Electronic Supplementary Material (ESI) for Green Chemistry.

Environmentally benign glycosylation of aryl pyranosides and aryl/alkyl furanosides demonstrating the versatility of thermostable CGTase from *Thermoanaerobacterium sp*.

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General Experimental Details

All reagents were purchased from commercial sources and were used without further purification unless noted. *Thermonanerobacter sp.* CGTase (Toruzyme® 3.0 L) was a gift of Novozymes A/S (Bagvaerd, Denmark). Unless otherwise stated, all reactions were monitored by TLC on Silica Gel 60 F_{254}. TLC spots were detected under 254 nm light or by staining with cerium ammonium molybdate solution. Column chromatography was performed on Silica Gel (40-63 μm). Optical rotations were measured at 20 °C. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are given in δ units (ppm) and referenced to MeOD (3.31 ppm). Coupling constants *J* were calculated in Hertz (Hz). Proton and carbon NMR peaks were unambiguously assigned by COSY (double quantum filtered with gradient pulse for selection), HSQC (gradient echo-anti echo selection and shape pulse) and HMBC (echo-anti echo gradient selection, magnitude mode) correlation experiments. For each oligosaccharide isolated, the reducing end (bearing PNP or alkyl chain) was quoted as “a”, and the letter increased toward the non-reducing end (for example the sugar after was quoted as “b”). High Resolution Mass were measured by electrospray with a MS/MS ZabSpec TOF Micromass using *m*-nitrobenzylic alcohol as a matrix and accelerated caesium ions for ionization (Centre Regional des Mesures Physiques de l’Ouest, Université de Rennes 1).

Kinetics of the enzymatic reaction with *p*NP glycosides

The synthesis ability of the CGTases from *Thermoanaerobacter sp.* was previously investigated and the reaction with the enzyme was optimized to efficiently produce the primary coupling product. Typically, CGTase (10 µL, 2.34 mg/mL) was added to 1.5 mL microtubes containing β-cyclodextrin (100 mg, 0.1 mM) and various carbohydrates (0.2 mM) in 50 mM phosphate buffer, pH 6.0 (1 mL) at 50°C. The reaction mixtures were incubated in a thermomixer (Eppendorf) during 72 hours. 50 µL samples were withdrawn at different intervals and diluted with 950 µL of acetonitrile/water (50 : 50) followed by a filtration before chromatography analysis.

HPLC analysis

Chromatographic analysis were carried out on an Agilent 1200 HPLC system (Agilent Technologies, Mexico), equipped with a ChemStation software, a micro-vacuum degasser G1322A, a quartenary pump G1311A, an autosampler G1329A, a thermostatic column compartment G1316A), and a diode array detector G1315B. An analytical Alltech® Prevail™ carbohydrate ES column (Analytical, 4.6*250 mm, 5 µm, Grace) was used for chromatographic separation at 35 °C. Using acetonitrile (mobile phase A) and purified and distilled water (mobile phase B) at a flow rate of 1 mL / min, HPLC analysis started with 20 % B followed by gradient to 50% B over 40 min, then by a gradient step for 1 min back to 20 % B, before isocratic elution with starting conditions within 30 min. The injection volume of each sample was 10 µL. Simultaneous monitoring was performed at 300, 368 and 400 nm.

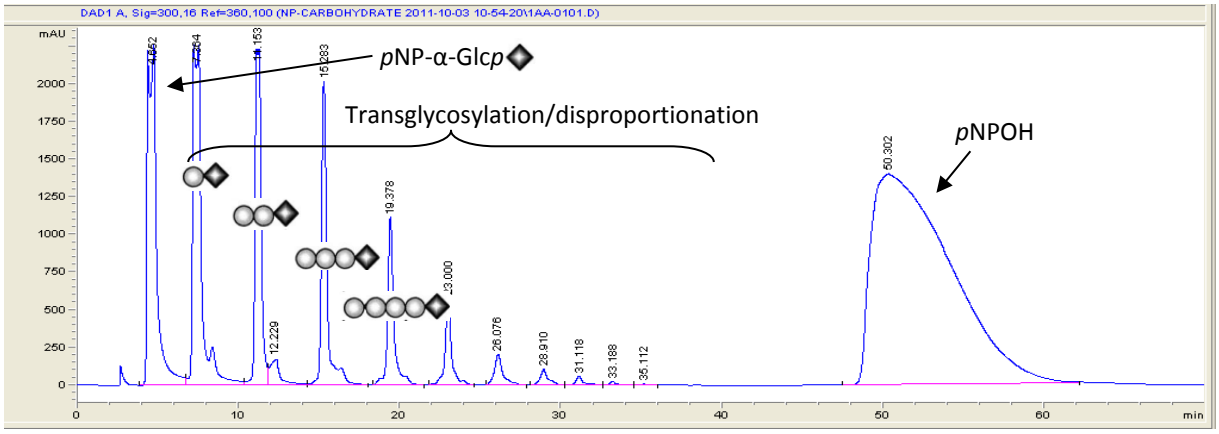


Figure 1 : *HPLC chromatograms of the reaction with pNP α-D-Glcp* ***1*** *after 72 hours incubation*

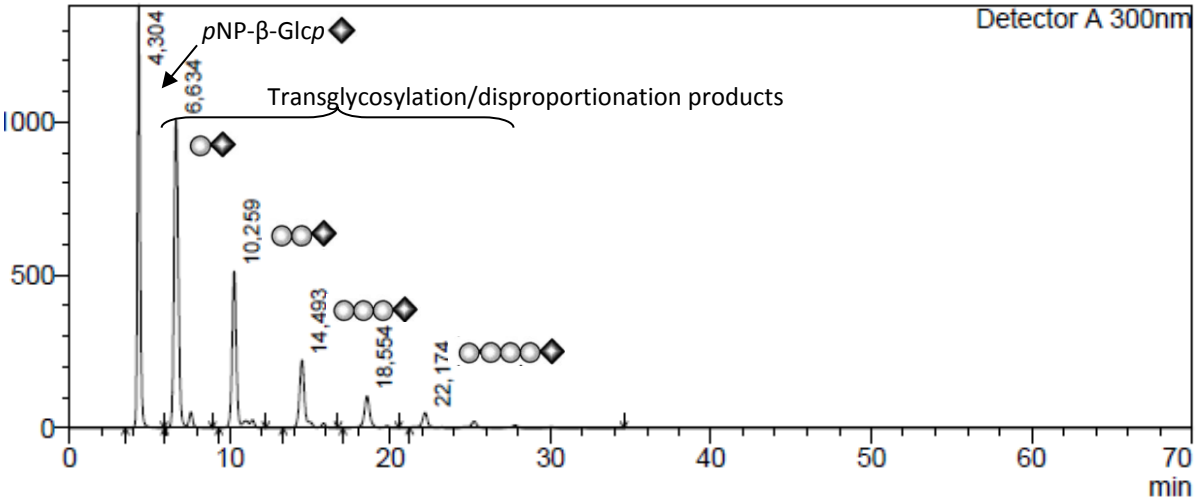


Figure 2 : *HPLC chromatograms of the reaction with pNP β-D-Glcp* ***2*** *after 72 hours incubation*

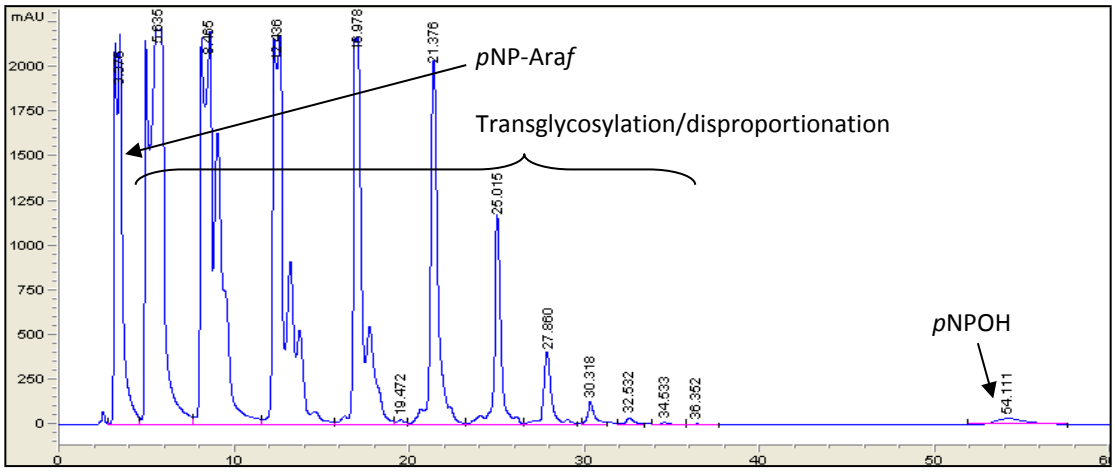


Figure 3 : *HPLC chromatograms of the reaction with pNP α-L-Araf* ***3*** *after 72 hours incubation*

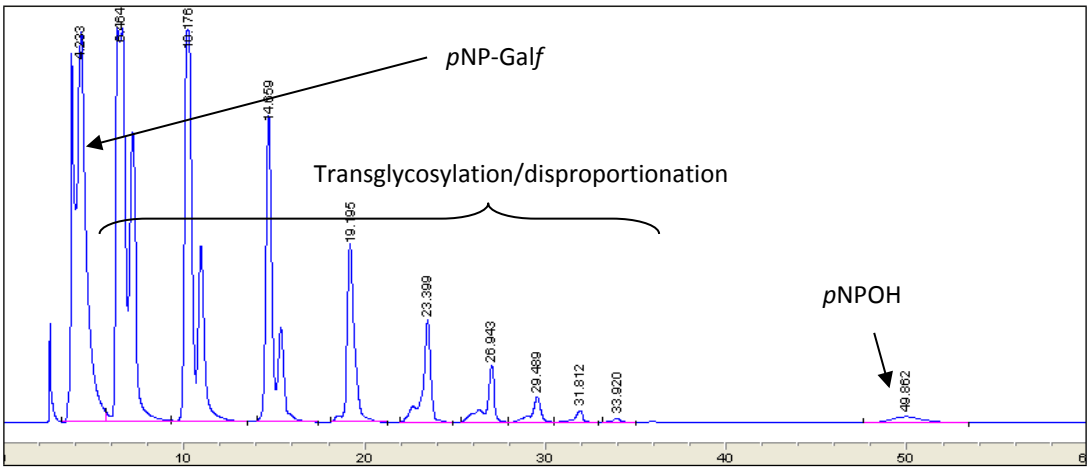


Figure 4 : *HPLC chromatograms of the reaction with pN β-D-Galf* ***4*** *after 72 hours incubation*

UPLC analysis

The samples collected during the development work were analyzed using an Acquity-LCT premier XE UPLC system from Waters equipped with a Acquity UPLC® BEH Amide column (BEH : Ethylene Bridged Hydride, 1.7 µm 2.1*100 mm, Waters) at flow rate 0.2 mL /min. Column temperature was maintained at 35 °C. The mobile phases consisted of A (ACN /H2O, 9:1) and B (ACN/H2O, 3:7) both containing either 0.1 vol % sodium hydroxide. A linear gradient with increasing proportion of B (0 min = 10 % B, 5 min = 70 % B, 10 minutes = 10 % B) was used. The injected sample volume was 5 µL and detected by a mass spectrometer with electrospray ionization. The instruments were operated in negative ion electrospray mode at a cone voltage of 40 V and capillary voltage of 28000.

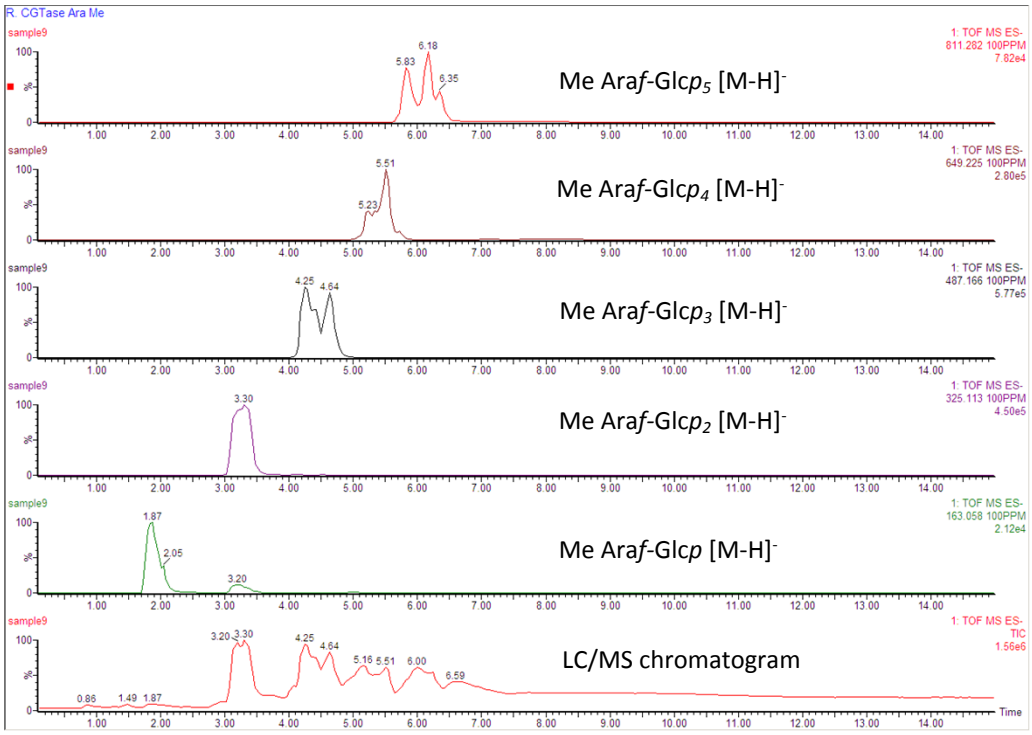


Figure 5 *: UPLC/MS analysis of the glucosylation reaction with methyl arabinofuranoside after 72 hours.*

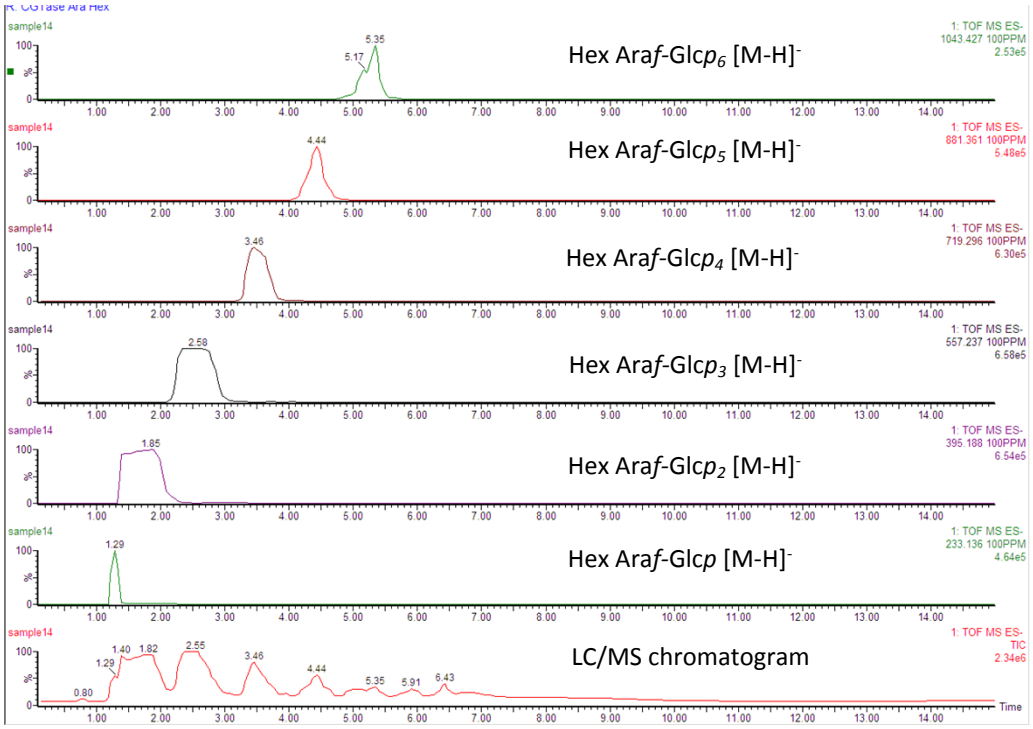
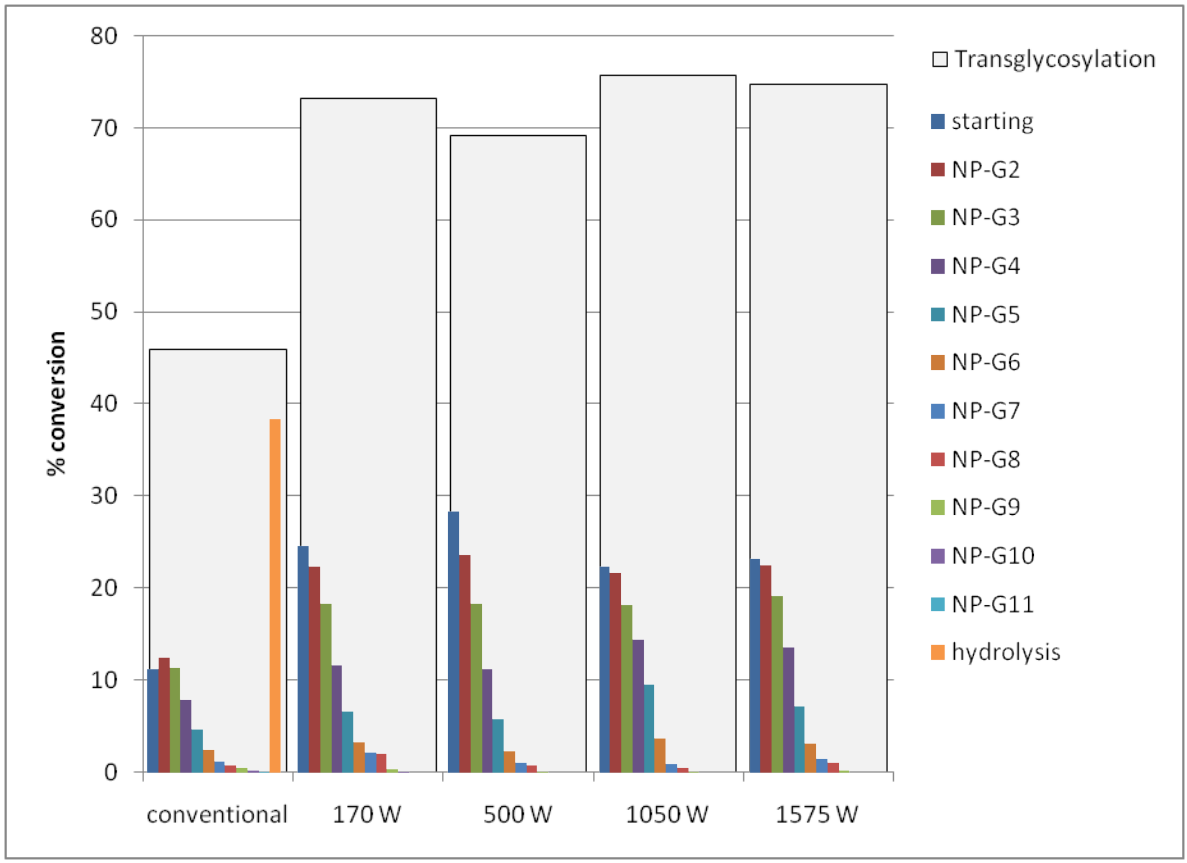


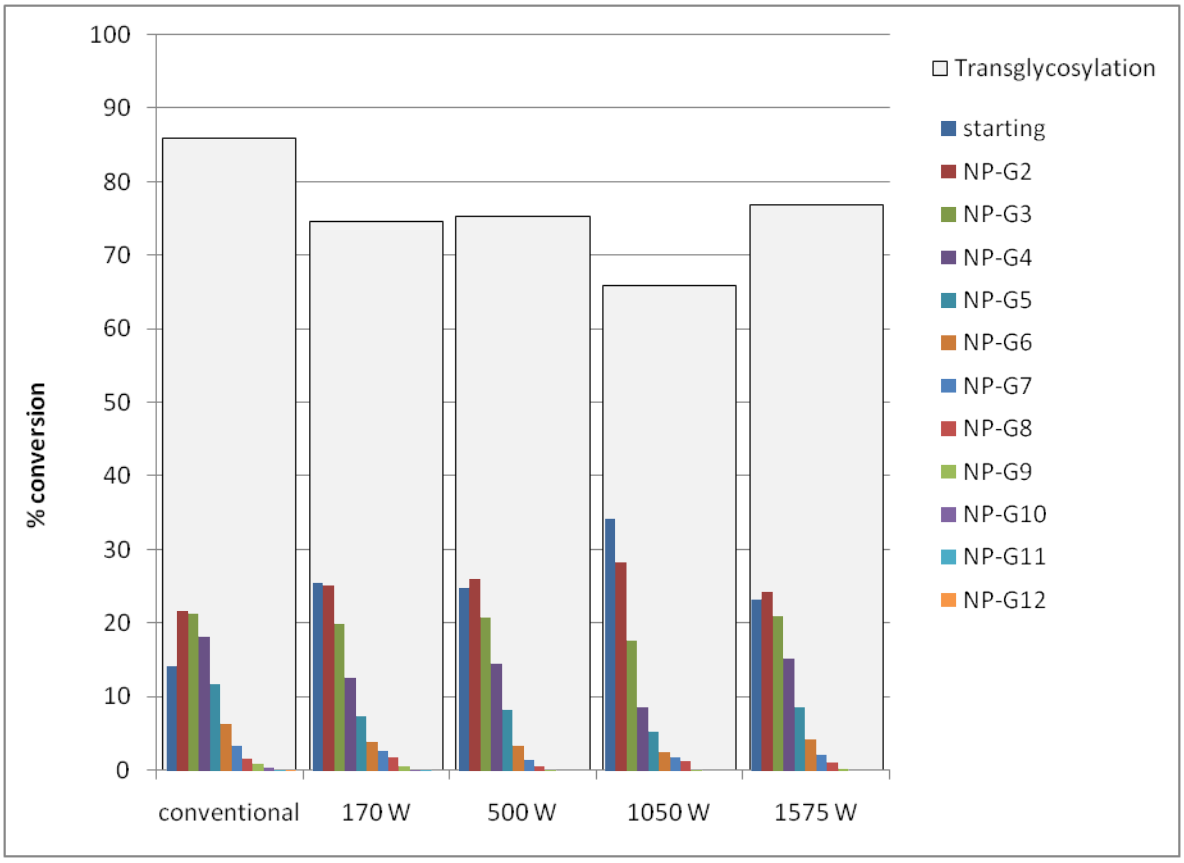
Figure 6: *UPLC /MS analysis of the glucosylation reaction with hexyl arabinofuranoside after 72 hours.*

Microwave assisted reaction between aryl glycoside and cyclodextrin in presence of CGTase

Microwave-assisted enzymatic reactions were performed in phosphate buffer only. CGTase (10 µL, 2.34mg/mL) was added to the substrate solutions (1 mL) containing 50 mM Na_2HPO_4 buffer (pH 6.0), β-cyclodextrin (10%, 100 mg, 0.1 mM) and various carbohydrates (0.2 mol/L). The reaction mixture was introduced in the microwave equipment and irradiated with a variable power. The reactions were stopped by reducing the temperature to room temperature and filtered through 0.22 µm Millipore express membrane.



Graph 1. Microwave power effect on trans-glycosylation and disproportionation yields on *p*NP α-Glc*p* **1**.



Graph 2. Microwave power effect on the trans-glycosylation and disproportionation yields on *p*NP β-Glc*p* **2**.

Transglycosylation reactions with glycoside acceptor in a preparative scale

Reaction conditions were implemented as previously described in a 1 mL final volume using a molar ratio glycoside/β-cyclodextrin 3/1 and CGTase (10 µL, 2.34 mg/mL). The resulting mixture was incubated at 50 °C during 72 h. Reaction mixture was lyophilized and the residue was purified by silica gel flash chromatrography using a eluant gradient AcOEt – (AcOH/H_2O, 1:1) from 90: 5 to 60 : 40. Elution of the products was monitored by UV detection and by TLC. Fractions corresponding to individual products were collected, evaporated and lyophilized.

Nitrophenyl β-D-maltoside (12).

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of of *p*-nitrophenyl β-D-glucopyranoside **1 (**60 mg, 0.2 mmol) in the presence of the CGTase wt and was isolated in 7% yield (6.5 mg, 0.014 mmol) after purification Further elution yield the byproduct nitrophenyl β-D-isomaltoside (**13**) in 2% yield (2 mg, 4.3 µmol).

Spectroscopic data correspond to those described in the literature.[1, 2]

12: δ_H(400 MHz, CD_3OD) 3. 97 – 3.30 (12H, m, H-2a, H-3a, H-4a, H-5a, H-6a, H-2b, H-3b, H-4b, H-5b, H-6b), 5.09 (1H, d, $J_{1b,2b}$ 3.2, H-1b), 5.21 (1H, t, $J_{1a,2a}$ 4.4, H-1a), 7.22 (2H, dd, Ph), 8.19 (2H, dd, Ph). δ_C (100 MHz, CD_3OD) 77.9 – 62.5, 80.7, 86.6, 102.7 (C-1b), 102.9 (C-1a), 117.8, 126.7. HRMS (ESI^-) calcd. for $C_{18}H_{24}NO_{13}$ $[M-H]^-$ 462,1326, found 462,1322.

13: δ_H(400 MHz, CD_3OD) 3. 97 – 3.30 (m, 12H, H-2a, H-3a, H-4a, H-5a, H-6a, H-2b, H-3b, H-4b, H-5b, H-6b), 4.80 (s, 1H, H-1b), 5.05 (d, 1H, $J_{1a,2a}$ 7.6 Hz, H-1a), 7.25 (d, 2H, *J* 9.2 Hz, Ph), 8.23 (d, 2H, *J* 9.2 Hz, Ph), δ_C (100 MHz, CD_3OD) 77.9 – 62.5, 94.6, 100.7 (C-1b), 101.7 (C-1a), 117.8, 126.9. HRMS (ESI^-) calcd. for $C_{18}H_{24}NO_{13}$ $[M-H]^-$ 462,1326, found 462,1324.

***p*-Nitrophenyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (14)**

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of of *p*-Nitrophenyl α-L-arabinofuranoside **3** (60 mg, 0.22 mmol) in the presence of the CGTase wt and was isolated in 17 % yield (14.5 mg) after purification. Further elution yield p-Nitrophenyl

α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**8**) in 10% yield (12.4 mg).

