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Synthesis of Amino-Bridged Oligosaccharide Mimetics

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Synthesis of amino-bridged oligosaccharides using reductive amination opens rapid access to novel glycomimetic target structures as potential ligands for the receptor protein NKR P1 of natural killer cells. Emphasis was laid on fast and facile synthetic routes. The carbonyl building blocks were easily obtained by oxidation with Dess–Martin periodinane or iodoxybenzoic acid (IBX). For the required amino-functionalized units, reduction of azide precursors was advantageous, and generation of the novel oligosaccharides was achieved by subsequent reductive amination. The target saccharide structures feature a bridging nitrogen atom inserted between two non-anomeric positions as well as including one anomeric position.

Introduction

The importance of carbohydrates in biological recognition processes increased in the last few decades. In particular, research focused on carbohydrate cell-cell communication, in which complex glycoconjugates are of great interest.[1] Initial biological studies require mainly simple mimetics of complex natural carbohydrate structures for potential drug design as well as for the investigation of glycoconjugate-structure relationship in biochemical processes.[2]

The role of carbohydrates as ligands for the receptor protein of the natural killer cell has been intensely studied.[3–5] As the natural killer cell is able to kill specific tumor cell lines,[6] the investigation of the ligand-receptor relationship is of utmost importance. The receptor protein NKR P1 of the natural killer cell was demonstrated to belong to the family of C-type lectin-like proteins which have a carbohydrate recognition domain.[7,8] For investigation of NK cell resistant tumor cells potential carbohydrate ligands were tested for their affinity to NKR P1.[9,10] Whereas complex carbohydrate synthesis often requires multiple-step pathways, rather facile accesses to glycomimetics are of interest for investigation of carbohydrate–protein interactions. These glycomimetics are mostly non-natural carbohydrate-derived structures that imitate the function of the natural derivative.[11]

Aim of this work was the synthesis of non-natural oligosaccharides using *N*-acetylhexosamine derivatives as building blocks. The structures were linked either through glycosidic or non-glycosidic amino bridges and expected to mimic natural *O*-glycosidic bonds as well as to provide new and unnatural pseudo-oligosaccharides. (Figure 1).

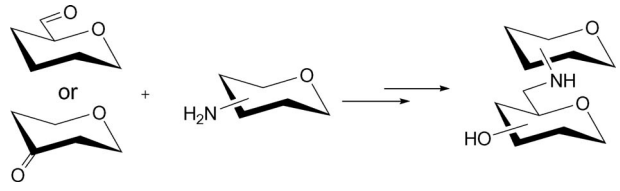

Figure 1. General synthetic scheme.

Emphasis was laid on classical chemical synthesis, however, mostly avoiding complex protective group chemistry. By using selective chemical synthesis the unnatural pseudo-oligosaccharides could be provided in a few facile and high yielding steps.

Unnatural linkages could be established in different ways.[12,13] In this contribution formation of the linkage was realized by using reductive amination[14,15] that selectively connects aldehydes or ketones with primary or secondary amines. For reduction of the imine sodium cyanoborohydride was applied[16] that easily forms the amino-linked disaccharide mimetics under very mild conditions.

Results and Discussion

Oxidation

As previously described[17] Dess–Martin oxidation is a mild and selective method to obtain 6-carbaldehydes from unprotected glycosides, however, the yields could not be enhanced to more than 50% (Scheme 1).

Therefore, as another oxidation reagent IBX (iodoxybenzoic acid), the precursor of the Dess–Martin periodinane, was employed. As reported IBX in DMSO shows about the same oxidative properties as periodinane.[18,19] Thus preparation of aldehydes **9** and **10**

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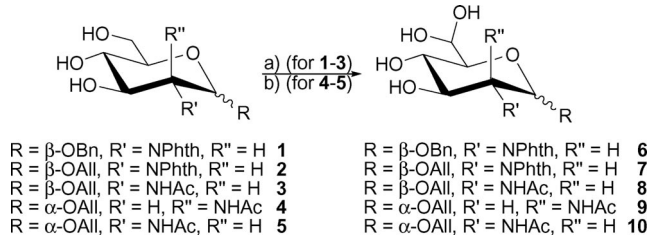
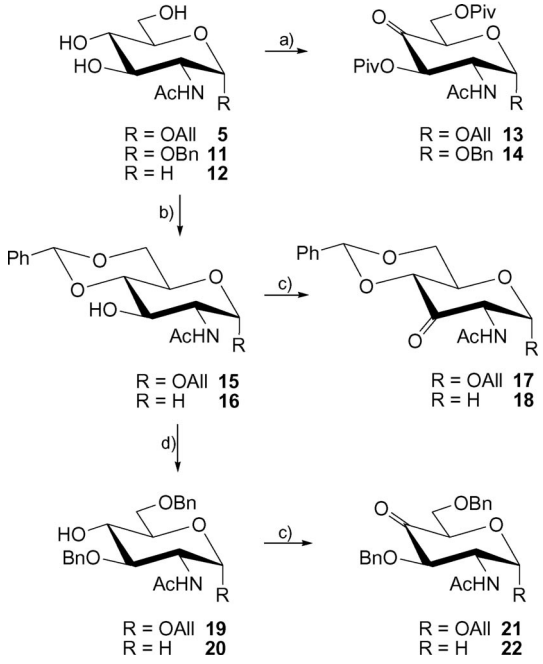


Scheme 1. Oxidation of glycosides with DMP or IBX: a) 1.2 equiv. DMP, DCM, MeCN, room temp., 2 h; b) 1.5 equiv. IBX, DMSO, room temp., 2 h.

with IBX provided 33 and 77% yield, which shows IBX to be as selective as the periodinane but more effective. The reaction of **10** was monitored using RP-HPLC. According to these data Dess–Martin oxidation took 35 min and was much faster, than oxidation with IBX (2 h). In case of the 3- and 4-keto sugars preparation was achieved by using Dess–Martin periodinane exclusively (Scheme 2).

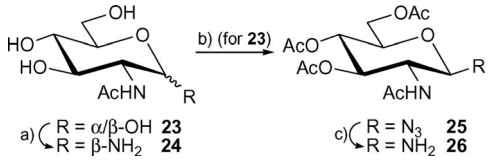


Scheme 2. Synthesis of keto sugars: a) 1. PivCl, DCM, pyridine, 0 °C, 2 h, 2. Dess–Martin periodinane, DCM, room temp., 24 h; b) benzaldehyde dimethyl acetal, THF, *p*TsA, 80 °C, 20 h; c) Dess–Martin periodinane, DCM, room temp., 24 h; d) 1. BnBr, NaOH/DMSO (1:10), room temp., 16 h, 2. $NaCNBH_3$, HCl, THF, room temp., 30 min.

The partially protected saccharides could be oxidized in good to very good yields. Treatment of glycosides **5**[20] and **11**[21] with pivaloyl chloride gave the partially protected glycosides[22,23] which could be oxidized with Dess–Martin periodinane in dichloromethane to give 4-keto sugars **13** and **14** in 87 and 85% yield, respectively. En route to the 3-keto sugars **17** and **18**, AllGlcNAc **5** and 1,5-anhydro-glucitol **12**[24] were transformed into the corresponding benzylidene-protected sugars which were oxidized with Dess–Martin periodinane in dichloromethane in 95% and 59% yield. Preparation of 4-keto sugars **20** and **21** started with benzylation of **15** and **16** followed by ring opening using sodium cyanoborohydride. The partially protected saccharides **19**[25] and **20**[26] obtained could be easily oxidized with periodinane and gave the desired products in 74% and 40% yield, respectively. These 3- and 4-keto sugars can now be employed as carbonyl building blocks for reductive amination to link sugar units by amino bridges.

Amino-Functionalized Building Blocks

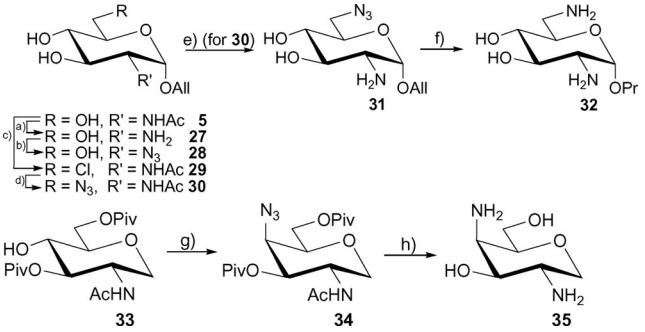
The easiest method for preparation of glycosylamines was reported by Kochetkov et al.[27,28] *N*-Acetylglucosamine **23** was transformed into glycosylamine **24** by reaction with saturated ammonium hydrogen carbonate solution, however, this glycosylamine is rather labile in aqueous media. Therefore, an alternative route was chosen using the acetylated glycosyl azide **25**[29] as precursor, which could be hydrogenated with palladium on charcoal in 94% yield to give the corresponding acetylated glycosylamine **26** (Scheme 3).



Scheme 3. Synthesis of glycosylamines: a) satd. NH_4HCO_3 solution, 37 °C, 80 h; b) 1. AcCl, room temp., 16 h, 2. NaN_3, DMF, 80 °C, 2 h; c) H_2, Pd/C, EtOAc, room temp., 72 h.

These building blocks can be used for preparation of novel oligosaccharide derivatives comprising the anomeric center.

For preparation of non-natural oligosaccharides 2-amino- and 6-amino-functionalized saccharides were synthesized as well as 2,6-diamino- and 2,4-diamino-saccharides (Scheme 4).

