

## **Supporting Information**

### **Copper-Catalyzed Enantioselective Propargylic Etherification of Propargylic Esters with Alcohols**

Kazunari Nakajima, Masashi Shibata, and Yoshiaki Nishibayashi\*

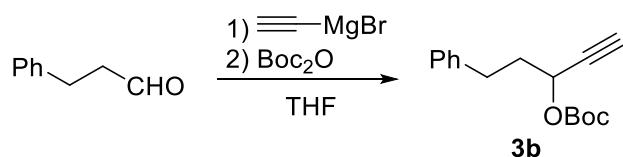
*Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113-8656, Japan*

#### **General Methods.**

$^1\text{H}$  NMR (270 MHz) and  $^{13}\text{C}$  NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using  $\text{CDCl}_3$  as a solvent unless otherwise noted. HPLC analyses were performed on Hitachi L-7100 and GL-7410 apparatuses equipped with a UV detector using 25 cm x 4.6 mm DAICEL Chiralcel OJ-H, OD, Chiralpak IC, ID columns. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Specific rotations were measured on a JASCO DIP-1000 polarimeter.

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods, then distilled under  $\text{N}_2$  and degassed before use. Optically active ligands (**L2**, **L5**),  $\text{CuOTf}\cdot 1/2\text{C}_6\text{H}_6$ , diisopropylethylamine, and (*S*)-1-phenylprop-2-yn-1-ol are commercially available reagents. Pybox ligands (**L1**,<sup>S1</sup> **L3**,<sup>S2</sup> **L4**,<sup>S3</sup> **L6**,<sup>S3</sup>), PNN ligands (**L7**,<sup>S4a</sup> **L8**,<sup>S4b</sup>), propargylic acetates (**1a**,<sup>S5</sup> **1b**,<sup>S6</sup>), and (*R*)-5-phenylpent-1-yn-3-ol<sup>S7</sup> were prepared according to the literature procedures.

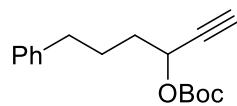
#### **Preparation of Propargylic Carbonates (3).**



A typical experimental procedure for the preparation of *tert*-butyl (5-phenylpent-1-yn-3-yl) carbonate (**3b**) is described below. In a 50 mL Schlenk flask were placed 3-phenylpropanal (0.870 mL, 6.60 mmol) and anhydrous THF (30 mL) under  $\text{N}_2$ . Ethylmagnesium bromide (0.5 M in THF, 20.0 mL, 10.0 mmol) was added to the solution at 0 °C and the mixture was allowed to warm to room temperature. After stirring for 1 h, the solution was cooled to 0 °C and di-*tert*-butyl dicarbonate (2.91 g, 13.3 mmol) was added to the solution. The mixture was kept at room temperature for 3 h and then

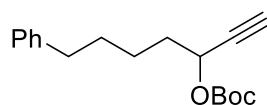
the reaction was quenched by saturated aqueous  $\text{NH}_4\text{Cl}$  (20 mL). The resulting mixture was extracted with diethyl ether (15 mL x 3) and the combined organic layers were dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography ( $\text{SiO}_2$ ) with hexane/ethyl acetate (95/5) to give **3b**<sup>88</sup> as a colorless oil (838 mg, 3.22 mmol, 48% yield).

Spectroscopic characterization of **3a**,<sup>89</sup> **3b**,<sup>88</sup> and **3f**<sup>88</sup> is described elsewhere. Spectroscopic data of other propargylic carbonates are described below:



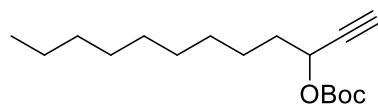
**3c**

**3c:** A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.31-7.25 (m, 2H), 7.19-7.16 (m, 3H), 5.17-5.15 (m, 1H), 2.65 (t,  $J$  = 6.8 Hz, 2H), 2.48 (d,  $J$  = 1.9 Hz, 1H), 1.84-1.82 (m, 4H), 1.49 (s, 9H).  $^{13}\text{C}$  NMR  $\delta$  152.6, 141.7, 128.38, 128.35, 125.9, 82.8, 80.8, 74.1, 66.5, 35.2, 34.2, 27.7, 26.6. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{22}\text{O}_3$  [M]: 274.1569. Found: 274.1580.



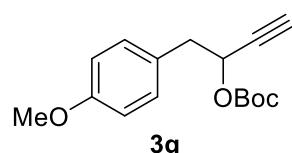
**3d**

**3d:** A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.30-7.25 (m, 2H), 7.20-7.15 (m, 3H), 5.15 (dt,  $J$  = 2.2 and 6.8 Hz, 1H), 2.63 (t,  $J$  = 7.6 Hz, 2H), 2.47 (d,  $J$  = 2.2 Hz, 1H), 1.88-1.80 (m, 2H), 1.72-1.61 (m, 2H), 1.57-1.44 (m, 11H).  $^{13}\text{C}$  NMR  $\delta$  152.6, 142.2, 128.33, 128.25, 125.7, 82.7, 80.9, 74.0, 66.6, 35.7, 34.5, 30.9, 27.7, 24.5. HRMS (EI) Calcd. for  $\text{C}_{18}\text{H}_{25}\text{O}_3$  [M+H]: 289.1804. Found: 289.1793.



**3e**

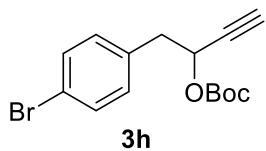
**3e:** A colorless oil.  $^1\text{H}$  NMR  $\delta$  5.14 (dt,  $J$  = 2.1 and 6.7 Hz, 1H), 2.47 (d,  $J$  = 2.1 Hz, 1H), 1.84-1.75 (m, 2H), 1.50 (s, 9H), 1.26 (br, 14H), 0.88 (t,  $J$  = 6.6 Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  152.6, 82.7, 81.0, 73.9, 66.7, 34.7, 31.8, 29.43, 29.39, 29.2, 29.0, 27.7, 24.8, 22.6, 14.1. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{31}\text{O}_3$  [M+H]: 283.2273. Found: 283.2266.



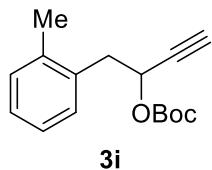
**3g**

**3g:** A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.19 (d,  $J$  = 8.8 Hz, 2H), 6.84 (d,  $J$  = 8.8 Hz, 2H), 5.30 (dt,  $J$  = 2.1 and 7.0 Hz, 1H), 3.78 (s, 3H), 3.12-2.96 (m, 2H), 2.48 (d,  $J$  = 2.1 Hz, 1H), 1.46 (s, 9H).  $^{13}\text{C}$  NMR  $\delta$  158.7,

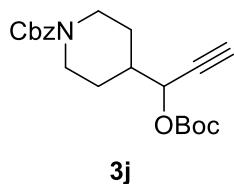
152.4, 130.7, 127.5, 113.8, 82.8, 80.5, 74.8, 67.4, 55.2, 40.3, 27.7. HRMS (EI) Calcd. for  $C_{16}H_{20}O_4$  [M]: 276.1362. Found: 276.1355.



**3h:** A colorless oil.  $^1H$  NMR  $\delta$  7.43 (d,  $J$  = 8.6 Hz, 2H), 7.16 (d,  $J$  = 8.6 Hz, 2H), 5.32 (dt,  $J$  = 2.1 and 6.9 Hz, 1H), 3.13-2.98 (m, 3H), 1.46 (s, 9H).  $^{13}C$  NMR  $\delta$  152.2, 134.4, 131.44, 131.40, 121.1, 83.0, 80.0, 75.2, 66.7, 40.4, 27.7. HRMS (EI) Calcd. for  $C_{15}H_{18}BrO_3$  [M+H]: 325.0439. Found: 325.0440.

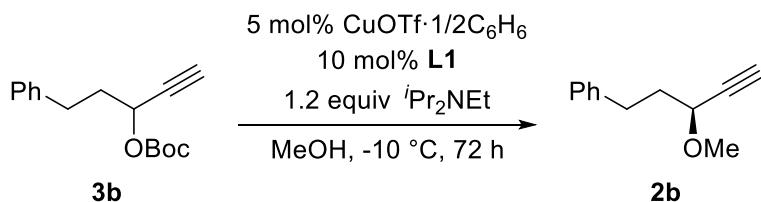


**3i:** A colorless oil.  $^1H$  NMR  $\delta$  7.25-7.21 (m, 1H), 7.16-7.11 (m, 3H), 5.38 (dt,  $J$  = 2.2 and 7.3 Hz, 1H), 3.21-3.05 (m, 2H), 2.47 (d,  $J$  = 2.2 Hz, 1H), 2.37 (s, 3H), 1.44 (s, 9H).  $^{13}C$  NMR  $\delta$  152.3, 136.9, 133.7, 130.5, 130.3, 127.1, 125.8, 82.8, 80.5, 74.7, 66.3, 38.4, 27.7, 19.5. HRMS (EI) Calcd. for  $C_{16}H_{20}O_3$  [M]: 260.1412. Found: 260.1404.



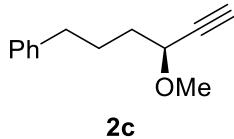
**3j:** A yellow solid, m.p. = 107.4-108.8 °C.  $^1H$  NMR  $\delta$  7.38-7.30 (m, 5H), 5.13 (s, 2H), 5.05 (dd,  $J$  = 2.1 and 6.1 Hz, 1H), 4.26 (brd,  $J$  = 10.8 Hz, 2H), 2.76 (brt,  $J$  = 12.4 Hz, 2H), 2.50 (d,  $J$  = 2.1 Hz, 1H), 1.96-1.72 (m, 3H), 1.52-1.33 (m, 11H).  $^{13}C$  NMR  $\delta$  155.2, 152.6, 136.8, 128.5, 127.9, 127.8, 83.0, 79.0, 75.3, 69.8, 67.1, 43.6, 43.5, 40.1, 27.7, 27.5, 27.0. HRMS (EI) Calcd. for  $C_{21}H_{27}NO_5$  [M]: 373.1889. Found: 373.1872.

**Copper-Catalyzed Enantioselective Propargylic Etherification of Propargylic Carbonates (3) with Aliphatic Alcohols.**

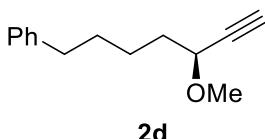


A typical experimental procedure for the reaction of *tert*-butyl (5-phenylpent-1-yn-3-yl) carbonate (**3b**) with methanol is described below. In a 20 mL Schlenk flask were placed CuOTf·1/2C<sub>6</sub>H<sub>6</sub> (2.6 mg, 0.010 mmol) and (*S*)-Me-pybox (**L1**) (5.0 mg, 0.020 mmol) under N<sub>2</sub>. Anhydrous methanol (1.0 mL) was added, and the mixture was magnetically stirred at 60 °C for 1 h. After the solution was cooled to -10 °C, **3b** (52.0 mg, 0.200 mmol) in anhydrous methanol (1.0 mL) and diisopropylethylamine (42.0 μL, 0.240 mmol) were added under N<sub>2</sub>, and the mixture was kept at -10 °C for 72 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by the column chromatography (SiO<sub>2</sub>) with hexane/diethyl ether (97/3) to give (3-methoxypent-4-yn-1-yl)benzene (**2b**)<sup>S10</sup> as a pale yellow oil (29.5 mg, 0.169 mmol, 85% yield). [α]<sup>25</sup><sub>D</sub> = -12.3 (c = 0.460, CHCl<sub>3</sub>). The enantiomeric excess of **2b** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.7 min (minor) and 7.3 min (major), 81% *ee*.

Isolated yields and spectroscopic data of other products (**2** and **4**) are described below:

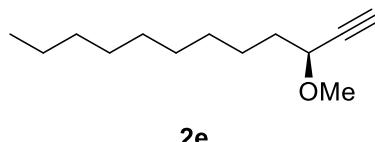


**2c:** 89% Yield. A colorless oil. <sup>1</sup>H NMR δ 7.30-7.27 (m, 2H), 7.25-7.14 (m, 3H), 3.97-3.91 (m, 1H), 3.39 (s, 3H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.42 (d, *J* = 1.9 Hz, 1H), 1.85-1.72 (m, 4H). <sup>13</sup>C NMR δ 142.1, 128.4, 128.3, 125.8, 82.6, 73.8, 70.9, 56.4, 35.5, 35.0, 26.9. HRMS (EI) Calcd. for C<sub>13</sub>H<sub>16</sub>O [M]: 188.1201. Found: 188.1200. [α]<sup>25</sup><sub>D</sub> = -34.1 (c = 0.820, CHCl<sub>3</sub>). The enantiomeric excess of **2c** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.2 min (minor) and 9.3 min (major), 78% *ee*.

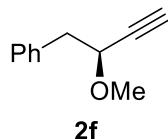


**2d:** 88% Yield. A colorless oil. <sup>1</sup>H NMR δ 7.30-7.25 (m, 2H), 7.19-7.14 (m, 3H), 3.93 (dt, *J* = 2.0 and 6.5 Hz, 1H), 3.40 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.43 (d, *J* = 2.0 Hz, 1H), 1.80-1.44 (m, 6H). <sup>13</sup>C NMR δ 142.5, 128.4, 128.3, 125.7, 82.7, 73.7, 71.0, 56.4, 35.8, 35.4, 31.2, 24.9. HRMS (EI) Calcd. for C<sub>14</sub>H<sub>18</sub>O [M]: 202.1358. Found: 202.1349. [α]<sup>25</sup><sub>D</sub> = -26.3 (c = 1.86, CHCl<sub>3</sub>). The enantiomeric excess

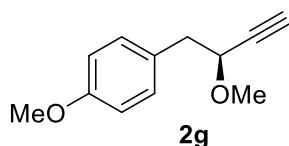
of **2d** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/<sup>i</sup>PrOH = 100/0, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 25.8 min (major) and 30.6 min (minor), 79% *ee*.



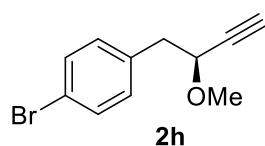
**2e:** 91% Yield. A colorless oil. <sup>1</sup>H NMR  $\delta$  3.93 (dt,  $J$  = 2.0 and 6.6 Hz, 1H), 3.41 (m, 3H), 2.43 (d,  $J$  = 2.0 Hz, 1H), 1.76-1.64 (m, 2H), 1.27 (br, 14H), 0.90-0.85 (brm, 3H). <sup>13</sup>C NMR  $\delta$  82.8, 73.6, 71.1, 56.4, 35.5, 31.9, 29.5, 29.30, 29.29, 25.1, 22.7, 14.1. HRMS (EI) Calcd. for C<sub>13</sub>H<sub>24</sub>O [M]: 196.1827. Found: 196.1832.  $[\alpha]^{25}_D$  = -38.5 ( $c$  = 0.605, CHCl<sub>3</sub>). The enantiomeric excess of **2e** was determined by HPLC analysis after conversion of **2e** into triazole **2e'** (*vide infra*).



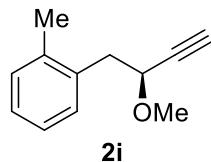
**2f:** 65% Yield. A pale yellow oil. <sup>1</sup>H NMR  $\delta$  7.33-7.23 (m, 5H), 4.14 (dt,  $J$  = 2.2 and 6.8 Hz, 1H), 3.41 (s, 3H), 3.10-2.94 (m, 2H), 2.45 (d,  $J$  = 2.2 Hz, 1H). <sup>13</sup>C NMR  $\delta$  137.0, 129.6, 128.2, 126.6, 82.1, 74.6, 72.0, 56.6, 42.0. HRMS (EI) Calcd. for C<sub>11</sub>H<sub>12</sub>O [M]: 160.0888. Found: 160.0895.  $[\alpha]^{25}_D$  = -24.6 ( $c$  = 0.790, CHCl<sub>3</sub>). The enantiomeric excess of **2f** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/<sup>i</sup>PrOH = 100/0, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 18.5 min (major) and 24.7 min (minor), 94% *ee*.



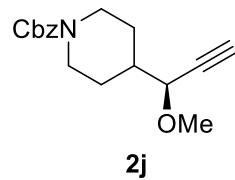
**2g:** 73% Yield. A pale yellow oil. <sup>1</sup>H NMR 7.19 (d,  $J$  = 8.6 Hz, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 4.09 (dt,  $J$  = 2.0 and 6.7 Hz, 1H), 3.79 (s, 3H), 3.41 (s, 3H), 3.03-2.88 (m, 2H), 2.45 (d,  $J$  = 2.0 Hz, 1H). <sup>13</sup>C NMR  $\delta$  158.4, 130.6, 129.1, 113.6, 82.2, 74.6, 72.3, 56.6, 55.2, 41.1. HRMS (EI) Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> [M]: 190.0994. Found: 190.0988.  $[\alpha]^{25}_D$  = -12.3 ( $c$  = 1.74, CHCl<sub>3</sub>). The enantiomeric excess of **2g** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/<sup>i</sup>PrOH = 97/3, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 13.1 min (major) and 20.6 min (minor), 95% *ee*.



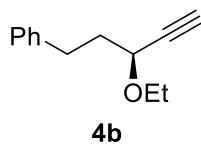
**2h:** 72% Yield. A pale yellow oil.  $^1\text{H}$  NMR  $\delta$  7.41 (d,  $J$  = 8.5 Hz, 2H), 7.15 (d,  $J$  = 8.5 Hz, 2H), 4.10 (dt,  $J$  = 2.1 and 6.5 Hz, 1H), 3.40 (s, 3H), 3.03-2.89 (m, 2H), 2.46 (d,  $J$  = 2.1 Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  135.9, 131.4, 131.3, 120.7, 81.7, 74.9, 71.6, 56.6, 41.3. HRMS (EI) Calcd. for  $\text{C}_{11}\text{H}_{11}\text{BrO}$  [M]: 237.9993. Found: 237.9988.  $[\alpha]^{25}\text{D} = -18.0$  ( $c$  = 1.16,  $\text{CHCl}_3$ ). The enantiomeric excess of **2h** was determined by HPLC analysis; DAICEL Chiraldak ID, hexane/ $^i\text{PrOH}$  = 99/1, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 10.8 min (major) and 12.8 min (minor), 95% ee.



**2i:** 89% Yield. A pale yellow oil.  $^1\text{H}$  NMR  $\delta$  7.26-7.21 (m, 1H), 7.15-7.12 (m, 3H), 4.14 (dt,  $J$  = 1.9 and 7.0 Hz, 1H), 3.42 (s, 3H), 3.13-2.96 (m, 2H), 2.44 (d,  $J$  = 1.9 Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR  $\delta$  136.7, 135.3, 130.23, 130.16, 126.8, 125.8, 82.2, 74.4, 71.4, 56.6, 39.0, 19.7. HRMS (EI) Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}$  [M]: 174.1045. Found: 174.1038.  $[\alpha]^{25}\text{D} = -27.3$  ( $c$  = 1.86,  $\text{CHCl}_3$ ). The enantiomeric excess of **2i** was determined by HPLC analysis; DAICEL Chiralcel OD, hexane/ $^i\text{PrOH}$  = 100/0, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 15.0 min (major) and 17.1 min (minor), 99% ee.

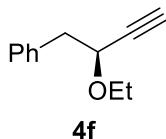


**2j:** 83% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.37-7.30 (m, 5H), 5.13 (s, 2H), 4.24 (brd,  $J$  = 11.9 Hz, 2H), 3.75 (dd,  $J$  = 2.0 and 5.8 Hz, 1H), 3.41 (s, 3H), 2.76 (brt,  $J$  = 13.0 Hz, 2H), 2.46 (d,  $J$  = 2.0 Hz, 1H), 1.85-1.73 (m, 3H), 1.50-1.26 (m, 2H).  $^{13}\text{C}$  NMR  $\delta$  155.2, 136.9, 128.4, 127.9, 127.8, 80.8, 75.1, 75.0, 66.9, 56.8, 43.8, 43.7, 40.8, 27.8, 27.3. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{21}\text{NO}_3$  [M]: 287.1521. Found: 287.1509.  $[\alpha]^{25}\text{D} = -13.2$  ( $c$  = 2.71,  $\text{CHCl}_3$ ). The enantiomeric excess of **2j** was determined by HPLC analysis; DAICEL Chiraldak IC, hexane/ $^i\text{PrOH}$  = 95/5, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 26.9 min (major) and 28.2 min (minor), 90% ee.



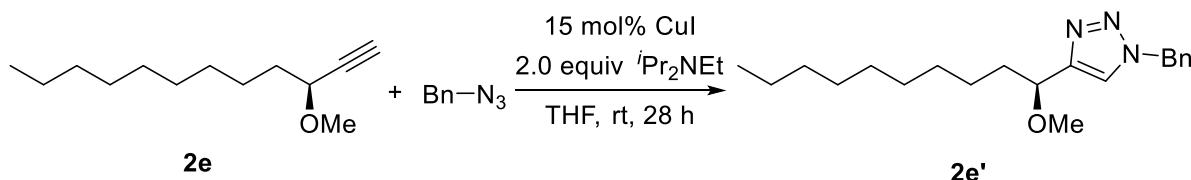
**4b:** 63% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.31-7.26 (m, 2H), 7.21-7.16 (m, 3H), 3.99 (dt,  $J$  = 2.2 and 6.8 Hz, 1H), 3.86-3.75 (m, 1H), 3.47-3.36 (m, 1H), 2.80 (t,  $J$  = 7.8 Hz, 2H), 2.44 (d,  $J$  = 2.2 Hz, 1H), 2.15-1.94 (m, 2H), 1.23 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  141.4, 128.5, 128.4, 125.9, 83.1, 73.5, 68.3, 64.4, 37.2, 31.3, 15.1. HRMS (EI) Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}$  [M]: 188.1201. Found: 188.1193.  $[\alpha]^{25}\text{D} = -18.7$

( $c = 1.03$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **4b** was determined by HPLC analysis; DAICEL Chiralcel OD, hexane/ $^i\text{PrOH} = 100/0$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 16.9 min (major) and 27.9 min (minor), 80% *ee*.



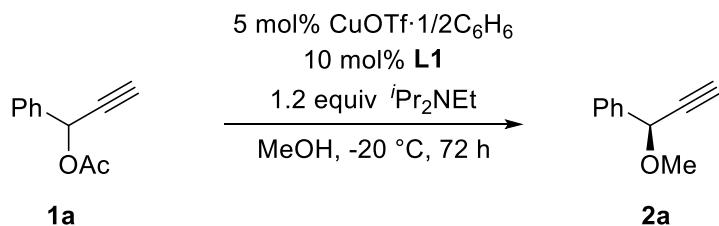
**4f:** 57% Yield. A pale yellow oil.  $^1\text{H}$  NMR  $\delta$  7.33-7.19 (m, 5H), 4.21 (dt,  $J = 1.9$  and 6.9 Hz, 1H), 3.87-3.75 (m, 1H), 3.48-3.37 (m, 1H), 3.11-2.93 (m, 2H), 2.41 (d,  $J = 1.9$  Hz, 1H), 1.20 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  137.2, 129.6, 128.1, 126.6, 82.7, 74.1, 70.3, 64.5, 42.2, 15.0. HRMS (EI) Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}$  [M]: 174.1045. Found: 174.1040.  $[\alpha]^{25}_D = -23.3$  ( $c = 0.800$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **4f** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH} = 100/0$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 12.9 min (major) and 18.3 min (minor), 93% *ee*.

### Synthesis of Triazole **2e'** from **2e**.



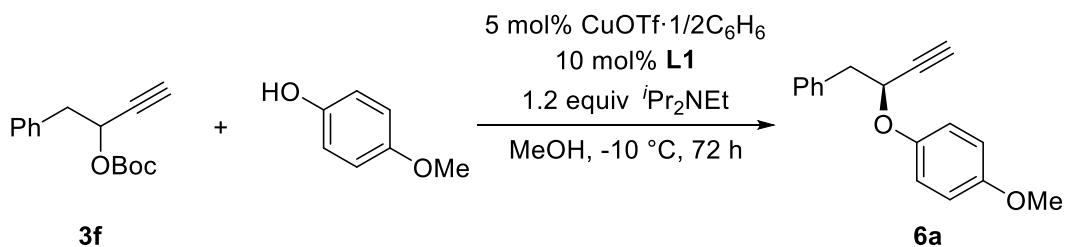
In a 20 mL Schlenk flask were placed 3-methoxydodec-1-yne (**2e**) (30.1 mg, 0.153 mmol), CuI (4.5 mg, 0.024 mmol), and anhydrous THF (1.5 mL) under  $\text{N}_2$ . Diisopropylethylamine (54.0  $\mu\text{L}$ , 0.310 mmol) and benzyl azide (22.5 mg, 0.169 mmol) were added to the solution at room temperature and the mixture was stirred for 28 h. Then, saturated aqueous  $\text{NH}_4\text{Cl}$  (5 mL) was added to the solution. The solution was extracted with diethyl ether (10 mL x 3) and the combined organic layers were dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography ( $\text{SiO}_2$ ) with hexane/ethyl acetate (75/25) to give 1-benzyl-4-(1-methoxydecyl)-1*H*-1,2,3-triazole (**2e'**) as a white solid (46.8 mg, 0.142 mmol, 93% yield), m.p. 52.6-54.5  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR  $\delta$  7.38-7.36 (m, 4H), 7.28-7.25 (m, 2H), 5.53 (s, 2H), 4.41 (t,  $J = 6.5$  Hz, 1H), 3.26 (s, 3H), 1.82-1.69 (m, 2H), 1.23 (br, 14H), 0.87 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  150.1, 134.7, 129.1, 128.7, 128.0, 120.7, 76.5, 56.8, 54.2, 35.9, 31.9, 29.5, 29.4, 29.3, 25.4, 22.7, 14.1. Anal. Calcd. for  $\text{C}_{20}\text{H}_{31}\text{N}_3\text{O}$ : C, 72.91; H, 9.48; N, 12.75. Found: C, 72.74; H, 9.23; N, 12.53.  $[\alpha]^{25}_D = -21.6$  ( $c = 0.105$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **2e'** was determined by HPLC analysis; DAICEL Chiralpak ID, hexane/ $^i\text{PrOH} = 85/15$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 12.1 min (major) and 16.2 min (minor), 80% *ee*.

**Copper-Catalyzed Enantioselective Propargylic Etherification of Propargylic Acetate (**1a**) with Methanol.**



In a 20 mL Schlenk flask were placed  $\text{CuOTf}\cdot 1/2\text{C}_6\text{H}_6$  (2.7 mg, 0.011 mmol) and (*S*)-Me-pybox (**L1**) (5.0 mg, 0.020 mmol) under  $\text{N}_2$ . Anhydrous methanol (1.0 mL) was added, and the mixture was magnetically stirred at 60 °C for 1 h. After the solution was cooled to -20 °C, **1a** (34.9 mg, 0.200 mmol) in anhydrous methanol (1.0 mL) and diisopropylethylamine (42.0  $\mu\text{L}$ , 0.240 mmol) were added under  $\text{N}_2$ , and the mixture was kept at -20 °C for 72 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by the column chromatography ( $\text{SiO}_2$ ) with hexane/diethyl ether (96/4) to give 1-methoxy-1-phenylprop-2-yne (**2a**)<sup>S11</sup> as a pale yellow oil (21.1 mg, 0.144 mmol, 72% yield).  $[\alpha]^{25}_D = -34.6$  ( $c = 0.495$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **2a** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $i\text{PrOH} = 97/3$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 15.6 min (minor) and 20.4 min (major), 71% *ee*.

