Supplementary Material

De novo synthesis and lectin binding studies of unsaturated carbapyranoses

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(2,5-Dimethoxyphenyl)methanol

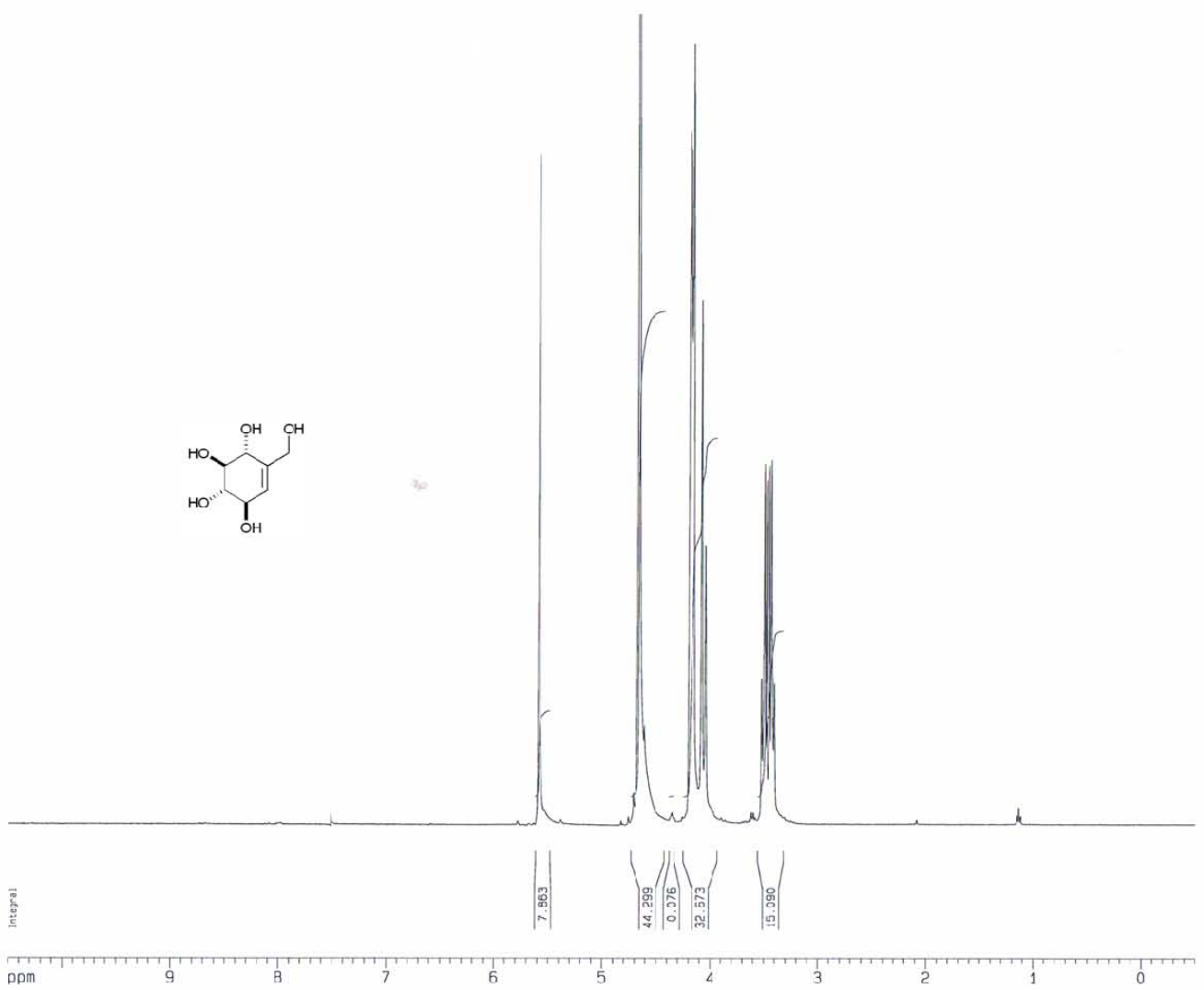
To a solution of 10.0 g (60.0 mmol) 2,5-dimethoxybenzaldehyde in 100 mL diethyl ether is added a solution of 3.4 g (90.0 mmol) sodium borohydride in 100 mL water. The mixture is stirred for 1 h at ambient temperature, the phases are separated and the aqueous phase is extracted with diethyl ether (3 x 50 mL). The combined organic layer is washed with brine (50 mL), dried over Na_2SO_4 and filtered. The solvent is evaporated to yield 10.0 g (59.5 mmol, 99 %) of a light yellow oil. ^{1}H-NMR (DMSO-*d*$_6$): δ 3.68 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 4.48 (d, 2H, *J* = 5.71 Hz, CH_2), 4.99 (t, 1H, *J* = 5.71 Hz, OH), 6.72 (dd, 1H, *J* = 3.12 and 8.81 Hz, H-4), 6.81 (d, 1H, *J* = 8.81 Hz, H-3), 6.99 (d, 1H, *J* = 3.12 Hz, H-6). ^{13}C-NMR (DMSO-*d*$_6$): δ 55.3, 55.6 (2 x OCH_3), 57.9 (CH_2), 111.0 (C-6), 111.5 (C-4), 113.3 (C-3), 131.7 (C-1), 150.1, 153.3 (C-2 and C-5). Anal. calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.59; H, 7.15 %.

2,5-Dimethoxybenzyl acetate

4.7 g (28.0 mmol) (2,5-Dimethoxyphenyl)methanol are dissolved in a cooled mixture (0 °C) of 10 mL triethylamine and 5 mL acetic anhydride and the reaction mixture is stirred for 1 h at ambient temperature. All volatiles are removed in vacuo and the residue is taken up in diethyl ether (100 mL). The organic phase is washed with 0.75 N HCl (3 x 20 mL), saturated aqueous $NaHCO_3$ (3 x 20 mL) and brine (20 mL). Evaporation of the solvent yields 4.7 g (22.4 mmol, 80 %) of a light yellow oil. ^{1}H-NMR (DMSO-*d*$_6$): δ 2.03 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.01 (s, 2H, CH_2), 6.84 (dd, 1H, *J* = 2.98 and 8.79 Hz, H-4), 6.88 (d, 1H, *J* = 2.98 Hz, H-6), 6.90 (d, 1H, *J* = 8.79 Hz, H-3). ^{13}C-NMR (DMSO-*d*$_6$): δ 20.5 (CH_3), 55.3, 55.8 (2 x OCH_3), 60.8 (CH_2), 111.9 (C-6), 113.5 (C-4), 115.4 (C-3), 124.9 (C-1), 151.1, 153.0 (C-2 and C-5), 170.2 (C=O). Anal. calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.79; H, 6.72 %.

(3,6-Dioxocyclohexa-1,4-dien-1-yl)methyl acetate

To a solution of 11.1 g (53.0 mmol) 2,5-dimethoxybenzyl acetate in 200 mL 1,4-dioxane are added 7.1 g (58.0 mmol) silver(I,III) oxide followed by 20 mL of 6 N nitric acid. After 15 min. at ambient temperature 480 mL chloroform and 120 mL water are added and the phases are separated. The organic layer is washed with saturated aqueous $NaHCO_3$ (3 x 200 mL) and brine (200 mL), dried over Na_2SO_4 and filtered. Removal of the solvent yields 7.9 g (44.1 mmol, 83 %) of a yellow solid. ^{1}H-NMR (DMSO-*d*$_6$): δ 2.09 (s, 3H, CH_3), 4.87 (d, 2H, *J* = 1.87 Hz, CH_2), 6.68 (d, 2H, *J* = 1.87 Hz, H-2), 6.86 (m, 2H, H-4 and H-5). ^{13}C-NMR (DMSO-*d*$_6$): δ 20.4 (CH3), 59.1 (CH2), 131.1 (C-2), 136.5, 136.6 (C-4 and C-5), 142.9 (C-1), 169.8, 186.2, 187.3 (3 x C=O). Anal. calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 60.12; H, 4.47 %.



