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Preparation and use of DMF-stabilized Iridium Nanoclusters as methylation catalysts using methanol as the C1 source

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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). All NMR spectra were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with TMS as an internal standard. All products were characterized by ^{1}H NMR, ^{13}C NMR and GC-MS. The products yield 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. Compounds **2a**[1], **2b**[2], **2c**[3], **2d**[2], **2e**[4], **2f**[1] **2g**[5], **2h**[6], **2i**[5], **2j**[7], **5a**[8], **5b**[8] and **5c**[8] were reported previously. High-resolution mass spectra were performed at Global Facility Center, Hokkaido University.

Experimental

Preparation of 0.1 M $IrCl_3$ aq. (A) : A mixture of $IrCl_3$(0.317 g) and distilled water (10 mL) was added to a vial bottle (10 mL), and allow the bottle to stand at room temperature overnight.

Synthesis of DMF-stabilized Ir NCs : DMF (50 mL) was added to a 300 mL three-necked round bottom flask, and the solution was preheated to 140 °C (± 2 °C) and stirred 1300 to 1500 rpm for 5 min. Then the 0.1 M $IrCl_3$ solution (A) was added to the hot DMF solution, which allowed to react for 10 h on stirring (1300 rpm-1500 rpm) at 140 °C (± 2 °C). The resulting clear red solution was used as 1 mM Ir NCs solution in DMF for further reaction. After vacuum evaporation of the solvent, the residue was re-dissolved in selected solvents such as DMF, D_2O, MeOH for the dynamic light scattering (DLS), NMR measurement and the β-methylation reactions.

$$\text{50 mL DMF} \xrightarrow[\text{140 °C, 5 min}]{\text{pre-heating}} \xrightarrow[\text{140 °C, 10 h}]{\text{0.1 M IrCl}_3\text{ aq.}} \text{1.0 mM Ir NCs}$$

Optical spectroscopy of DMF-stabilized Ir NCs : UV-visible absorption spectra were measured by using a JASCO V-670 spectrophotometer. Fluorescence emission spectra were measured by using JASCO FP-6200 fluorescence spectrophotometer at UV excitation of 350 nm.

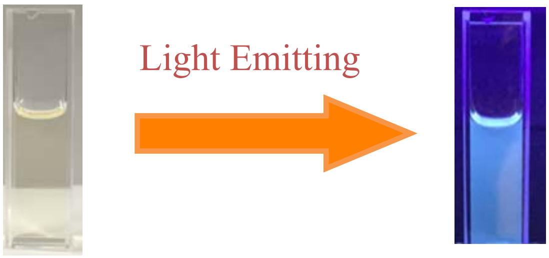


Fig.S1 photoluminescent by UV lamp (350 nm)

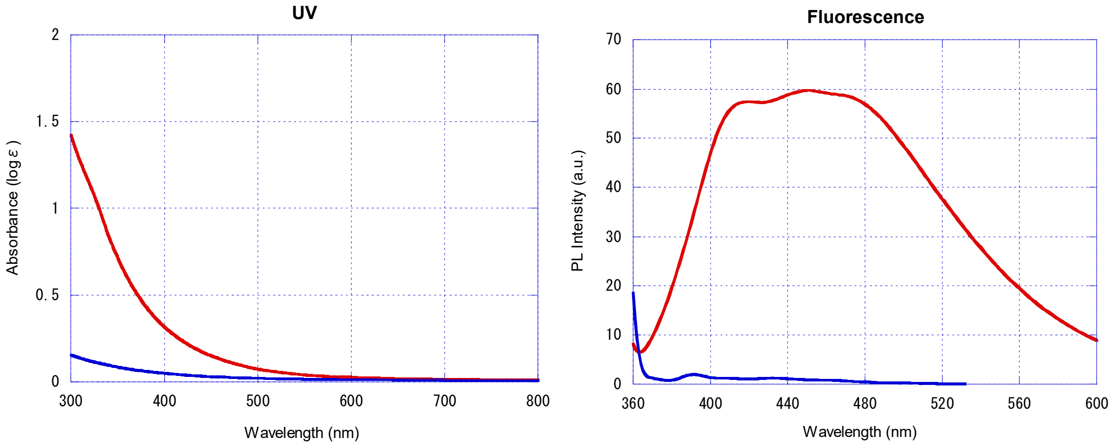


Fig. S2 (a) UV-visible absorption spectra of DMF-stabilized Ir NCs (red), and $IrCl_3$ as precursor (blue). (b) Photoluminescence emission spectra of DMF-stabilized Ir NCs (red), and $IrCl_3$ as precursor (blue)

Fig. S3 DMF-stabilized Ir NCs size distributions by TEM image

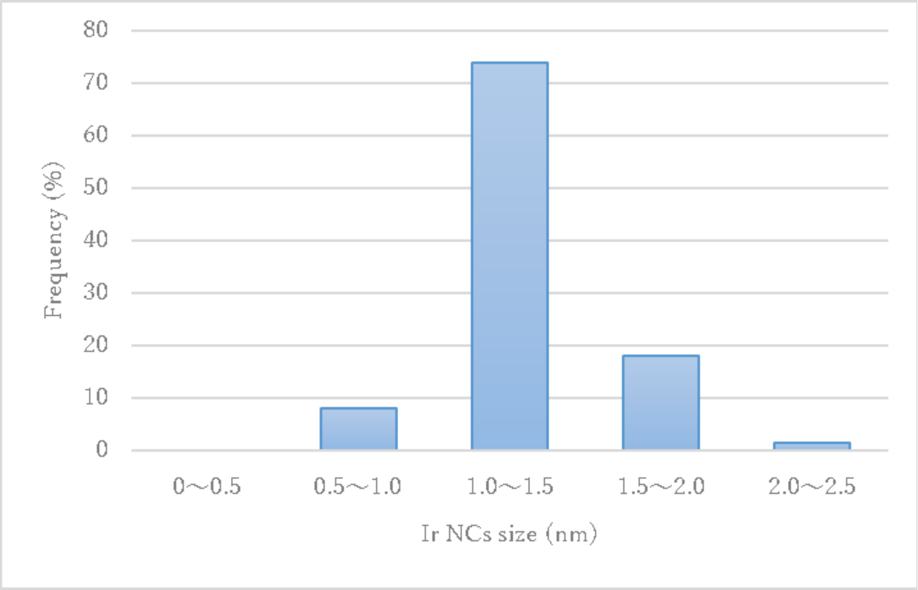


Fig. S4 ^1H NMR of DMF-stabilized Ir NCs

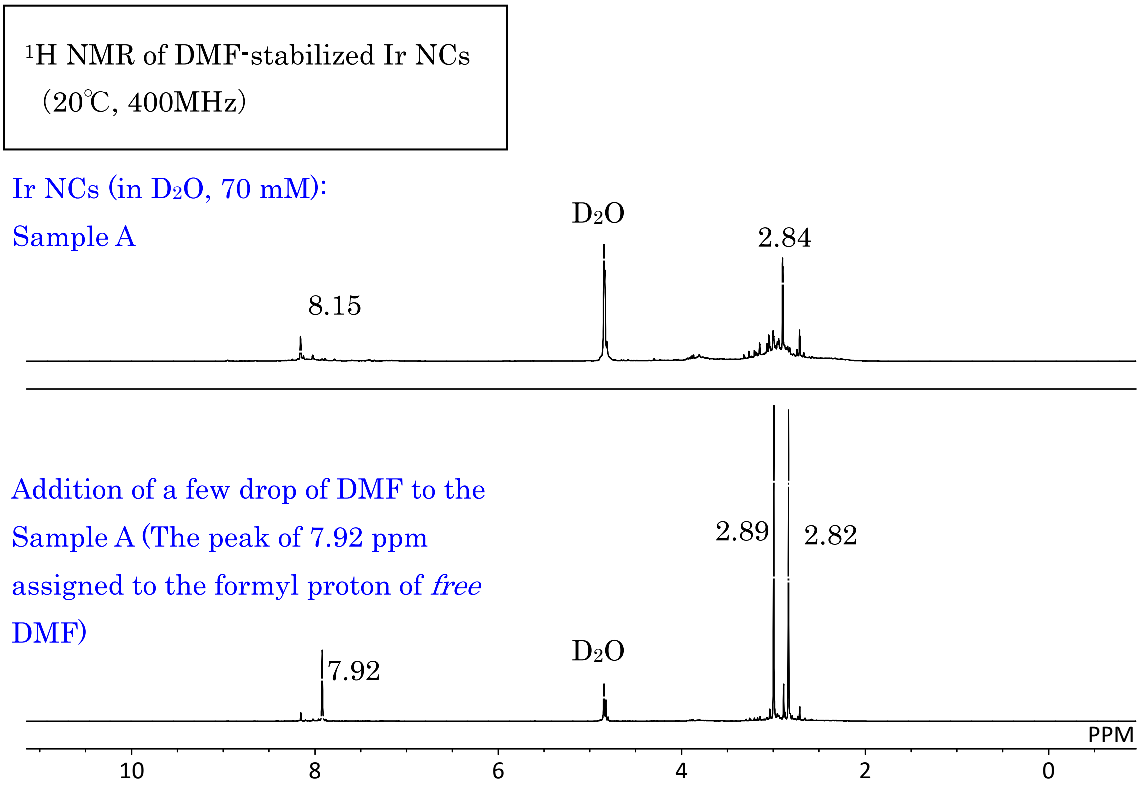


Fig. S5 XRD pattern of DMF-stabilized Ir NCs

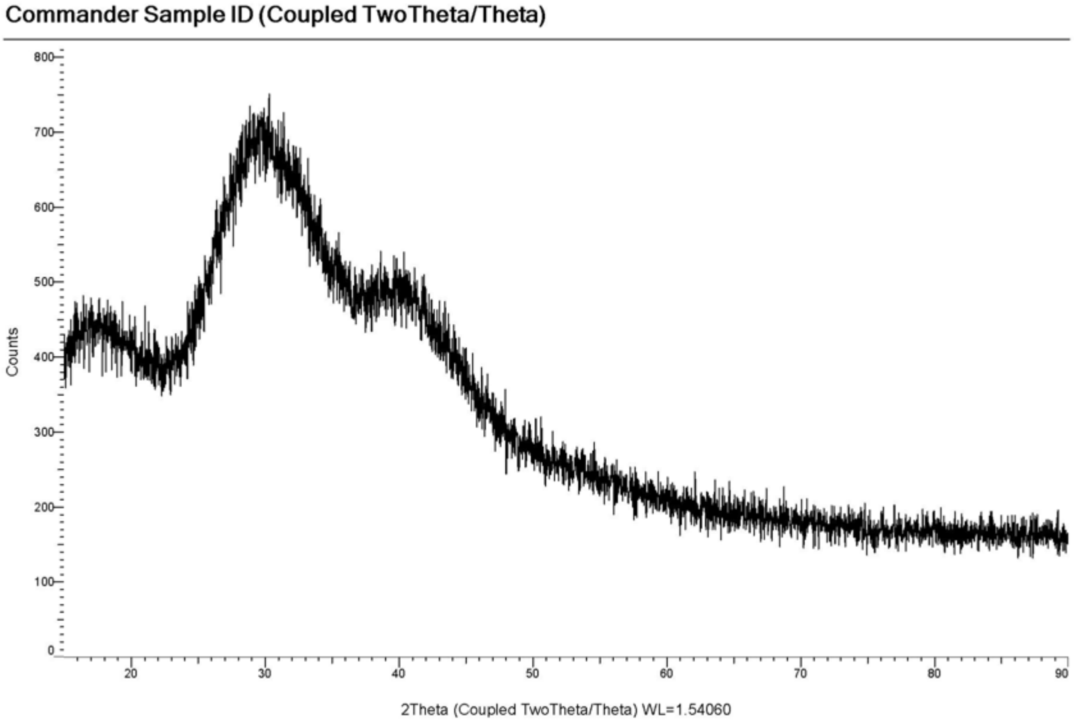


Fig. S6 XPS spectra of DMF-stabilized Ir NCs

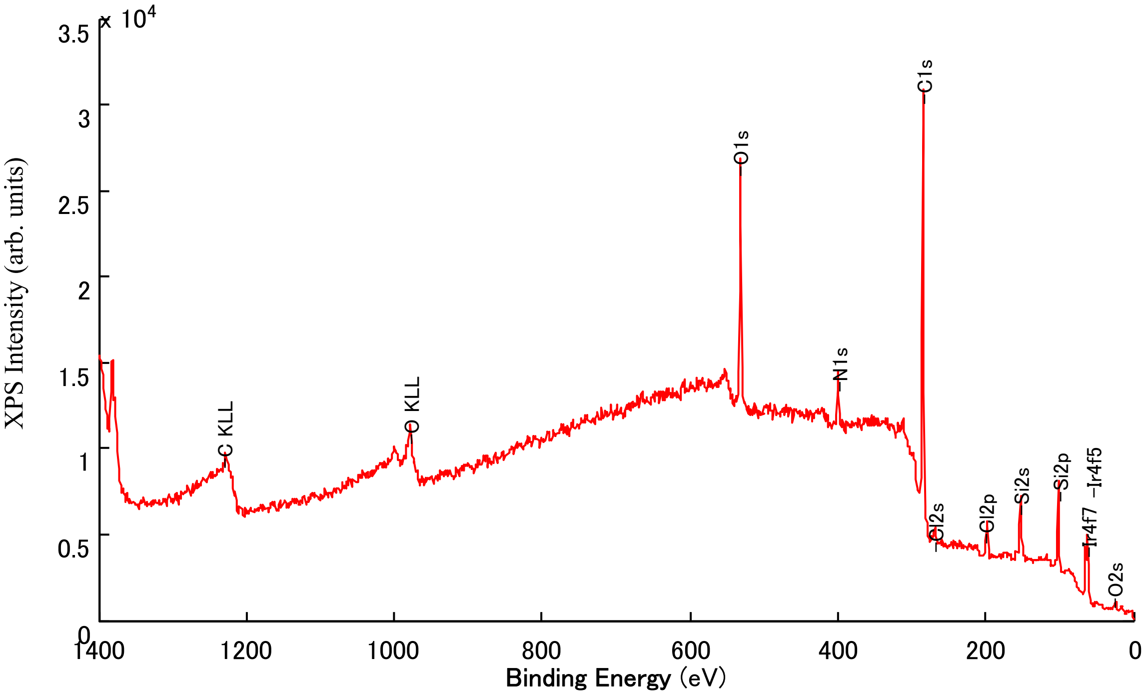


Fig. S7 FT-IR of free DMF(blue) and DMF-stabilized Ir NCs (orange)

