SUPPORTING INFORMATION

Iron-catalyzed selective oxidation of sulfides to sulfoxides with polyethylene glycol/O_2 system

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Supporting information **Page**

1. General experimental methods **2**

2. Conventional solvents and 18-crown-6 used for sulfide oxidation **2**

3. The ^{1}H NMR and ^{13}C NMR Charts for the sulfoxides **3**

1. General experimental methods

Caution

Experiments using compressed gases O_2 are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Materials

The sulfides were purchased from Sigma-Aldrich and Aladdin. The various Iron catalysts were purchased from Aladdin with >98% purity (Cu content was determined to be 0.013% w/w by using ICP method). The other organic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

NMR spectra were recorded on a Bruker 400 or Varian 400 spectrometer in $CDCl_3$. ^1H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^1H and ^{13}C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: $\delta_C = 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.26$ ppm). GC-MS were recorded on a Thermo Finnigan Polaris Q GC/MS. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17, 30 m×0.25 μm) using a flame ionization detector. ICP was measured on a ICP-9000 (N+M) Inductively coupled plasma emission spectrometer. Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum as eluant.

2. Conventional organic solvents and 18-crown-6 used for sulfide oxidation

Table S1 Solvent effect on the oxidation of thioanisole[a]

Entry	Solvent	Temp (°C)	Conv (%)[b]	Yield [b](%)	
				Sulfoxide	Sulfone
1	CH_2Cl_2	60	0	0	0
2	CH_3CN	80	0	0	0
3	CH_3OH	100	0	0	0
4	CH_3CH_2OH	100	0	0	0
5	$(CH_3CH_2O)_2$	100	0	0	0
6	1, 4-dioxane	100	0	0	0
7	CH_3CN/ CH_3OH	80	0	0	0
8	CH_3CN/CH_3CH_2OH	80	0	0	0

[a] All the experiments were carried out with 0.5 mmol (62 mg) of thioanisole, PEG-1000 (0.3 mmol, 300 mg,), $Fe(acac)_2$ (2 mol%, 2.4 mg), O_2 (2 MPa), 6 h. [b] Determined by GC using area normalization.

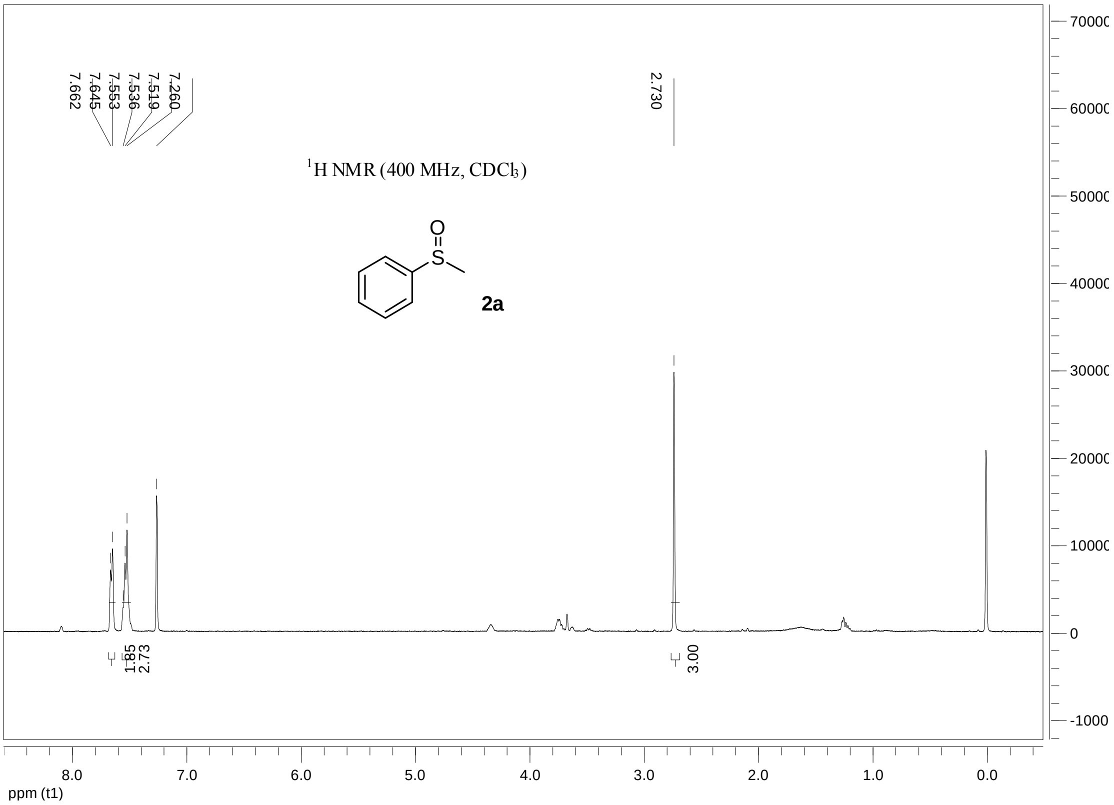
Table S2 Oxidation of thioanisole in 18-crown-6[a]

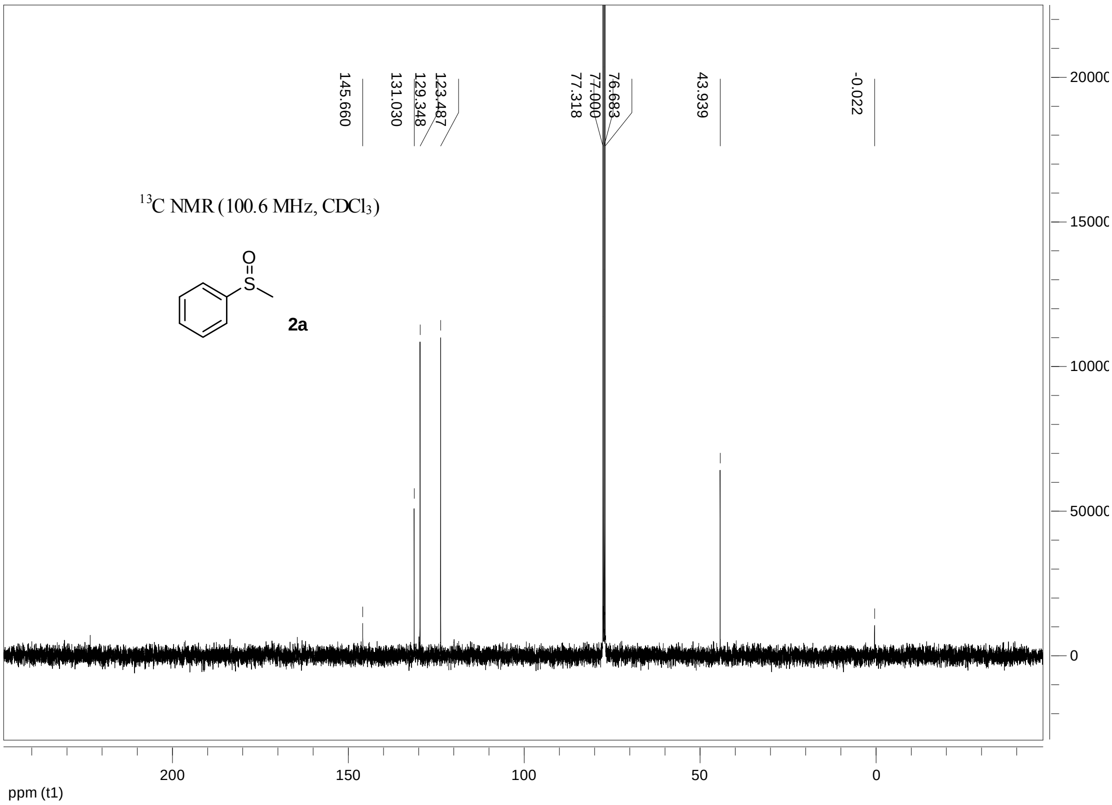
Entry	Temp (°C)	T(h)	Conv (%)[b]	Yield [b](%)	
				Sulfoxide	Sulfone
1[c]	100	12	<1	-	-
2	100	2	96	90	6
3[d]	100	2	<1	-	-

