Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Preparation of platinum nanoparticle catalyst locating near photocatalyst titanium oxide and its catalytic activity to convert benzyl alcohols to the corresponding ethers

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Contents

General Information

Commercially available chemicals and solvents were either used as it is from chemical suppliers. All reactions were performed under Ar atmosphere unless otherwise noted. For thin-layer chromatography (TLC), silica gel plates Merck 60 F_{254} were used. Column chromatography was performed with silica gel 60N (spherical, neutral, 63-210μm, Kanto Chemical Co., Inc.) unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL-300 (300 MHz, 75 MHz), JEOL JNM-AL-500 (500 MHz, 125 MHz) with tetramethylsilane as an internal standard. Chemistaion (TOKYO RIKAKIKAI CO., LTD PPS-CTRL) was used for preparation of PtNPs/TiO_2. LED light was purchased from OPTOCODE CO.

Experimental materials

Solvents were dried by molecular sieve 3A or 4A. Commercial reagents and Argon gas were used as received.

Preparation of PtNPs/TiO_2

$Na_2S_2O_8$ (4.0 g) was added in small portions to ice-cooled 98% H_2SO_4 (4.7 g) with continuous stirring to make piranha solution, and then crushed ice (13.0 g) and water (4.0 g) were added to the solution while the mixture was maintained below 15 ℃. When all the salt dissolved at room temperature, a powder of TiO_2 (500 mg) was dipped in the above mentioned piranha solution for 10 min with sonication (37 Hz) and left for another 1 h. The powder of TiO_2 was rinsed in succession H_2O (4 mL) and EtOH (12 mL) and filtered under reduced pressure. The powder was placed in a flask and dried *in vacuo*. The resulting solid was placed in a solution of $Pt(acac)_2$ (60.0 mg) and 4-methoxybenzyl alcohol (1.0 mL) in *p*-xylene (17 mL) and the reaction mixture was stirred at 130 ℃ for 12 h under a N_2 atmosphere. Then the solid was rinsed with *p*-xylene (10 mL) and EtOH (6 mL) and filtered under reduced pressure. The solid was dried *in vacuo* to give PtNPs/TiO_2 (587 mg).

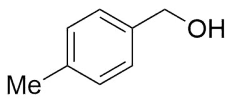
XANES experiments using hard X-ray

The X-ray absorption fine structure (XAFS) measurements were performed at hard X-ray beamline BL14B2 of SPring-8 in Japan. The incident hard X-rays were obtained using a silicon double crystal monochromator from synchrotron radiation from the 8GeV strong

ring. The net plane is (311) for the Pt L-absorption edge. The higher harmonics of the incident X-rays were reduced using two Rh-coated mirrors. The spectra of standard materials ($Pt(acac)_2$, $PtCl_2$, PtO_2), $PtNPs/TiO_2$ before the etherification reaction, and after the etherification were taken in the normal transition mode. The spectra of Pt foil, which is a standard material, was measured in the fluorescent X-ray yield method using a 19-elements Ge solid state detector. All the measurements were done at room temperature. The XAFS spectra were analyzed by ATHENA and ARTEMIS XAFS analysis package. For all measurements, data analysis to remove the background and qualitatively analyze the XANES was carried out manually. The da were normalized for variations in the primary X-ray intensity. A linear pre-edge was removed for each spectrum and the data were normalized by the height of the edge-jump. The theoretical scattering amplitude and phase shift function of the single scattering path was calculated by FEFF6.

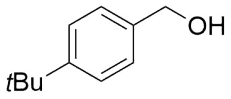
Preparation of benzyl alcohols (1a, 1c-1f, 1l, 1m)[1)]

General Procedure; To a solution of benzaldehyde (2.0 mmol, 1.0 eq.), which are commercially available, in MeOH (20 mL) was added $NaBH_4$ (8.0 mmol, 4.0 eq.) in portions in ice-water bath. The mixture was stirred at ambient temperature over 8 h. To the mixture was quenched by diluted HCl (1M). Organic compounds were extracted with $CHCl_3$ (10 mL×3). Organic layer was combined, washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure and the desired product was obtained without any further purification. If necessary, the obtained residue was purified by column chromatography (neutral flash silica gel, *n*-hexane / AcOEt) to get benzyl alcohol.



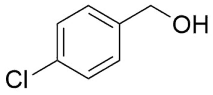
p-Tolylmethanol, **1a**[2)]

Following the general procedure, **1a** (2.01 g, 16.5 mmol, 97%) was obtained as a white crystal from 4-methylbenzaldehyde (2 mL, 17.0 mmol). m.p. 60-61 ℃ (recrystallized from AcOEt/hexane). lit.[2)] mp 60.2-61 ℃.



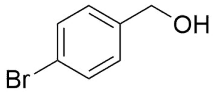
(4-(*tert*-Butyl)phenyl)methanol, **1c**[3)]

Following the general procedure, **1c** (300.5 mg, 2.03 mmol, 91%) was obtained as a pale yellow oil from 4-(*tert*-butyl)benzaldehyde (324.5 mg, 2.00 mmol).



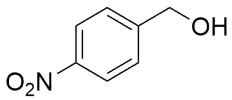
(4-Chlorophenyl)methanol, **1d**[4)]

Following the general procedure, **1d** (285.1 mg, 2.00 mmol, 94%) was obtained as a white needle from 4-chlorobenzaldehyde (297.6 mg, 2.12 mmol). m.p. 74-75 ℃ (recrystallized from AcOEt/hexane). lit.[5)] mp 74-76 ℃.



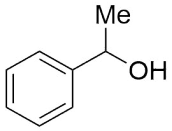
(4-Bromophenyl)methanol, **1e**[6)]

Following the general procedure, **1e** (362.4 mg, 1.94 mmol, 94%) was obtained as a white needle from 4-bromobenzaldehyde (382.1 mg, 2.07 mmol). m.p. 76-78 ℃ (recrystallized from AcOEt/hexane) lit.[7)] mp 76-78 ℃.



