Supporting Information

Nickel phosphide nanoalloy catalyst for the selective deoxygenation of sulfoxides to sulfides under ambient H_2 pressure

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References

1. General experimental details

$NiCl_2·6H_2O$, Nb_2O_5 and 4Å molecular sieves (4Å M.S.) were purchased from Wako Pure Chemical Industries (Japan). $CoCl_2·6H_2O$ and $Fe(CO)_5$ were purchased from Nacalai Tesque, Inc. (Japan), and Kanto Chemical Co., Inc., respectively. TiO_2 (JRC-TIO-15) and ZrO_2 (JRC-ZrO-6) were obtained from the Catalysis Society of Japan, respectively, as reference catalysts. SiO_2 (Q-6) was purchased from Fuji Silysia Chemicals (Japan). Al_2O_3 (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. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM-ESC400 spectrometer.

2. Catalyst preparations

Synthesis of nano-Co_2P

In a typical synthesis, $CoCl_2·6H_2O$ (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_2P.

Synthesis of nano-Fe_2P

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 $Fe(CO)_5$ 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_2P.

3. Characterization of metal phosphide nanoalloy catalysts

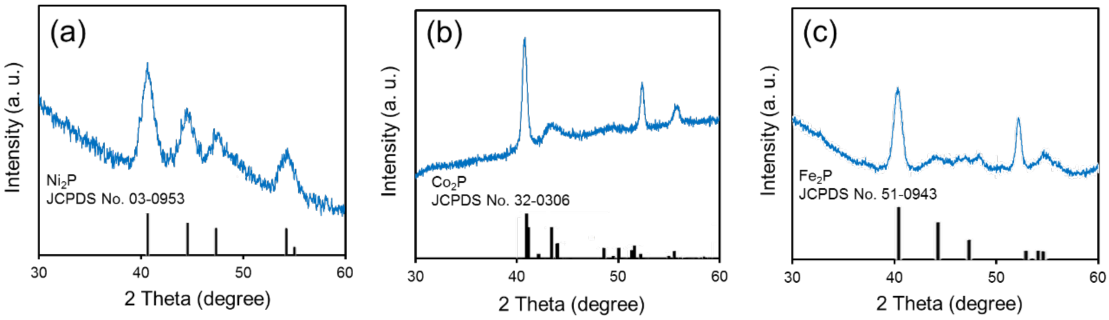


Fig. S1 XRD patterns of (a) nano-Ni_2P, (b) nano-Co_2P, and (c) nano-Fe_2P.

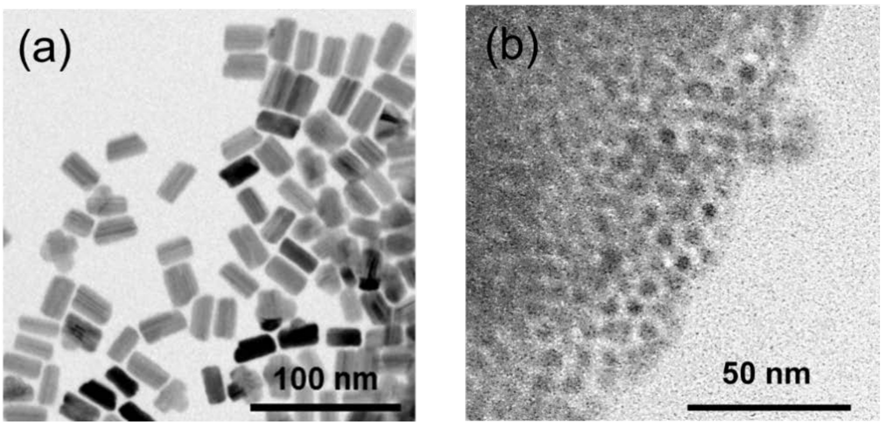


Fig. S2 TEM images of (a) nano-Co_2P, and (b) nano-Fe_2P.

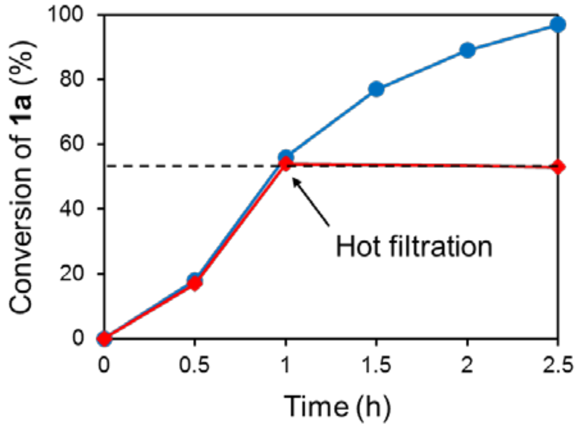


Fig. S3 Time course of the deoxygenation of **1a** using nano-Ni_2P/TiO_2. (●) Without catalyst filtration and (♦) with catalyst removal by hot filtration after 1 h. Reaction conditions: nano-Ni_2P/TiO_2 (5 mol% Ni), **1a** (0.5 mmol), toluene (3 mL), H_2 (10 bar), and 120 °C.

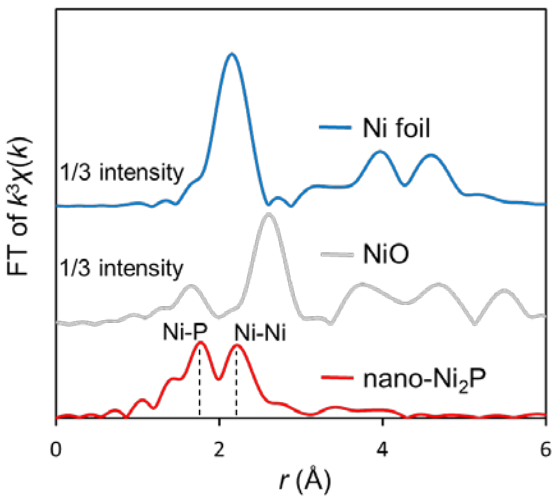


Fig. S4 Fourier transform k^3-weighted EXAFS of Ni foil, NiO, and nano-Ni_2P.

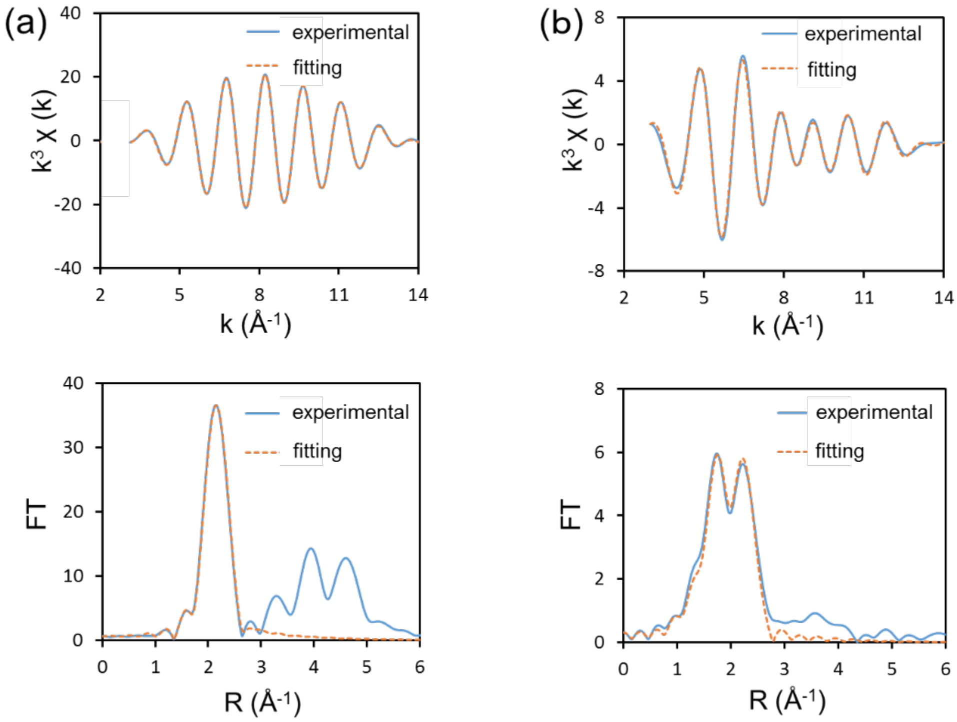


Fig. S5 EXAFS fitting curves in k-space (upper panel) and R-space (lower panel). (a) Ni foil and (b) nano-Ni_2P.

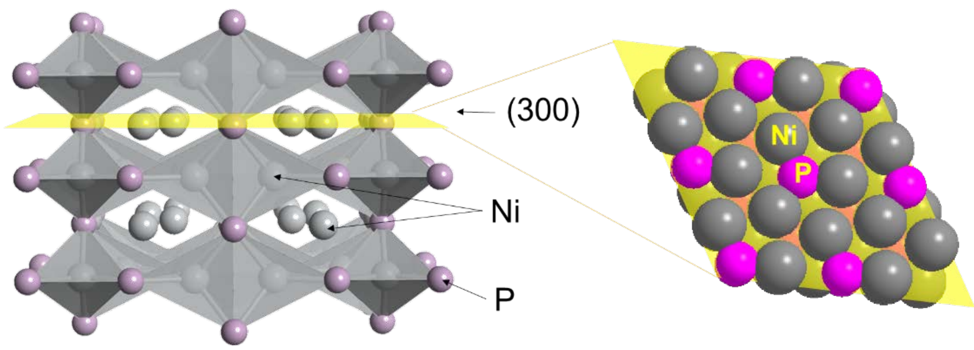


Fig. S6 Crystal structure of Ni_2P with a (300) plane.