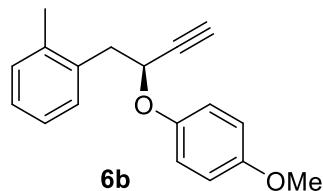
**Copper-Catalyzed Enantioselective Propargylic Etherification of Propargylic Carbonates (**3**) with Phenols.**



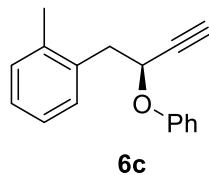
A typical experimental procedure for the reaction of *tert*-butyl (1-phenylbut-3-yn-2-yl) carbonate (**3f**) with 4-methoxyphenol is described below. In a 20 mL Schlenk flask were placed  $\text{CuOTf}\cdot 1/2\text{C}_6\text{H}_6$  (2.5 mg, 0.0099 mmol) and (*S*)-Me-pybox (**L1**) (5.0 mg, 0.020 mmol) under  $\text{N}_2$ . Anhydrous methanol (2.0 mL) was added, and the mixture was magnetically stirred at 60 °C for 1 h. After the solution was cooled to -10 °C, 4-methoxyphenol (49.4 mg, 0.398 mmol), **3f** (48.9 mg, 0.199 mmol), and diisopropylethylamine (42.0  $\mu\text{L}$ , 0.240 mmol) were added under  $\text{N}_2$ , and the mixture was kept at -10 °C for 72 h. The solvent was concentrated under reduced pressure, and the residue was purified by the column chromatography ( $\text{SiO}_2$ ) with hexane/diethyl ether (95/5) to give 4-methoxyphenyl 1-phenylbut-3-yn-2-yl ether (**6a**) as a colorless oil (38.0 mg, 0.151 mmol, 76% yield).  $^1\text{H NMR}$   $\delta$  7.35-7.21 (m, 5H), 6.95-6.89 (m, 2H), 6.83-6.77 (m, 2H), 4.79 (td,  $J = 6.6$  and 1.9 Hz, 1H), 3.75 (s, 3H), 3.27 (dd,  $J =$

13.6 and 6.6 Hz, 1H), 3.17 (dd,  $J$  = 13.6 and 6.6 Hz, 1H), 2.48 (d,  $J$  = 1.9 Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  154.6, 151.5, 136.5, 129.7, 128.3, 126.9, 117.4, 114.5, 81.9, 75.2, 69.9, 55.6, 42.1. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_2$  [M]: 252.1150. Found: 252.1146.  $[\alpha]^{25}_{\text{D}} = -100.7$  ( $c$  = 0.775,  $\text{CHCl}_3$ ). The enantiomeric excess of **6a** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH}$  = 95/5, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 20.4 min (major) and 24.5 min (minor), 97% *ee*.

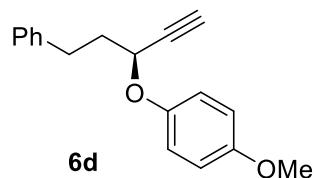
Isolated yields and spectroscopic data of other products (**6**) are described below:



**6b:** 69% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.32-7.25 (m, 1H), 7.20-7.13 (m, 3H), 6.94-6.88 (m, 2H), 6.83-6.77 (m, 2H), 4.79 (td,  $J$  = 6.9 and 2.0 Hz, 1H), 3.75 (s, 3H), 3.31 (dd,  $J$  = 14.0 and 6.9 Hz, 1H), 3.20 (dd,  $J$  = 14.0 and 6.9 Hz, 1H), 2.48 (d,  $J$  = 2.0 Hz, 1H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR  $\delta$  154.6, 151.5, 136.8, 134.9, 130.3, 130.2, 127.0, 125.8, 117.3, 114.4, 82.0, 75.0, 69.4, 55.6, 39.2, 19.7. HRMS (EI) Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_2$  [M]: 266.1307. Found: 266.1303.  $[\alpha]^{25}_{\text{D}} = -96.6$  ( $c$  = 1.50,  $\text{CHCl}_3$ ). The enantiomeric excess of **6b** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH}$  = 95/5, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 15.9 min (major) and 19.7 min (minor), 98% *ee*.

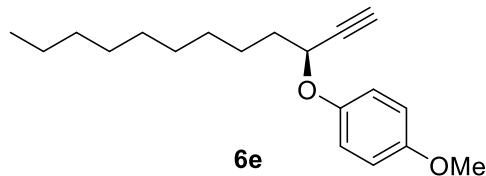


**6c:** 66% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.32-7.23 (m, 3H), 7.17-7.13 (m, 3H), 7.00-6.93 (m, 3H), 4.89 (td,  $J$  = 6.9 and 1.9 Hz, 1H), 3.34 (dd,  $J$  = 14.0 and 7.0 Hz, 1H), 3.23 (dd,  $J$  = 14.0 and 7.0 Hz, 1H), 2.48 (d,  $J$  = 1.9 Hz, 1H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR  $\delta$  157.4, 136.8, 134.7, 130.4, 130.3, 129.3, 127.0, 125.6, 121.5, 115.8, 81.8, 75.2, 68.1, 39.1, 19.7. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}$  [M]: 236.1201. Found: 236.1200.  $[\alpha]^{25}_{\text{D}} = -88.2$  ( $c$  = 0.910,  $\text{CHCl}_3$ ). The enantiomeric excess of **6c** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH}$  = 95/5, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 8.6 min (major) and 9.3 min (minor), 99% *ee*.

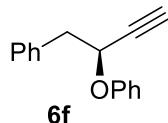


**6d:** 88% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.32-7.17 (m, 5H), 6.98-6.91 (m, 2H), 6.86-6.80 (m, 2H), 4.61 (td,  $J$  = 6.8 and 2.0 Hz, 1H), 3.76 (s, 3H), 2.89 (t,  $J$  = 7.7 Hz, 2H), 2.49 (d,  $J$  = 2.0 Hz, 1H), 2.35-

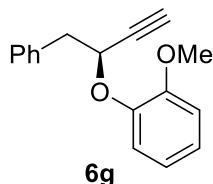
2.12 (m, 2H).  $^{13}\text{C}$  NMR  $\delta$  154.5, 151.5, 140.9, 128.53, 128.46, 126.1, 117.2, 114.5, 82.2, 74.7, 67.8, 55.6, 37.3, 31.2. HRMS (EI) Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_2$  [M]: 266.1307. Found: 266.1305.  $[\alpha]^{25}_{\text{D}} = -89.5$  ( $c = 1.60$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6d** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH}$  = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 16.7 min (major) and 32.4 min (minor), 91% *ee*.



**6e:** 69% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  6.99-6.93 (m, 2H), 6.86-6.80 (m, 2H), 4.62 (td,  $J = 6.8$  and 2.0 Hz, 1H), 3.77 (s, 3H), 2.46 (d,  $J = 2.0$  Hz, 1H), 1.99-1.83 (m, 2H), 1.58-1.48 (m, 2H), 1.31-1.27 (m, 12H), 0.91-0.86 (m, 3H).  $^{13}\text{C}$  NMR  $\delta$  154.4, 151.7, 117.2, 114.5, 82.6, 74.2, 68.8, 55.7, 35.8, 31.9, 29.51, 29.49, 29.3, 29.2, 25.1, 22.7, 14.1. HRMS (EI) Calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_2$  [M]: 288.2089. Found: 288.2095.  $[\alpha]^{25}_{\text{D}} = -101.6$  ( $c = 1.28$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6e** was determined by HPLC analysis; DAICEL Chiralcel OD, hexane/ $^i\text{PrOH}$  = 99/1, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 4.6 min (major) and 5.1 min (minor), 93% *ee*.

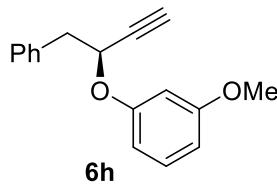


**6f:** 82% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.37-7.21 (m, 7H), 7.01-6.94 (m, 3H), 4.89 (td,  $J = 6.8$  and 1.9 Hz, 1H), 3.30 (dd,  $J = 13.8$  and 6.8 Hz, 1H), 3.20 (dd,  $J = 13.8$  and 6.8 Hz, 1H), 2.49 (d,  $J = 1.9$  Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  157.3, 136.4, 129.7, 129.4, 128.3, 126.9, 121.6, 115.8, 81.6, 75.3, 68.7, 42.1. HRMS (EI) Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}$  [M]: 222.1045. Found: 222.1055.  $[\alpha]^{25}_{\text{D}} = -118.3$  ( $c = 1.19$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6f** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH}$  = 98/2, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 11.9 min (major) and 13.6 min (minor), 97% *ee*.

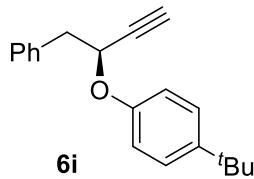


**6g:** 71% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.39-7.22 (m, 4H), 7.07-6.84 (m, 4H), 4.94 (td,  $J = 6.8$  and 2.2 Hz, 1H), 3.82 (s, 3H), 3.36 (dd,  $J = 13.5$  and 6.8 Hz, 1H), 3.23 (dd,  $J = 13.5$  and 6.8 Hz, 1H), 2.46 (d,  $J = 2.2$  Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  150.5, 146.7, 136.5, 129.8, 128.2, 126.8, 122.7, 120.7, 117.3, 112.4, 81.7, 75.5, 70.3, 56.0, 42.1. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_2$  [M]: 252.1150. Found: 252.1139.  $[\alpha]^{25}_{\text{D}} =$

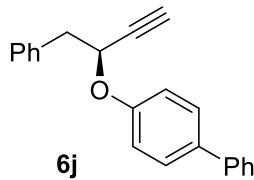
$-98.3$  ( $c = 1.67$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6g** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH} = 95/5$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 14.1 min (minor) and 14.9 min (major), 97% *ee*.



**6h:** 66% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.35-7.13 (m, 6H), 6.61-6.51 (m, 3H), 4.88 (td,  $J = 6.7$  and 1.9 Hz, 1H), 3.76 (s, 3H), 3.29 (dd,  $J = 13.6$  and 6.7 Hz, 1H), 3.18 (dd,  $J = 13.6$  and 6.7 Hz, 1H), 2.49 (d,  $J = 1.9$  Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  160.7, 158.5, 136.4, 129.75, 129.68, 128.3, 126.9, 107.8, 107.3, 102.2, 81.5, 75.4, 68.7, 55.2, 42.0. HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_2$  [M]: 252.1150. Found: 252.1160.  $[\alpha]^{25}_{\text{D}} = -135.4$  ( $c = 1.33$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6h** was determined by HPLC analysis; DAICEL Chiralcel OD, hexane/ $^i\text{PrOH} = 95/5$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 5.9 min (major) and 10.4 min (minor), 96% *ee*.

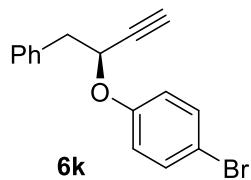


**6i:** 50% Yield. A colorless oil.  $^1\text{H}$  NMR  $\delta$  7.36-7.24 (m, 7H), 6.95-6.89 (m, 2H), 4.85 (td,  $J = 6.8$  and 2.0 Hz, 1H), 3.29 (dd,  $J = 13.9$  and 6.8 Hz, 1H), 3.18 (dd,  $J = 13.9$  and 6.8 Hz, 1H), 2.49 (d,  $J = 1.9$  Hz, 1H), 1.28 (s, 9H).  $^{13}\text{C}$  NMR  $\delta$  155.1, 144.2, 136.5, 129.7, 128.3, 126.9, 126.2, 115.7, 81.9, 75.2, 68.7, 42.1, 34.1, 31.5. HRMS (EI) Calcd. for  $\text{C}_{20}\text{H}_{22}\text{O}$  [M]: 278.1671. Found: 278.1682.  $[\alpha]^{25}_{\text{D}} = -105.3$  ( $c = 1.20$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6i** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/ $^i\text{PrOH} = 98/2$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time: 6.3 min (major) and 9.1 min (minor), 94% *ee*.



**6j:** 88% Yield. A white solid, m.p. = 52.9-53.8 °C.  $^1\text{H}$  NMR  $\delta$  7.46-7.39 (m, 4H), 7.34-7.12 (m, 8H), 7.00-6.94 (m, 2H), 4.84 (td,  $J = 6.8$  and 2.0 Hz, 1H), 3.24 (dd,  $J = 13.9$  and 6.8 Hz, 1H), 3.13 (dd,  $J = 13.9$  and 6.8 Hz, 1H), 2.42 (d,  $J = 2.0$  Hz).  $^{13}\text{C}$  NMR  $\delta$  156.9, 140.7, 136.4, 134.6, 129.7, 128.7, 128.3, 128.1, 126.9, 126.8, 126.7, 116.1, 81.6, 75.5, 68.8, 42.0. HRMS (EI) Calcd. for  $\text{C}_{22}\text{H}_{18}\text{O}$  [M]: 298.1358. Found: 298.1349.  $[\alpha]^{25}_{\text{D}} = -129.1$  ( $c = 2.03$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6j** was determined by

HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 26.2 min (major) and 60.2 min (minor), 96% *ee*.



**6k:** 57% Yield. A white solid, m.p. = 87.7–88.9 °C.  $^1\text{H}$  NMR  $\delta$  7.39–7.22 (m, 7H), 6.89–6.83 (m, 2H), 4.83 (td,  $J$  = 6.7 and 2.2 Hz, 1H), 3.28 (dd,  $J$  = 13.8 and 6.7 Hz, 1H), 3.19 (dd,  $J$  = 13.8 and 6.7 Hz, 1H), 2.50 (d,  $J$  = 2.2 Hz, 1H).  $^{13}\text{C}$  NMR  $\delta$  156.4, 136.2, 132.2, 129.7, 128.4, 127.0, 117.7, 113.9, 81.1, 75.7, 69.0, 42.0. HRMS (EI) Calcd. for  $\text{C}_{16}\text{H}_{13}\text{BrO}$  [M]: 300.0150. Found: 300.0143.  $[\alpha]^{25}_{\text{D}} = -104.4$  ( $c = 1.69$ ,  $\text{CHCl}_3$ ). The enantiomeric excess of **6k** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 9.1 min (major) and 12.5 min (minor), 98% *ee*.

### Investigation of Nonlinear Effect.

Experimental details of catalytic reactions of **3b** with methanol using **L1** with various *ee* values are summarized in Table S1.

**Table S1.** Nonlinear relationship between the *ee* value of **L1** and the *ee* value of **2b**.<sup>[a]</sup>

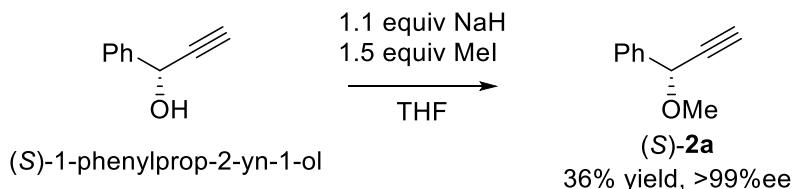
Entry	ee of <b>L1</b> (%)	Yield of <b>2b</b> (%) <sup>[b]</sup>	ee of <b>2b</b> (%) <sup>[c]</sup>
1	19	67	25
2	42	78	52
3	60	76	67
4	80	82	76
5	100	85	81

[a] Reactions of **3b** (0.20 mmol) in the presence of  $\text{CuOTf}\cdot 1/2\text{C}_6\text{H}_6$  (0.01 mmol), **L1** (0.02 mmol), and  $i\text{Pr}_2\text{NEt}$  (0.24 mmol) was carried out in  $\text{MeOH}$  (2 mL) at  $-10$  °C [b] Isolated yield. [c] Determined by HPLC.

### Synthesis of $[\text{Cu}_2(\text{L2})_2]\text{[OTf]}_2$ (5).

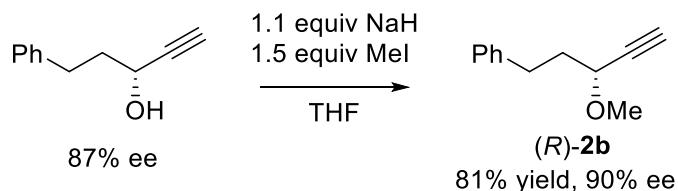
In a 50 mL Schlenk flask were placed  $\text{CuOTf} \cdot 1/2\text{C}_6\text{H}_6$  (125.6 mg, 0.499 mmol) and anhydrous  $\text{CH}_2\text{Cl}_2$  (25 mL) under  $\text{N}_2$ . (*S*)-Ph-pybox (**L2**) (185.0 mg, 0.501 mmol) was added to the solution, and then the mixture was magnetically stirred at room temperature for 1 h. The solution was concentrated *in vacuo* to about *ca.* 2 mL. Slow addition of diethyl ether (50 mL) to the obtained solution afforded a brown crystalline solid, which was collected by filtration and washed with diethyl ether (10 mL  $\times$  3) and dried *in vacuo* to afford  $[\text{Cu}_2(\text{L2})_2]\text{[OTf]}_2$  (**5a**)<sup>S12</sup> as a brown solid (249.6 mg, 0.214 mmol, 86% yield).

### Preparation of Optically Active Propargylic Ethers (*R*)-2a.



In a 20 mL Schlenk flask were placed sodium hydride (60% dispersion in paraffin liquid, 132 mg, 3.30 mmol) and anhydrous THF (15 mL) under  $\text{N}_2$ . (*S*)-1-Phenylprop-2-yn-1-ol (326 mg, 2.03 mmol) was added to the solution at 0 °C and the mixture was stirred at 0 °C for 30 min. Iodomethane (280  $\mu\text{L}$ , 4.50 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. Then, the reaction was quenched by saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL). The solution was extracted with diethyl ether (20 mL  $\times$  3) and the combined organic layers were dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography ( $\text{SiO}_2$ ) with hexane/ethyl acetate (97/3) to give (*S*)-1-methoxy-1-phenylprop-2-yne ((*S*)-**2a**) as a colorless oil (162 mg, 1.11 mmol, 37% yield).  $[\alpha]^{25}_D = +48.6$  ( $c = 0.530, \text{CHCl}_3$ ). The enantiomeric excess of (*S*)-**2a** was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254 \text{ nm}$ , retention time: 15.6 min (major; the peak of minor isomer was not observed), >99% *ee*.

### Preparation of Optically Active Propargylic Ethers (*R*)-2b.



In a 20 mL Schlenk flask were placed sodium hydride (60% dispersion in paraffin liquid, 89.3 mg, 2.23 mmol) and anhydrous THF (10 mL) under N<sub>2</sub>. (R)-5-phenylpent-1-yn-3-ol (326 mg, 2.03 mmol, 87% ee) was added to the solution at 0 °C and the mixture was stirred at 0 °C for 30 min. Iodomethane (190 µL, 2.99 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. Then, the reaction was quenched by saturated aqueous NH<sub>4</sub>Cl (10 mL). The solution was extracted with diethyl ether (10 mL x 3) and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO<sub>2</sub>) with hexane/ethyl acetate (97/3) to give (R)-(3-methoxypent-4-yn-1-yl)benzene ((R)-2b) as a colorless oil (286 mg, 1.64 mmol, 81% yield).  $[\alpha]^{25}_{\text{D}} = +13.8$  (*c* = 0.810, CHCl<sub>3</sub>). The enantiomeric excess of (R)-2b was determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/<sup>i</sup>PrOH = 97/3, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 6.9 min (major) and 7.6 min (minor), 90% ee.

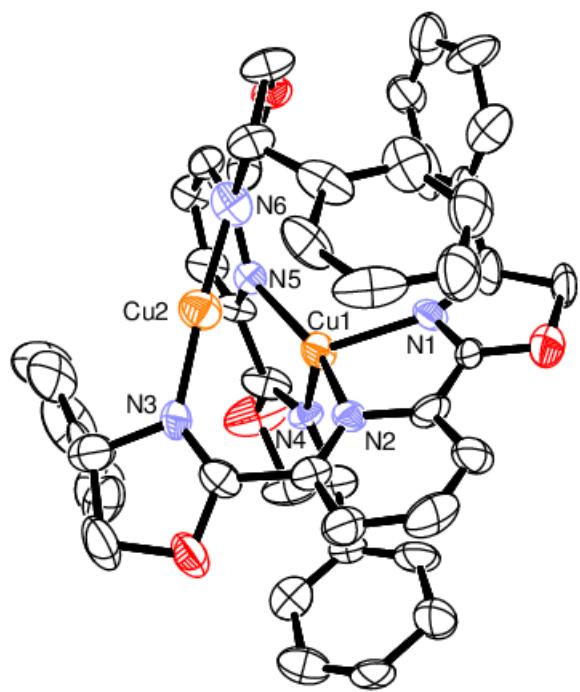
### X-ray Diffraction Studies.

Crystals of **5** and **6k** suitable for X-ray analyses were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O (**5**) and slow evaporation from Et<sub>2</sub>O (**6k**). Diffraction data were collected for the 2 $\theta$  range of 6 to 55° on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Cu-K $\alpha$  ( $\lambda$  = 0.71075 Å) radiation with VariMax optics. Intensity data were corrected for empirical absorptions, and for Lorentz and polarization effects. Structure solutions and refinements were carried out by using CrystalStructure package.<sup>S13</sup> The positions of non-hydrogen atoms were determined by direct methods (SHELX97 (**5**), SIR-97 (**6k**))<sup>S14</sup> and subsequent Fourier synthesis, and were refined on  $F_{\text{o}}^2$  using all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Anomalous dispersion effects were included in  $F_{\text{c}}$ , and neutral atom scattering factors and the values for  $\Delta f$  and  $\Delta f'$  were taken from ref. S15. ORTEP drawings of **5** and **6k** are depicted in Figures S1 and S2. Refinement of the Flack parameter<sup>S16</sup> for **6k** was refined to the value of 0.018(9), which clearly suggests that the absolute configuration of the major isomer of **6k** is (*S*) as shown in Figures S2. Details of the crystal and data collection parameters are summarized in Table S2.

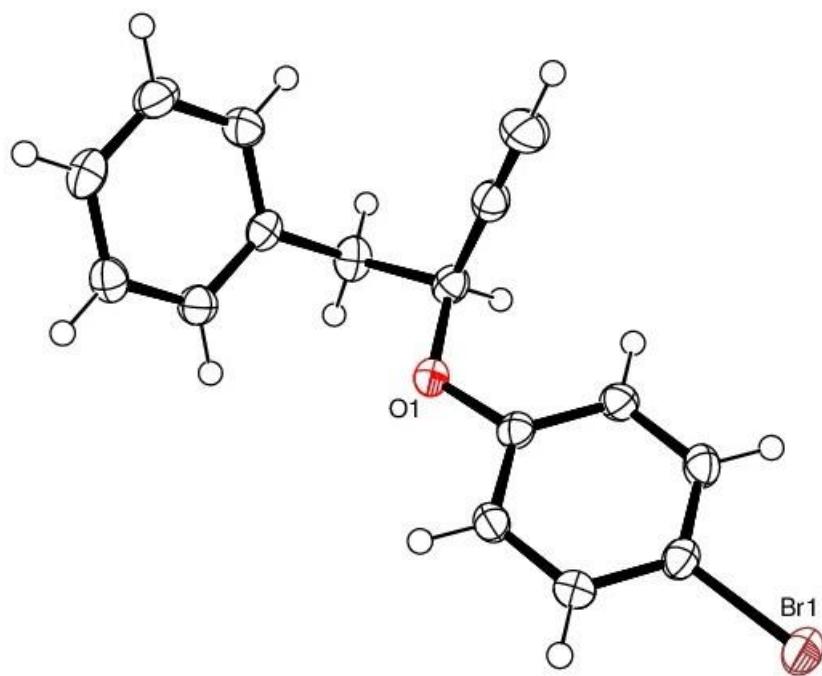
**Table S2.**

compound	<b>5</b>	<b>6k</b>
chemical formula	C <sub>48</sub> H <sub>39</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>6</sub> O <sub>10.50</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>13</sub> BrO
formula weight	1173.07	301.18
crystal size	0.34 x 0.21 x 0.18	0.20 x 0.10 x 0.05
crystal color, habit	orange, block	colorless, block
crystal system	orthorhombic	orthorhombic
space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
<i>a</i> (Å)	15.7607(8)	4.61(2)
<i>b</i> (Å)	16.9627(9)	10.41(3)
<i>c</i> (Å)	18.295(1)	27.47(7)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	90
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	4890.9(5)	1318(6)
<i>Z</i>	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.593	1.518
<i>F</i> (000)	2388.00	608.00
$\mu$ <sub>calcd</sub> (cm <sup>-1</sup> )	10.442	31.130
radiation	Mo-K $\alpha$ ( $\lambda$ = 0.71075 Å)	Mo-K $\alpha$ ( $\lambda$ = 0.71075 Å)
temperature (°C)	-150.0	-150.0
transmission factors rage	0.341-0.829	0.466-0.856
no. measured reflections	39722	12837
no. unique reflections	10707 ( <i>R</i> <sub>int</sub> = 0.0690)	2976 ( <i>R</i> <sub>int</sub> = 0.0451)
no. refined parameters	690	177
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.1089	0.0289
<i>wR</i> 2 (all data) <sup>b</sup>	0.1899	0.0669
GOF <sup>c</sup>	1.000	1.000
max/min residual peaks (e <sup>-</sup> /Å <sup>3</sup> )	+2.25/-1.62	+0.70/-0.49

<sup>a</sup>  $R$ 1 =  $\Sigma|F_o| - |F_c| / \Sigma|F_o|$ .<sup>b</sup>  $wR$ 2 =  $[\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$ ;  $w = 4F_o^2 / [pF_o^2 + q\sigma(F_o^2)]$ ;  $p = 0$  (**5**), 0.003 (**6k**);  $q = 7.92$  (**5**), 1 (**6k**).<sup>c</sup> GOF =  $[\Sigma w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$ .



**Figure S1.** ORTEP drawing of cationic part of **5**. All hydrogen atoms were omitted for clarity.



**Figure S2.** ORTEP drawing of **6k**.

## References and Notes.

(S1) Tse, M. K.; Bhor, S.; Klawonn, M.; Anilkumar, G.; Jiao, H.; Döbler, C.; Spannenberg, A.; Mägerlein, W.; Hugl, H.; Beller, M. *Chem. Eur. J.* **2006**, *12*, 1855.

(S2) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500.

(S3) Meng, J.-C.; Fokin, V. V.; Finn, M. G. *Tetrahedron Lett.* **2005**, *46*, 4543.

(S4) (a) Zhang, C.; Hu, X.-H.; Wang, Y.-H.; Zheng, Z.; Xu, J.; Hu, X.-P. *J. Am. Chem. Soc.* **2012**, *134*, 9585. (b) Zhu, F.-L.; Zou, Y.; Zhang, D.-Y.; Wang, Y.-H.; Hu, X. H.; Chen, S.; Xu, J.; Hu, X.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 1410.

(S5) Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777.

