

Supporting Information for:

Synthesis of Galactofuranose Containing Acceptor Substrates for Mycobacterial Galactofuranosyltransferases

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General Methods. Reactions were carried out in oven-dried glassware. All reagents were purchased from commercial sources and were used without further purification unless noted. Reaction solvents were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out at room temperature under a positive pressure of argon and were monitored by TLC on Silica Gel 60 F₂₅₄ (0.25 mm). TLC spots were detected under UV light or by charring with acidified *p*-anisaldehyde solution in EtOH. All organic solutions were dried with anhydrous MgSO₄. Unless otherwise indicated, all column chromatography was performed on Silica Gel (40–60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C. ¹H NMR spectra were recorded at 600 MHz, 500 MHz or 400 MHz, and chemical shifts were referenced to either TMS (0.0 ppm, CDCl₃), CD₃OD (3.30 ppm, CD₃OD) or HOD (4.78 ppm, D₂O). ¹H data were reported as though they were first order. ¹³C NMR (APT) spectra¹ were recorded at 125 MHz or 100 MHz, and ¹³C chemical shifts were referenced to internal CDCl₃ (77.23 ppm, CDCl₃), or CD₃OD (48.9 ppm, CD₃OD) or external acetone (31.07, D₂O). Assignments of resonances in NMR spectra were made using ¹H–¹H COSY and HMQC experiments. Organic solutions were concentrated under vacuum at < 40 °C. Electrospray mass spectra were recorded on samples suspended in mixtures of THF with MeOH and added NaCl.

Octyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (13) and **Octyl 2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (14)**. Compound **22**² (1.36 g, 1.61 mmol) was

dissolved in CH₂Cl₂ (75 mL), cooled to 0 °C, and trifluoroacetic acid (5% in CH₂Cl₂, 4.95 mL) was added dropwise. After stirring for 8 h, the reaction mixture was co-evaporated with toluene and concentrated to give a syrupy residue that was purified by column chromatography (8:1 hexanes–EtOAc) to give **13** (409 mg, 42%) and **14** (338 mg, 35%) as colorless syrups. The data for these compounds matched that previously reported.²

***p*-Tolyl 5-*O*-acetyl-2,3,6-tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (15).** To a solution of **28** (0.23 g, 0.38 mmol) in pyridine (10 mL), was added acetic anhydride (50 μL, 0.37 mmol). The reaction mixture was stirred for 2 h, poured into an ice–water mixture, and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried and concentrated. Co-evaporation with toluene removed all traces of pyridine and the residue was purified by column chromatography (4:1 hexanes–EtOAc) to give **15** as an amorphous white solid (0.22 g, 90%). *R*_f 0.36 (3:1 hexanes–EtOAc); [α]_D –61.2 (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.10–8.06 (m, 4 H, Ar), 8.00–7.98 (m, 2 H, Ar), 7.62–7.44 (m, 7 H, Ar), 7.36–7.32 (m, 4 H, Ar), 7.14 (d, 2 H, *J* = 9.0 Hz, Ar), 5.78 (app dt, 1 H, *J* = 6.9, 4.4 Hz, H-5), 5.77 (br s, 1 H, H-1), 5.64 (dd, 1 H, *J* = 1.6, 1.1 Hz, H-2), 5.63 (dd, 1 H, *J* = 4.7, 1.6 Hz, H-3), 4.86 (dd, 1 H, *J* = 4.7, 4.4 Hz, H-4), 4.68 (dd, 1 H, *J* = 11.8, 5.7 Hz, H-6_a), 4.56 (dd, 1 H, *J* = 11.8, 5.7 Hz, H-6_b), 2.34 (s, 3 H, ArCH₃), 2.01 (s, 3 H, C(=O)CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 170.0 (C=O), 166.0 (C=O), 165.4 (C=O), 165.3 (C=O), 138.3 (Ar), 133.6 (Ar), 133.1 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.3 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 91.4 (C-1), 82.0 (C-2), 81.0 (C-4), 77.4 (C-3), 69.7 (C-5),

63.2 (C-6), 21.1 (ArCH₃), 20.8 (C(=O)CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₃₆H₃₂O₉SNa: 663.1654. Found: 663.1659.

***p*-Tolyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (16).** Prepared from **27** (0.17 g, 0.29 mmol) in pyridine (10 mL), and acetic anhydride (35.0 μL, 0.37 mmol) as described for the synthesis of **15**, and the residue was purified by column chromatography (4:1 hexanes–EtOAc) to afford compound **16** as an amorphous white solid (0.17 g, 90%). *R_f* 0.38 (3:1 hexanes–EtOAc); [α]_D –30.3 (*c* 0.4, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.10–8.05 (m, 4 H, Ar), 7.90 (d, 2 H, *J* = 7.0 Hz, Ar), 7.62–7.45 (m, 7 H, Ar), 7.36–7.31 (m, 4 H, Ar), 7.14 (d, 2 H, *J* = 9.0 Hz, Ar), 5.92 (app dt, 1 H, *J* = 6.0, 5.0 Hz, H-5), 5.75 (d, 1 H, *J* = 0.9 Hz, H-1), 5.64–5.63 (m, 2 H, H-2, H-3), 4.86 (dd, 1 H, *J* = 5.0, 3.8 Hz, H-4), 4.53 (dd, 1 H, *J* = 11.8, 6.0 Hz, H-6_a), 4.45 (dd, 1 H, *J* = 11.8, 6.0 Hz, H-6_b), 2.34 (s, 3 H, ArCH₃), 2.01 (s, 3 H, C(=O)CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 170.5 (C=O), 165.7 (C=O), 165.5 (C=O), 165.3 (C=O), 133.6 (Ar), 133.4 (Ar), 133.3 (Ar), 133.1 (Ar), 130.0 (Ar), 129.0 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 91.5 (C-1), 82.3 (C-2), 81.3 (C-4), 77.8 (C-3), 70.2 (C-5), 62.7 (C-6), 21.2 (ArCH₃), 20.7 (C(=O)CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₃₆H₃₂O₉SNa: 663.1660. Found: 663.1659.

***p*-Tolyl 2,3,5,6-tetra-*O*-benzoyl-1-thio-β-D-galactofuranoside (17).** Methyl glycoside **24** (13.26 g, 21.70 mmol) was dissolved in CH₂Cl₂ (150 mL) at 0 °C and *p*-thiocresol (3.52 g, 28.3 mmol) was added. The reaction mixture was stirred for 15 min and BF₃·OEt₂ (17.9 mL, 141.03 mmol) was then slowly added. The solution was then allowed to stir for 8 h while

warming to rt before being neutralized with Et₃N and diluted with CH₂Cl₂. The organic layer was then washed successively a saturated aqueous solution of NaHCO₃, water and brine. The organic solution was dried and the solvent evaporated; the crude product was purified by chromatography (4:1 hexanes–EtOAc) to give **17** (13.57 g, 89%) as an amorphous white solid. *R_f* 0.38 (4:1 hexanes–EtOAc); [α]_D –82.0 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.07 (ddd, 4 H, *J* = 9.8, 8.5, 1.2 Hz, Ar), 7.96 (dd, 2 H, *J* = 8.0, 1.5 Hz, Ar), 7.89 (dd, 2 H, *J* = 8.0, 1.5 Hz, Ar), 7.60–7.45 (m, 8 H, Ar), 7.39–7.26 (m, 6 H, Ar), 7.07 (d, 2 H, *J* = 8.0 Hz, Ar), 6.10 (app dt, 1 H, *J* = 6.6, 5.0 Hz, H-5), 5.77 (d, 1 H, *J* = 1.8 Hz, H-1), 5.71 (dd, 1 H, *J* = 5.0, 1.8 Hz, H-3), 5.66 (app t, 1 H, *J* = 1.8 Hz, H-2), 4.95 (app t, 1 H, *J* = 5.0 Hz, H-4), 4.75 (dd, 1 H, *J* = 11.8, 7.0 Hz, H-6_a), 4.71 (dd, 1 H, *J* = 11.8, 7.0 Hz, H-6_b), 2.32 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.0 (C=O), 165.7 (C=O), 165.5 (C=O), 165.3 (C=O), 133.5 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 130.1 (Ar), 130.03 (Ar), 130.00 (Ar), 129.94 (Ar), 129.85 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.2 (Ar), 128.9 (Ar), 128.8 (Ar), 128.5 (Ar), 128.41 (Ar), 128.39 (Ar), 128.35 (Ar), 91.6 (C-1), 82.3 (C-2), 81.4 (C-4), 77.9 (C-3), 70.3 (C-5), 63.4 (C-6), 21.1 (ArCH₃). ESI-MS *m/z* calcd. for (M + Na) C₄₁H₃₄O₉SNa: 725.1872. Found: 725.1870.

***p*-Tolyl 2,3,5-tri-*O*-benzoyl-1-thio-β-L-arabinofuranoside (18).** Prepared from **29** (15.88 g, 35.60 mmol) in CH₂Cl₂ (75.0 mL) and *p*-thiocresol (4.40 g, 35.60 mmol) as described for the synthesis of **17** to afford **18** (18.0 g, 89%) as an amorphous white solid. *R_f* 0.38 (4:1 hexanes–EtOAc); [α]_D –90.4 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.14 (d, 2 H, *J* = 10.7 Hz, Ar), 8.06–8.00 (m, 4 H, Ar), 8.00–7.48 (m, 7 H, Ar), 7.42–7.30 (m, 4 H, Ar), 7.13 (d, 2

H, $J = 8.0$ Hz, Ar), 5.77 (d, 1 H, $J = 1.0$ Hz, H-1), 5.72 (dd, 1 H, $J = 1.0, 3.0$ Hz, H-2), 5.66 (dd, 1 H, $J = 5.0, 3.0$ Hz, H-3), 4.95 (app q, 1 H, $J = 5.0$ Hz, H-4), 4.75 (dd, 1 H, $J = 11.8, 5.0$ Hz, H-5_a), 4.71 (dd, 1 H, $J = 11.8, 5.0$ Hz, H-5_b), 2.32 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.2 (C=O), 165.6 (C=O), 165.4 (C=O), 138.2 (Ar), 133.64 (Ar), 133.56 (Ar), 133.1 (Ar), 133.0(Ar), 130.0 (Ar), 129.91 (Ar), 129.87 (Ar), 129.77 (Ar), 129.72 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.3 (Ar), 91.7 (C-1), 82.5 (C-2), 81.0 (C-4), 78.1 (C-3), 63.6 (C-5), 21.1 (ArCH₃). ESI-MS m/z calcd. for [M + Na]⁺ C₃₃H₂₈O₇SNa: 591.1513. Found: 591.1510.

Octyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside (20). Dithioacetal **19**³ (5.90 g, 20.60 mmol) was dissolved in 5% I₂ in octanol (w/v, 200 mL) at rt and stirred for 24 h. Excess I₂ was quenched by adding a saturated aqueous solution of Na₂S₂O₃ (20 mL). Next, a saturated aqueous solution of NaHCO₃ was added to neutralize the reaction mixture. The aqueous layer was washed three times with EtOAc and the combined organic layers were concentrated via azeotropic distillation with water to give an amorphous solid. To this crude mixture, pyridine was added followed by the addition of benzoyl chloride at 0 °C. The reaction mixture was stirred overnight, poured into an ice–water mixture, and extracted with CH₂Cl₂. The combined CH₂Cl₂ layers were washed with 1 M HCl, brine, dried, and concentrated. Column chromatography (4:1 hexanes–EtOAc) gave **20** (β/α = 9:1; 5.70 g, 39% over two steps). R_f 0.40 (α), 0.32 (β) (4:1 hexanes–EtOAc). The data for this material was identical to that reported previously.⁴

Octyl β -D-galactofuranoside (21). To a solution of compound **20** (β -anomer, 1.47 g, 2.08 mmol) in dry MeOH (50 mL) was added NaOMe–MeOH (0.1 M) dropwise until the pH of the reaction mixture turned 12. The reaction mixture was stirred at room temperature for 3 h and neutralized with glacial acetic acid. Concentration gave a syrup that was purified by flash chromatography (9:1 CH₂Cl₂–MeOH) to give the pure β -anomer **21** as an amorphous white solid (0.56 g, 92%). R_f 0.69 (9:1 CH₂Cl₂–MeOH). The data for this material was identical to that reported previously.⁴

Methyl 2,3,5,6-tetra-*O*-benzoyl- α/β -D-galactofuranoside (23). Dithioacetal **19**³ (0.50 g, 1.97 mmol) was dissolved in 2% I₂ in MeOH (w/v, 25 mL) at rt and stirred for 7 h. Excess I₂ was quenched by the increment addition of solid Na₂S₂O₃ until the solution was colorless. The reaction mixture was then neutralized by the addition of NaHCO₃ to the reaction mixture. Evaporation of the solvent gave the crude product as an amorphous yellow solid. Without further purification, pyridine was added to the crude mixture followed by the addition of benzoyl chloride at 0 °C. The reaction mixture was stirred overnight, poured into an ice–water mixture, and extracted with CH₂Cl₂. The combined CH₂Cl₂ layers were washed with 1 M HCl, brine, dried, and concentrated. Column chromatography (4:1 hexanes–EtOAc) gave **24** as an amorphous white solid (β/α = 9:1; 0.76 g, 71% over two steps). R_f 0.42 (β), 0.37 (α); (4:1 hexanes–EtOAc);. The data for this material was identical to that reported previously.⁴

***p*-Tolyl 1-thio- β -D-galactofuranoside (24).** To a solution of **17** (15.00 g, 21.34 mmol) in 3:1 MeOH–CH₂Cl₂ was added NaOMe in MeOH (0.1 M) dropwise until the pH of the reaction

mixture was 12. The solution was stirred at rt for 8 h and neutralized with glacial acetic acid. Concentration gave a yellow syrup that was purified by column chromatography (9:1 CH₂Cl₂–MeOH) to afford **24** (5.38 g, 88%) as an amorphous white solid. The data for this material matched that previously reported.⁶

***p*-Tolyl 6-*O*-trityl-1-thio-β-D-galactofuranoside (25).** To a solution of **24** (0.58 g, 2.04 mmol) in pyridine (10 mL), was added trityl chloride (0.85 g, 3.05 mmol). The reaction mixture was stirred at 50 °C overnight and was then poured into an ice–water mixture, and extracted with CH₂Cl₂. The combined organic layers were washed with brine and the organic solution was then dried and the solvent evaporated. Co-evaporation with toluene removed all traces of pyridine and the residue was purified by column chromatography (1:1 hexanes–EtOAc) to give **25** (0.85 g, 80%) as a colorless oil. *R*_f 0.12 (1:1 hexanes–EtOAc); [α]_D –91.9 (*c* 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 7.46–7.44 (m, 6 H, Ar), 7.44–7.21 (m, 11 H, Ar), 7.01–6.99 (d, 2 H, *J* = 8.5 Hz, Ar), 5.32 (d, 1 H, *J* = 3.4 Hz, H-1), 4.22–4.17 (m, 2 H, H-3, H-4), 4.12 (app t, 1 H, *J* = 3.4 Hz, H-2), 3.93 (app t, 1 H, *J* = 6.4 Hz, H-5), 3.36 (dd, 1 H, *J* = 9.5, 6.4 Hz, H-6_a), 3.25 (dd, 1 H, *J* = 9.5, 6.4 Hz, H-6_b), 2.41 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 143.5 (Ar), 137.7 (Ar), 132.6 (Ar), 129.9 (Ar), 129.8 (Ar), 128.7 (Ar), 127.9 (Ar), 127.2 (Ar), 92.5 (C-1), 87.1 (Ph₃C), 83.9 (C-4), 81.5 (C-2), 77.9 (C-3), 69.9 (C-5), 64.8 (C-6), 21.1 (ArCH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₃₂H₃₂O₅SNa: 551.1865. Found: 551.1863.

***p*-Tolyl 2,3,5-tri-*O*-benzoyl-6-*O*-trityl-1-thio-β-D-galactofuranoside (26).** Prepared from **25** (0.18 g, 0.33 mmol) in pyridine (5 mL) and benzoyl chloride (0.06 g, 0.21 mmol) as

described for the synthesis of **23**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to afford **25** (0.24 g, 87%) as an amorphous white solid. R_f 0.62 (3:1 hexanes–EtOAc); $[\alpha]_D -58.3$ (c 1.0, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ_{H}): 8.10 (dd, 4 H, $J = 9.2, 7.2$ Hz, Ar), 7.85 (dd, 2 H, $J = 7.9, 0.8$ Hz, Ar), 7.63–7.18 (m, 26 H, Ar), 7.02 (d, 2 H, $J = 8.4$ Hz, Ar), 5.90 (app dt, 1 H, $J = 6.0, 4.5$ Hz, H-5), 5.70 (d, 1 H, $J = 0.7$ Hz, H-1), 5.61–5.80 (m, 2 H, H-2, H-3), 5.10 (app t, 1 H, $J = 4.5$ Hz, H-4), 3.57 (dd, 1 H, $J = 10.1, 6.0$ Hz, H-6_a), 3.43 (dd, 1 H, $J = 10.0, 6.0$ Hz, H-6_b), 2.32 (s, 3 H, ArCH_3); $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ_{C}): 165.7 (C=O), 165.4 (C=O), 165.3 (C=O), 143.6 (Ar), 138.0 (Ar), 133.5 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 130.0 (Ar), 129.8 (Ar), 129.7 (Ar), 129.4 (Ar), 129.1 (Ar), 128.9 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 127.8 (Ar), 127.8 (Ar), 127.0 (Ar), 91.3 (C-1), 86.9 (Ph_3C), 82.4 (C-4), 81.3 (C-2), 78.0 (C-3), 72.1 (C-5), 62.9 (C-6), 21.2 (ArCH_3). ESI-MS m/z calcd. for $[\text{M} + \text{Na}]^+ \text{C}_{53}\text{H}_{44}\text{O}_8\text{SNa}$: 863.2649. Found: 863.2648.

***p*-Tolyl 2,3,5-tri-*O*-benzoyl-1-thio- β -D-galactofuranoside (27)** and ***p*-Tolyl 2,3,6-tri-*O*-benzoyl-1-thio- β -D-galactofuranoside (28)**. Compound **26** (0.82 g, 0.98 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to 0 °C, and trifluoroacetic acid (5% in CH_2Cl_2) (13.0 mL) was added dropwise. The reaction mixture was stirred for 12 h, co-evaporated with toluene and concentrated to give a syrup. The residue was purified by column chromatography (5:1 hexanes–EtOAc) to give **27** (0.17 g, 33%) and **28** (0.23 g, 44%) as colorless syrups. R_f 0.40 (**27**) and R_f 0.25 (**28**) (3:1 hexanes–EtOAc); Data for **27**: $[\alpha]_D -79.8$ (c 0.9, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ_{H}): 8.09 (dd, 4 H, $J = 7.0, 6.8$ Hz, Ar), 7.95 (d, 2 H, $J = 8.0$ Hz, Ar),

7.61–7.29 (m, 11 H, Ar), 7.11 (d, 2 H, $J = 8.0$ Hz, Ar), 5.76 (d, 1 H, $J = 0.9$ Hz, H-1), 5.69–5.65 (m, 3 H, H-2, H-3, H-5), 4.92 (app t, 1 H, $J = 4.7$ Hz, H-4), 4.06 (app t, 2 H, $J = 4.7$ Hz, H-6_a, H-6_b), 2.33 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.5 (C=O), 166.0 (C=O), 165.3 (C=O), 138.3 (Ar), 133.7 (Ar), 133.6 (Ar), 133.1 (Ar), 130.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.4 (Ar), 129.0 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 91.9 (C-1), 83.1 (C-4), 81.8 (C-2), 78.2 (C-3), 73.3 (C-5), 62.6 (C-6), 21.1 (ArCH₃). ESI-MS m/z calcd. for [M + Na]⁺ C₃₄H₃₀O₈SNa: 621.1556. Found: 621.1554. Data for **28**: [α]_D –5.3 (*c* 0.9, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.11 (dd, 2 H, $J = 6.5, 2.0$ Hz, Ar), 8.04 (dd, 4 H, $J = 13.0, 6.5$ Hz, Ar), 7.64–7.37 (m, 11 H, Ar), 7.12 (d, 2 H, $J = 7.5$ Hz, Ar), 5.74 (d, 1 H, $J = 1.8$ Hz, H-1), 5.73–5.72 (m, 2 H, H-2, H-3), 4.65 (dd, 1 H, $J = 5.0, 2.5$ Hz, H-4), 4.59–4.48 (m, 3 H, H-6_a, H-5, H-6_b), 2.33 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.5 (C=O), 166.0 (C=O), 165.3 (C=O), 138.3 (Ar), 133.7 (Ar), 133.5 (Ar), 133.3 (Ar), 130.0 (Ar), 130.0 (Ar), 129.89 (Ar), 129.87 (Ar), 129.78 (Ar), 129.73 (Ar), 129.4 (Ar), 128.95 (Ar), 128.90 (Ar), 128.58 (Ar), 128.55 (Ar), 128.4 (Ar), 92.0 (C-1), 83.2 (C-2), 81.8 (C-4), 78.2 (C-3), 69.0 (C-5), 66.1 (C-6), 21.1 (ArCH₃). ESI-MS m/z calcd. for [M + Na]⁺ C₃₄H₃₀O₈SNa : 621.1556. Found: 621.1554.

Octyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (30). Alcohol **14** (0.05 g, 0.08 mmol), thioglycoside **17** (0.06 g, 0.09 mmol), and activated, powdered 4 Å molecular sieves (200 mg) in CH₂Cl₂ (3 mL) were cooled at 0 °C. The reaction mixture was stirred for 15 min before *N*-iodosuccinimide (NIS, 0.03 g, 0.12 mmol),

and AgOTf (4.0 mg, 0.02 mmol) were added. The solution was stirred for a further 30 min before the reaction was quenched by the addition of Et₃N. The reaction mixture was then diluted with CH₂Cl₂ and filtered through a pad of Celite. The filtrate was washed with a saturated aqueous solution of Na₂S₂O₃, water and brine. The organic layer was then dried and the solvent evaporated. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to afford **30** (0.24 g, 87%) as a colorless oil. *R*_f 0.37 (5:1 hexanes–EtOAc); [α]_D –10.4 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ_H): 8.02–7.93 (m, 8 H, Ar), 7.91–7.75 (m, 4 H, Ar), 7.62–7.52 (m, 7 H, Ar), 7.48–7.39 (m, 16 H, Ar), 6.08 (app dt, 1 H, *J* = 7.0, 3.6 Hz, H-5'), 5.84 (dd, 1 H, *J* = 5.0, 1.4 Hz, H-3), 5.81 (s, 1 H, H-1'), 5.69 (d, 1 H, *J* = 1.2 Hz, H-2'), 5.63 (dd, 1 H, *J* = 5.1, 1.2 Hz, H-3'), 5.49 (dd, 1 H, *J* = 1.4, 0.6 Hz, H-2), 5.21 (br s, 1 H, H-1), 5.06 (dd, 1 H, *J* = 5.1, 3.6 Hz, H-4'), 4.79 (m, 5 H, H-6_a, H-6_a', H-5, H-6_b, H-6_b'), 4.53 (dd, 1 H, *J* = 5.0, 1.1 Hz, H-4), 3.72 (app dt, 1 H, *J* = 10.0, 6.0 Hz, octyl OCH₂), 3.47 (app dt, 1 H, *J* = 10.0, 6.0 Hz, octyl OCH₂), 1.64–1.61 (m, 2 H, octyl CH₂), 1.36–1.29 (m, 10 H, octyl CH₂), 0.88 (t, 3 H, *J* = 7.0 Hz, octyl CH₃); ¹³C NMR (100 MHz, CDCl₃, δ_C): 166.1 (C=O), 166.0 (C=O), 165.7 (C=O), 165.7 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 133.38 (Ar), 133.36 (Ar), 133.24 (Ar), 133.20 (Ar), 133.1 (Ar), 133.04 (Ar), 133.02 (Ar), 133.0 (Ar), 132.9 (Ar), 130.0 (Ar), 129.93 (Ar), 129.90 (Ar), 129.8 (Ar), 129.75 (Ar), 129.70 (Ar), 129.6 (Ar), 129.0 (Ar), 128.90 (Ar), 128.87 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 105.5 (C-1'), 105.2 (C-1), 82.4 (C-2'), 82.1 (C-2), 82.0 (C-4'), 81.7 (C-4), 80.6 (C-3), 77.9 (C-3'), 77.3 (C-5), 77.1 (C-5'), 69.5 (C-6'), 67.8 (octyl OCH₂), 63.0 (C-6), 31.9 (octyl CH₂), 29.6 (octyl CH₂),

29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.1 (octyl CH₂), 22.7 (octyl CH₂), 14.11 (octyl CH₃).

ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₉H₆₆O₁₈Na: 1205.4123. Found: 1205.4115.

Octyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (31). Prepared from **13** (0.05 g, 0.08 mmol) and donor **17** (0.06 g, 0.09 mmol), NIS (0.03 g, 0.12 mmol), and AgOTf (4.0 mg, 0.02 mmol) in CH₂Cl₂ (2 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give **31** (0.08 g, 89%) as a colorless oil. *R_f* 0.37 (5:1 hexanes–EtOAc); [α]_D –2.3 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ_H): 8.20–7.99 (m, 8 H, Ar), 7.97–7.90 (m, 4 H, Ar), 7.80 (dd, 2 H, *J* = 7.0, 2.0 Hz, Ar), 7.50–7.41 (m, 8 H, Ar), 7.35–7.26 (m, 8 H, Ar), 7.25–7.20 (m, 5 H, Ar), 6.08 (app dt, 1 H, *J* = 5.0, 3.6 Hz, H-5'), 5.92 (app dt, 1 H, *J* = 5.0, 3.9 Hz, H-5), 5.64–5.58 (m, 3 H, H-3, H-3', H-2), 5.45 (br s, 1 H, H-1'), 5.41 (dd, 1 H, *J* = 5.0, 1.0 Hz, H-2'), 5.28 (s, 1 H, H-1), 4.78 (dd, 1 H, *J* = 5.0, 3.4 Hz, H-4), 4.76–4.73 (m, 2 H, H-6_a', H-6_b'), 4.70 (dd, 1 H, *J* = 5.0, 3.6 Hz, H-4'), 4.23 (dd, 1 H, *J* = 10.5, 5.0 Hz, H-6_a), 4.06 (dd, 1 H, *J* = 10.5, 5.0 Hz, H-6_b), 3.75 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 3.52 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 1.63–1.40 (m, 2 H, octyl CH₂), 1.28–1.40 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.5, octyl CH₃); ¹³C NMR (100 MHz, CDCl₃, δ_C): 166.1 (C=O), 165.8 (C=O), 165.69 (C=O), 165.67 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 133.38 (Ar), 133.36, 133.2 (Ar), 133.19 (Ar), 133.1 (Ar), 133.07 (Ar), 133.04 (Ar), 133.02 (Ar), 132.97 (Ar), 132.9 (Ar), 130.0 (Ar), 129.93 (Ar), 129.90 (Ar), 129.8 (Ar), 129.75 (Ar), 129.70 (Ar), 129.6 (Ar), 129.0 (Ar), 128.89 (Ar), 129.87 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 106.5

(C-1'), 105.8 (C-1), 82.2 (C-2'), 81.4 (C-2), 81.8 (C-4'), 81.4 (C-4), 77.9 (C-3), 77.32 (C-3'), 77.30 (C-5), 77.1 (C-5'), 71.2 (C-6), 67.9 (octyl OCH₂), 63.7 (C-6'), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₉H₆₆O₁₈Na: 1205.4123. Found: 1205.4117.

Octyl 2,3,5,-tri-*O*-benzoyl-β-L-arabinofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (32). Prepared from **14** (35.3 mg, 0.06 mmol), donor **18** (40.8 mg, 0.08 mmol), NIS (19.7 mg, 0.09 mmol), and AgOTf (3.0 mg, 0.01 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**. The residue was then purified by chromatography (6:1 hexanes–EtOAc) to give disaccharide **32** (53.0 mg, 87%) as a colorless oil. *R_f* 0.45 (3:1 hexanes–EtOAc); [α]_D –10.9 (*c* 0.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ_H): 8.05–7.90 (m, 12 H, Ar), 7.61–7.21 (m, 18 H, Ar), 5.82 (dd, 1 H, *J* = 4.2, 1.7 Hz, H-3), 5.73 (s, 1 H, H-1'), 5.70 (d, 1 H, *J* = 1.4 Hz, H-2'), 5.58 (dd, 1 H, *J* = 5.0, 1.4 Hz, H-3'), 5.48 (d, 1 H, *J* = 1.7 Hz, H-2), 5.22 (s, 1 H, H-1), 4.82 (app dt, 1 H, *J* = 5.0, 4.5 Hz, H-4'), 4.78–4.64 (m, 4 H, H-5_a', H-6_b, H-6_a, H-5), 4.58–4.52 (m, 2 H, H-5_b', H-4), 3.75 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 3.52 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 1.63–1.59 (m, 2 H, octyl CH₂), 1.38–1.20 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.5 Hz, octyl CH₃); ¹³C NMR (100 MHz, CDCl₃, δ_C): 166.2 (C=O), 166.1 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 133.5 (Ar), 133.41 (Ar), 133.38 (Ar), 133.36 (Ar), 133.31 (Ar), 132.95 (Ar), 132.90 (Ar), 129.90 (Ar), 129.87 (Ar), 129.84 (Ar), 129.77 (Ar), 129.71 (Ar), 129.6 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.36 (Ar), 128.3 (Ar), 128.27 (Ar), 128.2 (Ar), 106.0 (C-1), 105.6 (C-1'), 82.3 (C-2), 82.0

(C-2'), 81.9 (C-4), 81.3 (C-4'), 77.8 (C-3), 77.4 (C-3'), 74.0 (C-5), 67.7 (C-5'), 64.7 (octyl OCH₂), 63.6 (C-6), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₁H₆₀O₁₆Na: 1071.3776. Found: 1071.3773.

Octyl 2,3,5,-tri-*O*-benzoyl-β-L-arabinofuranosyl-(1→6)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (33). Prepared from **13** (52.9 mg, 0.09 mmol), donor **18** (61.2 mg, 0.11 mmol), NIS (29.5 mg, 0.13 mmol) and AgOTf (4.5 mg, 0.02 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**. The residue was then purified by chromatography (6:1 hexanes–EtOAc) to give disaccharide **33** (82.0 mg, 89%) as colorless oil. *R_f* 0.43 (3:1 hexanes–EtOAc); [α]_D –20.3 (*c* 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ_H): 8.17–8.01 (m, 8 H, Ar), 7.97–7.81 (m, 4 H, Ar), 7.60–7.22 (m, 18 H, Ar), 5.89 (app dt, 1 H, *J* = 6.5, 5.0 Hz, H-5), 5.63 (d, 1 H, *J* = 6.0 Hz, H-3), 5.56 (d, 1 H, *J* = 4.0 Hz, H-3'), 5.47–5.42 (m, 2 H, H-2, H-2'), 5.35 (s, 1 H, H-1'), 5.29 (s, 1 H, H-1), 4.71–4.61 (m, 4 H, H-5_a', H-5_b', H-4, H-4'), 4.23 (dd, 1 H, *J* = 11.0, 5.0 Hz, H-6_a), 4.08 (dd, 1 H, *J* = 11.0, 5.0 Hz, H-6_b), 3.75 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 3.52 (app dt, 1 H, *J* = 9.5, 7.0 Hz, octyl OCH₂), 1.63–1.59 (m, 2 H, octyl CH₂), 1.38–1.20 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.5 Hz, octyl CH₃); ¹³C NMR (100 MHz, CDCl₃, δ_C): 166.1 (C=O), 165.8 (C=O), 165.7 (C=O), 165.5 (C=O), 165.1 (C=O), 165.2 (C=O), 133.4 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.98 (Ar), 132.95 (Ar), 130.0 (Ar), 129.9 (Ar), 129.89 (Ar), 129.83 (Ar), 129.80 (Ar), 129.7 (Ar), 129.2 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.40 (Ar), 128.37 (Ar), 128.35 (Ar), 128.31 (Ar), 128.2 (Ar), 106.1

(C-1), 105.7 (C-1'), 82.2 (C-2), 82.0 (C-2'), 81.4 (C-4), 81.2 (C-4'), 77.7 (C-3), 77.4 (C-3'), 71.4 (C-5), 67.8. (C-6'), 66.1 (octyl OCH₂), 63.5 (C-5'), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 octyl (CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₁H₆₀O₁₆Na: 1071.3776. Found: 1071.3773.

Octyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (34). Prepared from **14** (0.19 g, 0.31 mmol), donor **16** (0.16 g, 0.25 mmol), NIS (67.7 mg, 0.30 mmol) and AgOTf (12.9 mg, 0.05 mmol) in CH₂Cl₂ (10 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give disaccharide **34** (0.24 g, 89%) as a colorless oil. *R_f* 0.37 (3:1 hexanes–EtOAc); [α]_D –2.6 (*c* 1.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.20–7.90 (m, 8 H, Ar), 7.88–7.82 (m, 4 H, Ar), 7.58–7.16 (m, 18 H, Ar), 5.86 (app dt, 1 H, *J* = 6.5, 5.0 Hz, H-5'), 5.81 (dd, 1 H, *J* = 5.0, 1.0 Hz, H-3), 5.78 (s, 1 H, H-1'), 5.64 (d, 1 H, *J* = 1.4 Hz, H-2'), 5.54 (dd, 1 H, *J* = 4.3, 1.2 Hz, H-3'), 5.49 (d, 1 H, *J* = 1.0 Hz, H-2), 5.21 (s, 1 H, H-1) 4.93 (dd, 1 H, *J* = 5.0, 4.3 Hz, H-4'), 4.78–4.74 (m, 3 H, H-6_a, H-5, H-6_b), 4.56–4.39 (m, 3 H, H-6_a', H-6_b', H-4), 3.70 (app dt, 1 H, *J* = 9.5, 6.0 Hz, octyl OCH₂), 3.48 (app dt, 1 H, *J* = 9.5, 6.0 Hz, octyl OCH₂), 1.63–2.05 (s, 3 H, C(=O)CH₃), 1.63–1.59 (m, 2 H, octyl CH₂), 1.28–1.21 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 170.4 (C=O), 166.1 (C=O), 165.6 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 129.92 (Ar), 129.90 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.71 (Ar), 128.69 (Ar),

128.67 (Ar), 128.63 (Ar), 128.61 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 105.5 (C-1'), 105.3 (C-1), 82.3 (C-2'), 82.1 (C-2), 81.8 (C-4'), 81.7 (C-4), 77.7 (C-3), 77.1 (C-3'), 73.1 (C-5'), 70.3 (C-5), 67.6 (octyl OCH₂), 64.6 (C-6'), 62.9 (C-6), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 20.6 (C(=O)CH₃), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₄H₆₄O₁₈: 1143.3984. Found: 1143.3985.

Octyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (35) and Octyl 2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (36). Compound **34** (0.23 g, 0.21 mmol) was dissolved in CH₂Cl₂ (5 mL) and 3% methanolic HCl (12.0 mL) and the reaction mixture was stirred for 8 h. The solution was partially concentrated, diluted with CH₂Cl₂ and was washed with saturated NaHCO₃, water, and brine. The organic layer was then dried and the solvent was concentrated to a residue that was purified by column chromatography (4:1 hexanes–EtOAc) to give disaccharide **35** (0.17 g, 75%) as a colorless oil. Also isolated was **36** (0.05 g, 20%) as a colorless oil. Data for **35**: *R_f* 0.26 (3:1 hexanes–EtOAc); [α]_D –20.8 (*c* 2.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.20–7.90 (m, 8 H, Ar), 7.88–7.82 (m, 4 H, Ar), 7.59–7.42 (m, 8 H, Ar), 7.36–7.24 (m, 10 H, Ar), 5.83 (dd, 1 H, *J* = 5.3, 1.1 Hz, H-3), 5.79 (br s, 1 H, H-1'), 5.69 (dd, 1 H, *J* = 1.7, 0.5 Hz, H-2'), 5.58 (dd, 1 H, *J* = 4.2, 1.7 Hz, H-3'), 5.56–5.53 (m, 1 H, H-5'), 5.50 (d, 1 H, *J* = 1.1 Hz, H-2), 5.24 (br s, 1 H, H-1), 5.02 (dd, 1 H, *J* = 6.0, 4.2 Hz, H-4'), 4.78–4.66 (m, 3 H, H-5, H-6_a, H-6_b), 4.52 (dd, 1 H, *J* = 5.3, 3.4 Hz, H-4), 4.06–3.92 (m, 2 H, H-6'_a, H-6'_b), 3.74 (app dt, 1 H, *J* = 9.0, 7.0 Hz, octyl OCH₂), 3.48 (app dt, 1 H, *J* = 9.0, 7.0 Hz, octyl OCH₂),

1.63–1.59 (m, 2 H, octyl CH_2), 1.29–1.23 (m, 10 H, octyl CH_2), 0.85 (t, 3 H, $J = 9.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C): 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.6 (C=O), 165.5 (C=O), 165.2 (C=O), 133.7 (Ar), 133.4 (Ar), 133.30 (Ar), 133.27 (Ar), 133.1 (Ar), 133.0 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9 (Ar), 129.84 (Ar), 129.81 (Ar), 129.75 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.9 (Ar), 128.8 (Ar), 128.51 (Ar), 128.46 (Ar), 128.35 (Ar), 128.33 (Ar), 128.30 (Ar), 128.2 (Ar), 105.6 (C-1'), 105.5 (C-1), 82.4 (C-2'), 82.1 (C-2), 81.9 (C-4), 81.6 (C-4'), 77.7 (C-3'), 77.5 (C-3), 73.5 (C-5'), 73.0 (C-5), 67.7 (octyl OCH_2), 64.8 (C-6), 61.4 (C-6'), 31.8 (octyl CH_2), 29.5 (octyl CH_2), 29.44 (octyl CH_2), 29.3 (octyl CH_2), 26.2 (octyl CH_2), 22.7 (octyl CH_2), 14.2 (octyl CH_3). ESI-MS m/z calcd. for $[M + Na]^+ C_{62}H_{62}O_{17}$: 1101.3880. Found: 1101.3879. Data for **36**: R_f 0.25 (3:1 hexanes–EtOAc); 1H NMR (500 MHz, $CDCl_3$, δ_H) 8.20–7.90 (m, 10 H, Ar), 7.88–7.82 (m, 2 H, Ar), 7.59–7.26 (m, 16 H, Ar), 7.24–7.18 (m, 2 H, Ar), 5.83 (dd, 1 H, $J = 5.0, 1.0$ Hz, H-3), 5.76 (s, 1 H, H-1'), 5.73 (d, 1 H, $J = 1.8$ Hz, H-2'), 5.67 (dd, 1 H, $J = 5.0, 1.8$ Hz, H-3'), 5.46 (d, 1 H, $J = 1.3$ Hz, H-2), 5.19 (s, 1 H, H-1), 4.77–4.64 (m, 4 H, H-4', H-6a, H-6'a, H-6'b), 4.53–4.47 (m, 3 H, H-4, H-5, H-6b), 4.41–4.64 (m, 1 H, H-5'), 3.74 (app dt, 1 H, $J = 9.0, 7.0$ Hz, octyl OCH_2), 3.48 (dt, 1 H, $J = 9.0, 7.0$ Hz, octyl OCH_2), 1.63 (m, 2 H, octyl CH_2), 1.29–1.23 (m, 10 H, 5 x octyl CH_2), 0.85 (t, 3 H, $J = 9.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.7 (C=O), 165.5 (C=O), 165.1 (C=O), 133.5 (Ar), 133.4 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 130.02 (Ar), 130.01 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.03 (Ar), 129.01 (Ar), 128.9 (Ar), 128.6 (Ar), 128.55 (Ar), 128.49 (Ar), 128.4 (Ar), 128.3

(Ar), 128.22 (Ar), 128.19 (Ar), 128.16 (Ar), 128.15 (Ar), 105.6 (C-1'), 105.5 (C-1), 83.6 (C2'), 82.1 (C-2), 81.8 (C-4), 81.7 (C-4'), 77.7 (C-3'), 77.5 (C-3), 73.5 (C-5), 69.5 (C-5'), 67.6 (octyl O CH₂), 66.2 (C-6'), 64.6 (C-6), 31.8 (CH₂), 29.5 (octyl CH₂), 29.44 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.2 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₂H₆₂O₁₇: 1101.3880. Found: 1101.3879.

Octyl 2,3,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl)-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (37). Method 1:

Prepared from **35** (73.0 mg, 0.07 mmol), donor **17** (86.0 mg, 0.12 mmol), NIS (45.6 mg, 0.21 mmol) and AgOTf (3.5 mg, 0.01 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (5:1 hexanes–EtOAc) to give trisaccharide **37** (90.8 mg, 78%) as a colorless oil with the hydrolyzed donor eluting with the product (1:1 **37**–hydrolyzed donor ratio). *R_f* 0.22 (3:1 hexanes–EtOAc); **One-pot method:** Thioglycoside acceptor **28** (79.2 mg, 0.14 mmol), donor **49**⁷ (117.2 mg, 0.16 mmol), and activated, powdered 4 Å molecular sieves (200 mg) in CH₂Cl₂ (10 mL) were cooled to 0 °C. The mixture was stirred for 15 min, and TMSOTf (4.85 μL, 0.03 mmol) was slowly added. Donor consumption was monitored by thin-layer chromatography and after stirring for 1 h, acceptor **14** (16.4 mg, 0.03 mmol) was added to the reaction mixture. This was followed by the addition of NIS (11.1 mg, 0.05 mmol), AgOTf (1.4 mg, 0.005 mmol). The reaction mixture was then stirred for 30 min, neutralized with Et₃N, diluted with CH₂Cl₂ (5 mL) and filtered through Celite. The filtrate was washed successively with a saturated aqueous solution of Na₂S₂O₃ (10 mL), saturated aqueous

solution of NaHCO₃, water, and brine. The organic layer was dried and concentrated. The residue was purified by column chromatography (20:1 toluene–EtOAc) to give trisaccharide **37** (45.4 mg, 42%) as a colorless oil. *R_f* 0.40 (20:1 toluene–EtOAc); [α]_D –15.2 (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.01–7.92 (m, 16 H, Ar), 7.88–7.76 (m, 4 H, Ar), 7.59–7.17 (m, 24 H, Ar), 7.21–7.17 (m, 6 H, Ar), 6.11 (app dt, 1 H, *J* = 7.2, 3.9 Hz, H-5''), 5.98 (app dt, 1 H, *J* = 7.6, 4.8 Hz, H-5'), 5.82 (dd, 1 H, *J* = 5.1, 1.6 Hz, H-3''), 5.77 (s, 1 H, H-1'), 5.70 (dd, 1 H, *J* = 4.8, 1.4 Hz, H-3'), 5.66 (d, 1 H, *J* = 1.4 Hz, H-2'), 5.63 (dd, 1 H, *J* = 4.0, 1.5 Hz, H-3), 5.56 (d, 1 H, *J* = 1.6 Hz, H-2''), 5.33 (d, 1 H, *J* = 1.5 Hz, H-2), 5.25 (s, 1 H, H-1''), 5.23 (s, 1 H, H-1), 4.93 (app t, 1 H, *J* = 4.8 Hz, H-4'), 4.83–4.69 (m, 7 H, H-4'', H-5, H-6_a, H-6_b, H-6_a'', H-6_a', H-6_b''), 4.53 (dd, 1 H, *J* = 5.0, 4.0 Hz, H-4), 4.03 (dd, 1 H, *J* = 11.5, 7.6 Hz, H-6_b'), 3.70 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 3.47 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 1.58–1.53 (m, 2 H, octyl CH₂), 1.36–1.20 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.5, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.71 (C=O), 165.70 (C=O), 165.6 (C=O), 165.54 (C=O), 165.52 (C=O), 165.4 (C=O), 133.5 (Ar), 133.4 (Ar), 133.3 (Ar), 133.21 (Ar), 133.19 (Ar), 133.18 (Ar), 133.12 (Ar), 133.06 (Ar), 133.02 (Ar), 133.0 (Ar), 132.8 (Ar), 130.1 (Ar), 130.0 (Ar), 129.94 (Ar), 129.91 (Ar), 129.90 (Ar), 129.85 (Ar), 129.81 (Ar), 129.77 (Ar), 129.75 (Ar), 129.71 (Ar), 129.67 (Ar), 129.58 (Ar), 129.51 (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.93 (Ar), 128.91 (Ar), 128.89 (Ar), 128.8 (Ar), 128.52 (Ar), 128.5 (Ar), 128.42 (Ar), 128.40 (Ar), 128.37 (Ar), 128.31 (Ar), 128.25 (Ar), 128.2 (Ar), 106.7 (C-1), 105.5 (C-1''), 105.4 (C-1'), 82.5 (C-4'), 82.4 (C-4''), 82.3 (C-4), 82.2 (C-2'), 82.0 (C-2''), 81.9

(C-2), 77.9 (C-3'), 77.5 (C-3''), 77.4 (C-3), 73.1 (C-5), 71.7 (C-5'), 70.5 (C-5''), 67.7 (C-6'), 67.6 (octyl OCH₂), 64.6 (C-6''), 63.6 (C-6), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₆H₈₈O₂₆: 1679.5413. Found: 1679.5405.

Octyl 5-*O*-acetyl-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (38). Prepared from **13** (0.18 g, 0.30 mmol), donor **15** (0.25 g, 0.39 mmol), NIS (0.10 g, 0.45 mmol) and AgOTf (15.4 mg, 0.06 mmol) in CH₂Cl₂ (5 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give disaccharide **38** (0.34 g, 99%) as a colorless oil. *R_f* 0.27 (3:1 hexanes–EtOAc); [α]_D –2.5 (*c* 1.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.10–7.98 (m, 10 H, Ar), 7.59–7.21 (m, 20 H, Ar), 5.89 (app dt, 1 H, *J* = 7.5, 4.0 Hz, H-5'), 5.78 (app dt, 1 H, *J* = 7.5, 4.0 Hz, H-5), 5.60 (d, 1 H, *J* = 4.9 Hz, H-3'), 5.47 (dd, 1 H, *J* = 4.2, 1.0 Hz, H-3), 5.44 (d, 1 H, *J* = 1.0 Hz, H-2'), 5.41 (d, 1 H, *J* = 1.0 Hz, H-2), 5.36 (s, 1 H, H-1), 5.27 (s, 1 H, H-1'), 4.69–4.63 (m, 3 H, H-4, H-4', H-6_b), 4.60 (dd, 1 H, *J* = 12.0, 7.5 Hz, H-6_a), 4.19 (dd, 1 H, *J* = 10.5, 7.5 Hz, H-6'_a), 4.05 (dd, 1 H, *J* = 10.5, 7.5 Hz, H-6'_b), 3.75 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 3.47 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 2.03 (s, 3 H, C(=O)CH₃), 1.63–1.58 (m, 2 H, octyl CH₂), 1.28–1.24 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.0 Hz, octyl CH₃); ¹³C NMR (100 MHz, CDCl₃, δ_C): 170.0 (C=O), 166.0 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.1 (C=O), 133.5 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 130.2 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9 (Ar), 129.85 (Ar), 129.80 (Ar), 129.78 (Ar), 129.69 (Ar), 129.66 (Ar), 129.63

(Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.39 (Ar), 128.36 (Ar), 128.34 (Ar), 106.2 (C-1), 105.7 (C-1'), 82.2 (C-2'), 81.6 (C-2), 81.5 (C-4), 81.4 (C-4'), 77.5 (C-3'), 77.3 (C-3), 71.5 (C-5'), 71.7 (C-5'), 69.8 (C-5), 67.8 (octyl OCH₂), 66.3 (C-6), 63.5 (C-6'), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 20.8 (C(=O)CH₃), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₄H₆₄O₁₈: 1143.3984. Found: 1143.3983.