14: R_f = 0.55 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 10 (c 1.0 MeOH). δ_H(400 MHz, CD_3OD) 3.30 (1H, m, H-4b), 3.43 (1 H, dd, $J_{2b,1b}$ 4.0, $J_{2b,3b}$ 9.6, H-2b),. 3.77-3.63 (4 H, m, H-3b, H-6b, H-5a), 3.87 (2 H, m, H-5b, H-6'b), 4.03 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 6.0, H-3a), 4.27 (1 H, m, H-4a), 4.59 (1 H, dd, $J_{2a,1a}$ 1.2, $J_{2a,3a}$ 3.2, H-2a), 4.96 (d, 1 H, $J_{1b,2b}$ 4.0, H-1b), 5.71 (1 H, d, $J_{1a,2a}$ 1.2 Hz, H-1a), 7.22 (2 H, d, J 9.20 Hz, H_{Ph}), 8.20 (2 H, d, J 9.20, H_{Ph}). δ_C (100 MHz, CD_3OD) 62.5 (C-5a), 62.6 (C-6b), 71.8 (C-4b), 73.4 (C-2b), 74.3 (C-5b), 74.8 (C-3b), 81.3(C-2a), 85.6 (C-4a), 86.8 (C-3a), 101.8 (C-1b), 107.7 (C-1a), 117.7, 126.6, 143.5, 163.3 (C-Ph). HRMS (ESI^-) calcd. for $C_{17}H_{22}NO_{12}$ $[M-H]^-$ 432.1142, found 432.1160.

15: R_f = 0.32 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 10.4 (c 0.45 MeOH). δ_H(400 MHz, CD_3OD) 3.28 (1 H, m, H-4c), 3.48 (2 H, m, H-2b, H-2c), 3.55 (1 H, dd, $J_{4b,3b}$ 9.2 Hz, H-4b), 3.72-3.64 (3 H, m, H-5c, H-6c, H-3c), 3.75 (2 H, m, H-5a), 3.83 (1 H, m, H-6'c), 3.85 (2 H, m, H-6b), 3.91 (1 H, d, $J_{3b,4b}$ 9.2, H-3b), 4.01 (1 H, m, H-5b), 4.04 (1 H, dd, $J_{3a,2a}$ 1.6, $J_{3a,4a}$ 4.4, H-3a), 4.30 (1 H, dd, $J_{4a,3a}$ 4.4, $J_{4a,5a}$ 9.2, H-4a), 4.58 (1 H, d, $J_{2a,3a}$ 1.6, H-2a), 4.97 (1 H, d, $J_{1b,2b}$ 3.2, H-1b), 5.17 (1 H, d, $J_{1c,2c}$ 3.2, H-1c), 5.73 (1 H, s, H-1a), 7.20 (2 H, d, J 9.2, H_{Ph}), 8.24 (2 H, d, J 9.2, H_{Ph}). δ_C (100 MHz, CD_3OD) 62.0 (C-6b), 62.6 (C-5a), 62.8 (C-6c), 71.5 (C-4c), 72.7 (C-5b), 73.0 (C-2b), 74.2 (C-2c), 74.7 (C-3b), 74.9 (C-5c), 75.1 (C-3c), 80.7 (C-2a), 82.0 (C-4b), 86.3 (C-4a), 87.0 (C-3a), 101.7 (C-1b), 103.1 (C-1c), 107.6 (C-1a), 117.5, 126.7, 143.5, 163.2 (C-Ph). HRMS (ESI^-) calcd. for $C_{23}H_{32}NO_{17}$ $[M-H]^-$ 594.1670, found 594.1690.

***p*-Nitrophenyl α-D-glucopyranosyl-(1,3)-β-D-galactofuranoside (16)**

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of of *p*-Nitrophenyl β-D-galactofuranoside (60 mg, 0.02 mmol) in the presence of the CGTase wt and was isolated in 11 % yield (12 mg) after purification. Further elution yield *p*-Nitrophenyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-β-D-galactofuranoside (**17**) in 7% yield (20 mg).

16: R_f = 0.3 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 55 (c 0.2 MeOH). δ_H(400 MHz, CD_3OD) 3.30 (1 H, m, H-4b), 3.43 (1 H, dd, $J_{2b,1b}$ 4.0, $J_{2b,3b}$ 10, H-2b), 3.65 (4 H, m, H-6b, H-6a, H-3b), 3.79 (1 H, m, H-5a), 3.86 (2 H, m, H-5b, H-6'b), 4.14 (1 H, dd,

$J_{2a,3a}$ 3.6, $J_{3a,4a}$ 6.4, H-3a), 4.31 (1 H, m, H-4a), 4.58 (1 H, dd, $J_{2a,1a}$ 1.6, $J_{2a,3a}$ 3.6, H-2a), 4.98 (1 H, d, $J_{1b,2b}$ 4.0, H-1b), 5.70 (1 H, d, $J_{1a,2a}$ 1.6, H-1a), 7.22 (2 H, d, J 9.2, H_{Ph}), 8.21 (2 H, d, J 9.2, H_{Ph}). δ_C (100 MHz, CD_3OD) 62.7 (C-6b), 64.1 (C-6a),. 71.8 (C-4b), 72.3 (C-5a), 73.4 (C-2b), 74.4 (C-5b), 74.9 (C-3b), 81.2 (C-2a), 84.5 (C-4a), 87.4 (C-3a), 102.0 (C-1b), 107.7 (C-1a), 117.7, 126.6, 143.6, 163.3 (C-Ph). HRMS (ESI^-) calcd. for $C_{18}H_{24}NO_{13}$ $[M-H]^-$ 462.1248, found 462.1260.

17: R_f = 0.12 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 67 (c 0.5 MeOH). δ_H(400 MHz, CD_3OD) 3.27 (1 H, m, H-4c), 3.47 (1 H, dd, $J_{2c,1c}$ 3.6, $J_{2c,3c}$ 9.6, H-2c), 3.49 (1 H, dd, $J_{2b,1b}$ 3.6, $J_{2b,3b}$ 10.0, H-2b), 3.54 (1 H, dd, $J_{4b,3b}$ 8.8, $J_{4b,5b}$ 10.0, H-4b), 3.70- 3.62 (5 H, m, H-3c, H-5c, H-6a, H-6c), 3.78 (1 H, dd, $J_{6c,5c}$ 2.4 Hz, $J_{6c,6'c}$, H-6'c), 3.87-3.82 (3 H, m, H-5a, H-6b), 3.91 (1 H, dd, $J_{3b,4b}$ 8.8, $J_{3b,2b}$ 10.0, H-3b), 4.01 (1 H, m, H-5b), 4.15 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 5.6, H-3a), 4.34 (1 H, dd, $J_{4a,5a}$ 3.6, $J_{4a,3a}$ 5.6, H-4a), 4.57 (1 H, dd, $J_{2a,1a}$ 1.6, $J_{2a,3a}$ 3.2, H-2a), 4.99 (1 H, d, $J_{1b,2b}$ 3.6, H-1b), 5.16 (1 H, d, $J_{1c,2c}$ 3.6, H-1c), 5.72 (1 H, d, $J_{1a,2a}$ 1.6, Ha-1), 7.16 (2 H, d, J 9.2, H_{Ph}), 8.24 (2 H, d, J 9.2, H_{Ph}). δ_C (100 MHz, CD_3OD) 62.0 (C-6b), 62.6 (C-5a), 62.8 (C-6c), 71.5 (C-4c, C-6a), 72.7 (C-5b, C-5a), 73.0 (C-2b), 74.2 (C-2c), 74.7 (C-3b), 74.9 (C-5c), 75.1 (C-3c), 80.7 (C-2a), 82.0 (C-4b), 86.3 (C-4a), 87.0 (C-3a), 101.7 (C-1b), 103.1 (C-1c), 107.6 (C-1a), 117.5, 126.7, 143.5, 163.2 (C-Ph). HRMS (ESI^-) calcd. for $C_{24}H_{34}NO_{18}$ $[M-H]^-$ 624.1776, found 624.1779.

Methyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (18)

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of Methyl α-L-arabinofuranoside **11** (60 mg, 0.3 mmol) in the presence of the CGTase wt and was isolated in 14 % yield (16 mg) after purification. Further elution yield methyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**25**) in 11% yield (20 mg).

18: R_f = 0.25 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 15.6 (c 1.0 MeOH). δ_H(400 MHz, CD_3OD) 3.30 (1 H, m, H-4b), 3.36 (1 H, dd, $J_{2b,1b}$ 4.0, $J_{2b,3b}$ 9.6, H-2b), 3.37 (3 H, s, CH_3), 3.61-3.70 (2 H, m, H-3b, H-6b), 3.70 (1 H, dd, $J_{5a,4}$ 4.8, $J_{5a,5'a}$ 12.0, H-5a), 3.76 (1 H, dd, $J_{5'a,4}$ = 4.0 Hz, $J_{5'a,5}$ 12.0, H-5'a), 3.79-3.85 (2 H, m, H-5b, H-6'b), 3.88 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 6.2, H-3a), 4.09 (1 H, m, H-4a), 4.19 (1 H, dd, $J_{2a,1a}$ 1.2, $J_{2a,3a}$ 3.2, H-2a), 4.79 (1 H, d, $J_{1a,2a}$ 1.2, H-1a), 4.88 (1 H, d, $J_{1b,2b}$ 4.0, H-1b). δ_C(100 MHz, CD_3OD) 55.3 (CH_3), 62.7 (C-6b), 62.8 (C-5a), 72.9 (C-4b), 73.4 (C-2b), 74.1 (C-5b),

74.8 (C-3b), 81.6 (C-2a), 83.7 (C-4a), 86.7 (C-3a), 101.6 (C-1b), 110.6 (C-1a). HRMS (ESI^-) calcd. for $C_{12}H_{21}O_{10}$ $[M-H]^-$ 325.1135, found 325.1125.

25: R_f = 0.07 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 95 (c 0.5 MeOH). δ_H(400 MHz, CD_3OD) 3.30 (1 H, m, H-4c), 3.37 (3 H, s, CH_3), 3.40-3.48 (2 H, m, H-2c, H-2b), 3.52 (1 H, m, H-4b), 3.58-3.70 (3 H, m, H-3c, H-5c, H-6c), 3.70 (1 H, dd, $J_{5a,4a}$ 5.2, $J_{5a,5'a}$ 12.0, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 4.0, $J_{5'a,5a}$ 12.0, H-5'a), 3.75-3.90 (5 H, m, H-3b, H-5b, H-6b, H-6'c), 3.90 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 6.4, H-3a), 4.10 (1 H, m, H-4a), 4.17 (1 H, dd, $J_{2a,1a}$ 1.6, $J_{2a,3a}$ 3.2, H-2a), 4.78 (1 H, d, $J_{1a,2a}$ 1.6, H-1a), 4.90 (1 H, d, $J_{1b,2b}$ 4.0, H-1b), 5.11 (1 H, d, $J_{1c,2c}$ 3.6, H-1c). δ_C(100 MHz, CD_3OD) 55.3 (CH_3), 62.3 (C-6b), 62.7 (C-6c), 62.8 (C-5a), 71.6 (C-4c), 72.7 (C-5b), 73.5 (C-2b), 74.1 (C-2c), 74.2 (C-3b), 74.7 (C-5c), 75.1 (C-3c), 81.3 (C-2a), 81.9 (C-4b), 83.8 (C-4a), 86.7 (C-3a), 100.9 (C-1b), 102.9 (C-1c), 110.6 (C-1a). HRMS (ESI^-) calcd. for $C_{18}H_{31}O_{15}$ $[M-H]^-$ 487.1663, found 487.1655.

Ethyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (19)

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of ethyl α-L-arabinofuranoside **12** (53 mg, 0.30 mmol) in the presence of the CGTase wt and was isolated in 26 % yield (25 mg) after purification. Further elution yield propyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**26**) in 14% yield (20 mg).

19: R_f = 0.30 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D$ + 17.3 (c 0.85 in MeOH). δ_H(400 MHz, CD_3OD) 1.20 (3 H, t, J 7.1, CH_3), 3.28 (1 H, dd, $J_{4b,3b}$ 9.2, $J_{4b,5b}$ 9.8, H-4b), 3.39 (1 H, dd, $J_{2b,1b}$ 3.8, $J_{2b,3b}$ 9.8, H-2b), 3.44-3-53 (1 H, m, OCH_2CH_3), 3.62 (1 H, dd, $J_{3b,4b}$ 9.0, $J_{3b,2b}$ 9.8, H-3b), 3.66 (1 H, dd, $J_{6b,5b}$ 6.2, $J_{6b,6'b}$ 11.4, H-6b), 3.72-3.81 (2 H, m, OCH_2CH_3, H-5b), 3.69 (1 H, dd, $J_{5a,4a}$ 4.8, $J_{5a,5'a}$ 12.0, H-5a), 3.76 (1 H, dd, $J_{4a,5'a}$ 3.9, $J_{5'a,5a}$ 12.0, H-5'a), 3.85 (1 H, dd, $J_{6'b,5b}$ 2.3, $J_{6'b,6b}$ 11.4, H-6'b), 3.88 (1 H, dd, $J_{3a,2a}$ 3.5, $J_{3a,4a}$ 6.4, H-3a), 4.11 (1 H, ddd, $J_{4a,5'a}$ 3.9, $J_{4a,5a}$ 4.5, $J_{4a,3a}$ 6.4, H-4a), 4.20 (1 H, dd, $J_{2a,1a}$ 1.7, $J_{2a,3a}$ 3.5, H-2a), 4.89 (1 H, d, $J_{1a,2a}$ 1.7, H-1a), 4.89 (1 H, d, $J_{1b,2b}$ 3.8, H-1b). δ_C(100 MHz, CD_3OD) 15.4 (CH_3), 62.6 (C-6b), 62.8 (C-5a), 64.3 (OCH_2CH_3), 71.8 (C-4b), 73.5 (C-2b), 74.1 (C-5b), 74.9 (C-3b), 81.8 (C-2a), 83.4 (C-4a), 86.8 (C-3a), 101.2 (C-1b), 109.4 (C-1a). HRMS (ESI^-) calcd. for $C_{13}H_{23}O_{10}$ $[M-H]^-$ 339.1297, found 339.1298.

26: R_f = 0.1 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D$ + 63.3 (c 0.9 in MeOH). δ_H(400 MHz, CD_3OD) 1.21 (3 H, t, J 6.9, CH_3), 3.23-3.30 (1 H, m, H-4c), 3.42-3.51 (3 H, m, H-2c, H-2b, O*C*$H_2$$CH_3$), 3.52 (1 H, dd, J 9.1, J 9.6, H-4b), 3.63 (1 H, dd, J 9.1, J 9.6, H-3c), 3.57-3.71 (2 H, m, H-5c, H-6c), 3.68 (1 H, dd, $J_{5a,4a}$ 4.6, $J_{5a,5'a}$ 11.9, H-5a), 3.72-3.82 (1 H, m, O*C*$H_2$$CH_3$), 3.75 (1 H, dd, $J_{5'a,4a}$ 3.9, $J_{5'a,5a}$ 11.9, H-5'a), 3.79-3.92 (5 H, m, H-5b, H-6b, H-3b, H-6'c), 3.88 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 6.0, H-3a), 4.12 (1 H, ddd, $J_{4a,5'a}$ 3.9, $J_{4a,5a}$ 4.6, $J_{4a,3a}$ 6.0, H-4a), 4.20 (1 H, dd, $J_{2a,1a}$ 1.7, $J_{2a,3a}$ 3.2, H-2a), 4.89 (1 H, d, $J_{1a,2a}$ 1.7, H-1a), 4.91 (1 H, d, $J_{1b,2b}$ 4.4, H-1b), 5.15 (1 H, d, $J_{1c,2c}$ 3.8, H-1c). δ_C(100 MHz, CD_3OD) 15.5 (CH_3), 61.9 (C-6b), 62.6 (C-6c), 62.7 (C-5a), 64.1 (*C*$H_2$$CH_3$), 71.3 (C-4c), 72.4 (C-5b), 72.9, 74.0 (C-2c, C-2b), 74.5 (C-3b, C-5c), 74.9 (C-3c), 81.2 (C-2a), 81.7 (C-4b), 83.5 (C-4a), 86.7 (C-3a), 100.8 (C-1b), 102.8 (C-1c), 109.1 (C-1a). HRMS (ESI^-) calcd. for $C_{19}H_{33}O_{15}$ $[M-H]^-$ 501.1825, found 501.1821.

Propyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (20)

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of of propyl α-L-arabinofuranoside **13** (56 mg, 0.29 mmol) in the presence of the CGTase wt and was isolated in 21 % yield (22 mg) after purification. Further elution yield propyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**27**) in 13% yield (20 mg).

20: R_f = 0.38 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D$20 + 16.3 (*c* 0.27 in MeOH). δ_H(400 MHz, CD_3OD) 0.94 (3 H, t, J 7.8, CH_3), 1.60 (2 H, m, OCH_2C*H*$_2$), 3.28 (1 H, dd, $J_{4b,3b}$ 8.9, $J_{4b,5b}$ 9.8, H-4b), 3.25-3-43 (2 H, m, O*C*$H_2$$CH_2$, H-2b), 3.61 (1 H, dd, $J_{3b,4b}$ 8.9, $J_{3b,2b}$ 9.8, H-3b), 3.63-3.69 (2 H, m, H-6b, O*C*$H_2$$CH_2$), 3.69 (1 H, dd, $J_{5a,4a}$ 4.7, $J_{5a,5'a}$ 12.1, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 3.9, $J_{5'a,5a}$ 12.1, H-5'a), 3.77 (1 H, m, H-5b), 3.85 (1 H, dd, $J_{6'b,5b}$ 2.2, $J_{6'b,6b}$ 11.3, H-6'b), 3.87 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 6.7, H-3a), 4.11 (1 H, ddd, $J_{4a,5'a}$ 3.9, $J_{4a,5a}$ 4.7, $J_{4a,3a}$ 6.7, H-4a), 4.21 (1 H, dd, $J_{2a,1a}$ 1.7, $J_{2a,3a}$ 3.2, H-2a), 4.88 (1 H, d, $J_{1a,2a}$ 1.7, H-1a), 4.89 (1 H, d, $J_{1b,2b}$ 3.9, H-1b). δ_C(100 MHz, CD_3OD) 11.0 (CH_3), 23.9 (OCH_2*C*H_2), 62.6 (C-6b), 62.8 (C-5a), 70.5 (O*C*$H_2$$CH_2$), 71.8 (C-4b), 73.5 (C-2b), 74.1 (C-5b), 74.9 (C-3b), 81.8 (C-2a), 83.3 (C-4a), 87.0 (C-3a), 101.3 (C-1b), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{14}H_{25}O_{10}$ $[M-H]^-$ 353,1448, found 353,1437.

27: R_f = 0.19 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 60.5 (*c* 0.4 in MeOH). δ_H(400 MHz, CD_3OD) 0.95 (3 H, t, J 7.4, CH_3), 1.60 (2 H, m, OCH_2CH_2), 3.24-3.30 (1 H, m, H-4c), 3.34-3.43 (1 H, m, OCH_2CH_2), 3.45 (2 H, dd, $J_{2,1}$ 3.8, $J_{2,3}$ 9.5, H-2b, H-2c), 3.53 (1 H, dd, J 9.2, 9.5, H-4b), 3.63 (1 H, t, J 9.5, H-3c), 3.62-3.72 (3 H, m, H-5c, H-6c, OCH_2CH_2), 3.69 (1 H, dd, $J_{5a,4a}$ 4.6, $J_{5a,5'a}$ 11.9, H-5a), 3.75 (1 H, dd, $J_{5'a,4a}$ 3.6, $J_{5'a,5a}$ 11.9, H-5'a), 3.78-3.91 (5 H, m, H-5b, H-6b, H-3b, H-6'c), 3.87 (1 H, dd, $J_{3a,2a}$ 3.1, $J_{3a,4a}$ 6.2, H-3a), 4.13 (1 H, ddd, $J_{4a,5'a}$ 4.1, $J_{4a,5a}$ 4.6, $J_{4a,3a}$ 5.6, H-4a), 4.22 (1 H, dd, $J_{2a,1a}$ 1.4, $J_{2a,3a}$ 3.0, H-2a), 4.89 (1 H, d, $J_{1a,2a}$ 1.4, H-1a), 4.91 (1 H, d, $J_{1b,2b}$ 3.8, H-1b), 5.14 (1 H, d, $J_{1c,2c}$ 3.8, H-1c). δ_C(100 MHz, CD_3OD) 11.1 (CH_3), 24.0 (CH_2CH_3), 61.9 (C-6b), 62.7 (C-6c), 62.9 (C-5a), 70.4 (OCH_2CH_2), 71.5 (C-4c), 72.5 (C-5b), 73.0, 73.1 (C-2c, C-2b), 74.7 (C-3b), 74.8 (C-5c), 75.1 (C-3c), 81.2 (C-2a), 81.9 (C-4b), 84.0 (C-4a), 87.2 (C-3a), 101.2 (C-1b), 103.1 (C-1c), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{20}H_{35}O_{15}$ $[M-H]^-$ 515.1976, found 515.1970.

Butyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (21)

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of butyl α-L-arabinofuranoside **14** (67 mg, 0.32 mmol) in the presence of the CGTase wt and was isolated in 19 % yield (23 mg) after purification. Further elution yield butyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**28**) in 12% yield (20 mg).

21: R_f = 0.5 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 18.2 (*c* 0.5 in MeOH). δ_H(400 MHz, CD_3OD) 0.94 (3 H, t, J 7.4, CH_3), 1.40 (2 H, m, CH_2CH_3), 1.57 (2 H, m, OCH_2CH_2), 3.28 (1 H, dd, $J_{4b,3b}$ 8.9, $J_{4b,5b}$ 9.9, H-4b), 3.36-3-46 (1 H, m, OCH_2CH_2), 3.39 (1 H, dd, $J_{2b,1b}$ 4, $J_{2b,3b}$ 9.7, H-2b), 3.61 (1 H, dd, $J_{3b,4b}$ 8.9, $J_{3b,2b}$ 9.7, H-3b), 3.62-3.70 (2 H, m, H-6b, OCH_2CH_2), 3.69 (1 H, dd, $J_{5a,4a}$ 4.6, $J_{5a,5'a}$ 11.9, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 3.8, $J_{5'a,5a}$ 11.9, H-5'a), 3.74-3.80 (1 H, m, H-5b), 3.86 (1 H, dd, $J_{6'b,5b}$ 2.5, $J_{6'b,6b}$ 11.7, H-6'b), 3.87 (1 H, dd, $J_{3a,2a}$ 3.4, $J_{3a,4a}$ 6.5, H-3a), 4.10 (1 H, ddd, $J_{4a,5'a}$ 3.8, $J_{4a,5a}$ 4.6, $J_{4a,3a}$ 6.5, H-4a), 4.20 (1 H, dd, $J_{2a,1a}$ 1.8, $J_{2a,3a}$ 3.4, H-2a), 4.87 (1 H, d, $J_{1a,2a}$ 1.8, H-1a), 4.89 (1 H, d, $J_{1b,2b}$ 4, H-1b). δ_C(100 MHz, CD_3OD) 14.2 (CH_3), 20.4 (CH_2CH_3), 32.9 (OCH_2CH_2), 62.6 (C-6b), 62.8 (C-5a), 68.6 (OCH_2CH_2), 71.8 (C-4b), 73.5 (C-2b), 74.1 (C-5b), 74.9 (C-3b), 81.8 (C-2a), 83.4 (C-4a), 87.0 (C-3a), 101.3 (C-1b), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{15}H_{27}O_{10}$ $[M-H]^-$ 367.1604, found 367.1609.

28: R_f = 0.21 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 63.4 (*c* 0.35 in MeOH). δ_H(400 MHz, CD_3OD) 0.95 (3 H, t, J 7.3, CH_3), 1.41 (2 H, m, C*H*$_2$$CH_3$), 1.57 (2 H, m, OCH_2C*H*$_2$), 3.28 (1 H, t, J 9.4, H-4c), 3.40-3.47 (3 H, m, H-2b, H-2c, O*CH*$_2$$CH_2$), 3.52 (1 H, t, J 9.4, H-4b), 3.63 (1 H, t, J 9.4, H-3c), 3.64-3.72 (3 H, m, H-5c, H-6c, O*CH*$_2$$CH_2$), 3.69 (1 H, dd, $J_{5a,4a}$ 4.5, $J_{5a,5'a}$ 11.7, H-5a), 3.75 (1 H, dd, $J_{5'a,4a}$ 4.0, $J_{5'a,5a}$ 11.7, H-5'a), 3.78-3.91 (5 H, m, H-5b, H-6b, H-3b, H-6'c), 3.88 (1 H, dd, $J_{3a,2a}$ 2.8, $J_{3a,4a}$ 6.0, H-3a), 4.11 (1 H, ddd, $J_{4a,5'a}$ 4.0, $J_{4a,5a}$ 4.5, $J_{4a,3a}$ 6.0, H-4a), 4.21 (1 H, dd, $J_{2a,1a}$ 1.4, $J_{2a,3a}$ 2.8, H-2a), 4.87 (1 H, d, $J_{1a,2a}$ 1.4, H-1a), 4.90 (1 H, d, $J_{1b,2b}$ 3.8, H-1b), 5.14 (1 H, d, $J_{1c,2c}$ 3.7, H-1c). δ_C(100 MHz, CD_3OD) 14.2 (CH_3), 20.4 (*C*$H_2$$CH_3$), 32.8 ($OCH_2$*C*$H_2$), 62.0 (C-6b), 62.7 (C-6c), 62.9 (C-5a), 68.4 (O*C*$H_2$$CH_2$), 71.5 (C-4c), 72.6 (C-5b), 73.2, 73.3 (C-2c, C-2b), 74.7 (C-3b), 74.8 (C-5c), 75.1 (C-3c), 81.3 (C-2a), 81.9 (C-4b), 83.8 (C-4a), 87.2 (C-3a), 101.2 (C-1b), 103.1 (C-1c), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{21}H_{37}O_{15}$ $[M-H]^-$ 529.2132, found 529.2134.

***n*-pentyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (22)**

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of butyl α-L-arabinofuranoside **15** (60 mg, 0.27 mmol) in the presence of the CGTase wt and was isolated in 19 % yield (20 mg) after purification. Further elution yield butyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**29**) in 11% yield (17 mg).

