Supporting Information

Enabling the Serodiagnosis of American Tegumentary Leishmaniasis using Synthetic Aminopentyl-Galactofuranoside-containing Oligosaccharide Epitopes

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Carolina S. Touloumdjian,[a] *Emelie E. Reuber,*[b,c] *Fabienne Weber,*[b,c] *Renato E. Uncos,*[d] *Eleonora Elhalem,*[a,e] *Ana Bellomo,*[a,e] *María J. Comin,*[a,e] *Jorge D. Marco,*[d,e] *Peter H. Seeberger,*[b,c] *Lucía Gandolfi Donadío**[a,e]

[a] Departamento de Ingredientes Activos y Biorrefinerías, Instituto Nacional de Tecnología Industrial, San Martín, Buenos Aires, Argentina

[b] Department of Biomolecular Systems, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

[c] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany

[d] Instituto de Patología Experimental, Universidad Nacional de Salta, Salta, Argentina

[e] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), CABA, Argentina

***Corresponding author:** *lgandolfi@inti.gob.ar*

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1. General Information

Commercial grade reagents and solvents were used without further purification, except as indicated below. The solvents used were distilled, dried and stored according to standard procedures. All final products were at least 95% pure, as determined by ^{1}H NMR. Reaction monitoring was performed on Merck silica gel 60 F254 aluminum supported thin layer chromatography (TLC) plates. The TLC plates were visualized with UV light and by charging with 5% (v/v) sulfuric acid in ethanol, or with 0.1% (w/v) ninhydrin in ethanol, or with Hanessian solution (0.04 M solution ceric sulfate and ammonium molybdate in aqueous sulfuric acid). Column chromatography was performed on a Teledyne Isco Combi Flash Rf+ instrument under gradient elution conditions with RediSep disposable flash silica gel columns. Optical rotations were measured with a Perkin-Elmer 341 polarimeter. All melting points were determined on an Electrothermal IA9000 series digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were carried out on Bruker Fourier 300, 300 MHz or Bruker Avance DPX 400, 400 MHz spectrometer using $CDCl_3$, MeOD or D_2O as solvents. Chemical shifts (δ) are reported in ppm: in ^{1}H NMR spectra relative to TMS (δ = 0 ppm in $CDCl_3$), MeOH (δ = 3.34 ppm in MeOD) or acetone (δ = 2.22 ppm in D_2O); in ^{13}C NMR spectra relative to $CDCl_3$ (δ = 77.16 ppm in $CDCl_3$), MeOD (δ = 49.00 ppm in MeOD) or acetone (δ = 30.89 ppm in D_2O). Assignments of ^{1}H and ^{13}C NMR spectra were assisted by 2D ^{1}H COSY, HSQC, HMBC and ^{1}H,^{1}H-TOCSY experiments. The following abbreviations were used to indicate multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution positive ion electrospray ionization MS was conducted on a Waters Xevo G2S Q-TOF spectrometer.

2. Chemistry

2.1. General Procedures

General procedure for glycosylation

To a suspension of glycosyl trichloroacetimidate (1.0 equiv.) and acceptor (1.20 to 1.35 equiv.), both previously dried in vacuo, was added freshly activated powdered 4Å molecular sieves in anhydrous CH_2Cl_2 or Et_2O. The suspension was cooled (-15 to -40 °C) under Ar atmosphere and trimethylsilyl triflate (0.05 to 0.2 equiv.) was added slowly afterwards. The reaction mixture was stirred at the same temperature for 5 min to 30 min and then neutralized with triethylamine (TEA). The molecular sieves were filtered off, and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel or benzoylated without further purification.

General procedure for benzoylation

The 2-OH allyl glycoside (1.0 equiv.), previously dried in vacuo, was dissolved in anhydrous pyridine and cooled to 0 °C. Benzoyl chloride (3.9 to 5.9 equiv.) was then added dropwise, and the reaction mixture was allowed to warm to room temperature and stirred for 1 to 5.5 h. Upon completion (determined by TLC), the mixture was diluted with CH_2Cl_2 and extracted with water. The organic phase was sequentially washed with 5% HCl (2x), water, sat. $NaHCO_3$, and water until neutralization. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (toluene/EtOAc) to afford the pure product.

General procedure for deallylation

A methanolic suspension (total mixture concentration 0.5 M) of palladium acetate (0.4 to 0.8 equiv.) and triphenylphosphine (5 mol% relative to $Pd(AcO)_2$) was stirred at room temperature for 3 h to allow the formation of tetrakis(triphenylphosphine)palladium(0)

(0.4 to 0.8 equiv.). Diethylamine (DEA) (1 mol% relative to the catalyst) was then added, and the solution was stirred for an additional 15 min at room temperature. A solution of the allyl glycoside (1.0 equiv.) in anhydrous CH_2Cl_2 was added dropwise to the reaction mixture under continuous stirring. The reaction was allowed to proceed at room temperature for 24 h, with progression monitored by thin-layer chromatography (TLC). If incomplete conversion was observed, an additional portion of tetrakis(triphenylphosphine)palladium(0) (0.2 to 0.4 equiv.) in methanol (MeOH) was added, and the reaction mixture was stirred for another 24 h. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (toluene/EtOAc) to afford the pure hemiacetal.

General procedure for trichloroacetimidate formation

A solution of 1-OH glycoside (1.0 equiv.) and trichloroacetonitrile (6 equiv.) in anhydrous CH_2Cl_2 was cooled to 0 °C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.3–0.4 equiv.) was added dropwise, and the reaction mixture was stirred at 0 °C for 2 to 3 hours. Upon completion (determined by TLC), the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (toluene/EtOAc/TEA) to afford the pure glycosyl trichloroacetimidate.

General procedure for acetal hydrolysis

The protected glycoside was dissolved in 75% AcOH and stirred at 80 °C until complete conversion of the starting material was observed by TLC. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Residual acetic acid was removed by repeated co-evaporation with toluene (6x). If desired compound was identified in the crude product by NMR, it was subjected directly to debenzoylation without further purification.

General procedure for debenzoylation

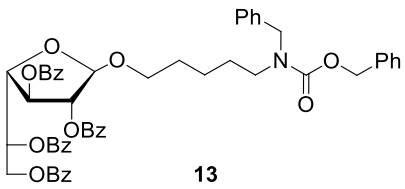
The protected glycoside was dissolved in MeOH, 1 M NaOH/MeOH (0.15 to 0.85 equiv. per benzoyl group) was added, and the mixture was stirred at room temperature for 2 to 7 h. The reaction mixture was then passed through a short column of Amberlite IR-120 H and the filtrate was concentrated under reduced pressure. The residue was subjected to successive cycles of dissolution in water and evaporation (6x). If the crude product was over 95% pure as determined by NMR, the reaction underwent hydrogenolysis without further purification. If purity was below 95%, the compound was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH).

General procedure for hydrogenolysis

The debenzoylated glycoside was dissolved in a mixture of MeOH/THF/H_2O/AcOH (10:5:4:1) (substrate concentration of 5 mM) and 10% wt. Pd/C catalyst (0.9 to 1.6 mg per mg of glycoside) was added. The solution was transferred to a hydrogenation vessel and purged with N_2/H_2 cycles (3x). The vessel was then pressurized with H_2 to 45 psi and mechanically stirred at room temperature for 2 to 7 days. The catalyst was removed by filtration through a pad of celite and the filtrate was concentrated under reduced pressure. Residual acetic acid was removed by repeated co-evaporation with toluene (6x). The residue was dissolved in water and purified using a reversed-phase solid-phase extraction cartridge (Maxi-Clean, C8). If necessary, further purification was performed by column chromatography on silica gel (acetonitrile/water/AcOH).[1] Fractions containing the pure compound were combined, concentrated, dissolved in water, and freeze-dried. All final compounds (**1**-**5**) were obtained as their corresponding ammonium acetate salts (**1'-5'**). The structures and nomenclature shown in the Supporting Information reflect these ammonium acetate forms.

2.2. Synthesis of compounds

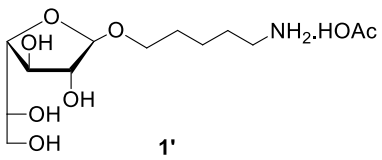
N-(Benzyl)benzyloxycarbonyl 5-aminopentyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside (13)



13

Glycosyl donor **6**[2] (0.84 g, 1.13 mmol) was reacted with **8**[3] (0.47 g, 1.44 mmol) in CH_2Cl_2 (39 mL) at -15 °C with TMSOTf (0.2 equiv.) for 30 min, according to the general procedure for glycosylation. Column chromatography in toluene/EtOAc 100:1 afforded **13** (0.94 g, 92%) as a syrup. R_f = 0.6 (toluene/EtOAc 9:1). $[\alpha]_D^{20}$ -6.8 (*c*=1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ (mixture of rotamers): 8.19 – 7.04 (m, 30H, 4 x PhCO, 2 x $PhCH_2$), 6.17 – 5.94 (m, 1H, H-5), 5.62 (d, *J* = 5.2 Hz, 1H, H-3), 5.44 (s, 1H, H-2), 5.33 – 5.22 (m, 1H, H-1), 5.22 – 5.09 (m, 2H, NCOOCH_2Ph), 4.87 – 4.67 (m, 2H, H-6a, H-6b), 4.62 (m, 1H, H-4), 4.56 – 4.39 (m, 2H, NCH_2Ph), 3.83 – 3.57 (m, 1H, OCH_aHCH_2), 3.57 – 3.35 (m, 1H, OCH$H_b$$CH_2$), 3.35 – 3.01 (m, 2H, CH_2CH_2N), 1.72 – 1.42 (m, 4H, 2 x CH_2), 1.42 – 1.15 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (mixture of rotamers): 166.2 (COPh), 165.8 (COPh), 165.7 (COPh), 165.5 (COPh), 156.8/156.2 (NCOO), 138.0 - 127.3 (4 x PhCO, 2 x $PhCH_2$), 105.7 (C-1), 82.2 (C-2), 81.3 (C-4), 77.6 (C-3), 70.3 (C-5), 67.5 (OCH_2CH_2), 67.2 (NCOOCH_2Ph), 63.6 (C-6), 50.6/50.3 (NCH_2Ph), 47.2/46.2 (CH_2CH_2N), 29.2 (CH_2), 28.0/27.5 (CH_2), 23.4 (CH_2). HRMS (ESI): m/z calcd. for $C_{54}H_{51}NO_{12}$ $[M+Na]^+$ 928.3309, found 928.3310.

5-Aminopentyl β-D-galactofuranoside, acetate (1')

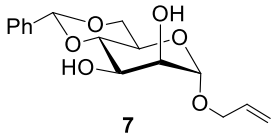


1'

5-Aminopentyl glycoside **13** (0.84 g, 0.93 mmol) was dissolved in MeOH (2.6 mL) and treated with NaOH 1 M in MeOH (0.6 equiv.) according to the general procedure for debenzoylation. The crude product was hydrogenated in the presence of Pd/C 10%

wt. (0.9 mg/mg of starting material) for 94 h according to the general procedure for hydrogenolysis. Column chromatography in ACN/H_2O/AcOH 9:1:0.1 afforded **1'** (231 mg, 77%), the ammonium acetate salt of compound **1**, as a syrup. R_f=0.65 (EtOH/H_2O/AcOH 7:1:1). $[\alpha]_D^{20}$ -49.3 (*c* =1, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 4.99 (d, *J* = 2.3 Hz, 1H, H-1), 4.14 – 3.98 (m, 2H, H-3, H-2), 3.95 (dd, *J* = 6.4, 4.1 Hz, 1H, H-4), 3.88 – 3.50 (m, 5H, H-5, H-6a, H-6b, OC$\underline{H}_2$CH_2), 3.06 – 2.92 (m, 2H, C$\underline{H}_2$NH_2), 1.91 (s, 3H, C$\underline{H}_3$COOH), 1.80 – 1.56 (m, 4H, 2 x CH_2), 1.54 – 1.34 (m, 2H, CH_2). ^{13}C NMR (75 MHz, D_2O) δ: 107.7 (C-1), 83.2 (C-4), 81.6 (C-2), 77.1 (C-3), 71.4 (C-5), 68.7 (O$\underline{C}$H$_2$CH$_2$), 63.4 (C-6), 40.0 ($\underline{C}$H$_2$NH$_2$), 28.7 (CH_2), 27.1 (CH_2), 23.9 ($\underline{C}$H$_3$COOH), 22.9 (CH_2). HRMS (ESI): m/z calcd. for $C_{11}H_{23}NO_6$ $[M+Na]^+$ 288.1423, found 288.1424.

Allyl 4,6-*O*-benzylidene-α-D-mannopyranoside (7)

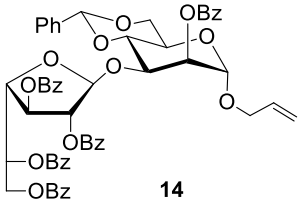


7

Anhydrous D-mannose (8.10 g, 45 mmol) was suspended in allyl alcohol (68 mL) and boron trifluoride diethyl etherate (0.4 mL, 3.2 mmol) was added slowly with stirring. The mixture was then heated at 70 °C and stirred under an argon atmosphere for 72 hours. The solution was neutralized with TEA (0.56 mL) and concentrated to yield allyl α,β-D-mannopyranoside (α/β ratio 15:1, ^{1}H NMR) as a colorless syrup. R_f = 0.66 (EtOAc/*i*-PrOH/H_2O 9:4:2). ^{1}H NMR (300 MHz, D_2O) δ (anomeric mixture): 6.08–5.88 (m, 1H, C$\underline{H}$=CH$_2$), 5.37 (dq, J = 17.3, 1.7 Hz, 1H, CH=C$\underline{H}_a$H), 5.29 (dd, J = 10.4, 1.1 Hz, 1H, CH=CH$\underline{H}_b$), 4.92 (d, J = 1.6 Hz, 0.9 H, H-1 α), 4.71 (d, J = 0.8 Hz, 0.1 H, H-1 β), 4.43–3.50 (m, 10H), 3.43–3.32 (m, 0.2 H). ^{13}C NMR (75 MHz, D_2O) δ (α-anomer): 133.2 ($\underline{C}$H=CH$_2$), 118.4 (CH=$\underline{C}$H$_2$), 99.0 (C-1), 72.8, 70.6, 70.0, 68.1, 66.8, 60.9. The dried crude product from the previous step (12 g) was suspended in anhydrous acetonitrile (200 mL), followed by addition of dry (1*S*)-(+)-10-camphorsulfonic acid (1.8 g, 7.75 mmol). After cooling to 0 °C, α,α-dimethoxytoluene

(8.7 mL, 58 mmol) was added dropwise with stirring. The mixture was stirred at 0 °C under argon for 2 h, then warmed up to room temperature and stirred for an additional 2 hours. The reaction was neutralized with TEA (1.3 mL) and concentrated. The resulting crude product was dissolved in CH_2Cl_2 (300 mL), extracted with sat. $NaHCO_3$ (250 mL), and the organic layer was washed with water (250 mL) and brine (250 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by column chromatography in toluene/EtOAc 7:3 afforded **7** (4.16 g, 30% over two steps) as a colorless solid. R_f = 0.61 (CH_2Cl_2/MeOH 9:1). Mp 144.6-146 °C, [lit.[4]148-149 °C (Et_2O)], $[\alpha]_D^{20}$ +69.9 (*c* =1, $CHCl_3$), [lit. [5]$[\alpha]_D^{23}$ +71.4 (*c* =1, $CHCl_3$)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 – 7.33 (m, 5H, PhCH), 6.00 – 5.81 (m, 1H, C<u>H</u>=CH_2), 5.55 (s, 1H, PhC<u>H</u>), 5.39 – 5.26 (m, 1H, CH=C<u>H$_a$</u>H), 5.26 – 5.18 (m, 1H, CH=CH<u>H$_b$</u>), 4.87 (d, *J* = 0.9 Hz, 1H, H-1), 4.32 – 4.13 (m, 2H, H-6a, OC<u>H$_a$</u>HCH=CH_2), 4.12 – 3.76 (m, 6H, H-3, H-2, OCH<u>H$_b$</u>CH=CH_2, H-4, H-5, H-6b), 2.88 (bs, 2H, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.3 - 126.4 (<u>C</u>H=CH_2, <u>Ph</u>CH), 117.9 (CH=<u>C</u>H_2), 102.4 (Ph<u>C</u>H), 99.5 (C-1), 79.0 (C-4), 71.1 (C-2), 68.9 (C-6), 68.7 (C-3), 68.4 (OCH_2CH=CH_2), 63.2 (C-5).

Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (14)

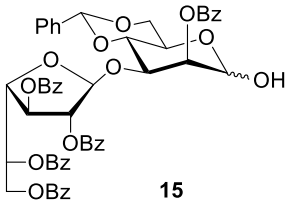


14

Glycosyl donor **6**[2] (3.38 g, 4.6 mmol) was reacted with **7** (1.75 g, 5.7 mmol) in CH_2Cl_2 (130 mL) at -30 °C with TMSOTf (0.05 equiv.) for 5 min, according to the general procedure for glycosylation. The foregoing crude product was dissolved in pyridine (52 mL) and treated with benzoyl chloride (3.9 equiv.) for 1 h, according to the general procedure for benzoylation. Column chromatography in toluene/EtOAc 20:1 afforded **14** (3.09 g, 68%) as an amorphous solid. R_f = 0.6 (toluene/EtOAc 9:1). Mp 79.4-81.7 °C. $[\alpha]_D^{20}$ -41.2 (*c*=1,

$CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.20 – 7.07 (m, 30H, 5 x PhCO, PhCH), 6.00 – 5.86 (m, 2H, CH=CH_2, H-5'), 5.65 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2), 5.56 (s, 1H, H-1'), 5.51 (s, 1H, PhCH), 5.40 (d, *J* = 5.1 Hz, 1H, H-3'), 5.34 (dq, *J* = 17.2, 1.6 Hz, 1H, CH=CH_aH), 5.34 (d, *J* = 1.0 Hz, 1H, H-2'), 5,26 (dq, *J* = 10.3, 1.3 Hz, 1H, CH=CHH_b), 5.02 (d, *J* = 1.6 Hz, 1H, H-1), 4.65 (dd, *J* = 5.1, 3.0 Hz, 1H, H-4'), 4.64 – 4.50 (m, 2H, H-6'a, H-3), 4.32 (dd, *J* = 10.1, 4.5 Hz, 1H, H-6a), 4.25 (ddt, *J* = 12.7, 5.2, 1.4 Hz, 1H, OCH_aHCH=CH_2), 4.19 (dd, *J* = 12.0, 3.3 Hz, 1H, H-6'b), 4.15 – 3.97 (m, 3H, H-4, OCHH_bCH=CH_2, H-5), 3.88 (t, *J* = 10.1 Hz, 1H, H-6b). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.2 (COPh), 165.8 (2 x COPh), 165.5 (COPh), 165.1 (COPh), 137.2 - 126.0 (CH=CH_2, 5 x PhCO, PhCH), 118.5 (CH=CH_2), 102.7 (C-1'), 102.2 (PhCH), 98.0 (C-1), 81.9 (C-4'), 81.4 (C-2'), 77.9 (C-3'), 77.6 (C-4), 70.2 (C-5'), 69.9 (C-3), 69.8 (C-2), 69.0 (C-6), 68.7 (OCH_2CH=CH_2), 64.2 (C-6'), 64.1 (C-5). HRMS (ESI): m/z calcd. for $C_{57}H_{50}O_{16}$ $[M+Na]^+$ 1013.2997, found 1013.3016.

2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (15)

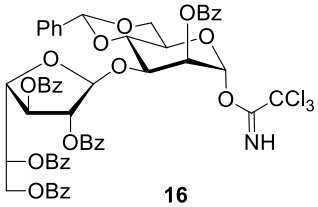


15

A solution of allyl glycoside **14** (2.60 g, 2.6 mmol) in CH_2Cl_2 (31 mL) was deallylated with tetrakis(triphenylphosphine)palladium(0) (0.8 equiv.), according to the general procedure for deallylation. Column chromatography in toluene/EtOAc 6:1 afforded **15** (2.27 g, 92%, α/β ratio ~6:1, ^1H NMR) as an amorphous solid. R_f = 0.44 (toluene/EtOAc 8:2). $[\alpha]_D^{20}$ -71.7 (*c* =1, $CHCl_3$). **15**α: ^1H NMR (400 MHz, $CDCl_3$) δ: 8.22 – 7.06 (m, 30H, 6 x PhCO, PhCH), 5.99 – 5.87 (m, 1H, H-5'), 5.67 (dd, *J* = 3.4, 1.4 Hz, 1H, H-2), 5.60 (s, 0.15H, H-1' β), 5.57 (s, 1H, H-1'), 5.50 (s, 1H, PhCH), 5.43 – 5.36 (m, 2H, H-3', H-1), 5.34 (bs, 1H, H-2'), 5.08 – 5.03 (m, 0.15H, H-1 β), 4.66 (dd, *J* = 5.2,

3.0 Hz, 1H, H-4'), 4.64 – 4.53 (m, 2H, H-3, H-6'a), 4.33 – 4.17 (m, 3H, H-6a, H-5, H-6'b), 4.10 (t, *J* = 9.6 Hz, 1H, H-4), 3.84 (t, *J* = 10.1 Hz, 1H, H-6b), 3.53 (d, *J* = 4.1 Hz, 1H, OH). **15**α: ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3 (COPh), 165.9 (2 x COPh), 165.6 (COPh), 165.2 (COPh), 137.2 - 126.0 (6 x PhCO, PhCH), 102.7 (C-1'), 102.5 (C-1' β), 102.2 (PhCH), 93.7 (C-1), 94.0 (C-1 β), 81.9 (C-4'), 81.5 (C-2'), 77.9 (C-3'), 77.6 (C-4), 70.2 (C-5'), 70.0 (C-2), 69.5 (C-3), 69.0 (C-6), 64.2 (C-5), 64.0 (C-6'). HRMS (ESI): m/z calcd. for $C_{54}H_{46}O_{16}$ $[M+Na]^+$ 973.2684, found 976.2710.

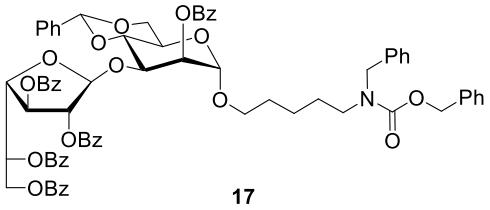
_O_-(2,3,5,6-tetra-_O_-benzoyl-β-D-galactofuranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranosyl) trichloroacetimidate (16)



16

A solution of hemiacetal **15** (2.86 g, 3.0 mmol) and trichloroacetonitrile (5 equiv.) in CH_2Cl_2 (30 mL) was treated with DBU (0.3 equiv.) for 3 h, according to the general procedure for trichloroacetimidate formation. Column chromatography in toluene/EtOAc/TEA 9:1:0.1 afforded **16** (2.52 g, 77%) as an amorphous solid. R_f = 0.76 (toluene/EtOAc/TEA 8:2:0.1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.77 (s, 1H, NH), 8.26 – 7.03 (m, 30H, 5 x PhCO, PhCH), 6.42 (d, *J* = 1.4 Hz, 1H, H-1), 6.03 – 5.89 (m, 1H, H-5'), 5.84 (dd, *J* = 3.5, 1.6 Hz, 1H, H-2), 5.61 (s, 1H, H-1'), 5.56 (s, 1H, PhCH), 5.44 (d, *J* = 5.2 Hz, 1H, H-3'), 5.37 (s, 1H, H-2'), 4.69 (dd, *J* = 4.9, 3.3 Hz, 1H, H-4'), 4.66 – 4.56 (m, 2H, H-6'a, H-3), 4.39 (dd, *J* = 10.3, 4.3 Hz, 1H, H-6a), 4.28 – 4.09 (m, 3H, H-4, H-6'b, H-5), 3.91 (t, *J* = 9.8 Hz, 1H, H-6b). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1 (COPh), 165.8 (COPh), 165.6 (COPh), 165.5 (COPh), 165.1 (COPh), 160.3 (C=NH), 136.9 - 125.4 (5 x PhCO, PhCH), 102.9 (C-1'), 102.2 (PhCH), 95.9 (C-1), 90.7 (CCl_3), 82.1 (C-4'), 81.6 (C-2'), 77.8 (C-3'), 77.0 (C-4), 70.2 (C-5'), 69.8 (C-3), 68.7 (C-6), 68.1 (C-2), 66.6 (C-5), 63.8 (C-6').

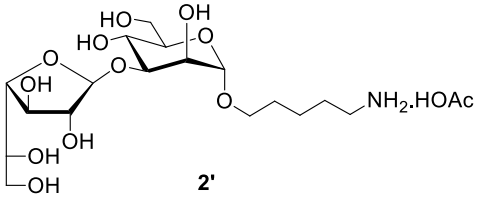
***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (17)**



17

Glycosyl donor **16** (50 mg, 0.046 mmol) was reacted with **8**[3] (18 mg, 0.055 mmol) in CH_2Cl_2 (3 mL) at -40 °C with TMSOTf (0.2 equiv.) for 5 min, according to general procedure for glycosylation. Column chromatography in toluene/EtOAc 95:5 afforded **17** (50 mg, 86%) as an amorphous solid. R_f = 0.5 (toluene/EtOAc 6:1). Mp 59-63.3 °C. $[\alpha]_D^{20}$ -33.9 (*c*=1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ (mixture of rotamers): 8.29 – 7.01 (m, 40H, 5 x PhCO, PhCH, 2 x $PhCH_2$), 5.98 – 5.87 (m, 1H, H-5'), 5.53 – 5.47 (m, 2H, H-2, H-1'), 5.50 (s, 1H, PhCH), 5.39 (d, *J* = 5.1 Hz, 1H, H-3'), 5.33 (s, 1H, H-2'), 5.24 – 5.11 (m, 2H, NCOOCH_2Ph), 4.97 – 4.86 (m, 1H, H-1), 4.70 – 4.42 (m, 5H, H-4', H-6'a, NCH_2Ph, H-3), 4.30 (dd, *J* = 9.1, 3.6 Hz, 1H, H-6a), 4.21 – 4.03 (m, 2H, H-6'b, H-4), 4.02 – 3.81 (m, 2H, H-5, H-6b), 3.78 – 3.52 (m, 1H, OCH_aHCH_2), 3.49 – 3.12 (m, 3H, OCH$H_b$$CH_2$, CH_2CH_2N), 1.75 – 1.44 (m, 4H, 2 x CH_2), 1.44 – 1.14 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (mixture of rotamers): 166.1 (COPh), 165.8 (COPh), 165.8 (COPh), 165.5 (COPh), 165.1 (COPh), 156.9/156.3 (NCOOCH_2Ph), 138.1 - 126.0 (5 x PhCO, PhCH, 2 x $PhCH_2$), 102.7 (C-1'), 102.2 (PhCH), 98.9 (C-1), 81.9 (C-4'), 81.4 (C-2'), 77.9 (C-3'), 77.6 (C-4), 70.2 (C-5'), 70.0 (C-3), 69.8 (C-2), 69.1 (C-6), 68.2 (OCH_2CH_2), 67.3 (NCOOCH_2Ph), 64.3 (C-6'), 64.0 (C-5), 50.7/50.4 (NCH_2Ph), 47.3/46.3 (CH_2CH_2N), 29.1 (CH_2), 28.0/27.6 (CH_2), 23.4 (CH_2). HRMS (ESI): m/z calcd. for $C_{74}H_{69}NO_{18}$ $[M+Na]^+$ 1282.4413, found 1282.4474.

5-Aminopentyl β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside, acetate (2')

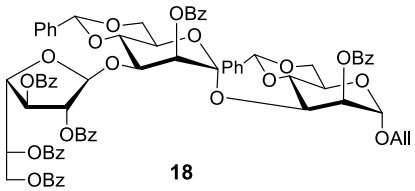


2'

5-Aminopentyl glycoside **17** (296 mg, 0.24 mmol) was dissolved in MeOH (3 mL) and treated with NaOH 1 M in MeOH (1.5 equiv.) according to the general procedure for debenzoylation. Column chromatography in CH_2Cl_2/MeOH 9:1 afforded *N*-(benzyl)benzyloxycarbonyl-5-aminopentyl β-D-galactofuranosyl-(1→3)-4,6-*O*-benzylidene-α-D-mannopyranoside (144 mg, 83%) as a syrup. R_f = 0.57 (CH_2Cl_2/MeOH 9:1). ^{1}H NMR (300 MHz, MeOD) δ (mixture of rotamers): 7.66 – 6.97 (m, 15H, PhCH, 2 x $PhCH_2$), 5.60 (s, 1H, PhCH), 5.22 – 5.12 (m, 2H, NCOOCH_2Ph), 5.09 (s, 1H, H-1'), 4.82 – 4.71 (m, 1H, H-1), 4.51 (s, 2H, NCH_2Ph), 4.23 – 4.14 (m, 1H, H-6a), 4.14 – 3.95 (m, 6H, H-2, H-3, H-4, H-4', H-2', H-3'), 3.87 – 3.72 (m, 2H, H-6b, H-5), 3.72 – 3.56 (m, 2H, H-5', OCH_aHCH_2), 3.50 (dd, *J* = 11.3, 7.2 Hz, 1H, H-6'a), 3.44 – 3.21 (m, 4H, H-6'b, OCH$H_b$$CH_2$, CH_2CH_2N), 1.70 – 1.44 (m, 4H, 2 x CH_2), 1.43 – 1.22 (m, 2H, CH_2). ^{13}C NMR (75 MHz, MeOD) δ (mixture of rotamers): 139.2 - 127.5 (PhCH, 2 x $PhCH_2$), 106.2 (C-1'), 103.1 (PhCH), 102.4 (C-1), 85.8 (C-4'), 82.4 (C-2'), 79.2 (C-3'), 78.3 (C-4), 73.0 (C-3), 72.5 (C-5'), 69.9 (C-6), 69.3 (C-2), 68.7 (OCH_2CH_2), 68.5/68.4 (NCOOCH_2Ph), 65.5 (C-5), 64.8 (C-6'), 51.6/51.4 (NCH_2Ph), 47.5 (CH_2CH_2N), 30.1 (CH_2), 28.9/28.5 (CH_2), 24.4 (CH_2). The above compound (144 mg, 0.20 mmol) was hydrogenated in the presence of Pd/C 10% wt. (1 mg/mg of starting material) for 2 days according to the general procedure for hydrogenolysis. Column chromatography in ACN/H_2O/AcOH 8:2:0.1 afforded **2'** (72 mg, 76%), the ammonium acetate salt of compound **2**, as a syrup. R_f = 0.62 (EtOH/H_2O/AcOH 7:1:1). $[\alpha]_D^{20}$ -26.8 (*c*=1, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 5.13 (d, *J* = 1.2 Hz, 1H, H-1'), 4.89 (d, *J* = 1.4 Hz, 1H, H-1), 4.15 (dd, *J* = 3.0, 1.6 Hz, 1H, H-2'), 4.12 (dd, *J* = 2.8, 2.0 Hz, 1H, H-2), 4.10 – 4.02 (m, 2H, H-3', H-4'), 3.92 – 3.81 (m, 3H, H-6a, H-3, H-5'), 3.80 – 3.61 (m,

6H, H-6b, OC$\underline{H}_a$HCH$_2$, H-4, H-6'a, H-5, H-6'b), 3.60 – 3.51 (m, 1H, OCH$\underline{H}_b$CH$_2$), 3.03 – 2.95 (m, 2H, C$\underline{H}_2$NH$_2$), 1.91 (s, 3H, C$\underline{H}_3$COOH), 1.76 – 1.60 (m, 4H, 2 x CH$_2$), 1.56 – 1.38 (m, 2H, CH$_2$). ^{13}C NMR (101 MHz, D$_2$O) δ: 105.0 (C-1'), 100.1 (C-1), 83.6 (C-4'), 82.0 (C-2'), 77.6 (C-3'), 76.2 (C-3), 73.3 (C-5), 71.4 (C-5'), 68.1 (O$\underline{C}$H$_2$CH$_2$), 67.4 (C-2), 65.7 (C-4), 63.4 (C-6'), 61.6 (C-6), 40.0 ($\underline{C}$H$_2$NH$_2$), 28.6 (CH$_2$), 27.1 (CH$_2$), 23.9 ($\underline{C}$H$_3$COOH), 23.1 (CH$_2$). HRMS (ESI): m/z calcd. for $C_{17}H_{33}NO_{11}$ $[M+Na]^+$ 450.1958, found 450.1951.

Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (18)

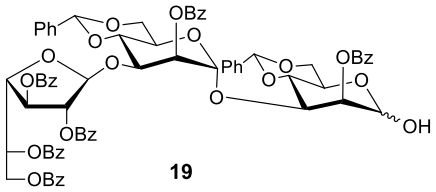


18

Glycosyl donor **16** (2.40 g, 2.2 mmol) was reacted with **7** (0.84 g, 2.7 mmol) in CH_2Cl_2 (77 mL) at -40 °C with TMSOTf (0.05 equiv.) for 10 min, according to the general procedure for glycosylation. The foregoing crude product was dissolved in pyridine (40 mL) and treated with benzoyl chloride (5.9 equiv.) for 1 h, according to the general procedure for benzoylation. Column chromatography in toluene/EtOAc 20:1 afforded **18** (2.46 g, 83%) as an amorphous solid. R_f = 0.44 (toluene/EtOAc 20:1). Mp 100.3-102.0 °C. $[\alpha]_D^{20}$ -62.2 (*c*=1, CHC l$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.25 – 7.06 (m, 40H, 6 x $\underline{Ph}$CO, 2 x $\underline{Ph}$CH), 6.01 – 5.86 (m, 1H, C$\underline{H}$=CH$_2$), 5.83 – 5.77 (m, 1H, H-5''), 5.74 (s, 1H, PhC$\underline{H}$), 5.65 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2'), 5.60 (dd, *J* = 3.6, 1.5 Hz, 1H, H-2), 5.40 – 5.37 (m, 2H, PhC$\underline{H}$, H-1'), 5.37 – 5.29 (m, 3H, CH=C$\underline{H}_a$H, H-3'', H-1''), 5.30 – 5.22 (m, 2H, CH=CH$\underline{H}_b$, H-2''), 5.04 (d, *J* = 1.5 Hz, 1H, H-1), 4.57 – 4.43 (m, 3H, H-6''a, H-4'', H-3), 4.39 (dd, *J* = 9.8, 3.5 Hz, 1H, H-3'), 4.34 (dd, *J* = 9.6, 4.1 Hz, 1H, H-6a), 4.30 – 4.20 (m, 3H, H-6'a, H-4, OC$\underline{H}_a$HCH=CH$_2$), 4.13 – 4.03 (m, 2H,

H-5', OCH$\underline{H_b}$CH=CH_2), 4.03 – 3.88 (m, 4H, H-5, H-4', H-6''b, H-6b), 3.78 (t, *J* = 10.2 Hz, 1H, H-6'b). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0 ($\underline{C}$OPh), 165.9 ($\underline{C}$OPh), 165.8 ($\underline{C}$OPh), 165.6 ($\underline{C}$OPh), 165.4 ($\underline{C}$OPh), 165.0 ($\underline{C}$OPh), 137.3 - 126.0 ($\underline{C}$H=CH_2, 6 x $\underline{Ph}$CO, 2 x $\underline{Ph}$CH), 118.4 (CH=$\underline{C}H_2$), 102.8 (C-1''), 102.2 (Ph$\underline{C}$H), 101.6 (Ph$\underline{C}$H), 100.2 (C-1'), 97.8 (C-1), 81.8 (C-4''), 81.2 (C-2''), 79.0 (C-4), 77.8 (C-3''), 77.4 (C-4'), 73.3 (C-3), 72.3 (C-2), 70.4 (C-5''), 69.9 (C-3'), 69.8 (C-2'), 68.9 (C-6, C-6'), 68.7 (O$\underline{C}H_2$CH=CH_2), 64.8 (C-5'), 64.0 (C-6''), 63.9 (C-5). HRMS (ESI): m/z calcd. for $C_{77}H_{68}O_{22}$ $[M+H]^+$ 1345.4281, found 1345.4343.

2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (19)

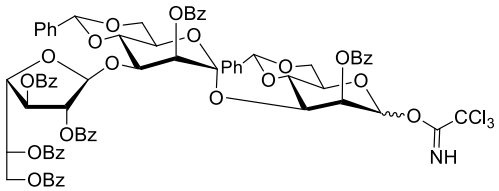


19

A solution of allyl glycoside **18** (1.15 g, 0.86 mmol) in CH_2Cl_2 (11 mL) was deallylated with tetrakis(triphenylphosphine)palladium(0) (0.4 equiv.), according to the general procedure for deallylation. In this case, after 24 h of stirring, 0.5 M methanolic solution of tetrakis(triphenylphosphine)palladium(0) (0.4 equiv.) was added. Column chromatography in toluene/EtOAc 5:1 afforded **19** (0.94 g, 84%, α/β ratio ~6:1, ^{1}H NMR) as an amorphous solid. R_f = 0.48 (toluene/ EtOAc 8:2). $[\alpha]_D^{20}$ -86.1 (*c*=1, $CHCl_3$). **19**α: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 – 6.98 (m, 40H, 6 x $\underline{Ph}$CO, 2 x $\underline{Ph}$CH), 5.86 – 5.78 (m, 1H, H-5''), 5.71 (s, 1H, PhC$\underline{H}$), 5.64 (dd, *J* = 3.5, 1.7 Hz, 1H, H-2'), 5.61 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2), 5.42 – 5.37 (m, 3H, PhC$\underline{H}$, H-1, H-1'), 5.37 – 5.32 (m, 2H, H-3'', H-1''), 5.24 (d, *J* = 1.0 Hz, 1H, H-2''), 4.57 – 4.46 (m, 3H, H-6''a, H-4'', H-3), 4.39 (dd, *J* = 9.9, 3.6 Hz, 1H, H-3'), 4.33 – 4.07 (m, 5H, H-6'a, H-6a, H-4, H-5, H-5'), 4.05 – 3.96 (m, 2H, H-4', H-6''b), 3.86 (t, *J* = 10.1 Hz, 1H, H-

6b), 3.80 (t, *J* = 10.3 Hz, 1H, H-6'b), 3.43 (d, *J* = 4.0 Hz, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0 (COPh), 165.9 (COPh), 165.8 (COPh), 165.6 (COPh), 165.4 (COPh), 165.0 (COPh), 137.3 - 126.1 (6 x PhCO, 2 x PhCH), 102.8 (C-1''), 102.2 (PhCH), 101.6 (PhCH), 100.1 (C-1'), 93.4 (C-1), 81.7 (C-4''), 81.2 (C-2''), 79.1 (C-4), 77.8 (C-3''), 77.4 (C-4'), 72.6 (C-3), 72.5 (C-2), 70.4 (C-5''), 69.9 (C-3'), 69.8 (C-2'), 68.9 (C-6, C-6'), 64.8 (C-5'), 64.1 (C-6''), 63.8 (C-5). HRMS (ESI): m/z calcd. for $C_{74}H_{64}O_{22}$ $[M+Na]^+$ 1327.3787, found 1327.3845.