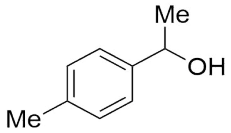
(4-Nitrophenyl)methanol, **1f**[3)]

Following the general procedure, **1f** (299.7 mg, 1.96 mmol, 92%) was obtained as a yellow needle from 4-nitrobenzaldehyde (320.2 mg, 2.12 mmol). m.p. 94-95 ℃ (recrystallized from EtOH). lit.[8)] mp 94-96 ℃.



1-Phenylethan-1-ol, **1l**[9)]

Following the general procedure, **1l** (247.7 mg, 2.03 mmol, 98%) was obtained as a colourless oil from acetophenone (249.6 mg, 2.07 mmol).

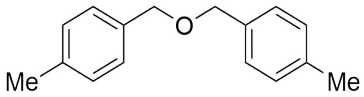


1-(*p*-Tolyl)ethan-1-ol, **1m**[10)]

Following the general procedure, **2m** (269.1 mg, 1.98 mmol, 94%) was obtained as a colourless oil from *p*-methylacetophenone (282.1 mg, 2.10 mmol).

Preparation of dibenzyl ethers (2a, 2c, 2g, 2h, 2i) or 3j.

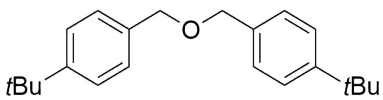
General Procedure; To a solution of benzyl alcohol (0.25 mmol, 1.0 eq.) in diethyl carbonate (1 mL, 0.25 M) was added PtNPs/TiO_2 (50 mg) after Ar substitution and the whole were stirred for 20 h at 75 ℃ with blue LED light (420 nm, 6 W × 2). The catalyst was removed by celite filtration and solvents were evaporated. The obtained residue was subjected to column chromatography (neutral flash silica gel, *n*-hexane / AcOEt) to give **2** or **3**.



4, 4'-(Oxybis(methylene))bis(methylbenzene), **2a**[11)]

Following the general procedure, **2a** (24.5 mg, 0.11 mmol, 89%) was obtained as a white plate from *p*-tolylmethanol **1a** (29.8 mg, 0.24 mmol). m.p. 60-61 ℃ (recrystallized from hexane). lit.[12)] mp 60-62 ℃.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.25 (4H, d, *J* = 7.9 Hz), 7.16 (4H, d, *J* = 7.9 Hz), 4.50 (4H, s), 2.34 (6H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 137.2, 135.3, 129.0, 127.9, 71.7, 21.2.

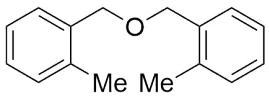


4, 4'-(Oxybis(methylene))bis(*tert*-butylbenzene), **2c**[13)]

Following the general procedure, **2c** (33.7 mg, 0.11 mmol, 76%) was obtained as a colourless oil from (4-(*tert*-butyl)phenyl)methan **1c** (47.2 mg, 0.29 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.31 (4H, d, *J* = 8.6 Hz), 7.24 (4H, d, *J* = 8.6 Hz), 4.46 (4H, s), 1.25 (18H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 150.5, 135.4, 127.6, 125.3, 71.8,

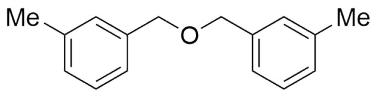
34.5, 31.3.



2, 2'-(Oxybis(methylene))bis(methylbenzene), **2g**[14)]

Following the general procedure, **2g** (13.0 mg, 0.057 mmol, 44%) was obtained as a white needle from *o*-tolylmethanol (47.2 mg, 0.29 mmol). m.p. 51-53 ℃ (recrystallized from AcOEt/hexane). lit.[15)] mp 51-52 ℃.

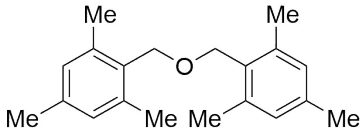
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.37-7.35 (2H, m), 7.22-7.15 (6H, m), 4.57 (4H, s), 2.33 (6H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 136.7, 136.2, 130.2, 128.7, 127.8, 125.8, 70.7, 18.8.



3, 3'-(Oxybis(methylene))bis(methylbenzene), **2h**[16)]

Following the general procedure, **2h** (5.0 mg, 0.022 mmol, 17%) was obtained as a colourless oil from *m*-tolylmethanol (47.2 mg, 0.29 mmol).

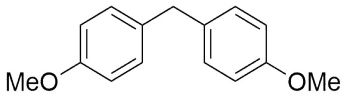
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.25 (2H, t, J = 8.0 Hz), 7.20 (2H, s), 7.17 (2H, d, J = 8.1 Hz), 7.12 (2H, d, J = 7.5), 4.53 (4H, s), 2.37 (6H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 138.2, 138.0, 128.6, 128.3, 128.3, 124.9, 72.2, 21.4.



2, 2'-(Oxybis(methylene))bis(1,3,5-trimethylbenzene), **2i**

Following the general procedure, **2h** (29.7 mg, 0.11 mmol, 82%) was obtained as a white plate from mesitylmethanol (38.4 mg, 0.26 mmol). m.p. 146-148 ℃ (recrystallized from EtOH). lit.[17)] mp 147-148 ℃.

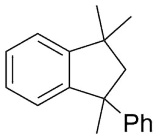
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.82 (4H, s), 4.55 (4H, s), 2.34 (12H, s), 2.23 (6H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 137.8, 137.5, 131.3, 128.8, 66.4, 21.0, 19.4; HRMS (MALDI) calcd for $C_{20}H_{26}ONa$: 305.1881 [$(M + H)^+$], found 305.1876.



Bis(4-methoxyphenyl)methane, **3j**[18)]

Following the general procedure, **3j** (26.9 mg, 0.11 mmol, 92%) was obtained as a colourless oil from commercial (4-methoxyphenyl)methanol (35.4 mg, 0.26 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.09 (4H, d, J = 8.7 Hz), 6.82 (4H, d, J = 8.7 Hz), 3.87 (2H, s), 3.78 (6H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 157.9, 133.7, 129.7, 113.8, 55.2, 40.1.