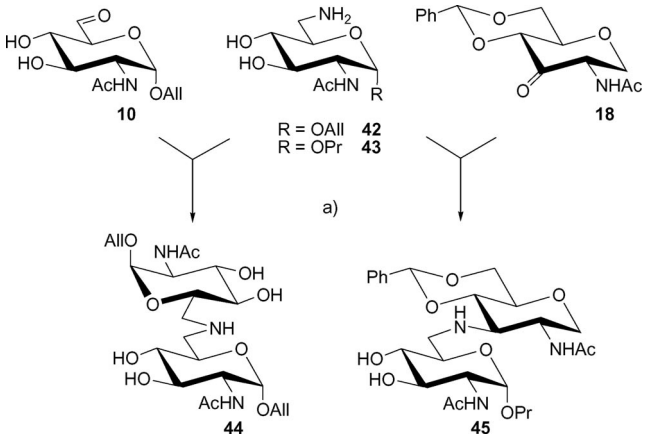


Scheme 4. Synthesis of diamino sugars: a) 2 N NaOH, 100 °C, 16 h; b) TfN_3, DCM, MeOH, DMAP, room temp., 16 h; c) 1. CCl_4, Ph_3P, pyridine, 0 °C, 2. 50 °C, 20 min, 3. MeOH, 50 °C, 20 min; d) NaN_3, DMF, 120 °C, 24 h; e) $Ba(OH)_2 \cdot 8H_2O$, H_2O, 120 °C, 3 h; f) H_2, Pd/C, MeOH, room temp., 72 h; g) 1. Tf_2O, DCM, pyridine, –35 °C → 0 °C, 4 h, 2. NaN_3, DMF, 80 °C, 3.5 h; h) 1. $Ba(OH)_2 \cdot 8H_2O$, H_2O, 110 °C, 16 h, 2. H_2, Pd/C, MeOH, room temp., 72 h.

Employing the diazo transfer with triflyl azide to the 2-amino component **27** led to the 2-azido sugar **28** in 42% yield. The primary hydroxy group of component **5** could be

selectively transformed into the halide **29** in 77% yield using carbon tetrachloride with triphenylphosphane in pyridine.[30,31] The halide **29** could be easily substituted with sodium azide in DMF to give the corresponding azide **30** in 60% yield, and deprotection of the acetyl group gave the 2-amino-6-azido-saccharide **31** in 83% yield. Upon hydrogenation the corresponding diamino-sugar **32** was obtained with the allyl group transformed to a propyl group.

For preparation of a 2,4-diamino-functionalized saccharide the partially protected anhydro glucitol **33** was reacted to give the 4-triflate and without further purification transferred into the epimeric *galacto* azide **34** in 60% yield over two steps. This in turn was transferred into the diamino component **35** in 80% yield.



Scheme 6. Reductive amination II: a) $NaCNBH_3$, MeOH, pH = 6, room temp., 20 h.

Reductive Amination

For linking the prepared aldehydo- and amino-functionalized saccharide building blocks reductive amination with sodium cyanoborohydride in aqueous methanol at pH 6 and room temperature could be employed.[17] The 2,6-*N*-linked structures **37**–**40** (Scheme 5) could be obtained in average to good yields without attempts for optimization.

An example of an amino-bridged structure comprising the anomeric center is the 1,6-*N*-linked structure **41** (Scheme 5). Carbaldehyde **10** was converted with glycosylamine **24** to give the disaccharide **41** in 23% yield. Again, compared to the 2,6-*N*-linked structures this disaccharide shows lower stabilities as also evident from the lower yield obtained. The transfer to 6,6-*N*-linked pseudo-disaccharides could be accomplished with carbaldehyde **10** and allyl 2-acetamido-6-amino-2,6-dideoxy-α-D-glucopyranoside (**42**) (Scheme 6). These structures provide another new unnatural form of *N*-linked disaccharides.

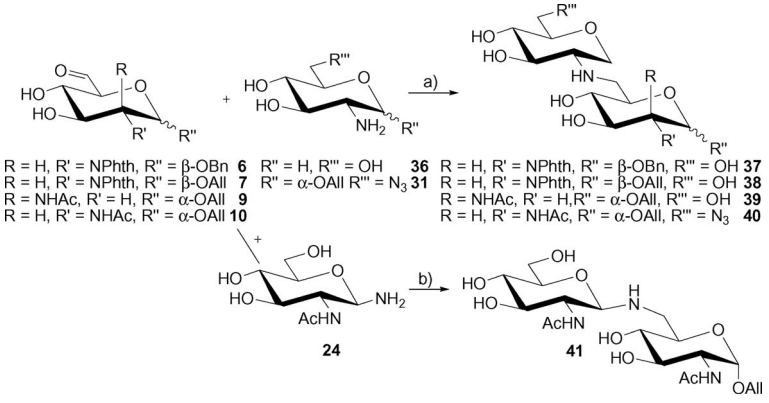
Another new *N*-linkage displays the 3,6-*N*-linked pseudo-disaccharide **45** obtained by reaction of 3-keto sugar **18** with 6-amino sugar **43**. In addition a small amount of the *gulo*-diastereomere was detected as well as both reduction products of keto sugar **18**. These results show that the standard reductive amination used for other linkages could not be applied here. However, optimization required is restricted by conditions to be adjusted between the reduction of ketones to alcohols at pH lower than 6 and pH higher than 8 leaving the optimum range for reductive amination with $NaCNBH_3$.[16]

Conclusions

These results demonstrate a fast and facile way to prepare unnatural oligosaccharide mimetics by using reductive amination. The aldehyde and keto sugars could be prepared under very mild and selective conditions with Dess–Martin periodinane. However, the synthesis of aldehydes was more effective if the oxidation was carried out with IBX. The amino-building blocks could be obtained by various methods. The easiest way is the synthesis of glycosylamines by Kochetkov et al.[27] Another route proceeds by reduction of azide precursors to the corresponding amines. Diamino sugars open access to novel higher oligosaccharides if converted with a carbaldehyde by reductive amination. This method displays an easy and fast approach to novel *N*-linked oligosaccharides to be tested as ligands for the receptor protein NKR P1 of natural killer cells.

Experimental Section

General Remarks: TLC was performed on aluminum sheets coated with silica gel 60 (Merck) and UV detection by heating with H_2SO_4



Scheme 5. Reductive amination I: a) $NaCNBH_3$, MeOH, H_2O, pH 6, room temp., 20 h; b) $NaCNBH_3$, THF, pH 6, room temp., 20 h.

(10% in EtOH). Aldehydes were detected by heating with 2,4-dinitrophenylhydrazine (0.2 M HCl) and amino-functionalized compounds with ninhydrin (0.2 M EtOH). Column chromatography was carried out on silica gel 60 (0.04–0.063 mm; Merck), and gel permeation chromatography on Sephadex LH20 with doubly distilled 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 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 an Apotec melting point apparatus and are uncorrected. The optical rotations were measured with a Perkin–Elmer 341 polarimeter at 20 °C (546 nm, Hg) or a Kruess P8000 polarimeter at 25 °C (589 nm, Na).

Oxidation General Procedure 1a: The monosaccharide (1.0 mmol) was suspended in acetonitrile (7.0 mL). A solution of Dess–Martin periodinane (1.2 mmol) in dichloromethane (10 mL) was added and stirred for 2 h at room temperature. The reaction mixture was diluted with dichloromethane/water (1:1) and the organic layer extracted with water. The aqueous layer was neutralized with a 2.0 N sodium hydroxide solution and concentrated. The residue was purified by column chromatography.

Oxidation General Procedure 1b: The monosaccharide (1 mmol) was dissolved in dichloromethane (10 mL). A solution of Dess–Martin periodinane (1.2 mmol) in dichloromethane (10 mL) was added and stirred for 2–24 h at room temperature. Sodium thiosulfate solution was added to the reaction mixture (4 g/100 mL H_2O) until two distinct phases were established. The organic layer was neutralized with sodium hydrogen carbonate, washed with water, dried, and concentrated. The residue was purified by column chromatography.

Reductive Amination General Procedure 2: Water was added dropwise to a solution of aldehyde (0.27 mmol) in methanol (1.5 mL) and amine (0.68 mmol, 2.5 equiv.) in methanol (1 mL) until complete dissolution. The pH of the solution was adjusted to 6 using either a 1 M solution of glacial acetic acid or a solution of 10% triethylamine in methanol. Then a 0.3 M sodium cyanoborohydride solution in methanol (0.6 mL) was added and the mixture stirred at room temperature overnight. The solution was concentrated and the residue was purified by gel permeation chromatography on Sephadex LH20 [water/methanol, (1:1)].

Benzyl 2-Deoxy-2-phthalimido-β-D-*gluco*-hexodialdo-1,5-pyranoside (6): Compound **1**[32] (1.0 g, 2.5 mmol) was suspended in acetonitrile (15 mL) and Dess–Martin periodinane (1.27 g, 3.02 mmol) in dichloromethane (20 mL) added. The mixture was stirred for 3 h at room temperature and then concentrated until dryness. The residue was purified by column chromatography [toluene/acetone (5:1→3:1→1:1)]. Product **6** (386 mg, 39%) could be obtained as a colorless solid; m.p. 148.4 °C. $[a]_D^{25}$ = –86.8 (*c* = 1.01, acetone), R_F = 0.40 (ethyl acetate). ^{1}H NMR (400 MHz, [D$_6$]acetone/D$_2$O): δ = 7.89–7.76 (m, 4 H, CH-Phth), 7.07–6.96 (m, 5 H, CH-Bn), 5.21 (d, $J_{5,6}$ = 2.4 Hz, 1 H, 6-H), 5.16 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H), 4.78 (d, $^2J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.5 Hz, 1 H, CH_2-Bn), 4.54 (d, 1 H, CH_2-Bn), 4.25 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.98 (dd, 1 H, 2-H), 3.62 (dd, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 3.40 (dd, 1 H, 5-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]acetone/D$_2$O): δ = 135.5 (CH-Phth), 129.0, 128.6, 128.5 (CH-Bn), 124.1 (CH-Phth), 98.6 (C-1), 90.0 (C-6), 77.9 (C-5), 72.4 (C-4), 71.7 (CH_2-Bn), 71.6 (C-3), 57.9 (C-2) ppm. $C_{21}H_{19}NO_7$ (396) ESI-MS: *m*/*z* = 420 [M + Na]$^+$, 817 [2M + Na]$^+$.