_O_-(2,3,5,6-tetra-_O_-benzoyl-β-D-galactofuranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α,β-D-mannopyranosyl) trichloroacetimidate (20)

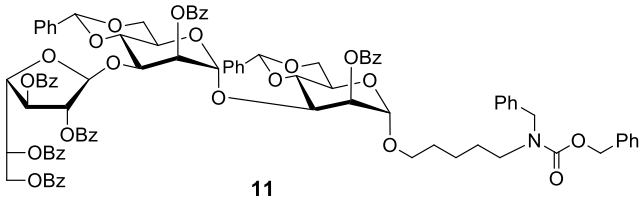


20

A solution of hemiacetal **19** (0.91 g, 0.69 mmol) and trichloroacetonitrile (6 equiv.) in CH_2Cl_2 (8.9 mL) was treated with DBU (0.4 equiv.) for 2 h, according to the general procedure for trichloroacetimidate formation. Column chromatography in toluene/TEA 10:0.1 afforded **20** (0.83 g, 83%, α/β ratio 9:1, ^{1}H NMR) as an amorphous solid. R_f = 0.72 (toluene/EtOAc/TEA 8:2:0.1). **20α**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (s, 1H, NH), 8.29 – 7.06 (m, 40H, 6 x PhCO, 2 x PhCH), 6.46 (d, *J* = 1.7 Hz, 1H, H-1), 5.87 – 5.80 (m, 1H, H-5''), 5.79 – 5.74 (m, 2H, H-2, PhCH), 5.67 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2'), 5.47 – 5.39 (m, 2H, H-1', PhCH), 5.38 – 5.33 (m, 2H, H-3'', H-1''), 5.26 (d, *J* = 1.0 Hz, 1H, H-2''), 4.61 – 4.50 (m, 3H, H-3, H-6''a, H-4''), 4.44 – 4.33 (m, 3H, H-3', H-6a, H-4), 4.22 (dd, *J* = 10.1, 4.7 Hz, 1H, H-6'a), 4.19 – 4.09 (m, 2H, H-5, H-5'), 4.09 – 3.90 (m, 3H, H-4', H-6''b, H-6b), 3.81 (t, *J* = 10.1 Hz, 1H, H-6'b). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.0 (COPh), 165.8 (COPh), 165.5 (2 x COPh), 165.4 (COPh), 165.0 (COPh), 160.0

(C=NH), 137.2 - 126.0 (6 x PhCO, 2 x PhCH), 102.8 (C-1''), 102.2 (PhCH), 101.6 (PhCH), 100.2 (C-1'), 95.5 (C-1), 90.8 (CCl_3), 81.8 (C-4''), 81.2 (C-2''), 78.4 (C-4), 77.8 (C-3''), 77.3 (C-4'), 72.4 (C-3), 70.6 (C-2), 70.4 (C-5''), 69.8 (C-3'), 69.6 (C-2'), 68.8 (C-6'), 68.5 (C-6), 66.4 (C-5), 64.9 (C-5'), 64.1 (C-6'').

_N_-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,5,6-tetra-_O_-benzoyl-β-D-galactofuranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranoside (11)

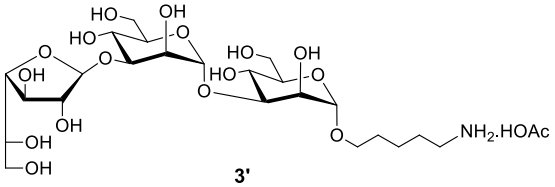


11

Glycosyl donor **20** (0.65 g, 0.45 mmol) was reacted with **8**[3] (180 mg, 0.55 mmol) in Et_2O (27 mL) at -30 °C with TMSOTf (0.2 equiv.) for 20 min, according to the general procedure for glycosylation. Column chromatography in toluene/EtOAc 12:1 afforded **11** (0.66 g, 91%) as an amorphous solid. R_f = 0.62 (toluene/EtOAc 6:1). Mp 74.7-76.3 °C. $[\alpha]_D^{20}$ -51.8 (*c*=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of rotamers): 8.25 – 7.01 (m, 50H, 6 x PhCO, 2 x PhCH, 2 x $PhCH_2$), 5.84 – 5.77 (m, 1H, H-5''), 5.74 (s, 1H, PhCH), 5.65 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2'), 5.55 (d, *J* = 2.8 Hz, 1H, H-2), 5.39 – 5.35 (m, 2H, H-1', PhCH), 5.36 – 5.31 (m, 2H, H-1'', H-3''), 5.24 (s, 1H, H-2''), 5.20 – 5.11 (m, 2H, $NCOOCH_2Ph$), 4.97 – 4.90 (m, 1H, H-1), 4.58 – 4.45 (m, 4H, H-6''a, NCH_2Ph, H-4''), 4.45 – 4.34 (m, 2H, H-3, H-3'), 4.34 – 4.18 (m, 3H, H-6a, H-6'a, H-4), 4.13 – 4.02 (m, 1H, H-5'), 4.03 – 3.86 (m, 4H, H-4', H-6b, H-5, H-6''b), 3.76 (t, *J* = 10.1 Hz, 1H, H-6'b), 3.71 – 3.57 (m, 1H, OCH_aHCH_2), 3.51 – 3.33 (m, 1H, $OCHH_bCH_2$), 3.32 – 3.15 (m, 2H, CH_2CH_2N), 1.73 – 1.44 (m, 4H, 2 x CH_2), 1.42 – 1.20 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ (mixture of rotamers): 166.0 (COPh), 166.0 (COPh), 165.8 (COPh), 165.6 (COPh), 165.4 (COPh), 165.0 (COPh), 156.9/156.3 (NCOO), 138.1 - 126.1 (6 x

PhCO, 2 x PhCH, 2 x $PhCH_2$), 102.8 (C-1''), 102.2 (PhCH), 101.6 (PhCH), 100.3 (C-1'), 98.6 (C-1), 81.8 (C-4''), 81.2 (C-2''), 79.0 (C-4), 77.8 (C-3''), 77.4 (C-4'), 73.6 (C-3), 72.4 (C-2), 70.4 (C-5''), 69.9 (C-3'), 69.8 (C-2'), 69.0 (C-6), 68.9 (C-6'), 68.3 (OCH_2CH_2), 67.3 ($NCOOCH_2Ph$), 64.8 (C-5'), 64.1 (C-6''), 63.8 (C-5), 50.8/50.5 (NCH_2Ph), 47.3/46.3 (CH_2CH_2N), 29.2 (CH_2), 28.1/27.7 (CH_2), 23.5 (CH_2). HRMS (ESI): m/z calcd. for $C_{94}H_{87}NO_{24}$ $[M+Na]^+$ 1636.5515, found 1636.5621.

5-Aminopentyl β-D-galactofuranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranoside, acetate (3')

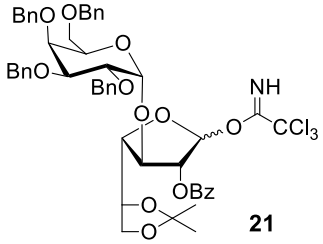


3'

5-Aminopentyl glycoside **11** (75 mg, 0.046 mmol) was dissolved in MeOH (0.48 mL) and treated with NaOH 1 M in MeOH (2.4 equiv.) according to the general procedure for debenzoylation. Column chromatography in CH_2Cl_2/MeOH 12:1 afforded *N*-(benzyl)benzyloxycarbonyl-5-aminopentyl β-D-galactofuranosyl-(1→3)-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-α-D-mannopyranoside (25 mg, 55%) as a syrup. R_f = 0.58 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{20}$ +6.6 (*c*=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of rotamers): 7.54 – 7.02 (m, 20H, 2 x PhCH, 2 x $PhCH_2$), 5.51 (s, 1H, PhCH), 5.48 (s, 1H, PhCH), 5.33 (s, 1H, H-1'), 5.28 – 5.04 (m, 3H, H-1'', $NCOOCH_2Ph$), 4.78 – 4.68 (m, 1H, H-1), 4.53 – 4.33 (m, 2H, NCH_2Ph), 4.32 – 3.88 (m, 11H), 3.88 – 3.69 (m, 4H, H-5', H-5, H6-b, H-6'b), 3.64 – 3.45 (m, 2H, H-5'', OCH_aHCH_2), 3.37 – 3.07 (m, 5H, $OCHH_bCH_2$, H-6''a, H-6''b, NCH_2CH_2), 1.71 – 1.37 (m, 4H, 2 x CH_2), 1.37 – 1.10 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ (mixture of rotamers): 156.9/156.4 (NCOO), 138.0 - 126.2 (2 x PhCH, 2 x $PhCH_2$), 104.8 (C-1''), 102.0 (PhCH), 101.6 (PhCH), 101.4 (C-1'), 100.5 (C-1), 86.1 (C-4''), 79.8 (C-2''), 78.9 (C-4), 78.4 (C-3''), 76.7 (C-4'), 72.8 (C-3*), 71.6 (C-

3'*), 71.4 (C-2), 70.8 (C-5''), 68.8 (C-6, C-6'), 68.3 (C-2'), 67.9 (O<u>C</u>H_2CH_2), 67.4 (NCOO<u>C</u>H_2Ph), 64.6 (C-5'), 63.9 (C-6''), 63.7 (C-5), 50.7/50.4 (N<u>C</u>H_2Ph), 47.2/46.3 (N<u>C</u>H_2CH_2), 29.2 (CH_2), 28.0/27.6 (CH_2), 23.4 (CH_2). *Assignments may be interchanged. HRMS (ESI): m/z calcd. for $C_{52}H_{63}NO_{18}$ $[M+Na]^+$ 1012.3943, found 1012.3962. The above compound (25 mg, 0.025mmol) was hydrogenated in the presence of Pd/C 10% wt. (1.6 mg/mg of starting material) for 7 days according to the general procedure for hydrogenolysis. Column chromatography in ACN/H_2O/AcOH 9:1:0.1 afforded **3'** (8.2 mg, 50%), the ammonium acetate salt of compound **3**, as a syrup. R_f = 0.55 (EtOH/H_2O/AcOH 7:1:1). $[\alpha]_D^{20}$ +6.2 (*c*=1, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 5.19 – 5.14 (m, 2H, H-1', H-1''), 4.84 (d, *J* = 1.9 Hz, 1H, H-1), 4.27 (dd, *J* = 3.1, 1.9 Hz, 1H, H-2'), 4.16 (dd, *J* = 3.1, 1.7 Hz, 1H, H-2''), 4.11 – 4.05 (m, 3H, H-2, H-3'', H-4''), 3.99 (dd, *J* = 9.4, 3.2 Hz, 1H, H-3'), 3.93 – 3.61 (m, 14H), 3.60 – 3.51 (m, 1H, OCH<u>H$_b$</u>CH_2), 3.05 – 2.97 (m, 2H, C<u>H_2</u>NH_2), 1.91 (s, 3H, C<u>H_3</u>COOH), 1.78 – 1.58 (m, 4H, 2 x CH_2), 1.53 – 1.38 (m, 2H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ: 105.1 (C-1''), 102.7 (C-1'), 100.2 (C-1), 83.6 (C-4''), 82.0 (C-2''), 78.9 (C-3), 77.7 (C-3''), 76.0 (C-3'), 73.9 (C-5'), 73.6 (C-5), 71.4 (C-5''), 70.4 (C-2), 68.1 (O<u>C</u>H_2CH_2), 67.4 (C-2'), 66.8 (C-4), 65.8 (C-4'), 63.4 (C-6''), 61.7 (C-6'*), 61.5 (C-6*), 40.0 (<u>C</u>H_2NH_2), 28.6 (CH_2), 27.2 (CH_2), 24.0 (<u>C</u>H_3COOH), 23.1 (CH_2). *Assignments may be interchanged. HRMS (ESI): m/z calcd. for $C_{23}H_{43}NO_{16}$ $[M+H]^+$ 590.2660, found 590.2663.

_O_-(2,3,4,6-tetra-_O_-benzyl-α-D-galactopyranosyl-(1→3)-2-_O_-benzoyl-5,6-_O_-isopropylidene-α,β-D-galactofuranosyl) trichloroacetimidate (21)

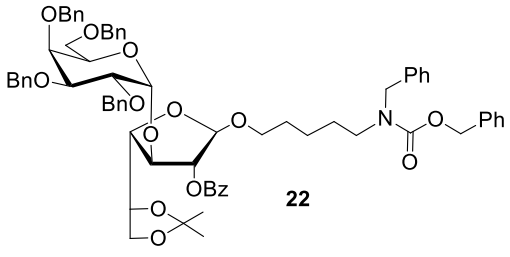


A suspension of dry 2-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone[6] (**10**; 1.52 g; 4.7 mmol) and powdered 4Å molecular sieves in anhydrous Et_2O (23 mL) was cooled

to -15 °C under Ar atmosphere, and trimethylsilyl triflate (34 μL; 0.19 mmol) was added. Then, a solution of *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl) trichloroacetimidate[7] (**9**; 2.55 g; 3.7 mmol) in Et_2O was slowly added (48 mL) and the mixture was stirred at -15 °C for 40 min. After complete consumption of the starting imidate (determined by TLC), the crude reaction mixture was diluted with CH_2Cl_2 (200 mL), the molecular sieves were filtered off, and the solution was washed with water (2 × 100 mL). The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography (toluene/EtOAc 25:1) to afford 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropyliden-D-galactono-1,4-lactone (2.63 g, 84%) as a colorless syrup. R_f = 0.55 (toluene/EtOAc 6:1). Mp 118.3-120.9 °C, [lit.[6] 133-134 °C]. $[\alpha]_D^{20}$ +48.9 (*c*=1, $CHCl_3$), [lit.[6] $[\alpha]_D$ +53.3 (*c*=1, $CHCl_3$)]. ^1H and ^{13}C NMR data of this intermediate were identical to those previously reported.[6] The above disaccharide (2.63 g, 3.11 mmol) was dried in vacuo and suspended in a solution of bis(2-butyl-3-methyl)borane (23.1 mmol) in anhydrous THF (10.5 mL) and cooled to 0 °C. The reaction mixture was stirred for 24 h at room temperature, cooled to 0 °C and water (6 mL) was very slowly added. After stirring for 20 min, H_2O_2 (4.2 mL) was slowly added, while the aqueous layer was kept at pH 8 with KOH 2.5 M. The crude mixture was diluted with water (110 mL) and extracted with CH_2Cl_2 (2 x 60 mL). The combined organic layers were washed with water (100 mL), dried over anhydrous Na_2SO_4 and concentrated. Boric acid was eliminated by co-evaporation with MeOH (6 x 12 mL), and the product was purified by column chromatography (9:1 toluene-EtOAc) to afford 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene -α,β-D-galactofuranose (1.39 g, 53%, β/α ratio 2:1, ^1H NMR) as an amorphous solid. R_f = 0.32 (4:1 toluene/EtOAc). $[\alpha]_D^{20}$ +60.7 (*c*=1, $CHCl_3$), [lit.[6] $[\alpha]_D$ +65.5 (*c*=1, $CHCl_3$)]. ^1H and ^{13}C NMR data of this intermediate were identical to those previously reported.[6]

A solution of the above 1-OH disaccharide (1.39 g, 1.6 mmol) and trichloroacetonitrile (0.5 mL, 5 mmol) in CH_2Cl_2 (26.5 mL) was cooled to 0 °C. DBU (50 µL, 0.33 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 1.5 h. Upon completion of the reaction (determined by TLC), the solution was concentrated, and the residue was purified by flash column chromatography on silica gel (10:0.3 toluene/TEA) to afford **21** (1.32 g, 81%, β/α ratio 4:1, ^{1}H NMR) as a syrup. R_f = 0.66 and 0.47 (toluene/EtOAc/TEA 6:1:0.07). ^{1}H NMR (300 MHz, $CDCl_3$) δ (anomeric mixture): 8.61 (s, 0.8H, NH β), 8.41 (s, 0.2H, NH α), 8.14 – 7.02 (m, 25H, PhCO, 4 x $PhCH_2$), 6.66 (d, *J* = 4.7 Hz, 0.2H, H-1 α), 6.47 (s, 0.8H, H-1 β), 5.67 (d, *J* = 1.1 Hz, 0.8H, H-2 β), 5.51 (dd, *J* = 7.6, 4.7 Hz, 0.2H, H-2 α), 5.10 (d, *J* = 3.5 Hz, 0.8H, H-1' β), 5.03 – 3.37 (m, 19H), 3.30 – 3.19 (m, 0.2H), 1.45 – 1.39 (m, 3H, CH_3 α, CH_3 β), 1.37 – 1.33 (m, 3H, CH_3 α, CH_3 β).

_N_-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,4,6-tetra-_O_-benzyl-α-D-galactopyranosyl-(1→3)-2-_O_-benzoyl-5,6-_O_-isopropylidene-β-D-galactofuranoside (22)

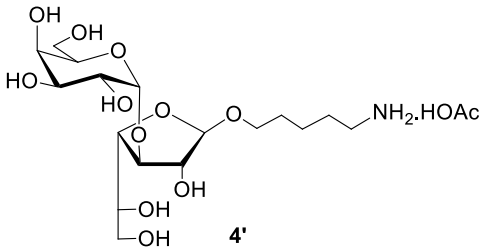


22

Glycosyl donor **21** (0.78 g, 0.79 mmol) was reacted with **8**[3] (350 mg, 1.07 mmol) in CH_2Cl_2 (19.5 mL) at -15 °C with TMSOTf (0.1 equiv.) for 30 min, according to the general procedure for glycosylation. Column chromatography in hexane/EtOAc 8:2 afforded **22** (0.66 g, 72%) as a syrup. R_f = 0.67 (toluene/EtOAc 8:2). $[\alpha]_D^{20}$ +17.4 (*c*=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of rotamers): 8.09 – 6.96 (m, 35H, PhCO, 6 x $PhCH_2$), 5.39 (bs, 1H, H-2), 5.21 – 5.11 (m, 2H, NCOOCH_2Ph), 5.08 – 4.99 (m, 2H, H-1, H-1'), 4.89 (d, *J* = 11.3 Hz, 1H, OCH_aHPh), 4.83 – 4.68 (m, 3H, OCH_aHPh, OCH_2Ph),

4.64 (d, *J* = 11.7 Hz, 1H, OCH$\underline{H_b}$Ph), 4.55 – 4.41 (m, 3H, OCH$\underline{H_b}$Ph, NC$\underline{H_2}$Ph), 4.38 – 4.19 (m, 3H, H-5, OC$\underline{H_2}$Ph), 4.18 – 3.99 (m, 5H, H-4, H-3, H-5', H-2', H-4'), 3.99 – 3.86 (m, 3H, H-6a, H-6b, H-3'), 3.78 – 3.57 (m, 1H, OC$\underline{H_a}$HCH$_2$), 3.50 (t, *J* = 8.6 Hz, 1H, H-6'a), 3.46 – 3.32 (m, 2H, OCH$\underline{H_b}$CH$_2$, H-6'b), 3.31 – 3.10 (m, 2H, CH$_2$C$\underline{H_2}$N), 1.61 – 1.41 (m, 7H, 2 x CH$_2$, CH$_3$), 1.39 – 1.18 (m, 5H, CH$_3$, CH$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ (mixture of rotamers): 165.6 ($\underline{C}$OPh), 156.8/156.3 (NCOO), 138.9 - 127.4 ($\underline{Ph}$CO, 6 x $\underline{Ph}$CH$_2$), 109.9 ($\underline{C}$(CH$_3$)$_2$), 106.0 (C-1), 99.4 (C-1'), 84.0 (C-3), 82.7/82.6 (C-2), 81.8/81.7 (C-4), 79.0 (C-3'), 76.4 (C-2'*), 75.6 (C-5), 75.0 (O$\underline{C}$H$_2$Ph), 74.8 (C-4'*), 73.7 (O$\underline{C}$H$_2$Ph), 73.4 (O$\underline{C}$H$_2$Ph), 72.8 (O$\underline{C}$H$_2$Ph), 69.8 (C-5'), 68.3 (C-6'), 67.6 (O$\underline{C}$H$_2$CH$_2$), 67.3 (NCOO$\underline{C}$H$_2$Ph), 65.7 (C-6), 50.6/50.3 (N$\underline{C}$H$_2$Ph), 47.3/46.3 (CH$_2\underline{C}$H$_2$N), 29.2 (CH$_2$), 28.0/27.6 (CH$_2$), 26.6 (CH$_3$), 25.5 (CH$_3$), 23.4 (CH$_2$). HRMS (ESI): m/z calcd. for $C_{70}H_{77}NO_{14}$ $[M+Na]^+$ 1178.5242, found 1178.5228.

5-Aminopentyl α-D-galactopyranosyl-(1→3)-β-D-galactofuranoside, acetate (4')

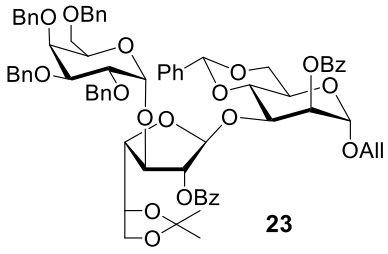


4'

5-Aminopentyl glycoside **22** (0.60 g, 0.52 mmol) was deprotected following the general procedure for acetal hydrolysis. The crude product was dissolved in MeOH (4.2 mL) and treated with NaOH 1 M in MeOH (0.8 equiv.) according to the general procedure for debenzoylation. The obtained mixture was hydrogenated in the presence of Pd/C 10% wt. (1.2 mg/mg of starting material) for 7 days according to the general procedure for hydrogenolysis. Column chromatography in ACN/H$_2$O/AcOH 8:2:0.1 afforded **4'** (174 mg, 69%), the ammonium acetate salt of compound **4**, as a syrup. R_f = 0.52 (EtOH/H$_2$O/AcOH 7:1:1). $[\alpha]_D^{20}$ +29.1 (*c*=1, H$_2$O). ^{1}H NMR (400 MHz, D$_2$O) δ: 5.06 (d, *J* = 2.9 Hz, 1H, H-1'), 5.04 (d, *J* = 1.8 Hz, 1H, H-1), 4.26 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 4.17 (dd, *J* = 6.3, 4.0

Hz, 1H, H-4), 4.10 – 4.03 (m, 2H, H-5', H-3), 4.02 – 3.99 (m, 1H, H-4'), 3.92 – 3.82 (m, 3H, H-5, H-2', H-3'), 3.83 – 3.56 (m, 6H), 3.03 – 2.97 (m, 2H, C$\underline{H_2}$N), 1.92 (s, 3H, C$\underline{H_3}$COOH), 1.77 – 1.60 (m, 4H, 2 x CH_2), 1.52 – 1.40 (m, 2H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ: 108.1 (C-1), 100.3 (C-1'), 85.1 (C-3), 82.3 (C-4), 80.1 (C-2), 72.0 (C-5'), 71.5 (C-5), 69.84 (C-3'*), 69.79 (C-4'), 68.8 (C-2'*), 68.6 (O$\underline{C}H_2CH_2$), 63.3 (C-6), 61.7 (C-6'), 40.0 ($\underline{C}H_2NH_2$), 28.7 (CH_2), 27.1 (CH_2), 23.9 ($\underline{C}H_3COOH$), 22.9 (CH_2). *Assignments may be interchanged. HRMS (ESI): m/z calcd. for $C_{17}H_{33}NO_{11}$ $[M+Na]^+$ 450.1951, found 450.1956.

Allyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (23)

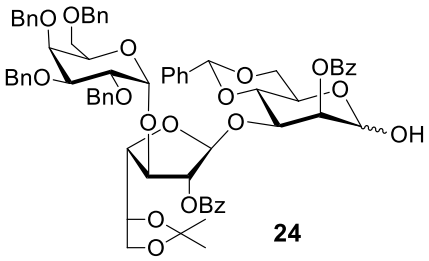


23

Glycosyl donor **21** (1.13 g, 1.1 mmol) was reacted with **7** (432 mg, 1.4 mmol) in CH_2Cl_2 (28 mL) at -15 °C with TMSOTf (0.1 equiv.) for 25 min, according to the general procedure for glycosylation. The foregoing crude product was dissolved in pyridine (18 mL) and treated with benzoyl chloride (4.7 equiv.) for 5.5 h, according to the general procedure for benzoylation. Column chromatography in toluene/EtOAc 15:1 afforded **23** (0.78 g, 57%) as an amorphous solid. R_f = 0.5 (toluene/EtOAc 9:1). Mp 63.4 - 65.0 °C. $[\alpha]_D^{20}$ -10.4 (*c*=1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 – 7.02 (m, 35H, 2 x $\underline{Ph}$CO, 4 x $\underline{Ph}CH_2$, $\underline{Ph}$CH), 6.02 – 5.80 (m, 1H, C$\underline{H}$=CH_2), 5.59 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2), 5.55 (s, 1H, PhC$\underline{H}$), 5.49 – 5.42 (m, 2H, H-1', H-2'), 5.31 (dq, *J* = 17.3, 1.5 Hz, 1H, CH=C$\underline{H_a}$H), 5.23 (dq, *J* = 10.4, 1.3 Hz, 1H, CH=CH$\underline{H_b}$), 5.18 (d, *J* = 3.7 Hz, 1H, H-1''), 4.97 (d, *J* = 1.5 Hz, 1H, H-1), 4.80 (d, *J* = 11.4 Hz, 1H, OC$\underline{H_a}$HPh), 4.70 (d, *J* = 11.7 Hz, 1H, OC$\underline{H_a}$HPh), 4.62 – 4.47 (m, 2H, H-3,

OCH$\underline{H_b}$Ph), 4.45 – 4.35 (m, 2H, OC$\underline{H_a}$HPh, OCH$\underline{H_b}$Ph), 4.34 – 4.06 (m, 7H, OCH$\underline{H_b}$Ph, H-4', OC$\underline{H_2}$Ph, OC$\underline{H_a}$HCH=CH_2, H-6a, H-5'), 4.06 – 3.87 (m, 6H, OCH$\underline{H_b}$CH=CH_2, H-4, H-5'', H-5, H-3', H-2''), 3.83 (dd, *J* = 8.5, 6.2 Hz, 1H, H-6'a), 3.73 – 3.64 (m, 2H, H-4'', H-6'b), 3.60 – 3.45 (m, 2H, H-6b, H-3''), 3.33 (t, *J* = 8.7 Hz, 1H, H-6''a), 3,16 (dd, *J* = 8.5, 5.1 Hz, 1H, H-6''b), 1.40 (s, 3H, CH_3), 1.31 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9 ($\underline{C}$OPh), 165.1 ($\underline{C}$OPh), 139.2 - 126.2 ($\underline{C}$H=CH_2, 2 x $\underline{Ph}$CO, 4 x $\underline{Ph}CH_2$, $\underline{Ph}$CH), 118.4 (CH=$\underline{C}H_2$), 110.0 ($\underline{C}(CH_3)_2$), 102.7 (C-1'), 101.1 (Ph$\underline{C}$H), 98.2 (C-1), 98.1 (C-1''), 84.4 (C-3'), 83.1 (C-4'), 80.9 (C-2'), 79.2 (C-3''), 77.0 (C-4), 76.9 (C-2''), 75.7 (C-5'), 74.82 (O$\underline{C}H_2$Ph), 74.77 (C-4''), 73.5 (O$\underline{C}H_2$Ph), 73.3 (O$\underline{C}H_2$Ph), 72.7 (O$\underline{C}H_2$Ph), 69.5 (C-3), 69.4 (C-2), 69.3 (C-5''), 68.7 (C-6, O$\underline{C}H_2$CH=CH_2), 68.1 (C-6''), 65.6 (C-6'), 64.2 (C-5), 26.7 (CH_3), 25.5 (CH_3). HRMS (ESI): m/z calcd. for $C_{73}H_{76}O_{18}$ $[M+H]^+$ 1263.4929, found 1263.4962.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (24)

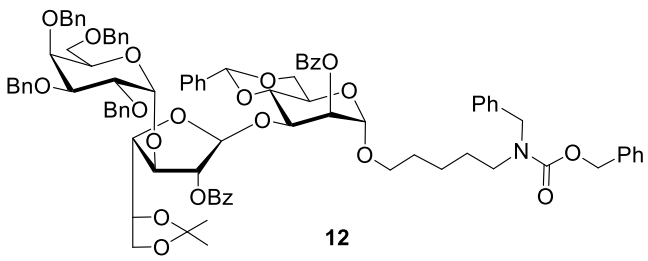


24

A solution of allyl glycoside **23** (0.50 g, 0.4 mmol) in CH_2Cl_2 (7.8 mL) was deallylated with tetrakis(triphenylphosphine)palladium(0) (0.8 equiv.), according to the general procedure for deallylation. In this case, after 24 h of stirring, 0.5 M methanolic solution of tetrakis(triphenylphosphine)palladium(0) (0.2 equiv.) was added. Column chromatography in toluene/EtOAc 9:1 afforded **24** (395 mg, 82%, α/β ratio 5:1, ^{1}H NMR) as an amorphous solid. R_f = 0.53 (toluene/ EtOAc 3:1). $[\alpha]_D^{20}$ -32.0 (*c*=1, $CHCl_3$). **23**α: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 – 7.07 (m, 35H, 2 x $\underline{Ph}$CO, 4 x $\underline{Ph}CH_2$, $\underline{Ph}$CH), 5.70

(dd, *J* = 3.4, 0.8 Hz, 0.2H, H-2 β), 5.61 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2), 5.56 (s, 0.2H, H-1' β), 5.55 (s, 1H, PhC<u>H</u>), 5.54 (s, 0.2H, PhC<u>H</u> β), 5.46 – 5.44 (m, 2H, H-1', H-2'), 5.30 (dd, *J* = 4.1, 1.4 Hz, 1H, H-1), 5.19 (d, *J* = 3.8 Hz, 0.2H, H-1'' β), 5.15 (d, *J* = 3.7 Hz, 1H, H-1''), 5.05 – 4.97 (m, 0.2H, H-1 β), 4.81 (d, *J* = 11.3 Hz, 1H, OC<u>H</u>$_a$HPh), 4.71 (d, *J* = 11.7 Hz, 1H, OC<u>H</u>$_a$HPh), 4.64 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3), 4.54 (d, *J* = 11.6 Hz, 1H, OCH<u>H</u>$_b$Ph), 4.46 (d, *J* = 11.8 Hz, 1H, OC<u>H</u>$_a$HPh), 4.41 (d, *J* = 11.4 Hz, 1H, OCH<u>H</u>$_b$Ph), 4.35 (d, *J* = 11.8 Hz, 1H, OCH<u>H</u>$_b$Ph), 4.28 (t, *J* = 6.0 Hz, 1H, H-4'), 4.24 – 3.98 (m, 7H, OC<u>H</u>$_2$Ph, H-6a, H-5, H-5' H-5'', H-4), 3.96 – 3.90 (m, 2H, H-2'', H-3'), 3.79 (dd, *J* = 8.6, 5.9 Hz, 1H, H-6'a), 3.76 – 3.73 (m, 1H, H-4''), 3.64 (dd, *J* = 8.5, 6.9 Hz, 1H, H-6'b), 3.62 – 3.52 (m, 2H, H-6b, H-3''), 3.32 (t, *J* = 8.5 Hz, 1H, H-6''a), 3.18 (dd, *J* = 8.7, 5.3 Hz, 1H, H-6''b), 1.37 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). **23**α: ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9 (<u>C</u>OPh), 165.1 (<u>C</u>OPh), 139.2 - 126.2 (2 x <u>Ph</u>CO, 4 x <u>Ph</u>CH_2, <u>Ph</u>CH), 110.0 (<u>C</u>$(CH_3)_2$), 102.9 (C-1'), 102.7 (C-1' β), 101.2 (Ph<u>C</u>H), 101.0 (Ph<u>C</u>H β), 98.3 (C-1''), 98.1 (C-1'' β), 94.0 (C-1 β), 93.8 (C-1), 84.3 (C-3'), 82.9 (C-4'), 81.1 (C-2'), 79.2 (C-3''), 77.3 (C-4), 76.8 (C-2''), 75.6 (C-5'), 74.8 (C-4'',O<u>C</u>H_2Ph), 73.5 (O<u>C</u>H_2Ph), 73.3 (O<u>C</u>H_2Ph), 72.7 (O<u>C</u>H_2Ph), 69.9 (C-2), 69.4 (C-5''), 69.3 (C-3), 68.8 (C-6), 68.2 (C-6''), 65.5 (C-6'), 64.1 (C-5), 26.5 (CH_3), 25.5 (CH_3). HRMS (ESI): m/z calcd. for $C_{70}H_{72}O_{18}$ $[M+Na]^+$ 1223.4617, found 1223.4673.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside** (**12**).



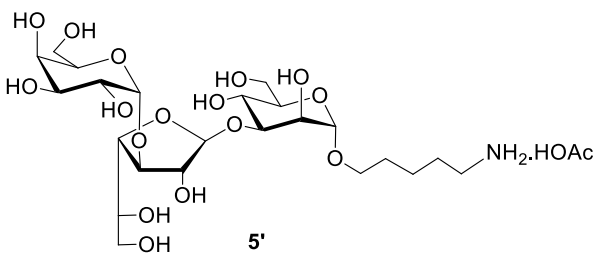
12

A solution of hemiacetal **24** (374 mg, 0.3 mmol) and trichloroacetonitrile (6 equiv.) in

CH_2Cl_2 (3.8 mL) was treated with DBU (0.4 equiv.) for 2.5 h, according to the general procedure for trichloroacetimidate formation. Column chromatography in toluene/TEA 10:0.1 afforded *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside) trichloroacetimidate (362 mg, 86%) as an amorphous solid. R_f = 0.74 (toluene/EtOAc/TEA 8:2:0.1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.76 (s, 1H, NH), 8.20 – 7.05 (m, 35H, 2 x PhCO, 4 x $PhCH_2$, PhCH), 6.39 (d, *J* = 1.5 Hz, 1H, H-1), 5.78 (dd, *J* = 3.7, 1.7 Hz, 1H, H-2), 5.54 (s, 1H, PhCH), 5.50 (s, 1H, H-1'), 5.47 (d, *J* = 1.6 Hz, 1H, H-2'), 5.17 (d, *J* = 3.7 Hz, 1H, H-1''), 4.80 (d, *J* = 11.4 Hz, 1H, OCH_aHPh), 4.71 (d, *J* = 11.7 Hz, 1H, OCH_aHPh), 4.60 (dd, *J* = 9.7, 3.7 Hz, 1H, H-3), 4.53 (d, *J* = 11.7 Hz, 1H, $OCHH_bPh$), 4.43 – 4.36 (m, 2H, OCH_aHPh, $OCHH_bPh$), 4.34 – 4.03 (m, 8H, H-4', $OCHH_bPh$, OCH_2Ph, H-6a, H-5', H-4, H-5), 4.03 – 3.88 (m, 3H, H-5'', H-3', H-2''), 3.84 (dd, *J* = 8.5, 6.0 Hz, 1H, H-6'a), 3.76 – 3.64 (m, 2H, H-6'b, H-4''), 3.58 – 3.45 (m, 2H, H-6b, H-3''), 3.32 (t, *J* = 8.7 Hz, 1H, H-6''a), 3.14 (dd, *J* = 8.5, 5.0 Hz, 1H, H-6''b), 1.39 (s, 3H, CH_3), 1.31 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.7 (COPh), 165.1 (COPh), 160.5 (C=NH), 139.2 - 125.5 (2 x PhCO, 4 x $PhCH_2$, PhCH), 110.0 ($C(CH_3)_2$), 102.9 (C-1'), 101.2 (PhCH), 98.1 (C-1''), 96.2 (C-1), 90.8 (CCl_3), 84.2 (C-3'), 83.0 (C-4'), 81.0 (C-2'), 79.2 (C-3''), 76.9 (C-2''), 76.4 (C-4), 75.6 (C-5'), 74.9 (OCH_2Ph), 74.7 (C-4''), 73.5 (OCH_2Ph), 73.4 (OCH_2Ph), 72.7 (OCH_2Ph), 69.43 (C-3), 69.38 (C-5''), 68.4 (C-6), 68.1 (C-6''), 67.9 (C-2), 66.6 (C-5), 65.6 (C-6'), 26.7 (CH_3), 25.5 (CH_3). The glycosyl imidate (362 mg, 0.27 mmol) was reacted with **8**[3] (109 mg, 0.33 mmol) in CH_2Cl_2 (12.3 mL) at -30 °C with TMSOTf (0.1 equiv.) for 15 min, according to the general procedure for glycosylation. Column chromatography in toluene/EtOAc 5:1 afforded **12** (371 mg, 91%) as an amorphous solid. R_f = 0.64 (toluene/EtOAc 6:1). Mp 50.7-52.2 °C. $[\alpha]_D^{20}$ -7.2 (*c*=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of

rotamers): 8.18 – 7.11 (m, 45H, 2 x PhCO, 6 x $PhCH_2$, PhCH), 5.57 – 5.52 (m, 2H, H-2, PhCH), 5.48 (s, 1H, H-1'), 5.45 (d, *J* = 1.5 Hz, 1H, H-2'), 5.22 – 5.12 (m, 3H, H-1'', $NCOOCH_2Ph$), 4.92 – 4.84 (m, 1H, H-1), 4.80 (d, *J* = 11.3 Hz, 1H, OCH_aHPh), 4.70 (d, *J* = 11.7 Hz, 1H, OCH_aHPh), 4.57 – 4.47 (m, 4H, H-3, $OCHH_bPh$, NCH_2Ph), 4.42 – 4.35 (m, 2H, $OCHH_bPh$, OCH_aHPh), 4.30 (dd, *J* = 6.3, 5.6 Hz, 1H, H-4'), 4.26 (d, *J* = 11.8 Hz, 1H, $OCHH_bPh$), 4.22 (d, *J* = 11.5 Hz, 1H, OCH_aHPh), 4.15 – 4.06 (m, 3H, $OCHH_bPh$, H-6a, H-5'), 4.04 – 3.94 (m, 2H, H-5'', H-4), 3.93 – 3.79 (m, 4H, H-2'', H-3', H-5, H-6'a), 3.74 – 3.56 (m, 3H, H-4'', H-6'b, OCH_aHCH_2), 3.55 – 3.45 (m, 2H, H-6b, H-3''), 3.41 – 3.18 (m, 4H, $OCHH_bCH_2$, H-6''a, CH_2CH_2N), 3.15 (dd, *J* = 8.5, 5.0 Hz, 1H, H-6''b), 1.66 – 1.46 (m, 4H, CH_2 x 2), 1.39 (s, 3H, CH_3), 1.38 – 1.21 (m, 5H, CH_3, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ (mixture of rotamers): 166.0 (COPh), 165.1 (COPh), 156.9/156.3 (NCOO), 139.2 - 126.2 (2 x PhCO, 6 x $PhCH_2$, PhCH), 110.0 ($C(CH_3)_2$), 102.6 (C-1'), 101.0 (PhCH), 99.1 (C-1), 98.0 (C-1''), 84.4 (C-3'), 83.3 (C-4'), 80.9 (C-2'), 79.2 (C-3''), 76.95 (C-4), 76.91 (C-2''), 75.8 (C-5'), 74.8 (OCH_2Ph), 74.7 (C-4''), 73.5 (OCH_2Ph), 73.3 (OCH_2Ph), 72.7 (OCH_2Ph), 69.5 (C-3), 69.4 (C-2), 69.3 (C-5''), 68.7 (C-6), 68.2 (OCH_2CH_2), 68.1 (C-6''), 67.3 ($NCOOCH_2Ph$), 65.5 (C-6'), 64.0 (C-5), 50.8/50.5 (NCH_2Ph), 47.3/46.4 (CH_2CH_2N), 29.2 (CH_2), 28.1/27.6 (CH_2), 26.7 (CH_3), 25.4 (CH_3), 23.5 (CH_2). HRMS (ESI): m/z calcd. for $C_{90}H_{95}NO_{20}$ $[M+Na]^+$ 1532.6345, found 1532.6471.