22: R_f = 0.5 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 20.6 (*c* 0.7 in MeOH). δ_H(400 MHz, CD_3OD) 0.92 (3 H, t, J 6.9, CH_3), 1.30-1.40 (4 H, m, C_2*H*$_4$$CH_3$), 1.53-1.65 (2 H, m, OCH_2C*H*$_2$), 3.29 (1 H, dd, $J_{4b,3b}$ 9.0, $J_{4b,5b}$ 9.9, H-4b), 3.36-3-45 (1 H, m, O*CH*$_2$$CH_2$), 3.39 (1 H, dd, $J_{2b,1b}$ 3.9, $J_{2b,3b}$ 9.7, H-2b), 3.62 (1 H, dd, $J_{3b,4b}$ 9.0, $J_{3b,2b}$ 9.7, H-3b), 3.62-3.75 (2 H, m, H-6b, O*CH*$_2$$CH_2$), 3.72 (1 H, dd, $J_{5a,4a}$ 4.3, $J_{5a,5'a}$ 12.0, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 3.6, $J_{5'a,5a}$ 12.0, H-5'a), 3.73-3.81 (1 H, m, H-5b), 3.85 (1 H, dd, $J_{6'b,5b}$ 2.5, $J_{6'b,6b}$ 11.9, H-6'b), 3.85 (1 H, dd, $J_{3a,2a}$ 3.5, $J_{3a,4a}$ 6.3, H-3a), 4.10 (1 H, ddd, $J_{4a,5'a}$ 3.6, $J_{4a,5a}$ 4.3, $J_{4a,3a}$ 6.3, H-4a), 4.21 (1 H, dd, $J_{2a,1a}$ 1.6, $J_{2a,3a}$ 3.5, H-2a), 4.87 (1 H, d, $J_{1a,2a}$ 1.6, H-1a), 4.89 (1 H, d, $J_{1b,2b}$ 3.9, H-1b). δ_C(100 MHz, CD_3OD) 14.4 (CH_3), 23.5, 29.5 (*C*$_2$$H_4CH_3$), 30.4 ($OCH_2$*C*$H_2$), 62.6 (C-6b), 62.8 (C-5a), 68.9 (O*C*$H_2$$CH_2$), 71.8 (C-4b), 73.5 (C-2b), 74.1 (C-5b), 74.9 (C-3b), 81.8 (C-2a), 83.4 (C-4a), 87.0 (C-3a), 101.3 (C-1b), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{16}H_{29}O_{10}$ $[M-H]^-$ 381.1766, found 381.1765.

29: R_f = 0.21 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 57.1 (*c* 0.7 in MeOH). δ_H(400 MHz, CD_3OD) 0.93 (3 H, t, J 7.1, CH_3), 1.30-1.42 (4 H, m, $C_2H_4CH_3$), 1.53-1.65 (2 H, m, OCH_2CH_2), 3.28 (1 H, t, J 9.1, H-4c), 3.37-3.47 (3 H, m, H-2b, H-2c, OCH_2CH_2), 3.52 (1 H, t, J 9.4, H-4b), 3.63 (1 H, t, J 9.0, H-3c), 3.59-3.72 (3 H, m, H-5c, H-6c, OCH_2CH_2), 3.69 (1 H, dd, $J_{5a,4a}$ 5.0, $J_{5a,5'a}$ 11.7, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 3.9, $J_{5'a,5a}$ 11.7, H-5'a), 3.79-3.92 (5 H, m, H-5b, H-6b, H-3b, H-6'c), 3.88 (1 H, dd, $J_{3a,2a}$ 3.0, $J_{3a,4a}$ 6.2, H-3a), 4.11 (1 H, ddd, $J_{4a,5'a}$ 4.0, $J_{4a,5a}$ 4.6, $J_{4a,3a}$ 6.2, H-4a), 4.20 (1 H, dd, $J_{2a,1a}$ 1.5, $J_{2a,3a}$ 3.0, H-2a), 4.87 (1 H, d, $J_{1a,2a}$ 1.5, H-1a), 4.90 (1 H, d, $J_{1b,2b}$ 3.8, H-1b), 5.14 (1 H, d, $J_{1c,2c}$ 3.8, H-1c). δ_C(100 MHz, CD_3OD) 14.5 (CH_3), 23.5, 29.5 ($C_2H_4CH_3$), 30.4 (OCH_2CH_2), 62.0 (C-6b), 62.7 (C-6c), 62.8 (C-5a), 68.7 (OCH_2CH_2), 71.5 (C-4c), 72.6 (C-5b), 73.1, 74.3 (C-2c, C-2b), 74.7 (C-3b), 74.8 (C-5c), 75.1 (C-3c), 81.4 (C-2a), 81.9 (C-4b), 83.7 (C-4a), 87.2 (C-3a), 101.2 (C-1b), 103.1 (C-1c), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{22}H_{39}O_{15}$ $[M-H]^-$ 543.2294, found 543.2300.

***n*-Hexyl α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (23)**

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of 60 mg (0.26 mmol) of *n*-hexyl α-L-arabinofuranoside and in the presence of the CGTase wt and was isolated in 25 % yield (25 mg) after purification. Further elution yield *n*-hexyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-α-L-arabinofuranoside (**30**) in 10% yield (13.6 mg).

23: R_f = 0.5 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 22.5 (c 1.0 MeOH). δ_H(400 MHz, CD_3OD) 0.91 (3 H, t, *J* 6.8, CH_3), 1.32 (6 H, m, C_3H_6), 1.58 (2 H, m, OCH_2CH_2), 3.28 (1 H, dd, $J_{4b,3b}$ 8.4, $J_{4b,5b}$ 10.0, H-4b), 3.40 (1 H, dd, $J_{2b,1b}$ 4.0, $J_{2b,3b}$ 9.6, H-2b), 3.42 (1 H, m, OCH_2CH_2), 3.61 (1 H, dd, $J_{3b,4b}$ 8.4, $J_{3b,2b}$ 9.6, H-3b), 3.64-3.68 (2 H, m, H-6b, OCH_2CH_2), 3.69 (1 H, dd, $J_{5a,4a}$ 4.2, $J_{5a,5'a}$ 12.4, H-5a), 3.72 (1 H, dd, $J_{5'a,4a}$ 4.0, $J_{5'a,5a}$ 12.4, H-5'a), 3.82 (1 H, dd, $J_{5b,6b}$ 2.4, $J_{5b,4b}$ 10.0, H-5b), 3.84 (1 H, m, H-6'b), 3.86 (1 H, dd, $J_{3a,2a}$ 3.6, $J_{3a,4a}$ 6.4, H-3a), 4.09 (1 H, m, H-4a), 4.20 (1 H, dd, $J_{2a,1a}$ 1.6, $J_{2a,3a}$ 3.6, H-2a), 4.88 (1 H, d, $J_{1a,2a}$ 1.6, H-1a), 4.90 (d, 1H, $J_{1b,2b}$ 4.0, H-1b). δ_C(100 MHz, CD_3OD) 14.4 (CH_3), 32.8, 30.6, 26.9, 23.7 (C_4H_8), 62.6 (C-6b), 62.7 (C-5a), 68.9 (OCH_2CH_2), 71.8 (C-4b), 73.5 (C-2b), 74.1 (C-5b), 74.9 (C-3b), 81.8 (C-2a), 83.3 (C-4a), 87.0 (C-3a), 101.3 (C-1b), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{17}H_{29}O_{10}$ $[M-H]^-$ 395.1917, found 395.1880.

30: R_f = 0.3 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 56.5 (c 0.2 MeOH). δ_H(400 MHz, CD_3OD) 0.91 (3 H, t, CH_3), 1.33 (6 H, m, C_3H_6), 1.58 (2 H, m, OCH_2CH_2), 3.28 (1 H, m, H-4c), 3.35-3.46 (3 H, m, H-2b, H-2c, OCH_2CH_2), 3.52 (1 H, m, H-4b), 3.62-3.74 (4 H, m, H-3c, H-5c, H-6c, OCH_2CH_2), 3.70 (1 H, dd, $J_{5a,4a}$ 5.2, $J_{5a,5'a}$ 12.0, H-5a), 3.76 (1 H, dd, $J_{5'a,4a}$ 4.0, $J_{5'a,5a}$ 12.0, H-5'a), 3.86-3.81 (5 H, m, H-3b, H-5b, H-6b, H-6'c), 3.90 (1 H, dd, $J_{3a,2a}$ 2.8, $J_{3a,4a}$ 6.4, H-3a), 4.10 (1 H, m, H-4a), 4.17 (1 H, dd, $J_{2a,1a}$ 1.2, $J_{2a,3a}$ 2.8, H-2a), 4.79 (1 H, d, $J_{1a,2a}$ 1.2, H-1a), 4.90 (1 H, d, $J_{1b,2b}$ 4.0, H-1b), 5.13 (1 H, d, $J_{1c,2c}$ 3.6, H-1c). δ_C(100 MHz, CD_3OD) 14.4 (CH_3), 32.7, 30.6, 26.9, 23.7 (C_4H_8), 61.9 (C-6b), 62.7 (C-6c), 62.8 (C-5a), 68.7 (OCH_2CH_2), 71.4 (C-4c), 72.6 (C-5b), 73.1 (C-2c), 74.2 (C-2b), 74.6 (C-3b), 74.7 (C-5c), 75.0 (C-3c), 81.4 (C-2a), 81.9 (C-4b), 83.6 (C-4a), 87.0 (C-3a), 101.1 (C-1b), 101.3 (C-1c), 109.5 (C-1a). HRMS (ESI^-) calcd. for $C_{23}H_{41}O_{15}$ $[M-H]^-$ 557.2445, found 557.2365.

***n*-Octyl α-D-glucopyranosyl-(1,3)-β-D-galactofuranoside (24)**

This compound was obtained according to the described general procedure for transglycosylation with glycoside acceptor by incubation of 100 mg (0.34 mmol) of *n*-octyl β-D-galactofuranoside and in the presence of the CGTase wt and was isolated in 5% yield (7.5 mg) after purification. Further elution yield *n*-octyl α-D-glucopyranosyl-(1,4)-α-D-glucopyranosyl-(1,3)-β-D-galactofuranoside (**31**) in 3% yield (6.3 mg).

24: R_f = 0.56 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 32.7 (c 1.0 MeOH). δ_H(400 MHz, CD_3OD) 0.89 (3H, t, J 6.8, CH_3), 1.28-1.32 (10H, m, CH_2), 1.60-1.63 (2H, m, OCH_2CH_2), 3.28 (1 H, m, H-4b), 3.42 (1 H, dd, $J_{2b,1b}$ 3.8, $J_{2b,3b}$ 11, H-2b), 3.46 (1H, t, J 6.7, OCH_2), 3.53-3.65 (5H, m, H-5a, H6a, H-3b, H-6b), 3.72 (1H, dd, J 5.0, H-4a), 3.80 (1H, dt, J 6.7, J 9.5, OCH_2), 3.89 (2 H, m, H-5b, H-6'b), 3.94 (1H, m, H-2a), 4.12 (1 H, dd, $J_{2a,3a}$ 3.2, $J_{3a,4a}$ 6.5, H-3a), 4.86 (1H, d, $J_{1a,2a}$ 1.5, H-1a), 4.98 (1 H, d, $J_{1b,2b}$ 4.0, H-1b). δ_C(100 MHz, CD_3OD) 15.2 (CH_3), 24.4, 31.4, 31.2, 31.1, 27.9 [$(CH_2)_5CH_3$], 33.7 (OCH_2CH_2), 62.7 (C-6b), 65.4 (C-6a), 69.6 (OCH_2), 71.8 (C-4b), 73.2 (C-5a), 73.4 (C-2b), 74.4 (C-5b), 74.9 (C-3b), 84.0 (C-2a), 84.9 (C-4a), 87.4 (C-3a), 102.0 (C-1b), 110.0 (C-1a). HRMS (ESI^-) calcd. for $C_{20}H_{37}O_{11}$ $[M-H]^-$ 453,2336, found 453,2332.

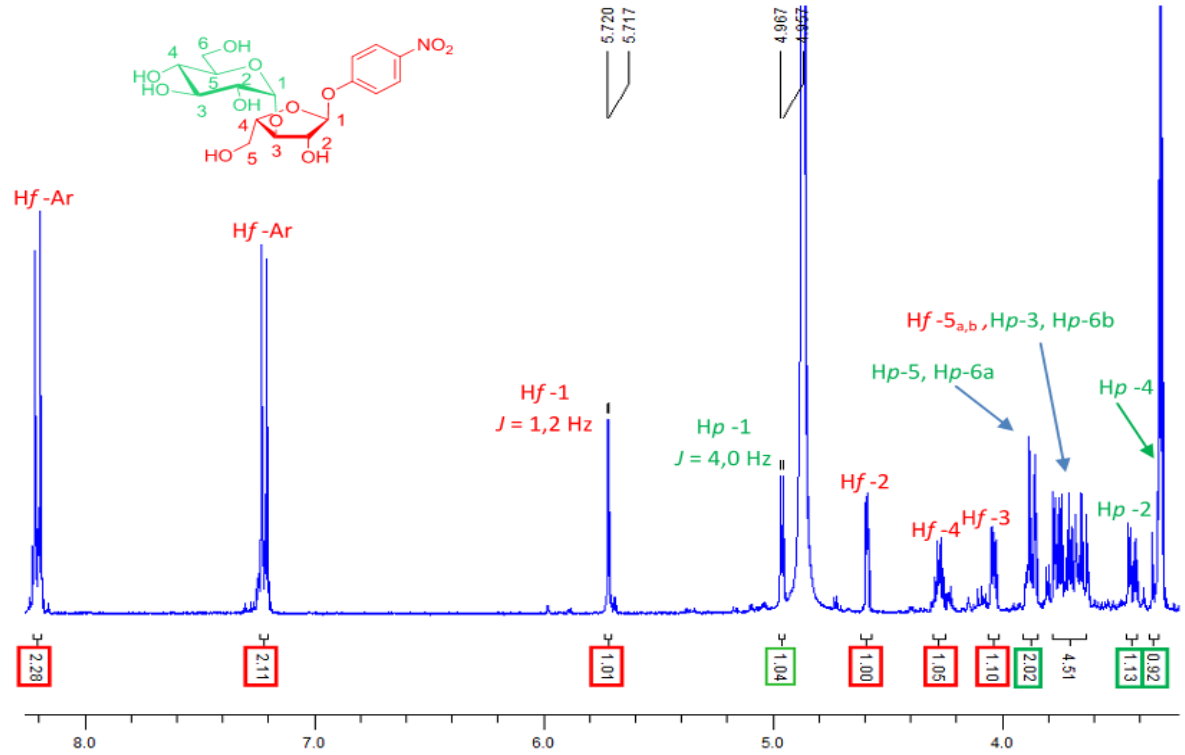
31: R_f = 0.4 (AcOEt/AcOH/H_2O, 7:2:2), $[\hat{I} \pm]_D^{20}$ + 56.5 (c 0.2 MeOH). δ_H(400 MHz, CD_3OD) 0.90 (3H, t, J 7, CH_3), 1.30-1.35 (10H, m, CH_2), 3.50 (1 H, dd, $J_{2b,1b}$ 3.6,

$J_{2b,3b}$ 10.0, H-2b), 1.61-1.63 (2H, m, OCH_2CH_2), 3.27 (1 H, m, H-4c), 3.45-3-47 (2H, m,H-2c, OCH_2), 3.52-3.70 (7H, m, H-5a, H6a, H-4b, H-3c, H-5c, H-6c), 3.72 (1H, dd, J 5.0, H-4a), 3.78 (1 H, dd, $J_{6c,5c}$ 2.4 Hz, $J_{6c,6'c}$ 12, H-6'c), 3.80 (1H, dt, J 6.7, J 9.5, OCH_2), 3.85-3.92 (3 H, m, H-3b, H-6b), 3.98-4.05 (2H, m, H-2a, H-5b), 4.15 (1 H, dd, $J_{3a,2a}$ 3.2, $J_{3a,4a}$ 5.6, H-3a), 4.88 (1H, d, $J_{1a,2a}$ 1.5, H-1a), 4.99 (1 H, d, $J_{1b,2b}$ 3.6, H-1b), 5.16 (1 H, d, $J_{1c,2c}$ 3.6, H-1c) δ_C(100 MHz, CD_3OD) 15.1 (CH_3), 24.5, 27.9, 31.2, 31.6, 31.7 [(CH_2)$_5CH_3$], 34.0 (OCH_2CH_2), 62.2 (C-6b), 62.5 (C-6c), 65.5 (C-6a), 69.3 (OCH_2), 71.5 (C-4c), 72.7 (C-5b), 73.0 (C-2b), 73.2 (C-5a), 74.2 (C-2c), 74.7 (C-3b), 74.9 (C-5c), 75.1 (C-3c), 82.0 (C-4b), 84.0 (C-2a), 84.9 (C-4a), 87.4 (C-3a), 101.7 (C-1b), 103.1 (C-1c), 110.0 (C-1a). HRMS (ESI^-) calcd. for $C_{26}H_{47}O_{16}$ $[M-H]^-$ 615,2864, found 615,2860.

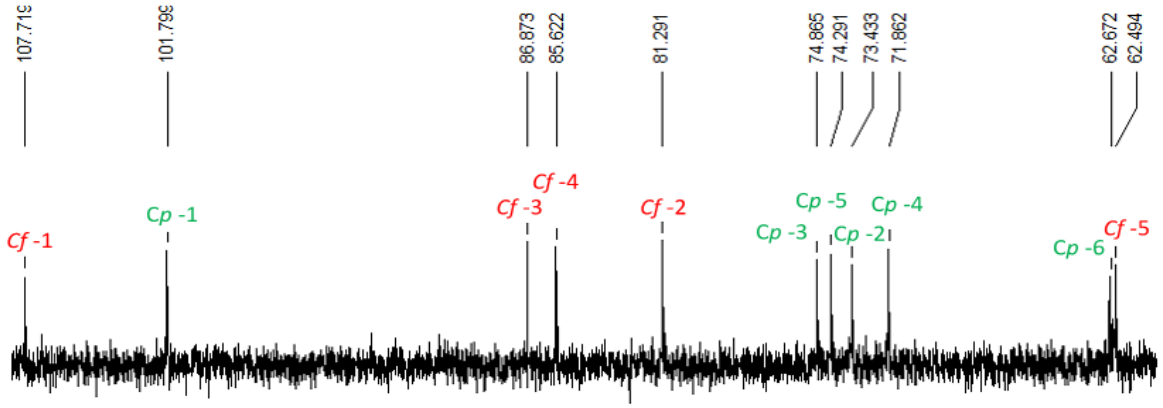
1. S. J. Gebbie, I. Gosney, P. R. Harrison, I. M. F. Lacan, W. R. Sanderson and J. P. Sankey, *Carbohydr. Res.*, 1998, **308**, 345-348

2. A. Tramice, G. Andreotti and A. Trincone, *Mar. Biotechnol.*, 2011, **13**, 773-781.

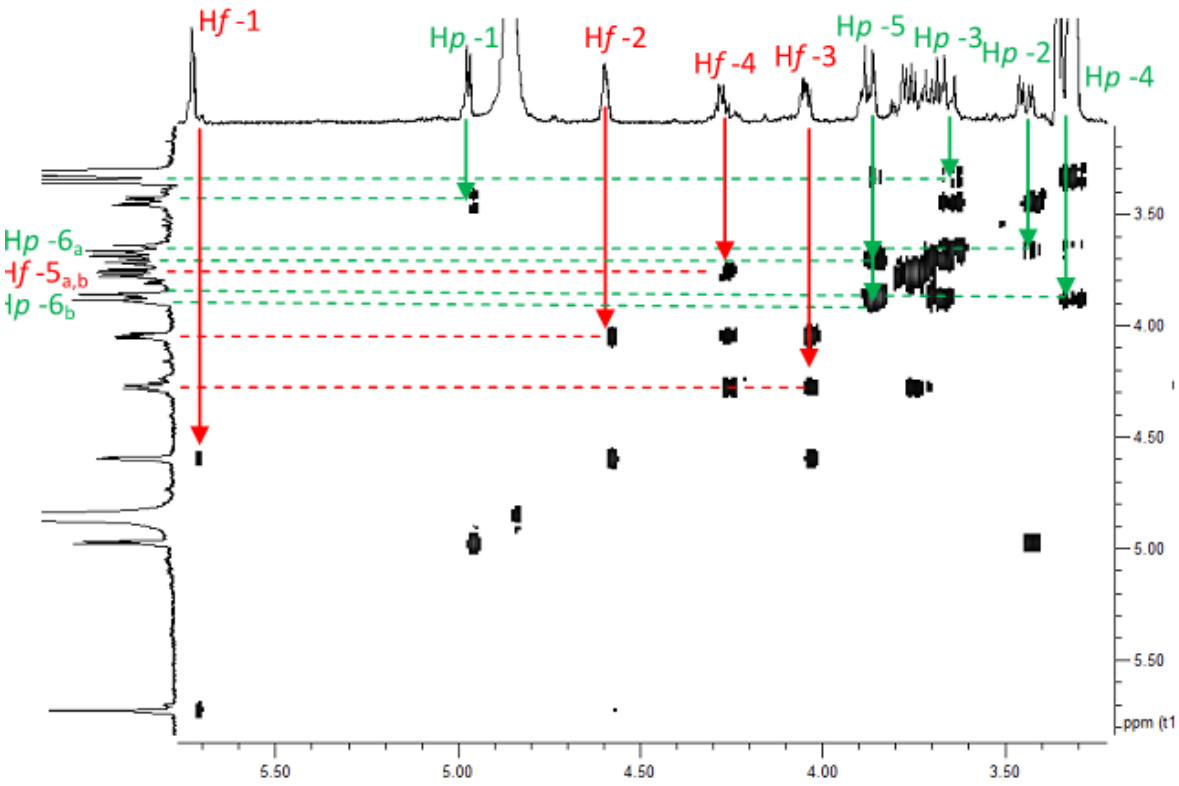
NMR characterisation of isolated compounds 14 and 15 from action of CGTase in presence of cyclodextrin and *p*NP Ara*f* 3



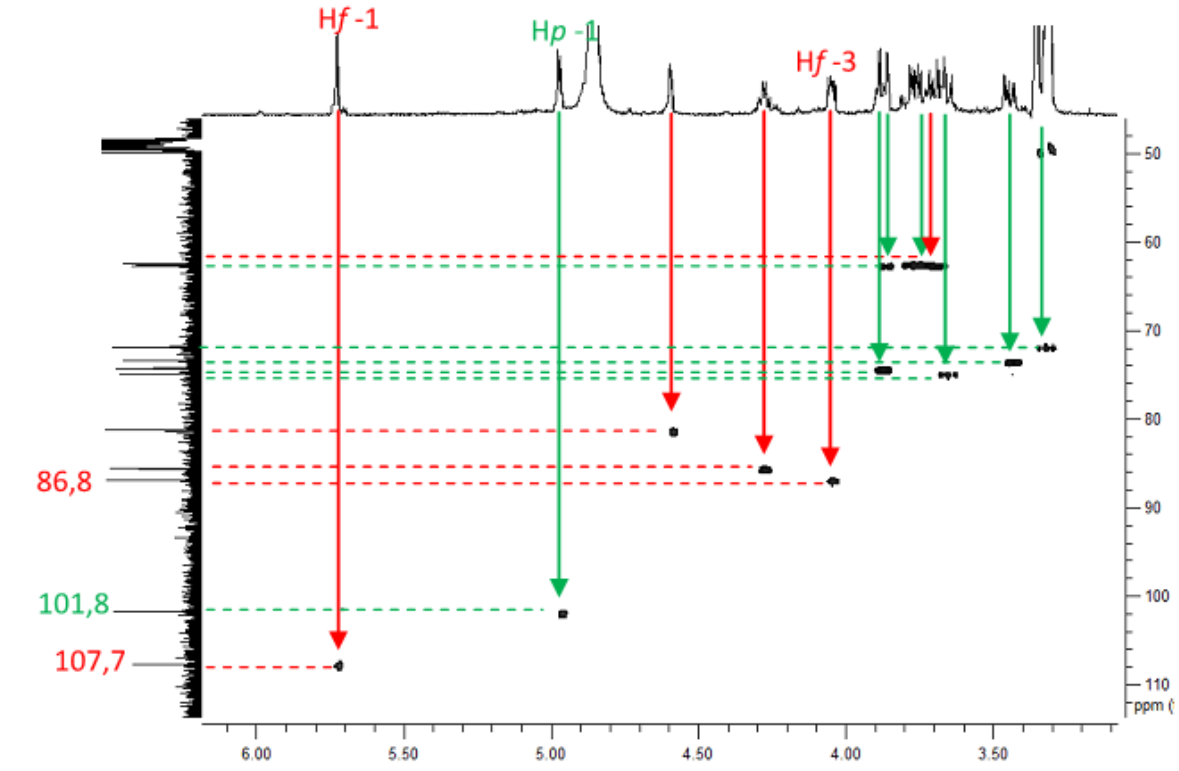
*[1]H NMR spectrum of isolated disaccharide **14**.*



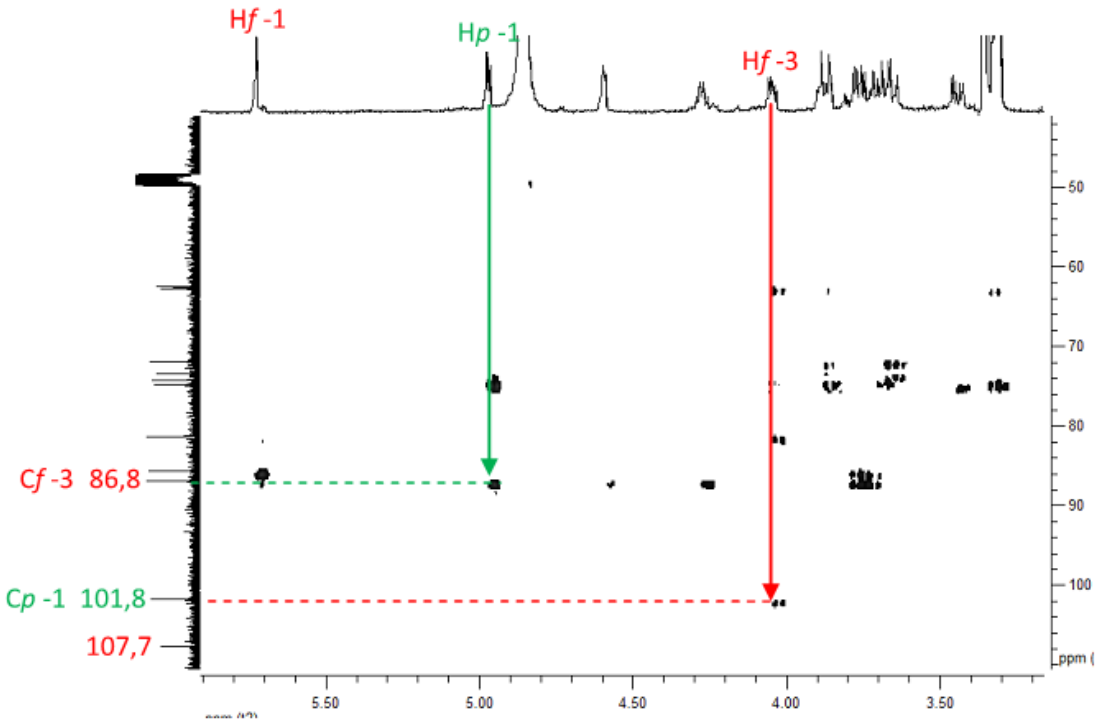
*[13]C NMR spectrum of isolated disaccharide **14**.*



