Electronic Supplementary Information

Surfactant-free single-nano-sized colloidal Cu nanoparticles for use as an active catalyst of Ullmann-coupling reaction

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General

GLC analysis was performed with a flame ionization detector using a 0.22 mm×25 m capillary column (BP-5). ^{1}H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as an internal standard. The products were characterized by ^{1}H NMR, ^{13}C NMR, and GC-MS. The yields of products were estimated from the peak areas based on the internal standard technique using GC.

All starting materials were commercially available and used without any purification. $CuCl_2$ was obtained from Wako Chemical Co. All solvents and other regents were obtained from Wako Chemical Co, TCI and ALDRICH and were used without further purification.

Compounds **3a**[1], **3b**[1,2], **3c**[1,2], **3d**[1,2], **3e**[2], **3f**[2], **3g**[2], **3h**[1], **3i**[1] were reported previously.

Experimental details

Preparation of Cu NPs. A solution of 15 μL of 0.1 M aqueous $CuCl_2$ was added to 15 mL of *N, N*-dimethylformamide (DMF) that had been preheated to 140 °C, and the DMF solution was refluxed in a 140 °C oil bath with stirring for 8 h. The surfactant-free copper nanoparticles (Cu NPs) were obtained as the 0.1 mM Cu NPs in DMF. After vacuum evaporation of excess solvent, the residue was redissolved in selected solvents such as methanol, acetonitrile (MeCN), and *N*-methylpyrrolidone (NMP) for the TEM measurement and the Ullmann O-Arylation.

Preparation of 0.01 mM Cu NPs in DMF (10^{-3} mol %)

The DMF solution of 1 mL of the prepared 0.1 mM Cu NPs was added to 10 mL of DMF, and the solution of 0.01 mM Cu NPs in DMF was prepared.

Photophysical property. Fluorescence excitation and emission spectra were obtained on a JASCO FP-6200 fluorospectrophotometer. at UV excitation of 350 nm (Figure S1)

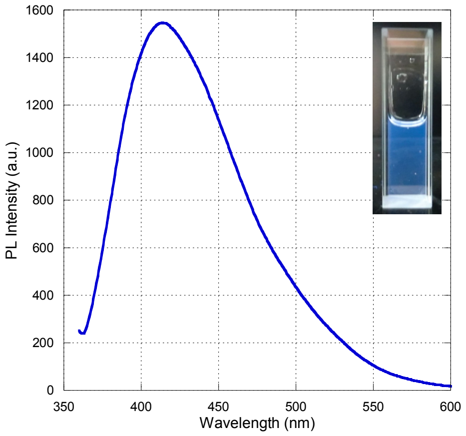


Figure S1. Photoluminescene emission spectra of DMF-protected Cu NPs.

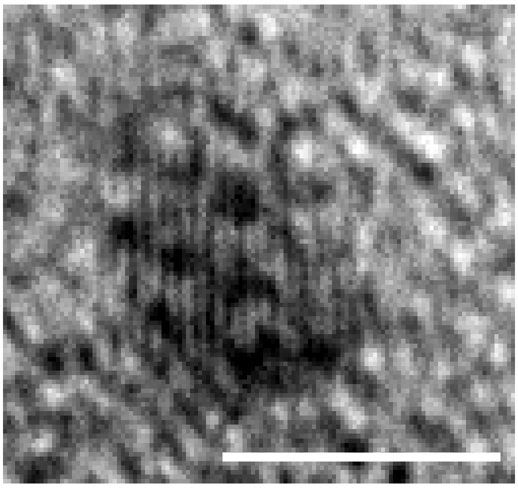


Figure S2. The high-magnification TEM image of Cu NPs showed that the crystal lattice fringes are 0.2 nm apart, which agrees with the d value of the (111) planes of the metallic Cu crystal. Bar : 3nm.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded with a Quantera SXM spectrometer (Physical Electronics, Inc.) using the monochromatic Al Kα line at 1486.7 eV. The base pressure was approximately 2 × 10^{-8} Torr. To compensate for charging effect, binding energies were referenced to C 1s at 284.7 eV of hydrocarbon.

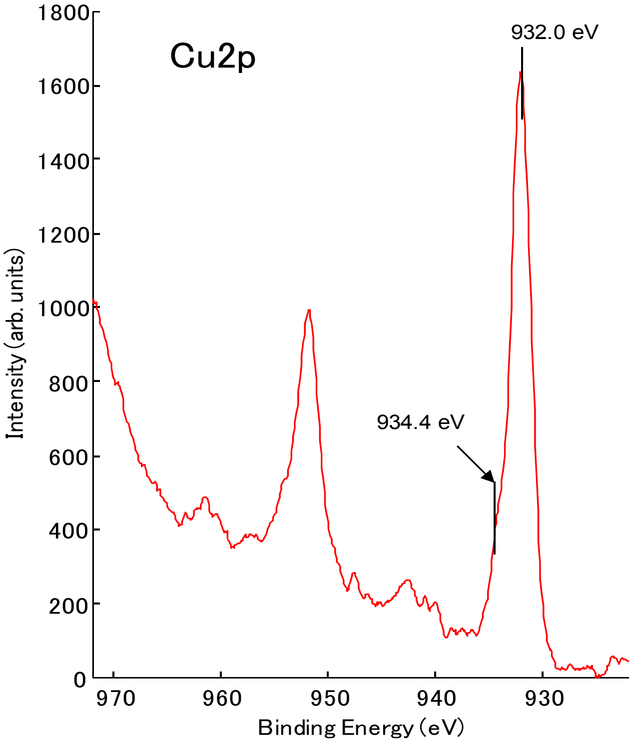


Figure S3. XPS spectrum of dried Cu NCs

Transmission electron microscopy (TEM). A drop of Cu NPs dispersed in methanol was placed on a carbon-coated Cu grid, and HR-TEM (high resolution TEM) image was obtained with a Hitachi H-9500 at an acceleration voltage of 300 kV. The raw magnification of the image was × 1,000,000.

Dynamic Light Scattering (DLS). A Nanoparticle analyser model SZ-100 with a 100mW laser and an interference optical filter at wavelength of 532nm (HORIBA, Japan) was used to perform dynamic light scattering for samples 200 μL (40 mM solution in DMF) in volume . The DLS measurement was performed at 25 ^{o}C.