(S6) Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2012**, *134*, 8770.

(S7) (a) Molander, G. A.; Sommers, E. M. *Tetrahedron Lett.* **2005**, *46*, 2345. (b) Midland, M. M.; Tramontano, A.; Kazubski, A.; Graham, R. S.; Tsai, D. J. S.; Cardin, D. B. *Tetrahedron* **1984**, *40*, 1371.

(S8) Evans, P. A.; Lawler, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4970.

(S9) Yoshida, M.; Okada, T.; Shishido, K. *Tetrahedron* **2007**, *63*, 6996.

(S10) Harada, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, K.; Oku, A. *J. Am. Chem. Soc.* **1996**, *118*, 11377.

(S11) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019.

(S12) Panera, M.; Díez, J.; Merino, I.; Rubio, E.; Gamasa, M. P. *Inorg. Chem.* **2009**, *48*, 11147.

(S13) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

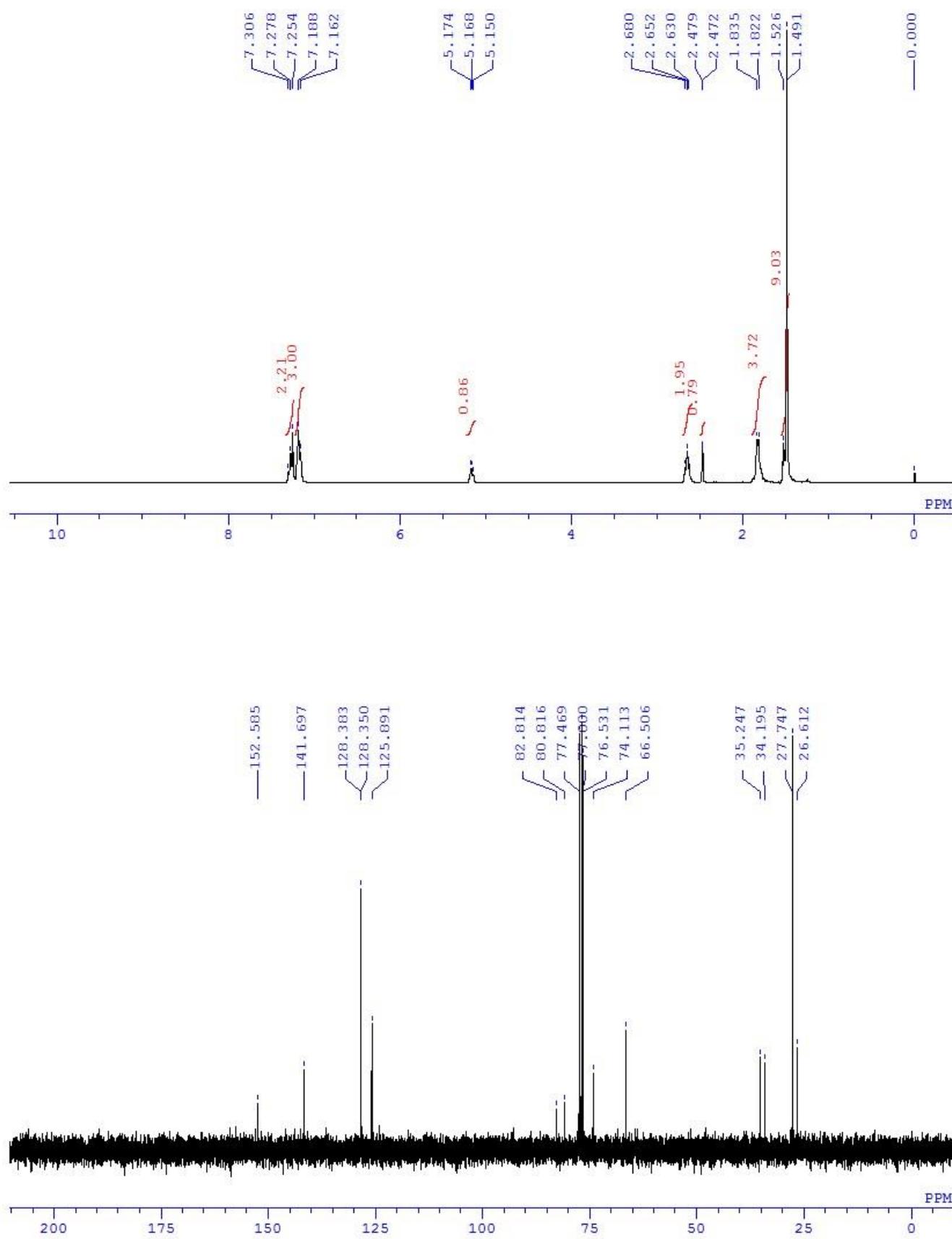
(S14) (a) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122. (b) Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.

(S15) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974). (b) Creagh, D. C.; McAuley, W. J. "International Tables for Crystallography", Vol C, (Wilson, A. J. C., ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

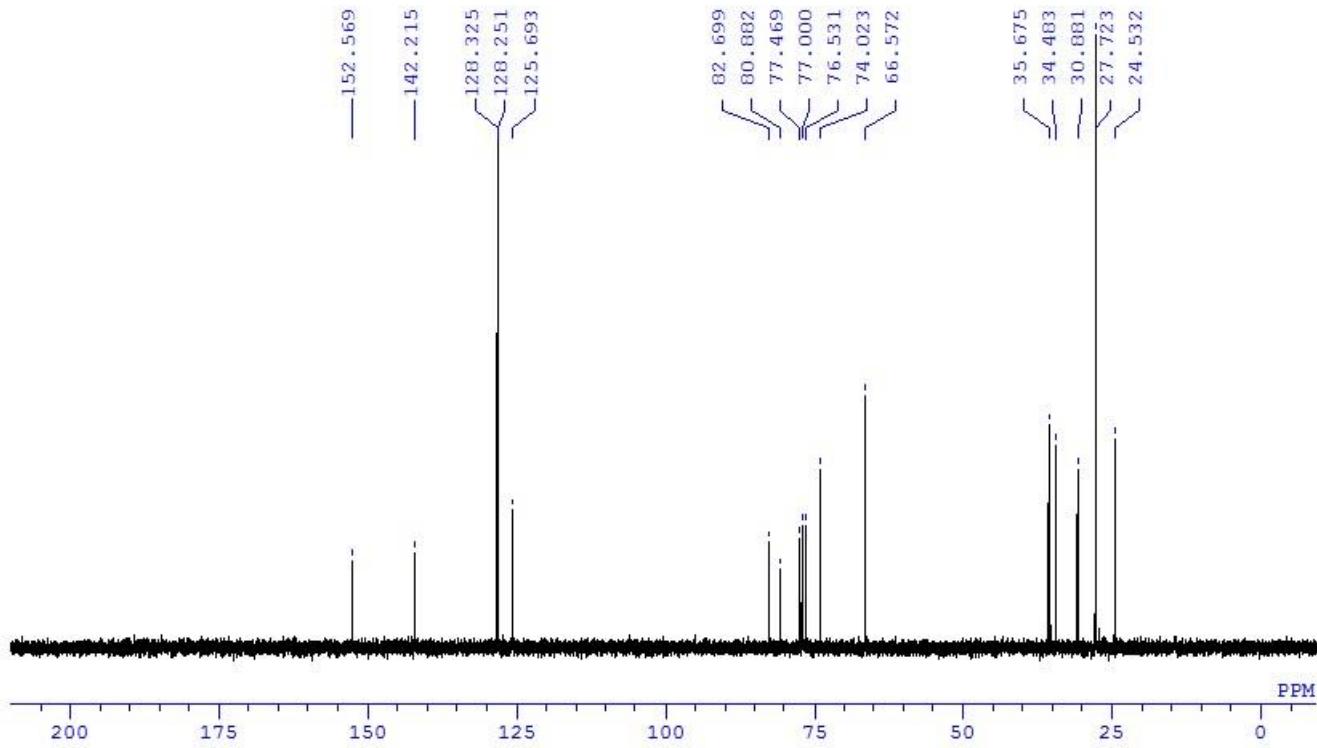
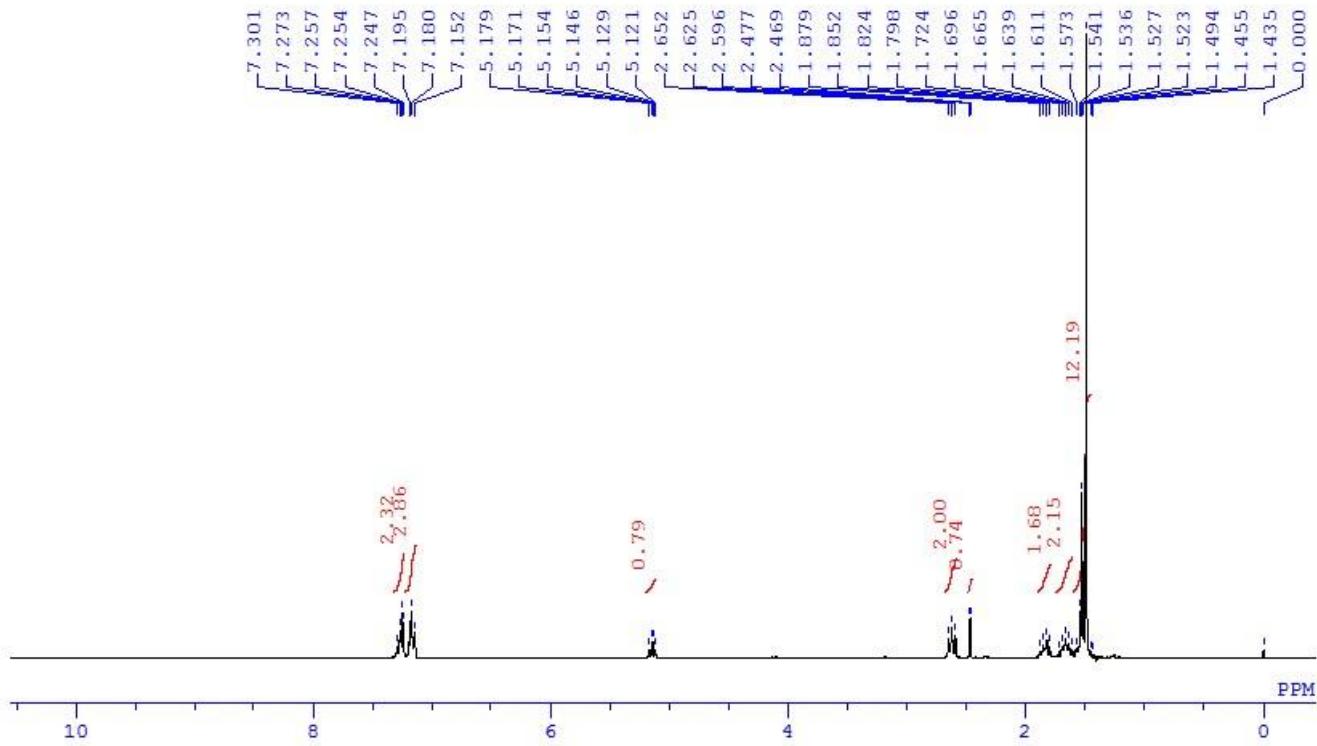
(S16) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

<sup>1</sup>H and <sup>13</sup>C NMR Spectra.

