

## Supplementary Information

### Construction and characterization of magnetic nanoparticles supported Cu complex: A stable and active nanocatalyst for synthesis of heteroaryl-aryl and di-heteroaryl sulfides

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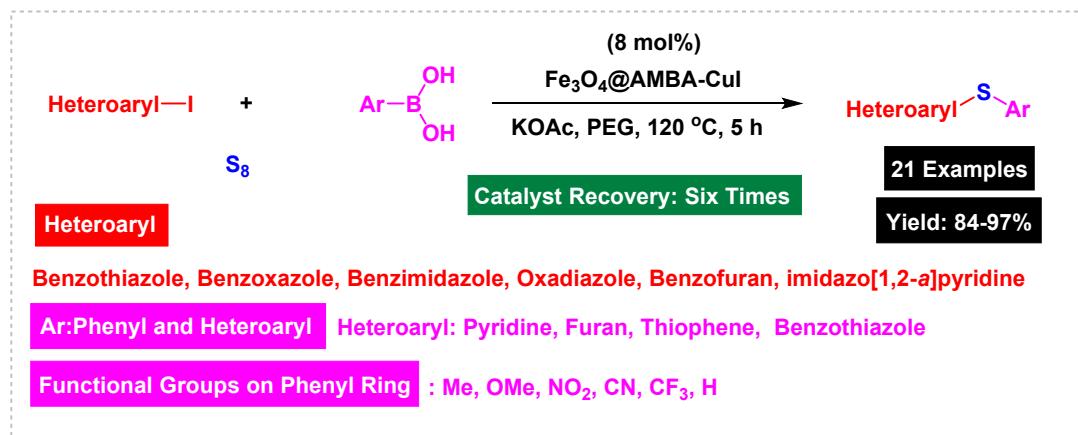
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#### Abstract

Diaryl and di-heteroaryl sulfides exist in the structure of many drugs and important biological compounds, also these compounds are well-known in medicinal chemistry due to important biological and pharmaceutical activities. Therefore, the development of novel, ecofriendly and efficient catalytic systems for the preparation of diaryl and di-heteroaryl sulfides is a very attractive and important challenge in organic synthesis. In this attractive methodology, we wish to introduce  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  nanomaterials as a novel and efficient magnetically recoverable catalyst for the preparation of heteroaryl-aryl and di-heteroaryl sulfides with high yields through reaction of heteroaryl halides with aryl or heteroaryl boronic acids and  $\text{S}_8$  as sulfur source under ecofriendly conditions. This catalytic system was very efficient and practical for a diverse range of heteroaryl substrates including benzothiazole, benzoxazole, benzimidazole, oxadiazole, benzofuran, imidazo[1,2-a]pyridine, because the desired diaryl and di-heteroaryl sulfides were prepared with high yields. The reusability-experiments revealed that the  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  nanocatalyst can be magnetically separated and reused at least six runs without significant decrease in its catalytic activity. VSM and ICP-OES analyzes confirmed that despite using the  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  nanocatalyst 6 times, the magnetic properties and stability of the catalyst were still maintained. Although all the obtained heteroaryl-aryl and di-heteroaryl sulfide products are known and previously reported, but synthesis of this number of heteroaryl-aryl and di-heteroaryl sulfides has never been reported by any methods.



**Keywords:** Diaryl and di-heteroaryl sulfides,  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  nanocatalyst, Magnetic separation, Pharmaceutical chemistry, Sulfur source.

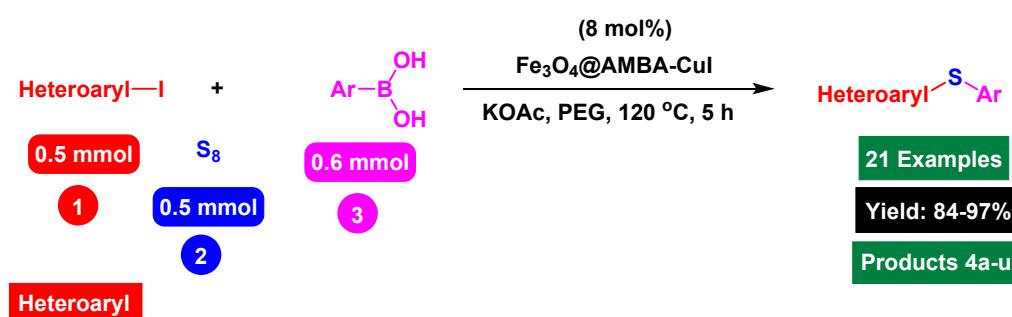
## Supplementary Information

### Experimental

#### General procedure for preparation of heteroaryl-aryl and di-heteroaryl sulfides catalyzed by $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$ nanocomposite

In a round bottomed flask, a mixture of heteroaryl iodides (0.5 mmol), aryl or heteroaryl boronic acids (0.6 mmol), S<sub>8</sub> (0.5 mmol) KOAc (2 equiv) and  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  catalyst (8 mol%) was stirred in PEG-400 at 120 °C for 5h (the progress of the reaction was monitored by thin-layer chromatography (TLC)). After completion of the reaction, the  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  was magnetically separated and reaction mixture was cooled to room temperature and H<sub>2</sub>O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude material was purified with chromatography column on silica gel (EtOAc/n-hexane) give the heteroaryl-aryl and di-heteroaryl sulfides products with 84-97%. All heteroaryl-aryl and di-heteroaryl sulfides products are previously reported and known. HNMR and CNMR were used in order to identify the structure of the heteroaryl-aryl and di-heteroaryl sulfide products

Scope of heteroaryl iodides and aryl or heteroaryl boronic acids for synthesis of heteroaryl-aryl and di-heteroaryl sulfides catalyzed by  $\text{Fe}_3\text{O}_4@\text{AMBA-CuI}$  nanomaterial.



**Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine**

**Ar:Phenyl and Heteroaryl    Heteroaryl: Pyridine, Furan, Thiophene, Benzothiazole**

**Functional Groups on Phenyl Ring : Me, OMe, NO<sub>2</sub>, CN, CF<sub>3</sub>, H**

Entry	Heteroaryl Halide	Aryl Boronic Acid	Product (Sulfide)
1			 95% Product 4a

## Supplementary Information

2			 94% <b>Product 4b</b>
3			 92% <b>Product 4c</b>
4			 96% <b>Product 4d</b>
5			 92% <b>Product 4e</b>
6			 91% <b>Product 4f</b>
7			 97% <b>Product 4g</b>
8			 86% <b>Product 4h</b>

## Supplementary Information

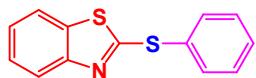
9			 96% Product 4i
10			 93% Product 4j
11			 91% Product 4k
12			 85% Product 4l
13			 92% Product 4m
14			 86% Product 4n
15			 84% Product 4o"/>

## Supplementary Information

16			 88% Product 4l
17			 88% Product 4q
18			 90% Product 4r
19			 87% Product 4s
20			 91% Product 4t
21			 92% Product 4u

## Supplementary Information

### NMR Data for heteroaryl-aryl and di-heteroaryl sulfide products

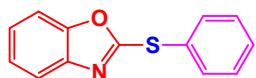


95%

Product 4a

<https://doi.org/10.1002/chem.201600800>

**2-(phenylthio)benzo[d]thiazole:** mp: 32–34 °C,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06–8.02 (m, 2H), 7.64–7.60 (m, 2H), 7.58–7.46 (m, 5H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 155.0, 135.6, 135.1, 130.8, 130.4, 126.7, 124.5, 122.1, 120.7.



94%

Product 4b

<https://doi.org/10.1021/acs.joc.9b02371>

**2-(phenylthio)benzo[d]oxazole:** Colorless oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.64 (m, 2H), 7.63 – 7.61 (m, 2H), 7.20 – 7.17 (m, 2H), 7.16 – 7.14 (m, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 152.3, 142.9, 135.1, 130.3, 129.9, 127.2, 124.7, 123.8, 119.4, 110.3.

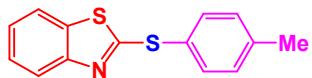


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Product 4c

<https://doi.org/10.1016/j.tet.2006.02.071>

**1-methyl-2-(phenylthio)-1H-benzo[d]imidazole:** mp: 65–67 °C,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61–7.57 (m, 2H), 7.48–7.45 (m, 2H), 7.38 (t,  $J = 4.3$  Hz, 3H), 7.23 – 7.21 (m, 2H), 3.78 (s, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 135.2, 131.5, 130.2, 129.8, 122.4, 118.6, 110.3, 32.9.

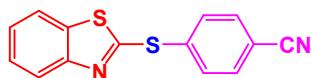


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Product 4d

<https://doi.org/10.1016/j.tet.2021.132564>

**2-(p-tolylthio)benzo[d]thiazole:** mp: 69–71 °C,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.60–7.57 (m, 2H), 7.37–7.33 (m, 1H), 7.32–7.25(m, 2H), 7.23–7.20 (m, 1H), 2.50(s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 153.6, 135.9, 134.1, 130.5, 130.2, 129.7, 126.3, 124.2, 121.5, 120.8, 22.5.



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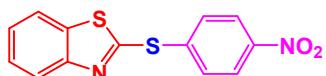
Product 4e

DOI

<https://doi.org/10.1039/C7CC03107F>

## Supplementary Information

**4-(benzo[d]thiazol-2-ylthio)benzonitrile:** mp: 110-112 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.7 Hz, 1H), 7.69–7.65 (m, 3H), 7.46–7.40(m, 2H), 7.31 (d, J = 4.5 Hz, 1H), 7.29 (d, J = 4.6 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.2, 153.4, 136.5, 136.2, 135.7, 130.3, 128.5, 126.3, 124.6, 122.0, 120.1.

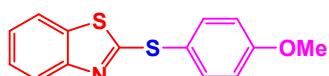


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Product 4f

DOI: 10.1039/C9NJ04440J

**2-((4-nitrophenyl)thio)benzo[d]thiazole:** mp: 86-89 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00–7.95 (m, 2H), 7.65–7.63 (m, 2H), 7.45–7.41 (m, 2H), 7.20–7.14 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.1, 158.3, 142.8, 141.3, 139.5, 138.0, 130.2, 129.7, 128.6, 127.9, 118.4, 115.7.

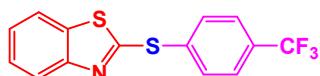


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Product 4g

<https://doi.org/10.1016/j.tet.2021.132564>

**2-((4-methoxyphenyl)thio)benzo[d]thiazole:** mp: 55-57 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.84 (d, J = 7.6 Hz, 1H), 7.65-7.60 (m, 2H), 7.38–7.35 (m, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.22-7.00 (m, 3H), 3.89(s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.2, 161.0, 154.9, 137.6, 135.7, 126.12, 124.3, 121.5, 120.8, 120.2, 115.5.

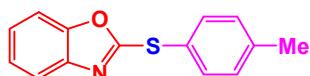


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Product 4h

DOI <https://doi.org/10.1039/C7CC03107F>

**2-((4-(trifluoromethyl)phenyl)thio)benzo[d]thiazole:** mp: 58-60 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.02 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 3H), 7.69–7.65 (m, 2H), 7.64–7.60(m, 1H), 7.59-7.57(m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.2, 141.0, 140.9, 139.5, 137.4, 136.5, 130.6, 129.7, 129.1, 128.7, 127.9, 127.3.



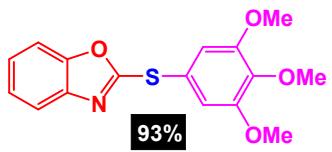
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Product 4i

<https://doi.org/10.1021/acs.joc.8b01644>

**2-(p-tolylthio)benzo[d]oxazole:** Colorless oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, J = 7.7 Hz, 2H), 7.61-7.55 (m, 2H), 7.31–7.24 (m, 2H), 7.21-7.18 (m, 2H), 2.54(s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.0, 155.2, 143.6, 141.5, 138.7, 130.5, 129.7, 127.3, 126.1, 120.3, 115.2, 22.5.

## Supplementary Information



Product 4j

<https://doi.org/10.1021/jo402586v>

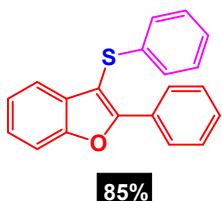
**2-((3,4,5-trimethoxyphenyl)thio)benzo[d]oxazole:** mp: 127-129 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.43 (td, J = 7.7, 1.3 Hz, 1H), 7.26 (td, J = 7.5, 1.3 Hz, 1H), 7.10 (s, 2H), 3.85 (s, 6H), 3.64 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.2, 155.3, 145.6, 141.2, 135.8, 130.7, 126.7, 125.3, 124.1, 121.0, 120.8, 58.9, 58.2.



Product 4k

DOI <https://doi.org/10.1039/D2OB02216H>

**bis(benzo[d]thiazol-2-yl)sulfane:** mp: 100-102 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (dd, J = 8.6 Hz, 2H), 7.65-7.60 (m), 7.45-7.40(m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.8, 141.6, 137.0, 135.9, 134.5, 130.2, 129.2, 127.3, 125.9.



Product 4l

<https://doi.org/10.1021/jo9016309>

**2-phenyl-3-(phenylthio)benzofuran:** mp: 66-68 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.24 (dd,J = 8.3 Hz, 2H), 7.56(d, J = 8.2 Hz, 1H), 7.48-7.41 (m, 5H), 7.37-7.23 (m, 5H), 7.22-7.16(m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.8, 153.2, 136.5, 130.6, 129.7, 129.4, 129.0, 128.7, 127.3, 126.5, 125.9, 125.4, 123.4, 120.5, 111.3, 104.9.

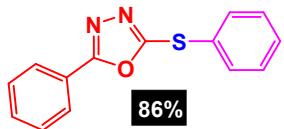


Product 4m

DOI <https://doi.org/10.1039/D0OB00684J>

**2-(pyridin-2-ylthio)benzo[d]thiazole:** mp: 66-68 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.26 (d, J = 1.8 Hz, 1H), 8.81 (dd, J = 4.9, 1.7 Hz, 1H), 8.29 (ddd, J = 8.1, 2.3, 1.8 Hz, 1H), 7.55–7.45 (m, 4H), 7.44 (ddd, J = 8.1, 4.9, 1.8 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.3, 154.6, 149.7, 136.5, 135.1, 132.5, 129.8, 128.9, 126.3, 122.4.

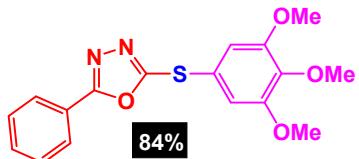
## Supplementary Information



**Product 4n**

<https://doi.org/10.1016/j.tet.2011.02.064>

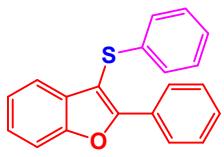
**2-phenyl-5-(phenylthio)-1,3,4-oxadiazole:** mp: 60-62 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (d, J = 7.6 Hz, 2 H), 7.70-7.64 (m, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.49-7.42 (m, 5 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.9, 166.1, 133.8, 132.4, 130.8, 130.2, 129.8, 127.6, 126.4, 123.9.



**Product 4o**

<https://doi.org/10.1021/jo402586v>

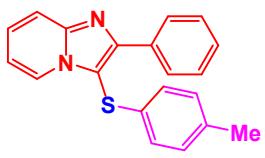
**2-phenyl-5-((3,4,5-trimethoxyphenyl)thio)-1,3,4-oxadiazole:** mp: 140-142 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (d, J = 6.7 Hz, 2H), 7.52-7.50 (m, 3H), 6.95 (s, 2H), 3.97 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.6, 163.9, 153.2, 140.3, 132.3, 130.0, 126.4, 123.7, 121.5, 111.3, 61.7, 55.5



**Product 4l**

DOI: 10.1055/s-0037-1612082

**2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine:** mp: 92-94 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.25 (d, 1H, J = 6.8 Hz), 8.18 (d, 2H, J = 7.6 Hz), 7.71 (d, 1H, J = 9.2 Hz), 7.45 (t, 2H, J = 7.7 Hz), 7.38 (d, 1H, J = 7.3 Hz), 7.30 (t, 1H, J = 8 Hz), 7.17 (t, 2H, J = 7.6 Hz), 7.11 (t, 1H, J = 7.6 Hz), 6.97 (d, 2H, J = 7.6 Hz), 6.85 (t, 1H, J = 6.7 Hz); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 151.0, 147.2, 133.5, 129.7, 128.5, 128.3, 127.4, 126.2, 125.6, 125.3, 124.5, 117.3, 112.2, 106.3.

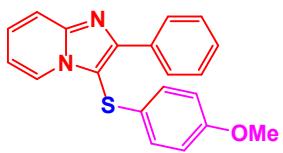


**Product 4q**

DOI: 10.1055/s-0037-1612082

**2-phenyl-3-(p-tolylthio)imidazo[1,2-a]pyridine:** mp: 135-137 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (d, 1H, J = 6.5 Hz), 8.21 (d, 2H, J = 7.5 Hz), 7.71 (d, 1H, J = 9.1 Hz), 7.46 (t, 2H, J = 7.6 Hz), 7.37 (d, 1H, J = 7.3 Hz), 7.28 (t, 1H, J = 8 Hz), 7.02 (d, 2H, J = 8 Hz), 6.95 (d, 2H, J = 8.1 Hz), 6.87 (t, 1H, J = 6.7 Hz), 2.38 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.0, 145.3, 136.8, 133.5, 131.2, 130.7, 129.7, 128.6, 128.0, 126.4, 125.7, 117.9, 112.4, 106.3, 21.3.

## Supplementary Information

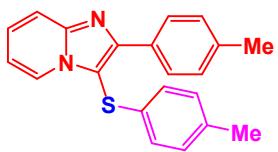


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Product 4r

DOI: 10.1055/s-0037-1612082

**3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-a]pyridine:** mp: 112-114 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.29 (d, 1H, J = 6.1 Hz), 8.22 (d, 2H, J = 8.2 Hz), 7.71 (d, 1H, J = 8.6 Hz), 7.42-7.40 (m, 2H), 7.35 (t, 1H, J = 5.7 Hz), 7.29-7.27 (m, 1H), 6.97 (d, 2H, J = 8.3 Hz), 6.85 (t, 1H, J = 5.6 Hz), 6.75 (d, 2H, J = 8.6 Hz), 3.70 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.6, 150.2, 146.7, 133.6, 130.9, 129.7, 128.8, 128.6, 127.7, 126.4, 125.7, 117.7, 115.9, 112.6, 107.4, 55.3.