Octyl 2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (39). Prepared from **38** (0.34 g, 0.06 mmol) in CH₂Cl₂ (20 mL) and 3% methanolic HCl (17.35 mL) as described for the synthesis of **35**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give disaccharide **39** (0.28 g, 85%) as a colorless oil. *R_f* 0.29 (2:1 hexanes–EtOAc); [α]_D –7.1 (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.20–7.90 (m, 8 H, Ar), 7.88–7.82 (m, 4 H, Ar), 7.58–7.22 (m, 18 H, Ar), 5.90 (app dt, 1 H, *J* = 5.9, 4.5 Hz, H-5), 5.61 (dd, 1 H, *J* = 3.7, 1.1 Hz, H-3'), 5.88 (dd, 1 H, *J* = 3.8, 0.7 Hz, H-3), 5.44 (d, 1 H, *J* = 1.1 Hz, H-2'), 5.42 (d, 1 H, *J* = 0.7 Hz, H-2), 5.35 (s, 1 H, H-1'), 5.26 (s, 1 H, H-1), 4.65 (dd, 1 H, *J* = 4.5, 3.8 Hz, H-4), 4.59 (dd, 1 H, *J* = 11.6, 6.9 Hz, H-6_a'), 4.52 (dd, 1 H, *J* = 4.8, 3.7 Hz, H-4'), 4.48–4.02 (m, 2 H, H-5', H-6_b'), 4.16 (dd, 1 H, *J* = 10.8, 5.9 Hz, H-6_a), 4.05 (dd, 1 H, *J* = 10.8, 5.9 Hz, H-6_b), 3.72 (app dt, 1 H, *J* = 9.4, 6.7 Hz, octyl OCH₂), 3.50 (app dt, 1 H, *J* = 9.4, 6.7 Hz, octyl OCH₂), 1.63–1.60 (m, 2 H, octyl CH₂), 1.28–1.20 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.1 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.1 (C=O), 133.5 (Ar), 133.4

(Ar), 133.3 (Ar), 133.3 (Ar), 133.03 (Ar), 133.0 (Ar), 129.9 (Ar), 129.83 (Ar), 129.79 (Ar), 129.71 (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.7 (Ar), 128.5 (Ar), 128.44 (Ar), 128.44 (Ar), 128.3 (Ar), 127.7 (Ar), 126.9 (Ar), 106.4 (C-1), 105.7 (C-1'), 82.6 (C-2), 82.1 (C-2'), 81.5 (C-4), 81.4 (C-4'), 78.0 (C-3'), 77.5 (C-3), 71.4 (C-5), 69.2 (C-5'), 66.4 (octyl OCH₂), 66.3 (C-6), 61.4 (C-6'), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₂H₆₂O₁₇: 1101.3881. Found: 1101.3879.

Octyl 2,3,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (41). Method 1:

Prepared from **39** (60.7 mg, 0.06 mmol), donor **17** (99.30 mg, 0.14 mmol), NIS (31.6 mg, 0.14 mmol) and AgOTf (2.9 mg, 0.01 mmol) in CH₂Cl₂ (2 mL) as described for the synthesis of **30**.

The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give trisaccharide **41** (90.8 mg, 91%) as a clear, colorless oil. *R_f* 0.22 (3:1 hexanes–EtOAc); **One-pot method:**

Thioglycoside acceptor **27** (46.2 mg, 0.08 mmol), donor **49**⁷ (74.4 mg, 0.10 mmol), and activated, powdered 4 Å molecular sieves (200.0 mg) in CH₂Cl₂ (7 mL) were cooled to 0 °C. The suspension was stirred for 15 min before TMSOTf (4.85 μL, 0.03 mmol) was slowly added.

Donor consumption was monitored by thin-layer chromatography and after stirring for 1 h, acceptor **13** (29.0 mg, 0.05 mmol) was added to the reaction mixture. This was followed by the addition of NIS (16.2 mg, 0.07 mmol), AgOTf (2.5 mg, 0.01 mmol). The reaction mixture was then stirred for 30 min, neutralized with Et₃N, diluted with CH₂Cl₂ (5 mL) and filtered through

Celite. The filtrate was washed successively with a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$, saturated aqueous solution of NaHCO_3 , water, and brine. The organic layer was dried, concentrated and the residue was purified by column chromatography (20:1 toluene–EtOAc) to give trisaccharide **41** (42.0 mg, 41%) as a clear colorless oil. R_f 0.58 (15:1 toluene–EtOAc); $[\alpha]_D -15.2$ (c 0.2, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ_{H}) 8.01–7.82 (m, 16 H, Ar), 7.59–7.17 (m, 34 H, Ar), 6.05 (app dt, 1 H, $J = 6.5, 4.7$ Hz, H-5''), 5.91 (app dt, 1 H, $J = 7.0, 3.9$ Hz, H-5), 5.83 (dd, 1 H, $J = 5.1, 1.0$ Hz, H-3'), 5.78 (s, 1 H, H-1''), 5.67 (d, 1 H, $J = 1.0$ Hz, H-2''), 5.62 (dd, 1 H, $J = 4.2, 1.0$ Hz, H-3''), 5.60 (d, 1 H, $J = 5.0$ Hz, H-3), 5.46 (d, 1 H, $J = 1.0$ Hz, H-2'), 5.43 (d, 1 H, $J = 1.0$ Hz, H-2), 5.33 (s, 1 H, H-1'), 5.27 (s, 1 H, H-1), 5.05 (dd, 1 H, $J = 4.7, 4.2$ Hz, H-4''), 4.83–4.64 (m, 7 H, H-4', H-5', H-4, H-6a', H-6b', H-6a'', H-6b''), 4.18 (dd, 1 H, $J = 10.6, 7.0$ Hz, H-6a), 4.04 (dd, 1 H, $J = 10.6, 7.0$ Hz, H-6b), 3.72 (app dt, 1 H, $J = 9.5, 6.7$ Hz, octyl OCH_2), 3.50 (app dt, 1 H, $J = 9.5, 6.7$ Hz, octyl OCH_2), 1.58–1.53 (m, 2 H, octyl CH_2), 1.28–1.20 (m, 10 H, octyl CH_2), 0.89 (t, 3 H, $J = 7.0$ Hz, octyl CH_3); $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ_{C}): 166.1 (C=O), 166.03 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 166.6 (C=O), 165.49 (C=O), 165.46 (C=O), 165.16 (C=O), 165.14 (C=O), 133.5 (Ar), 133.4 (Ar), 133.3 (Ar), 133.28 (Ar), 133.24 (Ar), 133.20 (Ar), 133.2 (Ar), 133.1 (Ar), 133.07 (Ar), 133.02 (Ar), 133.0 (Ar), 132.90 (Ar), 132.85 (Ar), 130.0 (Ar), 129.95 (Ar), 129.93 (Ar), 129.82 (Ar), 129.80 (Ar), 129.71 (Ar), 129.66 (Ar), 129.7 (Ar), 129.67 (Ar), 129.6 (Ar), 128.9 (Ar), 128.86 (Ar), 128.80 (Ar), 128.5 (Ar), 128.42 (Ar), 128.40 (Ar), 128.34 (Ar), 128.31 (Ar), 128.2 (Ar), 128.1 (Ar), 106.1 (C-1), 105.7 (C-1''), 105.3 (C-1'), 83.1 (C-4'), 82.9 (C-4''), 82.1 (C-4), 82.0 (C-2'), 81.7

(C-2''), 81.44 (C-2), 77.8 (C-3'), 77.6 (C-3''), 77.5 (C-3), 73.1 (C-5), 71.7 (C-5'), 70.5 (C-5''), 67.8 (C-6), 66.1 (octyl OCH₂), 64.9 (C-6''), 63.8 (C-6'), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₂). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₆H₈₈O₂₆: 1679.5413. Found: 1679.5405.

Octyl 5-*O*-acetyl-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl)-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (42).

Prepared from **35** (60.2 mg, 0.06 mmol), donor **15** (46.5 mg, 0.06 mmol), NIS (18.8 mg, 0.08 mmol) and AgOTf (2.8 mg, 0.01 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**.

The residue was purified by column chromatography (5:1 hexanes–EtOAc) to give trisaccharide

42 (69.0 mg, 78%) as a colorless oil. *R_f* 0.28 (3:1 hexanes–EtOAc); [α]_D –10.8 (*c* 1.5, CHCl₃);

¹H NMR (500 MHz, CDCl₃, δ_H) 8.20–7.90 (m, 14 H, Ar), 7.88–7.76 (m, 4 H, Ar), 7.59–7.32 (m, 21 H, Ar), 7.22–7.16 (m, 6 H, Ar), 5.95 (app dt, 1 H, *J* = 7.0, 4.3 Hz, H-5'), 5.82 (dd, 1 H, *J* = 5.3, 1.6 Hz, H-3''), 5.77 (s, 1 H, H-1'), 5.70 (app dt, 1 H, *J* = 7.9, 3.8 Hz, H-5''), 5.64 (dd, 1 H, *J* = 1.0, 0.5 Hz, H-2'), 5.60 (dd, 1 H, *J* = 3.8, 1.0 Hz, H-3'), 5.49 (dd, 1 H, *J* = 1.6, 0.5 Hz, H-2''), 5.42 (dd, 1 H, *J* = 5.1, 1.3 Hz, H-3), 5.33 (d, 1 H, *J* = 1.3 Hz, H-2), 5.21 (br s, 1 H, H-1''), 5.19 (s, 1 H, H-1), 4.91 (dd, 1 H, *J* = 4.3, 3.8 Hz, H-4'), 4.78–4.66 (m, 3 H, H-5, H-6_a, H-6_b), 4.62–4.58 (m, 2 H, H-4, H-6_a'), 4.56–4.49 (m, 2 H, H-4'', H-6_b'), 4.11 (dd, 1 H, *J* = 11.0, 7.9 Hz, H-6_a''), 3.98 (dd, 1 H, *J* = 11.0, 7.9 Hz, H-6_b''), 3.70 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 3.47 (app dt, 1 H, *J* = 9.5, 6.7 Hz, octyl OCH₂), 1.96 (s, 3 H, C(=O)CH₃), 1.58–1.53 (m, 2 H, octyl CH₂), 1.34–1.26 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.5 Hz, octyl CH₃); ¹³C NMR (125 MHz,

CDCl₃, δ_C): 170.0 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.4 (C=O), 165.2 (C=O), 164.9 (C=O), 133.44 (Ar), 133.41 (Ar), 133.37 (Ar), 133.33 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.95 (Ar), 132.9 (Ar), 132.8 (Ar), 130.0 (Ar), 129.89 (Ar), 129.88 (Ar), 129.82 (Ar), 129.79 (Ar), 129.77 (Ar), 129.71 (Ar), 129.67 (Ar), 129.66 (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 106.6 (C-1), 105.5 (C-1''), 105.4 (C-1'), 82.4 (C-4'), 82.3 (C-4''), 82.0 (C-4), 81.8 (C-2'), 81.6 (C-2''), 81.5 (C-2), 77.9 (C-3'), 77.2 (C-3''), 77.2 (C-3), 73.1 (C-5), 71.7 (C-5'), 70.0 (C-5''), 67.7 (C-6''), 67.6 (octyl OCH₂), 64.6 (C-6'), 63.6 (C-6), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃), 2.05 (C(=O)CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₁H₈₆O₂₆: 1617.5261. Found: 1617.5260.

Octyl 2,3,6-tri-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 6)-2,3,5-tri-*O*-benzoyl- β -D-galactofuranosyl)-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl- β -D-galactofuranoside (43). Prepared from **42** (20.0 mg, 0.01 mmol) in CH₂Cl₂ (2 mL) and 3% methanolic HCl (0.73 mL) as described for the synthesis of **35**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give disaccharide **45** (18.0 mg, 92%) as a colorless oil. R_f 0.09 (4:1 hexanes–EtOAc); $[\alpha]_D -2.8$ (c 1.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.20–7.90 (m, 16 H, Ar), 7.88–7.76 (m, 4 H, Ar), 7.59–7.17 (m, 25 H, Ar), 5.95 (app dt, 1 H, $J = 7.0, 4.8$ Hz, H-5'), 5.80 (dd, 1 H, $J = 4.2, 1.0$ Hz, H-3''), 5.77 (br s, 1 H, H-1'), 5.63 (dd, 1 H, $J = 1.5, 0.9$ Hz, H-2'), 5.57 (dd, 1 H, $J = 3.8, 1.5$ Hz, H-3'), 5.53 (dd, 1 H, $J = 4.7, 1.2$ Hz, H-3), 5.48 (d, 1 H, $J = 1.0$ Hz, H-2''), 5.37 (d, 1 H, $J = 1.2$ Hz, H-2), 5.22 (s, 1 H, H-1''), 5.16 (s, 1 H, H-1), 4.89 (dd, 1 H, $J = 4.8, 3.8$ Hz, H-4'), 4.76–4.74 (m, 1 H, H-6_a''), 4.73–4.68 (m, 2 H, H-5'', H-6_b''), 4.53–4.49 (m, 2 H, H-4, H-6_a), 4.44 (dd, 1 H, $J = 4.8, 4.2$ Hz, H-4''), 4.41 (dd, 1 H, $J = 11.4, 7.2$ Hz, H-6_b), 4.35 (app dt, 1 H, $J = 7.2, 3.4$ Hz, H-5), 4.08 (dd, 1 H, $J = 11.4, 7.0$ Hz, H-6_a'), 3.98 (dd, 1 H, $J = 11.4, 7.0$ Hz, H-6_b'), 3.69 (app dt, 1 H, $J = 9.5, 6.3$ Hz, octyl OCH₂), 3.47 (app dt, 1 H, $J = 9.5, 6.3$ Hz, octyl OCH₂), 1.63–1.60 (m, 2 H, octyl CH₂), 1.28–1.20 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, $J = 7.0$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.8 (C=O), 165.7 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 164.9 (C=O), 133.42 (Ar), 133.4 (Ar), 133.33 (Ar), 133.1 (Ar), 133.2 (Ar), 133.12 (Ar), 133.0 (Ar), 132.9 (Ar), 132.86 (Ar), 129.93 (Ar), 129.9 (Ar), 129.86 (Ar), 129.80 (Ar), 129.78 (Ar), 129.76 (Ar), 129.75 (Ar), 129.69 (Ar), 129.66 (Ar), 129.1 (Ar), 129.03 (Ar), 129.0 (Ar), 128.9 (Ar), 128.89 (Ar), 128.51 (Ar), 128.46

(Ar), 128.43 (Ar), 128.36 (Ar), 128.28 (Ar), 128.26 (Ar), 128.15 (Ar), 106.8 (C-1'), 105.5 (C-1''), 105.4 (C-1), 83.7 (C-4'), 82.4 (C-4), 82.3 (C-4''), 82.0 (C-2'), 81.8 (C-2''), 81.4 (C-2), 77.8 (C-3''), 77.3 (C-3'), 77.1 (C-3), 73.3 (C-5), 71.7 (C-5'), 69.3 (C-5''), 67.7 (C-6), 67.6 (C-6), 66.2 (C-6''), 64.7 (octyl OCH₂), 31.9 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.2 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₈₉H₈₄O₂₅: 1575.5159. Found: 1575.5157.

Octyl 2,3,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (45). **Method 1:** Prepared from **43** (20.0 mg, 0.01 mmol), donor **17** (18.1 mg, 0.03 mmol), NIS (4.3 mg, 0.02 mmol) and AgOTf (6.7 mg, 0.003 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (2:1 hexanes–EtOAc) to give tetrasaccharide **45** (14.9 mg, 70%) as an oil. *R_f* 0.33 (15:1 toluene–EtOAc). **Method 2:** Prepared from **14** (5.6 mg, 0.01 mmol), donor **57** (23.0 mg, 0.01 mmol), activated, powdered Å molecular sieves (50.0 mg), NIS (6.3 mg, 0.003 mmol) and AgOTf (1.2 mg, 0.0005 mmol) in CH₂Cl₂ (7 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (20:1 toluene–EtOAc) to give tetrasaccharide **45** (13.8 mg, 70%) as an oil. *R_f* 0.33 (15:1 toluene–EtOAc); [α]_D –7.8 (*c* 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.00–7.96 (m, 13 H, Ar), 7.90–7.79 (m, 15 H, Ar), 7.76–7.10 (m, 37 H, Ar), 5.99 (app dt, 1 H, *J* = 7.5, 5.3 Hz, H-5'''), 5.93 (app dt, 1 H, *J* = 8.0, 4.5 Hz, H-5'), 5.81 (dd, 1 H, *J* = 5.0, 1.5 Hz, H-3''), 5.77–5.76 (m, 3 H, H-3, H-1', H-1'''), 5.65

(br s, 1 H, H-2'), 5.645 (br s, 1 H, H-2'''), 5.61 (dd, 1 H, $J = 4.5, 1.3$ Hz, H-3'), 5.59 (dd, 1 H, $J = 4.5, 1.3$ Hz, H-3'''), 5.48 (d, 1 H, $J = 1.5$ Hz, H-2''), 5.34 (d, 1 H, $J = 1.5$ Hz, H-2), 5.20 (s, 1 H, H-1''), 5.18 (s, 1 H, H-1), 4.99 (dd, 1 H, $J = 5.3, 4.5$ Hz, H-4'''), 4.90 (app t, 1 H, $J = 4.5$ Hz, H-4'), 4.76–4.61 (m, 8 H, H-5'', H-5, H-6_a, H-6_b, H-6_a'', H-6_b'', H-6_a''', H-6_b'''), 4.58 (dd, 1 H, $J = 6.1, 3.0$ Hz, H-4), 4.50 (dd, 1 H, $J = 5.3, 3.9$ Hz, H-4''), 4.09 (dd, 1 H, $J = 11.4, 5.9$ Hz, H-6_a'), 3.97 (dd, 1 H, $J = 11.4, 5.9$ Hz, H-6_b'), 3.67 (app dt, 1 H, $J = 9.0, 6.5$ Hz, octyl OCH₂), 3.46 (app dt, 1 H, $J = 9.0, 6.5$ Hz, octyl OCH₂), 1.56–1.55 (m, 2 H, octyl CH₂), 1.33–1.21 (m, 10 H, octyl CH₂), 0.85 (t, 3 H, $J = 6.9$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.1 (C=O), 165.92 (C=O), 165.91 (C=O), 165.8 (C=O), 165.7 (C=O), 165.64 (C=O), 165.62 (C=O), 165.5 (C=O), 165.4 (2 x C=O), 165.2 (C=O), 165.1 (C=O), 165.07 (C=O), 133.4 (Ar), 133.3 (Ar), 133.25 (Ar), 133.2 (Ar), 133.1 (Ar), 133.05 (Ar), 133.0 (Ar), 132.94 (Ar), 132.9 (Ar), 132.8 (Ar), 129.93 (Ar), 129.9 (Ar), 129.81 (Ar), 129.79 (Ar), 129.76 (Ar), 129.69 (Ar), 129.66 (Ar), 129.6 (Ar), 129.2 (Ar), 129.0 (Ar), 128.91 (Ar), 128.89 (Ar), 128.72 (Ar), 128.5 (Ar), 128.4 (Ar), 128.36 (Ar), 128.3 (Ar), 128.25 (Ar), 128.21 (Ar), 128.17 (Ar), 128.1 (Ar), 128.08 (Ar), 106.6 (C-1''), 105.49 (C-1'''), 105.46 (C-1'), 105.45 (C-1), 82.9 (C-4), 82.4 (C-4'), 82.3 (C-4''), 82.1 (C-4'''), 82.0 (C-2'''), 82.0 (C-2'), 82.0 (C-2''), 82.0 (C-2), 77.83 (C-3', C-3'''), 77.80 (C-3, C-3''), 73.2 (C-5''), 72.7 (C-5), 71.8 (C-5'''), 70.6 (C-5'), 67.6 (C-6'), 67.5 (octyl OCH₂), 65.2 (C-6'''), 64.7 (C-6), 63.8 (C-6''), 31.8 (octyl CH₂), 29.5 (octyl CH₂), 29.4 (octyl CH₂), 29.2 (octyl CH₂), 26.1 (octyl CH₂), 22.6 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS m/z calcd. for [M + Na]⁺ C₁₂₃H₁₁₀O₃₄: 2155.169. Found: 2154.678.

Octyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl- β -D-galactofuranosyl)-(1 \rightarrow 6)-2,3,5-tri-*O*-benzoyl- β -D-galactofuranoside (46).

Prepared from **39** (111.4 mg, 0.10 mmol), donor **16** (46.5 mg, 0.06 mmol), NIS (64.9 mg, 0.29 mmol) and AgOTf (5.3 mg, 0.02 mmol) in CH₂Cl₂ (3 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give a mixture of trisaccharide **46** and the hydrolyzed donor (1:1 **46**–hydrolyzed donor) as oil. *R_f* 0.13 (3:1 hexanes–EtOAc). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₁H₈₆O₂₆: 1617.5261. Found: 1617.5253.

Octyl 2,3,5-tri-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 6)-2,3,6-tri-*O*-benzoyl- β -D-galactofuranoside (47). Prepared from acetylated trisaccharide **46** (not isolated pure) (68.5 mg, 0.04 mmol) in 1.0 mL CH₂Cl₂ (1.0 mL) and 3% methanolic HCl (2.49 mL) as described for the synthesis of **35**. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to give **47** (32.3 mg, 42% over two steps) as a colorless oil. *R_f* 0.17 (3:1 hexanes–EtOAc); [α]_D –20.4 (*c* 0.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H): 8.20–7.90 (m, 12 H, Ar), 7.88–7.76 (m, 8 H, Ar), 7.59–7.22 (m, 25 H, Ar), 5.95 (ddd, 1 H, *J* = 7.9, 5.0, 3.8 Hz H-5), 5.80 (dd, 1 H, *J* = 5.3, 1.0 Hz, H-3'), 5.76 (s, 1 H, H-1'), 5.65 (d, 1 H, *J* = 1.0 Hz, H-2'), 5.58 (dd, 1 H, *J* = 6.1, 1.0 Hz, H-3), 5.53 (d, 1 H, *J* = 4.8 Hz, H-3''), 5.52 (app dt, 1 H, *J* = 7.6, 3.8 Hz, H-5''), 5.43 (br s, 2 H, H-2'', H-2), 5.34 (s, 1 H, H-1), 5.26 (s, 1 H, H-1''), 4.99 (dd, 1 H, *J* = 4.8, 3.8 Hz, H-4''), 4.77–4.65 (m, 5 H, H-4', H-5', H-6_b', H-6_a', H-4), 4.18 (dd, 1 H, *J* = 11.4, 7.9 Hz, H-6_a), 4.05 (dd, 1 H, *J* = 11.4, 7.9 Hz, H-6_b),

4.01 (dd, 1 H, $J = 11.4, 5.0$ Hz, H-6_a'''), (dd, 1 H, $J = 11.4, 5.0$ Hz, H-6_b'''), 3.69 (app dt, 1 H, $J = 9.6, 6.3$ Hz, octyl OCH₂), 3.47 (app dt, 1 H, $J = 9.6, 6.3$ Hz, octyl OCH₂), 1.63–1.60 (m, 2 H, octyl CH₂), 1.28–1.21 (m, 10 H, octyl H₂), 0.89 (t, 3 H, $J = 7.0$, octyl CH₃); ESI-MS m/z calcd. for [M + Na]⁺ C₈₉H₈₄O₂₅: 1575.5160. Found: 1575.5158.

Octyl 2,3,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (48). Prepared from **53** (11.4 mg, 0.02 mmol), donor **13** (46.8 mg, 0.03 mmol), activated, powdered 4 Å molecular sieves (150.0 mg), NIS (12.8 mg, 0.06 mmol) and AgOTf (2.4 mg, 0.01 mmol) in CH₂Cl₂ (15 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (2:1 hexanes–EtOAc) to give tetrasaccharide **48** (30.0 mg, 75%) as a colorless oil. R_f 0.35 (15:1 toluene–EtOAc); $[\alpha]_D -10.8$ (c 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.05–7.74 (m, 20 H, Ar), 7.52–7.15 (m, 45 H, Ar), 6.01 (app dt, 1 H, $J = 7.5, 4.8$ Hz, H-5'''), 5.93–5.90 (m, 2 H, H-5'', H-5'), 5.81 (dd, 1 H, $J = 4.8, 1.2$ Hz, H-3'), 5.77 (s, 1 H, H-1''), 5.63 (dd, 1 H, $J = 1.2, 0.7$ Hz, H-2''), 5.62 (dd, 1 H, $J = 4.8, 1.2$ Hz, H-3''), 5.58 (d, 1 H, $J = 4.8$ Hz, H-3), 5.54 (d, 1 H, $J = 4.8$ Hz, H-3'''), 5.44 (d, 1 H, $J = 1.2$ Hz, H-2'), 5.43 (d, 1 H, $J = 1.2$ Hz, H-2), 5.323 (d, 1 H, $J = 1.2$ Hz, H-1'''), 5.318 (d, 1 H, $J = 1.2$ Hz, H-2'''), 5.26 (s, 1 H, H-1), 5.24 (s, 1 H, H-1'), 4.85 (app t, 1 H, $J = 4.8$ Hz, H-4''), 4.73–4.67 (m, 6 H, H-4''', H-5, H-6_a, H-6_b, H-6_a''', H-6_b'''), 4.66 (dd, 1 H, $J = 3.6, 4.8$ Hz, H-4), 4.61 (dd, 1 H, $J = 5.4, 3.0$ Hz, H-4'), 4.16 (dd, 1 H, $J = 10.5, 5.2$ Hz, H-6'_a), 4.12 (dd, 1 H, $J = 11.0, 6.0$ Hz, H-6'_b), 4.02 (dd, 1 H, $J = 10.5, 5.2$ Hz, H-6''_b), 3.97 (dd, 1 H, $J = 11.0, 6.0$

Hz, H-6_b''), 3.72 (app dt, 1 H, $J = 9.6, 6.6$ Hz, octyl OCH₂), 3.50 (app dt, 1 H, $J = 9.6, 6.6$ Hz, octyl OCH₂), 1.60–1.55 (m, 2 H, octyl CH₂), 1.33–1.19 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, $J = 7.2$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_c): 166.03 (C=O), 166.0 (C=O), 165.83 (C=O), 165.8 (C=O), 165.7 (C=O), 165.63 (C=O), 165.61 (C=O), 165.57 (C=O), 165.5 (C=O), 165.46 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 133.3 (Ar), 133.24 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.96 (Ar), 132.87 (Ar), 132.85 (Ar), 132.8 (Ar), 129.93 (Ar), 129.89 (Ar), 129.8 (Ar), 129.76 (Ar), 129.7 (Ar), 129.65 (Ar), 129.6 (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.47 (Ar), 128.42 (Ar), 128.4 (Ar), 128.35 (Ar), 128.32 (Ar), 128.3 (Ar), 128.25 (Ar), 128.22 (Ar), 128.17 (Ar), 128.12 (Ar), 106.7 (C-1), 106.1 (C-1'''), 105.8 (C-1''), 105.7 (C-1'), 82.7 (C-4), 82.5 (C-4''), 82.1 (C-2), 81.9 (C-2'), 81.84 (C-4'''), 81.83 (C-4'), 81.8 (C-2'''), 81.4 (C-2''), 77.7 (C-3''), 77.5 (C-3), 77.4 (C-3'''), 77.2 (C-3'), 73.2 (C-5), 71.9 (C-5'), 71.3 (C-5''), 70.5 (C-5'''), 67.74 (C-6''), 67.7 (octyl OCH₂), 66.1 (C-6), 65.1 (C-6'), 63.7 (C-6''), 31.8 (octyl CH₂), 29.45 (octyl CH₂), 29.4 (octyl CH₂), 29.2 (octyl CH₂), 26.1 (octyl CH₂), 22.6 (octyl CH₂), 14.1 (octyl CH₃). ESI-MS m/z calcd. for [M + Na]⁺ C₁₂₃H₁₁₀O₃₄: 2154.678. Found: 2154.68.

***p*-Tolyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (50).** Compound **27** (0.29 g, 0.48 mmol), donor **49**⁷ (0.46 g, 0.62 mmol), and activated, powdered 4 Å molecular sieves (0.57 g) in CH₂Cl₂ (25 mL) were cooled at 0 °C. The suspension was stirred for 15 min before TMSOTf (25.8 μL, 0.14 mmol) was added dropwise. The reaction mixture was then stirred for 1 h, neutralized with Et₃N,

diluted with CH₂Cl₂ and filtered through Celite. The filtrate was evaporated and the residue was purified by column chromatography (20:1 toluene–EtOAc) to give disaccharide **50** (0.51 g, 90%) as an amorphous white solid. *R_f* 0.37 (20:1 toluene–EtOAc); [α]_D –47.9 (*c* 0.7, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H): 8.06–8.03 (m, 8 H, Ar), 7.95 (dd, 2 H, *J* = 6.6, 4.0 Hz, Ar), 7.90 (dd, 2 H, *J* = 8.4, 1.2 Hz, Ar), 7.78 (dd, 2 H, *J* = 8.4, 1.2 Hz, Ar), 7.55–7.26 (m, 23 H, Ar), 7.04 (d, 2 H, *J* = 8.0 Hz, Ar), 6.05 (app dt, 1 H, *J* = 7.0, 3.7 Hz, H-5'), 5.93 (app dt, 1 H, *J* = 6.3, 4.5 Hz, H-5), 5.77 (d, 1 H, *J* = 1.0 Hz, H-1), 5.67 (dd, 1 H, *J* = 4.5, 2.4 Hz, H-3), 5.63 (dd, 1 H, *J* = 2.4, 1.0 Hz, H-2), 5.56 (dd, 1 H, *J* = 5.0, 1.0 Hz, H-3'), 5.42 (d, 1 H, *J* = 1.0 Hz, H-2'), 5.38 (s, 1 H, H-1'), 4.96 (app t, 1 H, *J* = 4.5 Hz, H-4), 4.75–4.71 (m, 2 H, H-4', H-6_a'), 4.64 (dd, 1 H, *J* = 11.9, 7.0 Hz, H-6_b'), 4.18 (dd, 1 H, *J* = 10.3, 6.3 Hz, H-6_a), 3.98 (dd, 1 H, *J* = 10.3, 6.3 Hz, H-6_b), 2.24 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C): 166.1 (C=O), 165.73 (C=O), 165.72 (C=O), 165.71 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 138.0 (Ar), 133.5 (Ar), 133.4 (Ar), 133.34 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.5 (Ar), 130.0 (Ar), 129.9 (Ar), 129.85 (Ar), 129.83 (Ar), 129.80 (Ar), 129.7 (Ar), 129.6 (Ar), 129.62 (Ar), 129.60 (Ar), 129.5 (Ar), 128.9 (Ar), 128.8 (Ar), 128.50 (Ar), 128.46 (Ar), 128.42 (Ar), 128.40 (Ar), 128.38 (Ar), 128.3 (Ar), 128.32 (Ar), 128.30 (Ar), 106.0 (C-1'), 91.4 (C-1), 82.5 (C-2), 82.02 (C-4'), 82.0 (C-2'), 81.6 (C-4), 77.8 (C-3), 77.6 (C-3'), 71.0 (C-5), 70.3 (C-5'), 65.6 (C-6), 63.8 (C-6') 21.0 (ArCH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₈H₅₆O₁₇S: 1199.3130. Found: 1199.3128

2,3,5,6-Tetra-*O*-benzoyl- β -D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-D-galactofuranose (51). To a solution of thioglycoside **50** (0.22 g, 0.18 mmol) in EtOAc (25 mL), was

added NBS (0.35 g, 1.80 mmol) and water (5 mL). The reaction mixture was allowed to stir for 4 h and then a saturated aqueous solution of sodium $\text{Na}_2\text{S}_2\text{O}_3$ was added. The organic layer was then washed with water, brine, dried and the solvent was evaporated. The crude product was purified by column chromatography (20:1 toluene–EtOAc) to obtain **51** (0.15 g, 74%, $\alpha:\beta = 1:3$) as an amorphous white solid. R_f 0.26 (20:1 toluene–EtOAc). The material had the same spectral properties as that reported previously.⁸

2,3,5,6-Tetra-*O*-benzoyl- β -D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-D-galactofuranosyl trichloroacetimidate (52). To a stirred solution of **51** (103.5 mg, 0.10 mmol) and trichloroacetonitrile (48.5 μL , 0.50 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C, was slowly added DBU (7.21 μL , 0.05 mmol). The reaction mixture was stirred at rt for 2 h and then concentrated at rt. The residue was purified by column chromatography (30:1:0.3 toluene–EtOAc– Et_3N) to furnish imidate **52** (85.0 mg, 85%, $\alpha:\beta = 1:9$) as an amorphous solid. R_f 0.60 (10:1 toluene–EtOAc). The material had the same spectral properties as that reported previously.⁸

***p*-Tolyl 2,3,5,6-tetra-*O*-benzoyl- β -D-galactofuranosyl (1→6)-2,3,5-tri-*O*-benzoyl- β -D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-1-thio- β -D-galactofuranoside (53).** Prepared from **28** (0.33 g, 0.27 mmol), donor **52** (0.12 g, 0.21 mmol), and activated, powdered 4 Å molecular sieves (0.35 g), TMSOTf (11.2 μL , 0.06 mmol) in CH_2Cl_2 (25 mL) as described for the synthesis of **50**. The residue was purified by column chromatography (30:1 toluene–EtOAc) to give trisaccharide **53** (0.26 g, 76%) as an amorphous white solid. R_f 0.54 (30:1

toluene–EtOAc); $[\alpha]_D -40.7$ (c 2.1, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ_{H}) 8.08–7.92 (m, 12 H, Ar), 7.86 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.81 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.75 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.51–7.16 (m, 34 H, Ar), 7.05 (d, 2 H, $J = 8.5$ Hz, Ar), 6.02 (app dt, 1 H, $J = 7.5, 4.0$ Hz, H-5''), 5.96–5.91 (m, 3 H, H-5', H-2, H-3''), 5.76 (s, 1 H, H-1), 5.71 (d, 1 H, $J = 2.5$ Hz, H-1'), 5.68 (app t, 1 H, $J = 2.5$ Hz, H-2''), 5.66–5.63 (m, 2 H, H-5, H-3), 5.55 (dd, 1 H, $J = 5.0, 1.0$ Hz, H-3'), 5.34 (d, 1 H, $J = 1.0$ Hz, H-2'), 5.24 (s, 1 H, H-1'), 4.90 (dd, 1 H, $J = 4.5, 4.5$ Hz, H-4), 4.79–4.67 (m, 6 H, H-4', H-4'', H-6_a', H-6_b', H-6_a'', H-6_b''), 4.09 (dd, 1 H, $J = 11.0, 6.5$ Hz, H-6_a), 3.97 (dd, 1 H, $J = 11.0, 6.5$ Hz, H-6_b), 2.37 (s, 3 H, ArCH_3); $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ_{C}): 166.1 (C=O), 166.0 (C=O), 165.8 (C=O), 165.7 (C=O), 165.68 (C=O), 165.56 (C=O), 165.52 (C=O), 165.3 (C=O), 165.2 (C=O), 165.2 (C=O), 138.0 (Ar), 133.7 (Ar), 133.6 (Ar), 133.52 (Ar), 133.48 (Ar), 133.3 (Ar), 133.29 (Ar), 133.22 (Ar), 133.19 (Ar), 133.12 (Ar), 133.08 (Ar), 133.05 (Ar), 133.02 (Ar), 133.0 (Ar), 132.93 (Ar), 132.89 (Ar), 132.88 (Ar), 132.7 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9 (Ar), 129.82 (Ar), 129.8 (Ar), 129.76 (Ar), 129.72 (Ar), 129.68 (Ar), 129.6 (Ar), 129.5 (Ar), 128.9 (Ar), 128.8 (Ar), 128.6 (Ar), 128.54 (Ar), 128.50 (Ar), 128.32 (Ar), 128.3 (Ar), 128.26 (Ar), 128.24 (Ar), 128.22 (Ar), 106.7 (C-1'), 105.8 (C-1''), 91.1 (C-1), 82.7 (C-2), 82.3 (C-2''), 82.0 (C-4'), 81.9 (C-2'), 81.9 (C-4''), 81.5 (C-4), 77.7 (C-3), 77.4 (C-3'), 77.3 (C-3''), 73.7 (C-5''), 71.8 (C-5), 70.5 (C-5'), 67.5 (C-6'), 64.6 (C-6''), 63.8 (C-6), 21.1 (ArCH_3). ESI-MS m/z calcd. for $[\text{M} + \text{Na}]^+$ $\text{C}_{95}\text{H}_{78}\text{O}_{25}\text{SNa}$: 1673.4445. Found: 1673.4441.

p-Tolyl 2,3,5,6-tetra-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl-1-thio- β -D-galactofuranoside (**54**). Prepared from **28** (0.26 g, 0.43 mmol), donor **49**⁷ (0.40 g, 0.53 mmol), and activated, powdered 4 Å molecular sieves (0.40 g) and TMSOTf (15.43 μ L, 0.06 mmol) in CH₂Cl₂ as described for the synthesis of **50**. The residue was purified by column chromatography (30:1 toluene–EtOAc) to give disaccharide **54** (0.43 g, 86%) as an amorphous white solid. *R*_f 0.25 (20:1 toluene–EtOAc); [α]_D –37.8 (*c* 0.7, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H): 8.04–7.83 (m, 14 H, Ar), 7.58–7.22 (m, 23 H, Ar), 7.20 (d, 2 H, *J* = 8.4 Hz, Ar), 6.01 (app dt, 1 H, *J* = 6.5, 4.5 Hz, H-5'), 5.90 (dd, 1 H, *J* = 3.0, 1.8 Hz, H-3), 5.77 (s, 1 H, H-1'), 5.71 (d, 1 H, *J* = 1.8 Hz, H-1), 5.68 (app t, 1 H, *J* = 1.8 Hz, H-2), 5.65 (d, 1 H, *J* = 1.2 Hz, H-2'), 5.62 (dd, 1 H, *J* = 4.5, 1.2 Hz, H-3'), 4.99 (app t, 1 H, *J* = 4.5 Hz, H-4'), 4.77 (dd, 1 H, *J* = 4.8, 3.0 Hz, H-4), 4.72–4.61 (m, 5 H, H-5, H-6_a, H-6_b, H-6_a', H-6_b'), 2.28 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C): 166.1 (C=O), 165.9 (C=O), 165.7 (C=O), 165.5 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 138.1 (Ar), 133.52 (Ar), 133.5 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.8 (Ar), 130.0 (Ar), 129.9 (Ar), 129.83 (Ar), 129.8 (Ar), 129.72 (Ar), 129.7 (Ar), 129.68 (Ar), 129.66 (Ar), 129.6 (Ar), 129.55 (Ar), 129.4 (Ar), 128.85 (Ar), 128.8 (Ar), 128.76 (Ar), 128.53 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.23 (Ar), 128.21 (Ar), 105.4 (C-1'), 91.2 (C-1), 82.3 (C-4), 82.2 (C-4'), 82.1 (C-2'), 81.5 (C-2), 77.8 (C-3), 77.1 (C-3'), 73.4 (C-5), 70.5 (C-5'), 64.4 (C-6'), 63.8 (C-6), 21.1 (ArCH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₆₈H₅₆O₁₇S: 1199.3130. Found: 1199.3128.

2,3,5,6-Tetra-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,5-tri-*O*-benzoyl-D-galactofuranose (55). Prepared from thioglycoside **54** (104.2 mg, 0.09 mmol), NBS (157.6 mg, 0.90 mmol), water (2 mL) in EtOAc (25 mL) as described for the synthesis of **51**. The crude product was purified by column chromatography to give **55** (68.0 mg, 72%, α : β = 1:3) as a syrup. R_f 0.11 (15:1 toluene–EtOAc); $[\alpha]_D -20.0$ (c 1.0, CHCl₃); The material had the same spectral properties as that reported previously.⁹

2,3,5,6-Tetra-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl-D-galactofuranosyl trichloroacetimidate (56). To a stirred solution of **55** (48.0 mg, 0.04 mmol) and trichloroacetonitrile (33.7 μ L, 0.33 mmol) in CH₂Cl₂ (5 mL) cooled to 0 °C, was slowly added DBU (3.41 μ L, 0.02 mmol). The reaction mixture was stirred at rt for 3 h and then concentrated. The residue was purified by column chromatography (30:1:0.3 toluene–EtOAc–Et₃N) to furnish imidate **56** (40.2 mg, 74%, α : β = 1:9) as an amorphous solid. R_f 0.60 (10:1 toluene–EtOAc); Data for β -anomer: ¹H NMR (CDCl₃, 500 MHz, δ_H) 8.76 (s, 1 H, NH), 8.06–7.16 (m, 35 H, Ar), 6.68 (br s, 1 H, H-1), 6.01 (app dt, 1 H, J = 6.5, 5.0 Hz, H-5'), 5.93 (dd, 1 H, J = 3.0, 1.8 Hz H-3), 5.78 (s, 1 H, H-1'), 5.76 (app t, 1 H, J = 1.8 Hz, H-2), 5.62 (d, 1 H, J = 1.2 Hz, H-2'), 5.56 (d, 1 H, J = 4.8 Hz, H-3'), 4.99 (dd, 1 H, J = 5.0, 4.5 Hz, H-4'), 4.82–4.78 (m, 6 H, H-4, H-5, H-6_a', H-6_b', H-6_a, H-6_b); ¹³C NMR (125 MHz, CDCl₃, δ_C): 166.0 (C=O), 165.6 (C=O), 165.6 (C=O), 165.44 (C=O), 165.42 (C=O), 165.40 (C=O), 165.0 (C=O), 160.4 (C=NH), 133.5 (Ar), 133.4 (Ar), 133.34 (Ar), 133.30 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.5 (Ar), 130.0 (Ar), 129.9 (Ar), 129.82 (Ar), 129.81 (Ar), 129.80 (Ar), 129.7 (Ar),

129.64 (Ar), 129.63 (Ar), 129.60 (Ar), 129.5 (Ar), 128.9 (Ar), 128.8 (Ar), 128.5 (Ar), 128.5 (Ar), 128.42 (Ar), 128.41 (Ar), 128.40 (Ar), 128.32 (Ar), 128.31 (Ar), 128.30 (Ar), 106.7 (C-1'), 105.1 (C-1), 83.4 (C-2), 81.8 (C-2'), 81.6 (C-4'), 80.9 (C-4), 77.5 (C-3), 76.9 (C-3'), 70.9 (C-5), 70.2 (C-5'), 65.6 (C-6'), 63.9 (C-6). ESI-MS m/z calcd. for $[M + Na]^+ C_{63}H_{50} Cl_3NO_{18}$: 1236.2030. Found: 1236.2032.

***p*-Tolyl 2,3,5,6-tetra-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-*O*-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 6)-2,3,5-tri-*O*-benzoyl-1-thio- β -D-galactofuranoside (57).**

Prepared from **27** (13.7 mg, 0.02 mmol), donor **56** (36.2 mg, 0.03 mmol), activated, powdered 4 Å molecular sieves (35.0 mg) and TMSOTf (1.24 μ L, 0.006 mmol) in CH_2Cl_2 (5 mL) as described for the synthesis of **50**. The residue was purified by column chromatography (30:1 toluene–EtOAc) to give trisaccharide **57** (27.2 mg, 72%) as an amorphous white solid. R_f 0.33 (15:1 toluene–EtOAc); $[\alpha]_D -8.3$ (c 0.2, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$, δ_H): 8.08–7.92 (m, 9 H, Ar), 7.86 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.81 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.75 (dd, 2 H, $J = 8.5, 1.5$ Hz, Ar), 7.51–7.16 (m, 37 H, Ar), 7.05 (d, 2 H, $J = 8.5$ Hz, Ar), 6.04 (app dt, 1 H, $J = 7.5, 4.5$ Hz, H-5''), 5.91 (app dt, 1 H, $J = 6.5, 4.4$ Hz, H-5), 5.80 (br s, 2 H, H-1'', H-3'), 5.73 (d, 1 H, $J = 1.5$ Hz, H-1), 5.69 (d, 1 H, $J = 1.5$ Hz, H-2''), 5.64 (dd, 1 H, $J = 4.4, 1.5$ Hz, H-3), 5.62 (app t, 1 H, $J = 1.5$ Hz, H-2), 5.61 (dd, 1 H, $J = 3.5, 1.5$ Hz, H-3''), 5.46 (d, 1 H, $J = 1.3$ Hz, H-2'), 5.28 (s, 1 H, H-1'), 5.06 (dd, 1 H, $J = 4.5, 3.5$ Hz, H-4''), 4.91 (app t, 1 H, $J = 4.4$ Hz, H-4), 4.76 (dd, 1 H, $J = 12.0, 7.5$ Hz, H-6_a''), 4.71–4.64 (m, 4 H, H-5', H-6_b'', H-6_a', H-6_b'), 4.59 (dd, 1 H, $J = 4.7, 3.5$ Hz, H-4'), 4.14 (dd, 1 H, $J = 10.2, 6.5$ Hz, H-6_a), 3.93 (dd, 1 H, $J =$

10.2, 6.5 Hz, H-6_b), 2.20 (s, 3 H, ArCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_c): 166.0 (C=O), 166.0 (C=O), 165.9 (C=O), 165.69 (C=O), 165.67 (C=O), 165.5 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 165.1 (C=O), 137.0 (Ar), 133.4 (Ar), 133.35 (Ar), 133.26 (Ar), 133.2 (Ar), 133.14 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.86 (Ar), 132.3 (Ar), 130.1 (Ar), 130.0 (Ar), 129.96 (Ar), 129.93 (Ar), 129.84 (Ar), 129.82 (Ar), 129.82 (Ar), 129.8 (Ar), 129.72 (Ar), 129.68 (Ar), 129.67 (Ar), 129.63 (Ar), 129.6 (Ar), 129.0 (Ar), 128.92 (Ar), 128.9 (Ar), 128.83 (Ar), 128.8 (Ar), 128.5 (Ar), 128.43 (Ar), 128.41 (Ar), 128.34 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 105.9 (C-1''), 105.2 (C-1'), 91.3 (C-1), 83.2 (C-4'), 82.5 (C-2), 82.1 (C-2''), 81.9 (C-4''), 81.7 (C-4), 81.5 (C-2'), 77.9 (C-3''), 77.8 (C-3), 77.6 (C-3'), 72.6 (C-5'), 70.9 (C-5''), 70.6 (C-5), 65.5 (C-6), 65.0 (C-6'), 63.8 (C-6''), 29.8 (ArCH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₅H₇₈O₂₅S: 1673.4445. Found: 1673.4441.

