DOI: 10.1002/ejoc.200600958

Synthesis of Novel Di- and Trisaccharide Mimetics with Non-Glycosidic Amino Bridges

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Keywords: Carbohydrates / Saccharide mimetics / Enzymatic glycosylation / Reductive amination / Dess–Martin oxidation / Non-glycosidically amino-bridged saccharides

Synthesis of novel di- and trisaccharides using enzymatic glycosylation, Dess–Martin oxidation and reductive amination allows rapid access to the target structures. Thus, a novel class of glycomimetics was obtained having nitrogen inserted as bridging atom between two non-anomeric positions. Novel di- and trisaccharide mimetics were designed using *N*-acetylglucosamine as a basis structure. A third monosaccharide unit was attached via an unnatural sugar–sugar bond without participation of the anomeric center. Their synthesis, proceeding via oxidation, glycosylation and reductive amination, required only a few steps, thus allowing rapid access to the target structures. Generation of the novel pseudo-disaccharide was achieved by Dess–Martin oxidation and a subsequent reductive amination.
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Introduction

The important role of carbohydrate derivatives in vital biological recognition processes has increasingly stimulated efforts in glycoconjugate research. Thus, biology studies require facile accesses to substantial quantities of complex oligosaccharides and glycoconjugates. Unnatural and modified oligosaccharides are needed as potential drug candidates as well as for the investigation of glycoconjugate structure-function relationships in biochemical processes. However, in contrast to other classes of natural products the synthesis of oligosaccharides needs individual protecting and activating groups and linking strategies. Universally applicable methodologies are seldomly available, thus mostly multiple step synthetic pathways are required. On the other hand carbohydrate components are often rather labile in vivo, since they are rapidly metabolised. Therefore, unnatural or modified oligosaccharides are of interest for investigation of glycoconjugate structure-function relationships as well as modulation or inhibition of biochemical processes. Such components termed glycomimetics are mostly non-natural carbohydrate-derived structures, which imitate or mimic the function of specific natural carbohydrate derivatives.[1] It can be expected that they show enhanced stability in vivo, particularly towards glycosidases and thus allow to study specific biological properties.

In this contribution an approach toward a novel class of glycomimetics is described. Emphasis was less on the synthesis of certain structures, but rather on the development of a fast and convenient methodology, which allows synthetic access to such glycomimetics in a few facile and high yielding steps. Of utmost importance are selective reactions, and both classical chemical as well as enzyme-catalysed transformations have to be considered. Due to the complexity of conventional oligosaccharide synthesis, enzymatic methods have experienced growing interest,[2–6] since no protection and deprotection steps are required and thus a rapid access to natural oligosaccharides is provided. However, so far application of enzymes for the formation of unnatural compounds is poorly investigated. Therefore, special emphasis in this project was on investigating enzymes for such a synthetic task.

As a common structural element in many biologically important glycoconjugates, such as *N*-linked oligosaccharides, human milk oligosaccharides[7] and ligands of various lectins,[8–10] *N*-acetyl-lactosamine (LacNAc) represented a promising basis for the design of interesting glycomimetics. To provide an element of resistance to enzymatic degradation another monosaccharide unit should be attached to the disaccharide via an unnatural sugar-sugar bond, without participation of anomeric centers (Figure 1). It can be expected that such a bond would not be cleaved by glycosidases. Further, the additional carbohydrate substituent may be supposed to exhibit a masking effect for the intraglycosidic LacNAc linkage[11] and thus prevent its cleavage by glycosidases as well.

Most previously described glycomimetics[12] contain carba-[13] or azasugars, with the ring-oxygen substituted by carbon or nitrogen,[14,15] or as in the C-glycosides having carbon instead of the anomeric oxygen.[16] Here it was envisaged to have nitrogen as a flexible bridging atom between two non-anomeric positions to arrive at a novel class of glycomimetics, not described so far.

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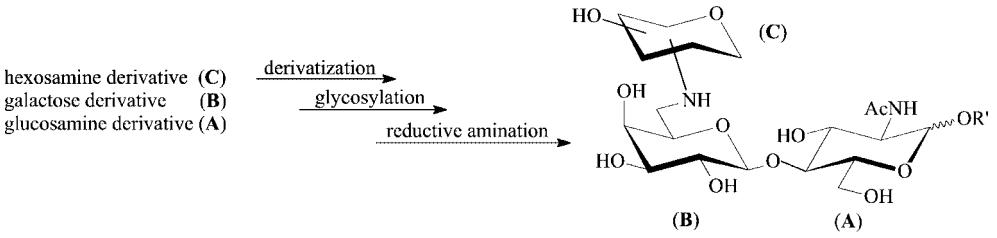


Figure 1. General synthetic Scheme.

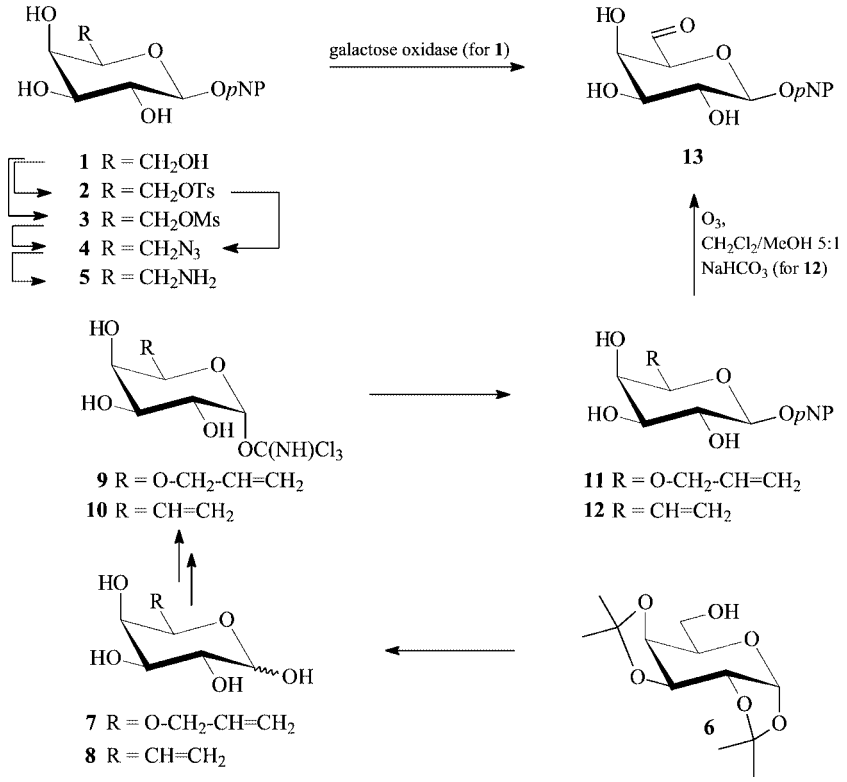
Thus, a synthetic approach to such glycomimetics starting with the three components **A** to **C** was dissected into three tasks: derivatization to generate aldehyde- or amino-functionalized saccharides, glycosylation to give LacNAc disaccharides and reductive amination to join the corresponding units (Figure 1).

Results and Discussion

Synthesis of Modified Galactosyl Donors

Modified galactose units B to be attached enzymatically to *N*-acetylglucosamine structures A employing the β-galactosidase (*Bacillus circulans*) to form β 1–4-linked LacNAc structures require the formation of various *p*-nitrophenyl β-D-galactopyranosides (Scheme 1). Synthesis of the 6-amino-substituted donor **5** was achieved in three steps. Esterification of **1** at C-6 with sulfonic acids gave the tosylate **2** or the mesylate **3** straightforwardly. Since the tosylate **2** could be too bulky to be accepted in the enzymatic glycosylation, the smaller mesylate **3** was prepared as well. Both sulfonates could be transferred into the desired azide **4** in 60% yield with some 4-nitrophenyl 3,6-anhydro-β-D-galactopyranoside as by-product. Final reduction of **4** in a Staudinger reaction gave the crystalline amine **5** in 94% yield.[17]

It was further of interest to investigate whether or not a donor structure with an aldehyde functionality would be accepted by this β-galactosidase. Therefore, the monosaccharide **13**[18] was synthesized bearing a substituent which can be transformed into an aldehyde group by ozonolysis. Starting with diacetone-D-galactose (**7**)[19] the 6-*O*-allyl ether **8** was prepared by phase-transfer catalysis according to Paulsen et al.[20] Further peracetylation, followed by re-



Scheme 1. Synthesis of modified *p*NPGal derivatives.

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gioselective deacetylation at the anomeric center, then transformation into the trichloroacetimidate **10**,[21] glycosylation with *p*-nitrophenol and deacetylation gave the β-galactopyranoside **12**. Employing the 6,7-olefin derivative **9**,[22] transformation into compound **11** and further into **13** was performed correspondingly.

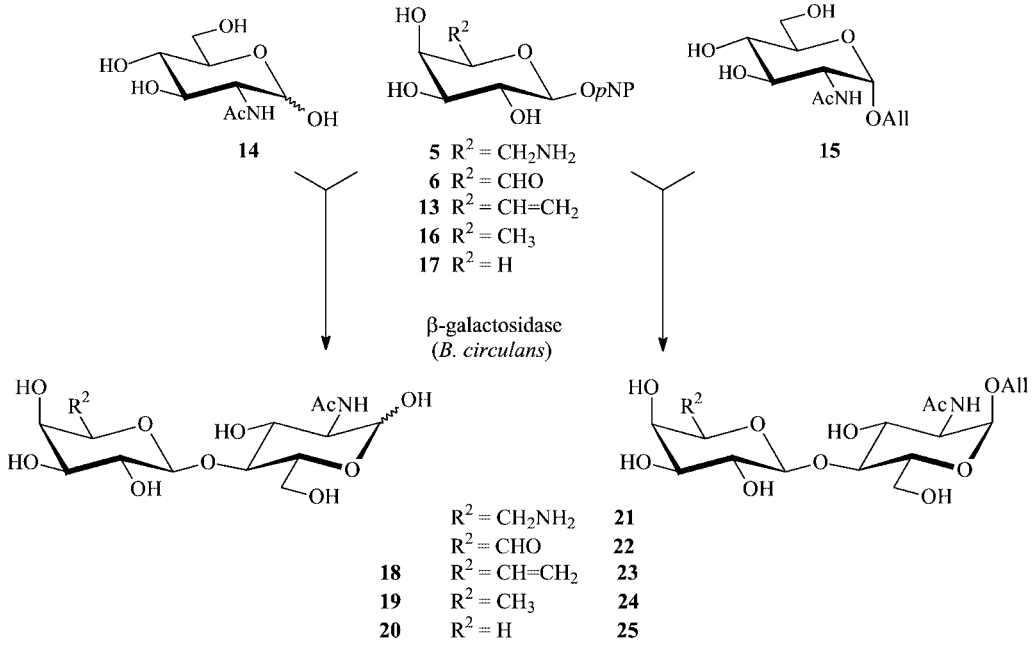
Cleavage of the olefinic compound **13** by ozonolysis led to the aldehyde **6** in a 47% yield. A much more efficient synthesis of aldehyde **6** could be performed by selective oxidation of *p*NP β-D-galactopyranoside (**1**). Best yields were obtained by galactose oxidase catalysed oxidation,[23] which gave the product **6** in nearly quantitative yield.

β-Galactosidase Catalysed Glycosylation

A synthetic access to the LacNAc-type disaccharides can be achieved in a few steps, carrying out the glycosylation by chemo-enzymatic methods. For this, an appropriate enzyme is the β-galactosidase from *Bacillus circulans* which catalyses the formation of a β 1–4 linkage, between a galactosyl donor and a 2-acetamido-glycosyl acceptor. The galactosidase from *B. circulans* is especially attractive for exploitation, due to its high yields and its extraordinary regioselectivity. Generally, the β 1–4-linked product is formed almost exclusively, with less than 5% β 1–6 isomer. Yields range from 18 to 66%, depending on the donor's leaving group and the utilized acceptor. These synthetic yields are quite considerable under the aspect that the natural task of glycosidases is to cleave oligosaccharides. As donor leaving groups, glucose, *p*-nitrophenol and *o*-nitrophenol are common but also others were investigated.[24] The acceptor may have a glucosyl or a galactosyl α/β-configuration with its anomeric center either unprotected or protected. An acetamido group at C-2 is required to control the regioselectivity, in other cases, e.g. with a hydroxyl group at C-2, a mixture of β 1–3-, β 1–4-, and β 1–6-linked regioisomeric disaccharides were obtained.[25]

Glycosidases often show a considerable flexibility with respect to variation of acceptor structures, but are mostly restricted to special donor structures. Concerning the β-galactosidase from *Bacillus circulans* different saccharides were recognized as acceptor molecules, however so far, there were only two derivatised galactosides published as donor molecules for the β-galactosidase from *Bacillus circulans*.[23,25,26] These results indicate that the primary alcohol function does not seem to be essential for recognition by the enzyme.

With the array of *p*NP galactopyranosides (Scheme 1) it could be investigated whether or not and to which extent these could function as donor substrates for β-galactosidase from *Bacillus circulans*. As uniform acceptor substrates 2-acetamido-2-deoxy-D-glucopyranose (**14**) as well as allyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**15**) were used in the enzymatic glycosylation. Reactions with compound **15** were performed at room temperature for 3 days, while reactions with GlcNAc (**14**) required 3 h at 55 °C.[27] Under these conditions, neither the 6-*O*-mesylate **3** nor the 6-azido-6-deoxy **4** compounds were accepted by the enzyme. However, reaction of amine **5** with acceptor **15** could be achieved and resulted in the formation of allyl 6-amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (**21**). Surprisingly, the 6,7-olefin structure **13** could be readily glycosylated to give both the disaccharides allyl 6,7-dideoxy-β-D-*galacto*-hept-6-enopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (**23**) and 6,7-dideoxy-β-D-*galacto*-hept-6-enopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (**18**) in 31% and 20%



Scheme 2. Enzymatic galactosylation employing modified *p*NPGal donors.

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yield, respectively. Again, 4-nitrophenyl 6-*O*-allyl-β-D-galactopyranoside (**12**) was not recognized. Reaction of the C-6 oxidized donor 4-nitrophenyl β-D-*galacto*-hexodialdopyranoside[23] (**6**) could be confirmed, and the disacccharide allyl β-D-*galacto*-hexodialdopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (**22**) was isolated in 68% yield. Further reactions employing the donors *p*NP-Fuc (**16**) and *p*NP-Ara (**17**) led to disaccharides **19** (66%) and **24** (76%) as well as **20** (6%) and **25** (13%), (Scheme 2) indicating excellent substrate properties of the 6-deoxy-D-*galacto* derivative in contrast to the L-*arabino* derivative. All yields refer to the amount of donor substrates used in the reactions.

Thus, the β-galactosidase from *B. circulans* showed a high flexibility with regard to C-6-modified galactopyranoside donor substrates.

