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Glycosyl Aldehydes, New Scaffolds for the Synthesis of Neo-Glycoconjugates *via* Bio-orthogonal Oxime Bond Formation

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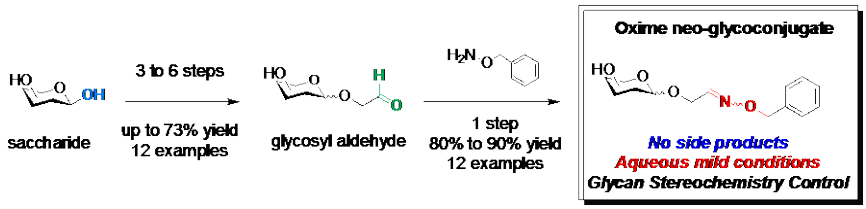

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Abstract. The straightforward preparation of glycosyl neo-conjugates by oxime (or hydrazone) bond formation represents a key bio-orthogonal tool in chemical biology. However, when this strategy is employed by reacting the reducing end of the glycan moiety, the configuration and the stereochemical information is lost due to partial (or total) opening of the glycan cyclic hemiacetal and the formation of the corresponding opened tautomers. We have completed the synthesis of a library of glycosyl aldehydes to be used as scaffold for the synthesis of neo-glycoconjugates via oxime bond formation. These glycosyl aldehydes constitute a simple and accessible alternative to avoid loosing of chiral information when conjugating, by oxime (or hydrazone) bonds, the aldehyde functionality present at the reducing end of natural carbohydrates.

Key words neoglycoconjugates, glycosyl aldehydes, oxime bond formation, carbohydrates, bioorthogonal chemistry, chemoselective ligation

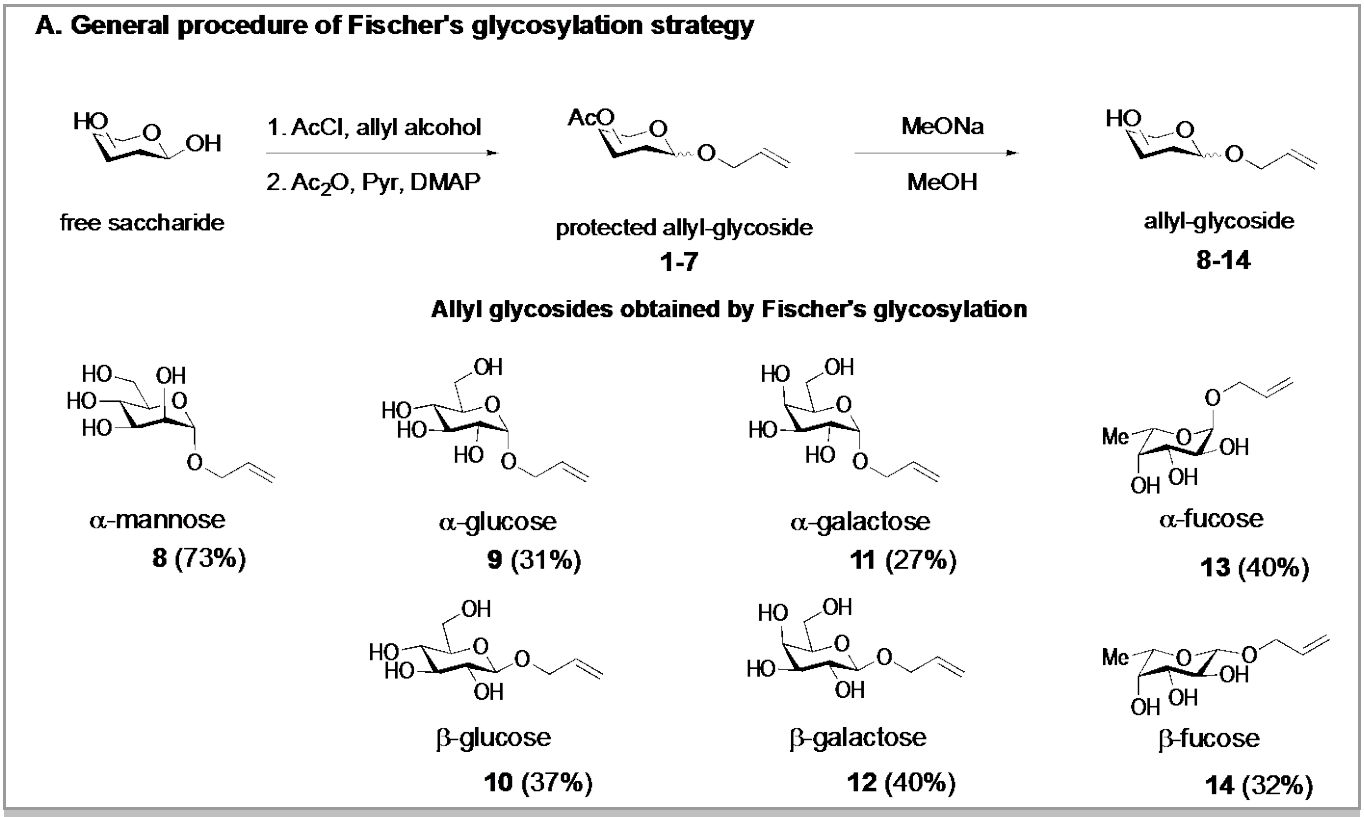
Introduction

Glycans are ubiquitous in nature and are not only an important source of metabolic energy. They are involved in numerous signaling and recognition events.[1] Carbohydrates cell-surface proteins interactions play important roles in many biological processes, such as viral and bacterial infections, cell recognition and adhesion, immune responses, fertilization, and cancer metastasis.[1] For this reason, the role of carbohydrates in the development of drugs, as vaccines, etc., is clearly growing.[2] Additionally, carbohydrates are becoming very important to the design and development of many diagnostic tools and for biosensors for clinical applications.[3] In the past decade, it increased the appreciation for the ubiquity of glycans and their ability to encode biochemical information. Furthermore, the understanding of how chemical information is encoded in glycan structures and how this information is read out by carbohydrate binding proteins (lectins) is a key challenge for glycobiology and beyond.[3a]

In nature, carbohydrates are present conjugated to other biomolecules forming glycopeptides and -proteins, glycolipids, glycosylated natural products, and more.[1,2] A wide variety of linkage chemistry connecting carbohydrates and aglycons (non-carbohydrate part of a conjugate) is observed. The most prevalent linkage types consist of O-alkyl glycosides (glycolipids and -proteins), glycosyl amides (N-glycoproteins), and heterocyclic glycosylamines (DNA/RNA). Neo-glycoconjugates, on the other hand, are non-natural glycoconjugates. These artificial glycoconjugates can, for example, incorporate a new linkage type or functionality onto the carbohydrate that enables the study of carbohydrate-protein interactions.[4] Designed glycoconjugates have become essential tools for glycobiology[5] such as glycoconjugates on arrays and surfaces, multivalent glycan scaffolds or in the tagging of glycans for bioimaging porpuses.[6]

Chemoselective reactions and, in particular, bioorthogonal reactions have been developed for the preparation of neo-glycoconjugates.[7-13] Bioorthogonal chemistry includes any chemical reaction that can occur inside of living systems without interfering with native biochemical processes.[7] A number of chemical ligation strategies have been developed that fulfill the requirements of bioorthogonality, including the 1,3-dipolar cycloaddition between azides and cyclooctynes,[8] between nitrones and cyclooctynes,[9] oxime/hydrazone formation from aldehydes and ketones,[10] the tetrazine ligation,[11] the isocyanide-based click reaction,[12] and most recently, the quadricyclane ligation.[13]

In this context, the hydrazone and the oxime bond formation have frequently been employed for the efficient chemical ligation of peptides[14] as well as for the conjugation of peptides with carbohydrates[15] and oligonucleotides.[16] A major advantage of these ligation techniques is that they do not require a coupling reagent or any chemical manipulations but mixing the two components such as the alcoxyamine and an aldehyde for the case of the oxime formation. In some of these examples, the aglycon was conjugated to the carbohydrate by oxime bond formation employing the reducing end of the carbohydrate. However, this strategy implies the ring opening and, consequently, the losing of natural tridimensional conformation of the carbohydrate.[17] In the case of monosaccharides and small oligosaccharides, in where the reducing carbohydrate residue is involved in the interaction with the receptor, the activity of the neo-glycoconjugates could be lost, and this type of chemoselective ligation is not suitable. Here we report the preparation of a glycosyl aldehydes library to synthesize neo-glycoconjugates via oxime bond formation. The process consists in the glycosylation with allyl alcohol followed by ozonolysis of the allyl group to afford the final



Scheme 1 . Flisher's glycosidation strategy for the synthesis of allyl-glycosides **8-14**.

aldehyde glycan. The reactivity of these glycosyl aldehydes was confirmed by reaction with *O*-benzylhydroxylamine. The corresponding oxime-bond formation was confirmed to proceed with quantitative conversions and excellent isolated yields in aqueous mild conditions.

Results

The target carbohydrate library was composed by the monosaccharides D-mannose (Man), D-glucose (Glc), D-galactose (Gal), L-fucose (Fuc), *N*-acetyl-D-galactosamine (GalNAc) and *N*-acetyl-D-glucosamine (GlcNAc), the disaccharides maltose and lactose and the branched mannose trisaccharide Manα1,3[Manα1,6]Man. We employed three different glycosylation strategies to prepare the key intermediate allyl-glycosides.

The Fischer methodology was employed to prepare allyl α-D-mannospyranoside (**8**) and the allyl α- and β-pyranoside of D-glucose (**9** and **10**), D-galactose (**11** and **12**) and L-fucose (**13** and **14**). The route started with glycosylation of the unprotected monosaccharides using acetyl chloride and allylalcohol at 60°C. This initial reaction produces a mixture of α and β isomers difficult to purify. Therefore, a transient protection of the free hydroxyl groups with Ac_2O, pyridine and a catalytic amount of 4-dimethylaminopyridine (DMAP) was performed to facilitate the purification of the anomers. After purification of both isomers by silica gel chromatography, the deprotection of the acetyl group using NaOMe in MeOH gave the allyl glycoside **8-14** in moderate to good isolated yields (27-73%, Scheme **1**). Fischer glycosylation reaction is an equilibrium process and lead to a mixture of ring size isomers and anomeric isomers, a clear limitation of the method if only one of the isomers is required. However, the application of this protocol allowed the access to reasonable amounts of both (α and β) allyl-glycopyranosides in a simple synthetic step.

The Fischer glycosylation of GlcNAc and GalNAc is not applicable due to the oxazoline trapping of the intermediates that inhibits the allyl glycosylation reactions. In addition, the application of the Koenigs-Knorr glycosylation with activated glycosyl donors, for this particular targets, could also lead to the formation of the collateral oxazoline product.[18] Therefore, due to the propensity of GlcNAc and GalNAc glycosyl donors to form this oxazoline, we decided to synthesize the allyl-glycosides of GlcNAc (**21**) and GalNAc (**22**) *via* the corresponding oxazoline donor and using TfOH as reaction promoter as shown in the Scheme **2**.

Starting from the GlcNAc (**15**) and GalNAc (**16**) the oxazoline was directly formed, following the procedure described by Hackman *et al.*,[19] using TMSOTf at 60°C in 1,2-DCE as solvent, the oxazolines **17** and **18** were obtained in quantitative yield. Subsequently, **17** and **18** were glycosylated using allyl alcohol as acceptor and TfOH as promoter in a sealed reaction vessel in DCM at 60°C. After SiO_2 chromatography purification, the peracetylated β-allyl glycosides of GlcNAc **19** and GalNAc **20** were obtained with excellent yields of 89% and 85%, respectively. Finally, deprotection of the acetyl group using NaOMe in MeOH gave the allyl glycosides **21** and **22** in quantitative yields. This stereoselective strategy lead only to the β isomers of GlcNAc and GalNAc as the attack of the allyl alcohol could only proceed from the β-face of the monosaccharides due to the blocking of the α face by the oxazoline ring.

In the case of lactose and maltose disaccharides, any of the glycosylation methods previously described could be applied. However, the application of the Fischer methodology in the synthesis of a disaccharide might lead to potential alcoholysis of the interglycosidic linkage.[20] Thus, β lactose and maltose allyl glycosides **25** and **28** were synthesized by direct glycosylation of peracetylated donor **23** and **26** with allyl alcohol using a big excess of $BF_3{\cdot}OEt_2$ as promoter,[21] followed by deprotection of the acetyl group using NaOMe in MeOH (Scheme **2**). The β stereochemical outcome of the glycosylation is determined by the presence of the neighboring acetyl group at position C2 that provides anchimeric assistance for the formation of a 1,2-*trans* stereochemical arrangement.

The allyl derivative of the branched mannose trisaccharide Manα1,3[Manα1,6]Man (**34**) was synthesized from the allyl α-mannose (**8**) following a multistep sequence[22] (Scheme **3**). The strategy starts with the selective protection of the primary hydroxyl group on C6 using the bulk TBDMS-Cl and imidazole to give **29** with a good isolated yield after chromatography purification (78%).[23] Compound **29** was treated with trimethyl orthoacetate and a catalytic amount of camphorsulphonic acid (CSA) to form the acetyl orthoester with the hydroxyl groups at positions C2 and C3. This orthoester was impossible to isolate due to the partial hydrolysis of the orthoester functionality during the chromatographic purification. Treatment of the orthoester intermediate with Bz_2O, Et_3N and a catalytic amount of DMAP gave the selective benzoylation of the hydroxyl group at position C4. Finally, addition of 1 M HCl lead to the partial hydrolysis of the orthoester to obtain compound **30** with the hydroxyl group at position C2 orthogonally protected with an acetate group and with the hydroxyl group at C3 unprotected.[24] After that, selective deprotection of the silyl protected primary hydroxyl group using TBAF in THF afforded the mannose **31** in good yield.

The benzoylated trichloroacetimidate glycosyl donor **32** was prepared following reported procedures.[22] The targeted trimannosides **33** incorporates the α linkage that it is favored due to the neighboring group at the C2 position of the glycosyl donors. The trisaccharide **33** was prepared by reaction of the glycosyl donor **32** with the glycosyl acceptors **31** using trimethylsilyltriflate (TMSOTf) as the promoter at 0°C with quantitative yield. Finally, the allyl-trisaccharide was prepared by the deprotection of acetyl and benzoyl groups using classical Zempler conditions (NaOMe/MeOH) to afford the final compound **34** in quantitative yield.

Finally, glycosyl aldehydes (**35**-**46**) were prepared by conversion of the allyl group to an aldehyde via ozonolysis with quantitative yields in all cases.[25] The analysis by NMR of these glycosyl aldehydes is not trivial, as at least three different species, in different ratios, could be identified by ^1H NMR spectroscopy in D_2O solution. These species could be assigned to the aldehyde, the hydrate and, in some cases, the cyclic six-membered ring hemiacetals formed via ring closure of the aldehyde with the hydroxyls in position OH-2.[26] However, these different intermediates could be trapped as oximes after condensation with the corresponding alkoxyamine (Scheme **4**). To exemplify the potential utility of the strategy for bioorthogonal conjugation, the glycosyl aldehydes were reacted with the *O*-benzylhydroxylamine to form the corresponding oxime neoglycoconjugates. This reaction was tested for all the prepared glycosyl aldehydes in physiological compatible conditions such as water at 40°C for 30 min. The final glycosyl acetaldehyde *O*-benzyl oximes (**47**-**58**) were purified by reverse phase HPLC and lyophilized to isolate the final products with excellent yields (80-90%).

