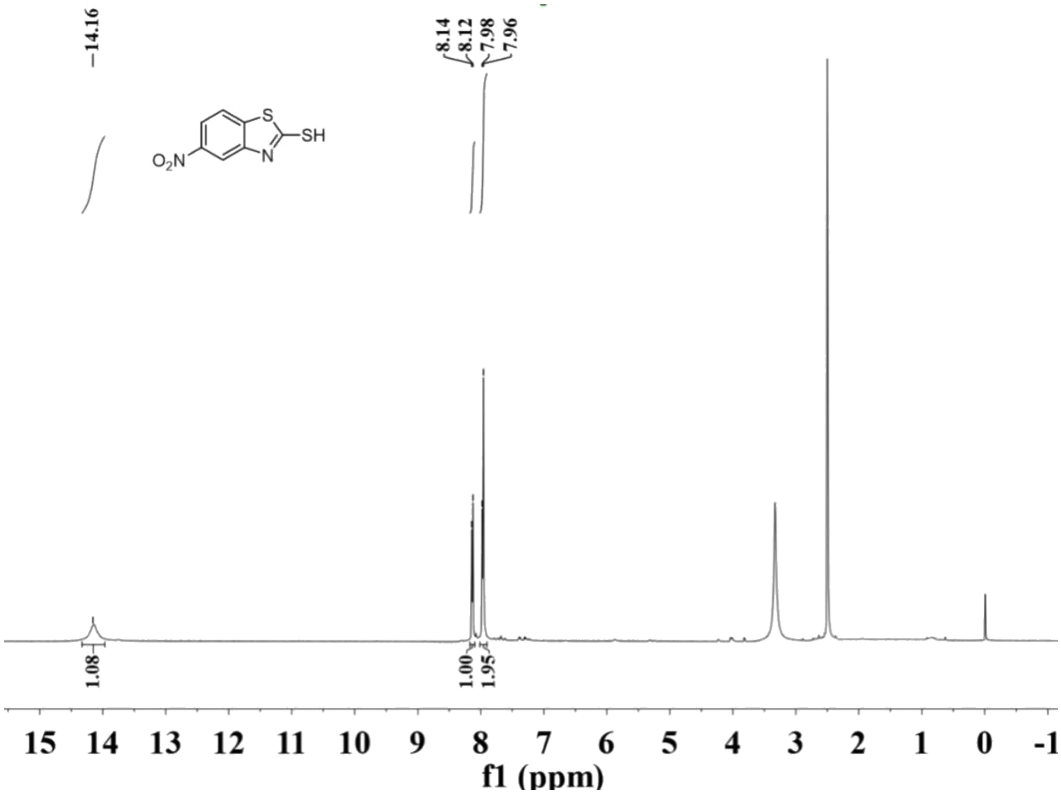
^{1}H NMR spectrum of compound **2l**



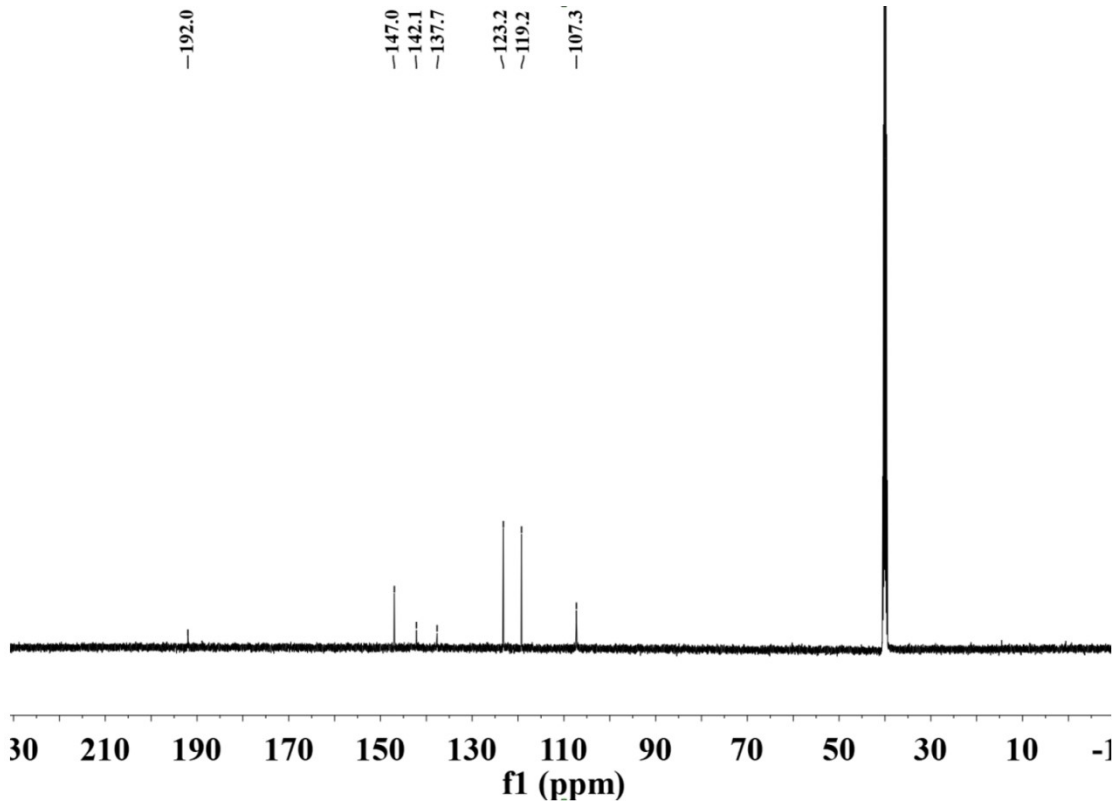
^{13}C NMR spectrum of compound **2l**



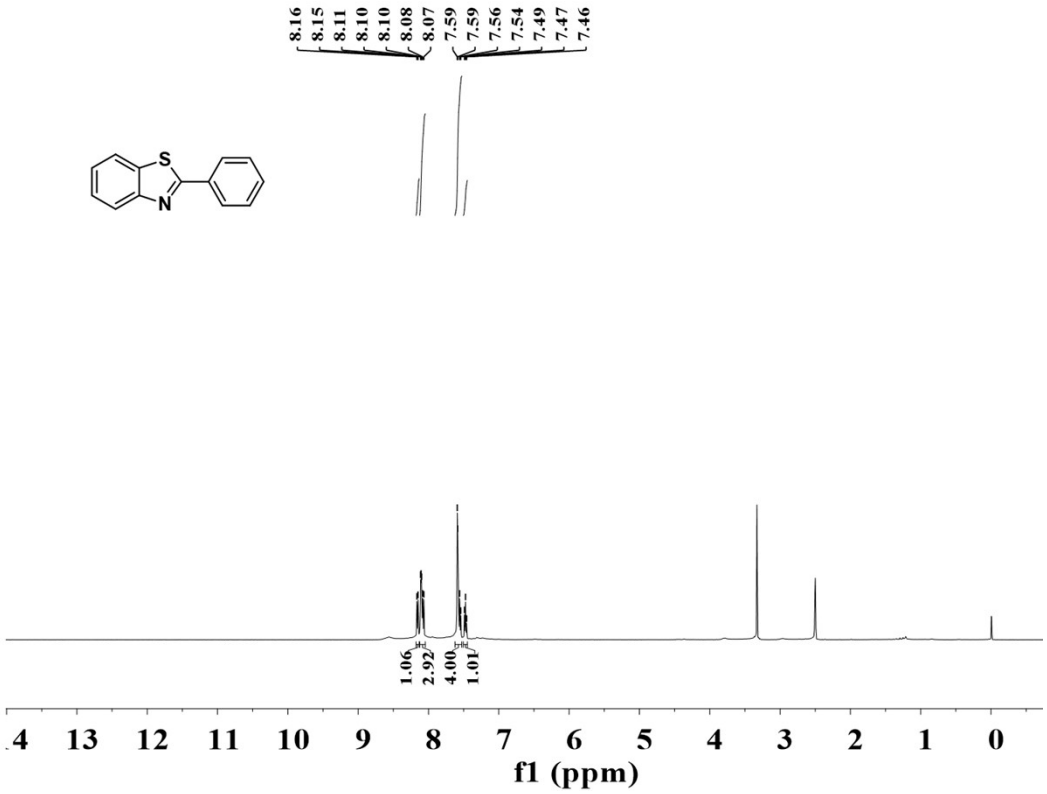
^{1}H NMR spectrum of compound **2m**



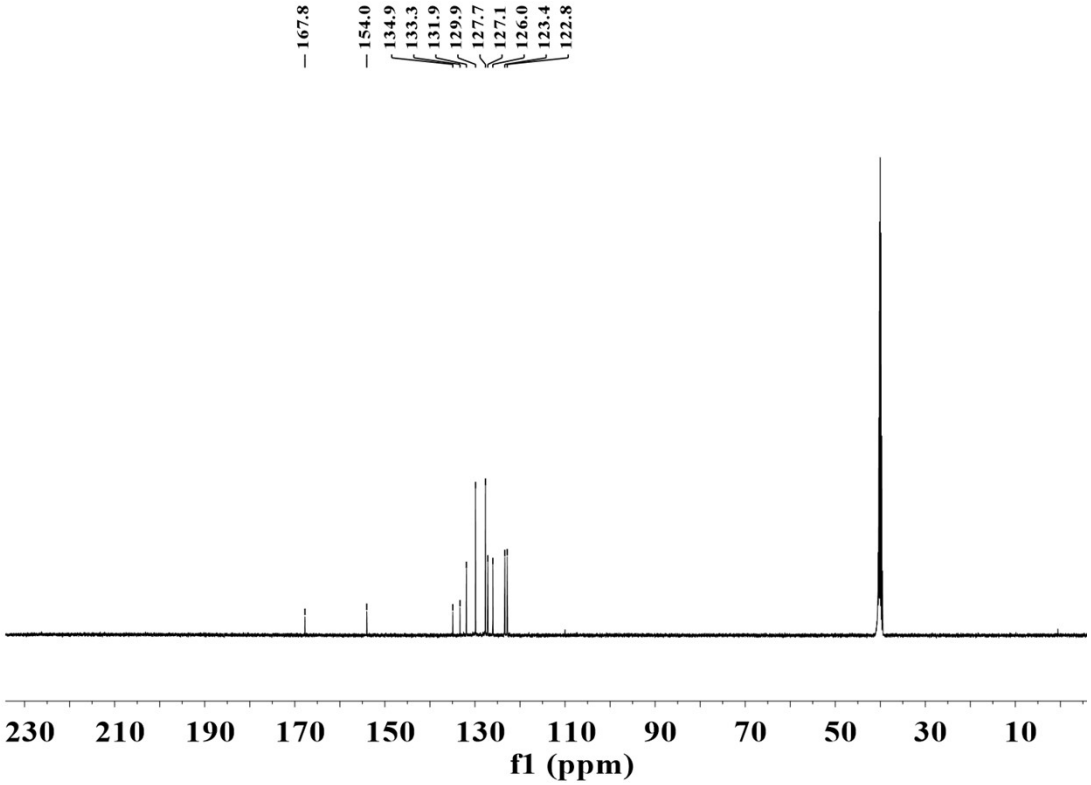
^{13}C NMR spectrum of compound **2m**



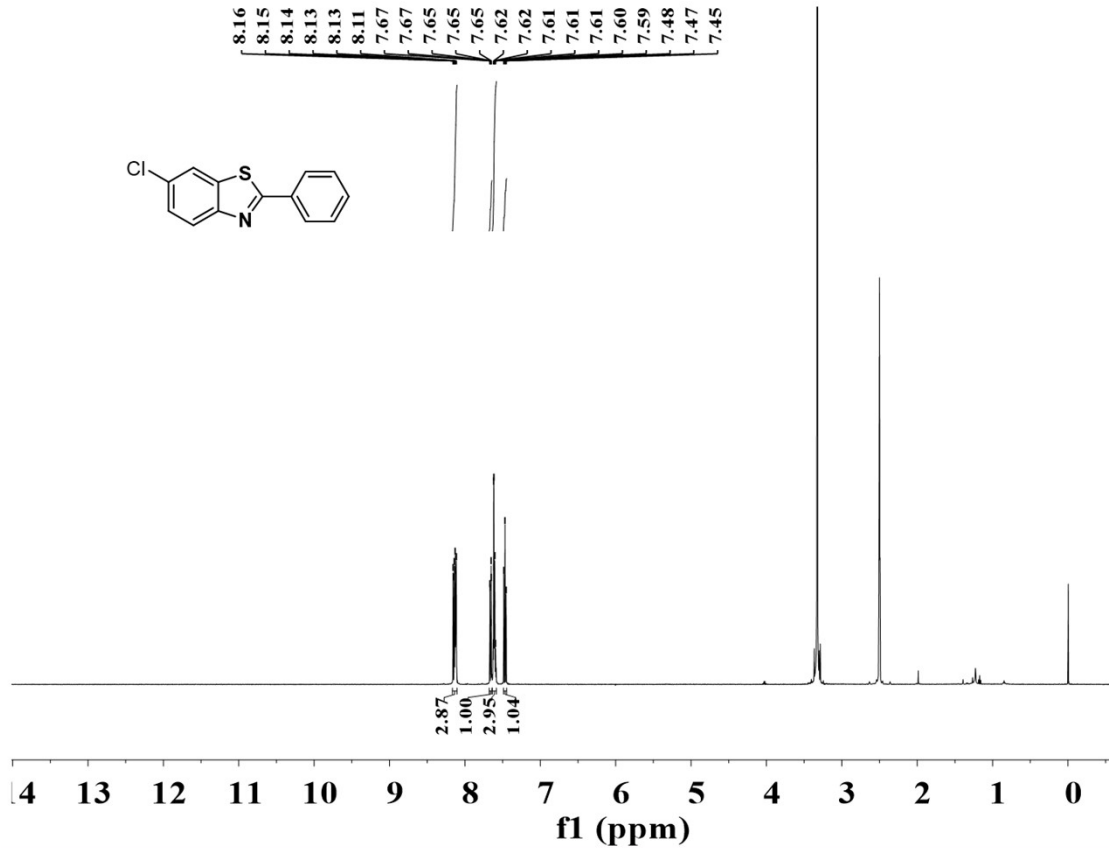
^{1}H NMR spectrum of compound **4a**



