# Conversion of Lactose into Mimics of *N*-Acetyllactosamine

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The α-*C*-Glycoside of *N*-acetyllactosamine **8** was synthesised from lactose by acetylation, conversion into the allyl α-*C*-glycoside **4**, exchanging the protecting groups for benzyl ethers, selective deprotection at the gluco-C-2 by iodocyclisation-reductive elimination, and conversion of the free hydroxyl group into an acetamido group by oxidation, oximation, stereoselective reduction and acetylation. Isomerization of the C-glycosidic appendage by conversion into a 2-oxypropyl group and treatment with base gave, after acetylation, the β-*C*-glycoside of *N*-acetyllactosamine **11**.

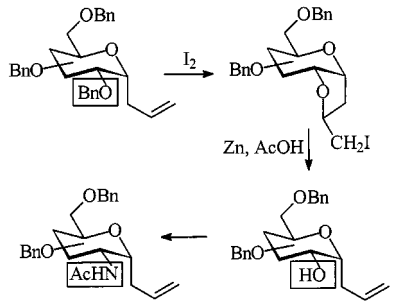
## Introduction

*N*-Acetyllactosamine [β-D-Gal-(1→4)-D-GlcNAc] is one of the most fundamental oligosaccharide sequences in glycoproteins and glycolipids and plays a central role in many cellular recognition phenomena.[1][2] It is, inter alia, a key constituent of the *lactoneo* glycosphingolipid family ($Le^x$, $Le^y$), which accumulate on the surface of cancer-cell membranes and are thus referred to as "tumour associated antigens".[3] Moreover, poly-*N*-acetyllactosamine is a significant carbohydrate component of lysosomal membrane glycoproteins,[4] and plays important roles in cytoplasm, to protect membrane glycoproteins from hydrolytic enzymes, and on the cell surface, to provide ligand structures for cell-adhesive molecules. For example, an abnormal expression of poly-*N*-acetyllactosamine have been observed in many kinds of tumor cells, including highly metastatic tumor cells.[4]

Since *N*-acetyllactosamine occurs in many biologically remarkable glycoconjugates, the synthesis of its analogues is a very attractive challenge. Recently carbadisaccharides related to *N*-acetyllactosamine have been synthesised,[5] but as far as we are aware, the C-glycosides of *N*-acetyllactosamine have never been reported.

In the course of our studies directed towards the synthesis of biologically relevant glycomimetics, we became interested in analogues of *N*-acetyllactosamine in which the *O*-glycosidic bond that links this disaccharide to peptidic or lipidic aglycons, both in the α and β anomeric configurations, is substituted by a more stable *C*-glycosidic bond.

We first considered the possibility of inducing the *C*-glycosylation reaction at the anomeric centre of the gluco-unit of lactosamino-derivatives. However, commercial lactosamine is very expensive, and most of the chemical[6] and enzymatic[7] methods developed to synthesise this disaccharide are rather complicated or suffer from high cost and limited availability of the enzymes. Only recently has a very interesting procedure to convert lactulose into lactosamine been reported.[8] Lactose, on the other hand, is obtained in large amounts as a by-product from dairies, and the *C*-glycosylation of the easily obtainable octaacetate **1** has been reported in the literature.[9] Therefore we have chosen lactose as a cheap starting material for the synthesis of the *C*-glycosides of *N*-acetyllactosamine, taking into account our recent observation that a polybenzylated allyl *C*-glucoside can be converted into the corresponding 2-amino-2-deoxy-*C*-glucoside according to the procedure reported in Scheme 1.[10]




Scheme 1. Conversion of an allyl C-glycopyranoside into its 2-acetamido-2-deoxy analogue

## Results and Discussion

Lactose was peracetylated,[11] and the obtained octaacetyllactose (**1**) was treated with allyltrimethylsilane and $BF_3{\cdot}OEt_2$ in order to obtain the allyl α-C-glycoside **2**.[9] However, TLC and $^{13}C$ NMR spectroscopic analysis of the reaction mixture constantly showed the presence of the β-anomer as a side product, which is difficult to separate. We observed that an efficient purification can be performed much more easily in a subsequent step of the synthesis. Therefore, crude **2** was deacetylated and then benzylated, affording the crude polybenzylated *C*-glycoside **3**. In order to effect the selective deprotection at C-2 of the glucosidic

