



Title	Nickel phosphide nanoalloy catalyst for the selective deoxygenation of sulfoxides to sulfides under ambient H <sub>2</sub> pressure
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# Supporting Information

## Nickel phosphide nanoalloy catalyst for the selective deoxygenation of sulfoxides to sulfides under ambient H<sub>2</sub> pressure

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### References

#### 1. General experimental details

NiCl<sub>2</sub>·6H<sub>2</sub>O, Nb<sub>2</sub>O<sub>5</sub> and 4Å molecular sieves (4Å M.S.) were purchased from Wako Pure Chemical Industries (Japan). CoCl<sub>2</sub>·6H<sub>2</sub>O and Fe(CO)<sub>5</sub> were purchased from Nacalai Tesque, Inc. (Japan), and Kanto Chemical Co., Inc., respectively. TiO<sub>2</sub> (JRC-TIO-15) and ZrO<sub>2</sub> (JRC-ZrO-6) were obtained from the Catalysis Society of Japan, respectively, as reference catalysts. SiO<sub>2</sub> (Q-6) was purchased from Fuji Silysia Chemicals (Japan). Al<sub>2</sub>O<sub>3</sub> (AKP-G015) was obtained from Sumitomo Chemical Co. Ltd. (Japan). Hydrotalcite (HT, AD-500NS) was obtained from Tomita Pharmaceutical Co. Ltd. (Japan). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed using an SII Nano Technology SPS7800 instrument. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM-ESC400 spectrometer.

#### 2. Catalyst preparations

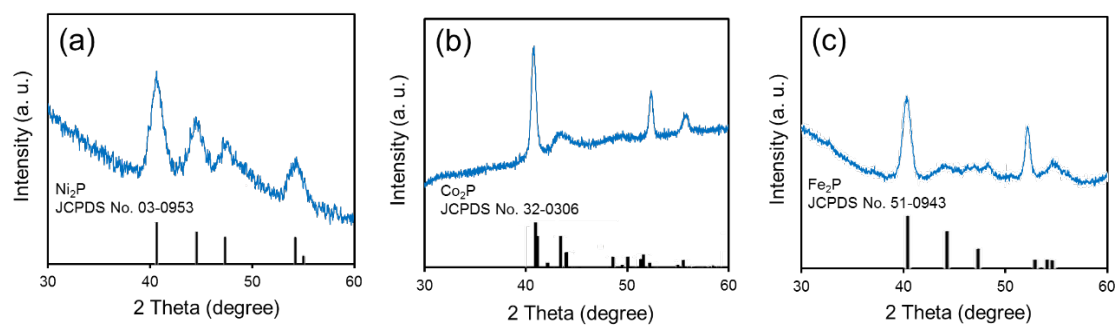
##### Synthesis of nano-Co<sub>2</sub>P

In a typical synthesis, CoCl<sub>2</sub>·6H<sub>2</sub>O (1.0 mmol) was combined with hexadecylamine (10 mmol) and triphenyl phosphite (10 mmol) in a Schlenk flask. The mixture was stirred at 150 °C and then the temperature increased to 290 °C with stirring, affording a black colloidal solution. The rest of the procedure was the same as that used to prepare nano-Ni<sub>2</sub>P.

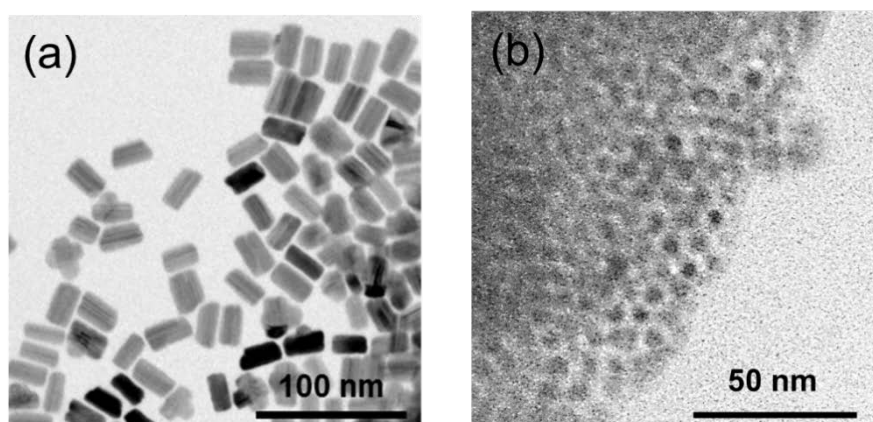
##### Synthesis of nano-Fe<sub>2</sub>P

In a typical synthesis, hexadecylamine (10 mmol) was combined with 1-octadecene (10 mL) and triphenyl phosphite (10 mmol) in a Schlenk flask. The mixture was stirred at 150 °C and then Fe(CO)<sub>5</sub> dissolved in 1-octadecene (5 mol/L) was added. The temperature increased to 300 °C with stirring, affording a black colloidal solution. The rest of the procedure was the same as that used to prepare nano-Ni<sub>2</sub>P.

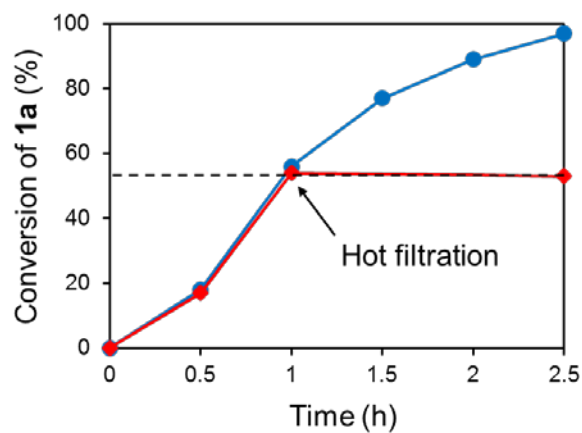
### 3. Characterization of metal phosphide nanoalloy catalysts



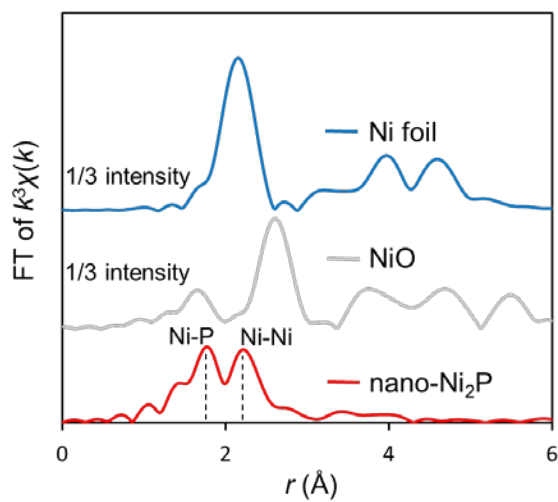
**Fig. S1** XRD patterns of (a) nano- $\text{Ni}_2\text{P}$ , (b) nano- $\text{Co}_2\text{P}$ , and (c) nano- $\text{Fe}_2\text{P}$ .



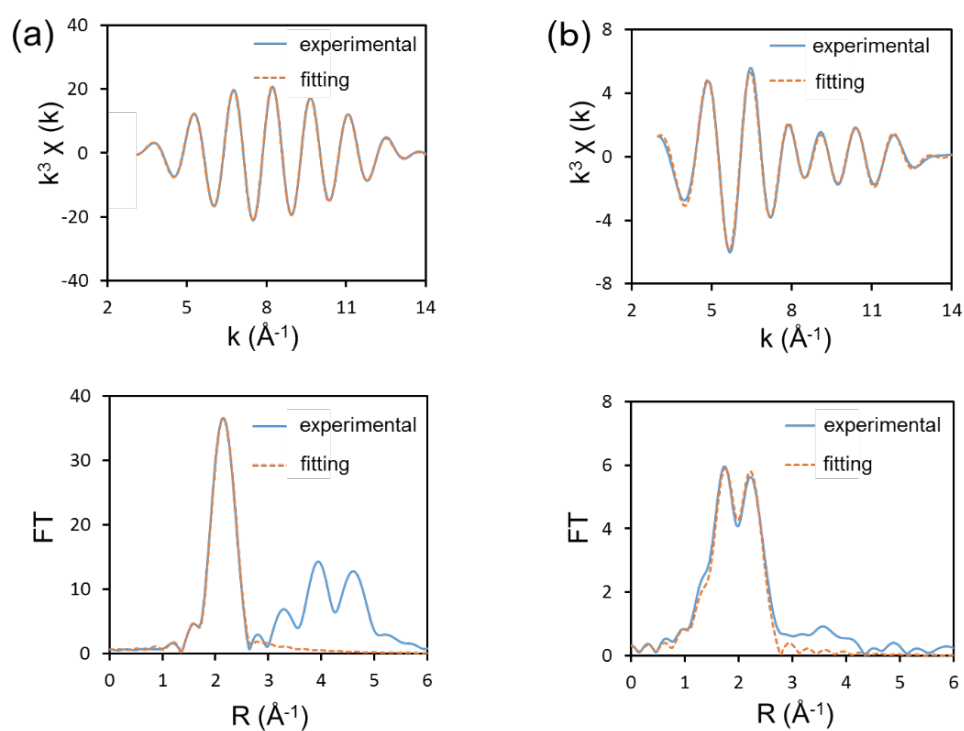
**Fig. S2** TEM images of (a) nano- $\text{Co}_2\text{P}$ , and (b) nano- $\text{Fe}_2\text{P}$ .