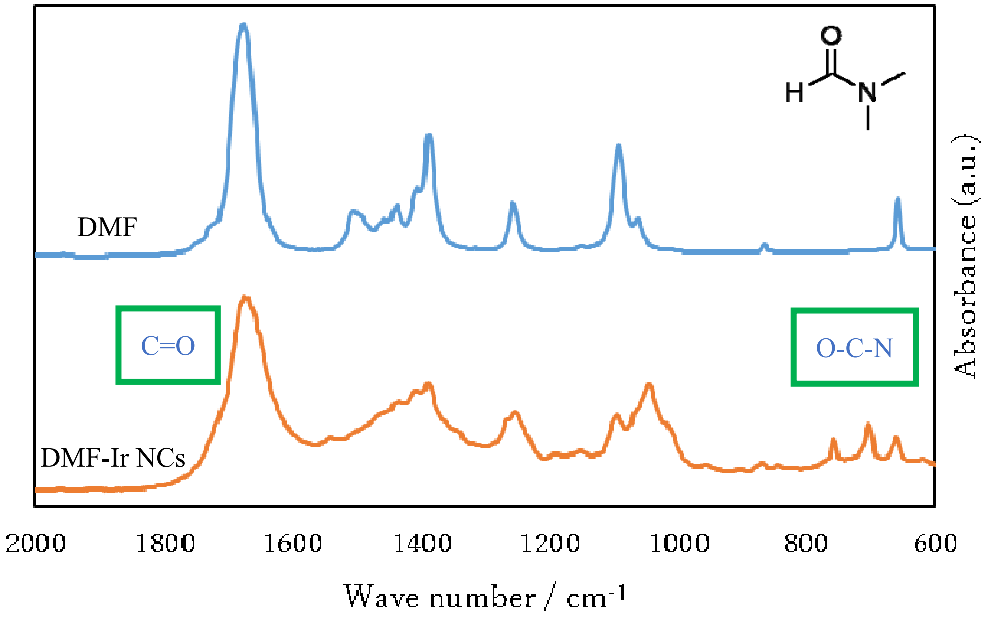
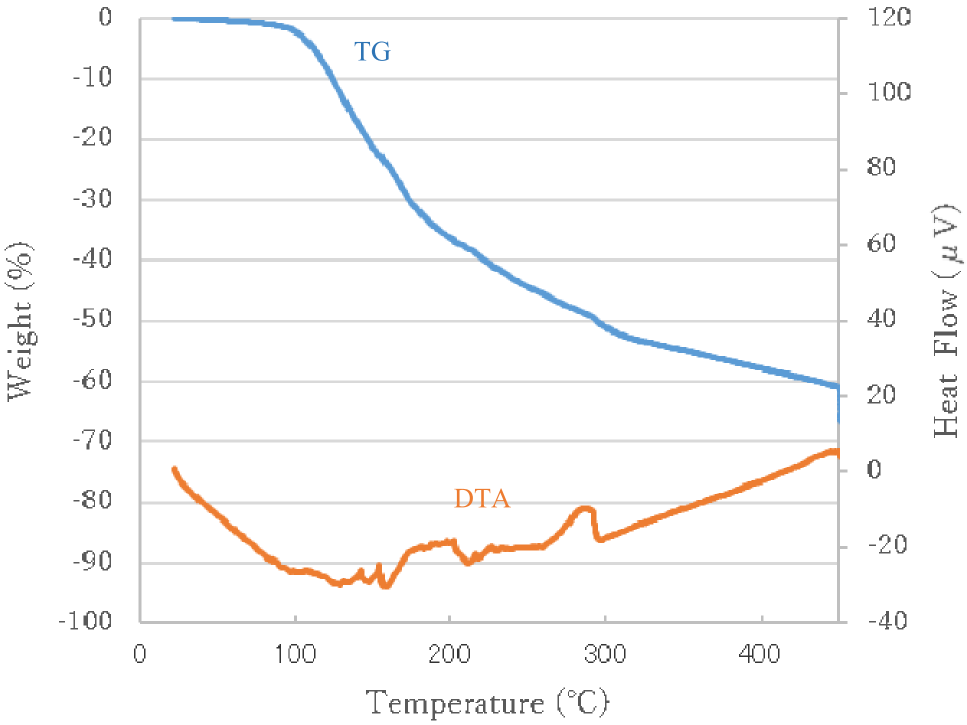


Fig. S8 TG-DTA for DMF-stabilized Ir NCs



A typical reaction procedure for Ir NCs catalyzed *β*-methylation of 1-phenylethanol 1a using methanol as C1 resource (Table 1, entry 12): A mixture of 1-phenylethanol **1a** (122 mg, 1.0 mmol), cesium carbonate (675 mg, 3.0 mmol) and 1 mM Ir NCs in methanol (2.0 mL) as a catalyst was stirred at 150 ^{o}C for 24 h under Ar atmosphere. The conversions and yields of products **2a** and **3a** were estimated from peak areas based on an internal standard (methyl benzoate) using GC. The reaction mixture was extracted with diisopropylether (30 mL×2), dried over sodium sulfate, and evaporated under vacuum and the product was obtained in 87 % yield (130 mg) as yellow oil.

A typical reaction procedure for Ir NCs catalyzed *N*-methylation of aniline 4a using methanol as C1 resource (Table S2, entry 1): A mixture of aniline **4a** (93 mg, 1.0 mmol), cesium carbonate (675 mg, 1.0 mmol) and 1 mM Ir NCs in methanol (2.0 mL) as a catalyst was stirred at 150 ^{o}C for 24 h under Ar atmosphere. The conversions and yields of product **5a** were estimated from peak areas based on an internal standard (methyl benzoate) using GC and the product **5a** were obtained in 87% yield. The reaction mixture was extracted with diisopropylether (30 mL×2), dried over sodium sulfate, and evaporated under vacuum and the product was obtained in 78% yield (84 mg) as yellow oil.

Mercury poisoning test for Ir catalyzed *β*-methylation of 1-phenylethanol 1a using methanol: A mixture of 1-phenylethanol **1a** (122 mg, 1.0 mmol), cesium carbonate (325 mg, 1.0 mmol), Hg (1 g, 5.0 mmol) and Iridium catalyst (0.001 mmol) in methanol (2.0 mL) was stirred at 150 ^{o}C for 24 h under Ar atmosphere. The conversions and yields of products **2a** and **3a** were estimated from peak areas based on an internal standard (methyl benzoate) using GC.

Compound **2k**. Yield 54% (92 mg), colorless liquid; ^{1}H NMR δ 7.27-7.11(m, 4H), 3.69 (d, *J* = 8.0 Hz, 2H), 2.95-2.84 (m, 1H), 1.43 (s, 1H), 1.26 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR δ 145.8(C), 134.3(C), 129.9(CH), 127.4(CH), 126.7(CH), 125.7(CH), 68.4(CH_2), 42.1(CH), 17.4(CH_3); IR (neat, cm^{-1}) 3300, 2929, 1597, 1570, 1429, 1082, 877, 783, 696; GC-MS (EI) *m/z* (relative intensity) 170(24) [M^+], 139(100), 103(87), 77(34), 51(8), 39(4); HRMS (EI) *m/z* calcd for $C_9H_{11}ClO$: 170.0498, found 170.0498

Conditions screening of *N*-methylation

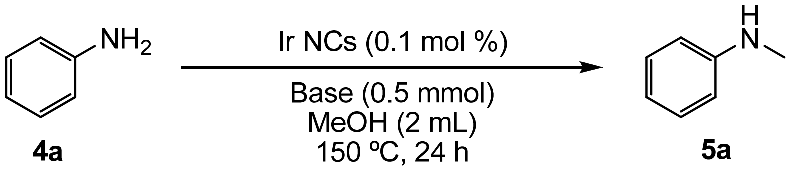


Table S1

Entry	Base	Conv. (%)	GC Yield (%)
1	Cs_2CO_3	>99	87 [78][a]
2	K_2CO_3	18	90
3	KO^{t}Bu	>99	94
4	KOH	18	92
5	Cs_2CO_3 (0.2 mmol)	>99	72
6	Cs_2CO_3 (without Ir NCs)	18	n.d.[b]

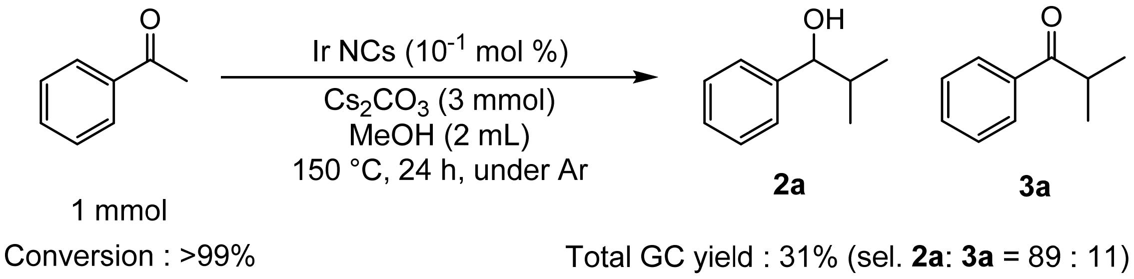
a) Isolated yield. b) Not detected.