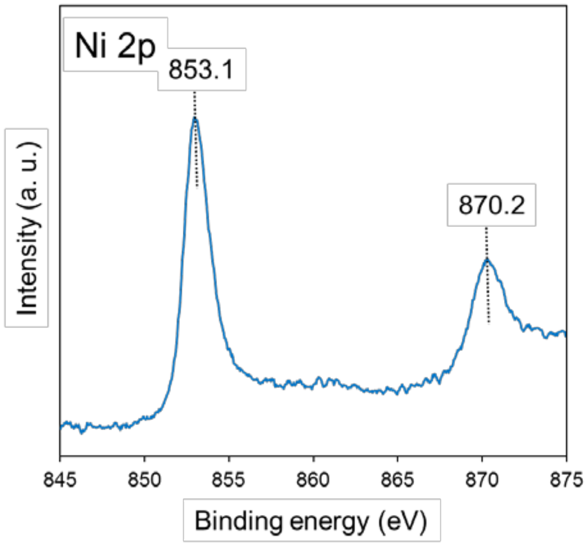


Fig. S7 Ni 2p XPS spectrum of nano-Ni_2P.

Table S1 Elemental analysis of fresh and used nano-Ni_2P/TiO_2 by ICP-AES

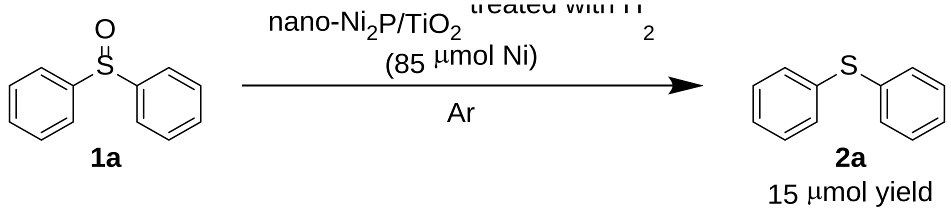
	Ni (wt.%)
Fresh nano-Ni_2P/TiO_2	0.99
Used nano-Ni_2P/TiO_2	0.98

Table S2 Curve fitting of Ni *K*-edge EXAFS for Ni foil and nano-Ni_2P

Sample	Shell	*CN* [a]	*r* (Å)[b]	DW [c]	R factor (%)
Ni foil	Ni–Ni	11 ± 0.1	2.48 ± 0.01	0.007 ± 0.002	2.4
nano-Ni_2P	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_2P (ideal)	Ni–P[d]	2.2	2.24	——	——
	Ni–Ni[e]	6.7	2.65	——	

[a] Coordination number. [b] Bond distance. [c] Debye–Waller factor. [d] Average of Ni–P whose bond lengths are less than 2.3 Å. [e] Average of Ni-Ni whose bond lengths are less than 2.7 Å.

4. Control experiment



Scheme S1 Deoxygenation of **1a** using nano-Ni_2P/TiO_2 treated with H_2. Reaction conditions: nano-Ni_2P/TiO_2 (0.85 μmol Ni) treated, **1a** (0.5 mmol), toluene (3 mL), Ar (1 bar), 120 °C, and 1 h. Before the reaction, nano-Ni_2P/TiO_2 was treated with H_2 (10 bar) at 120 °C for 1 h.

5. Comparison of activity between nano-Ni_2P and reported non-noble metal catalysts

Table S3 Deoxygenation of sulfides using H_2 catalyzed by non-noble metal catalysts

Catalyst	Conditions	Substrate	Yield of sulfide [%]	TON	Ref.
nano-Ni_2P/TiO_2	120 °C, 10 bar, 12 h in toluene	Diphenyl sulfoxide	92	92	***This work***
nano-Ni_2P/TiO_2	160 °C, 1 bar, 12 h in toluene	Diphenyl sulfoxide	97	19	***This work***
Co–Mo/NC-400	50 °C, 10 bar, 10 h in methanol	Diphenyl sulfoxide	100	--	***S1***
MoO_2Cl_2	120 °C, 50 bar, 20 h in toluene	Methyl phenyl sulfoxide	100	10	***S2***

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}H and ^{13}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}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.35 – 7.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 135.8, 131.0, 129.1, 127.0.

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

CAS registry No. [620-94-0]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.22 (d, *J* = 7.6 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 4H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 136.9, 132.9, 131.0, 129.9, 21.0.

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

CAS registry No. [831-91-4]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.31 – 7.21 (m, 10H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 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}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.26 – 7.25 (m, 4H), 7.13 – 7.09 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.4, 128.7, 126.6, 125.0, 15.8.

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

CAS registry No. [623-13-2]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 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}C NMR (100 MHz, $CDCl_3$, ppm): δ = 135.0, 134.7, 129.6, 127.3, 20.9, 16.5.

Dibutyl sulfide (*S3*) (2f)

CAS registry No. [544-40-1]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 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}C NMR (100 MHz, $CDCl_3$, ppm): δ = 31.8, 22.0, 13.6.

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

CAS registry No. [3698-89-3]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 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}C NMR (100 MHz, $CDCl_3$, ppm): δ = 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]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.84 – 2.81 (m, 4H), 1.95 – 1.92 (m 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 31.7, 30.9.

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

CAS registry No. [1618-26-4]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.56 (s, 2H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 40.1, 14.3.

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

CAS registry No. [5181-10-2]. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.29 – 7.22 (m, 8H); ^{13}C NMR

(100 MHz, $CDCl_3$, ppm): δ = 134.0, 133.5, 132.3, 129.5.

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

CAS registry No. [104-95-0]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 137.7, 131.8, 128.2, 118.6, 16.0.

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

CAS registry No. [1879-16-9]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.29 – 7.25 (m, 2H), 6.87 – 6.83 (m, 2H), 3.79 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.2, 130.3, 128.8, 114.6, 55.4, 18.1.

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

CAS registry No. [3446-89-7]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.92 (s, 1H), 7.78 – 7.75 (m, 2H), 7.34 – 7.31 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 191.1, 147.9, 133.0, 129.9, 125.2, 14.7.

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

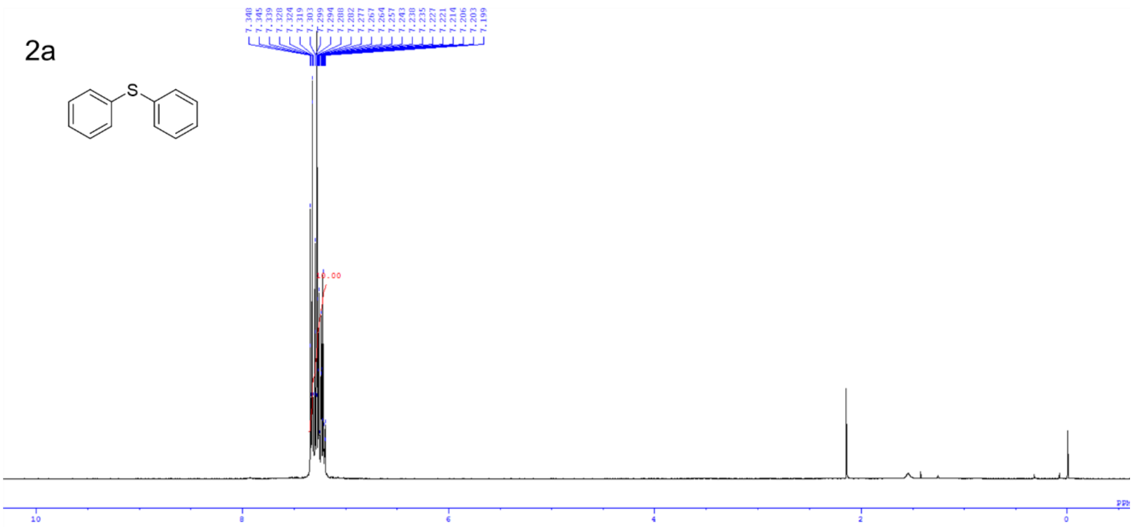
CAS registry No. [1778-09-2]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.87 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 197.2, 145.9, 133.6, 128.7, 125.0, 26.4, 14.8.

