Regiospecific Synthesis of 4-Deoxy-D-*threo*-hex-3-enopyranosides by Simultaneous Activation–Elimination of the Talopyranoside Axial 4-OH with the NaH/Im₂SO₂ System: Manifestation of the Stereoelectronic Effect

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A new and high-yielding method for the regioselective preparation of 4-deoxy- and 2,4-dideoxy-2-acetamido- β -D-threohex-3-enopyranosides has been developed. The process involves a simultaneous activation–elimination of the OH-4 group of β -D-talopyranosides and 2-acetamido-2-deoxy- β -D-talopyranosides, mediated by the NaH/N,N'-sulfuryldiimid-azole system at -30 °C. The same reaction applied on the analogous β -D-galactopyranosides takes place without any regioselectivity, affording mixtures of hex-3- and hex-4-enopyranosides. In the case of the methyl 2,3,6-tri-O-benzyl- α -D-talo- and α -D-galactopyranosides, the corresponding 4-O-imidazylates can be isolated by quenching the reactions

Introduction

Sulfonylation of sugar hydroxy groups is one of the most potent tool for their activation.^[1] The resulting sulfonates have been extensively used to perform bimolecular nucleophilic substitutions with a huge number of nucleophiles allowing: a) the introduction of different heteroatoms into the glycosyl framework (halogens, nitrogen, and sulfur),^[2] b) the epimerization of the stereogenic centre previously carrying the alcoholic function^[3] and c) deoxygenation.^[4] Other synthetic applications of carbohydrate sulfonates include the formation of cyclic anhydro derivatives, including epoxides,^[5] by intramolecular displacement and the installation of double bonds through classical base-promoted eliminations.

p-Toluenesulfonates (tosylates) and methanesulfonates (mesylates) were first introduced in carbohydrate chemistry in 1922^[6] and still represent the most widespread sulfonates in preparatively relevant syntheses of unsaturated sugars. In particular, 6-*O*-tosyl-pyranosides have been employed for the synthesis of 6-deoxy-hex-5-enopyranosides by treatment with several bases and, in particular, with the high-yielding NaH-DMF^[7] and NaH-HMPA systems.^[8] Elimination reactions of secondary tosylates are of less general use and

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at -30 °C. Upon warming these crude products to room temperature, the *a-talo-4-O*-imidazylate gives the corresponding hex-3-eno derivative in very high yield, but its *a-galacto* analogue gives the hex-4-enopyranoside enol ether in poor yield. The different regiochemical outcome between the *talo* and the *galacto* series has been attributed to the stereoelectronic effect exerted, exclusively in *talo*-configured compounds, by the axially disposed C-2 electronegative substituent, which selectively accelerates the breaking of the antiperiplanar C(3)–H bond.

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limited to specific cases^[9] in which a β -elimination could be favoured by an easily achievable antiperiplanar orientation between the leaving group and a single type of β -hydrogen.

The introduction of trifluoromethanesulfonates (triflates) has notably expanded the synthetically useful applications of nucleophilic substitution reactions, owing to the high nucleofugacity of this leaving group.^[10] Elimination reactions of triflates^[11] have been used for preparative purposes and also extensively investigated, owing to the presence of an alternative elimination pathway starting with an α -hydrogen abstraction, promoted by the strong electron-withdrawing effect of the triflyl group.^[11a] However, in the case of secondary triflates where two different types of hydrogen atoms flank the leaving group, mixtures of unsaturated derivatives are usually obtained.^[11b,11c]

Imidazole-1-sulfonates (imidazylates) have been proposed as efficient leaving groups characterised by an excellent nucleofugal ability and by the possibility of remote activation involving the basic nitrogen atom.^[12] Actually, significant improvements have been reported with imidazylates instead of tosylates and triflates, particularly in those reactions where the presence of unfavourable torsional or polar effects caused a lowering of yields (e.g. glucopyranoside 2-sulfonates.)^[13] Elimination reactions of imidazylates had been almost completely unknown,^[14] until we reported the formation of enol ethers 3,^[15] which occurred when the β -D-talopyranosides 1 were submitted to the protocol of the imidazylate preparation^[12] (Figure 1). This result was considered particularly surprising in view of the presence of



two different hydrogen atoms, H-3 and H-5, having an *anti* disposition with respect to the 4-*O*-imidazylate group on the putative intermediates **2**.





Figure 1. Transformation of 4-OH-containing β -D-talopyranosides into 4-deoxy- β -D-*threo*-hex-3-enopyranosides.

The β -D-*threo*-hex-3-enopyranosides **3** have not been described previously, whereas their *erythro* analogues have been occasionally reported as by-products during substitution^[16] or elimination^[11c] reactions of 4-*O*-sulfonyl-D-galactopyranosides. Moreover, this type of endocyclic sugar enol ether proved to be an interesting synthetic intermediate due to its application in the stereoselective synthesis of challenging β -D-mannopyranosides.^[17]

We present here a full account of the synthesis of 4-deoxy-D-*threo*-hex-3-enopyranosides starting from 6a-e as well as the extension of the activation–elimination procedure to other pyranosides 6f-i, characterised by an identical stereochemical relationship between the activable OH-4 group and the two contiguous stereogenic centres (C-3 and C-5), in order to clarify the structural parameters regulating the regioselective outcome of the elimination.

Synthesis of Substrates

Compounds 6a-i, selectively deprotected at C-4, were synthesised according to the general procedure illustrated in Scheme 1 and starting from derivatives 4a-i, obtained in a few steps from commercially available D-galactopyranosides, including lactose.

The galactopyranosides 4f-h and the 2-deoxy compound 4i have been prepared in accordance with methods previously reported in the literature,^[18] while the synthesis of the talopyranosides 4a,b and e was achieved starting from mixed acetals $7-9^{[19]}$ (Scheme 2) by a completely diastereoselective oxidation–reduction sequence.

As previously experienced for the oxidation of 7 to 10,^[20] the TPAP-NMO system^[21] effectively oxidised compound 8 and 9, giving access to the ulosides 11 and 12 in almost quantitative yield and without removal of the labile 6-Omethoxyisopropyl protecting group. The reduction of the two β-2-ulosides 10 and 11 (NaBH₄/MeOH) stereoselectively afforded the desired β -D-talopyranosides in excellent yields (94% and 98%, respectively). It is noteworthy that in these reductions, the D-talo stereoisomer was detected as the sole reaction product, evidently because of the cooperative effect of anomeric stereocontrol^[22] and of the steric hindrance of the β -face, exerted by the 3,4-O-isopropylidene protecting group, which is known to be much more effective in directing the hydride attack on β -D-lyxo-hexopyranosid-2-uloses^[23] than other substituents.^[24] However, our stereospecific epimerisation at C-2 of the mixed acetals 7 and 8 proved to be by far the most efficient synthetic methodology for the β -D-galacto to β -D-talo transformation, accessing compounds 13 and 14 in 85% and 60% overall yield, starting from methyl β-D-galactopyranoside and lactose, respectively.

The reduction of the α -uloside **12** yielded a 9:1 mixture of the α -talo (**15**) and α -galacto (**9**) diastereoisomers as a result of the opposite action of the steric effect exerted by the dioxolane ring and the anomeric stereocontrol of the methoxy group. Separation of **15** and **9** by flash chromatography was attempted with several eluents, but unfortunately, a satisfactory separation could not be obtained.



Scheme 1. General Procedure for the Preparation of 4-OH-containing D-galacto- and D-talopyranosides; Reagents and conditions: i: 80% AcOH aq, 50 °C; ii: a) Bu₂SnO, toluene, reflux; b) Bu₄NBr, BnBr, reflux.



Scheme 2. Preparation of protected D-talopyranosides; Reagents and conditions: i: TPAP, NMO, CH₂Cl₂; ii: NaBH₄, MeOH; iii: MeOH/H₂O, cat. AcOH; iv: KOH, 18-crown-6, BnBr.

The fully protected D-talopyranosides 4a and 4b were subsequently obtained (Scheme 2) in high yield starting from 13 and 14 through selective and mild acidic hydrolysis of the 6-O-methoxyisopropyl acetal, followed by benzylation. Performing the same sequence of reactions on the 15 + 9 mixture afforded a 9:1 diastereoisomeric mixture of 4e and 4h, which proved to be inseparable in our hands.



Scheme 3. Preparation of compound **4c**; Reagents and conditions: i: a) LiAlH₄, Et₂O, b) Ac₂O, MeOH; ii: KOH, 18-crown-6, BnBr.

The previously unreported methyl 2-acetamido-2-deoxy-3,4-*O*-isopropylidene- β -D-talopyranoside (4c) was obtained (Scheme 3) from the known oximino derivative 19,^[20] routinely obtained from the uloside 10. Reduction of 19 (Li-AlH₄/Et₂O), followed by *N*-acetylation and purification of the crude product, yielded the pure *N*-acetyl-D-talosamino derivative 20 (62% yield) and the *galacto* diastereoisomer 21 (17% yield, not shown). Benzylation of 20 gave, finally, 4c in high yield (84%). The preparation of the *N*-acetyl talosamino disaccharide derivative 4d, starting from lactose has been recently published as part of a project towards the synthesis of the β -D-ManNAcp-(1→4)-D-Glc disaccharide.^[17b]

Compounds 6a-i were finally obtained, as previously anticipated (Scheme 1), through a high-yielding hydrolysis of the 4a-i isopropylidene protecting groups and subsequent regioselective 3-O-benzylations. In particular, in the cases of the galactopyranoside diols 5f-h,^[25] treatment of the intermediate stannylidene acetals with BnBr gave the known methyl galactopyranosides 6f and 6h^[26] in excellent yields (>90%), as well as the previously unreported derivative **6**g. In full accordance with previous reports regarding the opening of 3,4-O-stannylidene acetals of galactopyranosides with several electrophiles^[27] (alkyl, acyl and sulfonyl halides), only the product arising from the electrophilic attack on the equatorial O-3 was detected, irrespective of the anomeric configuration. In the β -galacto series, the complete regioselectivity was attributed to the formation of dimeric stannylidene acetal species, which reacted with electrophiles only on the less hindered equatorial O-3 atom.^[27] An identical regioselective outcome was observed in the stannylidenation-benzylation of the 2-deoxy-diol 5i, obtained after hydrolysis of 4i.^[18d] It is noteworthy that the deacetonation of derivative 4i required very mild conditions in order to avoid both hydrolysis of the glycosidic linkage (80% ag AcOH) and the concurrent anomerization to the more stable α -anomer 22. After a prolonged reaction in MeOH, in the presence of a catalytic amount of TsOH (r.t., 30 h), the product 5i was revealed in a 35:65 ratio with 22. An excellent result (85% yield of anomerically pure 5i) was obtained by employing DDQ in 10% aq CH₃CN, proposed^[28] as a reagent operating under neutral conditions.

The transformation of compounds 4a-c and 4e into the talopyranosides 6a-c and 6e (Scheme 1) followed the same reaction sequence described above for the D-galacto compounds. The monosaccharide derivatives 4a and 4c were routinely de-isopropylidenated in almost quantitative yields. The hydrolysis of the 9:1 4h/4e mixture gave a crude product containing a 9:1 5e/5h mixture, which afforded pure 5e (88% yield) after chromatographic purification. In the case of the disaccharide 4b, the deacetonation step with 60% aq AcOH proved to be sufficiently regioselective, affording, after 3 h at room temperature, the diol 5b in a satisfactory 62% yield, along with the tetraol 23 (31%, Figure 2). Selectively deprotected talopyranosides 6a,b,c and 6e were finally obtained by benzylation of the intermediate stannylidene acetals of diols 5a,b,c and 5e. To the best of our knowledge, the reaction of 3,4-O-stannylidene acetals in the D-talopyranoside series with electrophiles has been previously reported only by our group^[17b] in the case of derivative **5d**, which reacted exclusively at the equatorial *O*-3, similarly to the reported *galacto* analogues.^[27] An identical result was obtained in the case of β -derivatives **5a**-**c**, accessing compounds **6a**-**c**, while the α -anomer **5e** gave an appreciable amount (9% yield) of the isomer **24**, along with predominant benzylation at *O*-3 (**6e**, 82% yield).

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Figure 2. Compounds 22-24 and 27e and 27h.

Results and Discussion

When the β -D-*talo* alcohols **6a**–d, previously transformed into their sodium salts with NaH in dry DMF, were treated at -30 °C with an excess (1.5 equiv.) of sulfuryldiimidazole (Im₂SO₂), fast and clean reactions took place, revealing the formation of faster-moving products (by TLC), containing exclusively the hex-3-enopyranosides 25a-d (Table 1), as ascertained by NMR analysis. We were not able to observe (by TLC or NMR) the formation of the putative intermediate 4-O-imidazylates at any stage of the reaction, because of their fast elimination under the reaction conditions. Pleasingly in any case, only abstraction of the trans-oriented H-3, promoted by the sodium imidazolate present in the reaction medium, was observed. After preliminary studies,^[15,17] we finally standardised the experimental conditions for this reaction (Table 1), which afforded pure enol ethers 25a-d in excellent yields (90-95%). Encouraged by the unexpected, completely regioselective abstraction of H-3 with respect to H-5, both of them presenting the same trans relationship with the leaving group at C-4, we extended the reaction to the β -D-galacto derivatives **6f** and **6g**. Under the same conditions as described above, the β -galacto compounds 6f and 6g showed an identical reactivity to that of their talo analogues. A simultaneous activationelimination process took place, but unfortunately, this time with an almost complete lack of regioselectivity, affording mixtures of hex-3- and hex-4-enopyranosides **25** and **26**. An identical result was also obtained in the case of the 2-deoxy derivative **6i**, suggesting a fundamental and specific role exerted by the axially disposed electronegative substituent at C-2 in the control of the regioselectivity.

Table 1. 4-Deoxy-hexenopyranoside formation by reaction of 6 with the NaH/Im₂SO₂ system.



[a] All reactions were performed at -30 °C for 1 h, warmed to room temperature and allowed to react for the reported time. [b] Evaluated through ¹³C NMR analysis on an inseparable mixture of **25f** and **26f**. [c] Estimated from the composition of two differently enriched mixtures of the two enol ethers (Experimental Section).