A typical reaction procedure for Cu NPs catalyzed Ullmann O-Arylation of 1a with 2a (Table 1, entry 2)

A mixture of iodobenzene **1a** (306 mg, 1.5 mmol), 3, 5-dimethylphenol **2a** (122 mg, 1.0 mmol), Cs_2CO_3 (652 mg, 2.0 mmol) and 0.1 mM Cu NPs in DMF (1 mL) as a catalyst was stirred at 140 ^{o}C for 24 h under Ar. The conversions and yields of products were estimated from peak areas based on an internal standard (tridecane) using GC and the product **3a** was obtained in quantitative yield. The product **3a** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane / ethyl acetate = 20 / 1) in 88% yield (174 mg). The highest turnover frequency was achieved 450 for 1 h.

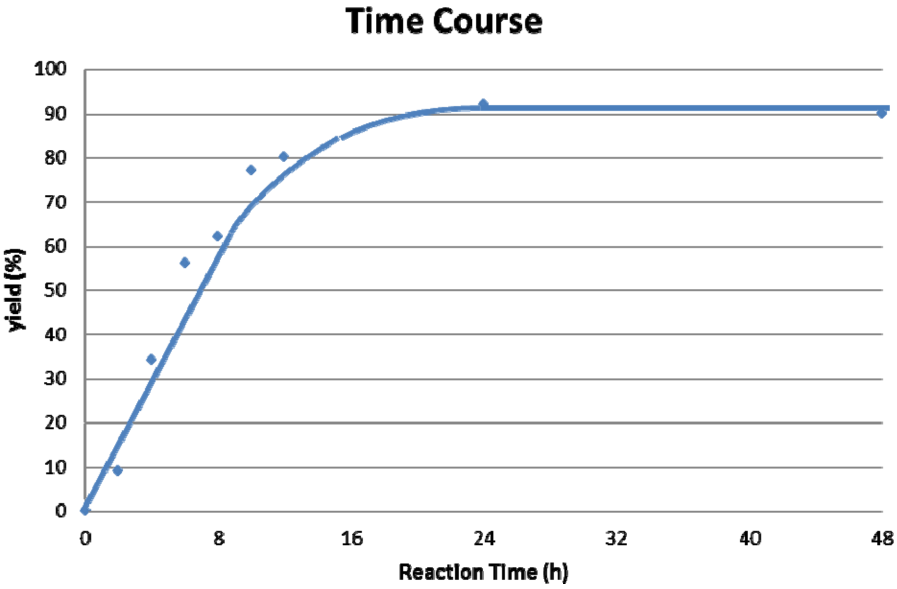


Figure S4. Time course for Ullmann O-Arylation reaction

A typical procedure for the catalyst-reusing sequence in the Cu NPs-catalyzed model reaction

After the reaction was performed under the conditions of entry 2, Table 1, iodobenzene **1a** (306 mg, 1.5 mmol), 3, 5-dimethylphenol **2a** (122 mg, 1.0 mmol) and Cs_2CO_3 (652 mg, 2.0 mmol) were added to the reaction mixture. It was used next catalytic sequence under the same reaction conditions as first cycle.

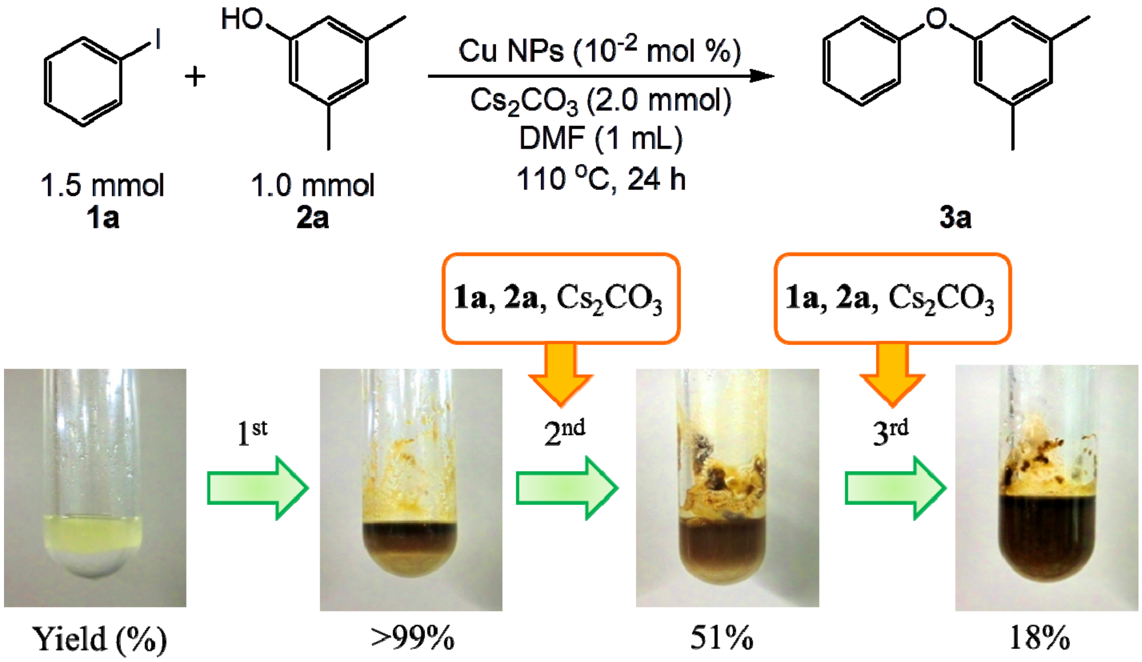


Figure S5. Depiction of the catalyst-reusing

Table S1. Catalyst-reusing

Cycle	**1st**	**2nd**	**3rd**
Yield (%)[a]	>99	51	18

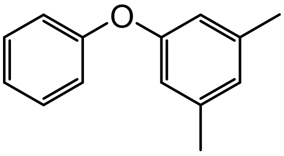
[a] GC yields (based on **2a**) were determined by average of three runs.