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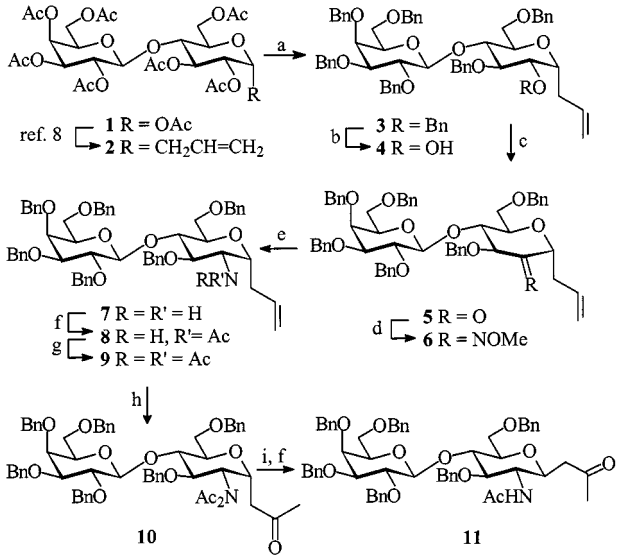
moiety, we treated crude **3** with iodine. At this stage a kinetic resolution occurred, the allyl α-*C*-glycoside **3** being more reactive than the β-anomer. After reductive elimination of the cyclic iodoether intermediate with zinc and acetic acid,[10] the allyl α-*C*-glycoside **4**, the gluco-C-2 hydroxyl group of which is deprotected, was easily separated from the completely protected β-anomer by chromatography. The whole process gave compound **4** in 31% overall yield from **1** (Scheme 2).




Scheme 2. (a) NaOMe 1 M, MeOH, then BnBr, NaH, DMF; (b) $I_2$, THF, then Zn, AcOH, MeOH/$Et_2O$; (c) DMSO/$Ac_2O$, 4Å m.s.; (d) $MeONH_2$, THF/MeOH/$H_2O$, pH 4.5; (e) $LiAlH_4$, THF; (f) $Ac_2O$, Py; (g) AcCl, $EtNiPr_2$, THF; (h) $Hg(OAc)_2$, THF/$H_2O$, then $Na_2PdCl_4$; (i) MeONa 1 M, MeOH

In order to convert the free hydroxyl group of **4** into an amino group, the approach based on the sequence oxidation-oximation-reduction was chosen. In α-glucopyranosides, in fact, the reduction of an oxime at C-2 stereoselectively occurs from the β-face, thus affording the equatorial amine.[12] Compound **4** was submitted to a Swern oxidation (DMSO/$Ac_2O$), and the obtained ketone **5** was converted into the corresponding oxime **6**. Stereoselective (*de* ≥ 95%) reduction with $LiAlH_4$ afforded the α-*C*-glycoside of lactosamine **7** in 49% overall yield from **4**. Acetylation with acetic anhydride in pyridine finally gave the α-*C*-glycoside of *N*-acetyllactosamine **8**.

The β-*C*-glycoside of *N*-acetyllactosamine was obtained by epimerization of the α-anomer. This epimerization occurs through a thermodynamically controlled retro-Michael/Michael reaction,[13] which requires a *C*-glycosidic appendage bearing an acidic hydrogen which is α to the anomeric position. The allylic group was then converted into a 2-oxopropyl group as follows: diacetate **9**, obtained from **8** (AcCl, $EtNiPr_2$, THF), was treated with $Hg(OAc)_2$ in THF/$H_2O$, then $Na_2PdCl_4$ in THF was added. The combined reactions afforded compound **10** in 82% yield. Epimerization of **10** was effected with a 1 M solution of NaOH, and acetylation of the product afforded the β-*C*-glycoside of *N*-acetyllactosamine **11** in 65% yield.

