Supporting Information

A Simple Metal-free Catalytic Sulfoxidation under Visible Light and Air

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General Information:

All reactions were carried out in glassware opened to the air unless specified. Chemicals without special descriptions were obtained from commercial sources, and were used without further purification. 0.05 M HCl/EtOH stock solution was prepared by adding 0.417 ml conc. HCl (~12 N) to 100 ml EtOH. Column chromatography was generally performed on silica gel (300-400 mesh). Thin layer chromatography (TLC) was visualized using UV light. ^{1}H-NMR spectra were recorded on Varian mercury 300 and Varian mercury 400 spectrometers. Chemical shifts are reported in parts per million (δ) relative to TMS (0.0 ppm) for ^{1}H-NMR data and $CDCl_3$ (77.16 ppm) for ^{13}C-NMR data. The abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet, m=multiple, and br= broad signal. Mass spectra were measured on Agilent LC-MS 1260/6120 (ESI) mass spectrometer.

General procedure for homogeneous catalysis (A):

To a solution of 0.05 M HCl in EtOH (4 ml), Rose Bengal (2 mol %) and sulfide (1.0 mmol) was added. The reaction was placed at a distance of about 5 cm from a 14 W fluorescent lamp, and stirred at room temperature. After the reaction completion monitored by GC, the mixture was filtered through basic alumina powder (200-300 mesh) and rinsed with EtOH (30 ml). The filtrate was concentrated under vacuum to give the desired product without further purification unless pointed out.

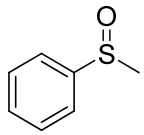
General procedure for solid-phase catalysis (B):

To a solution of 0.05 M HCl in EtOH (4 ml), polymer supported Rose Bengal (10 mol %) and sulfide (1.0 mmol) was added. The reaction was placed at a distance of about 5 cm from a 14 W fluorescent lamp, and stirred at room temperature. After the reaction completion monitored by GC, the mixture was filtered through a frit funnel and rinsed with EtOH (30 mL). The filtrate was concentrated under vacuum to give the desired product without further purification unless pointed out.

General procedure for recycling solid-phase catalysis:

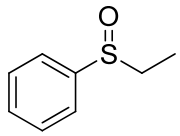
The procedure was similar to solid-phase catalysis. When the first oxidation finished, the mixture was filtered through frit funnel, and the catalyst was washed with EtOH. The recovered polymer supported Rose Bengal was directly used in the next reaction.

Methylsulfinylbenzene：



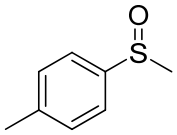
The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.54-7.50 (m, 3H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.50, 130.89, 129.21, 123.32, 43.80. MS (ESI) ($[M+H]^+$) 141.1.

Ethylsulfinylbenzene



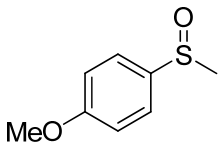
The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 2H), 7.51-7.49 (m, 3H), 2.95-2.86 (m, 1H), 2.80-2.71 (m, 1H), 1.18 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.94, 130.62, 128.84, 123.82, 49.90, 5.62. MS (ESI) ($[M+H]^+$) 155.0.

1-Methyl-4-(methylsulfinyl)benzene



The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.70 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.18, 141.16, 129.74, 123.23, 43.71, 21.12. MS (ESI) ($[M+H]^+$) 155.1.

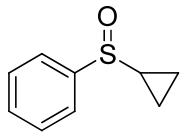
1-Methoxy-4-(methylsulfinyl)benzene



The title compound was prepared according to general procedure A and B.

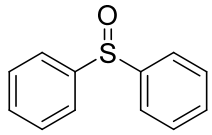
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.81, 136.37, 125.31, 114.71, 55.41, 43.84. MS (ESI) ($[M+H]^+$) 171.1.

Cyclopropylsulfinylbenzene



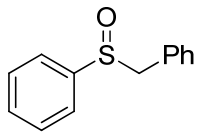
The title compound was prepared according to general procedure A and B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2H), 7.56-7.50 (m, 3H), 2.29-2.22 (m, 1H), 1.27-1.20 (m, 1H), 1.06-0.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.56, 130.60, 128.84, 123.65, 33.40, 3.11, 2.30. MS (ESI) ($[M+H]^+$) 167.1.

Sulfinyldibenzene



The title compound was prepared according to general procedure A and B. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.35-7.30 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.11, 130.48, 128.76, 124.05. MS (ESI) ($[M+H]^+$) 203.1.

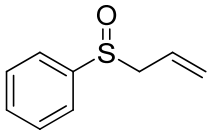
Benzylsulfinylbenzene



The title compound was prepared according to general procedure A and B. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5H), 7.23-7.17 (m, 3H), 6.95 (d, *J* = 7.1 Hz, 2H), 4.02 (d, *J* = 12.6 Hz, 1H), 3.97 (d, *J* = 12.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.37,

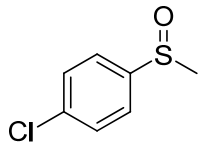
130.77, 130.01, 128.80, 128.49, 128.03, 127.84, 124.01, 62.99. MS (ESI) ($[M+H]^+$) 217.0.

Allylsulfinylbenzene



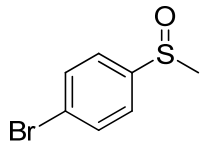
The title compound was prepared according to general procedure A and B. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.52-7.51 (m, 3H), 5.72-5.59 (m, 1H), 5.33 (d, *J* = 9.5 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 3.62-3.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.64, 130.83, 128.78, 125.00, 124.04, 123.58, 60.50. MS (ESI) ($[M+H]^+$) 167.1.

1-Chloro-4-(methylsulfinyl)benzene



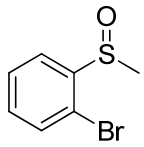
The title compound was prepared according to general procedure A and B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.52-7.49 (m, 2H), 2.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.03, 136.85, 129.36, 124.77, 43.76. MS (ESI) ($[M+H]^+$) 175.0.

1-Bromo-4-(methylsulfinyl)benzene



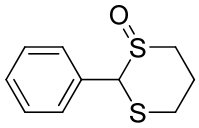
The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.63 (m, 2H), 7.60-7.48 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.77, 132.46, 125.32, 125.08, 43.91. MS (ESI) ($[M+H]^+$) 219.0.

1-Bromo-2-(methylsulfinyl)benzene



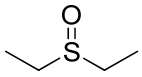
The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.60-7.54 (m, 2H), 7.37 (m, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.09, 132.83, 132.23, 128.66, 125.54, 118.30, 41.77. MS (ESI) ($[M+H]^+$) 219.0.

2-Phenyl-1, 3-dithiane 1-oxide



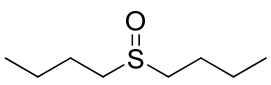
The title compound was prepared according to general procedure A and B. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 5H), 4.55 (s, 1H), 3.58-3.55 (m, 1H), 2.92-2.85 (m, 1H), 2.79-2.66 (m, 2H), 2.54-2.50 (m, 1H), 2.42-2.35 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.26, 129.10, 128.89, 128.54, 69.31, 54.54, 31.13, 29.33. MS (ESI) ($[M+H]^+$) 213.0.

Ethylsulfinylethane



The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74-2.67 (m, 4H), 1.34 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.82, 6.74. MS (ESI) ($[M+H]_+$) 107.1.

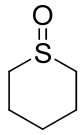
1-(Butylsulfinyl)butane



The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73-2.62 (m, 4H), 1.80-1.72 (m, 4H),

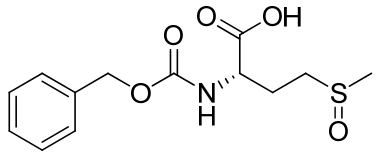
1.57-1.42 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 51.80, 24.30, 21.75, 13.40. MS (ESI) ($[M+H]^+$) 163.1.

Thiane 1-oxide



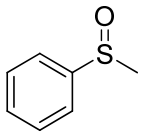
The title compound was prepared according to general procedure A and B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92-2.86 (m, 2H), 2.78-2.74 (m, 2H), 2.24-2.22 (m, 2H), 1.69-1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 48.27, 24.13, 18.47. MS (ESI) ($[M+H]^+$) 119.1.

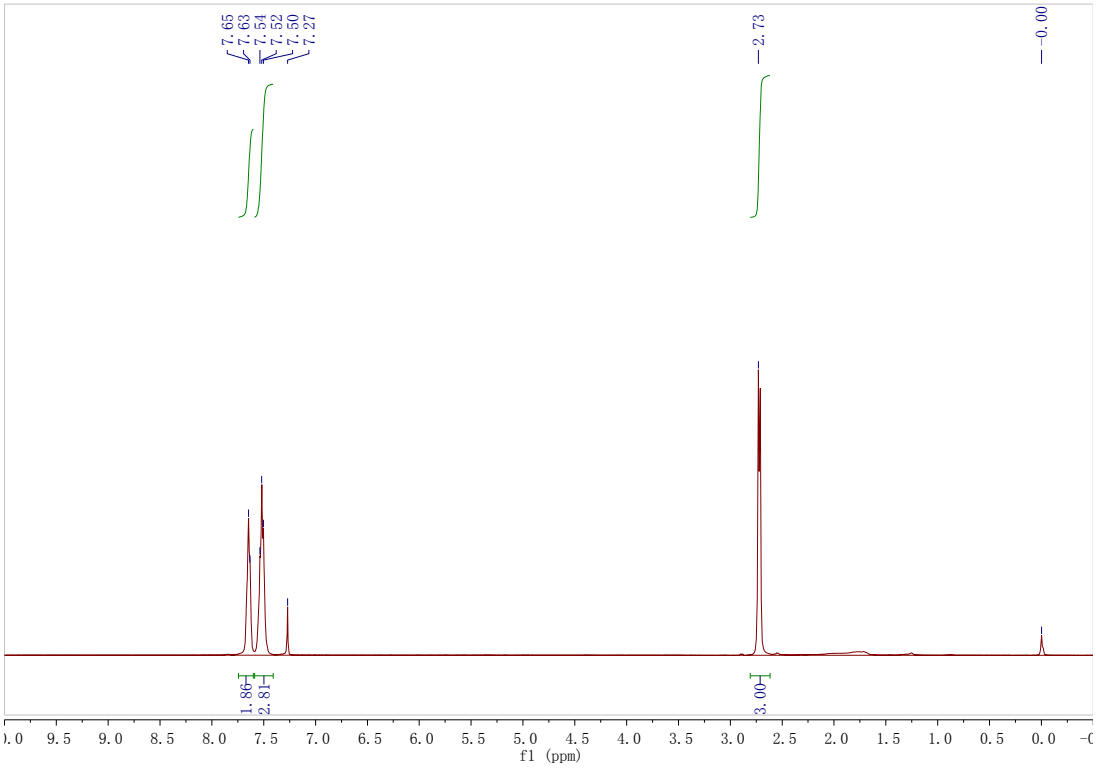
(2S)-2-(benzyloxycarbonylamino)-4-(methylsulfinyl)butanoic acid