Allyl 2-Deoxy-2-phthalimido-β-D-*gluco*-hexodialdo-1,5-pyranoside (7): Compound **2**[33] (1.279 g, 3.662 mmol) was suspended in acetonitrile (20 mL) and Dess–Martin periodinane (1.863 g, 4.395 mmol, 1.2 equiv.) in dichloromethane (30 mL) added. The reaction mixture was stirred for 2 h at room temperature, then concentrated and the residue was purified by column chromatography [toluene/acetone (5:1→3:1→1:1)]. Product **7** (447 mg, 37%) could be obtained as a colorless solid; m.p. 172.1 °C. $[a]_D^{25}$ = –41.7 (*c* = 0.72, acetone), R_F = 0.31 (toluene/acetone, 1:1). ^{1}H NMR (500 MHz, D$_2$O): δ = 8.00–7.86 (m, 4 H, CH-Phth), 5.71 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.2, $J_{CH\text{-}All,=CH2c}$ = 11.0, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 4.2, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.5 Hz, 1 H, CH-All), 5.39–5.29 (m, 2 H, 1-H, 6-H), 5.17 (dd, 1 H, =CH_2-All), 5.09 (dd, 1 H, =CH_2-All), 4.43–4.28 (m, 2 H, 3-H, -CH_2-All), 4.15 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 12.9 Hz, 1 H, CH_2-All), 4.05 (dd, $J_{1,2}$ = 8.6, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.66 (dd, $J_{3,4}$ = 8.7, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.59 (dd, $J_{5,6}$ = 2.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (101 MHz, D$_2$O): δ = 135.2 (CH-Phth) ppm. 133.0 (=CH-All), 118.7 (=CH_2-All), 97.6 (C-1), 88.0 (C-6), 76.8 (C-5), 71.1 (C-3), 70.6 (OCH_2-All), 70.5 (C-4), 56.7 (C-2) ppm. $C_{17}H_{17}NO_7$ (347.32) MALDI-TOF-MS: *m*/*z* = 369.4 [M + Na]$^+$, 385.4 [M + K]$^+$.

Allyl 2-Acetamido-2-deoxy-β-D-*gluco*-hexodialdo-1,5-pyranoside (8): Compound **3**[20] (353 mg, 1.35 mmol) was suspended in acetonitrile (8 mL) and treated with Dess–Martin periodinane (688.9 mg, 1.625 mmol) in dichloromethane (12 mL) after general procedure **1a**. The residue was purified by column chromatography [DCM/MeOH (8:1)] and product **8** (52.8 mg, 15%) could be obtained as a colorless solid; m.p. 170.5 °C, $[a]_D^{25}$ = –14.5 (*c* = 0.355, DMSO), R_F = 0.19 (DCM/MeOH, 5:1). ^{1}H NMR (400 MHz, D$_2$O): δ = 5.92 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.6, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.1, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.2 Hz, 1 H, CH-All), 5.36–5.24 (m, 3 H, 2× =CH_2-All, 6-H), 4.57 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 4.36 (dd, $^2J_{OCH2\text{-}All,OCH2\text{-}All}$ = 13.3 Hz, 1 H, -CH_2-All), 4.17 (dd, 1 H, -CH_2-All), 3.73 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.60–3.50 (m, 2 H, 3-H, 4-H), 3.39 (dd, $J_{4,5}$ = 9.5, $J_{5,6}$ = 2.1 Hz, 1 H, 5-H), 2.04 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D$_2$O): δ = 139.4 (=CH-All), 118.1 (=CH_2-All), 100.4 (C-1), 88.0 (C-6), 76.5 (C-5), 73.7 (C-3), 70.5 (OCH_2-All), 70.4 (C-4), 55.4 (C-2), 22.2 (CH_3-NHAc) ppm. $C_{11}H_{17}NO_6$ (259.26) ESI-MS: *m*/*z* = 541 [2M + Na]$^+$.

Allyl 2-Acetamido-2-deoxy-α-D-*manno*-hexodialdo-1,5-pyranoside (9): 1.) IBX oxidation: Compound **4**[34] (133 mg, 0.510 mmol) was dissolved in DMSO (2.5 mL) und IBX (211 mg, 0.763 mmol) was added. The reaction mixture was stirred for 2 h at room temperature, then diluted with water and filtered. The water was removed by freeze drying and the residue purified by column chromatography [DCM/MeOH (10:1)]. Product **9** (43 mg, 33%) could be obtained as a colorless solid. 2.) Dess–Martin oxidation: compound **4**[34] (340 mg, 1.30 mmol) was dissolved in acetonitrile (9 mL) and Dess–Martin periodinane (663 mg, 1.56 mmol) as well as dichloromethane (11 mL) added. The reaction mixture was treated for 2 h according to general procedure **1a**. The residue was purified by column chromatography [DCM/MeOH (12:1)]. Product **9** (91 mg, 27%) could be isolated as a colorless solid; m.p. 110 °C. $[a]_D^{24}$ = +32.2 (*c* = 0.115, MeOH), R_F = 0.32 (DCM/MeOH, 5:1). ^{1}H NMR (400 MHz, D$_2$O): δ = 5.98 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.5, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.3 Hz, 1 H, CH-All), 5.39 (dd, 1 H, =CH_2-All), 5.35–5.26 (m, 2 H, =CH_2-All, 6-H), 4.91 (s, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.36 (dd, $J_{2,3}$ = 4.7 Hz, 1 H, 2-H), 4.25 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 12.8 Hz, 1 H, -CH_2-All), 4.13–3.97 (m, 2 H, -CH_2-All, 3-H), 3.72–3.61 (m, 2 H, 4-H, 5-H), 2.06 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D$_2$O): δ = 133.2 (=CH-All), 118.5 (=CH_2-All), 98.2 (C-1), 87.9 (C-6), 73.4 (C-5),

69.2 (C-3), 68.2 (OCH_2-All), 67.5 (C-4), 52.5 (C-2), 21.9 (CH_3-NHAc) ppm. $C_{11}H_{17}NO_6$ (259.26) FAB-MS: *m*/*z* = 260.1 [M + H]$^+$. FAB-HRMS: found: 260.1135, calcd. 260.1134 [M + H]$^+$.

Allyl 2-Acetamido-2-deoxy-α-D-*gluco*-hexodialdo-1,5-pyranoside (10): AllGlcNAc **5**[20] (107.6 mg, 0.4123 mmol) was dissolved in DMSO (2.0 mL) and IBX (174 mg, 0.629 mmol) added. The reaction mixture was stirred for 2 h at room temperature. The reaction was diluted with water and the precipitate filtered. The water was removed by freeze drying and the residue purified by column chromatography [DCM/MeOH (12:1)]. Product **10** (82.7 mg, 77%) could be isolated as a colorless solid; m.p. 126–129 °C. $[\alpha]_D^{20}$ = +133 (*c* = 0.505, MeOH), R_F = 0.29 (DCM/MeOH, 5:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.97 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.7, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.2, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.2 Hz, 1 H, CH-All), 5.36 (dd, 1 H, =CH_2-All), 5.31–5.23 (m, 2 H, =CH_2-All, 6-H), 4.97 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.24 (dd, $^2J_{OCH2\text{-}All,CH2\text{-}All}$ = 13.1 Hz, 1 H, -CH_2-All), 4.04 (dd, 1 H, CH_2-All), 3.91 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.78 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.67 (dd, $J_{4,5}$ = 10.0, $J_{5,6}$ = 1.8 Hz, 1 H, 5-H), 3.56 (dd, 1 H, 4-H), 2.05 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 174.5 (CO-NHAc), 133.6 (=CH-All), 117.8 (=CH_2-All), 96.1 (C-1), 87.9 (C-6), 72.8 (C-5), 70.8 (C-3), 70.7 (C-4), 68.4 (OCH_2-All), 53.5 (C-2), 21.8 (CH_3-NHAc) ppm. $C_{11}H_{17}NO_6$ (259.26) FAB-MS: *m*/*z* = 260.1 [M + H]$^+$. FAB-HRMS: found: 260.1128, calcd. 260.1134 [M + H]$^+$.

Allyl 2-Acetamido-2-deoxy-3,6-di-*O*-pivaloyl-α-D-*xylo*-hexopyranoside-4-ulose (13): Allyl 2-acetamido-2-deoxy-3,6-di-*O*-pivaloyl-α-D-glucopyranoside[22] (1.52 g, 3.50 mmol) was dissolved in dry dichloromethane (15 mL) and Dess–Martin periodinane (1.81 g, 4.20 mmol) dissolved in dichloromethane (20 mL) added. The reaction mixture was treated according to general procedure **1b**. The residue was purified by column chromatography [petroleum ether/ethyl acetate (1:1)] and product **13** (1.30 g, 87%) could be isolated as a colorless amorphous solid. $[\alpha]_{546}^{20}$ = +116.7 (*c* = 0.15, $CHCl_3$), R_F = 0.25 (petroleum ether ether/ethyl acetate, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.90–5.81 (m, 1 H, CH-All), 5.79 (d, $J_{NH,2}$ = 9.2 Hz, 1 H, NH), 5.42 (d, 1 H, 3-H), 5.27 (dd, $J_{CH\text{-}All,=CH2t}$ = 17.2, $^2J_{=CH2c,=CH2t}$ = 1.5 Hz, 1 H, =CH_2-All), 5.22 (dd, $J_{CH\text{-}All,=CH2c}$ = 10.2 Hz, 1 H, =CH_2-All), 5.00 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.68 (ddd, $J_{2,3}$ = 11.7 Hz, 1 H, 2-H), 4.46 (dd, $J_{5,6a}$ = 3.1, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6aH), 4.41 (dd, $J_{5,6b}$ = 6.1 Hz, 1 H, 5-H), 4.27–4.18 (m, 2 H, 6b-H, -CH_2-All), 4.08–4.02 (m, 1 H, -CH_2-All), 1.91 (s, 3 H, CH_3-NHAc), 1.20 (s, 9 H, CH_3-Piv), 1.15 (s, 9 H, CH_3-Piv) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.2 (C-4), 178.5 (CO-Piv), 178.4 (CO-Piv), 169.8 (CO-NHAc), 133.0 (=CH-All), 119.4 (=CH_2-All), 96.8 (C-1), 74.0 (C-3), 72.4 (C-5), 69.5 (OCH_2-All), 61.9 (C-6), 53.6 (C-2), 39.3 [$C(CH_3)_3$], 39.2 [$C(CH_3)_3$], 27.6, 27.5, 27.4 [3× $C(CH_3)_3$], 23.9 (CH_3-NHAc) ppm. $C_{21}H_{33}NO_8$ (427.5) MALDI-TOF-MS: *m*/*z* = 450.4 [M + Na]$^+$, 466.3 [M + K]$^+$.