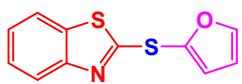


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Product 4s

DOI: 10.1055/s-0037-1612082

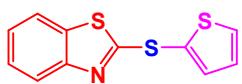
**2-(p-tolyl)-3-(p-tolylthio)imidazo[1,2-a]pyridine:** mp: 142-144 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.24 (d, 1H, J = 6.8 Hz), 8.12 (d, 2H, J = 7.8 Hz), 7.70 (d, 1H, J = 9.1 Hz), 7.33 (t, 1H, J = 7.6 Hz), 7.25 (d, 2H, J = 8.3 Hz), 7.02 (d, 2H, J = 7.7 Hz), 6.92 (d, 2H, J = 7.7 Hz), 6.83 (t, 1H, J = 6.7 Hz), 2.38 (s, 3H), 2.25 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 151.1, 146.3, 138.7, 134.3, 130.7, 129.7, 129.1, 128.2, 126.4, 125.1, 124.4, 117.6, 112.7, 105.9, 21.3, 20.6.



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Product 4t

**2-(furan-2-ylthio)benzo[d]thiazole:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, J = 8.5 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 9.2 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.6, 161.7, 137.6, 130.5, 129.3, 119.1, 115.3, 114.5.



92%

Product 4u

<https://doi.org/10.1016/j.tet.2014.10.075>

## Supplementary Information

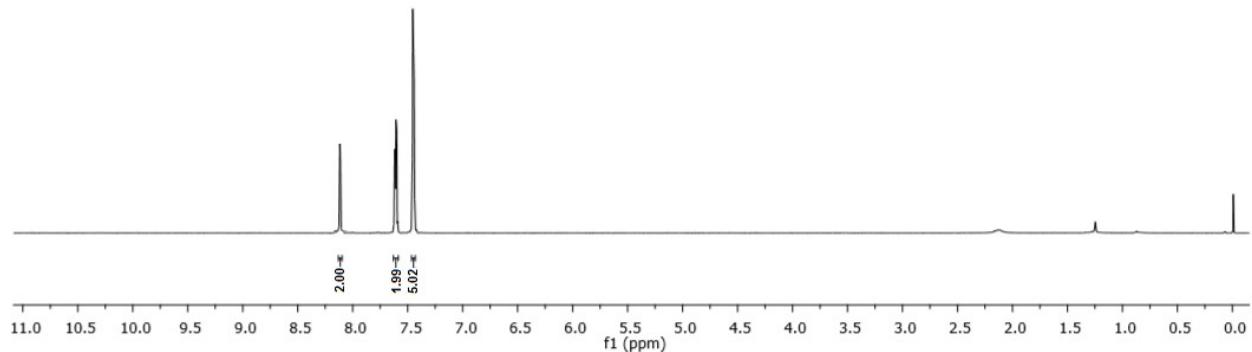
**2-(thiophen-2-ylthio)benzo[d]thiazole:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.21 (m, 2H), 7.14-7.10 (m, 2H), 6.97-6.93 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 149.8, 135.0, 134.7, 132.1, 130.8, 130.2, 128.3, 117.6, 116.3, 115.4.

**Table S1.** experimental conditions for NMR analysis

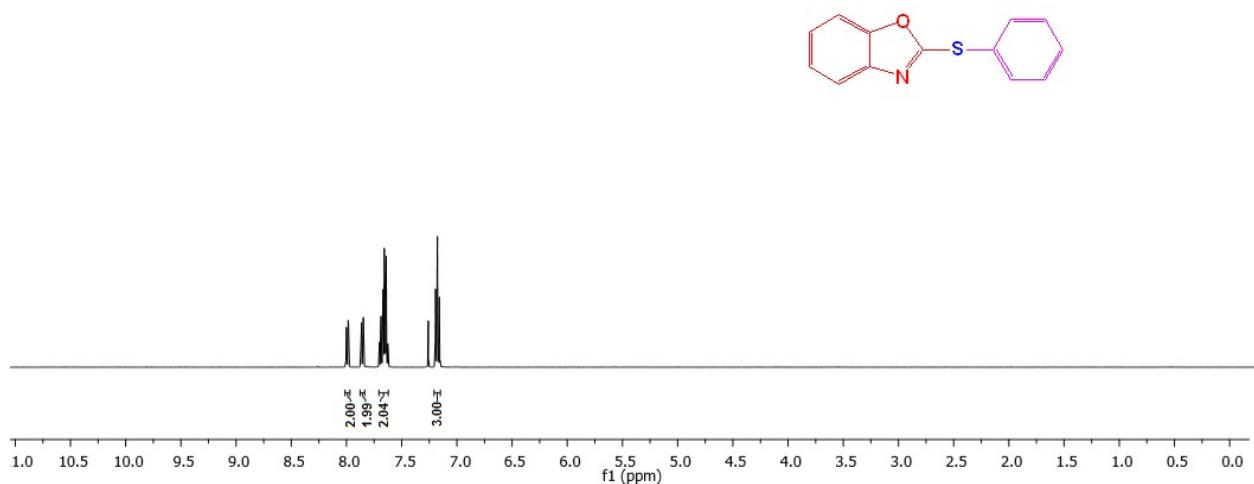
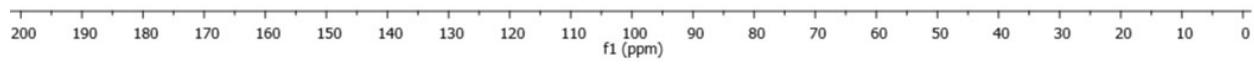
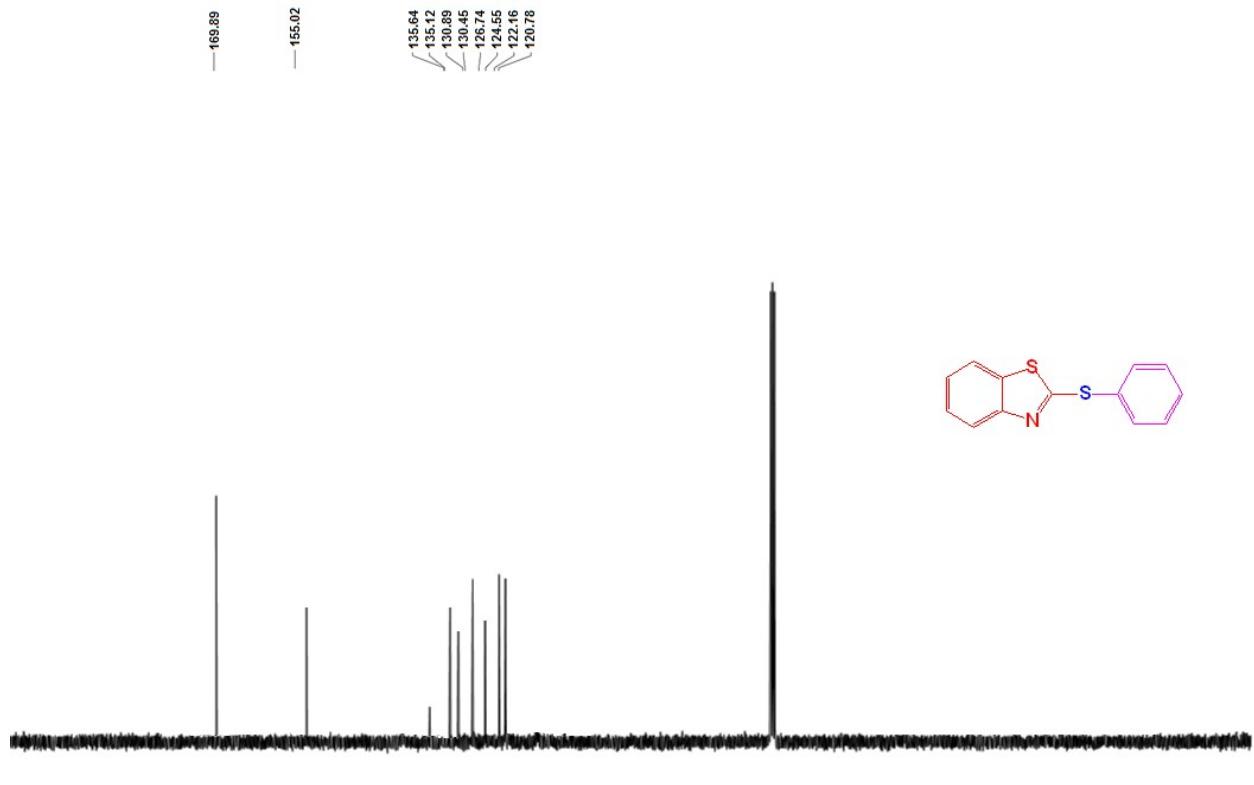
$^1\text{H}$ NMR		$^{13}\text{C}$ NMR	
F2 - Acquisition Parameters		F2 - Acquisition Parameters	
Date_	20230427	Date_	20230427
Time	14.20	Time	13.45
INSTRUM	spect	INSTRUM	spect
PROBHD	5 mm Multinucl	PROBHD	5 mm Multinucl
PULPROG	zg	PULPROG	zgpg
TD	16384	TD	65536
SOLVENT	$\text{CDCl}_3$	SOLVENT	$\text{CDCl}_3$
NS	10	NS	85
DS	0	DS	0
SWH	6265.664 Hz	SWH	13812.154 Hz
FIDRES	0.382426 Hz	FIDRES	0.210757 Hz
AQ	1.3074932 sec	AQ	2.3724532 sec
RG	32	RG	1625.5
DW	79.800 usec	DW	36.200 usec
DE	6.00 usec	DE	6.00 usec
TE	300.0 K	TE	300.0 K
D1	3.00000000 sec	D1	2.00000000 sec
		d11	0.03000000 sec
		d12	0.00002000 sec
===== CHANNEL f1 =====			
NUC1	$^{13}\text{C}$		
P1	10.00 usec		
PL1	0.00 dB		
SFO1	62.9015285 MHz		
===== CHANNEL f2 =====			
CPDPRG2	waltz16		
NUC2	$^1\text{H}$		
PCPD2	80.00 usec		
PL2	3.00 dB		
PL12	21.50 dB		
PL13	23.00 dB		
SFO2	250.1310005 MHz		
F2 - Processing parameters			
SI	32768		
SF	62.8955307 MHz		
WDW	EM		
SSB	0		
LB	8.00 Hz		

