

## Supporting Information

### The Direct Synthesis of Symmetrical Disulfides and Diselenide by Metal-Organic Framework MOF-199 as an Efficient Heterogenous Catalyst

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## Supplementary Information

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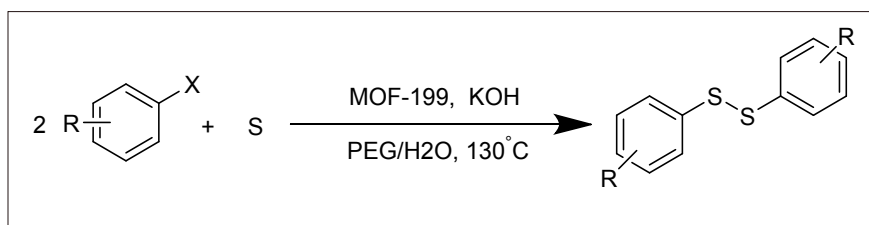
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## 1. General information

The reactions were performed under normal atmosphere condition. All reagents and solvents used in this work were obtained from Merck and were used without further purification. Analytical thin layer chromatography was performed using Merck silica gel GF<sub>254</sub> plates. Plate chromatography was performed using silica gel 60 PF<sub>254+366</sub>. All products are known and were characterized by comparison of their spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-Mass) and physical data with those of authentic samples. The NMR spectra were recorded at on a Bruker Avance NMR spectrometer in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> solution with TMS as internal standard. All shifts are given in ppm and all coupling constants (*J* values) were reported in Hertz (Hz). Elemental analyses were done on a Carlo-Erba EA1110 CHNO-S analyzer. The IR spectra were recorded at on a Bruker vertex 70 IR spectrometer.

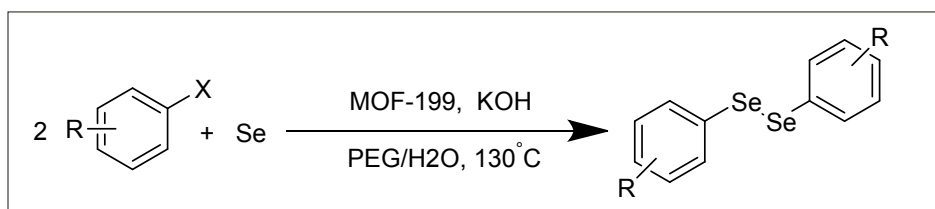
## 2. Experimental procedures and characterization data

### General procedure for the synthesis of diaryl disulfides derivatives

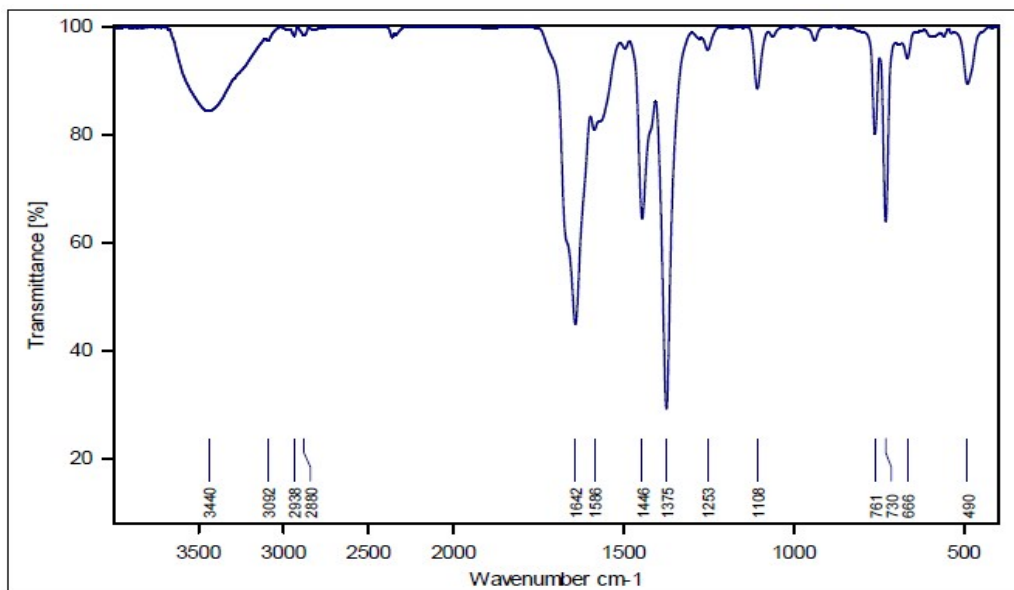


Symmetrical organic disulfides synthesis; typical experimental procedure. A mixture of iodobenzene (2.0 mmol), Sulfur (4.0 mmol) and MOF-199 (10 mg) were added to a flask containing 2ml DMF/H<sub>2</sub>O (20:1). The reaction continued at 130°C under atmospheric conditions until completion. The reaction progress was controlled by thin-layer chromatography. The reaction mixture was then filtered. The filtrate was evaporated under vacuum, CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added and the mixture was washed with H<sub>2</sub>O (2 × 15 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to give the crude diaryl disulfide, which was purified by plate chromatography (silica gel, n-hexane–ethyl acetate, 20:1).

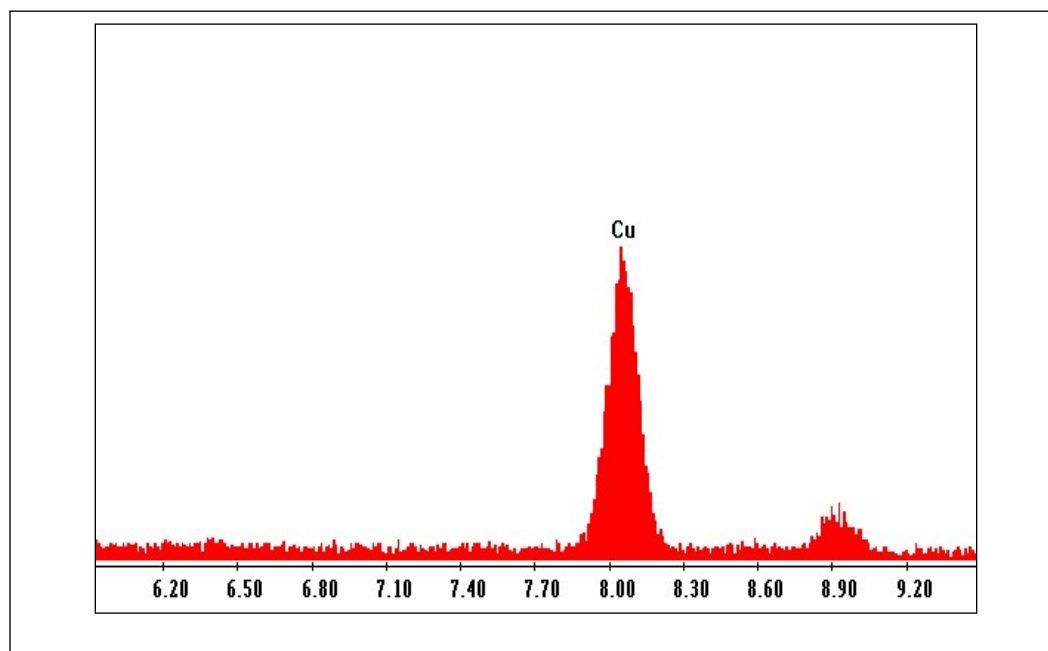
### General procedure for the synthesis of diaryl diselenides derivatives