[a] All the experiments were carried out with 0.5 mmol (62 mg) of thioanisole, 18-crown-6 (300 mg), $Fe(acac)_2$ (2 mol%, 2.4 mg), O_2 (2 MPa), unless otherwise noted. [b] Determined by GC using area normalization. [c] without $Fe(acac)_2$. [d] TEMPO (0.05 mmol) was added.

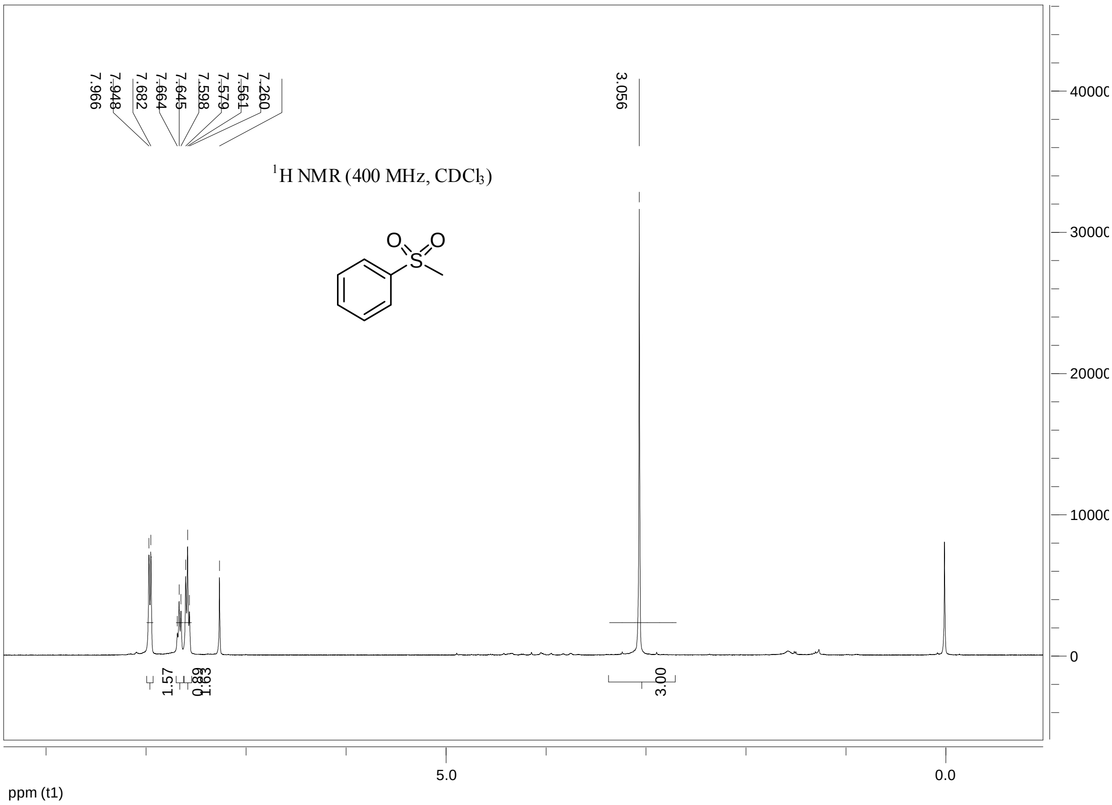
3. ^{1}H NMR and ^{13}C NMR charts for products