Octyl 2,3-Isopropylidene- α -L-rhamnopyranosyl-(1 \rightarrow 3)-2-acetamido-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside (58). To a solution of **62** (50.0 mg, 0.09 mmol) in acetone (5 mL) was added 2,2-dimethoxypropane (27.03 μ L, 0.22 mmol) and (1*S*)-(+)-camphorsulfonic acid (2.1 mg, 0.009 mmol). After 3 h of stirring, the pH of the solution was adjusted to 7 by adding Et₃N. Concentration gave a crude oil that was subsequently dissolved in CH₂Cl₂ (10 mL), washed with a saturated aqueous solution of NaHCO₃ and water. The organic layer was dried, concentrated to an oil and the residue was purified by column chromatography (2:1 hexanes–EtOAc) to furnish **58** (46.0 mg, 86%) as an amorphous white solid. *R_f* 0.59 (10:1 CH₂Cl₂–MeOH); [α]_D +2.6 (*c* 0.5, CHCl₃); ¹H NMR (500

MHz, CDCl₃, δ_H): 7.48–7.46 (m, 2 H, Ar), 7.35–7.33 (m, 3 H, Ar), 5.69 (d, 1 H, *J* = 10.0 Hz, NH), 5.51 (s, 1 H, PhCH), 5.05 (s, 1 H, H-1'), 4.71 (d, 1 H, *J* = 3.8 Hz, H-1), 4.40 (app dt, 1 H, *J* = 10.0, 3.8 Hz, H-2), 4.27 (app t, 1 H, *J* = 10.0 Hz, H-3), 4.10 (d, 1 H, *J* = 6.5 Hz, H-2'), 4.01 (dd, 1 H, *J* = 7.3, 6.5 Hz, H-3'), 3.99 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.88–3.68 (m, 4 H, H-6_a, H-6_b, H-5', octyl OCH₂), 3.59 (app dt, 1 H, *J* = 10.0, 5.0 Hz, H-5), 3.40 (app dt, 1 H, *J* = 9.8, 6.6 Hz, octyl OCH₂), 3.25 (dd, 1 H, *J* = 10.0, 7.3 Hz, H-4'), 2.02 (s, 3 H, C(=O)CH₃), 1.62–1.60 (m, 2 H, octyl OCH₂), 1.47 (s, 3 H, isopropylidene CH₃), 1.32–1.26 (m, 13 H, octyl CH₂, isopropylidene CH₃), 0.90 (t, 3 H, *J* = 6.9 Hz, octyl CH₃), 0.80 (d, 3 H, *J* = 6.2 Hz, H-6'); ¹³C NMR (125 MHz, CDCl₃, δ_C): 169.8 (C=O), 137.1 (Ar), 129.1 (Ar), 128.1 (Ar), 126.3 (Ar), 109.3 ((CH₃)₂C), 102.0 (PhCH), 98.3 (C-1'), 98.2 (C-1), 80.0 (C-4), 78.1 (C-3), 75.9 (C-2'), 75.0 (C-3'), 74.5 (C-4'), 68.9 (C-6), 68.3 (octyl OCH₂), 66.1 (C-5), 63.2 (C-5'), 53.6 (C-2), 31.8 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 27.9 (isopropylidene CH₃), 26.2 (octyl CH₂), 26.1 (isopropylidene CH₃), 23.4 (C(=O)CH₃), 22.6 (octyl CH₂), 16.8 (C-6'), 14.1 (octyl CH₃).

ESI-MS *m/z* calcd. for [M + Na]⁺ C₃₂H₄₉NO₁₀: 630.3249. Found: 630.3249.

Octyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside (61). Prepared from **59**¹⁰ (0.13 g, 0.31 mmol), donor **60**¹¹ (0.13 g, 0.40 mmol), activated, powdered 4 Å molecular sieves (365.0 mg), NIS (0.10 g, 0.46 mmol) and AgOTf (15.7 mg, 0.06 mmol) in CH₂Cl₂ (10 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (1:1 hexanes–EtOAc) to afford disaccharide **61** (0.19 g, 89%) as an amorphous white solid. *R_f* 0.28 (1:1

hexanes–EtOAc); $[\alpha]_D +32.5$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 7.52–7.50 (m, 2 H, Ar), 7.39–7.34 (m, 3 H, Ar), 5.63 (d, 1 H, *J* = 10.0 Hz, NH), 5.56 (s, 1 H, PhCH), 5.32 (dd, 1 H, *J* = 10.0, 3.5 Hz, H-3'), 4.98 (dd, 1 H, *J* = 3.5, 1.7 Hz, H-2'), 4.95–4.91 (m, 2 H, H-1', H-4'), 4.71 (d, 1 H, *J* = 3.6 Hz, H-1), 4.42 (app dt, 1 H, *J* = 10.0, 3.6 Hz, H-2), 4.26 (app dt, 1 H, *J* = 10.0, 4.5 Hz, H-5), 4.08–4.05 (m, 1 H, H-5'), 3.88 (app t, 1 H, *J* = 10.0 Hz, H-3), 3.83 (dd, 1 H, *J* = 10.0, 4.5 Hz, H-6_a), 3.76 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.71–3.65 (m, 2 H, H-6_b, octyl OCH₂), 3.38 (app dt, 1 H, *J* = 9.8, 6.7 Hz, octyl OCH₂), 2.09 (s, 3 H, C(=O)CH₃), 2.06 (s, 3 H, C(=O)CH₃), 1.98 (s, 3 H, C(=O)CH₃), 1.96 (s, 3 H, C(=O)CH₃), 1.61–1.58 (m, 2 H, octyl CH₂), 1.32–1.24 (m, 10 H, octyl CH₂), 0.89 (t, 3 H, *J* = 7.0 Hz, octyl CH₃), 0.69 (d, 3 H, *J* = 6.5 Hz, H-6'); ¹³C NMR (125 MHz, CDCl₃, δ_C): 170.3 (C=O), 170.1 (C=O), 170.0 (C=O), 169.8 (C=O), 137.2 (Ar), 129.1 (Ar), 128.1 (Ar), 126.4 (Ar), 102.0 (PhCH), 98.3 (C-1), 97.8 (C-1'), 80.3 (C-4), 76.0 (C-3), 71.5 (C-4'), 70.9 (C-2'), 69.0 (C-6), 68.5 (C-3'), 68.3 (octyl OCH₂), 66.3 (C-5'), 63.1 (C-5), 53.0 (C-2), 31.8 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.2 (octyl CH₂), 22.6 (octyl CH₂), 20.9 (2 x C(=O)CH₃), 20.7 (C(=O)CH₃), 16.6 (C-6'), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for (M + H⁺) C₃₅H₅₂NO₁₃: 694.3433. Found: 694.3408.

Octyl α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (62). Prepared from **61** (88.5 mg, 0.13 mmol) in 3:1 MeOH–CH₂Cl₂ (5 mL) and NaOMe in MeOH (0.1 M) as described for the synthesis of **24**. The residue was purified by column chromatography (9:1 CH₂Cl₂–MeOH) to afford **62** (52.0 mg, 72%) as an amorphous solid. *R_f* 0.24 (10:1 CH₂Cl₂–MeOH); $[\alpha]_D +3.9$ (*c* 0.3, MeOH); ¹H NMR (500 MHz, CD₃OD,

δ_{H}): 7.52–7.50 (m, 2 H, Ar), 7.39–7.34 (m, 3 H, Ar), 5.58 (s, 1 H, PhCH), 4.81 (br s, 1 H, H-1'), 4.71 (d, 1 H, $J = 3.7$ Hz, H-1), 4.22–4.18 (m, 2 H, H-2, H-4), 3.90 (app t, 1 H, $J = 9.4$ Hz, H-3), 3.86–3.70 (m, 3 H, H-5, H-5', octyl OCH₂), 3.67 (dd, 1 H, $J = 3.4, 1.8$ Hz, H-2'), 3.65–3.61 (m, 2 H, H-3', H-4'), 3.57 (dd, 1 H, $J = 9.6, 3.4$ Hz, H-6_a), 3.45 (app dt, 1 H, $J = 9.8, 6.4$ Hz, octyl OCH₂), 3.23 (app t, 1 H, $J = 9.6$ Hz, H-6_b), 2.00 (s, 3 H, C(=O)CH₃), 1.69–1.64 (m, 2 H, octyl CH₂), 1.43–1.28 (m, 10 H, octyl CH₂), 0.90 (t, 3 H, $J = 6.8$ Hz, octyl CH₃), 0.70 (d, 3 H, $J = 6.4$ Hz, H-6'); ¹³C NMR (125 MHz, CD₃OD, δ_{C}): 173.4 (C=O), 139.1 (Ar), 130.0 (Ar), 129.1 (Ar), 127.7 (Ar), 103.3 (PhCH), 102.6 (C-1), 99.6 (C-1'), 81.9 (C-4), 76.7 (C-3), 73.8 (C-4'), 72.5 (C-2'), 72.2 (C-6), 69.9 (C-3'), 69.8 (octyl OCH₂), 69.4 (C-5'), 64.5 (C-5), 55.3 (C-2), 33.0 (octyl CH₂), 30.52 (octyl CH₂), 30.51 (octyl CH₂), 30.4 (octyl CH₂), 27.3 (octyl CH₂), 23.7 (octyl CH₂), 22.6 (C(=O)CH₃), 17.6 (C-6'), 14.4 (octyl CH₃). ESI-MS m/z calcd for [M + Na]⁺ C₂₉H₄₅NO₁₀Na: 590.2936. Found. 590.2933.

Octyl 2,3,4,5-tetra-*O*-benzoyl- β -D-galactofuranosyl-(1→4)-2,3-isopropylidene- α -L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside (63). Prepared from **58** (44.8 mg, 0.07 mmol), donor **17** (56.9 mg, 0.08 mmol), activated, powdered 4 Å molecular sieves (70.0 mg), NIS (24.9 mg, 0.11 mmol) and AgOTf (3.8 mg, 0.01 mmol) in CH₂Cl₂ (5 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (10:1 toluene–EtOAc) to give trisaccharide **63** (74.0 mg, 85%) as an amorphous white solid. R_f 0.18 (10:1 toluene–EtOAc); $[\alpha]_{\text{D}} -32.4$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_{H}): 8.03–7.92 (m, 8 H, Ar), 7.57–7.25 (m, 15 H, Ar), 7.25–7.16 (m, 2 H, Ar),

6.05 (app dt, 1 H, $J = 7.5, 4.8$ Hz, H-5''), 5.78 (s, 1 H, H-1''), 5.70 (d, 1 H, $J = 10.0$ Hz, NH), 5.58 (dd, 1 H, $J = 4.8, 1.0$ Hz, H-3''), 5.53 (d, 1 H, $J = 5.0$ Hz, PhCH), 5.52 (d, 1 H, $J = 1.0$ Hz, H-2''), 5.10 (s, 1 H, H-1'), 4.73–4.71 (m, 3 H, H-1, H-6_a'', H-6_b''), 4.59 (app t, 1 H, $J = 4.8$ Hz, H-4''), 4.42 (app dt, 1 H, $J = 10.0, 3.7$ Hz, H-2), 4.31–4.26 (m, 2 H, H-3', H-5), 4.09–4.06 (m, 1 H, H-2'), 4.02–3.93 (m, 2 H, H-3, H-6_a), 3.85 (dd, 1 H, $J = 9.7, 4.4$ Hz, H-6_b), 3.78–3.69 (m, 2 H, H-5', octyl OCH₂), 3.64–3.53 (m, 2 H, H-4, H-4'), 3.41 (app dt, 1 H, $J = 9.5, 6.7$ Hz, octyl OCH₂), 3.33 (s, 3 H, C(=O)CH₃), 1.67–1.63 (m, 2 H, octyl CH₂), 1.48 (s, 3 H, isopropylidene CH₃), 1.35–1.25 (m, 13 H, isopropylidene CH₃, octyl CH₂), 0.92 (t, 3 H, $J = 6.9$ Hz, octyl CH₃), 0.82 (d, 3 H, $J = 6.2$ Hz, H-6'); ¹³C NMR (125 MHz, CDCl₃, δ_C): 169.8 (C=O), 166.0 (C=O), 165.7 (2 x C=O), 165.3 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.4 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 ((CH₃)₂C), 104.1 (C-1''), 101.7 (PhCH), 98.2 (C-1), 98.0 (C-1'), 82.2 (C-2''), 81.5 (C-4''), 80.0 (C-4), 78.1 (C-3''), 77.7 (C-3'), 76.5 (C-2'), 76.2 (C-3), 74.9 (C-4'), 70.4 (C-5''), 68.9 (C-6), 68.3 (octyl OCH₂), 64.4 (C-5), 63.4 (C-6''), 63.2 (C-5'), 53.6 (C-2), 31.8 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 29.24 (octyl CH₂), 29.21 (octyl CH₂), 27.8 (C(=O)CH₃), 26.4 (isopropylidene CH₃), 26.2 (isopropylidene CH₃), 22.7 (octyl CH₂), 17.2 (C-6'), 14.1 (octyl CH₃). ESI-MS m/z calcd. for (M + Na) C₆₆H₇₅NO₁₉Na: 1208.4826. Found: 1208.4831.

Octyl 2,3,4,5-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-

O-benzylidene-2-deoxy- α -D-glucopyranoside (64). Prepared from **58** (48.0 mg, 0.08 mmol), donor **58** (139.5 mg, 0.12 mmol), activated, powdered 4 Å molecular sieves (250.0 mg), NIS (30.2 mg, 0.13 mmol), AgOTf (4.1 mg, 0.02 mmol) in CH₂Cl₂ (5 mL) as described for the synthesis of **30**. The resulting residue was purified by column chromatography (2:1 hexanes–EtOAc) to give tetrasaccharide **64** (94.4 mg, 75%) as an oil. *R_f* 0.37 (1:1 hexanes–EtOAc); [α]_D –20.6 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H): 8.03–7.92 (m, 12 H, Ar), 7.84–7.80 (m, 4 H, Ar), 7.57–7.10 (m, 24 H, Ar), 6.03 (app dt, 1 H, *J* = 7.5, 5.0 Hz, H-5'''), 5.82 (dd, 1 H, *J* = 5.5, 1.2 Hz, H-3''), 5.81 (s, 1 H, H-1'''), 5.75 (s, 1 H, H-1''), 5.72 (d, 1 H, *J* = 10.0 Hz, NH), 5.65 (d, 1 H, *J* = 1.2 Hz, H-2''), 5.64 (dd, 1 H, *J* = 5.0, 1.3 Hz, H-3'''), 5.56 (d, 1 H, *J* = 1.3 Hz, H-2'''), 5.54 (s, 1 H, PhCH), 5.11 (s, 1 H, H-1'), 5.03 (app t, 1 H, *J* = 5.0 Hz, H-4'''), 4.78–4.64 (m, 6 H, H-1, H-5'', H-6_a'', H-6_b'', H-6_a''', H-6_b'''), 4.45–4.40 (m, 2 H, H-4'', H-2), 4.30–4.27 (m, 2 H, H-3', H-6_a), 4.10–4.06 (m, 1 H, H-2'), 4.00 (app t, 1 H, *J* = 10.0 Hz, H-3), 3.96–3.92 (m, 1 H, H-5'), 3.86 (app dt, 1 H, *J* = 10.0, 4.7 Hz, H-5), 3.78–3.69 (m, 2 H, H-6_b, octyl OCH₂), 3.61 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.57 (dd, 1 H, *J* = 10.0, 7.6 Hz, H-4'), 3.41 (app dt, 1 H, *J* = 9.8, 6.7 Hz, octyl OCH₂), 2.03 (s, 3 H, C(=O)CH₃), 1.65–1.58 (m, 2 H, octyl CH₂), 1.53 (s, 3 H, isopropylidene CH₃), 1.39–1.25 (m, 13 H, octyl CH₂, isopropylidene CH₃), 0.90 (t, 3 H, *J* = 7.0 Hz, octyl CH₃), 0.86 (d, 3 H, *J* = 6.0 Hz, H-6'); ¹³C NMR (125 MHz, CDCl₃, δ _C): 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.8 (Ar), 130.0 (Ar), 129.9 (Ar), 129.81 (Ar), 129.76 (Ar), 129.73 (Ar), 129.7 (Ar),

129.63 (Ar), 129.6 (Ar), 129.0 (Ar), 128.97 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.28 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 109.3 ((CH₃)₂C), 105.5 (C-1'''), 104.0 (C-1''), 101.7 (PhCH), 98.2 (C-1), 98.1 (C-1'), 82.8 (C-4''), 82.2 (C-4'''), 82.0 (C-2'''), 81.9 (C-2''), 80.0 (C-4), 77.8 (C-3), 77.7 (C-3'''), 77.6 (C-3'), 76.4 (C-2'), 76.2 (C-4'), 74.8 (C-3''), 72.8 (C-5''), 70.5 (C-5'''), 68.9 (C-6), 68.3 (octyl OCH₂), 64.8 (C-6'''), 64.4 (C-5), 63.7 (C-6''), 63.1 (C-5'), 53.6 (C-2), 31.8 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 27.9 (C(=O)CH₃), 26.3 (isopropylidene CH₃), 26.2 (octyl CH₂), 23.4 (isopropylidene CH₃), 22.6 (octyl CH₂), 17.2 (C-6'), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₉₃H₉₇NO₂₇Na: 1682.6140. Found: 1682.6145.

Octyl 2,3,4,5-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (65). Prepared from **58** (12.3 mg, 0.02 mmol), donor **53** (50.1 mg, 0.03 mmol), activated, powdered 4 Å molecular sieves (150.0 mg), NIS (11.4 mg, 0.05 mmol) and AgOTf (2.6 mg, 0.01 mmol) in CH₂Cl₂ (5 mL) as described for the synthesis of **30**. The residue was purified by column chromatography (2:1 hexanes–EtOAc) to give pentasaccharide **65** (33.0 mg, 77%) as an oil. *R_f* 0.23 (1:1 hexanes–EtOAc); [α]_D –7.8 (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H): 8.01–7.92 (m, 13 H, Ar), 7.80 (dd, 4 H, *J* = 10.0, 3.0 Hz, Ar), 7.74 (d, 2 H, *J* = 7.5 Hz, Ar), 7.50–7.06 (m, 36 H, Ar), 6.02 (app dt, 1 H, *J* = 8.0, 4.5 Hz, H-5'''), 5.91 (app dt, 1 H, *J* = 8.0, 4.0 Hz, H-5''''), 5.81 (d, 1 H, *J* = 5.5 Hz, H-3''), 5.77 (s, 1 H, H-1'''), 5.75 (s, 1 H,

H-1'''), 5.64–5.63 (m, 2 H, H-3''''', H-2'''''), 5.56–5.53 (m, 3 H, H-3''', H-2'', H-1''), 5.32 (s, 1 H, H-2'''), 5.23 (s, 1 H, PhCH), 5.10 (s, 1 H, H-1'), 4.85 (app t, 1 H, $J = 4.0$ Hz, H-4'''''), 4.73–4.65 (m, 8 H, H-1, H-5'', H-4''', H-6_a'', H-6_b'', H-6_a'''', H-6_b''''), 4.42–4.38 (m, 2 H, H-2, H-4''), 4.29–4.26 (m, 2 H, H-3', H-6_a), 4.12–4.08 (m, 2 H, H-2', H-6_a''''), 4.01–3.83 (m, 4 H, H-3, H-5', H-6_b'''', H-5), 3.77–3.68 (m, 2 H, H-6_b, octyl OCH₂), 3.61 (app t, 1 H, $J = 9.0$ Hz, H-4), 3.54 (dd, 1 H, $J = 10.0, 7.5$ Hz, H-4'), 3.39 (app dt, 1 H, $J = 9.5, 6.8$ Hz, octyl OCH₂), 2.02 (s, 3 H, C(=O)CH₃), 1.63–1.56 (m, 2 H, octyl CH₂), 1.43 (s, 3 H, isopropylidene CH₃), 1.33–1.26 (m, 13 H, octyl CH₂, isopropylidene CH₃), 0.92 (t, 3 H, $J = 7.0$ Hz, octyl CH₃), 0.83 (d, 3 H, $J = 6.0$ Hz, C-6'); ¹³C NMR (125 MHz, CDCl₃, δ_c): 169.8 (C=O), 166.1 (C=O), 166.0 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.3 (C=O), 165.2 (C=O), 165.0 (C=O), 137.1 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.89 (Ar), 132.86 (Ar), 129.94 (Ar), 129.9 (Ar), 129.82 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.6 (Ar), 129.1 (Ar), 128.9 (Ar), 128.54 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 ((CH₃)₂C), 106.7 (C-1'''''), 105.8 (C-1'''), 104.0 (C-1''), 101.7 (PhCH), 98.2 (C-1'), 98.1 (C-1), 82.6 (C-4'''''), 82.0 (C-4'''), 81.9 (2 C, C-2'', C-2'), 81.8 (C-2'''''), 80.1 (C-4), 77.8 (C-3''), 77.8 (C-3'), 77.6 (C-3'''''), 77.4 (C-3'''), 76.4 (C-3), 76.2 (C-4'), 74.9 (C-2'), 73.1 (C-5''), 71.8 (C-5'''), 70.5 (C-5'''''), 68.9 (C-6), 68.3 (octyl OCH₂), 67.7 (C-6'''''), 64.9 (C-6'''), 64.4 (C-5'), 63.7 (C-6''), 63.2 (C-5), 53.6 (C-2), 31.8 (octyl CH₂), 29.7 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 27.9 (isopropylidene CH₃), 26.4 (isopropylidene CH₃), 26.2 (octyl CH₂), 23.4 (C(=O)CH₃), 22.6

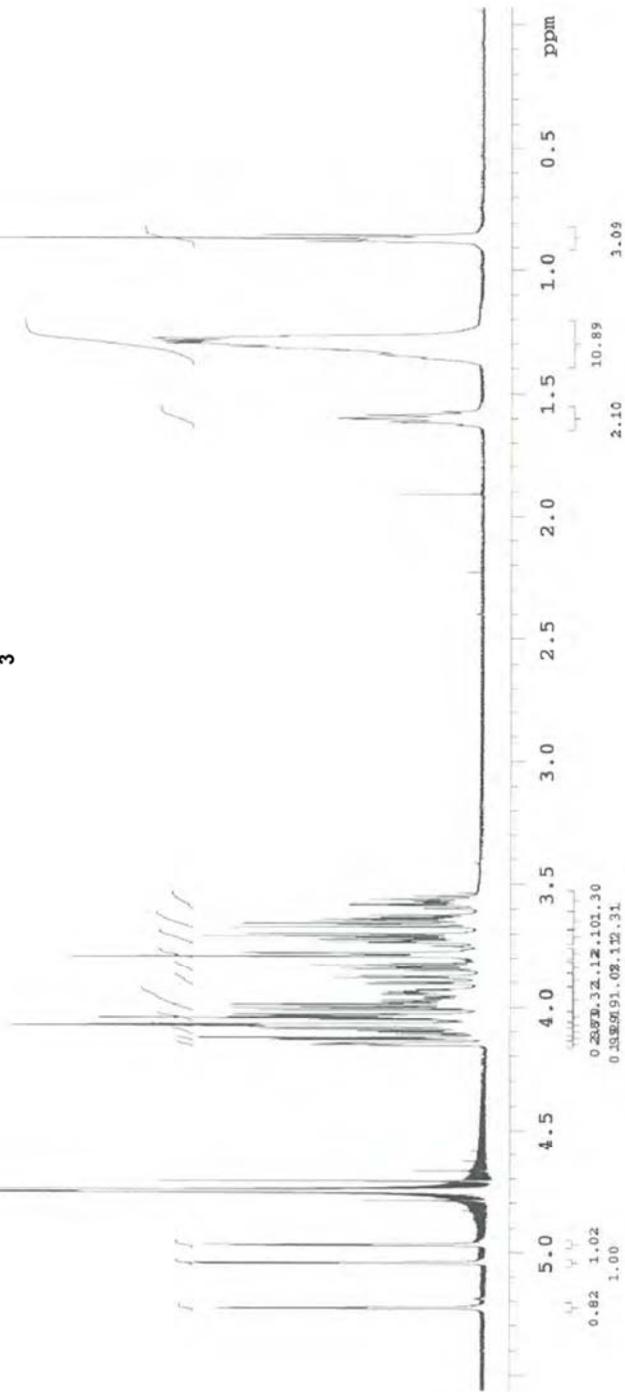
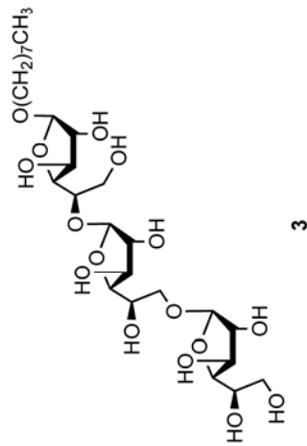
(octyl CH₂), 17.2 (C-6'), 14.1 (octyl CH₃). ESI-MS *m/z* calcd. for [M + Na]⁺ C₁₂₀H₁₁₉NO₃₅Na: 2157.75. Found: 2157.80.

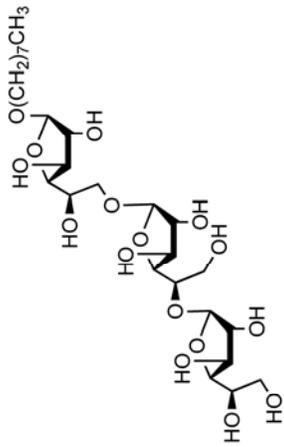
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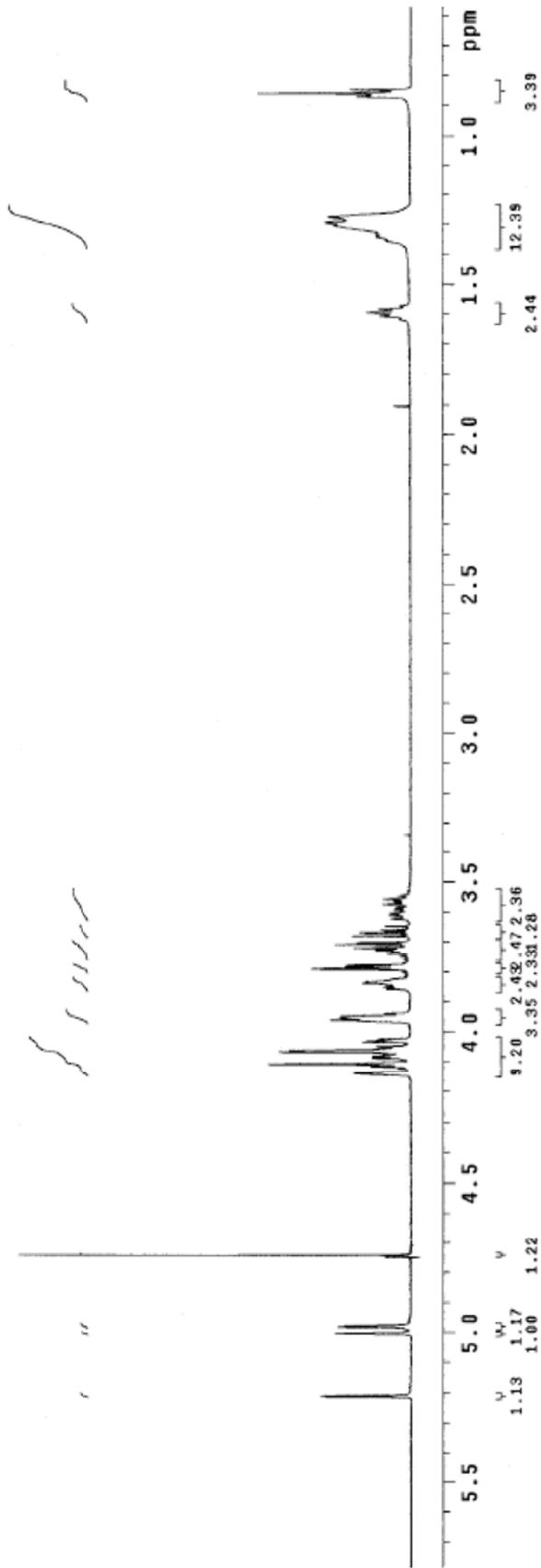
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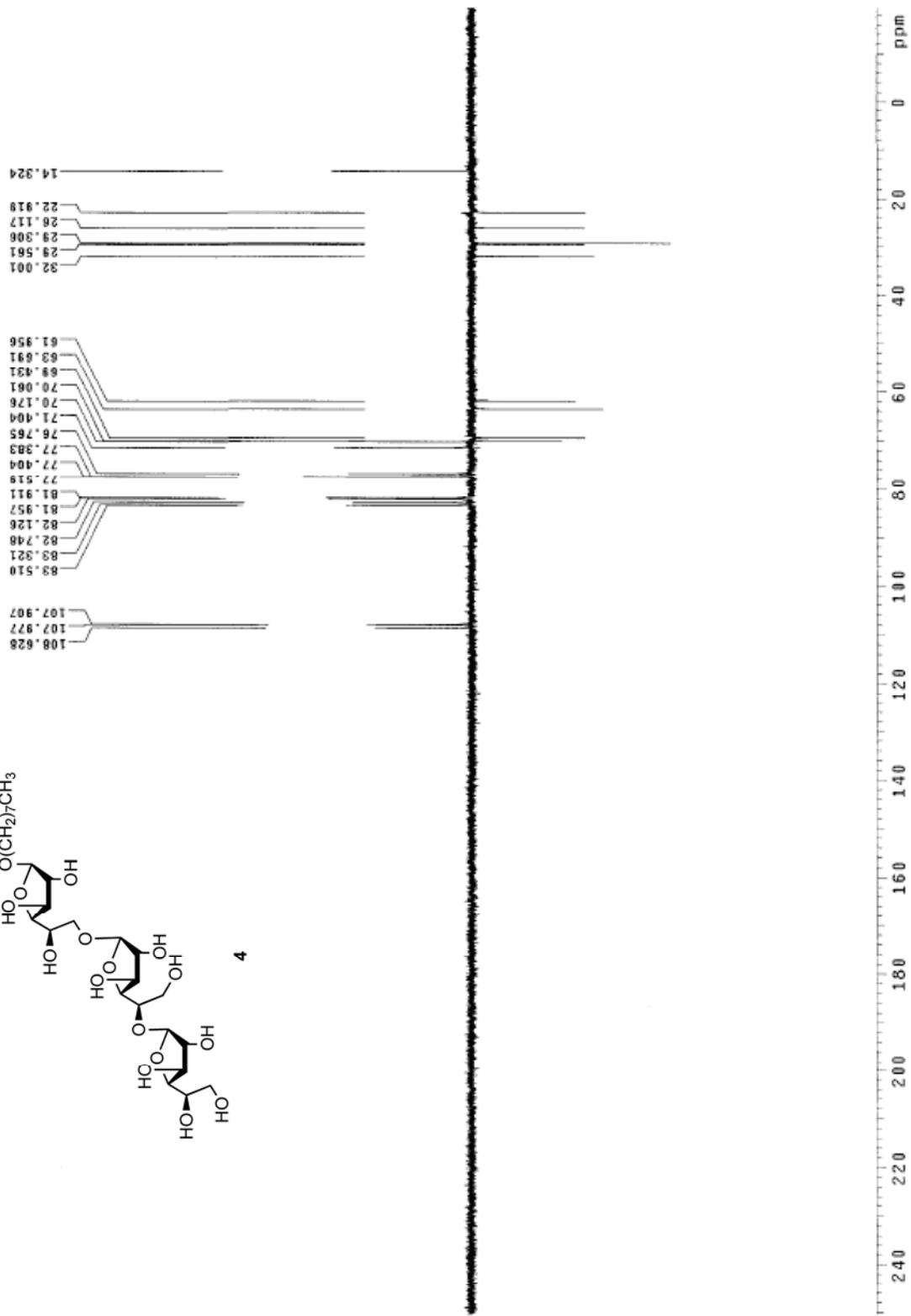
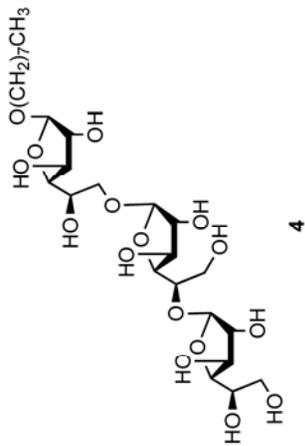
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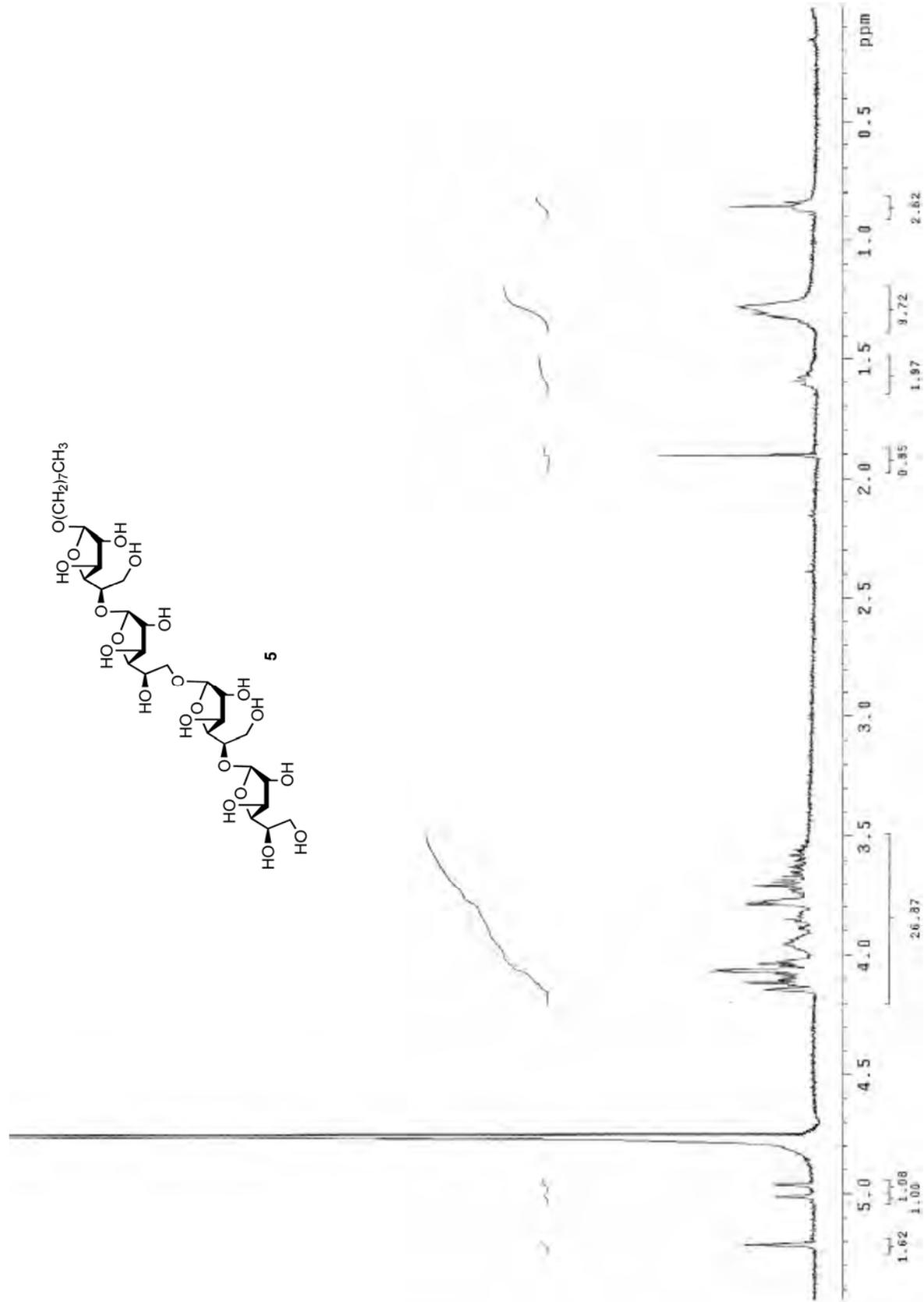


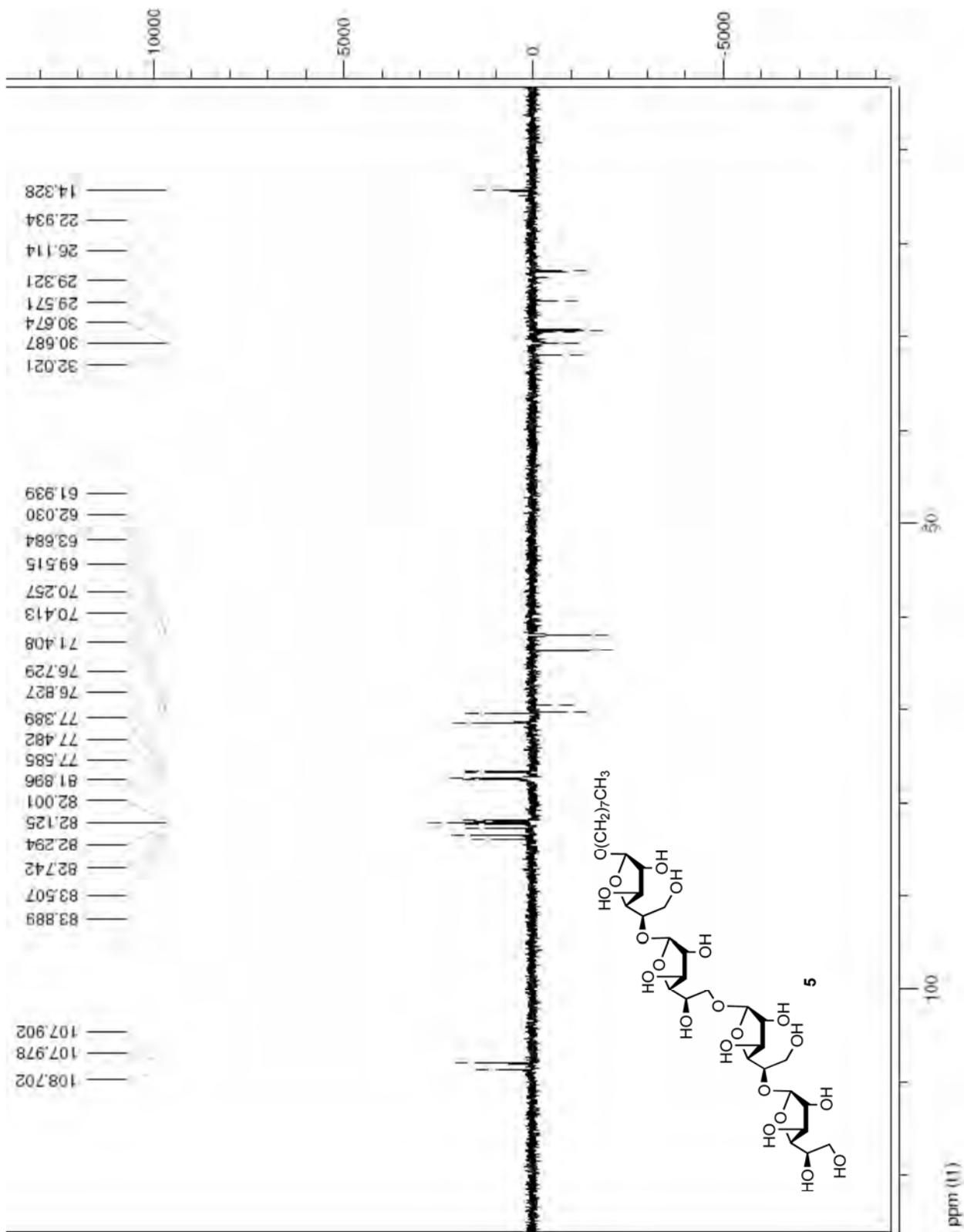


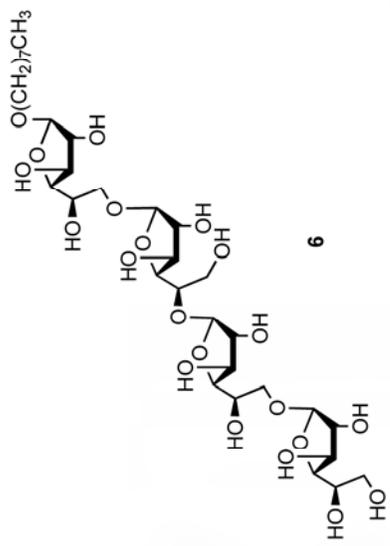
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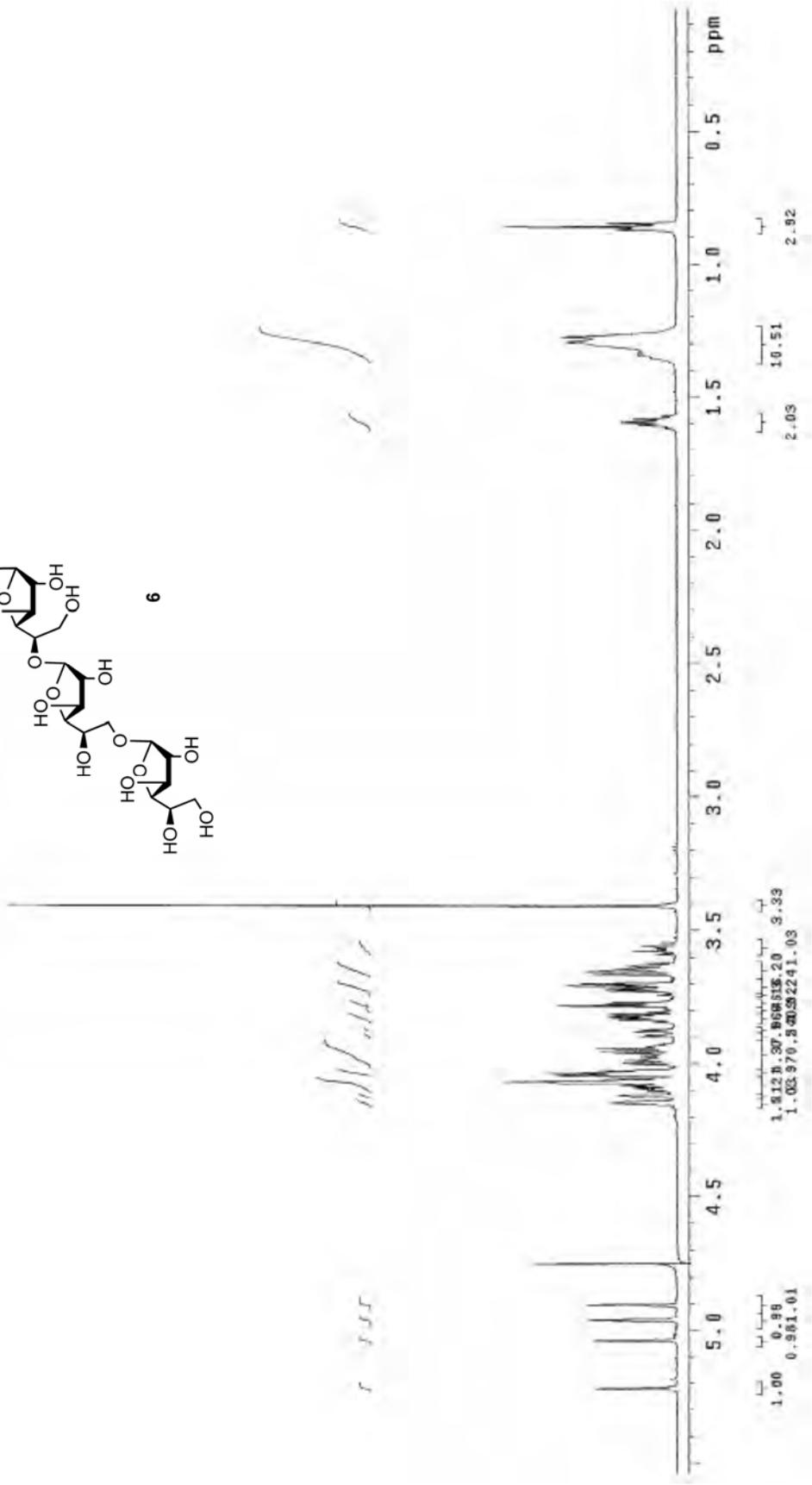


