

# Supplementary Materials: Iridium-Catalyzed Transfer Hydrogenation of Ketones and Aldehydes Using Glucose as a Sustainable Hydrogen Donor

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## General

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on JEOL ECX-500 and ECS-400 spectrometers (JEOL Ltd., Tokyo, Japan). Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph (GL Sciences Inc., Tokyo, Japan) with a capillary column (GL-Sciences and InertCap Pure WAX (GL Sciences Inc., Tokyo, Japan)). Silica-gel column chromatography was carried out by using Wako-gel C-200 (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan). Ketones and aldehydes were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) or nacalai tesque (Kyoto, Japan). Distilled water and *N,N*-dimethylacetamide (super dehydrated) were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). The compounds,  $[\text{Cp}^*\text{IrCl}_2]_2$  ( $\text{Cp}^*$  = -pentamethylcyclopentadienyl) [1] and iridium complexes **1-4** were prepared according to the literature methods [2, 3, 4, 5].

## General procedure for transfer hydrogenation of acetophenone to 1-phenylethanol using glucose (Table 1)

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst (0.1 mol% Ir), acetophenone (2.0 mmol), glucose (4.0 mmol), base (5.0 or 10.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the mixture was diluted with toluene (50 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard.

## General procedure for transfer hydrogenation of ketones to corresponding the corresponding secondary alcohols using glucose (Table 2)

### Conditions A

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), ketone (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.),  $\text{Na}_2\text{CO}_3$  (10.6 mg, 0.10 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the products were extracted with dichloromethane (20 mL  $\times$  3). After evaporation of the solvent, the yield was determined by  $^1\text{H}$  NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane).

**1-Phenylethanol (6a)** [6]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.33 (m, 4H, aromatic), 7.31–7.25 (m, 1H, aromatic), 4.91 (qd,  $J$  = 6.5, 3.5 Hz, 1H,  $\text{CHOH}$ ), 1.85 (d, 3.5 Hz, 1H,  $\text{CHOH}$ ), 1.50 (d,  $J$  = 6.0 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 128.6, 127.5, 125.5, 70.4, 25.2.

**1-(3'-Methylphenyl)ethanol (6b)** [7]:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (t,  $J$  = 8.0 Hz, 1H, aromatic), 7.23–7.15 (m, 2H, aromatic), 7.09 (d,  $J$  = 7.2 Hz, 1H, aromatic), 4.87 (qd,  $J$  = 6.4, 2.8 Hz, 1H,  $\text{CH(OH)CH}_3$ ), 2.36 (s, 3H,  $\text{ArCH}_3$ ), 1.80 (br, 1H, OH), 1.49 (d,  $J$  = 6.4 Hz, 3H,  $\text{CH(OH)CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 138.3, 128.6, 128.4, 126.2, 122.6, 70.6, 25.3, 21.6.

**1-(4'-Trifluoromethylphenyl)ethanol (6c)** [7]:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J$  = 8.0 Hz, 2H, aromatic), 7.42 (d,  $J$  = 8.4 Hz, 2H, aromatic), 4.88 (q,  $J$  = 2.4 Hz, 1H,  $-\text{CH(OH)CH}_3$ ), 2.93 (br, 1H, OH), 1.44 (d,  $J$  = 6.4 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 129.6 (q,  $J_{\text{CF}_3}$  = 31.7 Hz), 125.7, 125.4 (q,  $J_{\text{CF}_3}$  = 3.9 Hz), 124.3 (q,  $J_{\text{CF}_3}$  = 271.2 Hz), 69.8, 25.3.

**1-(4'-Nitrophenyl)ethanol (6d)** [6]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (dt,  $J$  = 9.0, 2.0 Hz, 2H, aromatic), 7.55 (ddt,  $J$  = 8.5, 2.0, 0.5 Hz, 2H, aromatic), 5.03 (q,  $J$  = 6.5 Hz, 1H,  $\text{CH}(\text{OH})\text{CH}_3$ ), 2.16 (br, 1H, OH), 1.52 (d,  $J$  = 6.5 Hz,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 147.3, 126.2, 123.9, 69.6, 25.6.

**1-(4'-Cyanophenyl)ethanol (6e)** [8]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J$  = 8.5, 1.0 Hz, 2H, aromatic), 7.49 (d,  $J$  = 8.0 Hz, 2H, aromatic), 4.97 (ddd,  $J$  = 13.0, 4.0, 2.5 Hz,  $\text{CH}(\text{OH})\text{CH}_3$ ), 1.92 (d,  $J$  = 4.0 Hz, OH), 1.50 (d,  $J$  = 6.0 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.4, 132.2, 126.1, 118.9, 110.5, 69.3, 25.2.

**Methyl-4-(1-hydroxyethyl)benzoate (6f)** [9]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (dt,  $J$  = 8.0, 2.0 Hz, 2H, aromatic), 7.43 (d,  $J$  = 8.0 Hz, 2H, aromatic), 4.95 (q,  $J$  = 5.5 Hz, 1H,  $\text{CH}(\text{OH})\text{CH}_3$ ), 3.90 (s, 3H,  $\text{C}(\text{O})\text{OCH}_3$ ), 2.19 (br, 1H, OH), 1.49 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}(\text{OH})\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 151.1, 130.0, 129.3, 125.4, 70.1, 52.2, 25.4.

**2,2,2-Trifluoro-1-phenylethanol (6g)** [10]:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.45 (m, 2H, aromatic), 7.45-7.37 (m, 3H, aromatic), 5.03 (m, 1H,  $\text{CHOHCF}_3$ ), 2.60-2.58 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 129.7, 128.8, 127.6, 124.3 (q,  $J_{\text{CF}_3}$  = 280.1 Hz), 72.9 (q,  $J_{\text{CF}_3}$  = 32.1 Hz).

**1-Phenyl-1-propanol (6h)** [11]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.31 (m, 4H, aromatic), 7.29-7.23 (m, 1H, aromatic), 4.58 (t,  $J$  = 6.5 Hz, 1H,  $\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ ), 1.96-1.98 (br, 1H, OH), 1.86-1.70 (m, 2H,  $\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ ), 0.91 (t,  $J$  = 7.5 Hz,  $\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 128.5, 127.6, 126.1, 76.1, 32.0, 10.3.

**4-Phenylbutan-2-ol (6i)** [11]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.26 (m, 2H, aromatic), 7.23-7.17 (m, 3H, aromatic), 3.84 (sep,  $J$  = 6.0 Hz, 1H,  $\text{CH}(\text{OH})$ ), 2.80-2.64 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.85-1.72 (m, 2H,  $\text{CH}_2$ ), 1.34 (br, 1H, OH), 1.23 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 128.5, 125.9, 67.5, 40.9, 32.2, 23.7.

**Cyclohexanol (6j)** [11]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.61 (m, 1H,  $\text{CH}_2\text{CHOHCH}_2$ ), 1.92-1.88 (m, 2H,  $\text{CH}_2$ ), 1.78-1.68 (m, 2H,  $\text{CH}_2$ ), 1.59-1.51 (m, 1H,  $\text{CH}_2$ ), 1.37 (s, 1H,  $\text{CH}_2$ ), 1.35-1.24 (m, 4H,  $\text{CH}_2$ ), 1.22-1.12 (m, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  70.4, 35.6, 25.5, 24.3.

**Cycloheptanol (6k)** [12]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (m, 1H,  $\text{CH}_2\text{CHOHCH}_2$ ), 1.92 (m, 2H,  $\text{CH}_2$ ), 1.65 (m, 2H,  $\text{CH}_2$ ), 1.61-1.50 (m, 6H,  $\text{CH}_2$ ), 1.40 (m, 2H,  $\text{CH}_2$ ), 1.30 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  72.9, 37.7, 28.2, 22.7.

### Conditions B

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), ketone (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.),  $\text{Na}_2\text{CO}_3$  (10.6 mg, 0.10 mmol, 5.0 mol%) and *N,N*-dimethylacetamide (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and the products were extracted with a mixed solvent having a volume ratio of hexane :  $\text{AcOEt}$  of 1 : 1 (20 mL  $\times$  3). After evaporation of the solvent, the yield was determined by  $^1\text{H}$  NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane).

**1-(4'-Methoxyphenyl)ethanol (6l)** [6]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dt,  $J$  = 8.5, 2.0 Hz, 2H, aromatic), 6.89 (dt,  $J$  = 9.0, 2.0 Hz, 2H, aromatic), 4.86 (q,  $J$  = 6.0 Hz, 1H,  $\text{CHOH}$ ), 3.81 (s, 3H, OMe), 1.78-1.75 (br, 1H, OH), 1.48 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 138.1, 126.8, 113.9, 70.1, 55.4, 25.2.

**1-(2'-Methoxyphenyl)ethanol (6m)** [12]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (dd,  $J$  = 7.5, 1.5 Hz, 1H, aromatic), 7.28-7.22 (m, 1H, aromatic), 6.97 (td,  $J$  = 7.5, 1.0 Hz, 1H, aromatic), 6.88 (d,  $J$  = 8.0 Hz, 1H, aromatic), 5.09 (quint,  $J$  = 6.5 Hz,  $\text{CH}(\text{OH})\text{CH}_3$ ), 3.87 (s, 3H, OMe), 2.69 (d,  $J$  = 5.0 Hz, OH), 1.51 (d,  $J$  = 7.0 Hz,  $\text{CH}(\text{OH})\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 133.5, 128.4, 126.2, 120.9, 110.5, 66.7, 55.4, 22.9.

**1-(4'-Chlorophenyl)ethanol (6n)** [6]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.27 (m, 4H, aromatic), 4.89 (m, 1H,  $\text{CHOH}$ ), 1.91-1.84 (br, 1H,  $\text{CHOH}$ ), 1.47 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 133.2, 128.7, 126.9, 69.9, 25.4.

1-(3'-Chlorophenyl)ethanol (**6o**) [7]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (t,  $J$  = 2.0 Hz, 1H, aromatic), 7.30-7.22 (m, 3H, aromatic), 4.88 (qd,  $J$  = 6.5, 3.5 Hz,  $\text{CH}(\text{OH})\text{CH}_3$ ), 1.92 (d,  $J$  = 3.5 Hz, 1H, OH), 1.48 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 134.5, 129.9, 127.7, 125.8, 123.7, 70.0, 25.4.

1-(2'-Chlorophenyl)ethanol (**6p**) [13]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J$  = 8.0, 2.0 Hz, 1H, aromatic), 7.33-7.27 (m, 2H, aromatic), 7.20 (td,  $J$  = 8.0, 2.0 Hz, 1H, aromatic), 5.28 (qd, 6.5, 3.5 Hz, 1H,  $\text{CH}(\text{OH})\text{CH}_3$ ), 2.13 (d,  $J$  = 4.0 Hz, 1H, OH), 1.48 (d,  $J$  = 6.5 Hz,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.2, 131.7, 129.5, 128.5, 127.3, 126.4, 67.1, 23.6.

1-(4'-Bromophenyl)ethanol (**6q**) [6]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (dt,  $J$  = 8.5, 2.5, 1.5 Hz, 2H, aromatic), 7.24 (d,  $J$  = 8.5 Hz, 2H, aromatic), 4.85 (q,  $J$  = 6.5 Hz, 1H,  $\text{CH}(\text{OH})\text{CH}_3$ ), 1.98 (br, 1H, OH), 1.46 (d,  $J$  = 6.5 Hz, 3H,  $\text{CH}(\text{OH})\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 131.7, 127.3, 121.3, 69.9, 25.4.

*General procedure for transfer hydrogenation of aldehydes to the corresponding primary alcohols using glucose (Table 3)*

### Conditions A

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), aldehyde (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.),  $\text{Na}_2\text{CO}_3$  (10.6 mg, 0.10 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the products were extracted with dichloromethane (20 mL  $\times$  3). After evaporation of the solvent, the yields were determined by  $^1\text{H}$  NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane).

Benzyl alcohol (**8a**) [14]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.35 (m, 4H, aromatic), 7.33-7.28 (m, 1H, aromatic), 4.70 (d,  $J$  = 6.0 Hz, 2H,  $\text{CH}_2(\text{OH})$ ), 1.75 (t,  $J$  = 6.0 Hz, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 128.6, 127.7, 127.1, 65.2.

*p*-Methylbenzyl alcohol (**8b**) [14]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J$  = 8.0 Hz, 2H, aromatic), 7.14 (d,  $J$  = 8.0 Hz, 2H, aromatic), 4.57 (d,  $J$  = 3.5 Hz, 2H,  $\text{ArCH}_2\text{OH}$ ), 2.33 (s, 3H, Me), 2.23-2.12 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 137.4, 129.3, 127.2, 65.2, 21.2.

*p*-Cyanobenzyl alcohol (**8c**) [12]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.57 (m, 2H, aromatic), 7.46-7.41 (m, 2H, aromatic), 4.73 (s, 2H,  $\text{CH}_2$ ), 2.61 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 132.3, 127.1, 119.0, 110.9, 64.1.

*m*-Nitrobenzyl alcohol (**8d**) [15]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H, aromatic), 8.16 (dd,  $J$  = 8.5, 1.0 Hz, 1H, aromatic), 7.71 (dd,  $J$  = 8.0, 1.0 Hz, 1H, aromatic), 7.54 (t,  $J$  = 8.0 Hz, 1H, aromatic), 4.84 (s, 2H,  $\text{CH}_2$ ), 1.95 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 143.0, 132.8, 129.6, 122.6, 121.6, 64.0.

*o*-Nitrobenzyl alcohol (**8e**) [15]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (dd,  $J$  = 8.0, 1.0 Hz, 1H, aromatic), 7.75 (d,  $J$  = 7.0 Hz, 1H, aromatic), 7.69 (td,  $J$  = 7.5, 1.0 Hz, 1H, aromatic), 7.49 (td,  $J$  = 8.0, 1.0 Hz, 1H, aromatic), 4.99 (d,  $J$  = 6.0 Hz, 2H,  $-\text{CH}(\text{OH})-$ ), 2.53 (t,  $J$  = 7.0 Hz, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.7, 136.9, 134.3, 130.2, 128.7, 125.2, 62.7.

Methyl-4-(hydroxymethyl)benzoate (**8f**) [16]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J$  = 8.0 Hz, 2H, aromatic), 7.37 (d,  $J$  = 8.0 Hz, 2H, aromatic), 4.69 (s, 2H,  $\text{CH}_2(\text{OH})$ ), 3.88 (s, 3H,  $\text{OCH}_3$ ), 3.21 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 146.3, 129.8, 129.0, 126.4, 64.4, 52.2.

### Conditions B

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), aldehyde (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.),  $\text{Na}_2\text{CO}_3$  (10.6 mg, 0.10 mmol, 5.0 mol%) and *N,N*-dimethylacetamide (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and the products were extracted with a mixed solvent having a volume ratio of hexane :  $\text{AcOEt}$  of 1 : 1 (20 mL  $\times$  3). After evaporation of the solvent, the yield was determined by  $^1\text{H}$  NMR analysis using 1,3,5-trimethoxybenzene as an

internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane).

*p*-Methoxybenzyl alcohol (**8g**) [14]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (dt,  $J$  = 9.0, 3.0, 2.0 Hz, 2H, aromatic), 6.89 (dt,  $J$  = 8.5, 3.0, 2.0 Hz, 2H, aromatic), 4.60 (s, 2H,  $\text{CH}_2$ ), 3.80 (s, 3H, OMe), 1.87 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 133.2, 128.8, 114.0, 65.1, 55.4.

*p*-Chlorobenzyl alcohol (**8h**) [14]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.23 (m, 4H, aromatic), 4.62 (s, 2H,  $\text{ArCH}_2\text{OH}$ ), 2.21 (br, 1H,  $\text{ArCH}_2\text{OH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 133.4, 128.8, 128.4, 64.6.

*p*-Bromobenzyl alcohol (**8i**) [12]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dt,  $J$  = 8.5, 2.0 Hz, 2H, aromatic), 7.23 (d,  $J$  = 8.5 Hz, 2H, aromatic), 4.65 (s, 2H,  $\text{CH}_2$ ), 1.87 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 131.7, 128.7, 121.6, 64.7.

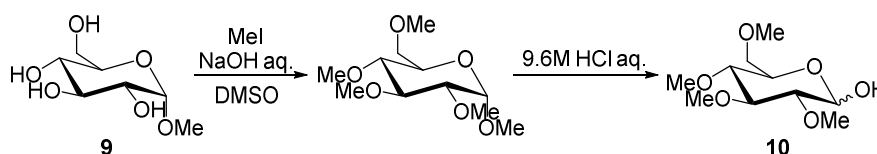
*p*-tert-Butylbenzyl alcohol (**8j**) [17]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J$  = 8.0 Hz, 2H, aromatic), 7.30 (d,  $J$  = 8.5 Hz, 2H, aromatic), 4.64 (d,  $J$  = 1.5 Hz, 2H,  $\text{CH}_2$ ), 1.32 (d,  $J$  = 2.0 Hz, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 138.0, 127.0, 125.6, 65.2, 34.6, 31.5.

2,6-Dichlorobenzyl alcohol (**8k**) [18]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.28 (m, 2H, aromatic), 7.18 (m, 1H, aromatic), 4.95 (d,  $J$  = 3.5 Hz,  $\text{CH}_2\text{OH}$ ), 2.31 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 135.7, 129.9, 128.5, 60.2.

2-Naphthalenemethanol (**8l**) [19]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83–7.75 (m, 3H, aromatic), 7.72 (s, 1H, aromatic), 7.49–7.38 (m, 3H, aromatic), 4.76 (s, 2H,  $\text{CH}_2$ ), 2.33 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 133.4, 133.0, 128.3, 128.0, 127.8, 126.2, 126.0, 125.5, 125.3, 65.4.

1-Naphthalenemethanol (**8m**) [15]:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  = 8.0 Hz, 1H, aromatic), 7.88–7.74 (m, 2H, aromatic), 7.54–7.36 (m, 4H, aromatic), 5.05 (s, 2H,  $\text{CH}_2$ ), 2.30–2.10 (br, 1H, OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.3, 133.8, 131.3, 128.7, 128.6, 126.4, 126.0, 125.5, 125.4, 123.7, 63.6.

Preparation of 2,3,4,6-tetra-*O*-methyl-*D*-glucopyranose (**10**). (Equation 2) [20]



In a two-necked round-bottomed flask, aqueous NaOH (50 wt%, 4.0 mL), methyl  $\alpha$ -D-glucopyranoside (**9**) (1.94 g, 10.0 mmol) and DMSO (35 mL) were placed. After stirring the mixture at room temperature for 5 minutes, iodomethane (3.3 mL, 50 mmol) was added. The mixture was stirred at room temperature for 4 hours. The reaction mixture was poured into water (100 mL) and extracted with EtO. An intermediate product was obtained after evaporation of the organic layer. (colorless oil, 1.64 g, 6.5 mmol, 65% yield).

In a round-bottomed flask, above intermediate product (1.64 g, 6.5 mmol) and aqueous HCl (9.6 M, 25 mL) were placed. The mixture was stirred at 60 °C for 16 hours. After cooling to room temperature, the crude product was obtained by evaporation of the reaction mixture. After purifying by column chromatography (eluent = EtOH/ $\text{CH}_2\text{Cl}_2$ ), the product **10** was obtained (653.5 mg, 2.8 mmol, 43% yield).

2,3,4,6-tetra-*O*-methyl-*D*-glucopyranose (**10**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.31 (d,  $J$  = 3.5 Hz, 1H), 4.56 (d,  $J$  = 7.5 Hz, 0.5H), 3.91 (dt,  $J$  = 10.5 Hz, 2.5 Hz, 1H), 3.70 (q,  $J$  = 7.0 Hz, 1H), 3.66–3.60 (m, 6H), 3.59–3.5 (m, 6H), 3.53–3.50 (m, 4H), 3.42–3.30 (m, 5H), 3.22–3.05 (m, 3H), 2.97 (dd,  $J$  = 9.0, 8.0 Hz, 0.5 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  96.9, 90.5, 86.4, 84.7, 83.1, 81.9, 79.7, 79.7, 74.1, 71.6, 71.4, 69.6, 60.9, 60.8, 60.5, 60.4, 59.1, 58.7.

Reaction of acetophenone using  $\alpha$ -D-glucopyranoside (**9**) (equation 1)

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (1.0 mg, 0.002 mmol, 0.1 mol%Ir), acetophenone (240.5 mg, 2.0 mmol),  $\alpha$ -D-glucopyranoside (777.3 mg, 4.0 mmol, 2.0 equiv.),  $\text{Na}_2\text{CO}_3$  (10.5 mg, 0.1 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours.

After cooling to room temperature, the mixture was diluted with toluene (50 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard. No reaction occurred.