In order to evaluate the possible influence of the anomeric configuration on the reaction outcome, we treated the two α derivatives **6e** and **6h**, belonging to the *talo* and the *galacto* series, respectively, with the NaH/Im₂SO₂ system. In both cases, we observed, in the first stage of the reaction (1 h at -30 °C), the complete disappearance of the starting material and the formation of a major slower-moving product (by TLC). Stimulated by the different reactivity of these two compounds compared to all the β -configured ones, the crude mixtures were quenched at this stage, and the corresponding 4-*O*-imidazylates **27e** and **27h** (Figure 2) were isolated. In a repetition of these reactions, when the crude mixtures containing **27e** and **27h** were warmed to room temperature, the 4-*O*-imidazylates slowly disappeared. In the case of the *talo* derivative **27e**, the 4-deoxy-D-*threo*-hex-3-

enopyranoside **25e** was the only isolated product (90% yield), while in the case of the *galacto* compound **27h**, the known 4-deoxy-D-*erythro*-hex-4-enopyranoside **26h**,^[11a] derived by the elimination with opposite regiochemistry, was obtained in a very poor yield (12%), because of concurrent reaction pathways.^[29]

From the results collected in Table 1, it can be summarised that: (a) talo-configured 4-O-imidazylate intermediates of both the α and β series, afforded the 4-deoxy-hex-3-enopyranosides (25) with complete regioselectivity, while their galacto and 2-deoxy analogues gave mixtures of 4-deoxy-hex-3- (25) and hex-4-pyranosides (26) and (b) 4-O-imidazylates belonging to the β anomeric configuration of both the talo and the galacto series, gave spontaneous eliminations even at low temperature (-30 °C), under the strongly basic reaction medium, while their a-analogues (27e and 27h) proved to be quite stable under the same conditions and could be isolated. Although the latter observation shows a huge difference between α and β anomers, this is not particularly surprising since it can be tentatively explained by taking into account Richardson's general observations.^[30] Richardson noted: a) that the anomeric configuration exerts a strong influence on the reactivity of sulfonates and on the substitution/elimination ratio obtained in their displacement reactions and b) a lower reaction rate for the anomer having the minor dipolar moment that is, in both the D-galacto and D-talo series, the α anomer.

Much more surprising is the complete regioselectivity observed in the reaction of the talo 4-O-imidazylates, evidently due to the presence of the axial electronegative substituent at C-2. It is reasonable to suppose that, in the presence of a strong base such as the imidazolate anion, at low temperature and in DMF, the mechanism of the elimination reactions is an E2-like process with a strong E1cb character. In particular, we hypothesise a transition state with the intermediate 4-O-imidazylates in the most likely chair conformation and a considerable degree of "carbanion character" at C-3. In the case of talo-configured imidazylates, the incoming non-bonding lone pair (in the sp^3 carbanion orbital) could be stabilised by the parallel axially disposed substituent at C-2 (Z = OBn or NHAc in Figure 3). This negative hyperconjugation could arise from the $n \rightarrow \sigma *_{C(2)-Z}$ delocalization of the non-bonding lone pair into the antiperiplanar antibonding $\sigma_{C(2)-Z}$ orbital.^[31] Because of this stereoelectronic assistance, H-3 should be more acidic in this case and more easily abstracted than H-5.

In the case of *galacto*- and 2-deoxy- 4-*O*-imidazylates (W = OBn or H in Figure 3), the stereoelectronic assistance to the C(3)–H bond breaking cannot be offered neither by the antibonding $\sigma_{*C(2)-W}$ orbital for geometrical reasons nor by the antiperiplanar $\sigma_{*C(2)-H}$ antibonding orbital, since the C–H bond is a good σ donor but a poor σ_{*} acceptor.^[32]

A spectroscopic manifestation of these hyperconjugative interactions can be found in the experimental ${}^{1}J_{C-H}$ values. Recent results from Cuevas and co-workers indicate that any stereoelectronic interaction weakening an axial C–H bond is manifested in a smaller ${}^{1}J_{C-Hax}$ value, relative to that of ${}^{1}J_{C-Hea}$.^[33] Starting from these considerations, we



Figure 3. Stereoelectronic interactions affecting the regioselectivity of 4-*O*-imidazylate eliminations.

compared (Table 2) the ${}^{1}J_{C-H}$ values of a strictly similar couple of talo- and galactopyranosides (6a and 6f), in order to determine if there is spectroscopic evidence of the stereoelectronic effect exerted by the axial benzyloxy group at C-2 of **6a**. As expected, both the axial ${}^{1}J_{C1-H1}$ and ${}^{1}J_{C3-H3}$ values of the talo compound 6a were smaller than the analogous coupling constants in the galactopyranoside 6f (Table 2). These data confirm that the σ^* acceptor ability of the C-2 axial benzyloxy group in the *talo* derivative **6a** is definitely higher than that of the axial H-2 in the corresponding galacto isomer 6f. Moreover, they reveal the fundamental role played by the axial substituent stereoelectronic effect in weakening an antiperiplanar C-H bond, which, to the best of our knowledge, has never been observed before. Of course, we are fully aware that the structure and interactions present in 6a and 6f are, by far, more complex than models reported in the literature, and that both the origin^[33] and the magnitude of the ${}^{1}J_{C-H}$ values can be affected by torsional effects of the substituents.^[34] However, the ${}^{1}J_{C-H}$ values completely agree with considerations we used to explain the regiospecificity observed in the elimination reactions of talo 4-O-imidazylates.

Table 2. Comparison between ${}^1\!J_{\rm C-H}$ values of a talo- and galactopyranoside couple.

HO OBn OBn BnO H H H H		HO OBn HO HO BnO H BnO H 6f	
	$^{1}J_{\mathrm{C-H}}$	$^{1}J_{\mathrm{C-H}}$	$\Delta J = J_{gal} - J_{tal}$
C-1	154.1	156.4	2.3
C-2	140.4	145.0	4.6
C-3	137.3	139.6	2.3
C-4	145.0	145.7	0.7
C-5	138.1	136.6	-1.5
C-6	143.4	143.0	-0.4

In conclusion, we have reported a full account of a new regiospecific methodology for the high-yielding, one-pot synthesis of previously unreported 4-deoxy-*threo*-hex-3-enopyranosides and their 2-acetamido analogues, starting

from talopyranosides selectively deprotected at C-4. Preparation of this uncommon class of sugars has been reported in detail, and their reactivity in the elimination reactions has been compared to that exhibited by the analogous galactopyranosides. A specific role of the C-2 axial substituent in determining the regiospecificity of the elimination of the axial 4-O-imidazylate intermediates has been demonstrated and tentatively explained on the basis of stereoelectronic effects, never invoked before to explain the regioselectivity of sulfonate elimination reactions. Further studies on other stereoisomeric series are ongoing in order to define the scope and limitations of this highly regiocontrolled synthetic methodology for the preparation of useful and challenging hexenopyranoside enol ethers.

Experimental Section

General: Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 polarimeter at 20±2 °C. ¹H and ¹³C NMR measurements were performed with a Bruker AC 200 instrument operating at 200 MHz and 50 MHz, respectively, in an appropriate solvent (Me₄Si as an internal standard). Coupled ¹³C NMR measurements were performed with a Varian INOVA600 spectrometer operating at 150 MHz. NMR signal assignments were made, when possible, with the aid of DEPT experiments, for comparison with values for known compounds and applying the known additivity rules,^[35] and, in the case of mixtures, referring to the differences in the peak intensities. All reactions were followed by TLC on Kieselgel 60 F254 with detection by UV light and/or with ethanolic 10% phosphomolybdic or sulfuric acid and heating. Kieselgel 60 (Merck, 70-230 mesh and 230-400 mesh, respectively) was used for column and flash chromatography. Solvents were dried by distillation according to standard procedures[36] and storage over 4-Å molecular sieves, activated for at least 24 h at 400 °C. MgSO₄ was used as a drying agent for solutions. After isolation, all 6-O-(1methoxy-1-methylethyl) derivatives 10-12 and 13-15 were stored at -18 °C in the presence of a trace of Et₃N. Elemental analyses and optical rotations of these compounds were not performed, and their purity was determined by NMR spectroscopy.

General Procedure for the Oxidation of 7–9: A mixture of alcohol (1 mmol) and pre-dried 4-methylmorpholine *N*-oxide (NMO, 1.8 equiv.) in anhydrous CH_2Cl_2 (20 mL) containing 4 Å powdered molecular sieves (1 g) was stirred for 30 min at room temperature under argon. Tetrapropylammonium perruthenate (TPAP, 0.05 equiv.) was added, and the resulting green mixture was stirred for 1–3 h at room temperature until TLC revealed complete oxidation of the starting material. The mixture was filtered through a celite-silica gel-celite triple alternate pad, and the filter was washed with CH_2Cl_2 and EtOAc. The organic phase was concentrated in vacuo and afforded the 2-ulose derivatives **10–12** almost pure by NMR spectroscopy.

General Procedure for the Reduction of 10–12: A solution of the crude 2-uloside (1 mmol) in MeOH (20 mL) was cooled to 0 °C under argon and treated with an excess of NaBH₄ (3 equiv.). The solution was left to react until TLC analysis showed complete disappearance of the starting material (30 min–1 h). H₂O was added (10 mL), and the resulting solution stirred for an additional 30 min. MeOH was evaporated under reduced pressure, and the residue was extracted with CH₂Cl₂ (4×20 mL). The organic extracts were

dried, filtered and concentrated. The crude products were composed of **13–15** exclusively, as determined by NMR.

General Procedure for the Demethoxyisopropylation of 13–15: A solution of 6-O-(1-methoxy-1-methylethyl) derivative (1 mmol) in MeOH/H₂O (10:1, 5 mL) was treated with AcOH (28 μ L) and heated to 50 °C while stirring. After 1 h, TLC analysis revealed the complete deprotection of the starting material. The solution was then cooled to room temperature and coevaporated with toluene (4 × 20 mL). Purification of the crude residue by flash chromatography on silica gel gave products 16–18.

Methyl 3,4-O-Isopropylidene-β-D-talopyranoside (16): Oxidation of alcohol 7^[19] (6.49 g, 21.2 mmol), performed as described above, gave crude methyl 3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-β-D-lyxo-hexopyranosid-2-ulose (10, 6.40 g, quantitative yield) as a clear syrup.^[20] Reduction of crude 10 (5.56 g, 18.3 mmol) with NaBH₄ in MeOH, according to the reported general procedure, afforded a clear syrup constituted exclusively by 13 (5.27 g, 94% yield). Some data for methyl 3,4-O-isopropylidene-6-O-(1methoxy-1-methylethyl)- β -D-talopyranoside (13): $R_{\rm f} = 0.33$ (EtOAc). ¹H NMR (200 MHz, C₆D₆): δ = 4.30 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H), 3.93 (m, 2 H, H-3, 4-H), 3.84 (dd, J_{6a,6b} = 9.6 Hz, J_{5,6a} = 3.0 Hz, 1 H, 6a-H), 3.78 (dd, $J_{5,6b} = 5.7$ Hz, 1 H, 6b-H), 3.55 (m, 1 H, 5-H), 3.47 (dd, J_{2.3} = 4.7 Hz, 1 H, 2-H), 3.24 (s, 3 H) and 3.16 (s, 3 H) (OCH₃-1, OCH₃-MIP), 1.30 (s, 6 H, 2×CH₃-MIP), 1.59 [s, 3 H, C(CH₃)₂], 1.20 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, C_6D_6): $\delta = 109.9 [C(CH_3)_2], 100.3 (C-1), 100.1 [C(CH_3)_2-MIP],$ 73.5, 72.5, 70.9 (C-3, C-4, C-5), 66.7 (C-2), 61.1 (C-6), 55.7 (OCH₃-1), 48.3 (OCH₃-MIP), 25.6 [C(CH₃)₂], 25.3 [C(CH₃)₂], 24.7 (CH₃-MIP), 24.6 (*C*H₃-MIP) ppm.

Hydrolysis of crude **13** (3.05 g, 10.0 mmol) was performed according to the described general procedure. The crude product was purified by flash chromatography, eluting with EtOAc, and gave pure **16** (96% yield from 7) as a white solid. $R_{\rm f} = 0.16$ (EtOAc); m.p. 69–72 °C (EtOAc/hexane). $[\alpha]_{\rm D}^{20} = -21.2$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 4.46$ (d, $J_{1,2} = 1.9$ Hz, 1 H, 1-H), 4.32 (dd, $J_{2,3} = 4.7$ Hz, $J_{3,4} = 6.6$ Hz, 1 H, 3-H), 4.22 (dd, $J_{4,5} = 2.3$ Hz, 1 H, 4-H), 4.00 (dd, $J_{6a,6b} = 12.5$ Hz, $J_{5,6b} = 8.2$ Hz, 1 H, 6b-H), 3.90–3.73 (m, 4 H, H-2, H-5, 6a-H, OH), 3.54 (s, 3 H, OCH₃), 2.51 (br. s, 1 H, OH), 1.58 [s, 3 H, C(CH₃)₂], 1.36 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 110.1$ [$C(CH_3)_2$], 100.4 (C-1), 73.4, 72.4, 71.6 (C-3, C-4, C-5), 66.1 (C-2), 62.1 (C-6), 56.5 (OCH₃), 25.2 [$C(CH_3)_2$], 25.1 [$C(CH_3)_2$] ppm. $C_{10}H_{18}O_6$ (234.25): calcd. C 51.27, H 7.75; found C 51.29, H 7.74.