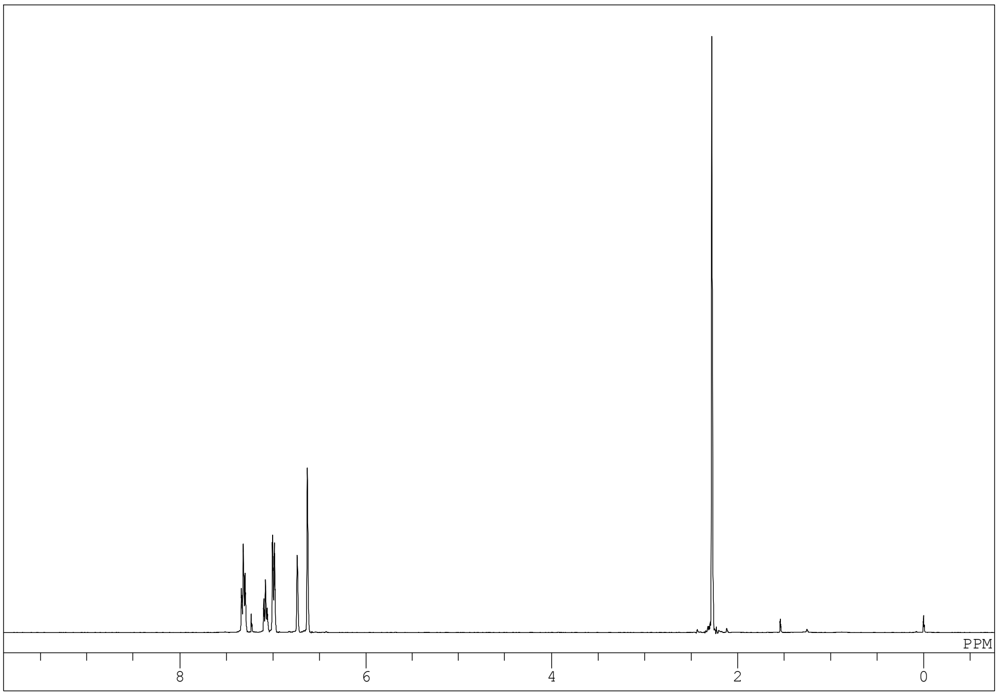
References

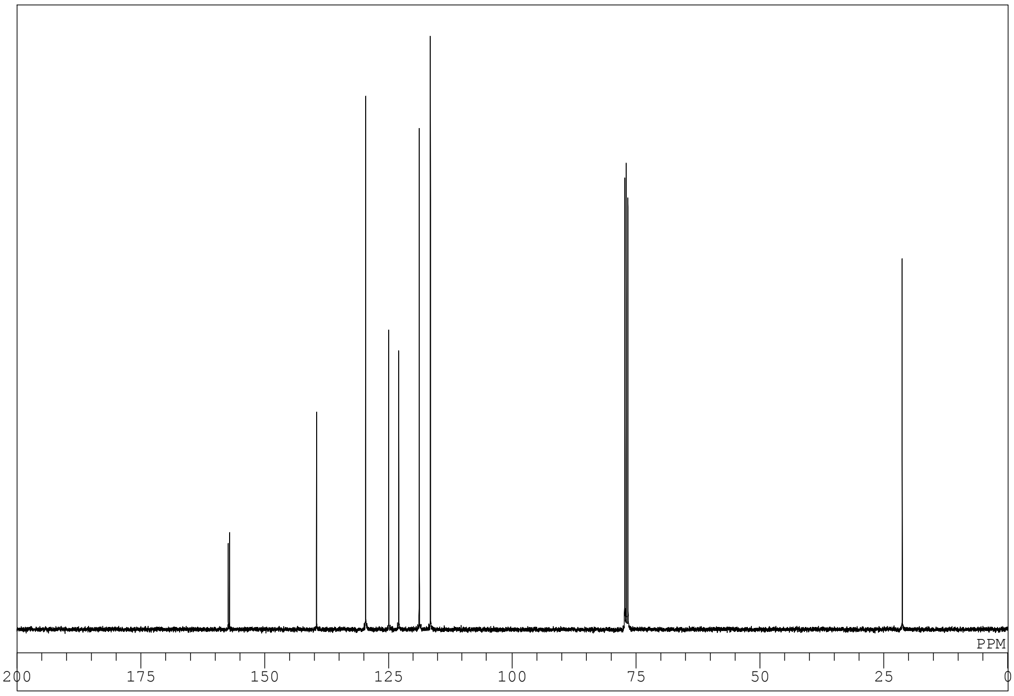
(1) H. J. Cristau, P. P. Cellier, S. Hamada, J. –F. Spindler and M. Taillefer, *Org. Lett.*, 2004, **6**, 913.

(2) A. B. Naidu, E. A. Jaseer and G. Sekar, *J. Org. Chem.* 2009, **74**, 3675.

3a







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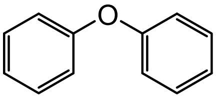

