ELECTRONIC SUPPLEMENTARY INFORMATION

Metal-free and VOC-free *O*-glycosylation in supercritical CO_2

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Contents

1. General Methods

All reagents were purchased from Sigma Aldrich, Alfa Aesar or Carbosynth chemical companies. Carbon dioxide (CO_2, CP grade 5.3 and SCF grade 99.995%) was supplied by Praxair. Dichloromethane (DCM) was distilled from CaH_2. CH_3CN was pre-died over 4 Å MS, distilled and then stored with activated 4Å MS. Toluene was stored with activated 4Å MS, THF was distilled from sodium and Et_3N was stored with activated 4Å MS. 4Å MS were activated by heating under high vacuum at 260 ^oC for 10 h and then were stored at 165 ^oC.

^1H and ^{13}C NMR spectra were recorded on a Varian® Mercury VX 400 or on a Bruker® Avance Ultrashield (400 MHz and 100 MHz respectively) spectrometer. NMR signals were fully assigned by COSY, HSQC, NOESY and HMBC experiments. Coupling constants (*J*) are reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, bd = broad doublet, bt = broad triplet, bq = broad quartet and app = apparent. Infrared (IR) spectra were recorded on a JASCO FTIR-600 plus Fourier Transform Infrared Spectrophotometer. ESI MS were run on an Agilent® 1100 Series LC/MSD instrument. Melting points (m.p.) were recorded with a Reichert apparatus. Optical rotations were measured on a Perkin–Elmer® 241 polarimeter with a path length of 1.0 dm and are reported with implied units of 10^{-1} deg cm^2 g^{-1}. Concentrations (c) are given in g/100 ml.

Thin layer chromatography (TLC) was carried out on 0.25 mm E. Merck® aluminum backed sheets coated with 60 F_{254} silica gel. Visualization of the silica plates was achieved using a UV lamp (λmax = 254 nm) and/or by heating plates that were dipped in a H_2SO_4/ethanol (1:15). Flash chromatography was carried out using forced flow of the indicated solvent on Fluka® or Merck® silica gel 60 (230-400 mesh).

2. General Procedures

A. General procedure for the preparation of galactopyranosyl bromides

Compounds **1**, **4** and **5** were prepared as previously reported[1] with minor changes during work-up.

A solution of HBr (20 mL, 33 wt % in acetic acid) was slowly added to a solution of the peracylated sugar (10 mmol, 1.0 equiv.) in DCM (40 mL) at 0 ^{o}C and the mixture was allowed to warm up to room temperature. After 3h, the reaction was cooled at -10 ^{o}C and water (100 mL) was added. Then, solid $NaHCO_3$ was added in small amounts until neutralization. The two phases were separated and the aqueous layer was extracted with DCM (3 x 25 mL). The combined organic layers were washed with brine and then dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was either dissolved with the minimum amount of Et_2O and precipitated with hexanes or purified by flash chromatography to afford the pure product as an amorphous colourless solid which was directly submitted to glycosylation reaction.

B. General procedure for the preparation of galactopyranosyl chlorides

Compounds **2** and **6** were prepared as previously reported[2] with minor changes during work-up.

Thionyl chloride (10 mmol, 2 equiv.) and $SnCl_4$ (5 mmol, 1 equiv) were added to a solution of peracylated sugar (5 mmol, 1 equiv.) in anhydrous DCM (70 mL). The mixture was stirred at room temperature until completion of the reaction was observed by TLC. The mixture was then poured onto a mixture of saturated $NaHCO_3$ solution and ice. Then, the two phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude residue was purified using flash chromatography to afford the galactopyranosyl chloride as a colorless solid.

C. General procedure for glycosylations with galactopyranosyl bromides (1, 4 and 5) in *sc*CO_2.

Galactopyranosyl bromide (0.365 mmol, 1 equiv.), glycosyl acceptor (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr Reactor) which was quickly sealed. It was then purged with CO_2, charged with the pressure of the CO_2 cylinder (ca. 800 Psi) and heated with a heating mantle to 60 ^oC. Once the temperature was reached, compressed CO_2 was added until a pressure of 1500 Psi. The start of the reaction is defined as the time at which the CO_2 pressure reaches 1500 Psi.

After stirring the reaction mixture at 60 ^oC and 1500 Psi until completion (14 h for donor 1 and between 20-24h for donors 4 and 5), the reactor was cooled to 0 ^oC and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with CH_2Cl_2 and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^1H NMR for the determination of the α:β ratio. Finally, the residue was purified by flash column chromatography using Hexane-AcOEt mixtures to give the glycosylated products.

D. General procedure for glycosylations with galactopyranosyl chlorides (2 and 6) in *sc*CO_2.

The galactopyranosyl chloride (0.365 mmol, 1 equiv.), glycosyl acceptor (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr reactor) which was quickly sealed. Then it was purged with CO_2, charged with the pressure of the CO_2 cylinder (ca. 800 Psi) and heated at 90 ^oC. Once the temperature was reached, compressed CO_2 was added until 1500 Psi. The start of the reaction is defined as the time at which the CO_2 pressure reaches 1500 Psi.

After stirring the reaction mixture at 90 ^oC and 1500 Psi for 24 h, the reactor was cooled to 0 ^oC and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with CH_2Cl_2 and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^1H NMR for the determination of the α:β ratio. Finally, the residue was purified by flash column chromatography using Hexane-AcOEt mixtures to give the glycosylated products.

E. General procedure for glycosylations with galactopyranosyl bromide 7 in *sc*CO_2.

Galactopyranosyl bromide (0.365 mmol, 1 equiv.), glycosyl acceptor (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr Reactor) which was quickly sealed. It was then purged with CO_2, charged with the pressure of the CO_2 cylinder (ca. 800 Psi) and heated with a heating mantle to 40 ^oC. Once the temperature was reached, compressed CO_2 was added until a pressure of 1500 Psi. The start of the reaction is defined as the time at which the CO_2 pressure reaches 1500 Psi.

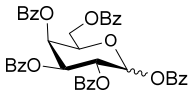
After stirring the reaction mixture at 40 ^oC and 1500 Psi until completion (3 h for acceptor **a**, **b** and 14h for acceptor **f**), the reactor was cooled to 0 ^oC and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with CH_2Cl_2 and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^1H NMR for the determination of the α:β ratio. Finally, the residue was purified by flash column chromatography using Hexane-AcOEt mixtures to give the glycosylated products.

F. General procedure for the preparation of galactosyl orthoesters (13a-c) in *sc*CO_2.

The glycosyl donor (0.365 mmol, 1 equiv.), glycosyl acceptor (1.1 mmol, 3 equiv.), 2,6-lutidine (1.1 mmol, 3 equiv.) and ca. 100 mg of 4Å MS were added to the reactor (25 mL Parr Reactor) and it was quickly sealed. The reactor was purged with CO_2, charged with the pressure of the CO_2 cylinder (ca. 800 Psi) and it was heated with a heating mantle to 60 ^oC. Once the temperature was reached, compressed CO_2 was added until 1500 Psi. The start of the reaction is defined as the time at which the CO_2 pressure reaches 1500 Psi. After stirring the reaction mixture at 60 ^oC and 1500 Psi for 24 h, the reactor was cooled to 0 ^oC and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with CH_2Cl_2 and the residue was concentrated and purified by flash chromatography on silica gel to give the products as a mixture of *endo* and *exo* orthoesters.

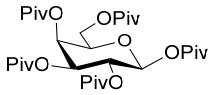
3. Synthetic procedures and characterization data

1,2,3,4,6-Penta-*O*-benzoyl-D-galactopyranose[3]



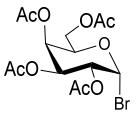
1,2,3,4,6-Penta-*O*-benzoyl-D-galactopyranoside was prepared as reported[1] with some procedure modifications. Et_3N (78 mL, 550 mmol, 20 equiv.) was added to a vigorously stirred suspension of galactose (5.00 g, 27.75 mmol) and DMAP (0.340 g, 2.77 mmol, 0.1 equiv.) in DCM (55 mL) and the mixture was heated at reflux under argon. Benzoyl chloride (25.75 mL, 222 mmol, 8 equiv.) was then added with caution and the mixture was allowed to react for 48 h. Excess of benzoyl chloride was quenched with MeOH and the suspension was cooled with an ice bath. The reaction mixture was concentrated under vacuum. The crude product was dissolved in DCM and washed first with saturated NH_4Cl solution (3 × 30 mL) and then with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude residue was purified by column chromatography using EtOAc/Hexane (1:2) to yield 14.7 g (72%) of 1,2,3,4,6-Penta-*O*-benzoyl-D-galactopyranose as a colourless solid. Product identity was confirmed by comparison to previously published data.

1,2,3,4,6-Penta-*O*-pivaloyl-β-D-galactopyranose[4]



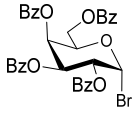
1,2,3,4,6-Penta-*O*-pivaloyl-β-D-galactopyranoside was prepared as previously reported[2] using 5.00 g (27.75 mmol) of D-galactose to afford 11.17 g (67%) of the title compound as a colourless solid. Spectroscopic data were in agreement with those reported.

2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (1)[1]



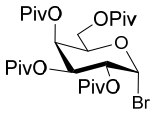
The reaction was performed as described in the general procedure A starting from 3.90 g (10 mmol) of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranoside. The crude product was dissolved with Et_2O and precipitated with hexanes to afford 4.10 g (quantitative yield) of the title compound as a colourless solid. Spectroscopic data were consistent with those reported.

2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (4)[5]



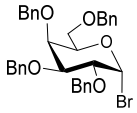
The reaction was performed as described in the general procedure A starting from 3.50 g (5 mmol) of 1,2,3,4,6-penta-*O*-benzoyl-D-galactopyranoside. The crude product was purified using flash chromatography to afford 3.03 g (92%) of the title compound as a yellowish solid. Product identity was confirmed by comparison to previously published data.

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (5)[6]



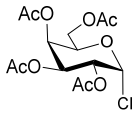
The reaction was performed as described in the general procedure A starting from 8.80 g (14.65 mmol) of 1,2,3,4,6-penta-*O*-pivaloyl-β-D-galactopyranoside. The crude product was purified using flash chromatography to afford 6.6 g (78 %) of the title compound as a colourless solid.

2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide (7)[7]



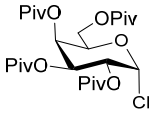
The reaction was performed as reported. 1-*O*-Acetyl-2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranose (2.00 g, 3.43 mmol) was dissolved in dry dichloromethane (34 mL) and cooled to -15 ºC. Then, bromotrimethylsilane (4.5 mL, 34.3 mmol) was added dropwise with stirring and the mixture was allowed to warm up to room temperature. After 24 h full conversion was observed by ^{1}H NMR using a small aliquot. Evaporation of the solvent gave 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **7** (1.88 g, 3.12 mmol, 91%) as a slightly brown syrup which was used without further purification. Spectroscopic data were consistent with those reported.

2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl chloride (2)[8]



The reaction was performed as described in the general procedure B with 1.95 g (5 mmol) of 1,2,3,4,6-penta-*O*-β-acetyl-D-galactopyranoside. The crude product was purified using flash chromatography to afford 1.66 g (91 %) of the title compound as a colourless solid. Spectroscopic data were in agreement with those reported.

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl chloride (6)



The reaction was performed as described in the general procedure B starting from 2.20 g (3.66 mmol) of 1,2,3,4,6-penta-*O*-β-pivaloyl-D-galactopyranoside. The crude product was purified using flash chromatography to afford 1.6 g (82 %) of the title compound as colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, $J_{1,2}$ = 4.0 Hz, 1H, H-1), 5.53 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.2 Hz, 1H, H-4), 5.49 (dd, $J_{3,2}$ = 10.4 Hz, $J_{3,4}$ = 3.3 Hz, 1H, H-3), 5.20 (dd, $J_{2,3}$ = 10.4 Hz, $J_{2,1}$ = 4.0 Hz, 1H, H-2), 4.54 (t, $J_{5,6}$ = 6.9 Hz, 1H, H-5), 4.11 (dd, $J_{6a,6b}$ = 11.2 Hz, $J_{6a,5}$ = 6.9 Hz, 1H, H-6a), 4.03 (dd, $J_{6b,6a}$ = 11.2 Hz, $J_{6b,5}$ = 6.9 Hz, 1H, H-6b), 1.24 (s, 9H, Piv), 1.17 (s, 9H, Piv), 1.17 (s, 9H, Piv), 1.12 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 177.5, 176.9, 176.6 (4 x C=O), 91.3 (C-1), 69.7 (C-5), 67.9 (C-2), 67.1 (C-3), 66.7 (C-4), 60.6 (C-6), 39.0 (C, Piv), 38.7 (C, Piv), 38.7 (C, Piv), 38.7 (C, Piv), 27.1 (CH_3, Piv), 27.0 (CH_3, Piv), 27.0 (CH_3, Piv), 26.9 (CH_3, Piv). **HRMS:** *m/z* calcd for $C_{26}H_{43}O_9ClNa$: 557.2488; found: 557.2488. $[\alpha]_D^{25}$ +68.3 (*c* 0.50, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2971, 2918, 2872, 2849, 1738, 1279, 1125, 1106, 762.

Benzyl 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (3a)

I. Method C. From **1**:

According to the general glycosylation procedure C, compound **3a** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of

benzyl alcohol (1.46 mmol, 4 equiv.) to afford the desired compound (104 mg, 65%, α:β = 1:3.8) as a colorless syrup. The α:β ratio was calculated from the peak area ratio of H1'aβ (4.90 ppm) and H1'aα (4.73 ppm) in the ^{1}H NMR crude spectrum.

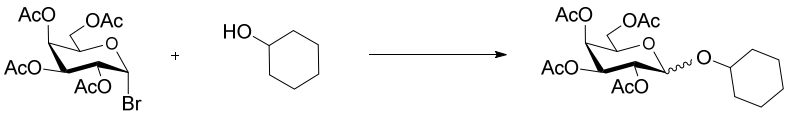
II. Method D. From **2**:

According to the general glycosylation procedure D, compound **3a** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl chloride (**2**) (134 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of benzyl alcohol (1,46 mmol, 4 equiv.) to afford **3a** (80 mg, 50%, α:β = 1:3.4) as a colourless syrup. The α:β ratio of the product was calculated from the peak area ratio of H-4'α (5.45 ppm) and H-3'β (4.98 ppm) in the ^{1}H NMR crude spectrum.

(3a-β):[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H, Ar), 5.39 (dd, $J_{4',3'}$ = 3.4 Hz, $J_{4',5'}$ = 0.9 Hz, 1H, H-4'), 5.28 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 4.98 (dd, $J_{3',2'}$ = 10.4 Hz, $J_{3',4'}$ = 3.4 Hz, 1H, H-3'), 4.92 (d, $J_{1a,1b}$ = 12.3 Hz, 1H, H-1a), 4.63 (d, $J_{1b,1a}$ = 12.3 Hz, 1H, H-1b), 4.51 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.22 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 6.5 Hz, 1H, H-6'a), 4.15 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.8 Hz, 1H, H-6'b), 3.89 (td, $J_{5',6'}$ = 6.7 Hz, $J_{5',4'}$ = 1.0 Hz, 1H, H-5'), 2.16 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.98 (s, 3H, Ac).

Ciclohexyl 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (3b)

I. Method C. From **1**:



According to the general glycosylation procedure C, compound **3b** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of cyclohexanol (1.46 mmol, 4 equiv.) to afford **3b** (132 mg, 85%, α:β = 1:5.7) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1'α (5.25 ppm) and H-2'β (5.18 ppm) in the ^{1}H NMR crude spectrum.

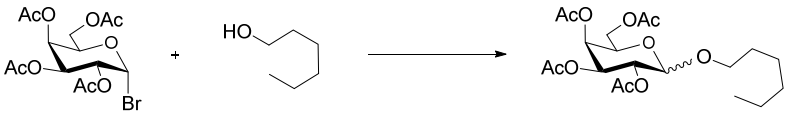
II. Method D. From **2**:

According to the general glycosylation procedure D, compound **3b** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl chloride (**2**) (134 mg, 0.365 mmol, 1 equiv.) and 0.15 mL (1.46 mmol, 4 equiv.) of cyclohexanol to afford **3b** (114 mg, 73%, α:β = 1:1.2) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-4'α (5.42 ppm) and H-2'β (5.19 ppm) in the ^{1}H NMR crude spectrum.

(3b-β):[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (dd, $J_{4',3'}$ = 3.4 Hz, $J_{4',5'}$ = 1.1 Hz, 1H, H-4'), 5.19 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.01 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 4.53 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.19 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 6.5 Hz, 1H, H-6'), 4.10 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 7.2 Hz, 1H, H-6'), 3.92 – 3.85 (m, 1H, H-5'), 3.66 – 3.57 (m, 1H, H-1), 2.14 (s, 3H, Ac), 2.04 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.92 – 1.63 (m, 4H, Cy), 1.53 – 1.38 (m, 2H, Cy), 1.38 – 1.16 (m, 4H, Cy).

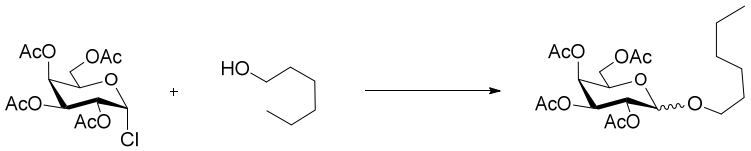
Hexyl 2,3,4,6-tetra-*O*-acetyl-α/β-D-galactopyranoside (3c)

I. Method C. From **1**:



According to the general glycosylation procedure C, compound **3c** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.) and 0.18 mL of 1-hexanol (1.46 mmol, 4 equiv.) to afford the desired compound (126 mg, 80%, α:β = 1:4.6) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-4'α (5.45 ppm) and H-2'β (5.20 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column for characterization purposes.

II. Method D. From **2**:

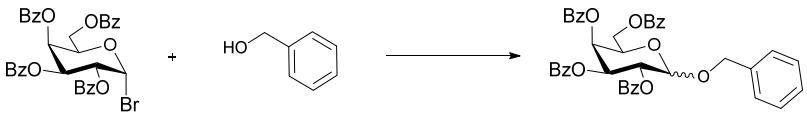


According to the general glycosylation procedure D, compound **3c** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl chloride (**2**) (134 mg, 0.365 mmol, 1 equiv.) and 0,18 mL of 1-hexanol (1,46 mmol, 4 equiv.) to afford **3c** (101 mg, 64%, α:β = 1:4.3) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-4'α (5.45 ppm) and H-3'β (5.01 ppm) in the ^{1}H NMR crude spectrum.

(3c-β): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.38 (dd, $J_{4',3'}$ = 3.4 Hz, $J_{4',5'}$ = 1.1 Hz, 1H, H-4'), 5.20 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.01 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.4 Hz, 1H, H-3'), 4.45 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.18 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 6.5 Hz, 1H, H-6'a), 4.12 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 7.0 Hz, 1H, H-6'b), 3.93 – 3.85 (m, 2H, H-5', H-1a), 3.46 (dt, $J_{1'b,1'a}$ = 9.6 Hz, $J_{1b,2}$ = 6.9 Hz, 1H, H-1b), 2.14 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.64 – 1.48 (m, 2H, H-2), 1.37 – 1.20 (m, 6H, 3xCH_2), 0.88 (t, $J_{6,5}$ = 6.9 Hz, 3H, H-6).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 170.3, 170.2, 169.4 (4x C=O), 101.3 (C-1'), 70.9 (C-3'), 70.5 (C-5'), 70.3 (C-1), 68.9 (C-2'), 67.0 (C-4'), 61.3 (C-6'), 31.5 (CH_2), 29.3 (CH_2, C-2), 25.5 (CH_2), 22.6 (CH_2), 20.7 (CH_3, Ac), 20.7 (2xCH_3, Ac), 20.6 (CH_3, Ac), 14.0 (CH_3). **HRMS:** *m/z* calcd for $C_{20}H_{32}O_{10}Na$: 455.1888; found: 455.1885.$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ -8.2 (*c* 0.32, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}**:** 2924, 2855, 1746, 1367, 1215, 1076, 1043.

(3c-α): ^{1}H NMR (400 MHz, CDCl3) δ 5.45 (dd, $J_{4',3'}$ = 3.4 Hz, $J_{4',5'}$ = 1.2 Hz, 1H, H-4'), 5.35 (m, 1H, H-3'), 5.13 – 5.08 (m, 2H, H-1', H-2'), 4.25 – 4.18 (m, 1H, H-5'), 4.11 (dd, $J_{6'a,6'b}$ =11.2 Hz, $J_{6'a,5'}$ = 6.1 Hz, 1H, H-6'a), 4.07 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 7.1 Hz, 1H, H-6'b), 3.68 (dt, $J_{1a,1b}$ = 9.8 Hz, $J_{1a,2}$ = 6.5 Hz, 1H, H-1a), 3.41 (dt, $J_{1b,1a}$ = 9.8 Hz, $J_{1b,2}$ = 6.6 Hz, 1H, H-1b), 2.14 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.62 – 1.54 (m, 2H, H-2), 1.39 – 1.24 (m, 6H, 3xCH_2), 0.89 (t, $J_{6,5}$ = 6.9 Hz, 3H, H-6). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.43, 170.43, 170.3, 170.1 (4x C=O), 96.0 (C-1'), 68.7 (C-1), 68.2 (C-4'), 68.1 (C-2'), 67.7 (C-3'), 66.1 (C-5'), 61.8 (C-6'), 31.5 (CH_2), 29.2 (CH_2, C-2), 25.7 (CH_2), 22.6 (CH_2), 20.8 (CH_3, Ac), 20.7 (CH_3, Ac), 20.7 (CH_3, Ac), 20.7 (CH_3, Ac), 14.0 (C-6). **HRMS:** *m/z* calcd for $C_{20}H_{32}O_{10}Na$: 455.1888; found: 455.1889. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +114.3 (c 1.30, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2930, 1746, 1225, 1051.

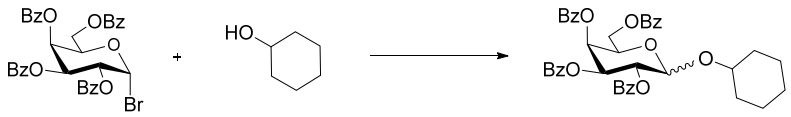
Benzyl 2,3,4,6-tetra-*O*-benzoyl-D-galactopyranoside (8a)



According to the general glycosylation procedure C, compound **8a** was prepared from 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (**4**) (240 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of benzyl alcohol (1.46 mmol, 4 equiv.) to afford **8a** (127 mg, 51%, α:β = 1:24) as a colorless syrup. The α:β ratio was calculated from the peak area ratio of H-3'β (5.55 ppm) and H-1'α (5.5 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

(8a-β): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H, Ar), 8.08 – 8.03 (m, 2H, Ar), 7.95 – 7.89 (m, 2H, Ar), 7.81 – 7.76 (m, 2H, Ar), 7.65 – 7.36 (m, 10H, Ar), 7.28 – 7.15 (m, 7H, Ar), 5.98 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 1.0 Hz, 1H, H-4'), 5.88 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.55 (dd, $J_{3',2'}$ = 10.4 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 4.97 (d, $J_{1a,1b}$ = 12.5 Hz, 1H, H-1a), 4.82 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.75 (d, $J_{1b,1a}$ = 12.5 Hz, 1H, H-1b), 4.72 (dd, $J_{6'a,6'b}$ = 11.3 Hz, $J_{6'a,5'}$ = 6.7 Hz, 1H, H-6'a), 4.45 (dd, $J_{6'b,6'a}$ = 11.3 Hz, $J_{6'b,5'}$ = 6.5 Hz, 1H, H-6'b), 4.29 (td, $J_{5',6'}$ = 6.6 Hz, $J_{5',4'}$ = 1.1 Hz, 1H, H-5'). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.5, 165.5, 165.2 (4 x C=O), 136.4 (C, Ar), 133.6 (CH, Ar), 133.3 (CH, Ar), 133.2 (CH, Ar), 133.2 (CH, Ar), 130.0 (CH, Ar), 129.8 (CH, Ar), 129.8 (2 x CH, Ar), 129.4 (C, Ar), 129.3 (C, Ar), 129.0 (C, Ar), 128.7 (C, Ar), 128.6 (CH, Ar), 128.5 (CH, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.0 (CH, Ar), 128.0 (CH, Ar), 99.5 (C-1'), 71.7 (C-3'), 71.4 (C-5'), 70.5 (C-1), 69.7 (C-2'), 68.1 (C-4'), 62.1 (C-6'). **HRMS:** *m/z* calcd for $C_{41}H_{34}O_{10}Na$: 709.2044; found: 709.2034. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +79.3 (*c* 1.56, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2924, 2855, 1746, 1367, 1215, 1076, 1043.

Cyclohexyl 2,3,4,6-tetra-*O*-benzoyl-D-galactopyranoside (8b)



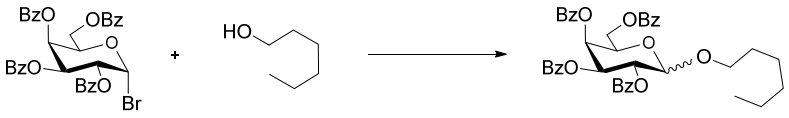
According to the general glycosylation procedure C, compound **8b** was prepared from 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (**4**) (240 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of cyclohexanol (1.46 mmol, 4 equiv.) to afford **8b** (178 mg, 72%, α:β = 1:5.3) as a colorless syrup. The α:β ratio was calculated from the peak area ratio of H-2'β (5.78 ppm) and H-2'α (5.65

ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

(8b-β): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H, Ar), 8.05 – 8.01 (m, 2H, Ar), 7.98 – 7.94 (m, 2H, Ar), 7.82 – 7.77 (m, 2H, Ar), 7.65 – 7.35 (m, 10H, Ar), 7.27 – 7.21 (m, 2H, Ar), 5.99 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 0.9 Hz, 1H, H-4'), 5.78 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.60 (dd, $J_{3',2'}$ = 10.4, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 4.91 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.68 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.8 Hz, 1H, H-6'a), 4.43 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.6 Hz, 1H, H-6'b), 4.32 (td, $J_{5',6'}$ = 6.6 Hz, $J_{5',4'}$ = 0.9 Hz, 1H, H-5'), 3.73 – 3.65 (m, 1H, H-1), 2.01 – 1.92 (m, 1H, Cy), 1.80 – 1.39 (m, 5H, Cy), 1.34 – 1.05 (m, 4H, Cy). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.6, 165.6, 165.2 (4xC=O), 133.5 (CH, Ar), 133.2 (CH, Ar), 133.2 (CH, Ar), 133.1 (CH, Ar), 130.1 (CH, Ar), 129.7 (CH, Ar), 129.7 (CH, Ar), 129.6 (CH, Ar), 129.5 (C, Ar), 129.4 (C, Ar), 129.0 (C, Ar), 128.8 (C, Ar), 128.5 (CH, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 100.3 (C-1'), 78.8 (C-1), 71.9 (C-3'), 71.2 (C-5'), 69.9 (C-2'), 68.1 (C-4'), 62.0 (C-6'), 33.3 (CH_2, Cy), 31.7 (CH_2, Cy), 25.3 (CH_2, Cy), 23.8 (CH_2, Cy), 23.7 (CH_2, Cy). **HRMS:** *m/z* calcd for $C_{40}H_{38}O_{10}Na$: 701.2357; found: 701.2352. $[\alpha]_D^{25}$ +84.1 (*c* 0.74, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}**:** 3070, 2935, 2853, 1722, 1257, 1091, 1068, 706.

(8b-α): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.96 (m, 6H, Ar), 7.82 – 7.78 (m, 2H, Ar), 7.64 – 7.35 (m, 10H, Ar), 7.28 – 7.22 (m, 2H, Ar), 6.03 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 1.2 Hz, 1H, H-4'), 6.00 (dd, $J_{3',2'}$ = 10.4 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 5.64 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{2',1'}$ = 3.8 Hz, 1H, H-2'), 5.56 (d, $J_{1',2'}$ = 3.8 Hz, 1H, H-1'), 4.78 – 4.73 (m, 1H, H-5'), 4.57 (dd, $J_{6'a,6'b}$ = 11.4 Hz, $J_{6'a,5'}$ = 7.5 Hz, 1H, H-6'a), 4.41 (dd, $J_{6'b,6'a}$ = 11.4 Hz, $J_{6'b,5'}$ = 5.4 Hz, 1H, H-6'b), 3.66 – 3.58 (m, 1H, H-1), 1.98 – 1.90 (m, 1H, Cy), 1.77 – 1.08 (m, 9H, Cy). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.1 (2xC=O), 165.6 (C=O), 165.6 (C=O), 133.5 (CH, Ar), 133.3 (CH, Ar), 133.15 (CH, Ar), 133.1 (CH, Ar), 129.9 (CH, Ar), 129.7 (CH, Ar), 129.7 (2xCH, Ar), 129.55 (C, Ar), 129.3 (C, Ar), 129.2 (C, Ar), 129.2 (C, Ar), 128.6 (CH, Ar), 128.4 (CH, Ar), 128.4 (CH, Ar), 128.2 (CH, Ar), 95.3 (C-1'), 77.2 (C-1), 69.4 (C-4'), 69.4 (C-2'), 68.6 (C-3'), 66.9 (C-5'), 62.9 (C-6'), 33.4 (CH_2, Cy), 31.6 (CH_2, Cy), 25.4 (CH_2, Cy), 23.9 (CH_2, Cy), 23.7 (CH_2, Cy). **HRMS:** *m/z* calcd for $C_{40}H_{38}O_{10}Na$: 701.2357; found:701.2350. $[\alpha]_D^{25}$ +130.1 (*c* 1.16, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 3064, 3020, 2935, 2857, 1719, 1264, 1093, 1068, 1025, 707.

