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Glycosyl Aldehydes: New Scaffolds for the Synthesis of Neoglycoconjugates via Bioorthogonal Oxime Bond Formation

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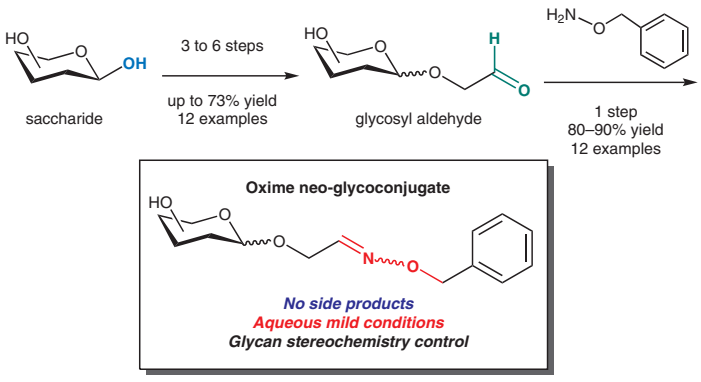

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Abstract The straightforward preparation of glycosyl neoconjugates by oxime (or hydrazone) bond formation represents a key bioorthogonal tool in chemical biology. However, when this strategy is employed by reacting the reducing end of the glycan moiety, the configuration and the stereochemical information is lost due to partial (or complete) 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 neoglycoconjugates via oxime bond formation. These glycosyl aldehydes constitute a simple and accessible alternative to avoid loss 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

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] Interactions between carbohydrates and cell-surface proteins 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 for the design and development of many diagnostic tools and for biosensors for clinical applications.[3] In the past decade, appreciation of the ubiquity of glycans and their ability to encode biochemical information has increased. 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 conjugated to other biomolecules, forming glycopeptides and glycoproteins, glycolipids, glycosylated natural products, and more.[1,2] A wide variety of linkage chemistry connecting carbohydrates and aglycons (noncarbohydrate part of a conjugate) is observed. The most prevalent linkage types consist of O-alkyl glycosides (glycolipids and glycoproteins), glycosyl amides (*N*-glycoproteins), and heterocyclic glycosylamines (DNA/RNA). Neoglycoconjugates, 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 purposes.[6]

Chemoselective reactions and, in particular, bioorthogonal reactions have been developed for the preparation of neoglycoconjugates.[7–13] Bioorthogonal chemistry includes any chemical reaction that can occur inside 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]

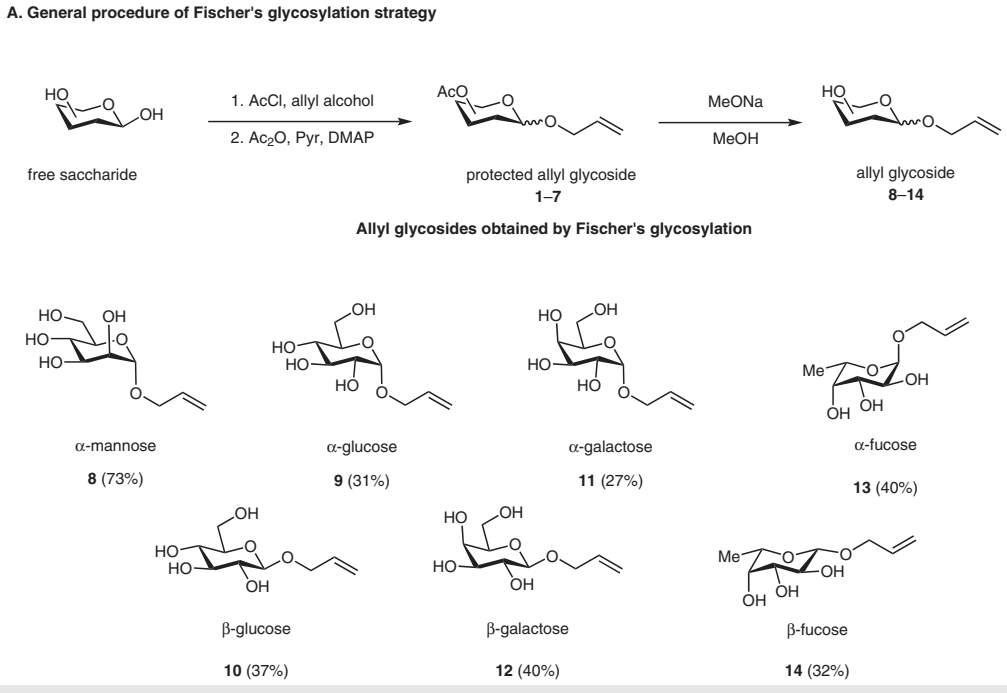
In this context, hydrazone and the oxime bond formation have frequently been employed for the efficient chemical ligation of peptides[14] as well as for the conjugation of peptides with carbohydrates[15] and oligonucleotides.[16] A

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 in the case of 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 loss of natural tridimensional conformation of the carbohydrate.[17] In the case of monosaccharides and small oligosaccharides, in which the reducing carbohydrate residue is involved in the interaction with the receptor, the activity of the neoglycoconjugates could be lost, and this type of chemoselective ligation is not suitable. Herein, we report the preparation of a glycosyl aldehyde library to synthesize neoglycoconjugates through oxime bond formation. The process consists of glycosylation with allyl alcohol followed by ozonolysis of the allyl group to afford the final 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.

The target carbohydrate library was composed of 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 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 allyl alcohol at 60 °C. This initial reaction produced a mixture of α- and β-isomers that was difficult to purify. Therefore, a transient protection of the free hydroxyl groups with Ac_2O, pyridine and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (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 that leads to a mixture of ring size isomers and anomeric isomers, which is a clear limitation of the method when only one of the isomers is required. However, the application of this protocol allowed access to reasonable amounts of both (α and β) allylglycopyranosides in a simple synthetic step.

The Fischer glycosylation of GlcNAc and GalNAc is not applicable because the oxazoline traps the intermediates and 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, given to the propensity of GlcNAc and Gal-



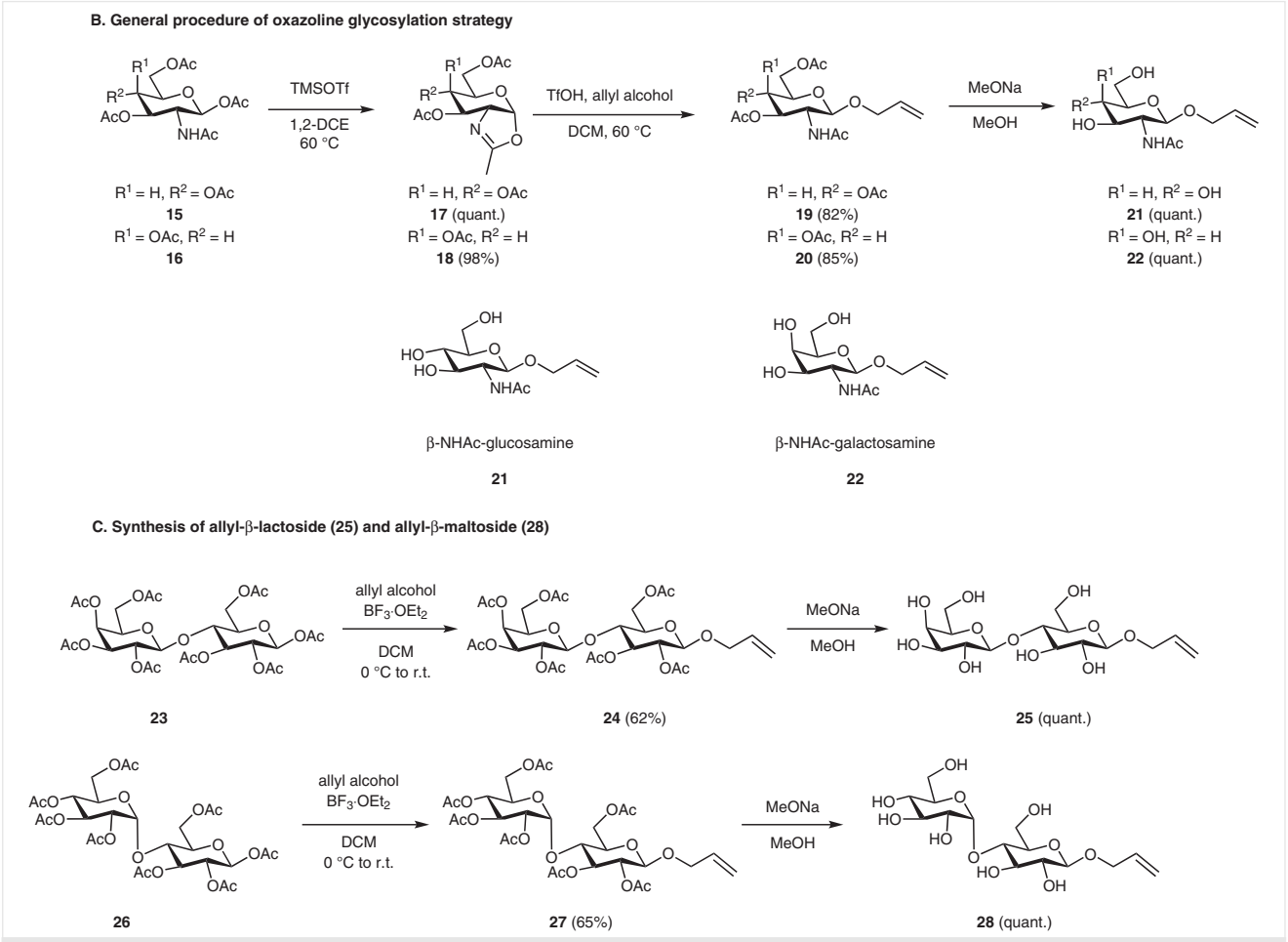
Scheme 1 Fisher's glycosidation strategy for the synthesis of allyl-glycosides **8–14**

NAc 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.

