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Stereoselective preparation of four 3-*C*-mannosylated D- and L-glucals from a single starting compound

Zuzana Lövyova, Kamil Parkan, Ladislav Kniežo *

Department of Chemistry of Natural Compounds, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

The corresponding oxadiene, prepared from the starting perbenzylated α-D-mannopyranosylethanal was subjected to stereoselective cycloaddition reactions with *R* and *S* methyl (ethenyloxy)(phenyl)acetates. From the two obtained diastereoisomeric cycloadducts, 3-*C*-α-D-mannosylated 1,2-D-glucal and 3-*C*-α-D-mannosylated 1,2-L-glucal were prepared. A simple epimerisation of the starting α-D-mannopyranosylethanal afforded perbenzylated β-D-mannopyranosylethanal, which was converted to 3-*C*-β-D-mannosylated 1,2-D-glucal or to 3-*C*-β-D-mannosylated 1,2-L-glucal by the same procedure. The structure of the obtained 3-*C*-α-D-mannosylated 1,2-D-glucal has been confirmed independently by its transformation to the known peracetylated methyl α-*C*-(1→3)-mannobioside. The prepared glucals are suitable precursors for the synthesis of stable glycoconjugates with non-hydrolyzable mannose-containing epitopes.

1. Introduction

Communication systems used on a molecular level by living organisms, are not limited to only the four letters of the genetic alphabet. A detailed study of the role played by saccharides in living organisms revealed that in addition to the two well-known 'alphabet' types (represented by amino acids and nucleotides), another 'alphabet' type that is utilized in biological recognition processes may also be formed by monosaccharides.[1] Using this alphabet, the cell surface carbohydrates mediate interactions between themselves and other cells (including immunodifferentiation, cell adhesion, cell differentiation, and regulation of cell growth) as well as between cells and antibodies, viruses, bacteria, peptide hormones or toxins. Among these interactions, mannose-containing ligands occupy a significant position because they are present on the surface of a large number of pathogens, such as viruses (including HIV), bacteria, fungi, and parasites. Aside from other lectins, they are also recognized by the carbohydrate recognition domain of lectin DC-SIGN, principally expressed by dendritic cells in genital and intestinal mucosa.[2] It has been shown that the inhibition of the recognition process between the mannose-containing ligands present, e.g., in HIV glycoprotein gp 120 and lectin DC-SIGN, may inhibit an infection process at one of the earliest stages.[3] In the studies of these and similar processes, it could be useful to obtain *C*-glycoside or *C*-oligosaccharide analogs of saccharides, which can mimic the structure of natural saccharide epitopes but are by far more stable in the organism because of their resistance to the ubiquitous glycosidases. The quest for effective synthetic methods leading to glycoconjugates with non-hydrolyzable saccharide mimetics is therefore very desirable. For the synthesis of the glycoconjugates mentioned, one might advantageously utilize the reactivity of the C=C bond in 1,2-glucals[4] because of its reactivity, which enables one- or two-step stereoselective preparations of *gluco*-[5] or mannopyranosyl glycosides,[6] glycosides of glucosamine[7] or mannosamine,[8] and some *C*-glycosides.[9] One can envisage that these or similar reactions of *C*-mannosylated 1,2-glucals may also be utilized for their attachment to an oligosaccharide, peptide or lipid moieties, either by glycosidic or C–C bonding, thus enabling the synthesis of various stable glycoconjugates with non-hydrolyzable mannose-containing epitopes. Therefore, we decided to prepare diastereoisomeric 3-*C*-mannosylated 1,2-glucals **1**–**4** as precursors for the synthesis of non-hydrolyzable glycoconjugates, using an approach to the preparation of 3-*C*-glycosylated D- and L-1,2-glucals that was recently published by our group.[10]

Thus, in the present paper, we describe a method enabling the conversion of the starting perbenzylated α-D-mannopyranosylethanal **5** into either of the two 3-*C*-α-D-mannosylated 1,2-glucals, namely 1,5-anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-*C*-[(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)methyl]-D-*arabino*-hex-1-enitol **1** or 1,5-anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-*C*-[(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)methyl]-L-*arabino*-hex-1-enitol **2**. Following facile epimerization of aldehyde **5** to β-D-mannopyranosylethanal **6**, it is possible to obtain any of the two 3-*C*-β-D-mannosylated 1,2-glucals by the same procedure, namely

* Corresponding author. Tel.: +420 220 444 265; fax: +420 220 444 422; e-mail address: Ladislav.Kniezo@vscht.cz (L. Kniežo).

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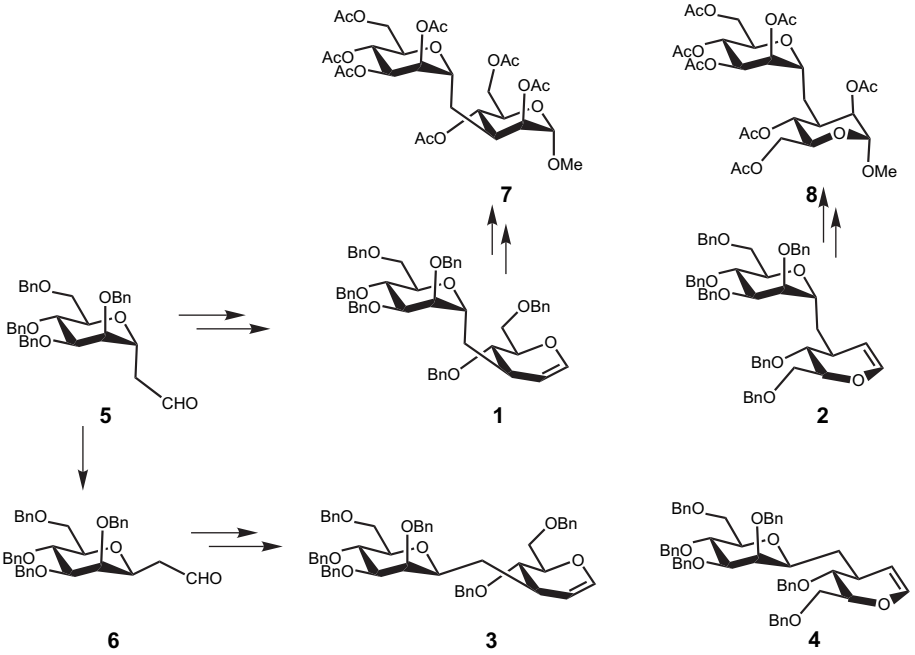
1,5-anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-*C*-[(2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)methyl]-D-*arabino*-hex-1-enitol **3** and 1,5-anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-*C*3,4,6-tetra-*O*-[(2,-benzyl-β-D-mannopyranosyl)methyl]-L-*arabino*-hex-1-enitol **4**. The structure of the obtained glucal **1** has been confirmed independently by its transformation to the known peracetylated methyl α-*C*-mannobioside **7**.[11] By the same manner, glucal **2** was converted to the diastereomeric *C*-disaccharide **8** with L-mannopyranose at the reducing end (Scheme 1).

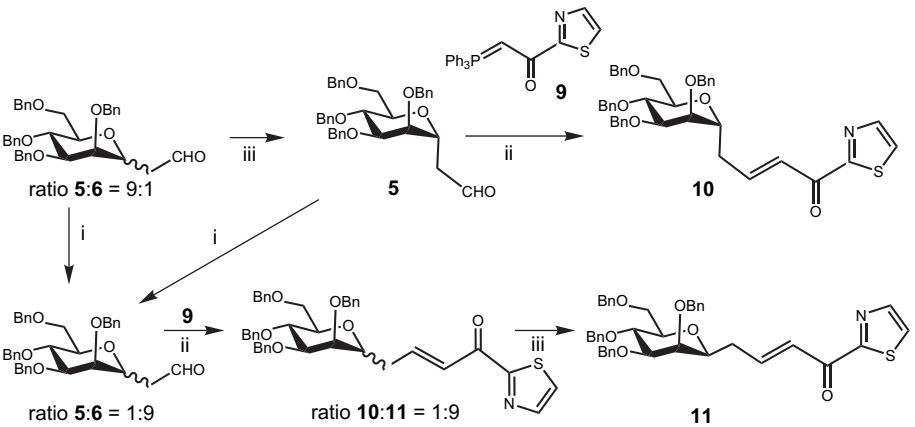


Scheme 1. Synthetic route to 3-*C*-mannosylated glucals **1**–**4**.

2. Results and discussion

The starting perbenzylated α-D-mannopyranosylethanal **5** is a known compound,[12] and the best method of its preparation is ozonolysis or dihydroxylation of the C=C bond (and its subsequent oxidative cleavage) of perbenzylated α-D-mannopyranosylpropene, accessible by stereoselective allylation of the D-mannopyranosyl cation generated from suitable precursors.[13] Because we required a greater amount (more than 10 g) of pure α-D-mannopyranosylethanal **5** and its β-isomer **6**, stereoselective synthesis of multigram amounts of pure perbenzylated α-D-mannopyranosylpropene did not appear to be practical. Therefore, we tried to obtain the aldehyde **5** through a more economic approach, from the readily accessible mixture of peracetylated α- and β-D-mannopyranosylpropenes.[14] Although this mixture is not separable by simple column chromatography, our preliminary experiments have shown that replacement of the acetyl protecting groups by benzyl groups and subsequent ozonolysis of the C=C bond leads to a mixture of perbenzylated α- and β-D-mannopyranosylethanals **5** and **6** that are separable (as shown by TLC) by chromatography on silica gel.

We prepared the mixture of peracetylated α- and β-D-mannopyranosylpropenes using a slight modification of the original procedure.[14] A solution of peracetylated D-mannose, 4 equiv of allyltrimethylsilane, and 5.5 equiv of $BF_3 \cdot Et_2O$ was refluxed in acetonitrile for 5 h. Following a workup of the reaction mixture, an unseparable mixture of peracetylated α- and β-D-mannopyranosylpropenes was afforded in 75% yield. Replacement of the acetyl protecting groups by benzyl groups and the subsequent ozonolysis gave a mixture of perbenzylated α- and β-D-mannopyranosylethanals **5** and **6** in the ratio of 9:1 (as determined by integration of the −CHO protons in the ^{1}H NMR spectrum; α anomer: triplet at 9.71 ppm, β anomer: triplet at 9.56 ppm). Chromatography of this mixture on silica gel afforded pure perbenzylated α-D-mannopyranosylethanal **5** in good yield, which in the Wittig reaction with ((2-thiazolylcarbonyl)methylen)triphenylphosphorane **9**[15] gave the only product substituted oxadiene **10**, which is



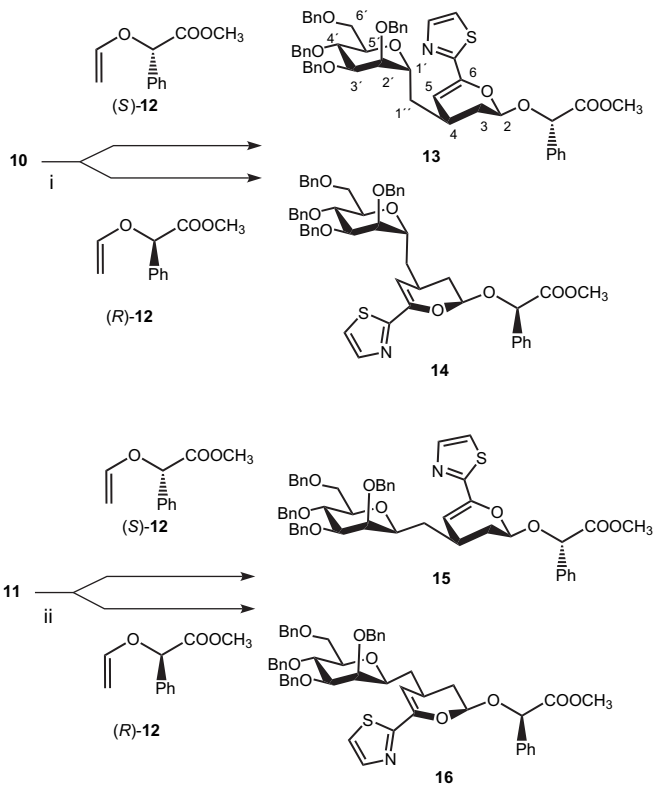
Scheme 2. Synthesis of **10** and **11**. Reagents and conditions: (i) 1% K_2CO_3/MeOH, rt, sonication, 6 h; (ii) **9**, $CHCl_3$, 50 °C, 48 h; (iii) flash chromatography.

the intermediate for the synthesis of glucal **1** or **2** (Scheme 2). It is evident that, alternatively, the described processes[13] may be used for the preparation of pure perbenzylated α-mannopyranosylpropene, which can be converted to aldehyde **5** by ozonolysis and subsequently converted to oxadiene **10** by reaction with phosphorane **9**.

To synthesize the substituted oxadiene **11**, which is an intermediate for the synthesis of glucals **3** and **4**, we made use of the epimerization of α-D-mannopyranosylethanal **5**. This epimerization was described to proceed in methanolic solution with either MeONa[16] or proline in a microwave oven.[17] In the first case, however, the arising β-D-mannopyranosylethanal **6** was not isolated but was reduced in situ to the corresponding alcohol. In the second case, the reaction was performed with only 0.4 mmol of aldehyde **5**. For epimerization of multigram amounts of the aldehyde **5**, a 1% methanolic solution of K_2CO_3 proved to be useful. After adding smaller amounts (≤0.5 g) of pure aldehyde **5** into a stirred solution of 1% methanolic K_2CO_3 at room temperature, equilibrium was achieved after about 2 days, and according to the ^{1}H NMR, the equilibrium mixture consisted of aldehydes **5** and **6** in the ratio of 1:12. Epimerization of greater amounts of the aldehyde was slower, and moreover, signals of other products began to appear in the ^{1}H NMR spectrum. However, the epimerization can be markedly accelerated by sonication. Thus, when 7 g of the starting aldehyde (or a mixture of aldehydes 5:6=9:1) was sonicated for 6 h at room temperature, the equilibrium mixture contained solely compounds **5** and **6** in the ratio of 1:9, whereas after longer periods of sonication, traces of the side product began to appear. Attempts to separate β-D-mannopyranosylethanal **6** from the remnants of the starting α-D-mannopyranosylethanal **5** by chromatography on silica gel were not very successful, and we isolated the pure β-D-mannopyranosylethanal **6** in a maximum yield of about 35%. The low yield is most likely due to relatively rapid decomposition of **6** (unlike **5**) on silica gel. Therefore, we abandoned purification attempts at this step and directly subjected the mixture of aldehydes **5** and **6** (1:9) to the Wittig reaction with ((2-thiazolylcarbonyl)-methylen)triphenylphosphorane **9**. The minor α-epimer **10** in the obtained mixture of oxadienes **10** and **11** was then removed by chromatography on silica gel, affording pure intermediate **11** in a good yield.

The obtained intermediates **10** and **11** were subjected to cycloaddition reactions with both enantiomers of methyl (ethenyloxy)(phenyl)acetate, (*R*)-**12** and (*S*)-**12**, easily obtainable from cheap and commercially accessible enantiomers of mandelic acid.[18] The cycloadditions were accelerated by sonication and proceeded at room temperature in the presence of 0.15 equiv of Eu(fod)$_3$ .The reaction time was 48 h for the α-D-mannopyranosyl derivative **10** and 24 h for the β-D-mannopyranosyl derivative **11**. NOE experiments confirmed the cis-relation of substituents on the C-2 and C-4 atoms of the 3,4-dihydro-2*H*-pyran ring in all of the obtained cycloadducts **13**–**16**. On the basis of analogy with similar cycloadditions that we had studied earlier,[10,18b,19] we can assume with great certainty that, similar to all preceding cases, the vinyl ether (*S*)-12 afforded cycloadducts **13** and **15** with 2*R*,4*R*-configuration and the vinyl ether (*R*)-**12** gave cycloadducts **14** and **16** with 2*S*,4*S*-configuration on the 3,4-dihydro-2*H*-pyran ring (Scheme 3).