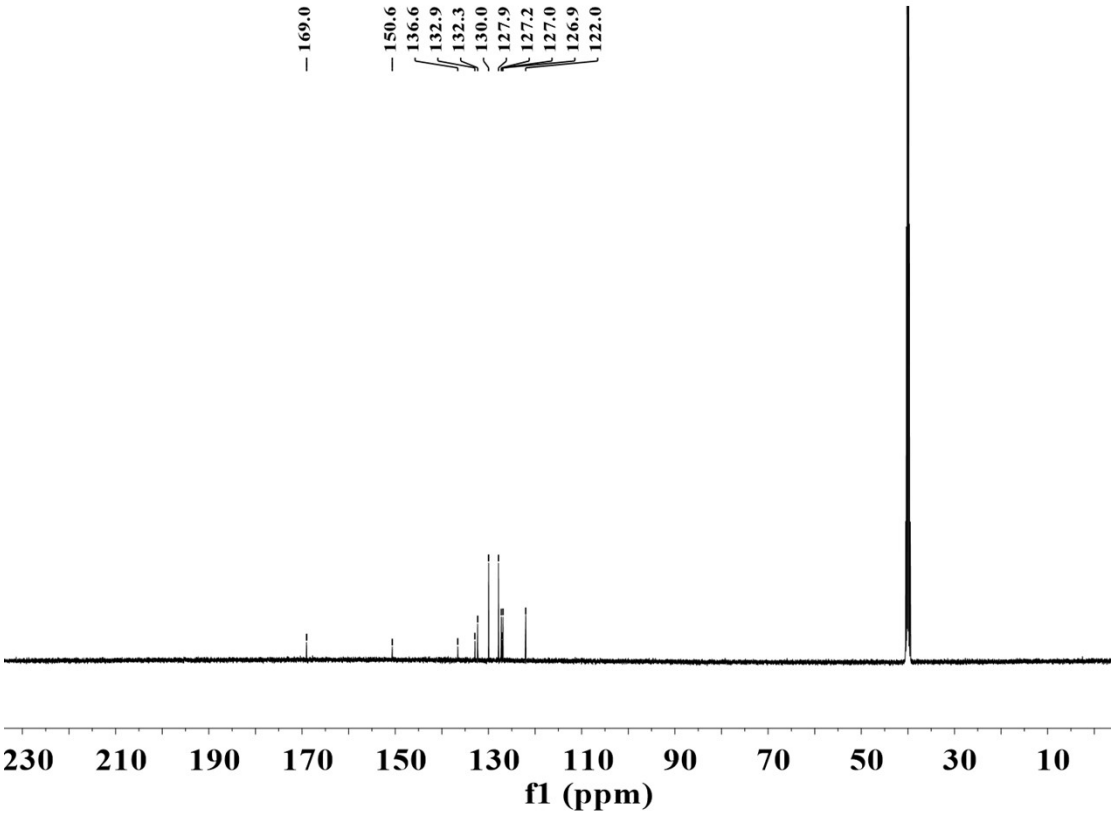
^{13}C NMR spectrum of compound **4a**



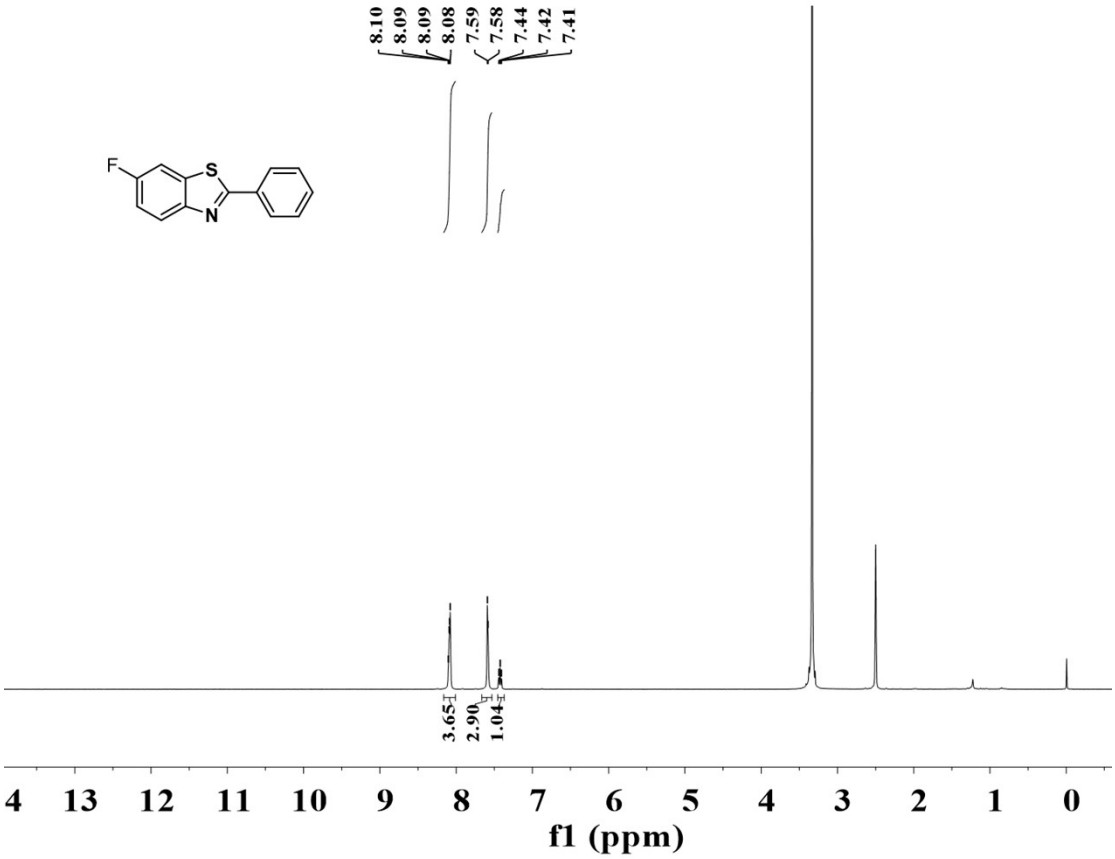
^{1}H NMR spectrum of compound **4b**



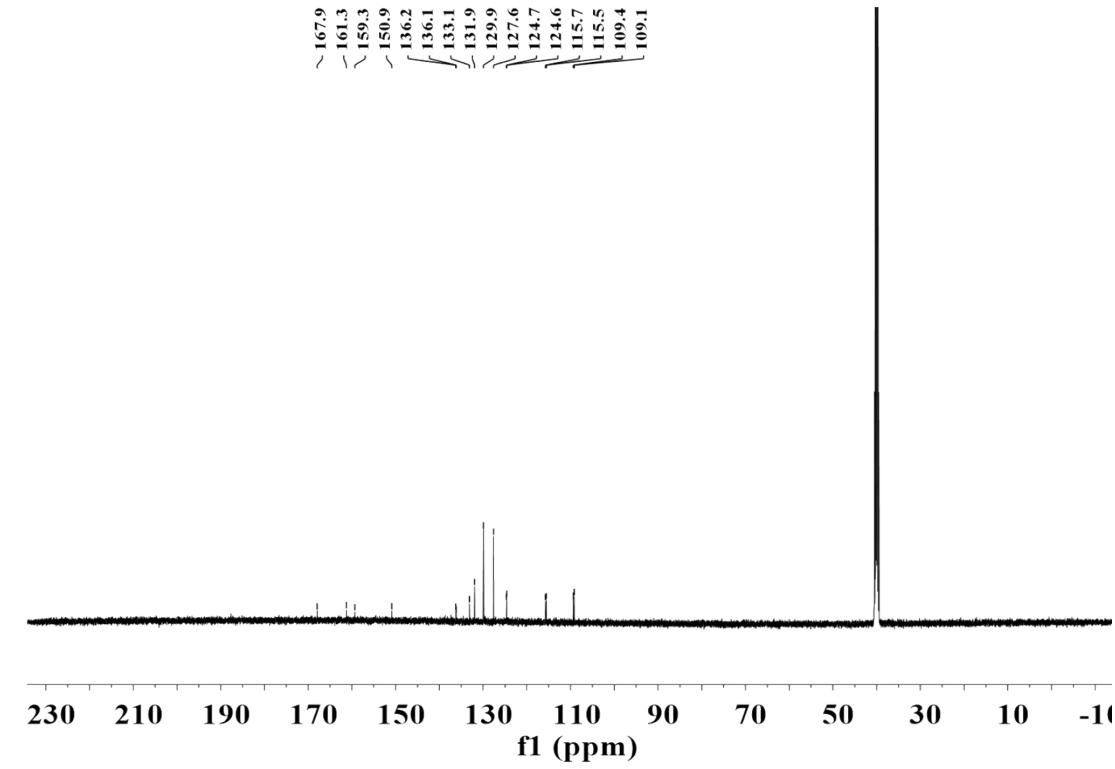
^{13}C NMR spectrum of compound **4b**



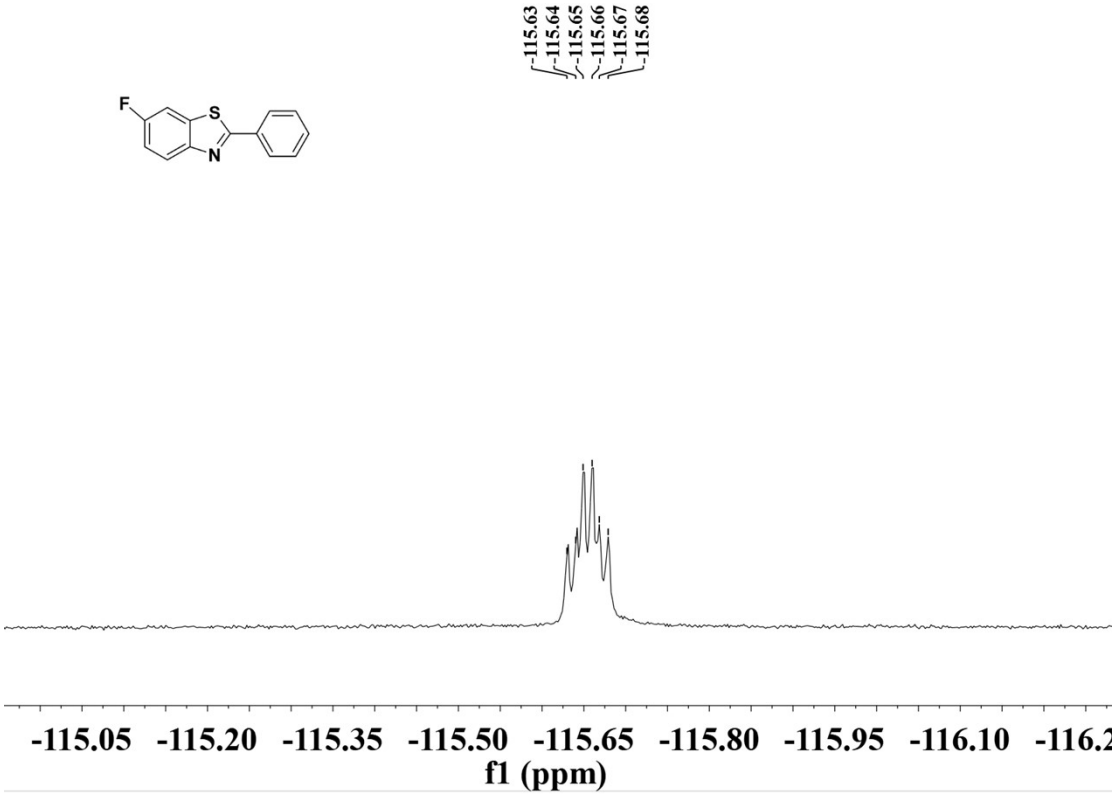
^{1}H NMR spectrum of compound **4c**



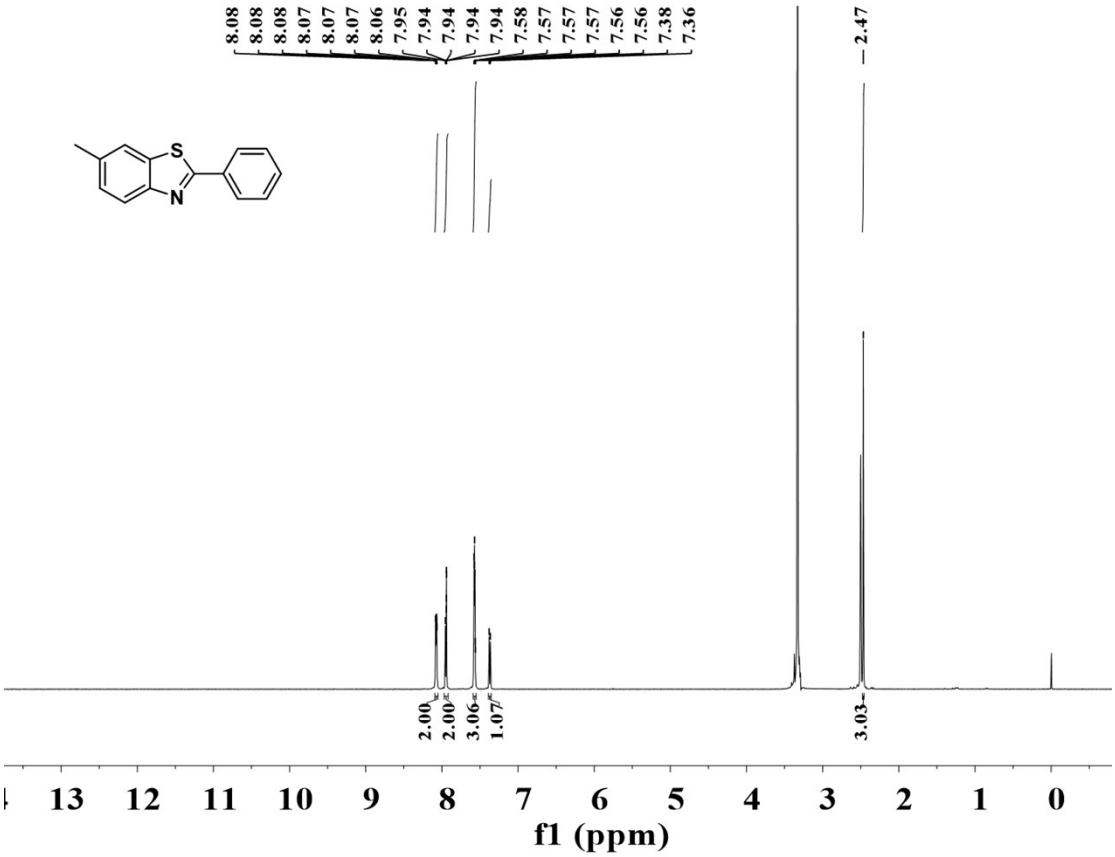
^{13}C NMR spectrum of compound **4c**



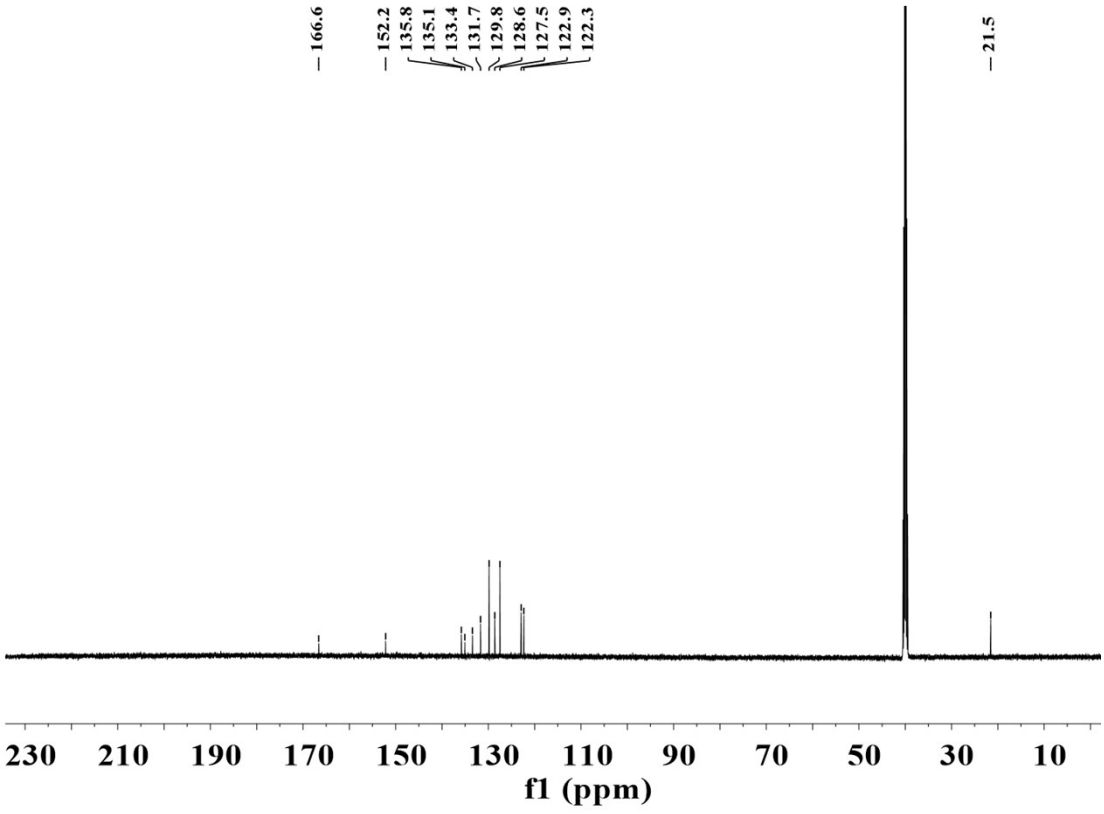