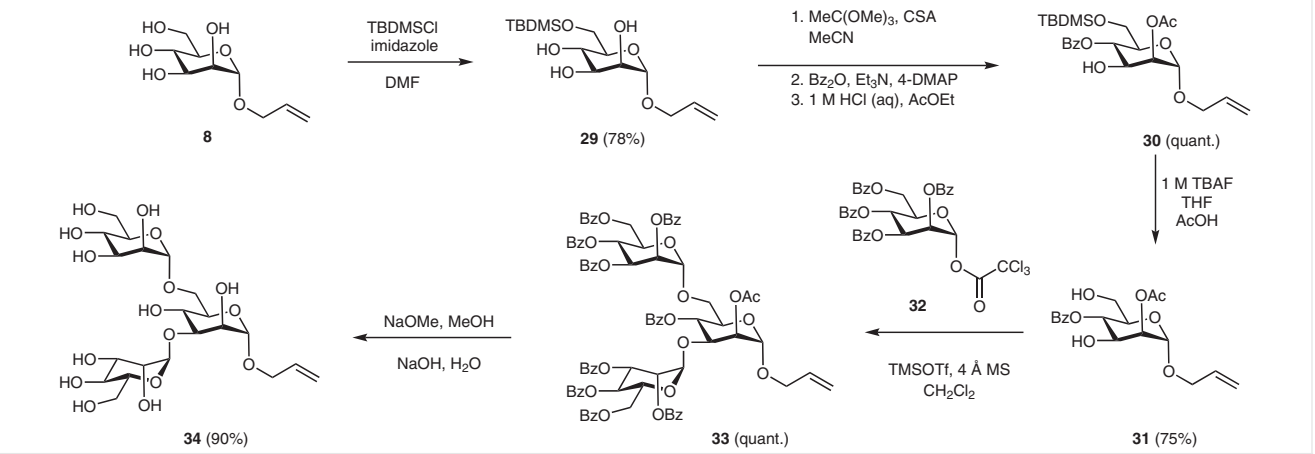
Starting from the GlcNAc (**15**) and GalNAc (**16**), the oxazoline was directly formed by following the procedure described by Hackam and co-workers,[19] using TMSOTf at 60 °C in 1,2-dichloroethane (DCE) as solvent, the oxazolines **17** and **18** were obtained in quantitative yield. Subsequently, **17** and **18** were glycosylated by using allyl alcohol as acceptor and TfOH as promoter in a sealed reaction vessel in CH_2Cl_2 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 allyl glycosides **21** and **22** in quantitative yields. This stereoselective strategy led only to the β-isomers of GlcNAc and GalNAc because 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 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 large 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 was determined by the presence of the neighboring acetyl group at position C2, which 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**) by following a multistep sequence[22] (Scheme 3). The strategy starts with selective protection of the primary hydroxyl group on C6 by using the bulky TBDMS-Cl and imidazole to give **29** with a good isolated yield after chromatography purification (78%).[23] Compound



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



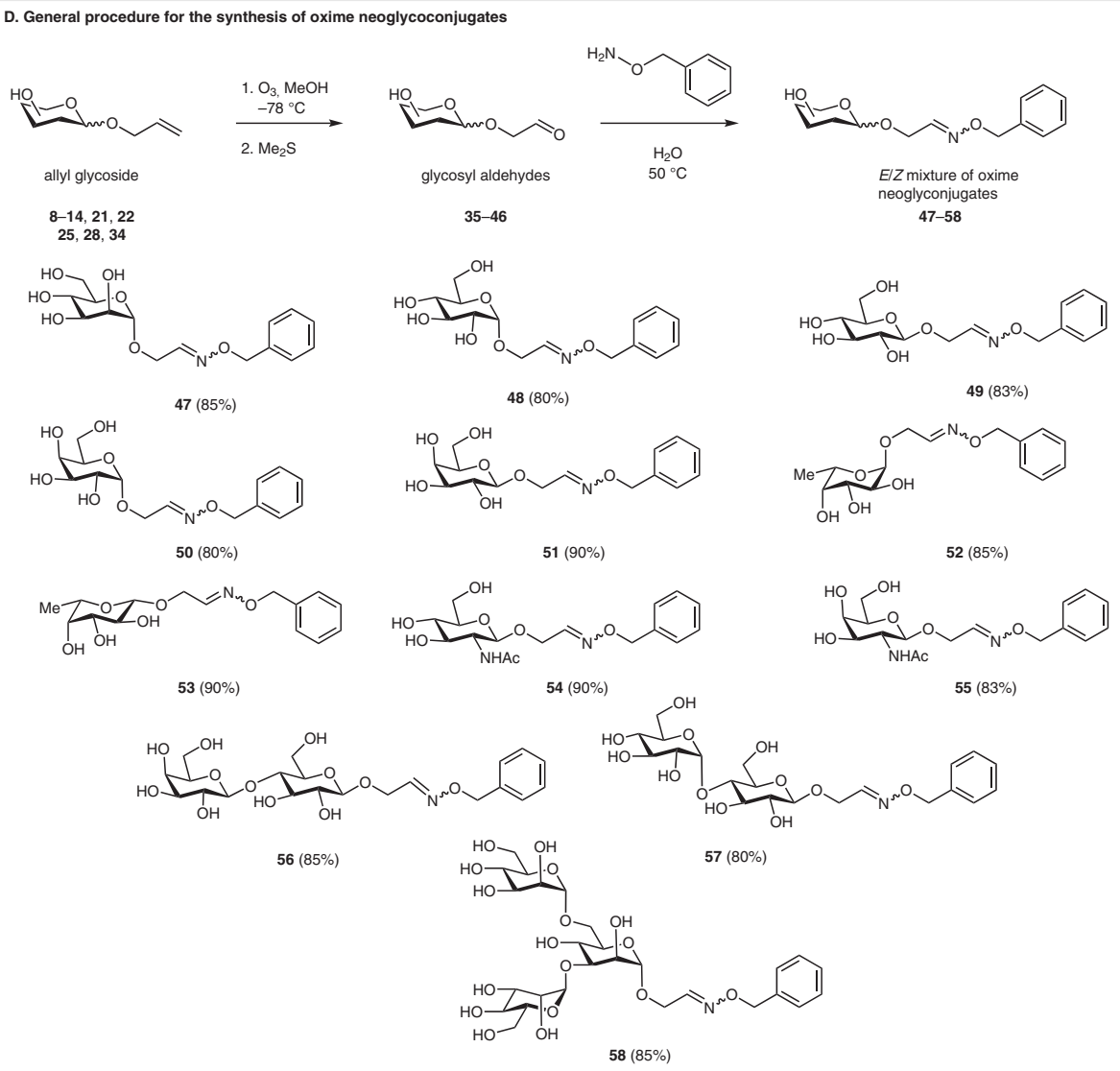
Scheme 3 Synthetic strategy for the synthesis of branched mannose trisaccharide Manα1,3[Manα1,6]Man (**34**)

29 was treated with trimethyl orthoacetate and a catalytic amount of 10-camphorsulfonic acid (CSA) to form the acetyl orthoester with the hydroxyl groups at positions C2 and C3. It was not possible to isolate this orthoester because of 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 led to 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 tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) afforded mannose **31** in good yield.

The benzoylated trichloroacetimidate glycosyl donor **32** was prepared by following reported procedures.[22] The targeted trimannosides **33** incorporates the α-linkage, which is favored because of the neighboring group at the C2 position of the glycosyl donors. Trisaccharide **33** was prepared by reaction of glycosyl donor **32** with glycosyl acceptors **31** using trimethylsilyltriflate (TMSOTf) as promoter at 0 °C with quantitative yield. The allyl trisaccharide was prepared by deprotection of acetyl and benzoyl groups under classical Zemplén 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 into an aldehyde through ozonolysis, with quantitative yields in all cases.[25] Analysis by NMR spectroscopy of these glycosyl aldehydes is not trivial, because at least three different species, in different ratios, could be identified by ^{1}H 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 through 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 demonstrate the potential utility of the strategy for bioorthogonal conjugation, the glycosyl aldehydes were reacted with *O*-benzylhydroxylamine to form the corresponding oxime neoglycoconjugates. This reaction was tested for all the prepared glycosyl aldehydes under physiologically 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%).

The straightforward preparation of glycosyl neoconjugates by oxime (or hydrazone) bond formation represents a key bioorthogonal 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 complete) 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., alkoxyamines) to afford the corresponding oximes under physiologically compatible conditions. The methodology included a Fischer strategy for **43**–**53**, oxazoline strategy for **54**–**55**, and direct glycosylation of peracetylated donor for **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 spectroscopic 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 intramolecular addition of the hydroxyls to the aldehyde function. However, these complex mixtures were readily resolved by reaction with the alkoxyamine nucleophiles, leading to the final oxime products.



Scheme 4 Synthesis of oxime neoglycoconjugates **47–58**

In summary, we have completed the synthesis of a library of glycosyl aldehydes to be used as scaffold for the synthesis of neoglycoconjugates via chemoselective ligation reactions, in particular, as oxime bond formation. These glycosyl aldehydes constitute a simple and accessible alternative to avoid loss 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 alkoxyamines by incubation in water at 40 °C. This strategy minimizes the potential loss of the natural tridimensional conformation of the carbohydrate when directly conjugated by oxime bonds to the organic scaffolds such as rigid molecules, peptides, and polymers.

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 with a Bruker AC 500 with solvent peaks as reference. ^1H and ^{13}C NMR spectra were obtained from solutions in $CDCl_3$ and CD_3OD and D_2O at 298 K. Coupling constants (J) are reported in Hz. Splitting patterns are described by as: 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. ^1H NMR spectra are reported as: 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 electrospray

ionization (ESI) with a Bruker Microtof mass spectrometer using MeOH or CH_3CN/H_2O as solvent system. High-performance liquid chromatography (HPLC) semipreparative purification was carried out with a JASCO MD-4015 with an Agilent Eclipse XDB-C18 column [Nucleosil 100–7 C18; Gradient: H_2O (0.1% TFA)/CH_3CN (0.1% TFA), 95:5→5:95 (0→10 min)]. t_R retention time.

Protected Allyl Glycosides 1–7; General Procedure A

A solution of AcCl (530 µL, 7.45 mmol) in allyl alcohol (18 mL) was stirred at r.t. for 1 h, 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 h. The mixture was cooled to r.t., then the reaction was 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 material and the solution was stirred at r.t. for 2 h. The mixture was diluted in EtOAc (100 mL) and washed with HCl 1 M (3 × 100 mL), $NaHCO_3$ sat. soln (3 × 100 mL) and brine (100 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude material was purified by silica gel column chromatography (Hex/EtOAc) to obtain the α- and β-pyranosyl isomers of monosaccharides **1**–**7**.

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

According to General Procedure A, the residue was purified by flash chromatography on silica gel (Hex/EtOAc, 2:1) to afford the corresponding α-pyranosyl isomer **1**.

Yield: 3.15 g (73%); colorless solid; R_f 0.42 (hexane/EtOAc, 2:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.92 (dddd, *J* = 17.0, 10.3, 6.3, 5.3 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.39 (dd, *J* = 10.0, 3.4 Hz, 1 H, H3), 5.33 (ddd, *J* = 17.2, 3.0, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.31 (t, *J* = 10.1, 1.5 Hz, 1 H, H4), 5.29–5.24 (m, 2 H, H2 + $OCH_2CH{=}CH_2$), 4.89 (d, *J* = 1.7 Hz, 1 H, H1), 4.30 (dd, *J* = 12.2, 5.3 Hz, 1 H, H6), 4.21 (ddt, *J* = 12.8, 5.3, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.13 (dd, *J* = 12.2, 2.5 Hz, 1 H, H6), 4.08–4.00 (m, 2 H, H5 + $OCH_2CH{=}CH_2$), 2.17 (s, 3 H, $OCOCH_3$), 2.12 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.01 (s, 3 H, $OCOCH_3$).

^{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 (C1), 70.1 (C2), 69.5 (C3), 69.1 ($OCH_2CH{=}CH_2$ or C5), 69.0 ($OCH_2CH{=}CH_2$ or C5), 66.6 (C4), 62.9 (C6), 21.3 ($OCOCH_3$), 21.1 ($OCOCH_3$), 21.1 ($OCOCH_3$), 21.0 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{24}NaO_{10}$: 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 General 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, 1 H, $OCH_2CH{=}CH_2$), 5.51 (t, *J* = 9.8 Hz, 1 H, H3), 5.32 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.23 (ddd, *J* = 10.4, 3.0, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.11 (d, *J* = 3.7 Hz, 1 H, H1), 5.07 (t, *J* = 9.8 Hz, 1 H, H4), 4.90 (dd, *J* = 10.2, 3.8 Hz, 1 H, H2), 4.26 (dd, *J* = 12.3, 4.5 Hz, 1 H, H6), 4.20 (ddt, *J* = 13.0, 5.2, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.09–4.00 (m, 3 H, H5 + H6 + $OCH_2CH{=}CH_2$), 2.10 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.03 (s, 3 H, $OCOCH_3$), 2.01 (s, 3 H, $OCOCH_3$).