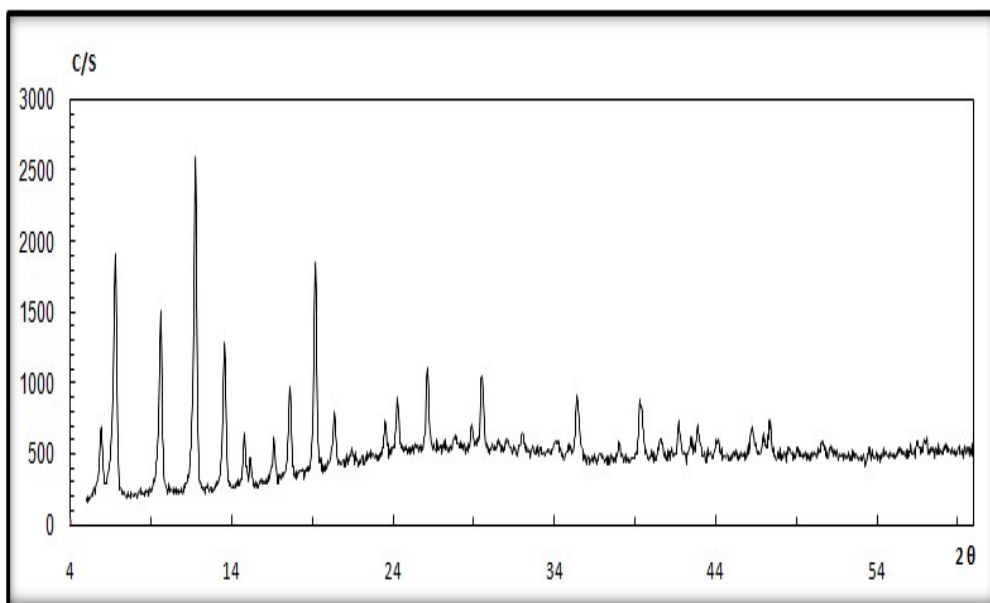
Symmetrical organic diselenides synthesis; typical experimental procedure. A mixture of iodobenzene (2.0 mmol), selenide (2.0 mmol) and MOF-199 (10 mg) were added to a flask containing 2ml DMF/H<sub>2</sub>O (20:1). The reaction continued at 130°C under atmospheric conditions until completion. The reaction progress was controlled by thin-layer chromatography. The reaction mixture was then filtered. The filtrate was evaporated under vacuum, CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added and the mixture was washed with H<sub>2</sub>O (2 × 15 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to give the crude diaryl diselenide, which was purified by plate chromatography (silica gel, n-hexane–ethyl acetate, 20:1).



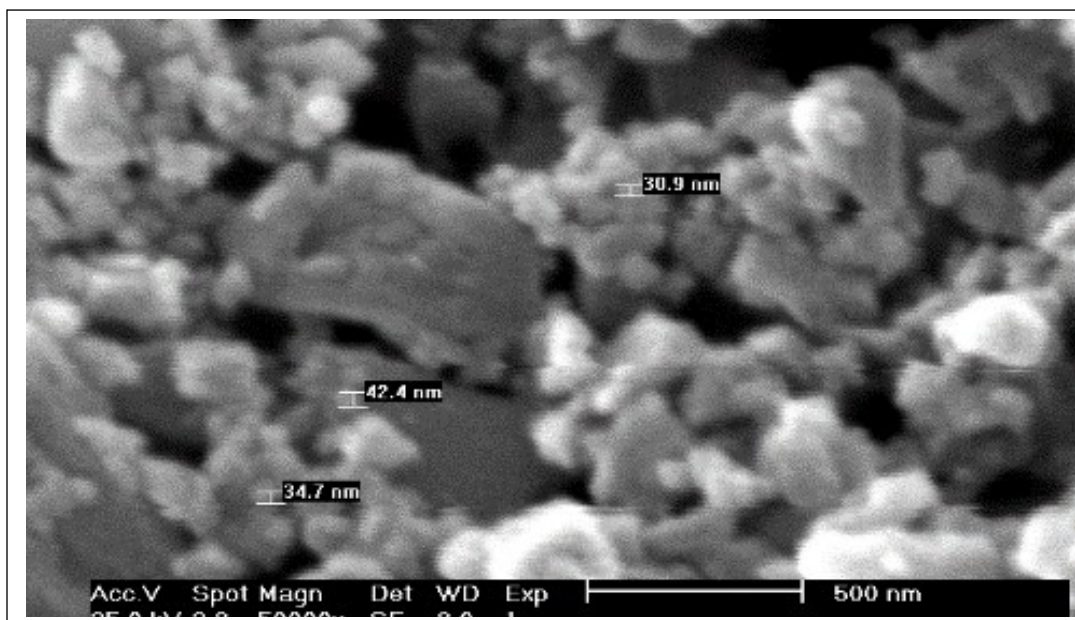
FT-IR spectra of the MOF-199



Energy-dispersive X-ray spectroscopy of the MOF-199



X-ray powder diffractogram of the MOF-199



SEM micrograph of the MOF-199.

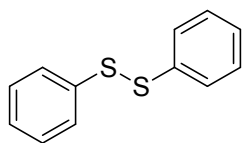
### General procedure for the synthesis of MOF-199

The procedure to prepare MOF-199 was according to Ref [1a,1b]. Benzenetricarboxylic acid (500 mg, 2.38 mmol) was mixed in 12 mL of a 1:1:1 mixture of DMF/EtOH/H<sub>2</sub>O. Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (860 mg, 4.31 mmol) was mixed with 12 mL of the same solvent and the mixtures were combined with stirring. Triethylamine (0.5 mL) was added to the reaction mixture, which was stirred for 24 h. The product was collected by filtration, washed twice with DMF (25ml), and finally dried.

### Characterization of MOF-199

Fourier transform infrared (FT-IR) spectra (Fig 1a) shows absorption in the waves numbers 3440, 1642 and 1446cm<sup>-1</sup> that are related to water molecule, carbonyl group of Benzenetricarboxylic acid and double bonds of benzene in order. It also shows the incorporation of Cu metal inside the framework organic and a uniform distribution of the particles throughout the framework, confirmed by EDX analysis (Fig 1b). X-ray powder diffraction patterns (Fig 1c) shows the presence of The main diffraction peak in the 2θ=11. Scanning electron microscopy (Fig 1d) shows existence crystales in nano-size.

### Experimental procedures and characterization data



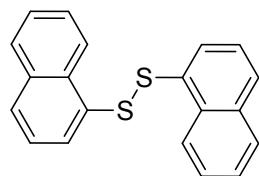
#### Diphenyl disulfide (Table 2, Entry1)<sup>2,3</sup>

The product was obtained (ethyl acetate/ *n*-hexane, 1:20) as a White solid in 98% yield. mp = 53-56 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.24–7.36 (m, 6H), 7.54 (m, 4H) .

<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 137.0, 129.1, 127.5, 127.2.

Elemental analysis calculated for C<sub>12</sub>H<sub>10</sub>S<sub>2</sub>: % = C, 66.01; H, 4.62; S, 29.37. Found: C, 66.49; H, 4.47; S, 29.96. GC-Mass (EI): *m/z* = 218.0 [M<sup>+</sup>].



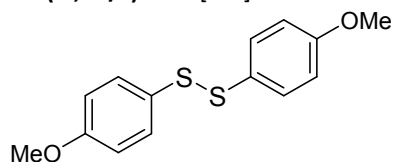
#### Bis (1-naphthalene) disulfide (Table 2, Entry 6)<sup>2,3</sup>

The product was obtained (ethyl acetate/ *n*-hexane, 1:20) as a yellow solid in 75% yield. mp = 92-99 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.41-8.50(d, 2H, *J*=8.4Hz), 7.82-7.95(m, 4H), 7.34-7.7(m, 8H).

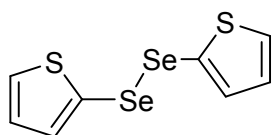
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 134.1, 132.6, 130.3, 129.9, 128.6, 128.0, 126.8, 126.6, 125.9, 125.1.

MS (EI, *m/z*): 318 [M<sup>+</sup>].



**Bis(4-methoxyphenyl) disulfide (Table 2, Entry11)<sup>3,4</sup>**

The product was obtained (ethyl acetate/ *n*-hexane, 1:5) as a White solid in 84% yield. mp = 41–43 °C . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 3.82 (s, 6H), 6.87 (d, *J* = 8.4 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 55.3, 114.7, 127.4, 132.7, 159.0.

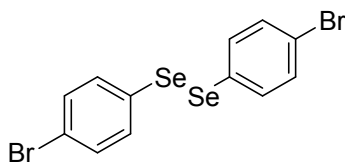


**Bis(thiophen-2-yl) Disulfide (Table 2, Entry 24)<sup>5</sup>**

The product was obtained (ethyl acetate/ *n*-hexane, 1:10) as a Dark orange oil in 88% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz): δ = 7.03 (m, 2H), 7.26 (m, 2H), 7.5 (m, 2H).

MS (EI, m/z): 326 [M<sup>+</sup>].



**Bis(4-mathoxyphenyl) disulfide (Table 2, Entry 31)<sup>5,6</sup>**

The product was obtained (ethyl acetate/ *n*-hexane, 1:5) as a Dark orange oil in 92% yield..