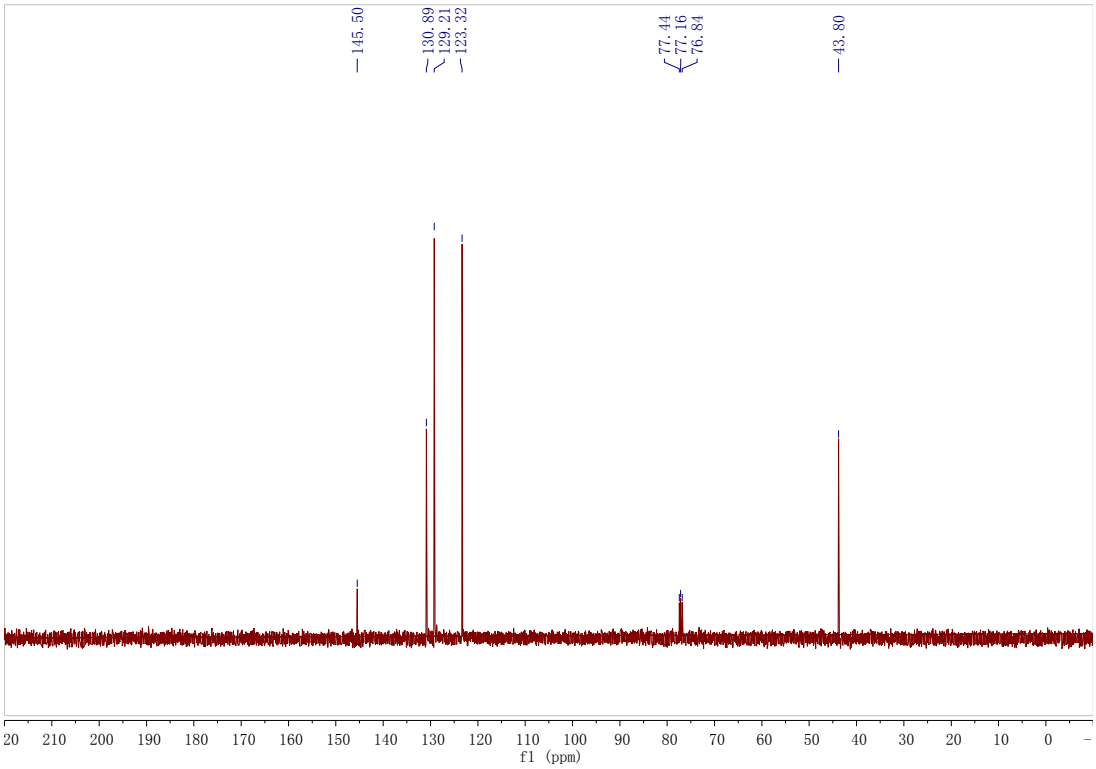


A mixture of diastereomers of the title compound was prepared according to general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (br, 1H), 7.29 (s, 5H), 6.73-6.32 (m, 1H), 5.05 (s, 2H), 4.39 (s, 1H), 2.95-2.62 (m, 2H), 2.51-2.49 (m, 3H), 2.28 (s, 1H), 2.11 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.29, 156.24, 136.10, 128.39, 128.05, 127.98, 66.86, 52.91, 52.63, 49.16, 49.07, 37.14, 37.08, 25.47, 25.20. MS (ESI) ($[M+H]^+$) 300.0.

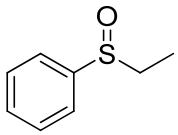
Methylsulfinylbenzene:

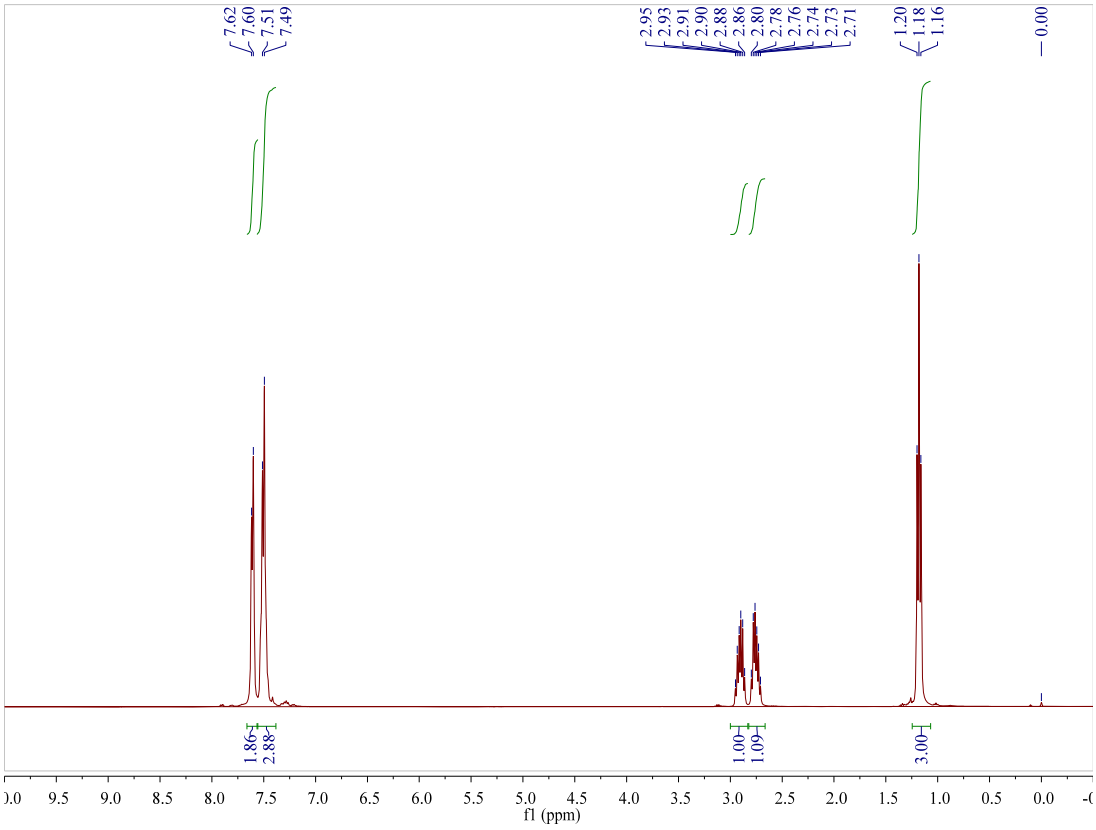


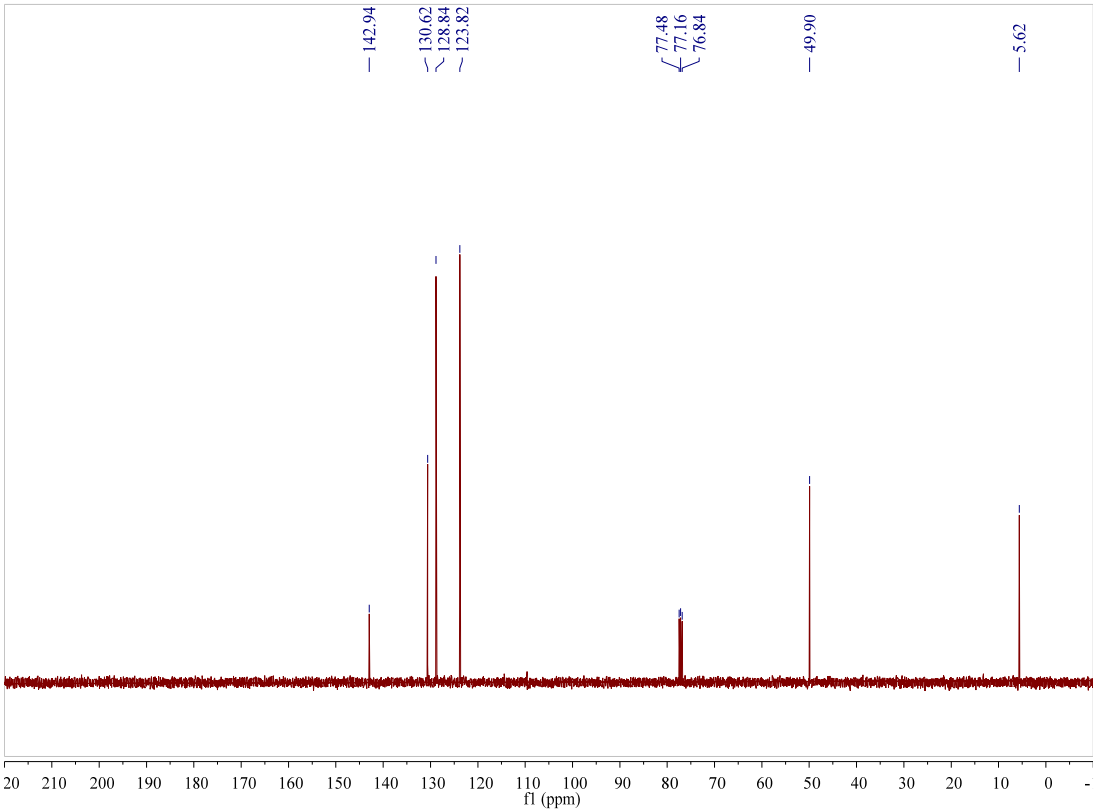




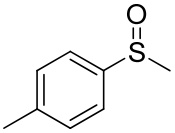
Ethylsulfinylbenzene

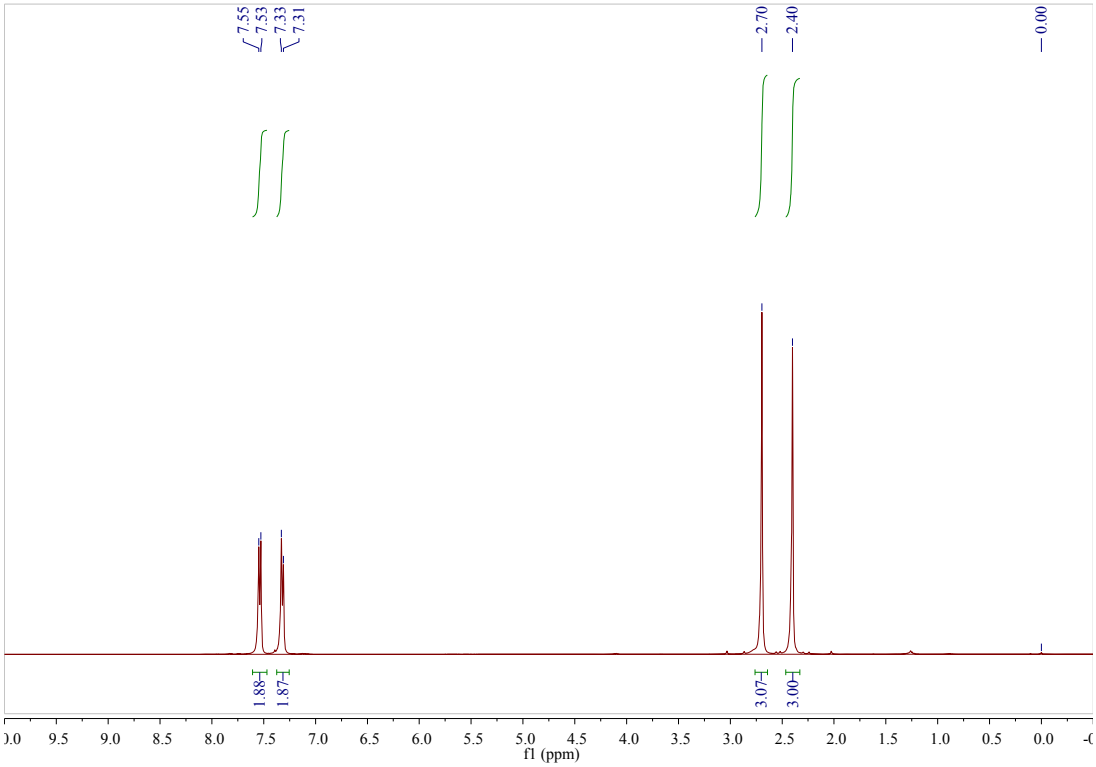


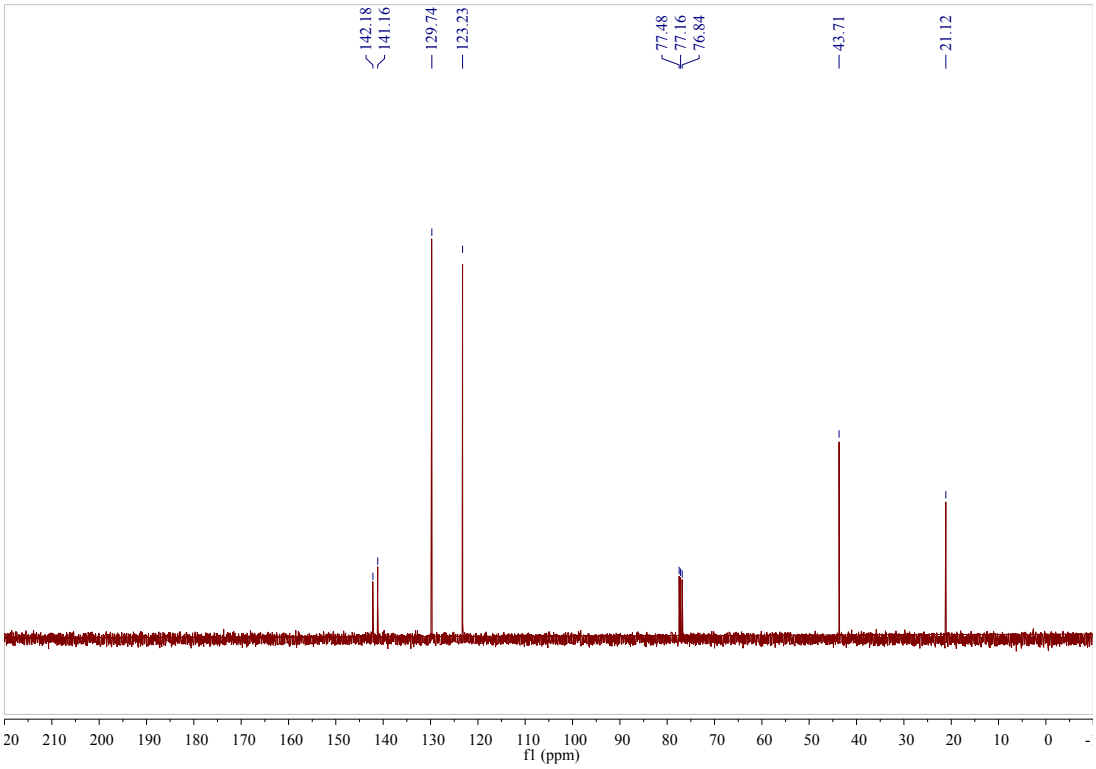




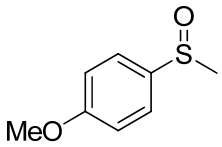
1-Methyl-4-(methylsulfinyl)benzene

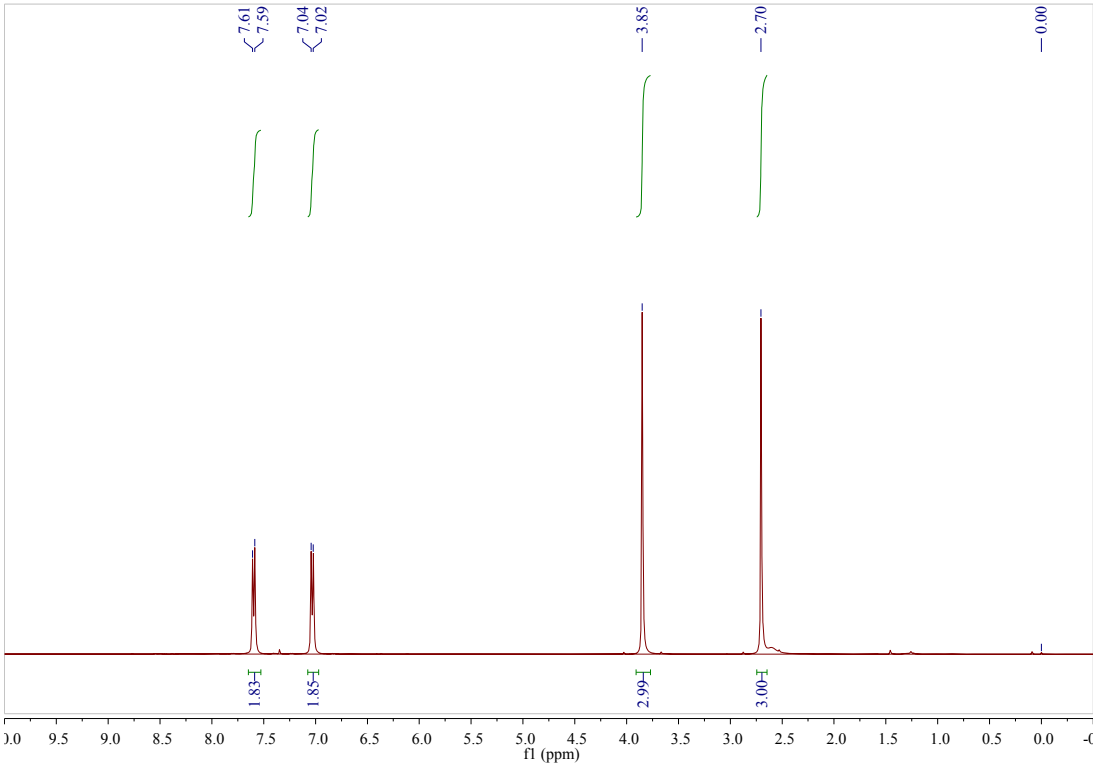