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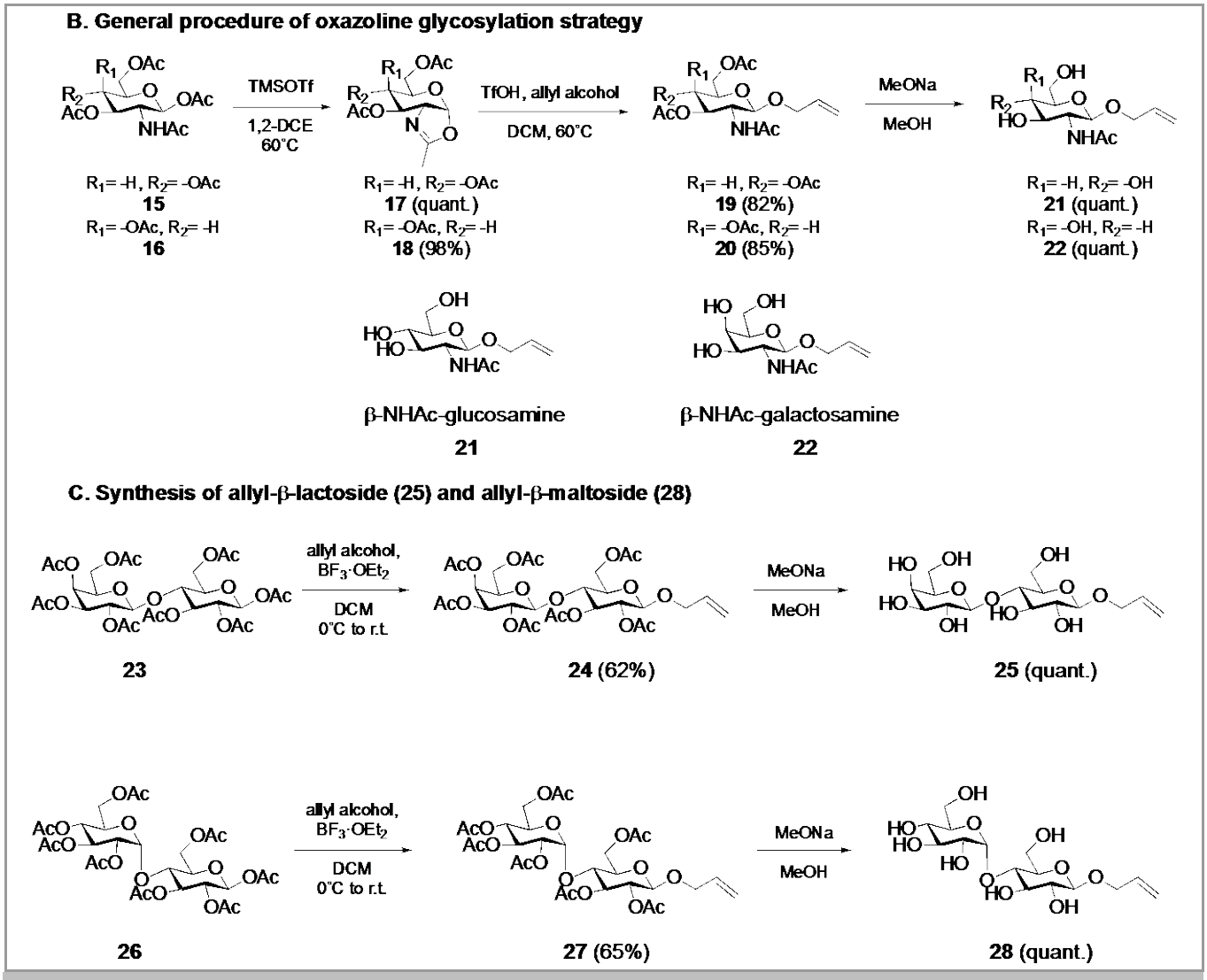
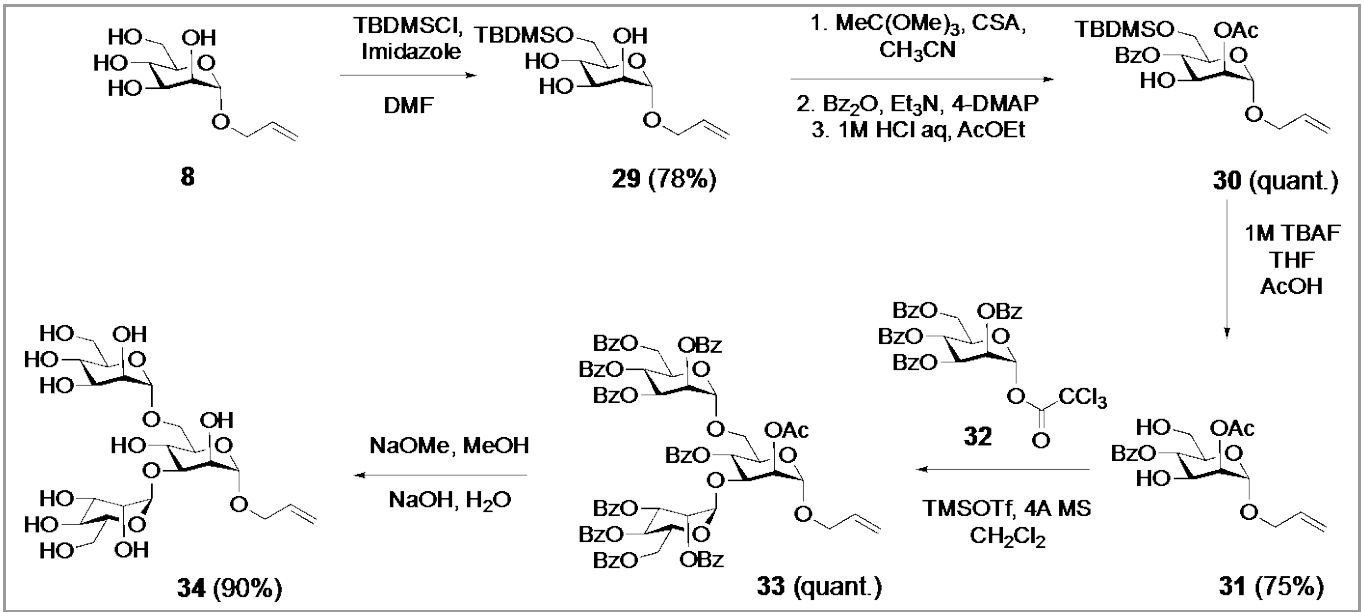
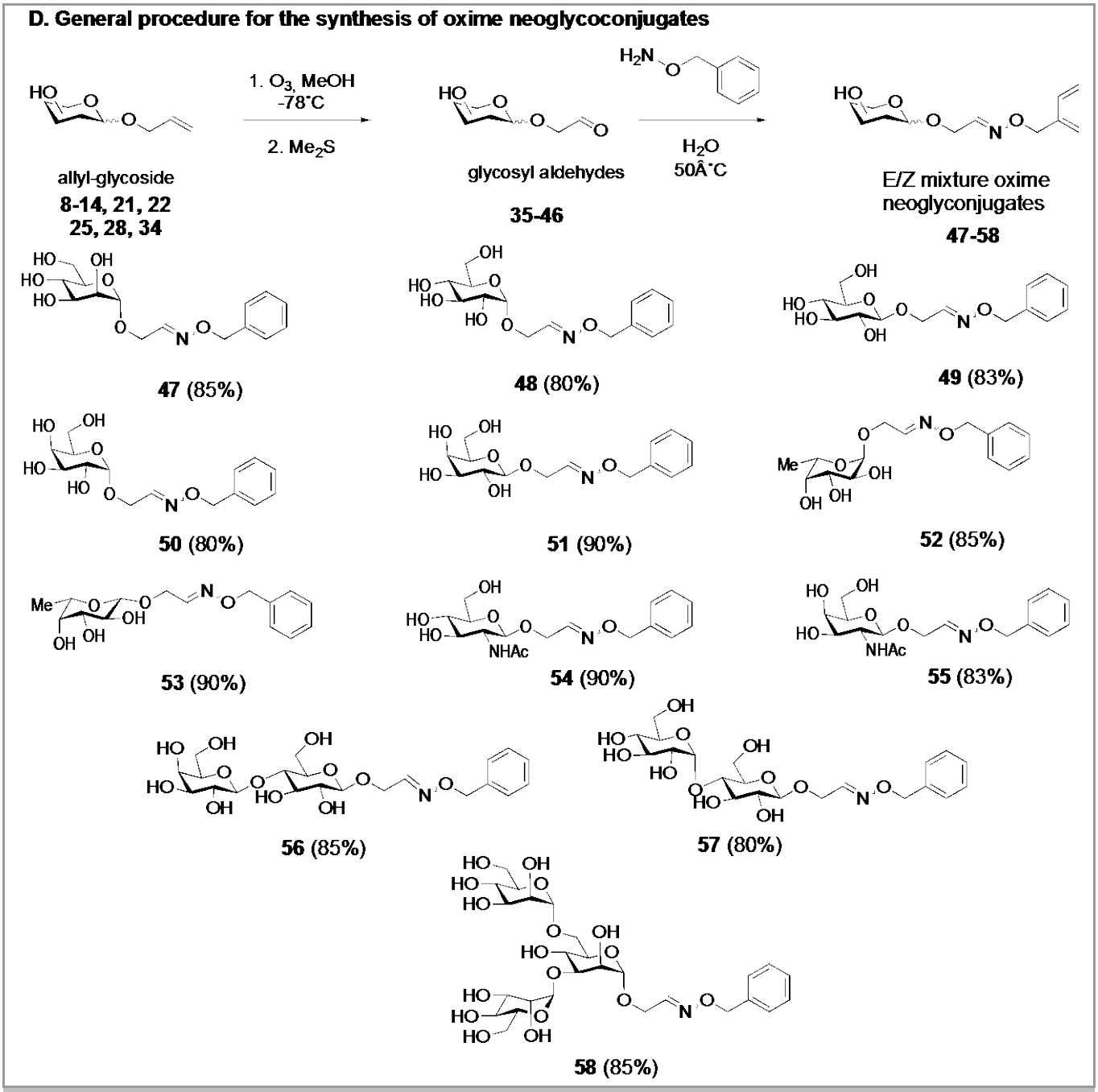


Scheme 2. Synthetic strategy for the synthesis of allyl-glycosides **21**, **22**, **25** and **28**.



Scheme 3. Synthetic strategy for the synthesis of branched mannose trisaccharide Manα1,3[Manα1,6]Man (**34**).



Scheme 4. Synthesis of oxime neoglycoconjugates **47**-**58**.

Discussion

The straightforward preparation of glycosyl neo-conjugates by oxime (or hydrazone) bond formation represents an key bio-orthogonal tool in chemical biology.[27] However, when this strategy is employed by reacting the reducing end of the glycan moiety, the configuration and the stereochemical information of the reducing glycan is lost due to partial (or total) opening of the glycan cyclic hemiacetal and the formation of the corresponding opened tautomers.[17] The objective of this work was to develop and to study the scope of simple synthetic strategies for the preparation of glycosyl aldehydes that could be efficiently conjugated with the corresponding nucleophiles (i.e. alcoxyamines) to afford the corresponding oximes in physiological compatible conditions. The methodology employed including the Fischer strategy for **43**-**53**, oxazolines strategy for **54**-**55** and direct glycosylation of peracetylated donor for the **56**-**57**. We also demonstrate that a multistep sequence employing glycosyl donor and acceptors could be employed for the preparation of tri-mannosyl branched glycan aldehydes. The NMR spectroscopy analysis of some of these synthesized aldehydes showed a mixture of different species such as the targeted aldehyde, the corresponding hydrate and products of inter or intra addition of the hydroxyls to the aldehyde function. However, these complex mixtures were readily resolved by reaction with the alcoxyamine nucleophiles leading to the final oxime products. In summary, we have completed the synthesis of a library of glycosyl aldehydes to be used as scaffold for the synthesis of neo-glycoconjugates via

chemoselective ligation reactions, in particular, as oxime bond formation. These glycosyl aldehydes constitute a simple and accessible alternative to avoid loosing of chiral information when conjugating the aldehyde functionality present at the reducing end of natural carbohydrates. The synthesized glycosyl aldehydes were bioorthogonally conjugated with the corresponding alcoxyamines by incubation in water at 40°C. This strategy minimizes the potential loses in the natural tridimensional conformation of the carbohydrate when directly conjugated by oxime bonds to the organic scaffolds such as rigid molecules, peptides and polymers.

Procedures

Reagents and solvents were purchased as reagent grade and used without further purification. Silica gel 60 (230-400 mesh, 0.015-0.04 mm) for column chromatography was purchased from Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from Merck and visualized by UV light. NMR spectra were recorded on a Bruker AC 500 with solvent peaks as reference. ^{1}H and ^{13}C NMR spectra were obtained from solutions in $CDCl_3$ and MeOD and D_2O at 298K. Coupling constants (*J*) are reported in Hz. Splitting patterns are described by using the following abbreviations: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dddd, doublet of doublet of doublet of doublet; td, triplet of doublet; dt, doublet of triplet; m, multiplet. ^{1}H-NMR spectra are reported in this order: chemical shift; multiplicity; coupling constant(s); number(s) of proton. All the assignments were confirmed by one- and two-dimensional NMR experiments (COSY and HSQC). HRMS spectra were recorded with an Electrospray (**ESI**) on a Bruker Microtof mass spectrometer using MeOH or CH_3CN/H_2O as solvent system. High-performance liquid chromatography (HPLC) semi preparative purification was carried out on JASCO MD-4015 with an Agilent Eclipse XDB-C18 column. Gradient: (Nucleosil 100-7 C18, H_2O (0,1% TFA)/CH_3CN (0,1% TFA) 95:5→ 5:95 (0→ 10min). R_t: retention time.

General Procedure for the Synthesis of protected allyl-glycosides 1-7.

(Procedure A) A solution of AcCl (530 µL, 7.45 mmol) in allyl alcohol (18 mL) was stirred at room temperature for 1 hour. Then, the monosaccharide (Man, Glc, Gal or Fuc) (2.0 g) was added (in one portion) and the mixture was stirred at 60°C for 3 hours. The reaction was cooled to room temperature, quenched by dropwise addition of Et_3N (2 mL) and the solvent was evaporated under reduce pressure. Ac_2O (15 mL), Pyr (30 mL) and a catalytic amount of DMAP were subsequently added to the crude and the solution was stirred for 2 hours at room temperature. The reaction was diluted in EtOAc (100 mL) and washed with HCl 1M (3x 100 mL), $NaHCO_3$ sat. soln. (3 x100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$ anh. and the solvent was evaporated. Finally the reaction crude were purified by silica gel column chromatography using as eluent a mixture of Hex-EtOAc to obtain the α and β pyranosyl isomers of the monosaccharides **1-7.**

Allyl-2,3,4,6-tetra-O-acetyl-α-D-mannopyranose (1)

According to the previously described procedure A, the residue was purified by flash chromatography on silica gel (Hex/EtOAc, 2:1) to afford the corresponding α pyranosyl isomer **1** (3.15 g, 73%) as a colorless solid.

R_f: 0.42 (hexane/EtOAc, 2:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.92 (dddd, 1H, *J*=17.0, 10.3, 6.3, 5.3 Hz, -OCH_2CH=CH_2), 5.39 (dd, 1H, *J*=10.0, 3.4 Hz, H_3), 5.33 (ddd, 1H, *J*=17.2, 3.0, 1.5 Hz, -OCH_2CH=CH_2), 5.31 (t, 1H, *J*=10.1, 1.5 Hz, H_4), 5.29-5.24(m, 2H, H_2 + -OCH_2CH=CH_2), 4.89 (d, 1H, *J*=1.7 Hz, H_1), 4.30 (dd, 1H, *J*=12.2, 5.3 Hz, H_6), 4.21 (ddt, 1H, *J*=12.8, 5.3, 1.4, -OCH_2CH=CH_2), 4.13 (dd, 1H, *J*=12.2, 2.5 Hz, H_6) 4.08-4.00 (m, 2H, H_5 + -OCH_2CH=CH_2), 2.17 (s, 3H, -OCOCH_3), 2.12 (s, 3H, -OCOCH_3), 2.06 (s, 3H, -OCOCH_3), 2.01 (s, 3H, -OCOCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0 (C=O), 170.4 (C=O), 170.2 (C=O), 170.1 (C=O), 133.3 (-OCH_2CH=CH_2), 118.8 (-OCH_2CH=CH_2), 97.0 (C_1), 70.1 (C_2), 69.5 (C_3), 69.1 (-OCH_2CH=CH_2 or C_5), 69.0 (-OCH_2CH=CH_2 or C_5), 66.6 (C_4), 62.9 (C_6), 21.3 (-OCOCH_3), 21.1 (-OCOCH_3), 21.1 (-OCOCH_3), 21.0 (-OCOCH_3).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}NaO_{10}$ $[M+Na]^+$: 411.1267; found: 411.1259.

Allyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (2) and Allyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (3)

According to the previously described procedure A, the residue was purified by flash chromatography on silica gel (Hex/EtOAc, 3:1) to afford the corresponding α pyranosyl isomer **2** (1.34 g, 31%) and α pyranosyl isomer **3** (1.60 g, 37%) as colorless solids.

