

## Supporting Information

### A Novel Approach Towards Synthesis of Benzothiazole and Benzimidazole: Eosin Y Catalyzed Photo-Triggered C-S and C-N Bond Formation

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## 1. General Information

All chemicals and solvents were purchased from Sigma Aldrich and used without purification. Melting points were measured on the Stewart melting point apparatus in one side open capillary and are uncorrected. The progress of the reaction was monitored by thin-layer chromatography on a glass plate coated with silica gel G-234 and fluorescent silica gel. UV lamp and iodine chamber was used for the visualization of the reaction spot. High-Resolution Mass Spectrometry (HRMS) was performed using a SCIEX X500R QTOF (TOF-MS) system.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance 500 MHz spectrometer in DMSO  $d_6$  using TMS as internal standard 500 MHz ( $^1\text{H}$ ) and 126 MHz ( $^{13}\text{C}$ ). All chemical shifts were reported in ppm with reference to the DMSO peak (2.50 for  $^1\text{H}$  and 39.50 for  $^{13}\text{C}$  NMR). All coupling constants are reported in hertz (Hz). Abbreviations are, s: singlet, d: doublet, t: triplet, q: quartet, bs: broad singlet, dd: double doublet. All products synthesized were confirmed by using melting point,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and comparison with the literature reports.

## 2. Experimental Procedures

### 2.1 General procedure for the synthesis of compound 3a-3w

A 25 mL RB flask equipped with a magnetic stirring bar was charged with methyl arene **1a** (1.0 mmol), 2-aminothiophenol **2a** (1.2mmol), Eosin Y (2 mol %), and solvent (3 mL). The mixture was stirred at room temperature and irradiated with blue LEDs light strips for 1.2 h under the open air. The progress of the reaction was monitored via TLC. The precipitate obtained was filtered and washed with ethanol after the completion of the reaction. The desired product was obtained in good yields after recrystallization using ethanol.

## 3. Optimization

We started our observations using a visible-light photoredox reaction of methylarene **1a** with 2-aminothiophenol**2a**, which was selected as the model reaction to optimize the reaction conditions under blue LED irradiation in ambient air at room temperature (**Table S1**). Firstly, we investigated the role of various photocatalysts using ethanol as a solvent (**Table S1, entries 1-4**). Eosin Y was the most active catalyst, yielding product **3a** in 52% (**Table S1, entry 4**). Next, different solvents were optimized (**Table S1, entries 5-11**), and water gave a good yield of 60% (**Table S1, entry 5**). It was observed that using water/ethanol in a 1:1 ratio led to a marginal increase of 70% in yield (**Table S1, entry 12**). Encouraged by the finding, a different ratio of ethanol and water (**Table S1, entries 12-15**) was tried. We got the best result (90%) using a mixture in the ratio of 1:2 (**Table S1, entry 14**). Further, we tried the reaction without blue LED but failed to give the desired product **3a** (**Table S1, entry 16**). Then, we varied the loading of Eosin Y from 3 mol% to 4 mol% (**Table S1, entries 17-18**) and found the exact yield on increasing the mol% of the photocatalyst. We tried extending the reaction time (**Table S1, entries 19**) but failed to get a better yield of product **3a**. Afterthat, under the same reaction condition, the influence of light on the reaction was investigated, and no product was formed in the absence of light (**Table S2, entry 1**), indicating the essential role of light irradiation. To further explore the impact of different light sources, purple, green, and white LED lights and a 20W CFL were used instead of the blue LED (**Table S2, entries 2-5**). The results showed that these light sources produced comparable 65-69% yields. In addition, the effect of atmospheric air was examined, and the reaction under oxygen produced almost the exact yield as under air (**Table S2, entry 7**).

**Table S1. Initial Optimization of the Reaction Conditions for the Synthesis of Compound 3a.**

Entry	Light source	Catalyst (mol %)	Solvent	Time (h)	Yields <sup>b</sup> %
1	Blue LED	Rhodamine B (2)	EtOH	3	30
2	Blue LED	Rose Bengal (2)	EtOH	3	35
3	Blue LED	Acridine red (2)	EtOH	3	32
4	Blue LED	Esoin Y (2)	EtOH	3	52
5	Blue LED	Esoin Y (2)	H <sub>2</sub> O	3	60
6	Blue LED	Esoin Y (2)	Methanol	3	35
7	Blue LED	Esoin Y (2)	DMF	3	20
8	Blue LED	Esoin Y (2)	Acetonitrile	3	25
9	Blue LED	Esoin Y (2)	DMSO	3	10
10	Blue LED	Esoin Y (2)	Toluene	3	30
11	Blue LED	Esoin Y (2)	THF	3	25
12	Blue LED	Esoin Y (2)	EtOH:H <sub>2</sub> O (1:1)	1.5	70
13	Blue LED	Esoin Y (2)	EtOH:H <sub>2</sub> O (2:1)	1.5	60
<b>14</b>	<b>Blue LED</b>	<b>Esoin Y (2)</b>	<b>EtOH:H<sub>2</sub>O (1:2)</b>	<b>1.5</b>	<b>90</b>
15	Blue LED	Esoin Y (2)	EtOH:H <sub>2</sub> O (1:4)	1.5	80
16	None	Esoin Y (2)	EtOH:H <sub>2</sub> O (1:2)	1.5	NR
17	Blue LED	Esoin Y (3)	EtOH:H <sub>2</sub> O (1:2)	1.5	91
18	Blue LED	Esoin Y (4)	EtOH:H <sub>2</sub> O (1:2)	1.5	92
19	Blue LED	Esoin Y (3)	EtOH:H <sub>2</sub> O (1:2)	4	90

<sup>(a)</sup>Reaction Condition: Methyl arene (1.0mmol), 2-aminothiophenol (1.2mmol), catalyst (2 mol %), solvent (3mL), Blue LED (1.5 h) under open air at room temperature. <sup>(b)</sup>Isolated yield.

**Table S2. Optimization of different colour LED.**

Entry	variations in the reaction conditions	Yield (%) <sup>b</sup>
1	in dark	nr
2	green LEDs instead of blue LEDs	60
3	White LEDs instead of blue LEDs	65

4	Purple LEDs instead of blue LEDs	69
5	20W CFL instead of blue LEDs	65
6	Blue LEDs	90
7	under O <sub>2</sub> atmosphere	85

<sup>(a)</sup>Reaction Condition: Methyl arene (1.0mmol), 2-aminothiophenol (1.2mmol), catalyst (2 mol %), solvent (3mL), Blue LED (1.5 h) under open air at room temperature. <sup>(b)</sup>Isolated yield.

## 4. Mechanistic Studies

### 4.1 Radical trapping experiments by TEMPO/ HRMS data

Several mechanistic investigations were performed to investigate the mechanism of the visible light photoredox. At first, 2, 2, 6, 6-tetramethylpiperidinoxy (TEMPO) (radical scavengers) (2 mol %) was added to the reaction system, and the trace amount of the **3a** was formed, and TEMPO adducts **4a** and **5a** were detected in HRMS data from the crude reaction mixture (Figure S1 and S2). These results suggested that the reaction passes through the radical pathway.

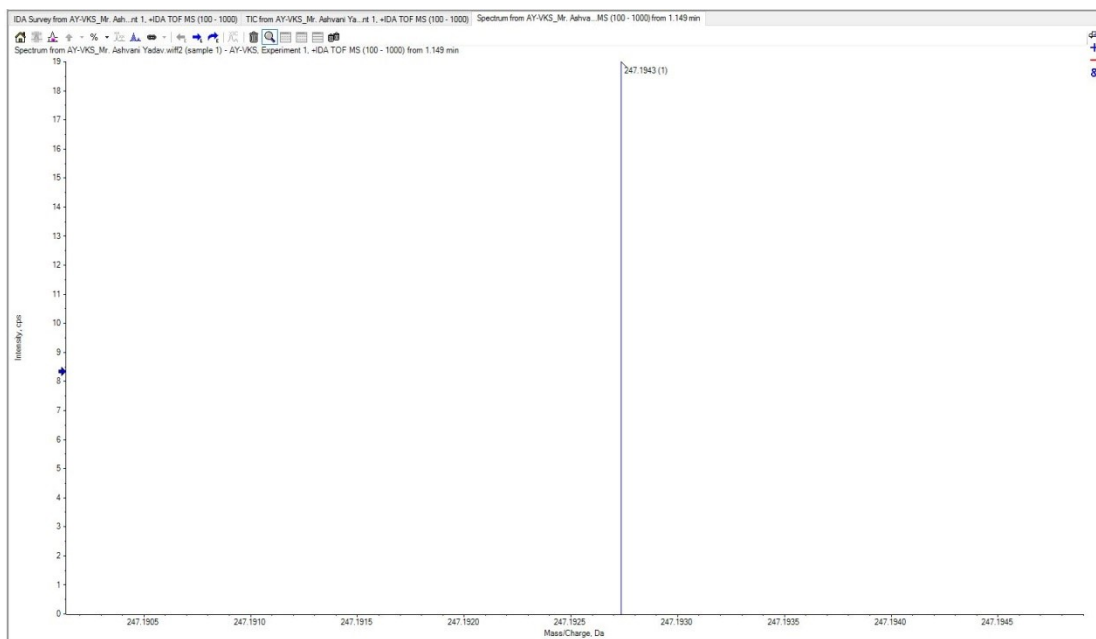
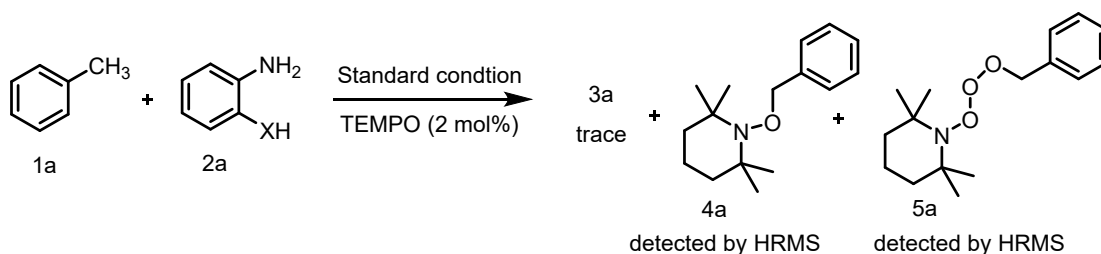


Figure S1. HRMS of adduct **4a**

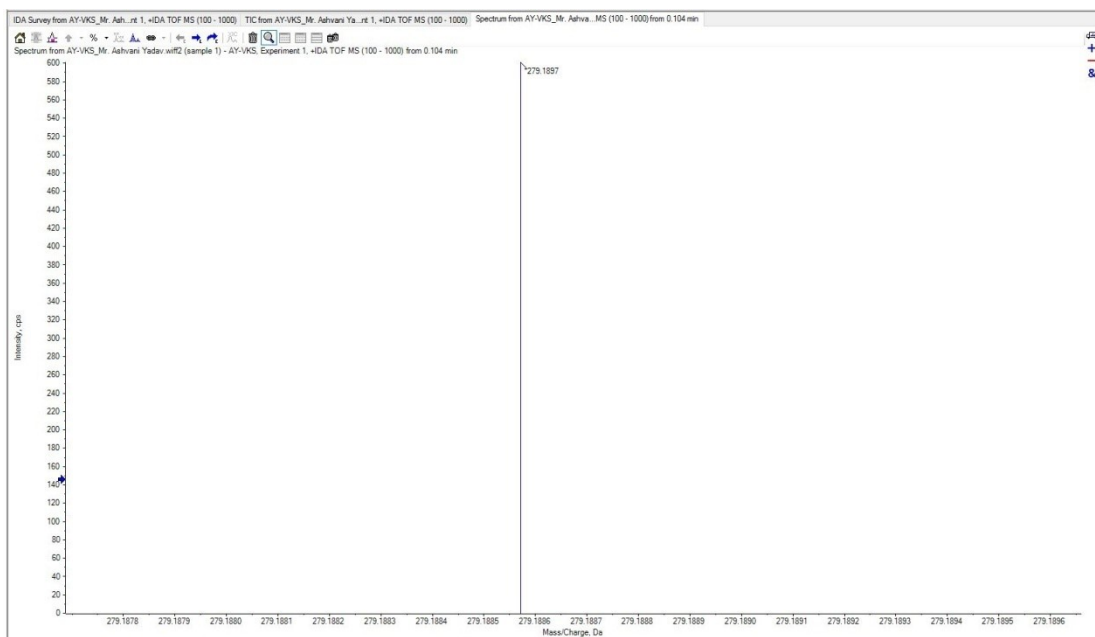


Figure S2. HRMS of adduct 5a

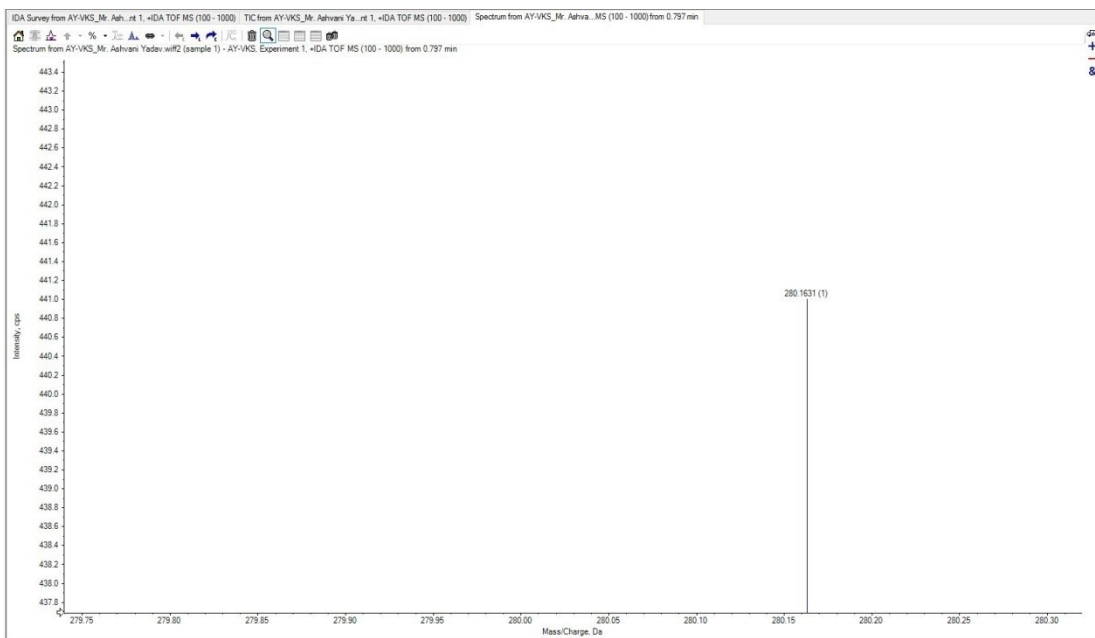
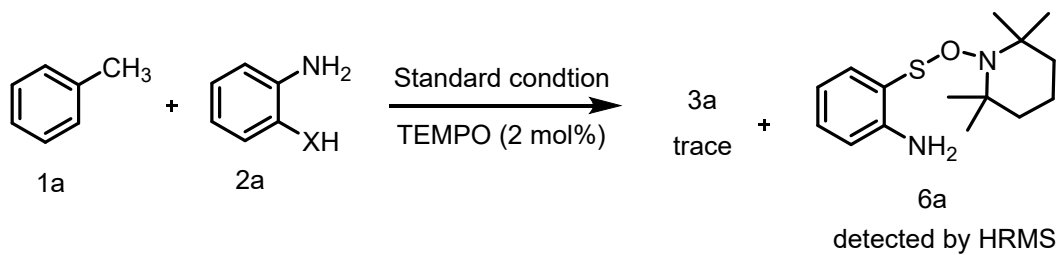


Figure S3. HRMS of adduct 6a

## 4.2 UV/Vis absorption spectrometry

SHIMADZU UV-800 UV-visible spectrophotometer was used to record UV- visible spectroscopy of reactants and reaction mixture. The sample was prepared by mixing of 1a, 2a, and mixture (1a+2a) (Fig S4) and 1a (1a+esoin Y) in methanol solvent [Conc. Reaction mixture =  $1.25 \times 10^{-4}$  mol/L] in a light path quartz UV cuvette.

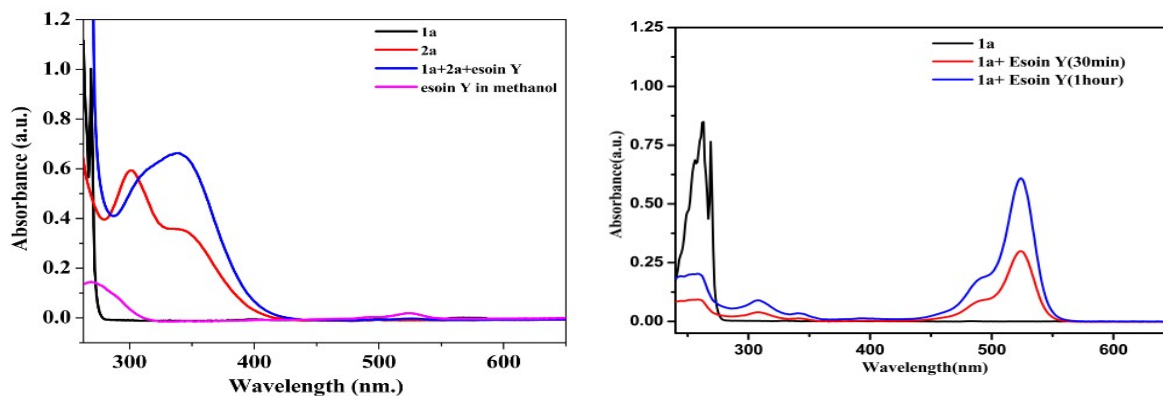


Figure S4. (A) UV-vis absorption spectra of (1a+2a), UV-vis absorption spectra (1a+esoin y)

## 4.3 Stern-Volmer Fluorescence Plots and quenching experiments.

In a Fluorescence experiment, the solution of **1a** in methanol was added to the appropriate amount of **2a**. The addition of **2a** was repeated 5 consecutive times. We recorded the emission spectra after each addition. All the solutions were excited at 280nm, and the emission was acquired from 0 nm to 500 nm. The result shown in Fig S5 indicates that **2a** quenches the excited state of **1a** and its emission.

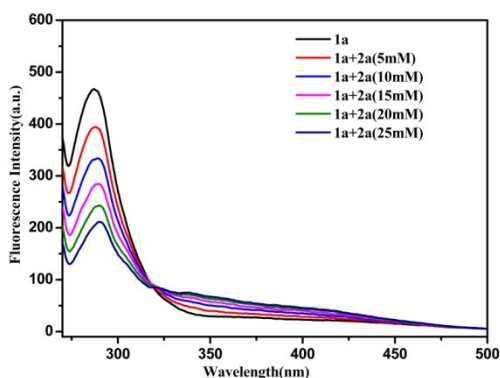


Figure S5. The fluorescence emission spectra of 1a with different concentrations of quencher 2a.

#### 4.4 Light-Dark cycle experiment

The reaction between 1b and 2a was conducted under the standard conditions on a 1.0 mmol scale. The reaction mixture was subjected to sequential periods of stirring under visible light irradiation (blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with column chromatography to give the corresponding products 3a. The yield of 3a was measured by weight of the product (Figure 7)

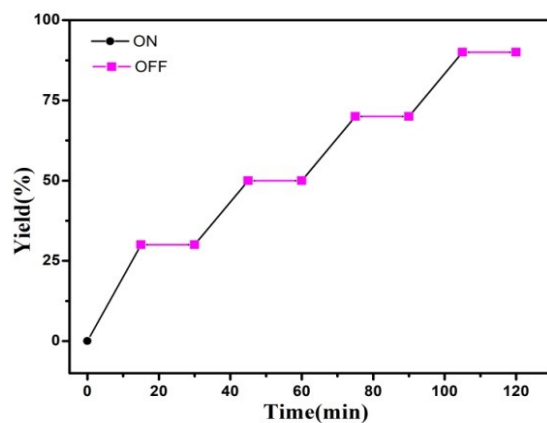
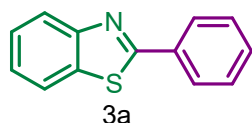


Figure S6. Light-Dark cycle experiment

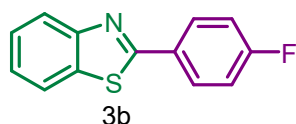
## 5. Characterization Data of the Products

### 2-Phenylbenzothiazole (3a) <sup>1</sup>



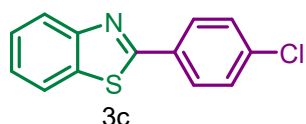
Yield 90%; Yellow solid; m.p. 115–116 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 8.18–8.15 (d, J = 8.0 Hz, 3H), 8.04–8.02 (m, 1H), 7.80–7.77 (m, 2H), 7.59–7.47 (d, J = 8.3, 1.2 Hz 3H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 166.6, 153.9, 135.0, 132.9, 132.5, 129.5, 127.3, 126.2, 125.4, 123.5, 122.9 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>9</sub>NS 212.0456, found: 212.0451.

### 2-(4-Fluorophenyl)benzothiazole (3b) <sup>2</sup>



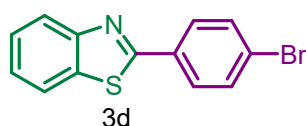
Yield 91%; Yellow solid; m.p. 101–102 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 8.17–8.15 (m, 1H), 8.08–8.06 (d, J = 8.0 Hz, 1H), 7.57–7.56 (dd, J = 8.3, 1.2 Hz, 2H), 7.54–7.47 (m, 2H), 7.46–7.41 (m, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 166.6, 165.2, 163.4, 154.1, 134.9, 130.1, 127.2, 125.9, 123.5, 122.9, 117.0 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>FNS 230.0361, found: 230.0350.

### 2-(4-Chlorophenyl)benzothiazole (3c) <sup>3</sup>



Yield 90%; Yellow solid; m.p. 111–112 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 8.17–8.15 (d, J = 8.0 Hz, 2H), 8.08–8.06 (m, 1H), 7.57–7.56 (d, J = 7.56 Hz, 2H), 7.57–7.54 (dd, J = 8.3, 1.2 Hz, 1H), 7.49–7.41 (m, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 166.5, 163.3, 153.9, 135.0, 130.2, 127.2, 126.2, 123.3, 122.9, 117.0, 116.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>ClNS 246.0066, found: 246.0069.