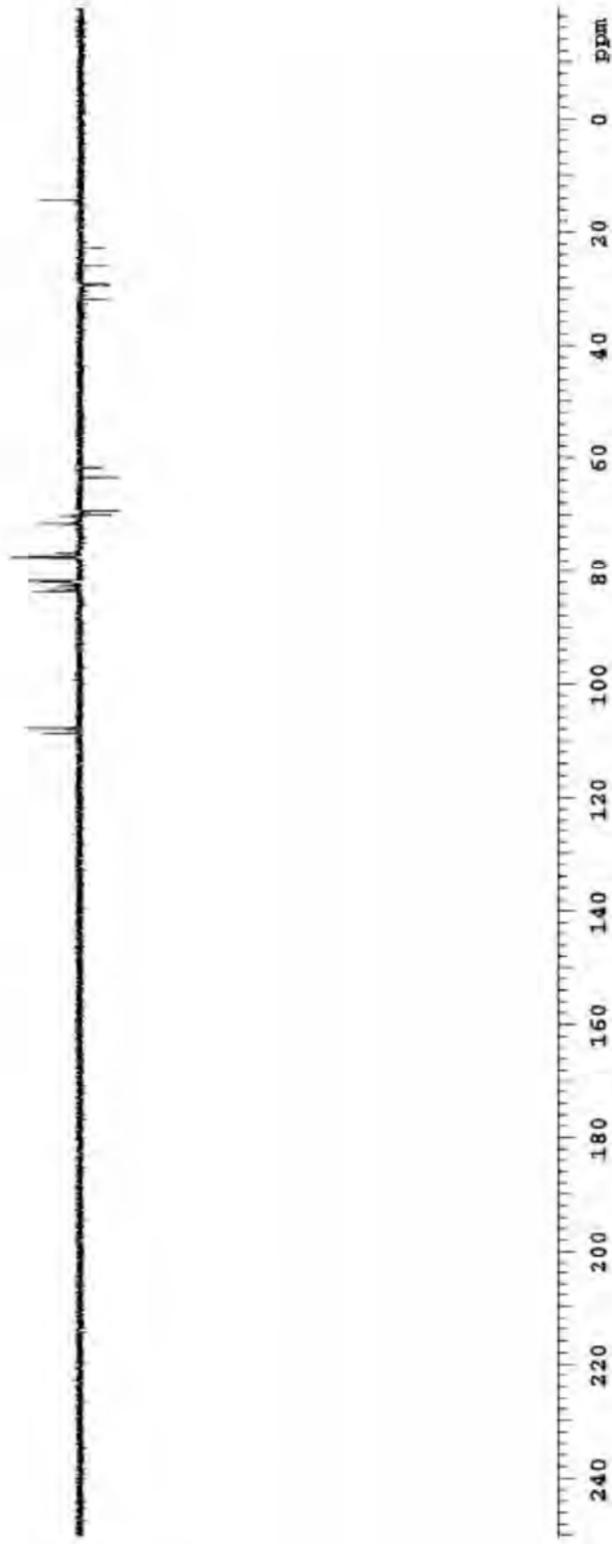
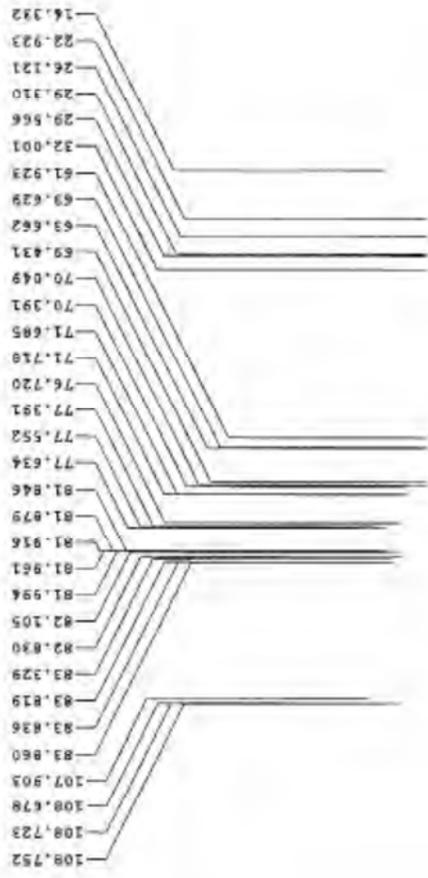
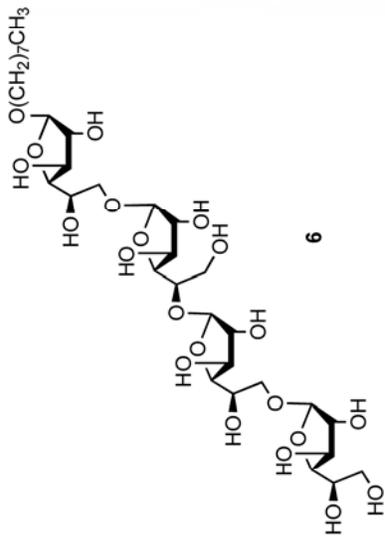


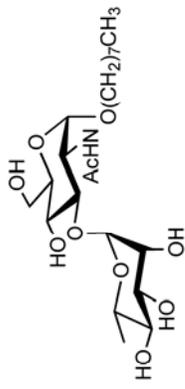




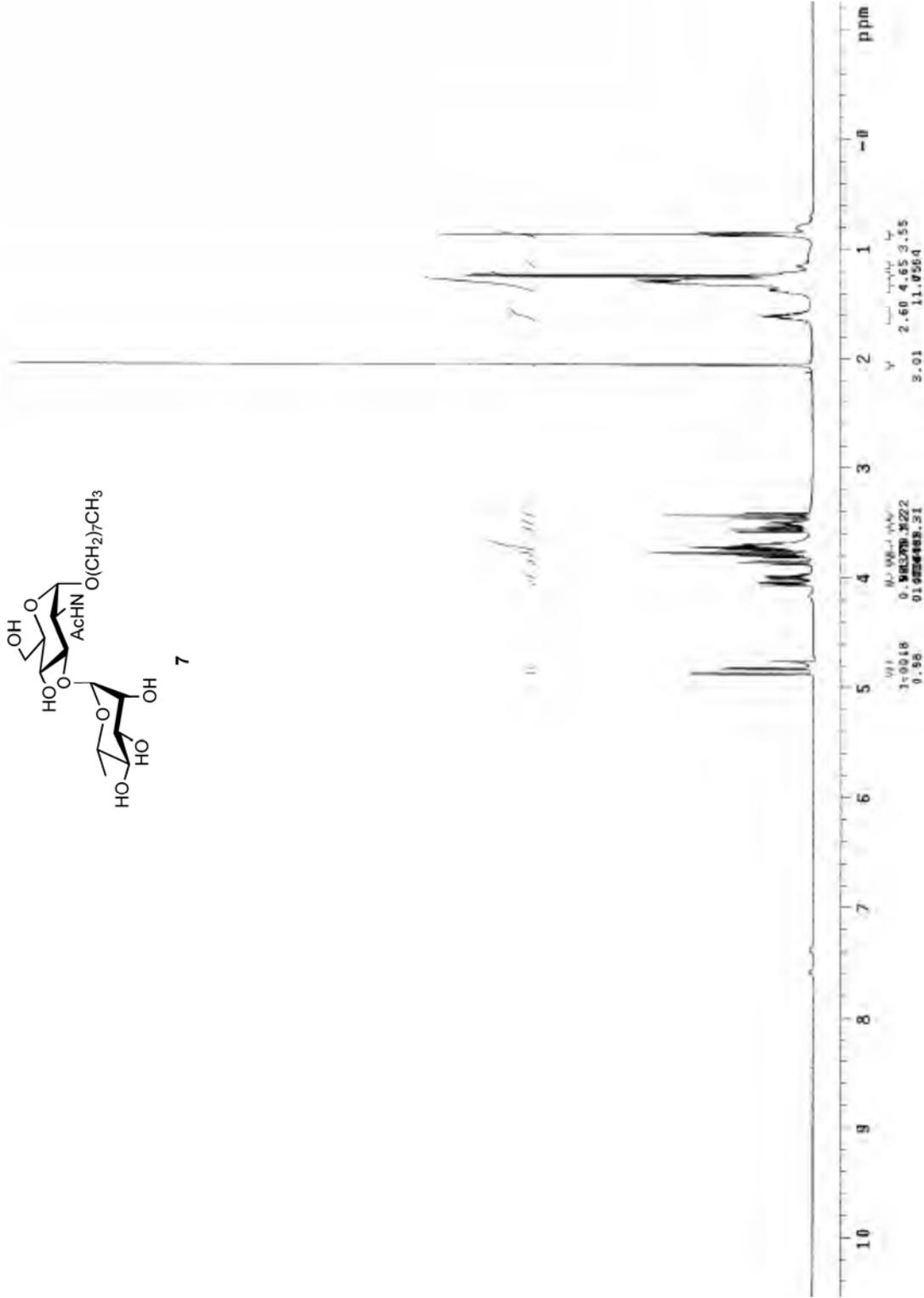
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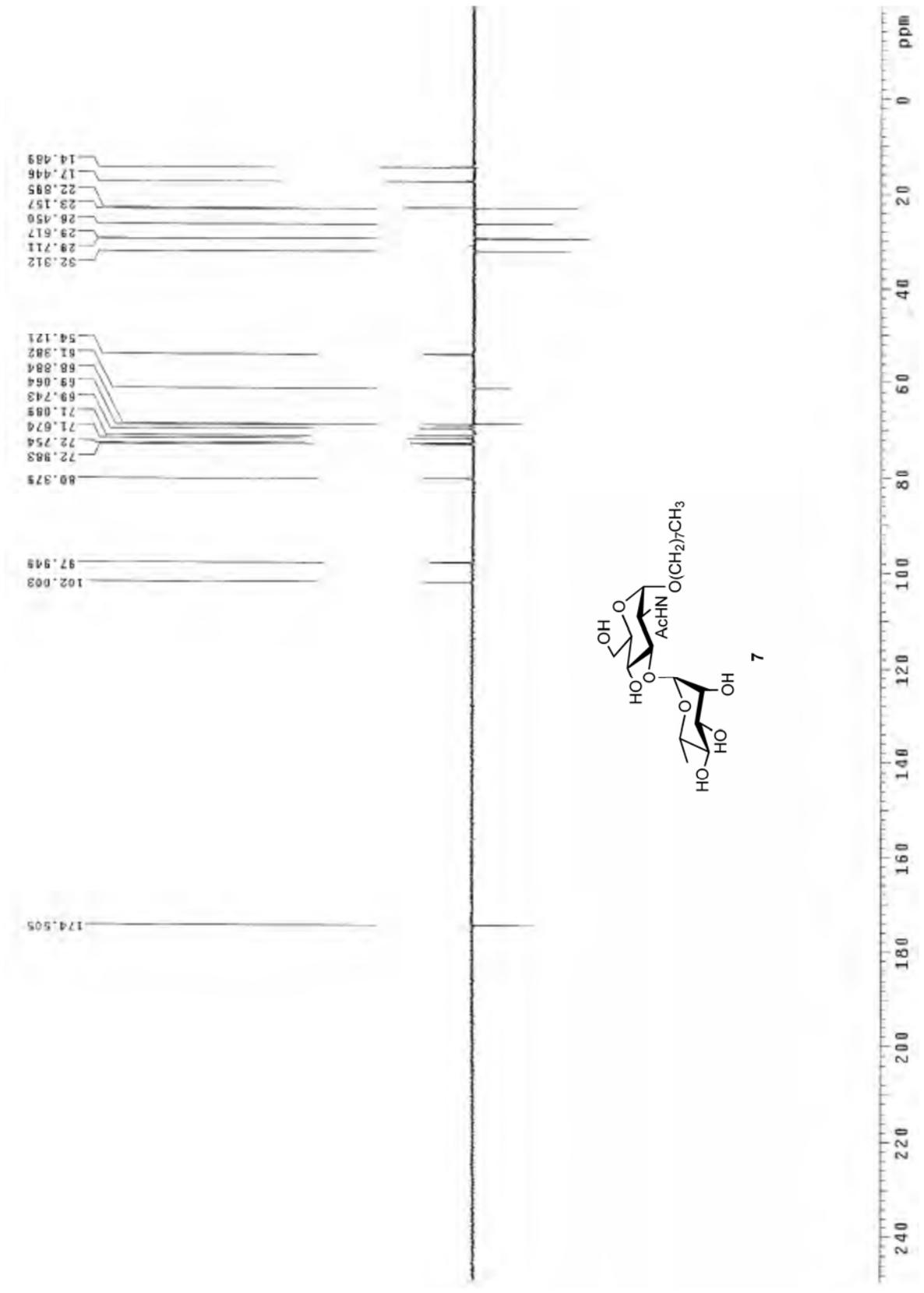


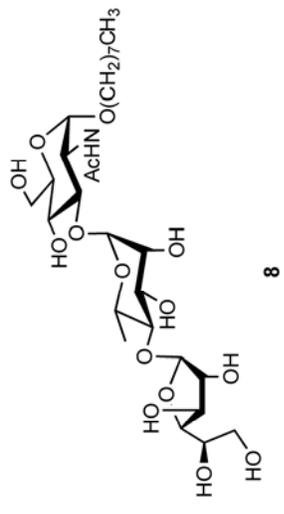




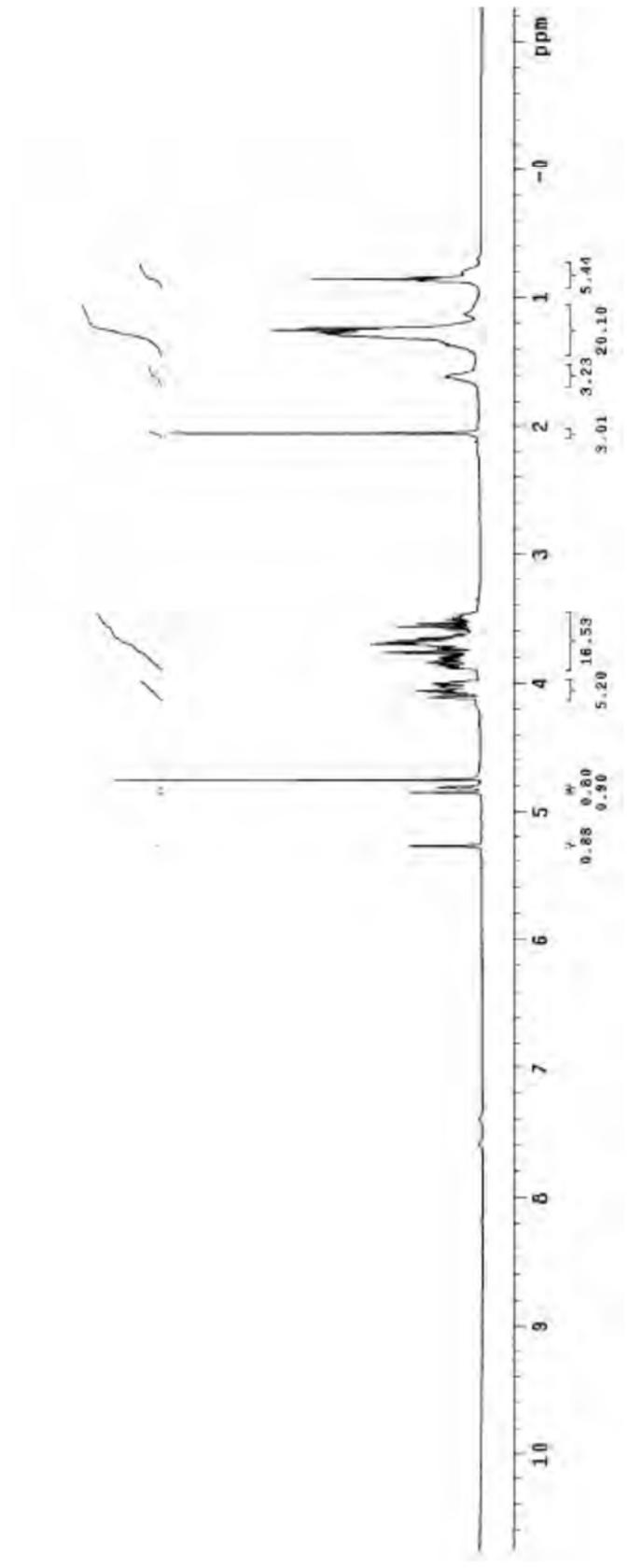
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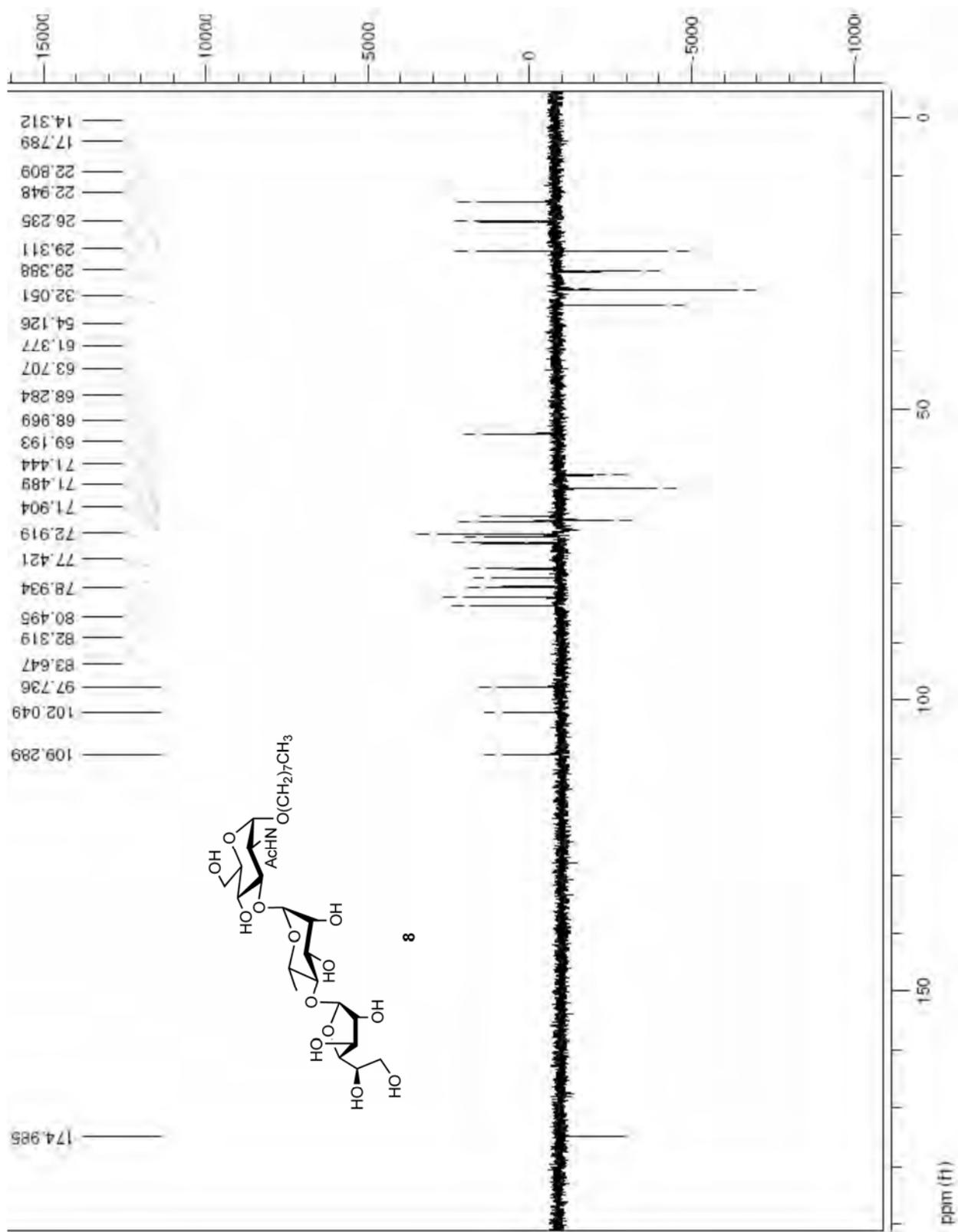


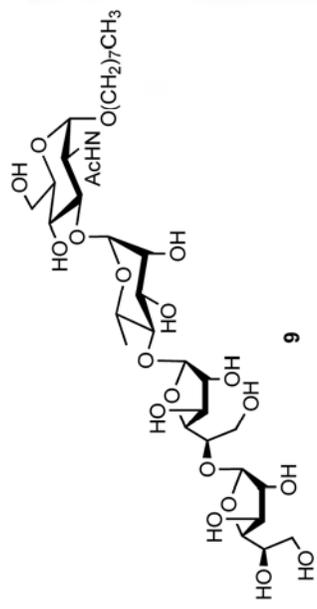


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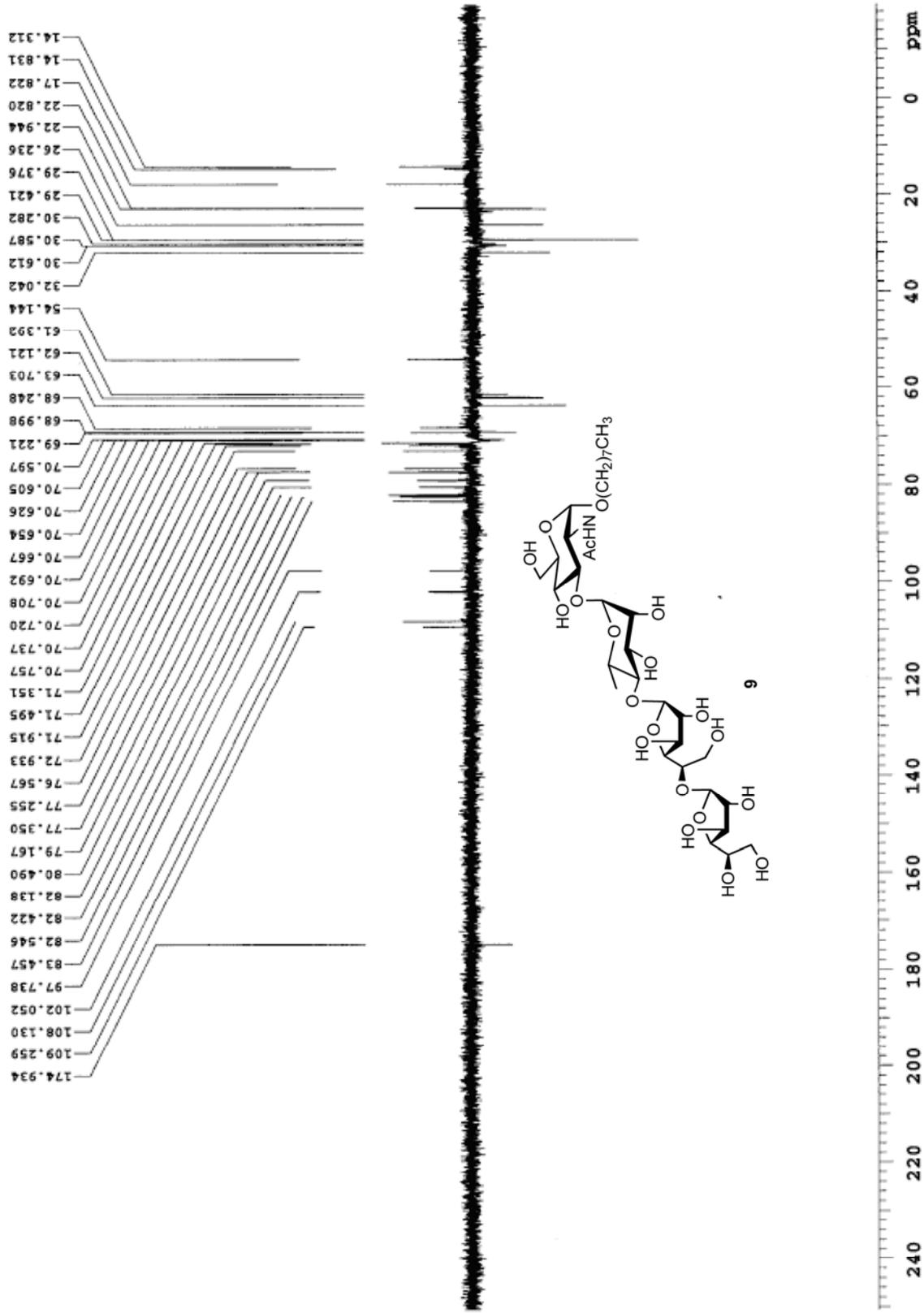
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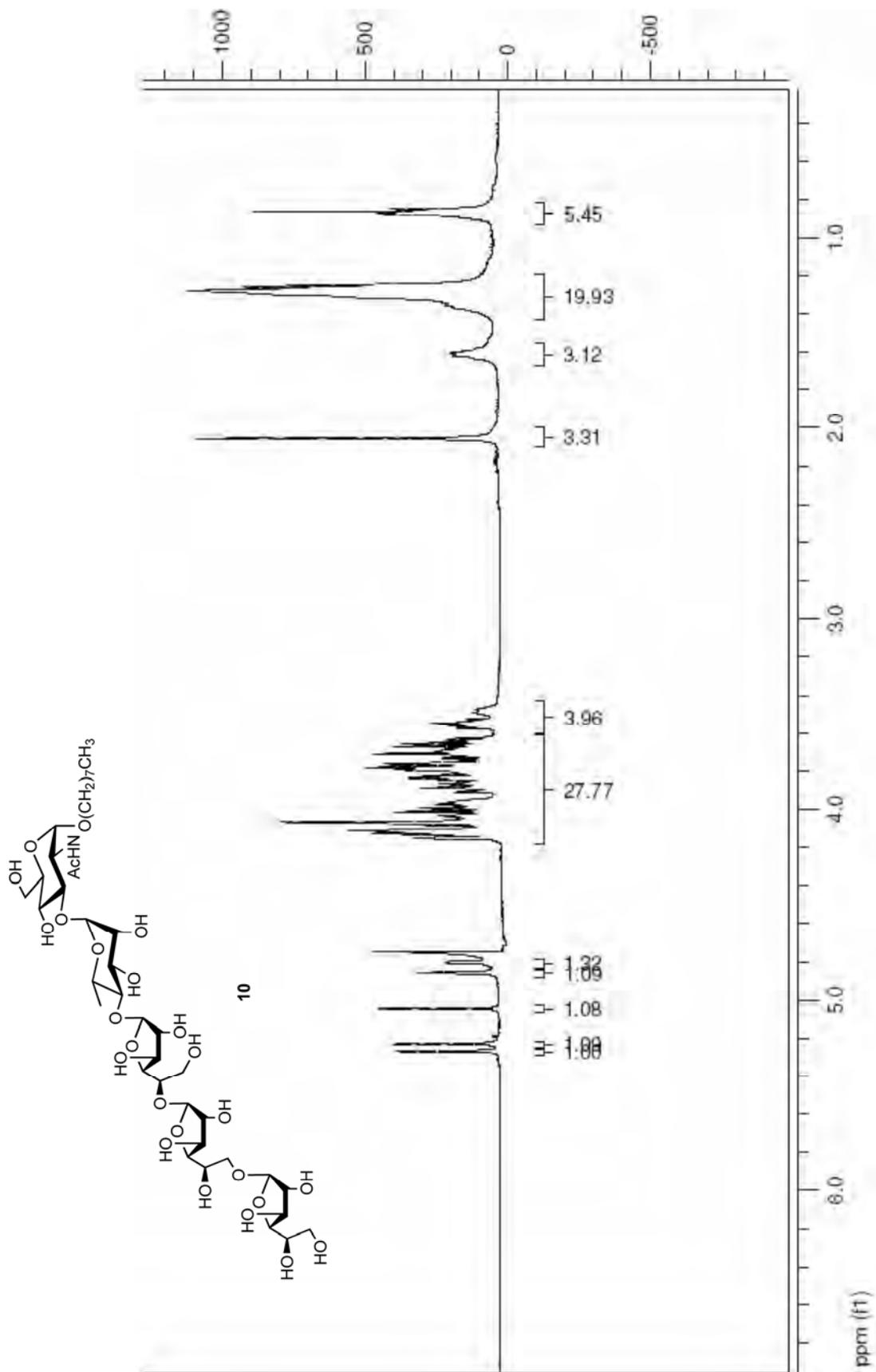


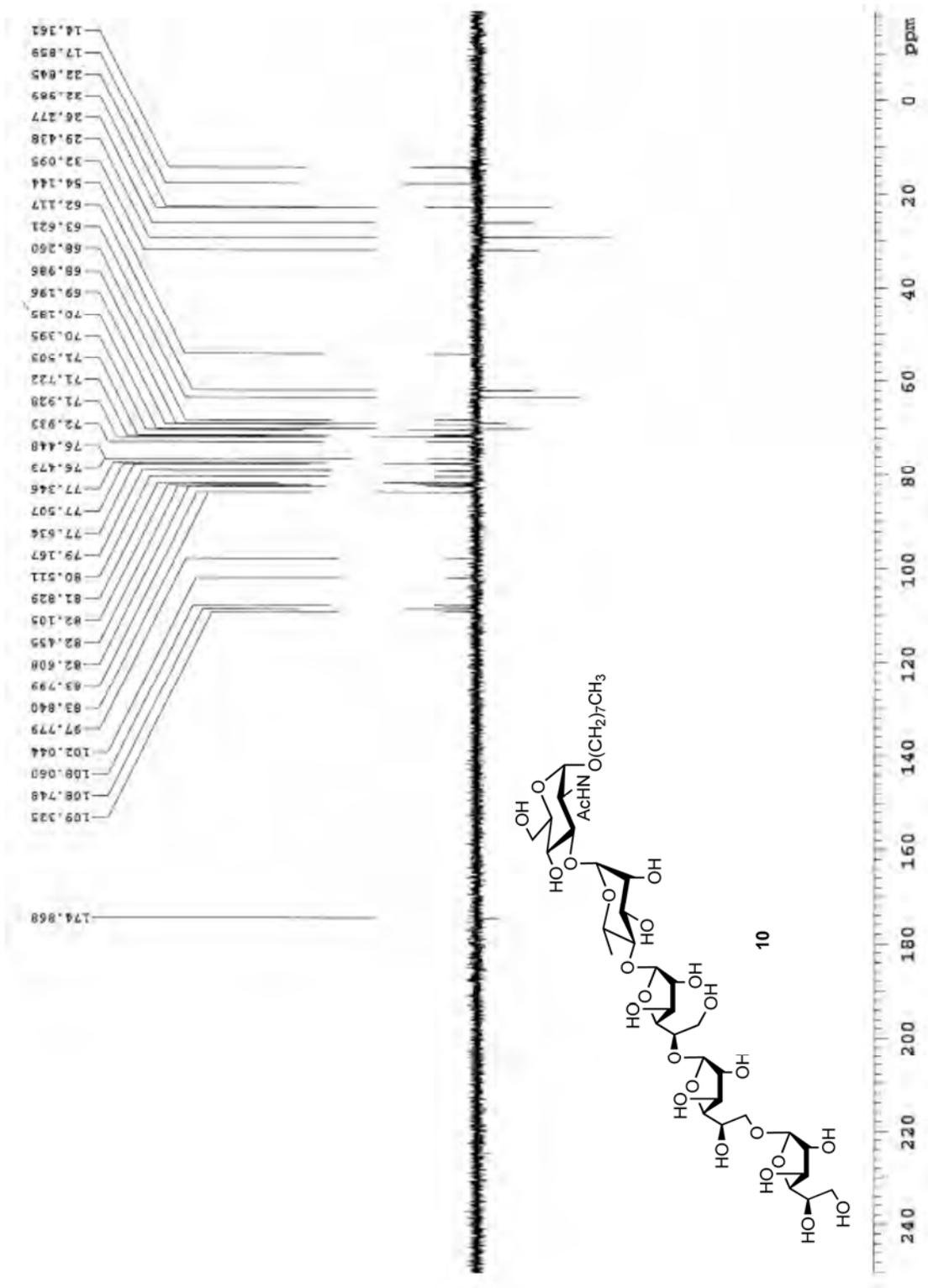


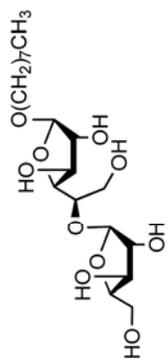
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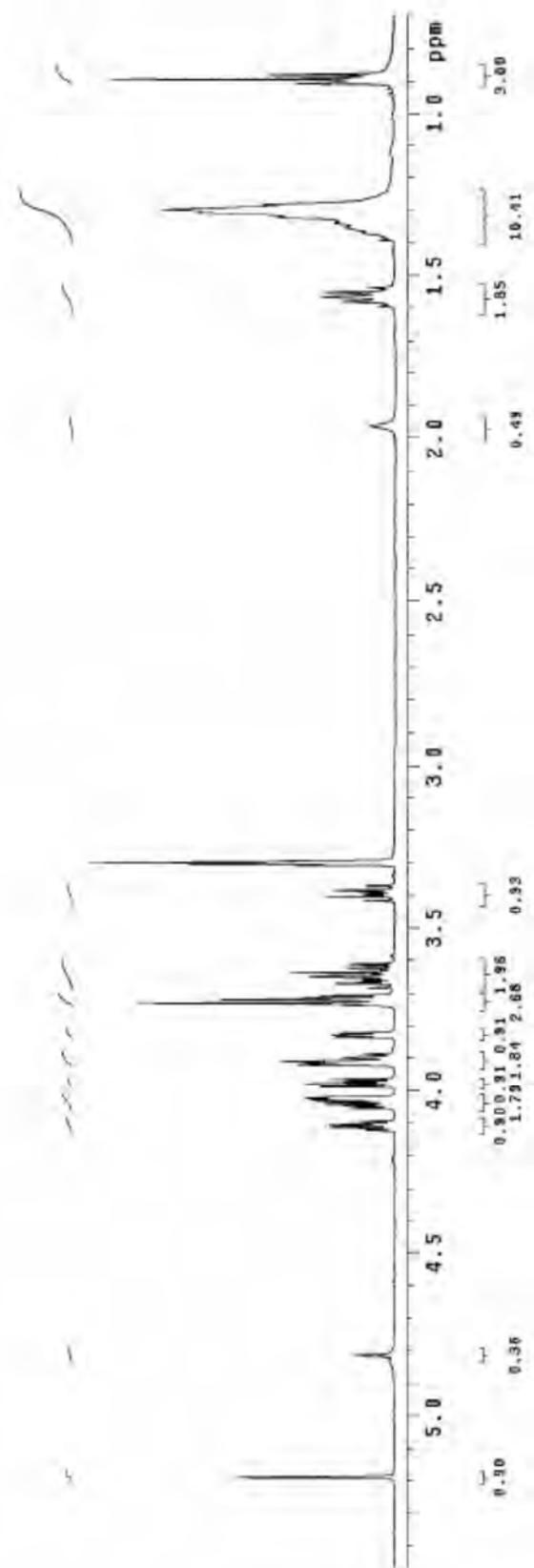


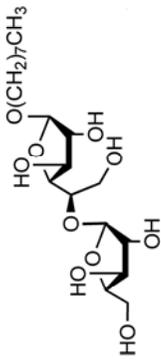




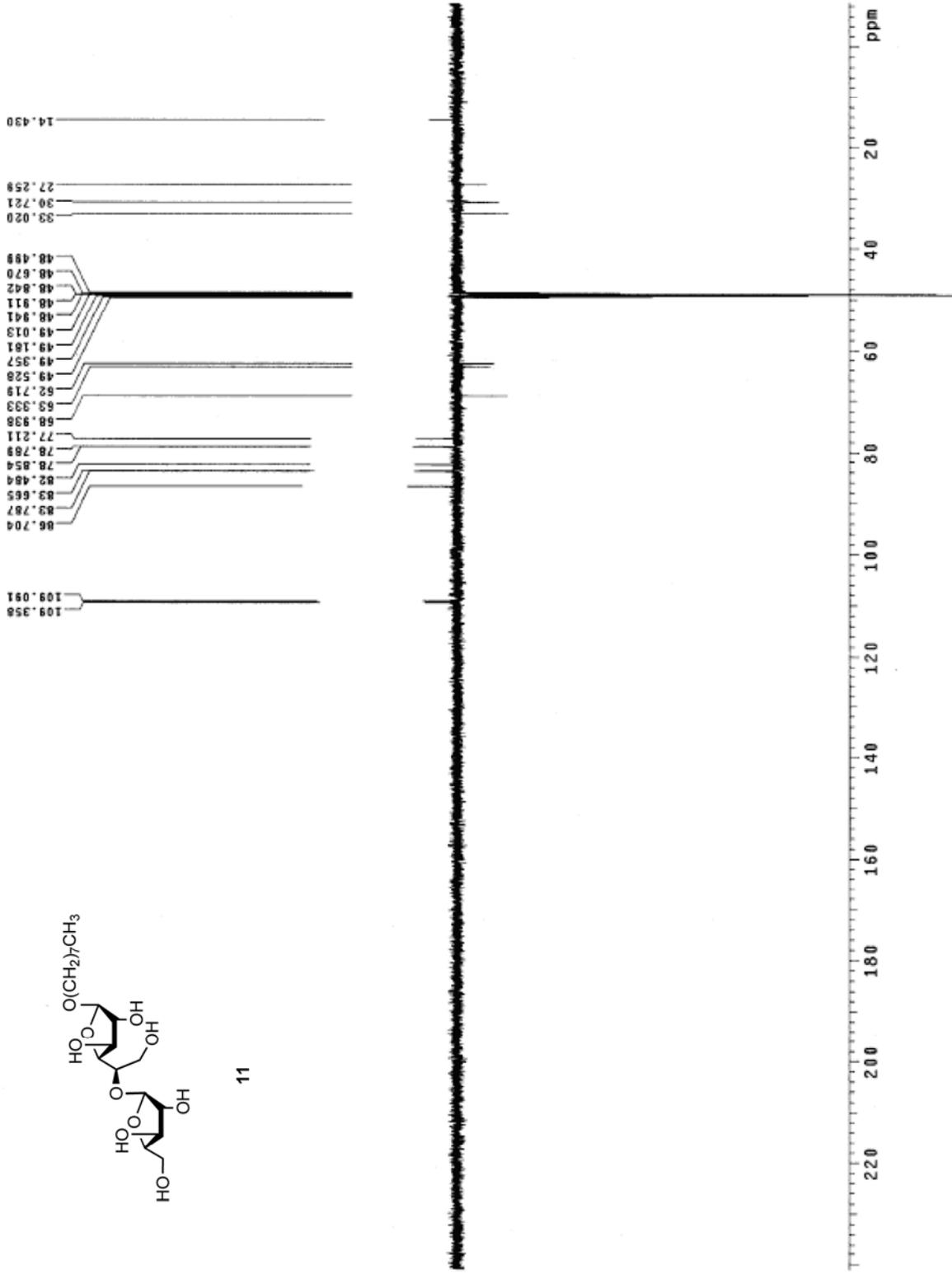


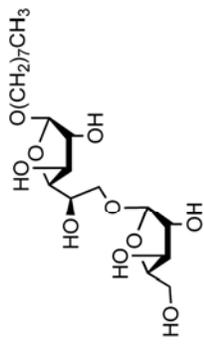
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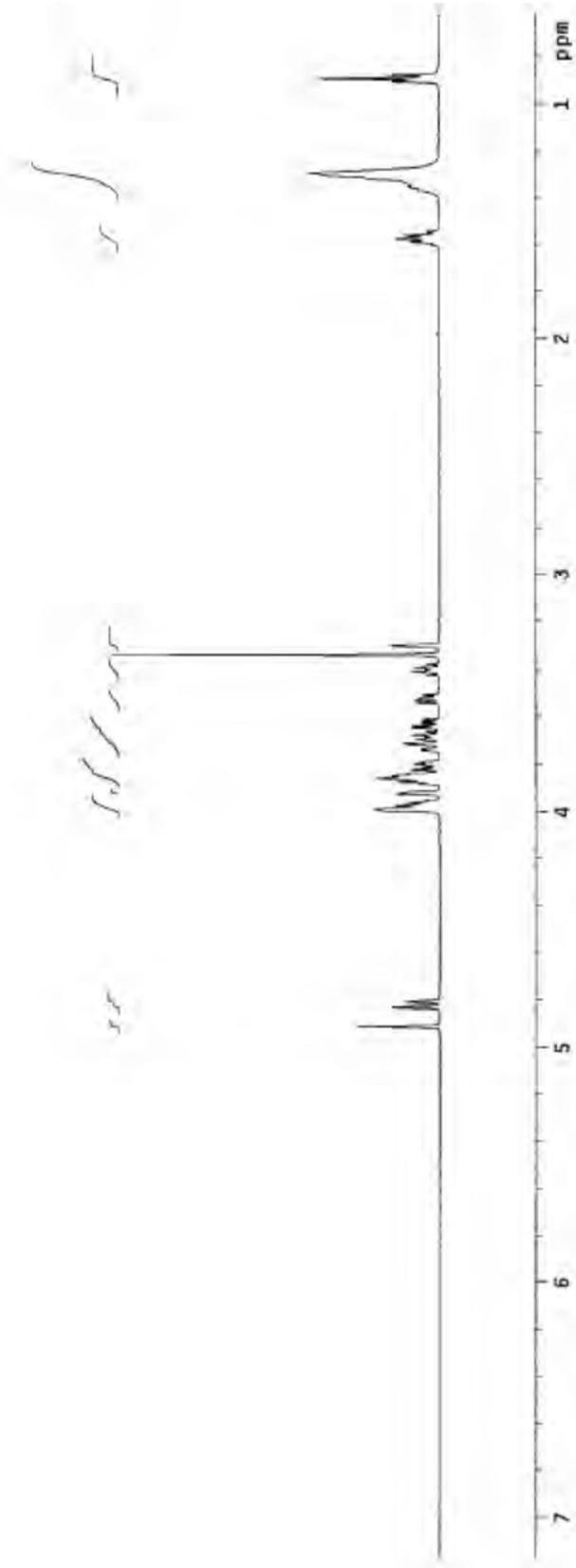


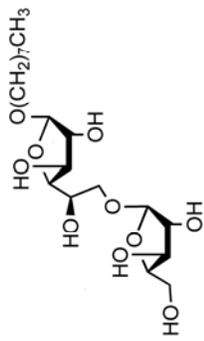
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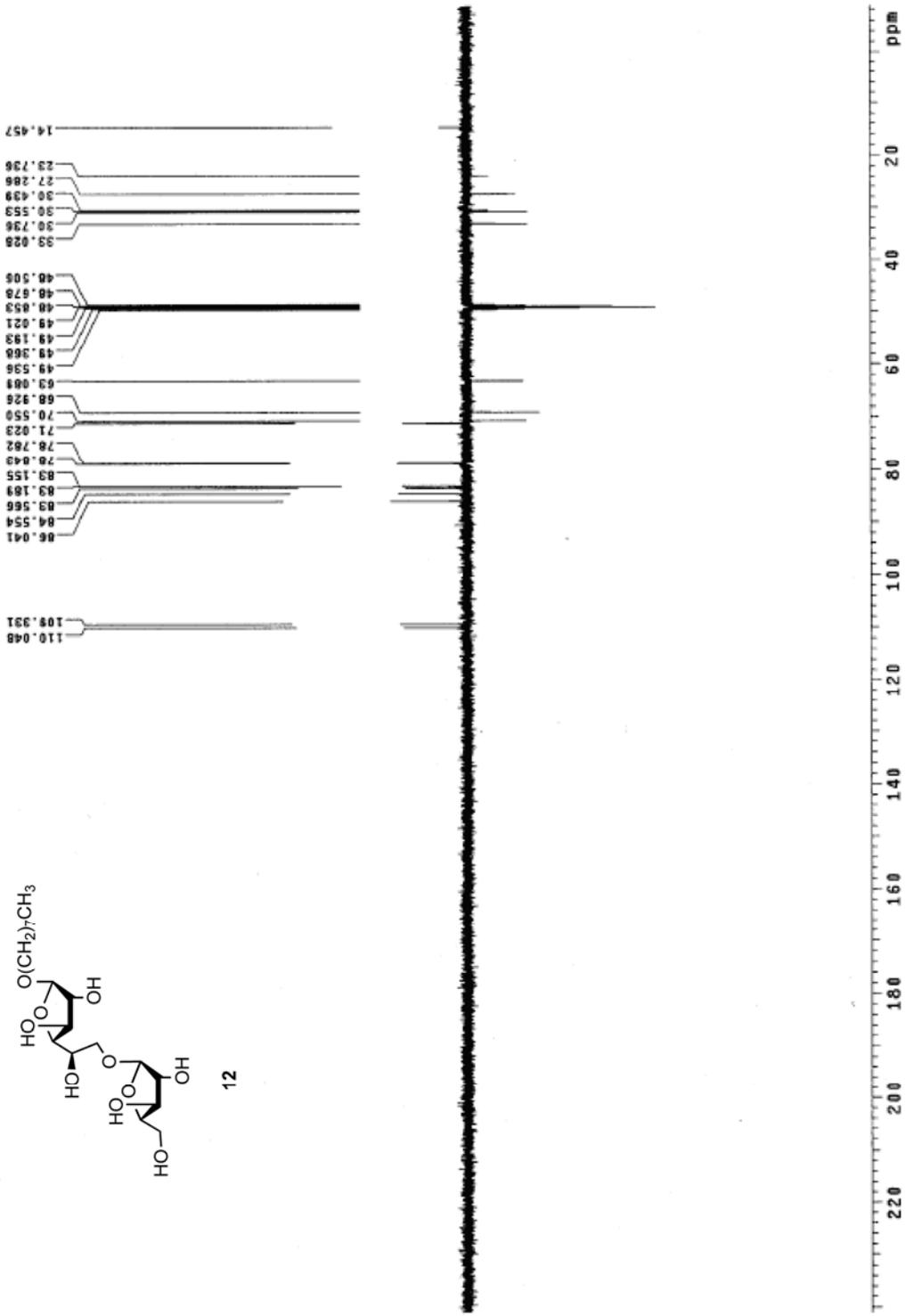