^{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 (C1), 70.7 (C2), 70.1 (C3), 68.8 ($OCH_2CH{=}CH_2$), 68.5 (C4), 67.3 (C5), 61.9 (C6), 20.7 ($OCOCH_3$), 20.7 ($OCOCH_3$), 20.7 ($OCOCH_3$), 20.6 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{24}NaO_{10}$: 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, 1 H, $OCH_2CH{=}CH_2$), 5.28 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.24–5.19 (m, 2 H, H3 + $OCH_2CH{=}CH_2$), 5.10 (t, *J* = 9.7 Hz, 1 H, H4), 5.03 (dd, *J* = 9.6, 8.0 Hz, 1 H, H2), 4.57 (d, *J* = 8.0 Hz, 1 H, H1), 4.35 (ddt, *J* = 13.2, 4.7, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.27 (dd, *J* = 12.3, 4.7 Hz, 1 H, H6), 4.15 (dd, *J* = 12.3, 2.4 Hz, 1 H, H6), 4.11 (ddt, *J* = 13.2, 6.1, 1.2 Hz, 1 H, $OCH_2CH{=}CH_2$), 3.70 (ddd, *J* = 10.0, 4.7, 2.5 Hz, 1 H, H5), 2.10 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.03 (s, 3 H, $OCOCH_3$), 2.01 (s, 3 H, $OCOCH_3$).

^{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 (C1), 72.9 (C3), 71.8 (C5), 71.3 (C2), 70.0 ($OCH_2CH{=}CH_2$), 68.4 (C4), 61.9 (C6), 20.7 ($OCOCH_3$), 20.7 ($OCOCH_3$), 20.6 ($OCOCH_3$), 20.6 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{24}NaO_{10}$: 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 General 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, 1 H, $OCH_2CH{=}CH_2$), 5.47 (dd, *J* = 3.4, 1.3 Hz, 1 H, H4), 5.39 (ddd, *J* = 11.9, 3.4, 1.6 Hz, 1 H, H3), 5.32 (ddd, *J* = 17.3, 3.4, 1.7 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.24 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.18–5.14 (m, 2 H, H1 + H2), 4.26 (td, *J* = 6.6, 1.4 Hz, H5), 4.20 (ddt, *J* = 13.1, 5.2, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.13–4.09 (m, 2 H, 2 H6), 4.03 (ddt, *J* = 13.1, 6.1, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 2.15 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.00 (s, 3 H, $OCOCH_3$).

^{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 ($OCH_2CH{=}CH_2$), 118.0 ($OCH_2CH{=}CH_2$), 95.3 (C1), 68.8 ($OCH_2CH{=}CH_2$), 68.1 (C4), 68.1 (C2), 67.6 (C3), 66.4 (C5), 61.7 (C6), 20.8 ($OCOCH_3$), 20.7 ($OCOCH_3$), 20.7 ($OCOCH_3$), 20.6 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{24}NaO_{10}$: 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, *J* = 17.3, 10.5, 6.1, 4.9 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.37 (dd, *J* = 3.5, 1.2 Hz, 1 H, H4), 5.30–5.17 (m, 3 H, H2 + $OCH_2CH{=}CH_2$), 5.01 (dd, *J* = 10.4, 3.5 Hz, 1 H, H3), 4.50 (d, *J* = 8.0 Hz, 1 H, H1), 4.35 (ddt, *J* = 13.2, 5.0, 1.6 Hz, 1 H, $OCH_2CH{=}CH_2$),

4.17 (dd, J = 11.3, 6.5 Hz, 1 H, H6), 4.15–4.06 (m, 2 H, H6 + OCH_2CH=CH_2), 3.89 (td, J = 6.7, 1.3 Hz, 1 H, H_5), 2.14 (s, 3 H, OCOCH_3), 2.04 (s, 3 H, OCOCH_3), 2.03 (s, 3 H, OCOCH_3), 1.97 (s, 3 H, OCOCH_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$_2$CH=CH$_2$), 117.9 (OCH$_2$CH=CH$_2$), 100.5 (C1), 71.3 (C3), 71.0 (C5), 70.4 (OCH$_2$CH=CH$_2$), 69.2 (C2), 67.4 (C4), 61.7 (C6), 21.1 (OCOCH$_3$), 21.0 (OCOCH$_3$), 21.0 (OCOCH$_3$), 20.9 (OCOCH$_3$).

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{24}NaO_{10}$: 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 General 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, 1 H, OCH$_2$CH=CH$_2$), 5.41 (dd, 1 H, J = 10.9, 3.3 Hz, H3), 5.35–5.29 (m, 2 H, H4 + OCH$_2$CH=CH$_2$), 5.23 (dd, J = 10.4, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.16 (dd, J = 10.8, 3.7 Hz, 1 H, H2), 5.11 (d, J = 3.6 Hz, 1 H, H1), 4.23–4.16 (m, 2 H, H5 + OCH$_2$CH=CH$_2$), 4.03 (dd, J = 13.3, 6.2 Hz, 1 H, OCH$_2$CH=CH$_2$), 2.18 (s, 3 H, OCOCH$_3$), 2.09 (s, 3 H, OCOCH$_3$), 2.00 (s, 3 H, OCOCH$_3$), 1.16 (d, J = 6.7 Hz, 3 H, H6).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0 (C=O), 170.8 (C=O), 170.4 (C=O), 133.9 (OCH$_2$CH=CH$_2$), 118.0 (OCH$_2$CH=CH$_2$), 95.7 (C1), 71.6 (C4), 69.0 (OCH$_2$CH=CH$_2$), 68.6 (C2 or C3), 68.5 (C2 or C3), 64.9 (C5), 21.2 (OCOCH$_3$), 21.1 (OCOCH$_3$), 21.0 (OCOCH$_3$), 16.2 (C6).

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{22}NaO_8$: 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, 1 H, OCH$_2$CH=CH$_2$), 5.20 (d, J = 17.2 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.17–5.10 (m, 3 H, H2 + H4 + OCH$_2$CH=CH$_2$), 4.95 (dd, J = 10.5, 3.2 Hz, 1 H, H3), 4.42 (d, J = 7.9 Hz, 1 H, H1), 4.29 (dd, J = 13.4, 4.7 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.02 (dd, J = 13.3, 6.0 Hz, 1 H, OCH$_2$CH=CH$_2$), 3.72 (q, J = 6.4, 1 H, H5), 2.10 (s, 3 H, OCOCH$_3$), 1.98 (s, 3 H, OCOCH$_3$), 1.91 (s, 3 H, OCOCH$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.1 (C=O), 170.6 (C=O), 169.9 (C=O), 134.0 (OCH$_2$CH=CH$_2$), 117.7 (OCH$_2$CH=CH$_2$), 100.3 (C1), 71.8 (C3), 70.7 (C2 or C4), 70.3 (C2 or C4), 69.6 (OCH$_2$CH=CH$_2$), 69.4 (C5), 21.2 (OCOCH$_3$), 21.1 (OCOCH$_3$), 21.0 (OCOCH$_3$), 16.5 (C6).

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

Deprotected Allyl Glycosides 8–14; General Procedure B

To a solution of protected glycosides (0.07 mmol) in anhydrous MeOH (1.5 mL), NaOMe (0.01 mmol) was added in one portion and the solution was stirred at r.t. After TLC showed a complete conversion (ca. 1 h) Amberlite IRA 120H$^+$ 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 monosaccharides **8–14**.

Allyl-α-D-mannopyranose (8)

According to General Procedure B, compound **8** was obtained (404 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 5.96 (dddd, J = 17.3, 10.7, 6.0, 5.1 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.32 (dq, J = 17.3, 1.8 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.19 (dq, J = 10.4, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.81 (d, J = 1.7 Hz, 1 H, H1), 4.24 (ddt, J = 13.1, 5.1, 1.6 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.03 (ddt, J = 13.1, 6.0, 1.4 Hz, 1 H, OCH$_2$CH=CH$_2$), 3.85 (dd, J = 11.8, 2.4 Hz, 1 H, H6), 3.83 (dd, J = 3.4, 1.7 Hz, 1 H, H2), 3.76–3.70 (m, 2 H, H3 + H6), 3.63 (t, J = 9.5 Hz, 1 H, H4), 3.55 (ddd, J = 9.8, 5.8, 2.3 Hz, 1 H, H5).

^{13}C NMR (CD_3OD, 125 MHz): δ = 135.9 (OCH$_2$CH=CH$_2$), 117.6 (OCH$_2$CH=CH$_2$), 101.1 (C1), 75.1 (C5), 73.1 (C3), 72.6 (C2), 69.2 (OCH$_2$CH=CH$_2$), 69.1 (C4), 63.4 (C6).

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

Allyl-α-D-glucopyranose (9)

According to General Procedure B, compound **9** was obtained (315 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.10–5.91 (m, 1 H, OCH$_2$CH=CH$_2$), 5.36 (ddd, J = 17.3, 3.4, 1.7 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.19 (ddd, J = 10.5, 3.0, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.85 (d, J = 3.7 Hz, 1 H, H1), 4.25 (ddt, J = 13.0, 5.2, 1.6 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.06 (ddt, J = 13.0, 6.0, 1.4 Hz, 1 H, OCH$_2$CH=CH$_2$), 3.83 (dd, J = 11.8, 2.4 Hz, 1 H, H6), 3.72–3.66 (m, 2 H, H3 + H6), 3.60 (ddd, J = 10.0, 5.6, 2.4 Hz, 1 H, H5), 3.42 (dd, J = 9.7, 3.8 Hz, 1 H, H2), 3.37–3.27 (m, 1 H, H4).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.0 (OCH$_2$CH=CH$_2$), 117.9 (OCH$_2$CH=CH$_2$), 99.6 (C1), 75.5 (C3), 74.2 (C2), 74.0 (C5), 72.5 (C4), 69.7 (OCH$_2$CH=CH$_2$), 69.1 (C4), 63.1 (C6).

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

Allyl-β-D-glucopyranose (10)

According to General Procedure B, compound **10** was obtained (315 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 5.99 (dddd, J = 17.2, 10.5, 6.1, 5.2 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.35 (dq, J = 17.3, 1.7 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.18 (dq, J = 10.5, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.40 (ddt, J = 13.1, 5.1, 1.6 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.32 (d, J = 7.8 Hz, 1 H, H1), 4.17 (ddt, J = 13.1, 6.0, 1.4 Hz, 1 H, OCH$_2$CH=CH$_2$), 3.85 (dd, J = 11.9, 2.1 Hz, 1 H, H6), 3.39–3.25 (m, 5 H, H3 + H4 + H5), 3.22 (dd, J = 9.8, 7.8 Hz, 1 H, H2).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.2 (OCH$_2$CH=CH$_2$), 117.8 (OCH$_2$CH=CH$_2$), 103.8 (C1), 78.5 (C3), 78.4 (C5), 75.5 (C2), 72.1 (C4), 71.5 (OCH$_2$CH=CH$_2$), 63.4 (C6).

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

Allyl-α-D-galactopyranose (11)

According to General Procedure B, compound **11** was obtained (250 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 5.97 (dddd, J = 17.3, 10.4, 6.1, 5.2 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.33 (ddd, J = 17.3, 3.4, 1.7 Hz, 1 H, OCH$_2$CH=CH$_2$), 5.16 (ddd, J = 10.4, 3.0, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.86 (d, J = 3.3 Hz, 1 H, H1), 4.22 (ddt, J = 13.0, 5.2, 1.5 Hz, 1 H, OCH$_2$CH=CH$_2$), 4.03 (ddt, J = 13.0, 6.1, 1.4 Hz, 1 H, OCH$_2$CH=CH$_2$), 3.88 (dd, J = 2.7, 1.3 Hz, 1 H, H4), 3.81 (td, J = 6.0, 1.2 Hz, 1 H, H5), 3.76 (t, J = 2.6 Hz, 2 H, H2+H3), 3.70 (dd, J = 6.1, 2.0 Hz, 2 H, 2 H6).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.1 ($OCH_2CH=CH_2$), 117.9 ($OCH_2CH=CH_2$), 99.9 (C1), 72.9 (C2), 71.9 and 71.5 (C4 and C5), 70.7 (C3), 69.8 ($OCH_2CH=CH_2$), 63.1 (C6).