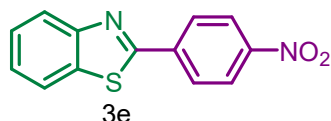
### 2-(4-Bromophenyl)benzothiazole (3d) <sup>1</sup>





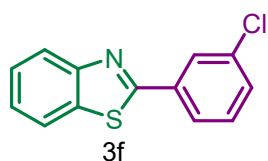
Yield 90%; Yellow powder; m.p. 132-133 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.14-8.13 (m, 2H), 7.63-7.62 (d, J = 8.0 Hz, 1H), 7.51-7.49 (d, J = 7.56 Hz, 1H), 7.19-7.16 (m, 1H), 7.15-7.11 (d, J = 8.26 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 166.5, 163.2, 154.2, 135.2, 130.0, 127.2, 125.9, 123.4, 122.6, 117.2, 116.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>BrNS 289.9561, found: 289.9553.

### 2-(4-Nitrophenyl)benzothiazole (3e) <sup>1</sup>



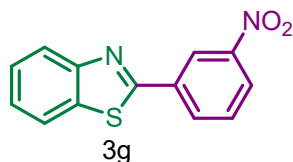
Yield 91%; Yellow powder; m.p. 230-231 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (m, 2H), 8.31-8.29 (m, 2H), 8.17-8.15 (d, J = 8.26 Hz, 1H), 8.00-7.98 (d, J = 8.12 Hz, 1H), 7.60-7.59 (m, 1H), 7.58-7.49 (m, 1H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.9, 153.7, 135.3, 133.0, 130.1, 126.8, 126.0, 125.2, 123.8, 122.4, 121.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S 257.0307, found: 257.0315.

### 2-(3-Chlorophenyl)benzothiazole (3f) <sup>4</sup>



Yield 85%; White solid; m.p. 98-99 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.13-8.12 (d, J = 1.6 Hz, 1H), 8.04-8.82 (s, 1H), 7.63-7.61 (d, J = 8.0 Hz, 2H), 7.47-7.44 (m, 4H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 164.6, 153.6, 135.4, 135.0, 133.1, 130.2, 126.9, 126.4, 125.9, 125.3, 123.8, 122.5, 121.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>9</sub>ClNS 246.0066, found: 246.0061.

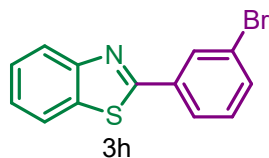
### 2-(3-Nitrophenyl)benzothiazole (3g) <sup>5</sup>



Yield 92%; White solid; m.p. 186-187 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.40-8.31 (m, 1H), 8.17-8.15 (d, J = 8.26 Hz, 1H), 8.00-7.98 (d, J = 8.20 Hz, 1H), 7.59-7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, 2H), 7.50-7.49 (d, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 164.9, 153.9, 135.3, 135.2,

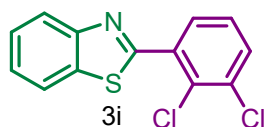
133.0, 130.1, 126.8, 126.0, 125.5, 125.2, 123.8, 122.4, 121.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S 257.0307, found: 257.0330.

### 2-(3-Bromophenyl)benzothiazole (3h) <sup>4</sup>



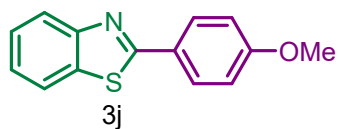
Yield 85%; White solid; m.p. 89–91 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.13-8.04 (m, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.63-7.61 (d, J = 8.0 Hz, 2H), 7.47-7.44 (dd, J = 8.1 Hz, 4H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 162.7, 152.4, 136.8, 136.2, 133.5, 132.3, 131.0, 130.5, 127.6, 126.6, 125.8, 123.7, 121.6 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>8</sub>BrNS 289.9561, found: 288.9553.

### 2-(2,3-Dichlorophenyl)benzothiazole (3i)



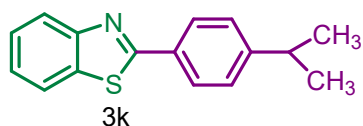
Yield 85%; White solid; m.p. 134-135 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.26-8.24 (m, 1H), 8.16-8.14 (d, J = 8.1 Hz, 1H), 7.99-7.97 (d, J = 8.0 Hz, 1H), 7.59-7.55 (dd, J = 8.1 Hz, 2H), 7.48-7.42 (m, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 162.9, 152.6, 136.7, 136.2, 133.2, 132.3, 131.9, 130.4, 127.6, 126.7, 125.6, 123.6, 121.6 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>7</sub>Cl<sub>2</sub>NS 279.9673, found: 278.9661.

### 2-(4-Methoxyphenyl)benzothiazole (3j) <sup>4</sup>



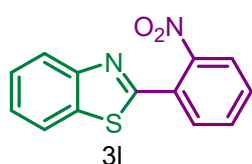
Yield 86%; Yellow solid; m.p. 125-127 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.14–8.12 (m, 2H), 7.63-7.62 (dd, J = 8.0, 0.5 Hz, 1H), 7.51-7.49 (d, J = 8.3, 1.2 Hz, 2H), 7.19-7.16 (ddd, J = 8.3, 1.2 Hz, 1H), 7.15–7.11 (m, 2H) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 160.8, 152.2, 144.4, 135.7, 128.6, 123.4, 122.3, 121.8, 118.8, 114.7, 111.7, 55.3 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>14</sub>H<sub>11</sub>NOS 242.0561, found: 242.0552.

### 2-(4-N,N-dimethyle)benzothiazole (3k) <sup>2</sup>



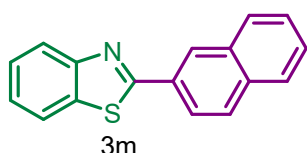
Yield 85%; Yellow powder; m.p. 170-171 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01-7.98 (d, 3H), 7.87-7.86 (d,  $J = 7.8, 1.2$  Hz, 1H), 7.47-7.34 (d, 1H), 7.33-7.28 (d, 1H), 6.78-6.77 (m, 2H), 3.08 (s, 6H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 154.4, 152.2, 134.6, 128.9, 125.9, 124.2, 122.3, 121.4, 121.4, 111.7, 40.2 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{16}\text{H}_{15}\text{NS}$  254.0925, found: 254.0436.

### 2-(2-Nitrophenyl)benzothiazole (3l) <sup>5</sup>



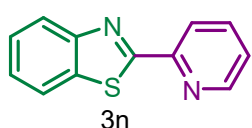
Yield 92%; White solid; m.p. 123-125 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12-8.10 (d,  $J = 1.6$  Hz, 1H), 8.04-8.82 (s, 1H), 7.63-7.61 (d,  $J = 8.0$  Hz, 2H), 7.47-7.44 (m, 4H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.33, 153.60, 148.99, 135.84, 133.36, 131.82, 130.92, 128.16, 126.59, 125.88, 124.52, 123.98, 121.58 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}$  257.0307, found: 256.0315.

### 2-(Naphthalene-2-yl)benzothiazole (3m) <sup>2</sup>



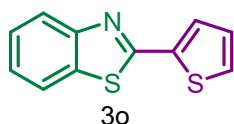
Yield 87%; White solid; m.p. 123-125 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 1.0$  Hz, 1H), 8.25-8.23 (dd,  $J = 8.6, 1.8$  Hz, 1H), 8.16-8.14 (d,  $J = 8.1$  Hz, 1H), 8.01-7.90 (m, 4H), 7.59-7.53 (m, 3H), 7.45-7.42 (dd,  $J = 8.1, 1.2$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.1, 154.5, 135.2, 134.5, 133.2, 131.0, 128.8, 127.9, 127.6, 127.5, 126.9, 126.4, 125.3, 124.3, 123.4, 121.7 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{17}\text{H}_{12}\text{NS}$  263.0690, found: 263.0699.

### 2-(Pyridin-2-yl)benzothiazole (3n) <sup>2</sup>



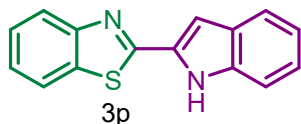
Yield 84%; Yellow powder; m.p. 133-135 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.69 (d, J = 7.8 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 7.8, 1H), 7.52-7.49 (d, 1H), 7.43-7.41 (d, J = 8.0, Hz, 1H), 7.40 (d, J = 7.9, 1H), 7.38-7.35 (dd, J = 8.2, 7.7 Hz, 1H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.4, 154.3, 151.4, 149.6, 136.9, 136.1, 126.3, 125.7, 125.3, 123.6, 122.0, 120.7 ppm. HRMS (ESI): m/z: [M+H<sup>+</sup>] calculated for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>S 213.0408, found: 213.0420.

### 2-(Thiophen-2-yl)benzothiazole (3o) <sup>2</sup>



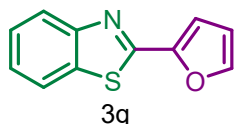
Yield 84%; White solid; m.p. 97-99 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 7.84 (dd, J = 8.0, 1.1 Hz, 1H), 7.73 (dd, J = 8.0, 1.1 Hz, 1H), 7.72 (dd, J = 3.7, 1.1 Hz, 1H), 7.62-7.51 (m, 1H), 7.50-7.22 (m, 3H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 147.5, 144.0, 135.0, 134.2, 129.2, 128.7, 127.1, 123.1, 122.2, 119.0, 111.7 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>11</sub>H<sub>7</sub>NS<sub>2</sub> 218.0020, found: 217.0030.

### 2-(1H-Indol-2-yl)benzothiazole (3p) <sup>6</sup>



Yield 83%; Yellow solid; m.p. 146-148 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 11.00 (s, 1H), 8.34-8.32 (d, J = 8.2 Hz, 1H), 7.88-7.87 (d, J = 8.0, 1.2 Hz, 1H), 7.70-7.68 (m, 1H), 7.57-7.49 (dd, 2H), 7.27-7.18 (m, 3H), 5.83 (s, 1H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 150.0, 136.8, 136.5, 136.1, 126.9, 126.0, 123.9, 122.8, 121.9, 120.7, 119.3, 118.8, 112.3, 110.9, 105.5 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>S 251.0565, found: 250.0575.

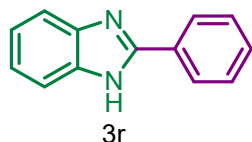
### 2-(Furan-2-yl)benzothiazole (3q) <sup>4</sup>



Yield 84%; Yellow solid; m.p. 104-106 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 8.16 (d, J = 8.2 Hz, 1H), 8.04-8.02 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 1.8, 0.5 Hz, 1H), 7.37 (ddd, J = 8.0, 1.2 Hz, 1H), 6.61 (ddd, J = 8.0, 1.2 Hz, 1H), 6.80 (dd, J = 3.5, 0.5 Hz, 1H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-

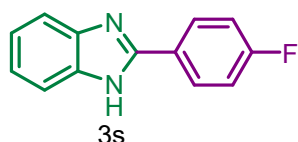
d<sub>6</sub>):  $\delta$  157.3, 153.8, 148.6, 146.6, 134.0, 127.3, 125.9, 123.1, 122.9, 113.5, 112.4 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>11</sub>H<sub>7</sub>NOS 202.0248, found: 201.0259.

### 2-Phenylbenzimidazole (3r) <sup>3</sup>



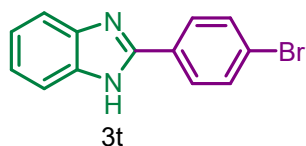
Yield 90%; Yellow powder; m.p. 293-294 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.91 (s, 1H), 8.20-8.18 (d, 2H), 7.68 (s, 1H), 7.58-7.55 (d, 3H), 7.50 (d, 1H), 7.49-7.18 (m, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta$  151.7, 144.3, 135.5, 130.6, 130.3, 129.4, 126.9, 122.9, 122.1, 119.3, 111.8 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub> 195.0844, found: 194.0860.

### 2-(4-Fluorophenyl)benzimidazole (3s) <sup>7</sup>



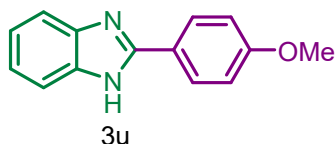
Yield 91%; Yellow powder; m.p. 256-258 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.91 (s, 1H), 8.25-8.22 (d, J = 8.3 Hz, 2H), 7.67- 7.66 (d, J = 8.32 Hz, 2H), 7.43-7.42 (m, 2H), 7.39-7.21 (s, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta$  164.7, 162.9, 151.0, 144.3, 135.4, 129.0, 127.2, 123.0, 122.2, 119.5, 116.5, 111.6 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>9</sub>FN<sub>2</sub> 213.0750, found: 212.0770.

### 2-(4-Bromophenyl)benzimidazole (3t) <sup>1</sup>



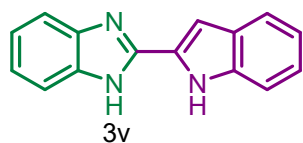
Yield 90%; White solid; m.p. 294-296 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.01 (s, 1H), 8.14-8.12 (d, J = 8.3 Hz, 2H), 7.78-7.61 (m, 4H), 7.23-7.22 (d, J = 8.1Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta$  150.7, 132.5, 129.9, 128.8, 123.7, 122.7 ppm. HRMS (ESI) [M+H<sup>+</sup>] calculated for C<sub>13</sub>H<sub>9</sub>BrN<sub>2</sub> 272.9950, found: 272.9980.

### 2-(4-Methoxyphenyl)benzimidazole (3u) <sup>1</sup>



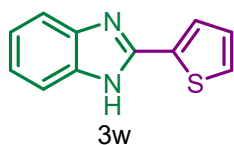
Yield 86%; White solid; m.p. 222-224 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  12.72 (s, 1H), 8.14 (d,  $J$  = 8.0Hz, 2H), 7.63-7.61 (m, 2H), 7.18–7.15 (m, 4H), 7.22 (d,  $J$  = 7.6Hz, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  161.0, 151.8, 144.4, 135.4, 128.5, 123.2, 122.5, 121.9, 118.9, 114.8, 111.5, 55.8 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$  225.0950, found: 225.0980.

### 2-(1H-Indol-2-yl)benzimidazole (3v) <sup>8</sup>



Yield 83%; Yellow solid; m.p. 160-161 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.67 (s, 1H), 11.00 (s, 1H) 8.34-8.33 (dd,  $J$  = 2.8, 0.9 Hz, 1H), 7.88-7.87 (d,  $J$  = 5.0, 0.7 Hz, 1H), 7.57-7.56 (dd,  $J$  = 5.0, 2.9 Hz, 1H), 7.27-7.19 (m, 1H), 6.84-6.83 (m, 4H), 5.83 (s, 1H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  150.4, 136.9, 136.3, 127.3, 125.8, 124.3, 123.2, 121.7, 120.6, 119.1, 112.7, 111.4, 105.9 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{15}\text{H}_{11}\text{N}_3$  234.0953, found: 234.0920.

### 2-(Thiophen-3-yl)benzimidazole (3w) <sup>7</sup>

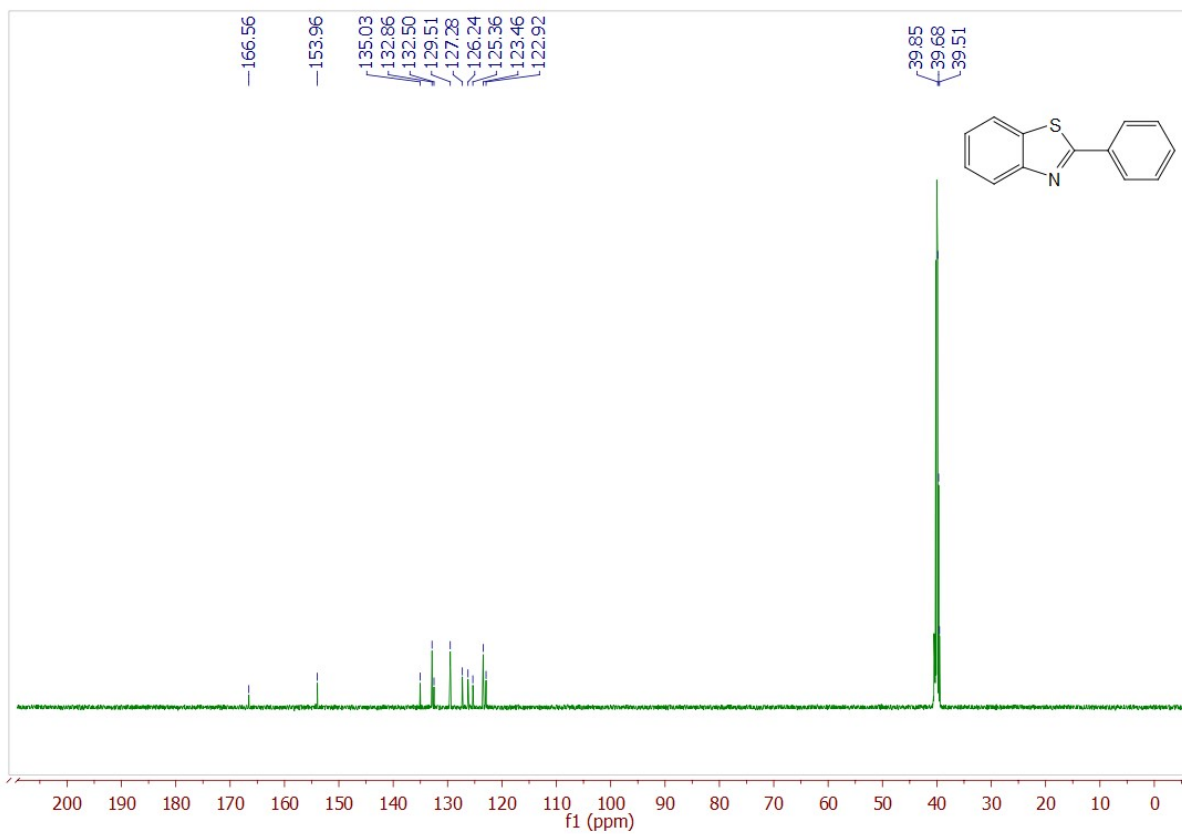
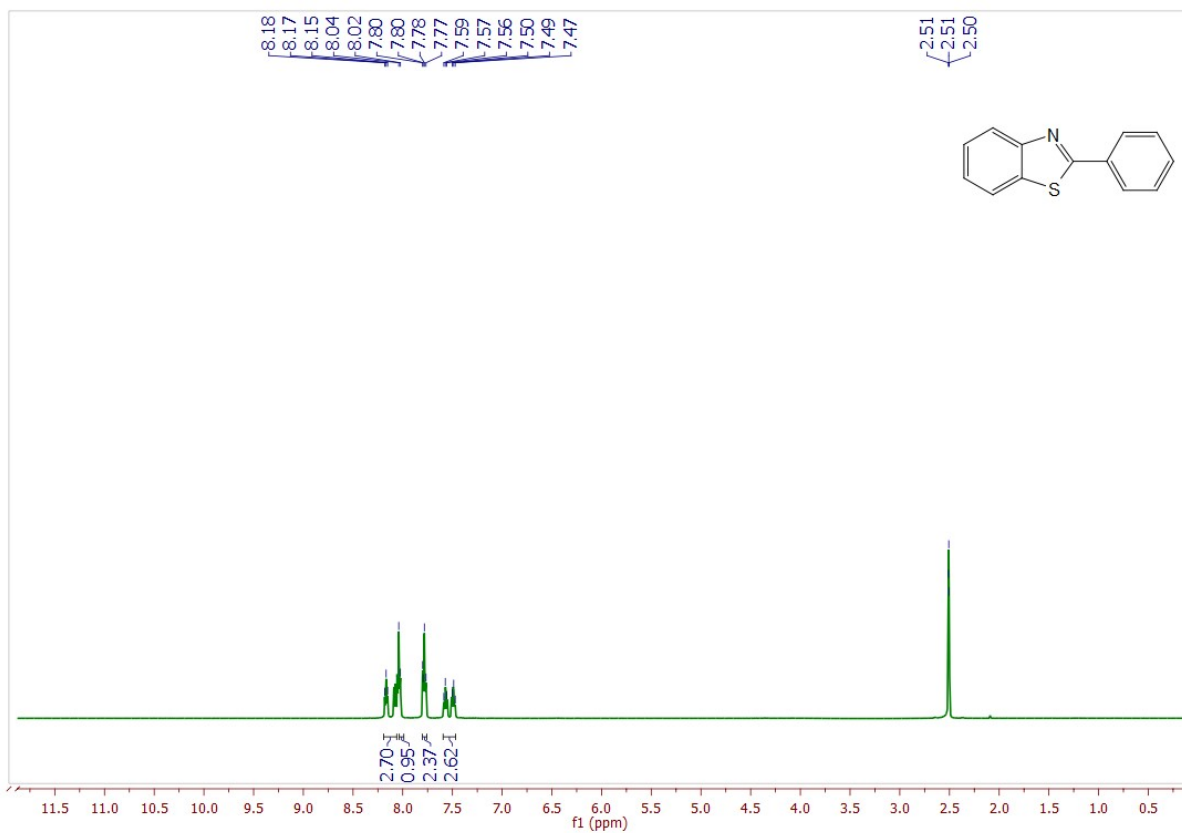


Yield 84%; White solid; m.p. 280 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  12.92 (s, 1H), 7.84-7.83 (dd,  $J$  = 2.8, 0.9 Hz, 1H), 7.73-7.72 (dd,  $J$  = 5.0, 0.7 Hz, 1H), 7.62-7.51 (dd,  $J$  = 5.0, 2.9 Hz, 1H), 7.50 (s, 1H), 7.25-7.20 (m, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  147.4, 144.2, 135.4, 134.2, 129.2, 128.6, 127.0, 123.0, 122.2, 118.9, 111.6 ppm. HRMS (ESI)  $[\text{M}+\text{H}^+]$  calculated for  $\text{C}_{11}\text{H}_8\text{N}_2\text{S}$  201.0408, found: 201.0430.

- 1 P. K. Sahu, RSC Adv., 2017, **7**, 42000–42012.
- 2 H. S. Hwang, S. Lee, S. S. Han, Y. K. Moon, Y. You and E. J. Cho, J. Org. Chem., 2020, **85**, 11835–11843.
- 3 Y. Cheng, J. Yang, Y. Qu and P. Li, Org. Lett., 2012, **14**, 98–101.
- 4 L. Ye, J. Chen, P. Mao, Z. Mao, X. Zhang and M. Yan, Tetrahedron Lett., 2017, **58**, 874–876.
- 5 R. Fazaeli and H. Aliyan, Appl. Catal. Gen., 2009, **353**, 74–79.
- 6 F. Diwan, M. H. Shaikh, M. Shaikh and M. Farooqui, Org. Commun., 2019, **12**, 13.
- 7 Z. Wang, T. Song and Y. Yang, Synlett, 2019, **30**, 319–324.
- 8 V. K. A. Kalalbandi and J. Seetharamappa, Synth. Commun., 2016, **46**, 626–635.