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

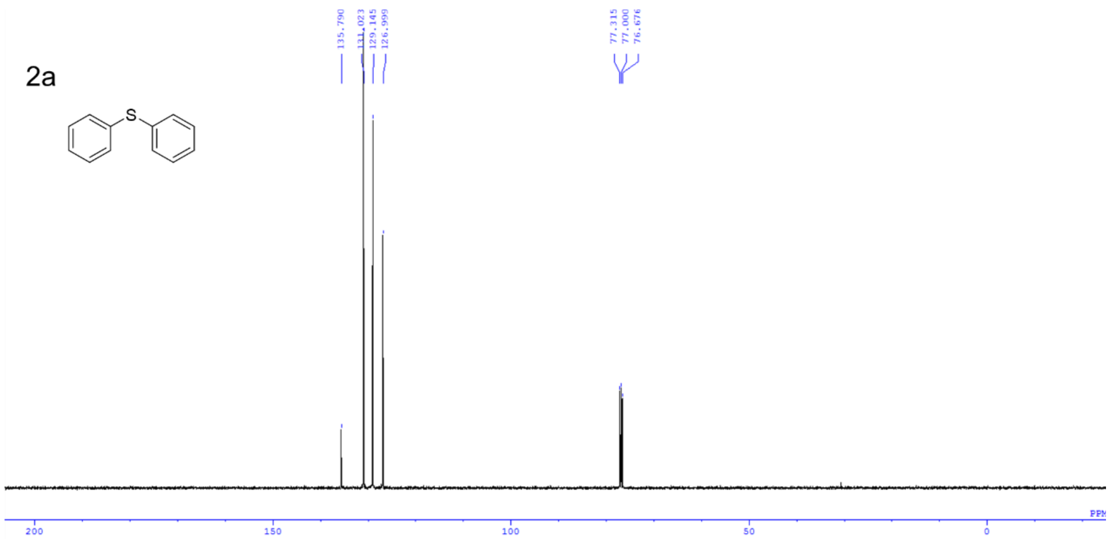
CAS registry No. [5296-64-0]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.32 – 7.30 (m, 2H), 7.26 –

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}C NMR (100 MHz, $CDCl_3$, ppm): δ = 135.9, 133.6, 129.8, 128.8, 126.2, 117.6, 37.2.

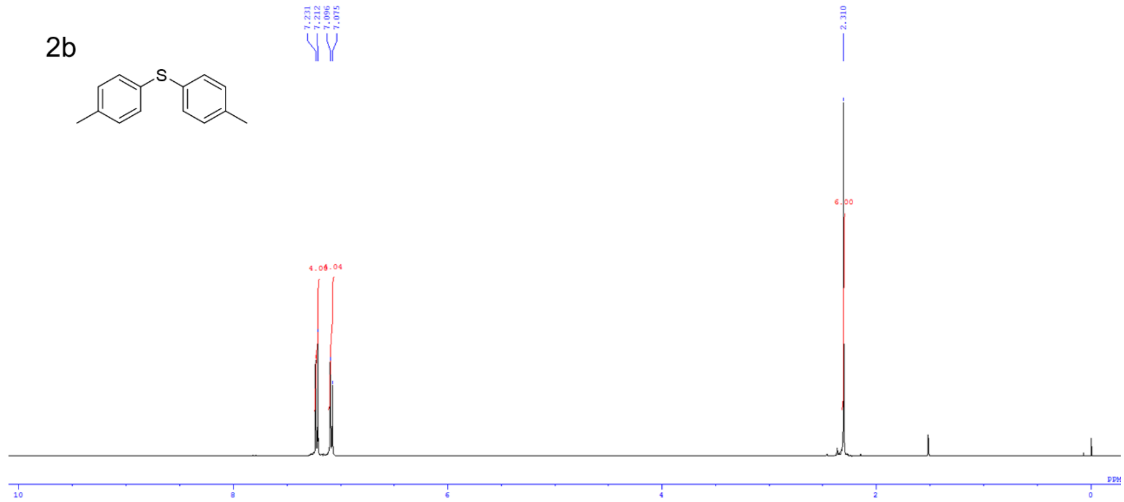
7. ^{1}H NMR and ^{13}C NMR spectra of products