## Supplementary Information

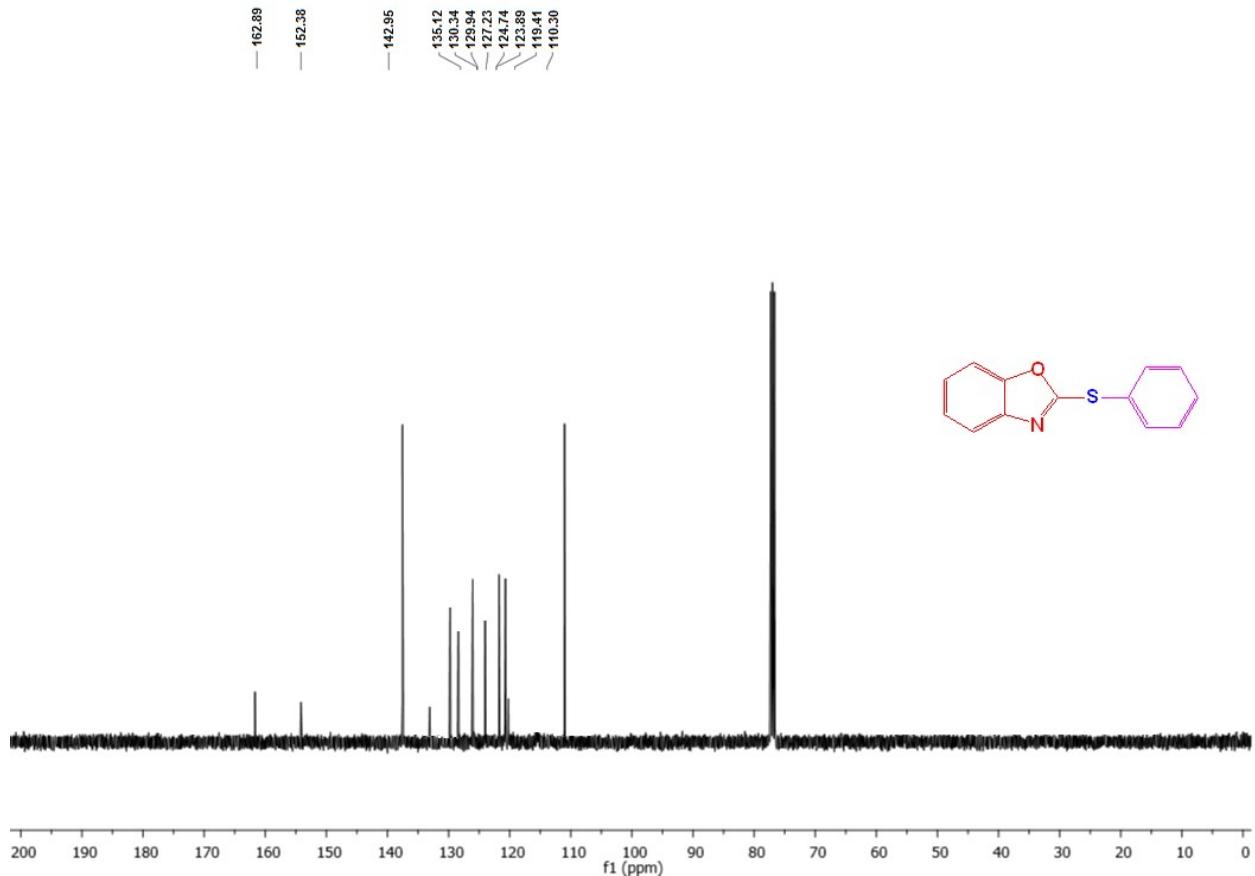
	GB	0
	PC	1.40



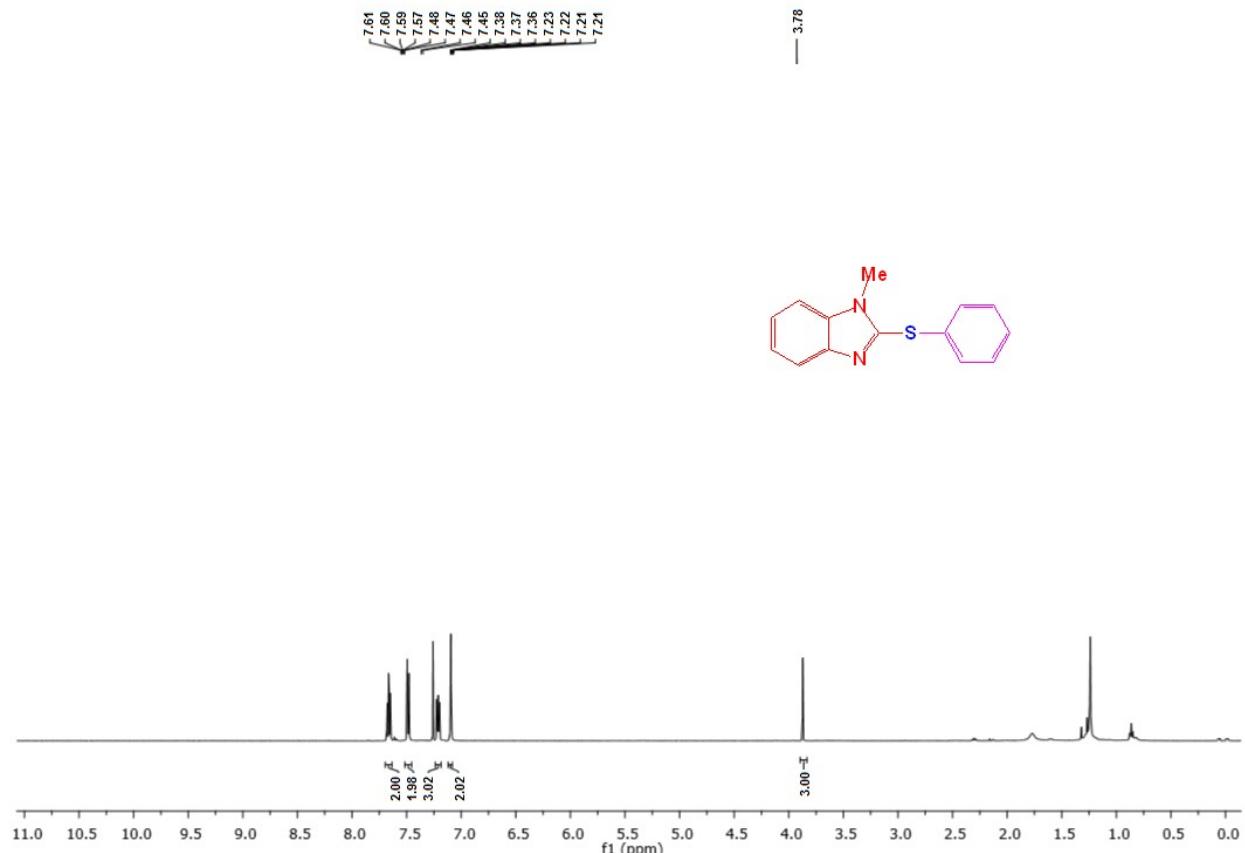
## Supplementary Information



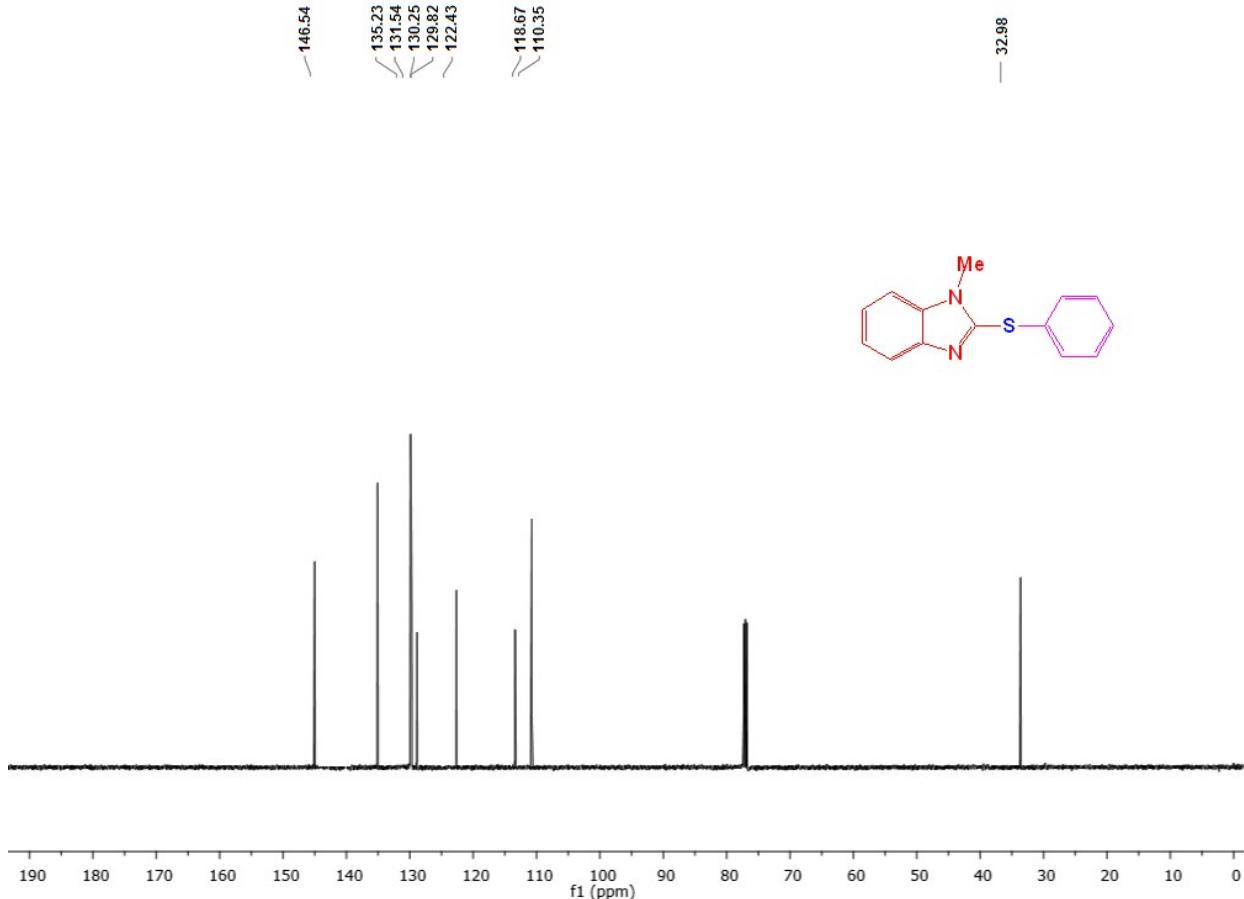
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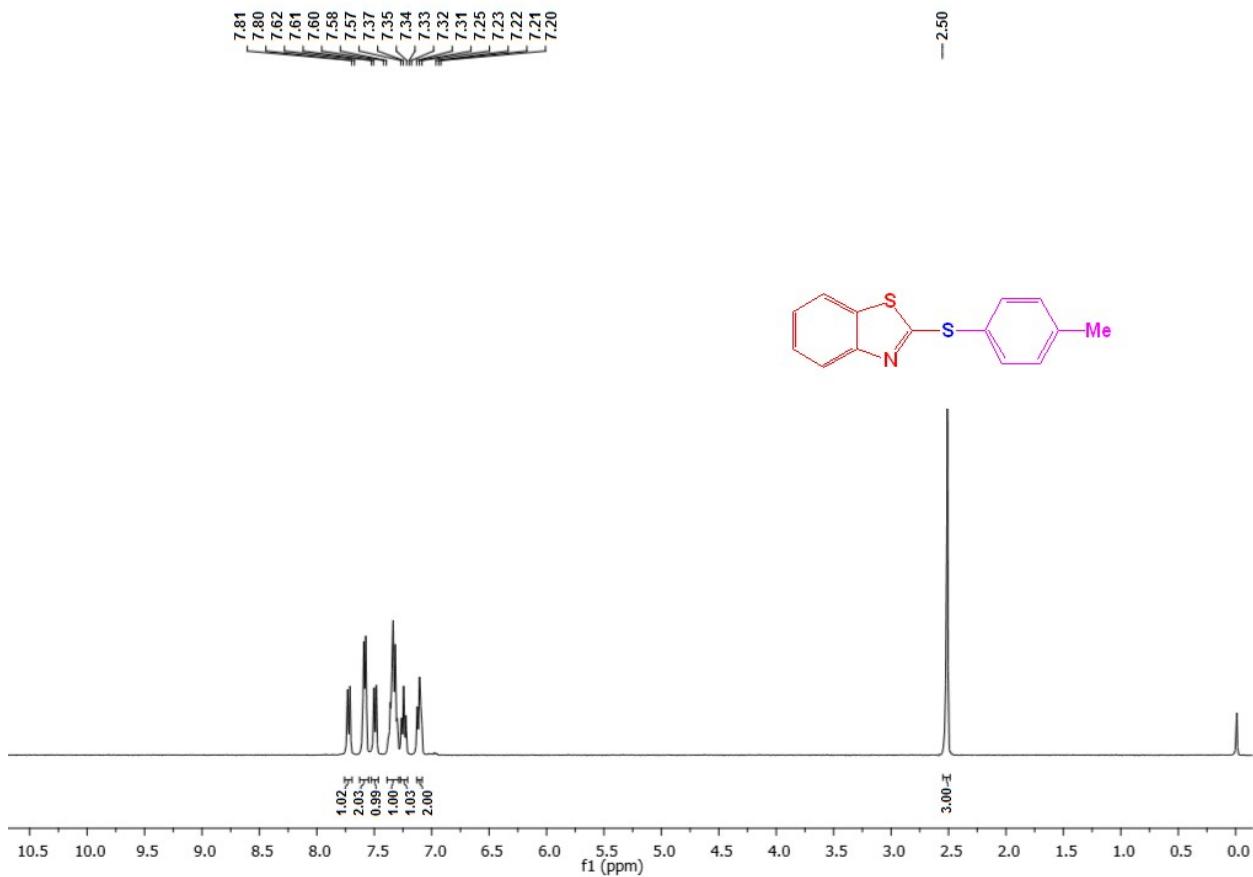
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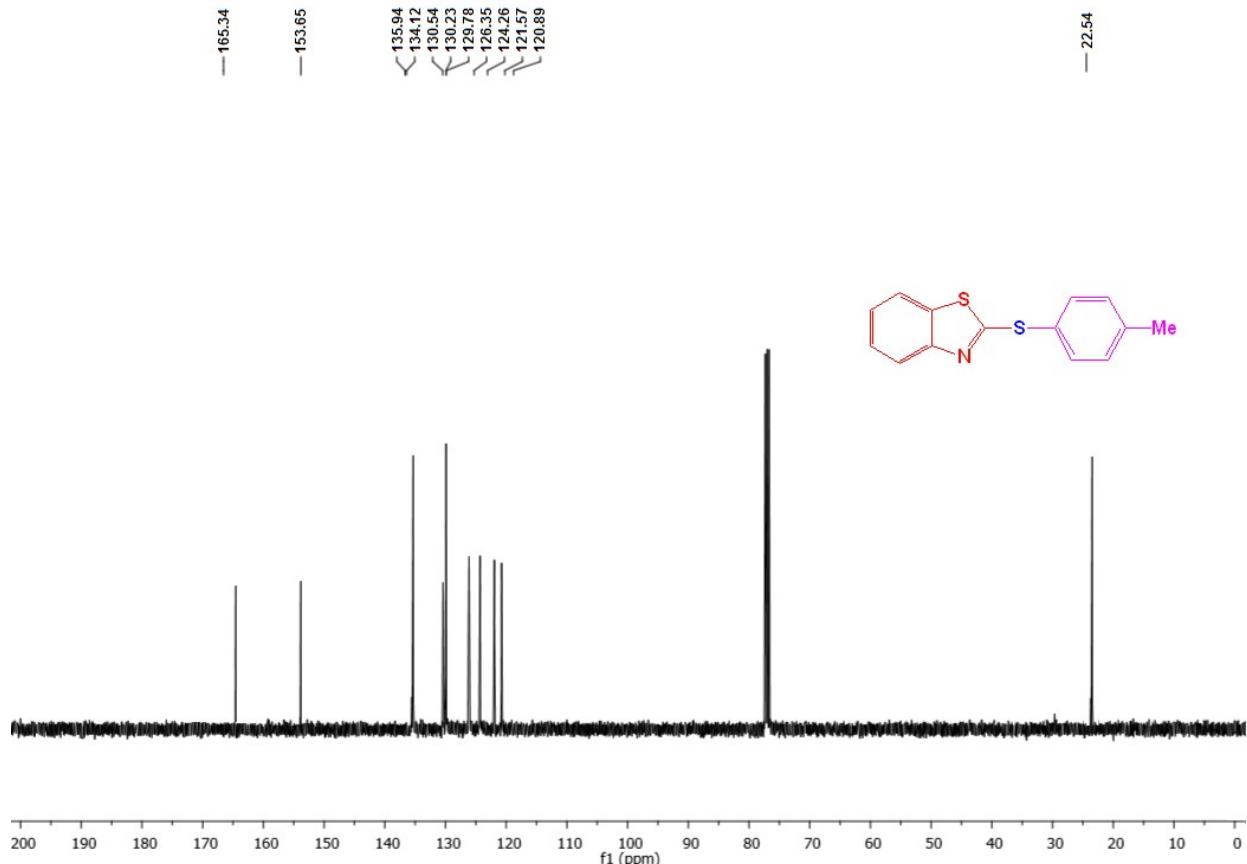
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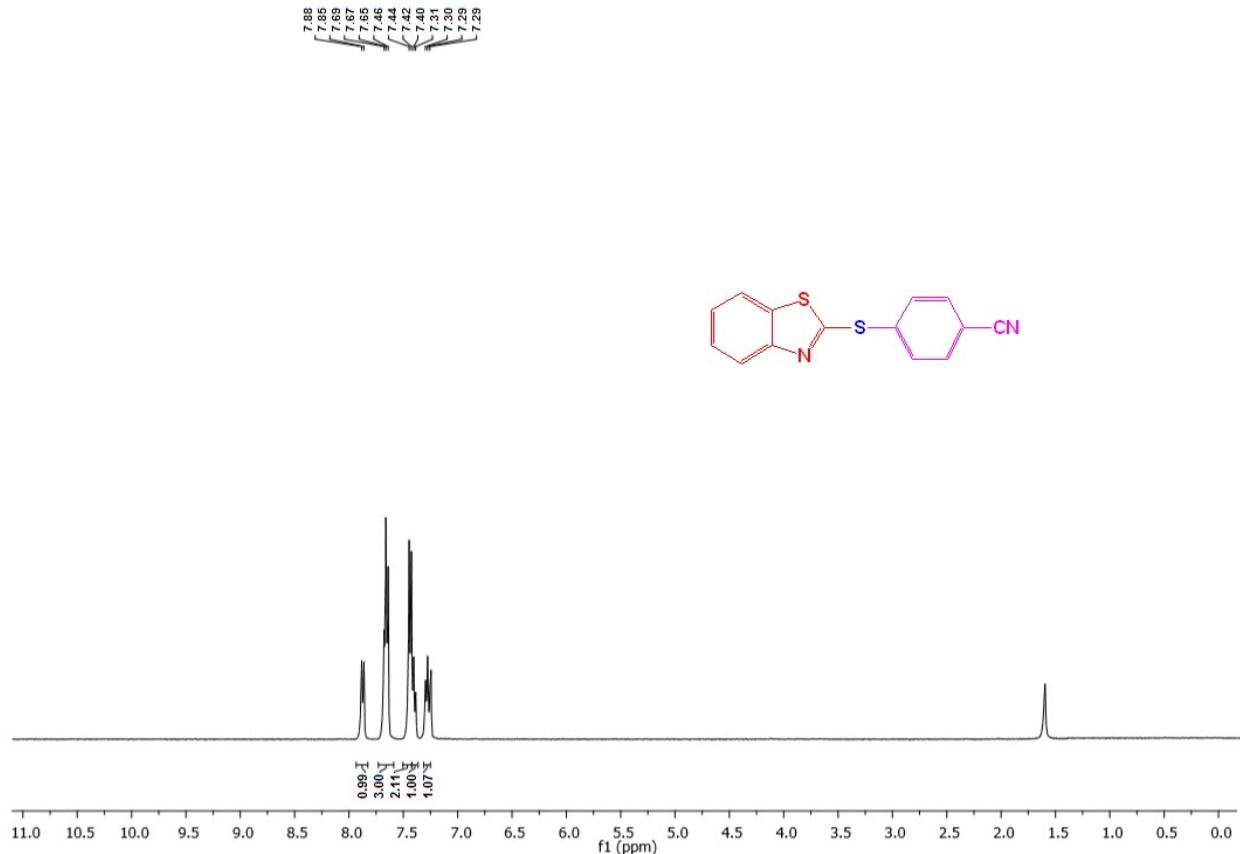
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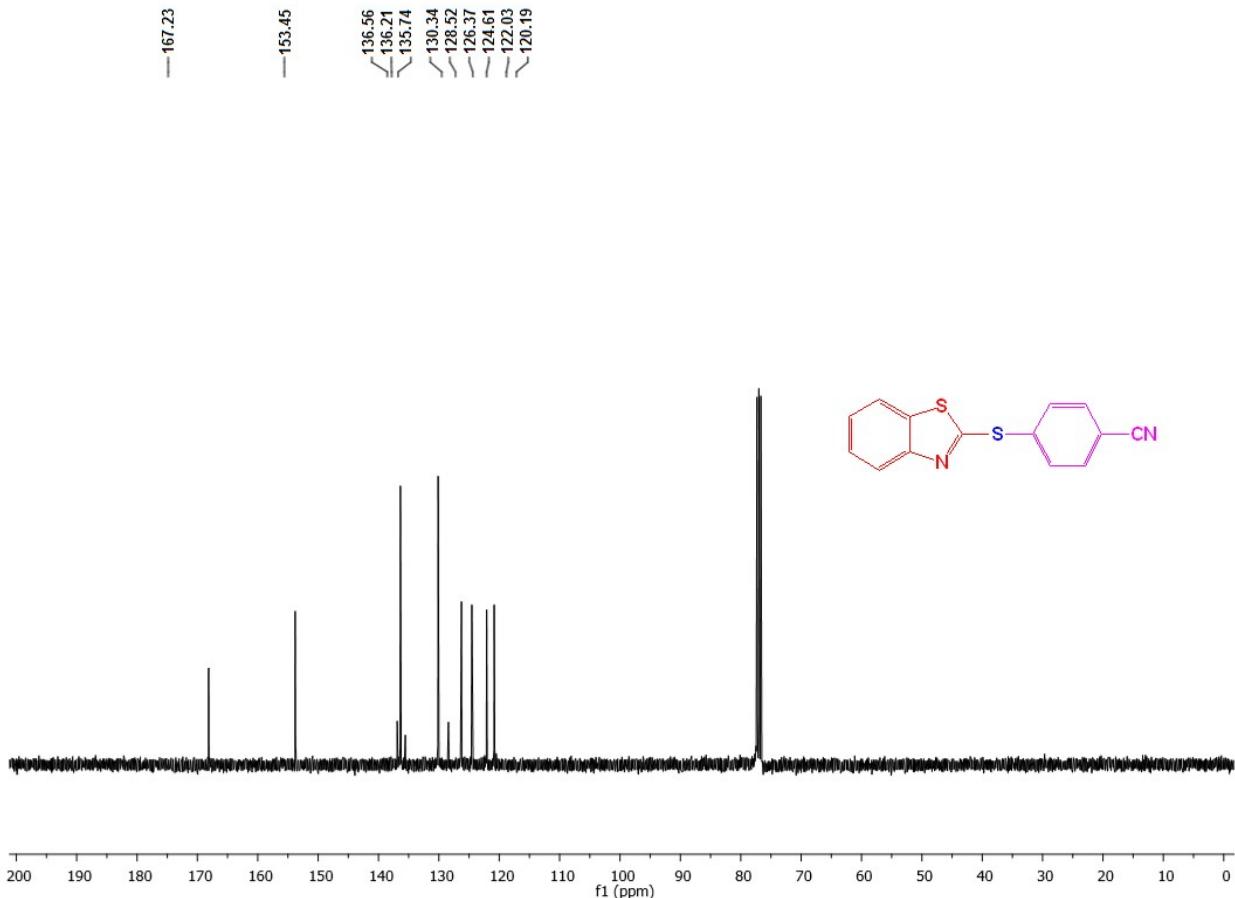