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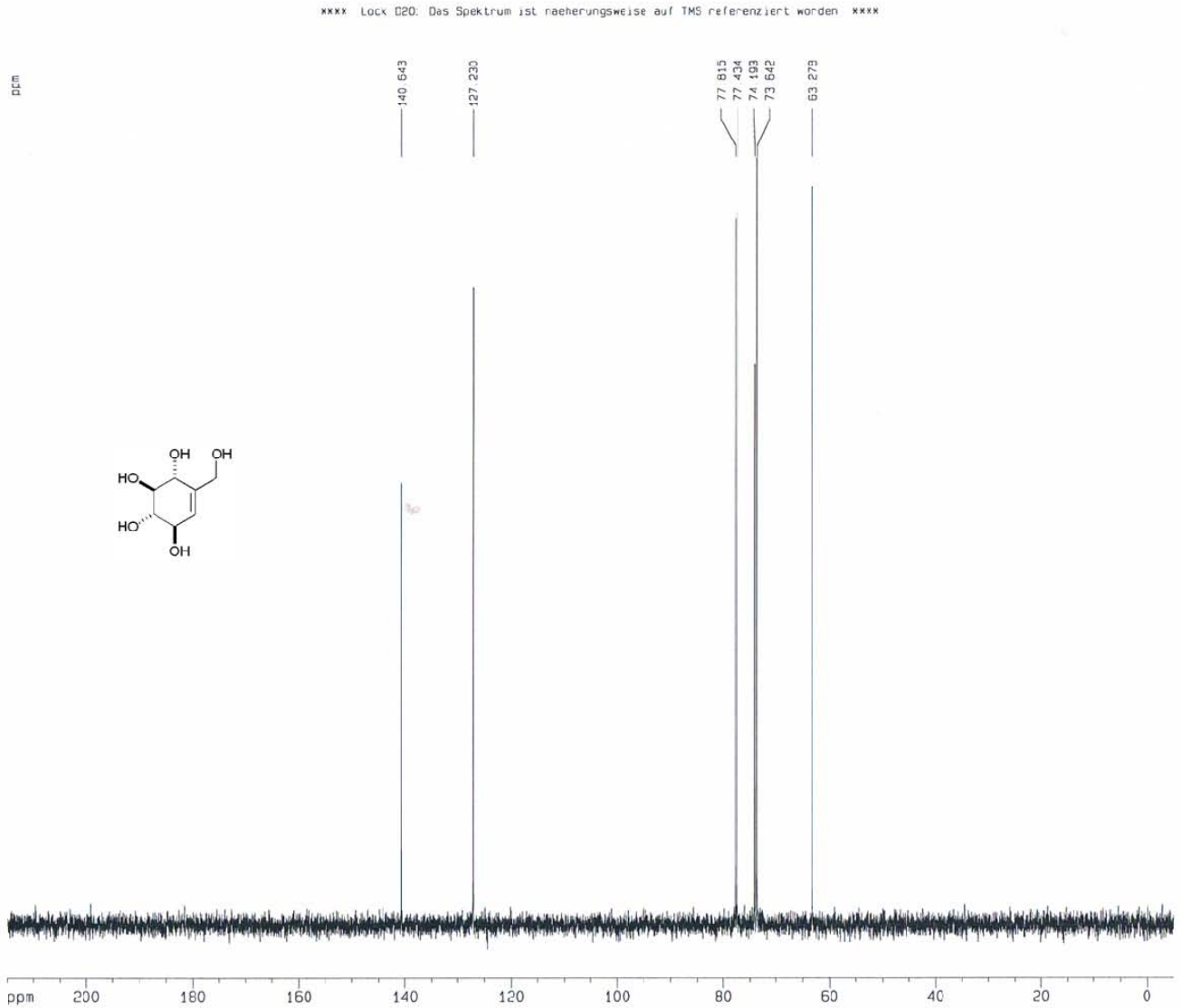

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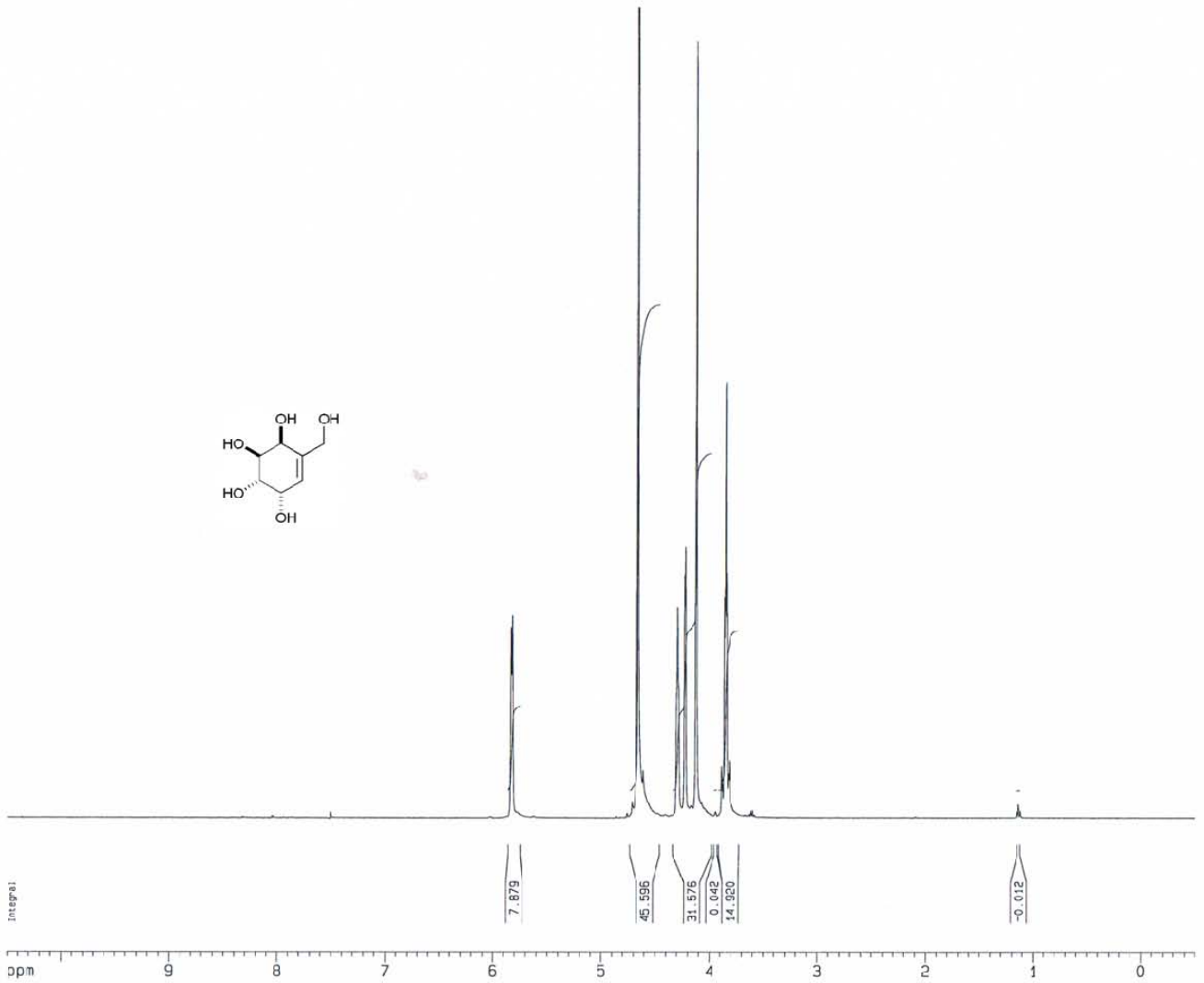