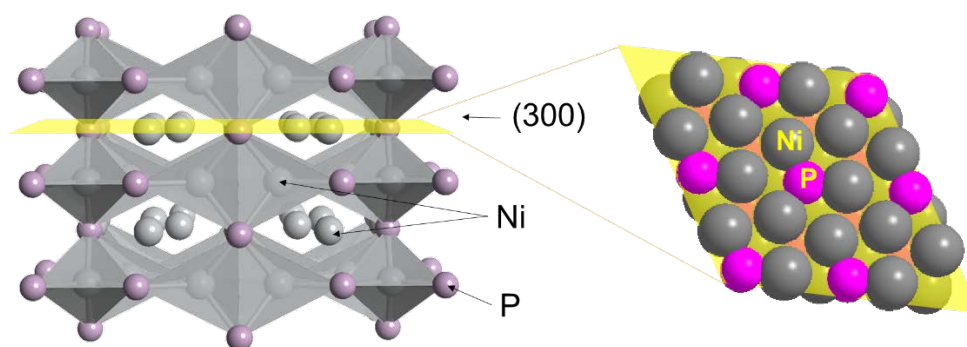
**Fig. S3** Time course of the deoxygenation of **1a** using nano-Ni<sub>2</sub>P/TiO<sub>2</sub>. (●) Without catalyst filtration and (◆) with catalyst removal by hot filtration after 1 h. Reaction conditions: nano-Ni<sub>2</sub>P/TiO<sub>2</sub> (5 mol% Ni), **1a** (0.5 mmol), toluene (3 mL), H<sub>2</sub> (10 bar), and 120 °C.



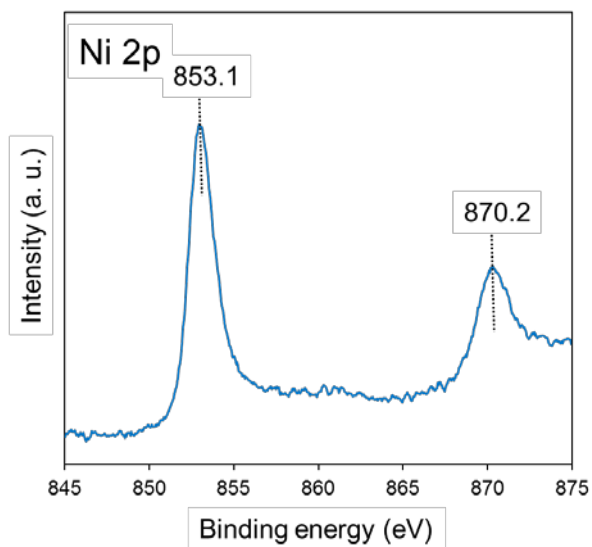
**Fig. S4** Fourier transform  $k^3$ -weighted EXAFS of Ni foil, NiO, and nano-Ni<sub>2</sub>P.



**Fig. S5** EXAFS fitting curves in k-space (upper panel) and R-space (lower panel). (a) Ni foil and (b) nano-Ni<sub>2</sub>P.



**Fig. S6** Crystal structure of Ni<sub>2</sub>P with a (300) plane.



**Fig. S7** Ni 2p XPS spectrum of nano-Ni<sub>2</sub>P.

**Table S1** Elemental analysis of fresh and used nano-Ni<sub>2</sub>P/TiO<sub>2</sub> by ICP-AES

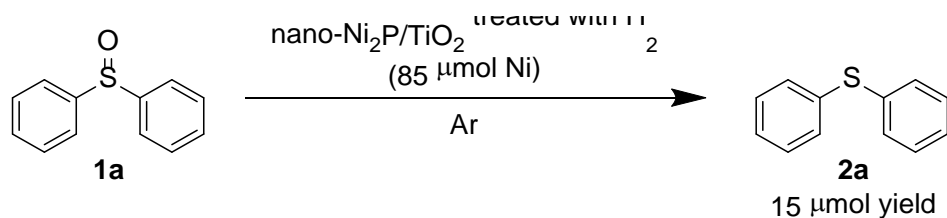
	Ni (wt.%)
Fresh nano-Ni <sub>2</sub> P/TiO <sub>2</sub>	0.99
Used nano-Ni <sub>2</sub> P/TiO <sub>2</sub>	0.98

**Table S2** Curve fitting of Ni *K*-edge EXAFS for Ni foil and nano-Ni<sub>2</sub>P

Sample	Shell	CN <sup>a</sup>	<i>r</i> (Å) <sup>b</sup>	DW <sup>c</sup>	R factor (%)
Ni foil	Ni–Ni	11 ± 0.1	2.48 ± 0.01	0.007 ± 0.002	2.4
nano-Ni <sub>2</sub> P	Ni–P	2.1 ± 0.2	2.21 ± 0.03	0.008 ± 0.004	7.5
	Ni–Ni	2.2 ± 0.2	2.58 ± 0.03	0.008 ± 0.004	
bulk Ni <sub>2</sub> P (ideal)	Ni–P <sup>d</sup>	2.2	2.24	—	—
	Ni–Ni <sup>e</sup>	6.7	2.65	—	

<sup>a</sup> Coordination number. <sup>b</sup> Bond distance. <sup>c</sup> Debye–Waller factor. <sup>d</sup> Average of Ni–P whose bond lengths are less than 2.3 Å. <sup>e</sup> Average of Ni–Ni whose bond lengths are less than 2.7 Å.

#### 4. Control experiment



**Scheme S1** Deoxygenation of **1a** using nano-Ni<sub>2</sub>P/TiO<sub>2</sub> treated with H<sub>2</sub>. Reaction conditions: nano-Ni<sub>2</sub>P/TiO<sub>2</sub> (0.85  $\mu\text{mol}$  Ni) treated, **1a** (0.5 mmol), toluene (3 mL), Ar (1 bar), 120 °C, and 1 h. Before the reaction, nano-Ni<sub>2</sub>P/TiO<sub>2</sub> was treated with H<sub>2</sub> (10 bar) at 120 °C for 1 h.

#### 5. Comparison of activity between nano-Ni<sub>2</sub>P and reported non-noble metal catalysts

**Table S3** Deoxygenation of sulfides using H<sub>2</sub> catalyzed by non-noble metal catalysts

Catalyst	Conditions	Substrate	Yield of sulfide [%]	TON	Ref.
nano-Ni <sub>2</sub> P/TiO <sub>2</sub>	120 °C, 10 bar, 12 h in toluene	Diphenyl sulfoxide	92	92	<i>This work</i>
nano-Ni <sub>2</sub> P/TiO <sub>2</sub>	160 °C, 1 bar, 12 h in toluene	Diphenyl sulfoxide	97	19	<i>This work</i>
Co–Mo/NC-400	50 °C, 10 bar, 10 h in methanol	Diphenyl sulfoxide	100	--	<i>S1</i>
MoO <sub>2</sub> Cl <sub>2</sub>	120 °C, 50 bar, 20 h in toluene	Methyl phenyl sulfoxide	100	10	<i>S2</i>



## 6. Characterization data of products

All the reaction products were characterized by GC-MS and NMR. The retention times (GC-MS) and chemical shifts ( $^1\text{H}$  and  $^{13}\text{C}$ ) of the products were in agreement with those of authentic samples or previously reported values.

### Dimethyl sulfide (S3) (2a)

CAS registry No. [139-66-2].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.35 - 7.20$  (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 135.8, 131.0, 129.1, 127.0$ .

### Bis(4-methylphenyl) sulfide (S3) (2b)

CAS registry No. [620-94-0].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.22$  (d,  $J = 7.6$  Hz, 4H), 7.08 (d,  $J = 8.4$  Hz, 4H), 2.31 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 136.9, 132.9, 131.0, 129.9, 21.0$ .

### Benzyl phenyl sulfide (S4) (2c)

CAS registry No. [831-91-4].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.31 - 7.21$  (m, 10H), 4.11 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 137.4, 136.3, 129.8, 128.8, 128.4, 127.1, 126.3, 39.0$ .

### Thioanisole (S3) (2d)

CAS registry No. [100-68-5].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.26 - 7.25$  (m, 4H), 7.13 – 7.09 (m, 1H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 138.4, 128.7, 126.6, 125.0, 15.8$ .

### (4-Methylthio)toluene (S3) (2e)

CAS registry No. [623-13-2].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.18$  (d,  $J = 8.8$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 2.45 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 135.0$ , 134.7, 129.6, 127.3, 20.9, 16.5.

**Dibutyl sulfide (S3) (2f)**

CAS registry No. [544-40-1].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 2.51$  (t,  $J = 7.6$  Hz, 4H), 1.63 – 1.53 (m, 4H), 1.46 – 1.38 (m, 4H), 0.92 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 31.8$ , 22.0, 13.6.

**Dodecyl Methyl Sulfide (S5) (2g)**

CAS registry No. [3698-89-3].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 2.49$  (t,  $J = 7.4$  Hz, 2H), 2.09 (s, 3H), 1.63 – 1.56 (m, 2H), 1.39 – 1.26 (m, 18H), 0.88 (t,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 34.3$ , 31.9, 29.6, 29.5, 29.3, 29.2, 28.8, 22.7, 15.5, 14.1.

**Tetrahydrothiophen (S3) (2h)**

CAS registry No. [110-01-0].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 2.84$  – 2.81 (m, 4H), 1.95 – 1.92 (m 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 31.7$ , 30.9.

**Bis(methylthio)methane (S6) (2i)**

CAS registry No. [1618-26-4].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 3.56$  (s, 2H), 2.09 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 40.1$ , 14.3.