Hexyl 2,3,4,6-tetra-*O*-benzoyl-D-galactopyranoside (8c)



According to the general glycosylation procedure C, compound **8c** was prepared from 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (**4**) (240 mg, 0.365 mmol, 1 equiv.) and 0,18 mL of 1-hexanol (1.46 mmol, 4 equiv.) to afford the desired glycoside (198 mg, 80%, α:β = 1:2.9) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1'α (5.44 ppm) and H-1'β (4.84 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

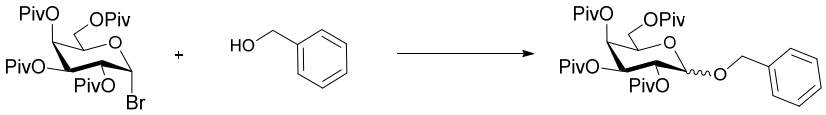
(8c-β): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 2H, Ar), 8.05 – 8.01 (m, 2H, Ar), 7.99 – 7.95 (m, 2H, Ar), 7.81 – 7.78 (m, 2H, Ar), 7.64 – 7.35 (m, 10H, Ar), 7.27 – 7.22 (m, 2H, Ar), 6.00 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 1.0 Hz, 1H, H-4'), 5.80 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.61 (dd, $J_{3',2'}$ = 10.4 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 4.81 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.70 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 6.5 Hz, 1H, H-6'a), 4.42 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.8 Hz, 1H, H-6'b), 4.33 (td, $J_{5',6'}$ = 6.6 Hz, $J_{5',4'}$ = 1.0 Hz, 1H, H-5'), 3.98 (dt, $J_{1'a,1'b}$ = 9.8 Hz, $J_{1a,2}$ = 6.2 Hz, 1H, H-1a), 3.57 (dt, $J_{1'b,1'a}$ = 9.8 Hz, $J_{1b,2}$ = 6.8 Hz, 1H, H-1b), 1.62 – 1.46 (m, 2H, H-2), 1.29 – 1.16 (m, 2H, H-3), 1.16 – 1.01 (m, 4H, H-4, H-5), 0.74 (t, $J_{6',5'}$ = 7.1 Hz, 3H, H-6). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0 (C=O), 165.6 (C=O), 165.5 (C=O), 165.2 (C=O), 133.5 (CH, Ar), 133.2 (CH, Ar), 133.2 (CH, Ar), 133.1 (CH, Ar), 130.0 (CH, Ar), 129.8 (CH, Ar), 129.7 (CH, Ar), 129.7 (CH, Ar), 129.4 (2xC, Ar), 129.0 (C, Ar), 128.7 (C, Ar), 128.6 (CH, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 101.7 (C-1'), 71.7 (C-3'), 71.2 (C-5'), 70.6 (C-1), 69.8 (C-2'), 68.1 (C-4'), 62.0 (C-6'), 31.4 (C-4), 29.3 (C-2), 25.4 (C-3), 22.4 (C-5), 13.9 (C-6). **HRMS:** *m/z* calcd for $C_{40}H_{40}O_{10}Na$: 703.2514; found: 703.2524. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +88.3 (*c* 1.10, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2931, 1727, 1267, 1095, 1070, 709.

(8c-α): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H, Ar), 8.05 – 7.97 (m, 4H, Ar), 7.83 – 7.77 (m, 2H, Ar), 7.65 – 7.34 (m, 10H, Ar), 7.28 – 7.22 (m, 2H, Ar), 6.04 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 1.0 Hz, 1H, H-4'), 6.01 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 5.68 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 3.7 Hz, 1H, H-2'), 5.42 (d, $J_{1',2'}$ = 3.7 Hz, 1H, H-1'), 4.67 – 4.57 (m, 2H, H-5', H-6'a), 4.41 (dd, $J_{6'b,6'a}$ = 10.8 Hz, $J_{6'b,5'}$ = 5.4 Hz, 1H, H-6'b), 3.80 (dt, $J_{1'a,1'b}$ = 9.8 Hz, $J_{1a,2}$ = 6.4 Hz, 1H, H-1a), 3.49 (dt, $J_{1'b,1'a}$ = 9.8 Hz, $J_{1b,2}$ = 6.6 Hz, 1H, H-1b), 1.66 – 1.54 (m, 2H, H-2), 1.36 – 1.24 (m, 2H, H-3), 1.24 – 1.12 (m, 4H, H-4, H-5), 0.80 (t, $J_{6',5'}$ = 7.1 Hz, 3H, H-6). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 166.0, 165.6, 165.6 (4 x C=O), 133.5 (CH, Ar), 133.3 (CH, Ar), 133.2 (CH, Ar), 133.1 (CH, Ar), 129.9 (CH, Ar), 129.8 (CH,

Ar), 129.7 (CH, Ar), 129.7 (CH, Ar), 129.5 (C, Ar), 129.2 (C, Ar), 129.2 (C, Ar), 129.2 (C, Ar), 128.6 (CH, Ar), 128.4 (CH, Ar), 128.4 (CH, Ar), 128.2 (CH, Ar), 96.5 (C-1'), 69.3 (C-2'), 69.2 (C-4'), 68.8 (C-1), 68.5 (C-3'), 66.8 (C-5'), 62.7 (C-6'), 31.4 (C-4), 29.3 (C-2), 25.7 (C-3), 22.5 (C-5), 13.9 (C-6). **HRMS:** *m/z* calcd for $C_{40}H_{40}O_{10}Na$: 703.2514; found: 703.2515. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +148.4 (*c* 1.3, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 3063, 2926, 2855, 1723, 1266, 1095, 1069, 709.

Benzyl 2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranoside (9a)

I. Method C. From **5**:



According to the general glycosylation procedure C, compound **9a** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.15 mL of benzyl alcohol (1.46 mmol, 4 equiv.) to afford **9a** (180 mg, 81%, α:β = 1:6.1) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1aβ (4.88 ppm) and H-5'α (4.32 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

I. Method D. From **6**:

According to the general glycosylation procedure D, compound **9a** was prepared from 2,3,4,6-tetra-O-pivaloyl-α-D-galactopyranosyl chloride (**6**) (195 mg, 0.365 mmol, 1 equiv.) and 0.15 mL (1.46 mmol, 4 equiv.) of benzyl alcohol to afford **9a** (170 mg, 77%, α:β = 1:4.9) as a colourless syrup. The α:β ratio of the product was calculated from the peak area ratio of H-1β (4.9 ppm) and H-5'α (4.32 ppm) in the ^{1}H NMR crude spectrum.

(9a-β):[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.40 (dd, $J_{4',3'}$ = 3.3 Hz, $J_{4',5'}$ = 0.8 Hz, 1H, H-4'), 5.30 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.08 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, 1H, H-3'), 4.88 (d, $J_{1a,1b}$ = 11.9 Hz, 1H, H-1a), 4.61 (d, $J_{1b,1a}$ = 11.9 Hz, 1H, H-1b), 4.58 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.21 (dd, $J_{6'a,6'b}$ = 11.0 Hz, $J_{6'a,5'}$ = 6.8 Hz, 1H, H-6'a), 4.05 (dd, $J_{6'b,6'a}$ = 11.0 Hz, $J_{6'b,5'}$ = 6.9 Hz, 1H, H-6'b), 3.96 (td, $J_{5',6'}$ = 6.8 Hz, $J_{5',4'}$ = 0.8 Hz, 1H, H-5'), 1.27 (s, 9H, Piv), 1.20 (s, 9H, Piv), 1.11 (s, 9H, Piv), 1.10 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 177.3, 176.9, 176.7 (4 x

C=O), 136.4 (C, Ar), 128.4 (CH, Ar), 128.0 (CH, Ar), 128.0 (CH, Ar), 99.6 (C-1'), 71.0 (C-3', C-5'), 70.5 (C-1), 68.7 (C-2'), 66.8 (C-4'), 61.3 (C-6'), 39.0 (C, Piv), 38.7 (C, Piv x3), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv).

(9a-α): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H, Ar), 5.53 – 5.48 (m, 2H, H-3', H-4'), 5.18 (d, $J_{1',2'}$ = 3.7 Hz, 1H, H-1'), 5.18 – 5.11 (m, 1H, H-2'), 4.73 (d, $J_{1a,1b}$ = 11.9 Hz, 1H, H-1a), 4.50 (d, $J_{1b,1a}$ = 11.9 Hz, 1H, H-1b), 4.32 (t, $J_{5',6'}$ = 6.8 Hz, 1H, H-5'), 4.10 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 7.3 Hz, 1H, H-6'a), 4.01 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.4 Hz, 1H, H-6'b), 1.26 (s, 9H, Piv), 1.20 (s, 9H, Piv), 1.14 (s, 9H, Piv), 1.12 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 177.7, 177.2, 176.9 (4 x C=O), 136.6 (C, Ar), 128.5 (CH, Ar, x2), 128.0 (CH, Ar), 128.0 (CH, Ar, x2), 95.1 (C-1'), 69.4 (C-1), 68.1(C-2'), 67.8(C-3'), 67.8(C-4'), 67.0 (C-5'), 61.8 (C-6'), 39.1 (C, Piv), 38.7 (3 x C, Piv), 27.2 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.0 (CH_3, Piv). **HRMS:** *m/z* calcd for $C_{33}H_{50}O_{10}Na$: 629.3296; found: 629.3301.

Cyclohexyl 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranoside (9b)

I. Method C. From **5**:

According to the general glycosylation procedure C, compound **9b** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.15 mL (1.46 mmol, 4 equiv.) of cyclohexanol to afford **9b** (142 mg, 65%, α:β = 1:19) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1'β (4.54 ppm) and H-5'α (4.29 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

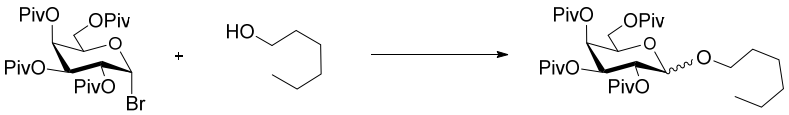
II. Method D. From **6**:

According to the general glycosylation procedure D, compound **9b** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl chloride (**6**) (134 mg, 0.365 mmol, 1 equiv.) and 0.15 mL (1.46 mmol, 4 equiv.) of cyclohexanol to afford **9b** (138 mg, 63%, α:β = 1:8.1) as a colourless

syrup. The α:β ratio of the product was calculated from the peak area ratio of H-1'β (4.60 ppm) and H-5'α (4.35 ppm) in the ^{1}H NMR crude spectrum.

(9b-β):[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.38 (dd, $J_{4',3'}$ = 3.3 Hz, $J_{4',5'}$ = 1.1 Hz, 1H, H-4'), 5.18 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 7.8 Hz, 1H, H-2'), 5.08 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, 1H, H-3'), 4.60 (d, $J_{1',2'}$ = 7.8 Hz, 1H, H-1'), 4.15 (dd, $J_{6'a,6'b}$ = 11.0 Hz, $J_{6'a,5'}$ = 7.0 Hz, 1H, H-6'a), 4.00 (dd, $J_{6'b,6'a}$ = 11.0 Hz, $J_{6'b,5'}$ = 6.6 Hz, 1H, H-6'b), 3.93 (td, $J_{5',6'}$ = 6.8 Hz, $J_{5',4'}$ = 1.1 Hz, 1H, H-5'), 3.60 – 3.50 (m, 1H, H-1), 1.98 – 1.15 (m, 10H, Cy), 1.25 (s, 9H, Piv), 1.17 (s, 9H, Piv), 1.15 (s, 9H, Piv), 1.10 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 177.3, 177.0, 176.6 (4 x C=O), 99.9 (C1), 78.4 (C-1), 71.2 (C-3'), 70.8 (C-5'), 68.9 (C-2'), 66.9 (C-4'), 61.5 (C-6'), 39.0 (C, Piv), 38.7 (C, Piv, x2), 38.7 (C, Piv), 33.5 (CH_2), 31.9 (CH_2), 27.2 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.0 (CH_3, Piv), 25.4 (CH_2), 24.1 (CH_2 x2). **HRMS:** *m*/*z* calcd for $C_{32}H_{54}O_{10}Na$: 621.3609; found: 621.3611.

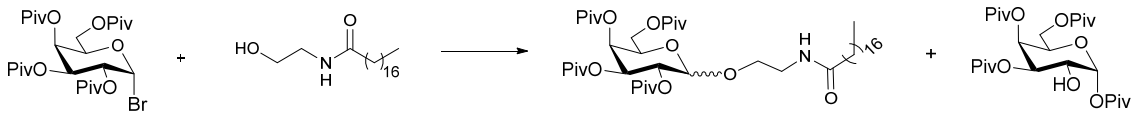
Hexyl 2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranoside (9c)



According to the general glycosylation procedure C, compound **9c** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.18 mL of 1-hexanol (1.46 mmol, 4 equiv.) to afford **9c** (132 mg, 60%, α:β = 1:19) as an amorphous colourless solid. The α:β ratio was calculated from the peak area ratio of H1'aβ (3.43 ppm) andH1'aα (3.34 ppm) in the ^{1}H NMR crude spectrum.

(9c-β): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dd, $J_{4',3'}$ = 3.3 Hz, $J_{4',5'}$ = 1.0 Hz, 1H, H-4'), 5.20 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 7.9 Hz, 1H, H-2'), 5.08 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, 1H, H-3'), 4.48 (d, $J_{1',2'}$ = 7.9 Hz, 1H, H-1'), 4.17 (dd, $J_{6'a,6'b}$ = 10.9 Hz, $J_{6'a,5'}$ = 6.7 Hz, 1H, H-6'a), 4.02 (dd, $J_{6'b,6'a}$ = 10.9 Hz, $J_{6'b,5'}$ = 7.1 Hz, 1H, H-6'b), 3.94 (td, $J_{5',6'}$ = 6.9 Hz, $J_{5',4'}$ = 1.1 Hz, 1H, H-5'), 3.89 – 3.80 (m, 1H, H-1a), 3.44 (dt, $J_{1'b,1'a}$ = 9.5 Hz, $J_{1b,2}$ = 7.0 Hz, 1H, H-1b), 1.63 – 1.49 (m, 2H, H-2), 1.25 (s, 9H, Piv), 1.21 – 1.35 (m, 6H, Hex), 1.17 (s, 9H, Piv), 1.15 (s, 9H, Piv), 1.10 (s, 9H, Piv), 0.86 (t, *J* = 6.9 Hz, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.9, 177.3, 176.9, 176.6 (4 x C=O), 101.4 (C-1'), 71.0 (C-3'), 70.8 (C-5'), 70.1 (C-1), 68.7 (C-2'), 66.8 (C-4'), 61.2 (C-6'), 39.0 (C, Piv), 38.7 (2x C, Piv), 38.7 (C, Piv), 31.6 (CH_2, Hex), 29.5 (C-2), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.0 (CH_3, Piv), 27.0 (CH_3, Piv), 25.6 (CH_2, Hex), 22.5 (CH_2, Hex), 14.0 (C-6). **HRMS:** *m*/*z* calcd for $C_{32}H_{56}O_{10}Na$: 623.3766; found: 623.3762. $[\alpha]_D^{25}$ +0.4 (*c* 1.02, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2962, 2935, 2872, 1737, 1138, 1075.

1-(2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranosyl)-*N*-octadecanoyl-2-aminoethanol (9d) and 1,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranose



According to the general glycosylation procedure C, compound **9d** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.478 g of N-(2-hydroxyethyl) estearaminde (1.46 mmol, 4 equiv.) to afford **9d** (117 mg, 39%, α:β = 1:5.3) as a waxy solid. The α:β ratio was calculated from the peak area ratio of H-3'α and H-4'β (5.41 ppm) and H-1aβ (3.84 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes. 1,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranose was obtained as a byproduct (22%).

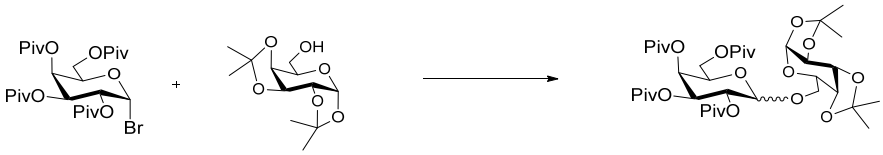
(9d-β): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (t, $J_{NH,2}$ = 5.3 Hz, 1H, NH), 5.41 (d, $J_{4',3'}$ = 3.3 Hz, 1H, H-4'), 5.20 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 7.8 Hz, 1H, H-2'), 5.11 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, 1H, H-3'), 4.52 (d, $J_{1',2'}$ = 7.8 Hz, 1H, H-1'), 4.16 (dd, $J_{6'a,6'b}$ = 10.8 Hz, $J_{6'a,5'}$ = 6.7 Hz, 1H, H-6'a), 4.07 – 3.94 (m, 2H, H-5', H-6'b), 3.87 – 3.80 (m, 1H, H-1a), 3.69 – 3.61 (m, 1H, H-1b), 3.49 – 3.41 (m, 2H, H-2), 2.20 – 2.10 (m, 2H, H-3), 1.68 – 1.55 (m, 2H, H-4), 1.27 (s, 9H, Piv), 1.34 – 1.21 (m, 28H, H-5 to H-18), 1.17 (s, 9H, Piv), 1.16 (s, 9H, Piv), 1.11 (s, 9H, Piv), 0.87 (t, $J_{19,18}$ = 6.8 Hz, 3H, H-19). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 177.2, 176.9, 176.8 (4 x C=O), 173.1 (N-C=O), 101.4 (C-1'), 71.2 (C-5'), 70.7 (C-3'), 69.0 (C-1), 68.8 (C-2'), 66.6 (C-4'), 61.1 (C-6'), 39.1 (C-2), 39.1 (C, Piv), 38.8 (C, Piv), 38.7 (C, Piv), 38.7 (C, Piv), 36.8 (C-3), 31.9 (CH_2), 29.7 (4 x CH_2), 29.7 (CH_2), 29.6 (2 x CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2 x CH_2), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.0 (2 x CH_3, Piv), 25.7 (C-4), 22.7 (CH_2), 14.1 (C-19). **HRMS:** *m/z* calcd for $C_{46}H_{83}NO_{11}Na$: 848.5858; found: 848.5846. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ -0.3 (*c* 1.27, $CHCl_3$). **FT-IR (ATR)** ν in cm^{-1}: 2924, 2854, 1741, 1279, 1143, 1075.

(9d-α): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, $J_{NH,2}$ = 5.4 Hz, 1H, NH), 5.49 – 5.41 (m, 2H, H-4', H-3'), 5.15 – 5.10 (m, 2H, H-2', H-1'), 4.25 (t, $J_{5',6'}$ = 6.8 Hz, 1H, H-5'), 4.09 (dd, $J_{6'a,6'b}$ = 11.2 Hz, $J_{6'a,5'}$ = 7.1 Hz, 1H, H-6'a), 4.00 (dd, $J_{6'b,6'a}$ = 11.2 Hz, $J_{6'b,5'}$ = 6.5 Hz, 1H, H-6'b), 3.79 – 3.71 (m, 1H, H-1a), 3.60 – 3.49 (m, 2H, H-1b, H-2a), 3.46 – 3.37 (m, 1H, H-2b), 2.19 – 2.14 (m, 2H, H-3), 1.68 – 1.58 (m, 2H, H-4), 1.35 – 1.22 (m, 28H, H-5 to H-18), 1.26 (s, 9H, Piv), 1.18 (s, 9H, Piv), 1.18 (s, 9H, Piv), 1.13 (s, 9H, Piv), 0.88 (t, $J_{19,18}$ = 6.9 Hz, 3H, H-19). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 177.6, 177.4, 176.9 (4 x C=O), 173.1 (N-C=O), 96.5 (C-1'), 68.1 (C-2'), 67.9 (C-1), 67.6 (C-3'), 67.5 (C-4'), 66.9

(C-5'), 61.7 (C-6'), 39.1 (C, Piv), 39.1 (C, Piv), 38.8 (C-2), 38.8 (C, Piv), 38.7 (C, Piv), 36.8 (C-3), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 27.2 (CH_3, Piv), 27.1 (2 x CH_3, Piv), 27.1 (CH_3, Piv), 25.7 (C-4), 22.7 (CH_2), 14.1 (C-19). **HRMS**: *m/z* calcd for $C_{46}H_{83}NO_{11}Na$: 848.5858; found: 848.5854. $[\alpha]_D^{25}$ = +49.9 (*c* 1.40, $CHCl_3$) **FT-IR (ATR)** ν in cm^{-1}: 2978, 2965, 2922, 2852, 1737, 1644, 1280, 1138, 1044.

1,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranose: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.28 (d, $J_{1,2}$ = 3.8 Hz, H-1), 5.48 (dd, $J_{4,3}$ = 3.2 Hz, $J_{4,5}$ = 1.3 Hz, H-4), 5.25 (dd, $J_{3,2}$ = 10.6 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 4.29 – 4.24 (app t, $J_{5,6}$ = 6.7 Hz, H-5), 4.15 (ddd, $J_{2,3}$ = 10.6 Hz, $J_{2,OH}$ = 8.6 Hz, $J_{2,1}$ = 3.8 Hz, H-2), 4.09 (dd, $J_{6a,6b}$ = 11.3 Hz, $J_{6a,5}$ = 7.3 Hz, H-6a), 3.99 (dd, $J_{6b,6a}$ = 11.3 Hz, $J_{6b,5}$ = 6.2 Hz, H-6b), 1.93 (d, $J_{OH,2}$ = 8.6 Hz, OH), 1.28 (s, 9H, Piv), 1.25 (s, 9H, Piv), 1.19 (s, 9H, Piv), 1.16 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.80, 177.85, 176.78, 176.52 (4 x C=O), 91.75 (C-1) , 70.59 (C-3), 69.26 (C-5), 67.34 (C-4), 67.20 (C-2), 61.45 (C-6), 39.33 (C, Piv), 39.08 (C, Piv), 38.94 (C, Piv), 38.68 (C, Piv), 27.14 (CH_3, Piv), 27.09 (CH_3, Piv), 27.04 (CH_3, Piv), 27.02 (CH_3, Piv). **HRMS**: *m/z* calcd for $C_{26}H_{44}O_{10}Na$: 539.2827; found: 539.2826. $[\alpha]_D^{25}$ +99.6 (*c* 1.00, $CHCl_3$) **FT-IR (ATR)** ν in cm^{-1}: 3505, 2974, 2935, 1739, 1281, 1144, 1093.

2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (9e)



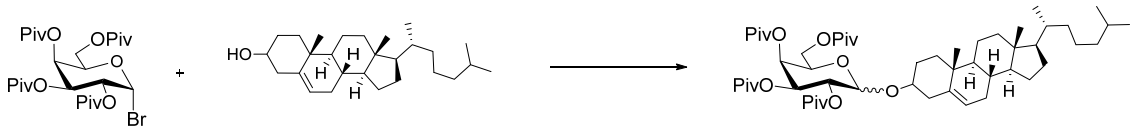
According to the general glycosylation procedure C, compound **9e** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.380 g (1.46 mmol, 4 equiv.) of 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose to afford **9e** (129 mg, 47%, α:β = 1:4) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-2'α and H-3'α (5.41 ppm) and H-4'β (5.38 ppm) in the ^{1}H NMR crude spectrum. A small fraction of the products was purified by column chromatography for characterization purposes.

(9e-β):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (d, $J_{1,2}$ = 4.9 Hz, 1H, H-1), 5.40 (dd, $J_{4',3'}$ = 3.4 Hz, $J_{4',5'}$ = 0.9 Hz, 1H, H-4'), 5.23 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 8.0 Hz, 1H, H-2'), 5.10 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.4 Hz, 1H, H-3'), 4.58 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1'), 4.57 (dd, $J_{3,4}$ = 7.9 Hz, $J_{3,2}$ = 2.4 Hz, 1H, H-3), 4.27 (dd, $J_{2,1}$ = 4.9 Hz, $J_{2,3}$ = 2.4 Hz, 1H, H-2), 4.21 (dd, $J_{4,3}$ = 7.9 Hz, $J_{4,5}$ = 1.9 Hz, 1H, H-4), 4.18 (dd, $J_{6'a,6'b}$ = 10.5 Hz, $J_{6'a,5'}$ = 6.1 Hz, 1H, H-6'a), 4.04 – 3.92 (m, 4H, H-6'b, H-5', H-6a, H-5), 3.65 (dd,

$J_{6b,6a}$ = 10.8 Hz, $J_{6b,5}$ = 6.7 Hz, 1H, H-6b), 1.50 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.26 (s, 9H, Piv), 1.18 (s, 9H, Piv), 1.17 (s, 9H, Piv), 1.11 (s, 9H, Piv). **HRMS:** *m*/*z* calcd for $C_{38}H_{62}NO_{15}Na$: 781.3981; found: 781.3974.

(9e-α): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (m, 3H, H-1, H-4', H-3'), 5.15 (dd, $J_{2',3'}$ = 10.1 Hz, $J_{2',1'}$ = 3.7 Hz, 1H, H-2'), 5.11 (d, $J_{1',2'}$ = 3.7 Hz, 1H, H-1'), 4.61 (dd, $J_{3,4}$ = 7.9 Hz, $J_{3,2}$ = 2.4 Hz, 1H, H-3), 4.32 – 4.28 (m, 1H, H-2, H-5'), 4.24 (dd, $J_{4,3}$ = 7.9 Hz, $J_{4,5}$ = 1.9 Hz, 1H, H-4), 4.09 (dd, $J_{6'a,6'b}$ = 11.1 Hz, $J_{6'a,5'}$ = 7.0 Hz, 1H, H-6'a), 4.01 (dd, $J_{6'b,6'a}$ = 11.1 Hz, $J_{6'b,5'}$ = 6.9 Hz, 1H, H-6'b), 3.98 – 3.93 (m, 1H, H-5), 3.75 (dd, $J_{6a,6b}$ = 9.7 Hz, $J_{6a,5}$ = 5.9 Hz, 1H, H-6a), 3.66 (dd, $J_{6b,6a}$ = 9.7 Hz, $J_{6b,5}$ = 7.4 Hz, 1H, H-6b), 1.56 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.25 (s, 9H, Piv), 1.19 (s, 9H, Piv), 1.18 (s, 9H, Piv), 1.12 (s, 9H, Piv). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 177.7, 177.3, 176.9 (4 x C=O), 109.2 (C, isopropyl), 108.6 (C, isopropyl), 96.4 (C-1'), 96.3 (C-1), 70.7 (C-4), 70.5 (C-2, C-3), 68.05 (C-2'), 67.7 (C-4', C-3'), 66.8 (C-5'), 66.6 (C-6), 66.0 (C-5), 61.4 (C-6'), 39.1 (C, Piv), 38.8 (C, Piv), 38.7 (C, Piv), 38.7 (C, Piv), 27.2 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 27.1 (CH_3, Piv), 26.2 (CH_3, isopropyl), 26.0 (CH_3, isopropyl), 24.9 (CH_3, isopropyl), 24.5 (CH_3, isopropyl). **HRMS:** *m*/*z* calcd for $C_{38}H_{62}O_{15}Na$: 781.3981; found: 781.3976. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +29.3 (*c* 0.50, $CHCl_3$) **FT-IR (ATR)** ν in cm^{-1}: 2961, 2922, 1737, 1280, 1257, 1211, 1138, 1071, 1045.