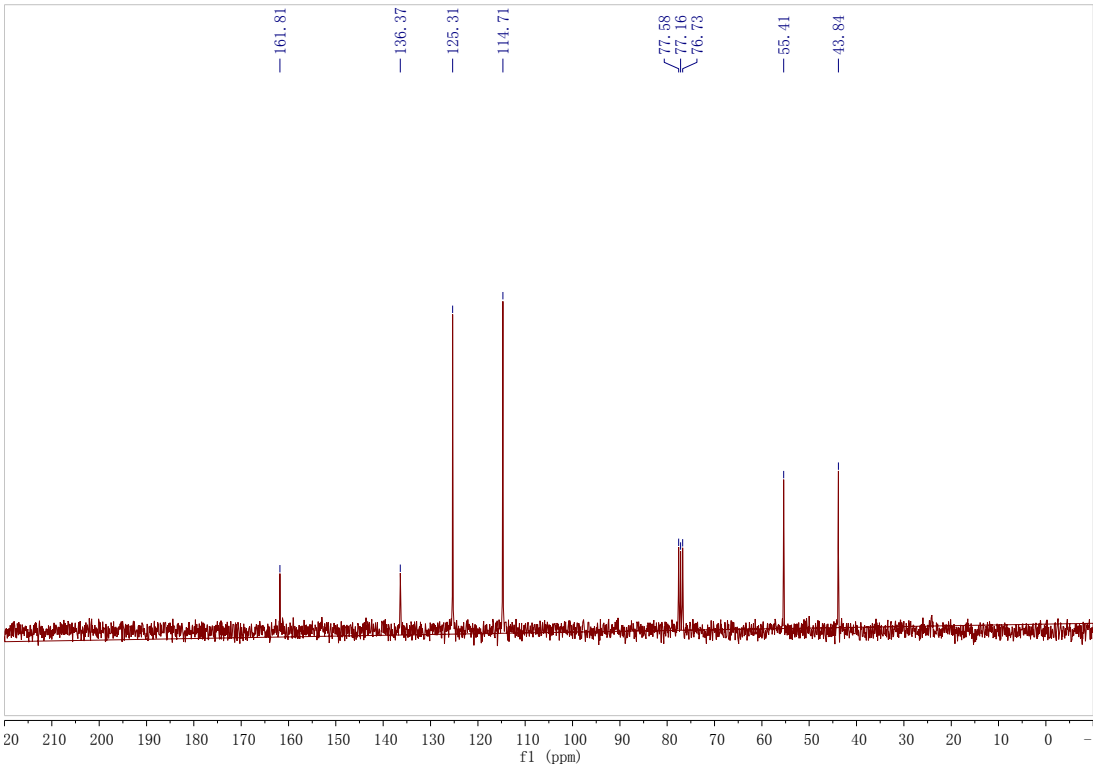




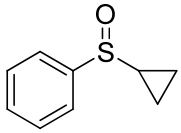
1-Methoxy-4-(methylsulfinyl)benzene

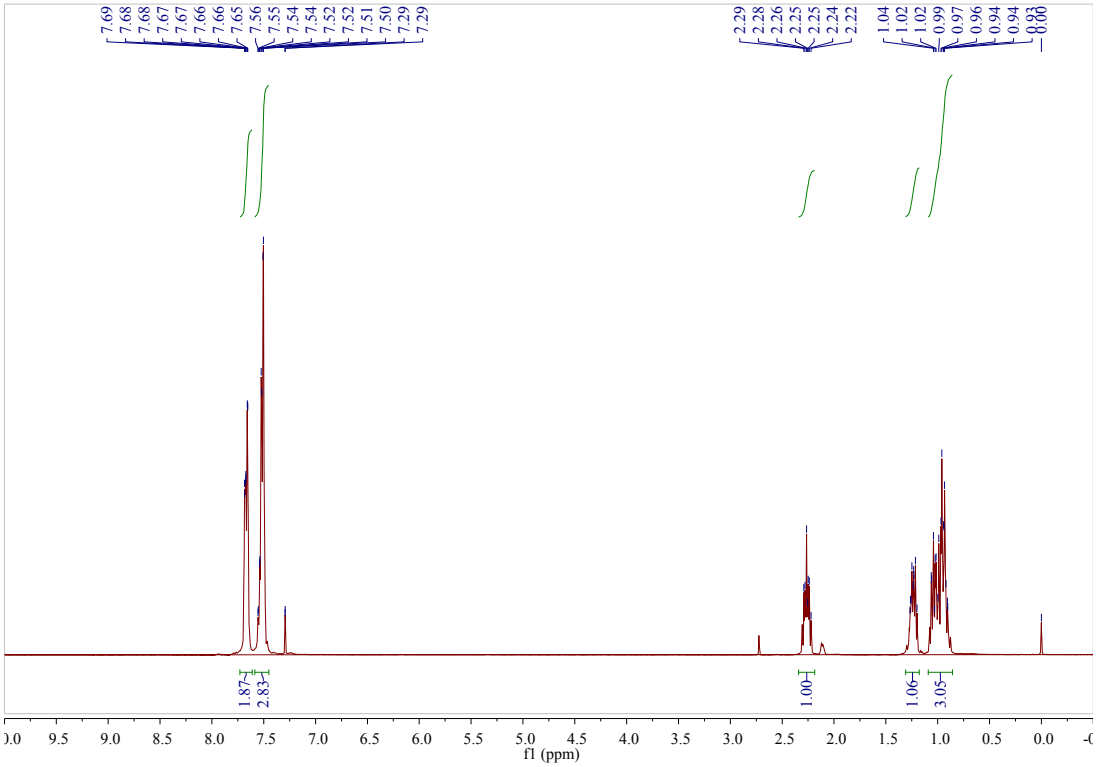


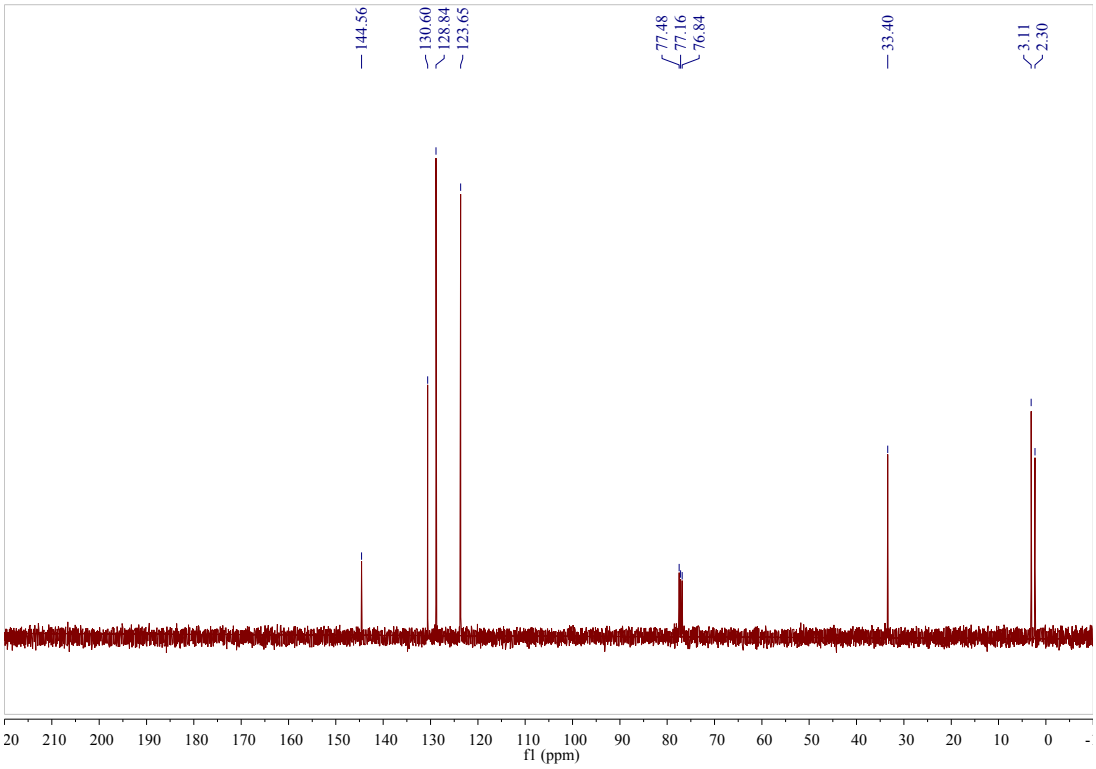




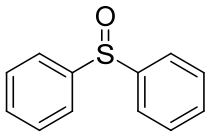
Cyclopropylsulfinylbenzene

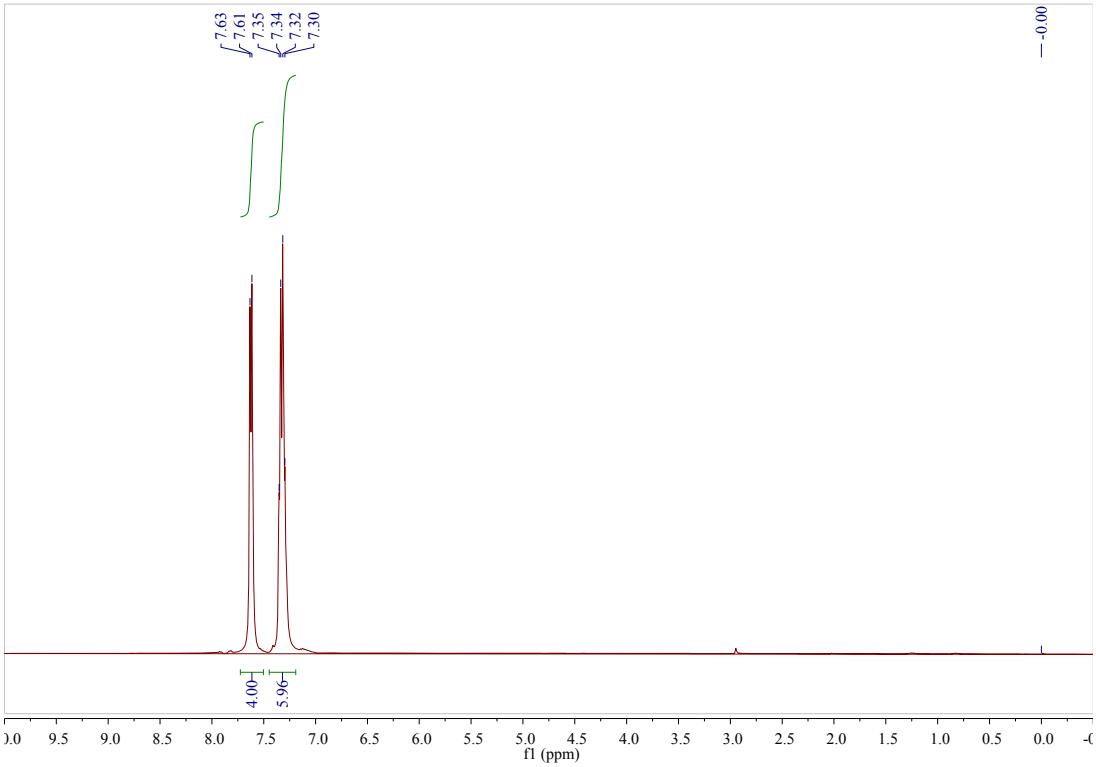


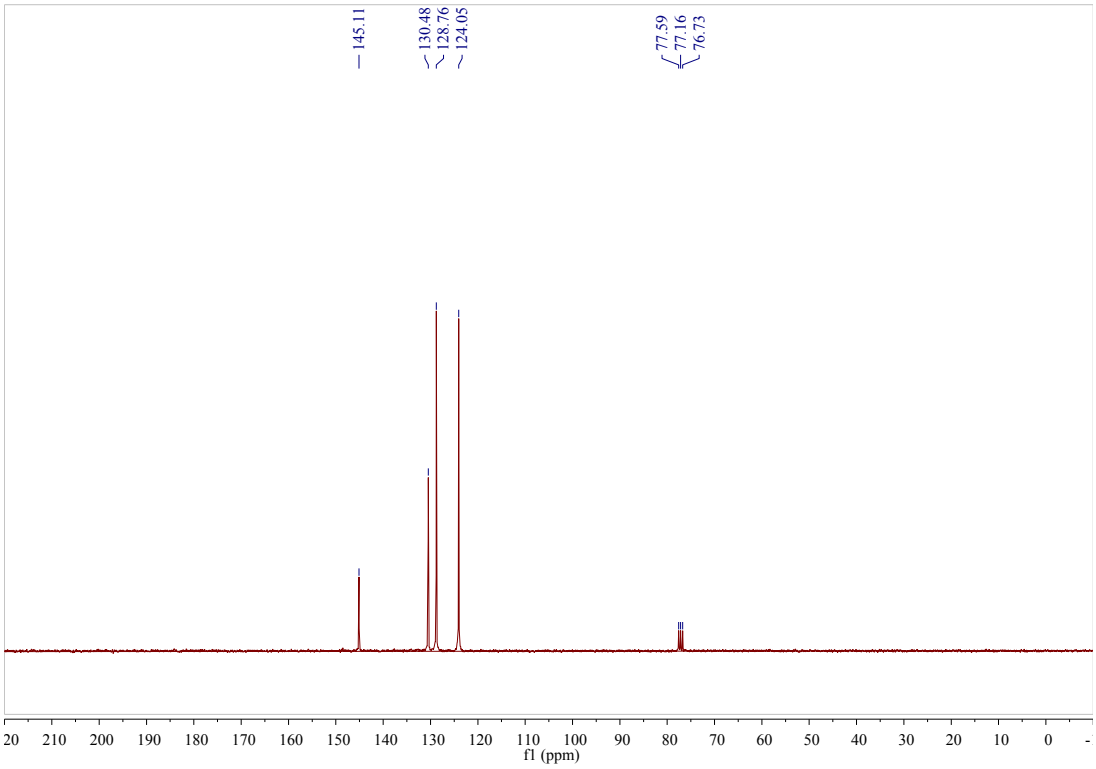