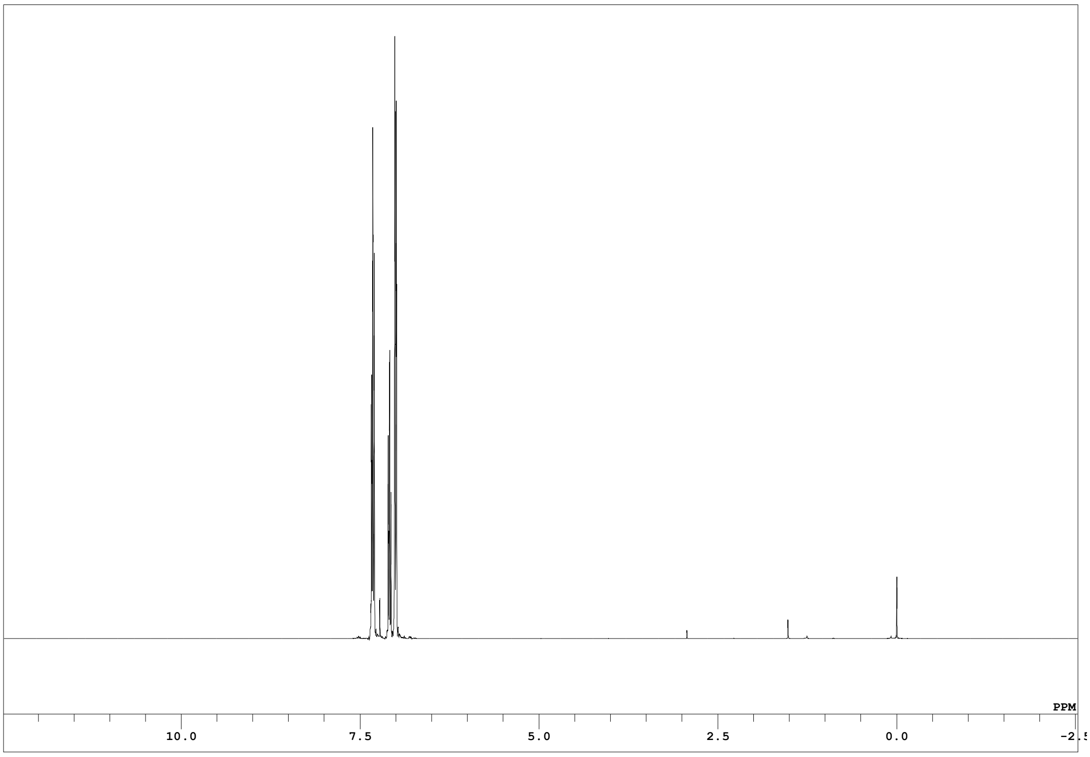

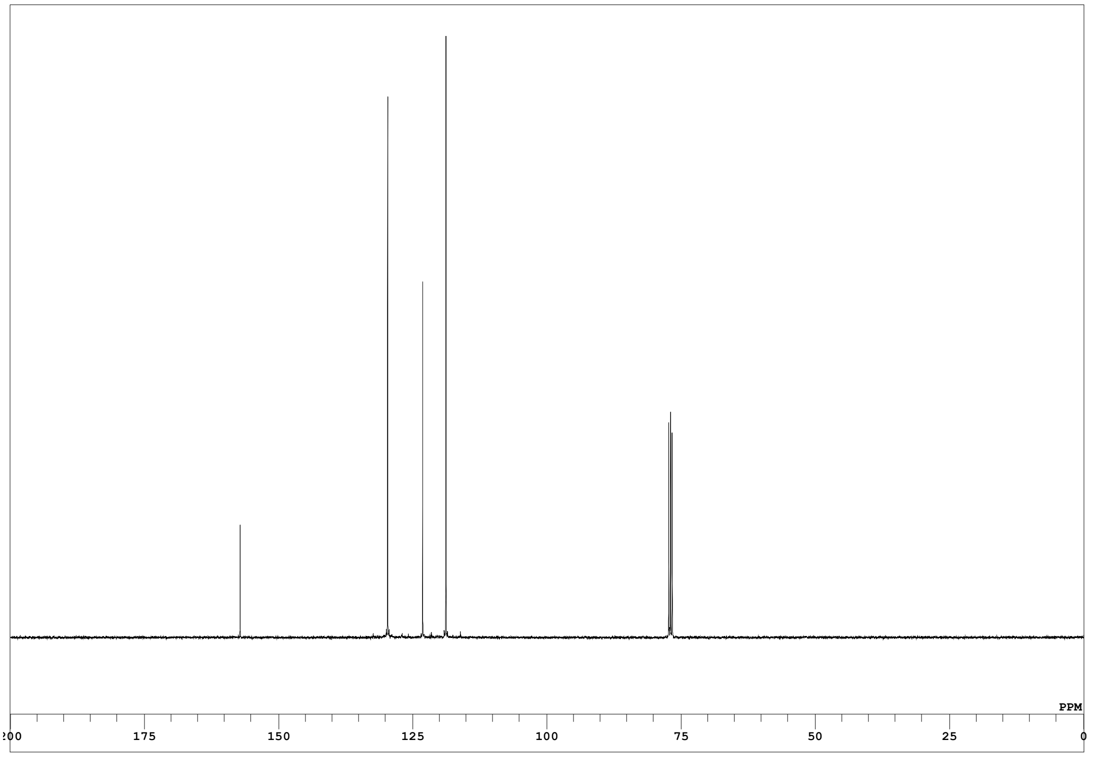

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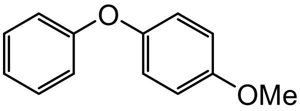