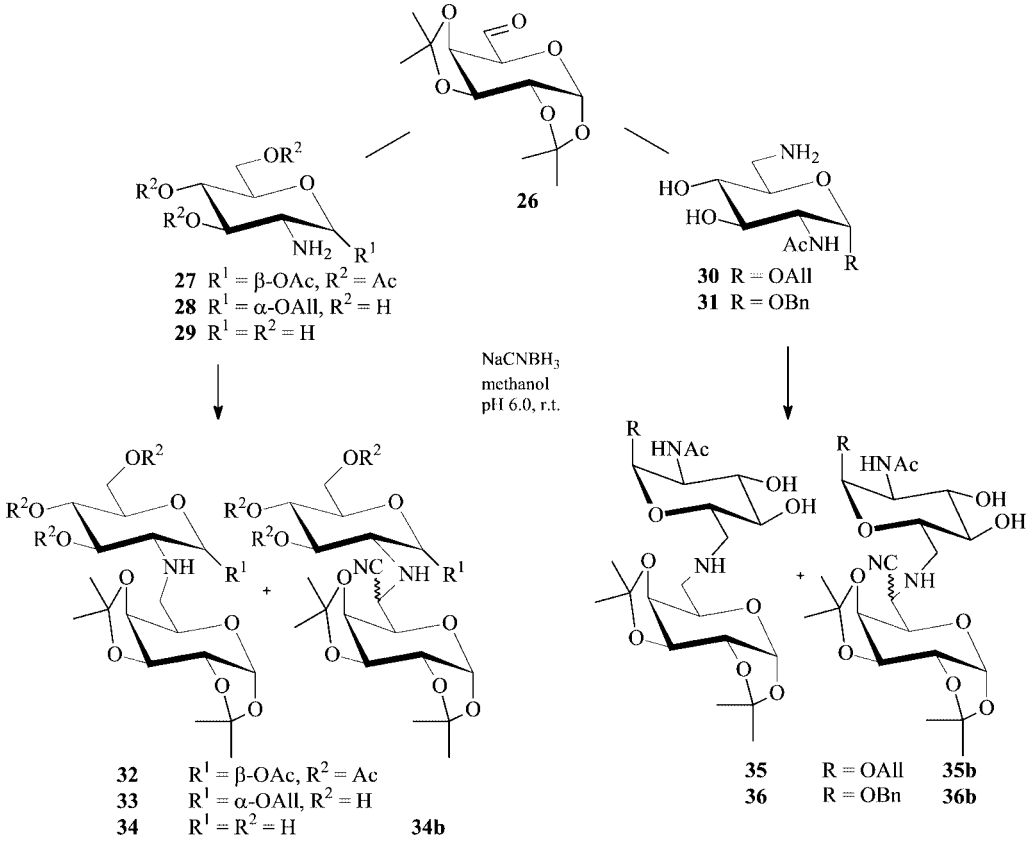
Reductive Amination

According to the general Scheme linking of the aldehydo- and amino-functionalized saccharide units would have to be performed mildly by reductive amination.[28–30] For initial studies the easily accessible diisopropylidene aldehydo galactose **26**[19,31] was chosen. As 2-amino sugars the glucoamine derivatives **27**[32] and **28**, obtained from **15** using a method according to Wong et al.,[23] as well as the 2-amino-1,5-anhydro-glucitol **29** were selected. The linkage formation was easily done with sodium cyanoborohydride in aqueous methanol at pH 6 and room temperature. Thus, the 2–6 via *N*-linked Gal-GlcN structures **32**–**34** could be obtained in 80%, almost quantitative, and 74% yield, respectively. In the latter case as side product the cyano adduct **34b** was observed in 24% yield.

Treatment of the same aldehyde with the 6-amino GlcNAc components **30** and **31**, obtained by Staudinger reduction[33] from the corresponding 6-azido precursors[34] again in about 50% yield gave the *N*-linked Gal-GlcNAc structures **35** and **36** this time via a 6–6 bridge. In both these cases the cyano adducts **35b** and **36b** (Scheme 3) appeared as side products in 10–30% yield.

En route to more advantageous preparation of aldehydo sugar derivatives the Dess–Martin oxidation[35] could be employed. Treatment of the GlcNAc glycosides **15**[36] and **37**[37] as well as the 1,5-anhydro-glucitol derivative **38**[38] with freshly prepared periodinane[39] gave the aldehydo compounds **39**–**41**. Without optimization they could be obtained in up to 50% yield.

As above, their transfer into 2–6 via *N*-linked disaccharide mimetics could be accomplished with allyl α-D-glucosamine **28** and 2-amino-1,5-anhydro-glucitol **29**. Thus compounds **43** and **44** were prepared in 50–80%, respectively. Correspondingly, with benzyl α-galactosamine **42** the mimetic structure **45** (Scheme 4) was obtained in 80% yield.



Scheme 3. Synthesis of disaccharide mimetics by reductive amination I.

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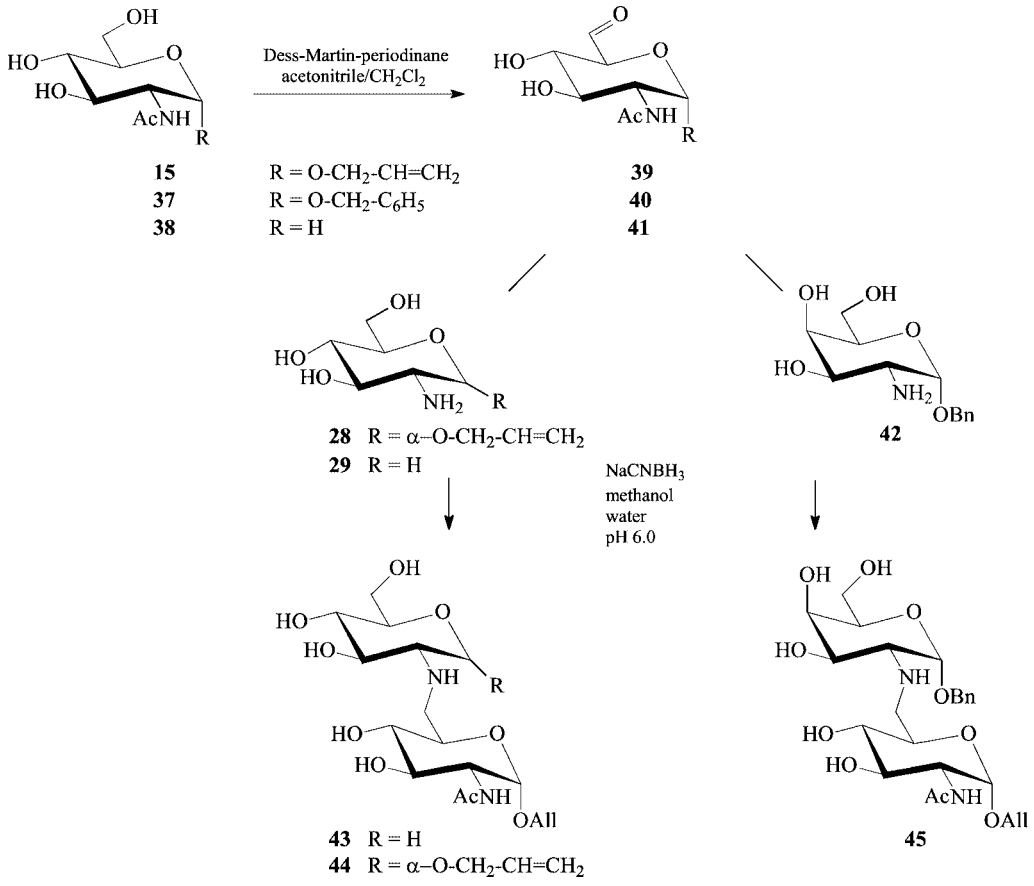
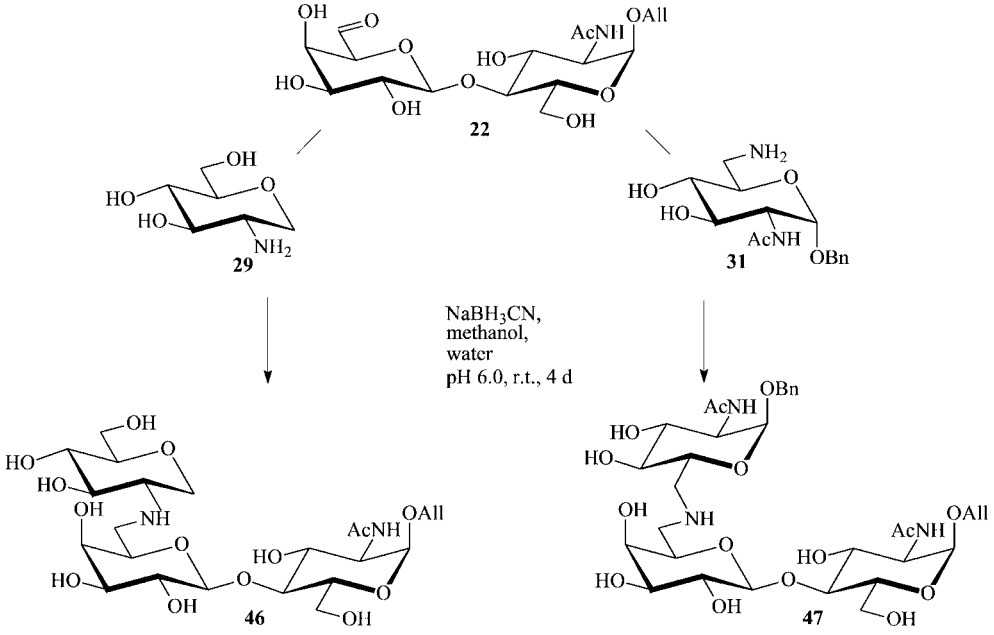


Scheme 4. Synthesis of disaccharide mimetics by reductive animation II.

Finally it was of interest to employ a disaccharide aldehyde with monosaccharide amines along the original outline. Thus, the C-6′-oxidized LacNAc **22**, obtained in good yields by galactosidase-catalyzed glycosylation was chosen as the substrate for the reductive aminations. As amino monosaccharide structures the 2-amino-1,5-anhydro-glucitol **29** and the benzyl glycoside of the 6-amino GlcNAc **31** were selected. Following the facily employed standard con-



Scheme 5. Reductive amination towards novel trisaccharide mimetics.

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ditions the reductive amination gave in quite satisfying yields the novel trisaccharide derivatives **46** and **47** (Scheme 5) comprising 6–6- and 6–2-*N*-linked glycosylated LacNAc mimetics. At room temperature complete conversion of the starting materials needed 4 days but by performing the reaction at 100 °C in a microwave oven a remarkable acceleration to 5 min was achieved.

Conclusion

To summarize the results, facile and rapid accesses to novel glycomimetics were elaborated employing among other reactions galactose oxidase-catalysed oxidation of *p*NP β-D-galactopyranoside, β-galactosidase-catalysed glycosylation, and finally reductive aminations with amino-functionalized carbohydrate units. The yields over all steps were up to about 50%. The enzymatic glycosylation with β-galactosidase (from *Bacillus circulans*) showed considerable flexibility for the enzyme substrates thus allowing for the synthesis of unusual disaccharide derivatives. Dess–Martin oxidation was found to be a selective chemical method to oxidize primary alcohol groups to aldehyde groups which could be reacted selectively with amino-functionalized carbohydrates to form novel pseudo-disaccharides. The formation of naturally occurring β-glycosides from easily cleavable α-allyl LacNAc structures will be addressed in further studies.

Experimental Section

General Remarks: TLC was performed on aluminium sheets coated with silica gel 60 (Merck) with UV detection by heating with H_2SO_4 (10% in EtOH). Aldehydes were detected by heating with 2,4-dinitrophenylhydrazine (0.2 M HCl) and amino-functionalized compounds with ninhydrine (0.2 M EtOH). Column chromatography was carried out on silica gel 60 (0.04–0.063 mm; Merck). Gelpermeation chromatography was carried out on Biogel P2 or Biogel P4 with bidistilled water or on Sephadex LH20 with bidistilled water/methanol (1:1). NMR spectra were recorded with a Bruker AMX-400 NMR (^{13}C: 100 MHz) or a DRX-500 NMR spectrometer (^{13}C: 125 MHz) and analyzed with the solvent peaks as references. Mass spectra were recorded with a Bruker Biflex II (MALDI-TOF, positive reflection mode, matrix: 2,5-dihydroxybenzoic acid) and with a VG Analytical 70–250S mass spectrometer (FAB mass spectra, *m*-nitrobenzyl alcohol). Melting points were determined with apotec melting point apparatus and are uncorrected. The optical rotations were measured on a Perkin–Elmer 341 polarimeter at 20 °C.

Enzymes were from Sigma Aldrich (β-Galactosidase: Lactase, EC 3.2.1.23, Biolacta®; Galactose Oxidase: D-Galactose: oxygen 6-oxidoreductase, EC 1.1.3.9).

Enzymatic Glycosylation. General Procedure 1: β-Galactosidase-catalysed glycosylation with allyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**15**) as acceptor: Glycosyl donor (100 μmol) and allyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**15**) (261 mg, 1 mmol, 10 equiv.) were dissolved in 50 mM potassium phosphate buffer (1.4 mL) pH 7.0 and acetonitrile (1.4 mL). Then a solution of 10 mg β-galactosidase (142 μL, 7 U) from *B. circulans* in 50 mM potassium phosphate buffer (1 mL) pH 7.0 was added. The reaction mixture was stirred for 3 d at room temperature. The reaction was stopped by short heating to 100 °C. The solvents were removed by freeze drying, and the residue was purified by gelpermeation chromatography using biogel P2 and water as eluent.

General Procedure 2: β-Galactosidase-catalysed glycosylation with 2-acetamido-2-deoxy-D-glucopyranose (**14**) as acceptor: Glycosyl donor (150 μmol) and 2-acetamido-2-deoxy-D-glucopyranose (**14**) (300 mg, 1.36 mmol, 9 equiv.) were dissolved in 50 mM sodium acetate buffer (4 mL) pH 5.0 at 55 °C. Then a solution of 10 mg β-galactosidase (80 μL, 4 U) from *B. circulans* in 50 mM potassium phosphate buffer (1 mL) pH 7.0 was added. The reaction mixture was incubated for 3 h at 55 °C, during which time the solution became bright yellow. The reaction was stopped by short heating to 100 °C. The solvents were removed by freeze drying, and the residue was purified by gelpermeation chromatography using biogel P2 and water as the eluent.

Reductive Amination. General Procedure 3: To a solution of aldehyde (0.15 mmol) and amine (0.45 mmol, 3 equiv.) in methanol (1 mL) was added water dropwise to reach complete solution. The pH of the solution was adjusted to 6 using either a 1 M solution of glacial acetic acid in methanol or a solution of 10% triethylamine in methanol. Then a 0.3 M methanolic sodium cyanoborohydride solution (0.2 to 0.25 mL) was added. The reaction mixture was stirred overnight and then concentrated. The residue was purified by column chromatography.

General Procedure 4: To a solution of aldehyde (0.36 mmol) in methanol (2.5 mL) and amine (1.02 mmol) in methanol (1.0 mL) was added water dropwise to reach complete solution. The pH of the solution was adjusted to 6 using a solution of 10% triethylamine in methanol (0.05 mL). Then a 0.3 M methanolic sodium cyanoborohydride solution (0.6 mL) was added and the mixture was stirred at room temp. overnight. The solution was concentrated and the residue was purified by gelpermeation chromatography on sephadex LH20 (water/methanol, 1:1).

Staudinger Reduction. General Procedure 5: The azide (1 mmol) was dissolved in THF/H_2O (4:1, 45 mL) and treated with triphenylphosphane (0.36 g, 1.36 mmol, 1.4 equiv.) and silica gel (1.00 g). The reaction mixture was stirred overnight at 50 °C, then the solvent was removed under reduced pressure and the residue purified by column chromatography.

4-Nitrophenyl 6-*O*-Tosyl-β-D-galactopyranoside (2): To a solution of compound **1** (1.80, 5.97 mmol) in pyridine (25 mL) was added dropwise at 0 °C tosyl chloride (1.40 g, 7.34 mmol) dissolved in pyridine (5.5 mL). After stirring for 2 h at room temperature the reaction was quenched by adding water (100 mL). The product was extracted using ethyl acetate, and the organic phase was washed with 5% hydrochloric acid, water and then dried with $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (DCM/MeOH, 7:1) to give **2** (1.40 g, 51%) as a colourless solid, m.p. 81 °C, $[\alpha]_D^{20} = -100$ (c = 0.5, CH_3OH). ^{1}H NMR (500 MHz, MeOD): δ = 8.19 (m, 2 H, *p*NP), 7.74 (m, 2 H, CH-Ts), 7.31 (m, 2 H, CH-Ts), 7.17 (m, 2 H, *p*NP), 5.00 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 4.31 (dd, $J_{5,6a}$ = 4.1, $J_{6a,6b}$ = 10.7 Hz, 1 H, 6a-H), 4.27 (dd, $J_{5,6b}$ = 7.9 Hz, 1 H, 6b-H), 4.05 (dd, 1 H, 5-H), 3.89 (d, $J_{3,4}$ = 3.5 Hz, 1 H, 4-H), 3.81 (dd, $J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 3.61 (dd, 1 H, 3-H), 2.40 (s, 3 H, CH_3-Ts) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 164.11, 146.95, 144.29, 134.71 (2× C-*p*NP, 2× C-Ts), 131.37 (CH-Ts), 129.62 (CH-Ts), 127.10 (CH-*p*NP), 118.19 (CH-*p*NP), 102.15 (C-1), 74.76, 74.73 (C-3, C-5), 72.08 (C-2), 71.16 (C-6), 70.35 (C-4), 21.93 (CH_3-Ts) ppm.

