

Supporting Information

Catalyst-free and Additive-free Method for the Synthesis of Benzothiazolethiones from *o*-Iodoanilines, DMSO and Potassium Sulfide

Xiaoming Zhu^{†‡}, Wenguang Li,[†] Xiai Luo,[†] Guobo Deng,[†] Yun, Liang^{†*} and Jianbin Liu^{†*}

[†]National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education, Key Laboratory of the Assembly and Application of Organic Functional Molecules, Hunan Normal University, Changsha, Hunan 410081, China

[‡]Key Laboratory of Functional Metal-Organic Compounds of Hunan Province, Hunan Province Universities Key Laboratory of Functional Organometallic Materials, College of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China.

Email: yliang@hunnu.edu.cn; 1485192973@qq.com.

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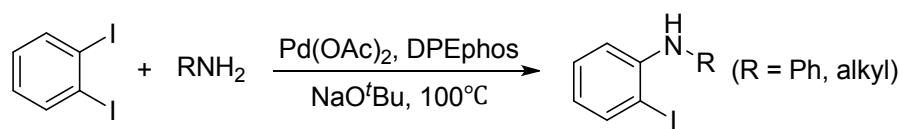
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1) General Information

^1H and ^{13}C NMR spectra were recorded on Bruker Avance-500 instrument (500 MHz for ^1H ; 125 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI (electrospray ionization). Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. GC analyses were recorded on Hunan Huasi Instrument Co. Ltd GC 8010 gas chromatograph spectrometer using FID. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE)/ethyl acetate (EA).

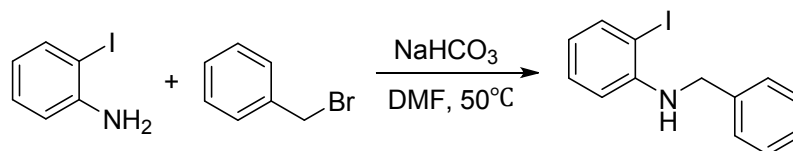
2) Synthesis of Starting Materials

Preparation of 1f-1i, 1n:¹



The sealed Schlenk tube was charged with 1,2-diodobenzene (3 mmol), the corresponding amine (1.5 equiv), Pd(OAc)₂ (0.5 mol %), DPEphos (0.75 mol %), NaOtBu (1.5 equiv) and toluene (8 mL). Then under the protection of nitrogen atmosphere, the mixture was stirred at 100 °C for 24 h. Then, cooled to room temperature, the mixture was filtered by a crude column with ethyl acetate as the eluent, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

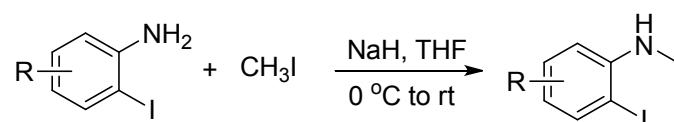
Preparation of 1j-1m, 1d:²



An oven-dried flask was charged with *o*-iodoaniline (2.6 mmol), the corresponding benzyl bromide (2 mmol), NaHCO₃ (4 mmol), and DMF (5 mL). The mixture was stirred at 50 °C, until complete consumption of starting material was

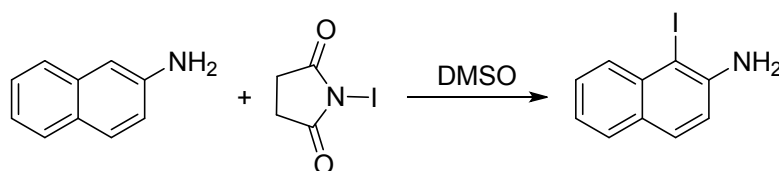
indicated by TLC. Then cooled to room temperature, the mixture was quenched with water and the organic layer extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography to afford the pure product.

Preparation of 1b, 1o-1q, 1s-1u:³



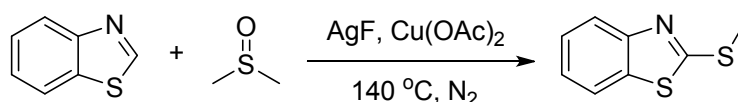
An oven-dried flask was charged with the corresponding *o*-iodoaniline (2 mmol), iodomethane (2 mmol), NaH (4 equiv) and THF (5 mL). The resulting mixture was stirred from 0 °C to rt, until complete consumption of starting material which was indicated by TLC. The mixture was quenched with water and the organic layer extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography to afford the pure product .

Preparation of 1u:⁴



NIS (2 mmol) was dissolved in anhydrous DMSO (15 mL) containing 2-naphthylamine (2 mmol). The resulting mixture was stirred for 6 h at room temperature. After the reaction was completed by TLC monitoring, the reaction mixture was quenched by water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford 1-iodonaphthalen-2-amine as a black solid with 88% yield.

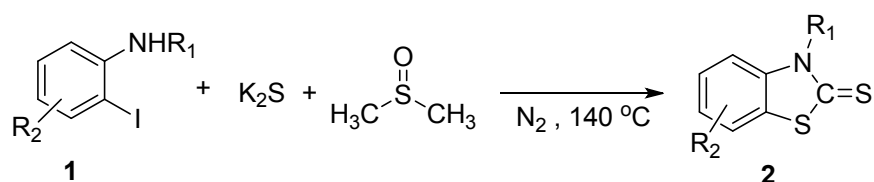
Preparation of H:⁵



Under an argon atmosphere, a Schlenk tube was charged with $\text{Cu}(\text{OAc})_2$ (74 mg, 0.4 mmol), AgF (5 mg, 0.04 mmol), benzothiazole (28 mg, 0.2 mmol), DMSO (1 ml). The resultant mixture was stirred at 140 °C for 15 h. After the reaction was completed by TLC monitoring, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the 2-(methylthio)benzo[*d*]thiazole as a white solid with 35 % yield.

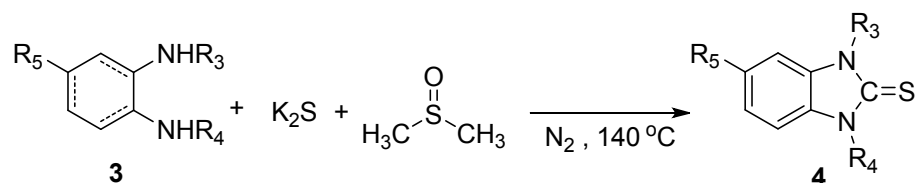
3) Typical Procedures

The Synthetic Procedure for Compounds 2:



The sealed Schlenk tube was charged with *o*-iodoanilines (0.3 mmol), K_2S (1.2 mmol), and DMSO (2 ml). Then, under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the pure product (2).

The Synthetic Procedure for Compounds 4:

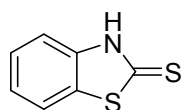


The sealed Schlenk tube was charged with 1,2-phenylenediamines (0.4 mmol), K_2S (1.2 mmol), and DMSO (2 ml). Then under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C. After the completion of the reaction (monitored by

TLC), the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the pure product (4).

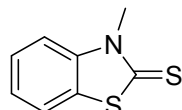
4) Characterization Data of Products

benzo[*d*]thiazole-2(3H)-thione (**2a**)⁶



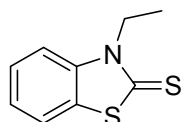
White solid (24 mg, 70%); mp: 190-192 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 13.77 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 - 7.26 (m, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 190.28, 141.73, 129.82, 127.62, 124.68, 122.24, 112.90.

3-methylbenzo[*d*]thiazole-2(3H)-thione (**2b**)⁶



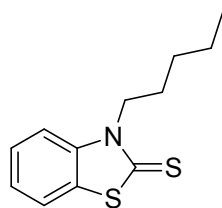
White solid (33 mg, 92%); mp: 100-102 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.43 - 7.40 (m, 1H), 7.32 - 7.29 (m 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 189.36, 141.96, 127.49, 126.95, 124.80, 121.24, 112.27, 33.10.

3-ethylbenzo[*d*]thiazole-2(3H)-thione (**2c**)⁷



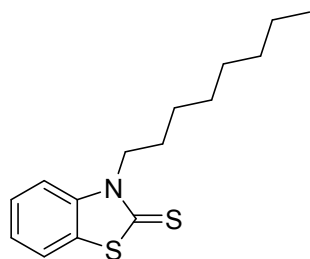
Colorless liquid (38 mg, 97%); ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 - 7.39 (m, 1H), 7.30 - 7.27 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.49 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.47, 141.01, 127.85, 126.87, 124.59, 121.35, 112.17, 41.29, 11.78.

3-pentylbenzo[*d*]thiazole-2(3H)-thione (**2d**)



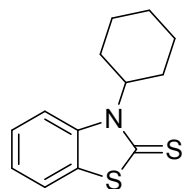
Yellow oil (37 mg, 81 %); ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.41 (t, *J* = 8.0 Hz, 2H), 1.85 - 1.79 (m, 2H), 1.47 - 1.38 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.85, 141.48, 127.87, 126.83, 124.56, 121.32, 112.31, 46.37, 28.91, 26.46, 22.32, 13.89; HRMS (ESI) *m/z* calcd for C₁₂H₁₆NS₂⁺ (M+H)⁺ 238.0719, found 238.0719.

3-octylbenzo[*d*]thiazole-2(3H)-thione (**2e**)¹



Yellow oil (38 mg, 67%); ¹H NMR (CDCl₃, 500 MHz) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 1.83 - 1.77 (m, 2H), 1.48 - 1.42 (m, 2H), 1.38 - 1.35 (m, 2H), 1.33 - 1.27 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.71, 141.39, 127.76, 126.78, 124.50, 121.24, 112.27, 46.33, 31.64, 29.10, 29.02, 26.75, 26.69, 22.50, 13.97.

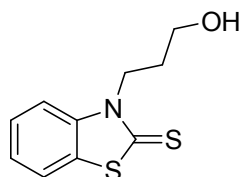
3-cyclohexylbenzo[*d*]thiazole-2(3H)-thione (**2f**)¹



Yellow solid (37 mg, 76%); mp: 115 - 117 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 5.76 (t, *J* = 12.5 Hz, 1H), 2.24 (q, *J* = 12.0 Hz, 2H), 1.97 (d, *J* = 13.0 Hz, 2H),

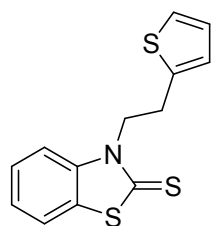
1.91 (d, $J = 11.0$ Hz, 2H), 1.83 (d, $J = 13.0$ Hz, 1H), 1.57 (q, $J = 13.0$ Hz, 2H), 1.36 - 1.31 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 189.26, 140.72, 127.39, 126.07, 123.98, 121.24, 114.00, 58.47, 28.53, 25.97, 25.34.

3-(3-hydroxypropyl)benzo[*d*]thiazole-2(3H)-thione (**2g**)



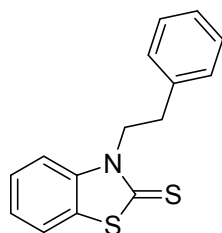
White solid (39 mg, 86%); mp: 82 - 84 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.52 (d, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.35 - 7.30 (m, 2H), 4.62 (t, $J = 6.0$ Hz, 2H), 3.61 (t, $J = 5.5$ Hz, 2H), 2.95 (s, 1H), 2.08 - 2.03 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 189.74, 141.25, 127.93, 127.12, 124.99, 121.44, 112.63, 57.96, 42.88, 30.08. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{NOS}_2^+$ ($\text{M}+\text{H}$) $^+$ 226.0355, found 226.0355.

3-(2-(thiophen-2-yl)ethyl)benzo[*d*]thiazole-2(3H)-thione (**2h**)¹



Yellow solid (31 mg, 55%); mp: 101-103 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.48 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.16 (d, $J = 5.0$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 6.93 - 6.88 (m, 2H), 4.65 (t, $J = 8.0$ Hz, 2H), 3.35 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 188.99, 141.39, 139.22, 127.64, 127.20, 126.91, 125.99, 124.66, 124.36, 121.37, 112.04, 47.65, 26.79.

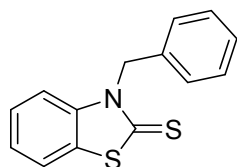
3-phenethylbenzo[*d*]thiazole-2(3H)-thione (**2i**)



Yellow solid (29 mg, 53%); mp: 105-107 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.46 (d, $J = 7.5$ Hz, 1H), 7.36 - 7.33 (m, 1H), 7.30 - 7.22 (m, 6H), 7.10 (d, $J = 8.0$ Hz, 1H), 4.59

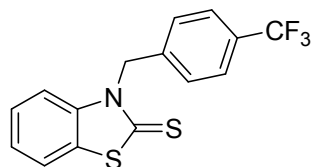
(s, $J = 8.0$ Hz, 2H), 3.08 (s, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 188.87, 141.41, 137.50, 128.93, 128.81, 127.76, 126.99, 126.93, 124.68, 121.42, 112.25, 47.78, 32.83; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{NS}_2^+$ ($\text{M}+\text{H}$) $^+$ 272.0562, found 272.0564.

3-benzylbenzo[*d*]thiazole-2(3H)-thione (**2j**)¹



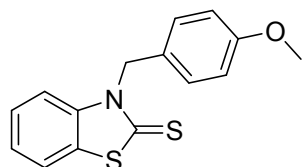
Pale yellow solid (36 mg, 68%); mp: 145-147 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.48 (d, $J = 7.5$ Hz, 1H), 7.34 - 7.24 (m, 7H), 7.11 (d, $J = 8.0$ Hz, 1H), 5.70 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 190.19, 141.45, 134.31, 128.91, 127.94, 127.55, 127.08, 126.94, 124.81, 121.28, 113.02, 49.49.

3-(4-(trifluoromethyl)benzyl)benzo[*d*]thiazole-2(3H)-thione (**2k**)¹



Yellow solid (34 mg, 52%); mp: 112-114 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.34 - 7.28 (m, 2H), 7.05 (d, $J = 8.5$ Hz, 1H), 5.75 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 190.28, 141.10, 138.29, 130.24 (q, $J = 32.44$ Hz), 127.48, 127.34, 127.14, 125.92 (q, $J = 3.65$ Hz), 125.09, 123.84 (q, $J = 270.61$ Hz), 121.51, 112.66, 48.88.

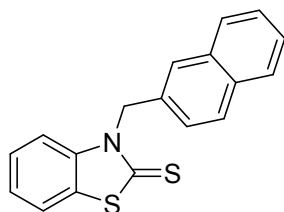
3-(4-methoxybenzyl)benzo[*d*]thiazole-2(3H)-thione (**2l**)



Pale yellow solid (25 mg, 44%); mp: 105-107 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.47 (d, $J = 7.5$ Hz, 1H), 7.31 - 7.24 (m, 4H), 7.15 (d, $J = 8.0$ Hz, 1H), 6.84 (d, $J = 8.5$ Hz, 2H), 5.63 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 189.97, 159.25, 141.43, 128.60, 127.57, 126.88, 126.37, 124.75, 121.23, 114.25, 113.03, 55.22, 48.98; HRMS

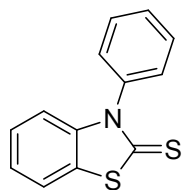
(ESI) m/z calcd for $C_{15}H_{14}NOS_2^+$ ($M+H$) $^+$ 288.0511, found 288.0512.

3-(naphthalen-2-ylmethyl)benzo[*d*]thiazole-2(3H)-thione (**2m**)¹



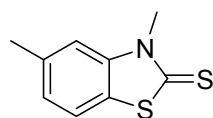
Yellow solid (32 mg, 51%); mp: 162-164 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.80 - 7.76 (m, 3H), 7.70 (s, 1H), 7.46 - 7.43 (m, 4H), 7.24 - 7.23 (m, 2H), 7.14 - 7.13 (m, 1H), 5.85 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 190.22, 141.41, 133.18, 132.86, 131.80, 128.91, 127.76, 127.68, 127.49, 126.95, 126.42, 126.19, 125.97, 124.83, 124.75, 121.28, 113.07, 49.68.

3-phenylbenzo[*d*]thiazole-2(3H)-thione (**2n**)¹



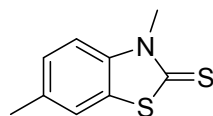
Yellow viscous oil (37 mg, 76%); ¹H NMR (CDCl₃, 500 MHz) δ 7.64 - 7.63 (m, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.31 - 7.24 (m, 2H), 6.72 (d, $J = 7.5$ Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 190.40, 143.28, 136.57, 130.13, 129.76, 128.21, 127.79, 126.82, 124.89, 121.08, 113.37.

3,5-dimethylbenzo[*d*]thiazole-2(3H)-thione (**2o**)⁸



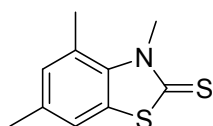
Pale yellow solid (21 mg, 53%); mp: 182-184 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.34 (d, $J = 8.5$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.02 (s, 1H), 3.83 (s, 3H), 2.47 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 189.62, 142.20, 137.44, 125.99, 124.37, 120.86, 112.82, 33.07, 21.59.

3,6-dimethylbenzo[*d*]thiazole-2(3H)-thione (**2p**)⁶



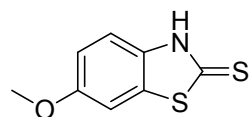
Yellow solid (31 mg, 79%); mp: 126-128 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.27 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.67, 139.92, 134.97, 127.90, 127.42, 121.28, 111.89, 33.07, 21.02.

3,4,6-trimethylbenzo[*d*]thiazole-2(3H)-thione (**2q**)



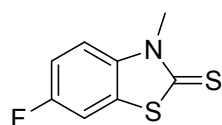
Pale yellow solid (29 mg, 70%); mp: 165-167 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.08 (s, 1H), 6.94 (s, 1H), 4.14 (s, 3H), 2.70 (s, 3H), 2.33 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 189.13, 138.83, 134.45, 132.11, 127.94, 122.64, 119.24, 37.13, 20.71, 20.63; HRMS (ESI) *m/z* calcd for C₁₀H₁₂NS₂⁺ (M+H)⁺ 210.0406, found 210.0406.

6-methoxybenzo[*d*]thiazole-2(3H)-thione (**2r**)¹



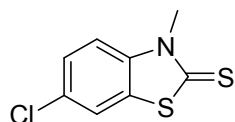
White solid (20 mg, 52%); mp: 200-202 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 13.51 (s, 1H), 7.33 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 3.76 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 188.84, 157.10, 135.67, 131.18, 115.26, 113.55, 106.36, 56.16.

6-fluoro-3-methylbenzo[*d*]thiazole-2(3H)-thione (**2s**)⁹



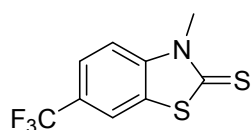
Yellow solid (21 mg, 51%); mp: 133-134 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.22 - 7.20 (m, 1H), 7.15 - 7.13 (m, 2H), 3.82 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.99, 160.13 (d, *J* = 244.8 Hz), 138.44, 128.60 (d, *J* = 10.0 Hz), 114.50 (d, *J* = 24.4 Hz), 112.80 (d, *J* = 8.6 Hz), 108.42 (d, *J* = 26.8 Hz), 33.23.

6-chloro-3-methylbenzo[*d*]thiazole-2(3H)-thione (**2t**)¹



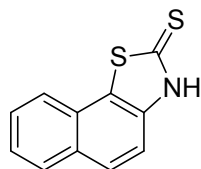
Yellow solid (32 mg, 76%); mp: 130-132 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 189.15, 140.61, 130.69, 128.70, 127.23, 120.97, 112.77, 33.17.

3-methyl-6-(trifluoromethyl)benzo[*d*]thiazole-2(3H)-thione (**2u**)



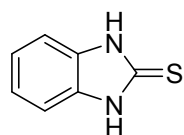
White solid (39 mg, 79%); mp: 127-129 °C; ¹H NMR(CDCl₃, 500 MHz) δ 7.73 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 190.48, 144.22, 127.96, 127.16 (q, *J* = 33.1 Hz), 124.26 (q, *J* = 3.6 Hz), 123.69 (q, *J* = 270.8 Hz), 118.54 (q, *J* = 3.8 Hz), 112.14, 33.27; HRMS (ESI) *m/z* calcd for C₉H₇F₃NS₂⁺ (M+H)⁺ 249.9967, found 249.9965.

naphtho[2,1-*d*]thiazole-2(3H)-thione (**2v**)¹⁰



Yellow solid (29 mg, 66%); mp: 219-221 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 14.01 (s, 1H), 8.01 (d, *J* = 8.5, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 188.87, 139.35, 130.30, 129.57, 128.78, 128.47, 126.62, 126.25, 124.84, 123.66, 113.07.

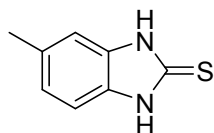
1H-benzo[*d*]imidazole-2(3H)-thione (**4a**)¹¹



Colorless solid (39 mg, 65%); mp: >250 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 12.53

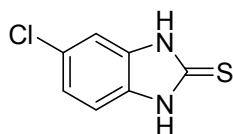
(s, 2H), 7.13 - 7.11 (m, 4H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 168.54, 132.69, 122.78, 109.94.

5-methyl-1H-benzo[*d*]imidazole-2(3H)-thione (**4b**)¹²



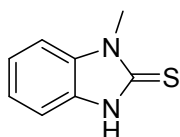
Pale yellow solid (36 mg, 55%); mp: >250 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 12.40 (s, 2H), 7.01 (s, J = 8.0 Hz, 1H), 6.94 - 6.91 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 168.23, 132.93, 132.11, 130.67, 123.66, 110.07, 109.58, 21.41.

5-chloro-1H-benzo[*d*]imidazole-2(3H)-thione (**4c**)¹²



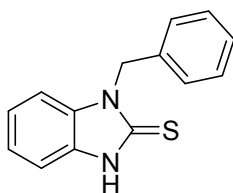
Gray solid (55 mg, 75%); mp: >250 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 12.66 (s, 2H), 7.13 - 7.10 (m, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 169.73, 133.69, 131.70, 127.15, 122.68, 110.99, 109.65.

1-methyl-1H-benzo[*d*]imidazole-2(3H)-thione (**4d**)¹³



Colorless solid (32 mg, 50%); mp: 191-193 °C; ^1H NMR (CDCl₃, 500 MHz) δ 11.87 (s, 1H), 7.29 - 7.28 (m, 1H), 7.22 - 7.17 (m, 2H), 7.14 - 7.12 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (CDCl₃, 125 MHz) δ 168.03, 133.22, 130.47, 123.35, 122.79, 110.16, 108.98, 30.43.

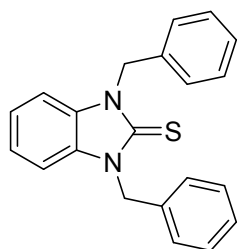
1-benzyl-1H-benzo[*d*]imidazole-2(3H)-thione (**4e**)¹⁴



Pale yellow solid (48 mg, 50%); mp: 186-187 °C; ^1H NMR (CDCl₃, 500 MHz) δ

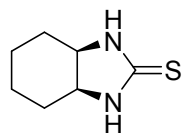
12.01 (s, 1H), 7.36 (d, $J = 7.5$ Hz, 2H), 7.32 - 7.24 (m, 4H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 5.55 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 168.52, 135.31, 132.55, 130.66, 128.74, 127.83, 127.44, 123.45, 122.88, 110.24, 109.79, 47.64.

1,3-dibenzyl-1H-benzo[d]imidazole-2(3H)-thione (**4f**)



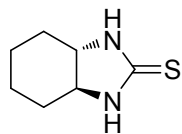
Yellow solid (60 mg, 46%); mp: 181-183 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.38 (d, $J = 7.0$ Hz, 4H), 7.32 - 7.29 (m, 4H), 7.27 - 7.23 (m, 2H), 7.09 - 7.04 (m, 4H), 5.63 (s, 4H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 170.97, 135.60, 131.97, 128.73, 127.77, 127.45, 123.02, 109.62, 48.54; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 331.1264, found 331.1263.

