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Synthesis of L-Pyranosides by Hydroboration of Hex-5-enopyranosides Revisited

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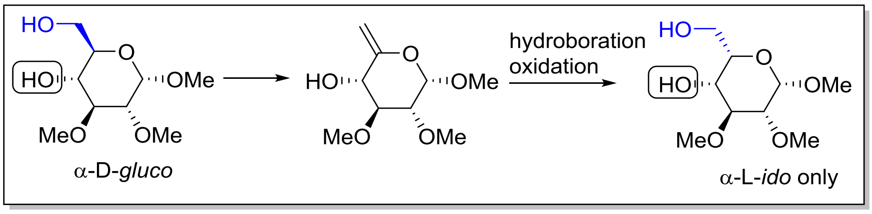


Abstract: Extensive study of the diastereoselective synthesis of L-pyranosides utilizing hydroboration of substituted *exo*-glucals (5-enopyranosides) obtained from D-sugars is presented. Based on this study we present the empirical rules describing the reaction stereoselectivity and the correlation between the yield of the L-*ido* product and the size of protecting groups used. Application of these guidelines revealed that the hydroboration of methyl 2,3-*O*-methyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside resulted in exclusive formation of L-*ido* product with high yield. This method can be successfully applied to the synthesis of L-iduronic acid being essential component of anticoagulant drugs with the diastereoselectivity superior to previously published protocols.

Introduction

Carbohydrates are one of the three most important components of living cells.[1] Although the D-sugars are most commonly distributed in the world, their L-isomers are also players in numerous biological processes.[2] The rare but biologically widespread L-sugars (mostly L-hexoses) have been found in numerous important natural products to only mention examples as alginates containing L-guluronic acid[3] or the well-known potent antitumor antibiotic Bleomycin comprising L-gulose (Fig. 1).[4] Among L-form sugar units, only a few such as L-arabinose, L-fucose, and L-rhamnose can be obtained from natural sources, thus chemical synthesis remains the most common source of pure L-sugars.[5] For instance, L-iduronic acid is a typical component of several mammalian glycosaminoglycans *i.e.* heparin, heparan sulfate[6] widely used as injectable blood thinner. L-Iduronic acid having several conformations in solution provides flexibility to the therapeutic polymer[7] and this sugar part is an essential component of polysaccharide-type synthetic anticoagulants as idraparinux (Fig. 1).[8]

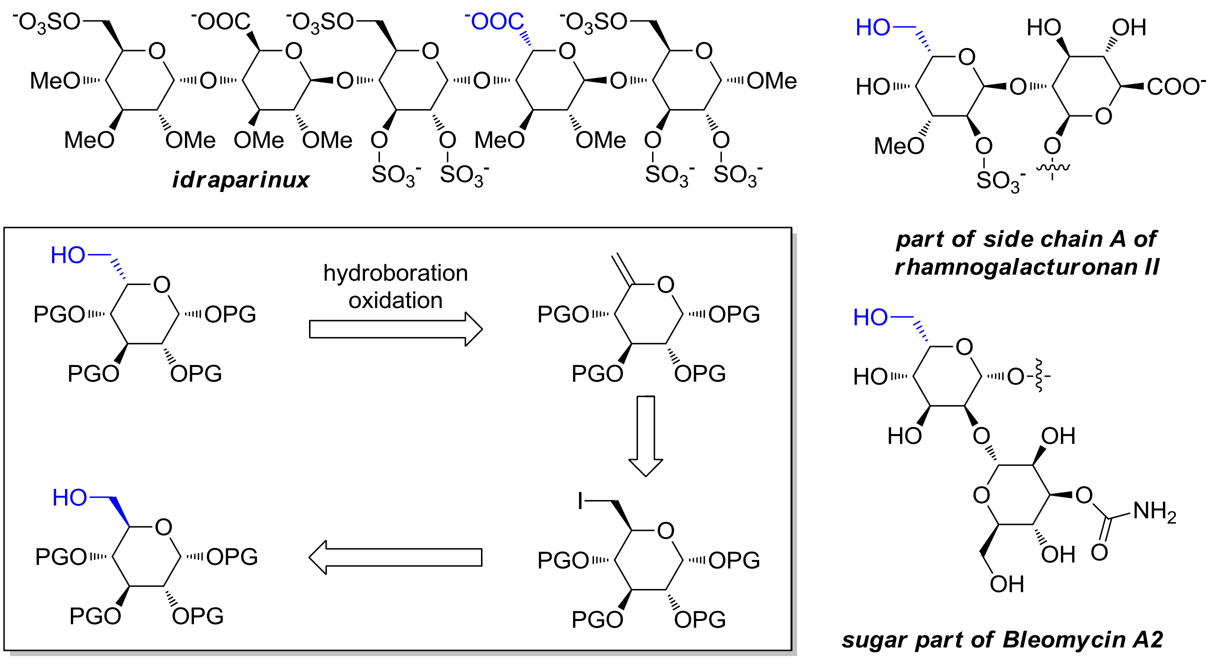


Fig 1. L-Hexoses as components of bioactive molecules and general retrosynthetic approach for synthesis of L-idose from D-glucose

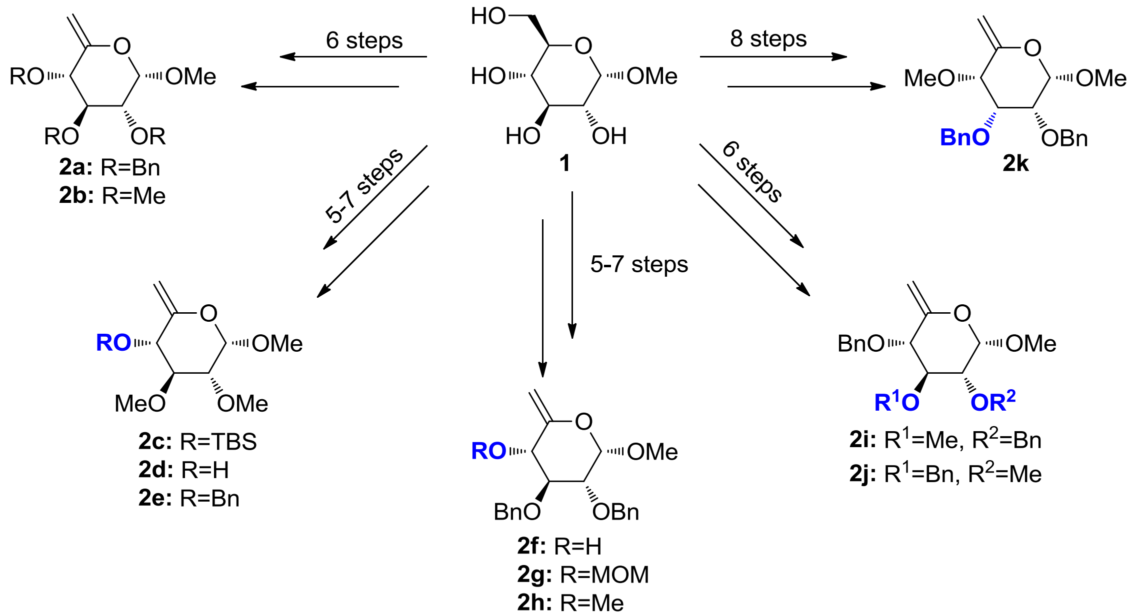
These interesting functions and increased medicinal interest in rare and unnatural carbohydrates along with the poor commercial availability of L-hexoses attracted chemists to develop reliable methods for the acquisition of L-hexoses and their derivatives.[5] Particularly, stereoselective hydroboration[9] of exocyclic alkenes constitutes valuable method for the epimerization at the C5 of D-sugars into corresponding L-antipodes.[10] Several reports have focused on the study of hydroboration/oxidation of 5-enopyranosides,[10-19] conveniently obtained by the elimination of 6-iodo-6-deoxy-D-glucose (Fig. 1). Initial study revealed that the addition of diborane to exocyclic alkene prepared from methyl glucoside, gave a mixture of the methyl D-glucoside and methyl L-idoside only slightly favoring the L-isomer (1:2.5).[10,11] Further, stereoselectivities ranging from 10:1 to 1:8 (L-*ido*/D-*gluco*) have been reported for the reactions of individual examples of protected *exo*-glucals under the treatment of borane/THF complex[12-17] and 9-BBN.[18-19] Interestingly, while the investigation on stereoselective transformation of various pyranosides appeared in the literature,[16] there is no systematic investigation on the kind of protecting groups and their influence on the reaction stereoselectivity.[19] Such investigation could be important for the planning strategy for the efficient total synthesis of natural products and drugs containing L-sugars, and particularly important L-iduronic acid being repeating unit of several mammalian glycosaminoglycans (GAG, heparin) and a crucial component of various synthetic anticoagulant drugs. Indeed, stereoselective C5 epimerisation in the glucose ring seems to be the most promising approach for preparation of the L-iduronic acid building block. Therefore, we present here our exhaustive studies on the hydroboration/oxidation of suitably protected methyl 6-deoxy-α- and β-D-*xylo*-hex-5-enopyranosides and the significant influence of the size of substituents on the reaction stereoselectivity.

Results and Discussion

Most of the previous studies described the hydroboration of *exo*-glucals with the α-anomeric configuration. This is rational approach, as the formation of required L-*ido* product occurs via the attack of electrophile at C5 from the opposite site to the anomeric substituent at

C1. On the other hand, heparin and heparin sulfate contain L-iduronic acid motifs incorporated with β-glycoside linkage and thus synthesis of L-iduronic acid with β-configured anomeric center seems to be crucial for the synthesis of anticoagulant drugs. Nevertheless, we started our systematic investigation from the synthesis of various methyl 6-deoxy-α-D-*xylo*-hex-5-enopyranosides (**2a-k**) from methyl α-D-glucoside (**1**, Scheme 1). Stereocontrolling auxiliaries of various size (H, Me, Bn, TBS, MOM) were located at C2, C3 and C4 with natural configuration of glucopyranoside. Sugars **2a** and **2b** possess the same benzyl or methyl ether at all three positions, while series **2c-e**, **2f-h** and **2i-j** differs by substituents at C4, C-3 and C2. Synthesis of **2k** required inversion at the C3 of pyranose ring, which was achieved by oxidation and stereoselective reduction of ketone by using $NaBH_4$.

Scheme 1. General Scheme of methyl α-5-enopyranosides synthesis

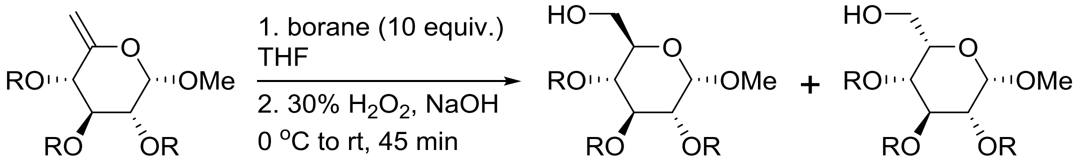


In all cases, treatment of suitably protected methyl α-D-glucopyranoside (methyl α-D-allopyranoside **2k**) with triphenylophosphine, iodine and imidazole afforded the 6-iodo derivatives isolated in high yield.[20] The dehydrohalogenation occurred easily by treatment of 6-iodo derivatives with potassium *tert*-butoxide. In some cases, however we used combined elimination with etherification at C4 (*O*-4) promoted by sodium hydride in the presence of

MeI or BnBr. Detailed information on the reaction protocols are presented in the Experimental Section.

Having in hand all desired compounds we attempted their hydroboration. At the initial stage various boranes and conditions were tested by using methyl 2,3,4-tri-*O*-benzyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (**2a**) and methyl 2,3,4-tri-*O*-methyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (**2b**) as the model substrates. The results are summarized in Table 1. In contrast to previous study,[19] the 9-borabicyclo[3.3.1]nonane (9-BBN) was not promising electrophile neither at low nor at elevated temperature (Table 1, entries 1,2). However, a low-temperature hydroboration of **2a** and **2b** with excess borane followed by oxidation yielded a mixture of D-*gluco* and L-*ido* isomers favoring formation of L-sugar, albeit in low stereoselectivity (entries 4 and 6). Interestingly, stereoselective formation of L-*ido* product was preferred in the case of methyl residues (**2b**, D-*gluco*/L-*ido* 1:8.5) while hydroboration of methyl 2,3,4-tri-*O*-benzyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (**2a**) was less selective (entry 4). Following the observation of Ikegami,[16] we used ten-fold excess of borane complex as essential amount for obtaining better stereoselectivity of L-*ido* product.