5-Aminopentyl α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside, acetate (5')



5'

5-Aminopentyl glycoside **12** (237 mg, 0.16 mmol) was deprotected following the general procedure for acetal

hydrolysis. The crude product was dissolved in MeOH (1.3 mL) and treated with NaOH 1 M in MeOH (1.7 equiv.) according to the general procedure for debenzoylation. Column chromatography in CH_2Cl_2/MeOH 12:1 rendered *N*-(benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside (120 mg, 65%) as an amorphous solid. R_f = 0.59 (CH_2Cl_2/MeOH 12:1). $[\alpha]_D^{20}$ +7.7 (*c*=1, $CHCl_3$). ^{1}H NMR (400 MHz, MeOD) δ (mixture of rotamers): 7.56 – 7.01 (m, 30H, 6 x $\underline{Ph}CH_2$), 5.22 – 5.10 (m, 2H, NCOOC$\underline{H_2}$Ph), 5.06 (s, 1H, H-1'), 5.00 (d, *J* = 3.5 Hz, 1H, H-1''), 4.83 (d, *J* = 11.3 Hz, 1H, OC$\underline{H_a}$HPh), 4.77 – 4.66 (m, 5H, 2 x OC$\underline{H_2}$Ph, H-1), 4.56 – 4.47 (m, 4H, OC$\underline{H_a}$HPh, OCH$\underline{H_b}$Ph, NC$\underline{H_2}$Ph), 4.44 (d, *J* = 11.9 Hz, 1H, OCH$\underline{H_b}$Ph), 4.38 – 4.30 (m, 2H, H-2', H-4'), 4.22 – 4.15 (m, 1H, H-5''), 4.05 (dd, *J* = 5.4, 2.8 Hz, 1H, H-3'), 4.02 – 3.89 (m, 3H, H-4'', H-2'', H-3''), 3.88 – 3.43 (m, 12H), 3.42 – 3.19 (m, 3H, OCH$\underline{H_b}$CH$_2$, $CH_2C\underline{H_2}$N), 1.67 – 1.40 (m, 4H, 2 x CH_2), 1.40 – 1.18 (m, 2H, CH_2). ^{13}C NMR (101 MHz, MeOD) δ (mixture of rotamers): 158.5/158.0 (NCOO), 140.1 - 128.4 (6 x $\underline{Ph}CH_2$), 106.9 (C-1'), 101.3 (C-1), 100.0 (C-1''), 86.8 (C-3'), 83.8 (C-4'), 80.5 (C-2'), 80.0 (C-3''), 77.9 (C-3), 77.2 (C-2''), 76.6 (C-4''), 75.9 (O$\underline{C}H_2$Ph), 74.6 (C-5), 74.5 (O$\underline{C}H_2$Ph), 74.3 (O$\underline{C}H_2$Ph), 74.0 (O$\underline{C}H_2$Ph), 72.6 (C-5'), 71.3 (C-5''), 70.6 (C-6''), 69.0 (C-2), 68.5 (NCOO$\underline{C}H_2$Ph), 68.4 (O$\underline{C}H_2CH_2$), 66.9 (C-4), 64.4 (C-6'), 63.1 (C-6), 51.6/51.4 (N$\underline{C}H_2$Ph), 48.5/47.5 ($CH_2\underline{C}H_2$N), 30.1 (CH_2), 29.0/28.5 (CH_2), 24.5 (CH_2). HRMS (ESI): m/z calcd. for $C_{66}H_{79}NO_{18}$ $[M+Na]^+$ 1196.5195, found 1196.5226. The obtained glycoside (120 mg, 0.1mmol) was hydrogenated in the presence of Pd/C 10% wt. (1.4 mg/mg of starting material) for 3 days according to the general procedure for hydrogenolysis. The reaction afforded **5'** (65 mg, 98%), the ammonium acetate salt of compound **5**, as a syrup. R_f = 0.5 (EtOH/H_2O/AcOH 7:1:1). $[\alpha]_D^{20}$ +30.7 (*c*=1, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 5.15 (d, *J* = 1.0 Hz, 1H, H-1'), 5.06 (d, *J* = 3.4 Hz, 1H, H-1''), 4.89 (d, *J* = 1.8 Hz, 1H, H-1), 4.38 (dd, *J* = 3.1, 1.5

Hz, 1H, H-2'), 4.26 (dd, *J* = 6.4, 3.9 Hz, 1H, H-4'), 4.13 – 4.08 (m, 2H, H-2, H-5''), 4.06 (dd, *J* = 6.4, 3.0 Hz, 1H, H-3'), 4.00 – 3.98 (m, 1H, H-4''), 3.92 – 3.82 (m, 5H, H-5', H-6a, H-3, H-3'', H-2''), 3.82 – 3.61 (m, 8H, H-6b, H-6''a, H-6''b, OC$\underline{H_a}$HCH$_2$, H-6'a, H-6'b, H-4, H-5), 3.60 – 3.51 (m, 1H, OCH$\underline{H_b}$CH$_2$), 3.04 – 2.97 (m, 2H, C$\underline{H_2}$NH$_2$), 1.90 (s, 3H, C$\underline{H_3}$COOH), 1.76 – 1.60 (m, 4H, 2 x CH$_2$), 1.55 – 1.38 (m, 2H, CH$_2$). ^{13}C NMR (101 MHz, D$_2$O) δ: 105.3 (C-1'), 100.3 (C-1''), 100.1 (C-1), 85.5 (C-3'), 82.3 (C-4'), 80.2 (C-2'), 76.1 (C-3), 73.4 (C-5), 72.0 (C-5''), 71.4 (C-5'), 69.9 (C-4'', C-3''), 68.8 (C-2''), 68.1 (O$\underline{C}$H$_2$CH$_2$), 67.5 (C-2), 65.7 (C-4), 63.5 (C-6'), 61.9 (C-6''), 61.6 (C-6), 40.0 ($\underline{C}$H$_2$NH$_2$), 28.6 (CH$_2$), 27.2 (CH$_2$), 23.9 ($\underline{C}$H$_3$COOH), 23.1 (CH$_2$). HRMS (ESI): m/z calcd. for $C_{70}H_{64}O_{21}$ $[M+Na]^+$ 612.2479, found 612.2482.

3. Antigenicity analysis of synthetic glycans

3.1. American tegumentary leishmaniasis

Sixteen archived human serum samples were obtained from individuals clinically suspected of having American tegumentary leishmaniasis *(ATL*) (Table S1). Diagnosis of clinical samples was assessed by ELISA with soluble antigens from *Leishmania braziliensis* amastigote and PCR. [8,9] The sera were collected from patients in a region where approximately 90% of infections are caused by *Leishmania braziliensis*, as demonstrated by Dr. Marco.[10,11]

The antigenicity evaluation by glycan microarray was carried out with 16 human sera samples from individuals living in northwestern Argentina: eight sera from individuals infected with *L. braziliensis* (*ATL +*) and eight sera from individuals not infected with *L. braziliensis* (*ATL –).* ATL + samples were tested for Chagas Disease and found negative. For glycan microarray immunoreactivity assays, both individual sera and pooled sera were employed. Two pools were analyzed: a positive pool consisting of 8 sera from

individuals infected with *L. braziliensis* (positive pool, *Pool ATL +*) and another 8 sera from not infected individuals (negative pool, *Pool ATL –*).

Table S1. Description on health status of human patients infected and non-infected with leishmaniasis. Sera were collected and tested for Immunofluorescent-antibody test, PCR before glycan array analysis.

Sample Name/Classification	*Date*	*Int. Ref.*	*Sex*	*Age*	*K-PCR*	*OD*	*OD/CO*	*ELISA result*
						L. braz. crude extract[8]		
"LEISH - #1"	9/6/2023	9994	F	28	negative	0.020	0.118	negative
"LEISH - #2"	2/15/2024	10075	M	54	negative	0.027	0.176	negative
"LEISH - #3"	4/7/2022	10076	F	25	negative	0.028	0.165	negative
"LEISH - #4"	10/30/2024	10122	M	65	negative	0.044	0.208	negative
"LEISH - #5"	11/9/2023	10131	M	46	negative	0.020	0.126	negative
"LEISH - #6"	11/16/2023	10177	M	51	negative	0.062	0.208	negative
"LEISH - #7"	11/25/2023	10195	M	38	negative	0.027	0.147	negative
"LEISH - #8"	12/19/2023	10210	F	30	negative	0.047	0.272	negative
"LEISH + #1"	11/3/2000	1257	M	24	positive	3.121	3.430	positive
"LEISH + #2"	10/10/2001	1406	M	53	positive	0.680	3.887	positive
"LEISH + #3"	10/16/2001	1409	F	49	positive	0.982	2.230	positive
"LEISH + #4"	11/26/2001	1439	M	28	positive	1.507	1.650	positive
"LEISH + #5"	7/5/2002	1857	M	18	positive	2.954	2.390	positive
"LEISH + #6"	8/14/2002	1861	M	39	positive	3.645	4.000	positive
"LEISH + #7"	9/9/2002	2019	F	21	positive	2.168	2.380	positive
"LEISH + #8"	5/9/2001	3288	M	29	positive	2.362	2.340	positive

"LEISH -": patients diagnosed as non ATL cases, "LEISH+": patients diagnosed as ATL cases; Int. Ref.: internal reference; K-PCR: kinetoplast DNA-PCR[9], OD: optical density average; CO: cut-off.

3.2. Chagas Disease

Serological diagnosis of clinical samples was performed using three methods: chemiluminescence microparticle immunoassay (Architect, Abbott, Germany), enzyme-linked immunosorbent assay (recombinant ELISA v3.0, Wiener, Argentina), and indirect hemagglutination test (HIDATEST, Laboratorio Lemos SRL, Argentina). The antigenicity evaluation by glycan microarray was carried out with twenty archived human serum samples divided into two pools: one consisting of 10 sera from individuals infected with T. cruzi (positive pool, Pool CD+) and another of 10 sera from individuals not infected (negative pool, CD-).

3.3. Ethical Approval for Human Studies

This study used stored human serum samples obtained from anonymous, randomized, and coded serum libraries belonging to *Leishmania* infected and uninfected individuals. The sampling and diagnosis procedures for the serum samples have been done at Instituto de Patología Experimental, Facultad de Ciencias de la Salud, Universidad Nacional de Salta (Salta, Argentina). All patients voluntarily requested the tests for the differential diagnosis of their lesions and consented to participate anonymously. The procedures were approved by the Bioethics Committee of the Health Ministry of Salta, Argentina, and followed the Declaration of Helsinki Principles (CONICET code: P-UE 22920170100106, approval number: EXP Nº 321-136934/2018-0#). Treatments and clinical follow-up were conducted by local physicians at the different medical institutions in Salta, Argentina, under the patients' informed consent.[8,10]

In the case of CD, archived human serum samples were obtained from anonymous, randomized, and coded serum libraries belonging to *T. cruzi* infected and uninfected individuals from the Parasitology Section of the Francisco Javier Muñiz Infectious Diseases Hospital (Buenos Aires, Argentina). The use of serum samples was obtained for diagnostic purposes and treated through a strict anonymization process and does not represent any risk to patients. The protection of privacy and confidentiality was guaranteed, complying with international and national ethical principles, allowing these materials to be used for research purposes without requiring additional informed consent.

3.4. Glycan Microarray

The glycans were dissolved at 0.1 mM in 50 mM sodium phosphate buffer pH 8.5 and printed in 64 identical fields to NEXTERION® 3-D Hydrogel coated glass slides (Schott) using a non-contact sciFLEXARRAYER S12 microarray spotter (Scienion, Berlin, Germany). After incubation overnight in a humidified box, the remaining reactive groups

of the slides were quenched with ethanolamine buffer (100 mM ethanolamine in 0,1 M NaPi, pH 9). The slides were blocked with 1% (w/v) bovine serum albumin (BSA) in phosphate buffered saline (PBS) and a 64 well incubation gasket (FlexWell Grid, Grace Bio Labs) was attached. The slides were incubated with ATL+/-, pool ATL+/-, pool CD+/- serum diluted 1:100 in 1% BSA-PBS for 1 h at 37° C. After three washes with PBS containing 0.1% (v/v) Tween-20 (PBS-T) the slides were incubated with goat anti-human IgG (IgG Fc-AF647, Southern Biotech), IgM (IgM, Alexa Fluor 488, Invitrogen), IgA (IgA-FITC, Southern Biotech), diluted 1:400 for 1 h at 37°C. The slides were washed twice with PBS-T. After removing the gasket, the slides were washed once with PBS and once with ddH_2O. The dried slides were scanned with InnoScan 1100 AL (Innopsys) at 488 nm and 635 nm, and intensities were evaluated with Mapix (Innopsys). IgM: 488, low laser power, gain 100; IgG: 635, high laser power, gain 5 The statistical analysis was performed with the software GraphPad Prism 10.4.0 (GraphPad Software, Inc.).

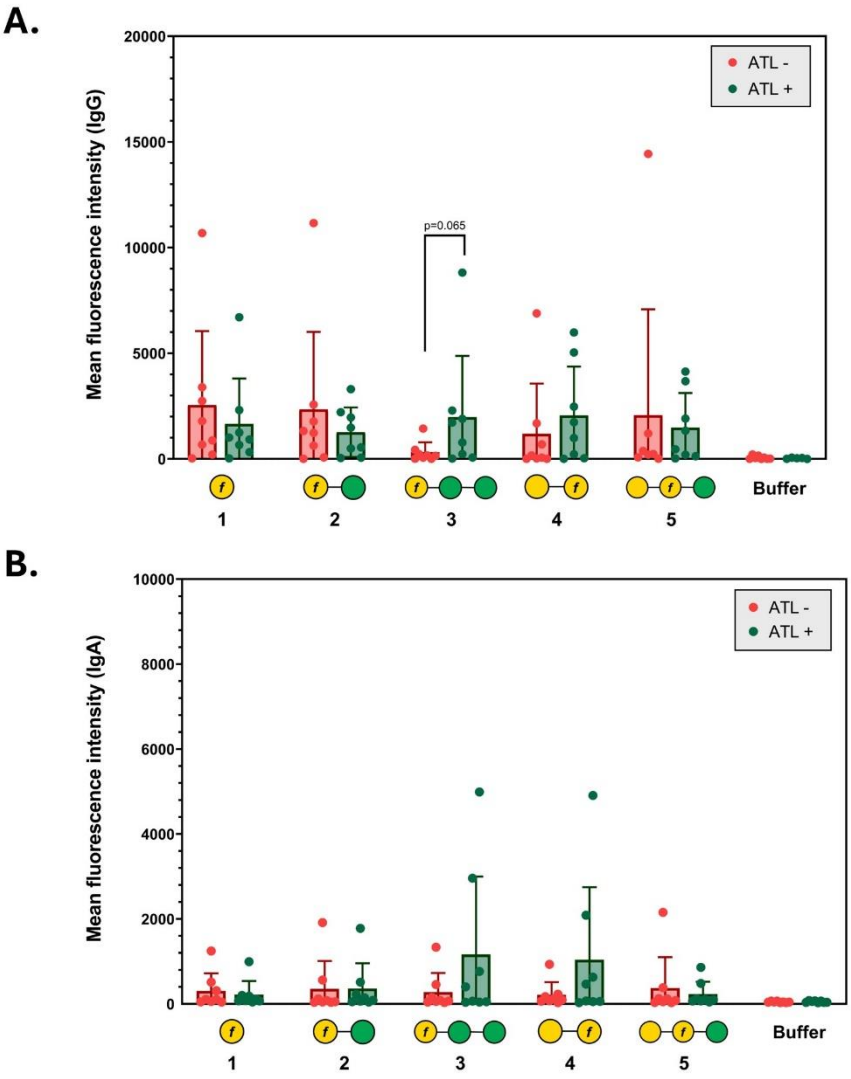


Figure S1. Glycan microarray-based antigenicity analysis of *Leishmania braziliensis*-related glycans. Mean fluorescence intensity of IgG (**graph A**) or IgA (**graph B**) antibodies in sera (dilution 1:100) from American tegumentary leishmaniasis (ATL) positive (ATL +; green) or negative (ATL -; red) patients bound to the synthetic glycans. Numbers **1**-**5** indicate the oligosaccharide antigen. Each dot represents a serum sample. Bars represent mean ± SEM. Positive and negative groups were compared using multiple Mann-Whitney test with (***) $p<0.0002$, (**) $p<0.0021$ and (*) $p<0.0332$.

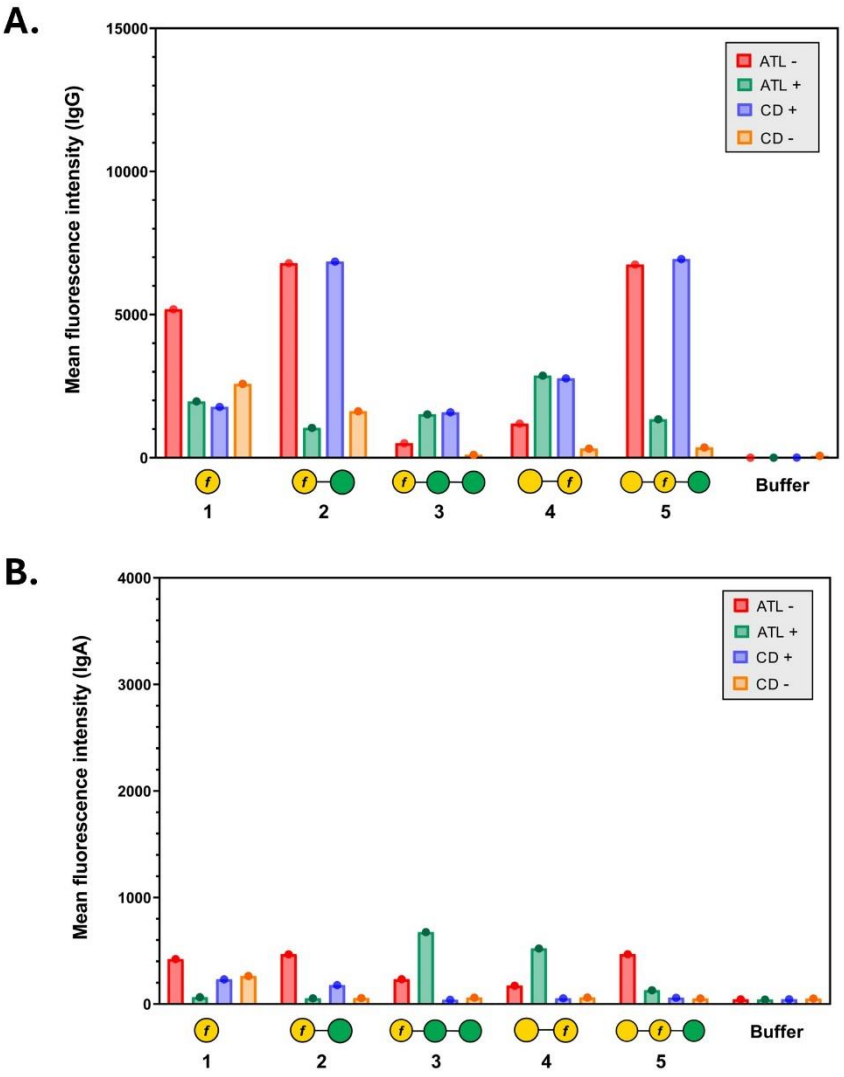


Figure S2. Comparative IgG and IgA response to synthetic *Leishmania braziliensis*-related glycans in sera from ATL and Chagas infected patients. Mean fluorescence intensity of IgG (**graph A**) or IgA (**graph B**) anti-glycan antibodies in pooled sera (dilution 1:100) from ATL positive (ATL +; $n = 8$; green) and negative (ATL -; $n = 8$; red) patients or Chagas disease positive (CD +; $n = 10$; blue) and negative (CD -; $n = 10$; orange) patients. Numbers **1-5** indicate the oligosaccharide antigen.

4. References

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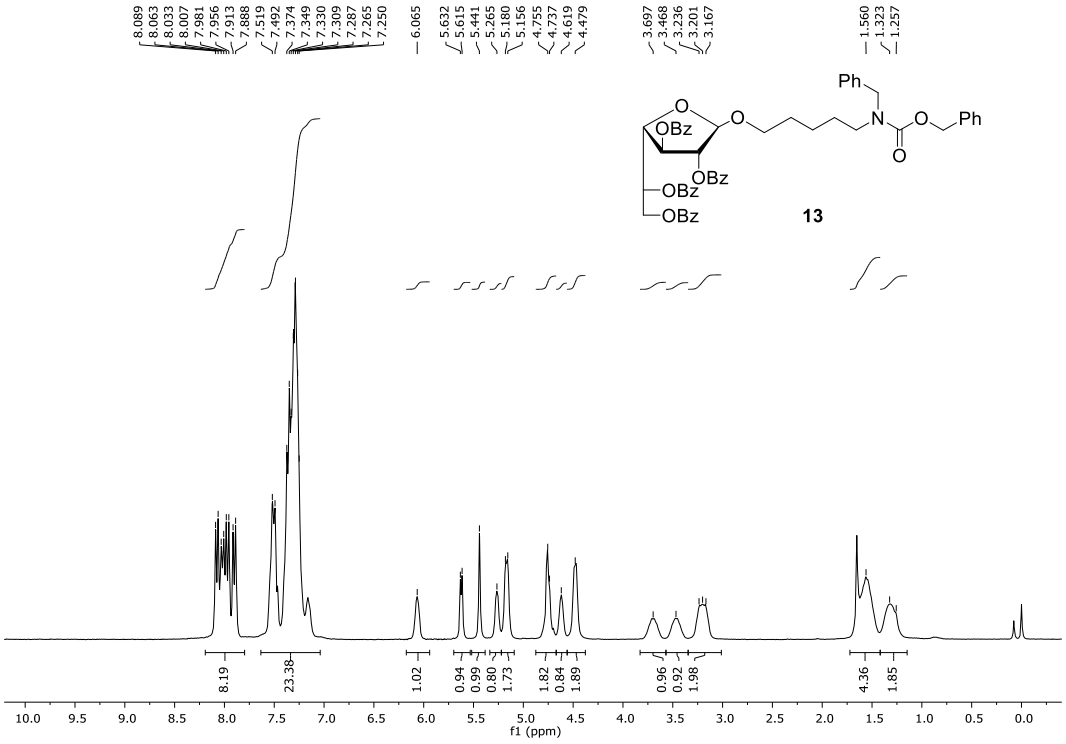
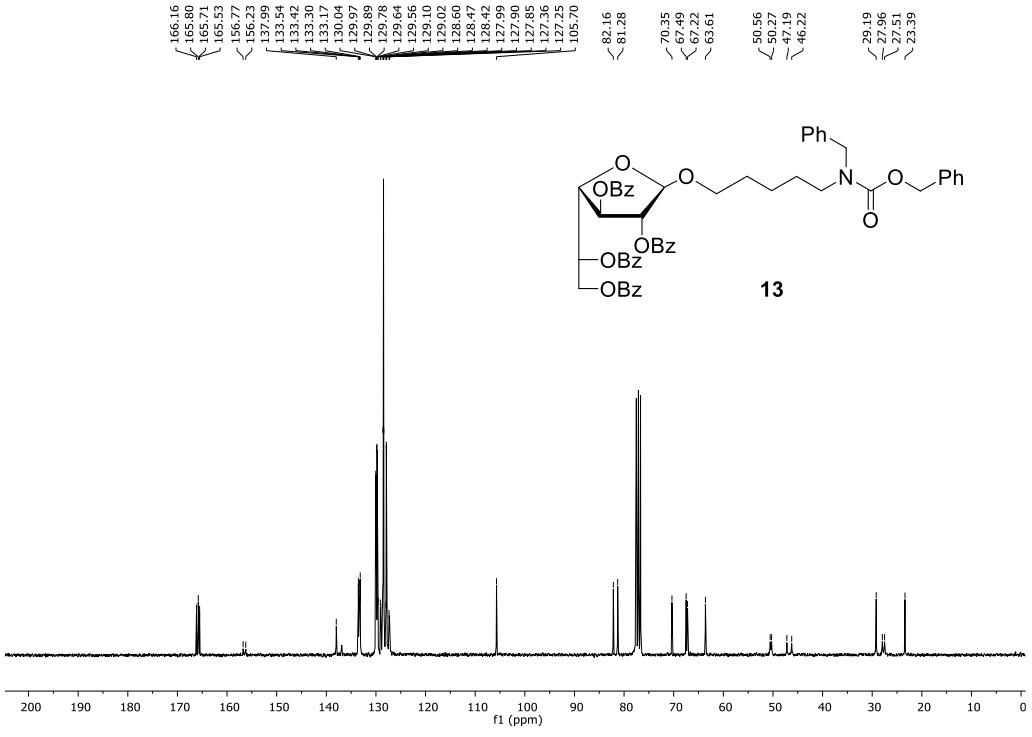
5. NMR Spectra

N-(Benzyl)benzyloxycarbonyl 5-aminopentyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside (13)

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



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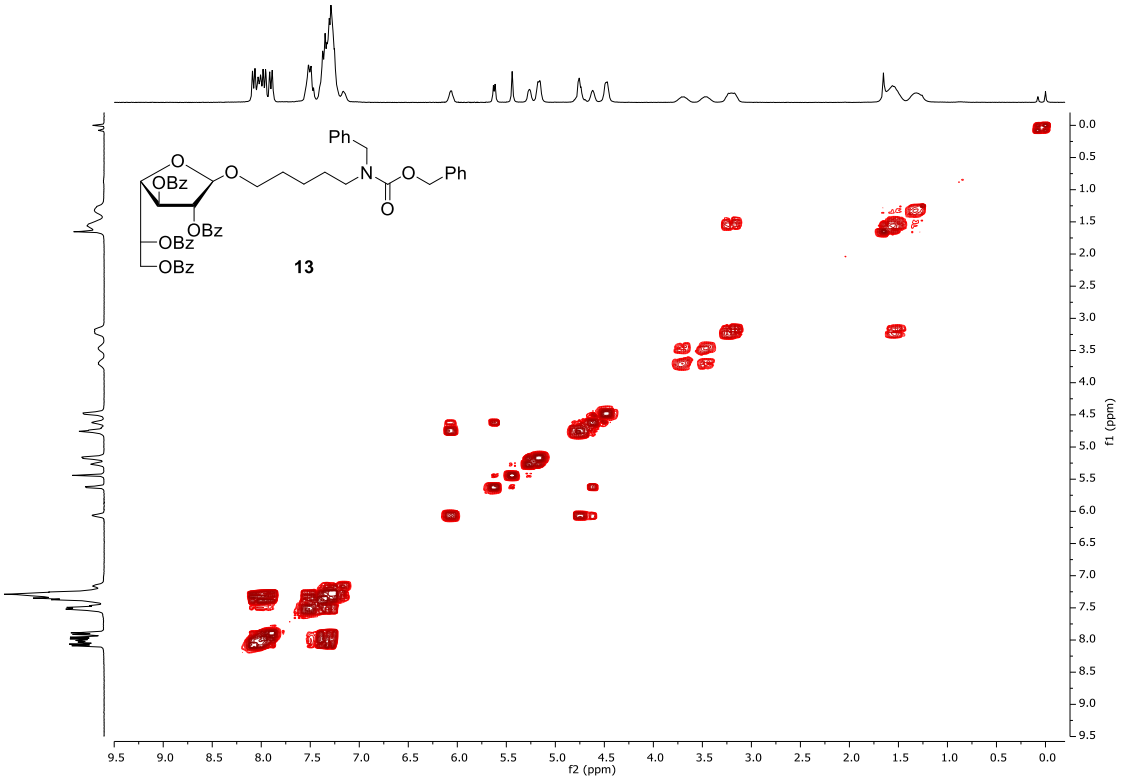
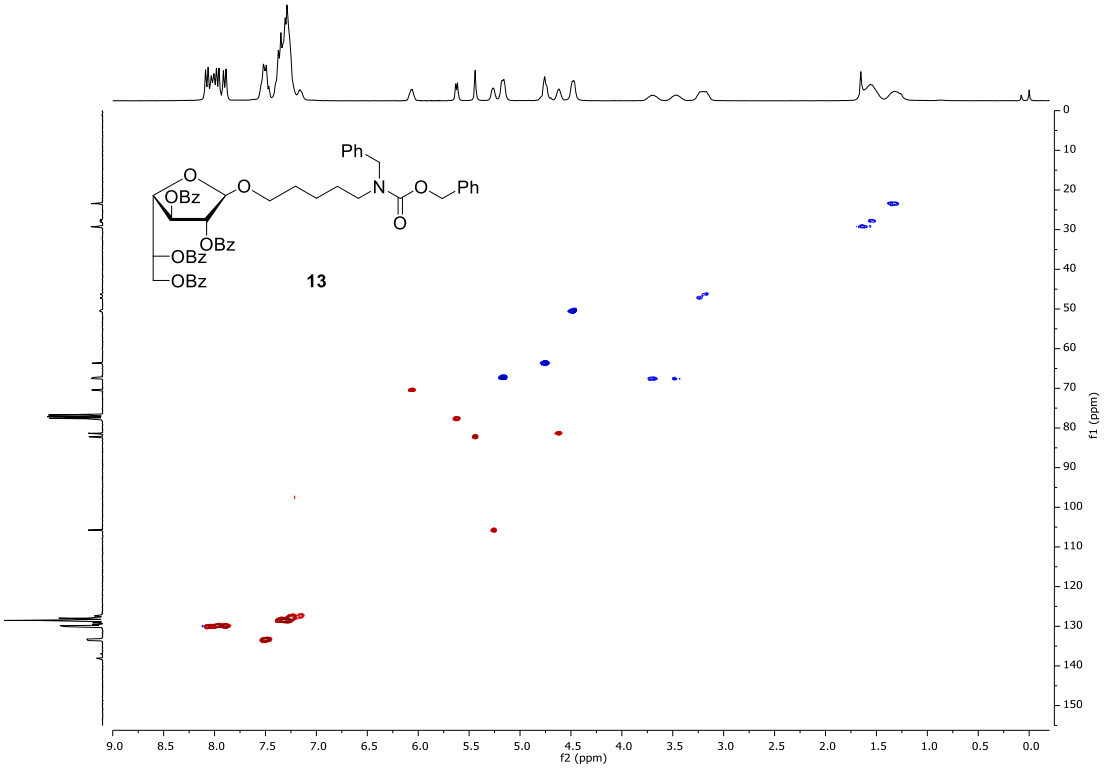
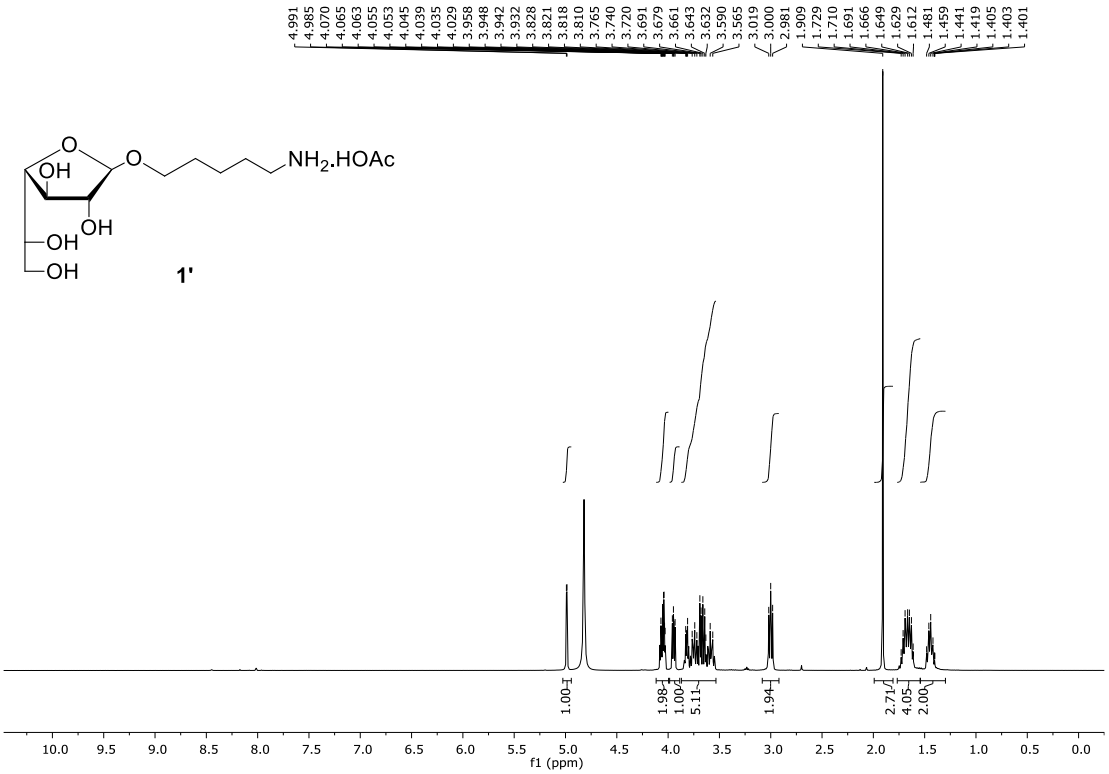


^{1}H-^{13}C decoupled HSQC NMR (300 MHz, $CDCl_3$)



5-Aminopentyl β-D-galactofuranoside, acetate (1')

^{1}H NMR (400 MHz, D_2O)



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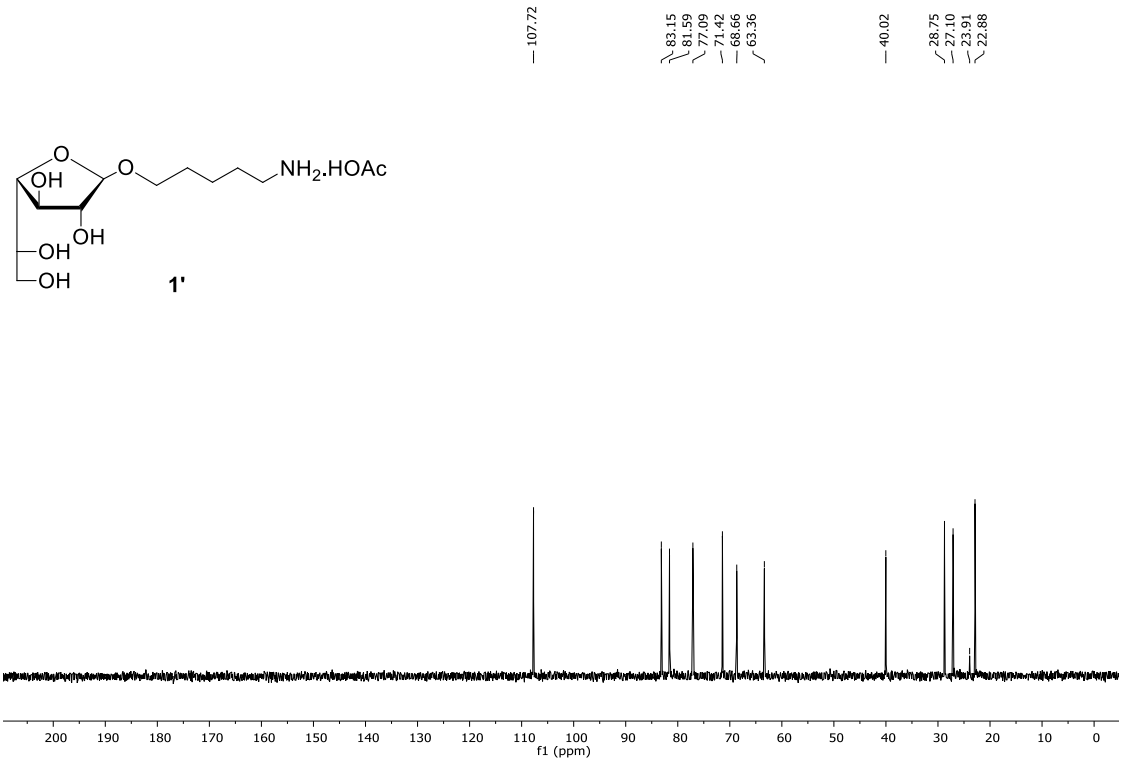

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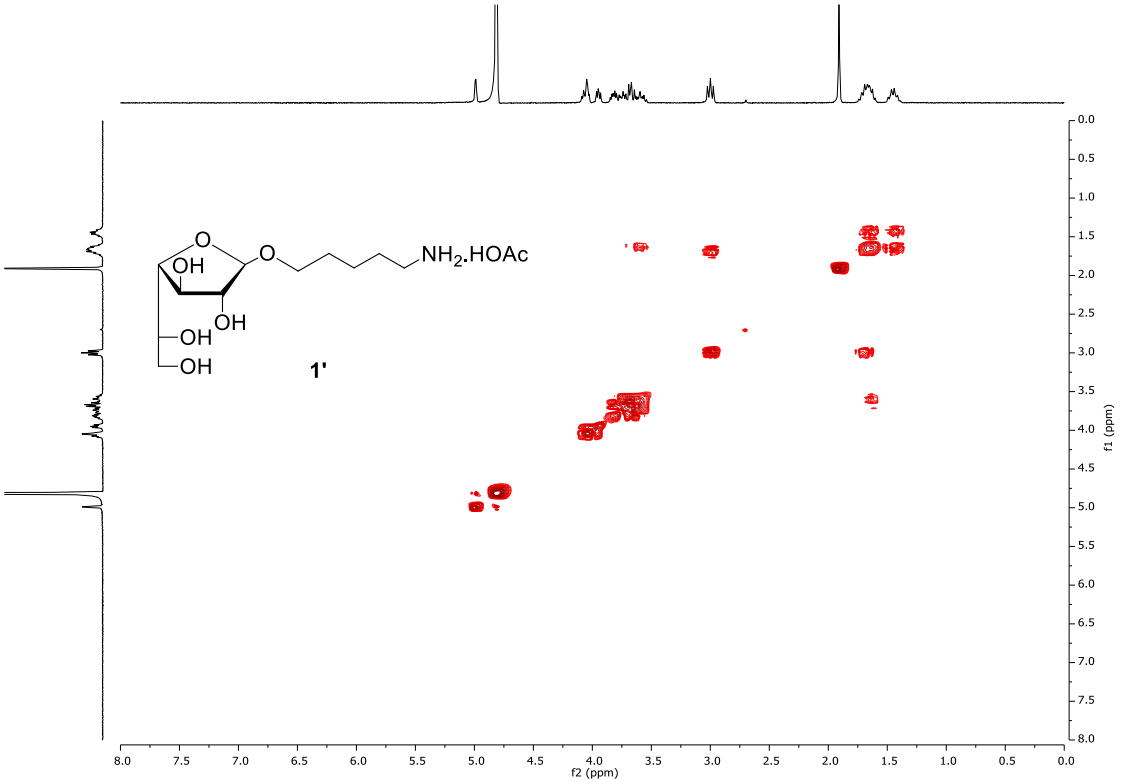

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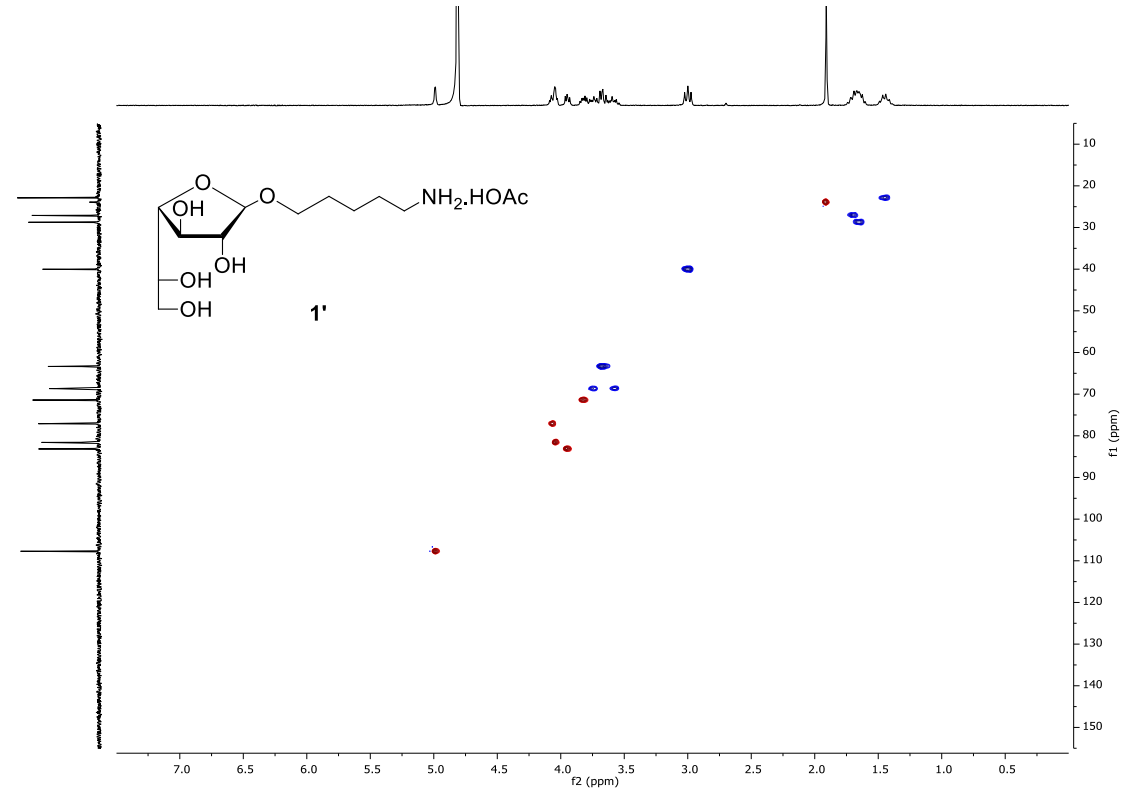