Cholesteryl 2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranoside (9f)

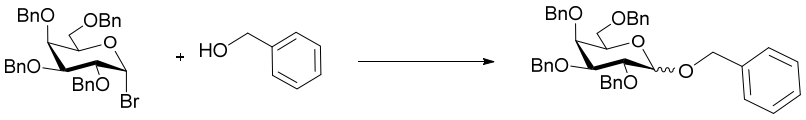


According to the general glycosylation procedure C, compound **9f** was prepared from 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.) and 0.564 g of cholesterol (1.46 mmol, 4 equiv.) to afford **9f** (180 mg, 56%, α:β = 1:11.5) as a colourless solid. The α:β ratio of the product was calculated from the peak area ratio of H-1'β (4.60 ppm) and H-5'α (4.36 ppm) in the ^{1}H NMR crude spectrum.

(9f-β):[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.39 (dd, $J_{4',3'}$ = 3.3 Hz, $J_{4',5'}$ = 0.9 Hz, 1H, H-4'), 5.32 (d, *J* = 5.0 Hz, 1H, H-chol), 5.19 (dd, $J_{2',3'}$ = 10.5 Hz, $J_{2',1'}$ = 7.9 Hz, 1H, H-2'), 5.09 (dd, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, 1H, H-3'), 4.61 (d, $J_{1',2'}$ = 7.9 Hz, 1H, H-1'), 4.16 (dd, $J_{6'a,6'b}$ = 10.9 Hz, $J_{6'a,5'}$ = 6.8 Hz, 1H, H-6'a), 4.01 (dd, $J_{6'b,6'a}$ = 10.9 Hz, $J_{6'b,5'}$ = 6.8 Hz, 1H, H-6'b), 3.98 – 3.92 (m, 1H, H-5'), 3.52 – 3.42 (m, 1H, H-1), 2.24 (d, *J* = 6.9 Hz, 2H, chol), 2.04 – 1.76 (m, 5H, chol), 1.66 – 0.83 (m, 69H, 4 x Piv, chol), 0.71 – 0.63 (m, 3H, chol). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9 (C=O), 177.3 (C=O), 177.0

(C=O), 176.6 (C=O), 140.3 (C=C), 122.0 (CH=C), 100.1 (C-1'), 80.0 (C-1), 71.1 (C-3'), 70.8 (C-5'), 68.8 (C-2'), 66.8 (C-4'), 61.4 (C-6'), 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 39.0, 38.9, 38.73, 38.72, 38.68, 37.1, 36.7, 36.1, 35.8, 31.9, 31.8, 29.6, 28.2, 28.0, 27.2, 27.13, 27.07, 27.04, 24.2, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8. **HRMS:** *m/z* calcd for $C_{53}H_{88}O_{11}Na$: 907.6270; found: 907.6269.

Benzyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10a)



According to the general glycosylation procedure E, compound **10a** was prepared from 220 mg of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide (**7**) (0.365 mmol, 1 equiv.) and 0.15 mL of benzyl alcohol (1.46 mmol, 4 equiv.) to afford **10a** (178 mg, 77%, α:β = 2.2:1) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1'α (5.03 ppm) and H-4'β (3.89 ppm) in the ^{1}H NMR crude spectrum. Spectroscopic data were in agreement with those reported.

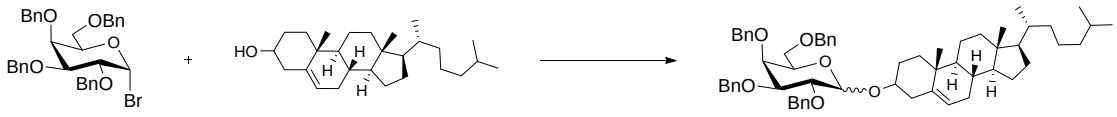
10a:[11] **^{1}H NMR** (400 MHz, DMSO-D6) δ 7.41 – 7.21 (m, 80H, Ar), 5.01 (d, $J_{1,2}$ = 3.4 Hz, 2.2H, H-1α), 4.82 – 4.41 (m, 33H, H-1'β, -C<u>H$_2$</u>Ph), 4.06 (d, $J_{4,3}$ = 1.8 Hz, 2.2H, H-4α), 3.99-3.92 (m, 4.4H, H-3α, H-5α), 3.90 (d, $J_{4,3}$ = 2.9 Hz, 1H, H-4β), 3.85 (dd, $J_{2,3}$ = 10.1 Hz, $J_{2,1}$ = 3.4 Hz, 2.2H, H-2α), 3.73 (t, $J_{5,6}$ = 6.5 Hz, 1H, H-5β), 3.66 (dd, $J_{3,2}$ = 9.7 Hz, $J_{3,4}$ = 2.9 Hz, 1H, H-3β), 3.62 – 3.45 (m, 7.4H, H-6α, H-6β, H-2β).**^{13}C NMR** (100 MHz, DMSO-D6) δ 139.0 (C-α, Ar), 138.8 (C-α, Ar), 138.8 (C-α, Ar), 138.8 (2xC-β, Ar), 138.7 (C-β, Ar), 138.2 (C-α, Ar), 138.2 (C-β, Ar), 137.84 (C-α, Ar), 137.8 (C-β, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.1 (CH, Ar), 128.1 (CH, Ar), 128.0 (CH, Ar), 127.8 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 127.6 (CH, Ar), 127.6 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.4 (CH, Ar), 127.3 (CH, Ar), 127.3 (CH, Ar), 127.2 (CH, Ar), 102.0 (C-1β), 96.0 (C-1α), 81.3 (C-3β), 79.0 (C-2β), 78.1, 75.8, 75.0, 74.1, 74.1, 74.1, 73.8, 72.6, 72.4, 71.6, 70.0, 69.1, 68.8, 68.6, 68.4.

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10b)

According to the general glycosylation procedure E, compound **10b** was prepared from 222 mg of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide (**7**) (0.368 mmol, 1 equiv.) and 0.16 mL of cyclohexanol (1.47 mmol, 4 equiv.) to afford **10b** (157 mg, 69%, α:β = 1.9:1) as a colourless syrup. The α:β ratio was calculated from the peak area ratio of H-1'α (5.03 ppm) and H-4'β (3.89 ppm) in the ^{1}H NMR crude spectrum.

10b:[12] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 57.2H, Ar), 5.03 (d, $J_{1',2'}$ = 3.7 Hz, 1.8H, H-1'α), 5.01 – 4.39 (m, 23.9H, H-1'β, -C<u>H</u>$_2$Ph), 4.10 – 3.96 (m, 7.4H, H-2'α, H-3'α, H-4'α, H-5'α), 3.89 (d, $J_{4',3'}$ = 2.5 Hz, 1H, H-4'β), 3.82 (dd, $J_{2',3'}$ = 9.7 Hz, $J_{2',1'}$ = 7.8 Hz, 1H, H-2'β), 3.70 (m, 1H, H-1β), 3.62 – 3.50 (m, 9.6H, H-1α, H-3'β, H-5'β, H-6'α, H-6'β), 2.04 – 1.15 (m, 28.6H, Cy). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.9 (C-α, Ar), 138.8 (C-β, Ar), 138.7 (2xC-α, Ar), 138.6 (C-β, Ar), 138.6 (C-β, Ar), 138.0 (C-α, Ar), 137.9 (C-β, Ar), 128.4 (CH, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.1 (CH, Ar), 127.9 (CH, Ar), 127.8 (CH, Ar), 127.7 (CH, Ar), 127.6 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.4 (CH, Ar), 127.3 (CH, Ar), 102.1 (C-1'β), 95.4(C-1'α), 82.4, 79.5, 79.1, 76.5, 75.3, 75.1, 75.1, 74.7, 74.4, 73.5, 73.5, 73.3, 73.1, 73.1, 73.0, 69.1, 69.1, 69.0, 33.7 (CH_2β, Cy), 33.3 (CH_2α, Cy), 31.8 (CH_2β, Cy), 31.5 (CH_2α, Cy), 25.6 (CH_2β, Cy), 25.6 (CH_2α, Cy), 24.5 (CH_2α, Cy), 24.2 (CH_2α, Cy), 24.1 (CH_2β, Cy), 23.9 (CH_2β, Cy).

Cholesteryl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10f)

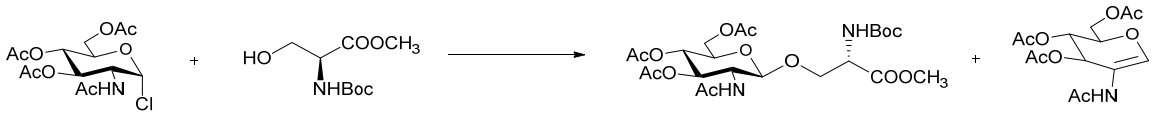


According to the general glycosylation procedure E, compound **10f** was prepared from 221 mg of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide (**7**) (0.366 mmol, 1 equiv.) and 0.564 g of Cholesterol (1.46 mmol, 4 equiv.) to afford **10f** (162 mg, 49%, α:β = 1.4:1) as a yellowish solid. The α:β ratio was calculated from the peak area ratio of C=C<u>H</u>β (5.34 ppm) and C=C<u>H</u>α (5.28 ppm) in the ^{1}H NMR crude spectrum.

10f:[13] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 48H, Ar), 5.34 (d, *J* = 5.1 Hz, 1H, C=C<u>H</u>β, Chol), 5.28 (d, *J* = 4.9 Hz, 1.4H, C=C<u>H</u>α, Chol), 5.00 (d, $J_{1',2'}$ = 3.7 Hz, 1.4H, H-1'α), 4.99 – 4.38 (m, 20.2H, , H-1'β, -C<u>H</u>$_2$Ph), 4.10 – 3.94 (m, 4.2H, H-2'α, H-3'α, H-5'α), 3.88 (d, $J_{4',3'}$ = 2.5 Hz, 1H, H-4'β), 3.82 (dd, $J_{2',3'}$ = 9.7 Hz, $J_{2',1'}$ = 7.8 Hz, 1H, H-2'β), 3.62 – 3.45 (m, 9.2H, H-1α, H-1β, H-3'β, H-5'β, H-6'α, H-6'β,), 2.49 – 2.25 (m, 4.8H, Chol), 2.07 – 1.78 (m, 14.4H, Chol), 1.71 – 0.84 (m, 76.8H, Chol), 0.69 (s, 7.2H, Chol). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.9 (<u>C</u>=CH, Chol), 140.7 (<u>C</u>=CH, Chol), 138.9

(C, Ar), 138.7 (C, Ar), 138.7 (C, Ar), 138.6 (C, Ar), 138.5 (C, Ar), 138.0 (C, Ar), 137.9 (C, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 128.1 (CH, Ar), 128.1 (CH, Ar), 127.9 (CH, Ar), 127.8 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 127.6 (CH, Ar), 127.6 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.5 (CH, Ar), 127.4 (CH, Ar), 127.4 (CH, Ar), 121.7 (C=CH, Chol), 121.6 (C=CH, Chol), 102.4 (C-1'β), 95.4 (C-1'α), 82.4, 79.6, 79.4, 79.2, 76.6, 76.4, 75.3, 75.1, 74.7, 74.4, 73.5, 73.4, 73.3, 73.3, 73.2, 73.0, 69.2, 69.1, 69.0, 56.7, 56.1, 50.1, 50.1, 42.3, 39.8, 39.7, 39.5, 39.0, 37.3, 37.1, 36.7, 36.1, 35.8, 31.9, 31.8, 29.8, 28.2, 28.0, 27.6, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8.

3-*O*-(3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-*N*-(*tert*-butyloxycarbonyl)-L-Serine methyl ester (12) and 2-acetamido-3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol 12'



11 **12** **12'**

According to the general glycosylation procedure C, compound **12** was prepared from 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride (**11**) (133 mg, 0.365 mmol, 1 equiv.) and 320 mg (1.46 mmol, 4 equiv.) of *N*-(*tert*-butoxycarbonyl)-L-serine methyl ester to afford 122 mg of an inseparable mixture of **12** (54%) and **12'** (12:12' = 4:1) as a yellowish solid. The yield is referred to compound **12**.

Spectroscopic data extracted from the mixture:

12: **^{1}H NMR** (400 MHz, CD_3OD) δ 5.22 (dd, $J_{4',5'}$ = 10.5 Hz, $J_{4',3'}$ = 9.4 Hz, 0.8H, H-4'), 4.98 (dd, $J_{3',2'}$ = 9.9 Hz, $J_{3',4'}$ = 9.4 Hz, 0.8H, H-3'), 4.68 (d, $J_{1',2'}$ = 8.5 Hz, 0.8H, H-1'), 4.35 (t, $J_{2,1}$ = 4.5 Hz, 0.8H, H-2), 4.29 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{6'a,5'}$ = 4.6 Hz, 0.8H, H-6'a), 4.16 – 4.07 (m, 1.6H, H-6'b, H-1a), 3.85 – 3.78 (m, 2.4H, H-2', H-5', H-1b), 3.73 (s, 2.4H, OMe), 2.07 (s, 2.4H, Ac), 2.00 (s, 2.4H, Ac), 1.98 (s, 2.4H, Ac), 1.94 (s, 2.4H, Ac), 1.45 (s, 7.2H, Boc). **^{13}C NMR** (100 MHz, CD_3OD) δ 173.6 (N-C=O), 172.3 (C=O), 172.1 (C=O), 171.6 (C=O), 157.6 (C=O, Boc), 102.0 (C-1'), 80.9 (C, Boc), 73.8 (C-4'), 73.0 (C-5'), 70.2 (C-1), 70.0 (C-3'), 63.1 (C-6'), 55.2 (C-2'), 55.2 (C-2), 52.9 (OCH_3), 28.7 (CH_3, Boc), 22.9 (CH_3, Ac), 20.7 (CH_3, Ac), 20.6 (CH_3, Ac), 20.6 (CH_3, Ac).

12': **^{1}H NMR** (400 MHz, CD_3OD) δ 6.88 (d, $J_{1,3}$ = 0.8 Hz, 0.2H, H-1), 5.57 (dt, $J_{3,4}$ = 4.9 Hz, $J_{3,1}$ = 0.8 Hz, 0.2H, H-3), 5.19 (dd, $J_{4,5}$ = 6.5 Hz, $J_{4,3}$ = 4.9 Hz, 0.2H, H-4), 4.50 – 4.45 (m, 0.2H, H-6a), 4.43 –

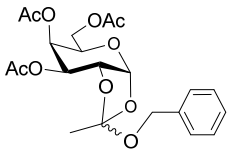
4.37 (m, 0.2H, H-5), 4.20 (dd, $J_{6b,6a}$ = 11.9 Hz, $J_{6b,5}$ = 3.1 Hz, 0.2H, H-6b), 2.06 (s, 0.6H, Ac), 2.06 (s, 0.6H, Ac), 2.04 (s, 0.6H, Ac), 1.96 (s, 0.6H, Ac). **^{13}C NMR** (100 MHz, CD_3OD) δ 173.2 (N-C=O), 172.1 (C=O), 171.9 (C=O), 171.2 (C=O), 143.8 (C-1), 112.3 (C-2), 75.1 (C-5), 68.7 (C-4), 68.5 (C-3), 62.2 (C-6), 22.7 (CH_3, Ac), 20.8 (CH_3, Ac), 20.7 (CH_3, Ac), 20.6 (CH_3, Ac).

HRMS found from the mixture:

HRMS **12**: *m*/*z* calcd for $C_{23}H_{37}N_2O_{13}$: 549.2290; found: 549.2288.

HRMS **12'**: *m*/*z* calcd for $C_{14}H_{19}NO_8Na$: 352.1003; found: 352.0995.

3,4,6-tri-*O*-acetyl-1,2-*O*-(1-benzyloxyethylidene)-α-D-galactopyranose (13a)

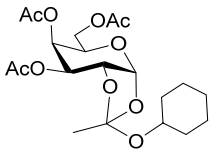


According to the general orthoester synthesis procedure F, compound **13a** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.), 0.11 mL of benzyl alcohol (1.1 mmol, 3 equiv.) and 0.13 mL of 2.6-lutidine (1.1 mmol, 3 equiv.) to afford **13a** (138 mg, 81%, *endo*:*exo* = 1:4.9) as a yellowish syrup. The *endo*:*exo* ratio of the product was calculated from the peak area ratio of H-1'$_{exo}$ (5.77 ppm) and H-1'$_{endo}$ (5.65 ppm) in the ^{1}H NMR crude spectrum.

13a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 5H, Ar), 5.79 (d, $J_{1exo-2exo}$ = 4.8 Hz, 0.83H, H-1'$_{exo}$), 5.64 (d, $J_{1'endo-2'endo}$ = 5.1 Hz, 0.17H, H-1'$_{endo}$), 5.41 – 5.34 (m, 1.17H, H-3'$_{endo}$, H-4'$_{exo}$, H-4'$_{endo}$), 5.03 (dd, $J_{3endo-4endo}$ = 6.7 Hz, $J_{3'endo-2'endo}$ = 3.4 Hz, 0.83H, H-3'$_{endo}$), 4.66 (d, *J* = 11.5 Hz, 1H, H-1a$_{endo}$), 4.58 (d, *J* = 11.5 Hz, 0.17H, H-1b$_{endo}$), 4.54 (d, *J* = 11.0 Hz, 0.83H, H-1a$_{exo}$), 4.50 (d, *J* = 11.1 Hz, 0.83H, endoH-1b$_{exo}$), 4.32 – 4.25 (m, 1H), 4.21 – 3.96 (m, 1H), 2.05 (s, 3H, Ac$_{endo}$, Ac$_{exo}$), 2.01 (s, 2.49H, Ac$_{exo}$), 2.00 (s, 3H, Ac$_{endo}$, Ac$_{exo}$), 1.97 (s, 0.51H, Ac$_{endo}$), 1.69 (s, 2.49H, $CH_{3\,exo}$), 1.59 (s, 0.51H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.51 (C=O, exo), 170.44 (C=O, endo), 170.09 (C=O, exo), 169.92 (C=O, endo), 169.89 (C=O, endo), 169.82 (C=O, exo), 137.39 (C, Ar, endo, exo), 128.44 (CH, Ar, endo, exo), 127.80 (CH, Ar, endo), 127.71 (CH, Ar, exo), 127.69 (CH, Ar, endo), 127.61 (CH, Ar, exo), 122.09 (C-orthoester, endo), 121.35 (C-orthoester, exo), 97.63 (C-1', endo), 97.56 (C-1', exo), 74.00 (C-2', endo), 73.92 (C-2', exo), 71.69 (C-3', endo), 71.43 (C-3', exo), 69.24 (C-5', endo), 69.14 (C-5', exo), 66.23 (C-4', endo), 65.95 (C-4', exo), 65.67 (C-1, endo), 65.05 (C-1, exo), 61.41 (C-6', exo), 61.36 (C-6', endo), 23.96 (CH_3, exo), 23.47 (CH_3, exo), 20.78 (2xAc, exo,

endo), 20.76 (Ac, exo), 20.74 (Ac, endo), 20.65 (Ac, endo), 20.61 (Ac, exo). **HRMS:** *m*/*z* calcd for $C_{21}H_{26}O_{10}Na$: 461.1418; found: 461.1412. **FT-IR (ATR)** ν in cm^{-1}: 3005, 2941, 2875, 1745, 1214, 1152, 1075, 1019, 733, 700.

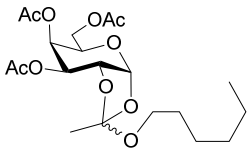
3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyclohexyloxyethylidene)-α-D-galactopyranose (13b)



According to the general orthoester synthesis procedure F, compound **13b** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.), 0,12 mL of cyclohexanol (1.1 mmol, 3 equiv.) and 0.13 mL of 2.6-lutidine (1.1 mmol, 3 equiv.) to afford **13b** (138 mg, 89%, *endo*:*exo* = 1:32.3) as a yellowish syrup. The *endo*:*exo* ratio was calculated from the peak area ratio of H-1'$_{exo}$ (5.77 ppm) and H-1'$_{endo}$ (5.65 ppm) in the ^{1}H NMR crude spectrum.

13b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (d, $J_{1',2'}$ = 4.9 Hz, 1H, H-1'), 5.41 (dd, $J_{4',3'}$ = 3.5 Hz, $J_{4',5'}$ = 2.4 Hz, 1H, H-4'), 5.05 (dd, $J_{3',2'}$ = 6.8 Hz, $J_{3',4'}$ = 3.5 Hz, 1H, H-3'), 4.33-4.29 (m, 1H, H-5'), 4.29 (dd, $J_{2',3'}$ = 6.8 Hz, $J_{2',1'}$ = 4.9 Hz, 1H, H-2'), 4.16 (dd, $J_{6'a,6'b}$ = 11.7 Hz, $J_{6'a,5'}$ = 7.0 Hz, 1H, H-6'a), 4.11 (dd, $J_{6'b,6'a}$ = 11.5 Hz, $J_{6'b,5'}$ = 6.6 Hz, 1H, H-6'b), 3.64 – 3.55 (m, 1H, H-1), 2.11 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.06 (s, 3H, Ac), 1.68 (s, 3H, CH_3), 1.88 – 1.09 (m, 10H, Cy). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.8 (3 x C=O), 121.0 (C-orthoester), 97.4 (C-1'), 73.1 (C-2'), 72.2 (C-1), 71.3 (C-3'), 68.9 (C-5'), 65.9 (C-4'), 61.5 (C-6'), 33.9 (C-2, CH_2, Cy), 33.9 (C-3, CH_2, Cy), 25.3 (CH_2, Cy), 24.4 (CH_2, Cy), 24.4 (CH_2, Cy), 24.1 (CH_3), 20.8 (CH_3, Ac), 20.7 (CH_3, Ac), 20.6 (CH_3, Ac).

3,4,6-tri-*O*-acetyl-1,2-*O*-(1-hexyloxyethylidene)-α-D-galactopyranose (13c)



According to the general orthoester synthesis procedure F, compound **13c** was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) (150 mg, 0.365 mmol, 1 equiv.), 0.14 mL of hexanol (1.1 mmol, 3 equiv.) and 0.13 mL of 2,6-lutidine (1.1 mmol, 3 equiv.) to afford **13c**

(129 mg, 82%, *endo*:*exo* = 1:4) as a yellowish syrup. The endo:exo ratio was calculated from the peak area ratio of H-1'$_{exo}$ (5.77 ppm) and H-1'$_{endo}$ (5.65 ppm) in the ^{1}H NMR crude spectrum.

13c: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.77 (d, $J_{1exo,2exo}$ = 4.8 Hz, 0.8H, H-1'$_{exo}$), 5.65 (d, $J_{1endo,2endo}$ = 5.2 Hz, 0.2H, H-1'$_{endo}$), 5.42 – 5.38 (m, 1H, H-4'$_{exo}$, H-4'$_{endo}$), 5.36 (dd, $J_{3endo,2endo}$ = 6.9 Hz, $J_{3endo,4endo}$ = 3.4 Hz, 0.2H, H-3'$_{endo}$), 5.03 (dd, $J_{3exo,2exo}$ = 6.5 Hz, $J_{3exo,4exo}$ = 3.5 Hz, 0.8H, H-3'exo), 4.34 – 4.26 (m, 1.8H, H-5'$_{exo}$, H-5'$_{endo}$, H-2'$_{exo}$), 4.19 (dd, $J_{2endo,3endo}$ = 6.9 Hz, $J_{2endo,1endo}$ = 5.2 Hz, 0.2H, H-2'$_{endo}$), 4.17 – 4.04 (m, 2H, H-6'$_{exo}$, H-6'$_{endo}$), 3.60 – 3.51 (m, 0.8H, H-6a$_{exo}$), 3.50 – 3.42 (m, 1.2H, H-6b$_{exo}$, H-6$_{endo}$), 2.09 (s, 0.6H, Ac$_{endo}$), 2.08 (s, 2.4H, Ac$_{exo}$), 2.04 (s, 2.4H, Ac$_{exo}$), 2.04 (s, 2.4H, Ac$_{exo}$), 2.03 (s, 0.6H, Ac$_{endo}$), 2.01 (s, 0.6H, Ac$_{endo}$), 1.63 (s, 2.4H, CH$_{3exo}$), 1.59 (s, 0.6H, CH$_{3endo}$), 1.57 – 1.46 (m, 2H, H-2$_{endo}$, H-2$_{exo}$), 1.37 – 1.23 (m, 6H, H-3$_{endo}$, H-3$_{exo}$, H-4$_{endo}$, H-4$_{exo}$, H-5$_{endo}$, H-5$_{exo}$), 0.92 – 0.86 (m, 3H, H-6$_{endo}$, H-6$_{exo}$). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ 170.7 (C=O$_{exo}$), 170.7 (C=O$_{endo}$), 170.3 (C=O$_{exo}$, C=O$_{endo}$), 170.2 (C=O$_{endo}$), 170.2 (C=O$_{exo}$), 122.0 (C-Orthoester$_{endo}$), 121.7 (C-Orthoester$_{exo}$), 98.3 (C-1'$_{endo}$), 97.8 (C-1'$_{exo}$), 74.5 (C-2'$_{exo}$), 73.8 (C-2'$_{endo}$), 72.1 (C-3'$_{endo}$), 71.7 (C-3'$_{exo}$), 69.5 (C-5'$_{exo}$), 69.5 (C-5'$_{endo}$), 66.6 (C-4'$_{endo}$), 66.4 (C-4'$_{exo}$), 64.0 (C-1$_{endo}$), 63.1 (C-1$_{exo}$), 62.1 (C-6'$_{endo}$), 62.0 (C-6'$_{exo}$), 32.0 (CH$_{2endo}$), 32.0 (CH$_{2exo}$), 29.9 (C-2$_{exo}$), 29.9 (C-2$_{endo}$), 26.2 (CH$_{2exo}$), 26.1 (CH$_{2endo}$), 24.1 (CH$_{3exo}$), 23.3 (CH$_{3endo}$), 23.0 (CH$_{2exo}$), 23.0 (CH$_{2endo}$), 20.9 (CH$_3$, Ac$_{exo}$, Ac$_{endo}$), 20.9 (CH$_3$, Ac$_{exo}$), 20.9 (CH$_3$, Ac$_{endo}$), 20.8 (CH$_3$, Ac$_{endo}$), 20.8 (CH$_3$, Ac$_{exo}$), 14.2 (C-6$_{endo}$, C-6$_{exo}$). **HRMS:** *m*/*z* calcd for $C_{38}H_{62}NO_{15}Na$: 455.1888; found: 455.1890.

Study of solvent relevance in the glycosylation.

Glycosylation with different solvents in a schlenck flask (Table 2, entries 2-6)

A solution of 85 mg of 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (0.146 mmol, 1 equiv.) and 61 µL of benzyl alcohol (0.584 mmol, 4 equiv.) in 10 mL of the corresponding solvent, was introduced in a schlenk flask containing ca. 40 mg of activated 4Å MS. The mixture was stirred at 60 ^{o}C over 20 h and it was then allowed to cool at room temperature, concentrated *in vacuo* and the residue was directly analysed by ^{1}H NMR for the conversion determination.

Glycosylation promoted by microwave irradiation (Table 2, entry 7)

A solution of 17 mg of 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (0.03 mmol, 1 equiv.) and 12 µL of benzyl alcohol (0.584 mmol, 4 equiv.) in 2 mL of toluene, was introduced in a microwave tube. The mixture was stirred at 60 ^{o}C and 100 W over 2

h. Once it was cooled at room temperature, the solvent was concentrated *in vacuo* and the residue was directly analysed by ^{1}H NMR for the conversion determination.

Glycosylation in reactor using DCM as solvent (Table 2, entry 8)

The reactor was charged with ca. 100 mg of activated 4Å MS and connected to vacuum for 1h. Then, a solution of 85 mg of 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (0.146 mmol, 1 equiv.) and 61 µL of benzyl alcohol (0.584 mmol, 4 equiv.) in 10 mL of DCM, was introduced inside the reactor by suction. The mixture was stirred at 60 ^{o}C over 20 h. Then it was allowed to cool at room temperature, concentrated *in vacuo* and the residue was directly analysed by ^{1}H NMR for the conversion determination.

Study of the relevance of the gas nature or supercritical conditions in the glycosylation reaction.

Glycosylation in *sc*Ar (Table 3, entry 2)

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.), 0.15 mL of cyclohexanol (1.46 mmol, 4 equiv.) and ca. 100 mg of 4Å MS were introduced to the reactor (25 mL Parr Reactor) and it was quickly sealed. The reactor was purged with Ar, charged with Ar until reaching the pressure of ca. 800 Psi and it was heated with a heating mantle at 60 ^{o}C. Once it reached the temperature, argon was introduced carefully to the reactor from the Ar cylinder to ca. 1500 Psi. After stirring the reaction mixture at 60 ^{o}C and 1500 Psi for 24 h, the reactor was cooled to 0 ^{o}C and the compressed Ar was then slowly leaked out. The residual solid in the reactor was washed out with ethyl acetate and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^{1}H NMR for the determination of the conversion.