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4-Nitrophenyl 6-*O*-Mesyl-β-D-galactopyranoside (3): To a solution of compound **1** (180 mg 0.598 mmol) in pyridine (7.5 mL), mesylchloride (57.5 μL, 0.745 mmol) was added dropwise at 0 °C. After stirring for 5.5 h at 0 °C the reaction was quenched by addition of water. The solution was concentrated and the residue was purified by column chromatography on silica gel (DCM/MeOH, 7:1). Product **3** (143 mg, 63%) was obtained as a colourless solid; m.p. 155 °C, $[a]_D^{20}$ = –93 (*c* = 0.25, CH_3OH). ^1H NMR (400 MHz, D_2O): δ = 8.12 (m, 2 H, *p*NP), 7.10 (m, 2 H, *p*NP), 5.10 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.41 (dd, $J_{5,6a}$ = 3.8, 1 H, $J_{6a,6b}$ = 11.2 Hz, 6a-H), 4.35 (dd, $J_{5,6b}$ = 8.2 Hz, 1 H, 6b-H), 4.11 (dd, 1 H, 5-H), 3.93 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 4-H), 3.75 (dd, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 3.67 (dd, 1 H, 3-H), 3.00 (s, 3 H, CH_3-Ms) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 162.05 (C-*p*NP), 146.95 (C-*p*NP), 126.44 (CH-*p*NP), 116.85 (CH-*p*NP), 100.06 (C-1), 73.42 (C-5), 72.61 (C-3), 70.50 (C-2), 70.03 (C-6), 68.50 (C-4), 36.95 (CH_3-Ms) ppm. $C_{13}H_{17}NO_{10}S$ (379.3): calcd. C 41.16, H 4.52, N 3.69; found C 41.10, H 4.65, N 3.68.

4-Nitrophenyl 6-Azido-6-deoxy-β-D-galactopyranoside (4)

Synthesis Starting from Tosylate 2: Compound **2** (1.46 g, 3.21 mmol) and sodium azide (1.05 g, 16.2 mmol) were dissolved in dry DMF (40 mL) and stirred for 14 h at 80 °C. Then the reaction mixture was cooled to room temperature and concentrated. The residue was taken up in ethyl acetate, washed with water, dried with $MgSO_4$, filtered, concentrated in vacuo and subsequently purified by flash chromatography on silica gel (DCM/MeOH, 12:1) to give **4** (0.63 g, 60%).

Synthesis Starting from Mesylate 3: Compound **3** (117 mg, 0.31 mmol) and sodium azide (100 mg, 1.54 mmol) were dissolved in dry DMF (4 mL) and stirred for 5 h at 80 °C. Then the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (DCM/MeOH, 12:1) to give 4-nitrophenyl 3,6-anhydro-β-D-galactopyranoside (53 mg, 60%) and 4-nitrophenyl 6-azido-6-deoxy-β-D-galactopyranoside (**4**) (39 mg, 39%).

4-Nitrophenyl 6-Azido-6-deoxy-β-D-galactopyranoside (4): Colourless solid, m.p. 205 °C (dec.), $[a]_D^{20}$ = –224 (*c* = 0.15, CH_3OH). ^1H NMR (400 MHz, MeOD): δ = 8.22 (m, 2 H, *p*NP), 7.25 (m, 2 H, *p*NP), 5.08 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 3.93 (ddd, $J_{4,5}$ = 1.0, $J_{5,6a}$ = 8.4 Hz, 1 H, 5-H), 3.84 (m, 2 H, 2-H, 4-H), 3.65 (dd, $J_{6a,6b}$ = 12.7 Hz, 1 H, 6a-H), 3.63 (dd, $J_{2,3}$ = 9.9, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 3.35 (dd, $J_{5,6b}$ = 4.1 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 127.01 (CH-*p*NP), 118.08 (CH-*p*NP), 102.31 (C-1), 76.38 (C-5), 74.85 (C-3), 72.15, 70.90 (C-2, C-4), 52.94 (C-6) ppm. $C_{12}H_{14}N_4O_7$ (326.3): calcd. C 44.17, H 4.32, N 17.17; found C 44.19, H 4.52, N 16.54.

4-Nitrophenyl 3,6-Anhydro-β-D-galactopyranoside: ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 8.21 (m, 2 H, pNP), 7.19 (m, 2 H, pNP), 5.82 (d, $J_{2\text{-OH},2}$ = 4.6 Hz, 1 H, 2-OH), 5.44 (s, 1 H, 1-H), 5.38 (d, $J_{4\text{-OH},4}$ = 3.8 Hz, 1 H, 4-OH), 4.27 (dd, $J_{4,5}$ = 1.8 Hz, 1 H, 4-H), 4.22 (dd, $J_{5,6b}$ = 2.8 Hz, 1 H, 5-H), 4.09 (d, $J_{2,3}$ = 4.6 Hz, 1 H, 3-H), 4.05 (dd, 1 H, 2-H), 3.85 (d, $J_{6a,b}$ = 9.7 Hz, 1 H, 6a-H), 3.80 (dd, 1 H, 6b-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 162.00 (C-pNP), 141.80 (C-pNP), 126.17 (CH-pNP), 116.89 (CH-pNP), 99.67 (C-1), 80.91 (C-3), 78.57 (C-5), 72.54 (C-2), 69.94 (C-6), 69.38 (C-4) ppm.

4-Nitrophenyl 6-Amino-6-deoxy-β-D-galactopyranoside (5): Azide **4** (90 mg, 0.27 mmol) was reacted according to general procedure 5. The product was purified by flash chromatography on silica gel [1. EE/MeOH (2:1) + 3% pyridine, 2. EE/MeOH (1:4) + 3% pyridine]. The amine **5** (76 mg, 94%) could be isolated as a yellow solid. M.p. 188 °C (dec.), $[a]_D^{20}$ = –66 (*c* = 0.28, CH_3OH). ^1H NMR (400 MHz, MeOD): δ = 8.30 (m, 2 H, *p*NP), 7.33 (m, 2 H, *p*NP), 5.16 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 3.99 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 4-H), 3.93 (m, 2 H, 2-H, 5-H), 3.72 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 3-H), 3.22 (dd, $J_{5,6a}$ = 7.6, $J_{6a,6b}$ = 13.5 Hz, 1 H, 6a-H), 3.10 (dd, $J_{5,6b}$ = 4.3 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 164.22 (C-*p*NP), 143.00 (C-*p*NP), 127.08 (CH-*p*NP), 118.06 (CH-*p*NP), 102.44 (C-1), 75.71 (C-5), 74.89 (C-3), 72.09 (C-2), 71.43 (C-4), 42.90 (C-6) ppm. $C_{12}H_{16}N_2O_7$ (300.3): calcd. C 48.00, H 5.37, N 9.33; found C 44.55, H 5.69, N 7.74. Contamination of amine **5** was detected.

4-Nitrophenyl β-D-*galacto*-Hexodialdo-1,5-pyranoside (6)

Synthesis by Ozonolysis: Under argon a solution of compound **13** (300 mg, 1.01 mmol) and sodium hydrogen carbonate (128 mg) in dry DCM/MeOH (5:1, 6 mL) was cooled to –50 °C. Ozone was added until the reaction mixture remained blue after 2.5 h. Excess of ozone was removed by discharging argon through the flask. Then triphenylphosphane (291 mg) was added and the mixture was stirred at room temperature for 36 h. The reaction mixture was concentrated and the residue was purified by column chromatography (DCM/MeOH, 9:1) to give **6** (143 mg, 47%) as a colourless solid.

Synthesis by Enzymatic Oxidation: A solution of compound **1** (303 mg, 1.01 mmol) and 500 mM aqueous copper sulfate (10 μL) in potassium phosphate buffer pH 7 (14 mL) were treated with catalase (90 μL, 3120 U) and galactose-oxidase (90 μL, 90 U) under oxygen atmosphere at room temperature for one day. The reaction was stopped by adding methanol (4 mL), the solvent was evaporated and the water was removed by freeze drying. The crude product (580 mg) contained product and salts. 102 mg of the crude product were purified by column chromatography (DCM/MeOH, 10:1) to give **6** (55 mg, 98%) as hydrate; m.p. 154 °C, $[a]_D^{20}$ = –87 (*c* = 0.15, H_2O), R_F = 0.29 (DCM/MeOH, 7:1). ^1H NMR (400 MHz, D_2O): δ = 8.24 (m, 2 H, *p*NP), 7.22 (m, 2 H, *p*NP), 5.16 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 5.11 (d, $J_{5,6}$ = 7.4 Hz, 1 H, 6-H), 4.14 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 4-H), 3.85 (dd, $J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.75 (dd, 1 H, 3-H), 3.61 (d, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 142.96 (C-*p*NP), 126.49 (CH-*p*NP), 116.87 (CH-*p*NP), 100.52 (C-1), 88.46 (C-6), 77.66 (C-5), 72.77 (C-3), 70.58 (C-2), 68.43 (C-4) ppm.

6-*O*-Allyl-D-galactopyranose (8): 1. Allyl bromide (31 mL), tetrabutylammonium hydrogen sulfate (6.53 g), and compound **7**[19] (5.07 g, 19.5 mmol) were vigorously stirred in a mixture consisting of dichloromethane (400 mL) and 50% sodium hydroxide solution (400 mL). After 5 h at room temperature the layers were separated. The aqueous layer was extracted with dichloromethane, the combined organic layers were washed with water, dried with $MgSO_4$, filtered and concentrated. Purification by column chromatography (PE/EE, 6:1) yielded 6-*O*-allyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4.57 g, 78%). Colourless syrup, $[a]_D^{20}$ = –60 (*c* = 0.5, $CHCl_3$), ref.[40] $[a]_D^{20}$ = –71.8, ref.[40] b.p.$_{0.03}$ = 86 °C, R_F = 0.39 (PE/EE, 4:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.79 (ddd, $J_{\text{CH-All,=CH2t}}$ = 17.3, $J_{\text{CH-All,=CH2c}}$ = 10.7 Hz, 1 H, CH-All), 5.41 (d, $J_{1,2}$ = 5.1 Hz, 1 H, 1-H), 5.15 (dd, $J_{\text{=CH2c,=CH2t}}$ = 1.5 Hz, 1 H, =CH_{2t}-All), 5.05 (d, 1 H, =CH_{2c}-All), 4.47 (dd, $J_{2,3}$ = 2.5, $J_{3,4}$ = 8.1 Hz,1 H, 3-H), 4.19 (dd, 1 H, 2-H), 4.13 (dd, $J_{4,5}$ = 2.0 Hz, 1 H, 4-H), 3.94–3.90 (m, 2 H, -CH_2-All), 3.85 (dd, $J_{5,6a}$ = 5.6, $J_{5,6b}$ = 6.6 Hz, 1 H, 5-H), 3.53 (dd, $J_{6a,6b}$ = 10.2 Hz, 1 H, 6a-H), 3.46 (dd, 1 H, 6b-H), 1.42 (s, 3 H, -CH_3), 1.32 (s, 3 H, -CH_3), 1.21 (s, 3 H, -CH_3), 1.19 (s, 3 H, -CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.22 (CH-All), 117.50 (=CH_2-All), 109.61 [-$C(CH_3)_2$], 108.81 [-$C(CH_3)_2$], 96.80 (C-1), 74.00 (-CH_2-All), 72.86 (C-4), 71.20 (C-3),

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71.10 (C-2), 69.02 (C-6), 67.15 (C-5), 26.22, 26.05, 25.00, 24.45 (4× -CH_3) ppm.

2. To a solution of 0.10 M hydrochloric acid (1060 mL, 106 mmol, 1.02 equiv.) and methanol (105 mL) was added 6-*O*-allyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (31.36 g, 104.4 mmol). After stirring for 2.5 h at 90 °C the reaction mixture was cooled to room temperature, neutralized with saturated sodium hydrogen carbonate solution and concentrated. Inorganic salts were removed by filtration through silica gel (chloroform/methanol, 6:1) to give **8** (26.02 g) as crude brown syrup, which was used in the following reaction without further purification.

A small amount of **8** was crystallized, washed with chloroform and characterized: colourless solid, m.p. 85 °C, $[\alpha]_D^{20}$ = –10 (*c* = 0.38, H_2O), R_F = 0.70 (EE/MeOH/H_2O, 7:3:1). ^{1}H NMR (400 MHz, MeOD): δ = 6.11 (m, 1 H, CH-All), 5.47 (dd, $J_{=CH2c,=CH2t}$ = 0.8 Hz, 1 H, =CH_{2c}-All), 5.33 (m, $J_{CH\text{-}All,=CH2t}$ = 17.3 Hz, 2 H, =CH_{2t}-All, 1-H), 4.34 (dd ≈ t, $J_{5,6a}$ = 6.6, $J_{5,6b}$ = 5.6 Hz, 1 H, 5-H), 4.22 (m, 3 H, 2-H, -CH_2-All), 4.06 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 1.3 Hz, 1 H, 4-H), 3.96 (dd, 1 H, 3-H), 3.92 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 3.84 (m, 2 H, 6a-H, 6b-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 136.50, 136.47 (CH-All), 117.79 (=CH_2-All), 99.11 (C-1β), 94.63 (C-1α), 75.40, 74.15 (C-5), 73.73, 73.67 (-CH_2-All), 71.68, 71.61 (C-4), 71.28, 71.11 (C-6), 71.02, 70.81, 70.44 71.20 (C-3, C-2) ppm.

2,3,4-Tri-*O*-acetyl-6-*O*-allyl-α-D-galactopyranosyl Trichloroacetimidate (10): Compound **8** (1.46 g, 6.76 mmol) dissolved in pyridine (90 mL) was cooled in an ice bath, and acetic anhydride (18 mL) was added dropwise. After 19 h stirring at room temperature the reaction mixture was diluted with toluene (30 mL), concentrated, codistilled with toluene, and the crude 1,2,3,4-tetra-*O*-acetyl-6-*O*-allyl-D-galactopyranose was dried in vacuo. 1,2,3,4-Tetra-*O*-acetyl-6-*O*-allyl-D-galactopyranose (2.85 g, 7.34 mmol) was dissolved in DMF (5.9 mL), ammonium carbonate (1.06 g, 13.58 mmol, 1.85 equiv.) was added and the reaction mixture was stirred at room temperature overnight. Dilution with dichloromethane (70 mL) was followed by excessive washing with brine. The aqueous phases were extracted with dichloromethane (30 mL), the combined organic phases dried with Na_2SO_4, filtered and concentrated. The product was isolated by column chromatography (toluene/EE, 1:1) to give 2,3,4-tri-*O*-acetyl-6-*O*-allyl-D-galactopyranose (1.59 g, 62%) as a colourless solid; m.p. 108 °C, R_F = 0.62 (PE/EE, 1:1), $[\alpha]_D^{20}$ = +91 (*c* = 0.35, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.99 (dddd, $J_{CH\text{-}All,=CH2c}$ = 8.9, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH2\text{-}All,CHAll}$ = 5.9, $J_{CH2\text{-}All,CHAll}$ = 6.1 Hz, 1 H, CH-All), 5.65 (d, $J_{1α,2α}$ = 3.8 Hz, 0.72 H, 1α-H), 5.61 (d, $J_{3α,4α}$ = 3.4, $J_{4,5}$ = 0.8 Hz, 0.72 H, 4α-H), 5.55 (dd, 0.72 H, 3α-H), 5.40 (dd, $J_{=CH2c,=CH2t}$ = 1.5 Hz, 1 H, =CH_{2t}-All), 5.34 (dd, 1 H, =CH_{2c}-All), 5.30 (dd, $J_{2α,3α}$ = 10.9 Hz, 0.72 H, 2α-H), 5.26 (dd, $J_{2β,3β}$ = 10.9, $J_{3β,4β}$ = 2.8 Hz, 0.28 H, 3β-H), 5.21 (dd, $J_{1β,2β}$ = 7.7 Hz, 0.28 H, 2β-H), 4.87 (d, 0.28 H, 1β-H), 4.59 (dd, $J_{5α,6aα}$ = 7.4, $J_{5α,6bα}$ = 4.7 Hz, 0.72 H, 5α-H), 4.16 (dd, 0.28 H, -CH_2-Allβ), 4.13 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.1, $J_{CH2\text{-}All,=CH2}$ = 1.8 Hz, 0.72 H, -CH_2-Allα), 4.10 (dd, 0.72 H, -CH_2-Allα), 4.09 (d, 0.28 H, 4β-H), 4.07 (dd, 0.28 H, -CH_2-Allβ), 4.03 (dd, $J_{5β,6aβ}$ = 6.7, $J_{5β,6bβ}$ = 4.9 Hz, 0.28 H, 5β-H), 3.71 (dd, $J_{6aβ,6bβ}$ = 10.1 Hz, 0.28 H, 6aβ-H), 3.64 (dd, $J_{6aα,6bα}$ = 10.8 Hz, 0.72 H, 6aα-H), 3.58 (dd, 0.28 H, 6bβ-H), 3.57 (dd, 0.72 H, 6bα-H), 2.26 (s, 3 H, Ac), 2.22 (s, 3 H, Ac), 2.13 (s, 3 H, Ac) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ ≈ 170.5 (3× CO-Ac), 134.33 (CH-All), 118.42 (-CH_2-Allα), 118.22 (-CH_2-Allβ), 96.19 (C-1β), 90.96 (C-1α), 72.78 (-CH_2-All); 69.40 (C-2), 68.26 (C-6), 68.22 (C-4), 67.94 (C-3), 67.71 (C-5), ≈21.0 (3× CH_3-Ac) ppm. $C_{17}H_{22}NO_9Cl_3$ (490.7): MALDI-TOF-MS: *m*/*z* = 385.01 $[M + Na]^+$, 369.08 $[M + K]^+$. Under argon 2,3,4-tri-*O*-acetyl-6-*O*-allyl-D-galactopyranose (2.42 g, 6.99 mmol) was dissolved in dry dichloromethane (27 mL) and treated with trichloroacetonitrile (8.72 mL, 86.96 mmol, 12.44 equiv.). A solution of 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) in dry dichloromethane (1.0 mL, 0.78 mmol DBU) was added dropwise, until the reaction mixture became deep brown. Stirring was continued at room temperature for 2.5 h, then the mixture was concentrated and purified by column chromatography (PE/EE, 3:1) to give **10** (1.86 g, 54%) as a colourless solid; m.p. 112 °C, R_F = 0.75 (PE/EE, 1:1), $[\alpha]_D^{20}$ = +100 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (s, 1 H, =NH), 6.47 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 5.74 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH2\text{-}All,CH\text{-}All}$ = 4.4, $J_{CH2\text{-}All,CH\text{-}All}$ = 5.7 Hz, 1 H, CH-All), 5.54 (d, $J_{3,4}$ = 2.7, $J_{4,5}$ = 0.8 Hz, 1 H, 4-H), 5.37 (dd, $J_{2,3}$ = 11.1 Hz, 1 H, 3-H), 5.30 (dd, 1 H, 2-H), 5.15 (dd, $J_{=CH2c,=CH2t}$ = 1.3 Hz, 1 H, =CH_2-All), 5.09 (dd, 1 H, =CH_2-All), 4.32 (dd ≈ t, $J_{5,6a}$ = 6.0, $J_{5,6b}$ = 6.6 Hz, 1 H, 5-H), 3.91 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 3.82 (dd, 1 H, -CH_2-All), 3.47 (dd, $J_{6a,6b}$ = 9.9 Hz, 1 H, 6a-H), 3.38 (dd, 1 H, 6b-H), 2.09 (s, 3 H, -CH_3), 1.96 (s, 3 H, -CH_3), 1.94 (s, 3 H, -CH_3) ppm. ^{13}C (125 MHz, $CDCl_3$): δ ≈ 170.4 (3× CO-Ac), 134.44 (CH-All), 118.07 (=CH_2-All), 94.15 (C-1), 72.84 (CH_2-All), 71.06 (C-2), 70.52 (C-3), 68.38 (C-4), 67.83 (C-6), 66.71 (C-5), ≈ 21.1 (3× CH_3-Ac) ppm.