Allyl 4,6-*O*-benzylidene-α-D-mannopyranoside (7)

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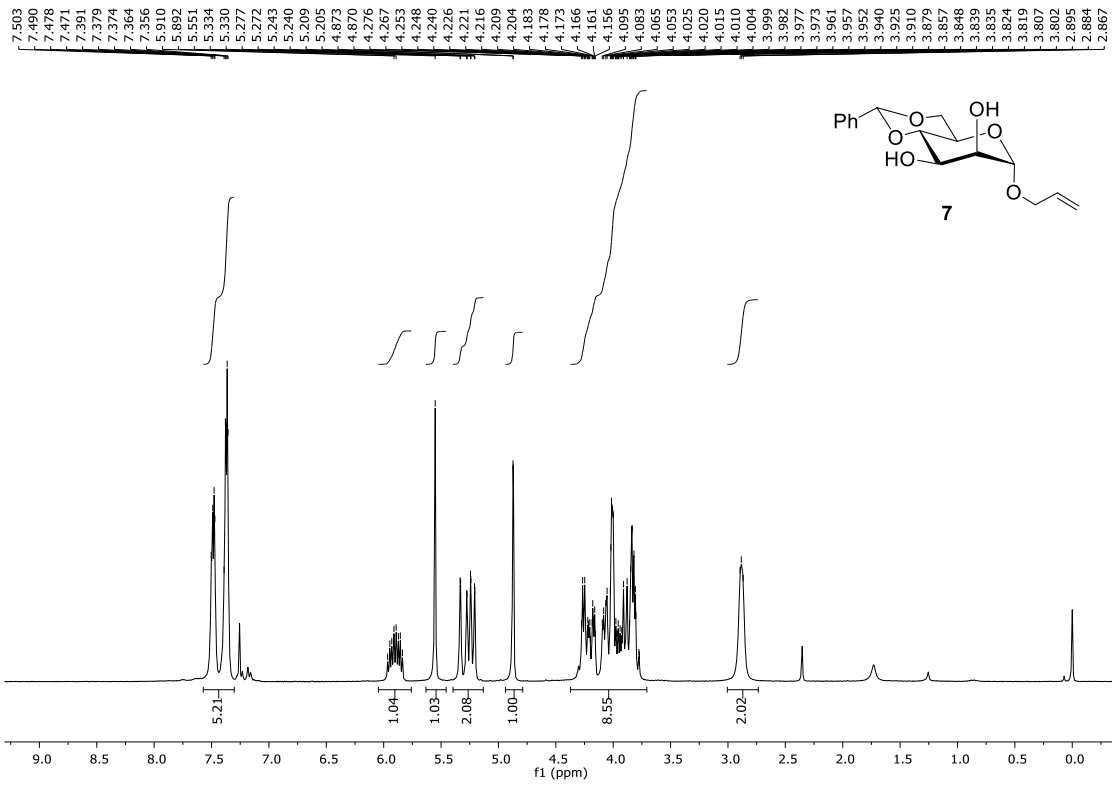
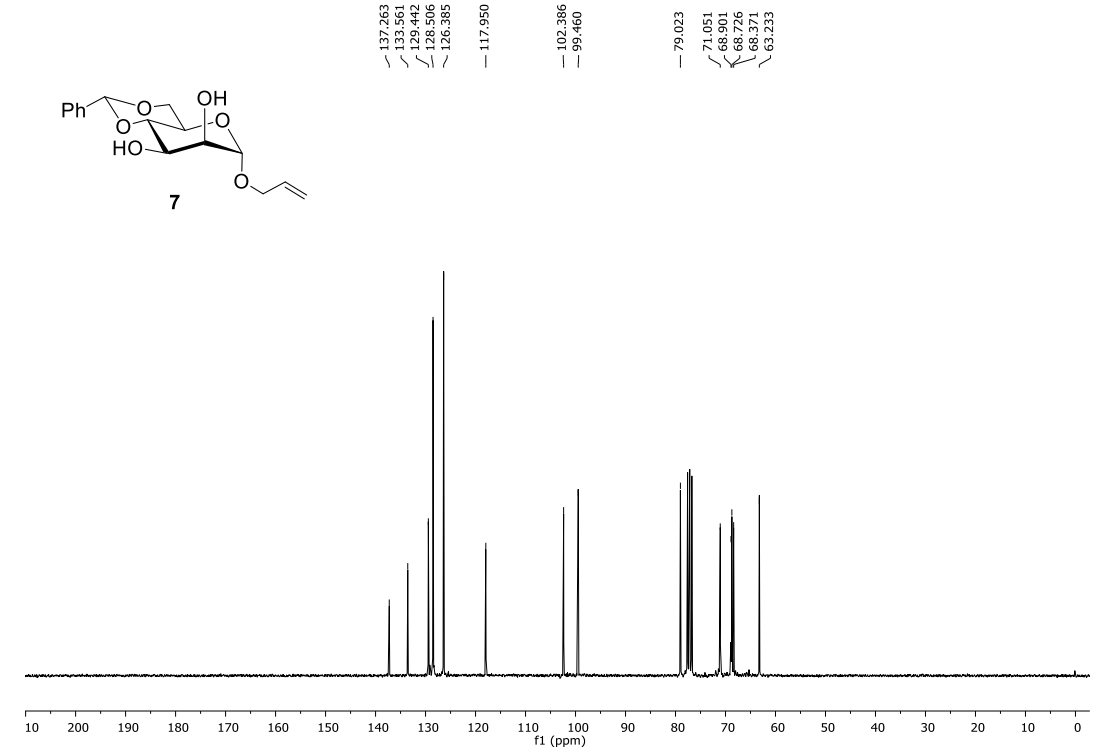
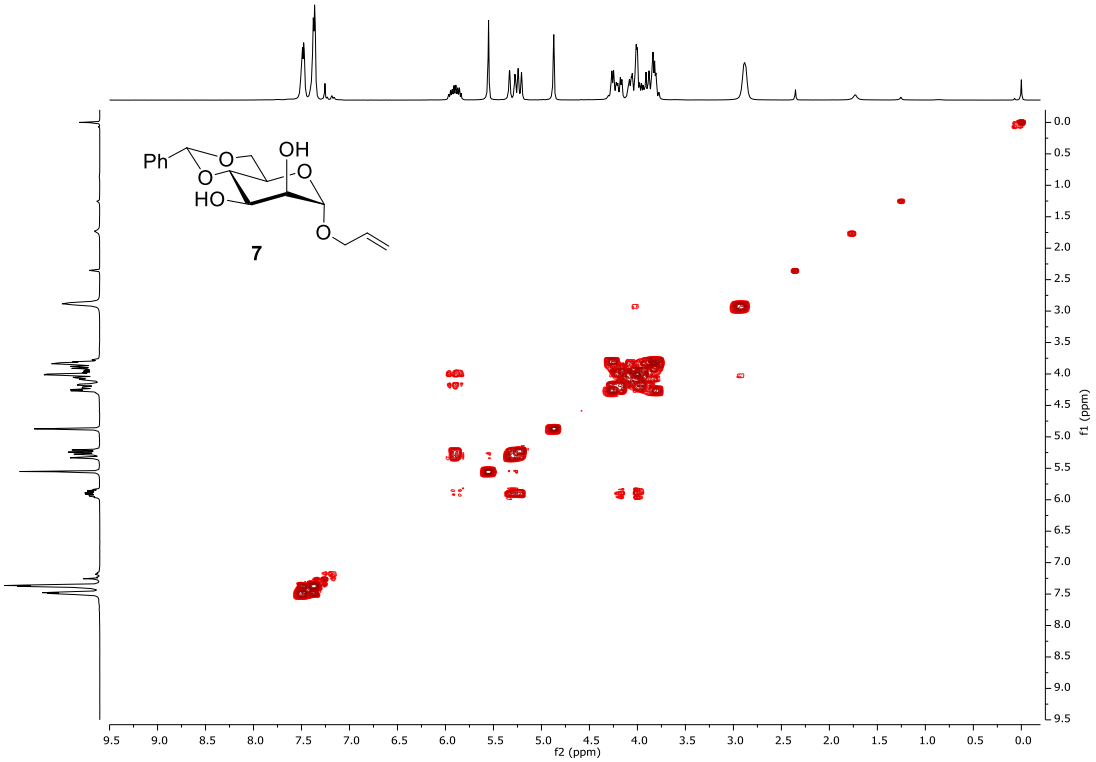


^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$)



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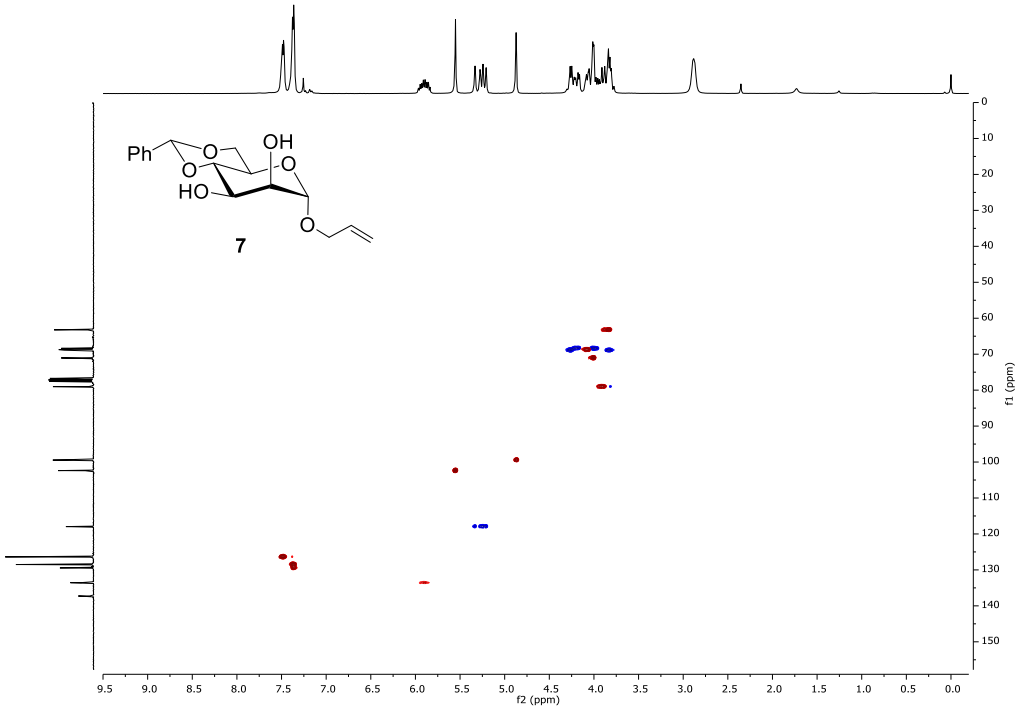
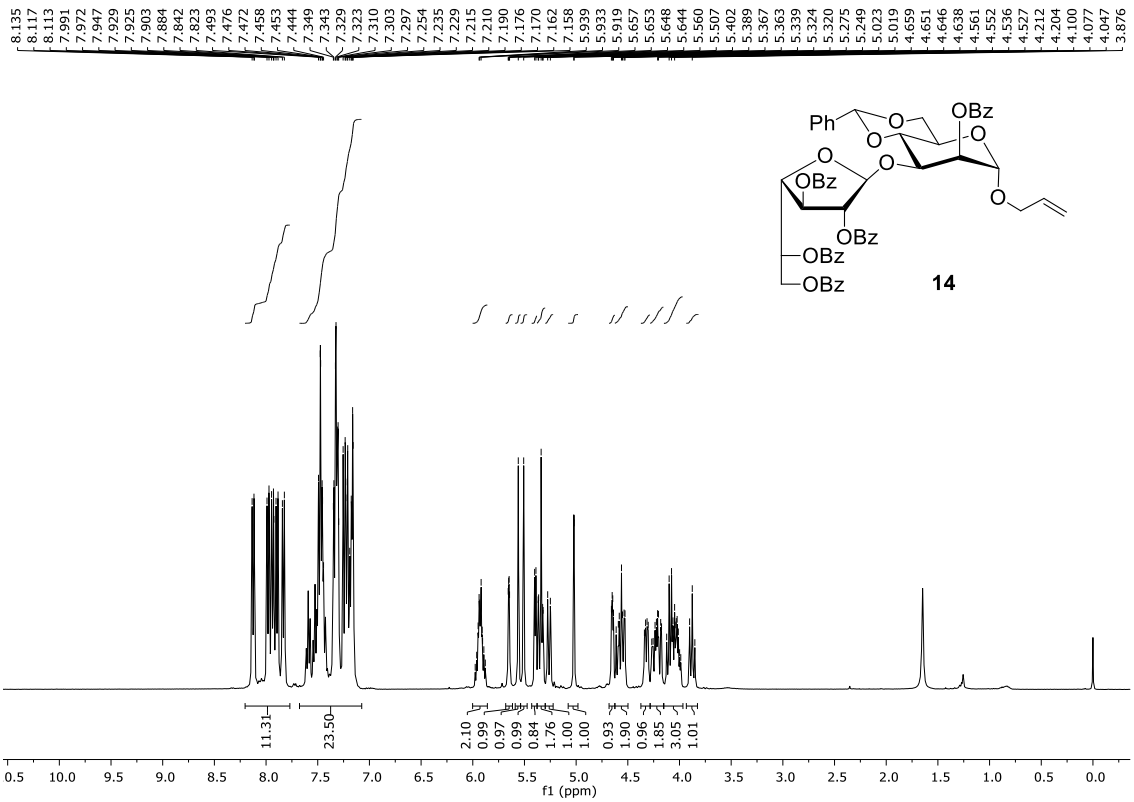


Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (14)

^{1}H NMR (400 MHz, $CDCl_3$)



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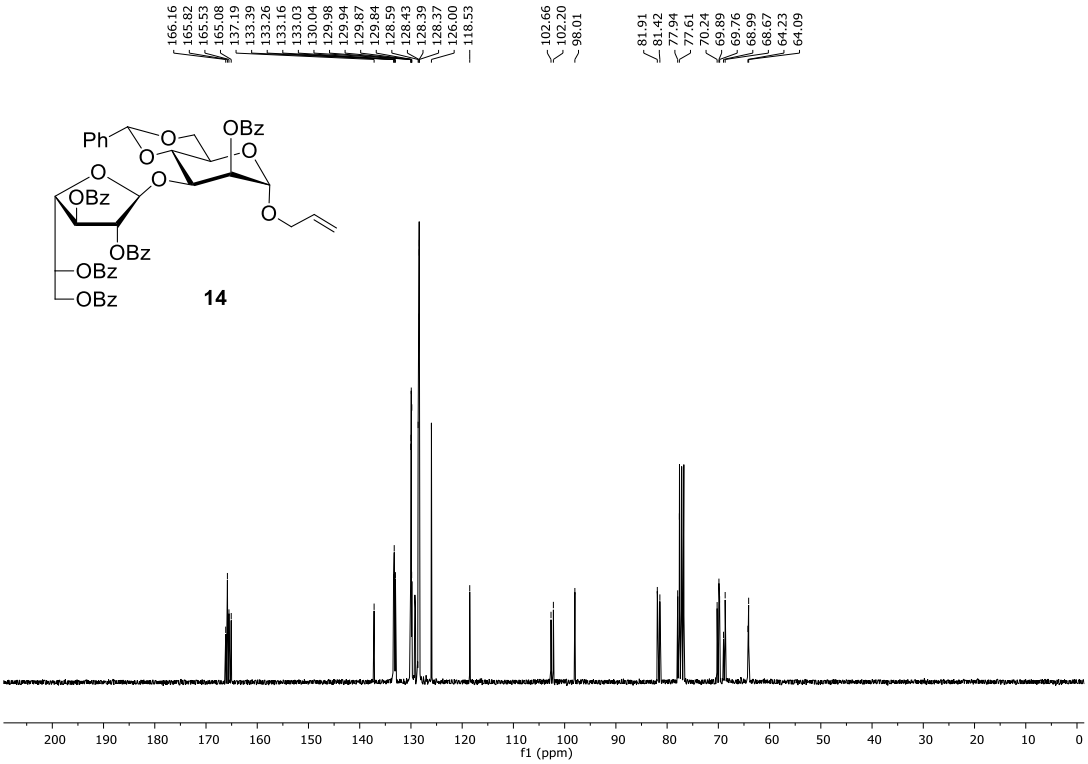

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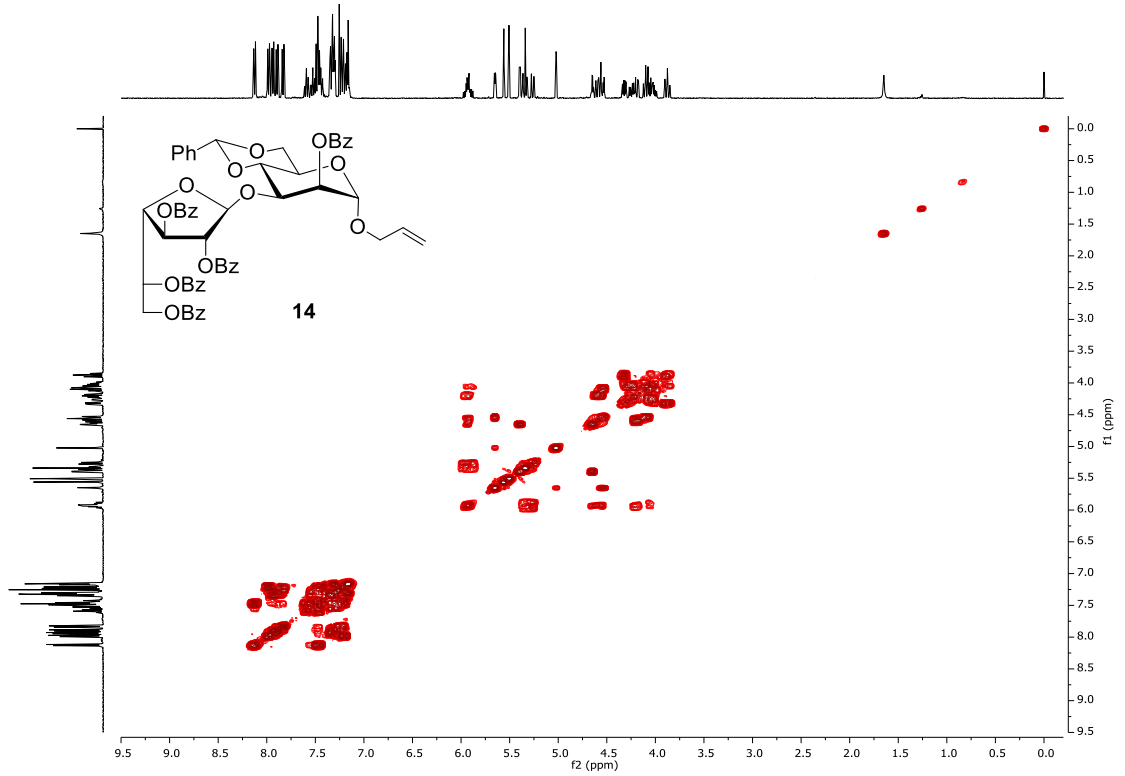

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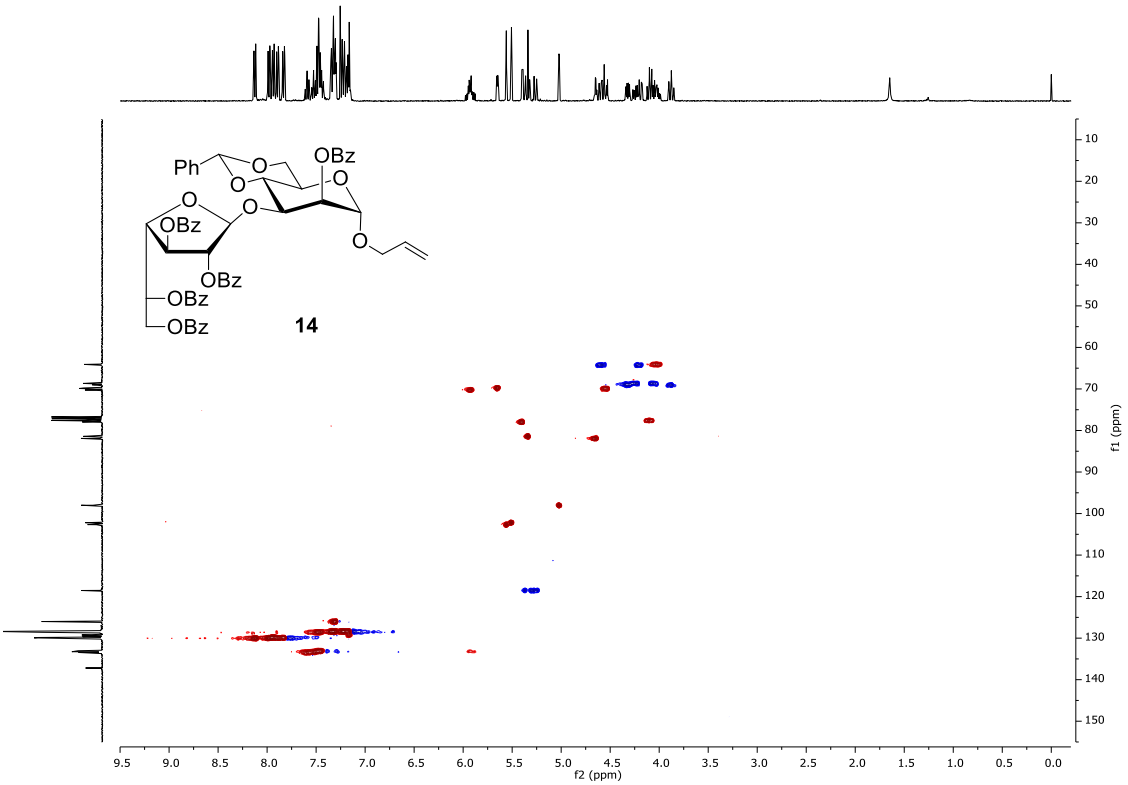

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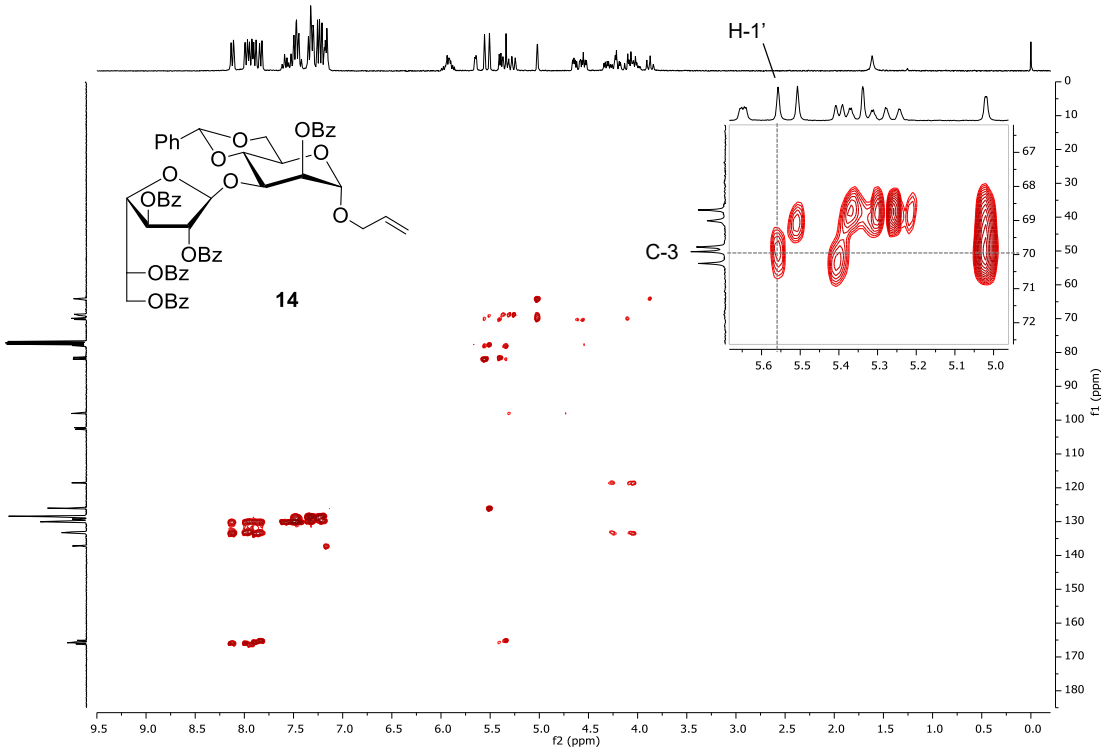
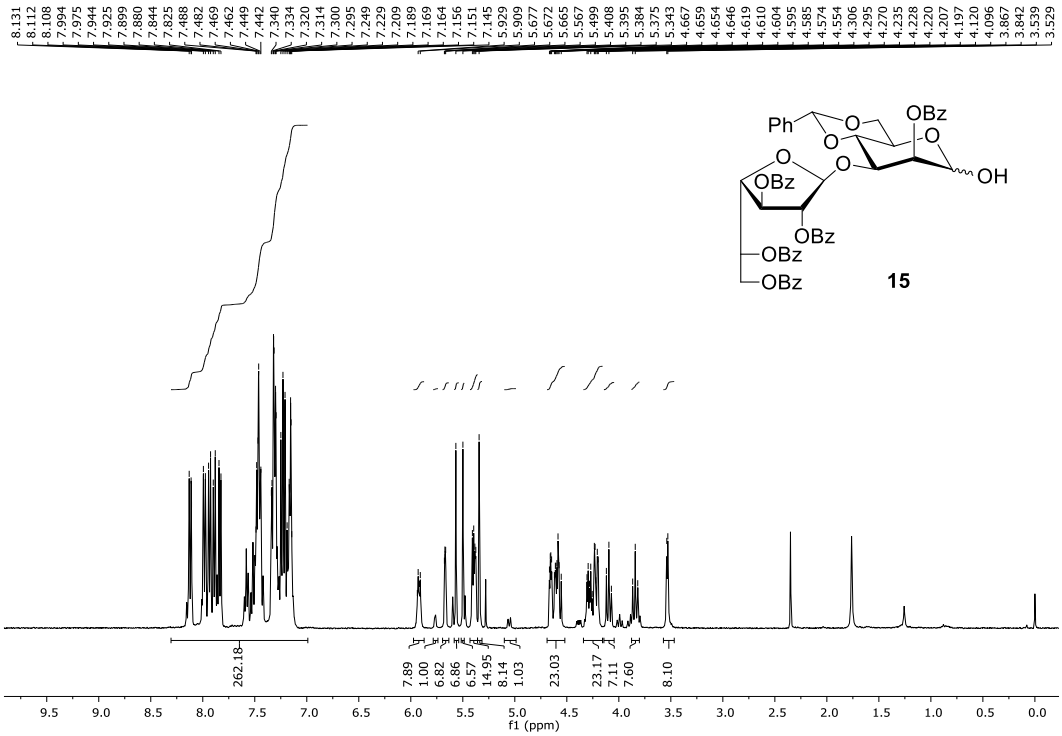


2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (15)

^{1}H NMR (400 MHz, $CDCl_3$)



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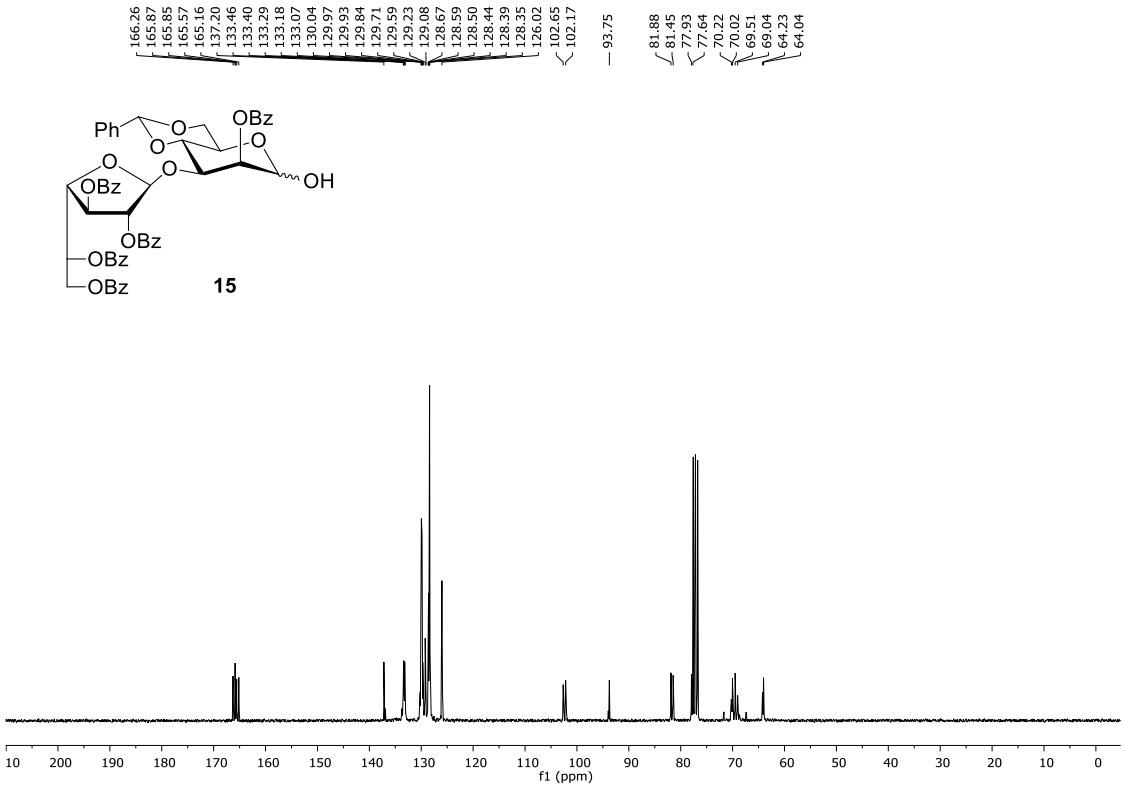

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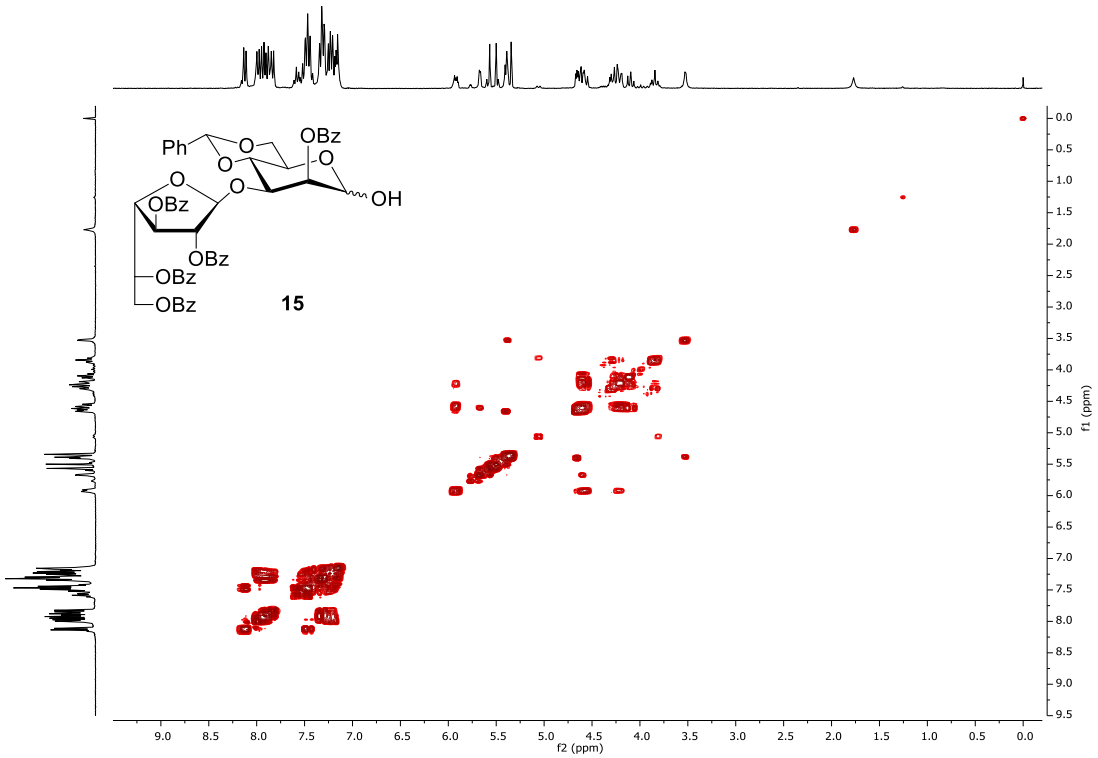
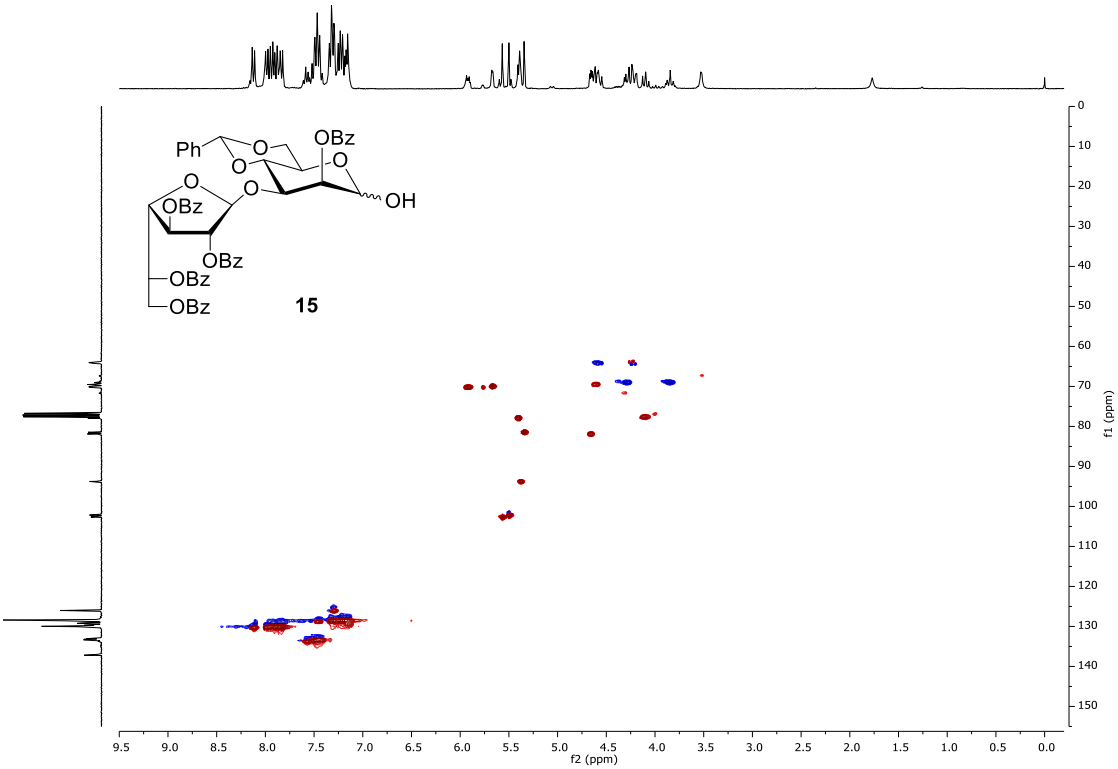
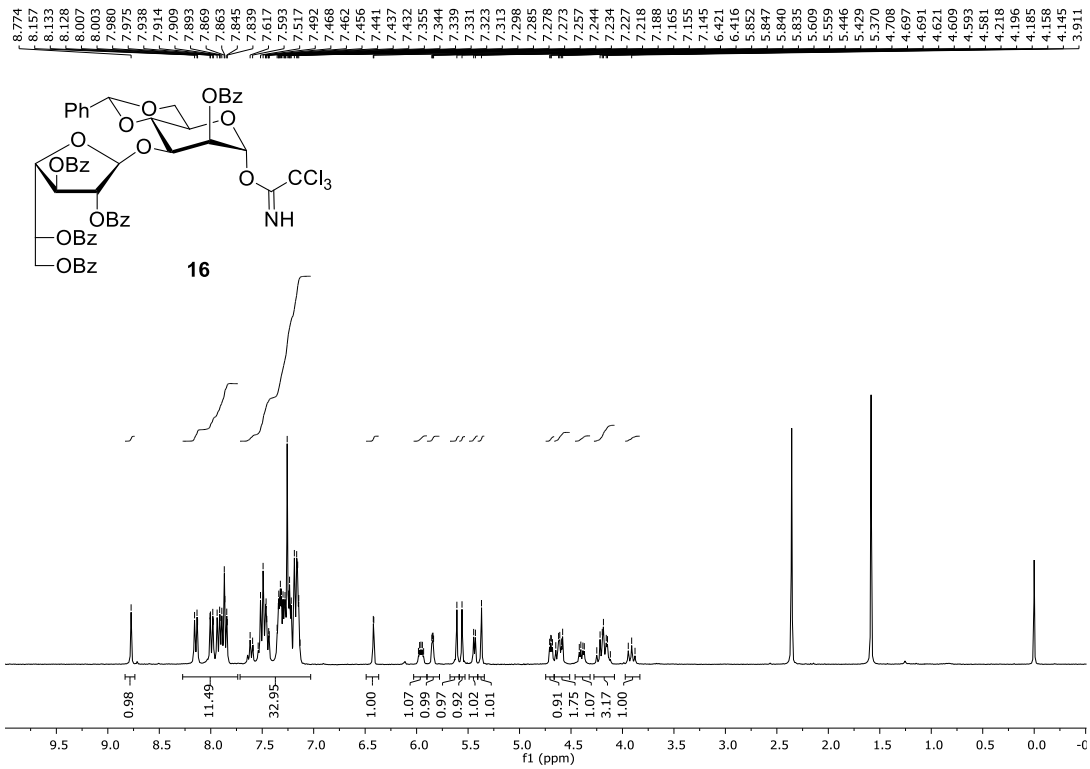


^{1}H-^{13}C decoupled HSQC NMR (300 MHz, $CDCl_3$)