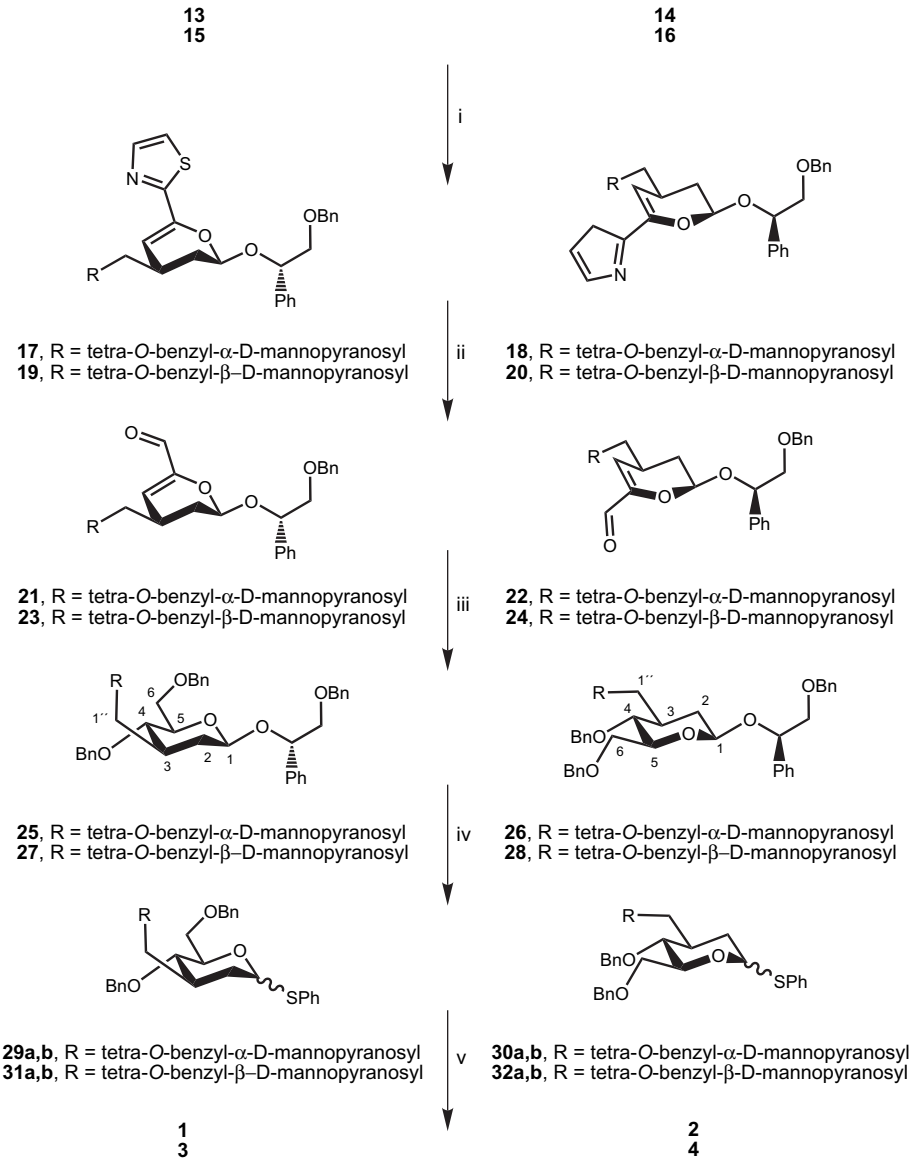
All four synthesized cycloadducts **13**–**16** were converted into the final glucal derivatives **1**–**4** using a procedure that was recently published by our group,[10] shown in Scheme 4. Reduction of the ester group in **13**–**16**, followed by benzylation of the resultant hydroxy group, afforded compounds **17**–**20**, which gave aldehydes **21**–**24** after transformation of the thiazole ring. Simultaneous reduction of the aldehyde group and hydroboration of the double bond by $BH_3\cdot Me_2S$ led to *C*-(1→3)-disaccharides **25**–**28**, having 2-deoxy-*arabino*-hexopyranose (compound **25**: $J_{3,4}$ 9.5 Hz, $J_{4,5}$ 9.7 Hz, compound **26**: $J_{3,4}$=$J_{4,5}$ 9.7 Hz, compound **27**: $J_{3,4}$=$J_{4,5}$ 9.7 Hz, and compound **28**: $J_{3,4}$=$J_{4,5}$ 9.4 Hz) at the reducing end, and these



Scheme 3. Stereoselective synthesis of **13**–**16**. Reagents and conditions: (i) (*R*)-**12** or (*S*)-**12**, Eu(fod)$_3$ (15 mol %), CH_2Cl_2, rt, sonication 48 h; (ii) (*R*)-**12** or (*S*)-**12**, Eu(fod)$_3$ (15 mol %), CH_2Cl_2, rt, sonication 24 h.

disaccharides were treated with thiophenol to give anomeric mixtures of thioglycosides **29a**,**b**–**32a**,**b**. Hydrolysis of the thioglycosides and subsequent mesylation and elimination of the formed hydroxy group led to glucals **1**–**4**. It is worth mentioning that in the synthesized structures with the α-D-mannopyranosyl moiety (e.g., **13**, **14**, **25**, **26**, and **2**), this non-reducing D-mannohexopyranose showed deviation from the normal $^4C_1$ conformation, as follows from lower values (6.4–7.3 Hz) of vicinal diaxial interactions between H-3′ and H-4′ and between H-4′ and H-5′ in the NMR spectra of these compounds. The same effect was also observed for α-*C*-(1→3)-mannobioside[11] and was explained by the steric congestion between the two monosaccharide moieties. In structures containing the β-D-mannopyranosyl moiety (**15**, **16**, **19**, **20**, **23**, **24**, **27**, **28**, **31a**, **3**, and **4**), this steric congestion is evidently not present because their β-D-mannohexopyranose moieties have 'normal' values of vicinal diaxial interactions between H-3′ and H-4′ and between H-4′ and H-5′ (in the range 9.2–9.7 Hz).

Because the assignment of the D- or L-configuration in glucals **1**–**4** is based only on analogy with similar previously studied cycloadditions,[10,18b,19] we decided to confirm the assignment unequivocally by transforming glucal **1** to the known peracetyl methyl α-*C*-(1→3)-mannobioside **7** that has already been prepared by coupling two D-mannohexopyranoses in an Sm_2I-promoted C-glycosylation.[11] The simplest way to transform glucal **1** to methyl *C*-mannobioside **7** is to perform an epoxidation with *m*-chloroperoxybenzoic acid in methanol, where formation of the α-epoxide should give rise to the corresponding methyl glucopyranoside derivative, whereas epoxidation from the β-face of the double bond should lead to the desired methyl mannopyranoside **7**. As indicated by the literature data, the diastereoselectivity of this epoxidation may depend significantly on the structure and substitution of the starting unsaturated saccharide. Thus, for example, epoxidation of 4-*O*-glycosylated glucal, namely hexa-*O*-methylmaltal, with *m*-chloroperoxybenzoic acid in

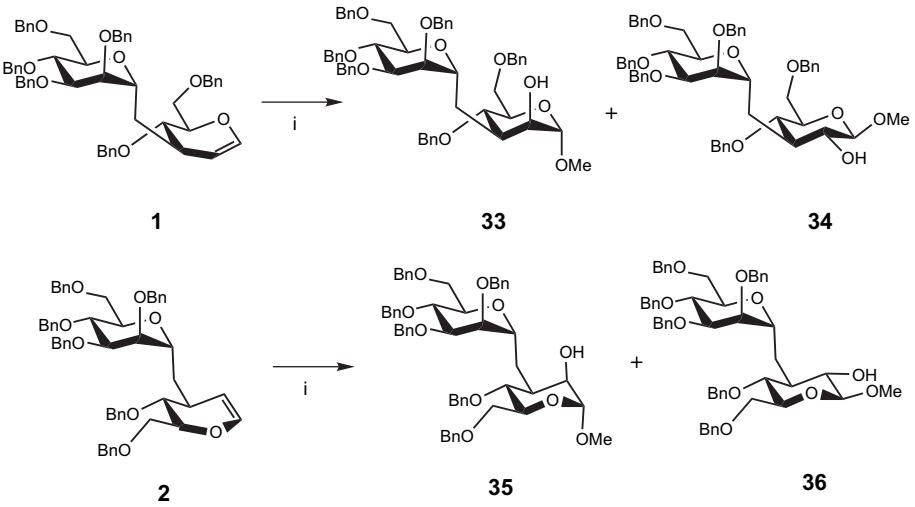


Scheme 4. Synthesis of glucals **1**–**4**. Reagents and conditions. (i) (a) $LiAlH_4$, THF, rt, 1 h; (b) NaH, BnBr, Bu_4NI, THF, 40 °C, 4 h, then rt 14 h; (ii) (a) MeOTf, MeCN, rt, 15 min; (b) $NaBH_4$, MeOH, rt, 15 min; (c) $AgNO_3$, MeCN/H_2O, rt, 20 min; (iii) (a) $Me_2S{\cdot}BH_3$, THF, rt, 16 h; (b) NaOH, H_2O_2, rt, 30 min; (c) NaH, BnBr, Bu_4NI, THF, 40 °C, 4 h, then rt 14 h; (iv) PhSH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 °C, then to rt 2 h; (v) (a) NBS, moist acetone (1% H_2O), −15 °C, 1 h, exclusion of light; (b) Ms_2O, *s*-collidine, CH_2Cl_2, 0 °C, 4 h.

methanol proceeded selectively from the α-face, affording solely methyl hexa-*O*-methyl-β-maltoside.[20] The same epoxidation of 3-*C*-glycosylated galactal, i.e., 4,6-di-*O*-benzyl-3-*C*-[(1*R*)-1,3,4,5,7-penta-*O*-benzyl-2,6-anhydro-D-*glycero*-L-*manno*-heptitol-1-*C*-yl]-3-deoxy-D-galactal, took place predominantly from the β-face under formation of methyl 4,6-di-*O*-benzyl-1,3-*C*-[(1*R*)-1,3,4,5,7-penta-*O*-benzyl-2,6-anhydro-D-*glycero*-L-*manno*-heptitol-1-*C*-yl]-3-deoxy-α-D-*talo*-pyranoside as the principal reaction product.[21]

We performed this simple epoxidation with glucal **1** and found that the reaction also proceeded preferentially from the β-face and that stereoselectivity of the epoxidation is practically the same as in the case of the *C*-glycosylated galactal.[21] The epoxidation afforded a mixture of two methyl glycosides **33** and **34**, which were easily separable by chromatography on silica gel (Scheme 5). The major product **33** was isolated chromatographically in 56% yield, and the minor product **34** was isolated in 20% yield. Both products had the same molecular weight (MS), corresponding to the expected methyl glycosides. In the ^1H NMR spectrum of **33**, the H-1 proton appeared as a broad singlet at 4.29 ppm, which corresponds to the methyl α-mannopyranoside structure, whereas in the spectrum of **34**, the H-1 proton appeared as a doublet at 4.13 ppm ($J_{1,2}$ 7.6 Hz), corresponding to methyl β-glucopyranoside. Moreover, debenzylation, followed by acetylation of the major product **33**, afforded a compound whose NMR spectra were identical with those published for peracetylated methyl α-*C*-(1→3)-mannobioside 7.[11] The only significant difference was the chemical shift of the methylene protons of the *C*-glycoside bond (H-1″a,b), described in the original paper as a multiplet at 1.40 to 1.24 ppm, which we found to be a multiplet at 1.88 to 1.83 ppm, partly overlapped with signals of acetyl groups. Chemical shifts of these protons were confirmed by using COSY and HMQC spectra. Because the chemical shifts and multiplicities of other protons were identical with the published values, we assume that the chemical shift of the *C*-glycoside methylene protons was assigned erroneously in the original paper.

By analogy, the same epoxidation of glucal **2** afforded a mixture of two methyl glycosides **35** and **36**, which were isolated by chromatography on silica gel in the yields of 51% and 20%, respectively. Similar to the preceding case, the H-1 proton in the major methyl



Scheme 5. Epoxidation of glucals **1** and **2**. Reagents and conditions: (i) MCPBA, MeOH, CH_2Cl_2, rt, 1.5 h.

glycoside **35** exhibited a broad singlet at 4.59 ppm, whereas in the methyl glycoside **36**, it appeared as a doublet at 4.11 ppm ($J_{1,2}$ 7.6 Hz). Debenzylation of methyl glycoside **35** followed by acetylation afforded *C*-disaccharide **8**, whose ^{1}H NMR spectrum was similar to that of compound **7**. However, it exhibited significant differences in chemical shifts or coupling constants for some protons. The most significant chemical shift differences (more than 0.1 ppm) were found for the protons H-1, H-2, H-3, and H-4 and for the methylene protons of the *C*-glycoside bond, which appeared as two discrete multiplets at 1.92 and 1.77 ppm. In regard to the coupling constants, the most significant deviations were observed for the H-3 proton.

Comparison of the NMR spectra of the obtained methyl glycosides **7** and **8** with the published spectra of methyl α-*C*-(1→3)-mannobioside showed convincing evidence that compound **7** is identical to the known methyl α-*C*-(1→3)-mannobioside, whereas compound **8** is its diastereoisomer. The differences in the H-3 proton coupling constants (for **7**: *J* 11.0, 5.5, 5.5, 3.0 Hz, and for **8**: *J* 11.2, 11.2, 3.1, 3.1 Hz) agree with the fact that *C*-disaccharides **7** and **8** differ in the absolute configuration of mannohexopyranose at the reducing end, which manifests itself in different conformational preferences of the *C*-aglycone bond. Thus, as follows from the obtained NMR spectra, the configuration for the cycloadducts **13** and **14** have been assigned correctly and compounds **1** and **3** are 3-*C*-mannosylated glucals with D-configuration, whereas compounds **2** and **4** are 3-*C*-mannosylated glucals with L-configuration.

3. Conclusion

In summary, we have reported a stereoselective synthesis of any of the four diastereoisomeric 3-*C*-mannosylated 1,2-glucals (1,5-anhydro-2,3-dideoxy-*arabino*-hex-1-enitols) **1**–**4** starting from the known α-D-mannopyranosylethanal **5**. The key step of the synthetic protocol is the cycloaddition of substituted oxadienes, prepared from starting aldehyde **5**, with chiral vinyl ethers derived from both enantiomers of mandelic acid. The final compounds were obtained in seven steps with overall yields 8.37% (for **1**), 9.17% (for **2**), 9.37% (for **3**), and 9.00% (for **4**). Epoxidation of glucals **1** or **2** in methanol afforded as the principal reaction products methyl glycosides of *C*-disaccharides **33** or **35** in 56% and 51% isolated yields, respectively. The obtained methyl glycoside **33** is a non-hydrolyzable analog of disaccharide α-D-Man-(1→3)-D-Man, which is significantly present in cell surface carbohydrates as the core branching region of asparagine-linked oligosaccharides. The simple epoxidation of glucal **1** and the subsequent facile chromatographic isolation of *C*-disaccharide **33** represent a good alternative to the published preparation of this structure.[11] Moreover, the prepared 3-*C*-mannosylated 1,2-glucals **1**–**4** are useful intermediates for preparation of various non-hydrolyzable mannose—containing (1→3)-disaccharide mimetics, which may serve either as tools for study of recognition processes with lectins or for synthesis of non-hydrolyzable glycoprotein or glycolipid epitopes.

4. Experimental

4.1. General methods

All solvents were purified by standard procedures. TLC was performed on HF_{254} plates (Merck), and the detection utilized either UV light or spraying with $Ce(SO_4)_2$ solution (5 g) in 10% H_2SO_4 (500 mL), with subsequent heating. Flash column chromatography was performed on silica gel (Merck, 100–160 μm) with solvents that had been distilled prior to use. Optical rotations were measured at 20 °C on a spectropolarimeter Autopol VI. ^{1}H (300 and 500 MHz) and ^{13}C (75 and 125.7 MHz) NMR spectra were recorded on Varian Oxford 300 and Bruker DRX 500 Avance spectrometers, using tetramethylsilane as an internal standard. The assignments of ^{1}H and ^{13}C signals were confirmed by homonuclear COSY and heteronuclear 2D correlated spectra, respectively. NOE connectivities were obtained using 1D ^{1}H DPFGSE-NOE experiments. Infrared spectra were recorded as $CHCl_3$ solutions on Nicolet 750 FT-IR spectrometer and are reported in wave numbers (cm^{-1}). Mass spectra and HPLC were performed on a 250×4.6 mm column packed with 5 μm Supelco BDS Hypersil C-18, with a mobile phase of MeOH/water, using an HP 1100 instrument equipped with a gradient pump, a column thermostat and, in addition to a UV detector, an Agilent G1956B single quadrupole system as an MS detector.