^{19}F NMR spectrum of compound **4c**



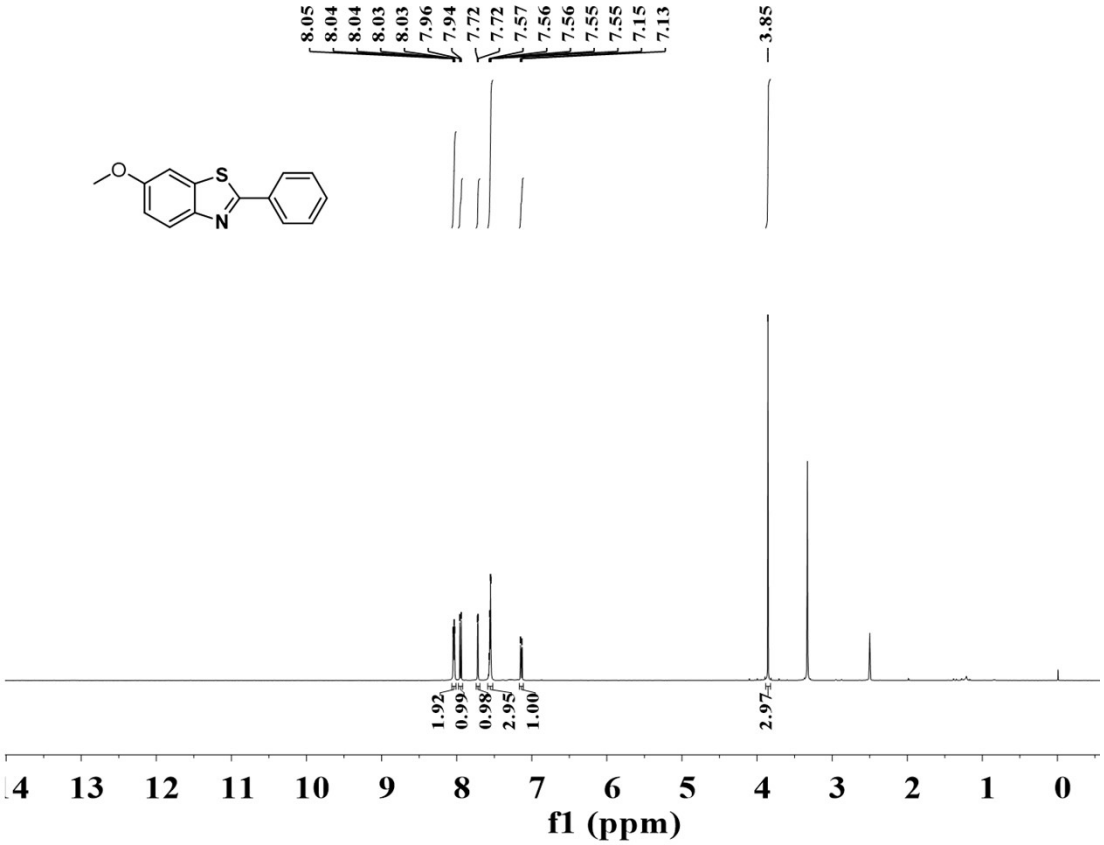
^{1}H NMR spectrum of compound **4d**



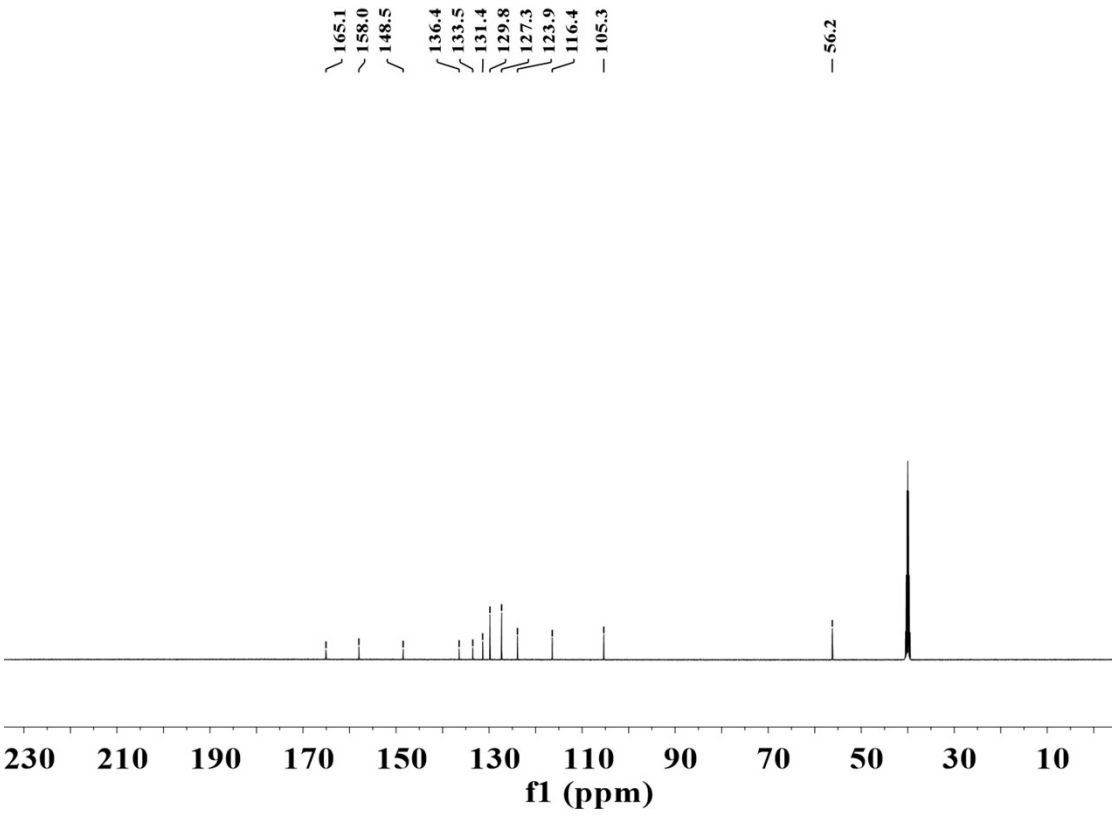
^{13}C NMR spectrum of compound **4d**



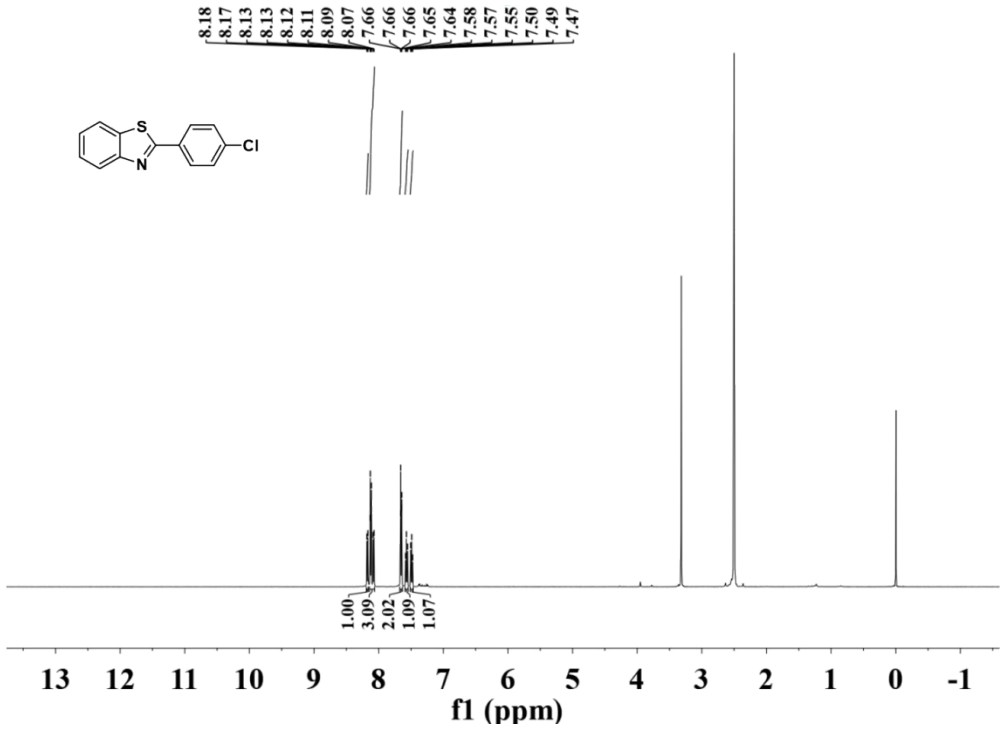
^{1}H NMR spectrum of compound **4e**



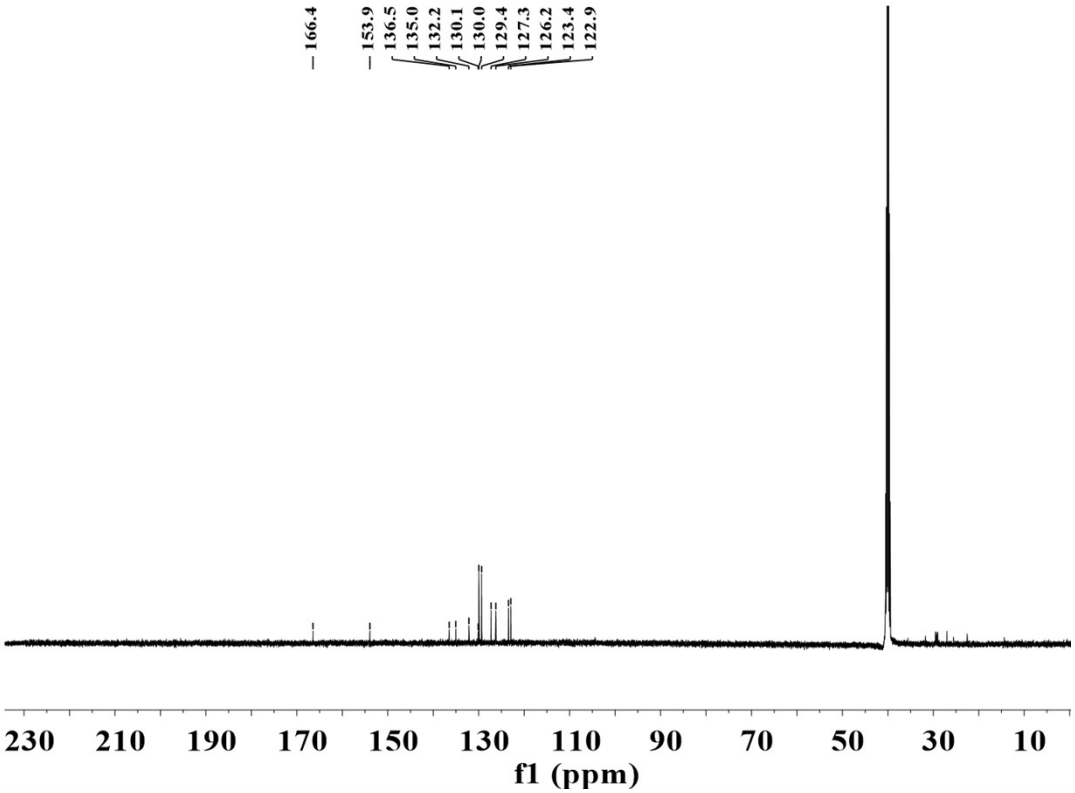
^{13}C NMR spectrum of compound **4e**



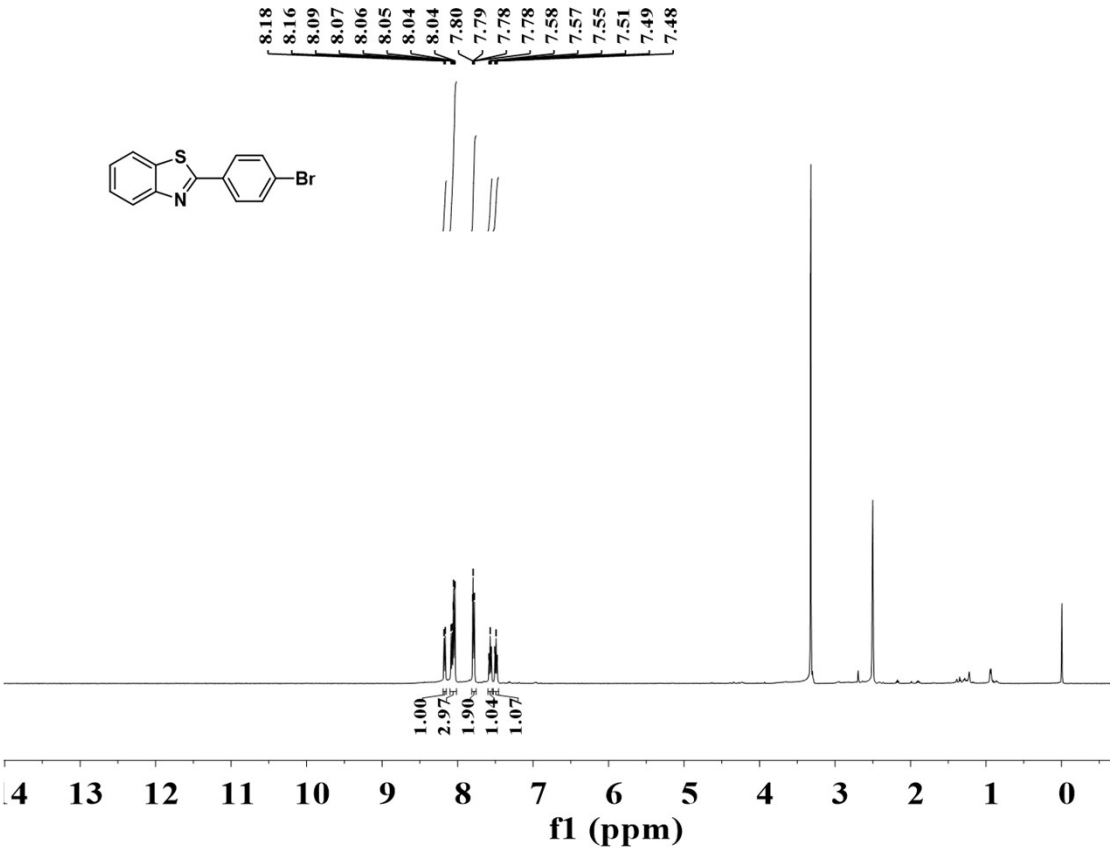
