Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Selective One-Pot Synthesis of Various Phenols from Diarylethanes

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Experimental

Genaral Remarks and Meterials

^{1}H and ^{13}C NMR were measured in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured as thin films on NaCl plate or KBr press disk. A GLC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). Mass spectra were determined at an ionizing voltage of 70 eV. The yields of products were estimated from the peak areas based on the internal standard technique using GLC. Diarylethanes **1** except **1b-d**, **1g**, and **1j**, were prepared by Beller method from the corresponding arenes with styrene (for **1a**, **1e-f**, **1k-m, 1o-p**)[1a] or 1-phenylethyl acetate (**1h-i**, **1n**)[1b] in the presence of iron catalyst. Compounds **1b-d** and **1j** are prepared by hydrogenation of 1,1-diphenylethylene, 1-(4-methylphenyl)-1-phenylethylene,[2a] 1-(3-methylphenyl)-1-phenylethylene[2b] and 1-(4-*tert*-butylphenyl)-1-phenylethylene[2c] with hydrogen gas (1 atm) on Pd/C.[3] All the diarylethanes **1** except **1i** and **1n,** and the product (**3-5**) are known compounds and reported previously (**1a,**[3a] **1b-c,**[3b] **1d**,[4] **1e-f**,[3a] **1g,**[5] **1h**,[6] **1j**,[7] **1k**,[8] **1l-m**,[3a] **1o**,[3b] **1p**,[9] **3a**,[10] **3b-c**,[11] **3d**,[10] **3e**,[12] **3h**,[13] **3i**,[14] **3j**,[15] **3k**,[16] **3n**,[17] **4a**,[18] **4f**,[19] **4g**,[20] **4l**,[21] **5a,**[22] and **9**[23]) Compound **1g** is commercially available and used without any purification.

A typical reaction was carried out as follows (Table 1, Entry 1): A mixture of 1-(4-methoxyphenyl)-1-phenylethane (**1a**) (637 mg, 3 mmol), NHPI (49 mg, 0.3 mmol, 10 mol%) and AIBN (15 mg, 0.09 mmol, 3 mol%) in acetonitrile (3.0 mL) was placed in a two-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 15 h. The reaction mixture was treated with a solution of sulfuric acid (29 mg, 0.3 mmol) in acetonitrile (1 mL) at 0 °C for 1 min. Removal of the solvent under

reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 15/1) to give the products, 4-methoxyphenol (**3a**) and acetophenone (**4a**) in 52% and 54% isolated yields, respectively as a pure form.