α isomer (2)

R_f: 0.29 (hexane/EtOAc, 3:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.92-5.84 (m, 1H, -OCH_2CH=CH_2), 5.51 (t, 1H, *J*=9.8Hz, H_3), 5.32 (ddd, 1H, *J*=17.2, 3.2, 1.6 Hz, -OCH_2CH=CH_2), 5.23 (ddd, 1H, *J*=10.4, 3.0, 1.5 Hz, -OCH_2CH=CH_2), 5.11 (d, 1H, *J*=3.7 Hz, H_1), 5.07 (t, 1H, *J*=9.8 Hz, H_4), 4.90 (dd, 1H, *J*=10.2, 3.8 Hz, H_2), 4.26 (dd, 1H, *J*=12.3, 4.5 Hz, H_6), 4.20 (ddt, 1H, *J*=13.0, 5.2, 1.4, -OCH_2CH=CH_2), 4.09-4.00 (m, 3H, H_5 + H_6 + -OCH_2CH=CH_2), 2.10 (s, 3H, -OCOCH_3), 2.07 (s, 3H, -OCOCH_3), 2.03 (s, 3H, -OCOCH_3), 2.01 (s, 3H, -OCOCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.6 (C=O), 171.1 (C=O), 171.1 (C=O), 169.6 (C=O), 133.1 (-OCH_2CH=CH_2), 118.2 (-OCH_2CH=CH_2), 94.8 (C_1), 70.7 (C_2), 70.1 (C_3), 68.8 (-OCH_2CH=CH_2), 68.5 (C_4), 67.3 (C_5), 61.9 (C_6), 20.7 (-OCOCH_3), 20.7 (-OCOCH_3), 20.7 (-OCOCH_3), 20.6 (-OCOCH_3).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}NaO_{10}$ $[M+Na]^+$: 411.1267; found: 411.1264.

β isomer (3)

R_f: 0.23 (hexane/EtOAc, 3:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.90-5.81 (m, 1H, -OCH_2CH=CH_2), 5.28 (ddd, 1H, *J*=17.2, 3.2, 1.6 Hz, -OCH_2CH=CH_2), 5.24-5.19 (m, 2H, H_3 + -OCH_2CH=CH_2), 5.10 (t, 1H, *J*=9.7 Hz, H_4), 5.03 (dd, 1H, *J*=9.6, 8.0 Hz, H_2), 4.57 (d, 1H, *J*=8.0 Hz, H_1), 4.35 (ddt, 1H, *J*=13.2, 4.7, 1.5 Hz, -OCH_2CH=CH_2), 4.27 (dd, 1H, *J*=12.3, 4.7 Hz, H_6), 4.15 (dd, 1H, *J*=12.3, 2.4 Hz, H_6), 4.11 (ddt, 1H, *J*=13.2, 6.1, 1.2 Hz, -OCH_2CH=CH_2), 3.70 (ddd, 1H, *J*=10.0, 4.7, 2.5 Hz, H_5), 2.10 (s, 3H, -OCOCH_3), 2.06 (s, 3H, -OCOCH_3), 2.03 (s, 3H, -OCOCH_3), 2.01 (s, 3H, -OCOCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.7 (C=O), 170.3 (C=O), 169.4 (C=O), 169.3 (C=O), 133.3 (-OCH_2CH=CH_2), 117.7 (-OCH_2CH=CH_2), 99.5 (C_1), 72.9 (C_3), 71.8 (C_5), 71.3 (C_2), 70.0 (-OCH_2CH=CH_2), 68.4 (C_4), 61.9 (C_6), 20.7 (-OCOCH_3), 20.7 (-OCOCH_3), 20.6 (-OCOCH_3), 20.6 (-OCOCH_3).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}NaO_{10}$ $[M+Na]^+$: 411.1267; found: 411.1263.

Allyl-2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose (4) and Allyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose (5)

According to the previously described procedure A, the residue was purified by flash chromatography on silica gel (Hex/EtOAc, 2.5:1) to afford the corresponding α pyranosyl isomer **4** (1.16 g, 27%) and β pyranosyl isomer **5** (1.72 g, 40%) as colorless solids.

α isomer (4)

R_f: 0.34 (hexane/EtOAc, 2.5:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.93-5.84 (m, 1H, -OCH_2CH=CH_2), 5.47 (dd, 1H, *J*=3.4, 1.3 Hz, H_4), 5.39 (ddd, 1H, *J*=11.9, 3.4, 1.6 Hz, H_3), 5.32 (ddd, 1H, *J*=17.3, 3.4, 1.7 Hz, -OCH_2CH=CH_2), 5.24 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz, -OCH_2CH=CH_2), 5.18-5.14 (m, 2H, H_1 + H_2), 4.26 (td, *J*=6.6, 1.4 Hz, H_5), 4.20 (ddt, *J*=13.1, 5.2, 1.5 Hz, -OCH_2CH=CH_2), 4.13-4.09 (m, 2H, 2H_6), 4.03 (ddt, 1H, *J*=13.1, 6.1, 1.4 Hz, -OCH_2CH=CH_2), 2.15 (s, 3H, -OCOCH_3), 2.09 (s, 3H, -OCOCH_3), 2.06 (s, 3H, -OCOCH_3), 2.00 (s, 3H, -OCOCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.4 (C=O), 170.4 (C=O), 170.3 (C=O), 170.0 (C=O), 133.2 (-OCH$_2$*C*H=CH$_2$), 118.0 (-OCH$_2$CH=*C*H$_2$), 95.3 (C_1), 68.8 (-O*C*H$_2$CH=CH$_2$), 68.1 (C_4), 68.1 (C_2), 67.6 (C_3), 66.4 (C_5), 61.7 (C_6), 20.8 (-OCO*C*H$_3$), 20.7 (-OCO*C*H$_3$), 20.7 (-OCO*C*H$_3$), 20.6 (-OCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}NaO_{10}$ [M+Na]$^+$: 411.1267; found: 411.1260.

β isomer (5)

R_f: 0.25 (hexane/EtOAc, 2.5:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.83 (dddd, 1H, *J*=17.3, 10.5, 6.1, 4.9 Hz, -OCH$_2$*CH*=CH$_2$), 5.37 (dd, 1H, *J*=3.5, 1.2 Hz, H$_4$), 5.30-5.17 (m, 3H, H$_2$ + -OCH$_2$CH=C*H*$_2$), 5.01 (dd, 1H, *J*=10.4, 3.5 Hz, H$_3$), 4.50 (d, 1H, *J*=8.0 Hz, H$_1$), 4.35 (ddt, 1H, *J*=13.2, 5.0, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.17 (dd, 1H, *J*=11.3, 6.5 Hz, H$_6$), 4.15-4.06 (m, 2H, H$_6$ + -OC*H*$_2$CH=CH$_2$), 3.89 (td, *J*=6.7, 1.3 Hz, H$_5$), 2.14 (s, 3H, -OCO*C*H$_3$), 2.04 (s, 3H, -OCO*C*H$_3$), 2.03 (s, 3H, -OCO*C*H$_3$), 1.97 (s, 3H, -OCO*C*H$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.8 (C=O), 170.6 (C=O), 170.5 (C=O), 169.8 (C=O), 133.7 (-OCH$_2$*C*H=CH$_2$), 117.9 (-OCH$_2$CH=*C*H$_2$), 100.5 (C_1), 71.3 (C_3), 71.0 (C_5), 70.4 (-O*C*H$_2$CH=CH$_2$), 69.2 (C_2), 67.4 (C_4), 61.7 (C_6), 21.1 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 20.9 (-OCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}NaO_{10}$ [M+Na]$^+$: 411.1267; found: 411.1262.

Allyl-2,3,4-tri-*O*-acetyl-α-L-fucopyranose (6) and Allyl-2,3,4-tri-*O*-acetyl- β-L-fucopyranose (7)

According to the previously described procedure A, the residue was purified by flash chromatography on silica gel (Hex/EtOAc, 4:1) to afford the corresponding α pyranosyl isomer **6** (1.29 g, 40%) and β pyranosyl isomer **7** (1.03 g, 32%) as colorless solids.

α isomer (6)

R_f: 0.55 (hexane/EtOAc, 1:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.94-5.84 (m, 1H, -OCH$_2$C*H*=CH$_2$), 5.41 (dd, 1H, *J*=10.9, 3.3 Hz, H$_3$), 5.35-5.29 (m, 2H, H$_4$ + -OCH$_2$CH=C*H*$_2$), 5.23 (dd, 1H, *J*=10.4, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 5.16 (dd, 1H, *J*=10.8, 3.7 Hz, H$_2$), 5.11 (d, 1H, *J*=3.6 Hz, H$_1$), 4.23-4.16 (m, 2H, H$_5$ + -OC*H*$_2$CH=CH$_2$), 4.03 (dd, 1H, *J*=13.3, 6.2 Hz, -OC*H*$_2$CH=CH$_2$), 2.18 (s, 3H, -OCO*C*H$_3$), 2.09 (s, 3H, -OCO*C*H$_3$), 2.00 (s, 3H, -OCO*C*H$_3$), 1.16 (d, 3H, *J*=6.7 Hz, H$_6$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0 (C=O), 170.8 (C=O), 170.4 (C=O), 133.9 (-OCH$_2$*C*H=CH$_2$), 118.0 (-OCH$_2$CH=*C*H$_2$), 95.7 (C_1), 71.6 (C_4), 69.0 (-O*C*H$_2$CH=CH$_2$), 68.6 (C_2 or C_3), 68.5 (C_2 or C_3), 64.9 (C_5), 21.2 (-OCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 16.2 (C_6).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{22}NaO_8$ [M+Na]$^+$: 353.1212; found: 353.1205.

β isomer (7)

R_f: 0.45 (hexane/EtOAc, 1:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.83-5.74 (m, 1H, -OCH$_2$C*H*=CH$_2$), 5.20 (d, 1H, *J*=17.2 Hz, -OCH$_2$C*H*=CH$_2$), 5.17-5.10 (m, 3H, H$_2$ + H$_4$ + -OCH$_2$CH=C*H*$_2$), 4.95 (dd, 1H, *J*=10.5, 3.2 Hz, H$_3$), 4.42 (d, 1H, *J*=7.9 Hz, H$_1$), 4.29 (dd, 1H, *J*=13.4, 4.7 Hz, -OC*H*$_2$CH=CH$_2$), 4.02 (dd, 1H, *J*=13.3, 6.0 Hz, -OC*H*$_2$CH=CH$_2$), 3.72 (q, 1H, *J*=6.4, H$_5$), 2.10 (s, 3H, -OCO*C*H$_3$), 1.98 (s, 3H, -OCO*C*H$_3$), 1.91 (s, 3H, -OCO*C*H$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.1 (C=O), 170.6 (C=O), 169.9 (C=O), 134.0 (-OCH$_2$*C*H=CH$_2$), 117.7 (-OCH$_2$CH=*C*H$_2$), 100.3 (C_1), 71.8 (C_3), 70.7 (C_2 or C_4), 70.3 (C_2 or C_4), 69.6 (-O*C*H$_2$CH=CH$_2$), 69.4 (C_5), 21.2 (-OCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 16.5 (C_6).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{22}NaO_8$ [M+Na]$^+$: 353.1212; found: 353.1209.

General Procedure for the Synthesis of deprotected allyl-glycosides 8-14.

(Procedure B) To a solution of protected glycosides (0.07 mmol) in 1.5 mL of dry MeOH, NaOMe (0.01 mmol) was added in one portion and the solution was stirred at room temperature. After TLC showed a complete conversion (around 1 hour) amberlite IRA 120 H$^+$ was added until pH 7 and the beads were filtered off. The solvent was evaporated under vacuum to obtain the α and β deprotected pyranosyl isomers of the monosacharides **8-14.**

Allyl-α-D-mannopyranose (8)

According to the previously described procedure B, compound **8** was obtained (404 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 5.96 (dddd, 1H, *J*=17.3, 10.7, 6.0, 5.1 Hz, -OCH$_2$*CH*=CH$_2$), 5.32 (dq, 1H, *J*=17.3, 1.8 Hz, -OCH$_2$CH=C*H*$_2$), 5.19 (dq, 1H, *J*=10.4, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 4.81 (d, 1H, *J*=1.7 Hz, H$_1$), 4.24 (ddt, 1H, *J*=13.1, 5.1, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.03 (ddt, 1H, *J*=13.1, 6.0, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.85 (dd, 1H, *J*=11.8, 2.4 Hz, H$_6$), 3.83 (dd, 1H, *J*=3.4, 1.7 Hz, H$_2$), 3.76-3.70 (m, 2H, H$_3$ + H$_6$), 3.63 (t, 1H, *J*=9.5 Hz, H$_4$), 3.55 (ddd, 1H, *J*=9.8, 5.8, 2.3, H$_5$).

^{13}C NMR (MeOD, 125 MHz): δ = 135.9 (-OCH$_2$*C*H=CH$_2$), 117.6 (-OCH$_2$CH=*C*H$_2$), 101.1 (C_1), 75.1 (C_5), 73.1 (C_3), 72.6 (C_2), 69.2 (-O*C*H$_2$CH=CH$_2$), 69.1 (C_4), 63.4 (C_6).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_6$ [M+Na]$^+$: 243.0845; found: 243.0837.

Allyl-α-D-glucopyranose (9)

According to the previously described procedure B, compound **9** was obtained (315 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 6.10-5.91 (m, 1H, -OCH$_2$C*H*=CH$_2$), 5.36 (ddd, 1H, *J*=17.3, 3.4, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.19 (ddd, 1H, *J*=10.5, 3.0, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 4.85 (d, 1H, *J*=3.7 Hz, H$_1$), 4.25 (ddt, 1H, *J*=13.0, 5.2, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.06 (ddt, 1H, *J*=13.0, 6.0, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.83 (dd, 1H, *J*=11.8, 2.4 Hz, H$_6$), 3.72-3.66 (m, 2H, H$_3$ + H$_6$), 3.60 (ddd, 1H, *J*=10.0, 5.6, 2.4 Hz, H$_5$), 3.42 (dd, 1H, *J*=9.7, 3.8 Hz, H$_2$), 3.37-3.27 (m, 1H, H$_4$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.0 (-OCH$_2$*C*H=CH$_2$), 117.9 (-OCH$_2$CH=*C*H$_2$), 99.6 (C_1), 75.5 (C_3), 74.2 (C_2), 74.0 (C_5), 72.5 (C_4), 69.7 (-O*C*H$_2$CH=CH$_2$), 69.1 (C_4), 63.1 (C_6).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_6$ [M+Na]$^+$: 243.0845; found: 243.0837.

Allyl-β-D-glucopyranose (10)

According to the previously described procedure B, compound **10** was obtained (315 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 5.99 (dddd, 1H, *J*=17.2, 10.5, 6.1, 5.2 Hz, -OCH$_2$*CH*=CH$_2$), 5.35 (dq, 1H, *J*=17.3, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.18 (dq, 1H, *J*=10.5, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 4.40 (ddt, 1H, *J*=13.1, 5.1, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.32 (d, 1H, *J*=7.8 Hz, H$_1$), 4.17 (ddt, 1H, *J*=13.1, 6.0, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.85 (dd, 1H, *J*=11.9, 2.1 Hz, H$_6$), 3.39-3.25 (m, 5H, H$_3$ + H$_4$ + H$_5$), 3.22 (dd, 1H, *J*=9.8, 7.8, H$_2$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.2 (-OCH$_2$*C*H=CH$_2$), 117.8 (-OCH$_2$CH=*C*H$_2$), 103.8 (C_1), 78.5 (C_3), 78.4 (C_5), 75.5 (C_2), 72.1 (C_4), 71.5 (-O*C*H$_2$CH=CH$_2$), 63.4 (C_6).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_6$ [M+Na]$^+$: 243.0845; found: 243.0837.

Allyl-α-D-galactopyranose (11)

According to the previously described procedure B, compound **11** was obtained (250 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 5.97 (dddd, 1H, *J*=17.3, 10.4, 6.1, 5.2 Hz, -OCH$_2$*CH*=CH$_2$), 5.33 (ddd, 1H, *J*=17.3, 3.4, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.16 (ddd, 1H, *J*=10.4, 3.0, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 4.86 (d, 1H, *J*=3.3 Hz, H$_1$), 4.22 (ddt, 1H, *J*=13.0, 5.2, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 4.03 (ddt, 1H, *J*=13.0, 6.1, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.88 (dd, 1H, *J*=2.7, 1.3 Hz, H$_4$), 3.81 (td, 1H, *J*=6.0, 1.2 Hz, H$_5$), 3.76 (t, 2H, *J*=2.6 Hz, H$_2$ + H$_3$), 3.70 (dd, 2H, *J*=6.1, 2.0 Hz, 2H$_6$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.1 (-OCH$_2$*C*H=CH$_2$), 117.9 (-OCH$_2$CH=*C*H$_2$), 99.9 (C$_1$), 72.9 (C$_2$), 71.9 and 71.5 (C$_4$ and C$_5$), 70.7 (C$_3$), 69.8 (-O*C*H$_2$CH=CH$_2$), 63.1 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_6$ [M+Na]$^+$: 243.0845; found: 243.0838.