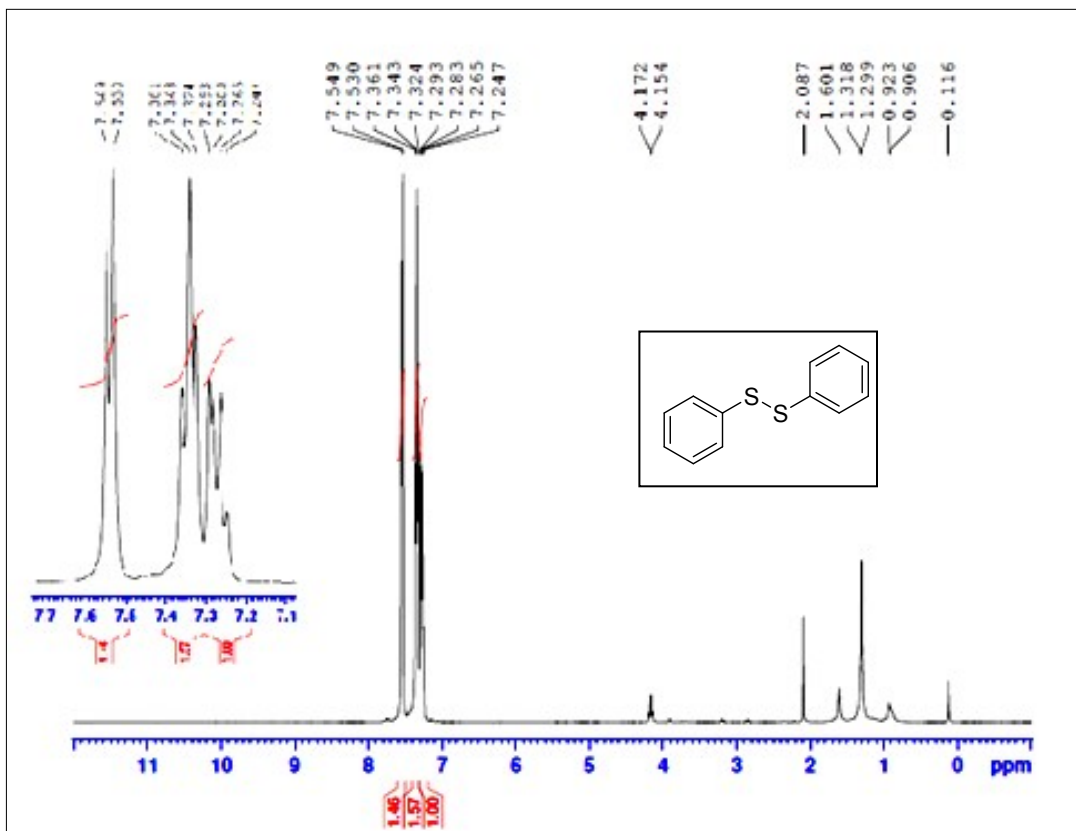
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 7.27-7.47 (m, 8H).

MS (EI, m/z): 470 [M<sup>+</sup>].

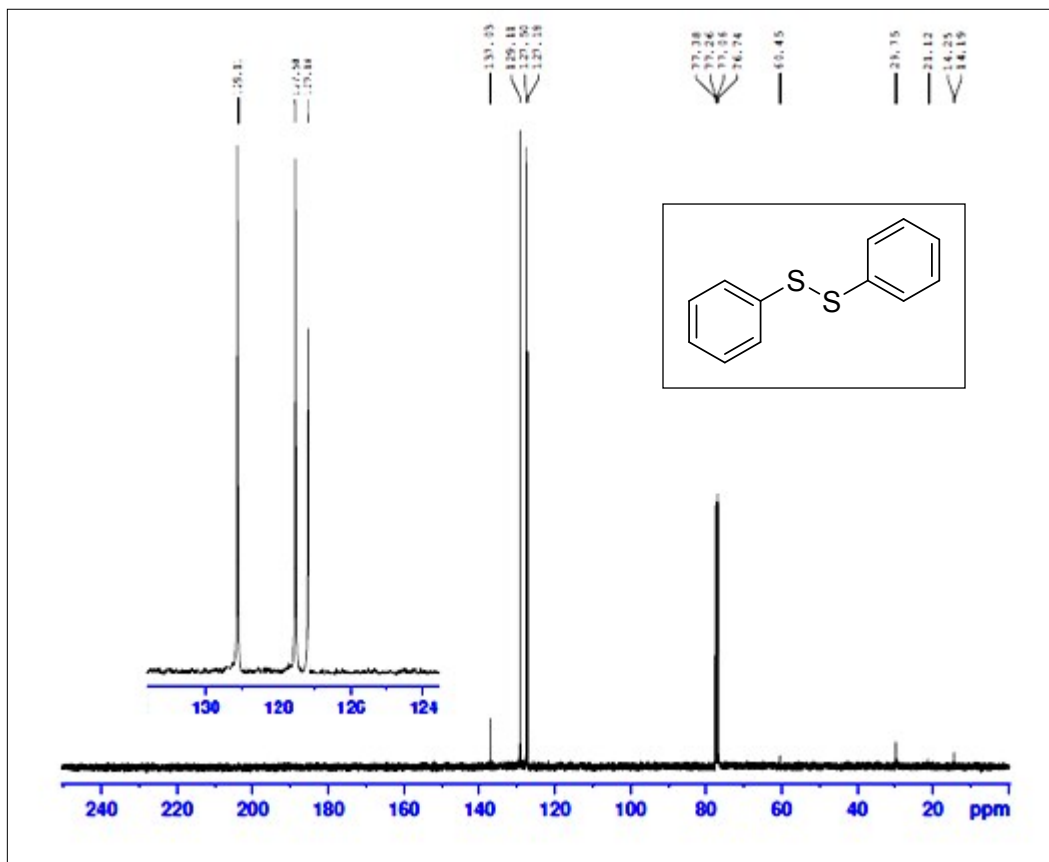
### 3. References

1. (a) E. J. Lenardo, R. G. Lara, M. S. Silva, R. G. Jacob, G Perin, *Tetrahedron Lett.* 2007, **48**, 7668; (b) D. J. Tranchemontagne, J. R. Hunt, O. M. Yaghi, *Tetrahedron.* 2008, **64**, 8553.
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3. M. Soleiman-Beigi, F. Mohammadi, *Synlett.* 2015, **26**, 911.
4. Z. Li, F. Ke, H. Deng, H. Xu, H. Xianga and X. Zhou, *Org. Biomol. Chem*, 2013, **11**, 2943.
5. M. Z. Kassaee, E. Motamedi, B. Movassagh and S. Poursadeghi, *Synthesis*, 2013, **45**, 2337.
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#### 4. Ms, $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for the products

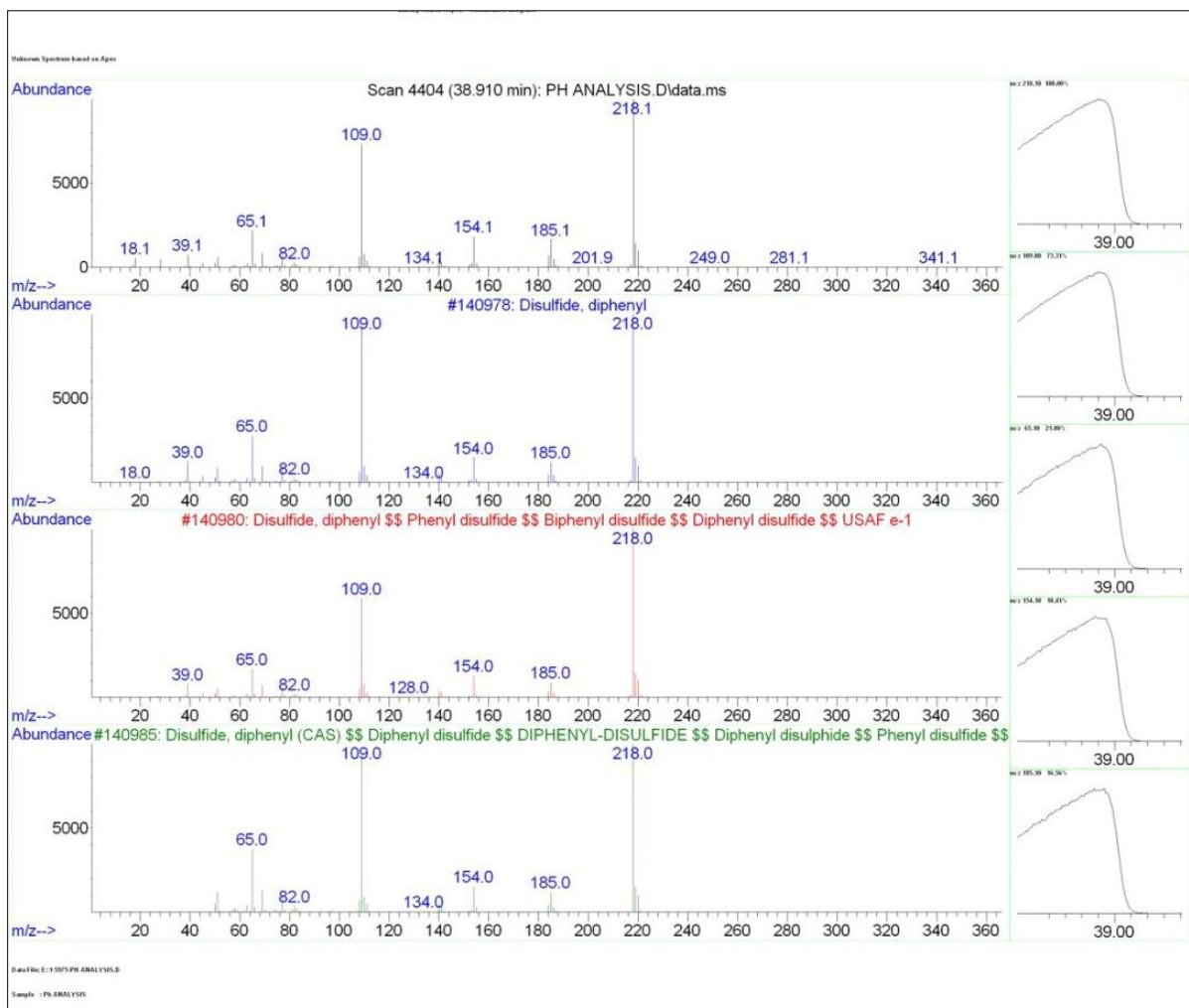
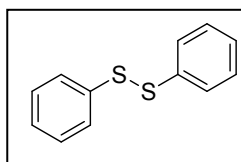