(3aR,7aS)-hexahydro-1H-benzo[d]imidazole-2(3H)-thione (**4ga**)¹⁵



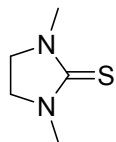
Pale yellow solid (26 mg, 42%); mp: 164-166 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 6.92 (s, 2H), 3.88 - 3.84 (m, 2H), 1.71 - 1.62 (m, 4H), 1.56 - 1.49 (m, 2H), 1.32 - 1.26 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 184.16, 56.04, 27.01, 19.89.

(3aS,7aS)-hexahydro-1H-benzo[d]imidazole-2(3H)-thione(**4gb**)¹⁶



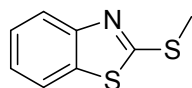
Pale yellow solid (28 mg, 46%); mp: 148-150 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 6.90 (s, 2H), 3.36 - 3.24 (m, 2H), 2.06 (d, $J = 12.0$ Hz, 2H), 1.83 - 1.75 (m, 2H), 1.50 - 1.43 (m, 2H), 1.34 - 1.24 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 187.09, 64.69, 28.88, 23.75.

1,3-dimethylimidazolidine-2-thione (**4h**)¹⁷



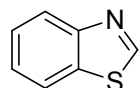
Colorless solid (7 mg, 24%); mp: 110-120 °C; ¹H NMR (CDCl₃, 500 MHz) δ 3.50 (s, 4H), 3.09 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 183.33, 48.18, 35.00.

2-(Methylthio)benzothiazole (**H**)⁵



white solid(13 mg, 35%); ¹H NMR (CDCl₃, 500 MHz) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 2.80 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 168.05, 153.35, 135.12, 126.04, 124.07, 121.37, 120.94, 15.91.

benzo[*d*]thiazole (**G**)¹



light yellow liquid(2 mg, 5%); ¹H NMR (CDCl₃, 500 MHz) δ 9.02 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.98 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 153.96, 153.14, 133.65, 126.17, 125.54, 123.60, 121.88.

5) References

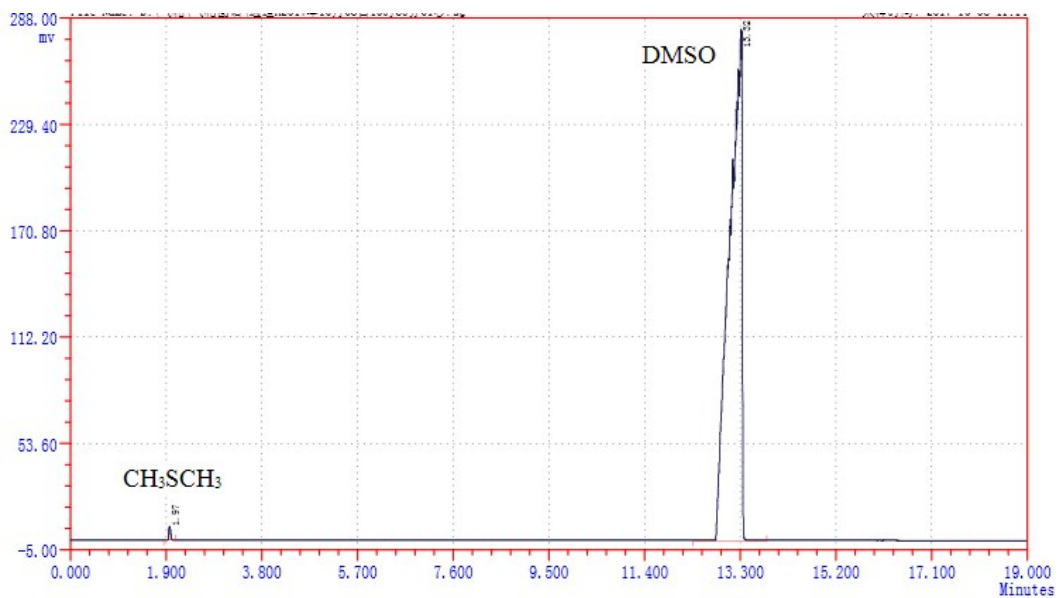
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- 7 Z.-J. Quan, R.-G. Ren, Y.-X. Da, Z. Zhang, X.-C. Wang, *Heteroat. Chem.*, 2011, **22**,

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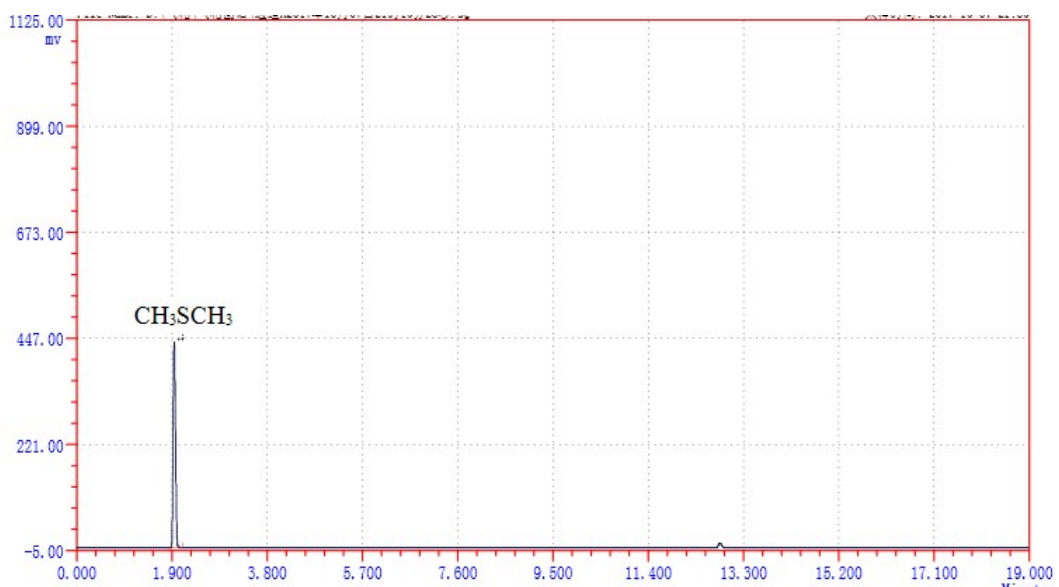
6) Mechanism Study

GC-MS and GC Analyses of the Composition of the Reactions

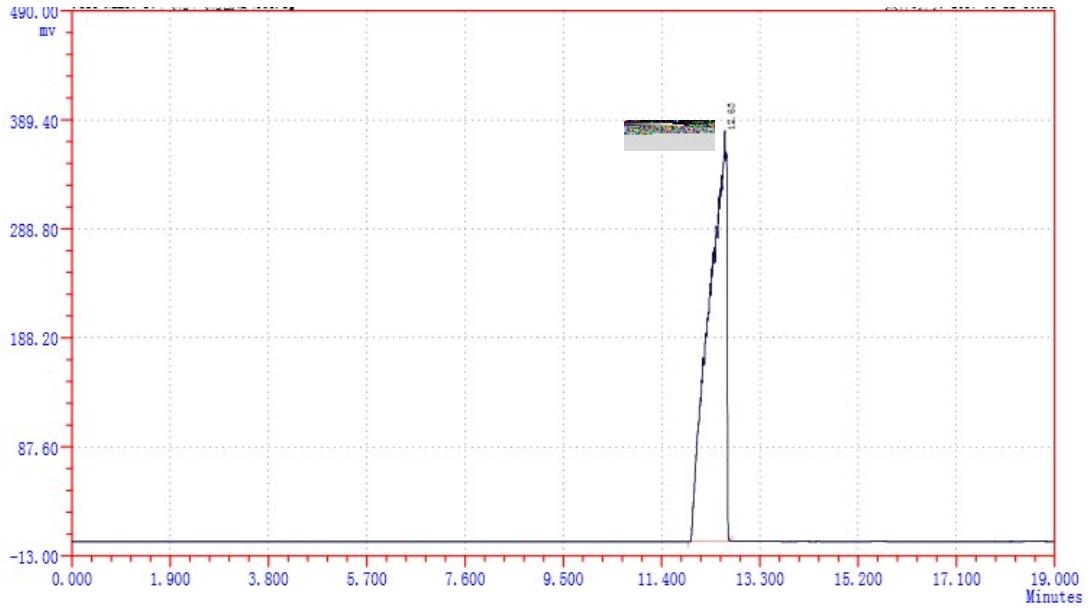
Experiment 1: The sealed Schlenk tube was charged with *o*-iodoaniline **1a** (0.2 mmol), K₂S (1.2 mmol), and methyl phenyl sulfoxide (0.5 mL). Then, under the protection of nitrogen atmosphere, the mixture was stirred at 140 °C for 12 h. Then, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was detected by GC-MS, and compounds **2aa**, **2ab** and **2ac** were detected from the reaction mixture via GC-MS analysis. The results revealed that the reaction mixture contained compounds **2aa**, **2ab** and **2ac**. The remaining combination of organic layer was dried over Na₂SO₄, and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the pure product **2a** in 60% yield.



GC analysis of standard sample methyl sulfide

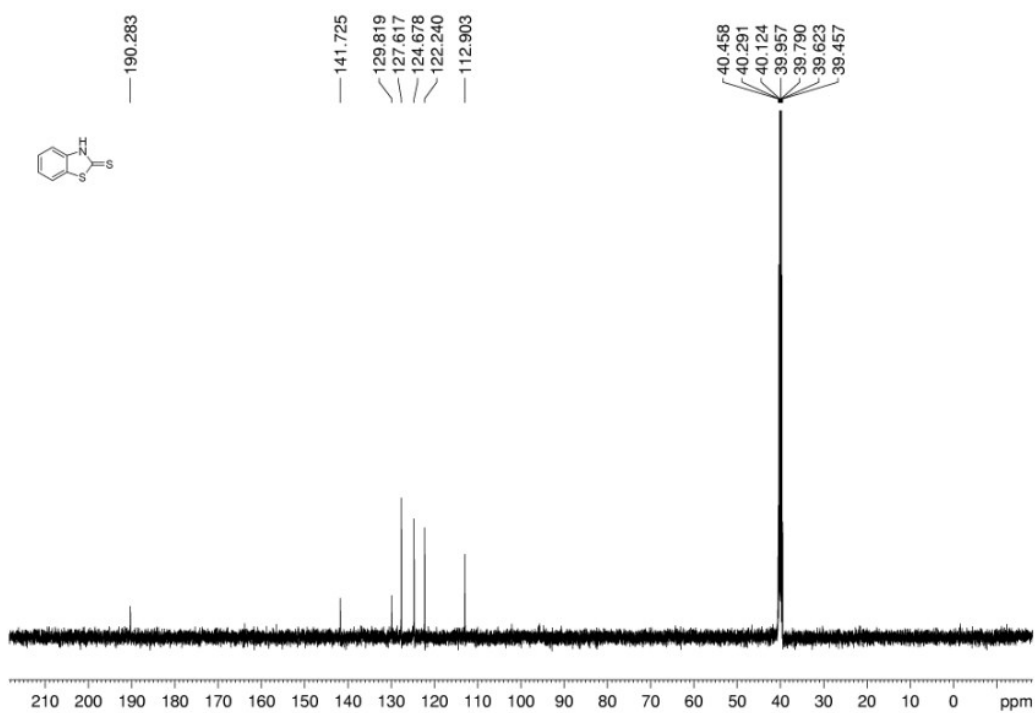
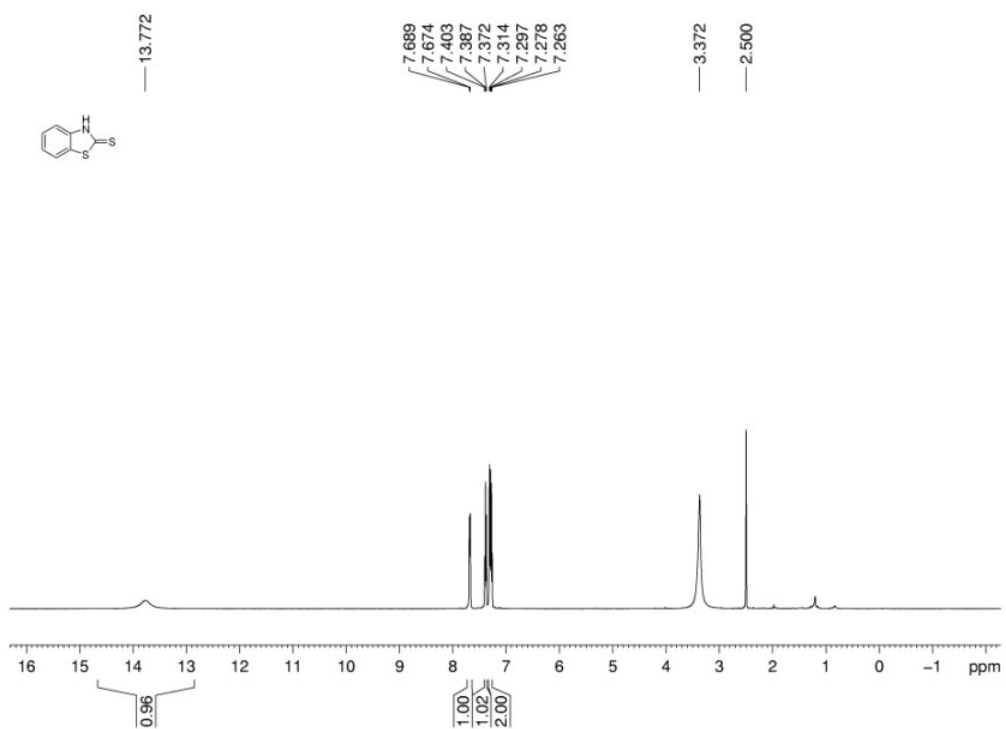


GC analysis of standard sample DMSO

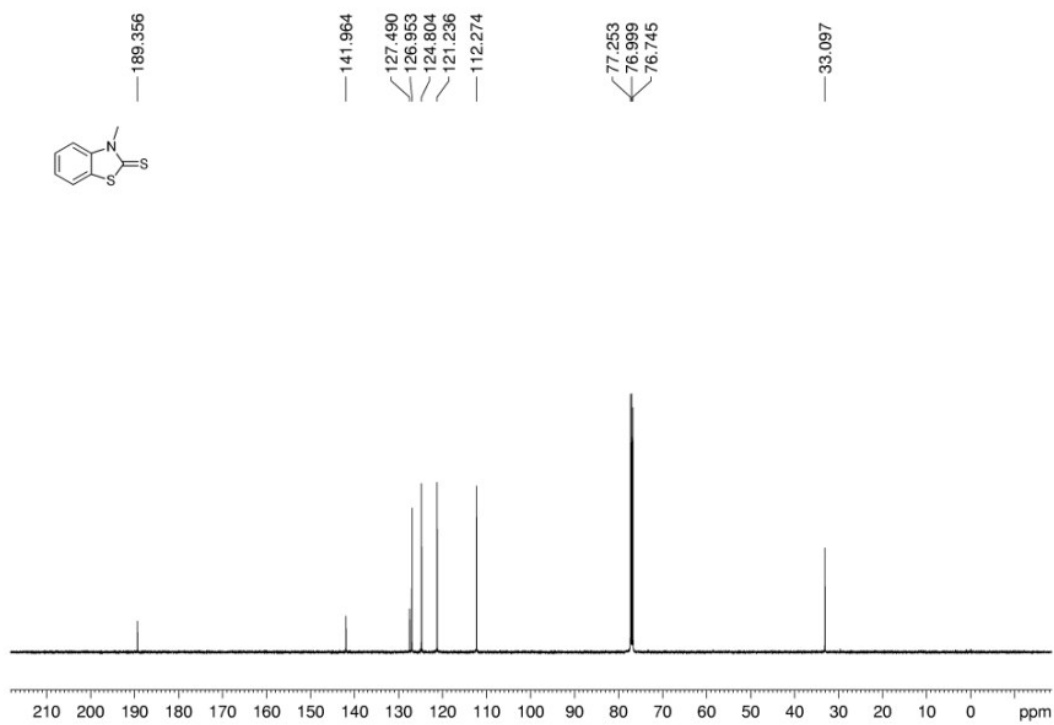
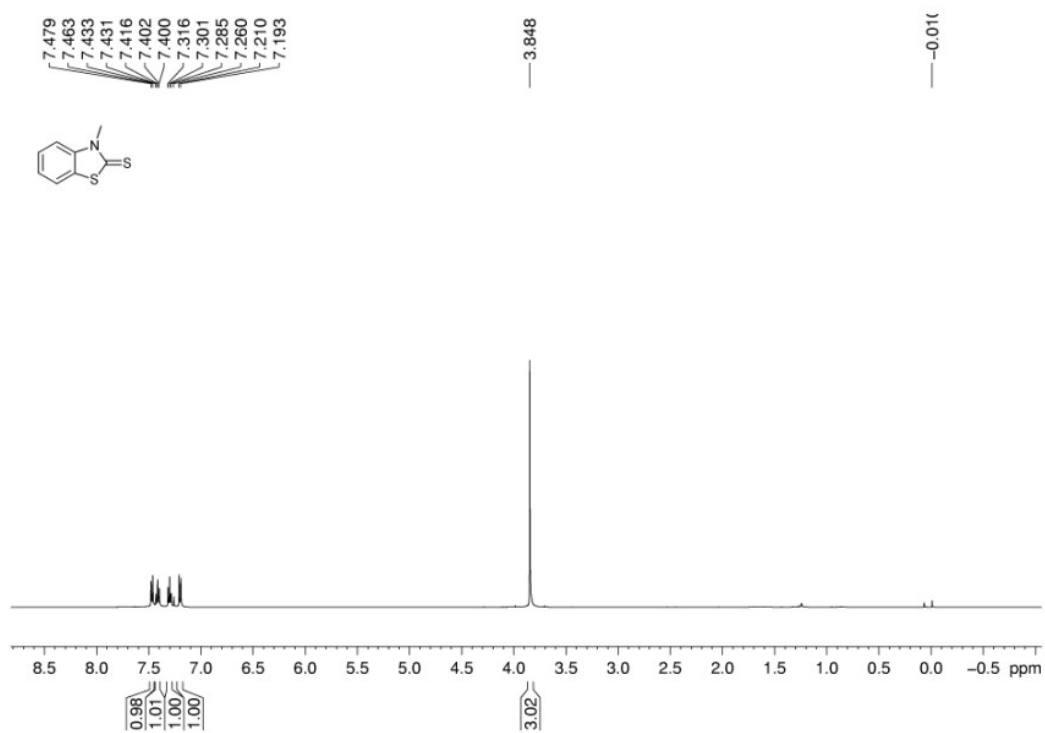


7) ^1H NMR and ^{13}C NMR Spectra of Products

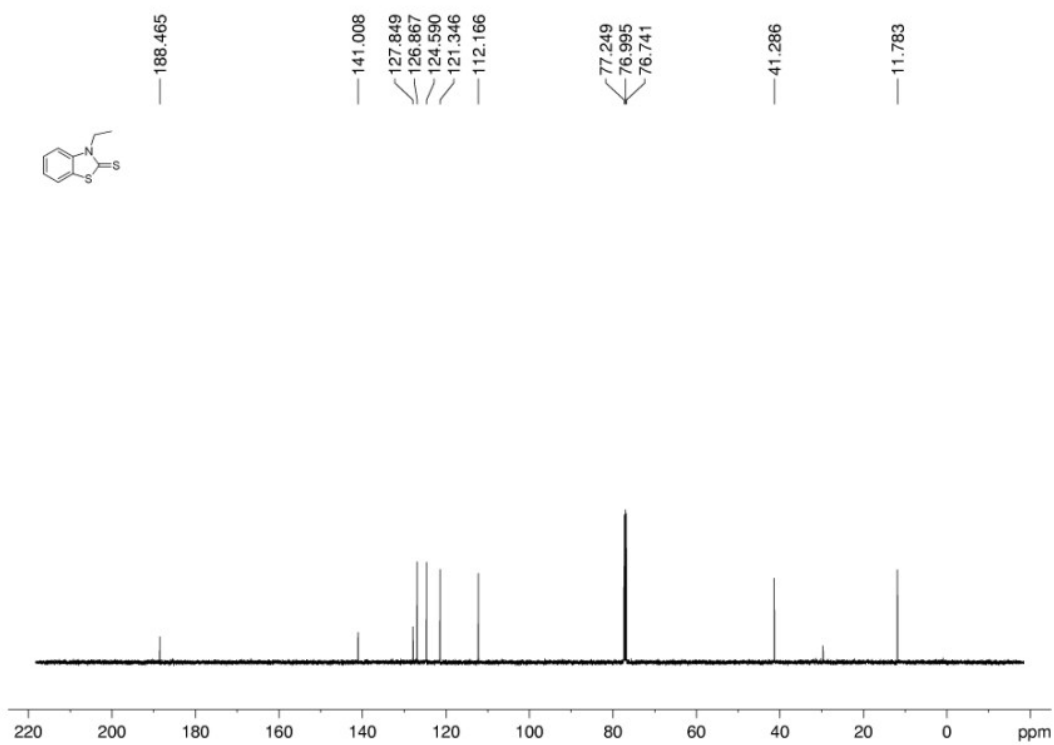
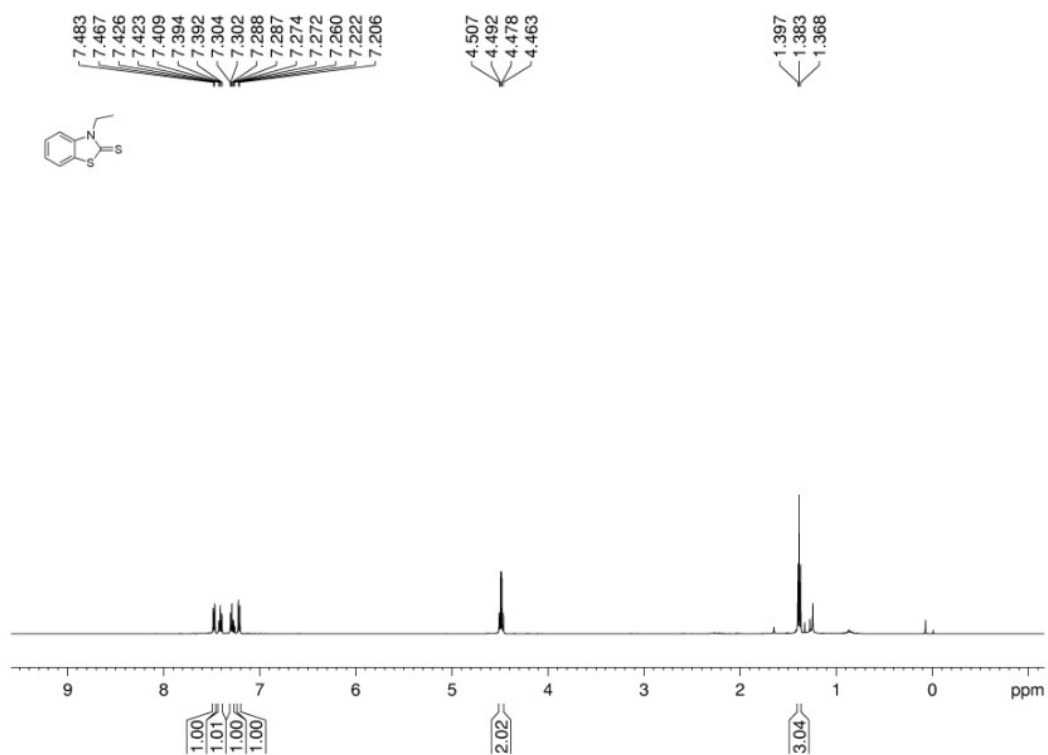
^1H and ^{13}C Spectrum of Compound **2a**