Oxidation of toluene in the presence of 1p (eq 2): An acetic acid (2.5 mL) solution of toluene (**7**) (92 mg, 1 mmol), NHPI (16 mg, 0.1 mmol, 10 mol%),$Co(OAc)_2$ (1 mg, 0.005 mmol, 0.5 mol%), and 1-mesityl-1-phenylethane (11 mg, 0.05 mmol, 5 mol%) was placed in a two-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 100 °C for 6 h. Removal of the solvent under reduced pressure afforded a cloudy solution. The product were esterified by ethanol (20 mL) and sulfuric acid (100 mg) at 80 °C for 15h. After the reaction, GC-MS analysis was performed. The conversions and yields of products were estimated from the peak areas, based on the GC internal standard technique.

1i: δ_H (270 MHz; $CDCl_3$, Me_4Si) 0.92 (t, ^3J(H,H)= 7.3 Hz, 3H), 1.57-1.65 (m, 5 H), 2.53 (t, ^3J(H,H) = 7.7 Hz, 2H), 4.11 (q, ^3J(H,H) = 7.3 Hz, 1H) and 7.05-7.35 (m, 9H); δ_C (67.5 MHz; $CDCl_3$, Me_4Si) 13.92, 21.93, 24.55, 37.62, 44.38, 125.90, 127.39, 127.58, 128.29, 128.38, 140.28, 143.53 and 146.61; ν_{max}/cm^{-1} 3023, 2963, 2928, 2869, 1599, 1505, 1284, 1492, 1451, 1029, 1026, 755 and 699; *m/z* (EI) 224.1566 (M^+. $C_{17}H_{20}$ requires 224.1565), 209 (100%), 195 (6), 181 (23), 167 (28), 91 (7) and 77 (8).

1n: δ_H (270 MHz; $CDCl_3$, Me_4Si) 1.59 (d, ^3J(H,H) = 7.3 Hz, 3H), 2.23 (s, 6 H), 3.68 (s, 3H), 4.03 (q, ^3J(H,H) = 7.3 Hz, 1H), 6.85 (s, 2H) and 7.12-7.32 (m, 5H); δ_C (67.5 MHz; $CDCl_3$, Me_4Si) 16.16, 21.99, 44.18, 59.60, 125.88, 127.49, 127.58, 127.82, 128.28, 130.43, 141.48 and 146.63; ν_{max}/cm^{-1} 3024, 2968, 2930, 2868, 2824, 1598, 1483, 1451,