Benzyl 2-Acetamido-2-deoxy-3,6-di-*O*-pivaloyl-α-D-*xylo*-hexopyranoside-4-ulose (14): Benzyl 2-acetamido-2-deoxy-3,6-di-*O*-pivaloyl-α-D-glucopyranoside[23] (1.11 g, 2.31 mmol) was dissolved in dry dichloromethane (15 mL) and Dess–Martin periodinane (1.18 g, 2.78 mmol) in dichloromethane (20 mL) was added. The reaction mixture was treated according to general procedure **1b** and the residue was purified by column chromatography [DCM/ethyl acetate (3:1)]. Product **14** (0.93 g, 85%) could be isolated as a colorless solid; m.p. 58.2 °C. $[\alpha]_D^{25}$ = +112 (*c* = 1.04, $CHCl_3$), R_F = 0.46 (DCM/ethyl acetate, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.49 (m, 5 H, CH-Bn), 5.85 (d, $J_{NH,2}$ = 9.7 Hz, 1 H, NH), 5.66 (d, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H), 5.27 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.99 (d, $^2J_{CH2Bn,CH2Bn}$ = 11.5 Hz, 1 H, CH_2-Bn), 4.90 (ddd, 1 H, 2-H), 4.77 (d, 1 H, CH_2-Bn), 4.70–4.64 (m, 2 H, 5-H, 6a-H), 4.49 (dd, $J_{5,6b}$ = 6.9, $^2J_{6a,6b}$ = 12.7 Hz, 1 H, 6b-H), 2.08 (s, 3 H, CH_3-NHAc), 1.39 (s, 9 H, CH_3-Piv), 1.38 (s, 9 H, CH_3-Piv) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.1 (C-4), 178.5 (CO-Piv), 169.7 (CO-NHAc), 129.1 (CH-Bn), 96.9 (C-1), 74.1 (C-3), 72.5 (C-5), 70.9 (CH_2-Bn), 61.8 (C-6), 53.6 (C-2), 39.3 [$C(CH_3)_3$], 39.2 [$C(CH_3)_3$], 27.6, 27.4 [2× $C(CH_3)_3$], 23.5 (CH_3-NHAc) ppm. $C_{25}H_{35}NO_8$ (477.5) MALDI-TOF-MS: *m*/*z* = 478.0 [M + H]$^+$, 500.0 [M + Na]$^+$, 516.0 [M + K]$^+$.

Allyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside-3-ulose (17): Compound **15**[25] (500 mg, 1.43 mmol) was suspended in dry dichloromethane (10 mL) and Dess–Martin periodinane (915 mg, 2.16 mmol, 1.5 equiv.) in dry dichloromethane (15 mL) was added. The reaction mixture was treated for 3 h according to general procedure **1b** and the residue was purified by column chromatography (petroleum ether/ethyl acetate, 1:3). Product **17** (474 mg, 95%) could be obtained as a colorless solid; m.p. 188.5 °C. $[\alpha]_D^{25}$ = +125.1 (*c* = 1.075, DMSO), R_F = 0.27 (petroleum ether/ethyl acetate, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 2 H, CH-Bn), 7.38–7.35 (m, 3 H, CH-Bn), 6.28 (d, $J_{2,NH}$ = 7.9 Hz, 1 H, NH), 5.84 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.0, $J_{CH\text{-}All,=CH2c}$ = 10.2, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.4 Hz, 1 H, CH-All), 5.59 (s, 1 H, PhC**H**OO), 5.38 (d, $J_{1,2}$ = 4.3 Hz, 1 H, 1-H), 5.31–5.21 (m, 2 H, =CH_2-All, =CH_2-All), 4.98 (ddd, $^4J_{2,4}$ = 1.3 Hz, 1 H, 2-H), 4.42–4.37 (m, 2 H, 4-H, 6a-H), 4.18 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 12.5 Hz, 1 H, -CH_2-All), 4.13 (ddd, $J_{4,5}$ = 9.9, $J_{5,6a}$ = 4.8, $J_{5,6b}$ = 2.0 Hz, 1 H, 5-H), 4.04–3.92 (m, 2 H, 6b-H, -CH_2-All), 2.08 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.5 (C-3), 170.5 (CO-NHAc), 133.1 (=CH-All), 129.3 (CH-Bn), 126.8 (CH-Bn), 118.9 (=CH_2-All), 102.4 (Ph*C*HOO), 100.6 (C-1), 83.0 (C-4), 69.8 (C-6), 69.4 (-CH_2-All), 66.7 (C-5), 59.3 (C-2), 23.5 (CH_3-NHAc) ppm. $C_{18}H_{21}NO_6$ (347.4) MALDI-TOF-MS: *m*/*z* = 348.1 [M + H]$^+$, 370.0 [M + Na]$^+$, 386.0 [M + K]$^+$.

2-Acetamido-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-3-ulose (18): Compound **16**[26] (300 mg, 1.02 mmol) was suspended in dichloromethane (15 mL) and Dess–Martin periodinane (526 mg, 1.24 mmol, 1.22 equiv.) in dichloromethane (18 mL) was added. The reaction mixture was treated for 16 h according to general procedure **1b** and the residue was purified by column chromatography [ethyl acetate]. Product **18** (175 mg, 59%) could be obtained as a colorless solid; m.p. 241 °C (dec.). $[\alpha]_D^{24}$ = +14.2 (*c* = 0.69, ethyl acetate), R_F = 0.36 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.47 (m, 2 H, CH-Bn), 7.43–7.33 (m, 3 H, CH-Bn), 6.40 (d, $J_{NH,2}$ = 5.2 Hz, 1 H, NH), 5.60 (s, 1 H, PhC**H**OO), 4.82 (ddd, $J_{1a,2}$ = 7.4, $J_{1b,2}$ = 8.9 Hz, 1 H, 2-H), 4.72 (dd, $^2J_{1a,1b}$ = 10.5 Hz, 1 H, 1a-H), 4.50–4.39 (m, 2 H, 4-H, 6a-H), 3.90 (dd, $J_{5,6b}$ = 10.1, $^2J_{6a,6b}$ = 10.6 Hz, 1 H, 6b-H), 3.67 (ddd, $J_{4,5}$ = 9.8, $J_{5,6a}$ = 4.8 Hz, 1 H, 5-H), 3.31 (dd, 1 H, 1b-H), 2.06 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.2 (C-3), 170.2 (CO-NHAc), 129.4, 128.3, 126.3 (CH-Bn), 101.9 (Ph*C*HOO), 82.9 (C-4), 75.4 (C-5), 72.4 (C-1), 69.3 (C-6), 56.5 (C-2), 23.0 (CH_3-NHAc) ppm. $C_{15}H_{17}NO_5$ (291.30) FAB-MS: *m*/*z* = 292.1 [M + H]$^+$. FAB-HRMS: found: 292.1175, calcd. 292.1185 [M + H]$^+$.

Allyl 2-Acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-*xylo*-hexopyranoside-4-ulose (21): Compound **19**[25] (260 mg, 0.589 mmol) was dissolved in dichloromethane (11 mL) and Dess–Martin periodinane (292 mg, 0.689 mmol) in dichloromethane (12 mL) added. The reaction mixture was treated for 20 h according to general procedure **1b** and the residue purified by column chromatography [petroleum ether/ethyl acetate (1:2)]. Product **21** (191 mg, 74%) could be isolated as an amorphous solid. $[\alpha]_D^{25}$ = +98.9 (*c* = 0.09, $CHCl_3$), R_F

= 0.42 (petroleum ether ether/ethyl acetate, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 10 H, CH-Bn), 5.89 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.2, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.2, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.4 Hz, 1 H, CH-All), 5.40 (d, $J_{NH,2}$ = 9.0 Hz, 1 H, NH), 5.30–5.20 (m, 2 H, 2× =CH_2-All), 5.10 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.94 (d, 1 H, CH_2-Bn), 4.65–4.55 (m, 3 H, 2-H, 2× CH_2-Bn), 4.47 (d, $^2J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.0 Hz, 1 H, CH_2-Bn), 4.53 (dd, $J_{5,6a}$ = 3.6, $J_{5,6b}$ = 6.3 Hz, 1 H, 5-H), 4.25 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 4.13–4.05 (m, 2 H, 3-H, -CH_2-All), 3.96 (dd, $^2J_{6a,6b}$ = 10.8 Hz, 1 H, 6a-H), 3.73 (dd, 1 H, 6b-H), 1.95 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.5 (C-4), 133.1 (=CH-All), 128.4–127.7 (CH-Bn), 118.3 (=CH_2-All), 96.4 (C-1), 79.3 (C-3), 73.8 (C-5), 73.7 (CH_2-Bn), 72.5 (CH_2-Bn), 69.0 (-CH_2-All), 67.7 (C-6), 54.1 (C-2), 23.3 (CH_3-NHAc) ppm. $C_{25}H_{29}NO_6$ (439.5) MALDI-TOF-MS: *m*/*z* = 462.5 [M + Na]$^+$, 478.5 [M + K]$^+$.