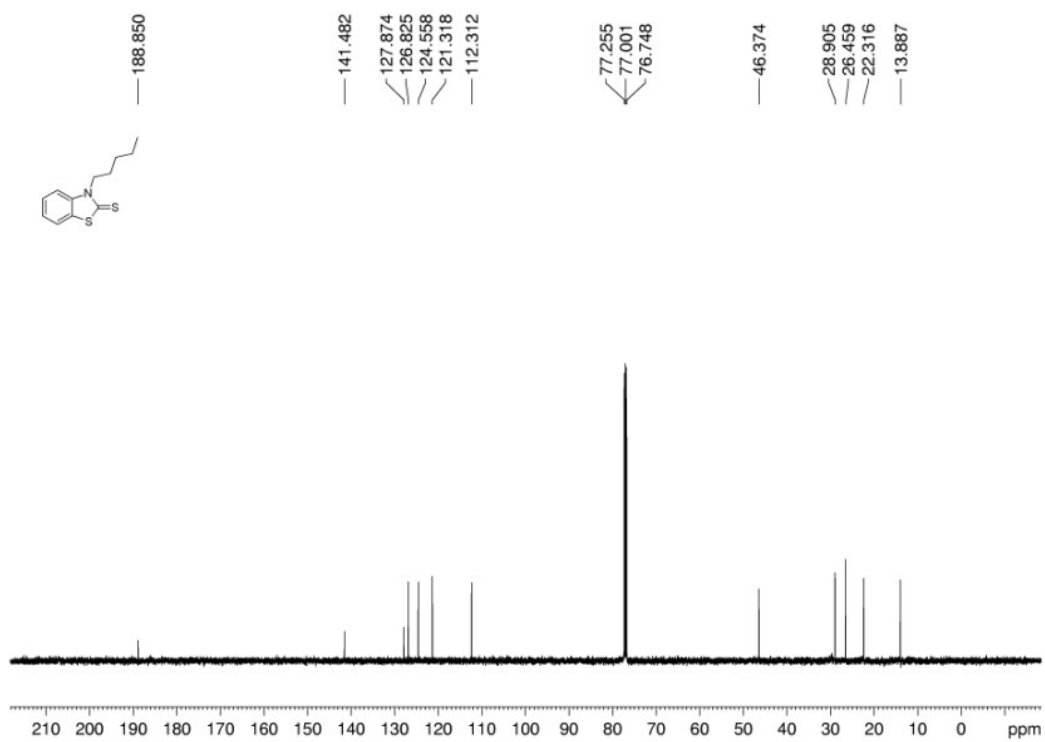
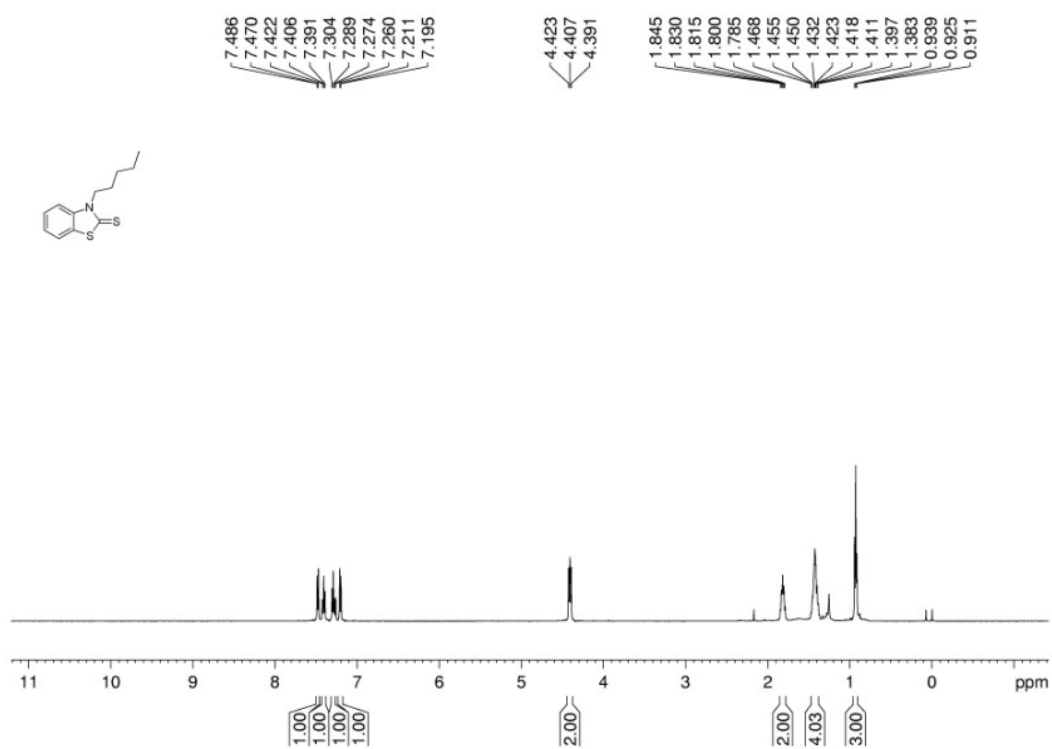
^1H and ^{13}C Spectrum of Compound **2b**



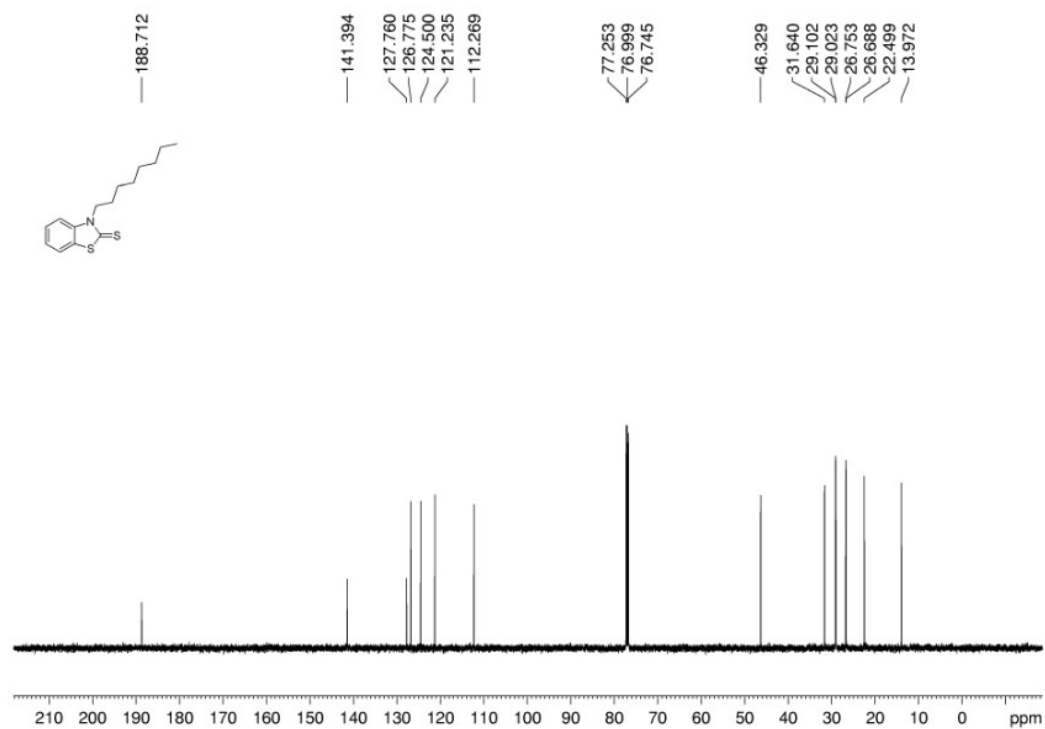
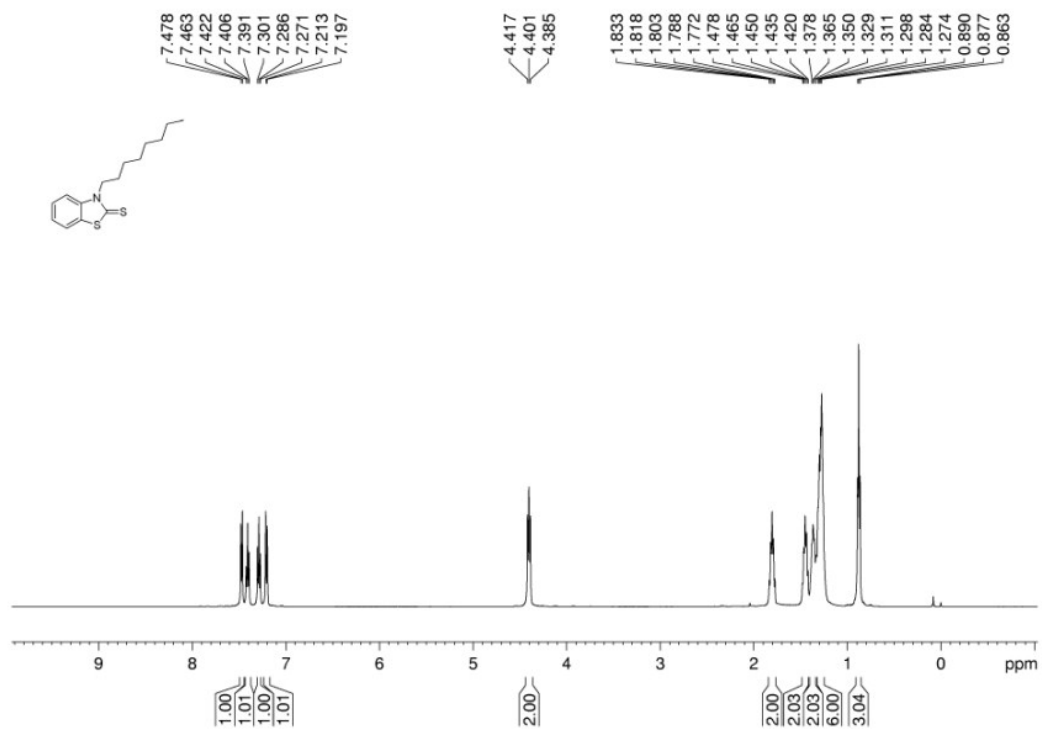
^1H and ^{13}C Spectrum of Compound **2c**



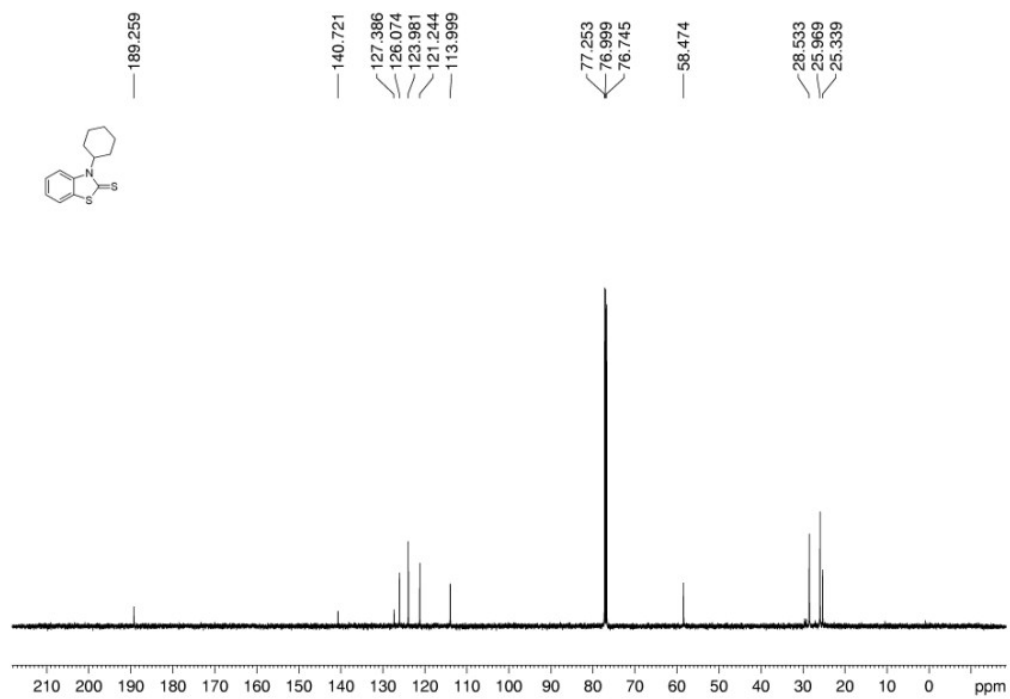
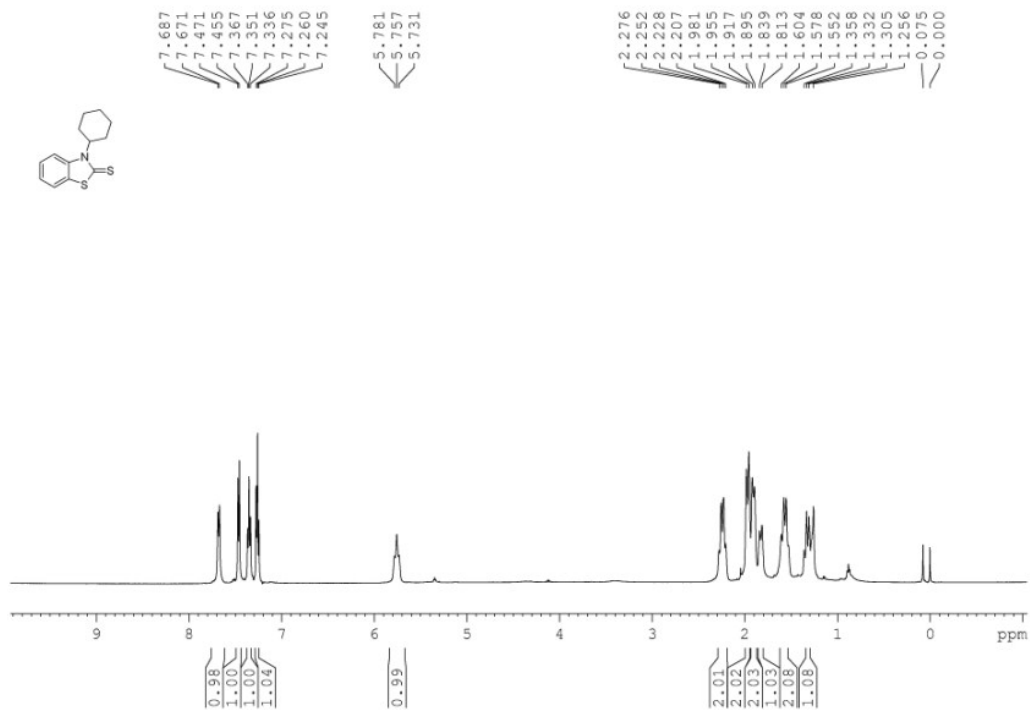
^1H and ^{13}C Spectrum of Compound **2d**



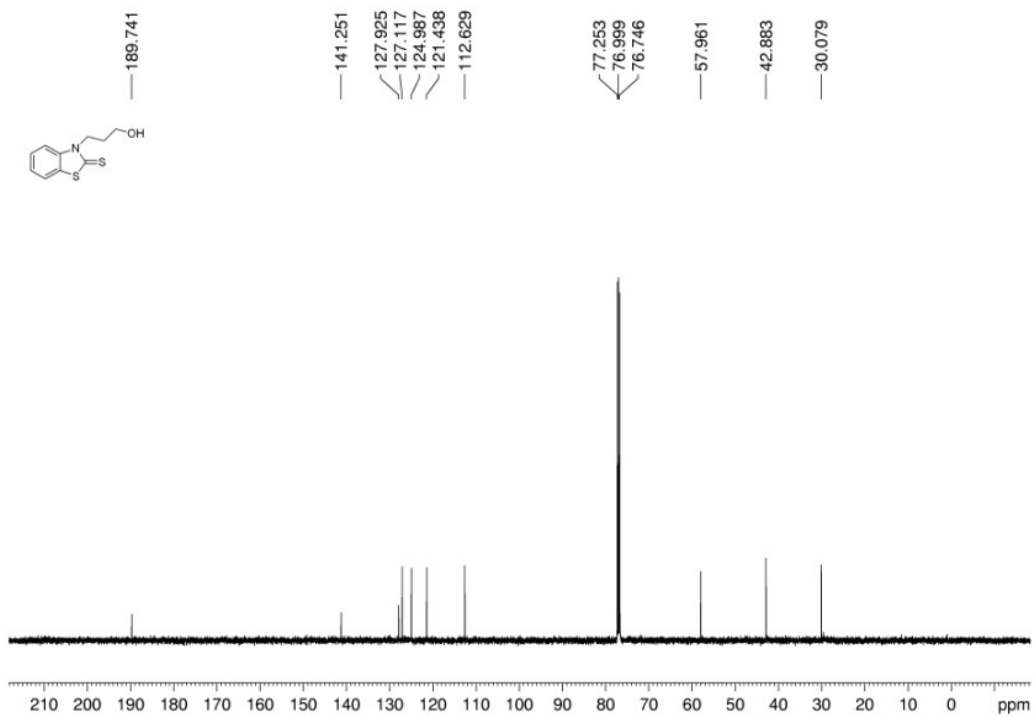
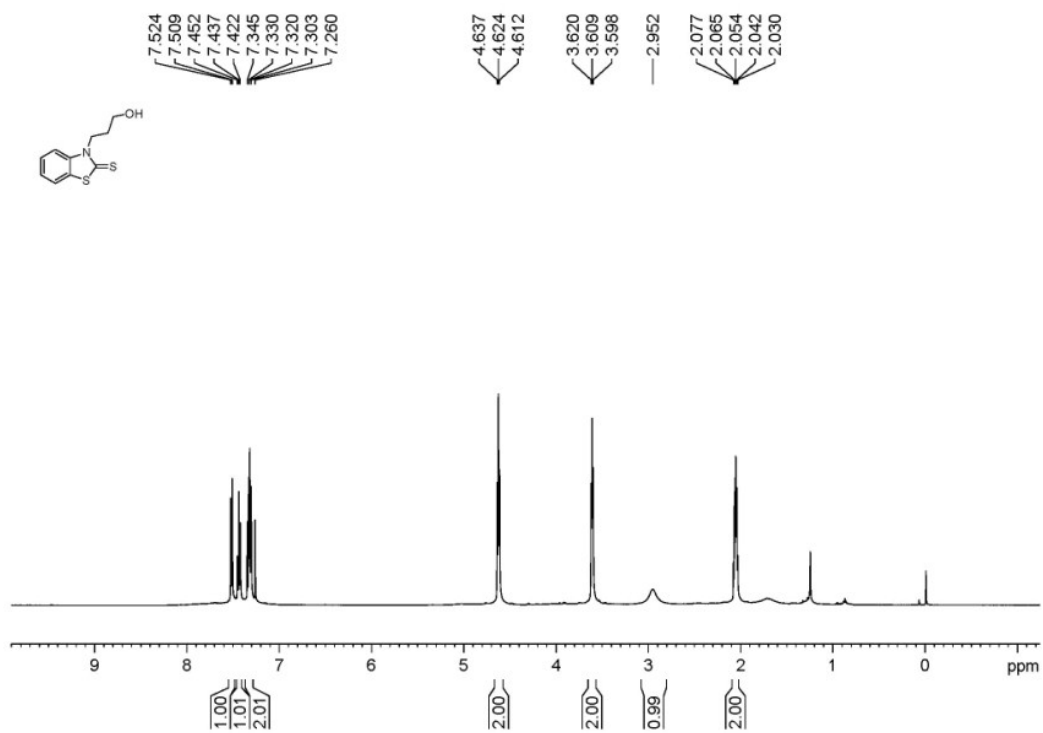
^1H and ^{13}C Spectrum of Compound **2e**



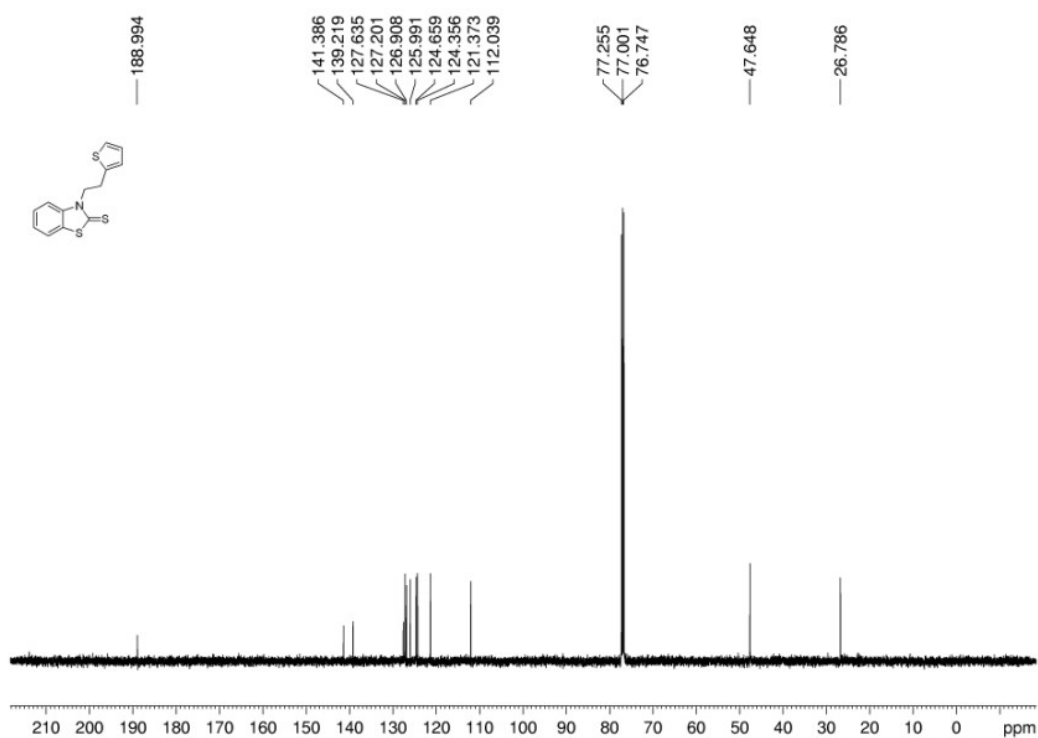
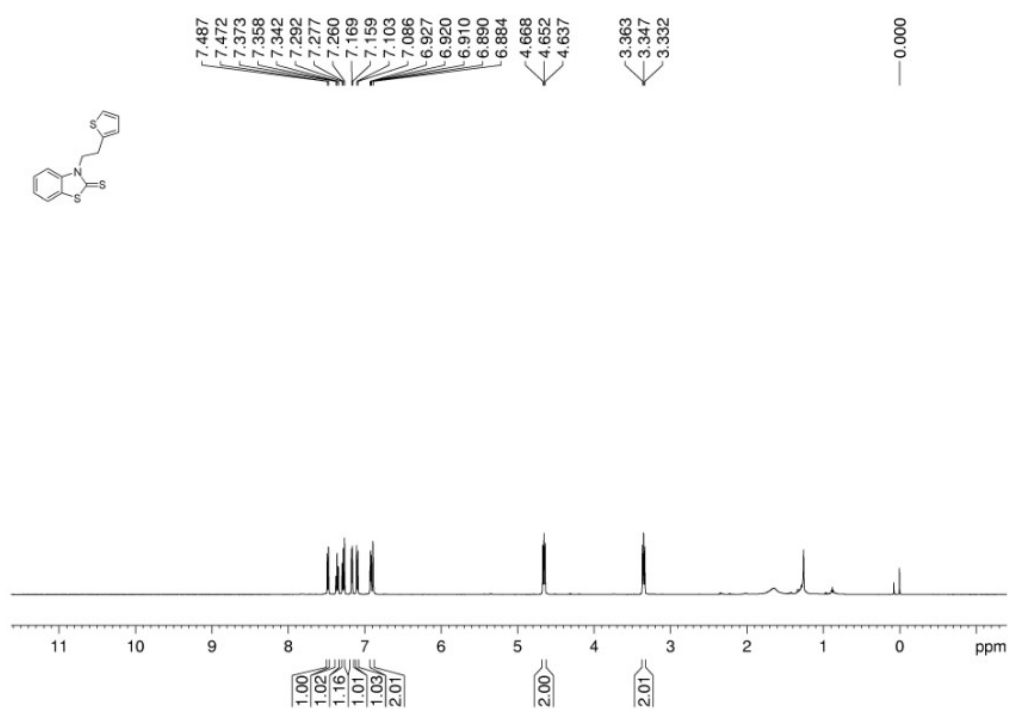
^1H and ^{13}C Spectrum of Compound **2f**