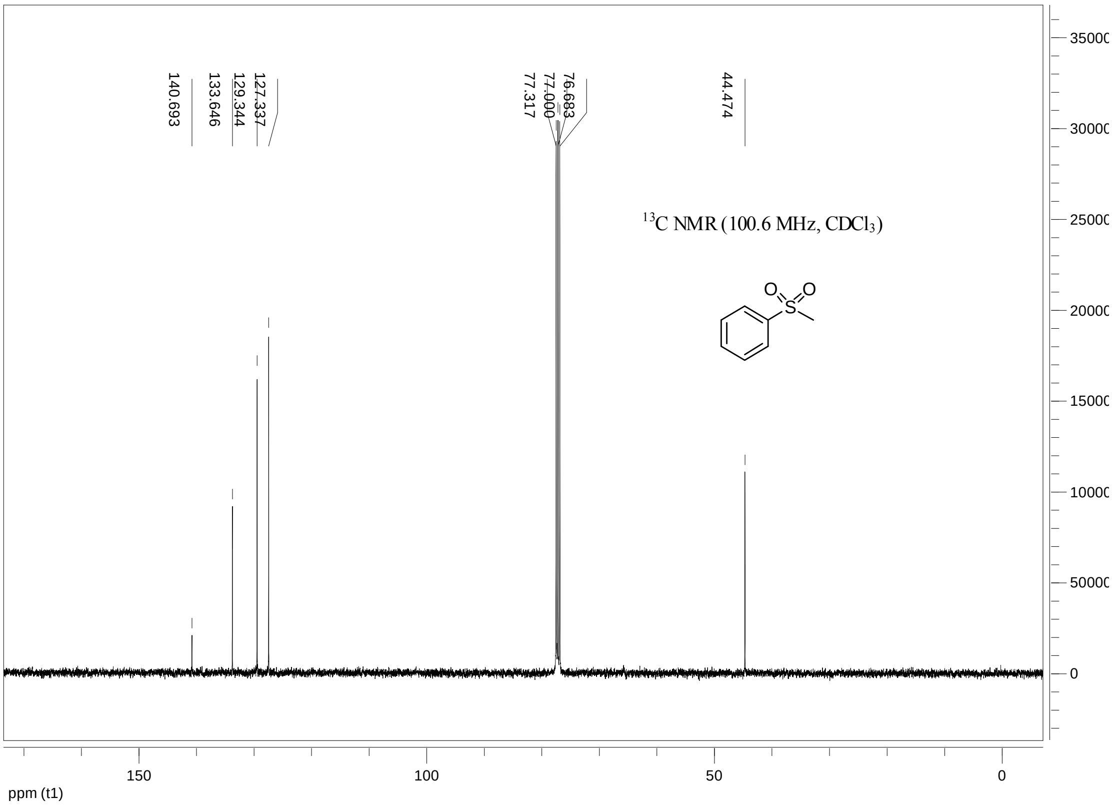
(Methylsulfinyl)benzene **2a**



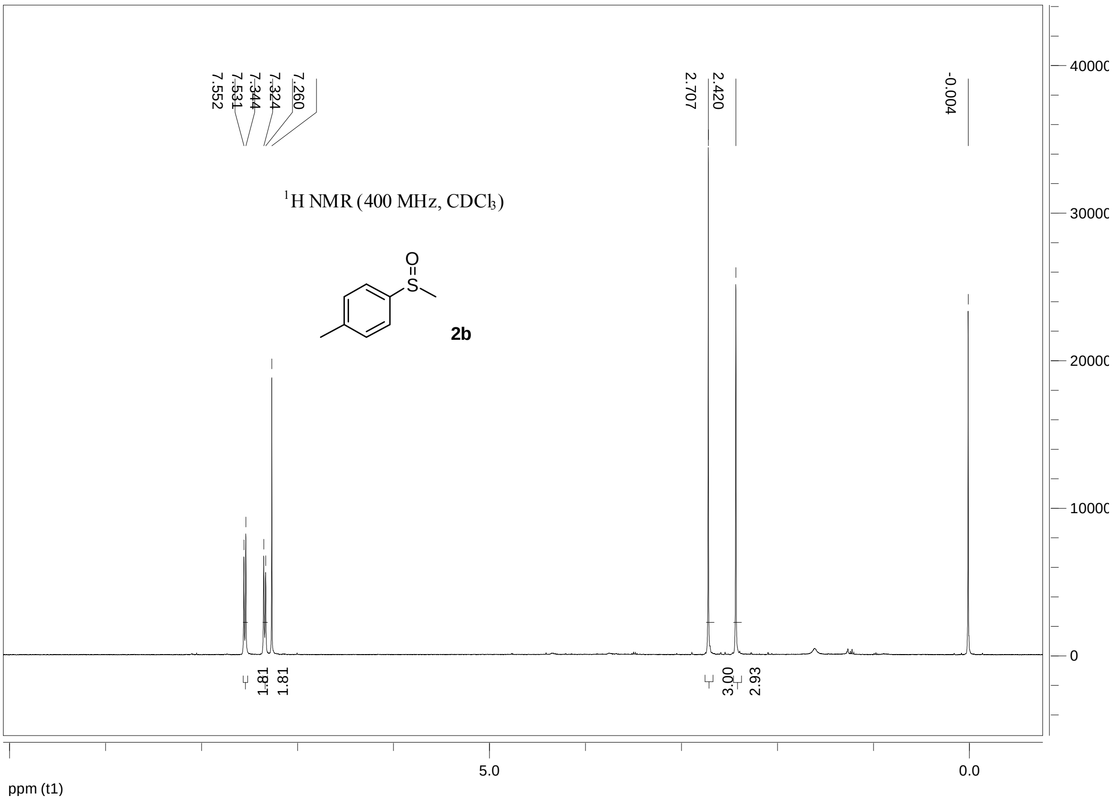


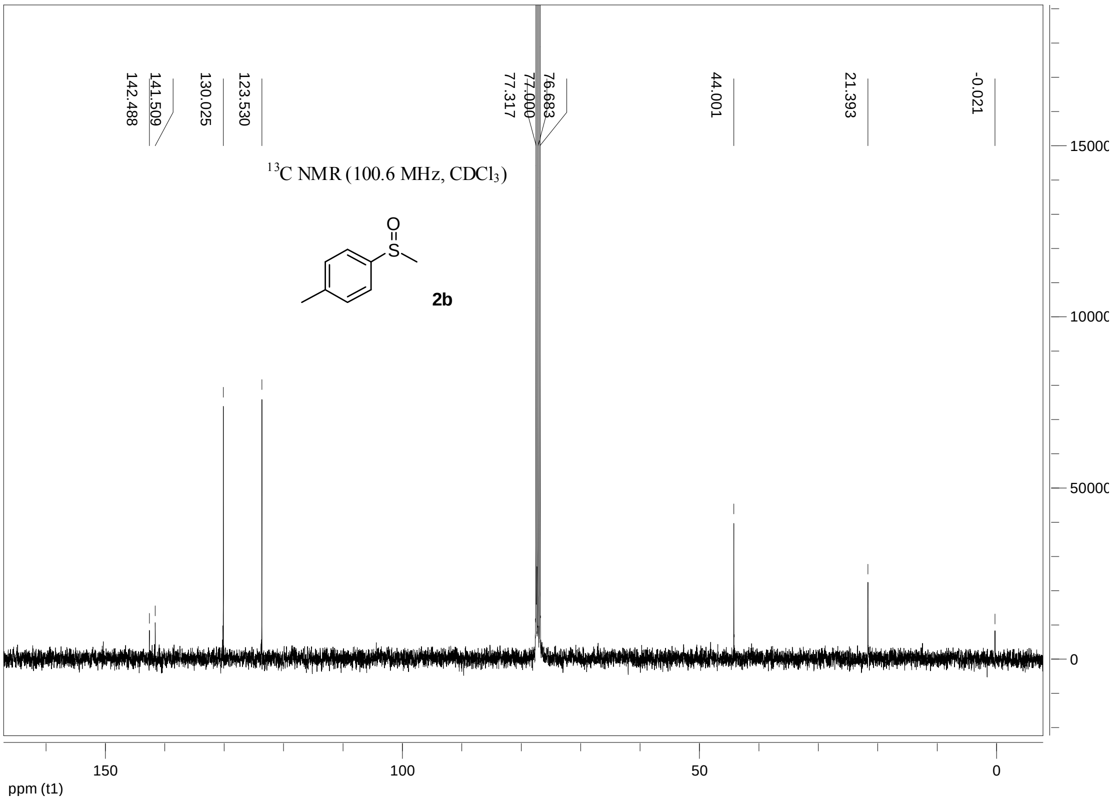