4-O-(3,4-O-Isopropylidene-β-D-talopyranosyl)-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose Dimethyl Acetal (17): Oxidation of alcohol 8^[18b] (9.0 g, 15.5 mmol) gave 11 (8.46 g, 94% yield) as a clear syrup, which was almost pure by NMR. Some data for 4-O-[3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-β-D-lyxohexopyranosyl-2-ulose]-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose dimethyl acetal (11): $R_{\rm f} = 0.53$ (9:1 CH₂Cl₂/Me₂CO). ¹H NMR (200 MHz, C₆D₆): δ = 5.20 (d, $J_{1',3'}$ = 0.7 Hz, 1 H, 1'-H), 4.77 (dd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 7.3 Hz, 1 H, 2-H), 4.50–3.50 (m, 11 Н, 1-Н, 3-Н, 4-Н, 5-Н, 6а-Н, 6b-Н, 3'-Н, 4'-Н, 5'-Н, 6'а-Н, 6'b-H), 3.24 (s, 3 H, OCH₃-1), 3.22 (s, 3 H, OCH₃-1), 3.17 (s, 3 H, OCH_3 -MIP), 1.42 (s, 6 H, 2×CH₃-MIP), 1.54 [s, 3 H, C(CH₃)₂], 1.40 [s, 3 H, C(CH₃)₂], 1.35 [s, 3 H, C(CH₃)₂], 1.32 [s, 3 H, C(CH₃)₂], 1.31 [s, 3 H, C(CH₃)₂], 1.20 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, C_6D_6): $\delta = 197.3$ (C-2'), 111.0 [C(CH_3)_2], 110.7 [C(CH₃)₂], 108.2 [C(CH₃)₂], 105.8 (C-1), 100.9 (C-1'), 100.2 [C(CH₃)₂-MIP], 78.4, 78.3, 78.2, 77.8 (C-3, C-5, C-3', C-4'), 76.7, 76.0 (C-2, C-4), 72.2 (C-5'), 65.9 (C-6), 59.9 (C-6'), 55.8 (OCH₃-1), 53.5 (OCH₃-1), 48.4 (OCH₃-MIP), 27.7 [C(CH₃)₂], 27.4 [C(CH₃)₂],

26.7 [C(*C*H₃)₂], 26.6 [C(*C*H₃)₂], 26.2 [C(*C*H₃)₂], 26.1 [C(*C*H₃)₂], 24.6 (*C*H₃-MIP), 24.5 (*C*H₃-MIP) ppm.

Reduction of crude uloside 11 (3.32 g, 5.74 mmol) gave 14 (3.30 g, 98% yield) as clear syrup, which was pure by NMR spectroscopy. Data for 4-O-[3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)B-D-talopyranosyl]-2,3:5,6-di-O-isopropylidene-aldehydo-Dglucose dimethyl acetal (14): $R_f = 0.18$ (9:1 CH₂Cl₂/Me₂CO). ¹H NMR (200 MHz, CDCl₃): δ = 4.90 (d, $J_{1',2'}$ = 2.2 Hz, 1 H, 1'-H), 4.53 (dd, $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 4.37 (d, 1 H, 1-H), 4.30-4.17 (m, 3 H, 4-H, 5-H, 6a-H), 4.10-4.00 (m, 2 H, H-6b, 3'-H), 3.95 (dd, $J_{3,4}$ = 1.4 Hz, 1 H, 3-H), 3.80 (ddd, $J_{5',6'a}$ = 3.9 Hz, $J_{5',6'b} = 6.0$ Hz, 1 H, $J_{4',5'} = 2.0$ Hz, 5'-H), 3.77 (dd, $J_{3',4'} = 6.2$ Hz, 1 H, 4'-H), 3.65 (dd, $J_{6'a,6'b}$ = 9.3 Hz, 1 H, 6'a-H), 3.58 (dd, 1 H, 6'b-H), 3.45 (m, 1 H, 2'-H), 3.43 (s, 6 H, 2×OCH₃-1), 3.21 (s, 3 H, OCH₃-MIP), 2.84 (d, $J_{2,OH}$ = 9.7 Hz, 1 H, OH), 1.58 [s, 3 H, C(CH₃)₂], 1.43 [s, 3 H, C(CH₃)₂], 1.42 [s, 3 H, C(CH₃)₂], 1.38 [s, 3 H, C(CH₃)₂], 1.36 [s, 3 H, C(CH₃)₂], 1.35, [s, 3 H, C(CH₃)₂], 1.34 (s, 6 H, $2 \times CH_3$ -MIP) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 110.0$ [C(CH₃)₂], 109.4 [C(CH₃)₂], 107.5 [C(CH₃)₂], 104.7 (C-1), 100.6 [C(CH₃)₂-MIP], 99.6 (C-1'), 77.8, 77.7 (C-3, C-5), 75.6, 74.5 (C-2, C-4), 73.6, 71.5, 71.4 (C-3', C-4', C-5'), 66.9 (C-2'), 64.8 (C-6), 59.7 (C-6'), 55.3 (OCH₃-1), 52.7 (OCH₃-1), 48.1 (OCH₃-MIP), 27.0 [C(CH₃)₂], 26.1 [C(CH₃)₂], 25.9 [C(CH₃)₂], 25.3 [C(CH₃)₂], 25.0 [C(CH₃)₂], 24.8 [C(CH₃)₂], 24.0 (CH₃-MIP), 23.9 (CH₃-MIP) ppm.

Hydrolysis of crude 14 (3.20 g, 5.52 mmol) gave 17 (2.10 g, 75% yield from 8) as a white solid after flash chromatography (2:8 hexane/EtOAc). $R_f = 0.22$ (2:8 hexane/EtOAc); m.p. 95–98 °C (EtOAc/ hexane). $[\alpha]_{D}^{20} = +18.3$ (c = 1.2, CHCl₃). ¹H NMR (200 MHz, CD₃CN/D₂O): δ = 4.59 (d, $J_{1',2'}$ = 1.2 Hz, 1 H, 1'-H), 4.44 (dd, $J_{1,2} = 6.8$ Hz, $J_{2,3} = 7.3$ Hz, 1 H, 2-H), 4.36 (d, 1 H, 1-H), 4.26-4.16 (m, 2 H, 3'-H, 5-H), 4.06 (dd, $J_{3',4'} = 5.9$ Hz, $J_{4',5'} = 2.2$ Hz, 1 H, 4'-H), 3.98 (dd, $J_{3,4}$ = 1.4 Hz, 1 H, 3-H), 3.97–3.94 (m, 2 H, 6a-H, 6b-H), 3.89 (dd, J_{4,5} = 4.4 Hz, 1 H, 4-H), 3.79–3.58 (m, 4 H, 2'-H, 5'-H, 6'a-H, 6'b-H), 3.41 (s, 3 H, OCH₃), 3.39 (s, 3 H, OCH₃), 1.46 [s, 3 H, C(CH₃)₂], 1.34 [s, 3 H, C(CH₃)₂], 1.33 [s, 3 H, C(CH₃)₂], 1.30 [s, 3 H, C(CH₃)₂], 1.28 [s, 3 H, C(CH₃)₂], 1.27 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CD₃CN/D₂O): δ = 110.5 [C(CH₃)₂], 110.4 [C(CH₃)₂], 108.8 [C(CH₃)₂], 107.6 (C-1), 101.8 (C-1'), 78.7, 78.2 (C-3, C-5), 76.2, 76.1, 75.2, 75.1, 72.2 (C-3', C-4', C-5', C-2, C-4), 67.4 (C-2'), 65.9 (C-6), 62.3 (C-6'), 57.4 (OCH₃), 54.6 (OCH₃), 27.4 [C(CH₃)₂], 26.8 [C(CH₃)₂], 26.7 [C(CH₃)₂], 25.9 [C(CH₃)₂], 25.7 [C(CH₃)₂], 25.5 [C(CH₃)₂] ppm. C₂₃H₄₀O₁₂ (508.56): calcd. C 54.32, H 7.93; found C 54.34, H 7.91.

Methyl 3,4-*O*-Isopropylidene-*α*-D-talopyranoside (18): Oxidation of alcohol 9^[19] (3.93 g, 12.8 mmol) afforded 12 (3.80 g, 97% yield) as a clear syrup, which was almost pure by NMR spectroscopy. Data for methyl 3,4-*O*-isopropylidene-6-*O*-(1-methoxy-1-methylethyl)-*α*-*D*-*lyxo*-hexopyranosyl-2-ulose (12): $R_{\rm f} = 0.65$ (95:5 CHCl₃/MeOH). ¹H NMR (200 MHz, C₆D₆): $\delta = 4.77$ (s, 1 H, 1-H), 4.51 (d, $J_{3,4} = 5.5$ Hz, 1 H, 3-H), 4.34 (ddd, $J_{5,6a} = 5.7$ Hz, $J_{5,6b} = 6.7$ Hz, $J_{4,5} = 1.9$ Hz, 1 H, 5-H), 4.18 (dd, 1 H, 4-H), 3.99 (dd, $J_{6a,6b} = 9.7$ Hz, 1 H, 6b-H), 3.89 (dd, 1 H, 6a-H), 3.22 (s, 3 H, OCH₃-1), 3.11 (s, 3 H, OCH₃-MIP), 1.37 (s, 6 H, $2 \times CH_3$ -MIP), 1.55 [s, 3 H, C(CH₃)₂], 1.28 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, C₆D₆): $\delta = 198.7$ (C-2), 110.6 [*C*(CH₃)₂], 100.9 (C-1), 100.1 [*C*(CH₃)₂-MIP], 78.0 (C-4), 76.0 (C-3), 67.5 (C-5), 60.4 (C-6), 54.8 (OCH₃-1), 48.3 (OCH₃-MIP), 27.4 [C(CH₃)₂], 26.3 [C(CH₃)₂], 24.5 (2 × CH₃-MIP) ppm.

Reduction of crude **12** (2.04 g, 6.7 mmol) with NaBH₄ in MeOH at -78 °C gave a clear syrup showing a single spot by TLC ($R_f = 0.40$, EtOAc). The NMR analysis revealed a mixture (1.95 g, 95% yield) of **15** and its *galacto* epimer **9**^[19] in a 9:1 ratio, as estimated

by the relative ¹H NMR signal integrations. Data for methyl 3,4-*O*-isopropylidene-6-*O*-(1-methoxy-1-methylethyl)- α -D-talopyranoside (15): ¹H NMR (200 MHz, CDCl₃): δ = 4.73 (d, $J_{1,2}$ = 5.4 Hz, 1 H, 1-H), 4.55 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 7.4 Hz, 1 H, 3-H), 4.32 (dd, $J_{4,5}$ = 1.9 Hz, 1 H, 4-H), 3.80 (ddd, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 7.2 Hz, 1 H, 5-H), 3.75–3.60 (m, 3 H, H-2, 6a-H, 6b-H), 3.45 (s, 3 H, OCH₃-1), 3.22 (s, 3 H, OCH₃-MIP), 2.81 (br. s, 1 H, OH), 1.36 (s, 6 H, 2 × CH₃-MIP), 1.51 [s, 3 H, C(CH₃)₂], 1.35 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 110.1 [*C*(CH₃)₂], 101.5 (C-1), 100.0 [*C*(CH₃)₂-MIP], 73.5, 73.3 (C-3, C-4), 68.9, 68.6 (C-2, C-5), 59.7 (C-6), 55.1 (OCH₃-1), 48.4 (OCH₃-MIP), 25.9 [*C*(CH₃)₂], 25.1 [C(CH₃)₂], 24.3 (2 × CH₃-MIP) ppm.

Hydrolysis of the **15** + **9** (1.52 g, 5.0 mmol) 9:1 mixture gave a white solid (1.15 g, quantitative yield) showing a single spot by TLC (R_f = 0.16, EtOAc). The NMR spectra showed a mixture of **18** and its *galacto* epimer in a 9:1 ratio. Some data for **18**: ¹H NMR (200 MHz, CDCl₃): δ = 4.75 (d, $J_{1,2}$ = 5.4 Hz, 1 H, 1-H), 4.54 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 7.5 Hz, 1 H, 3-H), 4.32 (dd, $J_{4,5}$ = 1.8 Hz, 1 H, 4-H), 3.88 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 7.5 Hz, 1 H, 6b-H), 3.81–3.66 (m, 3 H, H-2, H-5, 6a-H), 3.46 (s, 3 H, OCH₃), 3.35 (br. s, 2 H, OH), 2.10 (br. s, 2 H, OH), 1.52 [s, 3 H, C(CH₃)₂], 1.36 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 110.4 [*C*(CH₃)₂], 101.5 (C-1), 74.1, 73.5 (C-3, C-4), 69.2, 68.5 (C-2, C-5), 62.1 (C-6), 55.5 (OCH₃), 25.9 [C(CH₃)₂], 25.0 [C(CH₃)₂] ppm. C₁₀H₁₈O₆ (234.25): calcd. C 51.27, H 7.75; found C 51.24, H 7.71.

Methyl 2-Acetamido-2-deoxy-3,4-O-isopropylidene-β-D-talopyranoside (20) and Methyl 2-Acetamido-2-deoxy-3,4-O-isopropylidene-β-**D-galactopyranoside (21):** A solution of pure oxime **19**^[20] (988 mg, 4.0 mmol), in dry Et₂O (50 mL) was added dropwise to a suspension of LiAlH₄ (900 mg, 23.7 mmol) in dry Et₂O (80 mL) at room temperature under argon. The mixture was stirred for 10 min at room temperature and then heated to reflux. After 2 h, a TLC analysis (3:7 hexane/EtOAc) revealed the complete disappearance of the starting material. The reaction mixture was quenched by the addition of H₂O (1.0 mL), aq 15% NaOH (3.0 mL) and H₂O (1.0 mL), followed by an additional 15 min of stirring. The white precipitated solid was filtered and repeatedly washed with EtOAc. The organic phase was dried, filtered and the solvents were evaporated. The crude product was dissolved in MeOH (40 mL), treated with Ac₂O (4.0 mL) and left to react at room temperature overnight. The reaction mixture was then repeatedly co-evaporated with toluene $(4 \times 10 \text{ mL})$, and purification of the residue by flash chromatography (92:8 CH₂Cl₂/MeOH) allowed the isolation of two pure acetamido derivatives.

Data for 20: White solid (680 mg, 62% yield). $R_f = 0.36$ (92:8 CH₂Cl₂/MeOH); m.p. 139–142 °C. $[\alpha]_{20}^{D} = +7.5$ (c = 0.9, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 6.78$ (d, $J_{2,NH} = 9.2$ Hz, 1 H, NH), 4.72 (d, $J_{1,2} = 3.7$ Hz, 1 H, 1-H), 4.44–4.28 (m, 3 H, 2-H, 3-H, 4-H), 3.90–3.75 (m, 3 H, H-5, 6a-H, 6b-H), 3.44 (s, 3 H, OCH₃), 2.06 (s, 3 H, CH₃CO), 1.50 [s, 3 H, C(CH₃)₂], 1.31 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 170.2$ (C=O), 110.1 [C(CH₃)₂], 98.3 (C-1), 72.5, 71.7, 71.2 (C-3, C-4, C-5), 62.5 (C-6), 56.0 (OCH₃), 46.6 (C-2), 25.4 [C(CH₃)₂], 24.7 [C(CH₃)₂], 23.2 (CH₃CO) ppm. C₁₂H₂₁NO₆ (275.30): calcd. C 52.35, H 7.69, N 5.09; found C 52.38, H 7.68, N 4.99.