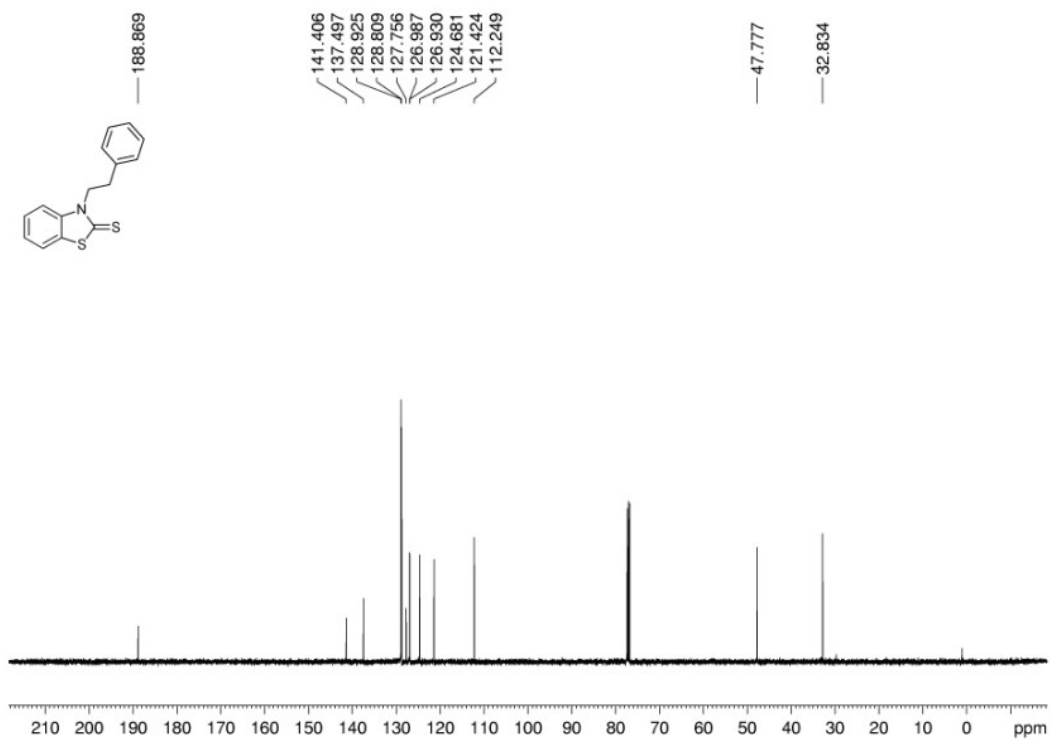
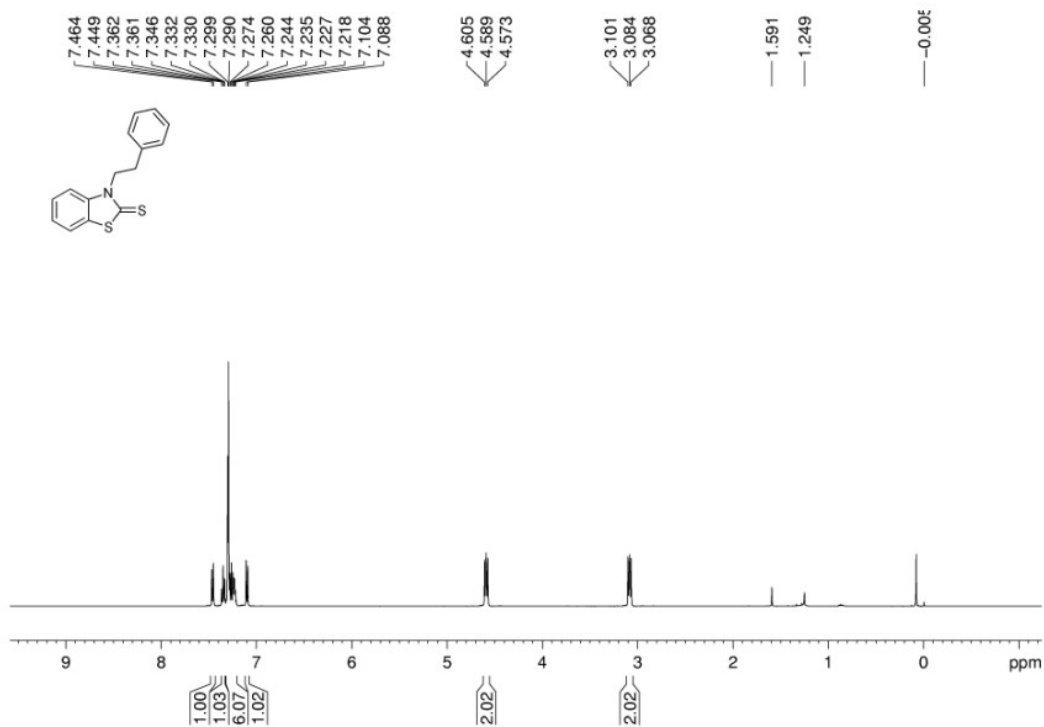
^1H and ^{13}C Spectrum of Compound **2g**



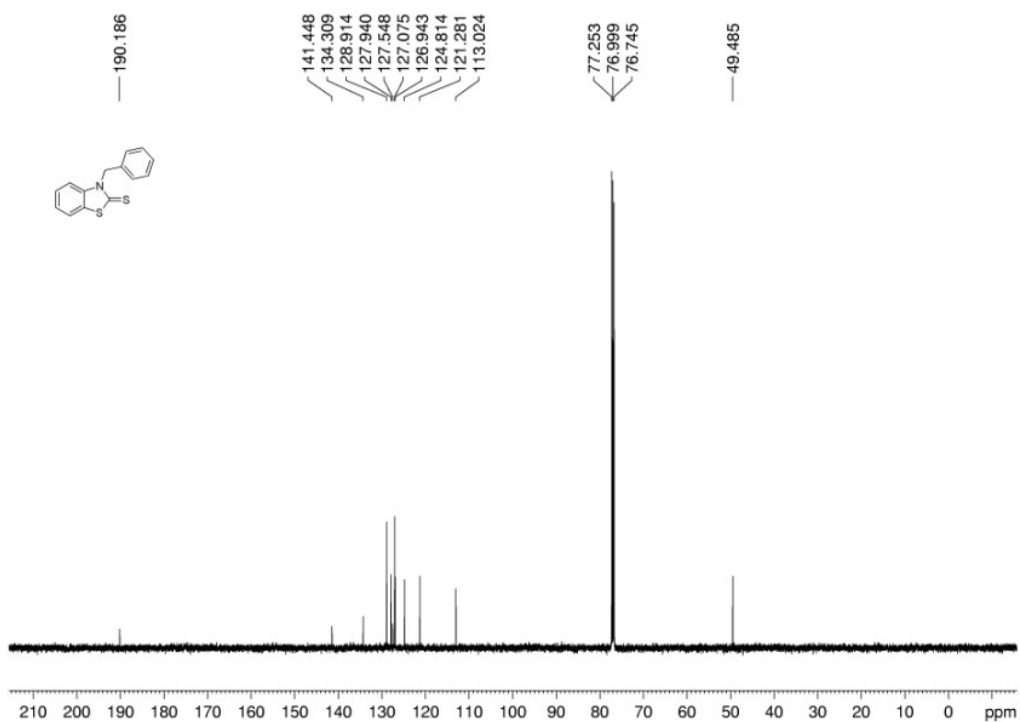
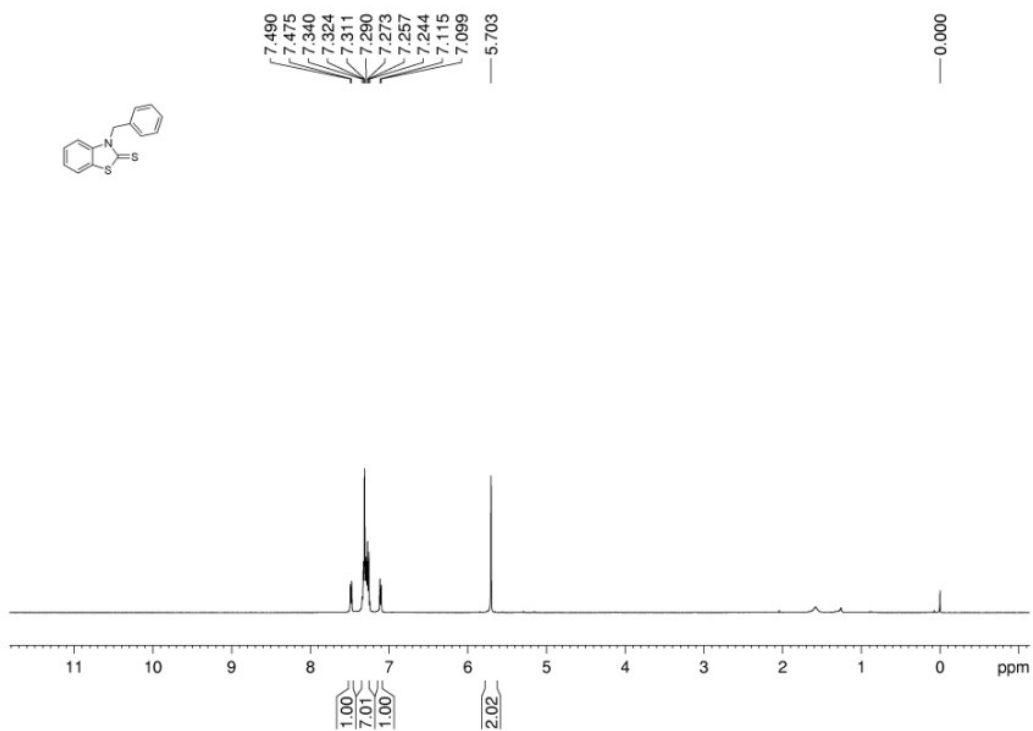
^1H and ^{13}C Spectrum of Compound **2h**



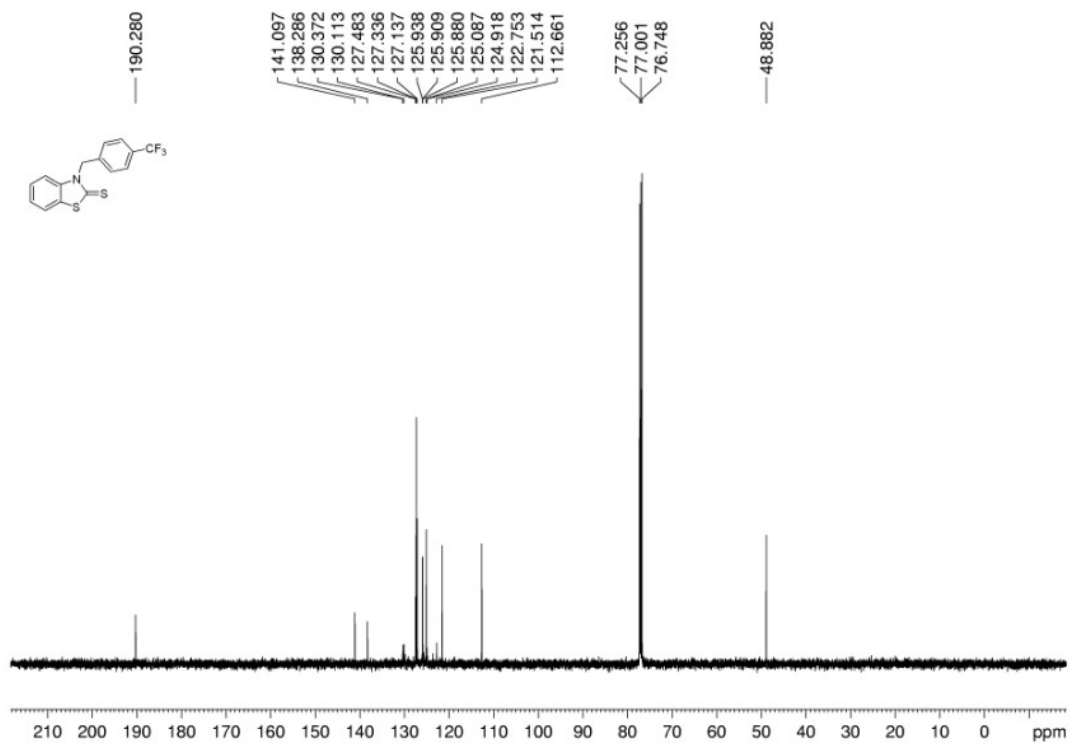
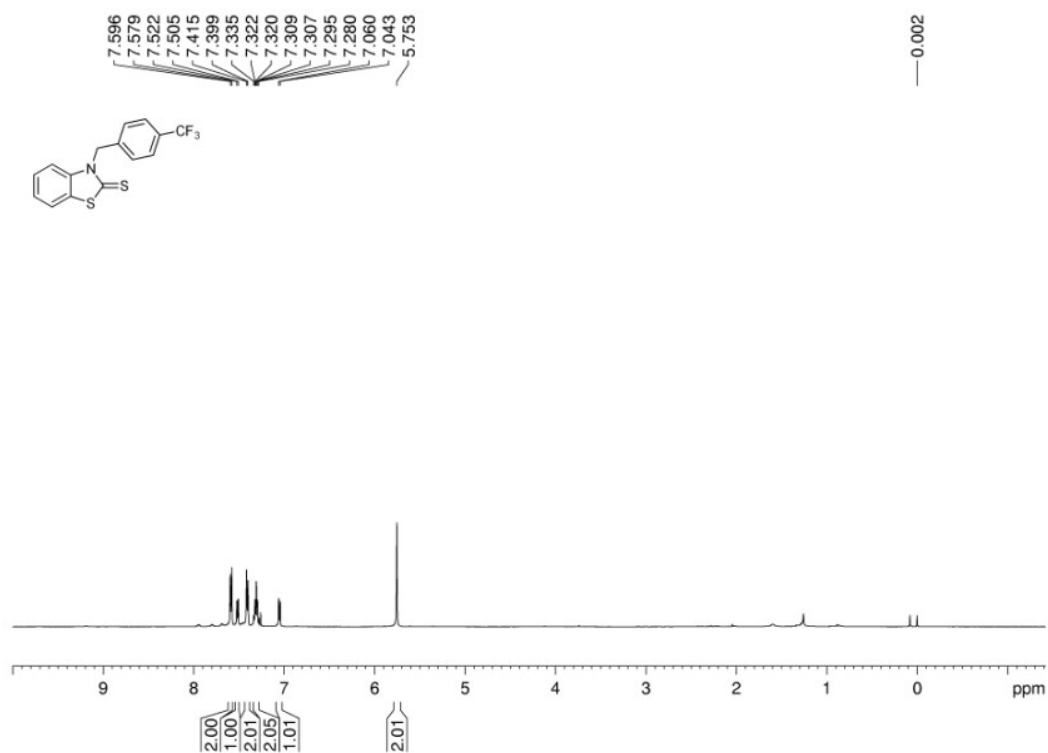
^1H and ^{13}C Spectrum of Compound **2i**



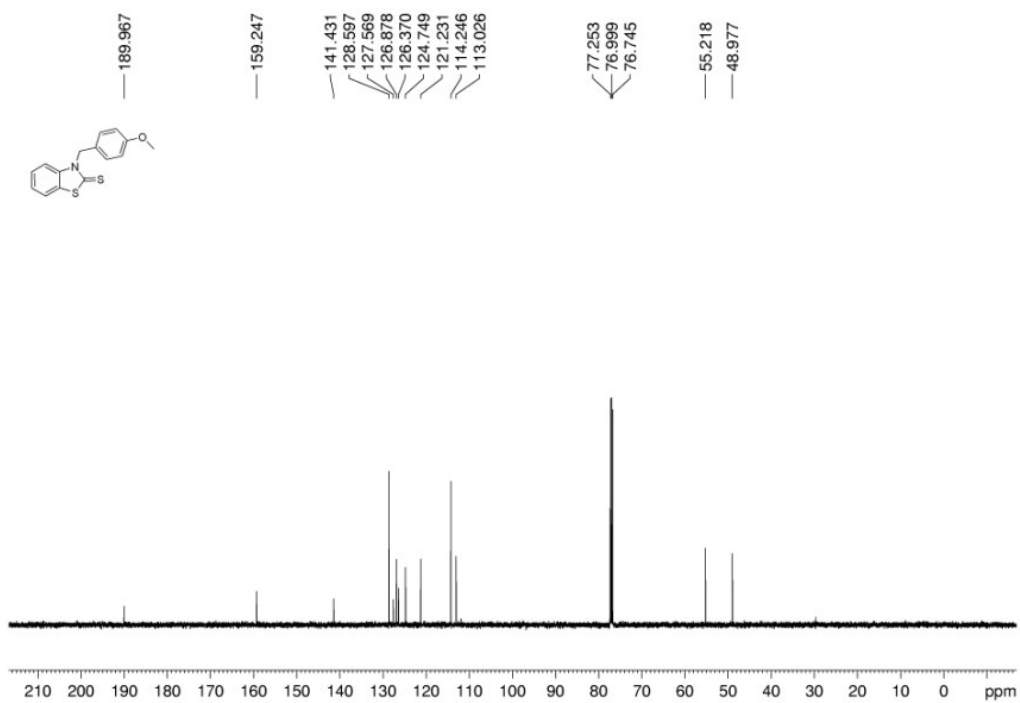
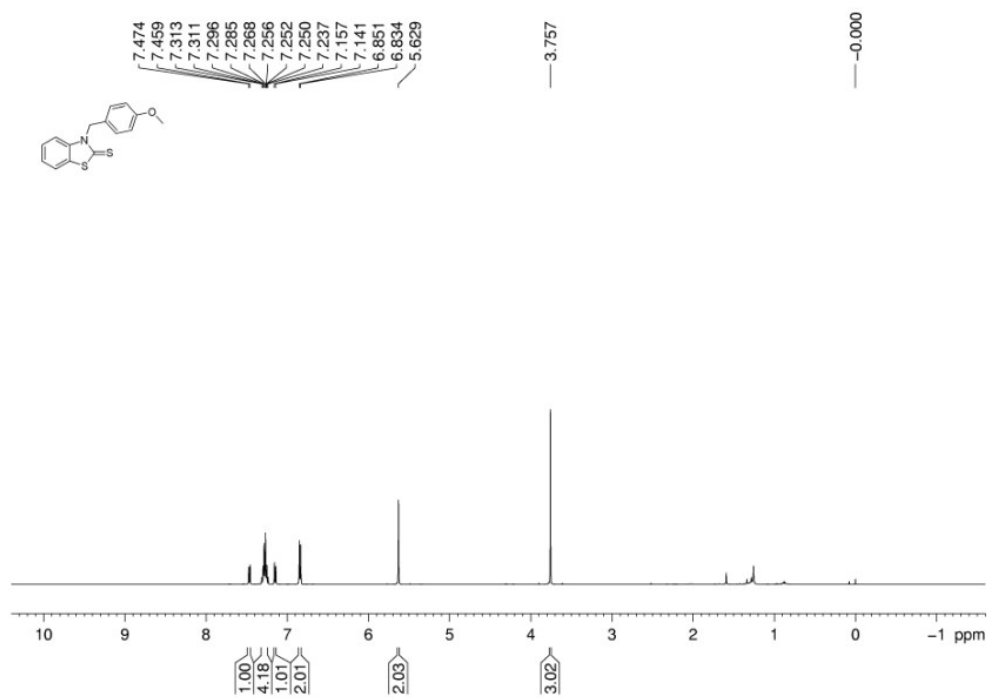
^1H and ^{13}C Spectrum of Compound **2j**



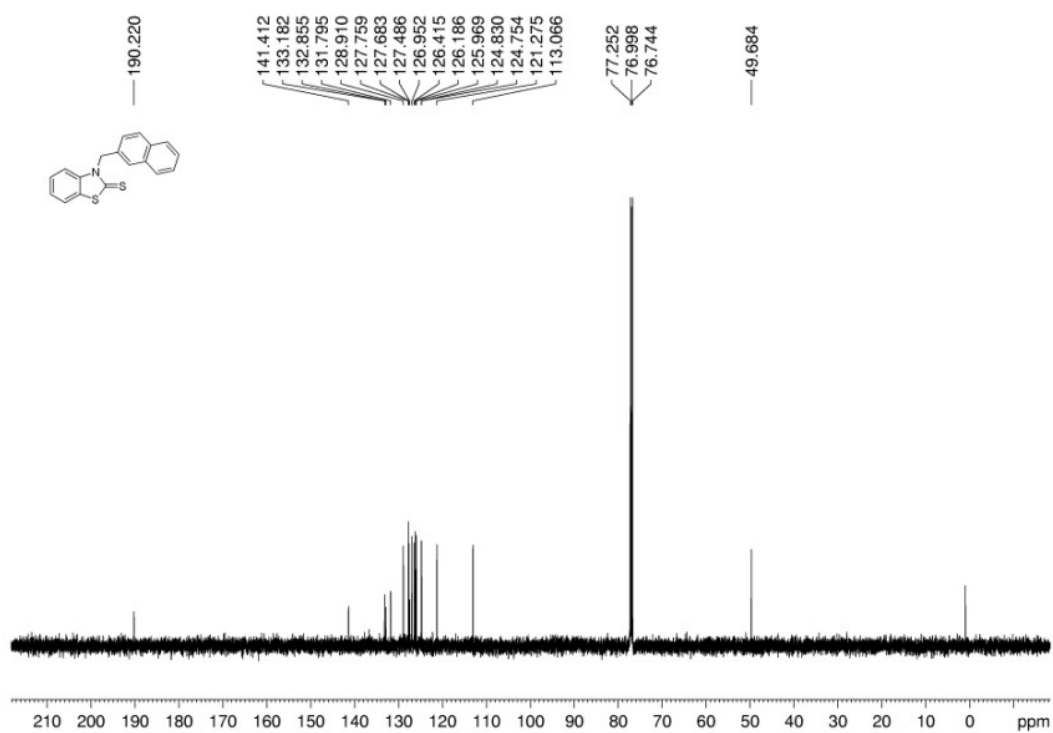
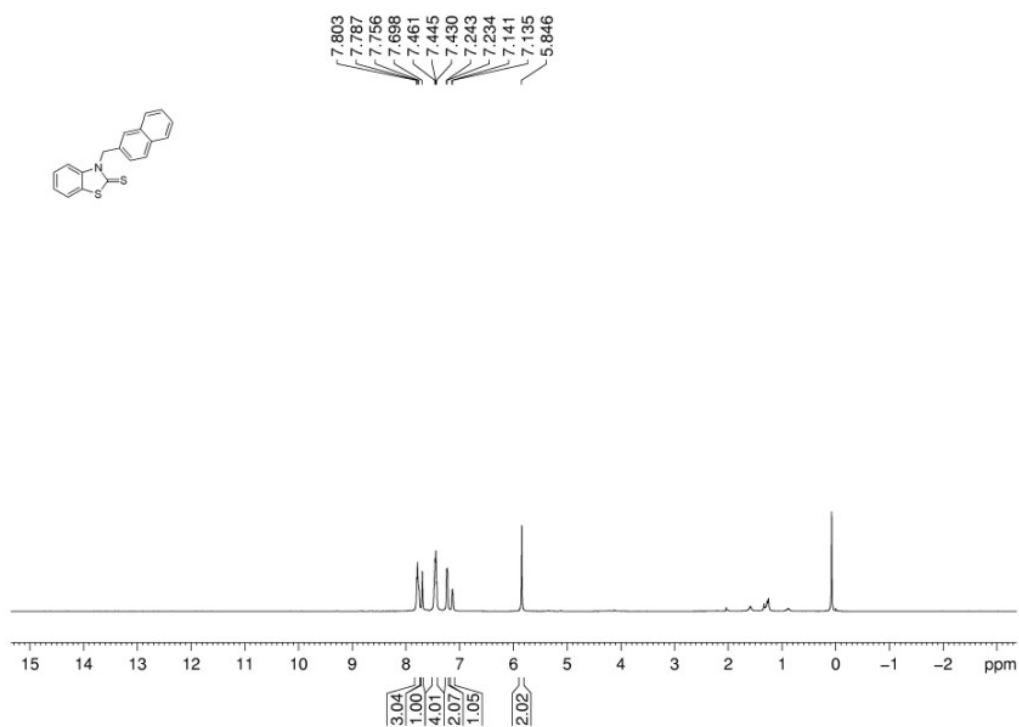
¹H and ¹³C Spectrum of Compound **2k**