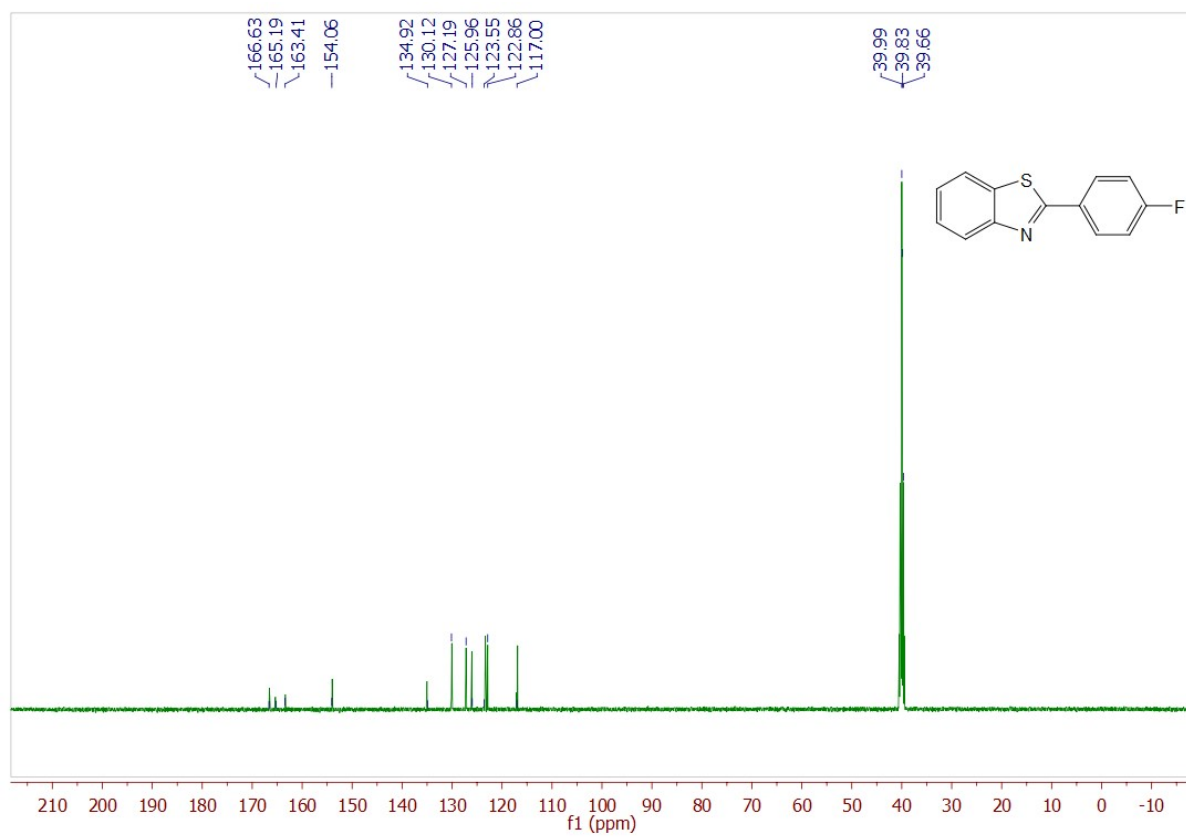
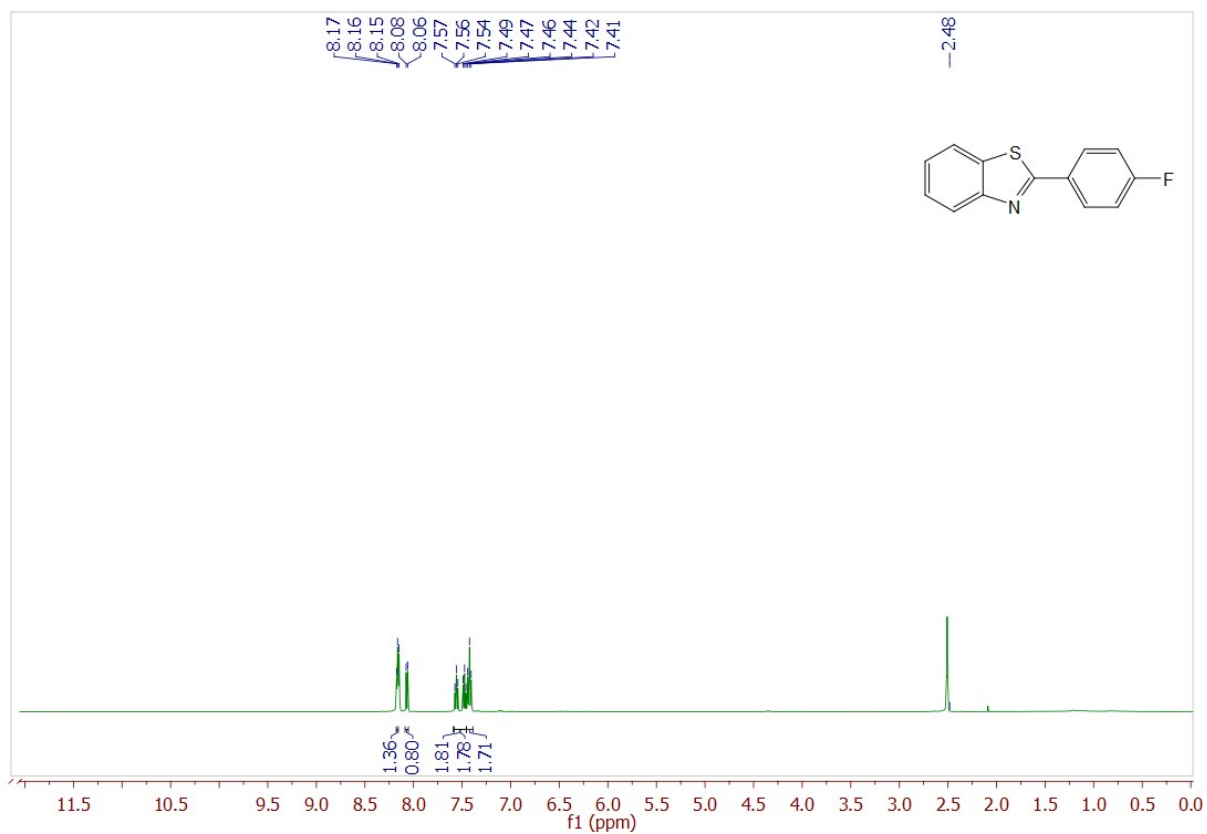
## 5.2 $^1\text{H}$ , $^{13}\text{C}$ NMR & Mass spectra of products

### $^1\text{H}$ and $^{13}\text{C}$ NMR (3a)

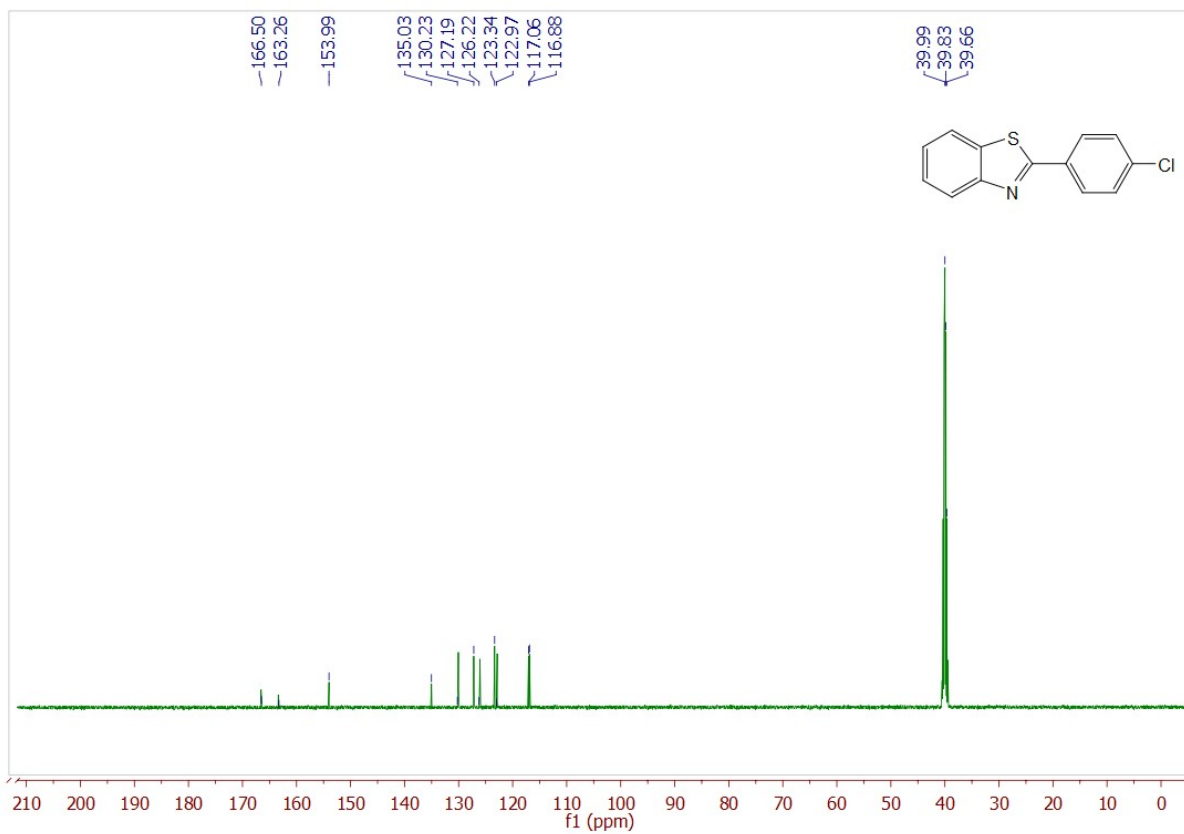
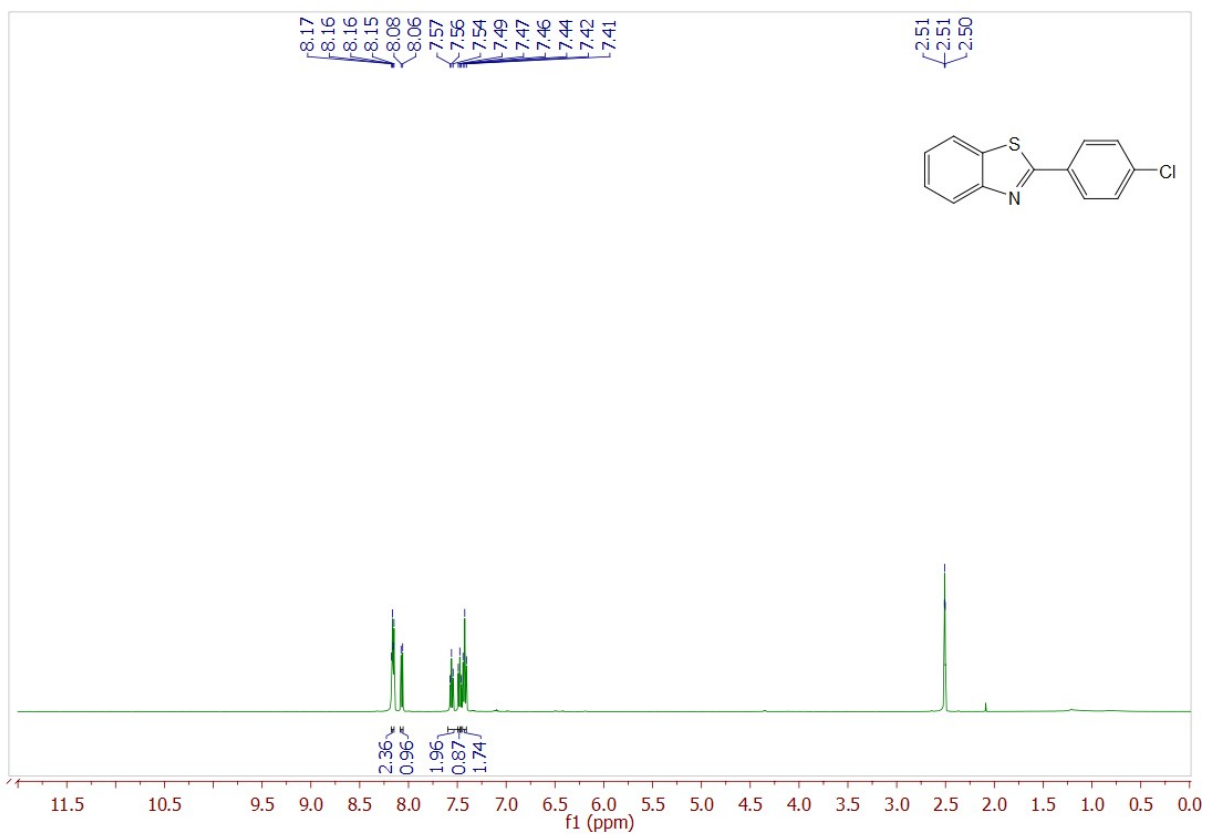




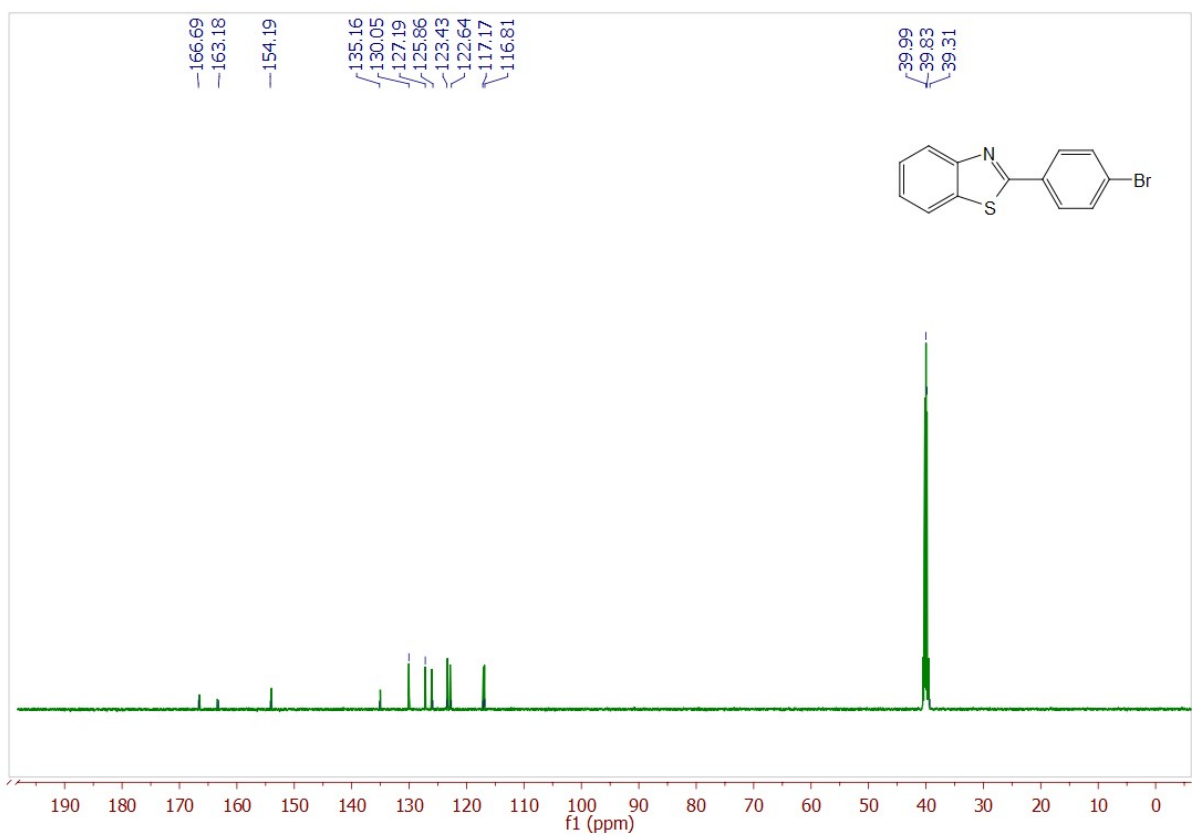
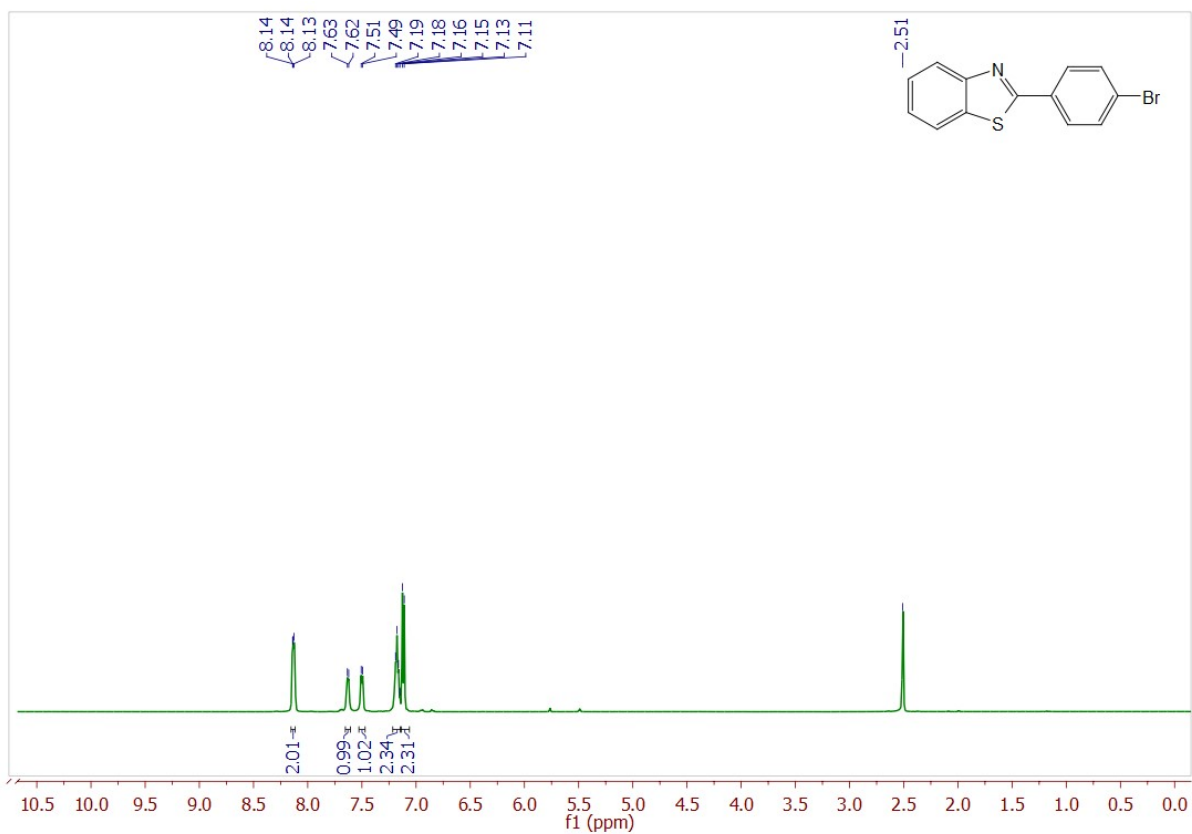
# $^1\text{H}$ and $^{13}\text{C}$ NMR (3b)