## Conclusion

In conclusion, this is the first example of the synthesis of *C*-glycosides of the biologically relevant disaccharide *N*-acetyllactosamine, in both the α and β anomeric configuration. Lactose was used as a cheap starting material, and the synthetic procedure exploited the possibility of converting a polybenzylated allyl *C*-glycoside into the corresponding 2-amino-2-deoxy derivative. The allyl or 2-oxopropyl *C*-glycosidic appendages of the obtained products are suitable for further functionalisation, in order to obtain different mimics of *N*-acetyllactosamine glycoconjugates.

## Experimental Section

**General Remarks:** NMR spectra were recorded on Bruker AC 300 spectrometer. Peak assignments were confirmed by COSY experiments. $CDCl_3$ was used as solvent and chemical shifts are reported in ppm downfield from tetramethylsilane (δ = 0). Coupling constants *J* are given in Hertz (Hz); multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. Melting points were determined with a Büchi apparatus and are not corrected. Optical rotations were measured at room temperature with a Perkin−Elmer 241 polarimeter. TLC was carried out on Merck Silica-gel 60 $F_{254}$ plates (0.25 mm thickness), and spots were visualized by spraying with a solution containing $H_2SO_4$ (31 mL), ammonium molybdate (21 g) and $Ce(SO_4)_2$ (1 g) in 500 mL water, or a 9:9:1 mixture of $H_2SO_4$/MeOH/$H_2O$, followed by heating at 110°C for 5 min. Flash chromatography (FC) was performed with Merck Silica-gel 60 (230−400 mesh). IR spectra were recorded on a Perkin−Elmer 681 spectrometer. Elemental analyses were performed using a Carlo Erba elemental analyser 1108.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-glucopyranosyl)-2-propene (4):** To a solution of lactose octaacetate **1** (34 g, 50 mmol) in $CH_3CN$ (170 mL) cooled to 0°C were added allyl trimethylsilane (50 mL, 250 mmol) and $BF_3{\cdot}Et_2O$ (32 mL, 250 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 5 h. The mixture was neutralised with satd. $NaHCO_3$ and extracted with AcOEt. The organic layers were dried ($Na_2SO_4$), filtered and the solvents evaporated under reduced pressure. The crude residue (33 g) was suspended in MeOH (100 mL) and 1 M NaOMe in MeOH (10 mL) was added. After stirring for 3 h at room temperature, the mixture became clear and it was neutralised with Amberlite IR-120 ($H^+$ form), filtered and the solvent evaporated. The oily residue (18 g) was dissolved in DMF (150 mL), and benzyl bromide (60 mL, 500 mmol) and sodium hydride (28 g, 700 mmol, portionwise!) were added. The reaction mixture was stirred at room temperature for 16 h, then the excess of sodium hydride was destroyed by slow addition of MeOH. The solution was concentrated to minimal volume, then diluted with AcOEt and washed with 5% aq. HCl and water. After drying ($Na_2SO_4$), filtration and evaporation of the solvent, the crude *C*-allyl lactoside **3** was obtained and used directly for the next steps without further purification. To a solution of the crude compound (19.7 g) in THF (250 mL) cooled to 0°C and kept in the dark, was added iodine (55 g, 218 mmol) with vigorous stirring. The mixture was allowed to warm to room temperature. After completion (1 h), the reaction mixture was diluted with AcOEt and the excess of iodine was reduced by washing with 5% aq. $Na_2S_2O_3$ until the organic phase became colourless. After washing with water, drying with $Na_2SO_4$, filtration and evaporation of the solvent, crude cyclic