1220, 1142, 1015, 874, 771, 756 and 699; *m/z* (EI) 240.1505 (M^+. $C_{17}H_{20}$ requires 240.1514), 225 (100%), 209 (7), 195 (11), 165 (8), 105 (7), 91 (5) and 77 (5).

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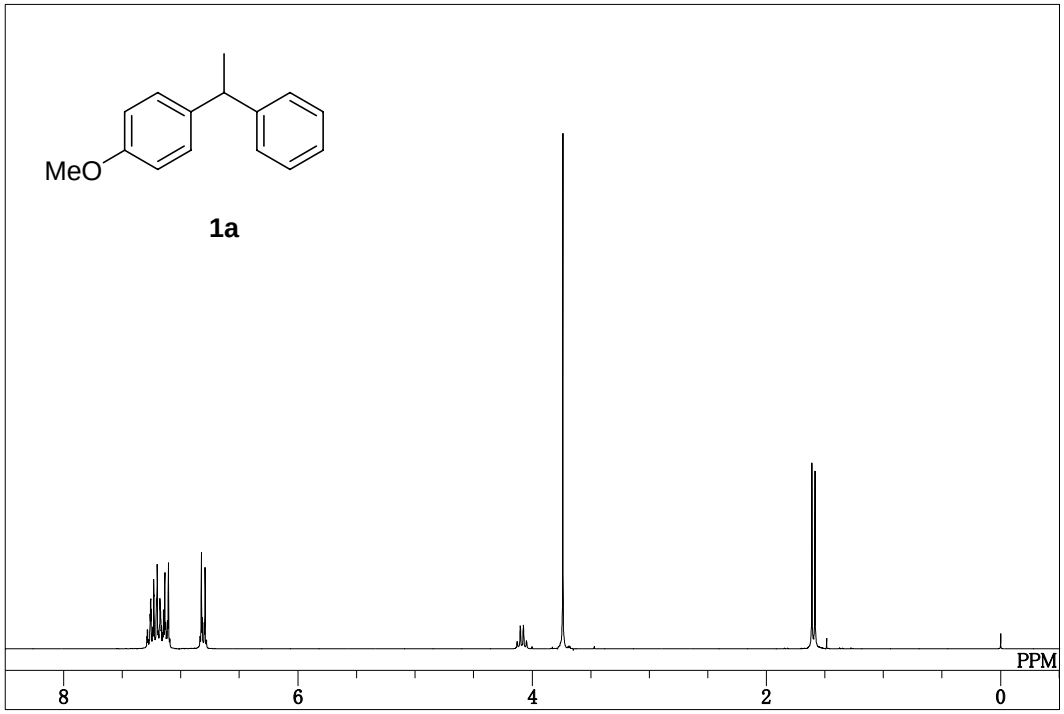
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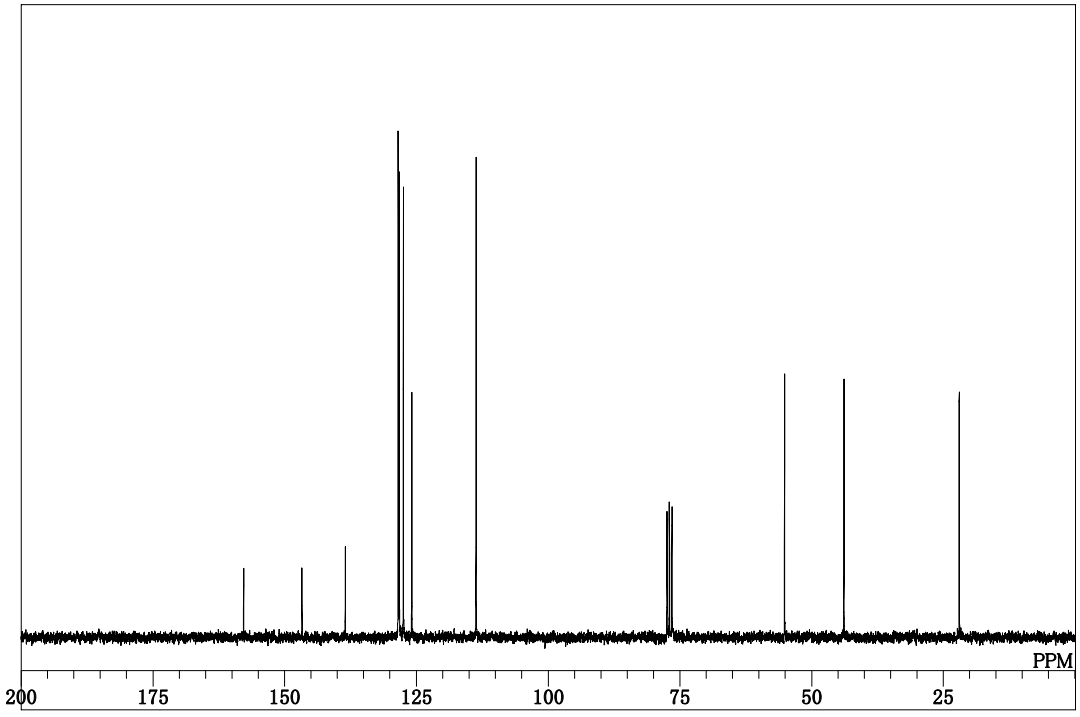
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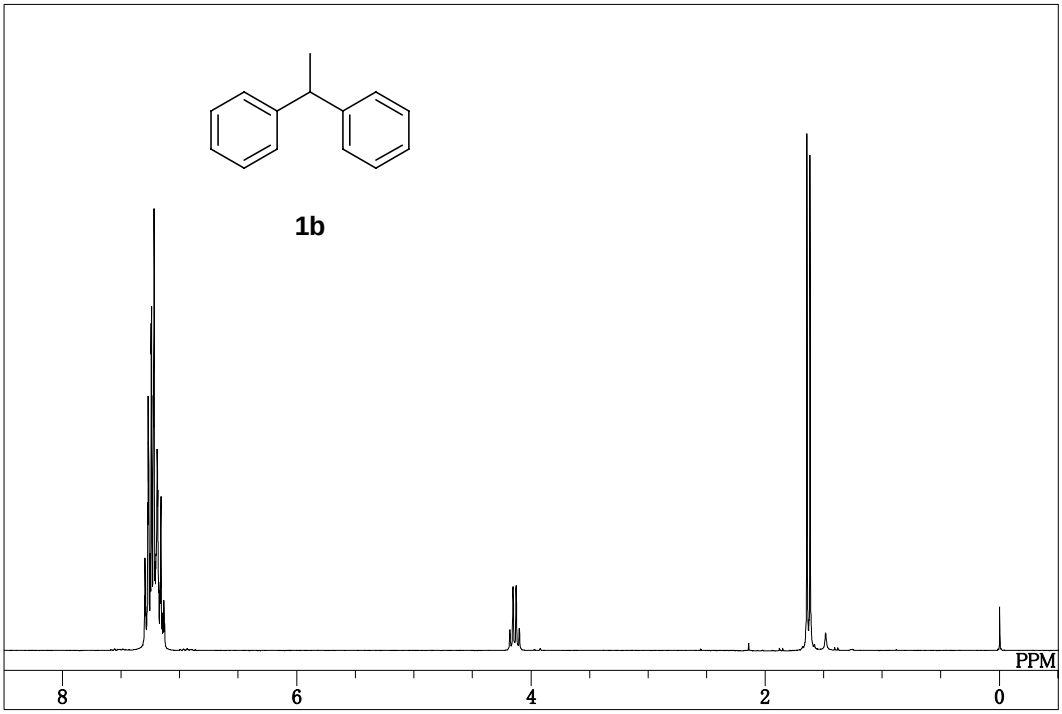
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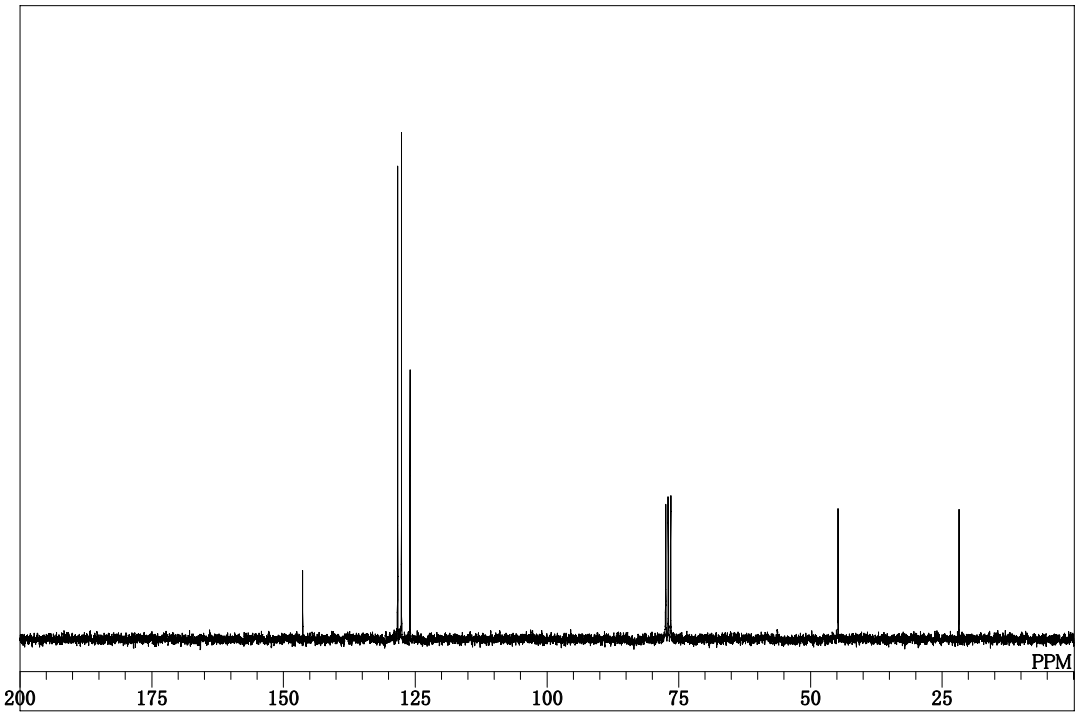
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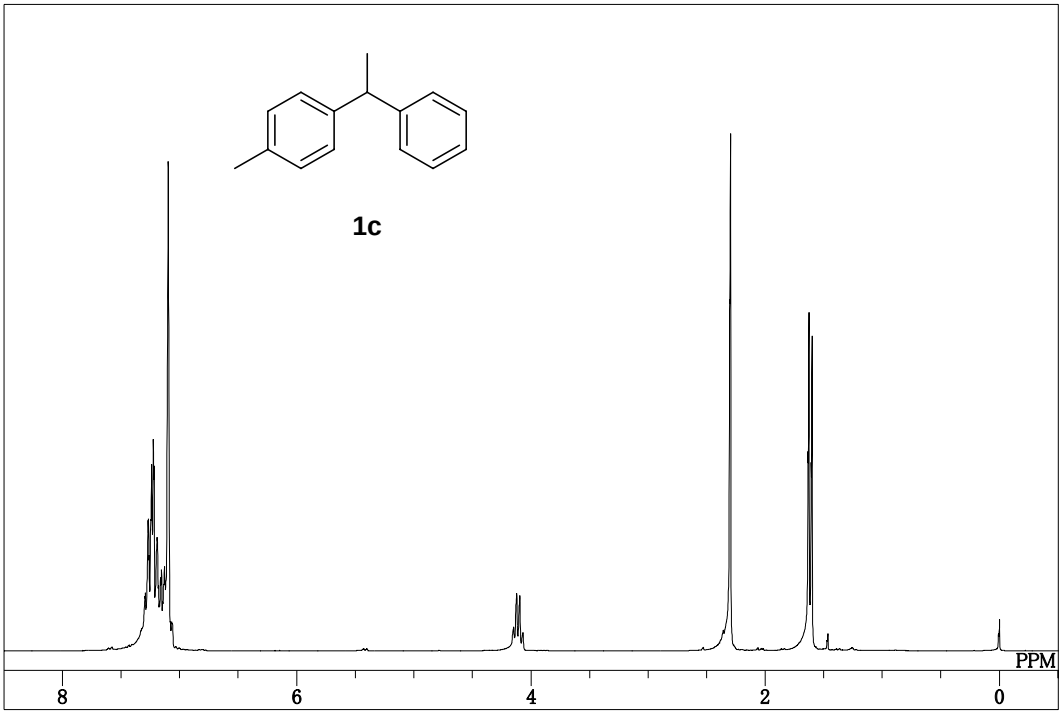
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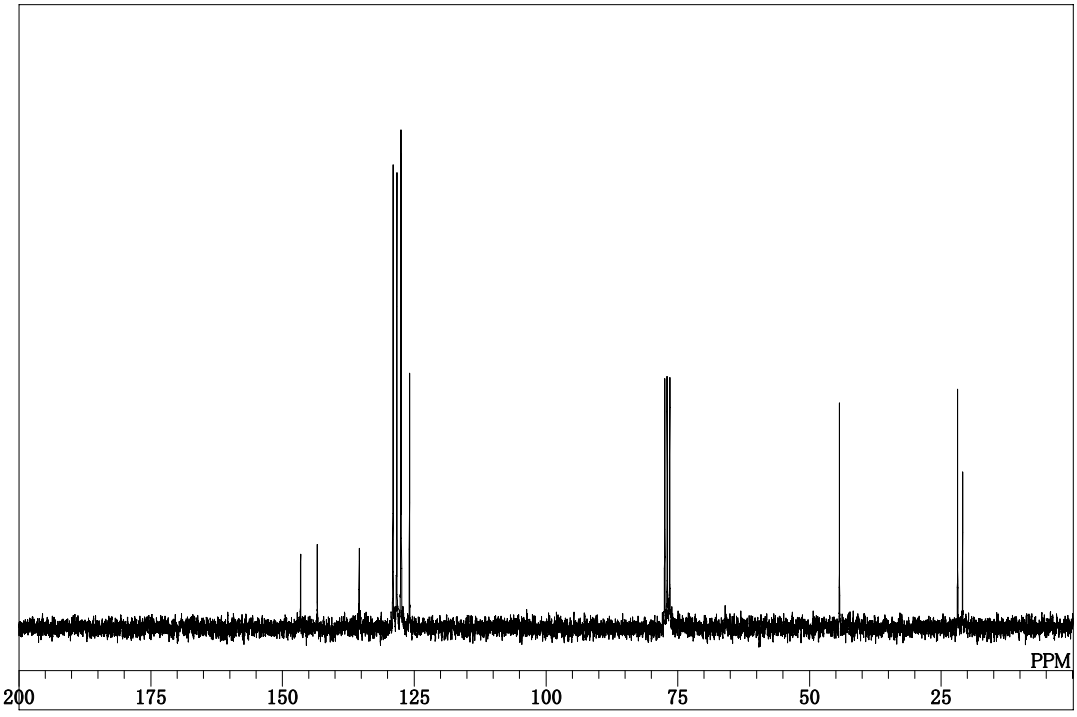
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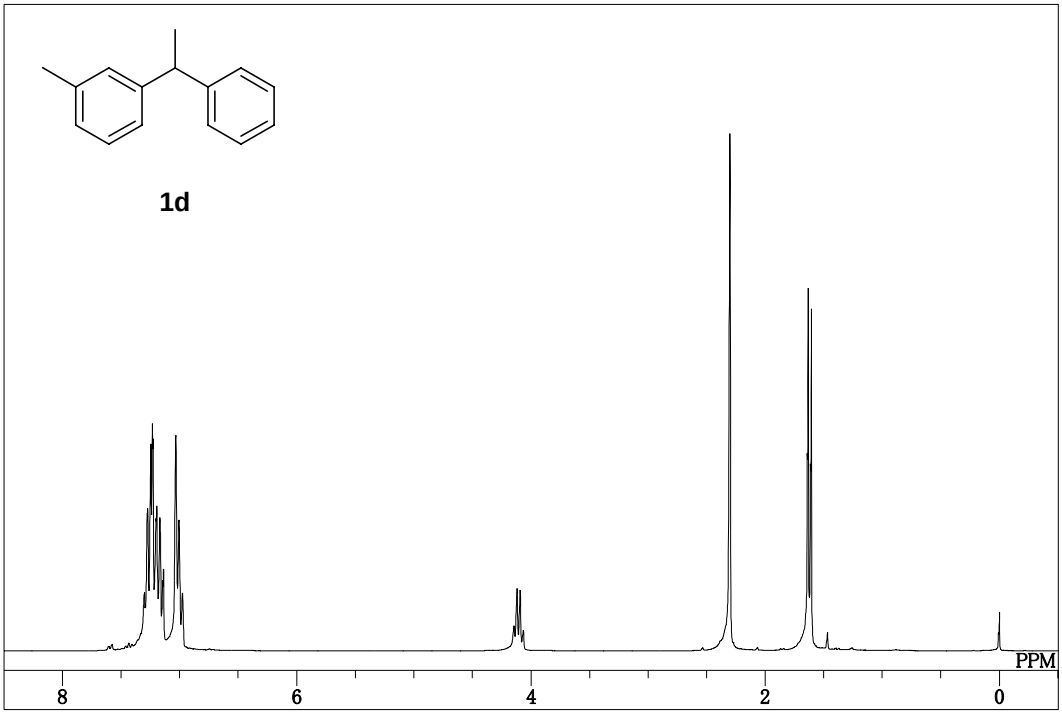
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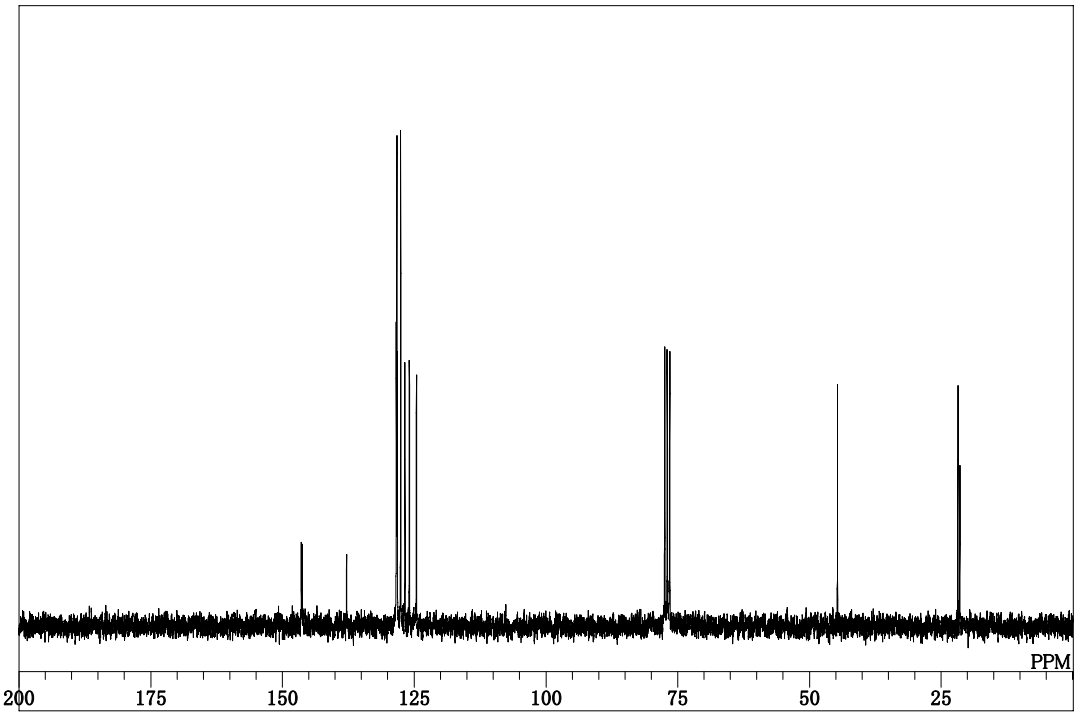
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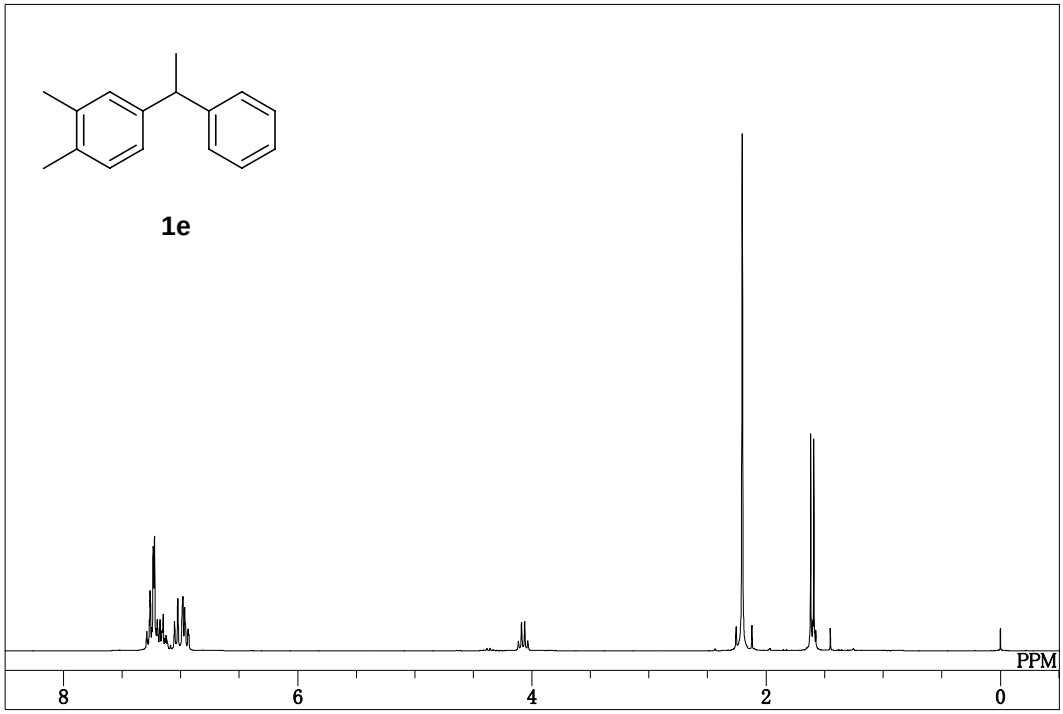