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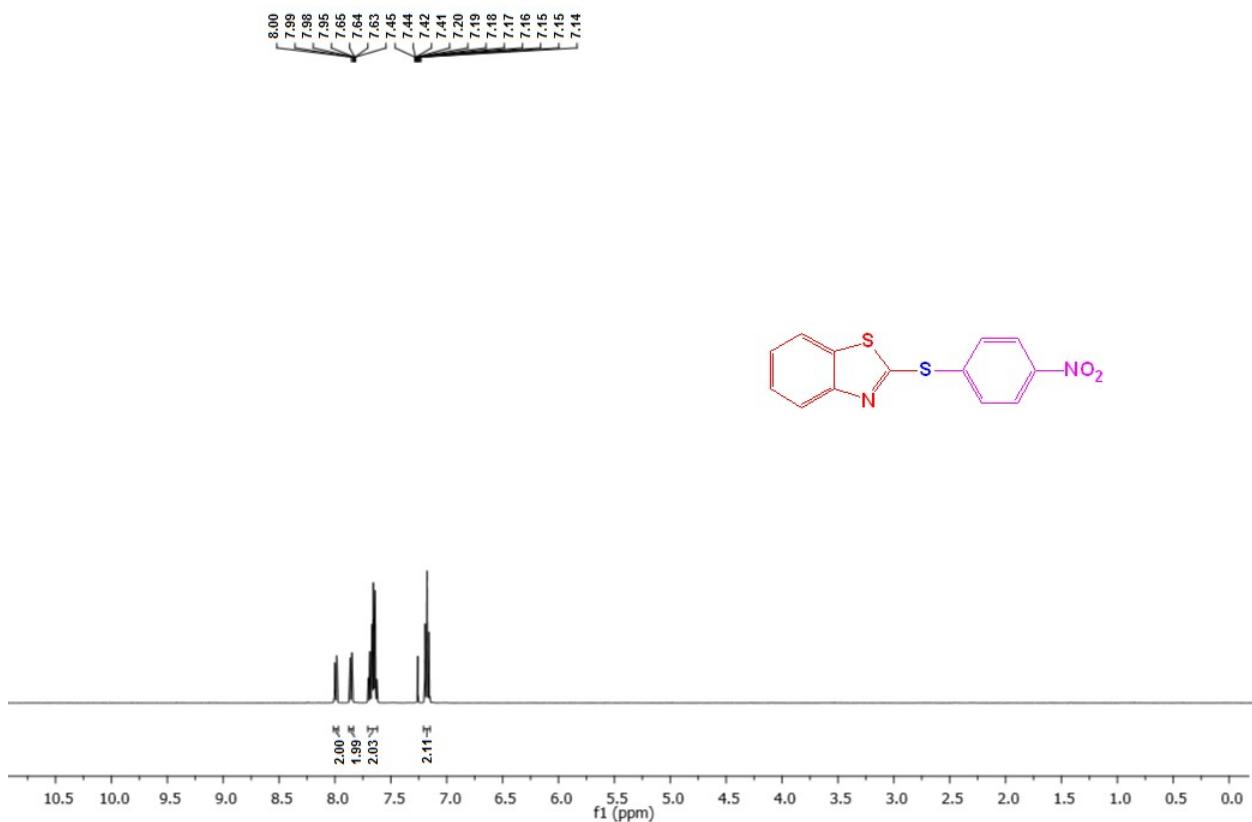
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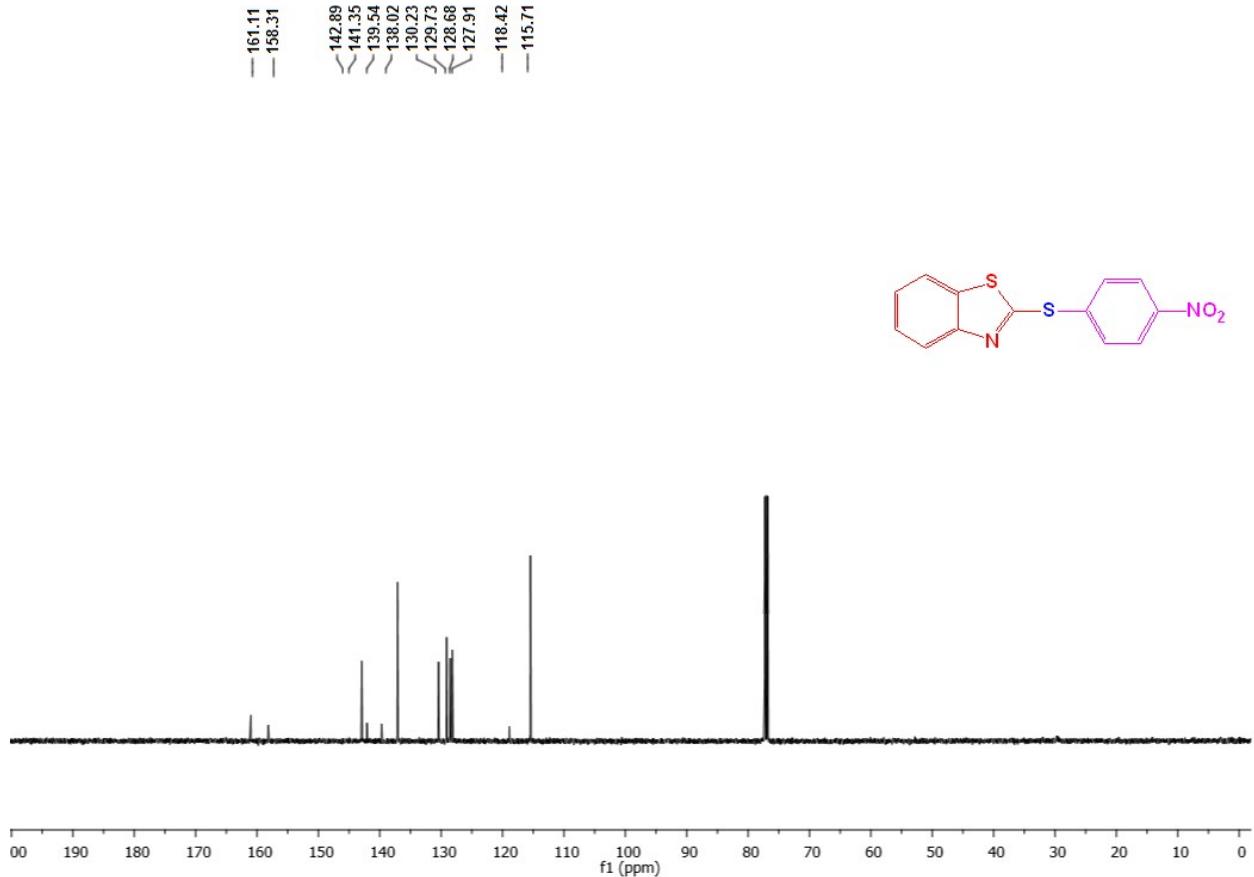
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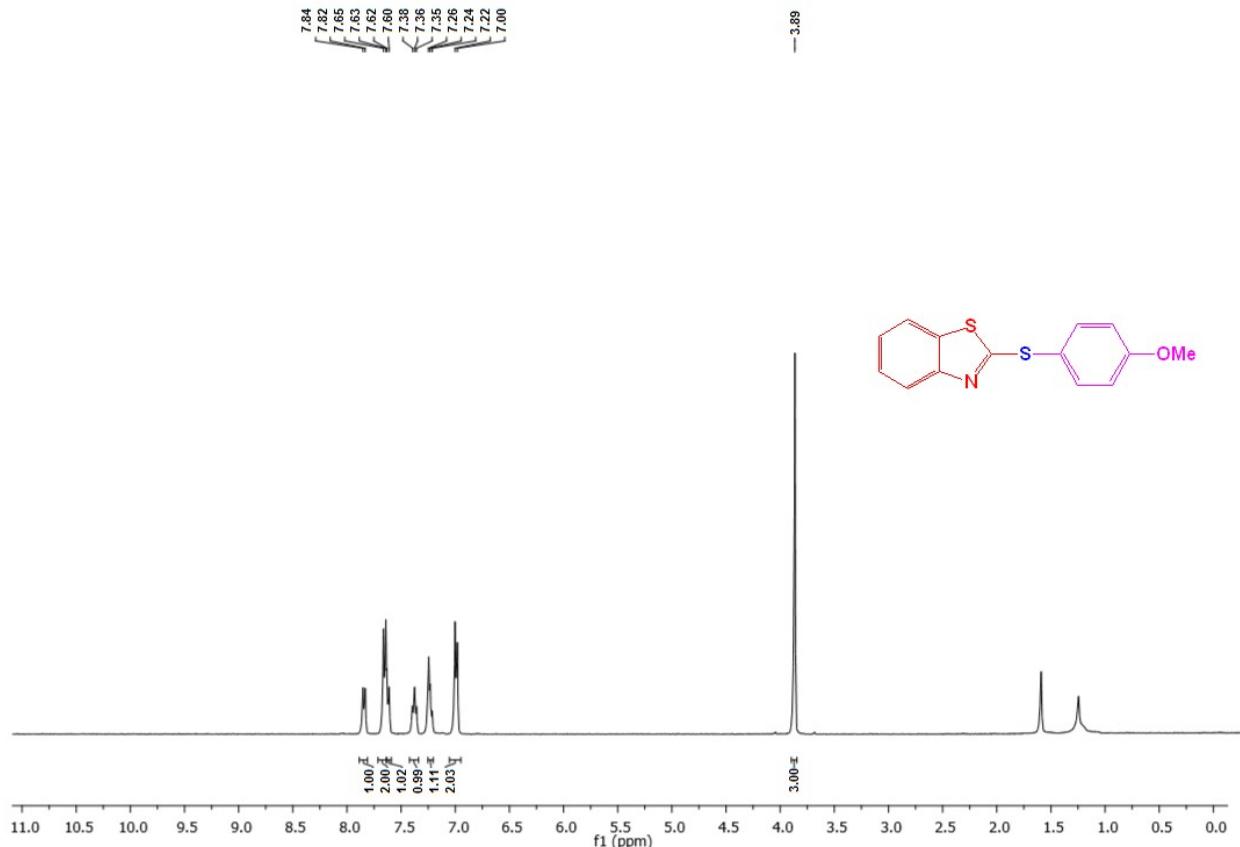
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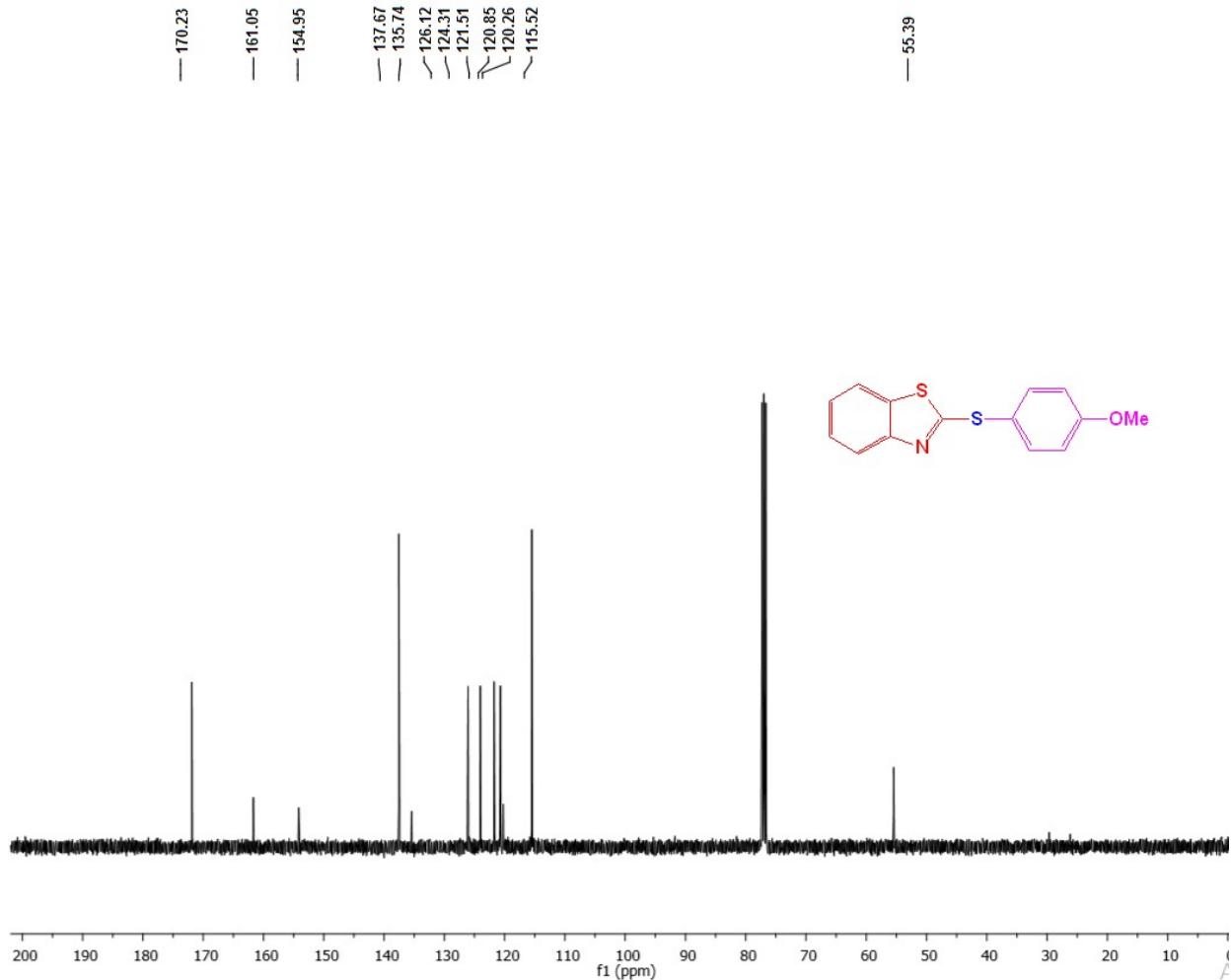
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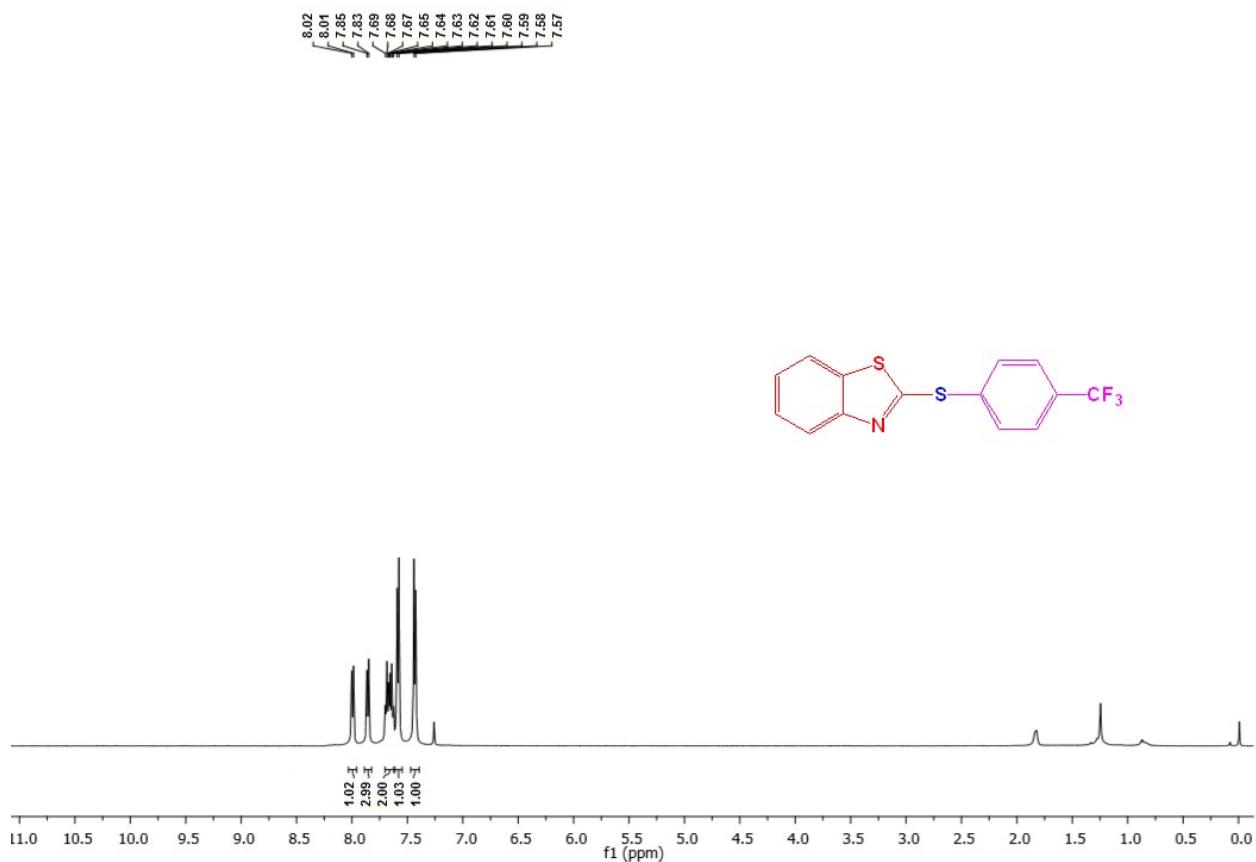
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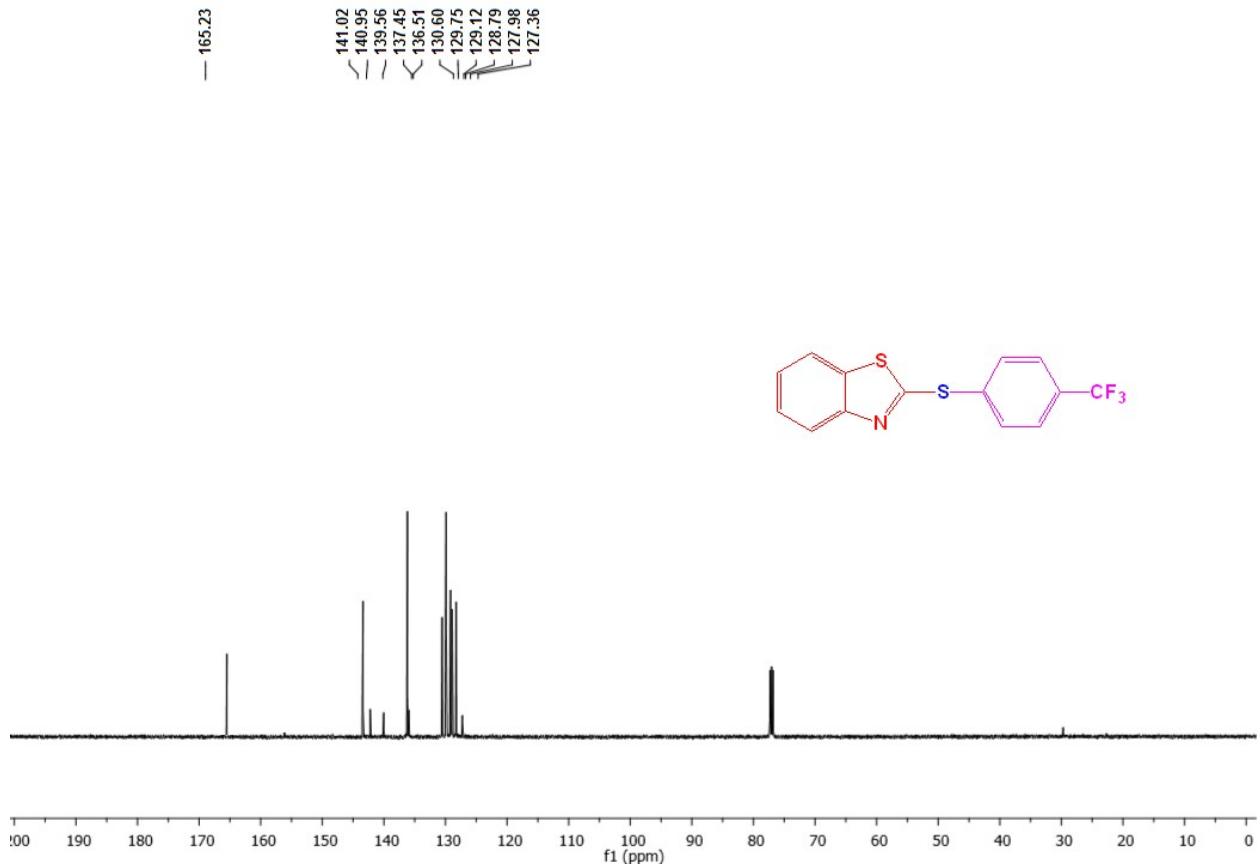