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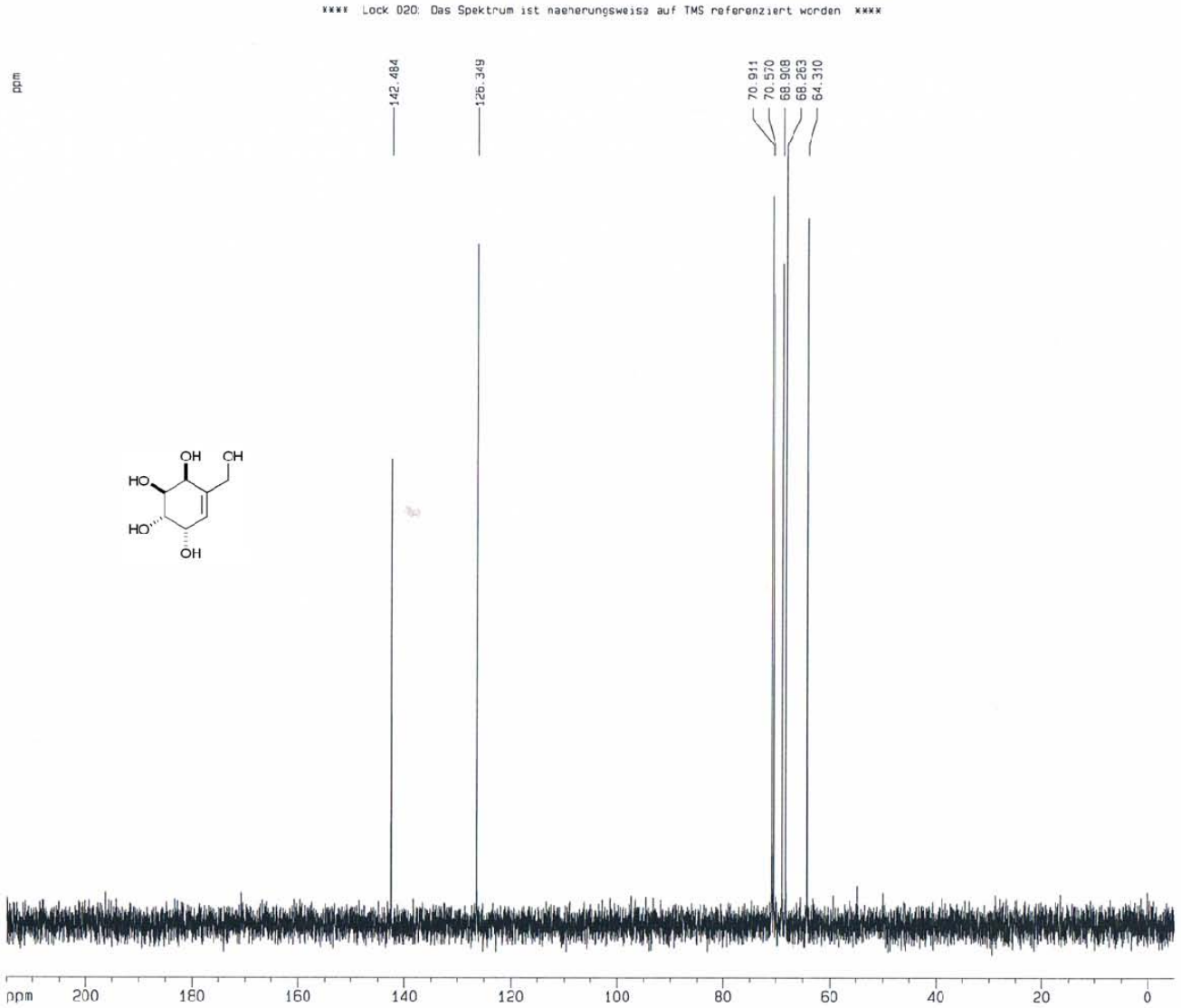