2,3,4-Tri-*O*-acetyl-6,7-dideoxy-α-D-*galacto*-hept-6-enopyranosyl Trichloroacetimidate (11): Compound **9**[22] (12.90 g, 2.9 mmol) was dissolved and stirred in dry pyridine (40 mL). Acetic anhydride (7.4 mL, 78.3 mmol) was added and the reaction mixture was stirred at room temperature overnight. Then pyridine was removed by co-distillation with toluene (50 mL), and the product was purified by column chromatography (PE/EE, 4:1) to give 1,2,3,4-tetra-*O*-acetyl-6,7-dideoxy-D-*galacto*-hept-6-enopyranose (3.30 g, 74%). This intermediate was dissolved in dry DMF (19 mL), hydrazine acetate (0.93 g, 15.7 mmol) was added and the mixture was stirred for 2 h at 60 °C. The reaction was terminated by addition of ethyl acetate (60 mL) and brine, then washed with water, dried with Na_2SO_4 and concentrated in vacuo. After purification by column chromatography (PE/EE, 3:1) 2,3,4-tri-*O*-acetyl-6,7-dideoxy-D-*galacto*-hept-6-enopyranose was isolated as a colourless oil (934 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (dddd, $J_{5,6}$ = 5.1 Hz, 1 H, 6-H), 5.46 (d, $J_{1α,2α}$ = 3.3 Hz, 1 H, 1α-H), 5.40–5.02 (m, $J_{6,7c}$ = 10.7, $J_{6,7t}$ = 16.3 Hz, 5 H, 2α+β-H, 3α+β-H, 4α+β-H, 7aα+β-H, 7bα+β-H), 4.74–4.66 (m, 2 H, 5α-H, 1β-H), 4.20–4.17 (m, 1 H, 5β-H), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.92 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.70 (CO-Ac), 171.00 (CO-Ac), 170.98 (CO-Ac), 133.07 (C-6), 118.18 (C-7), 95.90 (C-1β), 90.77 (C-1α), 74.12 (C-5β), 71.55, 69.19, 68.35 (C-2, C-3, C-4), 20.99, 20.96, 20.90 (3× CH_3-Ac) ppm. Under argon a solution of 2,3,4-tri-*O*-acetyl-6,7-dideoxy-D-*galacto*-hept-6-enopyranose (2.38 g, 7.87 mmol) in dry dichloromethane (30 mL) was treated with trichloroacetonitrile (9.8 mL) and 1.6 mL of a solution of DBU (0.73 mL) in dry dichloromethane (5.5 mL). The red-brown coloured solution was stirred for 2.5 h at room temperature, then concentrated and the residue was purified by flash chromatography (PE/EE, 6:1). Product **11** (2.63 g, 75%) was obtained as a colourless solid; m.p. 92 °C, $[\alpha]_D^{20}$ = +128 (*c* = 0.75, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H, NH), 6.58 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.64 (ddd, $J_{6,7c}$ = 10.7, $J_{6,7t}$ = 17.3 Hz, 1 H, 6-H), 5.47 (dd, $J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 5.41 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.1 Hz, 1 H, 3-H), 5.32 (dd, 1 H, 2-H), 5.30 (ddd, $J_{7c,7t}$ = 1.3 Hz, 1 H, 7_t-H), 5.19 (ddd, 1 H, 7_c-H), 4.66 (dd, $J_{5,6}$ = 5.3 Hz, 1 H, 5-H), 2.07 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.94 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.65, 170.53, 170.43 (3× CO-Ac), 161.40 (-C=NH), 131.93 (C-6), 119.20 (C-7), 94.19 (C-1), 72.37 (C-5),

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70.21 (C-4), 68.17 (C-3), 67.41 (C-2), 21.10, 21.00, 20.97 (3× CH_3-Ac) ppm.

4-Nitrophenyl 6-*O*-Allyl-β-D-galactopyranoside (12): Under argon compound **10** (1.86 g, 3.79 mmol) was dissolved in dry dichloromethane (10 mL), cooled to –10 °C and stirred. Then *p*-nitrophenol (525 mg, 3.79 mmol) and boron trifluoride–diethyl ether (0.5 mL, 3.79 mmol) were added. The reaction mixture was stirred at –10 °C for 2.5 h then diluted with dichloromethane (7 mL) and neutralized with saturated aqueous sodium hydrogen carbonate solution. The organic phase was washed with water, dried with Na_2SO_4, filtered and concentrated in vacuo. The remaining residue was purified by column chromatography (PE/EE, 3:1) to give 4-nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-allyl-β-D-galactopyranoside (935 mg, 53%). *N*-(2,3,4-Tri-*O*-acetyl-6-*O*-allyl-α-D-galactopyranosyl)trichloroacetamide (658 mg, 35%) and 4-nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-allyl-α-D-galactopyranoside (14 mg, 11%) were isolated as by-products.

4-Nitrophenyl 2,3,4-Tri-*O*-acetyl-6-*O*-allyl-β-D-galactopyranoside: Colourless foam, $[\alpha]_D^{20} = -2$ ($c = 0.60$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (m, 2 H, *p*NP), 7.03 (m, 2 H, *p*NP), 5.76 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.8 Hz, 1 H, CH-All), 5.45 (dd, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 5.44 (dd, $J_{4,5}$ = 0.8 Hz, 1 H, 4-H), 5.17 (dddd ≈ dq, $J_{=CH2c,=CH2t}$ = 1.8 Hz, 1 H, $=CH_{2t}$-All), 5.13 (dddd ≈ dq, $J_{CH2\text{-}All,=CH2}$ = 1.8 Hz, 1 H, $=CH_{2c}$-All), 5.09 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 5.07 (dd, $J_{3,4}$ = 3.6 Hz, 1 H, 3-H), 3.97 (ddd ≈ dt, $J_{5,6a}$ = 5.8, $J_{5,6b}$ = 5.4 Hz, 1 H, 5-H), 3.93–3.88 (m, 2 H, $-CH_2$-All), 3.51–3.47 (m, 2 H, 6a-H, 6b-H), 2.11 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.95 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.68, 170.48, 169.71 (3× CO-Ac), 161.82 (C-*p*NP), 143.56 (C-*p*NP), 134.37 (CH-All), 126.21 (CH-*p*NP), 118.04 ($=CH_2$-All), 117.03 (CH-*p*NP), 99.17 (C-1), 73.70 (C-5), 72.91 ($-CH_2$-All), 71.22 (C-3), 69.00 (C-4), 68.18 (C-6), 67.79 (C-2), 21.11, 21.06, 20.97 (3× CH_3-Ac) ppm. $C_{21}H_{25}NO_{11}$ (467.4): calcd. C 53.96, H 5.39, N 3.00; found C 52.91, H 5.46, N 2.61.

***N*-(2,3,4-Tri-*O*-acetyl-6-*O*-allyl-β-D-galactopyranosyl)trichloroacetamide:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (dd, $J_{1,NH}$ = 8.7 Hz, 1 H, NH), 5.76 (dddd, $J_{CH2\text{-}All,\text{-}CH}$ = 5.9, $J_{CH\text{-}All,=CH2c}$ = 10.1, $J_{CH\text{-}All,=CH2t}$ = 17.3 Hz, 1 H, CH-All), 5.47 (dd, $J_{3,4}$ = 3.4, $J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 5.17 (dddd ≈ dq, $J_{=CH2c,=CH2t}$ = 2.5 Hz, 1 H, $=CH_{2t}$-All), 5.14 (dd, $J_{2,3}$ = 8.7 Hz, 1 H, 3-H), 5.13–5.09 (m, 2 H, 2-H, $=CH_{2c}$-All), 5.06 (dd, $J_{1,2}$ = 8.9 Hz, 1 H, 1-H), 3.95–3.90 (m, 2 H, 5-H, $-CH_2$-All), 3.84 (dddd ≈ ddt, $J_{CH2\text{-}All,=CH2}$ = 1.8, $J_{CH2\text{-}All,\text{-}CH2\text{-}All}$ = 12.7 Hz, 1 H, $-CH_2$-All), 3.50 (dd, $J_{5,6a}$ = 5.6, $J_{6a,6b}$ = 9.9 Hz, 1 H, 6a-H), 3.39 (dd, $J_{5,6b}$ = 8.9 Hz, 1 H, 6b-H), 2.09 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.94 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.83 (3× CO-Ac), 162.37 (-NH-CO-), 134.42 (CH-All), 118.24 ($=CH_2$-All), 80.90 (C-1), 74.48 (C-5), 72.84 ($-CH_2$-All), 71.04, 68.73 (C-2, C-3), 67.97 (C-4), 67.50 (C-6), 21.06, 20.96 (3× CH_3-Ac) ppm. $C_{17}H_{22}NO_9Cl_3$ (490.7): MALDI-TOF-MS: *m*/*z* = 490.30, 492.30 $[M + H]^+$, 512.16, 514.16, 516.16 $[M + Na]^+$, 528.12, 530.11, 532.10 $[M + K]^+$. 4-Nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-allyl-β-D-galactopyranoside (222 mg, 0.47 mmol) was dissolved in methanol (1.2 mL) and treated with a solution of 25% aqueous ammonia (140 μL) in methanol (400 μL). The reaction mixture was stirred overnight at room temperature and upon complete deprotection, evaporated to dryness in vacuo. The residue was purified by flash chromatography (DCM/MeOH, 10:1) to give **12** (60 mg, 37%) as a colourless solid; m.p. 149 °C, $[\alpha]_D^{20} = -94$ ($c = 0.175$, MeOH). ^{1}H NMR (400 MHz, MeOD): δ = 8.43 (d, 2 H, *p*NP), 7.47 (d, 2 H, *p*NP), 6.14 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH2\text{-}All,CH\text{-}All}$ = 5.3, $J_{CH2\text{-}All,CH\text{-}All}$ = 6.6 Hz, 1 H, CH-All), 5.51 (dd, $J_{=CH2c,=CH2t}$ = 1.8 Hz, 1 H, $=CH_2$-All), 5.39 (dd, 1 H, $=CH_2$-All), 5.25 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.29–4.25 (m, 2 H, $-CH_2$-All), 4.17–4.11 (m, 2 H, 4-H, 5-H), 4.06 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.94 (dd, $J_{5,6a}$ = 4.8, $J_{6a,6b}$ = 10.2 Hz, 1 H, 6a-H), 3.91 (dd, $J_{5,6b}$ = 3.3 Hz, 1 H, 6b-H), 3.84 (dd, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 164.34 (C-*p*NP), 142.76 (C-*p*NP), 136.48 (CH-All), 126.95 (CH-*p*NP), 118.18 (CH-*p*NP), 117.43 ($=CH_2$-All), 102.55 (C-1), 76.13 (C-4 or C-5), 75.09 (C-3), 73.68 ($-CH_2$-All), 72.39 (C-2), 70.88 (C-6), 70.72 (C-4 or C-5) ppm. $C_{15}H_{19}NO_8$ (341.3): calcd. C 52.78, H 5.61, N 4.10; found C 52.62, H 5.64, N 3.89. FAB-MS: *m*/*z* = 342.2 $[M + H]^+$.

4-Nitrophenyl 6,7-Dideoxy-β-D-*galacto*-hept-6-enopyranoside (13): Under argon compound **11** (223 mg, 0.50 mmol) and *p*-nitrophenol (70 mg, 0.50 mmol) were dissolved in dichloromethane (1 mL) and cooled to –10 °C. Boron trifluoride etherate (12 μL) was added and stirred for 2 h at this temperature. The solution was neutralized with saturated sodium hydrogen carbonate solution and extracted with dichloromethane. The organic layers were washed with water, dried and concentrated. The residue was purified by column chromatography (PE/EE, 4:1). 4-Nitrophenyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-hept-6-enopyranoside (145 mg, 68%) was obtained as a colourless solid; m.p. 162 °C (ref.[41] 164 °C), $[\alpha]_D^{20} = +6$ ($c = 0.27$, $CHCl_3$), $R_F = 0.07$ (PE/EE, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (m, 2 H, *p*NP), 7.03 (m, 2 H, *p*NP), 5.69 (ddd, $J_{5,6}$ = 4.8, $J_{6,7c}$ = 10.9, $J_{6,7t}$ = 17.3 Hz, 1 H, 6-H), 5.47 (dd, $J_{1,2}$ = 7.9, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 5.41 (dd, $J_{3,4}$ = 3.3, $J_{4,5}$ = 1.1 Hz, 1 H, 4-H), 5.34 (ddd, $J_{7c,7t}$ = 1.3 Hz, 1 H, 7_t-H), 5.23 (ddd, 1 H, 7_c-H), 5.16 (d, 1 H, 1-H), 5.13 (dd, 1 H, 3-H), 4.35 (m, 1 H, 5-H), 2.09 (s, 3 H, Ac), 1.95 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170. 68, 170.48, 169.71 (3× CO-Ac), 161.82 (C-*p*NP), 143.56 (C-*p*NP), 131.49 (C-6), 126.22 (CH-*p*NP), 119.24 (C-7), 117.00 (CH-*p*NP), 99.07 (C-1), 74.57 (C-5), 71.20 (C-3), 69.48 (C-4), 68.82 (C-2), 21.09, 21.00, 20.97 (3× CH_3-Ac) ppm. $C_{19}H_{21}NO_{10}$ (423.4), MALDI-TOF-MS: *m*/*z* = 446.1 $[M + Na]^+$, 462.0 $[M + K]^+$. To a suspension of 4-nitrophenyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-hept-6-enopyranoside (535 mg, 1.26 mmol) in methanol (3.3 mL) was added a solution of a 25% aqueous ammonia (0.38 mL) in methanol (1.1 mL). After stirring for 24 h at room temperature the solution was concentrated and the residue dried under vacuum. Product **13** (375 mg, 100%) was obtained as a colourless solid; m.p. 174–178 °C (ref.[42] 173 °C), $[\alpha]_D^{20} = -95$ ($c = 0.20$, CH_3OH), $R_F = 0.41$ (CH_2Cl_2/MeOH, 7:1). ^{1}H NMR (400 MHz, MeOD): δ = 8.24 (m, 2 H, *p*NP), 7.25 (m, 2 H, *p*NP), 6.00 (ddd, $J_{5,6}$ = 5.4, $J_{6,7t}$ = 10.7, $J_{6,7c}$ = 17.0 Hz, 1 H, 6-H), 5.39 (ddd, $J_{7c,7t}$ = 1.3 Hz, 1 H, 7_t-H), 5.26 (ddd, 1 H, 7_c-H), 5.11 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.32 (dd, $J_{4,5}$ = 1.0 Hz, 1 H, 5-H), 3.90–3.87 (m, 2 H, 2-H, 4-H), 3.68 (dd, $J_{2,3}$ = 9.8, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 162.82 (C-*p*NP), 142.76 (C-*p*NP), 134.46 (C-6), 125.49 (CH-*p*NP), 116.55 (CH-*p*NP), 116.47 (C-7), 100.94 (C-1), 76.17 (C-5), 73.59 (C-3), 71.55, 70.66 (C-2, C-4) ppm. $C_{13}H_{15}NO_7$ (297.2): FAB-MS: *m*/*z* = 298.2 $[M + H]^+$.