(Methylsulfonyl)benzene



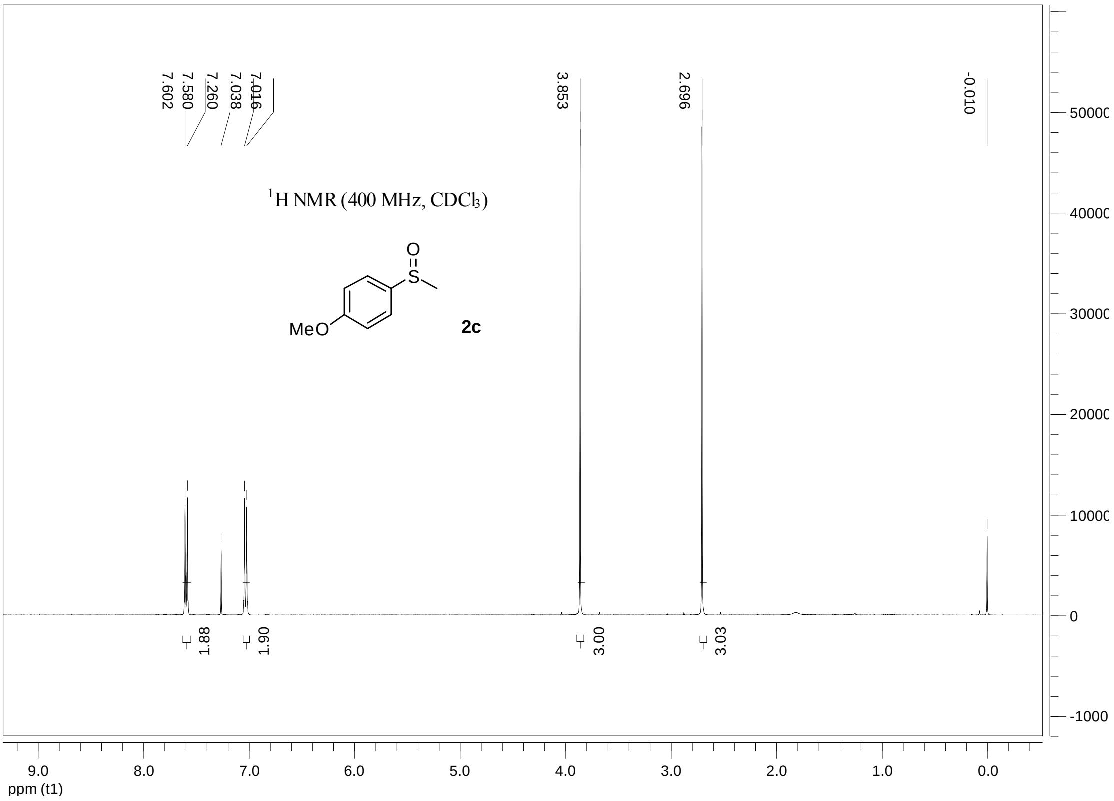


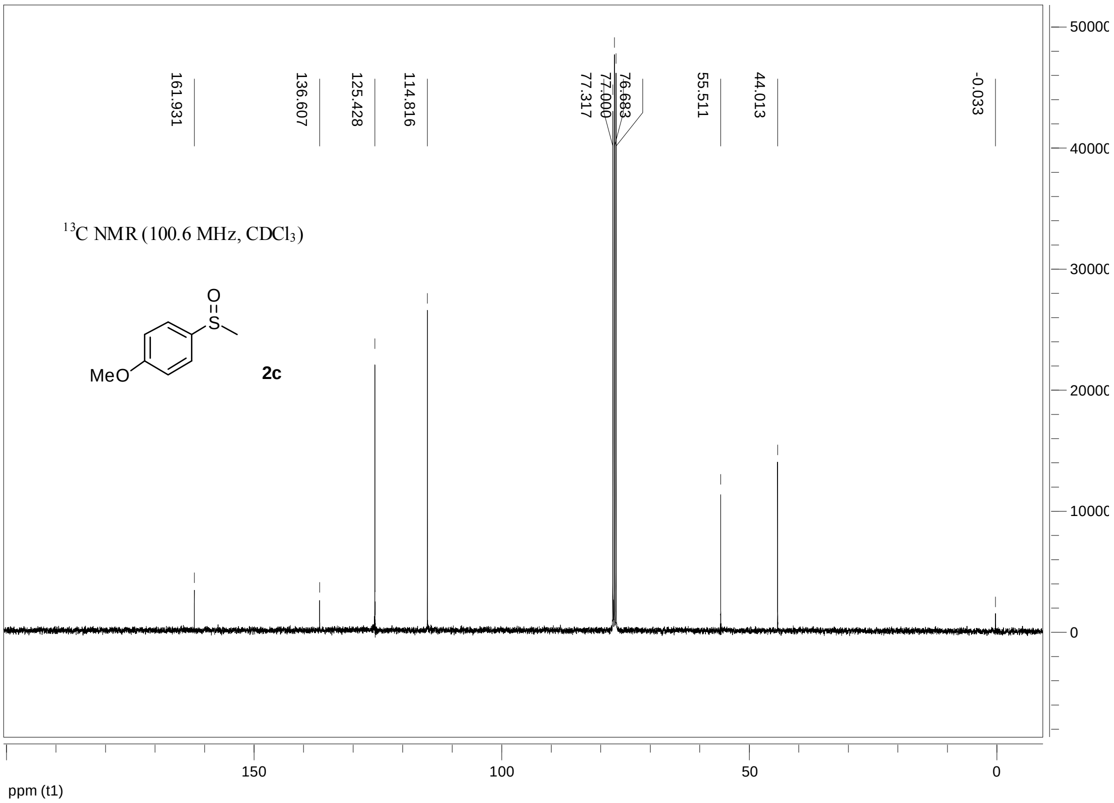
1-Methyl-4-(methylsulfinyl)benzene **2b**