*Reaction of acetophenone using 2,3,4,6-tetra-O-methyl-D-glucopyranose (10) (equation 2)*

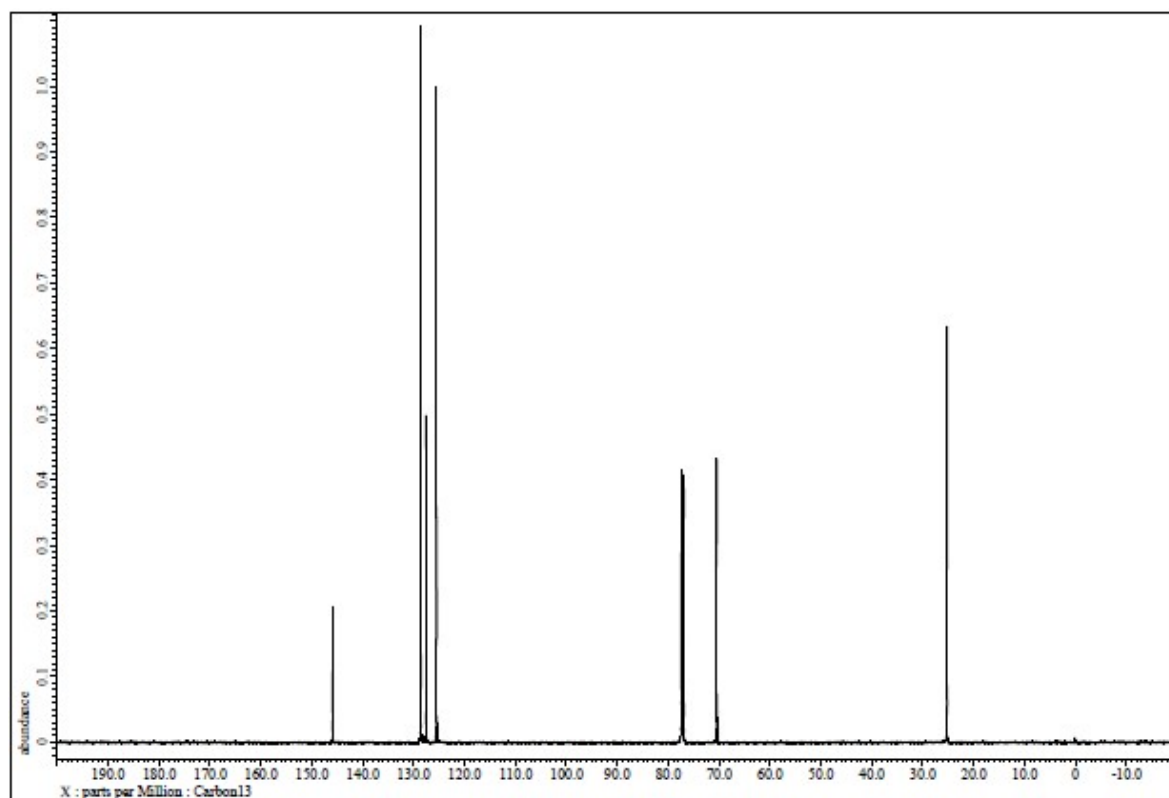
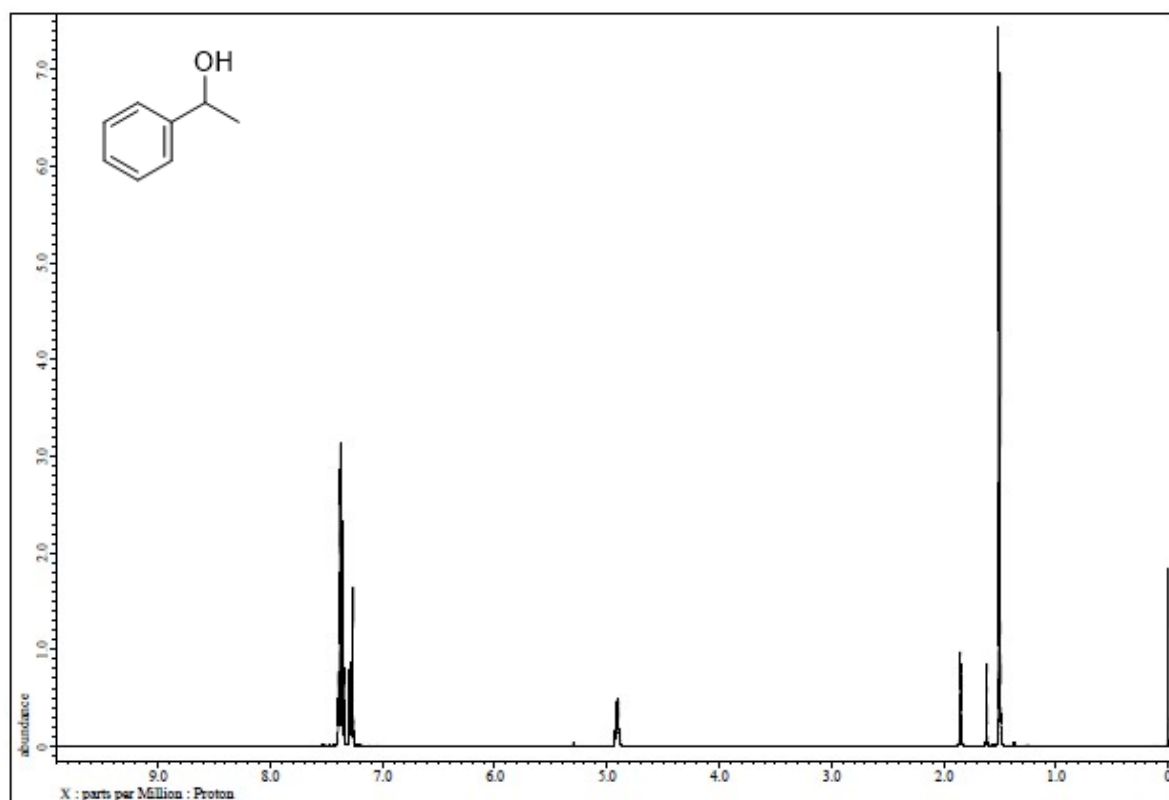
In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (1.1 mg, 0.002 mmol, 0.2 mol%Ir), acetophenone (120.6 mg, 1.0 mmol), 2,3,4,6-tetra-O-methyl-D-glucopyranose (472.4 mg, 2.0 mmol, 2.0 equiv.), Na<sub>2</sub>CO<sub>3</sub> (5.4 mg, 0.05 mmol, 5 mol%) and degassed distilled water (1.5 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 hours. After cooling to room temperature, the mixture was diluted with toluene (25 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard. The conversion and the yield were 97% and 97%, respectively.

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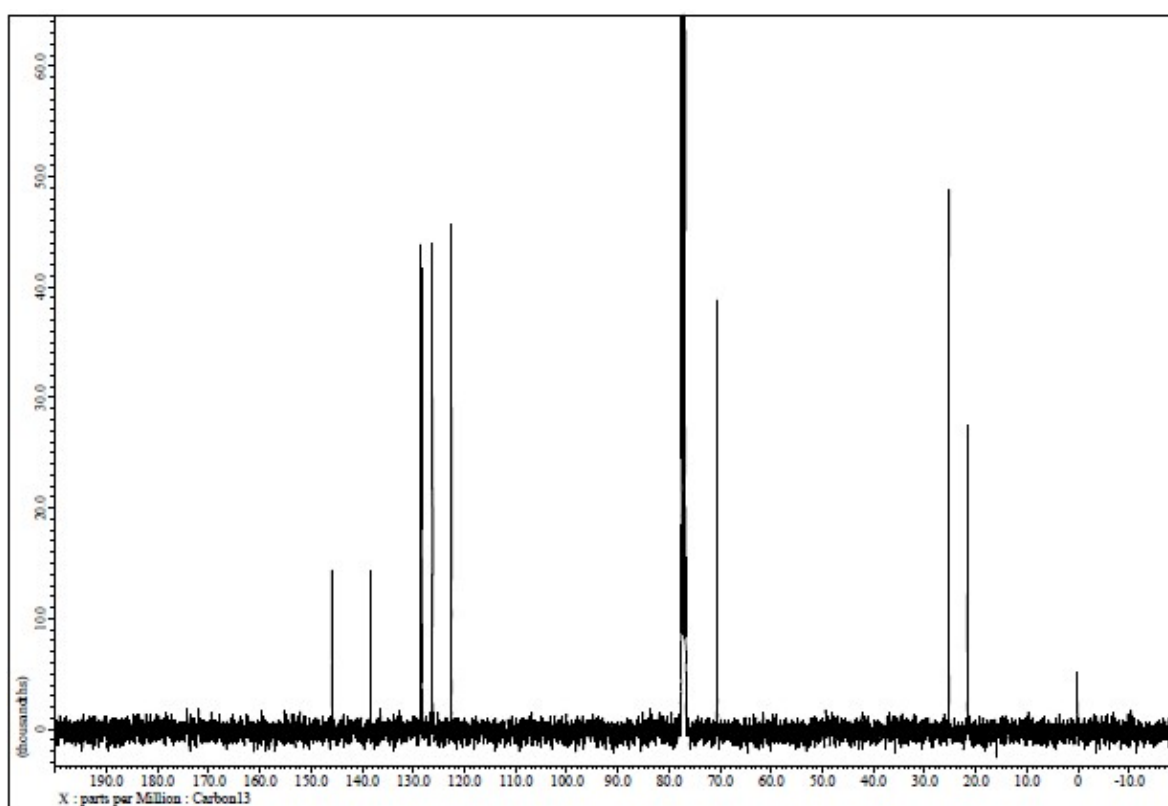
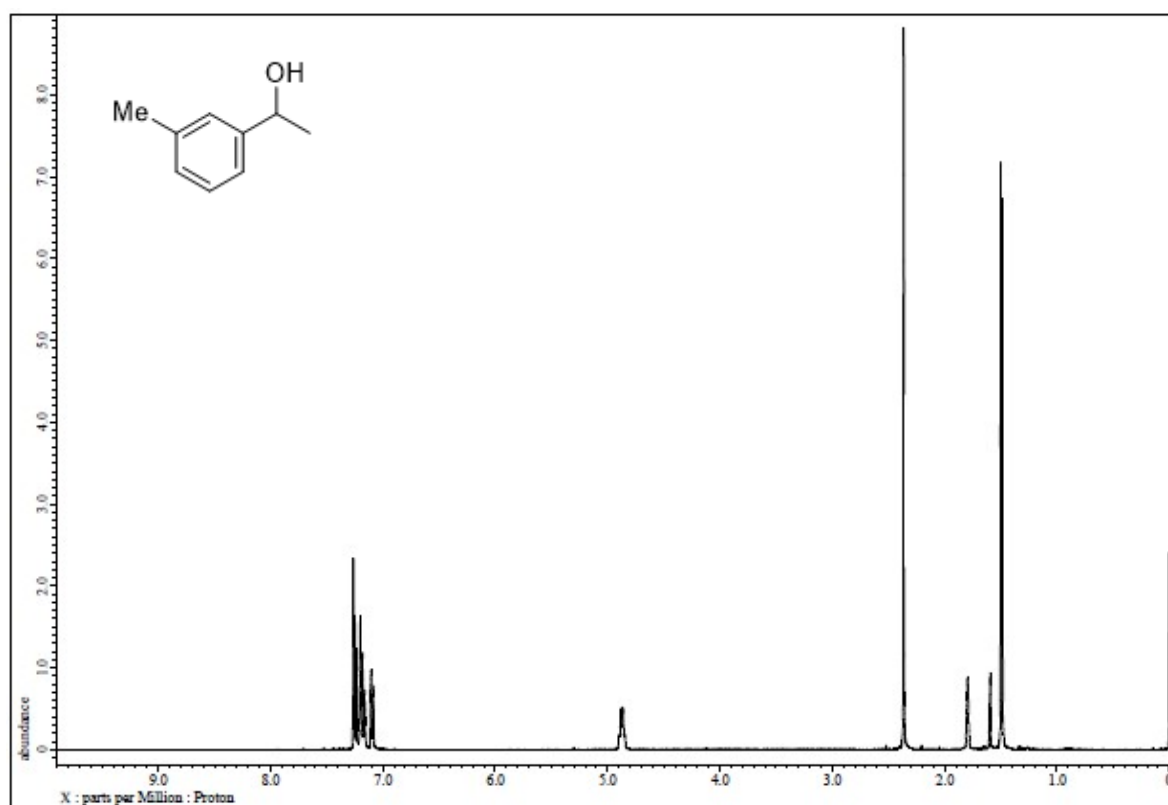
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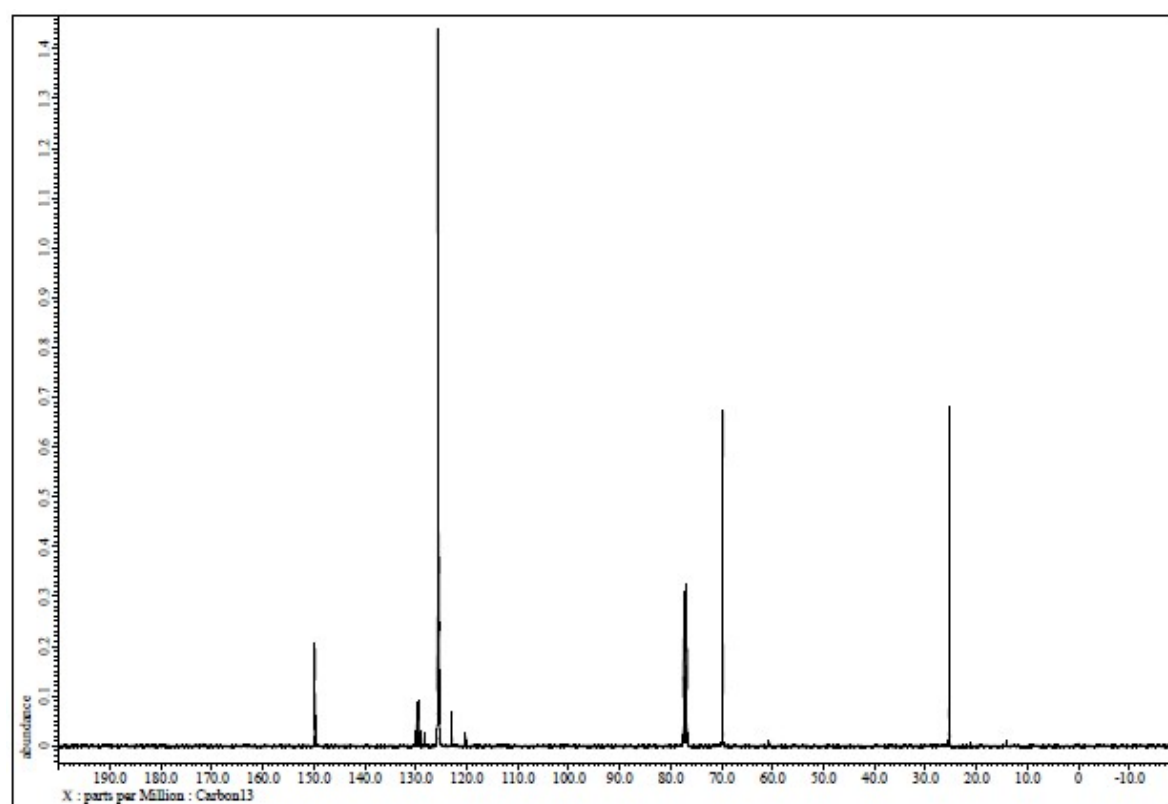
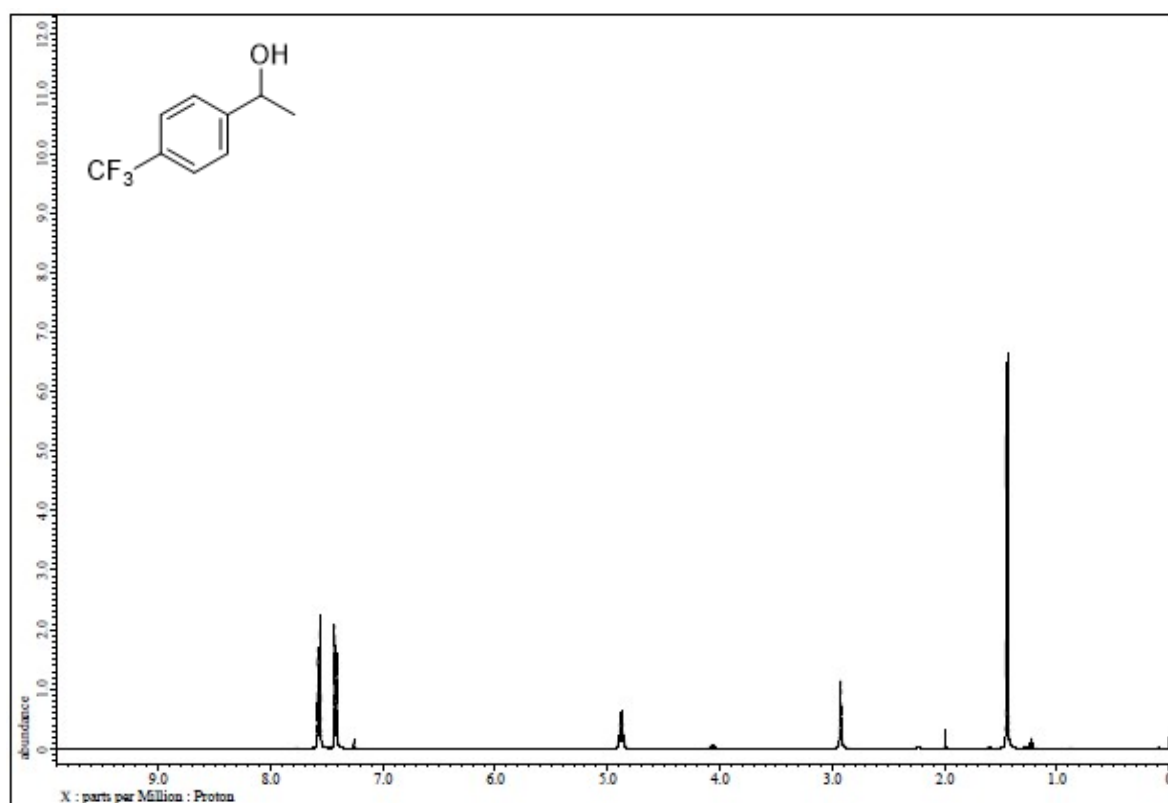


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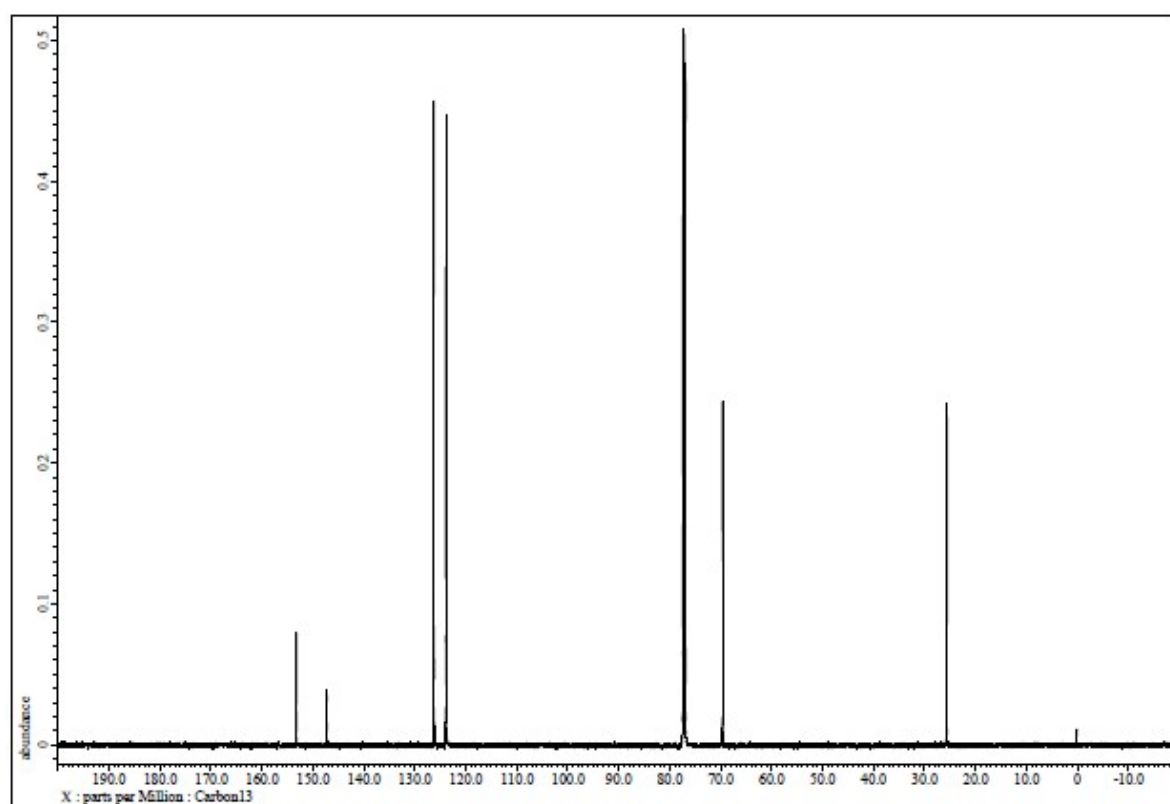
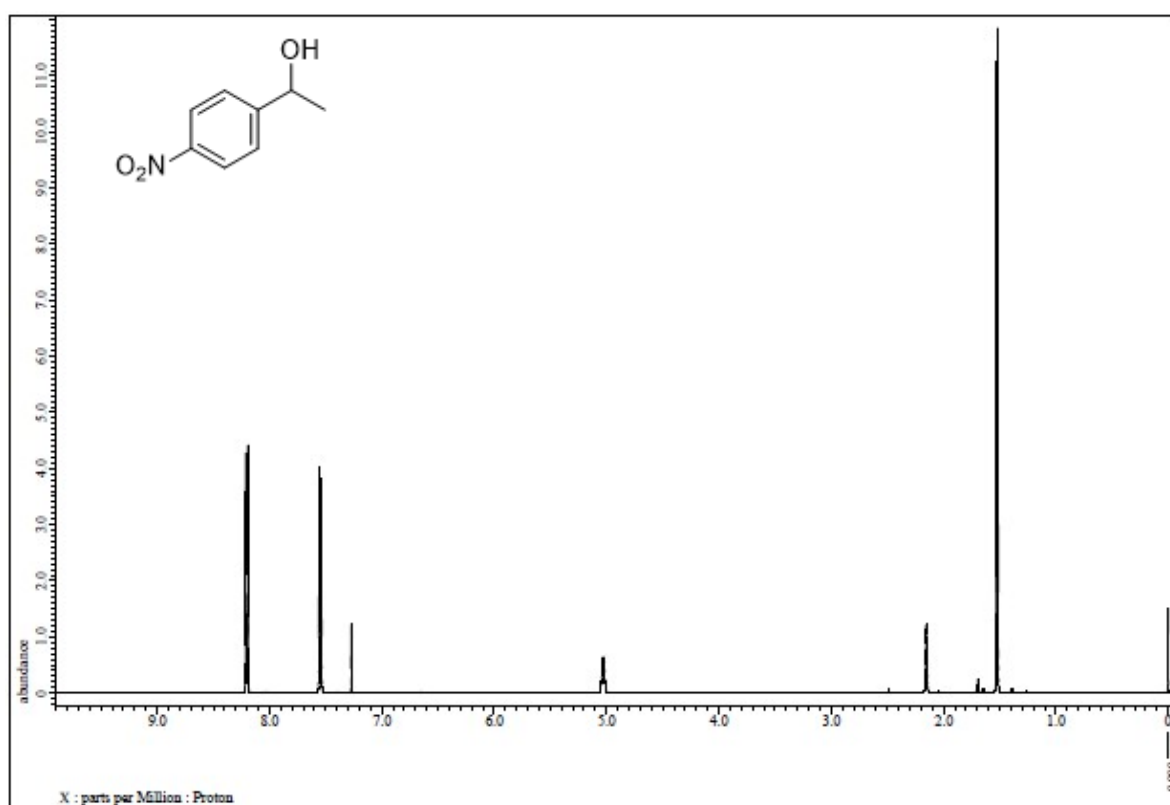