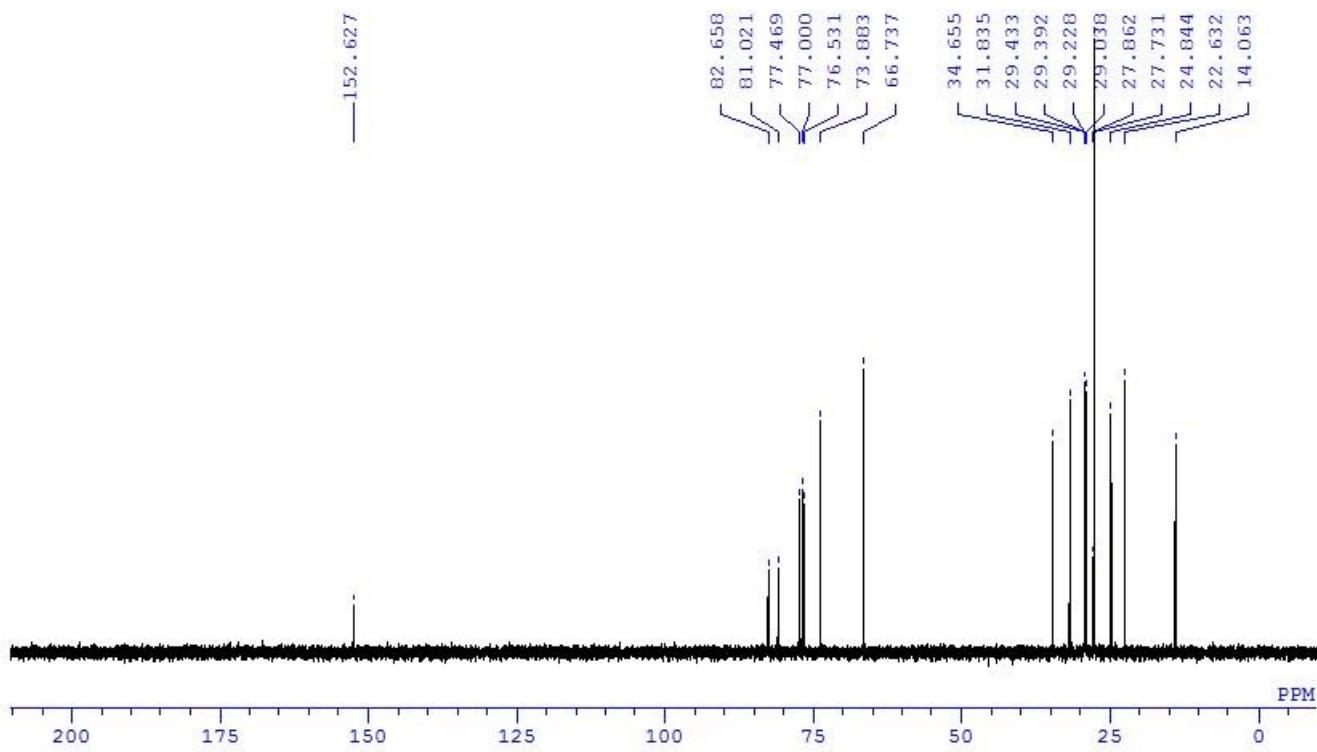
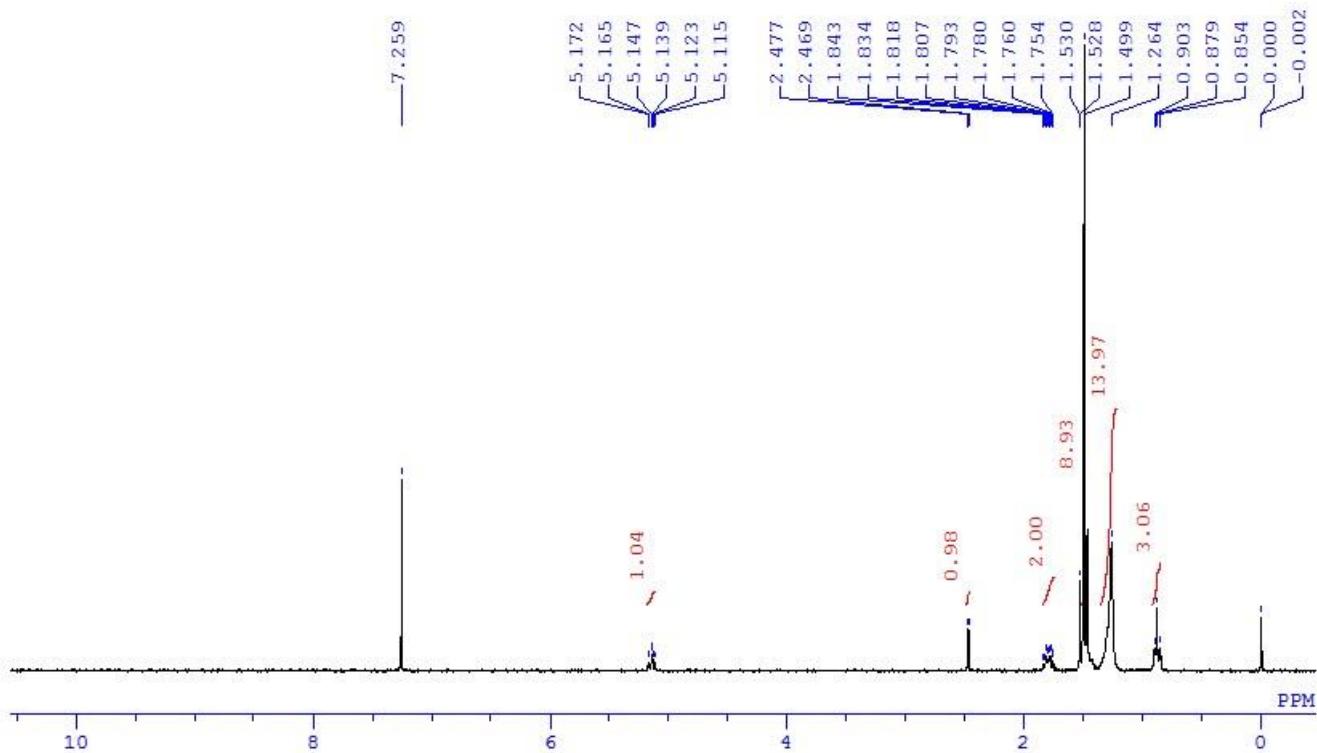
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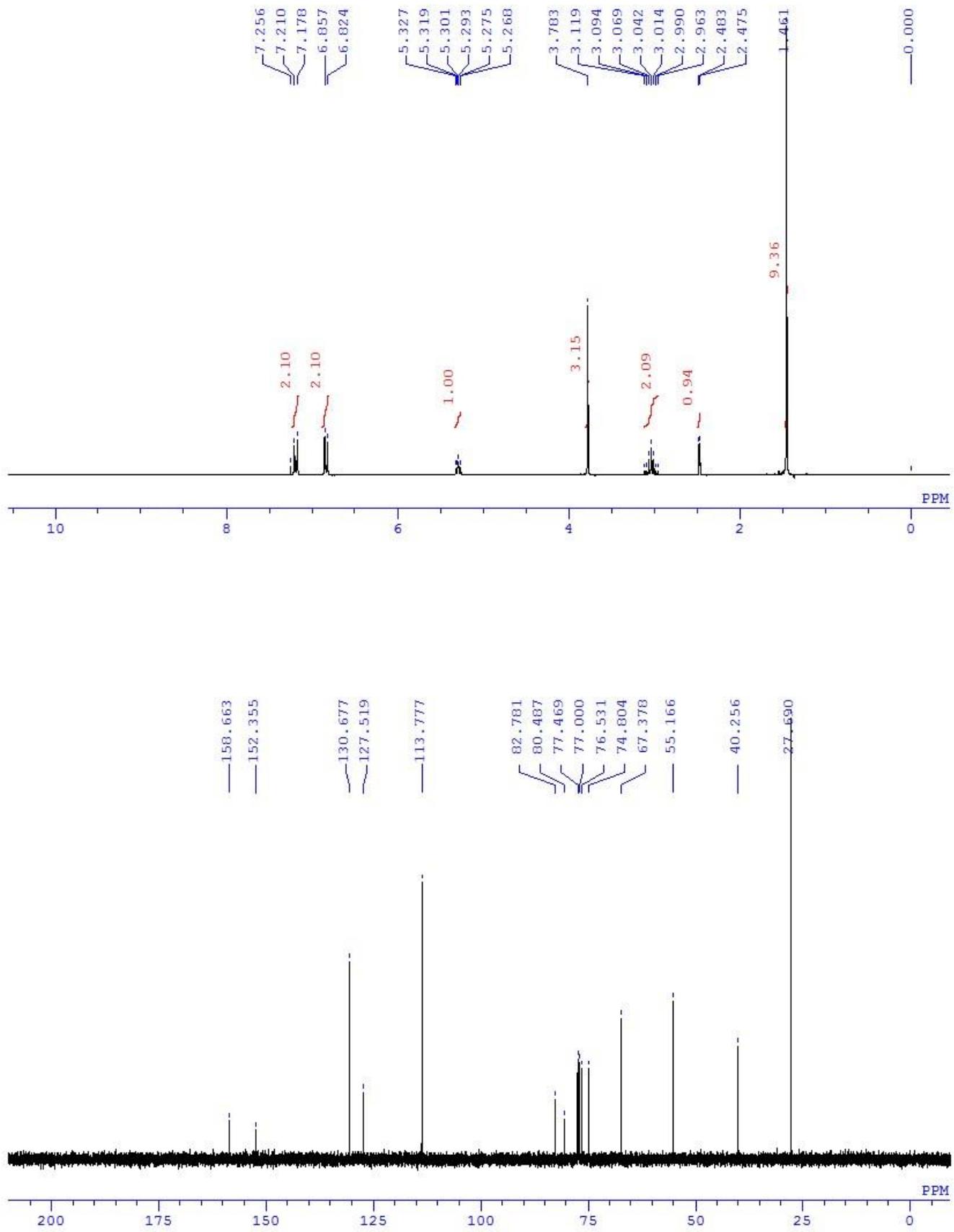
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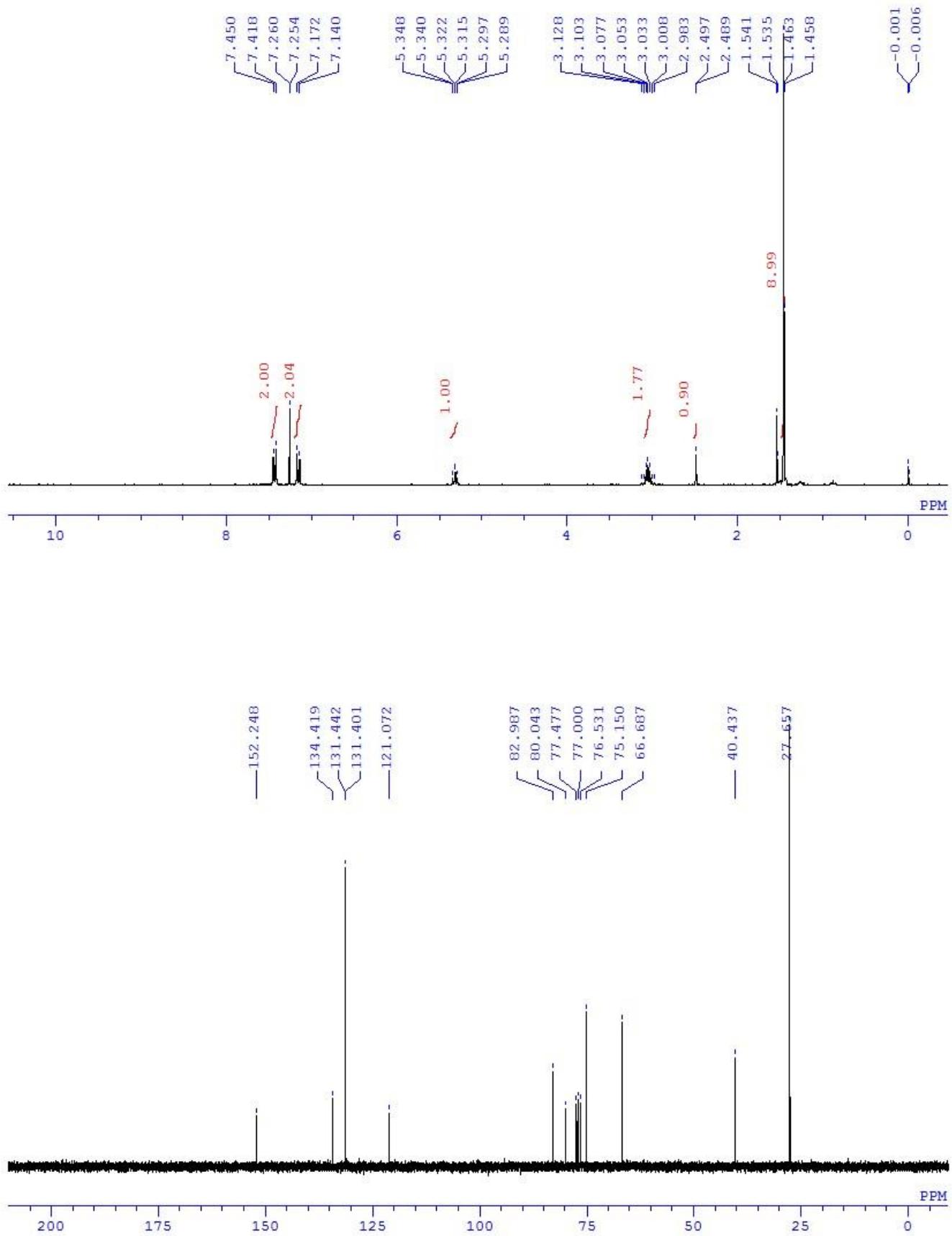
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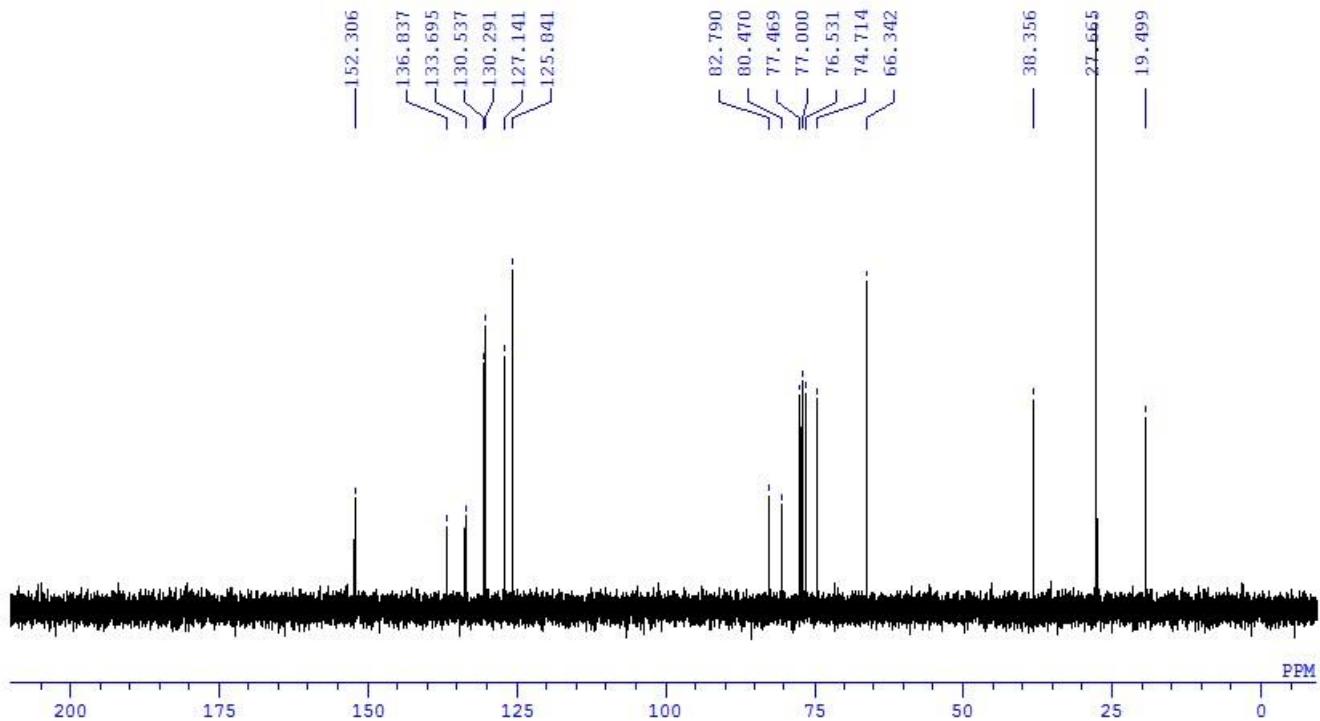
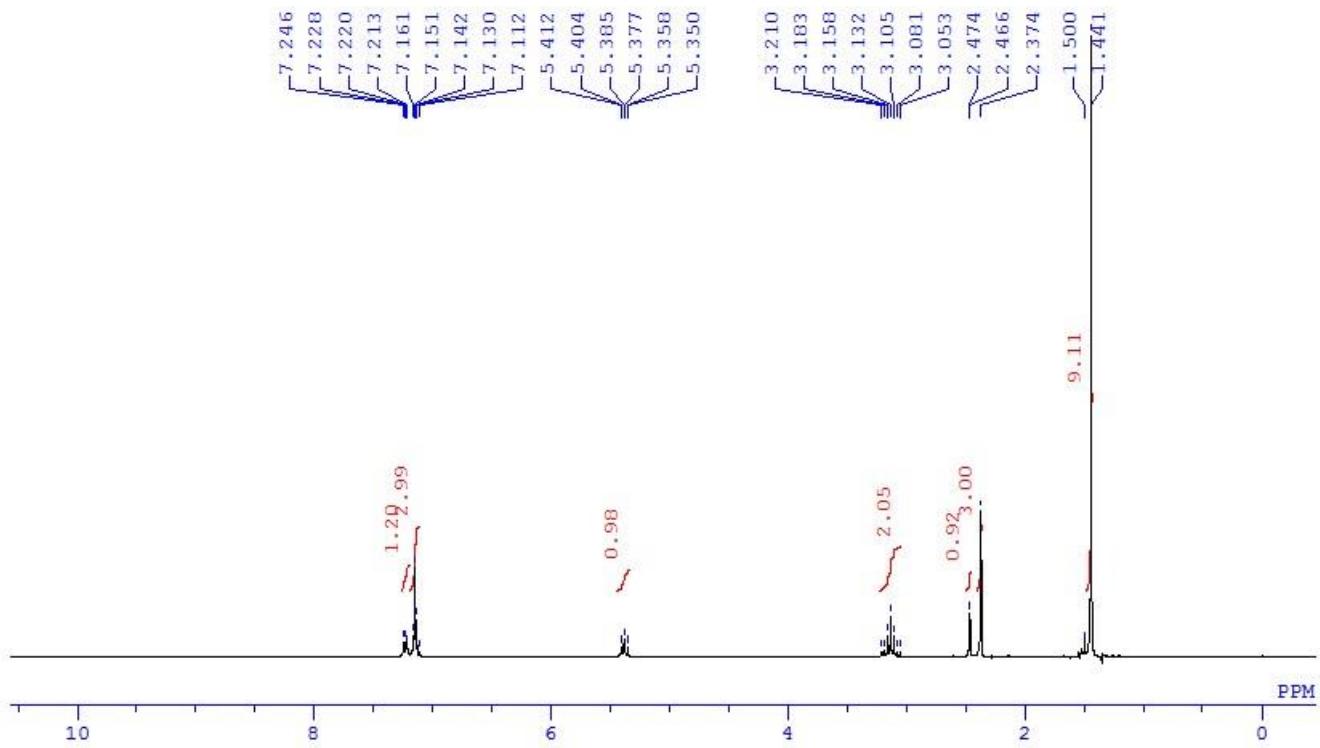
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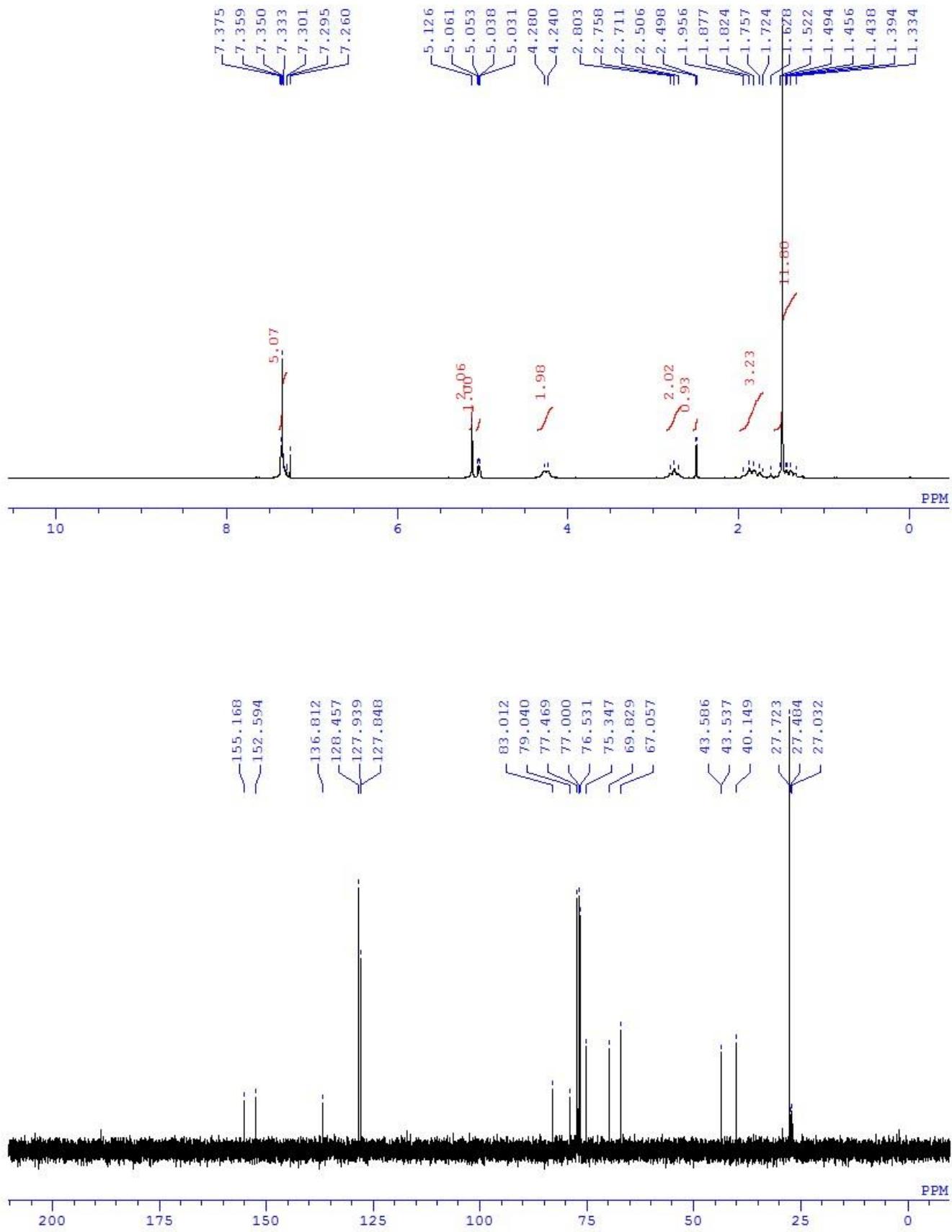
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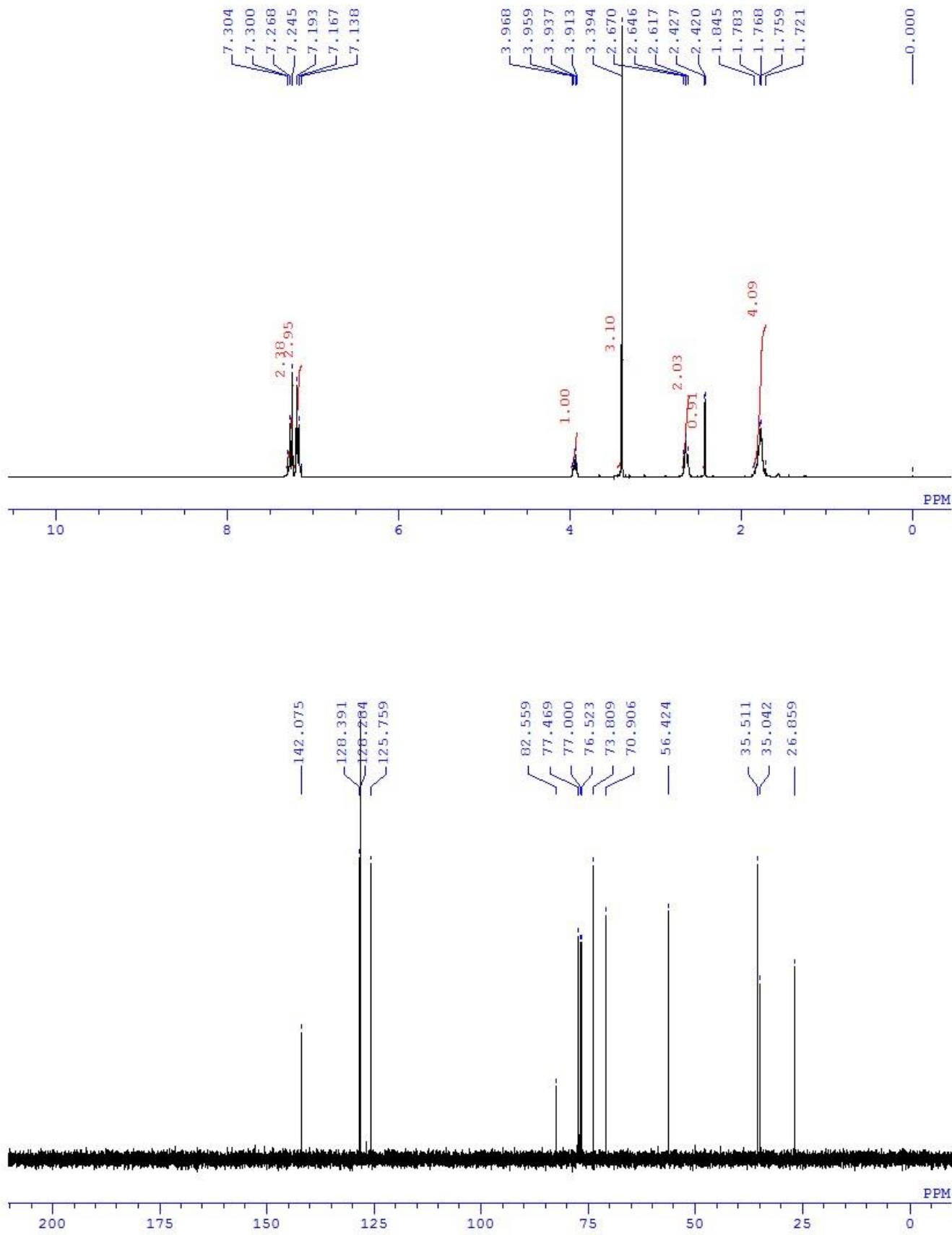
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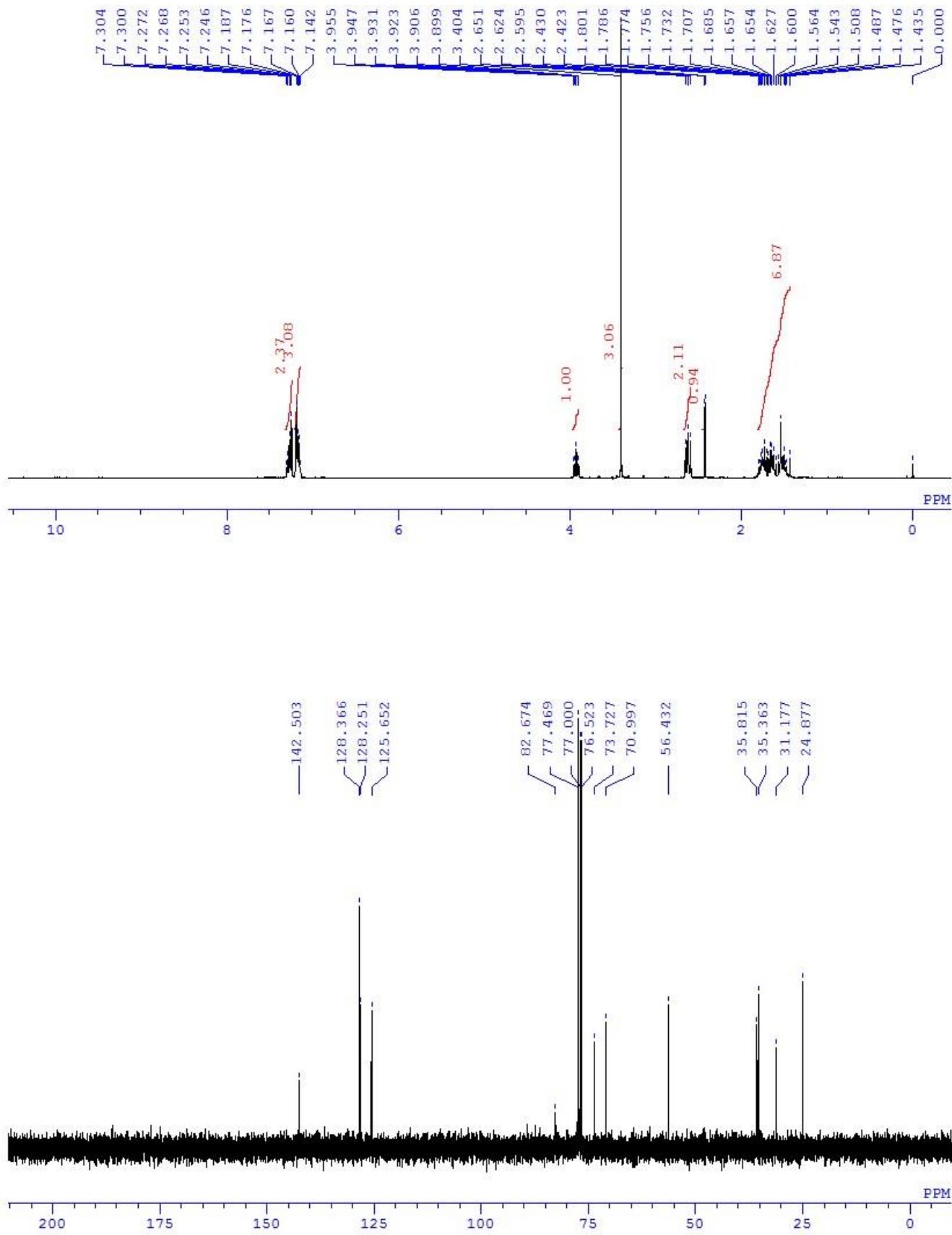
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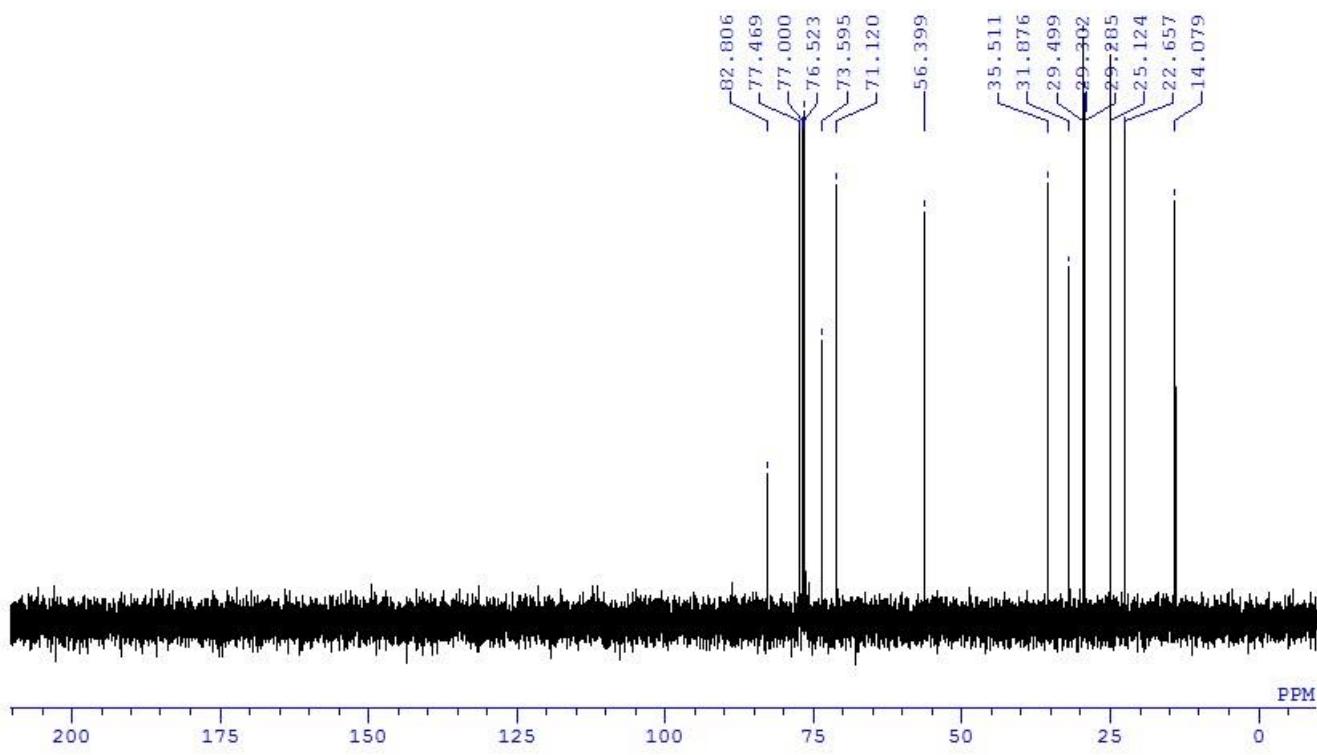
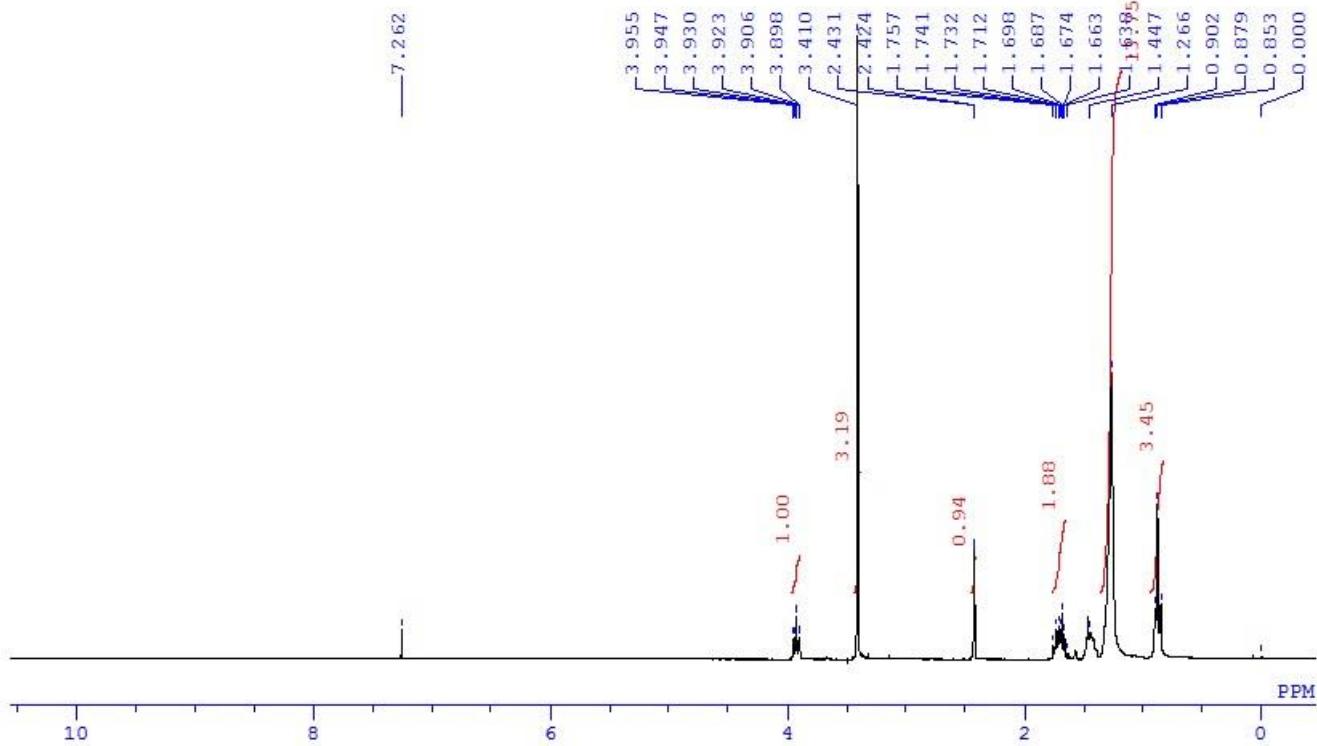
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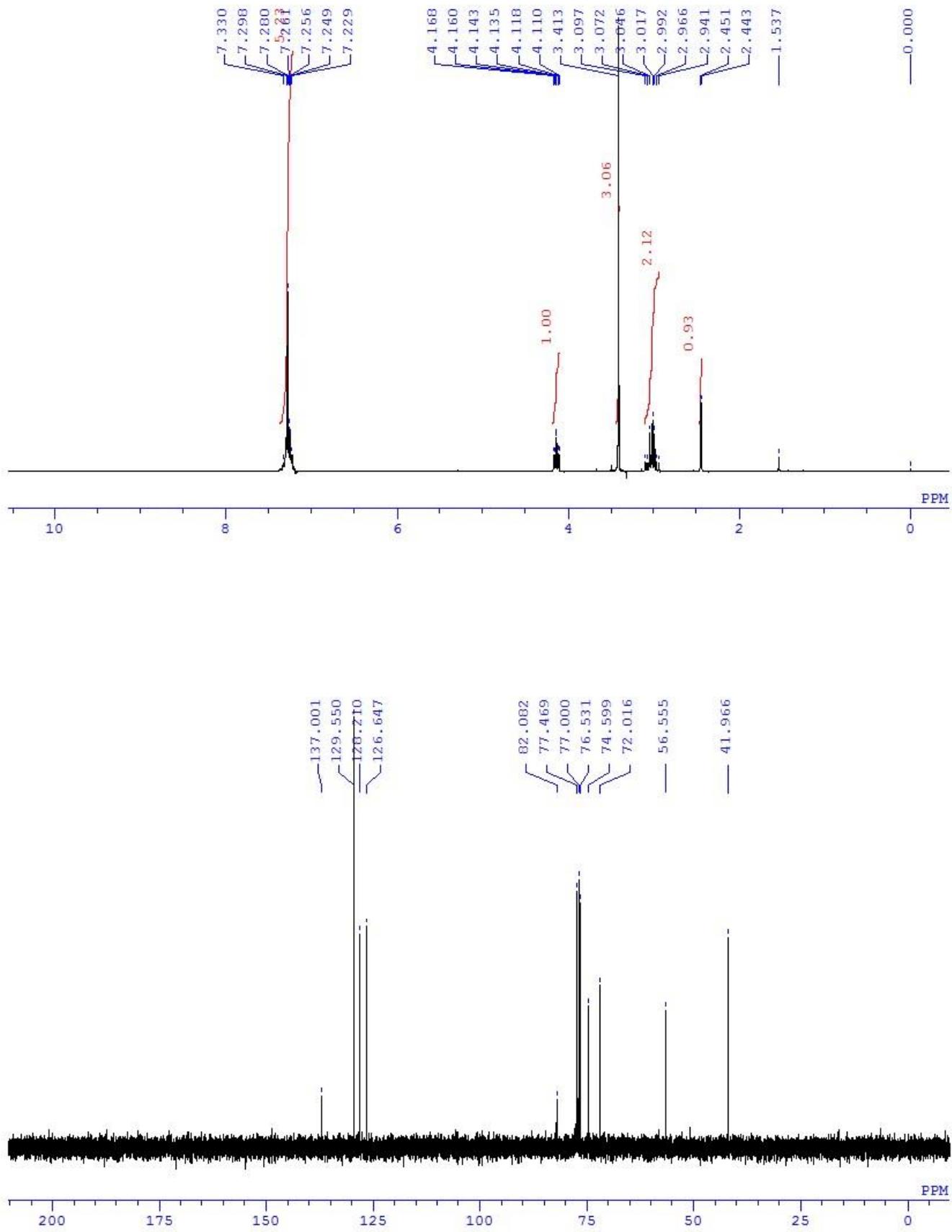
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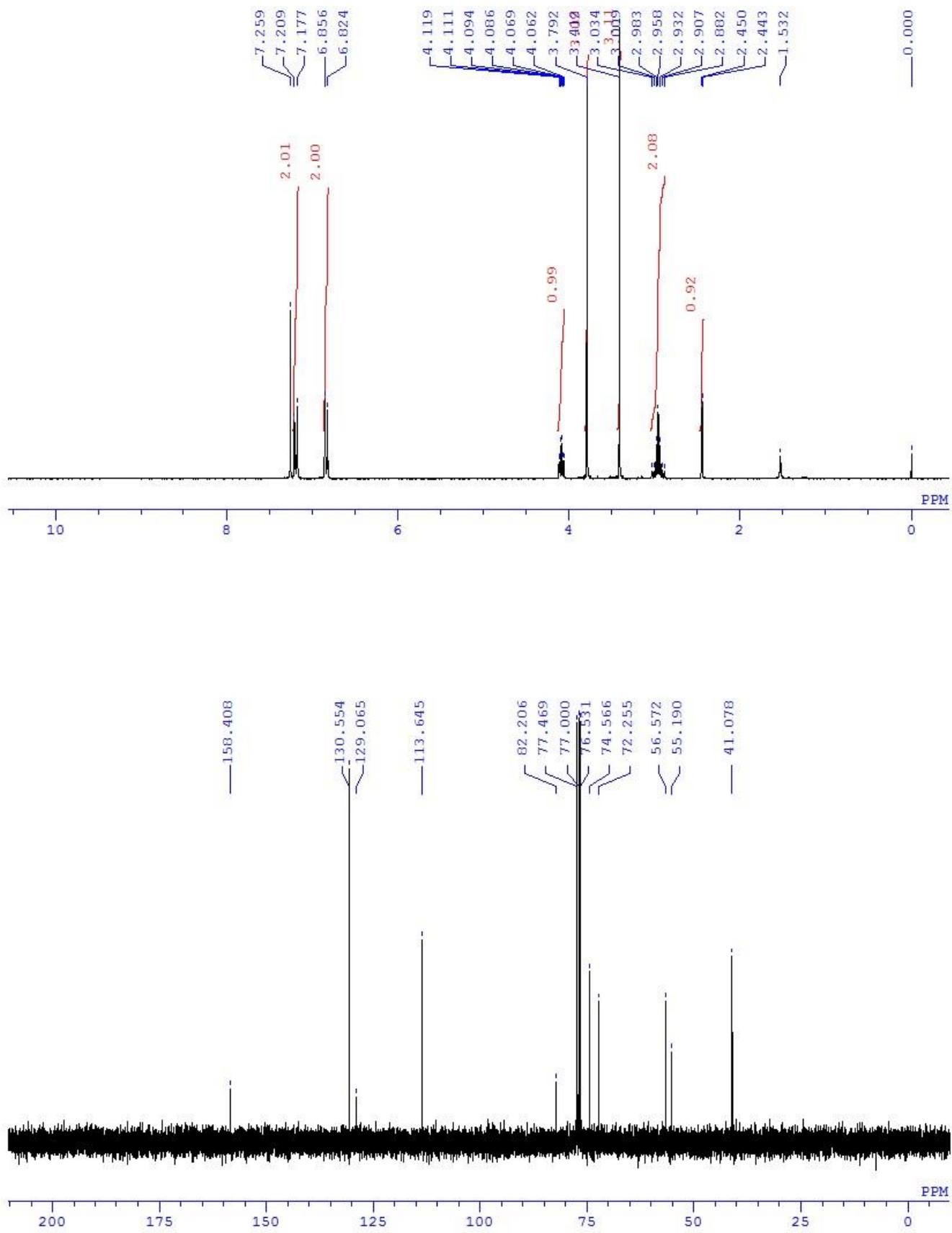