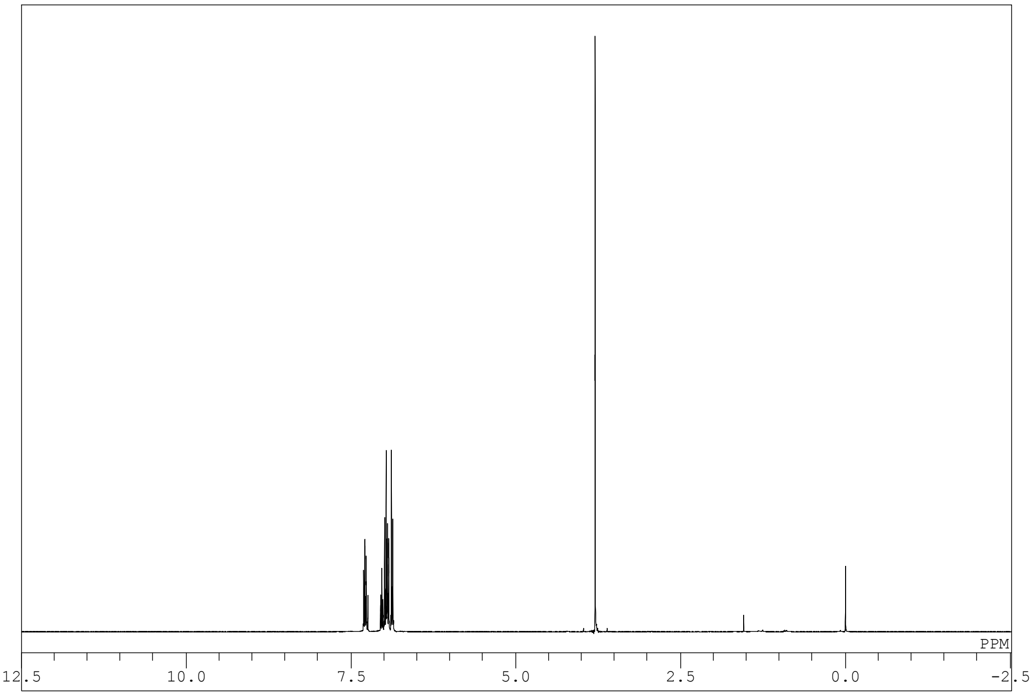

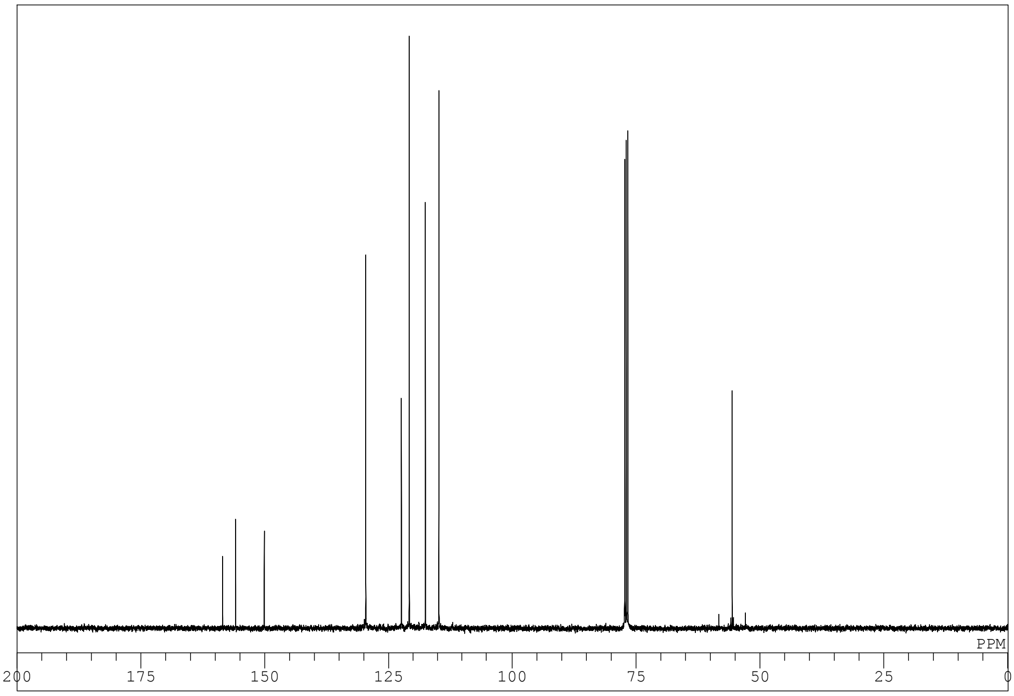

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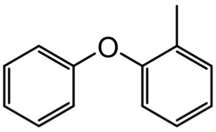

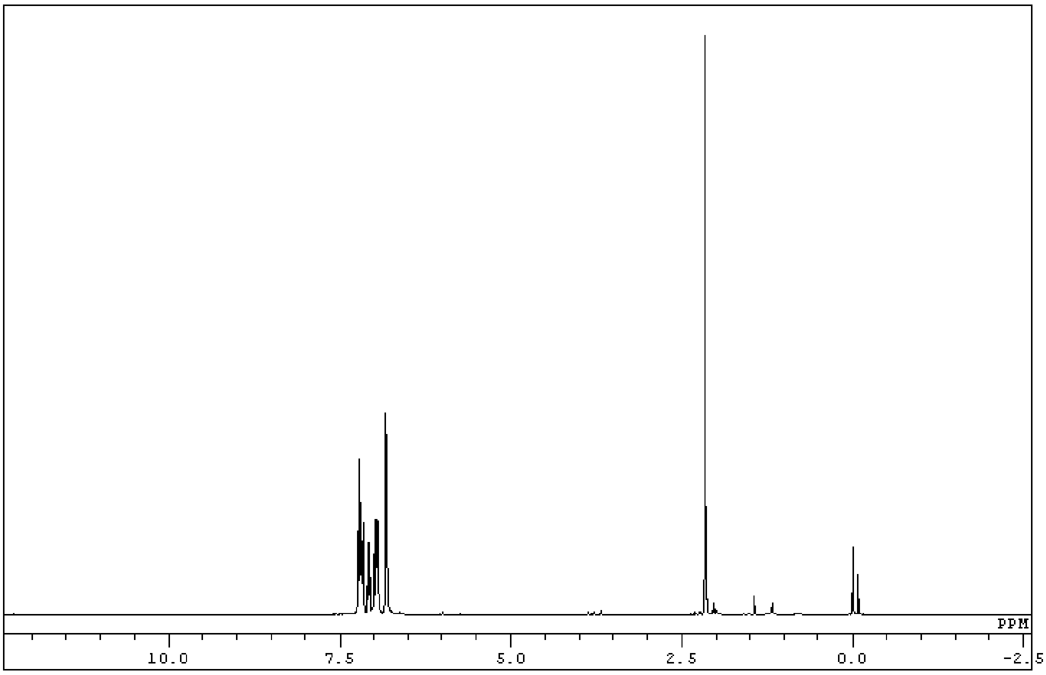

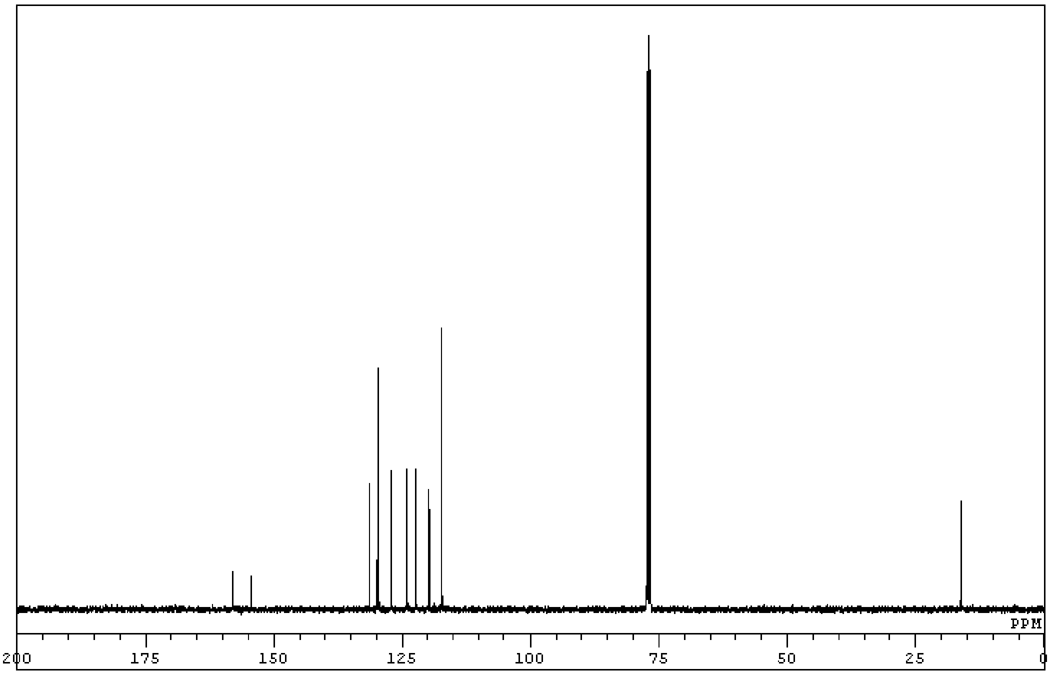

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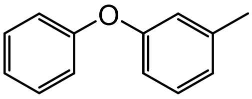