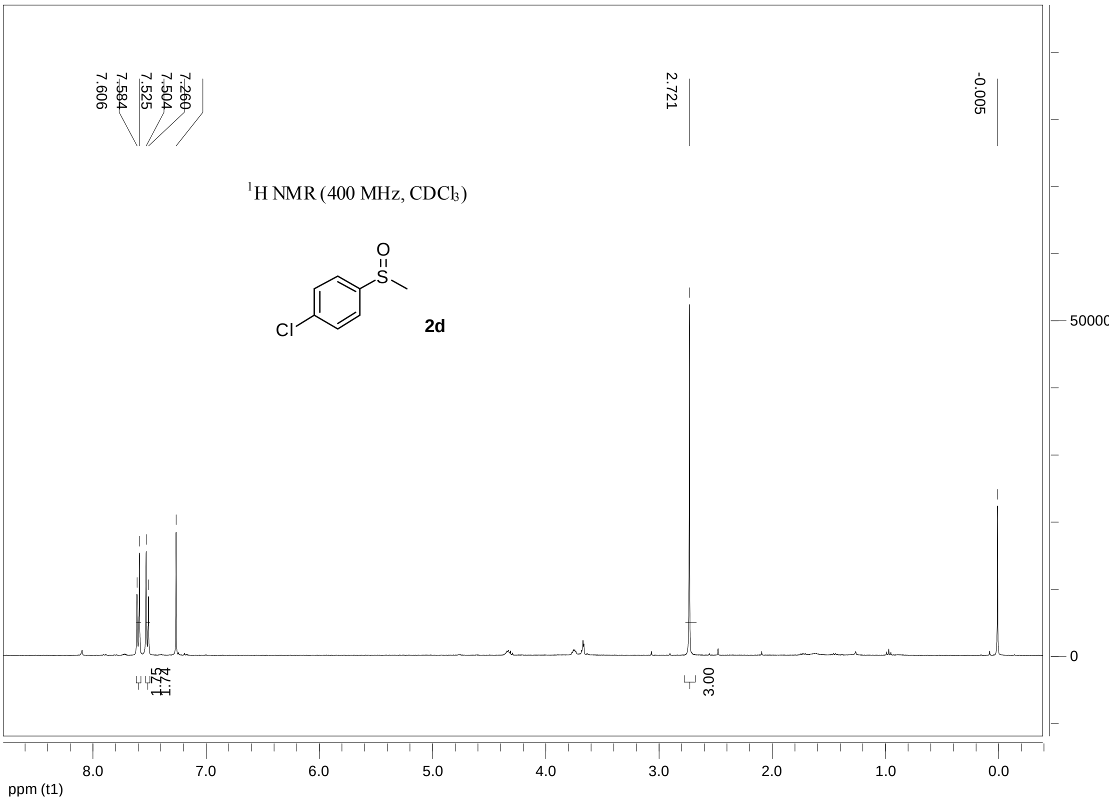


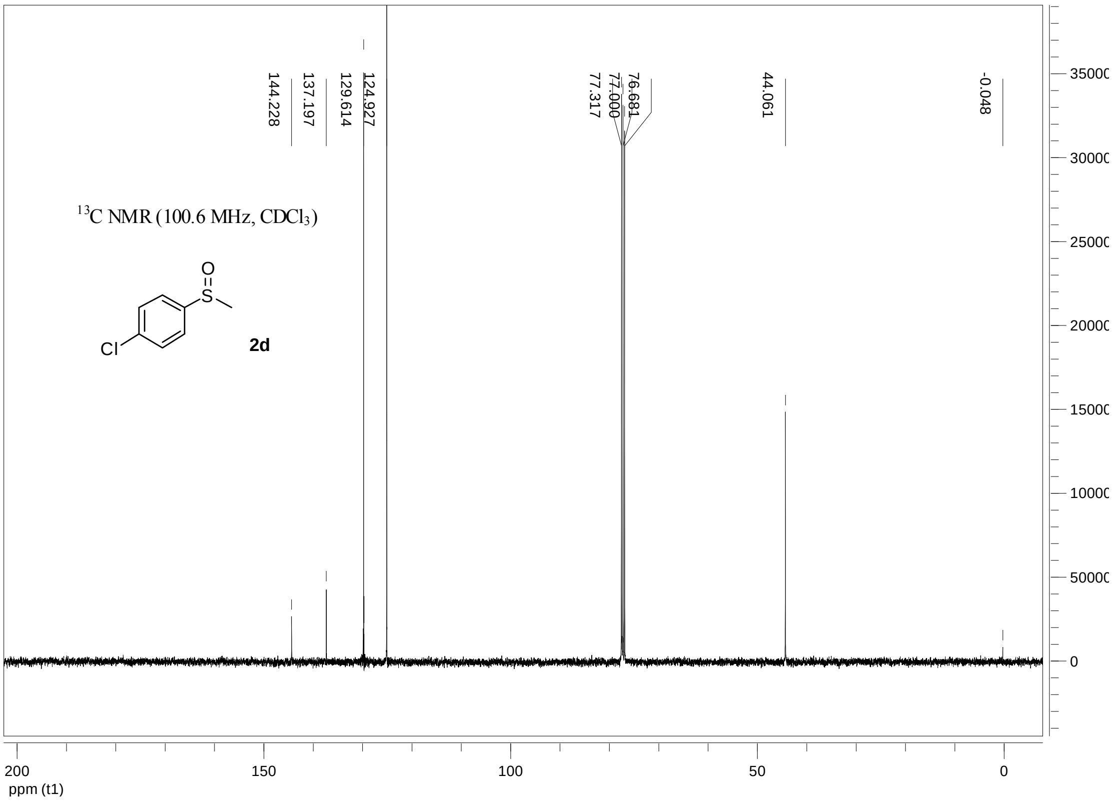
1-Methoxy-4-(methylsulfinyl)benzene **2c**