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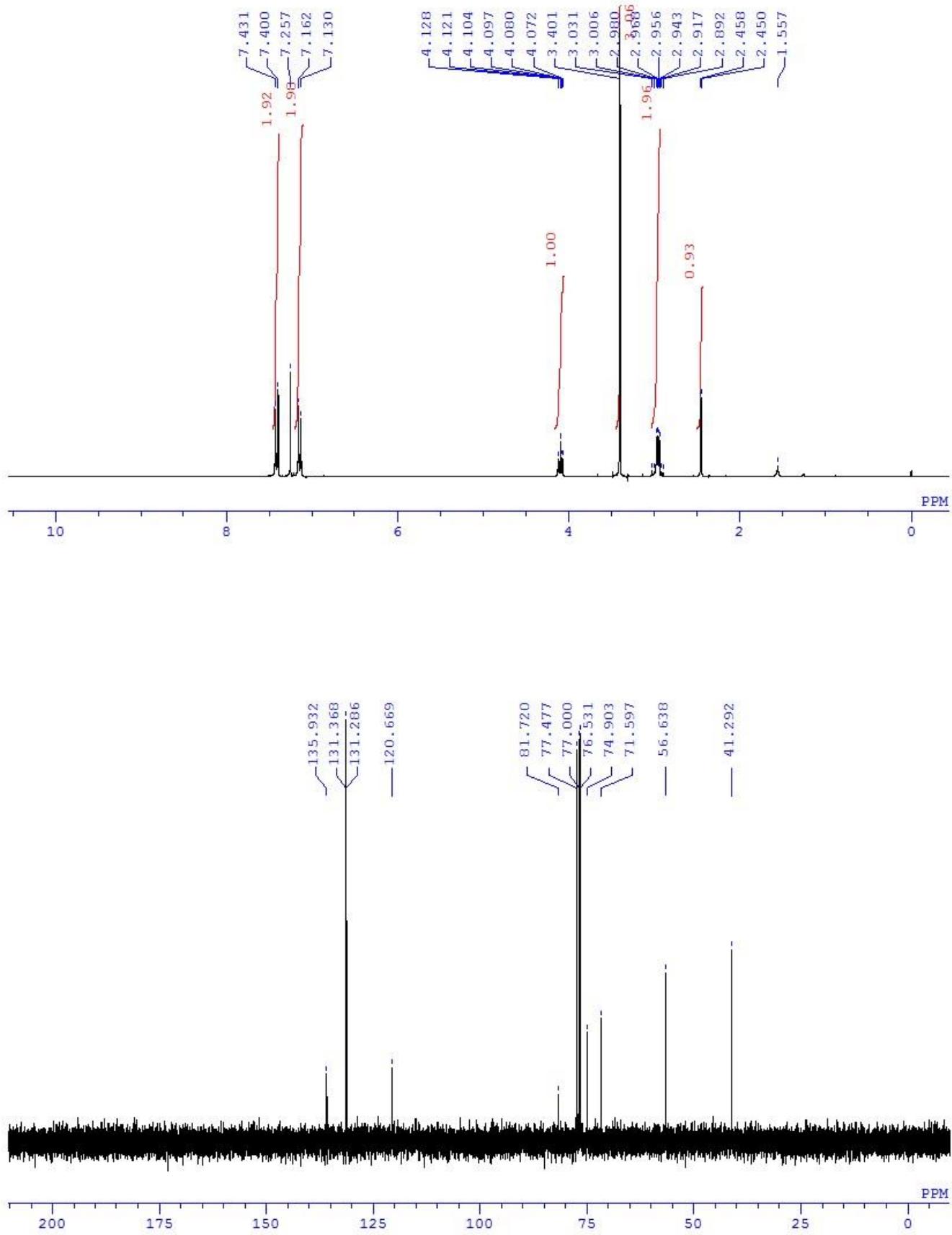
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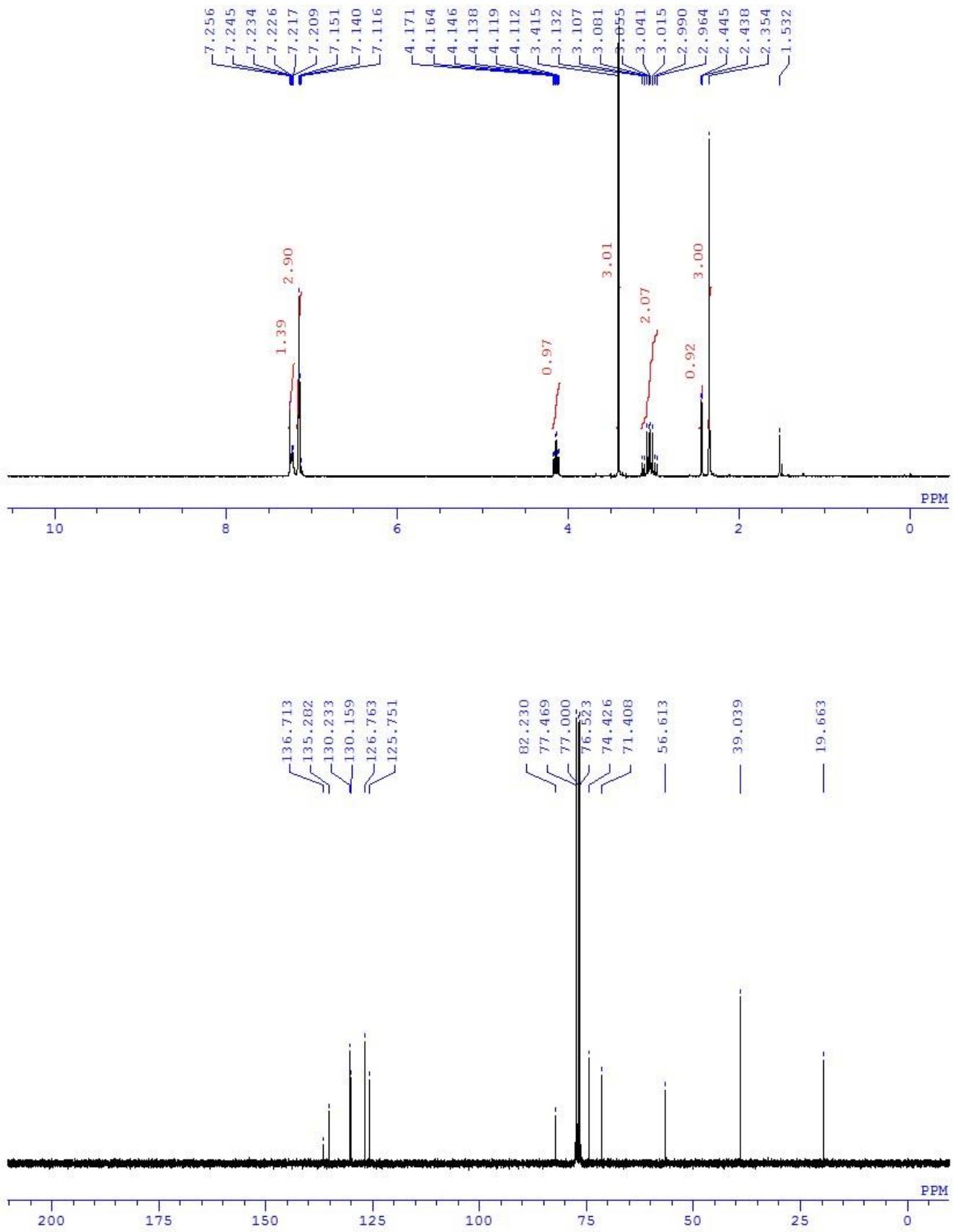
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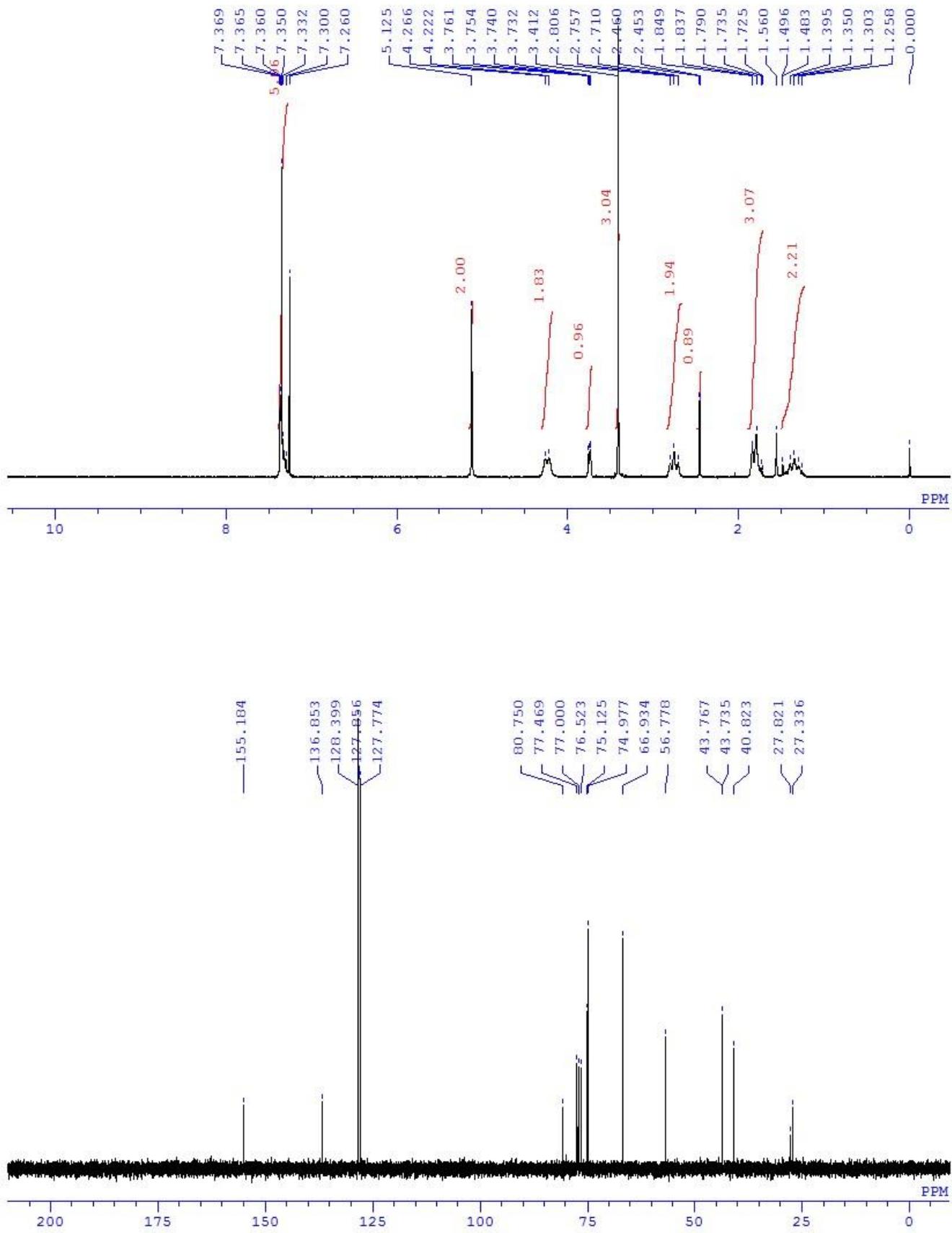
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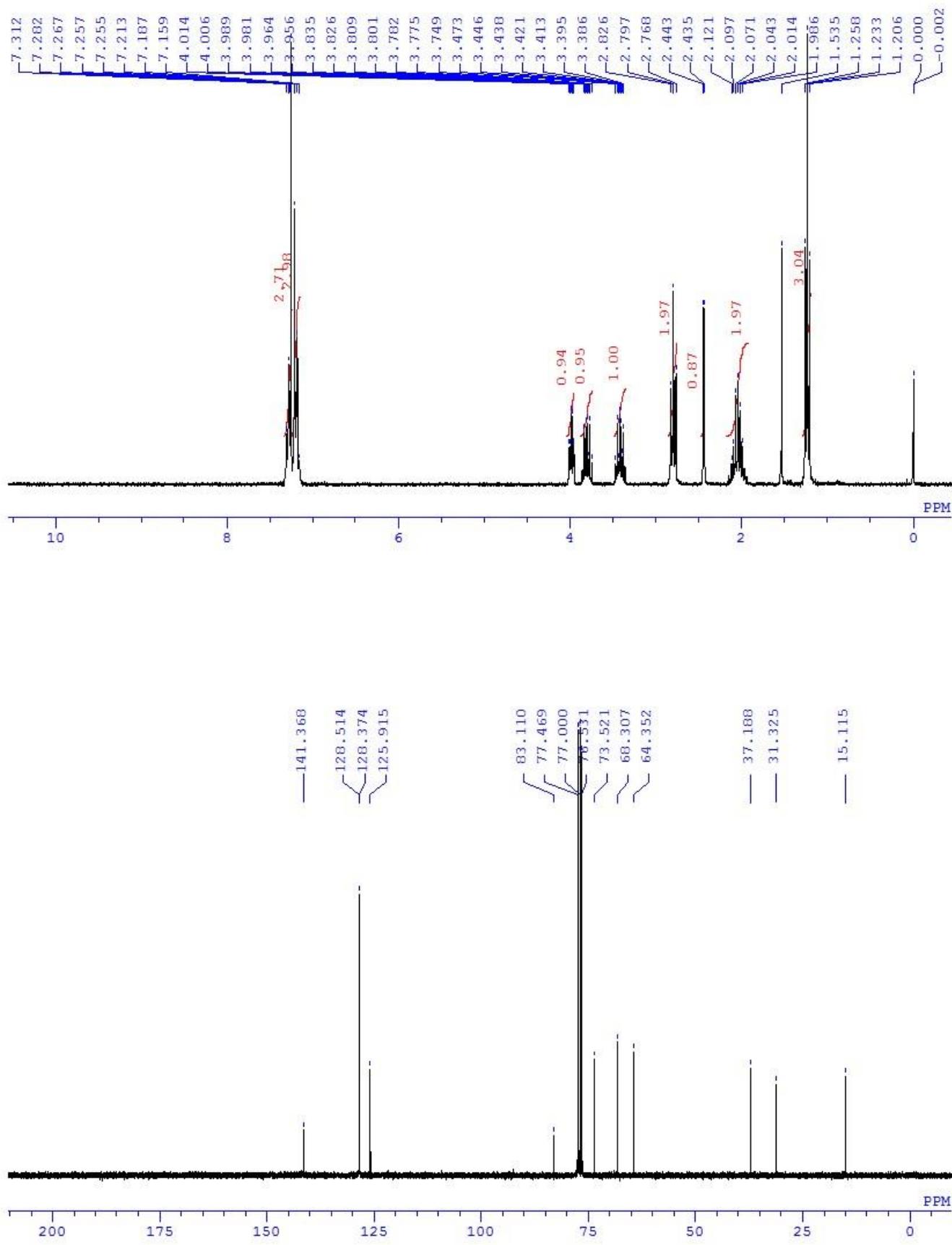
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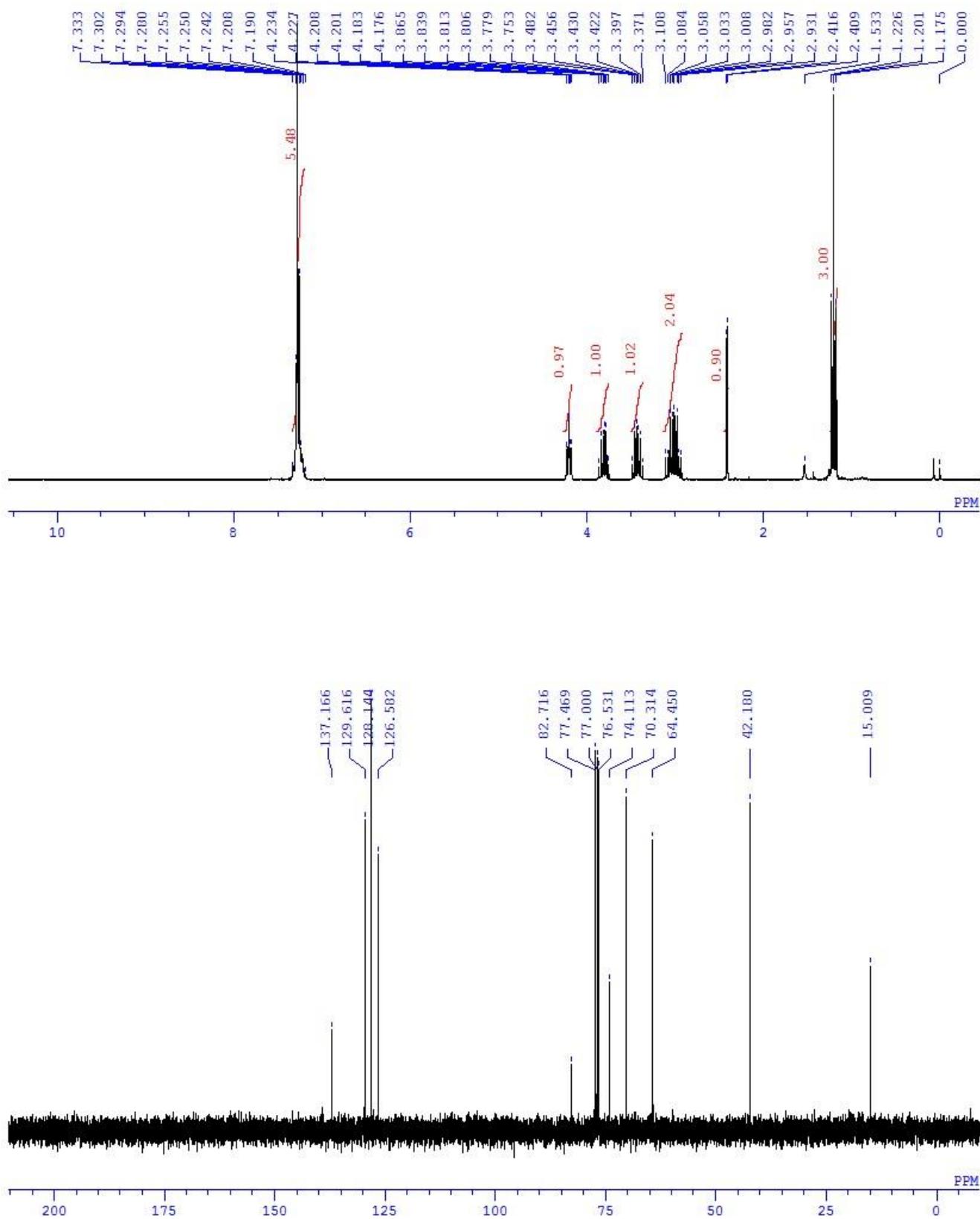
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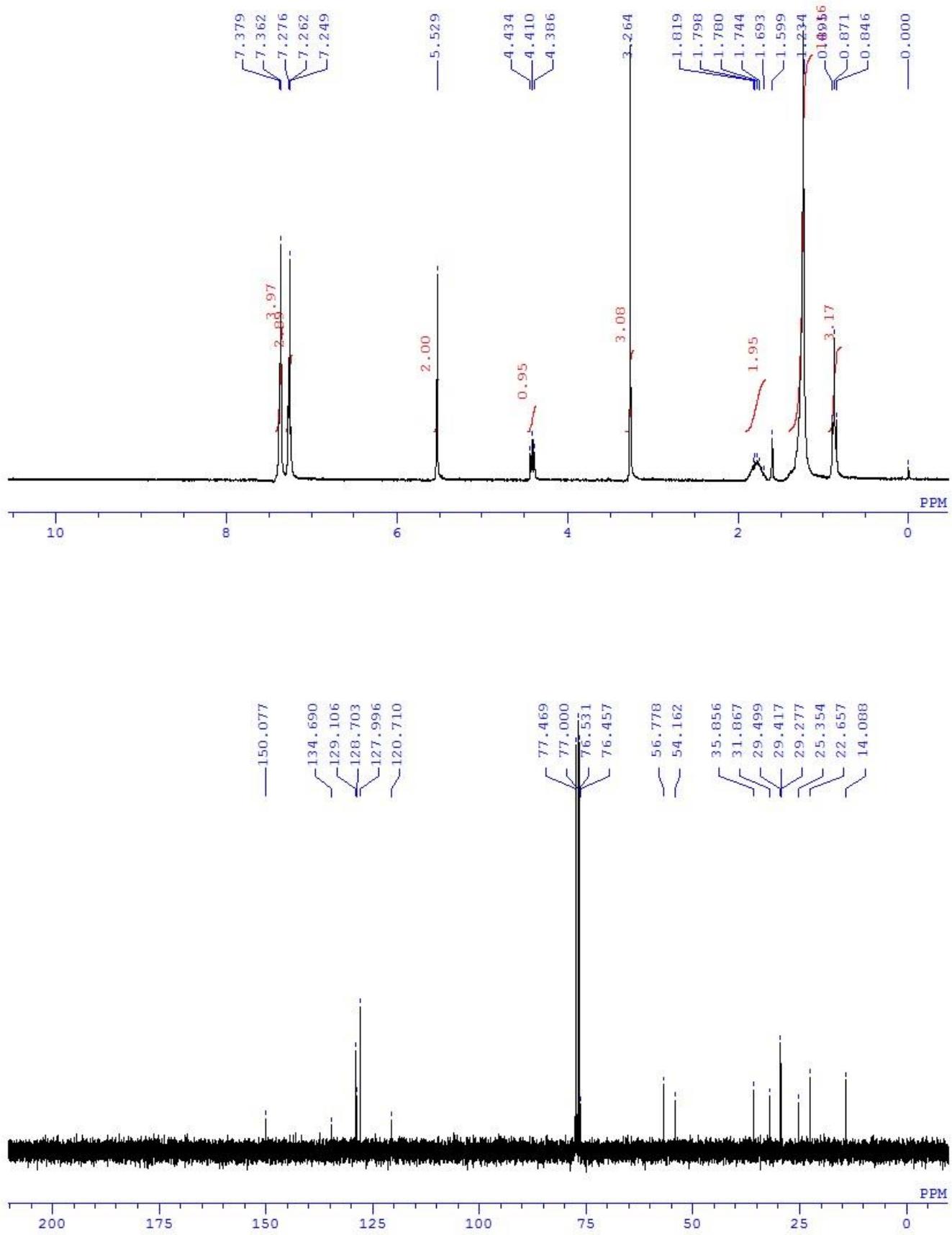
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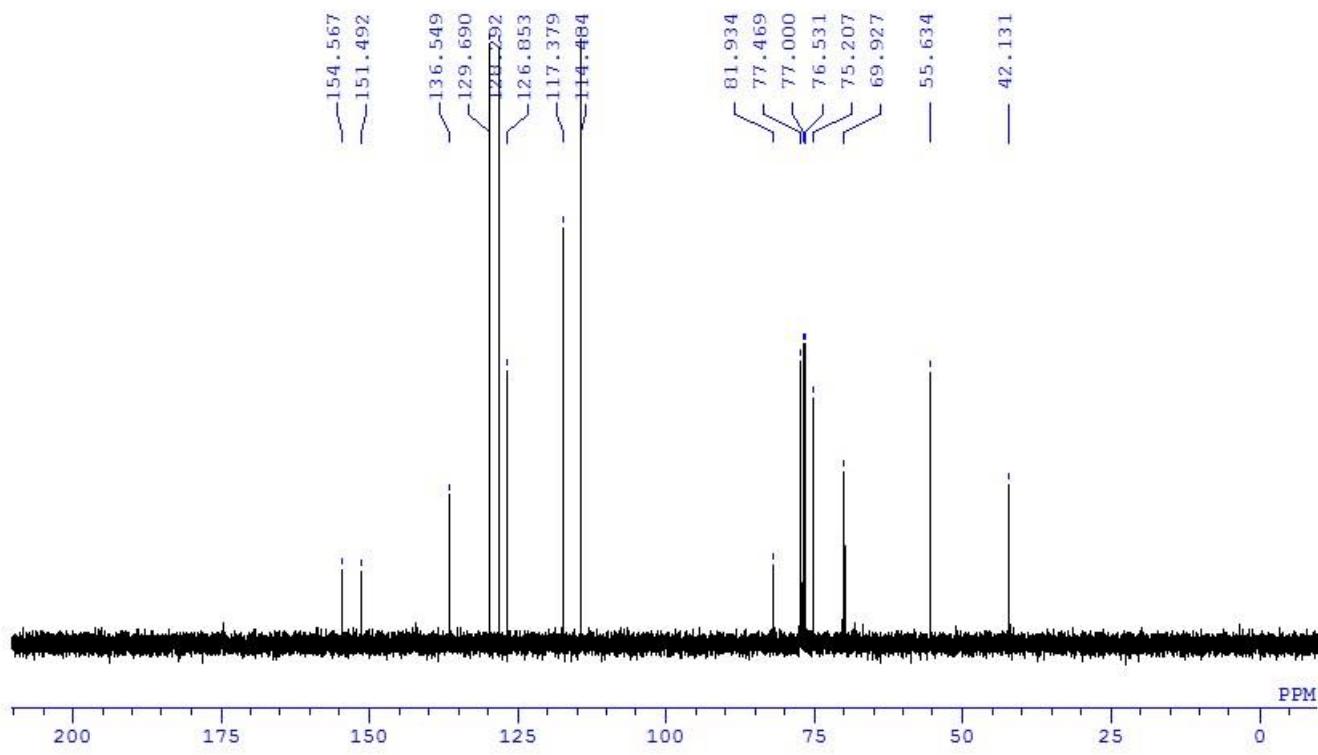
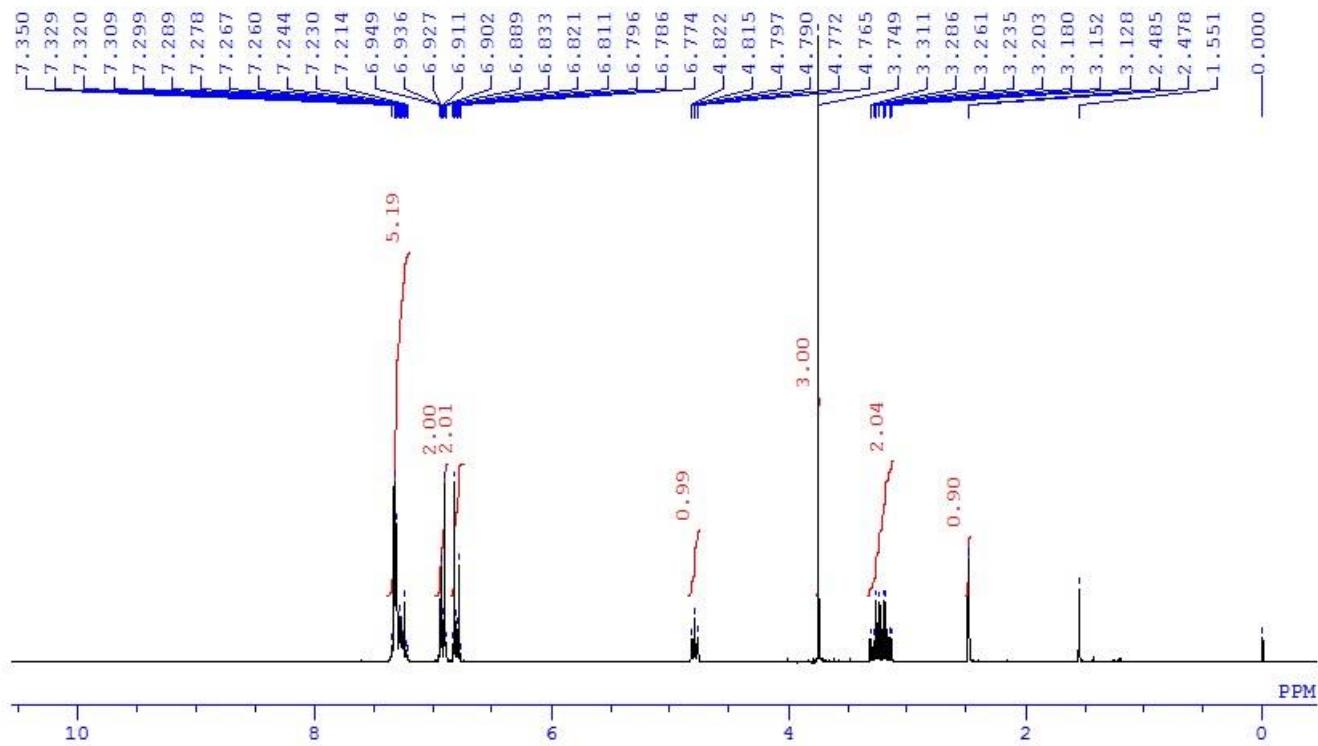
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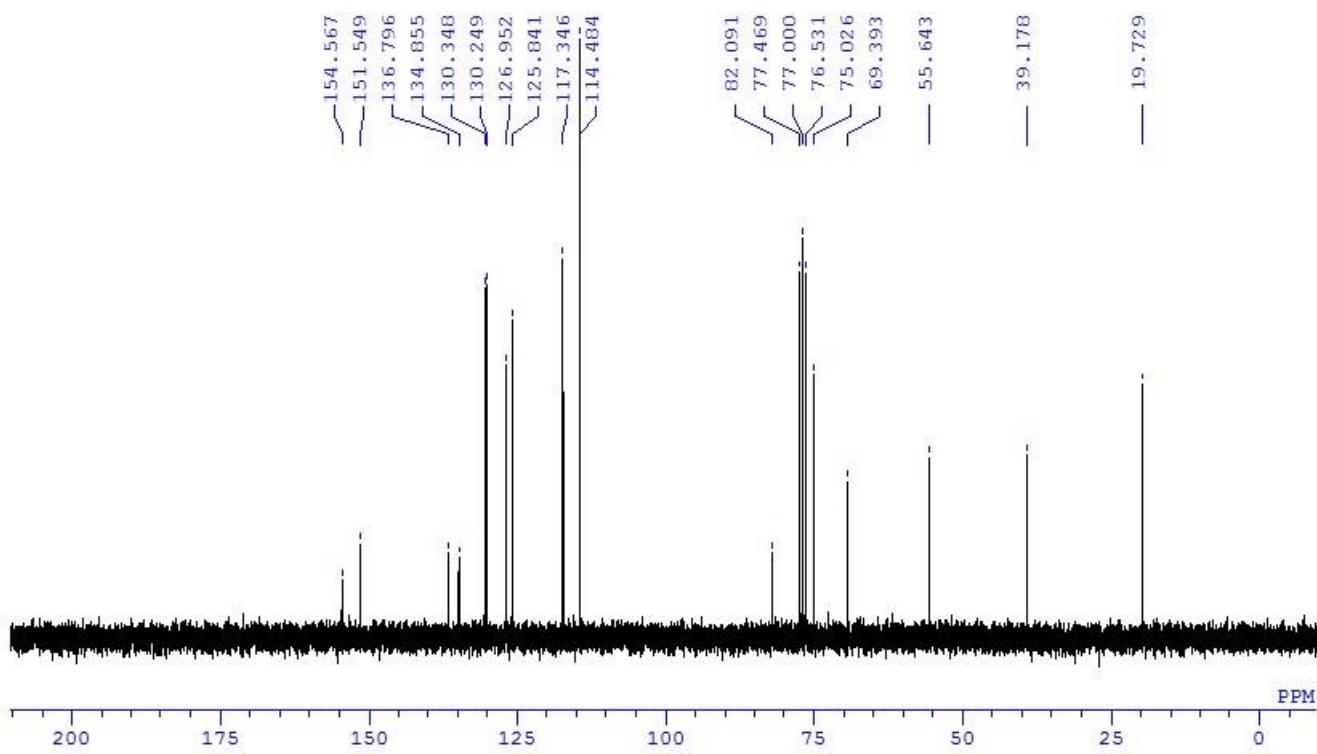
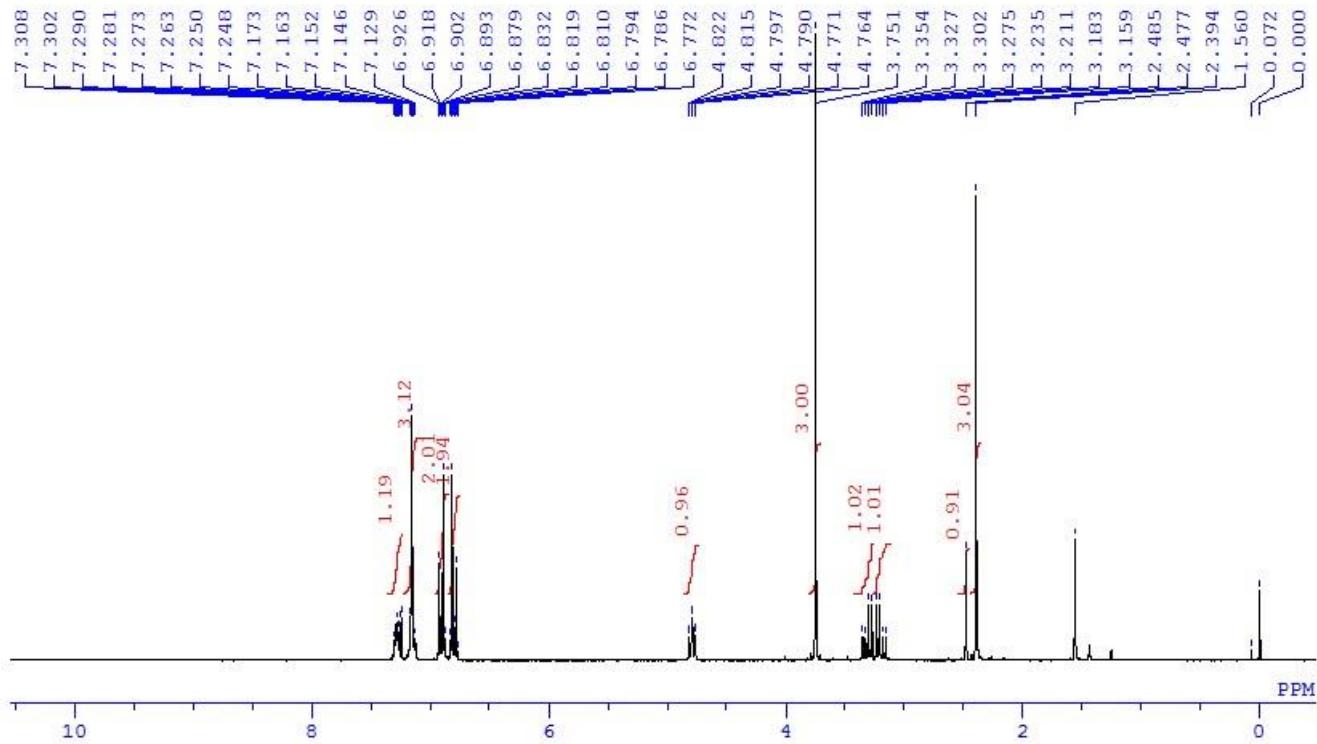
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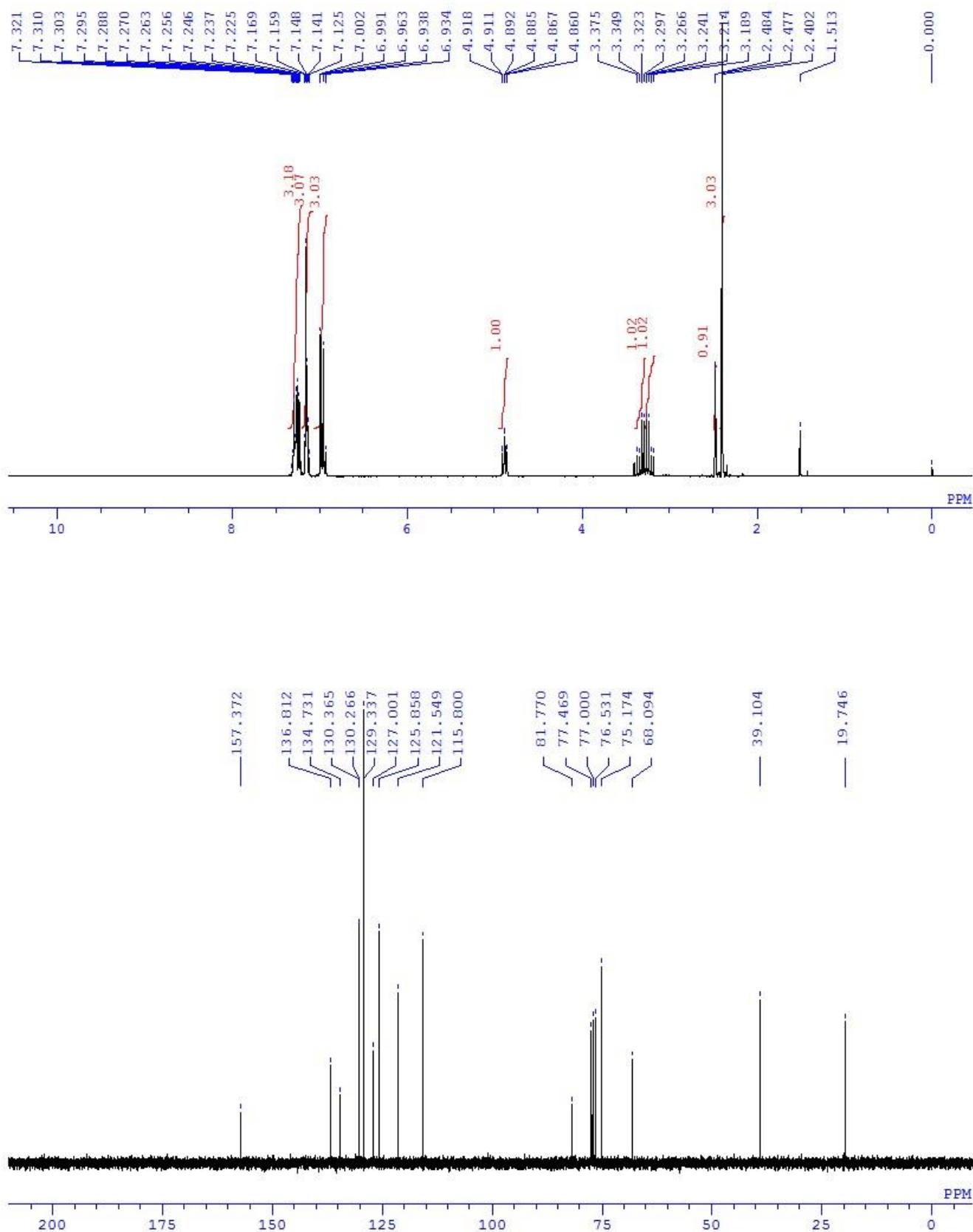