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F2 - Processing parameters

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1D NMR plot parameters

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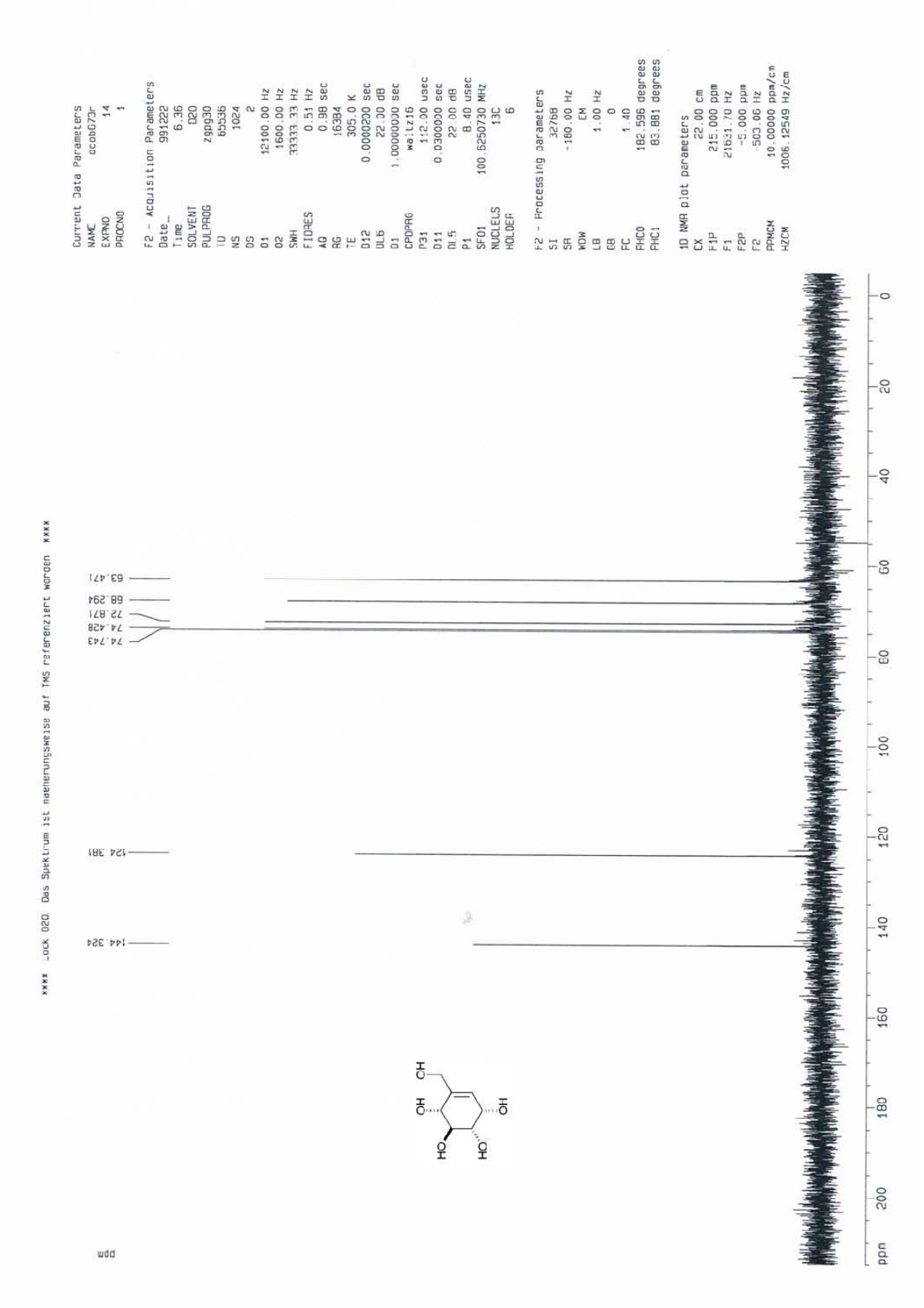