^{1}H NMR spectrum of compound **4f**



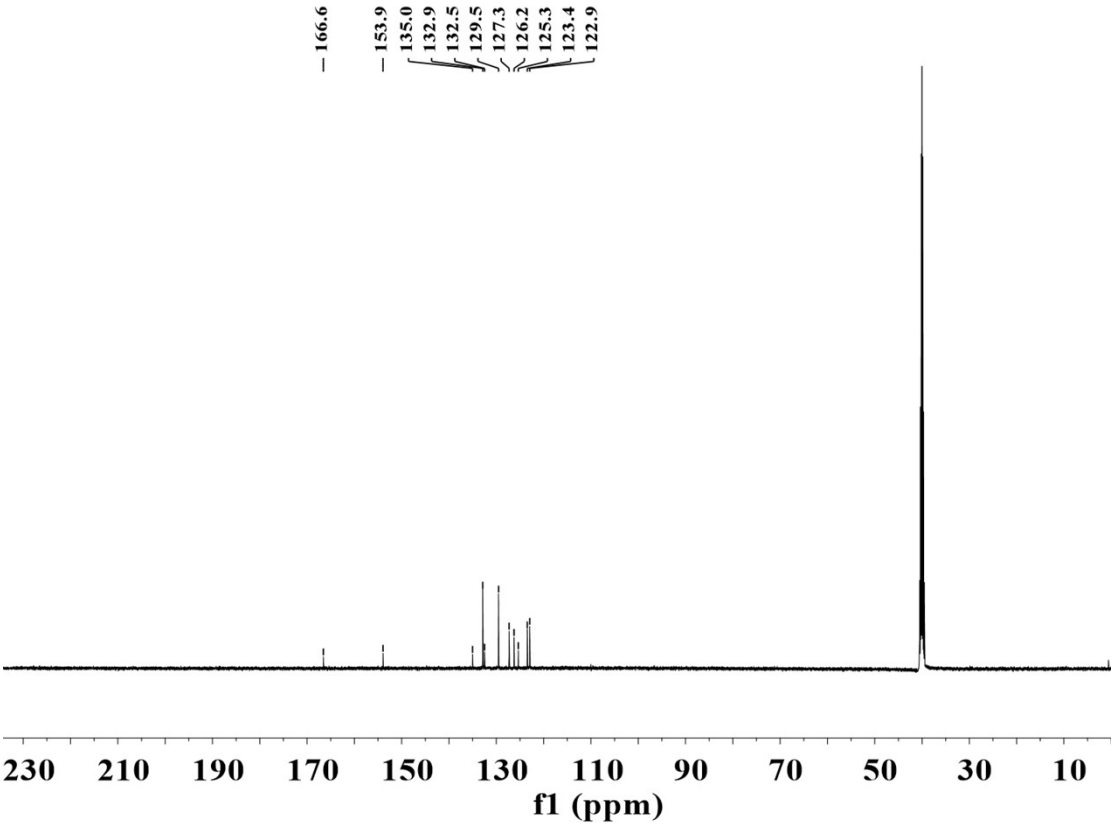
^{13}C NMR spectrum of compound **4f**



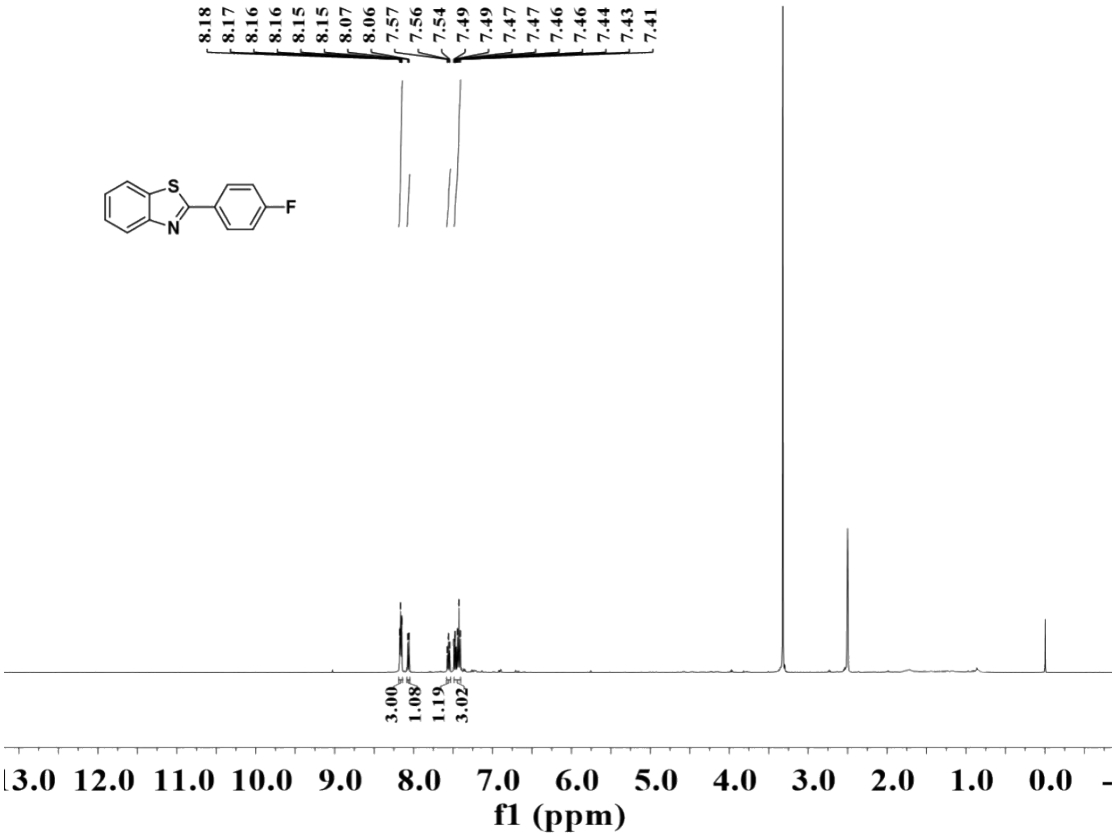
^{1}H NMR spectrum of compound **4g**



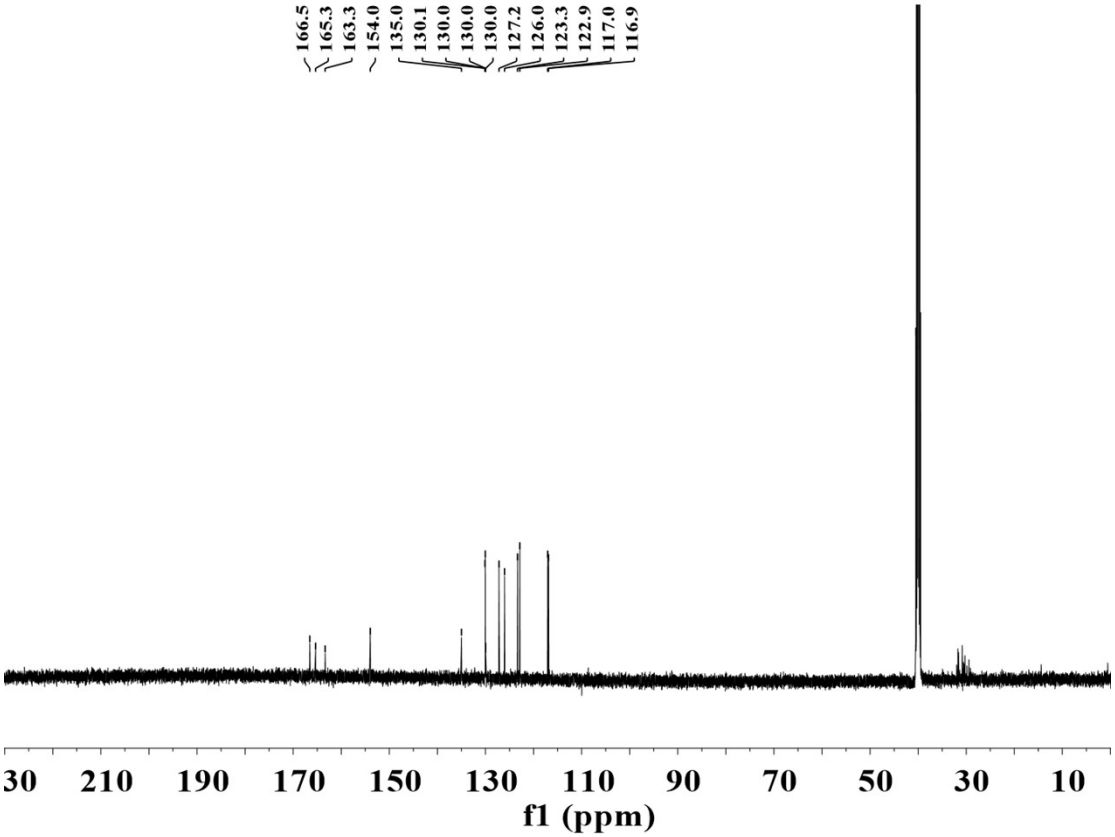
^{13}C NMR spectrum of compound **4g**



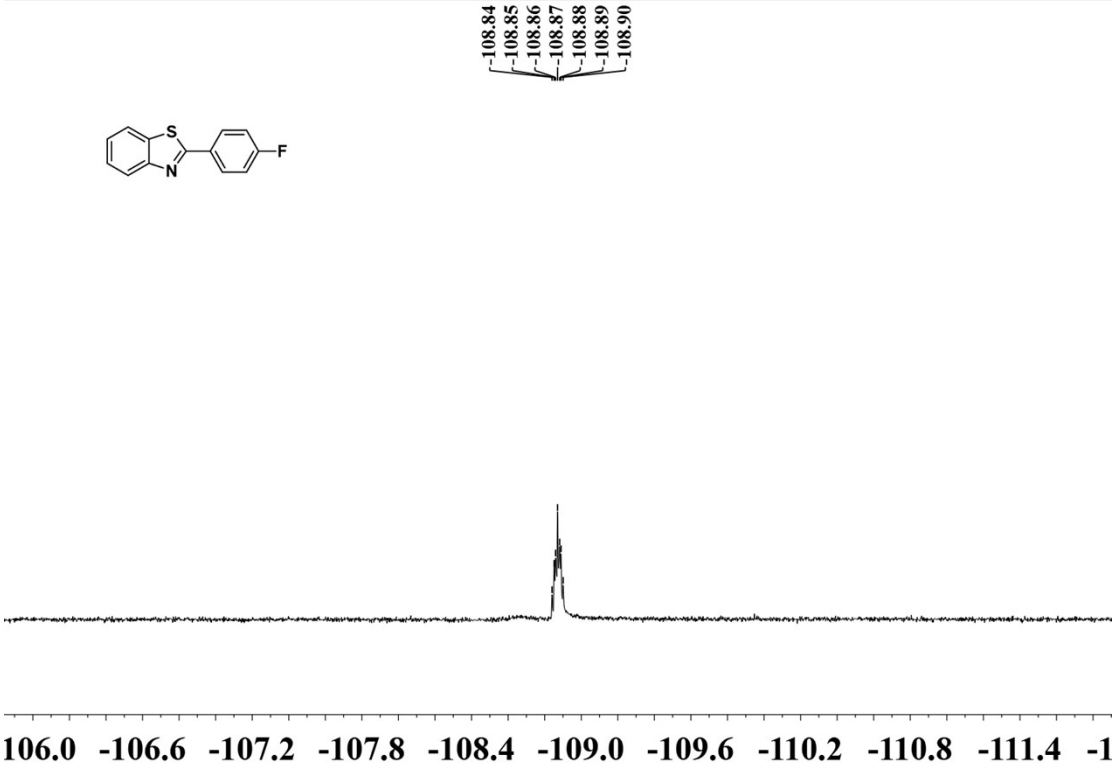
^{1}H NMR spectrum of compound **4h**



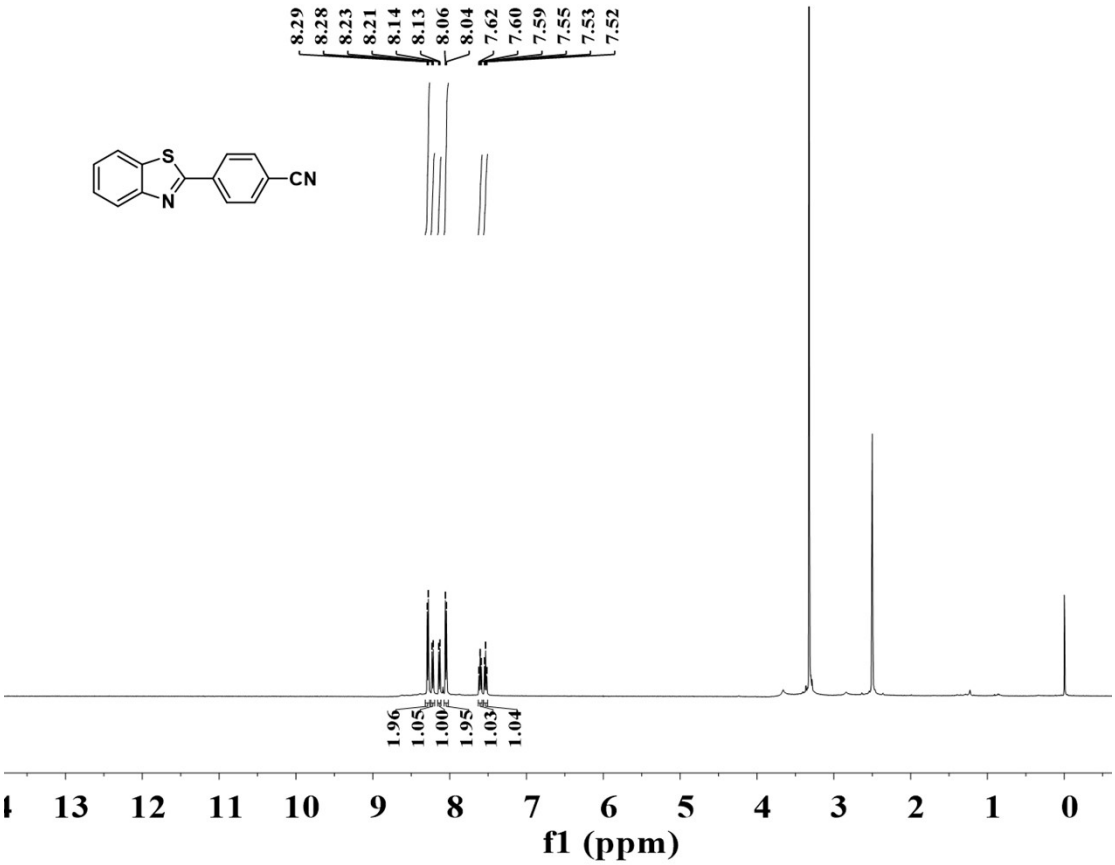