iodoether (16.9 g) was obtained. This compound was dissolved in a 1:1 MeOH/$Et_2O$ mixture (400 mL), then freshly activated powdered zinc (20.8 g, 318 mmol) and glacial AcOH (2.0 mL, 31.7 mmol) were added. The suspension was stirred at room temperature for 20 h, then filtered over a Celite pad, diluted with $CH_2Cl_2$, and washed with satd. $NaHCO_3$ until the pH was neutral. After drying ($Na_2SO_4$) and filtration, the solvent was removed by rotary evaporation. Purification by FC (petroleum ether/AcOEt, 8:3) gave compound **4** as a clear oil (14.8 g, 31% overall yield from lactose octaacetate). − $[\alpha]_D$ = +11.2 (*c* = 1, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.40−7.10 (m, 30 arom. H), 5.87 (ddt, 1 H, *J* = 17.9, *J* = 10.4, *J* = 3.0 Hz, H-2), 5.15 (dd, 1 H, *J* = 2.0 Hz, H-3a), 5.08 (dd, 1 H, H-3b), 4.96 (d, 1 H, *J* = 11.7 Hz, C*H*HPh), 4.88 (d, 1 H, *J* = 10.7 Hz, C*H*HPh), 4.78 (d, 1 H, C*H*HPh), 4.75 (d, 1 H, *J* = 11.4 Hz, C*H*HPh), 4.73 (s, 2 H, C$H_2$Ph), 4.60 (d, 1 H, C*H*HPh), 4.56 (d, 1 H, *J* = 12.1 Hz, C*H*HPh), 4.53 (d, 1 H, C*H*HPh), 4.45 (d, 1 H, C*H*HPh), 4.42 (s, 2 H, C$H_2$Ph), 4.36 (d, 1 H, *J* = 7.8 Hz, H-1′′), 4.08−3.82 (m, 6 H, H-1′, H-2′, H-3′, H-4′, H-6′a, H-4′′), 3.81 (dd, 1 H, *J* = 9.5, *J* = 7.8 Hz, H-2′′), 3.66 (dd, 1 H, *J* = 10.3, *J* = 5.3 Hz, H-6′b), 3.63 (m, 1 H, H-5′), 3.59−3.40 (m, 4 H, H-3′′, H-5′′, H-6′′a, H-6′′b), 2.45 (m, 2 H, H-1a, H-1b). − $C_{57}H_{62}O_{10}$ (907.11): calcd. C 75.47, H 6.89; found C 74.81, H 6.80.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-amino-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2-propene (7):** A mixture of $Ac_2O$ (37.2 mL) and DMSO (84 mL) was stirred at room temperature for 1 h in the presence of freshly activated 4 Å molecular sieves, then transferred with a syringe into a flask containing compound **4** (4.0 g, 4.4 mmol). After stirring for 2 h at room temperature, the reaction mixture was poured into ice cold water and extracted with $CH_2Cl_2$. The combined organic layers were washed with satd. $NaHCO_3$ and water, dried ($Na_2SO_4$), filtered and evaporated under reduced pressure. The crude residue (3.86 g) was dissolved in a 1:1 mixture THF/MeOH (60 mL), then a solution of *O*-methyl hydroxylamine hydrochloride (3.67 g, 44 mmol) and AcONa (6.53 g, 48 mmol) in water (25 mL), adjusted to pH = 4.5 with a few drops of glacial AcOH was added. The reaction mixture was stirred at room temperature for 4 h, then diluted with AcOEt and washed with satd. $NaHCO_3$ and water, dried ($Na_2SO_4$) and filtered. The solvent was removed under reduced pressure to give an oily residue (3.5 g) which used directly for the next step without further purification. The crude methyl oxime was dissolved in dry THF (17 mL) and 1 M $LiAlH_4$ in THF (26.6 mL) was added at 0°C. The reaction mixture was stirred at room temperature for 16 h, then the excess of $LiAlH_4$ was destroyed by slow addition of MeOH. The solution was diluted by addition of AcOEt and washed with 15% NaOH and water. The organic layer was dried ($Na_2SO_4$), filtered and evaporated under reduced pressure. Purification by FC (petroleum ether/AcOEt, 4:6) gave compound **7** as a clear oil (1.95 g, 49% overall yield from alcohol **4**). − $[\alpha]_D$ = +19.3 (*c* = 1, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz, 50°C): δ = 7.40−7.10 (m, 30 arom. H), 5.84 (ddt, 1 H, *J* = 17.2, *J* = 10.2, *J* = 5.0 Hz, H-2), 5.14 (dd, 1 H, *J* = 2.0 Hz, H-3a), 5.06 (dd, 1 H, H-3b), 4.93 (d, 1 H, *J* = 11.6 Hz, C*H*HPh), 4.84 (d, 1 H, *J* = 11.0 Hz, C*H*HPh), 4.79 (d, 1 H, *J* = 11.3 Hz, C*H*HPh), 4.77 (d, 1 H, C*H*HPh), 4.70 (s, 2 H, C$H_2$Ph), 4.57 (d, 1 H, C*H*HPh), 4.54 (d, 1 H, *J* = 12.0, C*H*HPh), 4.51 (d, 1 H, C*H*HPh), 4.45 (d, 1 H, *J* = 10.0 Hz, C*H*HPh), 4.42 (d, 1 H, C*H*HPh), 4.34 (d, 1 H, C*H*HPh), 4.31 (d, 1 H, *J* = 7.3 Hz, H-1′′), 4.05−3.90 (m, 2 H, H-1′, H-4′), 3.89−3.78 (m, 3 H, H-3′, H-6′a, H-4′′), 3.76 (dd, 1 H, *J* = 9.0 Hz, H-2′′), 3.65−3.55 (m, 2 H, H-6′′a, H-6′′b), 3.54−3.45 (m, 2 H, H-6′b, H-5′), 3.43−3.35 (m, 2 H, H-3′′, H-5′′), 3.16 (m, 2H, $NH_2$), 2.44 (m, 2 H, H-1a, H-1b). − $C_{57}H_{63}NO_9$ (906.13): calcd. C 75.54, H 7.01, N 1.55; found C 75.48, H 6.90, N 1.51.