1, 1, 3-Trimethyl-3-phenyl-2, 3-dihydro-*1H*-indene, **4k**[19)]

To a solution of commercial 2-phenylpropan-2-ol (34.4 mg, 0.25 mmol, 1.0 eq.) in nitromethane (1 mL) was added PtNPs/TiO_2 (50 mg) and the whole were stirred for 20 h at 75 ℃ with blue LED light. The catalyst was removed by celite filtration and solvents were evaporated. The obtained residue was subjected to column chromatography (neutral flash silica gel, *n*-hexane / AcOEt = 50:1) to give **4k** (22.8 mg, 0.096 mmol, 76%) as a white viscous liquid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.30-7.12 (9H, m), 2.43, 2.20 (2H, AB, J_{AB} = 13.2 Hz), 1.69 (3H, s), 1.35 (3H, s), 1.03 (3H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, 76 Hz) δ: 152.2, 151.0, 148.6, 127.9, 127.2, 126.7, 126.6, 125.4, 125.0, 122.5, 59.2, 50.7, 42.8, 30.9, 30.6, 30.3.

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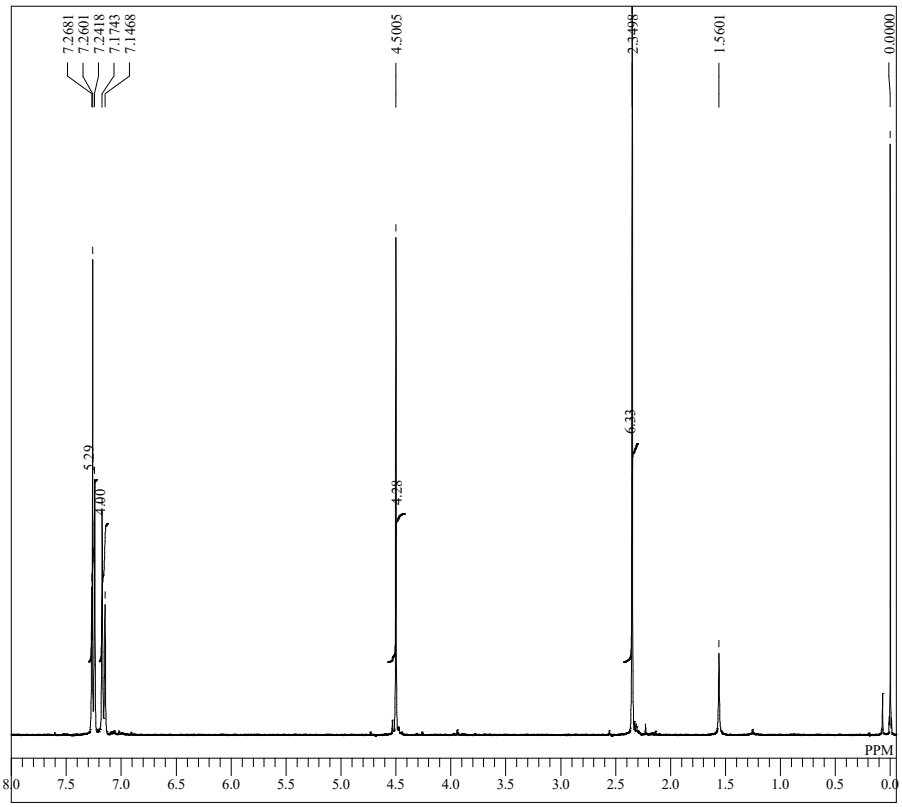
2a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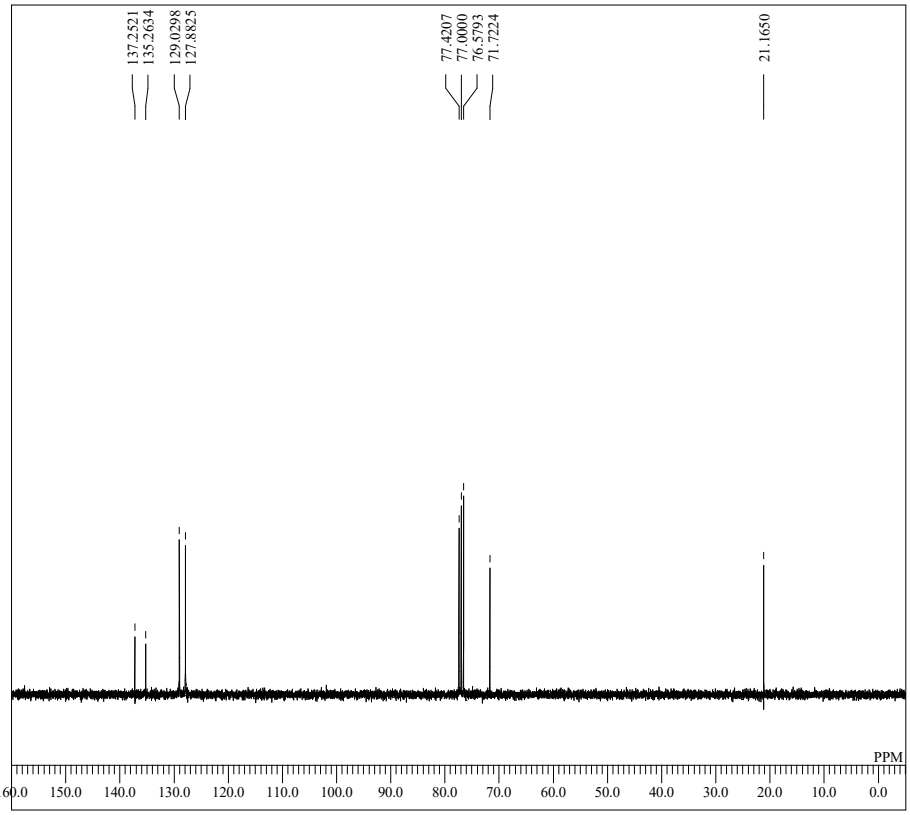
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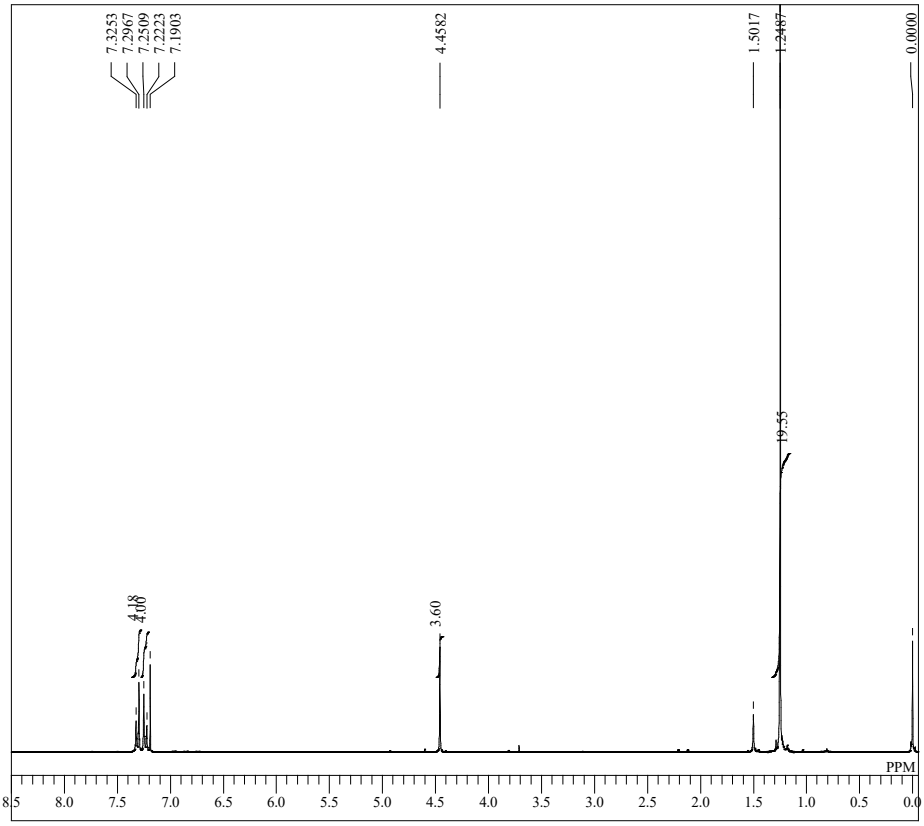
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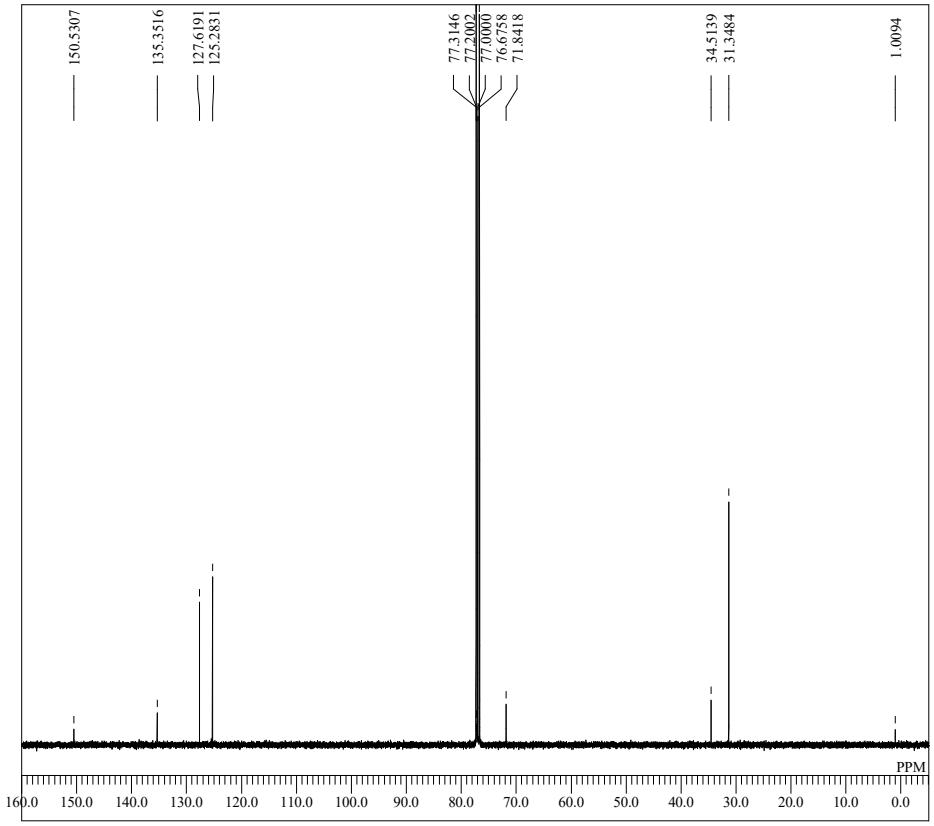
