Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Efficient Synthesis of *gem*-Dihydroperoxides with Molecular Oxygen and Anthraquinone under Visible Light Irradiation with Fluorescent Lamp

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1. General Considerations: All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL AL 400 spectrometer , JEOL EX 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) and JEOL ECA-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254). Flash column chromatography was performed with silica gel Kanto Chemical Co., Inc. 60N (40-50 mm spherical, neutral).

2. General Procedure. A Typical Example (Entry 1): Representative procedure of the dihydroperoxidation is as follows: A dry 2-propanol solution (5 mL) of the 4-*tert*-butylcyclohexanone (46.3 mg, 0.30 mmol) and AQN (6.2 mg, 0.03 mmol) in a pyrex tube equipped with O_2-balloon was stirred and irradiated externally with fluorescent lamp for 20 h. The reaction mixture was concentrated under reduced pressure, and the pure product (55.2 mg, 90%) was obtained by purification with preparative TLC.

3. NMR data:

All the products in the paper are known compounds that exhibited spectroscopic data identical to those reported in the literature.

4-*tert*-butylcyclohexane-1,1-diyl dihydroperoxide (2)[1-3]:

white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9H), 1.06 (tt, 1H, *J* = 0.5, 12.0Hz), 1.25 (dq, 2H, *J* = 3.6, 13.1Hz), 1.45 (dt, 2H, *J* = 4.1, 13.7Hz), 1.72 (br d, 2H, *J* = 10.8Hz), 2.29 (br d, 2H, *J* = 10.8Hz), 9.35 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 27.6, 29.7, 32.3, 47.4, 110.8

Cyclohexane-1,1-diyl dihydroperoxide (4)[1,2]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41-1.50 (m, 2H), 1.54-1.62 (m, 4H), 1.84 (t, 4H, *J*

= 6.2Hz), 8.93 (br s, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 25.0, 29.2, 110.5

2-Methylcyclohexane-1,1-diyl dihydroperoxide (6)[1]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, 3H, *J* = 7.2Hz), 1.37-1.74 (m, 7H), 1.90-1.95 (m, 1H), 2.26 (m, 1H), 8.58 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.3, 22.5, 24.9, 29.6, 32.0, 113.1

3-Methylcyclohexane-1,1-diyl dihydroperoxide (8)[4]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89-0.94 (m, 4H), 1.11 (t, 1H, *J* = 13.0Hz), 1.37 (dt, 1H, *J* = 4.1, 13.5Hz), 1.50 (tq, 1H, *J* = 2.4, 13.3Hz), 1.61-1.75 (m, 3H), 2.23 (br d, 2H, *J* = 13.2Hz), 9.20 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.1, 29.08, 29.14, 34.1, 37.5, 111.5

4-Methylcyclohexane-1,1-diyl dihydroperoxide (10)[3,4]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 6.8Hz), 1.21 (dq, 2H, *J* = 3.6, 12.8Hz), 1.52 (dt, 3H, *J* = 4.3, 13.3Hz), 2.21 (br d, 2H, *J* = 12.4Hz), 9.1 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 29.0, 30.6, 31.6, 110.9

Cyclooctane-1,1-diyl dihydroperoxide (12)[1]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50-1.68 (m, 10H), 1.86-1.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 24.9, 27.2, 27.9, 115.0

Adamantane-2,2-diyl dihydroperoxide (14)[1,2]:

white solid; ^{1}H NMR (400 MHz, DMSO-d6) δ 1.54-1.61 (m, 8H), 2.16 (br s, 2H), 10.7 (br s 2H); ^{13}C NMR (100 MHz, DMSO-d6) δ 26.5, 30.6, 33.1, 36.6, 38.8, 109.3

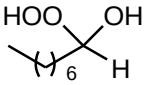
Nonane-2,2-diyl dihydroperoxide (16)[3]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.3Hz), 1.20-1.46 (m, 15H), 1.68-1.77 (m, 2H), 9.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 17.8, 22.6, 23.9, 29.1, 29.7, 31.7, 33.0, 112.6

Nonane-5,5-diyl dihydroperoxide (18)[1,3]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, 3H, *J* = 6.6Hz), 1.25-1.43 (m, 8H), 1.67-1.71 (m, 4H), 8.7 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 23.0, 25.8, 29.1, 114.4

1-Hydroperoxyoctan-1-ol (20) [3]:

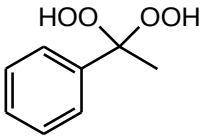


colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.11-1.63 (m, 12H), 5.12 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 24.5, 29.0, 29.3, 31.6, 32.9, 101.5

(4-Methoxyphenyl)methylene dihydroperoxide (22)[1,2]:

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.24 (s, 1H), 6.87 (d, 2H, J = 7.8Hz), 7.34 (d, 2H, J = 7.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 109.9, 113.8, 124.7, 128.5, 160.4

Phenylethane-1,1-diyl dihydroperoxide (24)[1-3]:



colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 3H), 7.34-7.42 (m, 3H) 7.48-7.52 (m, 2H), 8.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 111.4, 125.7, 128.4, 128.6, 138.2

4. References

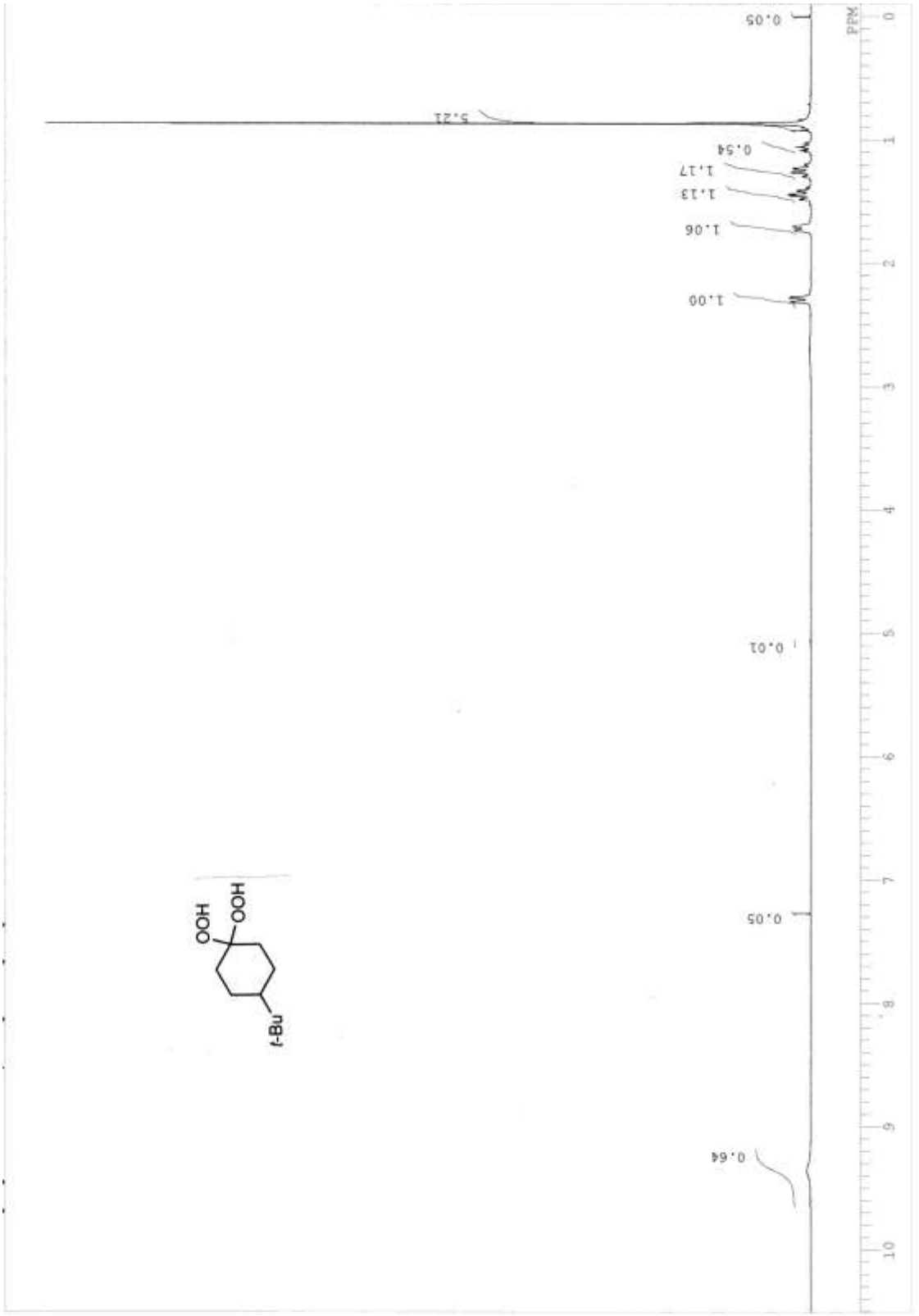
1) Ghorai, P.; Dussault, P. H. *Org. Lett.* **2008**, *10*, 4577-4579.

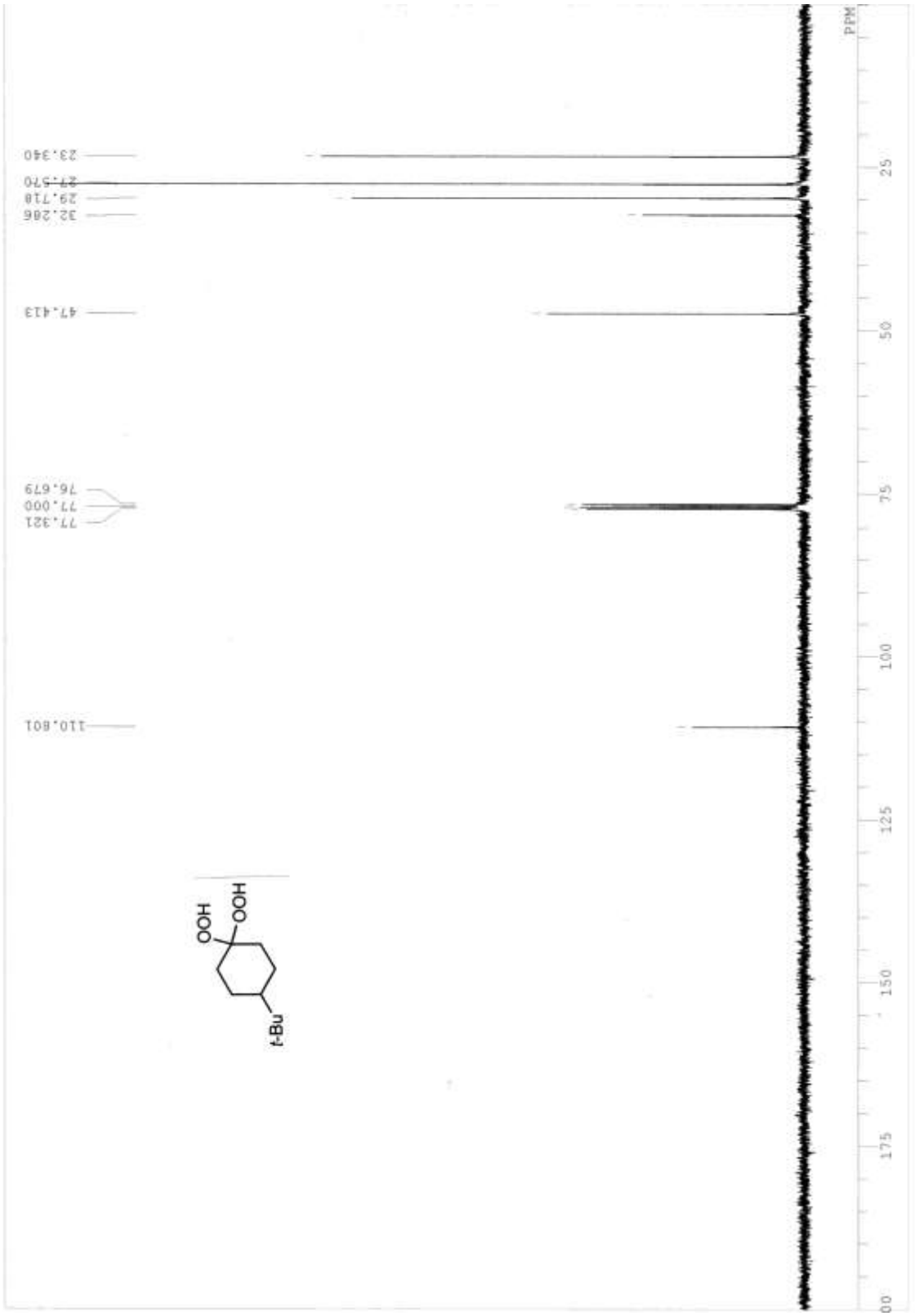
2) Li, Y.; Hao, H.-D.; Zhang, Q.; Wu, Y. *Org. Lett.* **2009**, *11*, 1615-1618.