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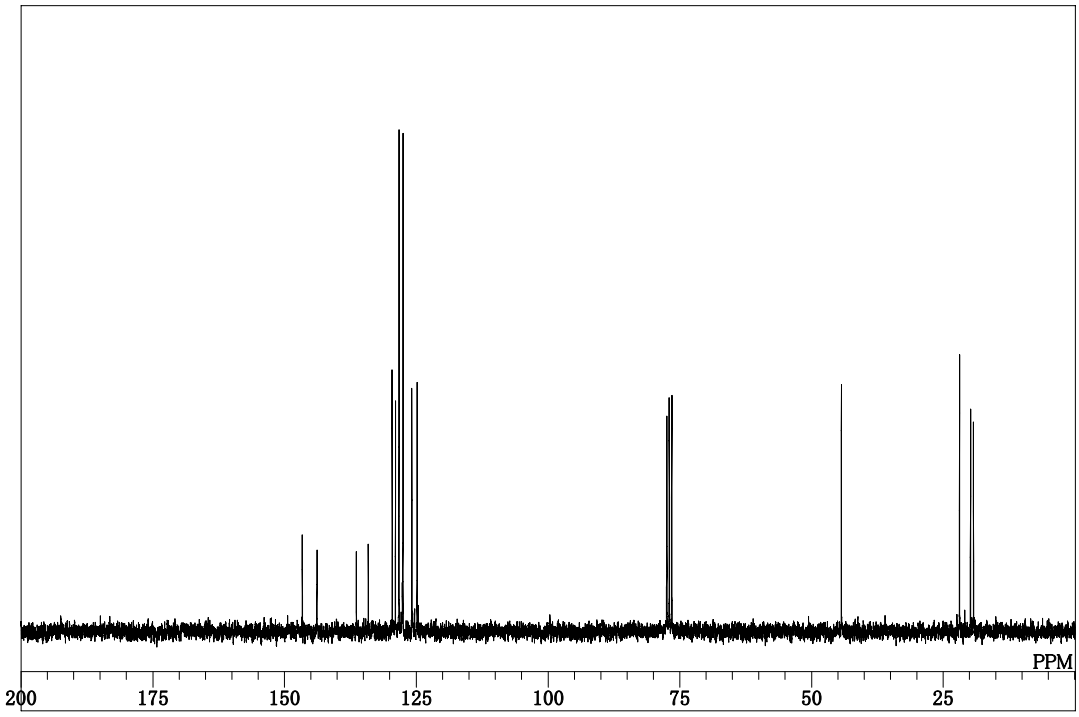
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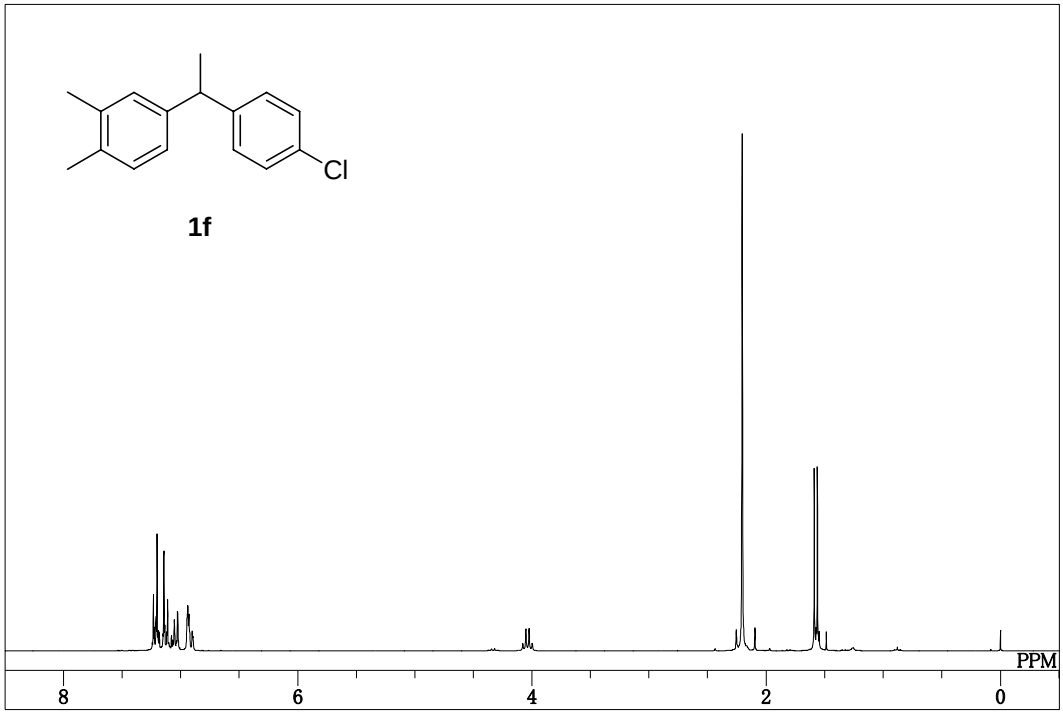
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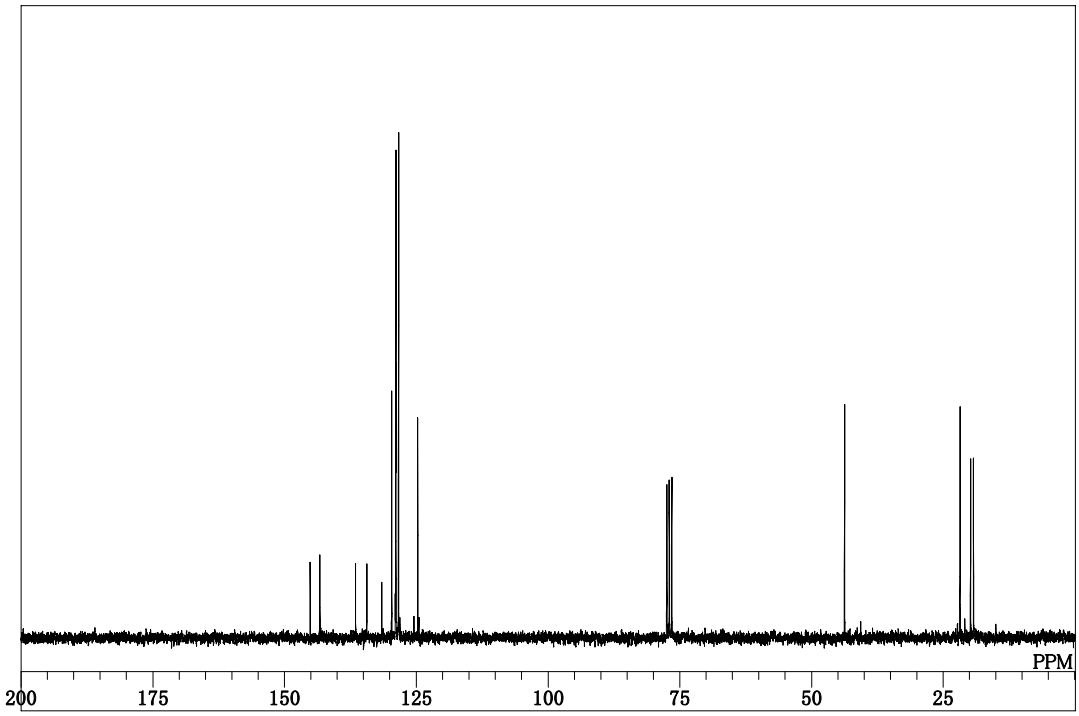
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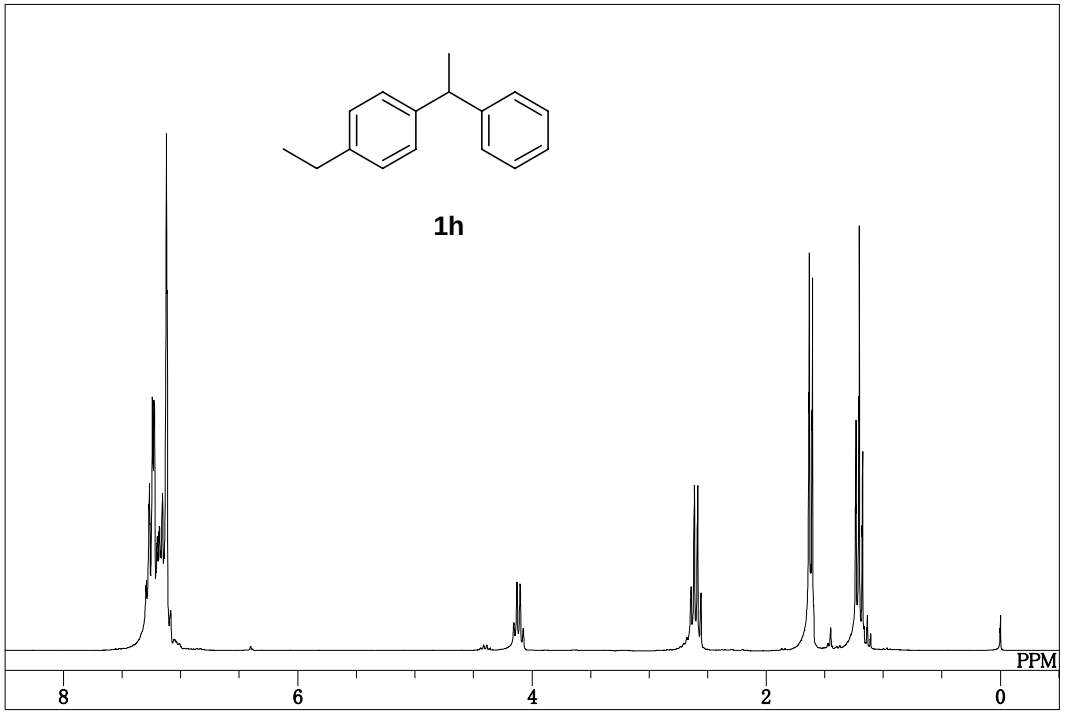
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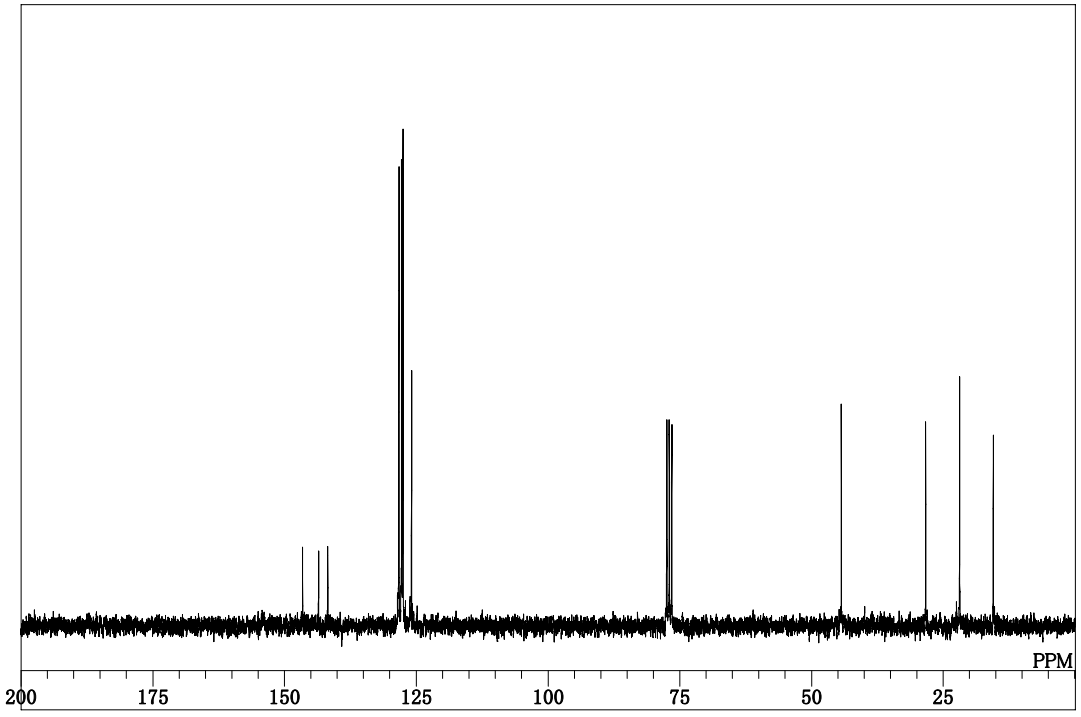
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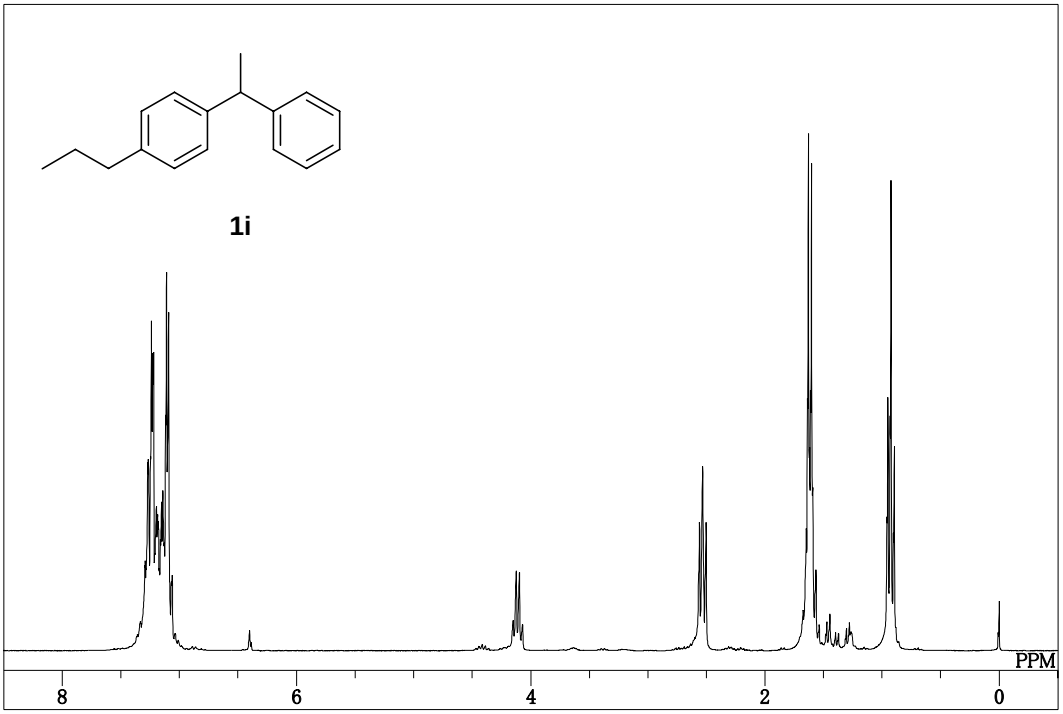
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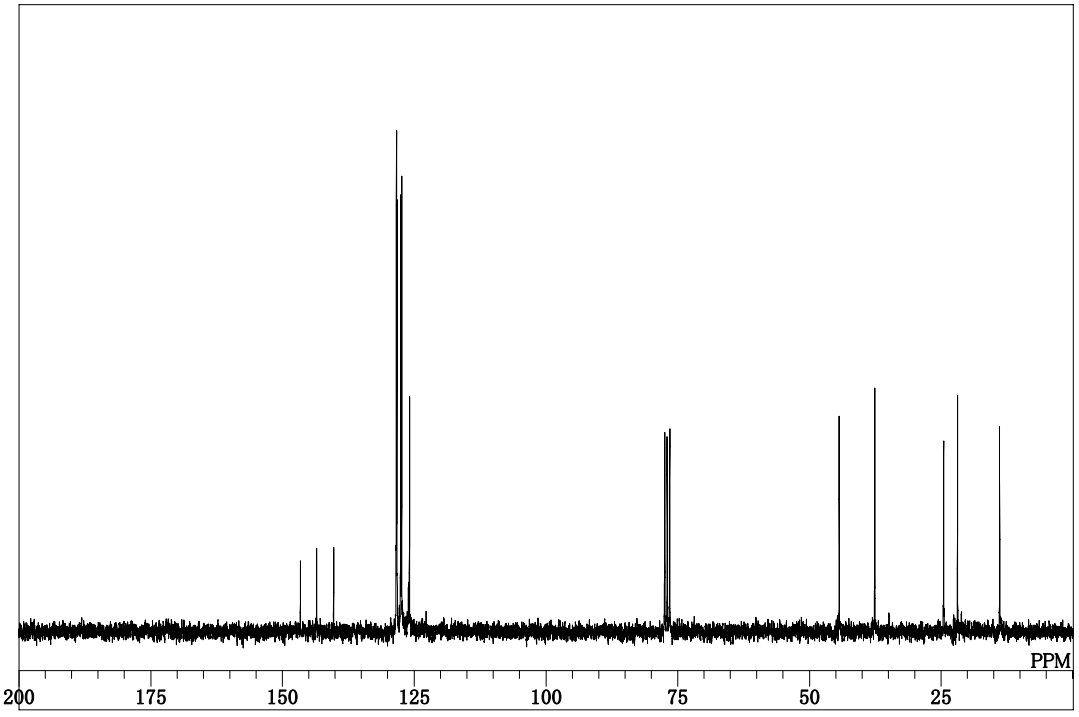
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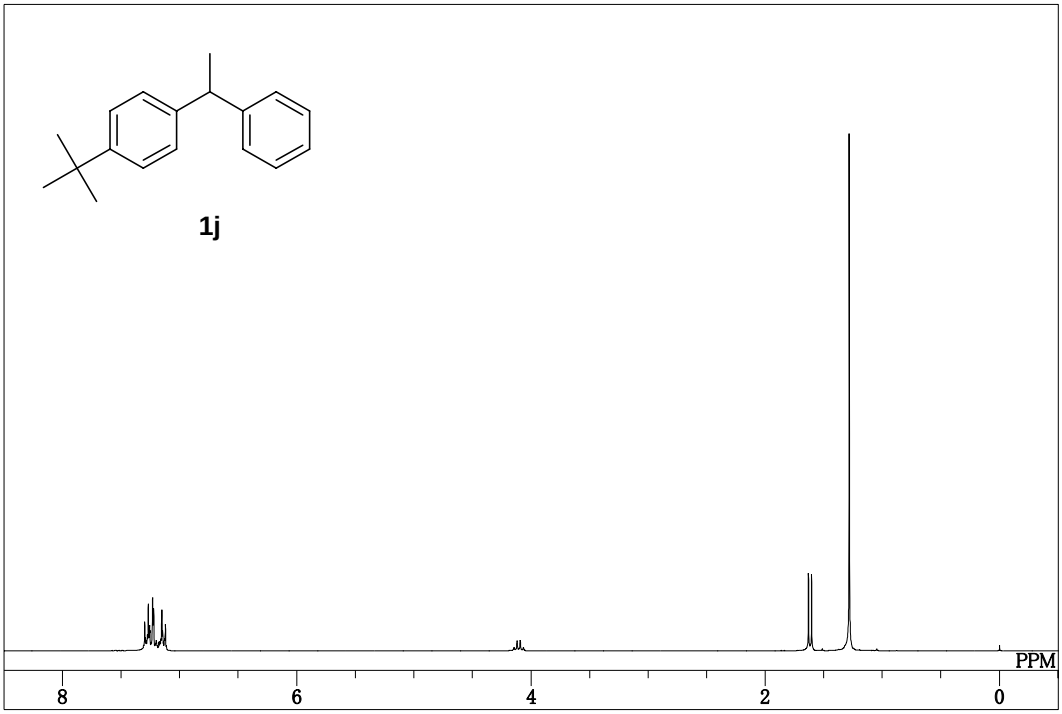
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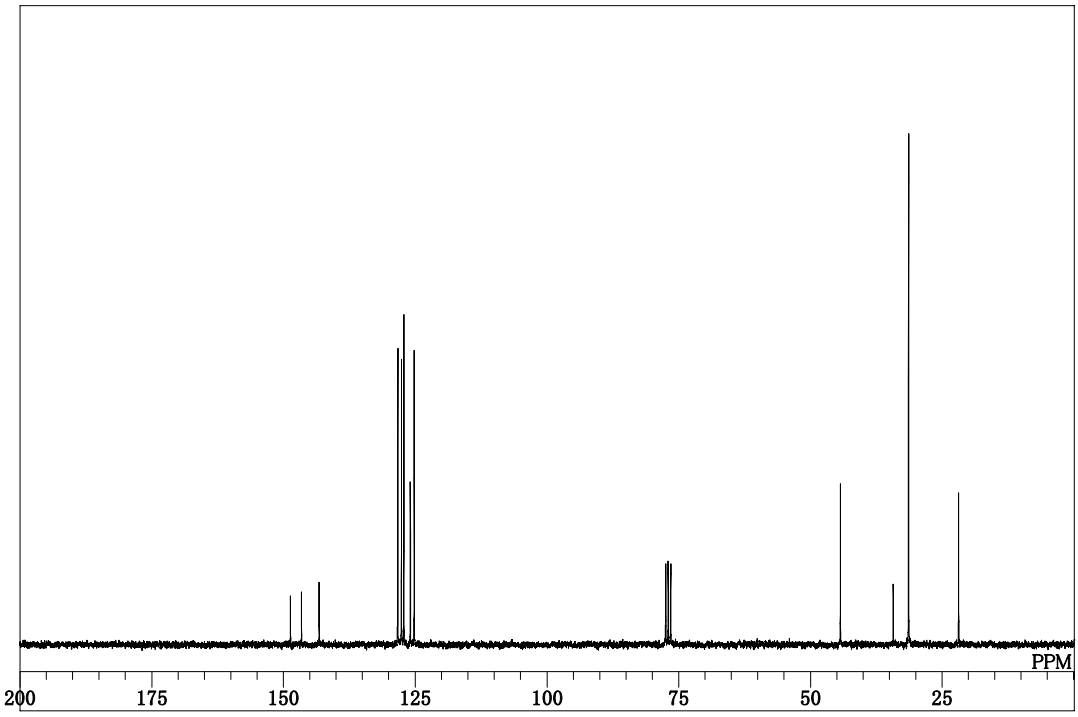
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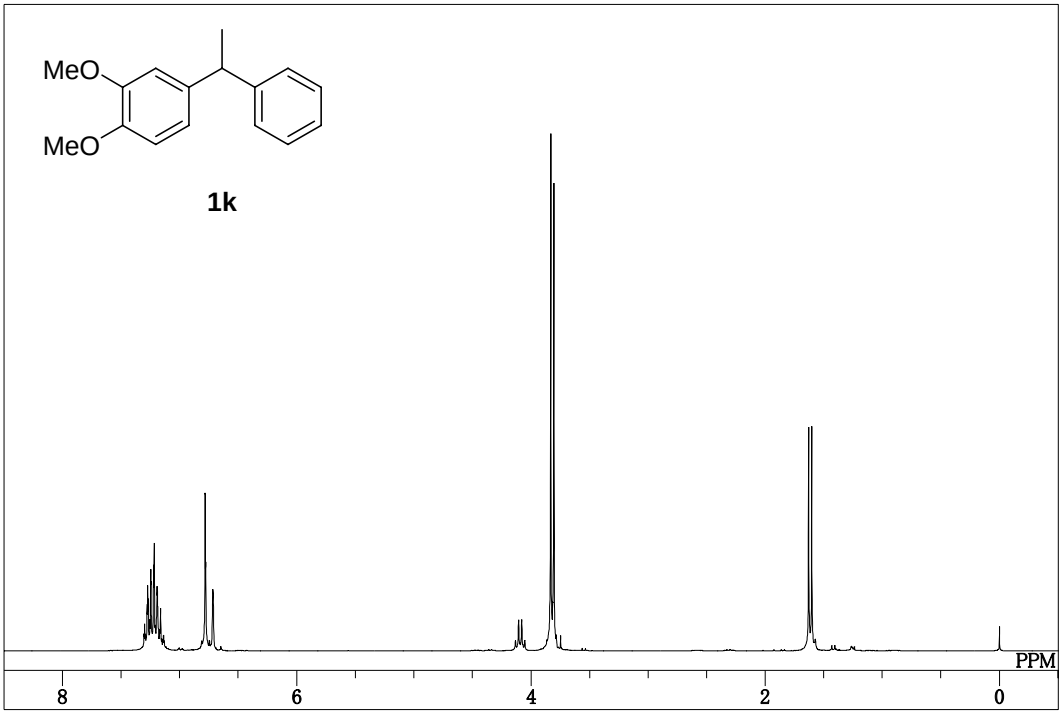
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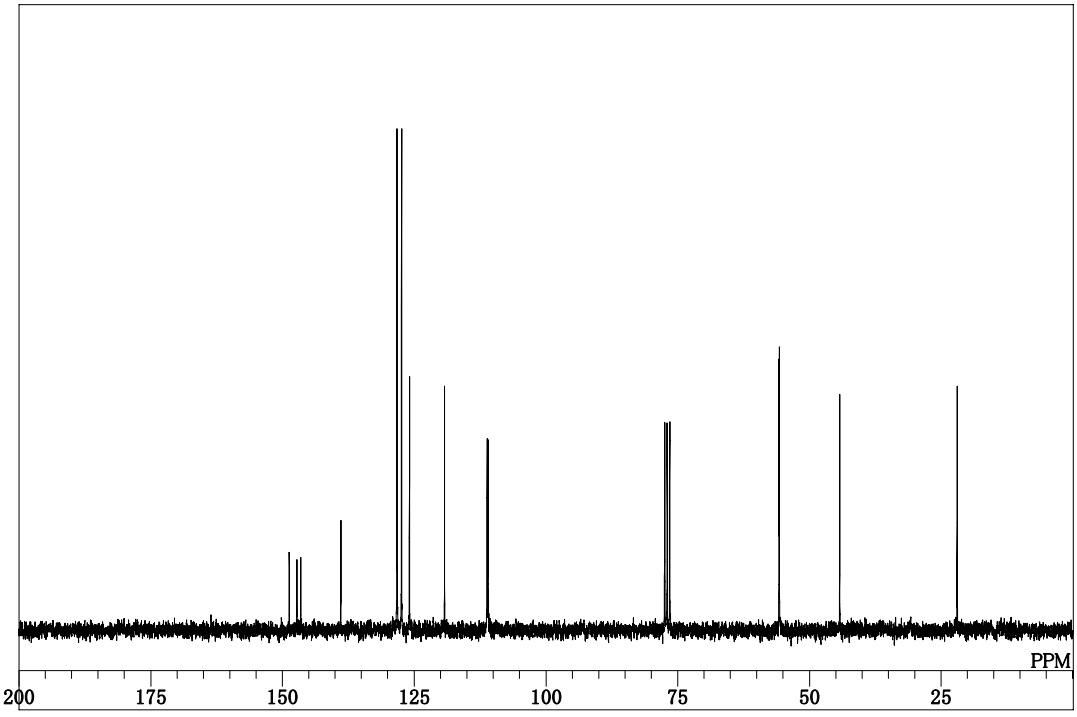
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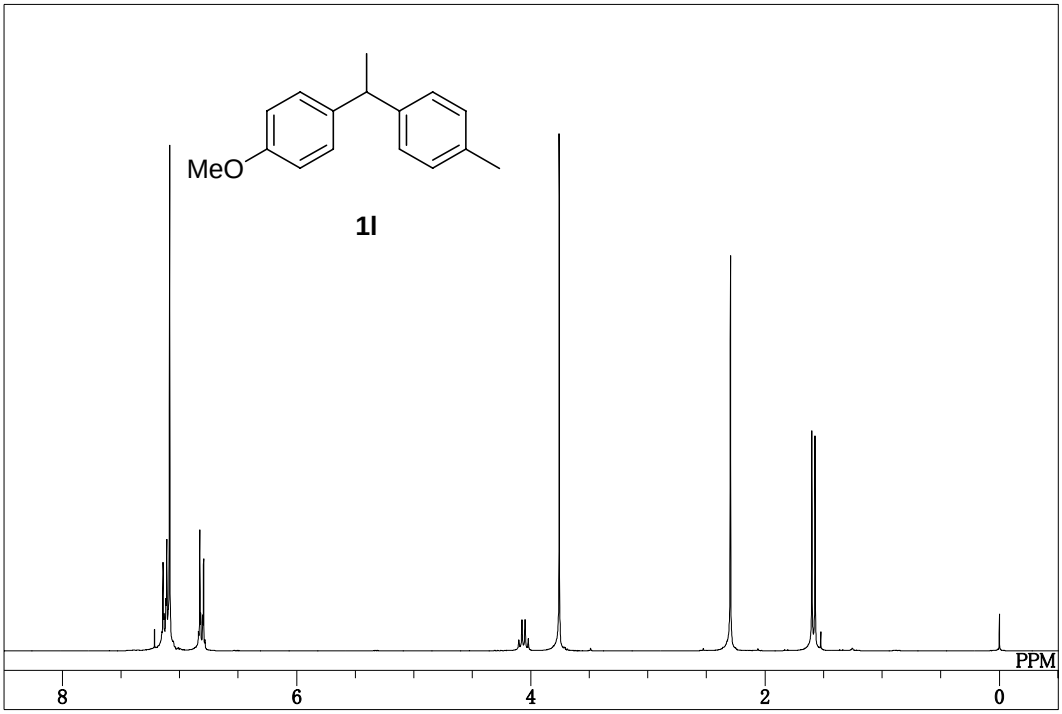
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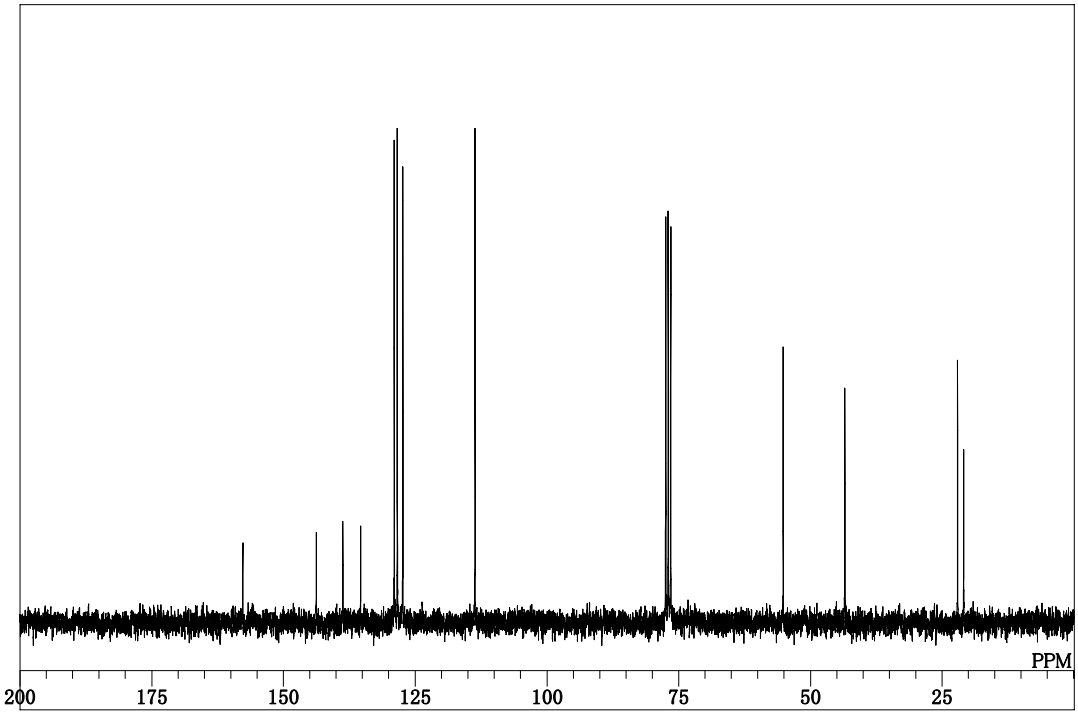