*4.1.1. (2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-ethanal (**5**).* Allyltrimethylsilane (60 mL, 368 mmol) and $BF_3{\cdot}Et_2O$ (65 mL, 492 mmol) were portionwise added to a solution of 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose (35 g, 93 mmol) in dry CH_3CN (500 mL). The mixture was refluxed for 5 h, then cooled to room temperature, and after concentration diluted with CH_2Cl_2 (500 mL). The solution was washed with 2 M NaOH under vigorous stirring to persisting alkaline reaction of the aqueous phase. The organic layer was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and the solvent

was evaporated. Chromatography of the residue (light petroleum/ethyl acetate, 3:1) afforded an unseparable mixture of α and β (2,3,4,6-tetra-*O*-acetyl-D-mannopyranosyl)-prop-2-enes (25 g, 75%); R_f=0.5 (light petroleum/ethyl acetate, 2:1). ESIMS: MH^+ found: 373.7. $C_{17}H_{25}O_9$ requires 373.2. The spectroscopic data were consistent with those reported.[14] A 0.1 M solution of MeONa in MeOH was added dropwise to the obtained mixture of peracetylated D-mannopyranosylprop-2-enes in MeOH (500 mL) to allow the alkaline reaction to persist, and the reaction mixture was stirred at room temperature. After 20 h, no starting compound was detected (TLC) in the reaction mixture, and the reaction was then neutralized with Dowex 50 (5 g) and filtered. Evaporation of the solvent and chromatography on silica gel (chloroform/MeOH, 5:1) afforded 13 g of a mixture of α and β D-mannopyranosylprop-2-enes; R_f=0.4 (chloroform/MeOH, 5:1). ESIMS: MH^+ found: 205.7. $C_9H_{17}O_5$ requires 205.2. The obtained mixture of D-mannopyranosylprop-2-enes was dissolved in dry tetrahydrofuran (400 mL). To this solution, we added 11.8 g (296.7 mmol) of a 60% suspension of NaH in mineral oil, and the reaction mixture was stirred at room temperature for 1 h. Then, tetrabutylammonium iodide (4.56 g, 12.3 mmol) was added, followed by dropwise addition of benzyl bromide (35.3 mL, 296.7 mmol). The reaction mixture was heated at 50 °C for 2 h and then stirred at room temperature for another 15 h. The excess hydride was decomposed by the addition of MeOH (5 mL), the solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and H_2O. The organic phases were combined, dried, and stripped of solvent, and the residue was chromatographed on silica gel (light petroleum/ethyl acetate, 12:1→9:1). This procedure yielded 33 g of a mixture of α and β perbenzylated D-mannopyranosylprop-2-enes; R_f=0.35 (light petroleum/ethyl acetate, 9:1). ESIMS: MH^+ found: 565.8. $C_{37}H_{41}O_5$ requires 565.7. The mixture obtained was dissolved in dry dichloromethane (200 mL) and was subsequently ozonized, after addition of anhydrous MeOH (40 mL) and cooling to −78 °C. After 20 min, the mixture did not contain (TLC) any starting compound, and the reaction was terminated by passing nitrogen through the mixture for 5 min. Then $NaHCO_3$ (4 g) (to prevent an acetalization) and then dimethyl sulfide (43 mL, 587 mmol) were added successively, and the stirred mixture was allowed to warm to room temperature. After stirring the mixture for 3 days at room temperature, the $NaHCO_3$ was filtered off, and the solvent was evaporated. ^{1}H NMR of the crude product showed the presence of a mixture of α and β perbenzylated D-mannopyranosylethanals **5** and **6** in a 9:1 ratio (aldehyde proton of the α-diastereoisomer as a triplet at 9.71 ppm and that of the β-diastereoisomer as a triplet at 9.56 ppm). Chromatography on a silica gel column (light petroleum/ethyl acetate, 9:1→5:1) afforded 23 g (60% from mixture of peracetylated D-mannopyranosylprop-2-enes) of (2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-ethanal **5**; R_f=0.35 (light petroleum/ethyl acetate, 3:1) and 6.5 g of a mixture of α and β of perbenzylated D-mannopyranosylethanals **5** and **6**; R_f=0.30 (light petroleum/ethyl acetate, 3:1). The spectroscopic data obtained for compound **5** were identical to those reported.[12b]

*4.1.2. (E)-4-(2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-1-(thiazol-2-yl)-but-2-en-1-one (**10**).* Ylide **9**[15] (17.2 g, 44.5 mmol) was added to a solution of aldehyde **5** (11.5 g, 20.3 mmol) in $CHCl_3$ (130 mL), and the mixture was stirred and heated at 50 °C. After 48 h, the reaction mixture did not show an aldehyde proton signal (9.71 ppm) in the ^{1}H NMR spectrum. The solvent was evaporated, and the residue was chromatographed on silica gel (light petroleum/ethyl acetate, 5:1→3:1), affording 9.6 g (70%) of compound **10** as a yellow viscous oil; [Found: C, 72.66; H, 5.96. $C_{41}H_{41}NO_6S$ requires C, 72.86; H, 6.11%]; R_f=0.3 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +9.5 (*c* 0.74, $CHCl_3$); ν_{max} 3011, 1671, 1625, 1454, 1390, 1094, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.89 (d, 1H, *J* 3.0 Hz, H-thiazol), 7.52 (d, 1H, *J* 3.0 Hz, H-thiazol), 7.15–7.40 (m, 22H, 4× C_6H_5, H-2, H-3), 4.64–4.44 (m, 8H, 4× O–CH_2–Ph), 4.16 (m, 1H, H-1′), 3.96 (dd, 1H, $J_{4',5'}$ 10.4 Hz, $J_{5',6'b}$ 5.0 Hz, H-5′), 3.91–3.76 (m, 3H, H-3′, H-6′a, H-4′), 3.72 (dd, 1H, $J_{6'a,6'b}$ 10.3 Hz, $J_{6'b,5'}$ 5.0 Hz, H-6′b), 3.62 (dd,1H, $J_{3',2'}$ 6.3 Hz, $J_{2',1'}$ 2.7 Hz, H-2′), 2.73–2.52 (m, 2H, H-4a, H-4b); ^{13}C NMR (125 MHz, $CDCl_3$) 180.9 (*C*-1), 167.8 (thiazol *C*-2), 146.7 (C-2), 144.4 (*C*–H thiazol), 138.1, 137.9, 137.7, 137.6 (4× *ipso* C_6H_5), 128.2–127.2 (20× C_6H_5), 126.3 (C-3), 126.0 (*C*–H thiazol), 75.4 (C-2′), 75.1, 74.3 (C-3′, C-4′), 73.9 (C-5′), 72.9, 72.7, 72.0, 71.2 (4× CH_2–Ph), 70.3 (C-5′), 68.4 (C-6′), 34.1 (C-4). ESIMS: MH^+, found: 676.4. $C_{41}H_{42}NO_6S$ requires 676.8.

*4.1.3. (E)-4-(2,3,4,6-Tetra-O-benzyl-β-D-mannopyranosyl)-1-(thiazol-2-yl)-but-2-en-1-one (**11**).* Aldehyde **5** (or the mixture of aldehydes **5** and **6** in a ratio of 9:1) (7.0 g, 12.3 mmol) was dissolved in a 1% methanolic solution of K_2CO_3 (270 mL) and was sonicated at room temperature. According to ^{1}H NMR, the reaction mixture contained the mixture of aldehydes **5** and **6** in a ratio of 1:9 after 6 h. The reaction was quenched by neutralization with acetic acid, the solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and a saturated NaCl solution. The organic phase was dried, the solvent evaporated, and the residue dissolved in $CHCl_3$. Ylide **9**[15] (10.5 g, 27.2 mmol) was added to the solution, and the mixture was heated at 50 °C. After 30 h, the reaction mixture did not show any aldehyde proton signals in the ^{1}H NMR spectrum. The solvent was evaporated, and the residue was chromatographed on silica gel (light petroleum/ethyl acetate, 5:1→3:1), affording 3.8 g (60%) of compound **11** as a yellow viscous oil; [Found: C, 72.64; H, 6.25. $C_{41}H_{41}NO_6S$ requires C, 72.86; H, 6.11%]; R_f=0.32 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +7.4 (*c* 0.74, $CHCl_3$); ν_{max} 3009, 1675, 1627, 1453, 1390, 1095, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.99 (d, 1H, H-thiazol, *J* 2.9 Hz), 7.65 (d, 1H, H-thiazol, *J* 2.9 Hz), 7.15–7.42 (m, 22H, 4× C_6H_5, H-2, H-3), 4.5–5.1 (m, 8H, 4× O–CH_2–Ph), 3.95 (dd, 1H, $J_{4',5'}$ 10.0 Hz, $J_{4',H\text{-}3'}$ 9.5 Hz, H-4′), 3.77 (m, 2H, H-2′, H-6′a), 3.70 (dd, 1H, $J_{6'a,6'b}$ 10.9 Hz, $J_{6'b,5'}$ 5.3 Hz, H-6′b), 3.64 (dd,1H, $J_{3',4'}$ 9.5 Hz, $J_{3',2'}$ 2.2 Hz, H-3′), 3.49 (m, 2H, H-1′, H-5′), 2.78 (m, 1H, H-4a), 2.49 (m, 1H, H-4b); ^{13}C NMR (125 MHz, $CDCl_3$) 181.4 (C-1), 168.1 (thiazol *C*-2), 147.0 (C-2), 144.7 (*C*–H thiazol), 138.4, 138.3, 138.2 (4× *ipso* C_6H_5), 128.5–127.4 (20× C_6H_5), 126.4 (*C*–H thiazol), 126.3 (C-3), 85.2 (C-3′), 79.9, 77.1 (C-1′, C-5′), 74.9 (C-2′, C-4′), 74.3, 73.5, 72.6 (4× CH_2–Ph), 69.5 (C-6′), 34.9 (C-4). ESIMS: MNH_4^+, found, 693.2. $C_{41}H_{42}N_2O_6S$ requires 693.3.

*4.1.4. Methyl (S)-2-phenyl-2-{[(2R,4R)-4-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl]oxy}acetate (**13**).* Eu(fod)$_3$ (2.10 g, 2.06 mmol) was added to a solution of compound **10** (9.0 g, 13.3 mmol) and chiral vinyl ether (*S*)-**12**[18] (3.9 g, 20.3 mmol) in dichloromethane (200 mL), and the reaction mixture was sonicated at room temperature. After 48 h, the mixture did not contain (TLC) any starting compound **10**. Evaporation of solvent and chromatography of the residue on silica gel (light petroleum/ethyl acetate, 3:1→2:1) afforded 8.7 g (75%) of compound **13** as a colorless foam; [Found: C, 71.78; H, 6.05. $C_{52}H_{53}NO_9S$ requires C, 71.95; H, 6.15%]; R_f=0.30 (light petroleum/ethyl acetate, 2:1); $[\alpha]_D^{20}$ +21.1 (*c* 1.36, $CHCl_3$); ν_{max} 3010, 1736, 1496, 1454, 1272, 1095, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.73 (d, 1H, H-thiazol, *J* 3.2 Hz), 7.45–7.15 (m, 26H, 5× C_6H_5, H-thiazol), 6.05 (d, INS> 1H, $J_{5,4}$ 3.7 Hz, H-5), 5.46 (s, 1H, Ph*CH*COOCH$_3$), 5.42 (dd, 1H, $J_{2,3ax}$ 5.5 Hz, $J_{2,3eq}$ 2.2 Hz, H-2), 4.73–4.42 (m, 8H, 4× O–CH_2–Ph), 4.18 (m, 1H, H-1′), 3.92–3.81 (m, 3H, H-4′, H-5′, H-6′a), 3.76 (dd, 1H, $J_{6'a,6'b}$ 10.5 Hz, $J_{6',5'}$ 3.3 Hz, H-6′b), 3.71 (dd, 1H, $J_{3',4'}$ 6.7 Hz, $J_{3',2'}$ 2.7 Hz, H-3′), 3.68 (s, 3H, COO*CH*$_3$), 3.49 (dd, 1H, $J_{2',1'}$ 4.3 Hz, $J_{3',2'}$ 2.7 Hz, H-2′), 2.67 (m, 1H, H-4), 2.23 (ddd, 1H, $J_{3eq,3ax}$ 13.7 Hz, $J_{3eq,4}$ 6.8 Hz, $J_{3eq,2}$ 2.2 Hz, H-3$_{eq}$), 2.04 (ddd, 1H, $J_{3eq,3ax}$ 13.7 Hz, $J_{3ax,4}$ 5.9 Hz, $J_{3ax,2}$ 5.5 Hz, H-3$_{ax}$), 1.89 (m, 1H, H-1″a), 1.70 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 170.8 (*C*OOCH$_3$), 163.9 (thiazol C-2), 143.1 (*C*–H thiazol), 143.0 (C-6), 138.4, 138.3, 138.2,

138.1, 136.1 (5× *ipso* C_6H_5), 128.4–127.1 (25× C_6H_5), 118.5 (*C*–H thiazol), 104.6 (C-5), 97.9 (C-2), 77.6 (PhCHCOOCH$_3$), 77.3 (C-3′), 76.6 (C-2′), 74.8, 73.4 (C-4′, C-5′), 73.6, 73.2, 72.0, 71.6 (4× CH_2–Ph), 71.1 (C-1′), 69.2 (C-6′), 52.2 (COOCH$_3$), 35.4 (C-1″), 32.8 (C-3), 27.1 (C-4). ESIMS: MH$^+$, found, 869.3. $C_{52}H_{54}NO_9S$ requires 869.1.

*4.1.5. Methyl (R)-2-phenyl-2-{[(2S,4S)-4-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl]oxy}acetate (**14**).* According to the same procedure described for the preparation of compound **13**, compound **10** (8.0 g, 11.8 mmol) and chiral vinyl ether (*R*)-**12**[18] (3.4 g, 17.8 mmol) afforded 8.2 g (80%) of compound **14** as a colorless foam; [Found: C, 71.75; H, 5.95. $C_{52}H_{53}NO_9S$ requires C, 71.95; H, 6.15%]; R_f=0.30 (light petroleum/ethyl acetate, 2:1); $[\alpha]_D^{20}$ −9.1 (*c* 0.99, $CHCl_3$); ν_{max} 3011, 1747, 1496,1454, 1272, 1096, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.73 (d, 1H, H-thiazol, *J* 3.2 Hz), 7.45–7.13 (m, 26H, 5× C_6H_5, H-thiazol), 5.95 (d,1H, $J_{5,4}$ 3.9 Hz, H-5), 5.46 (s, 1H, PhC*H*COOCH$_3$), 5.41 (dd, 1H, $J_{2,3ax}$ 6.0 Hz, $J_{2,3eq}$ 2.3 Hz, H-2), 4.73–4.42 (m, 8H, 4× O–CH_2–Ph), 4.18 (m, 1H, H-1′), 3.86 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 6.4 Hz, H-4′), 3.82–3.74 (m, 2H, H-3′, H, 6′a), 3.70 (m,5H, COOC*H*$_3$, H-5′, H-6′b), 3.52 (dd, 1H, $J_{2',3'}$ 4.8 Hz, $J_{2',1'}$ 3.0 Hz, H-2′), 2.71 (m, 1H, H-4), 2.18 (ddd, 1H, $J_{3eq,3ax}$ 13.6 Hz, $J_{3eq,4}$ 6.8 Hz, $J_{3eq,2}$ 2.3 Hz, H-3$_{eq}$), 1.98–1.79 (m, 2H, H-3, H-1″), 1.63 (m, 1H, H-1″); ^{13}C NMR (125 MHz, $CDCl_3$) 170.8 (*C*OOCH$_3$), 163.9 (thiazol C-2), 143.2, 143.1 (C-6, *C*–H thiazol), 138.4, 138.2, 138.1, 136.2 (5× *ipso* C_6H_5), 128.5–127.1 (25× C_6H_5), 118.4 (*C*–H thiazol), 106.1 (C-5), 98.3 (C-2), 77.7 (PhCHCOOCH$_3$), 77.1 (C-4′), 76.5 (C-2′), 74.8 (C-5′), 73.6, 73.3, 72.1, 71.6 (4× PhCH$_2$), 73.5 (C-3′), 70.1 (C-1′), 68.9 (C-6′), 52.2 (COOCH$_3$), 35.1 (C-1″), 31.5 (C-3), 26.9 (C-4). ESIMS: MH$^+$, found, 869.3. $C_{52}H_{54}NO_9S$ requires 869.1.