$^1\text{H}$  NMR spectrum of diphenyl disulfide (Table 2, Entry1)

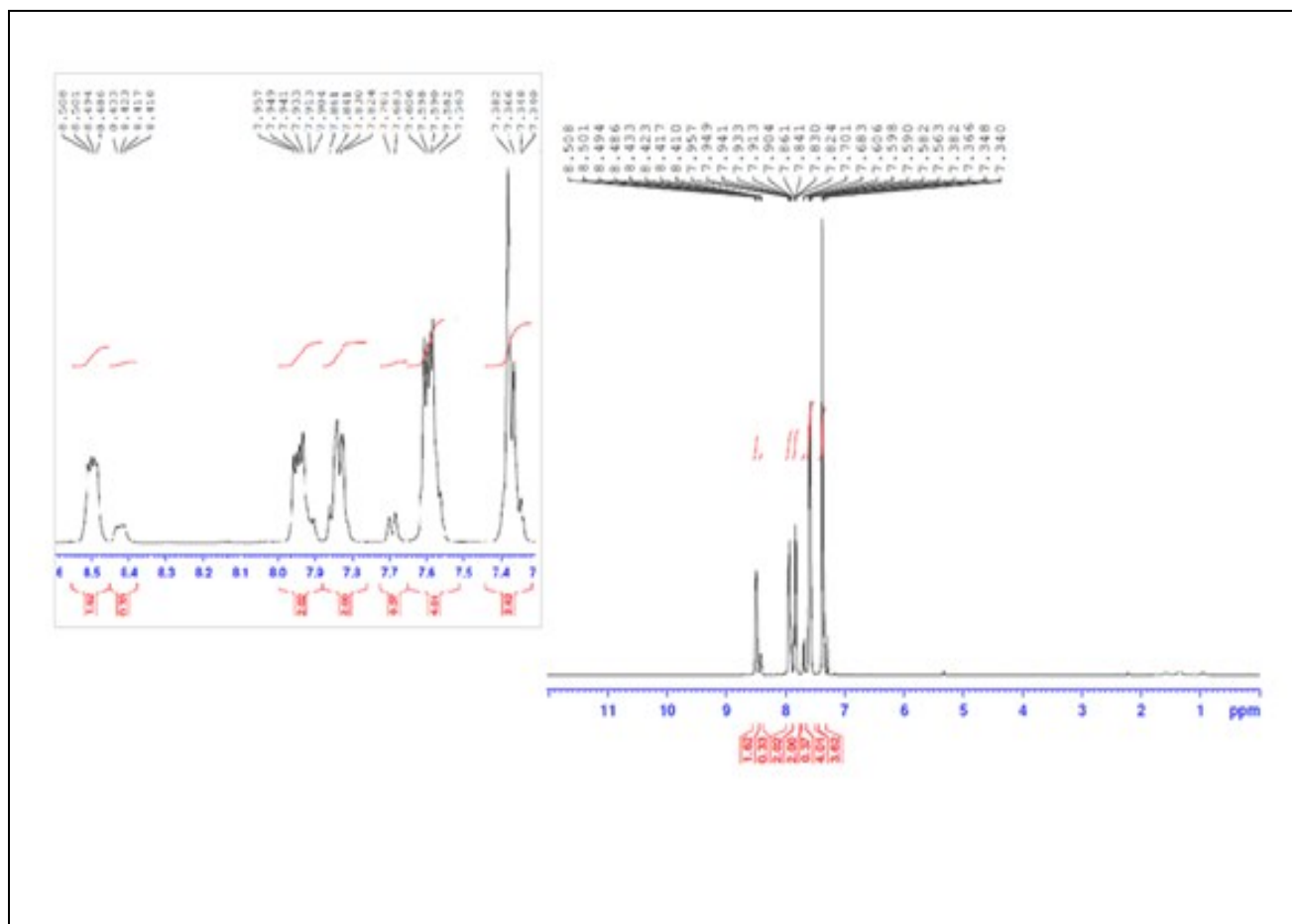
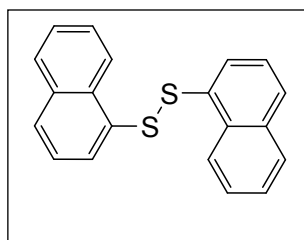


$^{13}\text{C}$  NMR spectrum of diphenyl disulfide (Table 2, Entry1)

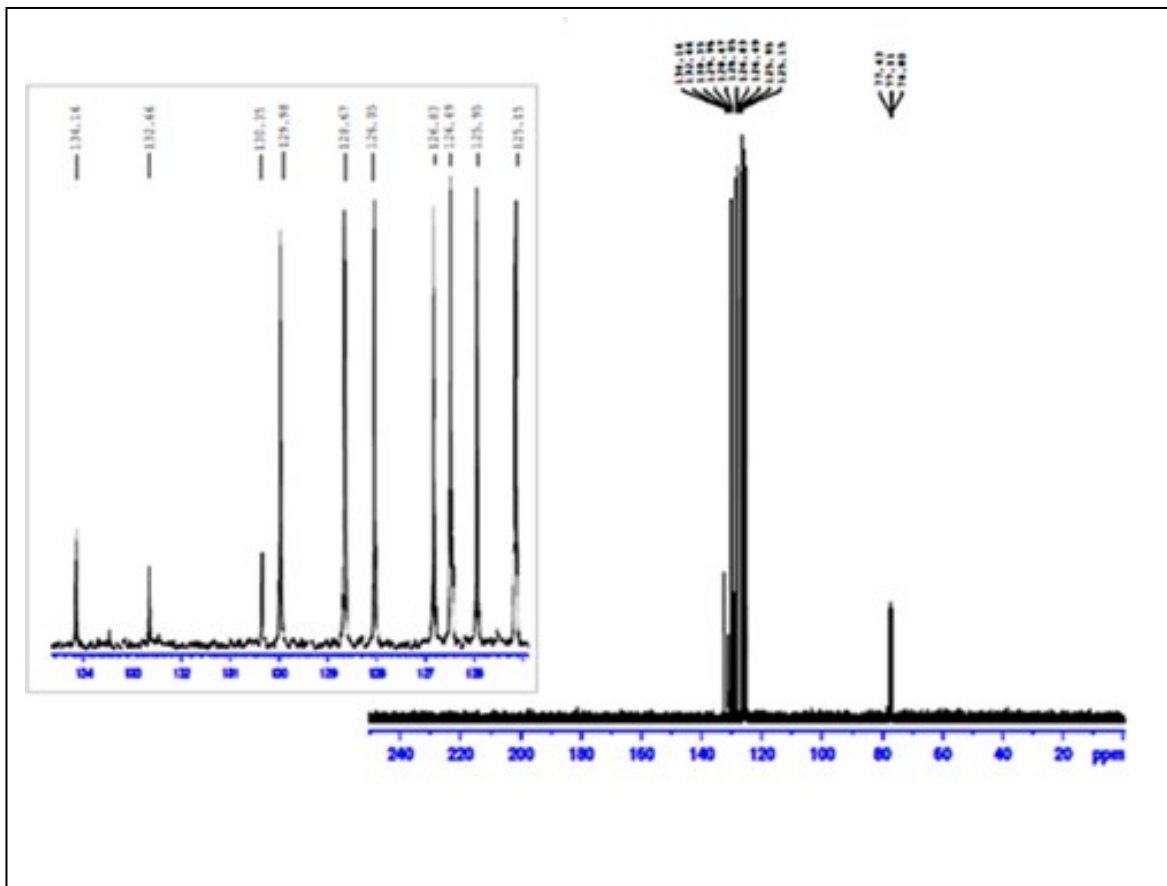
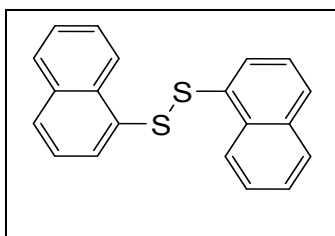