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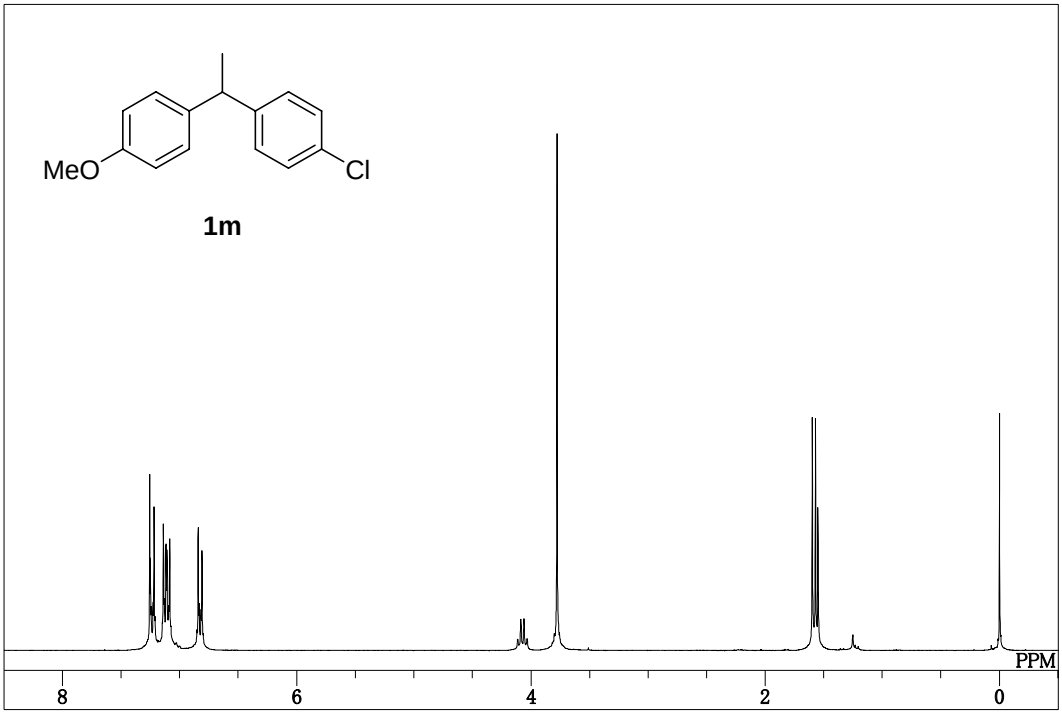
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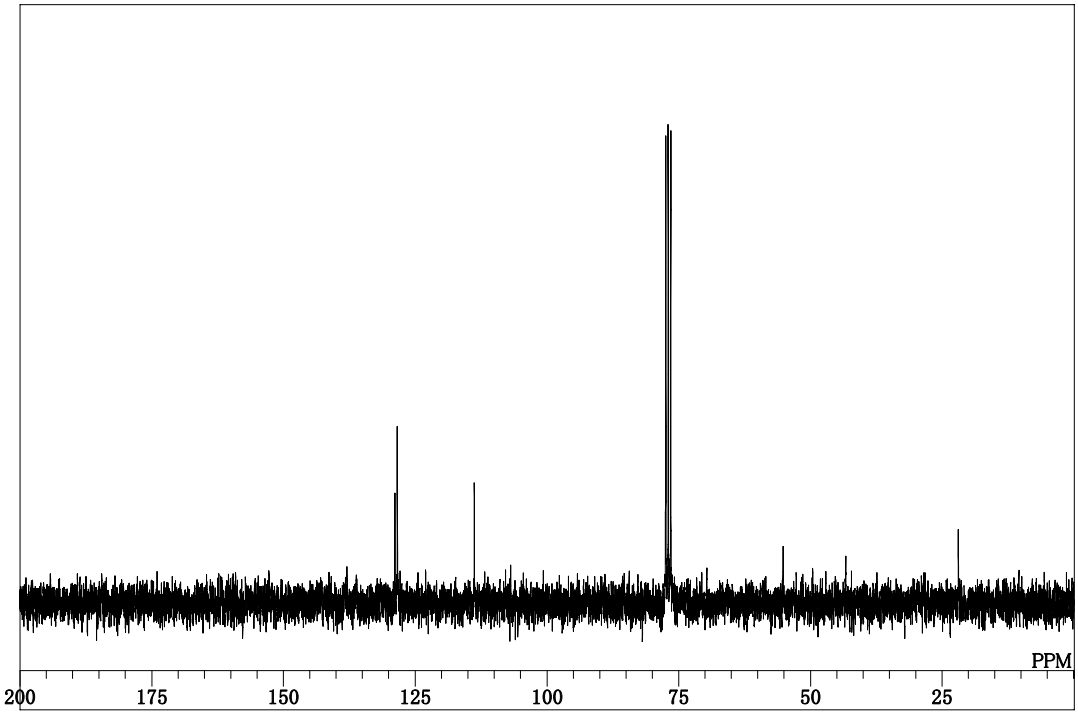
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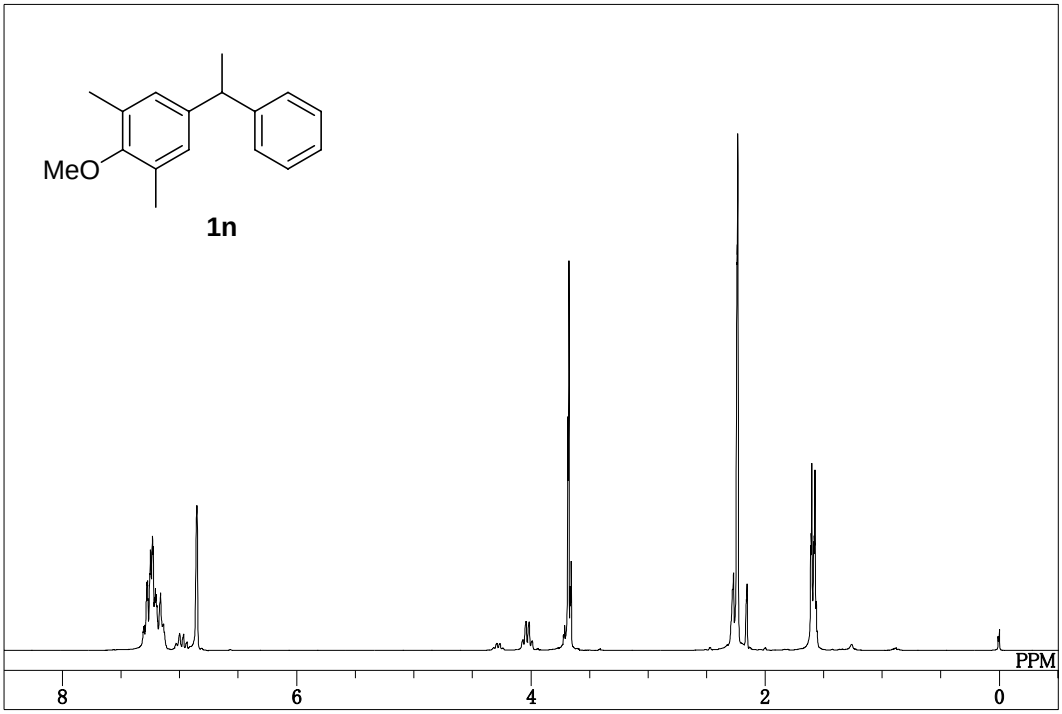
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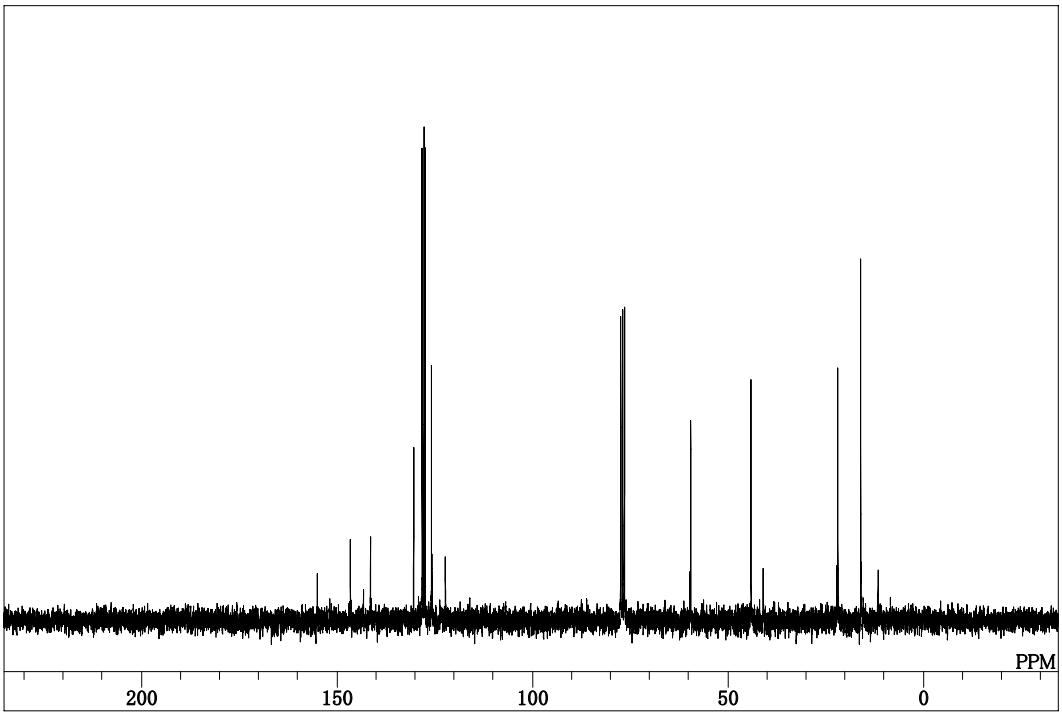
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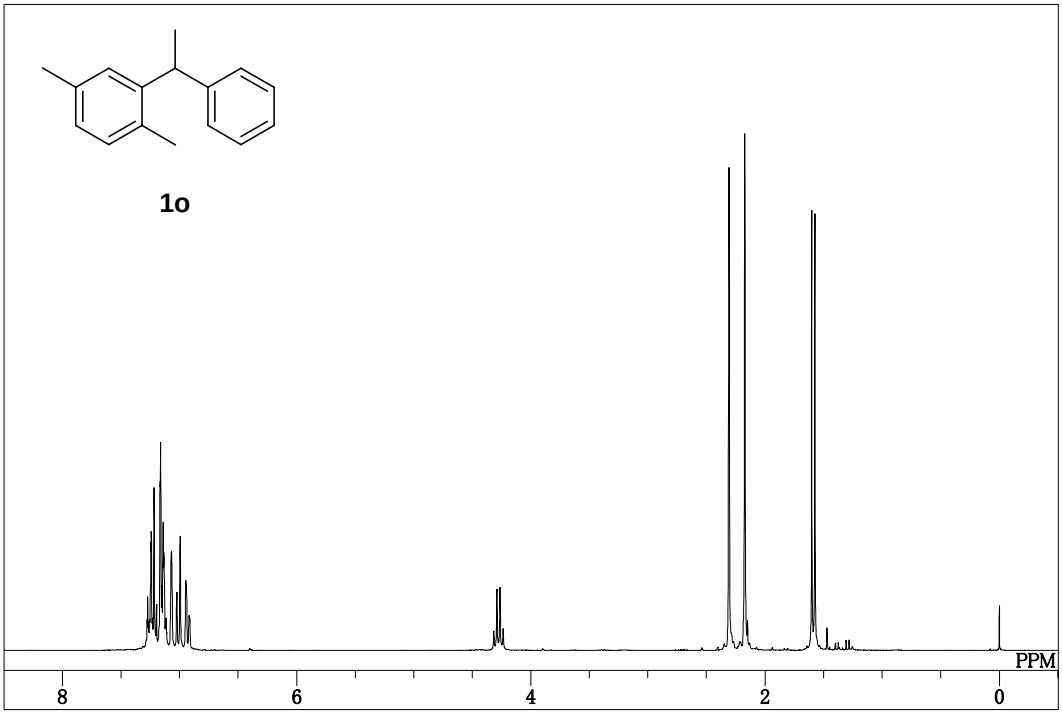
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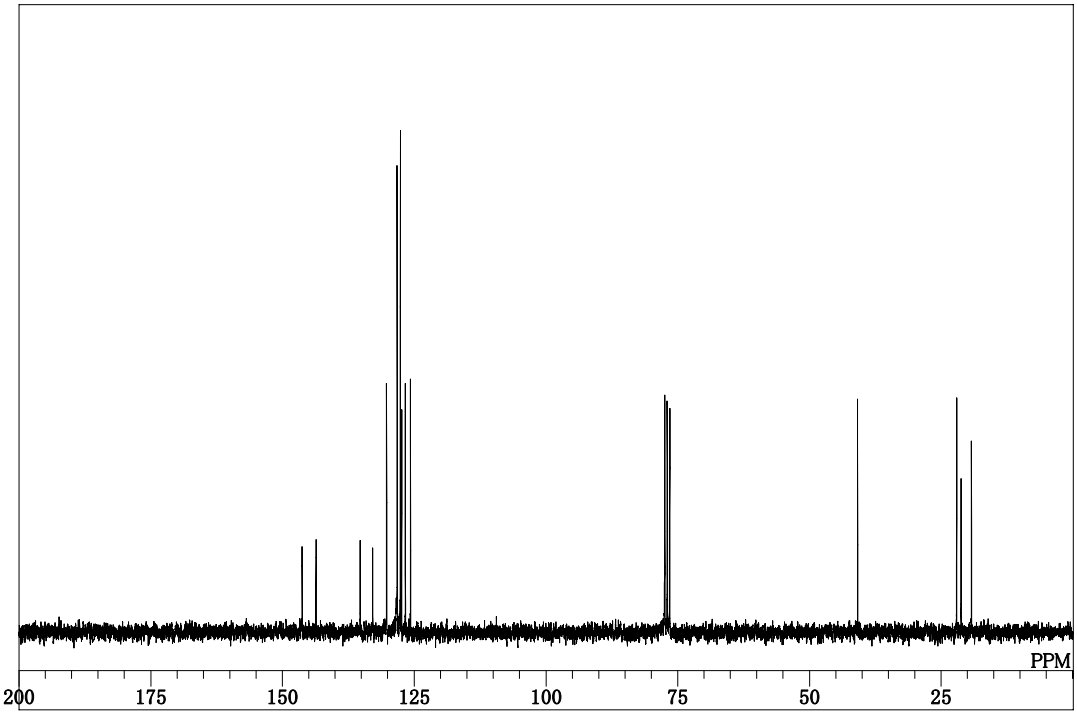
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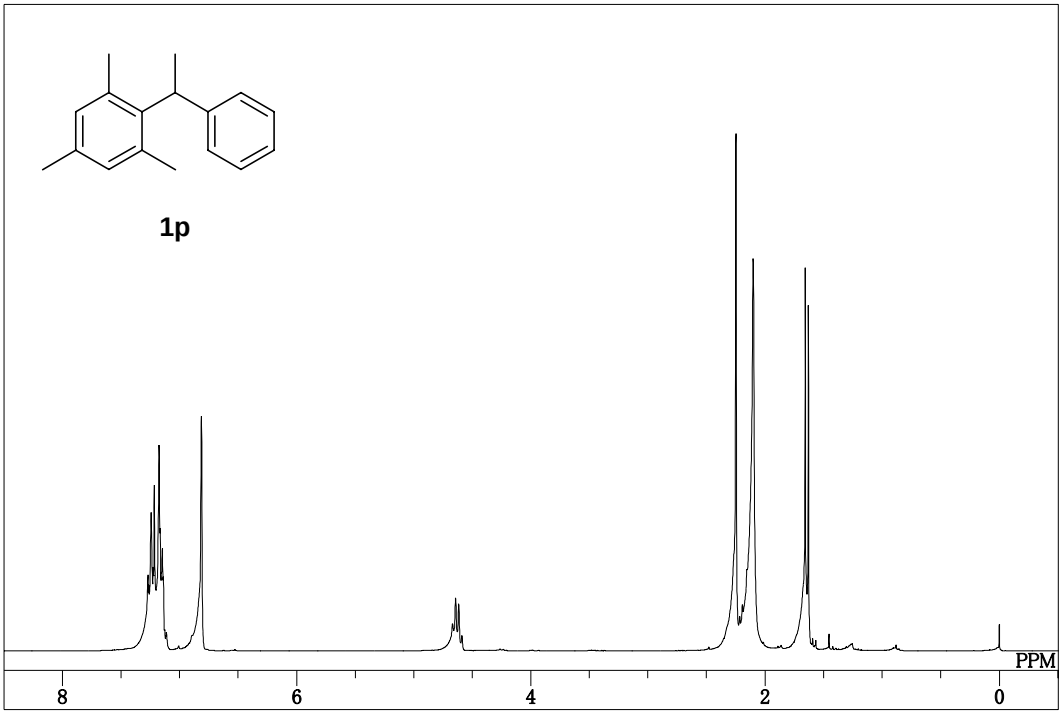
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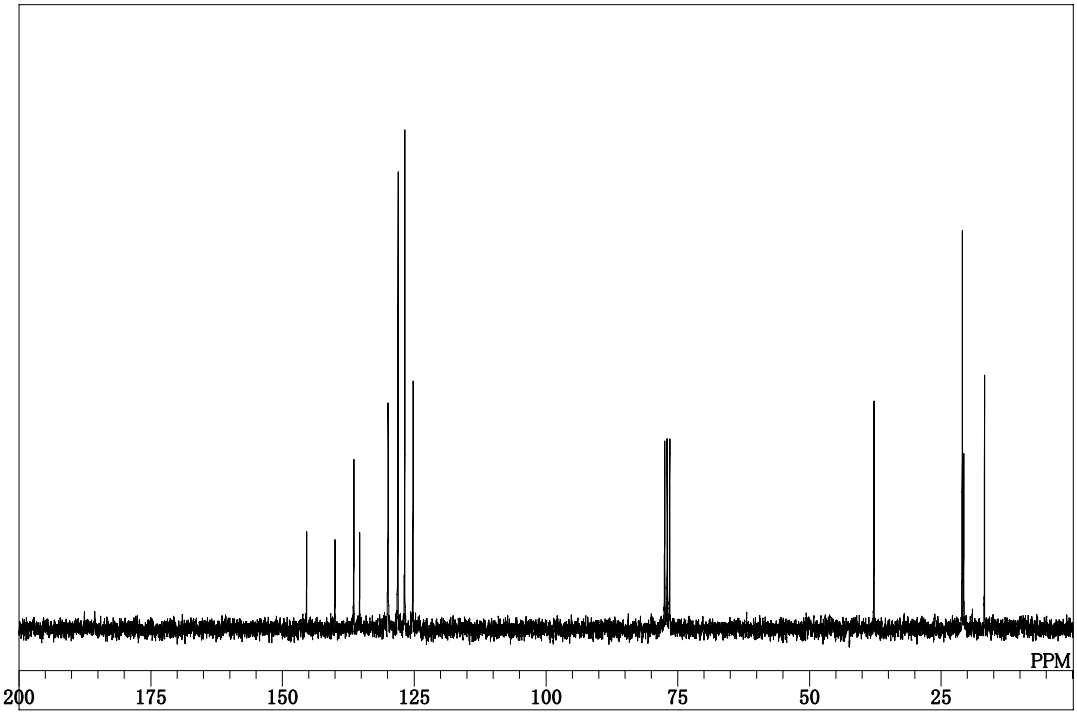
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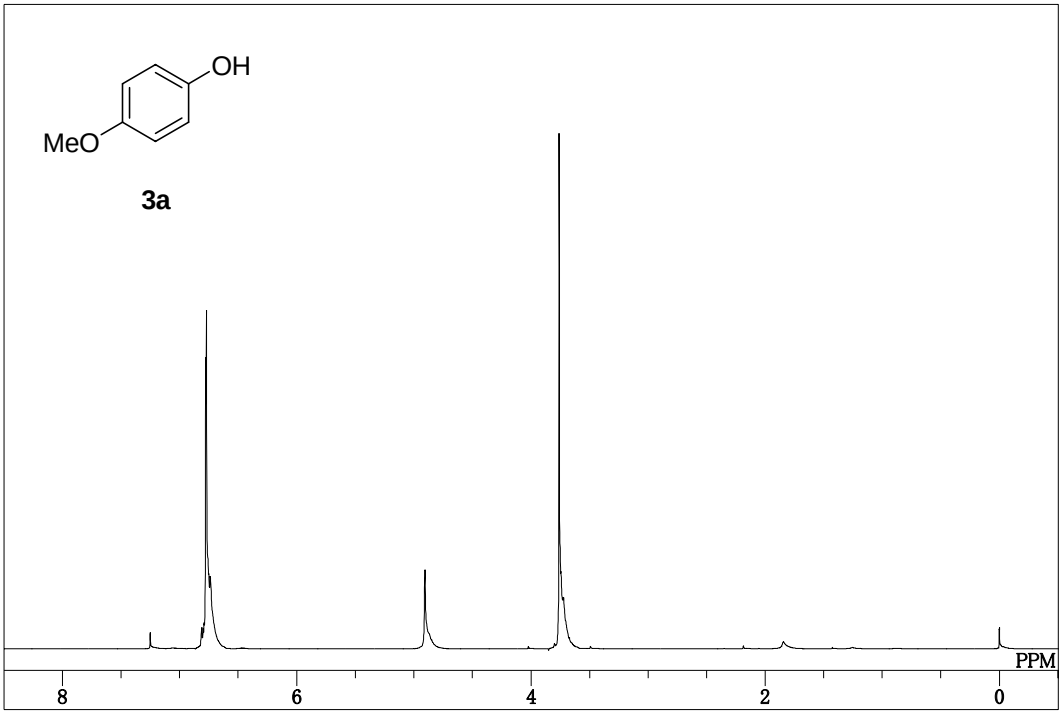
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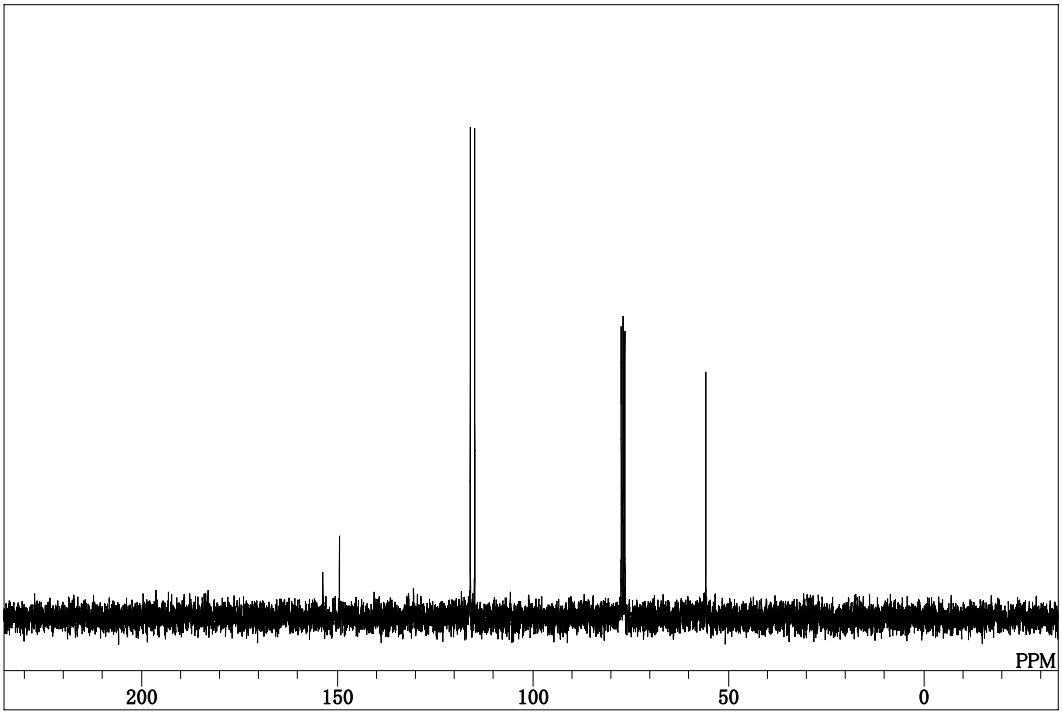
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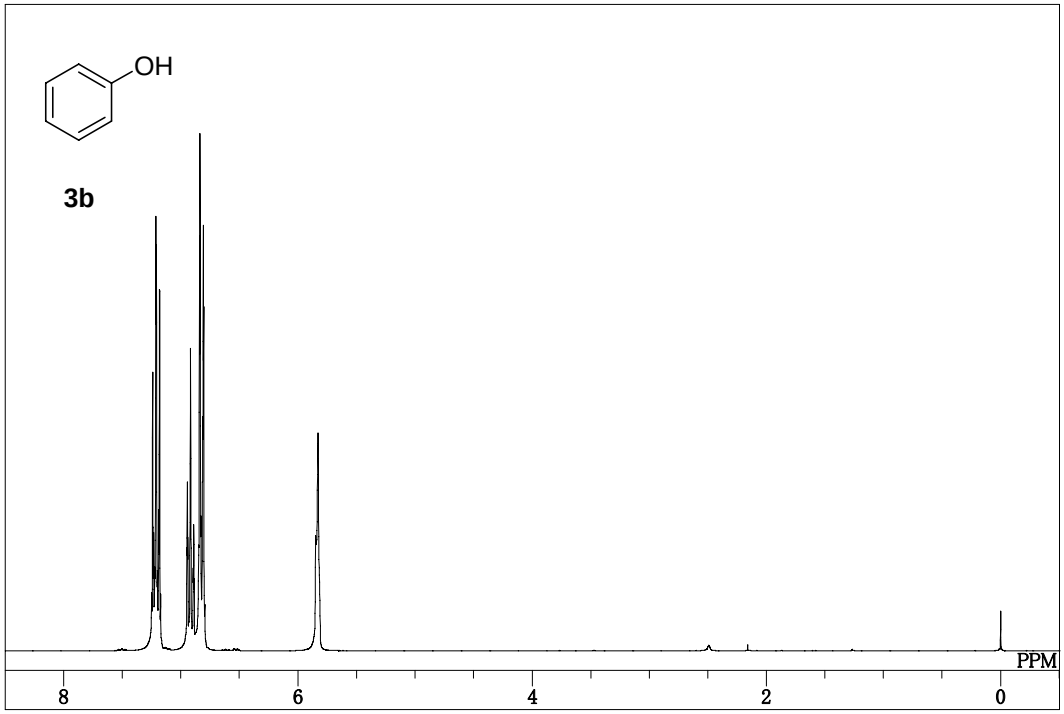
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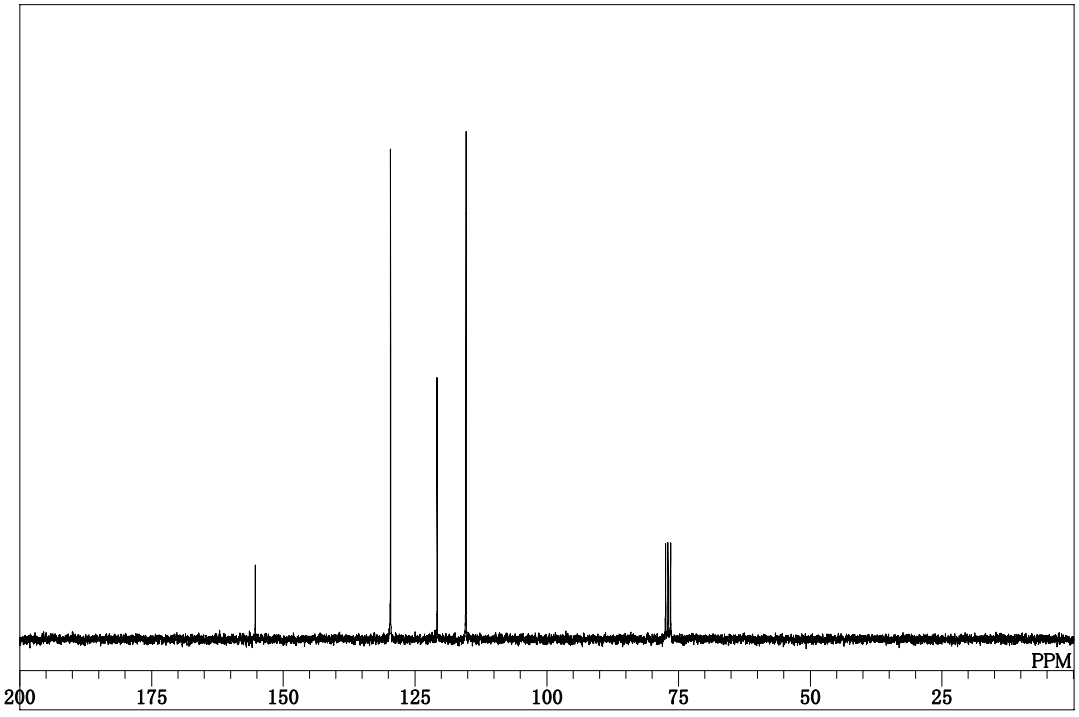
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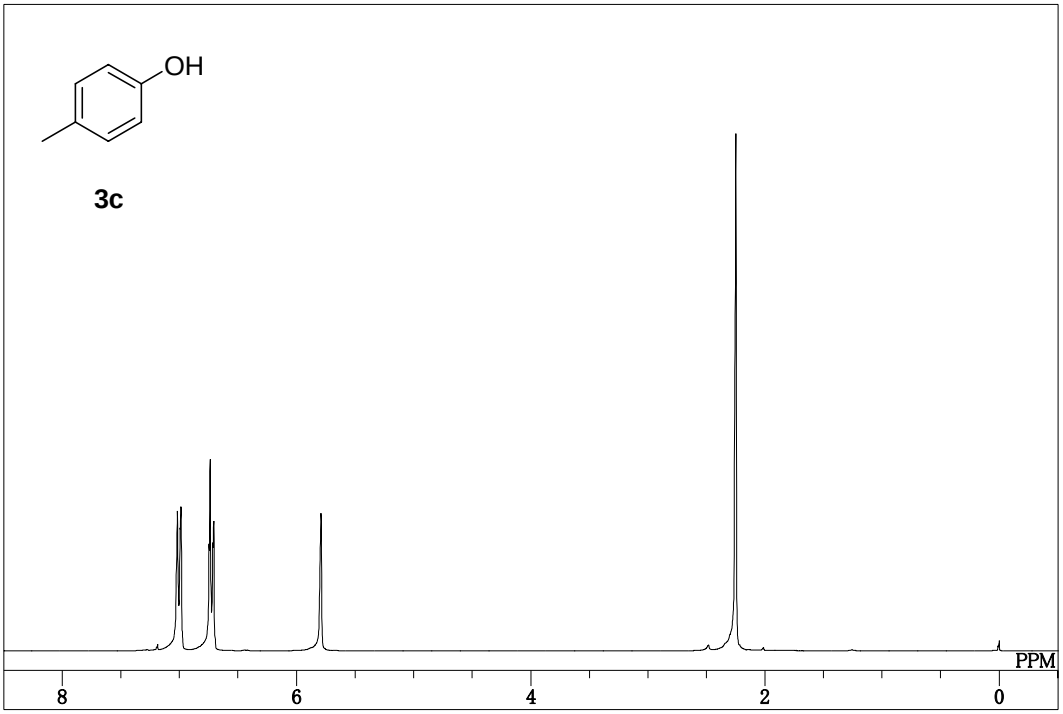