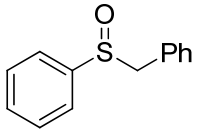
Sulfinyldibenzene

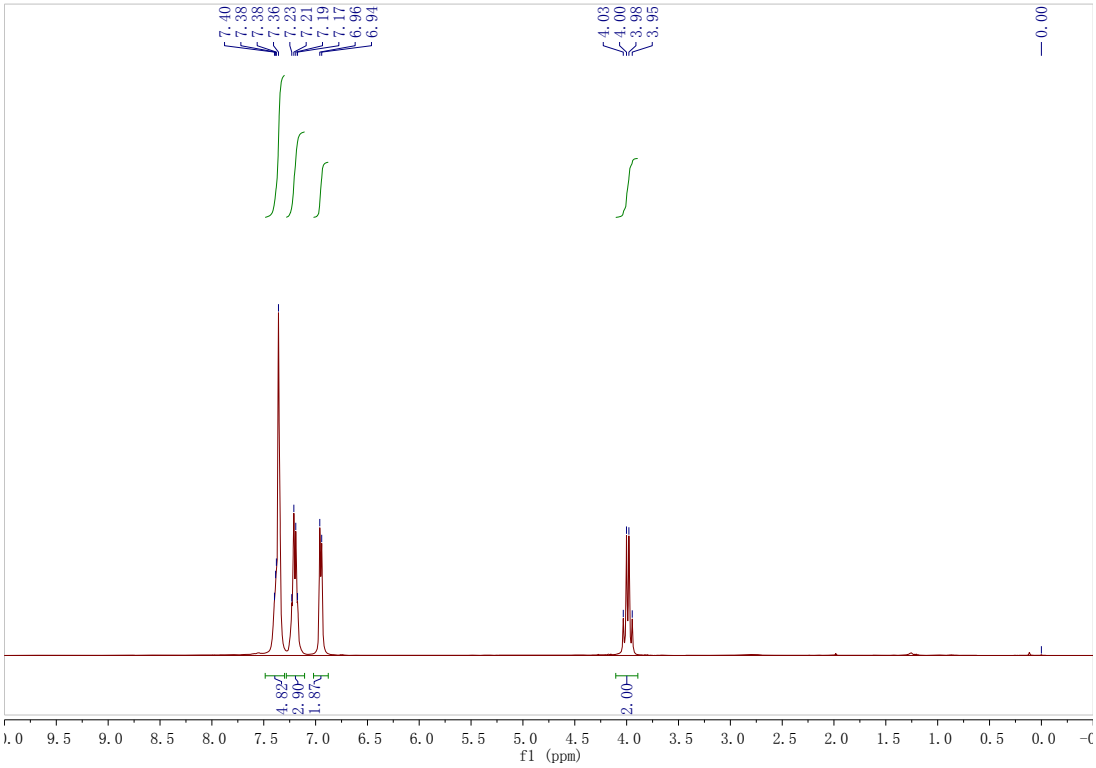


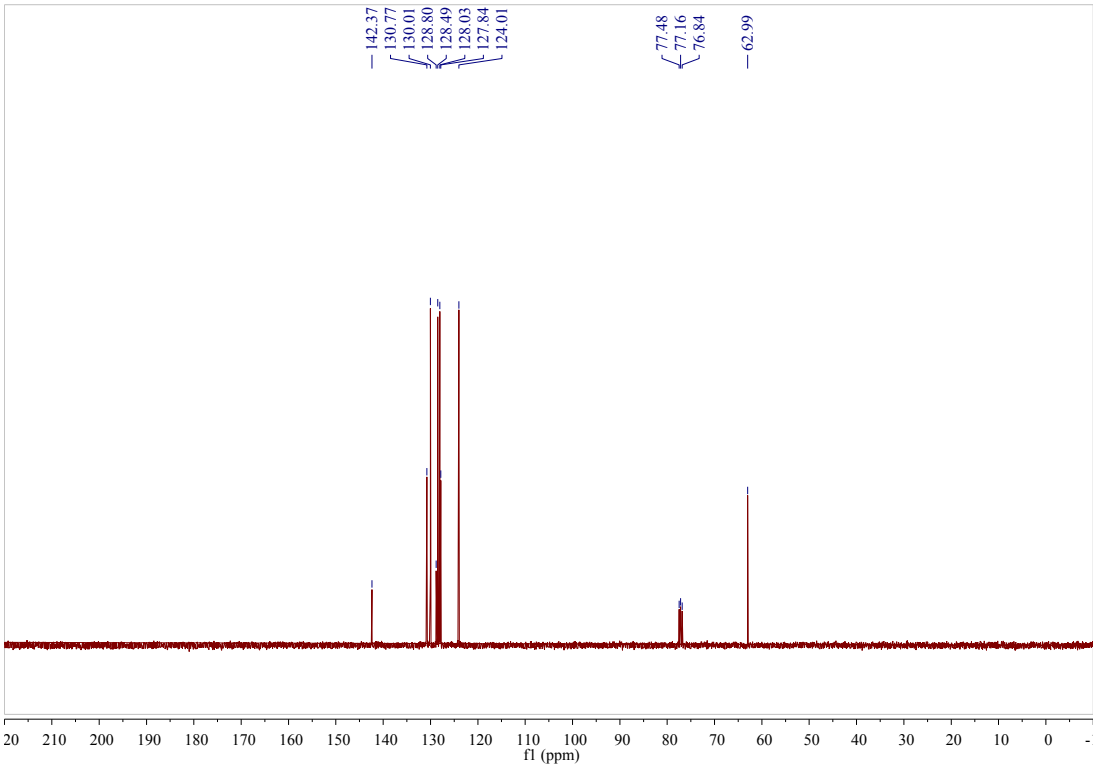




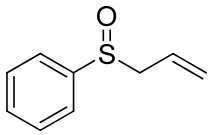
Benzylsulfinylbenzene

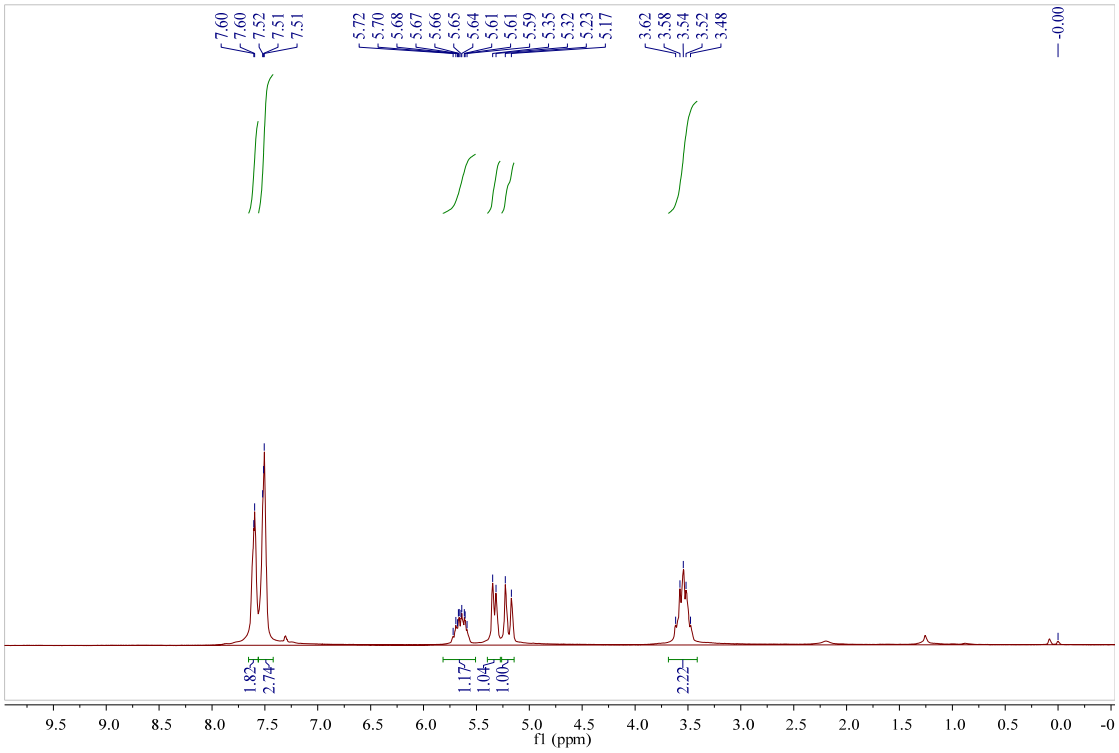


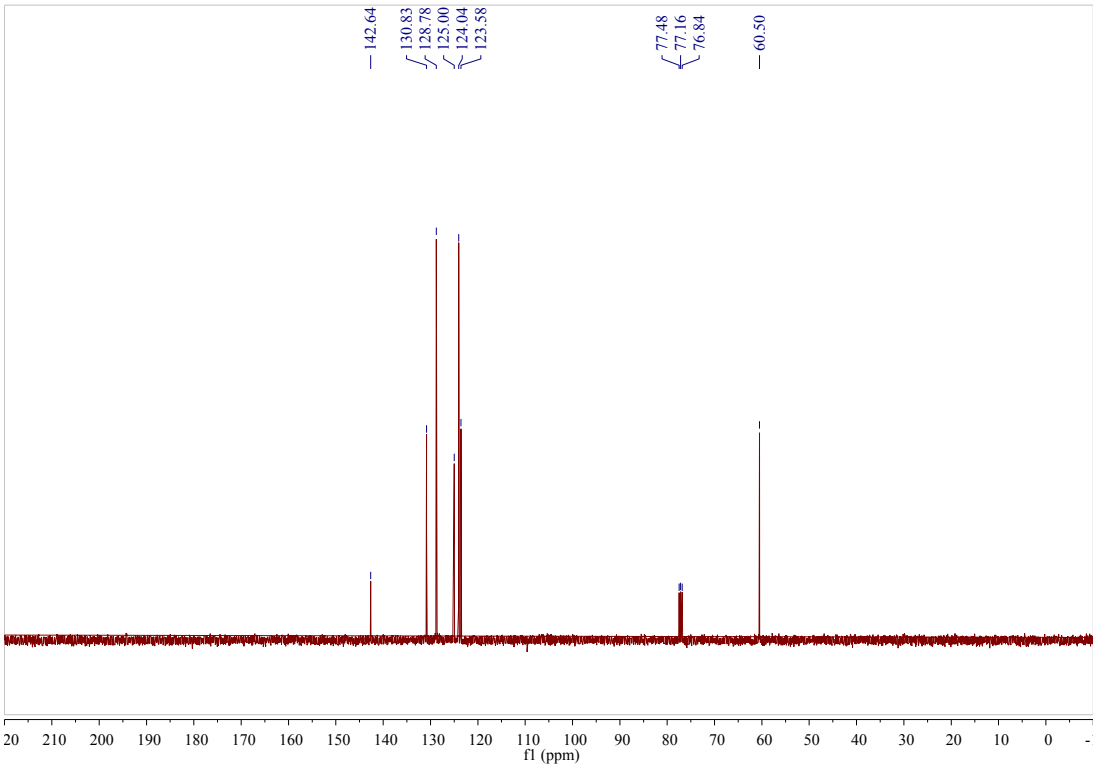




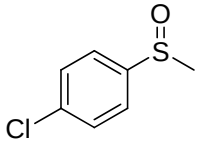
Allylsulfinylbenzene