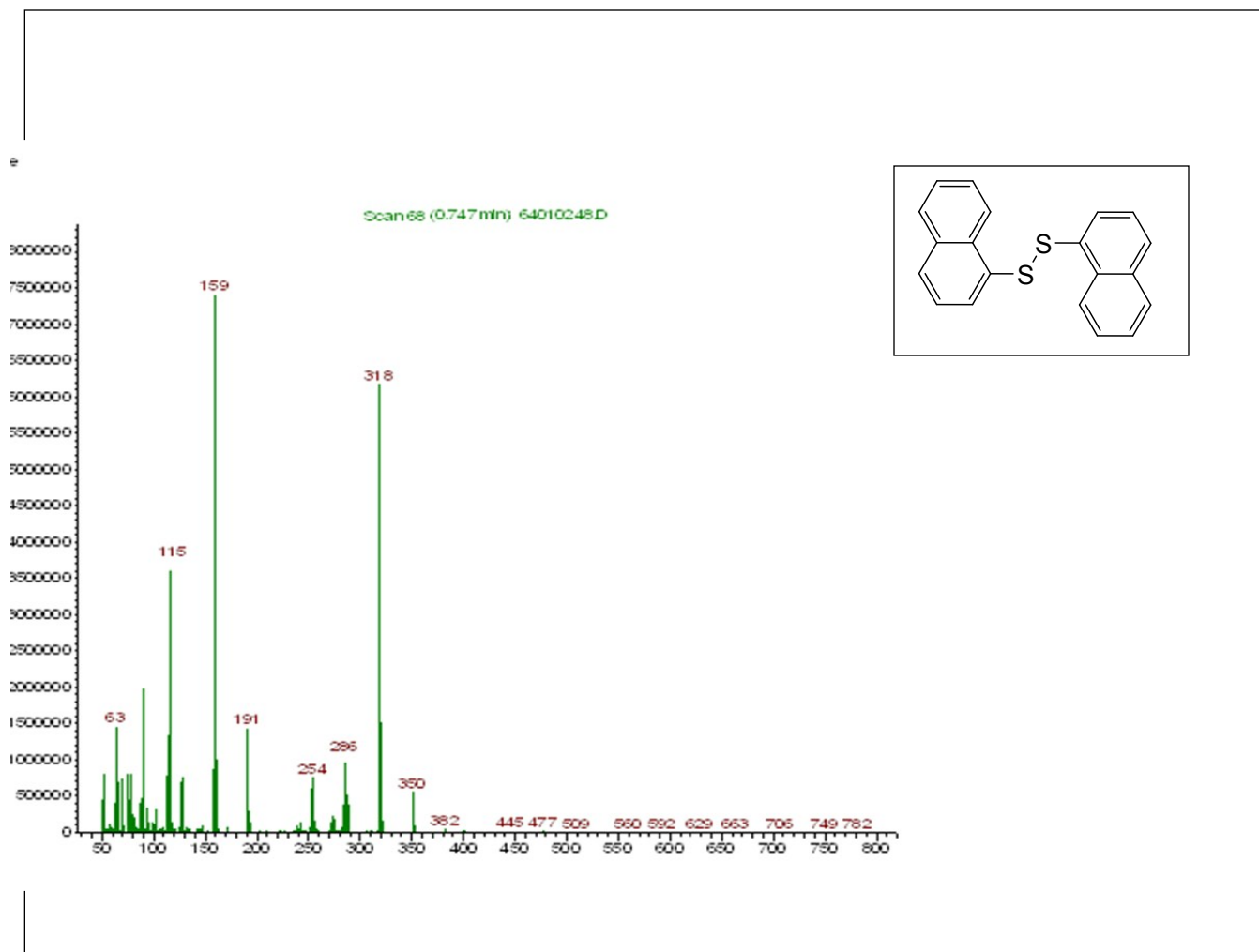
GC-Mass spectrum of diphenyl disulfide (Table 2, Entry1)



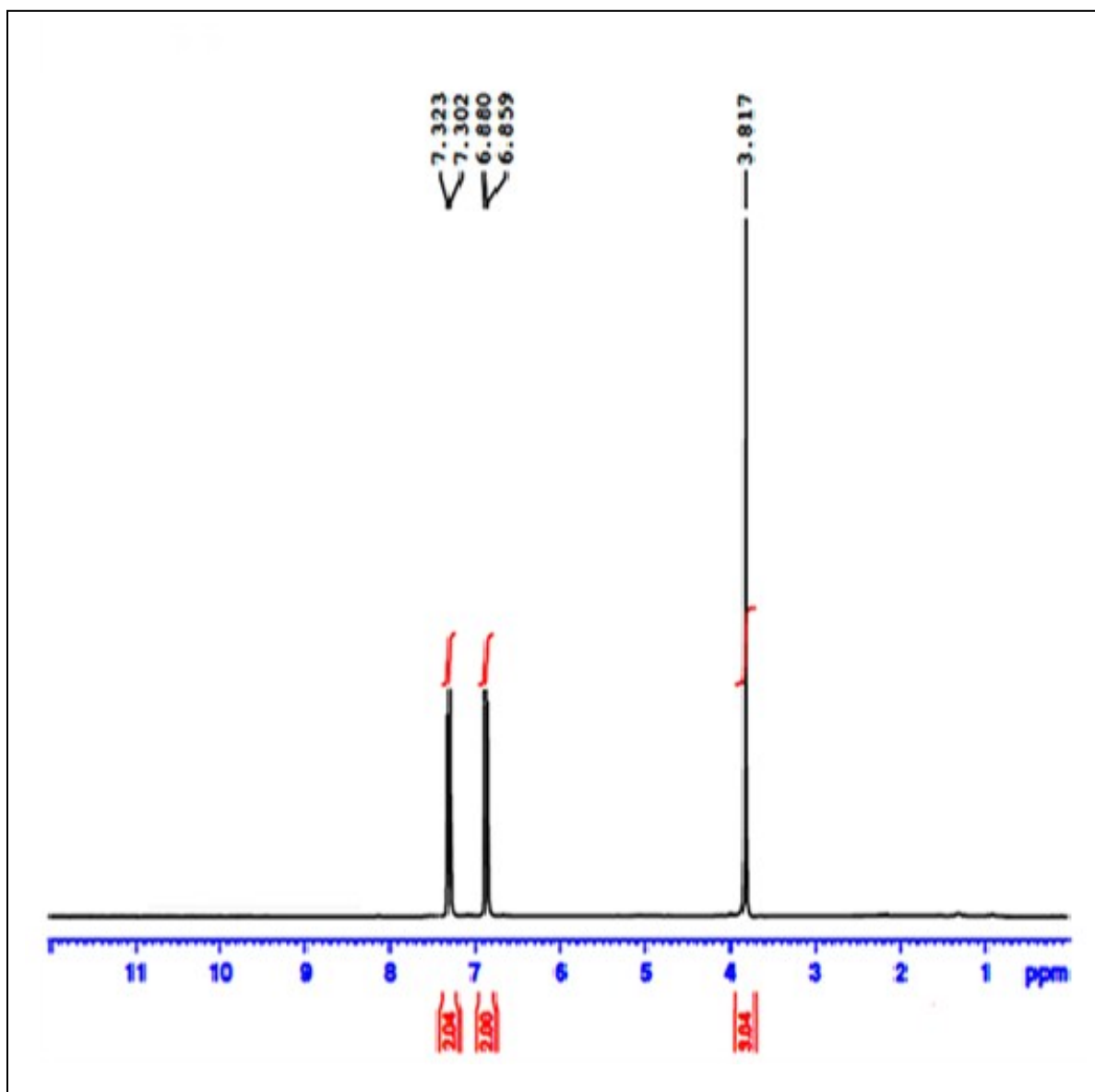
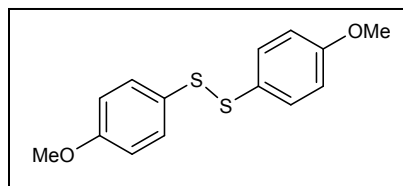
$^1\text{H}$  NMR spectrum of Bis (1-naphthalene) disulfide (Table 2, Entry 6)