Table S2

Entry[a]	Ir NCs (mol %)	Conv. (%)	GC Yield (%)	TON[b]
1	0.1	>99	87	870
2	0.01	90	80	8000
3	0.001	52	33	33000
4	0.0001	52	31	310000

a) Cs_2CO_3 was used as base. b) Turnover number (TON) = **5a** (mol)/IrNCs (mol)

Scheme S1. α-methylation of acetophenone with methanol using Ir NCs



Scheme S2. Reaction with paraformaldehyde

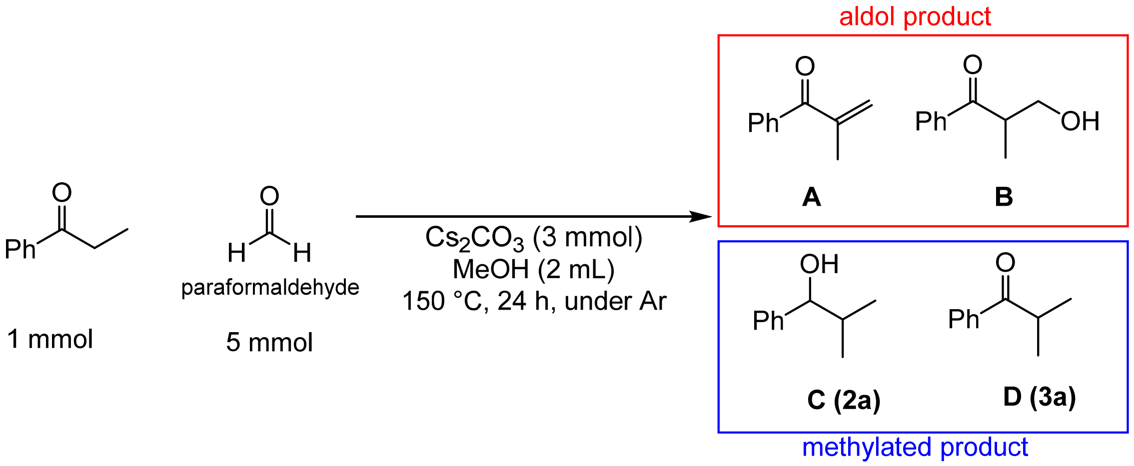
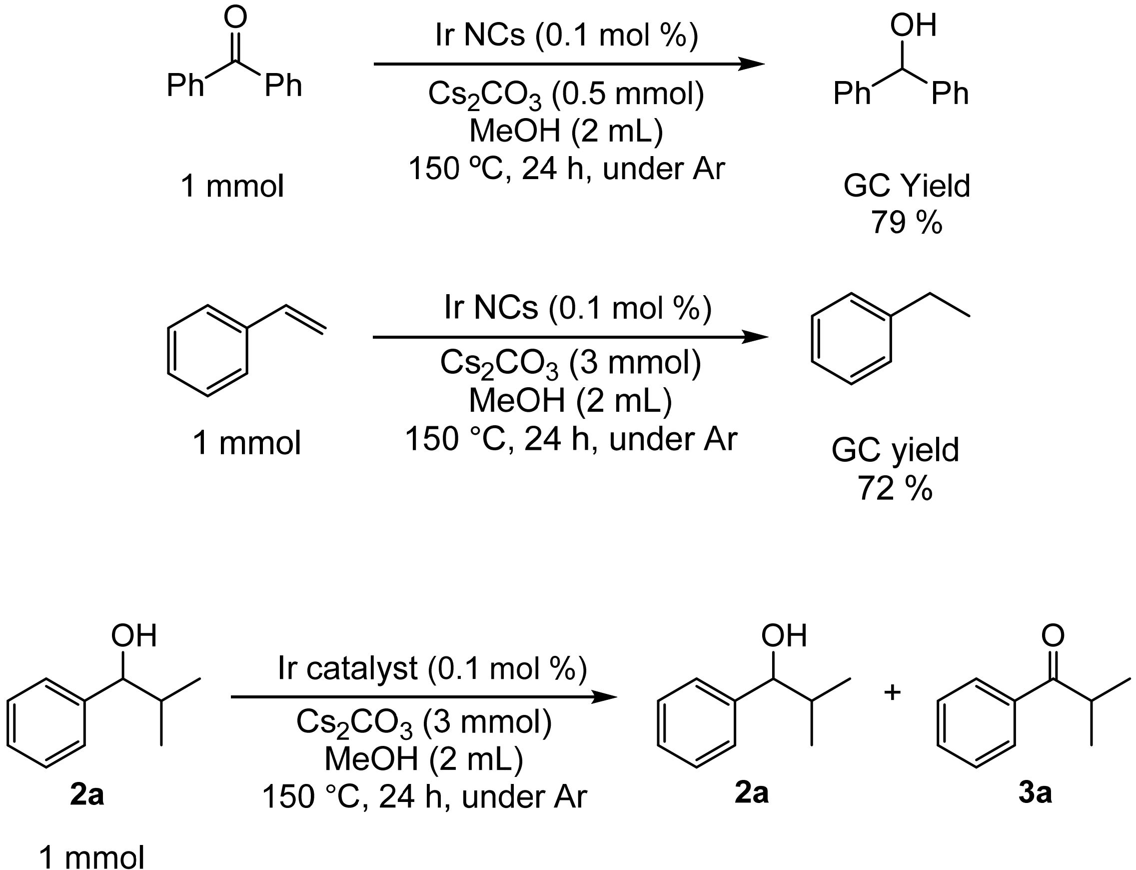


Table S3

Entry	**Conditions**	Conv. (%)	GC Yield (%)			
			A	**B**	**C(2a)**	**D(3a)**
1	as above	>99	n.d.[a]	n.d.[a]	2	3
2	without $(HCHO)_n$	35	n.d.[a]	n.d.[a]	trace	trace
3	add Ir NCs (0.1 mol %)	>99	n.d.[a]	n.d.[a]	12	n.d.[a]

a) Not detected by GC.

Scheme S3. Hydrogen transfer capability of Ir NCs using methanol



Ir catalyst	Selectivity (**2a** :**3a**)
Ir NCs	90 : 10
$IrCl_3$	74 : 26

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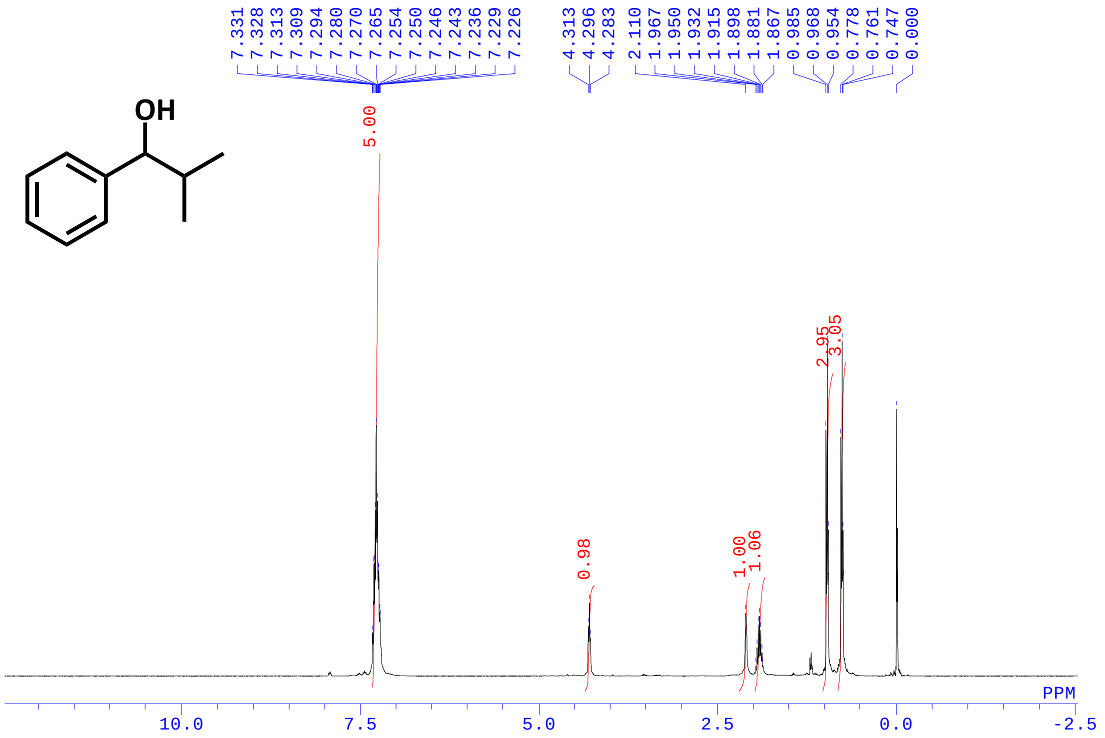
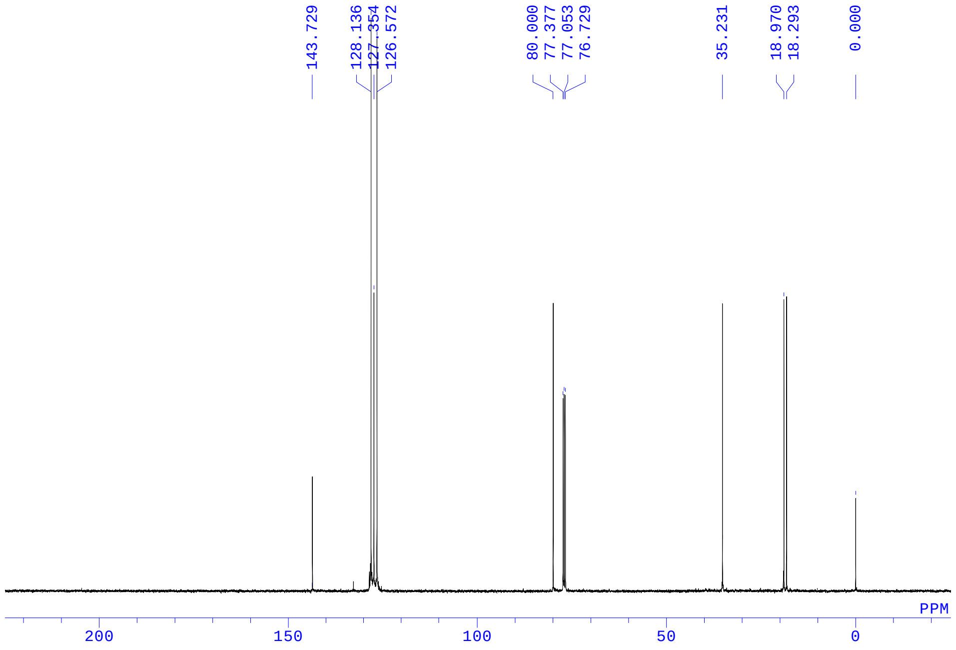
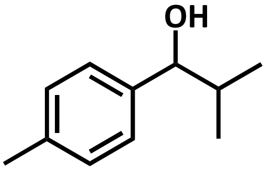
^{1}H NMR and ^{13}C NMR spectra

2a



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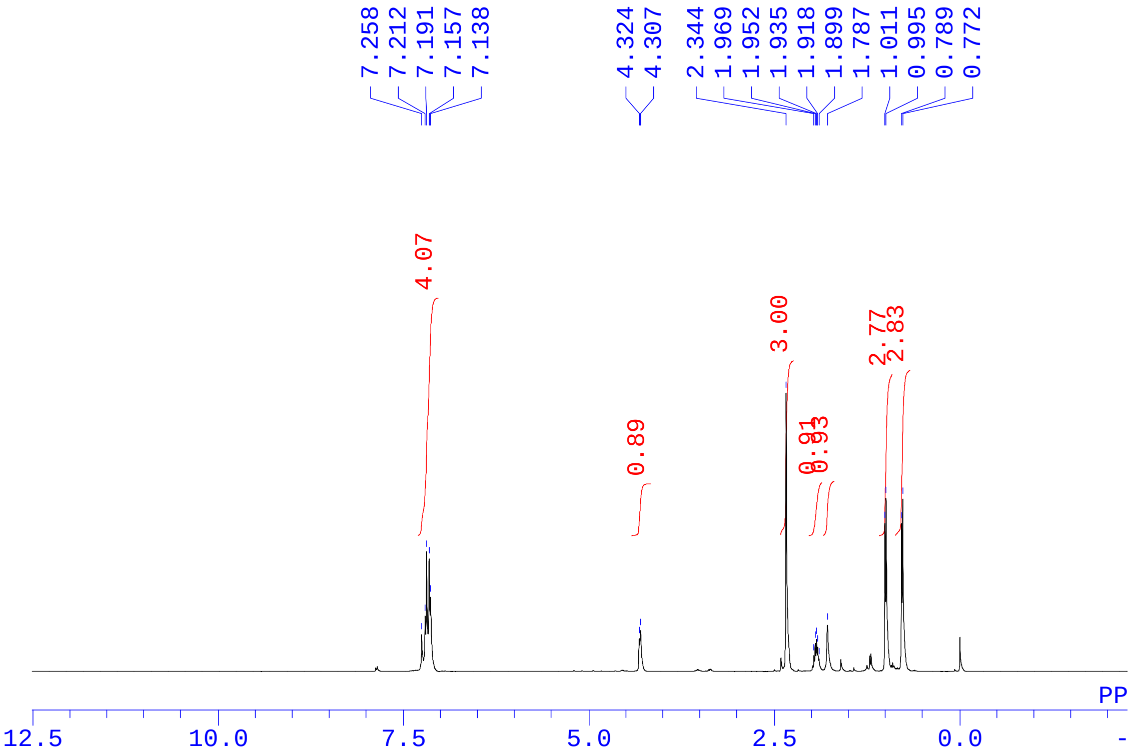
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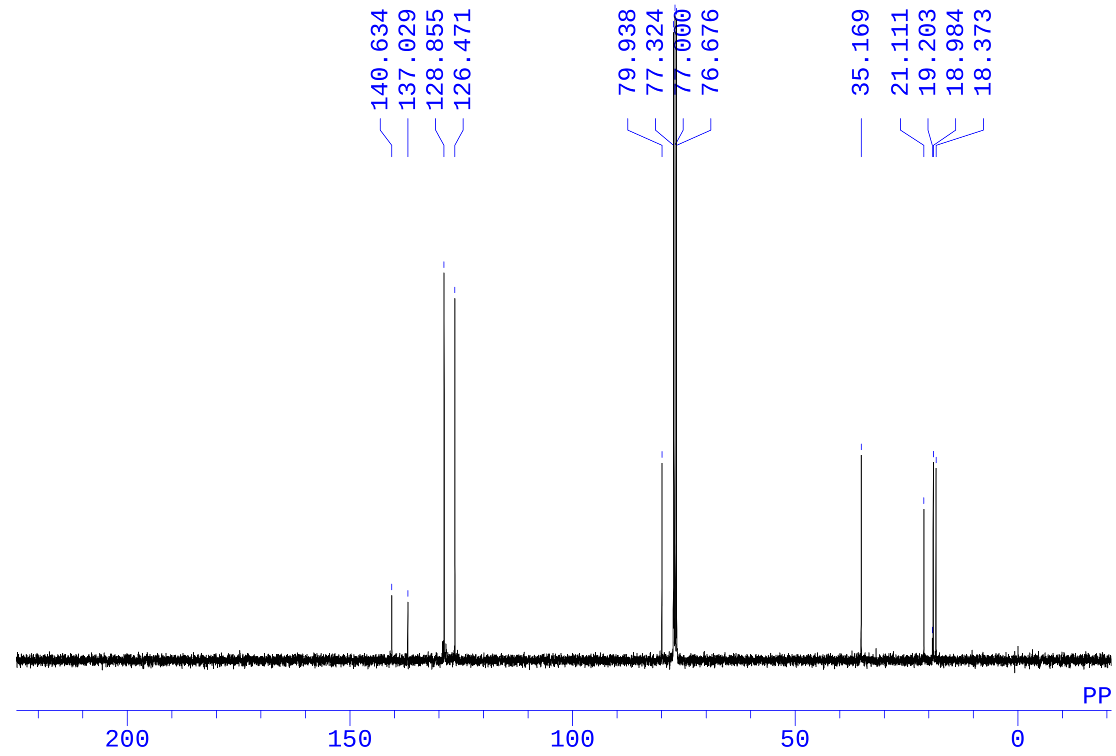
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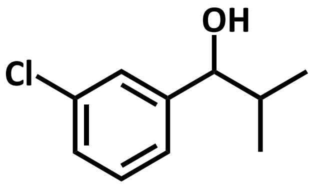