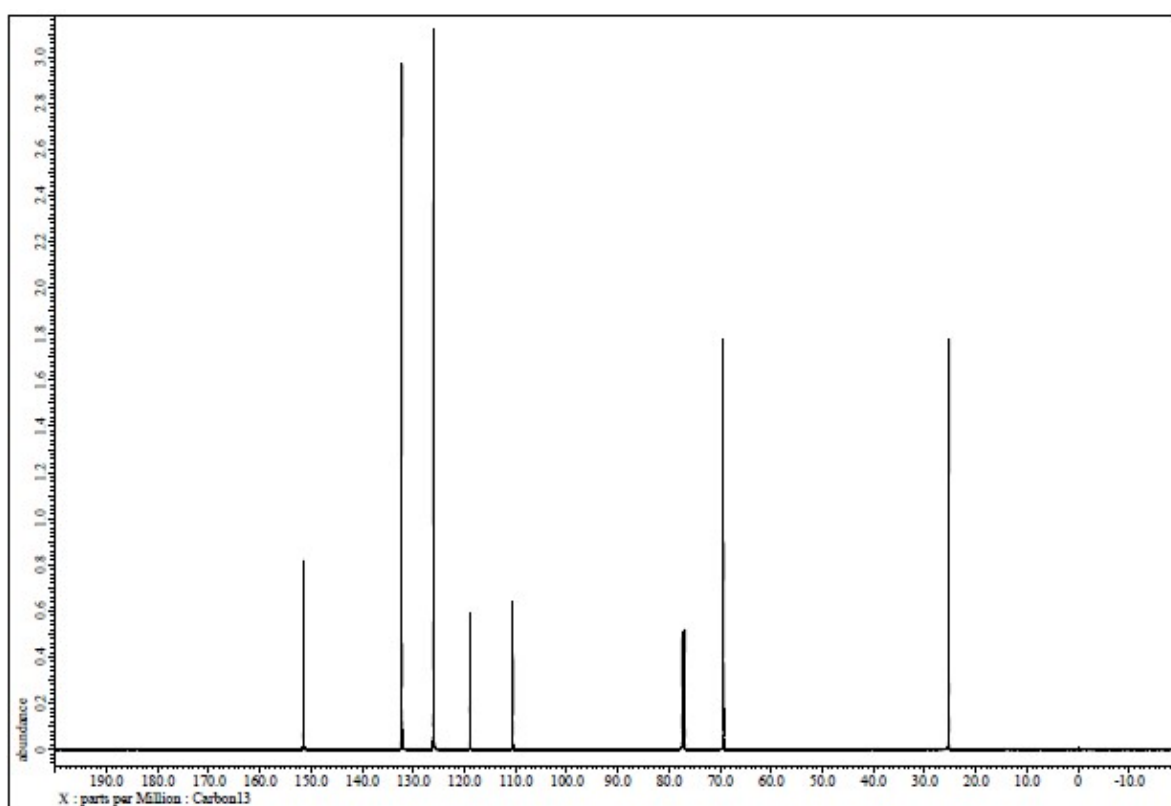
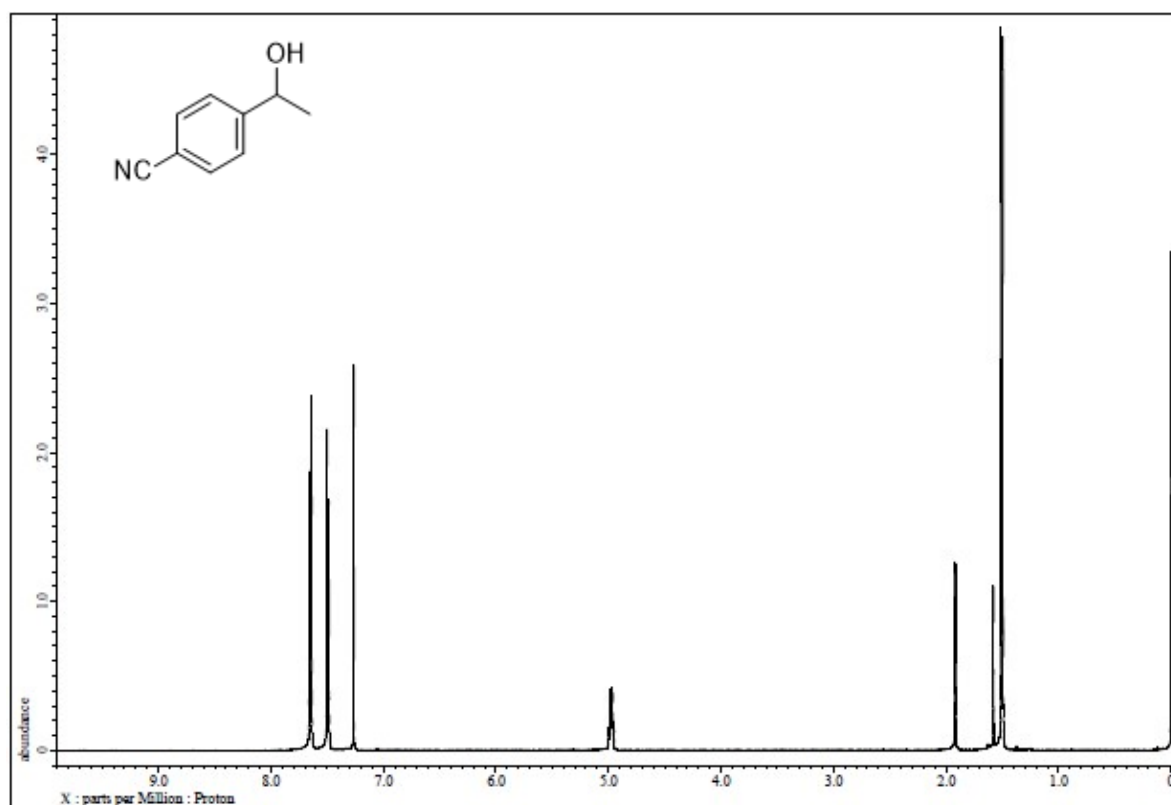
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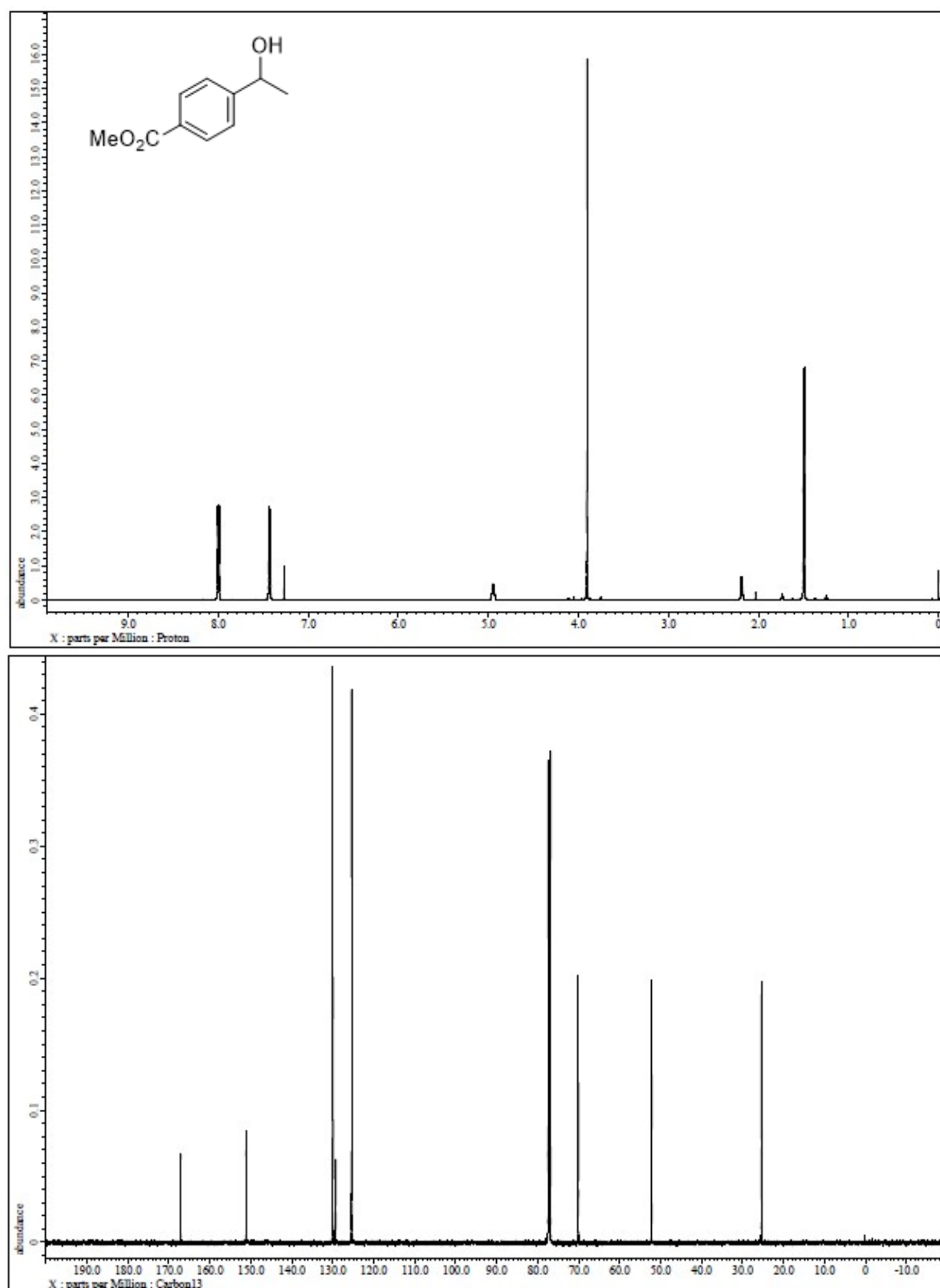
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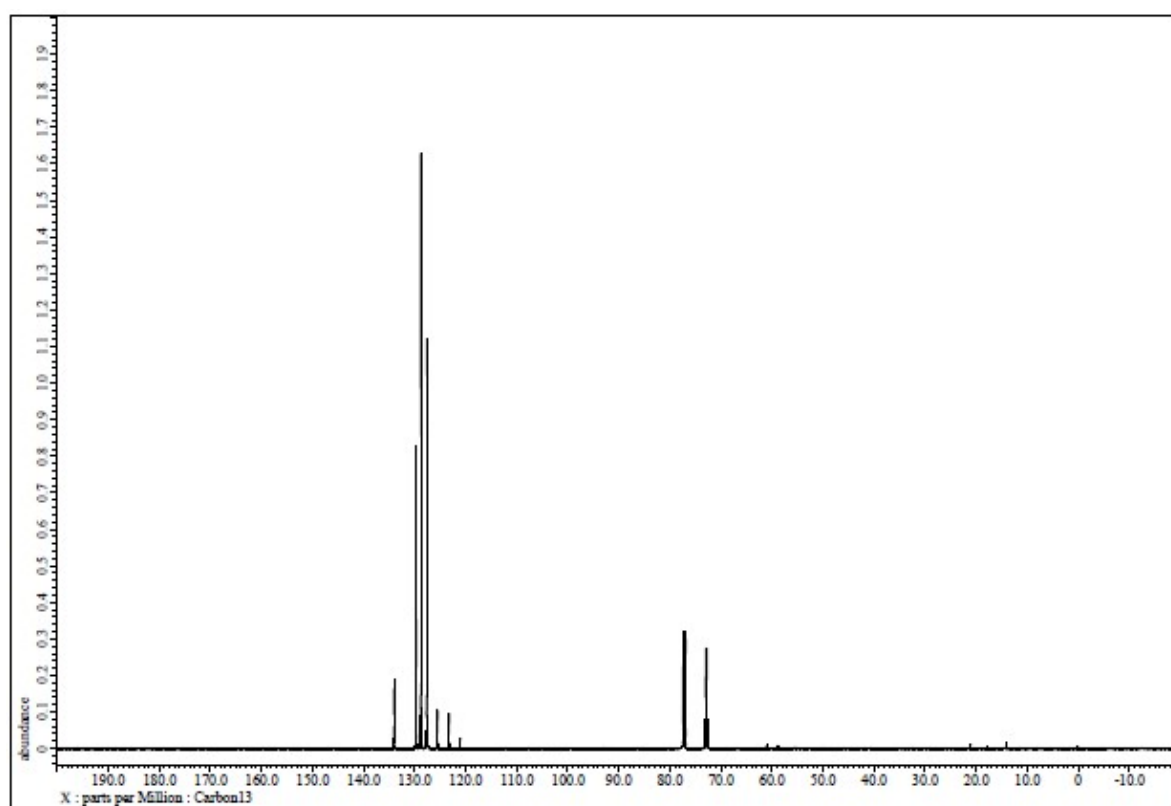
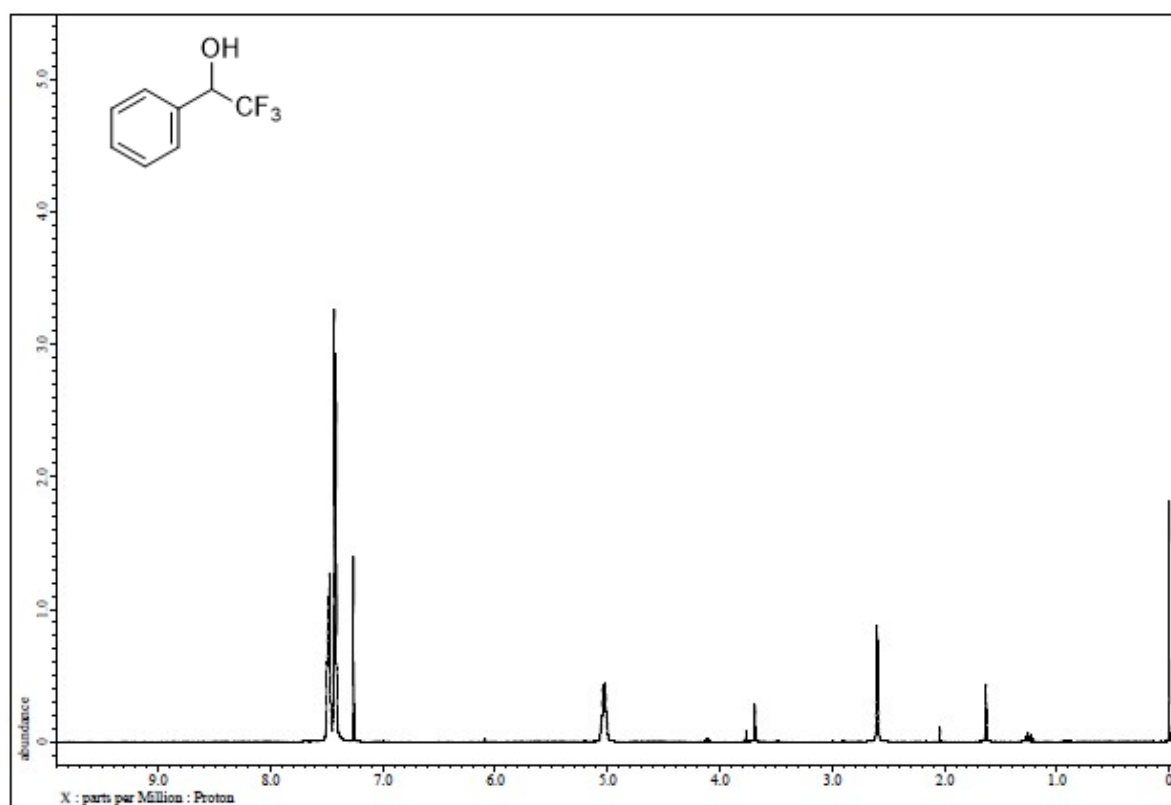
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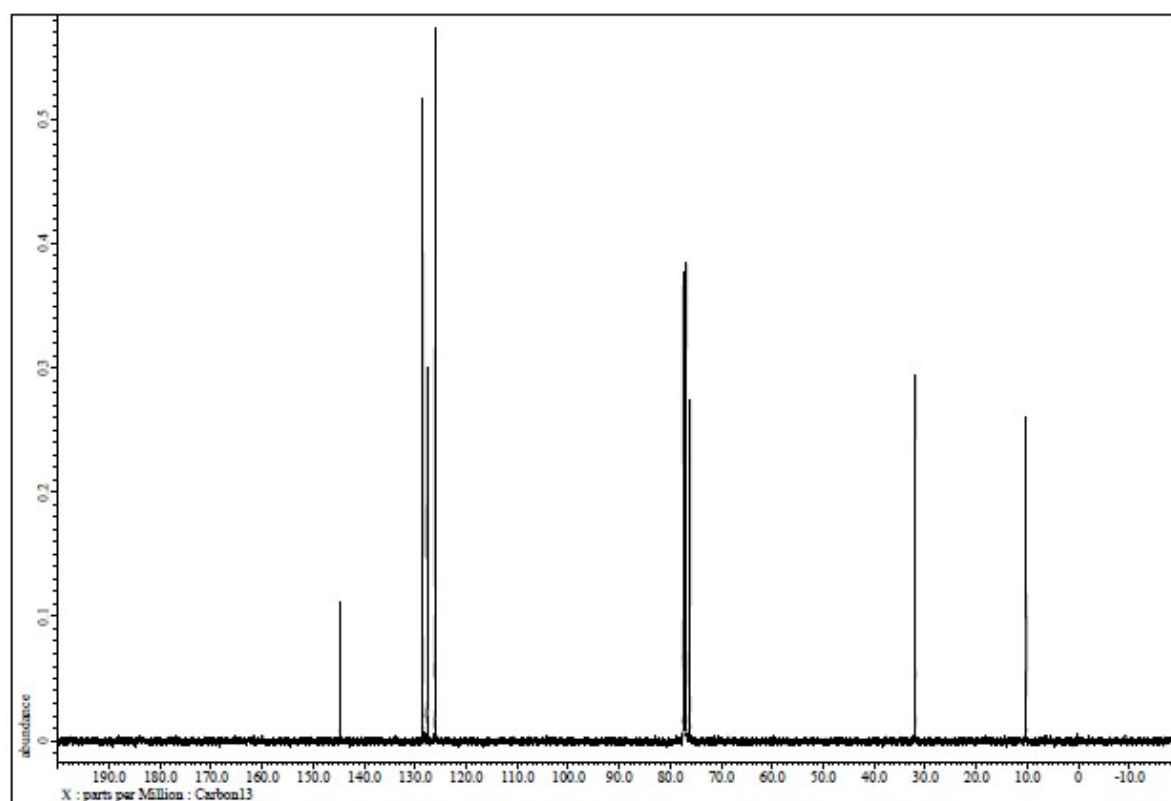
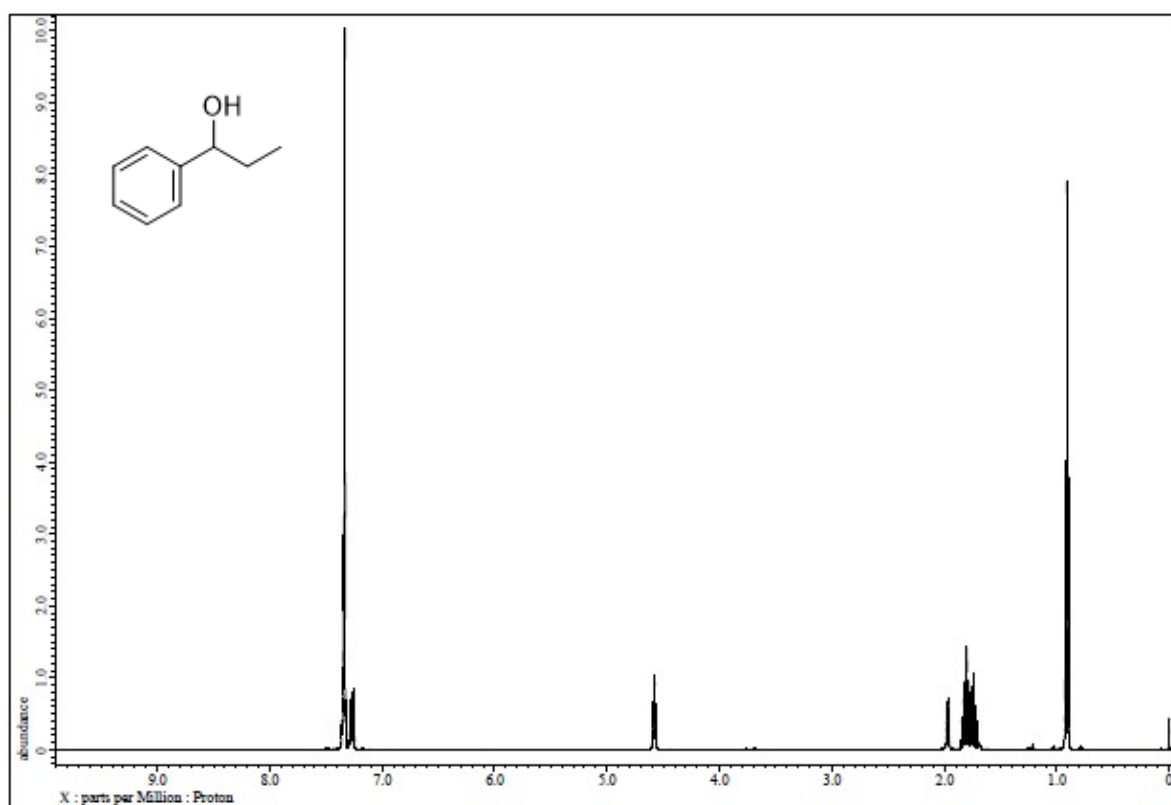
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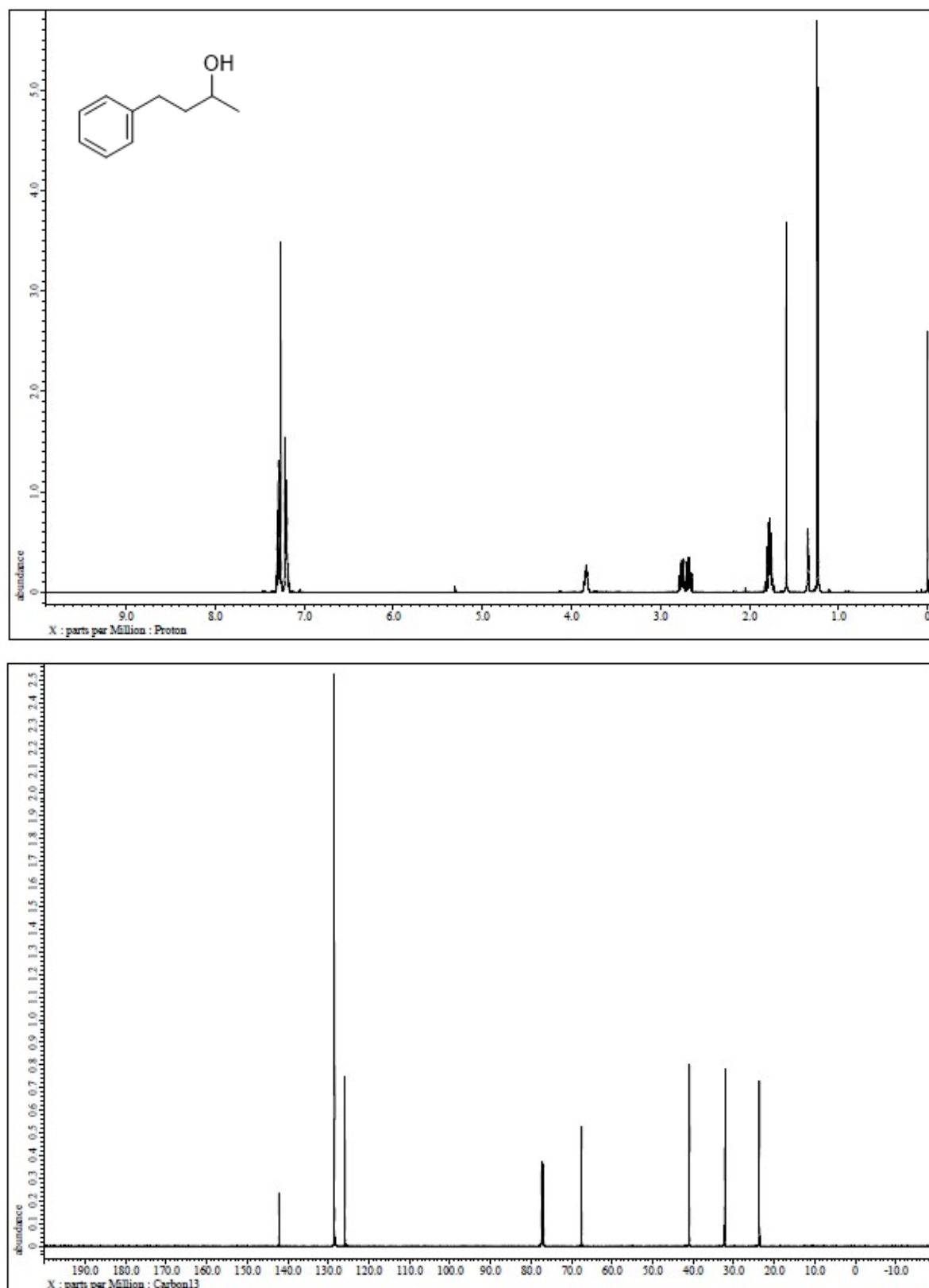
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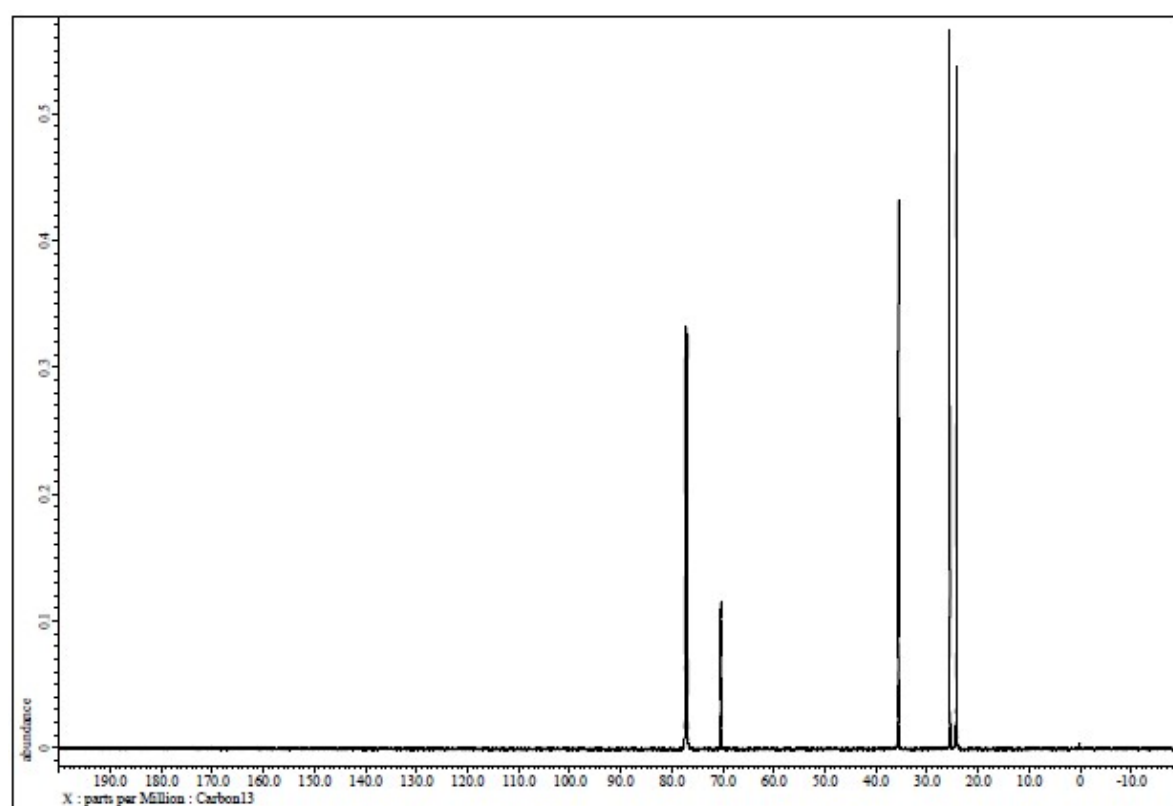
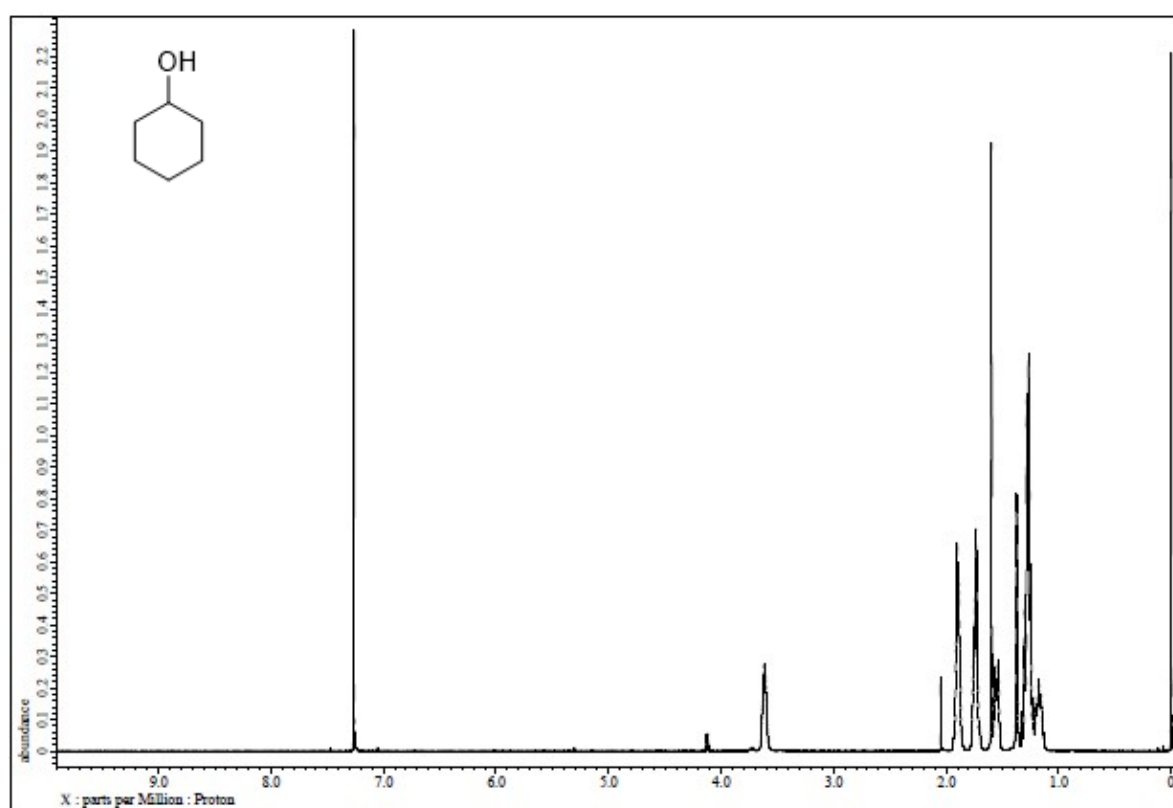
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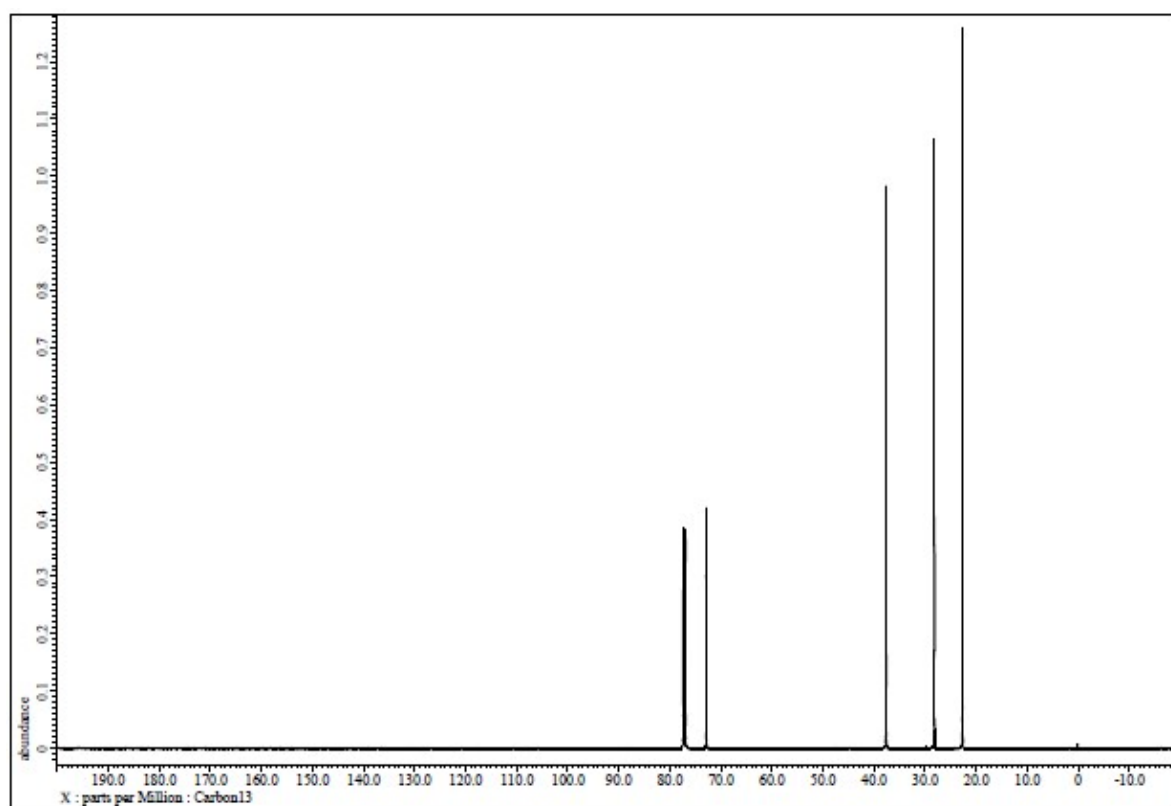
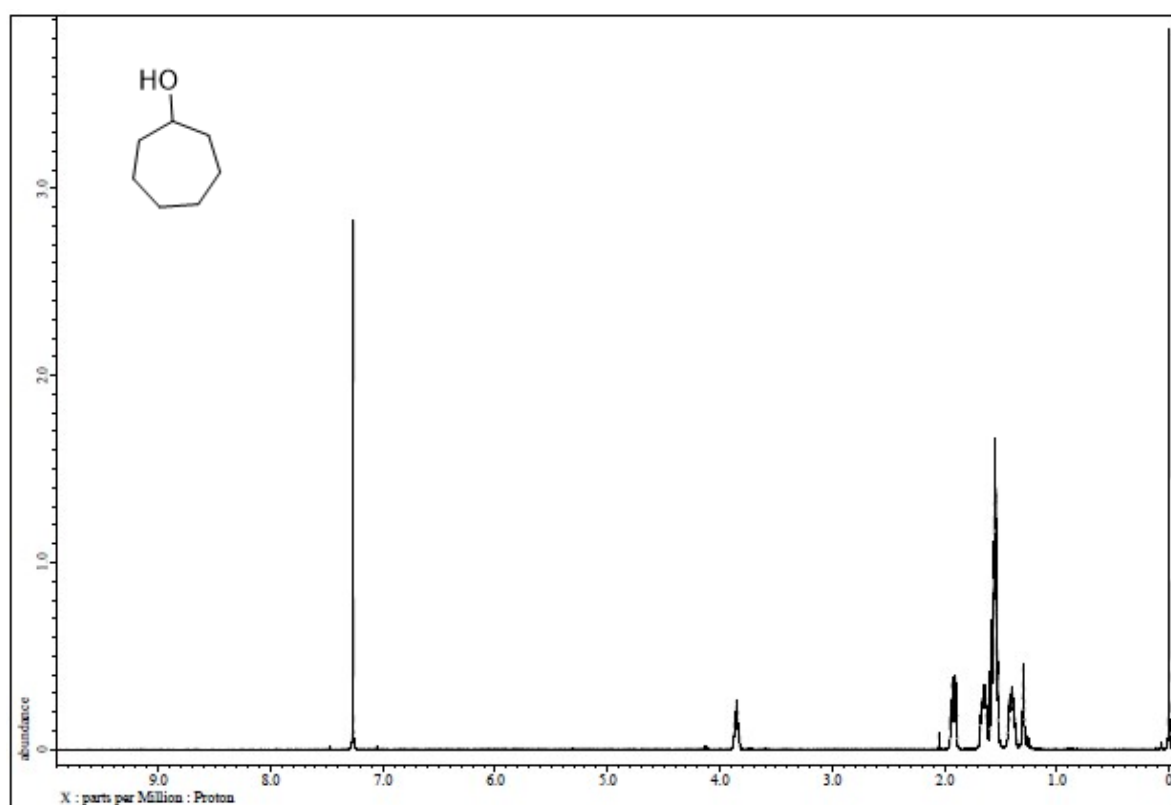