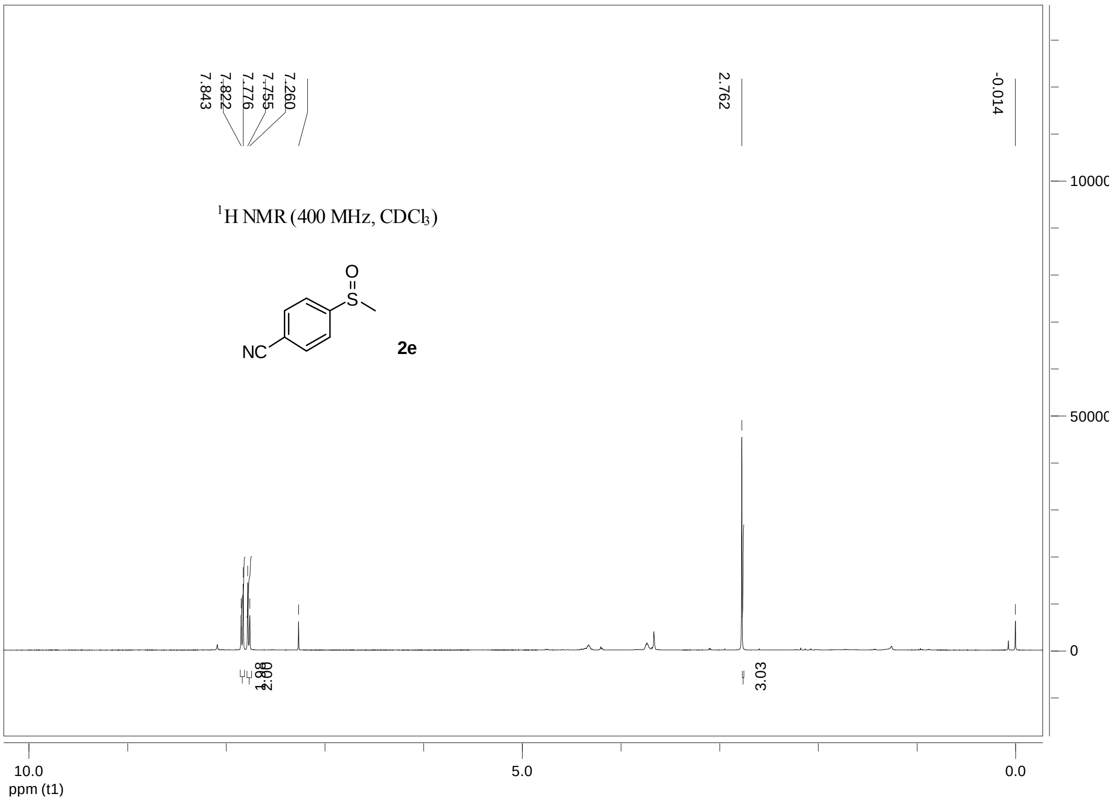


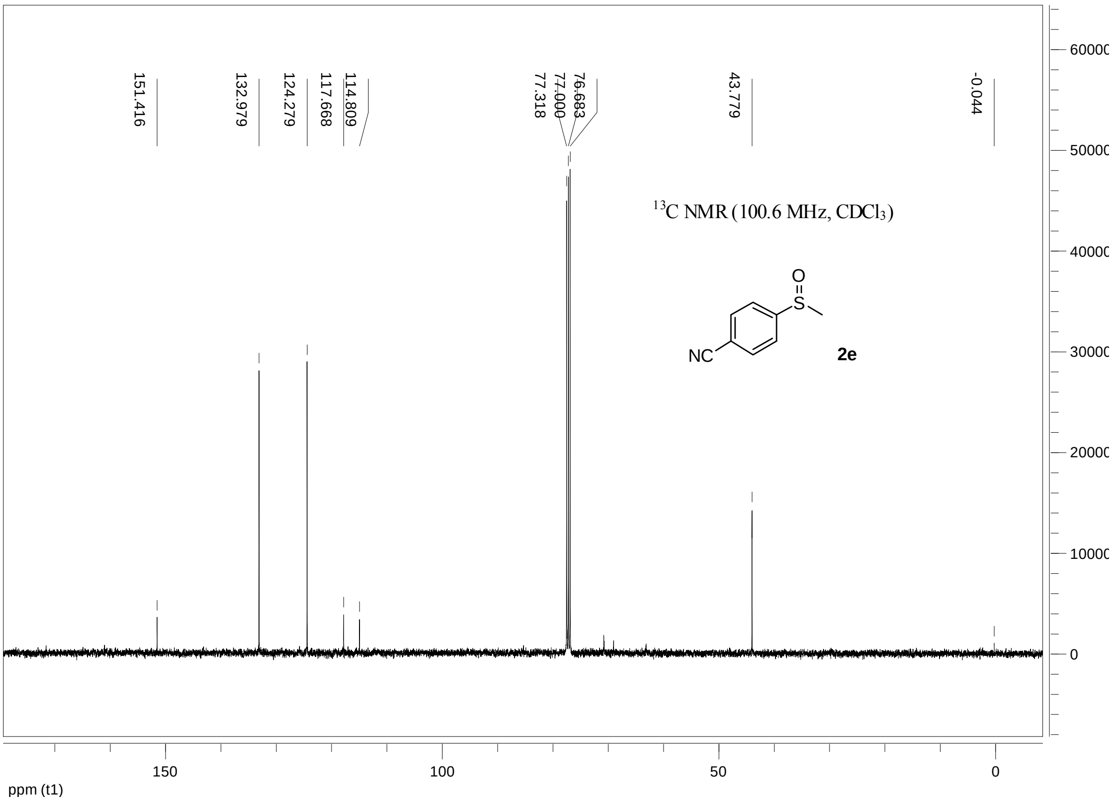
1-Chloro-4-(methylsulfinyl)benzene **2d**