*4.1.6. Methyl (S)-2-phenyl-2-{[(2R,4R)-4-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl]oxy}acetate (**15**).* According to the same procedure described for the preparation of compound **13** after 24 h of sonification, compound **11** (9.25 g, 13.69 mmol) and chiral vinyl ether (*S*)-**12** (3.94 g, 20.54 mmol) afforded 9.2 g (77%) of compound **15** as a colorless foam; [Found: C, 80.05; H, 6.25. $C_{52}H_{53}NO_9S$ requires C, 71.95; H, 6.15%]; R_f=0.30 (light petroleum/ethyl acetate, 2:1); $[\alpha]_D^{20}$ +15.0 (*c* 1.02, $CHCl_3$); ν_{max} 3015, 1745, 1497, 1456, 1272, 1096, 1028 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.77 (d, 1H, H-thiazol, *J* 2.6 Hz); 7.48–7.16 (m, 26H, 5× C_6H_5, H-thiazol), 5.96 (d,1H, $J_{5,4}$ 3.5 Hz, H-5), 5.49 (s, 1H, PhC*H*COOCH$_3$), 5.38 (dd, 1H, $J_{2,3ax}$ 6.4 Hz, $J_{2,3eq}$ 2.3 Hz, H-2), 4.51–5.15 (m, 8H, 4× O–CH_2–Ph), 3.95 (dd, 1H, $J_{4',5'}$ 10.0 Hz, $J_{4',3'}$ 9.5 Hz, H-4′), 3.77 (m, 2H, H-2′, H-6′a), 3.75 (s, 3H, COOC*H*$_3$), 3.70 (dd, 1H, $J_{6'a,6'b}$ 10.9 Hz, $J_{6'b,5'}$ 5.3 Hz, H-6′b), 3.64 (dd,1H, $J_{3',4'}$ 9.5 Hz, $J_{3',2'}$ 2.2 Hz, H-3′), 3.50–3.45 (m, 2H, H-1′, H-5′), 2.55 (m, 1H, H-4), 2.20–2.15 (m, 2H, H-3$_{eq}$, H-1″), 1.85 (m, 1H, H-3$_{ax}$), 1.57 (m, 1H, H-1″); ^{13}C NMR (75 MHz, $CDCl_3$) 171.2 (*C*OOCH$_3$), 164.3 (thiazol C-2), 143.6, 143.5 (C-6, *C*–H thiazol), 138.8, 138.7, 136.4 (5× *ipso* C_6H_5), 128.9–127.5 (25×C_6H_5), 118.9 (*C*–H thiazol), 106.0 (C-5), 98.7 (C-2), 85.7 (C-3′), 77.9 (PhCHCOOCH$_3$), 76.0, 75.8, 75.7 (C-5′, C-2′, C-1′), 75.8 (C-4′), 74.7, 73.7, 72.8 (4× PhCH$_2$), 70.0 (C-6′), 52.7 (COOCH$_3$), 36.9 (C-1″), 32.3 (C-3), 27.1 (C-4). ESIMS: MH$^+$, found, 869.2. $C_{52}H_{54}NO_9S$ requires 869.1.

*4.1.7. Methyl (R)-2-phenyl-2-{[(2S,4S)-4-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl]oxy}acetate (**16**).* According to the same procedure described for the preparation of compound **15**, compound **11** (9.0 g, 13.3 mmol) and chiral vinyl ether (*R*)-**12** (3.9 g, 20.3 mmol) afforded 9.3 g (80%) of compound **16** as a colorless foam; [Found: C, 71.70; H, 5.95. $C_{52}H_{53}NO_9S$ requires C, 71.95; H, 6.15%]; R_f=0.30 (light petroleum/ethyl acetate, 2:1); $[\alpha]_D^{20}$ −27.5 (*c* 1.48, $CHCl_3$); ν_{max} 3020, 1748, 1497, 1454, 1268, 1096, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.72 (d, 1H, H-thiazol, *J* 3.1 Hz), 7.48–7.10 (m, 26H, 5× C_6H_5, H-thiazol), 6.00 (d,1H, $J_{5,4}$ 3.5 Hz, H-5), 5.48 (s, 1H, PhC*H*COOCH$_3$), 5.42 (dd, 1H, $J_{2,3ax}$ 6.5 Hz, $J_{2,3eq}$ 2.0 Hz, H-2), 4.90–4.48 (m, 8H, 4× O–CH_2–Ph), 3.94 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 9.3 Hz, H-4′), 3.78–3.69 (m, 2H, H-6′a, H-6′b), 3.68 (s, 3H, COOC*H*$_3$), 3.62–3.56 (m, 2H, H-3′, H-2), 3.50 (m, 1H, H-1′), 3.45 (m, 1H, H-5′), 2.70 (m, 1H, H-4), 2.27 (ddd, 1H, $J_{3eq,3ax}$ 13.5 Hz, $J_{3eq,4}$ 7.1 Hz, $J_{2,3eq}$ 2.0 Hz, H-3$_{eq}$), 2.11 (m, 1H, H-1″a), 1.88 (ddd, 1H, $J_{3eq,3ax}$ 13.5 Hz, $J_{3ax,4}$ 6.9 Hz, $J_{2,3ax}$ 6.5 Hz, H-3$_{ax}$), 1.52 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 170.7 (*C*OOCH$_3$), 163.9 (thiazol C-2), 143.1 (C-6), 143.1 (*C*–H thiazol), 138.5, 138.4, 138.3, 13.2, 136.0 (5× *ipso* C_6H_5), 128.4–127.0 (25× C_6H_5), 118.5 (*C*–H thiazol), 104.2 (C-5), 98.1 (C-2), 85.0 (C-3′), 79.6 (C-5′), 77.4 (C-2′), 76.3 (PhCHCOOCH$_3$), 75.4 (C-4′), 75.3 (C-1′), 74.9, 74.4, 73.2, 72.3 (4× PhCH$_2$), 69.5 (C-6′), 52.2 (COOCH$_3$), 37.6 (C-1″), 33.5 (C-3), 26.42 (C-4). ESIMS: MH$^+$, found, 869.2. $C_{52}H_{54}NO_9S$ requires 869.1.

*4.1.8. (2R,4R)-2-[(S)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran (**17**).* Lithium aluminum hydride (0.9 g, 23.7 mmol) was added portionwise under argon to a solution of compound **13** (6.9 g, 7.9 mmol) in tetrahydrofuran (120 mL) that was pre-cooled to 0 °C, and the reaction mixture was stirred at room temperature for 1 h. After cautious addition of a 1 M solution of NaOH (10 mL), the reaction mixture was concentrated and partitioned between a 0.5 M solution of HCl and CH_2Cl_2. The organic layer was washed with $NaHCO_3$ solution and dried. The solvent was subsequently evaporated, and the residue was subjected to flash chromatography through a short column of silica gel in light petroleum/ethyl acetate (5:1). The obtained alcohol (6.34 g, R_f=0.4 in light petroleum/ethyl acetate, 4:1, *m*/*z* 839.6 [M+H]$^+$) was dissolved in tetrahydrofuran (300 mL), and the solution was stirred at room temperature for 1 h with a 60% suspension of NaH in mineral oil (1.9 g, 47.5 mmol). Then, benzyl bromide (2.7 mL, 18.7 mmol) and tetrabutylammonium iodide (0.71 g, 1.9 mmol) were added, and the reaction mixture was heated at 40 °C for 4 h and then stirred at room temperature for 14 h. MeOH (5 mL) was added, the solvent was evaporated in vacuo, and the residue was partitioned between dichloromethane and a saturated solution of $NaHCO_3$. Then, the organic layer was dried, the solvent was taken down, and the residue was chromatographed on silica gel in light petroleum/ethyl acetate (12:1→3:1). This procedure yielded 5.2 g (70%) of compound **17** as a pale yellow viscous oil; [Found: C, 74.75; H, 6.55. $C_{58}H_{59}NO_8S$ requires C, 74.89; H, 6.39%]; R_f=0.35 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +12.4 (*c* 1.43, $CHCl_3$); ν_{max} 3011, 1722, 1700, 1496, 1454, 1363, 1265, 1094, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.63 (d, 1H, H-thiazol, *J* 3.2 Hz), 7.38–7.09 (m, 30H, 6× C_6H_5), 7.04 (d, 1H, *J* 3.2 Hz, H-thiazol), 6.01 (d,1H, $J_{5,4}$ 3.7 Hz, H-5), 5.48 (dd, 1H, $J_{2,3eq}$ 2.2 Hz, $J_{2,3ax}$ 5.8 Hz, H-2), 4.94 (dd, 1H, *J* 8.2 Hz, *J* 3.5 Hz, PhC*H*CH$_2$OBn), 4.70–4.47 (m, 10H, 5× O–CH_2–Ph), 4.23 (ddd, 1H, $J_{1',1''a}$ 10.5 Hz, $J_{1',1''b}$ 4.5 Hz, $J_{1',2'}$ 3.0 Hz, H-1′), 3.95–3.86 (m, 2H, H-4′, H-5′), 3.85–3.72 (m, 3H, H-3′, H-6′a, H-6′b), 3.66 (dd, 1H, *J* 10.6 Hz, *J* 8.2 Hz, PhCHCH_{2a}OBn), 3.58 (dd, 1H, *J* 10.6 Hz, *J* 3.5 Hz, PhCHCH_{2b}OBn), 3.54 (dd, 1H, $J_{2',3'}$ 4.8 Hz, $J_{2',1'}$ 3.0 Hz, H-2′), 2.66 (m, 1H, H-4), 2.15 (ddd, 1H, $J_{3eq,3ax}$ 13.5 Hz, $J_{3eq,4}$ 6.9 Hz, $J_{2,3eq}$ 2.2 Hz, H-3$_{eq}$), 2.00–1.85 (m, 2H, H-1″a, H-3$_{ax}$), 1.80 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 164.2 (thiazol C-2), 143.5 (C-6), 142.6 (*C*–H thiazol), 139.6, 138.3, 138.2, 138.1, 138.1, 138.0 (6× *ipso* C_6H_5), 128.2–126.3 (30×C_6H_5), 118.3 (*C*–H thiazol), 103.5 (C-5), 100.2 (C-2), 80.9 (PhCHCH$_2$OBn), 76.9 (C-3′), 76.5 (C-2′), 74.7, 73.4 (C-4′, C-5′), 74.7 (PhCHCH$_2$OBn), 73.4, 73.1, 73.1, 71.9, 71.4 (5× PhCH$_2$, PhCHCH$_2$OBn), 70.8 (C-1′), 69.7 (C-1′), 69.0 (C-6′), 35.5 (C-1″), 33.4 (C-3), 27.3 (C-4). ESIMS: MH$^+$, found, 931.2. $C_{58}H_{60}NO_8S$ requires 931.2.

*4.1.9. (2S,4S)-2-[(R)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran (**18**).* Using the same procedure as described for the preparation of compound **17**, compound **14** (6.1 g, 7.03 mmol) was converted to compound **18** (pale yellow viscous oil, 4.6 g, 70%); [Found: C, 74.98; H, 6.25. $C_{58}H_{59}NO_8S$ requires C, 74.89; H, 6.39%];

R_f=0.35 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ −0.7 (*c* 1.57, $CHCl_3$); ν_{max} 3011, 1723,1699, 1496, 1454, 1363, 1266, 1099, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.63 (d, 1H, H-thiazol, *J* 3.2 Hz), 7.36–7.14 (m, 30H, 6× C_6H_5), 7.07 (d, 1H, H-thiazol, *J* 3.2 Hz), 5.88 (d,1H, $J_{5,4}$ 3.5 Hz, H-5), 5.47 (dd, 1H, $J_{2,3ax}$ 6.5 Hz, $J_{2,3eq}$ 1.9 Hz, H-2), 4.95 (dd, 1H, *J* 8.0 Hz, *J* 3.5 Hz, PhC*H*CH$_2$OBn), 4.70–4.47 (m, 10H, 5× O–CH_2–Ph), 4.17 (m, 1H, H-1′), 3.90–3.83 (m, 2H, H-4′, H-5′), 3.83–3.76 (m, 2H, H-6′a, H-3′), 3.73 (dd, 1H, $J_{6'a,6'b}$ 10.2 Hz, $J_{6'b,5'}$ 3.6 Hz, H-6′b), 3.68 (dd, 1H, *J* 10.7 Hz, *J* 8.0 Hz, PhCHCH_{2a}OBn), 3.60 (dd, 1H, *J* 10.7 Hz, *J* 3.5 Hz, PhCHCH_{2b}OBn), 3.55 (dd, 1H, $J_{2',3'}$ 4.9 Hz, $J_{2',1'}$ 3.0 Hz, H-2′), 2.72 (m, 1H, H-4), 2.23 (ddd, 1H, $J_{3eq,3ax}$ 13.3 Hz, $J_{3eq,4}$ 6.7 Hz, $J_{2,3eq}$ 1.9 Hz, H-3$_{eq}$), 1.93 (m, 1H, H-1″a), 1.83 (ddd, 1H, $J_{3eq,3ax}$ 13.3 Hz, $J_{3ax,4}$ 7.5 Hz, $J_{2,3ax}$ 6.5 Hz, H-3$_{ax}$), 1.69 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 164.2 (thiazol C-2), 143.6 (C-6), 142.8 (*C*–H thiazol), 139.6, 138.3, 138.2, 138.1, 138.1, 138.1 (6× *ipso* C_6H_5), 128.3–126.5 (30× C_6H_5), 118.4 (*C*–H thiazol), 105.0 (C-5), 100.7 (C-2), 81.0 (PhCHCH$_2$OBn), 77.0, 74.7, 73.5 (C-3′, C-4′, C-5′), 76.6 (C-2′), 74.8, 73.4, 73.3, 73.1, 72.1, 71.5 (5× PhCH$_2$, PhCHCH$_2$OBn), 69.7 (C-1′), 68.8 (C-6′), 35.4 (C-1″), 32.1 (C-3), 27.1 (C-4). ESIMS: MH^+, found, 931.2. $C_{58}H_{60}NO_8S$ requires 931.2.

*4.1.10. (2R,4R)-2-[(S)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran (**19**).* Using the same procedure as described for the preparation of compound **17**, compound **15** (7.1 g, 8.2 mmol) was converted to compound **19** (pale yellow viscous oil, 5.3 g, 70%); [Found: C, 75.05; H, 6.55. $C_{58}H_{59}NO_8S$ requires C, 74.89; H, 6.39%]; R_f=0.35 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +6.3 (*c* 1.81, $CHCl_3$); ν_{max} 3011, 1722, 1700, 1496, 1454, 1363, 1257, 1116, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.63 (d, 1H, *J* 3.2 Hz, H-thiazol,), 7.42–7.14 (m, 30H, 6× C_6H_5), 7.03 (d, 1H, *J* 3.2 Hz, H-thiazol,), 5.89 (d,1H, $J_{5,4}$ 3.2 Hz, H-5), 5.39 (dd, 1H, $J_{2,3ax}$ 7.1 Hz, $J_{2,3eq}$ 2.3 Hz, H-2), 4.98 (d, 1H, *J* 10.8 Hz, O–CH_2–Ph), 4.94 (dd, 1H, *J* 8.3 Hz, *J* 3.4 Hz, PhC*H*CH$_2$OBn), 4.89 (d, 1H, *J* 10.8 Hz, O–CH_2–Ph), 4.78–4.43 (m, 8H, 4× O–CH_2–Ph), 3.97 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 9.5 Hz, H-4′), 3.80–3.55 (m, 6H, PhCHCH_{2a}OBn, PhCHCH_{2b}OBn, H-6′a, H-6′b, H-2′, H-3′), 3.52–3.42 (m, 2H, H-1′, H-5′), 2.49 (m, 1H, H-4), 2.16 (m, 1H, H-1″a), 2.07 (ddd, 1H, $J_{3eq,3ax}$ 13.1 Hz, $J_{3eq,4}$ 6.9 Hz, $J_{2,3eq}$ 2.3 Hz, H-3$_{eq}$), 1.75 (ddd, 1H, $J_{3eq,3ax}$ 13.1 Hz, $J_{3ax,2}$ 7.1 Hz, $J_{3ax,4}$ 6.7 Hz, H-3$_{ax}$), 1.58 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 164.1 (thiazol C-2); 143.5 (C-6), 142.6 (*C*–H thiazol), 139.4, 138.3, 138.2, 138.1, 138.1, 137.9 (6× *ipso* C_6H_5), 128.2–126.3 (30×C_6H_5), 118.5 (*C*–H thiazol), 104.2 (C-5), 100.7 (C-2), 85.2 (C-3′), 81.2 (PhCHCH$_2$OBn), 79.7 (C-5′), 75.3, 75.1, 74.9 (C-1′, C-2′, C-4′), 74.9, 74.6, 74.0, 73.2, 73.1, 72.3 (5× PhCH$_2$, PhCHCH$_2$OBn), 69.4 (C-6′), 36.5 (C-1″), 32.7 (C-3), 27.0 (C-4). ESIMS: MH^+, found, 931.2. $C_{58}H_{60}NO_8S$ requires 931.2.