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

Allyl-β-D-galactopyranose (12)

According to General Procedure B, compound **12** was obtained (250 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.01 (dddd, *J* = 17.3, 10.4, 6.1, 5.2 Hz, 1 H, $OCH_2CH=CH_2$), 5.37 (ddd, *J* = 17.3, 3.4, 1.7 Hz, 1 H, $OCH_2CH=CH_2$), 5.19 (ddd, *J* = 10.5, 3.0, 1.5 Hz, 1 H, $OCH_2CH=CH_2$), 4.41 (ddt, *J* = 12.9, 5.3, 1.6 Hz, 1 H, $OCH_2CH=CH_2$), 4.30 (d, *J* = 7.7 Hz, 1 H, H1), 4.19 (ddt, *J* = 12.9, 6.1, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 3.87 (dd, *J* = 3.4, 1.1 Hz, 1 H, H4), 3.80 (dd, *J* = 11.4, 6.8 Hz, 1 H, H6), 3.76 (dd, *J* = 11.4, 5.5 Hz, 1 H, H6), 3.58 (dd, *J* = 9.7, 7.6 Hz, 1 H, H2), 3.53 (ddd, *J* = 6.7, 5.4, 1.2 Hz, 1 H, H5), 3.50 (dd, *J* = 9.7, 3.4 Hz, 1 H, H3).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.1 ($OCH_2CH=CH_2$), 117.7 ($OCH_2CH=CH_2$), 104.3 (C1), 76.0 (C5), 75.3 (C3), 72.8 (C2), 71.3 ($OCH_2CH=CH_2$), 70.6 (C4), 62.8 (C6).

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

Allyl-α-L-fucopyranoside (13)

According to General Procedure B, compound **13** was obtained (280 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.00 (dddd, *J* = 17.3, 10.3, 6.0, 5.3 Hz, 1 H, $OCH_2CH=CH_2$), 5.36 (ddd, *J* = 17.3, 3.4, 1.7 Hz, 1 H, $OCH_2CH=CH_2$), 5.21 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 4.84 (d, *J* = 3.0 Hz, 1 H, H1), 4.20 (ddt, *J* = 13.1, 5.3, 1.5 Hz, 1 H, $OCH_2CH=CH_2$), 4.07 (ddt, *J* = 13.1, 6.1, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 4.00 (q, *J* = 6.7 Hz, 1 H, H5), 3.82–3.76 (m, 2 H, H2 + H3), 3.70 (dd, *J* = 2.9, 1.3 Hz, 1 H, H4), 1.25 (d, *J* = 6.6 Hz, 3 H, 3 H6).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.2 ($OCH_2CH=CH_2$), 117.8 ($OCH_2CH=CH_2$), 100.0 (C1), 74.1 (C4), 72.1 (C2 or C3), 70.4 (C2 or C3), 69.9 ($OCH_2CH=CH_2$), 68.0 (C5), 17.0 (C6).

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

Allyl-β-L-fucopyranose (14)

According to General Procedure B, compound **14** was obtained (200 mg, quant.) as a colorless solid without further purification.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.00 (dddd, *J* = 17.1, 10.3, 6.0, 5.3 Hz, 1 H, $OCH_2CH=CH_2$), 5.36 (ddd, *J* = 17.3, 2.6, 1.3 Hz, 1 H, $OCH_2CH=CH_2$), 5.19 (ddd, *J* = 10.5, 2.8, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 4.36 (ddt, *J* = 12.9, 5.3, 1.6 Hz, 1 H, $OCH_2CH=CH_2$), 4.27 (d, *J* = 7.3 Hz, 1 H, H1), 4.15 (ddt, *J* = 12.9, 6.1, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 3.68–3.61 (m, 2 H, H4 + H5), 3.53 (dd, *J* = 9.7, 7.2 Hz, 1 H, H2), 3.49 (dd, *J* = 9.7, 3.2 Hz, 1 H, H3), 1.17 (d, *J* = 7.3 Hz, 3 H, 3 H6).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.3 ($OCH_2CH=CH_2$), 117.7 ($OCH_2CH=CH_2$), 104.3 (C1), 75.6 (C3), 73.4 (C4 or C5), 72.7 (C4 or C5), 72.3 (C2), 71.4 ($OCH_2CH=CH_2$), 17.1 (C6).

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

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 r.t. to a solution of peracetylated sugar **15** (2 g, 5.15 mmol) in anhydrous 1,2-dichloroethane (15 mL). The mixture was stirred for 4 h at 60 °C and allowed to cool to r.t. To this solution, triethylamine (2.9 mL) was added dropwise and, after 15 min at r.t., the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a $NaHCO_3$ sat. aq. soln (2 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, 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.[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 r.t. to a solution of peracetylated sugar **16** (2 g, 5.15 mmol) in anhydrous 1,2-dichloroethane (15 mL). The mixture was stirred for 4 h at 60 °C and allowed to cool to r.t. To this solution, triethylamine (2.9 mL) was added dropwise and, after 15 min at r.t., the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a $NaHCO_3$ sat. aq. soln (2 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, 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.[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 anhydrous 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 r.t., filtered through Celite and washed with CH_2Cl_2 (2 × 20 mL). The organic layer was washed with $NaHCO_3$ sat. aq. soln (2 × 50 mL) and brine (50 mL). The organic phase was dried over anhydrous $MgSO_4$, 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), to afford **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): δ = 5.86 (dddd, *J* = 16.9, 10.4, 6.3, 5.0 Hz, 1 H, $OCH_2CH=CH_2$), 5.54 (d, *J* = 8.8 Hz, 1 H, NHAc), 5.34–5.23 (m, 2 H, H3 + $OCH_2CH=CH_2$), 5.19 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 5.06 (t, *J* = 9.6 Hz, 1 H, H4), 4.71 (d, *J* = 8.3 Hz, 1 H, H1), 4.33 (ddt, *J* = 12.9, 5.0, 1.5 Hz, 1 H, $OCH_2CH=CH_2$), 4.25 (dd, *J* = 12.2, 4.8 Hz, 1 H, H6), 4.13 (dd, *J* = 12.3, 2.5 Hz, 1 H, H6), 4.08 (ddt, *J* = 13.0, 6.4, 1.4 Hz, 1 H, $OCH_2CH=CH_2$), 3.87 (dt, *J* = 10.6, 8.5 Hz, 1 H, H2), 3.70 (ddd, *J* = 10.0, 4.9, 2.5 Hz, 1 H, H5), 2.08 (s, 3 H, $OCOCH_3$), 2.02 ($OCOCH_3$), 2.01 ($OCOCH_3$), 1.94 ($NHCOCH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.3 (C=O), 171.1 (C=O), 170.6 (C=O), 169.8 (C=O), 133.9 ($OCH_2CH=CH_2$), 118.2 ($OCH_2CH=CH_2$), 100.1 (C1), 72.8 (C3), 72.2 (C5), 70.3 ($OCH_2CH=CH_2$), 69.1 (C4), 62.6 (C6), 55.2 (C2), 23.7 ($NHCOCH_3$), 21.1 ($OCOCH_3$), 21.1 ($OCOCH_3$), 21.0 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NNaO_9$: 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 anhydrous 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 r.t., filtered through Celite and washed with CH_2Cl_2 (2 × 20 mL). The organic layer was washed with $NaHCO_3$ sat. aq. soln (2 × 50 mL) and brine (50 mL). The organic phase was dried over anhydrous $MgSO_4$, 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), to afford **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, *J* = 17.0, 10.4, 6.3, 5.1 Hz, 1 H, OCH_2CH=CH_2), 5.46 (d, *J* = 8.6 Hz, 1 H, NHAc), 5.36 (dd, *J* = 3.4, 1.4 Hz, 1 H, H4), 5.33–5.25 (m, 2 H, H3 + OCH_2CH=CH_2), 5.22 (ddd, *J*=10.4, 3.0, 1.5 Hz, 1 H, OCH_2CH=CH_2), 4.74 (d, *J* = 8.4 Hz, 1 H, H1), 4.35 (ddt, *J* = 13.0, 5.1, 1.5 Hz, 1 H, OCH_2CH=CH_2), 4.20–4.06 (m, 3 H, 2 H6 + OCH_2CH=CH_2), 3.97 (dt, *J* = 11.2, 8.5 Hz, 1 H, H2), 3.91 (td, *J* = 6.1, 1.2 Hz, 1 H, H5), 2.14 (s, 3 H, $OCOCH_3$), 2.04 ($OCOCH_3$), 2.00 ($OCOCH_3$), 1.95 ($NHCOCH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.8 (C=O), 170.8 (C=O), 170.7 (C=O), 170.6 (C=O), 134.0 (OCH_2CH=CH_2), 118.2 (OCH_2CH=CH_2), 100.3 (C1), 71.1 (C5), 70.4 (OCH_2CH=CH_2), 70.3 (C3), 67.2 (C4), 61.9 (C6), 52.1 (C2), 23.9 ($NHCOCH_3$), 21.1 ($OCOCH_3$), 21.1 ($OCOCH_3$), 21.1 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NNaO_9$: 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 anhydrous MeOH (15 mL). The mixture was stirred at r.t., and the progress of the reaction was 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 (CD_3OD, 500 MHz): δ = 5.93 (dddd, *J* = 17.3, 10.6, 5.8, 4.9 Hz, 1 H, OCH_2CH=CH_2), 5.31 (ddd, *J* = 17.3, 3.6, 1.8 Hz, 1 H, OCH_2CH=CH_2), 5.17 (ddd, *J* = 10.5, 3.2, 1.6 Hz, 1 H, OCH_2CH=CH_2), 4.48 (d, *J* = 8.4 Hz, 1 H, H1), 4.38 (ddt, *J* = 13.3, 5.0, 1.7 Hz, 1 H, OCH_2CH=CH_2), 4.11 (ddt, *J* = 13.3, 5.8, 1.5 Hz, 1 H, OCH_2CH=CH_2), 3.92 (dd, *J* = 11.9, 2.3 Hz, 1 H, H6), 3.77–3.66 (m, 2 H, H2 + H6), 3.40–3.33 (m, 1 H, H4), 3.29 (ddd, *J* = 9.7, 5.9, 2.3 Hz, 1 H, H2).

^{13}C NMR (CD_3OD, 125 MHz): δ = 174.2 (C=O), 136.0 (OCH_2CH=CH_2), 117.3 (OCH_2CH=CH_2), 102.3 (C1), 78.4 (C5), 76.5 (C3), 72.6 (C4), 71.1 (OCH_2CH=CH_2), 63.2 (C6), 57.8 (C2), 23.3 ($NHCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{19}NaO_6$: 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 anhydrous MeOH (20 mL). The mixture was stirred at r.t. 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** (336 mg, quant.) as a colorless solid.