*2D NMR COSY spectrum of isolated disaccharide **14**.*



*2D NMR HSQC spectrum of isolated disaccharide **14**.*



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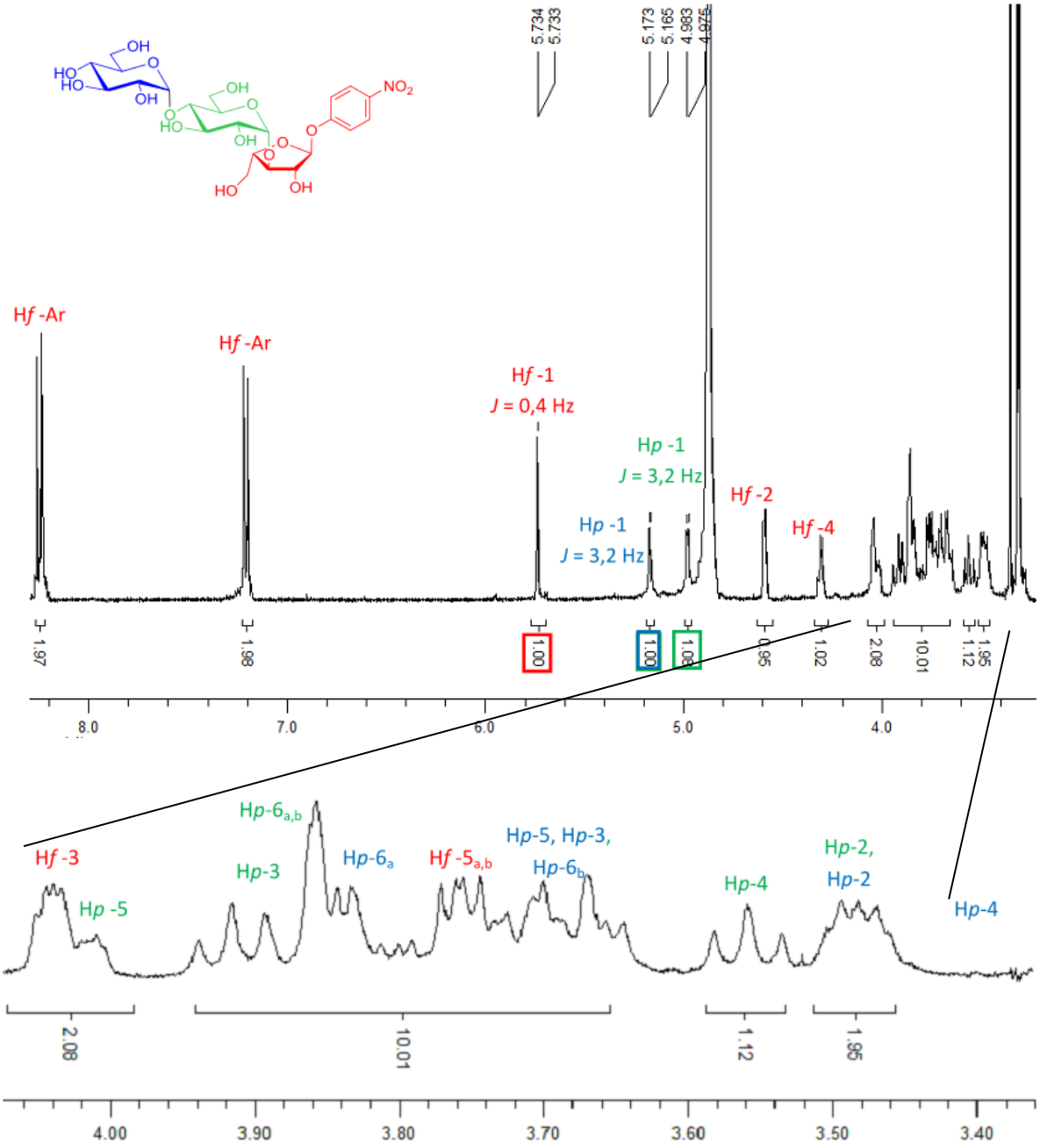
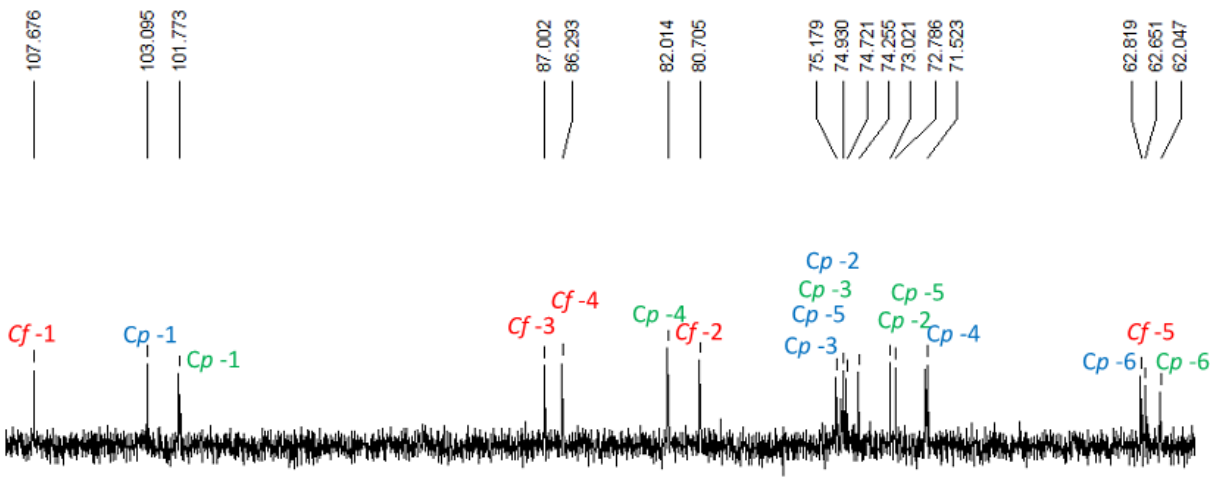
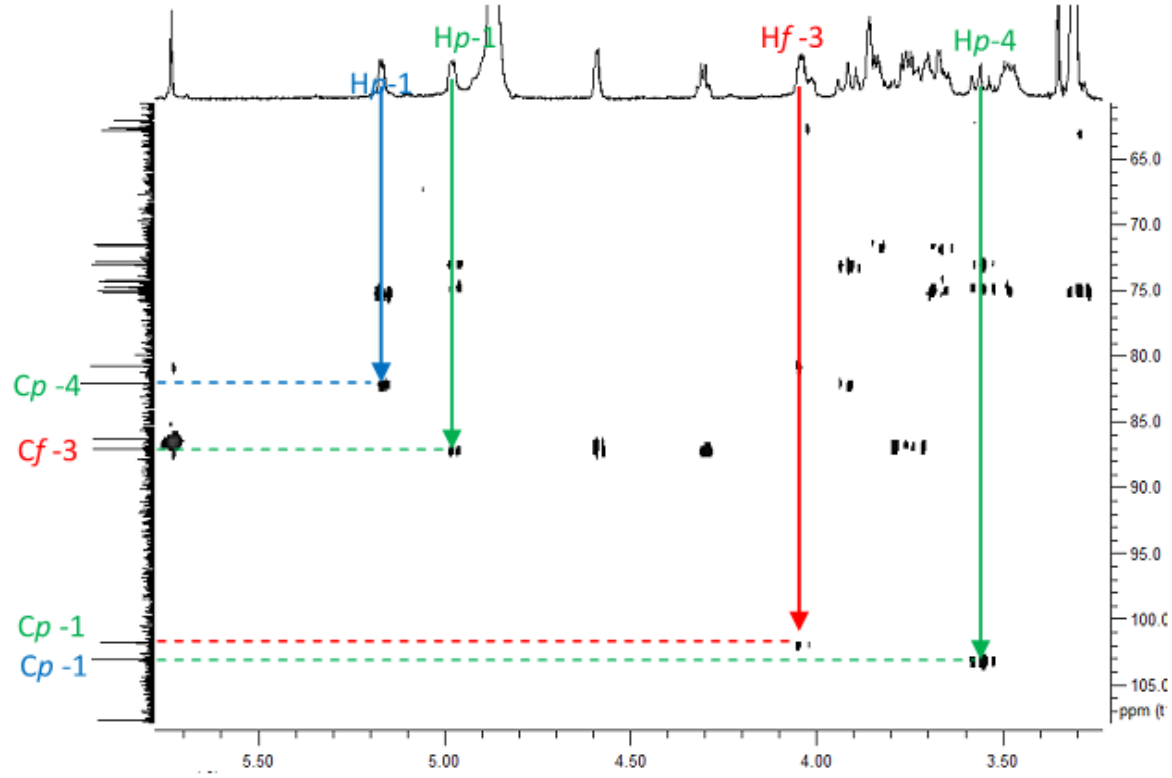


*[1]H NMR spectrum of isolated trisaccharide **15**.*

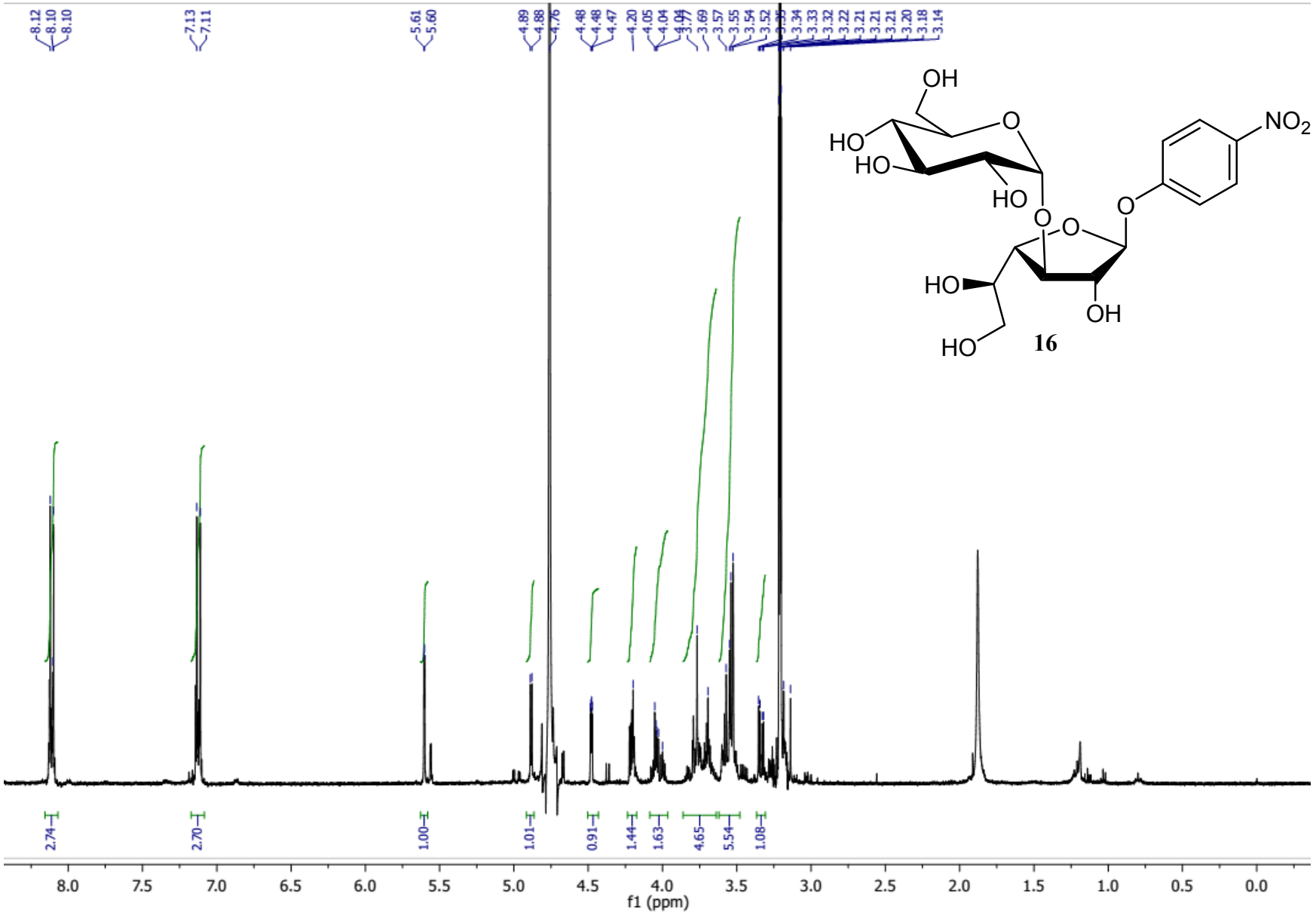


*^{13}C NMR spectrum of isolated trisaccharide **15**.*



*2D NMR HMBC spectrum of isolated trisaccharide **15**.*

NMR spectrum of isolated compounds 16-31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8.10
7.13
7.11
5.61
5.60
4.89
4.88
4.76
4.48
4.48
4.47
4.20
4.05
4.04
3.69
3.57
3.55
3.54
3.52
3.34
3.33
3.32
3.22
3.21
3.21
3.21
3.20
3.18
3.14
OH
HO
HO
HO
O
O
O
O
HO
HO
OH
NO2
16
2.74
2.70
1.00
1.01
0.91
1.44
1.63
4.65
5.54
1.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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1.0
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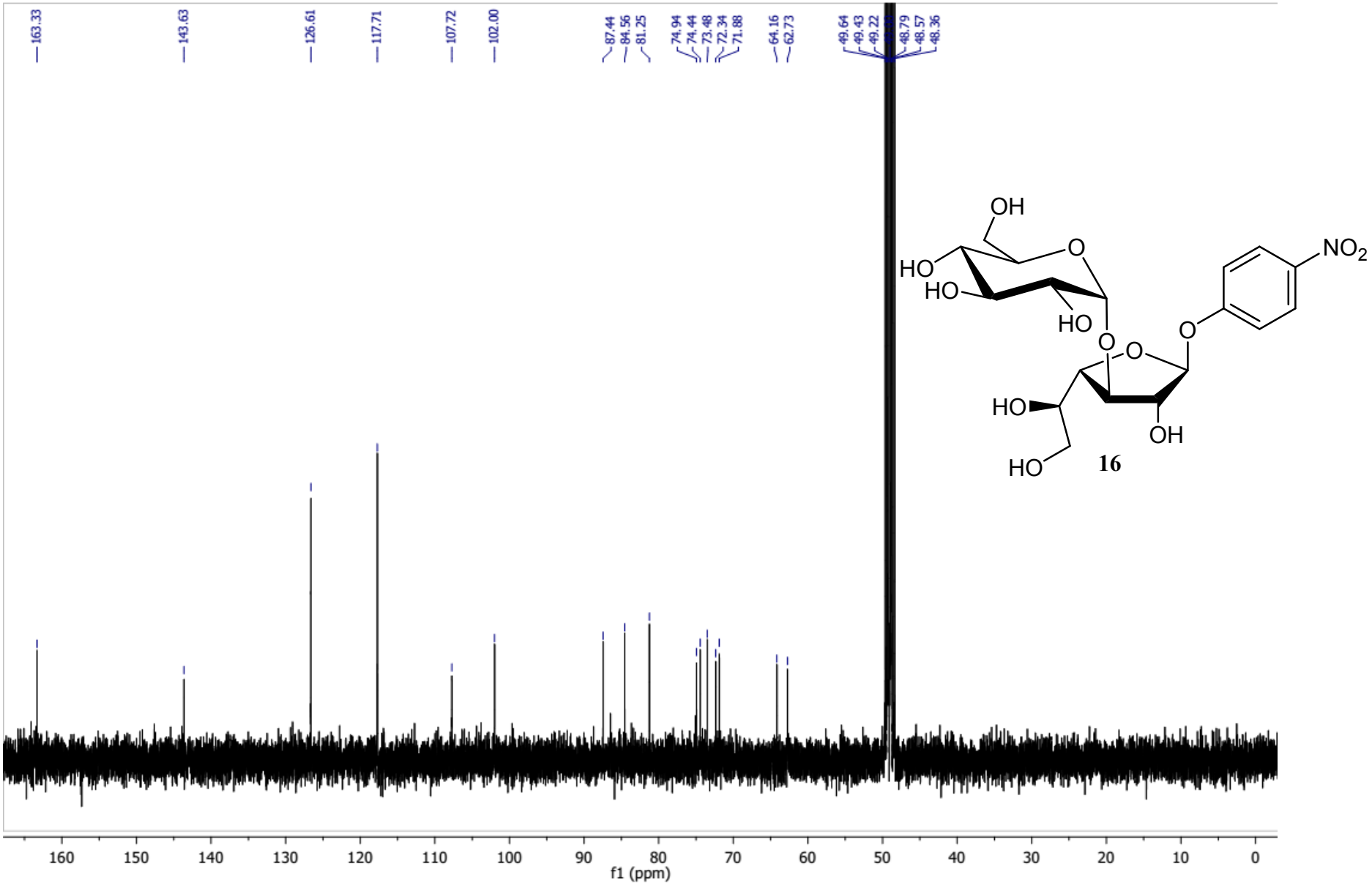
0.0
f1 (ppm)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72.34
71.88
64.16
62.73
49.64
49.43
49.22
48.79
48.57
48.36
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HO
HO
HO
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O
O
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HO
HO
OH
NO2
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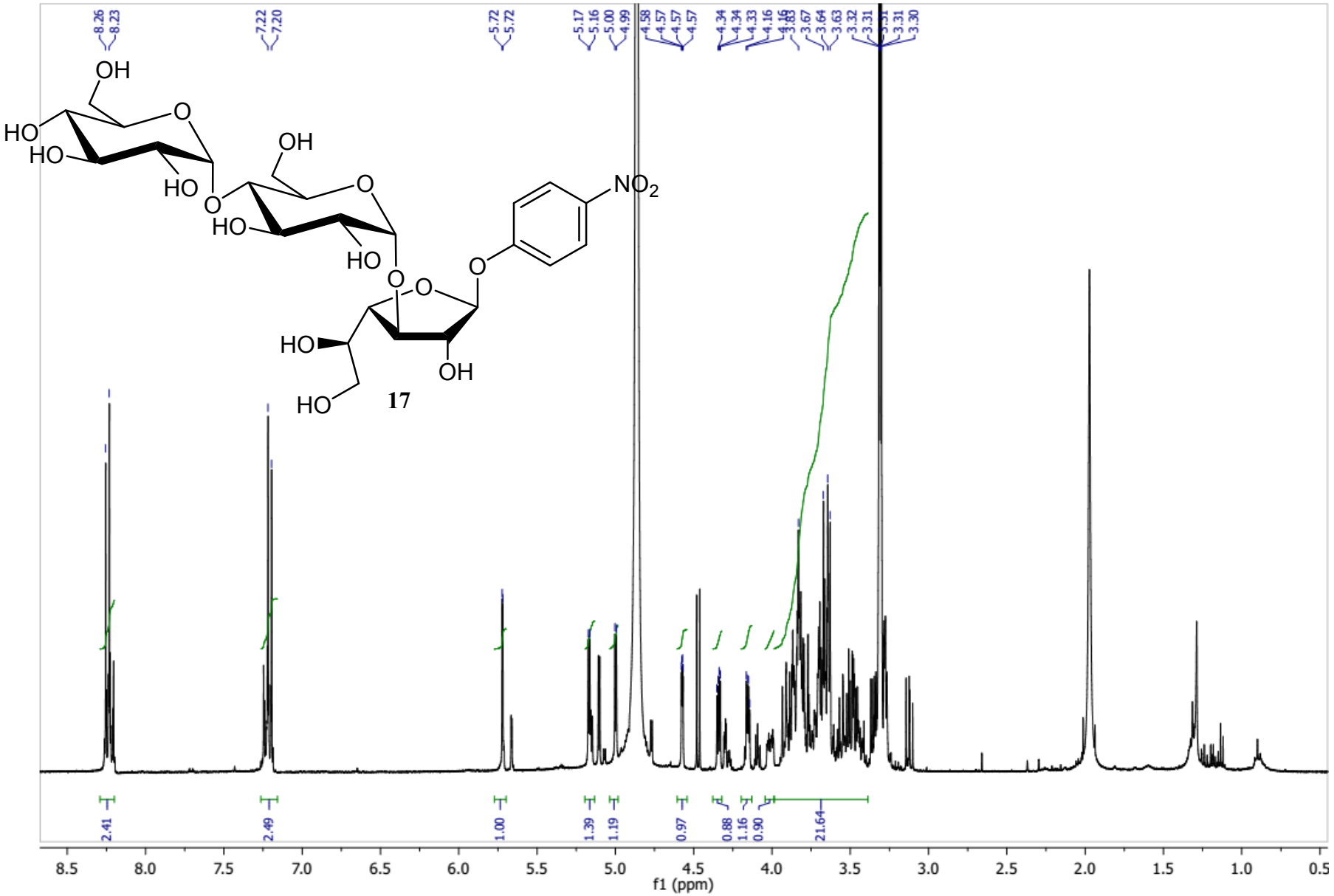
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

16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4.33
4.16
3.67
3.64
3.63
3.32
3.31
3.31
3.30
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O
OH
O
HO
HO
O
O
O
NO2
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OH
HO
17
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2.49
1.00
1.39
1.19
0.97
0.88
1.16
0.90
21.64
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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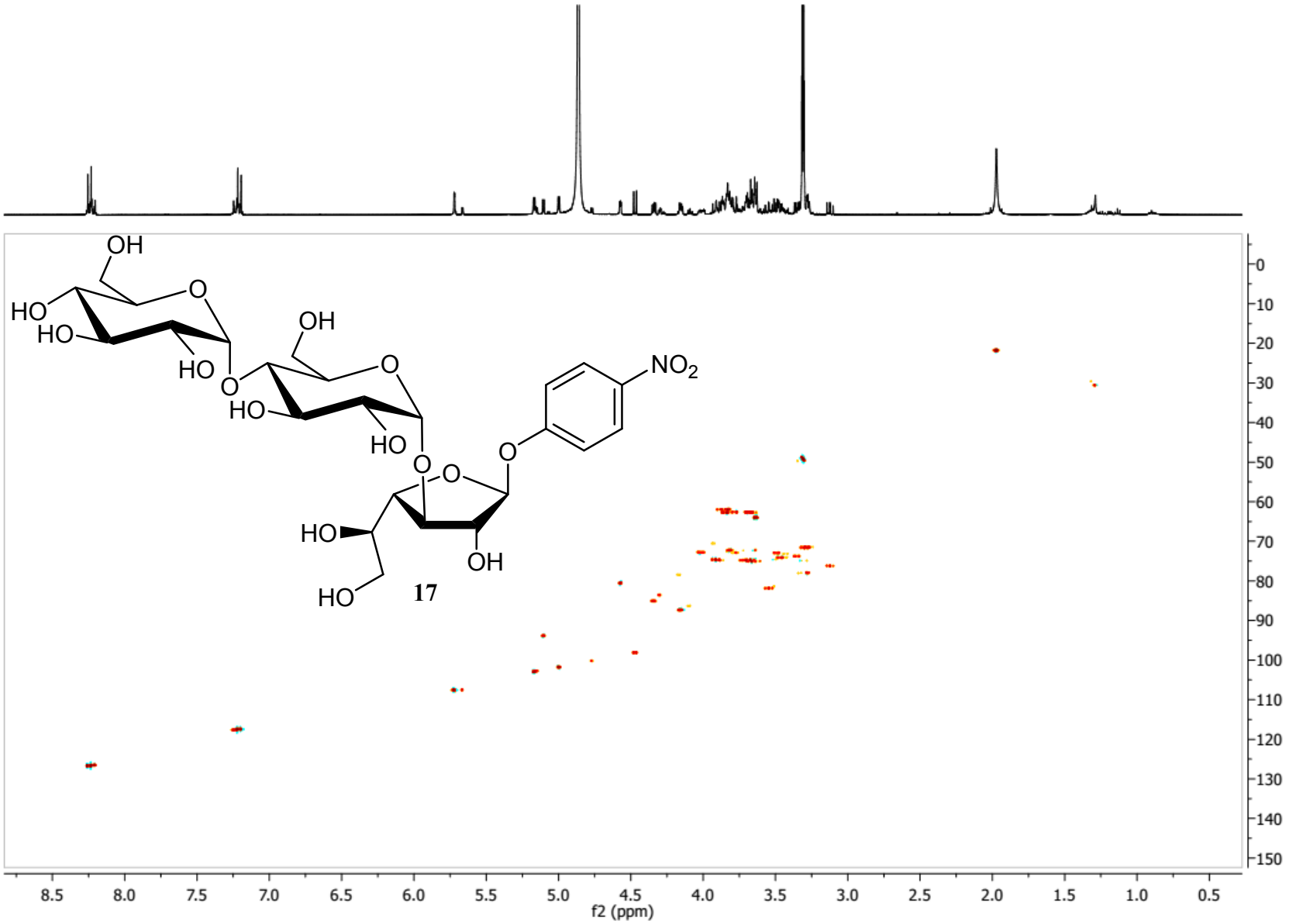
1.5
1.0
0.5
f1 (ppm)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OH
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10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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1.5
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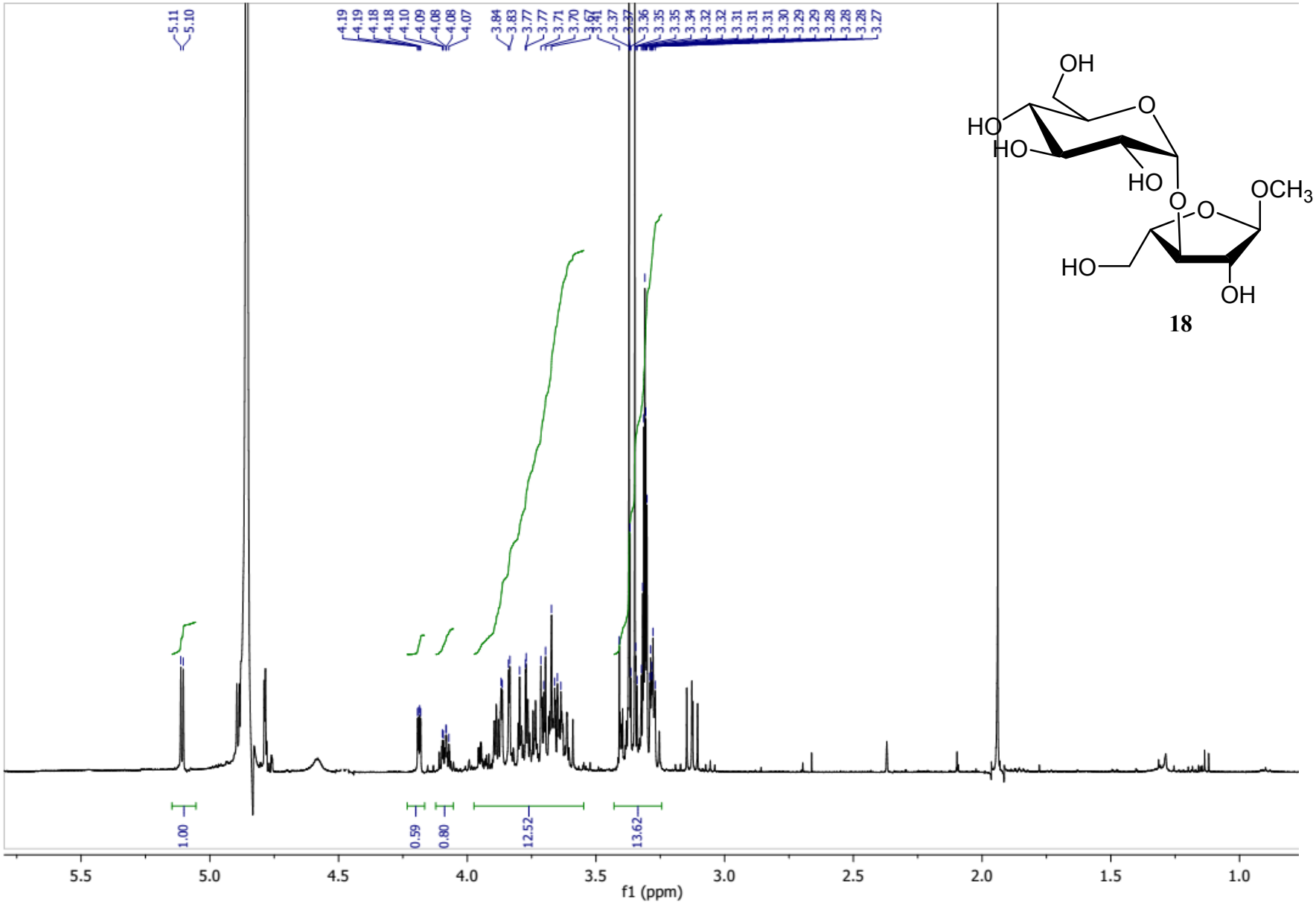
0.5
f2 (ppm)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3.31
3.31
3.31
3.30
3.29
3.29
3.28
3.28
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3.27
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0.80
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13.62
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
f1 (ppm)
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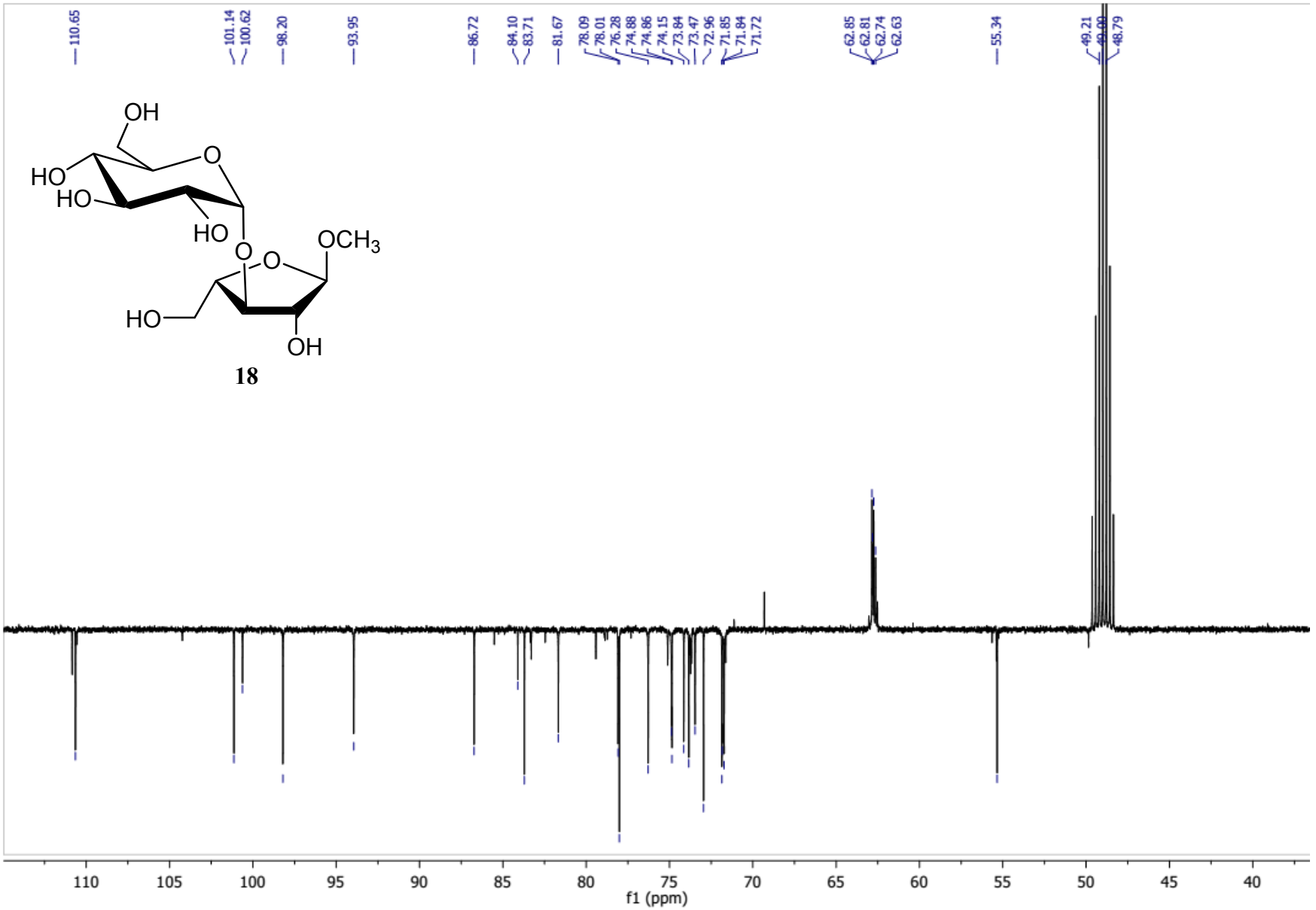
HO
HO
O
O
OCH3
HO
OH