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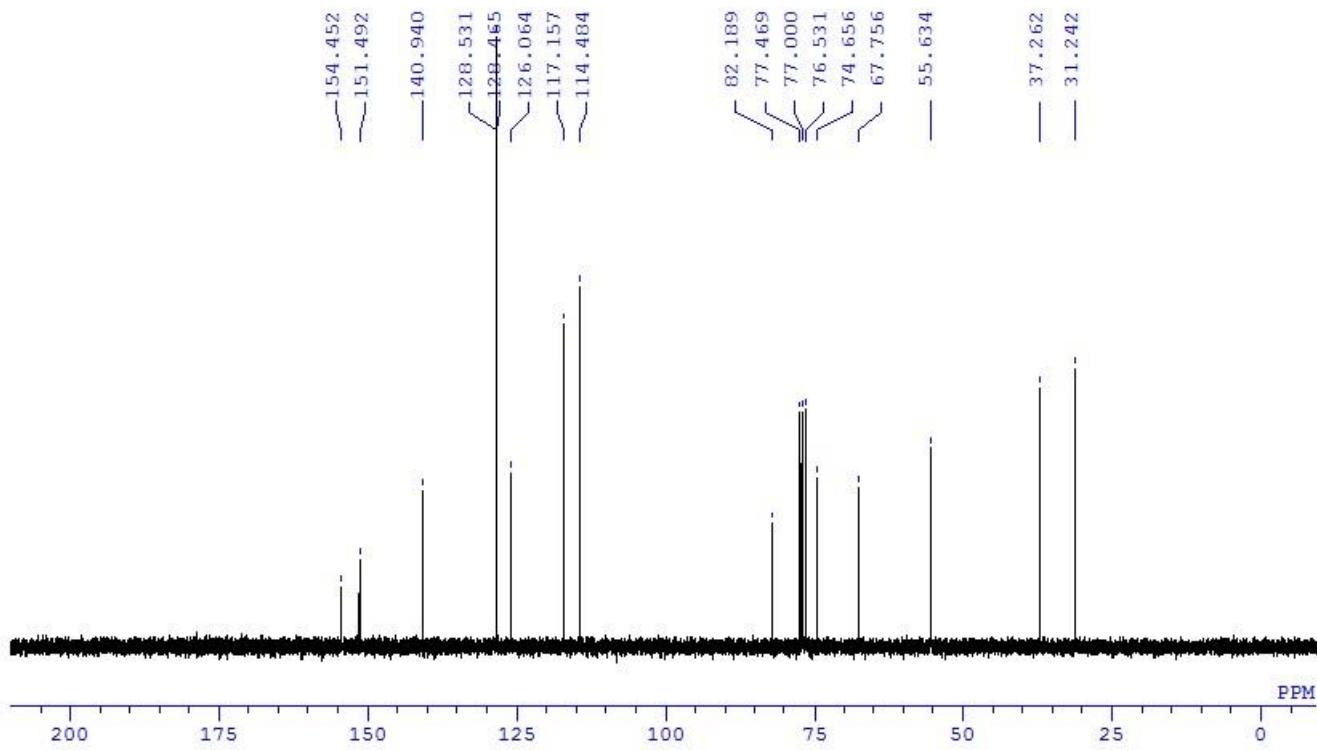
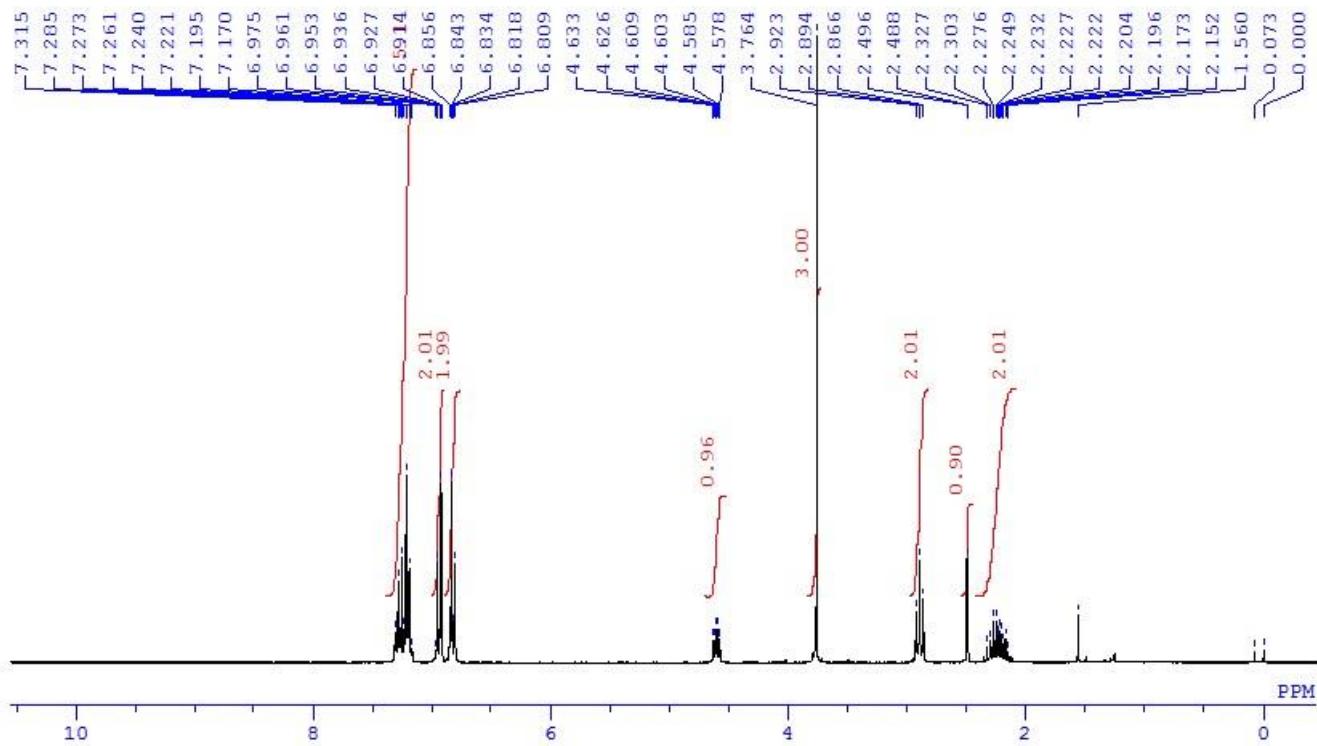
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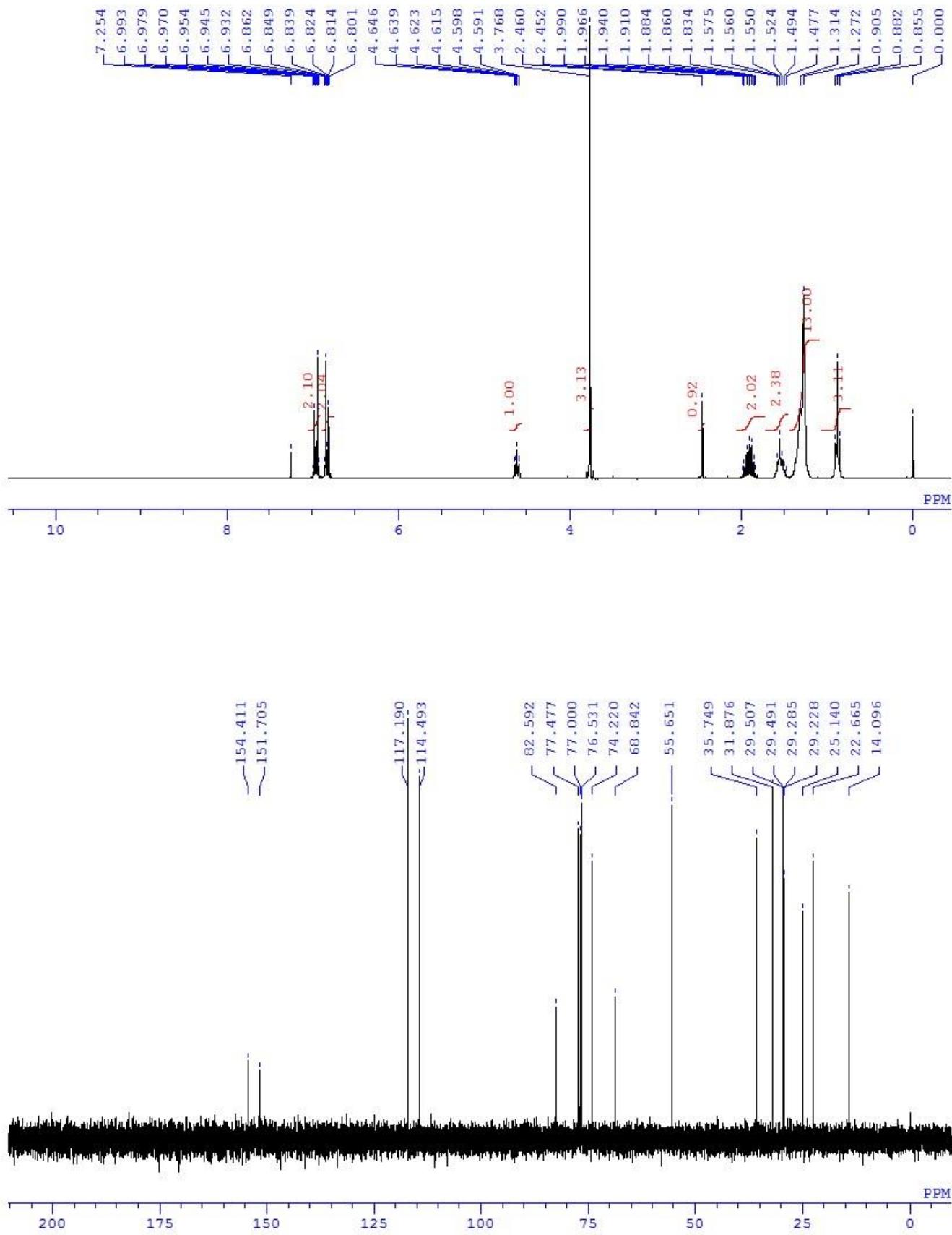
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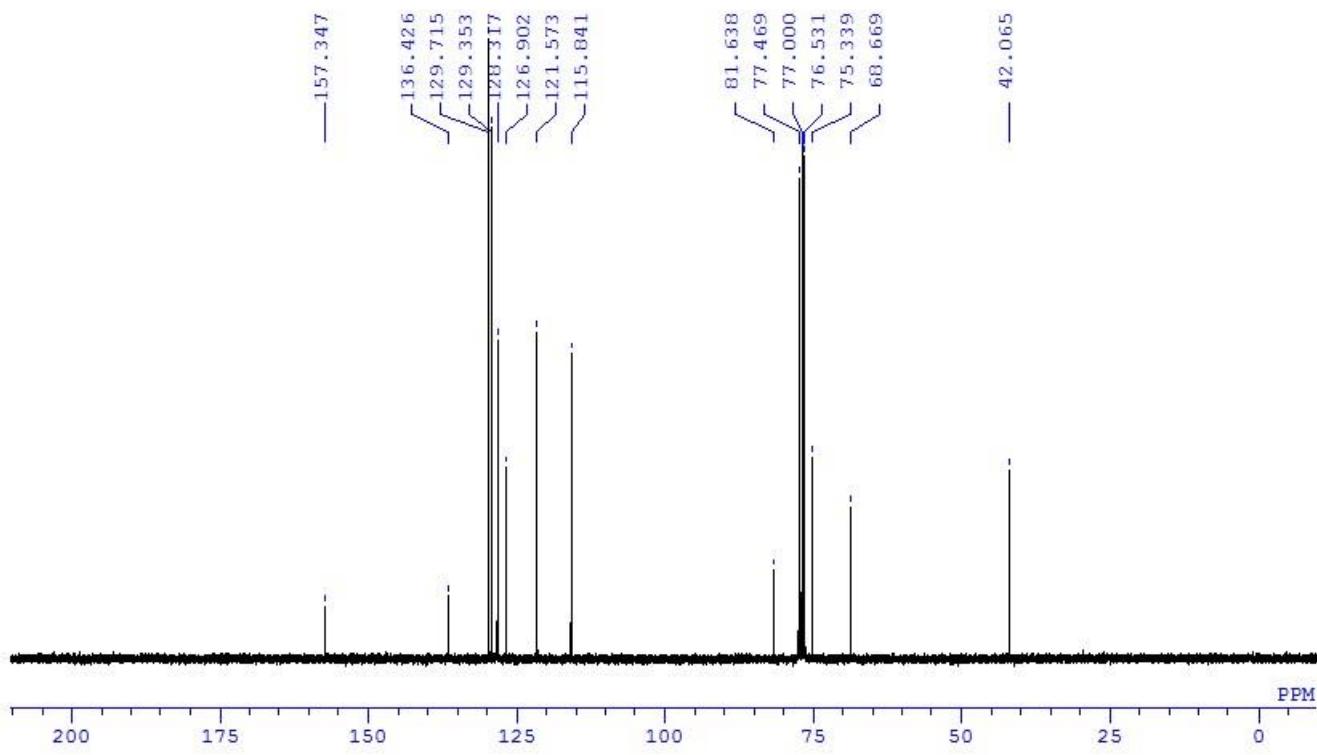
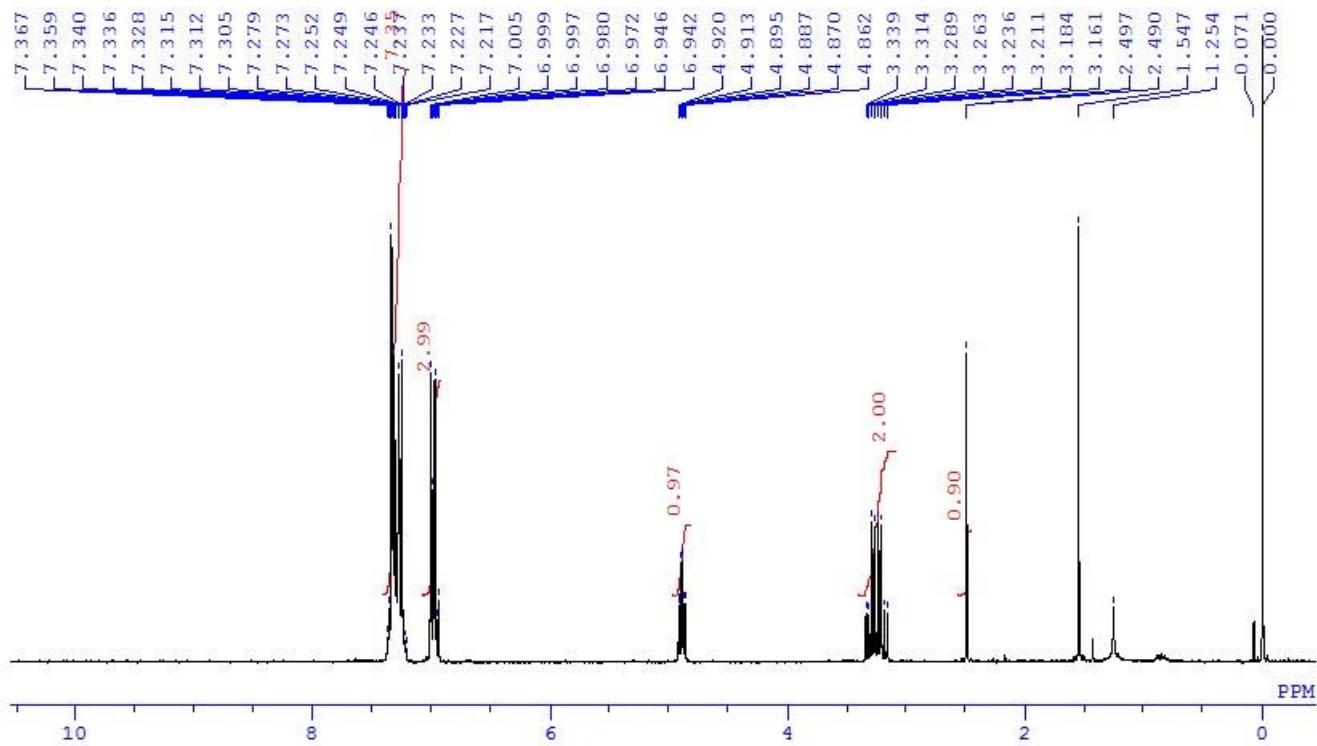
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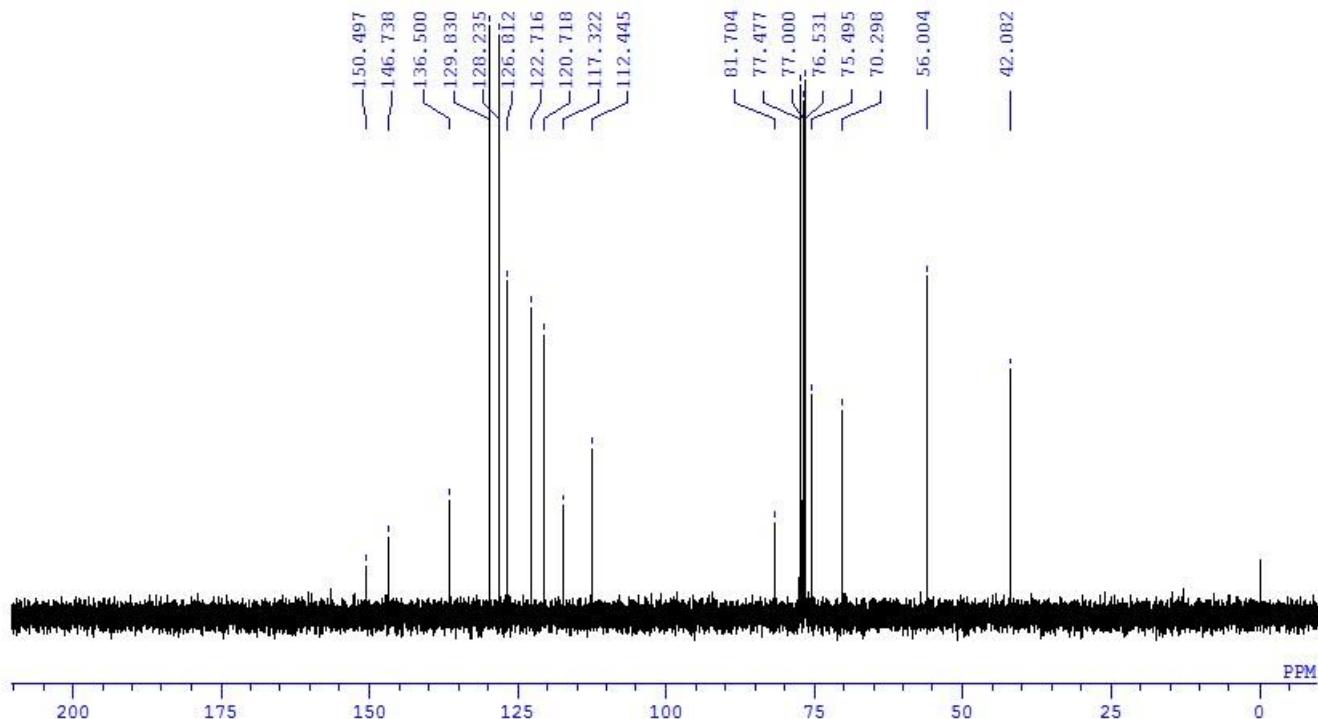
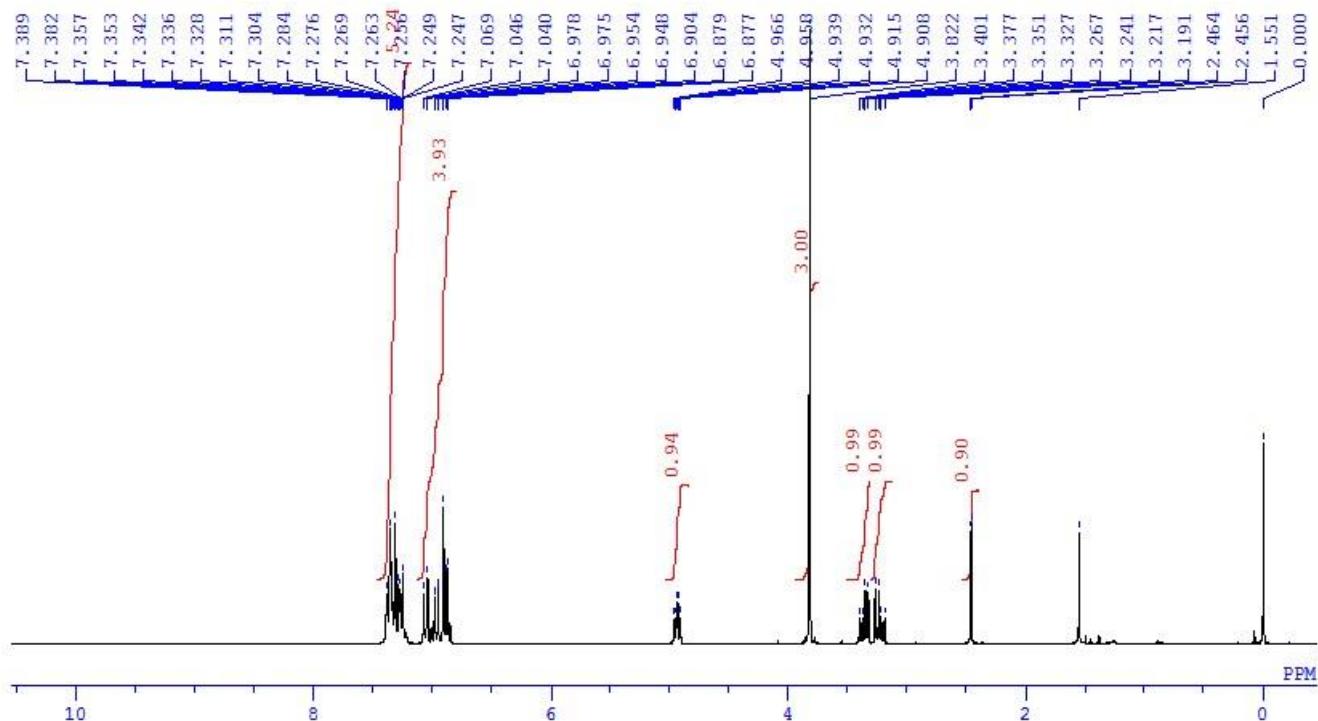
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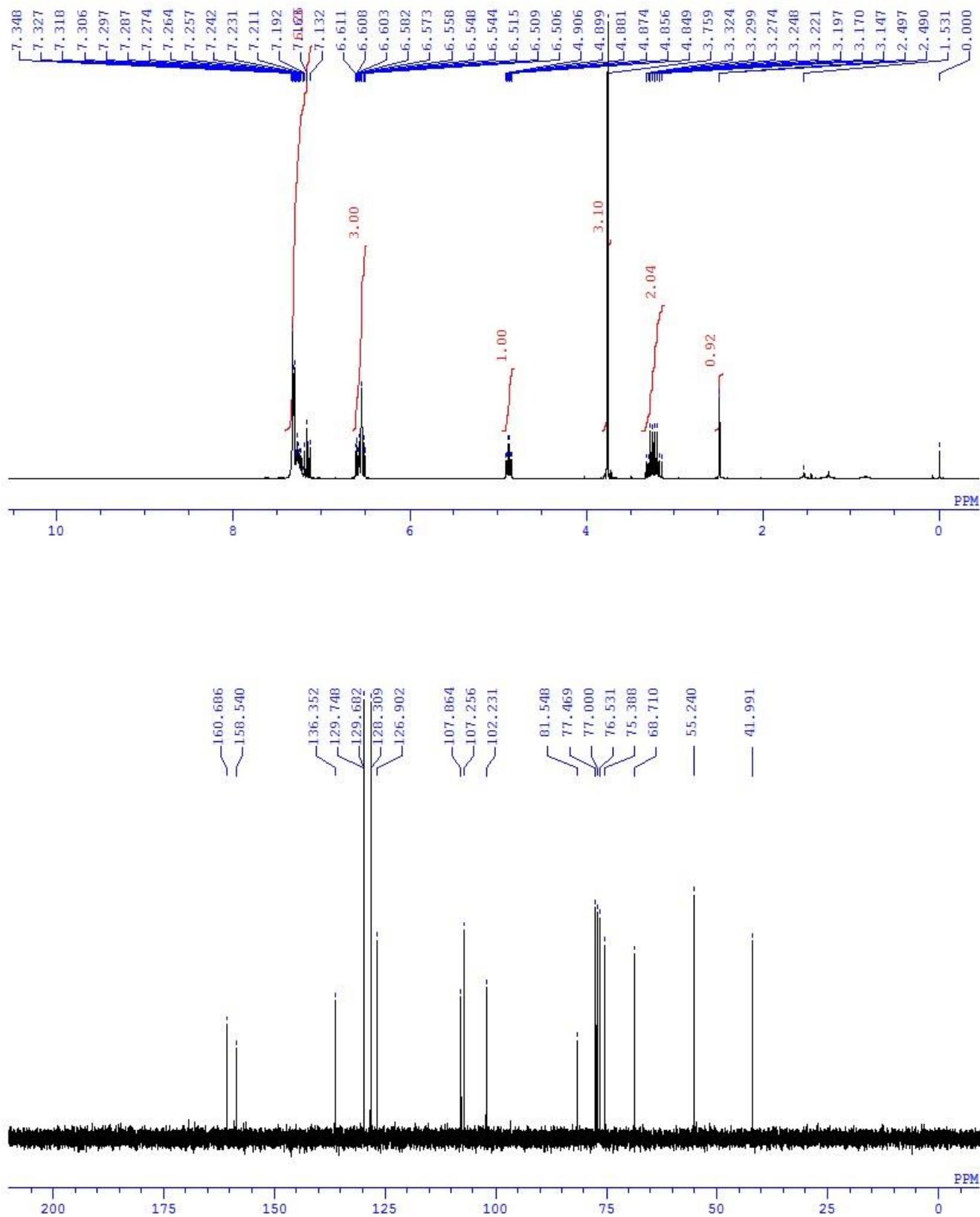
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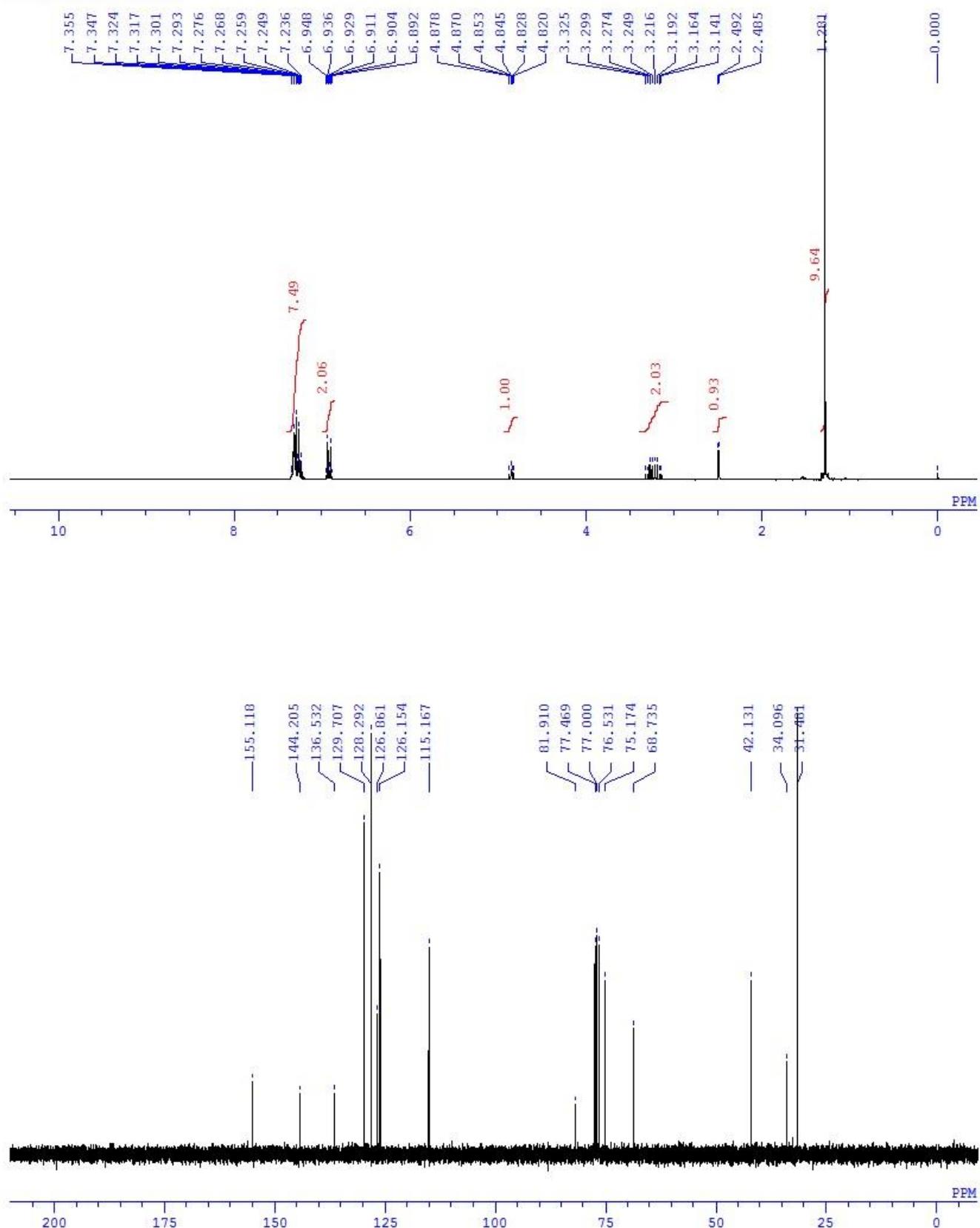
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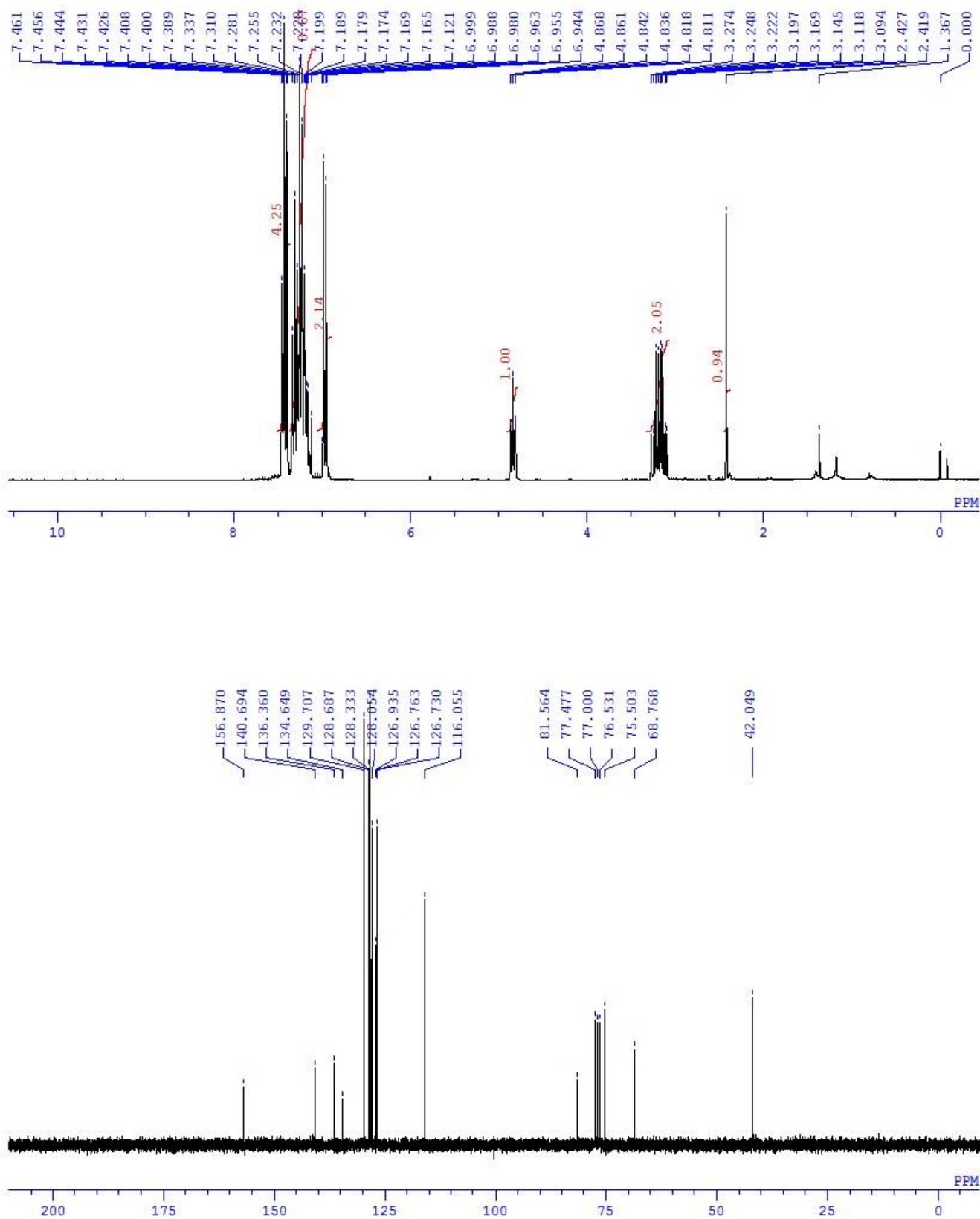
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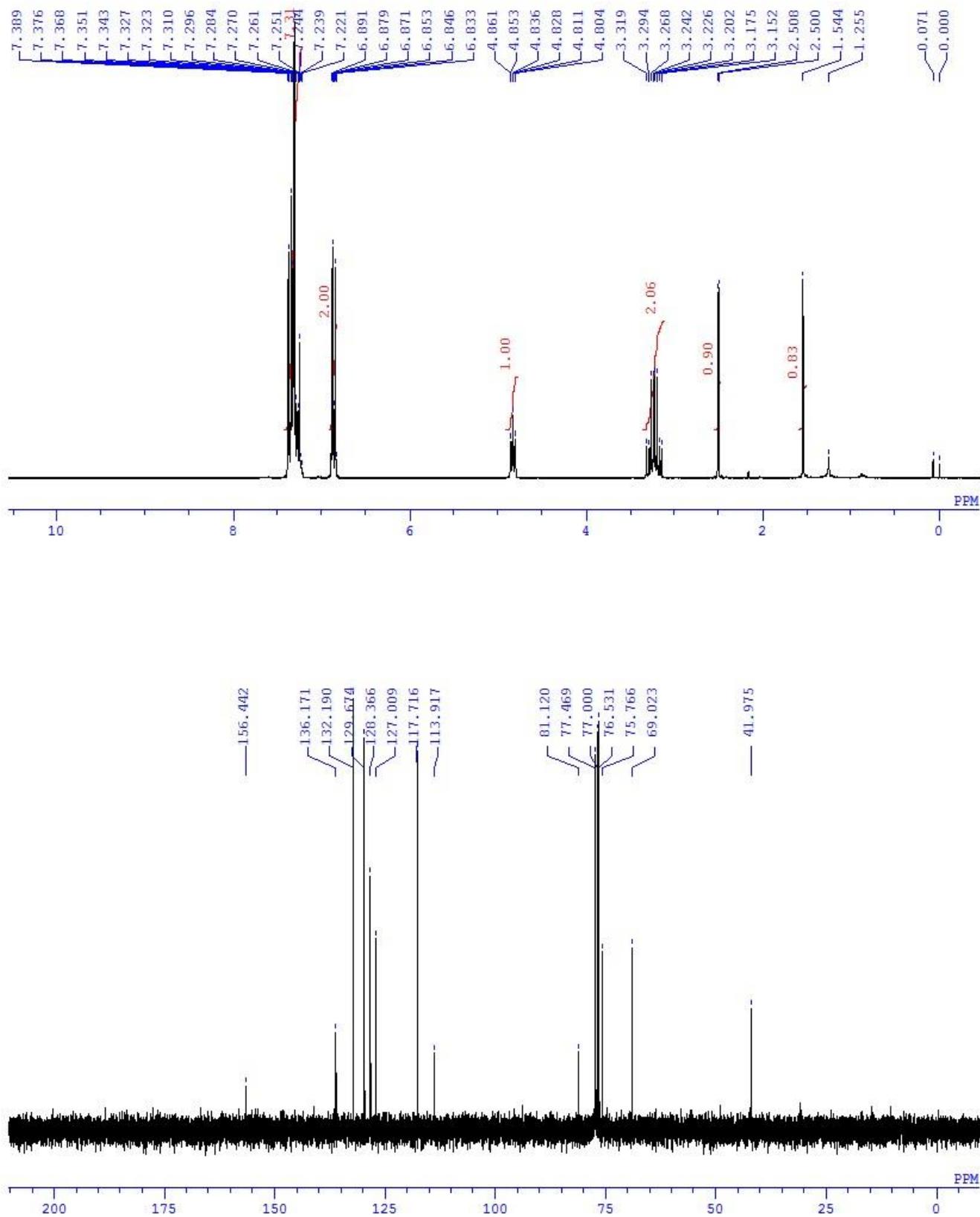
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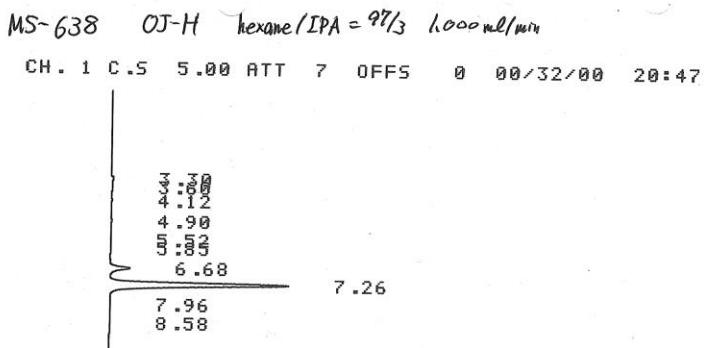