Allyl-β-D-galactopyranose (12)

According to the previously described procedure, compound **12** was obtained (250mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 6.01 (dddd, 1H, *J*=17.3, 10.4, 6.1, 5.2 Hz, -OCH$_2$*CH*=CH$_2$), 5.37 (ddd, 1H, *J*=17.3, 3.4, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.19 (ddd, 1H, *J*=10.5, 3.0, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 4.41 (ddt, 1H, *J*=12.9, 5.3, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.30 (d, 1H, *J*=7.7 Hz, H$_1$), , 4.19 (ddt, 1H, *J*=12.9, 6.1, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.87 (dd, 1H, *J*=3.4, 1.1 Hz, H$_4$), 3.80 (dd, 1H, *J*=11.4, 6.8 Hz, H$_6$), 3.76 (dd, 1H, *J*=11.4, 5.5 Hz, H$_6$), 3.58 (dd, 1H, *J*=9.7, 7.6 Hz, H$_2$), 3.53 (ddd, 1H, *J*=6.7, 5.4, 1.2 Hz, H$_5$), 3.50 (dd, 1H, *J*=9.7, 3.4, H$_3$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.1 (-OCH$_2$*C*H=CH$_2$), 117.7 (-OCH$_2$CH=*C*H$_2$), 104.3 (C$_1$), 76.0 (C$_5$), 75.3 (C$_3$), 72.8 (C$_2$), 71.3 (-O*C*H$_2$CH=CH$_2$), 70.6 (C$_4$), 62.8 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_6$ [M+Na]$^+$: 243.0845; found: 243.0837.

Allyl-α-L-fucopyranoside (13)

According to the previously described procedure, compound **13** was obtained (280mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 6.00 (dddd, 1H, *J*=17.3, 10.3, 6.0, 5.3 Hz, -OCH$_2$C*H*=CH$_2$), 5.36 (ddd, 1H, *J*=17.3, 3.4, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.21 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz, -OCH$_2$CH=C*H*$_2$), 4.84 (d, 1H, *J*=3.0 Hz, H$_1$), 4.20 (ddt, 1H, *J*=13.1, 5.3, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 4.07 (ddt, 1H, *J*=13.1, 6.1, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 4.00 (q, 1H, *J*=6.7 Hz, H$_5$), 3.82-3.76 (m, 2H, H$_2$ + H$_3$), 3.70 (dd, 1H, *J*=2.9, 1.3 Hz, H$_4$), 1.25 (d, 3H, *J*=6.6 Hz, 3H$_6$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.2 (-OCH$_2$*C*H=CH$_2$), 117.8 (-OCH$_2$CH=*C*H$_2$), 100.0 (C$_1$), 74.1 (C$_4$), 72.1 (C$_2$ or C$_3$), 70.4 (C$_2$ or C$_3$), 69.9 (-O*C*H$_2$CH=CH$_2$), 68.0 (C$_5$), 17.0 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_5$ [M+Na]$^+$: 227.0895; found: 243.0890.

Allyl-β-L-fucopyranose (14)

According to the previously described procedure, compound **14** was obtained (200 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (MeOD, 500 MHz): δ = 6.00 (dddd, 1H, *J*=17.1, 10.3, 6.0, 5.3 Hz, -OCH$_2$C*H*=CH$_2$), 5.36 (ddd, 1H, *J*=17.3, 2.6, 1.3 Hz, -OCH$_2$CH=C*H*$_2$), 5.19 (ddd, 1H, *J*=10.5, 2.8, 1.4 Hz, -OCH$_2$CH=C*H*$_2$), 4.36 (ddt, 1H, *J*=12.9, 5.3, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.27 (d, 1H, *J*=7.3 Hz, H$_1$), 4.15 (ddt, 1H, *J*=12.9, 6.1, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.68-3.61 (m, 2H, H$_4$ + H$_5$), 3.53 (dd, 1H, *J*=9.7, 7.2 Hz, H$_2$), 3.49 (dd, 1H, *J*=9.7, 3.2 Hz, H$_3$), 1.17 (d, 3H, *J*=7.3 Hz, 3H$_6$)

^{13}C NMR (MeOD, 125 MHz): δ = 136.3 (-OCH$_2$*C*H=CH$_2$), 117.7 (-OCH$_2$CH=*C*H$_2$), 104.3 (C$_1$), 75.6 (C$_3$), 73.4 (C$_4$ or C$_5$), 72.7 (C$_4$ or C$_5$), 72.3 (C$_2$), 71.4 (-O*C*H$_2$CH=CH$_2$), 17.1 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_9H_{16}NaO_5$ [M+Na]$^+$: 227.0895; found: 243.0891.

Synthesis Allyl-glycosides via oxazoline donors

2-Methyl-3,4,6-tri-O-acetyl-1,2-deoxy-α-D-glucopyrano[2,1,d]-2-oxazoline (17)

TMSOTf (1.0 mL, 5.40 mmol) was added at room temperature to a solution of peracetylated sugar **15** (2 g, 5.15 mmol) in dry 1,2-dichloroethane (15 mL). The mixture was stirred for 4 h at 60°C and allowed to cool to room temperature. To this solution, triethylamine (2.9 mL) was added dropwise and after 15 min at room temperature, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a $NaHCO_3$ sat. aq. soln. (2 x 50 mL). The organic layer was dried over anh. $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 50:1 → 30:1) to afford **17** (1.69 g, quant.) as a yellow oil.

Spectroscopic and physical data matched those reported in the literature.[19]

2-Methyl-3,4,6-tri-O-acetyl-1,2-deoxy-α-D-galactopyrano[2,1,d]-2-oxazoline (18)

TMSOTf (1.0 mL, 5.40 mmol) was added at room temperature to a solution of peracetylated sugar **16** (2 g, 5.15 mmol) in dry 1,2-dichloroethane (15 mL). The mixture was stirred for 4 h at 60°C and allowed to cool to room temperature. To this solution, triethylamine (2.9 mL) was added dropwise and after 15 min at room temperature, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a $NaHCO_3$ sat. aq. soln. (2 x 50 mL). The organic layer was dried over anh. $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 50:1 → 30:1) to afford **18** (1.60 g, 98%) as a yellow oil.

Spectroscopic and physical data matched those reported in the literature.[19]

Allyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose (19)

Freshly distilled allyl alcohol (1.3 mL, 18.83 mmol) was added dropwise to a mixture of oxazoline **17** (620 mg, 1.88 mmol) and powdered 4Å molecular sieves in dry CH_2Cl_2 (10 mL). The reaction vessel was sealed, heated at 70°C and trifluoromethanesulfonic acid (66 µL, 0.75 mmol) was then added and the reaction mixture was heated at 70°C for 4 h. The mixture was then allowed to cool to room temperature, filtered through celite and washed with CH_2Cl_2 (2 x 20 mL). The organic layer was washed with $NaHCO_3$ sat. aq. soln. (2 x 50 mL) and brine (50 mL). The organic phase was dried over anh. $MgSO_4$, filtered and concentrated under vacuum to remove the excess of allyl alcohol. The residue was purified by column chromatography on silica gel (CH_2Cl_2:MeOH, 100:0→100:1), afforded **19** (600 mg, 82%) as a colorless solid.

R_f: 0.58 (CH_2Cl_2:MeOH, 95:5)

^{1}H NMR ($CDCl_3$, 500 MHz): 5.86 (dddd, 1H, J=16.9, 10.4, 6.3, 5.0 Hz, -OCH$_2$*CH*=CH$_2$), 5.54 (d, 1H, *J*=8.8 Hz, N*H*Ac), 5.34-5.23 (m, 2H, H$_3$ + -OCH$_2$CH=C*H*$_2$), 5.19 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz -OCH$_2$CH=C*H*$_2$), 5.06 (t, 1H, *J*=9.6 Hz, H$_4$), 4.71 (d, 1H, *J*=8.3 Hz, H$_1$), 4.33 (ddt, 1H, *J*=12.9, 5.0, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 4.25 (dd, 1H, *J*=12.2, 4.8 Hz, H$_6$), 4.13 (dd, 1H, *J*=12.3, 2.5 Hz, H$_6$), 4.08 (ddt, 1H, *J*=13.0, 6.4, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 3.87 (dt, 1H, *J*=10.6, 8.5 Hz, H$_2$), 3.70 (ddd, 1H, *J*=10.0, 4.9, 2.5 Hz, H$_5$), 2.08 (s, 3H, -OCO*C*H$_3$), 2.02 (-OCO*C*H$_3$), 2.01 (-OCO*C*H$_3$), 1.94 (-NHCO*C*H$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.3 (C=O), 171.1 (C=O), 170.6 (C=O), 169.8 (C=O), 133.9 (-OCH$_2$*C*H=CH$_2$), 118.2 (-OCH$_2$CH=*C*H$_2$), 100.1 (C$_1$), 72.8 (C$_3$), 72.2 (C$_5$), 70.3 (-O*C*H$_2$CH=CH$_2$), 69.1 (C$_4$), 62.6 (C$_6$), 55.2 (C$_2$), 23.7 (-NHCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{25}NNaO_9$ [M+Na]$^+$: 410.1427; found: 410.1421.

Allyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranose (20)

Freshly distilled allyl alcohol (1.35 mL, 19.75 mmol) was added dropwise to a mixture of oxazoline **19** (650 mg, 1.97 mmol) and powdered 4Å molecular sieves in dry CH_2Cl_2 (10 mL). The reaction vessel was sealed, heated at 70°C and trifluoromethanesulfonic acid (70 µL, 0.79 mmol) was then added and the reaction mixture was heated at 70°C for 4 h. The mixture was then allowed to cool to room temperature, filtered through celite and washed with CH_2Cl_2 (2 x 20 mL). The organic layer was washed with $NaHCO_3$ sat. aq. soln. (2 x 50 mL) and brine (50 mL). The organic phase was dried over anh. $MgSO_4$, filtered and concentrated under vacuum to remove the excess of allyl alcohol. The residue was purified by column chromatography on silica gel (CH_2Cl_2:MeOH, 100:0→100:1), afforded **20** (645 mg, 85%) as a colorless solid.

R_f: 0.61 (CH_2Cl_2:MeOH, 100:5)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.87 (dddd, 1H, *J*=17.0, 10.4, 6.3, 5.1 Hz, -OCH$_2$C*H*=CH$_2$), 5.46 (d, 1H, *J*=8.6 Hz, NH*A*c), 5.36 (dd, 1H, *J*=3.4, 1.4 Hz, H$_4$), 5.33-5.25 (m, 2H, H$_3$ + -OCH$_2$CH=C*H*$_2$), 5.22 (ddd, 1H, *J*=10.4, 3.0, 1.5 Hz -OCH$_2$CH=C*H*$_2$), 4.74 (d, 1H, *J*=8.4Hz, H$_1$), 4.35 (ddt, 1H, *J*=13.0, 5.1, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 4.20-4.06 (m, 3H, 2H$_6$ + -OC*H*$_2$CH=CH$_2$), 3.97 (dt, 1H, *J*=11.2, 8.5 Hz, H$_2$), 3.91 (td, 1H, *J*=6.1, 1.2 Hz, H$_5$), 2.14 (s, 3H, -OCO*C*H$_3$), 2.04 (-OCO*C*H$_3$), 2.00 (-OCO*C*H$_3$), 1.95 (-NHCO*C*H$_3$)..

^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.8 (C=O), 170.8 (C=O), 170.7 (C=O), 170.6 (C=O), 134.0 (-OCH$_2$*C*H=CH$_2$), 118.2 (-OCH$_2$CH=*C*H$_2$), 100.3 (C$_1$), 71.1 (C$_5$), 70.4 (-O*C*H$_2$CH=CH$_2$), 70.3 (C$_3$), 67.2 (C$_4$), 61.9 (C$_6$), 52.1 (C$_2$), 23.9 (-NHCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.1 (-OCO*C*H$_3$), 21.1 (-OCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{25}NNaO_9$ [M+Na]$^+$: 410.1427; found: 410.1419.

Allyl-2-acetamido-2-deoxy-β-D-glucopyranose (21)

NaOMe (7 mg, 0.13 mmol) was added in one portion to a solution of **19** (300 mg, 0.78 mmol) in 15 mL of dry MeOH. The mixture was stirred at room temperature and followed by TLC. When full conversion was achieved, amberlite IRA 120 H$^+$ was added until pH 7 and the beads were filtered off. The solvent was evaporated under vacuum to obtain **21** as a colorless solid (203 mg, quant.).

^{1}H NMR (MeOD, 500 MHz): δ = 5.93 (dddd, 1H, *J*=17.3, 10.6, 5.8, 4.9 Hz, -OCH$_2$C*H*=CH$_2$), 5.31 (ddd, 1H, *J*=17.3, 3.6, 1.8 Hz, -OCH$_2$CH=C*H*$_2$), 5.17 (ddd, 1H, *J*=10.5, 3.2, 1.6 Hz, -OCH$_2$CH=C*H*$_2$), 4.48 (d, 1H, *J*=8.4 Hz, H$_1$), 4.38 (ddt, 1H, *J*=13.3, 5.0, 1.7 Hz, -OC*H*$_2$CH=CH$_2$), 4.11 (ddt, 1H, *J*=13.3, 5.8, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 3.92 (dd, 1H, *J*=11.9, 2.3 Hz, H$_6$), 3.77-3.66 (m, 2H, H$_2$ + H$_6$), 3.40-3.33 (m, 1H, H$_4$), 3.29 (ddd, 1H, *J*=9.7, 5.9, 2.3 Hz, H$_2$).

^{13}C NMR (MeOD, 125 MHz): δ = 174.2 (C=O), 136.0 (-OCH$_2$*C*H=CH$_2$), 117.3 (-OCH$_2$CH=*C*H$_2$), 102.3 (C$_1$), 78.4 (C$_5$), 76.5 (C$_3$), 72.6 (C$_4$), 71.1 (-O*C*H$_2$CH=CH$_2$), 63.2 (C$_6$), 57.8 (C$_2$), 23.3 (-NHCOCH$_3$).

HRMS (ESI): *m/z* calcd. for $C_{11}H_{19}NaO_6$ [M+Na]$^+$: 284.1110; found: 284.1105.

Allyl-2-acetamido-2-deoxy-β-D-galactopyranose (22)

NaOMe (10 mg, 0.19 mmol) was added in one portion to a solution of **20** (500 mg, 1.29 mmol) in 20 mL of dry MeOH. The mixture was stirred at room temperature and followed by TLC. When full conversion was achieved, amberlite IRA 120 H$^+$ was added until pH 7 and the beads were filtered off. The solvent was evaporated under vacuum to obtain **22** as a colorless solid (336 mg, quant.).

^{1}H NMR (MeOD, 500 MHz): δ = 5.91 (dddd, 1H, *J*=17.3, 10.6, 5.8, 4.9 Hz, -OCH$_2$C*H*=CH$_2$), 5.31 (ddd, 1H, *J*=17.2, 3.6, 1.8 Hz, -OCH$_2$CH=C*H*$_2$), 5.17 (ddd, 1H, *J*=10.7, 3.2, 1.6 Hz, -OCH$_2$CH=C*H*$_2$), 4.59 (s, 1H, NHAc), 4.46 (d, 1H, *J*=8.5 Hz, H$_1$), 4.38 (ddt, 1H, *J*=13.2, 5.0, 1.7 Hz, -OC*H*$_2$CH=CH$_2$), 4.12 (ddt, 1H, *J*=13.3, 5.8, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 3.98 (dd, 1H, *J*=10.7, 8.4 Hz, H$_2$), 3.87 (dd, 1H, *J*=3.4, 1.2 Hz, H$_4$), 3.82 (dd, 1H, *J*=11.4, 6.8 Hz, H$_6$), 3.78 (dd, 1H, *J*=11.4, 5.4 Hz, H$_6$), 3.64 (dd, 1H, *J*=10.7, 3.3 Hz, H$_3$), 3.53 (ddd, 1H, *J*=6.8, 5.4, 1.1 Hz, H$_5$), 2.02 (s, 3H, NHAc).

^{13}C NMR (MeOD, 125 MHz): δ = 174.5 (C=O), 136.1 (-OCH$_2$*C*H=CH$_2$), 117.3 (-OCH$_2$CH=*C*H$_2$), 102.6 (C$_1$), 77.2 (C$_5$), 73.7 (C$_3$), 70.1 (C$_4$), 71.1 (-O*C*H$_2$CH=CH$_2$), 70.1 (C$_4$), 62.9 (C$_6$), 54.7 (C$_2$), 23.4 (-NHCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{11}H_{19}NaO_6$ [M+Na]$^+$: 284.1110; found: 284.1106.

Synthesis allyl disaccharides

Allyl-per(acetylated) Lactose (24)

BF_3·Et$_2$O (0.9 mL, 7.35 mmol) was added drop wise to a cooled solution (0°C) of peracetyl-lactose **23** (1.0 g, 1.48 mmol) and allyl alcohol (150 µL, 2.21 mmol) in anhydrous DCM (10 mL). The reaction mixture was stirred at room temperature for 16 hours. The reaction was diluted with DCM (50 mL) and washed with water (3x, 50 mL), $NaHCO_3$ sat. soln (3x, 50 mL) and brine solution (50 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated to dryness. Finally, the residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to give **24** as a colorless solid (620 mg, 62%).