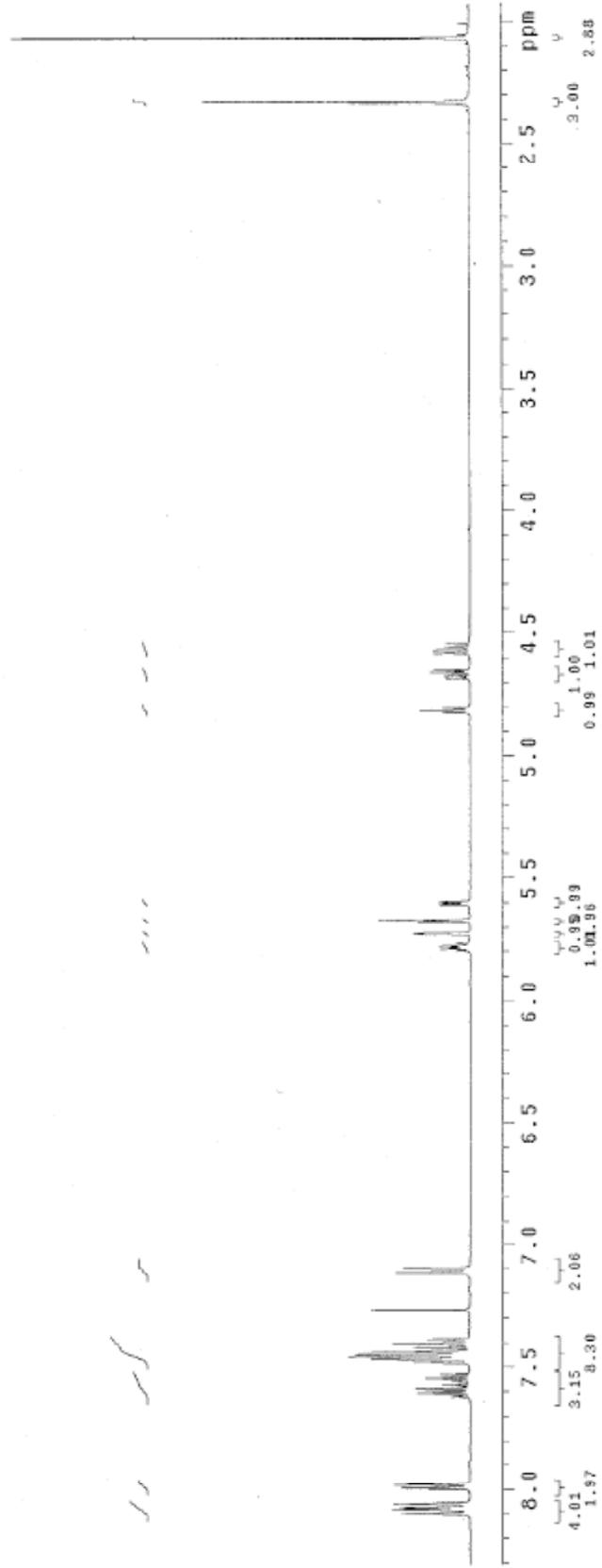
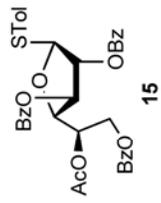
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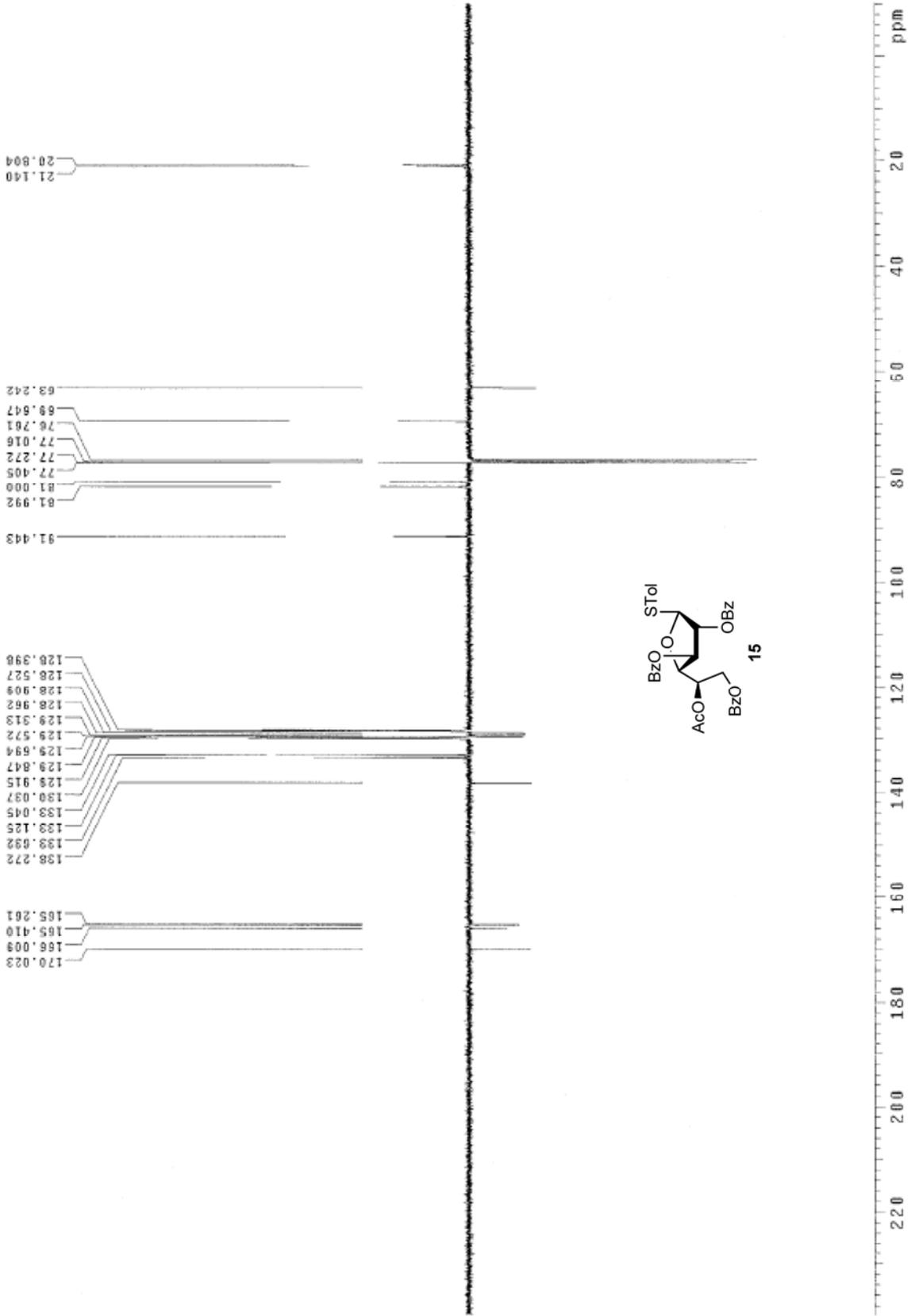


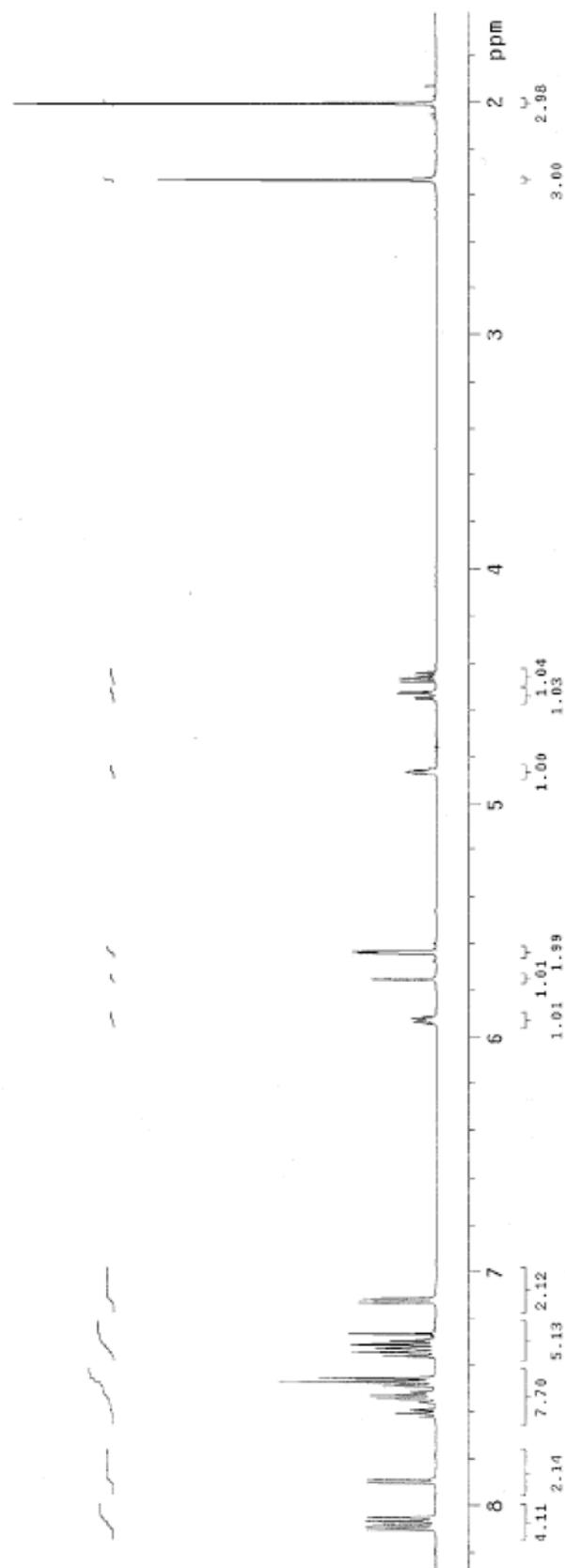
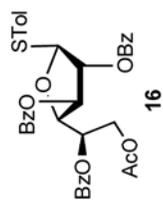


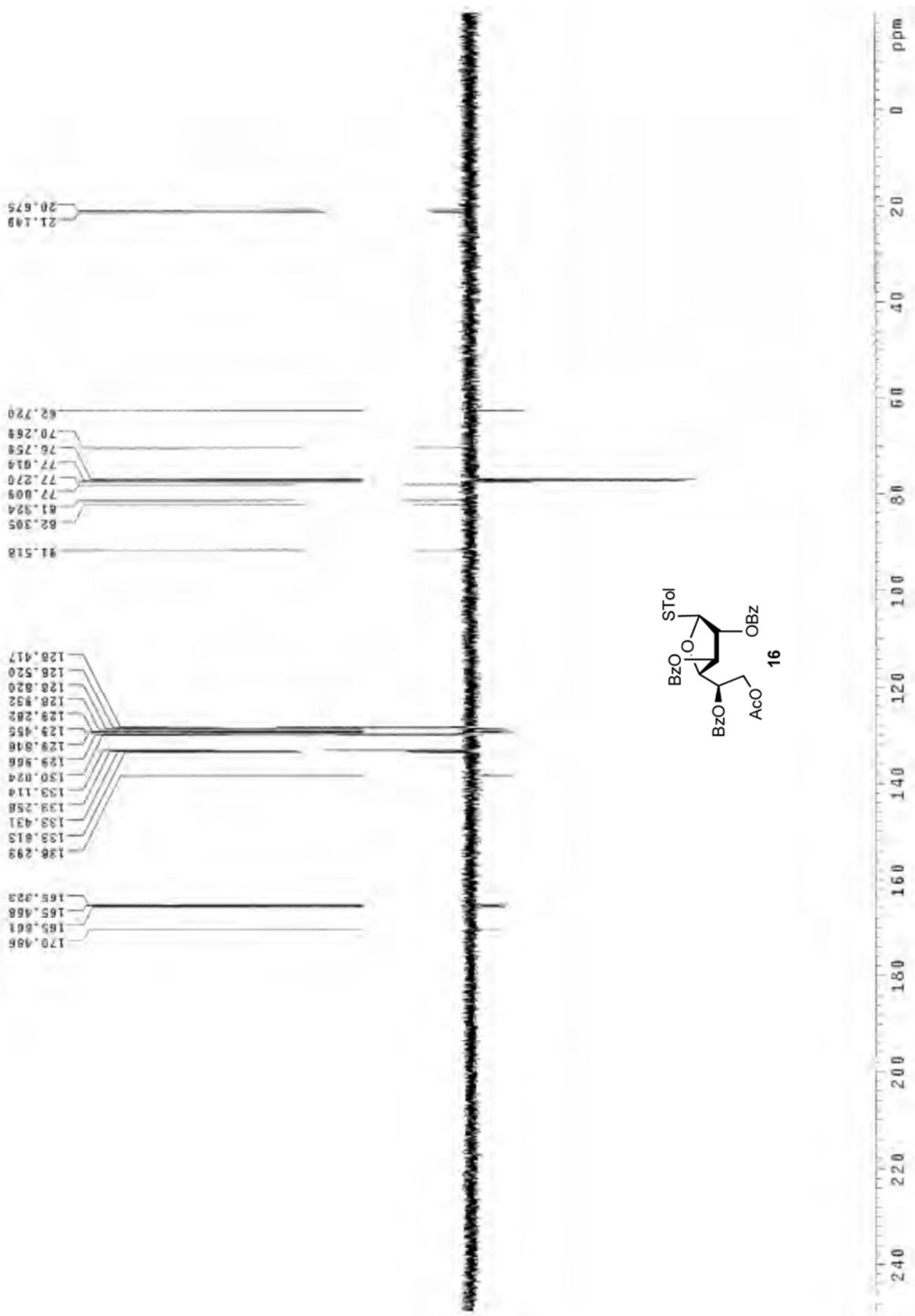
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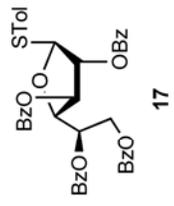




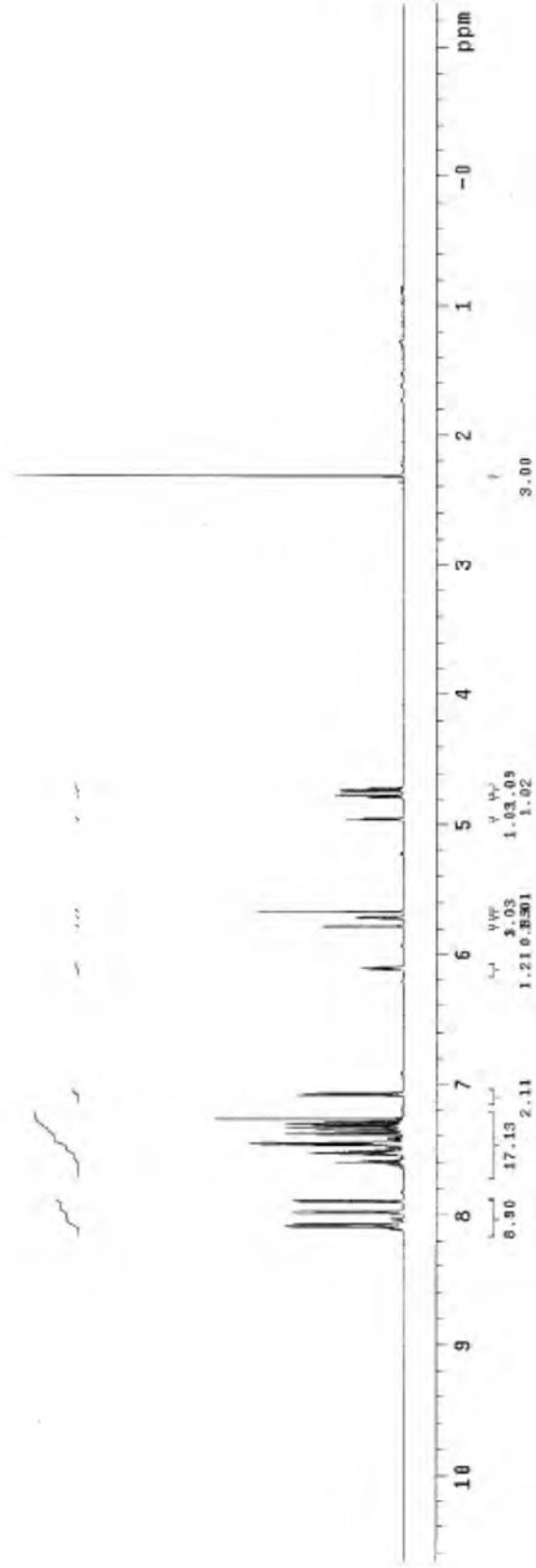


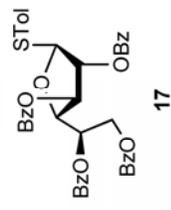
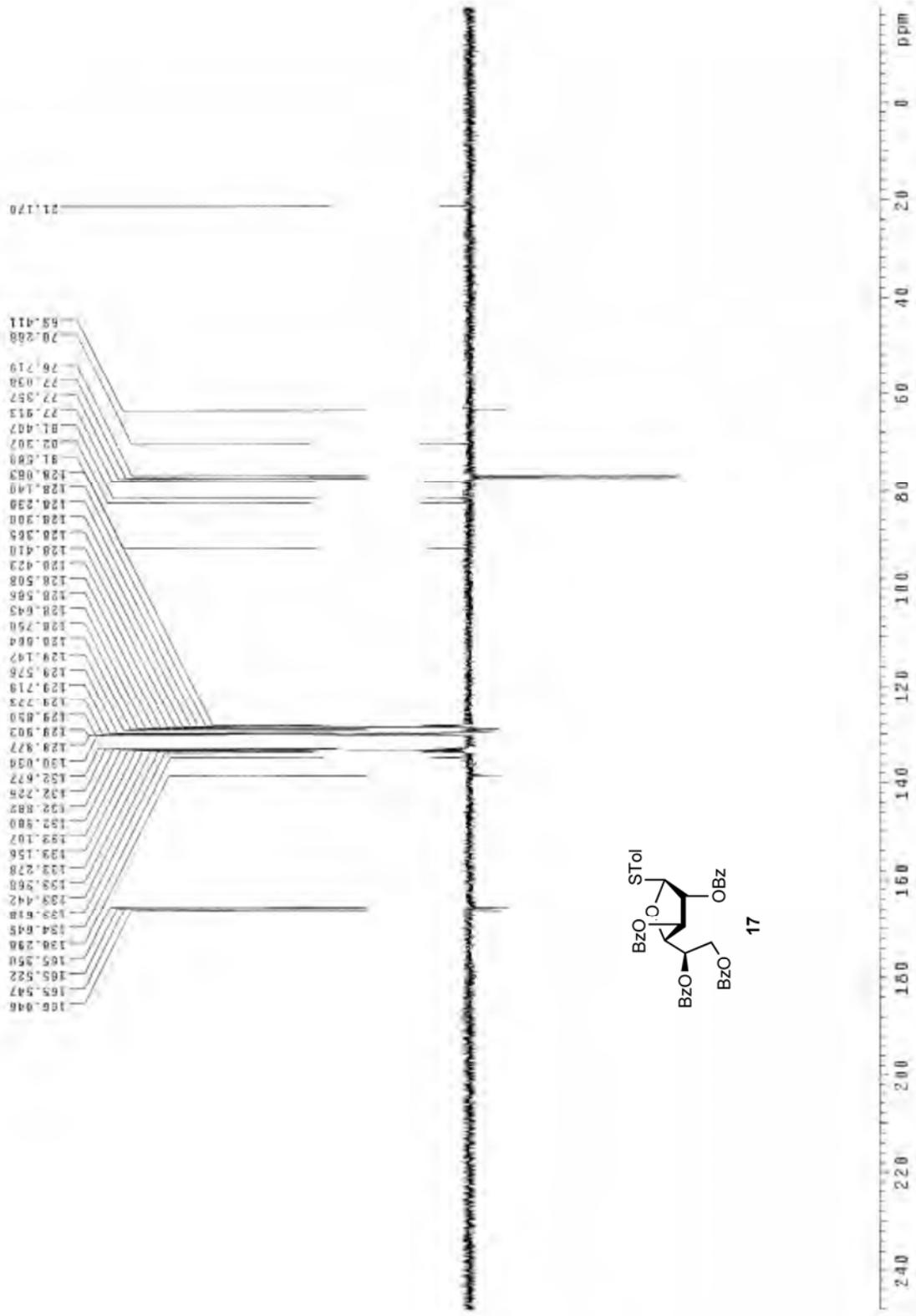


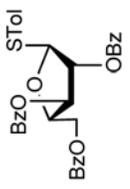




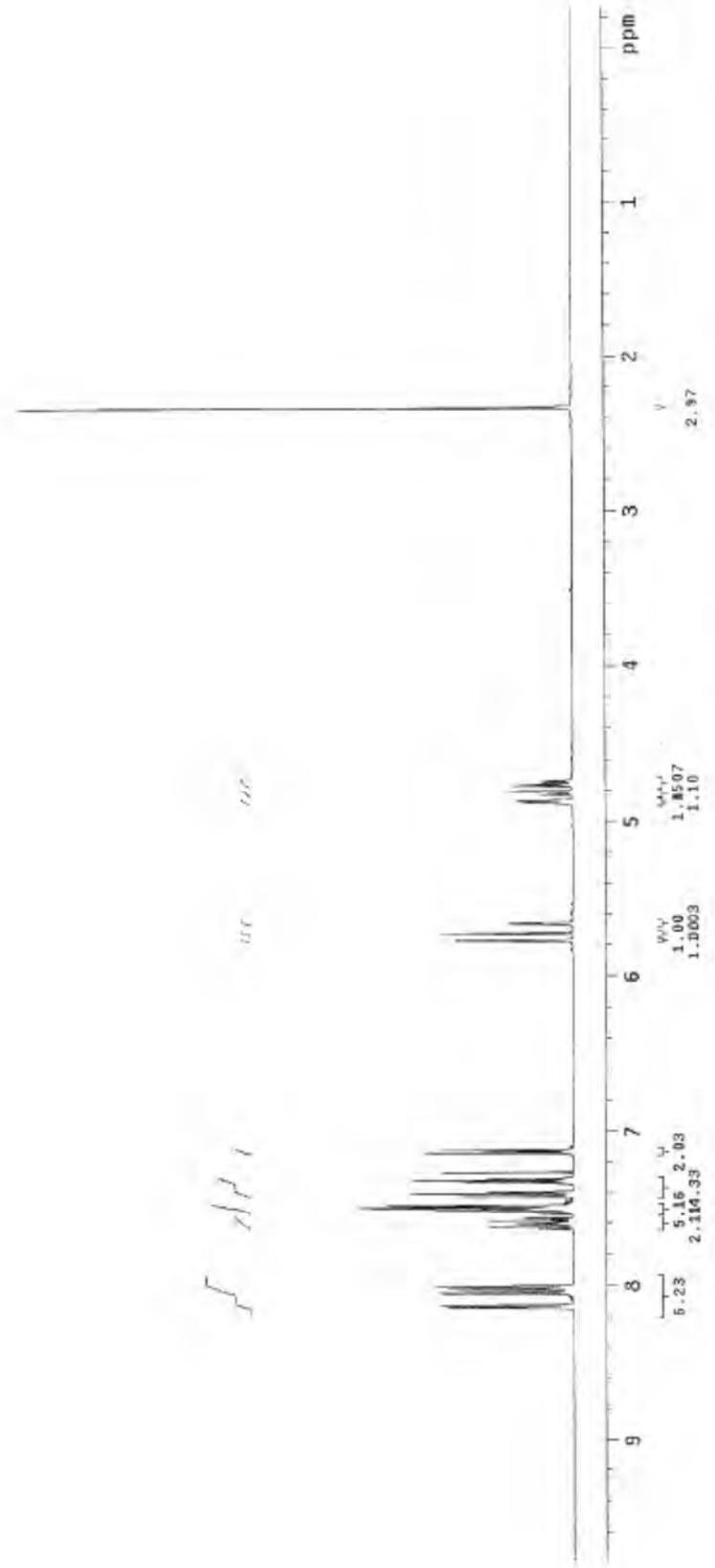
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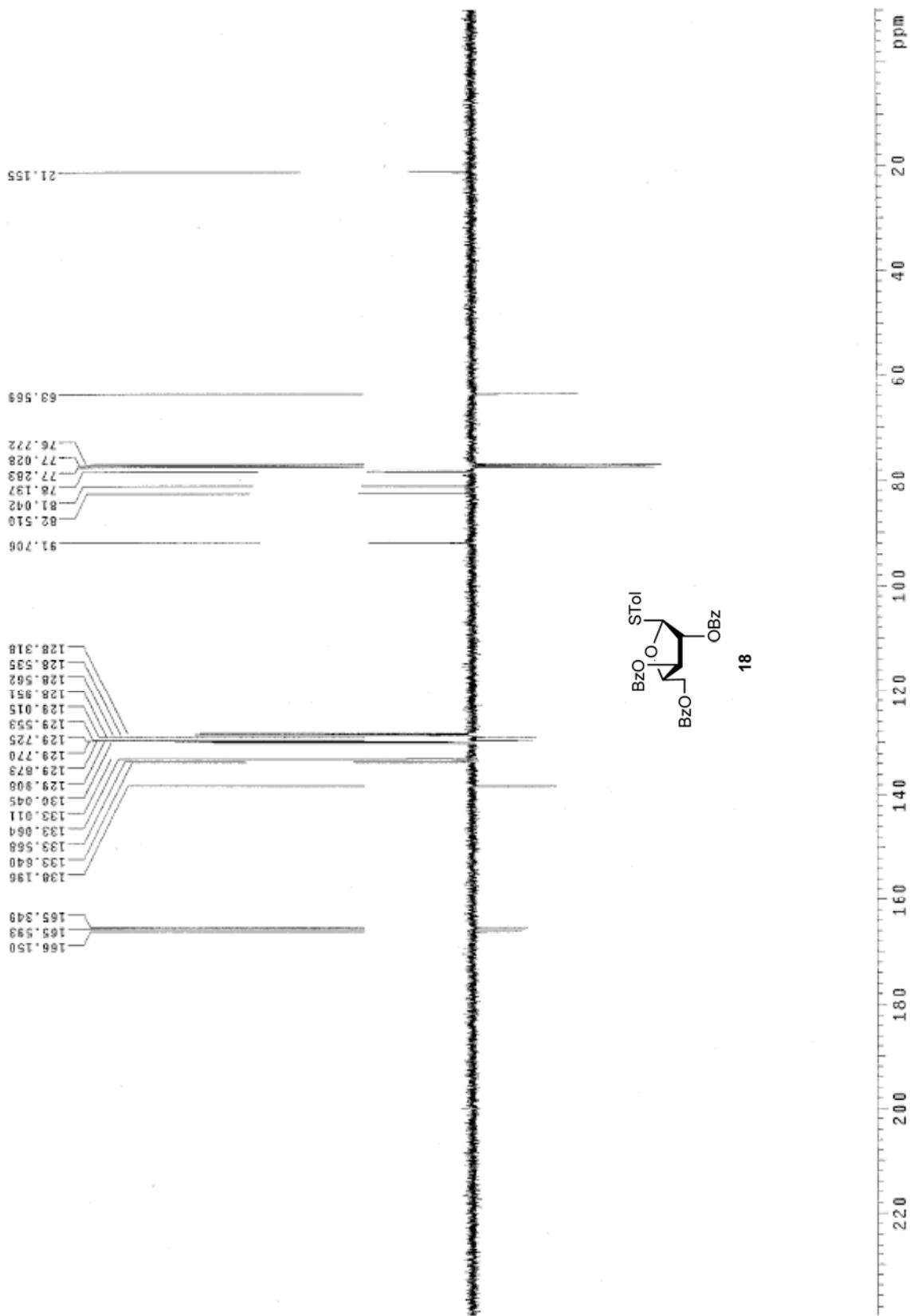


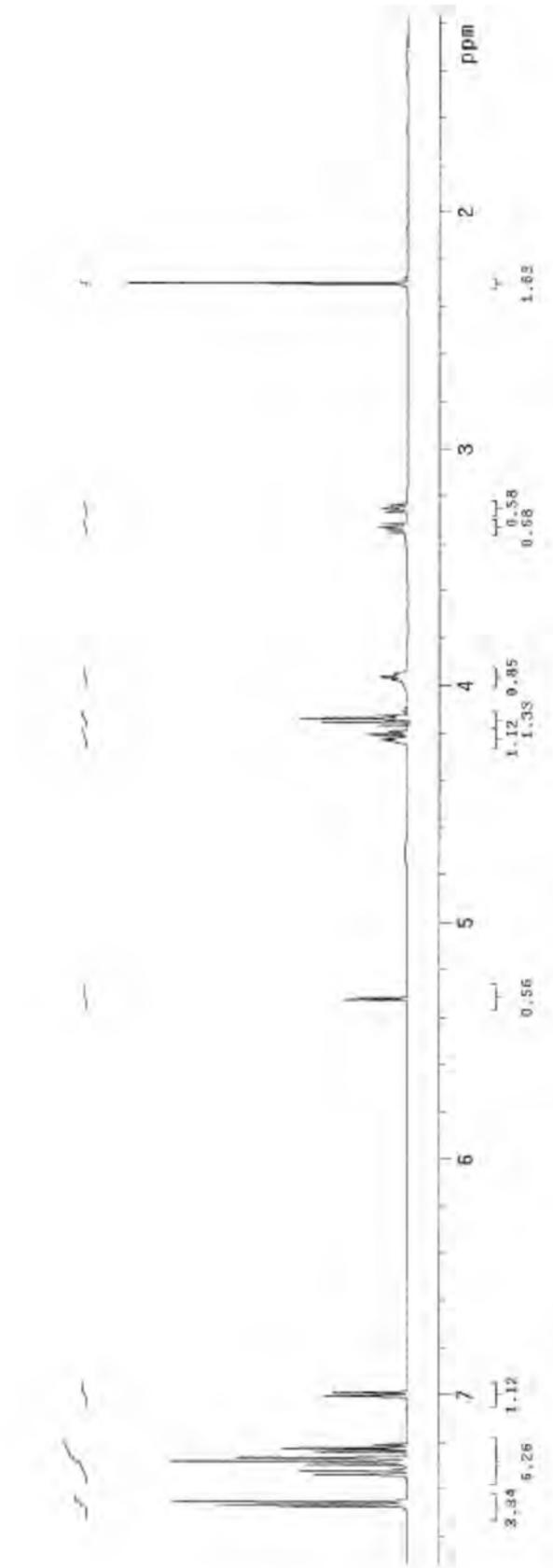
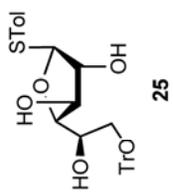


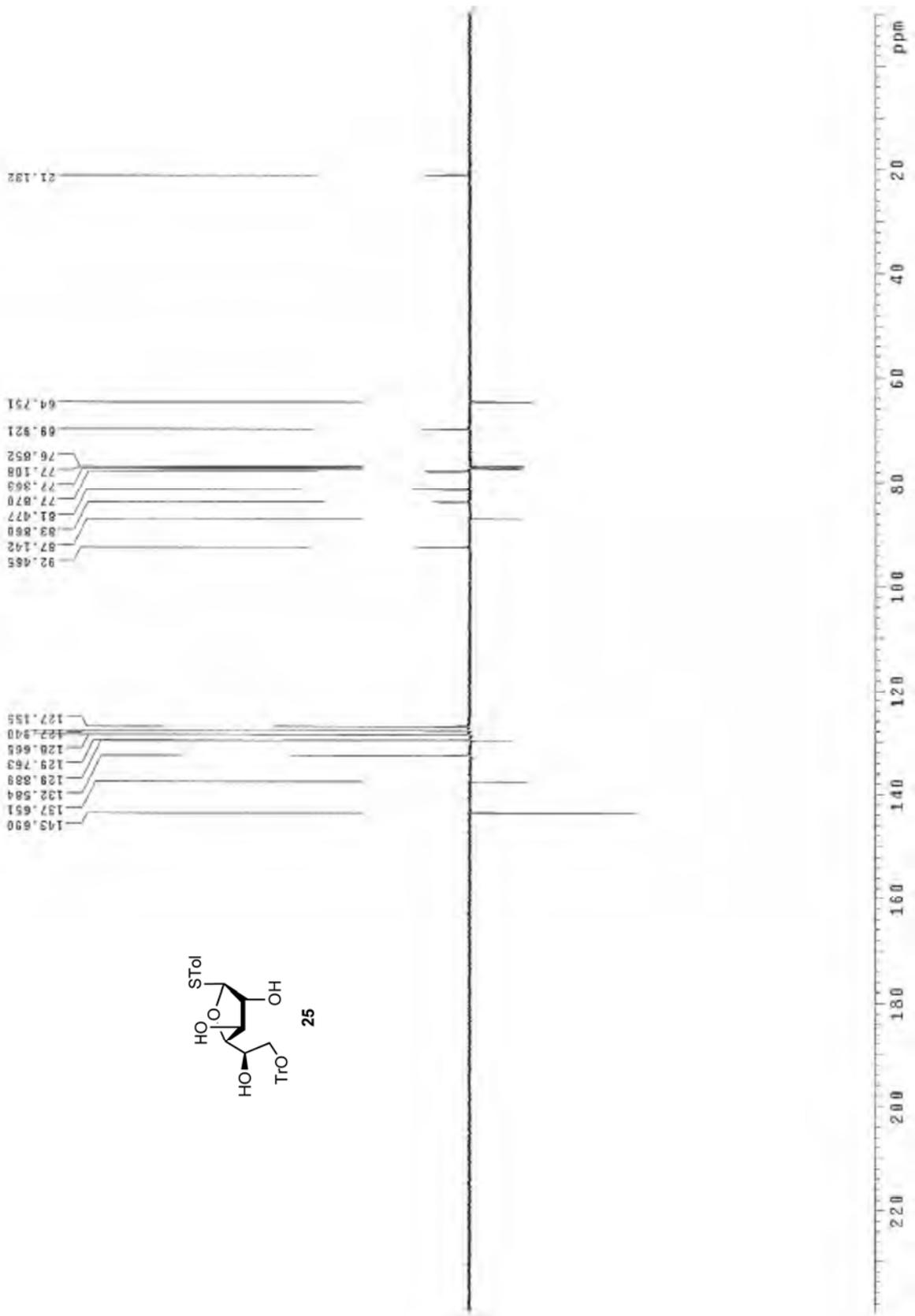
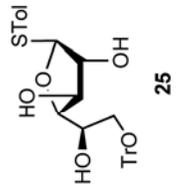


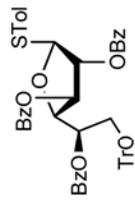
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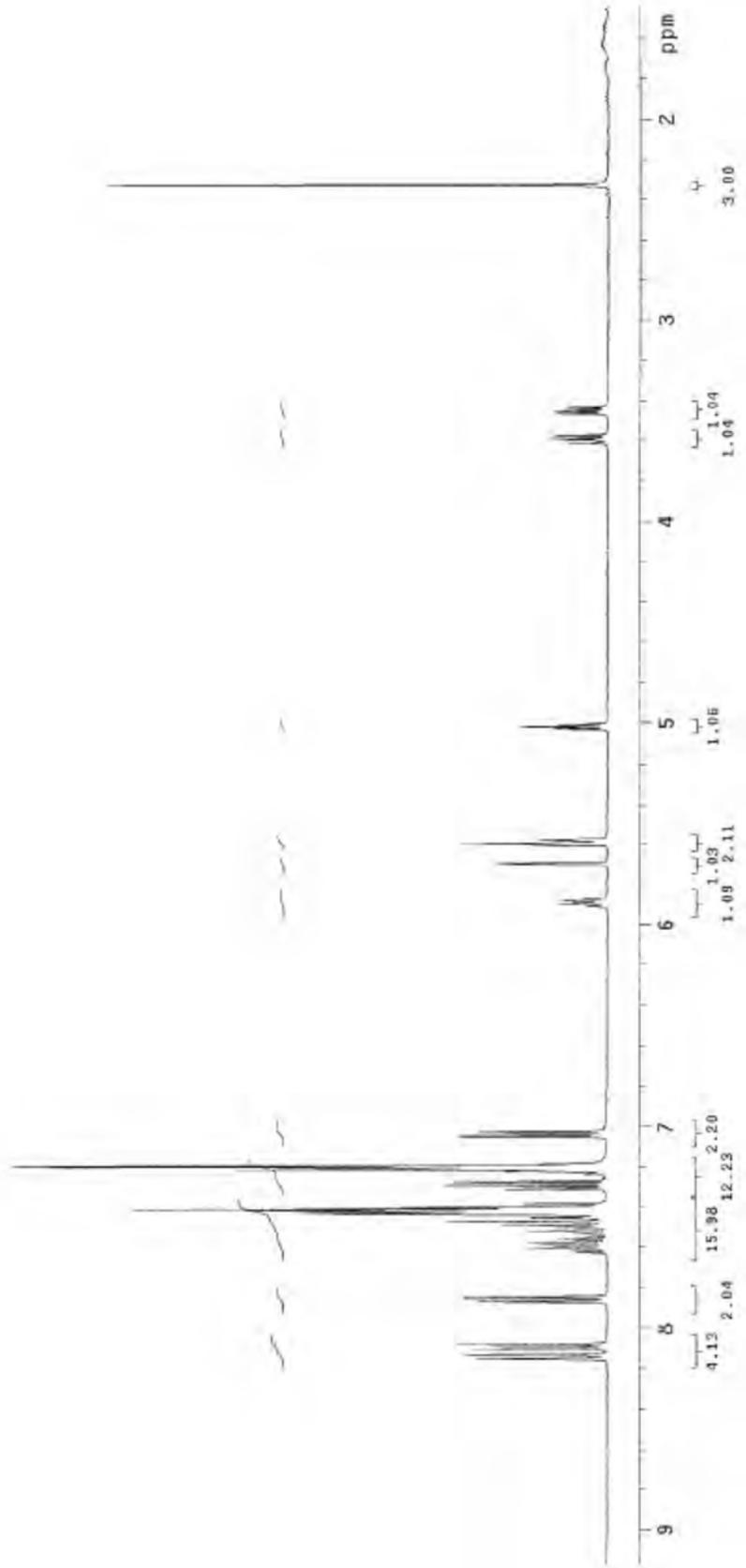


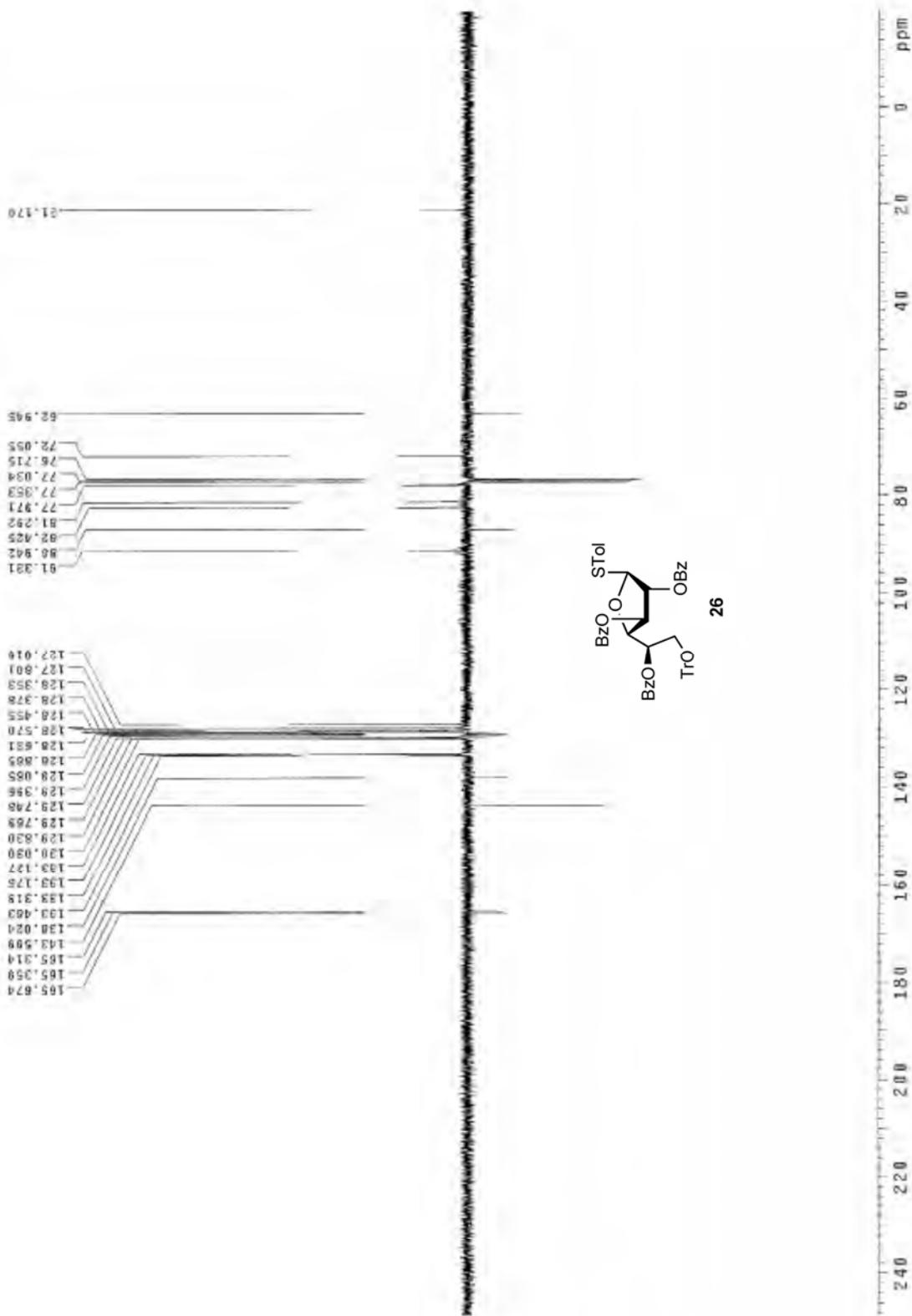


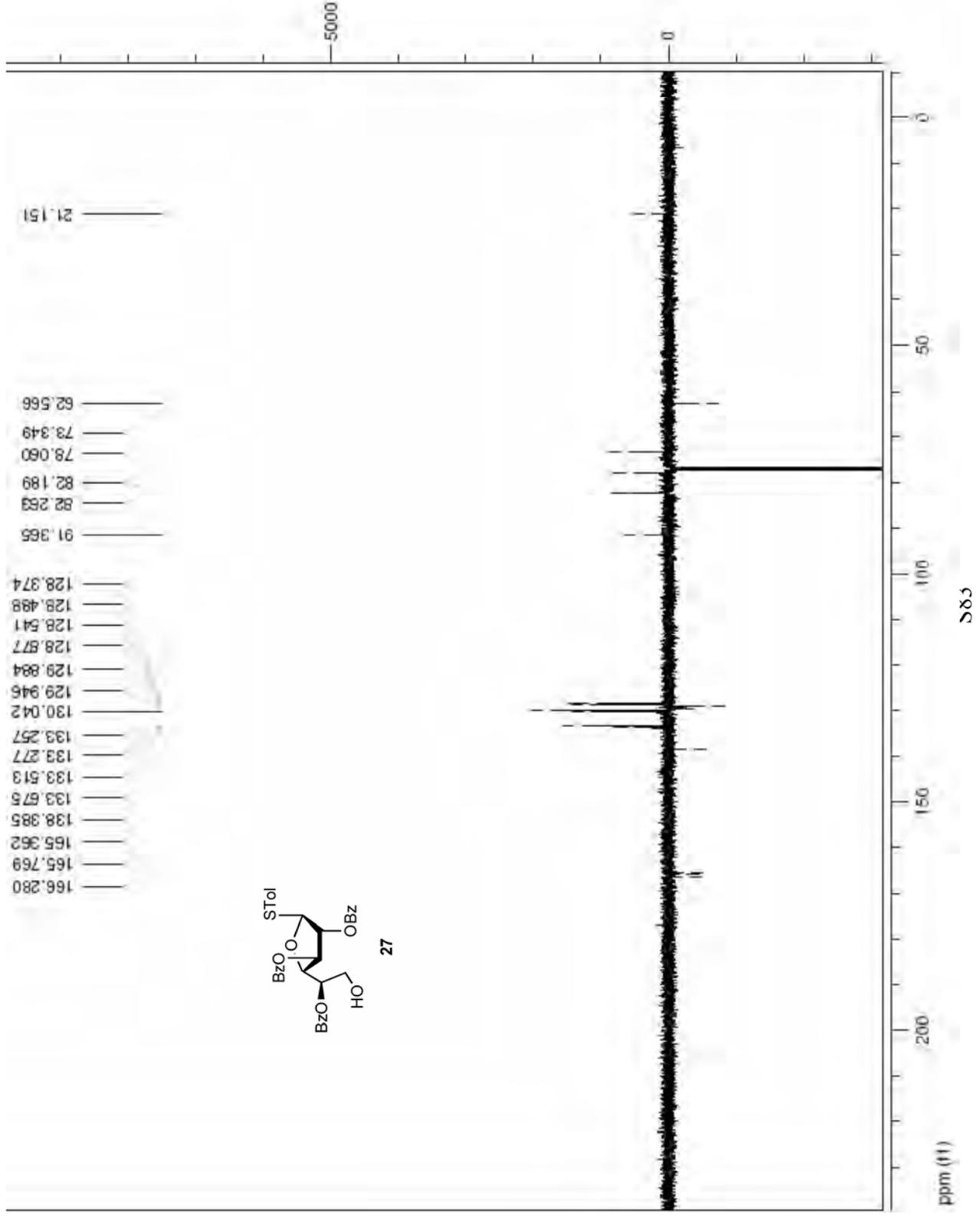


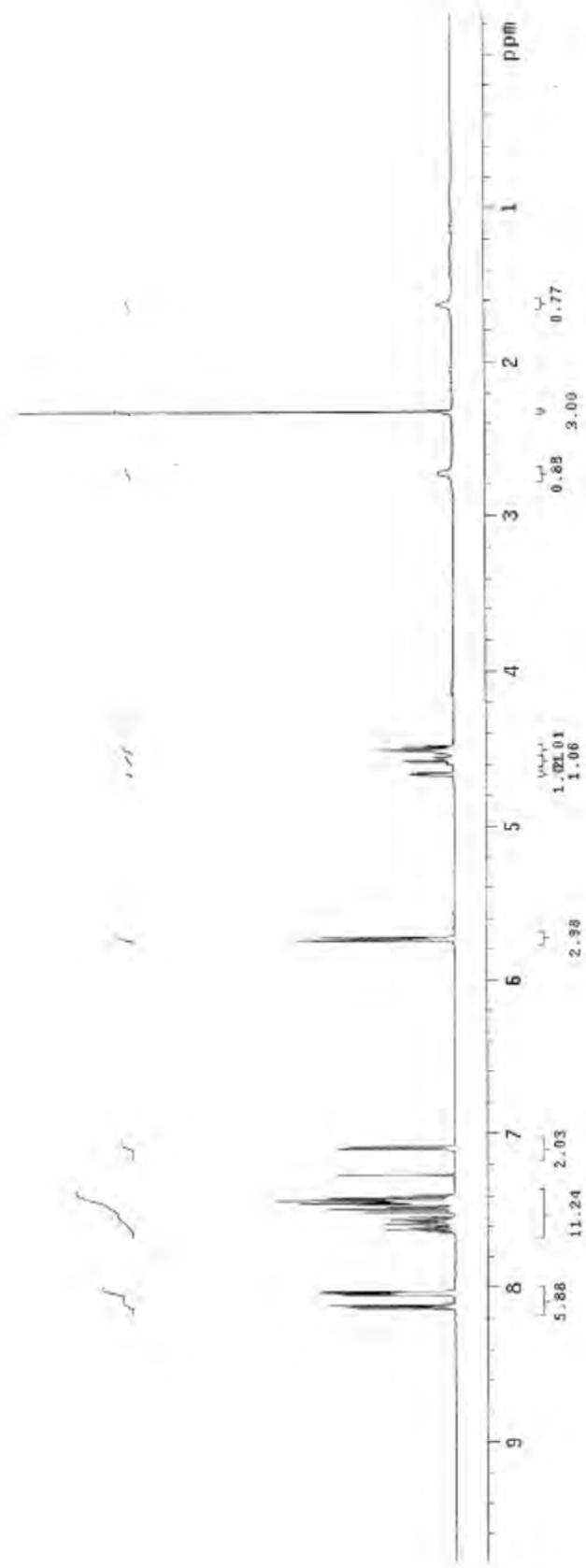
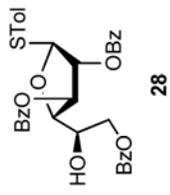