^{1}H NMR (CD_3OD, 500 MHz): δ = 5.91 (dddd, *J* = 17.3, 10.6, 5.8, 4.9 Hz, 1 H, OCH_2CH=CH_2), 5.31 (ddd, *J* = 17.2, 3.6, 1.8 Hz, 1 H, OCH_2CH=CH_2), 5.17 (ddd, *J* = 10.7, 3.2, 1.6 Hz, 1 H, OCH_2CH=CH_2), 4.59 (s, 1 H, NHAc), 4.46 (d, *J* = 8.5 Hz, 1 H, H1), 4.38 (ddt, *J* = 13.2, 5.0, 1.7 Hz, 1 H, OCH_2CH=CH_2), 4.12 (ddt, *J* = 13.3, 5.8, 1.5 Hz, 1 H, OCH_2CH=CH_2), 3.98 (dd, *J* = 10.7, 8.4 Hz, 1 H, H2), 3.87 (dd, *J* = 3.4, 1.2 Hz, 1 H, H4), 3.82 (dd, *J* = 11.4, 6.8 Hz, 1 H, H6), 3.78 (dd, *J* = 11.4, 5.4 Hz, 1 H, H6), 3.64 (dd, *J* = 10.7, 3.3 Hz, 1 H, H3), 3.53 (ddd, *J* = 6.8, 5.4, 1.1 Hz, 1 H, H5), 2.02 (s, 3 H, NHAc).

^{13}C NMR (CD_3OD, 125 MHz): δ = 174.5 (C=O), 136.1 (OCH_2CH=CH_2), 117.3 (OCH_2CH=CH_2), 102.6 (C1), 77.2 (C5), 73.7 (C3), 70.1 (C4), 71.1 (OCH_2CH=CH_2), 70.1 (C4), 62.9 (C6), 54.7 (C2), 23.4 ($NHCOCH_3$).

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

Allyl Disaccharides

Allyl Per(acetylated) Lactose (24)

$BF_3{\cdot}Et_2O$ (0.9 mL, 7.35 mmol) was added dropwise 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 CH_2Cl_2 (10 mL). The reaction mixture was stirred at r.t. for 16 h. The reaction was diluted with CH_2Cl_2 (50 mL) and washed with water (3 × 50 mL), $NaHCO_3$ sat. soln (3 × 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** (620 mg, 62%) as a colorless solid.

R_f 0.26 (hexane/EtOAc, 1:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.81 (dddd, *J* = 16.9, 10.8, 6.1, 4.9 Hz, 1 H, OCH_2CH=CH_2), 5.32 (dd, *J* = 3.4, 1.2 Hz, 1 H, H_{4B}), 5.23 (ddd, *J* = 17.2, 3.4, 1.7 Hz, 1 H, OCH_2CH=CH_2), 5.17 (t, *J* = 1.5 Hz, 1 H, H3A), 5.17 (ddd, *J* = 10.5, 3.0, 1.5 Hz, 1 H, OCH_2CH=CH_2), 5.08 (dd, *J* = 10.4, 7.9 Hz, 1 H, H2B), 4.96–4.86 (m, 2 H, H2A + H3B), 4.50 (d, *J* = 7.9 Hz, 1 H, H1A), 4.46 (d, *J* = 8.0 Hz, 1 H, H1B), 4.46–4.42 (m, 1 H, H6B), 4.27 (ddt, *J* = 13.2, 5.0, 1.6 Hz, 1 H, OCH_2CH=CH_2), 4.14–4.01 (m, 5 H, OCH_2CH=CH_2 + H5B + 2 H6A + H6B), 3.85 (ddd, *J* = 7.5, 6.3, 1.3 Hz, 1 H, OCH_2CH=CH_2), 3.78 (t, *J* = 9.4 Hz, 1 H, H4A), 3.57 (ddd, *J* = 9.9, 5.1, 2.1 Hz, 1 H, H5A), 2.12 (s, 3 H, $OCOCH_3$), 2.10 (s, 3 H, $OCOCH_3$), 2.03 ($OCOCH_3$), 2.02 (s, 6 H, $OCOCH_3$), 2.01 (s, 6 H, 2 × $OCOCH_3$), 1.94 (s, 3 H, $OCOCH_3$).

^{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_2CH=CH_2), 118.0 (OCH_2CH=CH_2), 101.5 (C1B), 99.7 (C1A), 76.7 (C4A), 73.3 (C3A), 73.0 (C5A), 72.1 (C2A), 71.4 (C3B), 71.1 (C5B), 70.4 (OCH_2CH=CH_2), 69.5 (C2B), 67.0 (C4B), 62.4 (C6A), 61.2 (C6A), 21.2 ($OCOCH_3$), 21.2 ($OCOCH_3$), 21.01 ($OCOCH_3$), 21.0 ($OCOCH_3$), 20.9 ($OCOCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{40}NaO_{18}$: 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 anhydrous MeOH (15 mL). The solution was stirred at r.t. and the progress of the reaction was 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** (254 mg, quant.) as a colorless solid.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.09–5.90 (m, 1 H, OCH_2CH=CH_2), 5.35 (ddd, *J* = 17.3, 3.4, 1.7 Hz, 1 H, OCH_2CH=CH_2), 5.21 (ddd, *J* = 10.4, 3.4, 1.7 Hz, 1 H,OCH_2CH=CH_2), 4.43–4.38 (m, 1 H, OCH_2CH=CH_2),4.40 (d, *J* = 7.5 Hz, 1 H, H1B), 4.38 (d, *J* = 7.8 Hz, 1 H, H1A), 4.19 (ddt, *J* = 12.9, 6.1, 1.5 Hz, 1 H, OCH_2CH=CH_2), 3.94 (dd, *J* = 3.5, 1.7 Hz, 1 H, H6A), 3.91–3.86 (m, 1 H, H6A), 3.86 (d, *J* = 3.2 Hz, 1 H, H4B), 3.82 (dd, *J* = 11.4, 7.4 Hz, 1 H, H6B), 3.74 (dd, *J* = 11.4, 7.4 Hz, 1 H, H6B), 3.66–3.55 (m, 3 H, H3A + H2B + H4B), 3.55–3.50 (m, 2 H, H4A + H3B), 3.43 (ddd, *J* = 9.5, 4.3, 2.6 Hz, 1 H, H5A), 3.31 (dd, *J* = 9.0, 7.9 Hz, 1 H, H2A).

^{13}C NMR (CD_3OD, 125 MHz): δ = 136.1 (OCH_2CH=CH_2), 117.9 (OCH_2CH=CH_2), 105.5 (C1), 103.7 (C1), 81.1, 77.5, 76.9, 75.3, 75.2, 73.0, 71.5, 70.7 (OCH_2CH=CH_2), 62.9 (C6), 62.3 (C6).

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

Allyl Per(acetylated) Maltose (27)

BF_3·Et_2O (0.9 mL, 7.35 mmol) was added to a cooled (0 °C) solution of peracetyl-maltose **26** (1.0 g, 1.48 mmol) and allyl alcohol (150 µL, 2.21 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred at r.t. for 16 h. The reaction was diluted with CH_2Cl_2 (50 mL) and washed with water (3 × 50 mL), $NaHCO_3$ sat. soln (3 × 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** (650 mg, 65%) as a colorless solid.

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

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.84 (dddd, *J* = 17.0, 10.8, 6.2, 4.9 Hz, 1 H, OCH_2CH=CH_2), 5.40 (d, *J* = 4.1 Hz, 1 H, H1B), 5.35 (t, *J* = 10.0 Hz, 1 H, H3B), 5.29–5.23 (m, 1 H, OCH_2CH=CH_2), 5.24 (t, *J* = 9.0 Hz, 1 H, H3A), 5.20 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, OCH_2CH=CH_2), 5.04 (t, *J* = 9.9 Hz, 1 H, H4B), 4.87–4.82 (m, 2 H, H2A + H2B), 4.58 (d, *J* = 7.9 Hz, 1 H, H1A), 4.48 (dd, *J* = 12.1, 2.8 Hz, 1 H, H6A), 4.30 (ddt, *J* = 13.2, 5.0, 1.6 Hz, 1 H, OCH_2CH=CH_2), 4.23 (ddd, *J* = 12.1, 8.2, 4.3 Hz, 2 H, H6A + H6B), 4.09 (ddt, *J* = 13.2, 6.2, 1.4 Hz, 1 H, OCH_2CH=CH_2), 4.04 (dd, *J* = 12.4, 2.2 Hz, 1 H, H6B), 4.00 (t, *J* = 10.0 Hz, 1 H, H4A), 3.96 (ddd, *J* = 10.3, 4.0, 2.3 Hz, 1 H, H5B), 3.96 (ddd, *J* = 9.6, 4.5, 2.8 Hz, 1 H, H5A), 2.14 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.08 ($OCOCH_3$), 2.02 (s, 6 H, $OCOCH_3$), 2.00 (s, 3 H, $OCOCH_3$), 1.99 (s, 3 H, $OCOCH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.9 (2 × 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 (C1A), 95.9 (C1B), 75.9 (C3A), 73.2 (C4A), 72.6 (C5A), 72.5 (C2A or C2B), 70.0 (C2A or C2B + OCH_2CH=CH_2), 69.8 (C3B), 68.9 (C5B), 68.5 (C4B), 63.2 (C6A), 62.0 (C6B), 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* [M + Na]$^+$ calcd for $C_{29}H_{40}NaO_{18}$: 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 anhydrous MeOH (15 mL). The solution was stirred at r.t. and the progress of the reaction was 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** (271 mg, quant.) as a colorless solid.

^{1}H NMR (CD_3OD, 500 MHz): δ = 6.03–5.93 (m, 1 H, OCH_2CH=CH_2), 5.33 (ddd, *J* = 17.2, 3.6, 1.8 Hz, 1 H, OCH_2CH=CH_2), 5.19–5.14 (m, 2 H, H1B + OCH_2CH=CH_2), 4.37 (ddd, *J* = 17.2, 3.6, 1.8 Hz, 1 H, OCH_2CH=CH_2), 4.32 (d, *J* = 7.8 Hz, 1 H, H1A), 4.15 (ddd, *J* = 12.9, 6.1, 1.5 Hz, 1 H, OCH_2CH=CH_2), 3.89 (dd, *J* = 12.2, 2.1 Hz, 1 H, H6B), 3.84–3.78 (m, 2 H, H6A + H6B), 3.71–3.58 (m, 4 H, H3A + H3B + H4B + H6A), 3.54 (t, *J* = 9.2 Hz, 1 H, H4A), 3.44 (dd, *J* = 9.7, 3.7 Hz, 1 H, H2B), 3.40–3.34 (m, 1 H, H5A), 3.28–3.21 (m, 2 H, H2A + H5B).

^{13}C NMR (CD_3OD, 125 MHz): δ = 135.6 (OCH_2CH=CH_2), 117.5 (OCH_2CH=CH_2), 103.3 (C1A), 102.9 (C1B), 81.2 (C4B), 77.8 (C4A or C3B), 76.6 (C5A), 75.1 (C3A), 74.7 (C2A), 74.7 (C4A or C3B), 74.1 (C2B), 71.5 (C5B), 71.1 (OCH_2CH=CH_2), 62.7 (C6A or C6B), 62.2 (C6A or C6B).