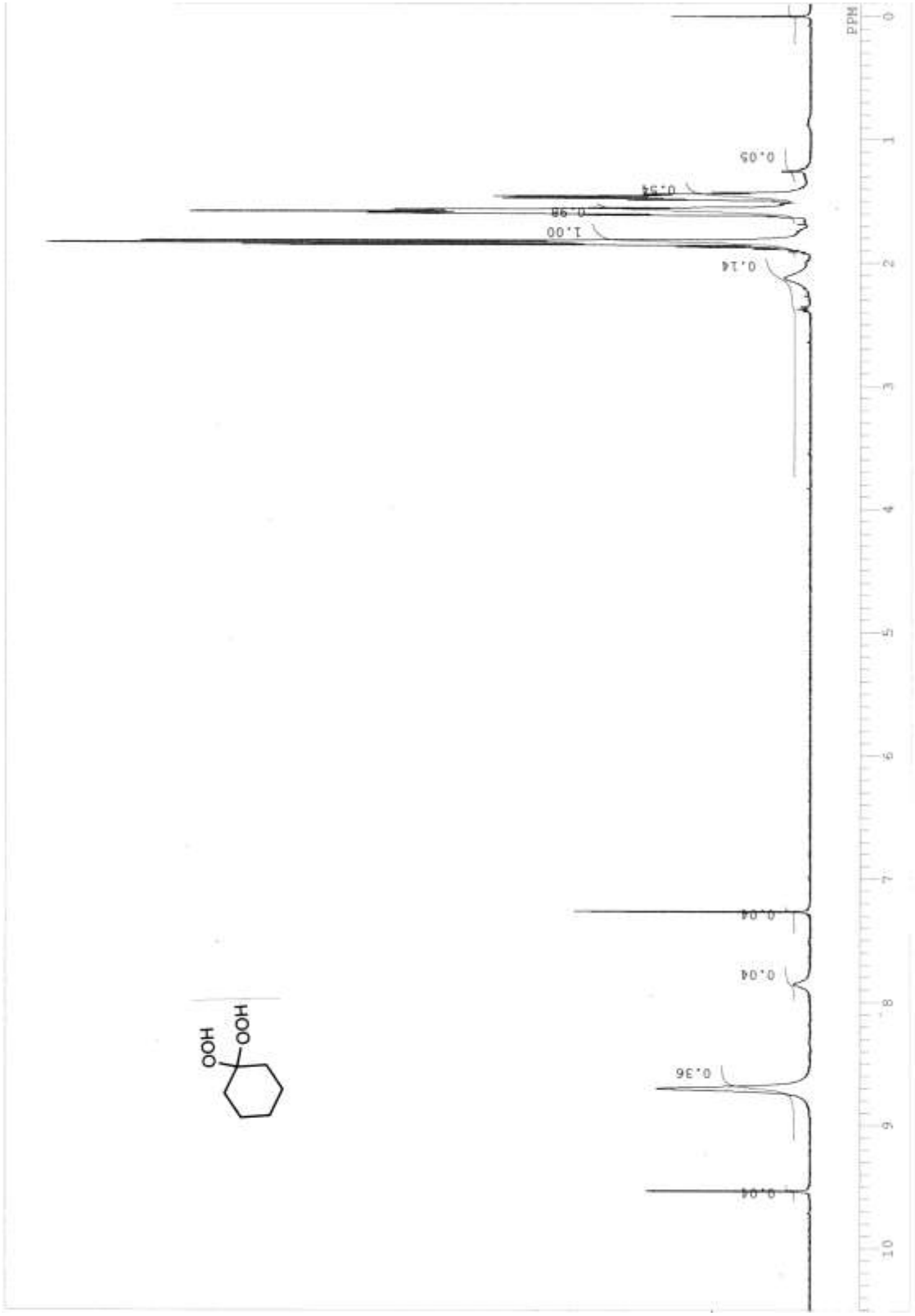
3) Žmitek, K.; Zupan, M.; Stavber, S.; Iskra, J. *J. Org. Chem.* **2007**, *72*, 6534-6540.

4) Žmitek, K.; Zupan, M.; Stavber, S.; Iskra, J. *Org. Lett.* **2006,** *8*, 2491-2494.

5. ^{1}H and ^{13}C NMR spectra



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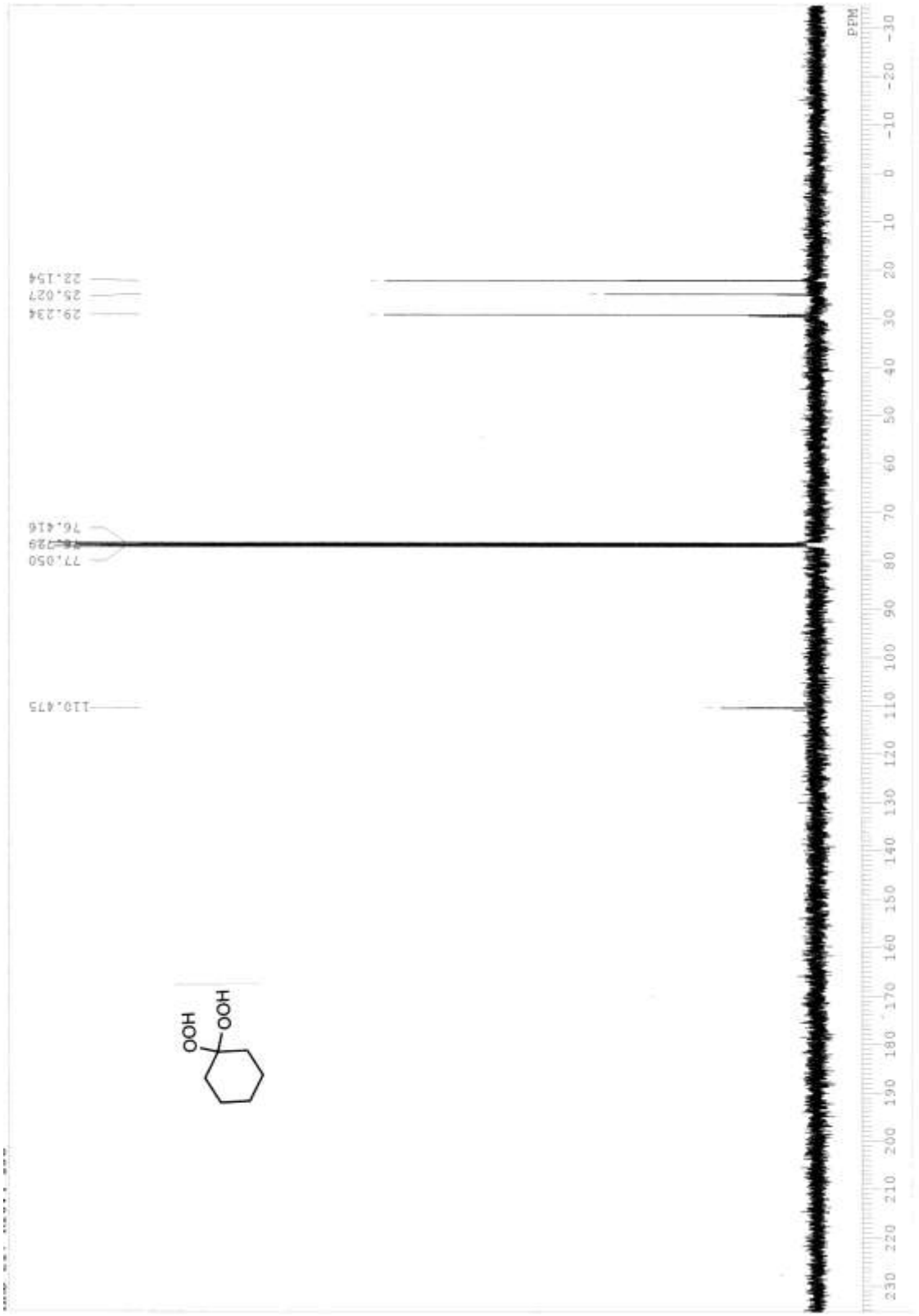
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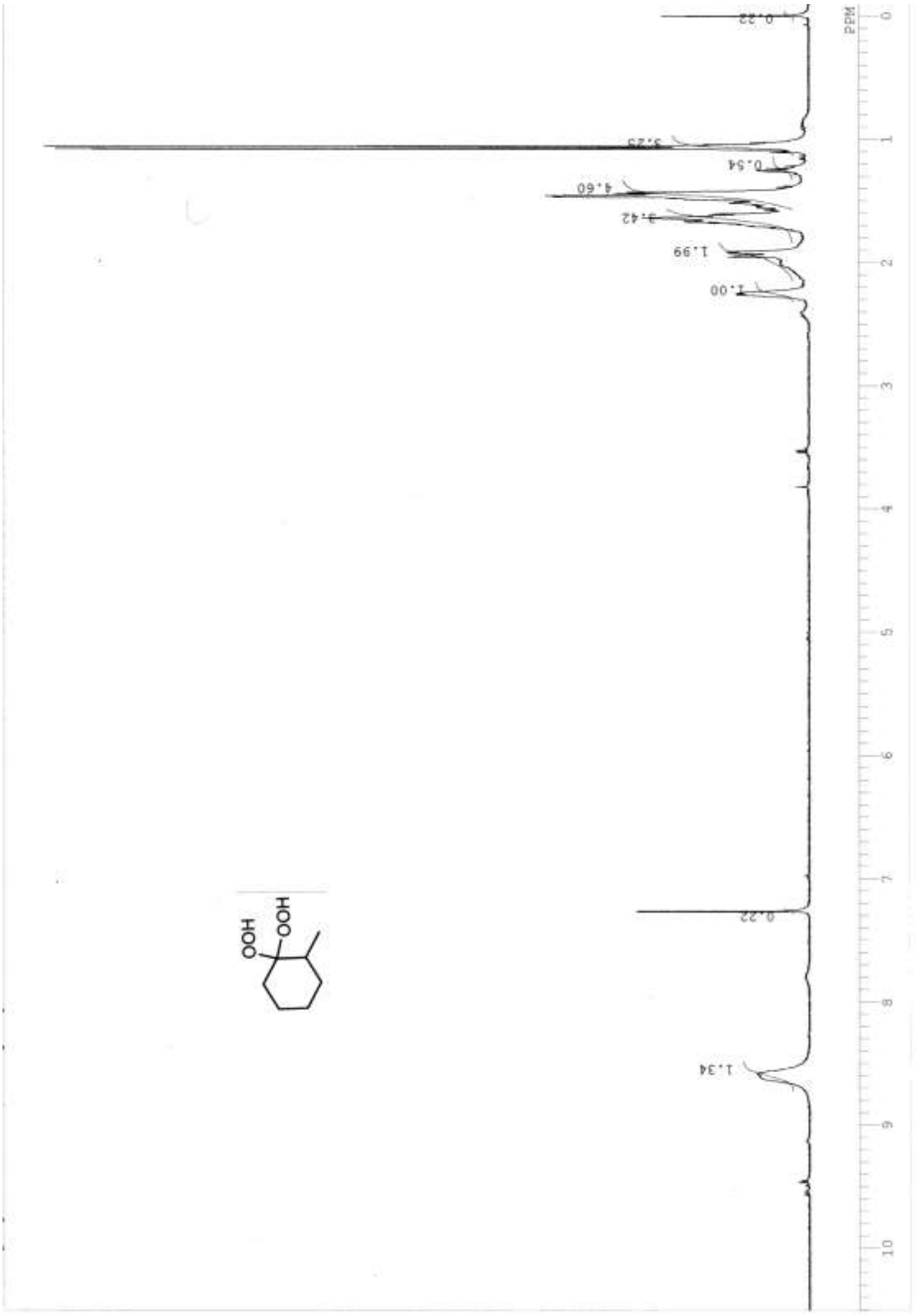