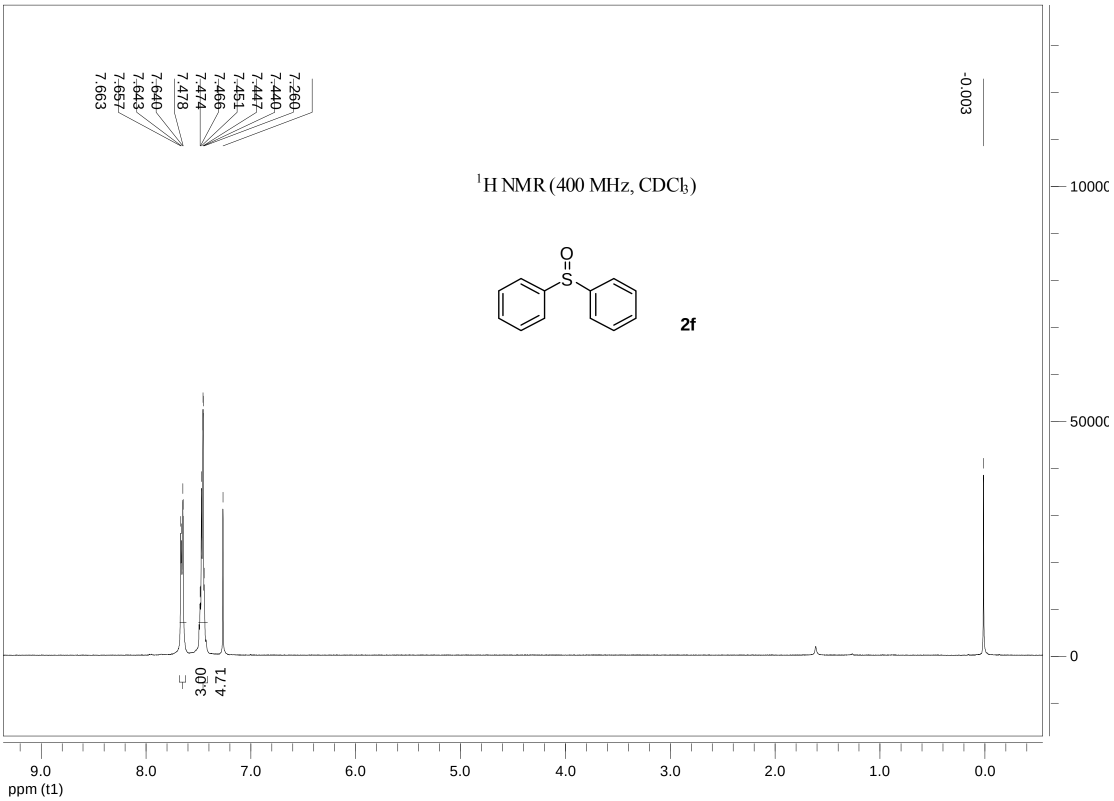


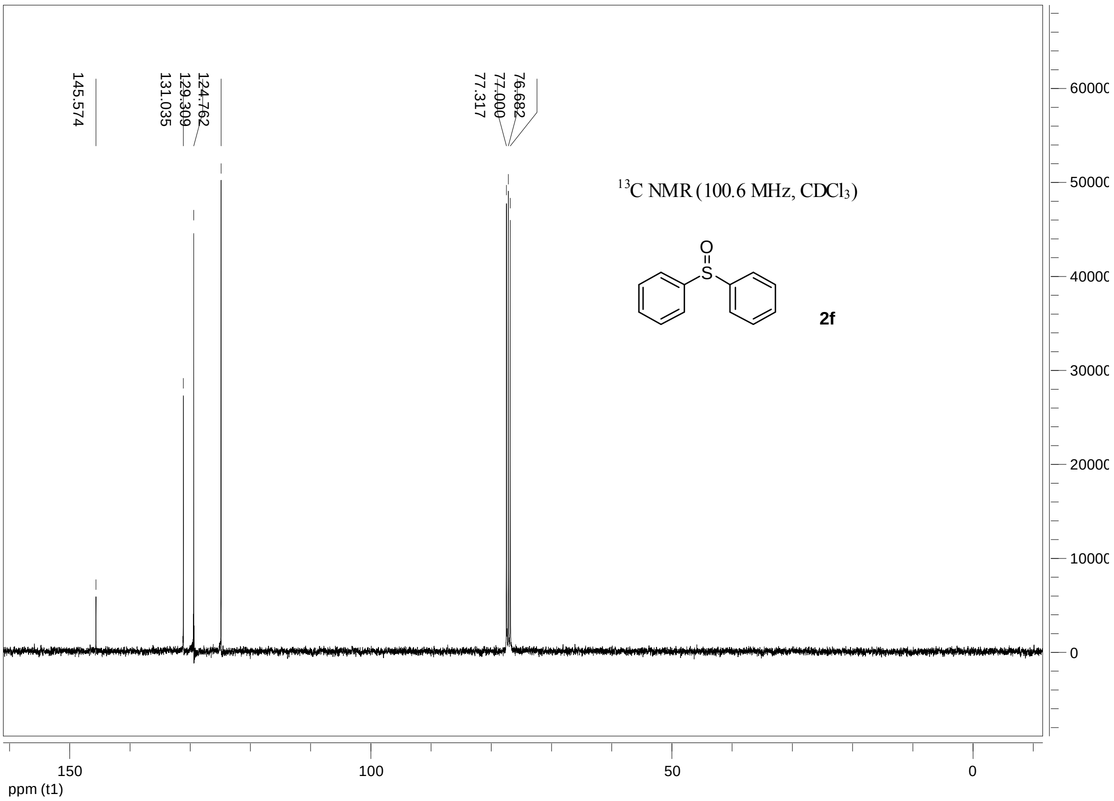
4-(Methylsulfinyl)benzonitrile **2e**



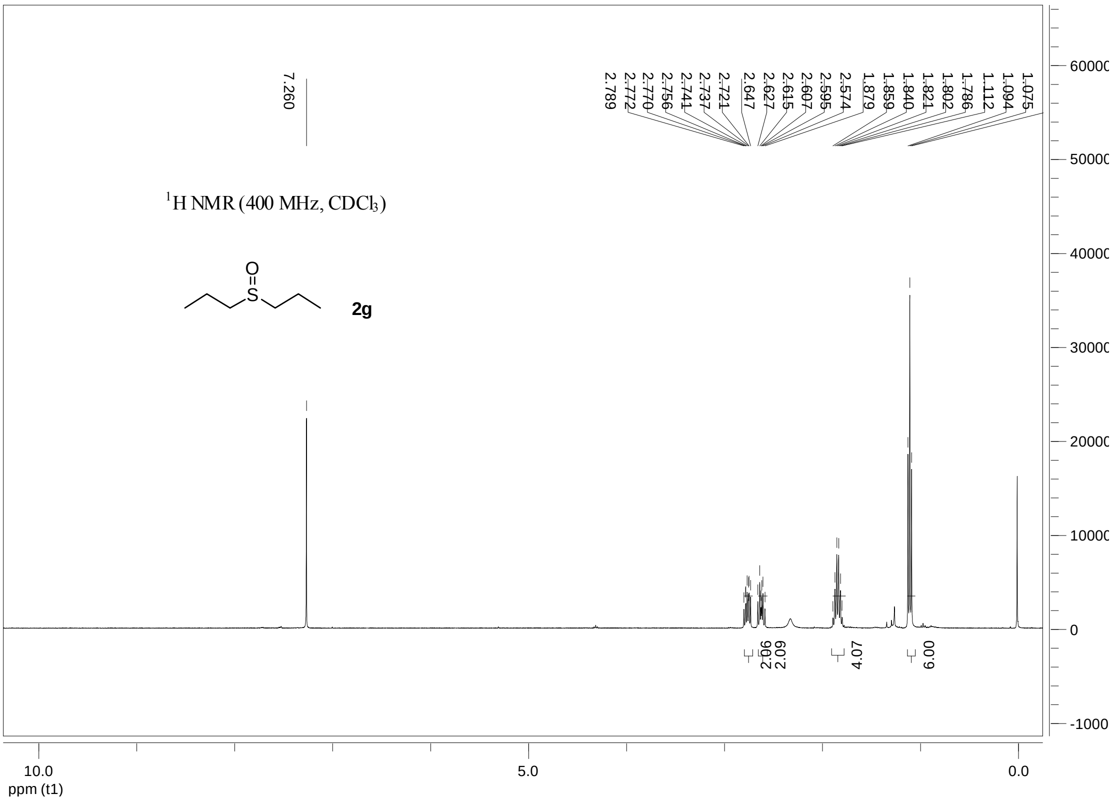


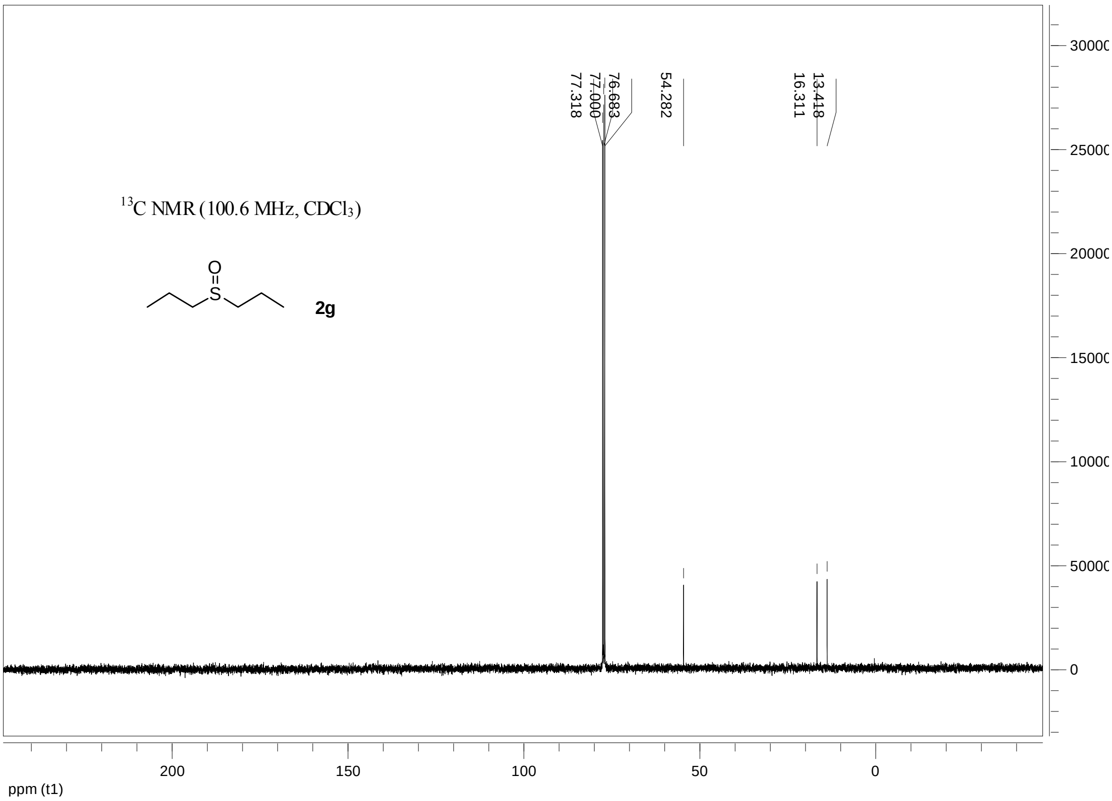
Sulfinyldibenzene **2f**



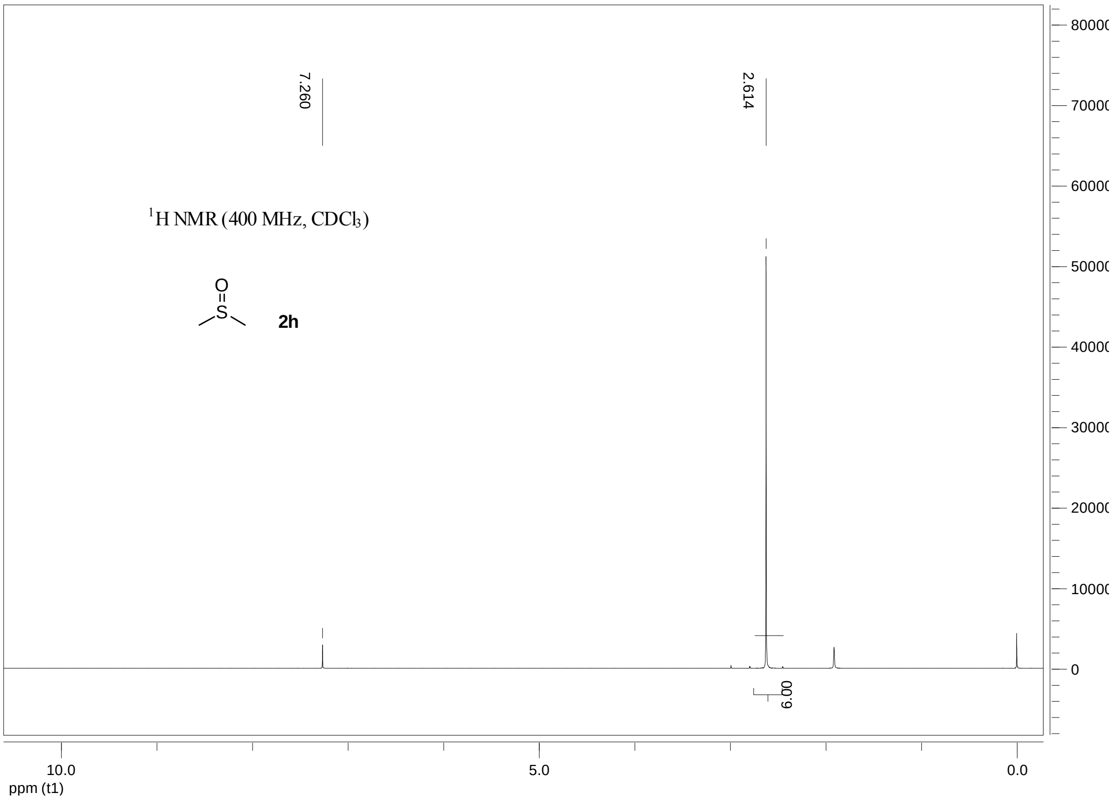