**4,4'-Dichloro diphenyl sulfide (S3) (2j)**

CAS registry No. [5181-10-2].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.29$  – 7.22 (m, 8H);  $^{13}\text{C}$  NMR

(100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 134.0, 133.5, 132.3, 129.5.

**4-Bromothioanisole (S7) (2k)**

CAS registry No. [104-95-0]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.12 (d,  $J$  = 8.4 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 137.7, 131.8, 128.2, 118.6, 16.0.

**4-Methoxythioanisole (S3) (2l)**

CAS registry No. [1879-16-9]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.29 – 7.25 (m, 2H), 6.87 – 6.83 (m, 2H), 3.79 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 158.2, 130.3, 128.8, 114.6, 55.4, 18.1.

**4-(Methylthio)benzaldehyde (S8) (2m)**

CAS registry No. [3446-89-7]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 9.92 (s, 1H), 7.78 – 7.75 (m, 2H), 7.34 – 7.31 (m, 2H), 2.53 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 191.1, 147.9, 133.0, 129.9, 125.2, 14.7.

**4'-(Methylthio)acetophenone (S5) (2n)**

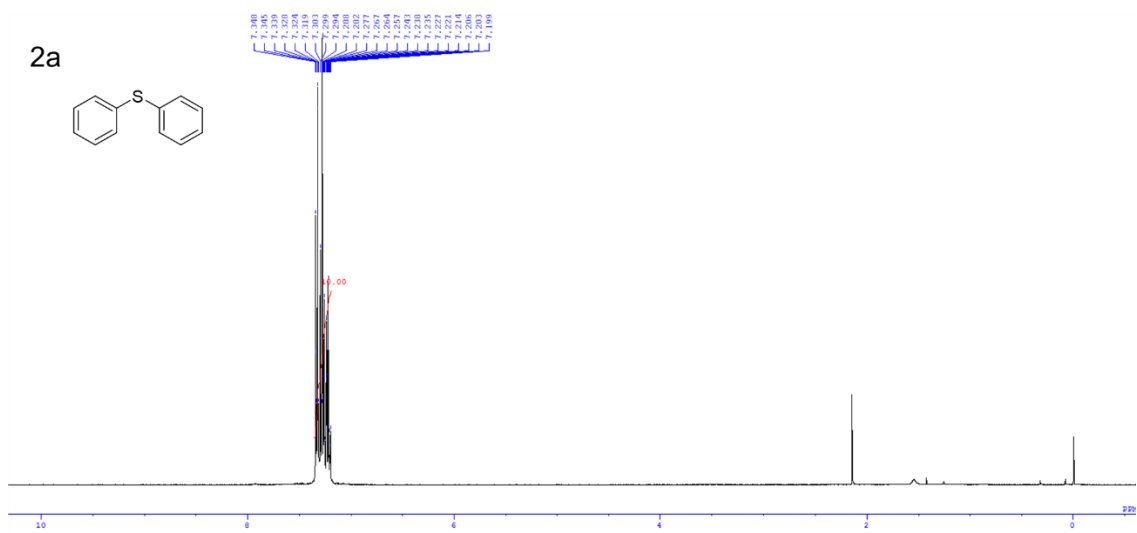
CAS registry No. [1778-09-2]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.87 (d,  $J$  = 8.8 Hz, 2H), 7.27 (d,  $J$  = 8.0 Hz, 2H), 2.57 (s, 3H), 2.52 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 197.2, 145.9, 133.6, 128.7, 125.0, 26.4, 14.8.

**Allyl phenyl sulfide (S9) (2o)**

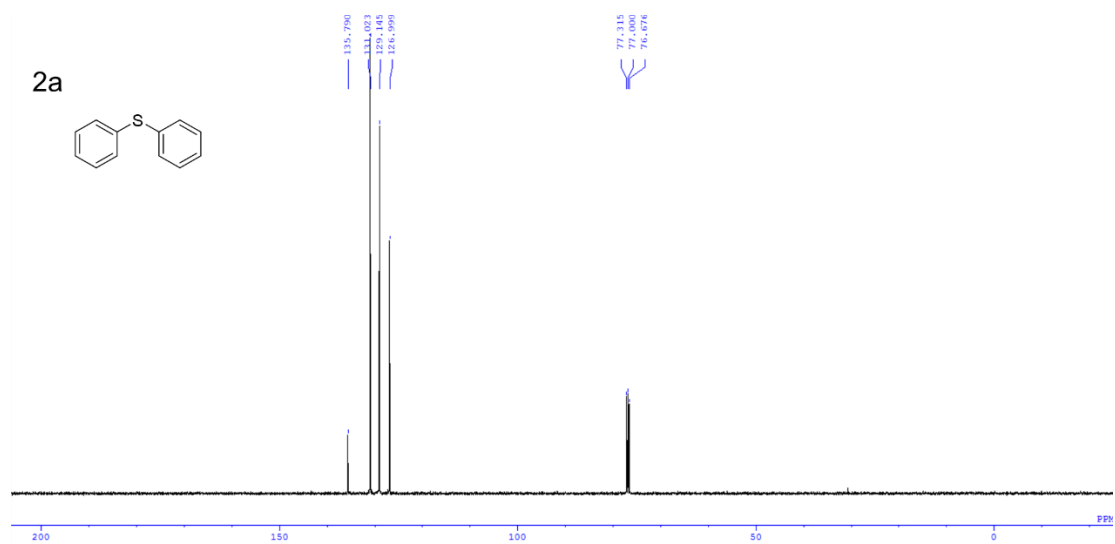
CAS registry No. [5296-64-0]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.32 – 7.30 (m, 2H), 7.26 –

7.22 (m, 2H), 7.14 (t,  $J = 7.4$  Hz, 1H), 5.90 – 5.80 (m, 1H), 5.13 – 5.02 (m, 2H), 3.51 (d,  $J = 6.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 135.9, 133.6, 129.8, 128.8, 126.2, 117.6, 37.2$ .

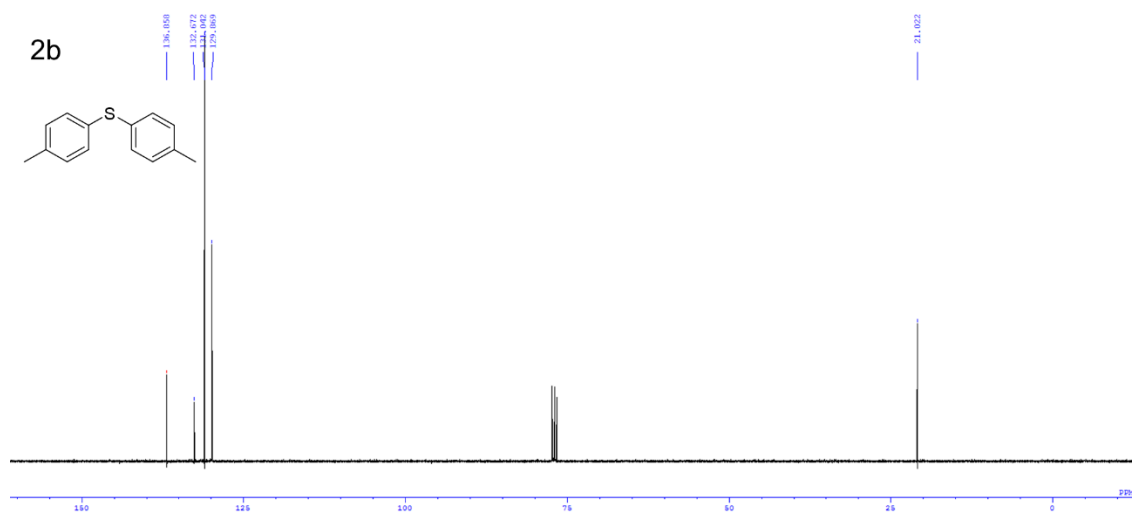
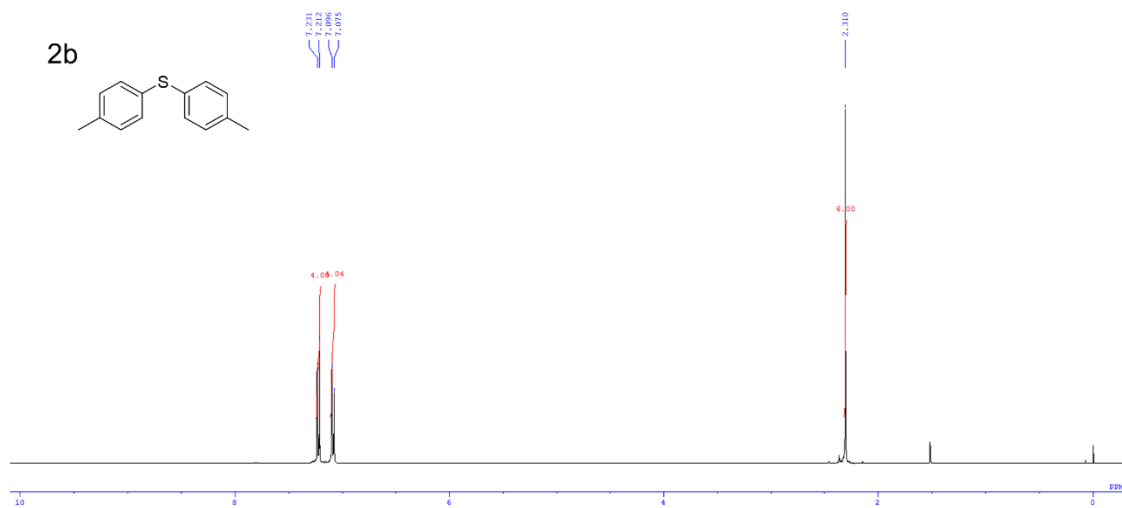
## 7. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of products