*4.1.11. (2S,4S)-2-[(R)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran (**20**).* Using the same procedure as described for the preparation of compound **17**, compound **16** (6.1 g, 7.03 mmol) was converted to compound **20** (pale yellow viscous oil, 4.6 g, 70%); [Found: C, 74.78; H, 6.25. $C_{58}H_{59}NO_8S$ requires C, 74.89; H, 6.39%]; R_f=0.35 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ −13.8 (*c* 1.26, $CHCl_3$); ν_{max} 3011, 1722, 1699, 1497, 1454, 1363, 1266, 1098, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.66 (d, 1H, H-thiazol, *J* 3.2 Hz), 7.42–7.16 (m, 30H, 8× C_6H_5), 7.13 (d, 1H, H-thiazol, *J* 3.2 Hz), 5.87 (d,1H, $J_{5,4}$ 3.2 Hz, H-5), 5.47 (dd, 1H, $J_{2,3ax}$ 6.7 Hz, $J_{2,3eq}$ 1.9 Hz, H-2), 5.10–4.95 (m, 2H, PhC*H*CH$_2$OBn, O–CH_2–Ph), 4.88 (d, 1H, *J* 10.8 Hz, O–CH_2–Ph), 4.90–4.48 (m, 8H, 4× O–CH_2–Ph), 3.94 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 9.4 Hz, H-4′), 3.80–3.68 (m, 4H, PhCHCH_{2a}OBn, PhCHCH_{2b}OBn, H-6′a, H-6′b), 3.67–3.57 (m, 2H, H-2′, H-3′), 3.53 (m, 1H, H-1′), 3.44 (ddd, 1H, $J_{4',5'}$ 9.4 Hz, $J_{5',6'b}$ 5.0 Hz, $J_{5',6'a}$ 1.7 Hz, H-5′), 2.68 (m, 1H, H-4), 2.21 (ddd, 1H, $J_{3eq,3ax}$ 13.3 Hz, $J_{3eq,4}$ 6.6 Hz, $J_{3eq,2}$ 1.9 Hz, H-3$_{eq}$), 2.11 (m, 1H, H-1″a), 1.75 (ddd, 1H, $J_{3eq,3ax}$ 13.3 Hz, $J_{3ax,4}$ 8.5 Hz, $J_{3ax,2}$ 6.7 Hz, H-3$_{ax}$), 1.42 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 164.5 (thiazol C-2), 143.7 (C-6), 142.9 (*C*–H thiazol), 139.7, 138.6, 138.5, 138.5, 138.4, 138.2 (6× *ipso* C_6H_5), 128.4–126.6 (30× C_6H_5), 118.7 (*C*–H thiazol), 103.3 (C-5), 100.9 (C-2), 85.3 (C-3′), 81.1 (PhCHCH$_2$OBn), 79.8 (C-5′), 76.2, 75.6 (C-2′, C-4′), 75.2 (C-1′), 75.1, 74.9, 74.4, 73.4, 73.3, 72.6 (5× PhCH$_2$, PhCHCH$_2$OBn), 69.7 (C-6′), 37.7 (C-1″), 34.5 (C-3), 27.2 (C-4). ESIMS: MH^+, found, 931.2. $C_{58}H_{60}NO_8S$ requires 931.2.

*4.1.12. (2R,4R)-2-[(S)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-6-formyl-3,4-dihydro-2H-pyran (**21**).* Molecular sieves (4 Å; 7.2 g) were added to a solution of compound **17** (5.3 g, 5.68 mmol) in acetonitrile (160 mL), and methyl triflate (0.96 mL, 8.45 mmol) was added dropwise. After stirring at room temperature for 15 min, MeOH (5 mL) was added, and the solvent was evaporated in vacuo. The residue was treated with MeOH (80 mL), and then, $NaBH_4$ (0.7 g, 18.6 mmol) was added in portions. After stirring at room temperature for 15 min, acetone (15 mL) was added, the reaction mixture was filtered through Super Cel and the filtrate was evaporated in vacuo. The residue was dissolved in acetonitrile (60 mL), and a solution of $AgNO_3$ (2.1 g, 12.36 mmol) in water (6 mL) was added under vigorous stirring. After stirring for 10 min, phosphate buffer (20 mL; pH 7) was added, and after 10 min, the acetonitrile was evaporated in vacuo, and the residue was partitioned between dichloromethane and phosphate buffer (pH 7). The organic phase was dried, the solvent was evaporated, and the residue was flash-chromatographed through a short silica gel column in light petroleum/ethyl acetate (7:1→5:1). This procedure resulted in a yield of 3.7 g (73%) of aldehyde **21** as a viscous oil; [Found: C, 76.74; H, 6.52. $C_{56}H_{58}O_9$ requires C, 76.86; H, 6.68%]; R_f=0.3 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +5.7 (*c* 1.2, $CHCl_3$); ν_{max} 3011, 2926, 2865, 1697, 1496, 1454, 1364, 1093, 1028, 986 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.75 (s, 1H, *H*CO), 7.40–7.10 (m, 30H, 6× C_6H_5), 5.81 (d, 1H, $J_{5,4}$ 4.3 Hz, H-5), 5.55 (m, 1H, H-2), 4.93 (dd, 1H, *J* 8.1, 3.5 Hz, PhC*H*CH$_2$OBn), 4.71–4.45 (m, 10H, 5× O–CH_2–Ph), 4.06 (ddd, 1H, $J_{1',1''a}$ 10.1 Hz, $J_{1',1''b}$ 5.2 Hz, $J_{1',2'}$ 2.8 Hz, H-1′), 3.98–3.73 (m, 4H, H-3′, H-4′, H-5′, H-6′a), 3.68 (dd, 1H, $J_{6'a,6'b}$ 10.2 Hz, $J_{6'b,5'}$ 3.7 Hz, H-6′b), 3.62 (m, 1H, PhCHCH_{2a}OBn), 3.57–3.48 (m, 2H, H-2′, PhCHCH_{2b}OBn), 2.64 (m, 1H, H-4), 2.10–1.91 (m, 3H, H-1″a, H-3$_{eq}$, H-3$_{ax}$), 1.85 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 186.3 (HCO); 148.7 (C-6), 139.3, 138.2, 138.1, 138.1 (6× *ipso* C_6H_5), 128.4–126.5 (30× C_6H_5), 125.2 (C-5), 98.3 (C-2), 79.8 (PhCHCH$_2$OBn), 76.8, 74.8, 73.7 (C-3′, C-4′, C-5′), 76.4 (C-2′), 74.6 (PhCHCH$_2$OBn), 73.3, 73.2, 73.1, 72.4, 71.8 (5× PhCH$_2$), 69.1 (C-1′), 68.8 (C-6′), 35.7 (C-1″), 32.1 (C-3), 26.5 (C-4). ESIMS: MNH_4^+, found 892.6. $C_{56}H_{62}NO_9$ requires 892.4.

*4.1.13. (2S,4S)-2-[(R)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-6-formyl-3,4-dihydro-2H-pyran (**22**).* Using the same procedure as described for the preparation of compound **21**, compound **18** (5.3 g, 5.68 mmol) was converted to aldehyde **22** (viscous oil, 3.8 g, 75%); [Found: C, 76.65; H, 6.56. $C_{56}H_{58}O_9$ requires C, 76.86; H, 6.68%]; R_f=0.3 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +10.0 (*c* 1.05, $CHCl_3$); ν_{max} 3019, 2925, 2865, 1696, 1496, 1454, 1364, 1096, 1028, 986 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.75 (s, 1H, *H*CO), 7.39–7.08 (m, 30H, 6× C_6H_5); 5.94 (d, 1H, $J_{5,4}$ 4.3 Hz, H-5); 5.56 (m,1H, H-2); 4.95 (dd, 1H, *J* 8.1, 3.6 Hz, PhC*H*CH$_2$OBn), 4.71–4.45 (m, 10H, 5× O–CH_2–Ph), 4.15 (ddd,1H, $J_{1',1''a}$ 11.0 Hz, $J_{1',1''b}$ 4.8 Hz, $J_{1',2'}$ 2.7 Hz, H-1′), 3.86–3.71 (m, 4H, H-3′, H-4′, H-5′, H-6′a), 3.69–3.60 (m, 2H, H-6′b, PhCHCH_{2a}OBn), 3.60–3.53 (m, 2H, H-2′, PhCHCH_{2b}OBn), 2.59 (m, 1H, H-4), 2.03–1.87 (m, 3H, H-1″a, H-3$_{eq}$, H-3$_{ax}$), 1.78 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 186.3 (HCO), 148.4 (C-6), 139.0, 138.0, 138.0, 137.9, 137.8 (6× *ipso* C_6H_5), 128.2–127.2 (30× C_6H_5), 126.4 (C-5), 98.1 (C-2) 79.3 (PhCHCH$_2$OBn), 76.4, 76.3 (C-2′, C-3′),

74.8, 73.3 (C-4′, C-5′), 74.5 (PhCH*C*H$_2$OBn), 73.4, 73.1, 72.0, 71.4 (5× PhCH$_2$), 71.0 (C-1′), 68.9 (C-6′), 34.8 (C-1″), 30.9 (C-3), 27.7 (C-4). ESIMS: MNH$_4^+$, found 892.6. $C_{56}H_{62}NO_9$ requires 892.4.

*4.1.14. (2R,4R)-2-[(S)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-6-formyl-3,4-dihydro-2H-pyran (**23**).* Using the same procedure as described for the preparation of compound **21**, compound **19** (5.1 g, 5.45 mmol) was converted to aldehyde **23** (viscous oil, 3.5 g, 73%); [Found: C, 76.74; H, 6.88. $C_{56}H_{58}O_9$ requires C, 76.86; H, 6.68%]; R_f=0.3 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +5.2 (*c* 1.24, $CHCl_3$); ν_{max} 3020, 2928, 2863, 1697, 1497, 1454, 1364, 1088, 1028, 986 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.78 (s, 1H, *H*CO), 7.43–7.15 (m, 30H, 6× C$_6$*H*$_5$), 5.84 (d, 1H, $J_{H\text{-}5,H-4}$ 4.10 Hz, H-5), 5.5 (m, 1H, H-2), 4.98 (d, 1H, *J* 11.7 Hz, O–C*H*$_2$–Ph), 4.95 (dd, 1H, *J* 7.7, 3.8 Hz, PhC*H*CH$_2$OBn), 4.89 (d, 1H, *J* 10.8 Hz, O–C*H*$_2$–Ph), 4.78–4.47 (m, 8H, 4× O–C*H*$_2$–Ph), 3.92 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 9.5 Hz, H-4′), 3.79–3.55 (m, 6H, H-2′, H-3′, H-6′a, H-6′b, PhCHC*H*$_{2a}$OBn, PhCHC*H*$_{2b}$OBn), 3.48–3.41 (m, 2H, H-1′, H-5′), 2.56 (m, 1H, H-4), 2.15 (ddd, 1H, $J_{1''a,1''b}$ 13.4, *J* 9.9, *J* 6.0 Hz, H-1″a), 1.95 (ddd, 1H, $J_{3eq,3ax}$ 13.9 Hz, $J_{4,3eq}$ 7.1 Hz, $J_{2,3eq}$ 2.2 Hz, H-3$_{eq}$), 1.84 (ddd, 1H, $J_{3eq,3ax}$ 13.9 Hz, $J_{2,3ax}$=$J_{4,3ax}$ 4.1 Hz, H-3$_{ax}$), 1.57 (ddd, 1H, $J_{1''a,1''b}$ 13.4 Hz, *J* 8.6, 2.3 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 186.3 (*H*CO), 148.6 (C-6), 139.2, 138.5, 138.4, 138.3, 138.1 (6× *ipso* C$_6$H$_5$), 128.4–127.2 (30× C$_6$H$_5$), 126.6 (C-5), 98.5 (C-2), 85.3 (C-3′), 79.8 (Ph*C*HCH$_2$OBn), 79.8 (C-5′), 76.2, 76.1, 75.4 (C-1′, C-2′, C-4′), 75.1, 74.7, 74.4, 73.4, 73.2 (5× PhCH$_2$), 72.6 (PhCHCH$_2$OBn), 69.8 (C-6′), 36.3 (C-1″), 31.1 (C-3), 27.5 (C-4). ESIMS: MNH$_4^+$, found 892.6. $C_{56}H_{62}NO_9$ requires 892.4.

*4.1.15. (2S,4S)-2-[(R)-2-(Benzyloxy)-1-phenylethoxy]-4-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-6-formyl-3,4-dihydro-2H-pyran (**24**).* Using the same procedure as described for the preparation of compound **21**, compound **20** (4.8 g, 5.16 mmol) was converted to aldehyde **24** (viscous oil, 3.4 g, 75%); [Found: C, 76.59; H, 6.75. $C_{56}H_{58}O_9$ requires C, 76.86; H, 6.68%]; R_f=0.3 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ −1.9 (*c* 1.13, $CHCl_3$); ν_{max} 3020, 2928, 2861, 1697, 1497, 1454, 1363, 1097, 1028, 987 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.82 (s, 1H, *H*CO); 7.43–7.15 (m, 30H, 6× C$_6$*H*$_5$), 5.71 (d, 1H, $J_{5,4}$ 4.1 Hz, H-5); 5.57 (m, 1H, H-2), 5.10 (d, 1H, *J* 11.7 Hz, O–C*H*$_2$–Ph), 4.95 (dd, 1H, *J* 8.1, 3.5 Hz, PhC*H*CH$_2$OBn), 4.89 (d, 1H, *J* 10.8 Hz, O–C*H*$_2$–Ph), 4.82–4.46 (m, 8H, 4× O–C*H*$_2$–Ph), 3.92 (dd, 1H, $J_{4',5'}$=$J_{4',3'}$ 9.2 Hz, H-4′), 3.75 (dd, 1H, $J_{6'a,6'b}$ 10.7 Hz, $J_{6'a,5'}$ 1.4 Hz, H-6′a), 3.71–3.64 (m, 2H, H-6′b, PhCHC*H*$_{2a}$OBn), 3.64–3.56 (m, 3H, H-2′, H-3′, PhCHC*H*$_{2b}$OBn), 3.42–3.34 (m, 2H, H-1′, H-5′), 2.59 (m, 1H, H-4), 2.15 (m, 1H, H-1″a), 2.03 (ddd, 1H, $J_{3eq,3ax}$ 13.8 Hz, $J_{3eq,4}$ 7.4 Hz, $J_{3eq,2}$ 2.4 Hz, H-3$_{eq}$), 1.88 (ddd, 1H, $J_{3eq,3ax}$ 13.8 Hz, $J_{3eq,4}$=$J_{3eq,2}$ 4.0 Hz, H-3$_{ax}$), 1.78 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 186.5 (*H*CO), 148.9 (C-6), 139.1, 138.5, 138.4, 138.3, 138.2 (6× *ipso* C$_6$H$_5$); 128.4–126.6 (30× C$_6$H$_5$), 125.2 (C-5), 98.5 (C-2), 85.2 (C-3′), 79.9 (C-5′), 79.2 (Ph*C*HCH$_2$OBn), 76.1 (C-2′), 75.7 (C-1′), 75.4 (C-4′), 75.1, 74.7, 74.4, 73.4, 73.3, 72.6 (5× Ph*C*H$_2$, PhCH*C*H$_2$OBn), 69.8 (C-6′), 36.8 (C-1″), 32.4 (C-3), 26.6 (C-4). ESIMS: MNH$_4^+$, found 892.6. $C_{56}H_{62}NO_9$ requires 892.4.

*4.1.16. (S)-2-Benzyloxy-1-phenylethyl 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-D-arabino-hexopyranoside (**25**).* A 2 M solution of $BH_3 \cdot Me_2S$ in tetrahydrofuran (7.4 mL, 14.7 mmol) was added dropwise to a solution of aldehyde **21** (3.7 g, 4.2 mmol) in tetrahydrofuran (80 mL) that was pre-cooled to 0 °C, and the reaction mixture was stirred at room temperature for 16 h. Then, a 30% NaOH solution (4.6 mL) and a 30% H_2O_2 (4.6 mL) were added in succession. The mixture was stirred at room temperature for 30 min and partitioned between ethyl acetate and a saturated NaCl solution. The organic phase was dried, the ethyl acetate evaporated in vacuo, and the residue was dissolved in tetrahydrofuran (150 mL). After addition of a 60% suspension of NaH in mineral oil (1 g, 25 mmol), the mixture was stirred at room temperature for 1 h. Benzyl bromide (3.1 mL, 25.8 mmol) and tetrabutylammonium iodide (0.49 g, 1.3 mmol) were added, and the reaction mixture was heated at 40 °C for 4 h. After stirring at room temperature for 14 h, MeOH (5 mL) was added, the solvent was evaporated in vacuo, and the residue was partitioned between dichloromethane and a saturated solution of $NaHCO_3$. The organic layer was dried, the solvent was removed in vacuo, and the residue was chromatographed on silica gel in light petroleum/ethyl acetate (12:1→8:1) to give 2.7 g (60%) of compound **25** as a viscous oil; [Found: C, 78.26; H, 6.75. $C_{70}H_{74}O_{10}$ requires C, 78.19; H, 6.94%]; R_f=0.56 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +2.5 (*c* 0.73, $CHCl_3$); ν_{max} 3011, 2922, 2867, 1496, 1454, 1364, 1087, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.42–7.13 (m, 40H, 8× C$_6$*H*$_5$); 4.91 (dd, 1H, *J* 7.8, 4.1 Hz, PhC*H*CH$_2$OBn), 4.73 (dd, 1H, $J_{1,2ax}$ 9.4 Hz, $J_{1,2eq}$ 1.6 Hz, H-1), 4.69 (d, 1H, H-1, *J* 11.2 Hz, O–C*H*$_2$–Ph), 4.60–4.30 (m, 13H, O–C*H*$_2$–Ph), 4.08 (ddd, 1H, $J_{1',1''b}$ 7.8 Hz, $J_{1',1''a}$ 4.4 Hz, $J_{1',2'}$ 3.1 Hz, H-1′), 3.85 (dd, 1H, $J_{4',5'}$=$J_{3',4'}$ 6.7 Hz, H-4′), 3.76–3.58 (m, 7H, H-3′, H-5′, H-6a, H-6b, H-6′a, PhCHC*H*$_{2a}$OBn, PhCHC*H*$_{2b}$OBn), 3.53 (dd, 1H, $J_{6'b,6'a}$ 11.2 Hz, $J_{6'b,5'}$ 1.6 Hz, H-6′b), 3.46 (dd, 1H, $J_{2',3'}$ 4.2 Hz, $J_{2',1'}$ 3.1 Hz, H-2′), 3.30 (ddd, 1H, $J_{4,5}$ 9.4 Hz, $J_{5,6a}$ 3.9 Hz, $J_{5,6b}$ 1.8 Hz, H-5), 3.16 (dd, 1H, $J_{4,5}$=$J_{3,4}$ 9.4 Hz, H-4), 2 0.18 (ddd, 1H, $J_{2eq,2ax}$ 12.6 Hz, $J_{2eq,3}$ 3.7 Hz, $J_{2eq,1}$ 1.6 Hz, H-2$_{eq}$), 1.86 (ddd, 1H, $J_{1''a,1''b}$ 13.8 Hz, $J_{1''a,1'}$ 4.4 Hz, $J_{1''a,3}$ 3.9 Hz, 1″a), 1.62 (m, 1H, H-3), 1.42 (ddd, 1H, $J_{2eq,2ax}$ 12.8 Hz, $J_{2ax,3}$=$J_{2ax,1}$ 9.4 Hz, H-2$_{ax}$), 1.33 (ddd, 1H, $J_{1''a,1''b}$ 13.8 Hz, $J_{1''b,3}$ 8.3 Hz, $J_{1''b,1'}$ 7.8 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 140.3, 138.6, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0 (8× *ipso* C$_6$H$_5$), 128.3–126.7 (40× C$_6$H$_5$), 101.5 (C-1), 79.3 (PhCHCH$_2$OBn), 78.3, 78.2 (C-5, C-4), 77.3 (C-3′), 75.9 (C-2′), 74.9 (C-4′), 74.7, 74.1, 73.7, 73.4, 73.3, 73.2, 72.2, 71.4 (7× PhCH$_2$, PhCHCH$_2$OBn), 73.4 (C-5′), 72.5 (C-1′), 69.2 (C-6′, C-6), 38.7 (C-3), 36.9 (C-2), 32.3 (C-1″). ESIMS: MNH$_4^+$, found 1092.7. $C_{70}H_{78}NO_{10}$ requires 1092.6.