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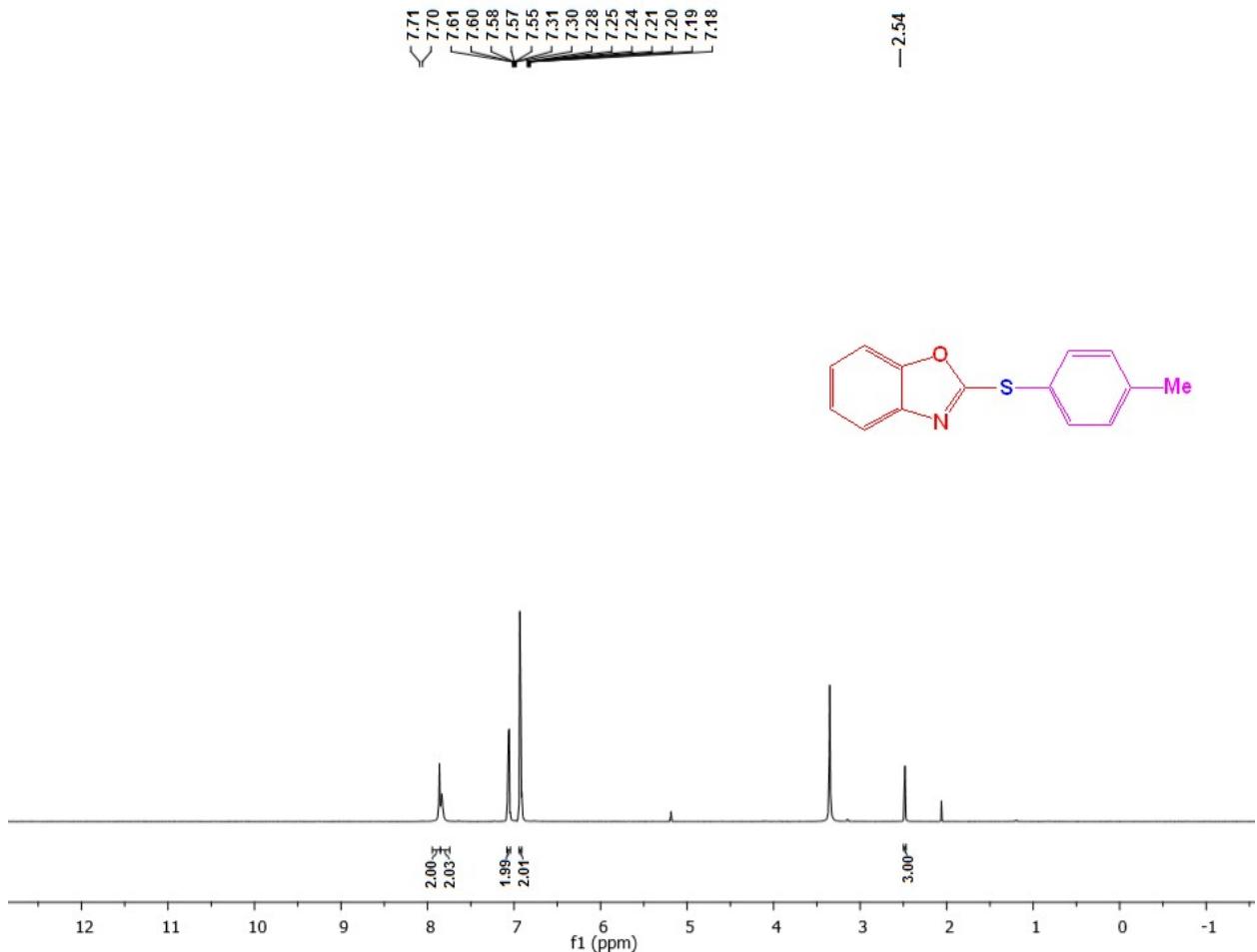
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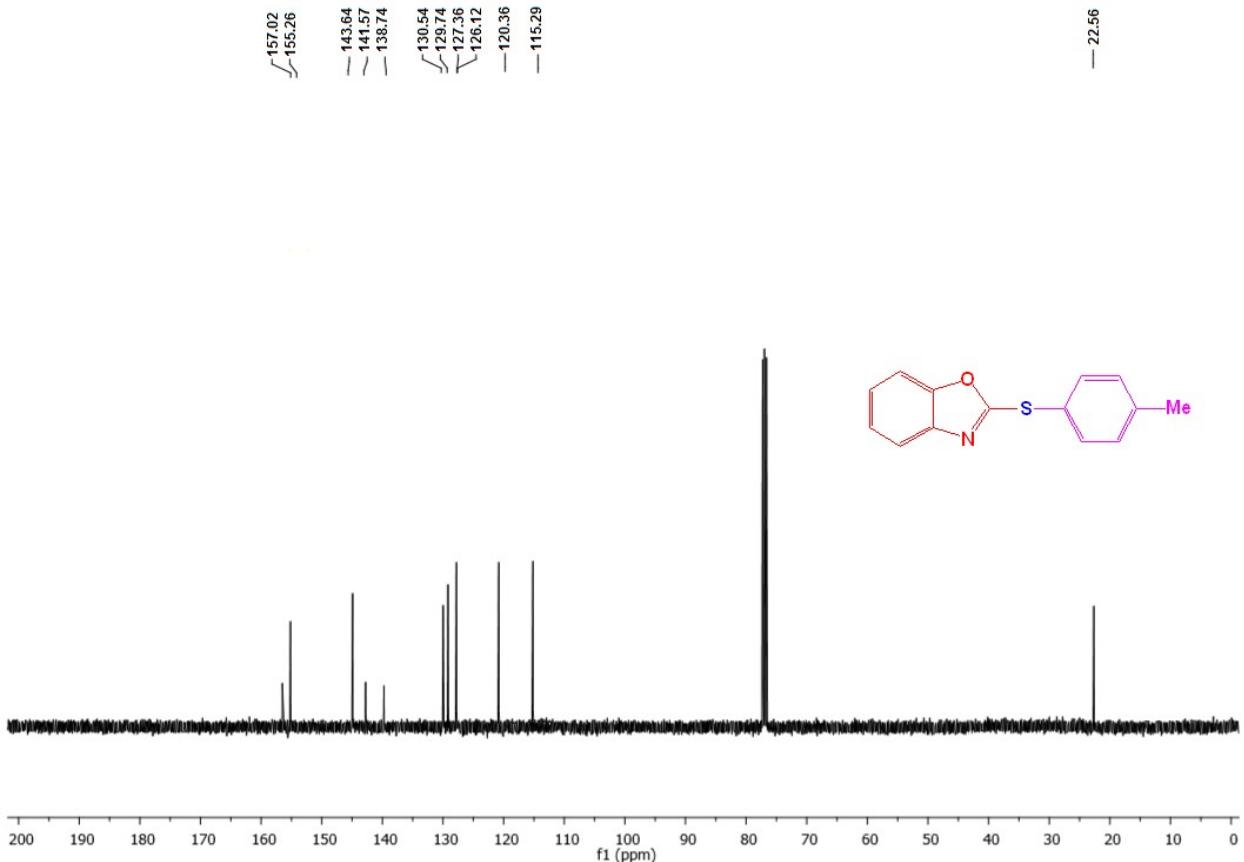
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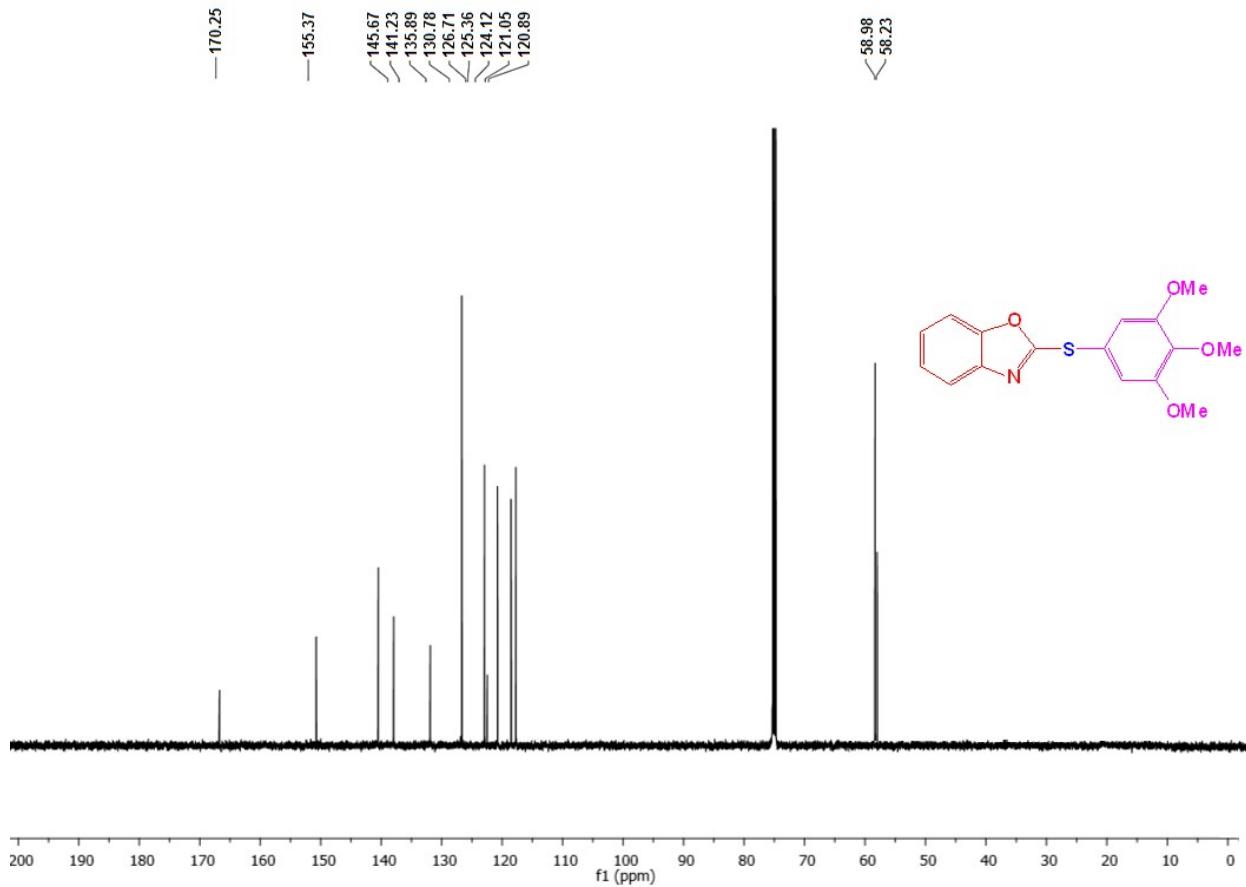
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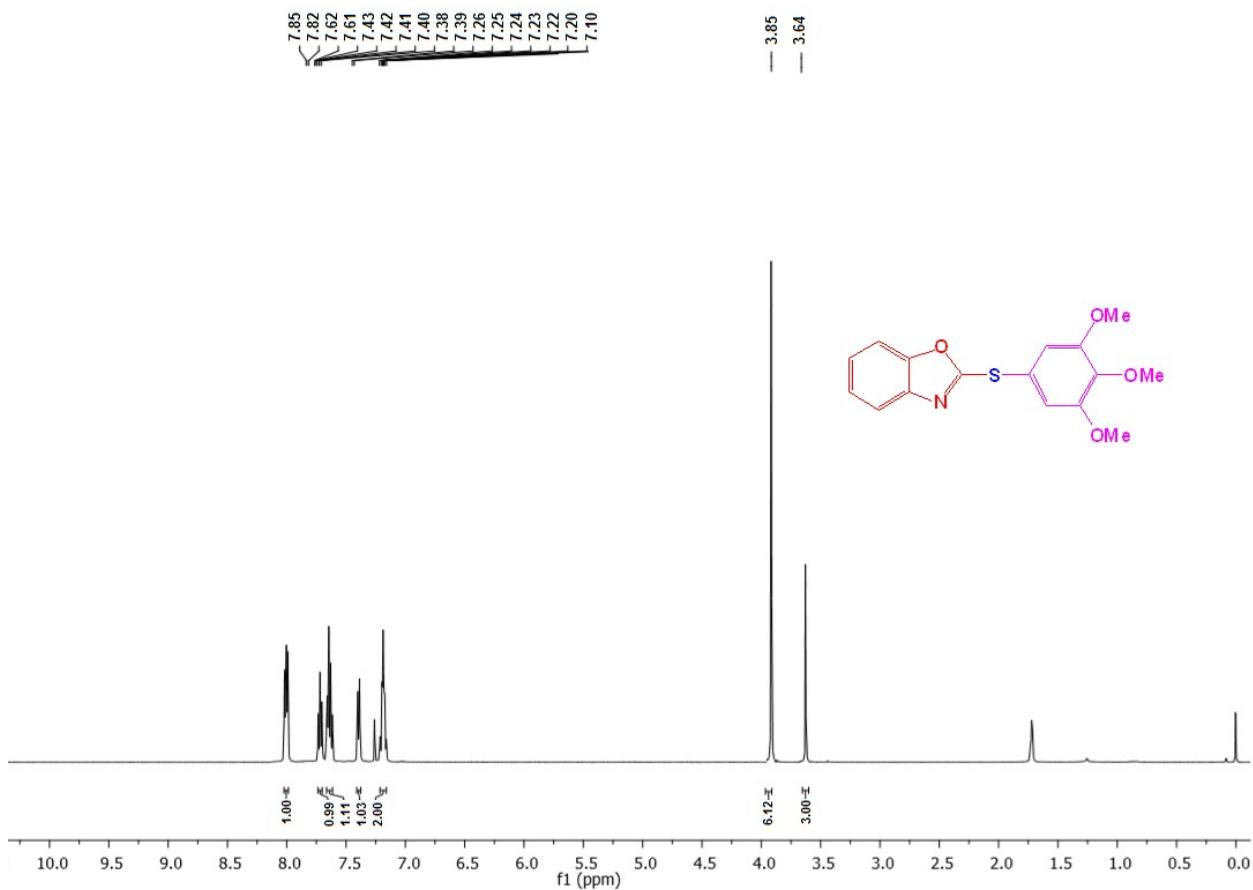
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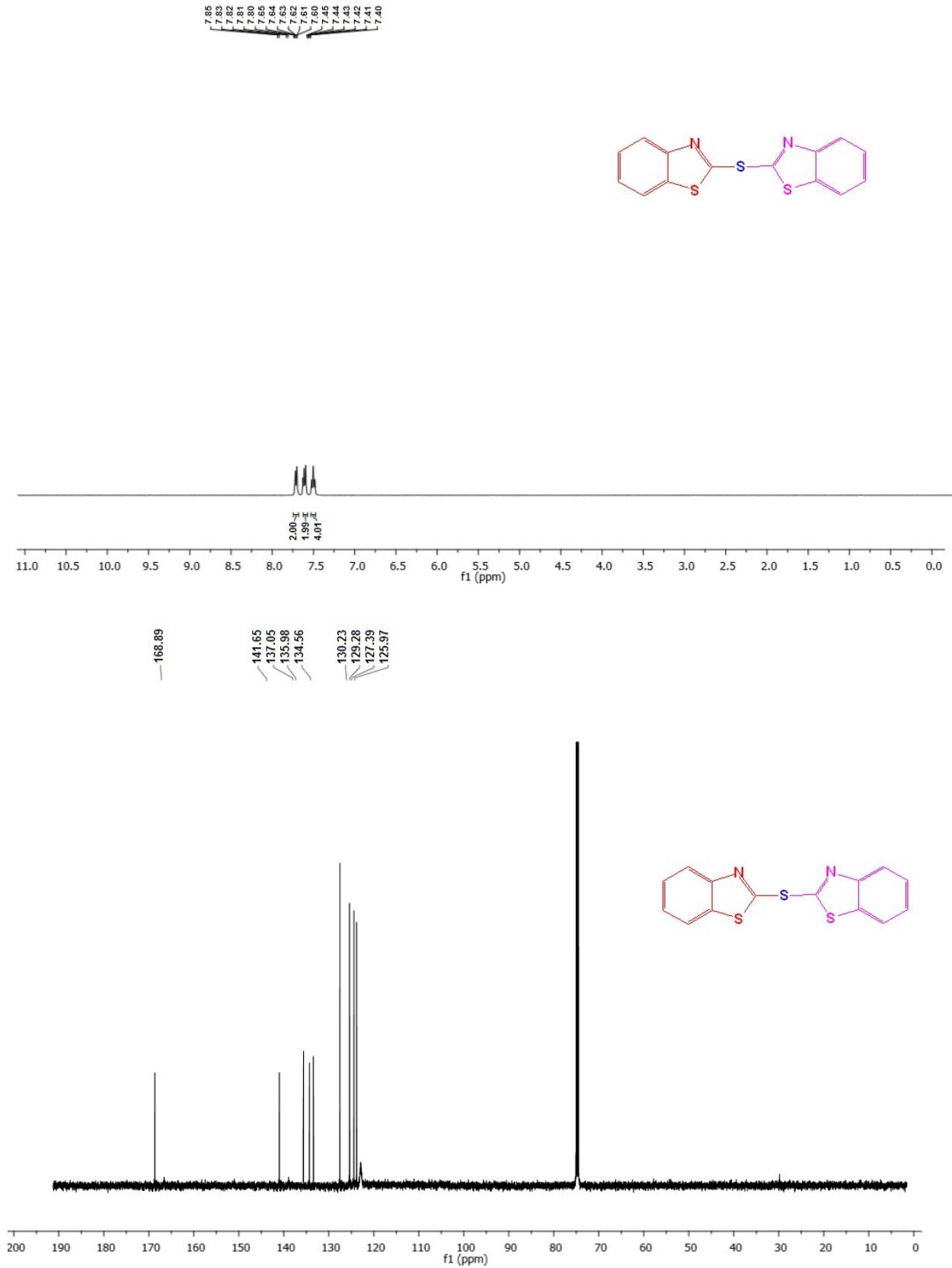
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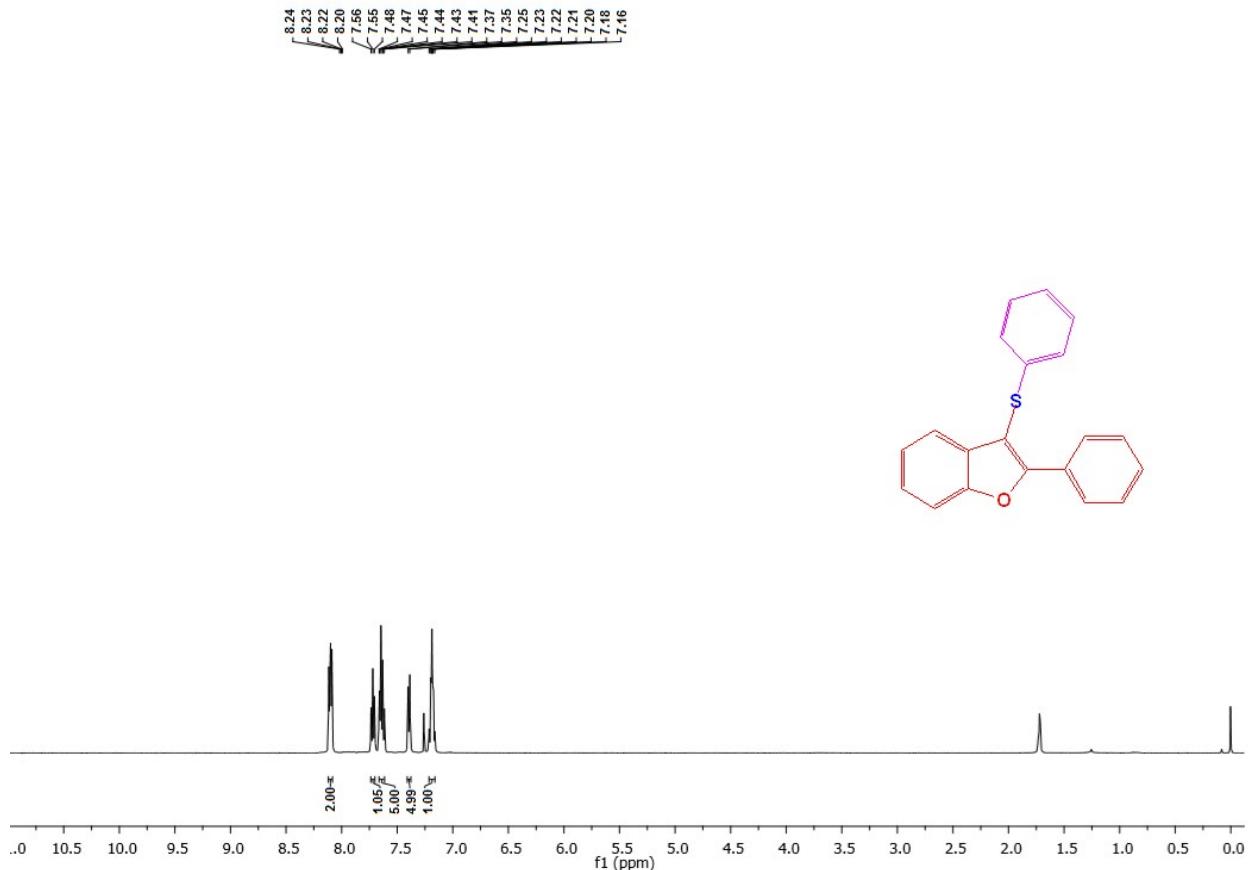