Table 1. Hydroboration/oxidation of methyl α-5-enoglucopyranosides 2a-b



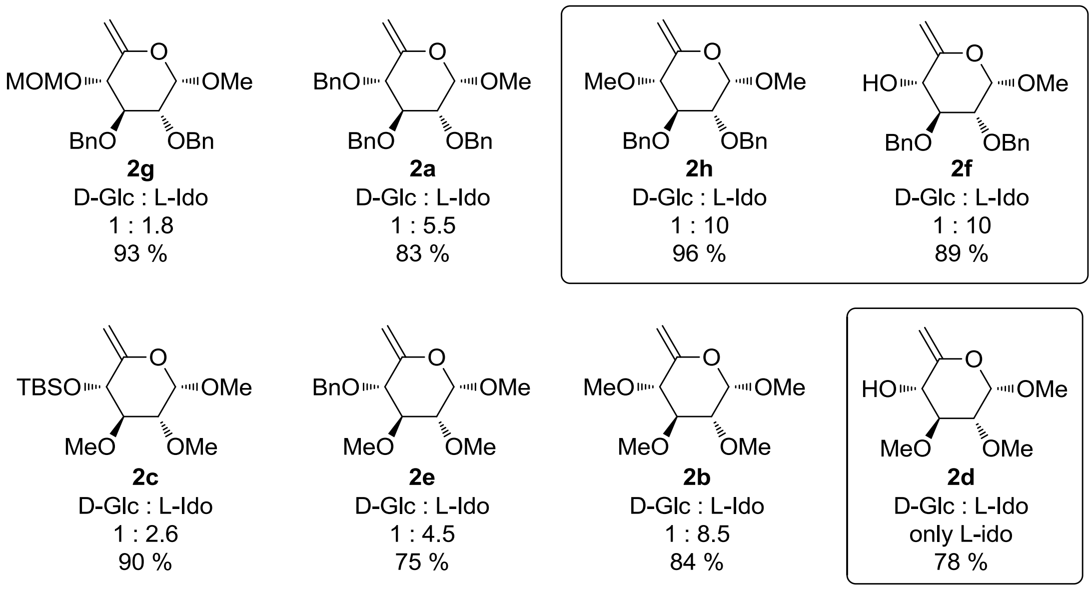
2a-b **3a-b** **4a-b**

Entry	Substrate	Borane	T [°C]	t [h][a]	Yield [%][b]	D-Glc : L-Ido[c]
1	**2a**	**9-BBN**	0	1.5	traces	-
2	**2a**	**9-BBN**[d]	65	2.5	traces	-
3	**2a**	**BH_3·THF**	rt	1.5	66	1 : 5.5
4	**2a**	**BH_3·THF**	0	1.5	83	1 : 5.5
5	**2a**	**BH_3·Me_2S**	0	1.5	78	1 : 3.4
6	**2b**	**BH_3·THF**	0	1.5	84	1 : 8.5
7	**2b**	**BH_3·Me_2S**	0	1.5	78	1 : 6.0

[a]Time of hydroboration reaction. [b]Yields for isolated diastereomers after column chromatography. [c]Diastereomers were separated by column chromatography. [d]2 Equiv. of borane was used.

With these optimized conditions we attempted systematic study protected methyl 6-deoxy-α-D-*xylo*-hex-5-enopyranosides. First essential results are summarized in Scheme 2. Thus, in a series of α-configured hex-5-enopyranosides with various substituents at C4 hydroboration stereoselectivity highly depends on the size of protective group attached to *O*-4, next to the reaction center. Smaller methyl substituent supported the formation of desired L-*ido* product (with up to 1:10 *dr*), while larger groups resulted in lower stereoselectivity. The same tendency was observed for 2,3-di-*O*-benzyl (**2a**, **2f-2h**) and 2,3-di-*O*-methyl (**2b**, **2c-2e**) derivatives.

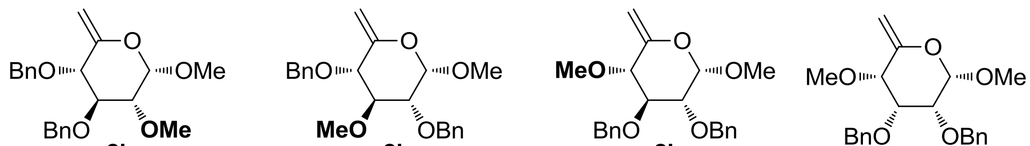
Scheme 2. Hydroboration/oxidation of methyl α-5-enoglucopyranosides 2a-h



The best results in terms of stereoselectivity was documented for methyl 2,3-di-*O*-methyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (**2d**). In this case, "inversed" L-*ido* product was formed exclusively, in high yield. However, synthetic application of **2f** seems also promising in the light of high stereoselectivity favoring L-*ido* isomer (1:10) and better applicability of benzyl groups for the synthetic purposes. Since satisfactory results were obtained by hydroboration of **2f** possessing free OH at C4 and because complete and easy separation of the isomers could be achieved by chromatography, this reaction can be recommended for the stereoselective inversion at C5 in the synthesis of L-iduronic acid from glucose.

Scheme 3 contains results with smallest substituent - methyl group - placed at the C2 (**2j**), C3 (**2i**) and finally C4 (**2h**) position. It confirms only the essential C4 position for obtaining the best stereoselectivity in the 6-deoxy-α-D-*xylo*-hex-5-enopyranoside series. However, epimerization at the C3 further enhanced the reaction selectivity. Hydroboration of methyl 2,3-di-*O*-benzyl-4-*O*-methyl-6-deoxy-α-D-*ribo*-hex-5-enopyranoside (**2k**) carried out under the same conditions resulted in a formation of L-*talo* isomer exclusively.

Scheme 3. Hydroboration/oxidation of methyl α-hex-5-enoglucopyranosides 2h-j and α-5-enoallopyranoside 2k



2j D-Glc : L-Ido 1 : 4.3 82 %

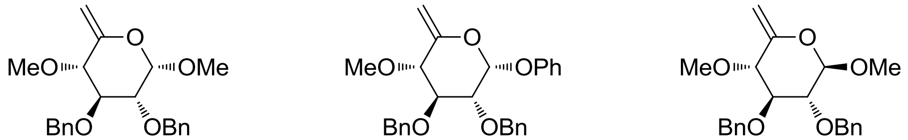
2i D-Glc : L-Ido 1 : 5.1 91 %

2h D-Glc : L-Ido 1 : 10 96 %

2k D-All : L-Tal only L-Tal 87 %

Previously presented results confirmed unambiguously the essential role of the C4 small substituent influencing the reaction stereoselectivity of the 6-deoxy-α-D-*xylo*-hex-5-enopyranoside series. However, changing the configuration at the anomeric carbon atom should have negative impact for the stereoselective formation of the L-*ido* product because of the anomeric substituent shielding the attack of the electrophilic reagent at the double bond. Indeed, comparison of the methyl α-hex-5-enopyranoside (**2h**) and methyl β-hex-5-enopyranoside (**2m**) clearly confirmed the role of the configuration at the anomeric center.

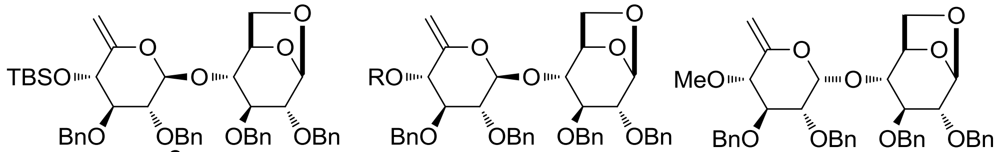
Scheme 4. Hydroboration/oxidation of hex-5-enopyranosides 2h, 2l-r



2h D-Glc : L-Ido 1 : 10 96 %

2l D-Glc : L-Ido 1 : 12 88 %

2m D-Glc : L-Ido 1 : 2.3 88 %



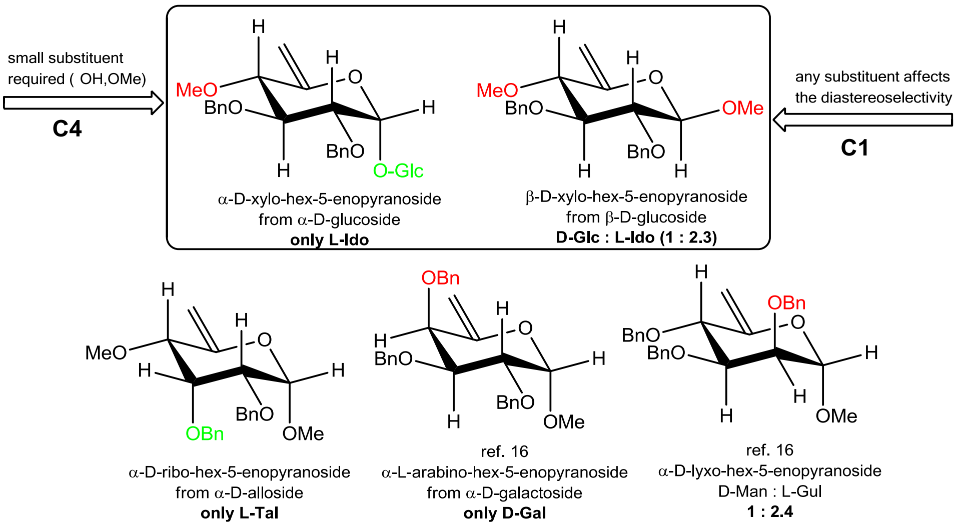
2o D-Glc : L-Ido 3.5 : 1 88%

D-Glc : L-Ido
2n: R=Me: 1.2 : 1
2p: R=H: 1.4 : 1
86%

2r D-Glc : L-Ido only L-Ido 88%

Stereoselectivity of the hydroboration was far less promising in the case of β-anomer **2m** barely reaching (1:2) ratio of D-/ L-forms. According to this rule, β-configured disaccharides should be less promising substrates for stereoselective hydroboration, unfortunately. Indeed, hydroboration-oxidation sequence of disaccharides (**2n-p**) having large β-oriented substituent at C1 confirmed lower stereoselectivy observed for such compounds. For these examples, similar results, ranging from predominance of D-*gluco* with **2o** to almost equal formation of D-*gluco*/L-*ido* for compounds **2n**/**2p** with smaller substituents at C4 documented again observed rules (Scheme 4). To ultimately confirm crucial influence on the stereoselectivity by C1 and C4 substituent configurations, we prepared and submitted for hydroboration α-configured disaccharide **2r** being analogue of **2n** with reversed configuration at C1. To our delight, only L-*ido*-configured sugar was formed with 88% yield in the reaction. This was ultimate confirmation of our expectation and shows that the efficient synthesis of β-configured disaccharides with L-iduronic acid requires inversion of the configuration in the α-configured monosaccharide prior to the subsequent glycosylation to appropriate β-disaccharides.

Scheme 5. Empirical rules for hydroboration of hex-5-enopyranosides



Conclusions

In conclusion, we examined diastereoselective hydroboration/oxidation of 5-enoglycopyranosides as a crucial step of the synthesis of L-iduronic acid from D-glucose. Based on these research we demonstrated that the reactions of various suitably protected 5-enopyranosides with borane afforded mixtures of D-*gluco* and L-*ido* pyranosides in the ratio highly dependent on the used protecting groups at C4 of glucose substrate. It was revealed that the reaction of α-configured monosaccharides and disaccharides possessing small substituents at C4 (OH, OMe) delivers L-*ido* pyranosides with high yield and stereoselectivities (Scheme 5). Particularly, application of these guidelines for the hydroboration of methyl 2,3-*O*-methyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside resulted in exclusive formation of L-*ido* product. It is rational as the formation of required L-*ido* product occurs via the attack of electrophile at C5 from the opposite site to the C4 substituent as well as the anomeric substituent at C1. However, the size of the substituent attached to anomeric center is not critical while the small substituent at C4 seems to be condition *sine qua non* for the high stereoselectivity en route the L-*ido* product. In contrast, any larger substituent attached at C1 with the β-configuration affects the reaction stereoselectivity and promotes the formation of the D-*gluco* derivative.

Experimental Section

General Information. All starting materials and reagents were purchased from commercial sources and used without purification. Dry THF was distilled from potassium to prior to use. Reactions were controlled using TLC on silica [alu-plates (0.2 mm)]. Plates were visualized with UV light (254 nm) and by treatment with: aqueous cerium(IV) sulfate solution with molybdic and sulfuric acid followed by heating. All organic solutions were dried over anhydrous sodium sulfate. Reaction products were purified by flash chromatography using silica gel 60 (240-400 mesh). Optical rotations were measured at room temperature with a digital polarimeter. IR spectra were recorded on an FT-IR spectrometer. $CDCl_3$, $(CD_3)_2CO$ and D_2O were used as NMR solvents. ^{1}H spectra were recorded with 600 MHz and referenced relative to: $CDCl_3$ - tetramethylsilane (δ = 0 ppm), $(CD_3)_2CO$ - residual solvent peak (δ = 2.05 ppm) and D_2O - acetonitrile (δ = 2.06 ppm). Data are reported as follows: chemical shift in parts per million (ppm) , multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet), coupling constants (in hertz) and integration. ^{13}C NMR spectra were measured at 150 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard: $CDCl_3$ (δ = 77.16 ppm), $(CD_3)_2CO$ (δ = 29.84 ppm) and D_2O (acetonitrile, δ = 1.47). High-resolution mass spectra were acquired using ESI-TOF method.