Data for 21: White solid (190 mg, 17% yield). $R_f = 0.26$ (92:8 CH₂Cl₂/MeOH); m.p. 91–92 °C. $[a]_D^{20} = +29.4$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 6.44$ (d, $J_{2,NH} = 7.7$ Hz, 1 H, NH), 4.83 (d, $J_{1,2} = 8.5$ Hz, 1 H, 1-H), 4.66 (dd, $J_{2,3} = 8.4$ Hz, $J_{3,4} = 5.4$ Hz, 1 H, 3-H), 4.18 (dd, $J_{4,5} = 1.5$ Hz, 1 H, 4-H), 4.04–3.83 (m, 3 H, H-5, 6a-H, 6b-H), 3.51 (s, 3 H, OCH₃), 3.18 (m, 1 H, 2-H), 2.01 (s, 3 H, CH₃CO), 1.52 [s, 3 H, C(CH₃)₂], 1.34 [s, 3 H,

C(*CH*₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 171.0 (C=O), 110.1 [*C*(CH₃)₂], 100.4 (C-1), 75.5, 73.7, 73.3 (C-3, C-4, C-5), 62.4 (C-6), 57.6 (C-2), 56.8 (OCH₃), 28.1 [C(*CH*₃)₂], 26.2 [C(*CH*₃)₂], 23.6 (*CH*₃CO) ppm. C₁₂H₂₁NO₆ (275.30): calcd. C 52.35, H 7.69, N 5.09; found C 52.37, H 7.68, N 5.01.

General Procedure for the Benzylation of 16–18 and 20: Starting material (1 mmol) was dissolved in THF/H₂O (99.5:0.5, 5 mL). Powdered KOH (4 equiv. per hydroxy group) and 18-crown-6 (0.05 equiv.) were added, and the resulting mixture was vigorously stirred at room temperature for 30 min. Benzyl bromide (2 equiv. per hydroxy group) was added, and the reacting mixture was stirred at room temperature until TLC analysis revealed the complete disappearance of the starting material and the formation of a major faster-moving product. MeOH (5 mL) was added, and the mixture was stirred for an additional 10 min. Solvents were evaporated in vacuo, and the residue was dissolved in CH₂Cl₂ (10 mL) and washed with H₂O (4 mL). The two phases were separated, and the aqueous phase was further extracted with CH₂Cl₂ (2×10 mL). The organic extracts were dried, concentrated under reduced pressure, and the residue was purified by flash chromatography.

Methyl 2,6-Di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-talopyranoside (4a): Benzylation of crude 16 (3.18 g, 13.6 mmol) gave 4a (5.29 g, 94% yield) as a white solid after flash chromatography (6:4 hexane/ EtOAc). $R_f = 0.36$ (6:4 hexane/EtOAc); m.p. 50–52 °C. $[\alpha]_{20}^{20} =$ -19.5 (c = 1.4, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.40$ -7.26 (m, 10 H, Ar-H), 4.78 (s, 2 H, PhCH₂), 4.56 (d, $J_{1,2} = 2.4$ Hz, 1 H, 1-H), 4.64, 4.54 (AB system, $J_{A,B} = 12.0$ Hz, 2 H, PhCH₂), 4.37 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7.3$ Hz, 1 H, 3-H), 4.20 (dd, $J_{4,5} =$ 1.8 Hz, 1 H, 4-H), 3.80–3.76 (m, 3 H, 5-H, 6a-H, 6b-H), 3.49 (dd, 1 H, 2-H), 3.47 (s, 3 H, OCH₃), 1.56 [s, 3 H, C(CH₃)₂], 1.33 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 138.1$ (Ar-C), 137.8 (Ar-C), 128.2–127.5 (Ar-CH), 110.2 [C(CH₃)₂], 99.6 (C-1), 73.4 (PhCH₂), 72.6 (PhCH₂), 72.1, 72.0, 71.6, 71.0 (C-2, C-3, C-4, C-5), 69.8 (C-6), 56.1 (OCH₃), 25.4 [C(CH₃)₂], 25.1 [C(CH₃)₂] ppm. C₂₄H₃₀O₆ (414.50): calcd. C 69.55, H 7.30; found C 69.57, H 7.31.

4-O-(2,6-Di-O-benzyl-3,4-O-isopropylidene-B-D-talopyranosyl)-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose Dimethyl Acetal (4b): Benzylation of 17 (2.0 g, 3.93 mmol) gave 4b (2.42 g, 90% yield) as a clear syrup after flash chromatography (6:4 hexane/ EtOAc). $R_{\rm f} = 0.34$ (6:4 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -6.3$ (c = 1.4, CHCl₃). ¹H NMR (200 MHz, CD₃CN): δ = 7.44–7.27 (m, 10 H, Ar-H), 4.73 (s, 2 H, PhCH₂), 4.67 (d, J_{1',2'} = 1.3 Hz, 1 H, 1'-H), 4.54 (s, 2 H, PhC H_2), 4.44 (dd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 4.34 (d, 1 H, 1-H), 4.29 (m, 1 H, 5-H), 4.19 (dd, $J_{2',3'}$ = 4.4 Hz, $J_{3',4'} = 6.1$ Hz, 1 H, 3'-H), 4.07 (dd, $J_{4',5'} = 2.7$ Hz, 1 H, 4'-H), 4.04 (dd, J_{3,4} = 1.6 Hz, 1 H, 3-H), 3.97–3.83 (m, 5 H, 5'-H, 6'b-H, 4-H, 6a-H, 6b-H), 3.72-3.61 (m, 2 H, 2'-H, 6'a-H), 3.32 (s, 3 H, OCH₃), 3.31 (s, 3 H, OCH₃), 1.39 [s, 3 H, C(CH₃)₂], 1.33 [s, 3 H, C(CH₃)₂], 1.31 [s, 3 H, C(CH₃)₂], 1.30 [s, 3 H, C(CH₃)₂], 1.28 [s, 3 H, C(CH₃)₂], 1.27 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CD₃CN): δ = 139.7 (Ar-C), 139.6 (Ar-C), 129.2 –128.2 (Ar-CH), 110.5 [C(CH₃)₂], 110.4 [C(CH₃)₂], 108.8, [C(CH₃)₂], 106.1 (C-1), 102.4 (C-1'), 78.4, 78.2, 77.3, 76.4 (C-2, C-3, C-4, C-5), 75.2 (PhCH₂), 73.7 (PhCH₂), 74.7, 74.4, 72.9, 72.1 (C-2', C-3', C-4', C-5'), 69.9 (C-6'), 66.1 (C-6), 56.0 (OCH₃), 54.34 (OCH₃), 27.4 [C(CH₃)₂], 27.2 [C(CH₃)₂], 26.9 [C(CH₃)₂], 26.1 [C(CH₃)₂], 26.0 [C(CH₃)₂], 25.3 [C(CH₃)₂] ppm. C₃₇H₅₂O₁₂ (688.81): calcd. C 64.52, H 7.61; found C 64.48, H 7.59.

Methyl 2-Acetamido-6-*O*-benzyl-2-deoxy-3,4-*O*-isopropylidene-β-Dtalopyranoside (4c): Benzylation of pure 20 (980 mg, 3.56 mmol) gave 4c (1.09 g, 84% yield) as a clear syrup after flash chromatography (2:8 hexane/EtOAc). $R_f = 0.10$ (2:8 hexane/EtOAc). $[\alpha]_{20}^{20} =$ +9.4 (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CD₃CN): δ = 7.38– 7.32 (m, 5 H, Ar-H), 6.71 (d, $J_{2,NH}$ = 9.3 Hz, 1 H, NH), 4.60, 4.53 (AB system, $J_{A,B}$ = 12.0 Hz, 2 H, PhC H_2), 4.49 (d, $J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.33 (dd, $J_{2,3}$ = 5.1 Hz, $J_{3,4}$ = 6.9 Hz, 1 H, 3-H), 4.26 (m, 1 H, H-2), 4.23 (dd, $J_{4,5}$ = 2.4 Hz, 1 H, 4-H), 4.05 (ddd, $J_{5,6a}$ = 6.7 Hz, $J_{5,6b}$ = 9.1 Hz, 1 H, 5-H), 3.73 (dd, $J_{6a,6b}$ = 10.2 Hz, 1 H, 6a-H), 3.66 (dd, 1 H, 6b-H), 3.37 (s, 3 H, OC H_3), 1.90 (s, 3 H, C H_3 CO), 1.41 [s, 3 H, C(C H_3)₂], 1.26 [s, 3 H, C(C H_3)₂] ppm. ¹³C NMR (50 MHz, CD₃CN): δ = 170.4 (C=O), 139.6 (Ar-C), 129.2– 128.4 (Ar-CH), 110.0 [C(CH₃)₂], 100.2 (C-1), 73.6 (PhCH₂), 73.0 (C-3), 72.7 (C-4), 71.9 (C-5), 70.4 (C-6), 56.5 (OCH₃), 48.3 (C-2), 26.1 [C(CH₃)₂], 25.4 [C(CH₃)₂], 23.3 (CH₃CO) ppm. C₁₉H₂₇NO₆ (365.43): calcd. C 62.45, H 7.55, N 3.83; found C 62.48, H 7.43, N 3.80.

Methyl 2,6-Di-*O*-benzyl-3,4-*O*-isopropylidene- α -D-talopyranoside (4e): Benzylation of 18 (impure because of its *galacto* epimer, 1.21 g, 5.16 mmol) gave a clear syrup showing a single spot by TLC analysis ($R_{\rm f} = 0.24$, 8:2 hexane/EtOAc). Flash chromatography of the crude (8:2 hexane/EtOAc) gave an inseparable mixture of 4e and its *galacto* epimer 4h^[18c] (1.71 g, 80% yield) in a 9:1 ratio, as estimated by NMR.

Data for 4e: ¹H NMR (200 MHz, CDCl₃): δ = 7.42–7.25 (m, 10 H, Ar-H), 4.83 (d, $J_{1,2}$ = 5.8 Hz, 1 H, 1-H), 4.81, 4.70 (AB system, $J_{A,B}$ = 12.4 Hz, 2 H, PhC H_2), 4.59, 4.52 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhC H_2), 4.47 (dd, 1 H, 3-H), 4.20 (dd, $J_{3,4}$ = 7.6 Hz, $J_{4,5}$ = 1.7 Hz, 1 H, 4-H), 3.71(ddd, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 7.0 Hz, 1 H, 5-H), 3.68 (dd, $J_{6a,6b}$ = 10.0 Hz, 1 H, 6a-H), 3.59 (dd, 1 H, 6b-H), 3.45 (s, 3 H, OC H_3), 3.43 (dd, $J_{2,3}$ = 2.8 Hz, 1 H, 2-H), 1.50 [s, 3 H, C(C H_3)₂], 1.33 [s, 3 H, C(C H_3)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 138.2 (Ar-C), 137.8 (Ar-C), 128.2–127.4 (Ar-CH), 110.4 [C(CH₃)₂], 101.4 (C-1), 75.0, 74.5, 74.4, 73.4 (C-2, C-3, C-4, C-5), 73.2 (PhCH₂), 72.3 (PhCH₂), 68.9 (C-6), 54.9 (OCH₃), 26.1 [C(CH₃)₂], 25.2 [C(CH₃)₂] ppm. C₂₄H₃₀O₆ (414.50): calcd. C 69.55, H 7.30; found C 69.53, H 7.28.

General Procedure for the De-O-isopropylidenation of 4a, 4c and 4e: The appropriate protected sugar (1 mmol) was dissolved in 80% aq AcOH (13 mL) and heated to 50 °C while stirring. After 3–5 h, TLC analysis revealed the complete disappearance of the starting material and formation of a more retained product. The solution was then cooled to room temperature and coevaporated with toluene (4×10 mL). The crude product was purified by flash chromatography.

Methyl 2,6-Di-*O*-benzyl-β-D-talopyranoside (5a): Hydrolysis of 4a (2.64 g, 6.36 mmol) gave 5a (2.37 g, 98% yield) as a clear syrup after flash chromatography (6:4 hexane/EtOAc). $R_{\rm f} = 0.17$ (6:4 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -82.3$ (c = 1.4, CHCl₃). ¹H NMR (200 MHz, CD₃CN): $\delta = 7.39-7.28$ (m, 10 H, Ar-H), 4.86, 4.66 (AB system, $J_{\rm A,B} = 11.4$ Hz, 2 H, PhCH₂), 4.55 (s, 2 H, PhCH₂), 4.36 (d, $J_{1,2} = 0.7$ Hz, 1 H, 1-H), 3.81 (m, 1 H, 2-H), 3.77–3.64 (m, 2 H, H-4, 6a-H), 3.61–3.53 (m, 3 H, 3-H,5- H, 6b-H), 3.50 (s, 3 H, OCH₃), 3.08 (br. s, 2 H, 2×OH) ppm. ¹³C NMR (50 MHz, CD₃CN): $\delta = 139.7$ (Ar-C), 139.5 (Ar-C), 129.2–128.4 (Ar-CH), 103.6 (C-1), 80.3 (C-2), 75.8 (C-5), 76.1 (PhCH₂), 73.7 (PhCH₂), 70.4 (C-6), 70.7, 69.8 (C-3, C-4), 57.2 (OCH₃) ppm. C₂₁H₂₆O₆ (374.43): calcd. C 67.36, H 7.00; found C 67.34, H 7.03.

4-*O*-(2,6-Di-*O*-benzyl-β-D-talopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (5b) and 4-*O*-(2,6-Di-*O*benzyl-β-D-talopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (23): A solution of 4b (1.13 g, 1.63 mmol) in 60% aq AcOH (22 mL) was stirred at room temperature. After 3 h, TLC analysis (2:8 hexane/EtOAc) revealed the complete disappearance of the starting material ($R_f = 0.65$) and formation of two products $(R_{\rm f} = 0.51 \text{ and } R_{\rm f} = 0.06)$. The reacting mixture was neutralised by the addition of aq 15% NaOH and extracted with EtOAc (4×20 mL). The organic phase was dried, filtered and concentrated in vacuo. Flash chromatography (EtOAc→95:5 EtOAc/MeOH) of the residue gave pure **5b** (652 mg, 62% yield), and **23** (314 mg, 31% yield).