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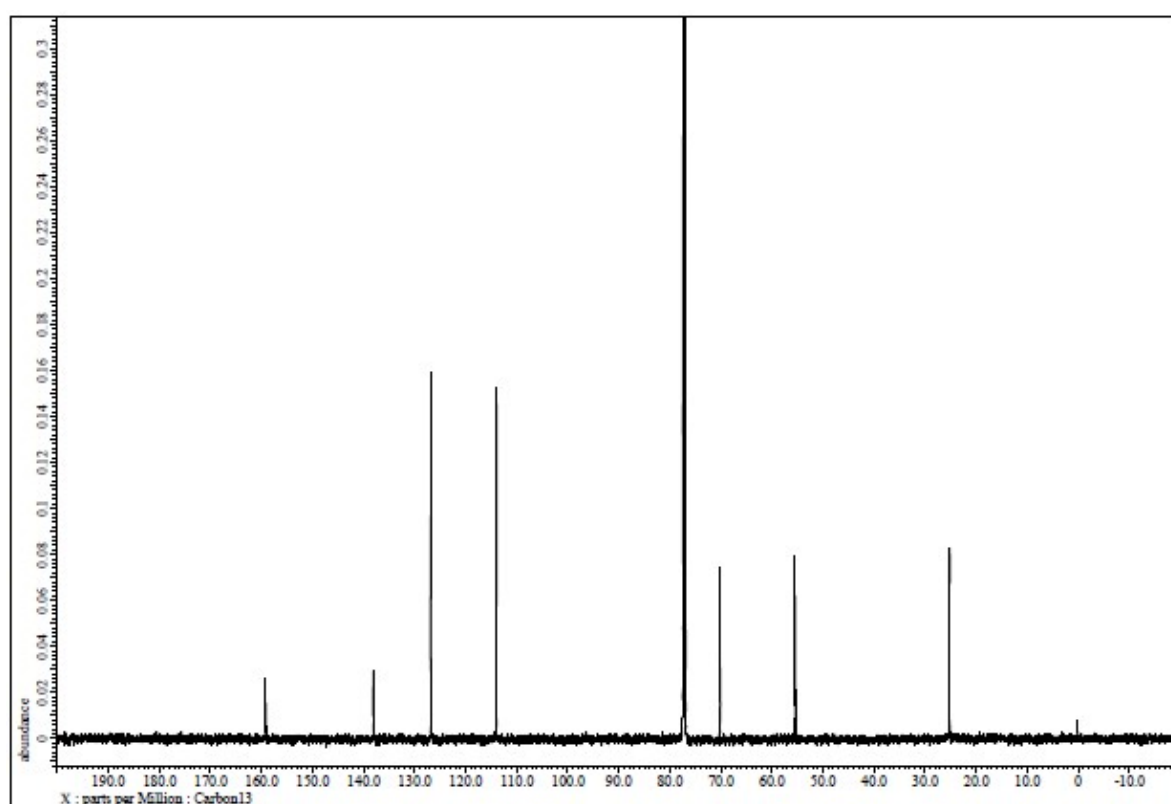
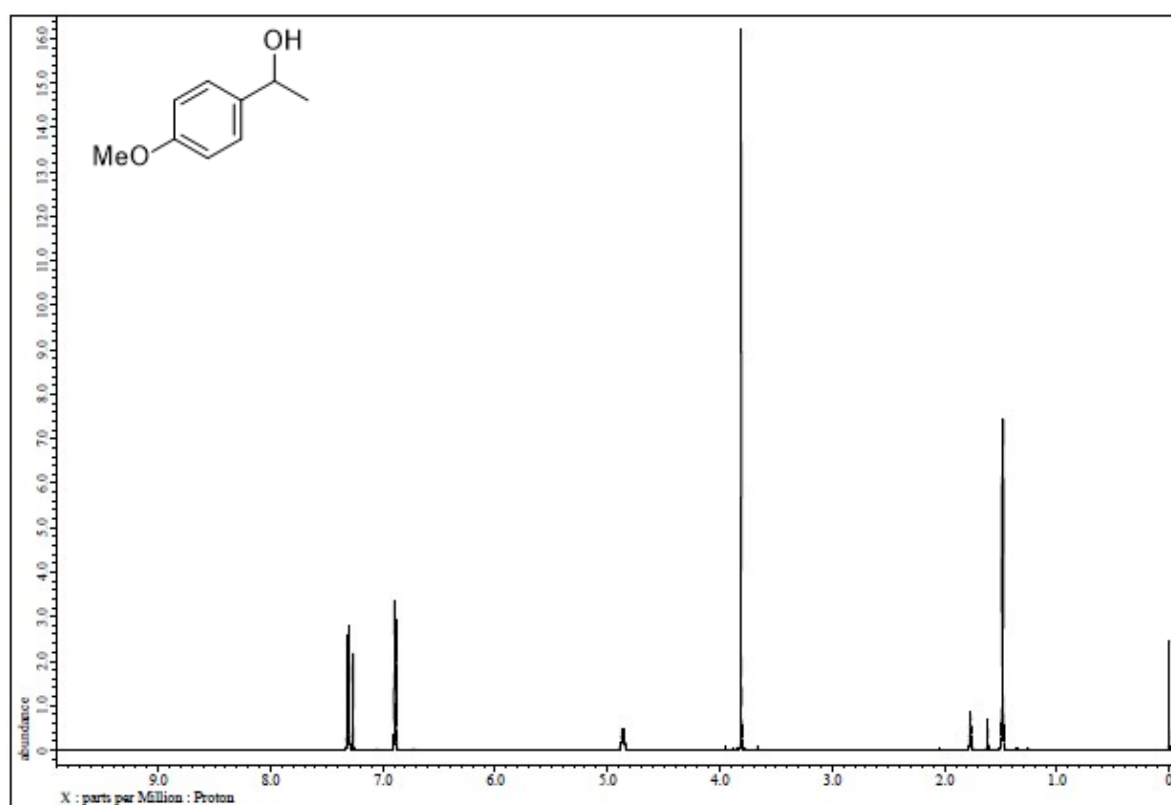