6,7-Dideoxy-β-D-*galacto*-hept-6-enopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (18): Compounds **13** (10 mg, 34 μmol) and **14** (75 mg, 340 μmol, 10 equiv.) were reacted according to general procedure 2. Disaccharide **18** (3 mg, 20%) was obtained as a colourless, amorphous solid. $[\alpha]_D^{20} = +224$ ($c = 0.13$, H_2O), R_F = 0.36 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 5.73 (ddd, $J_{5',6'}$ = 5.1, $J_{6',7'c}$ = 10.9, $J_{6',7't}$ = 17.6 Hz, 1 H, 6′-H), 5.18 (dd, $J_{7'c,7't}$ = 1.3 Hz, 1 H, $7'_t$-H), 5.14 (dd, 1 H, $7'_c$-H), 5.02 (d, $J_{1\alpha,2}$ = 2.3 Hz, 0.7 H, 1α-H), 4.52 (d, $J_{1\beta,2}$ = 7.6 Hz, 0.3 H, 1β-H), 4.28 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.07 (m, 1 H, 5′-H), 3.80–3.32 (m, 9 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 2′-H, 3′-H, 4′-H), 1.85

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(s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 133.47 (C-6′), 118.14 (C-7′), 103.50, 103.34 (C-1′), 95.27 (C-1β), 90.94 (C-1α), 79.24, 78.82 (C-4β), 75.76 (C-4α), 75.64 (C-5′), 75.25, 72.92, 71.83, 71.06, 70.92, 70.67, 70.61, 69.68, 68.96 (C-3, C-5, C-2′, C-3′, C-4′), 60.50, 60.38 (C-6), 56.63 (C-2β), 54.12 (C-2α), 22.57, 22.28 (CH_3-NHAc) ppm.

β-D-Fucopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (19): Compounds **16** (40 mg, 140 μmol) and **14** (300 mg, 1.36 mmol, 10 equiv.) were reacted according to general procedure 2. Disaccharide **20** (34 mg, 66%) was obtained as an amorphous yellow solid. $[\alpha]_D^{20}$ = –10 (*c* = 0.10, H_2O), R_F = 0.36 (EE/MeOH/H_2O, 7:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.33 (d, $J_{1\alpha,2\alpha}$ = 2.3 Hz, 0.6 H, 1α-H), 4.63 (m, 0.4 H, 1β-H), 4.56 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.12–4.06 (m, 1.1 H, 5α-H, 6aα-H), 4.04–3.95 (m, 4 H, 2α-H, 3α-H, 6bα-H, 5β-H, 6aβ-H, 6bβ-H, 5′-H), 3.89 (d, $J_{3',4'}$ = 3.3 Hz, 1 H, 4′-H), 3.82–3.77 (m, 2.8 H, 4α-H, 2β-H, 3β-H, 4β-H, 3′-H), 3.63 (m, $J_{2',3'}$ = 9.9 Hz, 1 H, H-2′), 2.18 (s, 3 H, NHAc), 1.38 (d, $J_{5',6'}$ = 6.4 Hz, 3 H, 6′-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 173.78 (CO-NHAc), 103.39 (C-1′), 95.21 (C-1β), 90.91 (C-1α), 79.88 (C-4α), 75.11 (C-4β), 73.09 (C-3′), 72.92 (C-3β), 71.56 (C-4′), 71.46 (C-5′), 71.05 (C-2′), 70.54 (C-3α), 69.68 (C-5), 60.52, 60.37 (C-6α and β), 56.00 (C-2β), 54.09 (C-2α), 22.56, 22.27 (CH_3-NHAcα and β), 15.70 (C-6′) ppm.

α-L-Arabinopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (20): Compounds **17** (40 mg, 150 μmol) and **14** (300 mg, 1.36 mmol), were reacted according to general procedure 2. Disaccharide **20** (3 mg, 6%) was obtained. ^{1}H NMR (400 MHz, D_2O): δ = 5.15 (br. s, 0.6 H, 1α-H), 4.67 (d, 0.4 H, 1β-H), 4.33 (d, 1 H, 1′-H), 3.93–3.76 (m, 6 H, 2α-H, 3-H, 5-H, 6a-H, 6b-H, 4′-H, 5a′-H), 3.64–3.59 (m, 4 H, 2β-H, 4-H, 3′-H, 5b′-H), 3.55–3.46 (m, 1.6 H, 4α-H or 4β-H, 2′-H), 1.99 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 103.76 (C-1′), 95.26 (C-1β), 90.96 (C-1α), 79.20 (C-4), 72.63 (C-3′), 71.38 (C-2′), 70.70, 69.51, 68.70 (C-3, C-5, C-4′), 66.81 (C-5′), 60.32 (C-6), 54.22 (C-2), 22.29 (CH_3-NHAc) ppm.

Allyl 6-Amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (21): Compounds **5** (36 mg, 116 μmol) and **15** (300 mg, 1.16 mmol, 10 equiv.) were reacted according to the general procedure 1 to give 356 mg yellow solid raw material of **21**. 114 mg were dissolved in dry pyridine (2 mL), cooled in a water bath and to this solution acetic anhydride (1 mL) was added dropwise. After stirring for 24 h at room temperature co-distillation with toluene was performed three times. The residue thus obtained was purified two times by column chromatography [PE/EE (1:4) and DCM/MeOH (6:1)]. Pure allyl 6-acetamido-2,3,4-tri-*O*-acetyl-6-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside (2 mg, ≈ 10%) was isolated. ^{1}H NMR (500 MHz, MeOD): δ = 5.87 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.7, $J_{CH\text{-}All,=CH2t}$ = 17.0, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.3 Hz, 1 H, CH-All), 5.23 (d, 1 H, =CH_2-All), 5.17 (d, $J_{3',4'}$ = 3.5 Hz, 1 H, 4′-H), 5.14–5.09 (m, 2 H, =CH_2-All, 3-H), 4.95 (dd, $J_{2',3'}$ = 10.4 Hz, 1 H, 3′-H), 4.89 (dd, 1 H, 2′-H), 4.69 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.55 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.37 (dd, $J_{5,6a}$ = 1.9, $J_{6a,6b}$ = 12.0 Hz, 1 H, 6a-H), 4.13–4.08 (m, 2 H, -CH_2-All, 2-H), 4.04 (dd, $J_{5,6b}$ = 6.0 Hz, 1 H, 6b-H), 3.95 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 3.84–3.79 (m, 2 H, 5-H, 5′-H), 3.75 (dd, $J_{3,4}$ = 8.8, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 3.36 (dd, $J_{5',6a'}$ = 8.2, $J_{6a',6b'}$ = 13.6 Hz, 1 H, 6a′-H), 3.12 (dd, $J_{5',6b'}$ = 6.3 Hz, 1 H, 6b′-H), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 1.83 (s, 6 H, 2× Ac), 1.81 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 131.68 (CH-All), 117.49 (=CH_2-All), 100.85 (C-1′), 96.35 (C-1), 76.48 (C-4), 71.58 (C-3, C-3′), 69.75 (C-2′ und C-5 or C-5′), 69.06 (C-5 or C-5′), 68.62 (-CH_2-All), 67.43 (C-4′), 62.68 (C-6), 52.59 (C-2), 38.02 (C-6′), 21.30–19.60 (7× CH_3-Ac) ppm.

Allyl β-D-*galacto*-Hexodialdo-1,5-pyranosyl-(1→4)-2-acetamido-2-deoxy-α-glucopyranoside (22): Compounds **6** (70 mg, 0.22 mmol) and **15** (300 mg, 1.15 mmol) were reacted in 50 mM potassium phosphate buffer pH 7.0 (4 mL) after addition of a solution consisting of 10 mg β-galactosidase (600 μL, 30 U) from *B. circulans* in 50 mM potassium phosphate buffer pH 7.0 (1 mL). After stirring for three days at room temperature water was removed by freeze-drying. The residue was purified by gel permeation chromatography on Sephadex LH 20 using EE/EE (1:1:1) EE/EE (11:11:11) methanol/water (1:1) to give **22** (65 mg, 68%) as a colourless solid; m.p. 219 °C (dec.), $[\alpha]_D^{20}$ = +7 (*c* = 0.15, H_2O), R_F = 0.31 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 6.05 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.7, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.6, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.6 Hz, 1 H, CH-All), 5.44 (dd, $J_{=CH2c,=CH2t}$ = 1.5 Hz, 1 H, =CH_2-All), 5.35 (dd, 1 H, =CH_2-All), 5.21 (d, $J_{5',6'}$ = 7.1 Hz, 1 H, 6′-H), 5.01 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 4.57 (d, $J_{1',2'}$ = 8.1 Hz, 1 H, 1′-H), 4.30 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.2 Hz, 1 H, -CH_2-All), 4.17 (d, $J_{3',4'}$ = 3.6 Hz, 1 H, 4′-H), 4.12 (dd, 1 H, -CH_2-All), 4.03–3.91 (m, 5 H, 2-H, 3-H, 5-H, 6a-H, 6b-H), 3.81 (dd, 1 H, 4-H), 3.75 (dd, $J_{2',3'}$ = 10.7 Hz, 1 H, 3′-H), 3.64 (dd, 1 H, 2′-H), 3.54 (dd, 1 H, 5′-H), 2.11 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 175.00 (CO-NHAc), 133.93 (CH-All), 118.34 (=CH_2-All), 103.60 (C-1′), 96.12 (C-1), 88.39 (C-6′), 80.04 (C-4), 77.29 (C-5′), 72.83 (C-3′), 71.08 (C-2′), 70.82 (C-5), 70.06 (C-3), 68.97 (-CH_2-All), 68.38 (C-4′), 60.35 (C-6), 53.59 (C-2), 22.23 (CH_3-NHAc) ppm. $C_{17}H_{24}NO_{11}$ (421.4): MALDI-TOF-MS: *m*/*z* = 444.2 $[M + Na]^+$, 460.1 $[M + K]^+$.

Allyl 6,7-Didesoxy-β-D-*galacto*-hept-6-enopyranosyl-(1→4)-2-acetamido-2-desoxy-α-D-glucopyranoside (23): Compounds **13** (32 mg, 108 μmol) and **15** (224 mg, 861 μmol) were reacted according to general procedure 1. Disaccharide **23** (14 mg, 31%) was obtained as a colourless syrup. $[\alpha]_D^{20}$ = –136 (*c* = 0.25, H_2O), R_F = 0.59 (EE/MeOH/H_2O, 7:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.83 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 23.4, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.1 Hz, 1 H, CH-All), 5.78 (ddd, $J_{6',7'c}$ = 10.9, $J_{6',7't}$ = 17.6 Hz, 1 H, 6′-H), 5.24 (m, $J_{7'c,7't}$ = 1.8 Hz, 1 H, 7′$_c$-H), 5.20 (m, 2 H, =CH_2-All, 7′$_t$-H), 5.12 (dd, $J_{=CH2c,=CH2t}$ = 1.5, $J_{CH2\text{-}All,=CH2}$ = 1.5 Hz, 1 H, =CH_2-All), 4.80 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 4.38 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.12 (dd, $J_{4',5'}$ = 1.3, $J_{5',6'}$ = 5.3 Hz, 1 H, 5′-H), 4.09 (dddd ≈ ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.0 Hz, 1 H, -CH_2-All), 3.91 (dddd ≈ ddt, 1 H, -CH_2-All), 3.82–3.71 (m, 6 H, 2-H, 3-H, 5-H, 6a-H, 6b-H, 4′-H), 3.59 (m, $J_{3',4'}$ = 3.6 Hz, 2 H, 3′-H, 4-H), 3.42 (dd, $J_{2',3'}$ = 9.9 Hz, 1 H, 2′-H), 1.92 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 175.00 (CO-NHAc), 133.93, 133.44 (C-6′, CH-All), 118.34, 118.11 (C-7′, =CH_2-All), 103.43 (C-1′), 96.17 (C-1), 79.65 (C-4), 75.60 (C-5′), 72.90 (C-3′), 71.03 (C-2′), 70.96, 70.89, 69.92 (C-3, C-5, C-4′), 68.97 (-CH_2-All), 60.23 (C-6), 53.65 (C-2), 22.22 (CH_3-NHAc) ppm.

Allyl β-D-Fucopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (24): Compounds **16** (33 mg, 116 μmol) and **15** (302 mg, 1.16 mmol) were reacted according to general procedure 1. Disaccharide **24** (36 mg, 76%) was obtained as a colourless syrup. $[\alpha]_D^{20}$ = +52 (*c* = 0.25, H_2O), R_F = 0.56 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 5.80–5.65 (m, 1 H, CH-All), 5.14 (d, $J_{CH\text{-}All,=CH2c}$ = 10.4 Hz, 1 H, =CH_2-All), 5.02 (d, $J_{CH\text{-}All,=CH2t}$ = 17.3 Hz, 1 H, =CH_2-All), 4.71 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 4.20 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 4.00 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.6, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.5 Hz, 1 H, -CH_2-All), 3.92 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.4 Hz, 1 H, -CH_2-All), 3.91 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.88–

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3.78 (m, 5 H, 3-H, 5-H, 6a-H, 6b-H, 5′-H), 3.72 (d, $J_{3',4'}$ = 3.3 Hz, 1 H, 4′-H), 3.66–3.60 (m, 2 H, 4-H, 3′-H), 3.46 (dd, $J_{2',3'}$ = 9.7 Hz, 1 H, 2′-H), 1.82 (s, 3 H, NHAc), 1.01 (d, $J_{5',6'}$ = 6.4 Hz, 3 H, 6′-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.78 (CO-NHAc), 133.97 (CH-All), 118.36 (=CH_2-All), 103.37 (C-1′), 96.19 (C-1), 79.83 (C-4), 73.11 (C-3′), 71.56 (C-4′), 71.46 (C-3 or C-5′), 71.06 (C-2′), 70.92 (C-3 or C-5′), 71.01 (C-5), 69.00 (-CH_2-All), 60.31 (C-6), 53.67 (C-2), 22.24 (CH_3-NHAc), 15.71 (C-6′) ppm.

Allyl α-L-Arabinopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside (25): Compounds **17** (32 mg, 116 μmol) and **15** (302 mg, 1.16 mmol) were reacted according to general procedure 1. Disaccharide **25** (6 mg, 13%), was obtained as a colourless syrup. $[\alpha]_D^{20}$ = +40 (*c* = 0.20, H_2O), R_F = 0.60 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 5.97–5.86 (m, 1 H, CH-All), 5.31 (dd, $J_{CH\text{-}All,=CH2c}$ = 10.7, $J_{CH2c,CH2t}$ = 1.5 Hz, 1 H, =CH_2-All), 5.22 (dd, $J_{CH\text{-}All,=CH2t}$ = 17.3 Hz, 1 H, =CH_2-All), 4.89 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.33 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 4.17 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.2 Hz, 1 H, -CH_2-All), 4.00 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.4 Hz, 1 H, -CH_2-All), 3.93–3.78, 3.67–3.61 (2× m, 1× 7 H, 1× 3 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 3′-H, 4′-H, 5a′-H, 5b′-H), 3.51 (dd, $J_{2',3'}$ = 9.7 Hz, 1 H, 2′-H), 2.00 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 173.00 (CO-NHAc), 133.98 (CH-All), 118.35 (=CH_2-All), 103.75 (C-1′), 96.24 (C-1), 79.15 (C-4), 72.64 (C-3′), 71.38 (C-2′), 71.07 (C-5), 69.84 (C-3), 68.98 (-CH_2-All), 68.69 (C-4′), 66.80 (C-5′), 60.25 (C-6), 53.79 (C-2), 22.25 (CH_3-NHAc) ppm.