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2-propene (8):** Compound 7 (1.9 g, 2.09 mmol) was dissolved in pyridine (15 mL), then $Ac_2O$ (2 mL) was added and the mixture was stirred overnight at room temperature. After addition of MeOH, the solution was concentrated to minimal volume and the residue was purified by FC (petroleum ether/AcOEt, 7:3) to afford compound 8 as a white solid (1.93 g, 97%), m.p. 71−72°C. − $[\alpha]_D$ = −3.6 (*c* = 1, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.50−7.15 (m, 30 arom. H), 6.38 (d, 1 H, *J* = 9.8 Hz, NH), 5.84 (ddt, 1 H, *J* = 19.5, *J* = 10.4, *J* = 6.8 Hz, H-2), 5.08 (dt, 1 H, H-3a), 5.03 (dt, 1 H, H-3b), 4.91 (d, 1 H, *J* = 11.2 Hz, C*H*HPh), 4.89 (d,1 H, *J* = 10.7, C*H*HPh), 4.79 (d, 1 H, C*H*HPh), 4.72 (s, 2 H, C$H_2$Ph), 4.57 (d,1 H, *J* = 11.8 Hz, C*H*HPh), 4.52 (d,1 H, C*H*HPh), 4.50 (s, 2 H, C$H_2$Ph), 4.46 (d, 1 H, *J* = 11.2 Hz, C*H*HPh), 4.42 (d, 1 H, C*H*HPh), 4.39 (d, 1 H, C*H*HPh), 4.35−4.22 (m, 2 H, H-1′′, H-3′), 4.14 (m, 1 H, H-2′), 4.00−3.80 (m, 3 H, H-1′, H-4′, H-4′′), 3.78−3.65 (m, 3 H, H-5′, H-6′a, H-2′′), 3.60−3.35 (m, 5 H, H-3′′, H-5′′, H-6′′a, H-6′′b, H-6′b), 2.20 (m, 2 H, H-1a, H-1b), 1.70 (s, 3 H, $CH_3$). − $C_{59}H_{65}NO_{10}$ (948.17): calcd. C 74.73, H 6.91, N 1.48; found C 74.60, H 6.80, N 1.44.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-*N,N*-diacetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2-propene (9):** To a solution of 8 (2.18 g, 2.3 mmol) in dry THF (25 mL) cooled to 0°C were added $EtN(iPr)_2$ (4.2 mL, 46 mmol) and AcCl (1.64 mL, 23 mmol), and the mixture stirred at room temperature for 16 h. After addition of MeOH, the reaction mixture was diluted with $CH_2Cl_2$ and washed three times with water. The organic layer was dried ($Na_2SO_4$), filtered and the solvent evaporated. FC (petroleum ether/AcOEt, 7:3) gave compound 9 (1.9 g, 82%) as a clear oil. − $[\alpha]_D$ = −9.4 (*c* = 1, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.40−7.10 (m, 30 arom H), 5.73 (ddt, 1 H, *J* = 15.3, *J* = 9.7, *J* = 5.0 Hz, H-2), 5.21 (d, 1 H, *J* = 10.8 Hz, C*H*HPh), 5.10 (dd, 1 H, *J* = 2.0 Hz, H-3a), 5.05 (dd, 1 H, H-3b), 4.93 (d, 1 H, *J* = 11.5 Hz, C*H*HPh), 4.83 (d, 1 H, *J* = 11.2 Hz, C*H*HPh), 4.78 (d, 1 H, C*H*HPh), 4.70 (s, 2 H, C$H_2$Ph), 4.57 (d, 1 H, *J* = 11.9 Hz, C*H*HPh), 4.53 (dd, 1 H, *J* = 9.5, *J* = 9.2 Hz, H-3′), 4.50 (d, 1 H, C*H*HPh), 4.34 (d, 1 H, *J* = 11.8 Hz, C*H*HPh), 4.33 (d, 1 H, *J* = 8.5 Hz, H-1′′), 4.32 (d, 1 H, C*H*HPh), 4.28 (d, 1 H, C*H*HPh), 4.16 (d, 1 H, C*H*HPh), 4.02 (m, 3 H, H-1′, H-2′, H-4′), 3.85 (m, 2 H, H-6′a, H-4′′), 3.75 (dd, 1 H, *J* = 9.8, *J* = 7.6 Hz, H-2′′), 3.50 (m, 2 H, H-5′, H-6′b), 3.44−3.26 (m, 4 H, H-3′′, H-5′′, H-6′′a, H-6′′b), 2.75 (m, 1 H, H-1a), 2.28 (2 s, 6 H, 2 $CH_3$), 2.20 (m, 1 H, H-1b). − $C_{61}H_{67}NO_{11}$ (990.20): calcd. C 73.98, H 6.82, N 1.42; found C 74.11, H 6.70, N 1.37.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-*N,N*-diacetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2-propanone (10):** Compound 9 (450 mg, 0.45 mmol) was dissolved in a mixture of THF/$H_2O$ (1.2:1), then $Hg(OAc)_2$ (162 mg, 0.51 mmol) was added and the reaction was stirred at room temperature until disappearance of the starting material was observed (TLC, 1 h). THF was added until the ratio THF/$H_2O$ became 3:1 (3.8 mL), then $Na_2PdCl_4$ (150 mg, 0.51 mmol) was added and the reaction mixture was warmed at 60°C for 2 h. After filtration over a Celite pad and dilution with $CH_2Cl_2$, the organic phase was washed with water, dried ($Na_2SO_4$), filtered and evaporated under reduced pressure. Purification by FC (petroleum ether/AcOEt, 2:1) afforded the ketone 10 (348 mg, 80%) as a clear oil. − $[\alpha]_D$ = −6.8 (*c* = 1, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.40−7.10 (m, 30 arom. H), 5.20 (d, 1 H, *J* = 10.8 Hz, C*H*HPh), 4.95 (d, 1 H, *J* = 11.5 Hz,