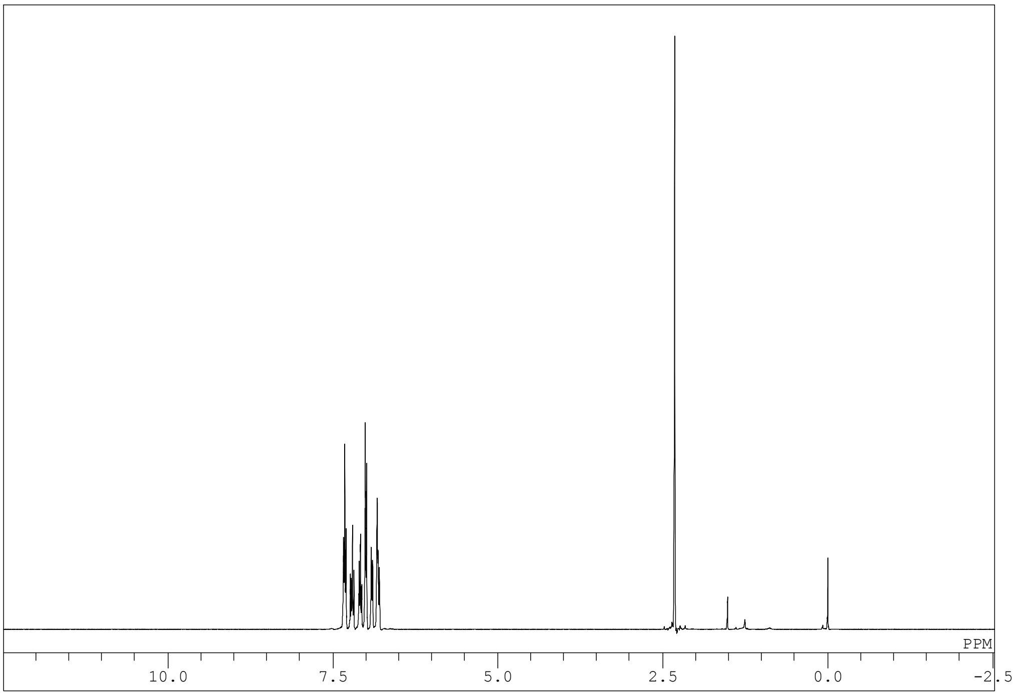

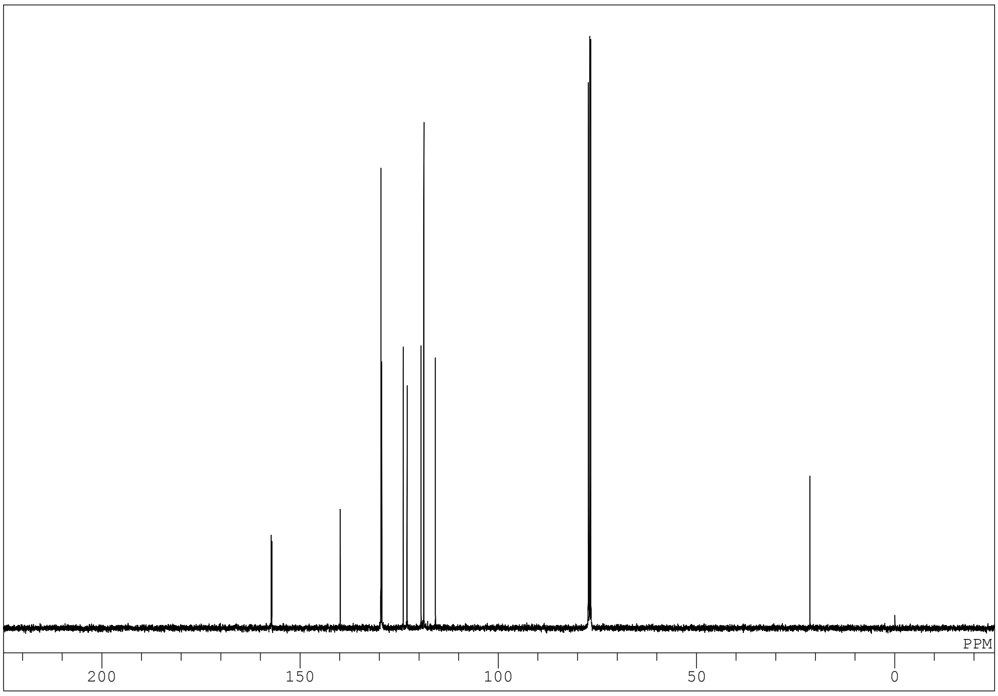

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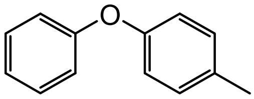