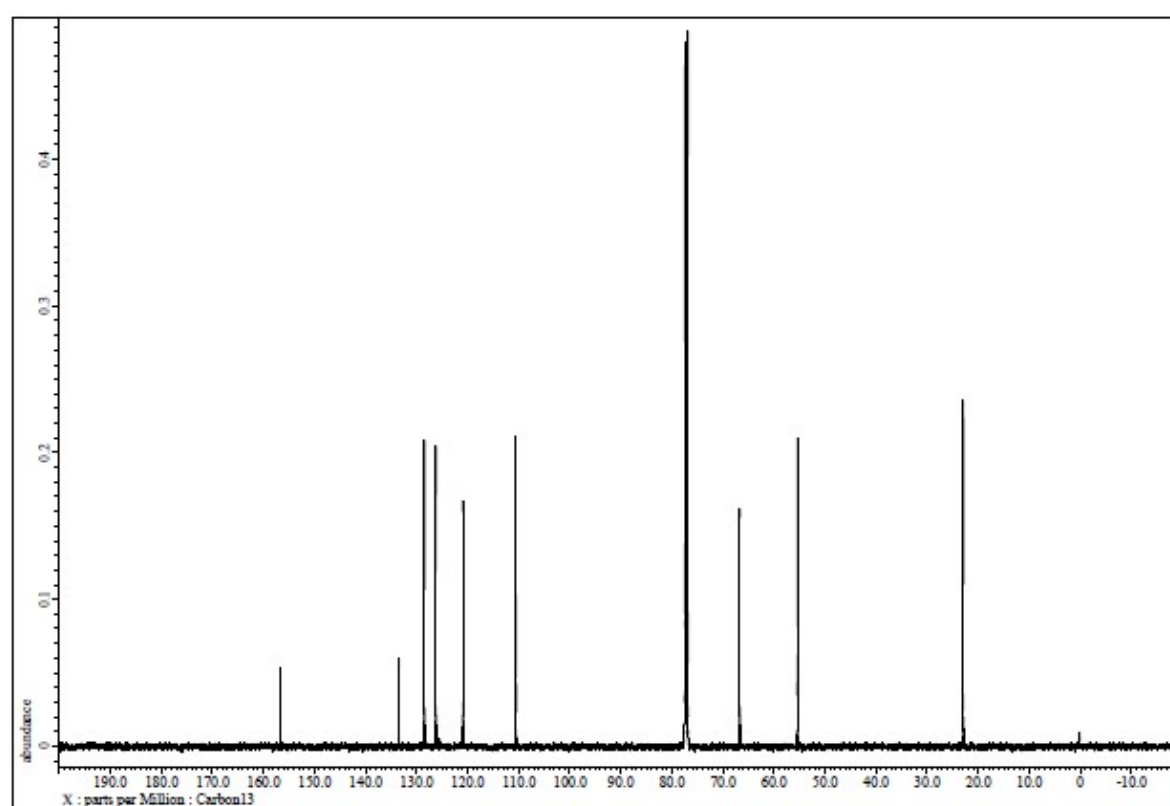
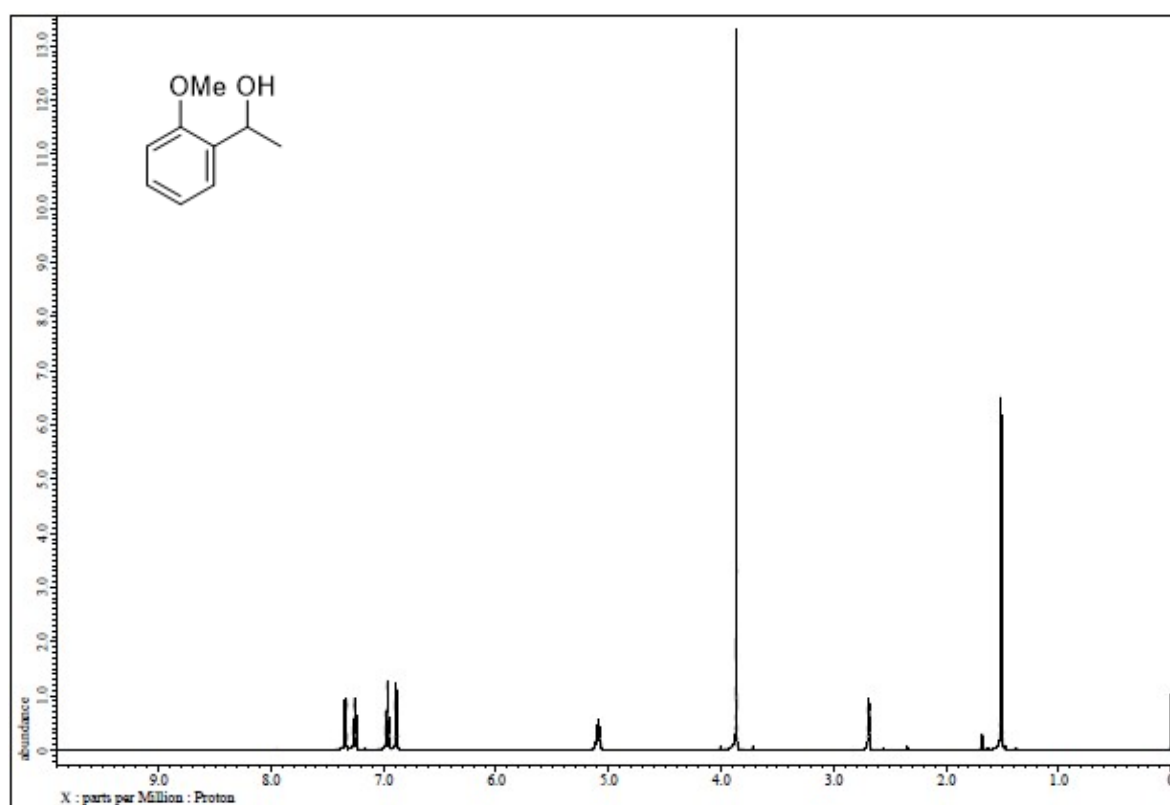
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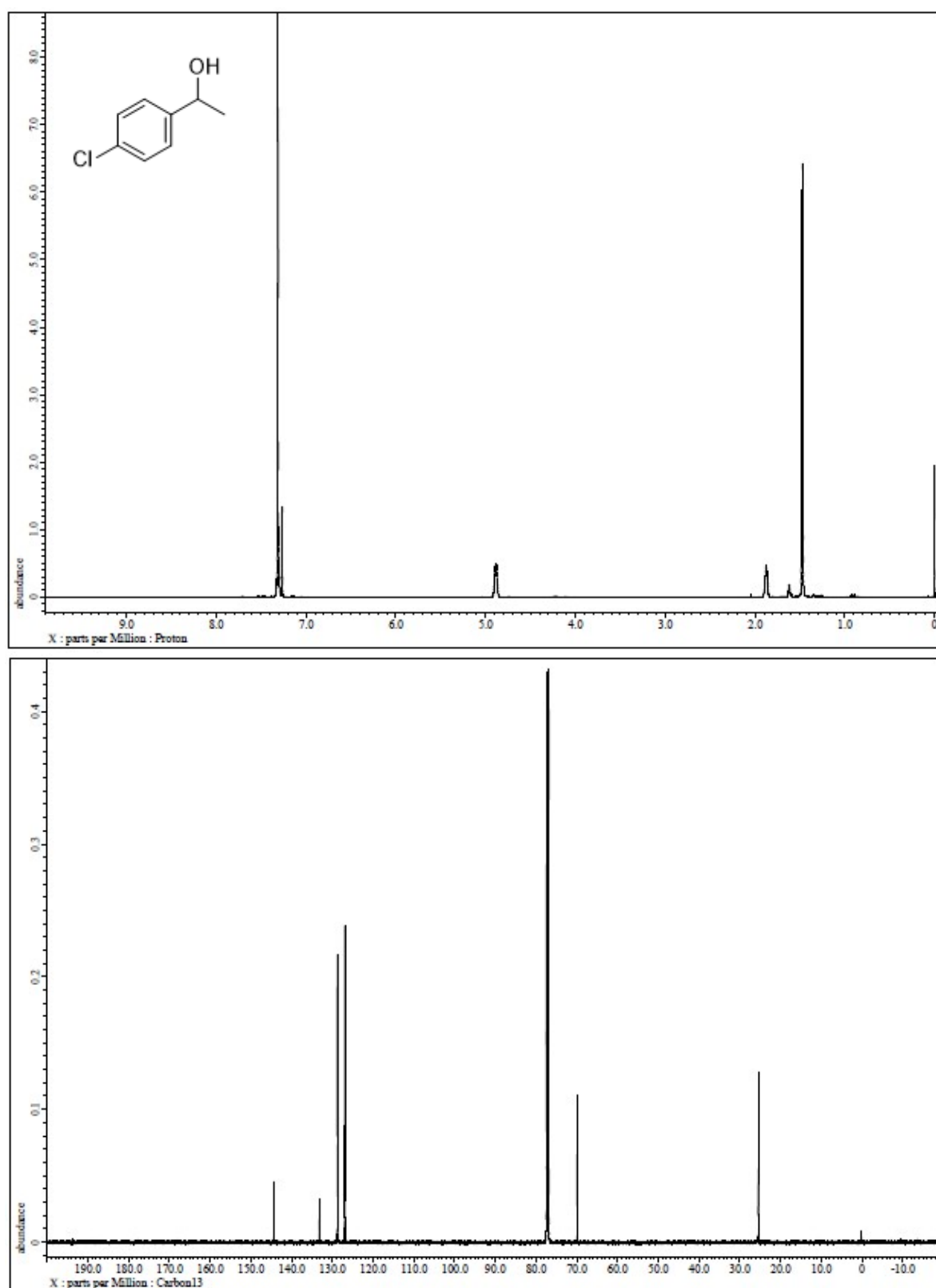


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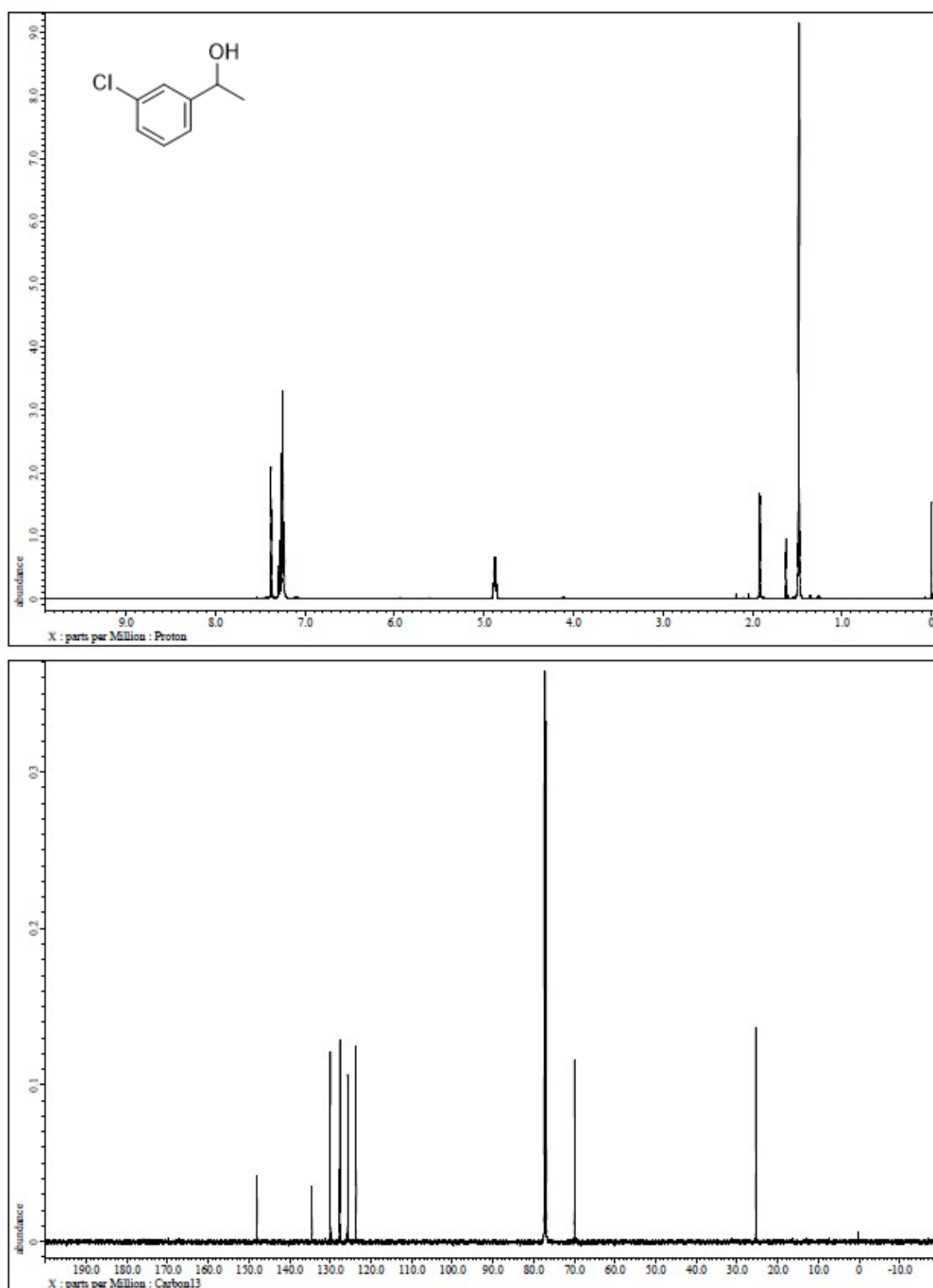


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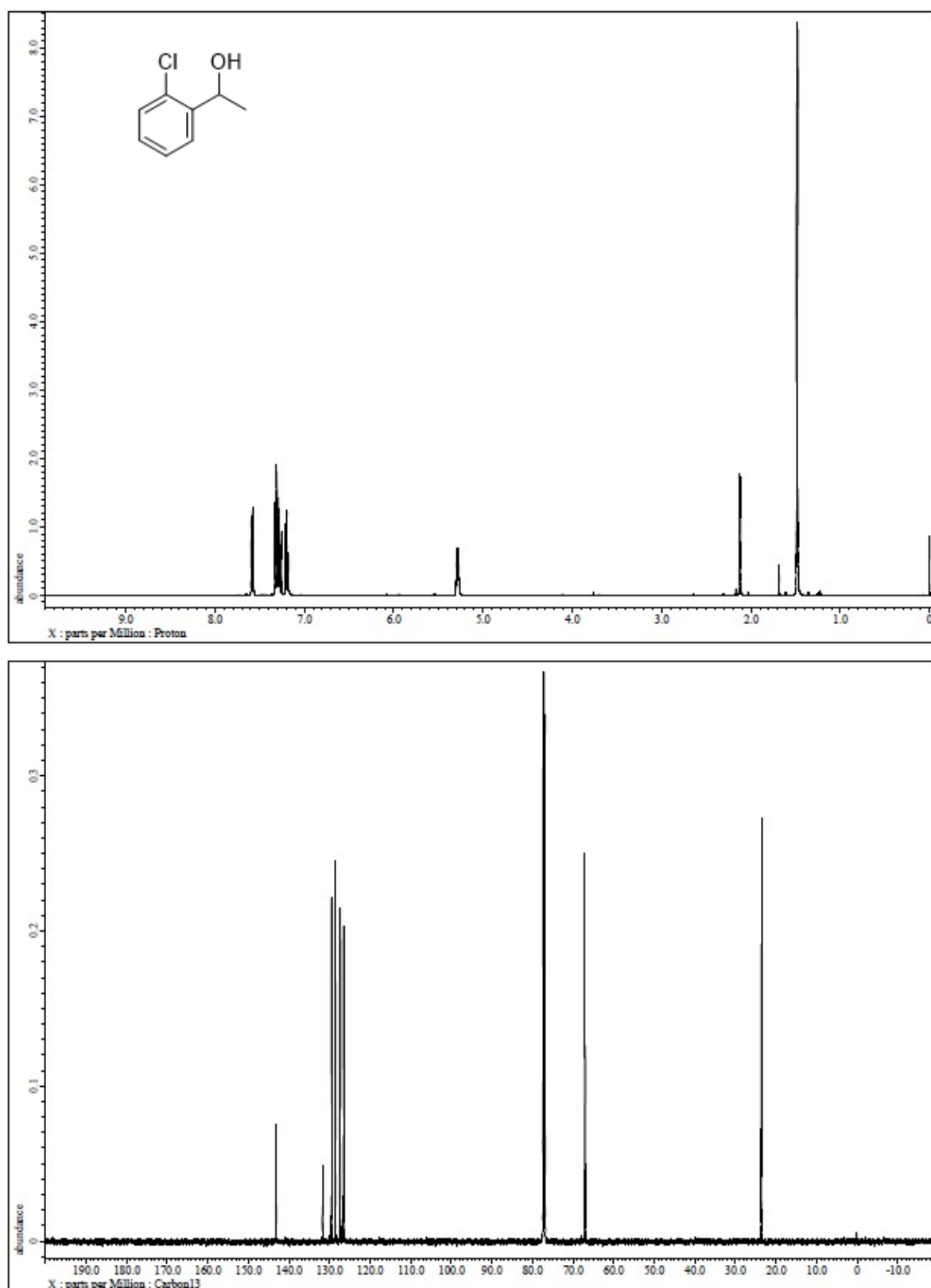