Data for 5b: Clear syrup. $R_f = 0.51$ (2:8 hexane/EtOAc). $[\alpha]_D^{20} =$ -40.3 (c = 0.9, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.34$ -7.26 (m, 10 H, Ar-H), 4.77 (s, 1 H, 1'-H), 5.07, 4.61 (AB system, $J_{A,B} = 11.4 \text{ Hz}, 2 \text{ H}, \text{PhC}H_2$, 4.54 (m, 1 H, 2-H), 4.57, 4.50 (AB system, $J_{A,B} = 12.0$ Hz, 2 H, PhC H_2), 4.36 (d, $J_{1,2} = 6.1$ Hz, 1 H, 1-H), 4.30 (dt, $J_{4.5} = 2.3$ Hz, $J_{5.6a} = J_{5.6b} = 6.9$ Hz, 1 H, 5-H), 4.20 (m, 1 H, 4-H), 4.19-3.95 (m, 4 H, 2'-H, 3-H, 6a-H, 6b-H), 3.79-3.48 (m, 5 H, 3'-H, 4'-H, 5'-H, 6'a-H, 6'b-H), 3.32 (s, 6 H, $2 \times OCH_3$), 3.03 (d, J = 13.0 Hz, 1 H, OH), 2.97 (d, J = 12.1 Hz, 1 H, OH), 1.39 [s, 3 H, C(CH₃)₂], 1.35 [s, 3 H, C(CH₃)₂], 1.34 [s, 3 H, C(CH₃)₂], 1.33 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, $CDCl_3$): $\delta = 138.0$ (Ar-C), 137.7 (Ar-C), 128.5–127.6 (Ar-CH), 109.9 [C(CH₃)₂], 107.8 [C(CH₃)₂], 104.8 (C-1), 102.5 (C-1'), 78.9, 78.4, 77.5 (C-2', C-3, C-5), 75.1, 74.9, 74.8 (C-5', C-2, C-4), 75.7 (PhCH₂), 73.4 (PhCH₂), 69.3, 69.2 (C-3', C-4'), 68.4 (C-6'), 64.8 (C-6), 55.4 (OCH₃), 52.9 (OCH₃), 26.9 [C(CH₃)₂], 26.8 [C(CH₃)₂], 26.5 [C(CH₃)₂], 24.9 [C(CH₃)₂] ppm. C₃₄H₄₈O₁₂ (648.75): calcd. C 62.95, H 7.46; found C 62.97, H 7.48.

Data for 23: White solid. $R_f = 0.12$ (95:5 EtOAc/MeOH); m.p. 51– 53 °C (EtOAc/hexane). $[\alpha]_{D}^{20} = -36.3$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.35–7.26 (m, 10 H, Ar-H), 4.71 (s, 1 H, 1'-H), 5.05, 4.62 (AB system, $J_{A,B} = 11.3$ Hz, 2 H, PhC H_2), 4.54 (s, 2 H, PhC H_2), 4.52 (dd, $J_{1,2}$ = 5.7 Hz, $J_{2,3}$ = 7.7 Hz 1 H, 2-H), 4.39 (d, 1 H, 1-H), 4.22 (dd, J_{3,4} = 1.3 Hz, 1 H, 3-H), 4.03 (dd, J_{4,5} = 5.3 Hz, 1 H, 4-H), 3.98-3.42 (m, 9 H, 2'-H, 3'-H, 4'-H, 5'-H, 6'a-H, 6'b-H, 5-H, 6a-H, 6b-H), 3.35 (br. s, 1 H, OH), 3.34 (s, 6 H, 2×OCH₃), 3.20 (br. s, 3 H, 3× OH), 1.40 [s, 3 H, C(CH₃)₂], 1.39 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 137.9 (Ar-C), 137.6 (Ar-C), 128.5-127.7 (Ar-CH), 110.0 [C(CH₃)₂], 104.7 (C-1), 101.2 (C-1'), 79.0, 77.1 (C-2', C-3), 75.7 (PhCH₂), 73.5 (PhCH₂), 76.1, 75.3, 75.0, 72.8 (C-5', C-2, C-4, C-5), 69.3, 69.2 (C-3', C-4'), 68.8 (C-6'), 63.4 (C-6), 55.5 (OCH₃), 53.6 (OCH₃), 26.9 [C(CH₃)₂], 26.8 [C(CH₃)₂] ppm. C₃₁H₄₄O₁₂ (608.68): calcd. C 61.17, H 7.29; found C 61.13, H 7.27.

Methyl 2-Acetamido-6-*O*-benzyl-2-deoxy-β-D-talopyranoside (5c): Hydrolysis of **4c** (538 mg, 1.47 mmol) gave **5c** (2.37 g, quantitative yield) as a solid foam. $R_{\rm f} = 0.26$ (92:8 CH₂Cl₂/MeOH). $[\alpha]_{\rm D}^{20} = -50.6$ (c = 1.6, CHCl₃). ¹H NMR (200 MHz, CD₃CN): $\delta = 7.37-7.32$ (m, 5 H, Ar-H), 6.69 (d, $J_{2,\rm NH} = 9.6$ Hz, 1 H, NH), 4.55 (s, 2 H, PhCH₂), 4.34 (d, $J_{1,2} = 1.7$ Hz 1 H, 1-H), 4.27 (m, 1 H, 2-H), 3.74 (m, 1 H, 4-H), 3.62 (dd, $J_{2,3} = 4.3$ Hz, $J_{3,4} = 2.5$ Hz, 1 H, 3-H), 3.71–3.60 (m, 3 H, 5-H, 6a-H, 6b-H), 3.40 (s, 3 H, OCH₃), 1.88 (s, 3 H, CH₃CO) ppm. ¹³C NMR (50 MHz, CD₃CN): $\delta = 173.7$ (C=O), 139.1 (Ar-C), 129.3–128.6 (Ar-CH), 102.0 (C-1), 75.1 (C-5), 73.7 (PhCH₂), 70.5 (C-6), 69.1 (C-4), 68.5 (C-3), 57.1 (OCH₃), 52.8 (C-2), 23.5 (CH₃CO) ppm. C₁₆H₂₃NO₆ (325.36): calcd. C 59.07, H 7.13, N 4.30; found C 59.10, H 7.11, N 4.27.

Methyl 2,6-Di-*O***-benzyl-***a***-D-talopyranoside (5e):** Hydrolysis of the 9:1 **4e/4h** mixture (1.32 g, 3.18 mmol) yielded a crude residue constituted by a 9:1 mixture of **5e/5h**.^[25c] Flash chromatography (1:1 hexane/EtOAc) gave pure **5e** (1.05 g, 88% yield) as a white solid. $R_{\rm f} = 0.37$ (1:1 hexane/EtOAc); m.p. 73–75 °C. $[a]_{\rm D}^{20} = +11.2$ (c = 1.1, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.35–7.24$ (m, 10 H, Ar-H), 4.85 (d, $J_{1,2} = 1.4$ Hz, 1 H, 1-H), 4.69, 4.57 (AB system, $J_{\rm A,B} = 11.4$ Hz, 2 H, PhC H_2), 4.63, 4.53 (AB system, $J_{\rm A,B} = 11.9$ Hz, 2 H, PhC H_2), 3.91 (bt, 1 H, 5-H), 3.82 (bt, 1 H, 3-H),

3.83–3.68 (m, 4 H, 2-H, 4-H, 6a-H, 6b-H), 3.37 (s, 3 H, OCH₃), 3.12 (d, $J_{3,OH} = 10.9$ Hz, 1 H, OH-3), 2.98 (d, $J_{4,OH} = 11.3$ Hz, 1 H, OH-4) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 138.1$ (Ar-C), 136.9 (Ar-C), 128.5–127.5 (Ar-CH), 98.4 (C-1), 78.5 (C-2), 73.7 (PhCH₂), 73.4 (PhCH₂), 70.4, 70.1 (C-3, C-5), 69.8 (C-6), 66.0 (C-4), 55.0 (OCH₃) ppm. C₂₁H₂₆O₆ (374.43): calcd. C 67.36, H 7.00; found C 67.33, H 7.02.

Methyl 3,6-Di-O-benzyl-2-deoxy-β-D-lyxo-hexopyranoside (5i): Method A [with MeOH/TsOH]: Compound 4i^[18d] (774 mg, 2.51 mmol) was dissolved in MeOH (7.5 mL), treated with TsOH (15 mg), and the reacting mixture was stirred at room temperature for 3 $h.^{\left[18d\right]}$ Et_3N (0.5 mL) was added, and the resulting solution was stirred for an additional 10 min. The mixture was concentrated in vacuo to give a yellow syrup showing a single spot by TLC analysis ($R_f = 0.23$, 1:9 hexane/EtOAc). Flash chromatography (1:9 hexane/EtOAc) gave a white solid mixture of diols 5i and 22 (541 mg, 80% yield) in a 85:15 ratio, as estimated by NMR spectroscopy. In a repetition of the experiment, the solution was stirred at room temperature for 30 h and a 35:65 mixture of 5i and 22 was obtained. Selected ¹H NMR signals (200 MHz, CDCl₃): δ = 4.85 (22, t, $J_{1,2ax} = J_{1,2eq} = 2.3$ Hz, 1 H, 1-H), 4.34 (5i, dd, $J_{1,2ax} =$ 9.7 Hz, $J_{1,2eq} = 2.3$ Hz, 1 H, 1-H) ppm. Selected ¹³C NMR signals $(50 \text{ MHz}, \text{CDCl}_3)$: $\delta = 101.2$ (5i, C-1), 98.7 (22, C-1), 73.5 (5i, C-5), 70.6 (22, C-6), 69.7 (5i, C-6), 68.5, 67.8 (5i, C-3, C-4), 69.0, 68.5, 65.5 (22, C-3, C-4, C-5), 56.5 (5i, OCH₃), 54.7 (22, OCH₃), 34.7 (5i, C-2), 32.7 (22, C-2) ppm. Method B [with 2,3-dichloro-5,6dicyano-1,4-benzoquinone (DDQ)]: Compound 4i^[18d] (820 mg, 2.66 mmol) was dissolved in a CH₃CN/H₂O (9:1, 16 mL), treated with DDQ (31 mg), and the resulting dark red reaction mixture was stirred at room temperature. After 7 h, a TLC analysis (2:8 hexane/EtOAc) revealed the complete disappearance of the starting material. The solution was then decolourised by the addition of charcoal (400 mg), and the mixture was stirred at room temperature for an additional 30 min. The suspension was filtered, and the solution was concentrated in vacuo. The residue (525 mg) was purified by flash chromatography (1:9 hexane/EtOAc) and gave pure 5i (606 mg, 85% yield) as a white solid. $R_{\rm f} = 0.23$ (1:9 hexane/ EtOAc); m.p. 81–82 °C, $[\alpha]_D^{20} = -42.4$ (c = 1.1, CHCl₃); ref.^[18d] $[\alpha]_{D}^{20} = -33$ (c = 3.6, CHCl₃), m.p. 81–82 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.36–7.29 (m, 5 H, Ar-H), 4.58 (s, 2 H, PhCH₂), 4.32 (dd, $J_{1,2eq} = 2.2$ Hz, $J_{1,2ax} = 9.7$ Hz, 1 H, 1-H), 3.81 (m, 1 H, 4-H), 3.68 (m, 1 H, 3-H), 3.75-3.50 (m, 3 H, 5-H, 6a-H, 6b-H), 3.50 (s, 3 H, OCH₃), 3.05 (d, $J_{4,OH}$ = 5.9 Hz, 1 H, OH-4), 2.90 (d, $J_{3,OH}$ = 8.6 Hz 1 H, OH-3), 2.00 (ddd, $J_{2ax,2eq} = 12.2$ Hz, $J_{2eq,3} = 5.0$ Hz, 1 H, 2eq-H), 1.70 (ddd, $J_{2ax,3}$ = 12.6 Hz, 1 H, 2ax-H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 137.8 (Ar-C), 128.1–127.4 (Ar-CH), 101.0 (C-1), 73.5 (C-5), 73.2 (PhCH2), 69.6 (C-6), 68.3, 67.5 (C-3, C-4), 56.2 (OCH₃), 34.3 (C-2) ppm. C₁₄H₂₀O₅ (268.31): calcd. C 62.67, H 5.71; found C 62.65, H 5.72.

General Procedure for the Stannylidenation–Benzylation of 5a–i: A mixture of the appropriate diol (1 mmol) and dibutyltin oxide (1.28 equiv.) in toluene (15 mL) was heated to reflux with a Dean–Stark apparatus overnight. Tetrabutylammonium bromide (0.5 equiv.) and benzyl bromide (1.36 equiv.) were added, and the reaction mixture was stirred at reflux until TLC analysis revealed the complete disappearance of the starting material (5–6 h). The solution was cooled to room temperature, concentrated to dryness, and the resulting residue was purified by flash chromatography, eluting first with hexane (100 mL) and then with the appropriate eluent.

Methyl 2,3,6-Tri-O-benzyl-β-D-talopyranoside (6a): Selective benzylation of 5a (1.19 g, 3.18 mmol) gave 6a (1.44 g, 97% yield) as a clear syrup after flash chromatography (7:3 hexane/EtOAc). $R_{\rm f} = 0.23$ (7:3 hexane/EtOAc). $[\alpha]_{10}^{20} = -47.1$ (c = 1.5, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.41-7.25$ (m, 15 H, Ar-H), 4.95, 4.80 (AB system, $J_{\rm A,B} = 11.9$ Hz, 2 H, PhC H_2), 4.59 (s, 2 H, PhC H_2), 4.67, 4.48 (AB system, $J_{\rm A,B} = 12.1$ Hz, 2 H, PhC H_2), 4.25 (d, $J_{1,2} = 0.7$ Hz, 1 H, 1-H), 4.05–3.91 (m, 3 H, 2-H, 4-H, 6a-H), 3.84 (dd, $J_{6a,6b} = 13.2$ Hz, 1 H, 6b-H), 3.73 (d, $J_{4,\rm OH} = 10.3$ Hz, 1 H, OH), 3.56 (s, 3 H, OCH₃), 3.47 (dt, $J_{4,5} = 1.0$ Hz, $J_{5,6a} = J_{5,6b} = 6.0$ Hz, 1 H, 5-H), 3.33 (t, $J_{2,3} = J_{3,4} = 3.0$ Hz, 1 H, 3-H) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 138.1$ (Ar-C), 137.8 (Ar-C), 137.7 (Ar-C), 128.3–126.8 (Ar-CH), 102.5 (C-1), 76.4 (C-2), 75.7, 75.6 (C-3, C-5), 75.1 (PhCH₂), 73.6 (PhCH₂), 69.4, 69.3 (C-6, PhCH₂), 66.8 (C-4), 57.0 (OCH₃) ppm. C₂₈H₃₂O₆ (464.56): calcd. C 72.39, H 6.94; found C 72.37, H 6.93.