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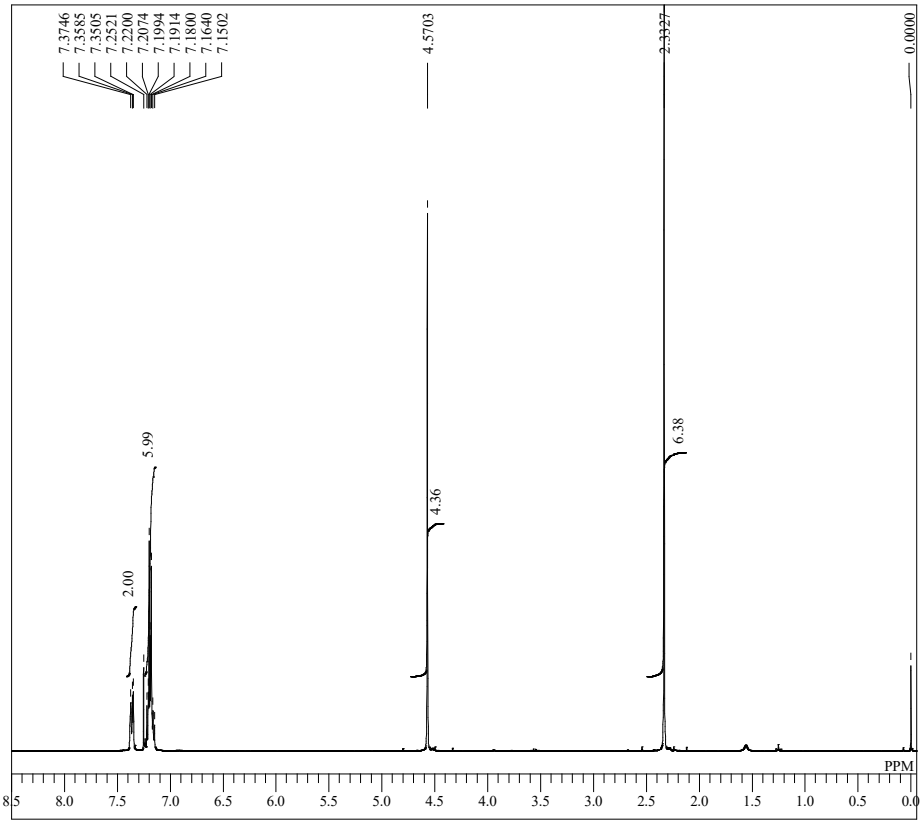
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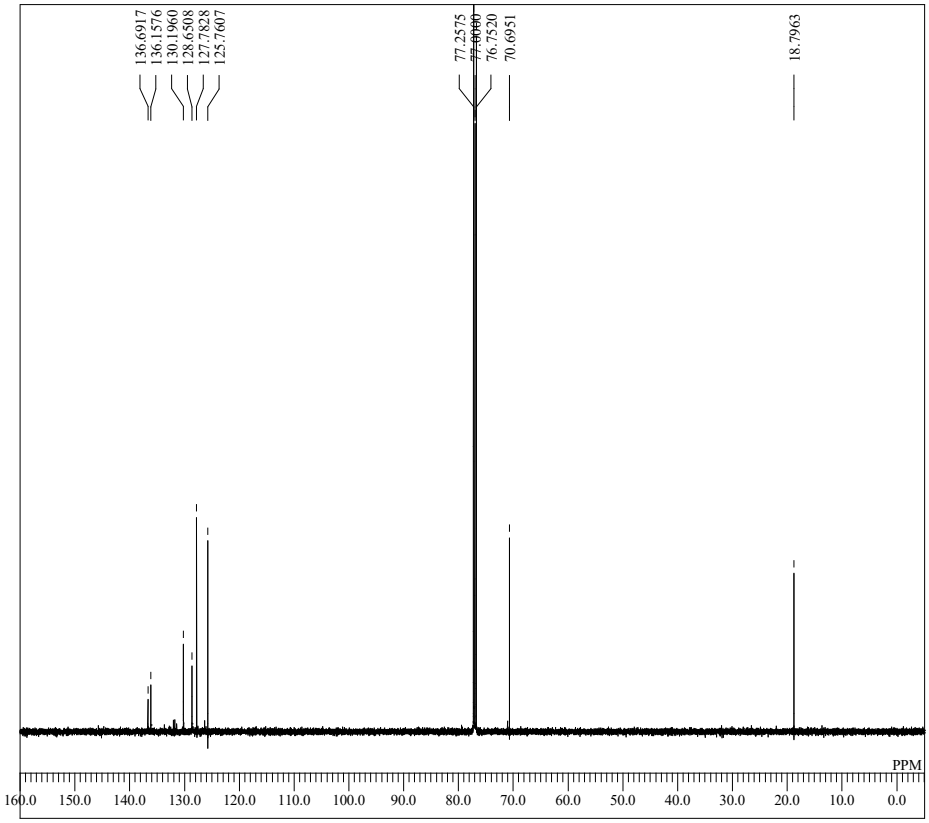
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127.7828
125.7607
77.2575
77.0060
76.7520
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18.7963
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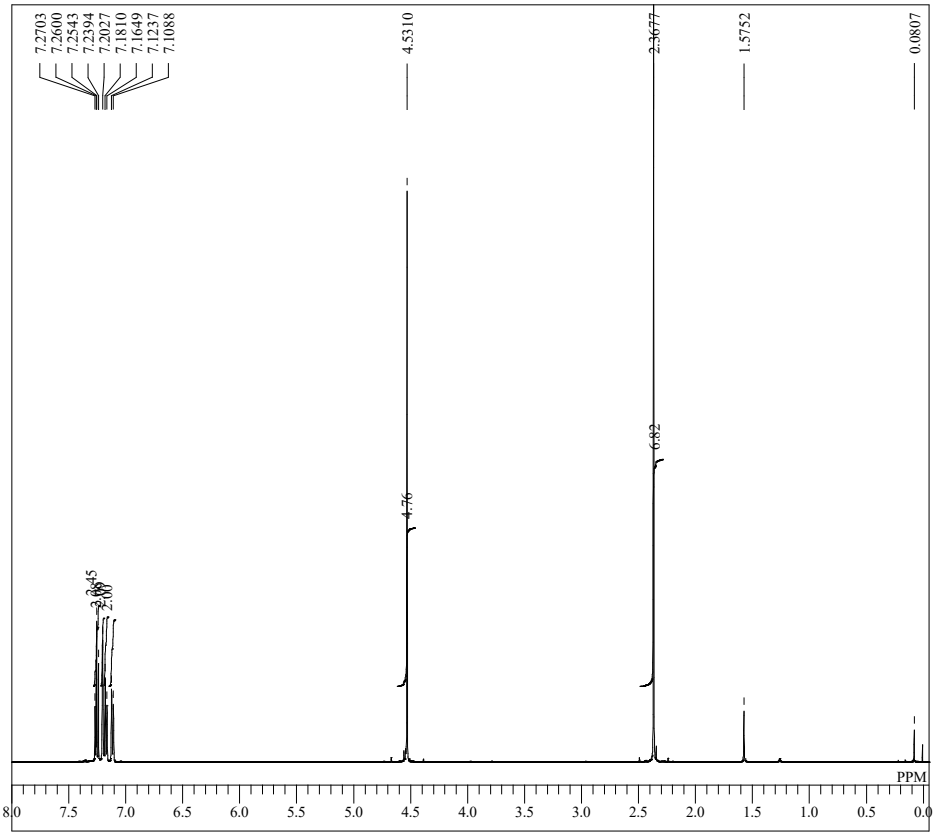