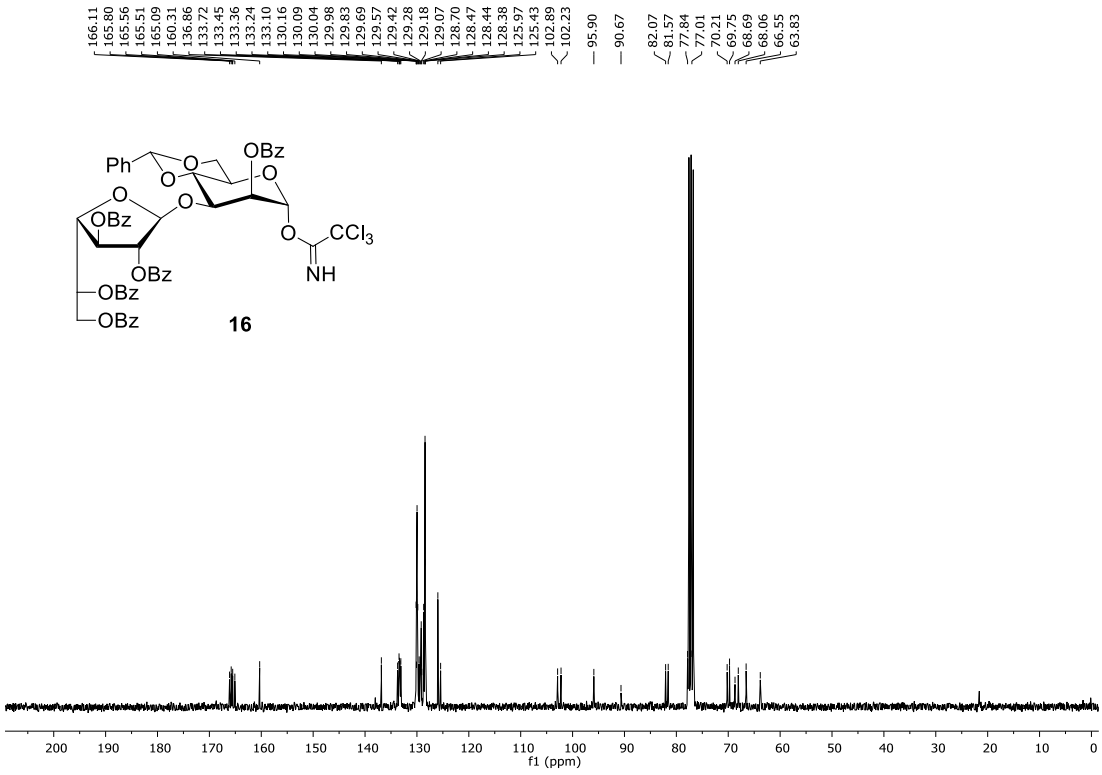


O-(2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl) trichloroacetimidate (16)

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



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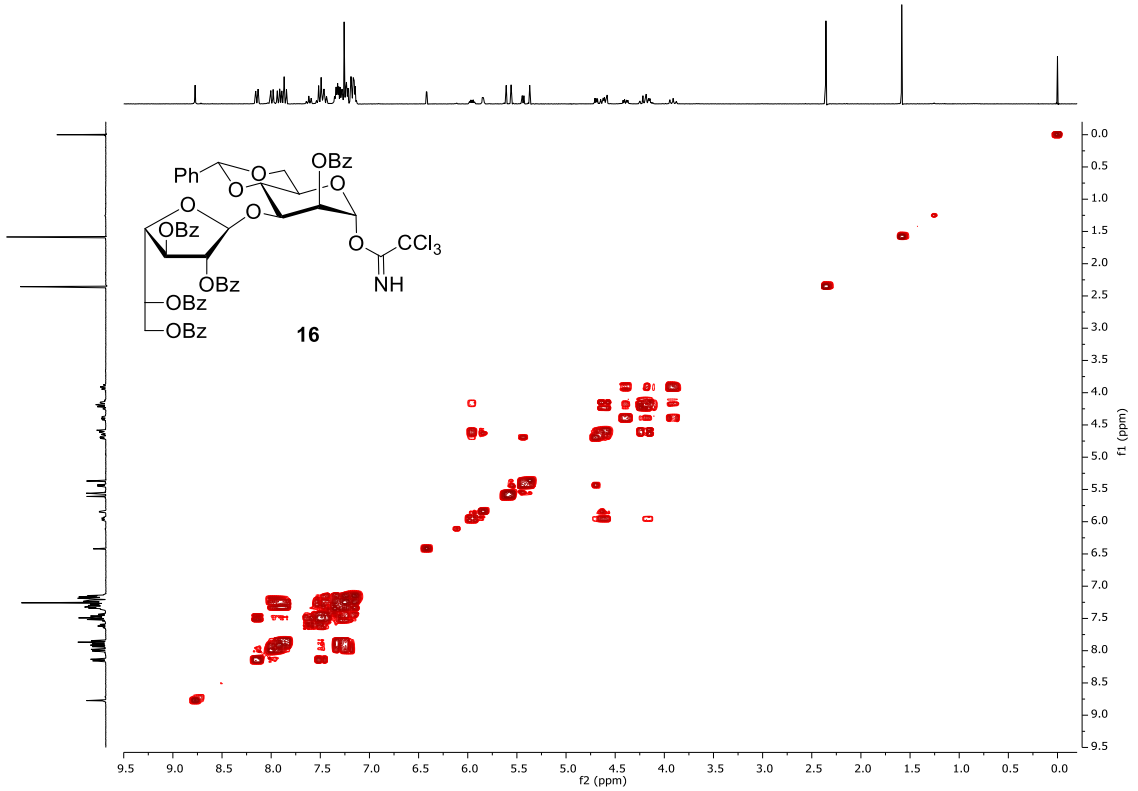

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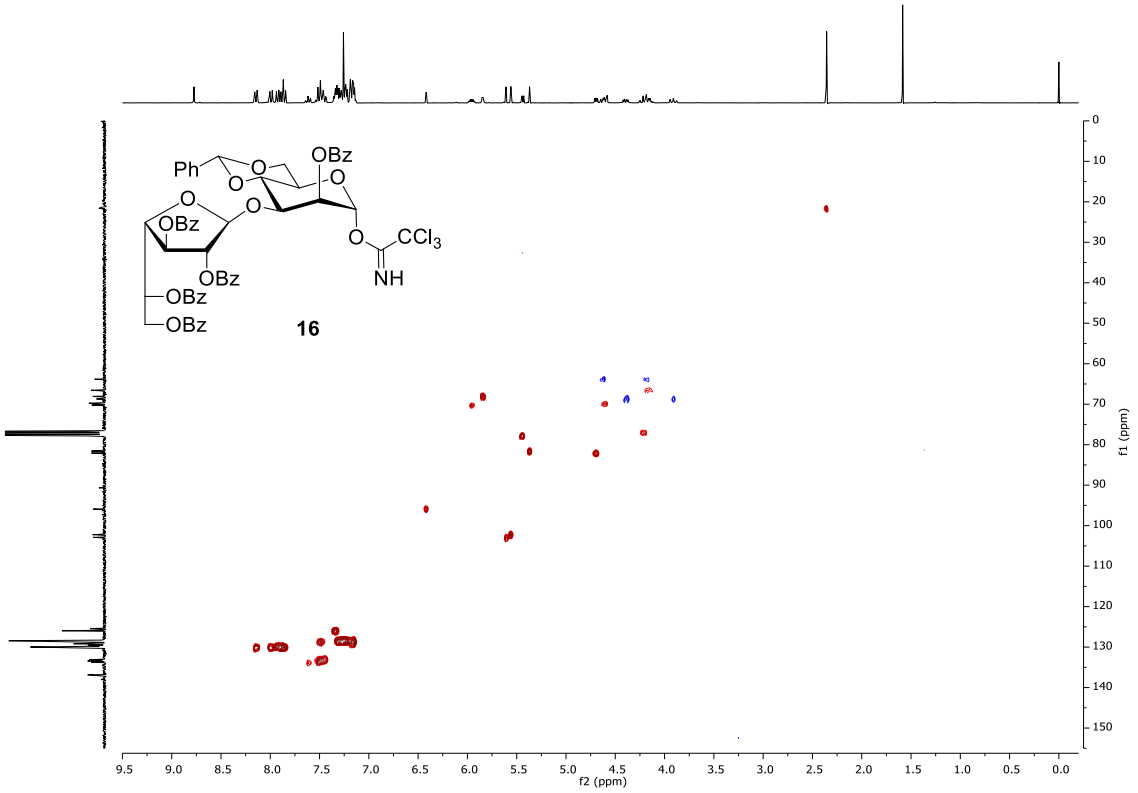
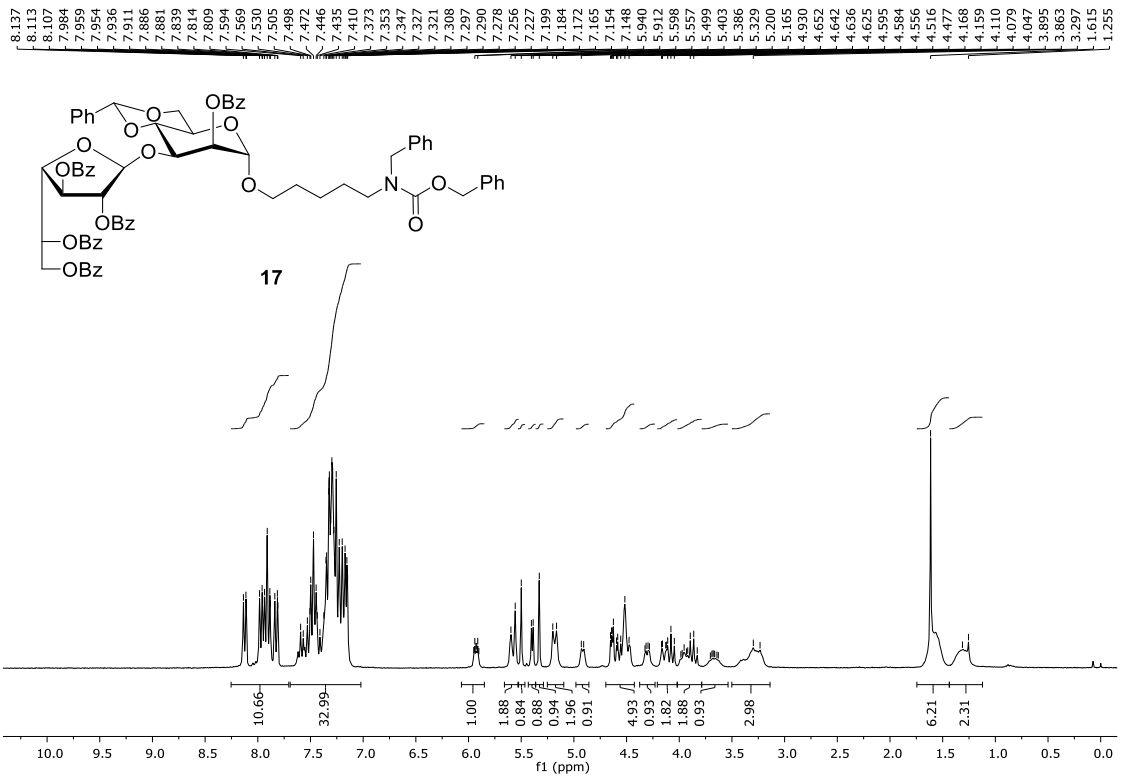
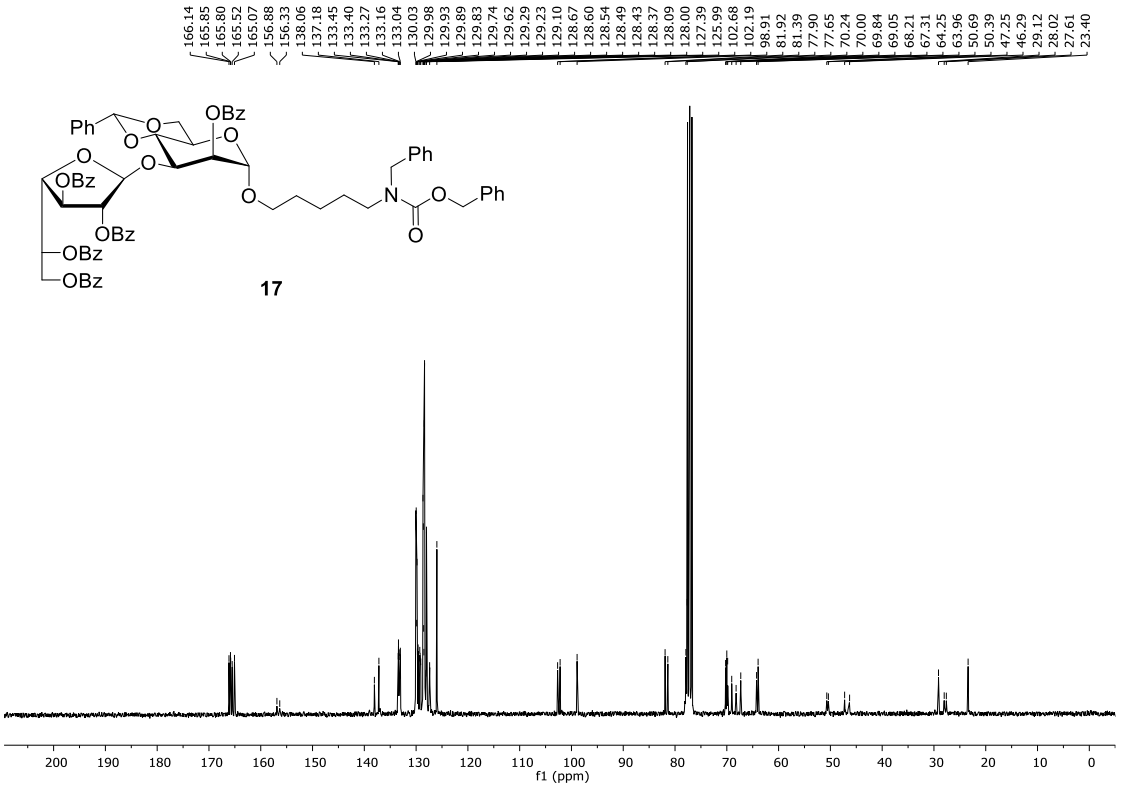


_N_-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,5,6-tetra-_O_-benzoyl-β-D-galactafuranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranoside (17)

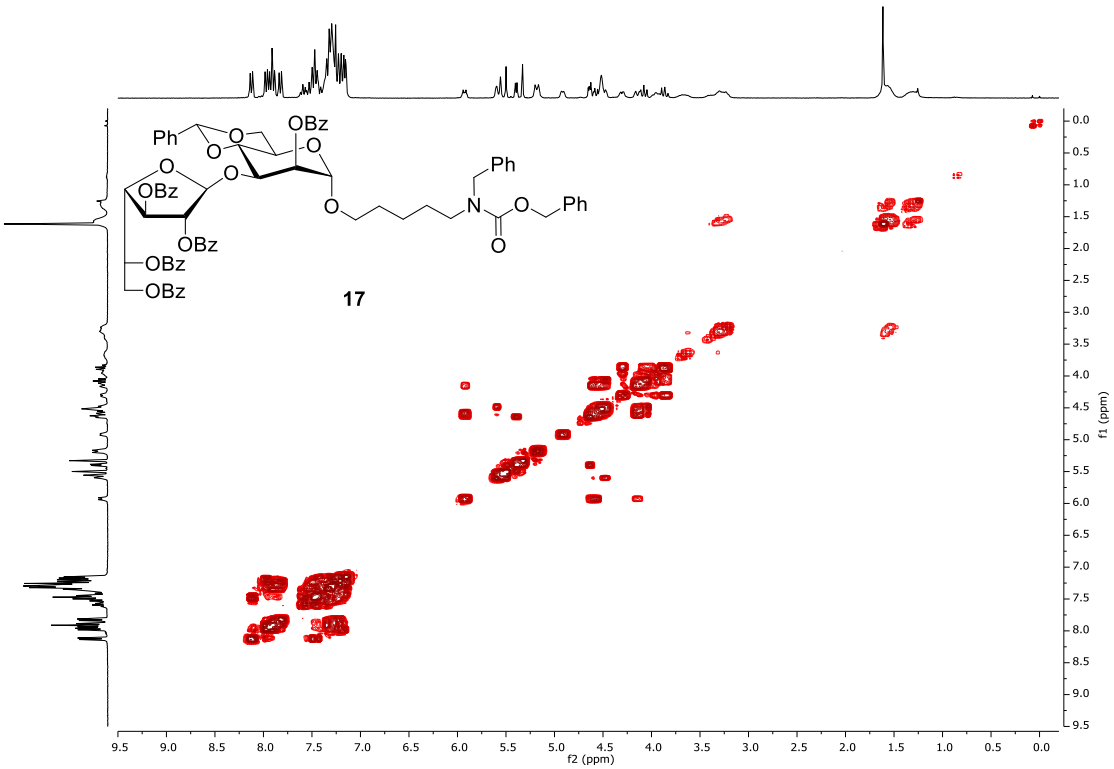
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$)



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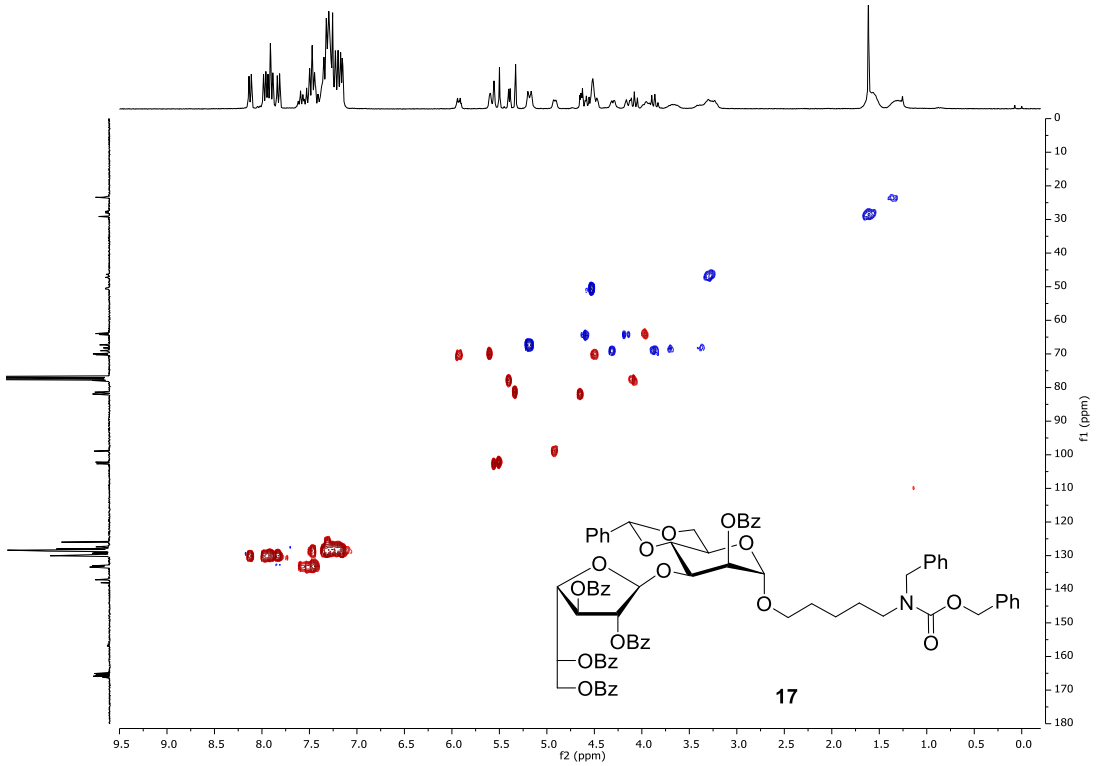
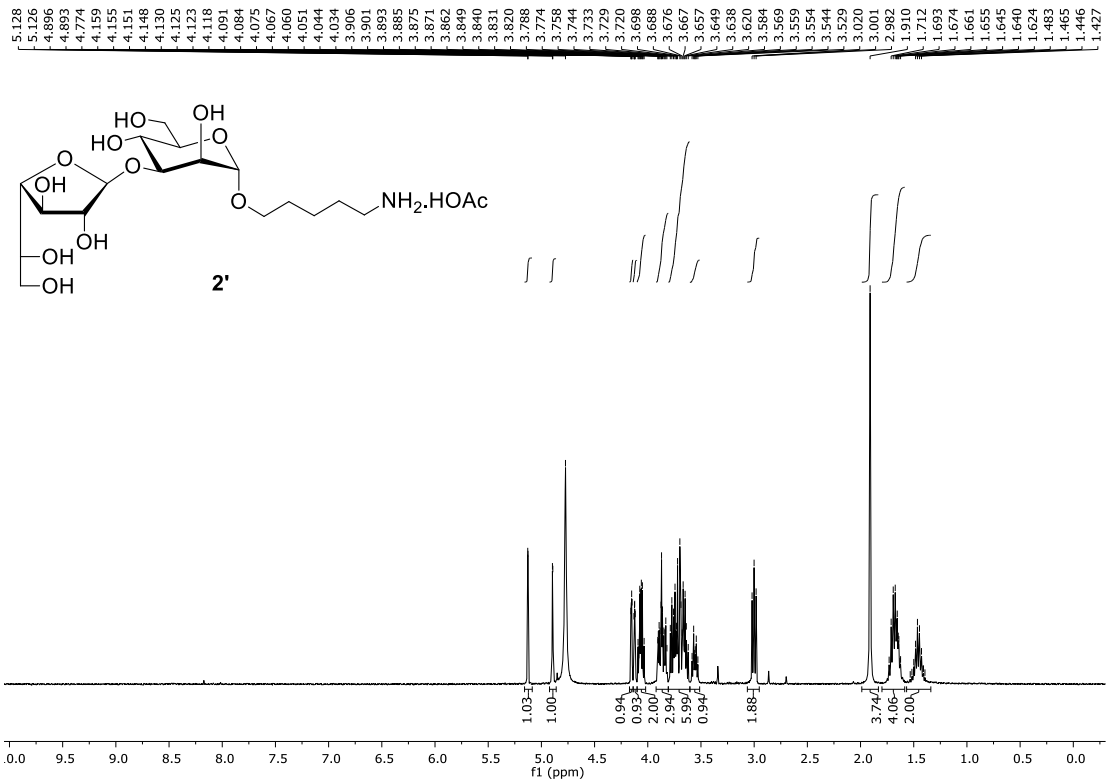


5-Aminopentyl β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside, acetate (2')

^{1}H NMR (400 MHz, D_2O)



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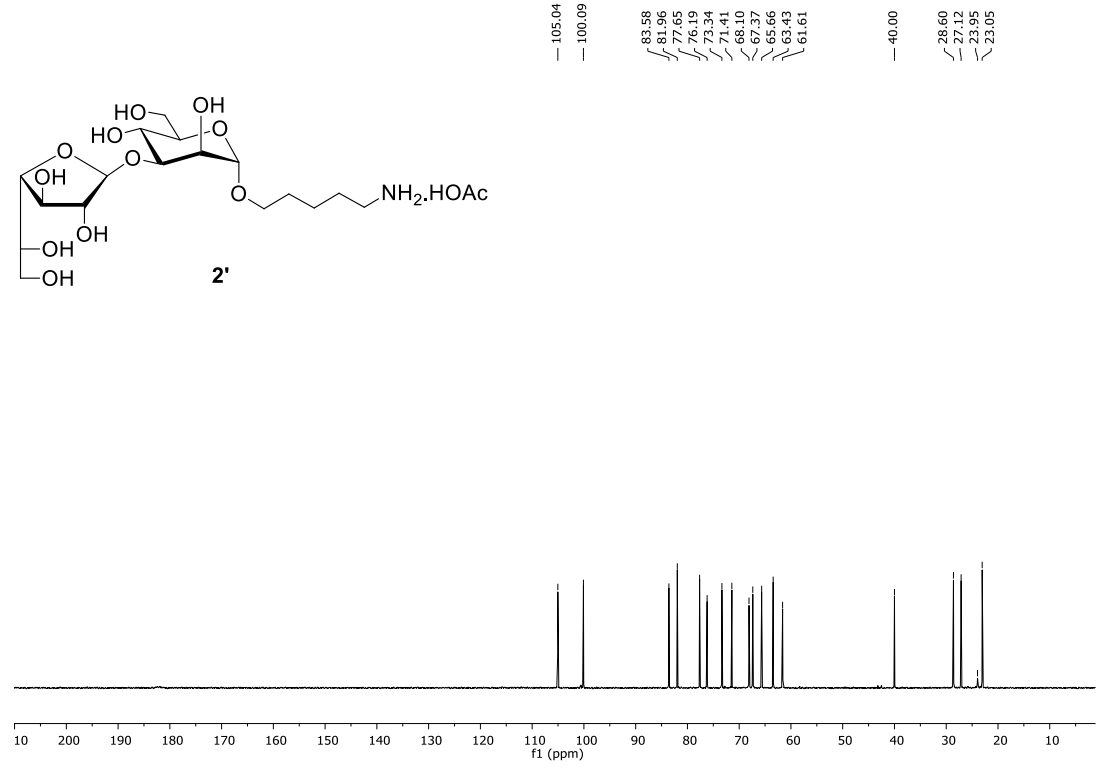

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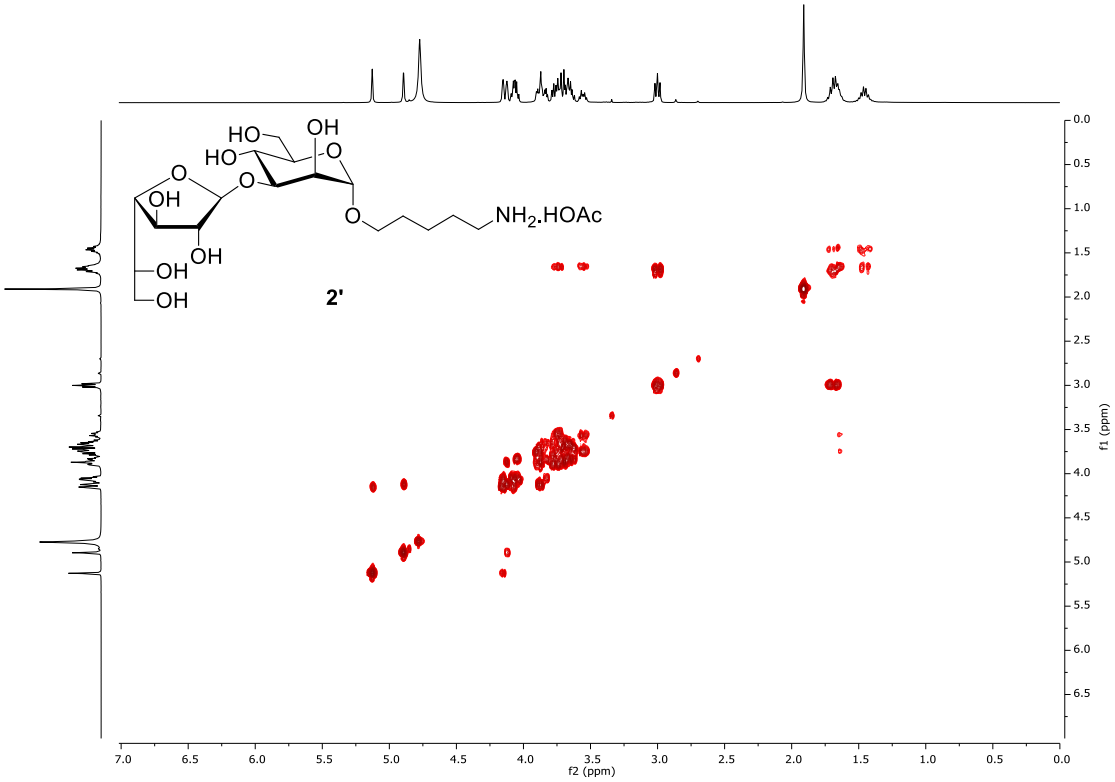

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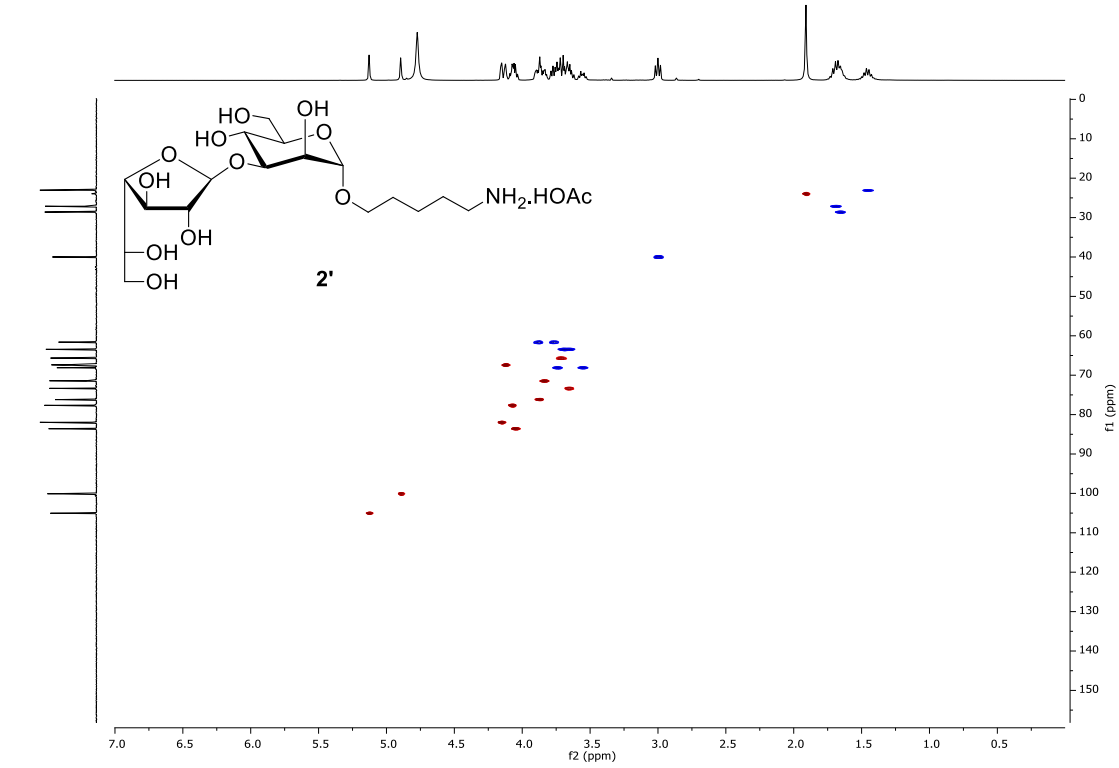
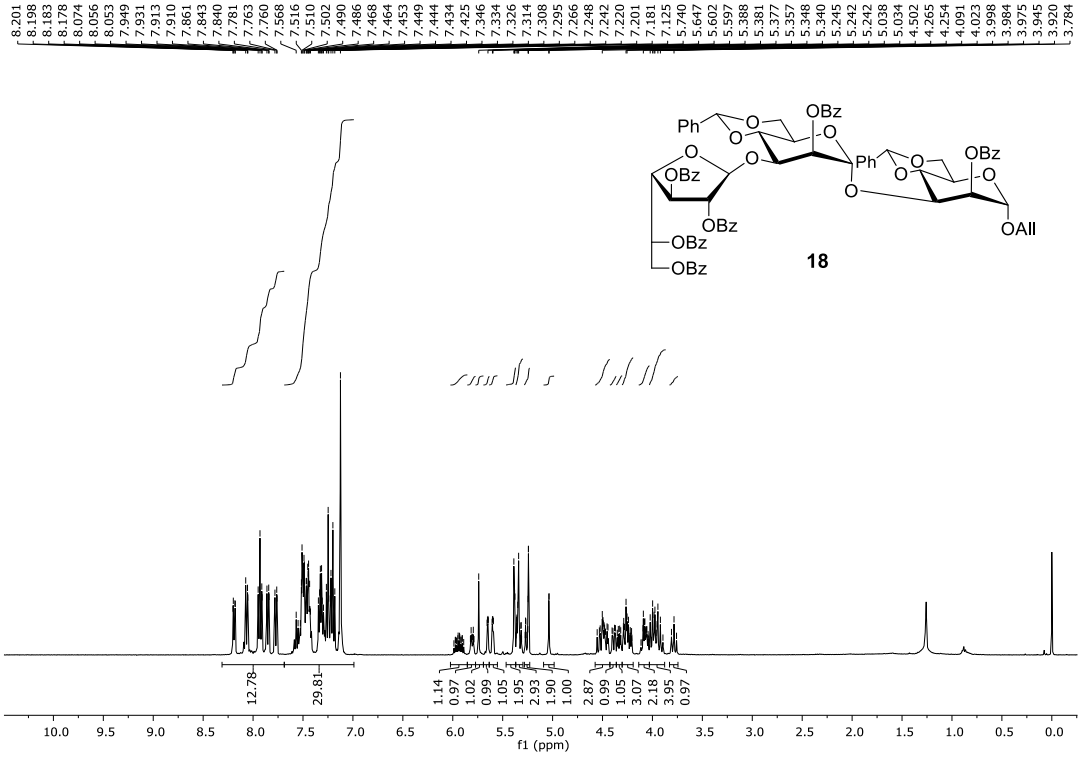


Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (18)

^{1}H NMR (400 MHz, $CDCl_3$)



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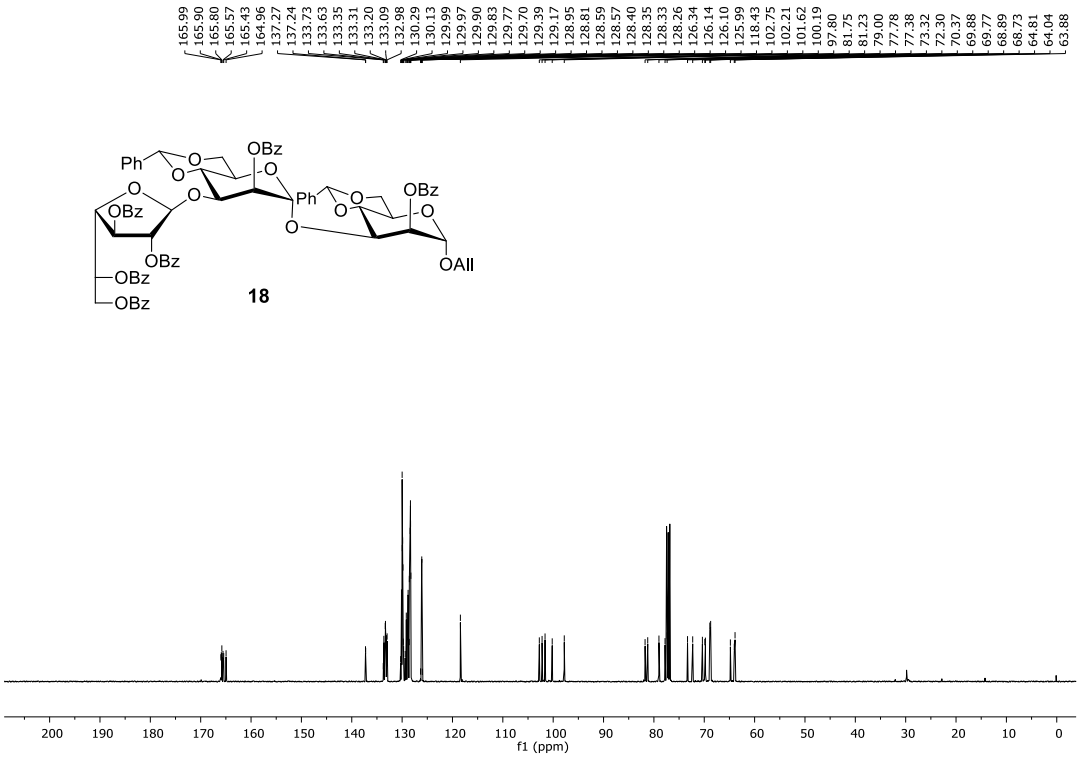

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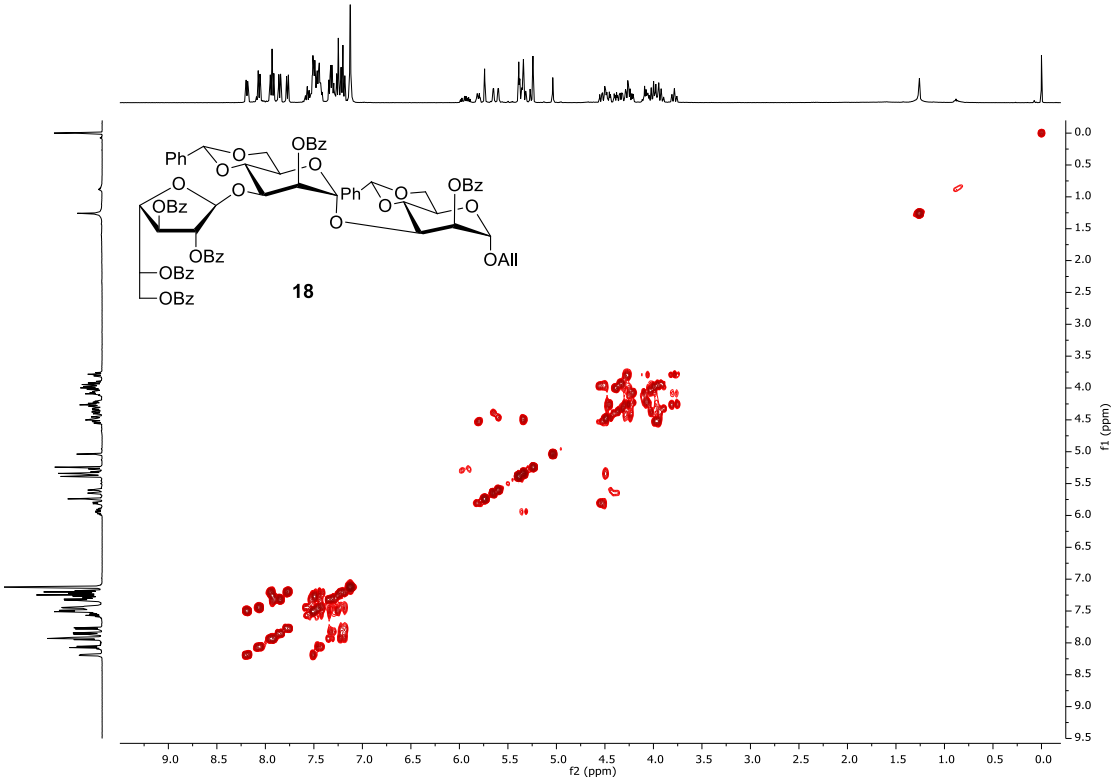