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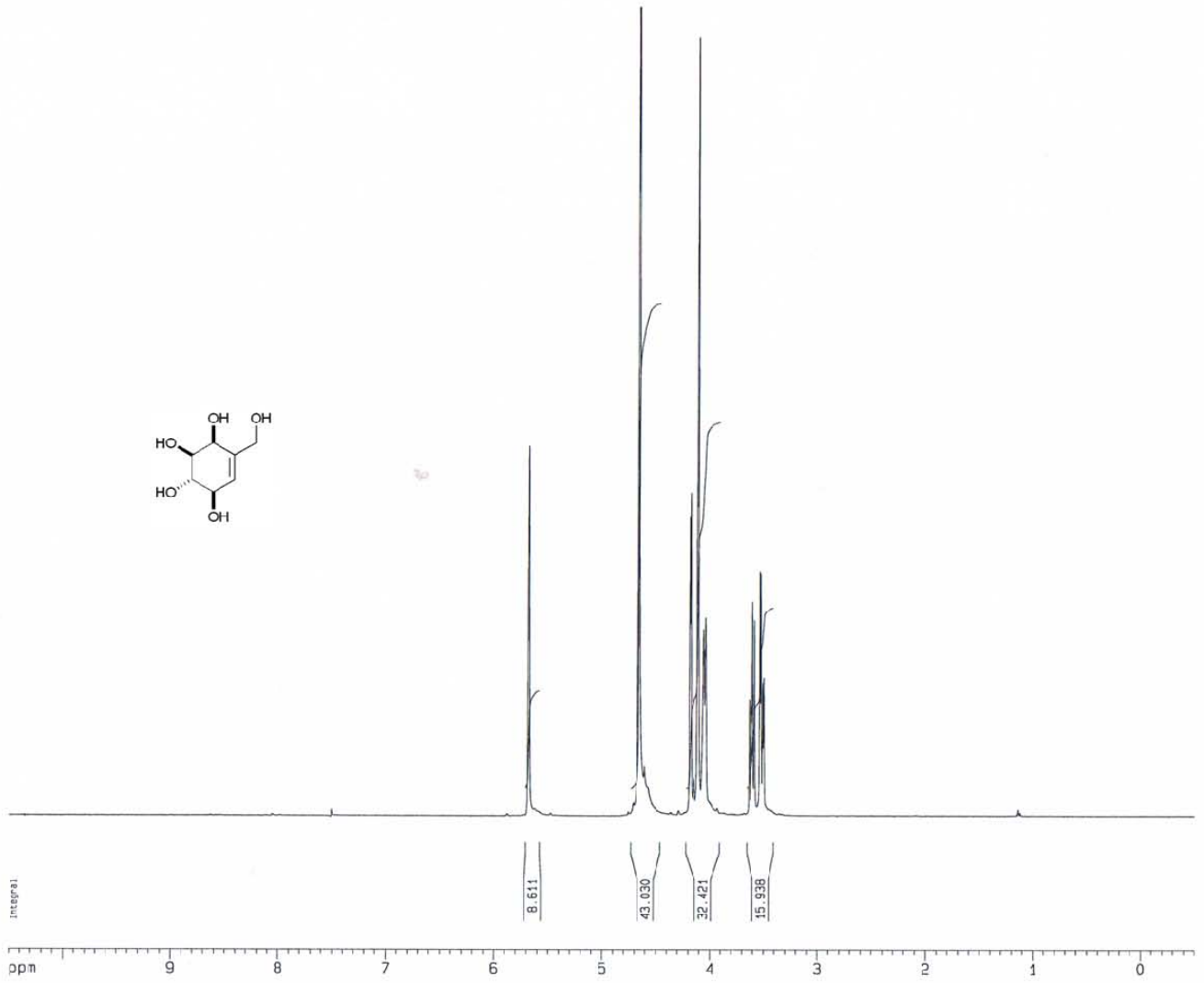

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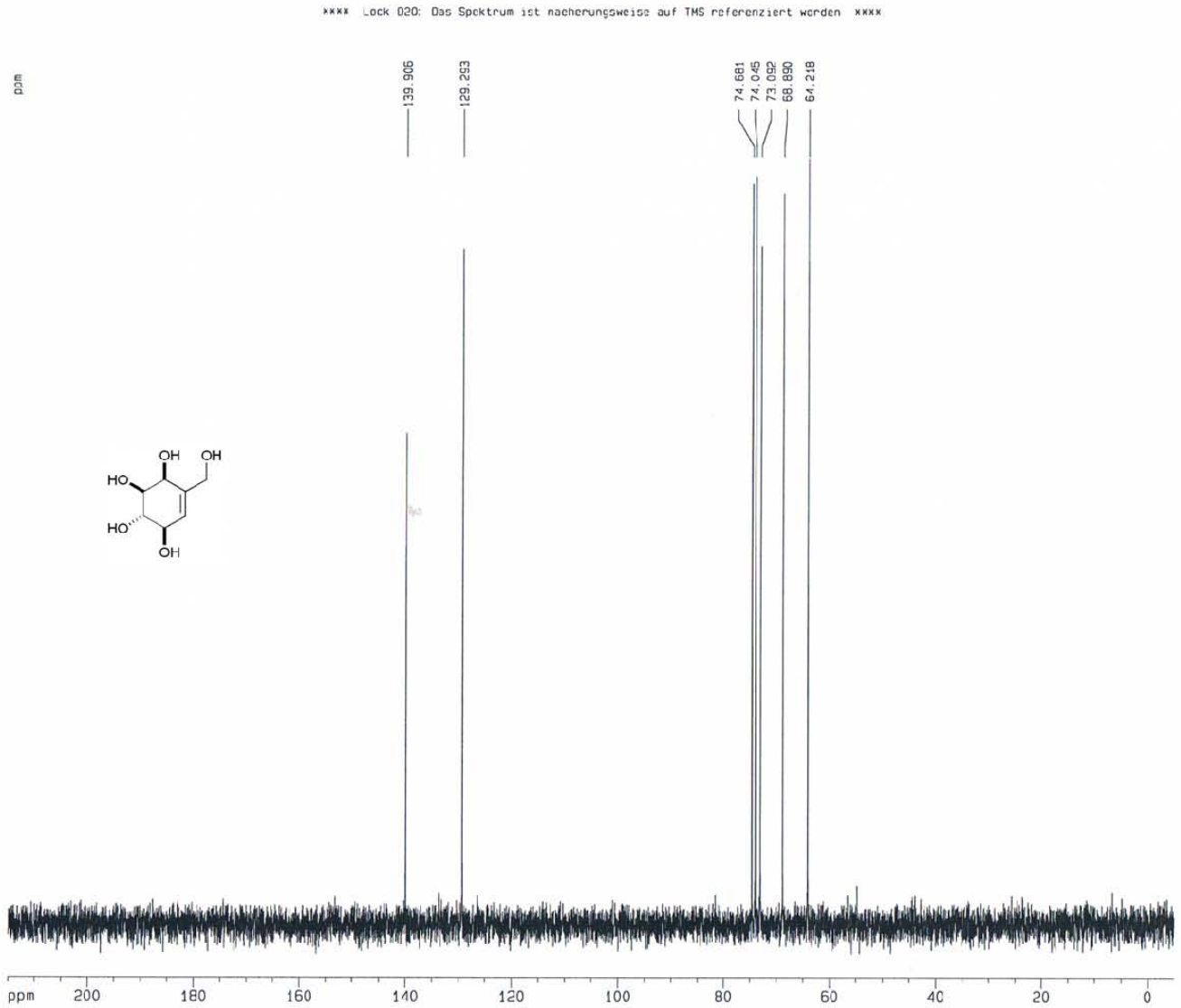