18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78.01
76.28
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74.15
73.84
73.47
72.96
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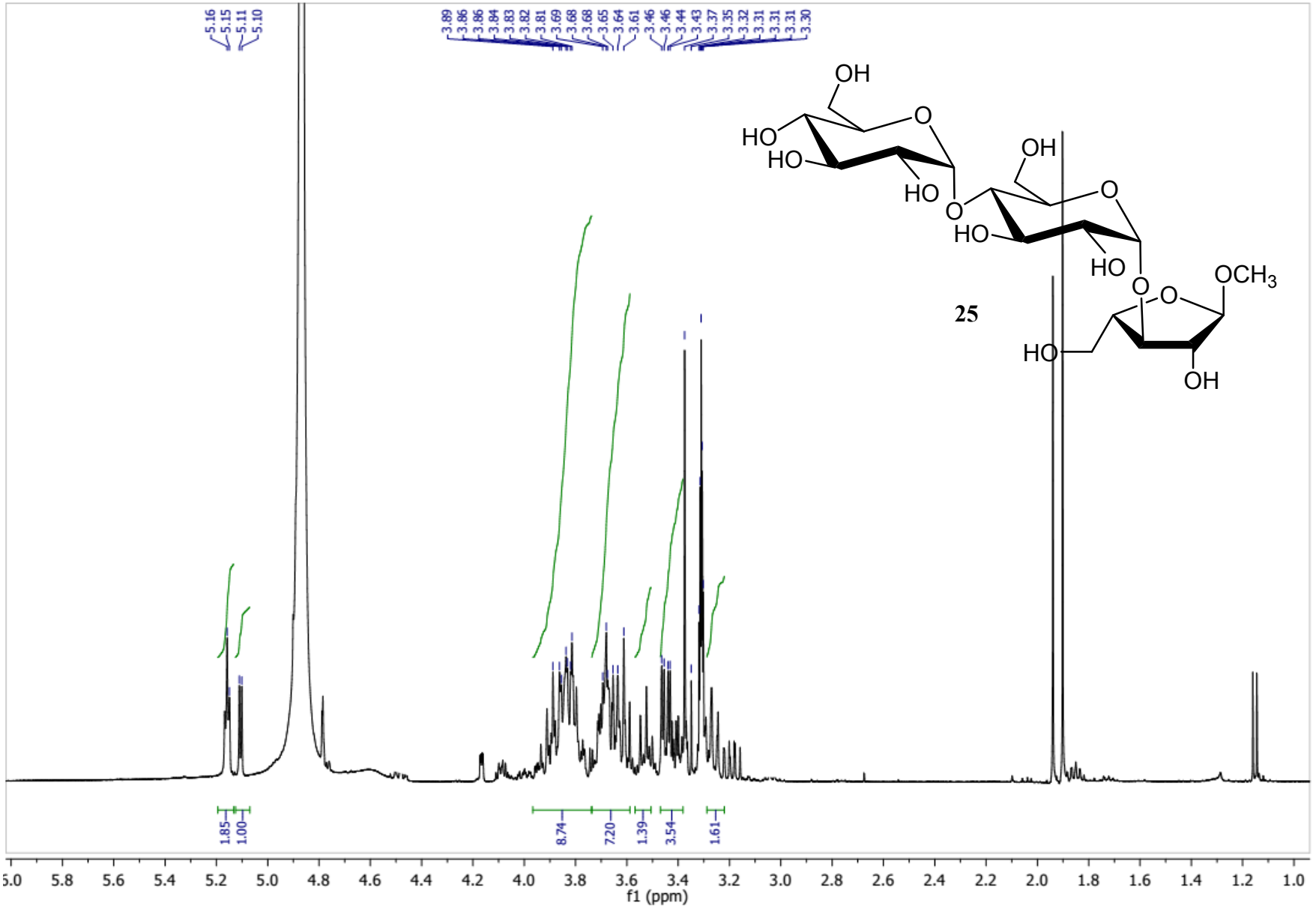
65
60
55
50
45
40
f1 (ppm)

18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HO
O
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HO
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7.20
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5.0
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4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
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1.4
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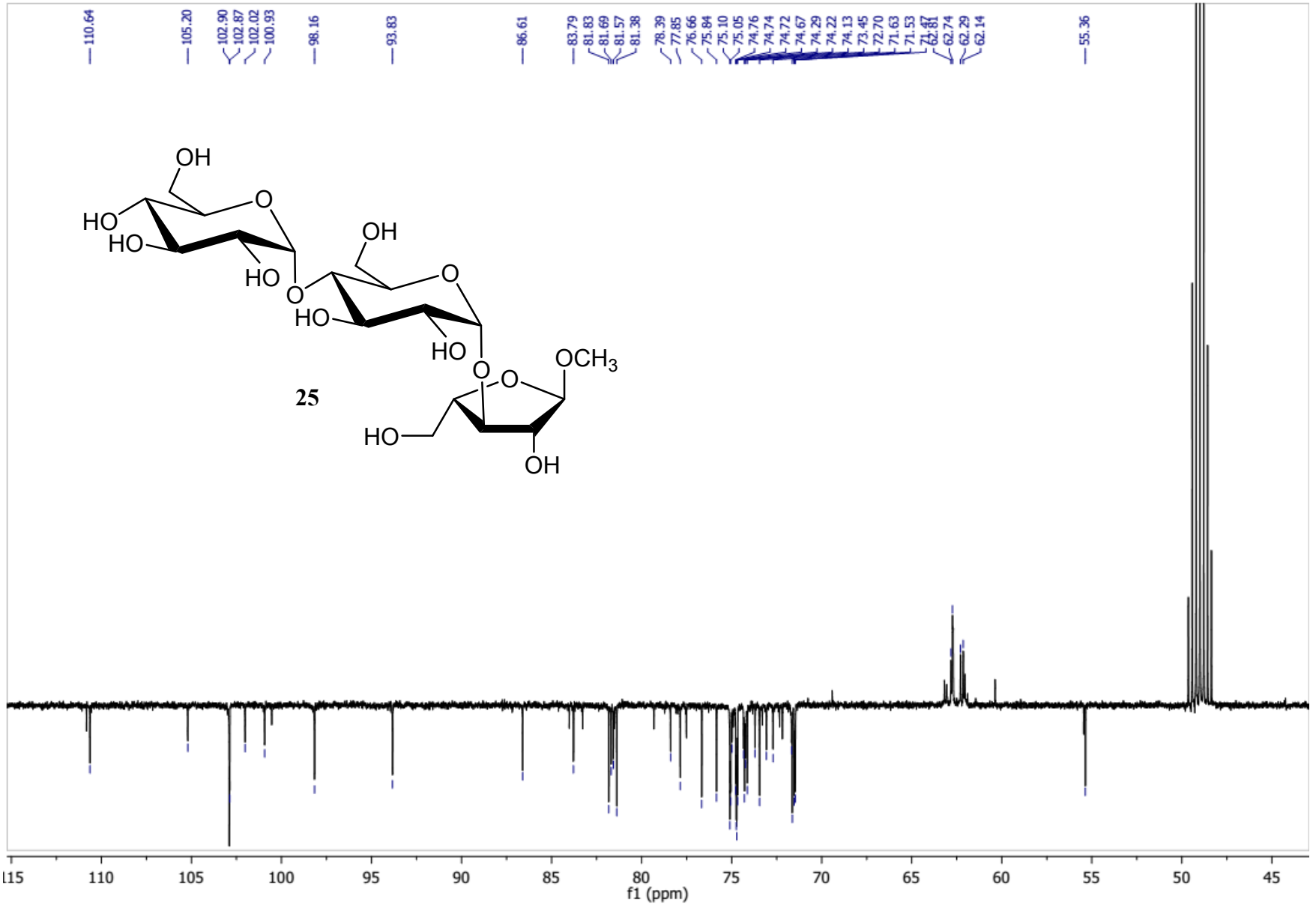
1.0
f1 (ppm)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74.13
73.45
72.70
71.63
71.53
62.74
62.29
62.14
55.36
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HO
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HO
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O
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O
HO
HO
O
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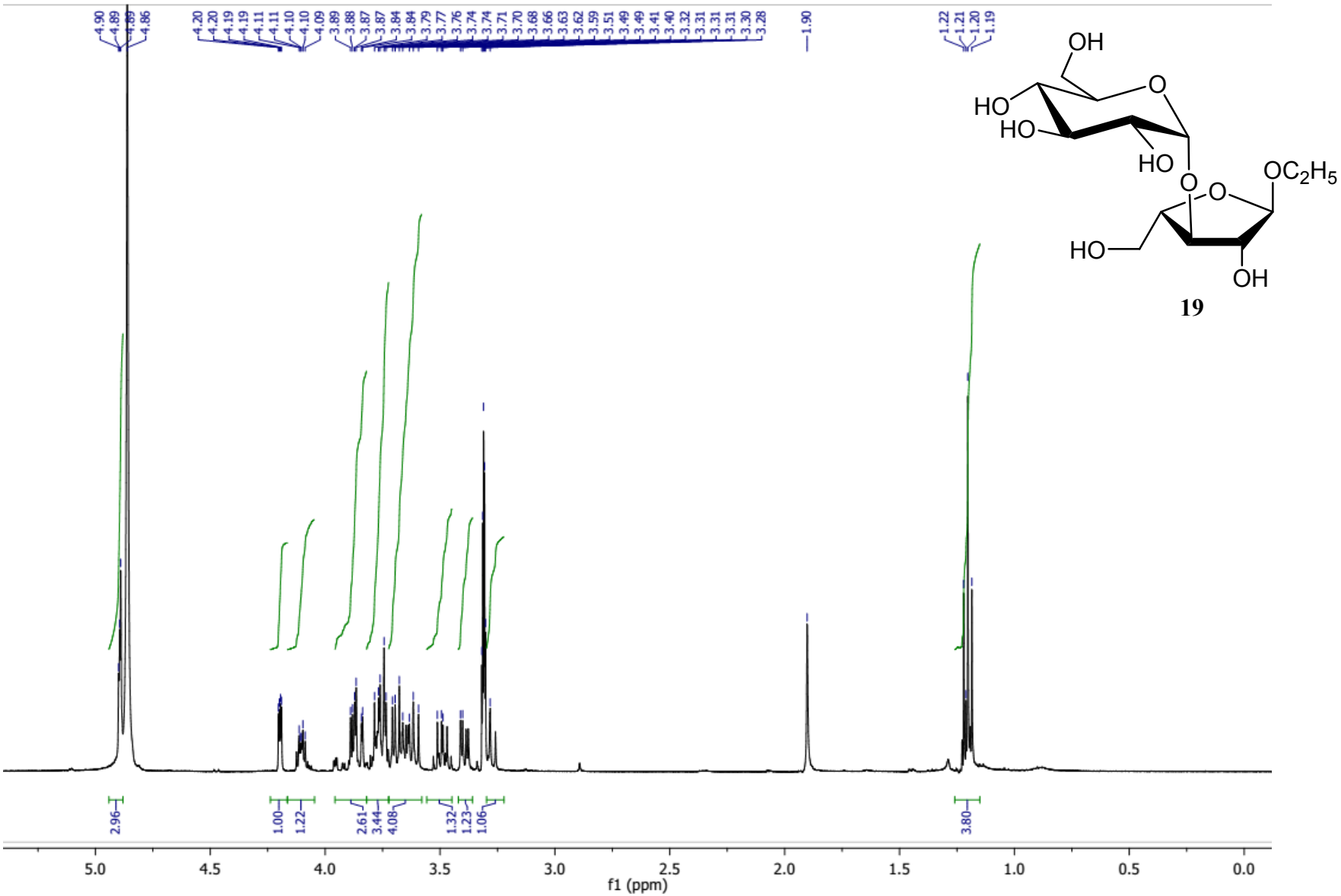
50
45
f1 (ppm)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3.31
3.31
3.30
3.28
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1.22
1.21
1.20
1.19
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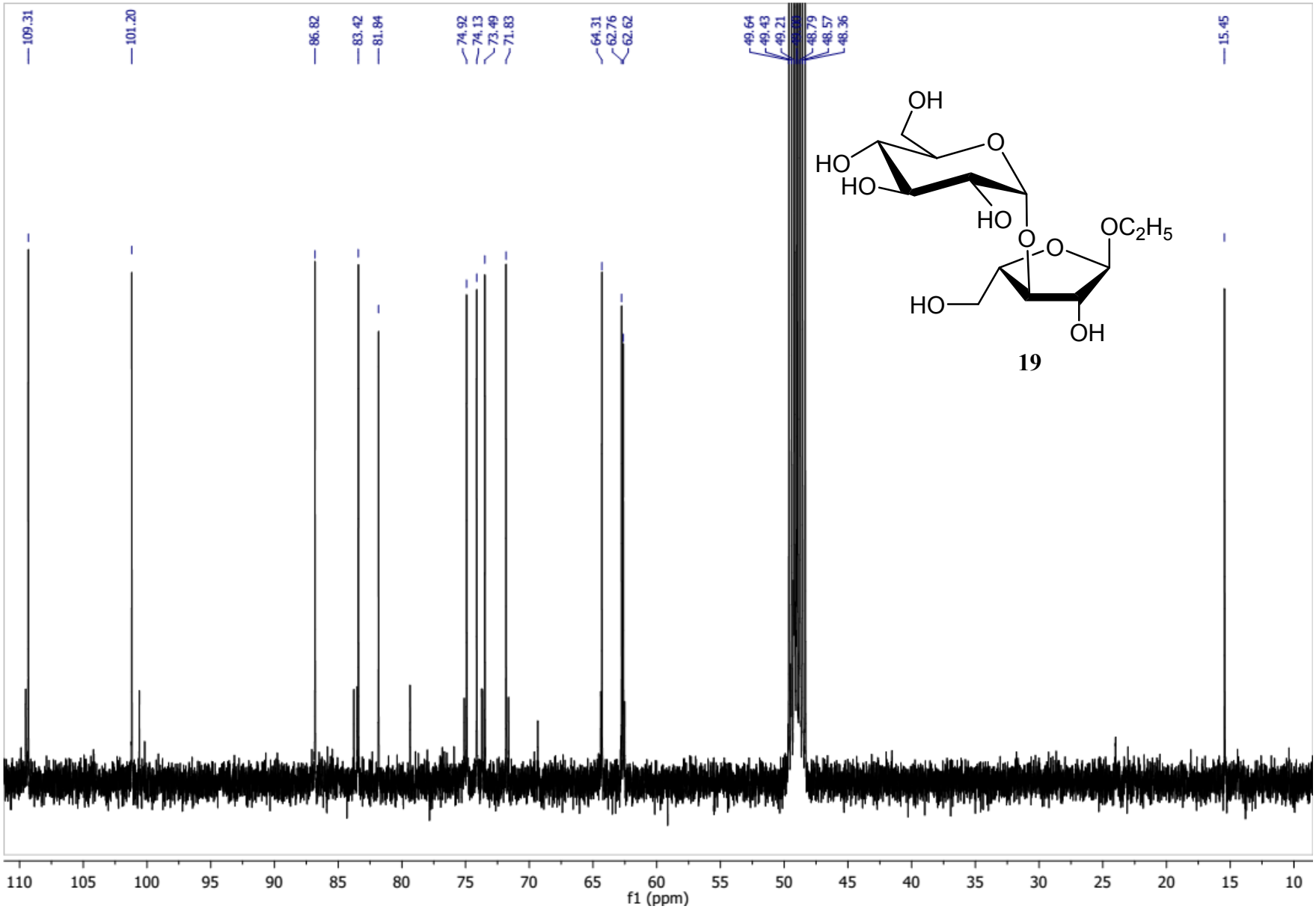
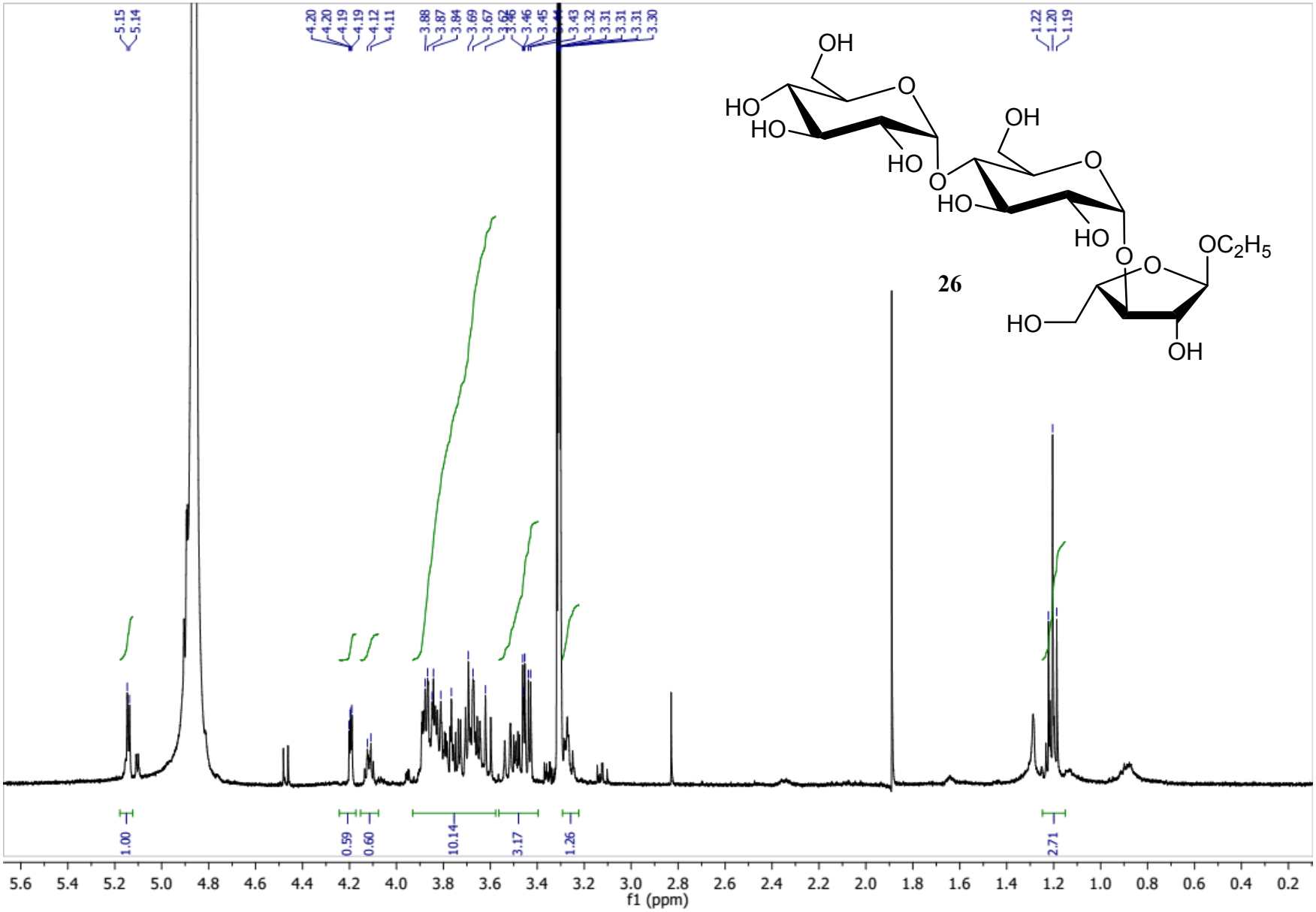
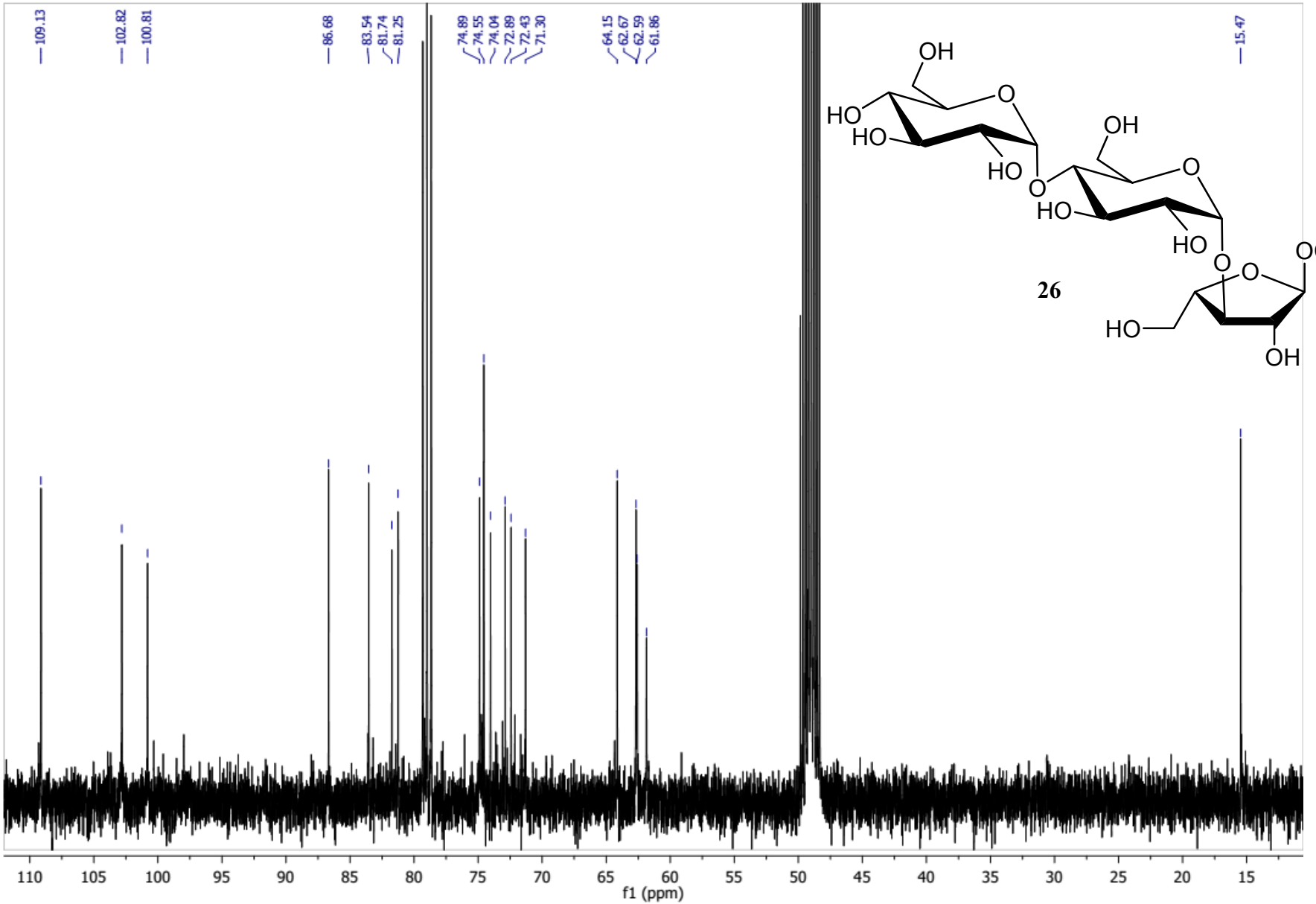
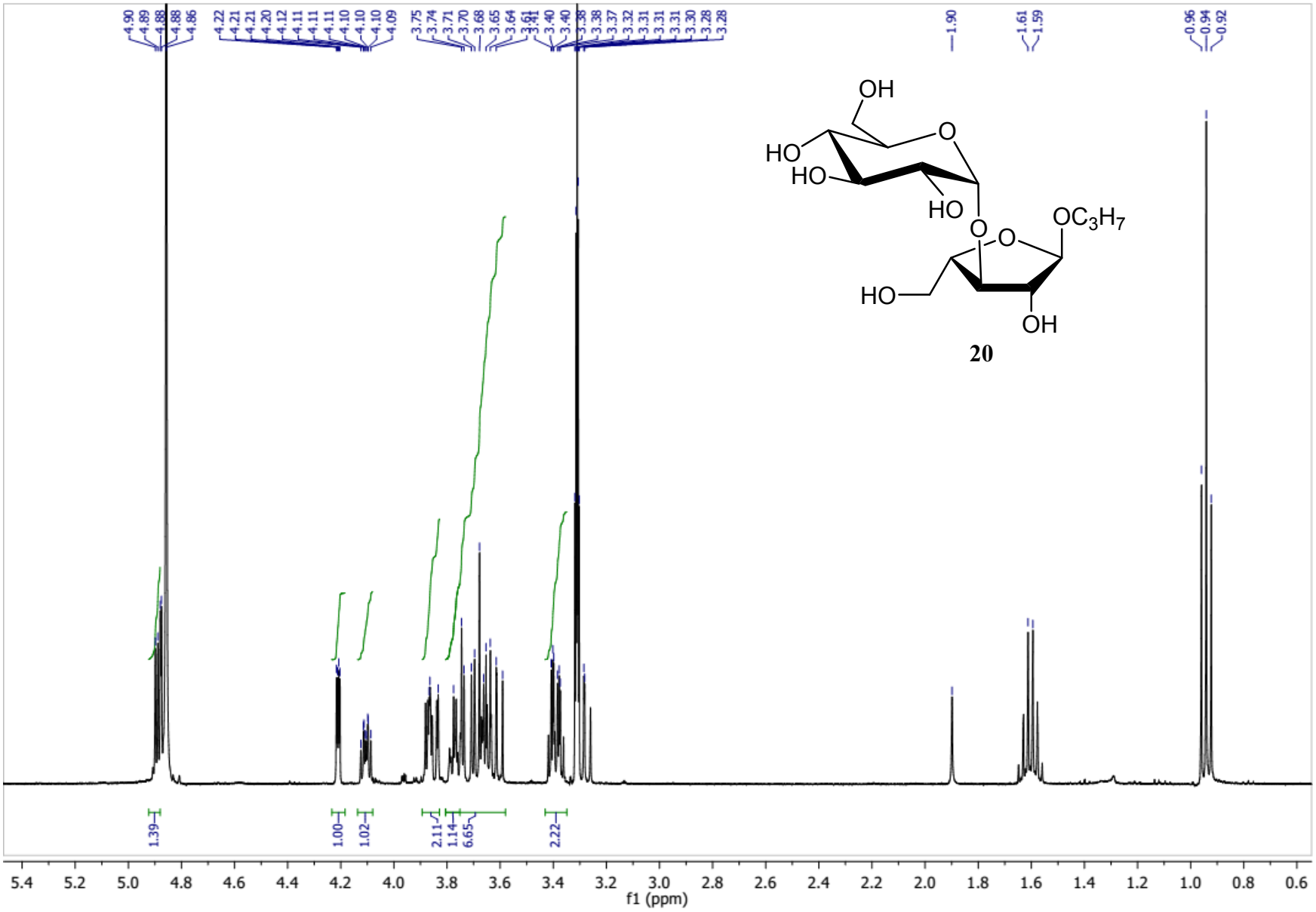
1.00
1.22
2.61
3.44
4.08
1.32
1.23
1.06
3.80
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
OH
HO
HO
HO
O
O
O
OC2H5
HO
OH