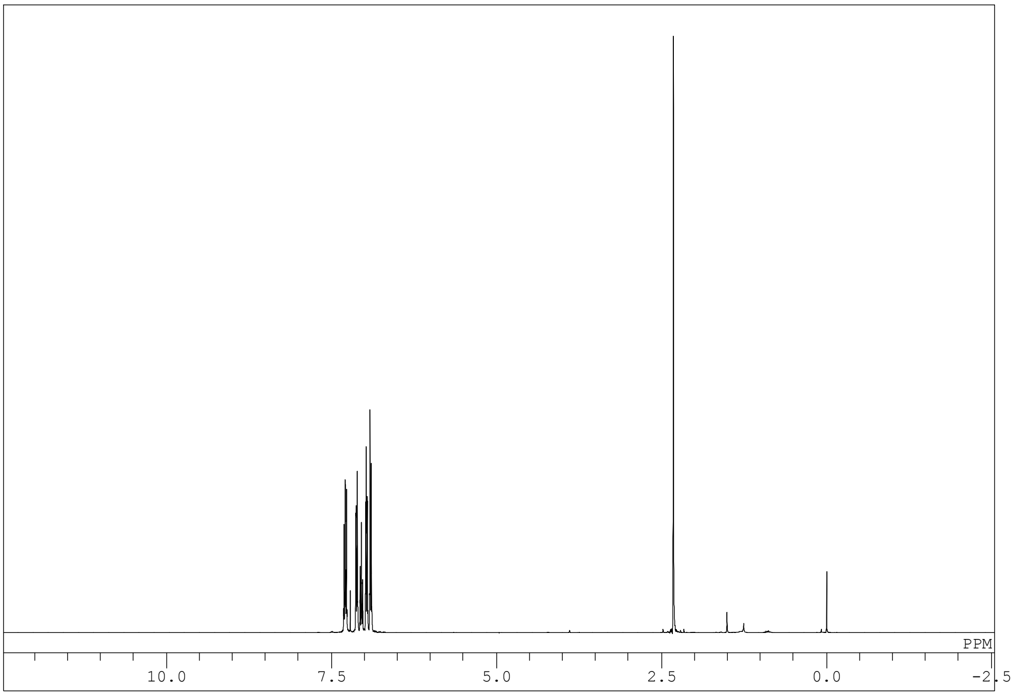

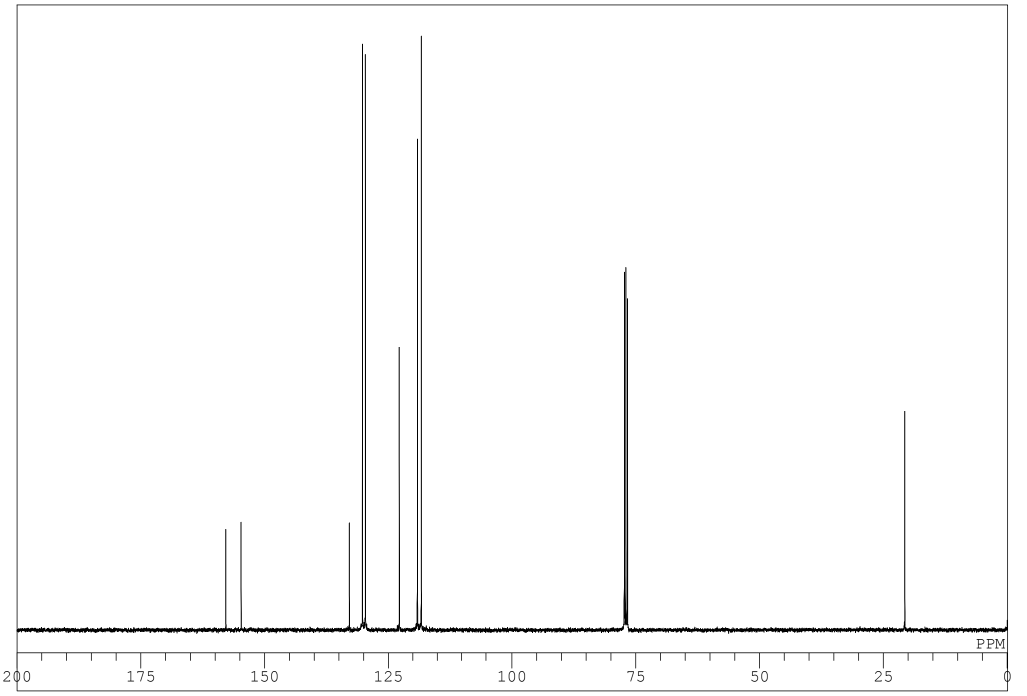

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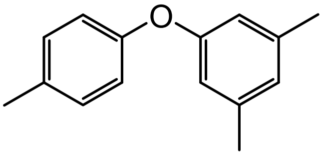