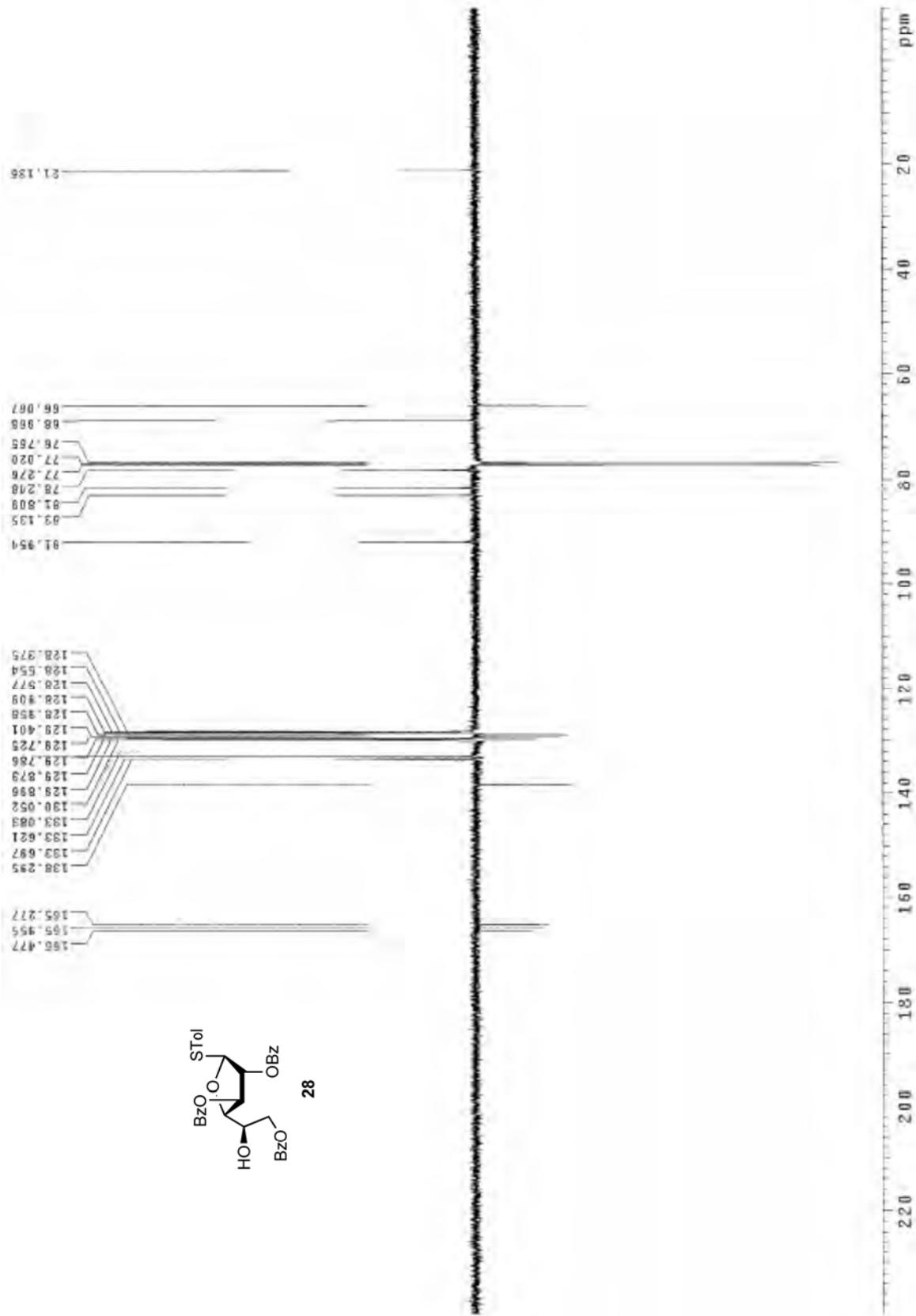
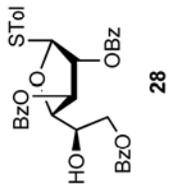
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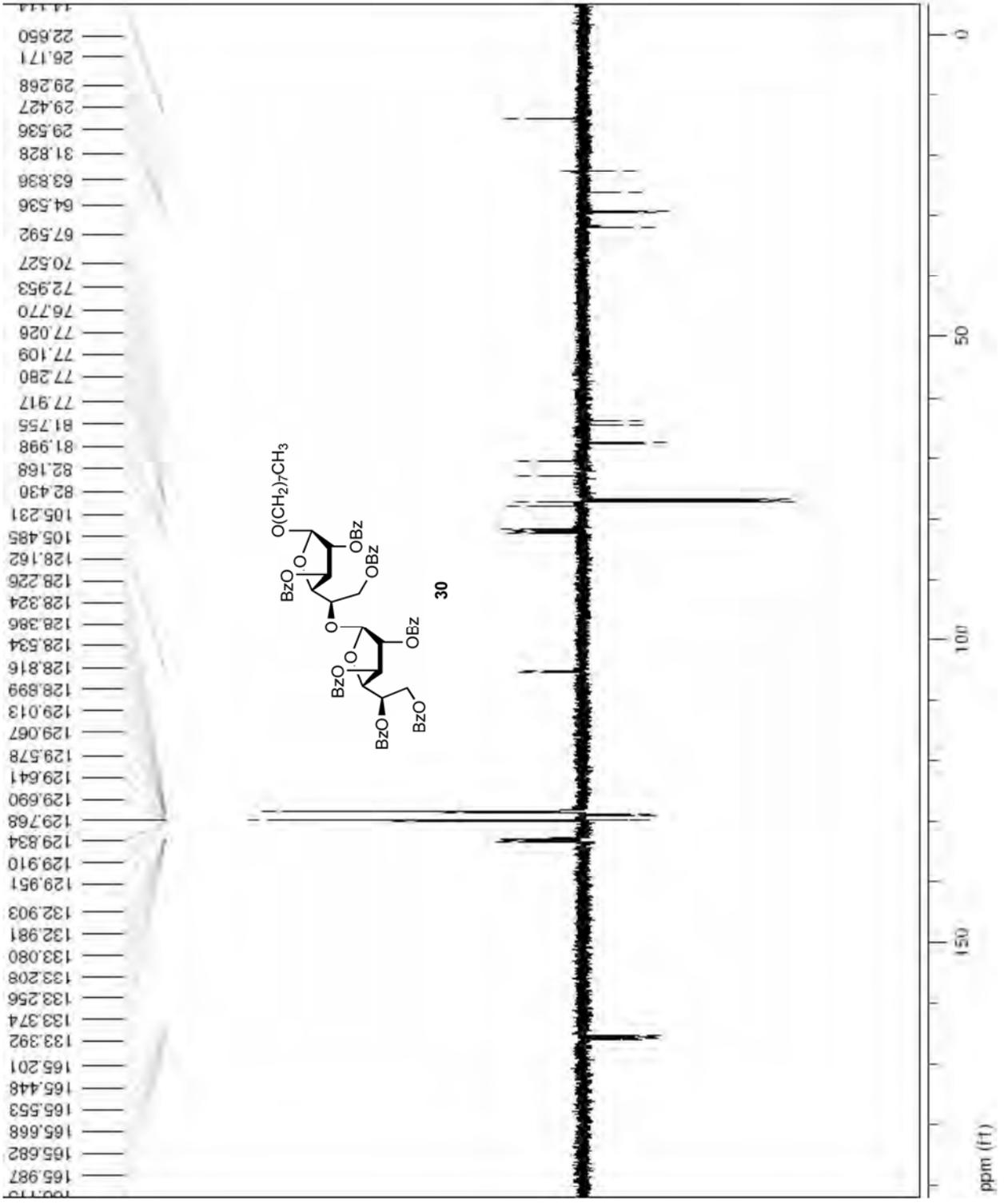


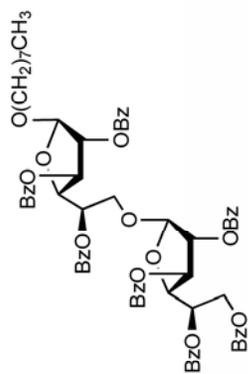




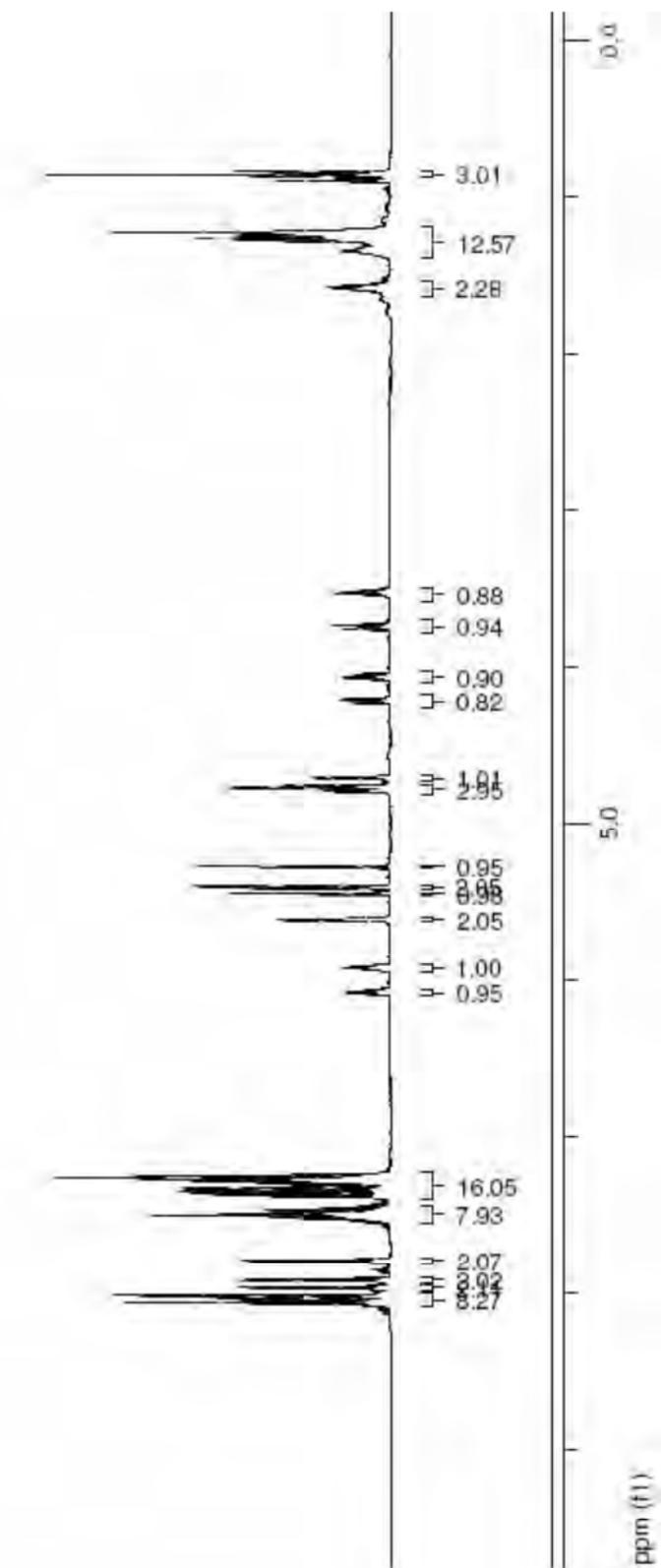


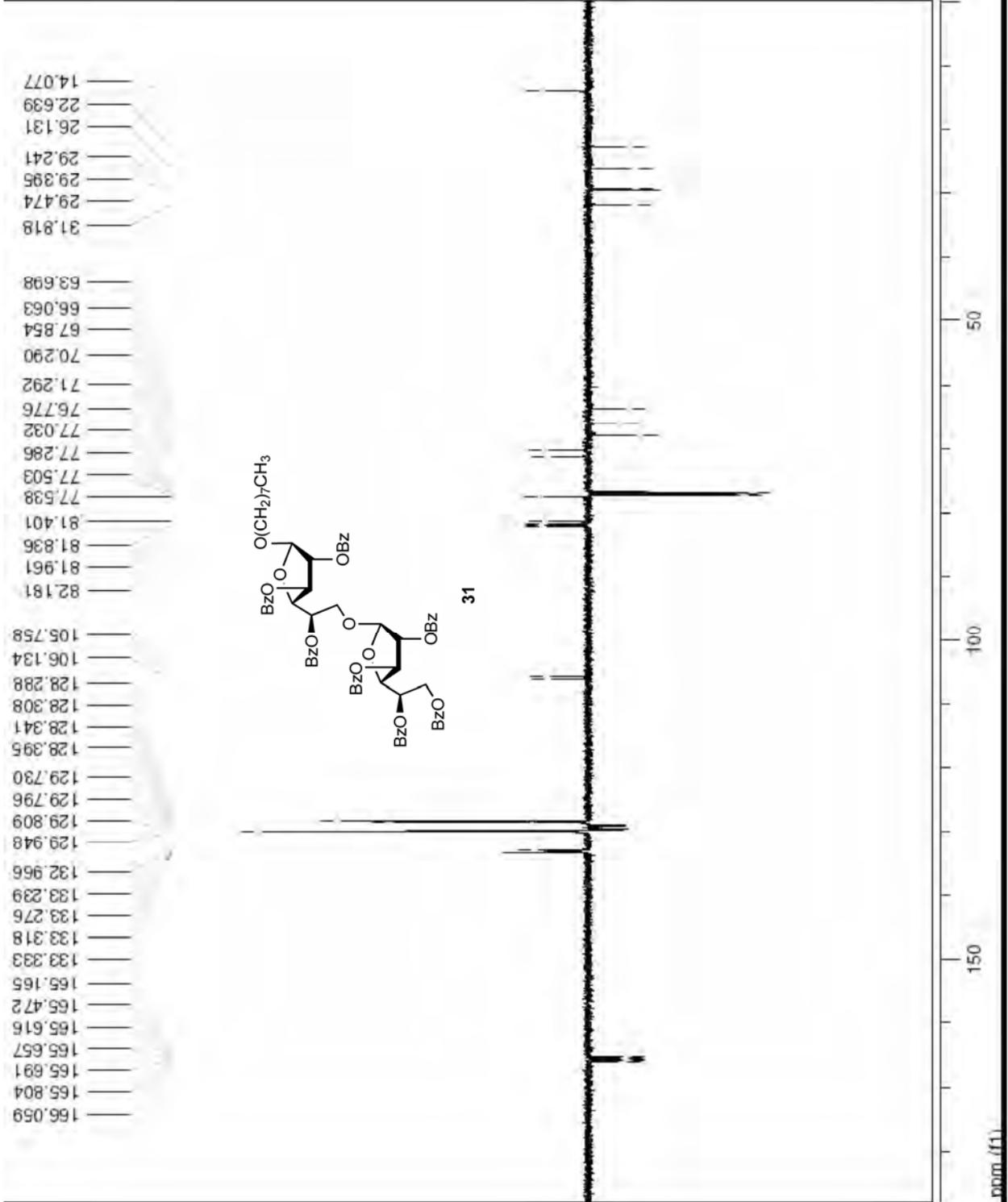


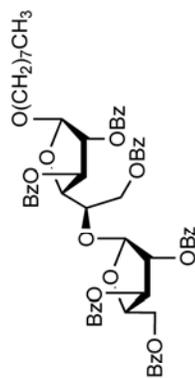




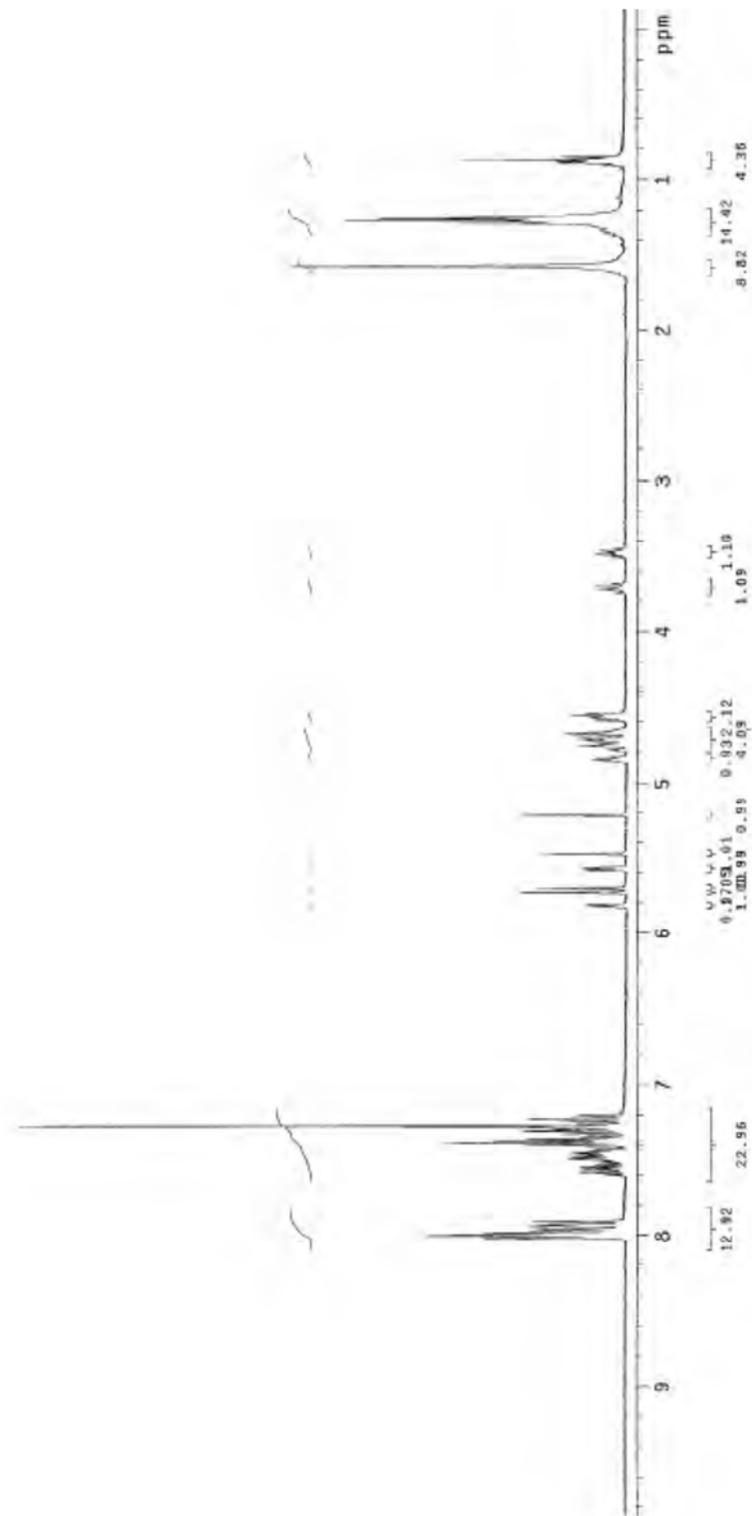
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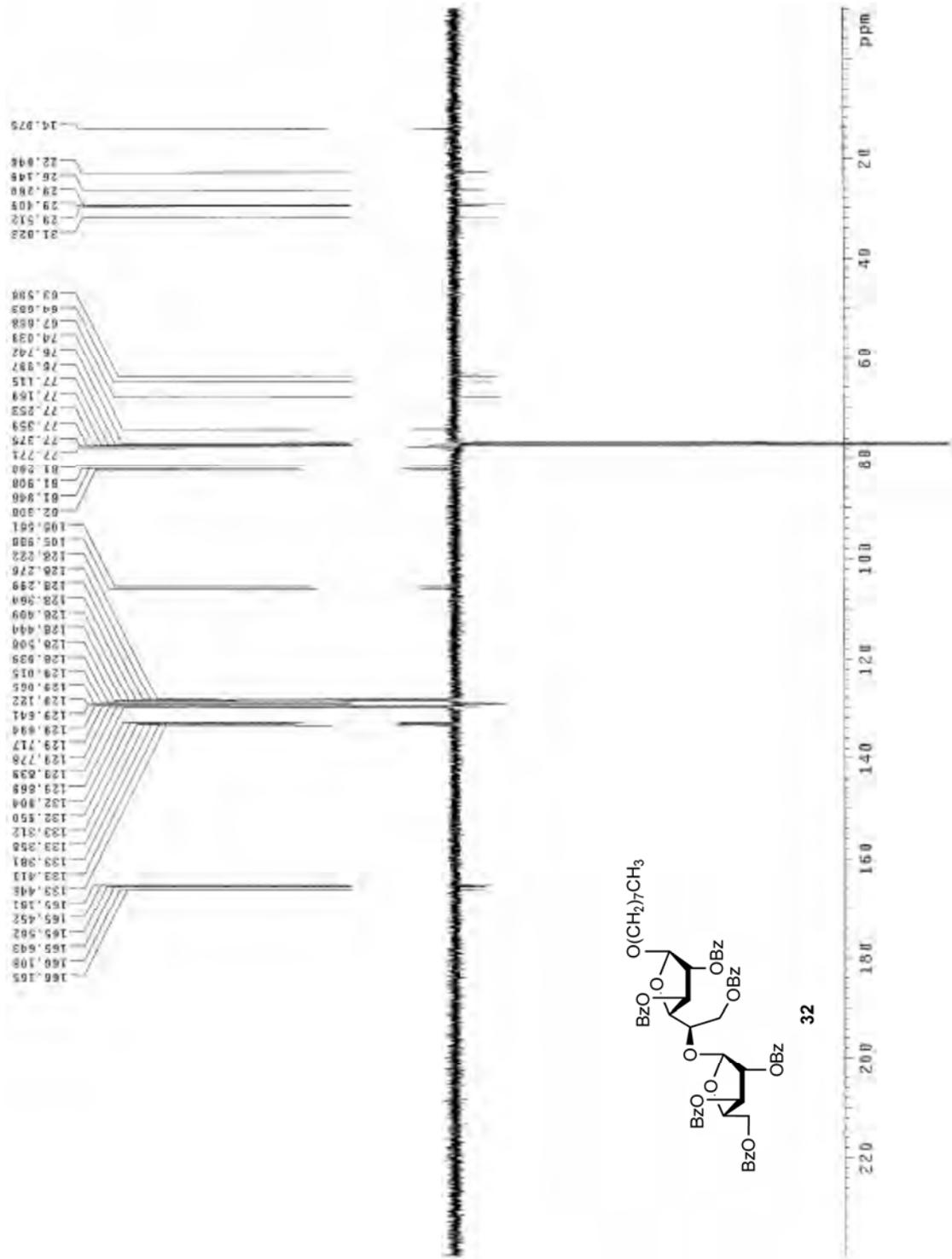


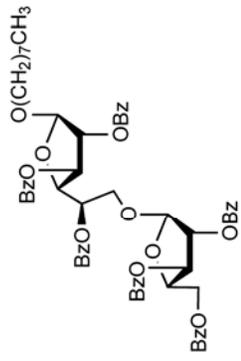


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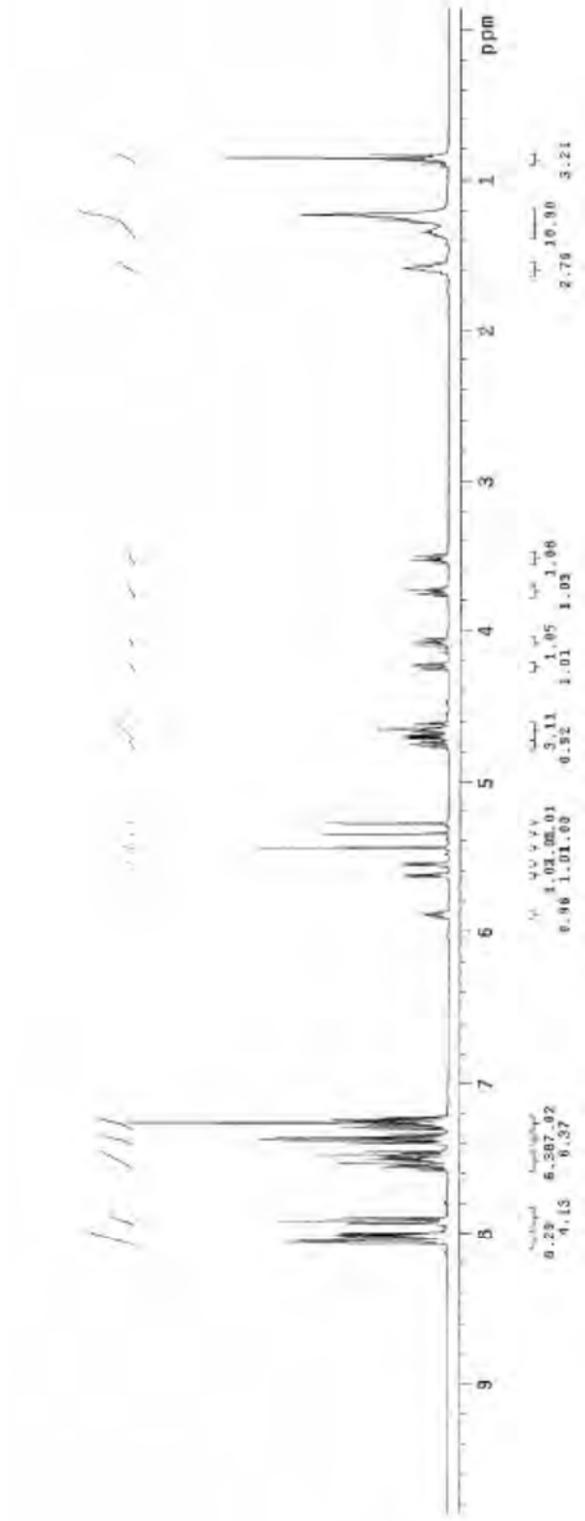


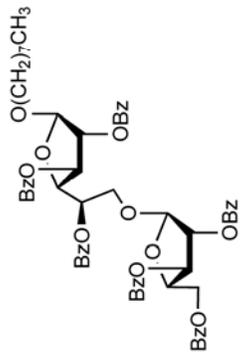
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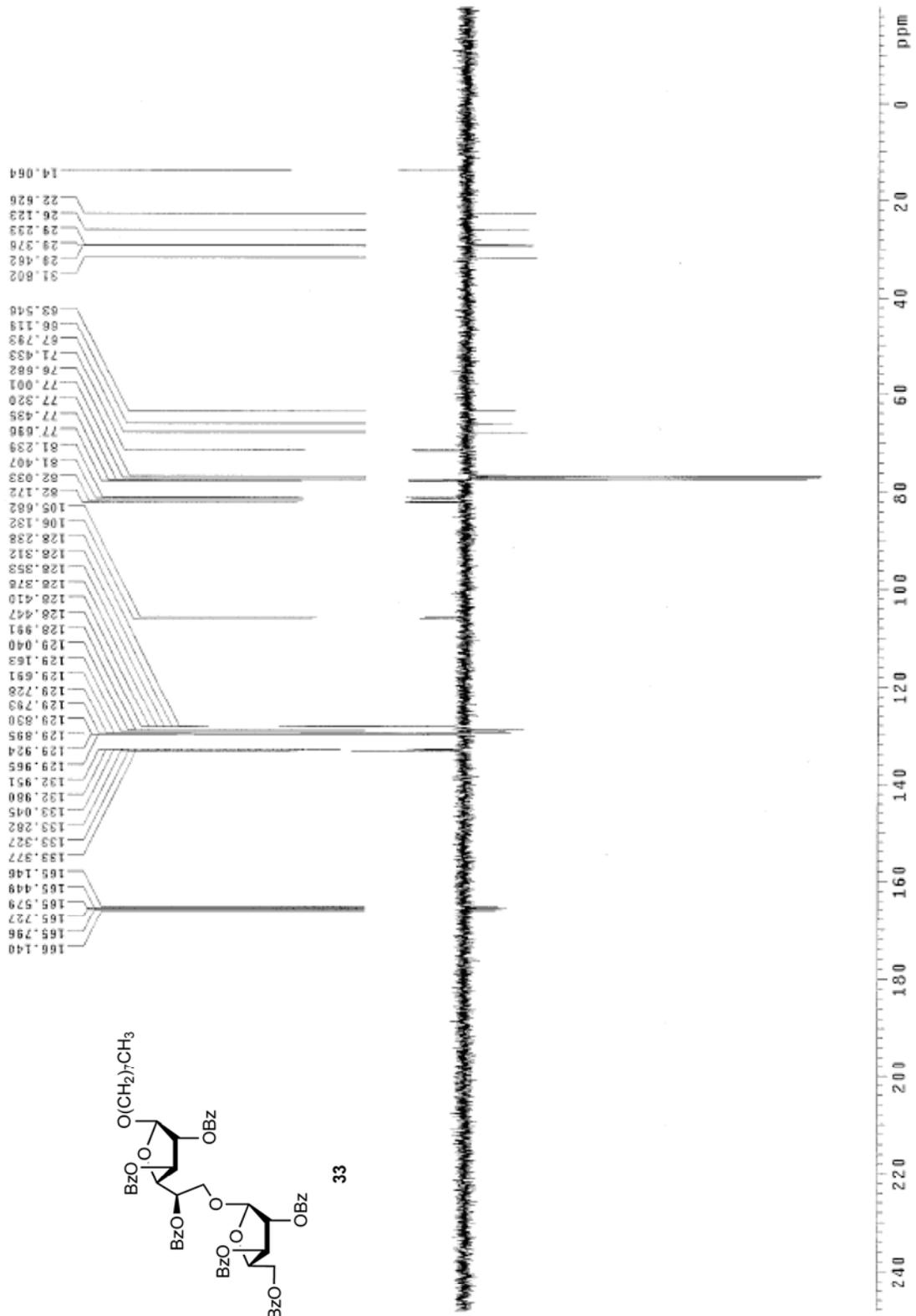


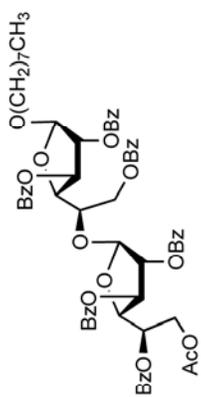
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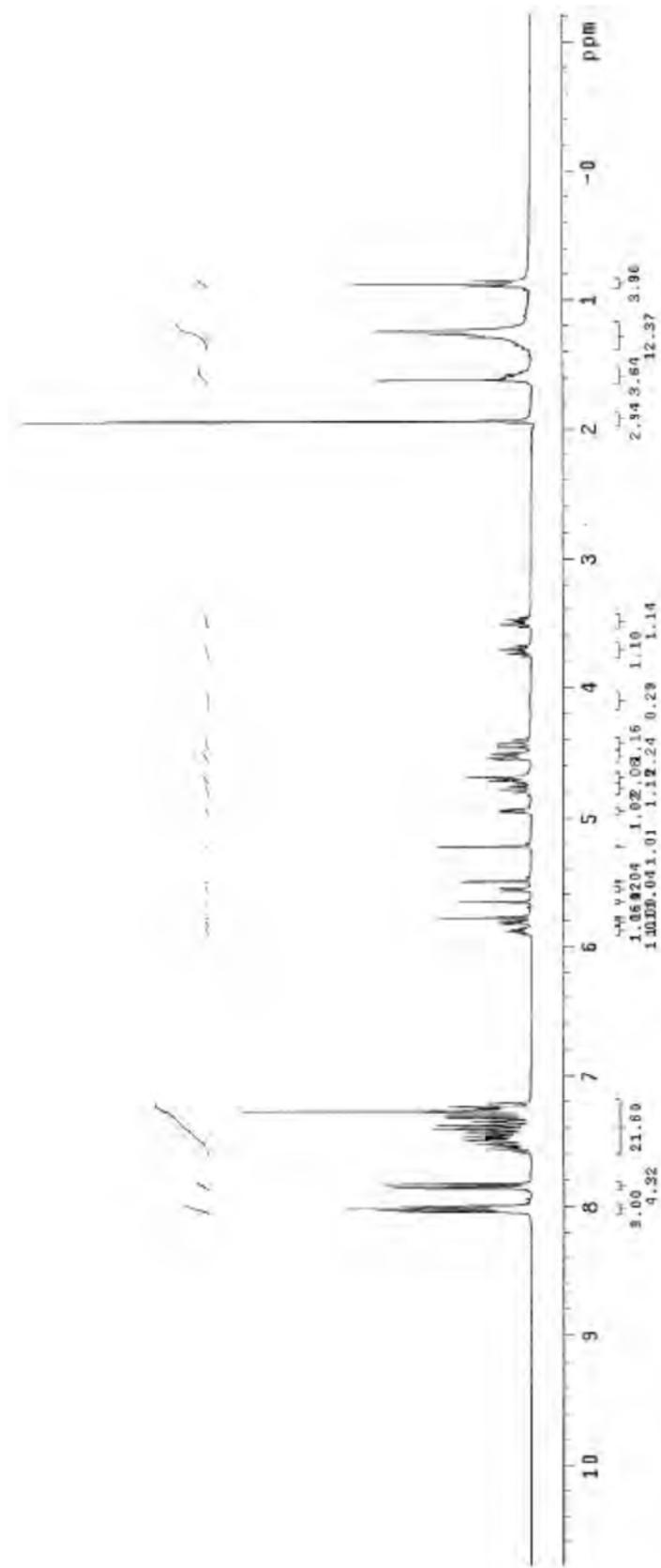


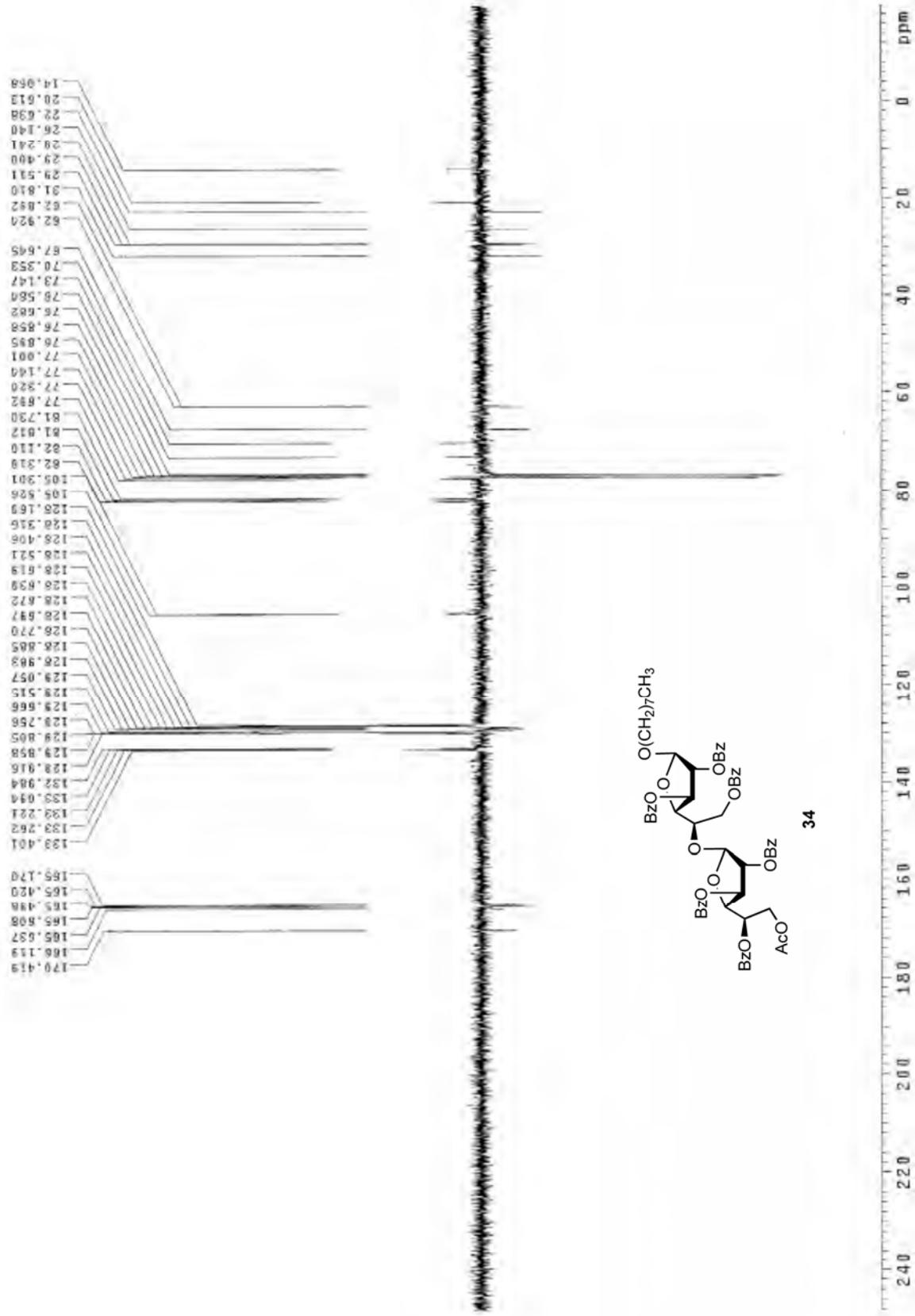
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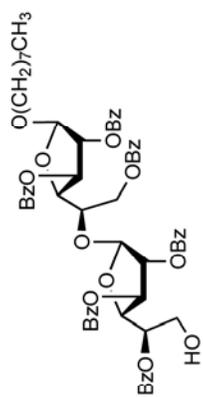




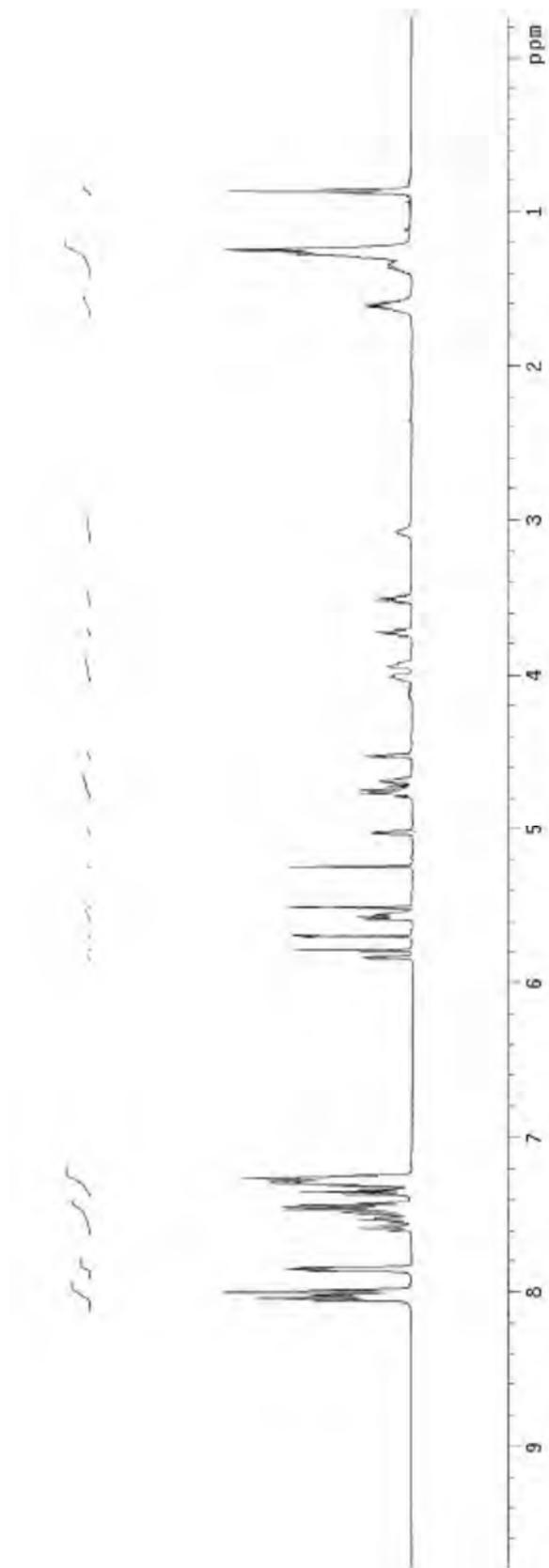
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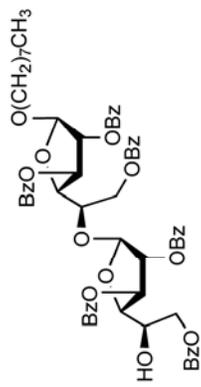




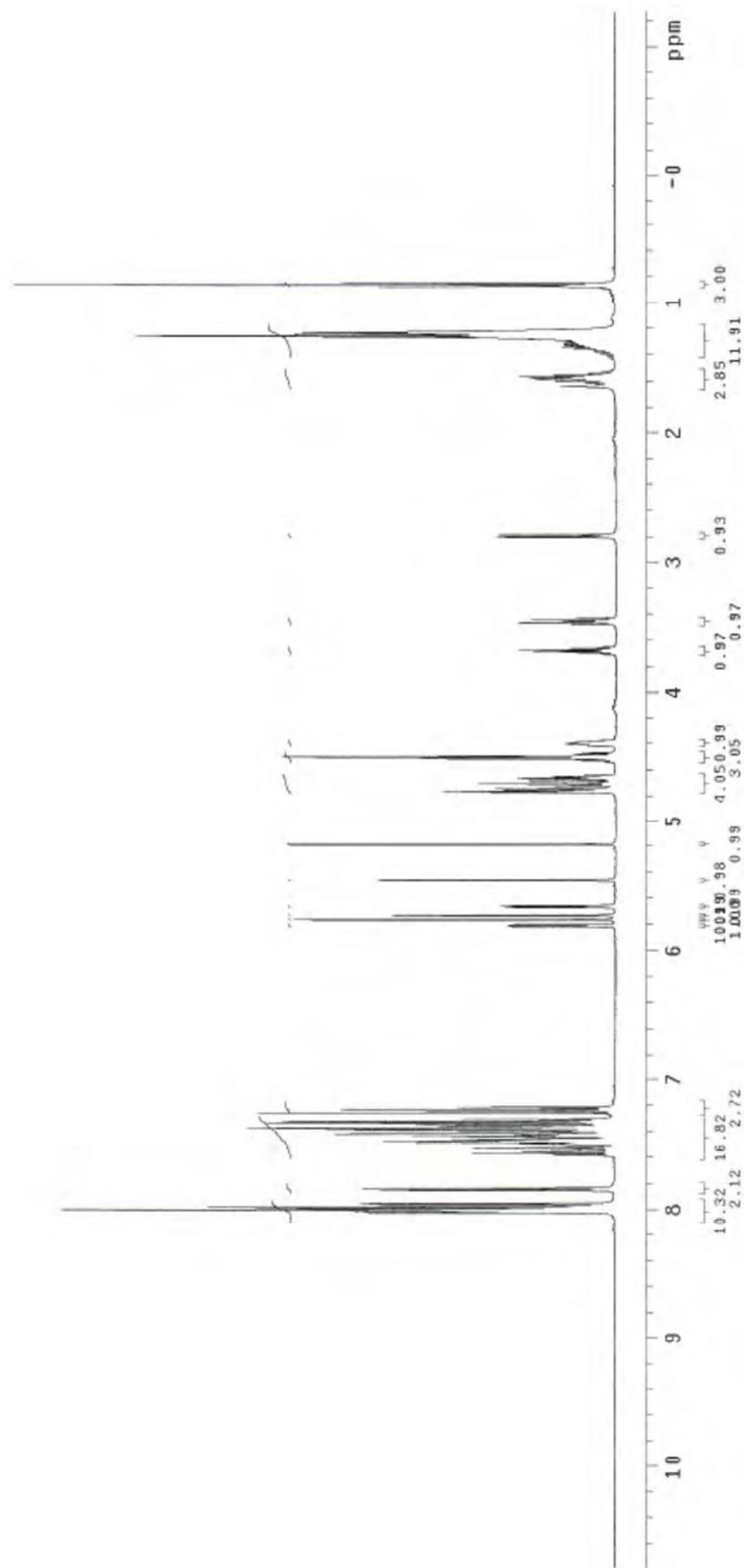


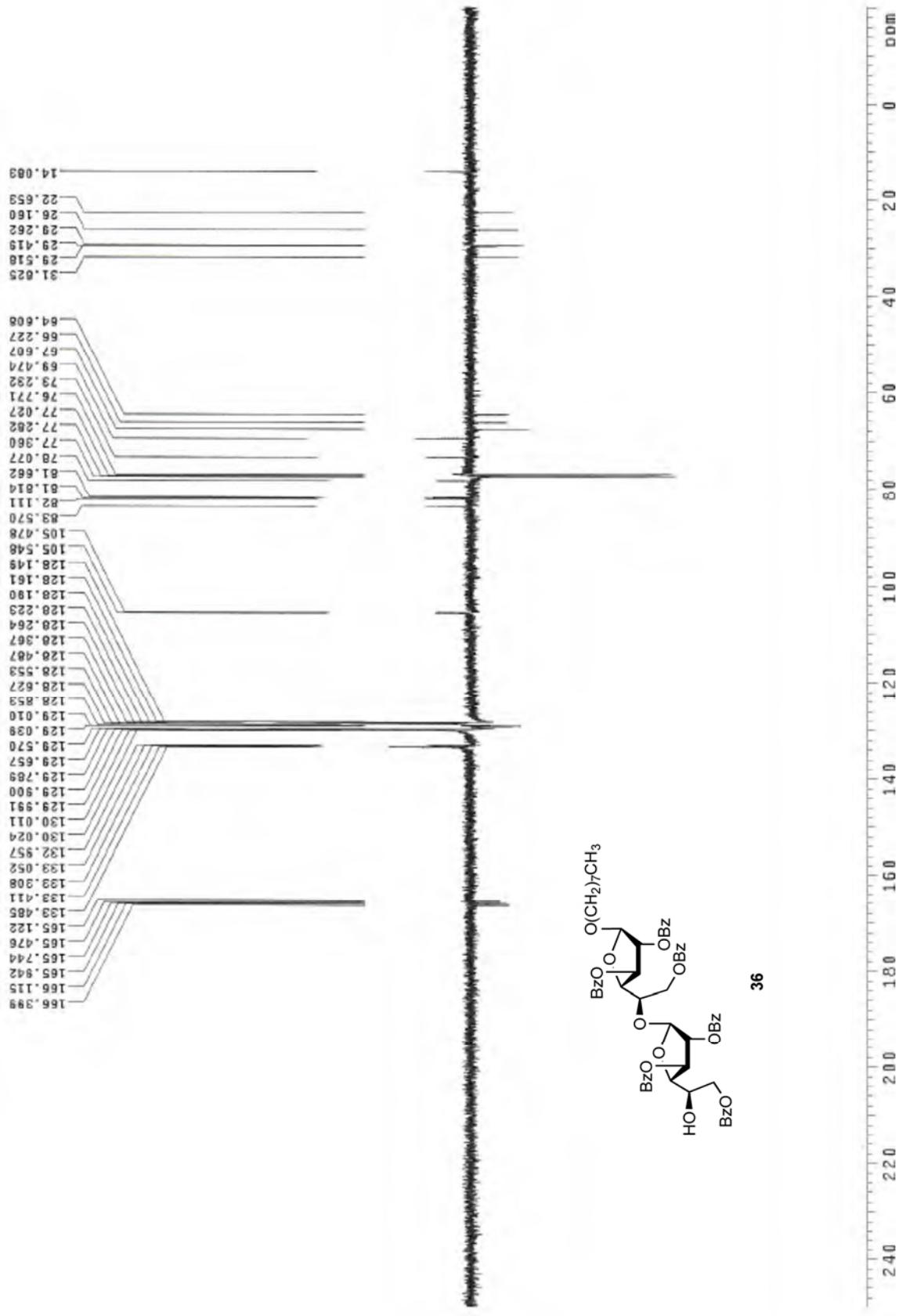
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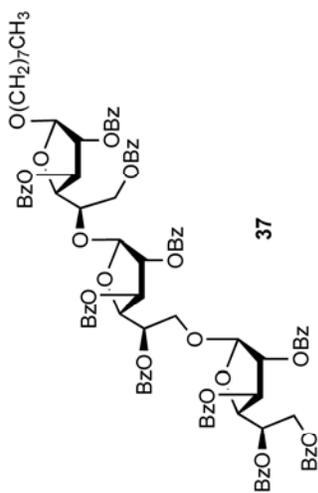