C*H*HPh), 4.82 (s, 2 H, C$H_2$Ph), 4.70 (s, 2 H, C$H_2$Ph), 4.64, (ddd, 1 H, $J$ = 7.8, $J$ = 5.7, $J$ = 5.6 Hz, H-1′), 4.55 (d, 1 H, $J$ = 11.9 Hz, C*H*HPh), 4.50 (d, 1 H, C*H*HPh), 4.41 (dd, 1 H, $J$ = 10.7, $J$ = 9.6 Hz, H-3′), 4.35 (d, 1 H, $J$ = 7.3 Hz, H-1′′), 4.34 (d, 1 H, C*H*HPh), 4.33 (d, 1 H, $J$ = 10.8 Hz, C*H*HPh), 4.27 (d, 1 H, C*H*HPh), 4.16 (d, 1 H, C*H*HPh), 4.09 (dd, 1 H, H-2′), 4.00, (t, 1 H, $J$ = 9.0 Hz, H-4′), 3.88−3.80 (m, 2 H, H-6′a, H-4′′), 3.75 (dd, 1 H, $J$ = 9.3 Hz, H-2′′), 3.58−3.45 (m, 2 H, H-5′, H-6′b), 3.44−3.27 (m, 4 H, H-6′′a, H-6′′b, H-3′′, H-5′′), 3.20 (dd, 1 H, $J$ = 17.0, $J$ = 7.8 Hz, H-1a), 2.76 (dd, 1 H, $J$ = 5.7 Hz, H-1b), 2.25 (s, 3 H, $CH_3$), 2.13 (s, 3 H, $CH_3$), 2.06 (s, 3 H, $CH_3$). − $C_{61}H_{67}NO_{12}$ (1006.20): calcd. C 72.80, H 6.72, N 1.39; found C 72.65, H 6.80, N 1.29.