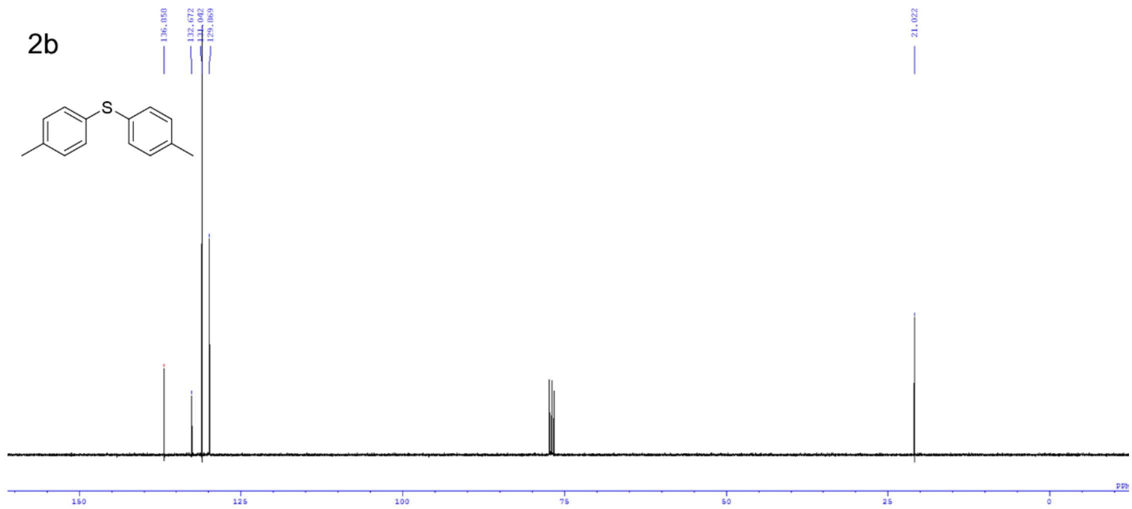
^{1}H NMR spectrum of **2a**



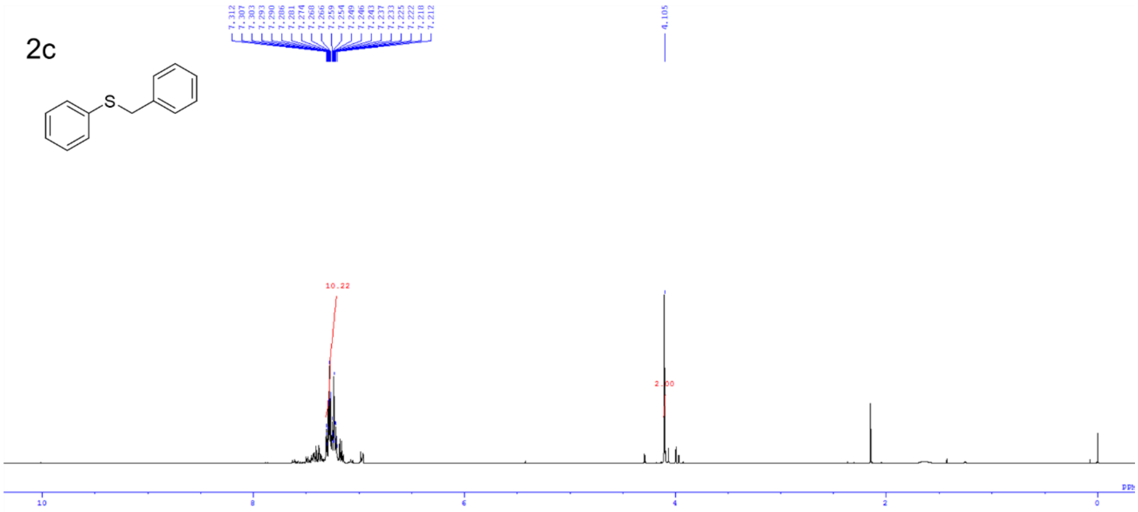
^{13}C NMR spectrum of **2a**



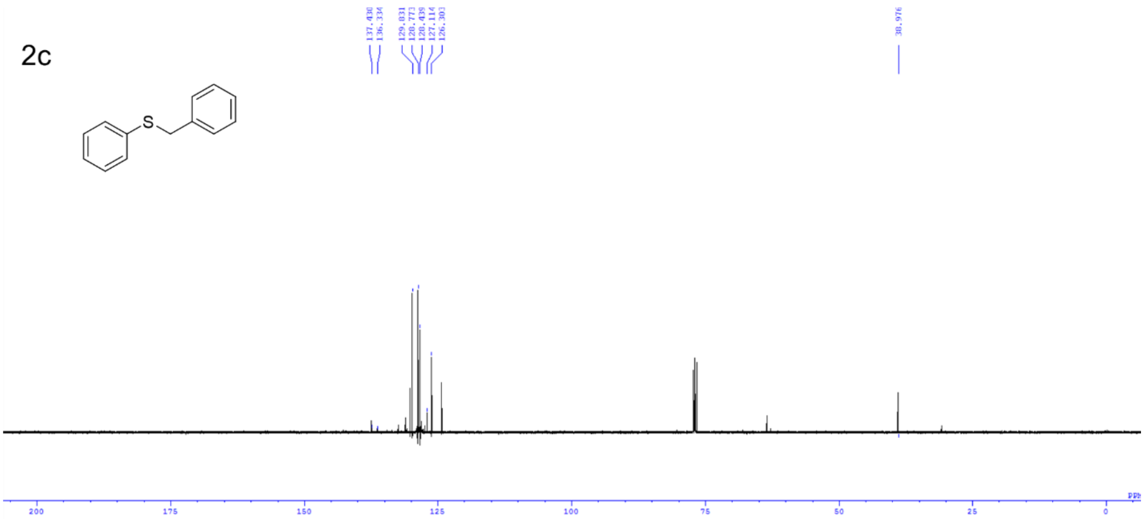
^{1}H NMR spectrum of **2b**



^{13}C NMR spectrum of **2b**



[1]H NMR spectrum of **2c**



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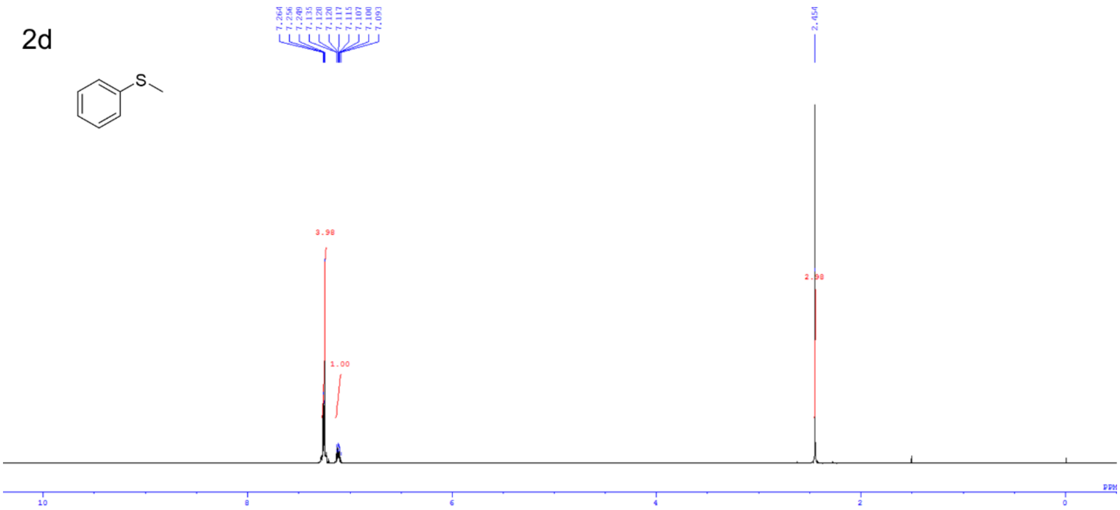

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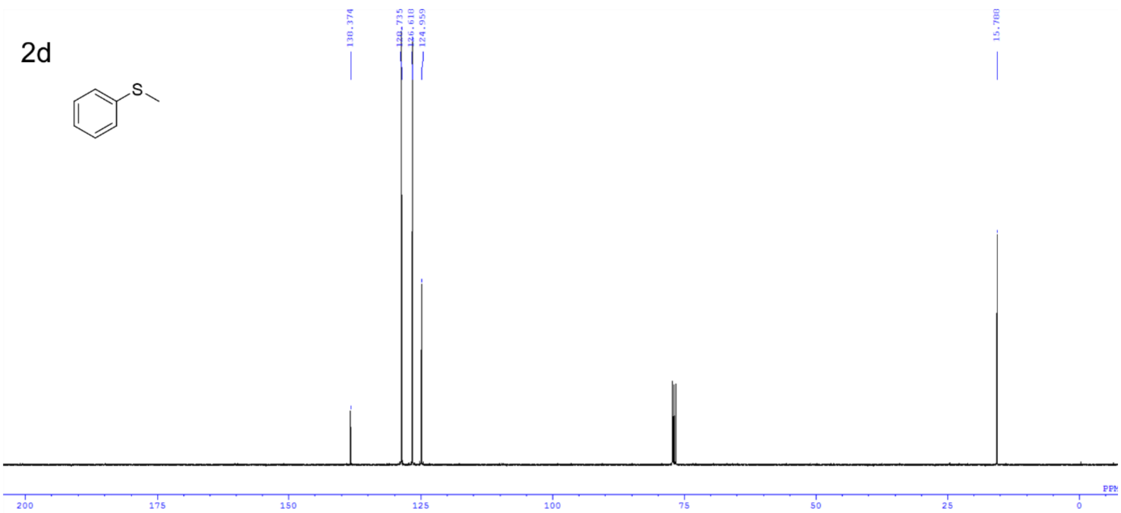
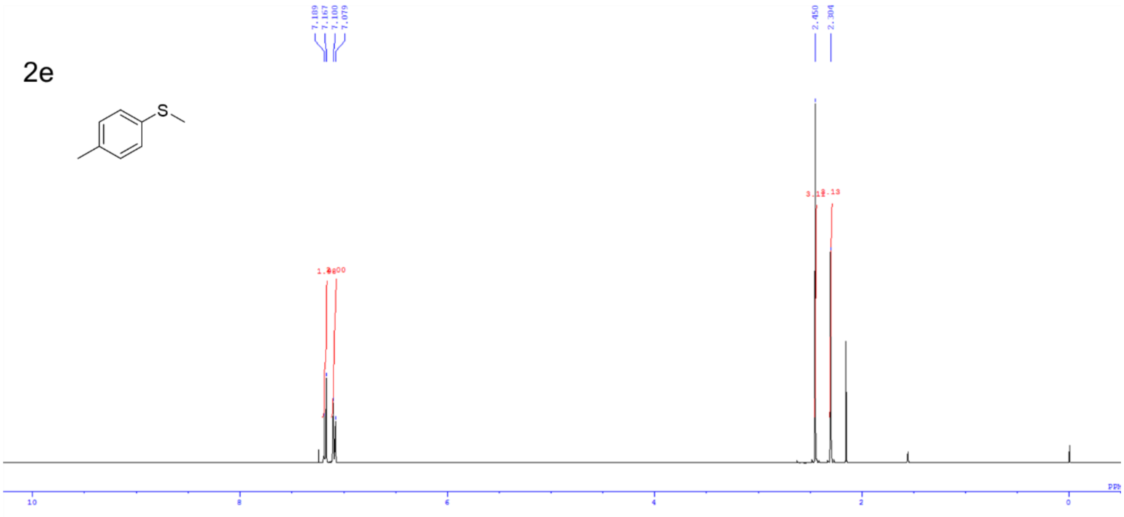


^{13}C NMR spectrum of **2d**

2e



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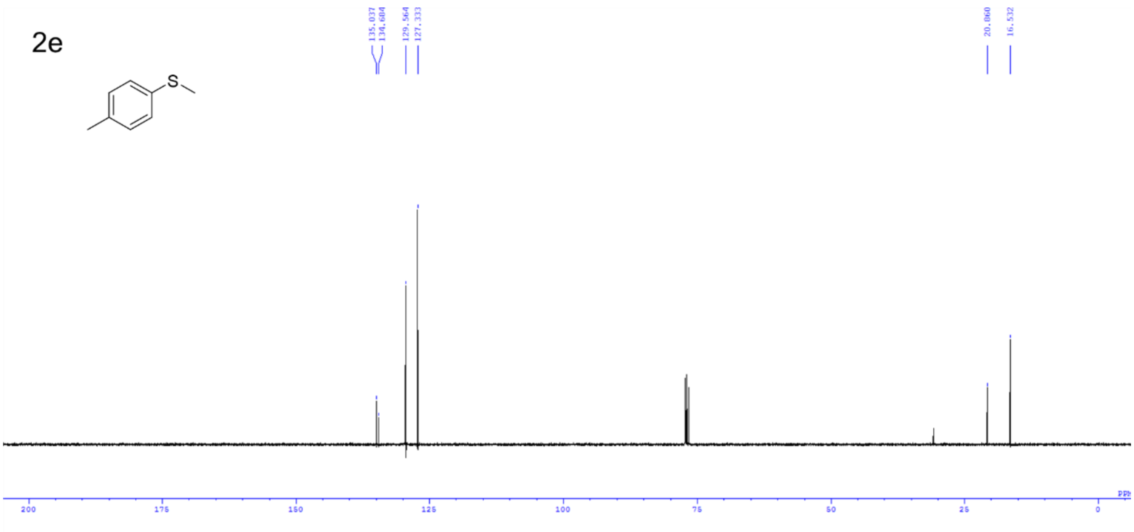
2e



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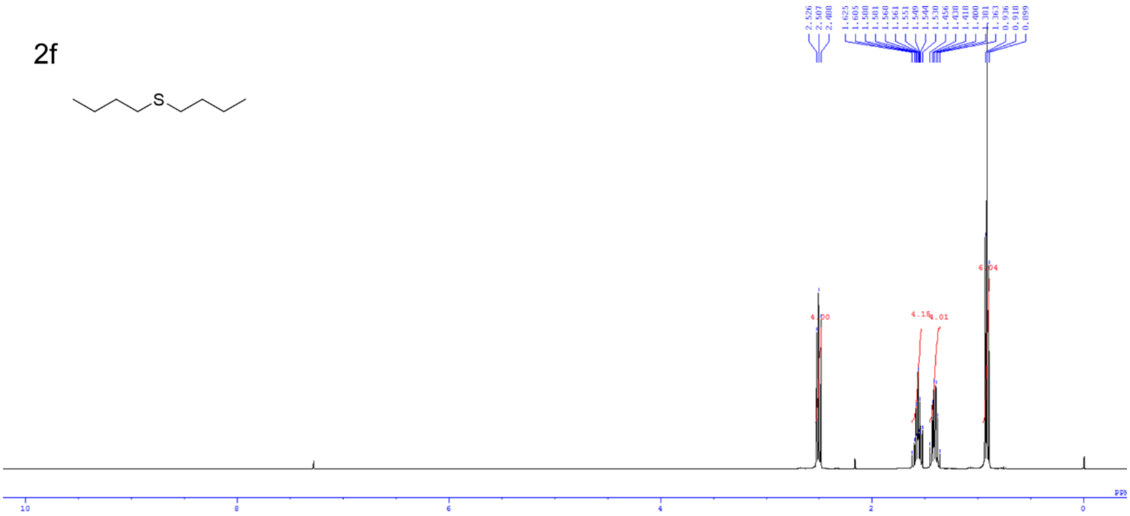