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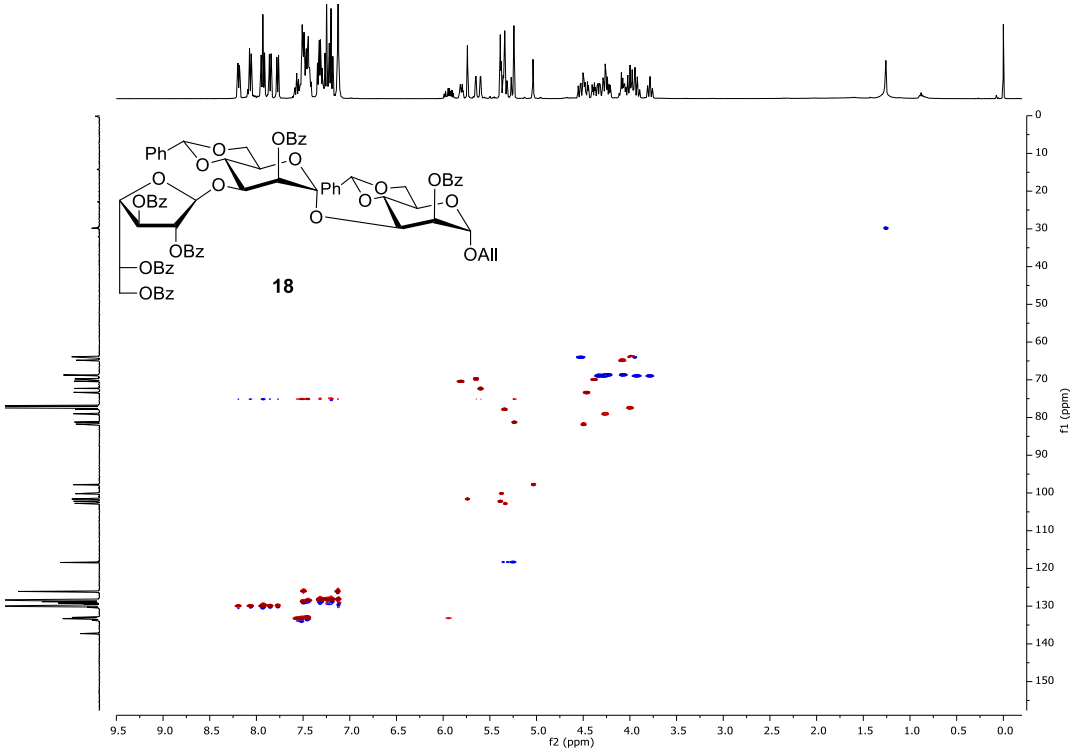
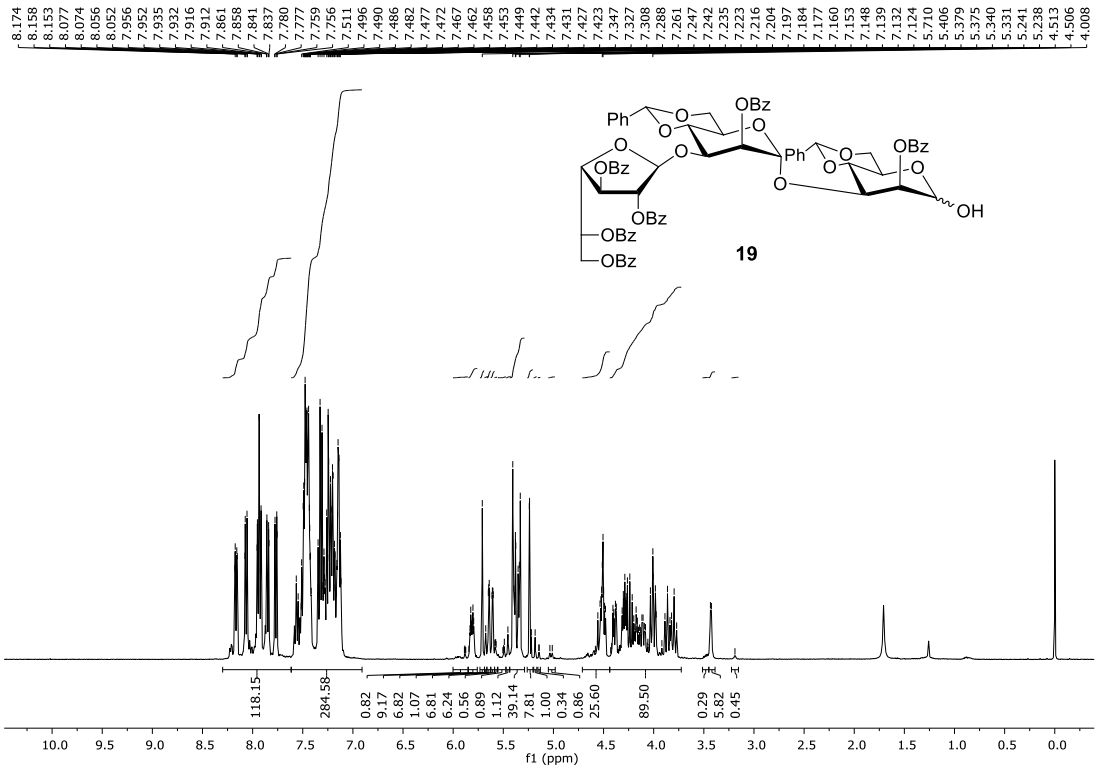
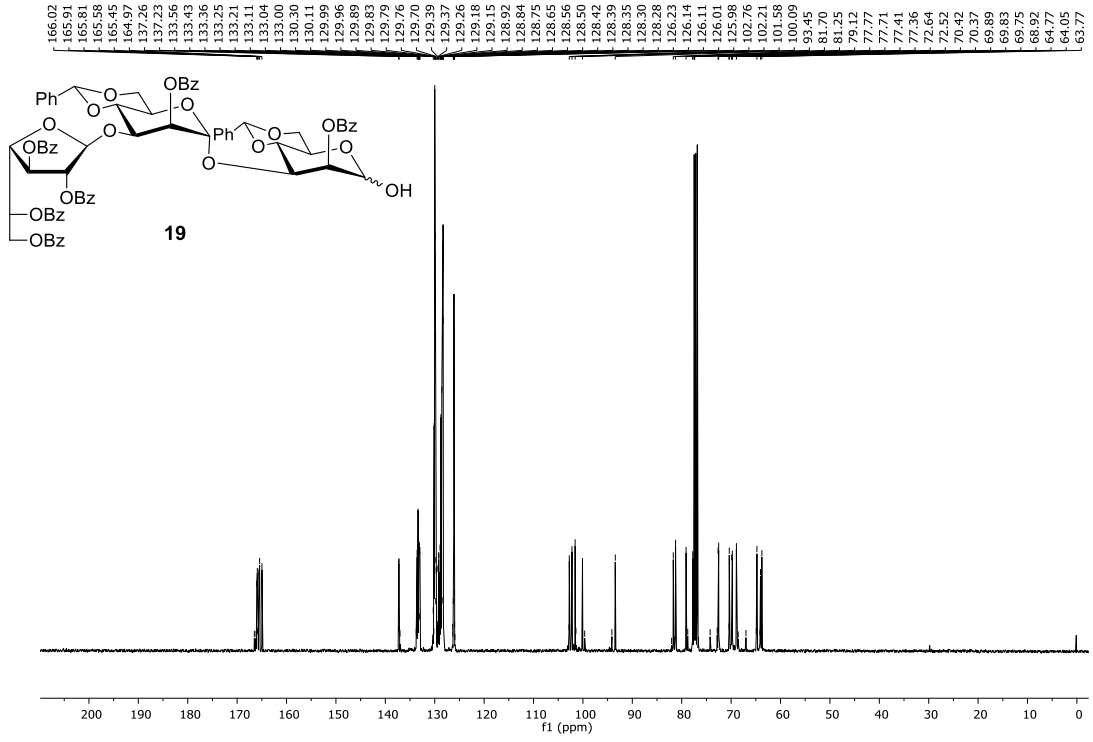


2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (19)

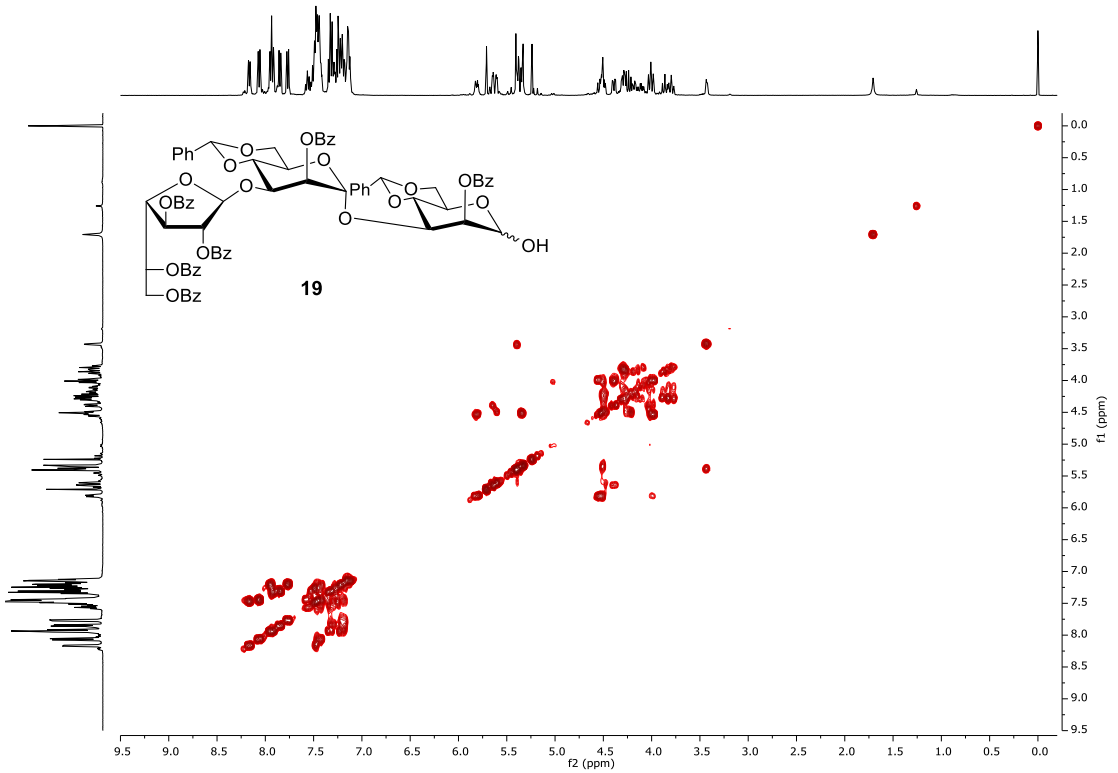
^{1}H NMR (400 MHz, $CDCl_3$)



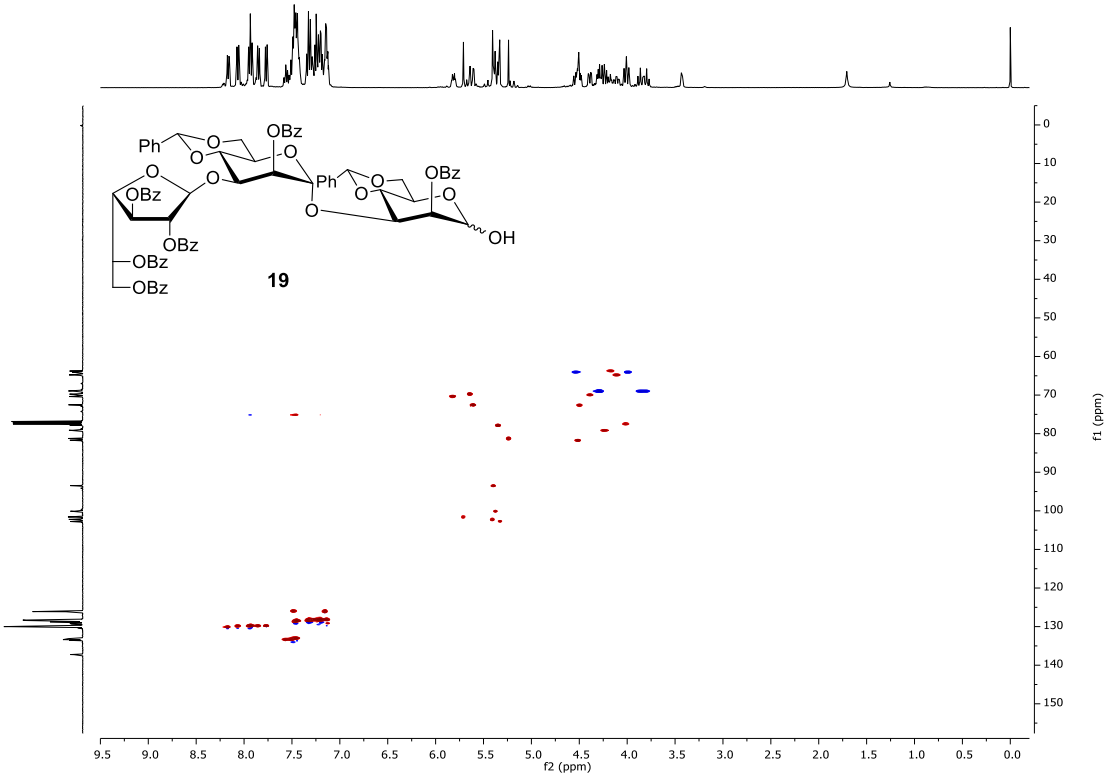
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)

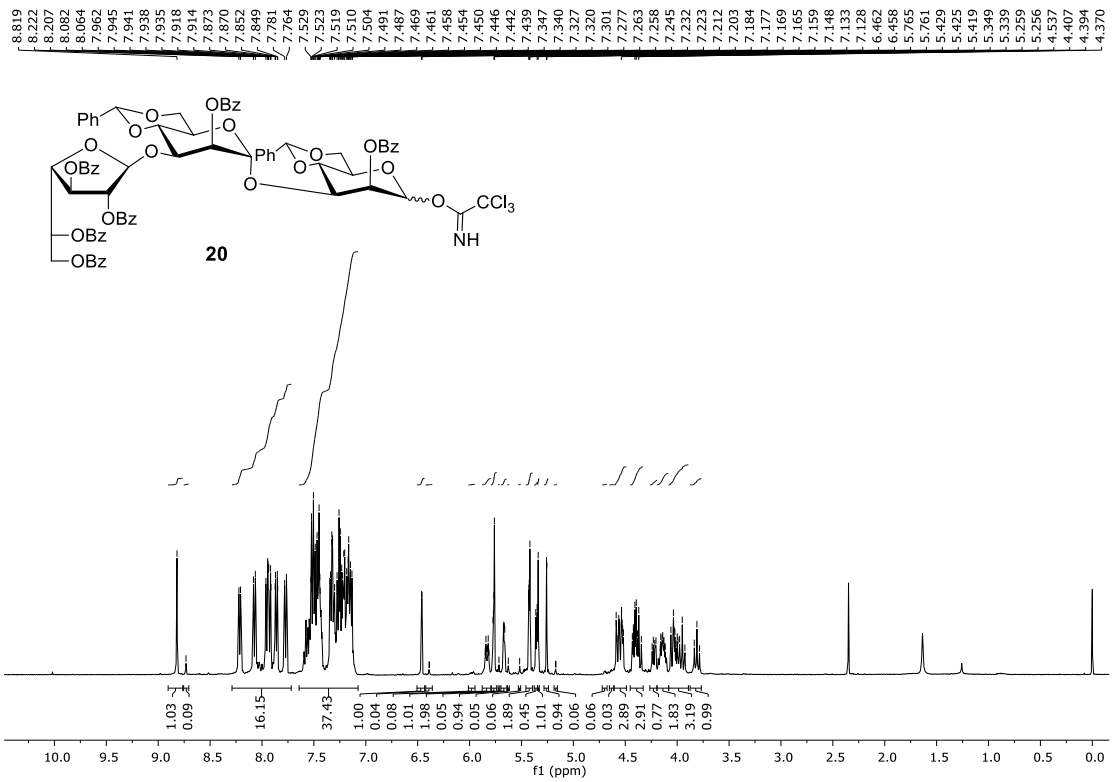


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

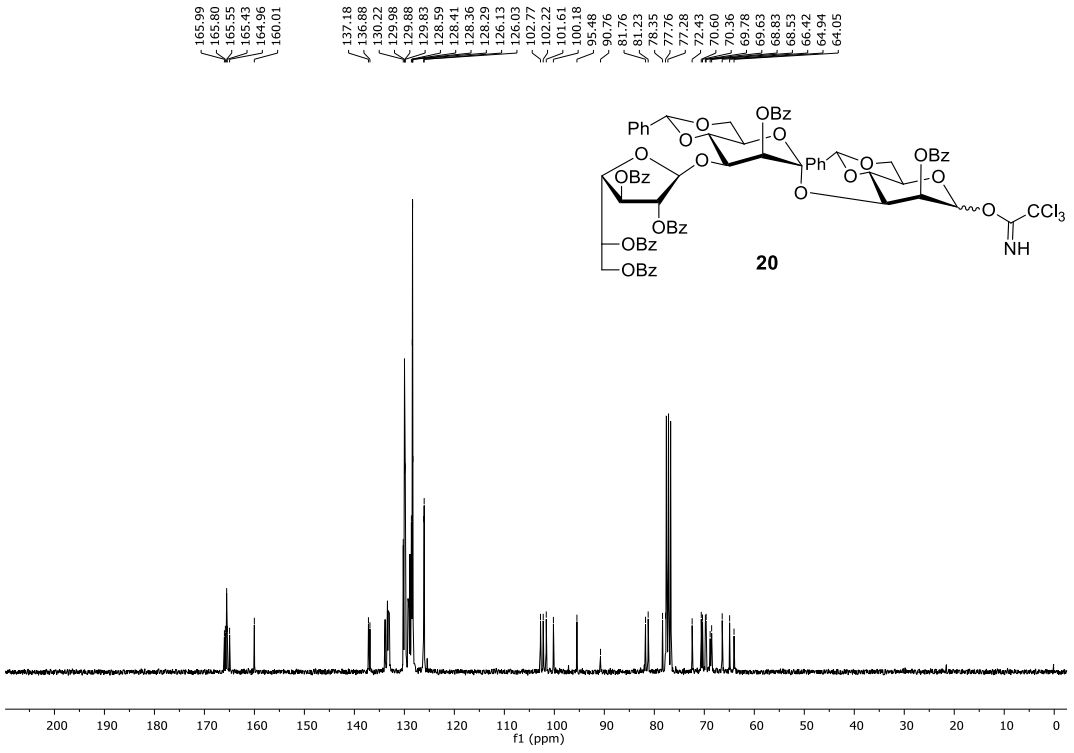


***O*-(2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranosyl) trichloroacetimidate (20)**

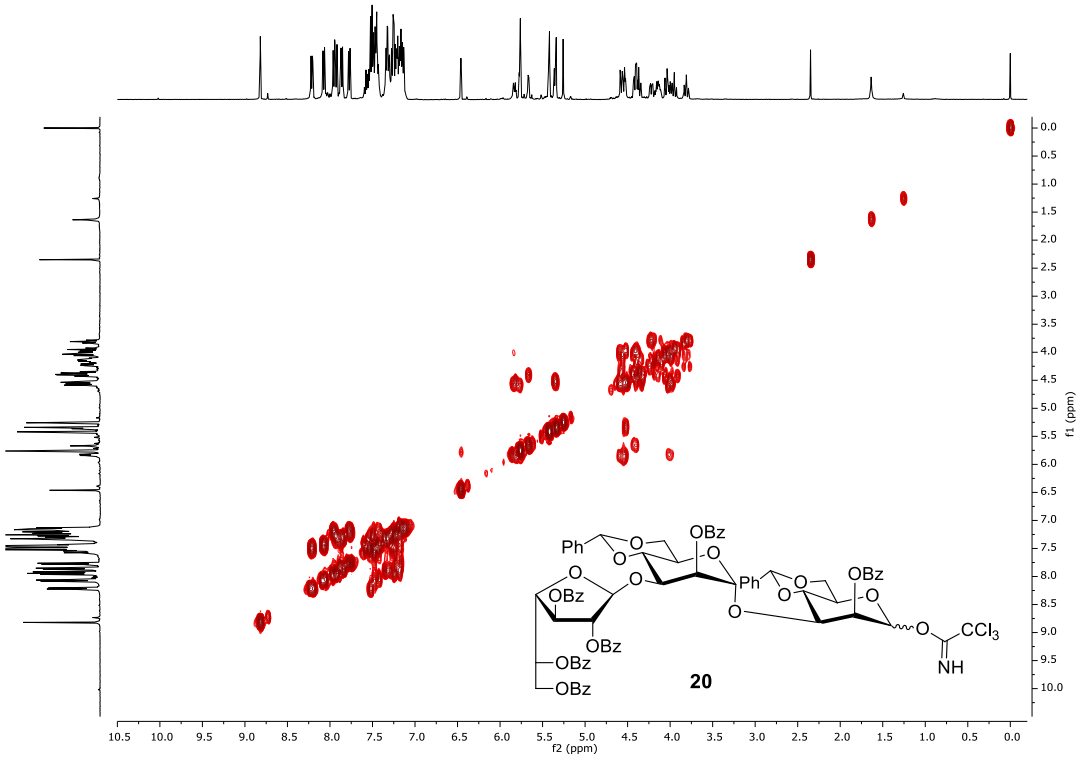
^{1}H NMR (400 MHz, $CDCl_3$)



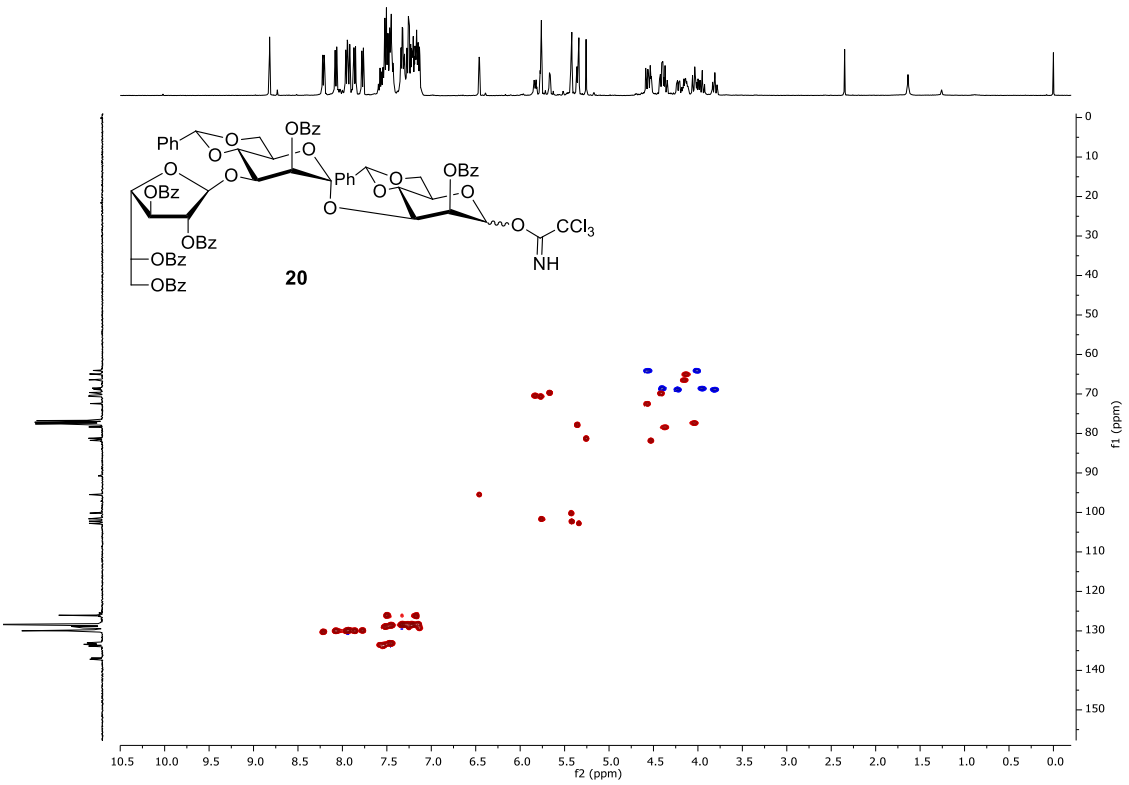
^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$)

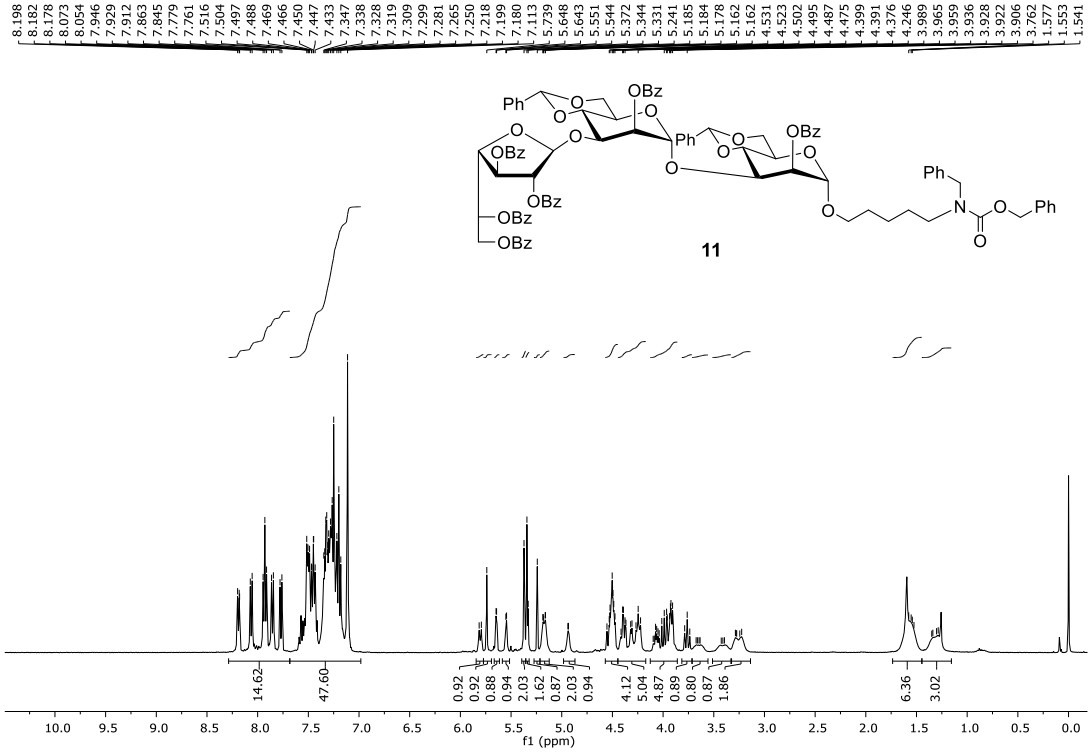


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

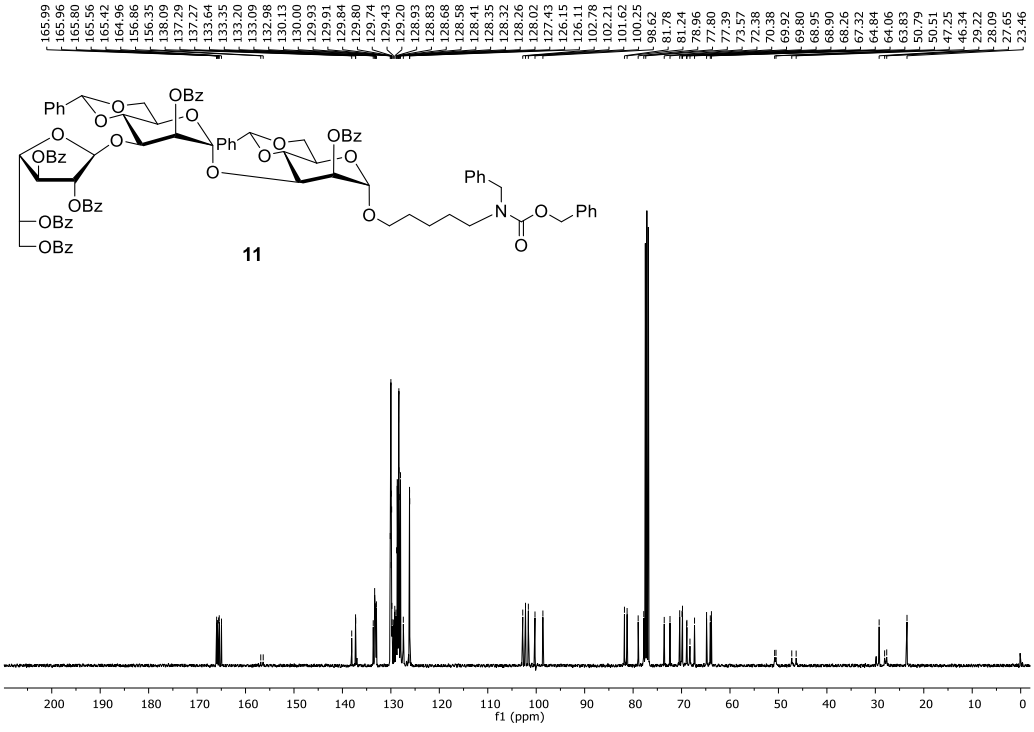


***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (11)**

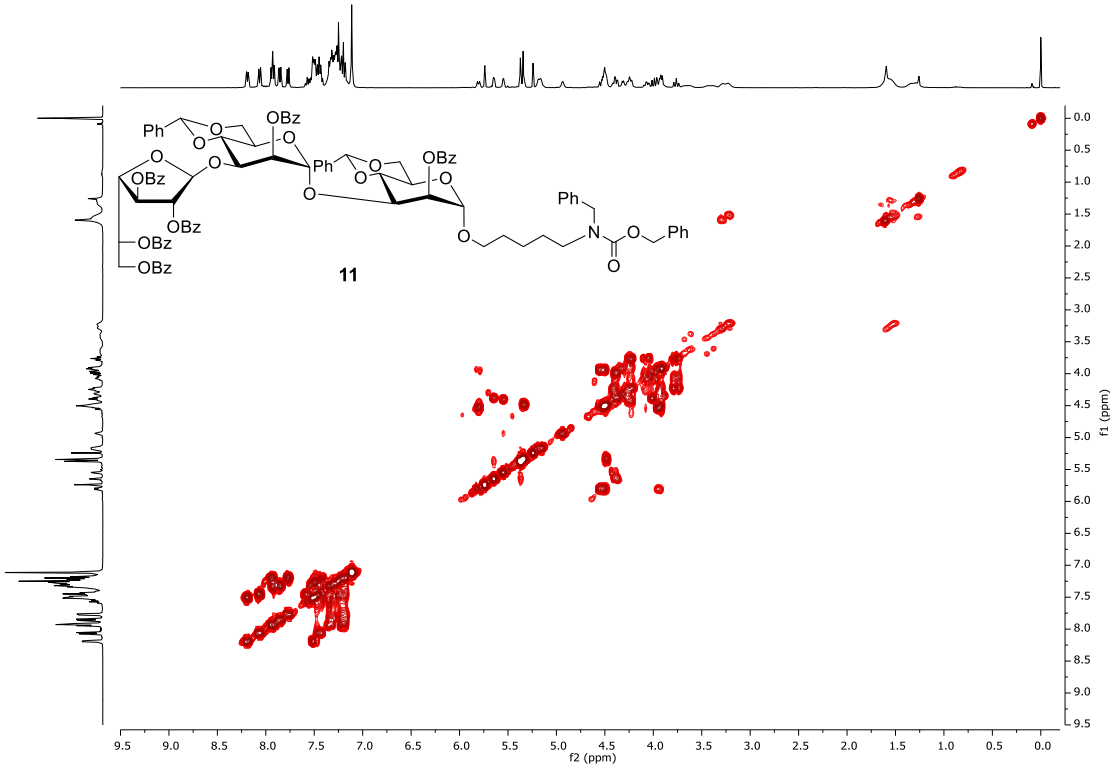
^{1}H NMR (400 MHz, $CDCl_3$)



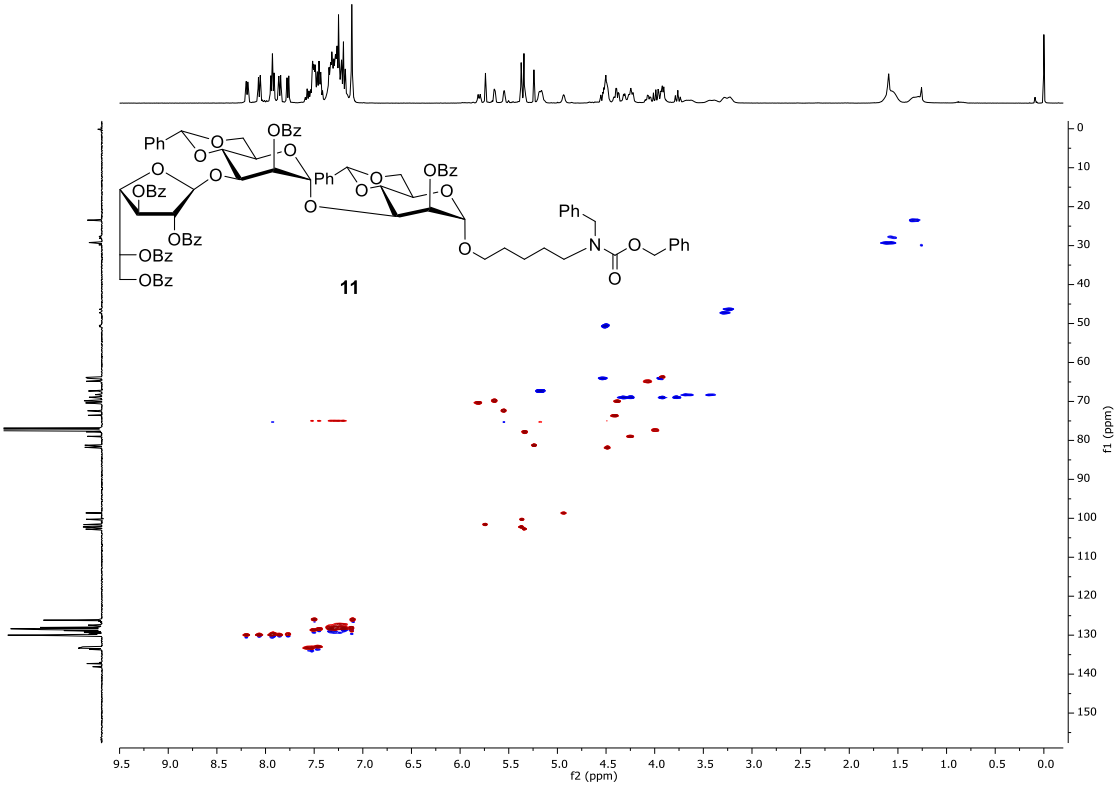
^{13}C NMR (101 MHz, $CDCl_3$)



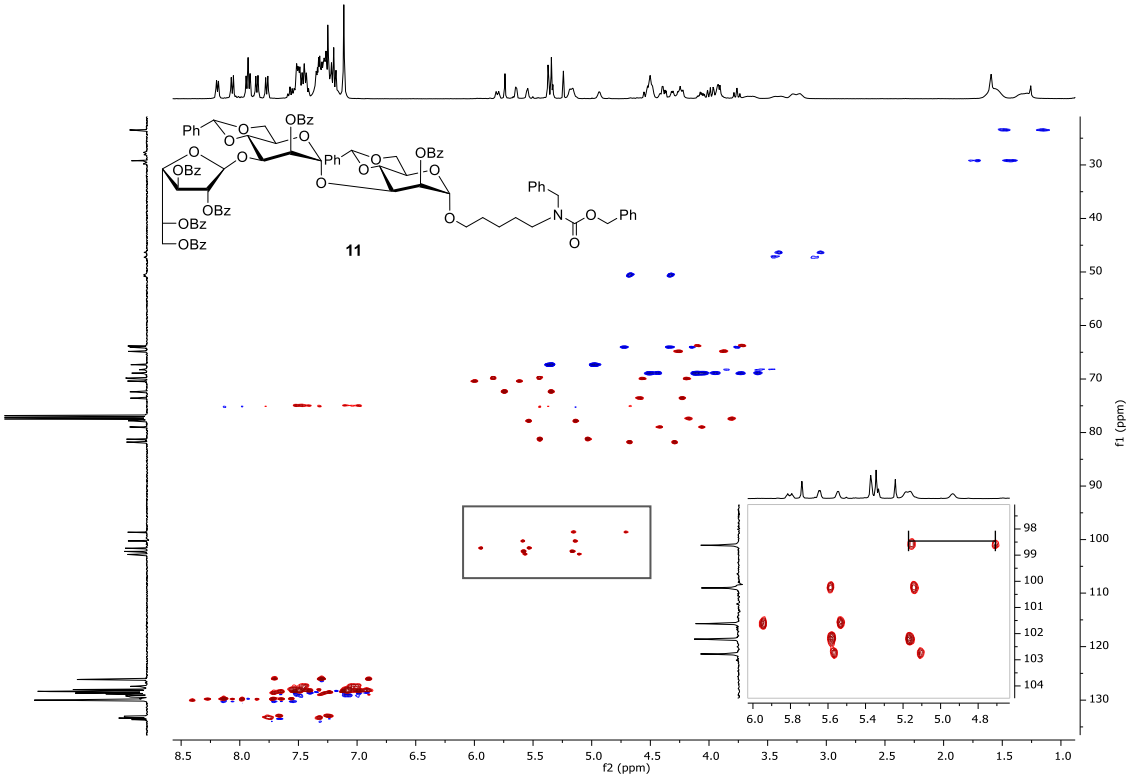
^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)



^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

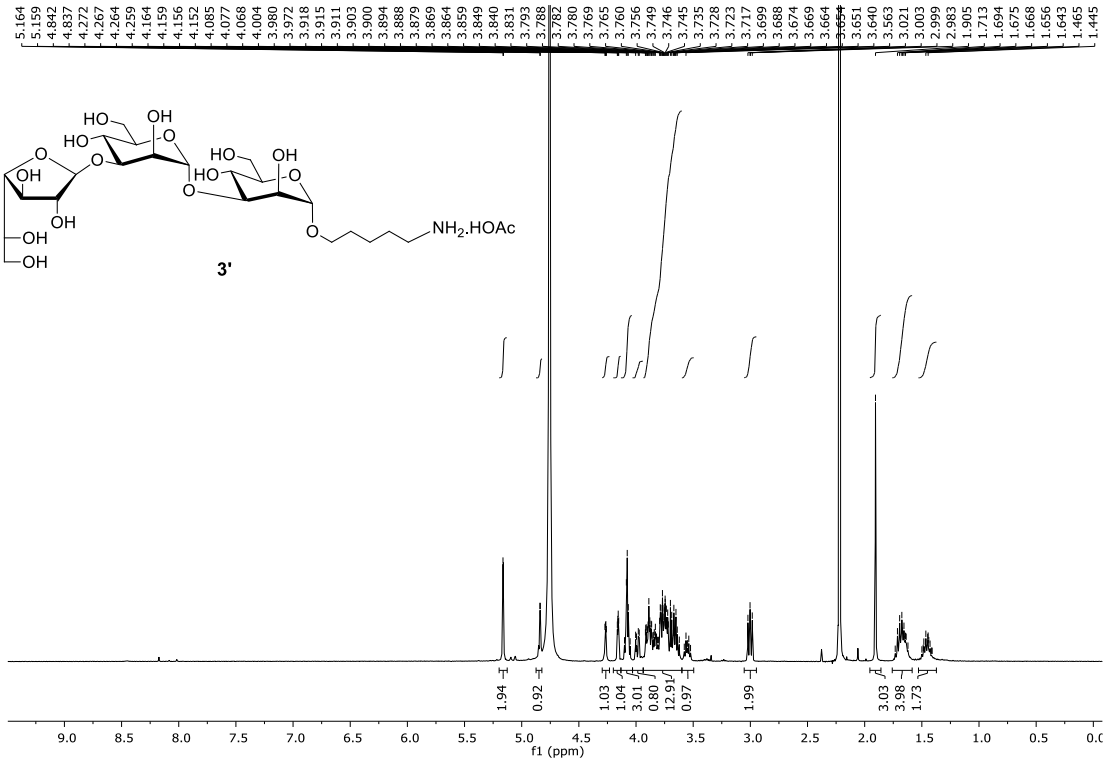


^{1}H-^{13}C coupled HSQC NMR (400 MHz, $CDCl_3$)