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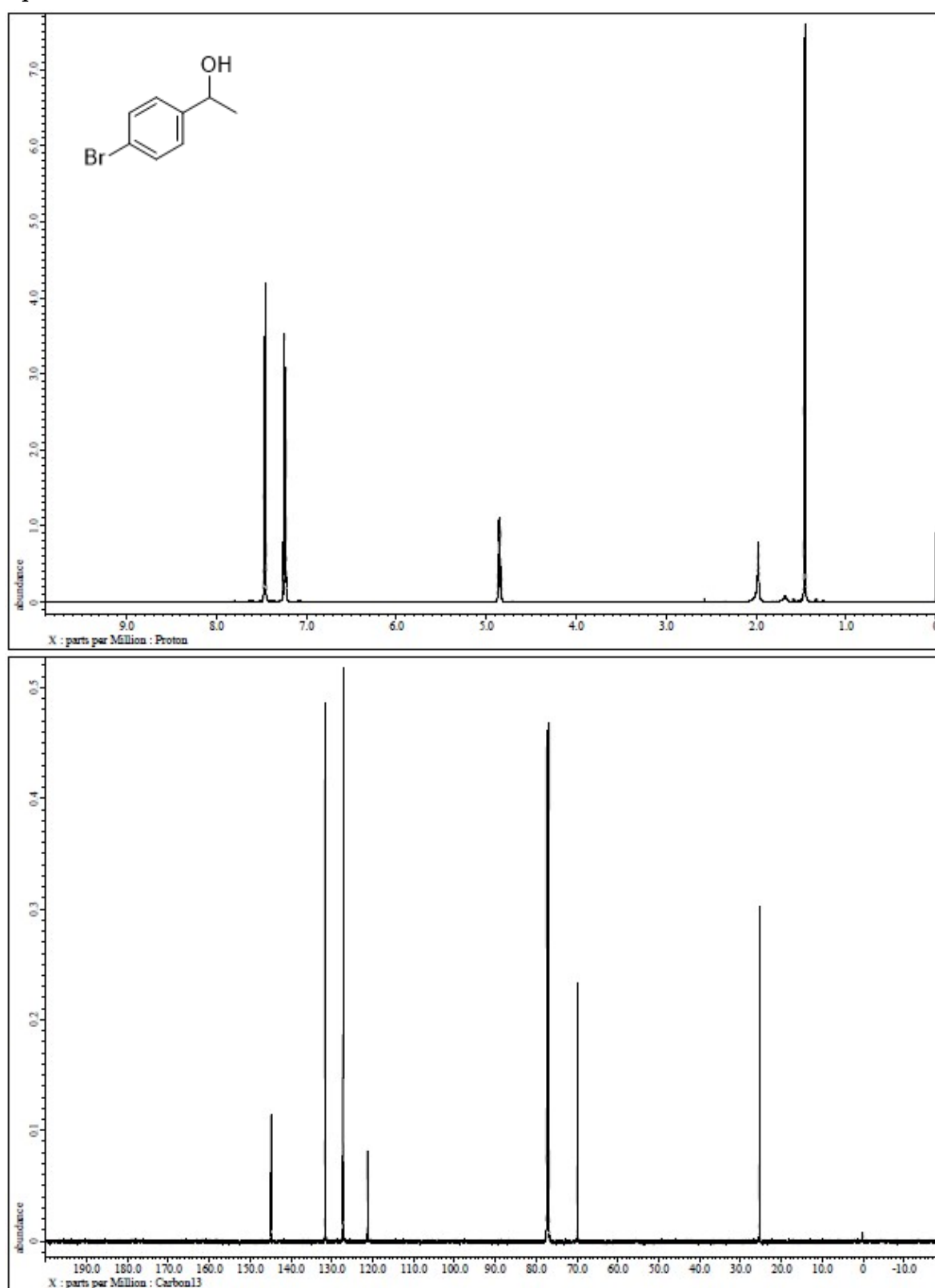
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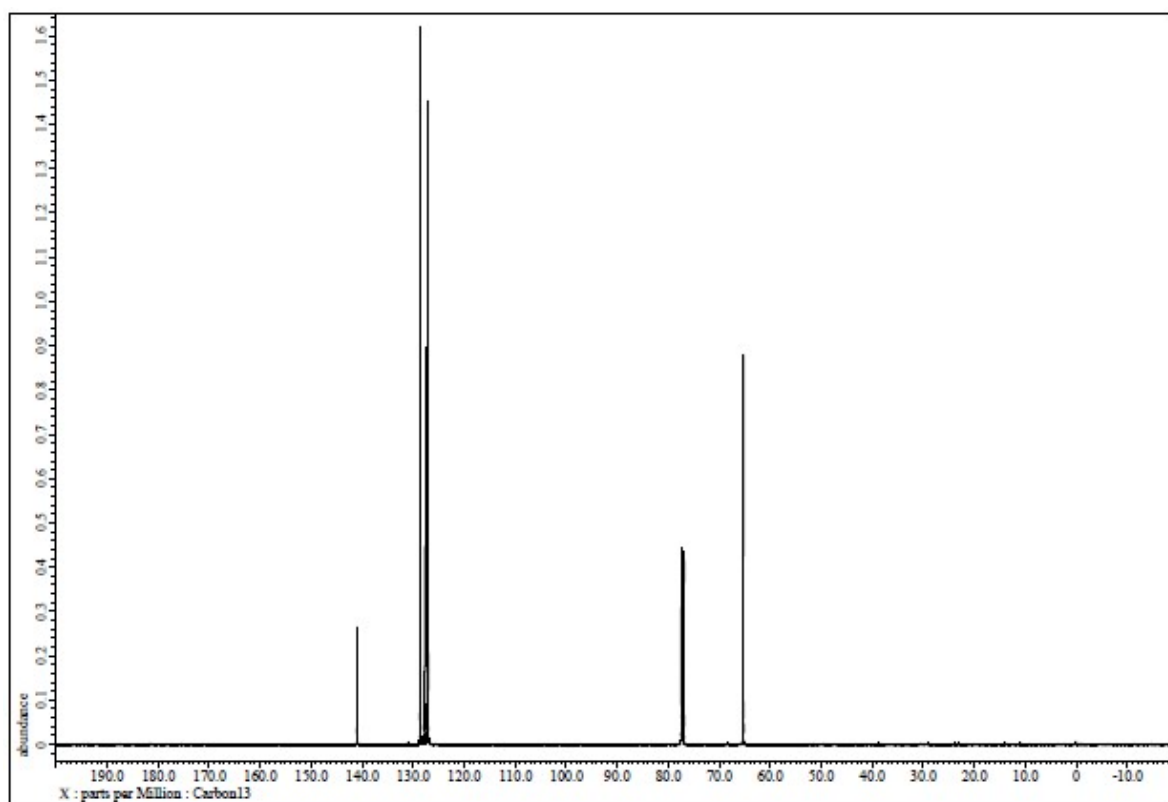
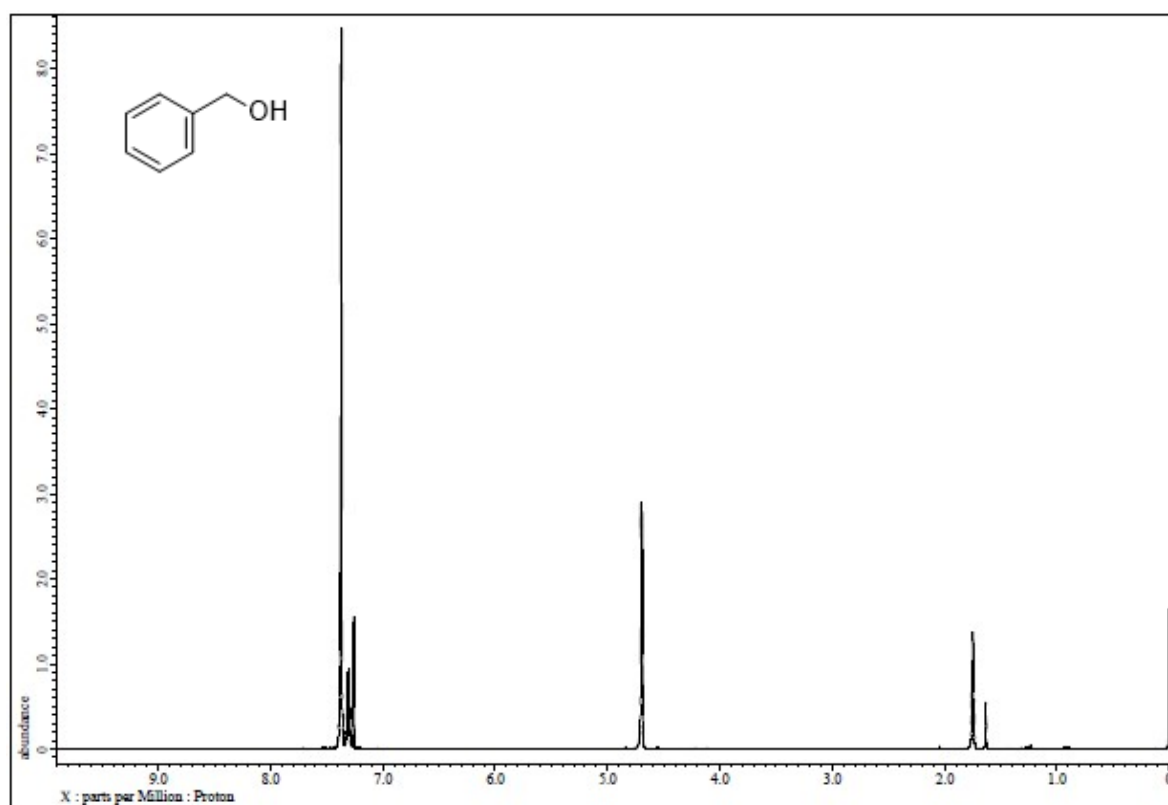
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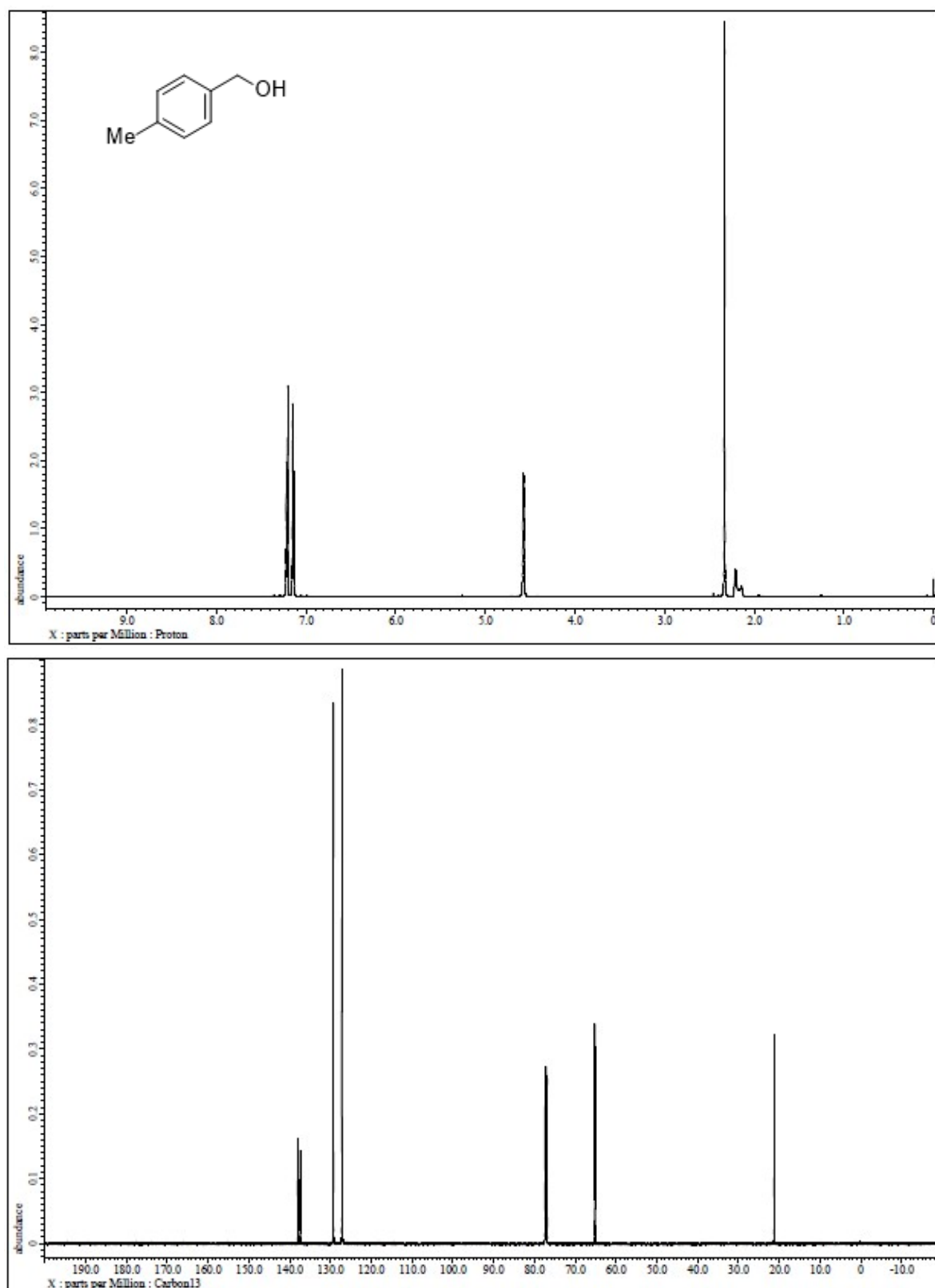


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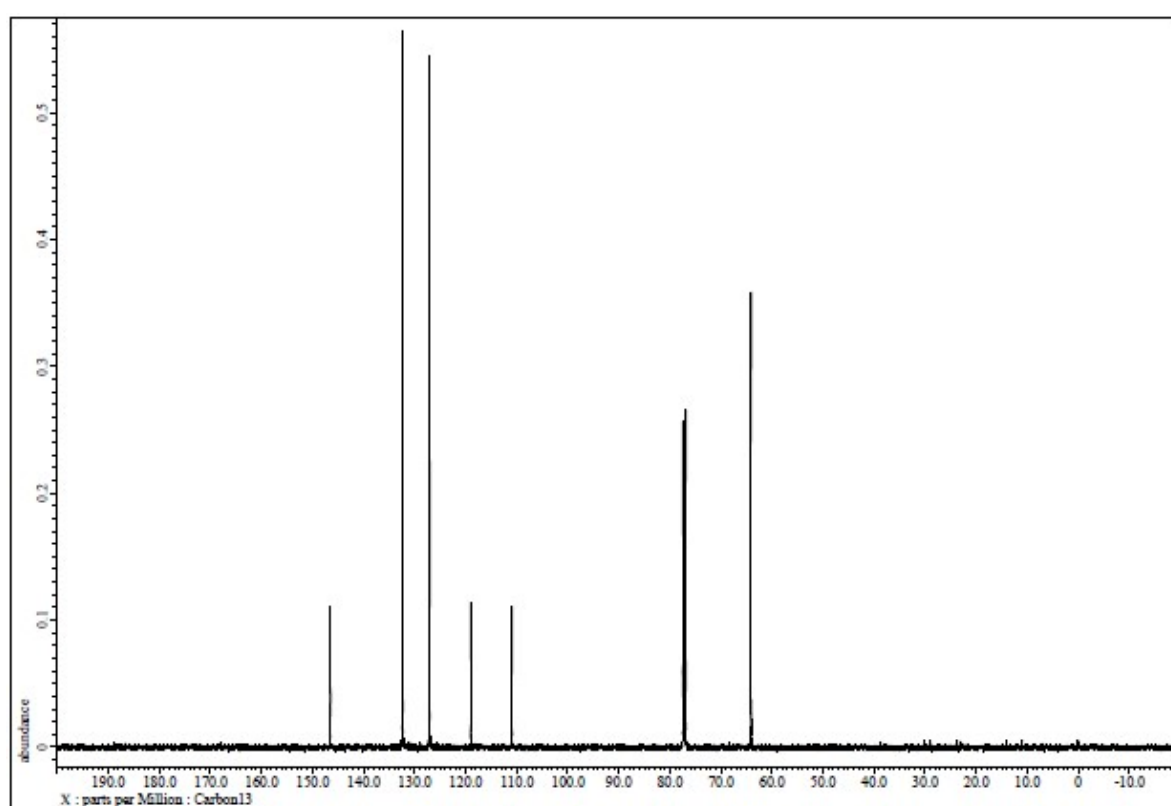
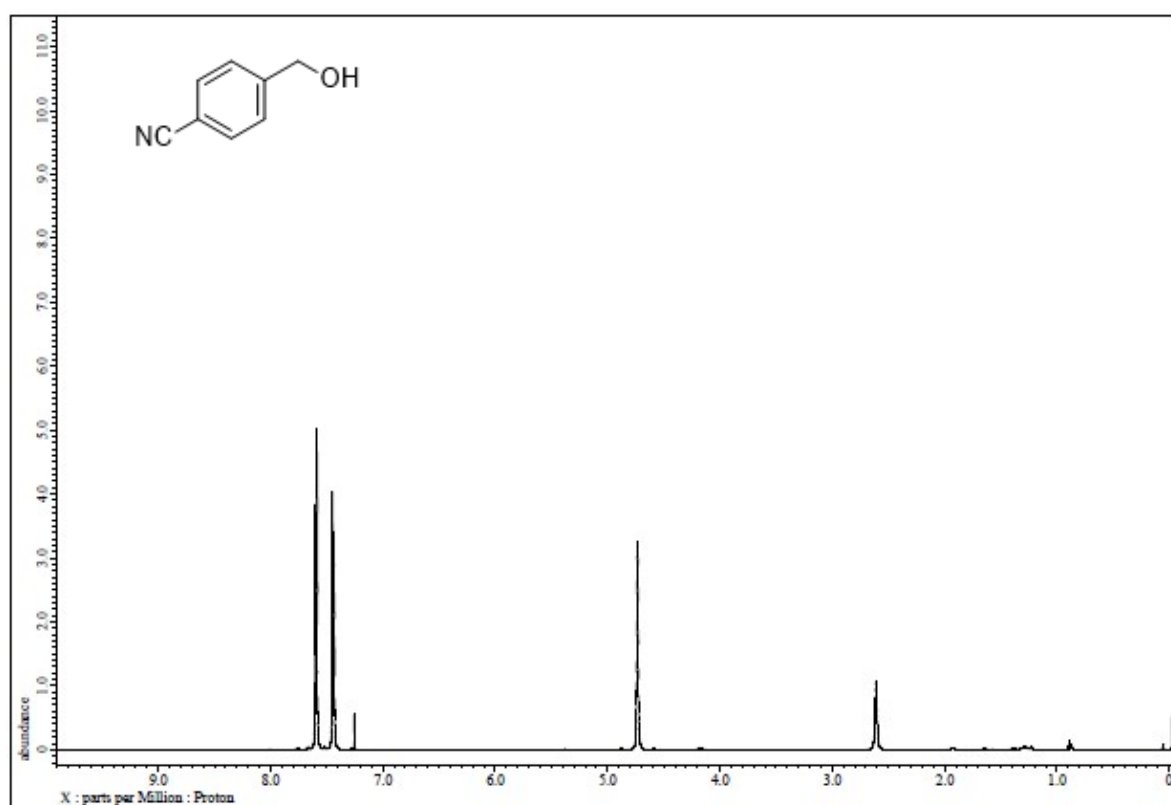