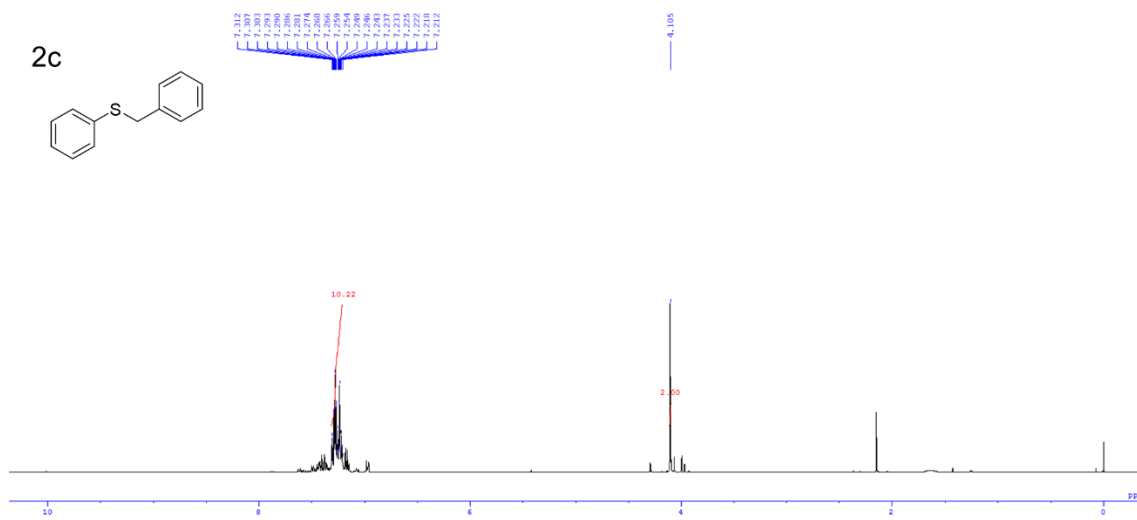


$^1\text{H}$  NMR spectrum of **2a**

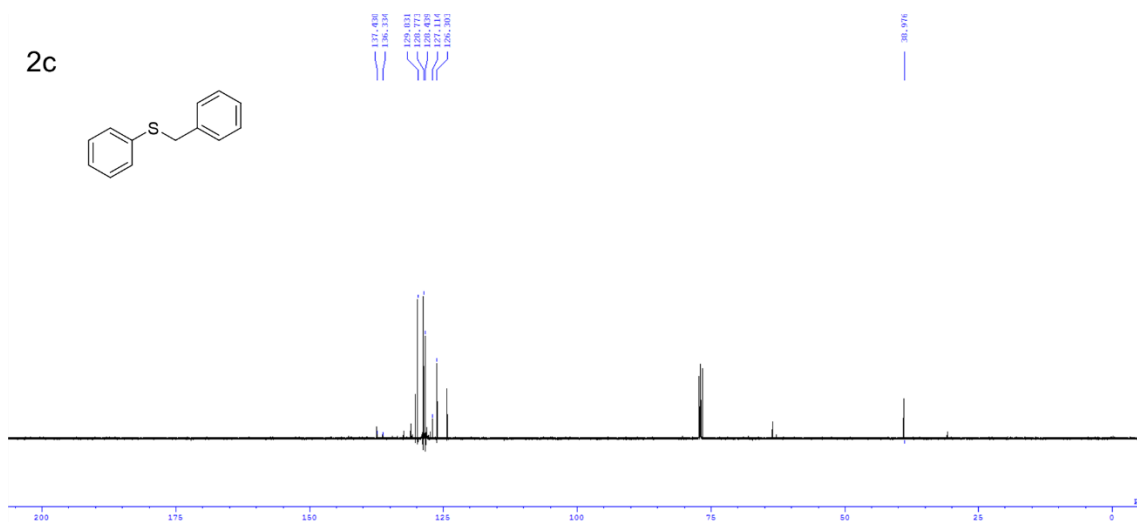


$^{13}\text{C}$  NMR spectrum of **2a**

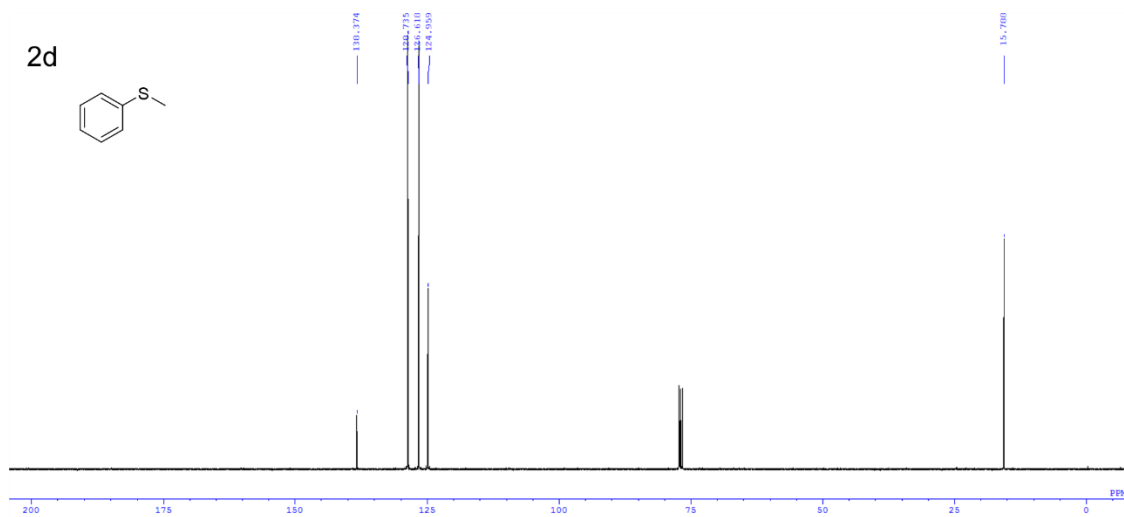
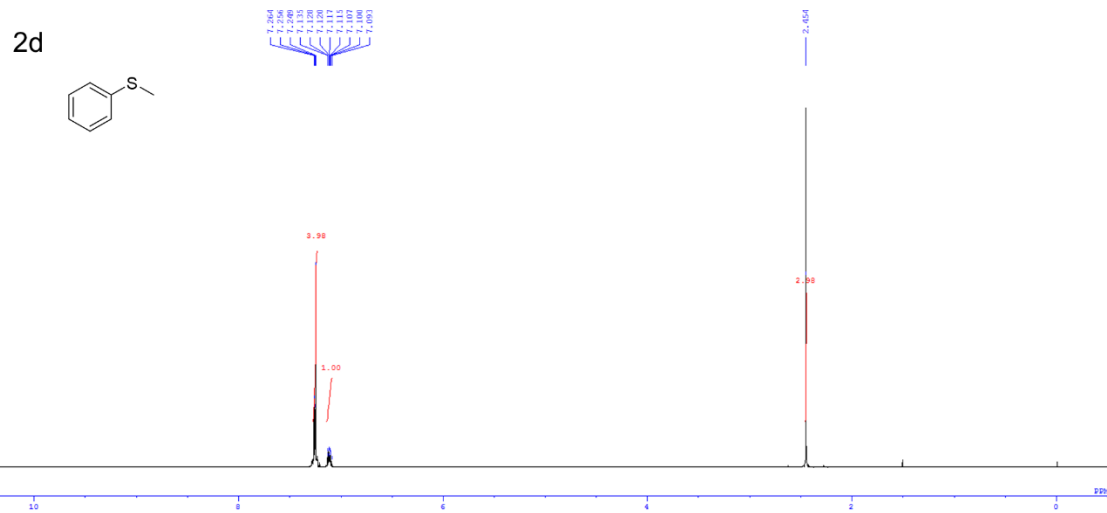