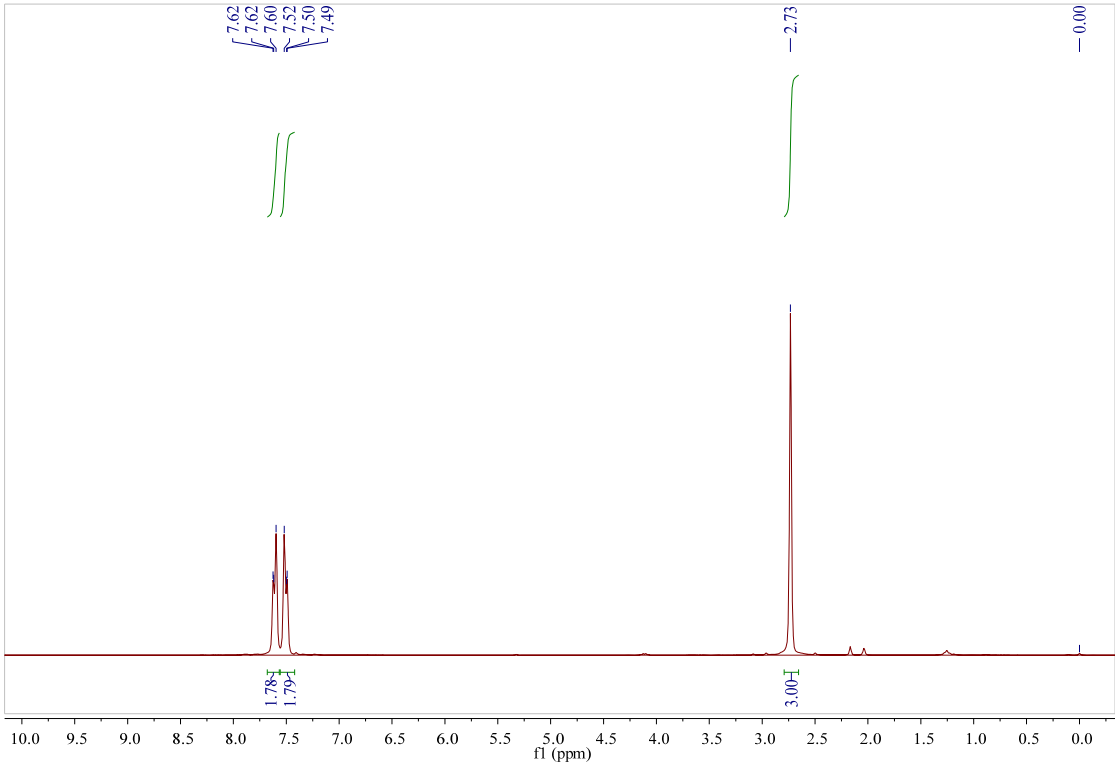


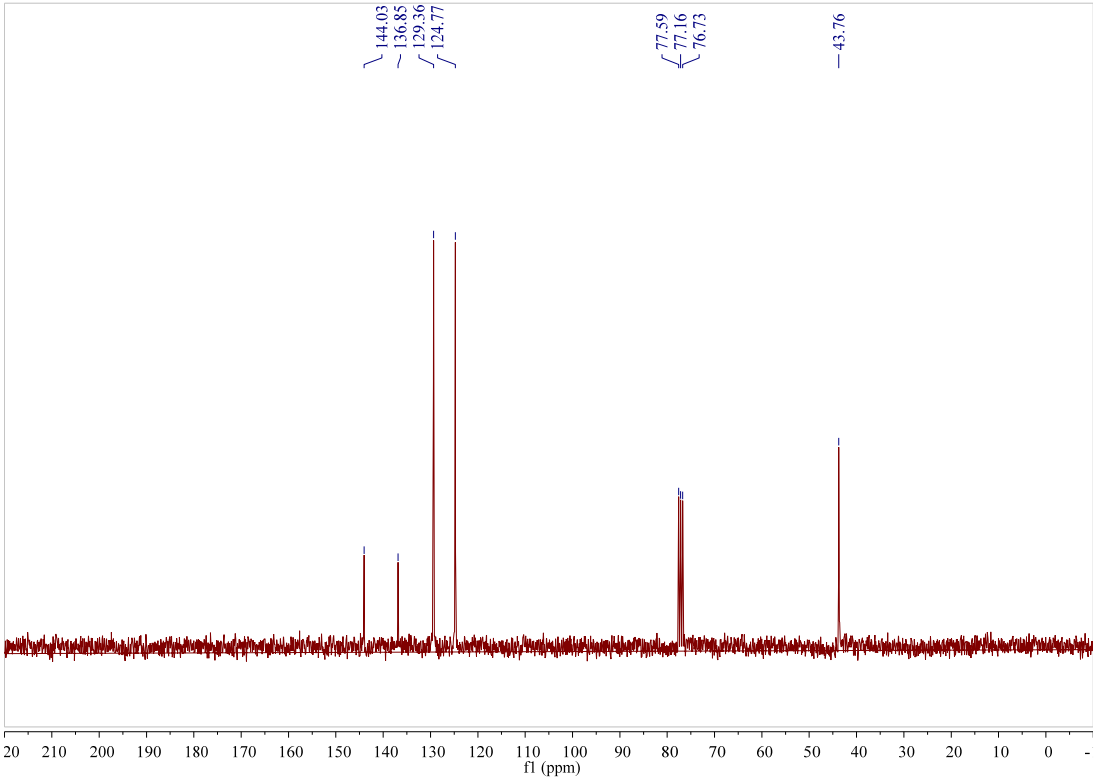




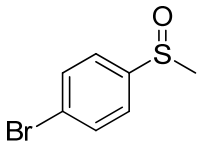
1-Chloro-4-(methylsulfinyl)benzene

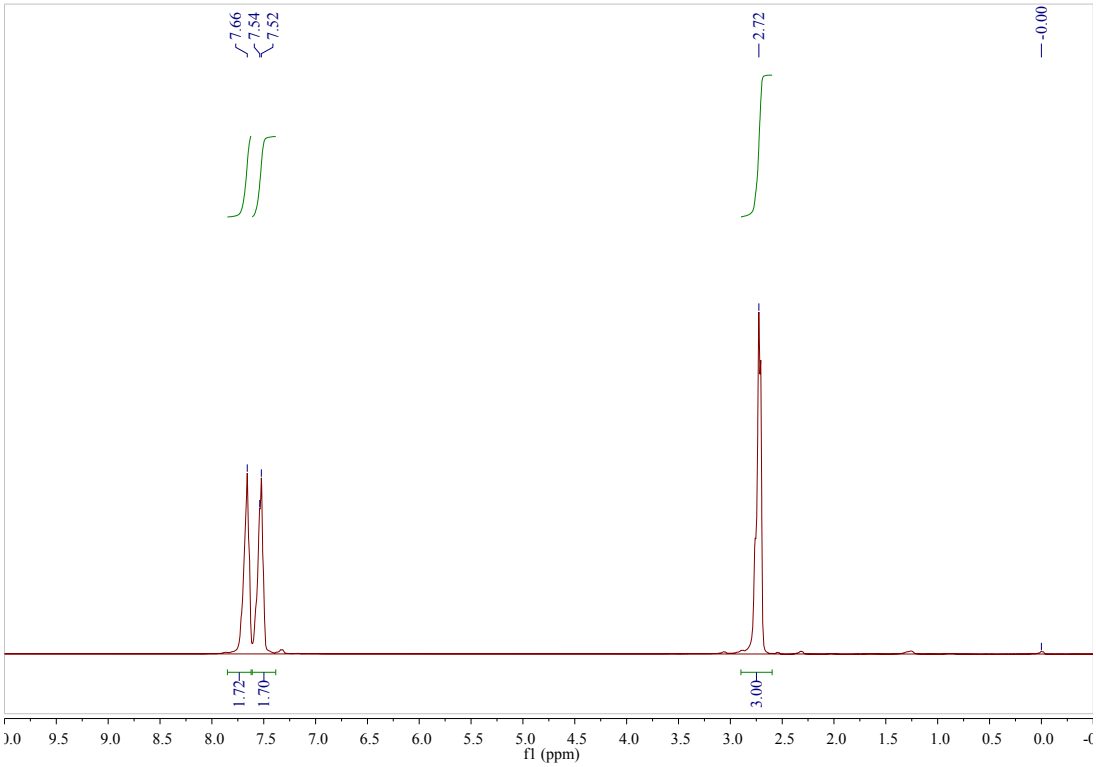


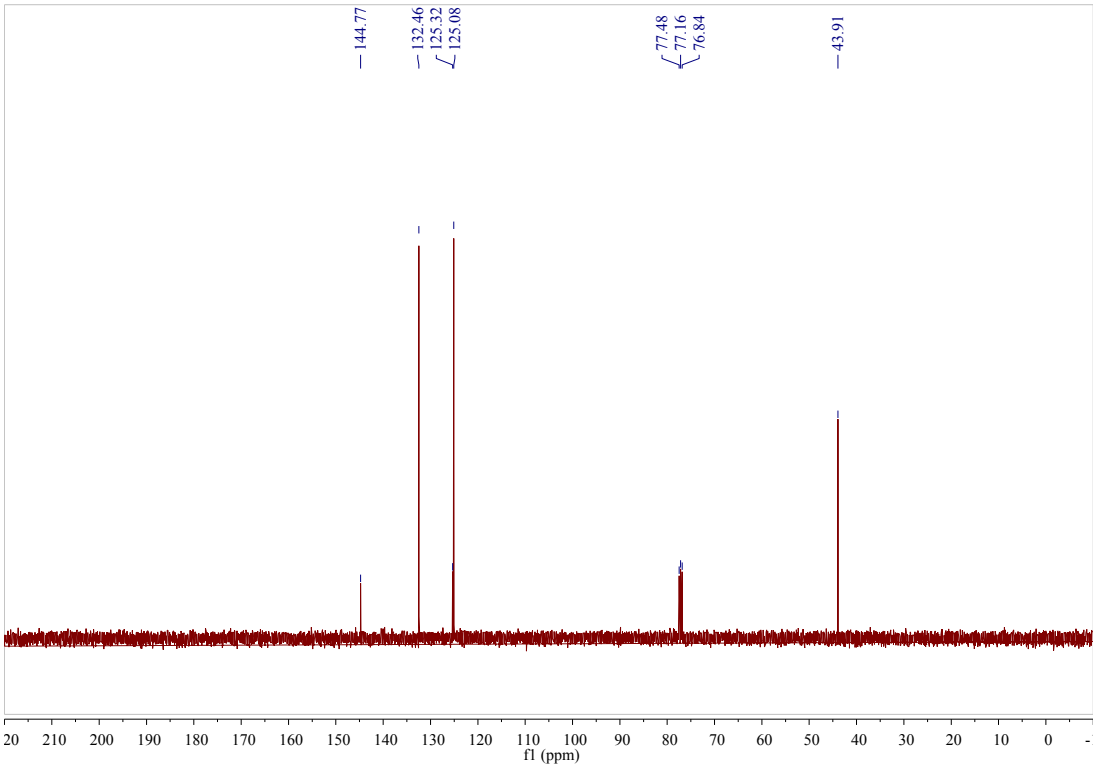




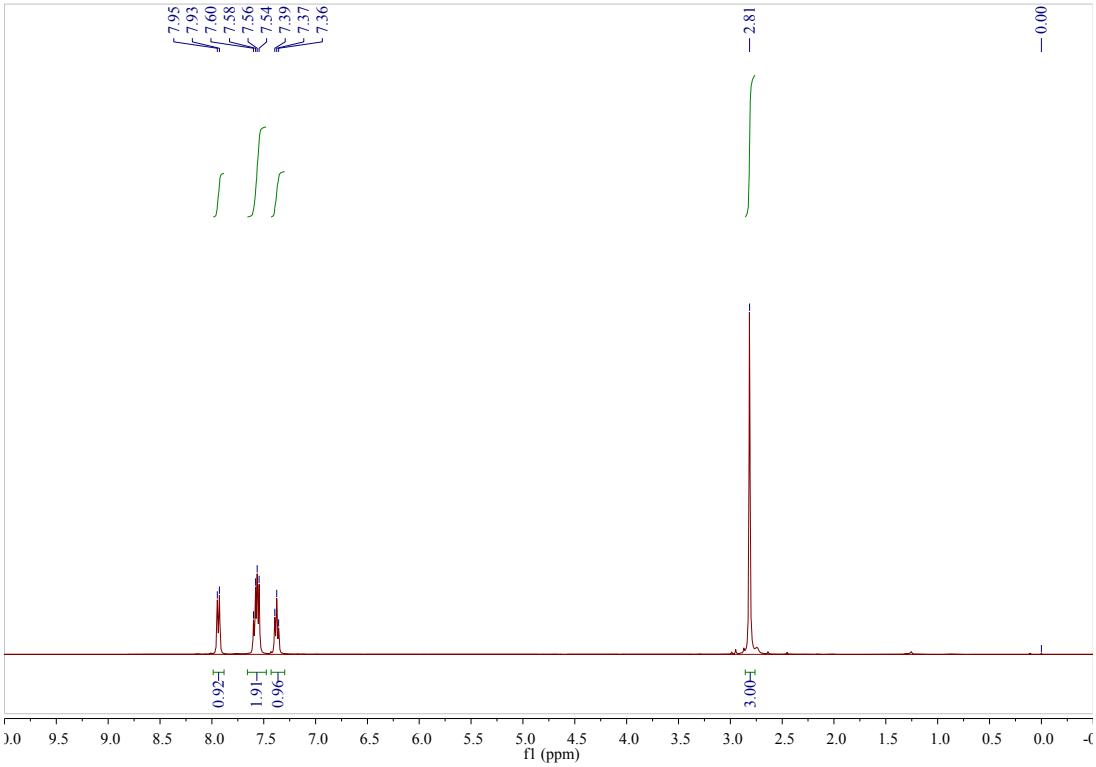
1-Bromo-4-(methylsulfinyl)benzene

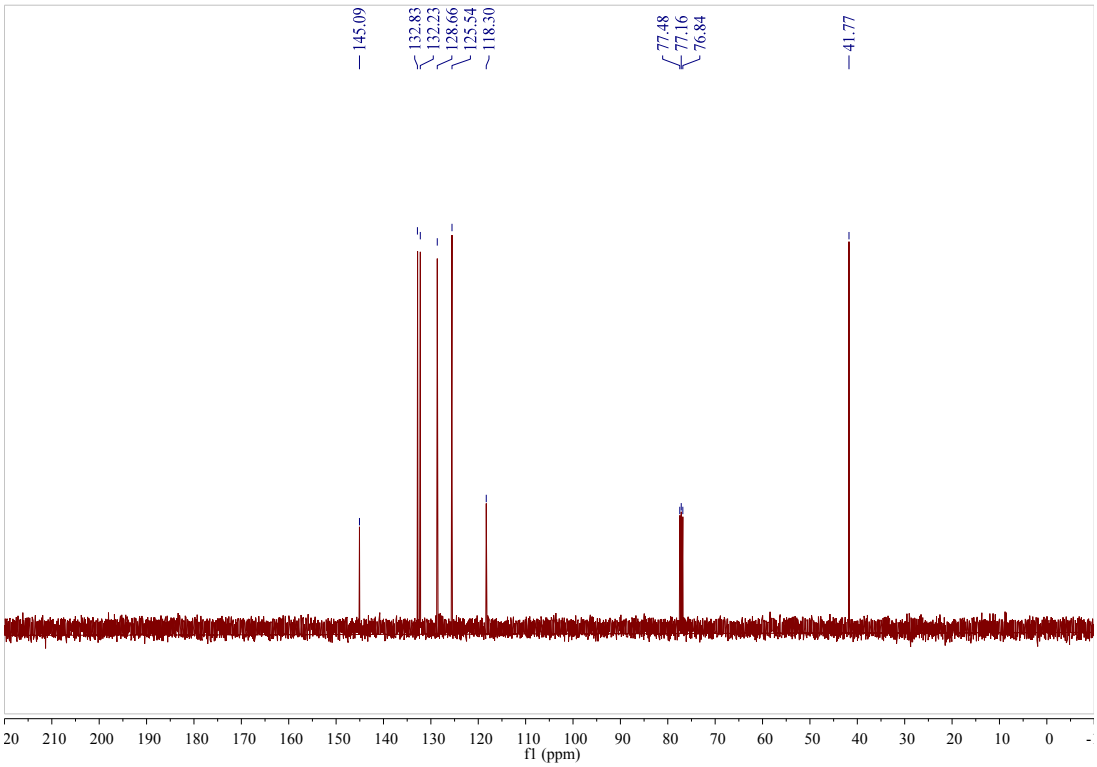