Glycosylation in subcritical CO_2 (Table 3, entry 3)

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.), 0.15 mL of cyclohexanol (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr Reactor) which was quickly sealed. It was then purged with CO_2, charged with CO_2 from the cylinder until reaching the pressure of ca. 650 Psi and heated with a heating mantle at 60 ^{o}C. Once the temperature was reached, the CO_2 pressure was 700 Psi. The start of the reaction is defined as the time at which the temperature reaches 60 ^{o}C.

After stirring the reaction mixture at 60 ^{o}C and 700 Psi for 24 h, the reactor was cooled to 0 ^{o}C and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with ethyl acetate and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^{1}H NMR for the conversion determination.

Glycosylation under neat conditions in a schlenk flask (Table 3, entry 4)

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.), 154 µL of cyclohexanol (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were introduced in a schlenk under inert atmosphere. After stirring at 60 ^{o}C for 24 h, the reaction mixture was cooled to room temperature and the residual solid in the schlenck flask was washed out with ethyl acetate and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^{1}H NMR for the determination of the conversion.

Glycosylation under neat conditions in the reactor (Table 3, entry 5)

2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.), 0.15 mL of cyclohexanol (1.46 mmol, 4 equiv.) and 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr reactor). After stirring the reaction mixture at 60 ^{o}C for 24 h, it was cooled to room temperature and the residual solid in the reactor was washed out with ethyl acetate and the solution was filtered over silica flash. The filtrate was concentrated *in vacuo* and the residue was analysed by ^{1}H NMR for the determination of the conversion.

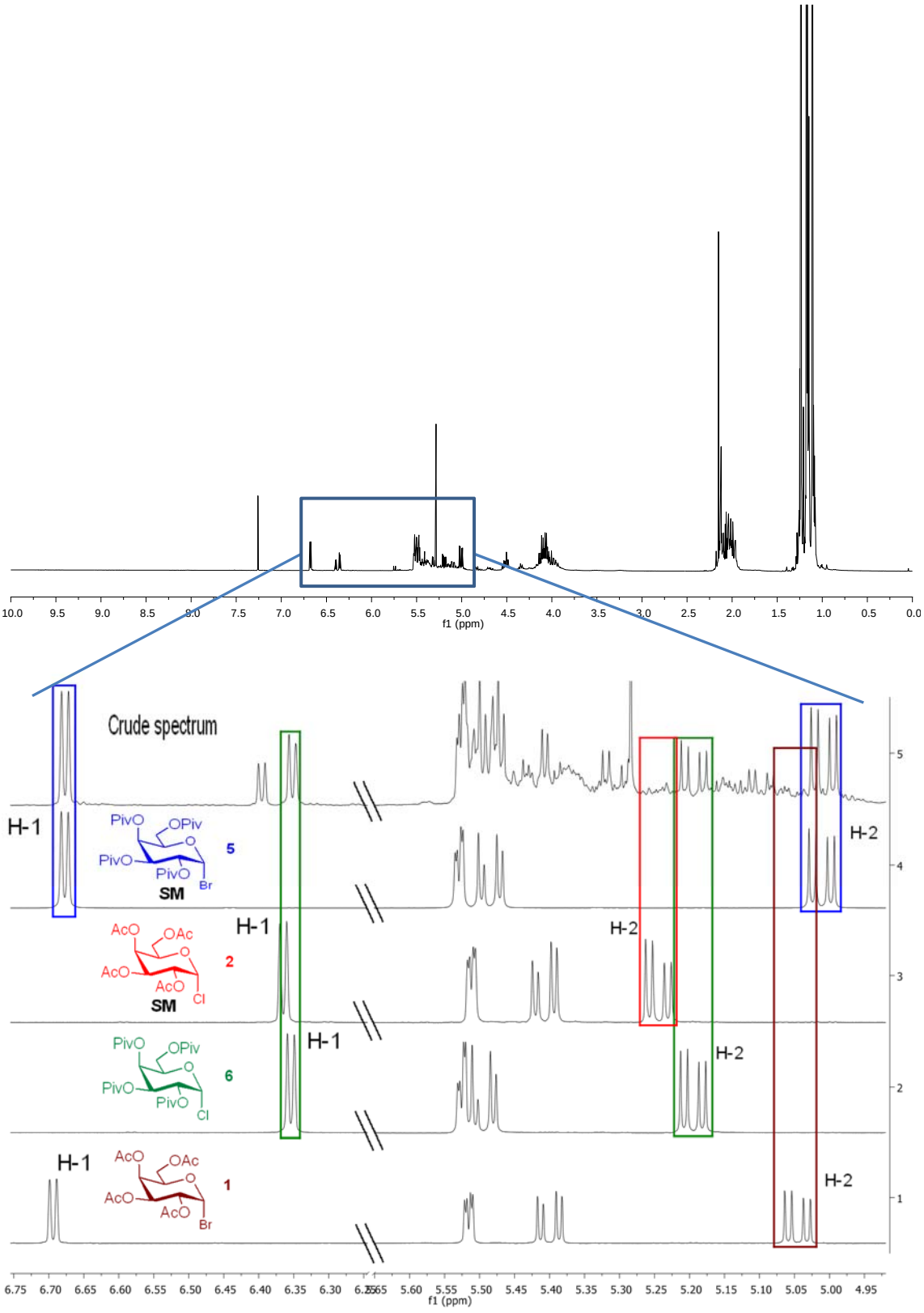
Halogen exchange experiment

2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl chloride (**2**) (134 mg, 0.365 mmol, 1 equiv.) and 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (**5**) (211 mg, 0.365 mmol, 1 equiv.), 4Å MS (ca. 100 mg) were placed inside the reactor (25 mL Parr Reactor) which was quickly sealed. It was then purged with CO_2, charged with the pressure of the CO_2 cylinder (ca. 800 Psi) and heated with a heating mantle to 90 ^{o}C. Once the temperature was reached, compressed CO_2 was added until a pressure of 1500 Psi. The start of the reaction is defined as the time at which the CO_2 pressure reaches 1500 Psi.

After stirring the reaction mixture at 90 ^{o}C and 1500 Psi for 15 h, the reactor was cooled to 0 ^{o}C and the compressed CO_2 was then slowly leaked out. The residual solid in the reactor was washed out with CH_2Cl_2 and the solution was filtered over silica gel. The filtrate was concentrated *in vacuo* and the residue was analysed by ^{1}H NMR.

The NMR spectra showed the formation of 2,3,4,6-tetra-*O*-Pivaloyl-α-D-galactopyranosyl chloride (**6**). This fact accounted for an halogen exchange. However, the fact that no traces of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**) could be rationalized by the formation of partially deacetylated compounds due to the higher lability of this protecting group. (NMR spectra is shown below)

Crude NMR spectrum of the halogen exchange experiment.



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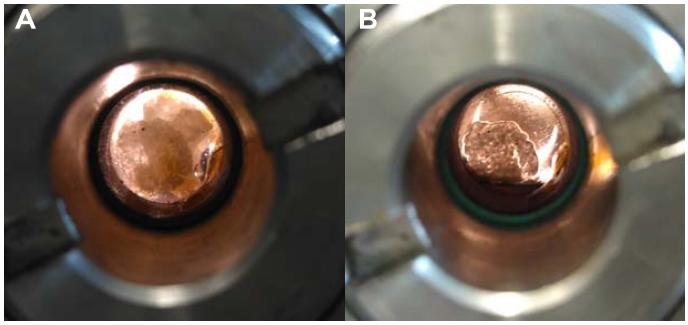
4. Additional images

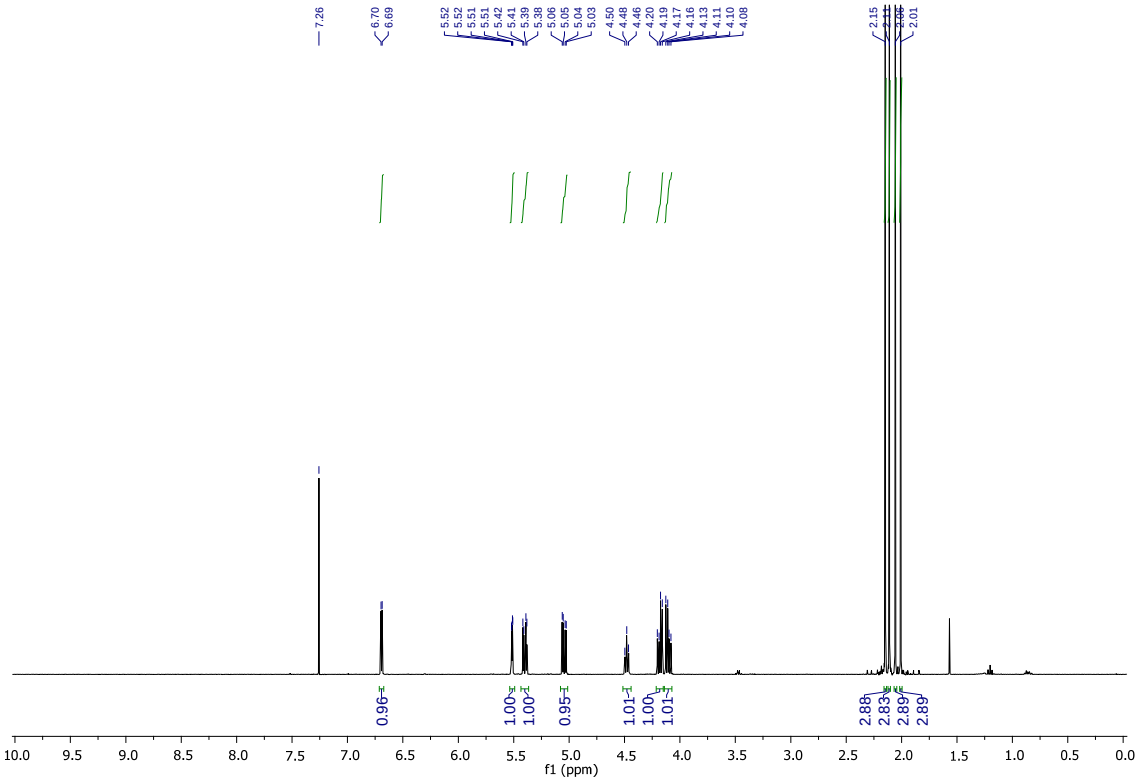


(a) Glycosyl donor **5** and cyclohexanol at atmospheric pressure and r.t. with a magnetic stirrer;

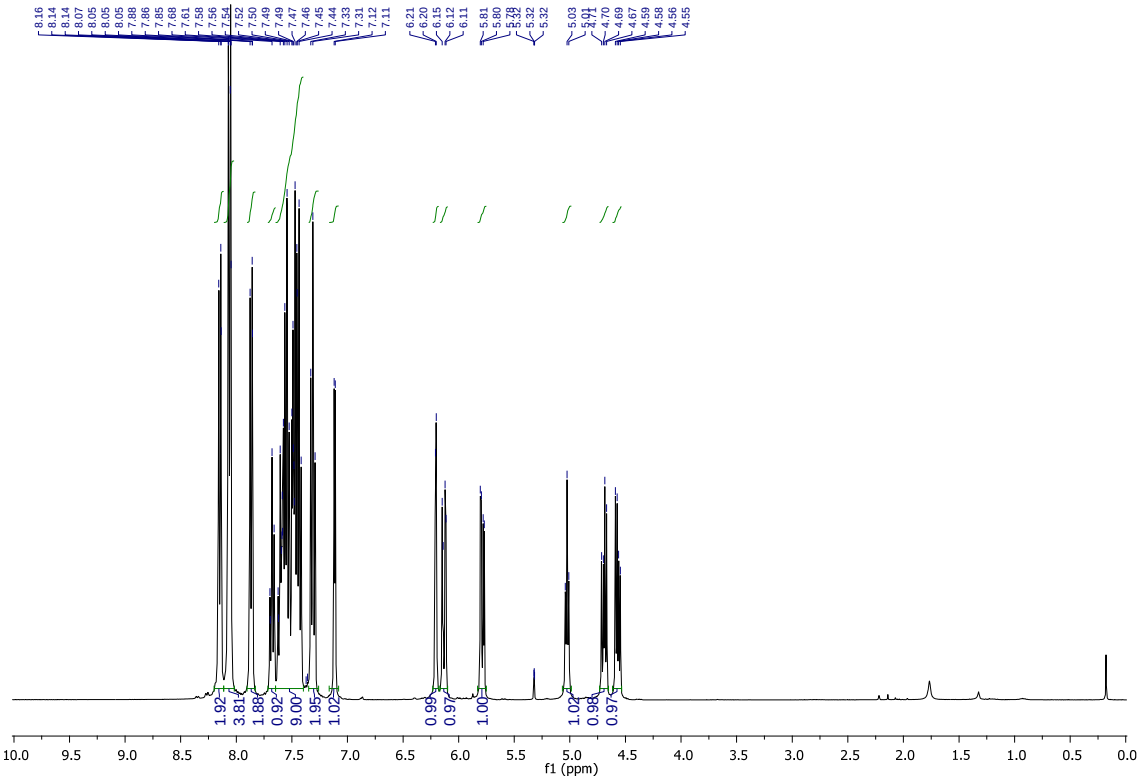
(b) Glycosyl donor **5** and cyclohexanol in Ar at 1500 Psi and 60 ^{o}C in a reactor with quartz windows.

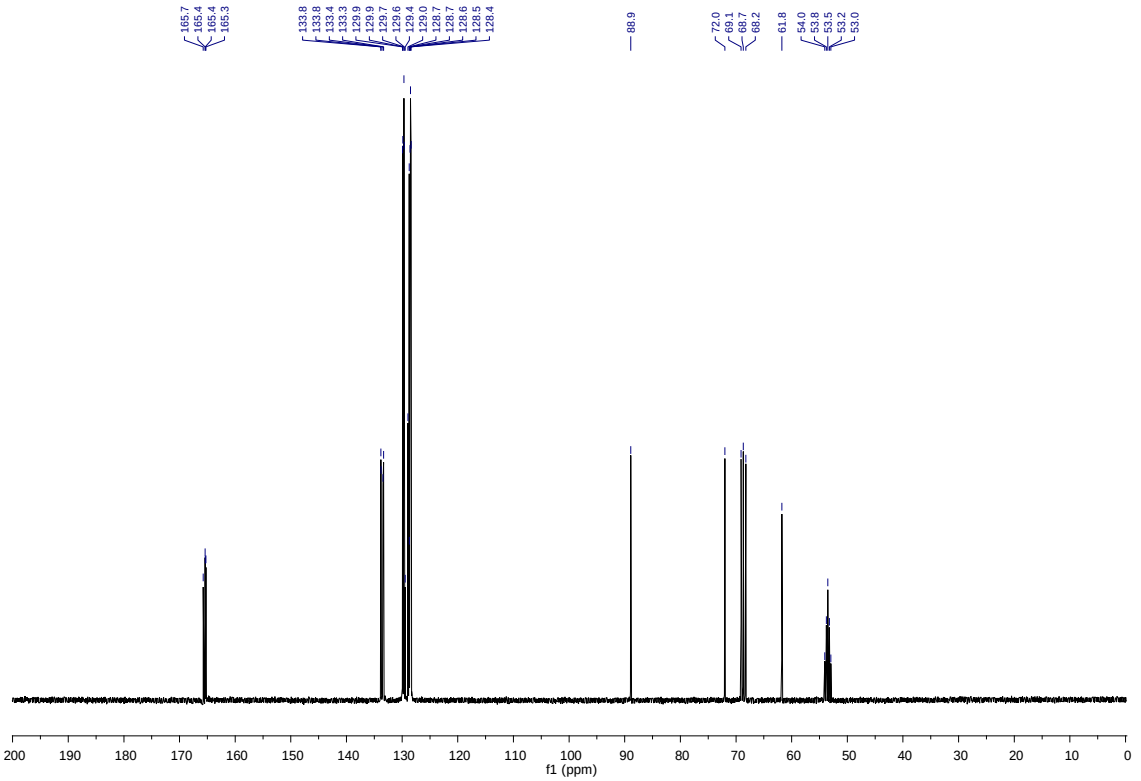
5. ^{1}H and ^{13}C NMR spectra

2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (1)

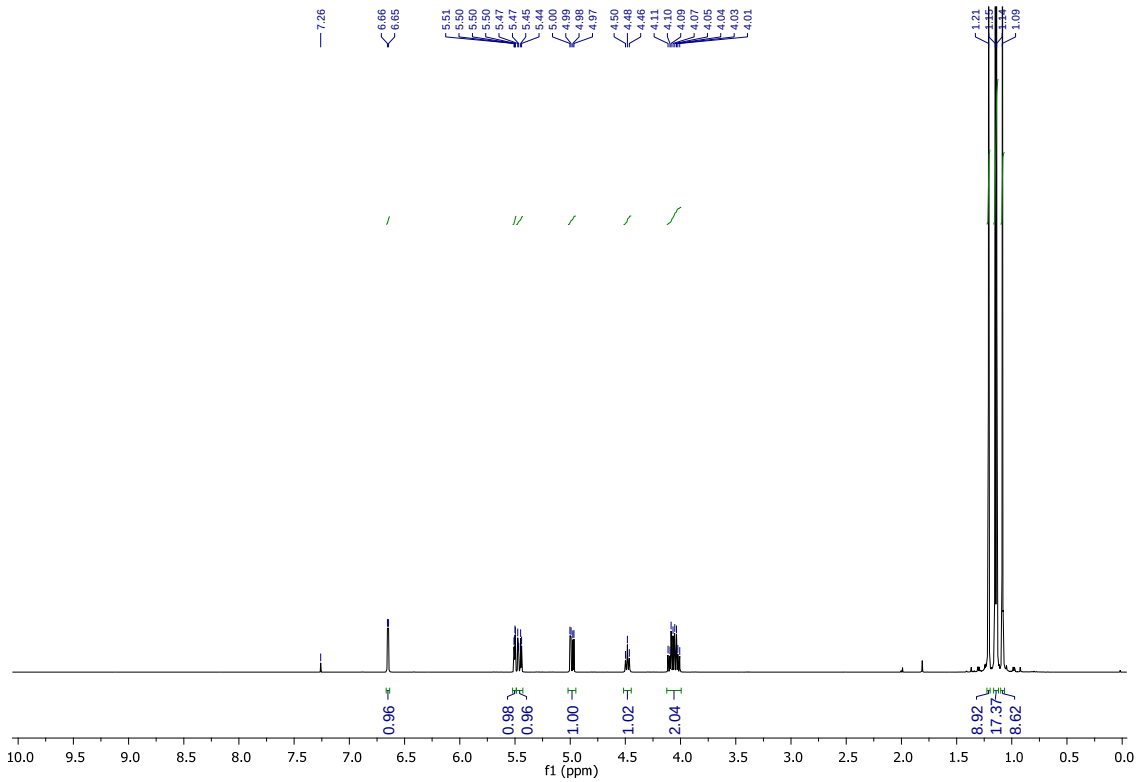


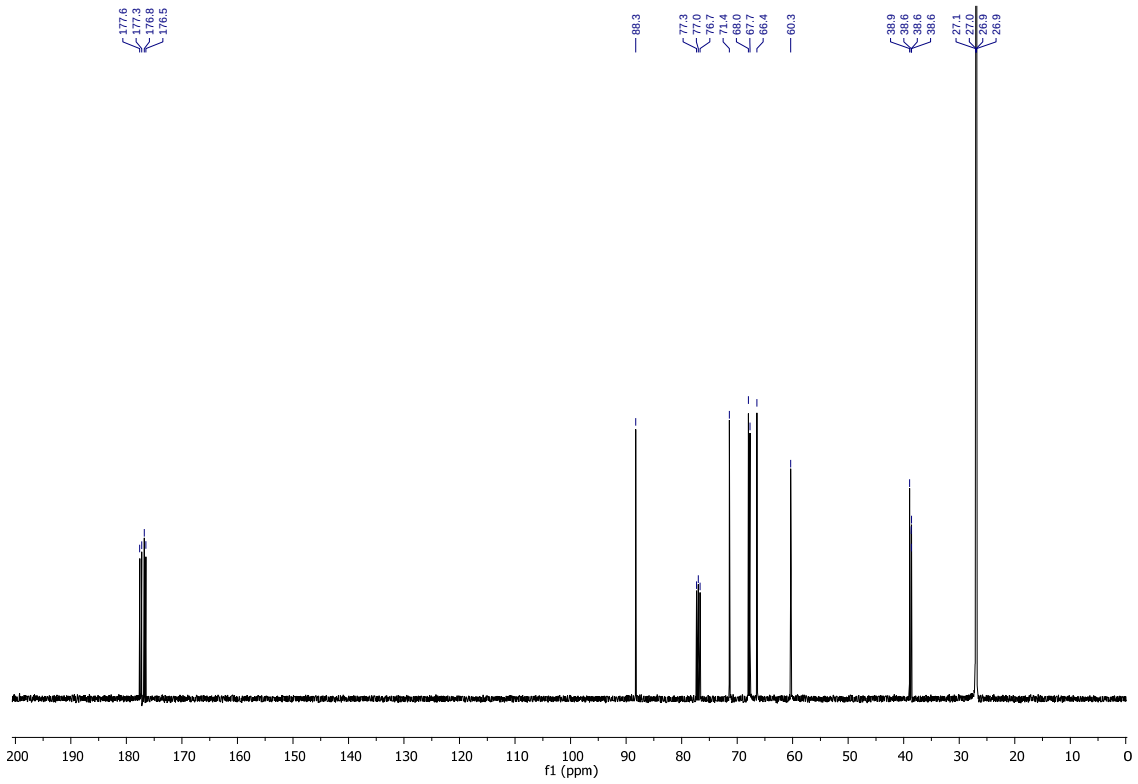
2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (4)



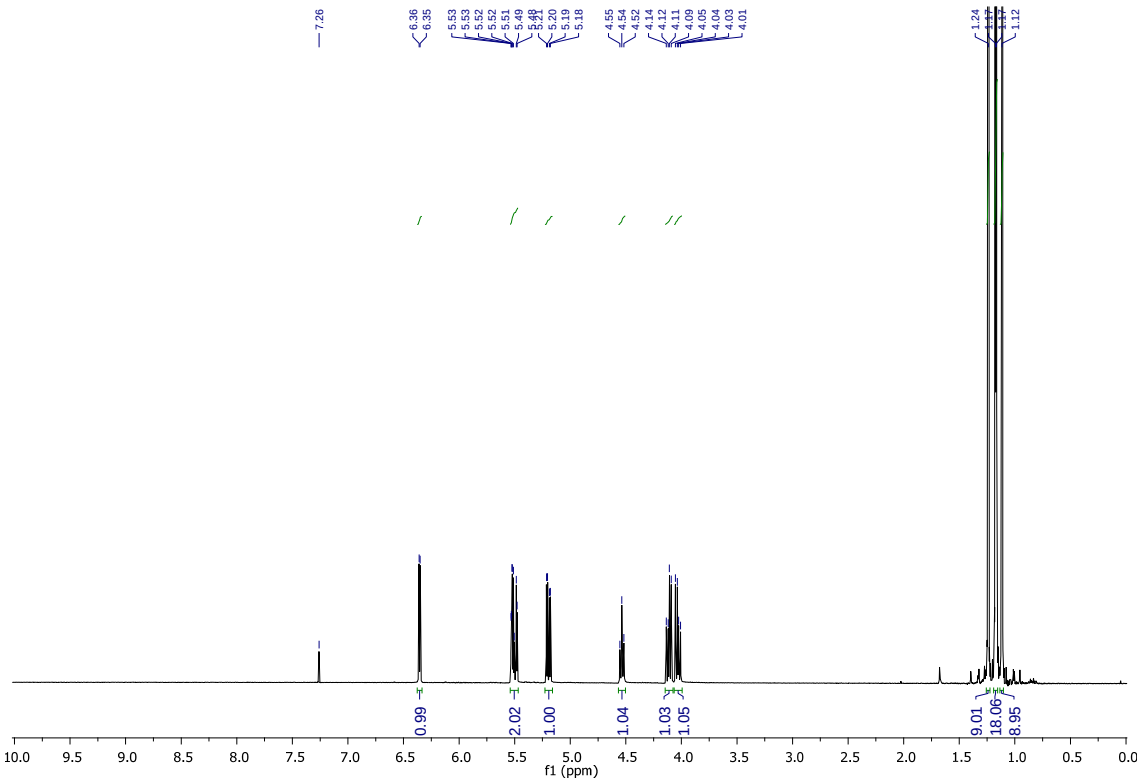


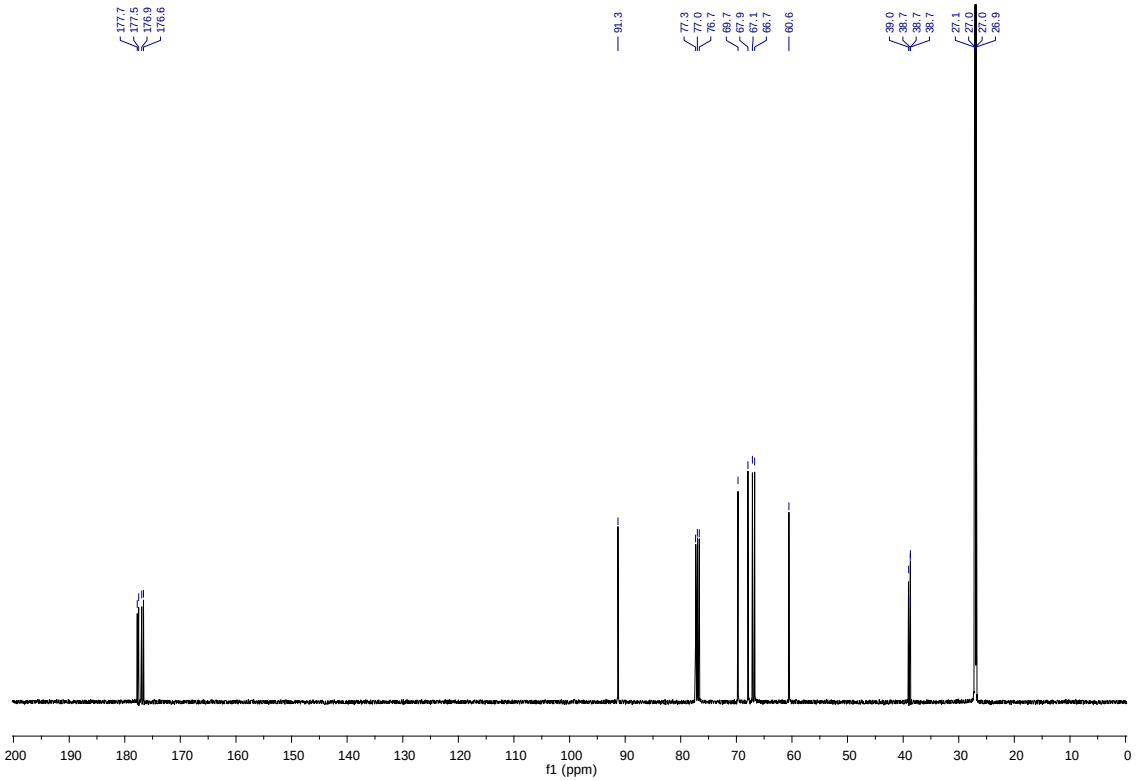
2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl bromide (5)