^{13}C NMR spectrum of compound **4h**



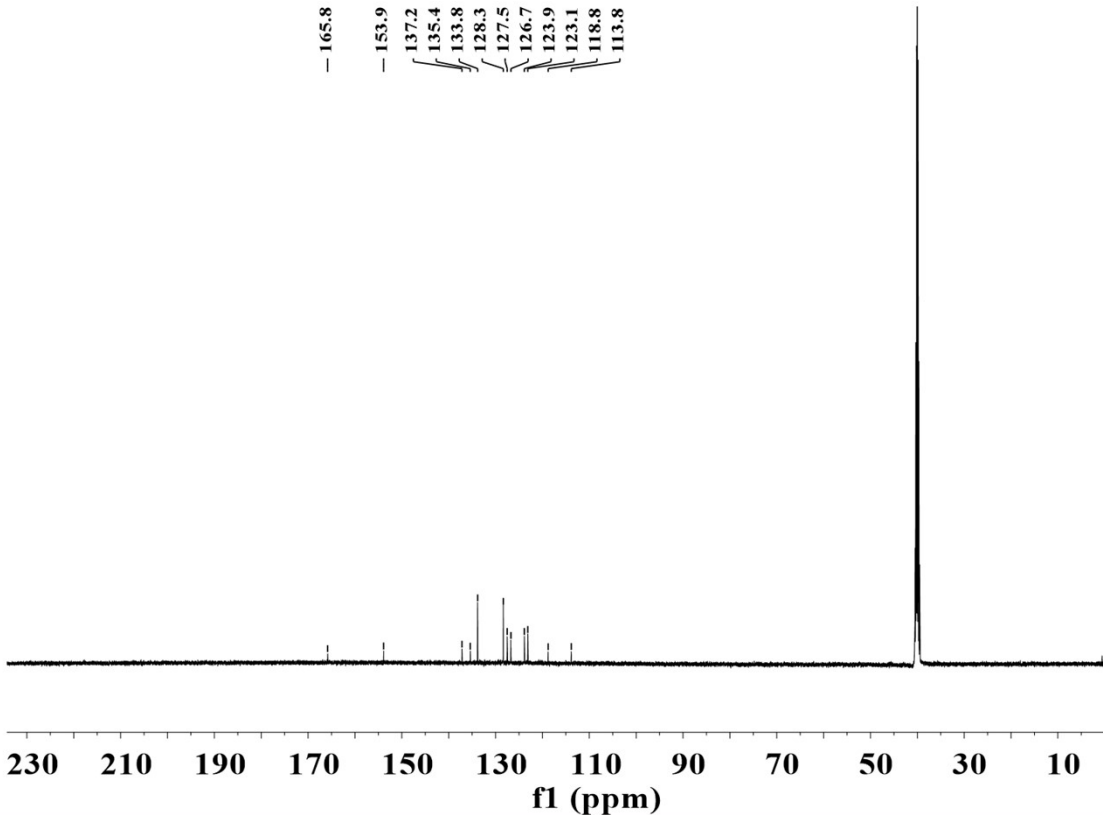
^{19}F NMR spectrum of compound **4h**



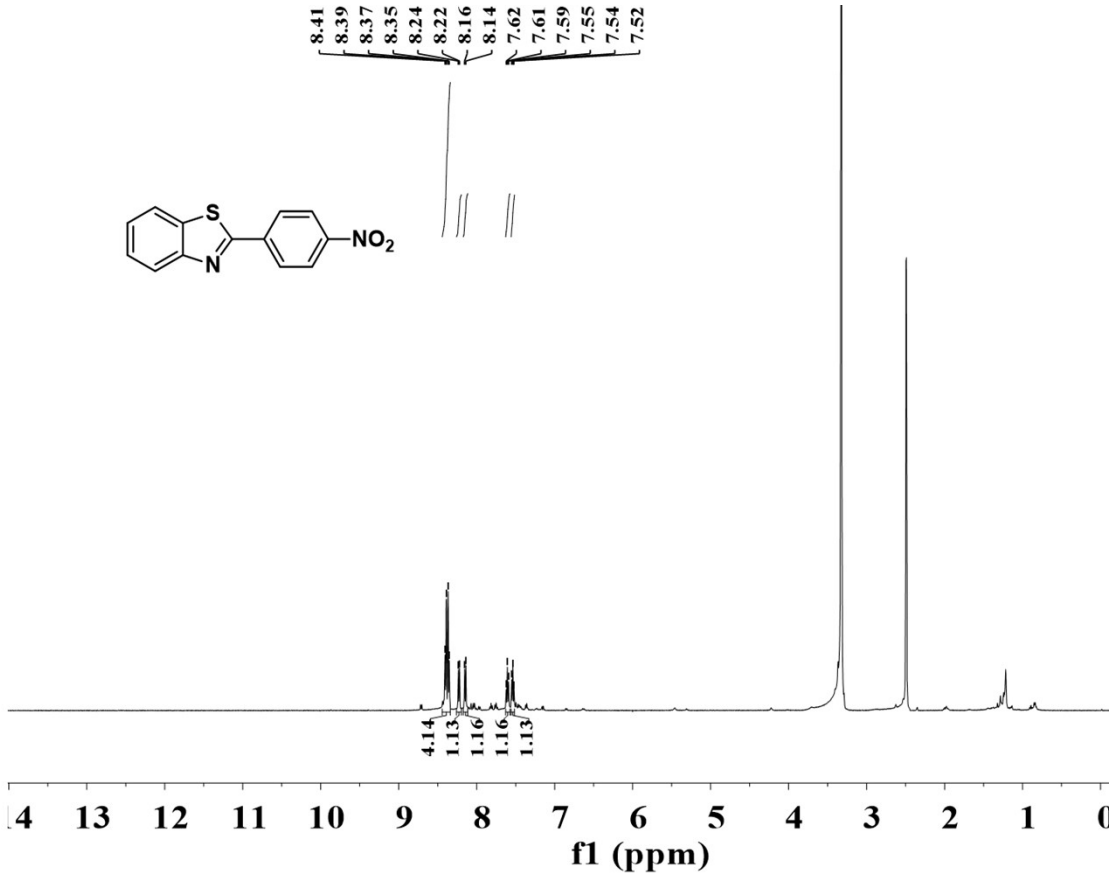
^{1}H NMR spectrum of compound **4i**



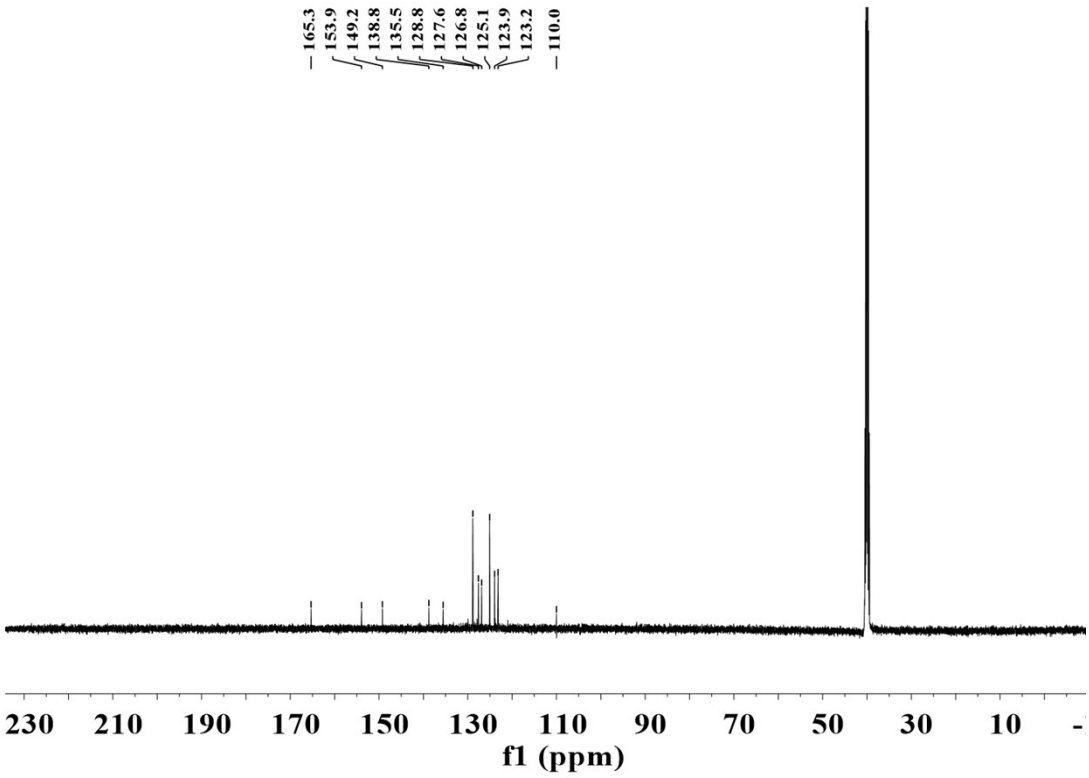
^{13}C NMR spectrum of compound **4i**



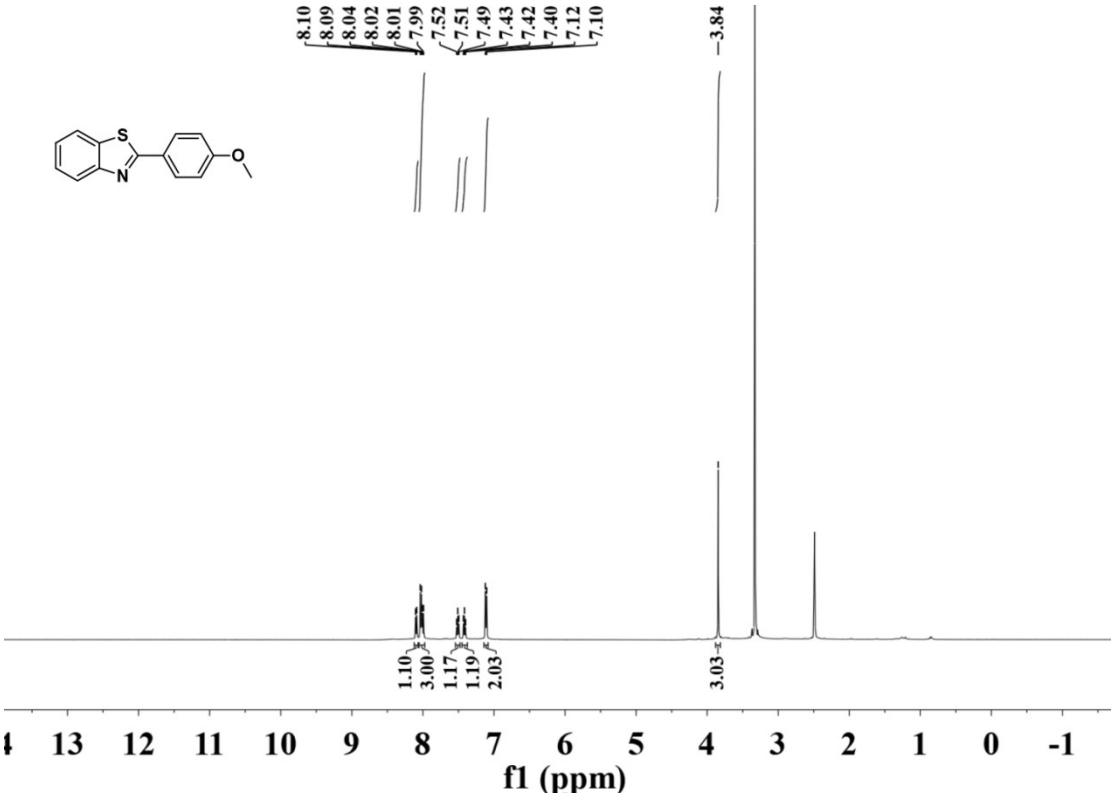
^{1}H NMR spectrum of compound **4j**



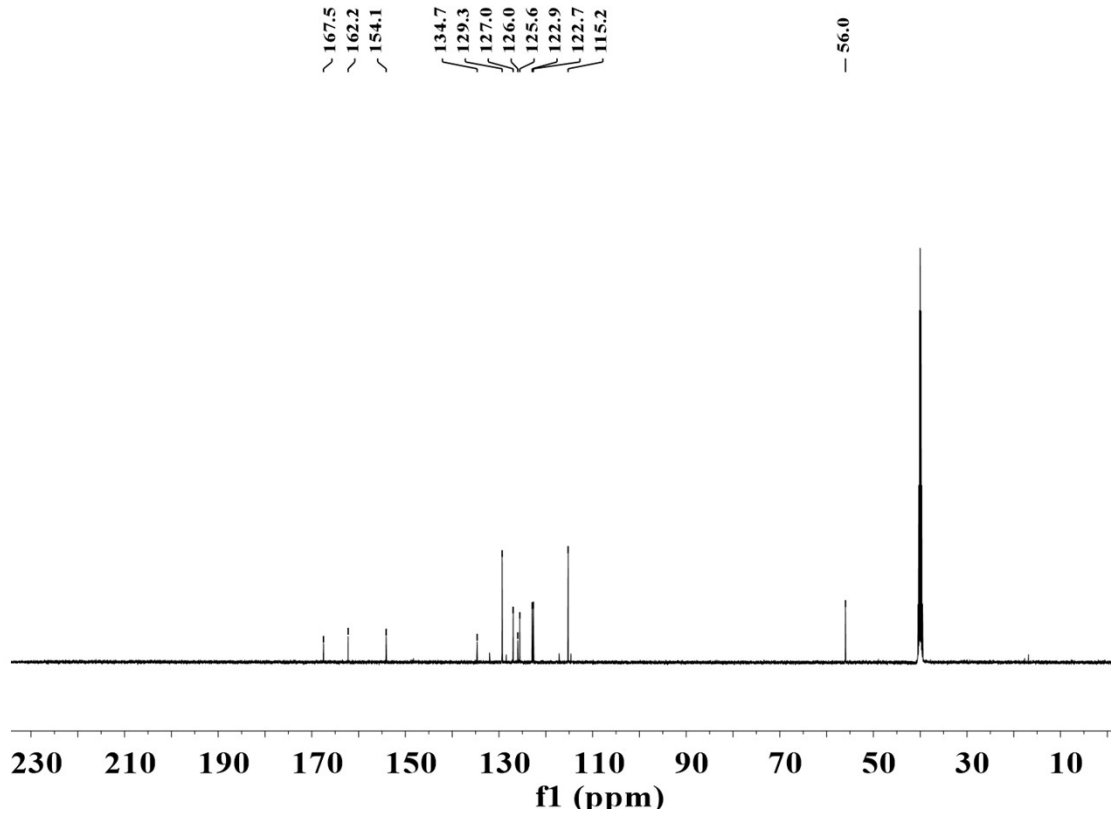
^{13}C NMR spectrum of compound **4j**