R_f: 0.26 (hexane:AcOEt, 1:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.81 (dddd, 1H, *J*=16.9, 10.8, 6.1, 4.9 Hz, -OCH$_2$C*H*=CH$_2$), 5.32 (dd, 1H, *J*=3.4, 1.2 Hz, H$_{4B}$), 5.23 (ddd, 1H, *J*=17.2, 1.7 Hz, -OCH$_2$CH=C*H*$_2$), 5.17 (t, 1H, *J*=1.5 Hz, H$_{3A}$), 5.17 (ddd, 1H, *J*=10.5, 3.0, 1.5 Hz, -OCH$_2$C*H*=CH$_2$), 5.08 (dd, 1H, *J*=10.4, 7.9 Hz, H$_{2B}$), 4.96-4.86 (m, 2H, H$_{2A}$ + H$_{3B}$), 4.50 (d, 1H, *J*= 7.9 Hz, H$_{1A}$), 4.46 (d, 1H, *J*= 8.0 Hz, H$_{1B}$), 4.46-4.42 (m, 1H,H$_{6B}$), 4.27 (ddt, 1H, *J*=13.2, 5.0, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.14 -4.01 (m, 5H, -OC*H*$_2$CH=CH$_2$ H$_{5B}$+ 2H$_{6A}$ + H$_{6B}$), 3.85 (ddd, 1H, *J*=7.5, 6.3, 1.3 Hz, -OCH$_2$C*H*=CH$_2$), 3.78 (t, 1H, *J*=9.4 Hz, H$_{4A}$), 3.57 (ddd, 1H, *J*=9.9, 5.1, 2.1 Hz, H$_{5A}$), 2.12 (s, 3H, -OCO*C*H$_3$), 2.10 (s, 3H, -OCO*C*H$_3$), 2.03 (-OCO*C*H$_3$), 2.02 (s, 6H, -OCO*C*H$_3$), 2.01 (s, 6H, 2 x -OCO*C*H$_3$), 1.94 (s, 3H, -OCO*C*H$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.7 (C=O), 170.7 (C=O), 170.5 (C=O), 170.4 (C=O), 170.2 (C=O), 170.0 (C=O), 169.4 (C=O), 133.7 (-OCH$_2$*C*H=CH$_2$), 118.0 (-OCH$_2$CH=*C*H$_2$), 101.5 (C$_{1B}$), 99.7 (C$_{1A}$), 76.7 (C$_{4A}$), 73.3 (C$_{3A}$), 73.0 (C$_{5A}$), 72.1 (C$_{2A}$), 71.4 (C$_{3B}$), 71.1 (C$_{5B}$), 70.4 (-O*C*H$_2$CH=CH$_2$), 69.5 (C$_{2B}$), 67.0 (C$_{4B}$), 62.4 (C$_{6A}$), 61.2 (C$_{6A}$), 21.2 (-OCO*C*H$_3$), 21.2 (-OCO*C*H$_3$), 21.01 (-OCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 20.9 (-OCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for HRMS (ESI): *m/z* calcd. for $C_{29}H_{40}NaO_{18}$ [M+Na]$^+$: 699.2112; found: 699.2107.

Allyl-β-Lactose (25)

NaOMe (5.0 mg, 0.10 mmol) was added in one portion to a solution of **24** (450 mg, 0.67 mmol) in 15 mL of dry MeOH. The solution was stirred at room temperature and followed by TLC. When full conversion was achieved, amberlite IRA 120 H$^+$ was added until pH 7 and the beads were filtered off. The solvent was evaporated under vacuum to obtain **25** as a colorless solid (254 mg, quant.).

^{1}H NMR (MeOD, 500 MHz): δ = 6.09-5.90 (m, 1H, -OCH$_2$C*H*=CH$_2$), 5.35 (ddd, 1H, *J*=17.3, 3.4, 1.7, -OCH$_2$CH=C*H*$_2$), 5.21 (ddd, 1H, *J*=10.4, 3.4, 1.7 Hz,-OCH$_2$CH=C*H*$_2$), 4.43-4.38 (m, 1H, -OC*H*$_2$CH=CH$_2$),4.40 (d, 1H, *J*=7.5 Hz, H$_{1B}$), 4.38 (d, 1H, *J*=7.8 Hz, H$_{1A}$), 4.19 (ddt, 1H, *J*=12.9, 6.1, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 3.94 (dd, 1H, *J*=3.5, 1.7 Hz, H$_{6A}$), 3.91-3.86 (m, 1H, H$_{6A}$), 3.86 (d, 1H, *J*=3.2 Hz, H$_{4B}$), 3.82 (dd, 1H, *J*=11.4, 7.4 Hz, H$_{6B}$), 3.74 (dd, 1H, *J*=11.4, 7.4 Hz, H$_{6B}$), 3.66-3.55 (m, 3H, H$_{3A}$ + H$_{2B}$ + H$_{4B}$), 3.55-3.50 (m, 2H, H$_{4A}$ + H$_{3B}$), 3.43 (ddd, 1H, *J*=9.5, 4.3, 2.6 Hz, H$_{5A}$), 3.31 (dd, 1H, *J*=9.0, 7.9 Hz, H$_{2A}$).

^{13}C NMR (MeOD, 125 MHz): δ = 136.1 (-OCH$_2$*C*H=CH$_2$), 117.9 (-OCH$_2$CH=*C*H$_2$), 105.5 (C$_1$) , 103.7 (C$_1$), 81.1, 77.5, 76.9, 75.3, 75.2, 73.0, 71.5, 70.7 (-OCH$_2$CH=*C*H$_2$), 62.9 (C$_6$), 62.3 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{26}NaO_{11}$ [M+Na]$^+$: 405.1373; found: 405.1370.

Allyl-per(acetylated) Maltose (27)

BF_3·Et$_2$O (0.9 mL, 7.35 mmol) was added to cooled (0°C) solution of peracetyl-maltose **26** (1.0 g, 1.48 mmol) and allyl alcohol (150 µL, 2.21 mmol) in anhydrous DCM (10 mL). The reaction mixture was stirred at room temperature for 16 hours. The reaction was diluted with DCM (50 mL) and washed with water (3x, 50 mL), $NaHCO_3$ sat. soln (3x, 50 mL) and brine solution (50 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated to dryness. Finally, the residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to give **27** as a colorless solid (650 mg, 65%).

R_f: 0.38 (hexane/EtOAc 1:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.84 (dddd, 1H, *J*=17.0, 10.8, 6.2, 4.9 Hz, -OCH$_2$C*H*=CH$_2$), 5.40 (d, 1H, *J*=4.1 Hz, H$_{1B}$), 5.35 (t, 1H, *J*=10.0 Hz, H$_{3B}$) 5.29-5.23 (m, 1H, -OCH$_2$CH=C*H*$_2$), 5.24 (t, 1H, *J*=9.0 Hz, H$_{3A}$), 5.20 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz, -OCH$_2$CH=C*H*$_2$), 5.04 (t, 1H, *J*=9.9 Hz, H$_{4B}$), 4.87-4.82 (m, 2H, H$_{2A}$ + H$_{2B}$), 4.58 (d, 1H, *J*=7.9 Hz, H$_{1A}$), 4.48 (dd, 1H, *J*=12.1, 2.8 Hz, H$_{6A}$), 4.30 (ddt, 1H, *J*=13.2, 5.0, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 4.23 (ddd, 2H, *J*=12.1, 8.2, 4.3 Hz, H$_{6A}$ + H$_{6B}$), 4.09 (ddt, 1H, *J*=13.2, 6.2, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 4.04 (dd, 1H, *J*=12.4, 2.2 Hz, H$_{6B}$), 4.00 (t, 1H, *J*=10.0 Hz, H$_{4A}$), 3.96 (ddd, 1H, *J*=10.3, 4.0, 2.3 Hz, H$_{5B}$), 3.96 (ddd, 1H, *J*=9.6, 4.5, 2.8 Hz, H$_{5A}$) 2.14 (s, 3H, -OCO*C*H$_3$), 2.09 (s, 3H, -OCO*C*H$_3$), 2.08 (-OCO*C*H$_3$), 2.02 (s, 6H, -OCO*C*H$_3$), 2.00 (s, 3H, -OCO*C*H$_3$), 1.99 (s, 3H, -OCO*C*H$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.9 (2 x C=O), 170.9 (C=O), 170.6 (C=O), 170.3 (C=O), 170.0 (C=O), 169.8 (C=O), 133.7 (-OCH_2CH=CH_2), 118.1 (-OCH_2CH=CH_2), 99.4 (C_{1A}), 95.9 (C_{1B}), 75.9 (C_{3A}), 73.2 (C_{4A}), 72.6 (C_{5A}), 72.5 (C_{2A} or C_{2B}), 70.0 (C_{2A} or C_{2B} + -OCH_2CH=CH_2), 69.8 (C_{3B}), 68.9 (C_{5B}), 68.5 (C_{4B}), 63.2 (C_{6A}), 62.0 (C_{6B}), 21.3 (-$OCOCH_3$), 21.3 (-$OCOCH_3$), 21.2 (-$OCOCH_3$), 21.1 (-$OCOCH_3$), 21.0 (-$OCOCH_3$), 21.0 (-$OCOCH_3$), 20.9 (-$OCOCH_3$).

HRMS (ESI): *m/z* calcd. for $C_{29}H_{40}NaO_{18}$ $[M+Na]^+$: 699.2112; found: 699.2106.

Allyl β-D-Maltose (28)

NaOMe (6.0 mg, 0.12 mmol) was added in one portion to a solution of **27** (480 mg, 0.71 mmol) in 15 mL of dry MeOH. The solution was stirred at room temperature and followed by TLC. When full conversion was achieved, amberlite IRA 120 H^+ was added until pH 7 and the beads were filtered off. The solvent was evaporated under vacuum to obtain **28** as a colorless solid (271 mg, quant.).

^{1}H NMR (MeOD, 500 MHz): δ = 6.03-5.93 (m, 1H, -OCH_2CH=CH_2), 5.33 (ddd, 1H, *J*= 17.2, 3.6, 1.8 Hz, -OCH_2CH=CH_2), 5.19-5.14 (m, 2H, H_{1B} + -OCH_2CH=CH_2), 4.37 (ddd, 1H, *J*= 17.2, 3.6, 1.8 Hz, -OCH_2CH=CH_2), 4.32(d, 1H, *J*=7.8 Hz, H_{1A}), 4.15 (ddd, 1H, *J*= 12.9, 6.1, 1.5 Hz, -OCH_2CH=CH_2), 3.89 (dd, 1H, *J*= 12.2, 2.1 Hz, H_{6B}), 3.84-3.78 (m, 2H, H_{6A} + H_{6B}), 3.71-3.58 (m, 4H, H_{3A} + H_{3B} + H_{4B} + H_{6A}), 3.54 (t, 1H, *J*=9.2 Hz, H_{4A}), 3.44(dd, 1H, *J*=9.7, 3.7 Hz, H_{2B}), 3.40-3.34 (m, 1H, H_{5A}), 3.28-3.21 (m, 2H, H_{2A} + H_{5B}).

^{13}C NMR (MeOD, 125 MHz): δ = 135.6 (-OCH_2CH=CH_2), 117.5 (-OCH_2CH=CH_2), 103.3 (C_{1A}), 102.9 (C_{1B}), 81.2 (C_{4B}), 77.8 (C_{4A} or C_{3B}), 76.6 (C_{5A}), 75.1 (C_{3A}), 74.7 (C_{2A}), 74.7(C_{4A} or C_{3B}), 74.1 (C_{2B}), 71.5 (C_{5B}), 71.1 (-OCH_2CH=CH_2), 62.7 (C_{6A} or C_{6B}), 62.2 (C_{6A} or C_{6B}).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373; found: 405.1368.

Synthesis of Allyl-Manα1,3[Manα1,6]Man

Allyl-6-*O*-*tert*-butyldimethyllsilyl-α-D-mannopyranose (29)

Imidazole (0.78 g, 11.44 mmol) and TBDMS-Cl (1.26 g, 8.39 mmol) were added to a solution of allyl mannose **8** (1.67 g , 7.62 mmol) in DMF (15 mL). The reaction mixture was stirred overnight at room temperature, diluted with DCM (150 mL) and washed with water (150 Ml) and brine (150 mL). The organic phase was dried over anh. $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (EtOAc/Hex, 1.5:1) to afford **29** (1.99 g, 78%) as a colorless oil.

R_f: 0.63 (hexane/EtOAc, 1:2)

^{1}H NMR ($CDCl_3$, 500 MHz): 5.89 (dddd, 1H, *J*=16.8, 10.4, 6.1, 5.1 Hz, -OCH_2CH=CH_2), 5.28 (ddd, 1H, *J*=17.2, 3.2, 1.6, -OCH_2CH=CH_2), 5.19 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz,-OCH_2CH=CH_2), 4.85 (d, 1H, *J*=1.6 Hz, H_1), 4.18 (ddt, 1H, *J*=12.9, 5.1, 1.5 Hz, -OCH_2CH=CH_2), 3.98 (ddt, 1H, *J*=12.9, 6.1, 1.4 Hz, -OCH_2CH=CH_2), 3.93 (dd, 1H, *J*=3.5, 1.7 Hz, H_2), 3.91-3.83 (m, 3H, H_3 + 2H_6), 3.77 (t, 1H, *J*=9.3 Hz, H_4), 3.62 (dt, 1H, J=9.5, 5.4 Hz, H_5), 0.91 (s, 9H, -C(CH_3)$_3$), 0.10 (s, 6H, 2CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 134.0 (-OCH_2CH=CH_2), 117.9 (-OCH_2CH=CH_2), 99.1 (C_1), 70.8, 70.9, 72.1, 71.1 (C_2, C_3, C_4, C_5), 68.4 (-OCH_2CH=CH_2), 65.1 (C_6), 26.3 (-C(CH_3)$_3$), 18.6 (-C(CH_3)$_3$), -5.1 (-CH_3), -5.0 (-CH_3).

HRMS (ESI): *m/z* calcd. for $C_{25}H_{34}NaO_6Si$ $[M+Na]^+$: 481.2022; found: 481.2017.

Allyl-2-*O*-acetyl-4-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranose (30)

Camphorsulfonic acid (0.20g, 0.84 mmol) and trimethyl orthoacetate (1.6 mL, 12.54 mmol) were sequentially added to a solution of **29** (1.40 g, 4.18 mmol) in CH_3CN (70 mL) and the reaction mixture was stirred at room temperature for 1 hour. The reaction was then quenched with Et_3N (650 μL) and the solvent was evaporated. The crude was dissolved in CH_2Cl_2 (60 mL) and Bz_2O (1.89 g, 8.36mmol), Et_3N (2.33 mL, 16.72 mmol) and 4-DMAP (50 Mg, 0.42 mmol) were sequentially added. The reaction mixture was stirred at room temperature for 1 hour. The solvent was evaporated and the crude residue was diluted with EtOAc (150 mL). The organic phase was washed with 1 M HCl (150 mL), sat. $NaHCO_3$ (150 mL) and water (150 mL), the organic phase was dried over anh. $MgSO_4$ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (hexane:EtOAc, 2.5:1) to obtain compound **30** as a colorless oil (1.31 g, 66%).

R_f: 0.20 (hexane/EtOAc, 2:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.05 (d, 2H, *J*=3.4 Hz, H_{Ar} ortho), 7.59 (t, 1H, *J*=7.5 Hz, H_{Ar} para), 7.46 (t, 2H, *J*=7.8 Hz, H_{Ar} meta), 5.99-5.87 (m, 1H, -OCH_2CH=CH_2), 5.36 (t, 1H, *J*=9.7 Hz, H_4), 5.34 (ddd, 1H, *J*=17.1, 3.4, 1.7 Hz, -OCH_2CH=CH_2), 5.24 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz, -OCH_2CH=CH_2), 5.12 (dd, 1H, *J*=3.6, 1.7 Hz, H_2), 4.95 (d, 1H, *J*=1.6 Hz, H_1), 4.27-4.23 (m, 1H, H_3), 4.22 (m , 1H, -OCH_2CH=CH_2) , 4.04 (m , 1H, -OCH_2CH=CH_2), 3.94 (ddd, 1H, *J*=10.0, 4.7, 2.8 Hz, H_5), 3.82-3.75 (m, 2H, 2H_6), 2.16 (s, 3H, -CO(CH_3)), 0.86 (s, 9H, -C(CH_3)$_3$), -0.01 (d, 6H, J=14.5 Hz, 2 CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.9 (C=O), 167.3 (C=O), 133.8 (-OCH_2CH=CH_2 + C_{AR}), 130.2 (C_{AR}), 129.9 (C_{AR}), 128.8 (C_{AR}), 118.1 (-OCH_2CH=CH_2), 96.7 (C_1), 73.1 (C_2), 71.6 (C_5), 70.9 (C_4), 69.4 (C_3), 68.7 (-OCH_2CH=CH_2), 62.8 (C_6), 26.2 (-C(CH_3)$_3$), 21.4 (-CO(CH_3)), 18.6 (-C(CH_3)$_3$), -5.1 (-CH_3), -5.0 (-CH_3).