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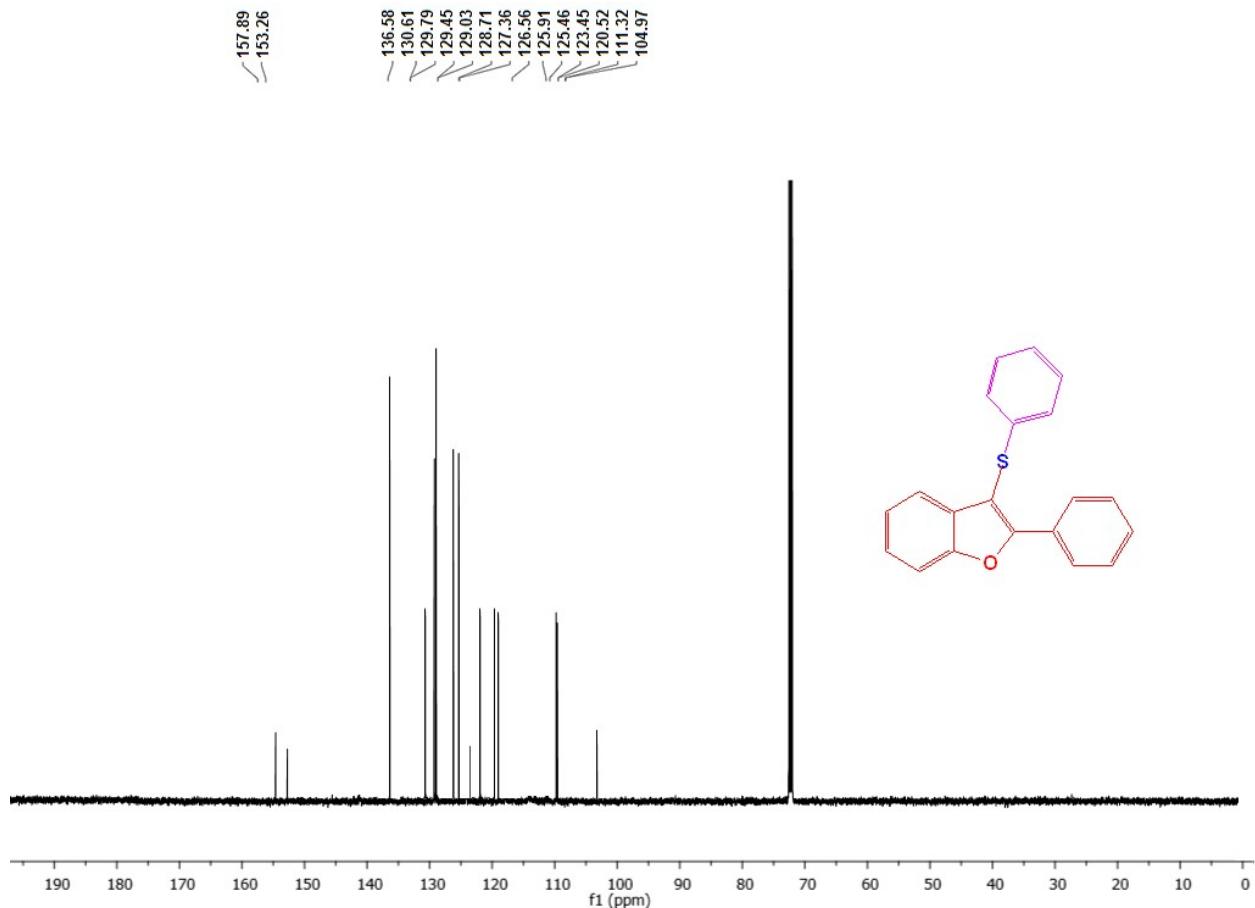
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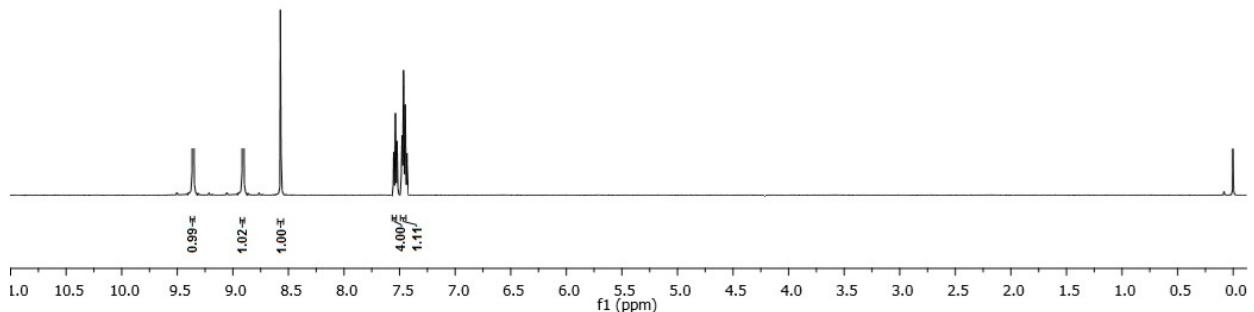
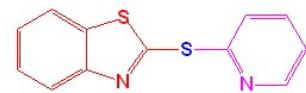
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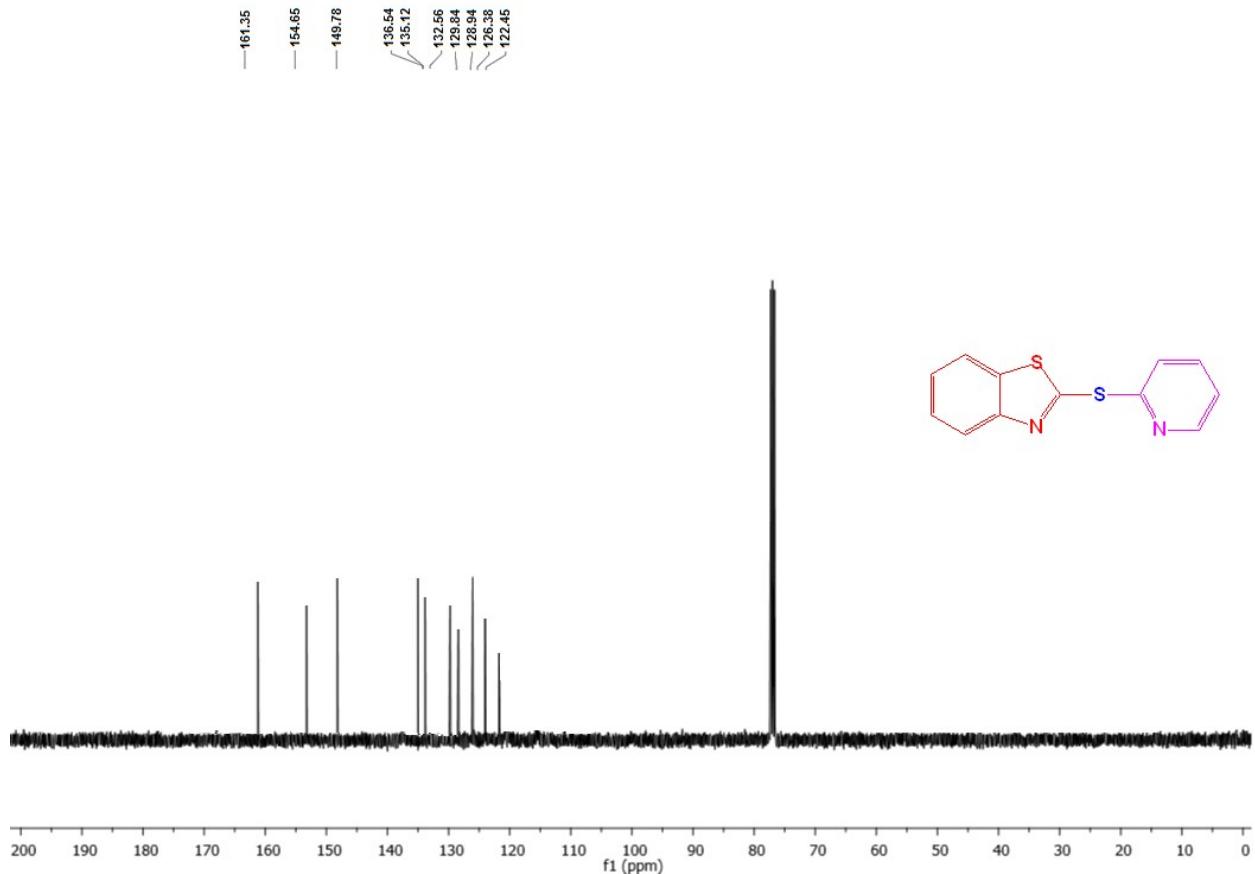
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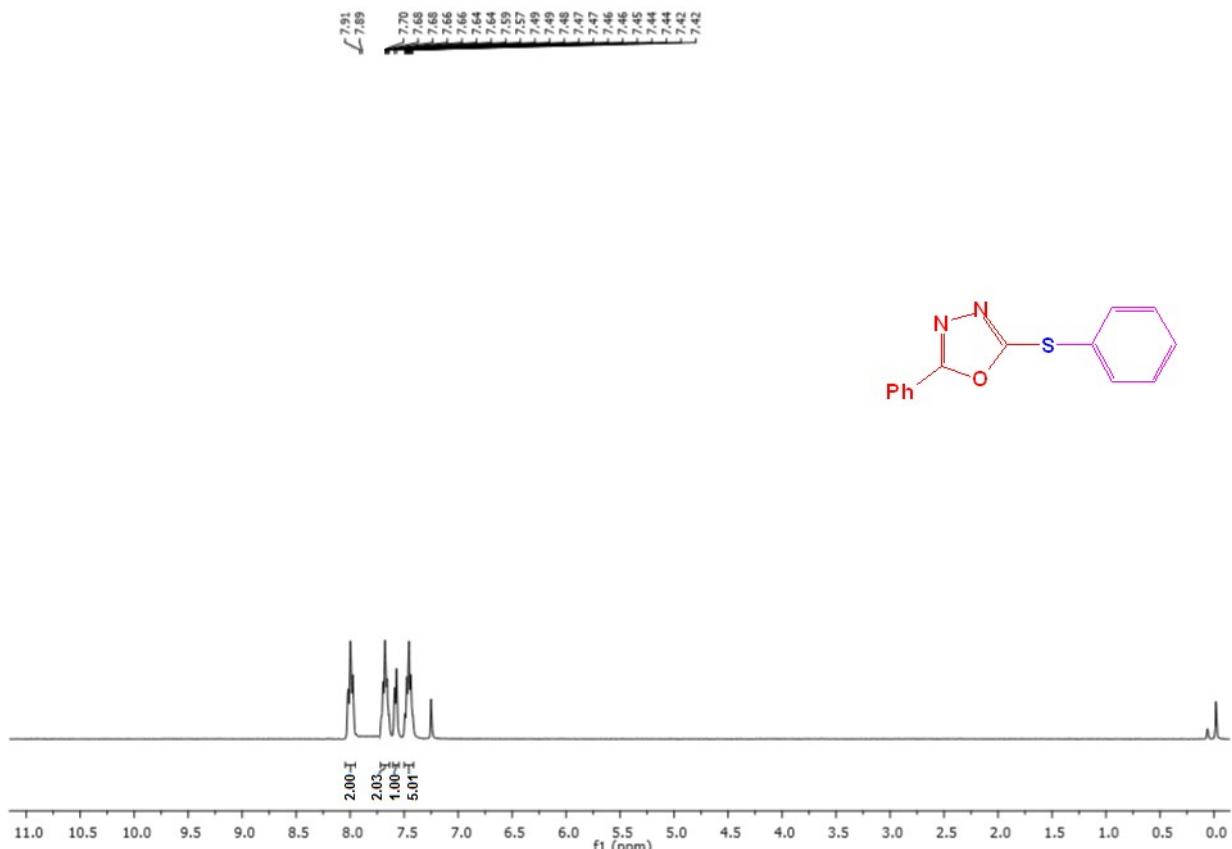
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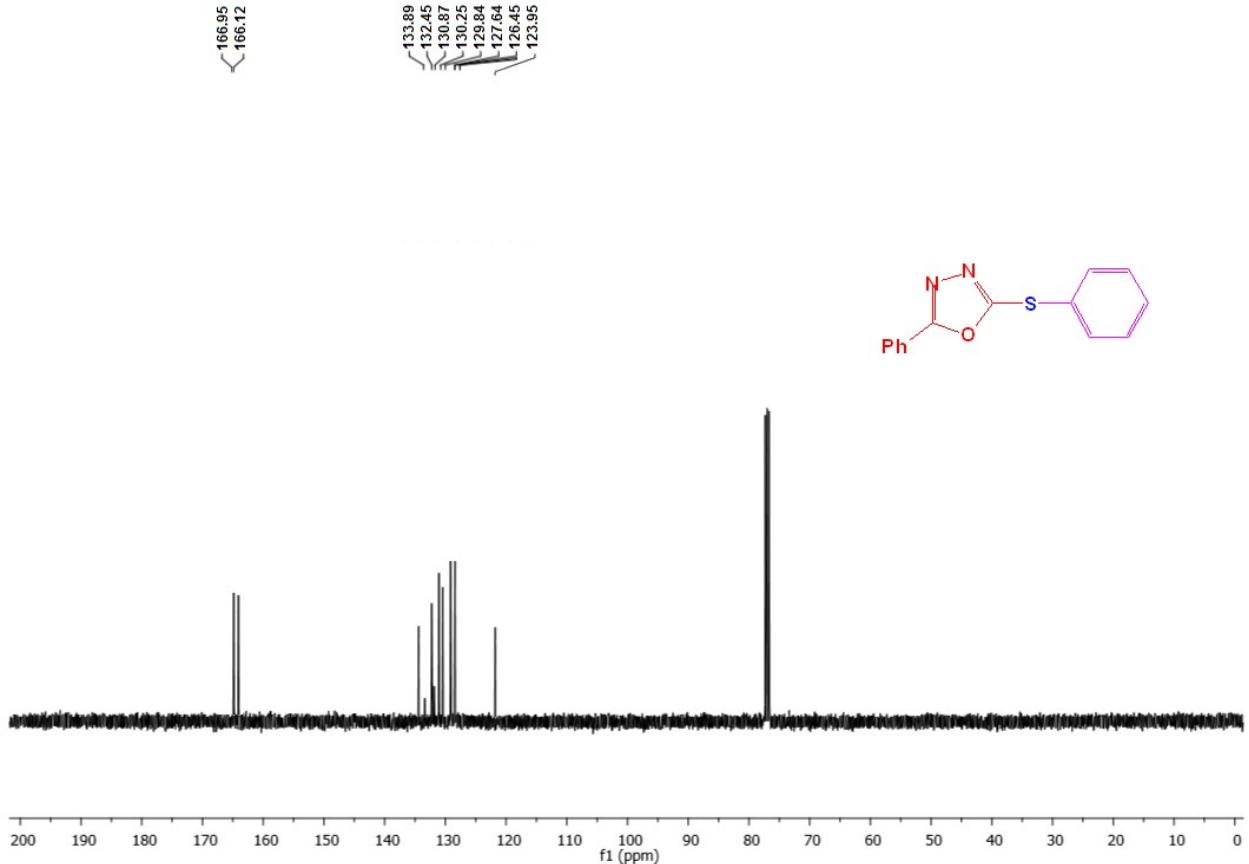
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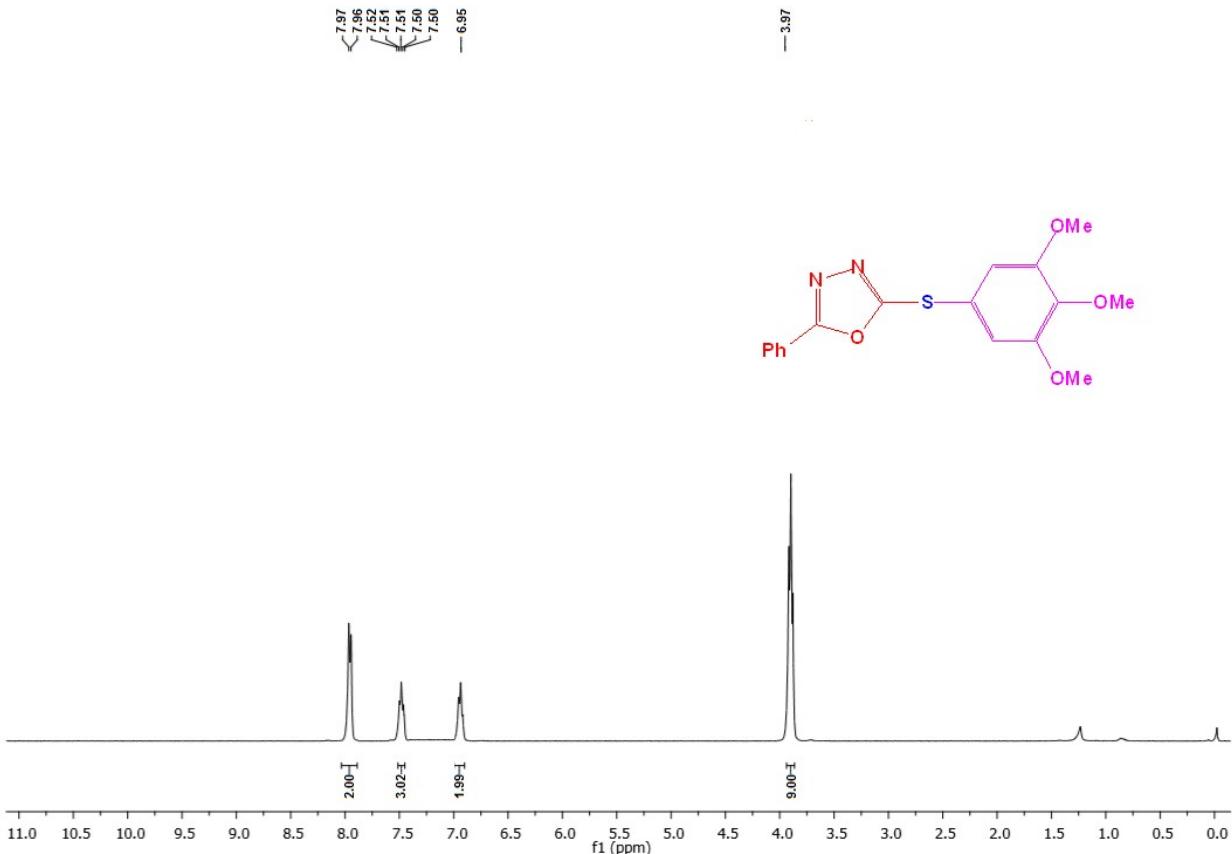