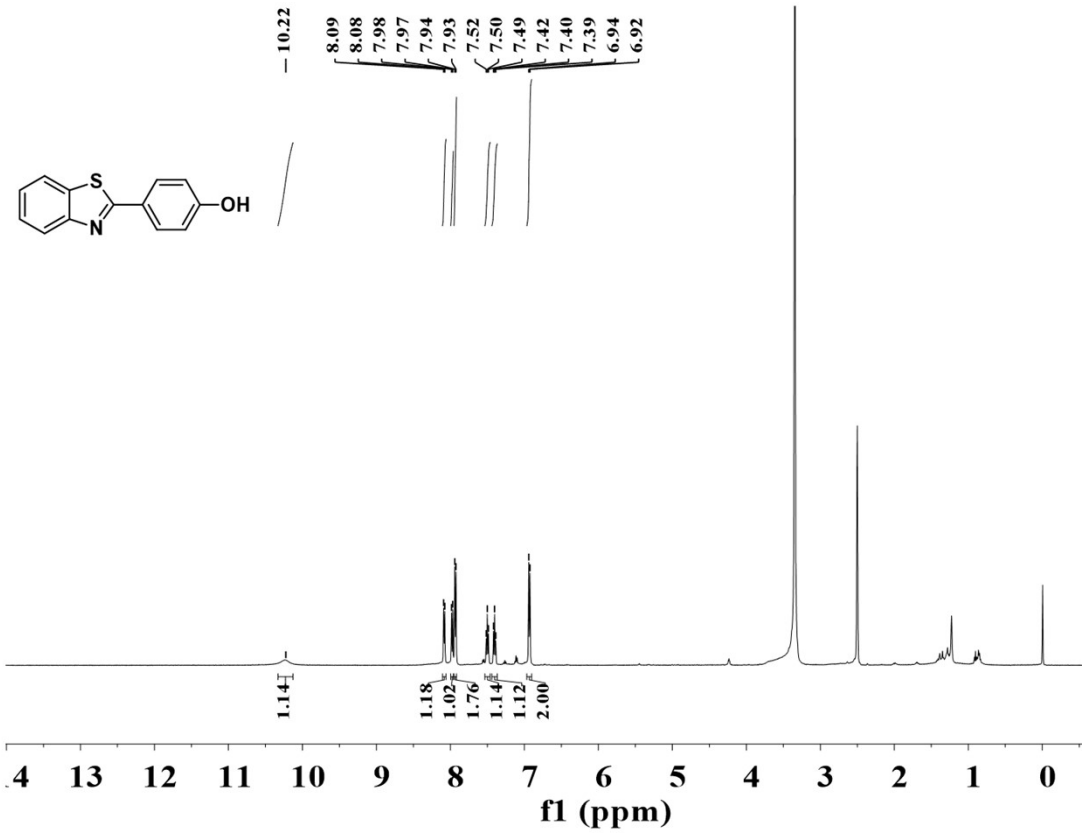
^{1}H NMR spectrum of compound **4k**



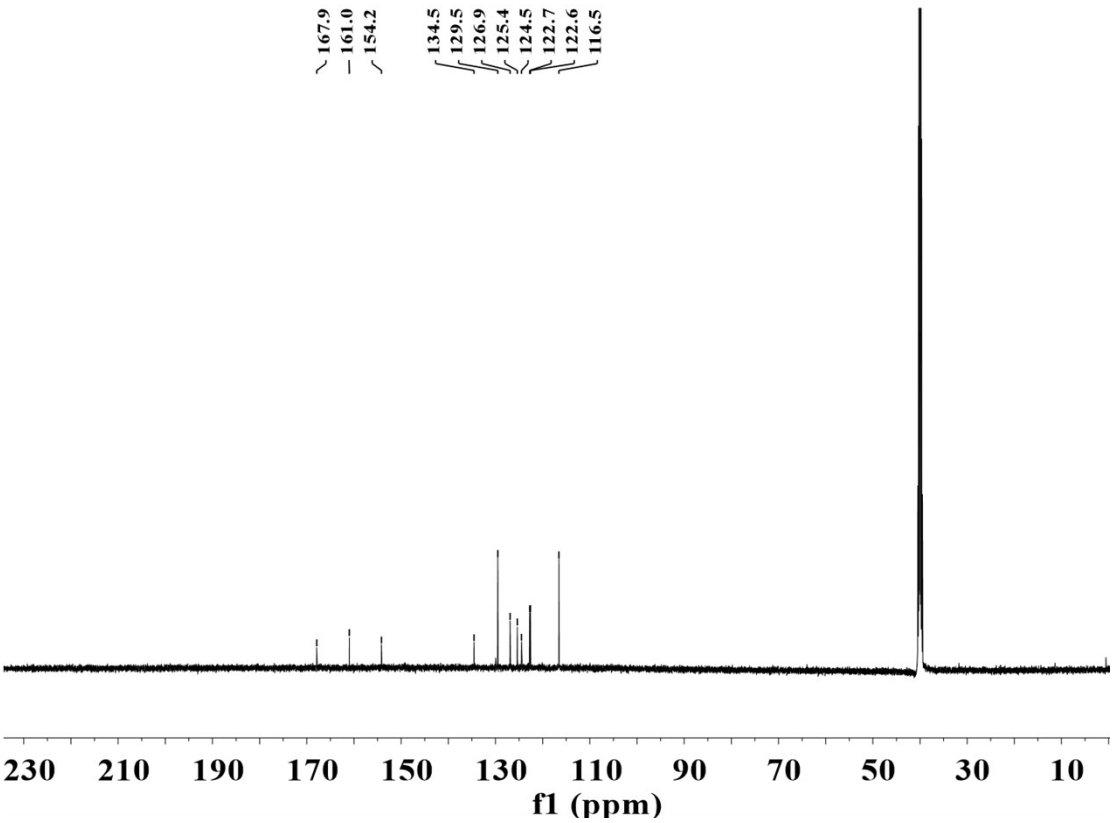
^{13}C NMR spectrum of compound **4k**



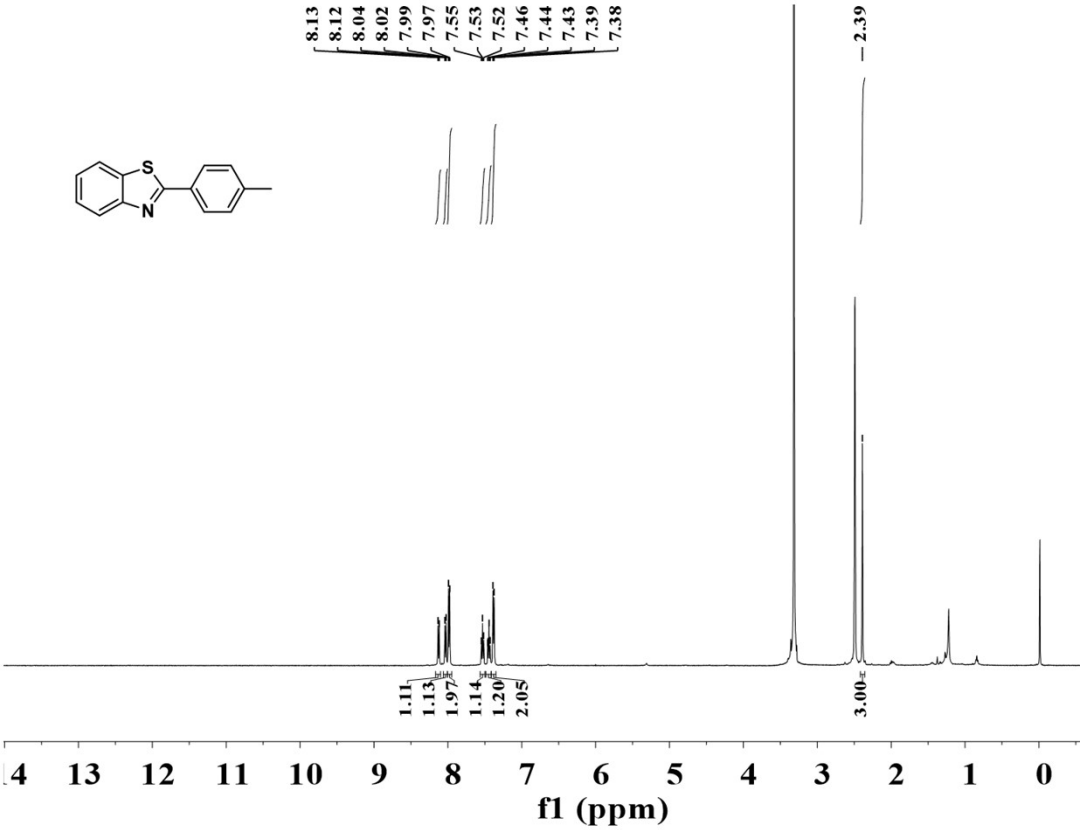
^{1}H NMR spectrum of compound **4l**



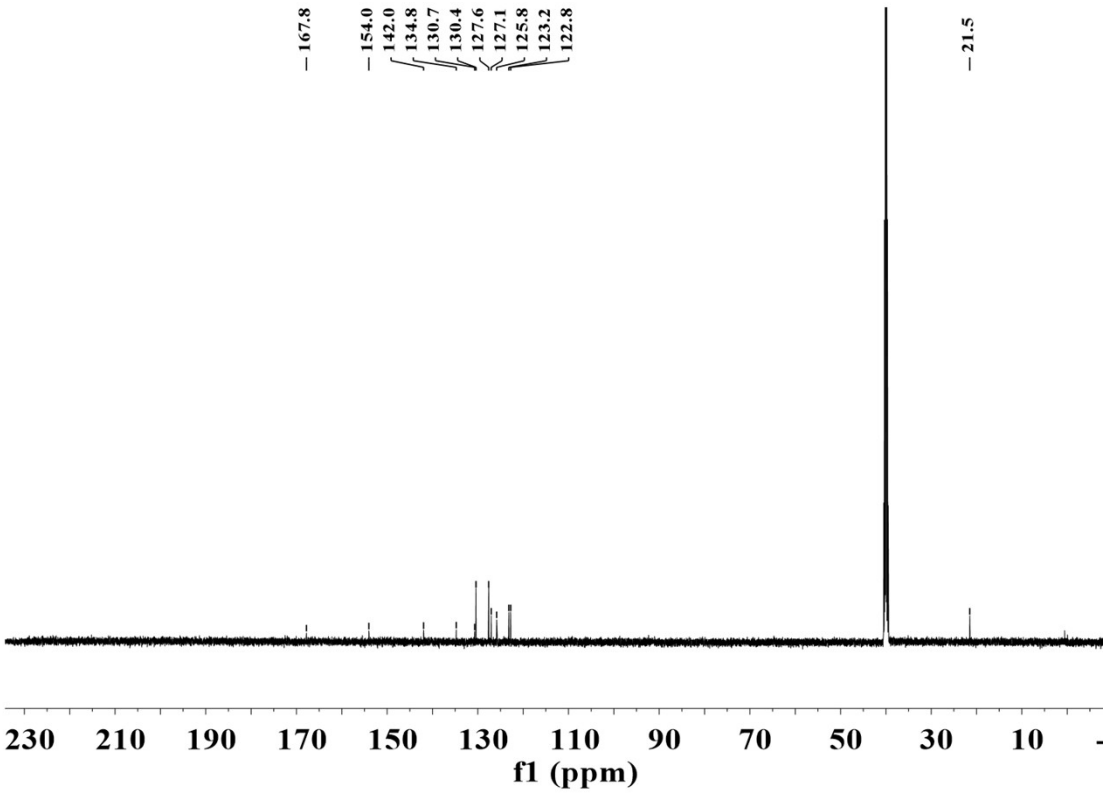
^{13}C NMR spectrum of compound **4l**



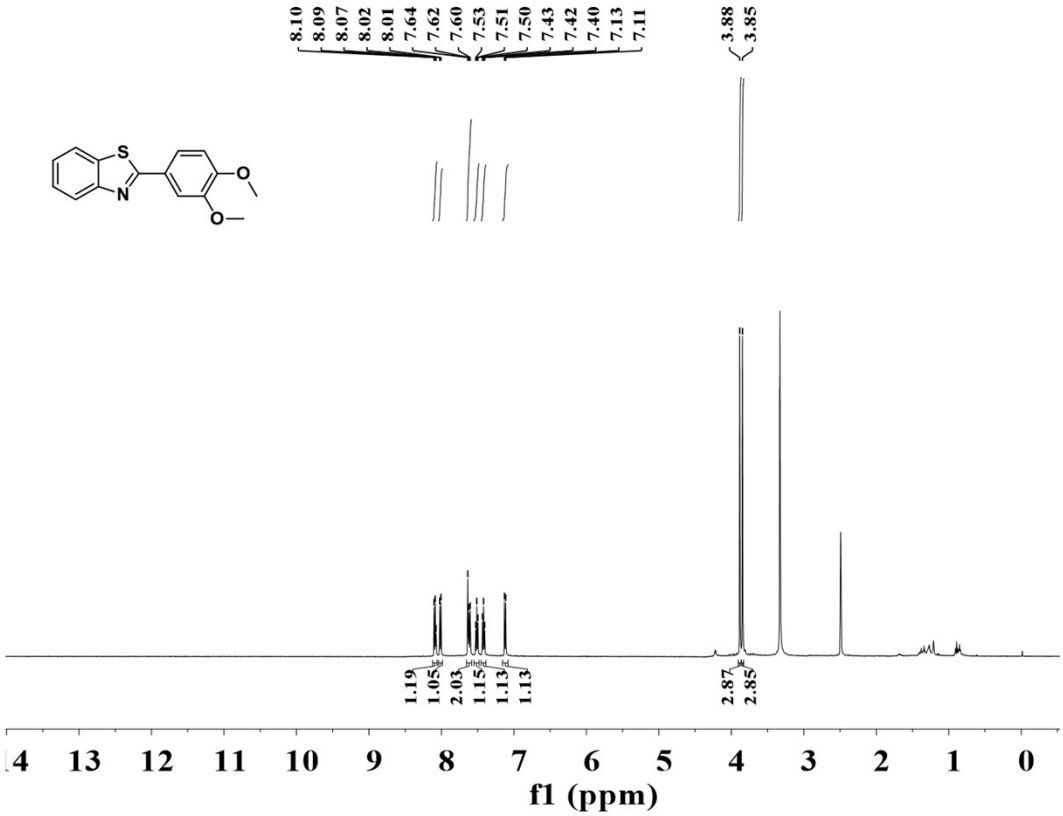
^{1}H NMR spectrum of compound **4m**