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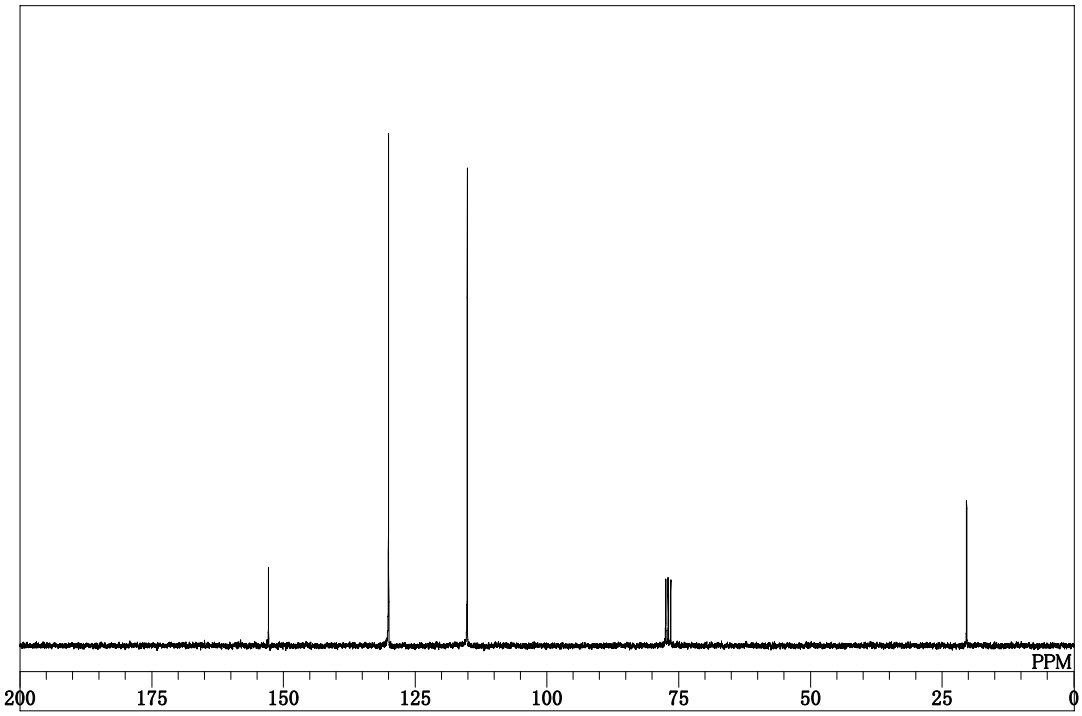
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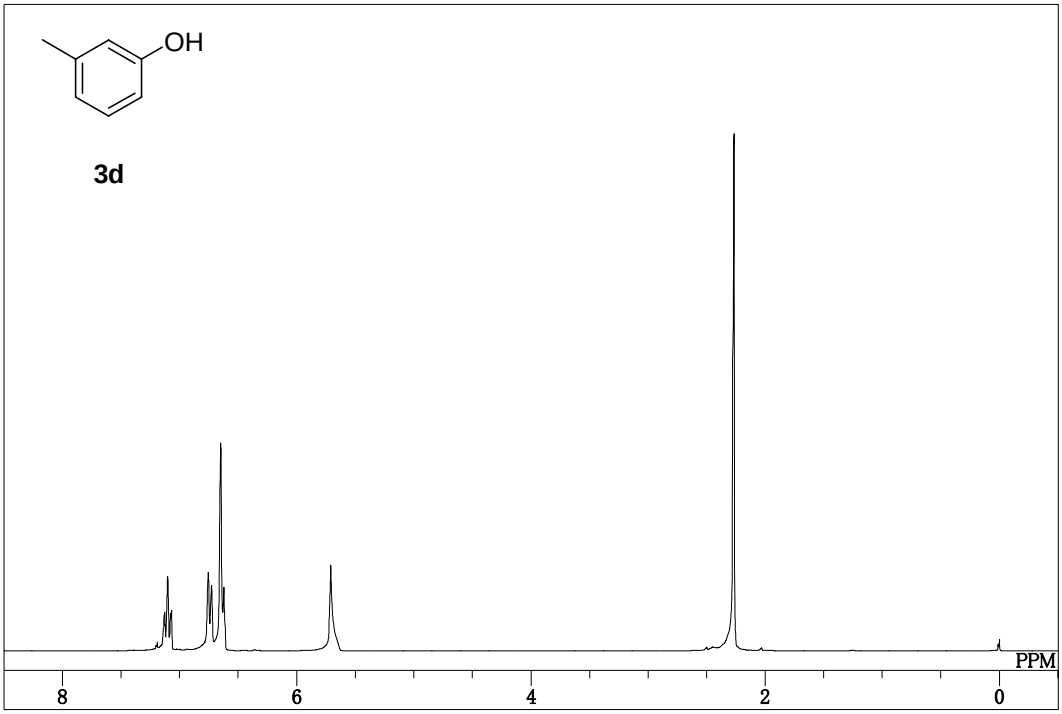
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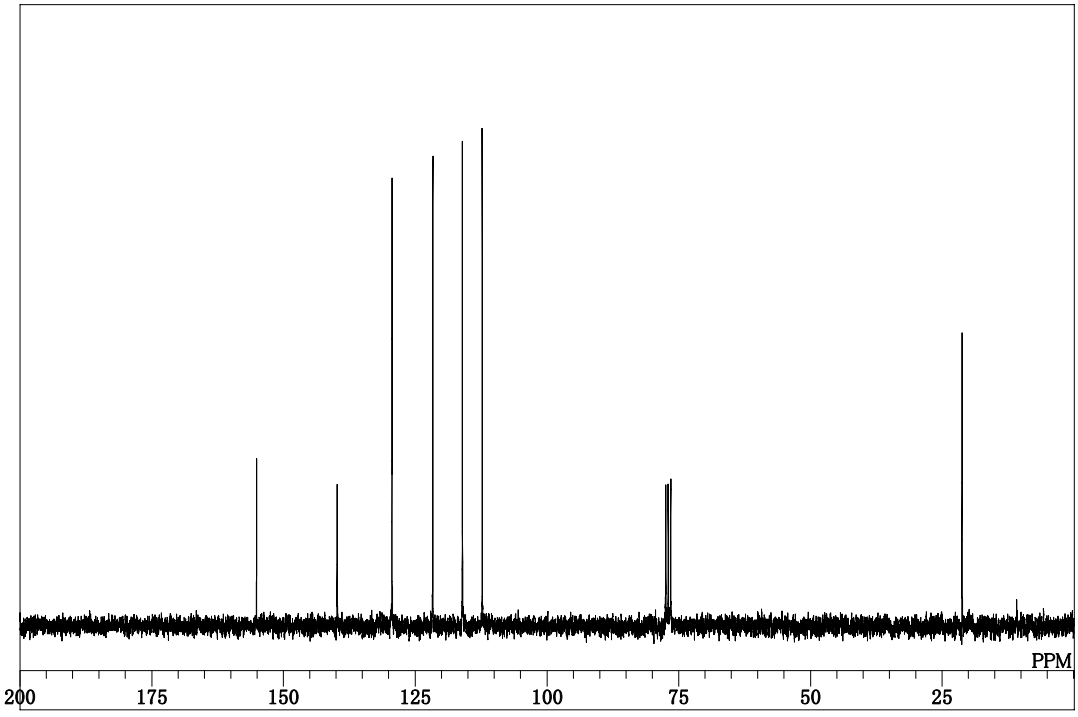
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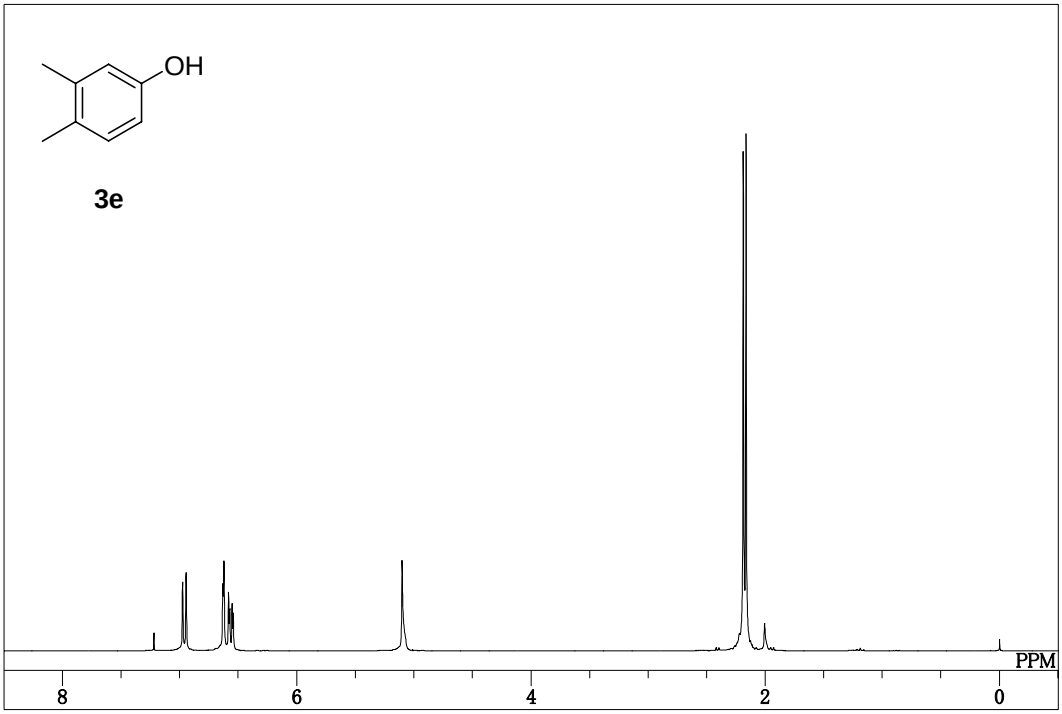
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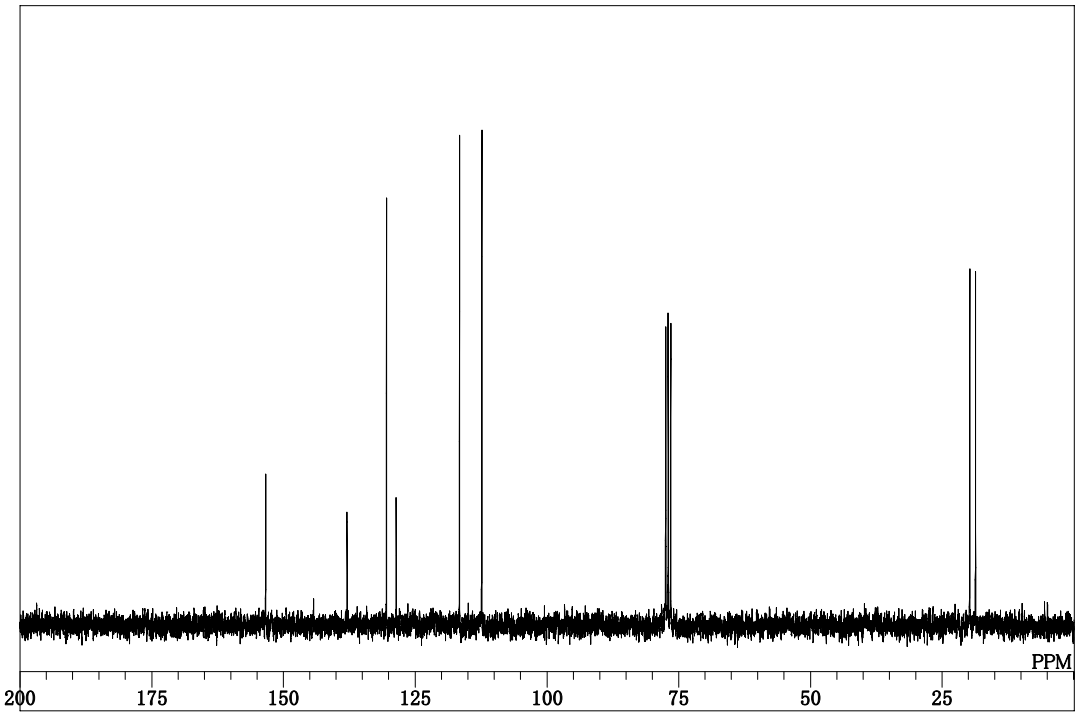
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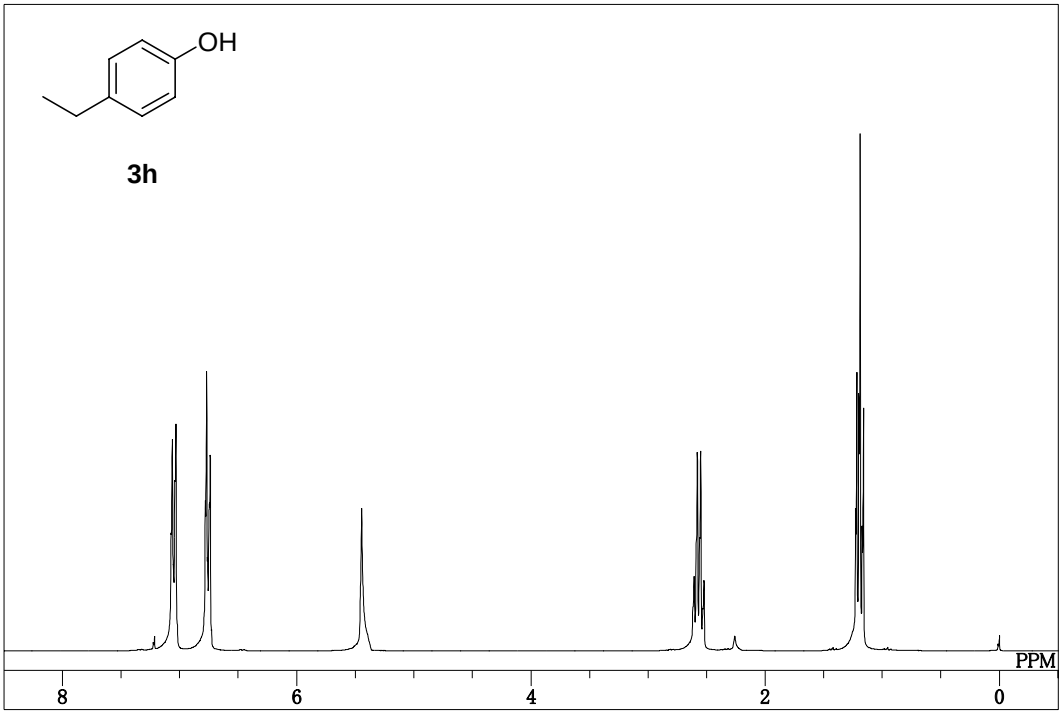
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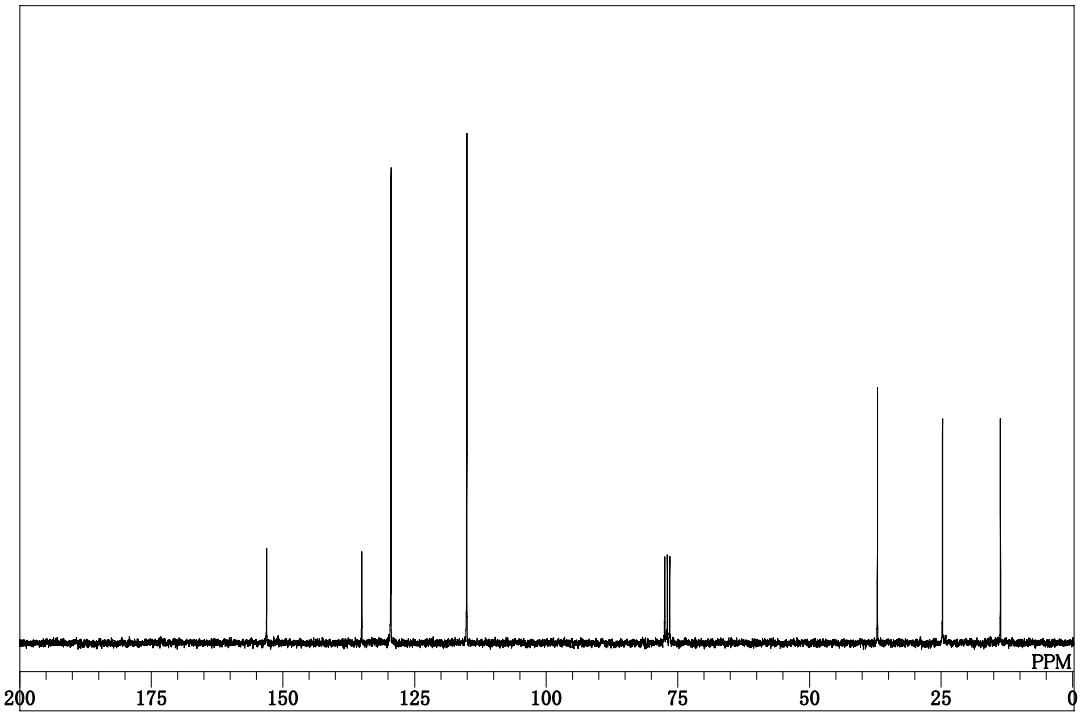
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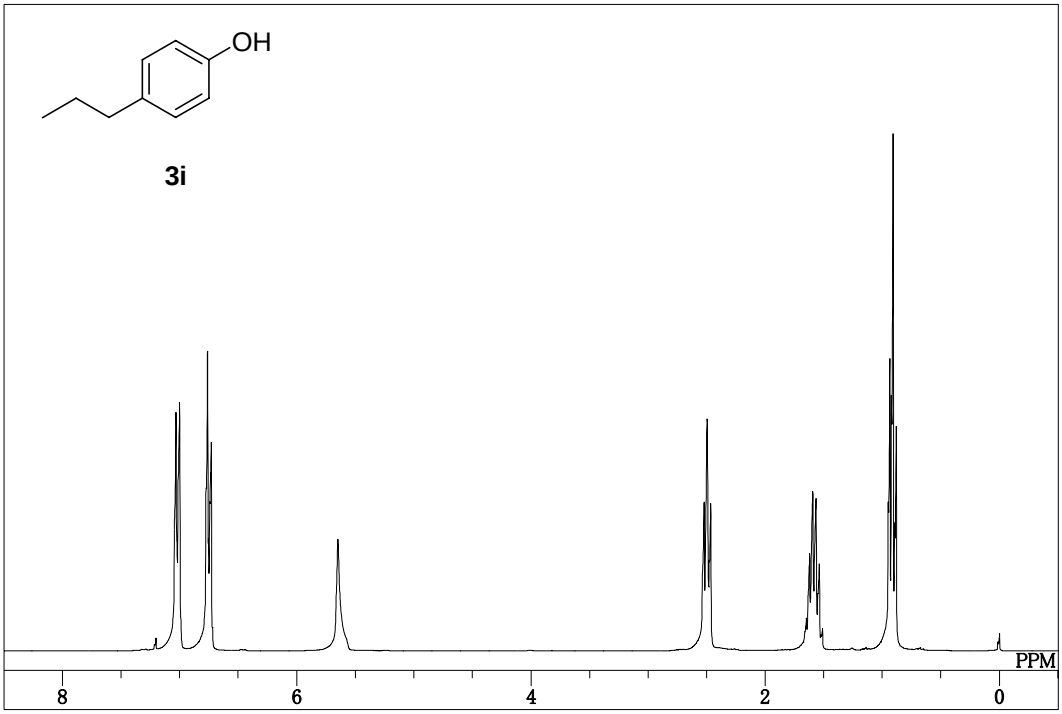
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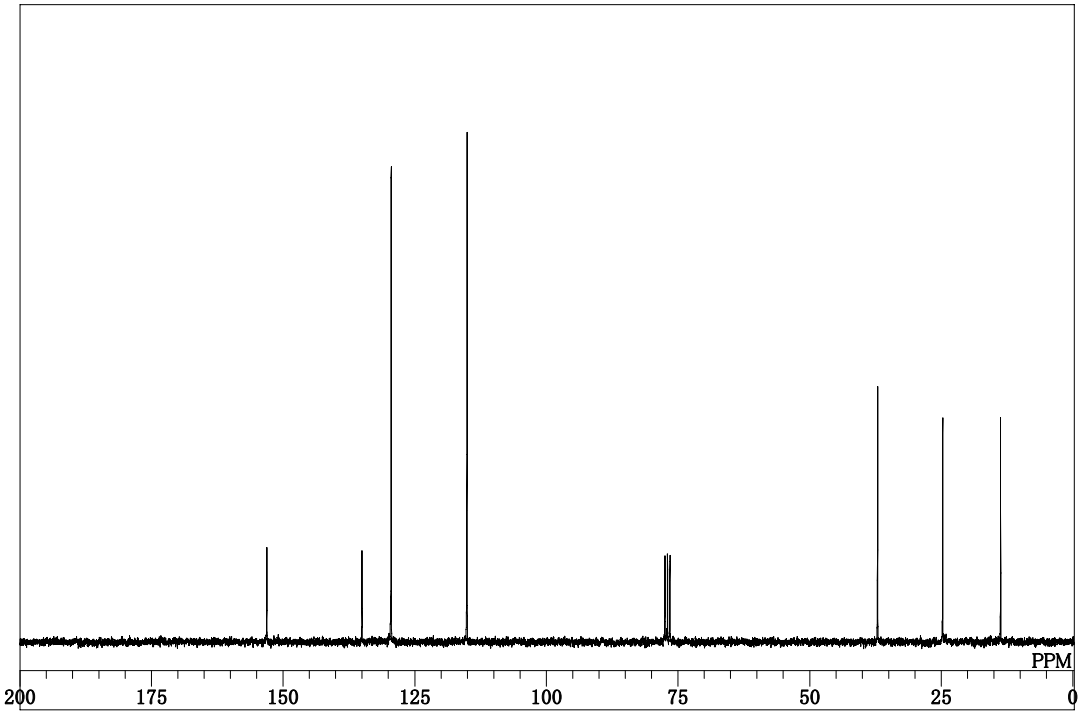
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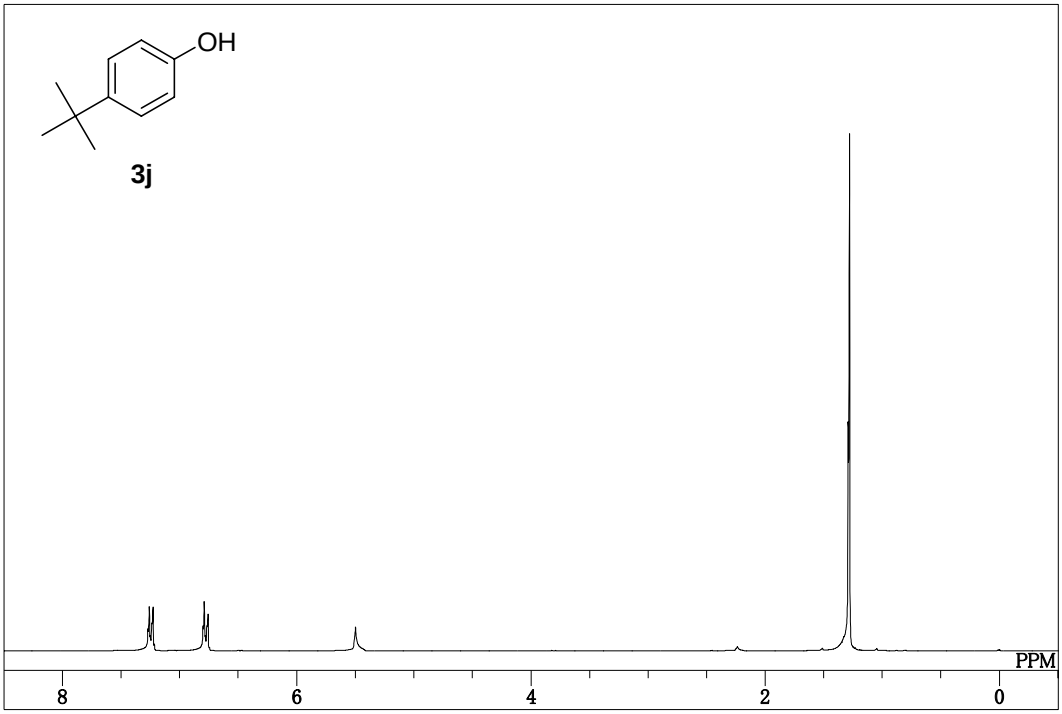
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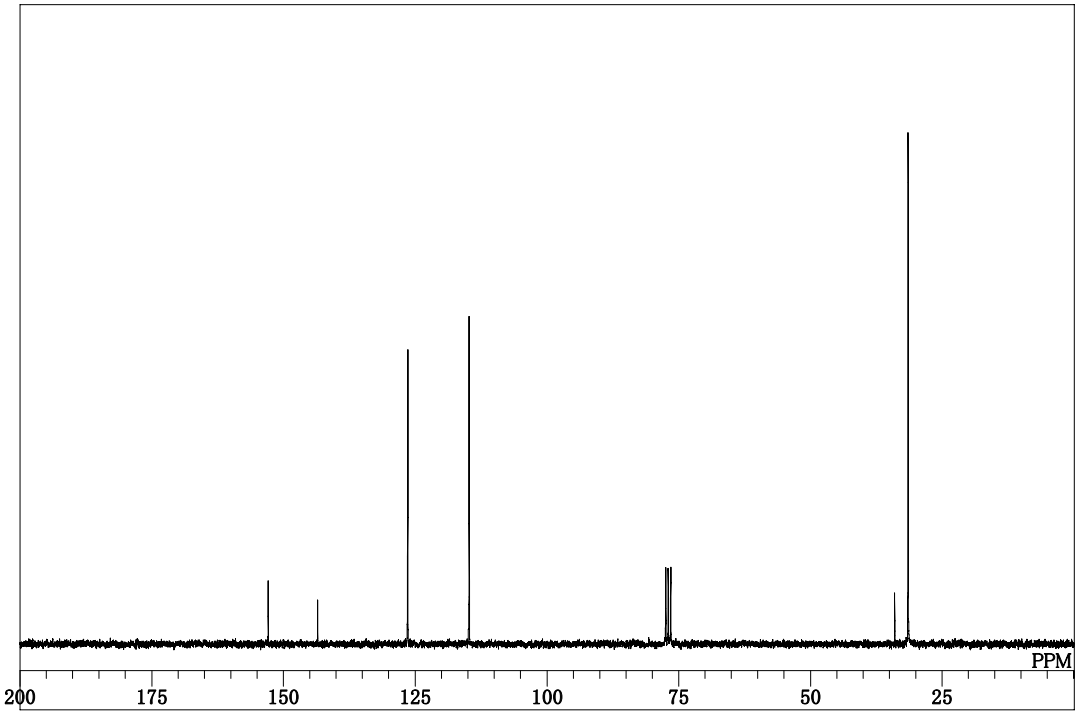
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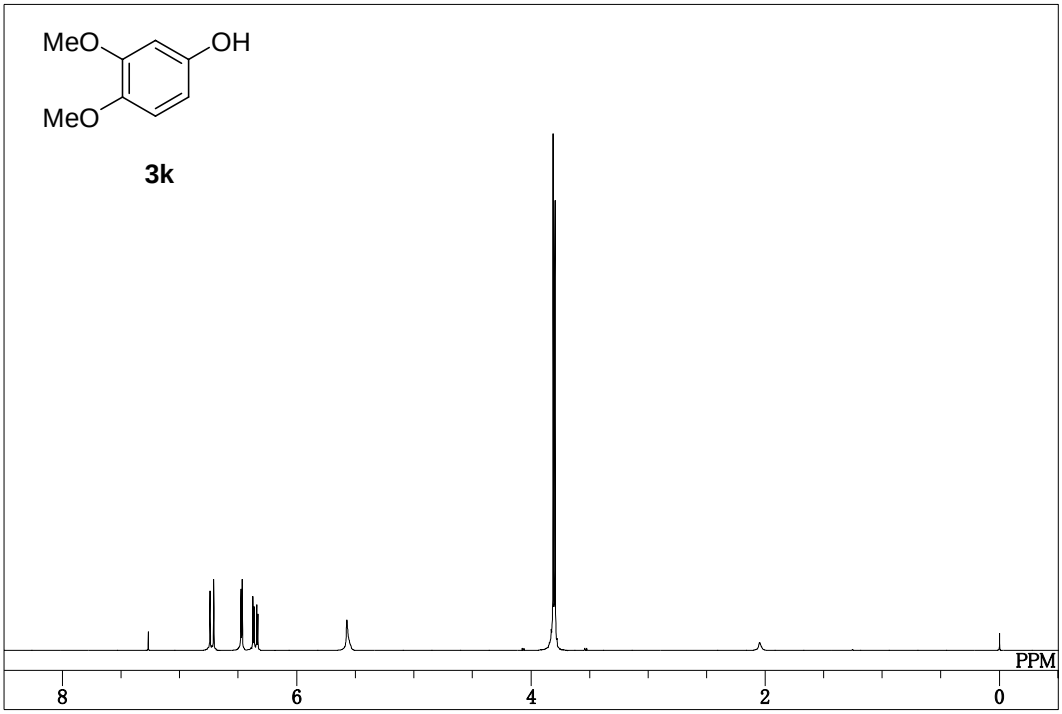
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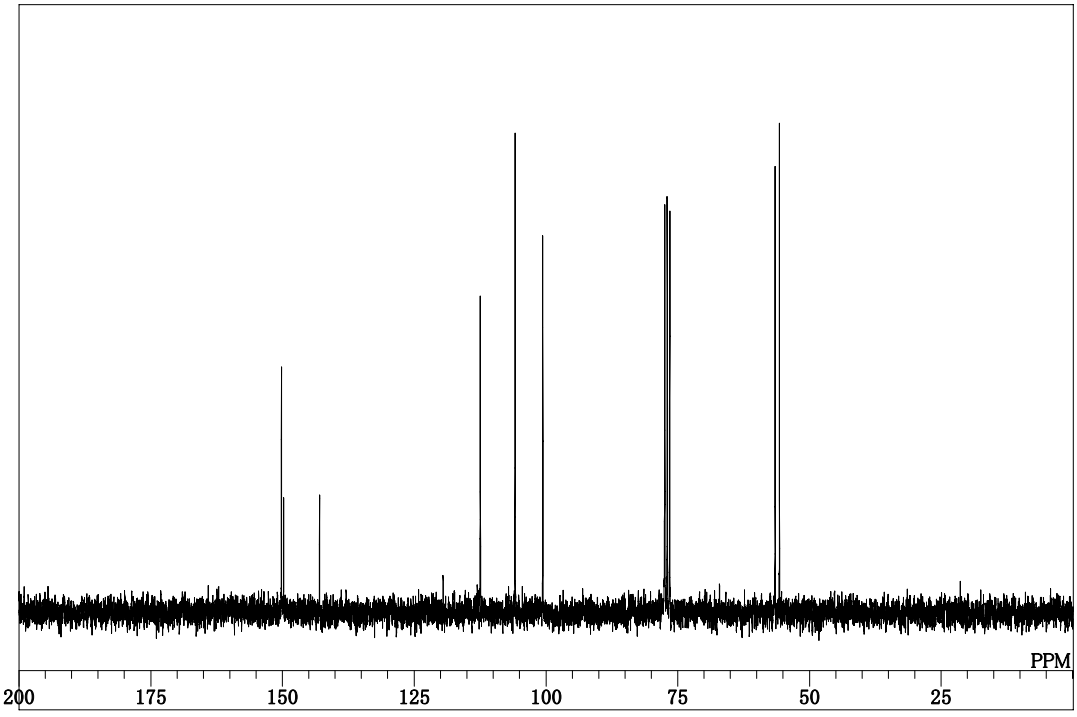
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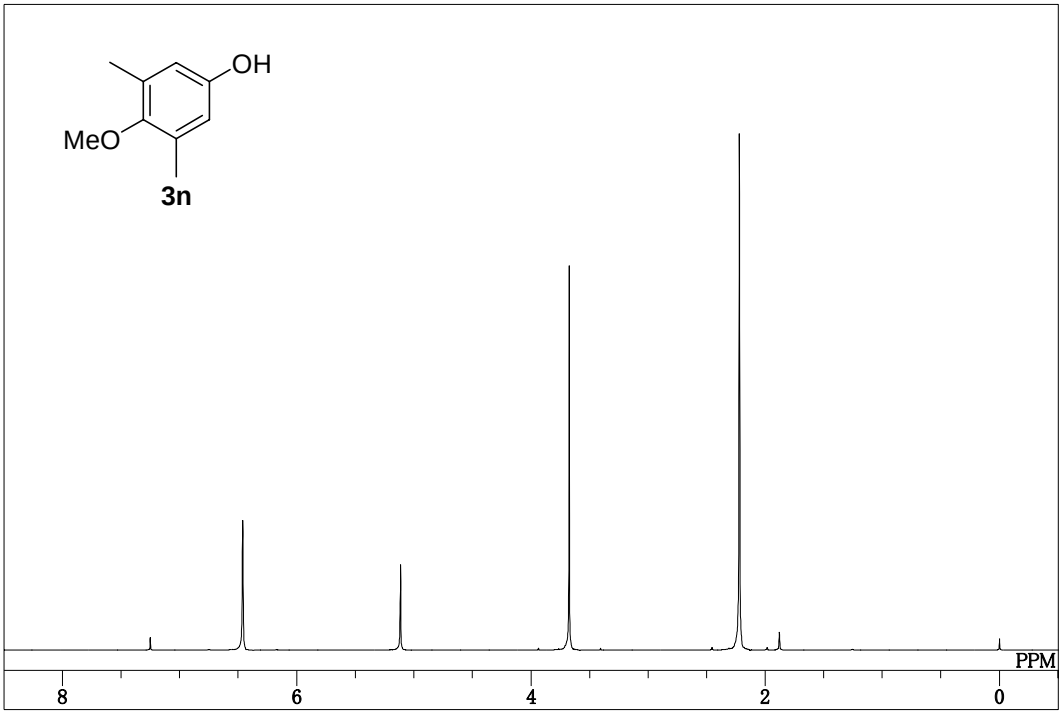