4-O-(2,3,6-Tri-O-benzyl-β-D-talopyranosyl)-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose Dimethyl Acetal (6b): Selective benzylation of 5b (640 mg, 0.98 mmol) gave 6b (716 mg, 98% yield) as a white solid after flash chromatography (7:3 hexane/EtOAc). $R_{\rm f}$ = 0.19 (7:3 hexane/EtOAc); m.p. 90–94 °C. $[\alpha]_{D}^{20} = -31.2$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.44–7.25 (m, 15 H, Ar-H), 4.93, 4.81 (AB system, $J_{A,B} = 11.6$ Hz, 2 H, PhC H_2), 4.66 (s, 1 H, 1'-H), 4.52 (m, 1 H, 2-H), 4.58, 4.49 (AB system, $J_{A,B}$ = 11.9 Hz, 2 H, PhC H_2), 4.64, 4.48 (AB system, $J_{A,B} = 12.3$ Hz, 2 H, PhC H_2), 4.34 (d, $J_{1,2}$ = 6.0 Hz, 1 H, 1-H), 4.25 (dt, $J_{5.6a}$ = $J_{5.6b}$ = 6.9 Hz, 1 H, 5-H), 4.13 (dd, $J_{3,4} = 1.4$ Hz, $J_{4,5} = 2.4$ Hz, 1 H, 4-H), 4.07–3.97 (m, 4 H, 2'-H, 5'-H, 6a-H, 6b-H), 3.93 (dd, $J_{2,3}$ = 7.6 Hz, 1 H, 3-H), 3.81 (dd, $J_{6'a,6'b} = 9.3$ Hz, $J_{5',6'b} = 7.1$ Hz, 1 H, 6'b-H), 3.77 (d, $J_{4',OH}$ = 10.7 Hz, 1 H, OH), 3.59 (dd, $J_{5',6'a}$ = 5.2 Hz, 1 H, 6'a-H), 3.46 (m, 1 H, 4'-H), 3.29 (s, 6 H, 2×OCH₃), 3.27 (t, $J_{2',3'} = J_{3',4'} = 2.9$ Hz, 1 H, 3'-H), 1.36 [s, 3 H, C(CH₃)₂], 1.35 [s, 3 H, $C(CH_3)_2$], 1.33 [s, 3 H, $C(CH_3)_2$], 1.28 [s, 3 H, $C(CH_3)_2$ ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 138.2$ (Ar-C), 138.0 (Ar-C), 137.8 (Ar-C), 128.4–127.6 (Ar-CH), 110.0 [C(CH₃)₂], 107.8 [C(CH₃)₂], 104.7 (C-1), 102.1 (C-1'), 78.4, 77.6, 76.6 (C-2', C-3, C-5), 75.7, 75.3, 74.9, 74.7 (C-3', C-5', C-2, C-4), 75.2 (PhCH₂), 73.5 (PhCH₂), 69.4, 68.6 (C-6', PhCH₂), 66.6 (C-4'), 64.9 (C-6), 55.4 (OCH₃), 52.8 (OCH₃), 27.0 [C(CH₃)₂], 26.7 [C(CH₃)₂], 26.5 [C(CH₃)₂], 24.9 [C(CH₃)₂] ppm. C₄₁H₅₄O₁₂ (738.87): calcd. C 66.65, H 7.37; found C 66.61, H 7.36.

Methyl 2-Acetamido-3,6-di-O-benzyl-2-deoxy-β-D-talopyranoside (6c): Selective benzylation of 5c (471 mg, 1.45 mmol) gave 6c (481 mg, 80% yield) as a clear syrup after flash chromatography (2:8 hexane/EtOAc). $R_{\rm f} = 0.13$ (2:8 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -81.5$ $(c = 1.0, \text{CHCl}_3)$. ¹H NMR (200 MHz, CDCl₃): $\delta = 7.35-7.27$ (m, 10 H, Ar-H), 6.73 (d, $J_{2,\rm NH}$ = 9.9 Hz, 1 H, NH), 4.79 (ddd, $J_{1,2}$ = 1.6 Hz, $J_{2,3} = 4.2$ Hz, 1 H, 2-H), 4.72, 4.37 (AB system, $J_{A,B} =$ 11.8 Hz, 2 H, PhCH₂), 4.57 (s, 2 H, PhCH₂), 4.25 (d, 1 H, 1-H), 3.89 (m, 1 H, 4-H), 3.81 (dd, $J_{6a.6b} = 9.8$ Hz, $J_{5.6b} = 5.7$ Hz, 1 H, 6b-H), 3.74 (dd, $J_{5.6a}$ = 5.4 Hz, 1 H, 6a-H), 3.50 (s, 3 H, OCH₃), 3.49 (m, 2 H, H-5, OH), 3.38 (dd, $J_{3,4}$ = 3.2 Hz, 1 H, 3-H), 2.00 (s, 3 H, CH₃CO) ppm. ¹³C NMR (50 MHz, CD₃CN): δ = 170.7 (C=O), 137.6 (Ar-C), 137.0 (Ar-C), 128.4-127.6 (Ar-CH), 101.3 (C-1), 73.9 (C-5), 73.8 (C-3), 69.7 (C-6), 73.5 (PhCH₂), 69.2 (PhCH₂), 67.6 (C-4), 56.8 (OCH₃), 47.7 (C-2), 23.5 (CH₃CO) ppm. C₂₃H₂₉NO₆ (415.48): calcd. C 66.49, H 7.04, N 3.37; found C 66.52, H 7.02, N 3.34.

Methyl 2,3,6-Tri-*O*-benzyl- α -D-talopyranoside (6e) and Methyl 2,4,6-Tri-*O*-benzyl- α -D-talopyranoside (24): Stannylidenation-benzylation of **5e** (520 mg, 1.39 mmol) gave a crude residue showing two spots by TLC ($R_f = 0.31$ and 0.21, 7:3 hexane/EtOAc). After chromatography (7:3 hexane/EtOAc), **6e** (527 mg, 82% yield) and 24 (57 mg, 9% yield) were isolated.

Data for 6e: Clear syrup; $R_f = 0.31$ (7:3 hexane/EtOAc). $[a]_D^{20} = +36.2$ (*c* = 1.1, CHCl₃). ¹H NMR (200 MHz, CD₃CN): δ = 7.42–7.28 (m, 15 H, Ar-H), 4.85 (d, $J_{1,2} = 1.7$ Hz, 1 H, 1-H), 4.76, 4.69 (AB system, $J_{A,B} = 11.5$ Hz, 2 H, PhC H_2), 4.67, 4.54 (AB system, $J_{A,B} = 11.8$ Hz, 2 H, PhC H_2), 4.67, 4.54 (AB system, $J_{A,B} = 11.8$ Hz, 2 H, PhC H_2), 4.54 (s, 2 H, PhC H_2), 3.95 (m, 1 H, 4-H), 3.82 (m, 1 H, 5-H), 3.79 (dd, $J_{2,3} = 4.8$ Hz, 1 H, 2-H), 3.69 (dd, $J_{6a,6b} = 9.9$ Hz, $J_{5,6a} = 5.1$ Hz, 1 H, 6a-H), 3.68 (s, 3 H, OC H_3), 3.67 (dd, $J_{3,4} = 5.0$ Hz, 1 H, 3-H), 3.64 (dd, $J_{5,6b} = 7.1$ Hz, 1 H, 6b-H), 3.49 (d, $J_{4,OH} = 10.0$ Hz, 1 H, OH) ppm. ¹³C NMR (50 MHz, CD₃CN): δ = 139.7 (Ar-C), 139.6 (Ar-C), 139.0 (Ar-C), 129.4–128.4 (Ar-CH), 100.1 (C-1), 77.5 (C-2), 74.2 (C-3), 74.3 (PhCH₂), 73.7 (PhCH₂), 71.4 (C-5), 70.9, 70.2 (C-6, PhCH₂), 68.5 (C-4), 55.2 (OCH₃) ppm. C₂₈H₃₂O₆ (464.56): calcd. C 72.39, H 6.94; found C 72.36, H 6.95.

Data for 24: Clear syrup; $R_f = 0.21$ (7:3 hexane/EtOAc). $[a]_{20}^{20} = +15.3$ (c = 0.9, CHCl₃). ¹H NMR (200 MHz, CD₃CN): $\delta = 7.39-7.24$ (m, 15 H, Ar-H), 4.83 (d, $J_{1,2} = 1.6$ Hz, 1 H, 1-H), 4.67, 4.54 (AB system, $J_{A,B} = 11.6$ Hz, 2 H, PhC H_2), 4.69, 4.52 (AB system, $J_{A,B} = 11.3$ Hz, 2 H, PhC H_2), 4.57, 4.50 (AB system, $J_{A,B} = 11.8$ Hz, 2 H, PhC H_2), 3.94 (dt, $J_{5,6a} = J_{5,6b} = 6.2$ Hz, 1 H, 5-H), 3.82 (t, $J_{2,3} = J_{3,4} = 4.0$ Hz, 1 H, 3-H), 3.68 (dd, $J_{4,5} = 1.8$ Hz, 1 H, 4-H), 3.62 (m, 2 H, 6a-H, 6b-H), 3.48 (dd, 1 H, 2-H), 3.31 (s, 3 H, OC H_3), 2.42 (br. s, 1 H, OH) ppm. ¹³C NMR (50 MHz, CD₃CN): $\delta = 140.1$ (Ar-C), 139.5 (Ar-C), 139.4 (Ar-C), 129.3–128.3 (Ar-CH), 99.6 (C-1), 78.1, 77.5 (C-2, C-4), 75.8 (PhCH₂), 73.8 (PhCH₂), 73.7 (PhCH₂), 70.3 (C-6), 70.1 (C-5), 67.4 (C-3), 55.2 (OCH₃) ppm. C₂₈H₃₂O₆ (464.56): calcd. C 72.39, H 6.94; found C 72.38, H 6.93.

Methyl 2,3,6-Tri-O-benzyl-β-D-galactopyranoside (6f): Selective benzylation of **5f**^[25a] (3.91 g, 10.46 mmol) gave **6f** (4.47 g, 92% yield) as a clear syrup after flash chromatography (7:3 hexane/ EtOAc). $R_{\rm f} = 0.37$ (7:3 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = +3.3$ (c = 1.0, CHCl₃); ref.^[26] $[\alpha]_D^{20} = +3.4$ (*c* = 3.6, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.36–7.22 (m, 15 H, Ar-H), 4.89, 4.71 (AB system, $J_{A,B} = 11.0 \text{ Hz}, 2 \text{ H}, \text{PhC}H_2$, 4.70 (s, 2 H, PhC H_2), 4.58 (s, 2 H, PhCH₂), 4.27 (d, J_{1.2} = 7.6 Hz, 1 H, 1-H), 4.00 (dd, 1 H, 4-H), 3.80 (dd, $J_{6a,6b}$ = 9.9 Hz, $J_{5,6a}$ = 5.5 Hz, 1 H, 6a-H), 3.72 (dd, $J_{5,6b}$ = 6.0 Hz, 1 H, 6b-H), 3.64 (dd, $J_{2,3} = 9.4$ Hz, 1 H, 2-H), 3.56 (s, 3 H, OCH₃), 3.54 (ddd, $J_{4,5} = 1.1$ Hz, 1 H, 5-H), 3.48 (dd, $J_{3,4} =$ 3.3 Hz, 1 H, 3-H), 2.60 (br. s, 1 H, OH) ppm. ¹³C NMR (50 MHz, $CDCl_3$): $\delta = 138.5$ (Ar-C), 137.9 (Ar-C), 137.8 (Ar-C), 128.4–127.5 (Ar-CH), 104.6 (C-1), 80.4 (C-2), 78.9 (C-3), 73.0 (C-5), 75.0 (PhCH₂), 73.6 (PhCH₂), 72.3 (PhCH₂), 69.1 (C-6), 66.7 (C-4), 56.9 (OCH_3) ppm.

4-O-[2,3,6-Tri-O-benzyl-β-D-galactopyranosyl)-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose Dimethyl Acetal (6g): Selective benzylation of 5g^[25b] (2.0 g, 3.08 mmol) gave 6g (2.1 g, 92% yield) as a clear syrup after flash chromatography (6:4 hexane/EtOAc). $R_{\rm f}$ = 0.47 (4:6 hexane/EtOAc). $[\alpha]_{D}^{20} = +1.3$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.39–7.25 (m, 15 H, Ar-H), 4.68 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, 1'-H), 4.72, 4.65 (AB system, $J_{A,B}$ = 11.7 Hz, 2 H, PhC H_2), 4.91, 4.63 (AB system, $J_{A,B} = 11.2$ Hz, 2 H, PhC H_2), 4.54 (dd, $J_{1,2}$ = 6.4 Hz, $J_{2,3}$ = 7.1 Hz, 1 H, 2-H), 4.59, 4.50 (AB system, $J_{A,B} = 11.9 \text{ Hz}, 2 \text{ H}, \text{PhC}H_2$, 4.34 (d, 1 H, 1-H), 4.29 (m, 1 H, 5-H), 4.20–3.92 (m, 5 H, 4'-H, 3-H, 4-H, 6a-H, 6b-H), 3.75 (dd, J_{2',3'} = 9.4 Hz, 1 H, 2'-H), 3.68-3.54 (m, 3 H, 5'-H, 6'a-H, 6'b-H), 3.48 (dd, $J_{3',4'}$ = 3.4 Hz, 1 H, 3'-H), 3.31 (s, 3 H, OCH₃), 3.30 (s, 3 H, OCH_3), 2.52 (d, $J_{4',OH}$ = 2.1 Hz, 1 H, OH), 1.43 [s, 3 H, C(CH₃)₂], 1.41 [s, 3 H, C(CH₃)₂], 1.40 [s, 3 H, C(CH₃)₂], 1.32 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 138.6 (Ar-C), 138.5 (Ar-C), 137.8 (Ar-C), 128.2–127.5 (Ar-CH), 110.2 [C(CH₃)₂], 108.4 [C(CH₃)₂], 105.1 (C-1), 103.1 (C-1'), 80.8, 79.3, 77.8, 77.5 (C-

2', C-3', C-2, C-3), 74.7, 74.2 (C4, C-5), 72.7 (C-5'), 75.3 (PhCH₂), 73.6 (PhCH₂), 72.3 (PhCH₂), 68.4 (C-6'), 66.4 (C-4'), 65.5 (C-6), 55.4 (OCH₃), 52.6 (OCH₃), 27.5 [C(CH₃)₂], 26.7 [C(CH₃)₂], 26.6 [C(CH₃)₂], 25.3 [C(CH₃)₂] ppm. C₄₁H₅₄O₁₂ (738.87): calcd. C 66.65, H 7.37; found C 66.62, H 7.35.