General Procedure A

Benzylation of hydroxyl groups: To a stirred solution of the starting material (1 mmol) in anhydrous DMF (10 mL) was added NaH - 60% dispersion in mineral oil - (2.0 equiv per OH group) at 0 °C. After 30 min, BnBr (2.0 equiv per OH group) was added at 0 °C, and the mixture was warmed to room temperature and stirred for 16 h. Subsequently, the reaction mixture was poured into ice-cold water and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure B

Benzylidene cleavage: The water (0.5 mL) and 1 M HCl (1 mL) were added to a stirred solution of 4,6-*O*-benzylidene protected derivative (1 mmol) in methanol (10 mL). The reaction mixture was then stirred for 1-3 h at 55 °C and neutralized with aq sat. $NaHCO_3$ (0.9 mL). Subsequently, solvents were concentrated under reduced pressure and residue was dissolved in ethyl acetate/water 1:1 solution. Organic layer was separated and water phase was extracted three times with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure C

Iodination: To a stirred solution of the starting material (1 mmol) in anhydrous toluene (25 mL) was added triphenylphosphine (1.2 equiv) and imidazole (2.6 equiv). The reaction mixture was then warmed to 70-75 °C and after 30 min iodine (1.2 equiv) was added. The temperature of reaction was held for 1-12 h and then cooled to room temperature. Subsequently, the reaction mixture was diluted with ethyl acetate and extracted with 10 % aq $Na_2S_2O_3$, water and brine. Organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure D

Silylation: To a stirred solution of the iodide (1 mmol) in anhydrous DCM (3 mL) was added 2,6-lutidine (1.5-2.0 equiv) at 0 °C. After 30 min, TBSOTf (1.2-1.5 equiv) was added in one portion at 0 °C, and the mixture was warmed to room temperature and stirred for 2-3 h. Subsequently, the reaction was quenched with Et_3N (1.5 equiv). After 5 min of stirring the mixture was diluted with DCM and extracted with water and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure E

Desilylation: To a stirred solution of the starting material (1 mmol) in anhydrous THF (20 mL) was added TBAF 1M solution in THF (2.0 equiv) at 0 °C. The mixture was then stirred at room temperature for 1-2 h. Subsequently, the reaction mixture was diluted with ethyl acetate and extracted with water and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure F1

Elimination of iodide: To a stirred solution of the iodide (1 mmol) in anhydrous THF (10 mL) was added *t*-BuOK (3.0 equiv) in one portion at 0 °C. After 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 24 h. Subsequently, the reaction mixture was diluted with ethyl acetate and extracted twice with water and once with brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure F2

Elimination of iodide with etherification of *O*-4 position: To a stirred solution of the iodide material (1 mmol) in anhydrous DMF (10 mL) was added MeI/BnBr/MOMCl (2.0 equiv) at 0 °C. After 30 min, NaH - 60% dispersion in mineral oil (10.0 equiv) was added at 0 °C, and the mixture was warmed to room temperature and stirred for 24-48 h. Subsequently, the reaction mixture was poured into ice-cold water and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

General Procedure G

Hydroboration/Oxidation: To a stirred solution of the starting material (0.3 mmol) in anhydrous THF (1 mL) was added a 1 M solution of borane THF complex in THF (10.0 equiv) at 0 °C. The temperature was held for 1.5 h. Then 30% H_2O_2 (1 mL) and 2 M NaOH aq sol. (1.5 mL) were added at 0 °C and the reaction mixture was stirred at room temperature for 50 min. Subsequently, the reaction mixture was diluted with ethyl acetate and extracted twice with aq sat. NH_4Cl, once with water and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

Following this procedure known compounds were synthesized: **3a**,[17] **4a**,[17] **3b**,[11] **4b**,[11] **3c**,[21] **3e**,[22] **3f**,[16] **4f**,[16] **3h**,[23] **3i**,[24] **3j**,[24] **3m**.[25]

Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-xylo-hex-5-enopyranoside (**2a**);[26] ^{1}H NMR (600 MHz, Acetone) δ 7.42 – 7.24 (m, 15H), 4.91 (d, *J* = 3.4 Hz, 1H), 4.89 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 2.1 Hz, 1H), 3.93 (ddd, *J* = 9.0, 2.0, 2.0 Hz, 1H), 3.85 (dd, *J* = 9.3, 9.2 Hz, 1H), 3.67 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.4, 140.1, 139.8, 139.5, 129.1, 129.0, 128.6, 128.6, 128.6, 128.4, 128.1, 99.7, 96.6, 81.7, 80.7, 80.4, 75.7, 74.9, 73.3, 55.5.

Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside (**3a**)[17] *and Methyl 2,3,4-tri-O-benzyl-β-L-idopyranoside* (**4a**);[17] Prepared according to general procedure G. Compound **2a** (151 mg, 0.338 mmol), $BH_3 \cdot THF$ (1M, 3.38 mL, 3.38 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (2 mL). Purified by column chromatography Hx-EA (2:1) to give first **3a** (13%, 20 mg, 0.043 mmol); Next eluted was **4a** (70%, 110 mg, 0.237 mmol).

Methyl 6-deoxy-2,3,4-tri-O-methyl-α-D-xylo-hex-5-enopyranoside (**2b**);[27] ^{1}H NMR (600 MHz, Acetone) δ 4.89 (d, *J* = 3.4 Hz, 1H), 4.66 (d, *J* = 2.0 Hz, 1H), 4.59 (d, *J* = 2.2 Hz, 1H), 3.52 (s, 3H), 3.52 (s, 3H), 3.51 – 3.49 (m, 1H), 3.43 (s, 3H), 3.37 (s, 3H), 3.34 (dd, *J* = 9.3, 9.1 Hz, 1H), 3.26 (dd, *J* = 9.4, 3.4 Hz, 1H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 99.3, 95.9, 83.2, 82.3, 82.1, 60.7, 60.1, 58.5, 55.4.

Methyl 2,3,4-tri-O-methyl-α-D-glucopyranoside (**3b**)[11] *and Methyl 2,3,4-tri-O-methyl-β-L-idopyranoside* (**4b**);[11] Prepared according to general procedure G. Compound **2b** (84 mg, 0.385 mmol), $BH_3 \cdot THF$ (1M, 3.85 mL, 3.85 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (2 mL). Purified by column chromatography MeOH-EA (1:25) to give first **3b** (9%, 8 mg, 0.034 mmol); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.80 (d, *J* = 3.6 Hz, 1H), 3.82 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.73 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.63 (s, 3H), 3.57 (s, 3H), 3.56 – 3.50 (m, 2H), 3.52 (s, 3H), 3.41 (s, 3H), 3.17 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.16 (dd, *J* = 9.9, 9.0 Hz, 1H), 1.81 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 97.7, 83.5, 82.0, 79.8, 70.7, 62.1, 61.0, 60.7, 59.2, 55.3. Next eluted was **4b** (75%, 68 mg, 0.287 mmol); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.72 (d, *J* = 3.4 Hz, 1H), 4.07 (td, *J* = 5.4, 5.4, 5.4 Hz, 1H), 3.90 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.82 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.70 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.58 (s, 3H), 3.53 (s, 3H), 3.52 (s, 3H), 3.52 (s, 3H), 3.38 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.22 (dd, *J* = 7.8, 3.4 Hz, 1H), 2.51 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 99.5, 80.4, 80.3, 78.4, 74.8, 63.1, 60.2, 59.7, 59.5, 57.0.

Synthesis of methyl 4-*O*-*tert*-butyldimethylsilyl-6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2c) and methyl 6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2d): *Methyl 4-O-tert-butyldimethylsilyl-6-deoxy-6-iodo-2,3-di-O-methyl-α-D-*

glucopyranoside (**6**); Prepared according to general procedure D. Compound **5**[28] (602 mg, 1.813 mmol), 2,6-lutidine (291 mg, 2.719 mmol), TBSOTf (575 mg, 2.175 mmol), DCM (6 mL), Et_3N (0.3 mL), 2 h. Purified by column chromatography Hx-EA (4:1). Yield: 97% (784 mg, 1.756 mmol) as colorless oil; $[\alpha]_D^{26}$ +77.4 (c 1.00, $CHCl_3$); IR (neat) 1463, 1376, 1249, 1162, 1091, 1051; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.84 (d, *J* = 3.6 Hz, 1H), 3.56 – 3.53 (m, 1H), 3.54 (s, 3H), 3.50 (s, 3H), 3.48 (s, 3H), 3.39 – 3.33 (m, 2H), 3.28 (dd, *J* = 8.6, 8.5 Hz, 1H), 3.25 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.22 (dd, *J* = 9.5, 3.6 Hz, 1H), 0.90 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 97.4, 83.0, 82.7, 74.9, 70.7, 61.3, 58.7, 55.7, 26.2, 18.3, 8.5, –3.7, –4.3; HRMS: calcd. for $C_{15}H_{31}IO_5Si$ $[M+Na]^+$: 469.0883, found 469.0859.

Methyl 4-O-tert-butyldimethylsilyl-6-deoxy-2,3-di-O-methyl-α-D-xylo-hex-5-enopyranoside (**2c**); Prepared according to general procedure F1. Compound **6** (739 mg, 1.656 mmol), *t*-BuOK (1M, 5 mL, 5 mmol), THF (20 mL). Purified by column chromatography Hx-EA (4:1). Yield: 84% (442 mg, 1.388 mmol) as colorless oil; $[\alpha]_D^{21}$ +60.7 (c 1.20, $CHCl_3$); IR (neat) 1664, 1473, 1252, 1162, 1112, 1087; ^{1}H NMR (600 MHz, Acetone) δ 4.92 (d, *J* = 3.3 Hz, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 4.62 (d, *J* = 2.2 Hz, 1H), 3.91 (ddd, *J* = 8.7, 2.1, 2.1 Hz, 1H), 3.51 (s, 3H), 3.43 (s, 3H), 3.39 (s, 3H), 3.29 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.25 (dd, *J* = 9.4, 8.7 Hz, 1H), 0.96 (s, 6H), 0.15 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 157.7, 99.2, 96.6, 84.0, 82.7, 73.1, 61.3, 58.3, 55.4, 26.3, 18.7, –4.4, –4.9; HRMS: calcd. for $C_{15}H_{30}O_5Si$ $[M+Na]^+$: 341.1760, found 341.1760.

Methyl 4-tert-butyldimethylsilyl-2,3-di-O-methyl-α-D-glucopyranoside (**3c**)[21] and *Methyl 4-tert-butyldimethylsilyl-2,3-di-O-methyl-β-L-idopyranoside* (**4c**); Prepared according to general procedure G. Compound **2c** (98 mg, 0.308 mmol), BH_3·THF (1M, 3.08 mL, 3.08 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.6 mL). Purified by column chromatography Hx-EA (2:1) to give mixture of **3c** and **4c** (90%, 93 mg, 0.276 mmol, **3c**:**4c** = 1:2.6). Another column chromatography was made to isolate part of pure **3c**; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.82 (d, *J* = 3.6 Hz, 1H), 3.81 (dd, *J* = 11.6, 2.7 Hz, 1H), 3.69 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.58 – 3.56 (m, 1H), 3.55 (s, 3H), 3.51 (s, 3H), 3.47 (dd, *J* = 9.5, 8.7 Hz, 1H), 3.43 (s, 3H), 3.36 (dd, *J* = 9.5, 8.7 Hz, 1H), 3.18 (dd, *J* = 9.5, 3.6 Hz, 1H), 0.90 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 97.5, 83.4, 82.9, 72.1, 70.7, 62.1, 61.4, 58.8, 55.3, 26.1, 18.2, –3.8, –4.90. Next eluted was **4c** as colorless oil; $[\alpha]_D^{22}$ +47.1 (c 1.00, $CHCl_3$); IR (neat) 3479, 1464, 1252, 1096, 1057; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.76 (d, *J* = 3.7 Hz, 1H), 3.97 – 3.92 (m, 2H), 3.83 (dd, *J* = 13.6, 7.5 Hz, 1H), 3.79 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.56 (s, 3H), 3.55 (dd, *J* = 8.7, 8.4 Hz, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 3.19 (dd, *J* = 8.7, 3.7 Hz, 1H), 0.91 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 99.4, 81.5, 79.7, 77.0, 72.3, 63.2, 61.0, 59.1, 57.2, 26.0, 18.2, –4.5, –4.8; HRMS: calcd. for $C_{15}H_{32}O_6Si$ $[M+Na]^+$: 359.1866, found 359.1858.

Methyl 6-deoxy-2,3-di-O-methyl-α-D-xylo-hex-5-enopyranoside (**2d**); Prepared according to general procedure E. Compound **2c** (268 mg, 0.841 mmol), TBAF (1M, 1.68 mL, 1.68 mmol), THF (20 mL). Purified by gradient column chromatography Hx-EA (2:1) to (1:1). Yield: 95% (164 mg, 0.799 mmol) as pale yellow oil; $[\alpha]_D^{26}$ +103.4 (c 1.30, $CHCl_3$); IR (neat) 3453, 1663, 1369, 1156, 1084, 1019; ^{1}H NMR (600 MHz, Acetone) δ 4.89 (d, *J* = 3.2 Hz, 1H), 4.76 (d, *J* = 2.1 Hz, 1H), 4.57 (d, *J* = 5.7 Hz, 1H), 4.55 (d, *J* = 2.3 Hz, 1H), 3.86 (dddd, *J* = 8.7, 5.7, 2.3, 2.1 Hz, 1H), 3.51 (s, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 3.29 (dd, *J* = 9.5, 8.7 Hz, 1H), 3.24 (dd, *J* = 9.5, 3.2 Hz, 1H); ^{13}C NMR (151 MHz, Acetone) δ 157.9, 99.2, 95.4, 83.9, 82.1, 72.1, 60.9, 58.3, 55.3; HRMS: calcd. for $C_9H_{16}O_5$ $[M+Na]^+$: 227.0895, found 227.0899.