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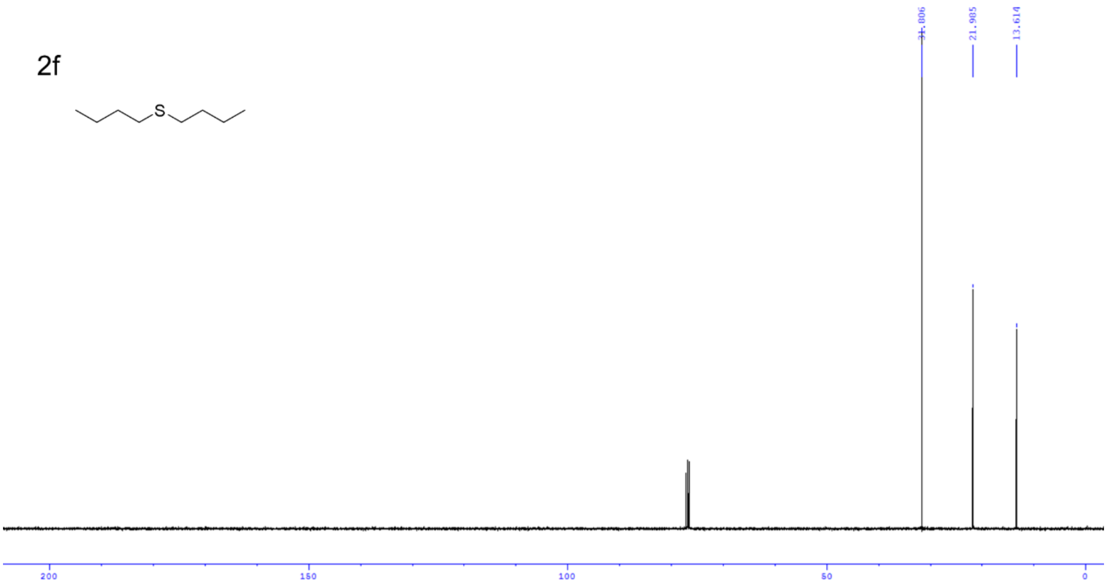

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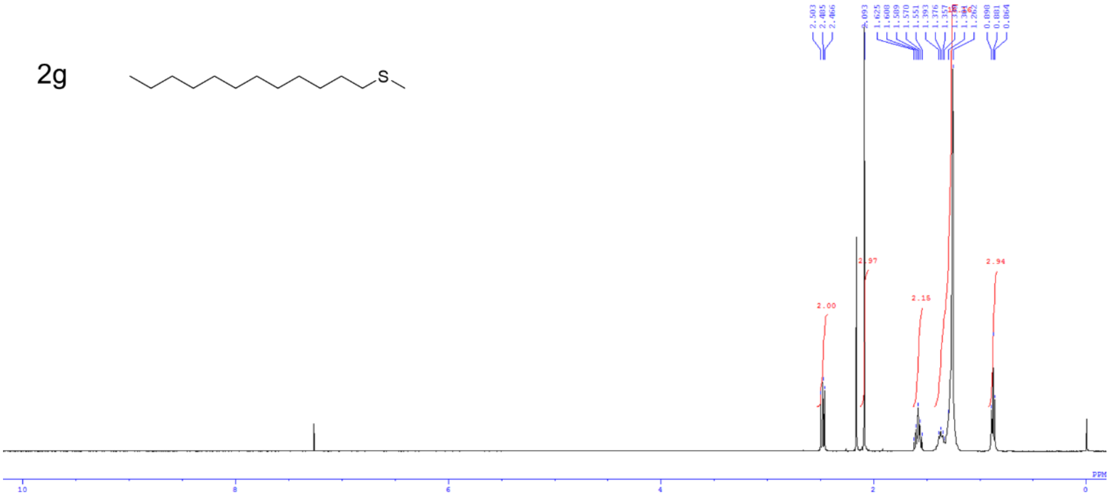
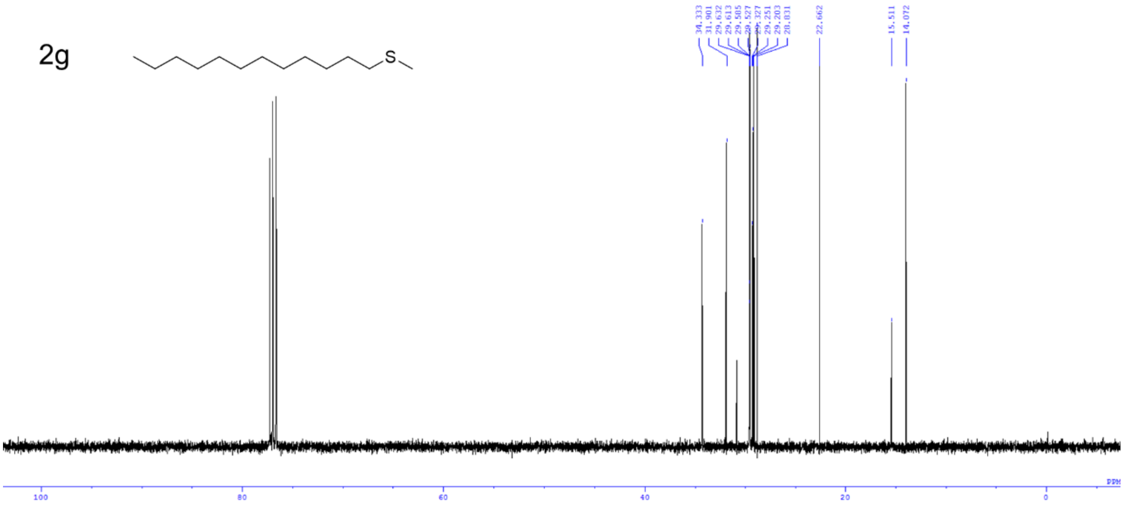
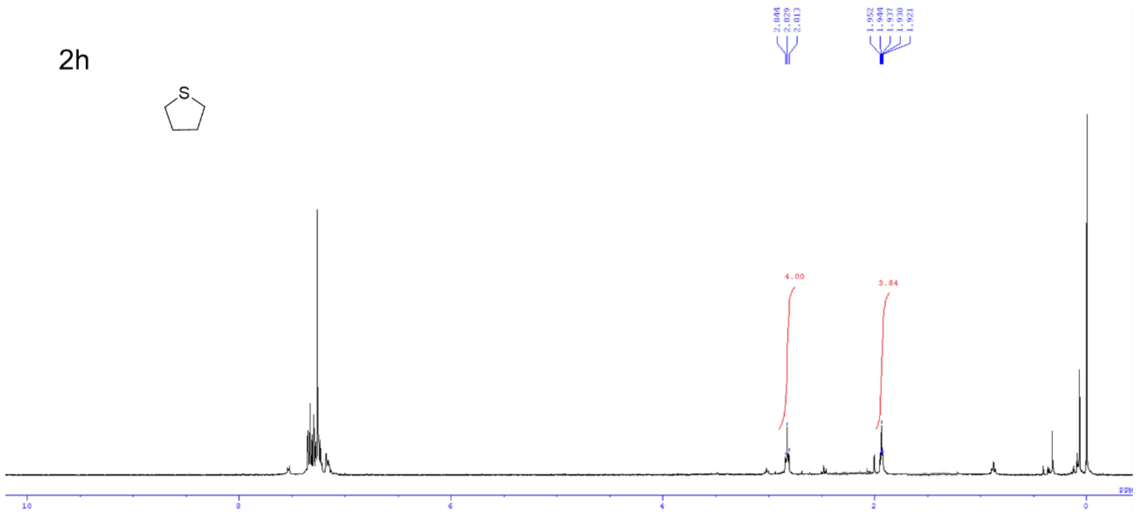