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1D NMR plot parameters

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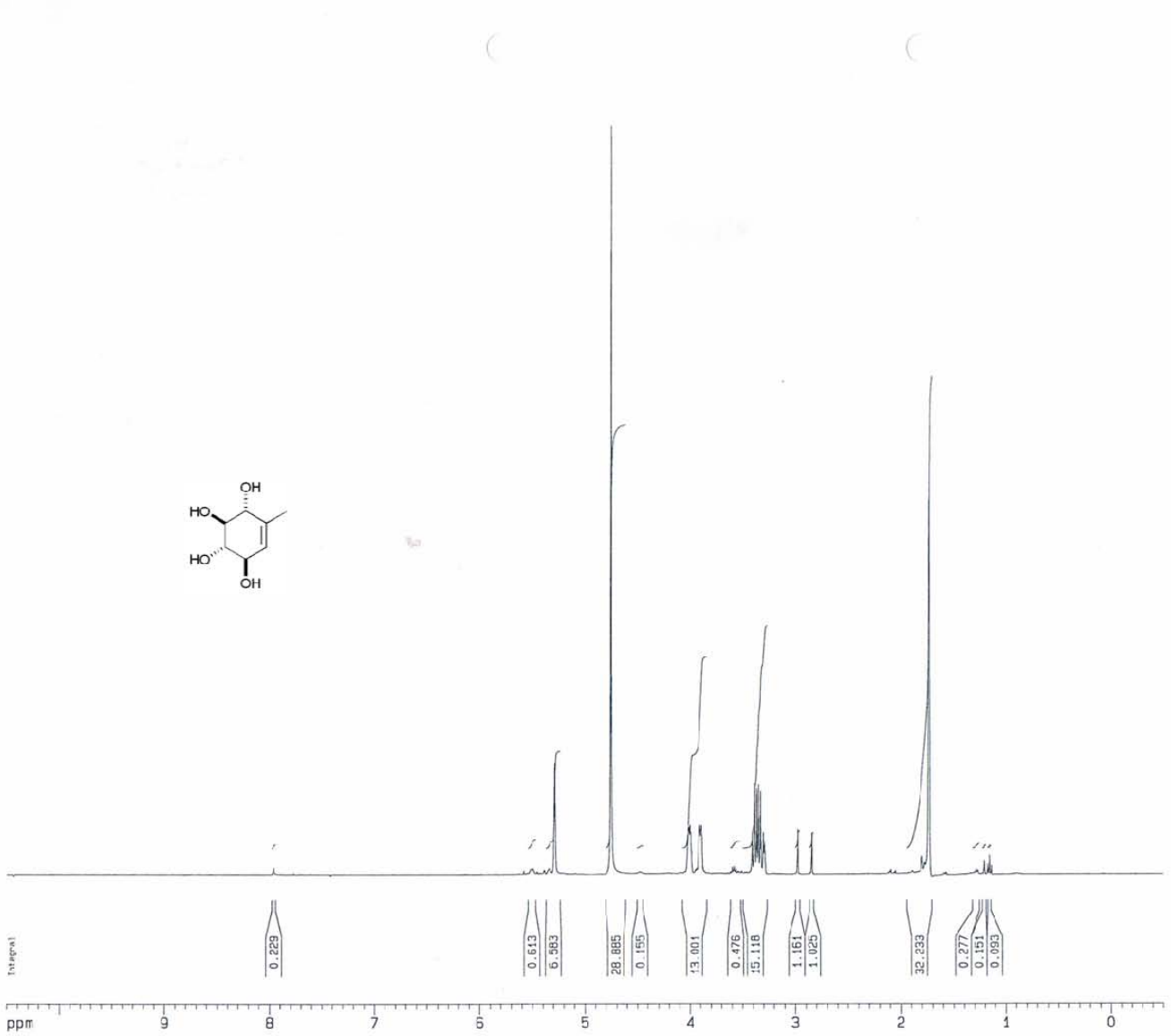


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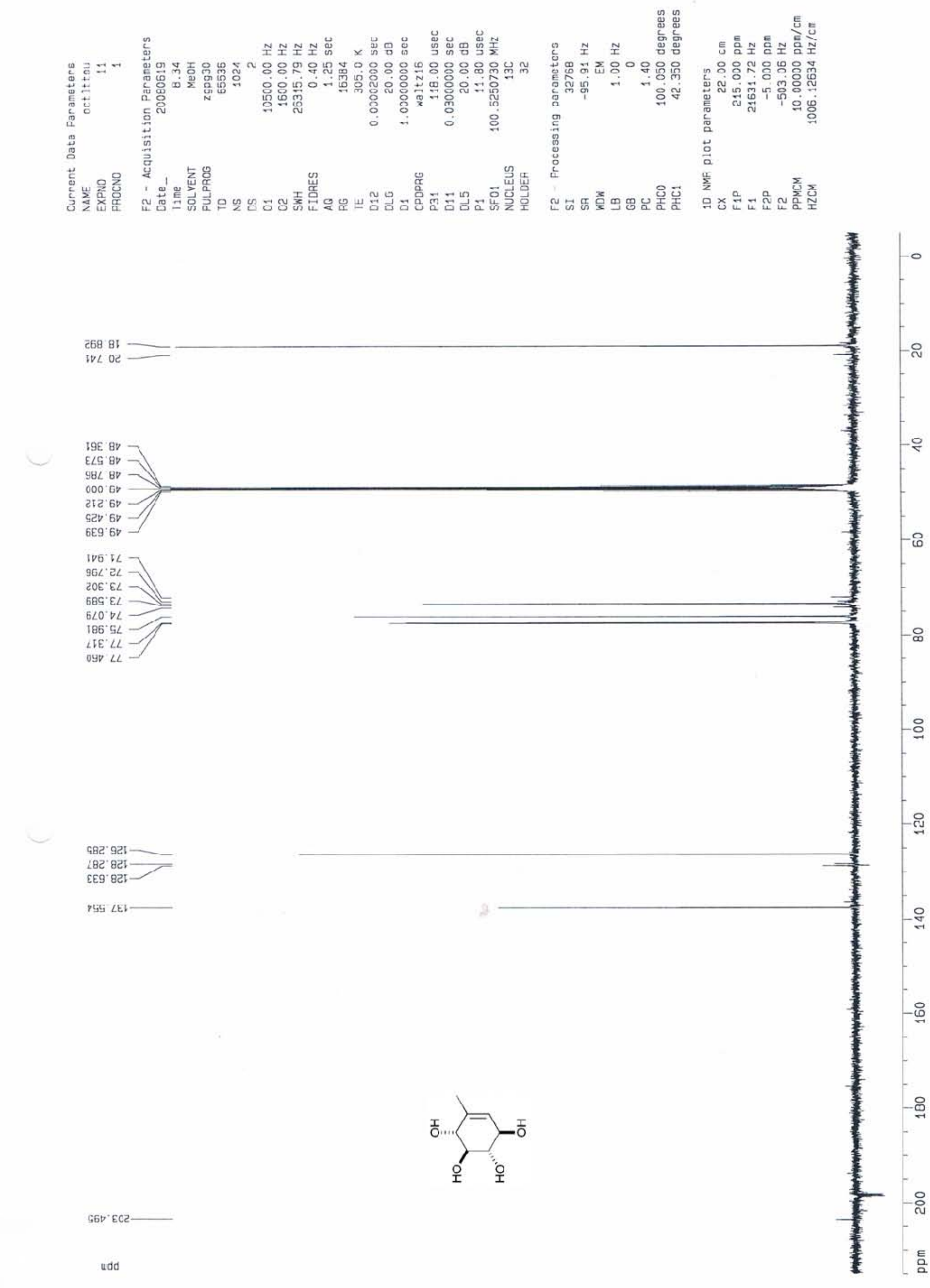