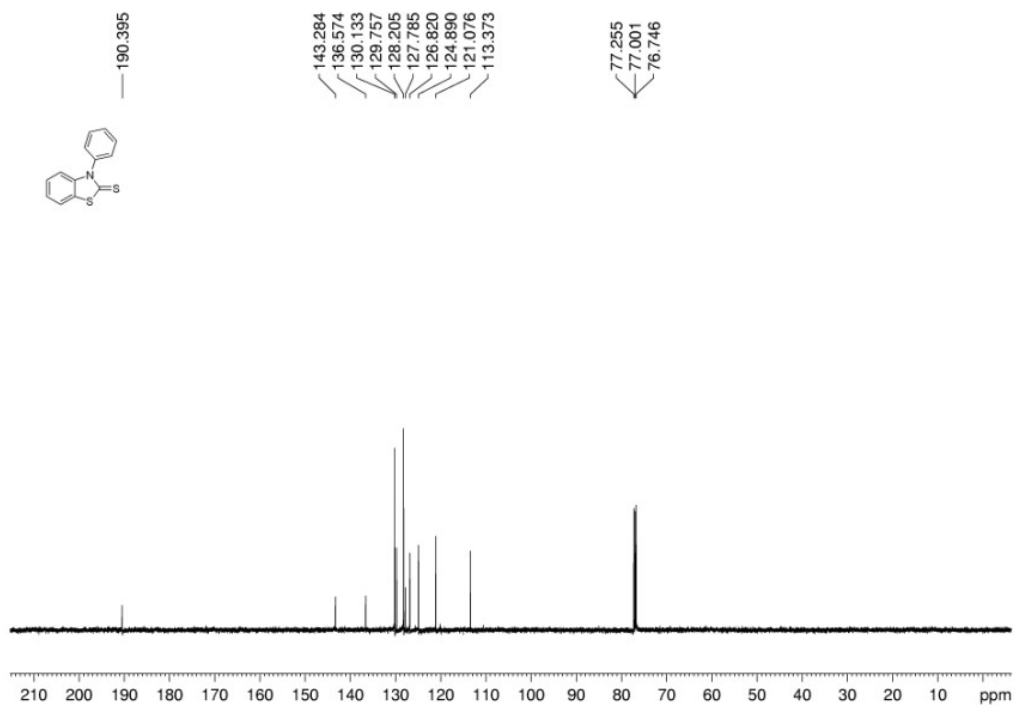
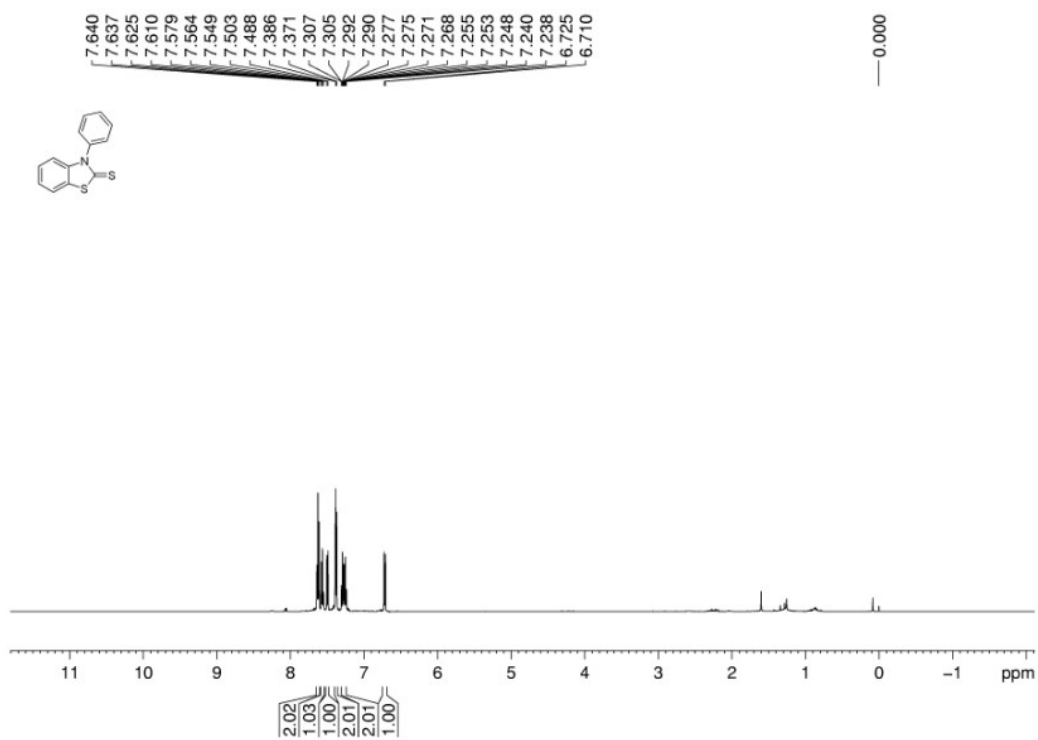
^1H and ^{13}C Spectrum of Compound **2I**



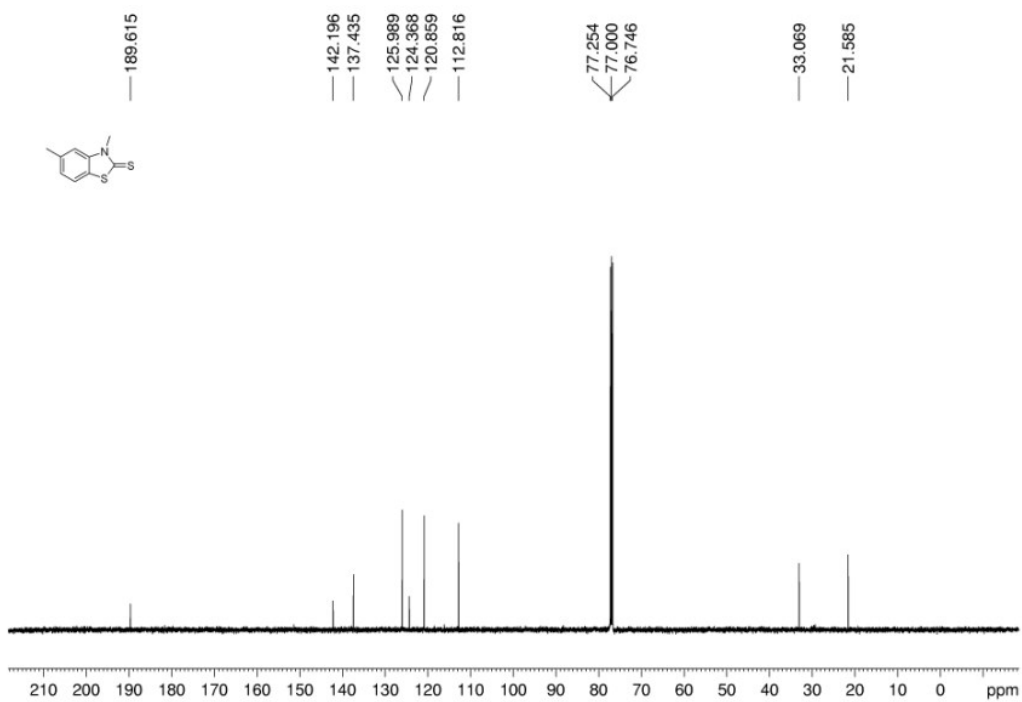
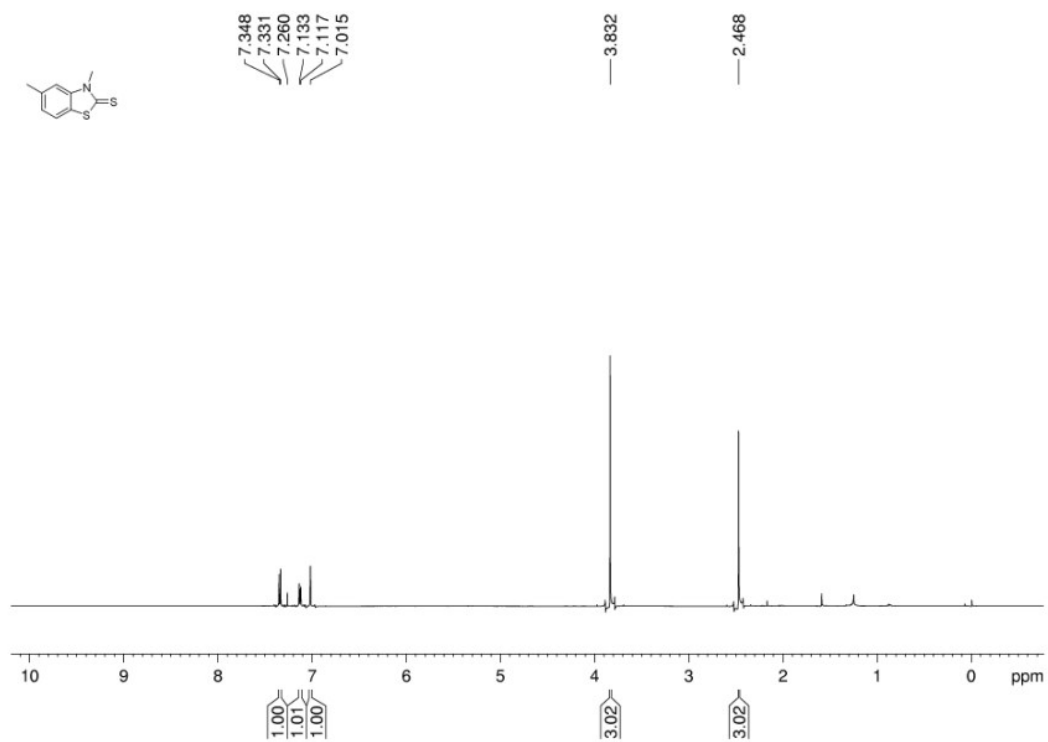
^1H and ^{13}C Spectrum of Compound **2m**



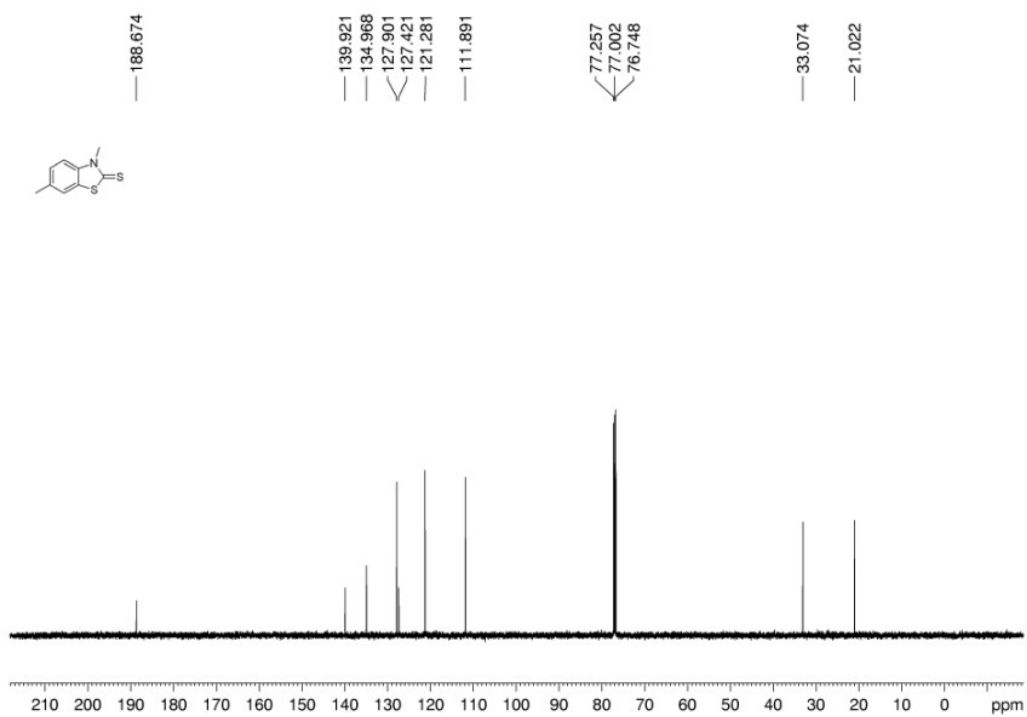
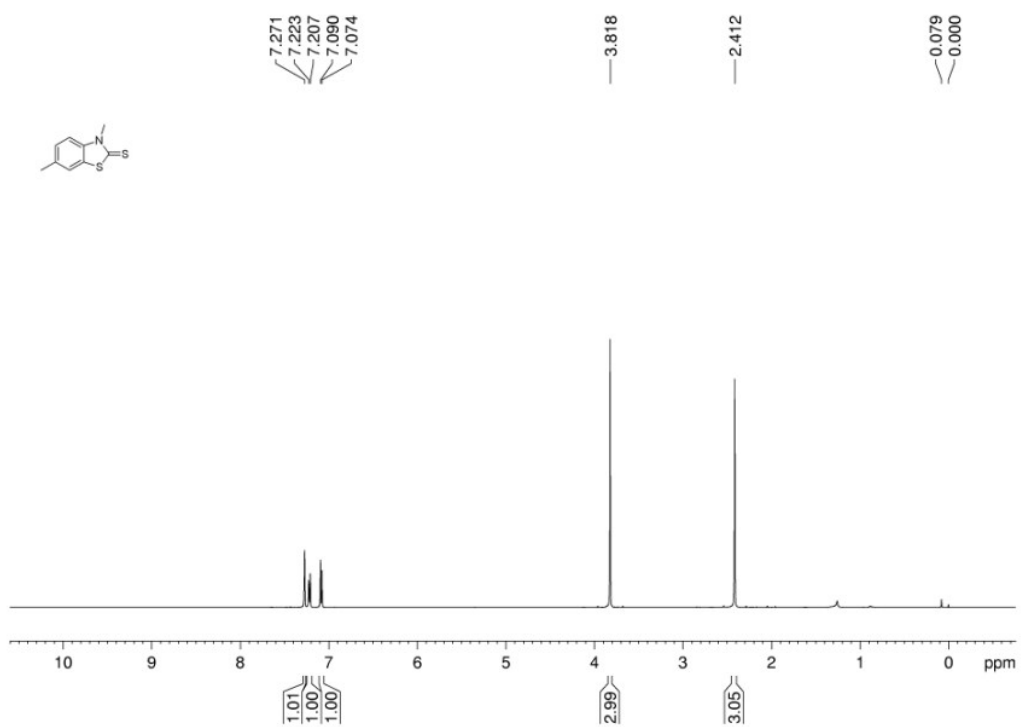
^1H and ^{13}C Spectrum of Compound **2n**



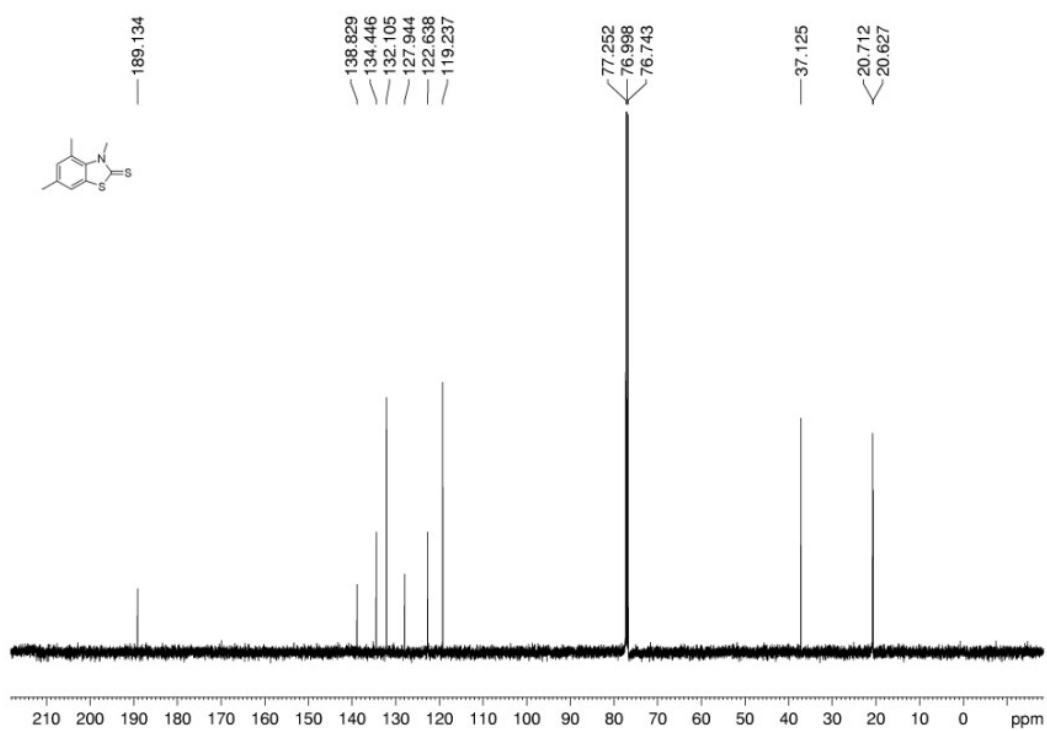
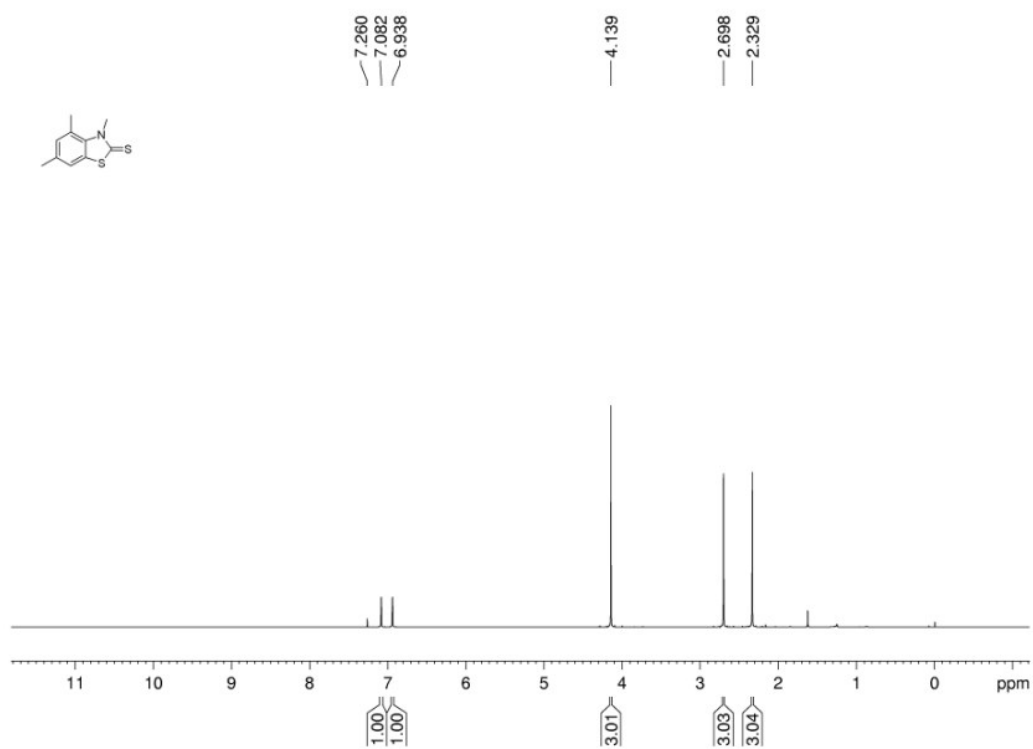
^1H and ^{13}C Spectrum of Compound **2o**