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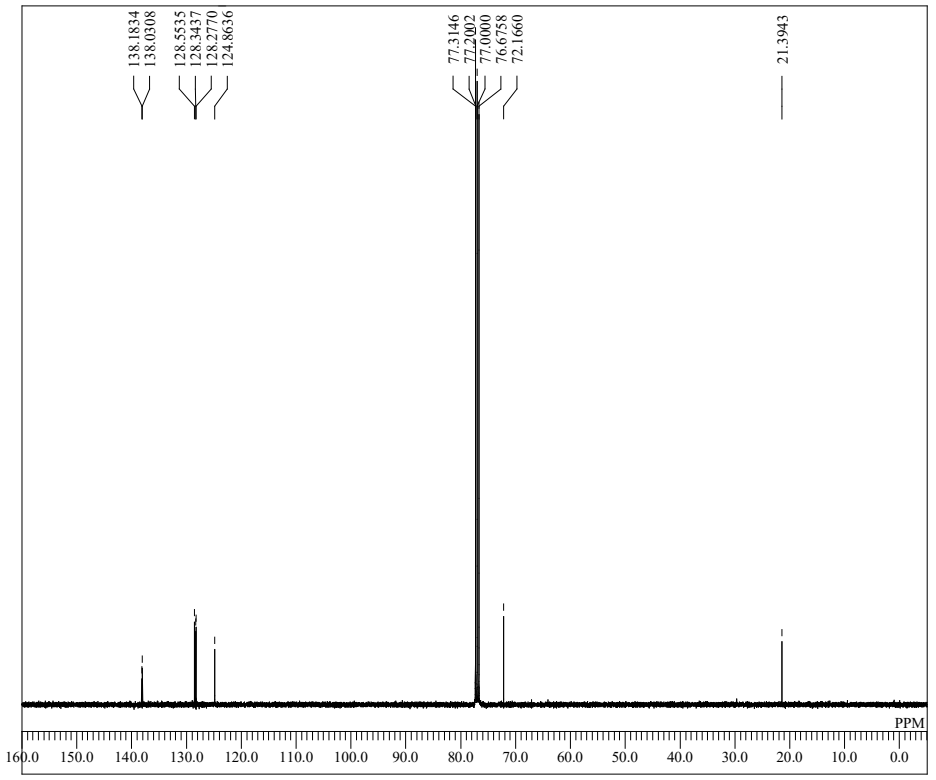
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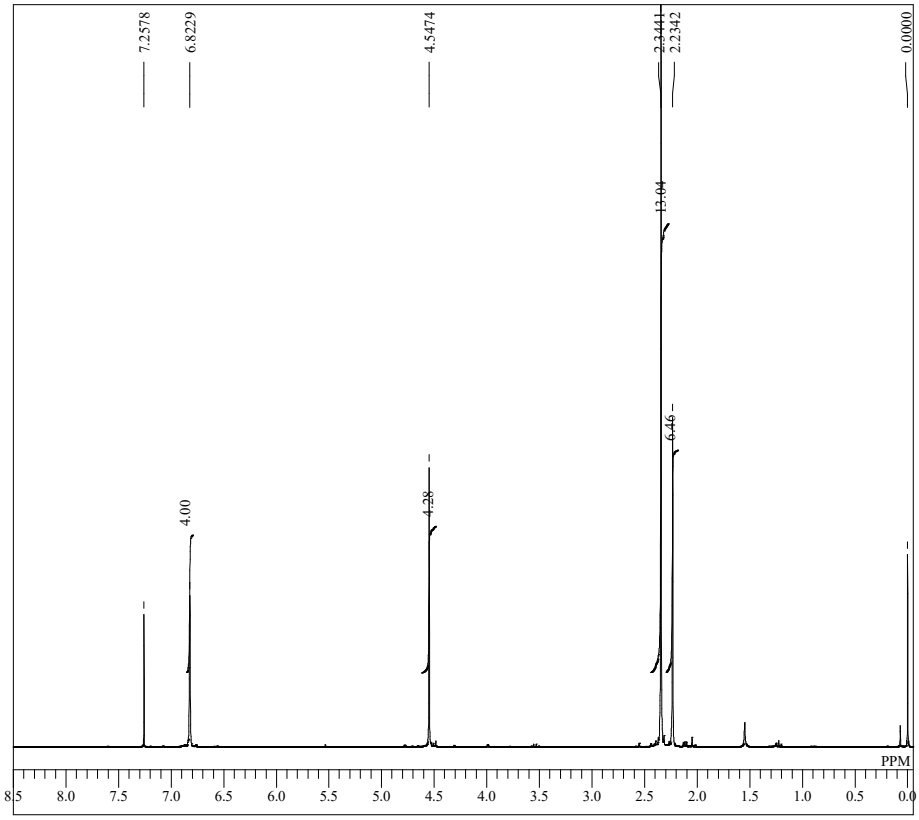
2i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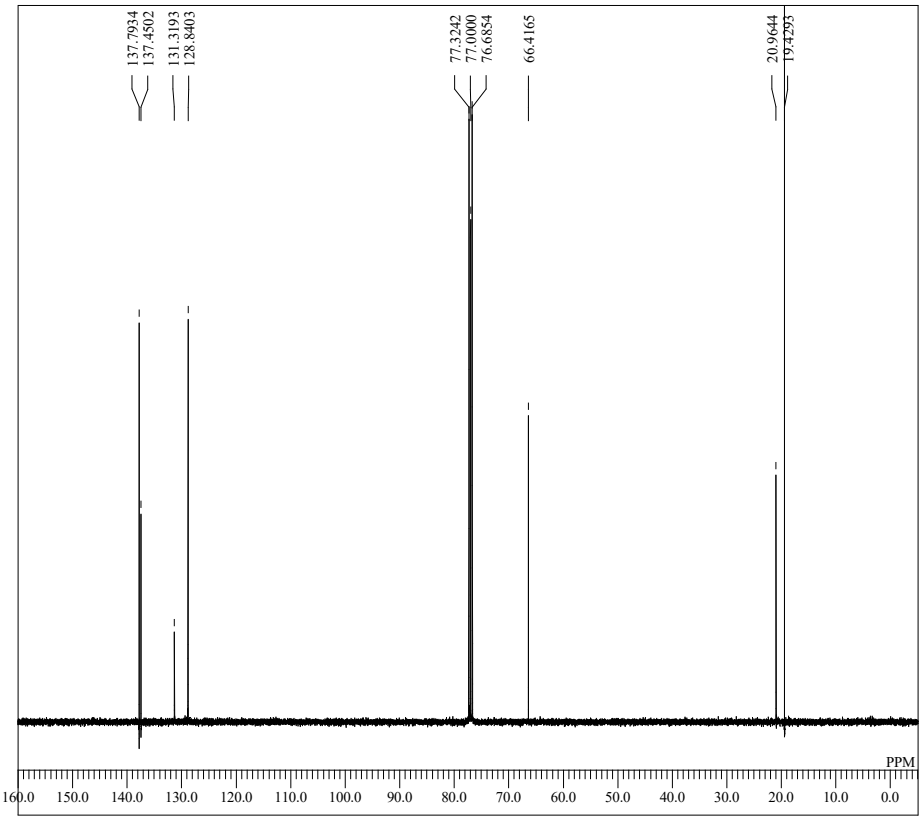
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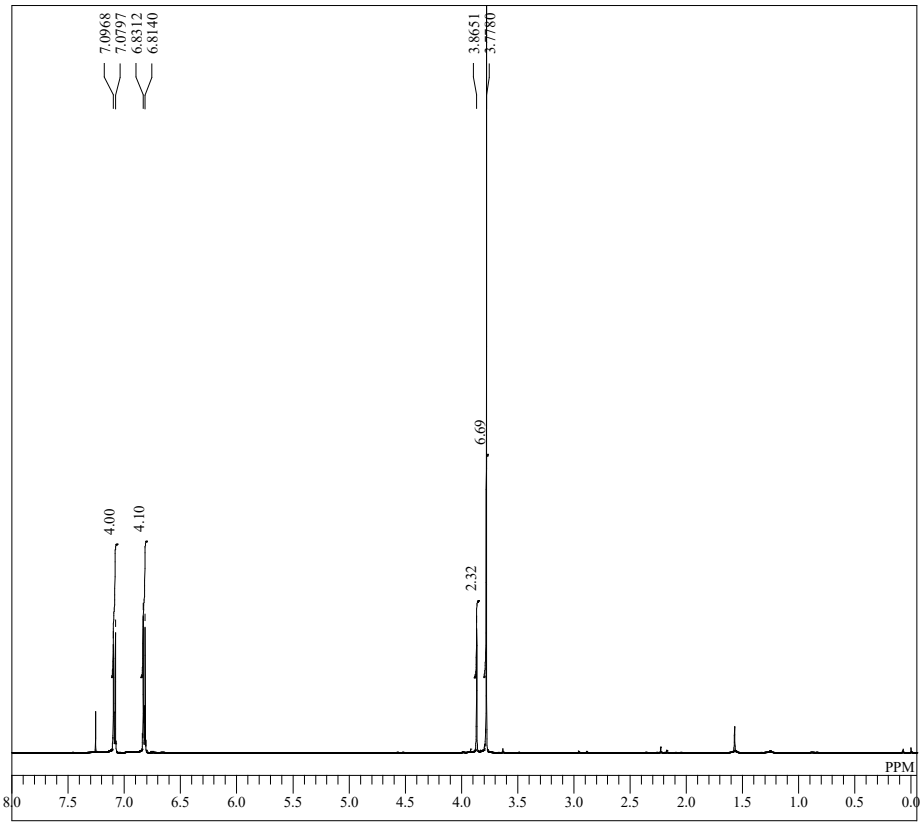