Allyl 2-Amino-2-deoxy-α-D-glucopyranoside (28): Compound **15** (915 mg, 3.5 mmol) and barium hydroxide octahydrate (14.18 mg, 44.9 mmol) in water (74 mL) were stirred for 3 h at 120 °C. After cooling to room temperature, the precipitate was filtered and the filtrate was treated with dry ice to remove the barium salts. The solvent was removed by freeze drying to give **28** (920 mg, 100%) as an amorphous, colourless solid. $[\alpha]_D^{20}$ = +59 (*c* = 0.65, MeOH), R_F = 0.07 (DCM/MeOH, 4:1). ^{1}H NMR (400 MHz, MeOD): δ = 5.96 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 4.81 (dddd ≈ dq, $J_{CH2\text{-}All,=CH2}$ = 1.4 Hz, 1 H, =CH_2-All), 5.18 (dddd ≈ dq, $J_{CH2\text{-}All,=CH2}$ = 1.5 Hz 1 H, =CH_2-All), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.24 (dddd ≈ ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.0 Hz, 1 H, -CH_2-All), 4.01 (dddd ≈ ddt, 1 H, -CH_2-All), 3.80 (dd, $J_{5,6a}$ = 2.3, $J_{6a,6b}$ = 12.0 Hz, 1 H, 6a-H), 3.69 (dd, $J_{5,6b}$ = 5.6 Hz, 1 H, 6b-H), 3.58 (ddd, $J_{4,5}$ = 9.9 Hz, 1 H, 5-H), 3.53 (dd ≈ t, 1 H, 3-H or 4-H), 3.31 (dd, 1 H, 3-H or 4-H), 2.71 (dd, $J_{2,3}$ = 9.9, $J_{3,4}$ = 9.7 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 135.81 (CH-All), 118.08 (=CH_2-All), 99.20 (C-1), 75.72 (C-3 or C-4), 74.65 (C-5), 72.35 (C-3 or C-4), 69.77 (-CH_2-All), 63.01 (C-6), 57.25 (C-2) ppm.

2-Amino-1,5-anhydro-2-deoxy-D-glucitol Hydrochloride (29): 2-Acetamido-3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-glucitol (**41**)[38] (0.6 g, 1.81 mmol) was solved in 2.5 M hydrochloric acid (5.0 mL) and stirred for 2 h at 110 °C. The reaction mixture was evaporated and the residue was solved in ethanol (1.0 mL). Diethyl ether was added until precipitation was completed. The residue was filtered and recrystallised from propanol/ethanol (1:1). Compound **29** (204 mg, 57%) could be obtained as a colourless solid; m.p. 190 °C, $[\alpha]_D^{20}$ = +17.8 (*c* = 1, H_2O), R_F = 0.34 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 4.28 (dd, $J_{1a,2}$ = 5.1, $J_{1a,1b}$ = 11.2 Hz, 1 H, 1a-H), 3.98 (dd, $J_{5,6a}$ = 2.3, $J_{6a,6b}$ = 12.2 Hz, 1 H, 6a-H), 3.81 (dd, $J_{5,6b}$ = 5.3 Hz, 1 H, 6b-H), 3.71 (dd, $J_{3,4}$ = 8.4, $J_{4,5}$ = 10.4 Hz, 1 H, 4-H), 3.64 (dd, 1 H, 1b-H), 3.54 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 3-H), 3.49 (ddd, 1 H, 5-H), 3.38 (ddd, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 80.96 (C-5), 73.98 (C-4), 70.16 (C-3), 65.88 (C-1), 61.01 (C-6), 51.74 (C-2) ppm. $C_6H_{14}ClNO_4$ (199.6): calcd. C 36.17, H 7.09, N 7.03; found C 36.22, H 7.07, N 7.02.

Allyl 2-Acetamido-6-amino-2,6-dideoxy-α-D-glucopyranoside (30): Allyl 2-acetamido-6-azido-2,6-dideoxy-α-D-glucopyranoside[34] (128 mg, 0.45 mmol) was reacted according to general procedure 5 and the product purified by column chromatography [EE/MeOH (1:9) + 3% pyridine]. Product **30** (113 mg, 97%) could be obtained as a colourless solid; m.p. 168 °C (dec.), $[\alpha]_D^{20}$ = +40 (*c* = 0.22, H_2O), R_F = 0.08 [EE/MeOH (1:9) + 3% pyridine]. ^{1}H NMR (400 MHz, D_2O): δ = 5.93 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1 Hz 1 H, CH-All), 5.43 (d, 1 H, =CH_2-All), 5.34 (dd, 1 H, =CH_2-All), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.19 (dddd ≈ ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.0 Hz, 1 H, -CH_2-All), 4.01 (dddd ≈ ddt, 1 H, -CH_2-All), 3.89 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.71 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.63 (ddd, $J_{4,5}$ = 9.9, $J_{5,6a}$ = 2.5, $J_{5,6b}$ = 7.4 Hz, 1 H, 5-H), 3.35 (dd, 1 H, 4-H), 2.98 (dd, $J_{6a,6b}$ = 13.7 Hz, 1 H, 6a-H), 2.76 (dd, 1 H, 6b-H), 2.00 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.86 (CO-NHAc), 134.07 (CH-All), 118.31 (=CH_2-All), 96.40 (C-1), 72.55 (C-5), 72.04 (C-4), 71.37 (C-3), 68.86 (-CH_2-All), 54.11 (C-2), 41.79 (C-6), 22.27 (CH_3-NHAc) ppm. $C_{11}H_{20}N_2O_5$ (260.3): calcd. C 50.75, H 7.74, N 10.76; found C 50.09, H 7.54, N 9.37.

Benzyl 2-Acetamido-6-amino-2,6-dideoxy-D-glucopyranoside (31): Benzyl 2-acetamido-6-azido-2,6-dideoxy-D-glucopyranoside[43] (1.54 g, 4.58 mmol) was reacted according to general procedure 5 and the product purified by column chromatography [EE/MeOH (4:1) + 3% pyridine]. Product **31** (986 mg, 69%) could be isolated as a colourless solid; m.p. 175 °C, $[\alpha]_D^{20}$ = +182 (*c* = 0.50, H_2O), R_F = 0.57 [PrOH/H_2O (7:3) + 1% NH_3]. ^{1}H NMR (400 MHz, D_2O): δ = 7.28–7.00 (m, 5 H, CH-Bn), 4.69 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.55 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.2 Hz, 1 H, CH_2-Bn), 4.33 (d, 1 H, -CH_2-Bn), 3.70 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.52 (dd, $J_{3,4}$ = 8.7 Hz, 1 H, 3-H), 3.45 (ddd, $J_{4,5}$ = 9.9, $J_{5,6a}$ = 2.8, $J_{5,6b}$ = 7.4 Hz, 1 H, 5-H), 3.05 (dd, 1 H, 4-H), 2.85 (dd, $J_{6a,6b}$ = 13.5 Hz, 1 H, 6a-H), 2.60 (dd, 1 H, 6b-H), 1.76 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 128.33, 128.17, 127.79 (CH-Bn), 96.65 (C-1), 73.01 (C-4), 72.20 (C-5), 71.37 (C-3), 69.44 (-CH_2-Bn), 54.36 (C-2), 42.55 (C-6), 21.43 (CH_3-NHAc) ppm.

(6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-(1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranos-2-yl)amine (32): The aldehyde **26**[19,31] (134 mg, 0.51 mmol) and amine **27**[32] (460 mg, 1.20 mmol) were stirred in methanol (5 mL) and reacted according to general procedure 3. After purification by column chromatography (PE/EE, 4:3) pure **32** (114 mg, 38%) was isolated as a yellow syrup. R_F = 0.14 (PE/EE, 4:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.45 (d, $J_{1',2'}$ = 8.5 Hz, 1 H, 1′-H), 5.38 (d, $J_{1,2}$ = 4.7 Hz, 1 H, 1-H), 4.97 (dd, 1 H, 3′-H or 4′-H), 4.93 (dd, 1 H, 3′-H or 4′-H), 4.48 (dd, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.21 (dd, 1 H, 2-H), 4.19 (dd, 1 H, 6a′-H), 4.60 (dd, $J_{4,5}$ = 1.6 Hz, 1 H, 4-H), 3.97 (dd, 1 H, 6b′-H), 3.69–3.62 (m, 2 H, 5-H, 5′-H), 2.83 (dd, $J_{5,6a}$ = 7.3, $J_{6a,6b}$ = 12.3 Hz, 1 H, 6a-H), 2.78 (dd, $J_{2',3'}$ = 9.1 Hz, 1 H, 2′-H), 2.75 (dd, $J_{5,6b}$ = 7.3 Hz, 1 H, 6b-H), 2.06 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.45 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.23 (s, 3 H, -CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.15, 170.12, 169.44 (4× CO-Ac), 109.67 [$C(CH_3)_2$], 96.73 (C-1), 95.09 (C-1′), 74.03 (C-3′ or C-4′), 72.91 (C-5′), 71.80 (C-4), 71.14 (C-3), 70.99 (C-2), 68.86 (C-3′ or C-4′), 67.06 (C-5), 62.26 (C-6′), 61.14 (C-2′), 47.68 (C-6), 26.46, 26.39, 25.37, 24.92 (4× CH_3), 21.47, 21.39, 21.15, 21.12 (4× CH_3-Ac) ppm. $C_{26}H_{39}NO_{14}$ (589.6): FAB-MS: *m/z* = 590.3 $[M + H]^+$.

(Allyl-2-deoxy-α-D-glucopyranosid-2-yl)(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)amine (33): The aldehyde **26** (47 mg, 0.18 mmol) and amine **28** (103 mg, 0.47 mmol) were reacted following general procedure 3. After purification by column

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chromatography (DCM/MEOH, 14:1) **33** (84 mg, 100%) could be isolated as an amorphous, colourless solid. $[\alpha]_D^{20}$ = +23 (*c* = 1.00, CH_3OH), R_F = 0.61 (DCM/MeOH, 4:1). ^1H NMR (400 MHz, MeOD): δ = 5.98 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.0, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.6, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.4 Hz, 1 H, CH-All), 5.53 (d, $J_{1,2}$ = 5.1 Hz, 1 H, 1-H), 5.35 (dd, 1 H, =CH_2-All), 5.20 (dd, 1 H, =CH_2-All), 5.06 (d, $J_{1',2'}$ = 3.3 Hz, 1 H, 1′-H), 4.65 (dd, $J_{2,3}$ = 2.3, $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.38 (dd, 1 H, 2-H), 4.29–4.22 (m, 2 H, 4-H, -CH_2-All), 4.07 (ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.7 Hz, 1 H, -CH_2-All), 3.96 (ddd, $J_{4,5}$ = 1.8, $J_{5,6a}$ = 8.4, $J_{5,6b}$ = 3.6 Hz, 1 H, 5-H), 3.82 (dd, $J_{5'6a'}$ = 2.3, $J_{6a',6b'}$ = 11.7 Hz, 1 H, 6a′-H), 3.69 (dd, $J_{5',6b'}$ = 5.6 Hz, 1 H, 6b′-H), 3.63 (dd, $J_{3',4'}$ = 9.2, $J_{4',5'}$ = 9.7 Hz, 1 H, 4′-H), 3.57 (ddd, 1 H, 5′-H), 3.32 (m, $J_{2',3'}$ = 10.4 Hz, 1 H, 3′-H), 3.05 (dd, $J_{6a,6b}$ = 12.7 Hz, 1 H, 6a-H), 2.91 (dd, 1 H, 6b-H), 2.73 (dd, 1 H, 2′-H), 1.55 (s, 3 H, -CH_3), 1.42 (s, 3 H, -CH_3), 1.36 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 135.81 (CH-All), 118.50 (=CH_2-All), 110.90 [$C(CH_3)_2$], 98.20 (C-1), 97.01 (C-1′), 74.27, 74.02, (C-3′, C-5′), 73.52 (C-4), 72.62 (C-3), 72.56 (C-4′), 72.25 (C-2), 69.68 (-CH_2-All), 68.22 (C-5), 63.23 (C-2′), 63.23 (C-6′), 48.42 (C-6), 29.79, 26.69, 25.56, 24.99 (4× CH_3) ppm.

(1,5-Anhydro-2-deoxy-glucitol-2-yl)(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)amine (34) and *N*-(1,5-Anhydro-2-deoxy-glucitol-2-yl)-6-amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-D,L-*glycero*-α-D-*galacto*-heptopyranurononitrile (34b): The aldehyde **26** (120 mg, 0.46 mmol) and amine **29** (240 mg, 1.20 mmol) were reacted according to general procedure 3. After purification by column chromatography (DCM/MeOH, 14:1) **34** (142 mg, 76%) could be isolated as a colourless solid. The byproduct **34b** (47 mg, 24%) could be isolated as a stereoisomeric mixture.

34: M.p. 169 °C, $[\alpha]_D^{20}$ = –18 (*c* = 0.25, CH_3OH), R_F = 0.30 (DCM/MeOH, 6:1). ^1H NMR (500 MHz, MeOD): δ = 5.54 (d, $J_{1,2}$ = 5.1 Hz, 1 H, 1-H), 4.66 (dd, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.39 (dd, 1 H, 2-H), 4.27 (dd, $J_{4,5}$ = 1.6 Hz, 1 H, 4-H), 4.12 (dd, $J_{1'e,1'a}$ = 11.4, $J_{1'e,2'}$ = 4.7 Hz, 1 H, 1e′-H), 3.97 (ddd, $J_{5,6a}$ = 8.5, $J_{5,6b}$ = 4.4 Hz, 1 H, 5-H), 3.85 (dd, $J_{5',6a'}$ = 2.2, $J_{6a',6b'}$ = 12.0 Hz, 1 H, 6a′-H), 3.65 (dd, $J_{5',6b'}$ = 5.7 Hz, 1 H, 6b′-H), 3.36 (dd, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 8.5 Hz, 1 H, 3′-H), 3.28 (dd, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 3.25–3.19 (m, 2 H, 1′a-H, 5′-H), 2.97 (dd, $J_{6a,6b}$ = 13.2 Hz,1 H, 6a-H), 2.92 (dd, 1 H, 6b-H), 2.76 (ddd ≈ dt, $J_{1'a,2'}$ = 10.4 Hz, 1 H, 2′-H), 1.52 (s, 3 H, -CH_3), 1.40 (s, 3 H, -CH_3), 1.33 (s, 6 H, 2× -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 109.43 [*C*-$(CH_3)_2$], 108.89 [*C*$(CH_3)_2$], 96.70 (C-1), 81.63 (C-5′), 76.45 (C-3′), 71.94 (C-4), 71.27 (C-4′), 71.12 (C-2), 70.80 (C-3), 67.91 (C-1′), 66.33 (C-5), 62.03 (C-6′), 59.01 (C-2′), 46.88 (C-6), 25.37, 24.17, 23.62 (4× CH_3) ppm. $C_{18}H_{31}NO_9$ (405.4): calcd. C 53.33, H 7.71, N 3.46; found C 49.78, H 7.78, N 3.34.