Methyl 2,3-di-O-methyl-β-L-idopyranoside (**4d**); Prepared according to general procedure G. Compound **2d** (71 mg, 0.348 mmol), BH_3·THF (1M, 3.48 mL, 3.48 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.8 mL). Purified by column chromatography EA. Yield: 79% (61 mg, 0.275 mmol) as colorless oil; $[\alpha]_D^{22}$ +25.1 (c 1.14, $CHCl_3$); IR (neat)

3485, 1447, 1374, 1154, 1099, 1043; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (d, *J* = 1.2 Hz, 1H), 3.98 (dd, *J* = 11.5, 7.0 Hz, 1H), 3.85 (ddd, *J* = 7.0, 4.5, 1.1 Hz, 1H), 3.81 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.67 – 3.64 (m, 2H), 3.58 (s, 3H), 3.57 (s, 3H), 3.44 (s, 3H), 3.44 – 3.42 (m, 1H), 2.24 (bs, 1H), 1.69 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 100.7, 77.6, 77.3, 75.1, 66.6, 62.8, 60.3, 58.0, 57.1; HRMS: calcd. for $C_9H_{18}O_6$ [*M*+Na]$^+$: 245.1001, found 245.0999.

Methyl 4-O-benzyl-6-deoxy-2,3-di-O-methyl-α-D-xylo-hex-5-enopyranoside (**2e**);[29] ^{1}H NMR (600 MHz, Acetone) δ 7.45 – 7.26 (m, 5H), 4.92 (d, *J* = 3.4 Hz, 1H), 4.79 (d, *J* = 2.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 2.1 Hz, 1H), 3.80 (ddd, *J* = 9.0, 2.1, 2.1 Hz, 1H), 3.55 (s, 3H), 3.46 – 3.43 (m, 1H), 3.44 (s, 3H), 3.38 (s, 3H), 3.30 (dd, *J* = 9.4, 3.4 Hz, 1H); ^{13}C NMR (151 MHz, Acetone) δ 155.4, 139.7, 129.1, 128.5, 128.3, 99.3, 96.4, 83.6, 82.2, 80.1, 74.7, 60.9, 58.5, 55.4.

Methyl 4-O-benzyl-2,3-di-O-methyl-α-D-glucopyranoside (**3e**)[22] and *Methyl 4-O-benzyl-2,3-di-O-methyl-β-L-idopyranoside* (**4e**); Prepared according to general procedure G. Compound **2e** (89 mg, 0.302 mmol), BH_3·THF (1M, 3.02 mL, 3.02 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.6 mL). Purified by column chromatography Hx-EA (1:2) to give first **3e** (12%, 11 mg, 0.035 mmol). Next eluted was **4e** (64%, 67 mg, 0.192 mmol) as colorless oil; $[\alpha]_D^{22}$ +57.6 (c 1.02, $CHCl_3$); IR (neat) 3481, 1497, 1453, 1373, 1096, 1053; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.71 (d, *J* = 3.4 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 3.97 (ddd, *J* = 5.5, 5.5, 5.5 Hz, 1H), 3.90 (dd, *J* = 11.9, 5.7 Hz, 1H), 3.81 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.74 (dd, *J* = 7.9, 7.9 Hz, 1H), 3.60 (dd, *J* = 7.7, 5.5 Hz, 1H), 3.59 (s, 3H), 3.52 (s, 3H), 3.51 (s, 3H), 3.22 (dd, *J* = 8.0, 3.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 128.7, 128.1, 128.1, 99.5, 80.6, 78.8, 77.8, 75.2, 73.9, 63.3, 60.4, 59.4, 57.0; HRMS: calcd. for $C_{16}H_{24}O_6$ [*M*+Na]$^+$: 335.1471, found 335.1472.

Synthesis of methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(methoxymethyl)-α-D-*xylo*-hex-5-enopyranoside (2g): *Methyl 2,3-di-O-benzyl-6-deoxy-4-O-(methoxymethyl)-α-D-xylo-hex-5-enopyranoside* (**2g**); Prepared according to general procedure F2. Compound **7**[30] (303 mg, 0.626 mmol), NaH (250 mg, 6.256 mmol), MOMCl (178 mg, 1.251 mmol), DMF (10 mL), 24 h. Purified by column chromatography Hx-EA (6:1). Yield: 78% (196 mg, 0.489 mmol) as colorless oil; $[\alpha]_D^{22}$ –7.3 (c 1.03, $CHCl_3$); IR (neat) 1663, 1497, 1454, 1150, 1090, 1044, 1027; ^1H NMR (600 MHz, Acetone) δ 7.41 – 7.24 (m, 10H), 4.91 (d, *J* = 3.4 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 6.5 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.72 (d, *J* = 6.5 Hz, 1H), 4.66 (d, *J* = 2.0 Hz, 1H), 4.01 (ddd, *J* = 9.2, 2.0, 2.0 Hz, 1H), 3.80 (dd, *J* = 9.4, 9.3 Hz, 1H), 3.68 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.40 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.4, 140.0, 139.7, 129.1, 129.0, 128.6, 128.6, 128.4, 128.2, 99.6, 98.0, 96.7, 81.6, 80.8, 76.9, 75.7, 73.2, 56.4, 55.5; HRMS: calcd. for $C_{23}H_{28}O_6$ $[M+Na]^+$: 423.1784, found 423.1766.

Methyl 2,3-di-O-benzyl-4-O-(methoxymethyl)-α-D-glucopyranoside (**3g**) and *Methyl 2,3-di-O-benzyl-4-O-(methoxymethyl)-β-L-idopyranoside* (**4g**); Prepared according to general procedure G. Compound **2g** (115 mg, 0.287 mmol), BH_3·THF (1M, 2.87 mL, 2.87 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.5 mL). Purified by column chromatography Hx-EA (1:1) to (1:2) to give first **3g** (33%, 40 mg, 0.096 mmol) as pale yellow oil; $[\alpha]_D^{21}$ +76.6 (c 1.06, $CHCl_3$); IR (neat) 3318, 1496, 1455, 1356, 1161, 1103, 1059, 1026; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.91 (d, *J* = 6.3 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 6.3 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 3.91 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.86 (d, *J* = 12.3 Hz, 1H), 3.75 (d, *J* = 10.9 Hz, 1H), 3.62 (ddd, *J* = 10.0, 3.4, 2.3 Hz, 1H), 3.57 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.49 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 2.53 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 138.2, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 99.0, 98.4, 81.7, 80.1, 76.4, 75.8, 73.5, 70.6, 61.9, 56.4, 55.4; HRMS: calcd. for $C_{23}H_{30}O_7$ $[M+Na]^+$: 441.1889, found 441.1878. Next eluted was **4g** (60%, 72 mg, 0.172 mmol) as colorless oil; $[\alpha]_D^{22}$ +65.1 (c 1.05, $CHCl_3$); IR (neat) 3481, 1496, 1454, 1363, 1149, 1099, 1036; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 10H), 4.76 (d, *J* = 6.6 Hz, 1H), 4.75 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.64 (d, *J* = 6.6 Hz, 1H), 4.58 (d, *J* = 3.2 Hz, 1H), 4.05 (ddd, *J* = 5.3, 5.2, 5.2 Hz, 1H), 3.98 (dd, *J* = 7.3, 7.3 Hz, 1H), 3.92 (dd, *J* = 12.1, 5.1 Hz, 1H), 3.88 (dd, *J* = 12.1, 4.9 Hz, 1H), 3.77 (dd, *J* = 7.2, 5.3 Hz, 1H), 3.51 (s, 3H), 3.49 (dd, *J* = 7.4, 3.2 Hz, 1H), 3.36 (s, 3H), 2.87 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 128.5, 128.5, 128.2, 128.0, 127.9, 127.9, 100.2, 97.5, 77.8, 77.0, 75.7, 75.4, 74.6, 73.9, 62.9, 57.1, 56.1; HRMS: calcd. for $C_{23}H_{30}O_7$ $[M+Na]^+$: 441.1889, found 441.1886.

Methyl 2,3-di-O-benzyl-6-deoxy-4-O-methyl-α-D-xylo-hex-5-enopyranoside (**2h**);[31] ^{1}H NMR (600 MHz, Acetone) δ 7.43 – 7.24 (m, 10H), 4.88 (d, *J* = 3.3 Hz, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.71 – 4.70 (m, *J* = 1.9 Hz, 1H), 4.63 (d, *J* = 2.1 Hz, 1H), 3.75 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.65 – 3.61 (m, 2H), 3.55 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 140.3, 139.8, 129.1, 129.0, 128.6, 128.3, 128.1, 99.7, 96.0, 82.6, 81.6, 80.5, 75.6, 73.3, 60.3, 55.5.

Methyl 2,3-di-O-benzyl-4-O-methyl-α-D-glucopyranoside (**3h**)[23] and *Methyl 2,3-di-O-benzyl-4-O-methyl-β-L-idopyranoside* (**4h**); Prepared according to general procedure G. Compound **2h** (140 mg, 0.378 mmol), BH_3·THF (1M, 3.78 mL, 3.78 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.9 mL). Purified by column chromatography Hx-EA (3:2) to (2:3) to give first **3h** (9%, 13 mg, 0.033 mmol) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 10H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 1H), 3.88 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.81 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.72 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.57 (ddd, *J* = 10.0, 4.0, 3.1 Hz, 1H), 3.56 (s, 3H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.37 (s, 1H), 3.23 (dd, *J* = 9.9, 9.1 Hz, 1H); ^{13}C NMR

(151 MHz, $CDCl_3$) δ 139.0, 138.3, 128.6, 128.5, 128.2, 128.1, 128.1, 127.7, 98.4, 81.9, 79.9, 79.9, 75.8, 73.6, 70.8, 62.1, 61.0, 55.4. Next eluted was **4h** (87%, 128 mg, 0.330 mmol) as colorless oil; $[\alpha]_D^{22}$ +25.1 (c 1.14, $CHCl_3$); IR (neat) 3485, 1496, 1454, 1362, 1091, 1052; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.78 (d, J = 11.1 Hz, 1H), 4.75 (d, J = 12.2 Hz, 1H), 4.71 (d, J = 11.1 Hz, 1H), 4.68 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 3.4 Hz, 1H), 4.08 (ddd, J = 5.4, 5.4, 5.4 Hz, 1H), 3.99 (dd, J = 7.9, 7.9 Hz, 1H), 3.91 (dd, J = 12.1, 5.3 Hz, 1H), 3.83 (dd, J = 12.1, 5.2 Hz, 1H), 3.49 (s, 3H), 3.48 (s, 3H), 3.47 (dd, J = 8.1, 3.4 Hz, 1H), 3.43 (dd, J = 7.8, 5.6 Hz, 1H), 2.36 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 138.4, 128.6, 128.5, 128.2, 128.0, 128.0, 127.8, 100.0, 80.8, 78.1, 76.9, 74.9, 74.8, 73.9, 63.2, 59.7, 57.0; HRMS: calcd. for $C_{22}H_{28}O_6$ $[M+Na]^+$: 411.1784, found 411.1763.

Synthesis of methyl 2,4-di-*O*-benzyl-6-deoxy-3-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2i): *Methyl 2-O-benzyl-6-deoxy-6-iodo-3-O-methyl-α-D-glucopyranoside* (**9**); Prepared according to general procedure C. Compound **8**[24] (616 mg, 2.065 mmol), PPh_3 (650 mg, 2.478 mmol), imidazole (366 mg, 5.369 mmol) I_2 (629 mg, 2.478 mmol), toluene (50 mL), 75 °C, 1 h. Purified by column chromatography Hx-EA (3:1). Yield: 88% (739 mg, 1.810 mmol) as colorless oil; $[\alpha]_D^{21}$ +42.5 (c 1.05, $CHCl_3$); IR (neat) 3436, 1454, 1372, 1066; ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 4.75 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 12.1 Hz, 1H), 4.61 (d, J = 3.5 Hz, 1H), 3.67 (s, 3H), 3.56 (dd, J = 10.7, 2.5 Hz, 1H), 3.54 (dd, J = 9.3, 9.0 Hz, 1H), 3.46 – 3.42 (m, 2H), 3.42 (s, 3H), 3.30 – 3.24 (m, 2H), 2.63 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 128.6, 128.1(2C), 98.3, 82.5, 79.9, 73.9, 73.1, 69.9, 61.6, 55.7, 7.2; HRMS: calcd. for $C_{15}H_{21}IO_5$ $[M+Na]^+$: 431.0331, found 431.0333.

Methyl 2,4-di-O-benzyl-6-deoxy-3-O-methyl-α-D-xylo-hex-5-enopyranoside (**2i**); Prepared according to general procedure F2. Compound **9** (353 mg, 0.865 mmol), NaH (346 mg, 8.647

mmol), BnBr (296 mg, 1.729 mmol), DMF (10 mL), 48 h. Purified by column chromatography Hx-EA (9:1). Yield: 80% (256 mg, 0.691 mmol) as white solid; mp 38-39 °C; $[\alpha]_D^{21}$ +1.3 (c 1.00, $CHCl_3$); IR (neat) 3662, 1497, 1454, 1365, 1089; ^1H NMR (600 MHz, Acetone) δ 7.44 – 7.39 (m, 4H), 7.38 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 4.85 (d, *J* = 2.8 Hz, 1H), 4.79 (d, *J* = 2.0 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 2.1 Hz, 1H), 3.83 – 3.80 (m, 1H), 3.60 (s, 3H), 3.56 – 3.52 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 139.8, 139.6, 129.1(2C), 128.5, 128.4, 128.3, 128.3, 99.7, 96.5, 83.6, 80.4, 80.1, 74.7, 73.2, 61.1, 55.4; HRMS: calcd. for $C_{22}H_{26}O_5$ $[M+Na]^+$: 393.1678, found 393.1683.