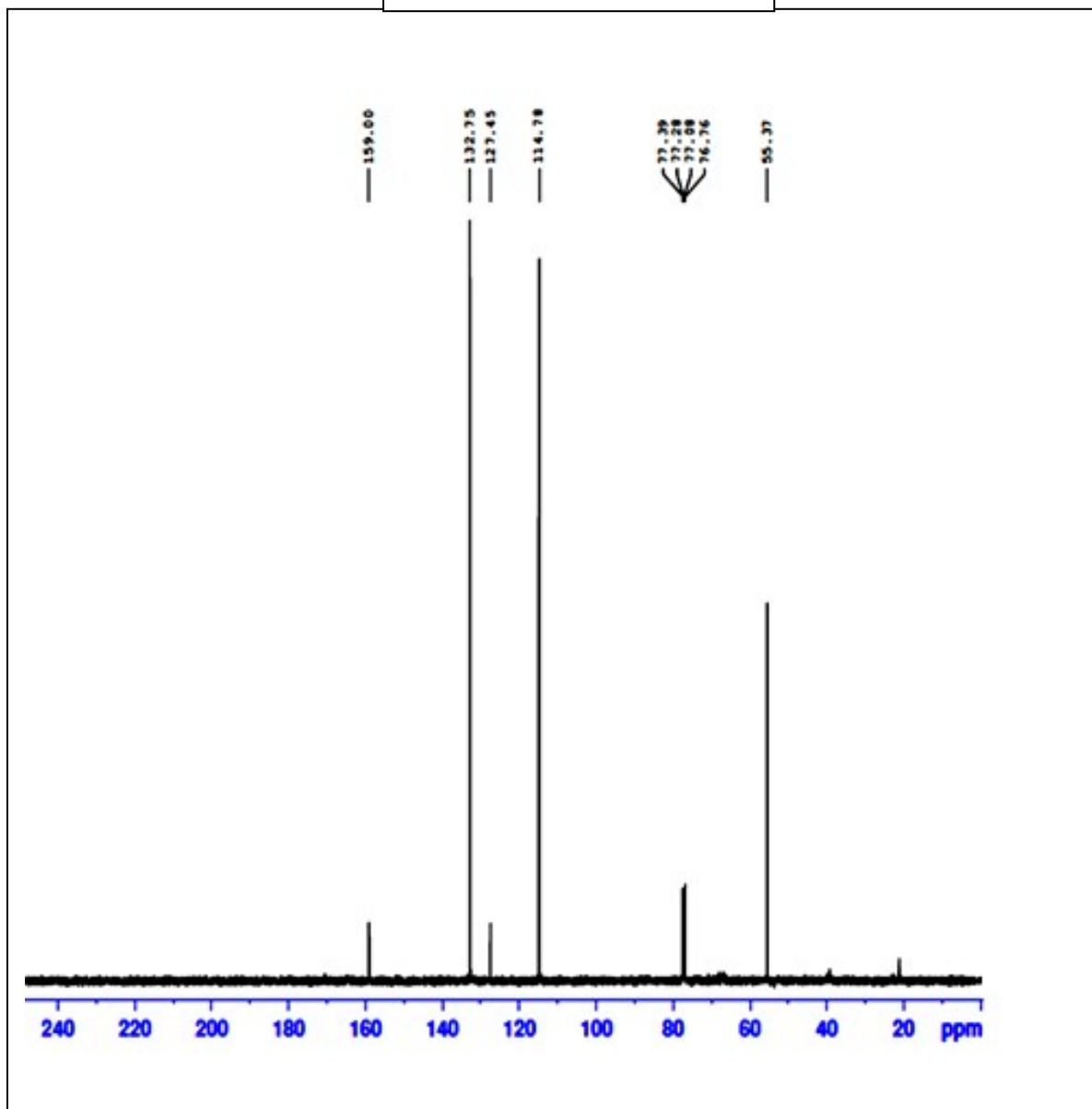
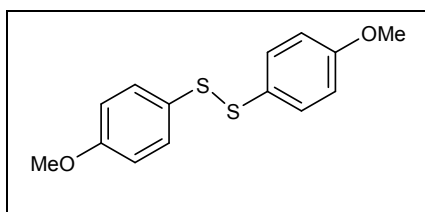
$^{13}\text{C}$  NMR spectrum of Bis (1-naphthalene) disulfide (Table 2, Entry 6)



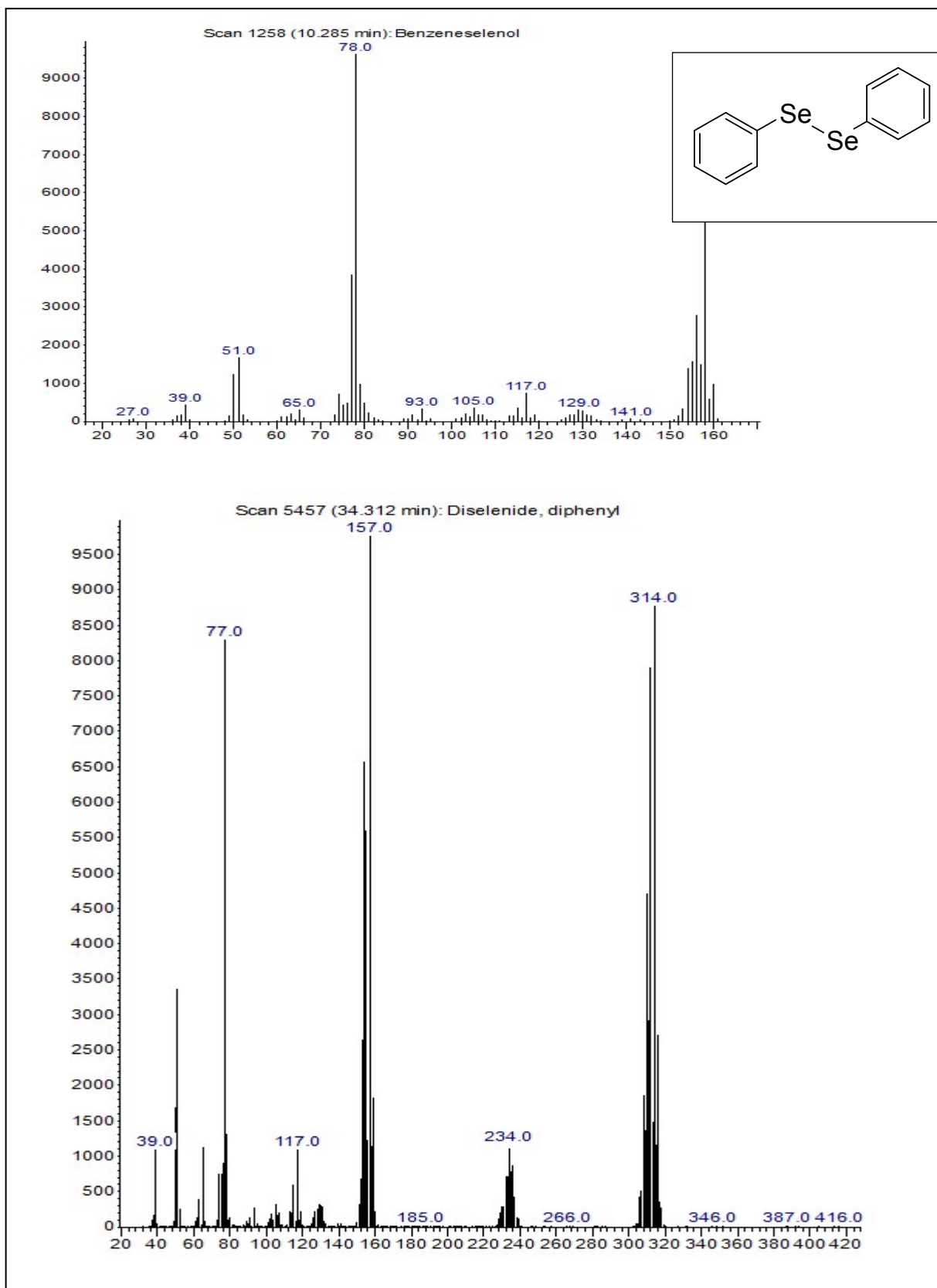
Mass spectrum of Bis (1-naphthalene) disulfide (Table 2, entry 6)