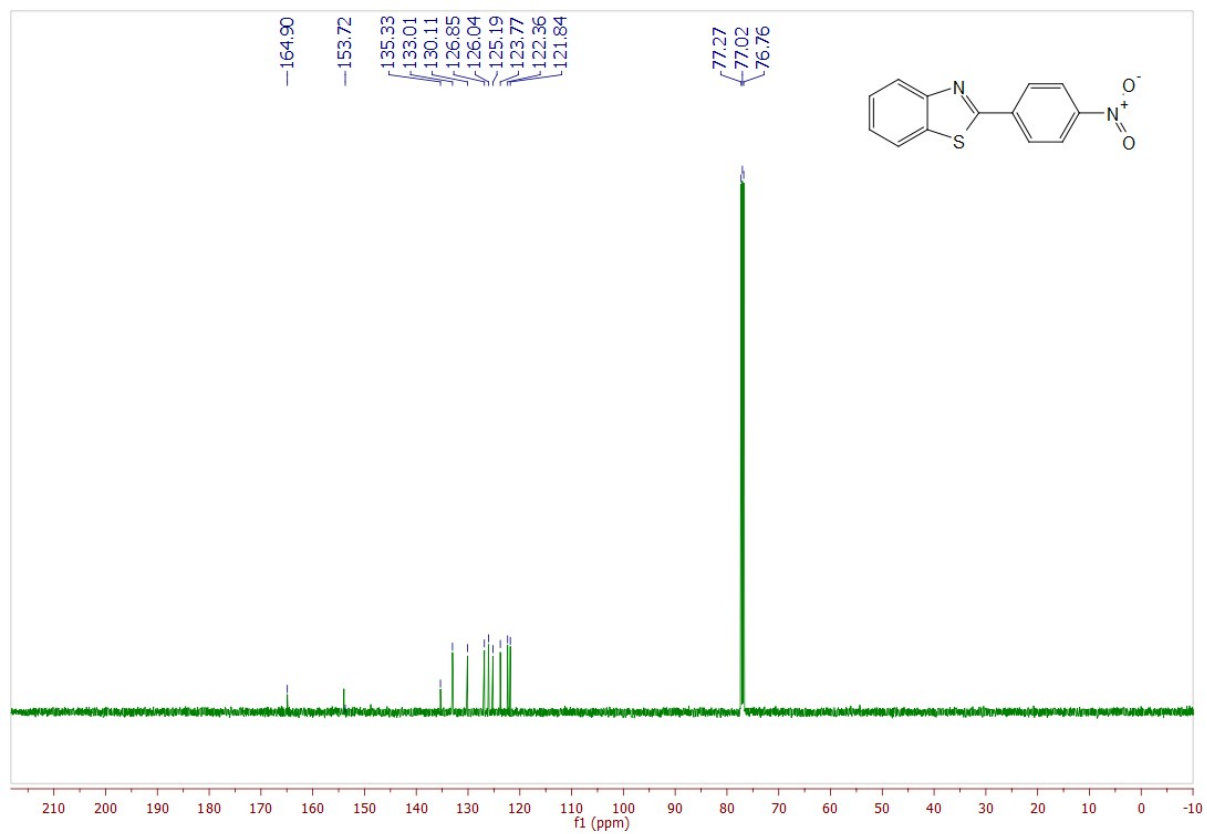
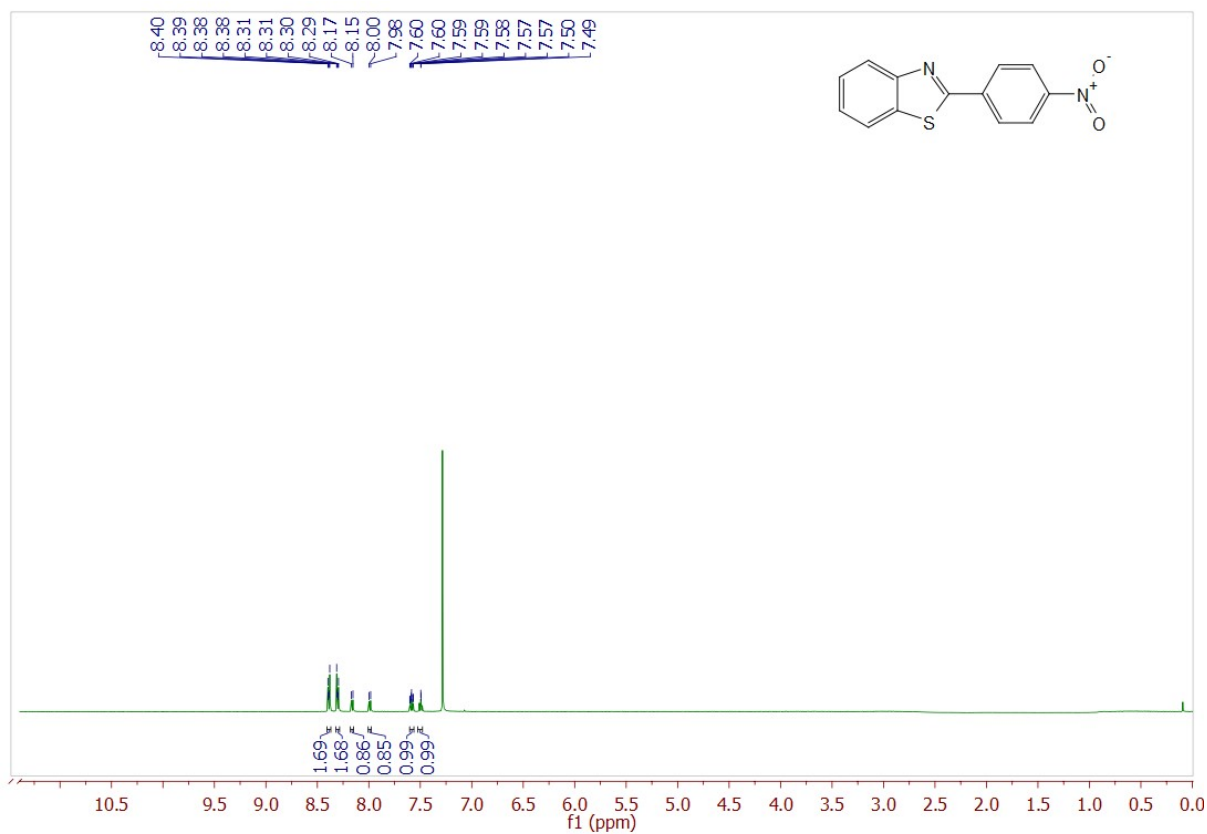
# <sup>1</sup>H and <sup>13</sup>C NMR (3c)



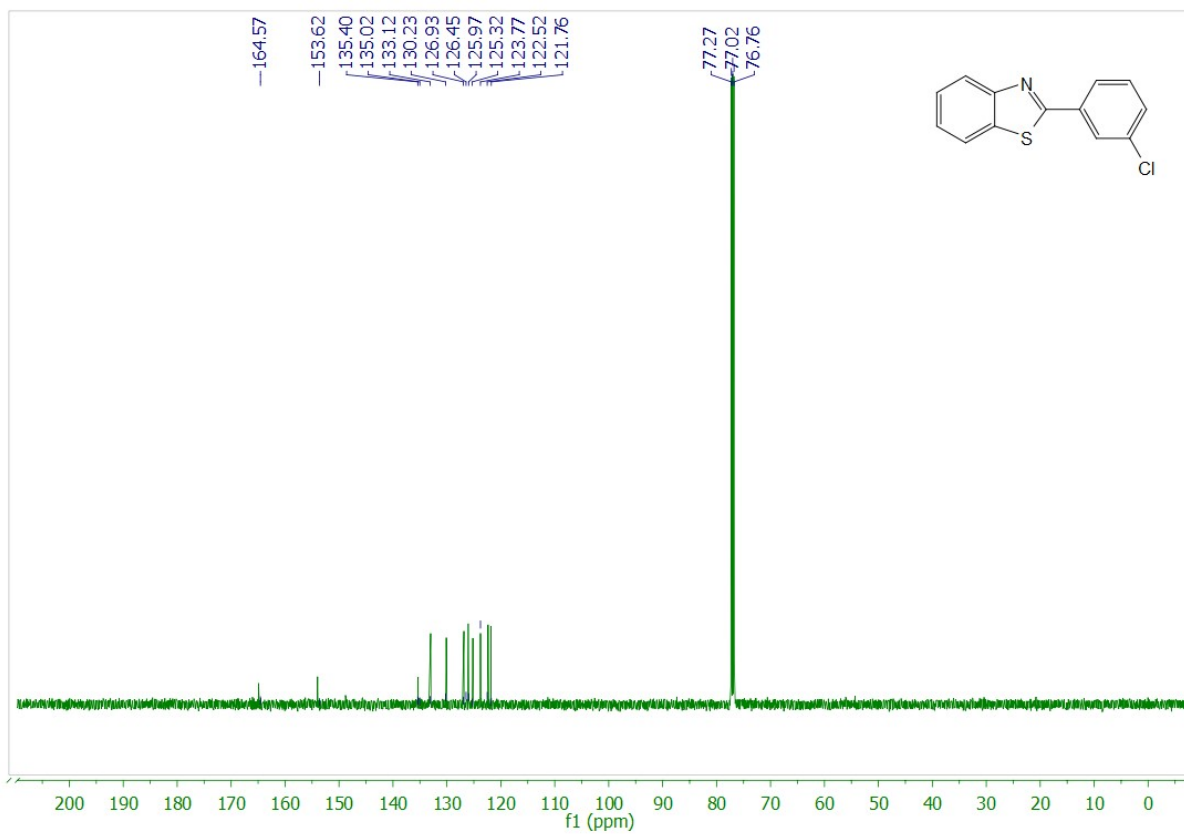
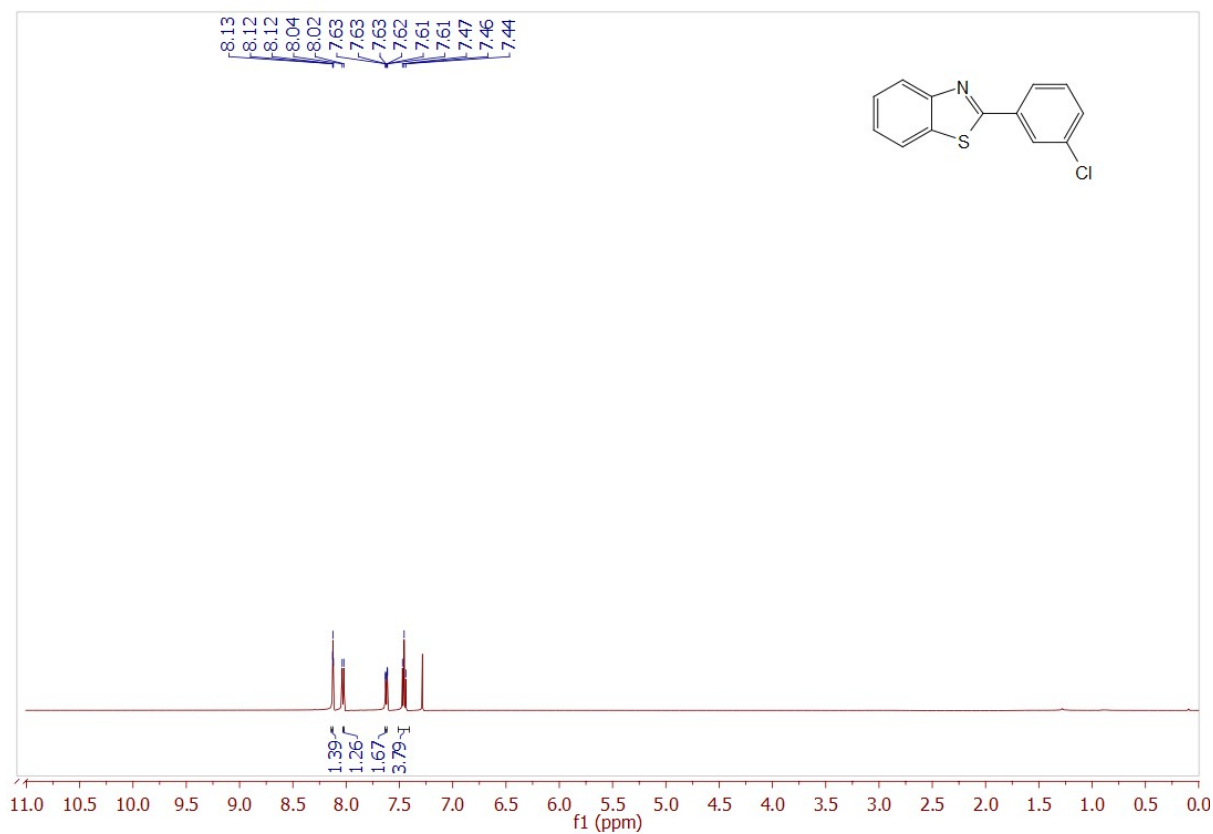
# <sup>1</sup>H and <sup>13</sup>C NMR (3d)



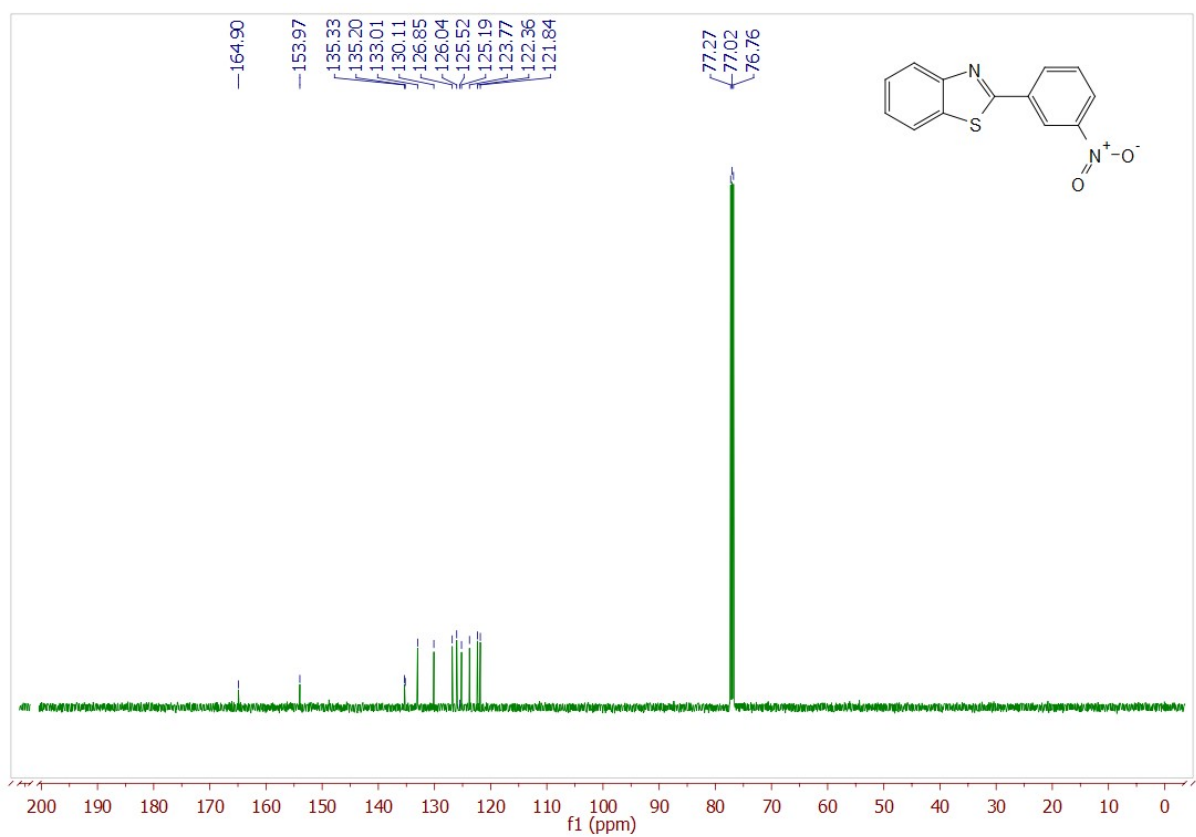
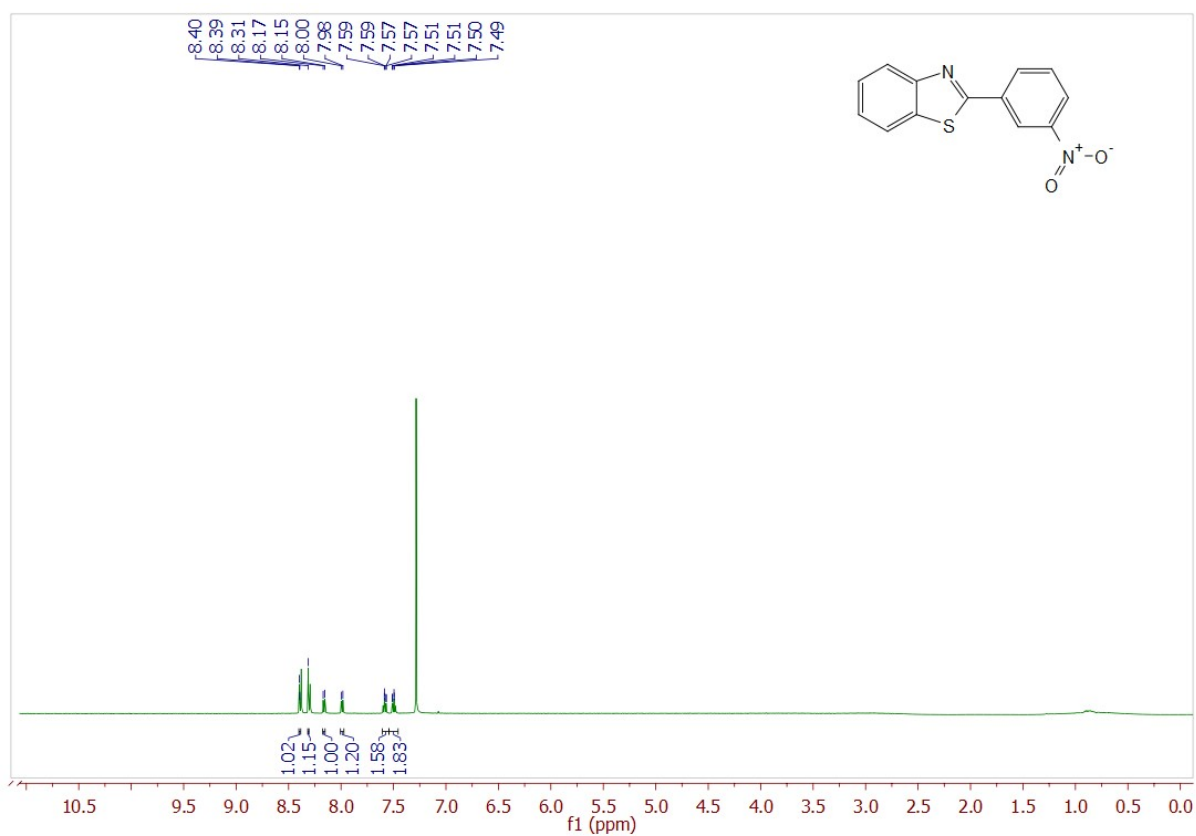
# <sup>1</sup>H and <sup>13</sup>C NMR (3e)



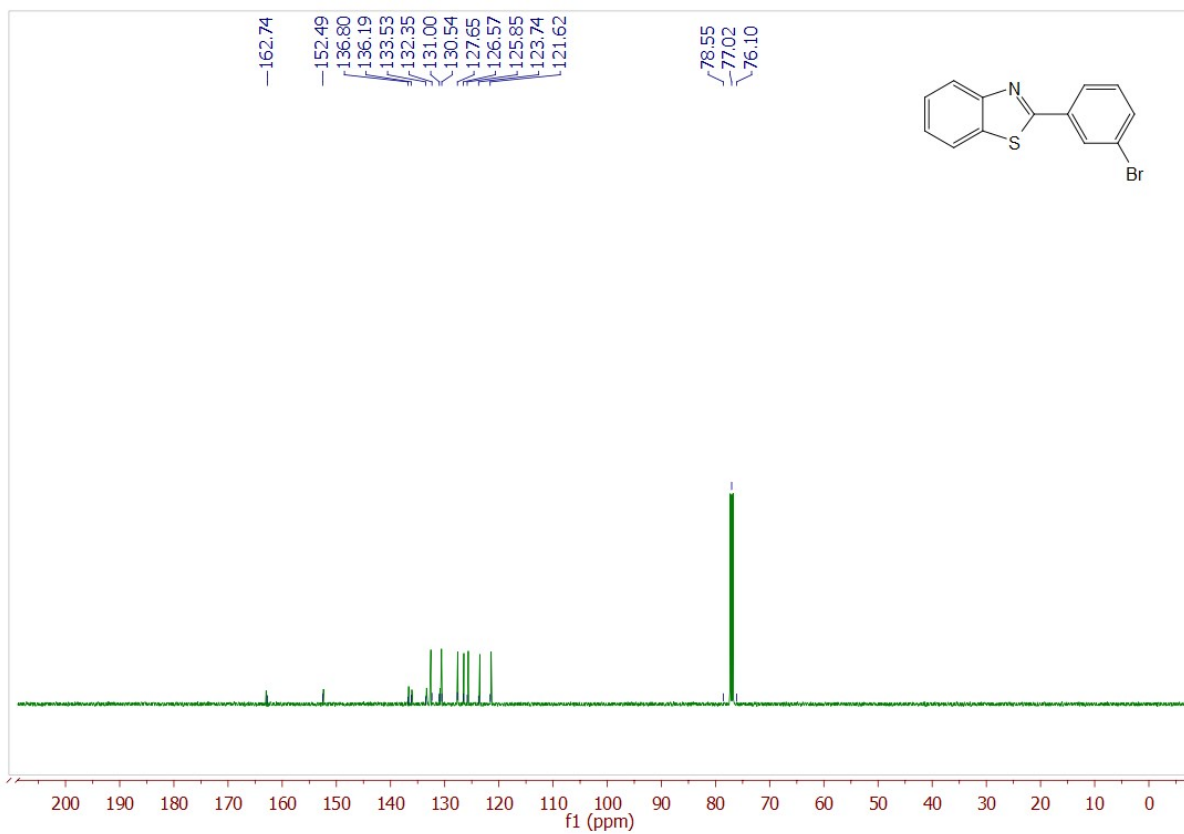
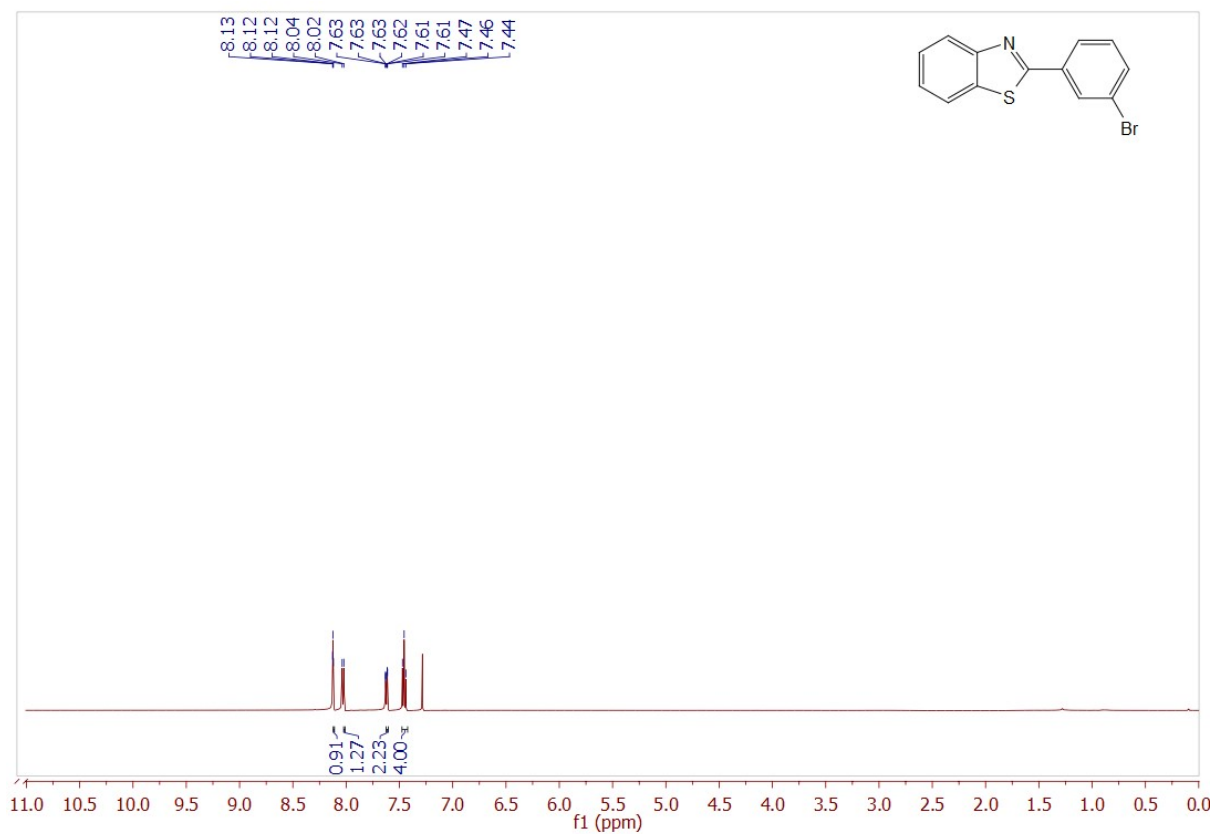
# <sup>1</sup>H and <sup>13</sup>C NMR (3f)