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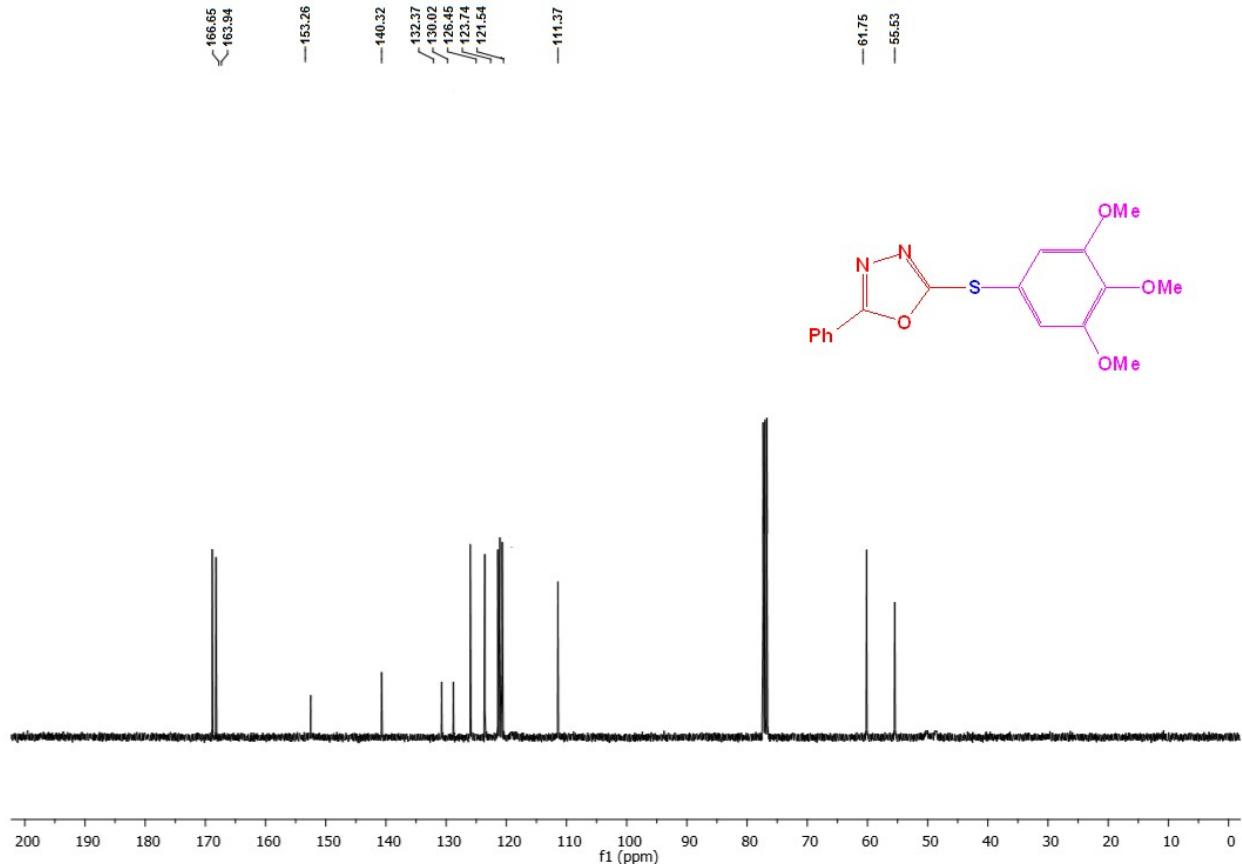
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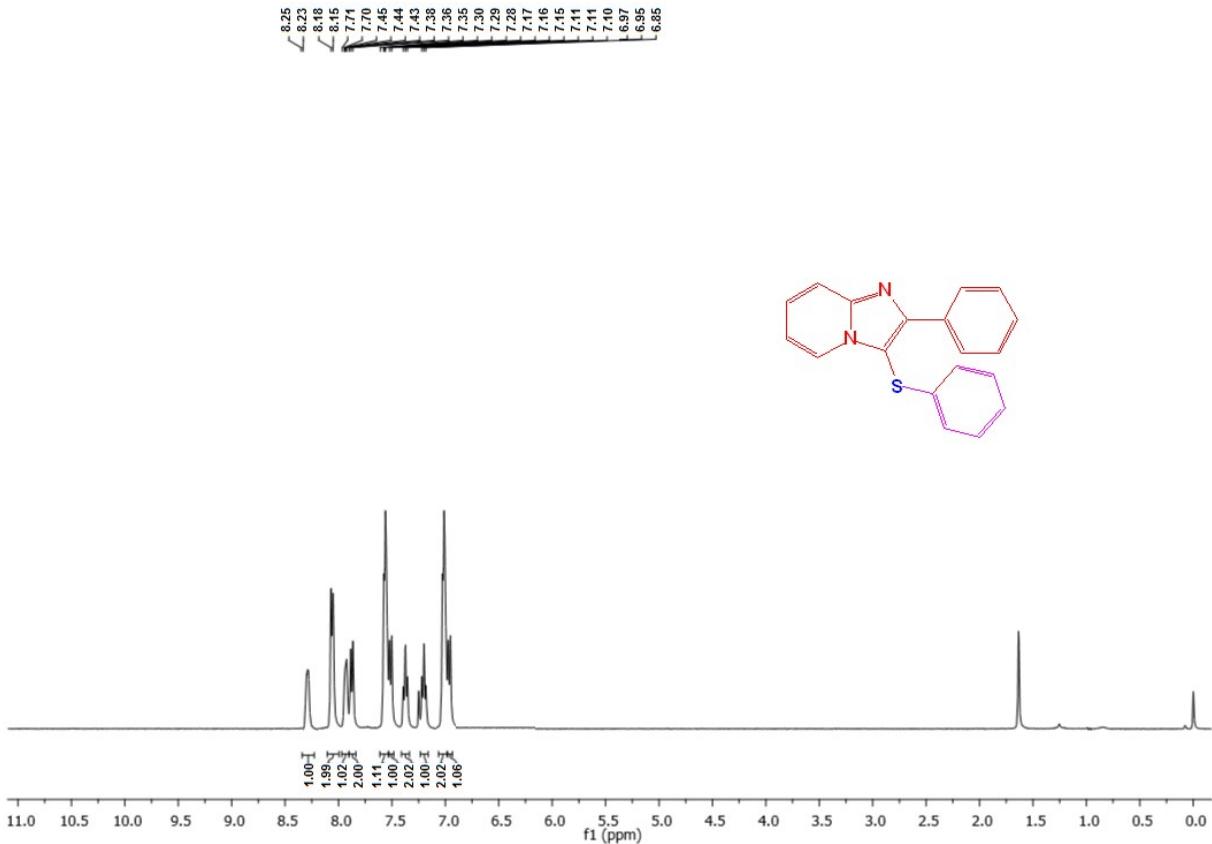
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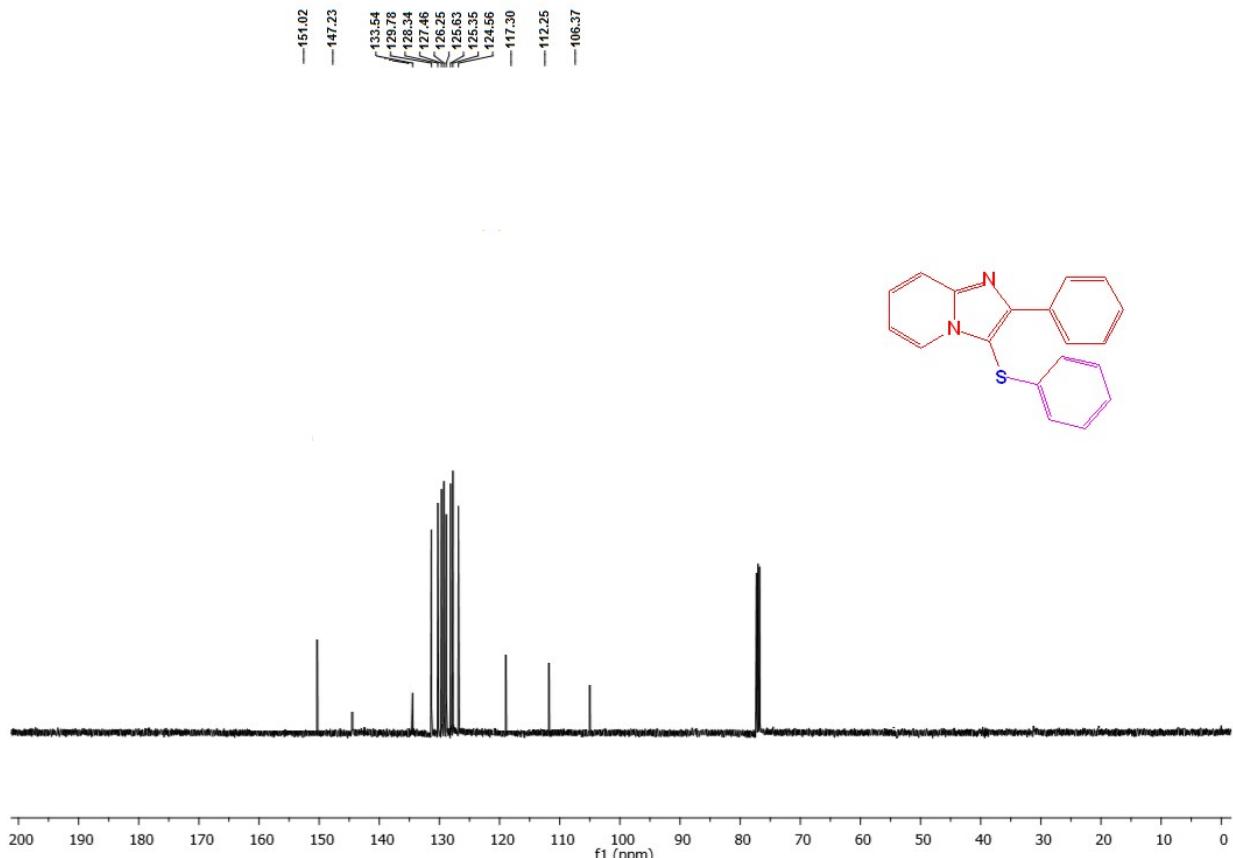
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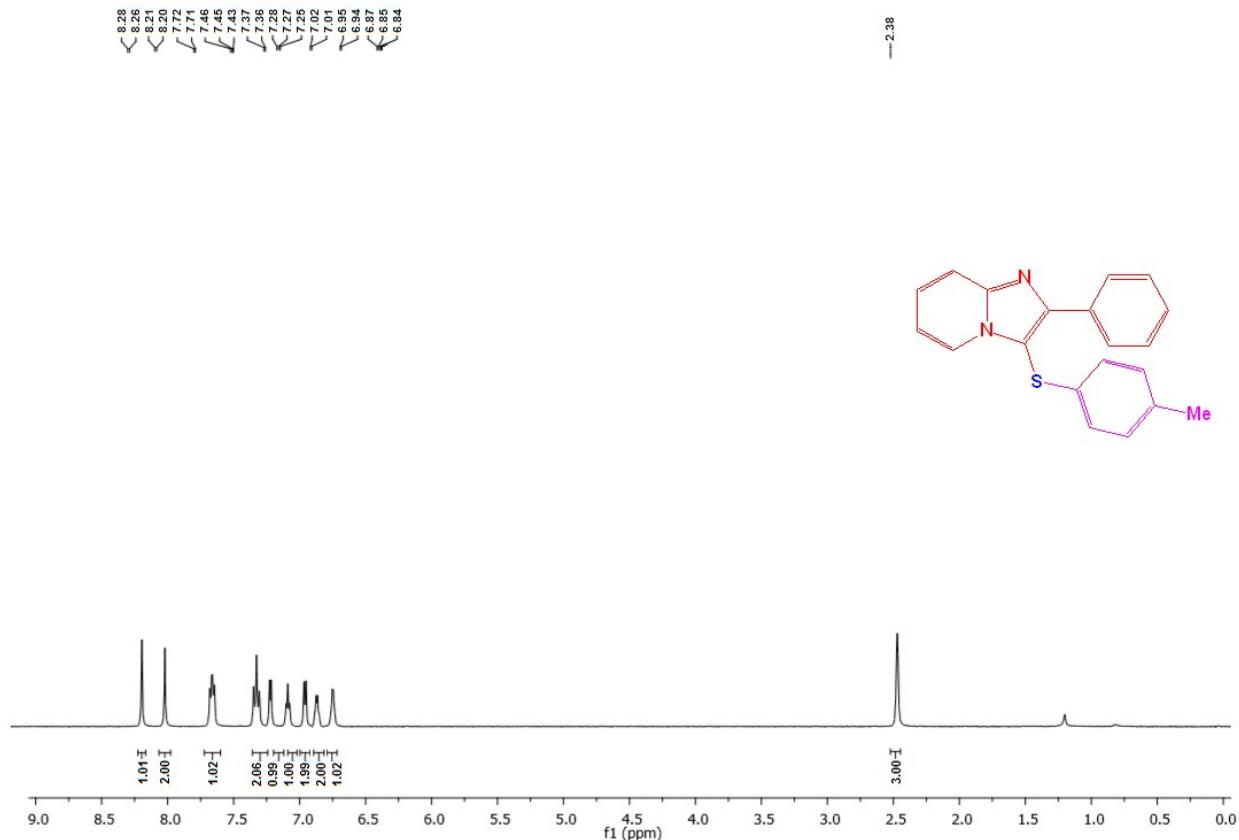
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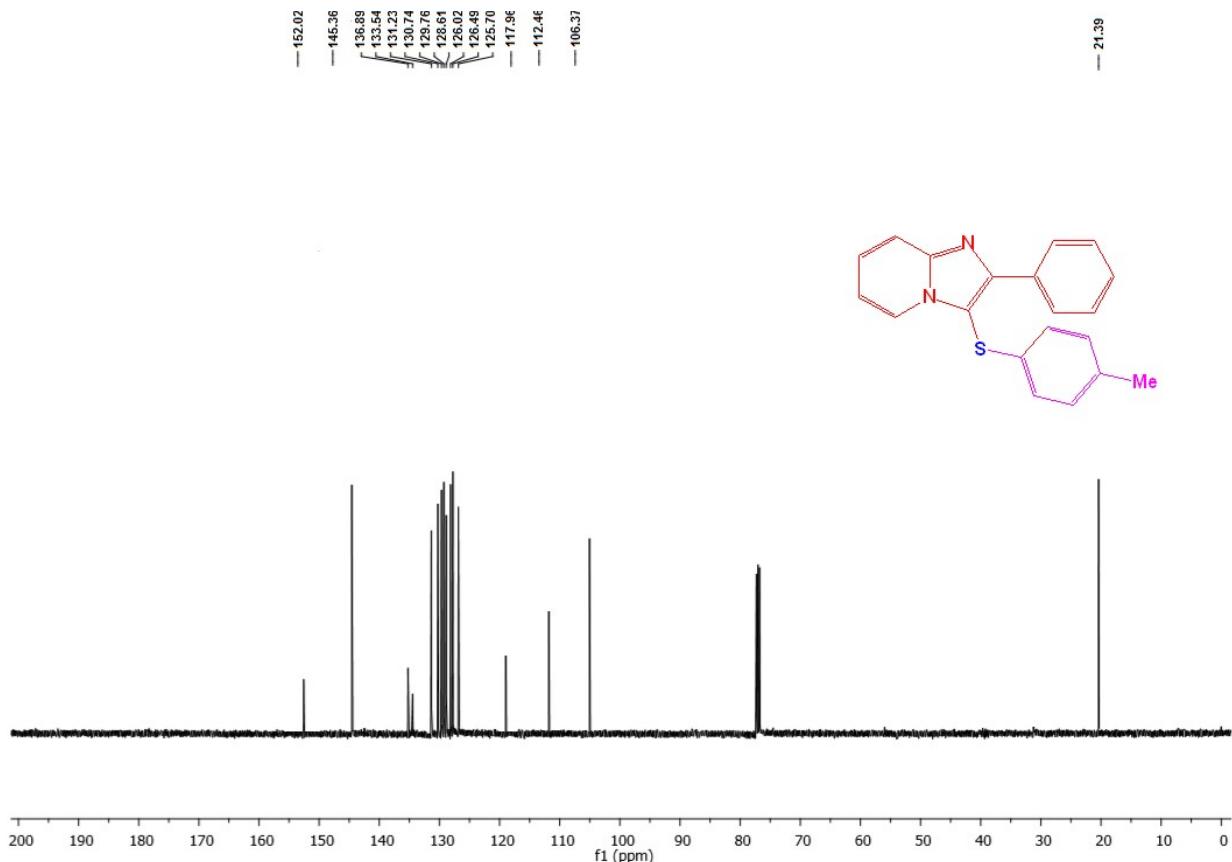
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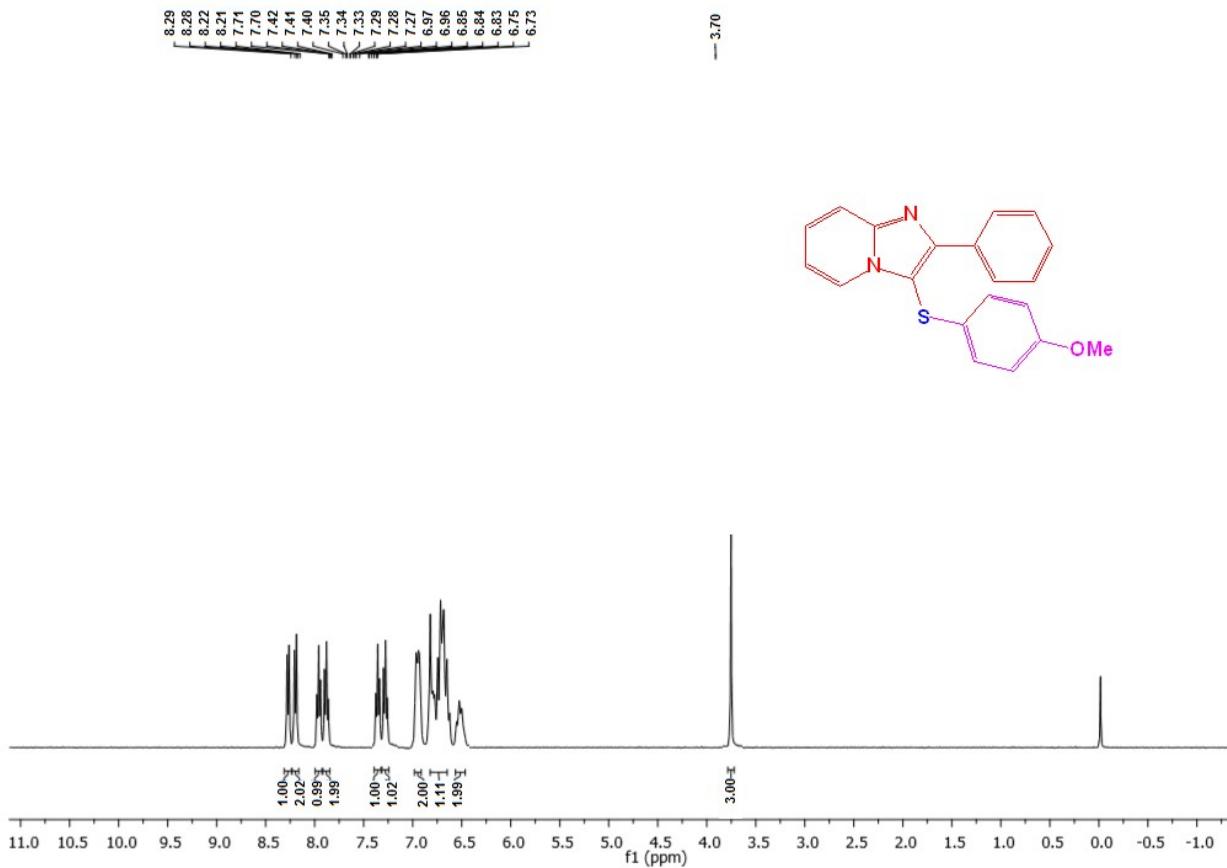