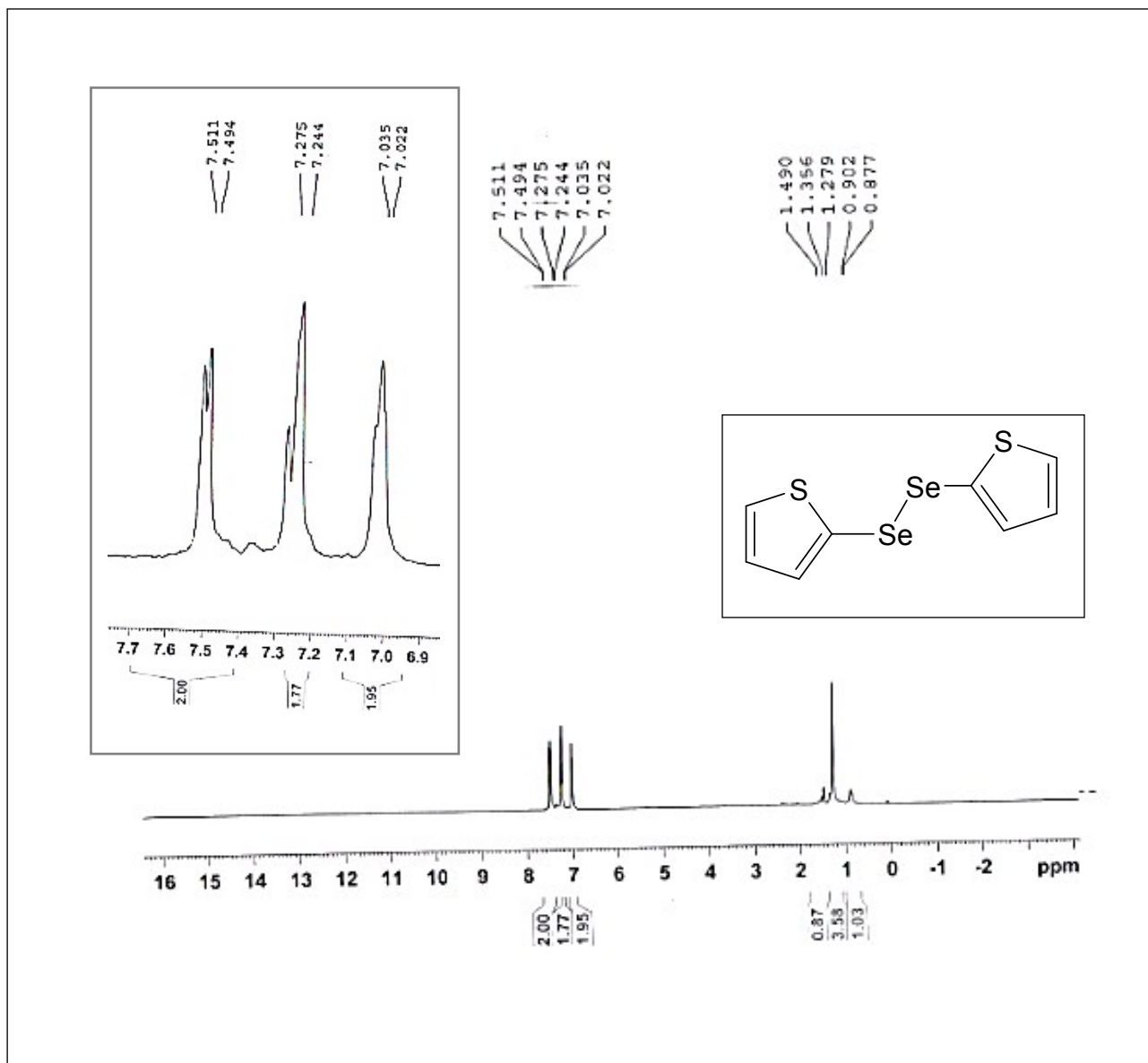
<sup>1</sup>H NMR spectrum of Bis(4-methoxyphenyl) disulfide (Table 2, Entry11)



<sup>13</sup>C NMR spectrum of Bis(4-methoxyphenyl) disulfide (Table 2, Entry11)

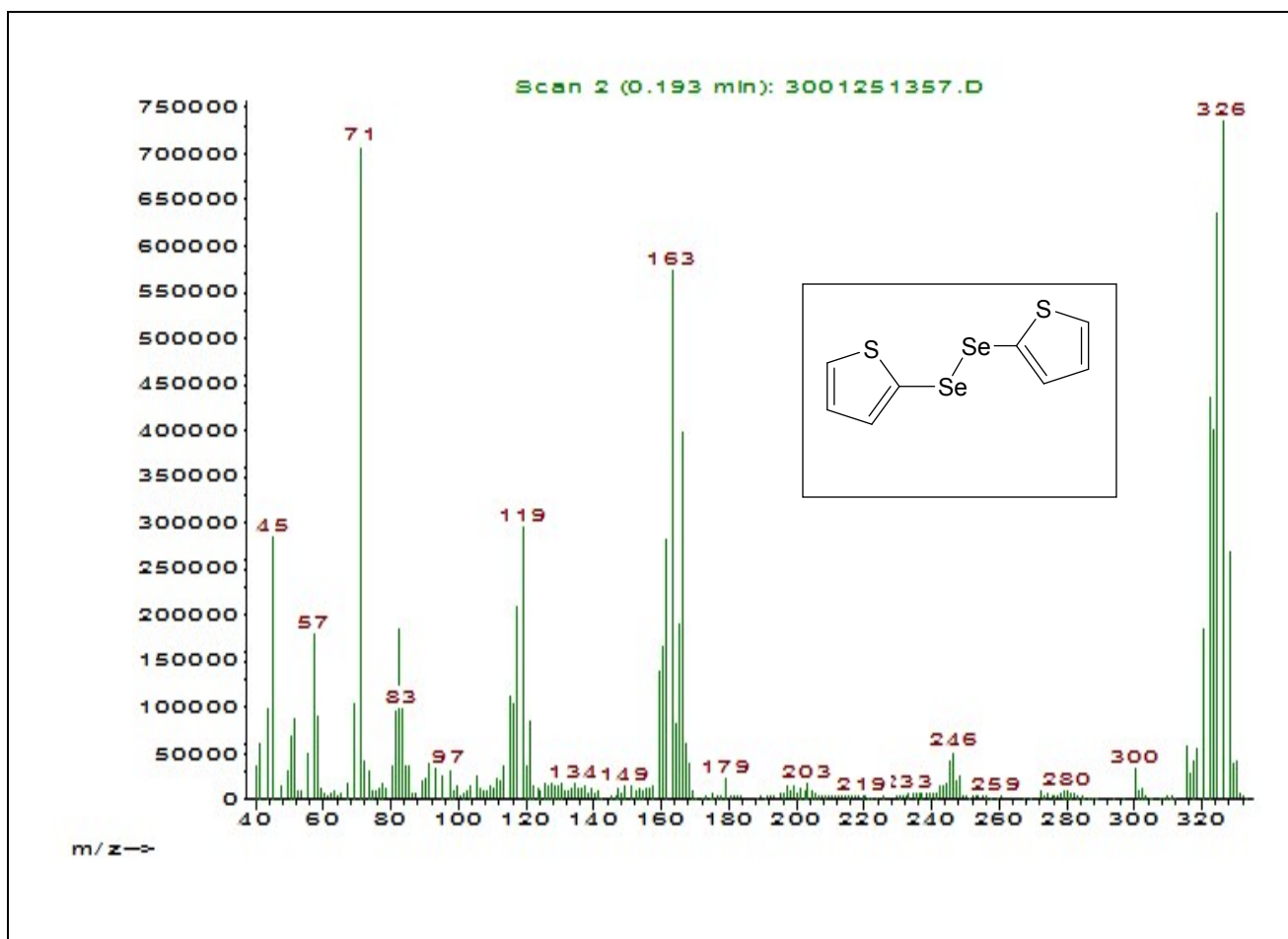


GC-Mass spectrum of diphenyl diselenide (Table 2, Entry17)