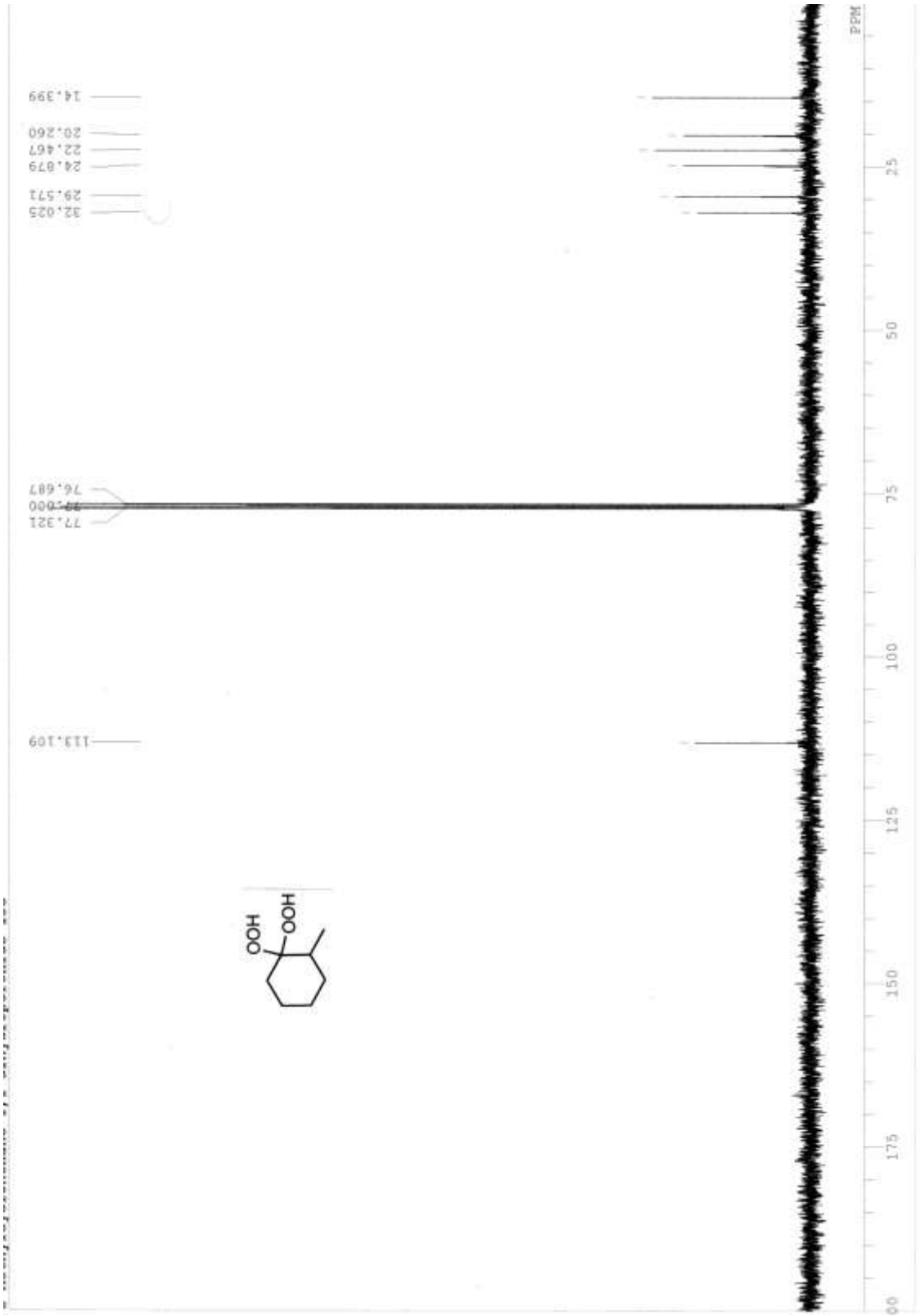

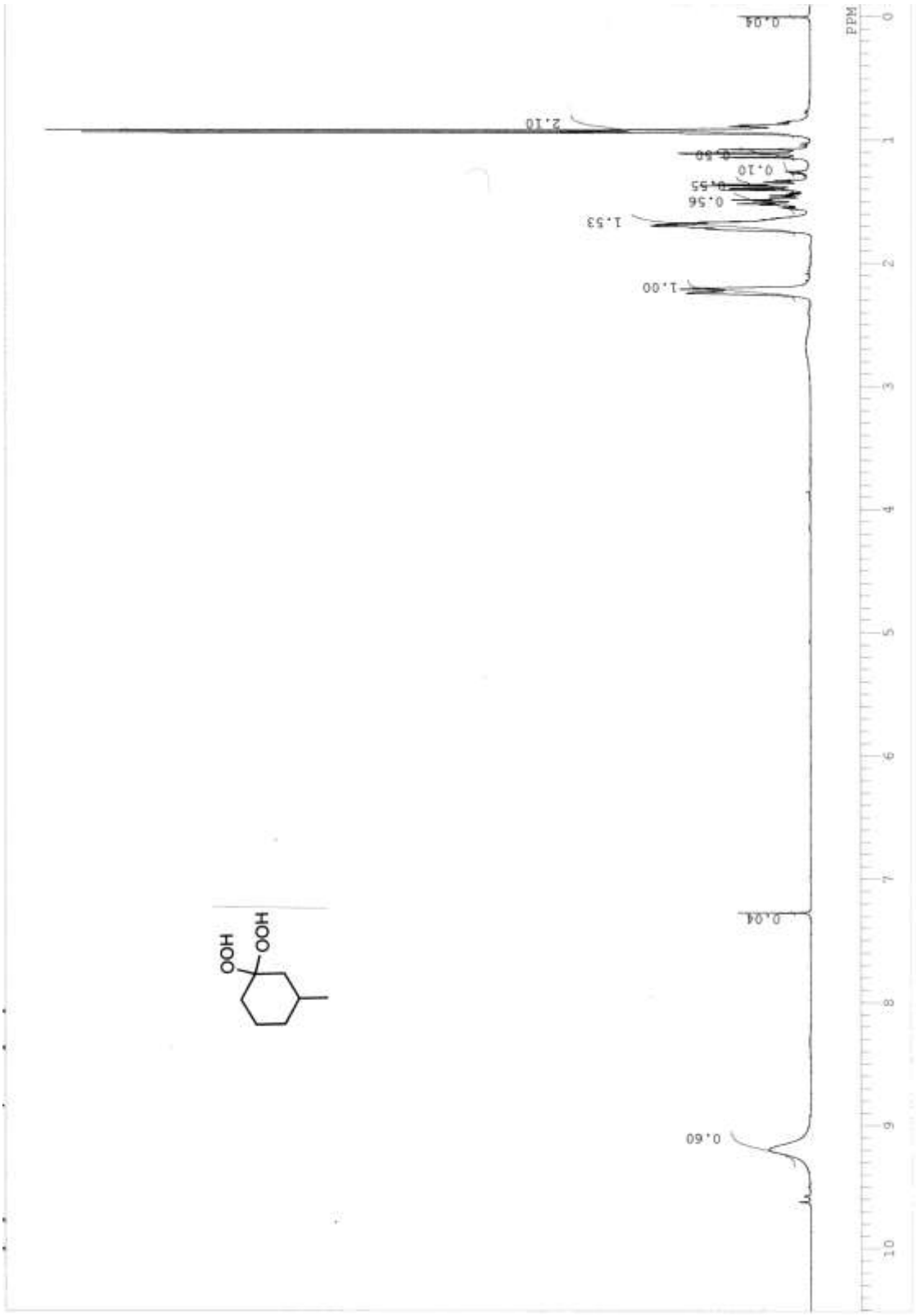

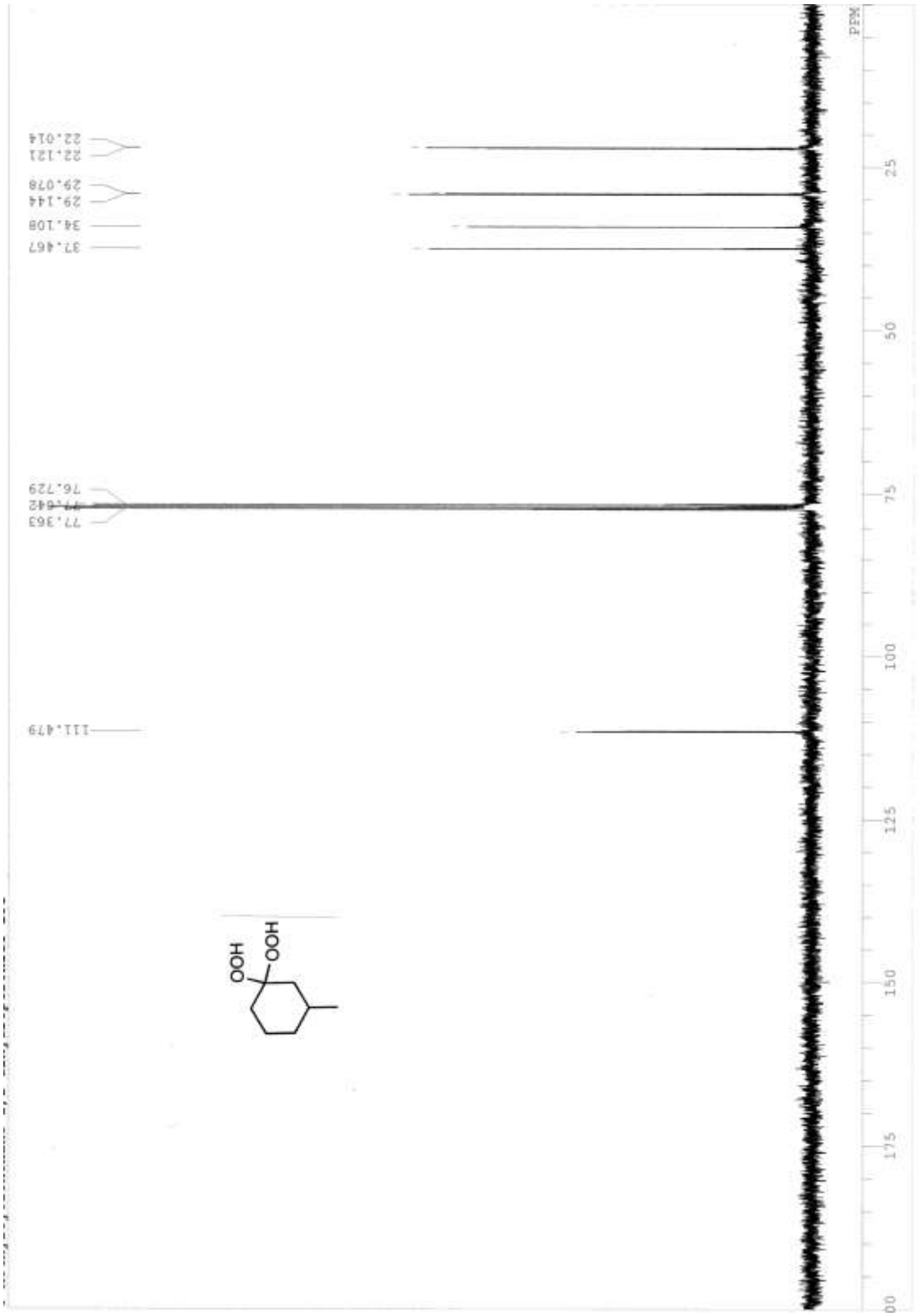