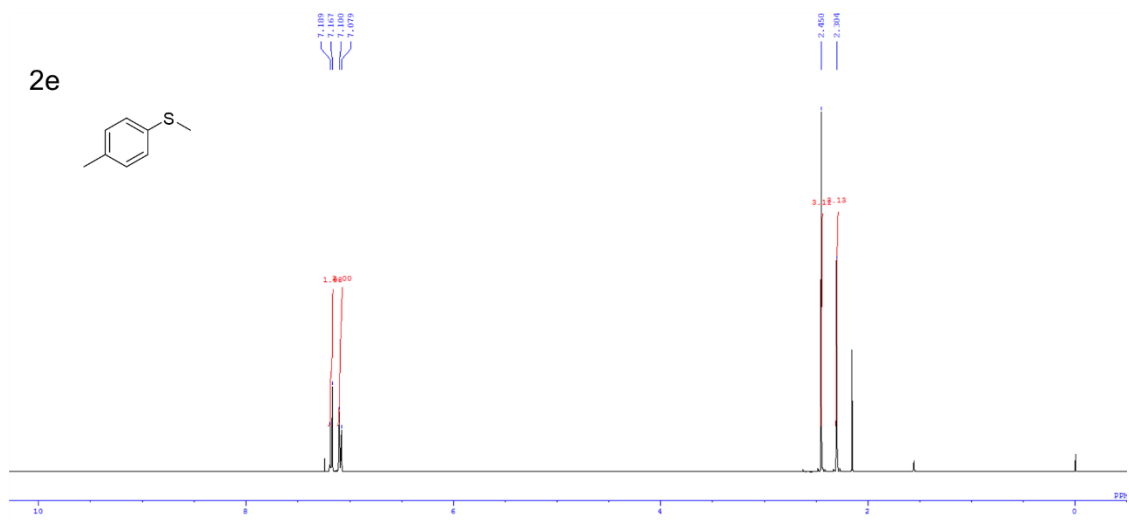
<sup>1</sup>H NMR spectrum of **2c**



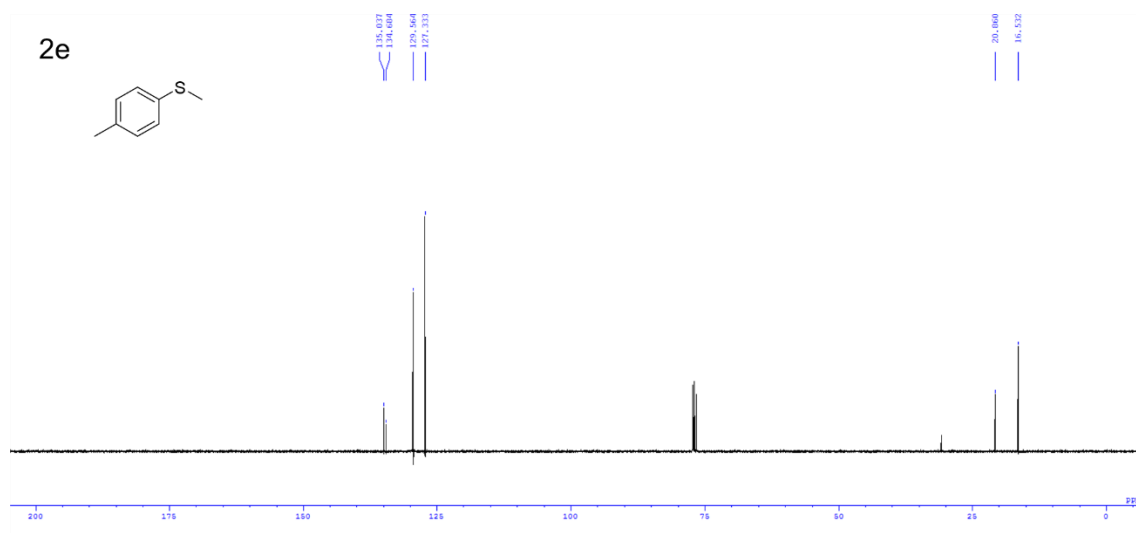
<sup>13</sup>C NMR spectrum of **2c**





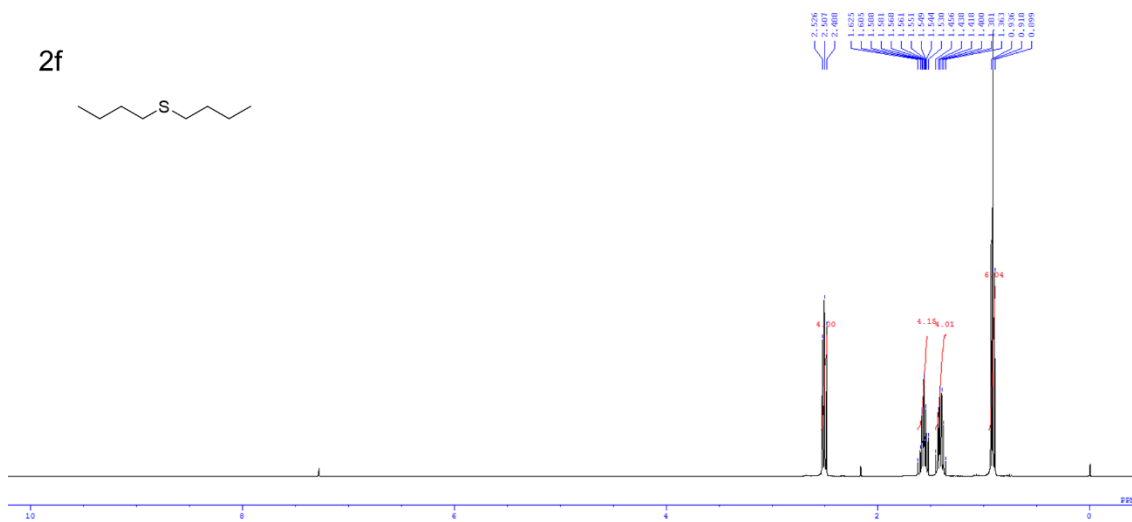
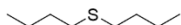


<sup>1</sup>H NMR spectrum of **2e**



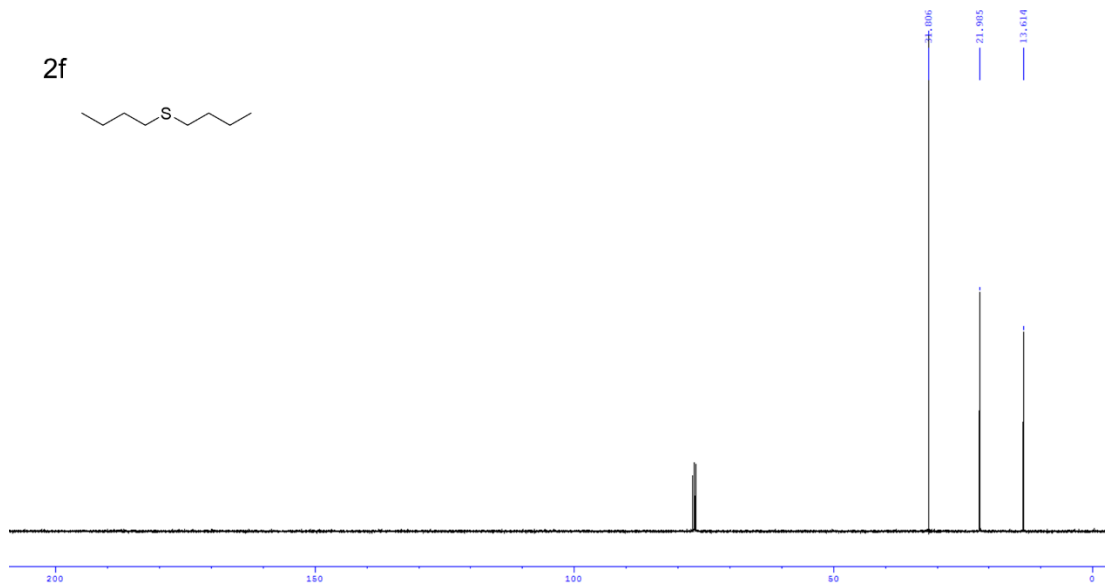
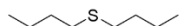
<sup>13</sup>C NMR spectrum of **2e**

2f

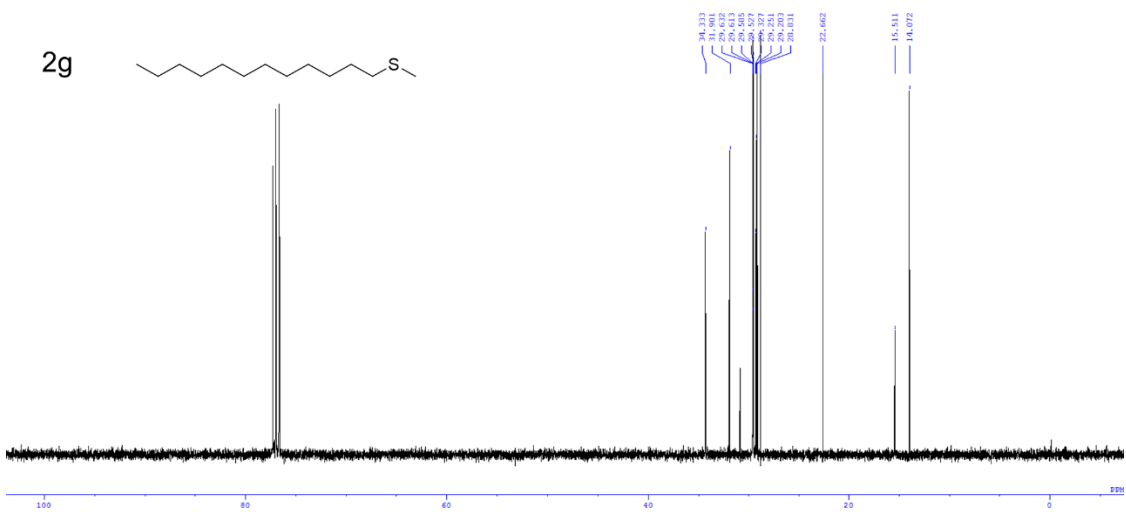
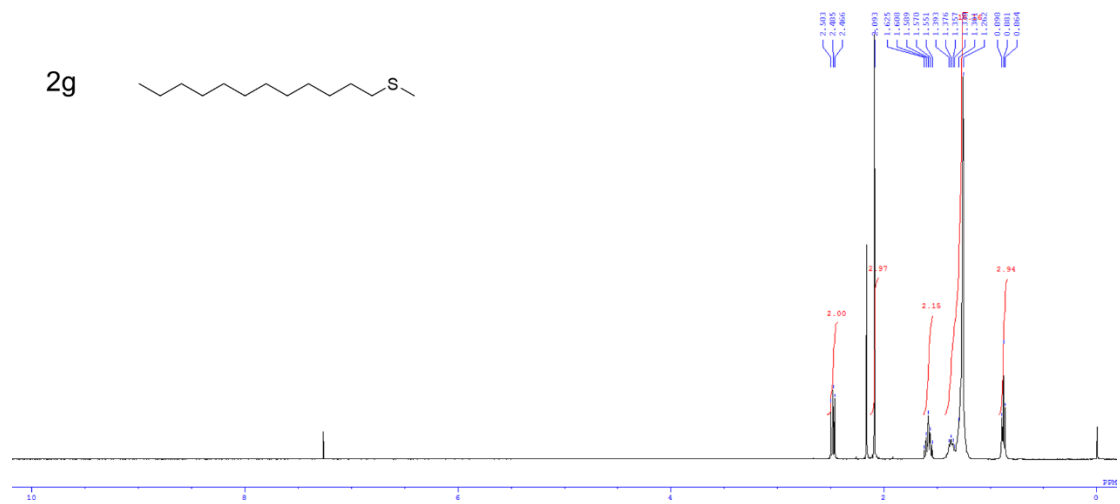