**1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-2-propanone (11):** Compound 10 (75 mg, 0.075 mmol) was dissolved in a 1 M NaOMe solution in MeOH (12 mL). After stirring at room temperature for 24 h, the reaction mixture was neutralised with Amberlite IR-120 (H+ form), filtered and the solvent removed by rotary evaporation. The oily residue (69 mg) was directly submitted to FC (petroleum ether/AcOEt, 1:1) to give 11 (47 mg, 65%) as a clear oil. − $[\alpha]_D$ = +1.1 ($c$ = 0.35, $CHCl_3$). − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.40−7.15 (m, 30 arom. H), 5.22 (br.s, 1 H, NH), 4.93 (d, 1 H, $J$ = 13.4 Hz, C*H*HPh), 4.86 (d, 1 H, $J$ = 11.7 Hz, C*H*HPh), 4.79 (s, 2 H, C$H_2$Ph), 4.70 (s, 2 H, C$H_2$Ph), 4.62 (d, 1 H, C*H*HPh), 4.52 (d, 1 H, C*H*HPh), 4.50 (d, 1 H, $J$ = 12.2 Hz, C*H*HPh), 4.41 (d, 1 H, $J$ = 7.6 Hz, H-1′′), 4.35 (d, 1 H, C*H*HPh), 4.35 (d, 1 H, $J$ = 12.0 Hz, C*H*HPh), 4.27 (d, 1 H, C*H*HPh), 3.99 (t, 1 H, $J$ = 8.8 Hz, H-4′), 3.86 (d, 1 H, $J$ = 2.8 Hz, H-4′′), 3.83−3.73 (m, 4 H, H-1′, H-2′, H-6′a, H-2′′), 3.58 (dd, 1 H, $J$ = 1.4 Hz, $J$ = 10.9, H-6′b), 3.49 (t, 1 H, H-3′), 3.43−3.34 (m, 5 H, H-5′, H-3′′, H-5′′, H-6′′a, H-6′′b), 2.74 (dd, 1H, $J$ = 16.8, $J$ = 6.3 Hz, H-1a), 2.63 (dd, 1 H, $J$ = 3.7 Hz, H-1b), 2.14 (s, 3 H, $CH_3$), 1.81 (s, 3 H, $CH_3$). − $C_{59}H_{65}NO_{11}$ (964.17): calcd. C 73.49, H 6.80, N 1.45; found C 73.70, H 6.87, N 1.50.

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