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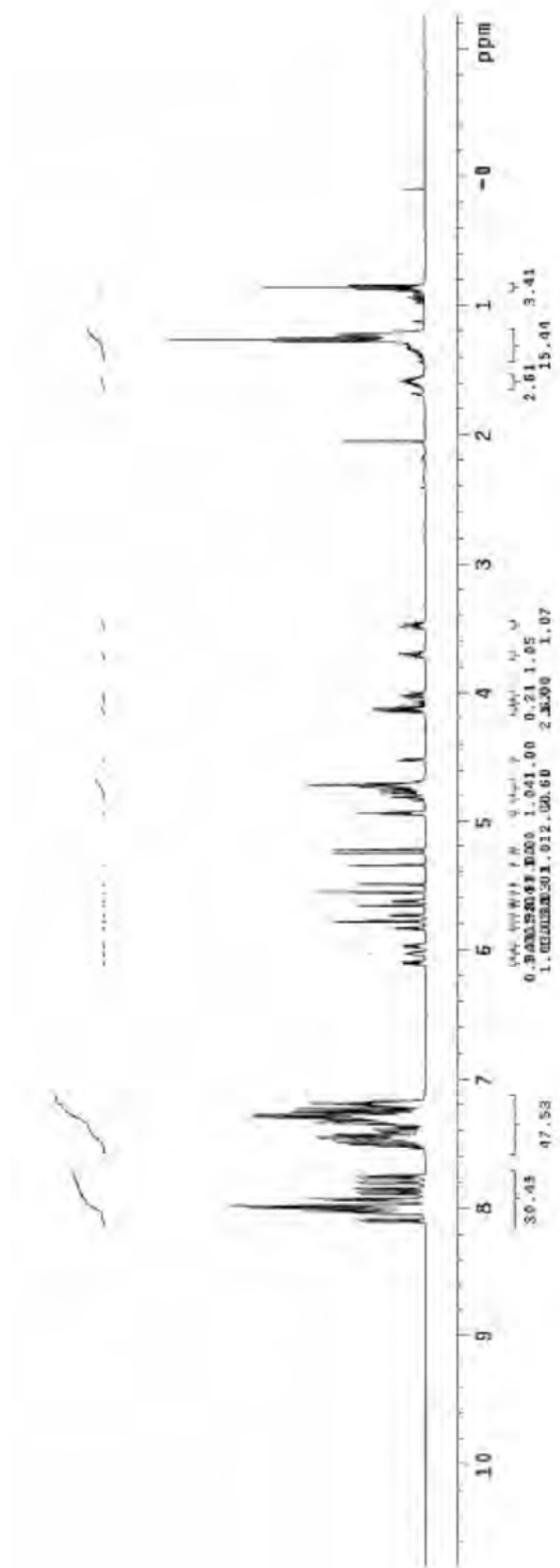


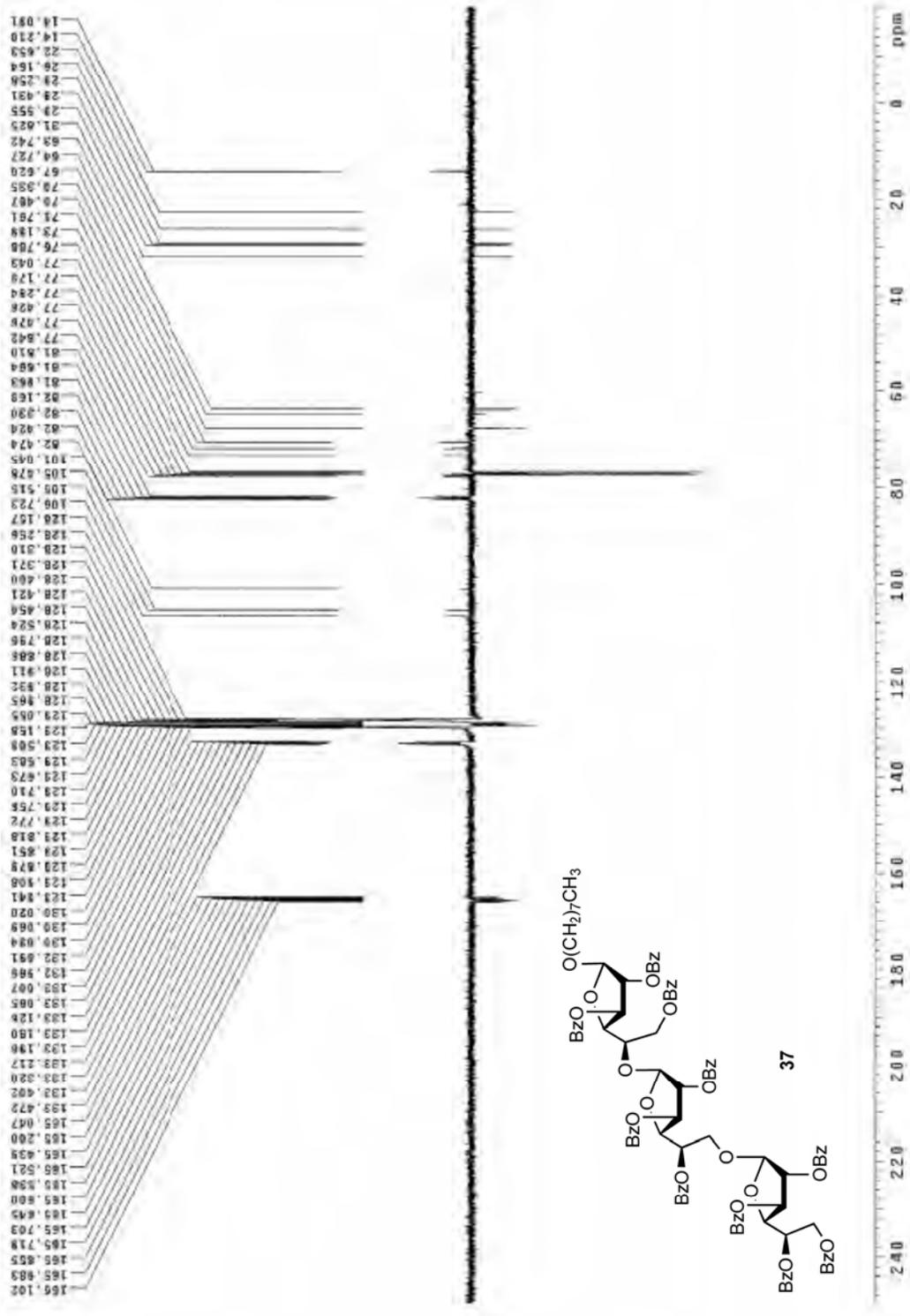


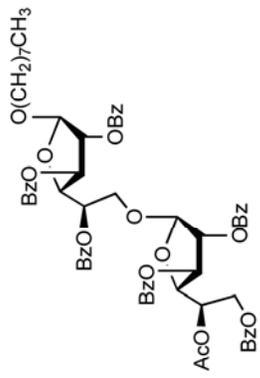
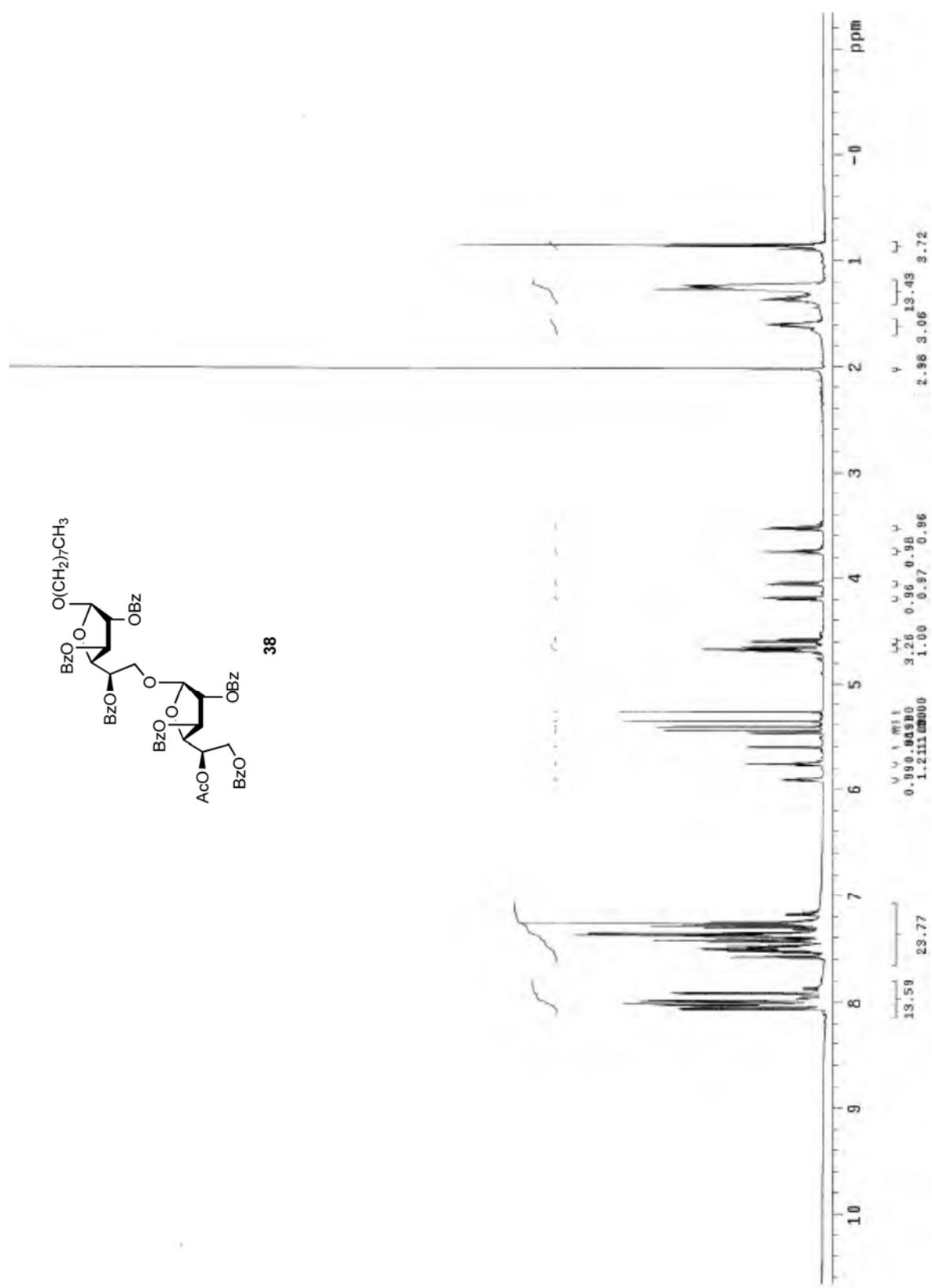
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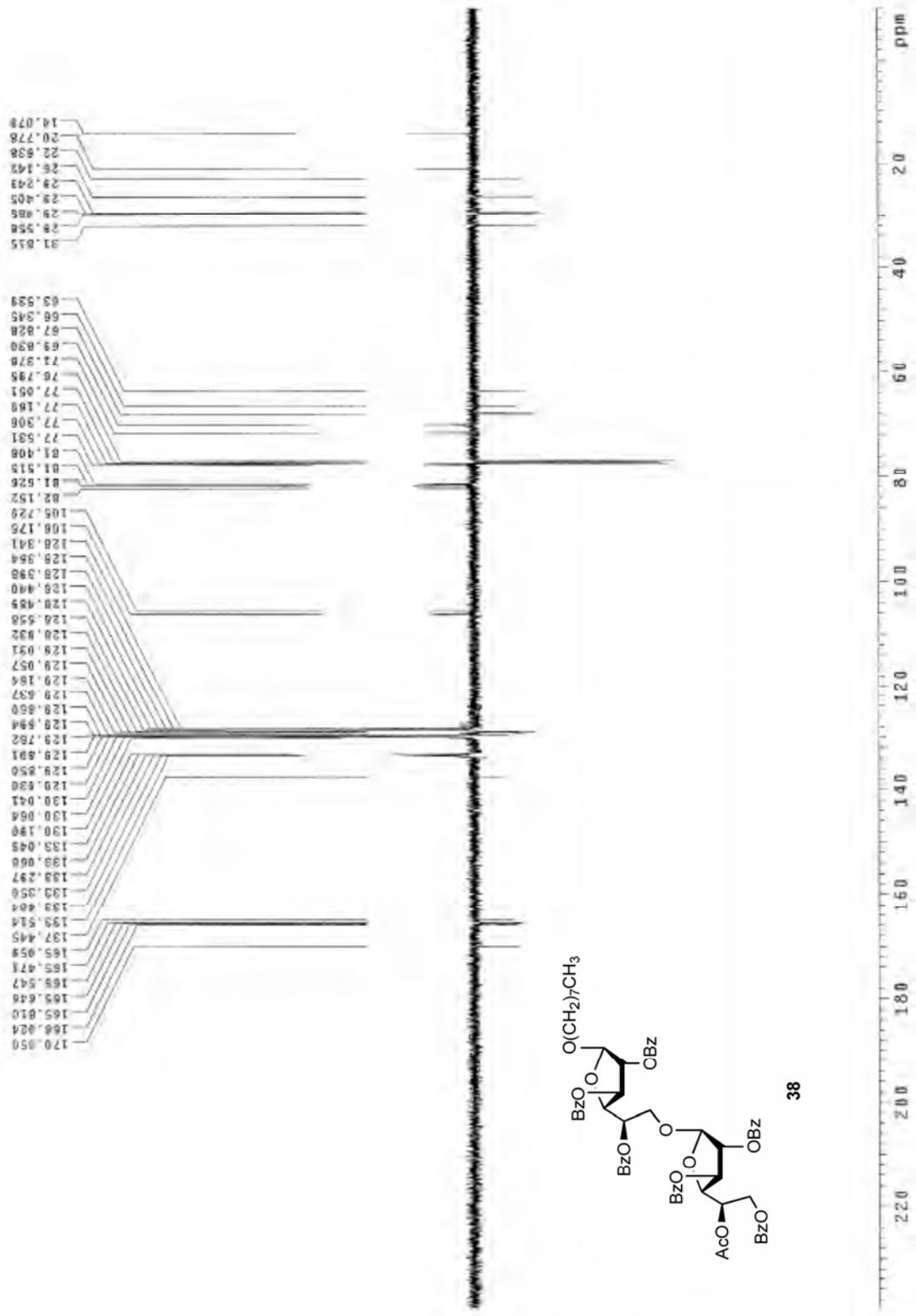
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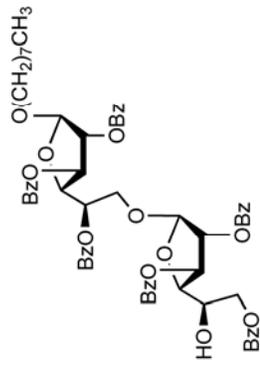




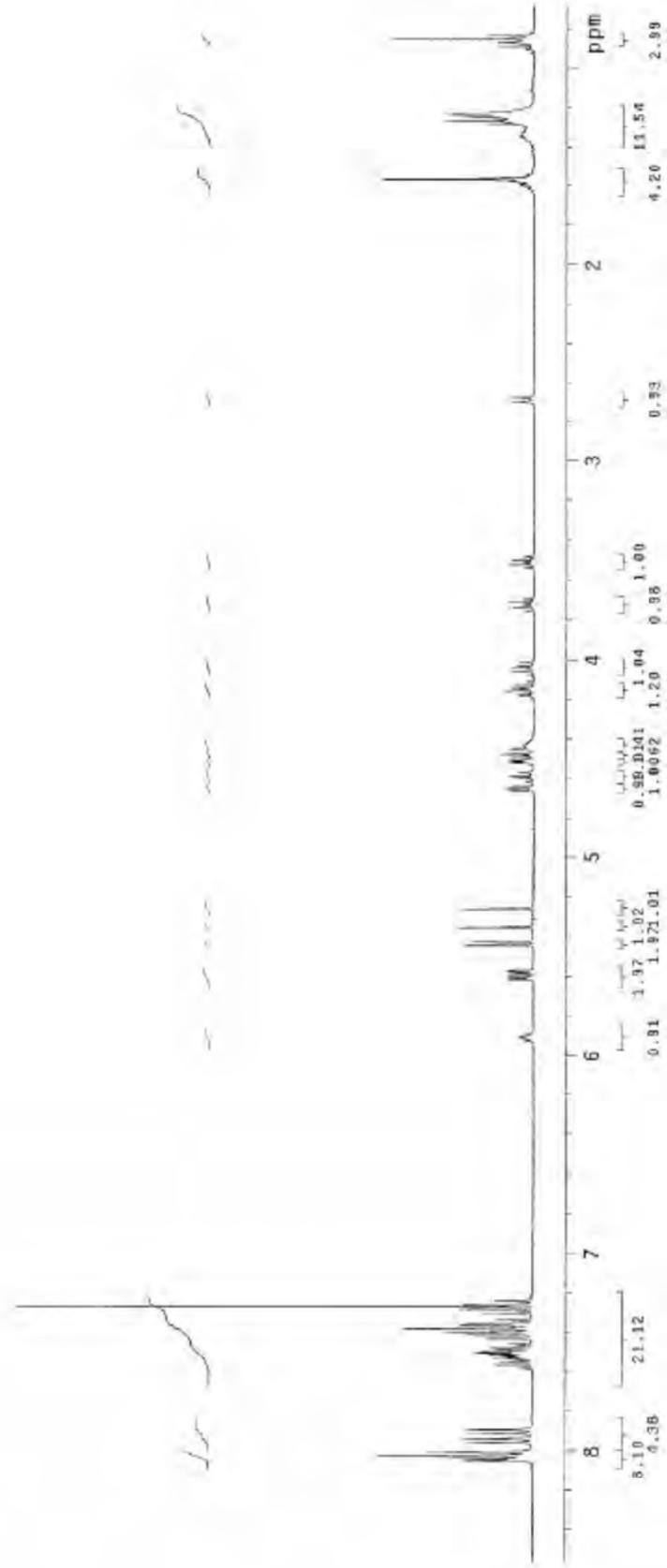


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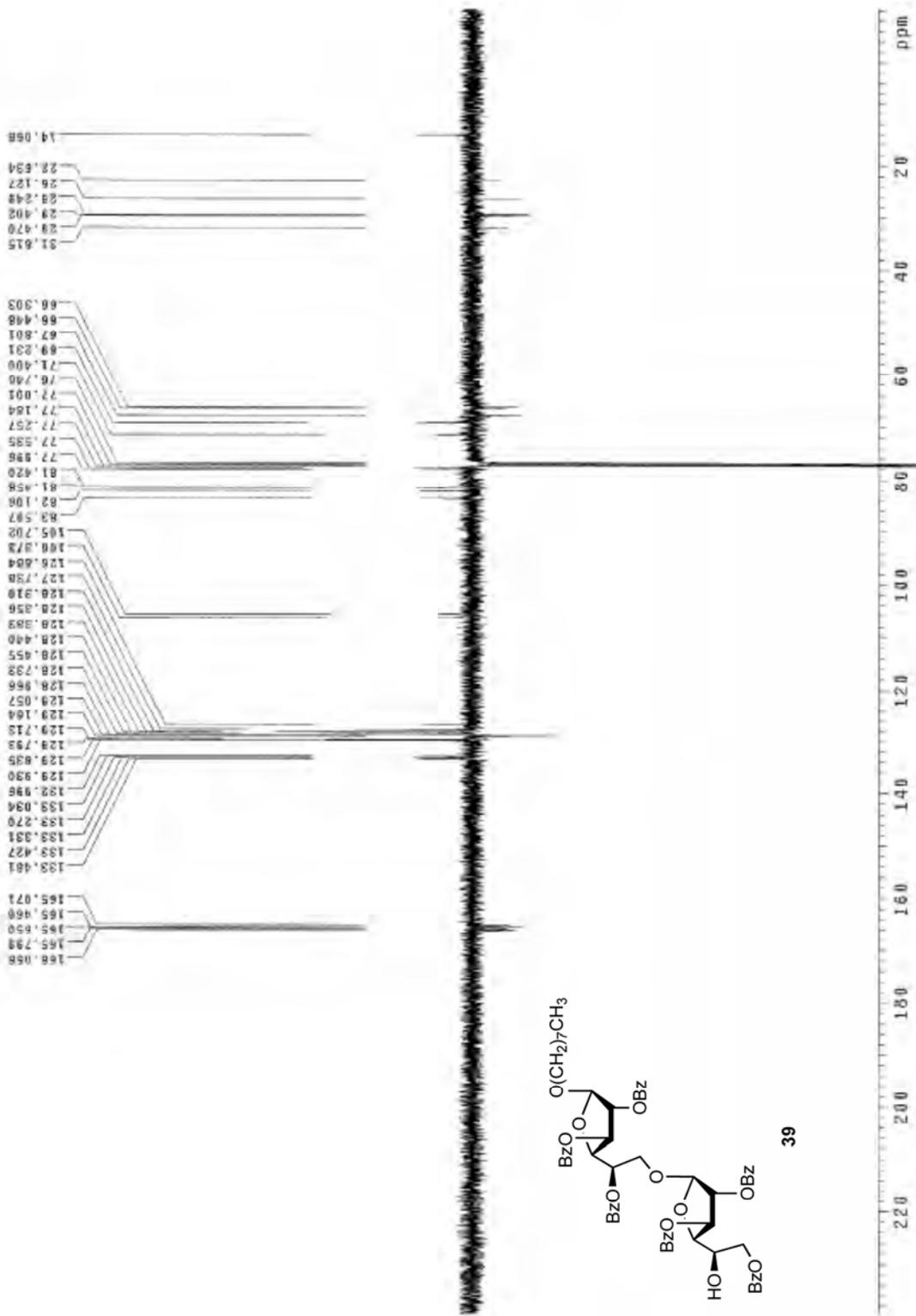


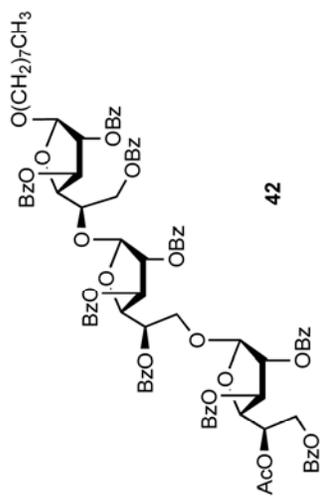


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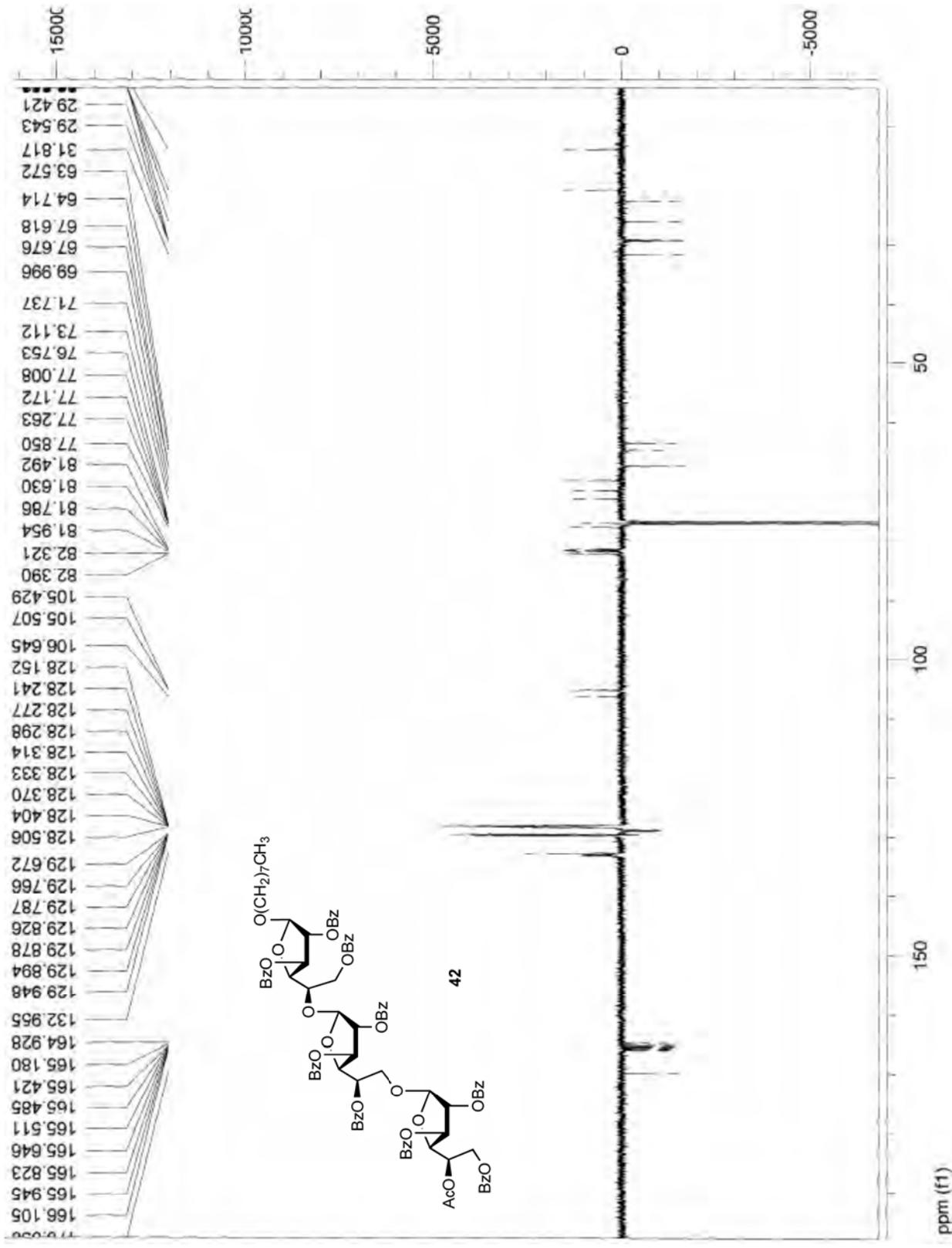
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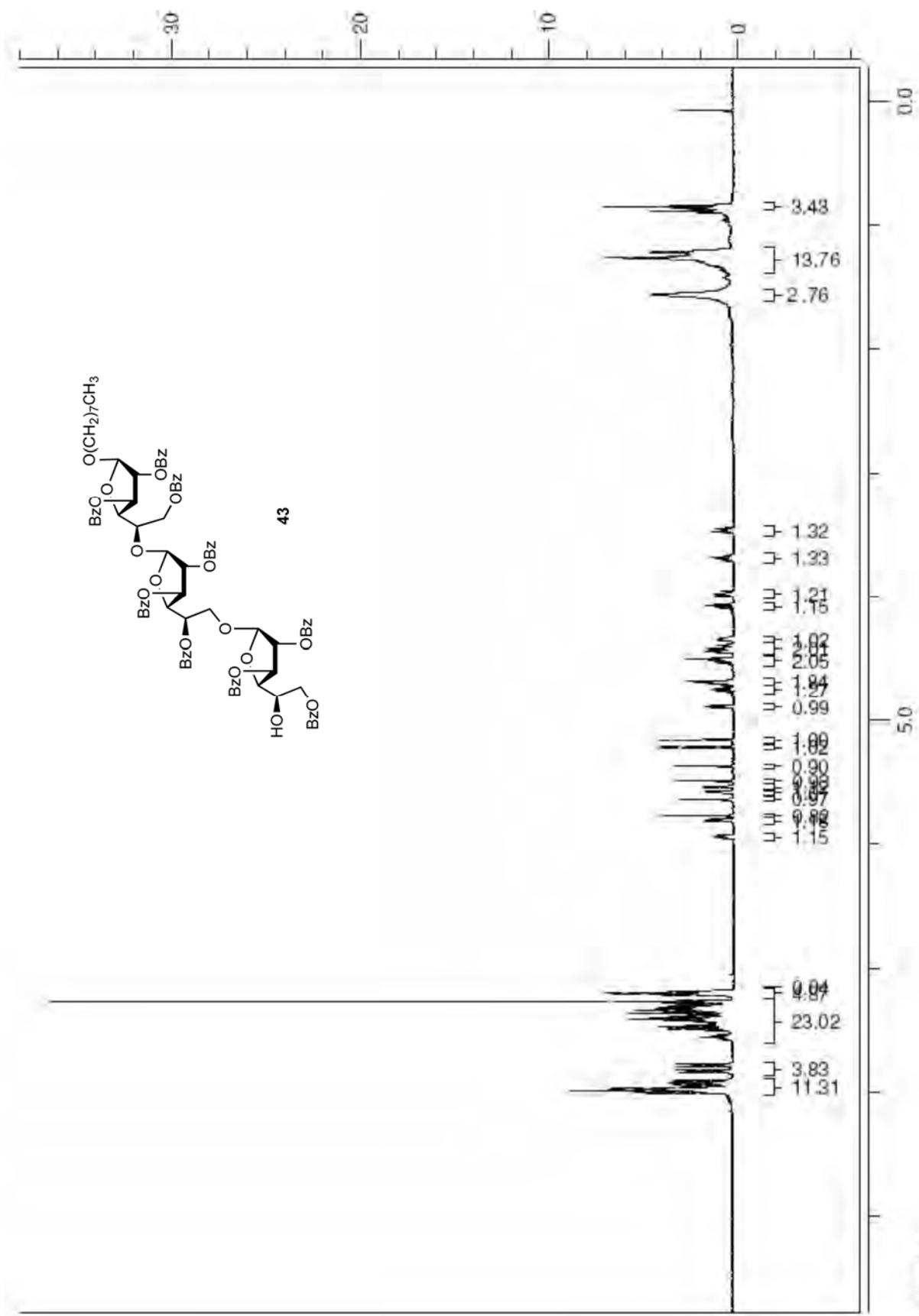


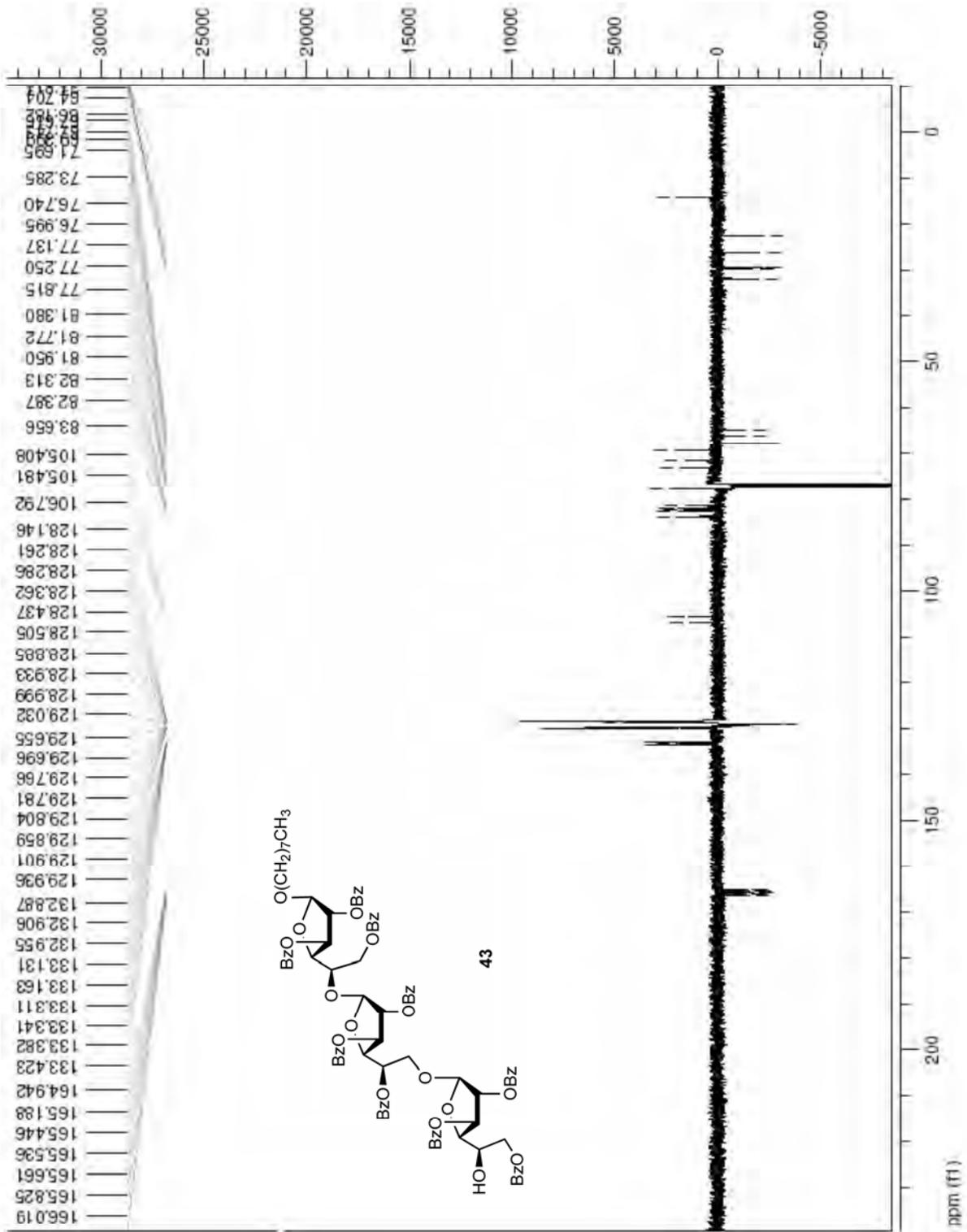


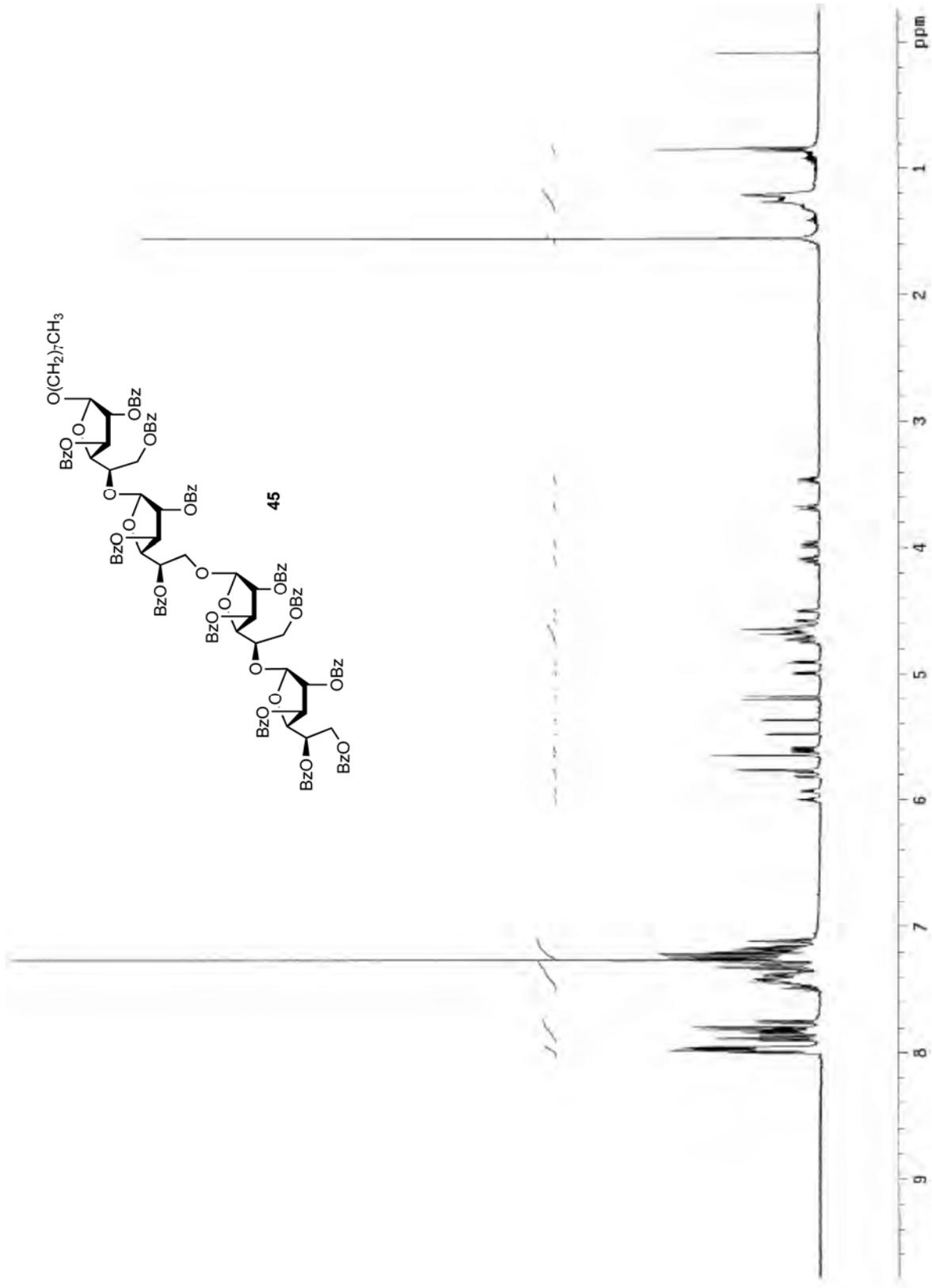
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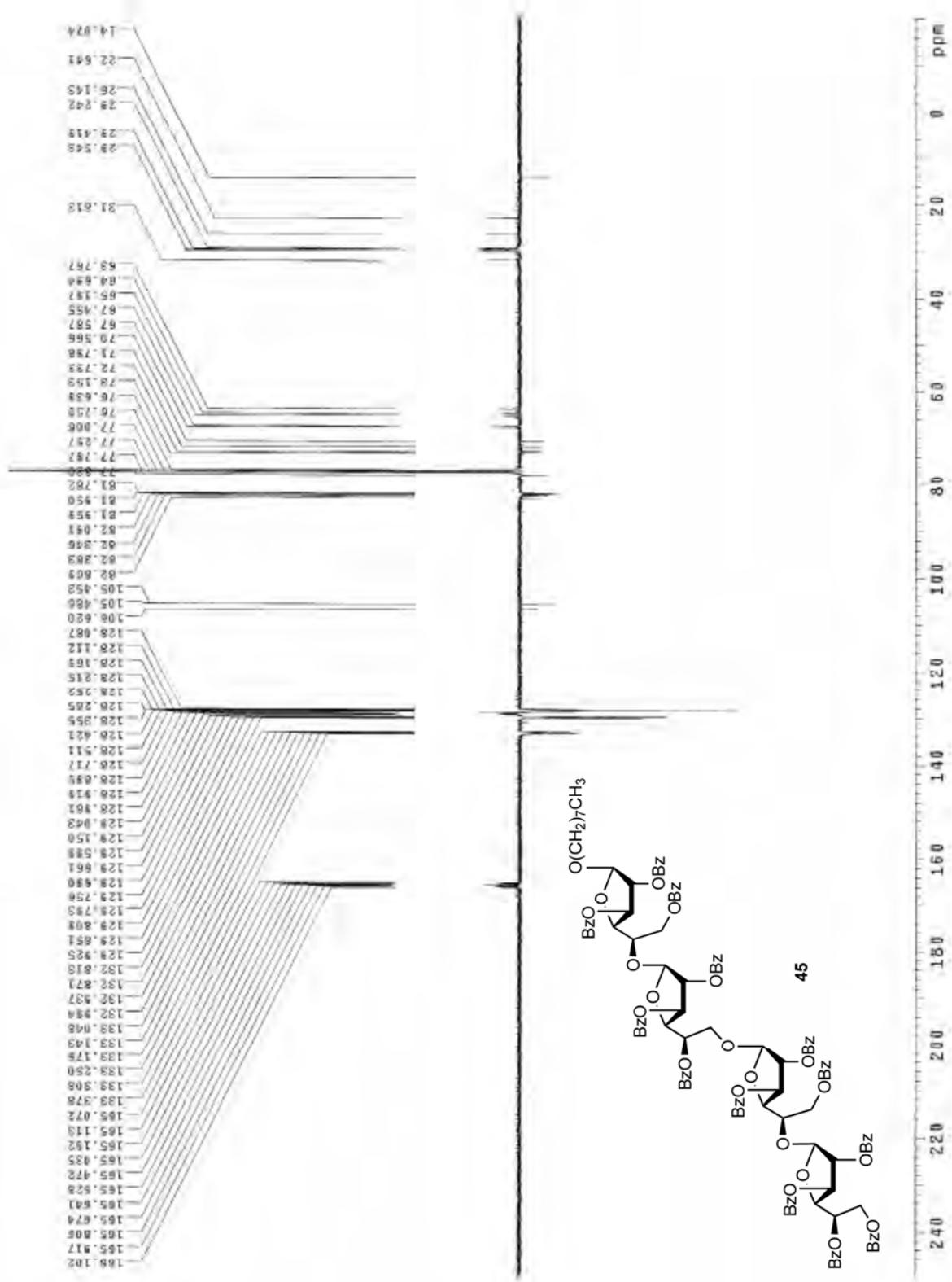