34b: R_F = 0.46 (DCM/MeOH, 6:1). ^1H NMR (400 MHz, MeOD): δ = 5.54 (d, $J_{1,2}$ = 4.8 Hz, 0.6 H, 1-H), 5.51 (d, $J_{1*,2*}$ = 5.1 Hz, 0.4 H, 1*-H), 4.72 (dd, $J_{2,3}$ = 2.3, $J_{3,4}$ = 7.9 Hz, 0.7 H, 3-H), 4.68 (dd, $J_{2*,3*}$ = 2.3, $J_{3*,4*}$ = 7.9 Hz, 0.4 H, 3*-H), 4.47–4.39 (m, 2 H, 2-H, 4-H, 2*-H, 4*-H), 4.10–4.04 (m, 1.3 H, 1′e-H, 1′e*-H, 6*-H), 3.99 (d, $J_{5,6}$ = 8.1 Hz, 0.7 H, 6-H), 3.93–3.89 (m, 1 H, 5-H, 5*-H), 3.82 (dd, $J_{5'6a'} = J_{5'*,6a'*}$ = 0.5, $J_{6a',6b'} = J_{6a'*,6b'*}$ = 11.7 Hz, 1 H, 6a′-H, 6a′*-H), 3.62 (dd, $J_{5',6b'} = J_{5'*,6b'*}$ = 5.6 Hz, 1 H, 6b′-H, 6b′*-H), 3.28–3.08 (m, 4 H, 1′a-H, 3′-H, 4′-H, 5′-H, 1′a*-H, 3′*-H, 4′*-H, 5′*-H), 2.82 (ddd ≈ dt, $J_{1'e,2'}$ = 4.6, $J_{1'a,2'}$ = 9.9, $J_{2',3'}$ = 9.9 Hz, 0.7 H, 2′-H), 2.77–2.70 (m, 0.3 H, 2′*-H), 1.53 (s, 0.9 H, -CH_3*), 1.50 (s, 2.6 H, CH_3), 1.33 (s, 4.4 H, 2× -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 120.28 (CN*), 118.33 (CN), 110.28 [*C*$(CH_3)_2$], 109.84 [*C*$(CH_3)_2$], 109.24 [*C*$(CH_3)_2$, *C*$(CH_3)_2$*], 96.82 (C-1, C-1*), 81.67 (C-5′), 81.39 (C-5′*), 78.72 (C-3′*), 76.83 (C-3′), 71.03 (C-4, C-4′, C-4*, C-4′*), 70.85 (C-2*), 70.77 (C-2), 70.64 (C-3*), 70.58 (C-3), 68.81 (C-5*), 68.70 (C-1′*), 68.30 (C-1′), 67.86 (C-5), 62.06 (C-6′), 62.03 (C-6′*), 59.27 (C-2′*), 57.82 (C-2′), 50.90 (C-6*), 48.97 (C-6), 25.18, 25.08, 24.05, 23.97, 23.65, 23.60 (4× CH_3, 4× CH_3*) ppm.

(Allyl-2-acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)amine (35) and *N*-(Allyl-2-acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)-6-amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-D,L-*glycero*-α-D-*galacto*-heptopyranurononitrile (35b): The aldehyde **26** (44 mg, 0.17 mmol) and amine **30** (96 mg, 0.37 mmol) were reacted according to general procedure 3. After purification by column chromatography (DCM/MeOH, 12:1) **35** (35 mg, 41%) could be isolated as an amorphous, colourless solid. The byproduct **35b** (10 mg, 11%) could also be isolated.

35: $[\alpha]_D^{20}$ = +21 (*c* = 0.65, CH_3OH), R_F = 0.39 (DCM/MeOH, 4:1). ^1H NMR (500 MHz, MeOD): δ = 5.95 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.1, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.0 Hz, 1 H, CH-All), 5.58 (d, $J_{1,2}$ = 5.0 Hz, 1 H, 1-H), 5.35 (dd, 1 H, =CH_2-All), 5.22 (dd, 1 H, =CH_2-All), 4.90 (d, $J_{1',2'}$ = 3.5 Hz, 1 H, 1′-H), 4.70 (dd, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.44 (dd, 1 H, 2-H), 4.30 (dd, $J_{4,5}$ = 1.5 Hz, 1 H, 4-H), 4.25 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.2, $J_{CH2\text{-}All,=CH2}$ = 1.6 Hz, 1 H, -CH_2-All), 4.12 (bd, $J_{5,6a}$ = 8.5 Hz, 1 H, 5-H), 4.05 (dd, $J_{CH2\text{-}All,=CH2}$ = 1.3 Hz, 1 H, -CH_2-All), 3.95–3.88, (m, 2 H, 2′-H, 5′-H), 3.71 (dd, $J_{2',3'}$ = 10.7, $J_{3',4'}$ = 8.8 Hz, 1 H, 3′-H), 3.40 (dd, $J_{5',6a'}$ = 3.2, $J_{6a',6b'}$ = 12.9 Hz, 1 H, 6a′-H), 3.29–3.24 (m, 2 H, 4′-H, 6a-H), 3.21–3.15 (m, 2 H, 6b-H, 6b′-H), 2.00 (s, 3 H, NHAc), 1.56 (s, 3 H, -CH_3), 1.44 (s, 3 H, -CH_3), 1.36 (s, 6 H, 2× -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 172.68 (CO-NHAc), 134.15 (CH-All), 116.96 (=CH_2-All), 109.80 [*C*$(CH_3)_2$], 109.17 [*C*$(CH_3)_2$], 96.79, 96.58 (C-1, C-1′), 73.50 (C-4′), 71.60, 71.06 (C-3′, C-3, C-4), 70.62 (C-2), 68.84 (-CH_2-All), 67.66 (C-5′), 64.14 (C-5), 54.05 (C-2′), 49.03 (C-6′), 47.30 (C-6), 25.24, 25.15, 23.90, 23.32 (4× CH_3), 21.47 (CH_3-NHAc) ppm. $C_{23}H_{38}N_2O_{10}$ (502.5): FAB-MS: *m*/*z* = 503.5 $[M + H]^+$.

35b: R_F = 0.63 (DCM/MeOH, 4:1). ^1H NMR (500 MHz, MeOD): δ = 5.90 (dddd, $J_{CH\text{-}All,=CH2c}$ = 10.2, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 5.49 (d, $J_{1,2}$ = 4.8 Hz, 1 H, 1-H), 5.29 (dddd ≈ dq, 1 H, =CH_2-All), 5.15 (dddd ≈ dq, 1 H, =CH_2-All), 4.74 (d, $J_{1',2'}$ = 3.8 Hz, 1 H, 1′-H), 4.69 (dd, $J_{2,3}$ = 2.3 $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.41–4.37 (m, 2 H, 2-H, 4-H), 4.16 (dddd ≈ ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.2, $J_{CH2\text{-}All,=CH2}$ = 1.5 Hz, 1 H, -CH_2-All), 4.00–3.92 (m, 3 H, -CH_2-All, 5-H, 6-H), 3.88 (dd, $J_{2',3'}$ = 8.7 Hz, 1 H, 2′-H), 3.71–3.60 (m, 2 H, 3′-H, 5′-H), 3.28 (dd, $J_{3'4'}$ = 8.7 Hz, 1 H, 4′-H), 3.02 (dd, $J_{5',6a'}$ = 3.1, $J_{6a',6b'}$ = 12.5 Hz, 1 H, 6a′-H), 2.94 (dd, $J_{5',6b'}$ = 7.4 Hz, 1 H, 6b′-H), 1.95 (s, 3 H, NHAc), 1.49 (s, 3 H, -CH_3),1.42 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.32 (s, 3 H, -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 134.33 (CH-All), 117.81, 116.77 (=CH_2-All, CN), 110.16 [*C*$(CH_3)_2$], 109.29 [*C*$(CH_3)_2$], 96.78, 96.52 (C-1, C-1′), 73.13 (C-4′), 71.53 (C-3′), 71.09 (C-2), 70.93 (C-4), 70.70 (C-5′), 70.37 (C-3), 68.26 (-CH_2-All), 67.63 (C-5), 54.30 (C-2′), 50.66 (C-6), 48.21 (C-6′), 25.20, 25.17, 23.95, 23.46 (4× CH_3), 21.46 (CH_3-NHAc) ppm. $C_{24}H_{37}N_3O_{10}$ (527.5): FAB-MS: *m*/*z* = 528.7 $[M + H]^+$.

(Benzyl-2-acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)amine (36), *N*-(Benzyl-2-acetamido-2,6-dideoxy-α-D-glucopyranoside-6-yl)-6-amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-D,L-*glycero*-α-D-*galacto*-heptopyranurononitrile (36b): The aldehyde **26** (93 mg, 0.35 mmol) and amine **31** (273 mg, 0.88 mmol) were reacted according to general procedure 3. After purification by column chromatography

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(DCM/MeOH, 12:1) **36** (92 mg, 48%) could be isolated as a colourless syrup. The byproduct **36b** (57 mg, 28%) could be isolated as a stereoisomeric mixture.

36: R_F = 0.20 (DCM/MeOH, 5:1). ^{1}H NMR (500 MHz, MeOD): δ = 7.41–7.29 (m, 5 H, CH-Bn), 5.58 (d, $J_{1,2}$ = 5.1 Hz, 1 H, 1-H), 4.90 (d, $J_{1',2'}$ = 3.5 Hz, 1 H, 1′-H), 4.79 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.3 Hz, 1 H, -CH_2-Bn), 4.69 (dd, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 4.54 (d, 1 H, -CH_2-Bn), 4.43 (dd, 1 H, 2-H), 4.27 (dd, $J_{4,5}$ = 1.9 Hz, 1 H, 4-H), 4.13 (ddd ≈ dt, $J_{5,6a}$ = 8.8, $J_{5,6b}$ = 1.9 Hz, 1 H, 5-H), 3.98 (ddd ≈ dt, $J_{5',6a'}$ = 3.2, $J_{5',6b'}$ = 9.1 Hz, 1 H, 5′-H), 3.89 (dd, $J_{2',3'}$ = 10.7 Hz, 1 H, 2′-H), 3.74 (dd, $J_{3',4'}$ = 9.1 Hz, 1 H, 3′-H), 3.41 (dd, $J_{6a',6b'}$ = 12.9 Hz, 1 H, 6a′-H), 3.31 (dd, $J_{6a,6b}$ = 13.2 Hz, 1 H, 6a-H), 3.26 (dd ≈ t, 1 H, 4′-H), 3.22–3.17 (m, 2 H, 6b-H, 6b′-H), 1.94 (s, 3 H, NHAc), 1.56 (s, 3 H, -CH_3), 1.39 (s, 3 H, -CH_3), 1.36 (s, 3 H, -CH_3), 1.35 (s, 3 H, -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 174.07 (CO-NHAc), 139.03 (C-Bn), 129.94, 129.63, 129.48 (CH-Bn), 111.33 [$C(CH_3)_2$], 110.71 [$C(CH_3)_2$], 98.11, 98.00 (C-1, C-1′), 75.01 (C-4′), 73.06 (C-4), 72.56, 72.43 (C-3′, C-3), 72.13 (C-2), 71.21 (-CH_2-Bn), 69.19 (C-5′), 65.65 (C-5), 55.56 (C-2′), 50.38 (C-6′), 49.09 (C-6), 26.71, 26.66, 25.39, 24.80 (4× CH_3), 22.93 (CH_3-NHAc) ppm. $C_{27}H_{40}N_2O_{10}$ (552.3): FAB-MS: m/z = 553.4 [M + H]$^+$.

36b: R_F = 0.60 (DCM/MeOH, 5:1). ^{1}H NMR (500 MHz, MeOD): δ = 7.43–7.30 (m, 5 H, CH-Bn), 5.55 (d, $J_{1,2}$ = 4.7 Hz, 1 H, 2× 1-H), 4.86 (d, $J_{1',2'}$ = 3.8 Hz, 1 H, 1′-H), 4.78 (d,$J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 11.7 Hz, 0.5 H, CH_2-Bn), 4.76 (d, 0.5 H, -CH_2-Bn), 4.74 (d, 0.5 H, -CH_2-Bn), 4.69 (dd, $J_{2,3}$ = 2.5, $J_{3,4}$ = 7.9 Hz, 0.5 H, 3-H), 4.52 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.0 Hz, 0.5 H, -CH_2-Bn), 4.51 (d, 0.5 H, -CH_2-Bn), 4.47–4.41 (m, 2 H, 2× 2-H, 2× 4-H), 4.09–4.04 (m, 1 H, 2× 6-H), 4.04–4.00 (m, 1 H, 2× 5-H), 3.94–3.90 (m, $J_{2',3'}$ = 10.7 Hz, 1 H, 2× 2′-H), 3.84–3.76 (m, 1 H, 2× 5′-H), 3.75–3.70 (m, 2 H, 2× 3′-H), 3.42 (dd ≈ t, 0.5 H, 4′-H), 3.35 (dd ≈ t, $J_{3',4'}$ = 8.9, $J_{4',5'}$ = 9.5 Hz, 0.5 H, 4′-H), 3.19 (dd, $J_{5'6a'}$ = 2.8, $J_{6a',6b'}$ = 12.6 Hz, 0.5 H, 6a′-H), 3.09 (dd, 0.5 H, 6a′-H), 3.02 (dd, $J_{5',6b'}$ = 6.3 Hz, 0.5 H, 6b′-H), 2.92 (dd, 0.5 H, 6b′-H), 1.92 (s, 3 H, NHAc), 1.56 (s, 1.5 H, -CH_3), 1.55 (s, 1.5 H, -CH_3), 1.45 (s, 1.8 H, -CH_3), 1.43 (s, 1.5 H, -CH_3), 1.39 (s, 1.9 H, -CH_3), 1.36 (s, 3.5 H, 2× -CH_3), 1.32 (s, 1.4 H, -CH_3) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 173.99 (CO-NHAc), 139.23 (C-Bn), 129.91, 129.61, 129.45 (CH-Bn), 120.50 (CN), 119.37 (CN), 111.66 [$C(CH_3)_2$], 111.30 [$C(CH_3)_2$], 110.81 [$C(CH_3)_2$], 98.22 (C-1), 97.77 (C-1′), 74.66 (C-4′), 72.95 (C-3′), 72.59 (C-3), 72.44, 72.20 (C-2, C-4), 72.02 (C-5′), 70.70 (-CH_2-Bn), 69.18 (C-5), 55.79 (C-2′), 52.61 (C-6), 49.46 (C-6′), 26.74, 25.51, 25.02, 23.00 (4× CH_3), 21.52 (CH_3-NHAc) ppm. $C_{28}H_{39}N_3O_{10}$ (577.3): FAB-MS: m/z = 578.5 [M + H]$^+$.

Allyl 2-Acetamido-2-deoxy-α-D-*gluco*-hexodialdo-1,5-pyranoside (39): To a suspension of **15**[36] (502 mg, 1.92 mmol) in acetonitrile (8 mL) was added Dess–Martin periodinane[39] (880 mg, 2.10 mmol) in dichloromethane (10 mL) and the mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water/dichloromethane (1:1) and the phases were separated. The aqueous phase was washed several times with dichloromethane, filtered, neutralized with 1 M sodium hydroxide solution and concentrated. The remaining water was removed by freeze drying and the residue was purified by column chromatography (DCM/MeOH, 12:1). Product **39** (242 mg, 49%) could be isolated as a colourless solid; m.p. 130 °C, $[\alpha]_{546}^{20}$ = +147 (c = 0.13, MeOH), R_F = 0.31 (DCM/MeOH, 5:1). ^{1}H NMR (D_2O, 400 MHz): δ = 5.88 (dddd, $J_{All\text{-}CH,\text{-}O\text{-}CH2}$ = 5.4 Hz, 1 H, All-CH), 5.27 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 15.8 Hz, 1 H, CH_2-All), 5.19 (d, $J_{5,6}$ = 1.8 Hz, 1 H, 6-H), 5.17 (dd, 1 H, CH_2-All), 4.87 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.15 (dd, $J_{\text{-}O\text{-}CH2,\text{-}O\text{-}CH2}$ = 12.9 Hz, 1 H, O-CH_2-All), 3.95 (dd, 1 H, O-CH_2-All), 3.82 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.6 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H) 3.58 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 5-H), 3.46 (dd, 1 H, 4-H), 1.95 (s, 3 H, CH_3-Ac) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 133.98 (All-CH), 118.22 (All-CH_2), 96.50 (C-1), 88.32 (C-6), 73.16 (C-5), 71.19 (C-3), 71.12 (C-4), 68.81 (O-CH_2-All), 53.90 (C-2), 22.20 (CH_3-Ac) ppm. $C_{11}H_{17}NO_6$ (259.3): calcd. C 50.97, H 6.56, N 5.41; found C 48.43, H 6.54, N 4.56; (mixture of **39** and **39**-hydrate).

Benzyl 2-Acetamido-2-deoxy-α-D-*gluco*-hexodialdo-1,5-pyranoside (40): To a suspension of **37**[37] (101 mg, 0.32 mmol) in acetonitrile (2.5 mL) was added Dess–Martin periodinane (185 mg, 0.44 mmol) in dichloromethane (5 mL). The mixture was stirred at room temperature for 3 h. The reaction was stopped by adding water/dichloromethane (1:1) and the phases were separated. The aqueous phase was washed with dichloromethane several times, filtered, neutralized with 1 M sodium hydroxide solution and concentrated. The remaining water was removed by freeze drying and the residue was purified by column chromatography (DCM/MeOH, 12:1). Product **40** (32 mg, 32%) could be isolated as a colourless solid; m.p. 89 °C, $[\alpha]_{546}^{20}$ = +148 (c = 0.23, MeOH), R_F = 0.30 (DCM/MeOH, 5:1). ^{1}H NMR (D_2O, 400 MHz): δ = 7.60–7.56 (m, 5 H, Ar-H), 5.42 (d, $J_{5,6}$ = 1.8 Hz, 1 H, 6-H), 5.12 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.68 (s, $^2J_{Ar\text{-}CH2,Ar\text{-}CH2}$ = 11.7 Hz, 1 H, CH_2-Ar), 3.99 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.89 (dd, $J_{4,5}$ = 1.0 Hz, 1 H, 5-H), 3.86 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.69 (dd, 1 H, 4-H), 2.08 (s, 1 H, CH_3-Ac) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 129.1 (CH-Ar), 128.7 (CH-Ar), 96.1 (C-1), 88.2 (C-6), 73.2 (C-5), 71.1 (C-3), 70.9 (C-4), 69.9 (CH_2-Bn), 53.9 (C-2), 22.1 (CH_3-Ac) ppm.