*4.1.17. (R)-2-(Benzyloxy)-1-fenylethyl 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-L-arabino-hexopyranoside (**26**).* Using the same procedure as described for the preparation of compound **25**, aldehyde **22** (1.9 g, 2.17 mmol) was converted to compound **26** (viscous oil, 1.4 g, 60%); [Found: C, 78.05; H, 7.05. $C_{70}H_{74}O_{10}$ requires C, 78.19; H, 6.94%]; R_f=0.58 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ +8.6 (*c* 1.03, $CHCl_3$); ν_{max} 3010, 2918, 2866, 1496, 1454, 1363, 1089, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.12 (m, 40H, 8× C$_6$*H*$_5$), 4.88 (dd, 1H, *J* 7.5, 4.0 Hz, PhC*H*CH$_2$OBn), 4.78 (dd, 1H, $J_{1,2ax}$ 9.4 Hz, $J_{1,2eq}$ 1.8 Hz, H-1), 4.77 (d, 1H, *J* 11.5 Hz, O–C*H*$_2$–Ph), 4.63–4.32 (m, 13H, O–C*H*$_2$–Ph), 4.08 (ddd, 1H, $J_{1',1''b}$ 11.9 Hz, $J_{1',2'}$=$J_{1',1''a}$ 3.2 Hz, H-1′), 3.88 (dd, 1H, $J_{4',5'}$=$J_{3',4'}$ 7.3 Hz, H-4′), 3.77–3.57 (m, 7H, H-3′, H-5′, H-6a, H-6b, H-6′a, PhCHC*H*$_{2a}$OBn, PhCHC*H*$_{2b}$OBn), 3.52 (dd, 1H, $J_{6'a,6'b}$ 11.1 Hz, $J_{6',5'}$ 1.5 Hz, H-6′b), 3.43 (dd, 1H, $J_{2',3'}$ 3.4 Hz, $J_{2',1'}$ 3.2 Hz, H-2′), 3.30 (ddd, 1H, $J_{5,4}$ 9.6 Hz, $J_{5,6a}$ 3.9 Hz, $J_{5,6b}$ 2.1 Hz, H-5), 3.14 (dd, 1H, $J_{4,5}$=$J_{3,4}$ 9.6 Hz, H-4), 2.21 (ddd, 1H, $J_{2eq,2ax}$ 12.8 Hz, $J_{2eq,3}$ 3.9 Hz, $J_{2eq,1}$ 1.8 Hz, H-2$_{eq}$), 2.06 (m, 1H, H-1″a), 1.90 (m, 1H, H-3), 1.30 (ddd, 1H, $J_{2eq,2ax}$=$J_{2ax,3}$ 12.8 Hz $J_{2ax,1}$ 9.4 Hz, H-2$_{ax}$), 0.85 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 140.3, 138.6, 138.5, 138.5, 138.3, 138.3, 138.1, 138.1 (8× *ipso* C$_6$H$_5$), 128.4–126.7 (40× C$_6$H$_5$), 101.6 (C-1), 79.3 (PhCHCH$_2$OBn), 78.1 (C-5, C-3′), 77.7 (C-4), 76.5 (C-2′), 75.0 (C-4′), 74.4, 73.9, 73.8, 73.4, 73.2, 72.9, 71.9, 71.4 (7× PhCH$_2$, PhCHCH$_2$OBn), 72.5 (C-5′), 69.4 (C-1′), 69.2 (C-6′, C-6), 35.7 (C-3), 35.6 (C-2), 31.2 (C-1″). ESIMS: MNH$_4^+$, found 1092.7. $C_{70}H_{78}NO_{10}$ requires 1092.6.

*4.1.18. (S)-2-(Benzyloxy)-1-fenylethyl 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-D-arabino-hexopyranoside (**27**).* Using the same procedure as described for the preparation of compound **25**, aldehyde **23** (3.4 g, 3.9 mmol) was converted to compound **27** (viscous oil, 2.9 g, 70%); [Found: C, 78.35; H, 6.74. $C_{70}H_{74}O_{10}$ requires C, 78.19; H, 6.94%]; R_f=0.6 (light

petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ −4.9 (*c* 0.78, $CHCl_3$); ν_{max} 3011, 2921, 2864, 1497, 1454, 1364, 1086, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.40–7.10 (m, 40H, 8× C_6H_5), 4.80 (d, 1H, *J* 11.8 Hz, O–CH_2–Ph), 4.90 (dd, 1H, *J* 7.6, 3.9 Hz, PhC*H*CH_2OBn), 4.86 (d, 1H, *J* 11.8 Hz, O–CH_2–Ph), 4.75 (dd, 1H, $J_{1,2ax}$ 9.5 Hz, $J_{1,2eq}$ 1.9 Hz, H-1), 4.72–4.29 (m, 12H, 6× O–CH_2–Ph), 3.95 (dd, 1H, $J_{4',5'}=J_{3',4'}$ 9.5 Hz, H-4′), 3.78–3.66 (m, 4H, H-2′, H-6a, H-6b, PhCHCH_{2a}OBn), 3.66–3.57 (m, 2H, H-6′a, PhCHCH_{2b}OBn), 3.56–3.48 (m, 2H, H-3′, H-6′b), 3.42–3.36 (m, 2H, H-1′, H-5′), 3.34 (ddd, 1H, $J_{5,4}$ 9.7 Hz, $J_{5,6b}$ 4.0 Hz, $J_{5,6a}$ 2.1 Hz, H-5), 3.14 (dd, 1H, $J_{4,5}=J_{3,4}$=9.7 Hz, H-4), 2.37 (m, 1H, H-1″a), 2.0 (ddd, 1H, $J_{2eq,2ax}$ 12.8 Hz, $J_{2eq,3}$ 3.9 Hz, $J_{1,2eq}$ 1.9 Hz, H-2_{eq}), 1.87 (m, 1H, H-3), 1.35 (ddd, 1H, $J_{2eq,2ax}$ 12.8 Hz, $J_{1,2ax}$ 9.5 Hz, $J_{3,2ax}$ 1.6 Hz, H-2_{ax}), 1.15 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 140.1, 138.7, 138.6, 138.4, 138.4, 138.3, 138.1, 138.0 (8× *ipso* C_6H_5); 128.3–126.6 (40× C_6H_5), 101.4 (C-1), 85.3 (C-3′), 79.9 (C-5′), 79.2 (PhCHCH_2OBn), 78.4 (C-4), 77.8 (C-5), 76.0 (C-2′), 75.3, 74.8 (C-4′, C-1′), 74.9, 74.6, 74.2, 73.5, 73.3, 73.3, 73.1, 72.4 (7× PhCH_2, PhCHCH_2OBn), 69.6 (C-6), 69.2 (C-6′), 36.3 (C-2), 35.9 (C-3), 34.7 (C-1″). ESIMS: MNH_4^+, found 1092.7. $C_{70}H_{78}NO_{10}$ requires 1092.6.

*4.1.19. (S)-2-(Methoxy)-1-fenylethyl 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-L-arabino-hexopyranoside (**28**).* Using the same procedure as described for the preparation of compound **25**, aldehyde **24** (1.3 g, 1.5 mmol) was converted to compound **28** (viscous oil, 0.9 g, 60%); [Found: C, 77.99; H, 7.04. $C_{70}H_{74}O_{10}$ requires C, 78.19; H, 6.94%]; R_f=0.6 (light petroleum/ethyl acetate, 3:1); $[\alpha]_D^{20}$ −9.6 (*c* 0.85, $CHCl_3$); ν_{max} 3010, 2923, 2865, 1497, 1454, 1363, 1095,1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.50–7.05 (m, 40H, 8× C_6H_5), 4.94 (d, 1H, *J* 11.7 Hz, O–CH_2–Ph), 4.92 (dd, 1H, *J* 8.0, 3.7 Hz, PhC*H*CH_2OBn), 4.85 (d, 1H, *J* 10.8 Hz, O–CH_2–Ph), 4.79 (dd, 1H, $J_{1,2ax}$ 9.5 Hz, $J_{1,2eq}$ 1.6 Hz, H-1), 4.74–4.28 (m, 12H, 6× O–CH_2–Ph), 3.95 (dd, 1H, $J_{4',5'}=J_{3',4'}$ 9.5 Hz, H-4′), 3.75–3.65 (m, 3H, H-6a, H-6b, PhCHCH_{2a}OBn), 3.65–3.58 (m, 2H, H-6′a, PhCHCH_{2b}OBn), 3.57 (br s, 1H, H-2′), 3.55–3.48 (m, 2H, H-3′, H-6′b), 3.42–3.36 (m, 2H, H-1′, H-5′), 3.33 (ddd, 1H, $J_{4,5}$ 9.4 Hz, $J_{5,6b}$ 4.4 Hz, $J_{5,6a}$ 1.8 Hz, H-5), 3.24 (dd, 1H, $J_{4,5}=J_{3,4}$ 9.4 Hz, H-4), 2.08 (ddd, 1H, $J_{2eq,2ax}$ 12.8 Hz, $J_{2eq,3}$ 4.1 Hz, $J_{2eq,1}$ 1.6 Hz, H-2_{eq}), 1.82–1.66 (m, 3H, H-3, H-1″a, H-1″b), 1.49 (ddd, 1H, $J_{2ax,2eq}$ 12.8 Hz, $J_{2ax,3}$ 12.6, $J_{2ax,1}$ 9.5 Hz, H-2_{ax}); ^{13}C NMR (125 MHz, $CDCl_3$) 140.2, 138.7, 138.6, 138.5, 138.4, 138.4, 138.3, 138.2 (8× *ipso* C_6H_5), 128.4–126.8 (40× C_6H_5), 101.7 (C-1), 85.4 (C-3′), 79.6 (C-5′), 79.4 (PhCHCH_2OBn), 78.6 (C-4), 78.5 (C-5), 77.1 (C-1′), 75.9 (C-2′), 75.5 (C-4′), 75.1, 74.8, 74.4, 74.3, 73.4, 73.3, 73.3, 72.6 (7× PhCH_2, PhCHCH_2OBn), 69.8 (C-6), 69.4 (C-6′), 38.2 (C-2), 36.9 (C-3), 33.9 (C-1″). ESIMS: MNH_4^+, found 1092.7. $C_{70}H_{78}NO_{10}$ requires 1092.6.

*4.1.20. Phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-α-D-arabino-hexopyranoside (**29a**) and phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-D-arabino-hexopyranoside (**29b**).* $BF_3{\cdot}Et_2O$ (0.50 mL, 3.76 mmol) and thiophenol (1.3 mL, 12.5 mmol) were added in an inert atmosphere to a solution of compound **25** (2.70 g, 2.50 mmol) in dichloromethane (150 mL) that was pre-cooled to −78 °C. The stirred reaction mixture was allowed to warm spontaneously to room temperature, and after 2 h, the reaction was quenched by cautious addition of 1 M NaOH. The reaction mixture was partitioned between dichloromethane and a saturated $NaHCO_3$ solution, the combined organic phases were dried and evaporated, and the residue was chromatographed on silica gel (light petroleum/ethyl acetate, 8:1), affording 1.9 g (80%) of a mixture of thioglycosides **29a**,**b** in a ratio α/β=3:1 (determined by integration of H-1 in ^1H NMR spectrum; for the α anomer d at 5.53 ppm, and for the β anomer dd at 4.65 ppm); R_f=0.35 (light petroleum/ethyl acetate, 4:1). Repeated chromatography afforded an analytical sample of the major α-diastereoisomer **29a** as a viscous oil; [Found: C, 76.38; H, 6.89. $C_{61}H_{64}O_8S$ requires C, 76.54; H, 6.69%]; ν_{max} 3011, 2913, 2868, 1585, 1497, 1454, 1364, 1088, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.47–7.13 (m, 35H, 7× C_6H_5), 5.53 (d, 1H, $J_{1,2ax}$ 5.4 Hz, H-1), 4.73–4.40 (m, 12H, 6× O–CH_2–Ph), 4.26 (m, 1H, H-5), 4.10 (m, 1H, H-1′), 3.85–3.73 (m, 3H, H-4′, H-5′, H-6a), 3.72–3.64 (m, 2H, H-3′, H-6′a), 3.61 (dd, 1H, *J* 1.4, 10.7 Hz, H-6′b), 3.50 (dd, 1H, *J* 3.3, 4.1 Hz, H-2′), 3.31 (dd, 1H, $J_{4,5}$ 9.7 Hz, $J_{3,4}$ 9.5 Hz, H-4), 2.41 (ddd, 1H, $J_{2eq,2ax}$ 13.9 Hz, $J_{2eq,3}$ 3.9 Hz, $J_{2eq,1}$ ~0 Hz, H-2_{eq}), 2.04 (m, 1H, H-3), 1.94 (m, 1H, H-1″a), 1.86 (ddd, 1H, $J_{2eq,2ax}$ 13.9 Hz, $J_{2ax,3}$ 12.6 Hz, $J_{2ax,1}$ 5.4 Hz, H-2_{ax}); 1.27 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 138.4, 138.3, 138.3, 138.2, 138.1, 137.9, 135.7 (7× *ipso* C_6H_5), 130.8–126.5 (35× C_6H_5), 84.7 (C-1), 78.4 (C-4), 77.2 (C-3′), 77.3 (C-3′), 76.1 (C-2′), 74.9 (C-4′), 73.9, 73.8, 73.4, 73.3, 72.0, 71.4 (6× PhCH_2), 73.5 (C-5′), 72.6 (C-5), 72.2 (C-1′), 69.4 (C-6), 69.3 (C-6′), 37.1 (C-3), 36.4 (C-2), 31.6 (C-1″). ESIMS: MNH_4^+, found 974.8. $C_{61}H_{68}NO_8S$ requires 974.5.

*4.1.21. Phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-α-L-arabino-hexopyranoside (**30a**) and phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-L-arabino-hexopyranoside (**30b**).* Using the same procedure as described for the preparation of compounds **29a**,**b**, compound **26** (1.4 g, 1.30 mmol) was converted to a mixture of thioglycosides **30a**,**b** (viscous oil 1.2 g, 80%) in a ratio α/β=1.3:1 (integration of H-1 in ^1H NMR spectrum; for the α anomer d at 5.58 ppm, for the β anomer dd at 4.75 ppm); R_f=0.4 (light petroleum/ethyl acetate, 4:1). ESIMS: MNH_4^+, found 974.8. $C_{61}H_{68}NO_8S$ requires 974.5. The obtained mixture was sufficiently pure to use in the next step without further purification.