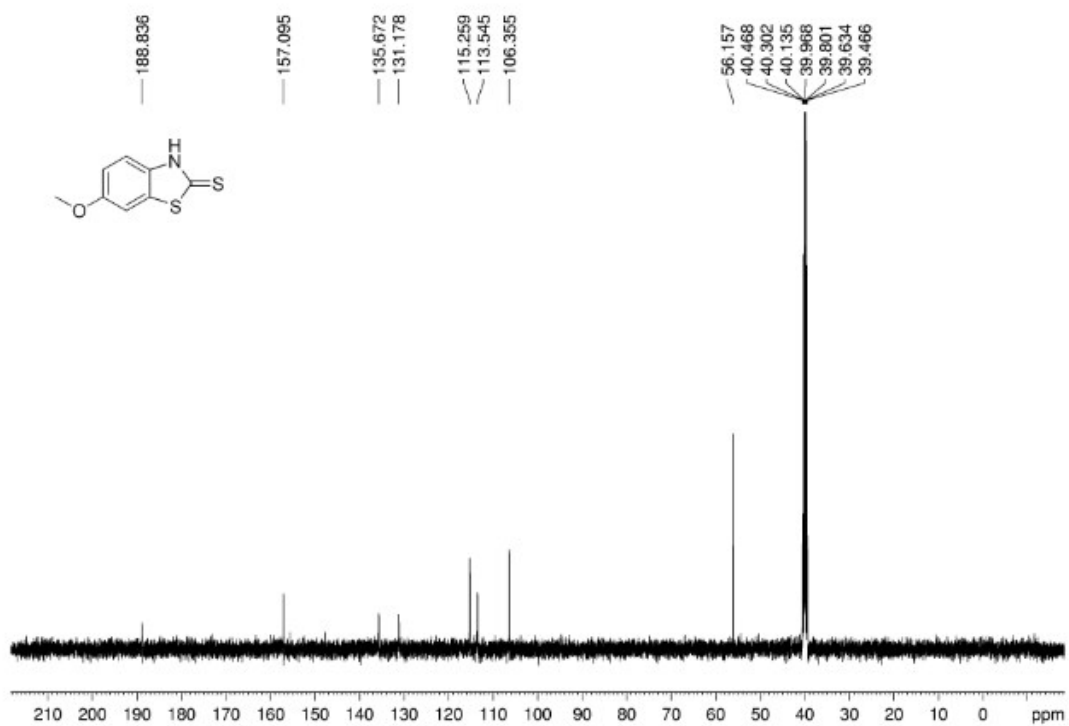
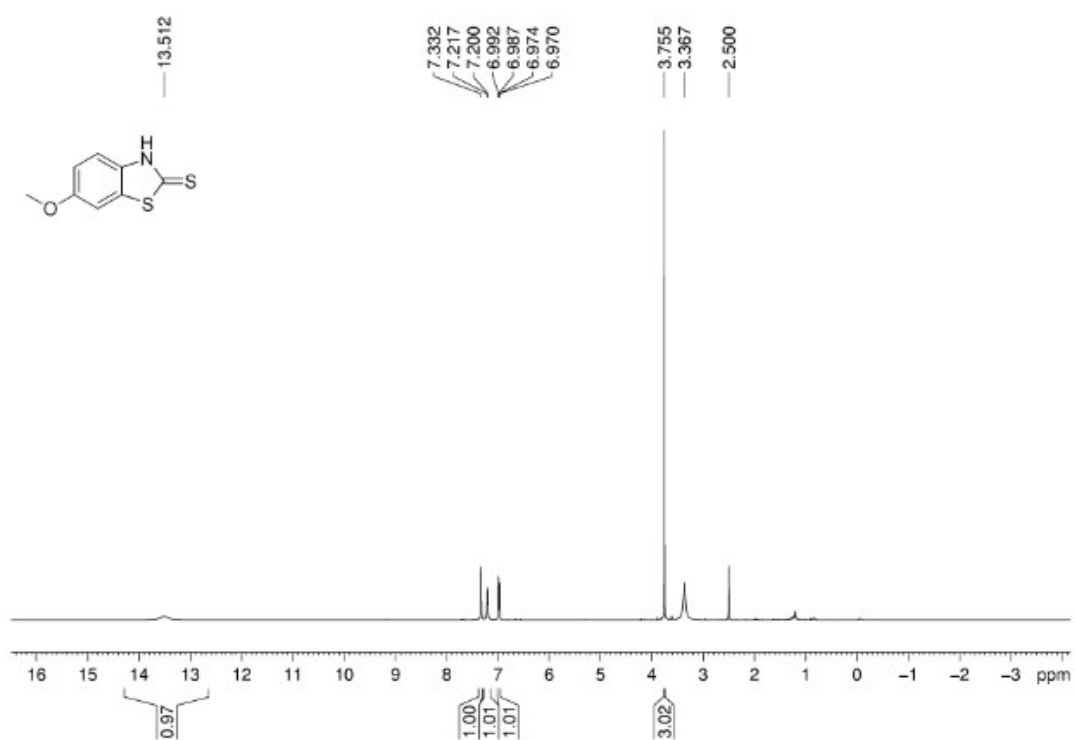
^1H and ^{13}C Spectrum of Compound **2p**



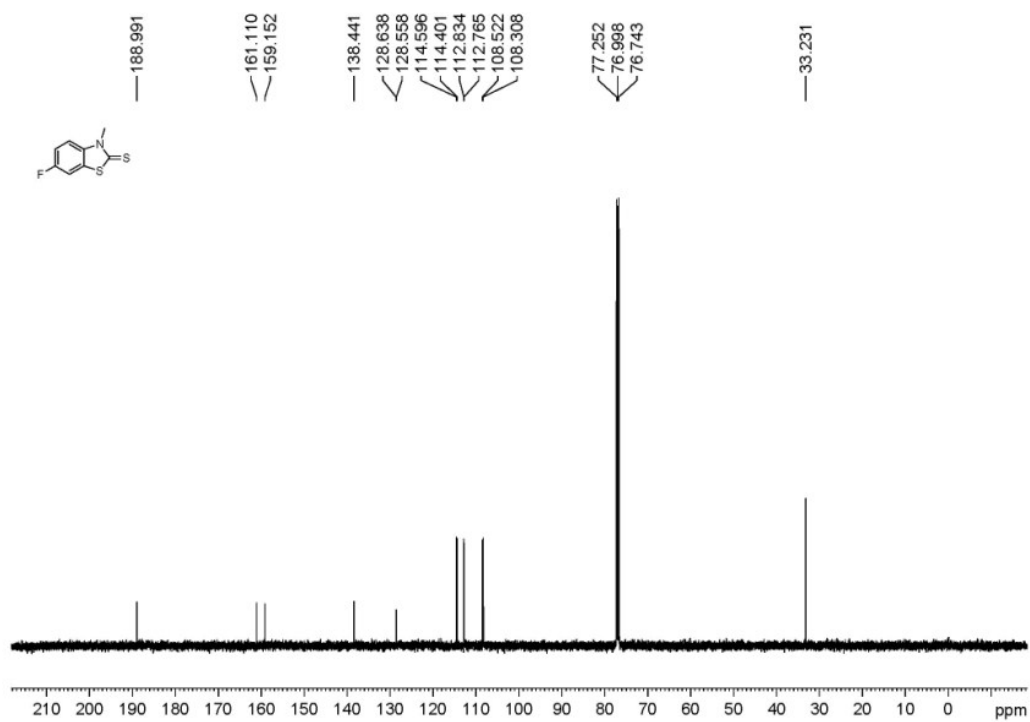
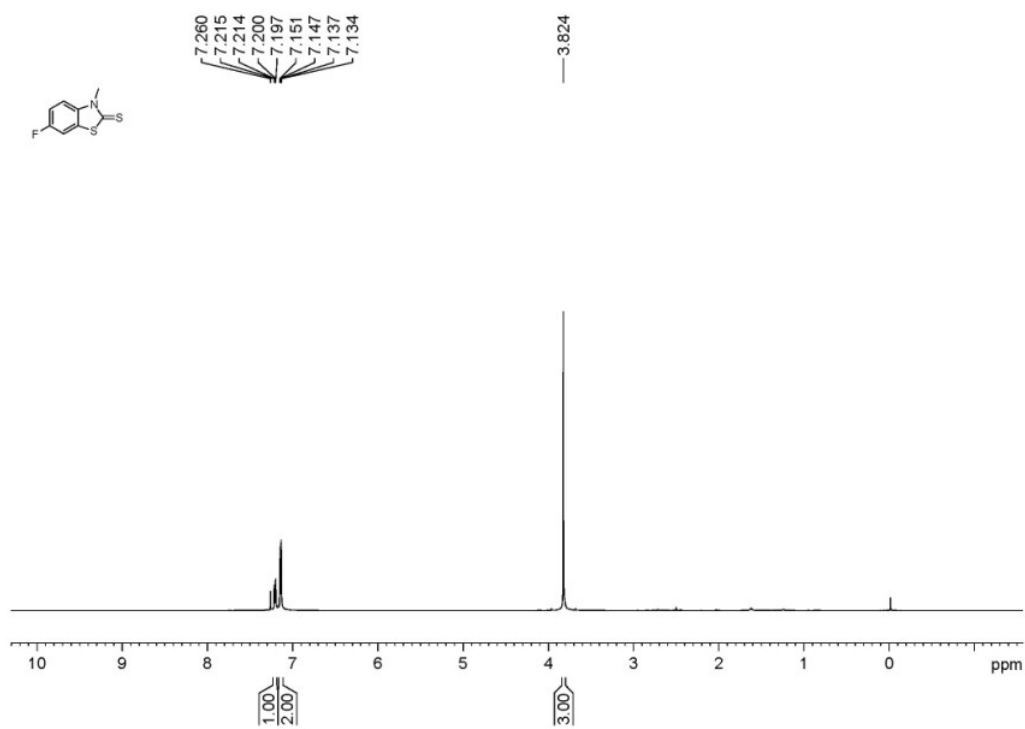
^1H and ^{13}C Spectrum of Compound **2q**



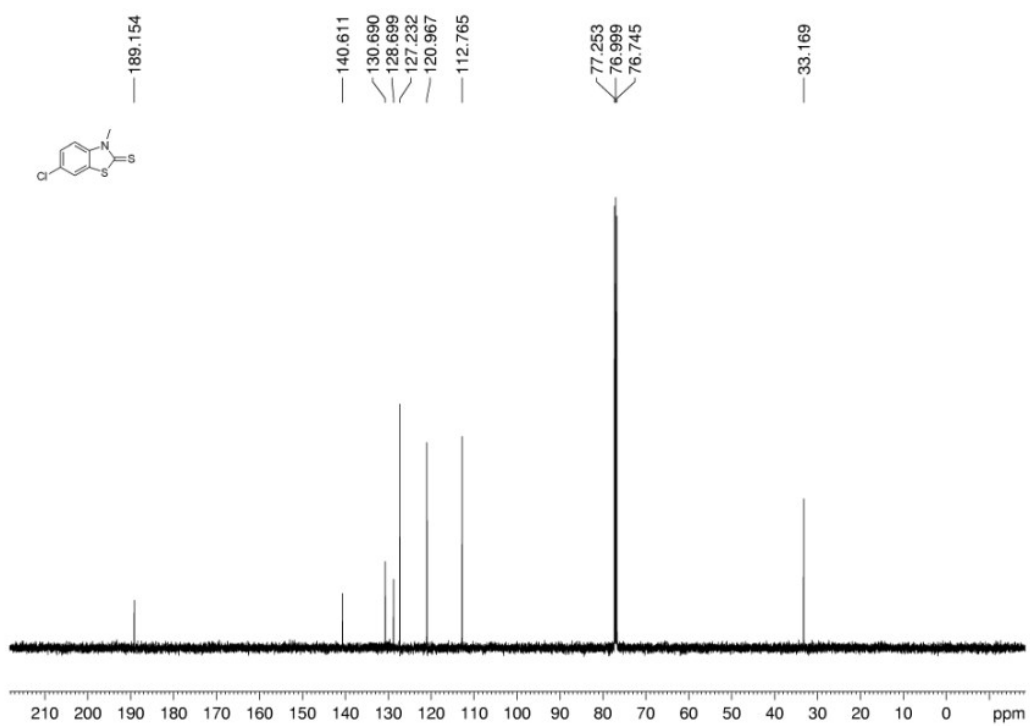
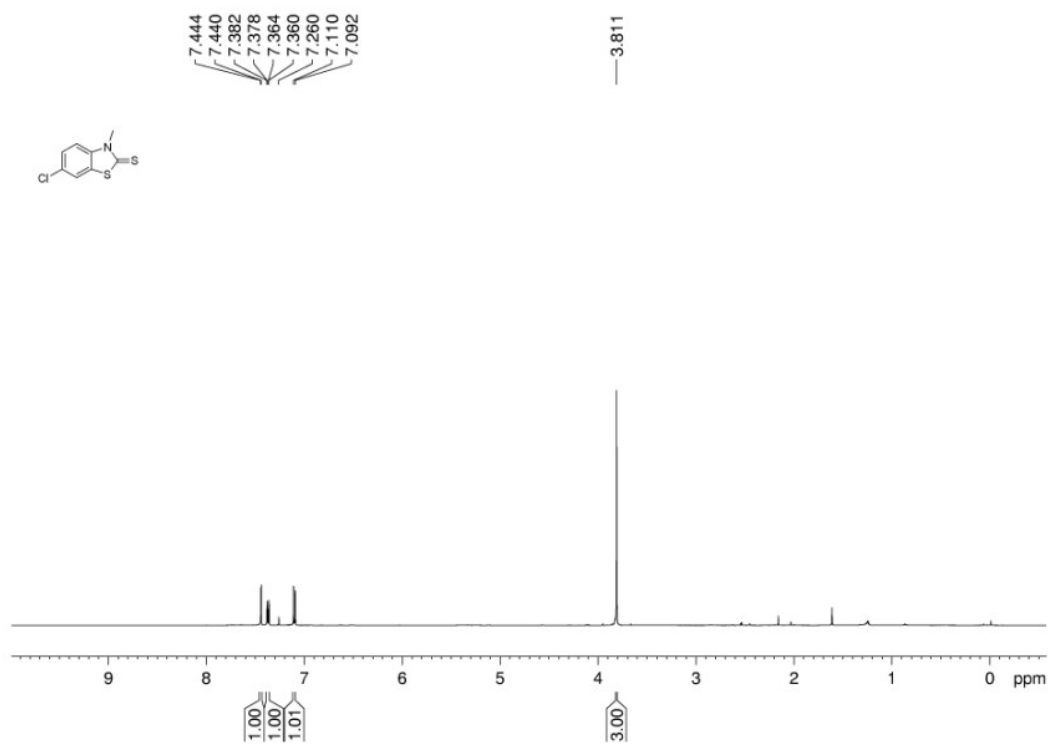
^1H and ^{13}C Spectrum of Compound **2r**



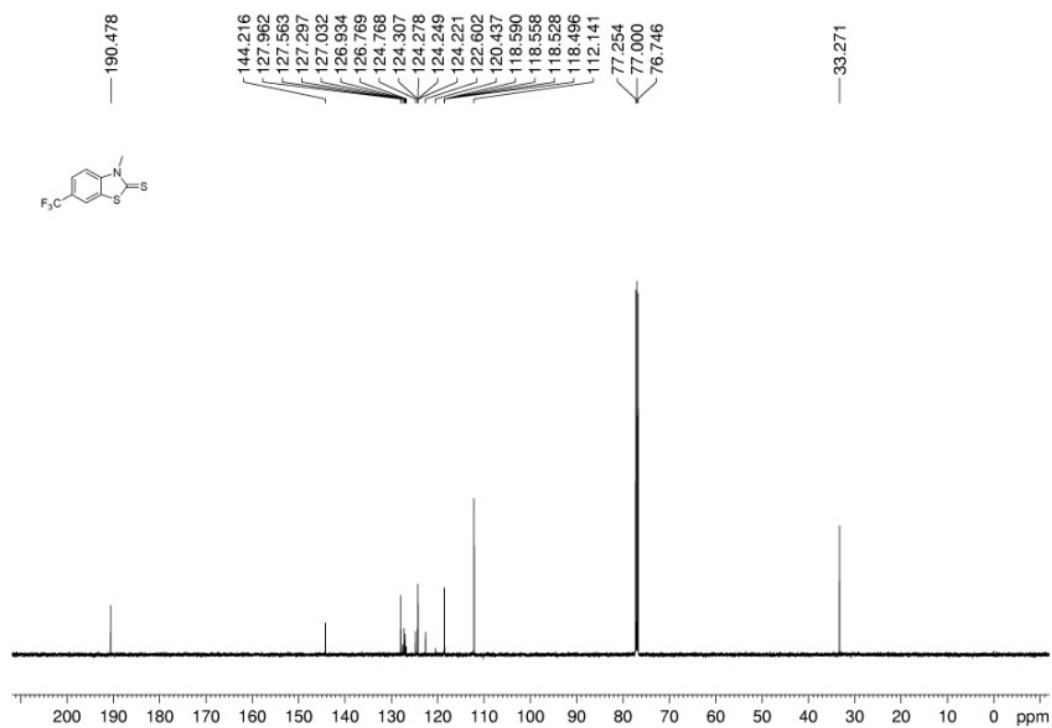
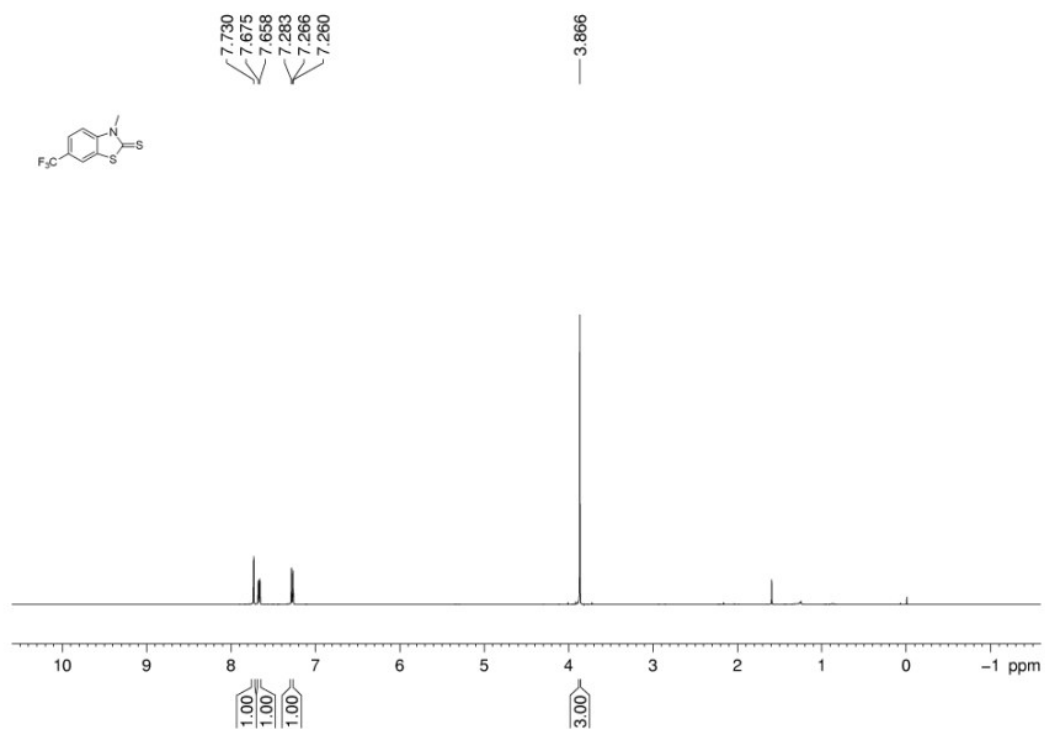
^1H and ^{13}C Spectrum of Compound **2s**



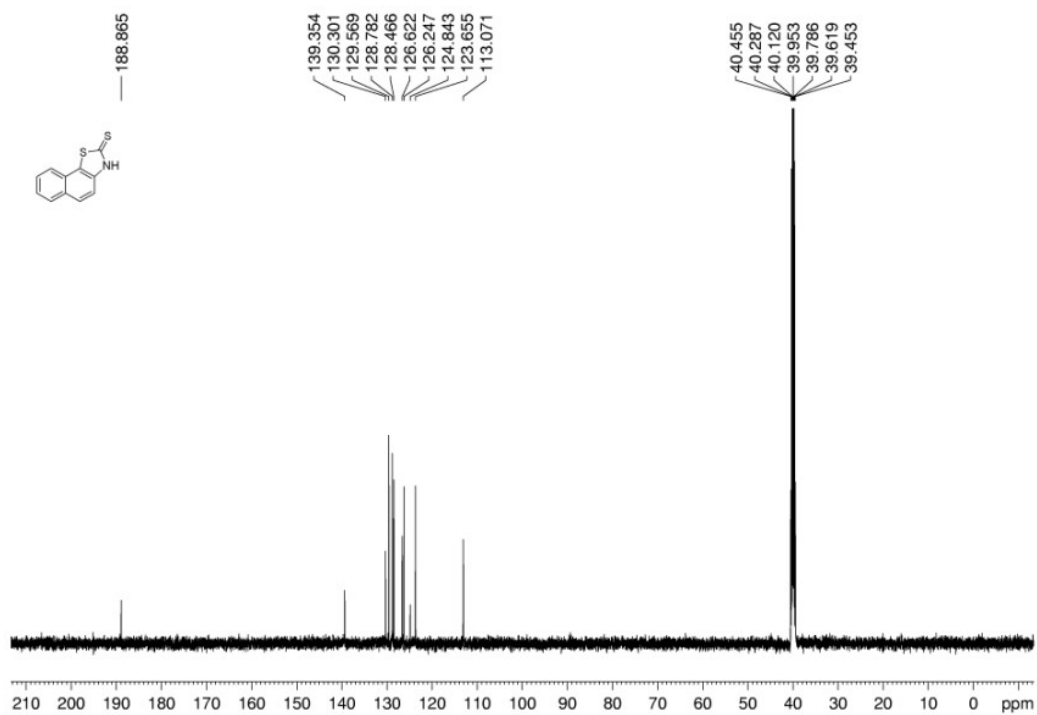
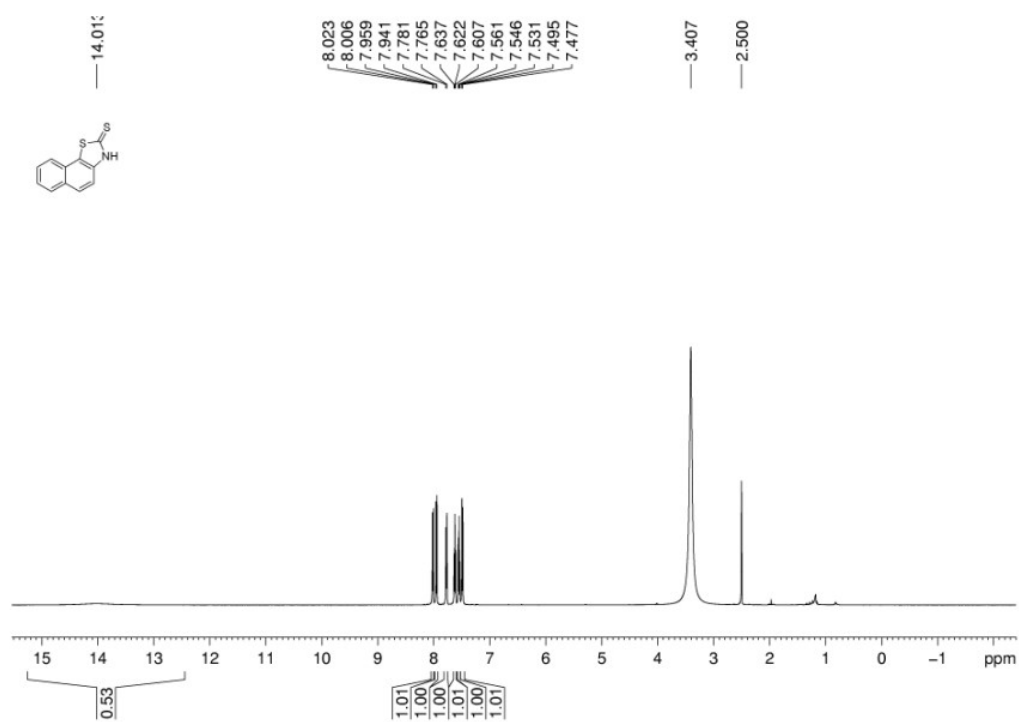
^1H and ^{13}C Spectrum of Compound **2t**