[1]H NMR spectrum of **2g**

2g



[13]C NMR spectrum of **2g**



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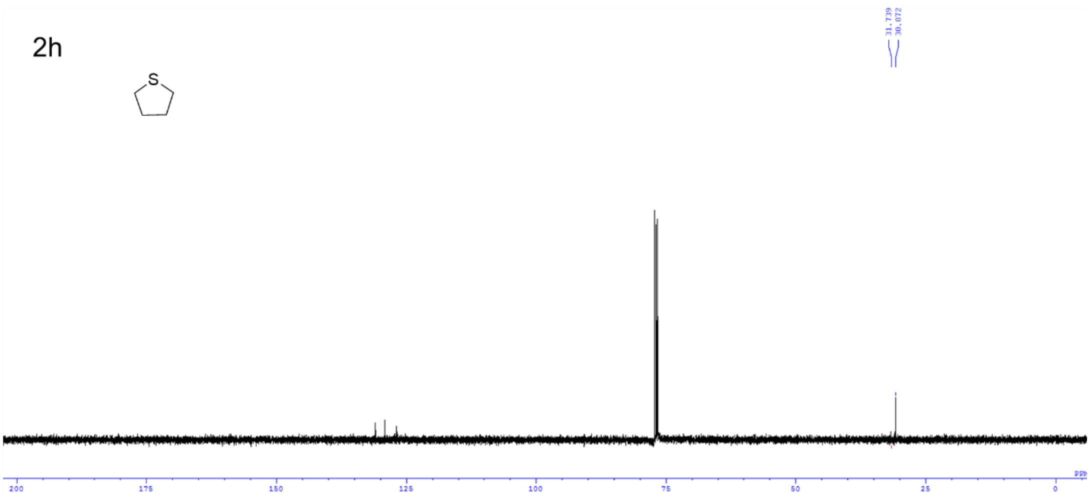
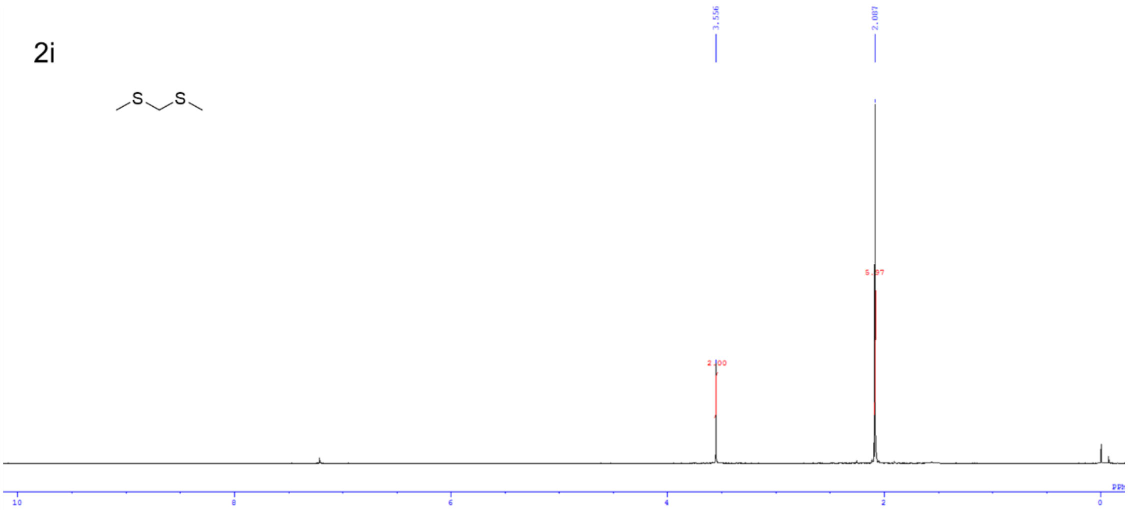


^{13}C NMR spectrum of **2h**



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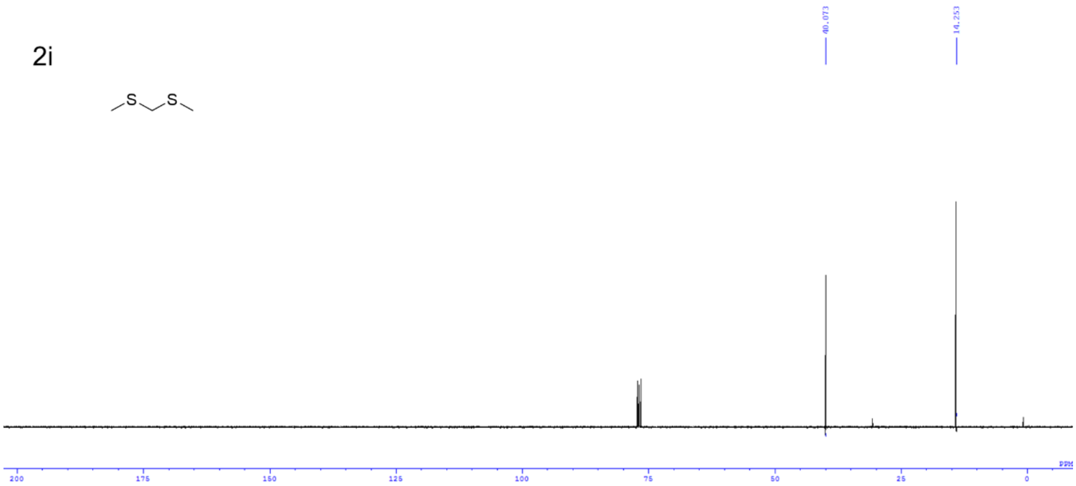
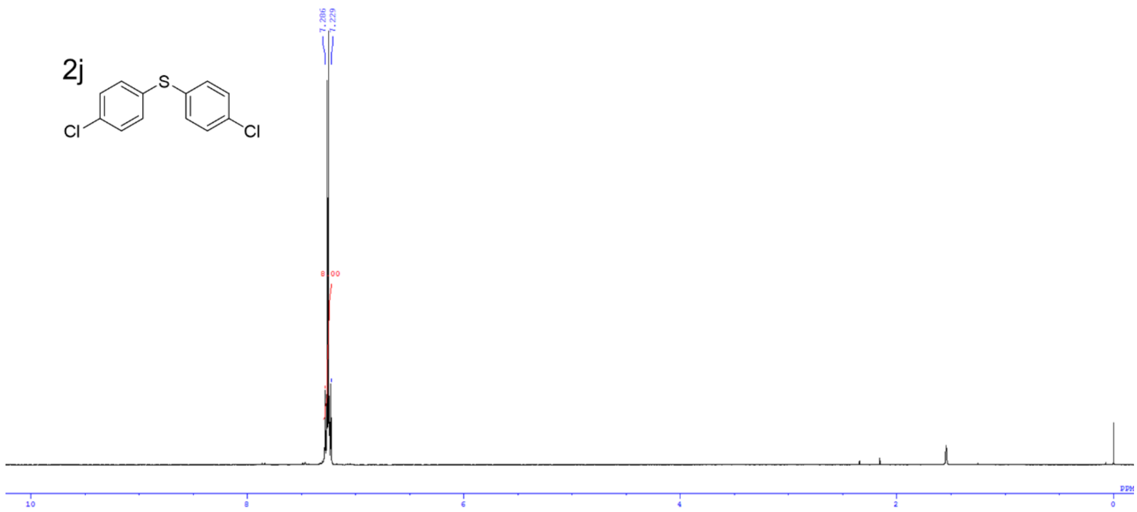


^{13}C NMR spectrum of **2i**



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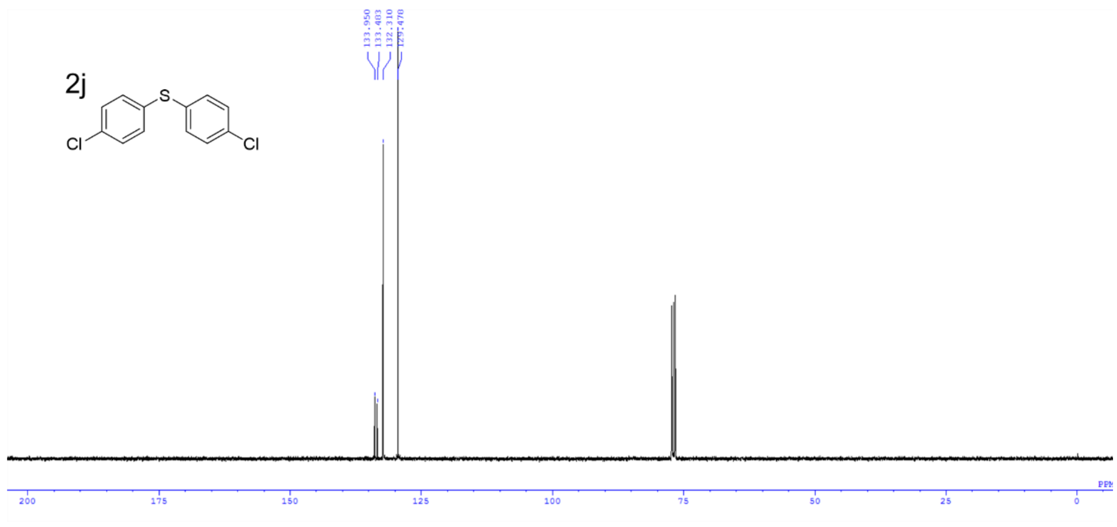
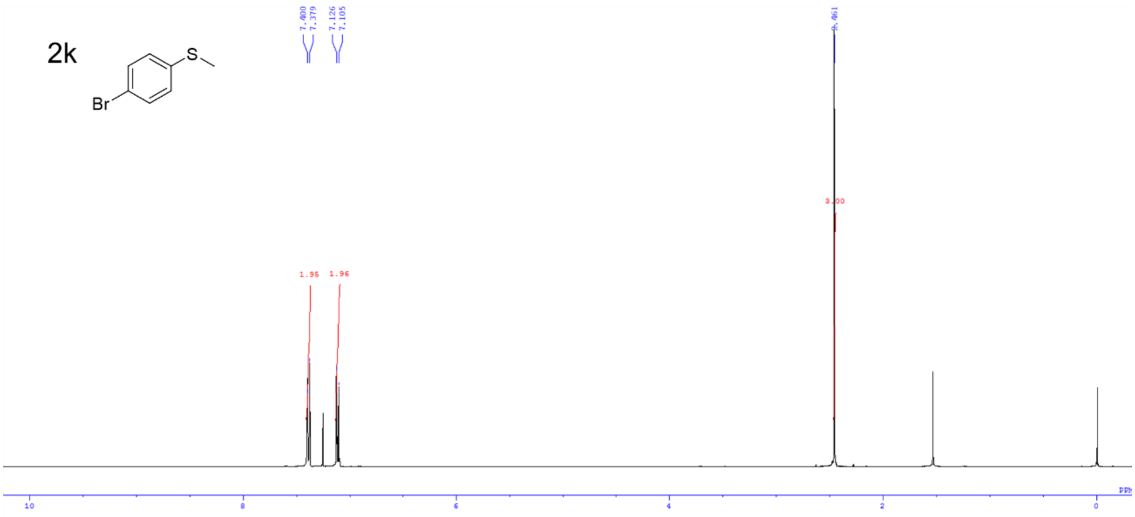
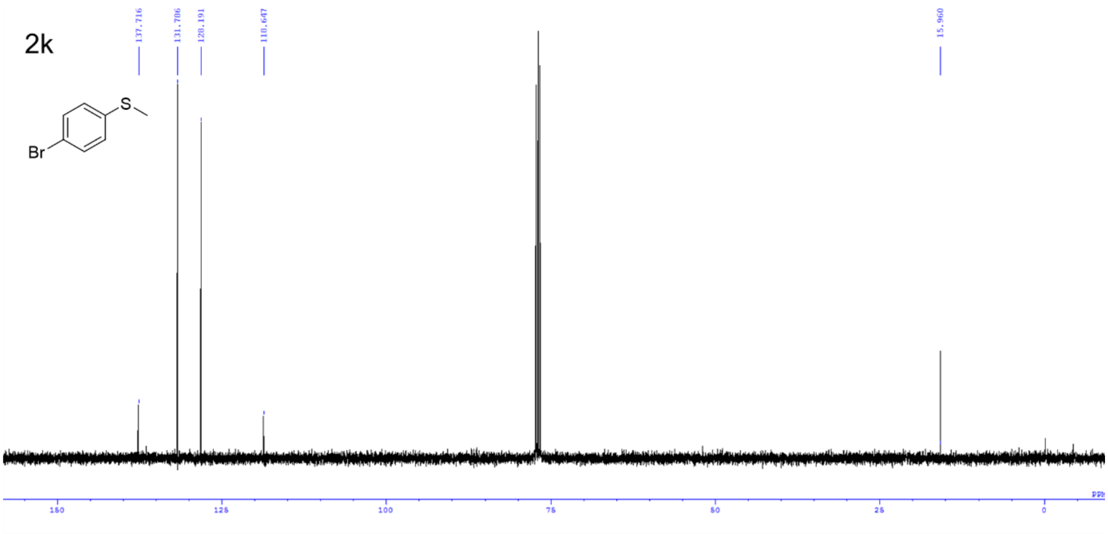