HRMS (ESI): *m/z* calcd. for $C_{34}H_{40}NaO_8Si$ $[M+Na]^+$: 627.2390; found: 627.2388.

Allyl-2-*O*-acetyl-4-*O*-benzoyl-α-D-mannopyranose (31)

AcOH (1.2 mL) and TBAF (THF solution (1M), 2.17 mL, 2.17 mmol) were sequentially added to a solution of **30** (1.05 g, 2.18 mmol) in THF (16 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (hexane:EtOAc, 1:1) to afford **31** as a colorless oil (601 mg, 75%).

R_f: 0.38 (hexane/EtOAc, 1:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.06(d, 2H, *J*=8.2 Hz, C_{Ar} ortho), 7.60 (t, 1H, *J*=7.5 Hz, C_{Ar} para), 7.46 (t, 2H, *J*=7.9 Hz, C_{Ar} meta), 5.97-5.87 (m, 1H, -OCH_2CH=CH_2), 5.36-5.30 (m, 2H, -OCH_2CH=CH_2 + H_4), 5.25 (ddd, 1H, *J*=10.4, 2.8, 1.4 Hz, -OCH_2CH=CH_2), 5.17 (dd, 1H, *J*=3.7, 1.7 Hz, H_2), 4.98 (d, 1H, *J*=1.7 Hz, H_1), 4.37-4.31 (m, 1H, H_3), 4.21 (ddt, 1H, *J*=12.9, 5.4, 1.5 Hz, -OCH_2CH=CH_2), 4.05 (ddt, 1H, *J*=12.9, 6.1, 1.4 Hz, -OCH_2CH=CH_2), 3.90 (ddd, 1H, *J*=10.1, 4.7, 2.8 Hz, H_5), 3.76 (d, 1H, *J*=12.7 Hz, H_6), 3.70 (dd, 1H, *J*=12.6, 4.2 Hz, H_6), 2.18 (s, 3H, -CO(CH_3)).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0 (C=O), 167.7 (C=O), 134.1 (C_{Ar}), 133.6 (-OCH_2CH=CH_2), 130.3 (C_{Ar}), 129.4 (C_{Ar}), 128.9 (C_{Ar}), 118.4 (-OCH_2CH=CH_2), 97.1 (C_1), 72.92 (C_2), 70.9 (C_5), 70.6 (C_4), 69.1 (-OCH_2CH=CH_2), 68.8 (C_3), 61.8 (C_6), 21.41 (-CO(CH_3)).

HRMS (ESI): *m/z* calcd. for $C_{18}H_{22}NaO_8$ $[M+Na]^+$: 389.1212; found: 389.1205.

Allyl-*O*-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl-(1-3)-*O*-[2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl-(1-6)]-2-*O*-acetyl-4-*O*-benzoyl-α-D-mannopyranose (33)

A mixture of the acceptor **31** (58 mg, 0.16 mmol) and the donor **32** (286 mg, 0.38 mmol) was co-evaporated from toluene three times. Powdered and activated 4 Å molecular sieves were added, and the mixture was kept under vacuum for few hours and then dissolved in dry DCM (5 mL). The mixture was cooled to 0°C for 15 min, followed by the addition of TMSOTf (8.5μl, 0.047mmol), and stirred for 30 min at 0°C The reaction was quenched by the addition of Et3N, filtered through celite and dried under vacuum. The crude was purified by flash column chromatography on silica gel hexane:EtOAc, 1.75:1) to obtain **33** as a colorless solid (254mg, quant.).

R_f: 0.56 (hexane/EtOAc, 1:2)

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.14 (dd, 2H, *J*=8.3, 1.4 Hz, 2H_{Ar}), 8.10-8.07 (m, 2H, 2H_{Ar}), 8.06-8.04 (m, 2H, 2H_{Ar}), 8.04-8.02 (m, 2H, 2H_{Ar}), 8.02-7.99 (m, 2H, 2H_{Ar}), 7.99-7.96 (m, 2H, 2H_{Ar}), 7.83 (dd, 2H, *J*=8.4, 1.4 Hz, 2H_{Ar}), 7.81-7.78 (m, 2H, 2H_{Ar}), 7.76 (dd, 2H, *J*=8.4, 1.4 Hz, 2H_{Ar}), 7.61-

7.47 (m, 6H, 6H_{Ar}), 7.46-7.20 (m, 21H, 21H_{Ar}), 6.10 (t, 1H, *J*=10.1 Hz, H_{4B}), 6.04 (t, 1H, *J*=10.1 Hz, H_{4C}), 6.00-5.90 (m, 2H, -OCH$_2$C*H*=CH$_2$+H_{3B}), 5.80-5.71 (m, 3H, H_{2B}+H_{4A}+H_{3C}), 5.52 (dd, 1H, *J*=3.5, 1.7 Hz, H_{2A}), 5.43 (ddd, 1H, *J*=17,3. 3.0, 1.5 Hz, -OCH$_2$CH=C*H*$_2$), 5.39 (dd, 1H, *J*=3.3, 1.8 Hz, H_{2C}), 5.32-5.28 (m, 2H, -OCH$_2$CH=C*H*$_2$ + H_{1C}), 5.12 (d, 1H, *J*=1.8 Hz, H_{1B}), 5.00 (d, 1H, *J*=1.6 Hz, H_{1A}), 4.70 (dd, 1H, *J*=12.2, 2.3 Hz, H_{6C}), 4.65-4.59 (m, 3H, H_{3A}+H_{5C}+H_{6C}), 4.55 (ddd, 1H, *J*=10.2, 4.5, 2.5 Hz, H_{5B}), 4.51 (dd, 1H, *J*=12.2, 4.1 Hz, H_{6B}), 4.41 (dd, 1H, *J*=12.1, 4.5 Hz, H_{6B}), 4.34 (ddt, 1H, *J*=12.9, 5.4, 1.4 Hz, -OC*H*$_2$CH=CH$_2$), 4.21 (ddd, 1H, *J*=10.3, 6.5, 2.1 Hz, H_{5A}), 4.16 (ddt, 1H, *J*=12.8, 6.2, 1.3 Hz, -OC*H*$_2$CH=CH$_2$), 4.10 (dd, 1H, *J*=11.2, 6.8 Hz, H_{6A}), 3.73 (dd, 1H, *J*=10.8, 2.2 Hz, H_{6A}), 2.36 (s, 3H, -COC*H*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.8 (C=O), 166.2 (C=O), 166.1 (C=O), 165.5 (C=O), 165.4 (C=O), 165.3 (C=O), 165.2 (C=O), 165.0 (C=O), 164.5 (C=O), 133.4 (C_{Ar}), 133.4 (C_{Ar}), 133.4 (C_{Ar}), 133.2 (C_{Ar}), 133.1 (C_{Ar}), 133.1 (C_{Ar}), 133.0 (C_{Ar}), 129.9 (C_{Ar}), 129.9 (C_{Ar}), 129.9 (C_{Ar}), 129.8 (C_{Ar}), 129.8 (C_{Ar}), 129.7 (C_{Ar}), 129.7 (C_{Ar}), 129.7 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 129.1 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 128.4 (C_{Ar}), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 118.7 (-OCH$_2$CH=*C*H$_2$), 99.2 (C_{1C}), 97.5 (C_{1B}), 96.5 (C_{1A}), 74.4, 71.1 (C_{2A}), 70.4, 70.2 (C_{2C}), 70.0, 69.8, 69.7, 69.22, 69.1, 68.9, 68.6 (-O*C*H$_2$CH=CH$_2$), 66.8, 66.6, 62.8 (C_6), 21.1 (-CO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{86}H_{74}NaO_{26}$ [M+Na]$^+$: 1545.4366; found: 1545.4361

Allyl-*O*-(α-D-mannopyranosyl-(1-3)-*O*-[α-D-mannopyranosyl-(1-6)]-α-D-mannopyranose (34)

NaOMe (50 mg, 0.93 mmol) was added in one portion to a solution of compound **33** (229 mg, 0.15 mmol) in MeOH/Toluene (4:1, 7.5 mL) and the reaction mixture was stirred at room temperature for 1 h. Aqueous NaOH (1M, 3 mL) was then added and the reaction mixture was heated at 50°C and stirred for 7 h. After neutralization with amberlite IRA 120 H^+, the solution was filtered and concentrated. The crude was dilute with water (10 mL) and washed with toluene (2x, 10 mL), the aqueous phase was separated and the water was evaporated to afford **34** (70 mg, 90%) as a colourless amorphous solid.

^{1}H NMR (D_2O, 500 MHz): δ = 5.85 (dddd, 1H, *J*=17.1, 10.4, 6.2, 5.4 Hz, -OCH$_2$C*H*=CH$_2$), 5.23 (ddd, 1H, *J*=17.2, 3.2, 1.6 Hz, -OCH$_2$CH=C*H*$_2$), 5.15 (ddd, 1H, *J*=10.4, 2.6, 1.3 Hz, -OCH$_2$CH=C*H*$_2$), 4.98 (d, 1H, *J*=1.7 Hz, H_1), 4.77 (d, 1H, *J*=1.8 Hz, H_1), 4.75 (d, 1H, *J*=1.8 Hz, H_1), 4.10 (ddt, 1H, J=12.9, 5.4, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 3.98 (dd, 1H, *J*=2.5, 1.7 Hz, H_2), 3.96 (ddd, 1H, *J*=6.7, 2.6, 1.3 Hz, -OC*H*$_2$CH=CH$_2$), 3.94 (dd, 1H, *J*=3.4, 1.7 Hz, H_2), 3.88 (dd, 1H, *J*=7.0, 4.4 Hz, H_6), 3.86 (dd, 1H, *J*=3.5, 1.7 Hz, H_2), 3.79-3.73 (m, 5H, H_3+2H_6), 3.71 (dd, 2H, *J*=8.9, 3.4 Hz), 3.67-3.57 (m, 4H, 3H_6), 3.56-3.50 (m, 3H).

^{13}C NMR (D_2O, 125 MHz): δ = 133.1 (-OCH$_2$*C*H=CH$_2$), 118.2 (-OCH$_2$CH=*C*H$_2$), 102.3 (C_1), 99.2 (C_1), 99.1 (C_1), 78.4, 73.2, 72.6, 71.0, 70.5, 70.2, 69.9 (C_2), 69.8 (C_2), 69.5 (C_2), 68.2 (-O*C*H$_2$CH=CH$_2$), 66.6, 66.6, 65.6, 65.1 (C_6), 60.9 (C_6), 60.8 (C_6).

HRMS (ESI): *m/z* calcd. for $C_{21}H_{36}NaO_{16}$ [M+Na]$^+$: 567.1901; found: 567.1895.

General Procedure for the Synthesis of oxime neoglycoconjugates

(Procedure C) Ozone was bubbled through a solution of allyl glycoside **16** (250 mg) in methanol (75 ml) at -78°C until the solution turned blue (~ 25 min). The solution was purged under N_2 flow to remove the excess of ozone and dimethyl sulfide (1 ml) was added. After a few minutes, nitrogen was again passed through the solution, which was then allowed to warm to room temperature. The solvent was removed under reduced pressure to afford glycosyl aldehydes **29**-**39** as a colorless oil (quant.) *O*-benzylhydroxylamine hydrochloride (1.1 equiv) was then added to the solution of the corresponding glycosyl aldehydes (10 mg, 1 equiv) in H_2O (1mL). The reaction was stirred at 40°C for 30 min and the final oxime was purified by semi preparative HPLC to obtain the *Z*/*E* mixture of neo-glycoconjugates (**47**-**58**).

(*E*/*Z*) α-D-mannopyranosyl acetaldehyde *O*-benzyl oxime (47)

According to the previously described procedure C, compound **47** was obtained (12.5 mg, 85%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.56 (dd, 1H, *J*= 6.3, 5.3 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.37-7.27 (m, 10H, 5H_{Ar} *E* isomer + 5H_{Ar} *Z* isomer), 6.93 (t, 1H, *J*=3.7 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.10 (s, 2H, CH_{2Bn} *Z* Isomer), 5.08 (s, 2H, CH_{2Bn} *E* Isomer), 4.82 (s, 1H, *J*=1.7 Hz, H_1 *E* isomer), 4.80 (d, 1H, *J*=1.7 Hz, H_1 *Z* isomer), 4.54 (dd, 1H, *J*=16.4, 3.6 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.41 (dd, 1H, *J*=16.4, 3.9 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.26 (dd, 1H, *J*=12.7, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.15 (dd, 1H, *J*=12.7, 6.3 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.86-3.84 (m, 3H, H_2 + H_6 *Z* isomer), 3.84-3.81 (m, 1H, H_2 + H_6 *E* isomer), 3.75-3.67 (m, 4H, H_3 + H_6 *Z* and *E* isomer), 3.66-3.61 (m, 2H, H_4 *Z* and *E* isomer), 3.56-3.50 (m, 2H, H_5 *Z* and *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 151.5 (-OCH$_2$-*C*H=N-O- *Z* isomer), 148.9 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.4 (C_{Ar}), 139.4 (C_{Ar}), 129.8 (C_{Ar}), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 129.3 (C_{Ar}), 129.3 (C_{Ar}), 102.3 (C_1 *Z* isomer), 101.8 (C_1 *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.4 (CH_{2Bn} *E* isomer), 75.5 (C_5 *Z* isomer), 75.4 (C_5 *E* isomer), 72.9 (C_3 isomer and *Z* isomer), 72.4 (C_2 isomer and *Z* isomer), 69.0 (C_4 *Z* isomer), 68.9 (C_4 *E* isomer), 65.5 (-OC*H*$_2$-CH=N-O- *E* isomer), 63.3 (-OC*H*$_2$-CH=N-O- *Z* isomer), 63.3 (C_6 *Z* and *E* isomer).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{21}NNaO_7$ [M+Na]$^+$: 350.1216; found: 350.1213.

(*E*/*Z*) α-D-glucopyranosyl acetaldehyde *O*-benzyl oxime (48)

According to the previously described procedure C, compound **48** was obtained (11.8 mg, 80%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.62 (dd, 1H, *J*=6.2, 5.4 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.39-7.28 (m, 10H, 5H_{Ar} *E* isomer + 5H_{Ar} *Z* isomer), 7.02 (t, 1H, *J*=3.7 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.12 (s, 2H, CH_{2Bn} *Z* Isomer), 5.09 (s, 2H, CH_{2Bn} *Z* Isomer), 4.86 (d, 1H, *J*=4.0 Hz, H_1 *E* isomer), 4.85 (d, 1H, *J*=4.0 Hz, H_1 *Z* isomer), 4.58 (dd, 1H, *J*=16.5, 3.6 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.45 (dd, 1H, *J*=16.5, 3.8 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.31 (dd, 1H, *J*=12.9, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.20 (dd, 1H, *J*=12.9, 6.2 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.83 (dt, 2H, *J*=11.9, 2.4 Hz, H_6 *Z* and *E* isomer), 3.73-3.63 (m, 4H, H_3 + H_6 *Z* and *E* isomer), 3.60 (ddd, 2H, *J*=10.1, 5.6, 2.3 Hz, H_5 *Z* and *E* isomer), 3.45 (dd, 1H, *J*=7.6, 3.8 Hz, H_2 *Z* or *E* isomer), 3.43 (dd, 1H, *J*=7.7, 3.8 Hz, H_2 *Z* or *E* isomer), 3.35-3.30 (m, 2H, H_4 *Z* and *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 151.8 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.2 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.4 (C_{Ar}), 129.8 (C_{Ar}), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 129.3 (C_{Ar}), 129.3 (C_{Ar}), 101.0 (C_1 *E* isomer), 100.5 (C_1 *Z* isomer), 77.7 (CH_{2Bn} *Z* isomer),, 77.4 (CH_{2Bn} *E* isomer), 75.4 (C_3 *Z* and *E* isomer), 74.5 (C_4 *Z* isomer), 74.4 (C_5 *E* isomer), 73.8 (C_2 *E* isomer), 73.8 (C_2 *Z* isomer), 72.2 (C_4 *Z* isomer), 72. 1 (C_4 *E* isomer), 66.1 (-OC*H*$_2$-CH=N-O- *E* isomer), 63.8 (-OC*H*$_2$-CH=N-O- *Z* isomer), 63.0 (C_6 *Z* isomer), 63.0 (C_6 *E* isomer).

HRMS (ESI): *m/z* calcd. for $C_{15}H_{21}NNaO_7$ [M+Na]$^+$: 350.1216; found: 350.1210.