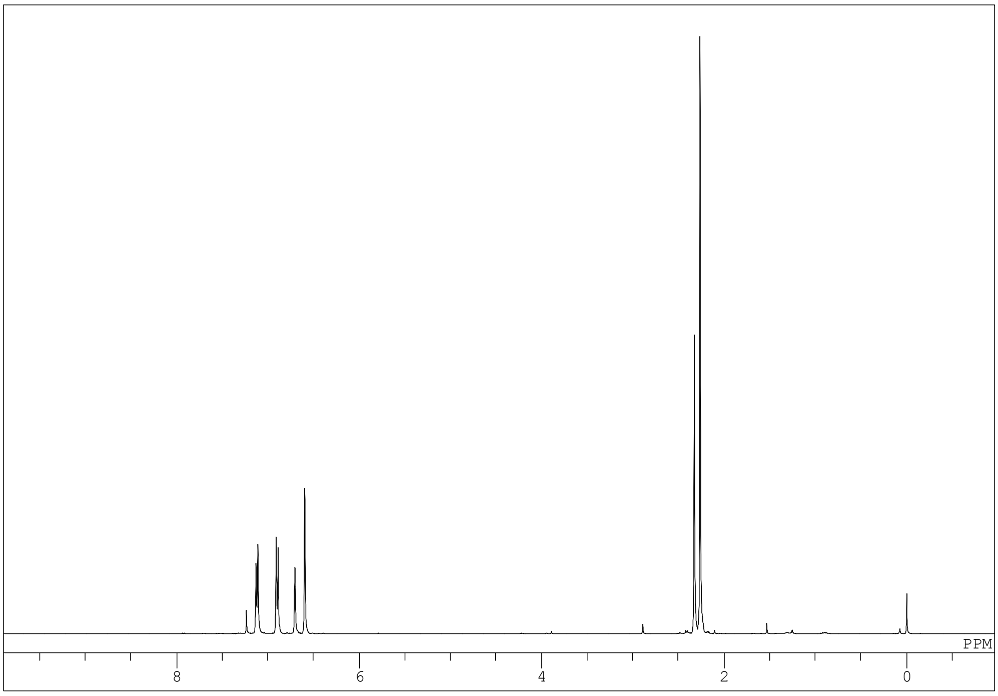

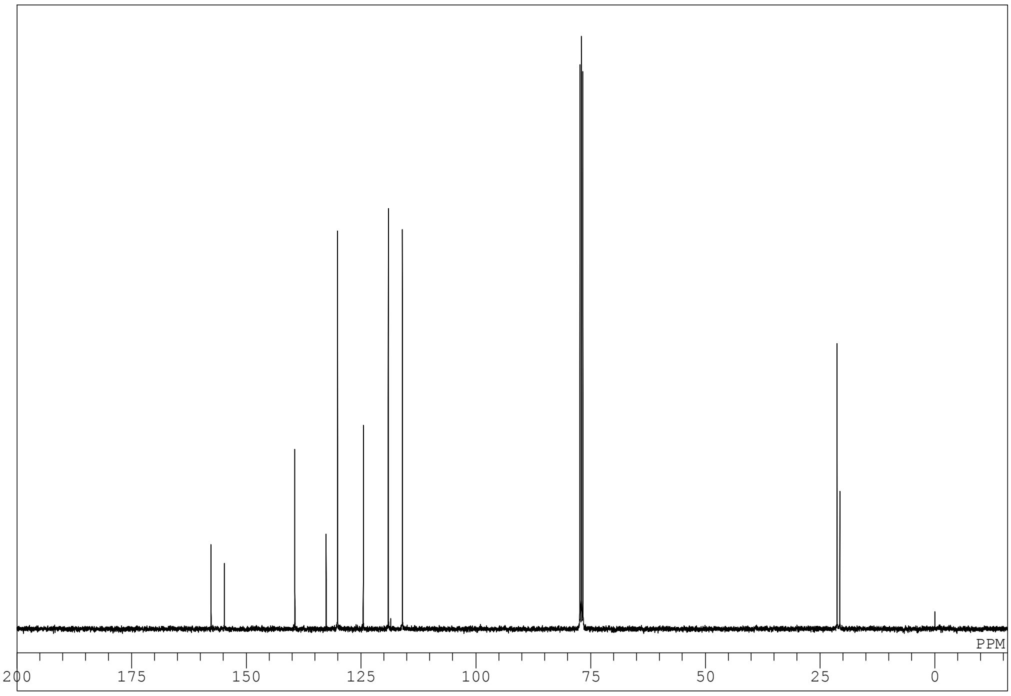

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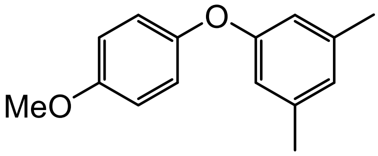

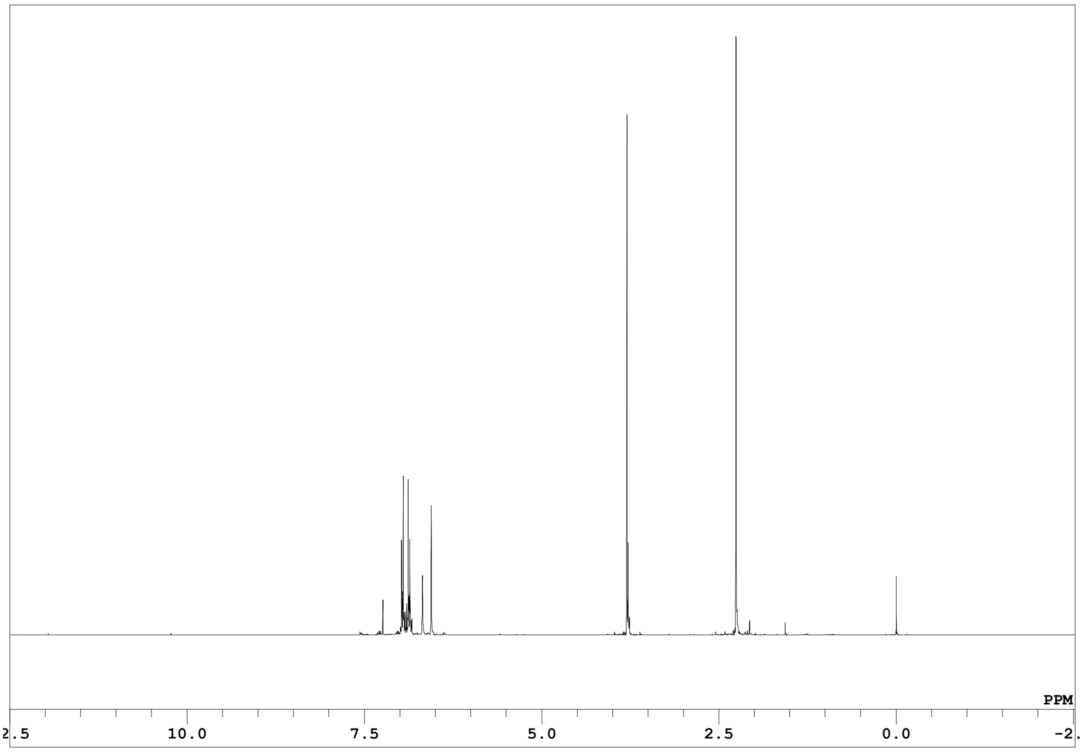

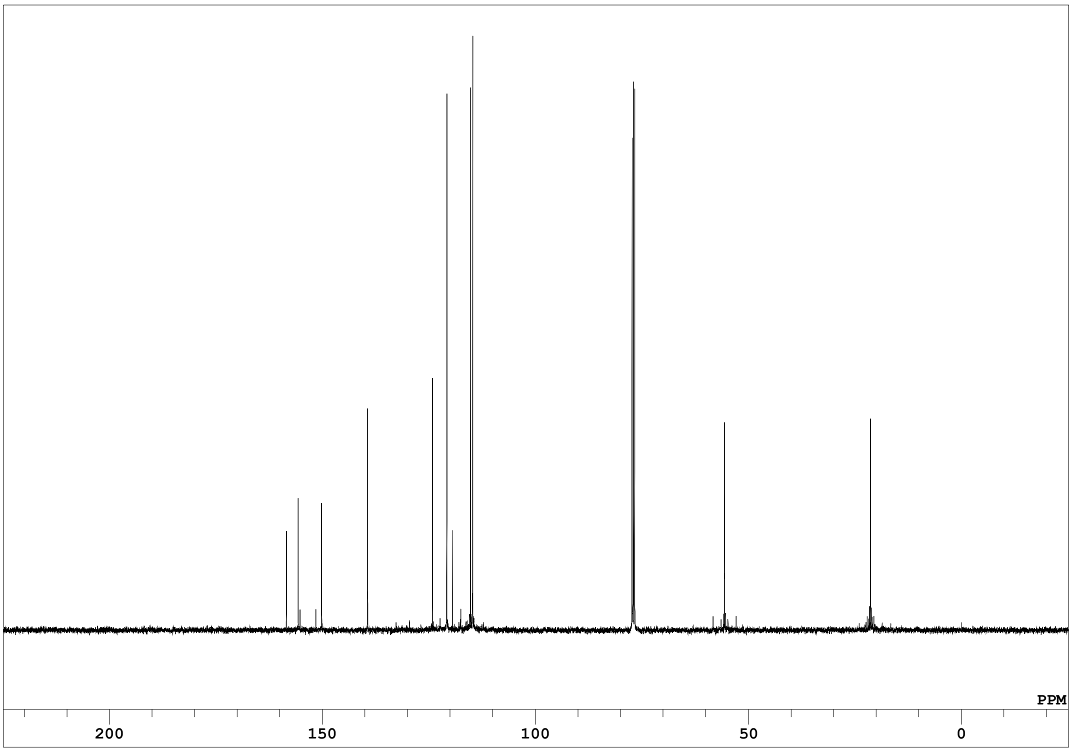

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