[13]C NMR spectrum of **2j**



^{1}H NMR spectrum of **2k**



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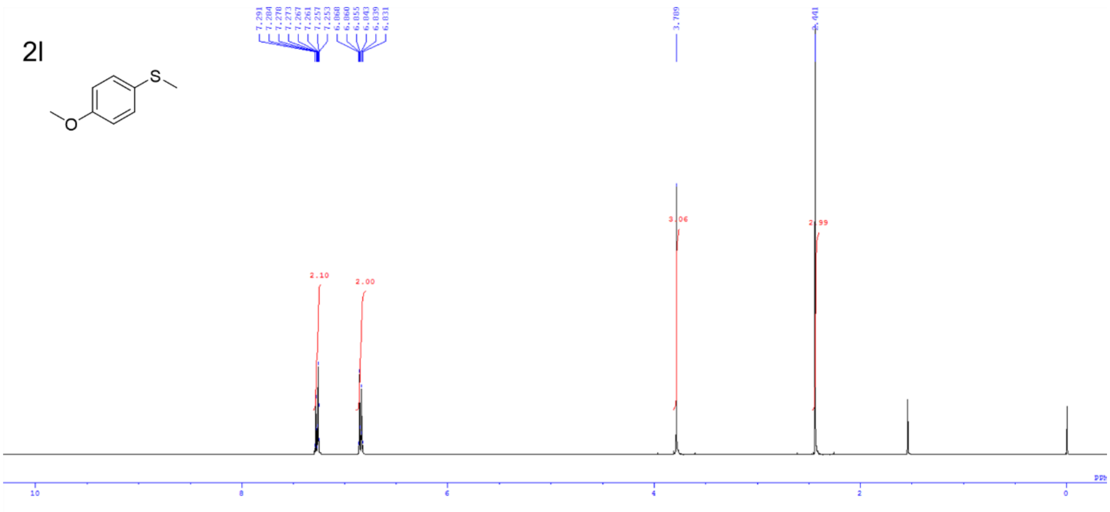
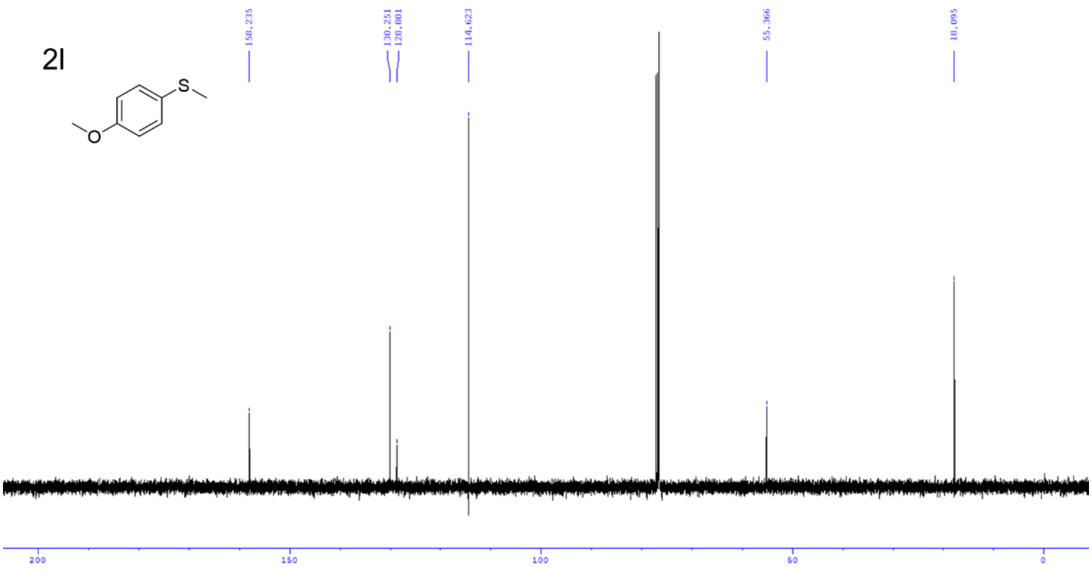
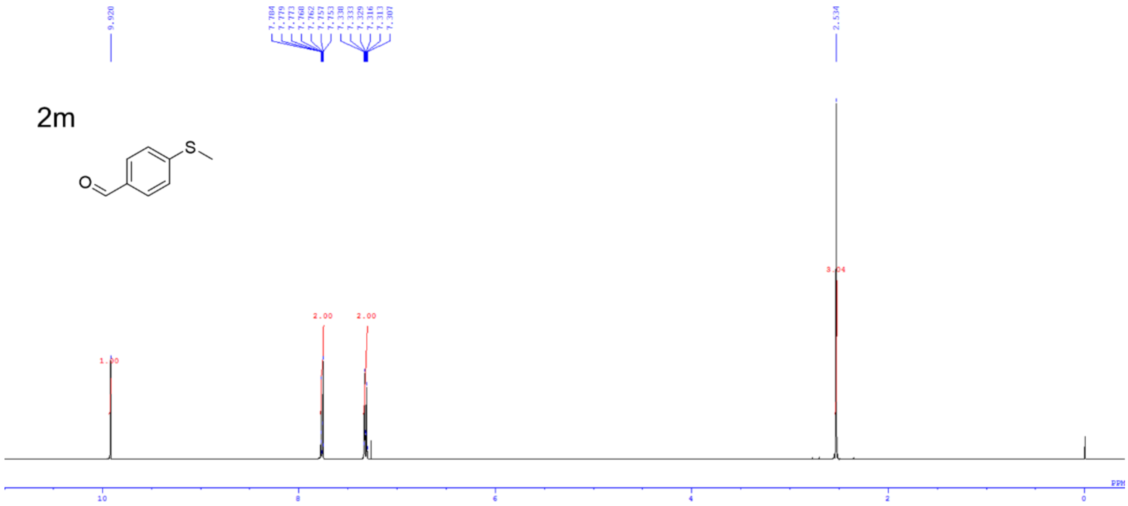