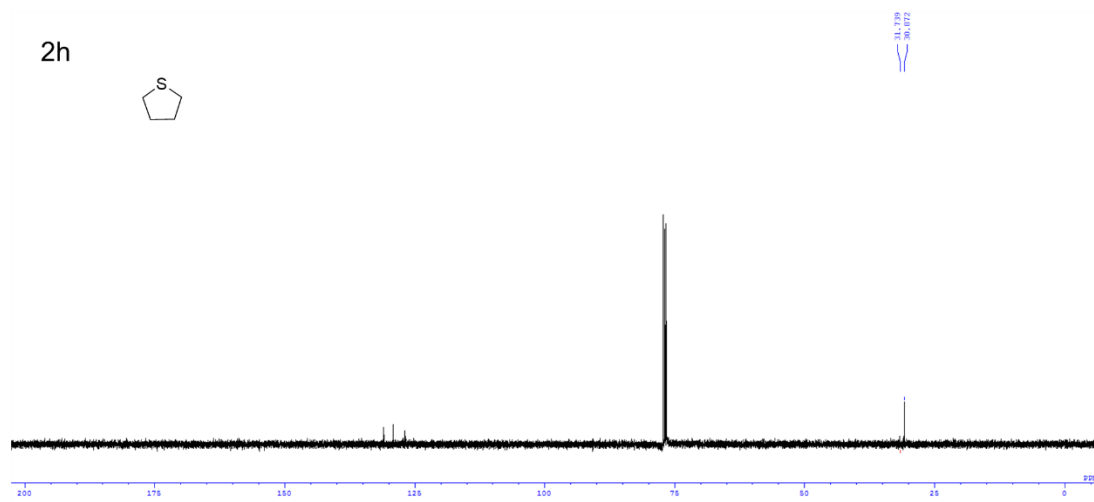
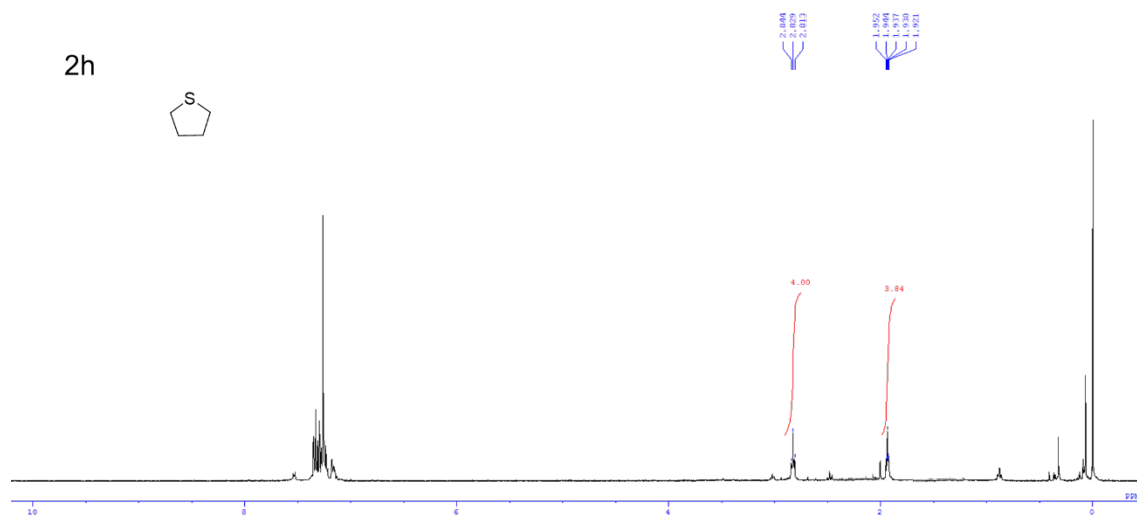
<sup>1</sup>H NMR spectrum of 2f

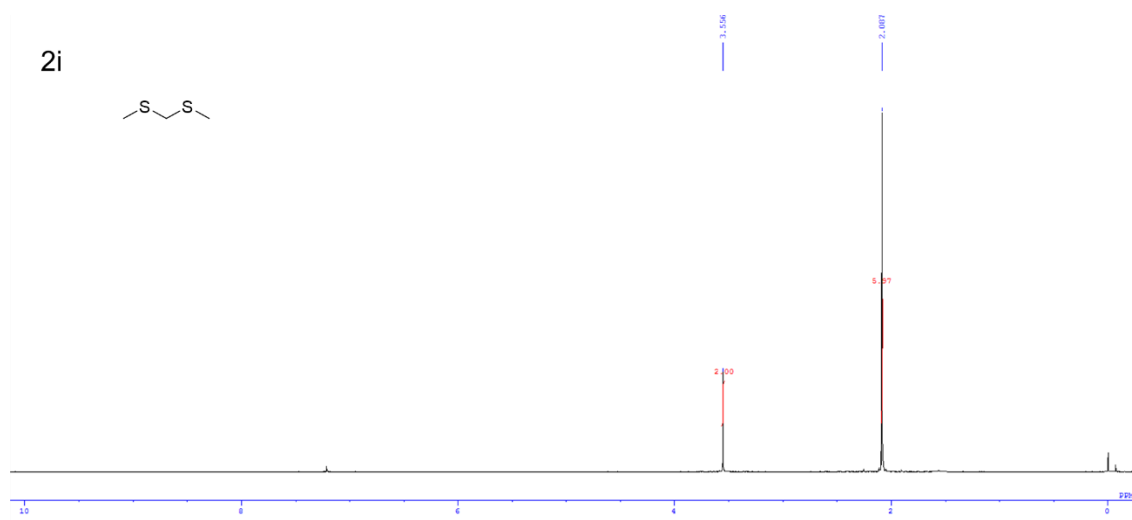
2f



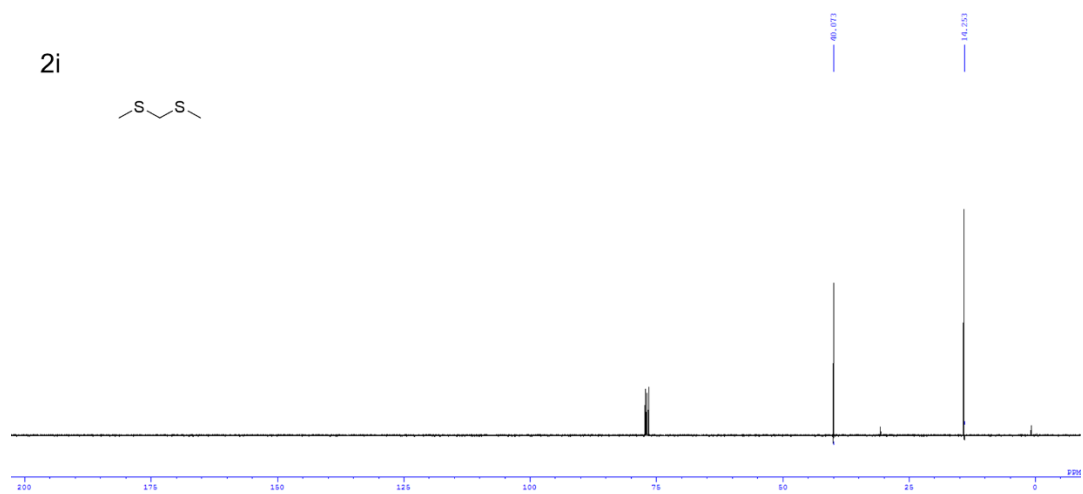
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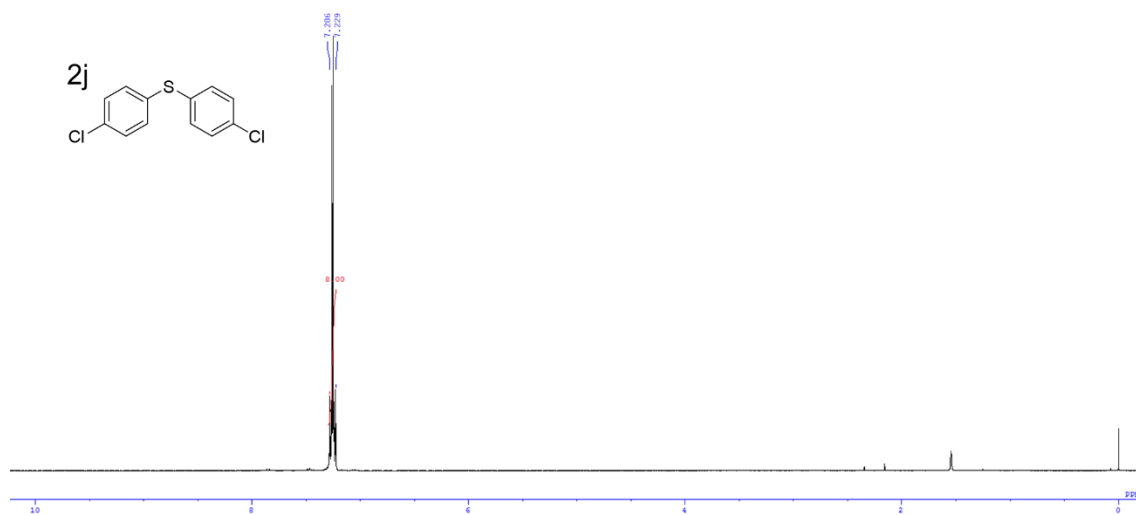