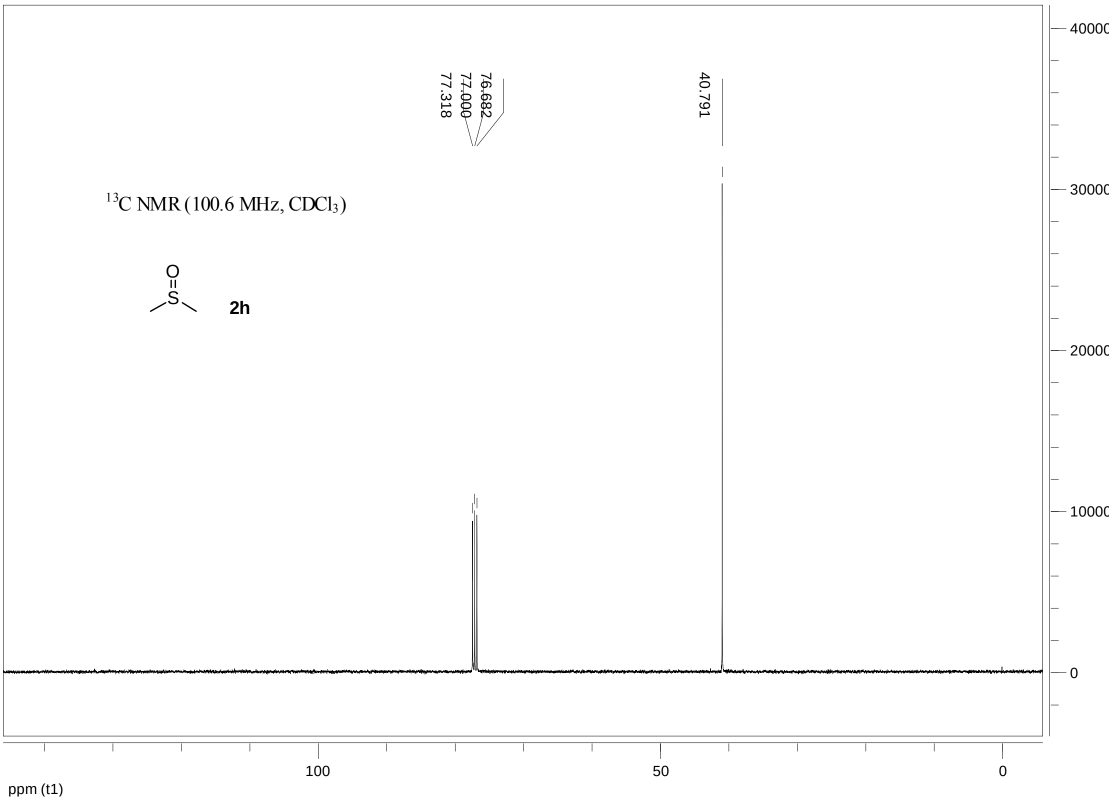
1-(Propylsulfinyl)propane **2g**





Dimethyl sulfoxide **2h**

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77.000
76.682
40.791
13C NMR (100.6 MHz, CDCl3)
O
S
2h
40000
30000
20000
10000
0
100
50
0
ppm (t1)