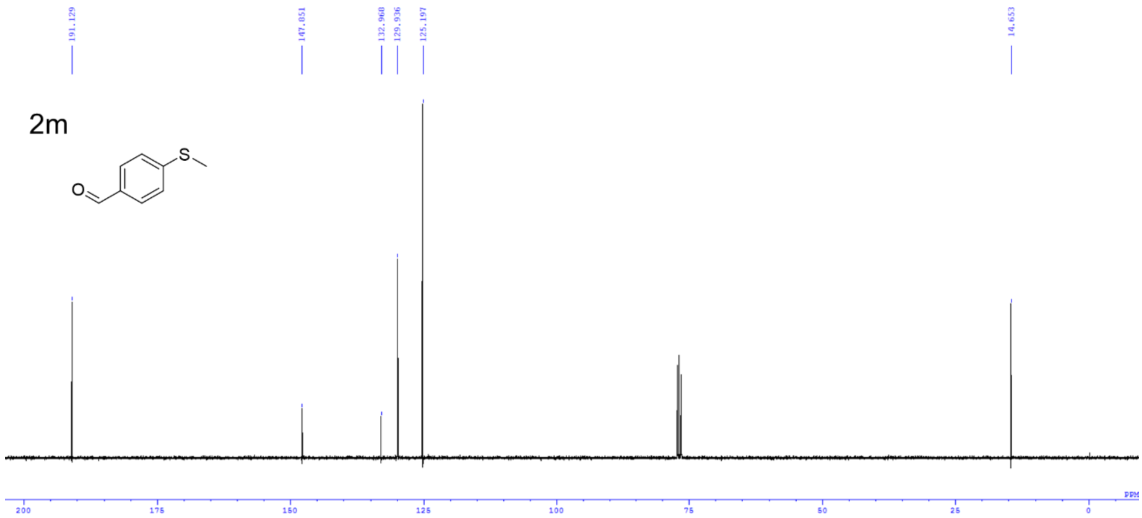
[1]H NMR spectrum of **2l**



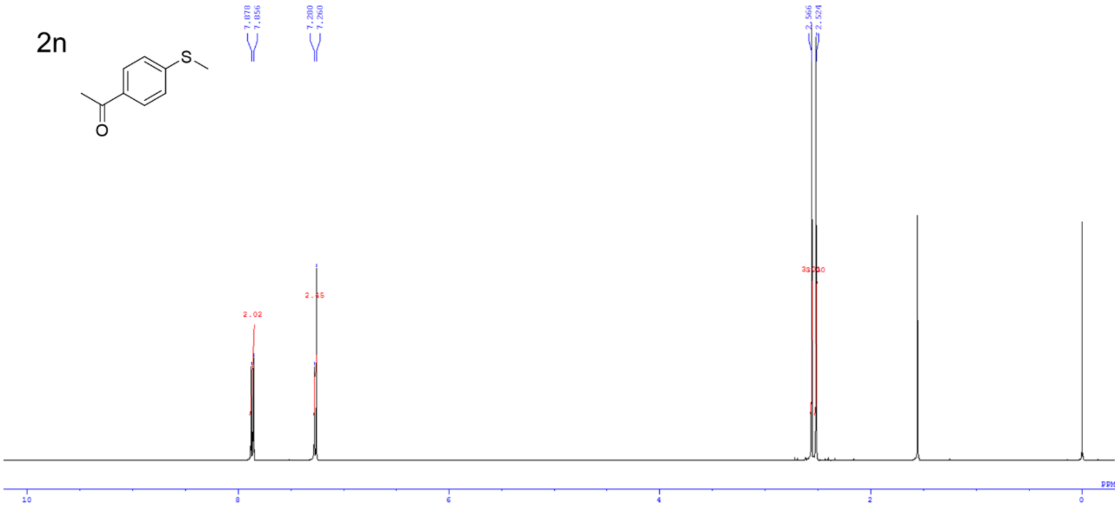
[13]C NMR spectrum of **2l**



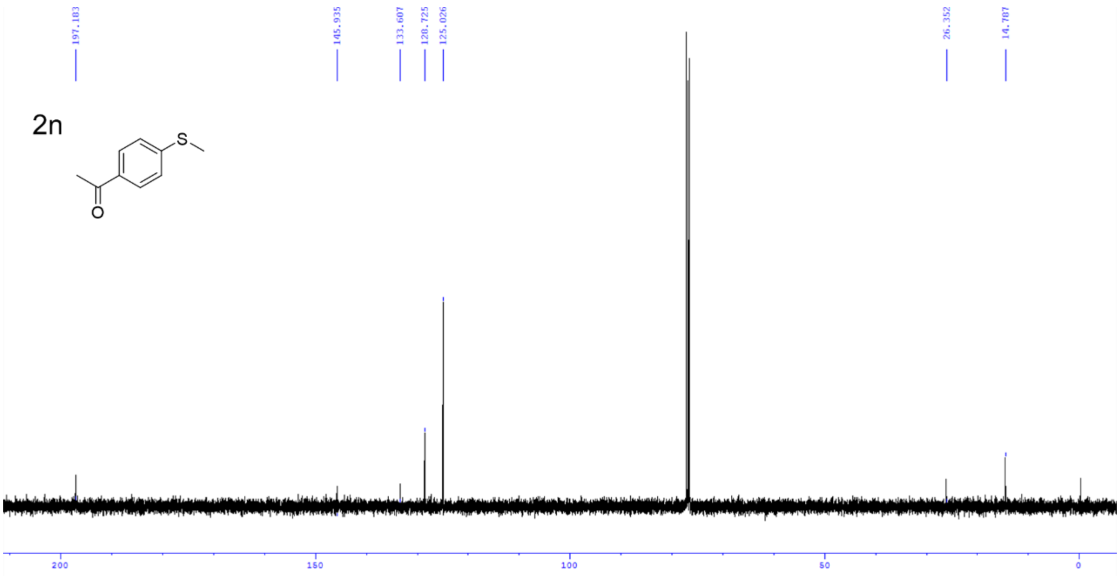
[1]H NMR spectrum of **2m**



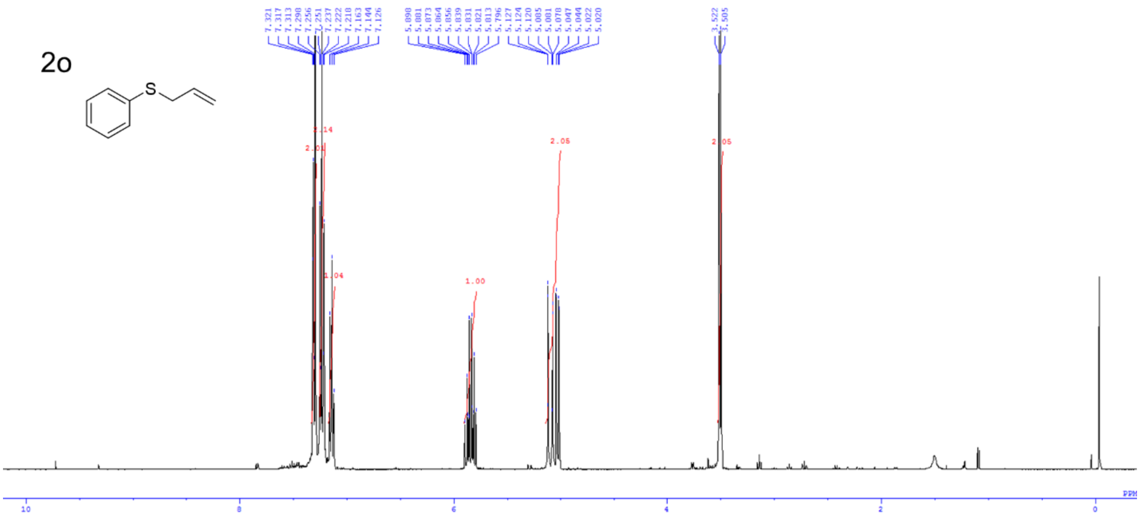
[13]C NMR spectrum of **2m**



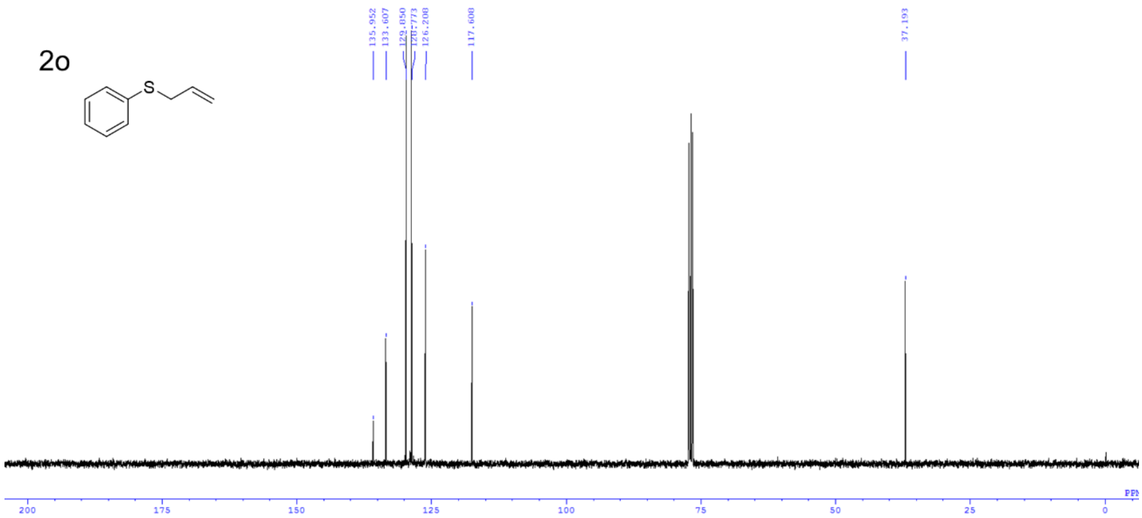
[1]H NMR spectrum of **2n**



[13]C NMR spectrum of **2n**



^{1}H NMR spectrum of **2o**



^{13}C NMR spectrum of **2o**

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