*4.1.22. Phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-α-D-arabino-hexopyranoside (**31a**) and phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-D-arabino-hexopyranoside (**31b**).* Using the same procedure as described for the preparation of compounds **29a**,**b**, compound **27** (2.9 g, 2.7 mmol) was converted to a mixture of thioglycosides **31a**,**b** (2.1 g, 81%), in a ratio α/β=3:1 (integration of H-1 in ^1H NMR spectrum; for the α anomer d at 5.56 ppm, for the β anomer dd at 4.67 ppm); R_f=0.46 (light petroleum/ethyl acetate, 4:1). Repeated chromatography afforded an analytical sample of the major α-diastereoisomer **31a** as a viscous oil; [Found: C, 76.38; H, 6.89. $C_{61}H_{64}O_8S$ requires C, 76.54; H, 6.69%]; ν_{max} 3011, 2915, 2867, 1585, 1497, 1454, 1363, 1086, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.46–7.10 (m, 35H, 7× C_6H_5), 5.58 (d, 1H, $J_{1,2ax}$ 5.3 Hz, H-1), 5.02 (d, 1H, *J* 11.6 Hz, O–CH_2–Ph), 4.86 (d, 1H, *J* 11.6 Hz, O–CH_2–Ph), 4.76–4.42 (m, 10H, 5× O–CH_2–Ph), 4.29 (m, 1H, H-5), 3.94 (dd, 1H, $J_{4',5'}=J_{3',4'}$ 9.5 Hz, H-4′), 3.81 (dd, 1H, $J_{6'a,6'b}$ 10.8 Hz, $J_{6'a,5'}$ 3.6 Hz, H-6′a), 3.80–3.71 (m, 2H, H-6a, H-6b), 3.69 (m, 1H, H-2′), 3.63 (dd, $J_{6'a,6'b}$ 10.8 Hz, 1H, $J_{6'a,5'}$ 1.6 Hz, H-6′$_b$), 3.53 (dd, 1H, $J_{3',4'}$ 9.4 Hz, $J_{3',2'}$ 2.4 Hz, H-3′), 3.42–3.37 (m, 2H, H-1′, H-5′), 3.34 (dd, 1H, $J_{4,5}=J_{4,3}$ 9.7 Hz, H-4), 2.38–2.22 (m, 2H, H-3, H-1″a), 2.05 (ddd, 1H, $J_{2eq,2ax}$ 13.8 Hz, $J_{2eq,3}$ 3.5 Hz, $J_{2eq,1}$ ~0 Hz, H-2_{eq}), 1.96 (ddd, 1H, $J_{2eq,2ax}$ 13.8 Hz, $J_{2ax,3}$ 12.6 Hz, $J_{2ax,1}$ 5.3 Hz, H-2_{ax}), 1.25 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 138.8, 138.7, 138.5, 138.5, 138.1, 138.0, 135.6 (7× *ipso* C_6H_5), 130.0–126.6 (35× C_6H_5), 85.4 (C-3′), 84.7 (C-1), 80.0 (C-5′), 78.4 (C-4), 76.3 (C-2′), 75.4, 75.2 (C-4′, C-1′), 75.0, 74.5, 73.6, 73.5, 73.4, 72.5 (6× PhCH_2, PhCHCH_2OBn), 72.2 (C-5), 69.7 (C-6), 69.3 (C-6′), 36.0 (C-2), 34.2 (C-1″), 34.1 (C-3). ESIMS: MNH_4^+, found 974.8. $C_{61}H_{68}NO_8S$ requires 974.5.

*4.1.23. Phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-L-arabino-hexopyranoside (**32a**) and phenyl-1-thio 2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-L-arabino-hexopyranoside (**32b**).* Using the same procedure as described for the preparation of compounds **29a**,**b**, compound **28** (0.9 g, 0.84 mmol) was converted to a mixture of thioglycosides **32a**,**b** (viscous oil,

0.7 g, 85%), in a ratio α/β=1.2:1 (integration of H-1 in ^{1}H NMR spectrum; for α anomer d at 5.64 ppm, for β anomer dd at 4.71 ppm); R_f=0.4 (light petroleum/ethyl acetate, 4:1). ESIMS: MNH_4^+, found 974.8. $C_{61}H_{68}NO_8S$ requires 974.5. The obtained mixture was sufficiently pure to use in the next step without further purification.

*4.1.24. 1,5-Anhydro-4,6-di-O-benzyl-2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-D-arabino-hex-1-enitol (**1**).* *N*-Bromosuccinimide (0.27 g, 1.5 mmol) was added to a solution of anomers **29a**,**b** (1.1 g, 1.1 mmol) in acetone (12 mL) containing 1% water. The reaction mixture was stirred at −15 °C under exclusion of light, and the reaction course was monitored by TLC (light petroleum/ethyl acetate, 3:1). After 40 min, the reaction mixture did not contain the starting compound, and the reaction was quenched by the addition of a $NaHCO_3$ solution to pH 8. After partitioning between dichloromethane and aqueous $NaHCO_3$, the organic phase was dried, the solvent was evaporated, and the residue was chromatographed on a short silica gel column in light petroleum/ethyl acetate (2:1), affording 0.83 g of 2,3-dideoxy-3-*C*-[(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-*O*-benzyl-D-*arabino*-hexopyranose (R_f 0.3, light petroleum/ethyl acetate (2:1); ESMSI: MH^+, found 865.7. $C_{55}H_{61}O_9$ requires 865.4.). The obtained compound was dissolved in dichloromethane (20 mL), and the solution was treated in an inert atmosphere at 0 °C with *s*-collidine (1.9 mL, 14.4 mmol) and mesyl anhydride (0.33 g, 1.9 mmol). The reaction mixture was stirred at 0 °C, and the reaction course was monitored by TLC (light petroleum/ethyl acetate, 3:1). After 4 h, the reaction mixture was partitioned between dichloromethane and aqueous $NaHCO_3$. The organic phase was dried, the solvent was evaporated, and the residue was chromatographed on silica gel in light petroleum/ethyl acetate (8:1), affording 0.63 g (65%) of compound **1** as a colorless syrup; [Found: C, 78.10; H, 6.80. $C_{55}H_{58}O_8$ requires C, 77.99; H, 6.90%]; R_f=0.5 (light petroleum/ethyl acetate, 4:1); $[\alpha]_D^{20}$ −10.3 (*c* 1.28, $CHCl_3$); ν_{max} 3011, 1650, 1497, 1454, 1364, 1096, 1028, 914 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.14 (m, 30H, 6× C_6H_5); 6.24 (dd, 1H, $J_{1,2}$ 6.0 Hz, $J_{1,3}$ 2.3 Hz, H-1), 4.75 (dd, 1H, $J_{1,2}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz, H-2); 4.73–4.44 (m, 12H, O–CH_2–Ph), 4.10 (ddd,1H, $J_{1',1''b}$ 8.3 Hz, $J_{2',1'}$ 4.2 Hz, $J_{1',1''a}$ 4.1 Hz, H-1′), 3.86–3.71 (m, 6H, H-4′, H-5′, H-5, H-6′a, H-6a, H-6b), 3.70–3.62 (m, 2H, H-3′, H-6′b), 3.50 (dd, 1H, $J_{4,5}$=$J_{4,3}$ 8.9 Hz, H-4), 3.47 (dd, 1H, $J_{2',1'}$,4.2 Hz, $J_{2',3'}$,3.2 Hz, H-2′), 2.33 (m, 1H, H-3), 1.67 (ddd, 1H, $J_{1''a,1''b}$ 14.2 Hz, $J_{1''a,1'}$ 4.1 Hz, $J_{1''a,3}$ 3.9 Hz, H-1″a), 1.45 (ddd,1H, $J_{1''a,1''b}$ 14.2 Hz, $J_{1''b,3}$ 8.4 Hz, $J_{1''b,1'}$ 8.3 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 142.6 (C-1), 138.4, 138.4, 138.3, 138.3, 138.2, 137.9 (6× *ipso* C_6H_5), 128.4–127.4 (30× C_6H_5), 102.9 (C-2), 78.0, 75.0, 73.4 (C-4′, C-5′, C-5), 77.6 (C-3′), 76.2, 75.9 (C-2′, C-4), 72.6 (C-1′), 74.1, 73.9, 73.6, 73.3, 72.1, 71.5 (6× PhCH_2), 69.3, 68.7 (C-6, C-6′), 38.6 (C-3), 31.8 (C-1″). ESIMS: MNH_4^+, found, 864.8. $C_{55}H_{62}NO_8$ requires 864.4.

*4.1.25. 1,5-Anhydro-4,6-di-O-benzyl-2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-L-arabino-hex-1-enitol (**2**).* Using the same procedure as described for the preparation of compound **1**, the mixture of compounds **30a**,**b** (0.8 g, 0.8 mmol) was converted to compound **2** (colorless syrup, 0.48 g, 65%); [Found: C, 77.75; H, 6.65. $C_{55}H_{58}O_8$ requires C, 77.99; H, 6.90%]; R_f=0.5 (light petroleum/ethyl acetate, 4:1); $[\alpha]_D^{20}$ +6.8 (*c* 0.45, $CHCl_3$); ν_{max} 3009, 1651, 1496, 1454, 1363, 1096, 1028, 914 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.39–7.14 (m, 30H, 6× C_6H_5), 6.30 (dd, 1H, $J_{1,2}$ 6.0 Hz, $J_{1,3}$ 2.3 Hz, H-1), 4.74 (d, 1H, *J* 11.4 Hz, O–CH_2–Ph), 4.66 (d, 1H, *J* 12.0 Hz, O–CH_2–Ph), 4.62 (dd, 1H, $J_{1,2}$ 6.0 Hz, $J_{2,3}$ 1.8 Hz, H-2), 4.61–4.43 (m, 10H, O–CH_2–Ph), 4.09 (ddd, $J_{1',1''b}$ 11.5 Hz, $J_{1',1''a}$=$J_{1',2'}$ 3.3 Hz, H-1′), 3.88 (dd, 1H, $J_{4',3'}$=$J_{4',5'}$ 7.0 Hz, H-4′), 3.85–3.67 (m, 6H, H-5′, H-5, H-6′a, H-6′b, H-6a, H-6b), 3.63 (dd, 1H, $J_{4',3'}$ 7.3 Hz, $J_{3',2'}$ 3.2 Hz, H-3′), 3.46–3.39 (m, 2H, H-2′, H-4), 2.50 (m, 1H, H-3), 1.91 (ddd, 1H, $J_{1''a,1''b}$ 13.8 Hz, $J_{1''a,3}$ 11.1 Hz, $J_{1''a,1'}$ 3.3 Hz, H-1″a), 0.96 (ddd, 1H, $J_{1''b,1''a}$ 13.8 Hz, $J_{1''b,1'}$ 11.5 Hz, $J_{1''b,3}$ 2.6 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 142.6 (C-1), 138.7, 138.5, 138.3, 138.3, 138.2, 137.9 (6× *ipso* C_6H_5), 128.5–127.4 (30× C_6H_5), 101.8 (C-2), 77.9 (C-5′or C-5), 77.8 (C-3′), 76.6, 76.1 (C-4, C-2′), 75.0 (C-4′), 72.9 (C-5′or C-5), 73.9, 73.8, 73.7, 73.2, 72.1, 71.6 (6× PhCH_2), 69.8 (C-1′), 69.2, 68.7 (C-6, C-6′), 35.2 (C-3), 3.8 (C-1″). ESIMS: MNH_4^+, found, 864.8. $C_{55}H_{62}NO_8$ requires 864.4.

*4.1.26. 1,5-Anhydro-4,6-di-O-benzyl-2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-D-arabino-hex-1-enitol (**3**).* Using the same procedure as described for the preparation of compound **1**, the mixture of compounds **31a**,**b** (1.4 g, 1.4 mmol) was converted to compound **3** (colorless syrup, 0.87 g, 70%); [Found: C, 77.85; H, 6.75. $C_{55}H_{58}O_8$ requires C, 77.99; H, 6.90%]; R_f=0.5 (light petroleum/ethyl acetate, 4:1); $[\alpha]_D^{20}$ −5.9 (*c* 1.03, $CHCl_3$); ν_{max} 3011, 1650, 1497, 1454, 1363, 1086, 1028, 914 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.38–7.15 (m, 30H, 6× C_6H_5), 6.31 (dd, 1H, $J_{1,2}$ 6.0 Hz, $J_{1,3}$ 2.3 Hz, H-1), 5.00 (d, 1H, *J* 11.7 Hz, O–CH_2–Ph), 4.86 (d, 1H, *J* 10.9 Hz, O–CH_2–Ph), 4.73–4.50 (10H, O–CH_2–Ph), 4.63 (dd, 1H, $J_{2,1}$ 6.0 Hz, $J_{2,3}$ 1.5 Hz, H-2), 3.94 (dd, 1H, $J_{4',3'}$=$J_{4',5'}$ 9.5 Hz, H-4′), 3.85–3.67 (m, 6H, H-5, H-6a, H-6b, H-6′a, H-6′b, H-2′), 3.54 (dd, 1H, $J_{3',4'}$ 9.5 Hz, $J_{2',3'}$ 2.7 Hz, H-3′), 3.47–3.35 (m, 3H, H-1′, H-4, H-5′), 2.51 (m, 1H, H-3), 2.29 (ddd, 1H, $J_{1''a,1''b}$ 14.0 Hz, *J* 9.2 Hz, *J* 5.3 Hz, H-1″a), 1.19 (ddd, 1H, $J_{1''a,1''b}$ 14.0 Hz, *J* 8.9 Hz, *J* 4.1 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 142.6 (C-1), 138.8, 138.7, 138.5, 138.5, 138.1, 137.9 (6× *ipso* C_6H_5), 128.4–127.3 (30× C_6H_5), 102.6 (C-2), 85.4 (C-3′), 80.1 (C-5′), 77.9 (C-5), 76.7, 76.2, 75.3 (C-1′, C-4, C-2′), 75.4 (C-4′), 75.1, 74.4, 73.8, 73.6, 73.5, 72.4 (6× PhCH_2), 69.7, 68.7 (C-6, C-6′), 35.6 (C-3), 35.1 (C-1″). ESIMS: MNH_4^+, found, 864.8. $C_{55}H_{62}NO_8$ requires 864.4.

*4.1.27. 1,5-Anhydro-4,6-di-O-benzyl-2,3-dideoxy-3-C-[(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)methyl]-L-arabino-hex-1-enitol (**4**).* Using the same procedure as described for the preparation of compound **1**, the mixture of compounds **32a**,**b** (0.7 g, 0.7 mmol) was converted to compound **4** (colorless syrup, 0.43 g, 70%); [Found: C, 77.79; H, 7.10. $C_{55}H_{58}O_8$ requires C, 77.99; H, 6.90%]; R_f=0.5 (light petroleum/ethyl acetate, 4:1); $[\alpha]_D^{20}$ +10.9 (*c* 0.39, $CHCl_3$); ν_{max} 3010, 1650, 1497, 1454, 1363, 1087, 1028, 915 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.09 (m, 30H, 6× C_6H_5), 6.29 (dd, 1H, $J_{1,2}$ 5.9 Hz, $J_{1,3}$ 2.0 Hz, H-1), 4.95 (d, 1H, *J* 11.7 Hz, O–CH_2–Ph), 4.86 (d, 1H, *J* 10.9 Hz, O–CH_2–Ph), 4.73 (dd, 1H, 1H, $J_{2,1}$ 5.9 Hz, $J_{2,3}$ 1.8 Hz, H-2), 4.66–4.45 (m, 10H, 5× O–CH_2–Ph), 3.88 (dd, 1H, $J_{4',3'}$=$J_{4',5'}$ 9.5 Hz, H-4′), 3.84–3.76 (m, 3H, H-6a, H-6b, H-5), 3.73 (dd, 1H, $J_{6'a,6'b}$ 10.8 Hz, $J_{6'a,5'}$ 1.8 Hz, H-6′a), 3.67 (dd, 1H, $J_{6'a,6'b}$ 10.8 Hz, $J_{6'b,5'}$ 5.8 Hz, H-6′b), 3.62 (br s, 1H, H-2′), 3.60–3.53 (m, 2H, H-4, H-3′), 3.45–3.35 (m, 2H, H-1′, H-5′), 2.39 (m, 1H, H-3), 1.83 (ddd, 1H, $J_{1''a,1''b}$ 14.1 Hz, $J_{1',1''a}$=$J_{3,1''a}$ 8.2 Hz, H-1″a), 1.64 (ddd, 1H, $J_{1''a,1''b}$ 14.1 Hz, $J_{1''b,1'}$=$J_{1''b,3}$ 3.9 Hz, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 142.5 (C-1), 138.8, 138.8, 138.5, 138.4, 138.3, 137.9 (6× *ipso* C_6H_5), 128.4–127.4 (30× C_6H_5), 103.3 (C-2), 85.3 (C-3′), 79.5 (C-5), 78.1 (C-5′), 77.5 (C-1′), 76.3, 76.2 (C-2′, C-4), 75.5 (C-4′), 75.1, 74.3, 74.3, 73.6, 73.4, 72.5 (6× PhCH_2), 69.9, 68.9 (C-6′, C-6), 38.1 (C-3), 34.1 (C-1″). ESIMS: MNH_4^+, found, 864.8. $C_{55}H_{62}NO_8$ requires 864.4.