Methyl 2,4-di-O-benzyl-3-O-methyl-α-D-glucopyranoside (**3i**)[24] and *Methyl 2,4-di-O-benzyl-3-O-methyl-β-L-idopyranoside* (**4i**); Prepared according to general procedure G. Compound **2i** (84 mg, 0.227 mmol), BH_3·THF (1M, 2.27 mL, 2.27 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.2 mL). Purified by column chromatography Hx-EA (3:2) to give first **3i** (15%, 13 mg, 0.033 mmol). Next eluted was **4i** (76%, 67 mg, 0.172 mmol) as white solid; mp 63-65 °C; $[\alpha]_D^{26}$ +40.5 (c 1.10, $CHCl_3$); IR (neat) 3460, 1497, 1454, 1095, 1055; ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 3.5 Hz, 1H), 3.94 (ddd, *J* = 5.7, 5.7, 4.9 Hz, 1H), 3.90 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.80 (dd, *J* = 11.8, 4.9 Hz, 1H), 3.76 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.60 (s, 3H), 3.58 (dd, *J* = 8.0, 5.7 Hz, 1H), 3.45 (s, 3H), 3.39 (dd, *J* = 8.2, 3.5 Hz, 1H), 2.76 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 138.0, 128.6, 128.5, 128.1, 128.1(2C), 127.9, 99.9, 79.2, 78.3, 78.1, 75.1, 73.9, 73.8, 63.3, 60.6, 57.0; HRMS: calcd. for $C_{22}H_{28}O_6$ $[M+Na]^+$: 411.1784, found 411.1788.

Synthesis of methyl 3,4-di-*O*-benzyl-6-deoxy-2-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2j): *Methyl 3-O-benzyl-2-O-methyl-α-D-glucopyranoside* (**11**); Prepared according to general procedure B. Compound **10**[24] (972 mg, 2.515 mmol), H_2O (1.25 mL), 1 M HCl (2.5 mL)

MeOH (25 mL), 55 °C, 1 h. Purified by column chromatography EA. Yield: 97% (728 mg, 2.440 mmol) as colorless oil; $[\alpha]_D^{26}$ +63.5 (c 1.20, $CHCl_3$); IR (neat) 3440, 1454, 1052; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 4.96 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 3.81 (dd, *J* = 11.8, 3.4 Hz, 1H), 3.76 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.72 (dd, *J* = 9.2, 9.1 Hz, 1H), 3.61 (ddd, *J* = 7.7, 3.8, 3.8 Hz, 1H), 3.54 (dd, *J* = 9.7, 9.0 Hz, 1H), 3.51 (s, 3H), 3.43 (s, 3H), 3.30 (dd, *J* = 9.6, 3.5 Hz, 1H), 2.55 (bs, 1H), 2.14 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 128.7, 128.0, 128.0, 97.6, 82.2, 81.4, 75.3, 70.9, 70.4, 62.5, 58.9, 55.4; HRMS: calcd. for $C_{15}H_{22}O_6$ $[M+Na]^+$: 321.1314, found 321.1313.

Methyl 3-O-benzyl-6-deoxy-6-iodo-2-O-methyl-α-D-glucopyranoside (**12**); Prepared according to general procedure C. Compound **11** (681 mg, 2.283 mmol), PPh_3 (718 mg, 2.739 mmol), imidazole (404 mg, 5.935 mmol) I_2 (695 mg, 2.739 mmol), toluene (50 mL), 75 °C, 1 h. Purified by column chromatography Hx-EA (4:1). Yield: 83% (775 mg, 1.898 mmol) as colorless oil; $[\alpha]_D^{21}$ +52.5 (c 0.90, $CHCl_3$); IR (neat) 3476, 1454, 1362, 1067; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 3.70 (dd, *J* = 9.2, 8.8 Hz, 1H), 3.54 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.53 (s, 3H), 3.49 (s, 3H), 3.40 (ddd, *J* = 9.2, 6.8, 2.5 Hz, 1H), 3.35 – 3.31 (m, 2H), 3.30 (dd, *J* = 10.7, 6.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 128.8, 128.1(2C), 97.6, 82.2, 80.8, 75.3, 73.6, 69.8, 58.8, 55.7, 7.3; HRMS: calcd. for $C_{15}H_{21}IO_5$ $[M+Na]^+$: 431.0331, found 431.0336.

Methyl 3,4-di-O-benzyl-6-deoxy-2-O-methyl-α-D-xylo-hex-5-enopyranoside (**2j**); Prepared according to general procedure F2. Compound **12** (327 mg, 0.801 mmol), NaH (320 mg, 8.010 mmol), BnBr (274 mg, 1.602 mmol), DMF (10 mL), 48 h. Purified by column chromatography Hx-EA (6:1). Yield: 85% (252 mg, 0.680 mmol) as colorless oil; $[\alpha]_D^{26}$ +6.6 (c 1.00, $CHCl_3$); IR (neat) 1662, 1497, 1454, 1356, 1091; ^1H NMR (600 MHz, Acetone) δ 7.40 – 7.24 (m, 10H), 4.97 (d, *J* = 3.4 Hz, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.79 (d, *J* = 11.9 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J*

= 2.1 Hz, 1H), 3.91 (ddd, *J* = 9.1, 2.0, 2.0 Hz, 1H), 3.75 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.47 (s, 3H), 3.42 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 140.1, 139.4, 129.1, 128.9, 128.6, 128.5, 128.3, 128.1, 99.2, 96.5, 82.4, 81.6, 80.1, 75.5, 74.8, 58.7, 55.4, HRMS: calcd. for $C_{22}H_{26}O_5$ [*M*+Na]$^+$: 393.1678, found 393.1682.

Methyl 3,4-di-O-benzyl-2-O-methyl-α-D-glucopyranoside (**3j**)[24] and *Methyl 3,4-di-O-benzyl-2-O-methyl-β-L-idopyranoside* (**4j**); Prepared according to general procedure G. Compound **2j** (95 mg, 0.256 mmol), BH_3·THF (1M, 2.56 mL, 2.56 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.3 mL). Purified by column chromatography Hx-EA (1:2) to give first **3j** (15%, 15 mg, 0.039 mmol). Next eluted was **4j** (67%, 67 mg, 0.172 mmol) as colorless oil; $[\alpha]_D^{25}$ +53.7 (c 1.02, $CHCl_3$); IR (neat) 3482, 1497, 1454, 1092, 1055; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 3.4 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.02 (dd, *J* = 7.7, 7.6 Hz, 1H), 4.00 (ddd, *J* = 5.5, 5.4, 5.4 Hz, 1H), 3.90 (dd, *J* = 11.9, 5.5 Hz, 1H), 3.85 (dd, *J* = 11.9, 5.4 Hz, 1H), 3.64 (dd, *J* = 7.6, 5.4 Hz, 1H), 3.52 (s, 3H), 3.52 (s, 3H), 3.30 (dd, *J* = 7.7, 3.4 Hz, 1H), 2.67 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 137.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 99.6, 80.6, 77.4, 76.5, 75.2, 74.8, 73.8, 63.2, 59.5, 57.0; HRMS: calcd. for $C_{22}H_{28}O_6$ [*M*+Na]$^+$: 411.1784, found 411.1780.

Synthesis of methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-*ribo*-hex-5-enopyranoside (2k): *Methyl 2-O-benzyl-4,6-O-benzylidene-α-D-allopyranoside* (**14**); Compound **13**[32] (749 mg, 2.022 mmol) was suspended in 69% aq EtOH (43 mL). Next solution of $NaBH_4$ (97 mg, 2.564 mmol) in H_2O (5 mL) was added. Subsequently, mixture was diluted with MeOH (10 mL). After 5.5 h of stirring the mixture was washed three times with DCM. Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

The residue was purified by column chromatography Hx-EA (2:1). Yield: 97% (731 mg, 1.963 mmol) as white solid; mp 75-77 °C; $[\alpha]_D^{22}$ +4.7 (c 1.00, $CHCl_3$); IR (neat) 3493, 1497, 1452, 1103; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.40 – 7.29 (m, 8H), 5.52 (s, 1H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.60 (d, *J* = 12.4 Hz, 1H), 4.46 – 4.41 (m, 1H), 4.34 (dd, *J* = 10.3, 5.2 Hz, 1H), 4.15 (ddd, *J* = 10.0, 10.0, 5.2 Hz, 1H), 3.70 (dd, *J* = 10.3, 10.3 Hz, 1H), 3.50 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.44 (s, 3H), 3.41 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.20 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 137.2, 129.2, 128.7, 128.3, 128.2, 128.1, 126.4, 102.1, 99.7, 78.9, 73.9, 70.5, 69.2, 67.0, 57.9, 56.0; HRMS: calcd. for $C_{21}H_{24}O_6$ $[M+Na]^+$: 395.1471, found 395.1476.

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-allopyranoside (**15**);[33] Prepared according to general procedure A. Compound **14** (680 mg, 1.826 mmol), NaH (146 mg, 3.652 mmol), BnBr (625 mg, 3.654 mmol), DMF (15 mL). Purified by column chromatography Hx-EA (4:1) to (7:3). Yield: 86% (727 mg, 1.572 mmol); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.22 (m, 15H), 5.45 (s, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.88 (d, *J* = 12.6 Hz, 1H), 4.70 (d, *J* = 4.1 Hz, 1H), 4.58 (d, *J* = 12.7 Hz, 1H), 4.44 (d, *J* = 12.7 Hz, 1H), 4.39 – 4.35 (m, 1H), 4.33 (dd, *J* = 10.0, 5.3 Hz, 1H), 4.19 (dd, *J* = 2.8, 2.8 Hz, 1H), 3.65 (t, *J* = 10.1, 10.1 Hz, 1H), 3.50 – 3.47 (m, 1H), 3.47 (s, 3H), 3.44 (dd, *J* = 3.8, 3.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.0, 137.7, 137.7, 129.2, 128.6, 128.4, 128.4, 128.1, 128.1, 128.0, 127.3, 126.4, 102.1, 99.1, 79.9, 74.8, 73.7, 72.3, 70.9, 69.5, 58.1, 56.3.

Methyl 2,3-di-O-benzyl-α-D-allopyranoside (**16**);[34] Prepared according to general procedure B. Compound **15** (700 mg, 1.513 mmol), H_2O (1 mL), 1 M HCl (2 mL) MeOH (20 mL), 55 °C, 3 h. Purified by column chromatography Hx-EA (1:4) Yield: 97% (550 mg, 1.469 mmol).

Methyl 2,3-di-O-benzyl-6-deoxy-6-iodo-α-D-allopyranoside (**17**); Prepared according to general procedure C. Compound **16** (495 mg, 1.322 mmol), PPh_3 (416 mg, 1.586 mmol), imidazole (234 mg, 3.437 mmol) I_2 (403 mg, 1.588 mmol), toluene (30 mL), 75 °C, 2 h.

Purified by column chromatography Hx-EA (4:1) to (7:3). Yield: 73% (468 mg, 0.966 mmol) as pale yellow oil; $[\alpha]_D^{15}$ +44.9 (c 1.07, $CHCl_3$); IR (neat) 3526, 1454, 1063; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H), 5.19 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 4.0 Hz, 1H), 4.71 (d, *J* = 12.3 Hz, 1H), 4.67 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.04 (dd, *J* = 3.1, 3.1 Hz, 1H), 3.65 – 3.60 (m, 1H), 3.55 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.52 – 3.51 (m, 1H), 3.51 (s, 3H), 3.28 – 3.23 (m, 1H), 3.24 (dd, *J* = 10.7, 7.5 Hz, 1H), 2.43 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 137.7, 128.7, 128.7, 128.3, 128.2, 128.0, 127.9, 98.2, 77.1, 75.5, 74.6, 71.9, 70.6, 67.8, 56.4, 7.9; HRMS: calcd. for $C_{21}H_{25}IO_5$ $[M+Na]^+$: 507.0644, found 507.0645.

Methyl 2,3-di-O-benzyl-6-deoxy-4-O-methyl-α-D-ribo-hex-5-enopyranoside (**2k**); Prepared according to general procedure F2. Compound **17** (338 mg, 0.698 mmol), NaH (279 mg, 6.975 mmol), MeI (198 mg, 1.395 mmol), DMF (10 mL), 24 h. Purified by column chromatography Hx-EA (3:1). Yield: 80% (206 mg, 0.556 mmol) as white solid; mp 78-80 °C; $[\alpha]_D^{27}$ +21.8 (c 1.06, $CHCl_3$); IR (neat) 2921, 2893, 1667, 1450, 1114, 1103; ^{1}H NMR (600 MHz, Acetone) δ 7.45 – 7.39 (m, 4H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 3H), 7.23 – 7.19 (m, 1H), 4.92 (d, *J* = 3.8 Hz, 1H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.77 (d, *J* = 12.3 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 1.6 Hz, 1H), 4.63 (d, *J* = 1.2 Hz, 1H), 4.33 (dd, *J* = 2.9, 2.9 Hz, 1H), 3.81 (dd, *J* = 3.8, 2.8 Hz, 1H), 3.78 – 3.76 (m, 1H), 3.41 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 154.1, 141.0, 139.7, 129.1, 128.7, 128.4, 128.3, 128.2, 127.6, 101.3, 96.2, 79.0, 77.4, 75.6, 73.8, 71.9, 57.5, 56.1; HRMS: calcd. for $C_{22}H_{26}O_5$ $[M+Na]^+$: 393.1678, found 393.1676.