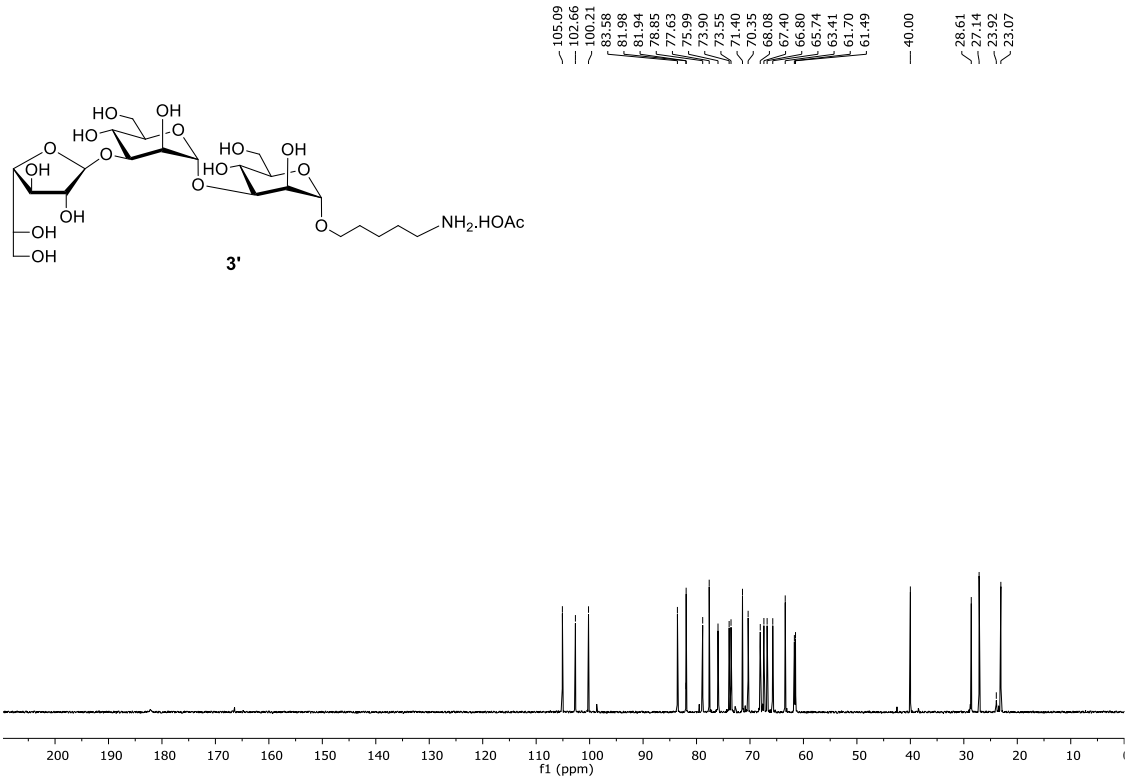


5-Aminopentyl β-D-galactofuranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranoside, acetate (3')

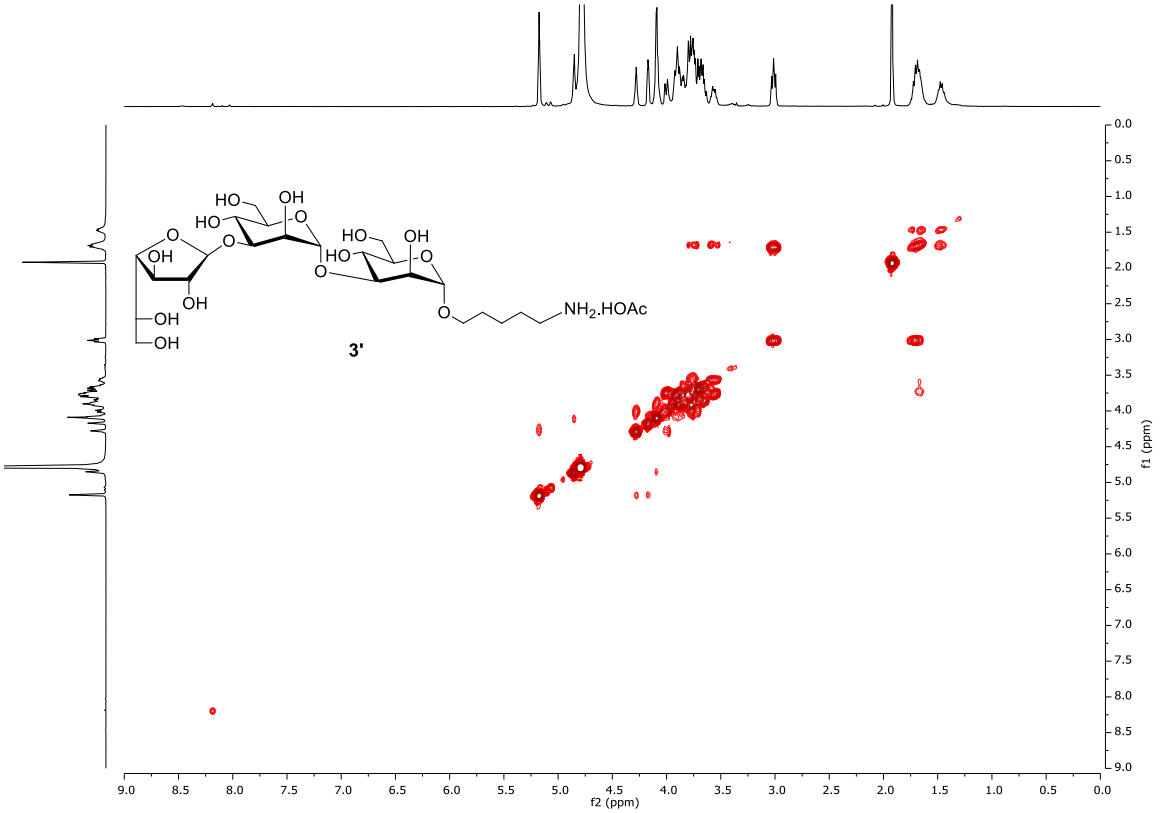
^{1}H NMR (400 MHz, D_2O)



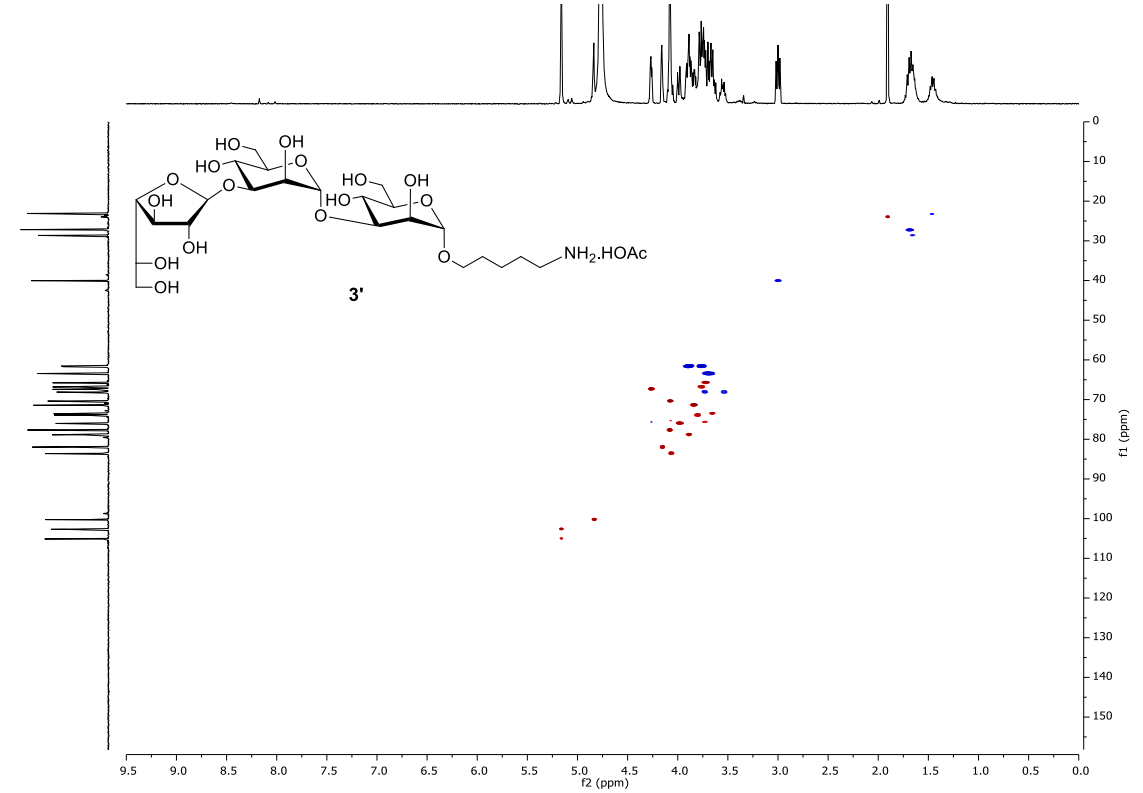
^{13}C NMR (101 MHz, D_2O)



^{1}H-^{1}H COSY NMR (400 MHz, D_2O)

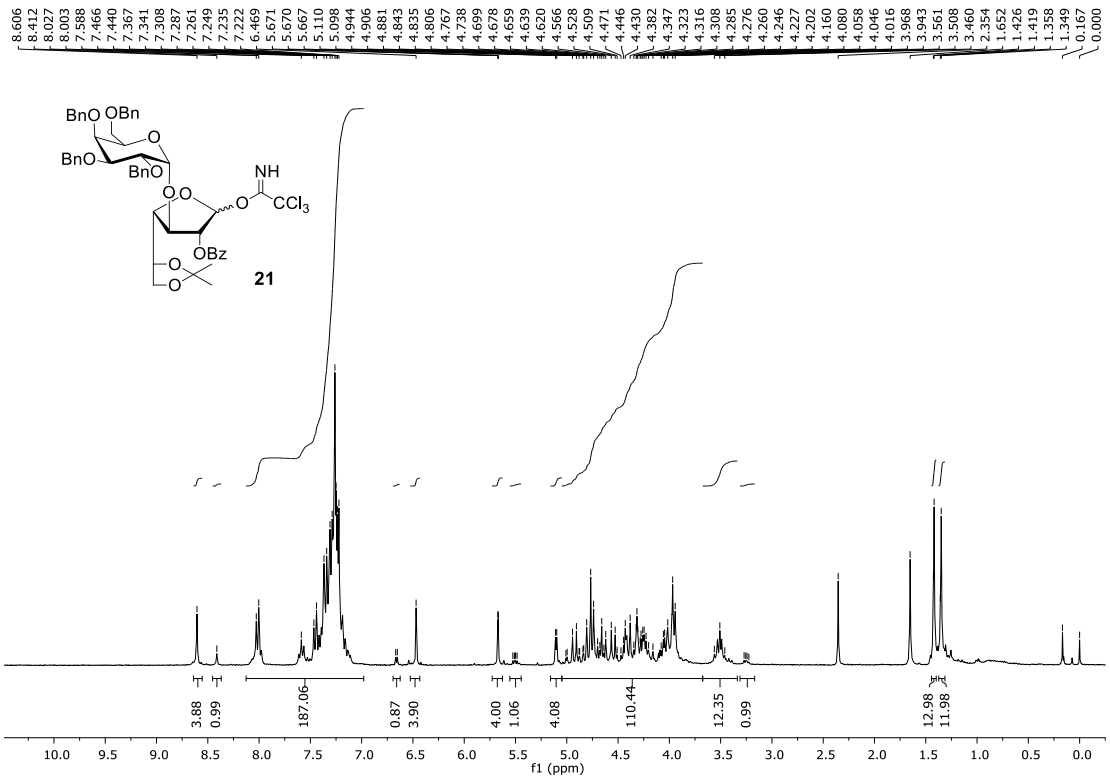


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, D_2O)

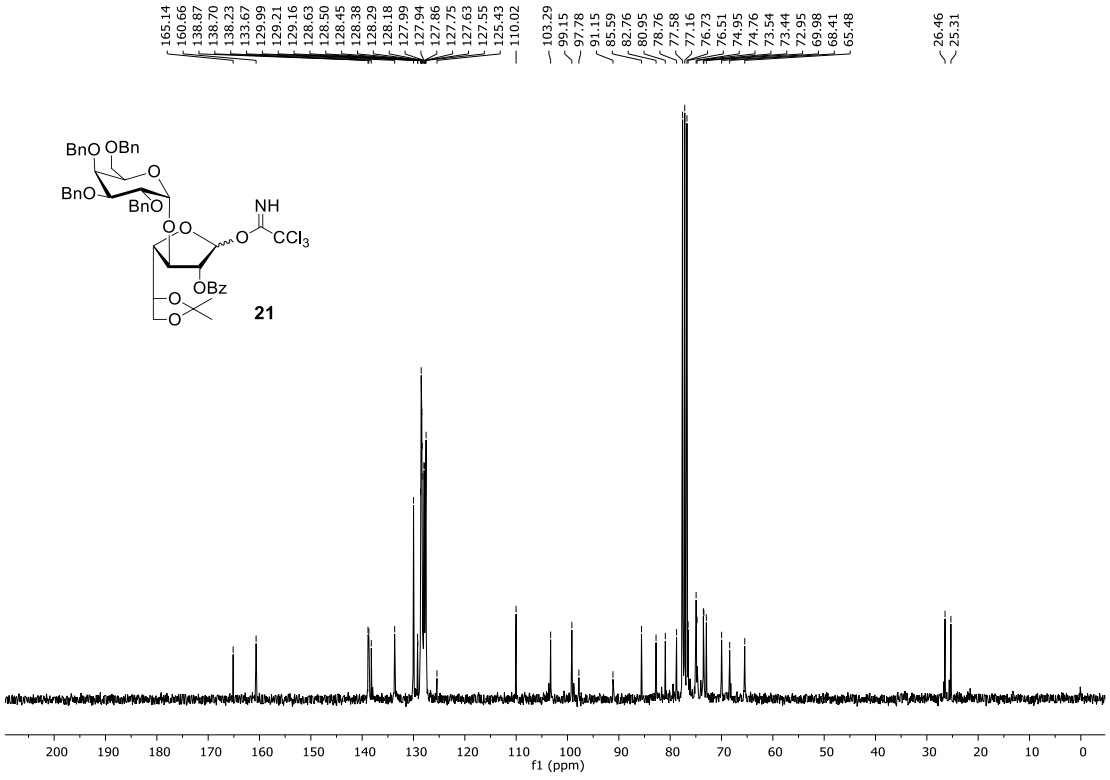


O-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl) trichloroacetimidate (21)

^{1}H NMR (300 MHz, $CDCl_3$)

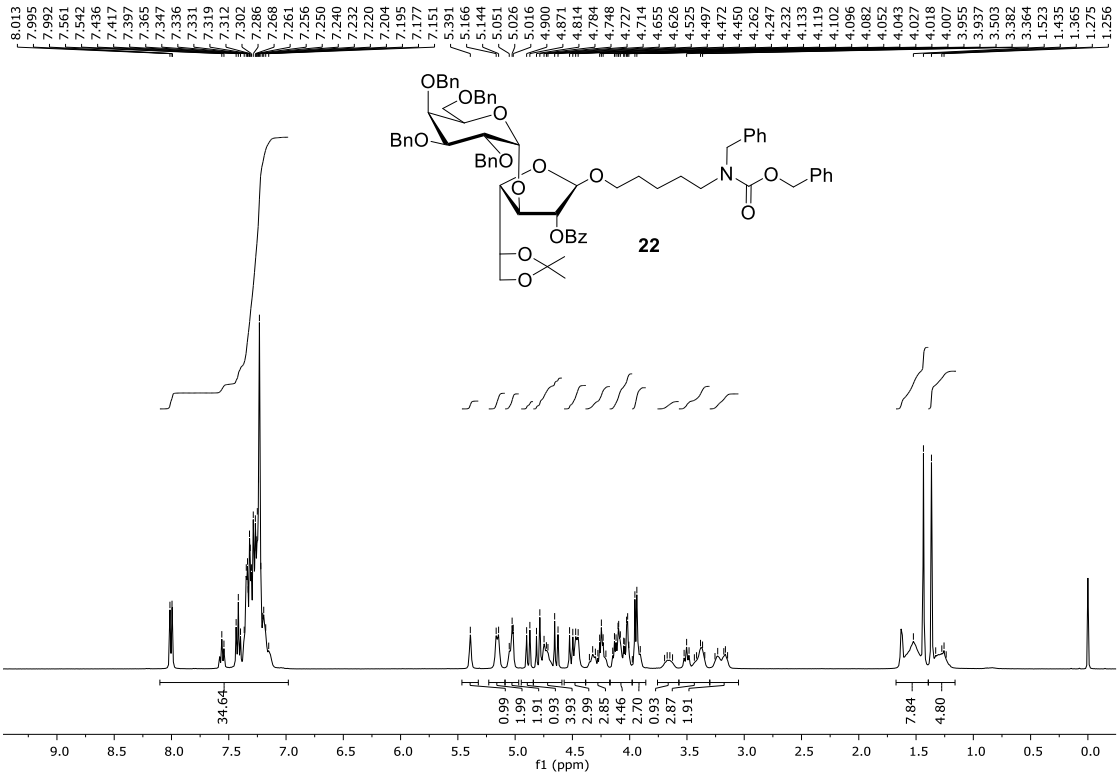


^{13}C NMR (75 MHz, $CDCl_3$)

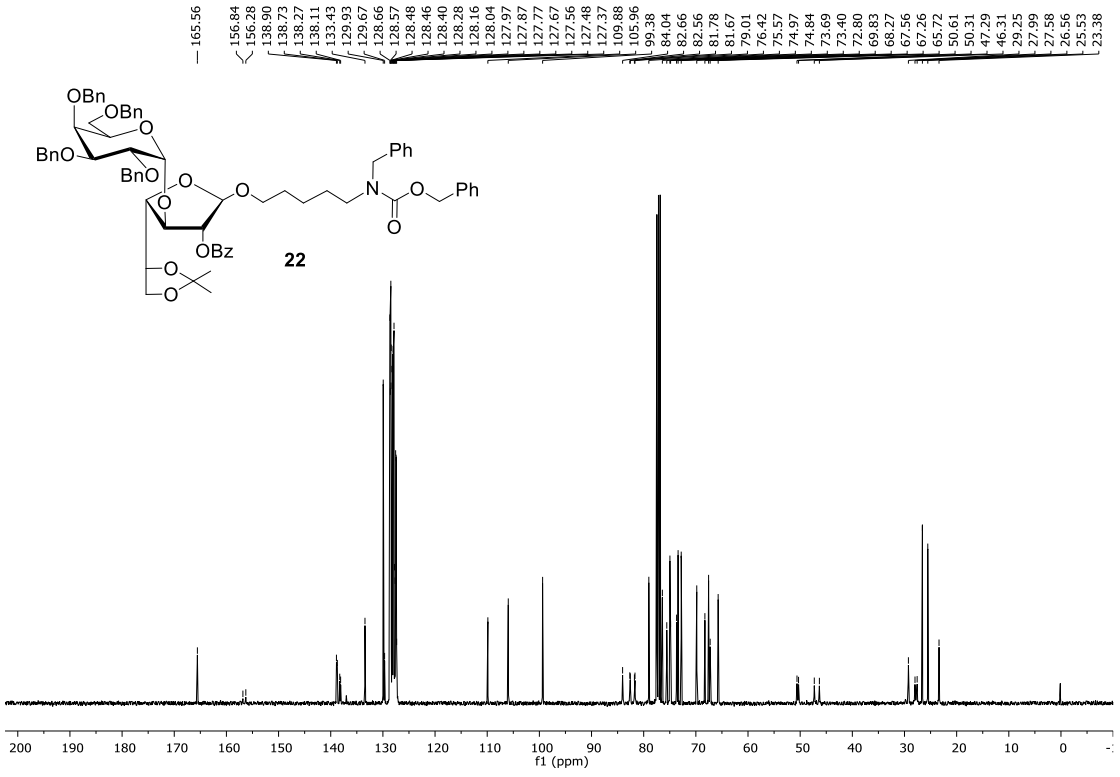


***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (22)**

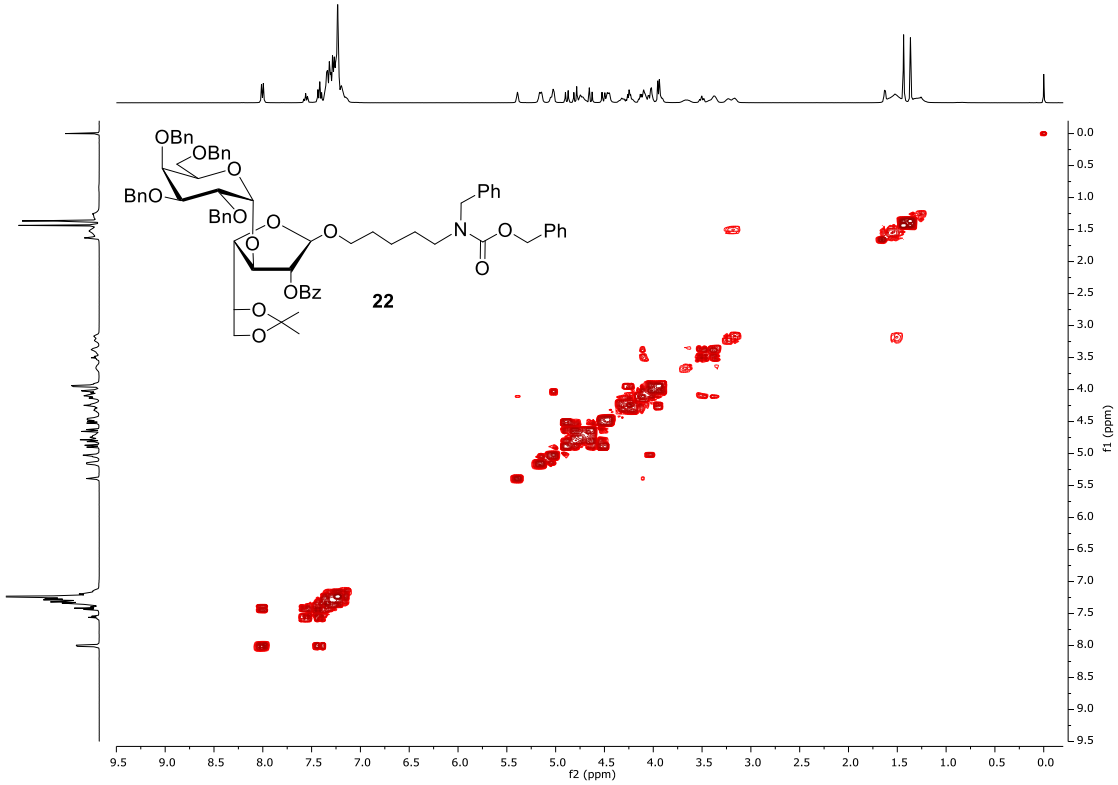
^{1}H NMR (400 MHz, $CDCl_3$)



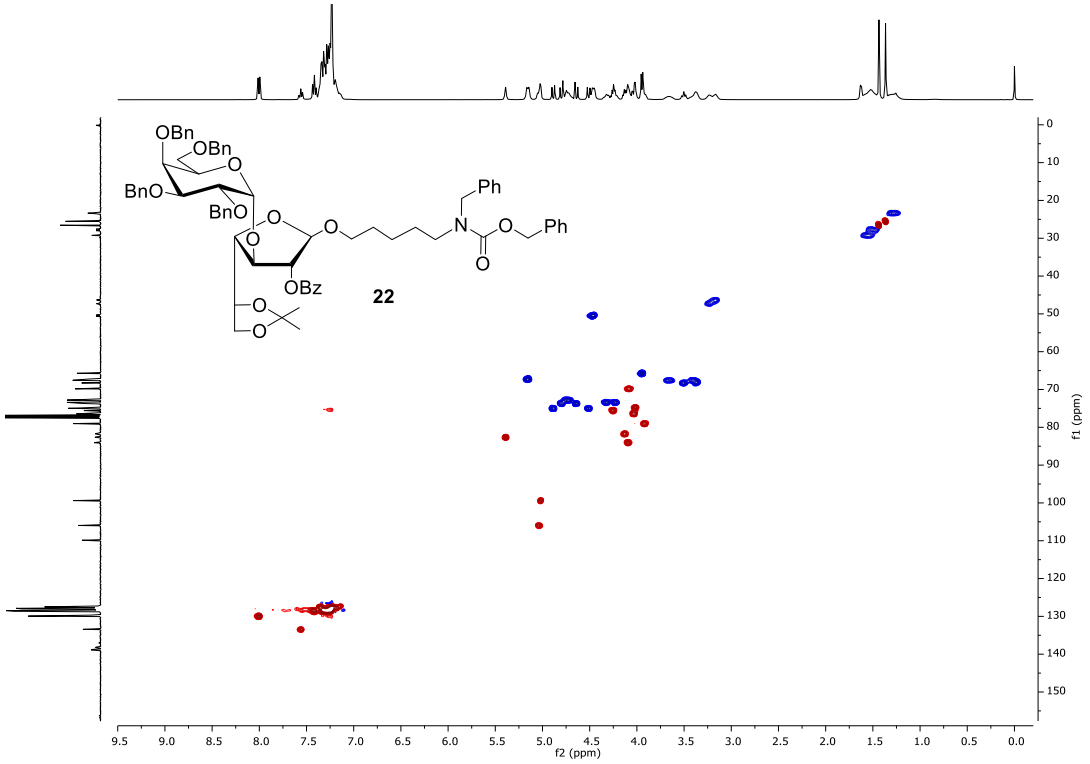
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)

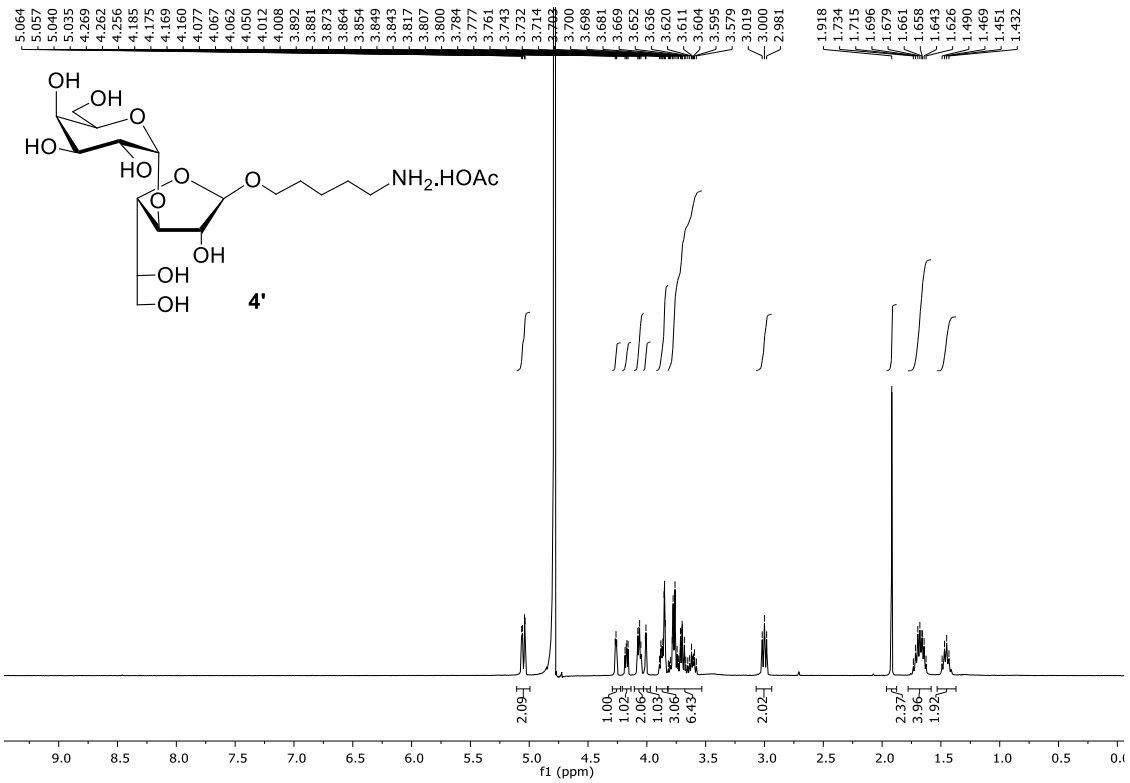


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

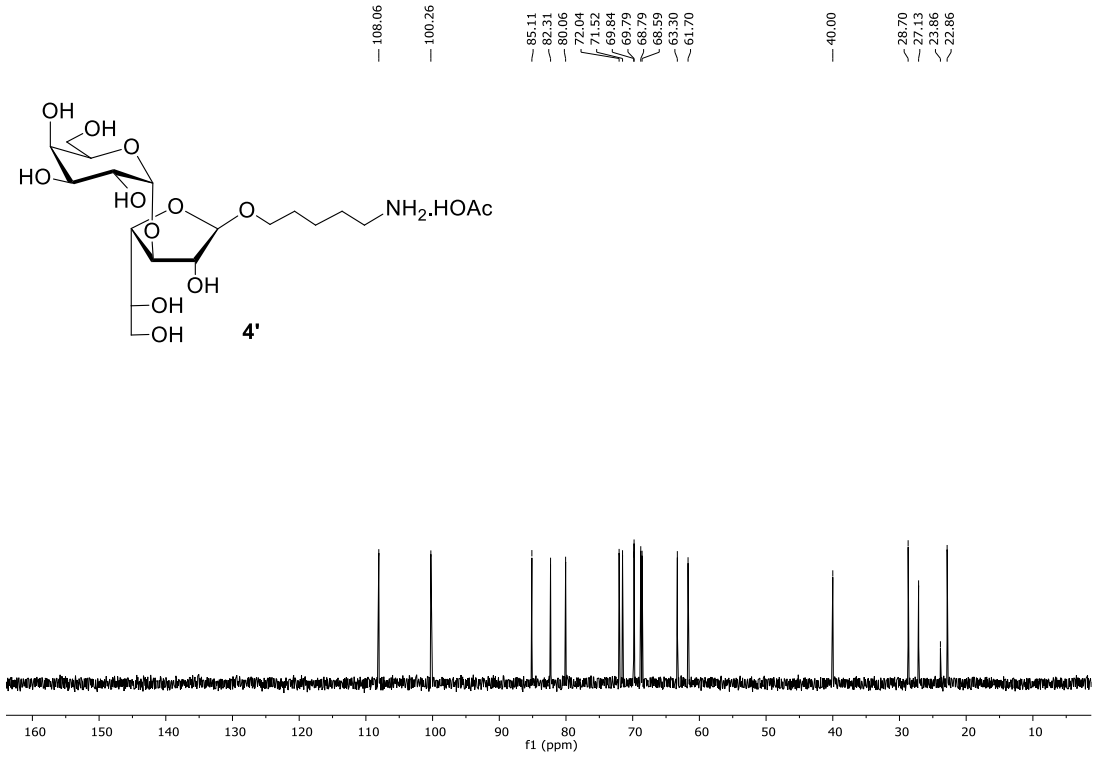


5-Aminopentyl α-D-galactopyranosyl-(1→3)-β-D-galactofuranoside, acetate (4')

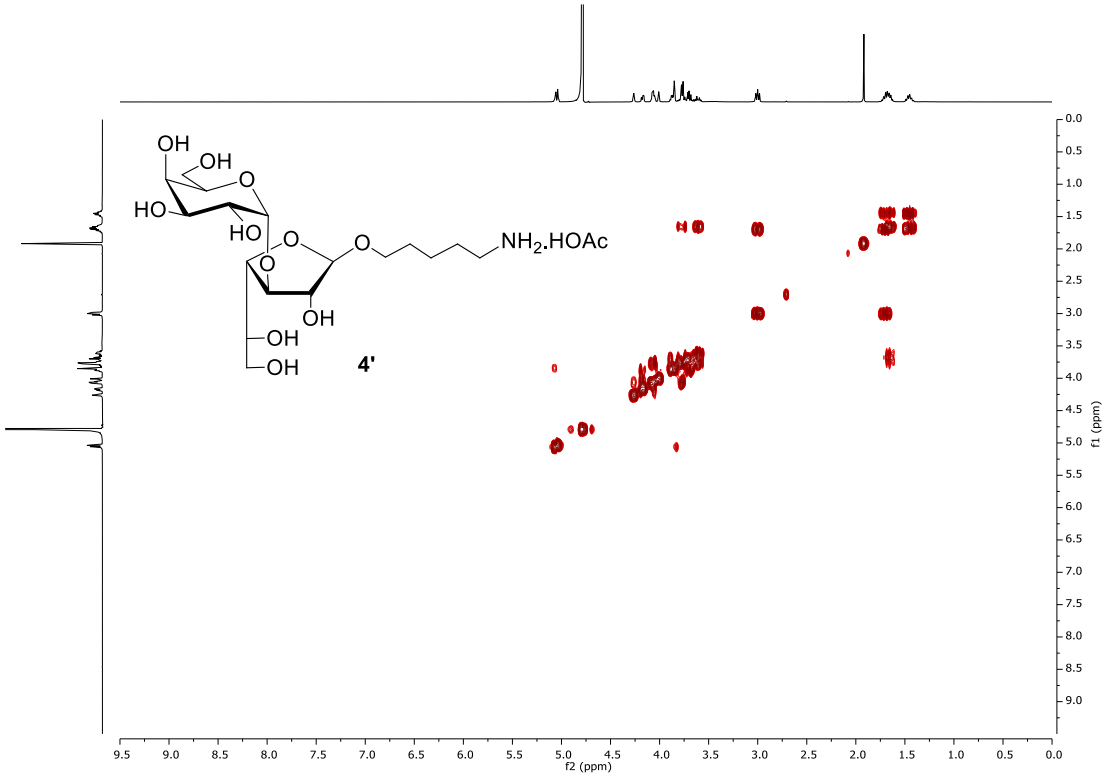
^{1}H NMR (400 MHz, D_2O)



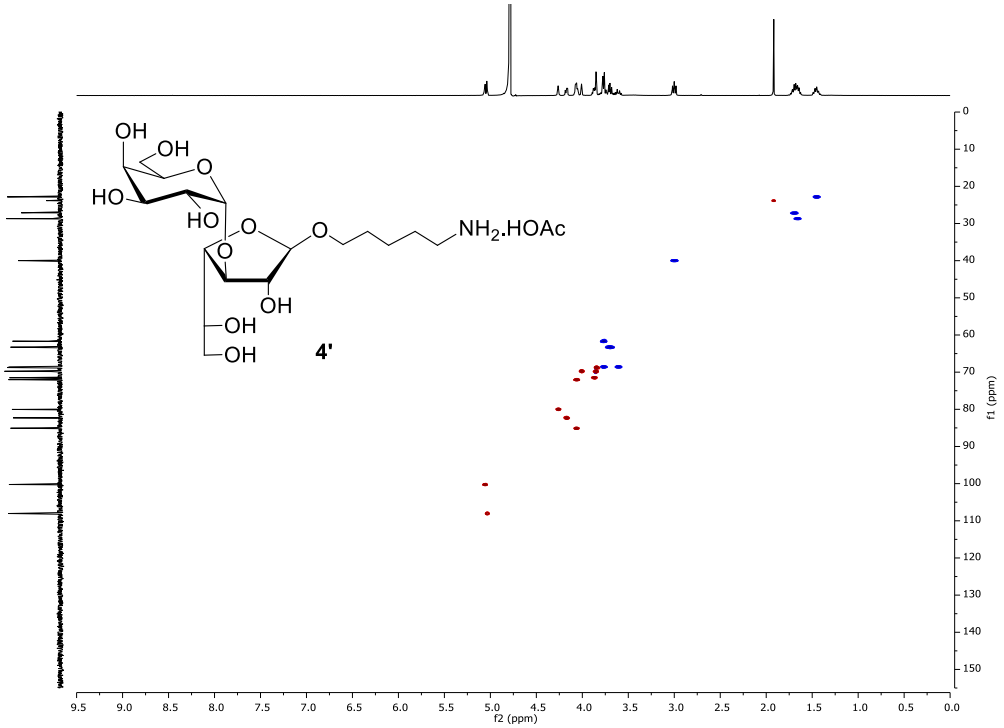
^{13}C NMR (101 MHz, D_2O)



^{1}H-^{1}H COSY NMR (400 MHz, D_2O)

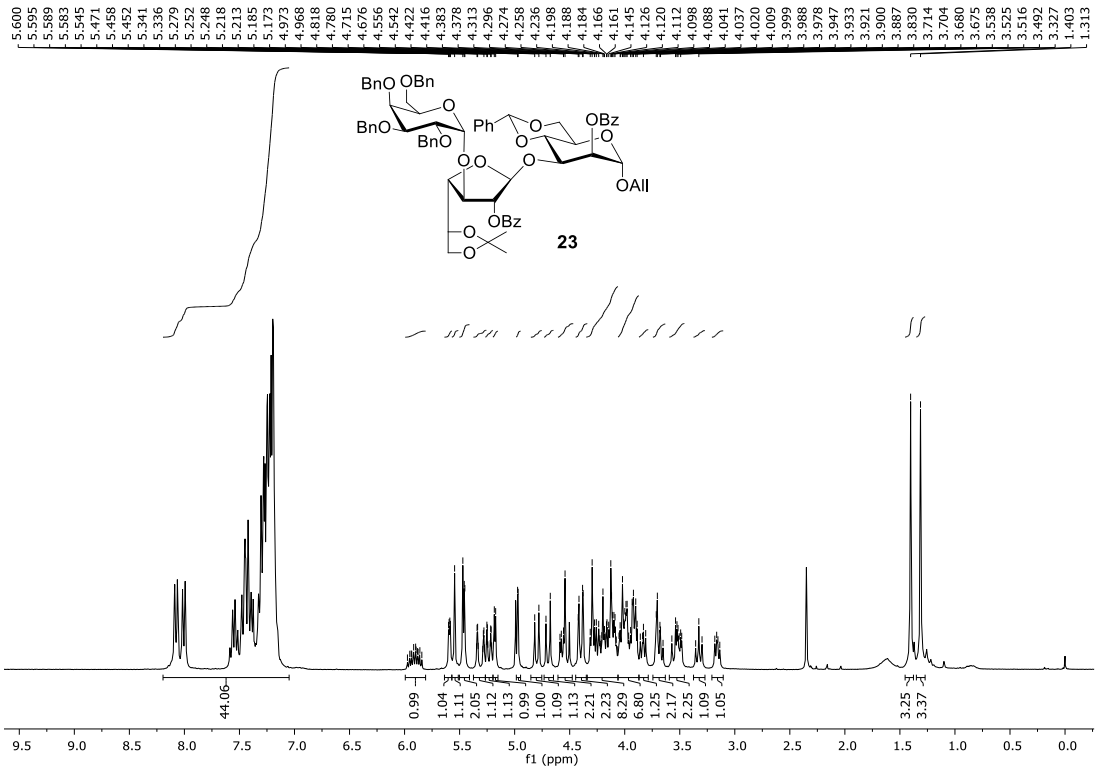


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, D_2O)

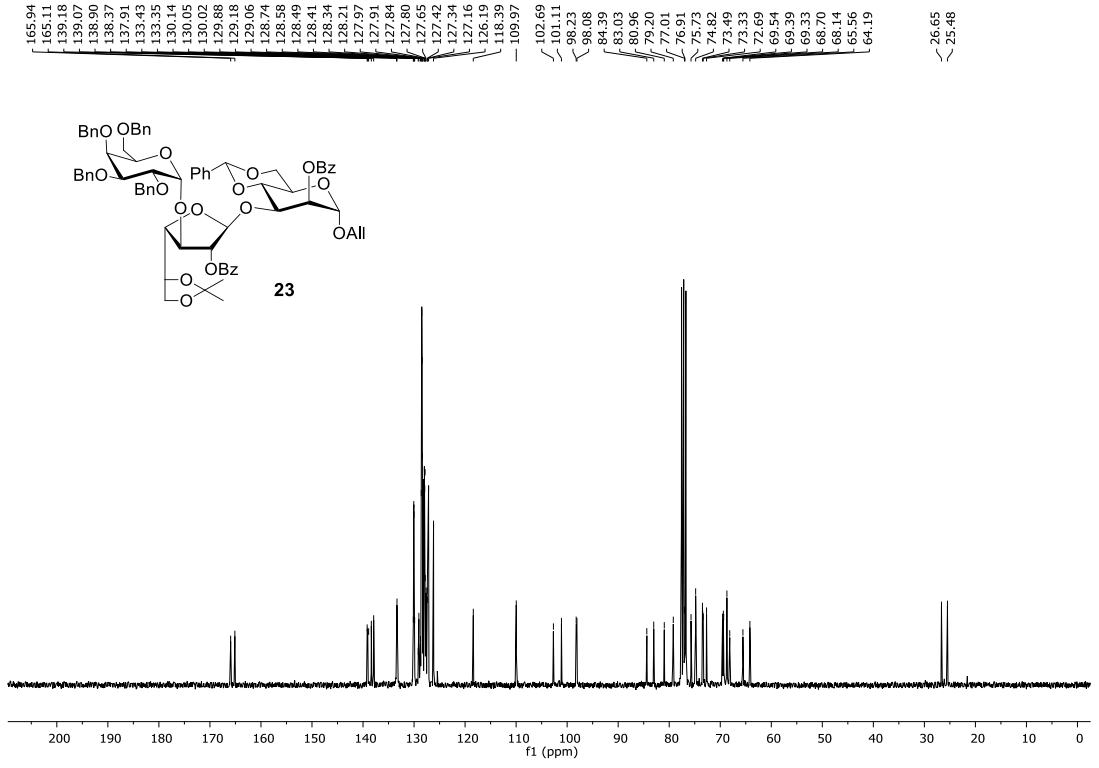


Allyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (23)