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

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 r.t., diluted with CH_2Cl_2 (150 mL) and washed with water (150 mL) and brine (150 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 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): δ = 5.89 (dddd, *J* = 16.8, 10.4, 6.1, 5.1 Hz, 1 H, OCH_2CH=CH_2), 5.28 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1 H, OCH_2CH=CH_2), 5.19 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H,OCH_2CH=CH_2), 4.85 (d, *J* = 1.6 Hz, 1 H, H1), 4.18 (ddt, *J* = 12.9, 5.1, 1.5 Hz, 1 H, OCH_2CH=CH_2), 3.98 (ddt, *J* = 12.9, 6.1, 1.4 Hz, 1 H, OCH_2CH=CH_2), 3.93 (dd, *J* = 3.5, 1.7 Hz, 1 H, H2), 3.91–3.83 (m, 3 H, H3 + 2 H6), 3.77 (t, *J* = 9.3 Hz, 1 H, H4), 3.62 (dt, *J* = 9.5, 5.4 Hz, 1 H, H5), 0.91 (s, 9 H, $C(CH_3)_3$), 0.10 (s, 6 H, $2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 134.0 (OCH_2CH=CH_2), 117.9 (OCH_2CH=CH_2), 99.1 (C1), 70.8, 70.9, 72.1, 71.1 (C2, C3, C4, C5), 68.4 (OCH_2CH=CH_2), 65.1 (C6), 26.3 ($C(CH_3)_3$), 18.6 ($C(CH_3)_3$), –5.1 (CH_3), –5.0 (CH_3).

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

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

Camphorsulfonic acid (0.20 g, 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 r.t. for 1 h. The reaction was then quenched with Et_3N (650 µL) and the solvent was evaporated. The crude material was dissolved in CH_2Cl_2 (60 mL) and Bz_2O (1.89 g, 8.36 mmol), 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 r.t. for 1 h. 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 anhydrous $MgSO_4$ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc, 2.5:1) to obtain **30** (1.31 g, 66%) as a colorless oil.

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

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.05 (d, *J* = 3.4 Hz, 2 H, H_{Ar} *ortho*), 7.59 (t, *J* = 7.5 Hz, 1 H, H_{Ar} *para*), 7.46 (t, *J* = 7.8 Hz, 2 H, H_{Ar} *meta*), 5.99–5.87 (m, 1 H, $OCH_2CH{=}CH_2$), 5.36 (t, *J* = 9.7 Hz, 1 H, H4), 5.34 (ddd, *J* = 17.1, 3.4, 1.7 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.24 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.12 (dd, *J* = 3.6, 1.7 Hz, 1 H, H2), 4.95 (d, *J* = 1.6 Hz, 1 H, H1), 4.27–4.23 (m, 1 H, H3), 4.22 (m, 1 H, $OCH_2CH{=}CH_2$), 4.04 (m, 1 H, $OCH_2CH{=}CH_2$), 3.94 (ddd, *J* = 10.0, 4.7, 2.8 Hz, 1 H, H5), 3.82–3.75 (m, 2 H, 2 H6), 2.16 (s, 3 H, $CO(CH_3)$), 0.86 (s, 9 H, $C(CH_3)_3$), –0.01 (d, *J* = 14.5 Hz, 6 H, 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 (C1), 73.1 (C2), 71.6 (C5), 70.9 (C4), 69.4 (C3), 68.7 ($OCH_2CH{=}CH_2$), 62.8 (C6), 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* [M + Na]$^+$ calcd for $C_{34}H_{40}NaO_8Si$: 627.2390; found: 627.2388.

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

AcOH (1.2 mL) and TBAF (1 M in THF, 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 r.t. 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** (601 mg, 75%) as a colorless oil.

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

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.06 (d, *J* = 8.2 Hz, 2 H, C_{Ar} *ortho*), 7.60 (t, *J* = 7.5 Hz, 1 H, C_{Ar} *para*), 7.46 (t, *J* = 7.9 Hz, 2 H, C_{Ar} *meta*), 5.97–5.87 (m, 1 H, $OCH_2CH{=}CH_2$), 5.36–5.30 (m, 2 H, $OCH_2CH{=}CH_2$ + H4), 5.25 (ddd, *J* = 10.4, 2.8, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.17 (dd, *J* = 3.7, 1.7 Hz, 1 H, H2), 4.98 (d, *J* = 1.7 Hz, 1 H, H1), 4.37–4.31 (m, 1 H, H3), 4.21 (ddt, *J* = 12.9, 5.4, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.05 (ddt, *J* = 12.9, 6.1, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 3.90 (ddd, *J* = 10.1, 4.7, 2.8 Hz, 1 H, H5), 3.76 (d, *J* = 12.7 Hz, 1 H, H6), 3.70 (dd, *J* = 12.6, 4.2 Hz, 1 H, H6), 2.18 (s, 3 H, $CO(CH_3)$).

^{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 (C1), 72.92 (C2), 70.9 (C5), 70.6 (C4), 69.1 ($OCH_2CH{=}CH_2$), 68.8 (C3), 61.8 (C6), 21.41 ($CO(CH_3)$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{22}NaO_8$: 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 acceptor **31** (58 mg, 0.16 mmol) and 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 a few hours and then dissolved in anhydrous CH_2Cl_2 (5 mL). The mixture was cooled to 0 °C for 15 min, followed by the addition of TMSOTf (8.5 µL, 0.047 mmol), and stirred for 30 min at 0 °C. The reaction was quenched by the addition of Et_3N, 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** (254 mg, quant.) as a colorless solid.

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

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.14 (dd, *J* = 8.3, 1.4 Hz, 2 H, 2 H_{Ar}), 8.10–8.07 (m, 2 H, 2 H_{Ar}), 8.06–8.04 (m, 2 H, 2 H_{Ar}), 8.04–8.02 (m, 2 H, 2 H_{Ar}), 8.02–7.99 (m, 2 H, 2 H_{Ar}), 7.99–7.96 (m, 2 H, 2 H_{Ar}), 7.83 (dd, *J* = 8.4, 1.4 Hz, 2 H, 2 H_{Ar}), 7.81–7.78 (m, 2 H, 2 H_{Ar}), 7.76 (dd, *J* = 8.4, 1.4 Hz, 2 H, 2 H_{Ar}), 7.61–7.47 (m, 6 H, 6 H_{Ar}), 7.46–7.20 (m, 21 H, 21 H_{Ar}), 6.10 (t, *J* = 10.1 Hz, 1 H, H4B), 6.04 (t, *J* = 10.1 Hz, 1 H, H4C), 6.00–5.90 (m, 2 H, $OCH_2CH{=}CH_2$ + H3B), 5.80–5.71 (m, 3 H, H2B + H4A + H3C), 5.52 (dd, *J* = 3.5, 1.7 Hz, 1 H, H2A), 5.43 (ddd, *J* = 17.3, 3.0, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.39 (dd, *J* = 3.3, 1.8 Hz, 1 H, H2C), 5.32–5.28 (m, 2 H, $OCH_2CH{=}CH_2$ + H1C), 5.12 (d, *J* = 1.8 Hz, 1 H, H1B), 5.00 (d, *J* = 1.6 Hz, 1 H, H1A), 4.70 (dd, *J* = 12.2, 2.3 Hz, 1 H, H6C), 4.65–4.59 (m, 3 H, H3A + H5C + H6C), 4.55 (ddd, *J* = 10.2, 4.5, 2.5 Hz, 1 H, H5B), 4.51 (dd, *J* = 12.2, 4.1 Hz, 1 H, H6B), 4.41 (dd, *J* = 12.1, 4.5 Hz, 1 H, H6B), 4.34 (ddt, *J* = 12.9, 5.4, 1.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.21 (ddd, *J* = 10.3, 6.5, 2.1 Hz, 1 H, H5A), 4.16 (ddt, *J* = 12.8, 6.2, 1.3 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.10 (dd, *J* = 11.2, 6.8 Hz, 1 H, H6A), 3.73 (dd, *J* = 10.8, 2.2 Hz, 1 H, H6A), 2.36 (s, 3 H, $COCH_3$).

^{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 ($OCH_2CH{=}CH_2$), 99.2 (C1C), 97.5 (C1B), 96.5 (C1A), 74.4, 71.1 (C2A), 70.4, 70.2 (C2C), 70.0, 69.8, 69.7, 69.22, 69.1, 68.9, 68.6 ($OCH_2CH{=}CH_2$), 66.8, 66.6, 62.8 (C6), 21.1 ($COCH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{86}H_{74}NaO_{26}$: 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 r.t. for 1 h. Aqueous NaOH (1 M, 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 material was diluted with water (10 mL) and washed with toluene (2 × 10 mL), the aqueous phase was separated and the water was evaporated to afford **34** (70 mg, 90%) as a colorless amorphous solid.

^{1}H NMR (D_2O, 500 MHz): δ = 5.85 (dddd, *J* = 17.1, 10.4, 6.2, 5.4 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.23 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1 H, $OCH_2CH{=}CH_2$), 5.15 (ddd, *J* = 10.4, 2.6, 1.3 Hz, 1 H, $OCH_2CH{=}CH_2$), 4.98 (d, *J* = 1.7 Hz, 1 H, H1), 4.77 (d, *J* = 1.8 Hz, 1 H, H1), 4.75 (d, *J* = 1.8 Hz, 1 H, H1), 4.10 (ddt, *J* = 12.9, 5.4, 1.5 Hz, 1 H, $OCH_2CH{=}CH_2$), 3.98 (dd, *J* = 2.5, 1.7 Hz, 1 H, H2), 3.96 (ddd, *J* = 6.7, 2.6, 1.3 Hz, 1 H, $OCH_2CH{=}CH_2$), 3.94 (dd, *J* = 3.4, 1.7 Hz, 1 H, H2), 3.88 (dd, *J* = 7.0, 4.4 Hz, 1 H, H6), 3.86 (dd, *J* = 3.5, 1.7 Hz, 1 H, H2), 3.79–3.73 (m, 5 H, H3 + 2 H6), 3.71 (dd, *J* = 8.9, 3.4 Hz, 2 H), 3.67–3.57 (m, 4 H, 3 H6), 3.56–3.50 (m, 3 H).

^{13}C NMR (D_2O, 125 MHz): δ = 133.1 ($OCH_2CH{=}CH_2$), 118.2 ($OCH_2CH{=}CH_2$), 102.3 (C1), 99.2 (C1), 99.1 (C1), 78.4, 73.2, 72.6, 71.0, 70.5, 70.2, 69.9 (C2), 69.8 (C2), 69.5 (C2), 68.2 ($OCH_2CH{=}CH_2$), 66.6, 66.6, 65.6, 65.1 (C6), 60.9 (C6), 60.8 (C6).

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

Oxime Neoglycoconjugates; General Procedure C

Ozone was bubbled through a solution of allyl glycoside **16** (250 mg) in MeOH (75 mL) at –78 °C until the solution turned blue (ca. 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 r.t. The solvent was removed under reduced pressure to af-

ford glycosyl aldehydes **29**–**39** (quant.) as a colorless oil. *O*-Benzylhydroxylamine hydrochloride (1.1 equiv) was then added to the solution of the corresponding glycosyl aldehydes (10 mg, 1 equiv) in H_2O (1 mL). The mixture was stirred at 40 °C for 30 min and the final oxime was purified by semipreparative HPLC to obtain the *Z*/*E* mixture of neoglycoconjugates **47**–**58**.