(*E*/*Z*) β-D-glucopyranosyl acetaldehyde *O*-benzyl oxime (49)

According to the previously described procedure C, compound **49** was obtained (12.2 mg, 83%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.63-7.54 (t, 1H, *J*=5.5 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.43-7.24 (m, 10H, 5H_{Ar} *E* isomer + 5H_{Ar} *Z* isomer), 7.00 (t, 1H, *J*=3.6 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 5.10 (s, 2H, CH_{2Bn} *Z* Isomer), 5.07 (s, 2H, CH_{2Bn} *Z* Isomer), 4.67 (dd, 1H, *J*=16.6, 3.5 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.55 (dd, 1H, *J*=16.6, 3.8 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.41 (dd, 1H, *J*=12.9, 5.3 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.30 (d, 1H, *J*=7.9 Hz, H_1 *Z* isomer), 4.29 (d, 1H, *J*=7.9 Hz, H_1 *E* isomer), 4.28 (dd, 1H, *J*=13.1, 6.2 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.86 (ddd, 2H, *J*=11.9, 3.7, 2.3 Hz, H_6 *Z* and *E* isomer), 3.68 (dd, 2H, *J*=12.0, 5.5 Hz, H_6 *Z* and *E* isomer), 3.40-3.16 (m, 8H, H_2 + H_3 + H_4 + H_5 *Z* and *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 152.3 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.6 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.5 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 105.0 (C$_1$ *Z* isomer), 104.4 (C$_1$ *E* isomer), 78.4 (C$_5$ *Z* and *E* isomer), 77.7 (CH$_{2Bn}$ *Z* isomer), 77.3 (CH$_{2Bn}$ *E* isomer), 75.4 (C$_2$ *Z* and *E* isomer), 71.9 (C$_4$ *Z* and *E* isomer), 67.5 (-O*C*H$_2$-CH=N-O- *E* isomer), 65.4(-O*C*H$_2$-CH=N-O- *Z* isomer), 63.1 (C$_6$ *Z* and *E* isomer).

H HRMS (ESI): *m/z* calcd. for C$_{15}$H$_{21}$NNaO$_7$ [M+Na]$^+$: 350.1216; found: 350.1213.

(*E/Z*) α-D-galactopyranosyl acetaldehyde *O*-benzyl oxime (50)

According to the previously described procedure, compound **50** was obtained (11.8 mg, 80%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.61 (t, 1H, *J*=5.7 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.40 (m, 10H, 5H$_{Ar}$ *E* isomer + 5H$_{Ar}$ *Z* isomer), 7.02 (t, 1H, *J*=3.7 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.10 (s, 2H, CH$_{2Bn}$ *E* isomer), 5.08 (s, 2H, CH$_{2Bn}$ *Z* isomer), 4.88 (s, 1H, *J*=4.0 Hz, H$_1$ *E* isomer or H$_1$ *Z* isomer), 4.85 (s, 2H, *J*=4.0 Hz, H$_1$ *E* isomer or H$_1$ *Z* isomer), 4.55 (dd, 1H, *J*=16.5, 3.5 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.43 (dd, 1H, *J*=16.5, 3.8 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.29 (dd, 1H , *J*=12.9, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.18 (dd, 1H, *J*=13.0, 6.1 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.91-3.88 (m, 2H, H$_4$ *E* isomer + H$_4$ *Z* isomer), 3.85-3.65 (m, 10, H$_2$ + H$_3$ + H$_5$ +2H$_6$ *E* and *Z* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 151.9 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.4 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.4(C$_{Ar}$), 129.8 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.3 (C$_{Ar}$), 101.3 (C$_1$ *E* isomer or *Z* isomer), 100.8 (C$_1$ *E* isomer or *Z* isomer), 77.8, 77.4, 73.3, 73.1, 71.8, 71.5, 70.5, 66.1 (-O*C*H$_2$-CH=N-O- *E* isomer), 64.0 (-O*C*H$_2$-CH=N-O- *Z* isomer), 63.2, 63.1.

HRMS (ESI): *m/z* calcd. for C$_{15}$H$_{21}$NNaO$_7$ [M+Na]$^+$: 350.1216; found: 350.1210.

(*E/Z*) β-D-galactopyranosyl acetaldehyde *O*-benzyl oxime (51)

According to the previously described procedure C, compound **51** was obtained (13.3 mg, 90%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.59 (dd, 1H, *J*=6.2, 5.3 Hz, -OCH$_2$-*C*H=N-O- *E* isomer), 7.38-7.27 (m, 10H, 5H$_{Ar}$ *E* isomer + 5H$_{Ar}$ *Z* isomer), 7.00 (t, 1H, *J*=3.6 Hz, -OCH$_2$-*C*H=N-O- *E* isomer), 5.09 (s, 2H, CH$_{2Bn}$ *Z* isomer), 5.07 (s, 2H, CH$_{2Bn}$ *E* isomer), 4.67 (dd, 1H, *J*=16.6, 3.5 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.55 (dd, 1H, *J*=16.6, 3.7 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.41 (dd, 1H, *J*=12.9, 5.2 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.31-4.24 (m, 3H, + -OC*H*$_2$-CH=N-O- *E* isomer + H$_1$ *E* and *Z* isomer), 4.01-3.95 (m, 2H, H$_5$ *Z* and *E* isomer), 3.85 (dd, 1H, *J*=3.4, 1.5 Hz, H$_4$ *E* isomer), 3.84 (dd, 1H, *J*=3.4, 1.5 Hz, H$_4$ *Z* isomer), 3.80-3.70 (m, 3H, 3H$_6$), 3.67-3.61 (m, 1H, H$_6$), 3.58-3.44 (m, 4H, H$_2$ + H$_3$ *Z* and *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 152.4 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.7 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.5 (C$_{Ar}$) 129.8 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.3 (C$_{Ar}$), 105.6 (C$_1$ *Z* isomer), 104. 9 (C$_1$ *E* isomer) 85.0 , 83.7 , 77.7 (CH$_{2Bn}$ *Z* isomer), 77.3 (CH$_{2Bn}$ *Z* isomer), 77.2 (C$_3$ *Z* or *E* isomer), 77.8 (C$_5$ *Z* or *E* isomer), 75.3 (C$_5$ *Z* or *E* isomer), 72.8, 70.7 (C$_4$ *Z* or *E* isomer), 70.7 (C$_4$ *Z* or *E* isomer), 67.5 (-O*C*H$_2$-CH=N-O- *E* isomer), 65.4 (-O*C*H$_2$-CH=N-O- *Z* isomer), 62.9 (C$_6$ *Z* and *E* isomer).

HRMS (ESI): *m/z* calcd. for C$_{15}$H$_{21}$NNaO$_7$ [M+Na]$^+$: 350.1216; found: 350.1212.

(*E/Z*) α-L-fucopyranosyl acetaldehyde *O*-benzyl oxime (52)

According to the previously described procedure C, compound **52** was obtained (13.7 mg, 85%) as a colorless solid after HPLC purification (R_t: 8.3 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.58 (t, 1H, *J*=5.7, -OCH$_2$-C*H*=N-O- *E* isomer), 7.38-7.26 (m, 10H, *E* isomer + 5H$_{Ar}$ *Z* isomer) 6.97 (t, 1H, *J*=3.7 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.10 (s, 2H, CH$_{2Bn}$ *Z* Isomer), 5.07 (s, 2H, CH$_{2Bn}$ *E* Isomer), 4.82 (d, 1H, *J*=3.1 Hz, H$_1$ *E* isomer), 4.78 (d, 1H, *J*=3.1 Hz, H$_1$ *Z* isomer), 4.48 (dd, 1H, *J*=16.4, 3.7 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.38 (dd, 1H, *J*=16.4, 3.8 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.22 (dd, 1H, *J*=12.9, 5.6 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.16 (dd, 1H, *J*=12.9, 6.2 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.96-3.90 (m, 2H, H$_5$ *E* and *Z* isomer), 3.77-3.72 (m, 4H, H$_2$ + H$_3$ *E* and *Z* isomer), 3.68-3.66 (m, 2H, H$_4$ *E* and *Z* isomer), 1.22 (d, 3H, *J*=5.6 Hz, H$_6$ *Z* isomer), 1.21 (d, 3H, *J*=6.7 Hz, H$_6$ *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 151.4 (-OCH$_2$-*C*H=N-O- *Z* isomer), 148.9 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.0 (C$_{Ar}$), 129.4 (C$_{Ar}$), 129.4 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.1 (C$_{Ar}$), 129.0 (C$_{Ar}$), 128.9 (C$_{Ar}$), 100.9 (C$_1$ *Z* isomer), 100.6 (C$_1$ *E* isomer), 77.4 (CH$_{2Bn}$ *Z* isomer), 77.0 (CH$_{2Bn}$ *E* isomer), 73.5 (C$_4$ *E* or *Z* isomer), 71.6 (C$_2$ or C$_3$ *E* isomer), 71.5 (C$_2$ or C$_3$ *Z* isomer), 69.9 (C$_2$ or C$_3$ *Z* isomer), 69.8 (C$_2$ or C$_3$ *E* isomer), 67.9 (C$_6$ *Z* isomer), 67.9 (C$_6$ *E* isomer), 65.9 (-O*C*H$_2$-CH=N-O- *E* isomer), 63.4 (-O*C*H$_2$-CH=N-O- *Z* isomer), 16.7 (C$_6$ *Z* isomer), 16.7(C$_6$ *E* isomer).

HRMS (ESI): *m/z* calcd. for C$_{15}$H$_{21}$NNaO$_6$ [M+Na]$^+$: 334.1267; found:334.1263.

(*E/Z*) β-L-fucopyranosyl acetaldehyde *O*-benzyl oxime (53)

According to the previously described procedure C, compound **53** was obtained (14.5 mg. 90%) as a colorless solid after HPLC purification (R_t: 8.3 min).

^{1}H NMR (MeOD, 500 MHz): δ = 7.57 (dd, 1H, *J*=6.2, 5.4 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.40-7.26 (m, 10H, 5H$_{Ar}$ *E* isomer + 5H$_{Ar}$ *Z* isomer) 6.98 (t, 1H, *J*=3.6 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.10 (s, 2H, CH$_{2Bn}$ *Z* isomer), 5.07 (s, 2H, CH$_{2Bn}$ *E* isomer), 4.60 (dd, 1H, *J*=16.6, 3.6 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.51 (dd, 1H, *J*=16.6, 3.7 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.34 (dd, 1H, *J*=12.9, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.25 (dd, 1H, *J*=12.9, 6.2 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.22 (d, 1H, *J*= 7.3 Hz, H$_1$ *Z* isomer), 4.20 (d, 1H, *J*= 7.3 Hz, H$_1$ *E* isomer), 3.68-3.54 (m, 4H, H$_4$ + H$_5$ *E* and *Z* isomer), 3.53-3.42 (m, 4H, H$_2$ + H$_3$ *E* and *Z* isomer)), 1.28 (d, 3H, *J*=5.6 Hz, H$_6$ *E* isomer or H$_6$ *Z* isomer), 1.26 (d, 3H, *J*=5.6 Hz, H$_6$ *E* isomer or H$_6$ *Z* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 152.5 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.6 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.6 (C$_{Ar}$), 139.5 (C$_{Ar}$), 129.7 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.2 (C$_{Ar}$), 105.4 (C$_1$ *Z* isomer), 104.7 (C$_1$ *E* isomer), 77.7 (CH$_{2Bn}$ *E* isomer), 77.3 (CH$_{2Bn}$ *E* isomer), 75.5 (C$_3$ or C$_2$ *E* and *Z* isomer), 73.4 (C$_5$ *E* and *Z* isomer), 72.5 (C$_4$ *E* or *Z* isomer), 72.5 (C$_4$ *E* or *Z* isomer), 72.4 (C$_3$ or C$_2$ *E* and *Z* isomer), 67.4 (-O*C*H$_2$-CH=N-O- E isomer), 65.2 (-O*C*H$_2$-CH=N-O- *Z* isomer), 17.1 (C$_6$ *E* and *Z* isomer).

HRMS (ESI): *m/z* calcd. for C$_{15}$H$_{21}$NNaO$_6$ [M+Na]$^+$: 334.1267; found: 334.1262.

(*E/Z*) 2-acetamido-2-deoxy-β-D-glucopyranosyl acetaldehyde *O*-benzyl oxime (54)

According to the previously described procedure C, compound **54** was obtained (12.6 mg, 90%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ =7.52 (dd, 1H, *J*=6.4, 5.4 Hz, -OCH$_2$-*C*H=N-O- *E* isomer), 7.38-7.27 (m, 10H, , 5H$_{Ar}$ *E* isomer + 5H$_{Ar}$ *Z* isomer), 6.90 (t, 1H, *J*=3.6 Hz, -OCH$_2$-*C*H=N-O- *Z* isomer), 5.09 (s, 2H, CH$_{2Bn}$ *Z* isomer), 5.06 (s, 2H, CH$_{2Bn}$ *E* isomer), 4.61 (dd, 1H, *J*=16.5, 3.5 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.49 (dd, 1H, *J*=16.6, 3.8 Hz, -OC*H*$_2$-CH=N-O- *Z* isomer), 4.46 (d, 1H *J*= 8.4 Hz, H$_1$ *E* isomer), 4.44 (d, 1H *J*= 8.4 Hz, H$_1$ *Z* isomer), 4.34 (dd, 1H, *J*=12.8, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.23 (dd, 1H, *J*=12.8, 6.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.88 (dt, 2H, *J*=12.0, 2.6 Hz, H$_6$ *Z* and *E* isomer), 3.77-3.61 (m, 4H, H$_4$ + H$_6$ *Z* and *E* isomer), 3.46 (dd, 2H, *J*=10.3, 8.7 Hz, H$_4$ *Z* and *E* isomer), 3.38-3.34 (m, 2H, H$_4$ *Z* and *E* isomer), 3.27 (tdd, 2H, *J*=9.9, 5.7, 2.3 Hz, H$_5$ *Z* and *E* isomer), 2.00 (s, 3H, -NHCO*C*H$_3$ *Z* isomer), 1.98 (s, 3H, -NHCO*C*H$_3$ *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 174.3 (C=O), 174.3 (C=O), 152.16 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.36 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.4 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.7 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.3 (C$_{Ar}$), 103.1 (C$_1$ *E* isomer), 102.5 (C$_1$ *E* isomer), 78.5 (C$_5$ *Z* isomer), 78.5 (C$_5$ *E* isomer), 77.7 (CH$_{2Bn}$ *Z* isomer), 77.4 (CH$_{2Bn}$ *E* isomer), 76.4 (C$_2$ *Z* and *E* isomer), 72.4 (C$_4$ *Z* and *E* isomer), 67.2 (-O*C*H$_2$-CH=N-O- *E* isomer), 65.1 (-O*C*H$_2$-CH=N-O- *Z* isomer), 63.1 (C$_6$ *E* isomer), 63.1 (C$_6$ *Z* isomer), 57.6 (C$_4$ *E* isomer), 57.6 (C$_4$ *Z* isomer), 23.4 (-NHCO*C*H$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}N_2NaO_7$ [M+Na]$^+$: 391.1481; found: 391.1477.

(*E/Z*) 2-acetamido-2-deoxy-β-D-galactopyranosyl acetaldehyde *O*-benzyl oxime (55)

According to the previously described procedure C, compound **55** was obtained (11.6 mg, 83%) as a colorless solid after HPLC purification (R_t: 8.5 min).

^{1}H NMR (MeOD, 500 MHz): δ =7.51 (dd, 1H, *J*=6.4, 5.4 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.40- 7.23 (m, 10H, 5H$_{Ar}$ *E* isomer + 5H$_{Ar}$ *Z* isomer), 6.90 (t, 1H, *J*=3.6 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer) 5.09 (s, 2H, CH$_{2Bn}$ *Z* Isomer), 5.06 (s, 2H, CH$_{2Bn}$ *E* Isomer), 4.62 (dd, 1H, *J*=16.6, 3.4 Hz, , -OC*H*$_2$-CH=N-O- *Z* isomer), 4.50 (dd, 1H, *J*=16.5, 3.8 Hz, , -OC*H*$_2$-CH=N-O- *Z* isomer), 4.43 (d, 1H, *J*=8.4 Hz, H$_1$ *E* isomer), 4.42 (d, 1H, *J*=8.4 Hz, H$_1$ *Z* isomer), 4.35 (dd, 1H, *J*=12.8, 5.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 4.23 (dd, 1H, *J*=12.8, 6.4 Hz, -OC*H*$_2$-CH=N-O- *E* isomer), 3.94 (dd, 1H, *J*=10.7,8.4 Hz, H$_2$ *Z* isomer), 3.93 (dd, 1H, *J*=10.7,8.4 Hz, H$_2$ *E* isomer) 3.85 (d, 2H, *J*=3.4, H$_2$ *Z* and *E* isomer), 3.79 (dd, 2H, *J*=11.4, 6.8 Hz, H$_6$ *Z* and *E* isomer), 3.75 (dd, 2H, *J*=11.3, 5.3 Hz, H$_6$ *Z* and *E* isomer), 3.60 (dd, 2H, *J*=10.6, 3.3 Hz, H$_3$ *Z* and *E* isomer), 3.50 (ddd, 2H, *J*=7.8, 6.6, 5.3 Hz, H$_5$ *Z* and *E* isomer), 2.00 (s, 3H, -NHCOCH$_3$ *Z* isomer), 1.98 (s, 3H, -NHCOCH$_3$ *E* isomer).