6k:



## HPLC Charts.

2b:



3009-12008

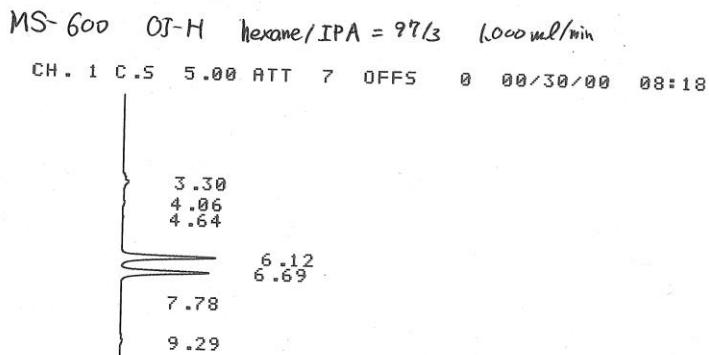
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FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

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8	7.26	277337	90.400	VB
TOTAL		306789	100.000	
PEAK REJ :		10000		

2b(rac):



D-2500 00/30/00 08:18

METHOD: TAG: 13 CH: 1

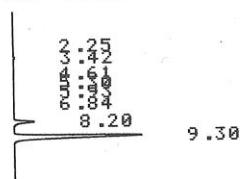
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NO.	RT	AREA	CONC	BC
4	6.12	128723	50.559	BV
5	6.69	125875	49.441	VB
TOTAL		254598	100.000	
PEAK REJ :		30000		

2c:

MS-692-2 OJ-H hexane/IPA = 98/2 1.060 ml/min

CH. 1 C.5 2.50 ATT 8 OFFS 0 00/39/00 22:19



D-2500

00/39/00 22:19

METHOD: TAG: 51 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
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8	9.30	561104	89.153	BB
TOTAL		629372	100.000	

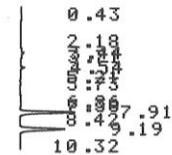
PEAK REJ :

50000

2c(rac):

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CH. 1 C.5 2.50 ATT 7 OFFS 0 00/34/00 00:26



D-2500

00/34/00 00:26

METHOD: TAG: 42 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

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12	9.19	83686	48.019	BB
TOTAL		174276	100.000	

PEAK REJ :

50000

2d:

MS-701 OT-H hexane/IPA = 100/0 1,000 mL/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 00/40/00 02:42

3:02  
5:42  
S.P. 9.50  
11.38  
14.22  
15.18  
20.10  
23.16  
25.78  
S.P. 30.00

D-2500

00/40/00 02:42

METHOD: TAG: 54 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
10	25.78	1182803	89.721	BB
11	30.56	135505	10.279	BB
TOTAL		1318308	100.000	

PEAK REJ : 50000

3009-12002

2d(rac):

MS-700-2 OT-H hexane/IPA = 100/0 1,000 mL/min

CH. 1 C.S. 1.25 ATT 8 OFFS 0 00/40/00 01:17

3:00  
9:30  
11:34  
13:54  
15:54  
23.63  
26.26  
30.72

D-2500

00/40/00 01:17

METHOD: TAG: 52 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
10	26.26	528663	48.431	BB
11	30.72	562911	51.569	BB
TOTAL		1091574	100.000	