(*E*/*Z*)-α-D-Mannopyranosyl Acetaldehyde *O*-Benzyl Oxime (47)

According to Procedure C, compound **47** (12.5 mg, 85%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.56 (dd, *J* = 6.3, 5.3 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.37–7.27 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 6.93 (t, *J* = 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.10 (s, 2 H, CH_{2Bn} *Z* isomer), 5.08 (s, 2 H, CH_{2Bn} *E* isomer), 4.82 (d, *J* = 1.7 Hz, 1 H, H1 *E* isomer), 4.80 (d, *J* = 1.7 Hz, 1 H, H1 *Z* isomer), 4.54 (dd, *J* = 16.4, 3.6 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.41 (dd, *J* = 16.4, 3.9 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.26 (dd, *J* = 12.7, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.15 (dd, *J* = 12.7, 6.3 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.86–3.84 (m, 3 H, H2 + H6 *Z* isomer), 3.84–3.81 (m, 1 H, H2 + H6 *E* isomer), 3.75–3.67 (m, 4 H, H3 + H6 *Z* and *E* isomer), 3.66–3.61 (m, 2 H, H4 *Z* and *E* isomer), 3.56–3.50 (m, 2 H, H5 *Z* and *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 151.5 (OCH_2-CH=N-O *Z* isomer), 148.9 (OCH_2-CH=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 (C1 *Z* isomer), 101.8 (C1 *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.4 (CH_{2Bn} *E* isomer), 75.5 (C5 *Z* isomer), 75.4 (C5 *E* isomer), 72.9 (C3 isomer and *Z* isomer), 72.4 (C2 isomer and *Z* isomer), 69.0 (C4 *Z* isomer), 68.9 (C4 *E* isomer), 65.5 (OCH_2CH=N-O *E* isomer), 63.3 (OCH_2CH=N-O *Z* isomer), 63.3 (C6 *Z* and *E* isomer).

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

(*E*/*Z*)-α-D-Glucopyranosyl Acetaldehyde *O*-Benzyl Oxime (48)

According to Procedure C, compound **48** (11.8 mg, 80%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.62 (dd, *J* = 6.2, 5.4 Hz, 1 H, OCH_2-CH=N-O *E* isomer), 7.39–7.28 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 7.02 (t, *J* = 3.7 Hz, 1 H, OCH_2-CH=N-O *Z* isomer), 5.12 (s, 2 H, CH_{2Bn} *Z* isomer), 5.09 (s, 2 H, CH_{2Bn} *Z* isomer), 4.86 (d, *J* = 4.0 Hz, 1 H, H1 *E* isomer), 4.85 (d, *J* = 4.0 Hz, 1 H, H1 *Z* isomer), 4.58 (dd, *J* = 16.5, 3.6 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.45 (dd, *J* = 16.5, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.31 (dd, *J* = 12.9, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.20 (dd, *J* = 12.9, 6.2 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.83 (dt, *J* = 11.9, 2.4 Hz, 2 H, H6 *Z* and *E* isomer), 3.73–3.63 (m, 4 H, H3 + H6 *Z* and *E* isomer), 3.60 (ddd, *J* = 10.1, 5.6, 2.3 Hz, 2 H, H5 *Z* and *E* isomer), 3.45 (dd, *J* = 7.6, 3.8 Hz, 1 H, H2 *Z* or *E* isomer), 3.43 (dd, *J* = 7.7, 3.8 Hz, 1 H, H2 *Z* or *E* isomer), 3.35–3.30 (m, 2 H, H4 *Z* and *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 151.8 (OCH_2-CH=N-O *Z* isomer), 149.2 (OCH_2-CH=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 (C1 *E* isomer), 100.5 (C1 *Z* isomer), 77.7 (CH_{2Bn} *Z* isomer),, 77.4 (CH_{2Bn} *E* isomer), 75.4 (C3 *Z* and *E* isomer), 74.5 (C4 *Z* isomer), 74.4 (C5 *E* isomer), 73.8 (C2 *E* isomer), 73.8 (C2 *Z* isomer), 72.2 (C4 *Z* isomer), 72. 1 (C4 *E* isomer), 66.1 (OCH_2CH=N-O *E* isomer), 63.8 (OCH_2CH=N-O *Z* isomer), 63.0 (C6 *Z* isomer), 63.0 (C6 *E* isomer).

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

(*E*/*Z*)-β-D-Glucopyranosyl Acetaldehyde *O*-Benzyl Oxime (49)

According to Procedure C, compound **49** (12.2 mg, 83%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.63–7.54 (t, *J* = 5.5 Hz, 1 H, OCH_2-CH=N-O *E* isomer), 7.43–7.24 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 7.00 (t, *J* = 3.6 Hz, 1 H, OCH_2-CH=N-O *E* isomer), 5.10 (s, 2 H, CH_{2Bn} *Z* isomer), 5.07 (s, 2 H, CH_{2Bn} *Z* isomer), 4.67 (dd, *J* = 16.6, 3.5 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.55 (dd, *J* = 16.6, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.41 (dd, *J* = 12.9, 5.3 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.30 (d, *J* = 7.9 Hz, 1 H, H1 *Z* isomer), 4.29 (d, *J* = 7.9 Hz, 1 H, H1 *E* isomer), 4.28 (dd, *J* = 13.1, 6.2 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.86 (ddd, *J* = 11.9, 3.7, 2.3 Hz, 2 H, H6 *Z* and *E* isomer), 3.68 (dd, *J* = 12.0, 5.5 Hz, 2 H, H6 *Z* and *E* isomer), 3.40–3.16 (m, 8 H, H2 + H3 + H4 + H5 *Z* and *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 152.3 (OCH_2-CH=N-O *Z* isomer), 149.6 (OCH_2-CH=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 (C1 *Z* isomer), 104.4 (C1 *E* isomer), 78.4 (C5 *Z* and *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.3 (CH_{2Bn} *E* isomer), 75.4 (C2 *Z* and *E* isomer), 71.9 (C4 *Z* and *E* isomer), 67.5 (OCH_2CH=N-O *E* isomer), 65.4 (OCH_2CH=N-O *Z* isomer), 63.1 (C6 *Z* and *E* isomer).

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

(*E*/*Z*)-α-D-Galactopyranosyl Acetaldehyde *O*-Benzyl Oxime (50)

According to Procedure C, compound **50** (11.8 mg, 80%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.61 (t, *J* = 5.7 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.40 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 7.02 (t, *J* = 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.10 (s, 2 H, CH_{2Bn} *E* isomer), 5.08 (s, 2 H, CH_{2Bn} *Z* isomer), 4.88 (s, 1 H, *J* = 4.0 Hz, H1 *E* isomer or H1 *Z* isomer), 4.85 (s, *J* = 4.0 Hz, 2 H, H1 *E* isomer or H1 *Z* isomer), 4.55 (dd, *J* = 16.5, 3.5 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.43 (dd, *J* = 16.5, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.29 (dd, *J* = 12.9, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.18 (dd, *J* = 13.0, 6.1 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.91–3.88 (m, 2 H, H4 *E* isomer+ H4 *Z* isomer), 3.85–3.65 (m, 10, H2 + H3 + H5 + 2 H6 *E* and *Z* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 151.9 (OCH_2-CH=N-O *Z* isomer), 149.4 (OCH_2-CH=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 (C1 *E* isomer or *Z* isomer), 100.8 (C1 *E* isomer or *Z* isomer), 77.8, 77.4, 73.3, 73.1, 71.8, 71.5, 70.5, 66.1 (OCH_2CH=N-O *E* isomer), 64.0 (OCH_2CH=N-O *Z* isomer), 63.2, 63.1.

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

(*E*/*Z*)-β-D-Galactopyranosyl Acetaldehyde *O*-Benzyl Oxime (51)

According to Procedure C, compound **51** (13.3 mg, 90%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.59 (dd, *J* = 6.2, 5.3 Hz, 1 H, OCH_2-CH=N-O *E* isomer), 7.38–7.27 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 7.00 (t, *J* = 3.6 Hz, 1 H, OCH_2-CH=N-O *E* isomer), 5.09 (s, 2 H, CH_{2Bn} *Z* isomer), 5.07 (s, 2 H, CH_{2Bn} *E* isomer), 4.67 (dd, *J* = 16.6, 3.5 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.55 (dd, *J* = 16.6, 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.41 (dd, *J* = 12.9, 5.2 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.31–4.24 (m, 3 H, OCH_2CH=N-O *E* isomer + H1 *E* and *Z* isomer), 4.01–3.95 (m, 2 H, H5 *Z* and *E* isomer), 3.85 (dd, *J* = 3.4, 1.5 Hz, 1 H, H4 *E* isomer), 3.84 (dd, *J* = 3.4, 1.5 Hz, 1 H, H4 *Z* isomer), 3.80–3.70 (m, 3 H, 3 H6), 3.67–3.61 (m, 1 H, H6), 3.58–3.44 (m, 4 H, H2 + H3 *Z* and *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 152.4 (OCH_2-CH=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 (C1 *Z* isomer), 104. 9 (C1 *E* isomer), 85.0, 83.7, 77.7 (CH_{2Bn} *Z* isomer), 77.3 (CH_{2Bn} *Z* isomer), 77.2 (C3 *Z* or *E* isomer), 77.8 (C5 *Z* or *E* isomer), 75.3 (C5 *Z* or *E* isomer), 72.8, 70.7 (C4 *Z* or *E* isomer), 70.7 (C4 *Z* or *E* isomer), 67.5 (OCH_2CH=N-O *E* isomer), 65.4 (OCH_2CH=N-O *Z* isomer), 62.9 (C6 *Z* and *E* isomer).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{21}NNaO_7$: 350.1216; found: 350.1212.

(*E*/*Z*)-α-L-Fucopyranosyl Acetaldehyde *O*-Benzyl Oxime (52)

According to Procedure C, compound **52** (13.7 mg, 85%) was obtained as a colorless solid after HPLC purification (t_R 8.3 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.58 (t, *J* = 5.7 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.38–7.26 (m, 10 H, *E* isomer + 5 H_{Ar} *Z* isomer), 6.97 (t, *J* = 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.10 (s, 2 H, CH_{2Bn} *Z* isomer), 5.07 (s, 2 H, CH_{2Bn} *E* isomer), 4.82 (d, *J* = 3.1 Hz, 1 H, H1 *E* isomer), 4.78 (d, *J* = 3.1 Hz, 1 H, H1 *Z* isomer), 4.48 (dd, *J* = 16.4, 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.38 (dd, *J* = 16.4, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.22 (dd, *J* = 12.9, 5.6 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.16 (dd, *J* = 12.9, 6.2 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.96–3.90 (m, 2 H, H5 *E* and *Z* isomer), 3.77–3.72 (m, 4 H, H2 + H3 *E* and *Z* isomer), 3.68–3.66 (m, 2 H, H4 *E* and *Z* isomer), 1.22 (d, *J* = 5.6 Hz, 3 H, H6 *Z* isomer), 1.21 (d, *J* = 6.7 Hz, 3 H, H6 *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 151.4 (OCH_2-CH=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 (C1 *Z* isomer), 100.6 (C1 *E* isomer), 77.4 (CH_{2Bn} *Z* isomer), 77.0 (CH_{2Bn} *E* isomer), 73.5 (C4 *E* or *Z* isomer), 71.6 (C2 or C3 *E* isomer), 71.5 (C2 or C3 *Z* isomer), 69.9 (C2 or C3 *Z* isomer), 69.8 (C2 or C3 *E* isomer), 67.9 (C6 *Z* isomer), 67.9 (C6 *E* isomer), 65.9 (OCH_2CH=N-O *E* isomer), 63.4 (OCH_2CH=N-O *Z* isomer), 16.7 (C6 *Z* isomer), 16.7 (C6 *E* isomer).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{21}NNaO_6$: 334.1267; found:334.1263.