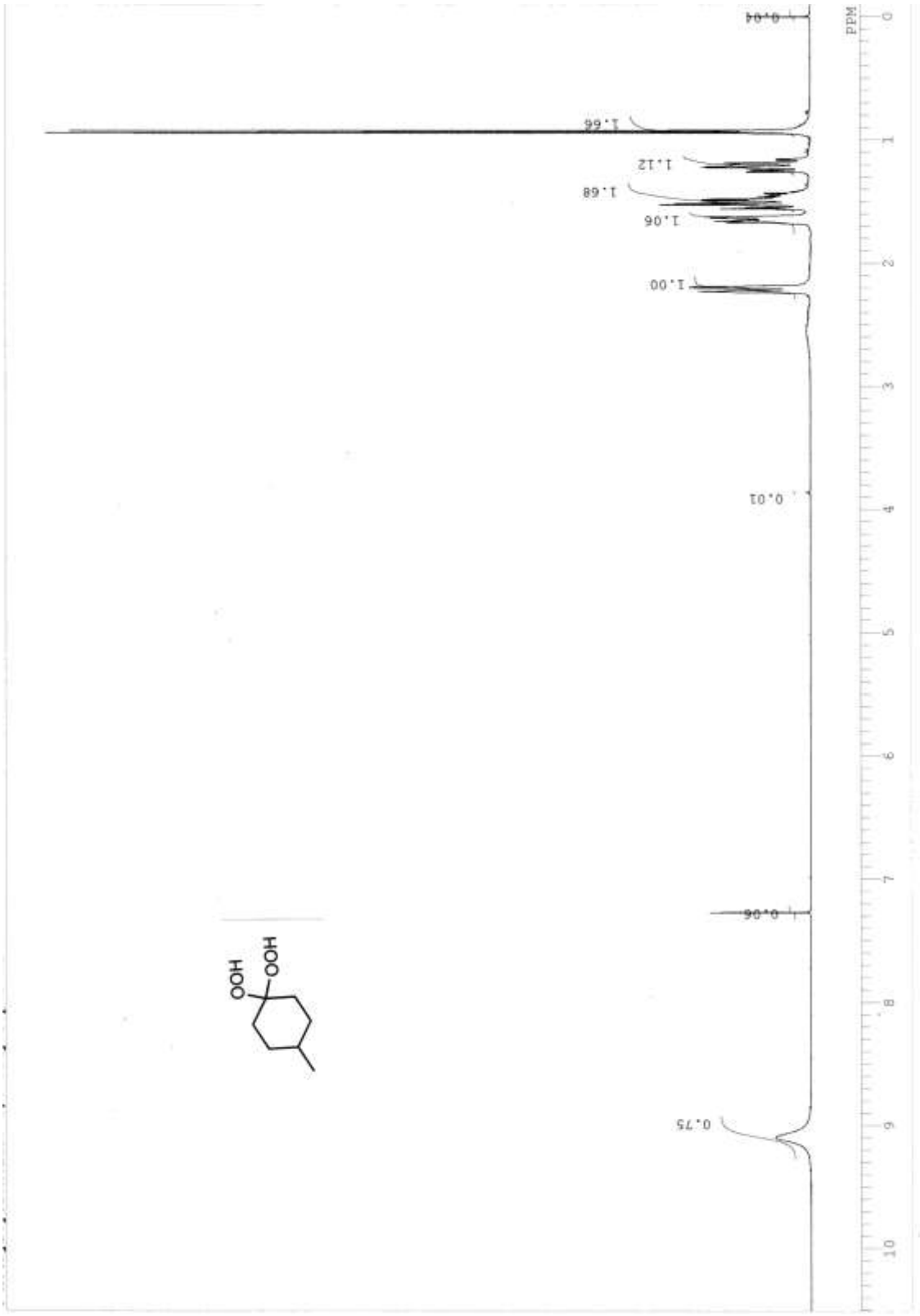
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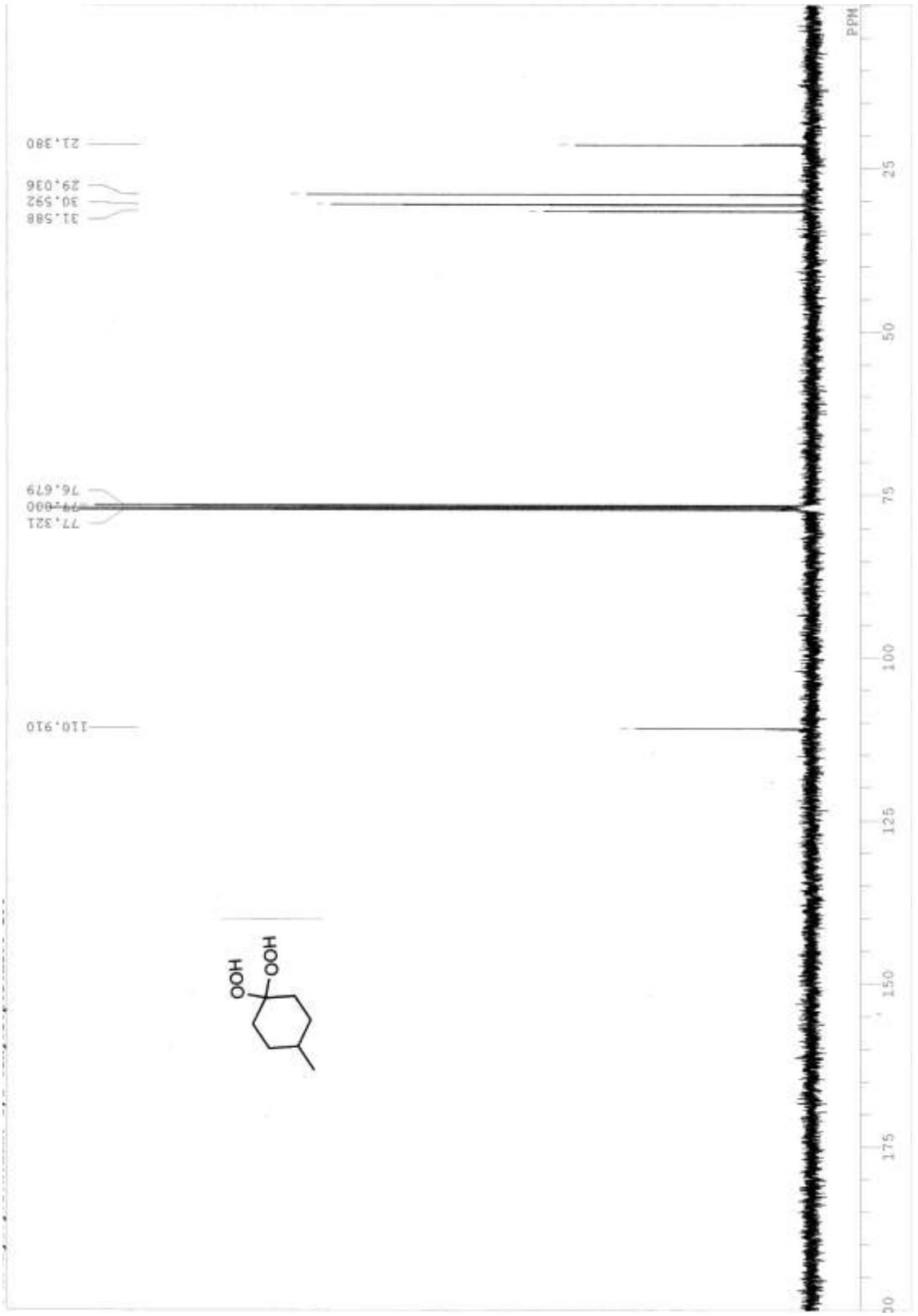