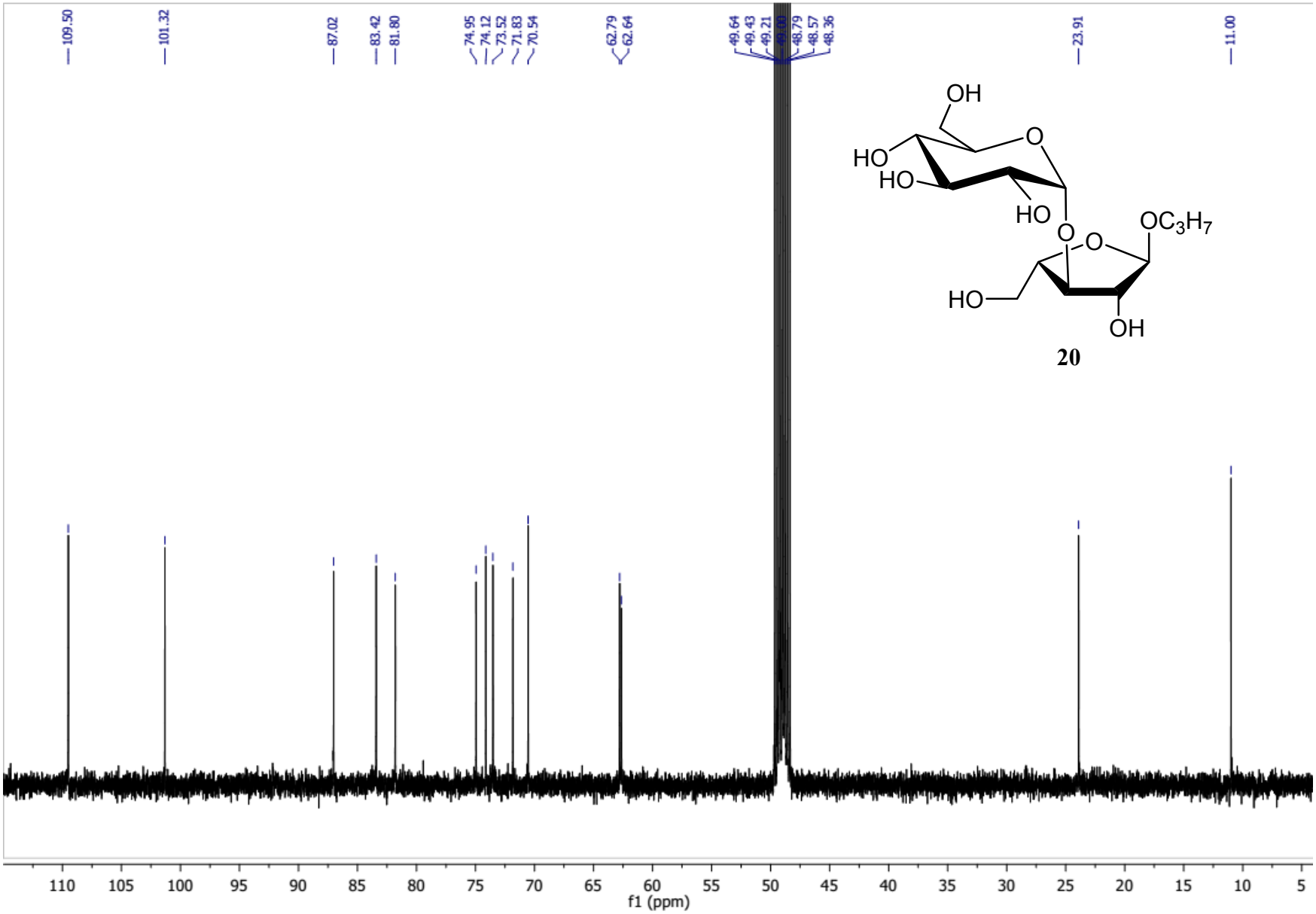
19

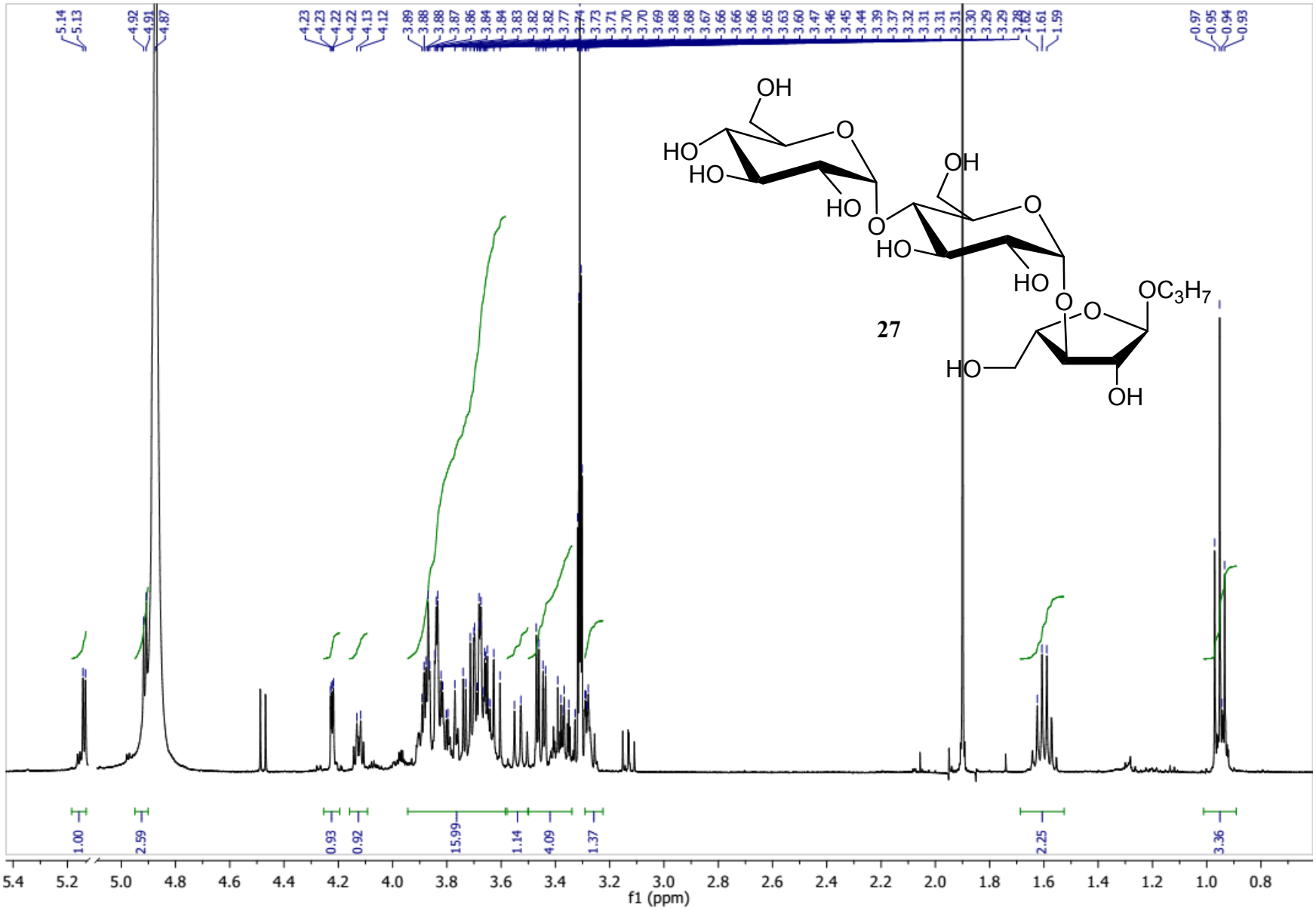

109.31
101.20
86.82
83.42
81.84
74.92
74.13
73.49
71.83
64.31
62.76
62.62
49.64
49.43
49.21
48.79
48.57
48.36
15.45
OH
HO
HO
HO
O
O
O
OC2H5
HO
OH
19
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

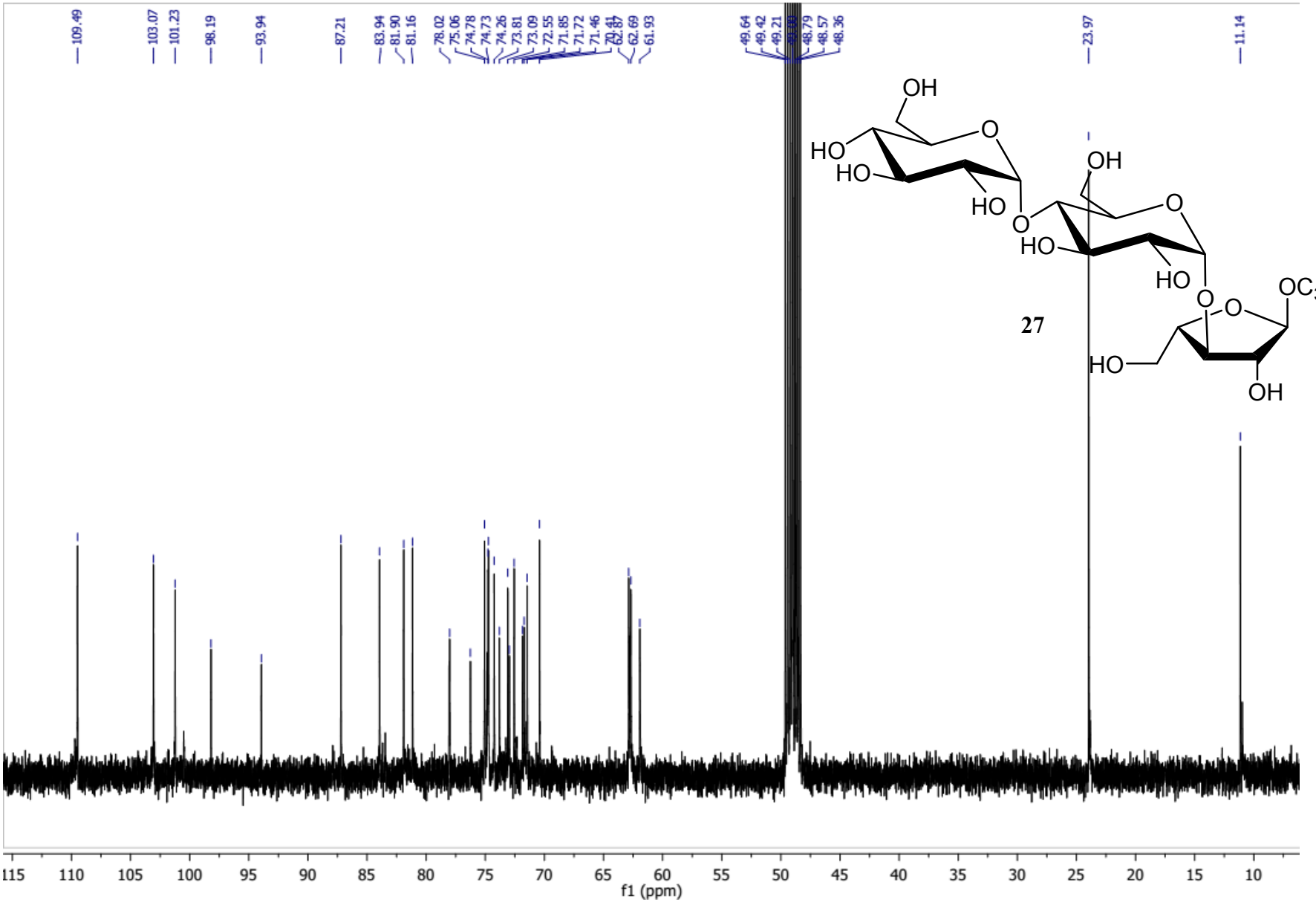

5.15
5.14
4.20
4.20
4.19
4.19
4.12
4.11
3.88
3.87
3.84
3.69
3.67
3.46
3.45
3.43
3.32
3.31
3.31
3.31
3.30
1.22
1.20
1.19
OH
HO
HO
O
HO
HO
OH
O
HO
HO
O
O
OC2H5
HO
OH
26
1.00
0.59
0.60
10.14
3.17
1.26
2.71
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f1 (ppm)

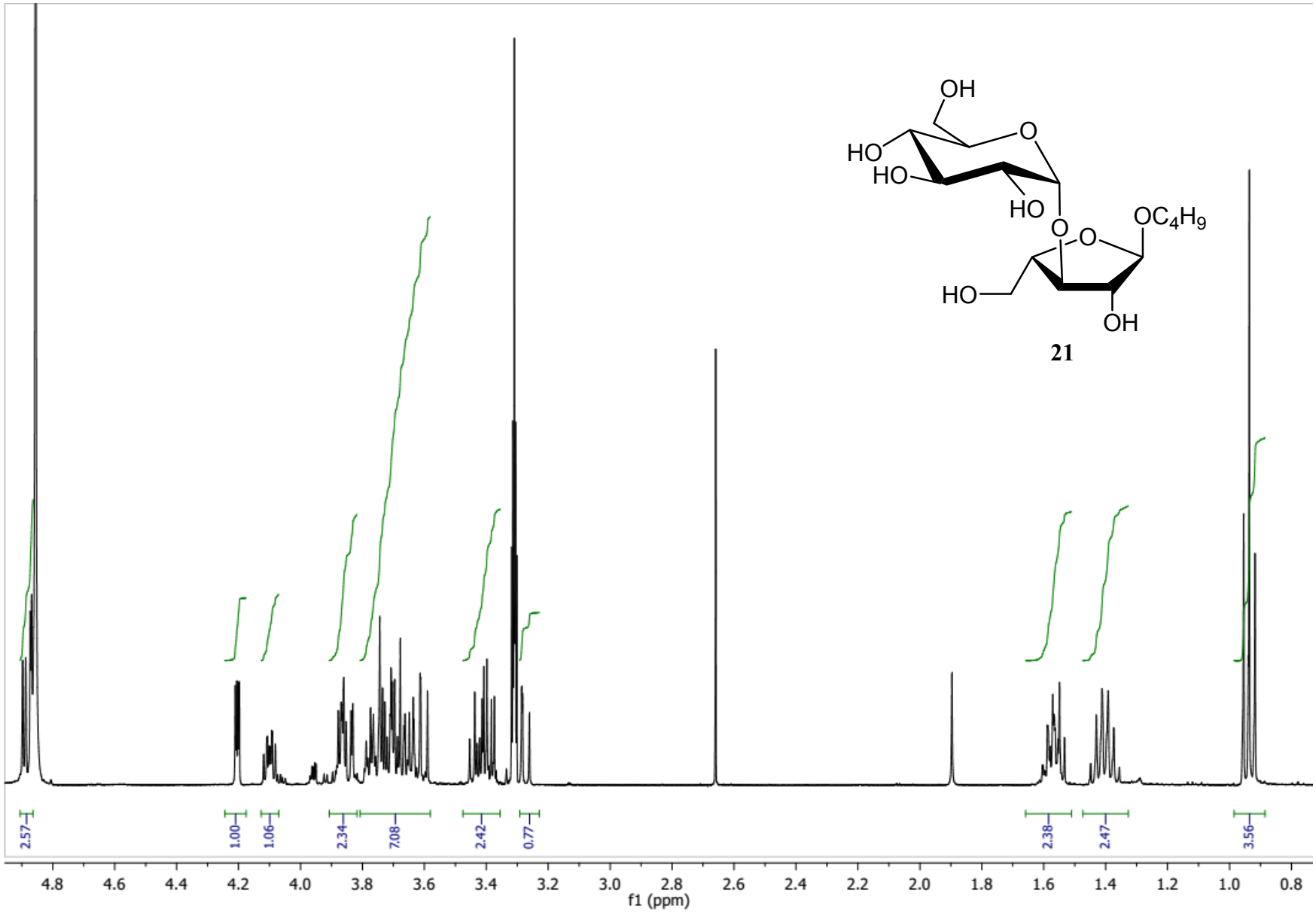

109.13
102.82
100.81
86.68
83.54
81.74
81.25
74.89
74.55
74.04
72.89
72.43
71.30
64.15
62.67
62.59
61.86
15.47
OH
HO
HO
HO
O
O
OH
HO
O
HO
O
O
OC2H5
HO
OH
26
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

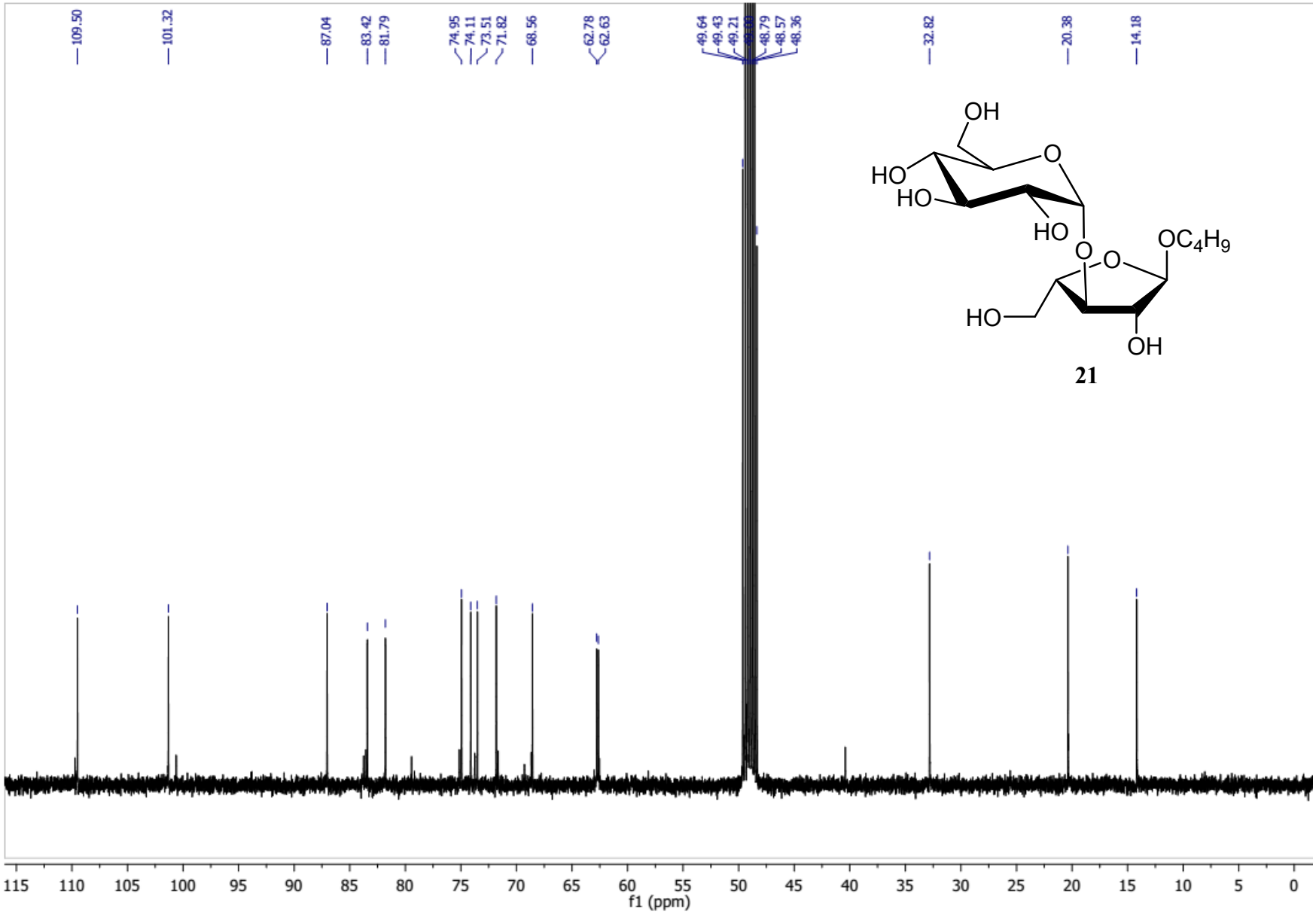

OH
HO
HO
O
HO
O
O
OC3H7
HO
OH
20
f1 (ppm)