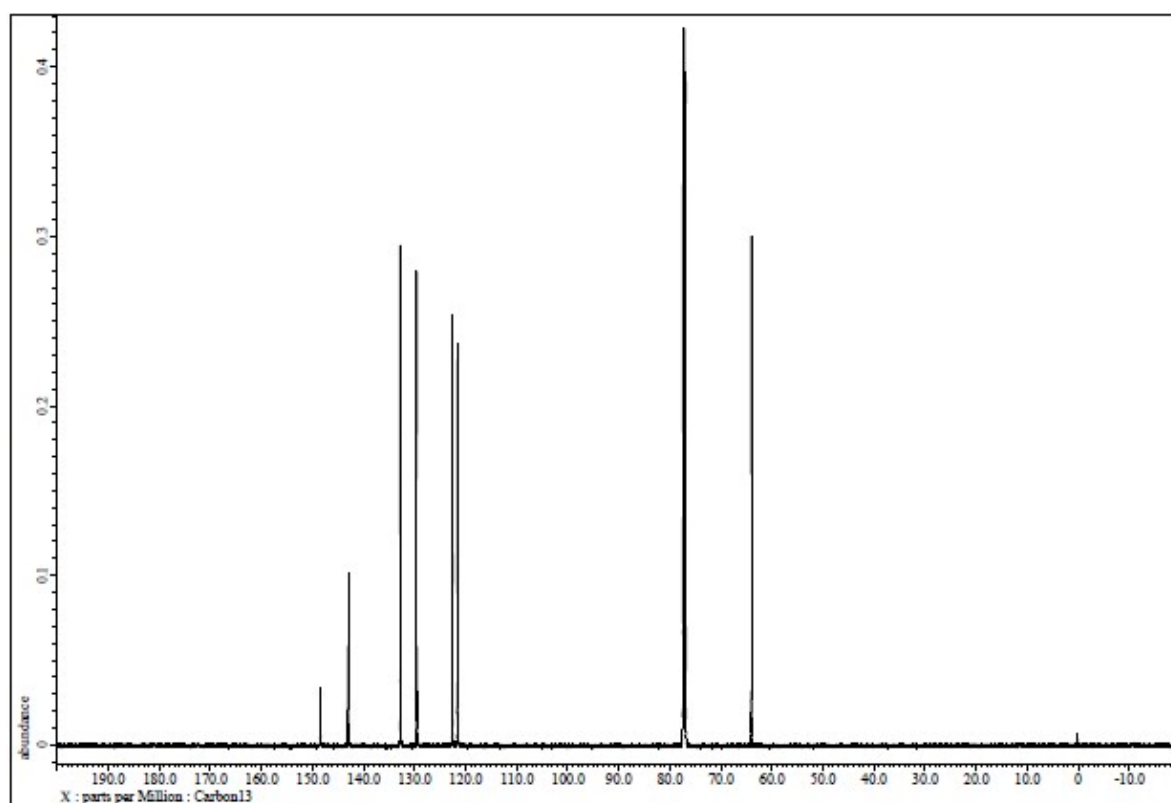
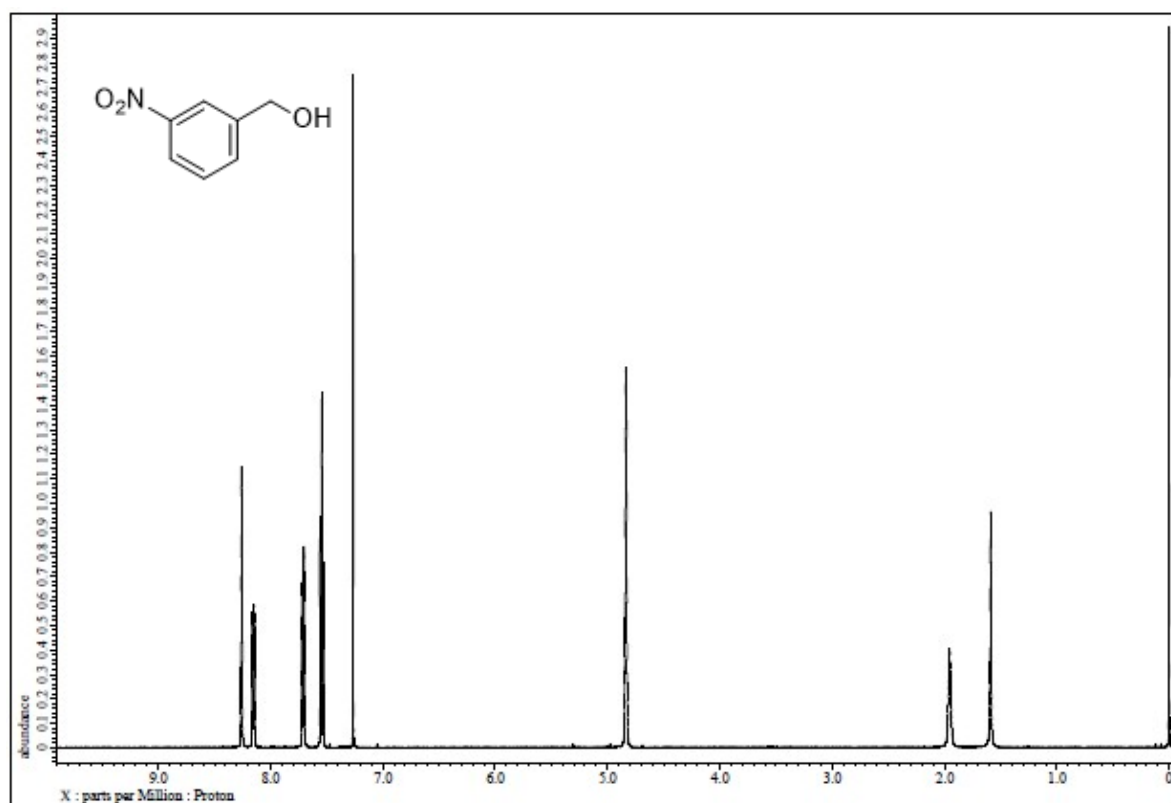
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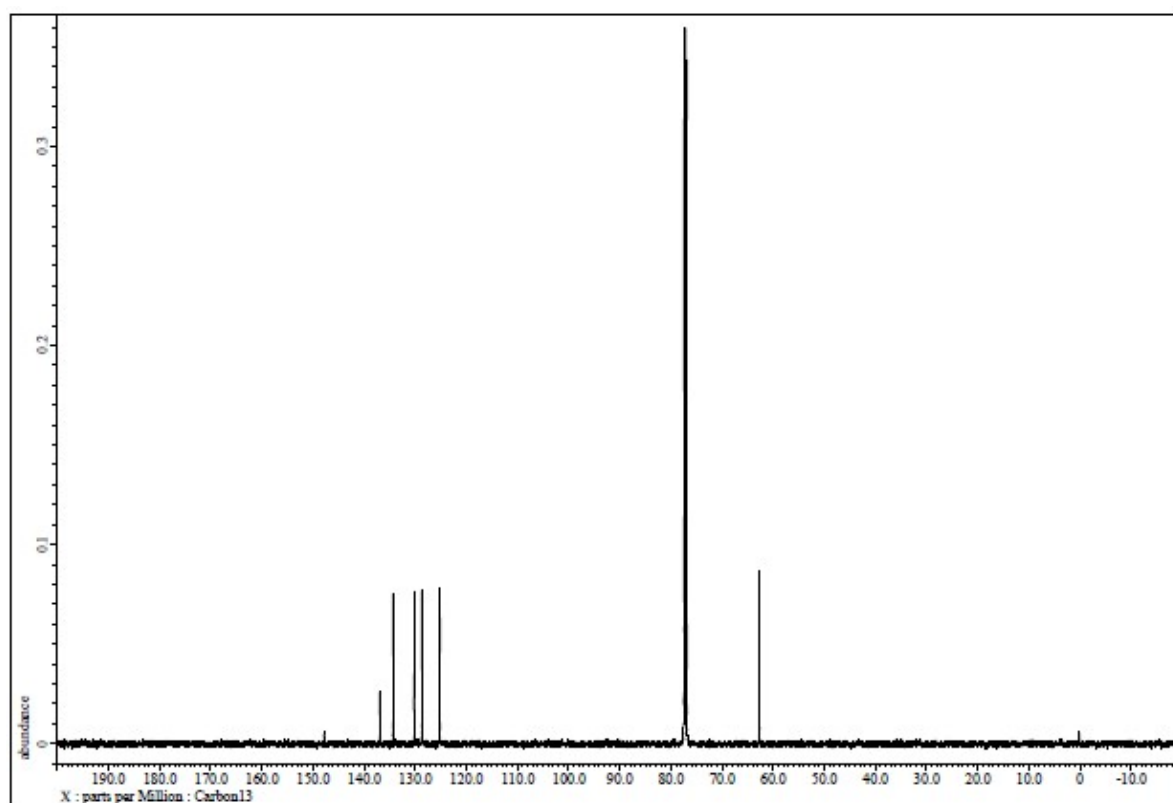
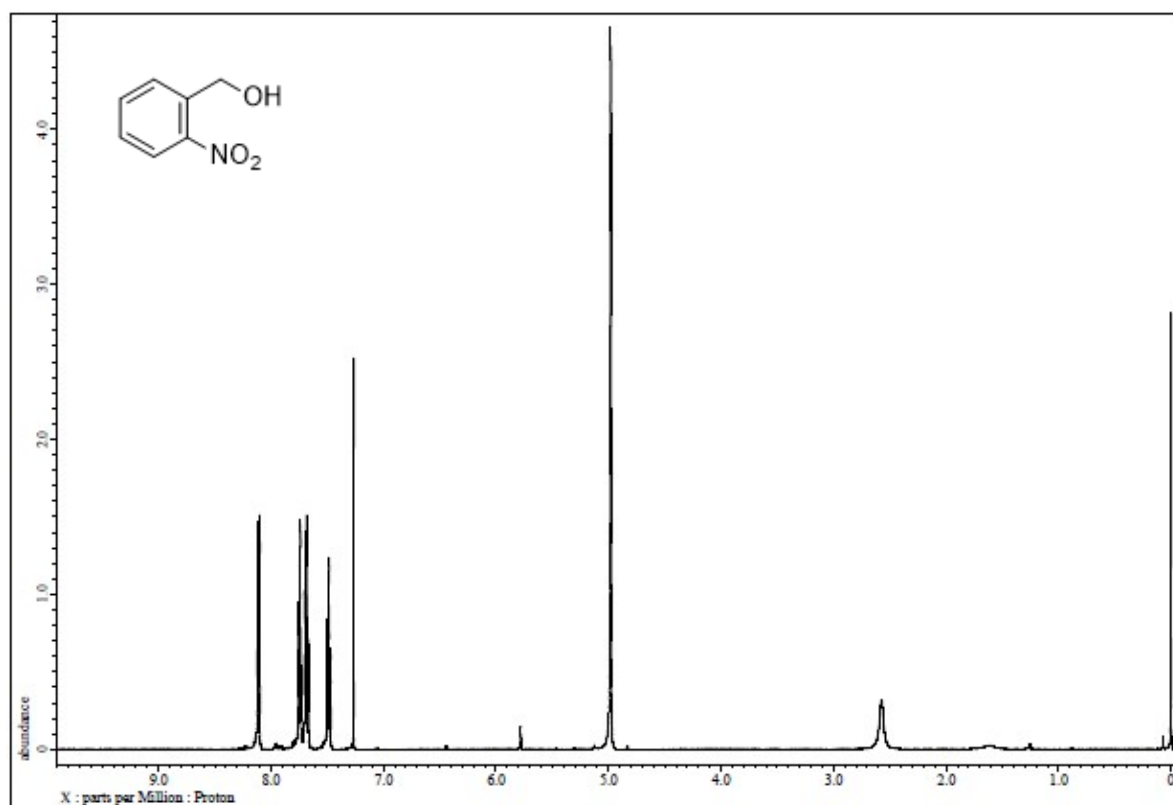
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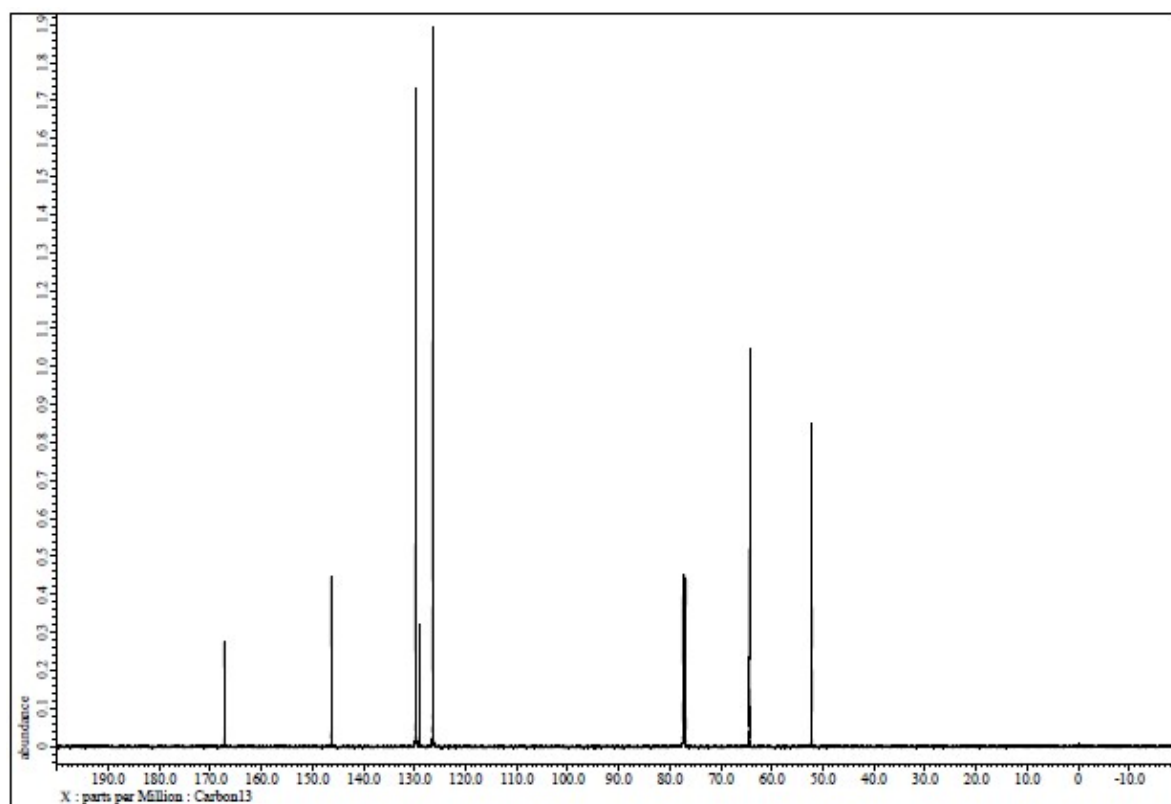
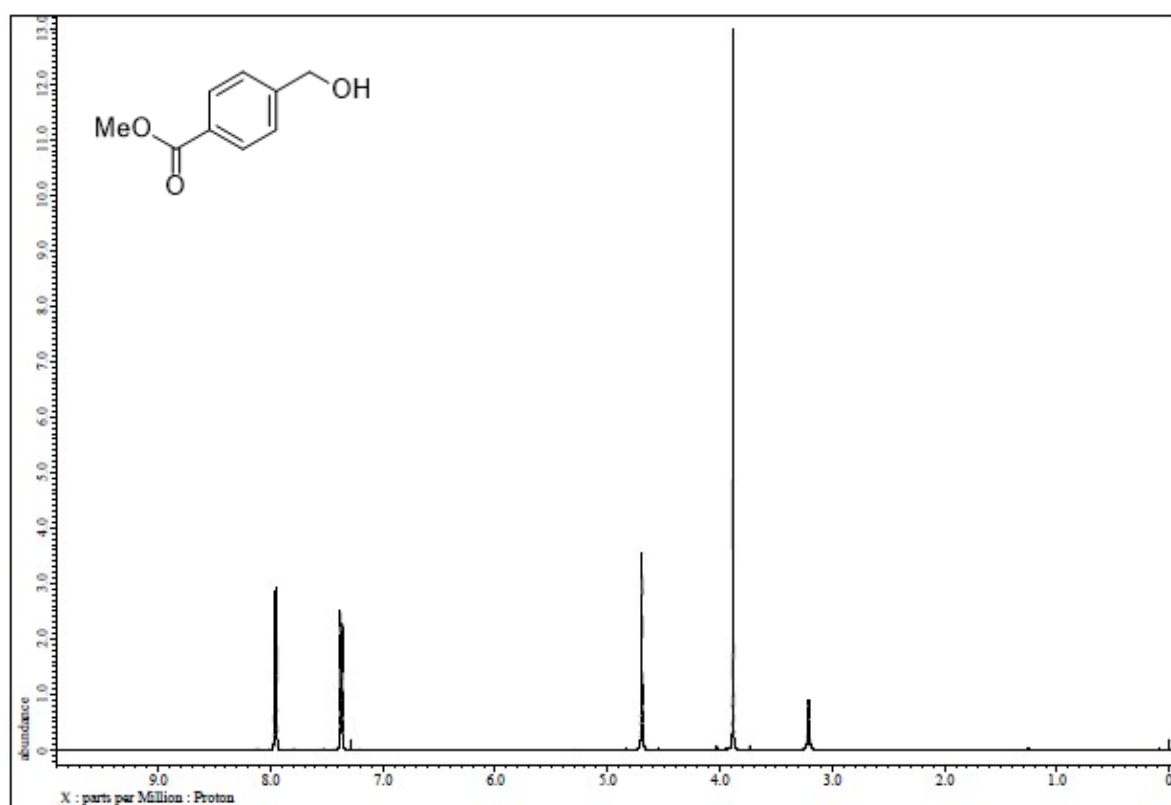
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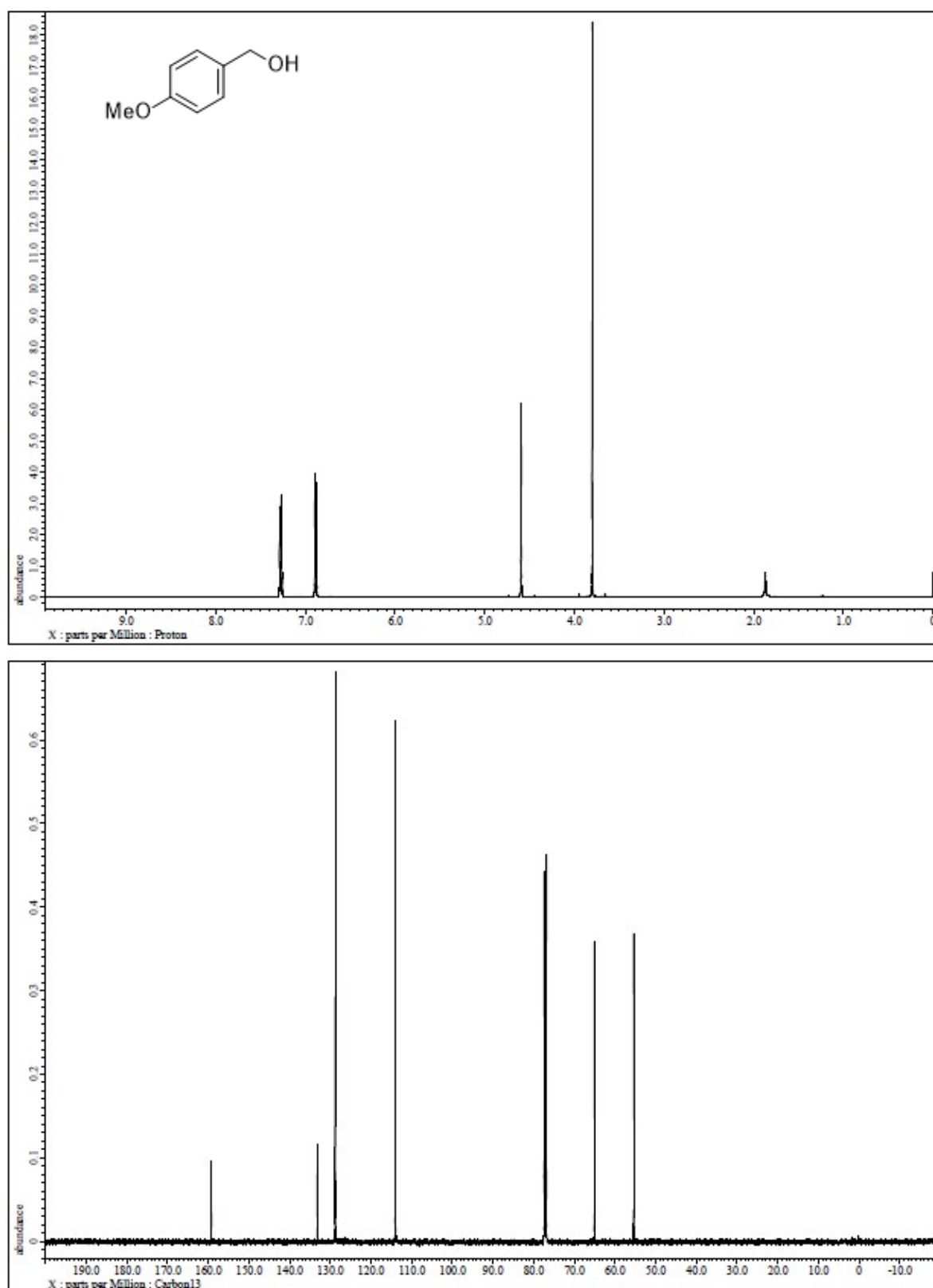
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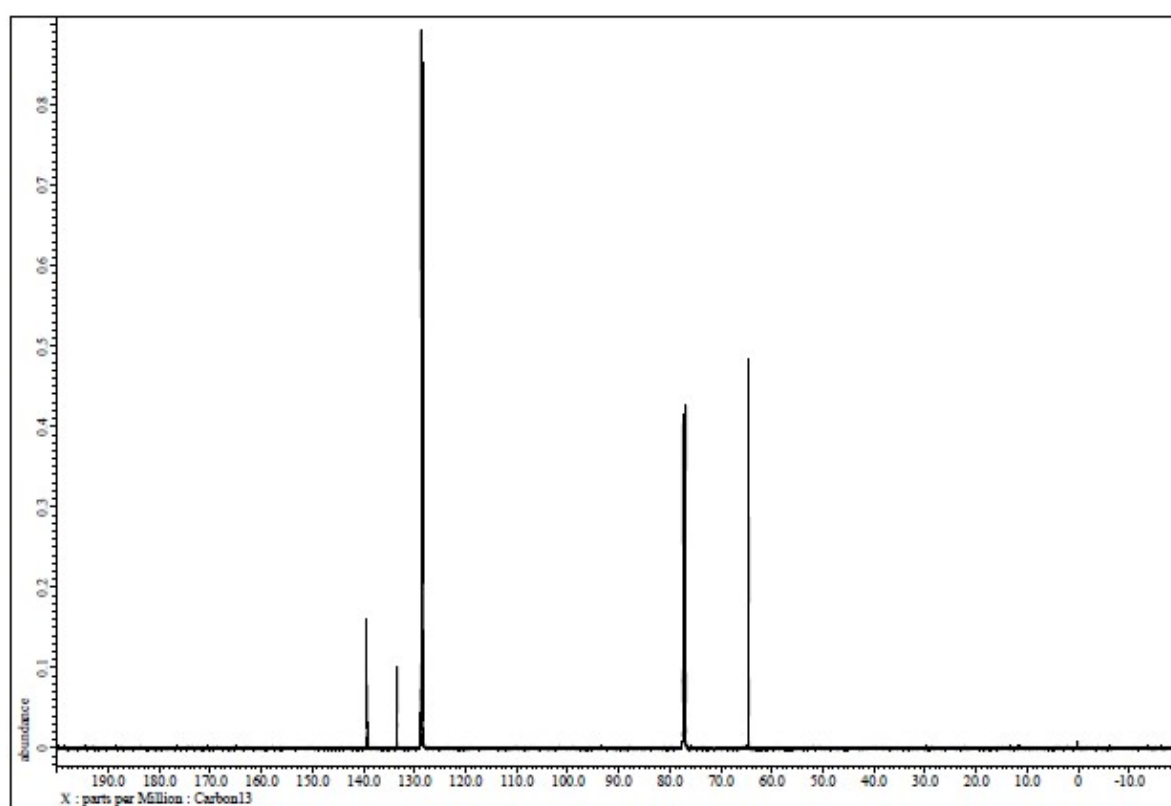
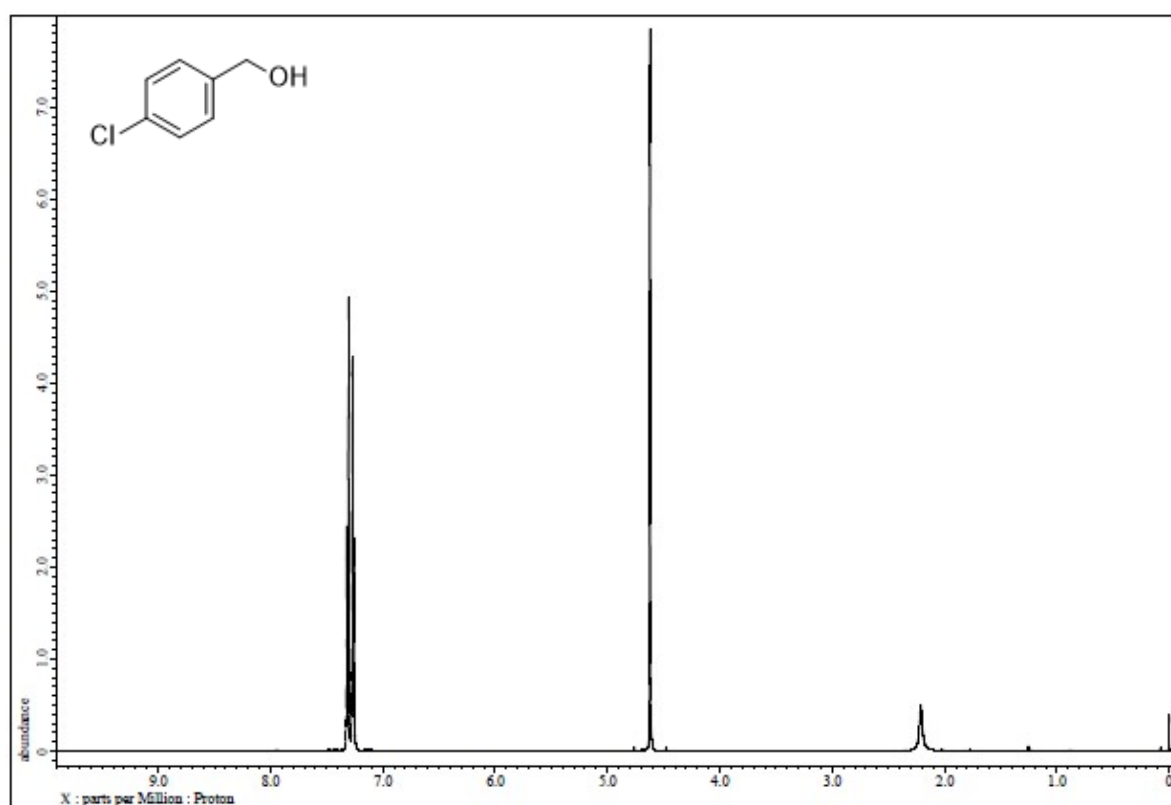
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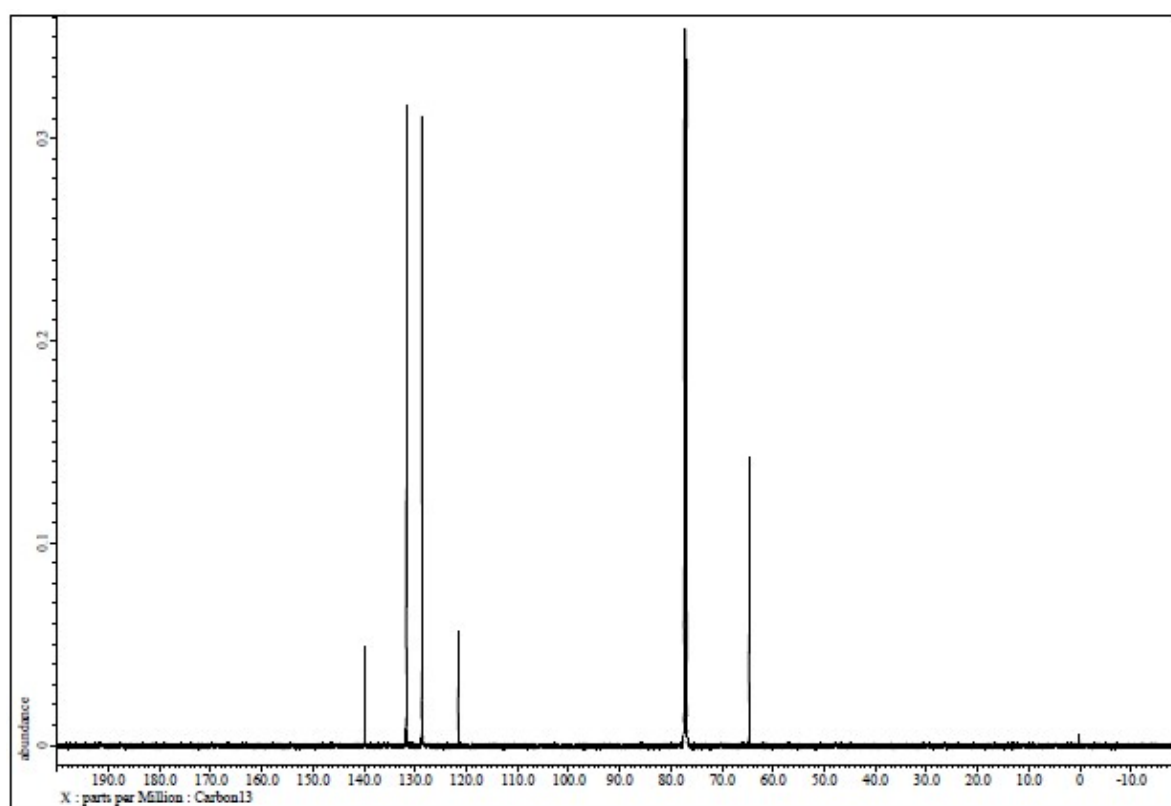
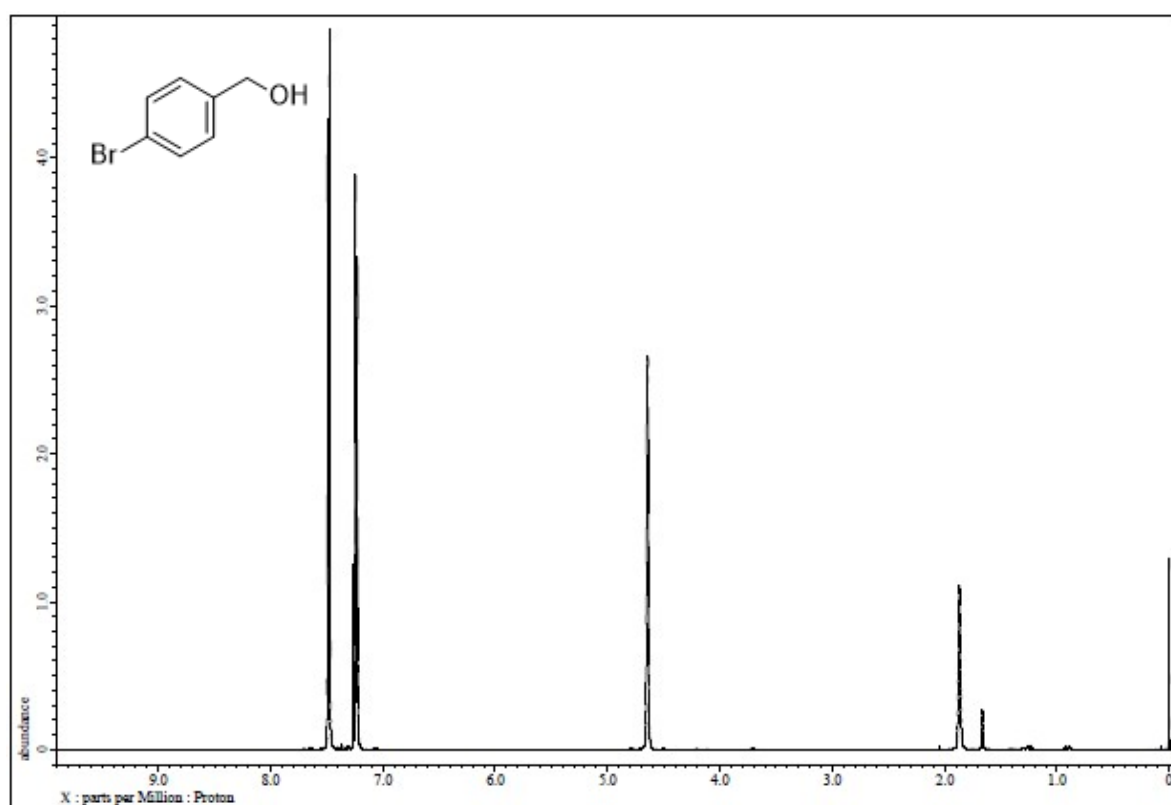
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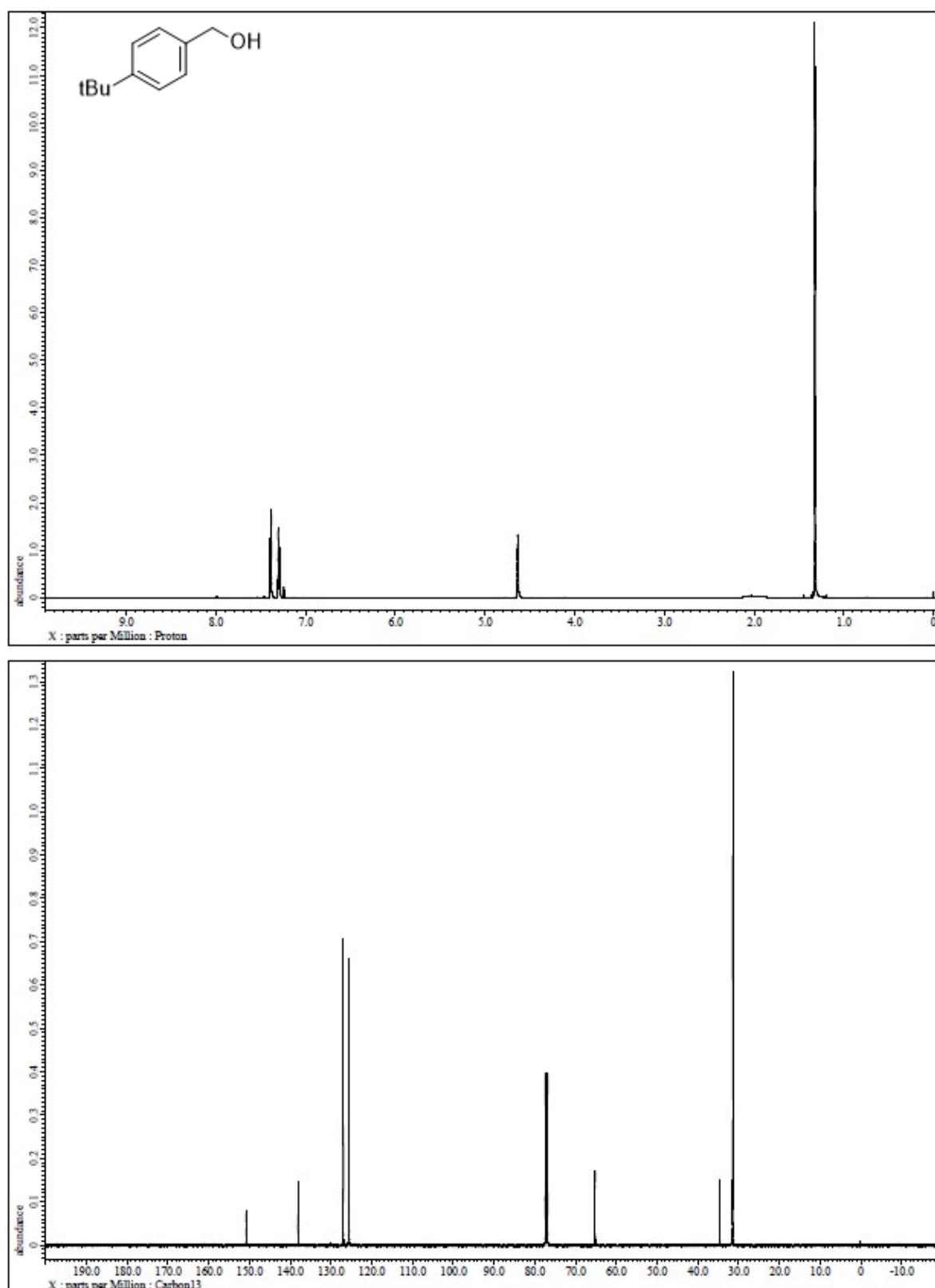