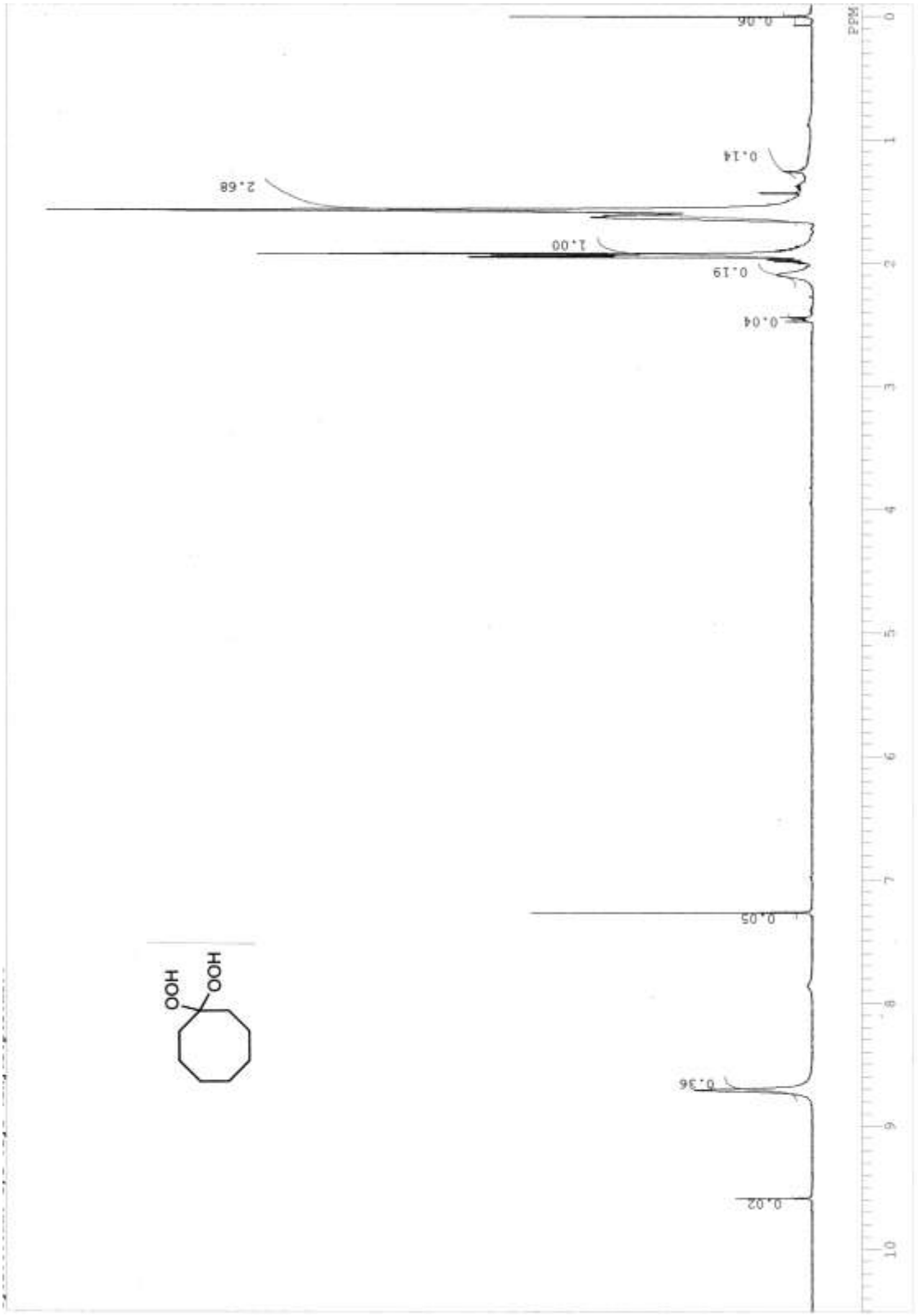
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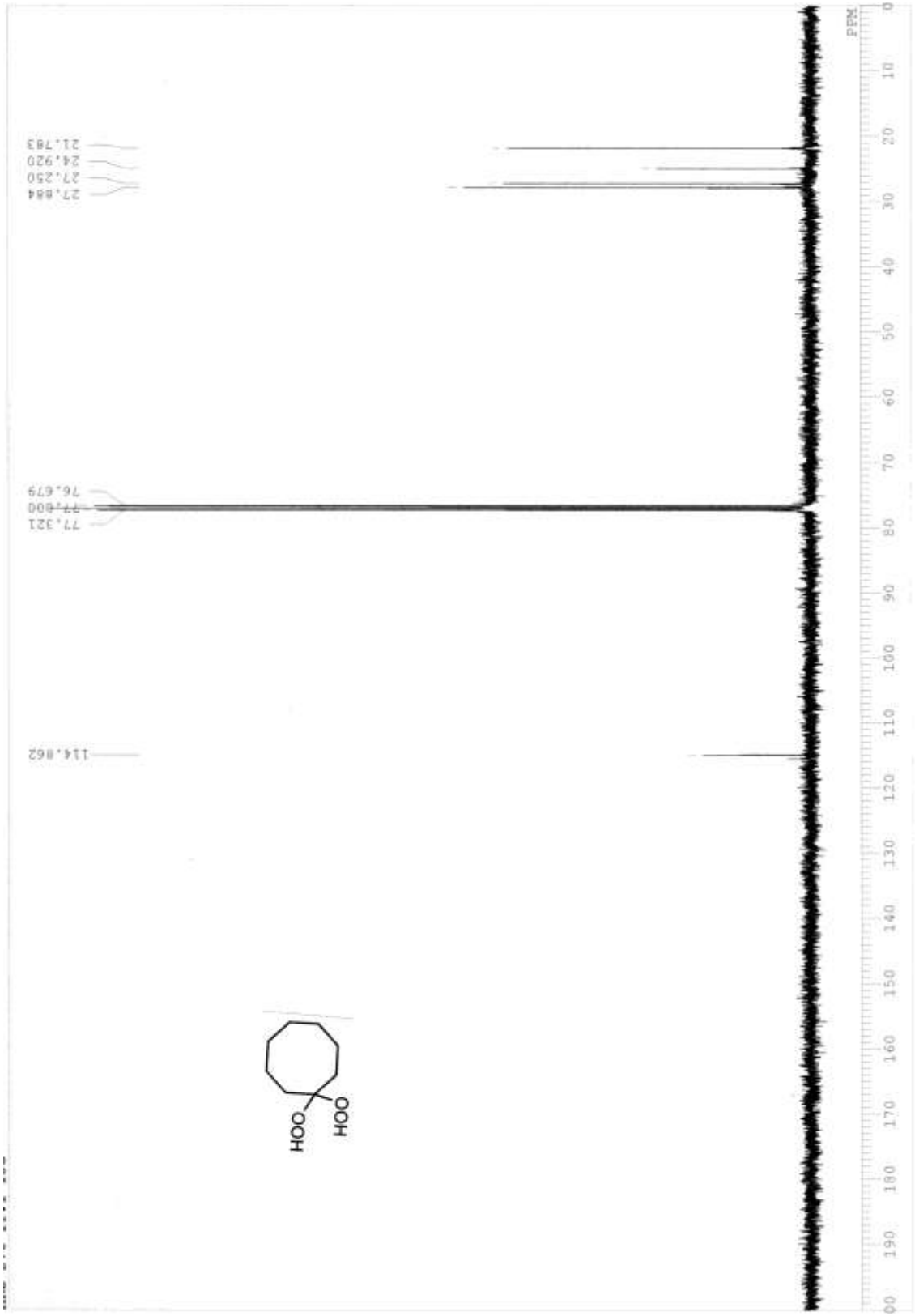
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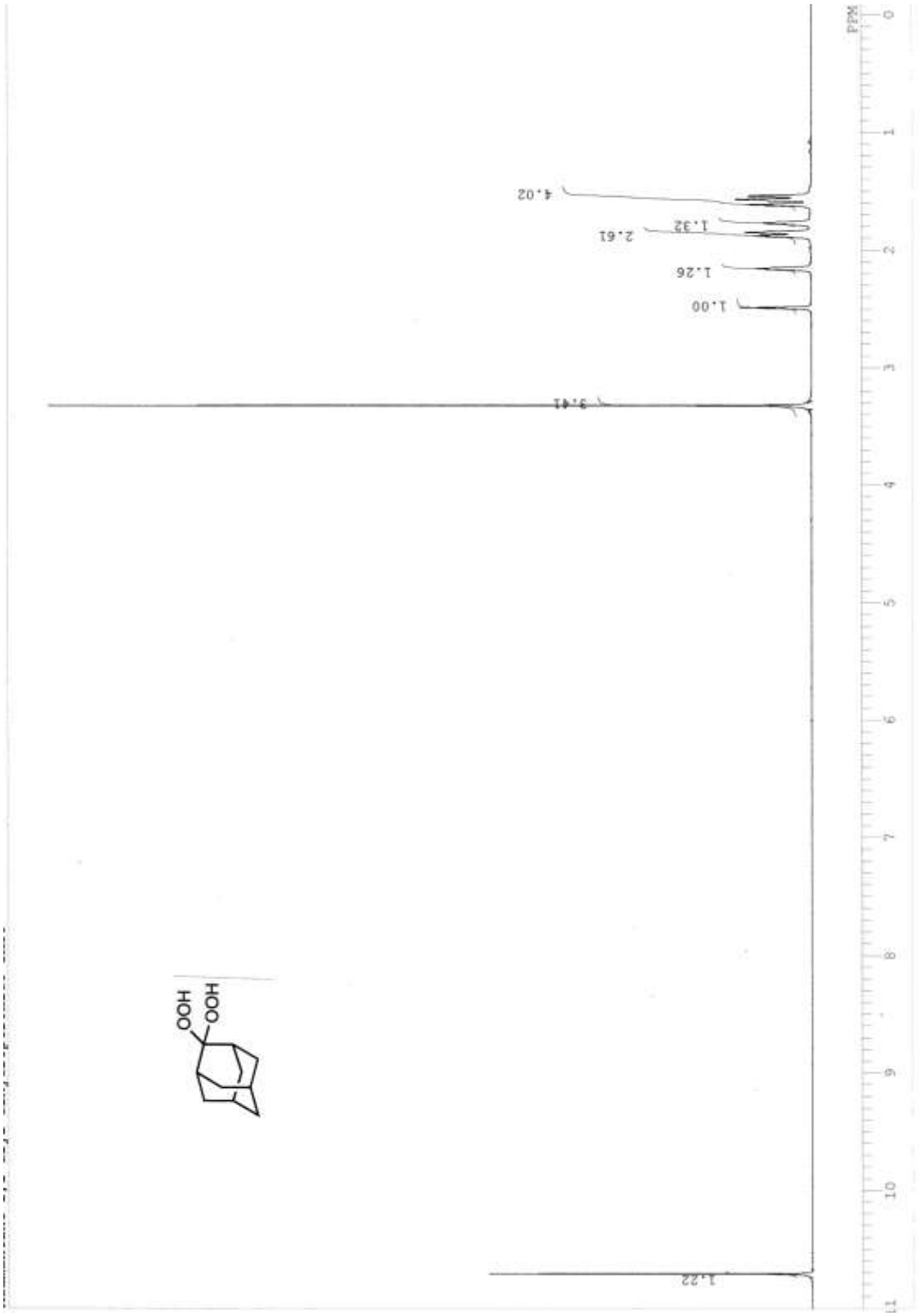