Methyl 2,3-di-O-benzyl-4-O-methyl-β-L-talopyranoside (**4k**); Prepared according to general procedure G. Compound **2k** (136 mg, 0.367 mmol), BH_3·THF (1M, 3.67 mL, 3.67 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.9 mL). Purified by column chromatography EA. Yield: 87% (124 mg, 0.319 mmol) as colorless oil; $[\alpha]_D^{26}$ +69.6 (c 1.07,

$CHCl_3$); IR (neat) 3463, 1496, 1453, 1113, 1065; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.34 – 7.18 (m, 8H), 4.97 (d, *J* = 12.9 Hz, 1H), 4.74 (d, *J* = 12.9 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 1.2 Hz, 1H), 4.05 (dd, *J* = 11.5, 7.3 Hz, 1H), 3.82 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.81 (s, 1H), 3.59 (s, 3H), 3.57 – 3.55 (m, 1H), 3.52 (s, 3H), 3.49 – 3.45 (m, 1H), 3.43 – 3.40 (m, 1H), 2.53 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.0, 137.9, 128.2, 127.9, 127.8, 127.4, 127.0, 127.0, 102.7, 78.4, 75.8, 75.5, 74.1, 73.9, 70.6, 62.2, 60.1, 56.6; HRMS: calcd. for $C_{22}H_{28}O_6$ [*M*+Na]$^+$: 411.1784, found 411.1781.

Synthesis of phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2l): *Phenyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside* (**18**);[35] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.03 (m, 20H), 5.57 (s, 1H), 5.44 (d, *J* = 3.7 Hz, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.26 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.19 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.00 (ddd, *J* = 10.0, 10.0, 4.9 Hz, 1H), 3.74 – 3.67 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 138.9, 138.1, 137.5, 129.7, 129.1, 128.6, 128.5, 128.4, 128.1, 128.1, 127.8, 126.2, 122.8, 117.1, 101.5, 96.5, 82.2, 79.2, 78.6, 75.5, 73.8, 69.0, 63.3.

Phenyl 2,3-di-O-benzyl-α-D-glucopyranoside (**19**); Prepared according to general procedure B. Compound **18** (658 mg, 1.254 mmol), H_2O (1 mL), 1 M HCl (2 mL) MeOH (20 mL), 55 °C, 3 h. Purified by column chromatography Hx-EA (2:1) to (1:1). Yield: 92% (504 mg, 1.155 mmol) as white solid; mp 121-123 °C; $[\alpha]_D^{26}$ +77.0 (c 1.00, $CHCl_3$); IR (neat) 3269, 1599, 1491, 1231, 1058; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 12H), 7.10 – 7.00 (m, 3H), 5.43 (d, *J* = 3.5 Hz, 1H), 5.07 (d, *J* = 11.4 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.01 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.77 – 3.66 (m, 4H), 3.64 (dd, *J* = 9.5, 3.5 Hz, 1H), 2.70 (bs, 1H), 2.06 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ

156.8, 138.8, 137.9, 129.6, 128.7, 128.6, 128.1, 128.1, 128.0, 122.7, 117.1, 95.7, 81.3, 79.7, 75.6, 73.2, 71.7, 70.1, 62.1; HRMS: calcd. for $C_{26}H_{28}O_6$ [*M*+Na]$^+$: 459.1784, found 459.1768.

Phenyl 2,3-di-O-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (**20**); Prepared according to general procedure C. Compound **19** (464 mg, 1.063 mmol), PPh_3 (335 mg, 1.277 mmol), imidazole (188 mg, 2.762 mmol) I_2 (324 mg, 1.277 mmol), toluene (40 mL), 70 °C, 3 h. Purified by column chromatography Hx-EA (4:1). Yield: 94% (545 mg, 0.997 mmol) as colorless oil; $[\alpha]_D^{22}$ +53.2 (c 0.80, $CHCl_3$); IR (neat) 3442, 1597, 1494, 1219, 1060; ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 12H), 7.15 – 7.03 (m, 3H), 5.47 (d, *J* = 3.5 Hz, 1H), 5.09 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.05 – 4.01 (m, 1H), 3.68 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.49 – 3.40 (m, 3H), 3.34 – 3.31 (m, 1H), 2.31 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 138.7, 137.9, 129.6, 128.8, 128.7, 128.2, 128.1, 128.0, 122.8, 117.2, 95.8, 80.7, 79.9, 75.6, 73.8, 73.1, 70.0, 7.6; HRMS: calcd. for $C_{26}H_{27}IO_5$ [*M*+Na]$^+$: 569.0801, found 569.0806.

Phenyl 2,3-di-O-benzyl-6-deoxy-4-O-methyl-α-D-xylo-hex-5-enopyranoside (**2l**); Prepared according to general procedure F2. Compound **20** (160 mg, 0.293 mmol), NaH (117 mg, 2.928 mmol), MeI (83 mg, 0.586 mmol), DMF (7 mL), 24 h. Purified by column chromatography Hx-EA (9:1). Yield: 93% (118 mg, 0.273 mmol) as colorless oil; $[\alpha]_D^{26}$ +74.3 (c 0.70, $CHCl_3$); IR (neat) 1666, 1598, 1495, 1454, 1090; ^1H NMR (600 MHz, Acetone) δ 7.47 – 7.02 (m, 15H), 5.75 (d, *J* = 3.4 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 2.0 Hz, 1H), 4.48 (dd, *J* = 2.1, 0.4 Hz, 1H), 3.98 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.85 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.76 (ddd, *J* = 4.1, 2.1, 2.1 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 157.8, 154.6, 140.1, 139.4, 130.2, 129.2, 129.0, 128.6, 128.5, 128.4, 128.1, 123.2, 117.9, 96.9, 96.8, 82.3, 81.6, 80.0, 75.7, 73.5, 60.3; HRMS: calcd. for $C_{27}H_{28}O_5$ [*M*+Na]$^+$: 455.1834, found 455.1835.

Phenyl 2,3-di-O-benzyl-4-O-methyl-α-D-glucopyranoside (**3l**) and *Phenyl 2,3-di-O-benzyl-4-O-methyl-β-L-idopyranoside* (**4l**); Prepared according to general procedure G. Compound **2l** (98 mg, 0.227 mmol), BH_3·THF (1M, 2.27 mL, 2.27 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.2 mL). Purified by column chromatography Hx-EA (7:3) to (3:2) to give first **3l** (7%, 7 mg, 0.016 mmol) as colorless oil; $[\alpha]_D^{26}$ +50.1 (c 0.54, $CHCl_3$); IR (neat) 3462, 1598, 1495, 1454, 1225, 1098; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 12H), 7.07 – 7.02 (m, 3H), 5.41 (d, *J* = 3.6 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.11 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.76 – 3.69 (m, 3H), 3.62 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.60 (s, 3H), 3.38 (dd, *J* = 9.3, 9.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 138.9, 138.1, 129.7, 128.6, 128.6, 128.1, 128.1, 128.1, 127.8, 122.7, 117.0, 95.7, 81.8, 79.8, 79.4, 75.8, 73.5, 71.7, 61.8, 61.1; HRMS: calcd. for $C_{27}H_{30}O_6$ $[M+Na]^+$: 473.1940, found 473.1943. Next eluted was **4l** (81%, 83 mg, 0.184 mmol) as colorless oil; $[\alpha]_D^{26}$ +89.4 (c 1.10, $CHCl_3$); IR (neat) 3493, 1598, 1495, 1223, 1100; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 12H), 7.08 – 7.01 (m, 3H), 5.44 (d, *J* = 3.2 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.73 (d, *J* = 12.2 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.20 – 4.16 (m, 1H), 4.07 (dd, *J* = 7.6, 7.4 Hz, 1H), 3.86 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.79 (dd, *J* = 12.1, 6.9 Hz, 1H), 3.64 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.49 (s, 3H), 3.50 – 3.47 (m, 1H), 2.14 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 138.4, 138.2, 129.8, 128.5, 128.5, 128.2, 128.0, 128.0, 127.9, 122.5, 116.2, 96.4, 80.2, 77.5, 76.4, 75.4, 74.8, 73.8, 63.1, 59.5; HRMS: calcd. for $C_{27}H_{30}O_6$ $[M+Na]^+$: 473.1940, found 473.1947.

Synthesis of methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-β-D-*xylo*-hex-5-enopyranoside (2m): *Methyl 2,3-di-O-benzyl-6-O-deoxy-6-iodo-β-D-glucopyranoside* (**21**);[36] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 10H), 4.95 (d, *J* = 11.6 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.37 – 4.33 (m, *J* = 7.5 Hz, 1H), 3.60 (s, 3H), 3.55 (dd, J = 10.6, 2.3 Hz, 1H), 3.45 – 3.40 (m, 2H), 3.32 (ddd, J = 8.6, 5.9, 2.5 Hz, 1H), 3.24 (dd, J = 10.6, 7.8 Hz, 1H), 3.16 – 3.12 (m, 1H), 2.25 (d, J = 2.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 138.4, 128.8, 128.5, 128.2, 128.2, 128.1, 127.9, 104.7, 83.4, 82.0, 75.3, 74.6, 74.2, 73.5, 57.3, 6.1.

Methyl 2,3-di-O-benzyl-6-deoxy-4-O-methyl-β-D-xylo-hex-5-enopyranoside (**2m**); Prepared according to general procedure F2. Compound **21** (539 mg, 1.113 mmol), NaH (445 mg, 11.129 mmol), MeI (316 mg, 2.226 mmol), DMF (10 mL), 24 h. Purified by column chromatography Hx-EA (9:1) to (6:1). Yield: 93% (384 mg, 1.034 mmol) as white solid; mp 62-64 °C; $[\alpha]_D^{23}$ –38.4 (c 1.00, $CHCl_3$); IR (neat) 1662, 1498, 1452, 1095, 1072; ^{1}H NMR (600 MHz, Acetone) δ 7.38 – 7.25 (m, 10H), 4.76 (d, J = 11.7 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.71 (d, J = 11.6 Hz, 1H), 4.70 (d, J = 5.8 Hz, 1H), 4.67 (d, J = 11.7 Hz, 1H), 4.57 (dd, J = 1.2, 0.5 Hz, 1H), 4.50 (dd, J = 1.3, 0.5 Hz, 1H), 3.90 – 3.88 (m, 1H), 3.55 – 3.51 (m, 2H), 3.50 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 139.7, 139.6, 129.0, 128.6, 128.6, 128.3, 128.2, 104.0, 93.0, 82.9, 82.3, 80.8, 73.9, 73.8, 58.8, 56.6; HRMS: calcd. for $C_{22}H_{26}O_5$ [M+Na]$^+$: 393.1678, found 393.1686.

Methyl 2,3-di-O-benzyl-4-O-methyl-β-D-glucopyranoside (**3m**)[25] and *Methyl 2,3-di-O-benzyl-4-O-methyl-α-L-idopyranoside* (**4m**); Prepared according to general procedure G. Compound **2m** (95 mg, 0.256 mmol), BH_3·THF (1M, 2.56 mL, 2.56 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.3 mL). Purified by column chromatography Hx-EA (3:2) to give first **3m** (27%, 27 mg, 0.070 mmol). Next eluted was **4m** (61%, 61 mg, 0.157 mmol) as white solid; mp 92-94 °C; $[\alpha]_D^{23}$ –23.4 (c 1.10, $CHCl_3$); IR (neat) 3276, 1498, 1453, 1101, 1063; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 10H), 4.76 (d, J = 11.6 Hz, 1H), 4.74 (d, J = 3.8 Hz, 1H), 4.70 (d, J = 11.9 Hz, 1H), 4.59 (d, J = 11.8 Hz, 1H), 4.57 (d, J = 11.5 Hz, 1H), 4.09 (ddd, J = 6.5, 4.2, 4.2 Hz, 1H), 3.93 (dd, J = 11.8, 6.5 Hz, 1H), 3.78 (dd, J = 11.0, 5.3 Hz, 1H), 3.73 (dd, J = 6.5, 5.3 Hz, 1H), 3.47 (dd, J = 6.5, 3.8 Hz, 1H), 3.43 (s, 3H), 3.43 – 3.42

(m, 1H), 3.42 (s, 3H), 2.26 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 138.2, 128.5, 128.1, 128.0, 127.9, 101.8, 80.2, 78.4, 77.0, 73.6, 73.4, 69.5, 62.4, 59.0, 55.7; HRMS: calcd. for $C_{22}H_{28}O_6$ [*M*+Na]$^+$: 411.1784, found 411.1779.