2-Acetamido-1,5-anhydro-3,6-di-*O*-benzyl-2-desoxy-D-*xylo*-hex-4-ulose (22): Compound **20**[26] (480 mg, 1.25 mmol) was dissolved in dry dichloromethane (10 mL) and Dess–Martin periodinane (634 mg, 1.49 mmol) in dichloromethane (12 mL) added. The reaction mixture was treated for 3 h according to general procedure **1b** and the residue purified by column chromatography (petroleum ether/ethyl acetate, 1:50). Product **22** (193 mg, 40%) could be isolated as an amorphous solid. $[\alpha]_D^{20}$ = +23.1 (*c* = 0.065, $CHCl_3$), R_F = 0.40 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.31 (m, 10 H, CH-Bn), 5.39 (d, $J_{NH,2}$ = 5.6 Hz, 1 H, NH), 4.88 (d, 1 H, CH_2-Bn), 4.65–4.53 (m, 2 H, 2× CH_2-Bn), 4.47 (d, $^2J_{CH2Bn,CH2Bn}$ = 11.8 Hz, 1 H, CH_2-Bn), 4.32 (dd, $J_{1a,2}$ = 4.5, $^2J_{1a,1b}$ = 11.7 Hz, 1 H, 1a-H), 4.15–4.05 (m, 3 H, 2-H, 3-H, 5-H), 3.88 (dd, $J_{5,6a}$ = 3.5, $^2J_{6a,6b}$ = 10.9 Hz, 1 H, 6aH), 3.77–3.68 (m, 2 H, 1bH, 6b-H), 1.89 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 128.8, 127.9 (*C*H-Bn), 81.1 (C-5), 80.2 (C-3), 72.9, 72.5 (CH_2-Bn), 68.2 (C-6), 67.4 (C-1), 54.0 (C-2), 23.1 (CH_3-NHAc) ppm. $C_{22}H_{25}NO_5$ (383.44) MALDI-TOF-MS: *m*/*z* = 405.5 [M + Na]$^+$, 421.5 [M + K]$^+$.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl Azide (25): 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[24] (2.0 g, 5.5 mmol) was dissolved in DMF (14 mL) and sodium azide (0.94 g, 0.085 mol) was added. The reaction mixture was stirred for 2 h at 50 °C. The mixture was diluted with chloroform and washed with water several times. The organic layer was dried, concentrated and the residue was purified by column chromatography (ethyl acetate). The product **25** (1.6 g, 79%) could be obtained as a colorless solid; m.p. 161 °C (m.p.[29] 166–167 °C). $[\alpha]_D^{20}$ = –18.9 (*c* = 0.55, $CHCl_3$), R_F = 0.32 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (d, $J_{NH,2}$ = 8.9 Hz, 1 H, NH), 5.46 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 5.32 (dd, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 4.97 (d, $J_{1,2}$ = 9.2 Hz, 1 H, 1-H), 4.49 (dd, $J_{5,6a}$ = 4.8, $^2J_{6a,6b}$ = 12.5 Hz, 1 H, 6a-H), 4.39 (dd, $J_{5,6b}$ = 2.3 Hz, 1 H, 6b-H), 4.13 (ddd, 1 H, 2-H), 4.00 (ddd, 1 H, 5-H), 2.32 (s, 3 H, CH_3-Ac), 2.26 (2× s, 6 H, 2× CH_3-Ac), 2.20 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3 (CO-Ac), 88.4 (C-1), 74.1 (C-5), 72.1 (C-3), 68.0 (C-4), 61.8 (C-6), 54.3 (C-2), 23.2 (CH_3-NHAc), 20.7, 20.6, 20.5 (3× CH_3-OAc) ppm. $C_{14}H_{20}N_4O_8$ (372.33) MALDI-TOF-MS: *m*/*z* = 394.9 [M + Na]$^+$, 410.9 [M + K]$^+$. IR: $\tilde{\nu}$ = 2103 cm^{-1} (N_3 valency).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylamine (26): Azide **25** (400 mg, 1.07 mmol) was dissolved in ethyl acetate (20 mL) under argon. To the solution was added Pd/C (2 spatula tips) and stirred for 72 h at room temperature under hydrogen. The catalyst was filtered through sodium sulfate and the filtrate concentrated. The product **26** (347.5 mg, 94%) was obtained as a colorless solid; m.p. 148.3 °C (dec.). $[\alpha]_D^{25}$ = –1.29 (*c* = 1.085, MeOH), R_F = 0.57 (ethyl acetate/propanol/water, 1:6:3). ^{1}H NMR (400 MHz, MeOD): δ = 5.16 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 4.96 (dd, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 4.31–4.16 (m, 2 H, 1-H, 6a-H), 4.09 (dd, $J_{5,6b}$ = 2.3, $^2J_{6a,6b}$ = 12.2 Hz, 1 H, 6b-H), 3.88–3.68 (m, 2 H, 2-H, 5-H), 2.04 (s, 3 H, CH_3-Ac), 2.00 (s, 3 H, CH_3-Ac), 1.98 (s, 3 H, CH_3-Ac), 1.92 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 172.4 (CO-Ac), 86.1 (C-1), 75.0 (C-3), 73.9 (C-5), 70.6 (C-4), 63.8 (C-6), 56.2 (C-2), 22.8 (CH_3-NHAc), 20.6 (3× CH_3-Ac) ppm. $C_{14}H_{22}N_2O_8$ (346.33) MALDI-TOF-MS: *m*/*z* = 347.0 [M + H]$^+$, 369.0 [M + Na]$^+$, 384.9 [M + K]$^+$.

Allyl 2-Azido-2-deoxy-α-D-glucopyranoside (28): AllGlcNAc **5**[20] (500 mg, 1.92 mmol) was suspended in 2 N sodium hydroxide (18 mL) and stirred overnight at 100 °C. After cooling to room temperature the reaction mixture was neutralized with 2 N hydrochloric acid, filtered through silica, and eluted with ethyl acetate/MeOH/H_2O (7:2:1) The filtrate was concentrated and the remaining water removed by freeze drying. The obtained amine was dissolved in methanol (20 mL) and DMAP (464 mg, 3.80 mmol) as well as freshly prepared triflyl azide (4.22 mmol) in dichloromethane (0.4 M) added. The reaction was stirred for 16 h at room temperature then concentrated, and the residue was purified by column chromatography (DCM/MeOH, 8:1). Product **28** (0.196 g, 42%) could be isolated as a yellow oil. $[\alpha]_D^{25}$ = +136.3 (*c* = 0.405, MeOH), R_F = 0.53 (DCM/MeOH, 5:1). ^{1}H NMR (400 MHz, MeOD): δ = 5.96 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.5, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.7, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.0 Hz, 1 H, CH-All), 5.36 (dd, 1 H, =CH_2-All), 5.16 (dd, 1 H, =CH_2-All), 4.93 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.24 (dd, $^2J_{CH2\text{-}All,CH2\text{-}All}$ = 13.2 Hz, 1 H, -CH_2-All), 4.04 (dd, 1 H, -CH_2-All), 3.81–3.79 (m, 2 H, 3-H, 6a-H), 3.68 (dd, $J_{5,6b}$ = 5.5, $^2J_{6a,6b}$ = 11.9 Hz, 1 H, 6b-H), 3.59 (ddd, $J_{4,5}$ = 9.8, $J_{5,6a}$ = 2.1 Hz, 1 H, 5-H), 3.35 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 4-H), 3.10 (dd, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 135.2 (=CH-All), 117.4 (=CH_2-All), 98.6 (C-1), 74.0 (C-5), 72.6 (C-3), 72.2 (C-4), 69.3 (OCH_2-All), 64.6 (C-2), 62.5 (C-6) ppm. IR: $\tilde{\nu}$ = -N_3-valency (2105) cm^{-1}. $C_9H_{15}N_3O_5$ (245.23) FAB-MS: *m*/*z* = 246.1 [M + H]$^+$. FAB-HRMS: found: 246.1081, calcd. 246.1090 [M + H]$^+$.

Allyl 2-Acetamido-6-chloro-2,6-dideoxy-α-D-glucopyranoside (29): AllGlcNAc **5**[20] (1.0 g, 3.8 mmol) was dissolved in pyridine (30 mL) and triphenylphosphane (2.26 g, 8.55 mmol) was added. At 0 °C carbon tetrachloride (3.7 mL, 38 mmol, 5.8 g) was slowly and dropwise added and then stirred for 20 min at 50 °C. For termination of the reaction methanol (5 mL) was added and stirring continued for 20 min at 50 °C. The mixture was concentrated and the residue, after co-distillation with toluene, purified by column chromatography (ethyl acetate/MeOH, 20:1→15:1→10:1). Product **29** (818 mg, 77%) could be obtained as a yellow solid; m.p. 154.5 °C, $[\alpha]_D^{25}$ = +146 (*c* = 0.815, MeOH), R_F = 0.45 (DCM/MeOH, 5:1) ^{1}H NMR (400 MHz, MeOD): δ = 5.94 (dddd, $J_{=CH\text{-}All,=CH2t}$ = 17.2, $J_{=CH\text{-}All,=CH2c}$ = 10.5, $J_{=CH\text{-}All,OCH2\text{-}All}$ = 5.1, $J_{=CH\text{-}All,OCH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 5.32 (dd, 1 H, =CH_2-All), 5.19 (dd, 1 H, =CH_2-All), 4.83 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.21 (dd, $^2J_{OCH2\text{-}All,OCH2\text{-}All}$ = 13.1 Hz, 1 H, -CH_2-All), 4.02 (dd, 1 H, -CH_2-All), 3.92 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.87 (dd, $J_{5,6a}$ = 1.6, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6a-H), 3.80–3.63 (m, 3 H, 3-H, 5-H, 6b-H), 3.36 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 1.98 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 174.1 (CO-NHAc), 135.7 (=CH-All), 118.1 (=CH_2-All), 98.1 (C-1), 73.7 (C-4), 73.6 (C-5), 73.0 (C-3), 69.6 (OCH_2-All), 55.7 (C-2), 46.1 (C-6), 22.9 (CH_3-NHAc) ppm. $C_{11}H_{18}ClNO_5$ (279.72) FAB-MS: *m*/*z* = 280.1 [M + H]$^+$. FAB-HRMS: found: 280.0950, calcd. 280.0952 [M + H]$^+$.