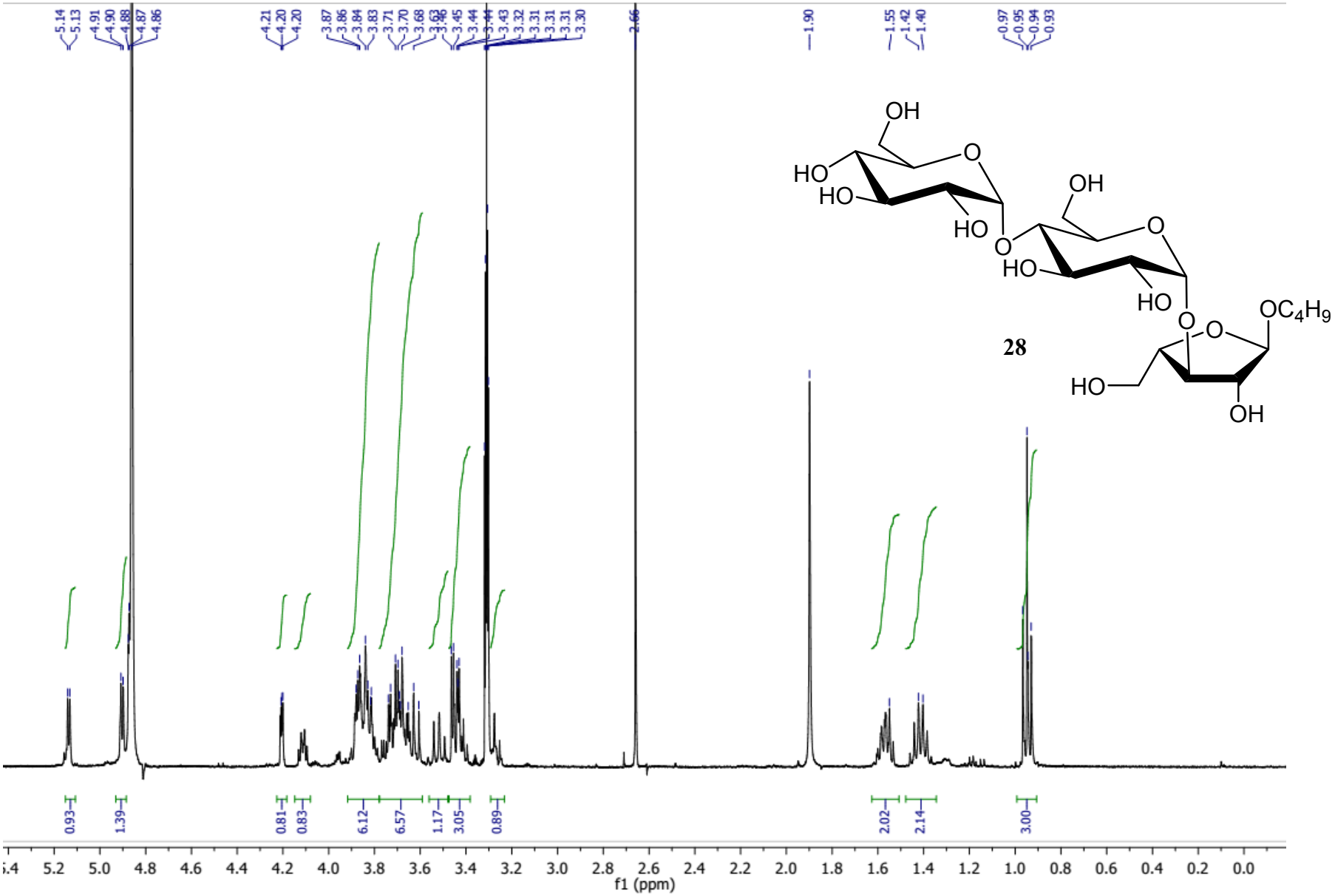

109.50
101.32
87.02
83.42
81.80
74.95
74.12
73.52
71.83
70.54
62.79
62.64
49.64
49.43
49.21
48.79
48.57
48.36
23.91
11.00
OH
HO
HO
HO
O
O
O
OC3H7
HO
OH
20
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

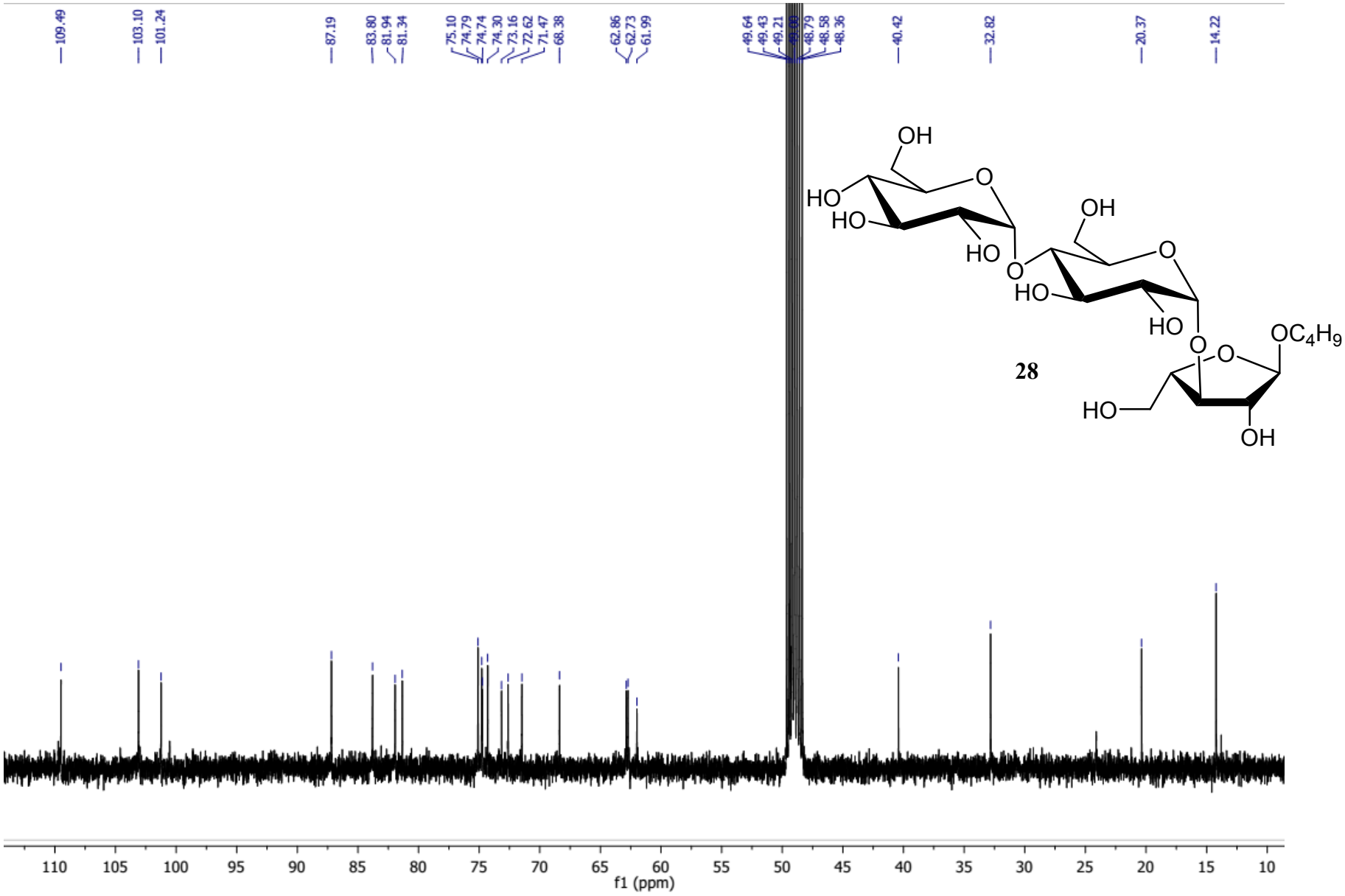

OH
HO
HO
HO
O
O
OH
HO
O
HO
O
O
OC3H7
HO
OH
27
f1 (ppm)

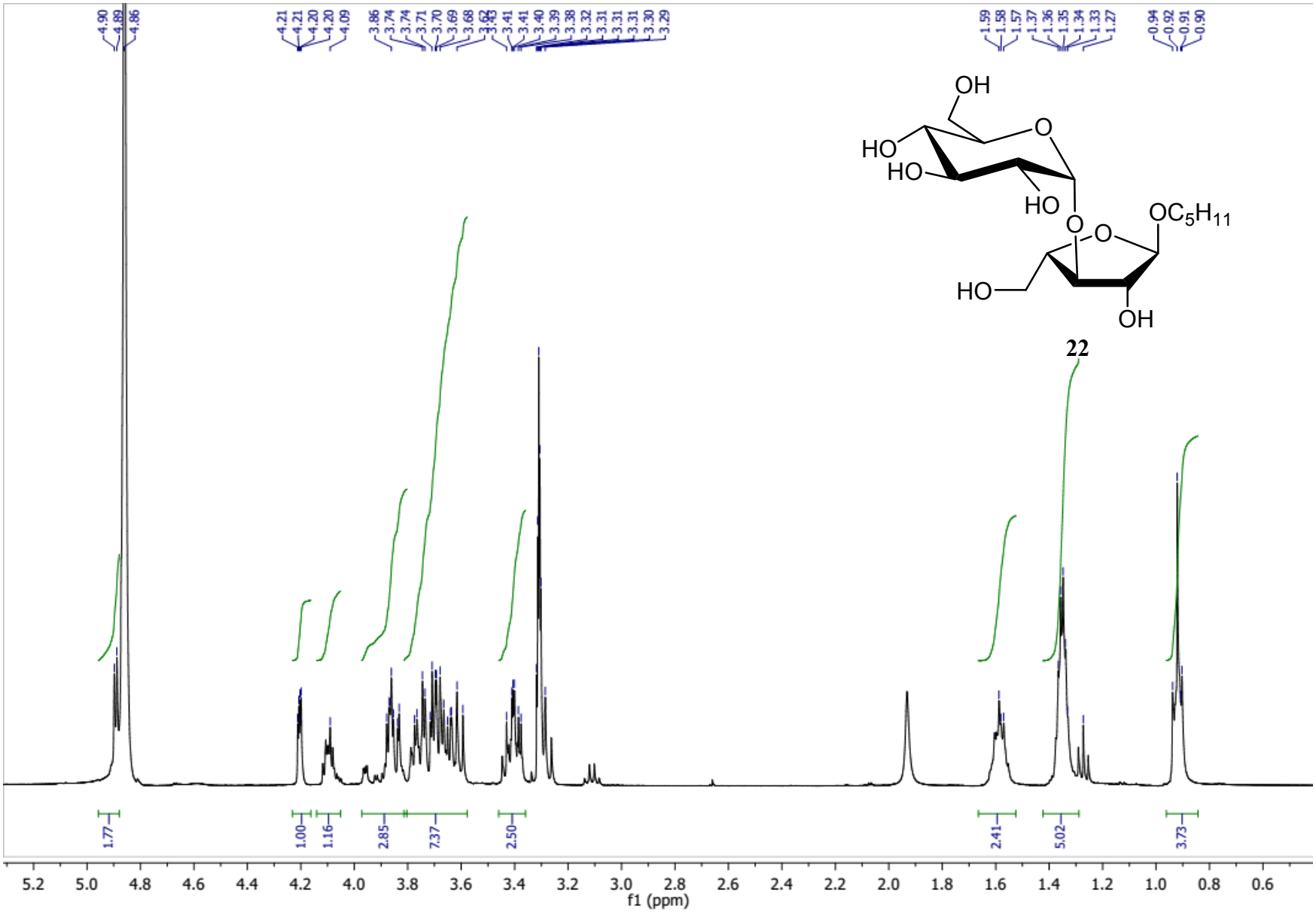

109.49
103.07
101.23
98.19
93.94
87.21
83.94
81.90
81.16
78.02
75.06
74.78
74.73
74.26
73.81
73.09
72.55
71.85
71.72
71.46
62.87
62.69
61.93
49.64
49.42
49.21
48.79
48.57
48.36
23.97
11.14
OH
HO
HO
HO
O
O
HO
OH
O
HO
HO
O
O
OC3H7
HO
OH
27
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

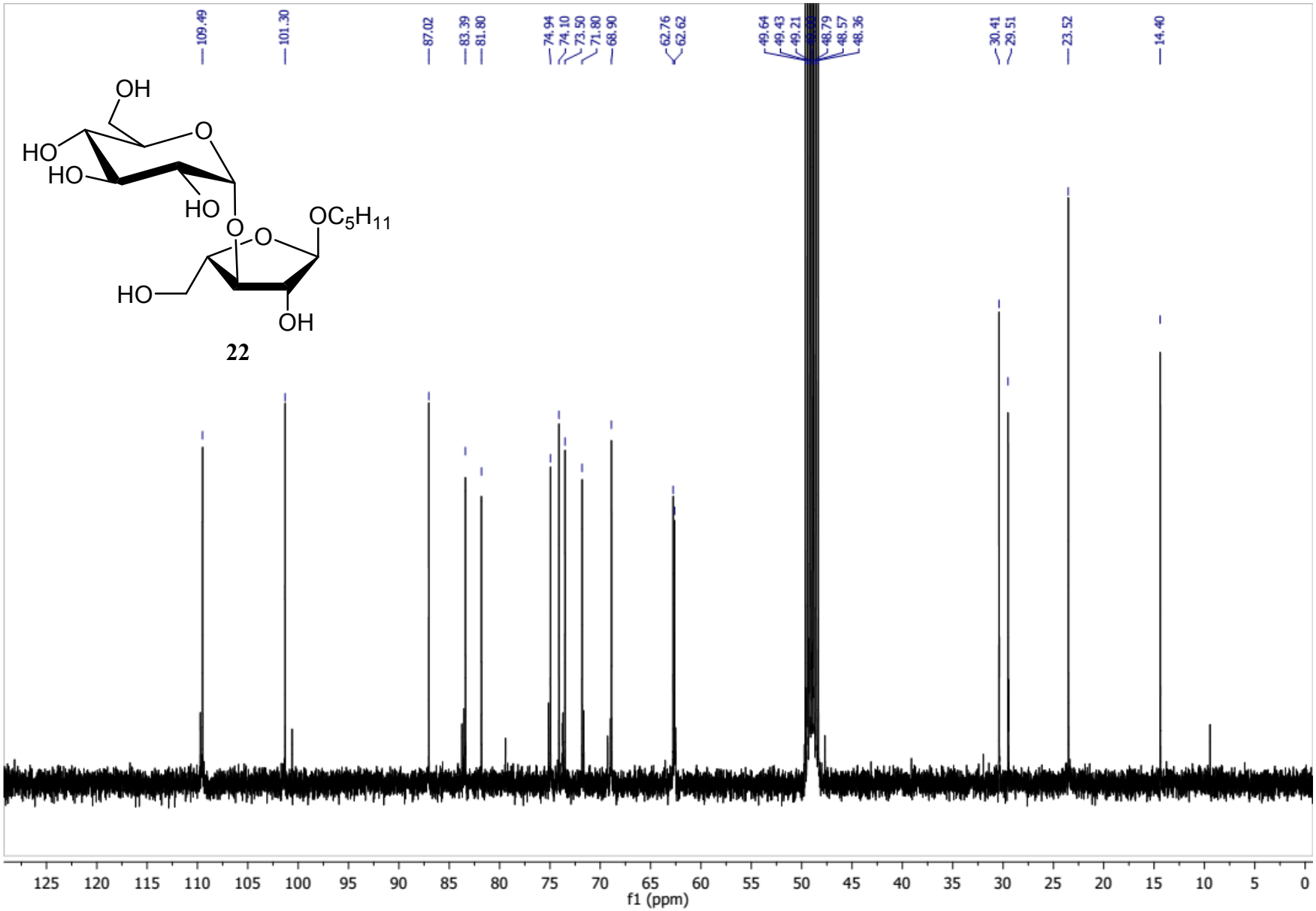

OH
HO
HO
HO
O
O
O
OC4H9
HO
OH
21
2.57
1.00
1.06
2.34
7.08
2.42
0.77
2.38
2.47
3.56
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f1 (ppm)

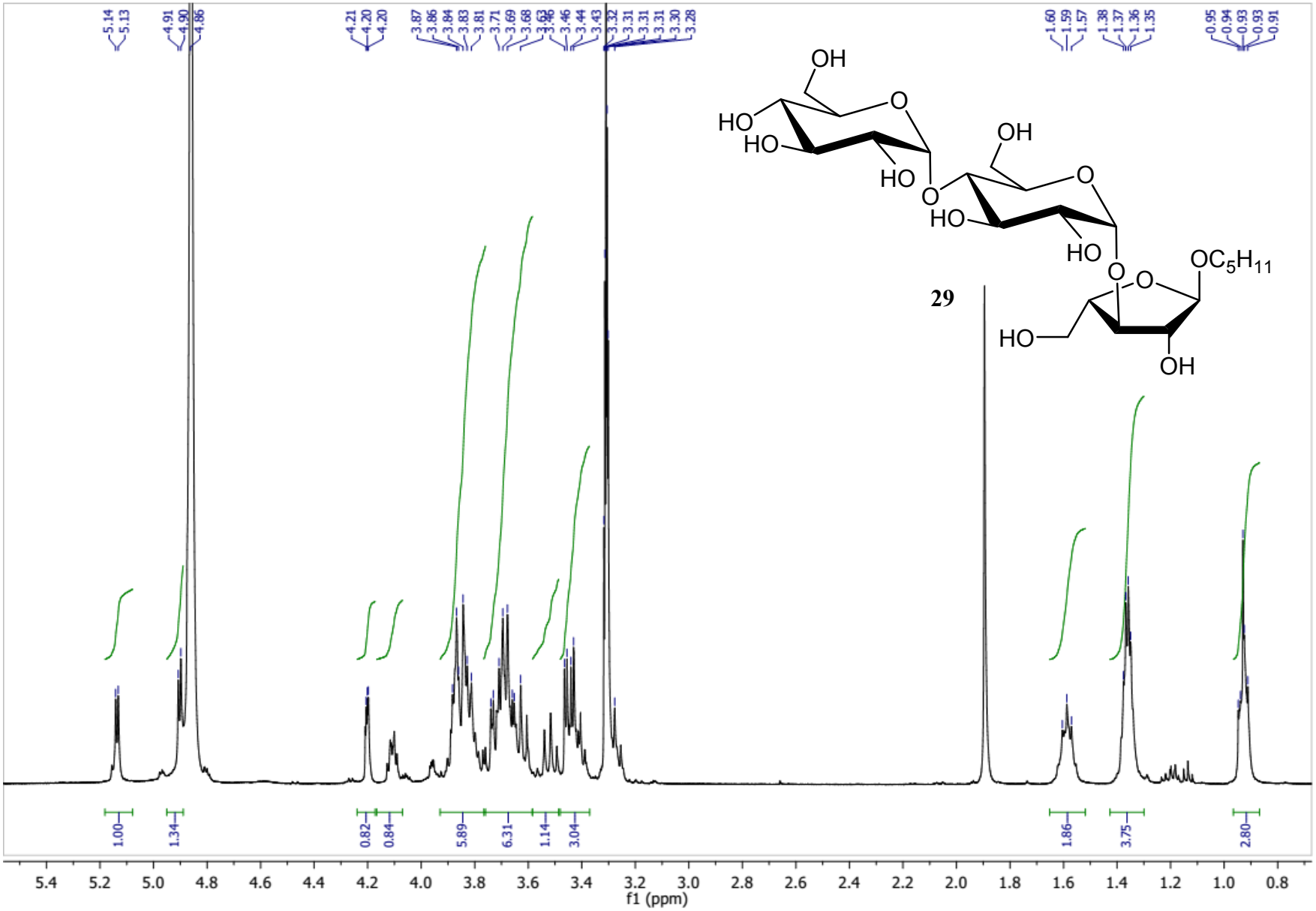

109.50
101.32
87.04
83.42
81.79
74.95
74.11
73.51
71.82
68.56
62.78
62.63
49.64
49.43
49.21
48.79
48.57
48.36
32.82
20.38
14.18
OH
HO
HO
HO
O
O
O
OC4H9
HO
OH
21
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

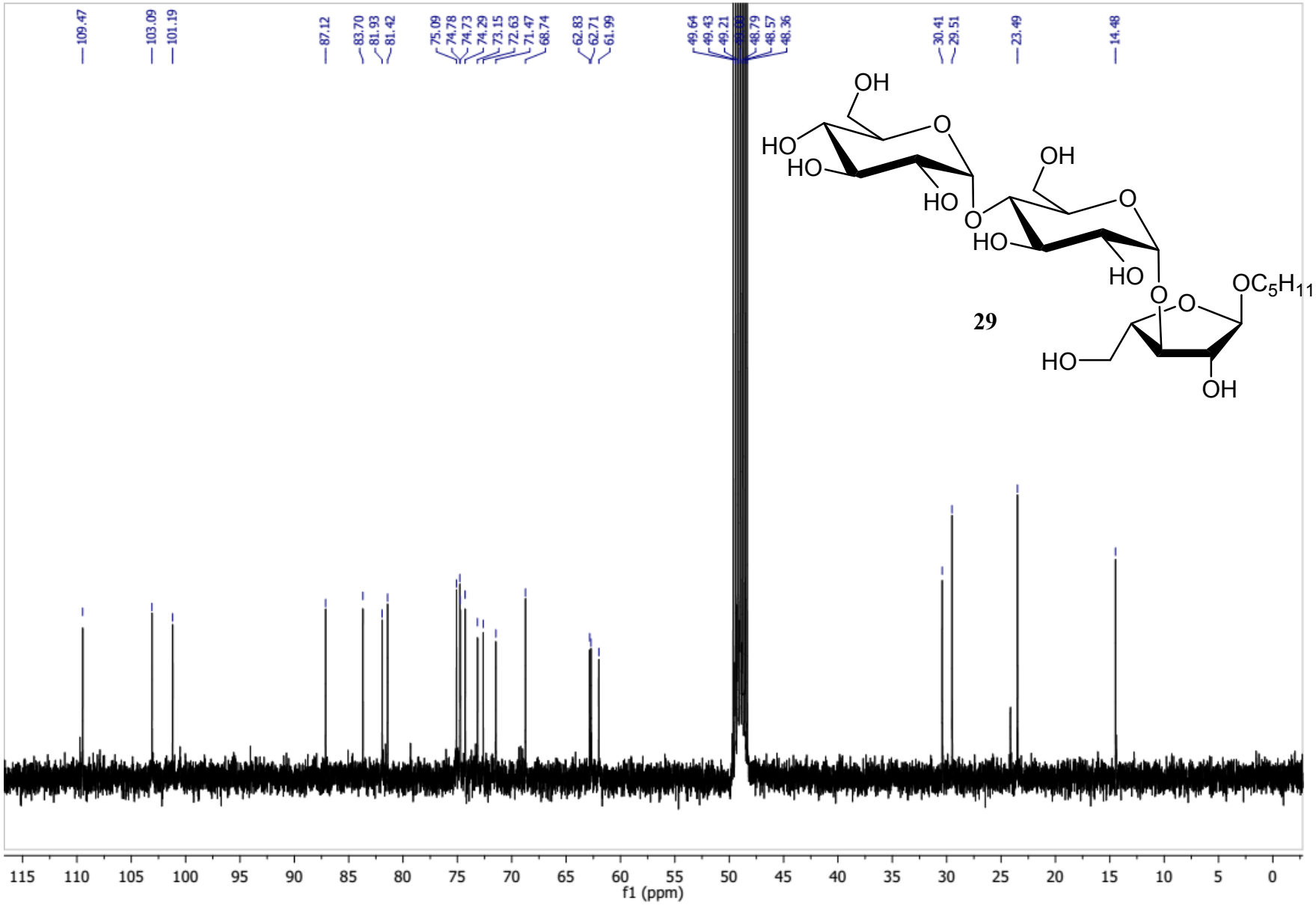

5.14
5.13
4.91
4.90
4.88
4.87
4.86
4.21
4.20
4.20
3.87
3.86
3.84
3.83
3.71
3.70
3.68
3.45
3.44
3.43
3.32
3.31
3.31
3.31
3.30
2.66
1.90
1.55
1.42
1.40
0.97
0.95
0.94
0.93
0.93
1.39
0.81
0.83
6.12
6.57
1.17
3.05
0.89
2.02
2.14
3.00
f1 (ppm)
OH
HO
HO
HO
O
O
OH
HO
HO
O
O
HO
O
O
OC4H9
HO
OH
28

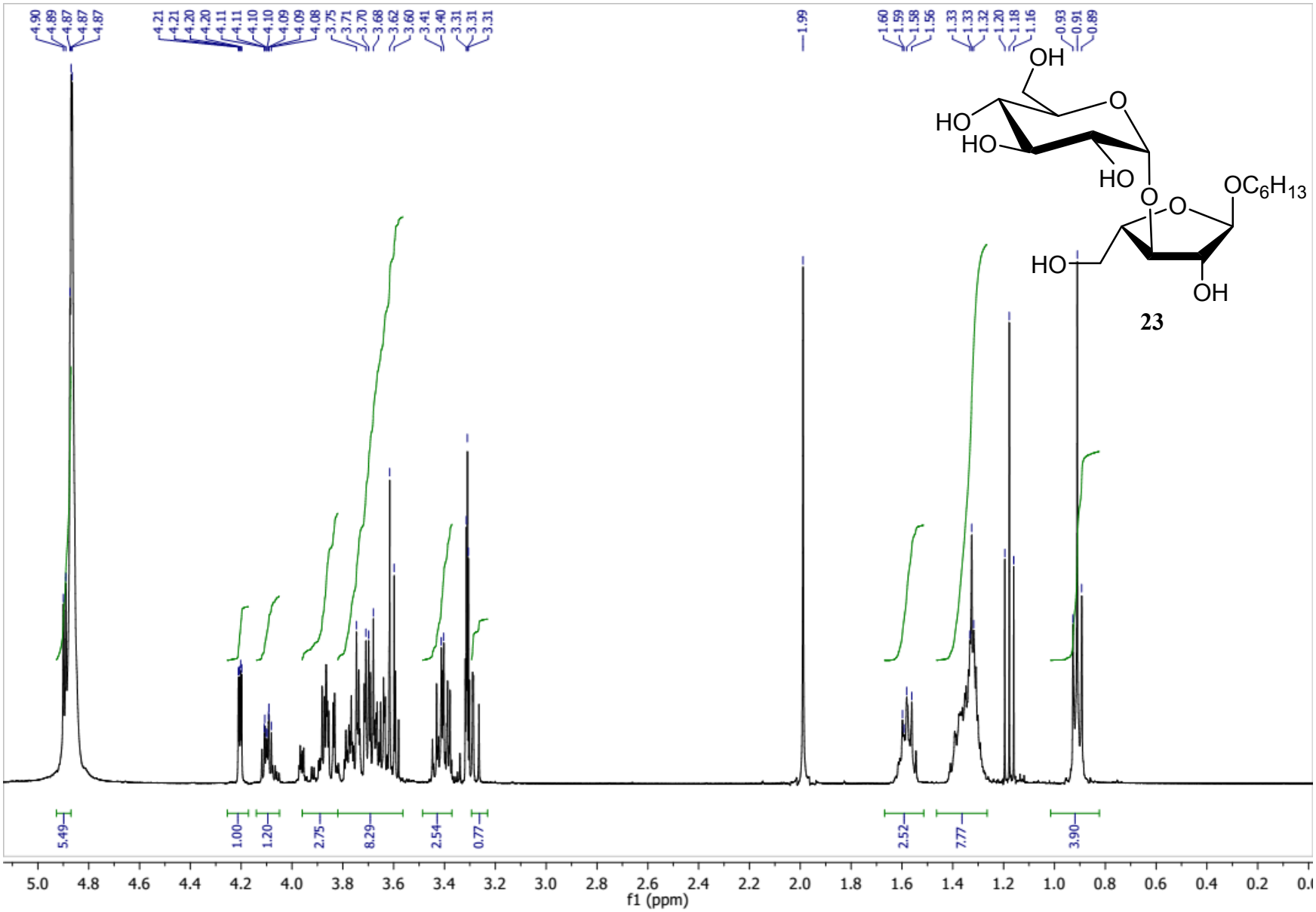

109.49
103.10
101.24
87.19
83.80
81.94
81.34
75.10
74.79
74.74
74.30
73.16
72.62
71.47
68.38
62.86
62.73
61.99
49.64
49.43
49.21
48.79
48.58
48.36
40.42
32.82
20.37
14.22
OH
HO
HO
HO
O
O
HO
OH
O
HO
HO
O
O
OC4H9
HO
OH
28
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