Synthesis of 1,6-anhydro-2,3-di-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-6-*O*-deoxy-4-*O*-methyl-β-D-*xylo*-hex-5-enopyranosyl)-β-D-glucopyranose (2n): *1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranose* (**23**); To stirred suspension of compound **22**[37] (1.7 g, 5.242 mmol) in MeCN (50 mL) benzaldehyde dimethylacetal (1.03 mL, 6.863 mmol) and camphorsulfonic acid (122 mg, 0.525 mmol) were added. The reaction mixture was heated to reflux and stirred for 3 h under an atmosphere of Ar. The reaction mixture was neutralised with Et_3N and after 10 min concentrated under reduced pressure. The residue was dissolved in Et_2O/H_2O (1:1). Water layer was separated and extracted three times with Et_2O. Then combined organic phases were backwashed with H_2O once. Subsequently, water was evaporated azeotropic with toluene under reduced pressure and residue was passed through short plug of silica gel EA-MeOH (5:1). Solvents were removed under reduced pressure and residue was dissolved in DMF (50 mL) then **23** was prepared according to general procedure A. NaH (1.676 g, 41.939 mmol), BnBr (7.173 g, 41.939 mmol). Purified by column chromatography Hx-EA (3:1). Yield: 71% (2.864 g, 3.706 mmol) as white solid; mp 86-88 °C; $[\alpha]_D^{26}$ –58.2 (c 1.10, $CHCl_3$); IR (neat) 2868, 1454, 1086; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.25 (m, 25H), 5.54 (s, 1H), 5.49 (s, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.91 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.68 (s, 1H), 4.57 (d, *J* = 7.3 Hz, 1H), 4.60 – 4.53 (m, 2H), 4.55 (d, *J* = 12.3 Hz, 1H), 4.45 (d, *J* = 12.2 Hz, 1H), 4.16 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.97 (d, *J* = 7.2 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.76 – 3.73 (m, 1H), 3.73 – 3.63 (m, 4H), 3.53 (dd, *J* = 8.5, 7.9 Hz, 1H), 3.36 (s, 1H), 3.27 (ddd, *J* = 9.8, 9.8, 5.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 138.4, 138.1, 138.0, 137.4, 129.1, 128.7, 128.6, 128.5, 128.4, 128.4, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.1, 126.1, 103.6, 101.3, 101.0, 82.0, 81.4, 81.0, 78.7, 76.1, 76.0, 75.7, 75.2, 74.3, 72.1, 71.5, 68.8, 66.2, 65.3; HRMS: calcd. for $C_{47}H_{48}O_{10}$ $[M+Na]^+$: 795.3145, found 795.3124.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranose (**3p**); Prepared according to general procedure B. Compound **23** (1.723 g, 2.229 mmol), H_2O (1.25 mL), 1 M HCl (2.5 mL) MeOH (25 mL), 55 °C, 3 h. Purified by column chromatography Hx-EA (1:2). Yield: 93% (1.420 g, 2.074 mmol) as pale yellow solid; mp 93-94 °C; $[\alpha]_D^{25}$ –58.4 (c 1.00, $CHCl_3$); IR (neat) 3296, 1497, 1454, 1084; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 20H), 5.50 (s, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.97 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.60 – 4.49 (m, 6H), 3.98 (dd, *J* = 7.3, 0.8 Hz, 1H), 3.81 – 3.79 (m, 1H), 3.76 – 3.74 (m, 1H), 3.72 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.74 – 3.70 (m, 1H), 3.66 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.53 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.45 (dd, *J* = 9.1, 7.6 Hz, 1H), 3.41 – 3.37 (m, 2H), 3.18 (ddd, *J* = 9.5, 4.7, 3.6 Hz, 1H), 2.44 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 138.4, 138.0, 137.8, 128.8, 128.6, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 127.8, 102.8, 100.8, 83.9, 81.7, 78.1, 76.4, 75.9, 75.3, 75.1, 74.9, 74.2, 72.2, 71.6, 70.3, 65.3, 62.6; HRMS: calcd. for $C_{40}H_{44}O_{10}$ $[M+Na]^+$: 707.2832, found 707.2832.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-6-O-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranose (**24**); Prepared according to general procedure C. Compound **3p** (1.227 g, 1.792 mmol), PPh_3 (564 mg, 2.150 mmol), imidazole (317 mg, 4.656 mmol) I_2 (546 mg, 2.151 mmol), toluene (55 mL), 75 °C, 12 h. After 3 h another portion of reagents was added PPh_3 (56 mg, 0.214 mmol), imidazole (64 mg, 0.925 mmol) I_2 (55 mg, 0.217 mmol). Purified by column chromatography Hx-EA (2:1). Yield: 93% (1.328 g, 1.671 mmol) as colorless oil; $[\alpha]_D^{26}$ –44.7 (c 1.00, $CHCl_3$); IR (neat) 3458, 1496, 1454, 1073; ^{1}H NMR (600 MHz, $CDCl_3$) δ

7.44 – 7.21 (m, 20H), 5.51 (s, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.67 – 4.60 (m, 5H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.04 (d, *J* = 7.2 Hz, 1H), 3.94 – 3.91 (m, 1H), 3.88 (s, 1H), 3.74 (dd, *J* = 6.9, 6.2 Hz, 1H), 3.51 (dd, *J* = 9.0, 7.7 Hz, 1H), 3.48 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.42 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.39 (s, 1H), 3.34 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.23 (dd, *J* = 10.7, 7.4 Hz, 1H), 3.11 (ddd, *J* = 9.5, 7.5, 2.4 Hz, 1H), 2.24 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 138.3, 138.2, 138.1, 128.9, 128.8, 128.5, 128.5, 128.3, 128.2, 127.9, 127.8, 102.6, 101.0, 83.2, 81.5, 76.9, 76.6, 75.8, 75.3, 74.8, 74.4, 73.6, 73.2, 72.1, 71.6, 65.1, 6.2; HRMS: calcd. for $C_{40}H_{43}IO_9$ $[M+Na]^+$: 817.1850, found 817.1842.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-6-O-deoxy-4-O-methyl-β-D-xylo-hex-5-enopyranosyl)-β-D-glucopyranose (**2n**); Prepared according to general procedure F2. Compound **24** (210 mg, 0.264 mmol), NaH (106 mg, 2.650 mmol), MeI (75 mg, 0.528 mmol), DMF (5 mL), 24 h. Purified by column chromatography Hx-EA (3:1). Yield: 96% (172 mg, 0.253 mmol) as colorless oil; $[\alpha]_D^{26}$ –53.8 (c 0.95, $CHCl_3$); IR (neat) 1661, 1497, 1454, 1093; ^{1}H NMR (600 MHz, Acetone) δ 7.41 – 7.22 (m, 20H), 5.45 (s, 1H), 5.10 (d, *J* = 6.1 Hz, 1H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.77 – 4.72 (m, 4H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.61 – 4.61 (m, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.54 (dd, *J* = 1.2, 0.5 Hz, 1H), 4.00 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.99 – 3.98 (m, 1H), 3.91 (ddd, *J* = 2.6, 1.3, 1.3 Hz, 1H), 3.83 – 3.81 (m, 1H), 3.66 (dd, *J* = 7.3, 6.0 Hz, 1H), 3.60 (t, *J* = 6.2 Hz, 1H), 3.53 (dd, *J* = 7.3, 6.3 Hz, 1H), 3.42 (s, 1H), 3.38 – 3.37 (m, 1H); ^{13}C NMR (151 MHz, Acetone) δ 155.3, 139.8, 139.5, 139.5, 139.4, 129.2, 129.1, 129.1, 129.0, 129.0, 128.5, 128.3, 128.3, 128.2, 102.1, 101.5, 93.7, 82.9, 82.0, 80.8, 78.5, 78.0, 77.9, 74.7, 74.0, 74.0, 72.5, 71.9, 65.8, 58.8; HRMS: calcd. for $C_{41}H_{44}O_9$ $[M+Na]^+$: 703.2883, found 703.2868.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-methyl-β-D-glucopyranosyl)-β-D-glucopyranose (**3n**) and *1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-methyl-α-L-*

idopyranosyl)-β-D-glucopyranose (**4n**); Prepared according to general procedure G. Compound **2n** (149 mg, 0.219 mmol), BH_3·THF (1M, 2.19 mL, 2.19 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.2 mL). Purified by column chromatography Hx-EA (1:1) to give first **4n** (39%, 60 mg, 0.086 mmol) as colorless oil; $[\alpha]_D^{26}$ –42.7 (c 1.00, $CHCl_3$); IR (neat) 3492, 1497, 1454, 1074; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 20H), 5.49 (s, 1H), 5.11 (d, *J* = 5.4 Hz, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.66 (dd, *J* = 5.9, 0.6 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.09 (dt, *J* = 7.8, 4.4 Hz, 1H), 3.97 (dd, *J* = 7.2, 0.6 Hz, 1H), 3.80 (s, 1H), 3.76 – 3.69 (m, 3H), 3.60 (dd, *J* = 8.2, 6.7 Hz, 1H), 3.58 (s, 1H), 3.52 (dd, *J* = 8.3, 5.4 Hz, 1H), 3.46 (dd, *J* = 6.6, 4.8 Hz, 1H), 3.45 (s, 3H), 3.38 (s, 1H), 2.66 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 137.7, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 100.6, 98.9, 81.5, 80.2, 79.6, 77.4, 76.4, 76.1, 74.4(2C), 74.3, 72.3, 71.8, 71.7, 65.9, 60.8, 59.2; HRMS: calcd. for $C_{41}H_{46}O_{10}$ $[M+Na]^+$: 721.2989, found 721.2990. Next eluted was **3n** (47%, 72 mg, 0.103 mmol) as colorless oil; $[\alpha]_D^{26}$ –27.5 (c 0.90, $CHCl_3$); IR (neat) 3468, 1497, 1454, 1089; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 20H), 5.50 (s, *J* = 7.1 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.58 – 4.56 (m, 1H), 4.53 (d, *J* = 12.3 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 3.96 (d, *J* = 7.2 Hz, 1H), 3.80 – 3.78 (m, 1H), 3.72 (s, 1H), 3.71 (dd, *J* = 7.3, 6.2 Hz, 1H), 3.68 (dd, *J* = 11.8, 2.6 Hz, 1H), 3.63 (dd, *J* = 11.8, 3.9 Hz, 1H), 3.54 (s, 3H), 3.49 (dd, *J* = 9.1, 9.1 Hz, 1H), 3.42 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.38 (s, 1H), 3.25 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.10 (ddd, *J* = 9.7, 4.1, 2.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 138.5, 138.1, 137.9, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 102.8, 100.8, 84.4, 82.0, 79.4, 78.6, 76.1, 75.9, 75.7, 75.2, 75.2, 74.4, 72.1, 71.6, 65.3, 62.0, 60.9; HRMS: calcd. for $C_{41}H_{46}O_{10}$ $[M+Na]^+$: 721.2989, found 721.2994.