Allyl 2-Acetamido-6-azido-2,6-dideoxy-α-D-glucopyranoside (30): Compound **29** (807 mg, 2.89 mmol) was dissolved in DMF (12 mL), sodium azide (958 mg, 14.7 mmol) was added and the reaction mixture was stirred for 24 h at 120 °C. After cooling to room temperature the solid was filtered and washed with acetonitrile. The filtrate was concentrated and the residue purified by column chromatography (ethyl acetate/MeOH, 15:1). Product **30** (498 mg, 60%) could be obtained as a colorless solid; m.p. 117.4 °C. $[\alpha]_D^{25}$ = +97.9 (c = 0.19, MeOH), R_F = 0.33 (ethyl acetate/MeOH, 10:1). ^{1}H NMR (400 MHz, MeOD): δ = 5.59 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.2, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,CH2\text{-}All}$ = 5.2, $J_{CH\text{-}All,CH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 5.33 (dd, 1 H, =CH_2-All), 5.20 (dd, 1 H, =CH_2-All) 4.85 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.21 (dd, $^2J_{OCH2\text{-}All,OCH2\text{-}All}$ = 13.1 Hz, 1 H, -CH_2-All), 4.03 (dd, 1 H, -CH_2-All), 3.96 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.75 (ddd, $J_{4,5}$ = 9.8, $J_{5,6a}$ = 2.3, $J_{5,6b}$ = 6.6 Hz, 1 H, 5-H), 3.66 (dd, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.51 (dd, $^2J_{6a,6b}$ = 13.2 Hz, 1 H, 6a-H), 3.41 (dd, 1 H, 6b-H), 3.34 (dd, 1 H, 4-H), 1.99 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 173.7 (CO-NHAc), 135.3 (=CH-All), 117.8 (=CH_2-All), 97.7 (C-1), 73.2 (C-4), 73.1 (C-5), 72.6 (C-3), 69.5 (OCH_2-All), 55.3 (C-2), 52.8 (C-6) 22.5 (CH_3-NHAc) ppm. IR: $\tilde{\nu}$ = -N_3-valency (2096) cm^{-1}. $C_{11}H_{18}N_4O_5$ (286.28) FAB-MS: m/z = 287.1 [M + H]$^+$. FAB-HRMS: found: 287.1355, calcd. 287.1356 [M + H]$^+$.

Allyl 2-Acetamido-2-amino-6-azido-2,6-dideoxy-α-D-glucopyranoside (31): Compound **30** (731 mg, 2.55 mmol) and barium hydroxide octahydrate (10.5 g, 33.3 mmol) in water (50 mL) were stirred for 3 h at 120 °C. After cooling to room temperature the reaction mixture was stirred for 24 h. The solid was filtered and the filtrate was extracted continuously until no product was detected in the aqueous phase. The organic phase was dried and the solvents evaporated in vacuo. Product **31** (515 mg, 83%) could be obtained as a yellow oil. $[\alpha]_D^{25}$ = +127 (c = 0.165, MeOH), R_F = 0.30 (ethyl acetate/MeOH/water, 7:3:1). ^{1}H NMR (400 MHz, MeOD): δ = 5.98 (dddd, $J_{=CH\text{-}All,=CH2t}$ = 17.2, $J_{=CH\text{-}All,=CH2c}$ = 10.4, $J_{=CH\text{-}All,OCH2\text{-}All}$ = 5.3, $J_{=CH\text{-}All,OCH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 5.36 (dd, 1 H, =CH_2-All), 5.20 (dd, 1 H, =CH_2-All), 4.86 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.25 (dd, $^2J_{OCH2\text{-}All,OCH2\text{-}All}$ = 12.9 Hz, 1 H, -CH_2-All), 4.04 (dd, 1 H, -CH_2-All), 3.73 (ddd, $J_{4,5}$ = 9.8, $J_{5,6a}$ = 2.3, $J_{5,6b}$ = 5.5 Hz, 1 H, 5-H), 3.52–3.37 (m, 3 H, 3-H, 6a-H, 6b-H), 3.24 (dd, $J_{3,4}$ = 8.9 Hz, 1 H, 4-H), 2.63 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 134.2 (=CH-All), 115.9 (=CH_2-All), 97.8 (C-1), 74.6 (C-3), 71.8 (C-5), 71.2 (C-4), 68.0 (OCH_2-All), 55.7 (C-2), 51.4 (C-6) ppm. IR: $\tilde{\nu}$ = -N_3-valency (2099) cm^{-1}. $C_9H_{16}N_4O_4$ (244.25) FAB-MS: m/z = 245.1 [M + H]$^+$. FAB-HRMS: found: 245.1252, calcd. 245.1250 [M + H]$^+$.

Propyl 2,6-Diamino-2,6-dideoxy-α-D-glucopyranoside (32): Azide **31** (107.8 mg, 0.4414 mmol) was dissolved in methanol (6 mL) and Pd/$CaCO_3$ (one spatula point) was added. The reaction mixture was stirred under hydrogen for 72 h at room temperature. After reaction has terminated the catalyst was filtered off over Celite and the filtrate was concentrated. The residue was purified by gel permeation chromatography on Sephadex LH20 (MeOH/water, 1:1). Product **32** (19.6 mg, 20%) could be isolated as an amorphous solid. $[\alpha]_D^{25}$ = +50 (c = 0.08, water), R_F = 0.53 (DCM/MeOH, 5:1). ^{1}H NMR (500 MHz, D_2O): δ = 5.18 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.99–3.86 (m, 2 H, 4-H, 5-H), 3.72 (ddd, $^2J_{OCH2\text{-}Pr,OCH2\text{-}Pr}$ = 12.2 Hz, 1 H, OCH_2-Pr), 3.55–3.34 (m, 4 H, OCH_2-Pr, 2-H, 3-H, 6a-H), 3.19 (dd, $J_{5,6b}$ = 8.9, $^2J_{6a,6b}$ = 13.4 Hz, 1 H, 6b-H), 1.71–1.58 (m, $J_{OCH2\text{-}Pr,CH2\text{-}Pr}$ = 2.8, $J_{OCH2\text{-}Pr,CH2\text{-}Pr}$ = 6.7 Hz, 2 H, CH_2-Pr), 0.94 (t, 3 H, CH_3-Pr) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 94.9 (C-1), 71.2 (C-3), 70.2 (OCH_2-Pr), 69.2, 68.7 (C-4, C-5), 53.6 (C-2), 49.4 (C-6), 21.8 (CH_2-Pr) ppm. $C_9H_{20}N_2O_4$ (220.27) ESI-MS: m/z = 243 [M + Na]$^+$.

2-Acetamido-1,5-anhydro-4-azido-2,4-dideoxy-3,6-di-*O*-pivaloyl-D-galactitol (34): Compound **33**[22] (1.50 g, 4.28 mmol) was dissolved under argon in dry dichloromethane (35 mL) and dry pyridine (2.0 mL). Trifluoromethane sulfuric acid anhydride (0.85 mL, 5.1 mmol) was slowly added at –35 °C and the reaction was stirred for 4 h at 0 °C. The mixture was diluted with dichloromethane and washed with 2.5 M hydrochloric acid. The organic layer was neutralized with saturated sodium hydrogen carbonate solution, washed with water, dried and concentrated.

The residue was dissolved in DMF (13 mL) sodium azide (1.3 g, 20 mmol) added and stirred for 3.5 h at 80 °C. The reaction mixture was diluted with chloroform and washed with water. The organic layer was dried, concentrated and the residue purified by column chromatography (petroleum ether ether/ethyl acetate, 1:2). Product **34** (1.03 g, 60%) could be obtained as a colorless solid; m.p. 119.8 °C. $[\alpha]_D^{20}$ = –52.6 (c = 1.01, $CHCl_3$), R_F = 0.33 (petroleum ether ether/ethyl acetate, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.49 (d, $J_{2,NH}$ = 8.3 Hz, 1 H, NH), 5.06 (dd, $J_{2,3}$ = 10.8, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 4.48 (dddd, $J_{1a,2}$ = 5.3, $J_{1b,2}$ = 11.0 Hz, 1 H, 2-H), 4.24 (dd, $J_{5,6a}$ = 6.3, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6a-H), 4.19–4.07 (m, 2 H, 1a-H, 6b-H), 3.89 (dd, $J_{4,5}$ = 1.5 Hz, 1 H, 4-H), 3.67 (ddd, $J_{5,6b}$ = 6.5 Hz, 1 H, 5-H), 3.10 (dd, $^2J_{1a,1b}$ = 11.1 Hz, 1 H, 1b-H), 1.91 (s, 3 H, CH_3-NHAc), 1.25 (s, 9 H, CH_3-Piv), 1.21 (s, 9 H, CH_3-Piv) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.4, 178.0 (2× *C*O-Piv), 169.9 (*C*O-NHAc), 75.2 (C-5), 73.4 (C-3), 68.8 (C-1), 62.9 (C-6), 61.1 (C-4), 47.0 (C-2), 39.3 [*C*(CH_3)$_3$], 27.1, 26.9 [C(*C*H_3)$_3$], 23.1 (CH_3-NHAc) ppm. $C_{18}H_{30}N_4O_6$ (398.45) MALDI-TOF-MS: m/z = 399.1 [M + H]$^+$, 421.1 [M + Na]$^+$, 437.0 [M + K]$^+$. IR: $\tilde{\nu}$ = 2104 cm^{-1} (N_3 valency).

2,4-Diamino-1,5-anhydro-2,4-dideoxy-D-galactitol (35): Compound **34** (771 mg, 1.94 mmol) and barium hydroxide octahydrate (5.24 g, 16.6 mmol) in water were stirred overnight at 110 °C. After cooling to room temperature, the precipitate was filtered and the water was removed by freeze drying. The residue was diluted with a small amount of water and the mixture treated with dry ice to remove the barium salts. The solvent was again removed by freeze drying. The residue was diluted in methanol (4 mL) and Pd/C (one spatula tip) added. The mixture was stirred under hydrogen for 72 h at room. Then the catalyst was filtered through sodium sulfate and the filtrate was concentrated. The residue was purified by gel permeation chromatography on Sephadex LH20 (MeOH/water, 1:1). Product **35** (253 mg, 80%) could be obtained as a colorless solid; m.p. 220 °C (dec.). $[\alpha]_D^{20}$ = +16 (c = 0.05, water), R_F = 0.34 (BuOH/AcOH/water, 5:2:2). ^{1}H NMR (400 MHz, D_2O): δ = 3.94–3.82 (m, 2 H, 1a-H, 3-H), 3.76–3.63 (m, 3 H, 5-H, 6a-H, 6b-H), 3.59–3.47 (m, 2 H, 1b-H, 4-H), 3.05 (ddd, $J_{1a,2}$ = 5.3, $J_{1b,2}$ = 10.8, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 78.1 (C-5), 68.4 (C-3), 61.6 (C-6), 61.3 (C-1), 52.6 (C-2), 46.1 (C-4) ppm. $C_6H_{14}N_2O_3$ (162.19) FAB-MS: m/z = 201.0 [M + K]$^+$.