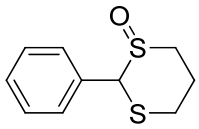


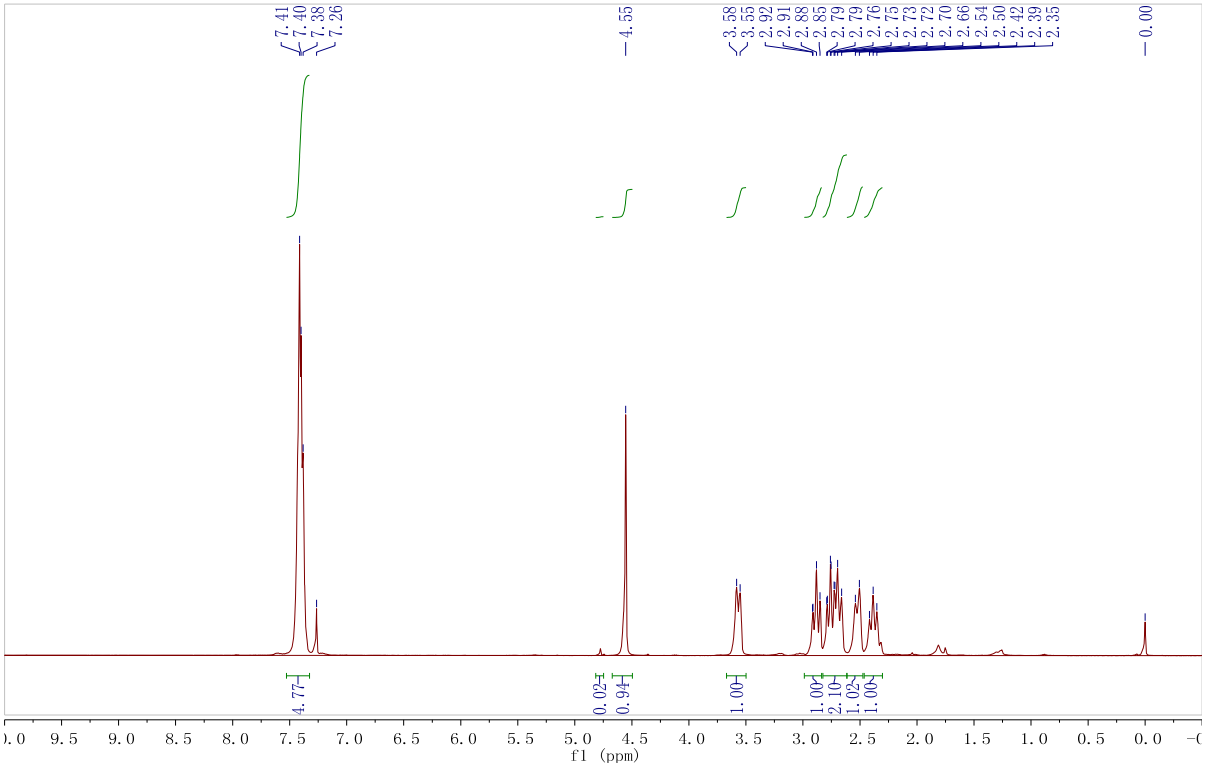
1-Bromo-2-(methylsulfinyl)benzene

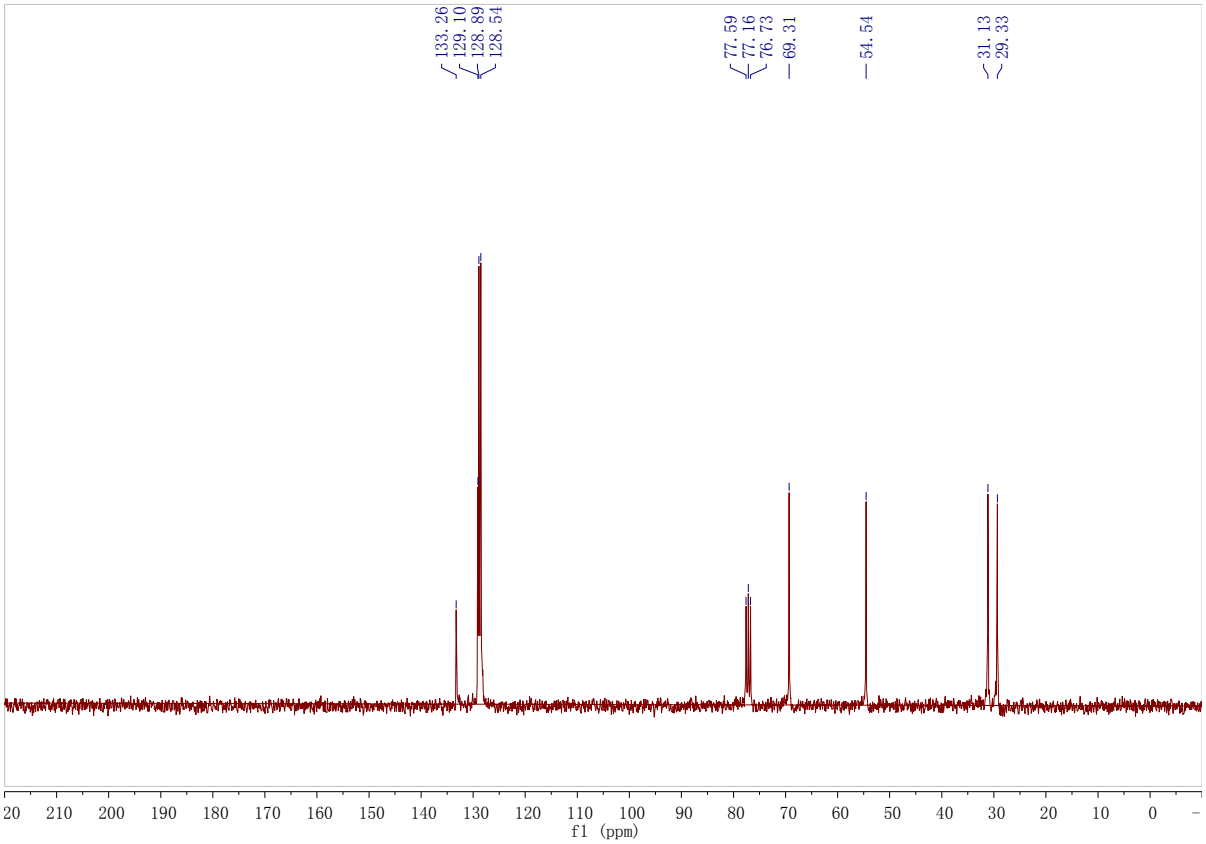




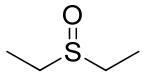
2-Phenyl-1, 3-dithiane 1-oxide

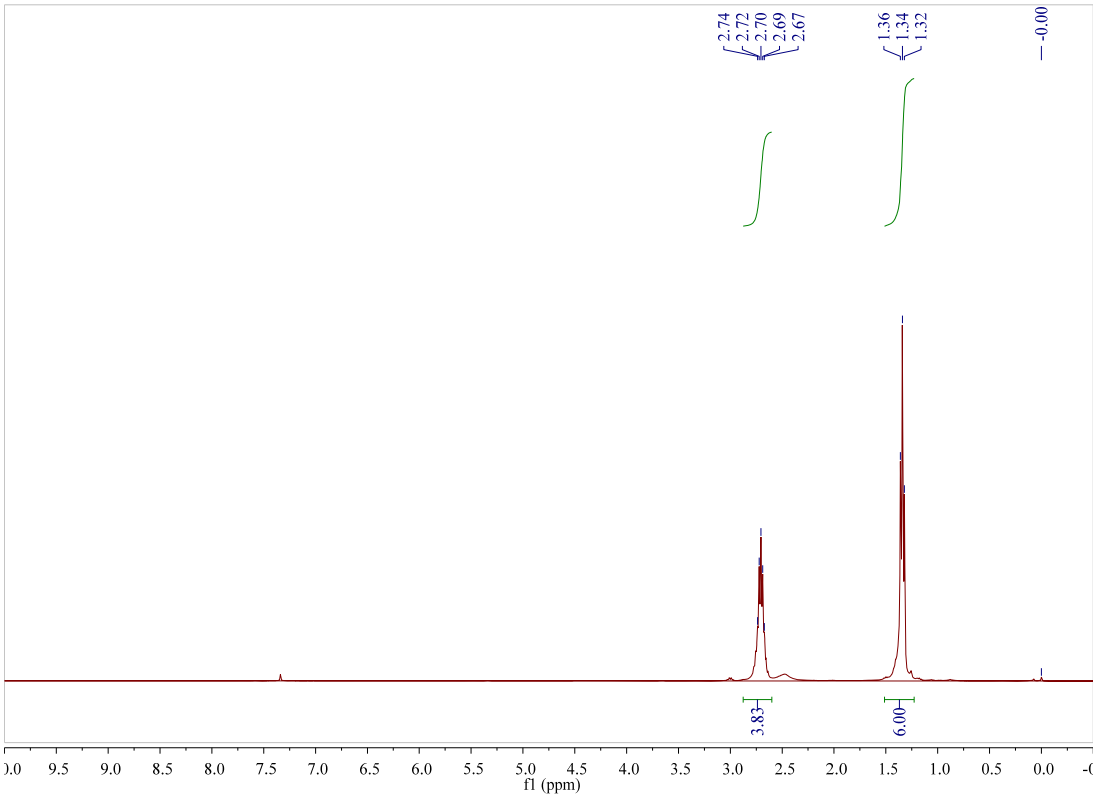


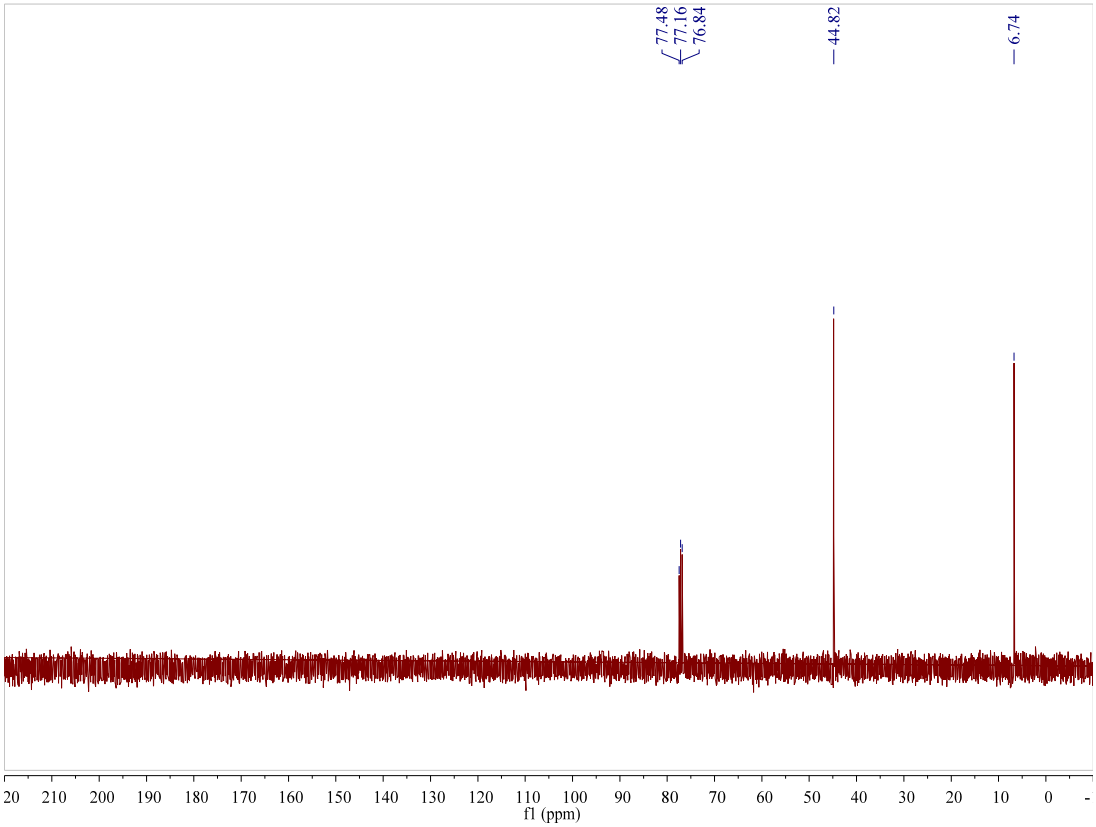




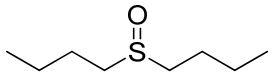