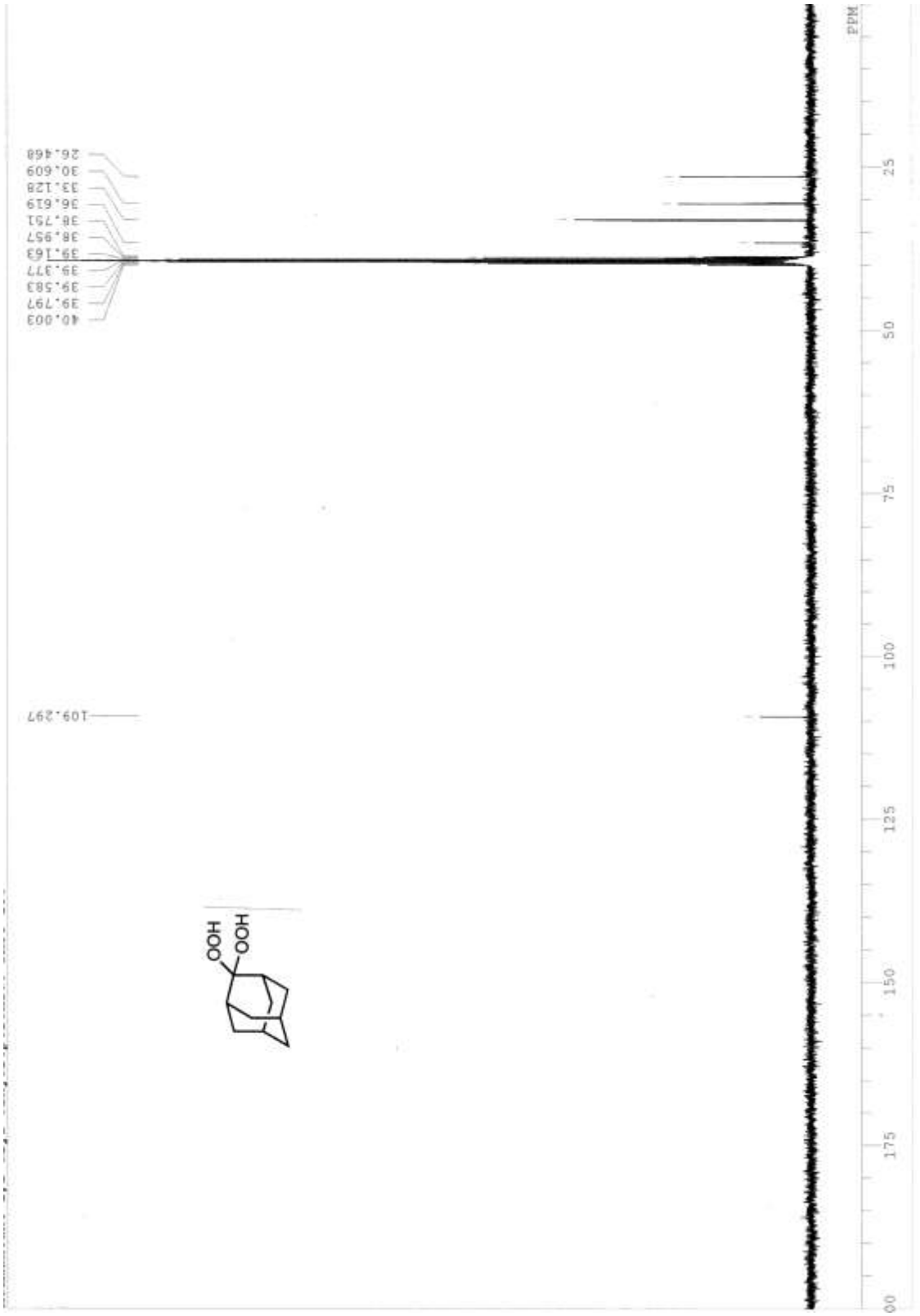

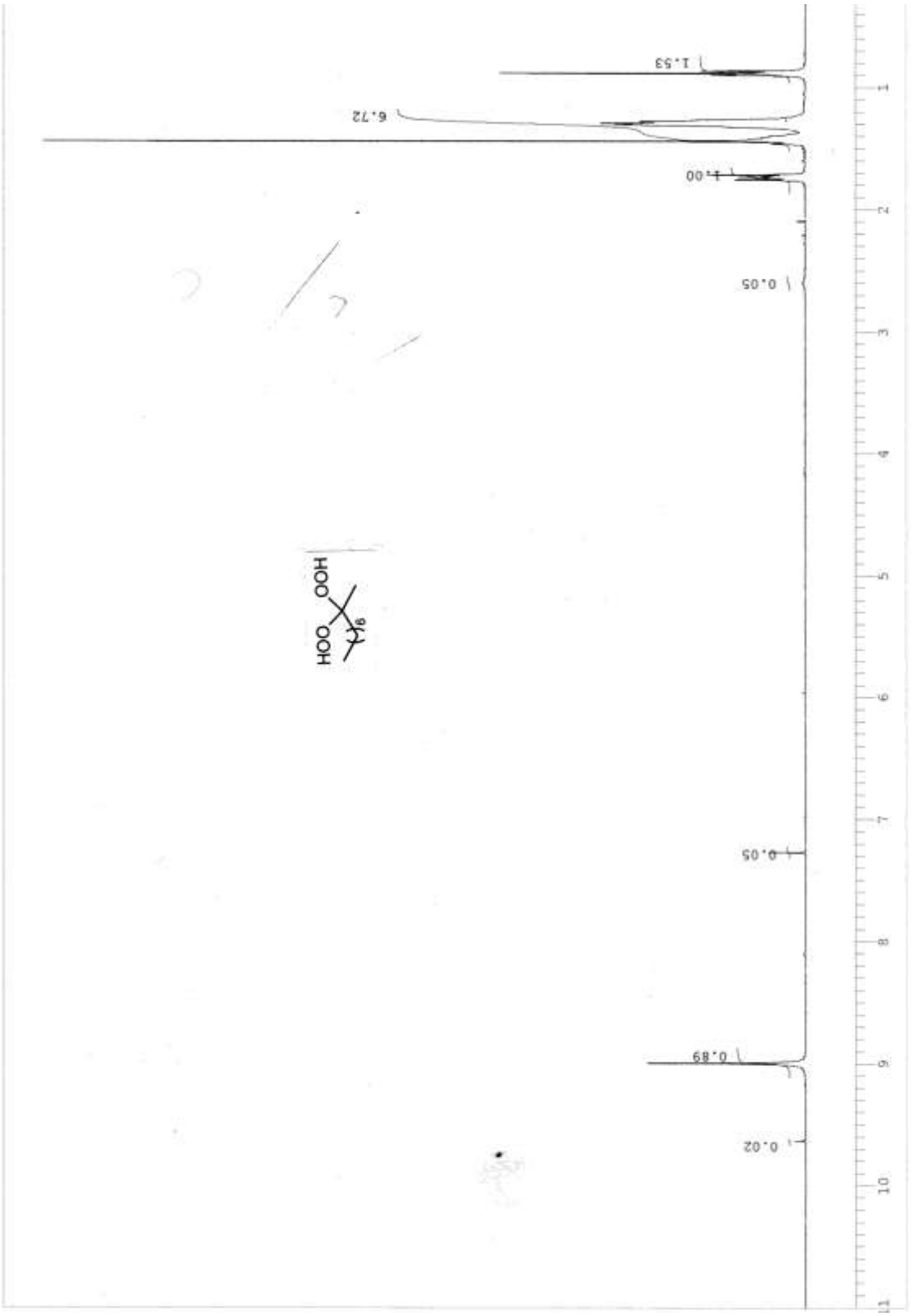

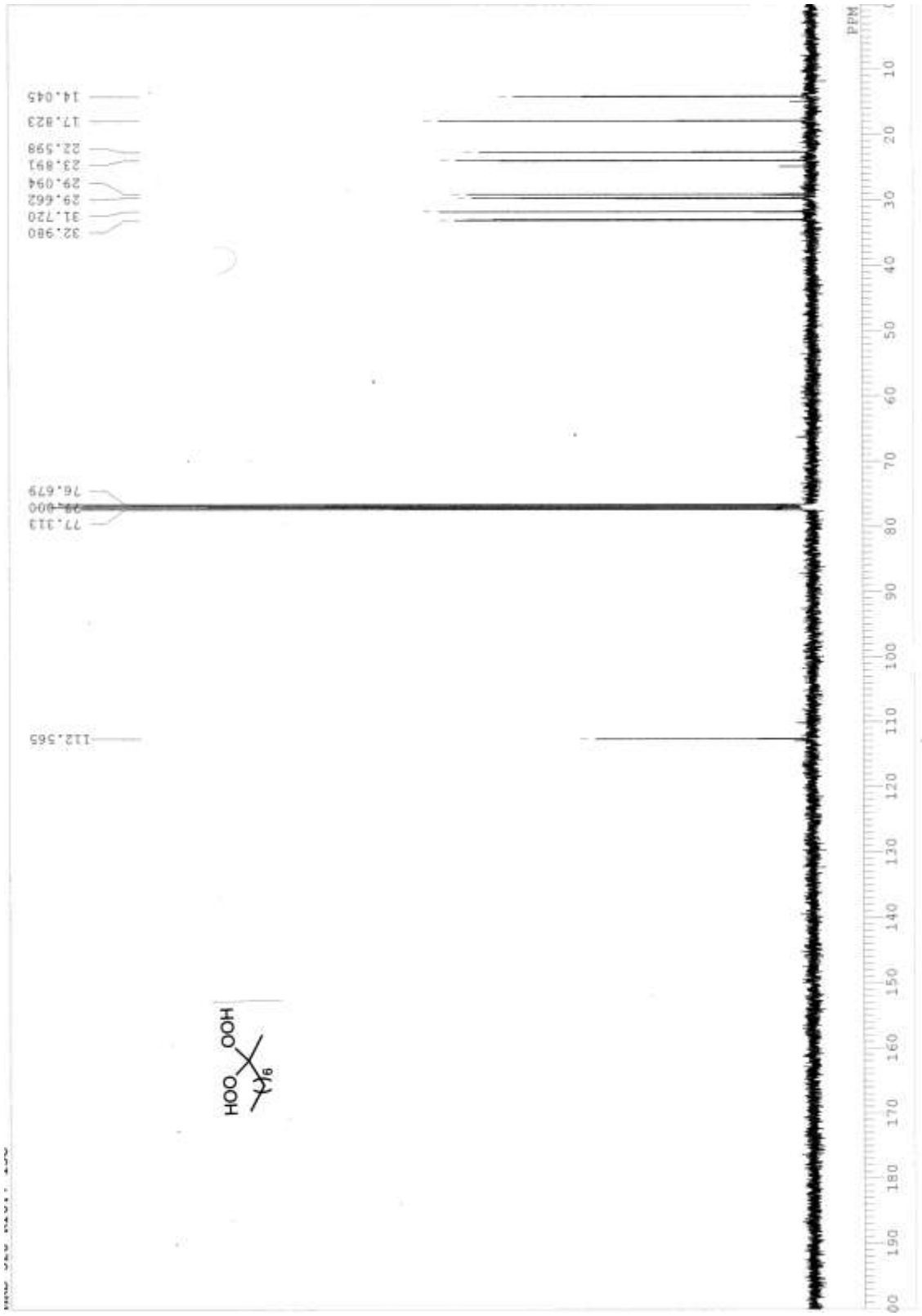
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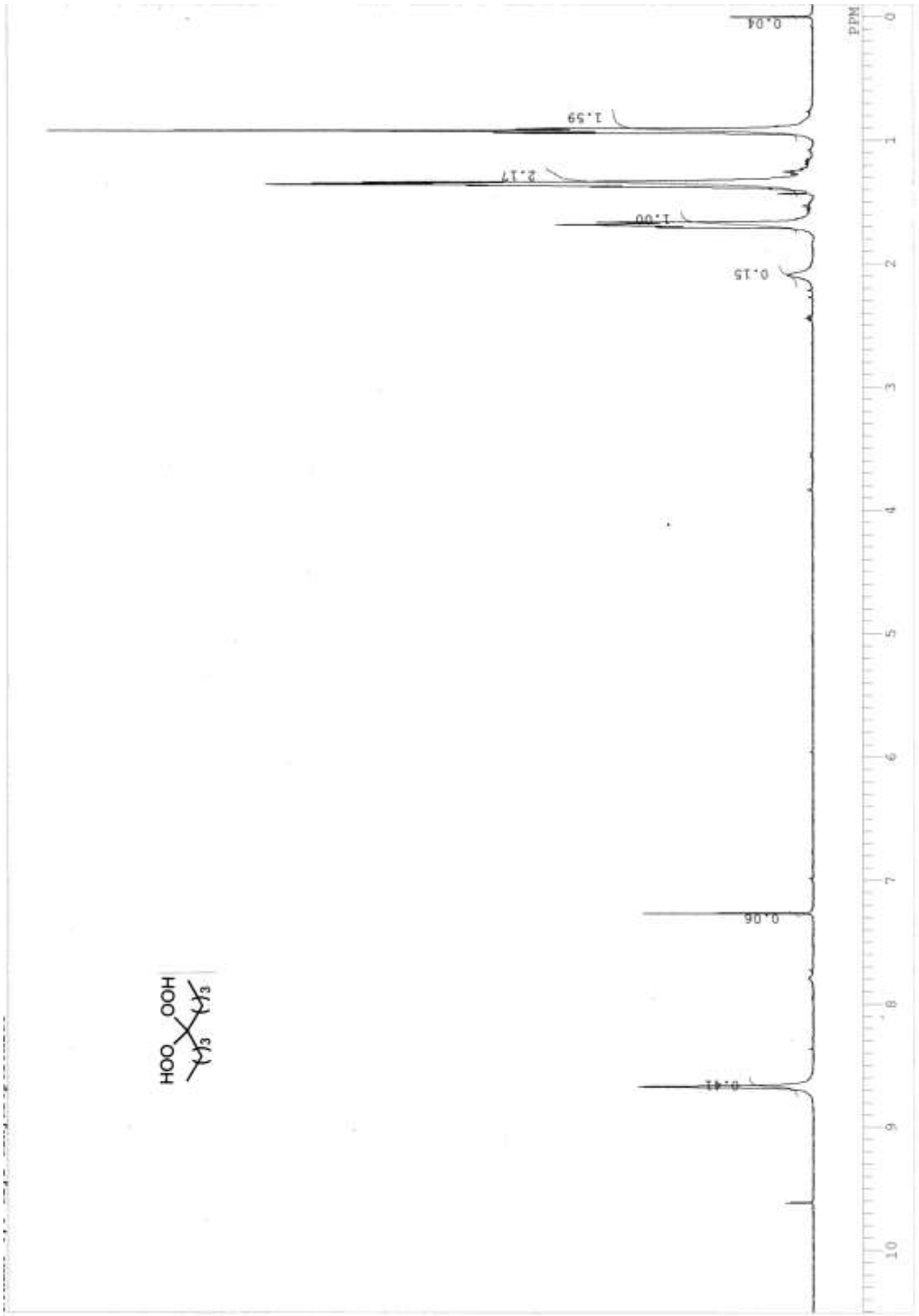