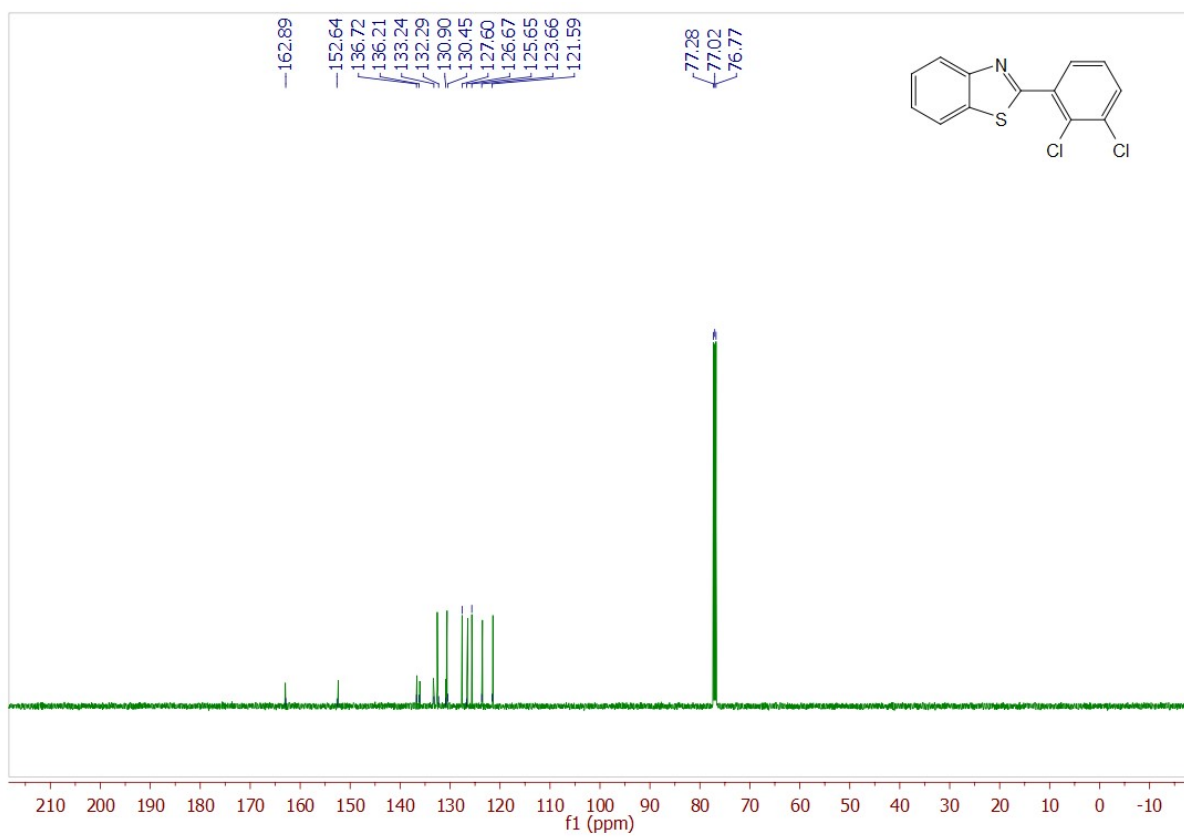
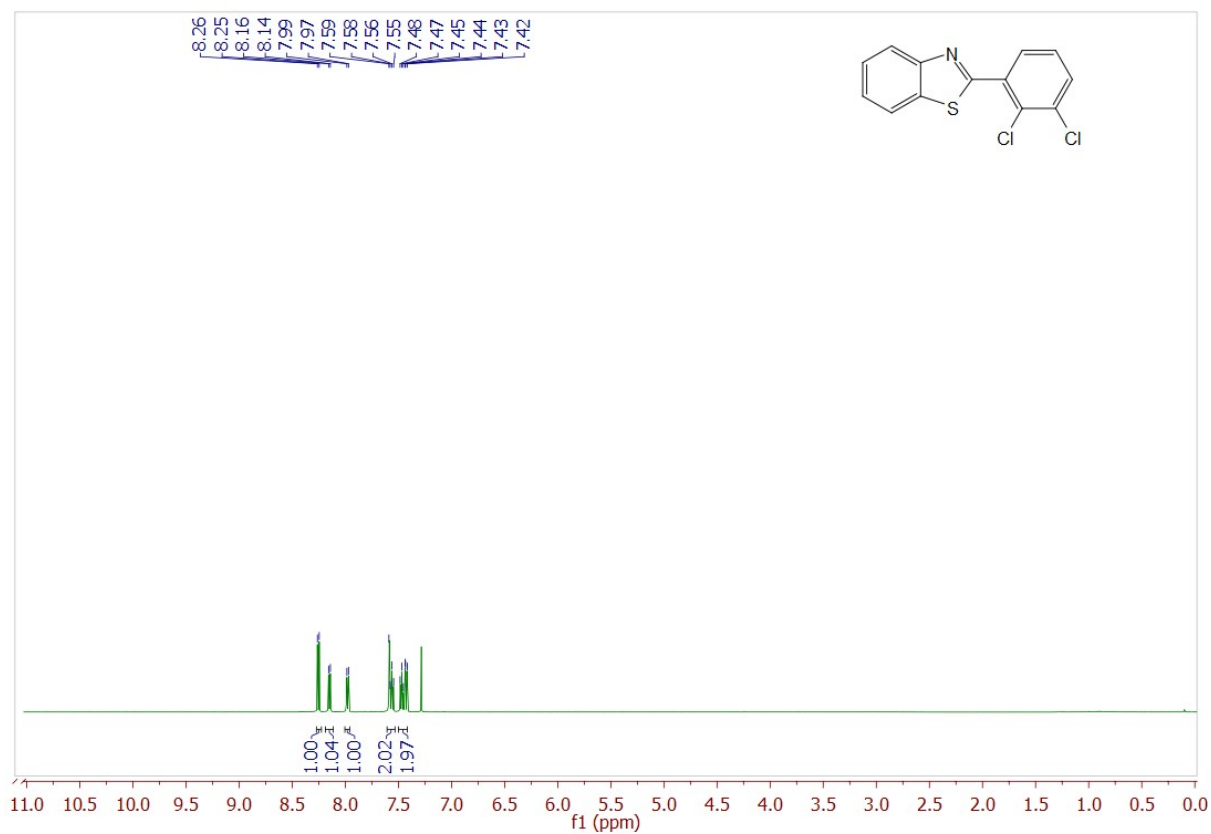
# $^1\text{H}$ and $^{13}\text{C}$ NMR (3g)



# <sup>1</sup>H and <sup>13</sup>C NMR (3h)

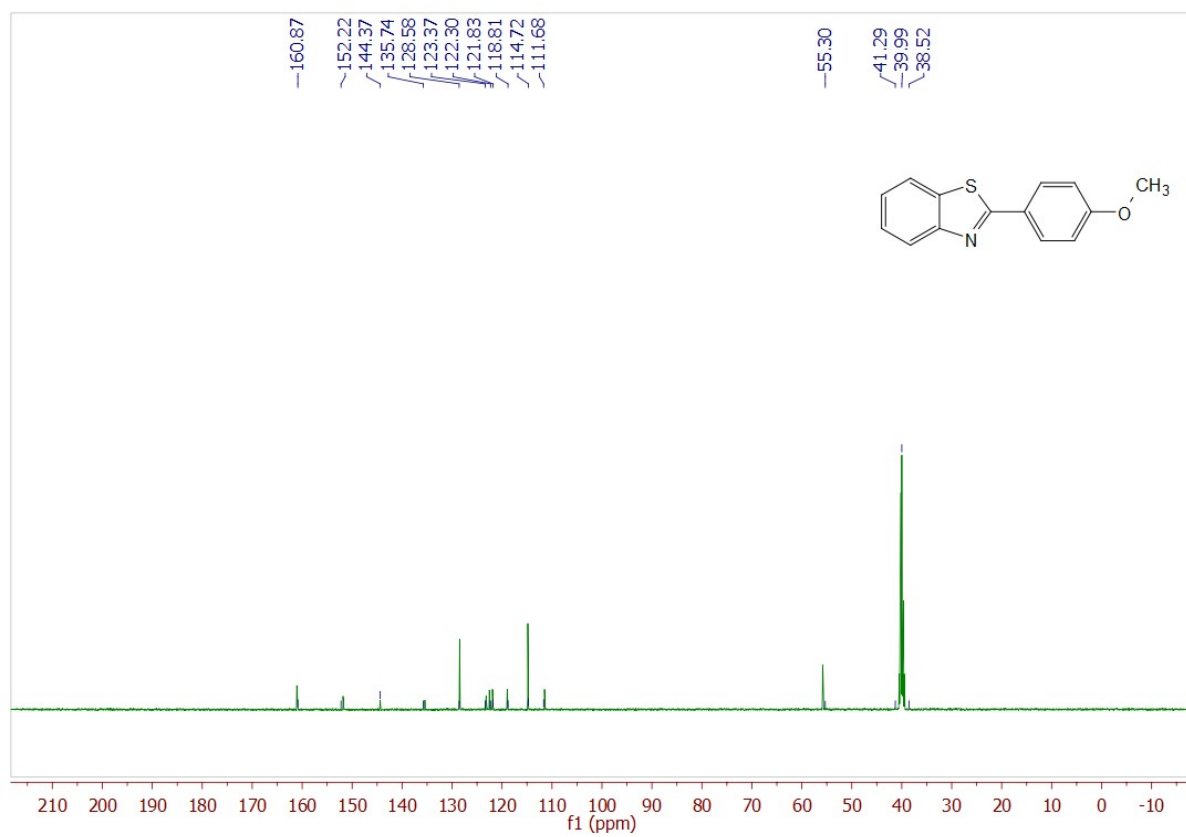
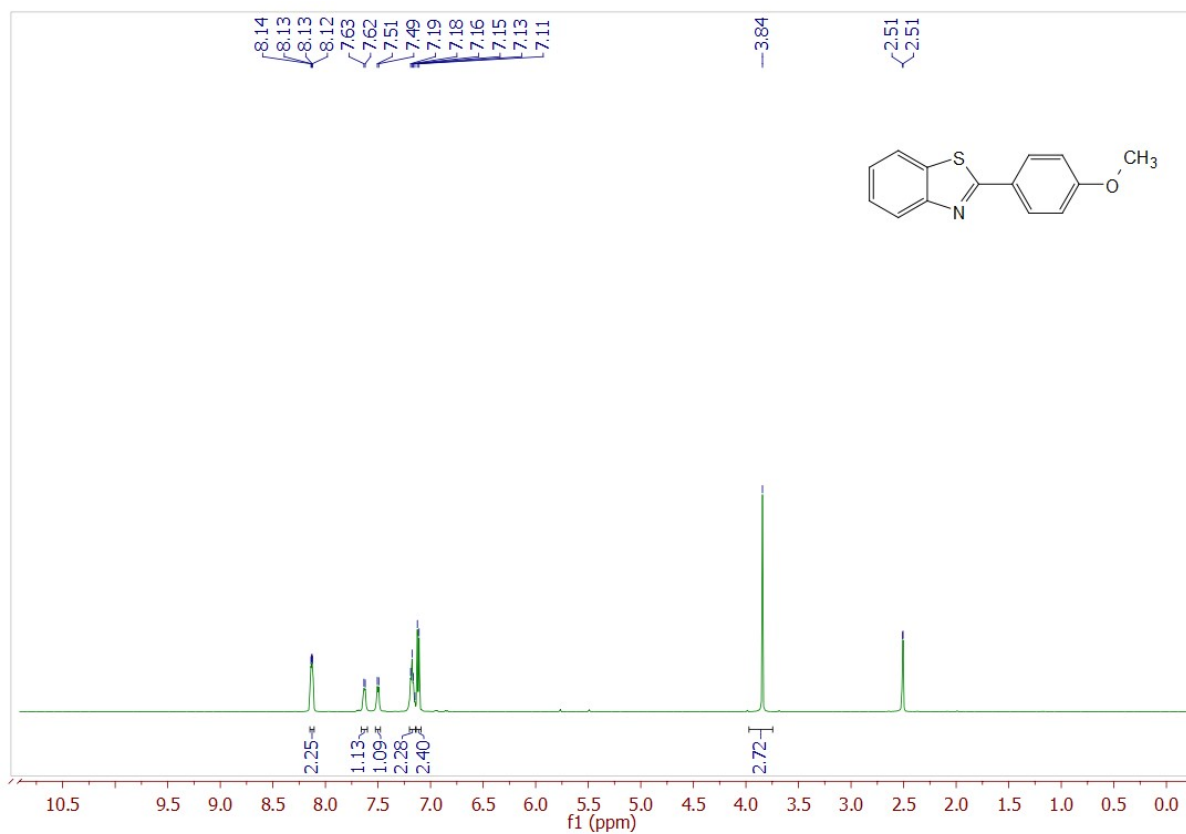


### $^1\text{H}$ and $^{13}\text{C}$ NMR (3i)

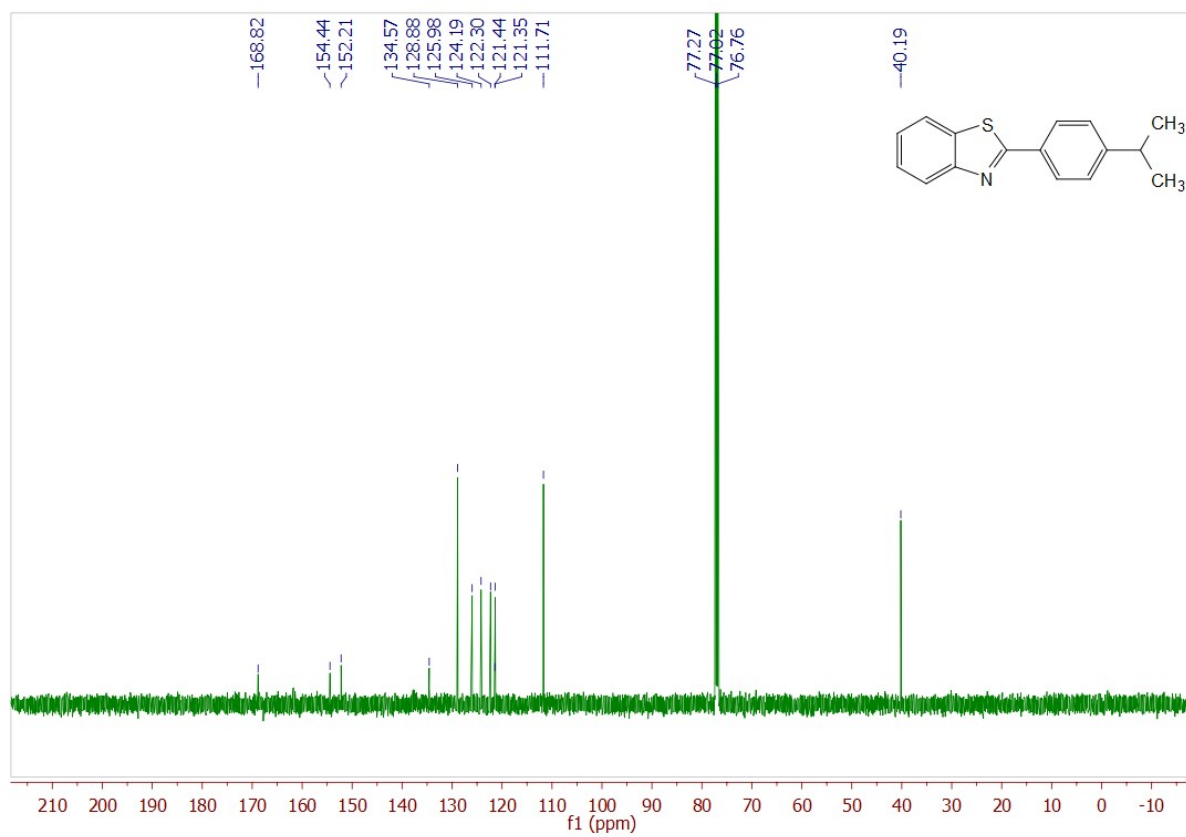
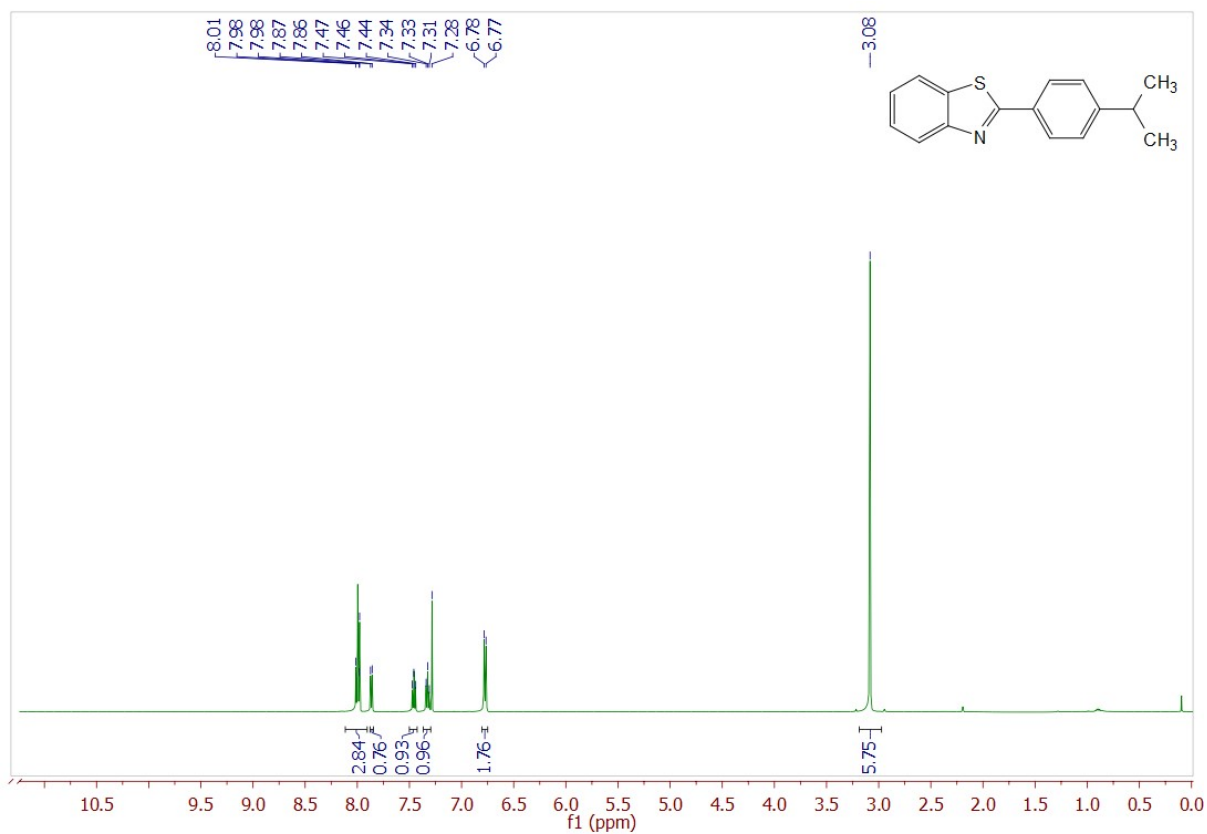