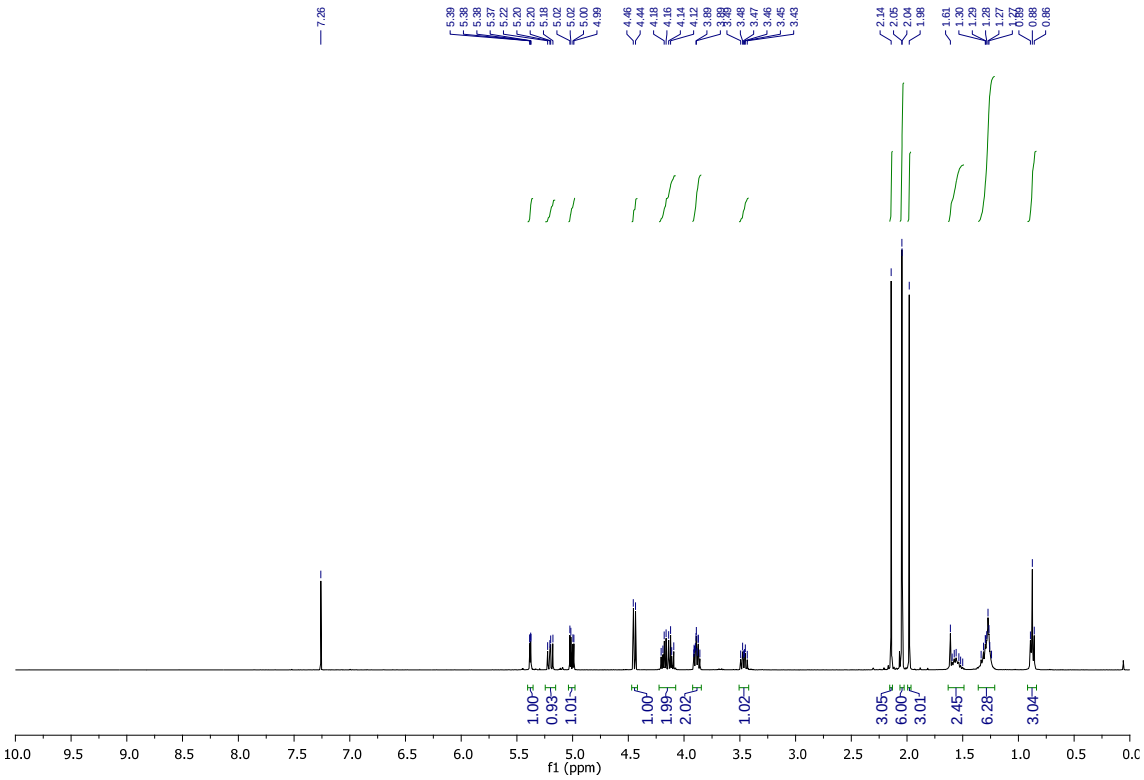


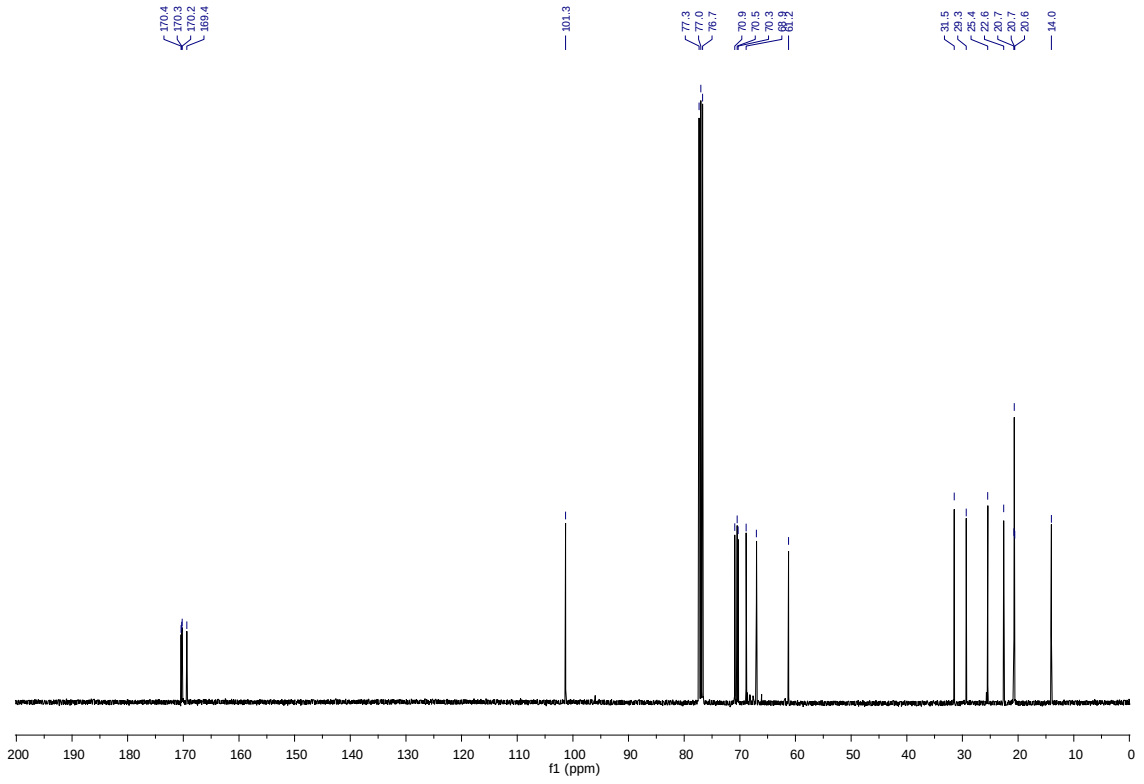
2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl chloride (6)



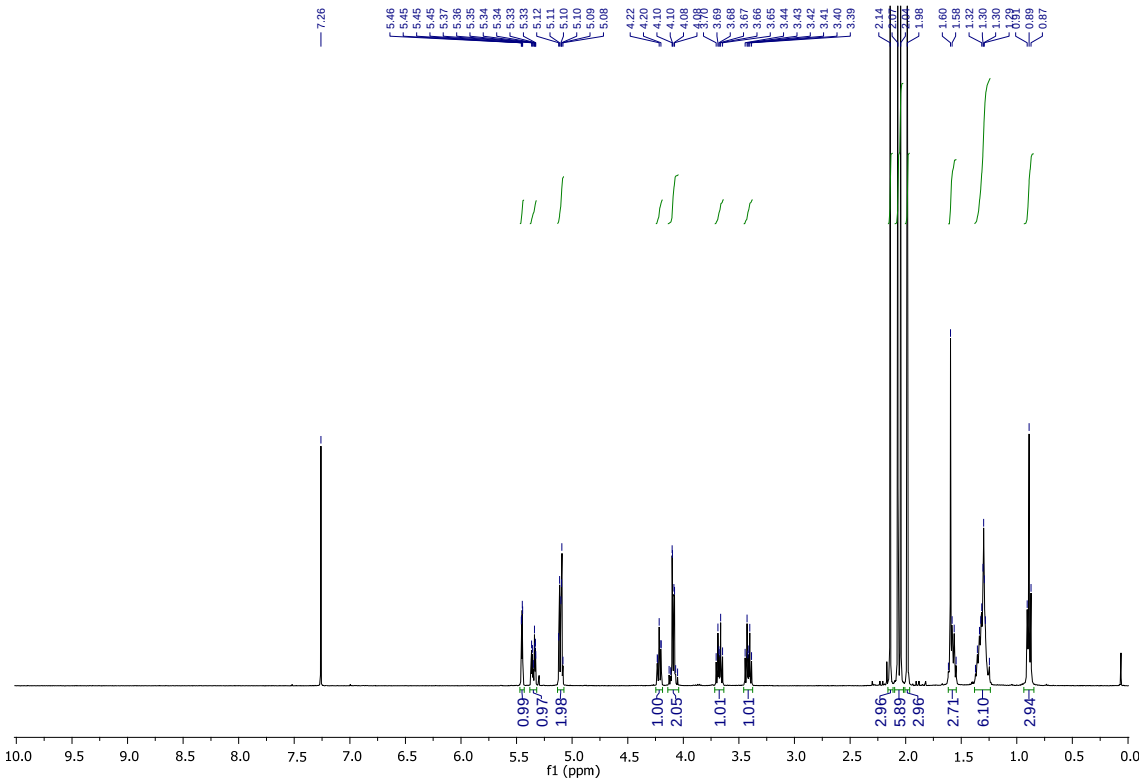


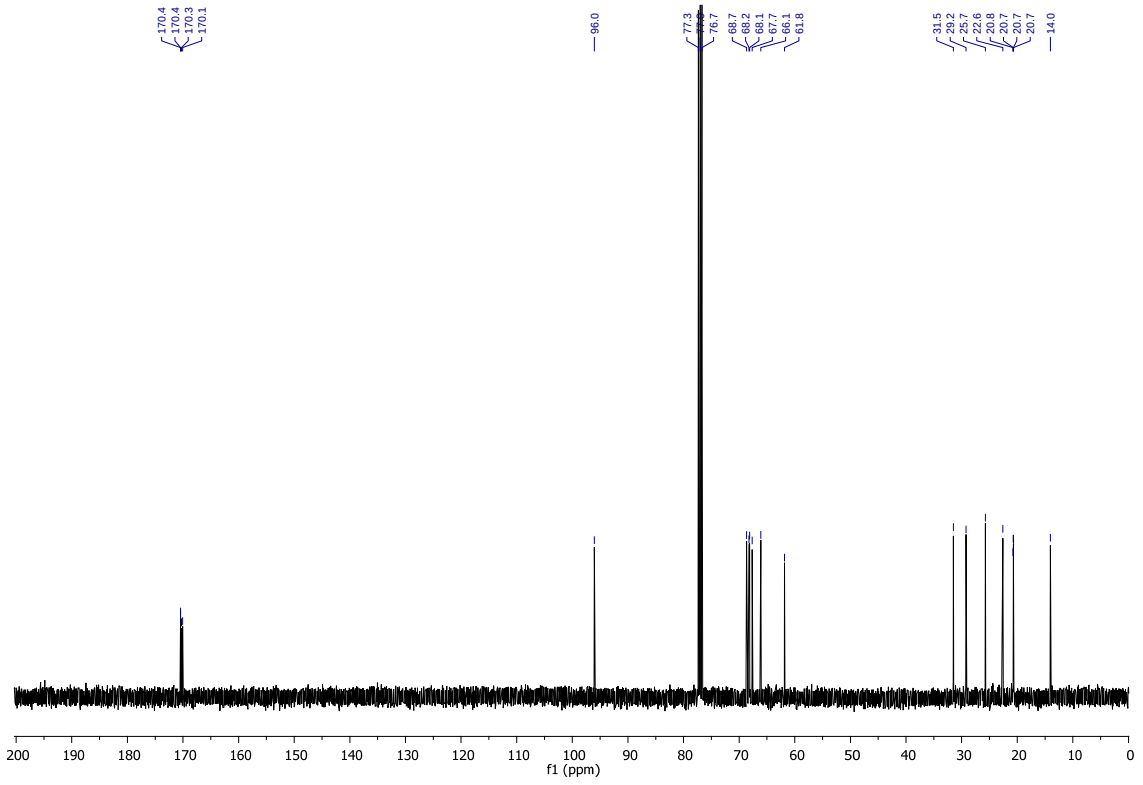
Hexyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (3c-β)



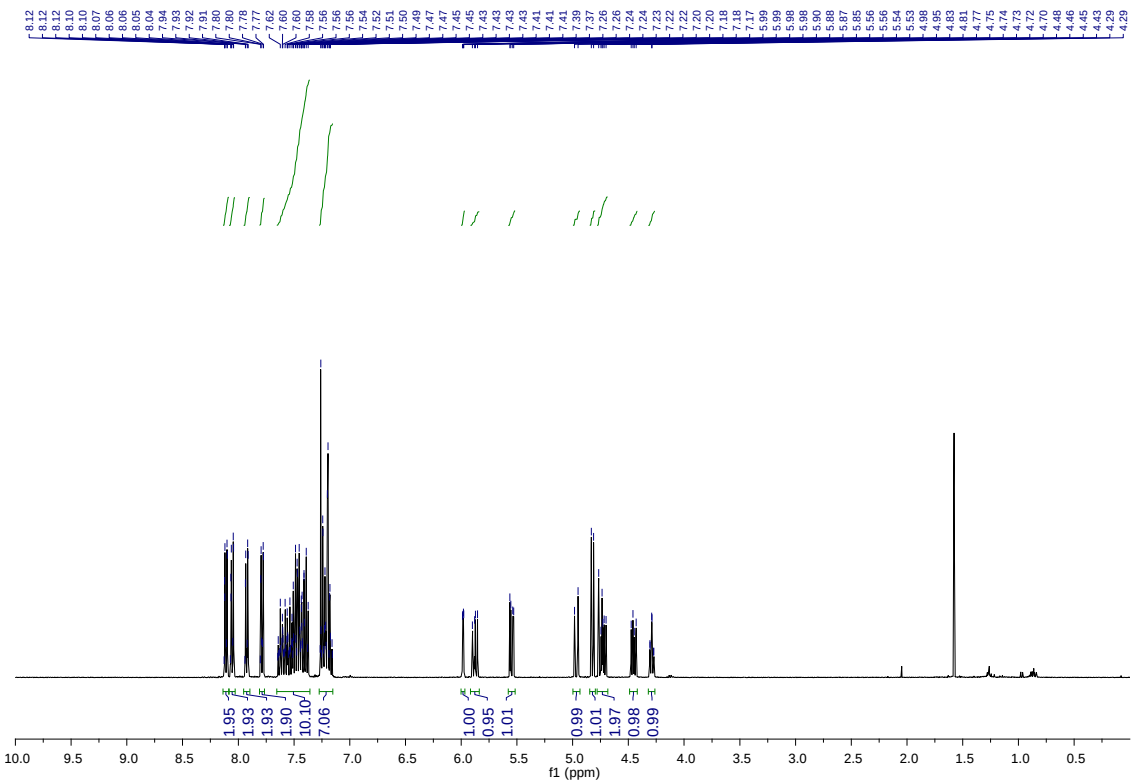


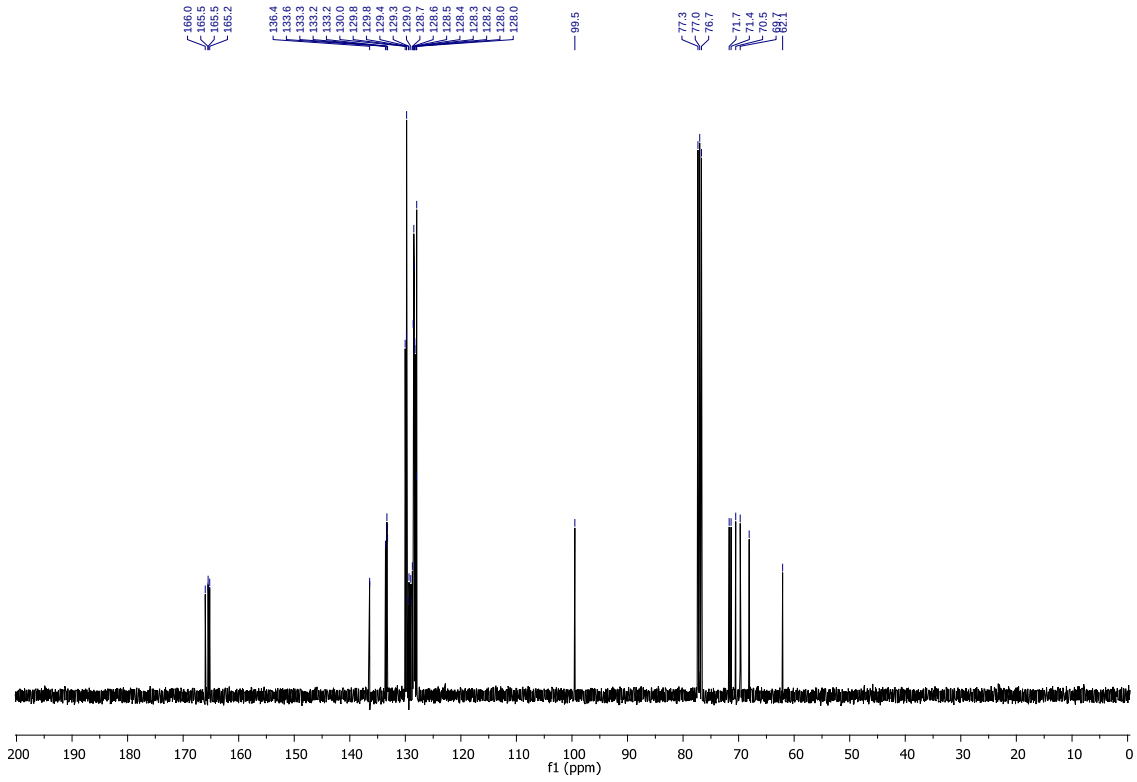
Hexyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (3c-α)



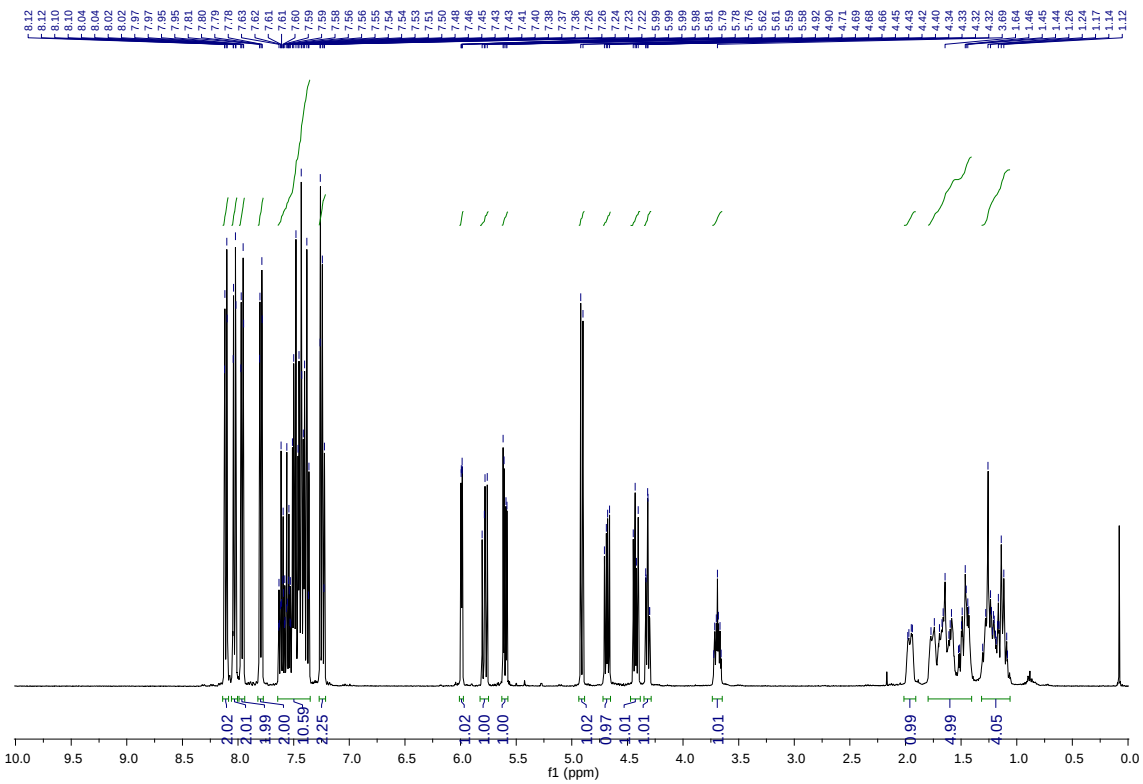


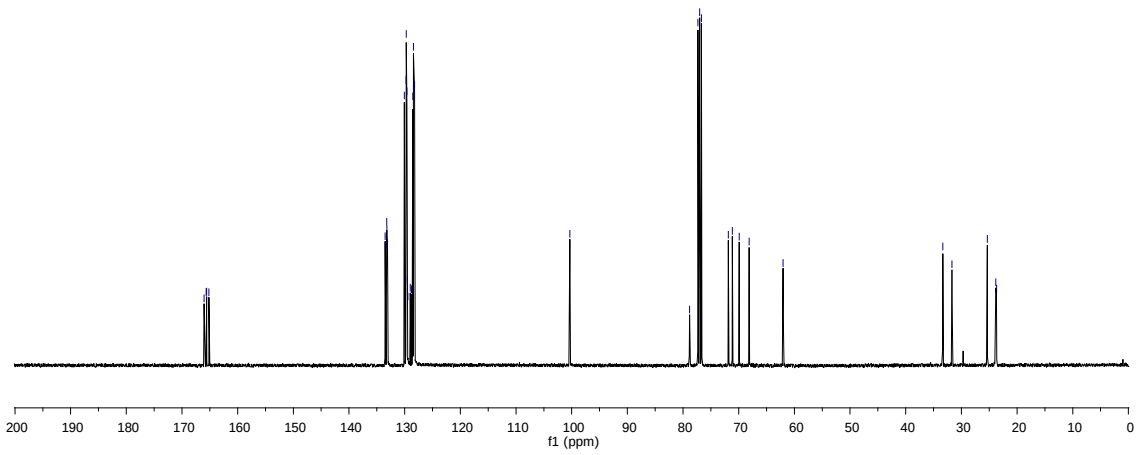
Benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (8a-β)



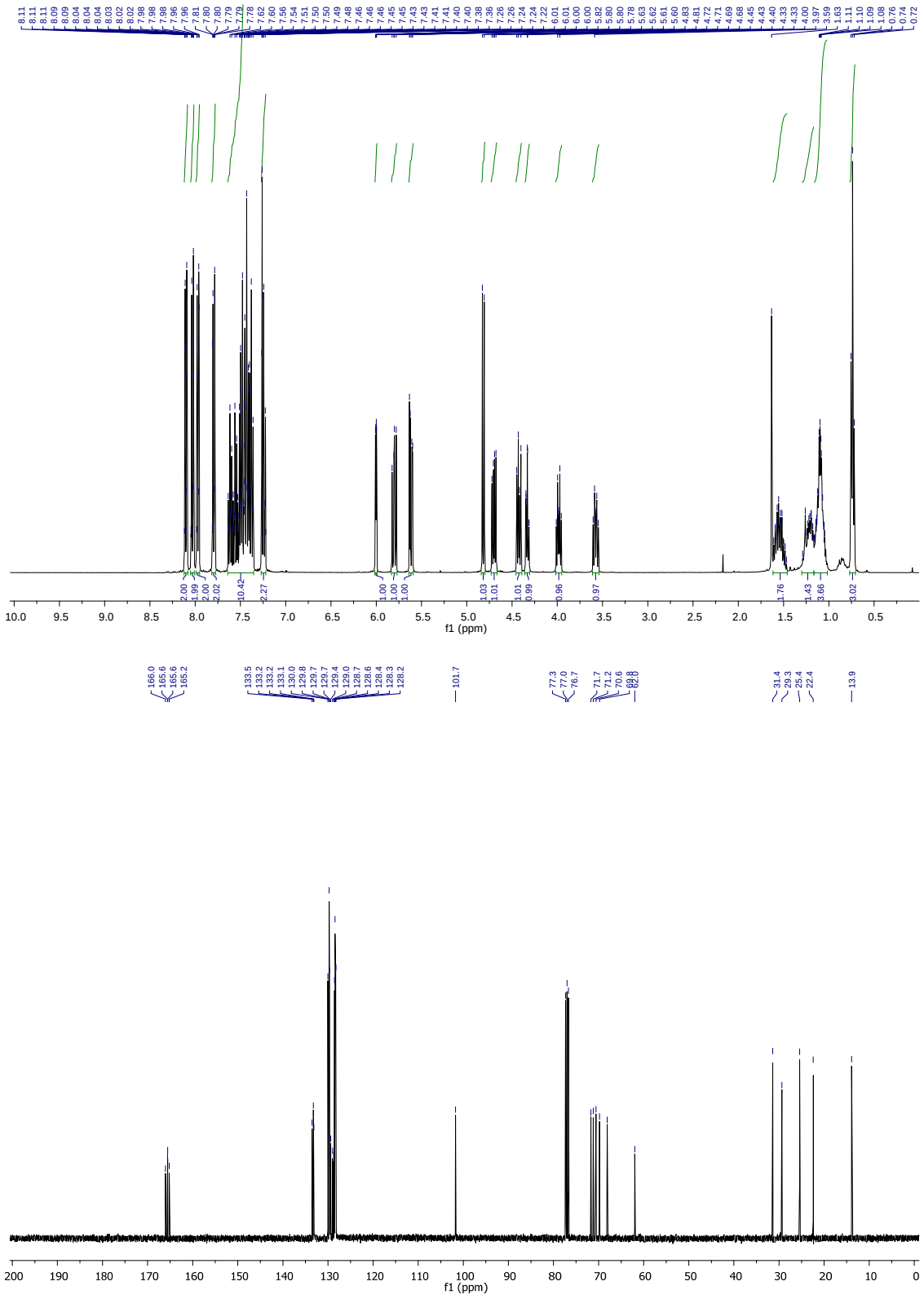


Cyclohexyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (8b-β)

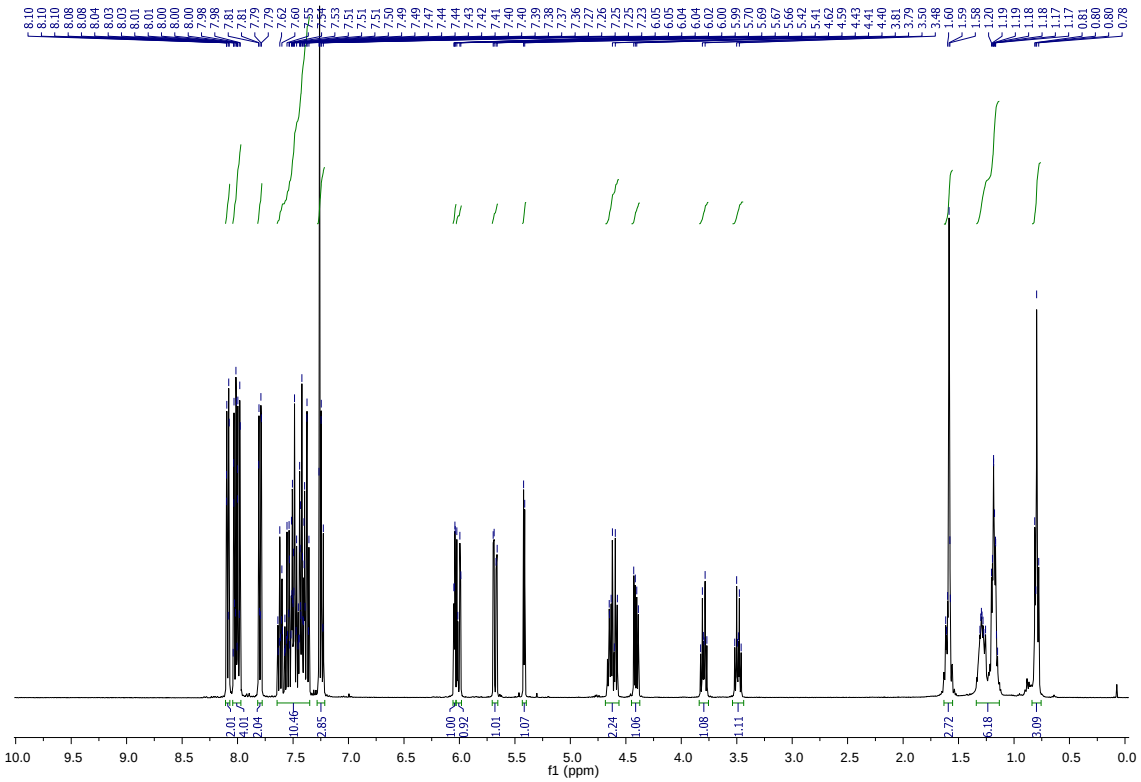


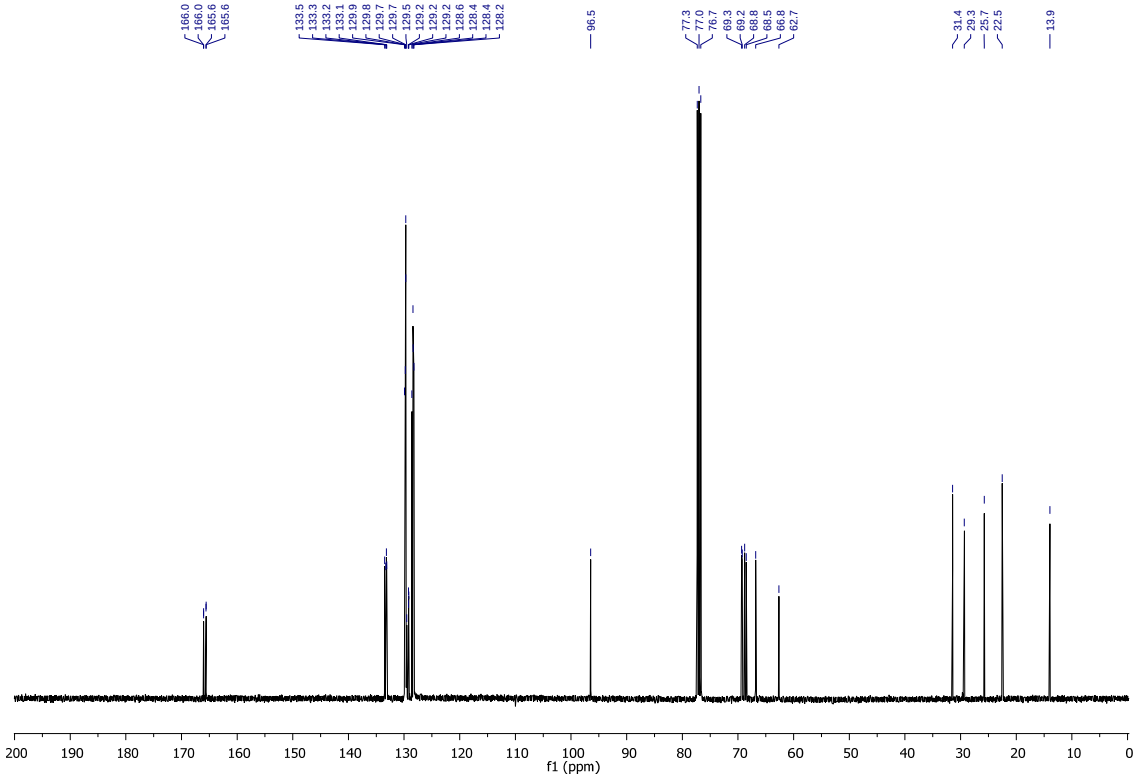


Hexyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (8c-β)