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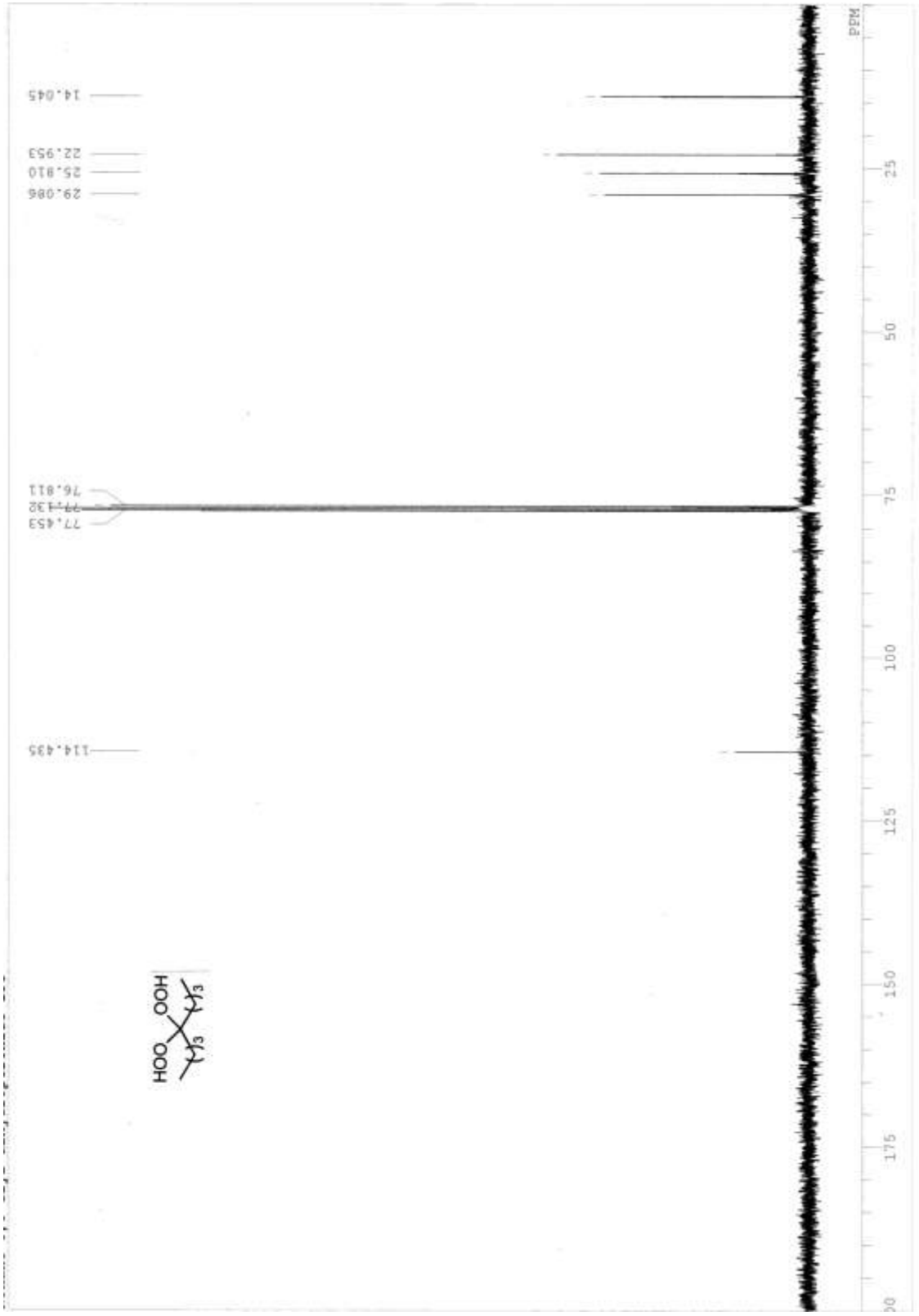
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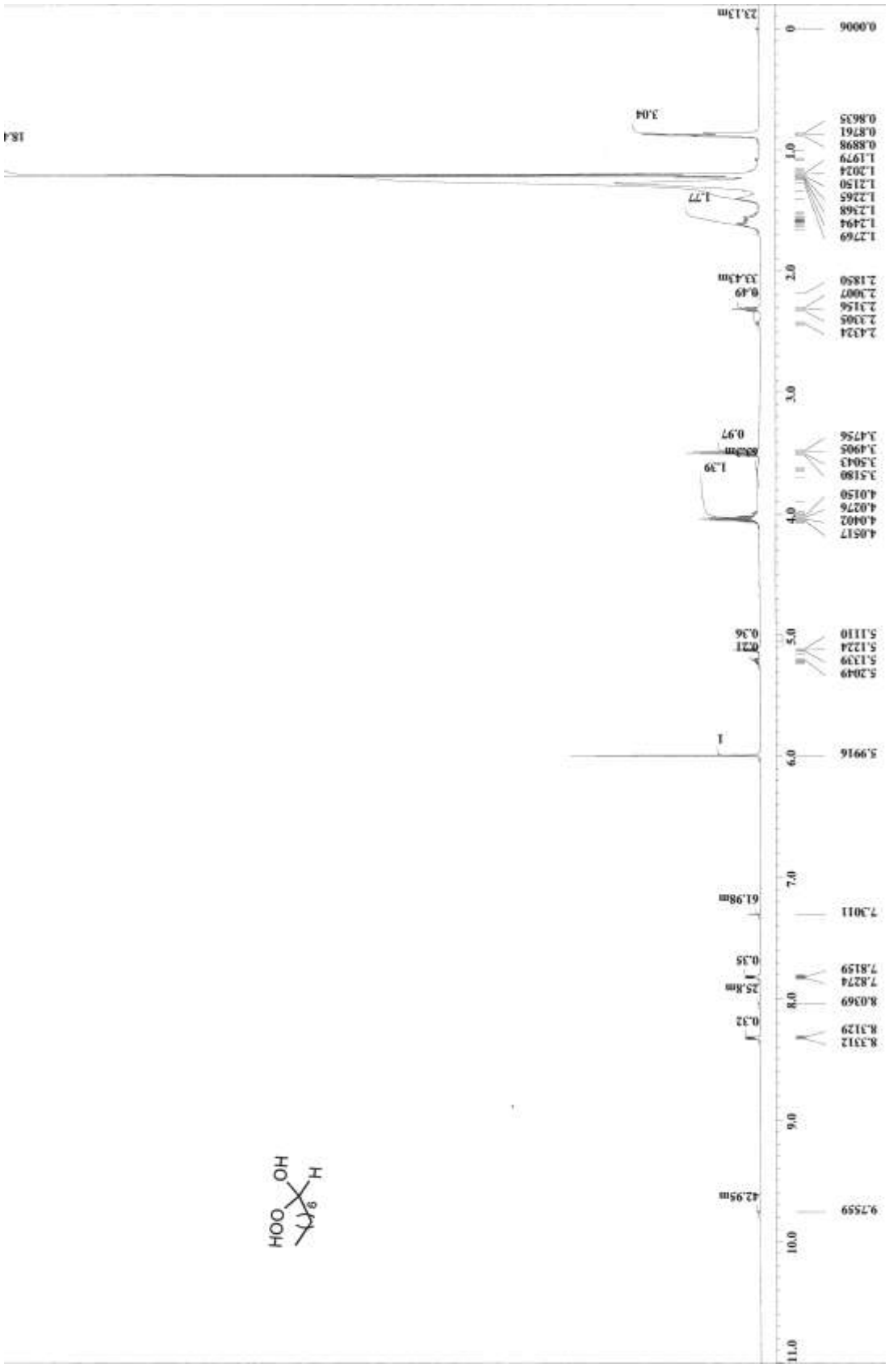