3j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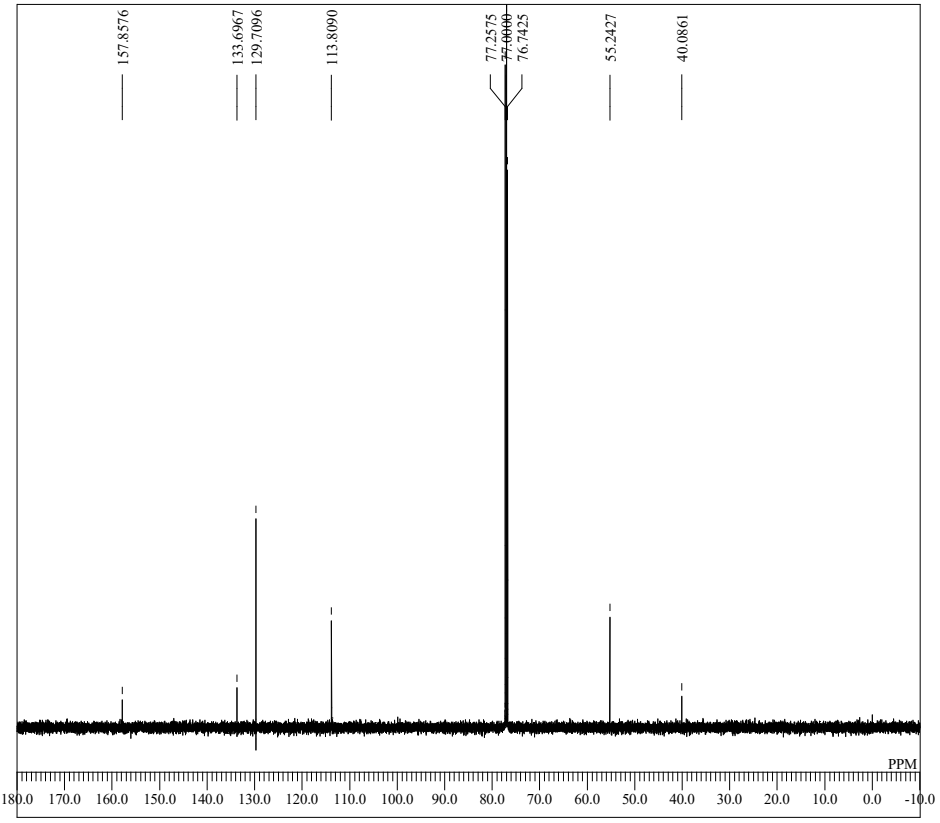
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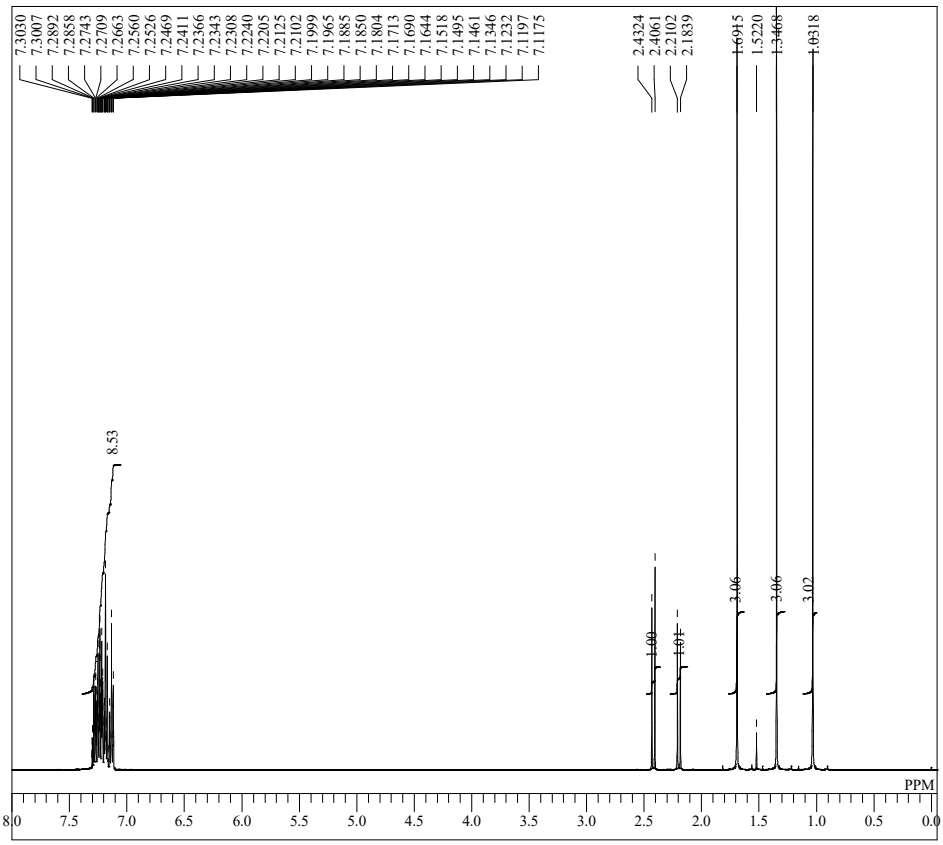
4k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3.06
3.02
PPM
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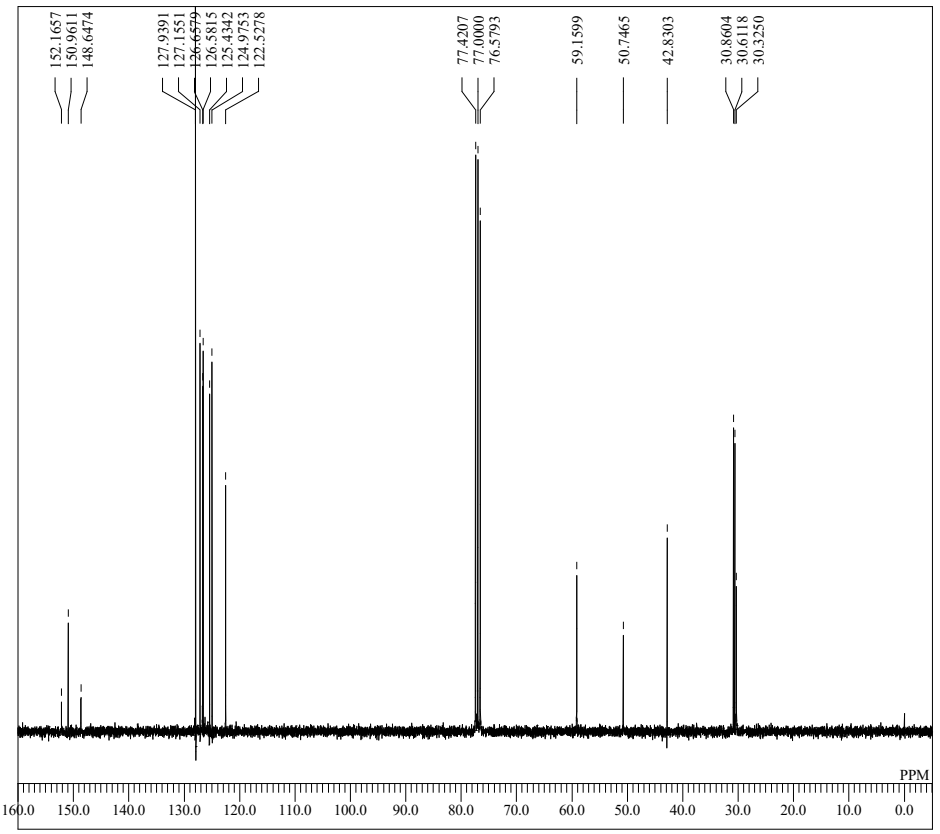
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