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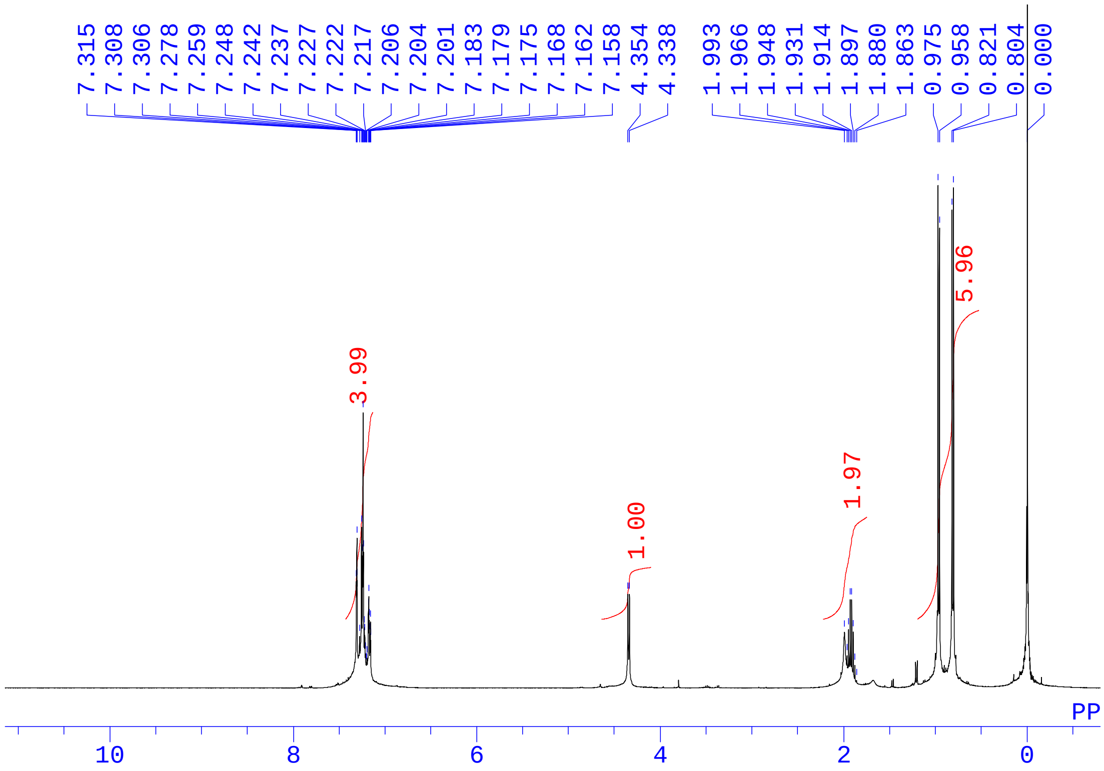

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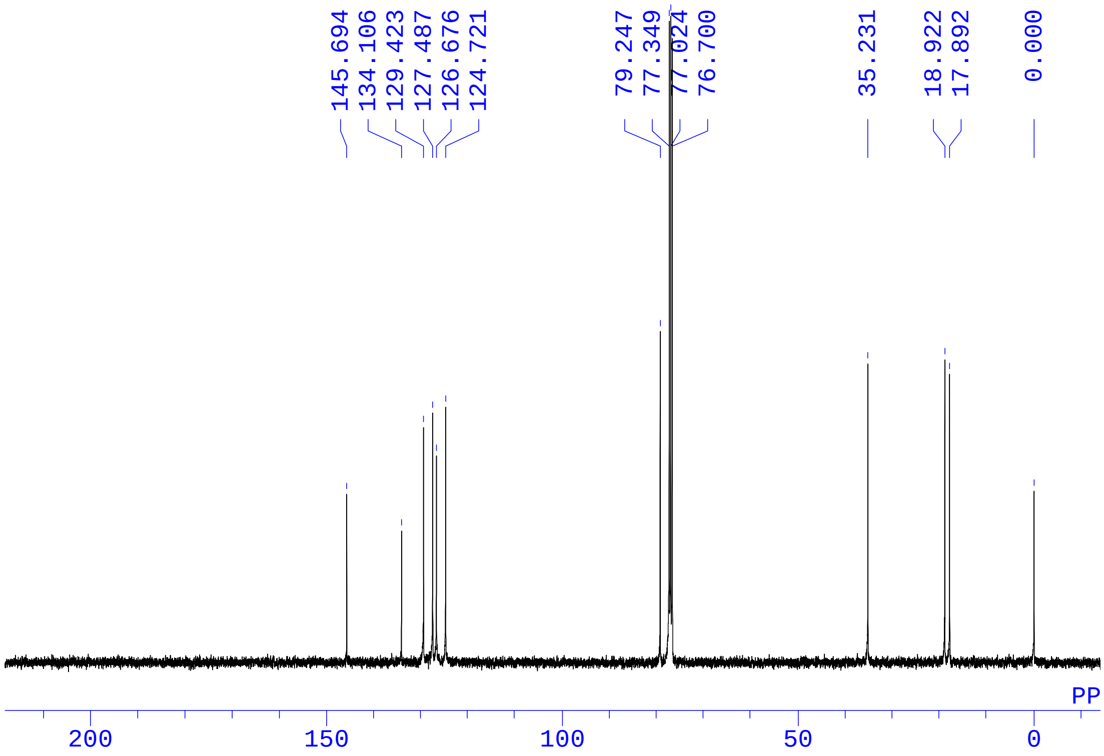

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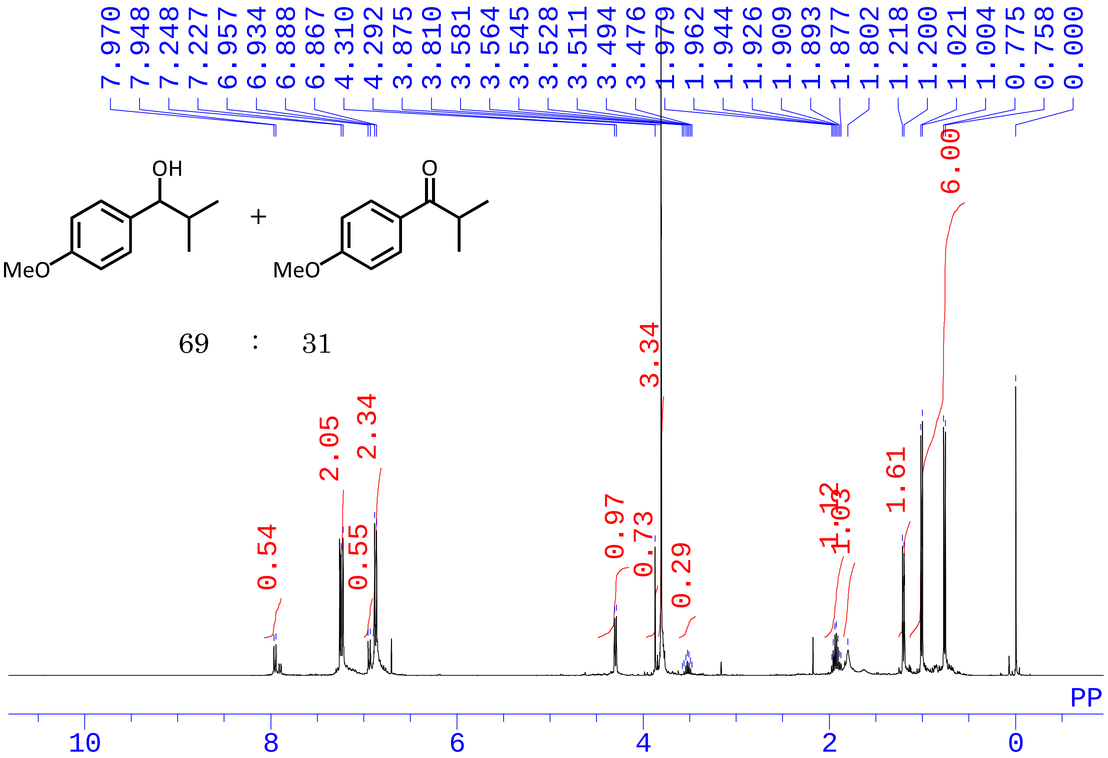