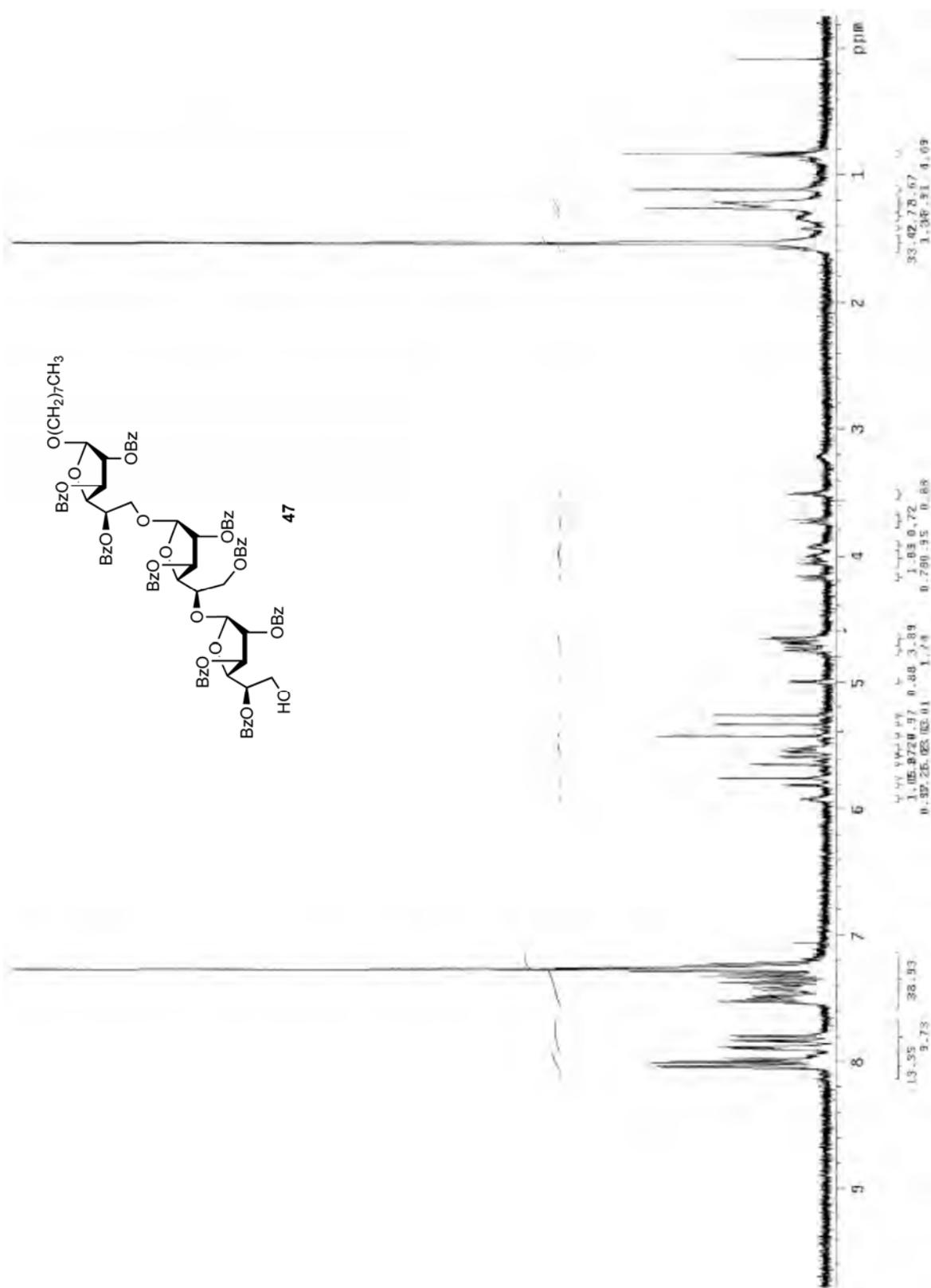


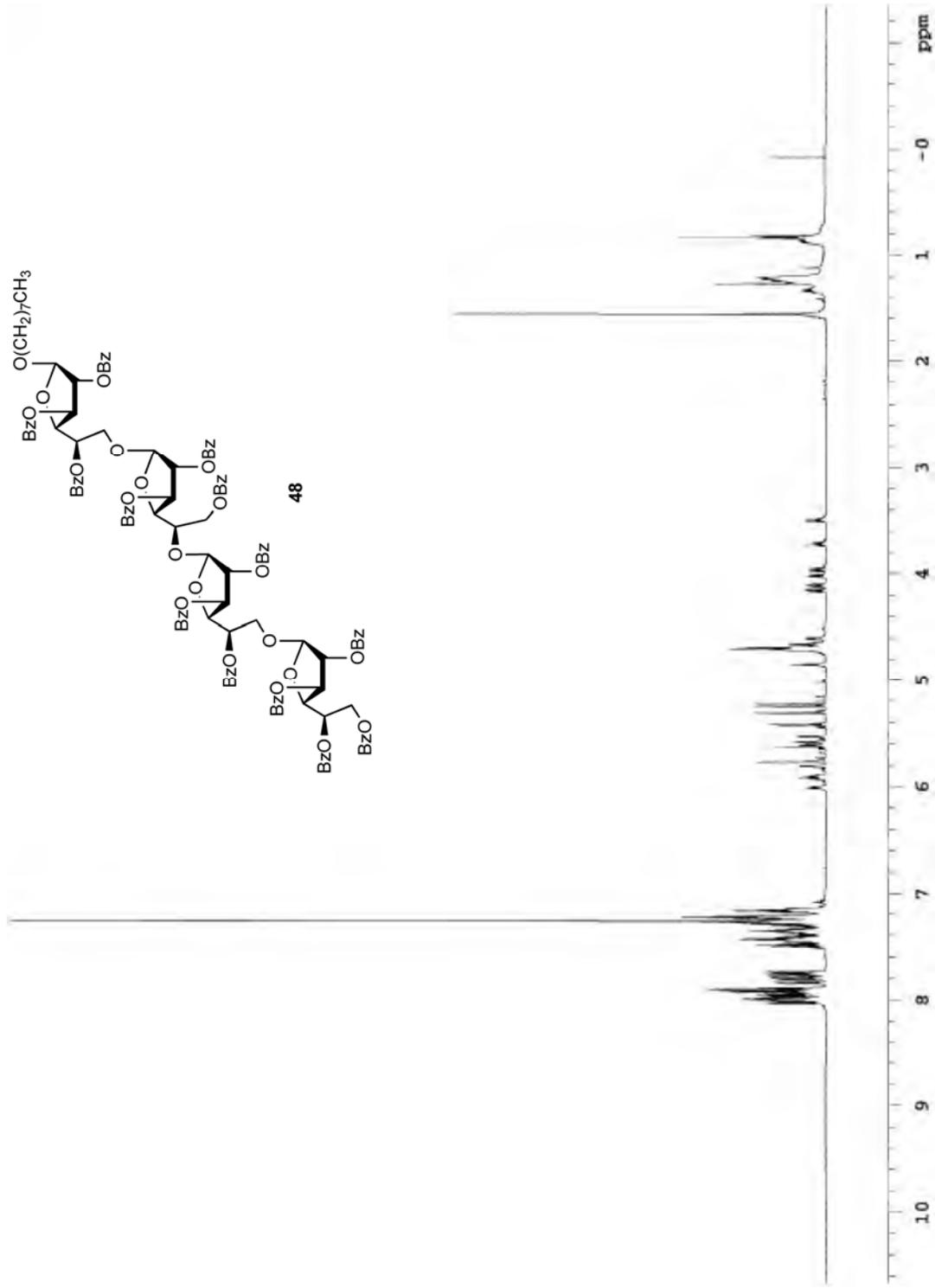


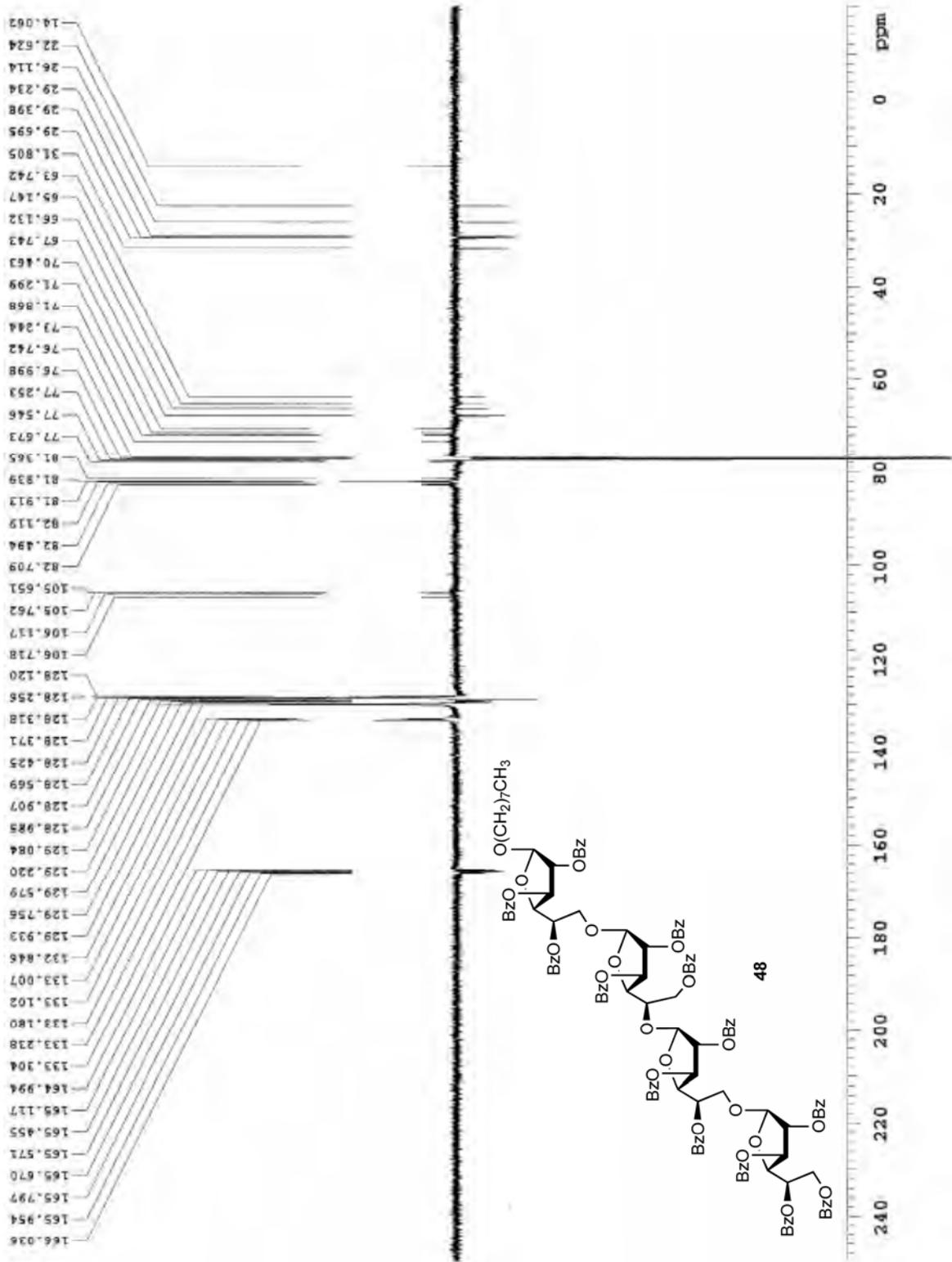


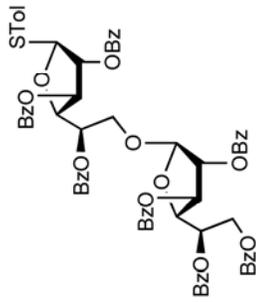




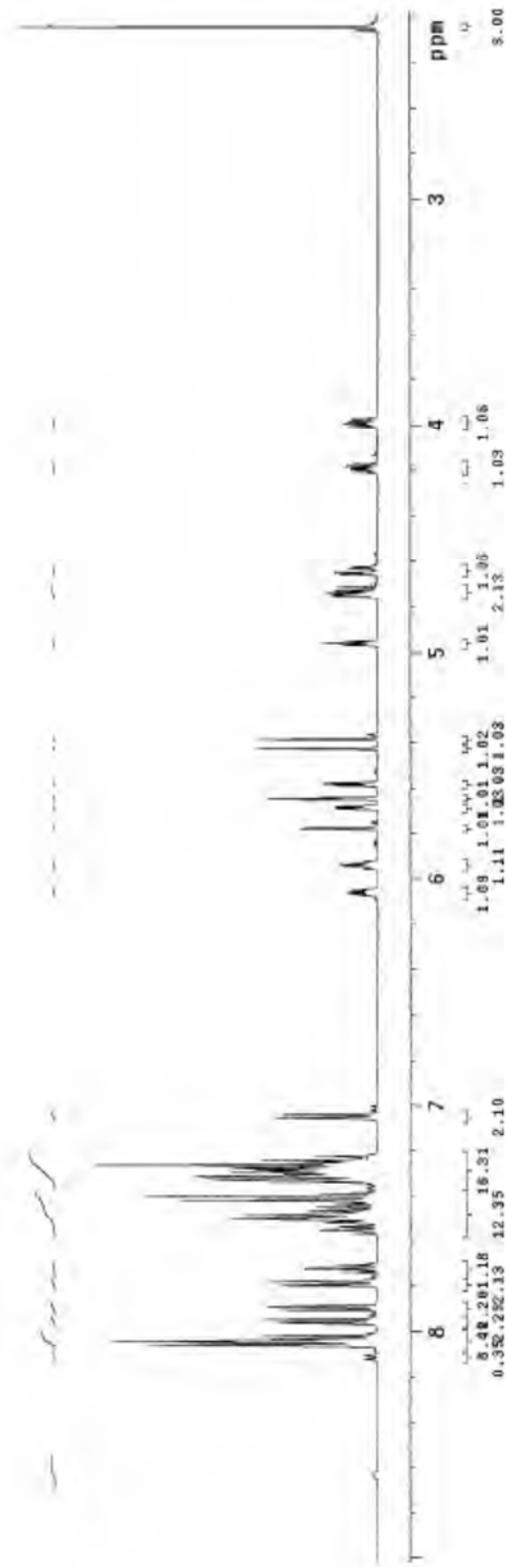




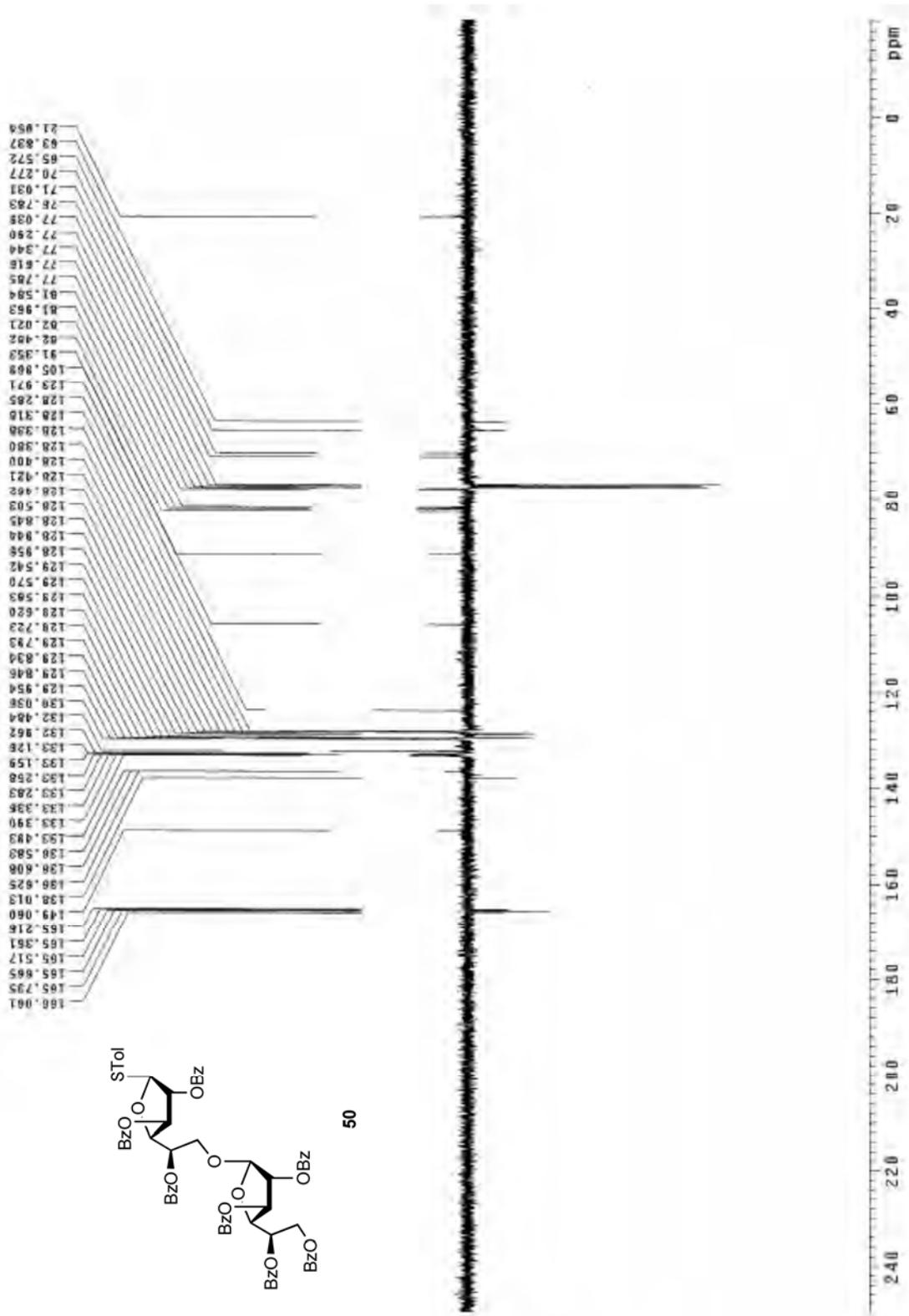




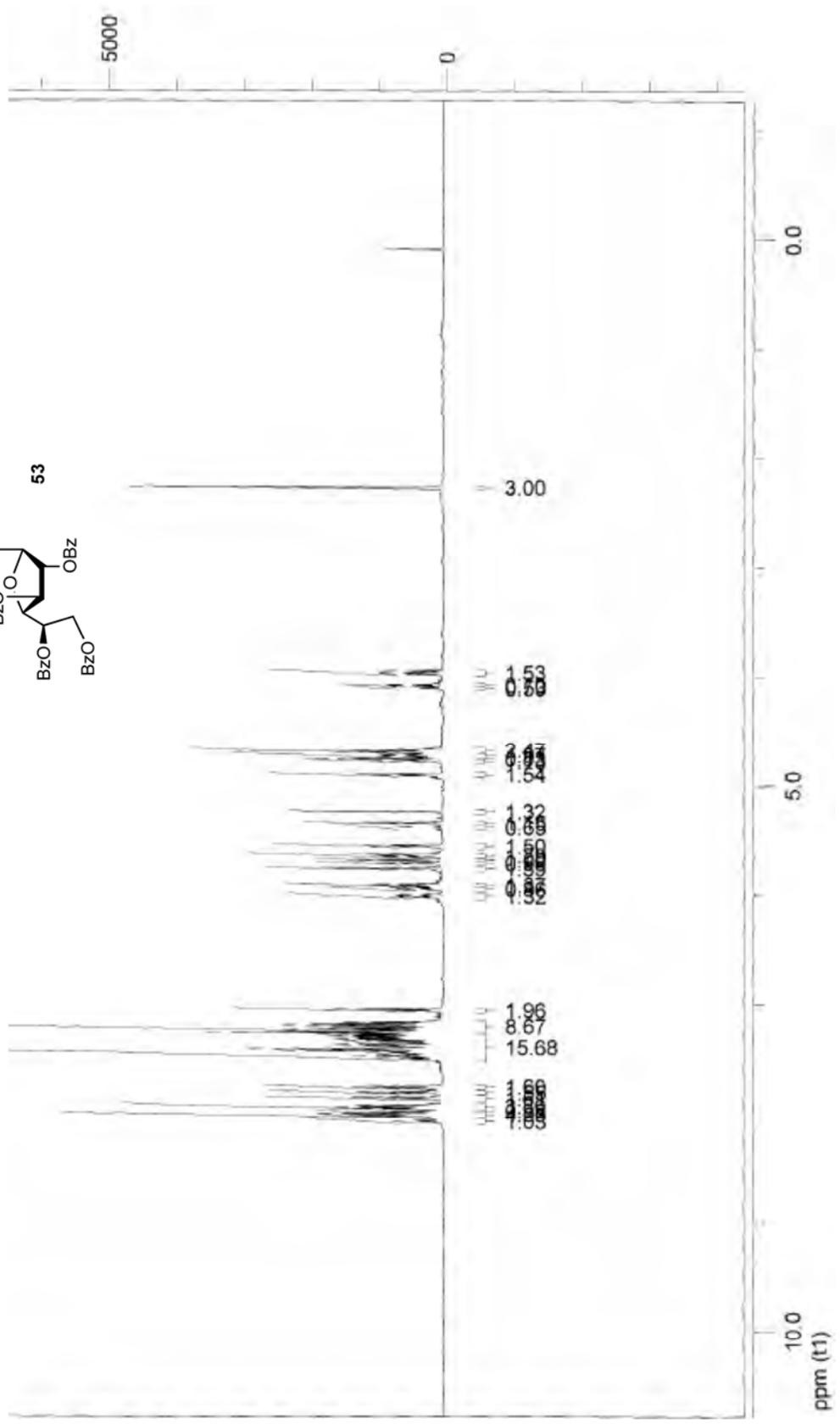
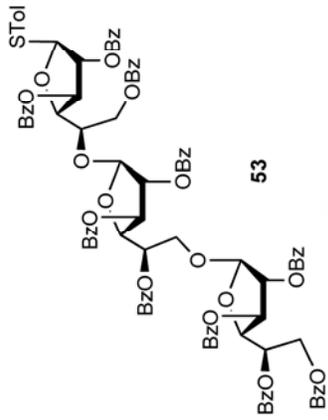
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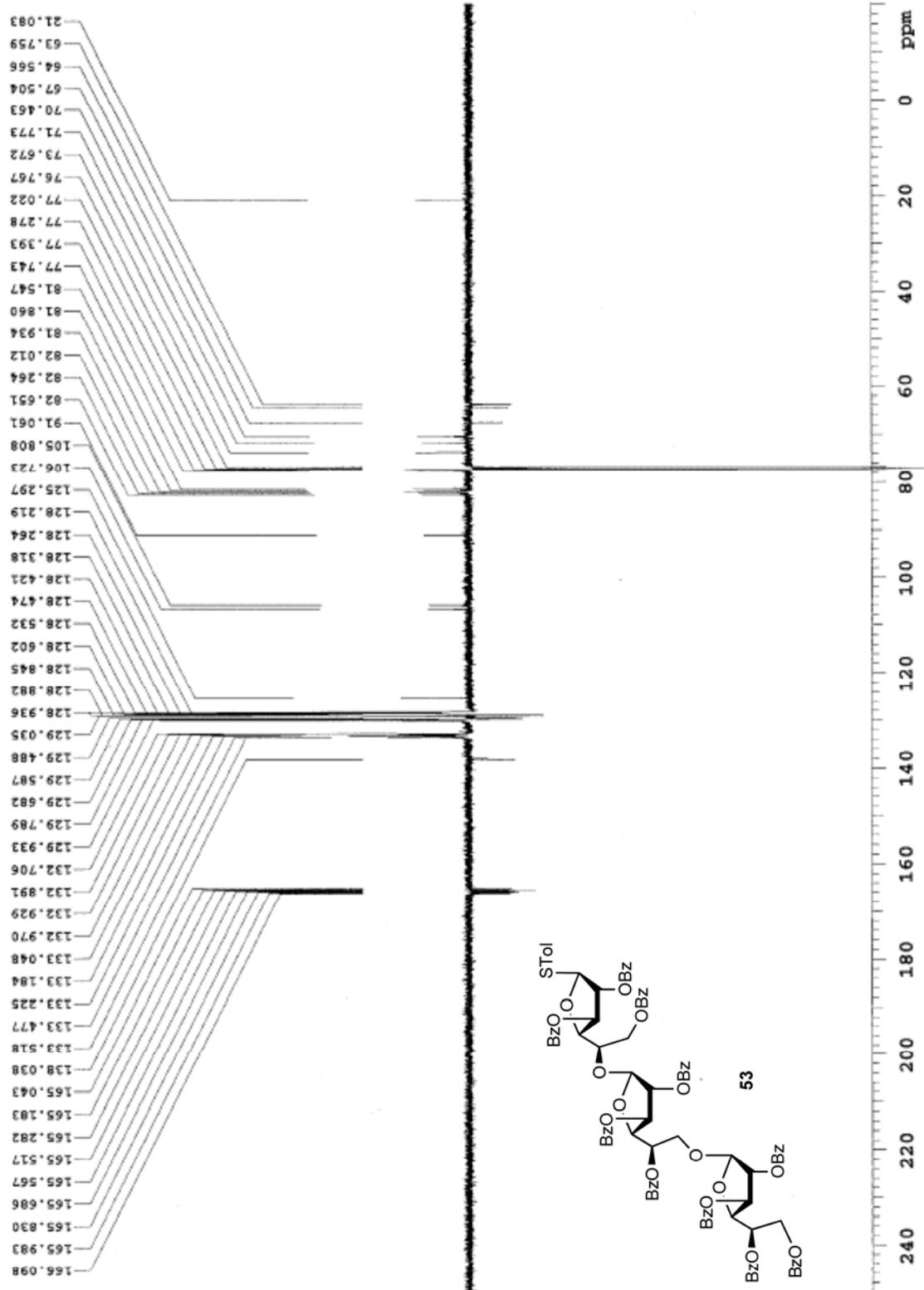


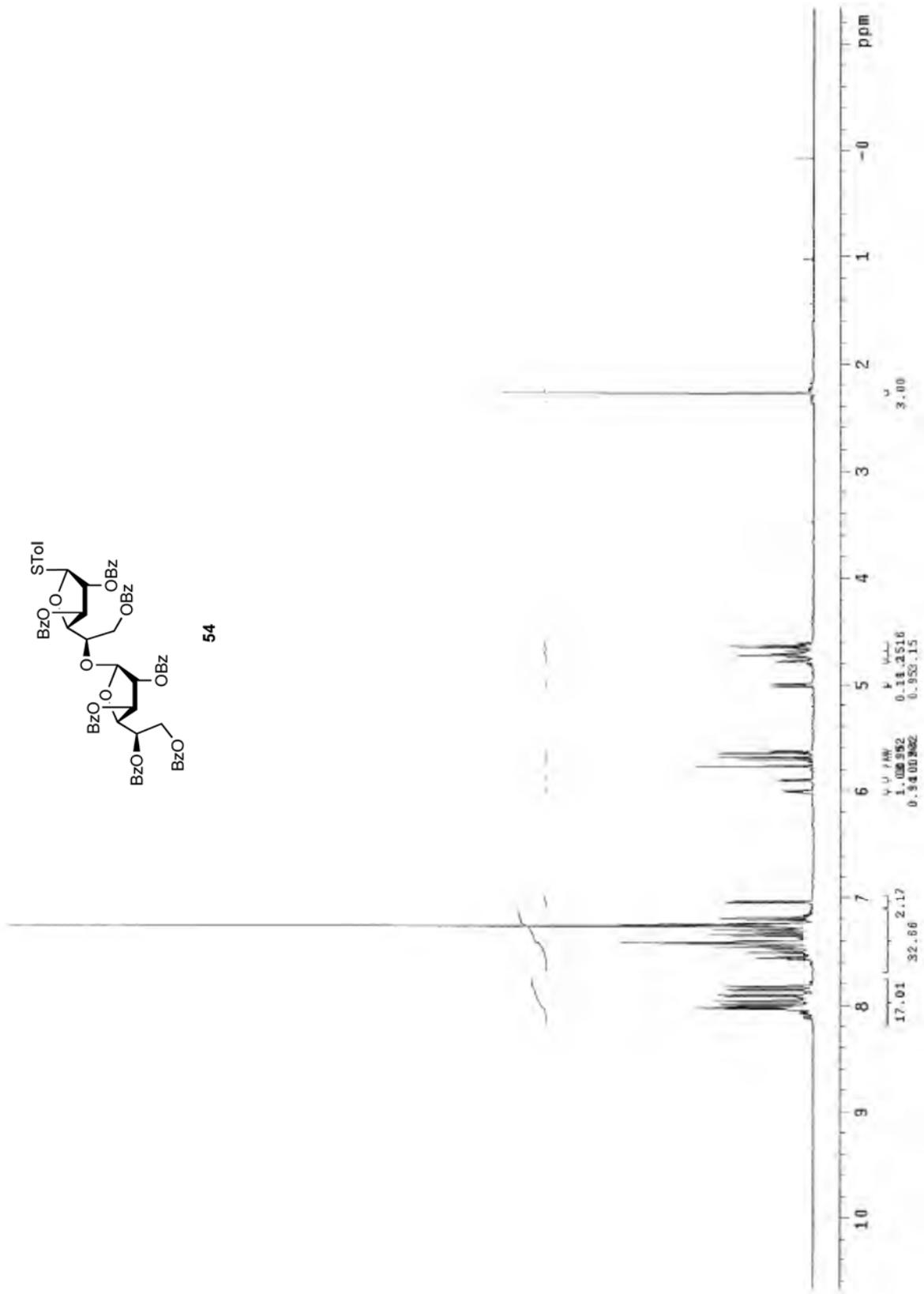
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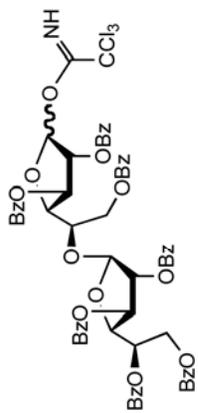




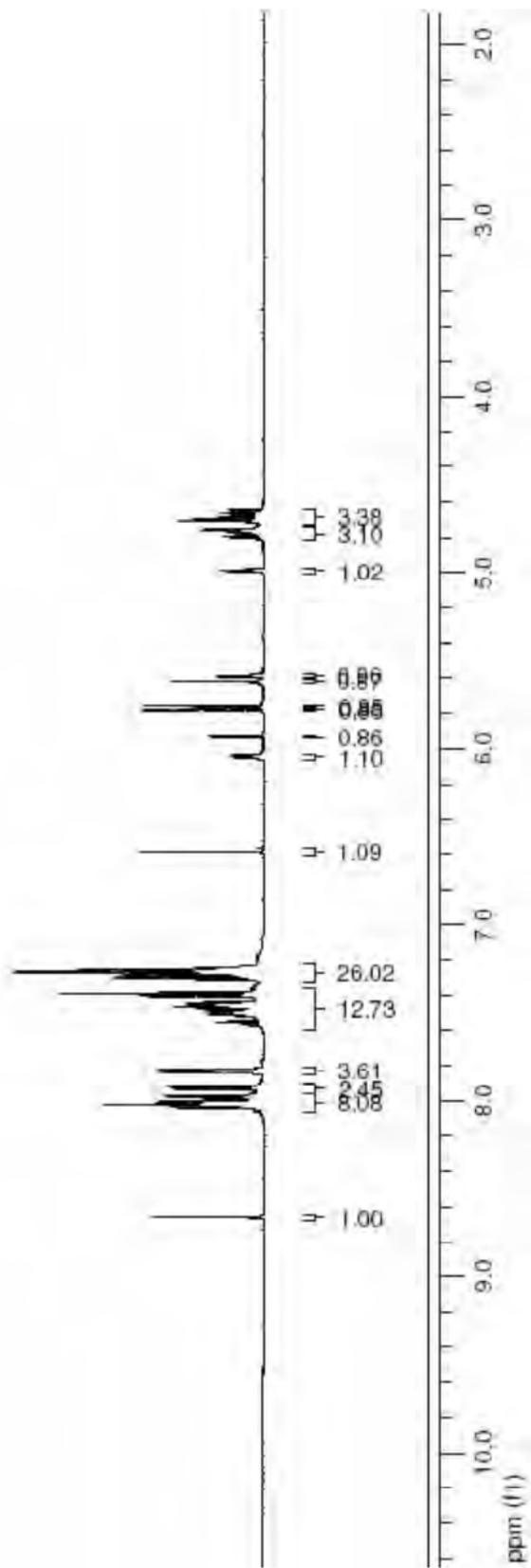


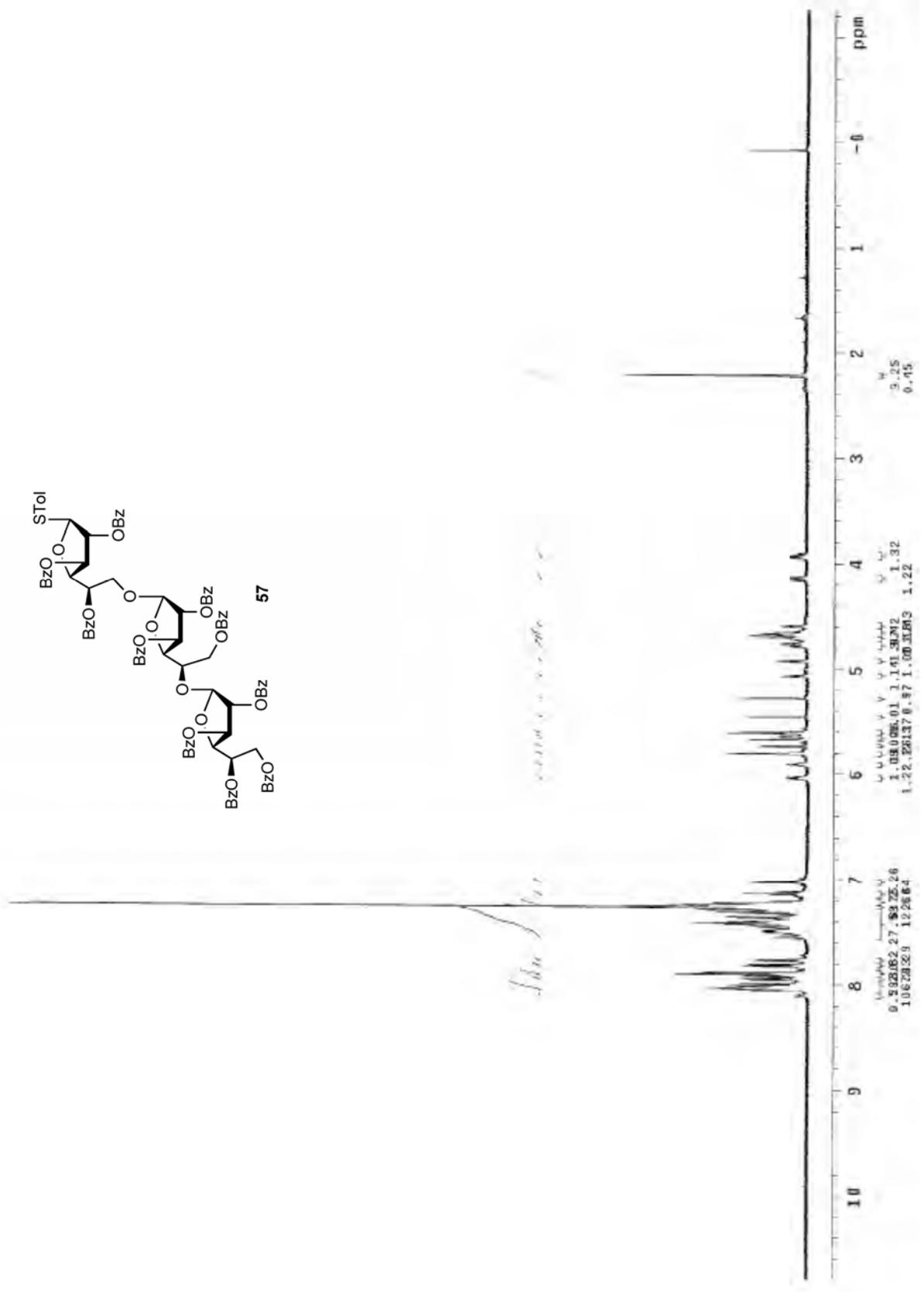
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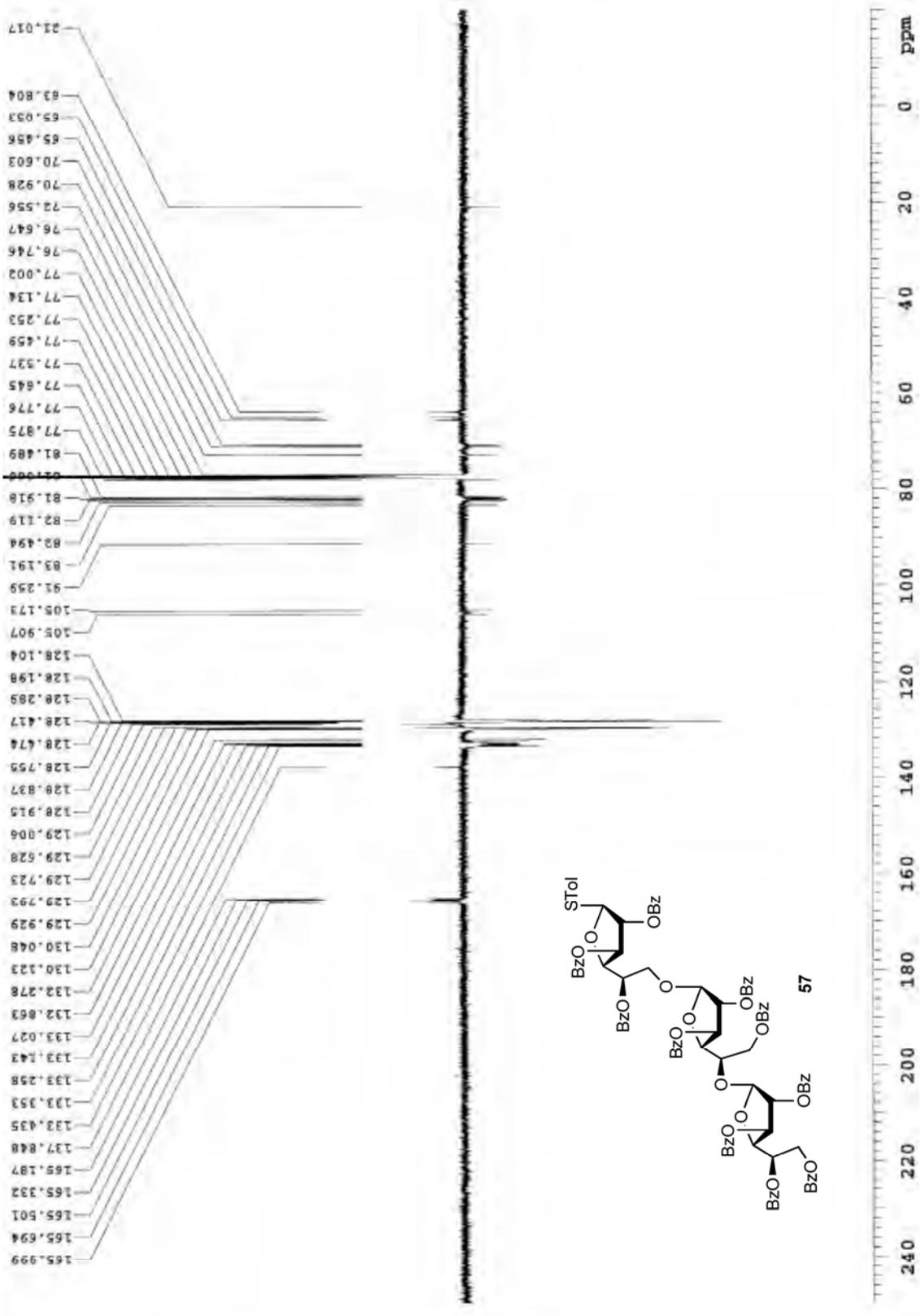
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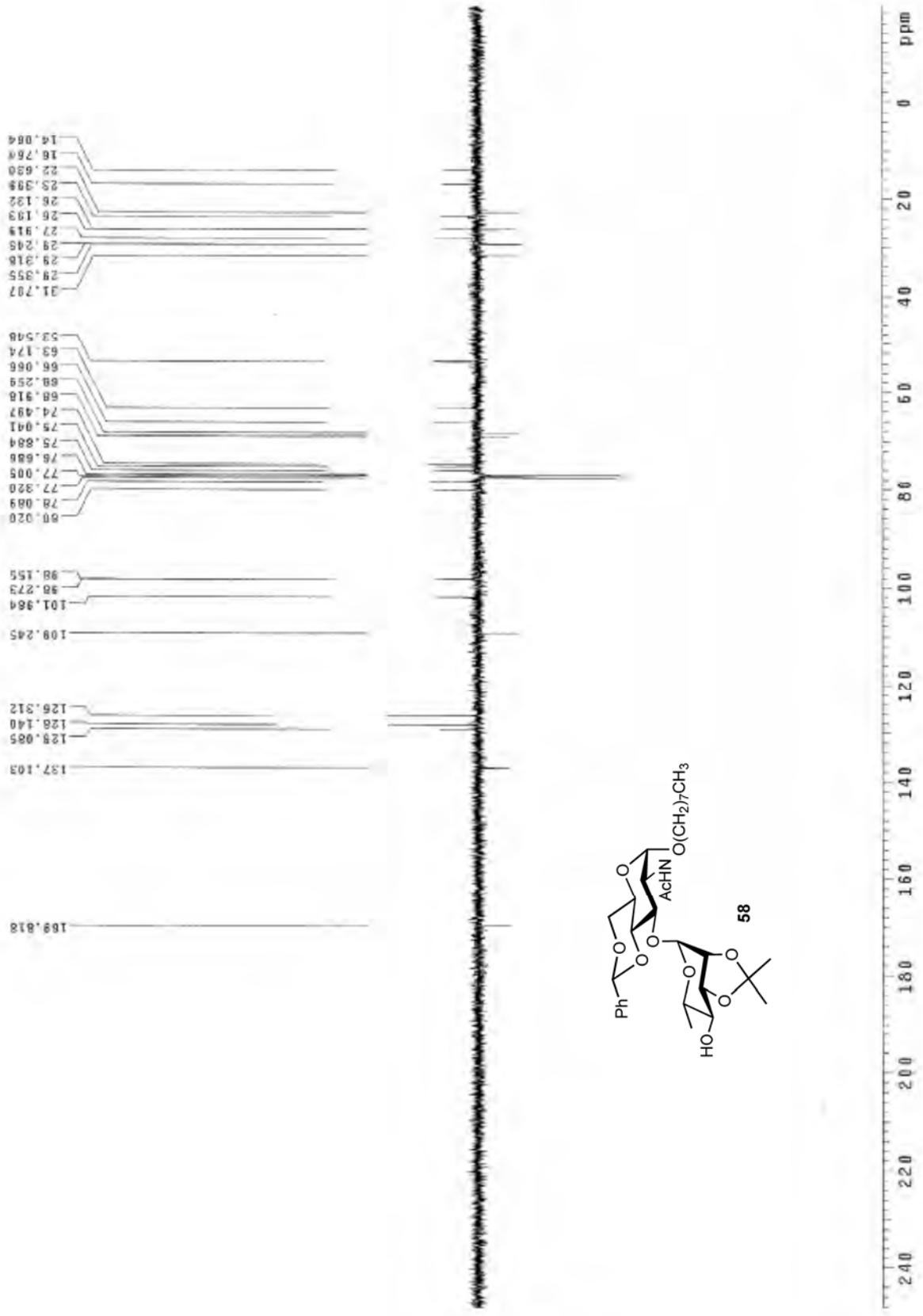


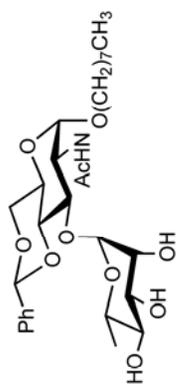
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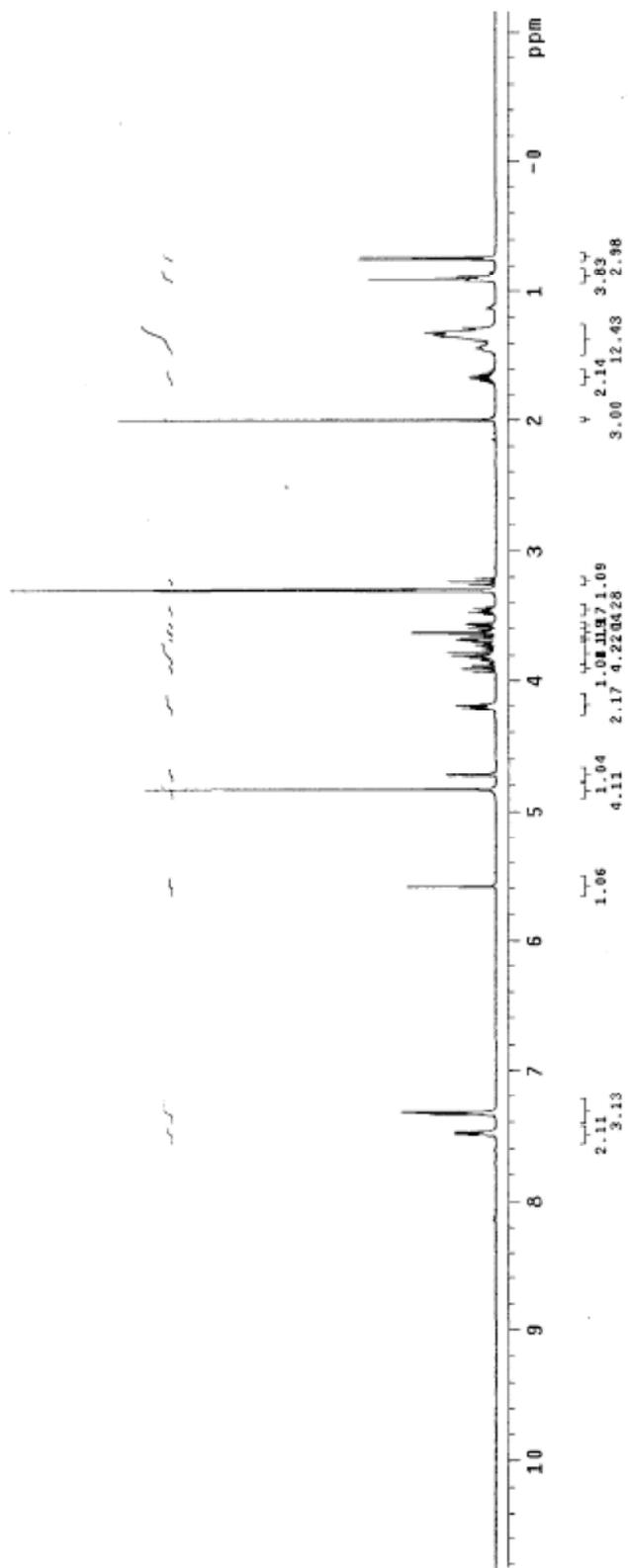


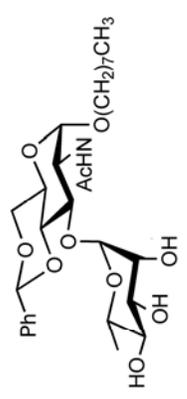
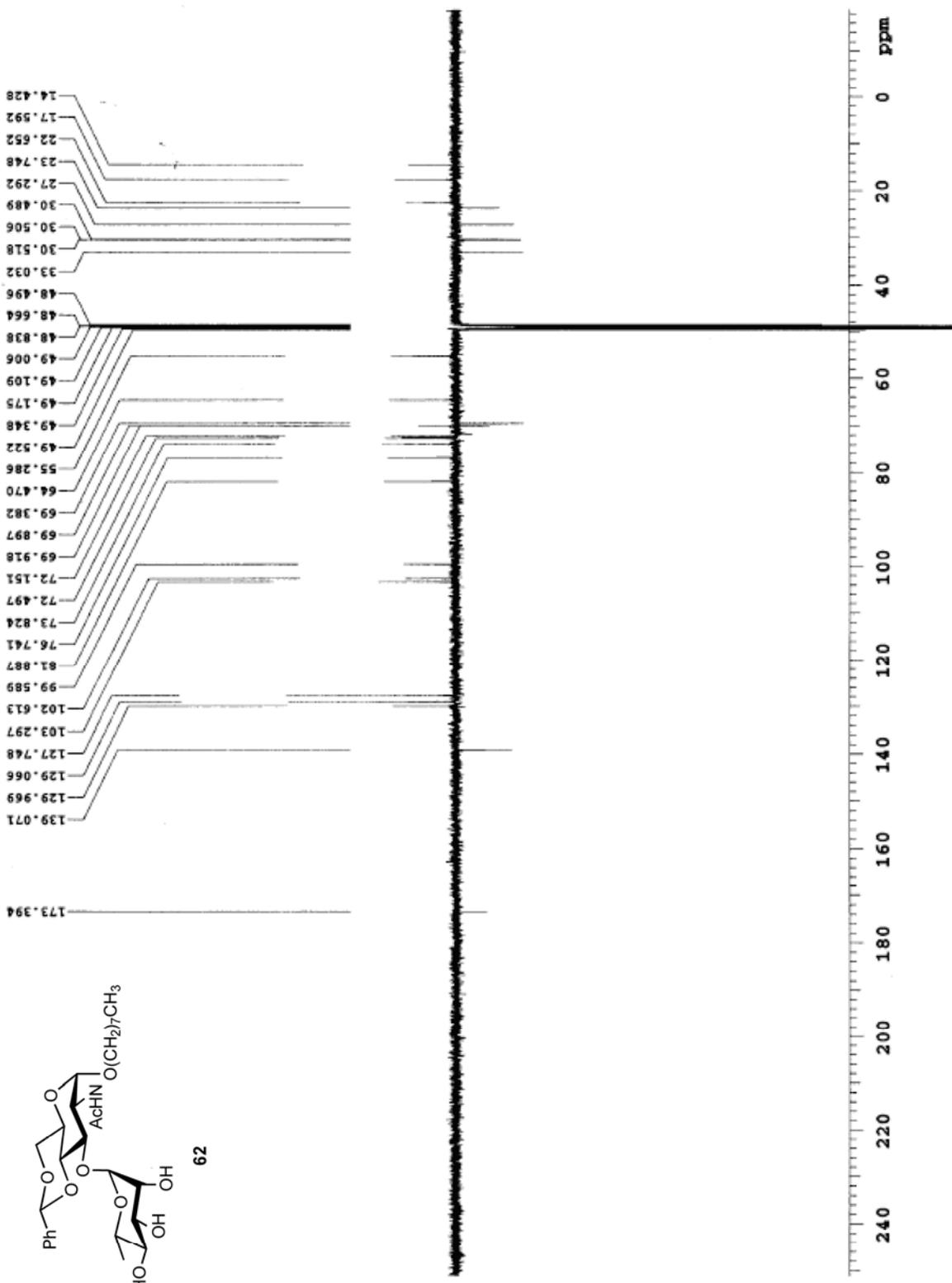


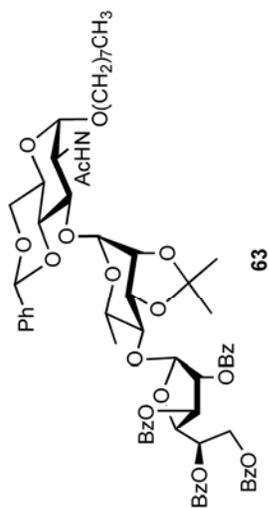




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