Methyl 2,3,6-Tri-O-benzyl-a-D-galactopyranoside (6h): Selective benzylation of **5h**^[25c] (1.86 g, 4.97 mmol) gave **6h** (2.11 g, 91% yield) as a clear syrup after flash chromatography (7:3 hexane/ EtOAc). $R_{\rm f} = 0.23$ (7:3 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = +32.7$ (c = 1.1, CHCl₃); ref.^[26] $[\alpha]_{D}^{20} = +34$ (c = 3.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.38–7.25 (m, 15 H, Ar-H), 4.80, 4.69 (AB system, $J_{A,B} = 11.6 \text{ Hz}, 2 \text{ H}, \text{PhC}H_2$, 4.68 (dd, $J_{1,2} = 4.1 \text{ Hz}, 1 \text{ H}, 1 \text{-H}$), 4.82, 4.66 (AB system, $J_{A,B} = 12.1 \text{ Hz}$, 2 H, PhCH₂), 4.60, 4.53 (AB system, $J_{A,B} = 11.0$ Hz, 2 H, PhC H_2), 4.05 (m, 1 H, 4-H), 3.86–3.92 (m, 3 H, 2-H, 3-H, 5-H), 3.73 (dd, $J_{6a,6b} = 9.9$ Hz, $J_{5,6b}$ = 6.3 Hz, 1 H, 6b-H), 3.66 (dd, $J_{5,6a}$ = 5.2 Hz, 1 H, 6a-H), 3.38 (s, 3 H, OCH₃), 2.62 (br. s, 1 H, OH) ppm. ¹³C NMR (50 MHz, $CDCl_3$): $\delta = 138.2$ (Ar-C), 138.0 (Ar-C), 137.8 (Ar-C), 128.3–127.5 (Ar-CH), 98.4 (C-1), 77.5, 75.6 (C-2, C-3), 73.5 (PhCH₂), 73.4 (PhCH₂), 72.6 (PhCH₂), 69.5 (C-6), 68.2, 67.9 (C-4, C-5), 55.2 (OCH₃) ppm.

Methyl 3,6-Di-O-benzyl-2-deoxy-β-D-lyxo-hexopyranoside (6i): Selective benzylation of 5i (600 mg, 2.24 mmol) gave 6i (787 mg, 98% yield) as a clear syrup after flash chromatography (6:4 hexane/ EtOAc). $R_{\rm f} = 0.36$ (6:4 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -11.9$ (c = 1.1, CHCl₃), ref.^[18d] $[\alpha]_{D}^{20} = -13$. ¹H NMR (200 MHz, CDCl₃): $\delta =$ 7.30-7.26 (m, 10 H, Ar-H), 4.60 (s, 2 H, PhCH₂), 4.64, 4.57 (AB system, $J_{A,B} = 12.1 \text{ Hz}$, 2 H, PhC H_2), 4.33 (dd, $J_{1,2eq} = 2.3 \text{ Hz}$, $J_{1,2ax} = 9.5$ Hz, 1 H, 1-H), 4.00 (m, 1 H, 5-H), 3.84 (dd, $J_{6a,6b} =$ 9.9 Hz, $J_{5,6b} = 5.9$ Hz, 1 H, 6b-H), 3.83 (dd, $J_{5,6a} = 5.9$ Hz, 1 H, 6a-H), 3.53 (ddd, $J_{3,4}$ = 3.0 Hz, $J_{2eq,3}$ = 5.0 Hz, $J_{2ax,3}$ = 11.9 Hz, 1 H, 3-H), 3.50 (s, 3 H, OCH₃), 3.49 (dd, $J_{4,5} = 5.3$ Hz, 1 H, 4-H), 2.03 (ddd, 1 H, J_{2ax,2eq} = 12.3 Hz, 2eq-H), 1.83 (ddd, 1 H, 2ax-H), 1.64 (br. s, 1 H, OH) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 138.0 (Ar-C), 137.6 (Ar-C), 128.5-126.7 (Ar-CH), 101.0 (C-1), 75.0, 73.7 (C-3, C-5), 73.7 (PhCH₂), 69.9, 69.5 (C-6, PhCH₂), 64.9 (C-4), 56.4 (OCH₃), 32.0 (C-2) ppm. $C_{21}H_{26}O_5$ (358.43): calcd. C 70.37, H 7.31; found C 70.34, H 7.32.

General Procedure for the Activation-Elimination Reaction of 6a-i: Sodium hydride (200 mg of a 60% dispersion in mineral oil, 5.0 mmol), was washed with dry hexane (4×1 mL) and suspended in dry DMF (5 mL). The mixture was treated with a solution of the appropriate alcohol (1.0 mmol) in dry DMF (20 mL) at room temperature under argon. The resulting mixture was stirred at room temperature for 30 min and then cooled to -30 °C. Solid Im₂SO₂ (290 mg, 1.46 mmol) was added, and the reacting mixture was stirred at -30 °C for an additional 1 h. The mixture was warmed to room temperature and further stirred until TLC analysis revealed the complete formation of a faster-moving product (see Table 1). The reaction was quenched by the addition of MeOH (1 mL), and the resulting solution was poured onto a mixture of ice and diethyl ether (20 mL). The two phases were separated, and the aqueous solution was further extracted with diethyl ether $(1 \times 20 \text{ mL})$. The organic extracts were dried, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-β-D-*threo*-hex-3-enopyranoside (25a): Activation–elimination of 6a (464 mg, 1.0 mmol) gave 25a (423 mg, 95% yield) as a clear syrup after chromatography (7:3 hexane/EtOAc + 0.1% Et₃N). $R_{\rm f} = 0.47$ (6:4 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -1.6$ (c = 1.1, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.38-7.21$ (m, 15 H, Ar-H), 4.92 (d, $J_{4.5} = 1.7$ Hz, 1 H, 4-H), 4.88, 4.79

(AB system, $J_{A,B} = 12.5$ Hz, 2 H, PhC H_2), 4.76, 4.68 (AB system, $J_{A,B} = 11.5$ Hz, 2 H, PhC H_2), 4.65, 4.56 (AB system, $J_{A,B} = 11.9$ Hz, 2 H, PhC H_2), 4.51 (d, 1 H, 1-H), 4.42 (m, 1 H, 5-H), 3.97 (t, $J_{1,2} = J_{2,5} = 1.9$ Hz, 1 H, 2-H), 3.72 (dd, $J_{6a,6b} = 9.7$ Hz, $J_{5,6a} = 5.6$ Hz, 1 H, 6a-H), 3.59 (s, 3 H, OC H_3), 3.55 (dd, $J_{5,6b} = 6.2$ Hz, 1 H, 6b-H) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 152.1$ (C-3), 138.8 (Ar-C), 138.0 (Ar-C), 136.3 (Ar-C), 128.2–127.6 (Ar-CH), 101.6 (C-1), 98.6 (C-4), 73.4 (PhCH₂), 73.1 (PhCH₂), 72.6 (PhCH₂), 72.5, 72.1 (C-2, C-5), 69.1 (C-6), 56.7 (OCH₃) ppm. C₂₈H₃₀O₅ (446.54): calcd. C 75.31, H 6.77; found C 75.32, H 6.76.

4-O-[2,3,6-Tri-O-benzyl-4-deoxy-β-D-threo-hex-3-enopyranosyl)-2,3:5,6-di-O-isopropylidene-aldehydo-D-glucose Dimethyl Acetal (25b): Activation-elimination of 6b (600 mg, 0.81 mmol) gave 25b (525 mg, 90% yield) as a clear syrup after chromatography (6:4 hexane/EtOAc + 0.1% Et₃N). $R_{\rm f} = 0.42$ (6:4 hexane/EtOAc). $[\alpha]_{\rm D}^{20}$ = +4.3 (c = 1.2, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 7.39– 7.20 (m, 15 H, Ar-H), 4.99 (d, $J_{4',5'}$ = 1.5 Hz, 1 H, H-4'), 4.90 (d, $J_{1',2'} = 1.9$ Hz, 1 H, 1'-H), 4.91, 4.79 (AB system, $J_{A,B} = 12.3$ Hz, 2 H, PhC H_2), 4.77, 4.69 (AB system, $J_{A,B}$ = 13.2 Hz, 2 H, PhC H_2), 4.66 (dd, $J_{1,2} = 6.0$ Hz, $J_{2,3} = 7.5$ Hz, 1 H, 2-H), 4.60, 4.52 (AB system, $J_{A,B} = 12.2$ Hz, 2 H, PhCH₂), 4.37 (d, 1 H, 1-H), 4.33 (m, 1 H, 5'-H-), 4.30 (dt, $J_{4,5} = 2.7$ Hz, $J_{5,6a} = J_{5,6b} = 6.9$ Hz, 1 H, 5-H), 4.18-3.95 (m, 5 H, 2'-H, 3-H, 4-H, 6a-H, 6b-H), 3.68 (dd, $J_{6'a,6'b} = 9.5$ Hz, $J_{5',6'a} = 5.3$ Hz, 1 H, 6'a-H), 3.47 (dd, $J_{5',6'b} =$ 6.6 Hz, 1 H, 6'b-H), 3.34 (s, 3 H, OCH₃), 3.32 (s, 3 H, OCH₃), 1.42 [s, 3 H, C(CH₃)₂], 1.38 [s, 3 H, C(CH₃)₂], 1.35 [s, 3 H, C(CH₃)₂], 1.34 [s, 3 H, C(CH₃)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 152.4 (C-3'), 138.7 (Ar-C), 138.1 (Ar-C), 136.5 (Ar-C), 128.3-127.2 (Ar-CH), 110.2 [C(CH₃)₂], 107.8 [C(CH₃)₂], 104.8 (C-1), 101.6 (C-1'), 99.3 (C-4'), 78.3, 77.7 (C-2, C-3), 74.9, 74.8 (C-4, C-5), 73.3 (PhCH₂), 73.1 (PhCH₂), 72.7 (PhCH₂), 72.9, 72.7 (C-2', C-5'), 69.2 (C-6'), 65.0 (C-6), 55.3 (OCH₃), 52.9 (OCH₃), 27.2 [C(CH₃)₂], 26.6 [C(CH₃)₂], 26.5 [C(CH₃)₂], 25.1 [C(CH₃)₂] ppm. C₄₁H₅₂O₁₁ (720.86): calcd. C 68.31, H 7.27; found C 68.33, H 7.25.

Methyl 2-Acetamido-3,6-di-O-benzyl-2,4-dideoxy-B-D-threo-hex-3enopyranoside (25c): Activation–elimination reaction of 6c (360 mg, 0.86 mmol) gave 25c (317 mg, 93% yield) as a clear syrup after flash chromatography (2:8 hexane/EtOAc + 0.1% Et₃N). $R_{\rm f} = 0.21$ (2:8 hexane/EtOAc). $[\alpha]_{D}^{20} = +2.2$ (c = 1.1, CHCl₃). ¹H NMR (200 MHz, CD₃CN): δ = 7.38–7.29 (m, 10 H, Ar-H), 6.32 (d, $J_{2,\rm NH}$ = 9.0 Hz, 1 H, NH), 4.86 (d, $J_{4,5}$ = 1.8 Hz, 1 H, 4-H), 4.80, 4.70 (AB system, $J_{A,B} = 12.0$ Hz, 2 H, PhC H_2), 4.58 (d, $J_{1,2} = 1.9$ Hz, 1 H, 1-H), 4.58-4.50 (m, 3 H, H-2, PhCH₂), 4.42 (m, 1 H, 5-H), 3.57 (dd, $J_{6a,6b}$ = 9.9 Hz, $J_{5,6 b}$ = 6.1 Hz, 1 H, 6b-H), 3.50 (dd, $J_{5,6a}$ = 4.9 Hz, 1 H, 6a-H), 3.41 (s, 3 H, OCH_3), 1.82 (s, 3 H, CH_3CO) ppm. ¹³C NMR (50 MHz, CD₃CN): δ = 152.6 (C-3), 138.7 (Ar-C), 137.2 (Ar-C), 128.7-127.2 (Ar-CH), 100.1 (C-1), 97.3 (C-4), 73.4 (PhCH₂), 73.3 (PhCH₂), 72.2 (C-5), 69.2 (C-6), 55.9 (OCH₃), 48.6 (C-2), 22.8 (CH₃CO) ppm. C₂₃H₂₇NO₅ (397.47): calcd. C 69.50, H 6.85, N 3.52; found C 69.48, H 6.87, N 3.49.

4-O-(2-Acetamido-3,6-di-O-benzyl-2,4-dideoxy-β-D-*threo*-hex-3enopyranosyl)-2,3:5,6-di-O-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (25d): Activation–elimination reaction of 5d^[17b] (525 mg, 0.76 mmol) gave 25d (465 mg, 91% yield) as a clear syrup after chromatography. The spectroscopic and analytical data of 25d completely agreed with those reported in the literature.^[17b]

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy- α -D-*threo*-hex-3-enopyranoside (25e) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(1-imidazolylsulfonyl)- α -D-talopyranoside (27e): The activation–elimination reaction of 6e (196 mg, 0.42 mmol) was performed as described in the general procedure and gave 25e (168 mg, 90% yield) as a clear syrup after flash chromatography (8:2 hexane/EtOAc + 0.1% Et₃N). $R_{\rm f} = 0.24$

(8:2 hexane/EtOAc). $[\alpha]_{D}^{20} = +73.3$ (c = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.38-7.22$ (m, 15 H, Ar-H), 4.95 (d, $J_{1,2} = 1.0$ Hz, 1 H, 1-H), 4.92 (d, $J_{4,5} = 1.9$ Hz, 1 H, 4-H), 4.76 (s, 2 H, PhCH₂), 4.74, 4.64 (AB system, $J_{A,B} = 12.1$ Hz, 2 H, PhCH₂), 4.64, 4.57 (AB system, $J_{A,B} = 12.0$ Hz, 2 H, PhCH₂), 4.45 (m, 1 H, 5-H), 3.81 (t, $J_{2,5} = 1.0$ Hz, 1 H, 2-H), 3.68 (dd, $J_{6a,6b} = 9.8$ Hz, $J_{5,6b} = 6.5$ Hz, 1 H, 6b-H), 3.54 (dd, $J_{5,6a} = 5.2$ Hz, 1 H, 6a-H), 3.45 (s, 3 H, OCH₃) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 150.2$ (C-3), 137.9 (Ar-C), 137.8 (Ar-C), 136.2 (Ar-C), 128.0–127.1 (Ar-CH), 100.3 (C-1), 97.2 (C-4), 72.7 (C-2), 73.1 (PhCH₂), 73.0 (PhCH₂), 71.0 (PhCH₂), 68.4 (C-6), 67.2 (C-5), 55.3 (OCH₃) ppm. C₂₈H₃₀O₅ (446.54): calcd. C 75.31, H 6.77; found C 75.29, H 6.78.