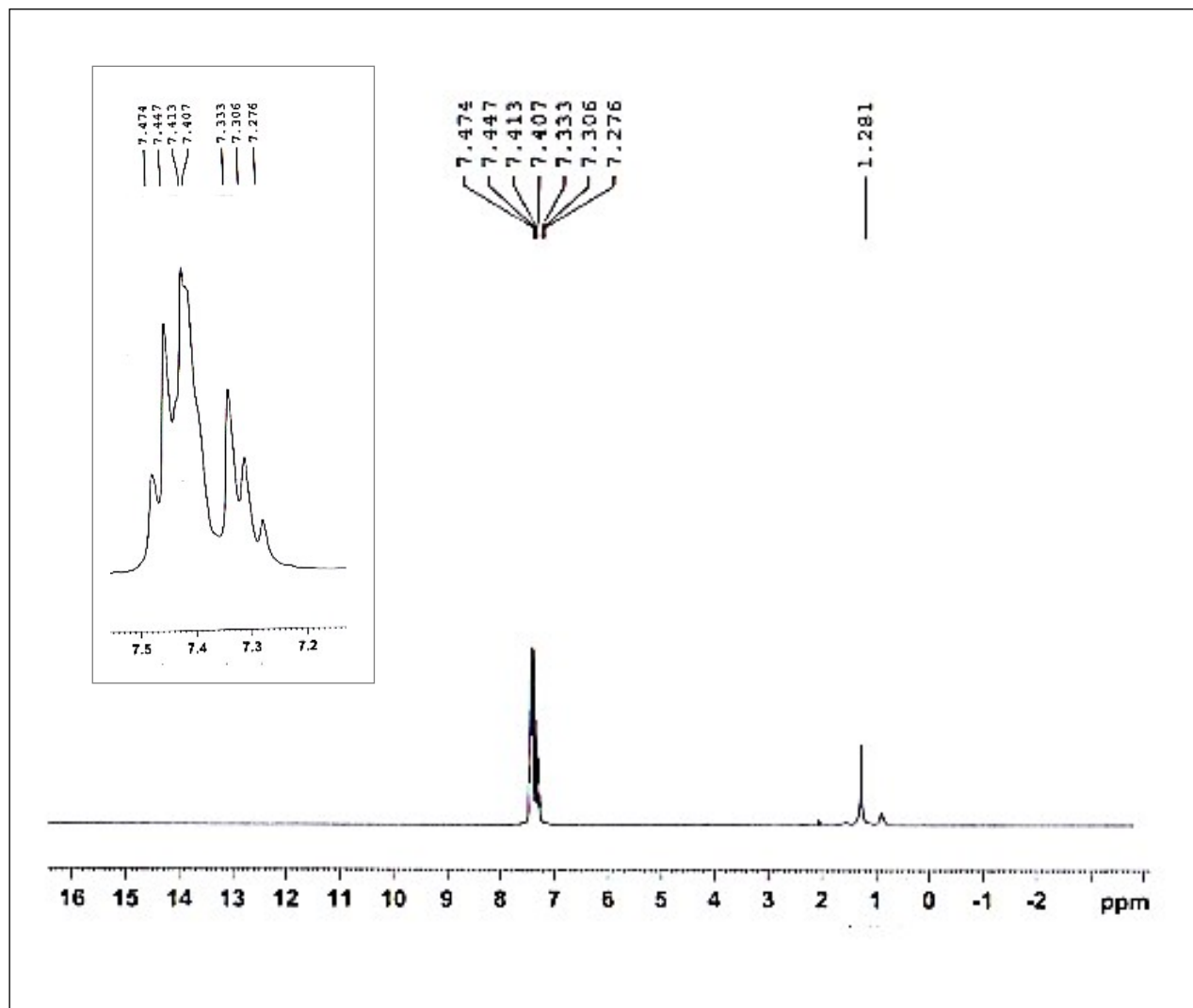
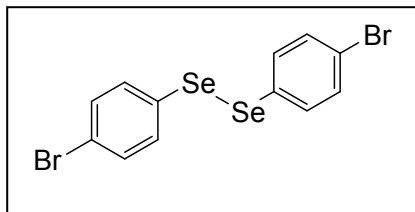


<sup>1</sup>H NMR spectrum of Bis(thiophen-2-yl) Diselenide (Table 2, Entry 24)

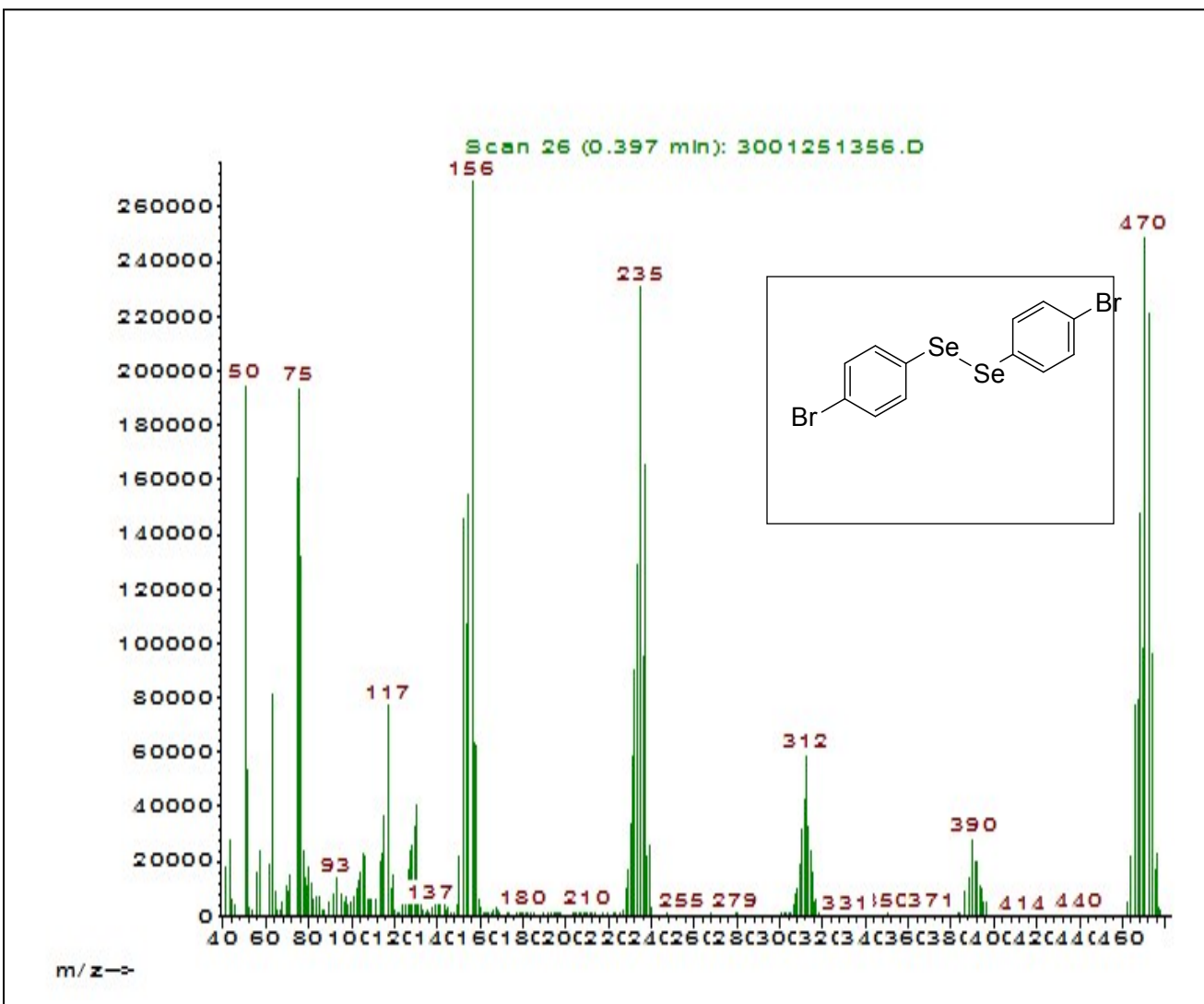




Mass spectrum of Bis(thiophen-2-yl) Diselenide (Table 2, entry 24)



<sup>1</sup>H NMR spectrum of Bis(4-bromophenyl) Diselenide (Table 2, entry 31)



Mass spectrum of Bis(4-bromophenyl) Diselenide (Table 2, entry 31)