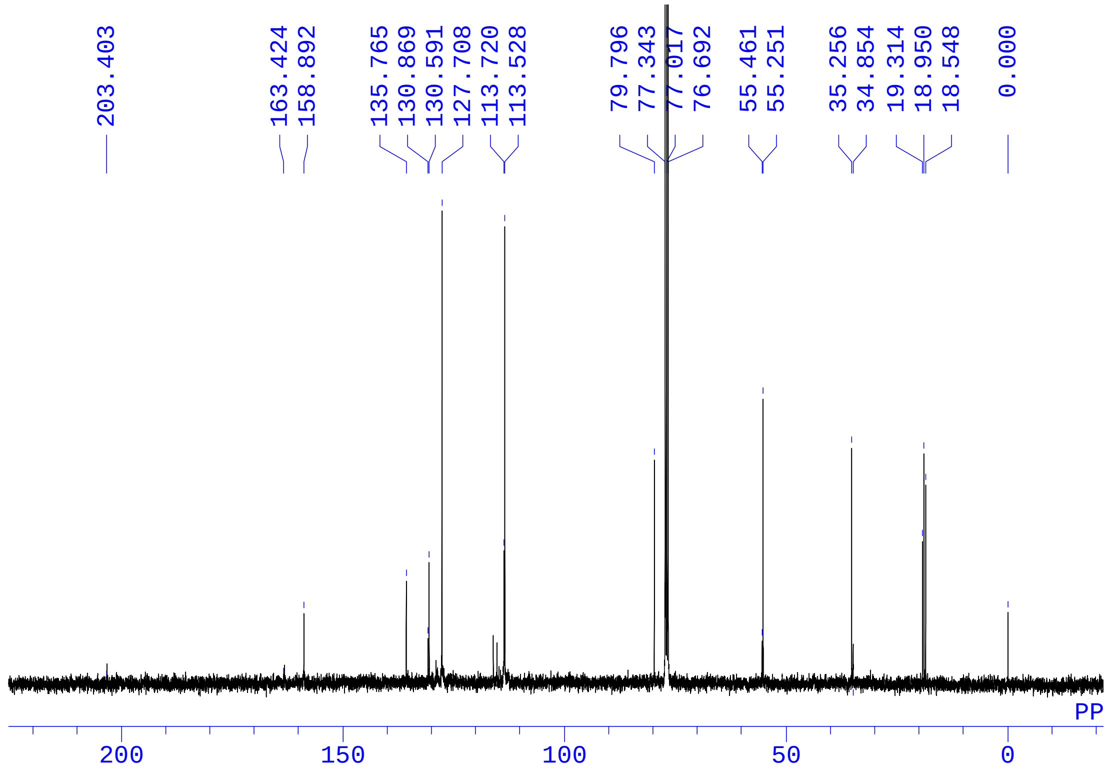

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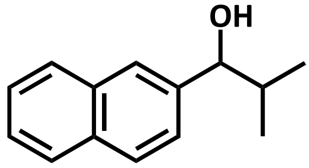
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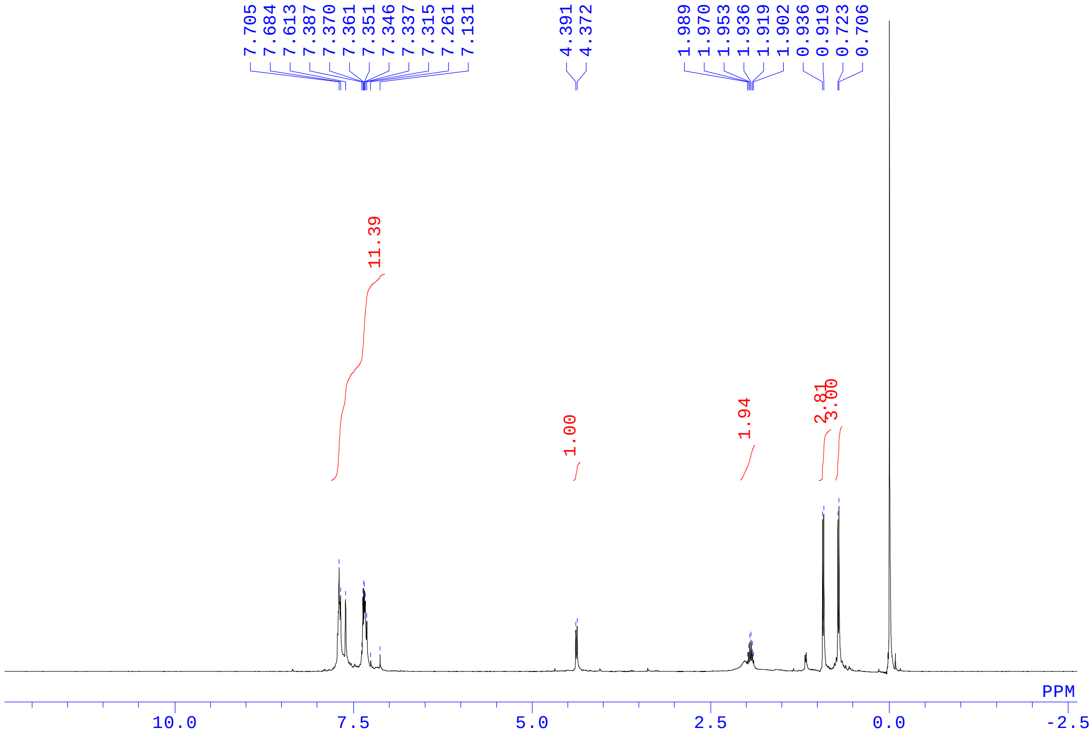
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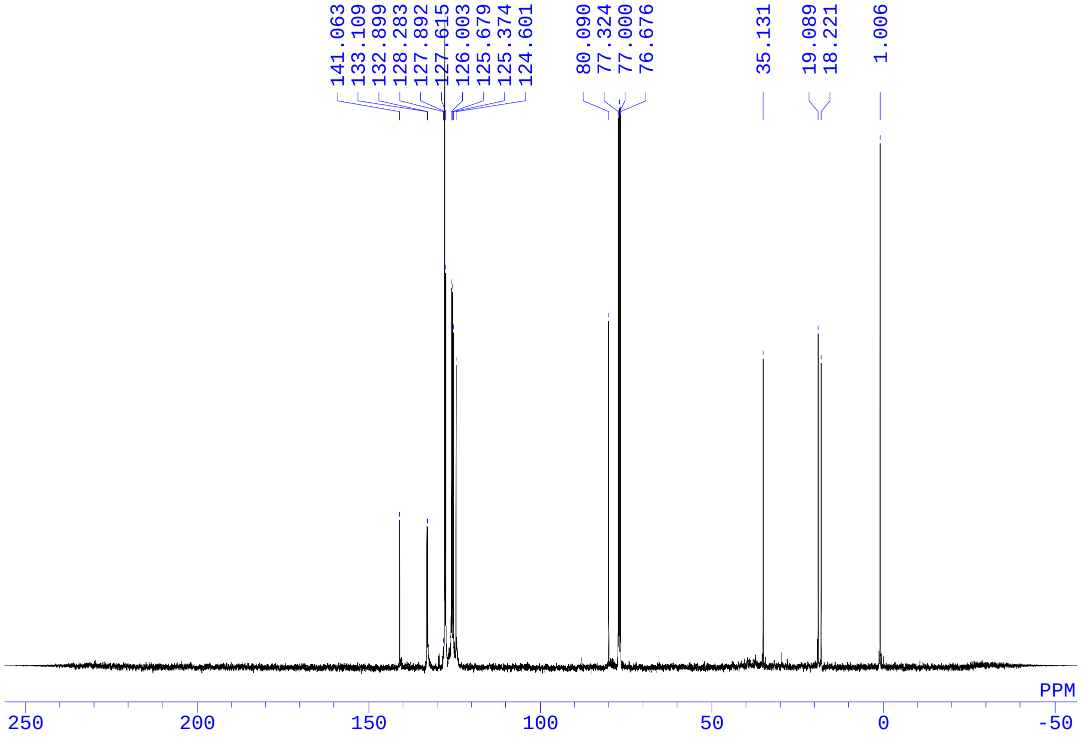
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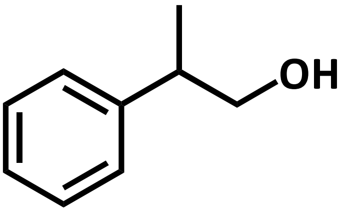
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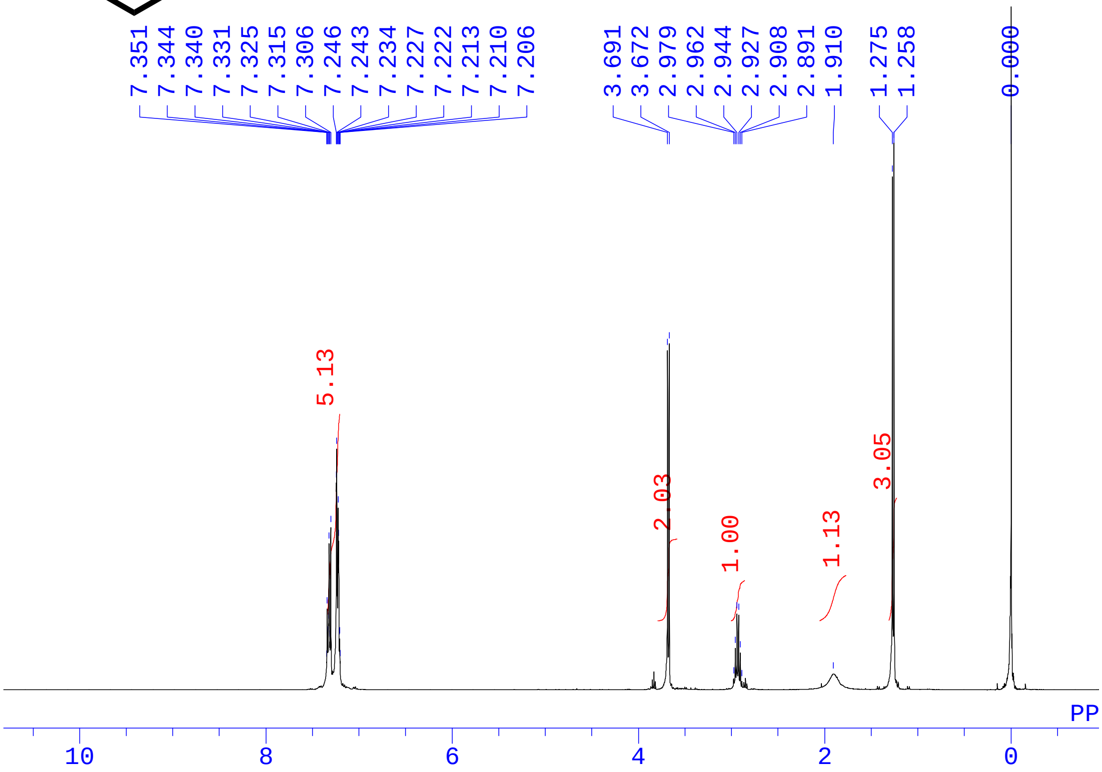
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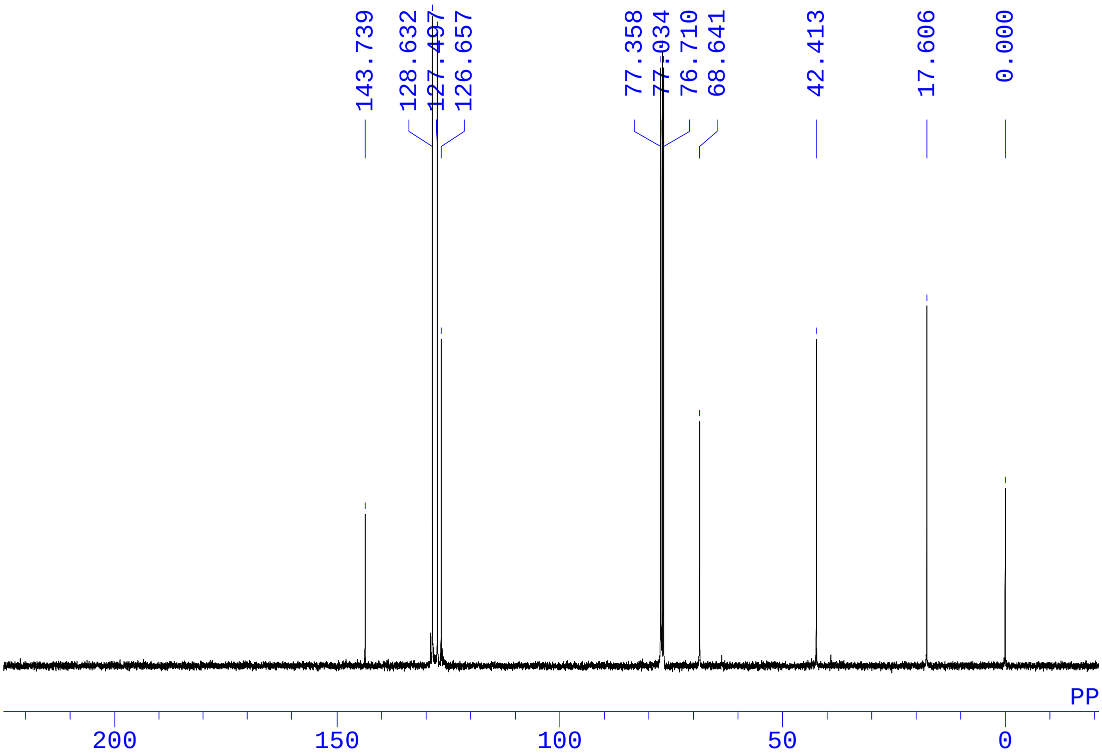
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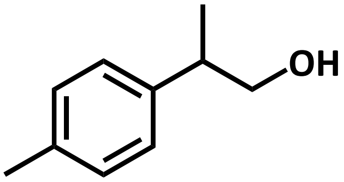
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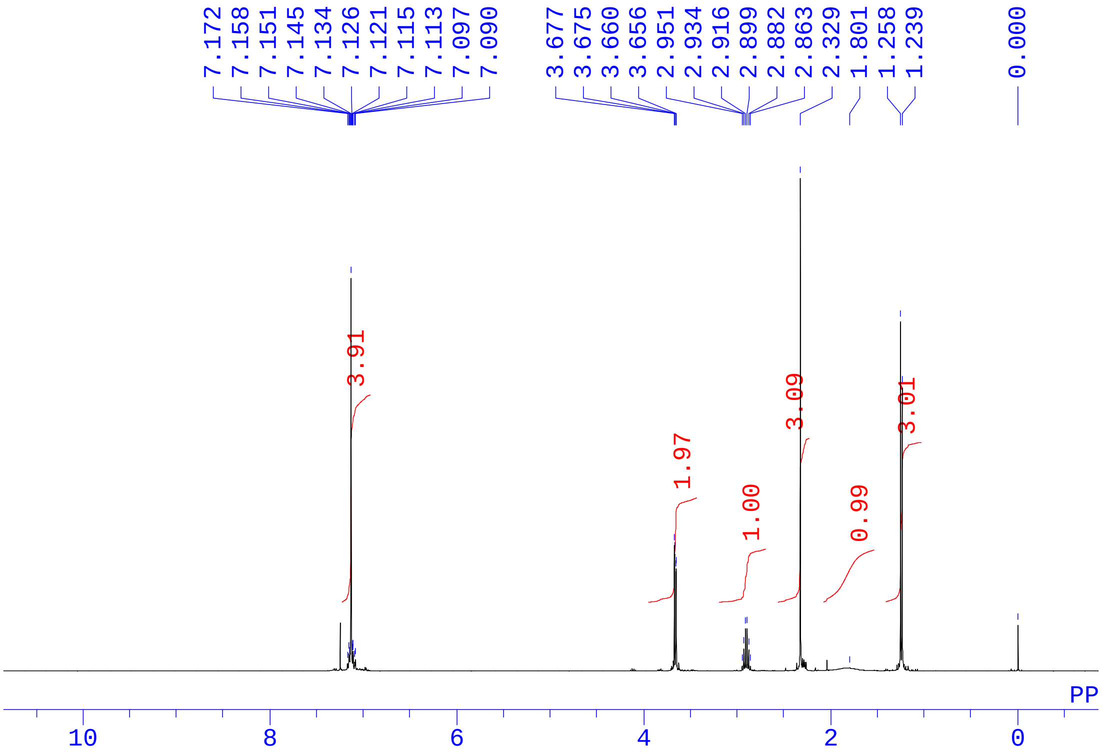
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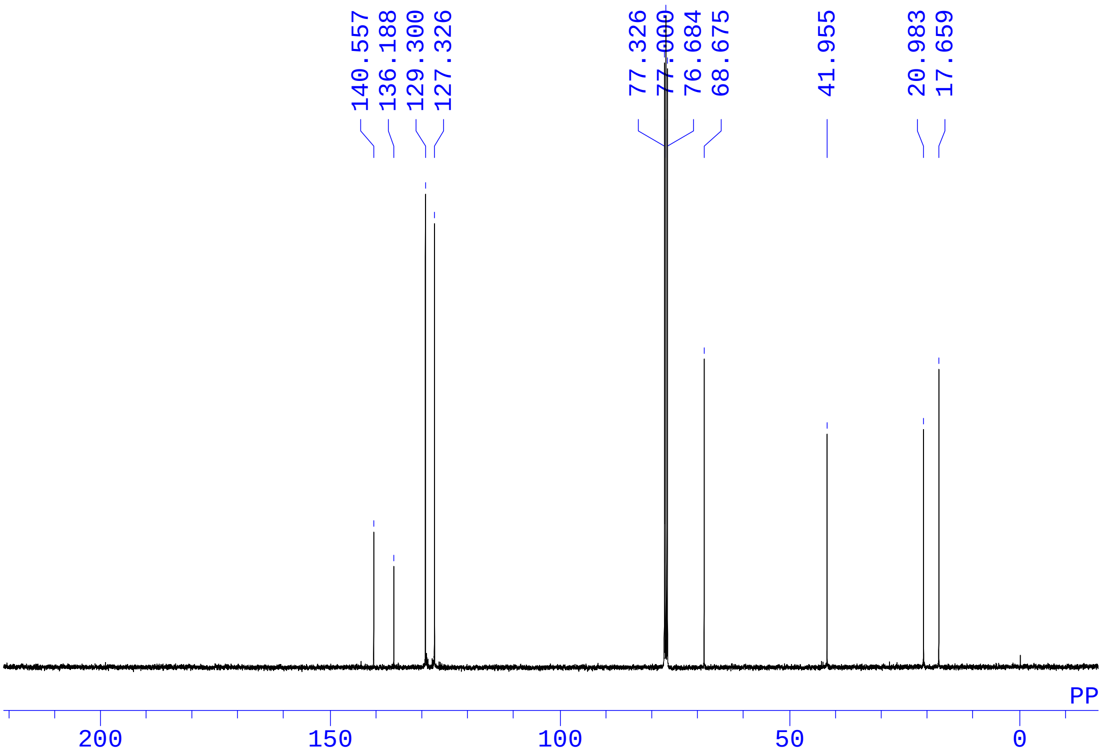
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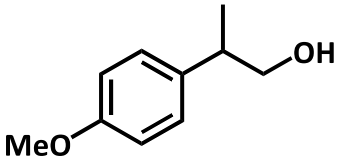