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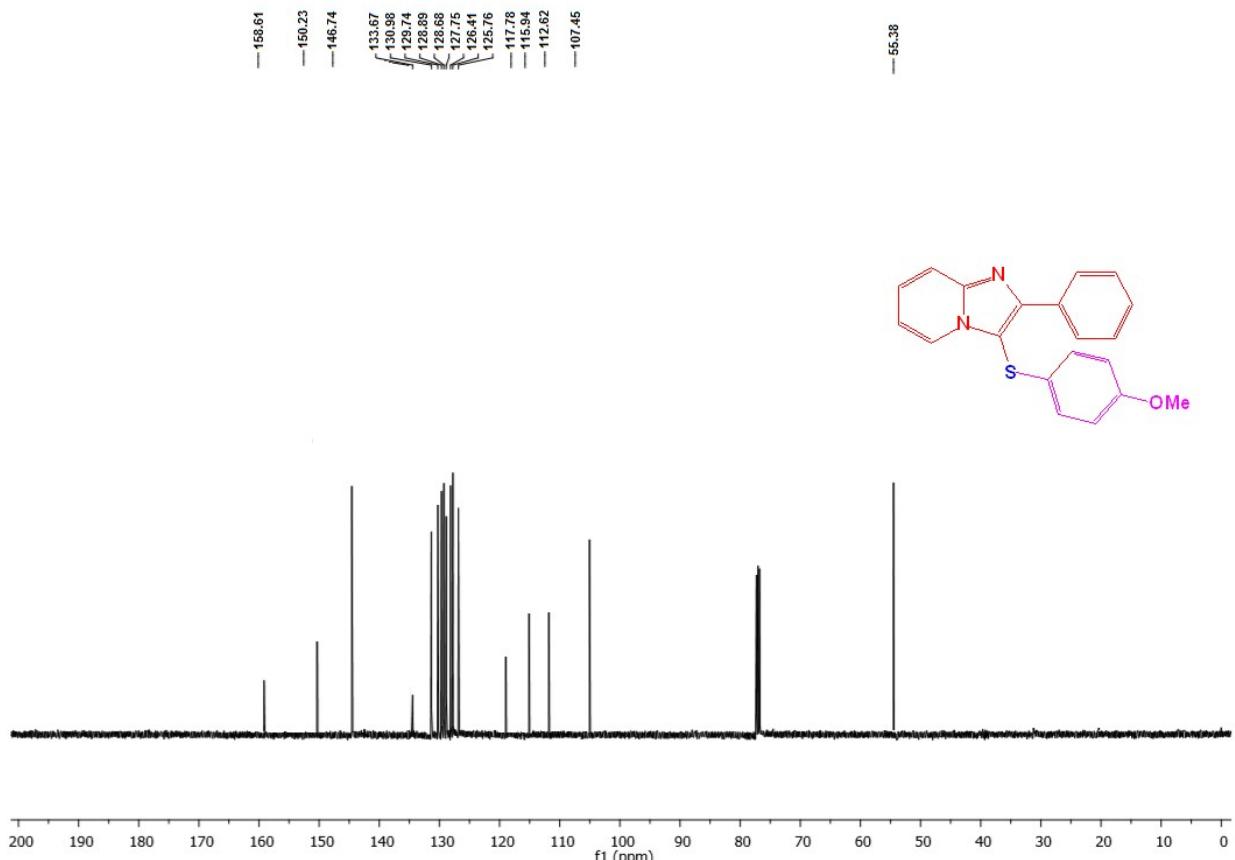
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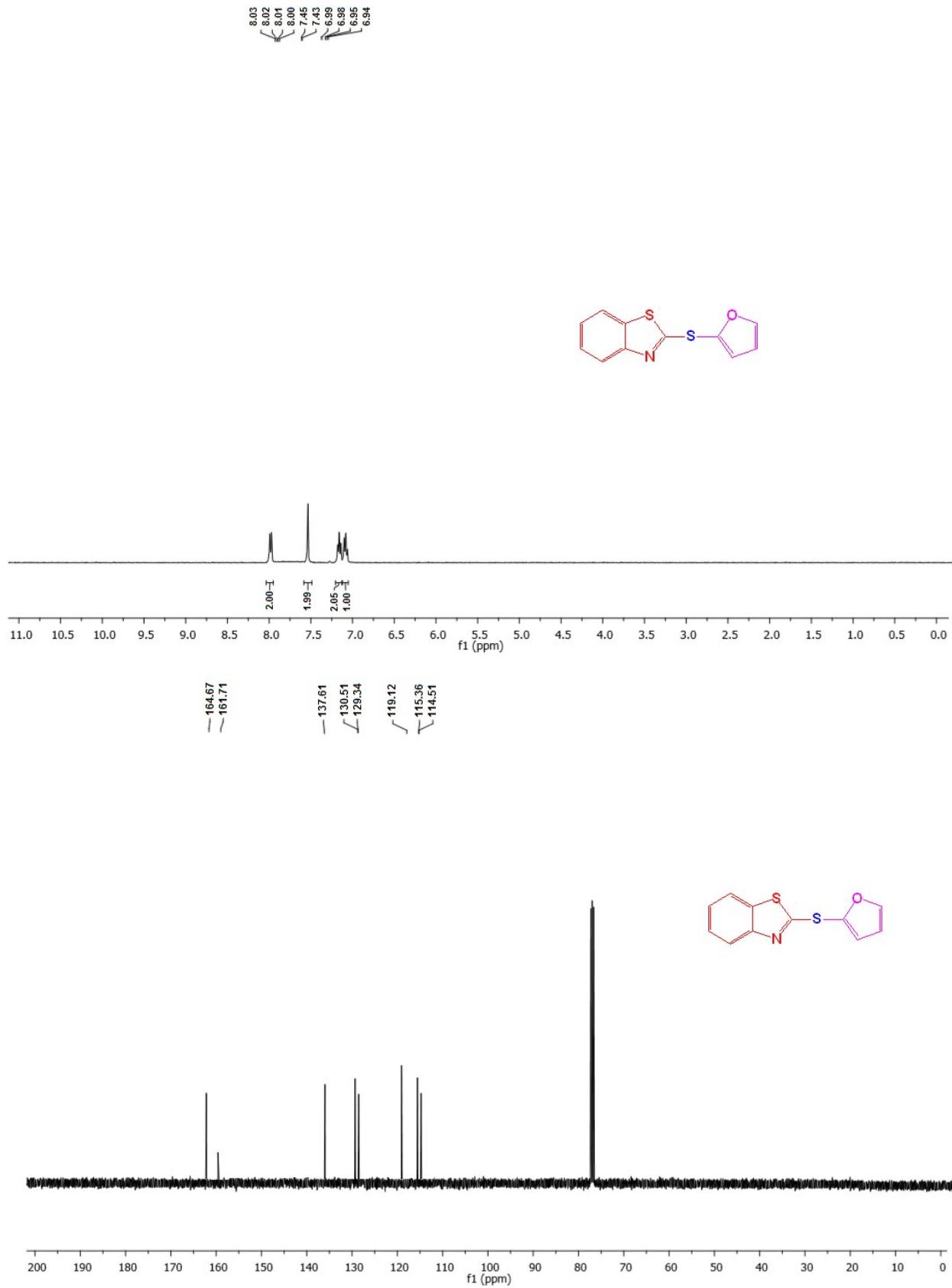
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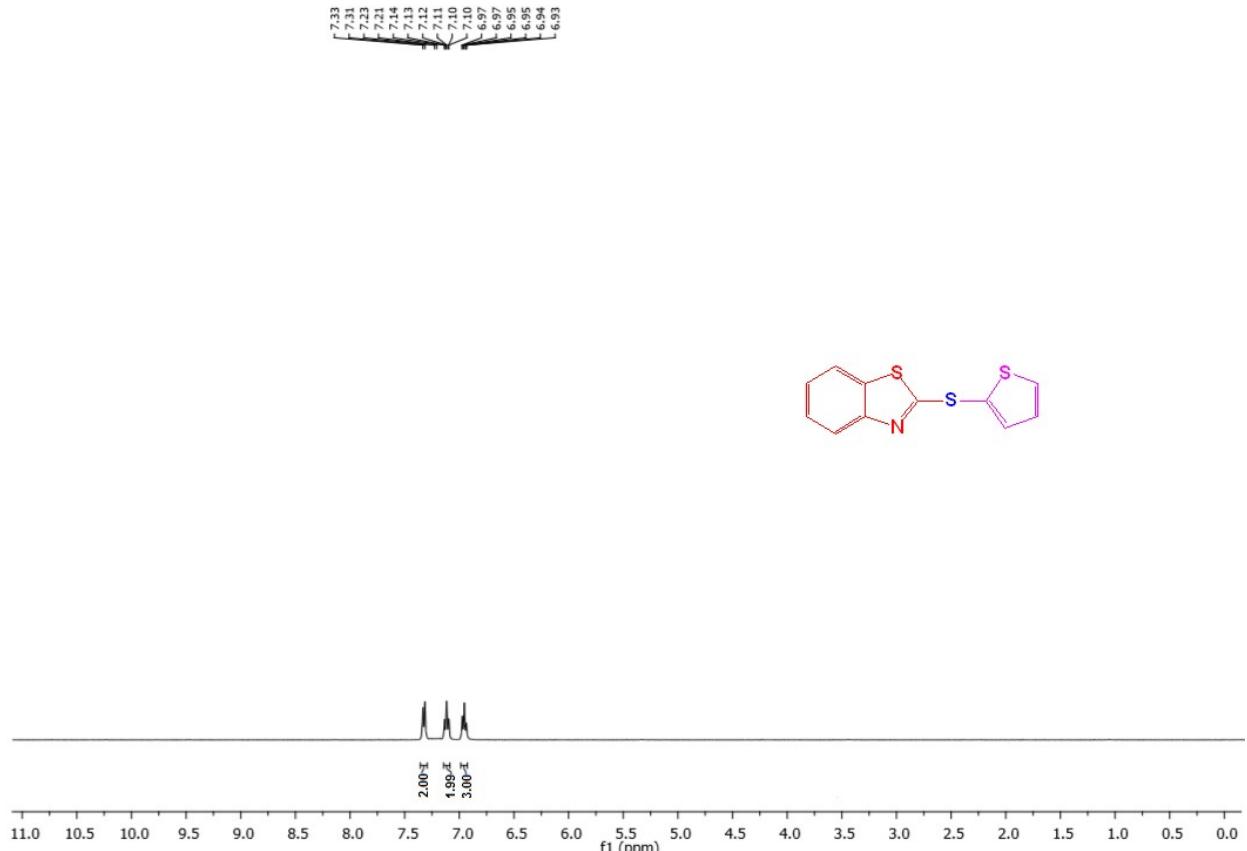
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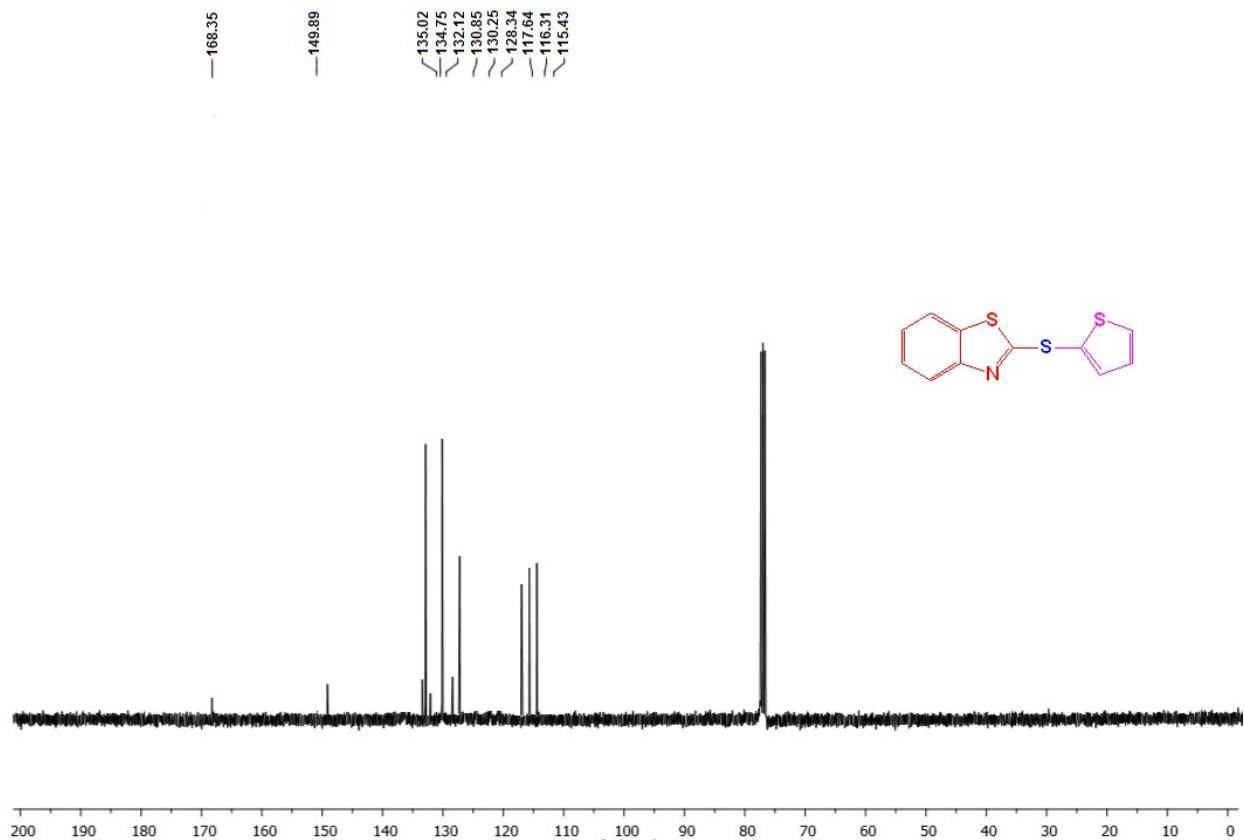
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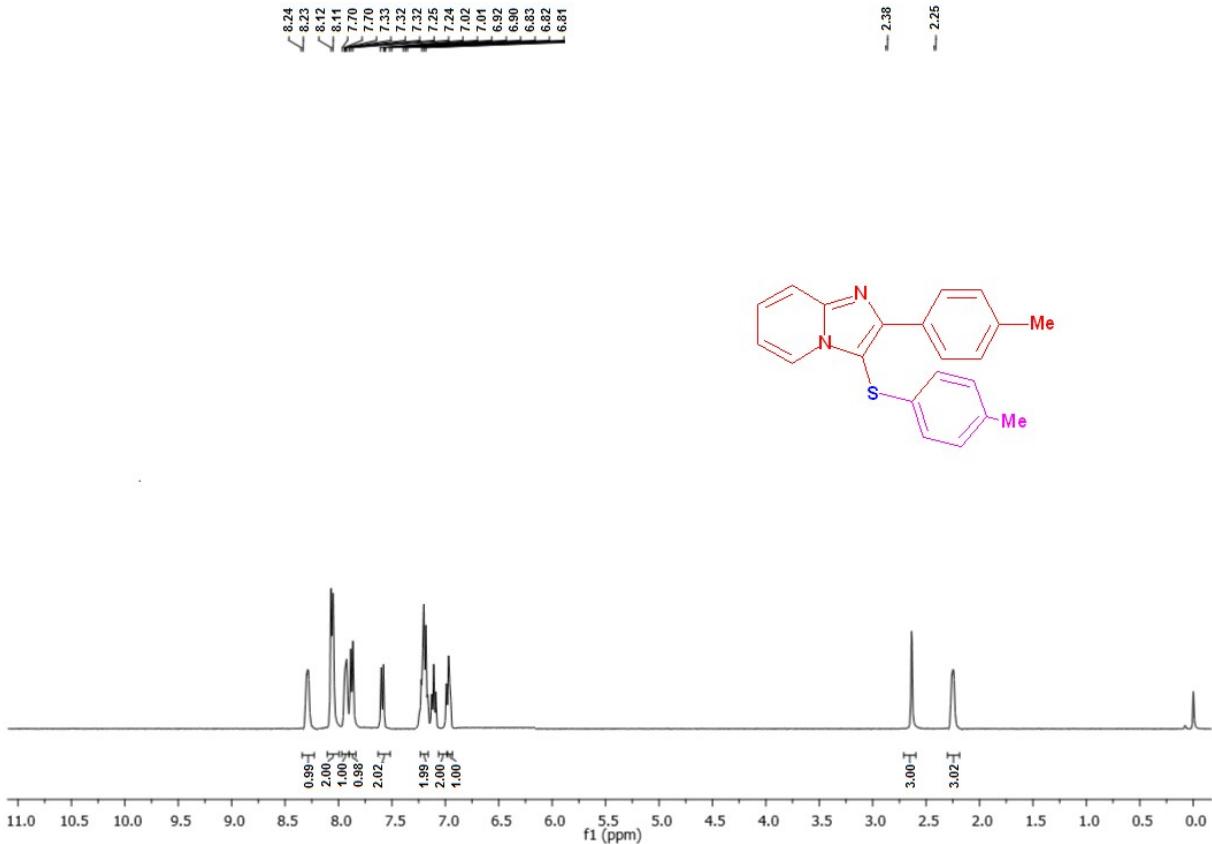
## Supplementary Information



## Supplementary Information



## Supplementary Information



## Supplementary Information