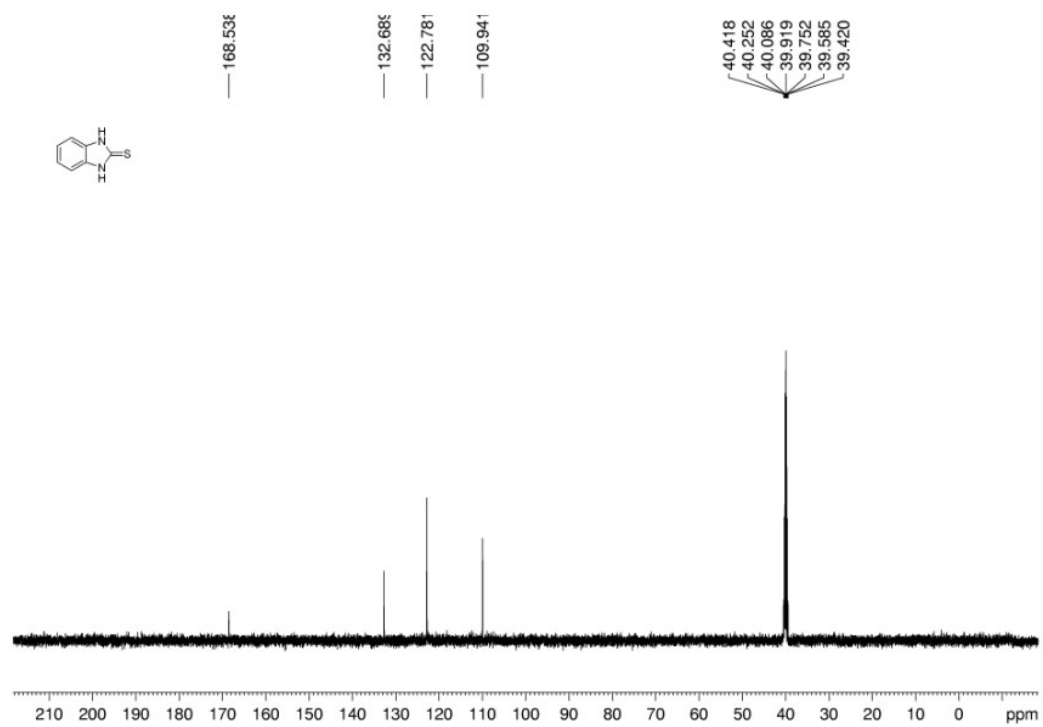
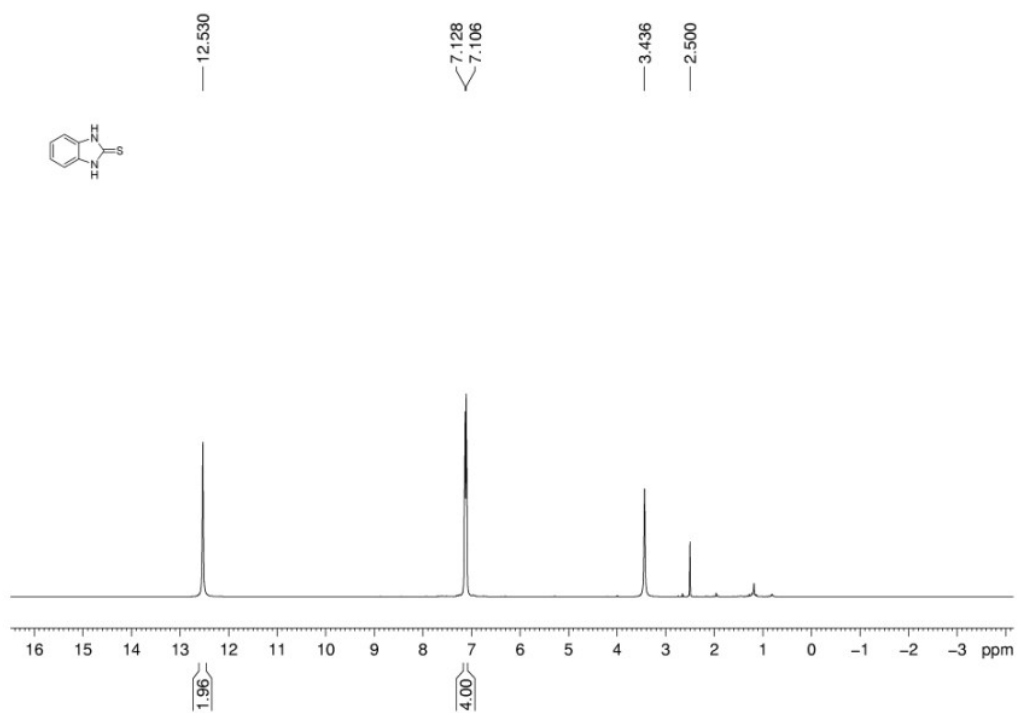
^1H and ^{13}C Spectrum of Compound **2u**



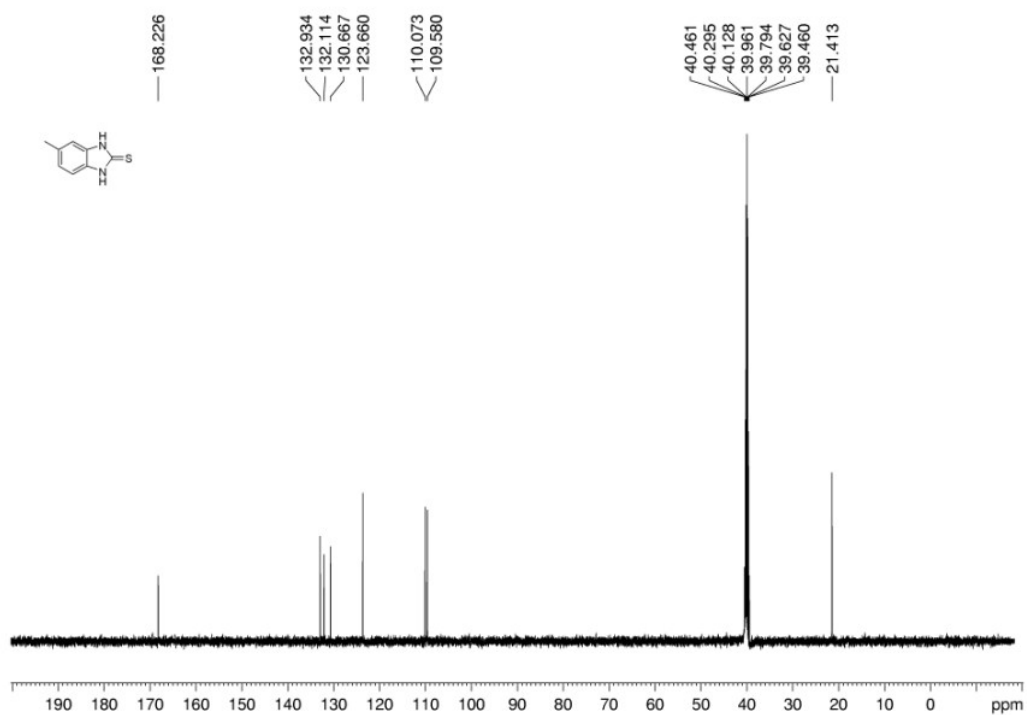
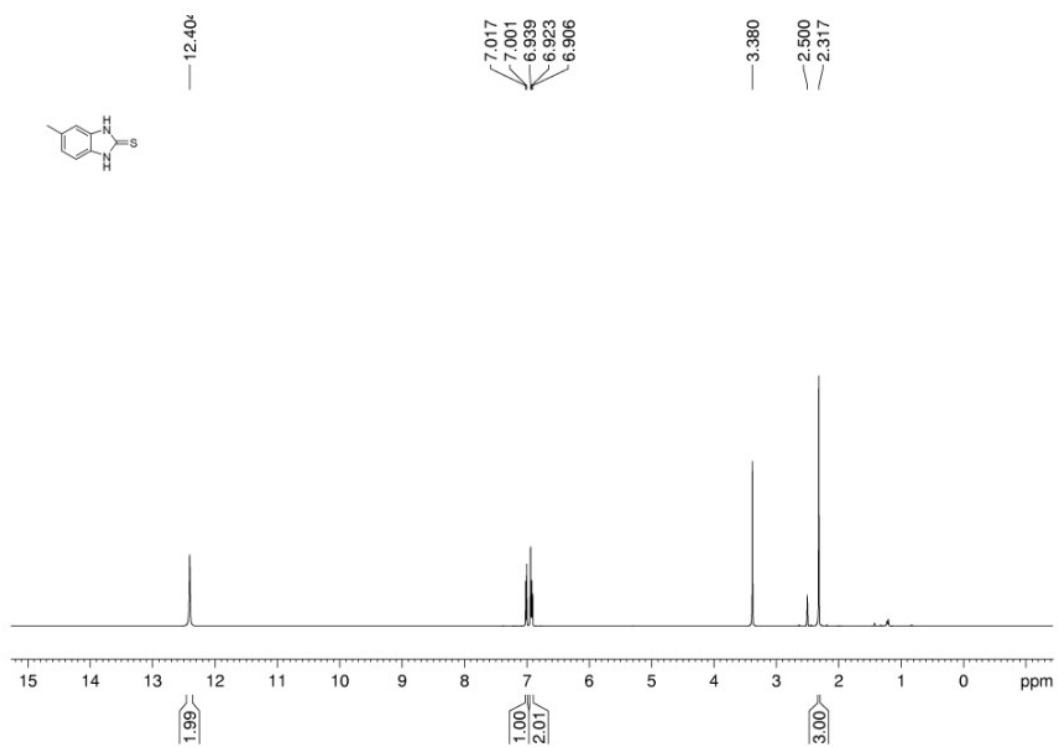
^1H and ^{13}C Spectrum of Compound **2v**



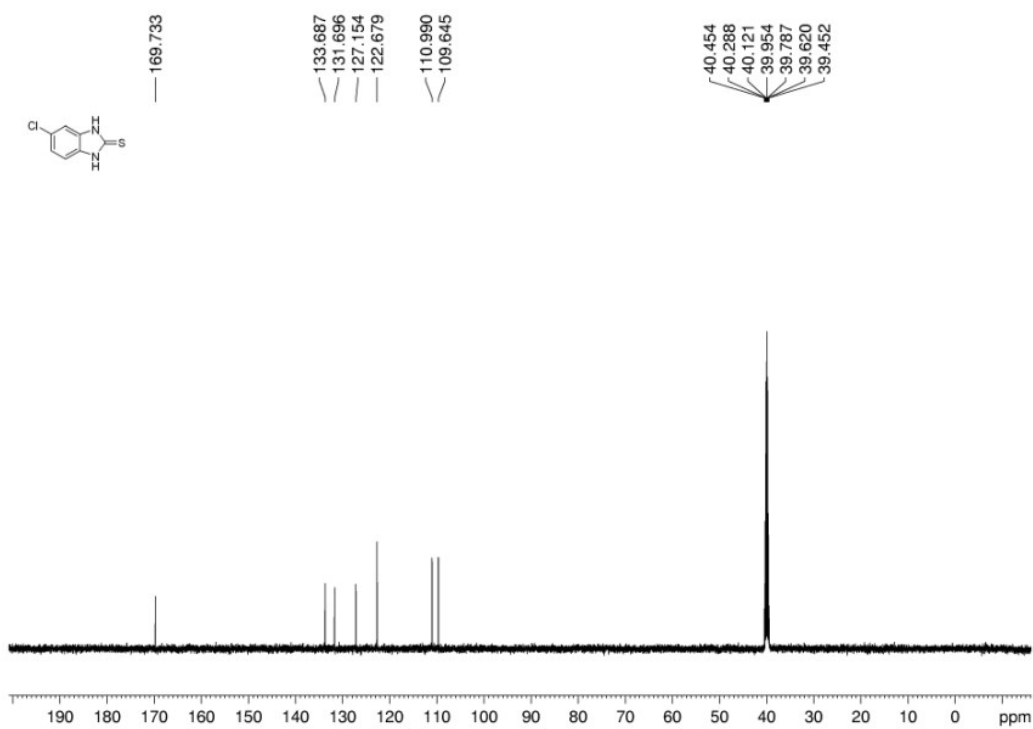
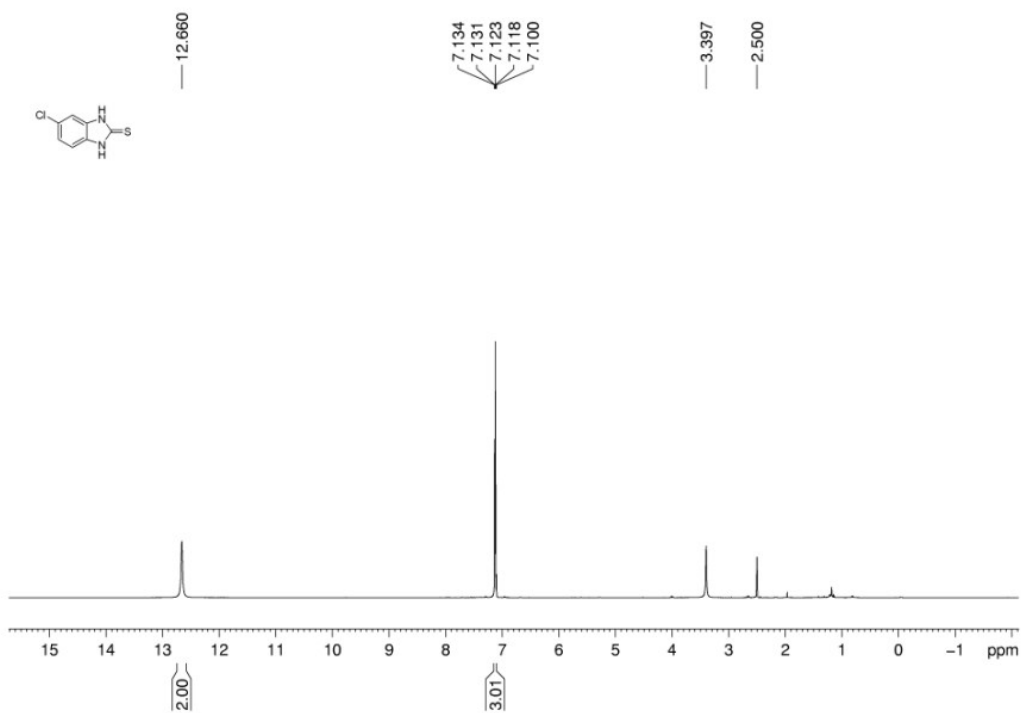
^1H and ^{13}C Spectrum of Compound **4a**



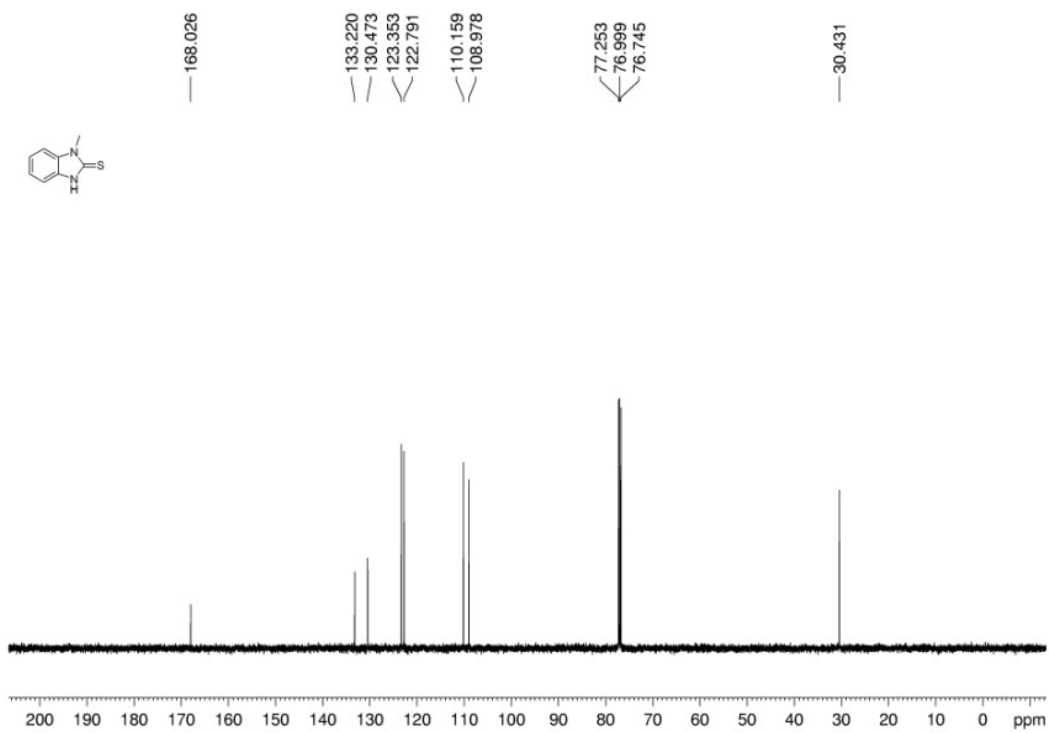
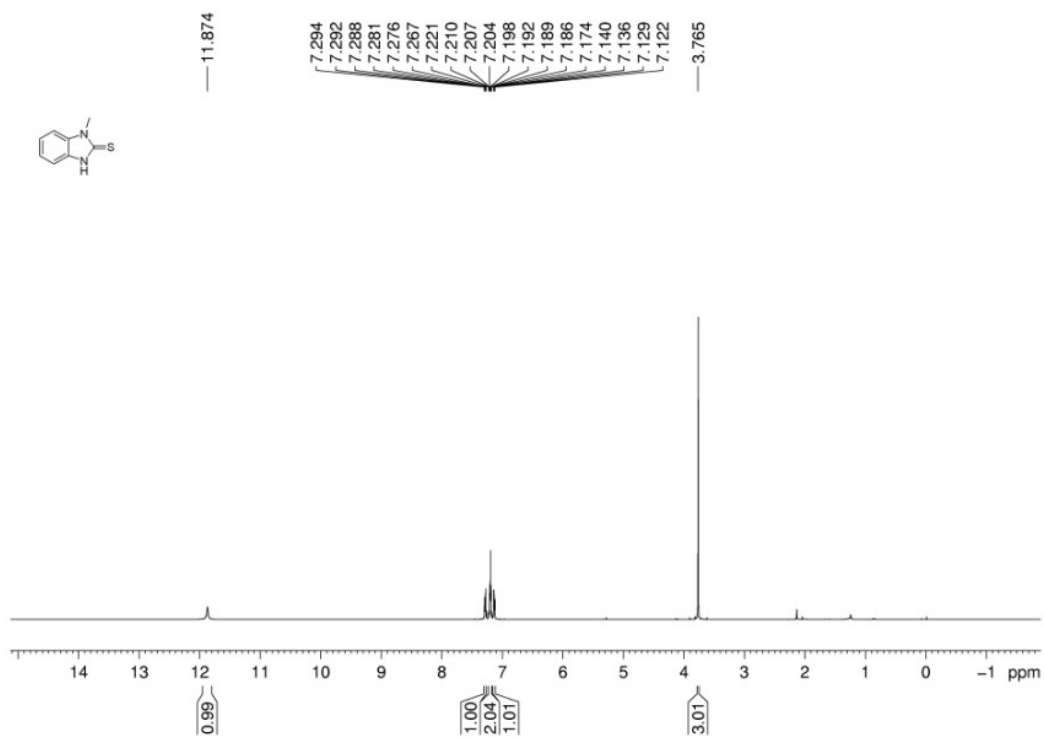
^1H and ^{13}C Spectrum of Compound **4b**



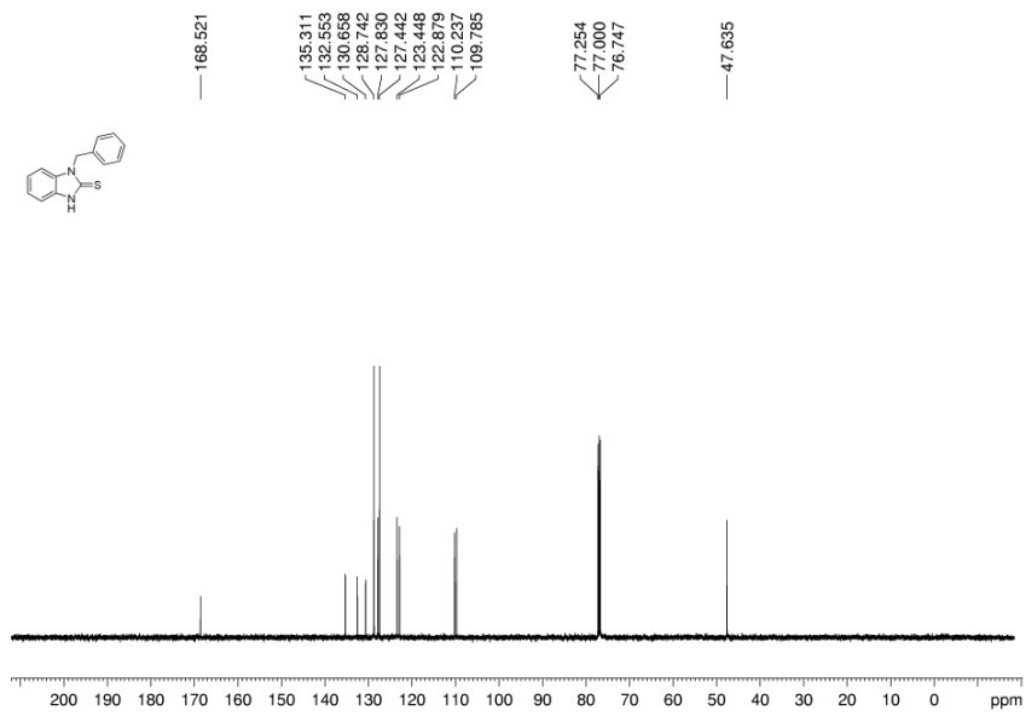
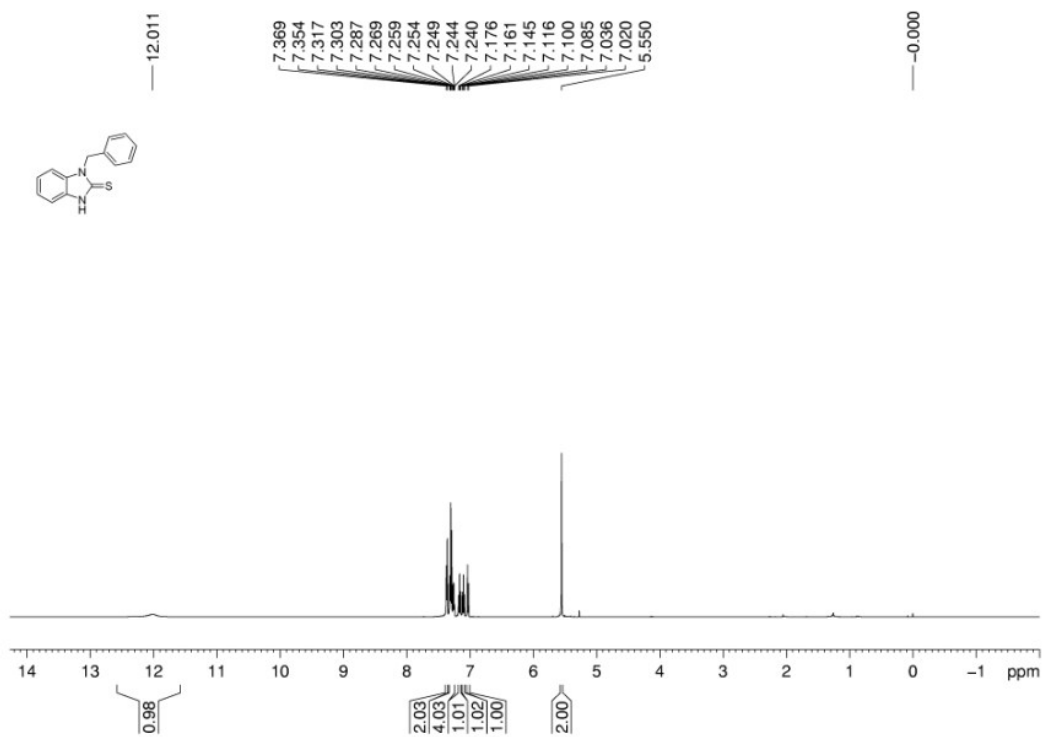
^1H and ^{13}C Spectrum of Compound **4c**