(*E*/*Z*)-β-L-Fucopyranosyl Acetaldehyde *O*-Benzyl Oxime (53)

According to Procedure C, compound **53** (14.5 mg. 90%) was obtained as a colorless solid after HPLC purification (t_R 8.3 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.57 (dd, *J* = 6.2, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.40–7.26 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 6.98 (t, *J* = 3.6 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.10 (s, 2 H, CH_{2Bn} *Z* isomer), 5.07 (s, 2 H, CH_{2Bn} *E* isomer), 4.60 (dd, *J* = 16.6, 3.6 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.51 (dd, *J* = 16.6, 3.7 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.34 (dd, *J* = 12.9, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.25 (dd, *J* = 12.9, 6.2 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.22 (d, *J* = 7.3 Hz, 1 H, H1 *Z* isomer), 4.20 (d, *J* = 7.3 Hz, 1 H, H1 *E* isomer), 3.68–3.54 (m, 4 H, H4 + H5 *E* and *Z* isomer), 3.53–3.42 (m, 4 H, H2 + H3 *E* and *Z* isomer), 1.28 (d, *J* = 5.6 Hz, 3 H, H6 *E* isomer or H6 *Z* isomer), 1.26 (d, *J* = 5.6 Hz, 3 H, H6 *E* isomer or H6 *Z* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 152.5 (OCH_2-CH=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 (C1 *Z* isomer), 104.7 (C1 *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.3 (CH_{2Bn} *E* isomer), 75.5 (C3 or C2 *E* and *Z* isomer), 73.4 (C5 *E* and *Z* isomer), 72.5 (C4 *E* or *Z* isomer), 72.5 (C4 *E* or *Z* isomer), 72.4 (C3 or C2 *E* and *Z* isomer), 67.4 (OCH_2CH=N-O E isomer), 65.2 (OCH_2CH=N-O *Z* isomer), 17.1 (C6 *E* and *Z* isomer).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{21}NNaO_6$: 334.1267; found: 334.1262.

(*E*/*Z*)-2-Acetamido-2-deoxy-β-D-glucopyranosyl Acetaldehyde *O*-Benzyl Oxime (54)

According to Procedure C, compound **54** (12.6 mg, 90%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.52 (dd, *J* = 6.4, 5.4 Hz, 1 H, OCH_2-*C*H=N-O *E* isomer), 7.38–7.27 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 6.90 (t, *J* = 3.6 Hz, 1 H, OCH_2-*C*H=N-O *Z* isomer), 5.09 (s, 2 H, CH_{2Bn} *Z* isomer), 5.06 (s, 2 H, CH_{2Bn} *E* isomer), 4.61 (dd, *J* = 16.5, 3.5 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.49 (dd, *J* = 16.6, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.46 (d, *J* = 8.4 Hz, 1 H, H1 *E* isomer), 4.44 (d, *J* = 8.4 Hz, 1 H, H1 *Z* isomer), 4.34 (dd, *J* = 12.8, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.23 (dd, *J* = 12.8, 6.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.88 (dt, *J* = 12.0, 2.6 Hz, 2 H, H6 *Z* and *E* isomer), 3.77–3.61 (m, 4 H, H4 + H6 *Z* and *E* isomer), 3.46 (dd, *J* = 10.3, 8.7 Hz, 2 H, H4 *Z* and *E* isomer), 3.38–3.34 (m, 2 H, H4 *Z* and *E* isomer), 3.27 (tdd, *J* = 9.9, 5.7, 2.3 Hz, 2 H, H5 *Z* and *E* isomer), 2.00 (s, 3 H, $NHCOCH_3$ *Z* isomer), 1.98 (s, 3 H, $NHCOCH_3$ *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 174.3 (C=O), 174.3 (C=O), 152.16 (OCH_2-CH=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 (C1 *E* isomer), 102.5 (C1 *E* isomer), 78.5 (C5 *Z* isomer), 78.5 (C5 *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.4 (CH_{2Bn} *E* isomer), 76.4 (C2 *Z* and *E* isomer), 72.4 (C4 *Z* and *E* isomer), 67.2 (OCH_2CH=N-O *E* isomer), 65.1 (OCH_2CH=N-O *Z* isomer), 63.1 (C6 *E* isomer), 63.1 (C6 *Z* isomer), 57.6 (C4 *E* isomer), 57.6 (C4 *Z* isomer), 23.4 ($NHCOCH_3$).

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

(*E*/*Z*)-2-Acetamido-2-deoxy-β-D-galactopyranosyl Acetaldehyde *O*-Benzyl Oxime (55)

According to Procedure C, compound **55** (11.6 mg, 83%) was obtained as a colorless solid after HPLC purification (t_R 8.5 min).

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.51 (dd, *J* = 6.4, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.40–7.23 (m, 10 H, 5 H_{Ar} *E* isomer + 5 H_{Ar} *Z* isomer), 6.90 (t, *J* = 3.6 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.09 (s, 2 H, CH_{2Bn} *Z* isomer), 5.06 (s, 2 H, CH_{2Bn} *E* isomer), 4.62 (dd, *J* = 16.6, 3.4 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.50 (dd, *J* = 16.5, 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 4.43 (d, *J* = 8.4 Hz, 1 H, H1 *E* isomer), 4.42 (d, *J* = 8.4 Hz, 1 H, H1 *Z* isomer), 4.35 (dd, *J* = 12.8, 5.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 4.23 (dd, *J* = 12.8, 6.4 Hz, 1 H, OCH_2CH=N-O *E* isomer), 3.94 (dd, *J* = 10.7, 8.4 Hz, 1 H, H2 *Z* isomer), 3.93 (dd, *J* = 10.7, 8.4 Hz, 1 H, H2 *E* isomer), 3.85 (d, *J* = 3.4, 2 H, H2 *Z* and *E* isomer), 3.79 (dd, *J* = 11.4, 6.8 Hz, 2 H, H6 *Z* and *E* isomer), 3.75 (dd, *J* = 11.3, 5.3 Hz, 2 H, H6 *Z* and *E* isomer), 3.60 (dd, *J* = 10.6, 3.3 Hz, 2 H, H3 *Z* and *E* isomer), 3.50 (ddd, *J* = 7.8, 6.6, 5.3 Hz, 2 H, H5 *Z* and *E* isomer), 2.00 (s, 3 H, $NHCOCH_3$ *Z* isomer), 1.98 (s, 3 H, $NHCOCH_3$ *E* isomer).

^{13}C NMR (CD_3OD, 125 MHz): δ = 174.6 (C=O), 152.2 (OCH_2-CH=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 (C1 *Z* isomer), 102.9 (C1 *E* isomer), 77.7 (CH_{2Bn} *Z* isomer), 77.3 (C5 *Z* isomer), 77.3 (C5 *E* isomer), 77.2 (CH_{2Bn} *E* isomer), 73.7 (C3 *Z* and *E* isomer), 70.0 (C4 *Z* and *E* isomer), 67.1 (OCH_2CH=N-O *E* isomer), 65.0 (OCH_2CH=N-O *Z* isomer), 62.9 (C2 *Z* and *E* isomer), 54.6 (C2 *E* isomer), 54.5 (C2 *Z* isomer), 23.4 ($NHCOCH_3$).

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

(*E*/*Z*)-*O*-β-D-Galactopyranosyl-(1-4)-β-D-glucopyranosyl Acetaldehyde *O*-Benzyl Oxime (56)

According to Procedure C, compound **56** (10.8 mg, 85%) was obtained as a colorless solid after HPLC purification (t_R 9.2 min).

^{1}H NMR (D_2O-CD_3OD, 500 MHz): δ = 7.53 (t, *J* = 5.5 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.42–7.22 (m, 10 H, H_{Ar}), 6.96 (t, *J* = 3.8 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.01 (s, 3 H, CH_{2Bn} *Z* isomer), 5.00 (s, 3 H, CH_{2Bn} *E* isomer), 4.55 (dd, *J* = 16.6, 3.8 Hz, 1 H, OCH_2CHN *Z* isomer), 4.49 (dd, *J* = 16.6, 3.8 Hz, 1 H, OCH_2CHN *Z* isomer), 4.39–4.20 (m, 6 H, OCH_2CHN *Z* isomer + H1A + H1B *Z* and *E* isomer), 3.79 (d, *J* = 3.4 Hz, 2 H, H4B *Z* and *E* isomer), 3.79–3.27 (m, 20 H, H3A + H4A + H5A + 2 H6A + H2B + H3B + H5B + 2 H6B *Z* and *E* isomer).

^{13}C NMR (D_2O-CD_3OD, 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 (C1), 102.9 (C1), 78.7, 76.3, 76.0, 75.8, 75.2, 74.8, 73.1, 71.4, 69.0, 66.1, 61.4 (C6), 60.3 (C6).

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

(*E*/*Z*)-*O*-α-D-Glucopyranosyl-(1-4)-β-D-glucopyranosyl Acetaldehyde O-Benzyl Oxime (57)

According to Procedure C, compound **57** (10.2 mg, 80%) was obtained as a colorless solid after HPLC purification (t_R 9.2 min).

^{1}H NMR (D_2O-CD_3OD, 500 MHz): δ = 7.53 (t, *J* = 5.6 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.42–7.26 (m, 10 H, H_{Ar}), 6.97 (t, *J* = 4.0 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.28–5.18 (m, 2 H, H_{1B} *Z* and *E* isomer), 5.03 (s, 3 H, CH_{2Bn} *E* isomer), 5.02 (s, 3 H, CH_{2Bn} *Z* isomer), 4.54 (td, *J* = 4.5, 1.9 Hz, 1 H, OCH_2CHN *Z* isomer), 4.34–4.17 (m, 3 H, OCH_2CHN *Z* isomer + H1A *Z* and *E* isomer), 3.81–3.43 (m, 18 H, H3A + H4A + 2 H6A + H2B + H3B + H4B + 2 H6B *Z* and *E* isomer), 3.37–3.26 (m, 2 H, H_{5A}), 3.24–3.13 (m, 4 H, H2A + H5B *Z* and *E* isomer).

^{13}C NMR (D_2O-CD_3OD, 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 (C1A), 100.4 (C1B), 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 (C6), 60.8 (C6).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{31}NNaO_{12}$: 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 Procedure C, compound **58** (10.0 mg, 85%) was obtained after HPLC purification (t_R 9.0 min).

^{1}H NMR (D_2O, 500 MHz): δ = 7.63 (t, *J* = 4.0 Hz, 1 H, OCH_2CH=N-O *E* isomer), 7.49 (m, 10 H, H_{Ar}), 7.02 (t, *J* = 4.0 Hz, 1 H, OCH_2CH=N-O *Z* isomer), 5.11 (s, 2 H, CH_{2Bn} *E* isomer), 5.10 (s, 2 H, CH_{2Bn} *Z* isomer), 5.05 (s, 2 H, H1B *Z* and *E* isomer), 4.83 (s, 1 H, H1A *Z* isomer), 4.82 (s, 1 H, H1A *E* isomer), 4.80 (s, 2 H, H1C *Z* and *E* isomer), 4.49 (ddd, *J* = 16.0, 4.1, 1.3 Hz, 1 H, OCH_2CHN *Z* isomer), 4.40 (ddd, *J* = 16.0, 4.0, 1.3 Hz, 1 H, OCH_2CHN- *E* isomer), 4.27–4.16 (m, 2 H, OCH_2CHN *E* isomer), 4.07 (d, *J* = 8.3 Hz, 1 H, H2C), 4.04–3.99 (m, 1 H, H2B), 3.95–3.88 (m, 4 H, H2A + H2B *Z* and *E* isomer), 3.87–3–81 (m, 13 H, H3B + H6 *Z* and *E* isomer), 3.81–3.76 (m, 3 H), 3.75–3.68 (m, 10 H), 3.66–3.54 (m, 10 H).

^{13}C NMR (D_2O, 125 MHz): δ = 152.2 (OCH_2-*C*H=N-O *Z* isomer), 149.9 (OCH_2-CH=N-O *E* isomer), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 102.8 (C1B), 100.7 (C1), 100.6 (C1), 99.9 (C1), 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 (C6), 64.6 (OCH_2CH=N-O *E* isomer), 61.96, 61.35 (OCH_2CH=N-O *Z* isomer).

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

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591082.

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