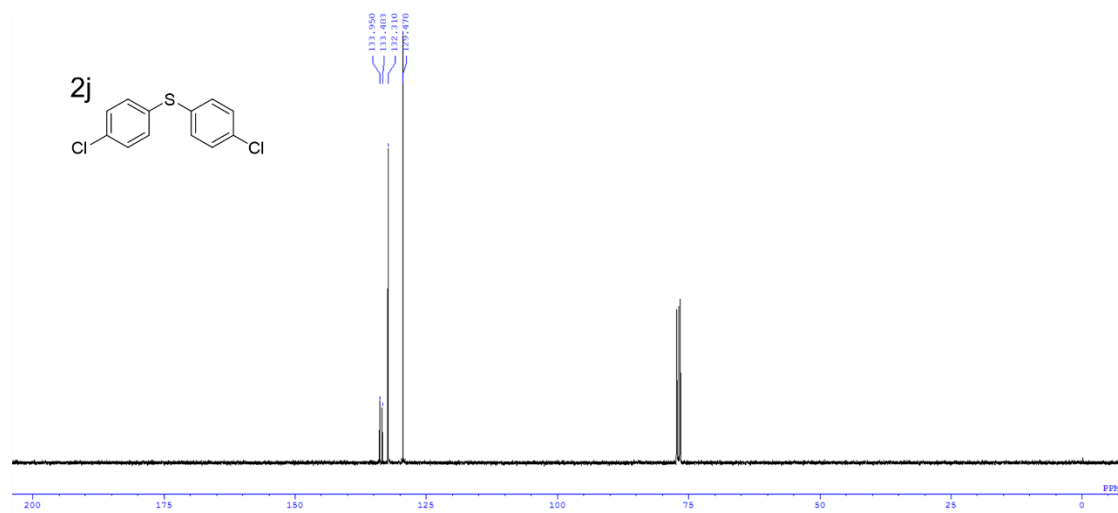
<sup>1</sup>H NMR spectrum of **2i**



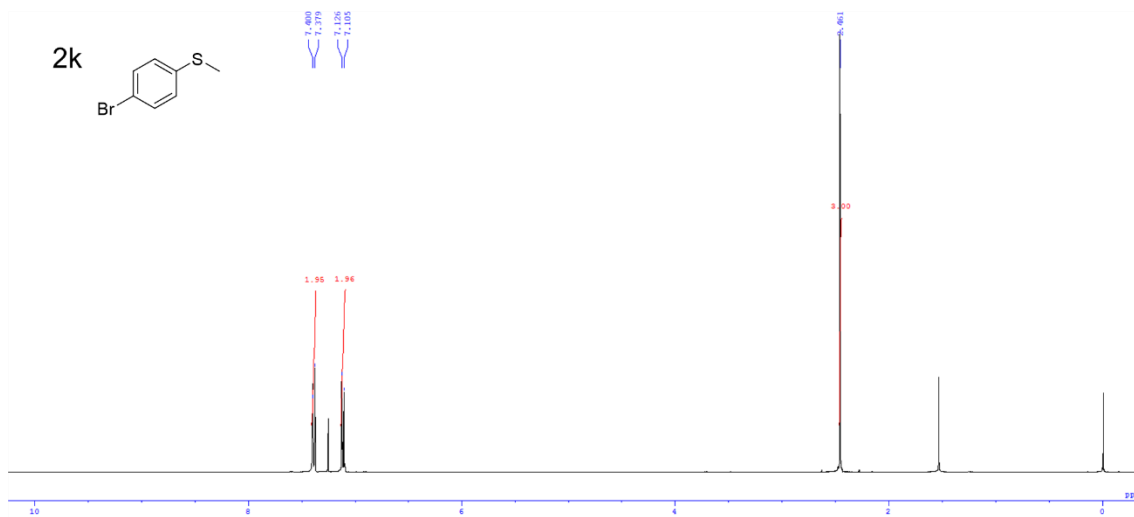
<sup>13</sup>C NMR spectrum of **2i**



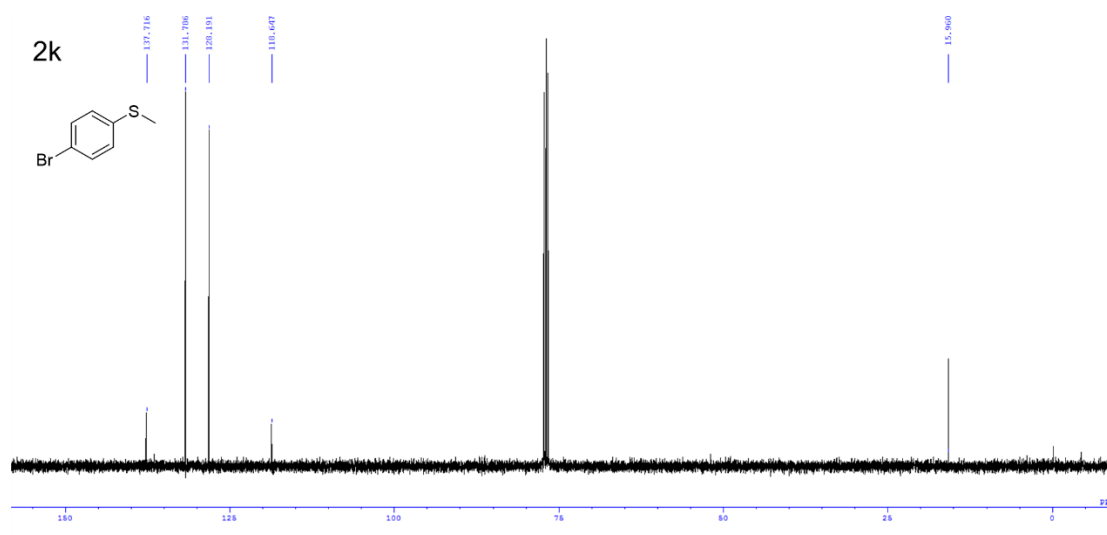
<sup>1</sup>H NMR spectrum of **2j**



<sup>13</sup>C NMR spectrum of **2j**



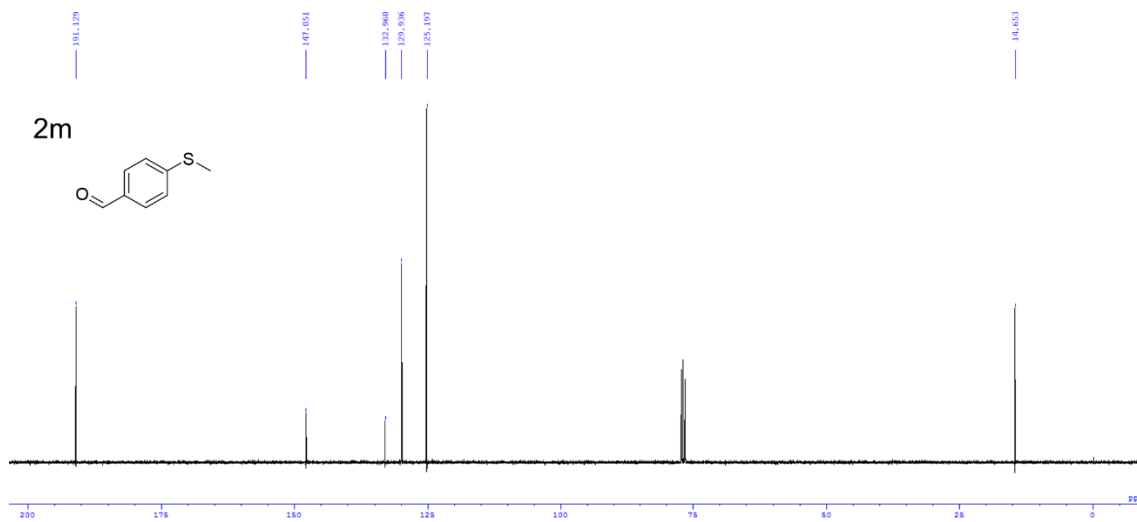
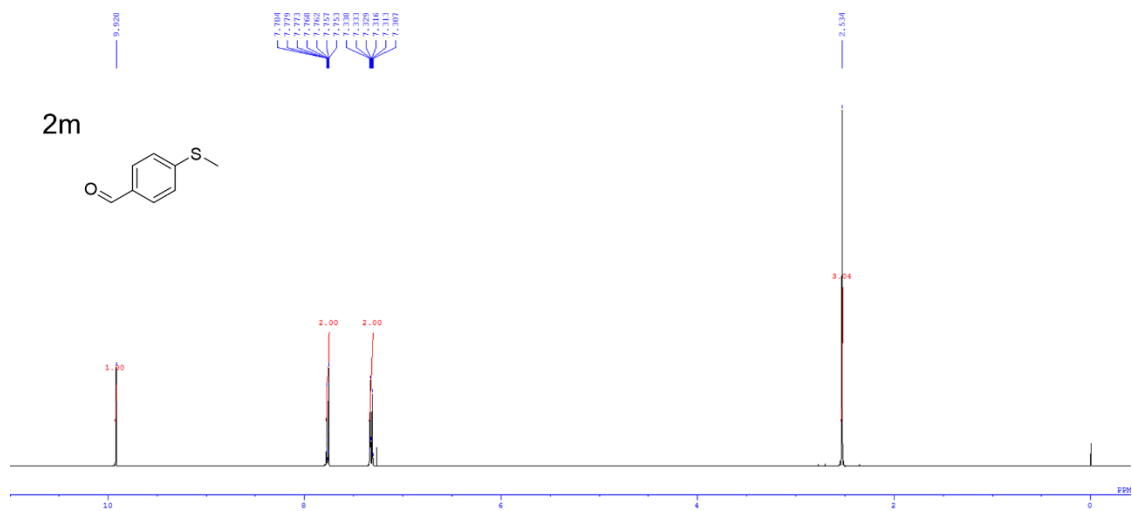
<sup>1</sup>H NMR spectrum of **2k**