2-Acetamido-1,5-anhydro-2-deoxy-hexodialdo-D-glucitol (41): To a suspension of **38** (122 mg, 0.59 mmol) in acetonitrile (3 mL) was added pyridine (0.05 mL) and Dess–Martin periodinane (280 mg, 0.7 mmol) in dichloromethane (6 mL). The mixture was stirred at room temperature for 4 h. The reaction was stopped by adding dichloromethane/water (1:1) and the phases were separated. The aqueous phase was washed with dichloromethane several times, filtered, neutralized with 1 M sodium hydroxide solution and concentrated. The remaining water was removed by freeze drying and the residue was purified by column chromatography (DCM/MeOH, 6:1) to give **41** (23 mg, 19%) as a colourless solid; m.p. 150 °C, $[\alpha]_{546}^{20}$ = –17.5 (c = 0.08, MeOH), R_F = 0.33 (DCM/MeOH, 3:1). ^{1}H NMR (D_2O, 400 MHz): δ = 5.18 (d, $J_{5,6}$ = 2.0 Hz, 1 H, 6-H), 3.90 (dd, $J_{1a,1b}$ = 11.2 Hz, 1 H, 1a-H), 3.78 (ddd, $J_{1a,2}$ = 5.1, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 3.49–3.44 (m, 2 H, 3-H, 4-H), 3.23 (dd, $J_{4,5}$ = 4.8 Hz, 1 H, 5-H), 3.17 (dd, 1 H, 1b-H), 1.96 (s, 3 H, CH_3-Ac) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 88.1 (C-6), 81.2 (C-5), 75.0 (C-3), 71.0 (C-4), 67.5 (C-1), 51.5 (C-2), 22.3 (CH_3-Ac) ppm.

Benzyl 2-Amino-2-deoxy-α-D-galactopyranoside (42): Benzyl 2-acetamido-2-deoxy-4,6-di-*O*-pivaloyl-α-D-galactopyranoside[44,45] (550 mg, 1.15 mmol) and barium hydroxide octahydrate (4.8 g, 13.30 mmol) in water (27 mL) were stirred at 100–120 °C for 16 h. After cooling to room temperature the precipitate was filtered and the filtrate was treated with dry ice to remove the barium salts. The solvent was removed by freeze drying to give **42** (580 mg, 100%) as a colourless solid; m.p. 145 °C, $[\alpha]_{546}^{20}$ = +62.9 (c = 0.55, MeOH), R_F = 0.07 (DCM/MeOH, 5:1). ^{1}H NMR (400 MHz, D_2O): δ = 7.53–7.43 (m, 5 H, CH-Bn), 5.27 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.82 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 11.5 Hz, 1 H, CH_2-Bn), 4.67 (d, 1 H, CH_2-Bn), 4.09–3.99 (m, 3 H, 3-H, 4-H, 5-H), 3.78–3.73 (m, $J_{5,6a}$ = 3.3, $J_{5,6b}$ = 4.8 Hz, 2 H, 6a-H, 6b-H), 3.48 (ddd, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 129.0 (CH-Bn), 95.4 (C-1), 71.7 (C-5), 70.2 (CH_2-Bn), 68.5 (C-3), 67.5 (C-4), 61.3 (C-6), 51.2 (C-2) ppm.

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(Allyl 2-Acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)(1,5-anhydro-2-deoxy-D-glucitol-2-yl)amine (43): The aldehyde **39** (92.5 g, 0.36 mmol) in methanol (2.5 mL) and amine **29** (204 mg, 1.02 mmol) in methanol (1.0 mL) were reacted according to general procedure 4. Compound **43** (112 mg, 78%) could be isolated as a colourless solid; m.p. 105 °C, $[\alpha]_{546}^{20}$ = +96 (*c* = 0.08, MeOH), R_F = 0.65 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 6.03 (dddd, 1 H, =CH-All), 5.41 (dd, $J_{CH\text{-}All,CH2c}$ = 10.4 Hz, 1 H, CH_2-All), 5.34 (dd, $J_{CH\text{-}All,CH2t}$ = 17.3 Hz, 1 H, CH_2-All), 5.00 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.32 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.1 Hz, 1 H, O-CH_2-All), 4.27 (dd, $J_{1a'1b'}$ = 11.2, $J_{1a',2'}$ = 4.8 Hz, 1 H, 1a′-H), 4.13 (dd, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1 Hz, 1 H, O-CH_2-All), 4.04–3.98 (m, 2 H, 2-H, 5′-H), 3.95 (dd, $J_{5',6a'}$ = 2.0, $J_{6a',6b'}$ = 12.3 Hz, 1 H, 6a′-H), 3.83 (dd, $J_{2,3}$ = 8.9, $J_{3,4}$ = 10.7 Hz, 1 H, 3-H), 3.77 (dd, $J_{5',6b'}$ = 5.3 Hz, 1 H, 6b′-H), 3.65 (dd, $J_{2'3'}$ = 8.6, $J_{3'4'}$ = 9.2 Hz, 1 H, 3′-H), 3.54–3.42 (m, 4 H, 1b′-H, 4′-H, 4-H, 5-H), 3.38 (dd, $J_{5,6a}$ = 6.1, $J_{6a,6b}$ = 13.2 Hz, 1 H, 6a-H), 3.21–3.05 (m, 2 H, 2′-H, 6b-H), 2.09 (s, 3 H, CH_3-Ac) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 134.02 (CH-All), 118.24 (=CH_2-All), 96.49 (C-1), 80.86 (C-5), 72.49 (C-4′), 71.03 (C-4), 70.45 (C-3), 69.21 (C-1′, -CH_2-All), 61.16 (C-6′), 58.07 (C-2′), 53.86 (C-2), 47.33 (C-6), 22.19 (CH_3-Ac) ppm. $C_{17}H_{30}N_2O_9$ (406.4): MALDI-TOF-MS: 407.5 $[M + H]^+$, 429.5 $[M + Na]^+$.

(Allyl 2-Acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)(allyl-2-deoxy-α-D-glucopyranos-2-yl)amine (44): The aldehyde **39** (90 mg, 0.34 mmol) in methanol (2.2 mL) and amine **28** (220 mg, 1.01 mmol) in methanol (1 mL) were reacted according to general procedure 4 to give **44** (66 mg, 42%) as a colourless solid; m.p. 187 °C, $[\alpha]_{546}^{20}$ = +133 (*c* = 0.03, H_2O), R_F = 0.64 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 5.98–5.84 (m, 2 H, 2× CH-All), 5.35–5.25 (m, 2 H, 2× = CH_2-All), 5.24–5.18 (m, 2 H, =CH_2-All), 5.09 (d, $J_{1',2'}$ = 3.6 Hz, 1 H, 1′-H), 4.86 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.23–4.13 (m, 2 H, 2× -CH_2-All), 4.05–3.95 (m, 2 H, 2× -CH_2-All), 3.87 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.84–3.75 (m, 3 H, 5-H, 2′-H, 5′-H), 3.73–3.59 (m, 6 H, 3-H, 4-H, 6a-H, 3′-H, 4′-H, 6a′-H), 3.40–3.26 (m, 2 H, 6b-H, 6b′-H), 1.97 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 117.92 (=CH_2-All), 97.56 (C-1′), 94.95 (C-1), 74.10, 73.41, 71.00 (C-3, C-4, C-5, C-3′, C-4′, C5′) 69.15 (-CH_2-All) 61.48 (C-6′), 54.21 (C-2), 54.02 (C-2′), 48.50 (C-6), 22.17 (CH_3-NHAc) ppm. $C_{20}H_{34}N_2O_{10}$ (462.5) MALDI-TOF-MS: *m*/*z* = 463.4 $[M + H]^+$, 485.4 $[M + Na]^+$.

(Allyl 2-Acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)(benzyl-2-deoxy-α-D-galactopyranos-2-yl)amine (45): The aldehyde **39** (100 mg, 0.39 mmol) in methanol (2.5 mL) and amine **42** (311 mg, 1.16 mmol) in methanol (1.5 mL) were reacted according to general procedure 4 to give **45** (155 mg, 76%) as a colourless solid; m.p. 150 °C, $[\alpha]_{546}^{20}$ = +119 (*c* = 0.32, H_2O), R_F = 0.44 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 7.60–7.48 (m, 5 H, CH-Bn), 6.01 (dddd, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1, $J_{CH\text{-}All,CH2c}$ = 10.4, $J_{CH\text{-}All,CH2t}$ = 17.3 Hz, 1 H, CH-All), 5.39 (dd, 1 H, =CH_2-All), 5.33 (dd, 1 H, =CH_2-All), 5.27 (d, $J_{1',2'}$ = 3.8 Hz, 1 H, 1′-H), 4.96 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.86 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 11.5 Hz, 1 H, CH_2-Bn), 4.68 (d, 1 H, CH_2-Bn), 6.40 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 4.11–3.98 (m, 4 H, -CH_2-All, 2-H, 4′-H, 5′-H), 3.91–3.77 (m, 5 H, 3-H, 5-H, 3′-H, 6a′-H, 6b′-H), 3.35 (dd, $J_{3,4}$ = 9.2 Hz, 1 H, 4-H), 3.08–3.00 (m, 2 H, 2′-H, 6a-H), 2.79 (dd, $J_{5,6b}$ = 8.6, $J_{6a,6b}$ = 12.2 Hz, 1 H, 6b-H), 2.14 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 129.42, 129.24, 128.93 (*C*H-Bn), 118.40 (=CH_2-All), 96.42 (C-1′), 95.02 (C-1), 73.11 (C-4), 72.21 (C-3), 72.12 (C-4′ or C-5′), 71.37 (C-3′, C-5), 69.98 (CH_2-Bn), 69.06 (CH_2-All), 67.54 (C-4′ or C-5′), 61.76 (C-6′), 57.87 (C-2′), 54.13 (C-2), 47.81 (C-6), 22.33 (CH_3-NHAc) ppm. $C_{24}H_{36}N_2O_{10}$ (512.6): MALDI-TOF-MS: *m*/*z* = 535.1 $[M + Na]^+$, 551.1 $[M + K]^+$.

[Allyl 6-Deoxy-β-D-galactopyranos-6-yl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside](1,5-anhydro-2-deoxy-glucitol-2-yl)amine (46): The disaccharide aldehyde **22** (61 mg, 0.15 mmol) and amine **29** (71 mg, 0.36 mmol) in methanol (1 mL). Purification by gelpermeation chromatography on sephadex LH 20 (water/methanol, 1:1) allowed isolation of compound **46** (61 mg, 73%) as a colourless solid; m.p. 165 °C (dec.), $[\alpha]_D^{20}$ = +57 (*c* = 0.35, H_2O), R_F = 0.47 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (500 MHz, D_2O): δ = 5.90 (ddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.0, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.1 Hz, 1 H, CH-All), 5.29 (d, 1 H, =CH_2-All), 5.20 (d, 1 H, =CH_2-All), 4.87 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.46 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.20 (d, $J_{1a'',1b''}$ = 11.4, $J_{1a'',2''}$ = 4.7 Hz, 1 H, 1a′′-H), 4.15 (dd, $J_{CH2\text{-}All,CH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 3.98 (dd, 1 H, -CH_2-All), 3.91 (dd, $J_{2,3}$ = 10.4, $J_{5',6a'}$ = 2.8, $J_{5',6b'}$ = 10.4 Hz, 2 H, 2-H, 5′-H), 3.86 (d, $J_{3',4'}$ = 3.2 Hz, 1 H, 4′-H), 3.84–3.76 (m, 6 H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 6a′′-H), 3.68–3.60 (m, 3 H, 3′-H, 3′′-H, 6b′′-H), 3.52–3.43 (m, 2 H, 2′-H, 1b′′-H), 3.40–3.26 (m, 4 H, 6a′-H, 6b′-H, 4′′-H, 5′′-H), 3.18 (dd, $J_{2'',3''}$ = 10.7 Hz, 1 H, 2′′-H), 1.98 (s, 3 H, NHAc) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 133.97 (CH-All), 118.41 (=CH_2-All), 102.63 (C-1′), 96.38 (C-1), 80.85 (C-5′′), 76.98 (C-4), 74.04 (C-3′′), 73.76 (C-3′), 72.68, 71.27, 71.21, 70.49, 70.19, 69.46 (C-3, C-5, C-2′, C-4′, C-5′, C-4′′), 69.00 (-CH_2-All), 65.19 (C-1′′), 61.10 (C-6′′), 60.06 (C-6), 57.83 (C-2′′), 53.82 (C-2), 46.81 (C-6′), 22.28 (CH_3-NHAc) ppm.

[Allyl 6-Deoxy-β-D-galactopyranos-6-yl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside](benzyl 2-acetamido-2,6-dideoxy-α-D-glucopyranosid-6-yl)amine (47): The disaccharide aldehyde **22** (75 mg, 0.18 mmol) and amine **31** (130 mg, 0.42 mmol) in methanol (1.2 mL) were reacted according to general procedure 3. Purification by gelpermeation chromatography on Sephadex LH 20 (water/methanol, 1:1) allowed isolation of compound **47** (53 mg, 41%) as a colourless solid; m.p. 180 °C (dec.), $[\alpha]_D^{20}$ = +33 (*c* = 0.15, H_2O), R_F = 0.54 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 7.35–7.25 (m, 5 H, CH-Bn), 5.82 (ddd, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.3 Hz, 1 H, CH-All), 5.22 (d, $J_{=CH2t,=CH2c}$ = 1.5, $J_{=CH2,CH2\text{-}All}$ = 1.5 Hz, 1 H, =CH_2-All), 5.13 (d, 1 H, =CH_2-All), 4.84 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.77 (d, $J_{1'',2''}$ = 2.8 Hz, 1 H, 1′′-H), 4.68 (d, $J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.0 Hz, 1 H, -CH_2-Bn), 4.43 (d, 1 H, -CH_2-Bn), 4.39 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.08 (dddd ≈ ddt, 1 H, -CH_2-All), 3.89 (dddd ≈ ddt, $J_{CH2\text{-}All,CH2\text{-}All}$ = 13.0 Hz, 1 H, -CH_2-All), 3.84–3.68 (m, 10 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 4′-H, 5′-H, 2′′-H, 5′′-H), 3.64 (dd, $J_{2'',3''}$ = 10.7, $J_{3'',4''}$ = 8.9 Hz, 1 H, 3′′-H), 3.58 (dd, $J_{3',4'}$ = 3.3 Hz, 1 H, 3′-H), 3.43 (dd, $J_{2',3'}$ = 9.9 Hz, 1 H, 2′-H), 3.26 (dd, $J_{4'',5''}$ = 9.7 Hz, 1 H, 4′′-H), 3.19–3.08 (m, 2 H, 6a′-H, 6a′′-H), 2.99–2.90 (m, 2 H, 6b′-H, 6b′′-H), 1.85 (s, 3 H, NHAc), 1.82 (s, 3 H, NHAc′′) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.68 (CO-NHAc), 137.37 (C-Bn), 133.98 (CH-All), 129.18, 128.88, 128.80 (CH-Bn), 118.37 (=CH_2-All), 102.74 (C-1′), 96.30 (C-1, C-1′′), 77.49 (C-4), 72.78 (C-4′′), 72.69 (C-3′), 71.83, 71.37, 71.20, 70.94, 69.98, 69.70, 69.02 (C-3, C-5, C-2′, C-4′, C-5′, C-3′′, C-5′′), 70.38 (-CH_2-Bn), 68.97 (-CH_2-All), 60.16 (C-6), 53.96 (C-2, C-2′′), 49.33, 48.77 (C-6′, C-6′′), 22.23, 22.17 (CH_3-NHAc, CH_3-NHAc′′) ppm.

Acknowledgments

Support of this work by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (SFB 470,A5) is gratefully acknowledged.

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Received: November 2, 2006
Published Online: January 19, 2007

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