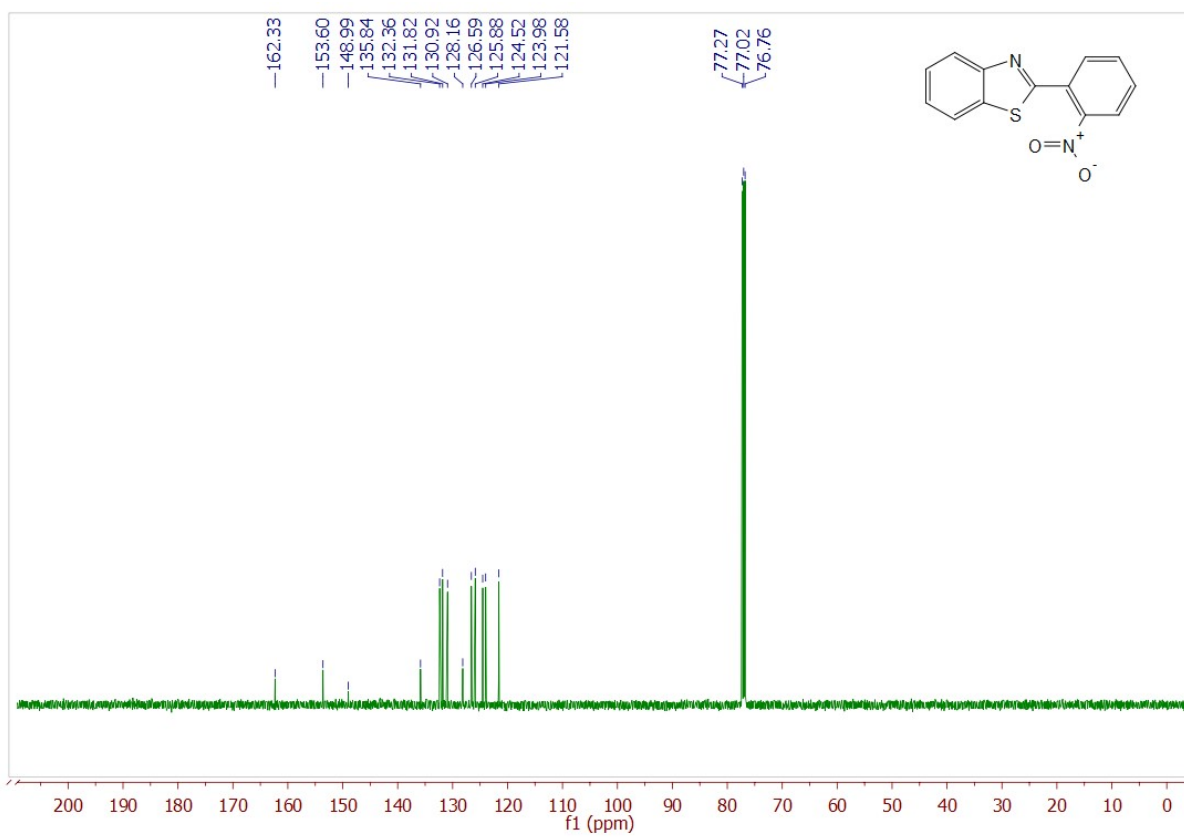
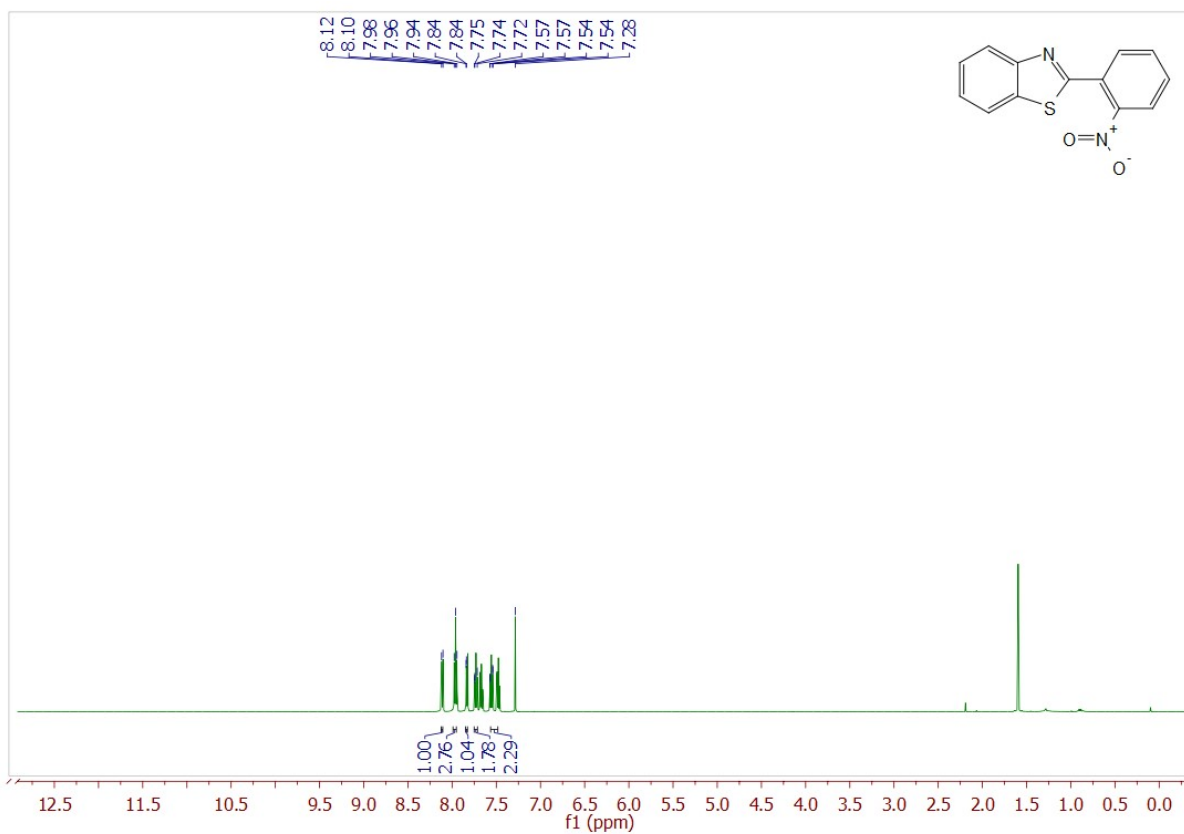
# <sup>1</sup>H and <sup>13</sup>C NMR (3J)



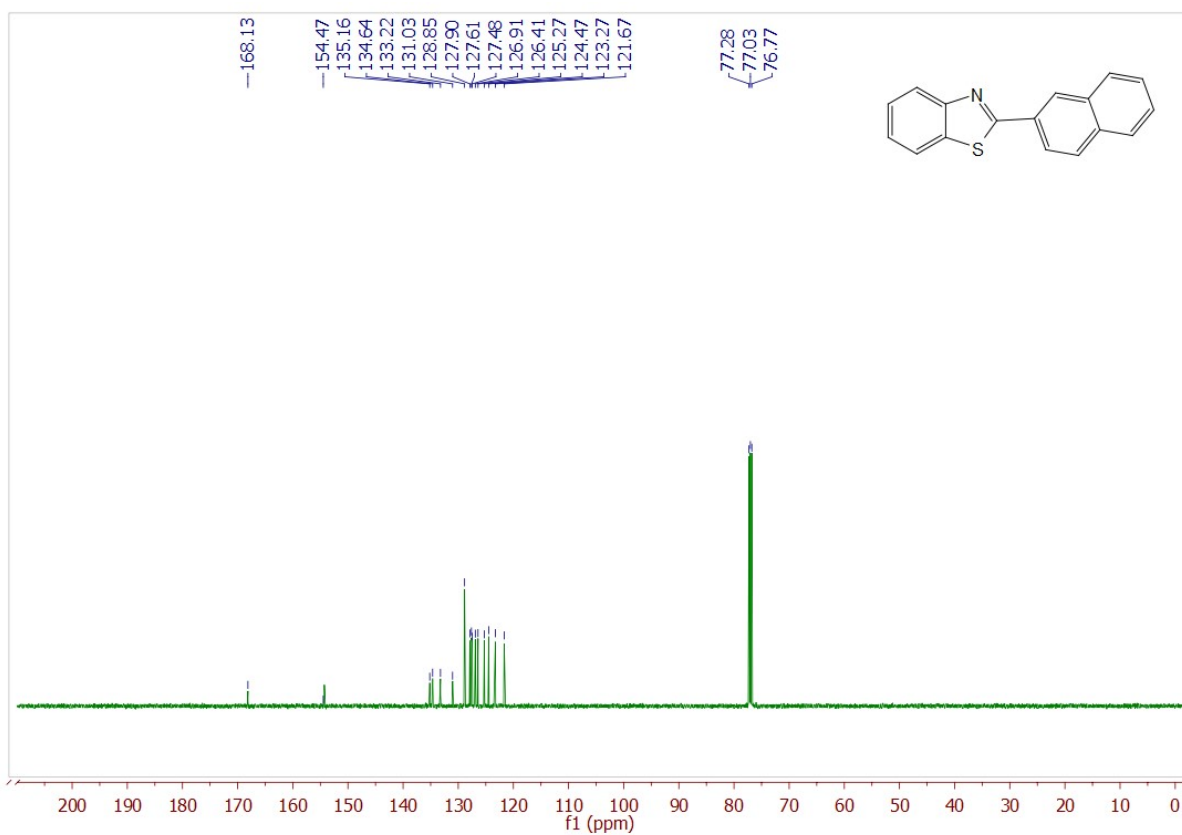
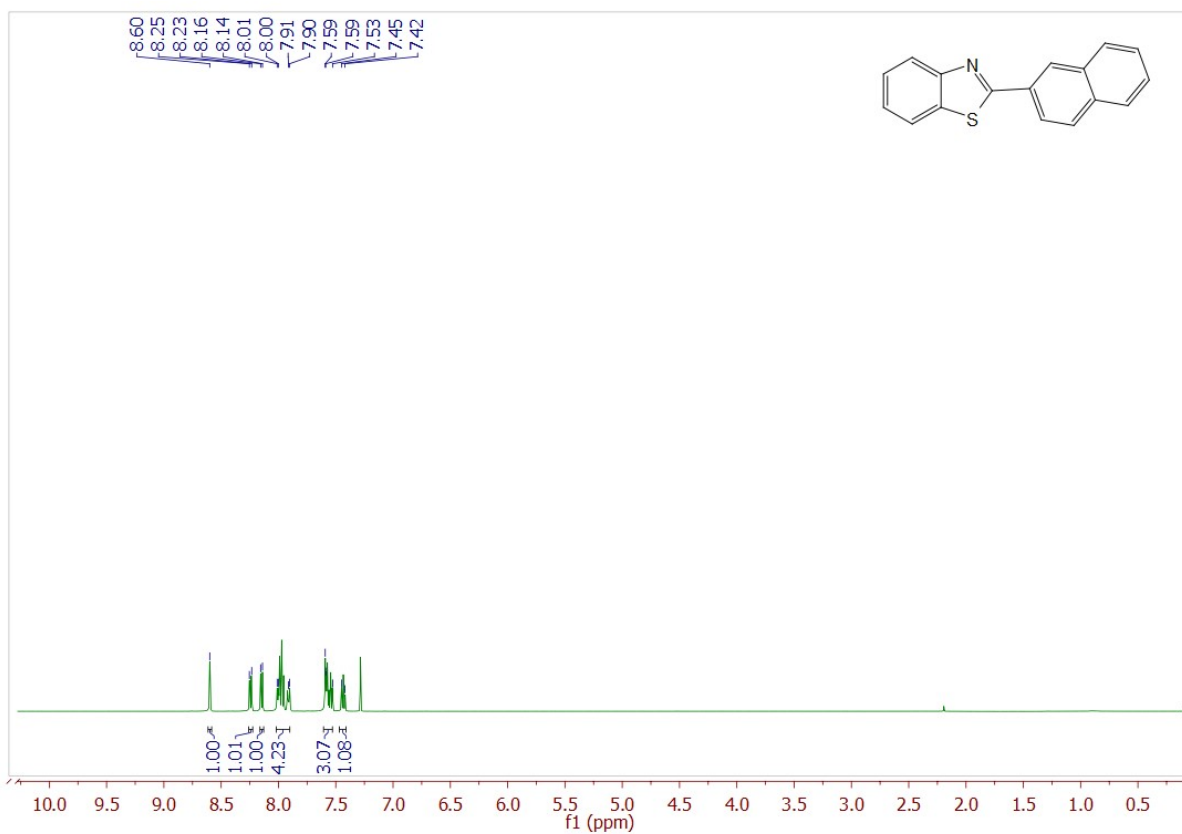
# <sup>1</sup>H and <sup>13</sup>C NMR (3k)



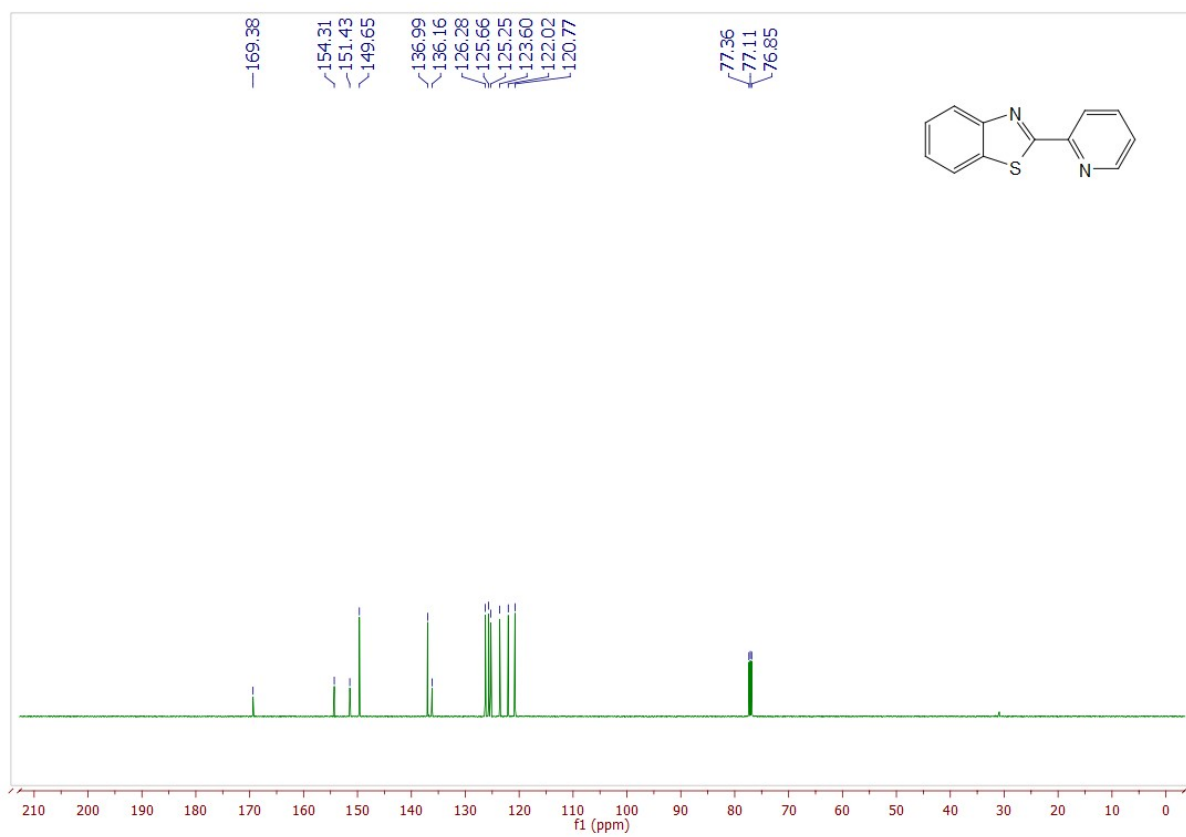
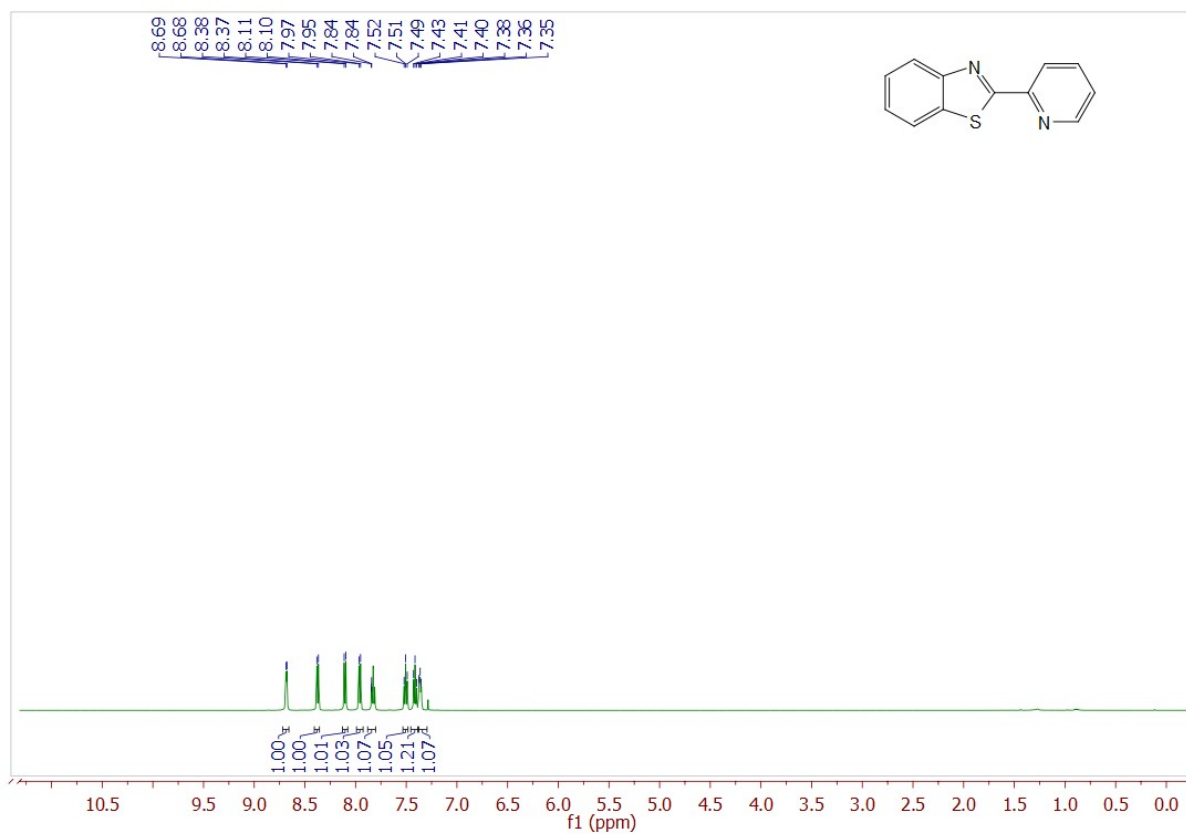
# <sup>1</sup>H and <sup>13</sup>C NMR (3l)



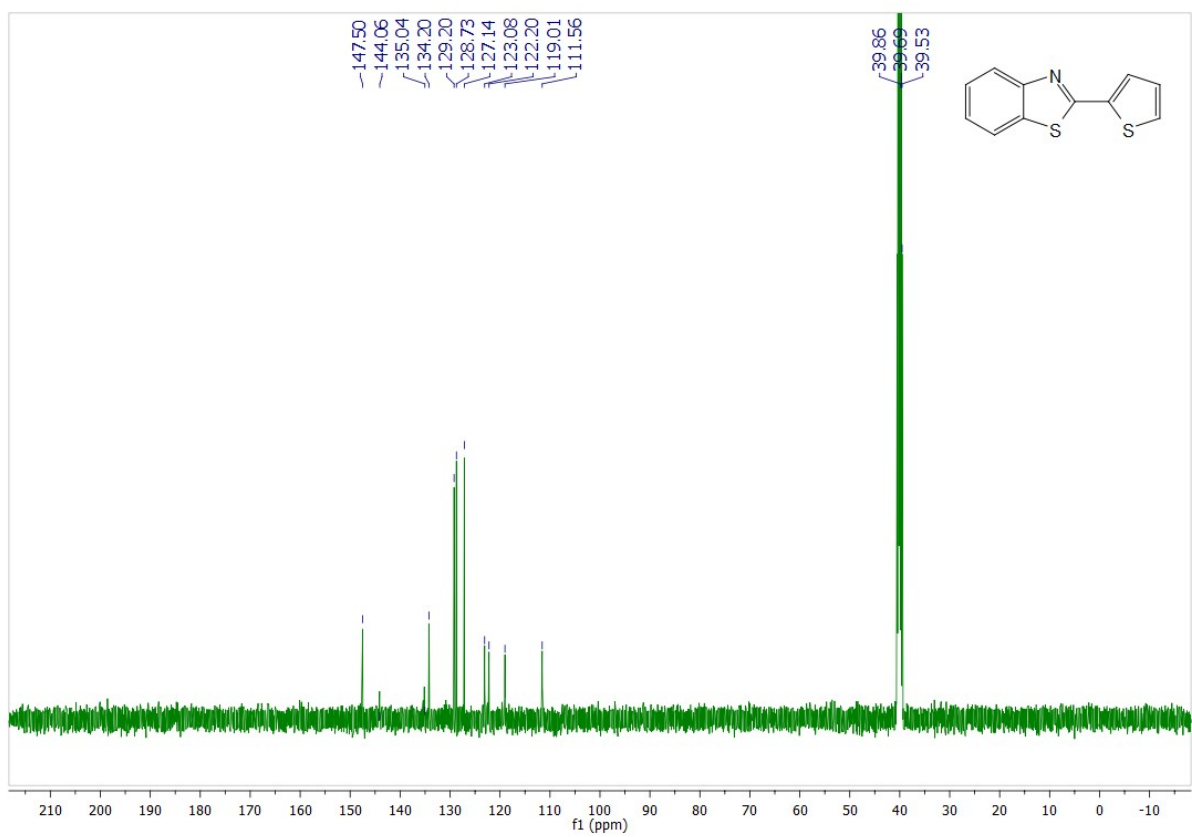
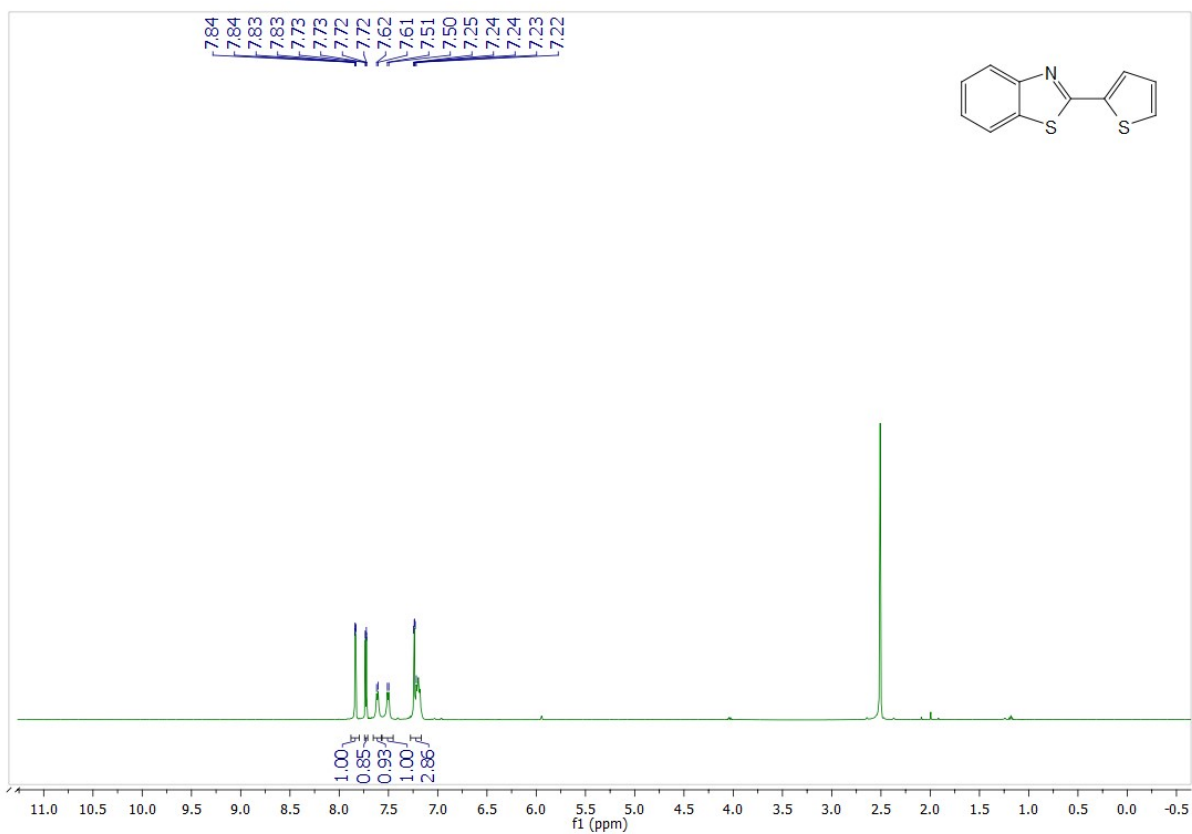
# <sup>1</sup>H and <sup>13</sup>C NMR (3m)