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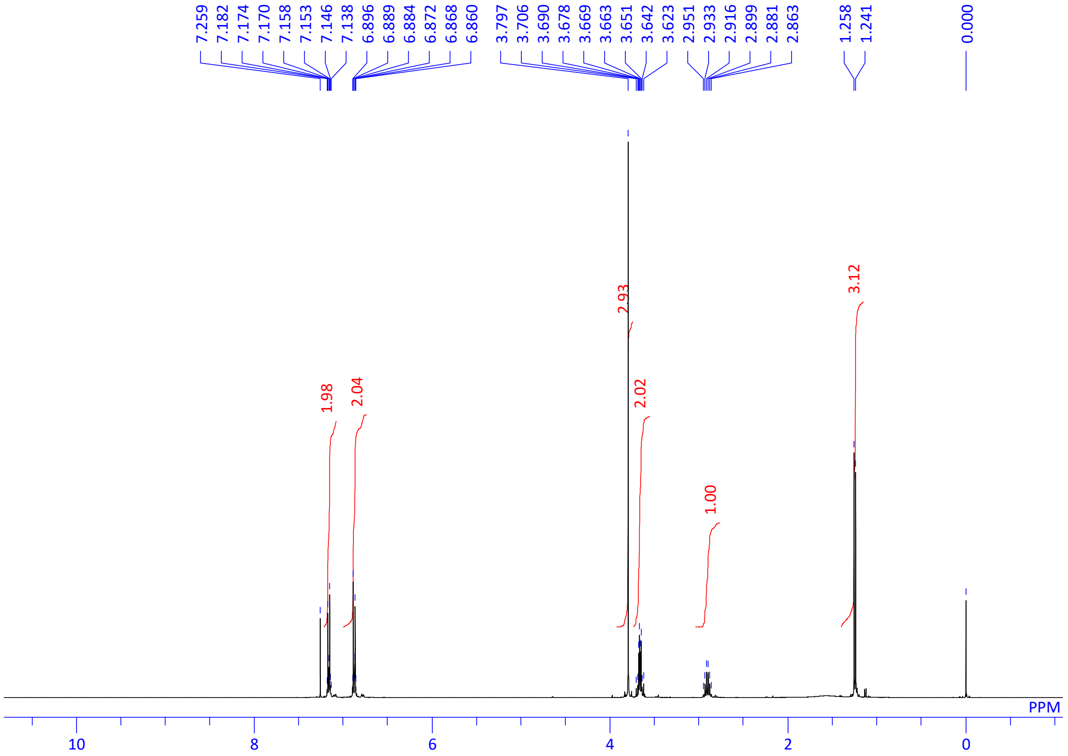

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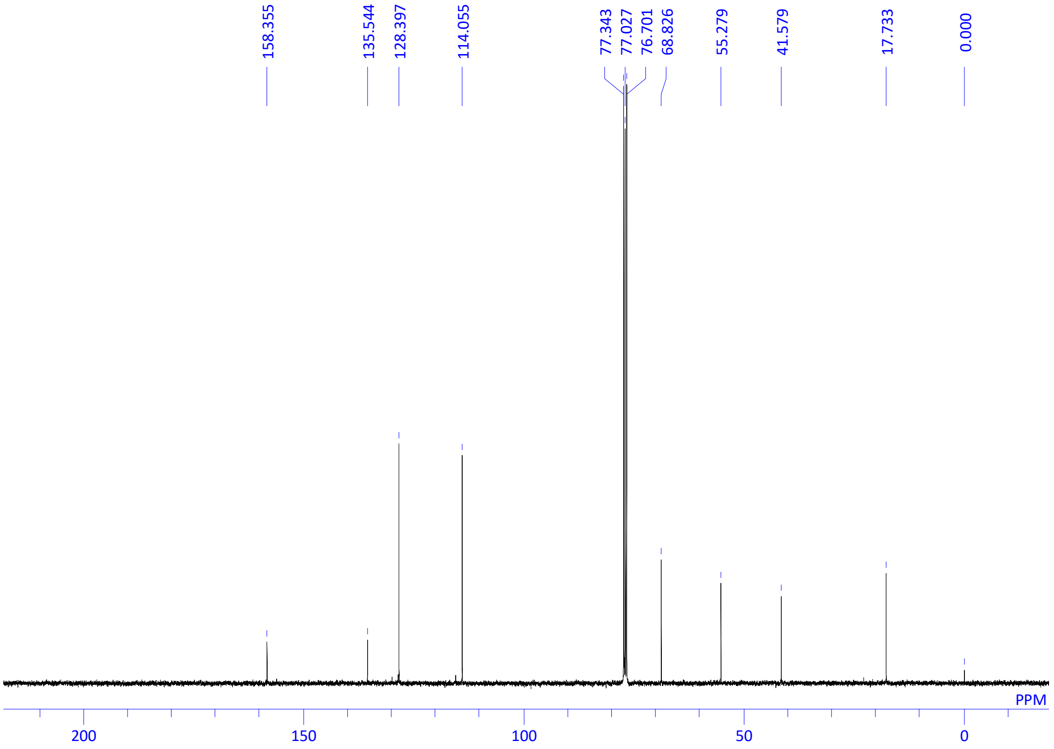