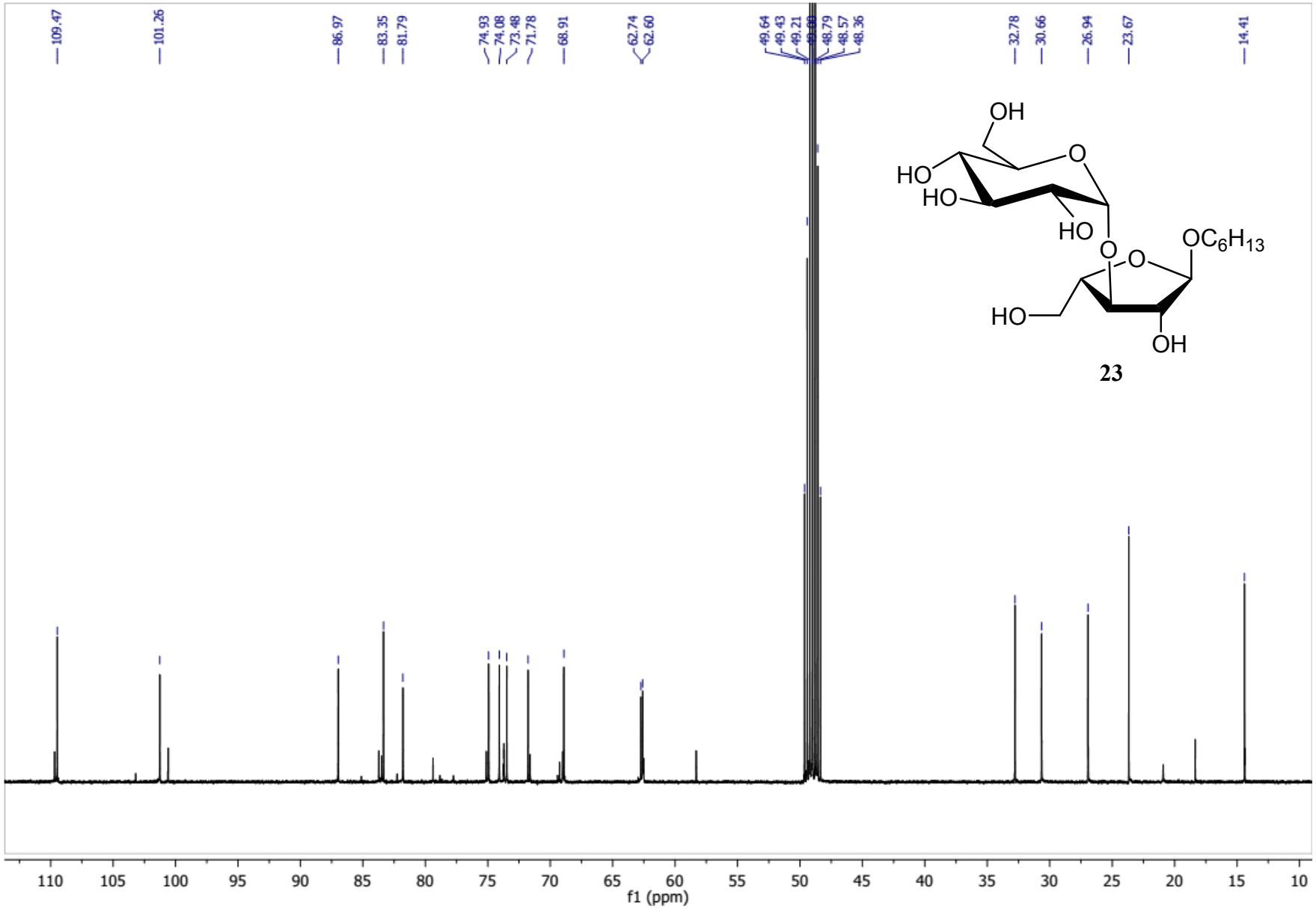

4.90
4.89
4.86
4.21
4.21
4.20
4.20
4.09
3.86
3.74
3.74
3.71
3.70
3.69
3.68
3.41
3.41
3.40
3.39
3.38
3.32
3.31
3.31
3.31
3.30
3.29
1.59
1.58
1.57
1.37
1.36
1.35
1.34
1.33
1.27
0.94
0.92
0.91
0.90
OH
HO
HO
HO
O
O
O
OC5H11
HO
OH
22
1.77
1.00
1.16
2.85
7.37
2.50
2.41
5.02
3.73
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f1 (ppm)

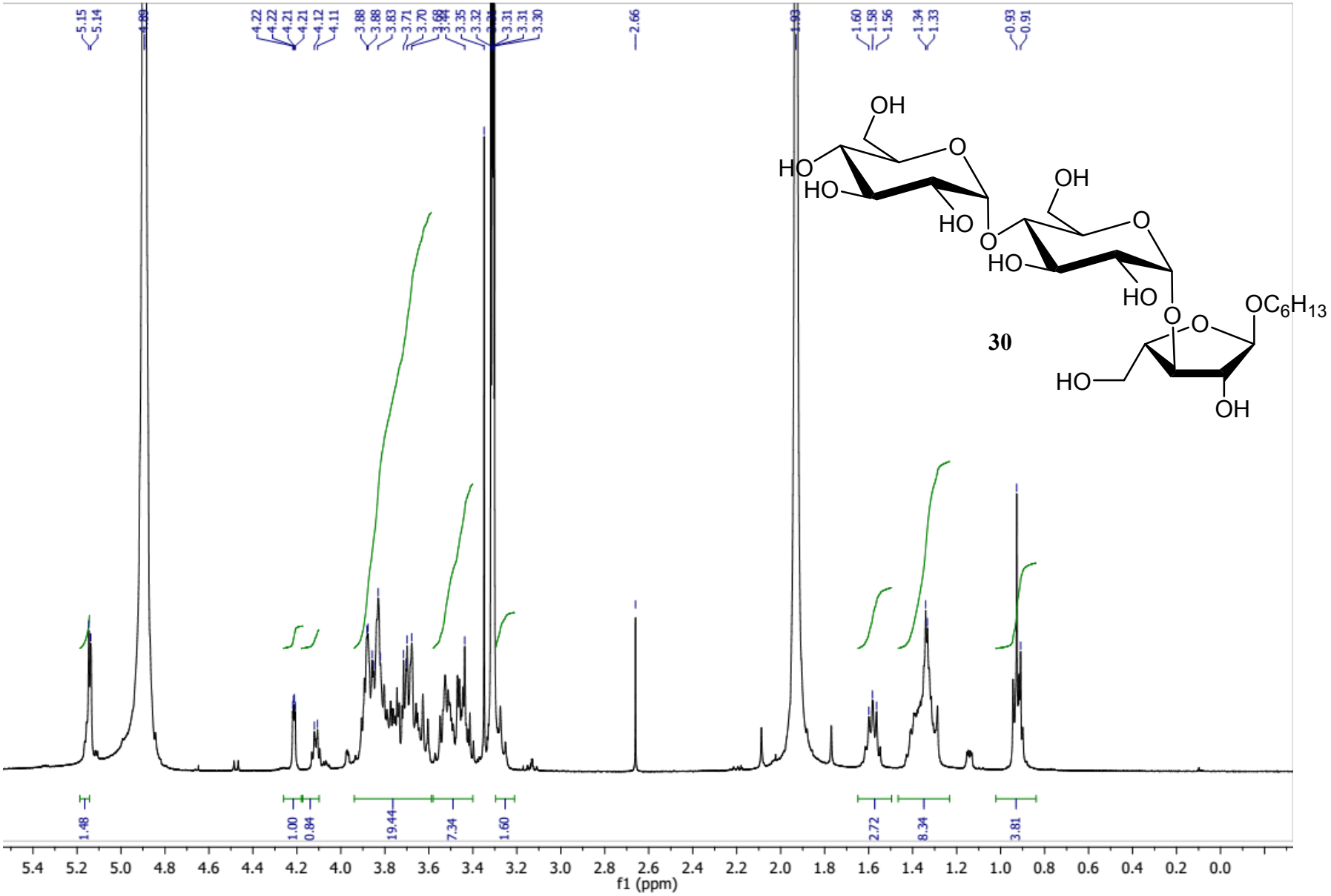

109.49
101.30
87.02
83.39
81.80
74.94
74.10
73.50
71.80
68.90
62.76
62.62
49.64
49.43
49.21
48.79
48.57
48.36
30.41
29.51
23.52
14.40
OH
HO
HO
HO
O
O
O
OC5H11
HO
OH
22
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

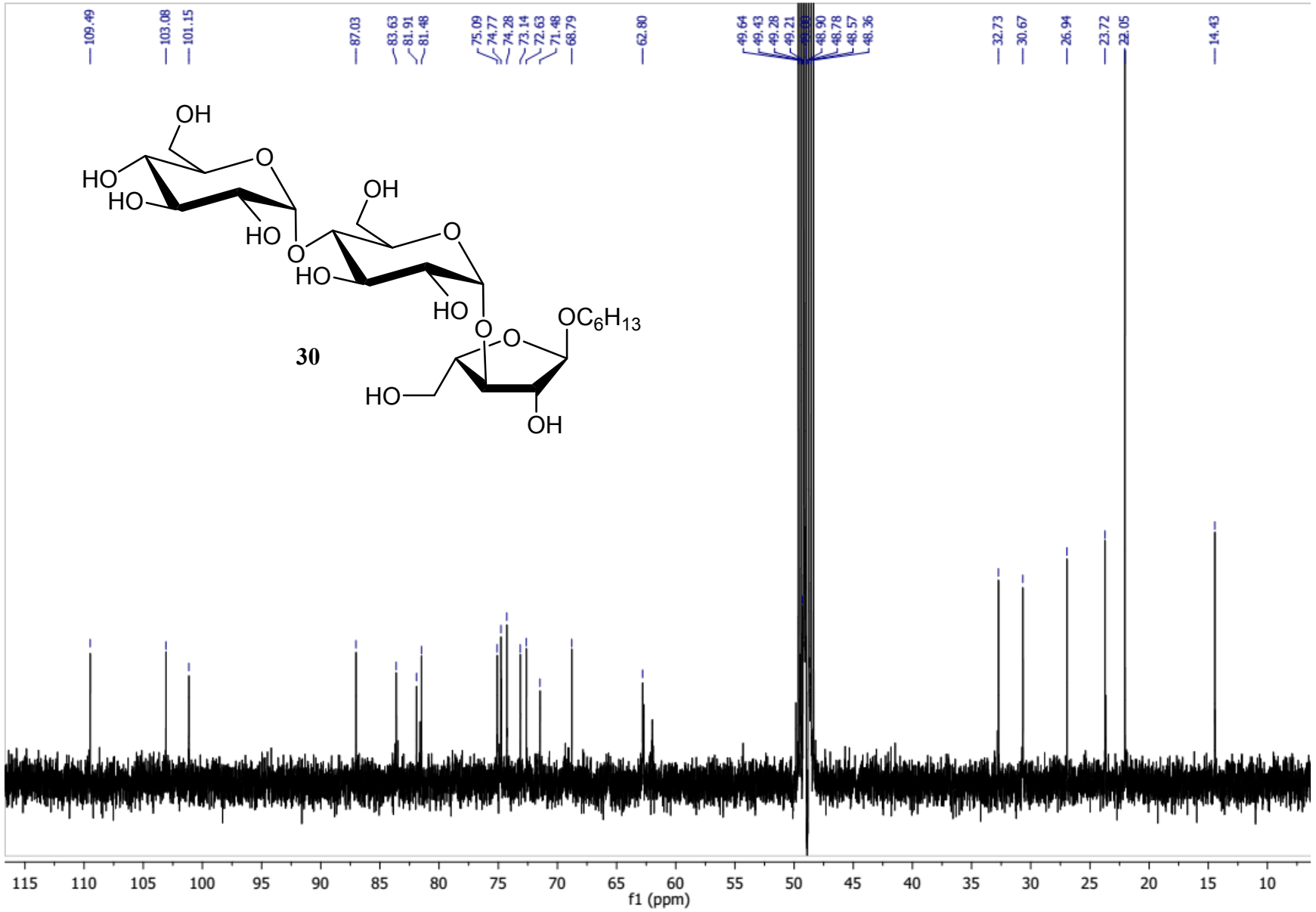

5.14
5.13
4.91
4.90
4.86
4.21
4.20
4.20
3.87
3.86
3.84
3.83
3.81
3.71
3.69
3.68
3.46
3.44
3.43
3.32
3.31
3.31
3.31
3.30
3.28
1.60
1.59
1.57
1.38
1.37
1.36
1.35
0.95
0.94
0.93
0.93
0.91
OH
HO
HO
O
HO
O
OH
O
HO
HO
O
O
OC5H11
HO
OH
29
1.00
1.34
0.82
0.84
5.89
6.31
1.14
3.04
1.86
3.75
2.80
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f1 (ppm)

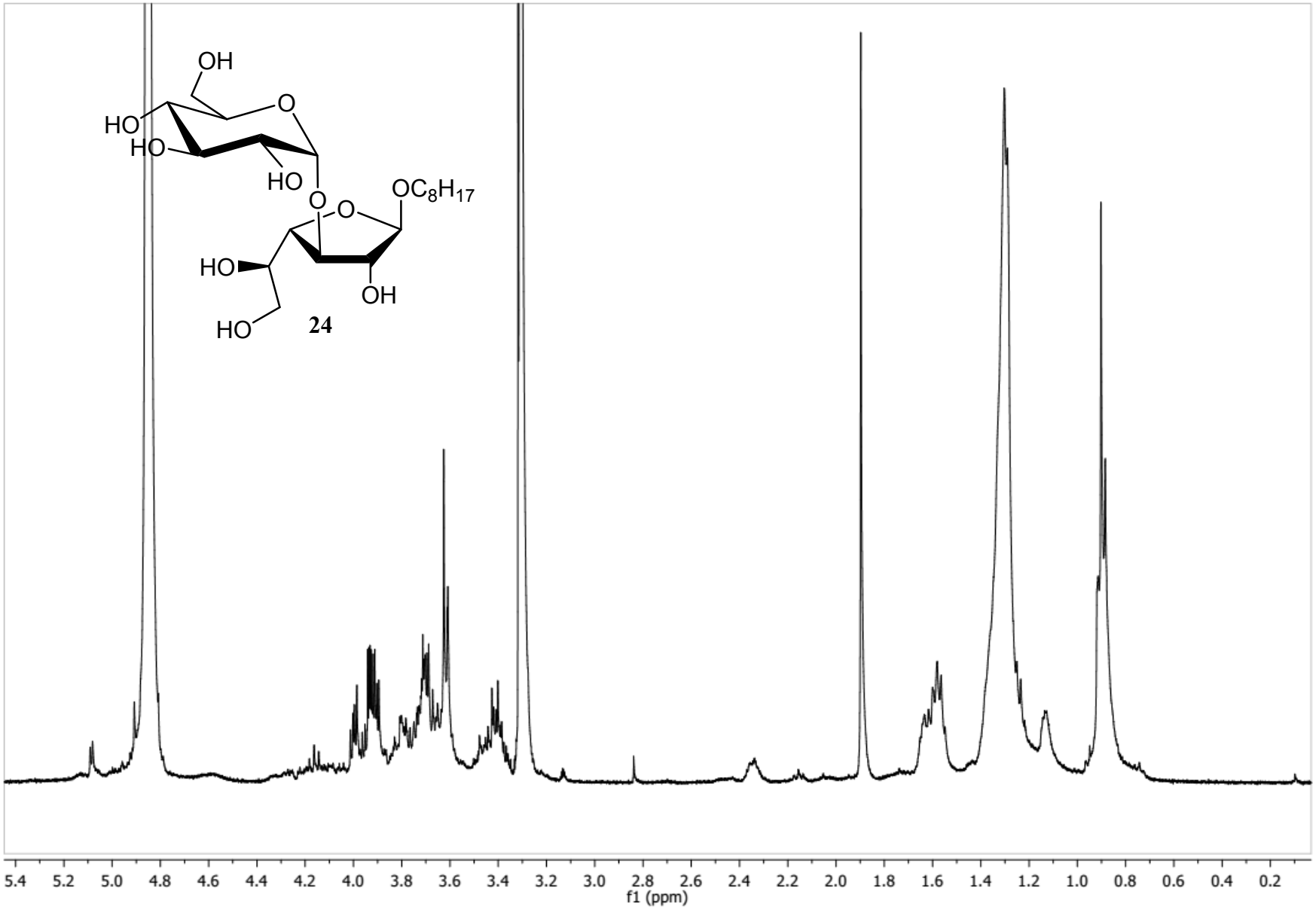

109.47
103.09
101.19
87.12
83.70
81.93
81.42
75.09
74.78
74.73
74.29
73.15
72.63
71.47
68.74
62.83
62.71
61.99
49.64
49.43
49.21
48.79
48.57
48.36
30.41
29.51
23.49
14.48
OH
HO
HO
O
HO
OH
O
HO
O
HO
HO
O
O
OC5H11
HO
OH
29
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

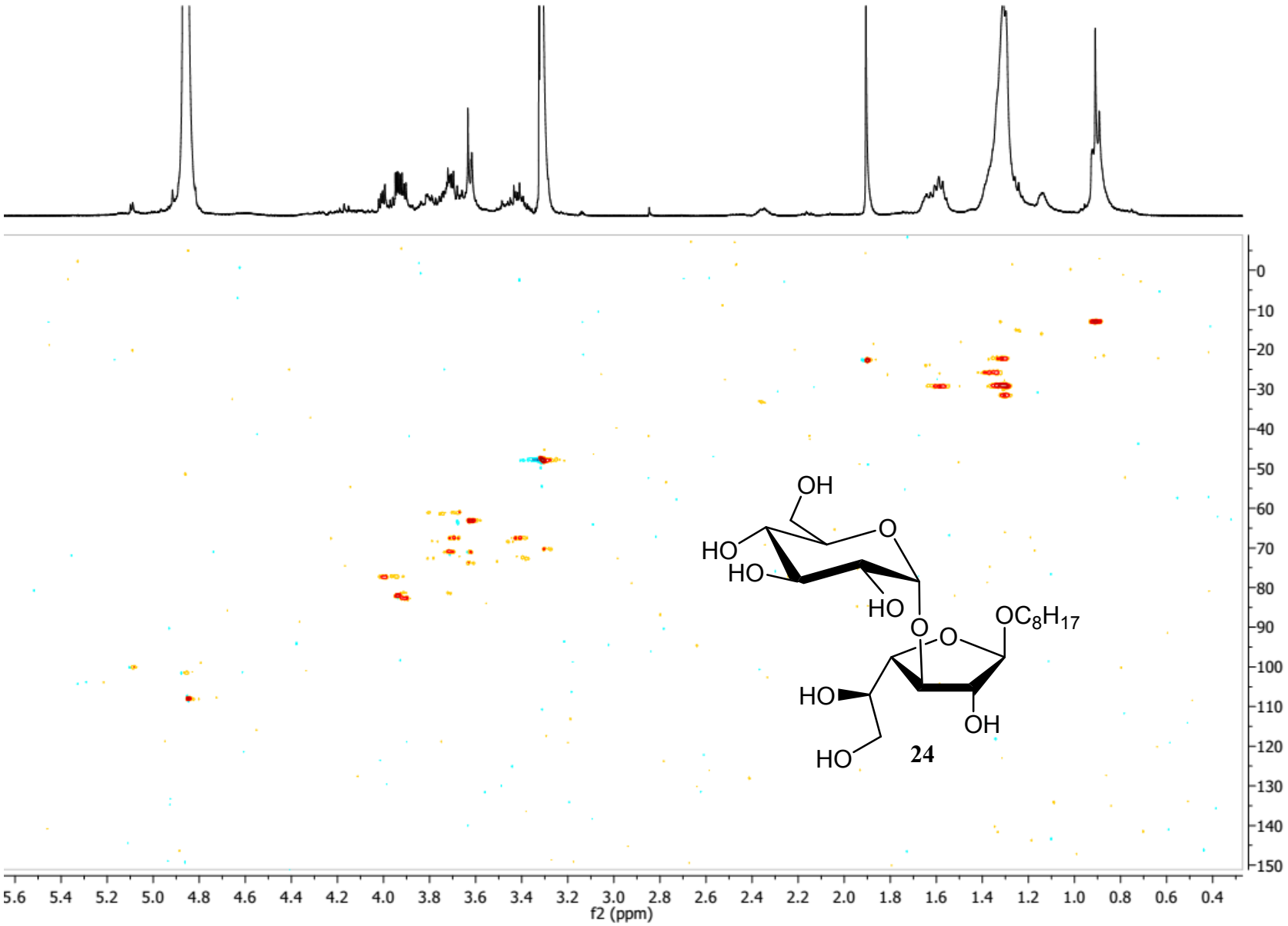

4.90
4.89
4.87
4.87
4.87
4.21
4.21
4.20
4.20
4.11
4.11
4.10
4.10
4.09
4.09
4.08
3.75
3.71
3.70
3.68
3.62
3.60
3.41
3.40
3.31
3.31
3.31
1.99
1.60
1.59
1.58
1.56
1.33
1.33
1.32
1.20
1.18
1.16
0.93
0.91
0.89
OH
HO
HO
HO
O
O
O
OC6H13
HO
OH
23
5.49
1.00
1.20
2.75
8.29
2.54
0.77
2.52
7.77
3.90
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
f1 (ppm)

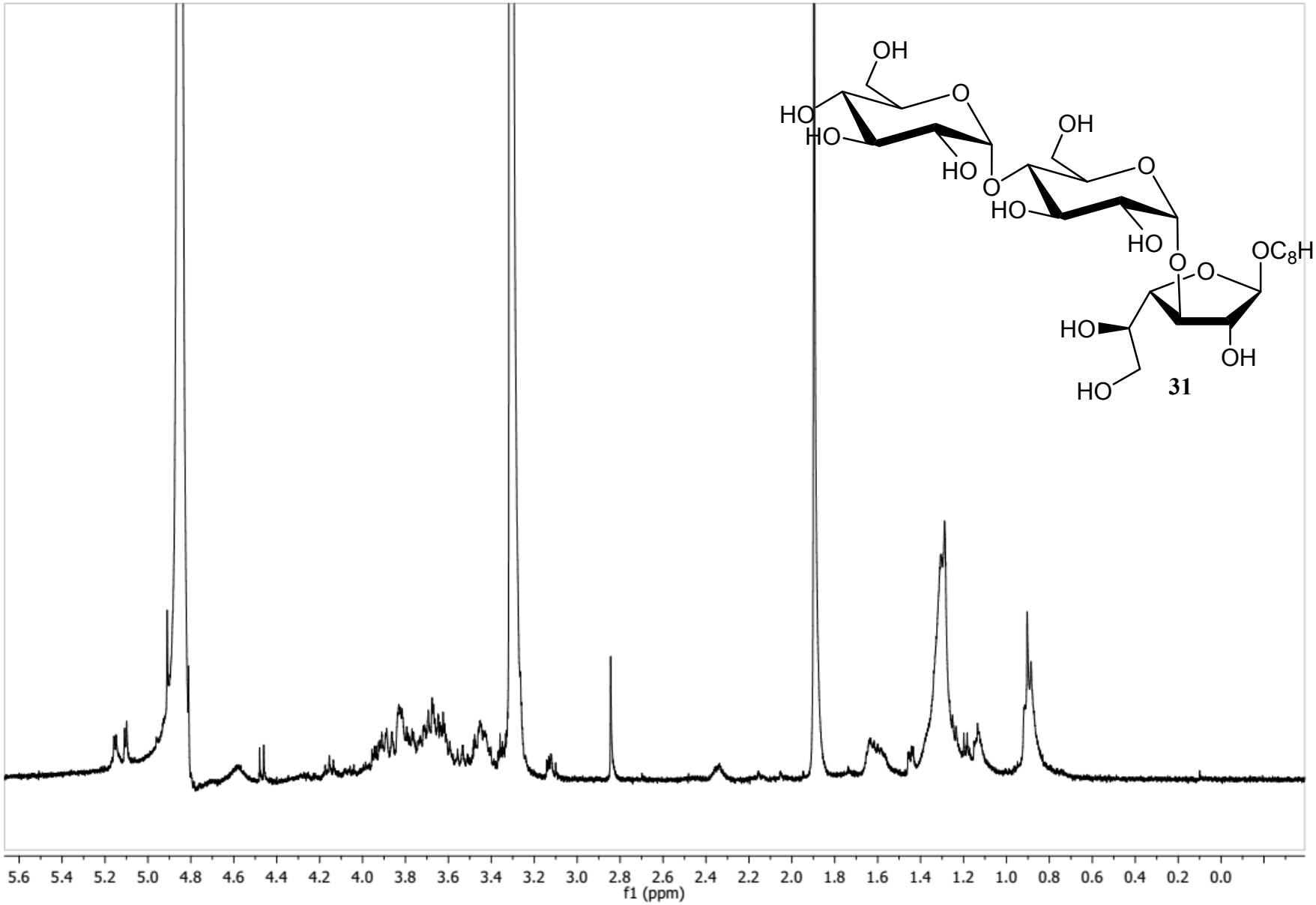

109.47
101.26
86.97
83.35
81.79
74.93
74.08
73.48
71.78
68.91
62.74
62.60
49.64
49.43
49.21
48.79
48.57
48.36
32.78
30.66
26.94
23.67
14.41
OH
HO
HO
HO
O
O
O
OC6H13
HO
OH
23
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


5.15
5.14
4.89
4.22
4.22
4.21
4.21
4.12
4.11
3.88
3.88
3.83
3.71
3.70
3.35
3.32
3.31
3.31
3.30
2.66
1.93
1.60
1.58
1.56
1.34
1.33
0.93
0.91
OH
HO
HO
HO
O
O
HO
OH
O
HO
O
O
OC6H13
HO
OH
30
1.48
1.00
0.84
19.44
7.34
1.60
2.72
8.34
3.81
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f1 (ppm)


109.49
103.08
101.15
87.03
83.63
81.91
81.48
75.09
74.77
74.28
73.14
72.63
71.48
68.79
62.80
49.64
49.43
49.28
49.21
48.90
48.78
48.57
48.36
32.73
30.67
26.94
23.72
22.05
14.43
OH
HO
HO
O
HO
O
OH
HO
O
HO
O
O
OC6H13
HO
OH
30
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


OH
HO
HO
HO
O
O
O
OC8H17
HO
HO
OH
24
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f1 (ppm)


OH
HO
HO
HO
O
O
O
OC8H17
HO
HO
OH
24
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150


OH
HO
HO
HO
O
O
OH
O
HO
HO
O
O
OC8H17
HO
HO
OH
31
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f1 (ppm)