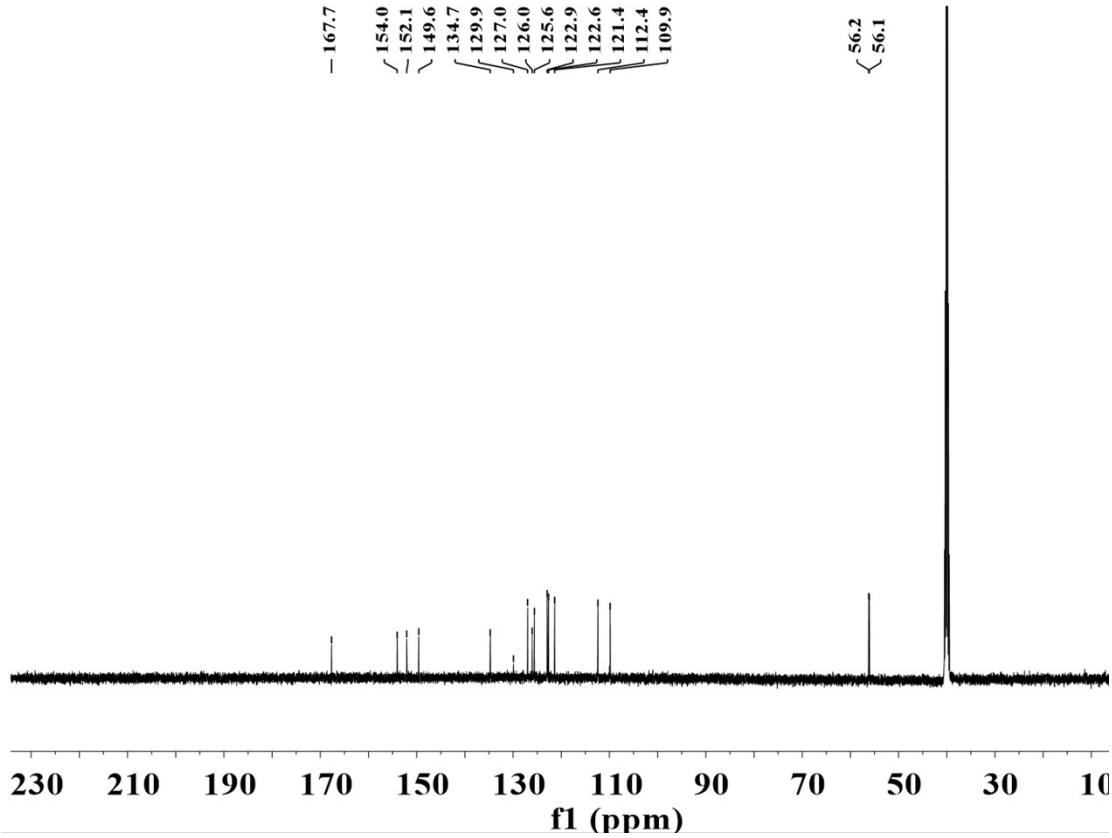
^{13}C NMR spectrum of compound **4m**



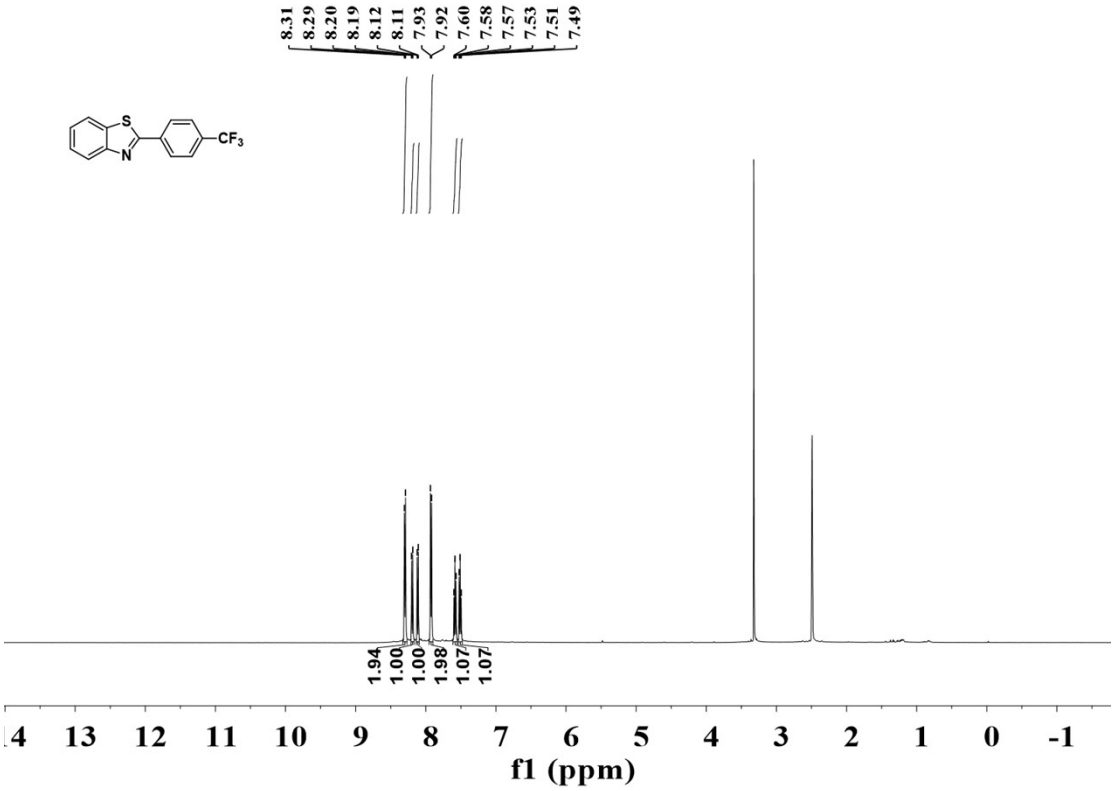
^{1}H NMR spectrum of compound **4n**



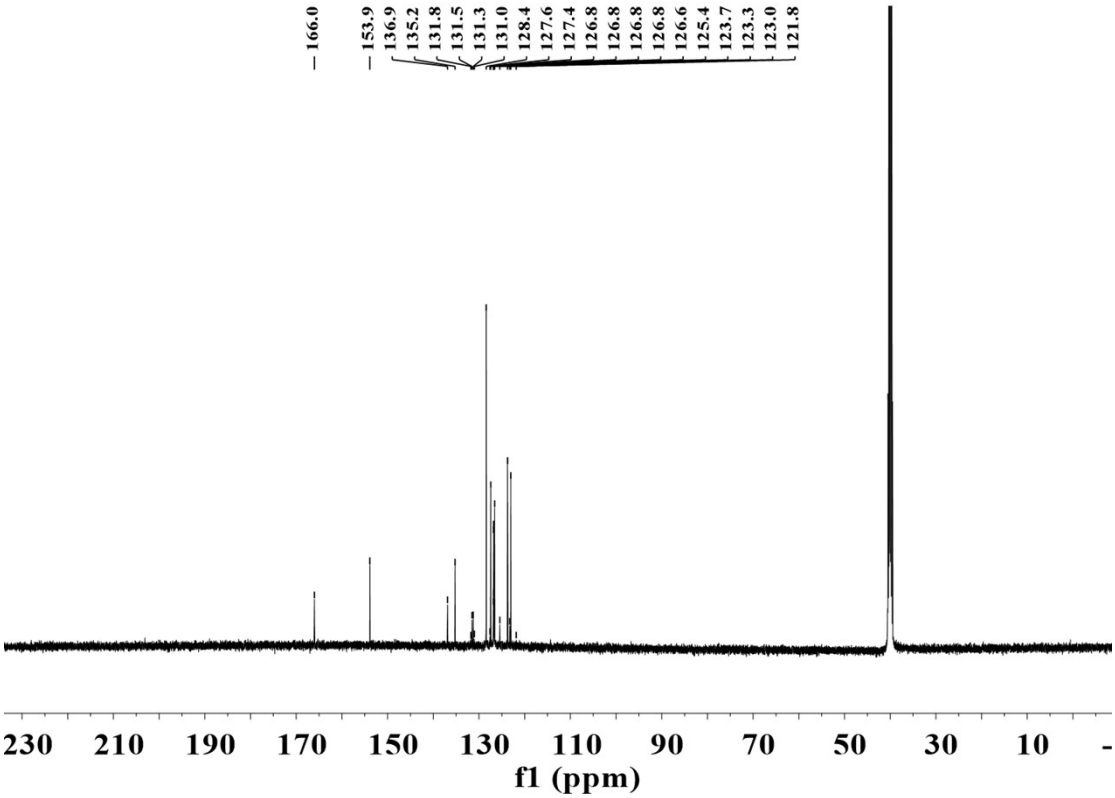
^{13}C NMR spectrum of compound **4n**



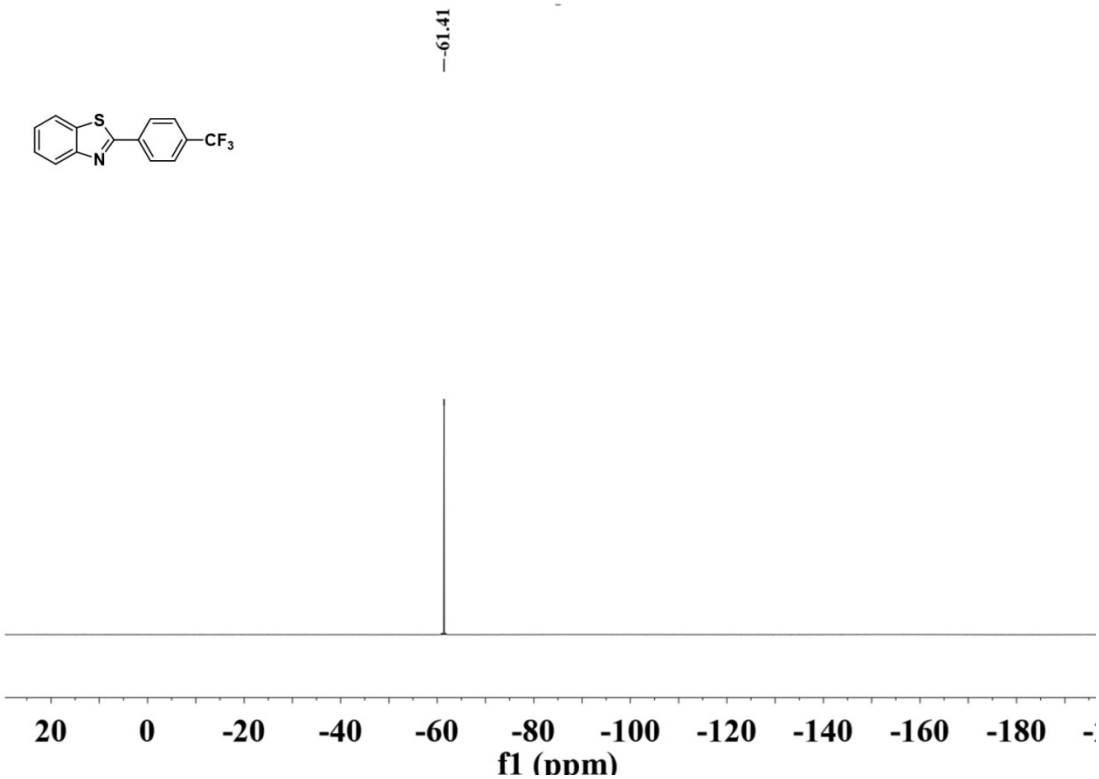
^{1}H NMR spectrum of compound **4o**



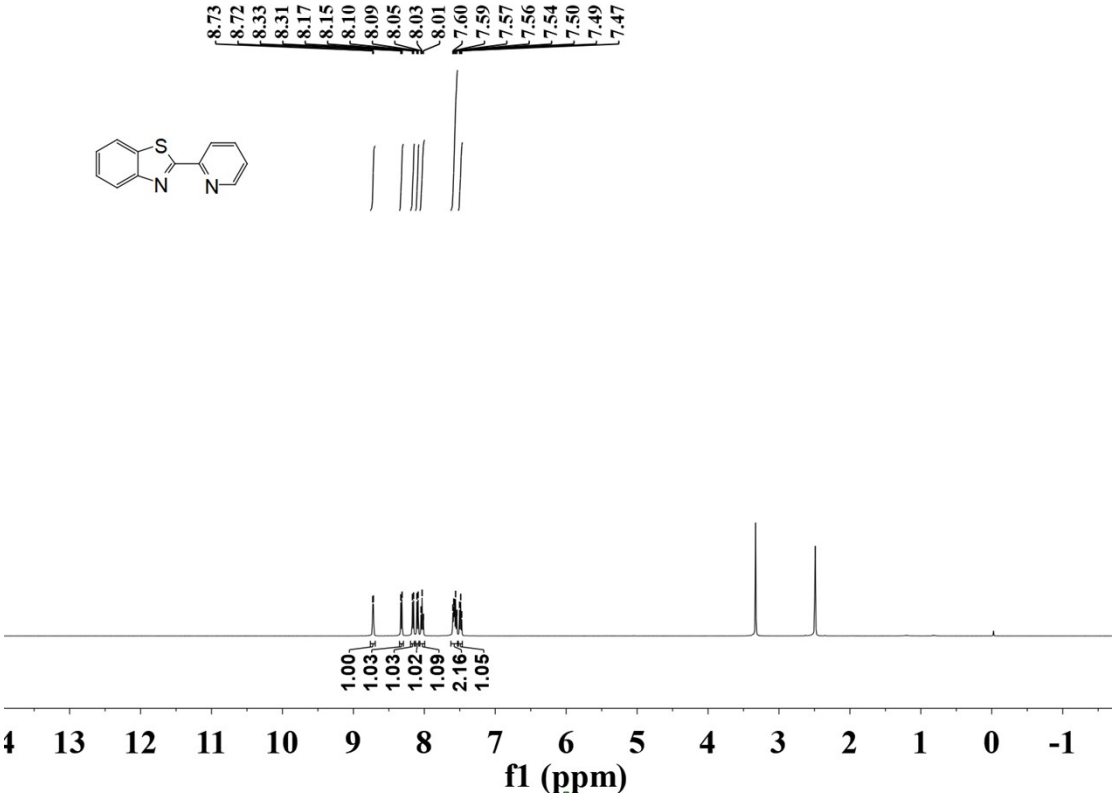
^{13}C NMR spectrum of compound **4o**



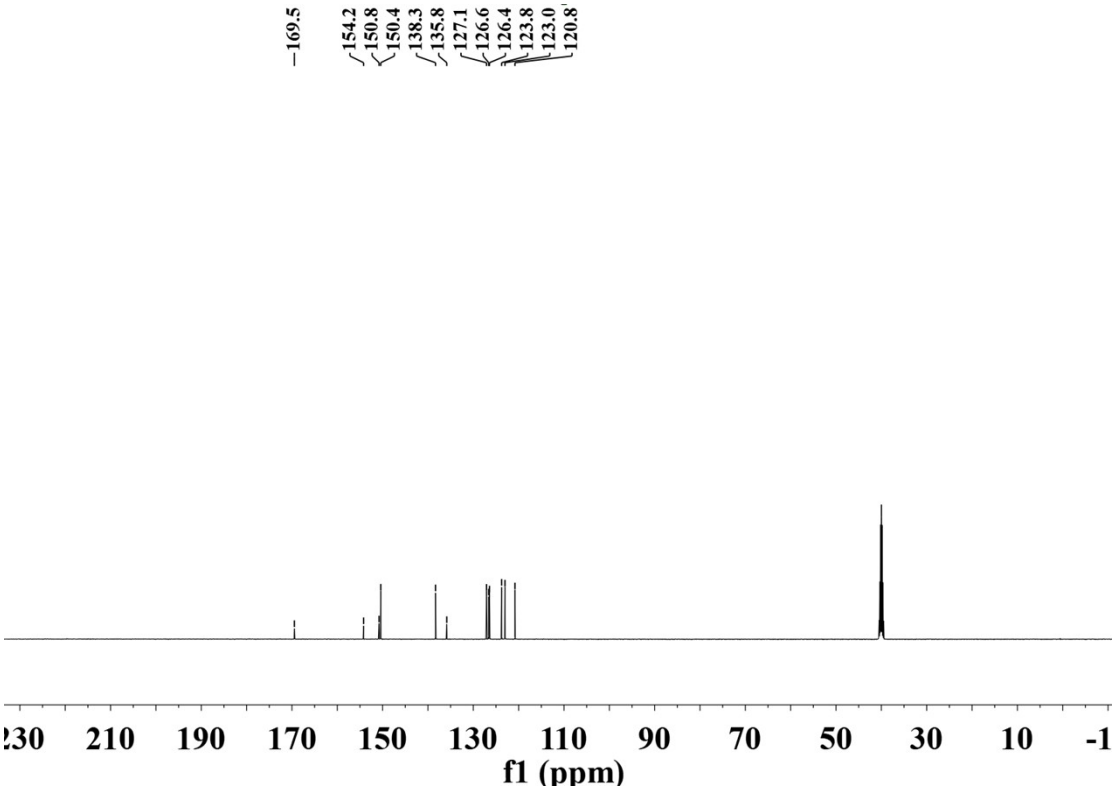