***N*-(Benzyl 2,6-dideoxy-2-phthalimido-β-D-glucopyranoside-6-yl)-(1,5-anhydro-2-deoxy-D-glucitol-2-yl)amine (37):** Aldehyde **6** (90.7 mg, 0.229 mmol) in methanol (2 mL) and amine **36**[17] (114 mg, 0.569 mmol) in methanol (1 mL) were treated according to general procedure **2**. After purification by gel permeation chromatography on Sephadex LH20 (methanol/water, 1:1) product **37** (45 mg, 36%) could be obtained as a colorless solid; m.p. 182.1 °C. $[\alpha]_D^{25}$ = –21.4 (c = 0.575, MeOH), R_F = 0.36 (ethyl acetate/MeOH/water, 7:3:1). ^{1}H NMR (400 MHz, [D_6]acetone): δ = 7.91–7.73 (m, 4 H, CH-Phth), 7.14–7.02 (m, 5 H, CH-Bn), 5.19 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H), 4.79 (d, $^2J_{CH2\text{-}Bn,CH2\text{-}Bn}$ = 12.4 Hz, 1 H, CH_2-Bn), 4.57 (d, 1 H, CH_2-Bn), 4.27 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 4.07–3.99 (m, 2 H, 1a′H, 2-H), 3.80 (dd, $J_{5',6a'}$ = 2.8,

$^2J_{6a',6b'}$ = 11.7 Hz, 1 H, 6a′H), 3.66–3.58 (m, 2 H, 5-H, 6b′-H), 3.41 (dd, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.34–3.28 (m, 2 H, 3′-H, 4′-H), 3.17 (ddd, $J_{4',5'}$ = 8.8, $J_{5',6b'}$ = 5.6 Hz, 1 H, 5′-H), 3.14–3.05 (m, 2 H, 1b′-H, 6a-H), 2.90 (dd, $J_{5,6b}$ = 7.1, $^2J_{6a,6b}$ = 13.2 Hz, 1 H, 6b-H), 2.65 (ddd, $J_{1a',2'}$ = 4.8, $J_{1b',2'}$ = 9.4, $J_{2',3'}$ = 10.4 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]acetone): δ = 135.1 (CH-Phth), 128.9, 128.4, 128.2 (CH-Bn), 122.8 (CH-Phth), 98.5 (C-1), 82.2 (C-5′), 78.0 (C-3′), 74.9 (C-5), 74.2 (C-4), 72.4 (C-4′), 72.1 (C-3), 71.2 (CH_2-Bn), 70.0 (C-1′), 63.2 (C-6′), 59.6 (C-2′), 58.3 (C-2), 48.7 (C-6) ppm. $C_{20}H_{35}N_5O_9$ (544.55) MALDI-TOF-MS: *m*/*z* = 544.9 [M + H]$^+$, 566.9 [M + Na]$^+$, 584.9 [M + K]$^+$.

***N*-(Allyl 2,6-dideoxy-2-phthalimido-β-D-glucopyranoside-6-yl)-(1,5-anhydro-2-deoxy-D-glucitol-2-yl)amine (38):** Aldehyde **7** (94 mg, 0.27 mmol) in methanol (2 mL) and amine **36**[17] (134.6 mg, 0.676 mmol) in methanol (1 mL) were treated according to general procedure **2**. After purification by gel permeation chromatography on Sephadex LH20 (methanol/water, 1:1) product **38** (95 mg, 71%) could be isolated as a colorless solid; m.p. 236 °C. $[\alpha]_D^{25}$ = +11.1 (*c* = 0.28, MeOH), R_F = 0.40 (ethyl acetate/MeOH/water, 7:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 7.97–7.73 (m, 4 H, CH-Phth), 5.65 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.1, $J_{CH\text{-}All,=CH2c}$ = 10.3, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.2, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.9 Hz, 1 H, CH-All), 5.26 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H), 5.09 (dd, 1 H, =CH_2-All), 5.01 (dd, 1 H, =CH_2-All), 4.33–4.18 (m, 2 H, -CH_2-All, 3-H), 4.16–4.01 (m, 2 H, -CH_2-All, 1a′-H), 3.96 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.82 (dd, $^2J_{6a',6b'}$ = 11.6 Hz, 1 H, 6a′-H), 3.72–3.61 (m, 2 H, 5-H, 6b′-H), 3.44–3.20 (m, 5 H, 4-H, 1b′-H, 3′-H, 4′-H, 5′-H), 3.12 (dd, $J_{5,6a}$ = 2.7, $^2J_{6a,6b}$ = 12.1 Hz, 1 H, 6a-H), 2.93–2.72 (m, 2 H, 2′-H, 6b-H) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 135.2 (CH-Phth), 133.3 (=CH-All), 123.8 (CH-Phth), 118.7 (=CH_2-All), 97.7 (C-1), 80.6 (C-5′), 74.0 (C-5), 72.4 (C-4, C-4′), 70.9 (CH_2-All), 70.7 (C-3), 70.3 (C-3′), 66.8 (C-1′), 61.2 (C-6′), 57.6 (C-2′), 56.9 (C-2), 47.4 (C-6) ppm. $C_{20}H_{35}N_5O_9$ (494.49) MALDI-TOF-MS: *m*/*z* = 516.5 [M + Na]$^+$.

***N*-(Allyl 2-acetamido-2,6-dideoxy-α-D-mannopyranoside-6-yl)-(1,5-anhydro-2-deoxy-D-glucitol-2-yl)amine (39):** Aldehyde **9** (131 mg, 0.506 mmol) was dissolved in methanol (2.5 mL) and amine **36**[17] in methanol (1.5 mL) was added. The reaction mixture was treated according to general procedure **2** and the residue was purified by gel permeation chromatography (methanol/water, 1:1). Product **39** (103 mg, 50%) could be isolated as a colorless solid; m.p. 98.5 °C. $[\alpha]_D^{24}$ = +50.1 (*c* = 0.715, H_2O), R_F = 0.27 (ethyl acetate/MeOH/H_2O, 7:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.89 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.1 Hz, 1 H, CH-All), 5.29 (dd, 1 H, =CH_2-All), 5.16 (dd, 1 H, =CH_2-All), 4.79 (d, $J_{1,2}$ = 1.3 Hz, 1 H, 1-H), 4.28 (dd, $J_{2,3}$ = 4.7 Hz, 1 H, 2-H), 4.22–4.12 (m, 2 H, -CH_2-All, 1a′-H), 4.02 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 13.0 Hz, 1 H, -CH_2-All), 3.94 (dd, $J_{3,4}$ = 9.8 Hz, 1 H, 3-H), 3.86–3.76 (m, 2 H, 5-H, 6a′-H), 3.62 (dd, $J_{5',6b'}$ = 5.5, $^2J_{6a',6b'}$ = 10.4 Hz, 1 H, 6b′-H), 3.55 (dd, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 8.2 Hz, 1 H, 3′-H), 3.47–3.27 (m, 5 H, 1b′-H, 4′-H, 5′-H, 4-H, 6a-H), 3.15–2.98 (m, 2 H, 2′-H, 6b-H), 1.96 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 174.8 (CO-NHAc), 133.3 (=CH-All), 118.4 (=CH_2-All), 98.2 (C-1), 80.5 (C-5′), 74.0 (C-3′), 70.2 (C-4′), 68.8 (C-3, C-4, C-5), 68.6 (-CH_2-All), 65.6 (C-1′), 60.8 (C-6′), 57.7 (C-2′), 52.6 (C-2), 46.8 (C-6), 22.0 (CH_3-NHAc) ppm. $C_{17}H_{30}N_2O_9$ (406.43) MALDI-TOF-MS: *m*/*z* = 406.8 [M + H]$^+$, 428.8 [M + Na]$^+$, 444.8 [M + K]$^+$.

***N*-(Allyl 2-acetamido-2,6-dideoxy-α-D-glucopyranoside-6-yl)-(allyl 6-azido-2,6-dideoxy-α-D-glucopyranose-2-yl)amine (40):** Aldehyde **10** (94 mg, 0.36 mmol) in methanol (2 mL) and amine **31** (220 mg, 0.901 mmol) in methanol (1 mL) were treated according to general procedure **2**. After purification by gel permeation chromatography (methanol/water, 1:1) product **40** (25 mg, 14%) could be isolated as a colorless solid; m.p. 133 °C. $[\alpha]_D^{25}$ = +124 (*c* = 0.11, MeOH), R_F = 0.70 (*i*PrOH/NH_3/H_2O, 5:1:2). ^{1}H NMR (400 MHz, D_2O): δ = 6.13–5.84 (m, 2 H, 2× CH-All), 5.48–5.23 (m, 4 H, 4× =CH_2-All), 5.11 (d, $J_{1',2'}$ = 3.7 Hz, 1 H, 1′-H′), 4.93 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 4.32–4.21 (m, 2 H, 2× -CH_2-All), 4.16–4.04 (m, 2 H, 2× -CH_2-All), 4.00–3.91 (m, 2 H, 2-H, 3′H), 3.81–3.72 (m, 3 H, 3-H, 5-H, 5′-H), 3.43–3.33 (m, 3 H, 4-H, 4′-H, 6a′-H), 3.21–3.06 (m, 3 H, 6a-H, 2′-H, 6b′-H), 2.91 (dd, $J_{5,6b}$ = 4.5, $^2J_{6a,6b}$ = 12.7 Hz, 1 H, 6b-H), 2.05 (s, 3 H, CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 133.5 (=CH-All), 118.1 (=CH_2-All), 96.1 (C-1), 95.9 (C-1′), 72.2 (C-4 ppm. C-4′), 71.8 (C-3), 70.7 (C-5, C-5′), 68.1 (C-3′), 54.4 (C-2′), 53.6 (C-2), 49.0 (C-6′), 47.6 (C-6), 22.0 (CH_3-NHAc) ppm. IR: $\tilde{\nu}$ = -N_3-valency (2102) cm^{-1}. $C_{20}H_{35}N_5O_9$ (487.50) MALDI-TOF-MS: *m*/*z* = 483.9 [M + Na – N_2]$^+$.