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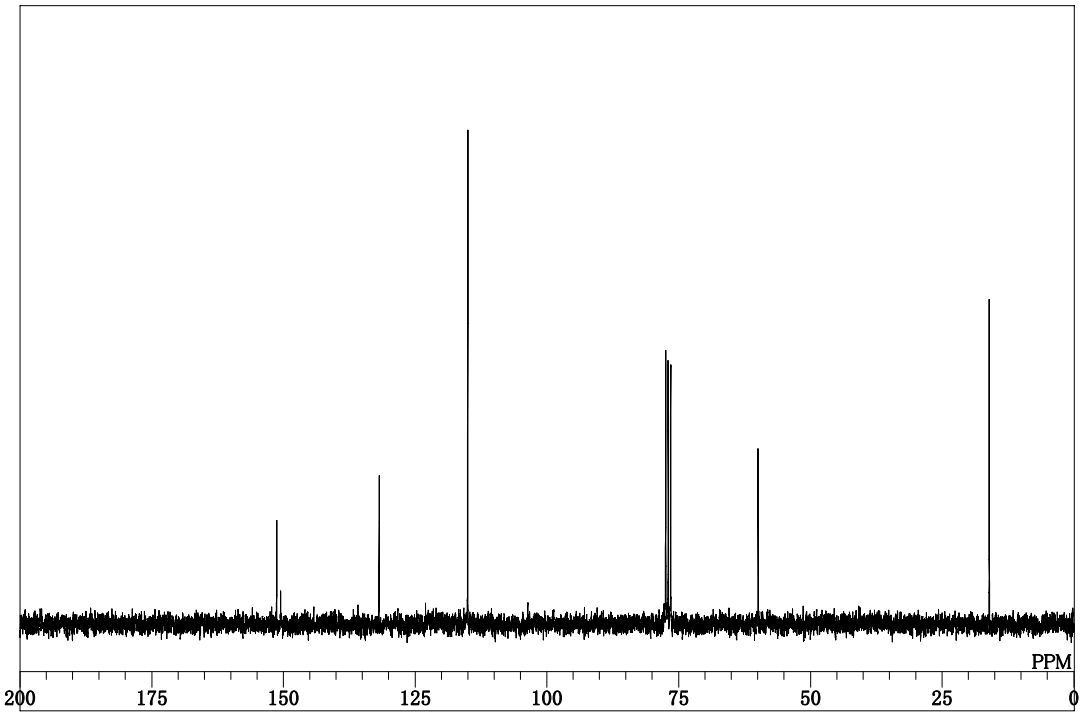
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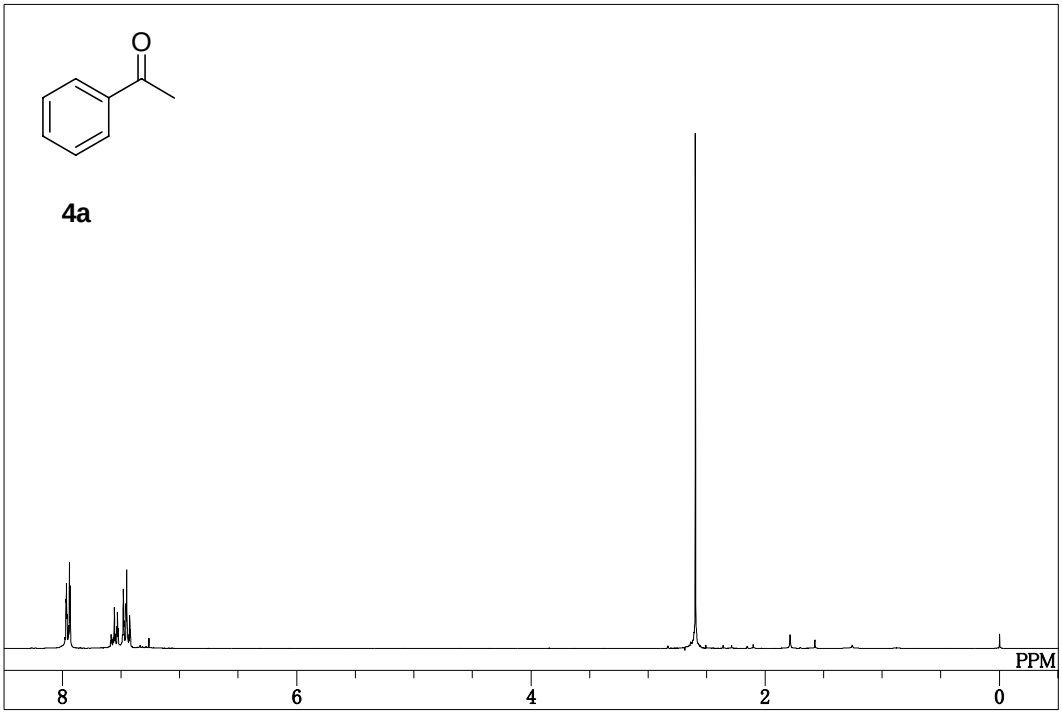
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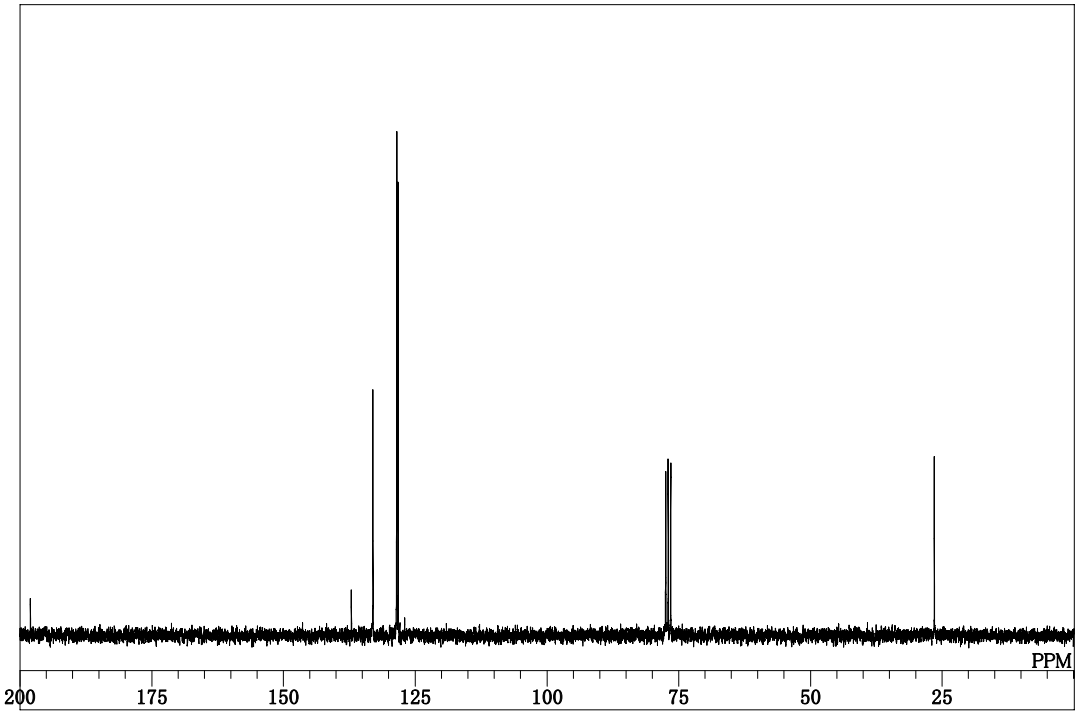
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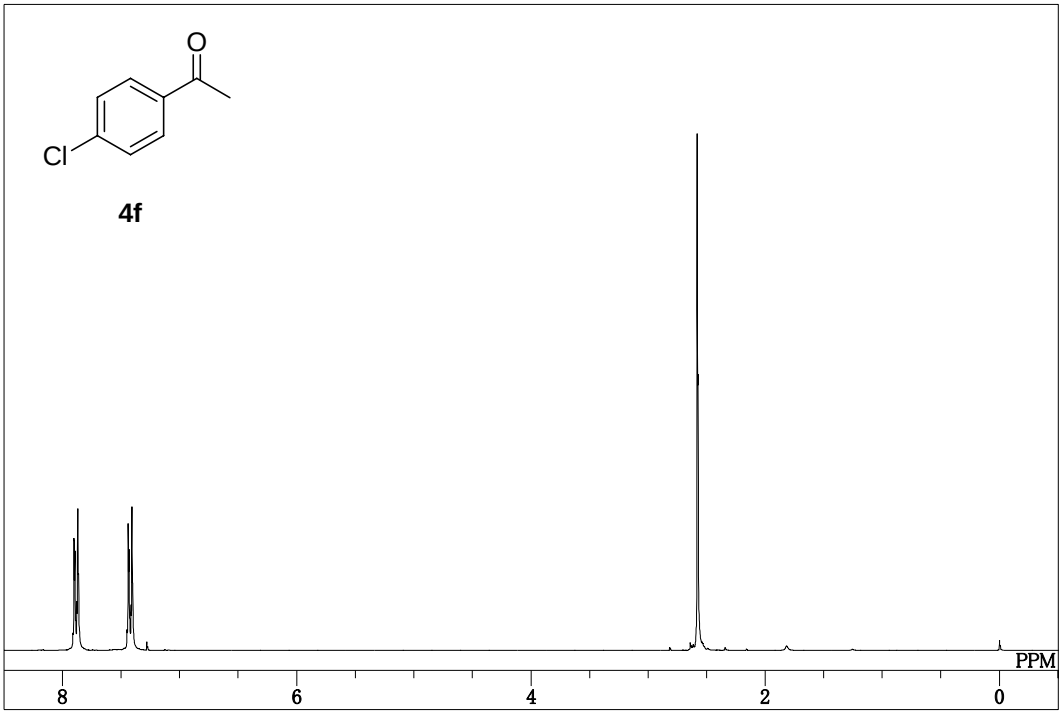
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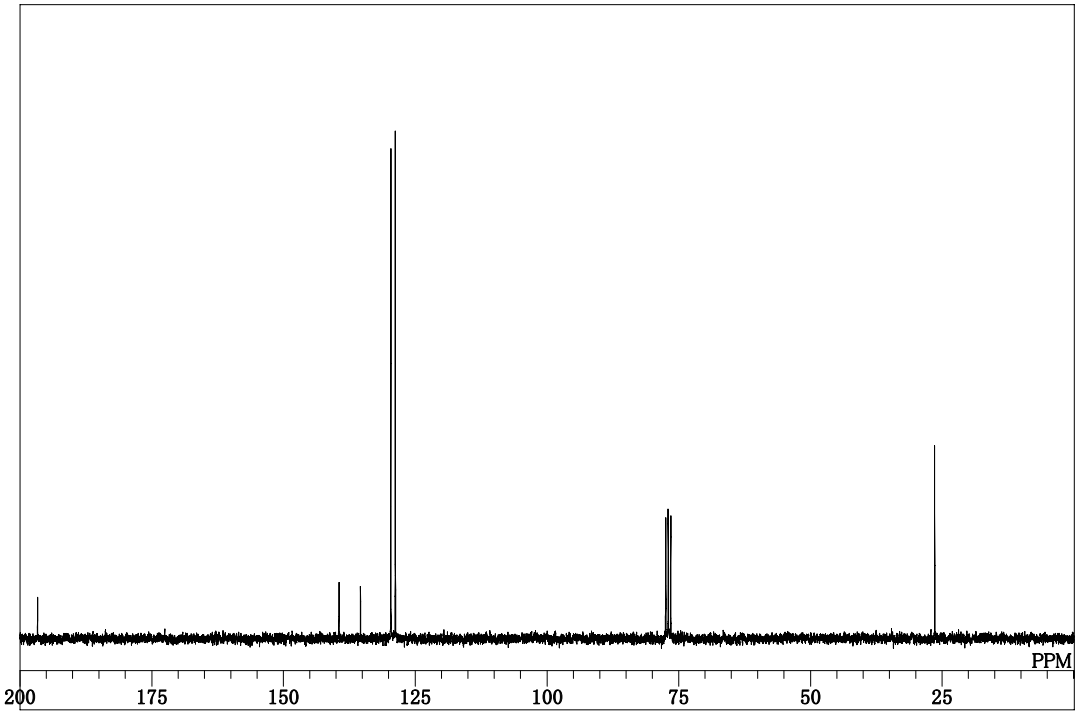
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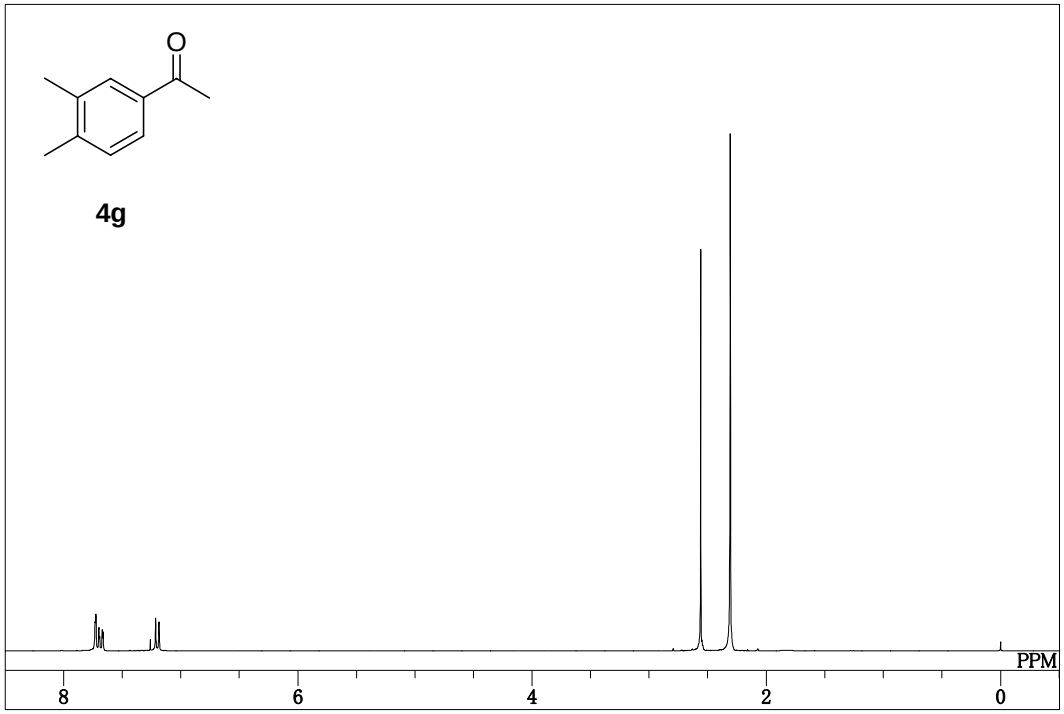
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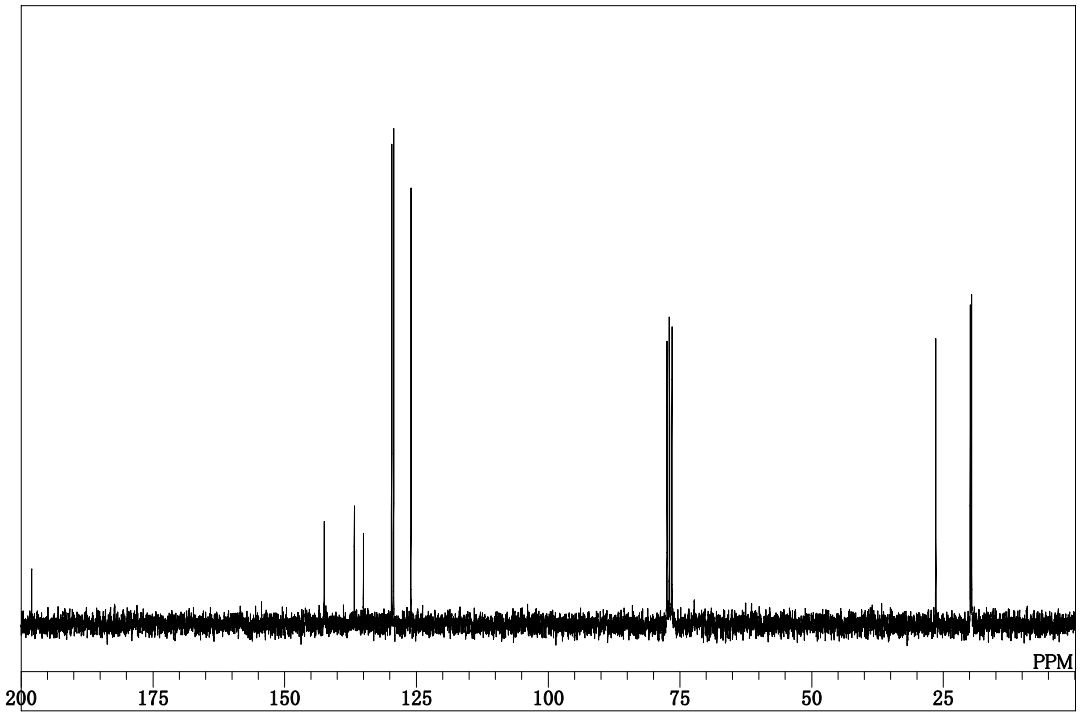
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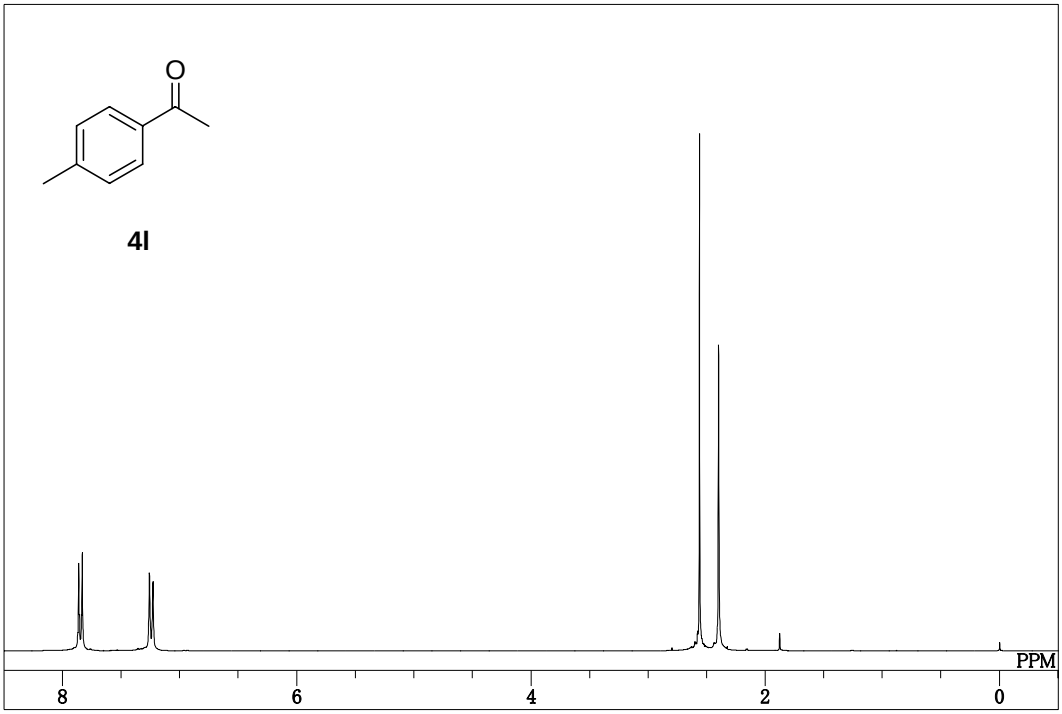
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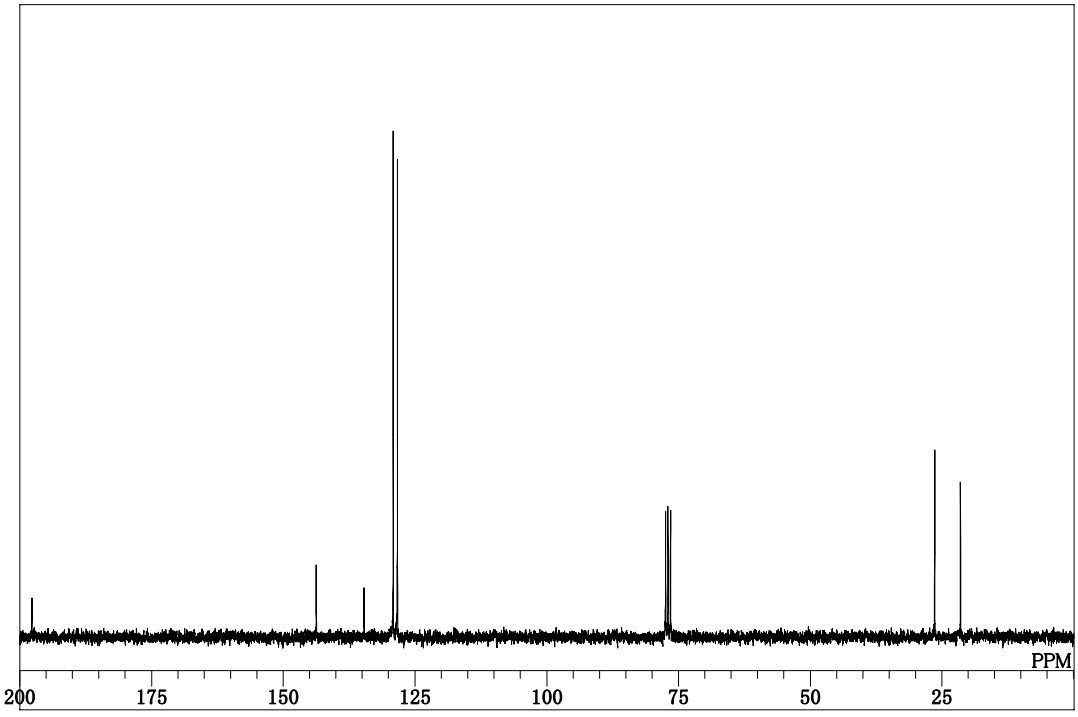
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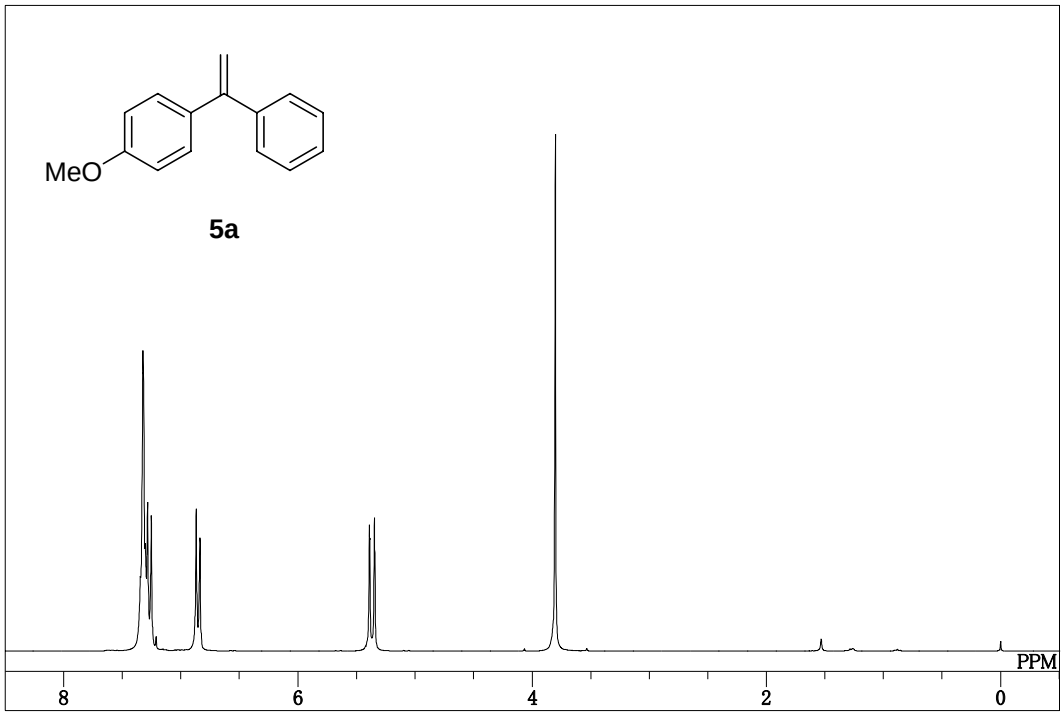
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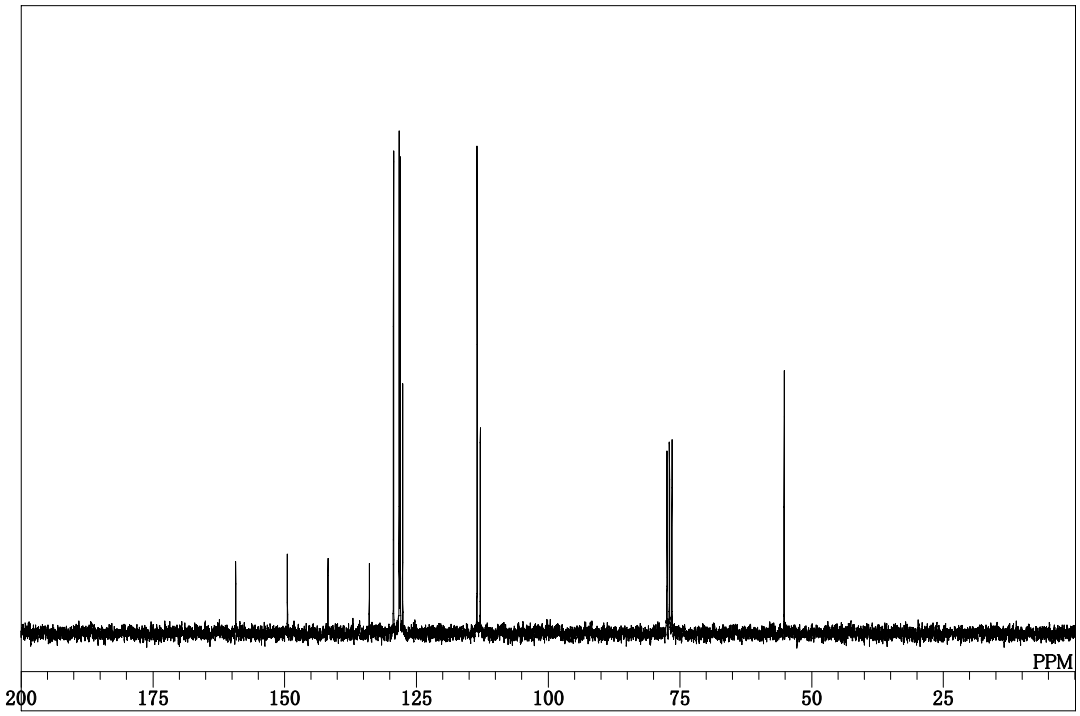
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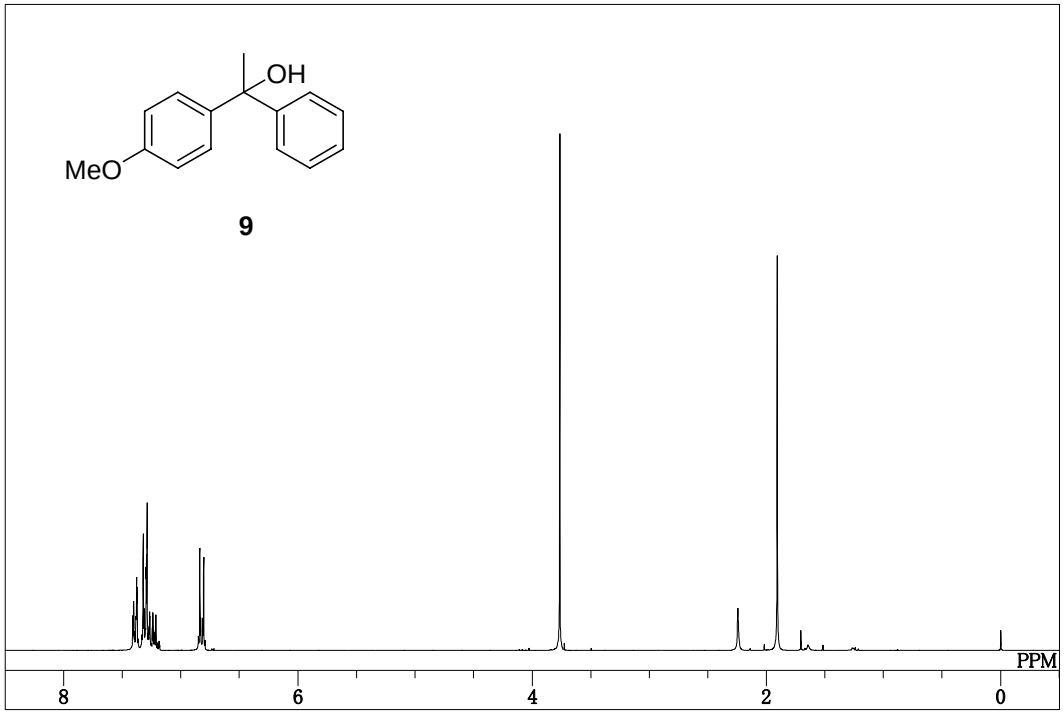

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