^{19}F NMR spectrum of compound **4o**


-61.41
S
N
CF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

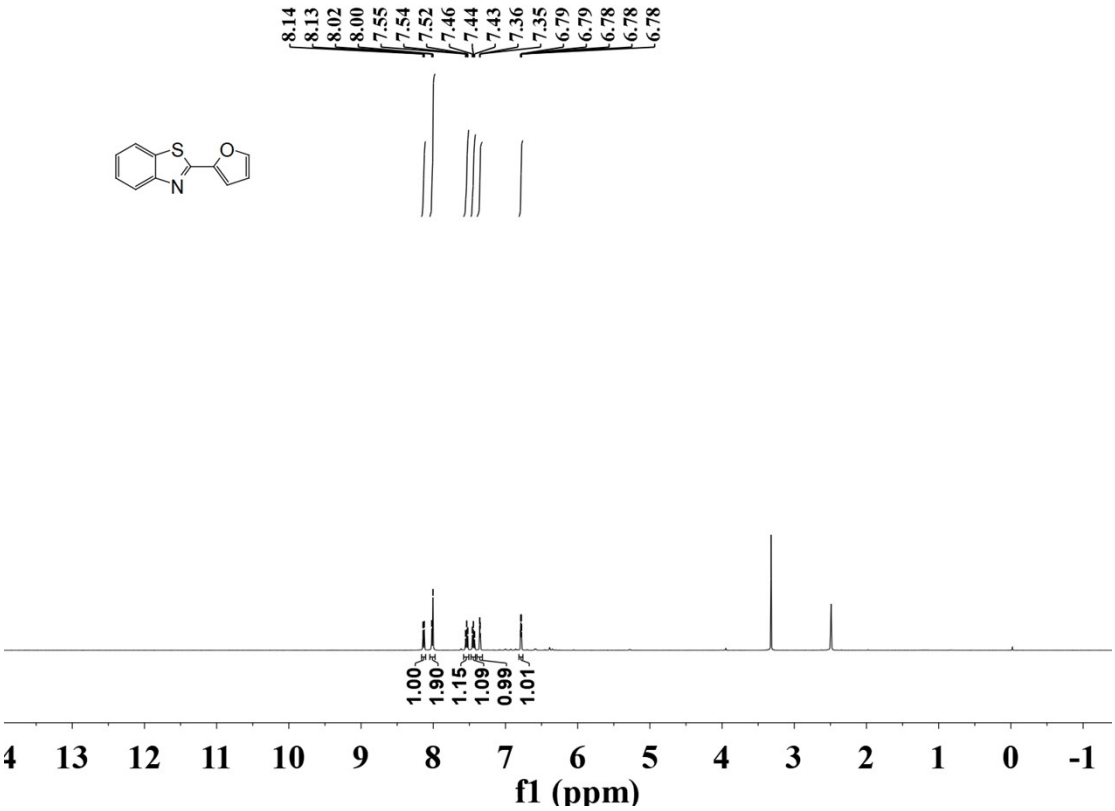
^{1}H NMR spectrum of compound **4p**



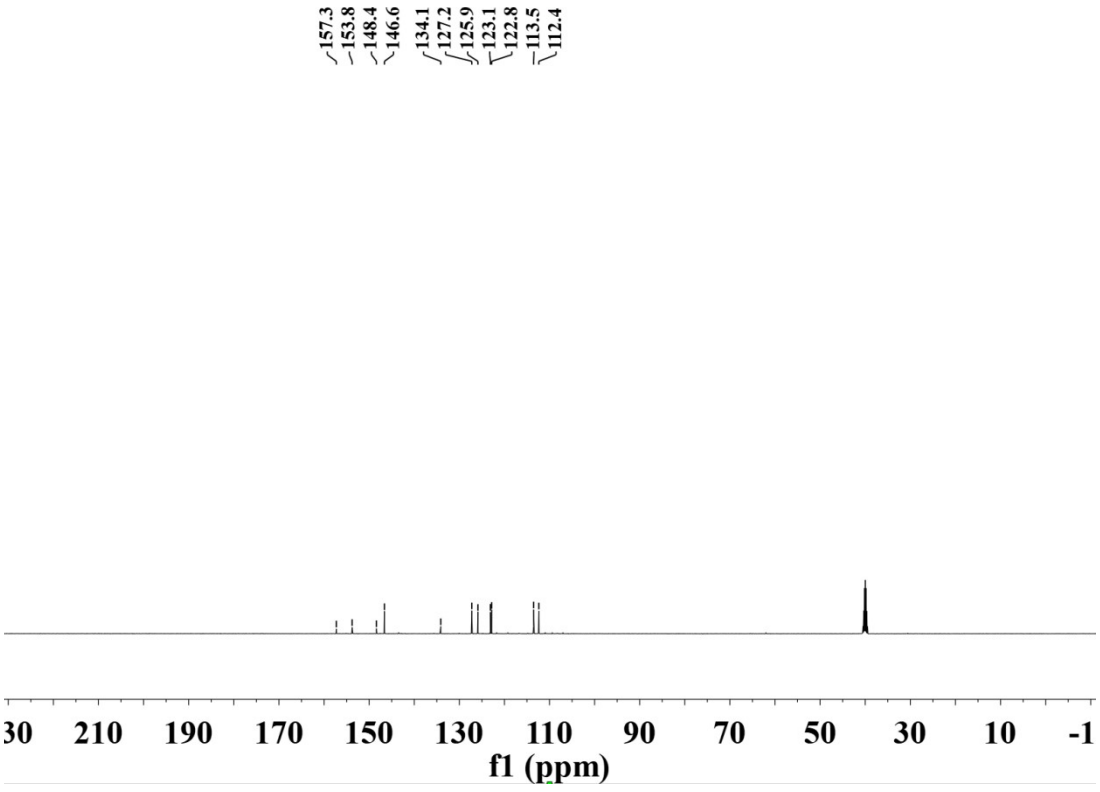
^{13}C NMR spectrum of compound **4p**



^{1}H NMR spectrum of compound **4q**



^{13}C NMR spectrum of compound **4q**



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