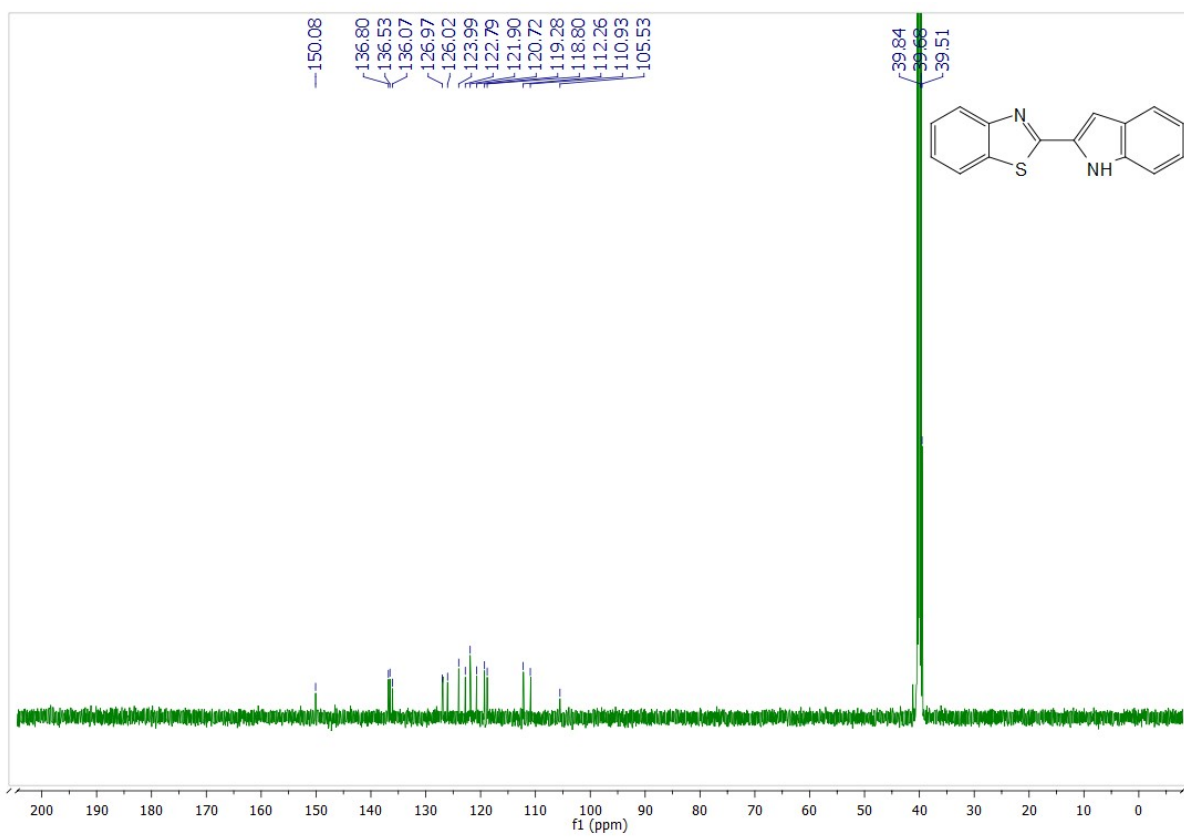
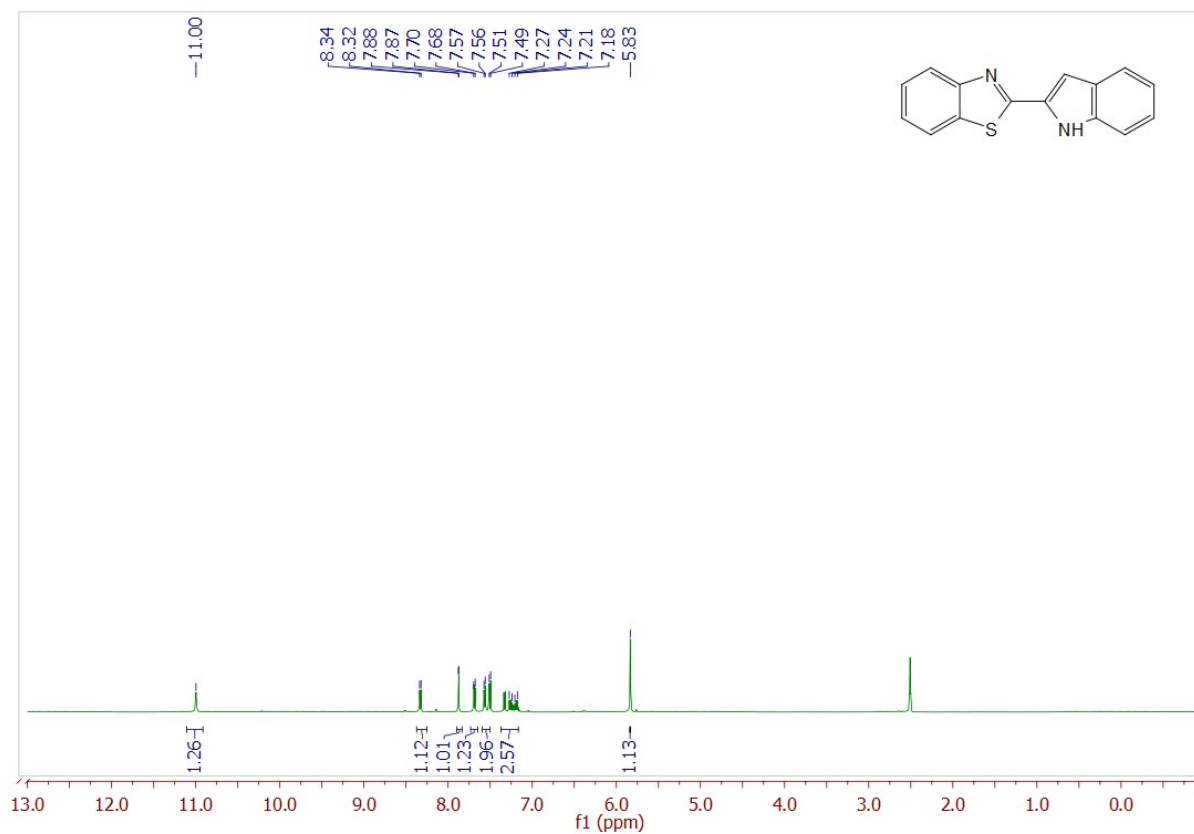
# <sup>1</sup>H and <sup>13</sup>C NMR (3n)



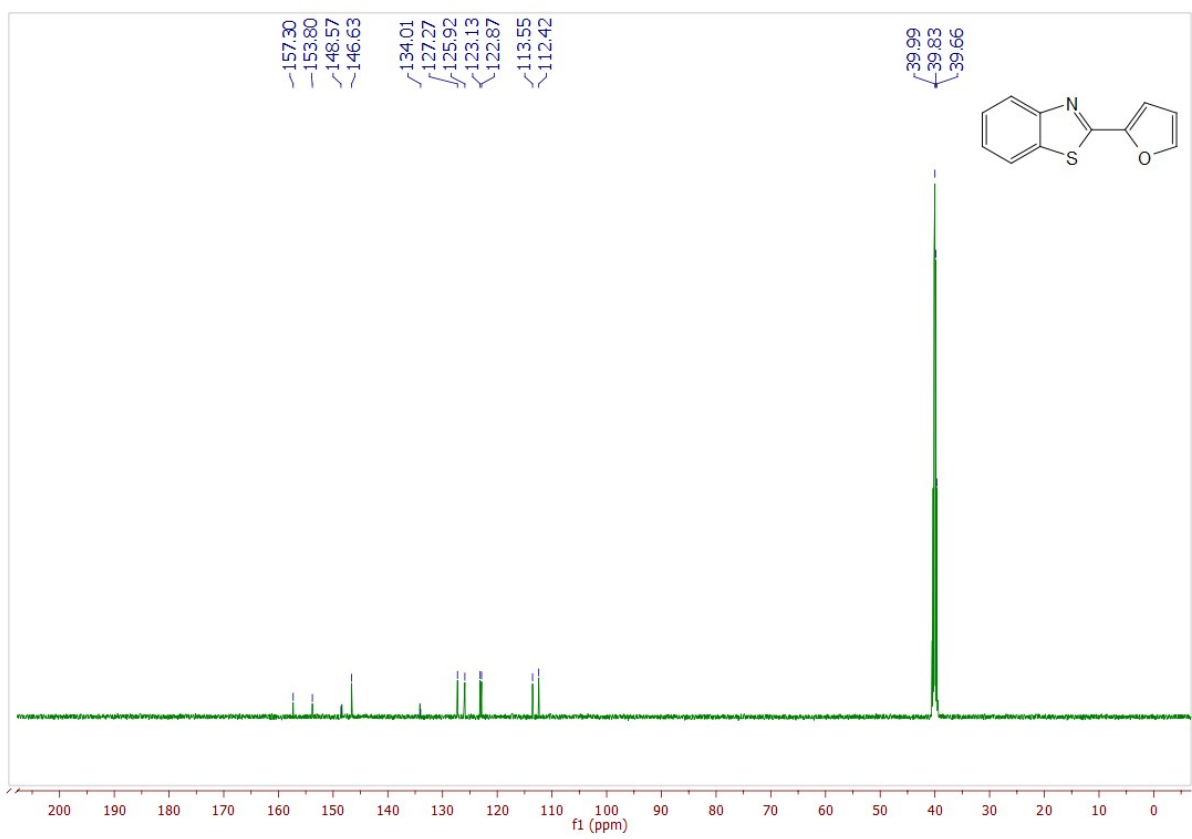
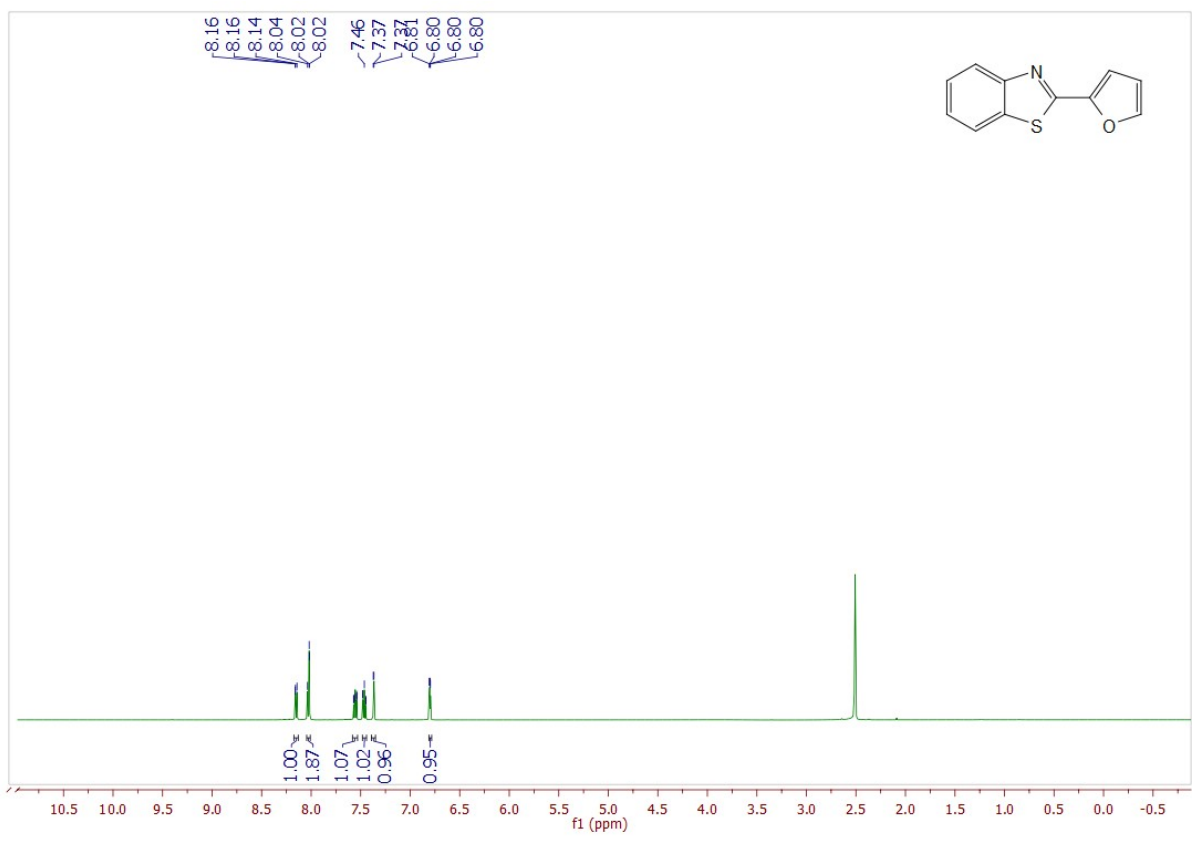
# <sup>1</sup>H and <sup>13</sup>C NMR (3o)



# $^1\text{H}$ and $^{13}\text{C}$ NMR (3p)

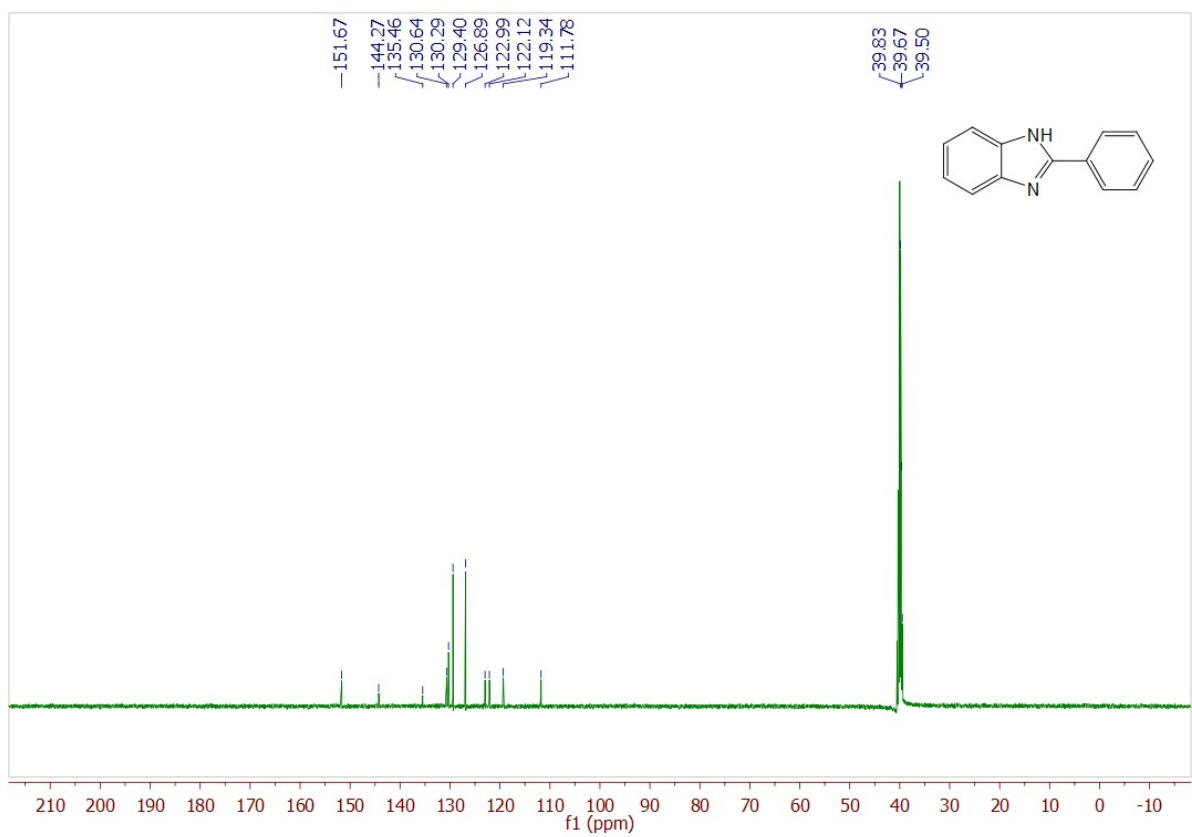
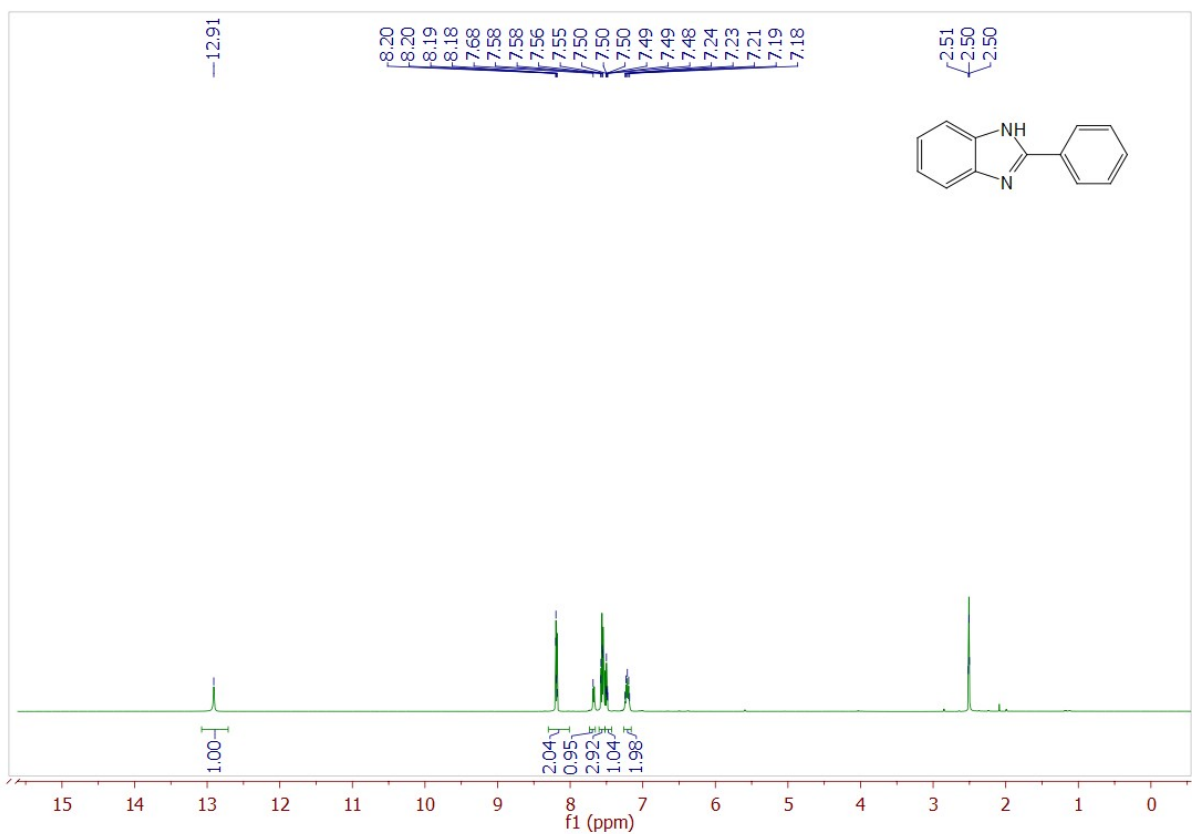


# <sup>1</sup>H and <sup>13</sup>C NMR (3q)

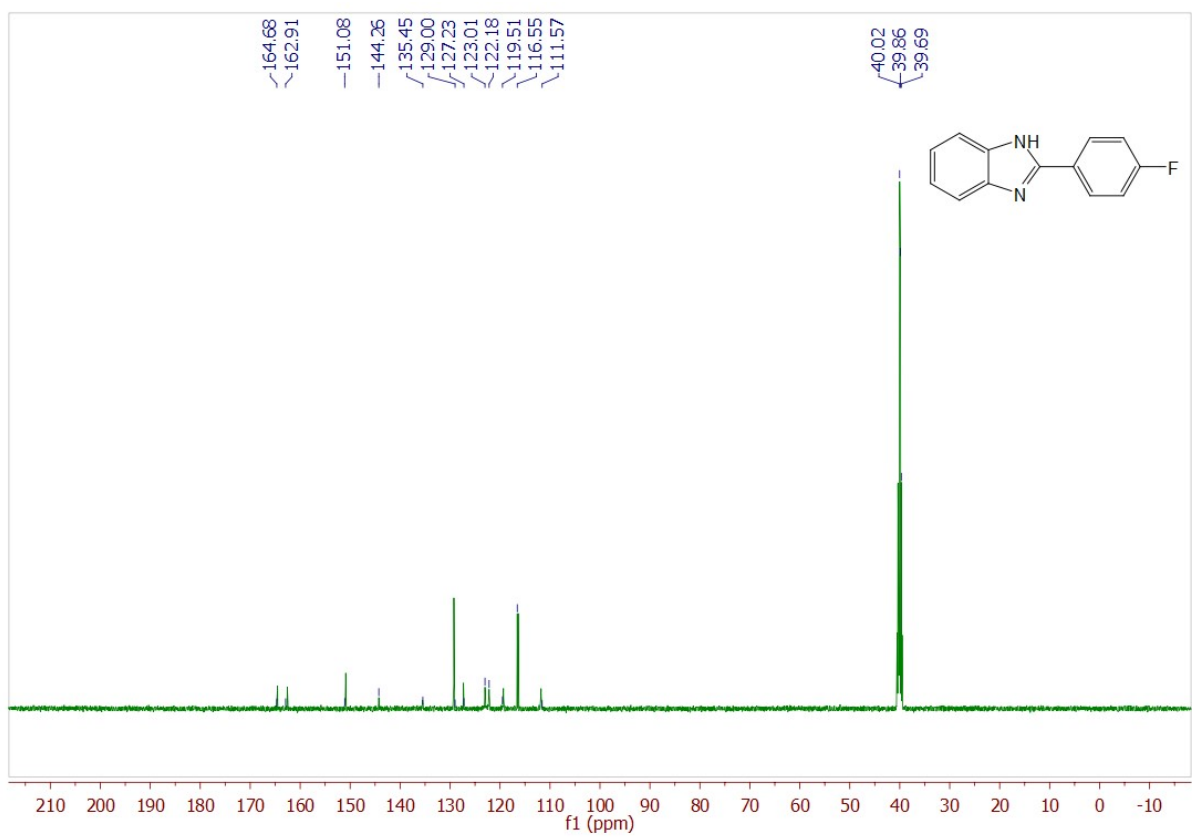
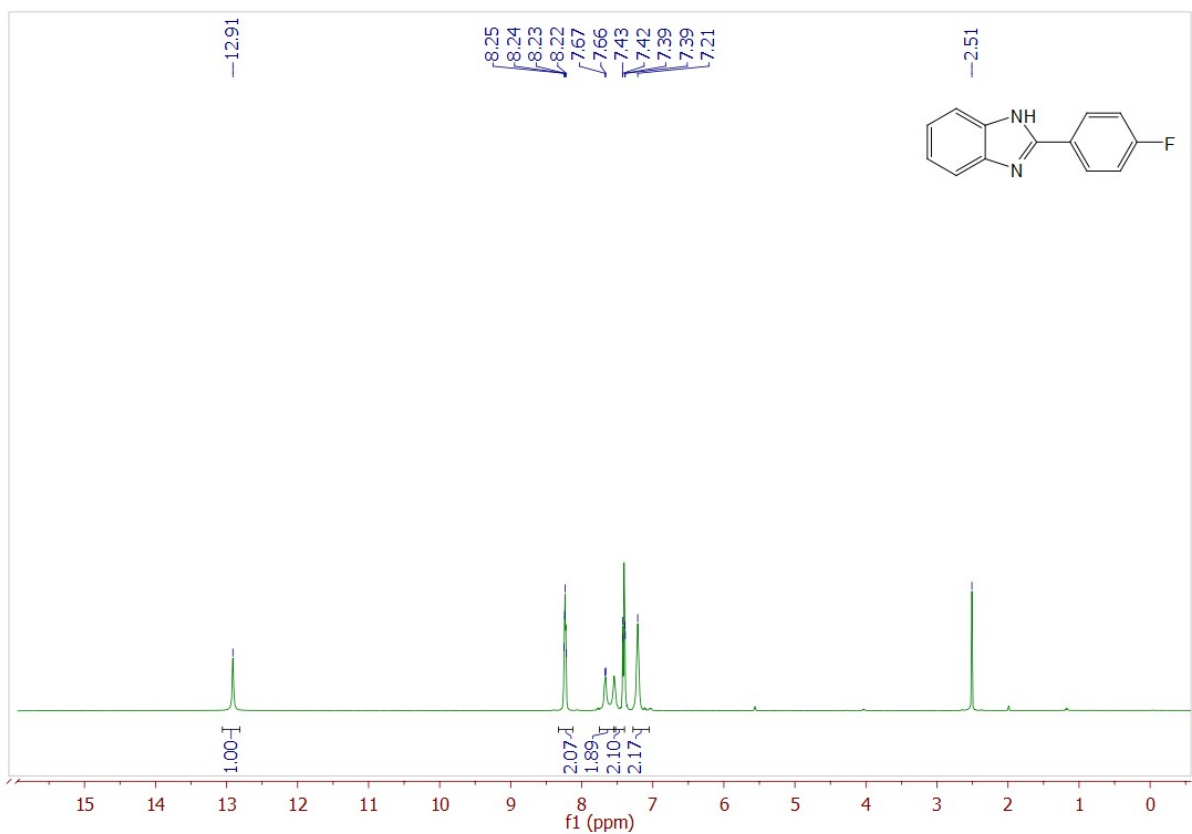