*4.1.28. Methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-α-D-mannopyranoside (**33**) and methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-β-D-glucopyranoside (**34**).* *m*-Chloroperoxybenzoic acid (77%) (150 mg, 0.67 mmol) was added, with stirring in an inert atmosphere, to a solution of **1** (470 mg, 0.56 mmol) in anhydrous MeOH (8 mL) and CH_2Cl_2 (2 mL) at room temperature. TLC showed that the reaction was complete after 1.5 h. The excess of peroxyacid was reduced by addition of aqueous $NaHCO_3$ (to pH=8), and the reaction mixture was partitioned between CH_2Cl_2 and H_2O. The

organic layer was dried and concentrated, and the residue was chromatographed on silica gel (light petroleum/ethyl acetate, 3:1) to yield **33** as a viscous oil (270 mg, 56%), R_f=0.36 (light petroleum/ethyl acetate, 2:1) and **34** as a viscous oil (120 mg, 25%), R_f=0.30 (light petroleum/ethyl acetate, 2:1). Compound **33**: [Found: C, 74.93; H, 6.75. $C_{56}H_{62}O_{10}$ requires C, 75.13; H, 6.93%]; $[\alpha]_D^{20}$ +6.3 (*c* 0.92, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 7.37–7.09 (m, 30H, 6× C_6H_5), 4.78–4.31 (m, 12H, O–CH_2–Ph), 4.28 (br s, 1H, H-1), 4.09–4.02 (m, 2H, H-1′, H-2), 3.94 (dd, 1H, $J_{4',3'}$=$J_{4',5'}$ 7.8 Hz, H-4′), 3.75–3.64 (m, 4H, H-5, H-6a, H-6b, H-6′a), 3.62 (dd, 1H, $J_{3',4'}$ 7.8 Hz, $J_{3',2'}$ 2.3 Hz, H-3′), 3.60–3.50 (m, 2H, H-5′, H-6′b), 3.50–3.40 (m, 2H, H-4, H-2′), 3.31 (s, 3H, OCH_3), 1.98 (m, 1H, H-3), 1.81 (ddd, 1H, $J_{1''a,1''b}$ 14.0 Hz, $J_{1''a,1'}$=$J_{1''a,3}$ 11.0 Hz, H-1″a), 1.56 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 138.3, 138.3, 138.2, 138.1, 138.1, 137.4 (6× *ipso* C_6H_5), 128.4–127.5 (30× C_6H_5), 100.9 (C-1), 78.2 (C-3′), 77.5 (C-4), 75.7 (C-5′), 75.0 (C-2′), 74.8 (C-2), 72.6 (C-4′), 77.7 (C-5), 74.2, 74.1, 73.5, 73.4, 72.1, 71.7 (6× PhCH_2), 70.1, 69.7 (C-6, C-6′), 67.8 (C-1′), 54.5 (OCH_3), 42.7 (C-3), 29.7 (C-1″). ESIMS: MNH_4^+, found 912.2. $C_{56}H_{66}NO_{10}$ requires 912.5. Compound **34**: $[\alpha]_D^{20}$ −3.8 (*c* 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.10 (m, 30H, 6× C_6H_5), 4.68–4.43 (m, 12H, 6× O–CH_2–Ph), 4.22–4.17 (m, 1H, H-1′), 4.11 (dd, 1H, $J_{1,2}$ 7.5 Hz, H-1), 3.98 (m, 1H, H-5′), 3.82 (dd, 1H, $J_{3',4'}$=$J_{4',5'}$ 5.8 Hz, H-4′), 3.79–3.68 (m, 5H, H-3′, H-6′a, H-6′b, H-6a, H-6b), 3.57–3.52 (m, 4H, H-2′, OCH_3), 3.45 (m, 1H, H-5), 3.35 (dd, 1H, $J_{3,4}$=$J_{4,5}$ 9.5 Hz, H-4), 3.21 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{1,2}$ 7.5 Hz, H-2), 2.08 (m, 1H, H-1″a), 1.80–1.67 (m, 2H, H-1″b, H-3); ^{13}C NMR (125 MHz, $CDCl_3$) 138.2, 138.2, 138.1, 138.1, 137.9, 137.8 (6× *ipso* C_6H_5), 128.3–127.4 (30× C_6H_5), 105.4 (C-1), 77.6 (C-5), 77.2 (C-4), 76.5 (C-2′), 76.1 (C-3′), 74.6 (C-4′), 74.1 (PhCH_2), 73.6 (C-5′), 73.5 (2× PhCH_2), 73.2 (PhCH_2), 72.8 (C-2), 72.2 (PhCH_2), 71.9 (C-1′), 71.3 (PhCH_2), 69.1, 68.7 (C-6, C-6′), 56.7 (OCH_3), 46.3 (C-3), 30.7 (C-1″). ESIMS: MNH_4^+, found 912.2. $C_{56}H_{66}NO_{10}$ requires 912.5.

*4.1.29. Methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)methyl]-4,6-di-O-benzyl-α-L-mannopyranoside (**35**) and methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl) methyl]-4,6-di-O-benzyl-β-L-glucopyranoside (**36**).* Using the same procedure as in the previous case, the glucal **2** (290 mg, 0.34 mmol) was converted to compounds **35** (viscous oil, 160 mg, 51%), R_f=0.30 (light petroleum/ethyl acetate, 2:1) and **36** (viscous oil, 76 mg, 24%), R_f=0.36 (light petroleum/ethyl acetate, 2:1). Compound **35**: [Found: C, 74.93; H, 6.75. $C_{56}H_{62}O_{10}$ requires C, 75.13; H, 6.93%]; $[\alpha]_D^{20}$ −4.2 (*c* 0.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.10 (m, 30H, 6× C_6H_5), 4.69 (d, 1H, *J* 11.4 Hz, O–CH_2–Ph), 4.65 (d, 1H, *J* 11.4 Hz, O–CH_2–Ph), 4.59 (br s, 1H, H-1), 4.57–4.34 (m, 10H, O–CH_2–Ph), 4.19 (m, 1H, H-1′), 3.87–3.82 (m, 2H, H-2, H-6a), 3.81–3.65 (m, 7H, H-5, H-3′, H-4′, H-5′, H-6b, H-6′a, H-6′b), 3.58–3.53 (m, 2H, H-2′, H-4), 3.3 (s, 3H, OCH_3), 2.19 (m, 1H, H-3), 1.93 (m, 1H, H-1″a), 1.64 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 138.5–138.1 (6× *ipso* C_6H_5), 128.3–127.3 (30× C_6H_5), 100.6 (C-1), 76.7 (C-3′), 76.1, 74.9, 73.8 (C-4, C-2′, C-2), 74.1, 73.5, 73.5, 73.2, 72.1, 71.5 (6× PhCH_2), 73.3, 72.0, 69.3 (C-4′, C-5, C-4′), 69.4, 69.0 (C-6, C-6′), 54.7 (OCH_3), 37.9 (C-3), 26.5 (C-1″). ESIMS: MNH_4^+, found 912.2. $C_{56}H_{66}NO_{10}$ requires 912.5. Compound **36**: $[\alpha]_D^{20}$ +5.6 (*c* 0.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 7.40–7.14 (m, 30H, 6× C_6H_5), 4.73–4.39 (m, 11H, O–CH_2–Ph), 4.33 (ddd, 1H, $J_{1',1''b}$ 10.4 Hz, $J_{1',1''a}$ 3.9 Hz, $J_{1',2'}$ 2.2 Hz, H-1′), 4.23 (d, 1H, 1H, *J* 11.0 Hz, O–CH_2–Ph), 4.10 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.94 (ddd, 1H, $J_{5',4'}$=$J_{5',6'a}$ 7.4 Hz, $J_{5',6'b}$ 2.8 Hz, H-5′), 3.77–3.65 (m, 5H, H-3′, H-4′, H-6a, H-6b, H-6′a), 3.63–3.56 (m, 2H, H-6′b, H-2), 3.53–3.48 (m, 4H, H-2′, OCH_3), 3.45 (ddd, 1H, $J_{4,5}$ 9.6 Hz, $J_{5,6a}$=$J_{5,6b}$ 3.3 Hz, H-5), 3.38 (dd, 1H, $J_{4,3}$ 10.5 Hz, $J_{4,5}$ 9.6 Hz, H-4), 2.16 (m, 1H, H-1″a), 1.84 (m, 1H, H-3), 1.56 (m, 1H, H-1″b); ^{13}C NMR (125 MHz, $CDCl_3$) 138.1–137.8 (6× *ipso* C_6H_5), 128.3–127.5 (30×C_6H_5), 105.6 (C-1), 77.8, 77.7 (C-5, C-3′), 76.4 (C-2′), 75.3 (C-4′), 74.9 (C-4), 73.9, 73.8, 73.5, 73.3 (4× PhCH_2), 72.8 (C-5′), 72.3, 71.6 (2× PhCH_2), 71.2 (C-2), 71.0 (C-1′), 69.6, 69.2 (C-6, C-6′), 56.7 (OCH_3), 45.0 (C-3), 25.5 (C-1″). ESIMS: MNH_4^+, found 912.2. $C_{56}H_{66}NO_{10}$ requires 912.5.

*4.1.30. Methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)methyl]-2,4,6-tri-O-acetyl-α-D-mannopyranoside (**7**).* 10% Pd/C (30 mg) were added to a solution of *C*-disaccharide **33** (150 mg, 0.17 mmol) in MeOH (15 mL) and glacial acetic acid (3 mL), and the reaction was stirred overnight under an atmosphere of hydrogen, then filtered through a pad of Celite and coevaporated three times with toluene. The obtained compound (methyl 3-deoxy-3-*C*-[(α-D-mannopyranosyl)methyl]-α-D-mannopyranoside, ESIMS: MNH_4^+, found 372.1. $C_{14}H_{30}NO_{10}$ requires 372.2) was dissolved in pyridine (16 mL) and Ac_2O (8 mL) and stirred overnight at room temperature. The reaction mixture was concentrated and coevaporated three times with toluene, and column chromatography (light petroleum/ethyl acetate, 2:1→1:2) yielded 55 mg (50%) of **7** as a viscous oil; [Found: C, 51.60; H, 6.05. $C_{28}H_{40}O_{17}$ requires C, 51.83; H, 6.17%]; R_f=0.67 ($CHCl_3$/MeOH, 15:1); $[\alpha]_D^{20}$ +10.7 (*c* 0.68, $CHCl_3$); ν_{max} 3034, 2932, 1744, 1371, 1142, 1048 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) 5.56 (dd, 1H, $J_{3',4'}$ 6.0 Hz, $J_{2',3'}$ 3.2 Hz, H-3′), 5.41 (dd, 1H, $J_{4,3}$=$J_{4,5}$ 10.5 Hz, H-4), 5.29 (dd, 1H, $J_{2',1'}$ 6.9 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.26 (dd, 1H, $J_{2,3}$ 3.0 Hz, $J_{2,1}$ 1.3 Hz, H-2), 5.18 (dd, 1H, $J_{3',4'}$ 6.0 Hz, $J_{4',5'}$ 4.4 Hz, H-4′), 4.76 (dd, 1H, $J_{6'a,6'b}$ 11.9 Hz, $J_{5',6'a}$ 8.0 Hz, H-6′a), 4.71 (d, 1H, $J_{2,1}$ 1.3 Hz, H-1), 4.41 (dd, 1H, $J_{6a,6b}$ 12.1 Hz, $J_{5,6a}$ 5.2 Hz, H-6a), 4.21–4.12 (m, 2H, H-1′, H-6b) 4.06 (ddd, 1H, $J_{5',6'a}$ 8.0 Hz, $J_{5',4'}$ 4.4 Hz, $J_{5',6'b}$ 3.7 Hz, H-5′), 4.02 (dd, 1H, $J_{6'a,6'b}$ 11.9 Hz, $J_{5',6'b}$ 3.7 Hz, H-6′b), 3.89 (ddd, 1H, $J_{5,4}$ 10.5 Hz, $J_{5,6a}$ 5.2 Hz, $J_{5,6b}$ 2.5 Hz, H-5), 3.0 (s, 3H, OCH_3), 2.58 (dddd, 1H, $J_{4,3}$ 10.5 Hz, $J_{1''a,3}$=$J_{1''b,3}$ 5.5 Hz, $J_{3,2}$ 3.0 Hz, H-3), 1.87 (s, 3H, $COOCH_3$), 1.86–1.84 (m, 2H, H-1″a, H-1″b), 1.82 (s, 3H, $COOCH_3$), 1.75 (s, 3H, $COOCH_3$), 1.71 (s, 3H, $COOCH_3$), 1.65 (s, 3H, $COOCH_3$), 1.57 (s, 3H, $COOCH_3$), 1.53 (s, 3H, $COOCH_3$); ^{13}C NMR (125 MHz, C_6D_6) 170.1–169.1 (7× $COOCH_3$), 97.8 (C-1), 73.0 (C-5′), 72.4 (C-2), 71.0 (C-1′), 70.3 (C-2′), 69.6 (C-5), 68.6 (C-4), 68.2 (C-4′), 68.1 (C-3′), 63.1 (C-6), 60.9 (C-6′), 54.5 (OCH_3), 37.1 (C-3), 29.1 (C-1″), 20.4–20.1 (7× $COOCH_3$). ESIMS: MNH_4^+, found 665.9. $C_{28}H_{44}NO_{17}$ requires 666.2.

*4.1.31. Methyl 3-deoxy-3-C-[(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)methyl]-2,4,6-tri-O-acetyl-α-L-mannopyranoside (**8**).* Using the same procedure as for the preparation of **7**, compound **35** (160 mg, 0.18 mmol) was converted to *C*-disaccharide **8** (viscous oil, 80 mg, 67%); [Found: C, 51.55; H, 6.35. $C_{28}H_{40}O_{17}$ requires C, 51.83; H, 6.17%]; R_f=0.67 ($CHCl_3$/MeOH, 15:1); $[\alpha]_D^{20}$ −6.9 (*c* 0.75, $CHCl_3$); ν_{max} 3011, 1671, 1625, 1454, 1390, 1094, 1028 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) 5.57 (dd, 1H, $J_{3',4'}$ 6.1 Hz, $J_{3',2'}$ 3.2 Hz, H-3′), 5.37 (br s, 1H, H-2), 5.30 (dd, 1H, $J_{4,3}$ 11.2 Hz, $J_{4,5}$ 10.5 Hz, H-4), 5.27 (dd, 1H, $J_{2',1'}$ 6.2 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.17 (dd, 1H, $J_{4',3'}$ 6.1 Hz, $J_{4',5'}$ 5.0 Hz, H-4′), 4.60 (br s, 1H, H-1), 4.61 (dd, 1H, $J_{6'a,6'b}$ 12.1 Hz, $J_{5',6'a}$ 8.7 Hz, H-6′a), 4.35 (dd, 1H, $J_{6a,6b}$ 12.2 Hz, $J_{5,6a}$ 5.3 Hz, H-6a), 4.25 (dd, 1H, $J_{6'a,6'b}$ 12.1 Hz, $J_{5',6'b}$ 3.4 Hz, H-6′b), 4.22–4.10 (m, 3H, H-1′, H-5′, H-6b), 3.88 (m, 1H, H-5), 2.98 (s, 3H, OCH_3), 2.73 (dddd, 1H, $J_{3,4}$=$J_{3,1''a}$ 11.2 Hz, $J_{3,1''b}$=$J_{3,2}$ 3 Hz, H-3), 1.92 (m, 1H, H-1″a), 1.87 (s, 3H, $COOCH_3$), 1.78 (m, 1H, H-1″b), 1.74 (s, 3H, $COOCH_3$), 1.73 (s, 3H, $COOCH_3$), 1.68 (s, 3H, $COOCH_3$), 1.66 (s, 3H, $COOCH_3$), 1.61 (s, 3H, $COOCH_3$), 1.58 (s, 3H, $COOCH_3$); ^{13}C NMR (125 MHz, C_6D_6) 170.1–169.3 (7× $COOCH_3$), 98.2 (C-1), 72.7 (C-5′), 70.5 (C-2′), 69.4, 69.3 (C-2, C-5), 68.6 (C-4′), 68.1 (C-3′), 67.9 (C-4), 67.3 (C-1′), 63.2 (C-6), 61.4 (C-6′), 54.4 (OCH_3), 35.1 (C-3), 27.0 (C-1″), 20.3–20.1 (7× $COOCH_3$). ESIMS: MNH_4^+, found 665.9. $C_{28}H_{44}NO_{17}$ requires 666.2.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.04.044. These data include MOL file and InChIKey of the most important compounds described in this article.

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