***N*-(Allyl 2-acetamido-2,6-dideoxy-α-D-glucopyranoside-6-yl)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)amine (41):** Compound **10** (100 mg, 0.386 mmol) was suspended in THF (3 mL) and amine **24**[27] (380 mg, 1.73 mmol) in THF (5 mL) added. The pH was adjusted to 6 by adding 1 M acetic acid solution dropwise. Then a 0.3 M solution of sodium cyanoborohydride in THF (1.0 mL) was added. The reaction mixture was stirred overnight at room temperature, concentrated and the residue purified by gel permeation chromatography on Sephadex LH20 (methanol/water, 1:1). Product **40** (41.6 mg, 23%) could be obtained as a yellow solid; m.p. 100.5 °C. $[\alpha]_{546}^{20}$ = +26 (*c* = 0.41, H_2O), R_F = 0.73 (*i*PrOH/NH_3/ethyl acetate 5:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.75 (dddd, $J_{CHAll,\text{-}CH2\text{-}All}$ = 5.3 Hz, 1 H, CH-All), 5.15 (dd, 1 H, =CH_2-All), 5.06 (dd, 1 H, =CH_2-All), 4.95 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.35 (d, $J_{1',2'}$ = 9.4 Hz, 1 H, 1′H), 4.25 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH\text{-}All}$ = 13.2 Hz, 1 H, -CH_2-All), 4.07 (dd, 1 H, -CH_2-All), 3.99–3.36 (m, 12 H, 2-H, 2′H, 3-H, 3′-H, 4-H, 4′-H, 5-H, 5′-H, 6a-H, 6a′-H, 6b-H, 6b′-H), 2.05 (s, 6 H, 2× CH_3-NHAc) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 133.7 (=CH-All), 117.9 (=CH_2-All) 96.0 (C-1), 85.9 (C-1′), 76.7 (C-5), 74.9 (C-4), 72.4 (C-5′), 71.0 (C-3′), 70.4 (C-4′), 70.3 (C-3), 68.6 (-CH_2-All), 61.2 (C-6, C-6′), 55.2 (C-2′), 53.7 (C-2), 21.9 (CH_3-NHAc) ppm. $C_{19}H_{33}N_3O_9$ (463.5): MALDI-TOF-MS: *m*/*z* = 502.1 [M + K]$^+$.

Propyl 2-Acetamido-6-amino-2,6-dideoxy-α-D-glucopyranoside (43): Compound **30** (493.6 mg, 1.724 mmol) was dissolved in methanol (22 mL) and Pd/$CaCO_3$ (one spatula point) added. The reaction mixture was stirred under hydrogen for 20 h at room temperature. The catalyst was filtered through Celite and washed with methanol. The filtrate was concentrated and the residue purified by column chromatography [ethyl acetate/MeOH (1:1→100% MeOH)]. Product **43** (370 mg, 82%) could be obtained as a yellow solid; m.p. 128 °C. $[\alpha]_D^{24}$ = +114 (*c* = 0.17, MeOH), R_F = 0.05 (ethyl acetate/MeOH, 1:1). ^{1}H NMR (400 MHz, MeOD): δ = 4.79 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.87 (dd, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 3.71–3.63 (m, 2 H, 3-H, OCH_2-Pr), 3.55 (ddd, $J_{4,5}$ = 10.0, $J_{5,6a}$ = 3.0, $J_{5,6b}$ = 7.2 Hz, 1 H, 5-H), 3.40–3.33 (m, 1 H, OCH_2-Pr), 3.22 (dd, $J_{3,4}$ = 8.3 Hz, 1 H, 4-H), 2.99 (dd, $^2J_{6a,6b}$ = 13.3 Hz, 1 H, 6a-H), 2.75 (dd, 1 H, 6b-H), 1.98 (s, 3 H, CH_3-NHAc), 1.70–1.57 (m, $J_{CH2\text{-}Pr,CH3\text{-}Pr}$ = 7.4 Hz, 2 H, CH_2-Pr), 0.97 (t, 3 H, CH_3-Pr) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 173.7 (*C*O-NHAc), 98.5 (C-1), 74.1 (C-4), 73.4 (C-5), 72.7 (C-3), 70.7 (OCH_2-Pr), 55.6 (C-2), 43.9 (C-6), 23.7 (CH_2-Pr), 22.5 (CH_3-NHAc), 11.0 (CH_3-Pr) ppm. $C_{11}H_{20}N_2O_5$ (262.30) FAB-MS: *m*/*z* = 263.2 [M + H]$^+$. FAB-HRMS: found: 263.1619, calcd. 263.1607 [M + H]$^+$.

Bis-*N*-(allyl 2-acetamido-2,6-dideoxy-α-D-glucopyranoside-6-yl)-amine (44): Aldehyde **10** (102 mg, 0.394 mmol) in methanol (2 mL) and amine **42**[17] (250 mg, 0.954 mmol) in methanol (2 mL) were

treated according to general procedure **2**. The residue was purified by gel permeation chromatography on Sephadex LH20 (methanol/water, 1:1) and product **44** (115 mg, 58%) could be isolated as a yellow solid; m.p. 230 °C (dec.). $[\alpha]_D^{20}$ = +123.7 (*c* = 0.135, H_2O), R_F = 0.16 (ethyl acetate/MeOH/H_2O, 7:3:1). ^{1}H NMR (400 MHz, D_2O): δ = 5.97 (dddd, $J_{CH\text{-}All,=CH2t}$ = 17.3, $J_{CH\text{-}All,=CH2c}$ = 10.4, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 5.2, $J_{CH\text{-}All,\text{-}CH2\text{-}All}$ = 6.1 Hz, 2 H, 2× CH-All), 5.36 (dd, 2 H, 2× =CH_2-All), 5.28 (dd, 2 H, 2× =CH_2-All), 4.96 (d, $J_{1,2}$ = $J_{1',2'}$ = 3.6 Hz, 2 H, 1-H, 1′-H), 4.24 (dd, $^2J_{\text{-}CH2\text{-}All,\text{-}CH2\text{-}All}$ = 13.1 Hz, 2 H, 2× -CH_2-All), 4.07 (dd, 2 H, 2× -CH_2-All), 4.03–3.92 (m, 4 H, 2-H, 2′-H, 5-H, 5′-H), 3.78 (dd, $J_{2,3}$ = $J_{2',3'}$ = 10.6, $J_{3,4}$ = $J_{3',4'}$ = 8.9 Hz, 2 H, 3-H, 3′-H), 3.52–3.33 (m, 4 H, 4-H, 4′-H, 6a-H, 6a′-H), 3.19 (dd, $^2J_{6a,6b}$ = $^2J_{6a',6b'}$ = 12.1 Hz, 2 H, 6b-H, 6b′-H), 2.05 (s, 6 H, 2× CH_3-Ac) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 174.5 (2× *C*O-Ac), 133.6 (2× =CH-All), 118.0 (2× =CH_2-All), 96.2 (C-1, C-1′), 72.2 (C-4, C-4′), 70.8 (C-3, C-3′), 68.8 (2× -CH_2-All), 68.0 (C-5, C-5′), 53.6 (C-2, C-2′), 48.7 (C-6, C-6′), 21.9 (2× *C*H_3-Ac) ppm. $C_{22}H_{37}N_3O_{10}$ (503.54) MALDI-TOF-MS: *m*/*z* = 504.4 $[M + H]^+$, 525.4 $[M + Na]^+$, 541.3 $[M + K]^+$.

***N*-(Propyl 2-acetamido-2-deoxy-α-D-glucopyranose-6-yl)-(1,5-anhydro-2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucitol-3-yl)amine (45):** Ketone **18** (59.2 mg, 0.203 mmol) in methanol (3 mL) and amine **43** (137 mg, 0.526 mmol) in methanol (4 mL) were treated according to general procedure 2. After purification by column chromatography [DCM/MeOH (9:1)] product **45** (22 mg, 20%) could be isolated as a colorless solid; m.p. 225.8 °C. $[\alpha]_D^{25}$ = +34 (*c* = 0.36, MeOH), R_F = 0.23 (DCM/MeOH/, 5:1). ^{1}H NMR (400 MHz, D_2O): δ = 7.49–7.36 (m, 5 H, CH-Bn), 5.70 (s, 1 H, PhCHOO), 4.68 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.27 (dd, $J_{5',6a'}$ = 5.0, $^2J_{6a',6b'}$ = 10.5 Hz, 1 H, 6a′-H), 4.07 (ddd, $J_{1b',2'}$ = 10.6, $J_{2',3'}$ = 10.3 Hz, 1 H, 2′-H), 3.90 (dd, $J_{1a',2}$ = 5.2, $^2J_{1a',1b'}$ = 11.4 Hz, 1 H, 1a′-H), 3.81–3.69 (m, 3 H, 2-H, 4′-H, 6b′-H), 3.66–3.49 (m, 3 H, 3-H, 5-H, 5′-H), 3.46–3.33 (m, 2 H, OCH_2-Pr, 1b′-H), 3.32–3.12 (m, 3 H, OCH_2-Pr, 4-H, 6a-H), 3.06 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 2.94 (dd, $J_{5,6b}$ = 8.0, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6b-H), 1.96 (s, 3 H, CH_3-NHAc), 1.94 (s, 3 H, CH_3-NHAc′), 1.48–1.37 (m, 2 H, CH_2-Pr), 0.77 (t, 3 H, CH_3-Pr) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 128.5, 125.9 (CH-Bn), 101.2 (PhCHOO), 96.3 (C-1), 79.0 (C-4′), 72.4 (C-4), 71.2 (C-5′), 70.7 (C-3), 69.9 (OCH_2-Pr), 69.7 (C-5), 68.0 (C-1′), 67.7 (C-6′), 60.7 (C-3′), 53.6 (C-2), 49.2 (C-2′), 47.7 (C-6), 21.8, 21.6 (CH_3-NHAc), 21.3 (CH_2-Pr) ppm. $C_{26}H_{39}N_3O_9$ (537.60) FAB-MS: *m*/*z* = 538.3 $[M + H]^+$. FAB-HRMS: found: 538.2772, calcd. 538.2765 $[M + H]^+$.

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