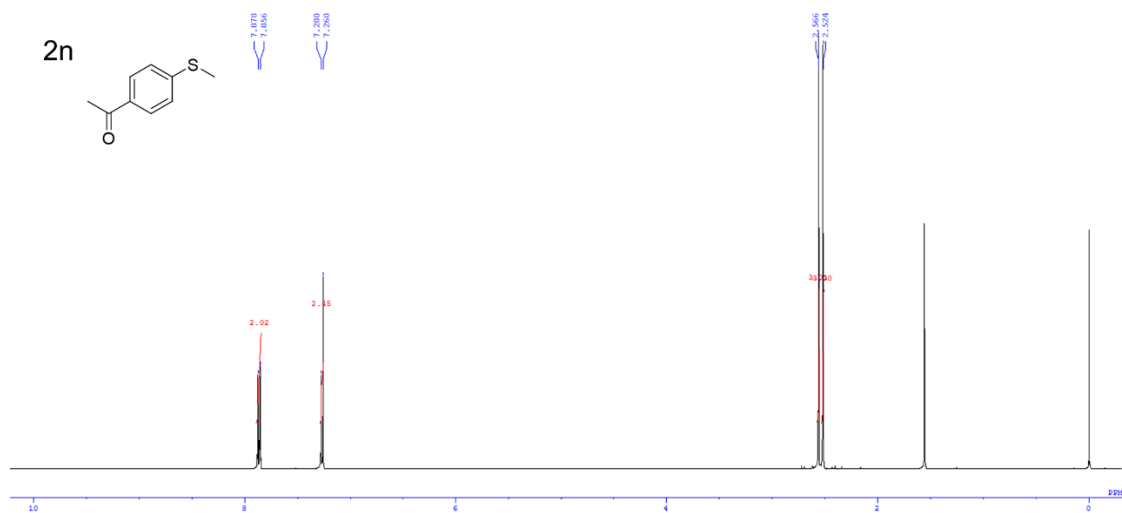


<sup>13</sup>C NMR spectrum of **2k**

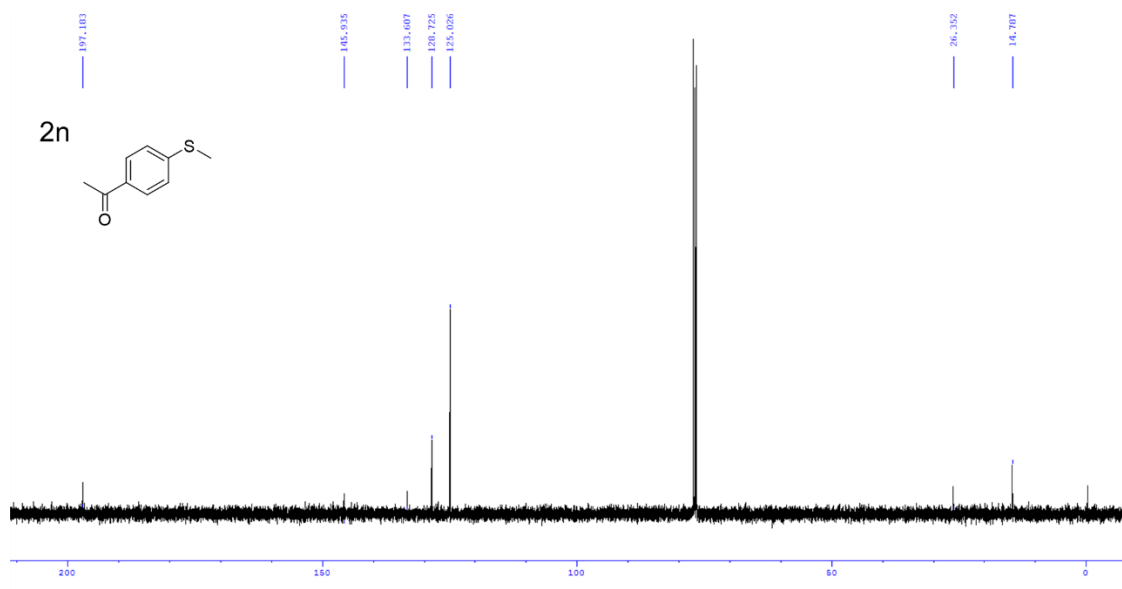




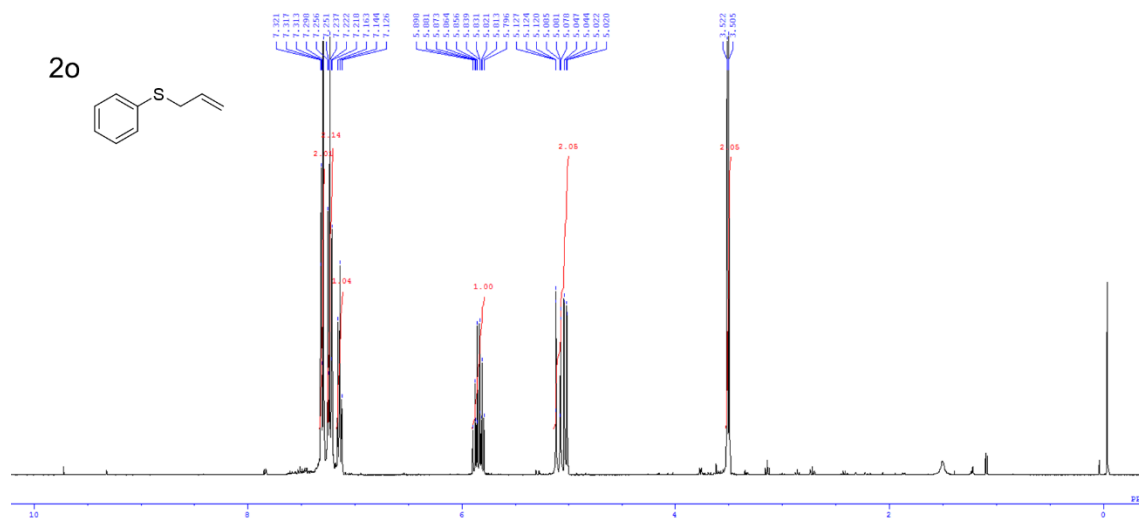




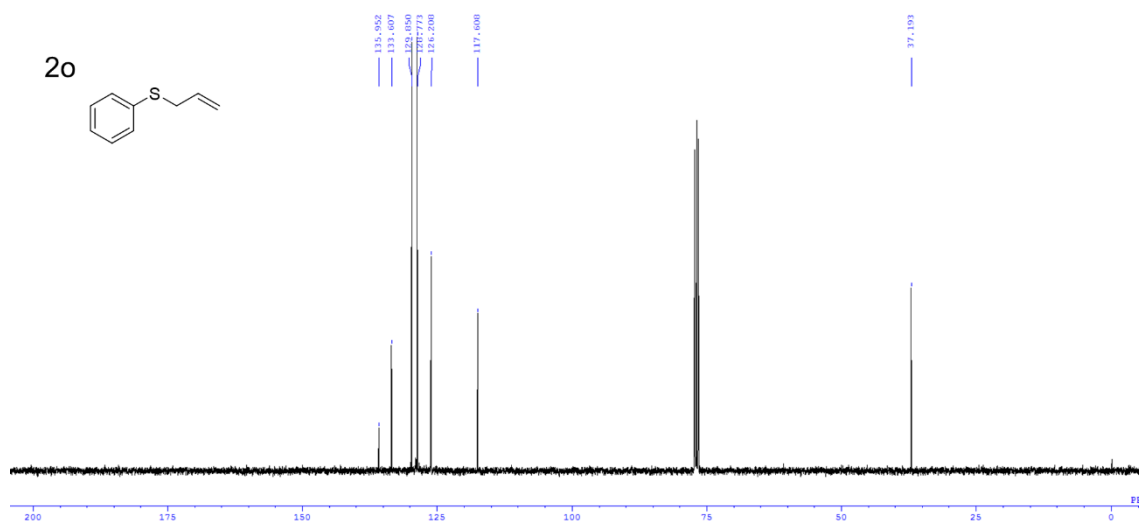
<sup>1</sup>H NMR spectrum of **2n**



<sup>13</sup>C NMR spectrum of **2n**



<sup>1</sup>H NMR spectrum of **2o**



<sup>13</sup>C NMR spectrum of **2o**

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