Ethylsulfinylethane

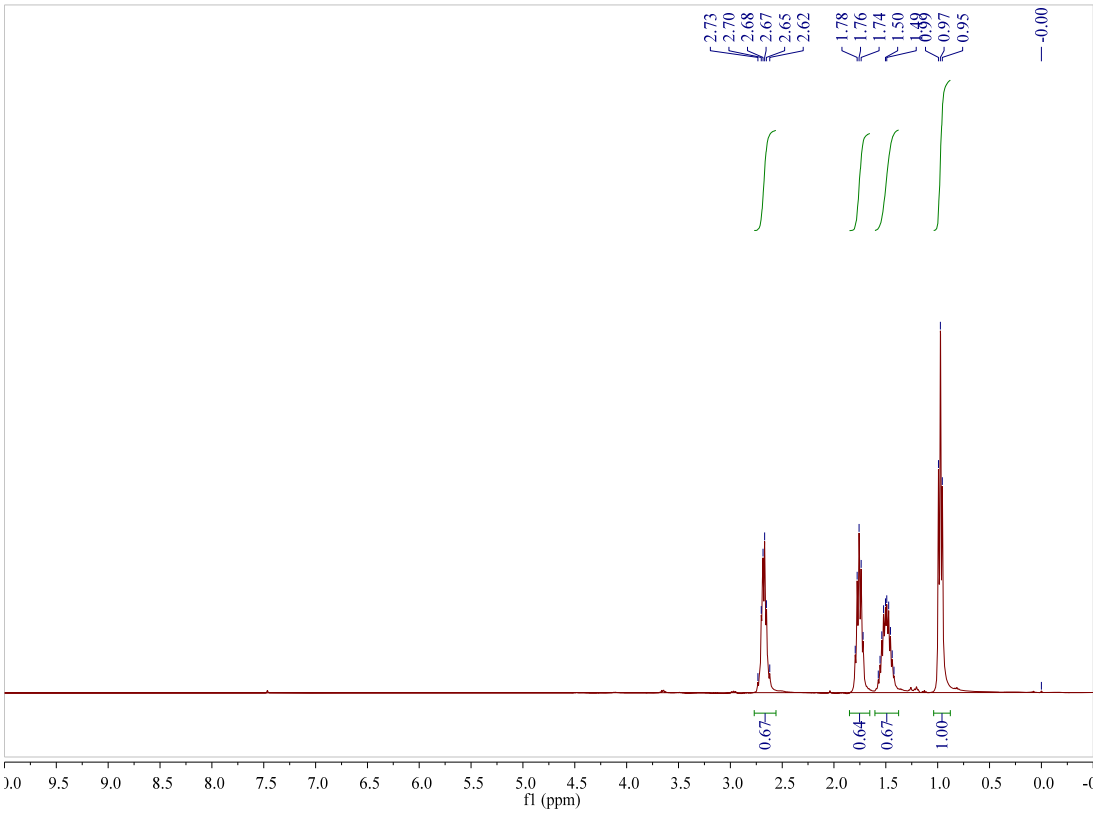


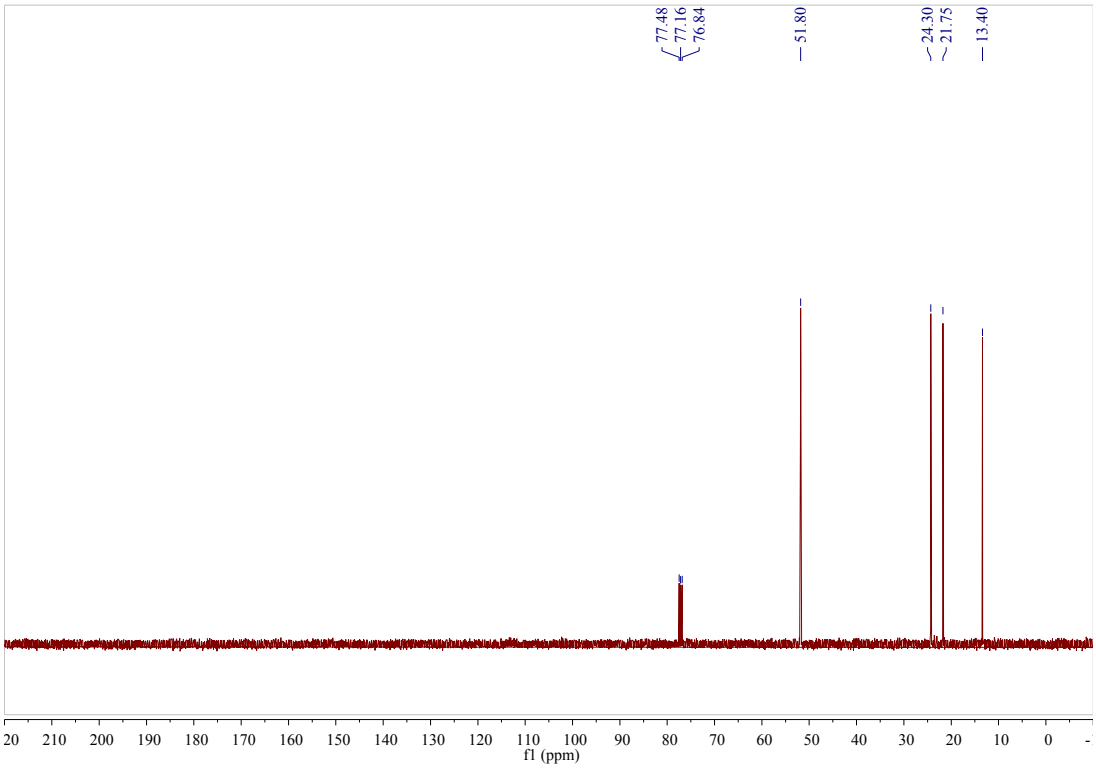




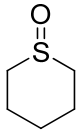
1-(Butylsulfinyl)butane

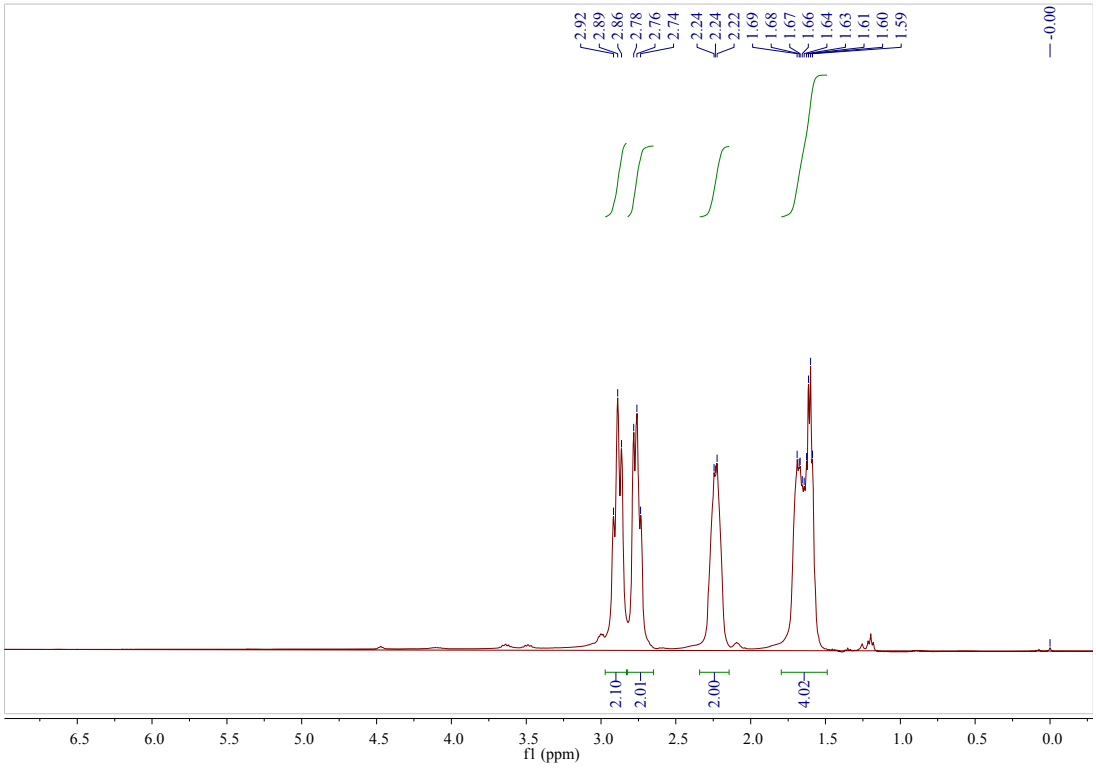


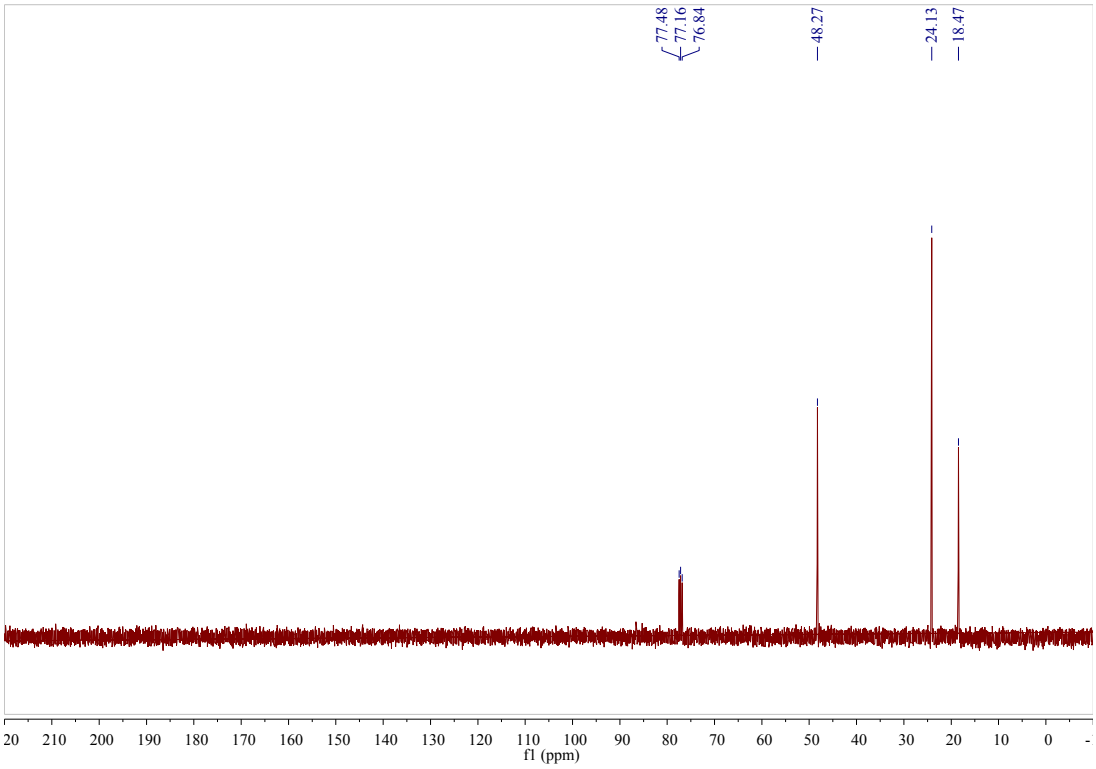




Thiane 1-oxide







(2S)-2-(benzyloxycarbonylamino)-4-(methylsulfinyl)butanoic acid