^{13}C NMR (MeOD, 125 MHz): δ = 174.6 (C=O), 152.2 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.4 (-OCH$_2$-*C*H=N-O- *E* isomer), 139.4 (C$_{Ar}$), 129.7 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.3 (C$_{Ar}$), 129.3 (C$_{Ar}$), 103.5 (C$_1$ *Z* isomer), 102.9 (C$_1$ *E* isomer), 77.7 (CH$_{2Bn}$ *Z* isomer), 77.3 (C$_5$ *Z* isomer), 77.3 (C$_5$ *E* isomer), 77.2 (CH$_{2Bn}$ *E* isomer), 73.7 (C$_3$ *Z* and *E* isomer), 70.0 (C$_4$ *Z* and *E* isomer), 67.1 (-O*C*H$_2$-CH=N-O- *E* isomer), 65.0 (-O*C*H$_2$-CH=N-O- *Z* isomer), 62.9 (C$_2$ *Z* and *E* isomer), 54.6 (C$_2$ *E* isomer), 54.5 (C$_2$ *Z* isomer), 23.4 (-NHCOCH$_3$).

HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}N_2NaO_7$ [M+Na]$^+$: 391.1481; found: 391.1477.

(*E/Z*) O-β-D-galactopyranosyl-(1-4)-β-D-glucopyranosyl acetaldehyde *O*-benzyl oxime (56)

According to the previously described procedure C, compound **56** was obtained (10.8 mg, 85%) as a colorless solid after HPLC purification (R_t: 9.2 min).

^{1}H NMR (D$_2$O-MeOD, 500 MHz): δ = 7.53 (t, 1H, *J*=5.5 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.42-7.22 (m, 10H, H$_{Ar}$), 6.96 (t, 1H, *J*=3.8 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.01 (s, 3H, CH$_{2Bn}$ *Z* isomer), 5.00 (s, 3H, CH$_{2Bn}$ *E* isomer), 4.55 (dd, 1H, *J*=16.6, 3.8 Hz, -OC*H*$_2$CHN *Z* isomer), 4.49 (dd, 1H, *J*=16.6, 3.8 Hz, -OC*H*$_2$CHN *Z* isomer), 4.39-4.20 (m, 6H, -OC*H*$_2$CHN *Z* isomer + H$_{1A}$ + H$_{1B}$ *Z* and *E* isomer), 3.79 (d, 2H, J=3.4 Hz, H$_{4B}$ *Z* and *E* isomer), 3.79-3.27 (m, 20H, H$_{3A}$ + H$_{4A}$ + H$_{5A}$ + 2H$_{6A}$ + H$_{2B}$ + H$_{3B}$ + H$_{5B}$ + 2H$_{6B}$ *Z* and *E* isomer).

^{13}C NMR (D$_2$O-MeOD, 125 MHz): δ = 151.6 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.4 (-OCH$_2$-*C*H=N-O- *E* isomer), 137.4 (C$_{Ar}$), 137.2 (C$_{Ar}$), 128.9 (C$_{Ar}$), 128.6 (C$_{Ar}$), 128.4 (C$_{Ar}$), 103.4 (C$_1$), 102.9 (C$_1$), 78.7, 76.3, 76.0, 75.8, 75.2, 74.8, 73.1, 71.4, 69.0, 66.1, 61.4 (C$_6$), 60.3 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_{21}H_{31}NNaO_{12}$ [M+Na]$^+$: 512.1744; found: 512.1738.

(*E/Z*) O-α-D-glucopyranosyl-(1-4)-β-D-glucopyranosyl acetaldehyde O-benzyl oxime (57)

According to the previously described procedure C, compound **57** was obtained (10.2 mg, 80%) as a colorless solid after HPLC purification (R_t: 9.2 min).

^{1}H NMR (D$_2$O-MeOD, 500 MHz): δ =7.53 (t, 1H, *J*=5.6 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.42-7.26 (m, 10H, H$_{Ar}$), 6.97 (t, 1H, *J*=4.0 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.28-5.18 (m, 2H, H$_{1B}$ *Z* and *E* isomer), 5.03 (s, 3H, CH$_{2Bn}$ *E* isomer), 5.02 (s, 3H, CH$_{2Bn}$ *Z* isomer), 4.54 (td, 1H, *J*=4.5, 1.9 Hz, -OC*H*$_2$CHN *Z* isomer), 4.34-4.17 (m, 3H, -OC*H*$_2$CHN *Z* isomer + H$_{1A}$ *Z* and *E* isomer), 3.81-3.43 (m, 18H, H$_{3A}$ + H$_{4A}$ + 2H$_{6A}$ + H$_{2B}$ + H$_{3B}$ + H$_{4B}$ + 2H$_{6B}$ *Z* and *E* isomer), 3.37-3.26 (m, 2H, H$_{5A}$), 3.24-3.13 (m, 4H, H$_{2A}$ + H$_{5B}$ *Z* and *E* isomer).

^{13}C NMR (D$_2$O-MeOD, 125 MHz): δ = 152.0 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.7 (-OCH$_2$-*C*H=N-O- *E* isomer), 137.3 (C$_{Ar}$), 129.1 (C$_{Ar}$), 129.0 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.7 (C$_{Ar}$), 128.6 (C$_{Ar}$), 101.6 (C$_{1A}$), 100.4 (C$_{1B}$), 77.7, 77.5, 76.4, 76.0, 74.9, 73.4, 73.2, 73.0, 72.2, 69.7, 66.0, 64.0, 60.9 (C$_6$), 60.8 (C$_6$).

HRMS (ESI): *m/z* calcd. for $C_{21}H_{31}NNaO_{12}$ [M+Na]$^+$: 512.1744; found: 512.1740.

O-α-D-mannopyranosyl-(1-3)-O-[α-D-mannopyranosyl-(1-6)]-α-D-mannopyranosyl acetaldehyde O-benzyl oxime (58)

According to the previously described procedure, compound **58** was obtained (10.0 mg, 85%) after HPLC purification (R_t: 9.0 min).

^{1}H NMR (D$_2$O, 500 MHz): δ =7.63 (t, 1H, *J*=4.0 Hz, -OCH$_2$-C*H*=N-O- *E* isomer), 7.49 (m, 10H, H$_{Ar}$), 7.02 (t, 1H, *J*=4.0 Hz, -OCH$_2$-C*H*=N-O- *Z* isomer), 5.11 (s, 2H, CH$_{2Bn}$ *E* Isomer), 5.10 (s, 2H, CH$_{2Bn}$ *Z* Isomer), 5.05 (s, 2H, H$_{1B}$ *Z* and *E* isomer), 4.83 (s, 1H, H$_{1A}$ *Z* Isomer), 4.82 (s, 1H, H$_{1A}$ *E* isomer), 4.80 (s, 2H, H$_{1C}$ *Z* and *E* Isomer), 4.49 (ddd, 1H, *J*=16.0, 4.1, 1.3 Hz, -OC*H*$_2$CHN *Z* isomer), 4.40 (ddd, 1H, *J*=16.0, 4.0, 1.3 Hz, -OC*H*$_2$CHN- *E* isomer), 4.27-4.16 (m, 2H, -OC*H*$_2$CHN *E* isomer), 4.07 (d, 1H, *J*=8.3 Hz, H$_{2C}$), 4.04-3.99 (m, 1H, H$_{2B}$), 3.95-3.88 (m, 4H, H$_{2A}$ +H$_{2B}$ *Z* and *E* Isomer), 3.87-3-81 (m, 13H, H$_{3B}$+H$_6$ *Z* and *E* Isomer), 3.81-3.76 (m, 3H), 3.75-3.68 (m, 10H), 3.66-3.54 (m, 10H).

^{13}C NMR (D$_2$O, 125 MHz) 152.2 (-OCH$_2$-*C*H=N-O- *Z* isomer), 149.9 (-OCH$_2$-*C*H=N-O- *E* isomer),, 129.2 (C$_{Ar}$), 128.9(C$_{Ar}$), 128.8 (C$_{Ar}$), 128.6 (C$_{Ar}$), 102.8 (C$_{1B}$), 100.7 (C$_1$), 100.6 (C$_1$), 99.9 (C$_1$), 78.8, 76.3 (CH$_{2Bn}$ *Z* isomer), 76.1 (CH$_{2Bn}$ *E* isomer), 73.7, 63.1, 71.8, 71.8, 71.0, 71.0, 70.8, 70.5, 70.3, 70.3, 69.9, 69.8, 60.4, 67.1, 65.9, 65.5 (C$_6$), 64.6 (-OC*H*$_2$-CH=N-O- *E* isomer), 61.96, 61.35(-OC*H*$_2$-CH=N-O- *Z* isomer).

HRMS (ESI): *m/z* calcd. for $C_{27}H_{41}NNaO_{17}$ [M+Na]$^+$: 674.2272; found: 674.2265.

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Supporting Information

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Primary Data

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References

(1) (a) Varki, A.; Cummings, R.; Esko, J.; Freeze, H.; Hart, G.; Marth, J. *Essentials of Glycobiology*, 2nd ed., Cold Spring Harbor Laboratory Press, New York, **2009**. (b) Wittman V. In Glycoscience (Eds.: B. Fraser-Reid, K. Tatsuta and J. Thiem), Springer-Verlag, Berlin, Germany, **2008**, 135; c) Varki, A. *Glycobiology* **2017**, 27, 3.

(2) (a) Roy, R. *Drug Discov. Today: Technol.* **2004**, *1*, 327. (b) Fernández-Tejada, A.; Cañada, F. J.; Jiménez-Barbero, J. *ChemMedChem* **2015**, *10*, 1291.

(3) (a) Bertozzi, C. R.; Kiessling, L. L. *Science* **2001**, *291*, 2357. (b) Raman, R.; Raguram, S.; Venkataraman, G.; Paulson, J. C.; Sasisekharan , R. *Nat. Methods* **2005**, *2*, 817. (c) Timmer, M. S.; Stocker, B. L.; Seeberger, P. H. *Curr. Opin. Chem. Biol.* **2007**, *11*, 59.

(d) Cunningham, S.; Gerlach, J. Q.; Kane, M.; Joshi, L. *Analyst* **2010**, 135, 2471–2480.
(4) Villadsen, K.; Martos-Maldonado, M. C.; Jensen, K. J.; Thygesen M. B. *ChemBioChem* **2017**, 18, 574.
(5) Larsen, K.; Thygesen, M. B.; Guillaumie, F.; Willats, W. G. T.; Jensen, K. J. *Carbohydr. Res.* **2006**, *341*, 1209.
(6) Godula, K.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2012**, *134*, 15732.
(7) (a) Sletten, E. M.; Bertozzi, C. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 6974. (b) Prescher, J. A.; Dube, D. H.; Bertozzi, C. R. *Nature* **2004** *430*, 873. (c) Prescher, J. A; Bertozzi, C. R. *Nat. Chem. Biol.* **2005**, *1*, 13.
(8) Baskin, J. M.; Prescher, J. A.; Laughlin, S. T.; Agard, N. J.; Chang, P. V.; Miller, I. A.; Lo, A.; Codelli, J. A.; Bertozzi, C. R. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 16793.
(9) Ning, X.; Temming, R. P.; Dommerholt, J.; Guo, J.; Blanco-Ania, D.; Debets, M. F.; Wolfert, M. A.; Boons, G.-J.; Van Delft, F. L. *Angew. Chem. Int. Ed.* **2010**, *49*, 3065.
(10) Yarema, K. J.; Mahal, L. K.; Bruehl, R. E.; Rodriguez, E. C.; Bertozzi, C. R. *J. Biol. Chem.* **1998**, 273, 31168.
(11) (a) Blackman, M. L.; Royzen, M.; Fox, J. M. J. Amer. Chem. Soc. **2008**, *130*, 13518. (b) Ehret, F.; Wu, H.; Alexander, S. C.; Devaraj, N. K. *J. Am. Chem. Soc.* **2015**, *137*, 8876. (c) Šečkutė, J.; Devaraj, N. K. *Curr. Opin. Chem. Biol.* **2013**, *17*, 761.
(12) Stöckmann, H.; Neves, A. A.; Stairs, S.; Brindle, K. M.; Leeper, F. J. *Org. Biomol. Chem.* **2011**, *9*, 7303.
(13) Sletten, E. M.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2011**, *133*, 17570.
(14) (a) Zhao, Y.; Kent, S.B; Chait, B.T.; *Proc. Natl. Acad. Sci. U.S.A.* **1997**, 94, 162. (b) Gehin, C.; Montenegro, J.; Bang, E.-K.; Cajaraville, A.; Takayama, S.; Hirose, H.; Futaki, S.; Matile, S.; Riezman, H. *J. Am. Chem. Soc.* **2013**, *135*, 9295. (c) Priegue, J. M.; Crisan, D. N.; Martínez-Costas, J.; Granja, J. R.; Fernandez-Trillo, F.; Montenegro, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 7492. (d) Crisan, D. N.; Creese, O.; Ball, R.; Brioso, J. L.; Martyn, B.; Montenegro, J.; Fernandez-Trillo, F. *Polym. Chem.* **2017**, *8*, 4576. (e) Pazo, M.; Fernández-Caro, H.; Priegue, J. M.; Lostalé-Seijo, I.; Montenegro, J. *Synlett* **2017**, *28*, 924. (f) Louzao, I.; García-Fandiño, R.; Montenegro, J. *J. Mat. Chem. B* **2017**, *5*, 4426. (g) Fuertes, A.; Marisa, J.; Granja, J. R.; Montenegro, J. *Chem. Commun.* **2017**, *53*, 7861.
(15) Cervigny, E.; Dumy, P.; Mutter, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1230.
(16) Forget, D.; Boturyn, D.; Defrancq, E.; Lhomme, J.; Dumy P. *Chem. Eur. J.* **2001**, 7, 3976.
(17) Kwase, Y. A.; Cochran, M.; Nitz, M. Protecting-Group-Free Glycoconjugate Synthesis: Hydrazide and Oxyamine Derivatives in N-Glycoside Formation. *Modern Synthetic Methods in Carbohydrate Chemistry: From Monosaccharides to Complex Glycoconjugates* **2013**, 67.
(18) Banoub, J.; Boullanger, P.; Lafont, D. *Chem. Rev.* **1992**, *92*, 1167.
(19) Wipf, P.; Eyer, B. R.; Yamaguchi, Y.; Zhang, F.; Neal, M. D.; Sodhi, C. P.; Good, M.; Branca, M.; Prindle Jr., T.; Lu, P.; Brodsky, J. L.; Hackam, D. J. *Tetrahedron Lett.* **2015**, *56*, 3097.
(20) (a) Zurabyan, S. E.; Bílik, V.; Bauer, S. *Chem. Zvesti* **1969**, *23*, 923. (b) Piekarska, B. *Roczn. Chem.* **1975**, *49*, 1919. (c) Cheetham, N. W. H.; Sirimanne, P. *Carbohydr. Res.* **1981**, 96, 126.
(21) Khamsi, J.; Ashmus, R. A.; Schocker, N. S.; Michael, K. *Carbohydr. Res.* **2012,** *357*, 147.
(22) (a) Reina, J. J.; Di Maio, A.; Ramos-Soriano, J.; Figueiredo, R. C.; Rojo, J. *Org. Biomol. Chem.,* **2016**, *14,* 2873. (b) Ramos-Soriano, J.; de la Fuente, M. C.; de la Cruz, N.; Figueiredo, R. C.; Rojo, J.; Reina, J. J. *Org. Biomol. Chem.*, **2017**, DOI: 10.1039/C7OB02286G.
(23) Reina, J. J.; Rojo, J. *Tetrahedron Lett.*, **2006**, *47*, 2475.
(24) Chang, S.-M.; Tu, Z.; Jan, H.-M.; Pan, J.-F.; Lin, C.-H. *Chem. Commun.* **2013**, *49*, 4265.
(25) Eichler, E.; Kihlberg, J.; Bundle, D. R. *Glycoconj. J.* **1991,** *8*, 69.
(26) Fang, T. T.; Zirrolli, J.; Bendiak, B. *Carbohydr. Res.* **2007**, *342*, 217.
(27) Villadsen, K.; Martos-Maldonado, M. C.; Jensen, K. J.; Thygensen, M. B. *ChemBioChem* **2017**, *18*, 574.

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