Synthesis of 1,6-anhydro-2,3-di-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-*O*-deoxy-β-D-*xylo*-hex-5-enopyranosyl)-β-D-glucopyranose (2o) and 1,6-anhydro-2,3-di-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-6-*O*-deoxy-β-D-*xylo*-hex-5-enopyranosyl)-β-D-glucopyranose (2p): *1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl-6-O-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranose* (**25**); Prepared according to general procedure D. Compound **24** (1.097 g, 1.380 mmol), 2,6-lutidine (296 mg, 2.762 mmol), TBSOTf (547 mg, 2.069 mmol), DCM (10 mL), Et_3N (0.3 mL), 3 h. Purified by column chromatography Hx-EA (4:1). Yield: 97% (1.215 g, 1.337 mmol) as white solid; mp 135-137 °C; $[\alpha]_D^{21}$ –6.6 (c 0.80, $CHCl_3$); IR (neat) 1466, 1247, 1109, 1092; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 20H), 5.50 (s, 1H), 5.07 (d, *J* = 11.5 Hz, 1H), 5.06 (d, *J* = 10.6 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.69 – 4.59 (m, 6H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.03 (dd, *J* = 7.2, 0.9 Hz, 1H), 3.92 – 3.90 (m, 2H), 3.73 (dd, *J* = 7.1, 6.0 Hz, 1H), 3.55 – 3.51 (m, 2H), 3.45 – 3.43 (m, 2H), 3.41 – 3.38 (m, 1H), 3.20 – 3.12 (m, 2H), 0.87 (s, 9H), 0.09 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 138.3, 138.3, 138.1, 128.7, 128.5, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.8, 127.8, 127.3, 127.1, 102.4, 101.1, 83.8, 82.3, 76.9, 76.8, 76.0, 75.8, 74.9, 74.7, 74.5, 73.7, 72.2, 71.6, 65.2, 26.1, 18.2, 7.2, –3.6, –4.2; HRMS: calcd. for $C_{46}H_{57}IO_9Si$ $[M+Na]^+$: 931.2714, found 931.2690.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl-6-O-deoxy-β-D-xylo-hex-5-enopyranosyl)-β-D-glucopyranose (**2o**); Prepared according to general procedure F1. Compound **25** (1.161 g, 1.277 mmol), *t*-BuOK (1M, 3.8 mL, 3.8 mmol), THF (20 mL). Purified by column chromatography Hx-EA (4:1). Yield: 96% (960 mg, 1.229 mmol) as colorless oil; $[\alpha]_D^{21}$ –39.1 (c 0.98, $CHCl_3$); IR (neat) 1663, 1454, 1253, 1073; ^{1}H NMR (600 MHz, Acetone) δ 7.41 – 7.23 (m, 20H), 5.46 (s, 1H), 5.01 (d, *J* = 6.4 Hz, 1H), 5.00 (d, *J* = 11.3 Hz, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.75 (dd, *J* = 5.7, 1.5 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 11.2 Hz, 1H), 4.70 (d, *J* = 1.6 Hz, 1H), 4.67 (d, *J* = 1.4 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.28 (ddd, *J* = 3.2, 1.6, 1.6 Hz, 1H), 4.03 – 4.02 (m, 1H), 4.01 (dd, *J* = 7.3, 1.1 Hz, 1H), 3.83 – 3.81 (m, 1H), 3.67 (dd, *J* = 7.2, 6.1 Hz, 1H), 3.63 (dd, *J* = 7.1, 6.4 Hz, 1H), 3.42 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.39 – 3.38 (m, 1H), 0.93 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (151 MHz, Acetone) δ 158.3, 139.7, 139.4, 129.2, 129.1, 129.1, 129.0, 128.9, 128.6, 128.5, 128.3, 128.3, 128.3, 128.3, 128.1, 102.8, 101.4, 94.4, 84.1, 82.3, 78.5, 77.7, 77.6, 74.9, 74.5, 74.3, 72.5, 72.1, 71.9, 65.7, 26.2, 18.6, –4.4, –4.7; HRMS: calcd. for $C_{46}H_{56}O_9Si$ $[M+Na]^+$: 803.3591, found 803.3568.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl-β-D-glucopyranosyl)-β-D-glucopyranose (**3o**) and *1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl-α-L-idopyranosyl)-β-D-glucopyranose* (**4o**); Prepared according to general procedure G. Compound **2o** (121 mg, 0.155 mmol), BH_3·THF (1M, 1.55 mL, 1.55 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1 mL). Purified by column chromatography Hx-EA (3:1) to (7:3) to give first **3o** (68%, 85 mg, 0.106 mmol) as colorless oil; $[\alpha]_D^{26}$ –15.9 (c 1.05, $CHCl_3$); IR (neat) 3499, 1497, 1454, 1253, 1073; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 20H), 5.50 (s, 1H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.59 – 4.50 (m, 6H), 3.94 (d, *J* = 7.2 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.75 – 3.68 (m, 3H), 3.62 – 3.55 (m, 2H), 3.46 (dd, *J* = 9.1, 7.8 Hz, 1H), 3.38 (s, 1H), 3.38 – 3.35 (m, 1H), 3.14 (ddd, *J* = 9.1, 5.4, 2.7 Hz, 1H), 1.94 (bs, 1H), 0.87 (s, 9H), 0.06 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 138.4, 138.0, 137.8, 128.6, 128.6, 128.4, 128.3, 128.2, 128.0, 128.0, 128.0, 127.8, 127.7, 127.2, 127.2, 102.6, 100.6, 84.5, 82.4, 78.3, 76.6, 76.6, 75.9, 75.2, 74.9, 74.4, 72.2, 71.6, 70.5, 65.4, 62.1, 26.0, 18.1, –3.7, –4.7; HRMS: calcd. for $C_{46}H_{58}O_{10}Si$ $[M+Na]^+$: 821.3697, found 821.3687. Next eluted was **4o** (19%, 24 mg, 0.030 mmol) as colorless oil; $[\alpha]_D^{26}$ –26.1 (c 0.75, $CHCl_3$); IR (neat) 3501, 1497, 1454, 1253, 1071; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 20H), 5.50 (s, 1H), 5.19 – 5.17 (m, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.73 – 4.70 (m, 2H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 4.00 – 3.97 (m, 1H), 3.96 (dd, *J* = 7.2, 0.7 Hz, 1H), 3.88 – 3.85 (m, 1H), 3.81 (s, 1H), 3.76 – 3.70 (m, 3H), 3.60 (d, *J* = 12.6 Hz, 1H), 3.41 – 3.37 (m, 3H), 2.94 (bs, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 138.6, 138.0, 137.7, 128.6 128.5, 128.5, 128.4, 128.0, 128.0, 127.9, 127.7, 127.6, 127.6, 100.5, 97.7, 81.6, 81.3, 77.5, 76.6, 75.9, 75.1, 75.0, 74.8, 74.5, 72.4, 72.2, 71.6, 66.1, 59.7, 25.9, 18.1, –4.5, –4.7; HRMS: calcd. for $C_{46}H_{58}O_{10}Si$ $[M+Na]^+$: 821.3697, found 821.3681.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-6-O-deoxy-β-D-xylo-hex-5-enopyranosyl)-β-D-glucopyranose (**2p**); Prepared according to general procedure E. Compound **2o** (489 mg, 0.626 mmol), TBAF (1M, 1.25 mL, 1.25 mmol), THF (20 mL). Purified by gradient column chromatography Hx-EA (3:1) to (7:3). Yield: 100% (417 mg, 0.625 mmol) as colorless oil; $[\alpha]_D^{25}$ –53.6 (c 0.95, $CHCl_3$); IR (neat) 3458, 1663, 1497, 1454, 1208, 1072; ^{1}H NMR (600 MHz, Acetone) δ 7.43 – 7.23 (m, 20H), 5.44 (s, 1H), 5.00 (d, *J* = 5.8 Hz, 1H), 4.98 (d, *J* = 11.3 Hz, 1H), 4.88 (d, *J* = 5.5 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 1.8 Hz, 1H), 4.75 – 4.73 (m, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 1.8 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.33 – 4.29 (m, 1H), 4.01 (dd, *J* = 7.2, 1.1 Hz, 1H), 4.01 – 4.00 (m, 1H), 3.82 – 3.81 (m, 1H), 3.67 (dd, *J* = 7.2, 6.0 Hz, 1H), 3.62 (dd, *J* = 7.3, 5.8 Hz, 1H), 3.44 (dd, *J* = 9.1, 7.3 Hz, 1H), 3.37 – 3.36 (m, 1H); ^{13}C NMR (151 MHz, Acetone) δ 158.7, 140.1, 139.5, 139.5, 139.4, 129.2, 129.1, 129.1, 129.0, 128.9, 128.6, 128.6, 128.5, 128.3, 128.3, 128.1, 102.6, 101.5, 93.1, 84.0, 82.3, 78.3, 77.7, 77.6, 74.7, 74.6, 74.2, 72.4, 71.9, 70.9, 65.7; HRMS: calcd. for $C_{40}H_{42}O_9$ [M+Na]$^+$: 689.2727, found 689.2717.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranose (**3p**) and *1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-α-L-idopyranosyl)-β-D-glucopyranose* (**4p**); Prepared according to general procedure G. Compound **2p** (214 mg, 0.321 mmol), BH_3·THF (1M, 3.21 mL, 3.21 mmol), THF (1 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1.7 mL). Purified by column chromatography Hx-EA (1:1) to (1:4) to give first **4p** (36%, 79 mg, 0.115 mmol) as colorless oil; $[\alpha]_D^{25}$ –70.2 (c 0.95, $CHCl_3$); IR (neat) 3497, 1496, 1454, 1099; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 20H), 5.46 (s, 1H), 5.12 (s, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.60 (s, 2H), 4.55 (d, J = 6.4 Hz, 1H), 4.53 (d, J = 11.8 Hz, 1H), 4.49 (d, J = 11.8 Hz, 1H), 4.47 (d, J = 11.8 Hz, 1H), 4.46 (d, J = 12.2 Hz, 1H), 4.41 (d, J = 12.2 Hz, 1H), 4.14 – 4.11 (m, 1H), 3.92 (dd, J = 7.3, 0.5 Hz, 1H), 3.78 (d, J = 3.2 Hz, 1H), 3.74 – 3.68 (m, 5H), 3.64 (m, 1H), 3.58 (dd, J = 11.9, 4.2 Hz, 1H), 3.35 (d, J = 3.1 Hz, 1H), 3.30 (d, J = 9.6 Hz, 1H), 2.25 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.1, 137.9, 137.7, 137.0, 128.7, 128.5, 128.5, 128.5, 128.4, 128.1, 127.9, 127.9, 127.7, 101.1, 96.3, 77.7, 77.6, 74.4, 74.4, 74.0, 73.2, 73.1, 72.8, 71.9, 71.6, 69.1, 68.1, 66.0, 63.4; HRMS: calcd. for $C_{40}H_{44}O_{10}$ [M+Na]$^+$: 707.2832, found 707.2837. Next eluted was **3p** (50%, 111 mg, 0.162 mmol).

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-6-O-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranose (**26**);[38] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 20H), 5.49 (s, 1H), 5.01 (d, J = 3.4 Hz, 1H), 4.99 (d, J = 11.5 Hz, 1H), 4.73 (d, J = 5.0 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 12.3 Hz, 1H), 4.57 (d, J = 12.3 Hz, 1H), 4.55 (d, J = 12.2 Hz, 1H), 4.53 (d, J = 12.0 Hz, 2H), 4.52 (d, J = 12.0 Hz, 2H), 4.48 (d, J = 12.2 Hz, 1H), 4.02 (d, J = 7.2 Hz, 1H), 3.88 (dd, J = 9.2, 9.2 Hz, 1H), 3.76 (s, 1H), 3.74 (dd, J = 7.2, 5.9 Hz, 1H), 3.69 – 3.64

(m, 2H), 3.55 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.49 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (s, 1H), 3.31 (dd, *J* = 9.1, 9.1 Hz, 1H), 3.25 (dd, *J* = 10.7, 7.5 Hz, 1H), 2.22 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 138.1, 138.0, 137.8, 128.8, 128.6, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 127.9, 127.6, 100.8, 97.0, 80.5, 79.4, 76.9, 76.8, 76.4, 75.5, 75.4, 73.9, 72.4, 72.0, 71.6, 70.9, 66.1, 7.4.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-6-O-deoxy-4-O-methyl-α-D-xylo-hex-5-enopyranosyl)-β-D-glucopyranose (**2r**); Prepared according to general procedure F2. Compound **26** (232 mg, 0.292 mmol), NaH (117 mg, 2.925 mmol), MeI (83 mg, 0.585 mmol), DMF (6 mL), 24 h. Purified by column chromatography Hx-EA (3:1). Yield: 89% (178 mg, 0.261 mmol) as colorless oil; $[\alpha]_D^{24}$ –20.5 (c 1.37, $CHCl_3$); IR (neat) 1660, 1497, 1454, 1087, 1026; ^{1}H NMR (600 MHz, Acetone) δ 7.41 – 7.18 (m, 20H), 5.42 (s, 1H), 5.31 (d, *J* = 3.4 Hz, 1H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.83 (d, *J* = 11.3 Hz, 1H), 4.74 (d, *J* = 2.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.66 – 4.61 (m, 5H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.96 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.88 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.84 (dd, *J* = 3.8, 1.0 Hz, 1H), 3.70 – 3.67 (m, 2H), 3.66 – 3.63 (m, 2H), 3.56 (s, 3H), 3.38 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (151 MHz, Acetone) δ 155.8, 140.2, 139.6, 139.5, 139.4, 129.1, 129.1, 129.0, 129.0, 128.7, 128.5, 128.4, 128.3, 128.3, 128.1, 101.6, 98.6, 96.4, 82.5, 81.2, 79.8(2C), 79.0, 78.5, 76.6, 75.6, 73.2, 72.8, 71.8, 67.0, 60.3; HRMS: calcd. for $C_{41}H_{44}O_9$ $[M+Na]^+$: 703.2883, found 703.2864.

1,6-Anhydro-2,3-di-O-benzyl-4-O-(2,3-di-O-benzyl-4-O-methyl-β-L-idopyranosyl)-β-D-glucopyranose (**4r**); Prepared according to general procedure G. Compound **2r** (127 mg, 0.187 mmol), BH_3·THF (1M, 1.87 mL, 1.87 mmol), THF (2 mL). Then 30% H_2O_2 (1 mL), 2 M NaOH (1 mL). Purified by column chromatography Hx-EA (1:2) to (1:4). Yield: 88% (115 mg, 0.165 mmol) as colorless oil; $[\alpha]_D^{26}$ +8.0 (c 1.03, $CHCl_3$); IR (neat) 3514, 1496, 1454, 1089, 1028; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 20H), 5.46 (s, 1H), 4.87 (d, *J* = 3.0

Hz, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.07 – 4.03 (m, 1H), 4.00 (dd, *J* = 12.0, 8.2 Hz, 1H), 3.97 (d, *J* = 6.7 Hz, 1H), 3.93 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.76 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.69 (dd, *J* = 7.1, 5.8 Hz, 1H), 3.65 – 3.63 (m, 1H), 3.62 (s, 1H), 3.50 (dd, *J* = 6.9, 3.0 Hz, 1H), 3.42 (s, 3H), 3.36 (dd, *J* = 6.7, 4.8 Hz, 1H), 3.35 – 3.34 (m, 1H), 3.15 (bs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 138.3, 138.0, 137.8, 128.5, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 100.7, 99.6, 79.6, 78.5, 76.9, 76.7, 75.7, 75.6, 75.0, 74.1, 74.1, 72.3, 71.8, 65.7, 62.1, 58.7; HRMS: calcd. for $C_{41}H_{46}O_{10}$ $[M+Na]^+$: 721.2989, found 721.2999.

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Supporting Information. ^{1}H and ^{13}C NMR spectra of all compounds and copies of the crude mixtures of NMR spectra for compounds **4a-c**, **4e**, **4f**, **4j**, **4n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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