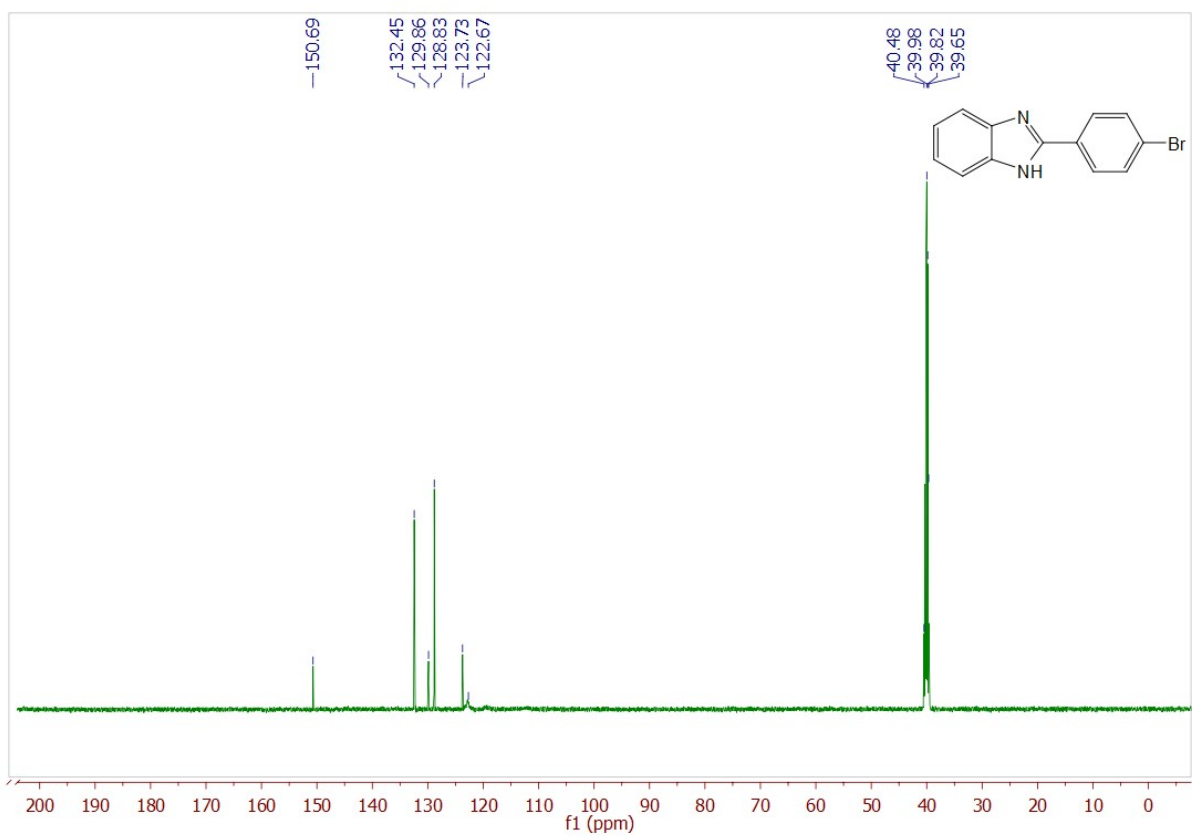
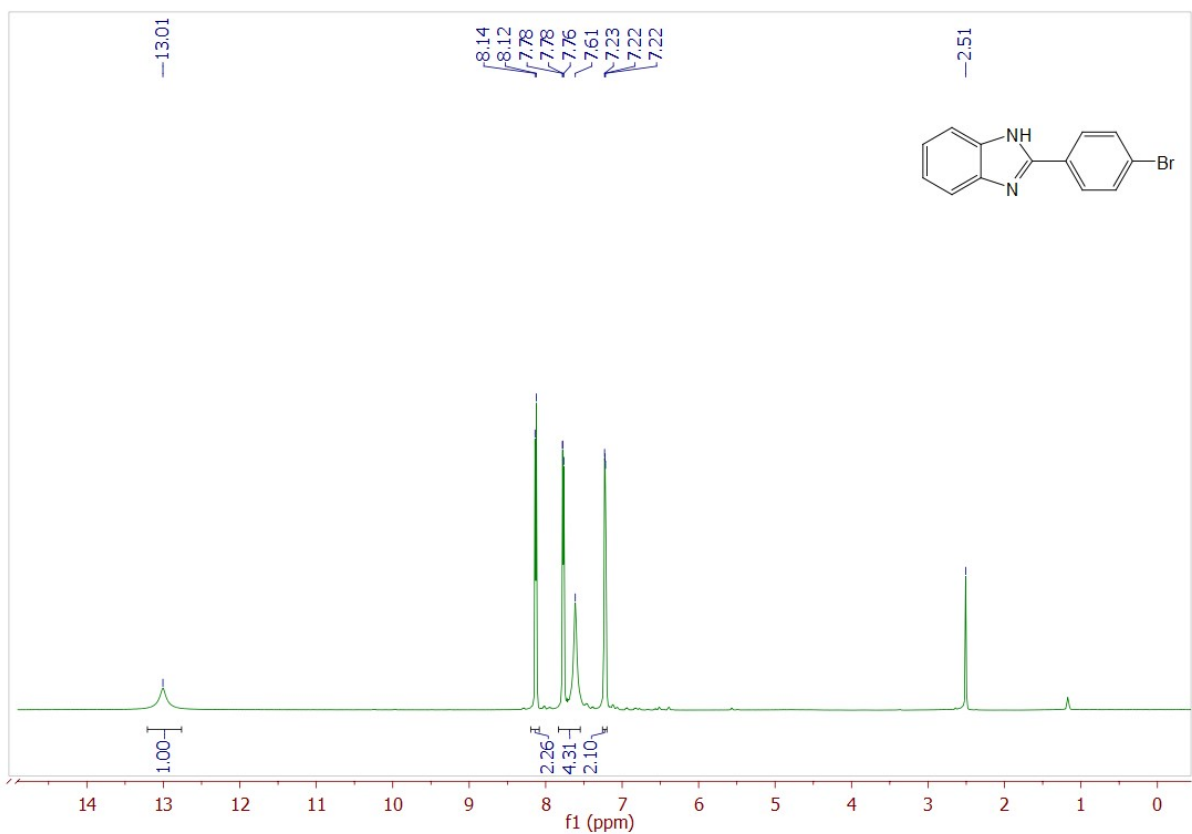
# $^1\text{H}$ and $^{13}\text{C}$ NMR (3r)



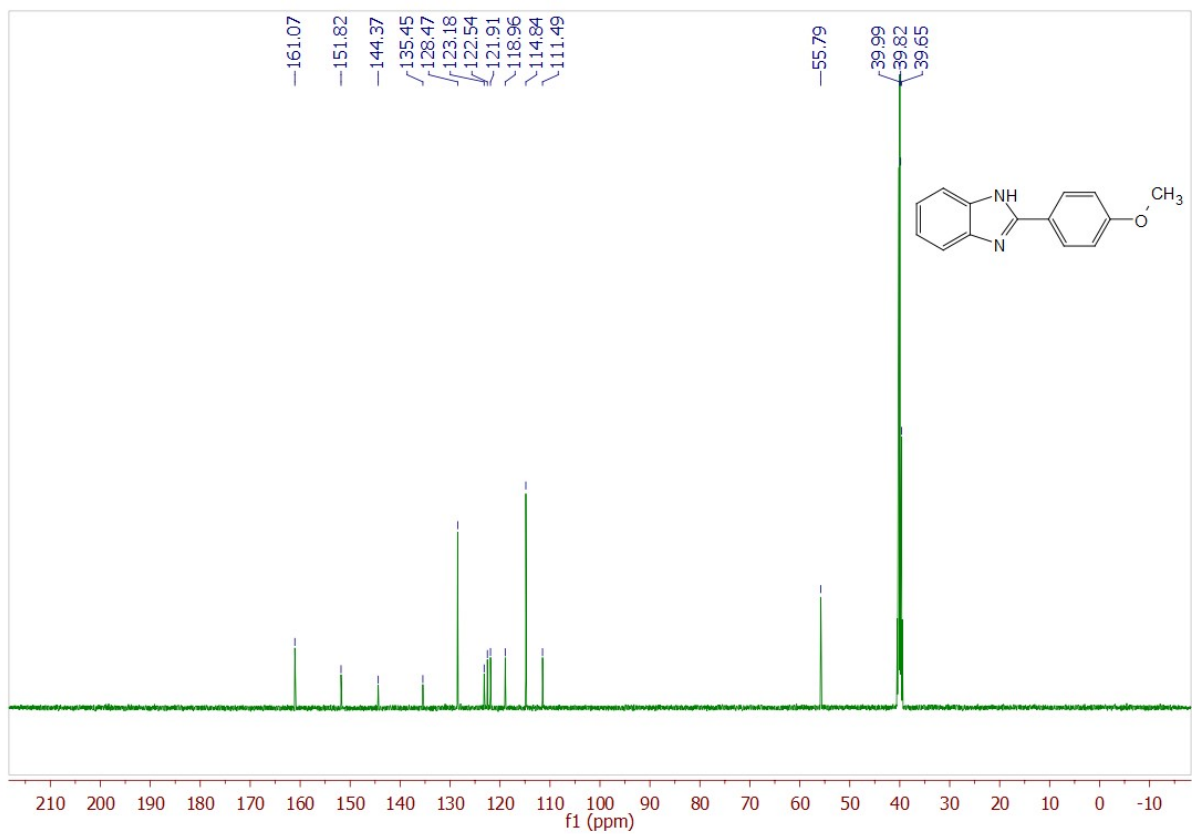
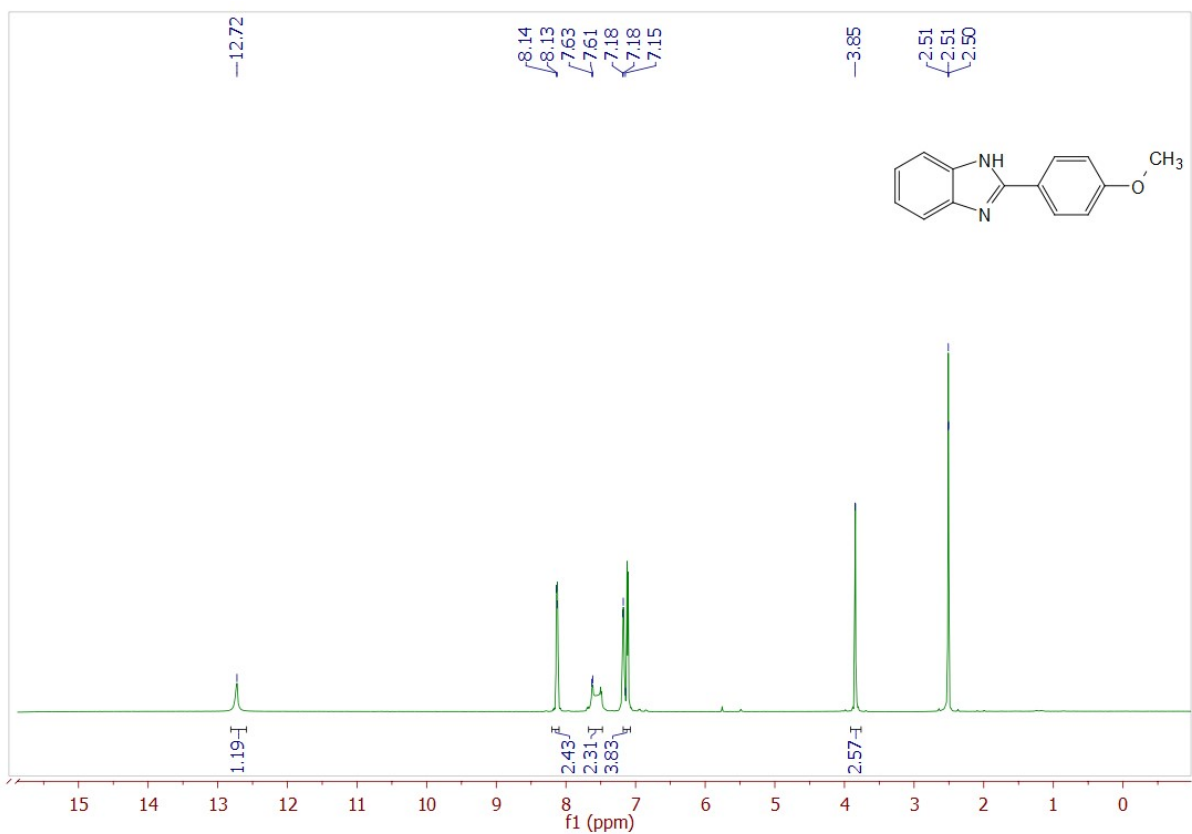
# <sup>1</sup>H and <sup>13</sup>C NMR (3s)



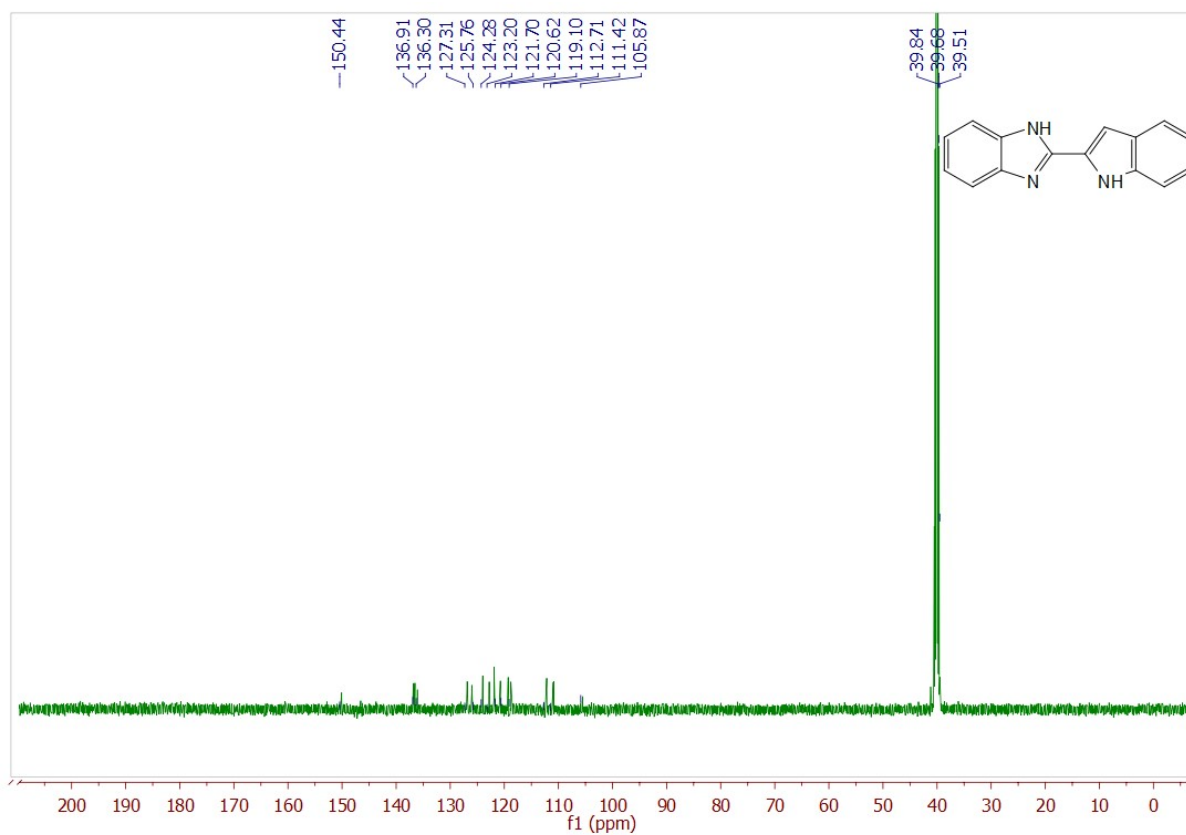
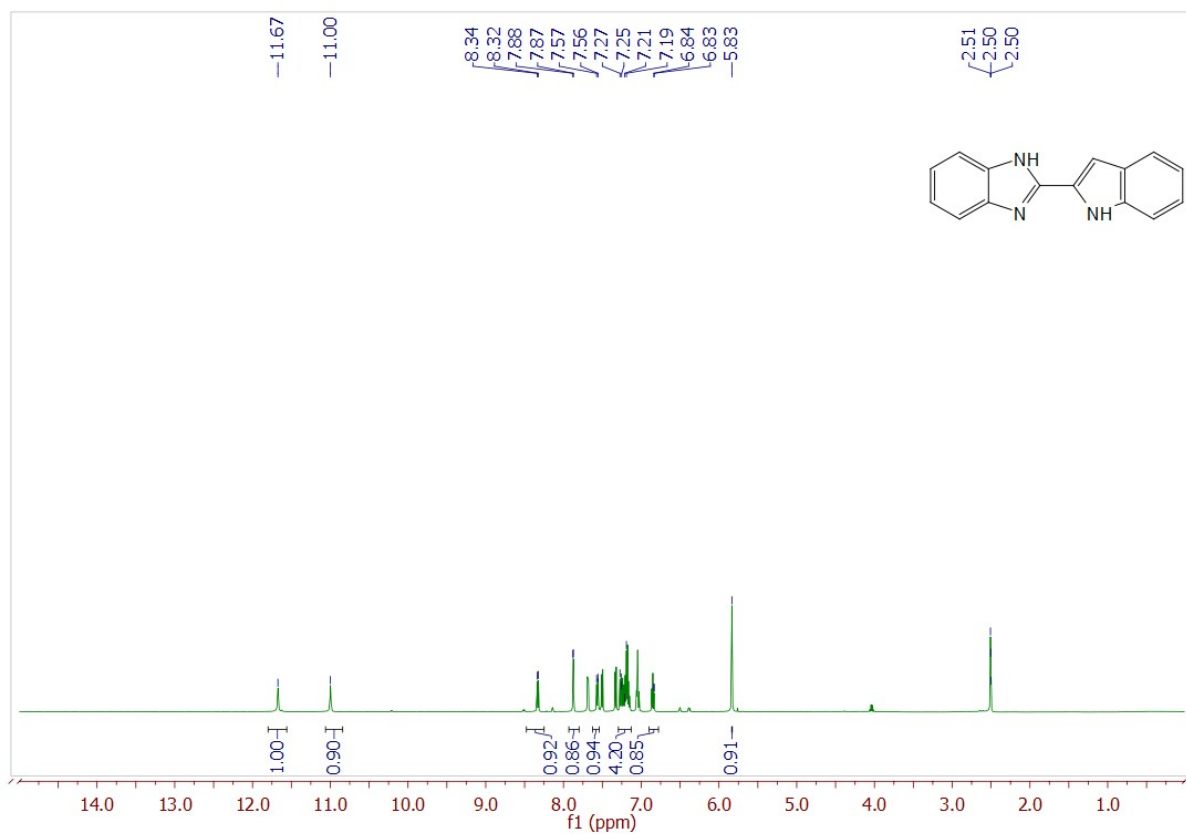
# $^1\text{H}$ and $^{13}\text{C}$ NMR (3t)



# <sup>1</sup>H and <sup>13</sup>C NMR (3u)



# <sup>1</sup>H and <sup>13</sup>C NMR (3v)



# $^1\text{H}$ and $^{13}\text{C}$ NMR (3w)