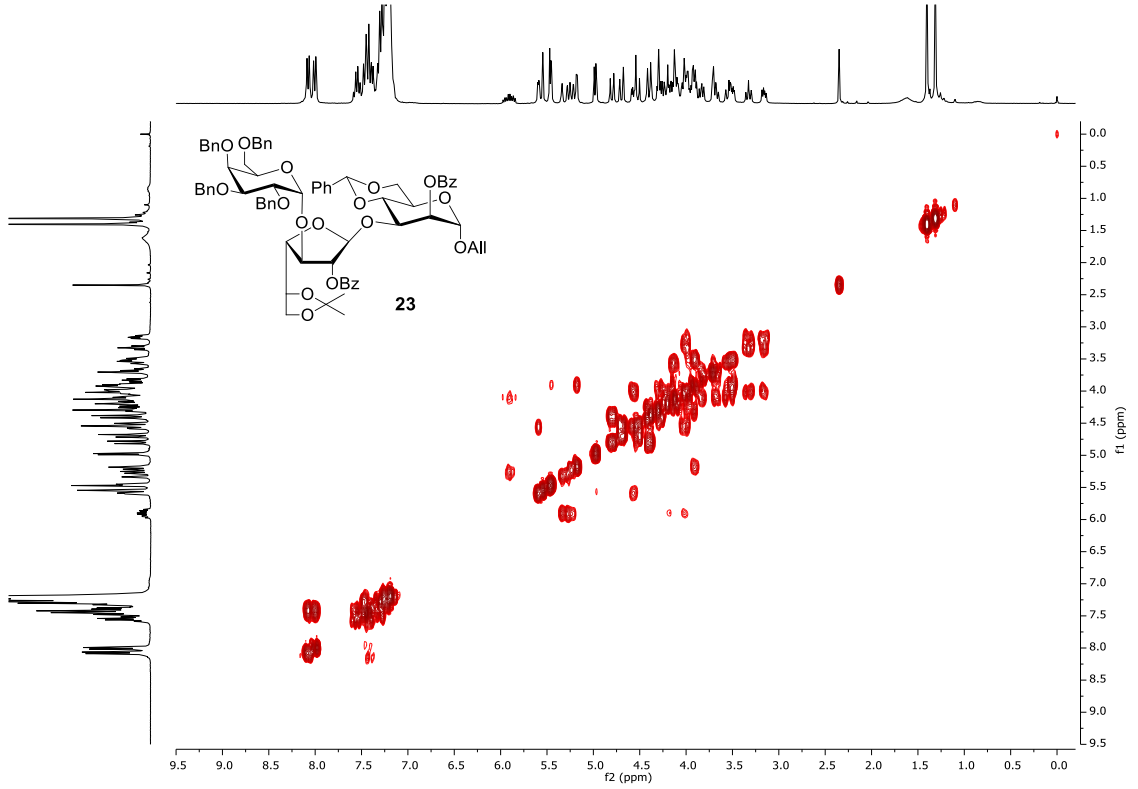
^{1}H NMR (300 MHz, $CDCl_3$)



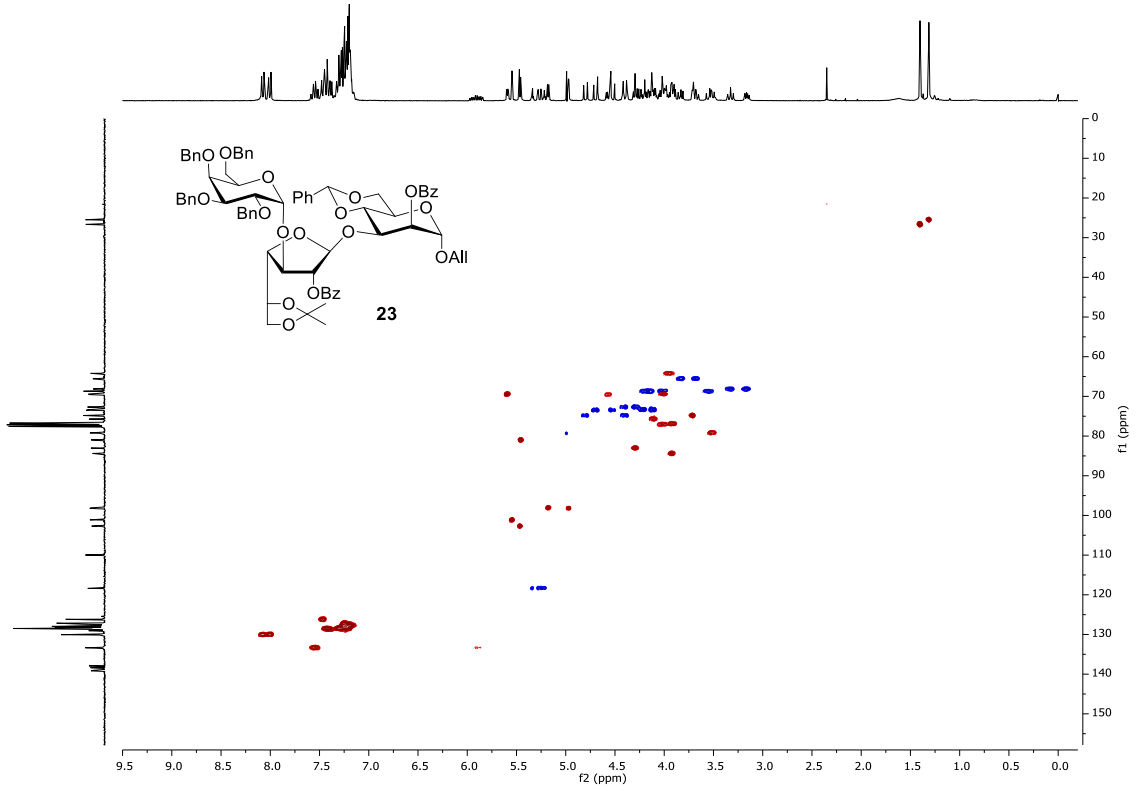
^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$)

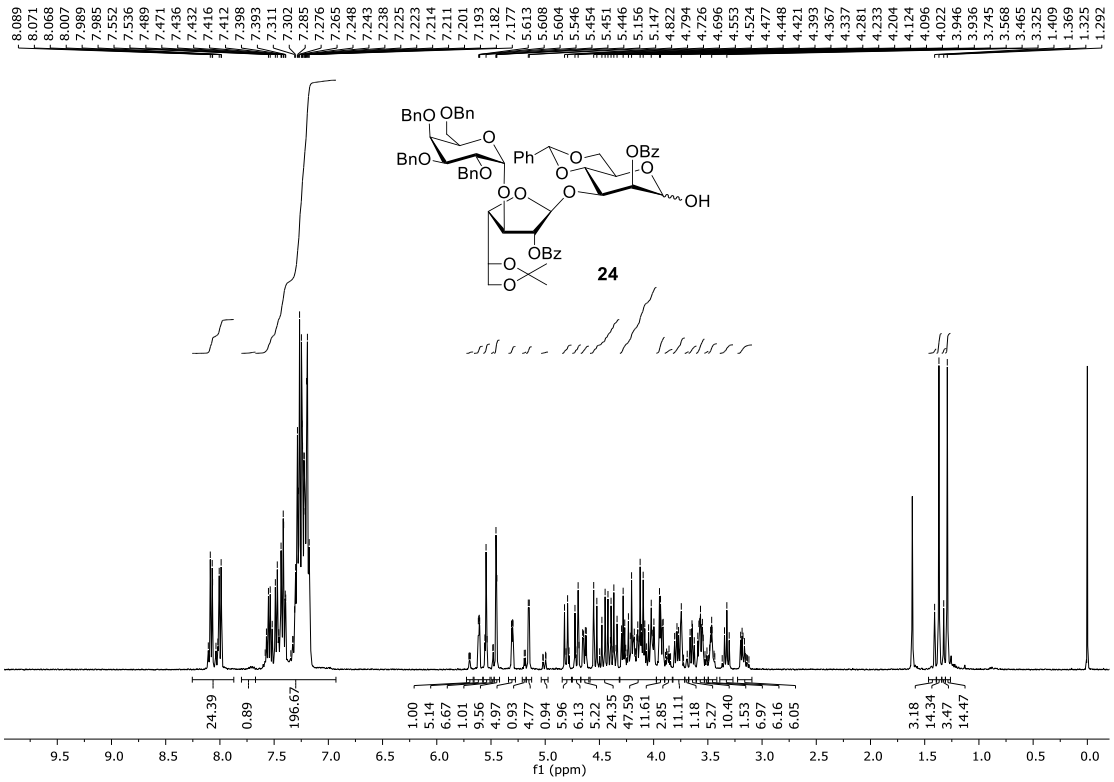


^{1}H-^{13}C decoupled HSQC NMR (300 MHz, $CDCl_3$)

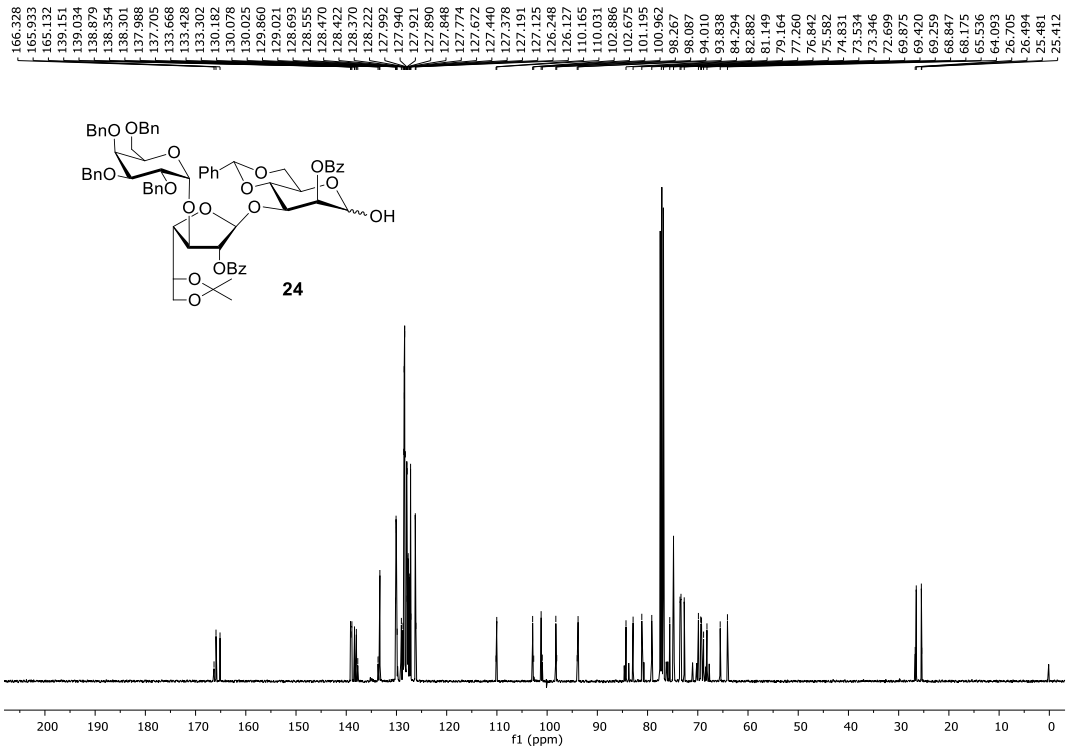


2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α,β-D-mannopyranose (24)

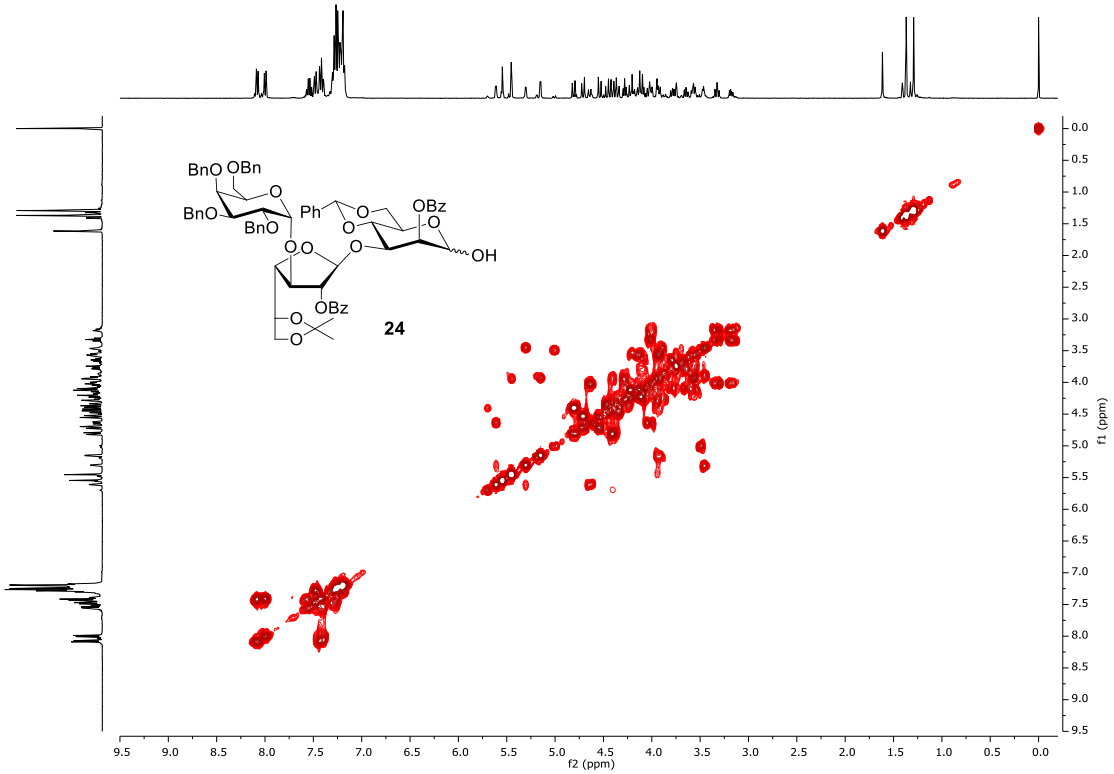
^{1}H NMR (400 MHz, $CDCl_3$)



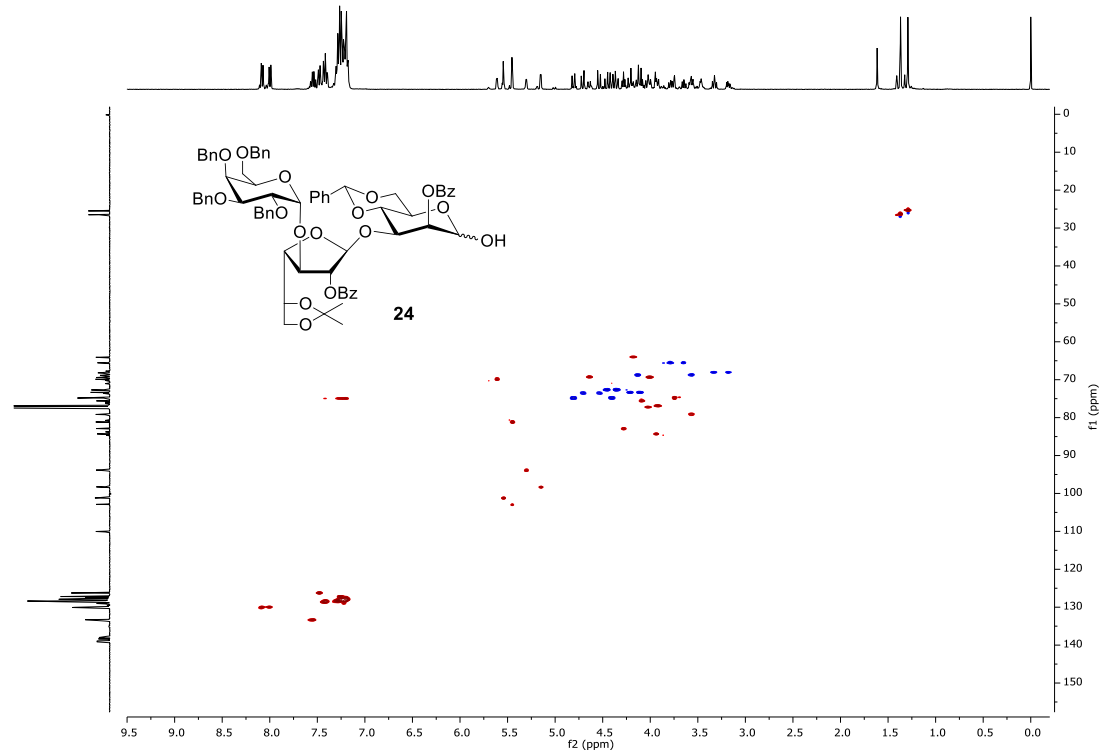
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)

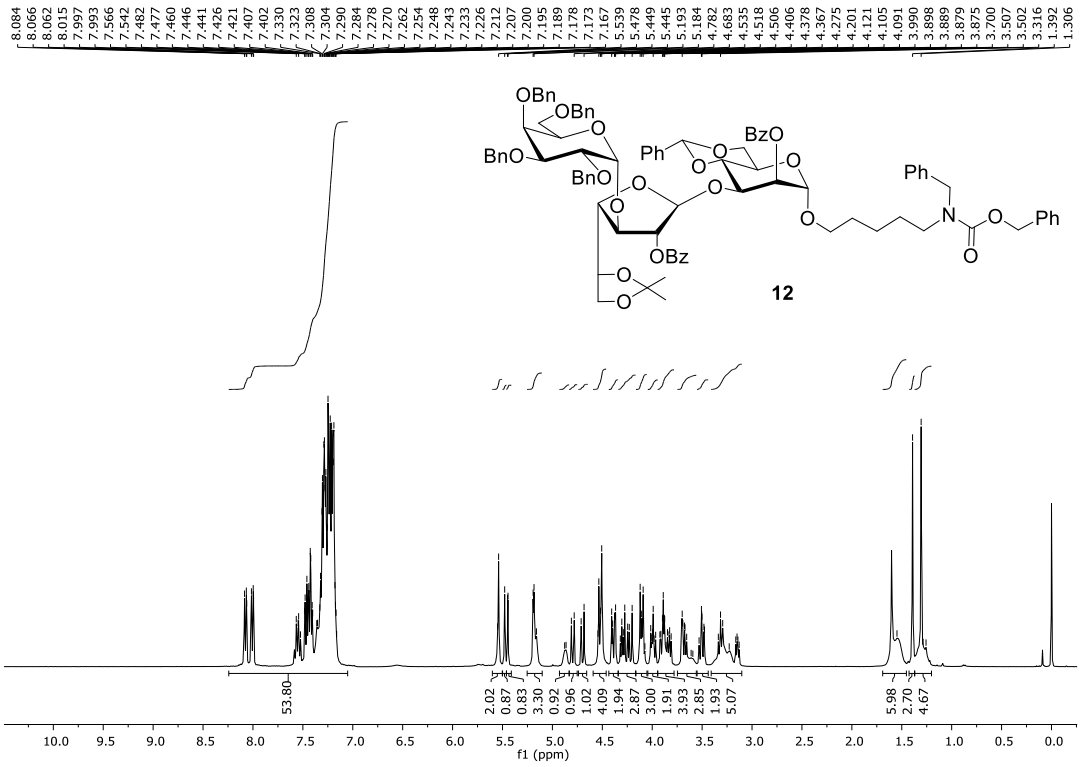


^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

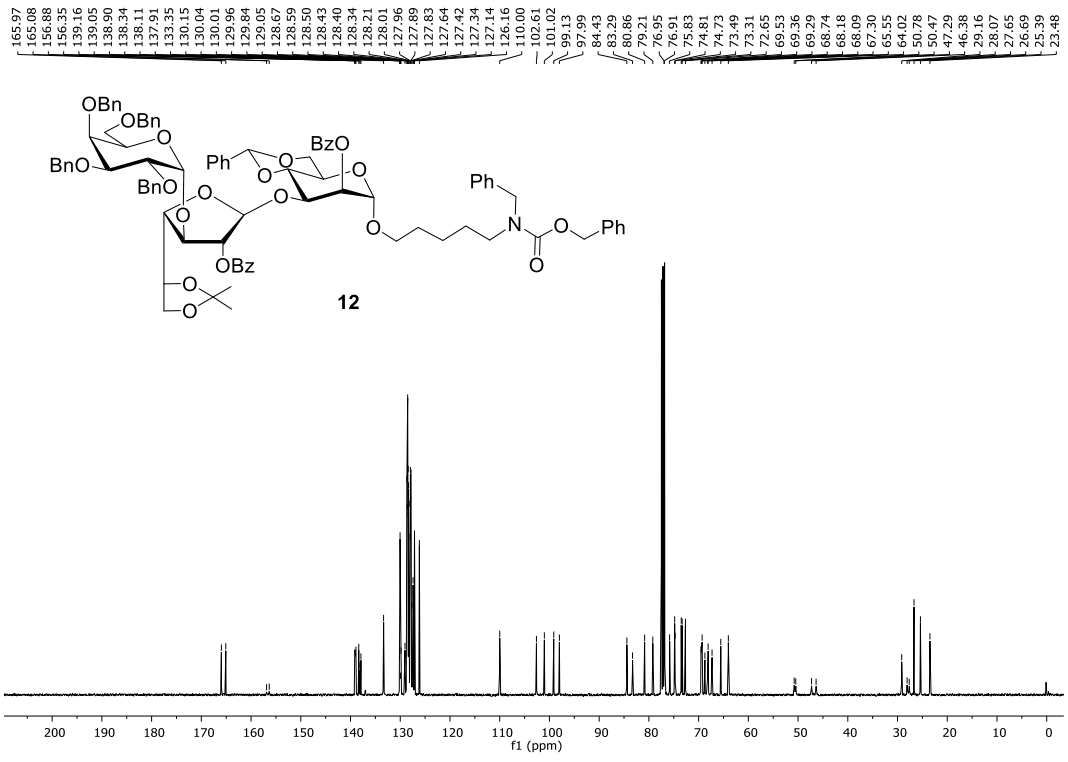


_N_-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2,3,4,6-tetra-_O_-benzyl-α-D-galactopyranosyl-(1→3)-2-_O_-benzoyl-5,6-_O_-isopropylidene-β-D-galactofuranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-α-D-mannopyranoside (12)

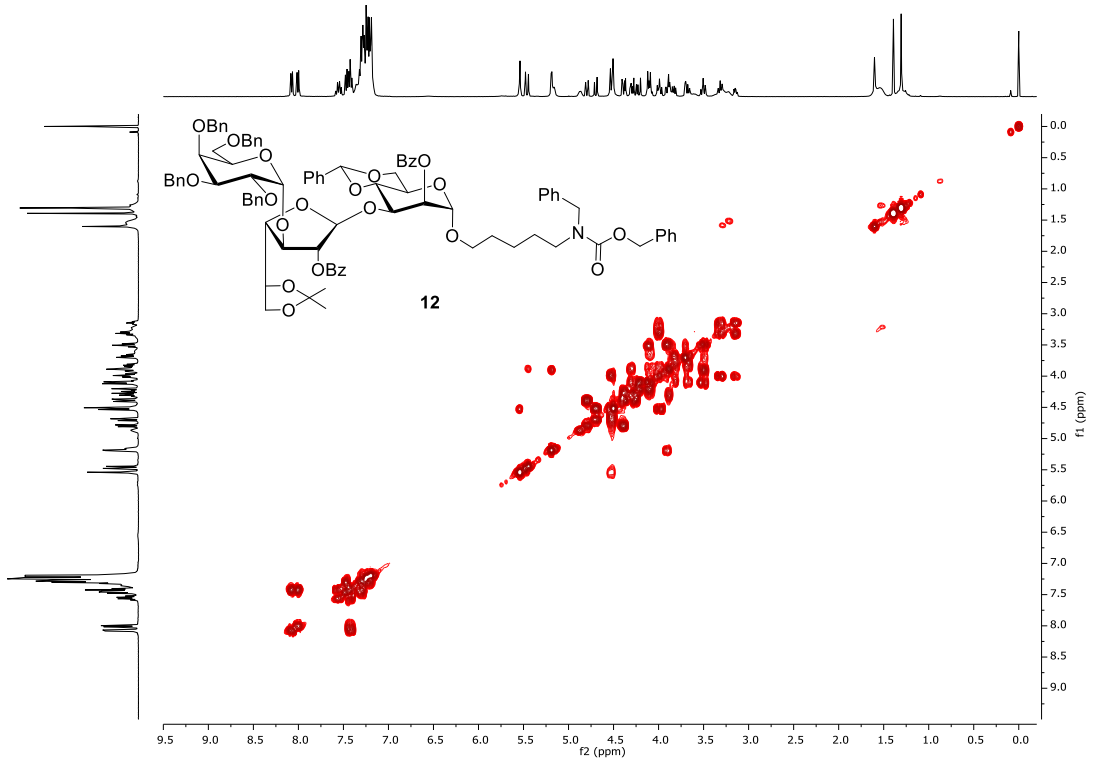
^{1}H NMR (400 MHz, $CDCl_3$)



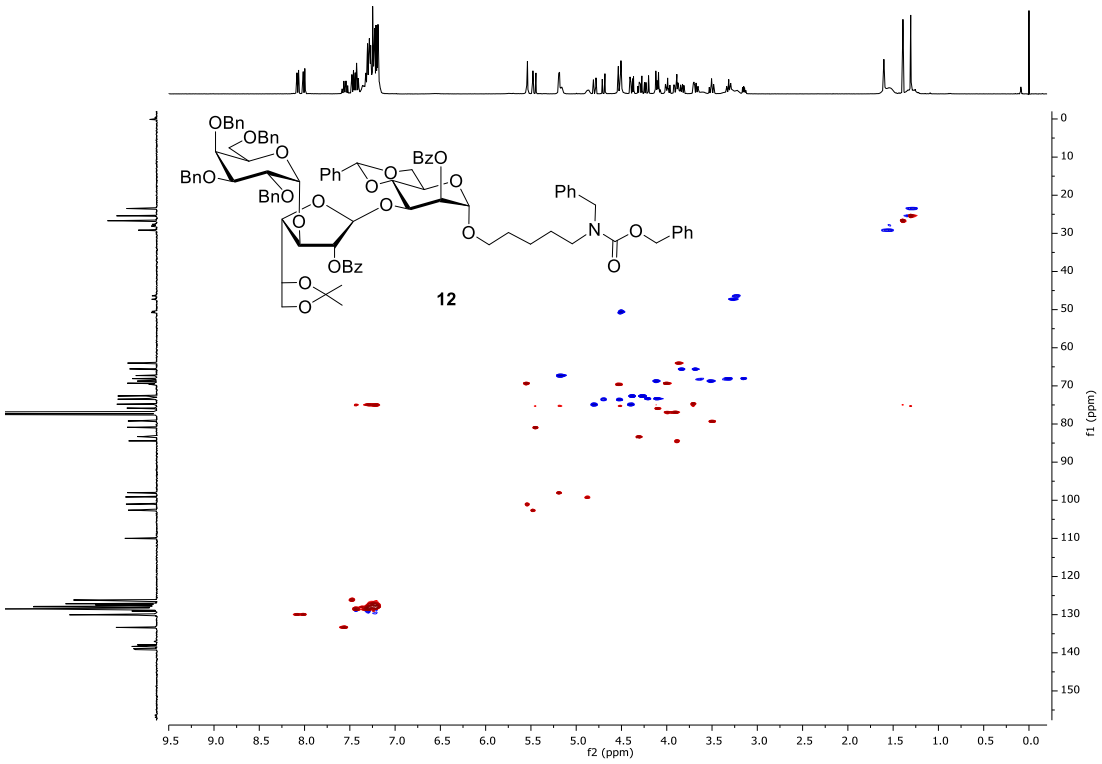
^{13}C NMR (101 MHz, $CDCl_3$)



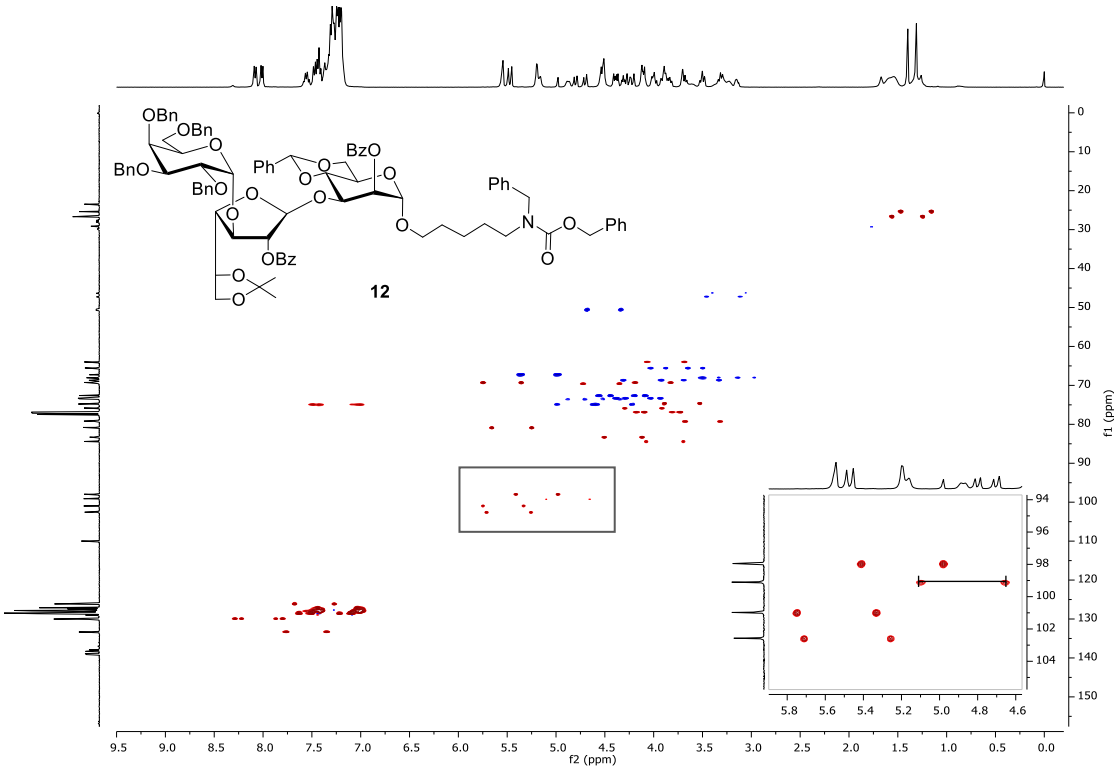
^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)



^{1}H-^{13}C decoupled HSQC NMR (400 MHz, $CDCl_3$)

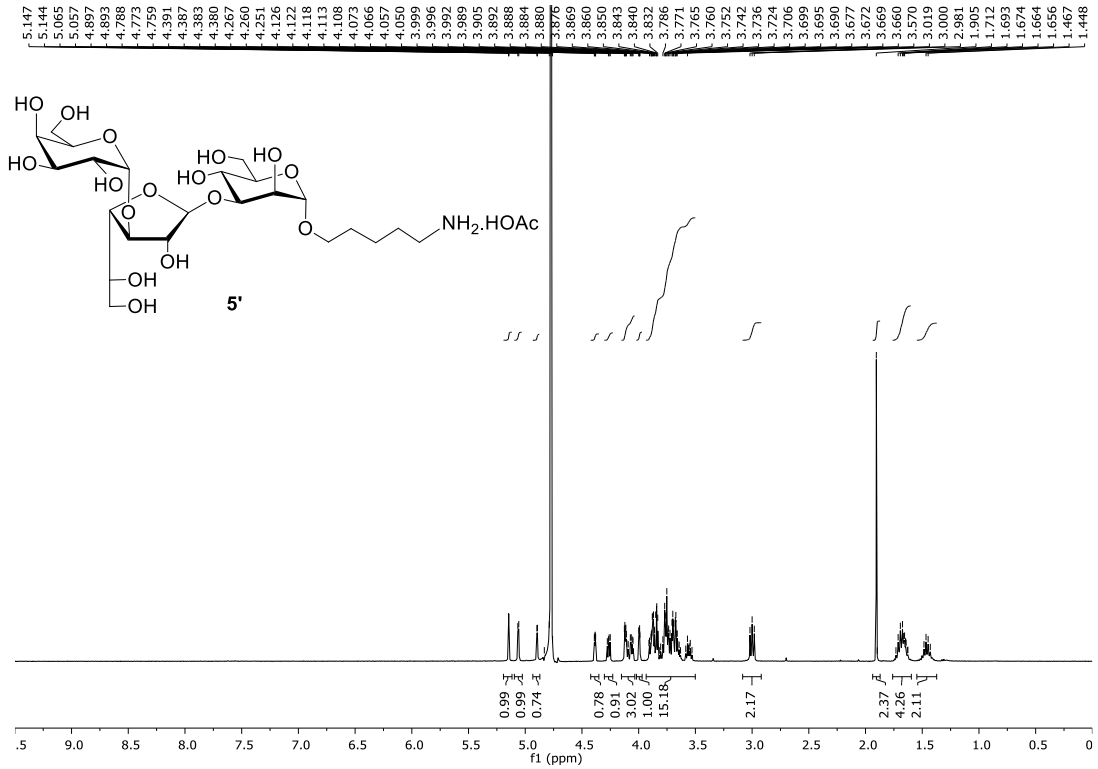


^{1}H-^{13}C coupled HSQC NMR (400 MHz, $CDCl_3$)

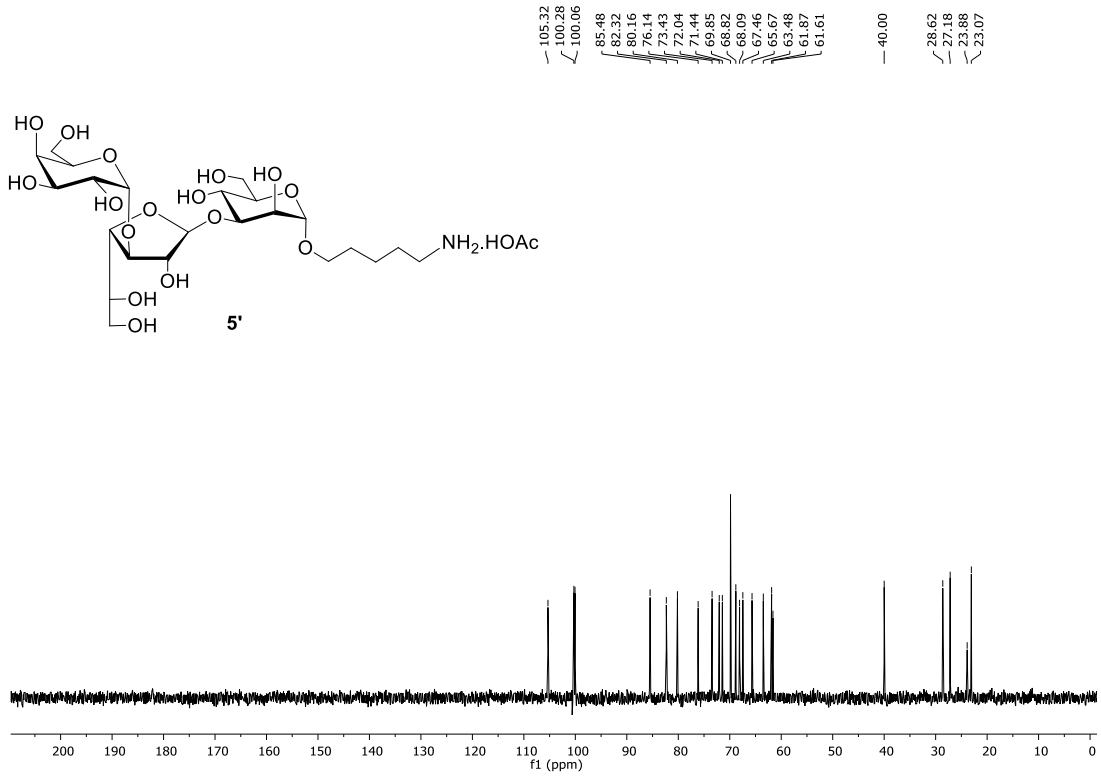


5-Aminopentyl α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside, acetate (5')

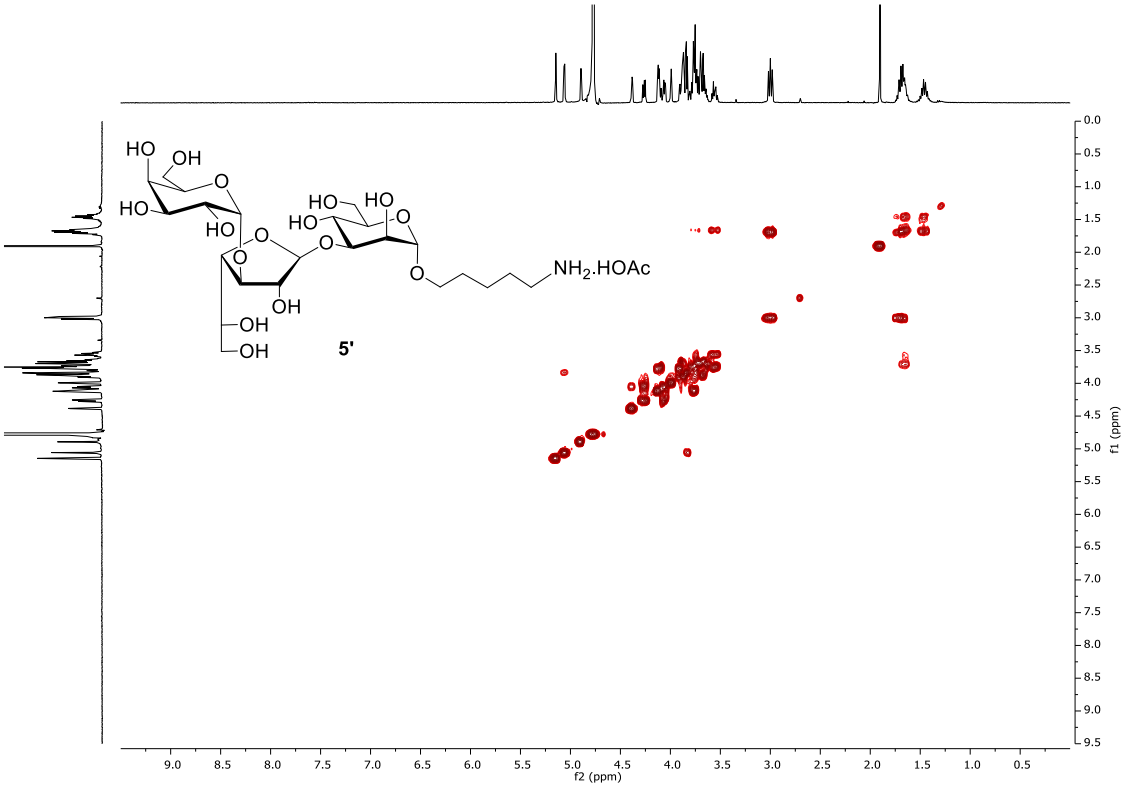
^{1}H NMR (400 MHz, D_2O)



^{13}C NMR (101 MHz, D_2O)



^{1}H-^{1}H COSY NMR (400 MHz, D_2O)



^{1}H-^{13}C decoupled HSQC NMR (400 MHz, D_2O)