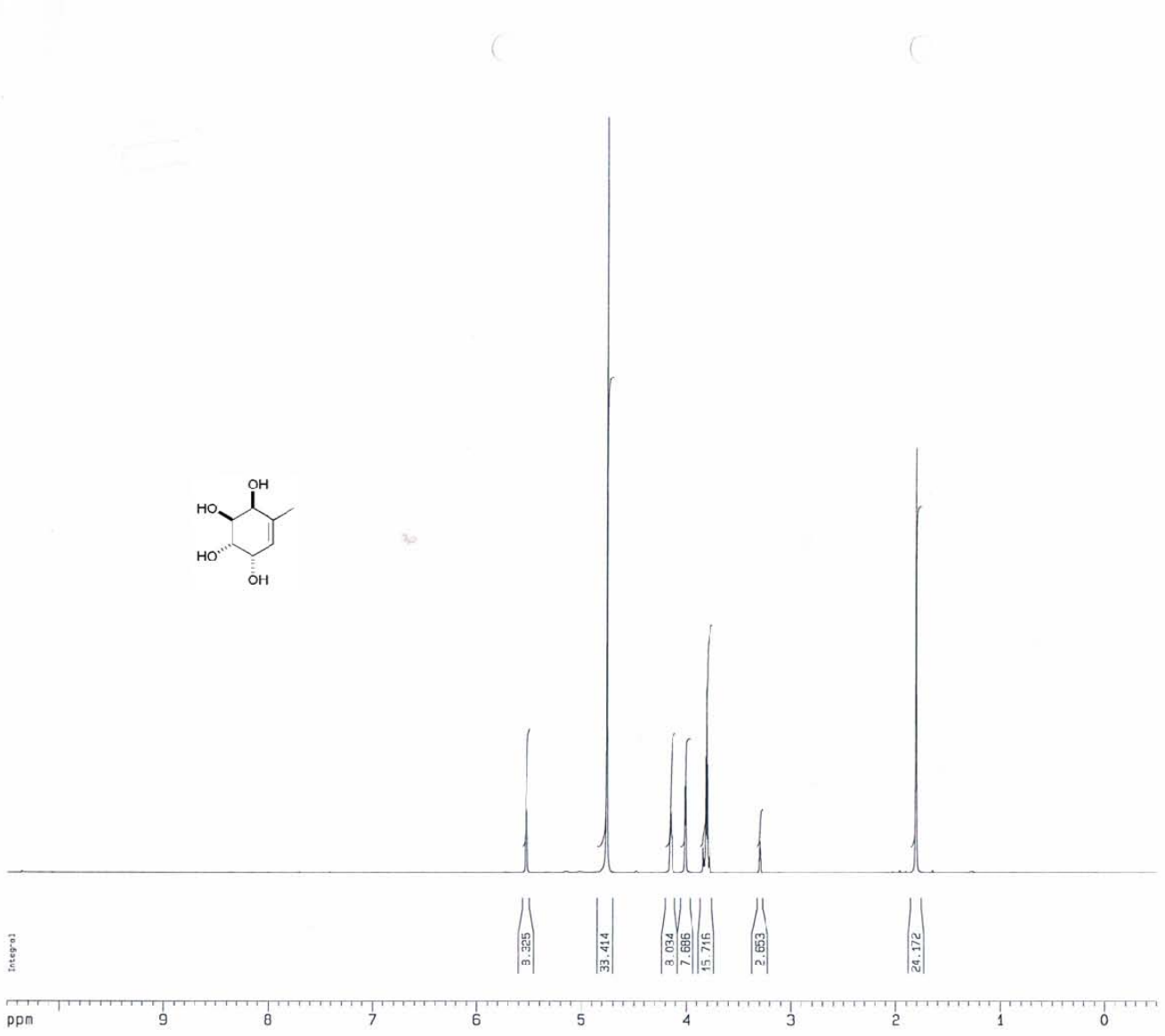

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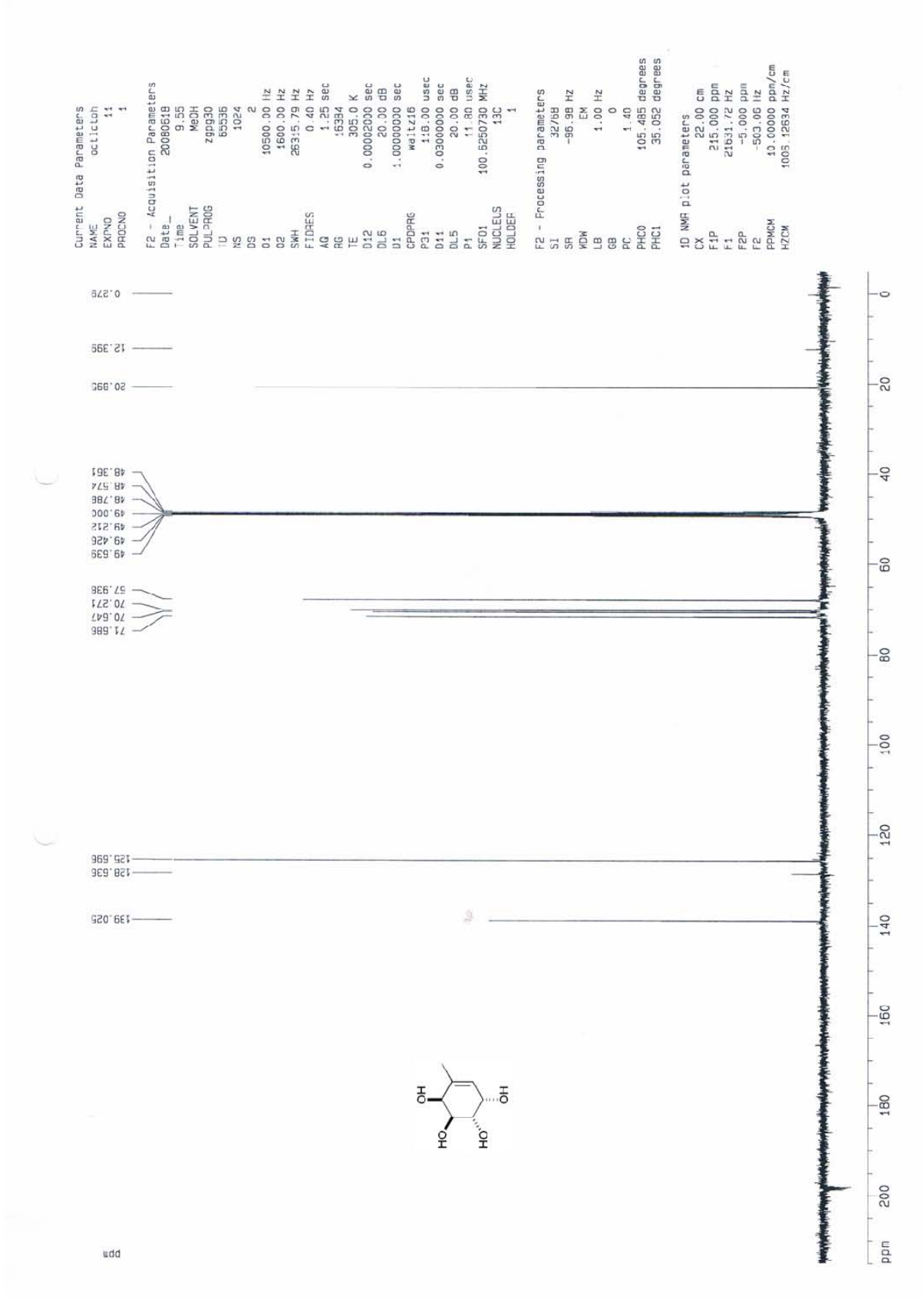
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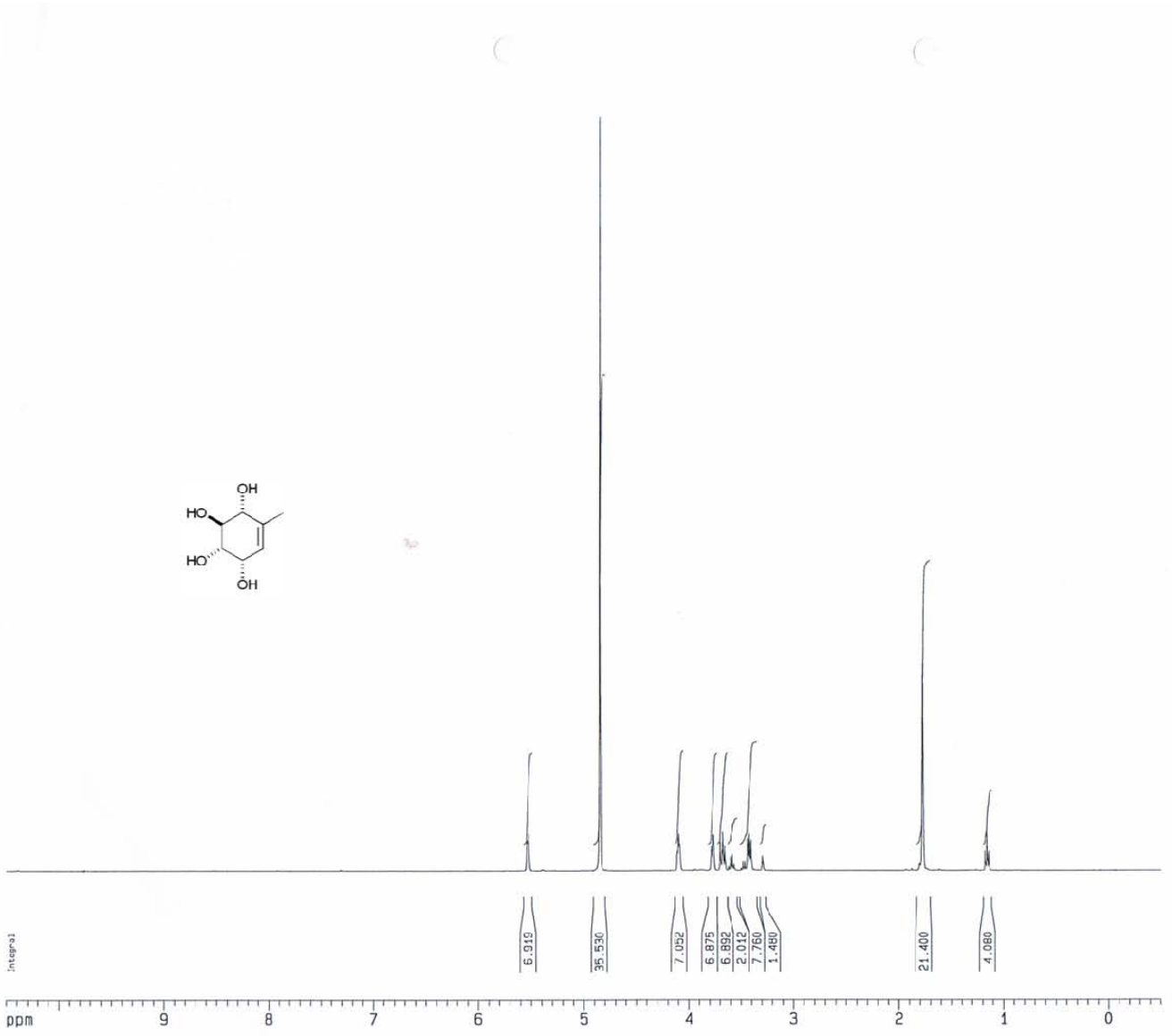