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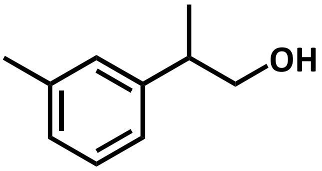
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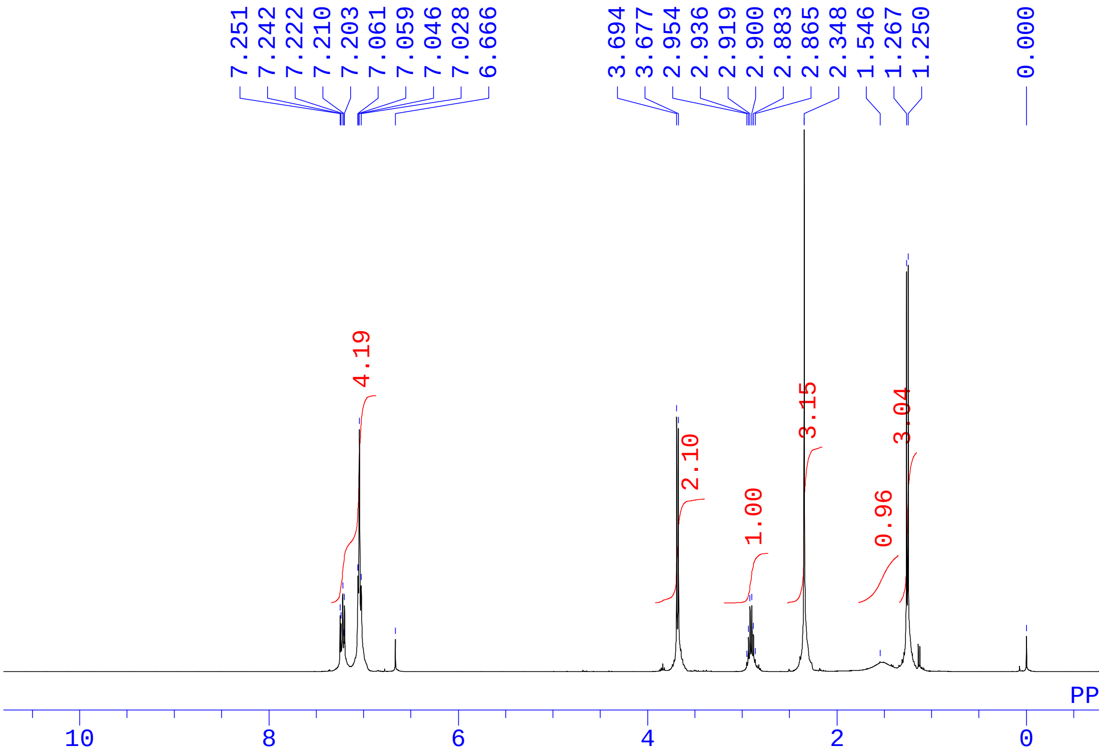
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7.222
7.210
7.203
7.061
7.059
7.046
7.028
6.666
3.694
3.677
2.954
2.936
2.919
2.900
2.883
2.865
2.348
1.546
1.267
1.250
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2.10
1.00
3.15
0.96
3.04
PP
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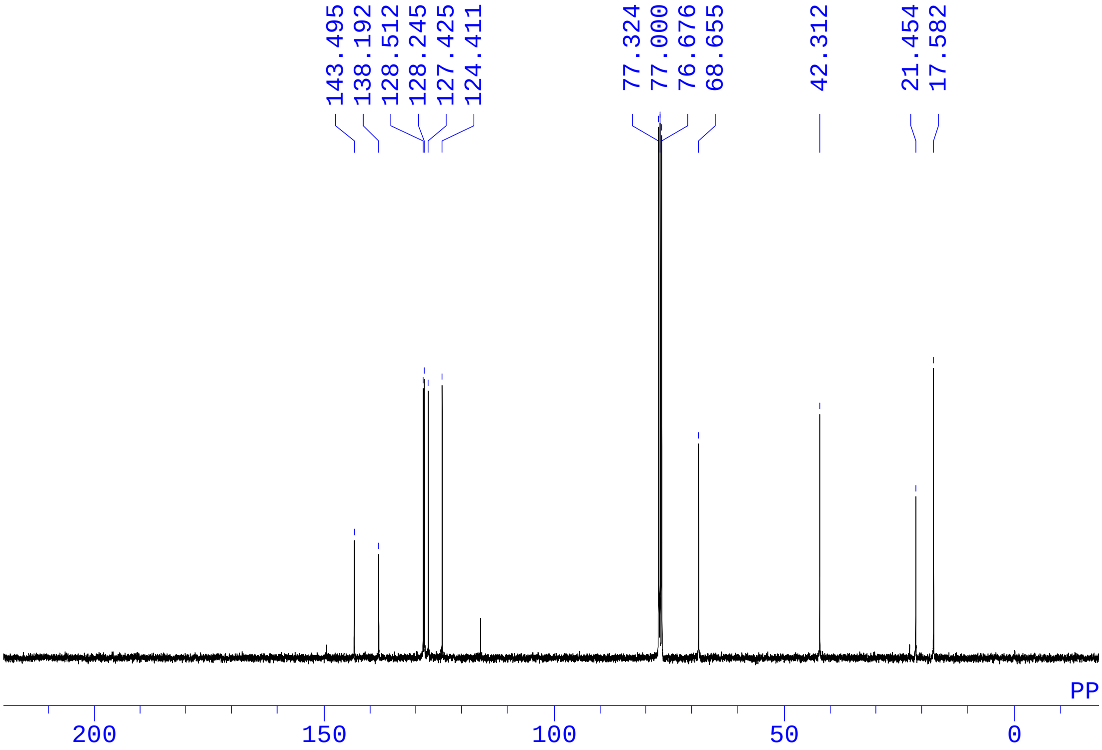
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PP
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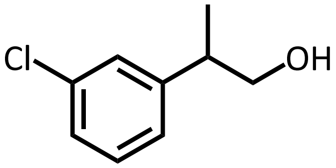
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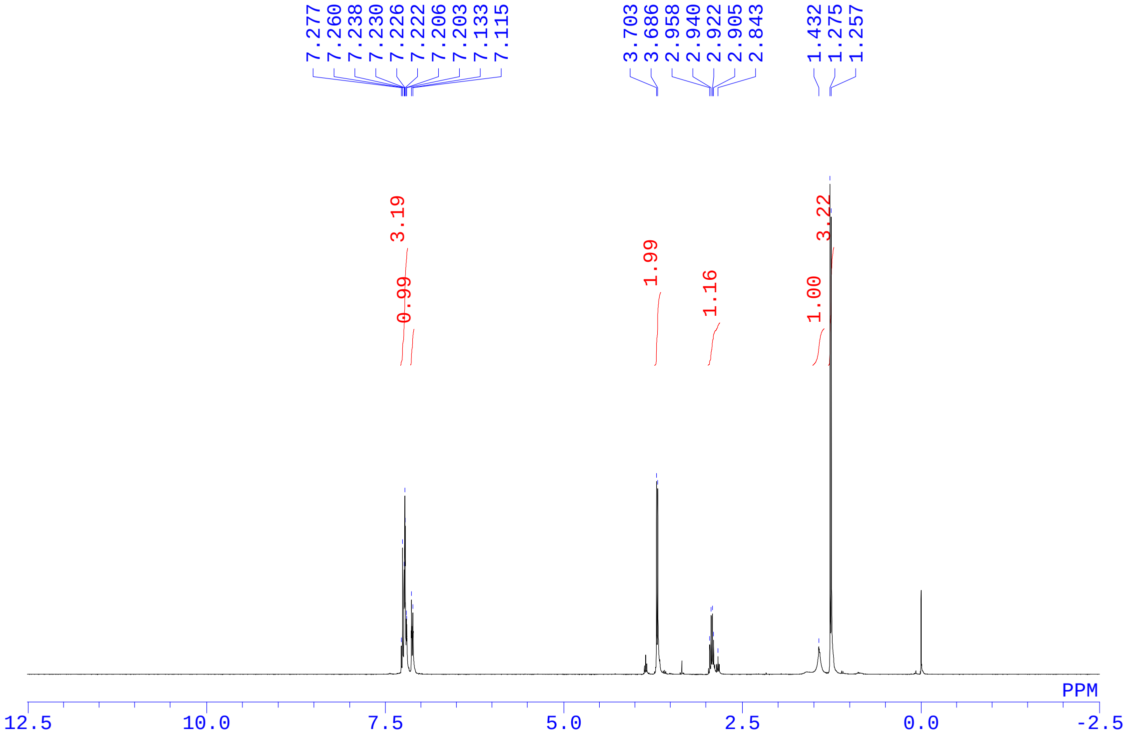
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7.226
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2.940
2.922
2.905
2.843
1.432
1.275
1.257
3.19
0.99
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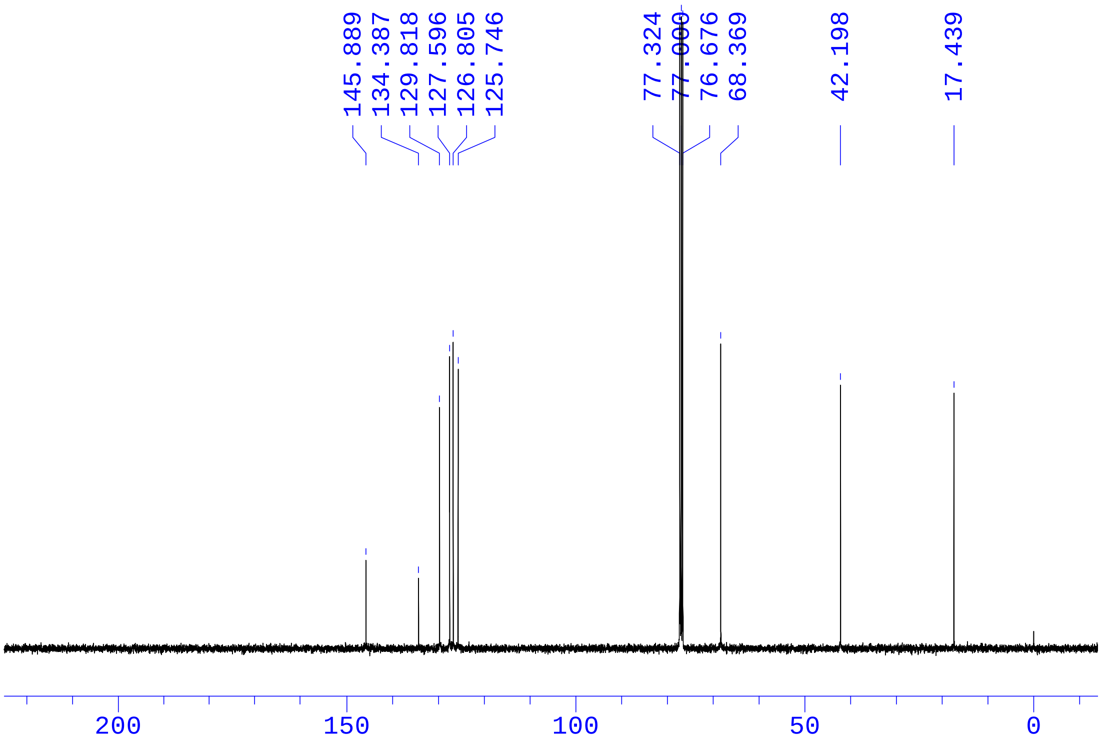
-2.5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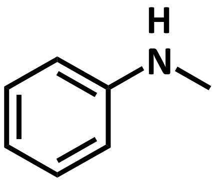
150
100
50
0