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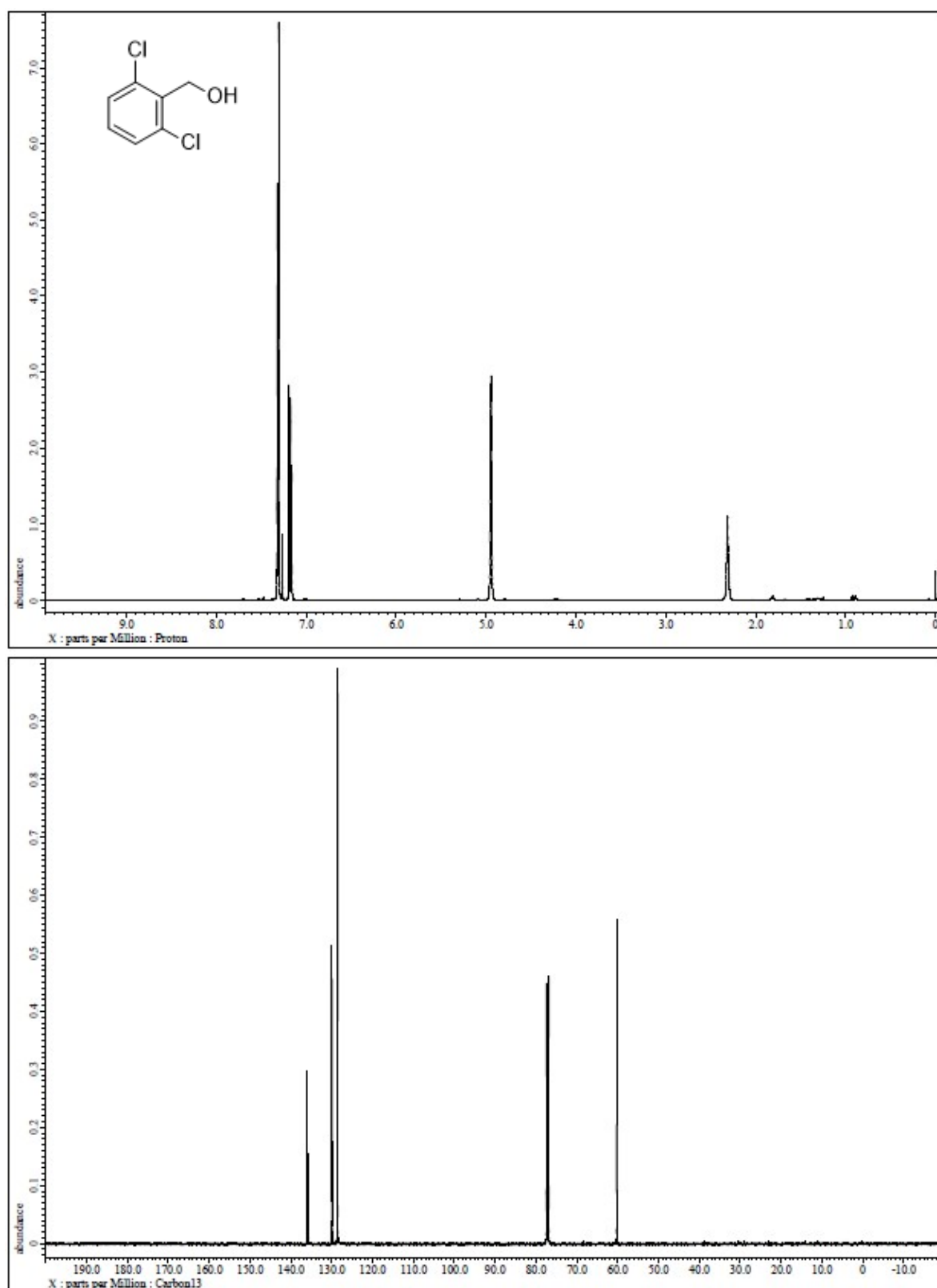




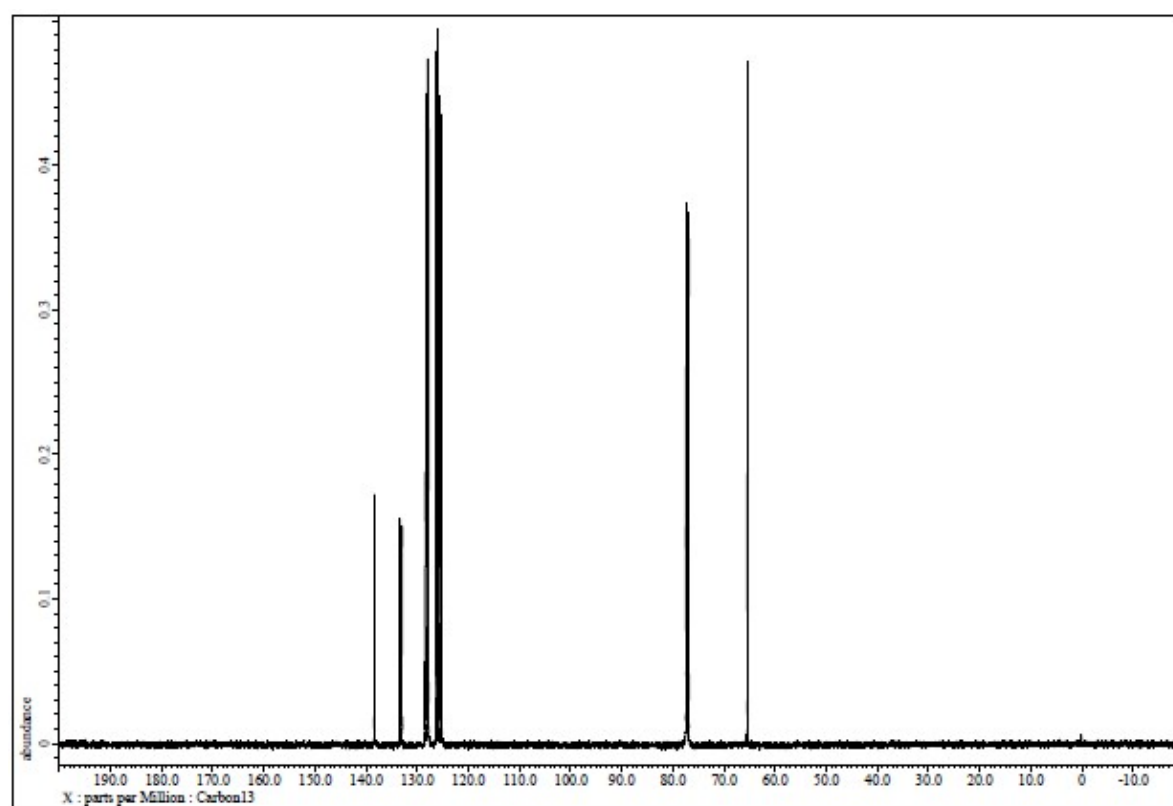
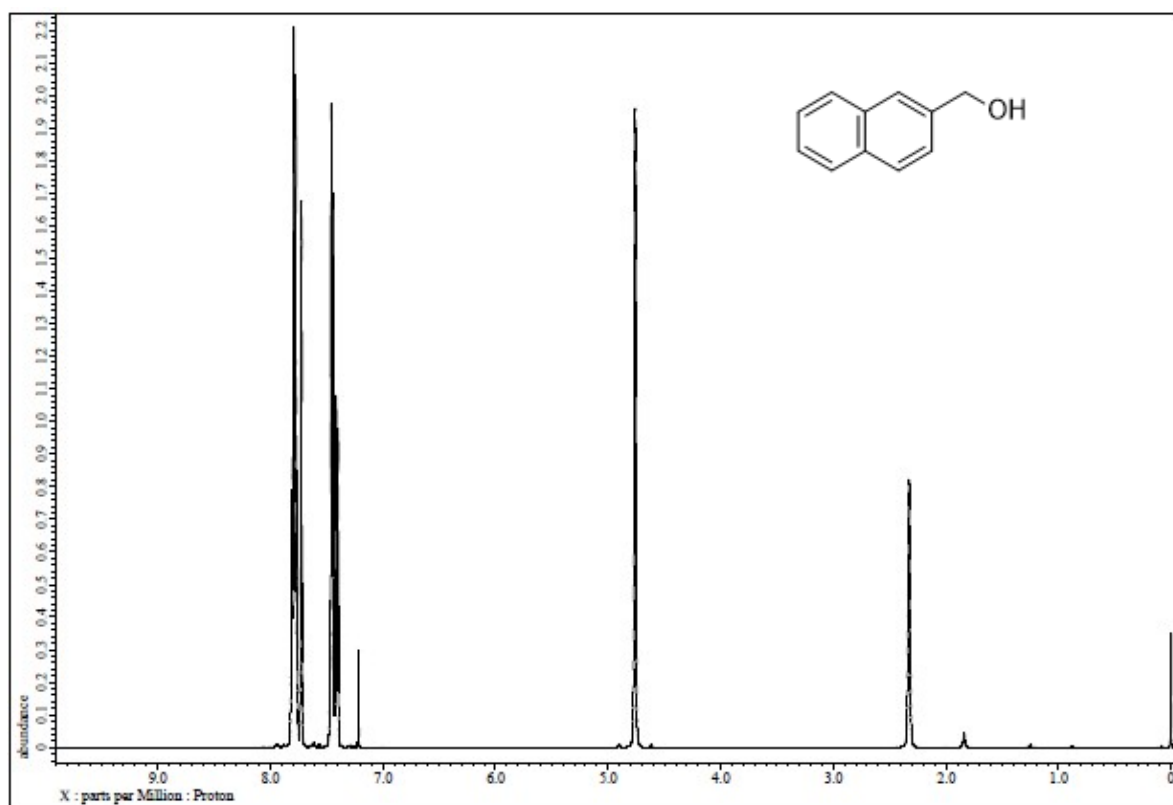
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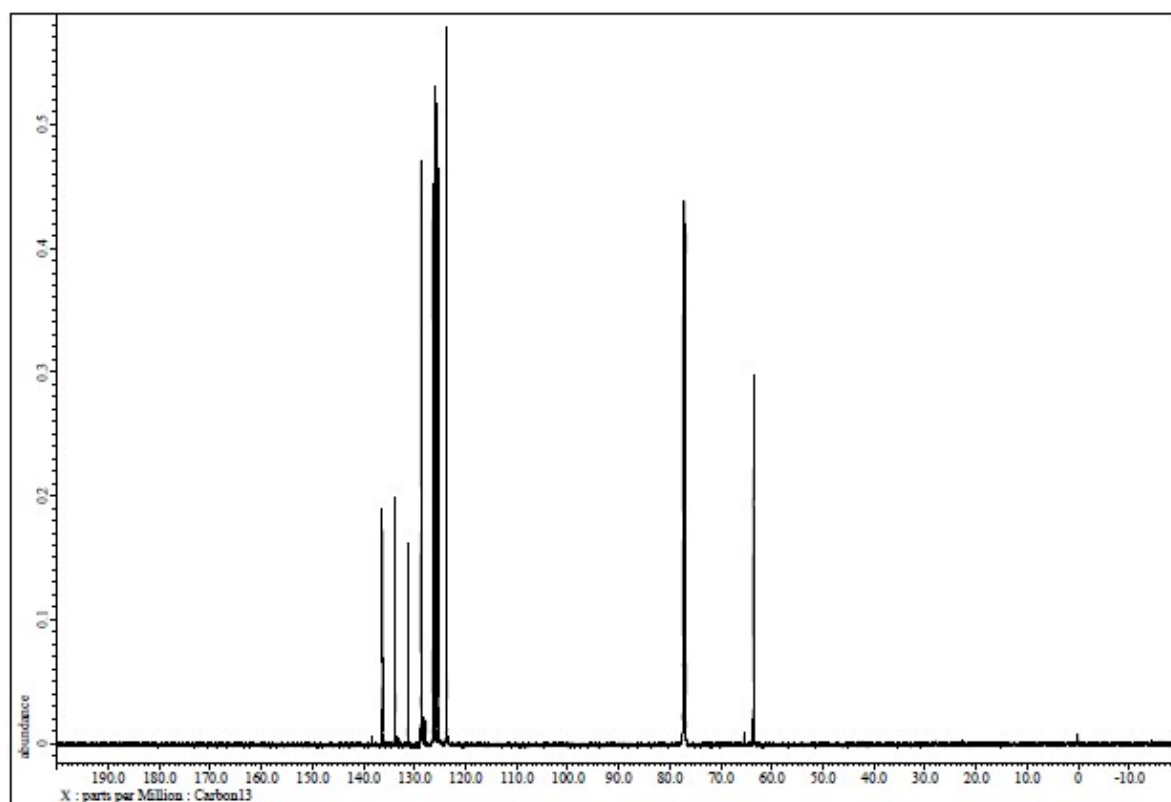
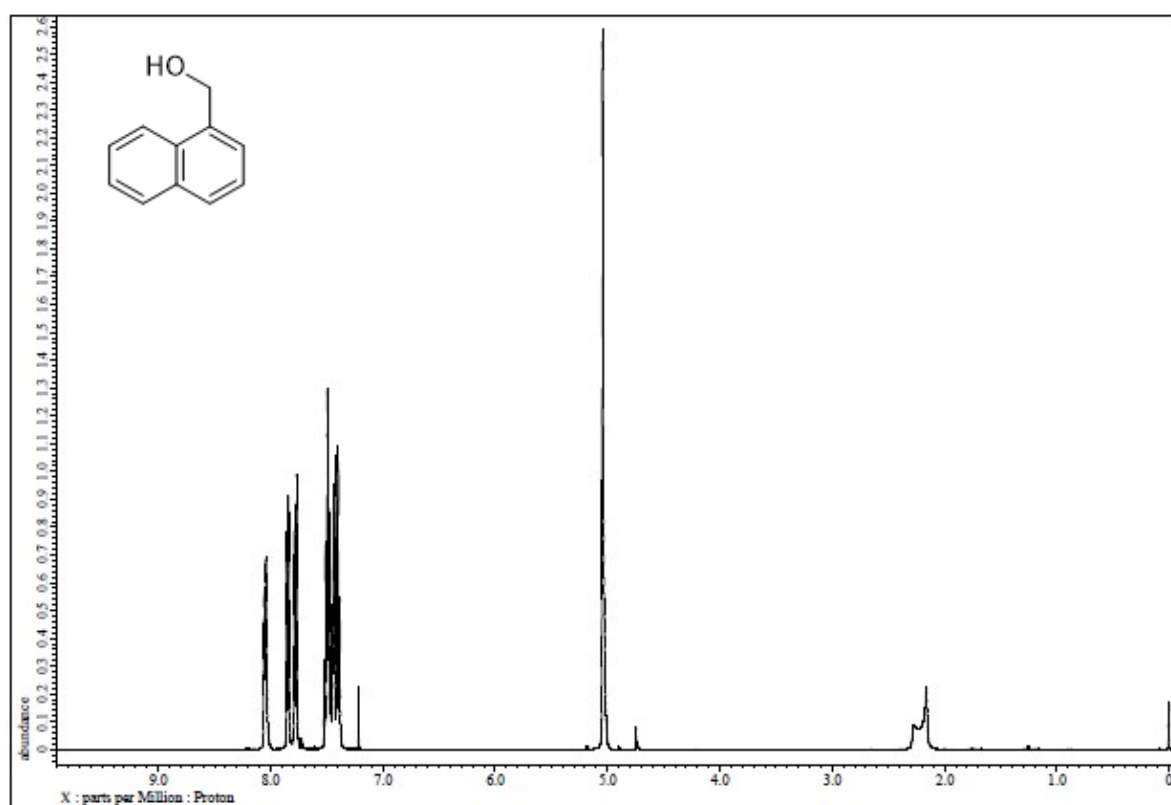
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