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PHC1 22.258 degrees

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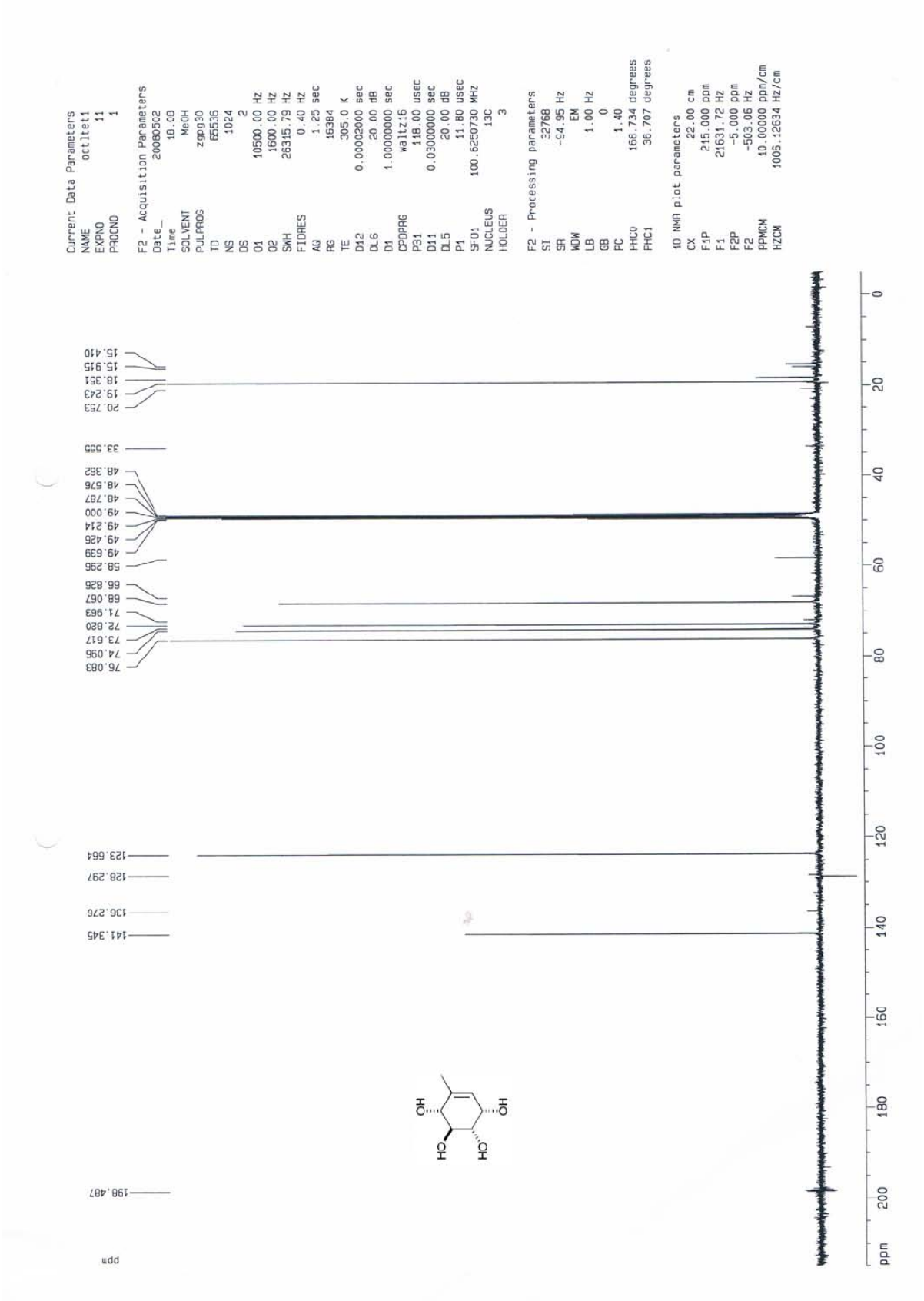
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SWH 26315.79 Hz
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F2P -5.000 ppm
F2 -503.06 Hz
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120
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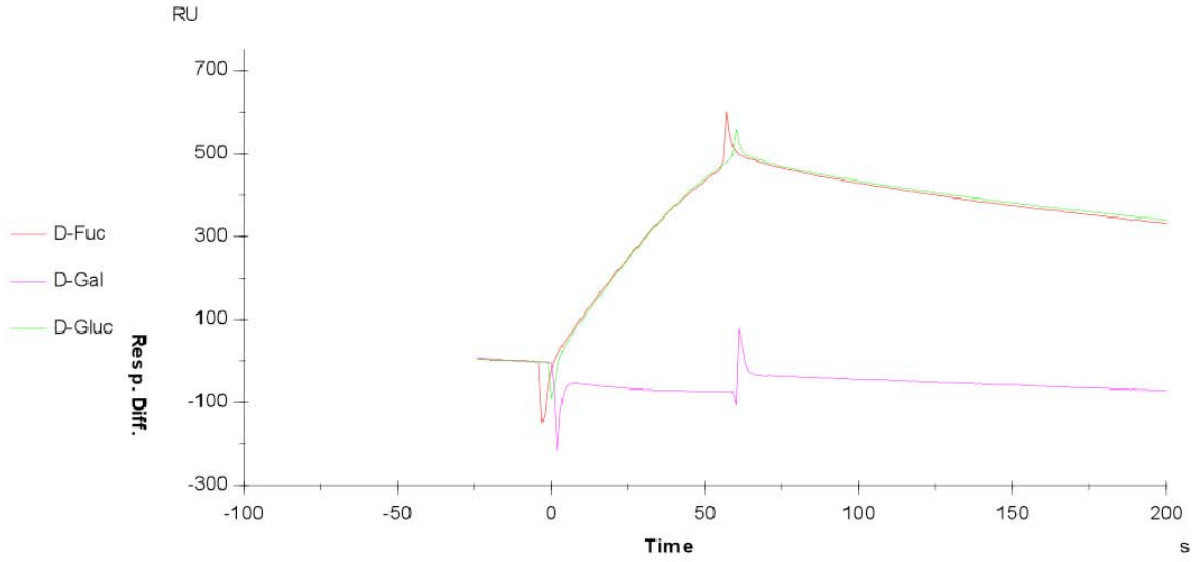
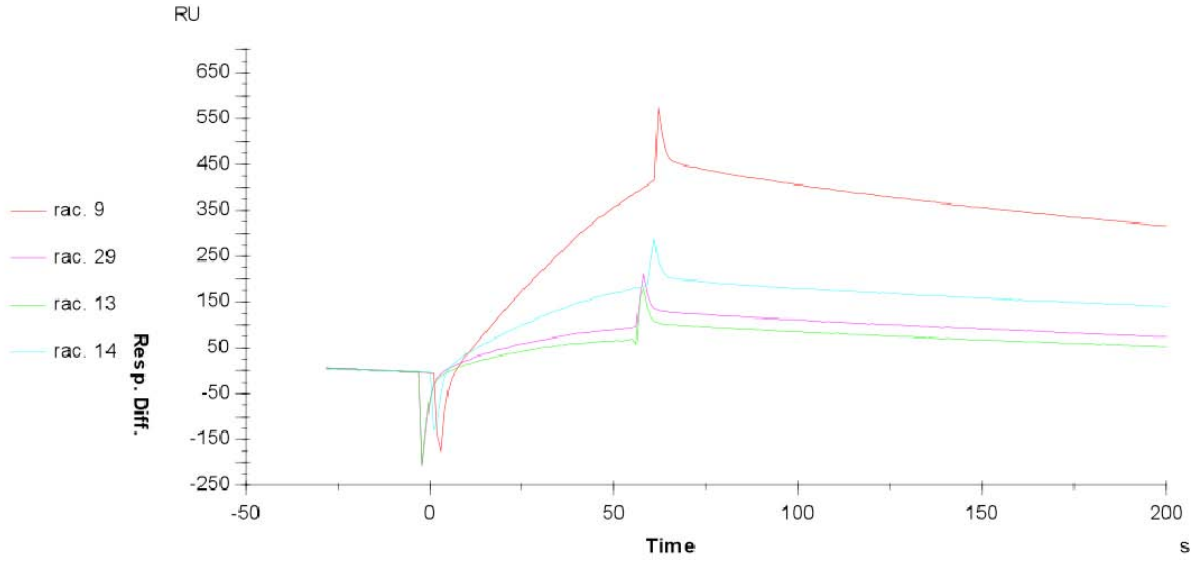
OH
OH
HO
HO

Ligand: ASF Analyte: ML I (2.5 µg/mL)



Ligand: ASF Analyte: ML I (2.5 µg/mL)



Ligand: ASF Analyte: ML I (2.5 μg/mL)