5a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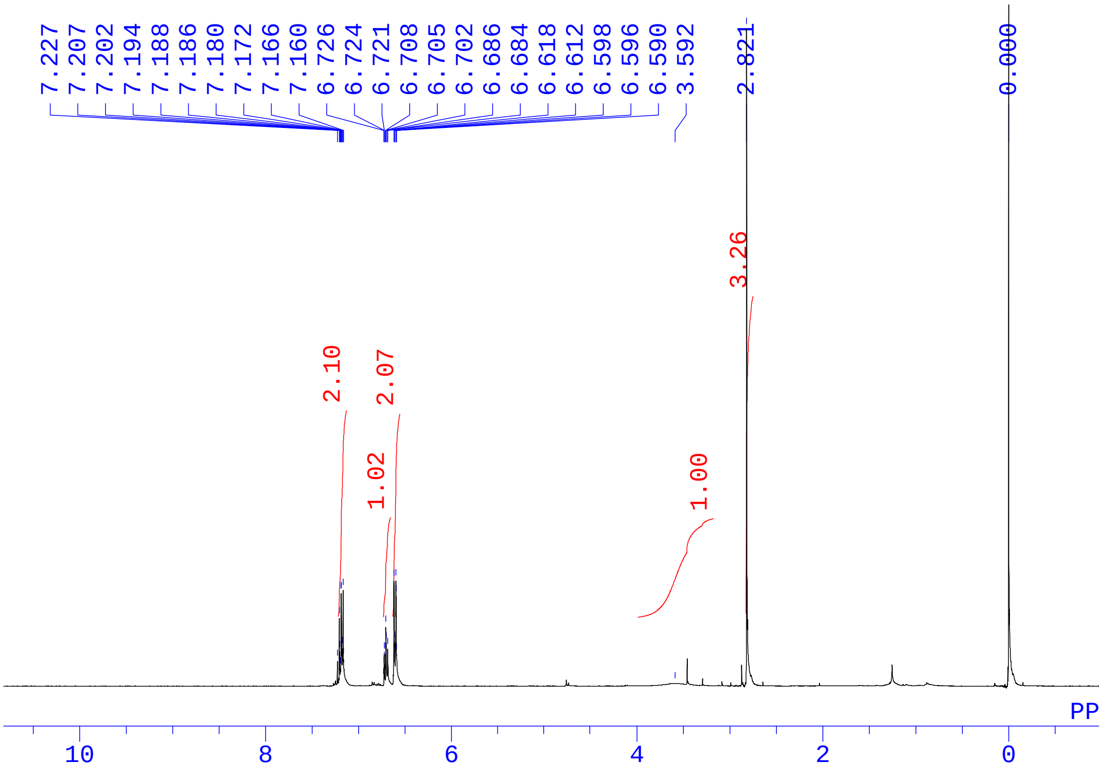
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6.708
6.705
6.702
6.686
6.684
6.618
6.612
6.598
6.596
6.590
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2.10
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1.02
1.00
PP
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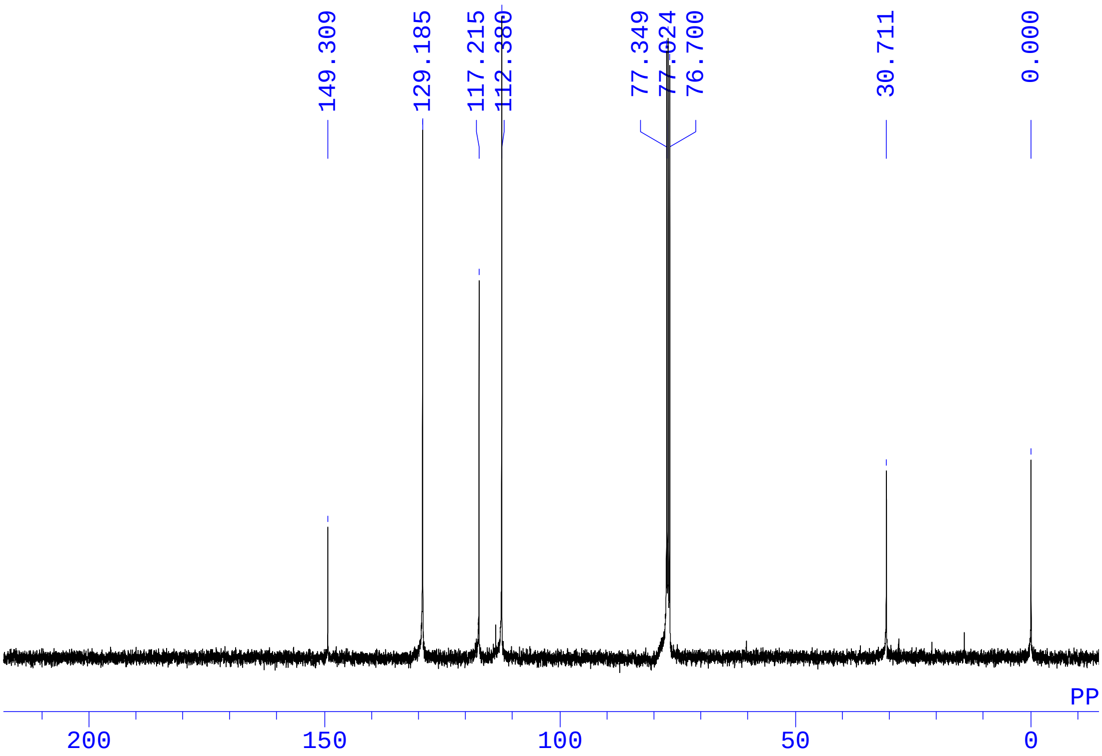
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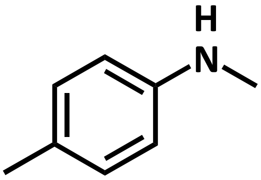
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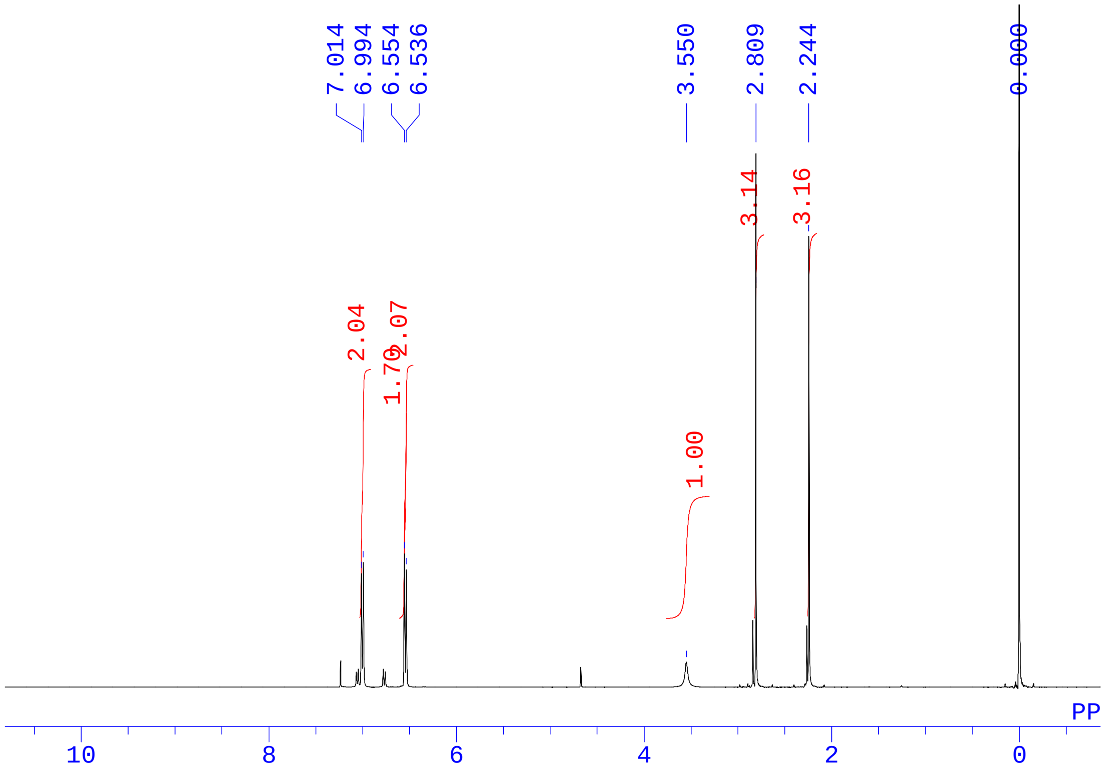
5b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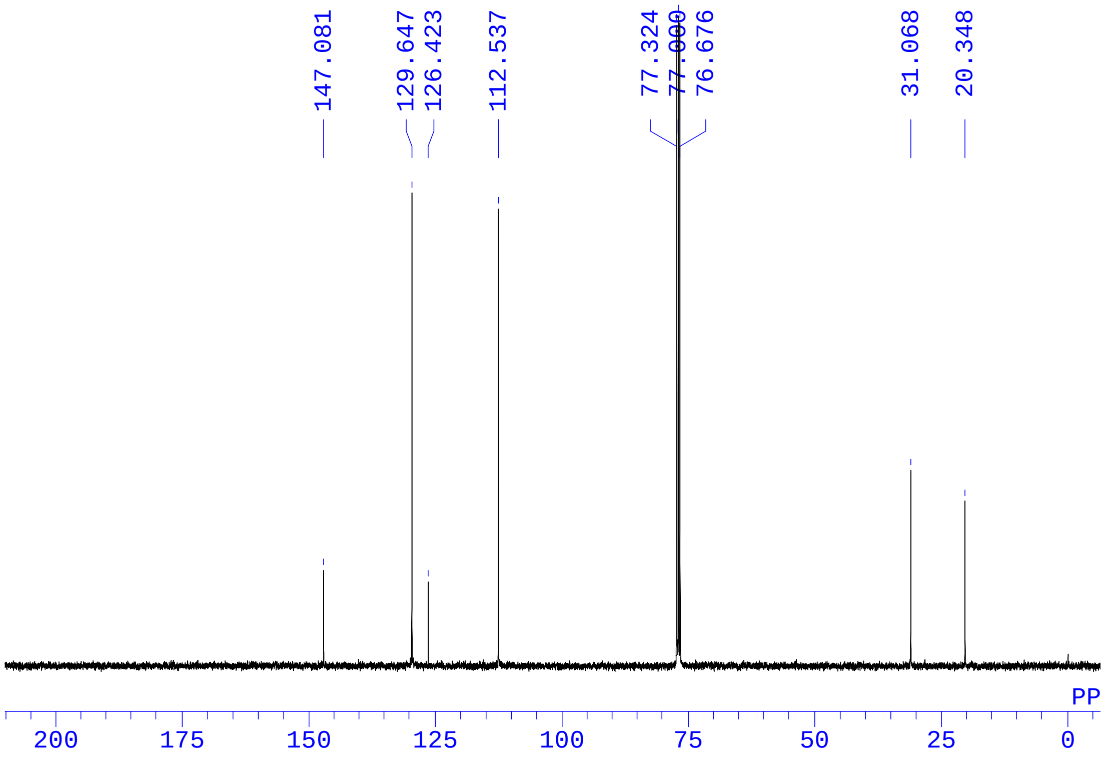
10
8
6
4
2
0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76.676
31.068
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75
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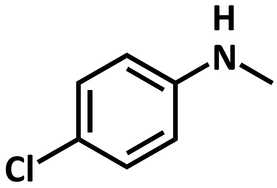
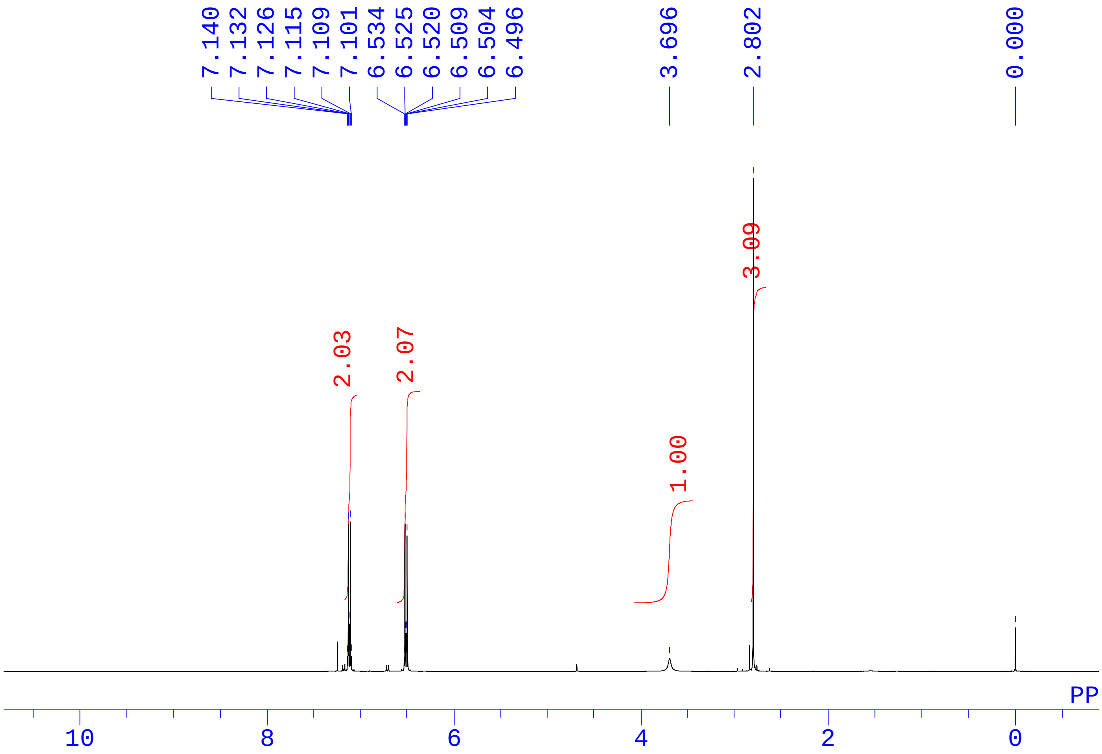
0

5c


H
N
Cl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6.504
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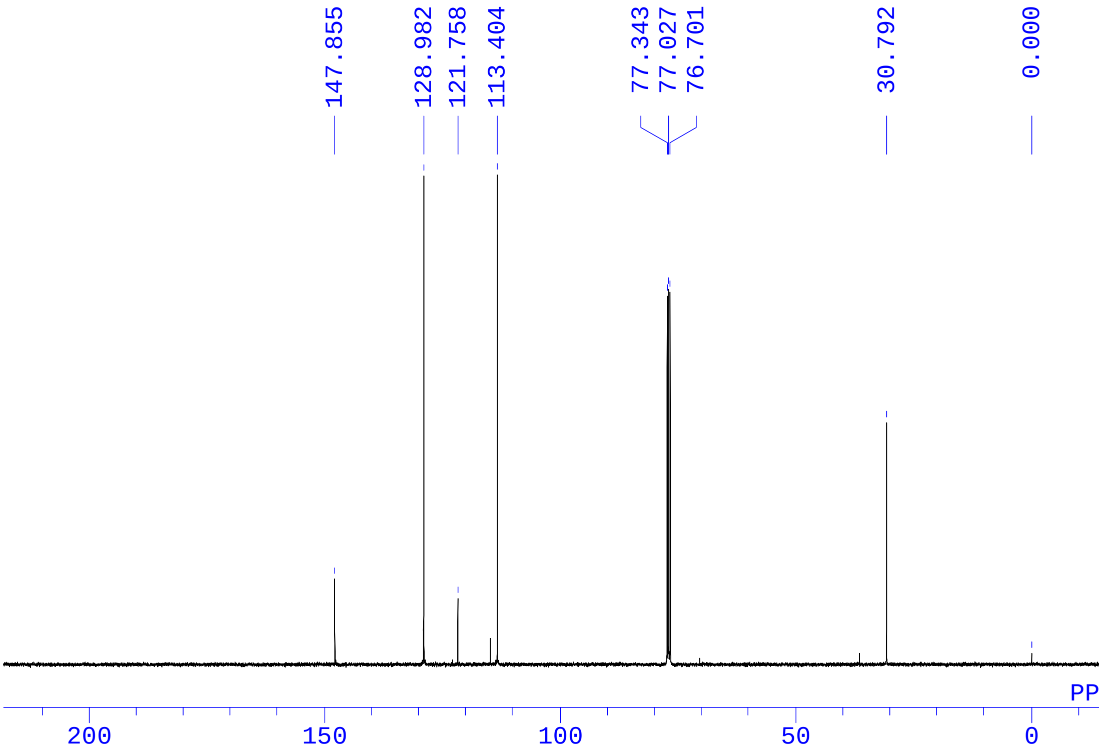
2.03
2.07
1.00
3.09
PP
10
8
6
4
2
0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121.758
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77.027
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30.792
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PP
200
150
100
50
0