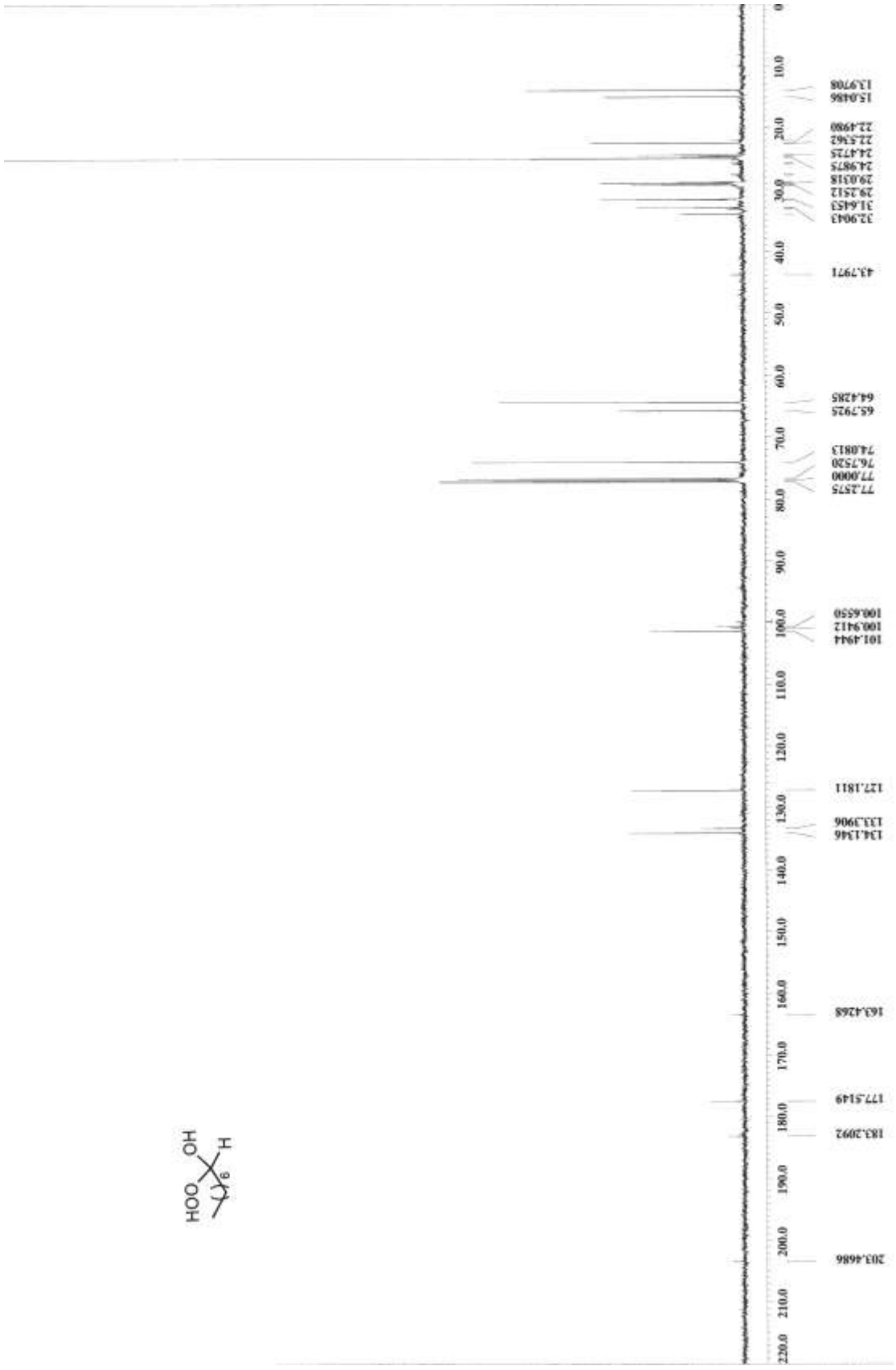
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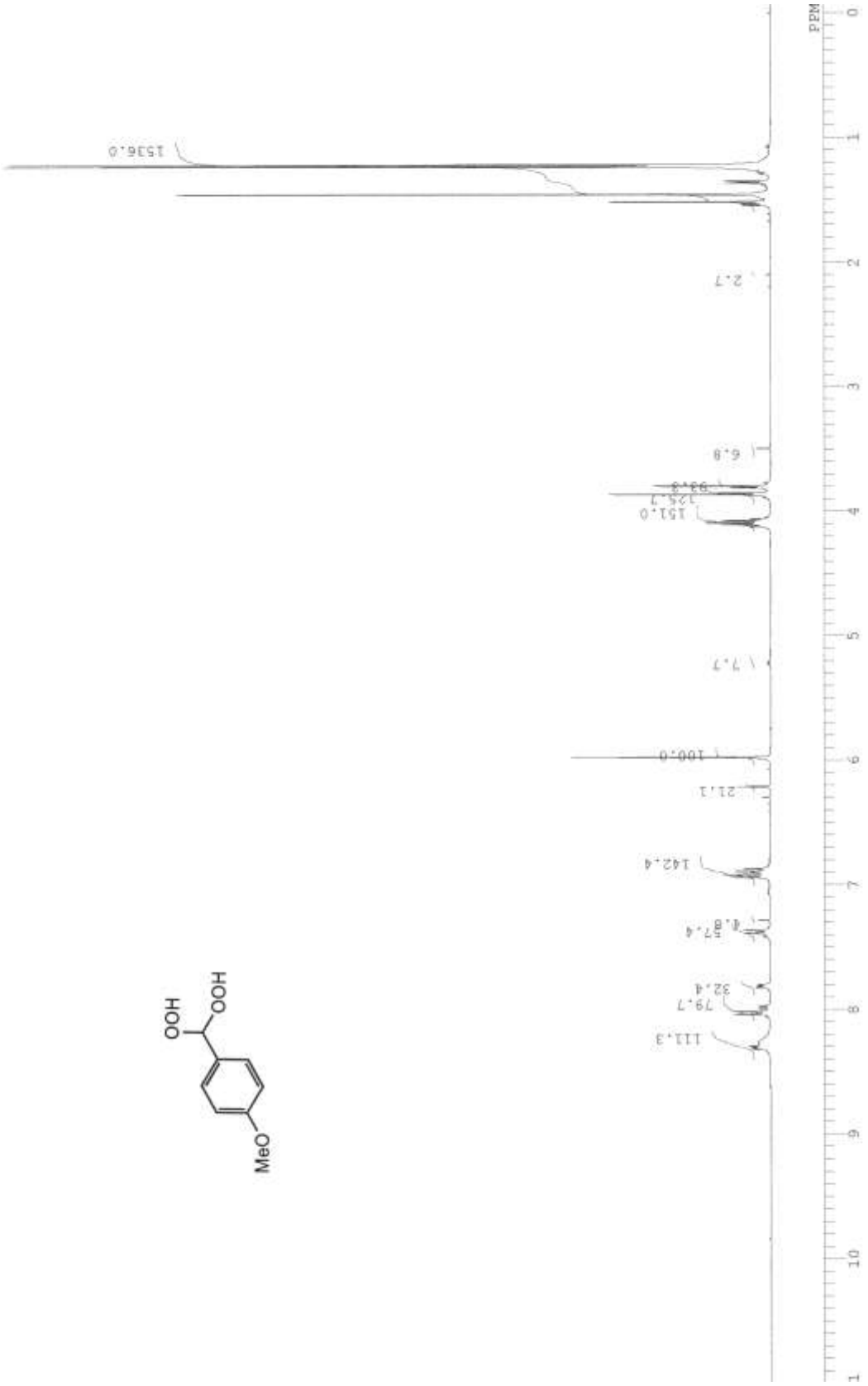
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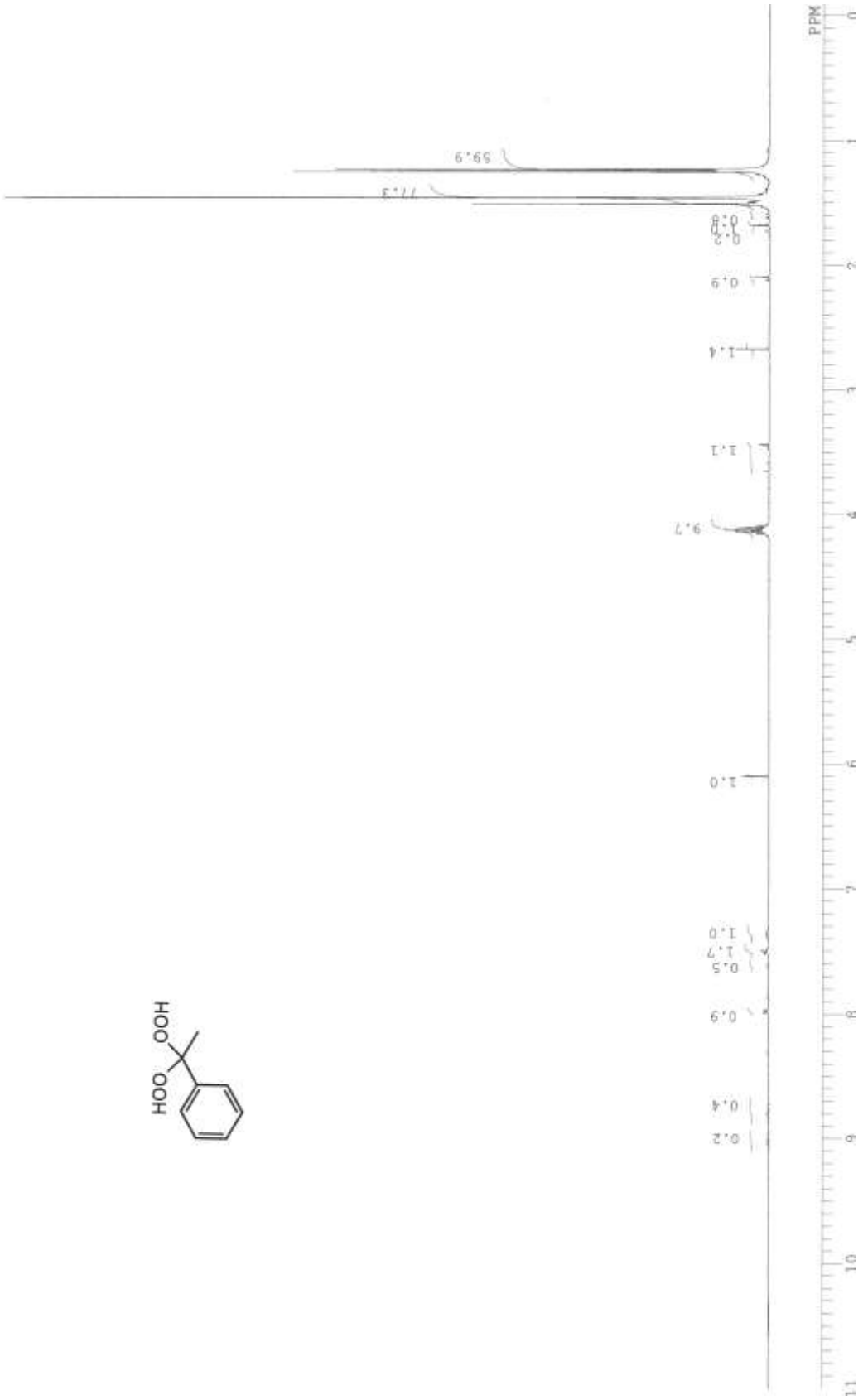
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