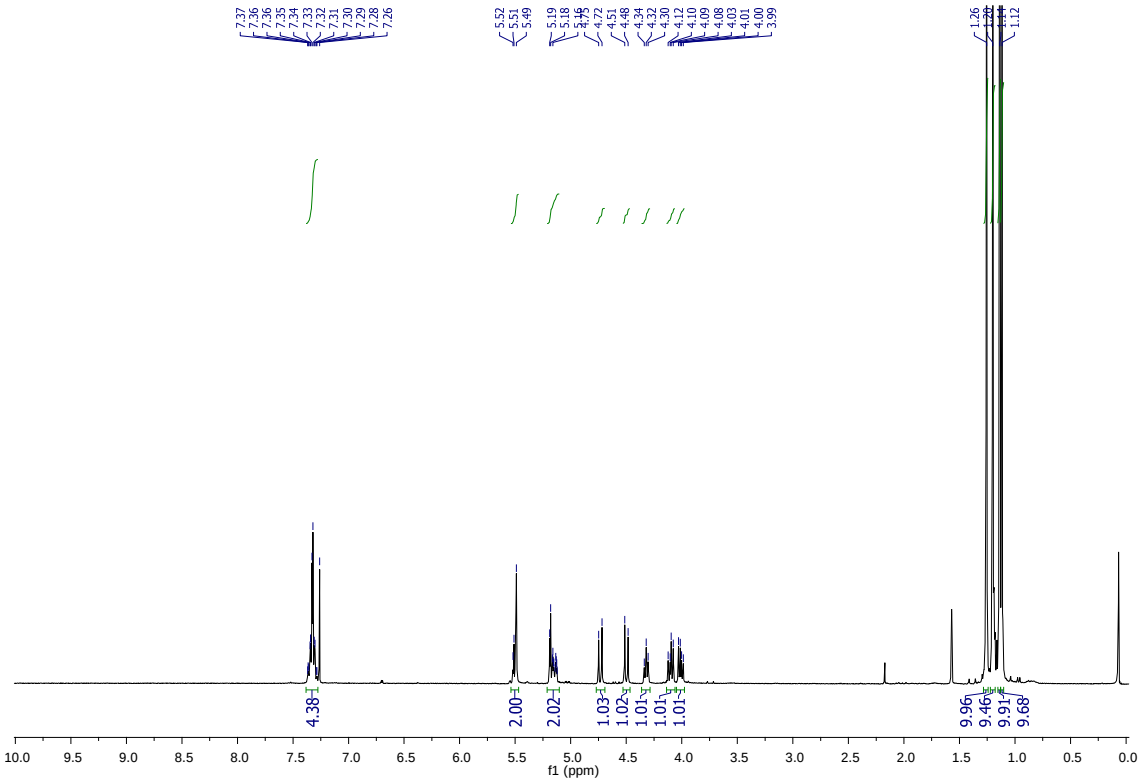


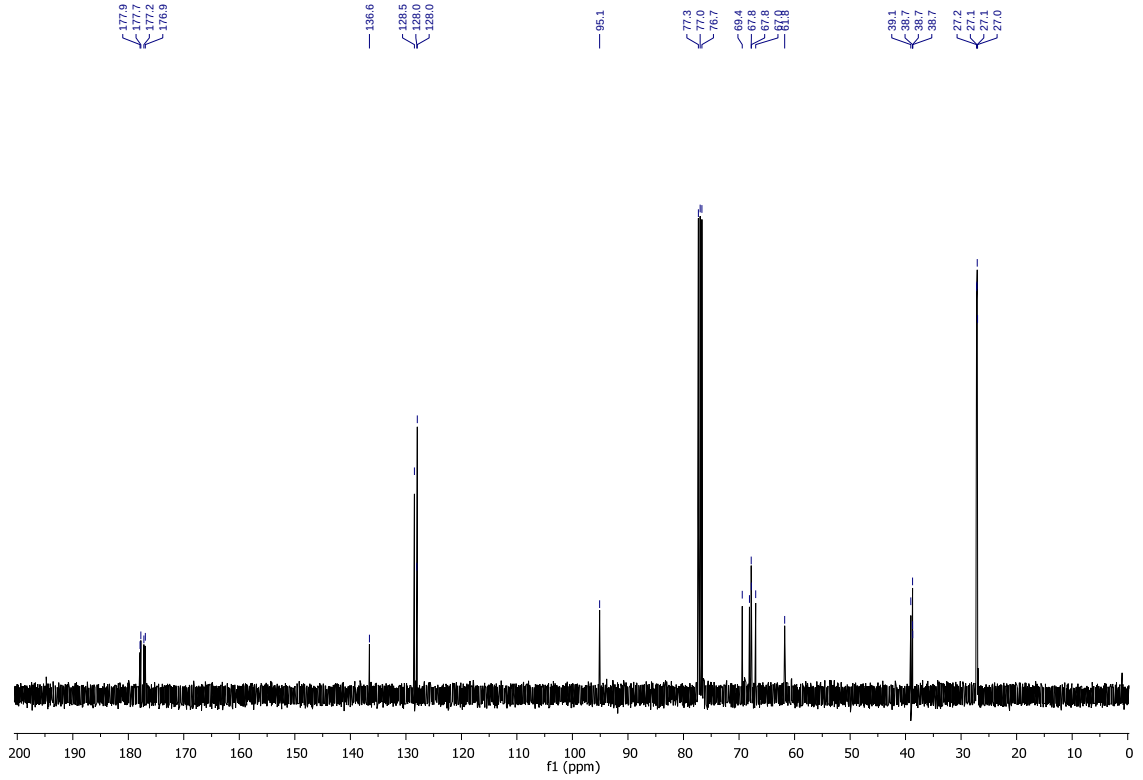
Hexyl 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranoside (8c-α)



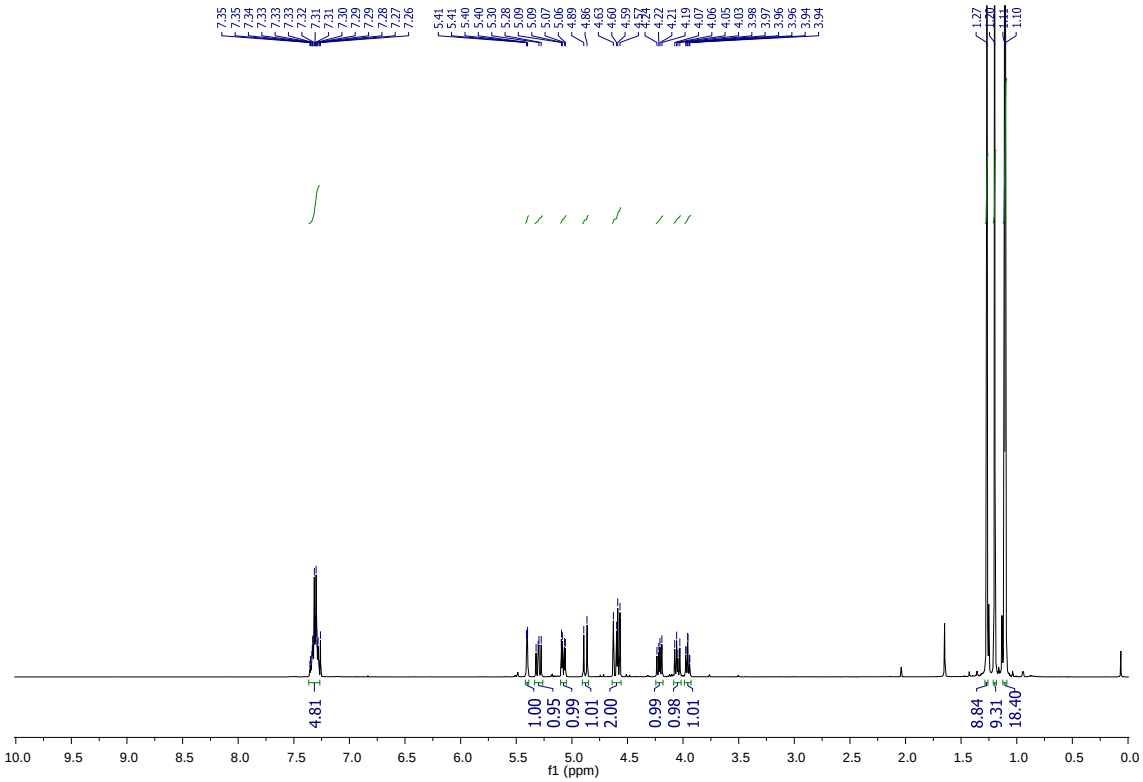


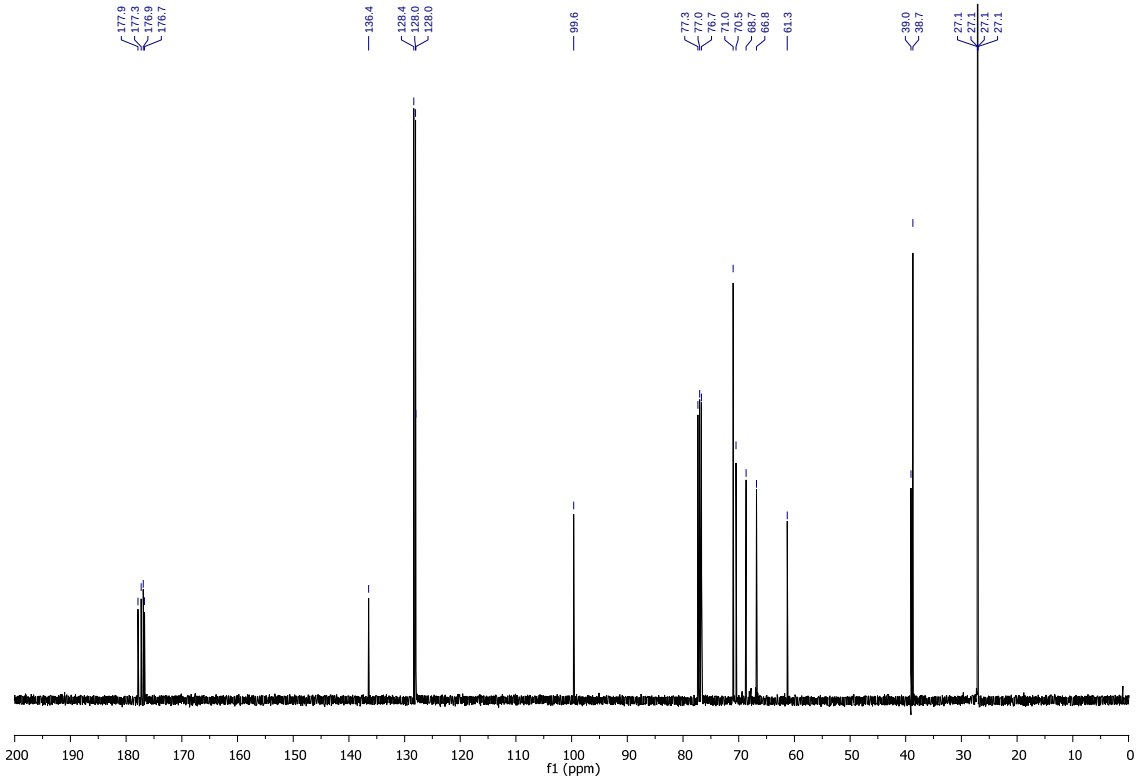
Benzyl 2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranoside (9a-α)



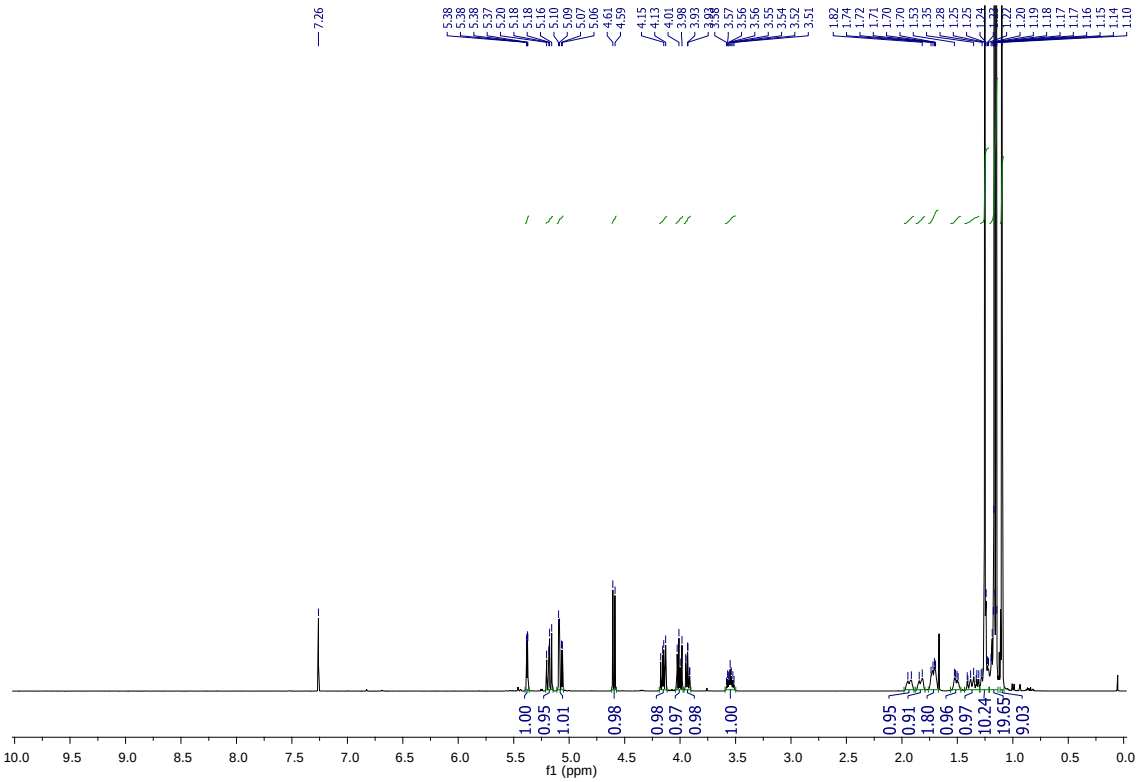


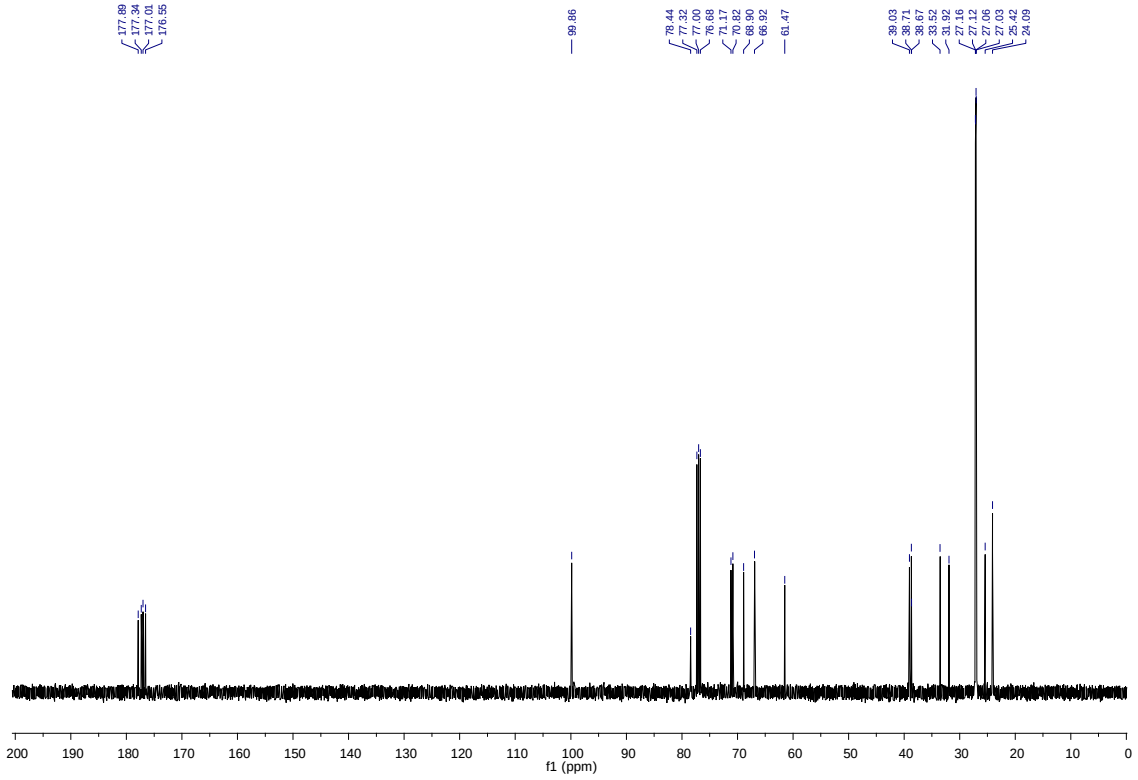
Benzyl 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranoside (9a-β)



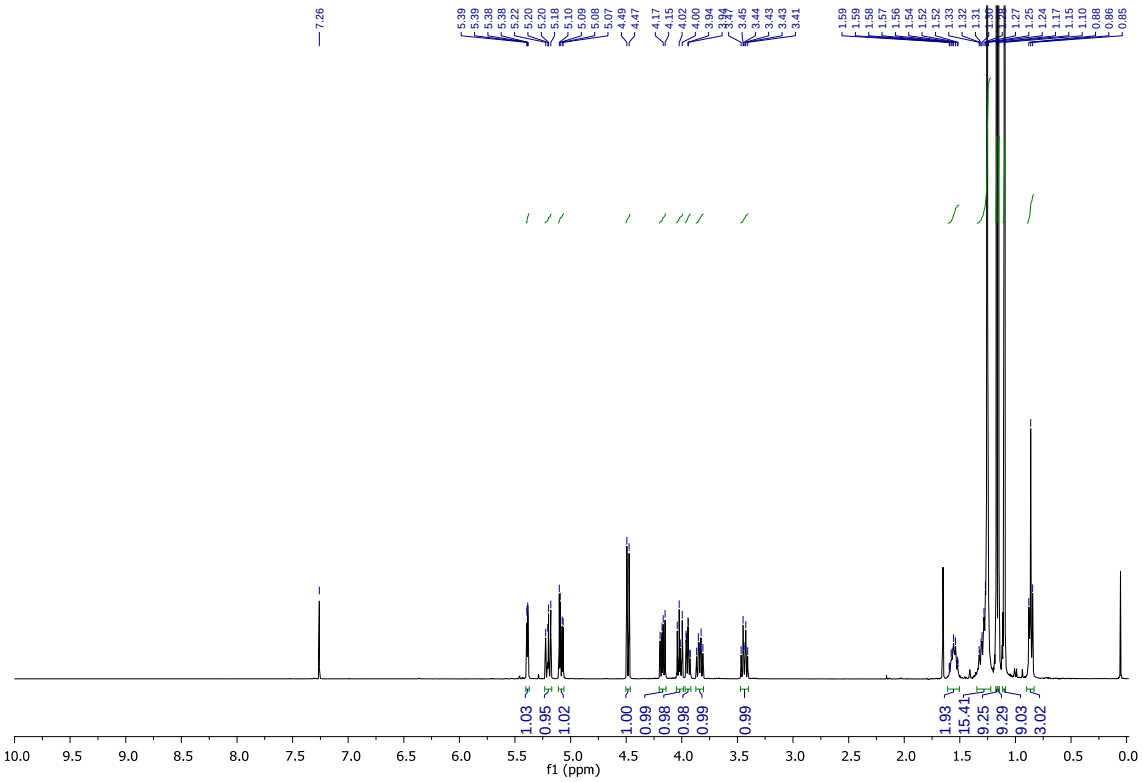


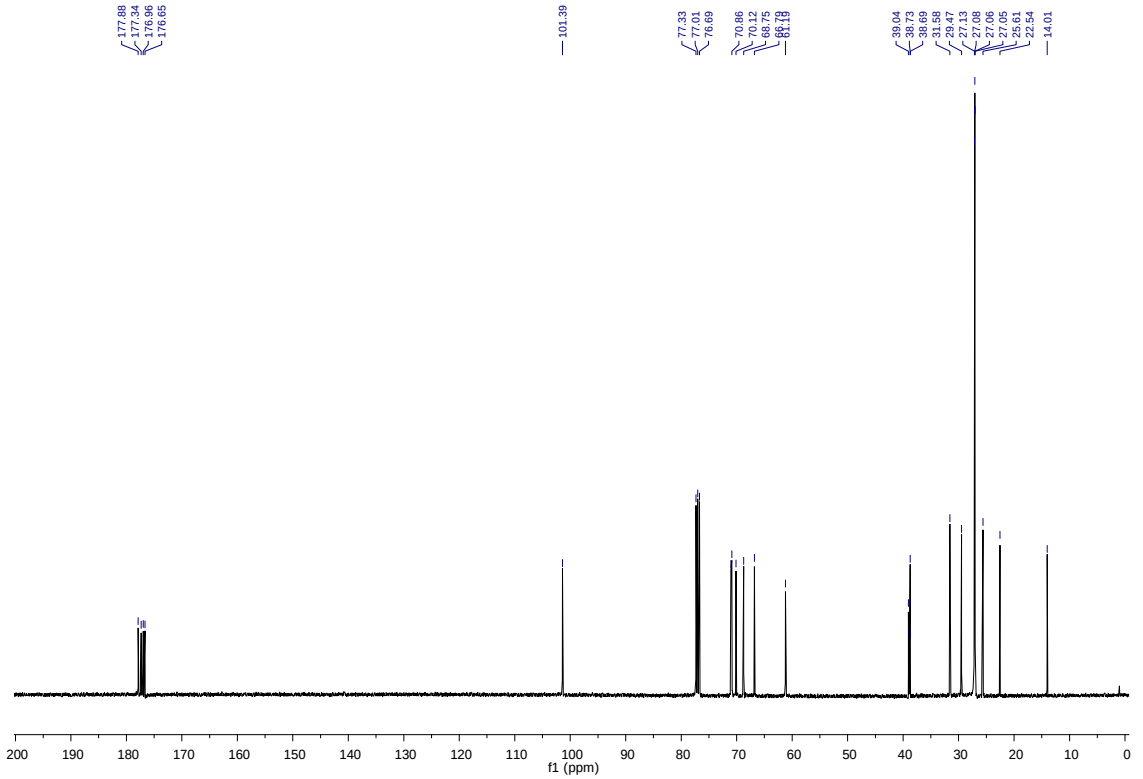
Cyclohexyl 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranoside (9b-β)



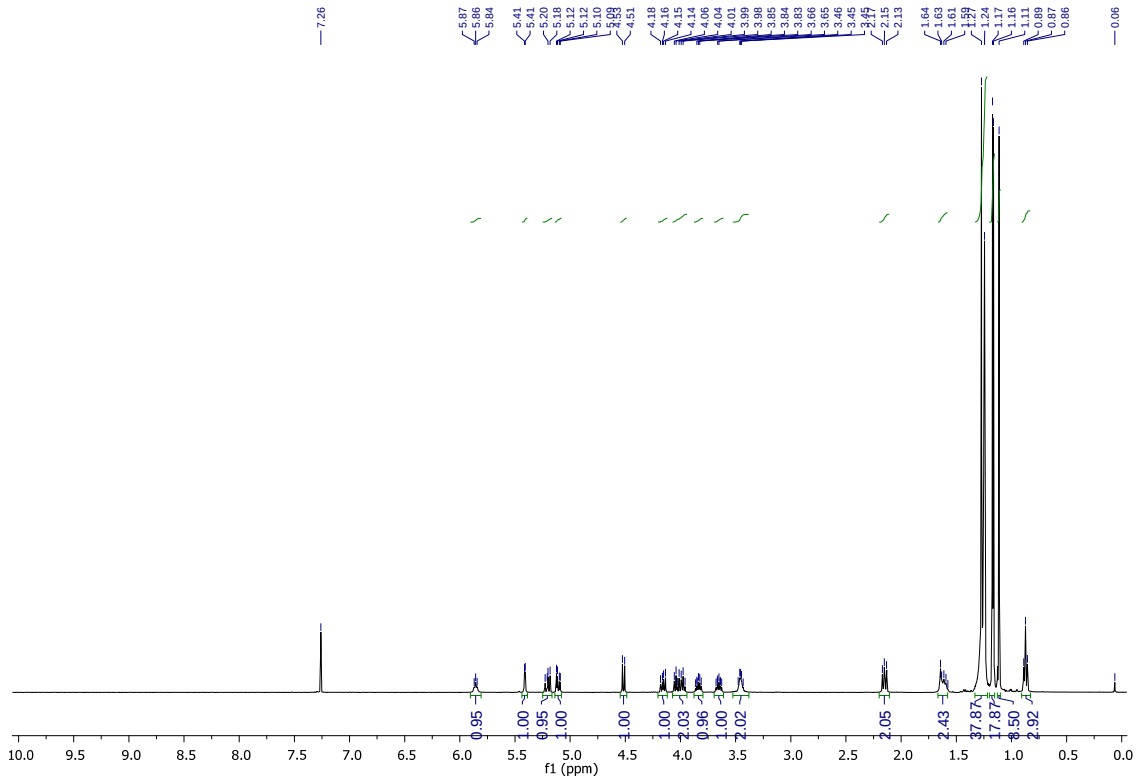


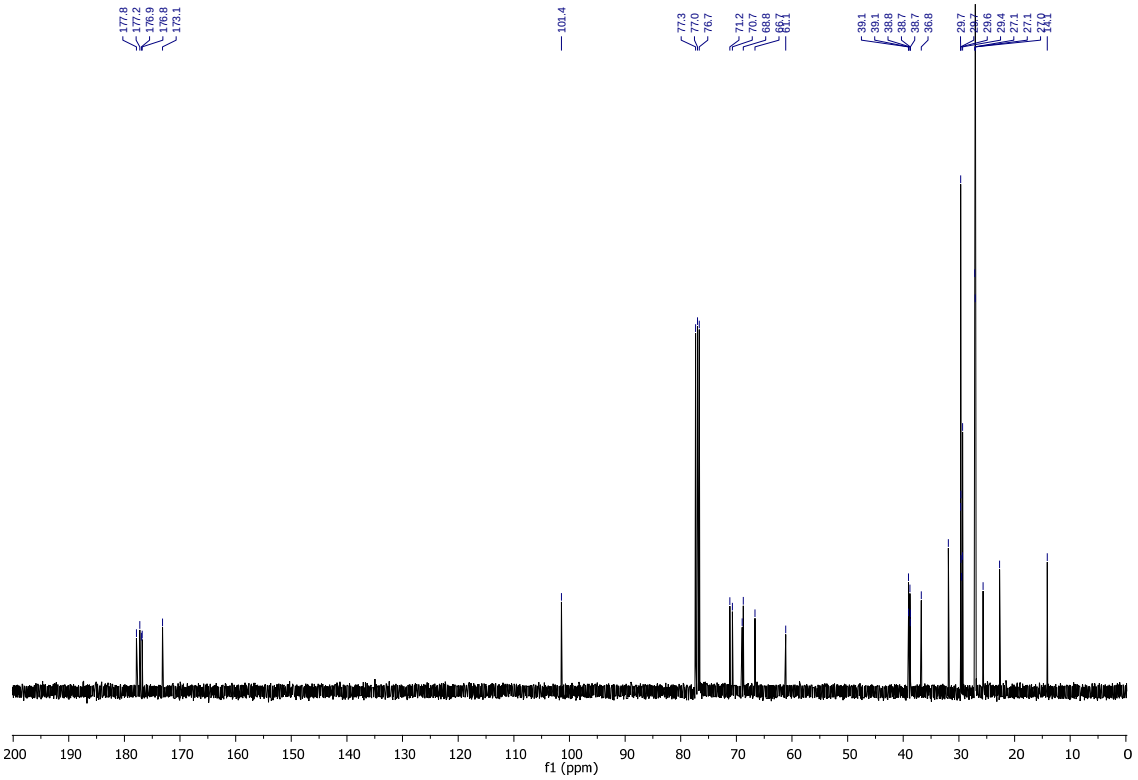
Hexyl 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranoside (9c-β)