PEAK REJ : 50000

2f:

MS-686-B-2 OJ-H hexane/IPA = 100/0 1,000 ml/min

CH. 1 C.S 2.50 ATT 8 OFFS 0 00/29/00 23:23

3.13  
4.52  
5.26  
6.91  
8.89  
  
14.58  
  
18.47  
  
24.68  
27.11

3009-12008

D-2500

00/29/00 23:23

METHOD: TAG: 40 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
5	8.89	71424	4.641	BB
8	18.47	1424943	92.599	BB
9	24.68	42461	2.759	BB
TOTAL		1538828	100.000	
PEAK REJ :		20000		

2f(rac):

MS-614-B OJ-H hexane 100% 1,000 ml/min

CH. 1 C.S 2.50 ATT 7 OFFS 0 00/11/00 02:31

5.P  
8.33  
9.33  
10.33  
11.33  
12.33  
13.92  
  
19.30  
  
24.35  
  
5.P 1600

D-2500

00/11/00 02:31

METHOD: TAG: 14 CH: 1

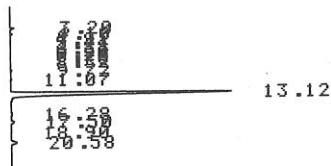
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
9	9.33	71898	25.451	VB
11	19.30	105303	37.275	BB
12	24.35	105300	37.274	BB
TOTAL		282501	100.000	
PEAK REJ :		50000		

2g:

09-12008

MS-726 OF-H hexane/IPA = 97/3 1.000 ml/min  
CH. 1 C.5 1.25 ATT 9 OFFS 0 00/58/00 23:32



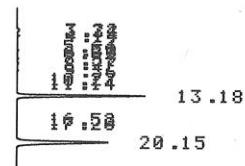
D-2500 00/58/00 23:32

METHOD: TAG: 81 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
12 13.12 2968460 97.429 BV  
16 20.58 78342 2.571 BB  
TOTAL 3046802 100.000  
PEAK REJ : 50000

2g(rac):

MS-725 OF-H hexane/IPA = 97/3 1.000 ml/min

CH. 1 C.5 1.25 ATT 8 OFFS 0 00/56/00 20:33



D-2500 00/56/00 20:33

METHOD: TAG: 75 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
12 13.18 640609 48.629 BB  
15 20.15 676717 51.371 BB  
TOTAL 1317326 100.000  
PEAK REJ : 50000

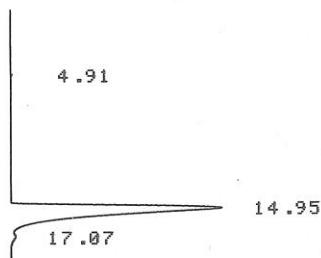
3009-120C



2i:

MS-744 OD hexane/IPA = 100/0 1,000 uL/min

CH. 1 C.S. 2.50 ATT 7 OFFS 0 00/90/00 23:39



D-2500

00/90/00 23:39

METHOD: TAG: 108 CH: 1

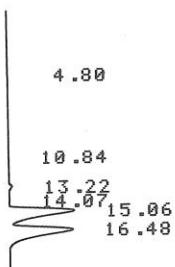
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	14.95	1527668	99.369	BU
3	17.07	9695	0.631	TBB
TOTAL		1537363	100.000	
PEAK REJ :		5000		

2i(rac):

MS-743 OD hexane/IPA = 100/0 1,000 uL/min

CH. 1 C.S. 2.50 ATT 8 OFFS 0 00/89/00 22:39



D-2500

00/89/00 22:39

METHOD: TAG: 107 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
5	15.06	777244	48.592	BU
6	16.48	822300	51.408	VB
TOTAL		1599544	100.000	
PEAK REJ :		50000		

2j:

MS-718 IC hexane/IPA = 95/5 1000ml/min

FILE # SYS 1 SEQ 2  
CH. 1 <D> C. S 1.25 ATT 7 OFFS 0 02/05/14 17:46

3.88
7.61
14.68
16.18
18.98
21.68
24.28
28.18
31.38

26.88

D 7500 INTEGRATOR REPORT

ANALYZED: 02/05/14 17:46 REPORTED: 02/05/14 18:25  
SYSTEM : 1

METHOD : OPERATOR:  
CHANNEL : 1 <DIGITAL> SEQ : 2

FILE : 0 MODULE T PROG : DETECTOR= 1  
CALC METHOD: AR/HIC <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
9	26.88	928778	94.799	BV
10	29.18	50053	5.201	TBB
TOTAL		979731	100.000	
PEAK REJ :		50000		

2j(rac):

MS-719 ~~IC~~ hexane/IPA = 95/5 1000ml/min

FILE # SYS 1 SEQ 1  
CH. 1 <D> C. S 1.25 ATT 7 OFFS 0 02/05/14 10:46

1.88
5.68
9.18
14.28
18.42
21.98
24.95
27.88
32.44

D 7500 INTEGRATOR REPORT

ANALYZED: 02/05/14 10:46 REPORTED: 02/05/14 11:13  
SYSTEM : 1

METHOD : OPERATOR:  
CHANNEL : 1 <DIGITAL> SEQ : 1

FILE : 0 MODULE T PROG : DETECTOR= 1  
CALC METHOD: AR/HIC <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
12	27.83	318567	40.593	BB
13	29.80	324963	50.497	BB
TOTAL		643530	100.000	
PEAK REJ :		50000		

4b:

9-12008

MS-693 OD hexane /IPA = 100/0 1.000 ml/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 00/35/00 02:18

4.80  
112.834  
16.88  
19.38  
27.90

D-2500

00/35/00 02:18

METHOD: TAG: 44 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	16.88	447198	89.889	BB
6	27.90	50300	10.111	BB
TOTAL		497498	100.000	

PEAK REJ : 50000

4b(rac):

12008

MS-682-2 OD hexane /IPA = 100/0 1.000 ml/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 00/28/00 02:48

4.40  
8.10  
10.46  
12.40  
15.67  
20.78  
26.19  
30.08

D-2500

00/28/00 02:48

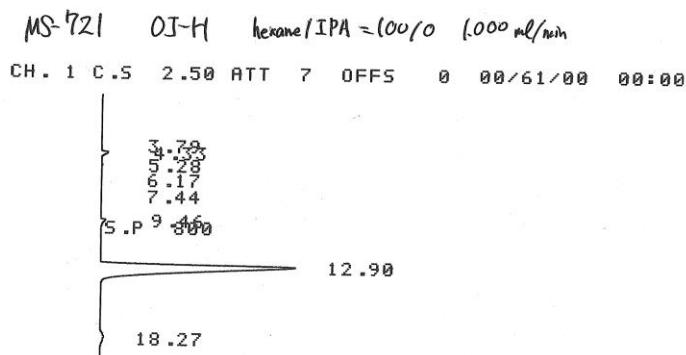
METHOD: TAG: 35 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
6	15.67	393486	47.821	BB
8	26.19	429338	52.179	BB
TOTAL		822824	100.000	

PEAK REJ : 50000

4f:



D-2500 00/61/00 00:00

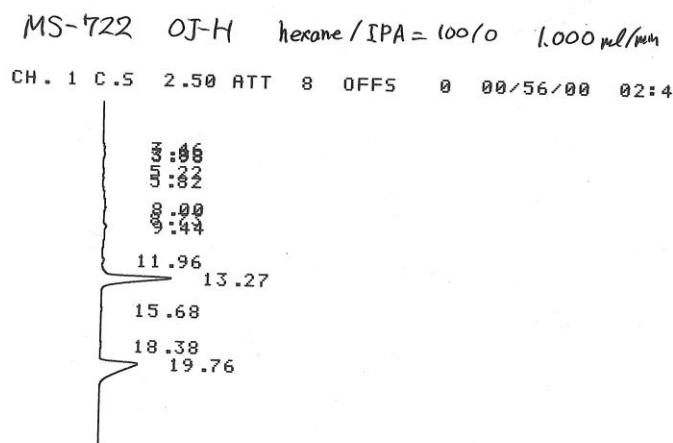
METHOD: TAG: 85 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
7	12.90	997608	96.719	BB
8	18.27	33846	3.281	BB
TOTAL		1031454	100.000	
PEAK REJ :		30000		

3003

4f(rac):



D-2500 00/56/00 02:48

METHOD: TAG: 74 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
10	13.27	599274	51.760	UU
13	19.76	558514	48.240	BB
TOTAL		1157788	100.000	
PEAK REJ :		50000		

2e':

MS-727-2 ID hexane/IPA = 85/15 1.000ml/min

D 7500 INTEGRATOR REPORT

ANALYZED: 02/08/14 15:15 REPORTED: 02/08/14 15:36  
 SYSTEM : 1  
 METHOD : OPERATOR:  
 CHANNEL : 1 <DIGITAL> SEQ : 2  
 FILE : 9 MODULE T PROG : DETECTOR= 1  
 CALC METHOD: AR/HIZ <AREA> COMPONENT TBL : 9  
 NO. RT AREA CONC BC  
 14 12.12 463332 90.087 BB  
 16 16.22 443300 9.913 BB  
 TOTAL 447712 100.000  
 PEAK REJ : 300000

2e'(rac):

MS-720-2 ID hexane/IPA = 85/15 (1,000 mL/min)

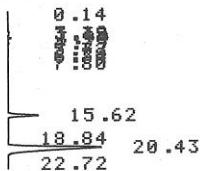
D-7500 INTEGRATOR REPORT

ANALYZED: 02/21/14 16:21 REPORTED: 02/21/14 16:42  
 SYSTEM : 1  
 METHOD : OPERATOR:  
 CHANNEL : 1 <DIGITAL> SEQ : 2  
 FILE : 0 MODULE T-PROG : DETECTOR= 1  
 CALC-METHOD: AR/HIZ <AREA> COMPONENT TBL : 0  
 NO. RT AREA CONC BC  
 11 11.88 25798 49.414 BB  
 13 15.64 26410 50.586 BB  
 TOTAL 52208 100.000  
 PEAK REJ : 20000

2a:

MS-674 OJ-H hexane/IPA = 95/5 1.000 ml/min

CH. 1 C.S. 1.25 ATT 8 OFFS 0 00/14/00 00:12



15.62	18.84	20.43	22.72
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D-2500

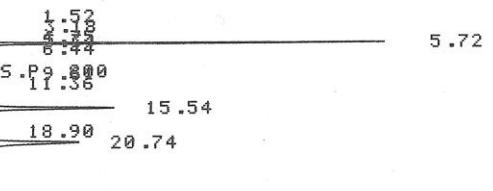
00/14/00 00:12

METHOD: TAG: 19 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
11 15.62 173996 14.409 BB  
13 20.43 1033517 85.591 BB  
TOTAL 1207513 100.000  
PEAK REJ : 30000

2a(rac):

MS-674-3 OJ-H h/I = 95/5 1.000 ml/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 00/15/00 00:08



5.72	15.54	20.74
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3009-12008

D-2500

00/15/00 00:08

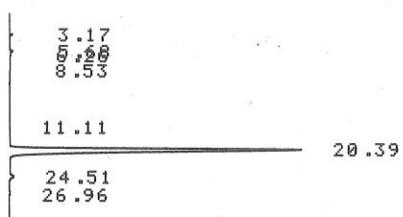
METHOD: TAG: 23 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
5 5.72 487484 41.481 VV  
9 15.54 343978 29.270 BB  
11 20.74 343738 29.249 BB  
TOTAL 1175200 100.000  
PEAK REJ : 50000

6a:

2014.7/29 PN-332

DJ-H, hex/IPA = 95/5, 1.000  $\mu$ l/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 07/29/14 15:19



D-2500

07/29/14 15:19

METHOD: TAG: 34 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
5	11.11	20050	1.360	BB
6	20.39	1436580	97.452	BB
7	24.51	17518	1.188	BB

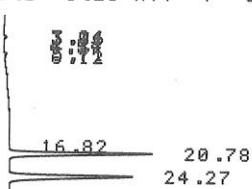
TOTAL 1474148 100.000  
PEAK REJ : 15000

6a(rac):

2014.7/29 PN-331

DJ-H, hex/IPA = 95/5, 1.000  $\mu$ l/min

CH. 1 C.S. 1.25 ATT 7 OFFS 0 00/24/00 17:02



D-2500

00/24/00 17:02

METHOD: TAG: 33 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

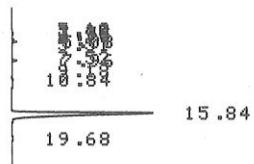
NO.	RT	AREA	CONC	BC
9	20.78	604755	49.799	BB
10	24.27	609648	50.201	BB

TOTAL 1214403 100.000  
PEAK REJ : 70000

6b:

2014.7/16 PN-~~305~~ 306  
OJ-H, hex/IPA=95/5, 1.000  $\mu$ l/min

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/11/00 13:52



D-2500 00/11/00 13:52

METHOD: TAG: 18 CH: 1

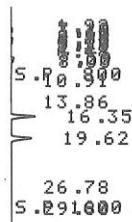
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	3.95	21350	0.785	UU
6	5.08	39551	1.453	UU
9	7.96	42916	1.577	VB
11	10.84	25455	0.935	BB
12	15.84	2570536	94.466	BB
13	19.68	21316	0.783	BB
TOTAL		2721124	100.000	
PEAK REJ :		21300		

6b(rac):

2014.7/16 PN-309  
OJ-H, hex/IPA=95/5, 1.000  $\mu$ l/min

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/11/00 13:17



D-2500 00/11/00 13:17

METHOD: TAG: 17 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

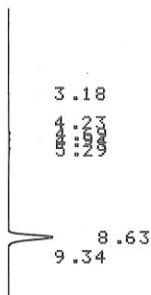
NO.	RT	AREA	CONC	BC
14	16.35	321257	49.551	BB
15	19.62	327076	50.449	BB
TOTAL		648333	100.000	
PEAK REJ :		50000		

6c:

2014-7/4 PN-305

OJ-H, hex/IPA = 95/5, 1.000 mL/min

CH. 1 C.S. 5.00 ATT 9 OFFS 0 00/00/00 00:07



D-2500

00/00/00 00:07

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	3.18	2930	0.781	BB
2	4.23	802	0.214	BB
3	4.69	4832	1.288	BV
4	4.94	4970	1.325	UV
5	5.29	6938	1.850	VB
6	8.63	352086	93.879	BV
7	9.34	2486	0.663	TBB

TOTAL

375044 100.000

PEAK REJ :

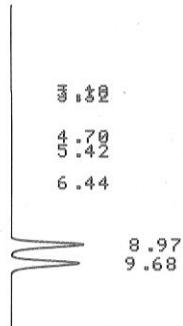
100

6c(rac):

2014-6-20 PN-297

OJ-H, hex/IPA = 95/5, 1.000 mL/min

CH. 1 C.S. 5.00 ATT 9 OFFS 0 01/89/00 20:16



D-2500

01/89/00 20:16

METHOD: TAG: 177 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
6	8.97	594547	49.218	BV
7	9.68	613450	50.782	VB

TOTAL

1207997 100.000

PEAK REJ :

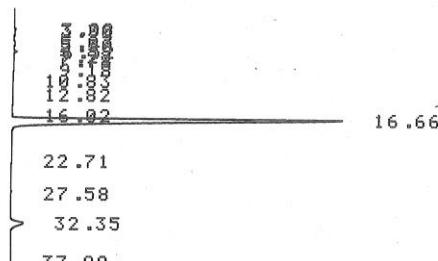
30000

6d:

2014-8/22 PN-293

OJ-H, hex/IPA = 90/10, 1.000 mL/min

CH. 1 C.S. 1.25 ATT 8 OFFS 0 08/22/14 16:51



D-2500

08/22/14 16:51

METHOD: TAG: 45 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
12	16.66	3500972	95.634	VB
15	32.35	159833	4.366	BB
TOTAL		3660905	100.000	

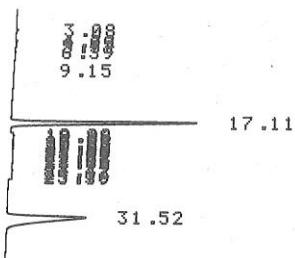
PEAK REJ: 40000

6d(rac):

2014-8/22 PN-292

OJ-H, hex/IPA = 90/10, 1.000 mL/min.

CH. 1 C.S. 1.25 ATT 7 OFFS 0 08/22/14 15:58



D-2500

08/22/14 15:58

METHOD: TAG: 44 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
7	17.11	682996	50.027	BB
25	31.52	682254	49.973	BB
TOTAL		1365250	100.000	

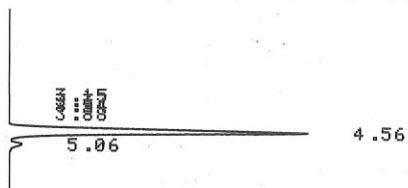
PEAK REJ: 40000

6e:

2014. 12/19 PN-385

~~OD~~, hex/IPA = 99/1, 1.000 mL/min  
OD

CH. 1 C.S. 5.00 ATT 10 OFFS 0 00/54/00 01:31



D-2500

00/54/00 01:31

METHOD: TAG: 52 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

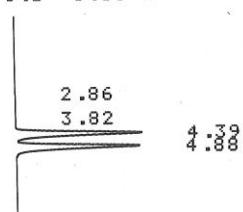
NO.	RT	AREA	CONC	BC
5	4.56	4391305	96.726	BV
6	5.06	148629	3.274	TBB
TOTAL		4539934	100.000	
PEAK REJ :		10000		

6e(rac):

2014. 12/19 PN-391

~~OD~~, hex/IPA = 99/1, 1.000 mL/min

CH. 1 C.S. 5.00 ATT 10 OFFS 0 00/54/00 02:22



D-2500

00/54/00 02:22

METHOD: TAG: 53 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

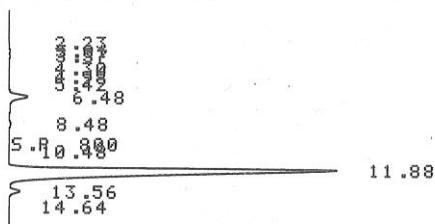
NO.	RT	AREA	CONC	BC
3	4.39	1584531	49.574	BV
4	4.88	1611739	50.426	VB
TOTAL		3196270	100.000	
PEAK REJ :		10000		

6f:

2014. 9/18 PN-344

OJ-H, hex/IPA = 98/2, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 10 OFFS 0 09/18/14 11:15



D-2500

09/18/14 11:15

METHOD: TAG: 74 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

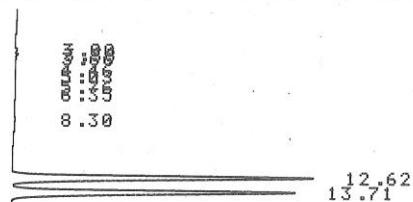
NO.	RT	AREA	CONC	BC
7	6.48	510993	3.822	VB
10	11.88	12637226	94.527	BU
11	13.56	220657	1.651	TBB
TOTAL		13368876	100.000	
PEAK REJ.:		50000		

6f(rac):

2014. 9/18 PN-355

OJ-H, hex/IPA = 98/2, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 8 OFFS 0 09/18/14 10:32



D-2500

09/18/14 10:32

METHOD: TAG: 72 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

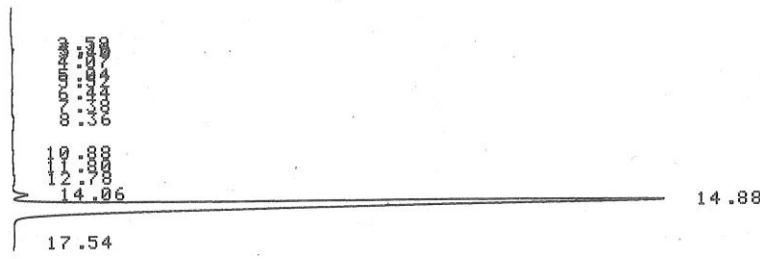
NO.	RT	AREA	CONC	BC
9	12.62	1727226	49.564	UU
10	13.71	1757598	50.436	VB
TOTAL		3484824	100.000	
PEAK REJ.:		50000		

6g:

2014-11-16 PN-379

OJ-H, hex/IPA = 95/5, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 8 OFFS 0 00/11/00 04:50



D-2500

00/11/00 04:50

METHOD: TAG: 11 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
13	14.06	78998	1.300	UV
14	14.88	5996138	98.700	UV
TOTAL		6075136	100.000	

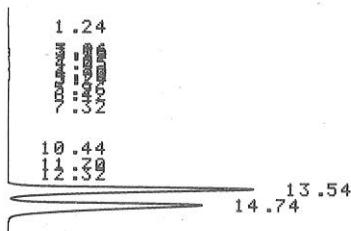
PEAK REJ: 50000

6g(rac):

2014-11-16 PN-380

OJ-H, hex/IPA = 95/5, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 10 OFFS 0 00/11/00 04:28



D-2500

00/11/00 04:28

METHOD: TAG: 10 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

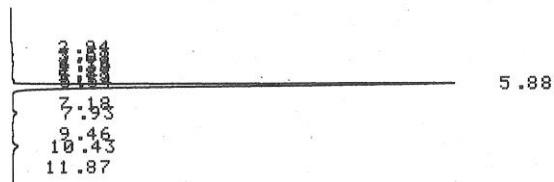
NO.	RT	AREA	CONC	BC
15	13.54	7545961	50.036	UV
16	14.74	7535224	49.964	UV
TOTAL		15081185	100.000	

PEAK REJ: 50000

6h:

2014. 12/19. PN-383  
OD, hex/IPA = 95/5, 1.000 ml/min

CH. 1 C.S. 2.50 ATT 10 OFFS 0 00/54/00 03:53



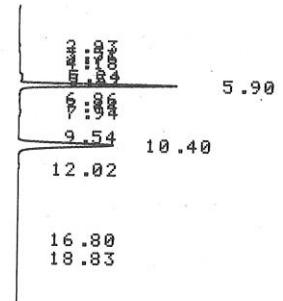
D-2500 00/54/00 03:53

METHOD: TAG: 56 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
9 5.88 6998882 98.016 UV  
13 10.43 141668 1.984 BV  
TOTAL 7140550 100.000  
PEAK REJ : 140000

6h(rac):

PN-381 2014. 12/19  
OD, hex/IPA = 95/5, 1.000 ml/min

CH. 1 C.S. 2.50 ATT 9 OFFS 0 00/54/00 03:26



D-2500 00/54/00 03:26

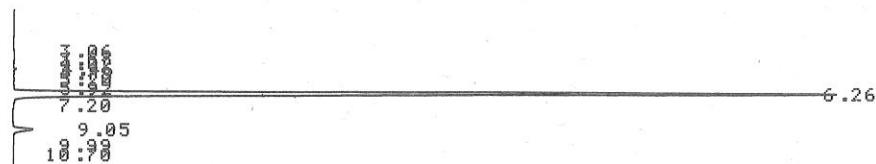
METHOD: TAG: 55 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA  
NO. RT AREA CONC BC  
7 5.90 1234934 49.977 UV  
12 10.40 1236090 50.023 BV  
TOTAL 2471024 100.000  
PEAK REJ : 40000

6i:

OJ-H, hex/IPA = 98/2, 1.000 mL/min

PN-366 2014.10/2

CH. 1 C.S. 2.50 ATT 9 OFFS 0 00/04/00 05:33



D-2500

00/04/00 05:33

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
8	6.26	7034077	97.186	UV
10	9.05	203634	2.814	BV

TOTAL

7237711 100.000

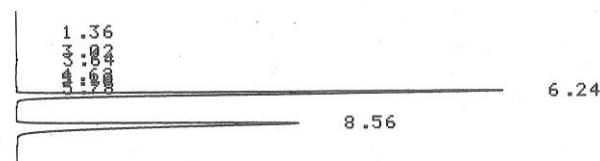
PEAK REJ : 50000

6i(rac):

2014.9/18 PN-356

OJ-H, hex/IPA = 98/2, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 9 OFFS 0 09/18/14 11:32



D-2500

09/18/14 11:32

METHOD: TAG: 75 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
7	6.24	3697506	49.419	UB
8	8.56	3784517	50.581	BB

TOTAL

7482023 100.000

PEAK REJ : 50000

6j:

2014 - 10/30 PN-376

OJ-H, hex/IPA = 90/10, 1.000 mL/min

CH. 1 C.S. 1.25 ATT 10 OFFS 0 00/03/00 21:41

9.70
11.19
13.15
13.34
19.03
21.38
23.42

26.23

S.P. 1600
31.74
34.48
40.54
47.55
53.87
60.24

D-2500

00/03/00 21:41

METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
21	26.23	44698404	98.203	BV
30	60.24	817833	1.797	BB
TOTAL		45516237	100.000	
PEAK REJ :		50000		

6j(rac):

2014. 10/8 PN-369

OJ-H, hex/IPA = 90/10, 1.000 mL/min

CH. 1 C.S. 1.25 ATT 9 OFFS 0 00/10/00 05:15

9.73
11.11
13.09
17.99
20.83

25.95

S.P. 1600
32.94
40.35
48.00
52.19

56.96

D-2500

00/10/00 05:15

METHOD: TAG: 11 CH: 1

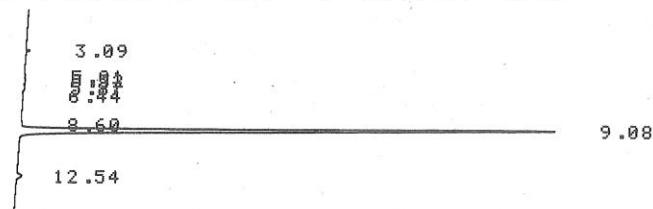
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
17	25.95	5525578	49.489	BB
23	56.96	5639747	50.511	BB
TOTAL		11165325	100.000	
PEAK REJ :		200000		

6k:

2014. 8/25 PN-340  
OJ-H, hex IPA = 90/10, 1.000 mL/min

CH. 1 C.S. 2.50 ATT 6 OFFS 0 08/25/14 15:19



D-2500 08/25/14 15:19

METHOD: TAG: 49 CH: 1

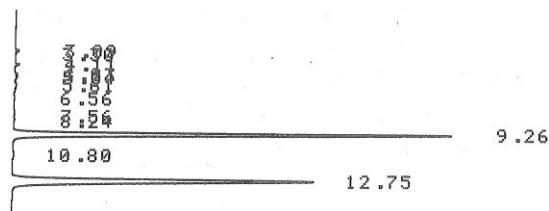
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
7	9.08	515926	98.844	VB
8	12.54	6036	1.156	TBB
TOTAL		521962	100.000	
PEAK REJ :		6000		

6k(rac):

2014. 8/21 PN-342  
OJ-H, hex IPA = 90/10, 1.000 mL/min.

CH. 1 C.S. 2.50 ATT 6 OFFS 0 08/21/14 12:54



D-2500 08/21/14 12:54

METHOD: TAG: 42 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
10	9.26	426742	49.770	BB
12	12.75	430679	50.230	BB
TOTAL		857421	100.000	
PEAK REJ :		200000		