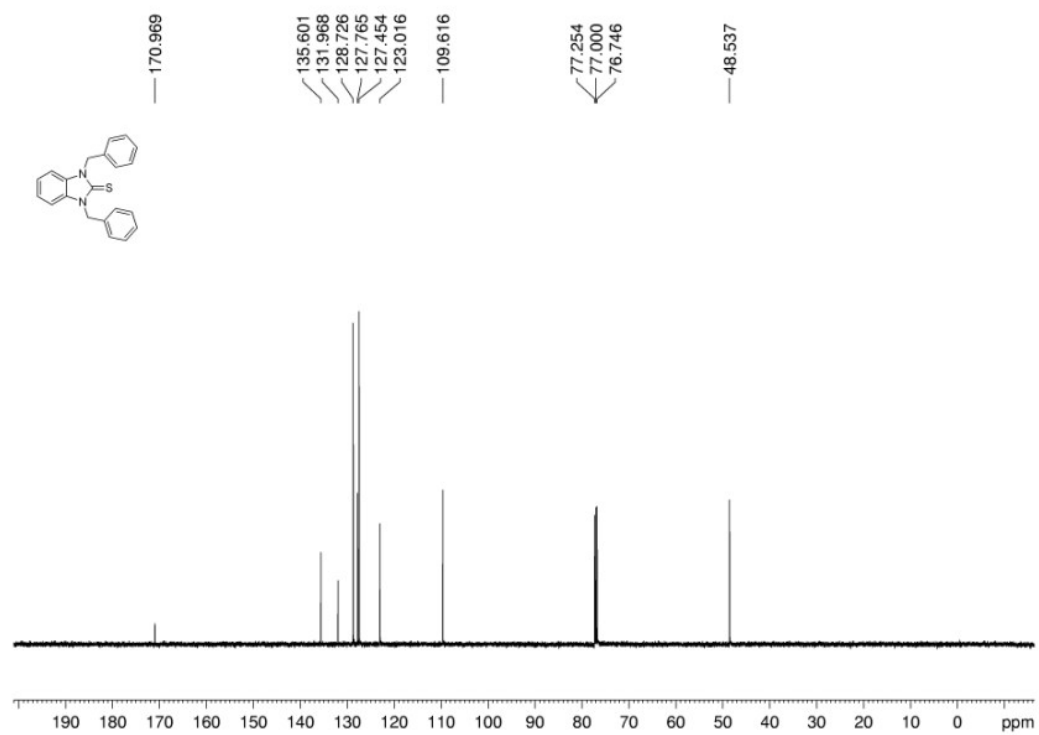
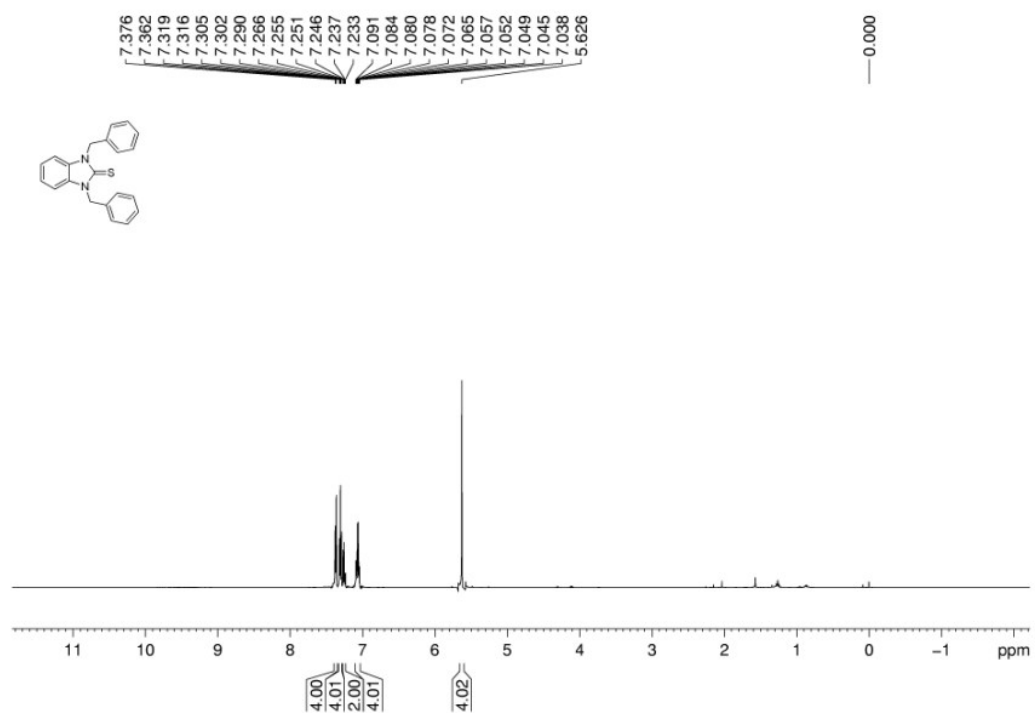
^1H and ^{13}C Spectrum of Compound **4d**



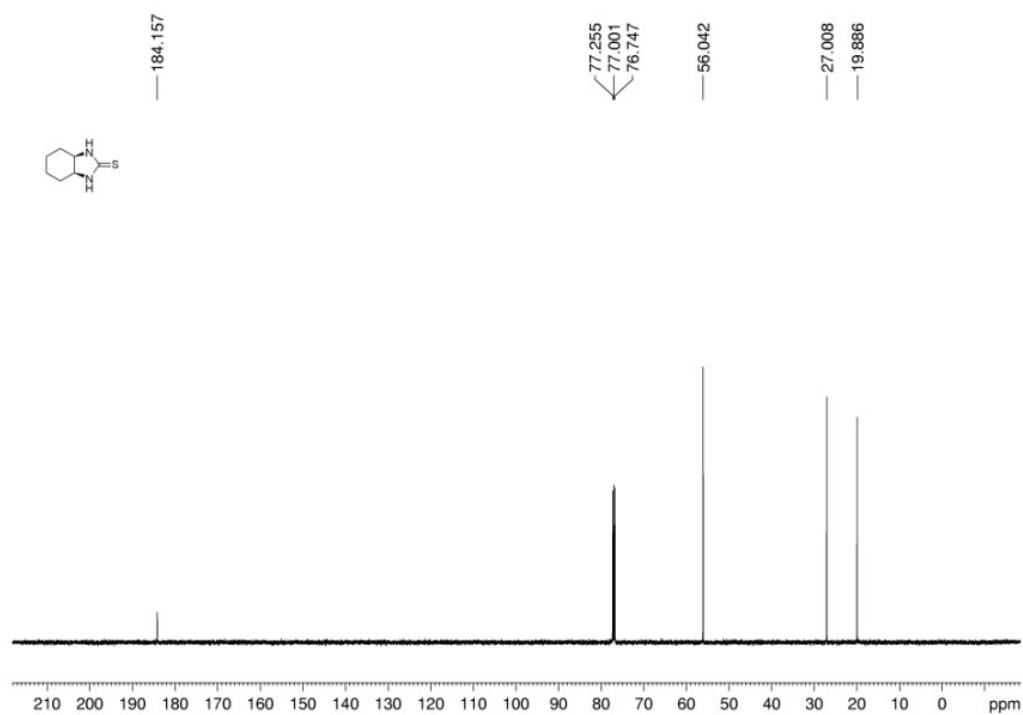
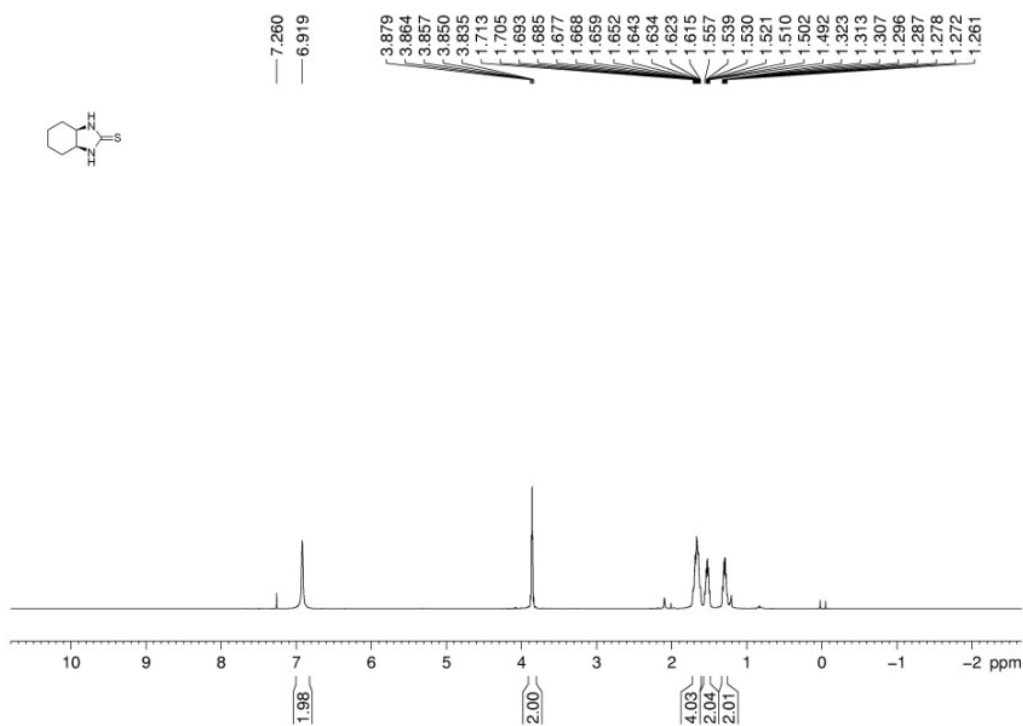
^1H and ^{13}C Spectrum of Compound **4e**



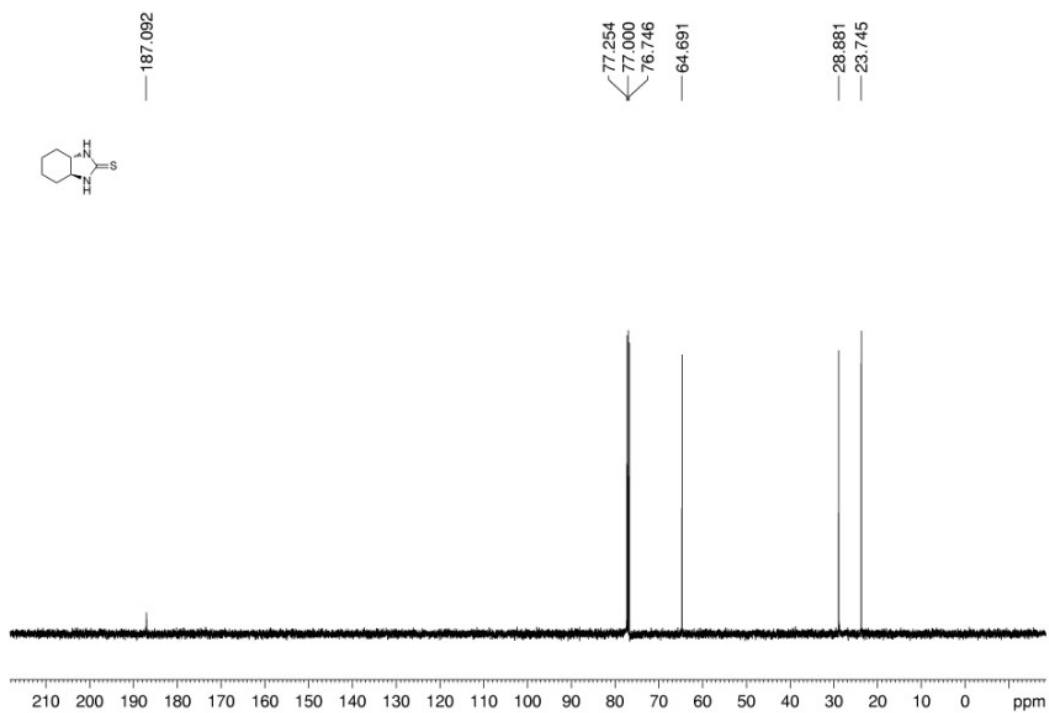
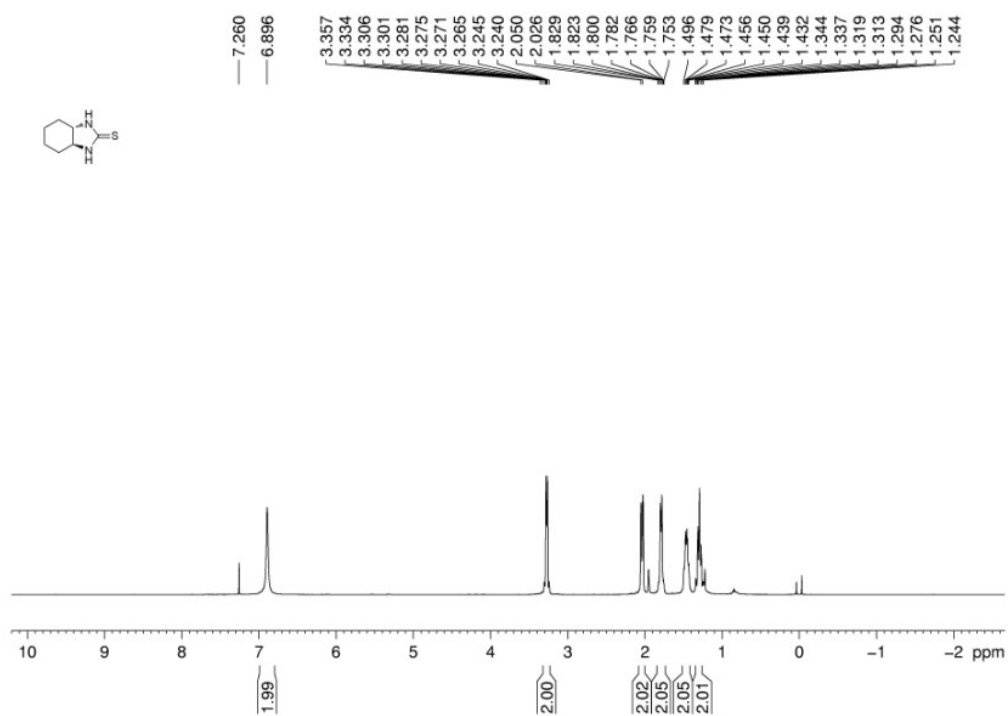
^1H and ^{13}C Spectrum of Compound **4f**



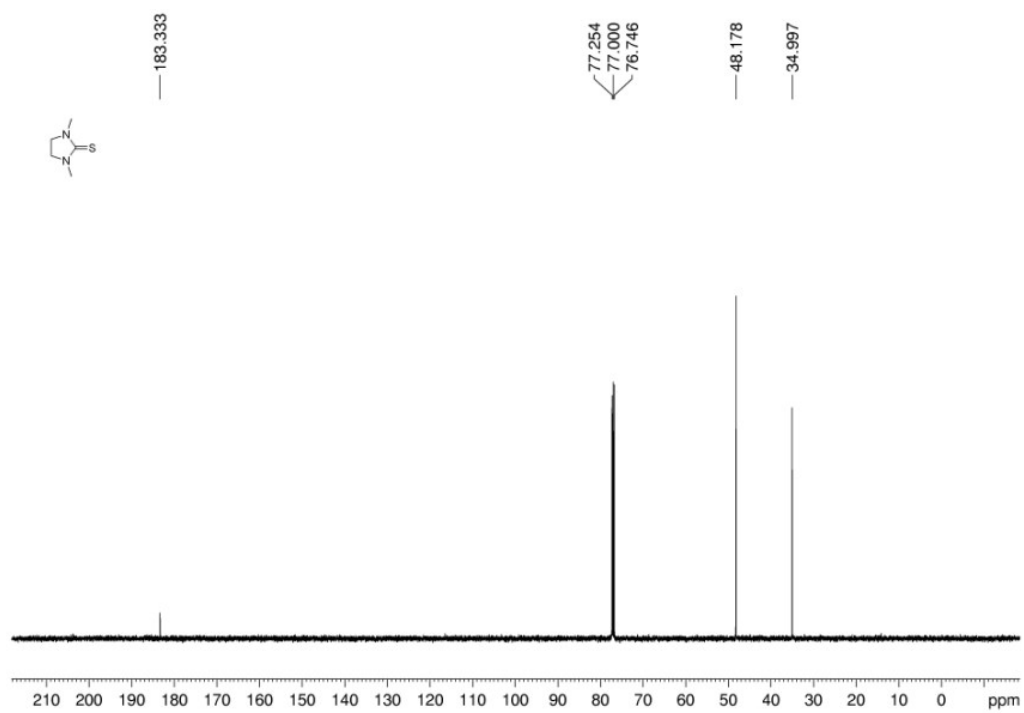
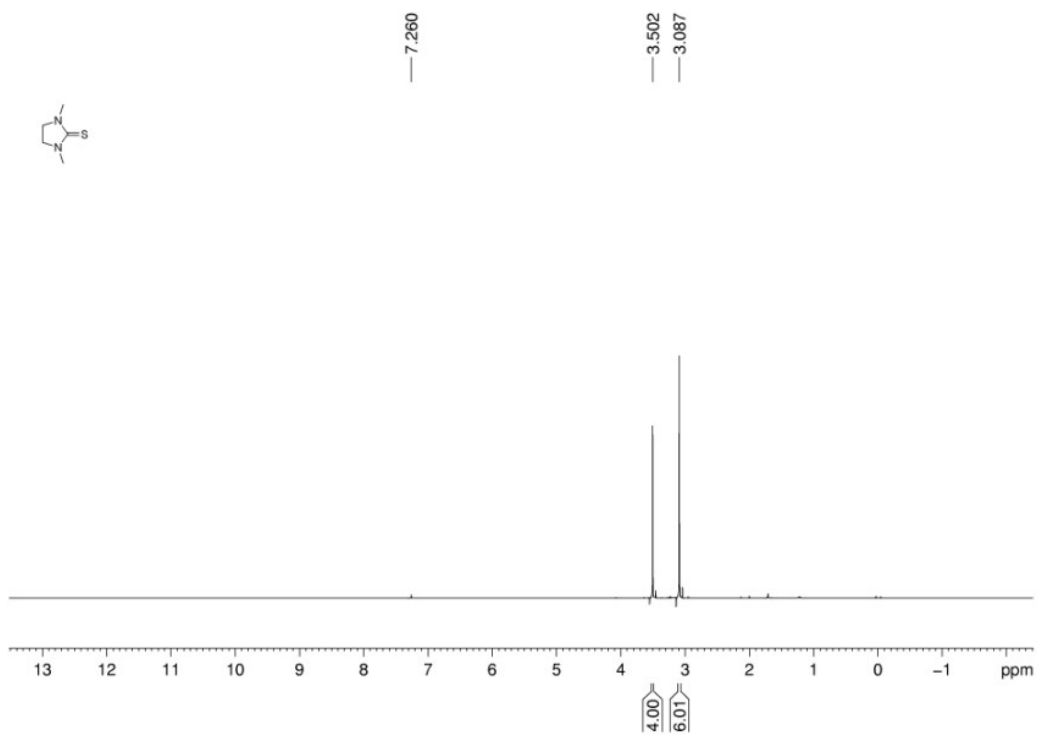
^1H and ^{13}C Spectrum of Compound **4ga**



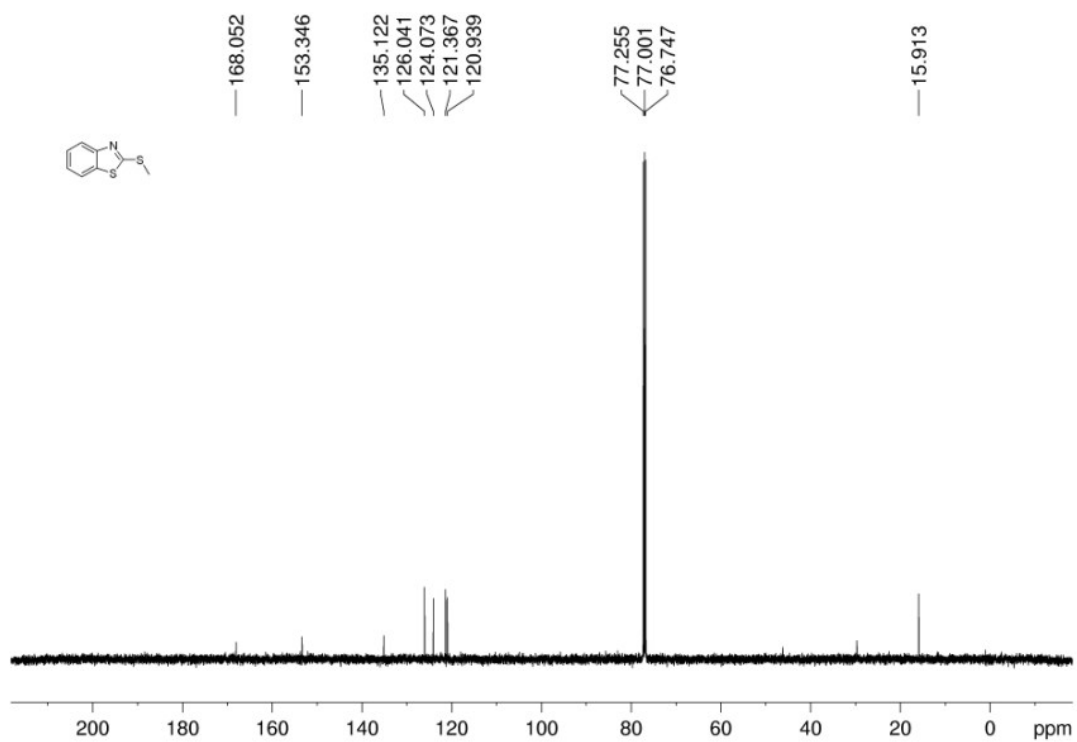
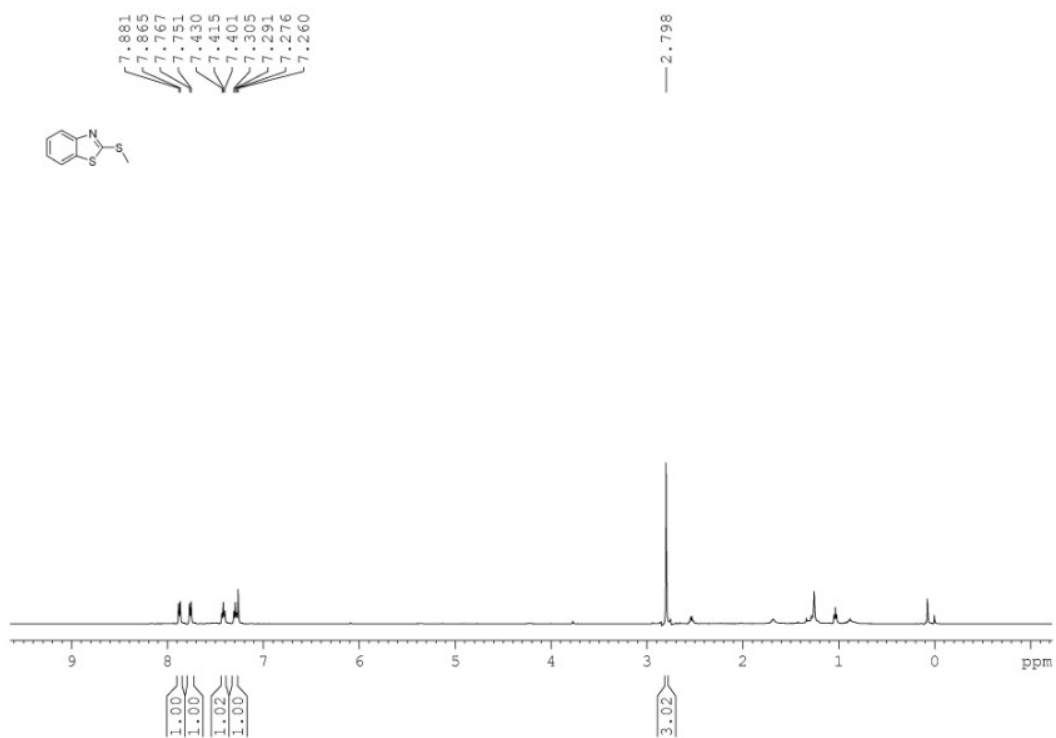
¹H and ¹³C Spectrum of Compound **4gb**



^1H and ^{13}C Spectrum of Compound **4h**



^1H and ^{13}C Spectrum of Compound **H**



^1H and ^{13}C Spectrum of Compound G