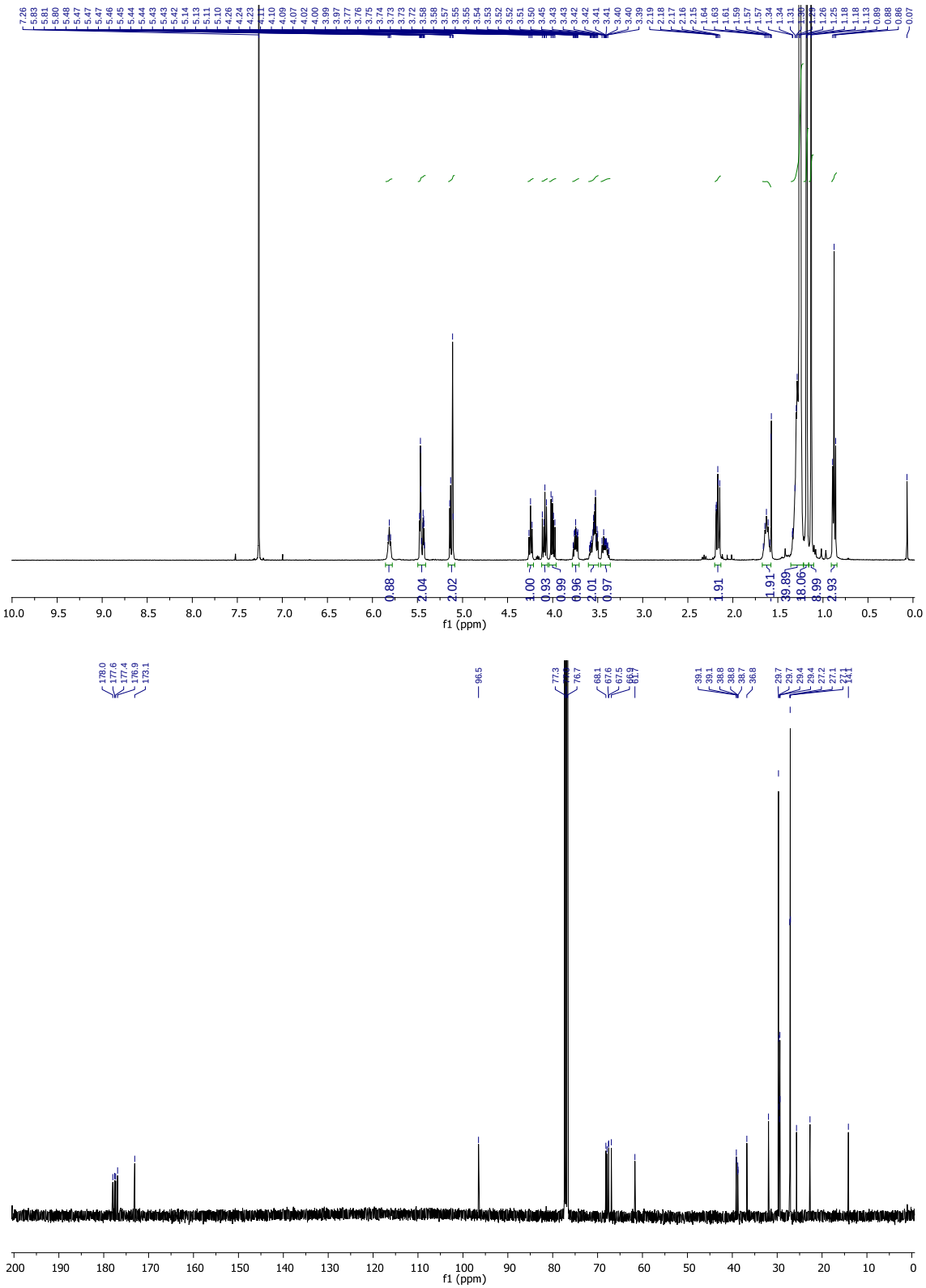


1-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-*N*-octadecanoyl-2-aminoethanol (9d- β)

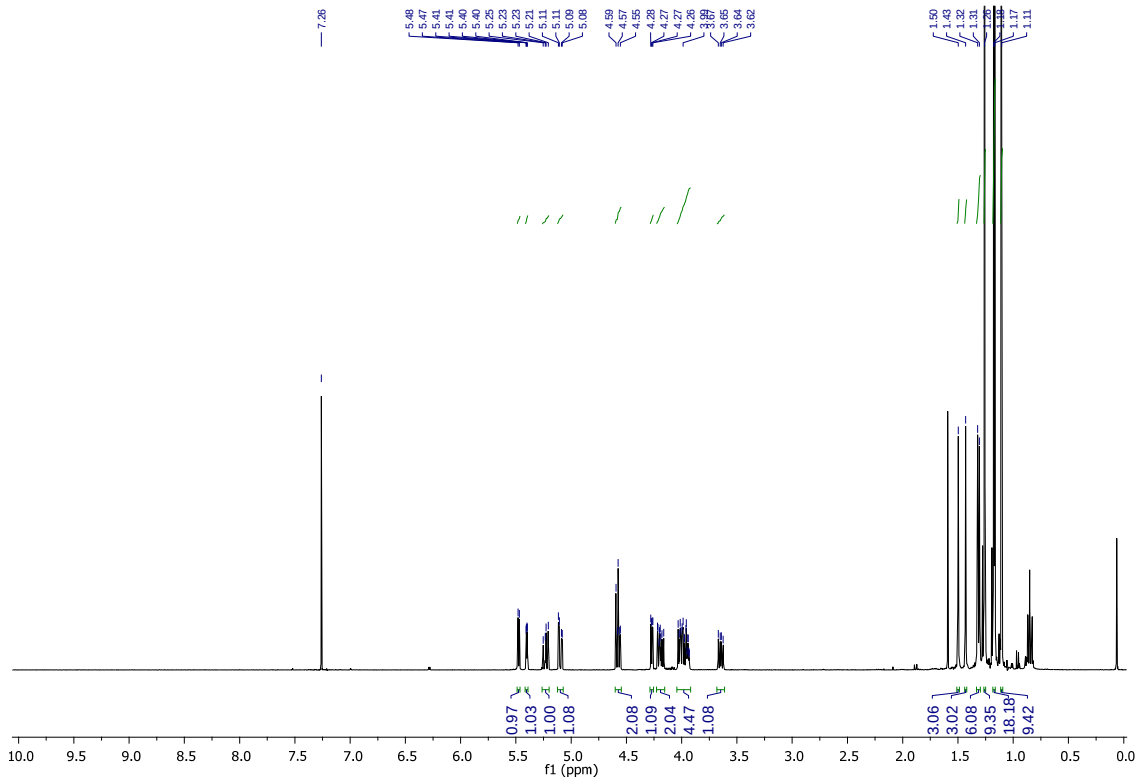


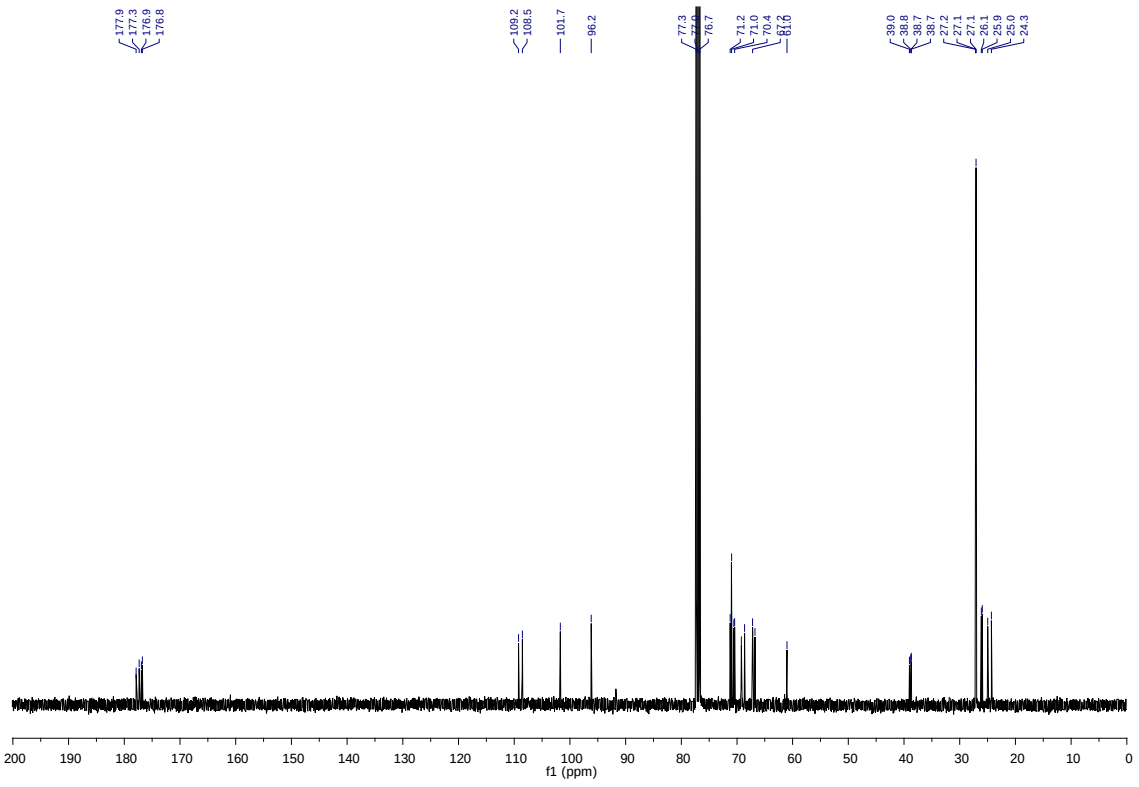


1-(2,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranosyl)-*N*-octadecanoyl-2-aminoethanol (9d- α)

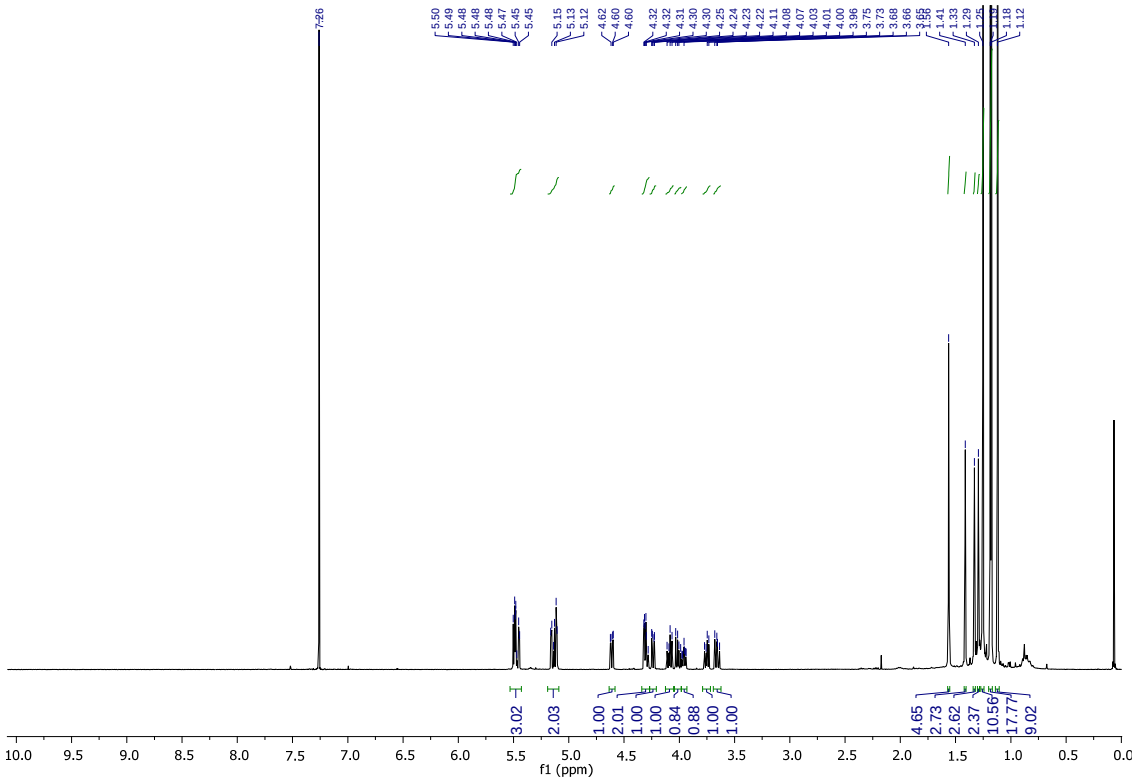


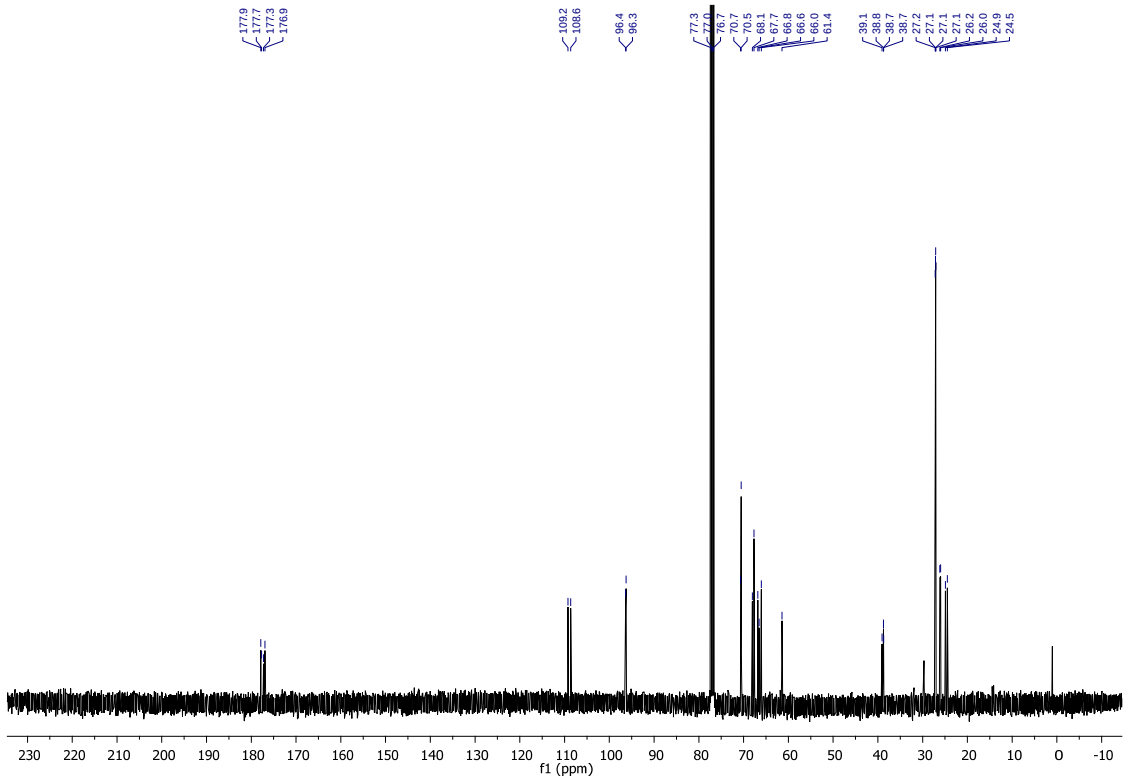
1,2:3,4-di-*O*-isopropylidene-6-*O*-(tetra-*O*-pivaloyl-β-D-galactopyranosyl)-α-D-galactose (9e-β)



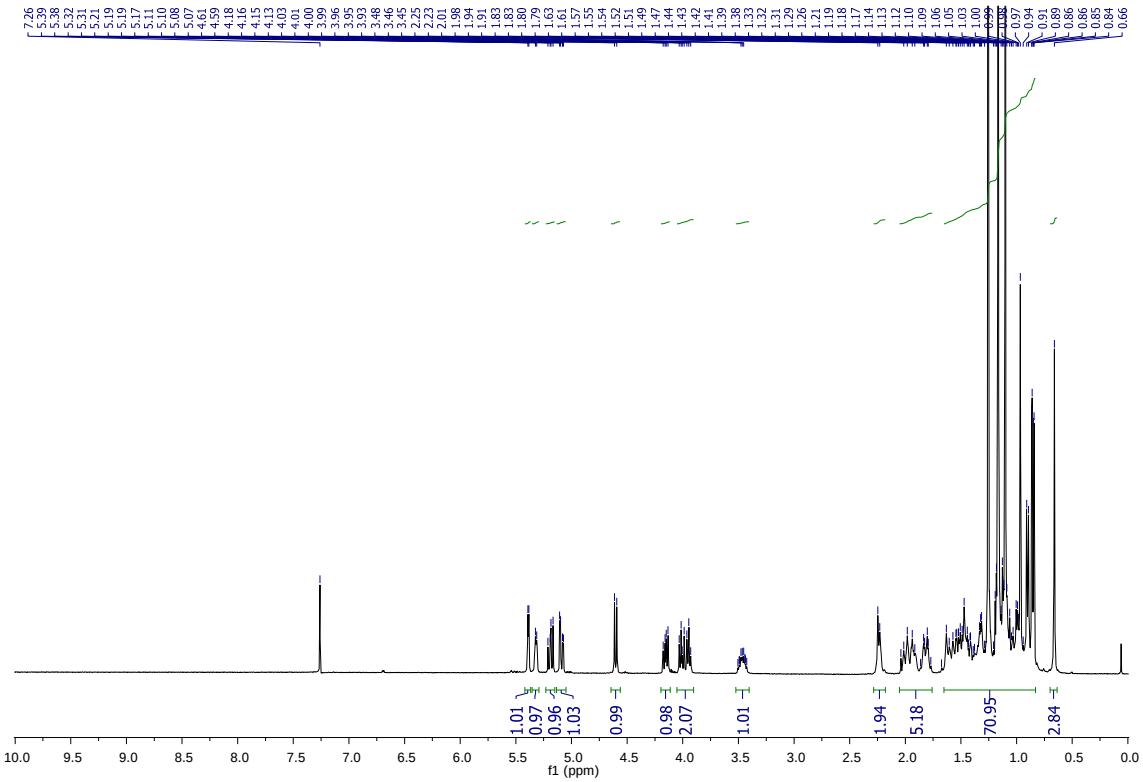


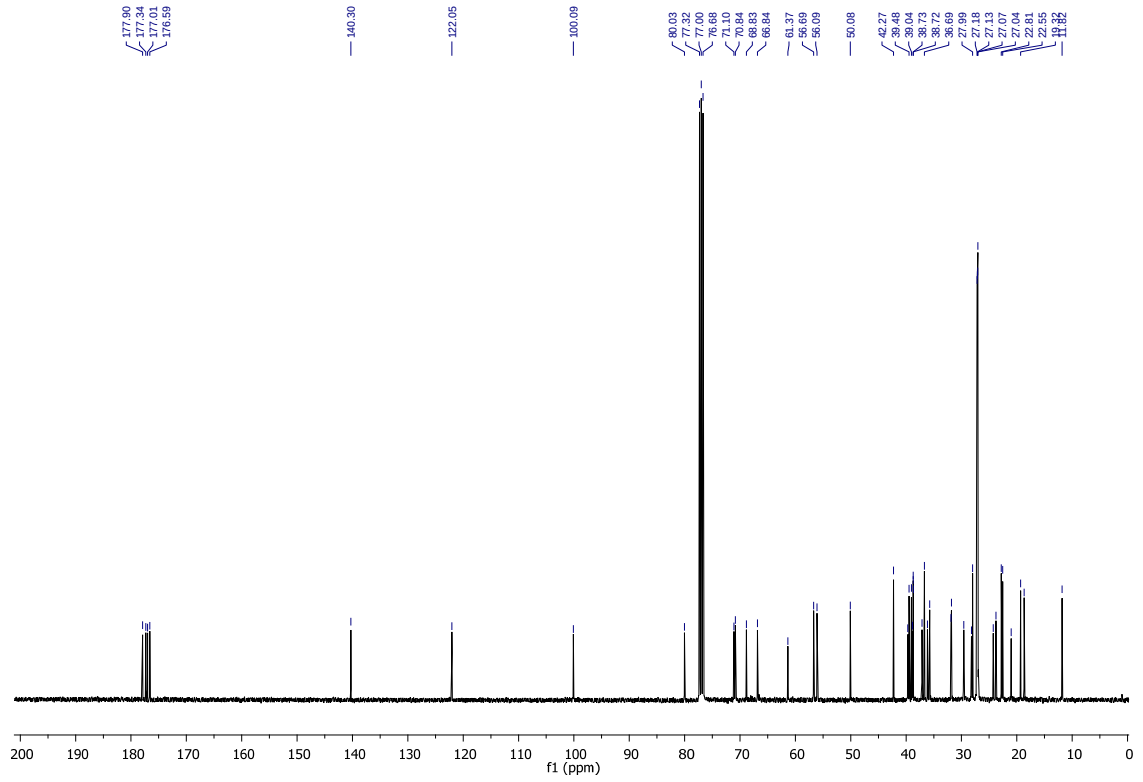
1,2:3,4-di-*O*-isopropylidene-6-*O*-(tetra-*O*-pivaloyl-α-D-galactopyranosyl)-α-D-galactose (9e-α)



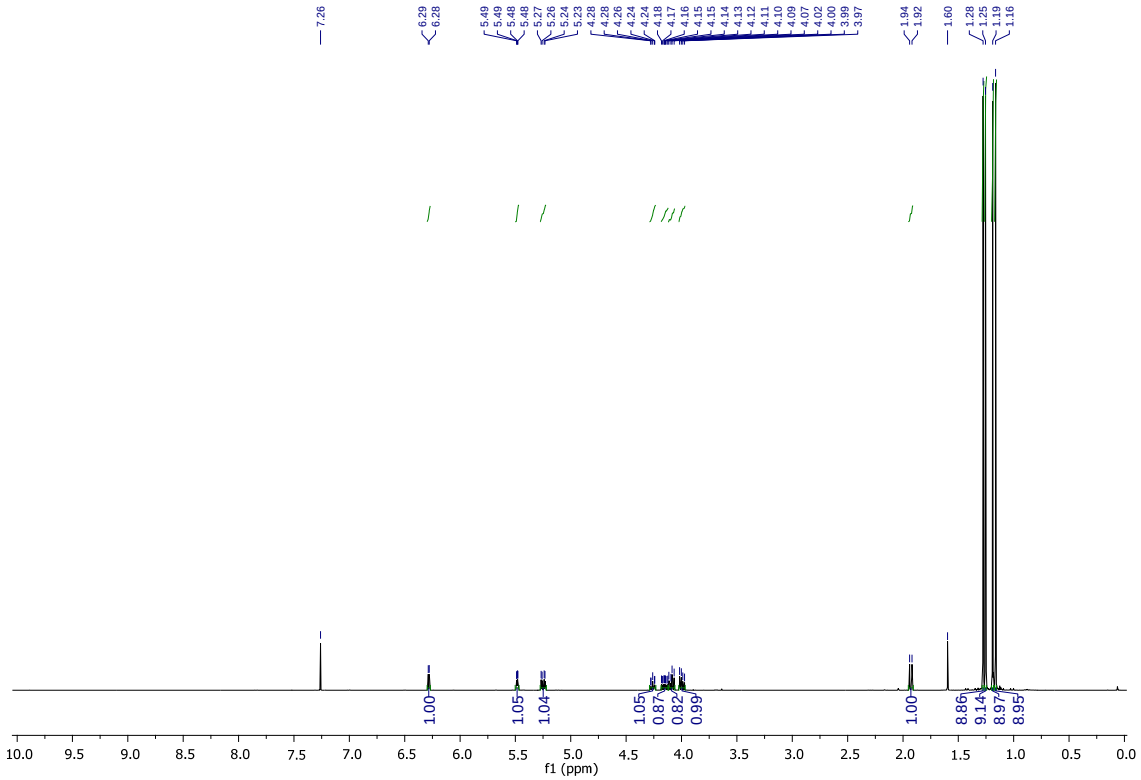


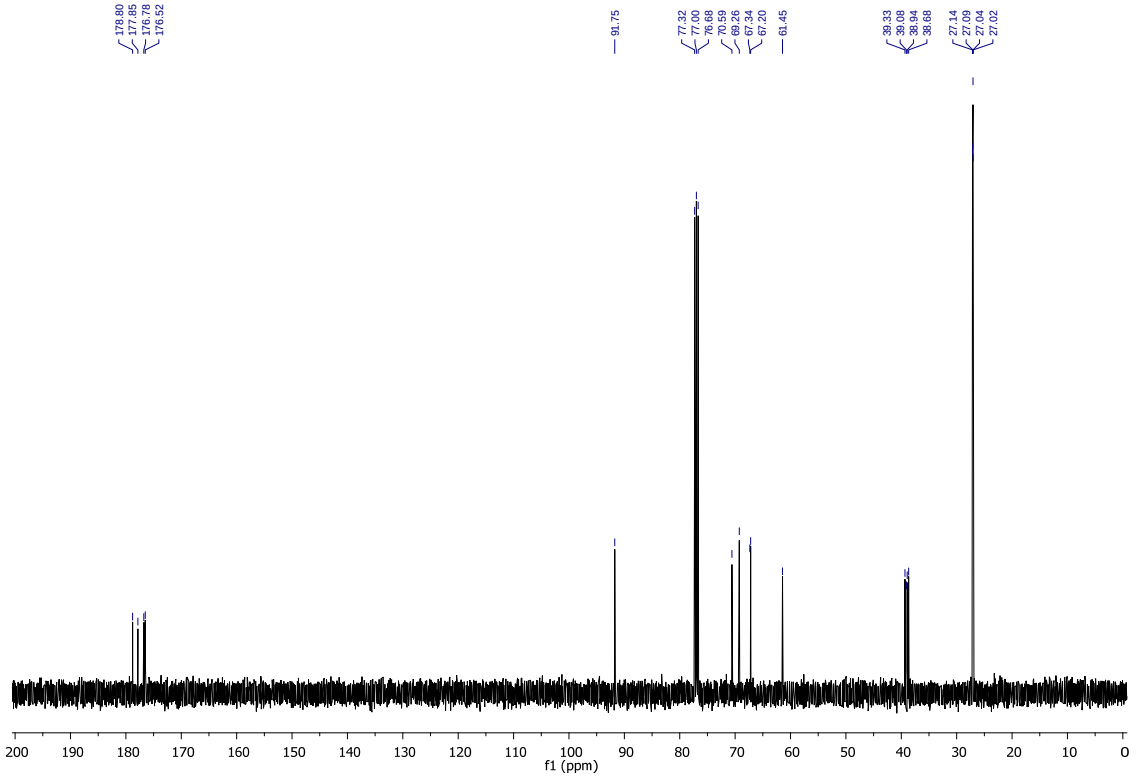
Cholesteryl 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranoside (9f-β)



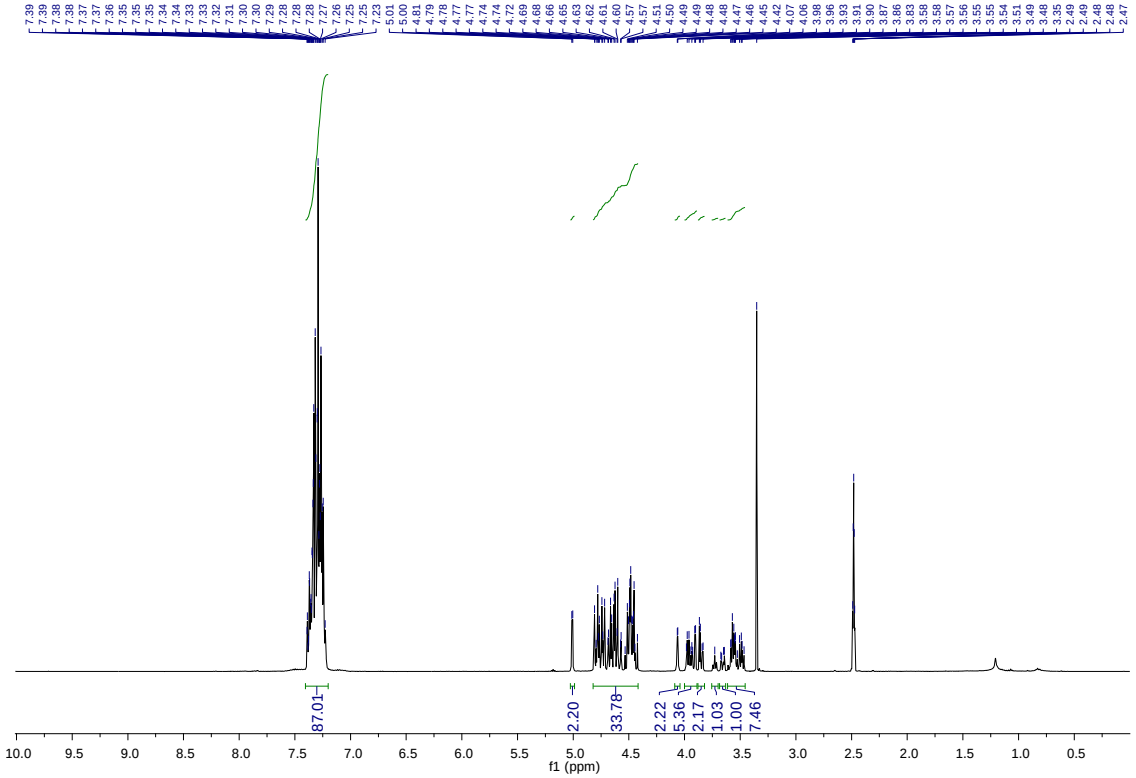


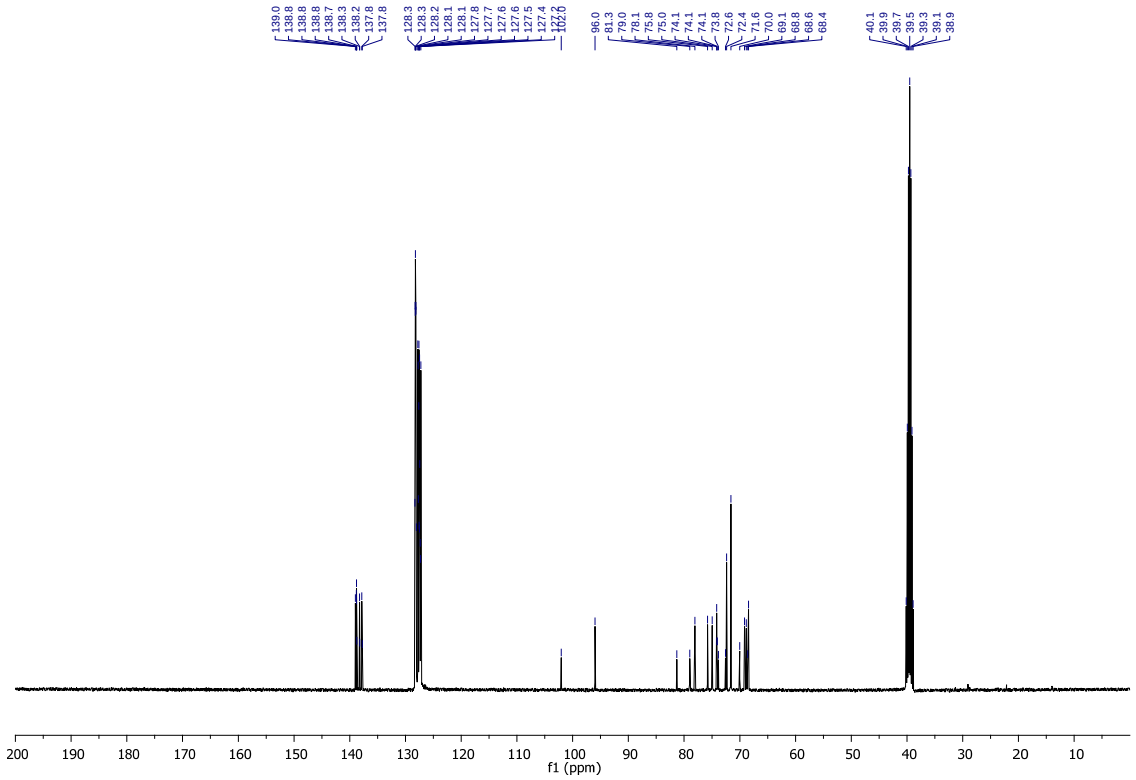
1,3,4,6-tetra-*O*-pivaloyl-α-D-galactopyranoside



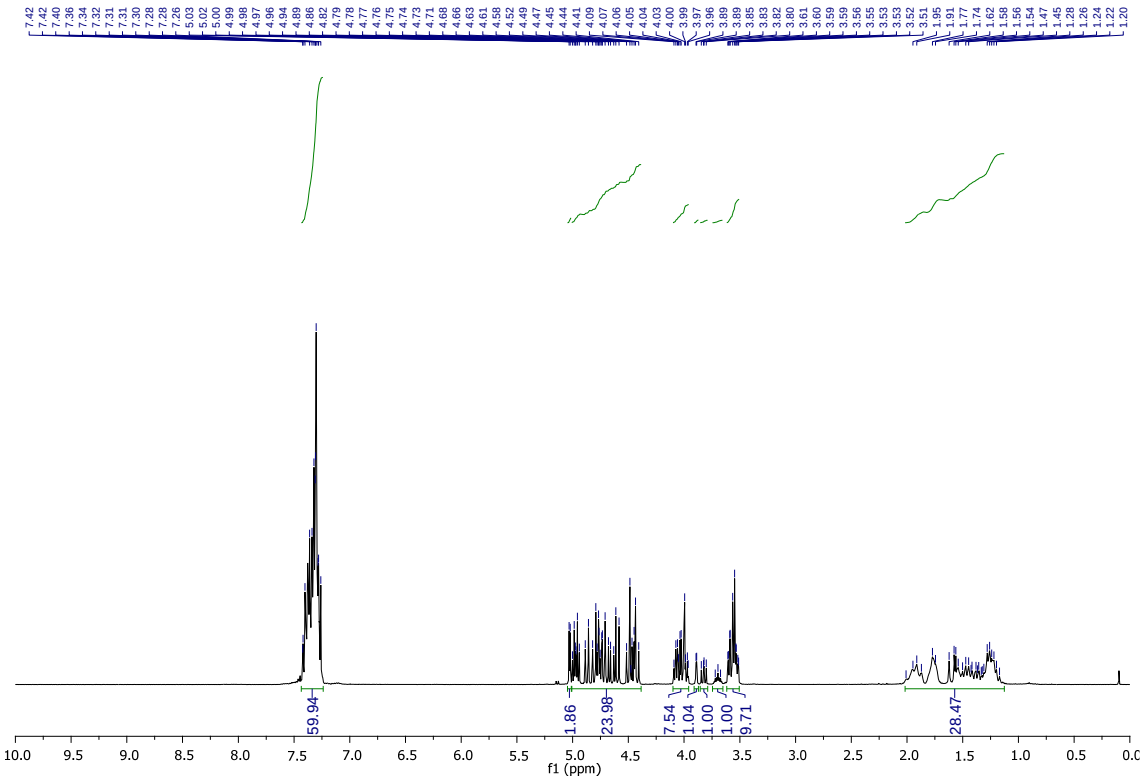


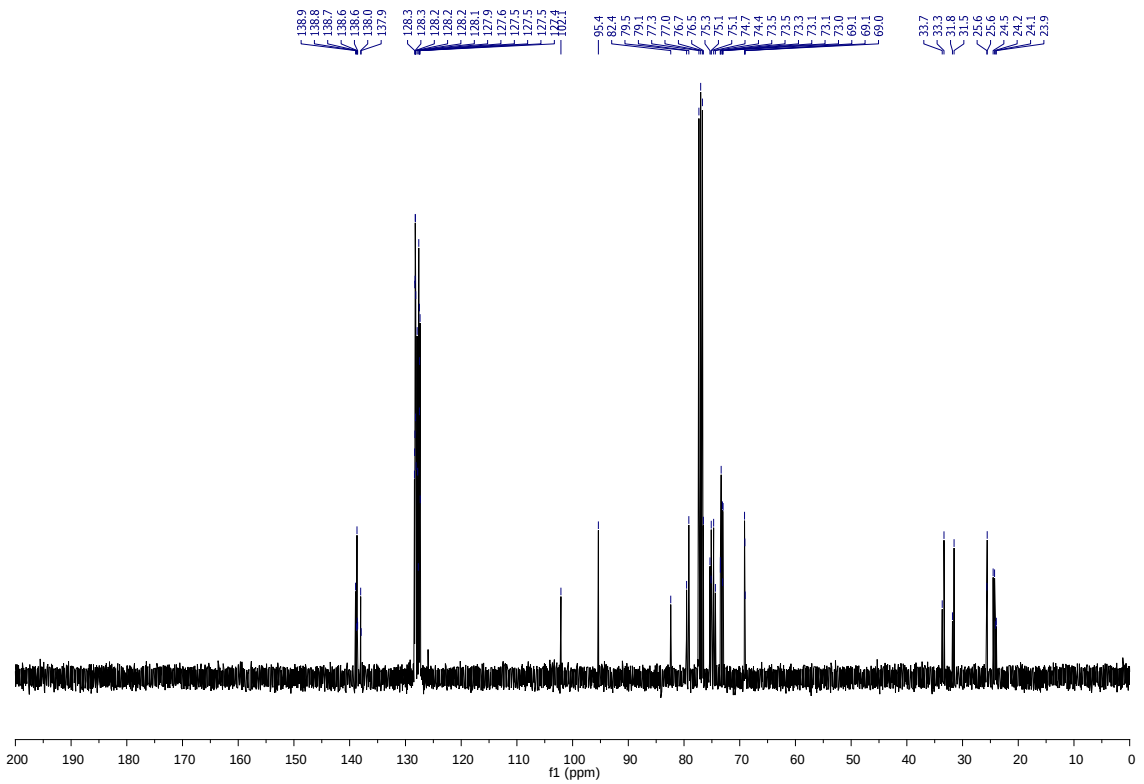
Benzyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10a)



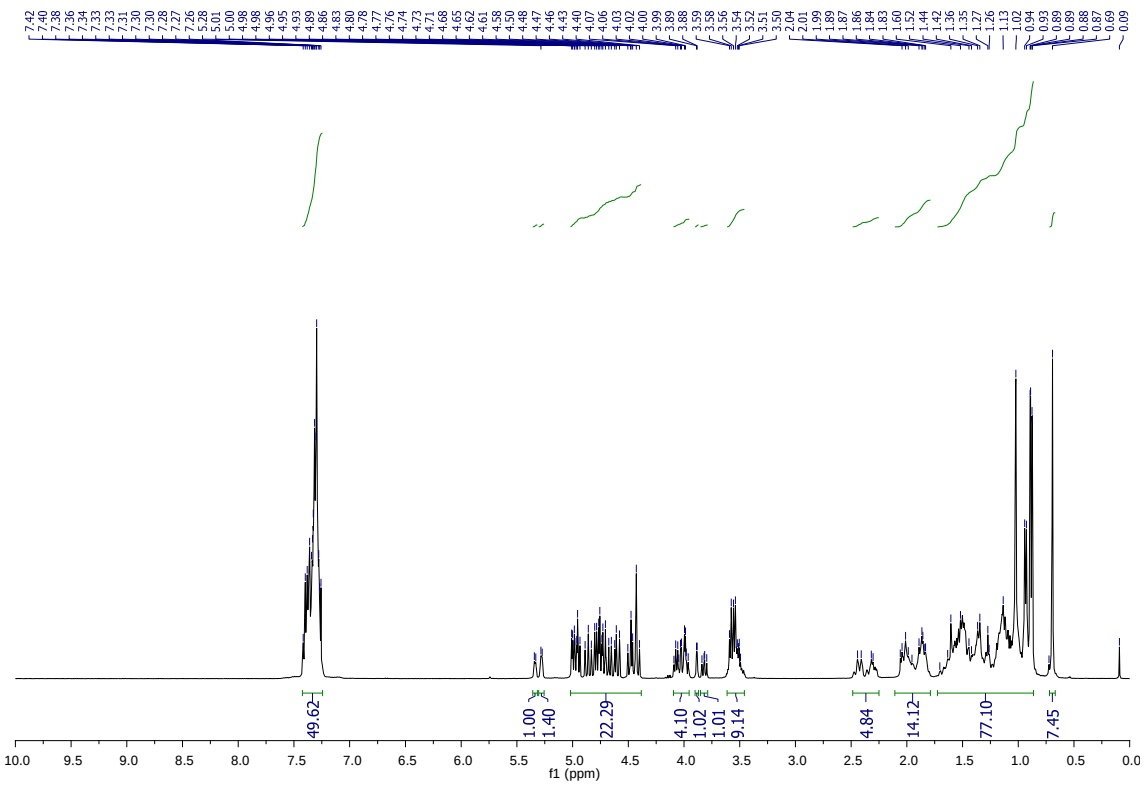


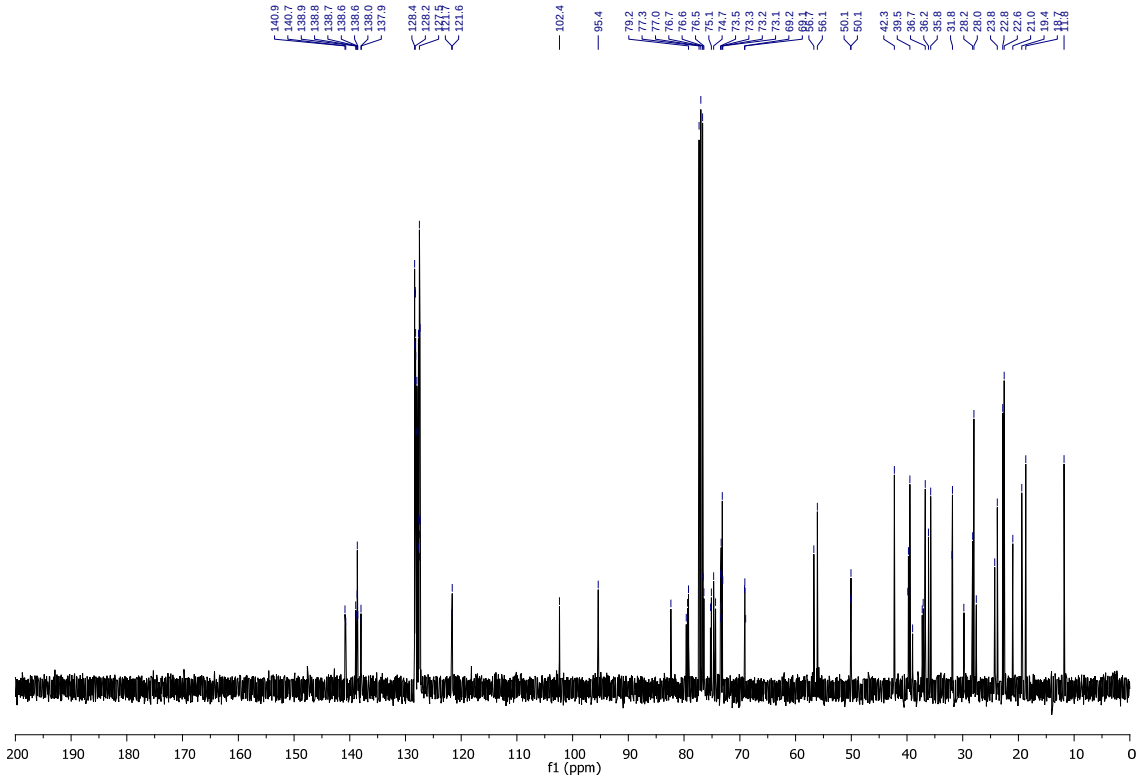
Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10b)



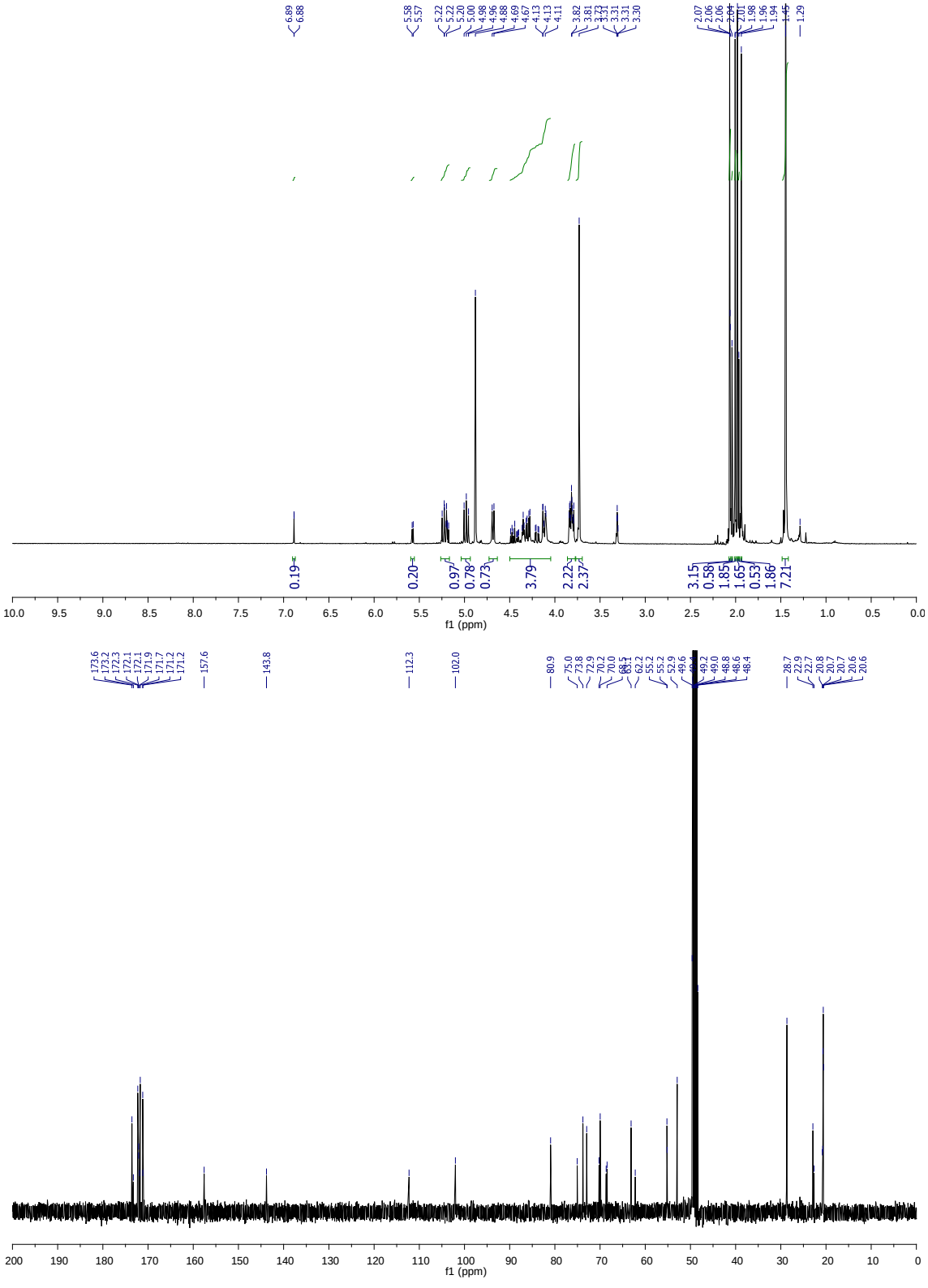


Cholesteryl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (10f)

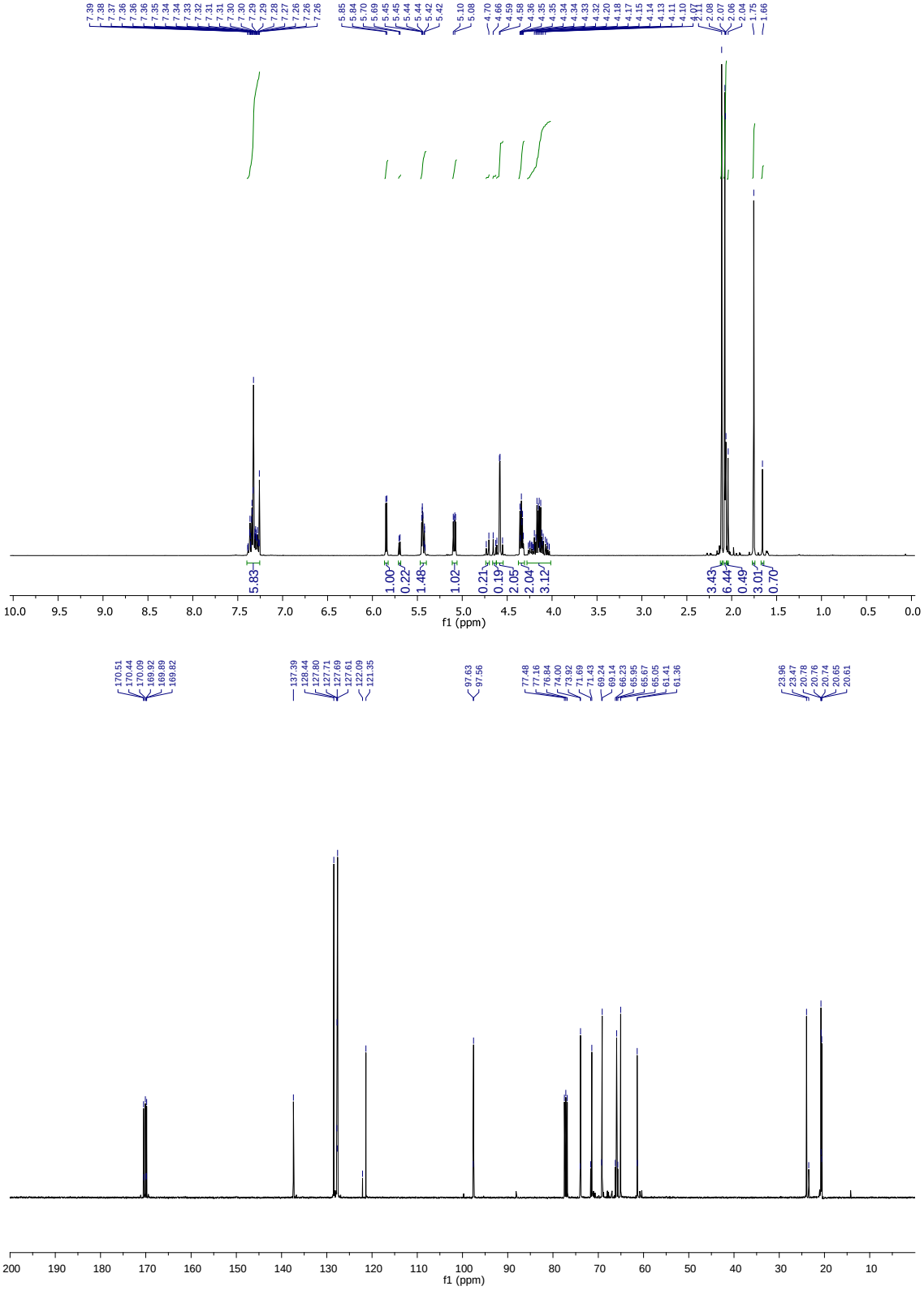




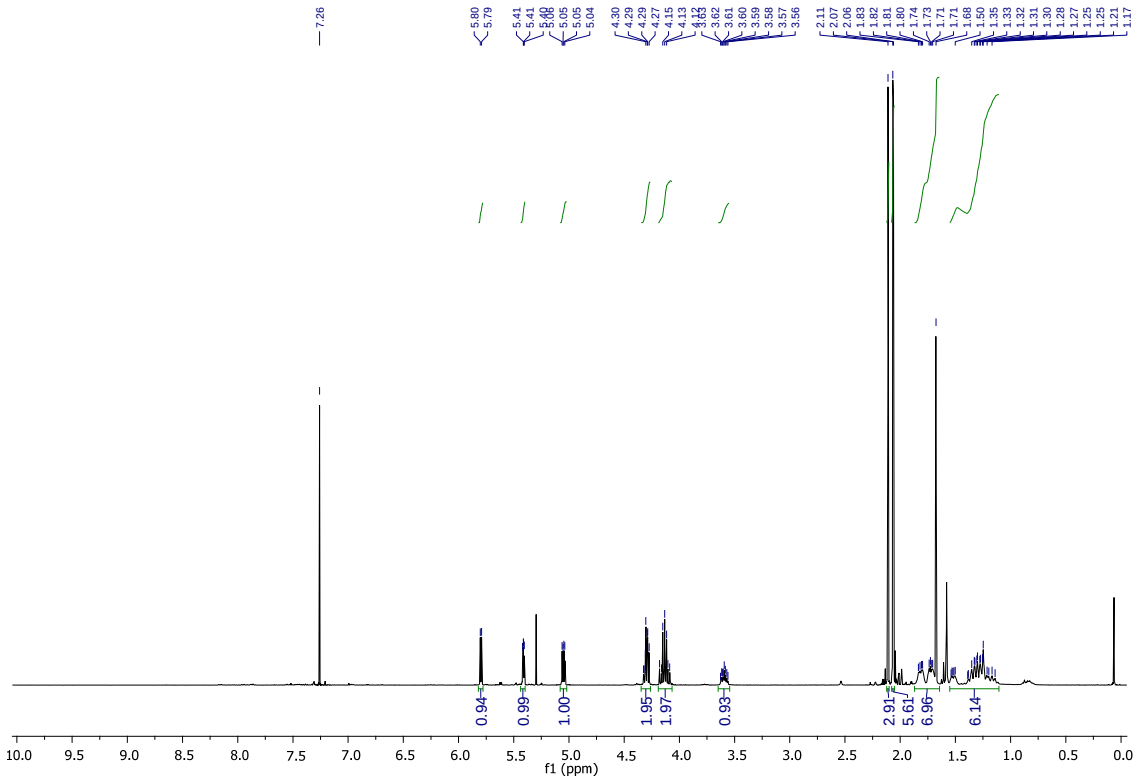
3-*O*-(3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-N-(*tert*-butyloxycarbonyl)-L-Serine methyl ester (12) and 2-acetamido-3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol (12')

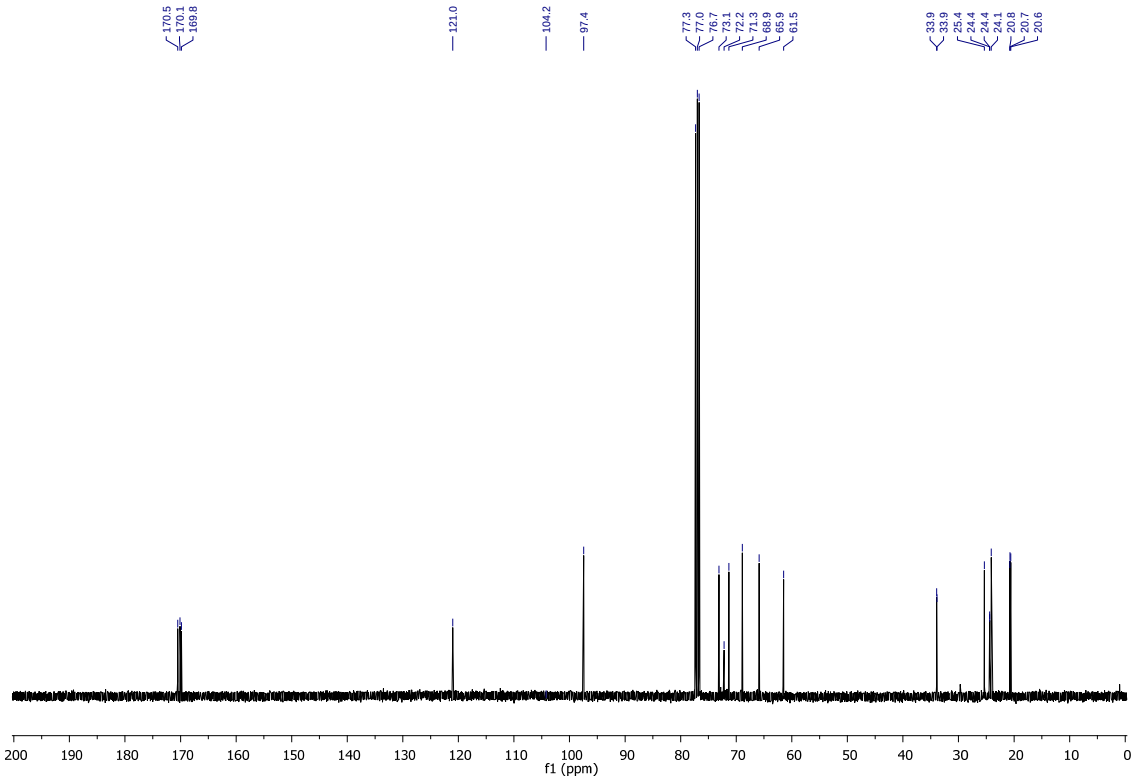


3,4,6-tri-*O*-acetyl-1,2-*O*-(1-benzyloxyethylidene)-α-D-galactopyranose (13a)



3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyclohexyloxyethylidene)-α-D-galactopyranose (13b)





3,4,6-tri-*O*-acetyl-1,2-*O*-(1-hexyloxyethylidene)-α-D-galactopyranose (13c)