In a repetition of the experiment, the reaction was set up as described in the general procedure, but it was quenched after 1 h at -30 °C and then rapidly worked up as usual. In this case, the NMR analysis of the crude product revealed the formation of compound **27e**.

Data for 27e: Clear syrup. ¹H NMR (200 MHz, CD₃CN): δ = 7.97 (s, 1 H, H-2'), 7.29–7.42 (m, 16 H, Ar-H and 4'-H), 6.96 (s, 1 H, 5'-H), 5.37 (dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 1.4 Hz, 1 H, 4-H), 4.83 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.59, 4.48 (AB system, $J_{A,B}$ = 12.0 Hz, 2 H, PhC H_2), 4.57 (s, 2 H, PhC H_2), 4.56, 4.52 (AB system, $J_{A,B}$ = 11.4 Hz, 2 H, PhC H_2), 4.10 (m, 1 H, 5-H), 3.79 (dd, 1 H, $J_{2,3}$ = 3.8 Hz, 3-H), 3.66–3.60 (m, 3 H, H-2, 6a-H, 6b-H), 3.31 (s, 3 H, OC H_3) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 138.1 (C-2'), 138.9 (Ar-C), 138.6 (Ar-C), 137.6 (Ar-C), 130.4 (C-5'), 128.9–128.0 (Ar-CH), 117.7 (C-4'), 100.2 (C-1), 82.7, 74.4, 72.5, 67.7 (C-2, C-3, C-4, C-5), 73.7 (PhCH₂), 73.4 (PhCH₂), 71.3 (PhCH₂), 68.7 (C-6), 55.4 (OCH₃) ppm.

Methyl 2,3,6-Tri-O-benzyl-4-deoxy-β-D-*erythro*-hex-3-enopyranoside (25f) and Methyl 2,3,6-Tri-O-benzyl-4-deoxy-α-L-*threo*-hex-4enopyranoside (26f): Activation–elimination of 6f (283 mg, 0.61 mmol) yielded a crude residue constituted by two enol ethers showing a single spot by TLC ($R_f = 0.33$, 8:2 hexane/EtOAc). Chromatography of the residue on silica gel (8:2 hexane/EtOAc + 0.1% Et₃N) gave an inseparable mixture of 25f and 26f (217 mg, 80% yield) in a 55:25 ratio, as estimated by NMR spectroscopy.

Selected ¹H NMR (200 MHz, CDCl₃) signals of **25**f: δ = 4.92 (d, $J_{4,5}$ = 2.3 Hz, 1 H, 4-H), 4.76 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.58 (m, 1 H, 5-H), 3.91 (dd, $J_{2,5}$ = 1.3 Hz, 1 H, 2-H), 3.61 (dd, $J_{6a,6b}$ = 9.4 Hz, $J_{5,6b}$ = 6.7 Hz, 1 H, 6b-H), 3.45 (s, 3 H, OCH₃), 3.44 (dd, $J_{5,6a}$ = 6.0 Hz, 1 H, 6a-H) ppm. Selected ¹³C NMR (50 MHz, CDCl₃) signals of **25**f: δ = 151.4 (C-3). 102.1 (C-1), 96.9 (C-4), 74.1 (C-2), 73.6 (PhCH₂), 73.2 (PhCH₂), 72.7 (PhCH₂), 71.0 (C-5), 69.0 (C-6), 55.9 (OCH₃) ppm. Spectroscopic data for the minor product **26f** completely agreed with those reported in the literature.^[37] C₂₈H₃₀O₅ (446.54): calcd. C 75.31, H 6.77; found C 75.27, H 6.74.

4-*O*-(2,3,6-Tri-*O*-benzyl-4-deoxy-β-D-*erythro*-hex-3-enopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (25g) and 4-*O*-(2,3,6-Tri-*O*-benzyl-4-deoxy-α-L-*threo*-hex-4-enopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (26g): Activation–elimination of 6g (500 mg, 0.68 mmol) gave a crude residue constituted by a 25g and 26g mixture in a 60:40 ratio, as estimated by NMR spectroscopy. Chromatography of the crude mixture on silica gel (8:2 hexane/EtOAc + 0.1% Et₃N) allowed a complete separation of the two enol ethers 25g (225 mg, 46% yield) and 26g (147 mg, 30% yield).

Data for 25g: Clear syrup; $R_{\rm f} = 0.18$ (2:8 hexane/EtOAc). $[\alpha]_{\rm D}^{20} = -30.4$ (c = 0.9, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.37 - 7.21$ (m, 15 H, Ar-H), 5.00 (d, $J_{1',2'} = 6.2$ Hz, 1 H, 1'-H), 4.92 (d, $J_{4',5'} = 1.2$ Hz, 1 H, 4'-H), 4.79 (s, 2 H, PhCH₂), 4.73, 4.70 (AB

system, $J_{A,B} = 11.3$ Hz, 2 H, PhC H_2), 4.54 (s, 2 H, PhC H_2), 4.52 (dd, $J_{1,2} = 6.4$ Hz, $J_{2,3} = 6.9$ Hz, 1 H, 2-H), 4.43 (m, 1 H, 5'-H), 4.36 (d, 1 H, 1-H), 4.18–3.98 (m, 6 H, 2'-H, 3-H, 4-H, 5-H, 6a-H, 6b-H), 3.58 (dd, $J_{6'a,6'b} = 9.6$ Hz, $J_{5',6'a} = 5.3$ Hz, 1 H, 6'a-H), 3.39 (dd, $J_{5',6'b} = 6.5$ Hz, 1 H, 6'b-H), 3.33 (s, 6 H, 2×OC H_3), 1.41 [s, 3 H, C(C H_3)₂], 1.40 [s, 3 H, C(C H_3)₂], 1.39 [s, 3 H, C(C H_3)₂], 1.33 [s, 3 H, C(C H_3)₂] ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 153.0$ (C-3'), 138.1 (Ar-C), 138.0 (Ar-C), 136.5 (Ar-C), 128.3–127.5 (Ar-CH), 110.2 [C(CH₃)₂], 108.3 [C(CH₃)₂], 105.0 (C-1), 102.2 (C-1'), 97.6 (C-4'), 78.0, 77.4 (C-3, C-5), 75.9, 74.9, 74.5 (C-2', C-2, C-4), 74.4 (PhCH₂), 73.3 (PhCH₂), 72.9 (PhCH₂), 71.1 (C-5'), 69.4 (C-6'), 65.5 (C-6), 55.3 (OCH₃), 52.8 (OCH₃), 27.4 [C(CH₃)₂], 26.7 [C(CH₃)₂], 26.6 [C(CH₃)₂], 25.2 [C(CH₃)₂] ppm. C₄₁H₅₂O₁₁ (720.86): calcd. C 68.31, H 7.27; found C 68.28, H 7.24.

Data for 26g: Clear syrup; $R_f = 0.18$ (2:8 hexane/EtOAc). $[\alpha]_D^{20} =$ +10.6 (c = 1.2, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.34$ -7.25 (m, 15 H, Ar-H), 5.31 (d, $J_{1',2'}$ = 6.9 Hz, 1 H, 1'-H), 5.07 (d, $J_{3',4'} = 3.1$ Hz, 1 H, 4'-H), 4.86, 4.68 (AB system, $J_{A,B} = 11.6$ Hz, 2 H, PhCH₂), 4.56 (s, 2 H, PhCH₂), 4.54 (s, 2 H, PhCH₂), 4.46 (dd, $J_{1,2} = 6.3$ Hz, $J_{2,3} = 7.4$ Hz, 1 H, 2-H), 4.35 (d, 1 H, 1-H), 4.30 (m, 1 H, 5-H), 4.14 (m, 3 H, 3'-H, 4-H, 6a-H), 4.06 (dd, $J_{3,4} = 5.9$ Hz, 1 H, 3-H), 3.98 (dd, $J_{6a,6b}$ = 8.8 Hz, $J_{5,6b}$ = 6.5 Hz, 1 H, 6b-H), 3.91 (br. s, 2 H, 6'a-H, 6'b-H), 3.75 (dd, $J_{2',3'} = 5.7$ Hz, 1 H, 2'-H), 3.36 (s, 6 H, 2×OCH₃), 1.41 [s, 3 H, C(CH₃)₂], 1.39 [s, 3 H, $C(CH_3)_2$], 1.38 [s, 3 H, $C(CH_3)_2$], 1.33, [s, 3 H, $C(CH_3)_2$] ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 149.6 (C-5'), 138.4 (Ar-C), 138.2 (Ar-C), 137.9 (Ar-C), 128.3–127.4 (Ar-CH), 110.2 [C(CH₃)₂], 108.3 [C(CH₃)₂], 105.2 (C-1), 101.0 (C-1'), 98.7 (C-4'), 78.2, 77.9, 77.7 (C-2', C-3, C-5), 74.9, 74.8, 74.5 (C-3', C-2, C-4), 73.7 (PhCH₂), 72.6 (PhCH₂), 70.9 (PhCH₂), 68.5 (C-6'), 65.3 (C-6), 55.7 (OCH₃), 52.9, (OCH₃), 27.3 [C(CH₃)₂], 26.6 [C(CH₃)₂], 26.5 [C(CH₃)₂], 25.2 [C(CH₃)₂] ppm. C₄₁H₅₂O₁₁ (720.86): calcd. C 68.31, H 7.27; found C 68.35, H 7.29.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-β-L-*threo*-hex-4-enopyranoside (26h) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(1-imidazolylsulfonyl)-α-D-galactopyranoside (27h): The activation–elimination reaction of 6h (354 mg, 0.76 mmol) was set up as described in the general procedure. The reaction was quenched after 1 h at -30 °C and worked up as usual. Chromatography (1:1 hexane/EtOAc) of the residue gave 26h (36 mg, 10% yield) and 27h (334 mg, 74% yield).

Data for 26h: Clear syrup; $R_f = 0.31$ (75:25 hexane/EtOAc). [*a*]₂₀²⁰ = +76.8 (*c* = 1.2, CHCl₃); ref.^[11a] [*a*]₂₀²⁰ = +78 (*c* = 1.0, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.38-7.22$ (m, 15 H, Ar-H), 5.03 (d, $J_{3,4} = 2.9$ Hz, 1 H, 4-H), 4.85 (d, $J_{1,2} = 2.4$ Hz, 1 H, 1-H), 4.80, 4.73 (AB system, $J_{A,B} = 12.3$ Hz, 2 H, PhC H_2), 4.62 (s, 2 H, PhC H_2), 4.56, 4.50 (AB system, $J_{A,B} = 11.9$ Hz, 2 H, PhC H_2), 4.24 (ddt, $J_{3,6a} = J_{3,6b} = 1.3$ Hz, 1 H, 3-H), 3.91 (br. s, 2 H, 6a-H, 6b-H), 3.78 (dd, $J_{2,3} = 6.9$ Hz, 1 H, 2-H), 3.50 (s, 3 H, OC H_3) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 148.6$ (C-5), 138.4 (Ar-C), 138.1 (Ar-C), 137.9 (Ar-C), 128.3–127.6 (Ar-CH), 99.7, 99.6 (C-1, C-4), 76.1, 73.2 (C-2, C-3), 73.0 (PhCH₂), 72.1 (PhCH₂), 71.3 (PhCH₂), 69.0 (C-6), 56.6 (OCH₃) ppm.

Data for 27h: Clear syrup; $R_f = 0.39$ (1:1 hexane/EtOAc). $[\alpha]_{20}^{20} = +39.3$ (c = 1.4, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.88$ (s, 1 H, Im-H2). 7.41–7.25 (m, 16 H, 15 Ar-H, Im-H4), 6.98 (s, 1 H, Im-H5), 5.36 (d, $J_{3,4} = 2.8$ Hz, 1 H, 4-H), 4.82, 4.69 (AB system, $J_{A,B} = 11.1$ Hz, 2 H, PhCH₂), 4.79, 4.57 (AB system, $J_{A,B} = 12.1$ Hz, 2 H, PhCH₂), 4.56 (d, $J_{1,2} = 3.6$ Hz, 1 H, 1-H), 4.51, 4.41 (AB system, $J_{A,B} = 11.2$ Hz, 2 H, PhCH₂), 4.03 (m, 1 H, 5-H), 3.96 (dd, $J_{2,3} = 10.8$ Hz, 1 H, 3-H), 3.60 (dd, 1 H, 2-H), 3.54 (dd, $J_{6a,6b} = 9.0$ Hz, $J_{5,6a} = 5.7$ Hz, 1 H, 6a-H), 3.45 (dd, $J_{5,6b} = 8.5$ Hz, 1 H, 6b-H), 3.35 (s, 3 H, OCH₃) ppm. ¹³C NMR (50 MHz, CDCl₃): δ

= 137.6 (Ar-C), 137.3 (Ar-C), 137.1 (Ar-C), 137.1 (Im-C2), 130.2 (Im-C5), 128.4–127.9 (Ar-CH), 118.2 (Im-C4), 98.6 (C-1), 83.5 (C-4), 74.9, 74.8 (C-2, C-3), 73.6 (PhCH₂), 73.5 (PhCH₂), 73.4 (PhCH₂), 67.2 (C-6), 66.7 (C-5), 55.6 (OCH₃) ppm. $C_{31}H_{34}N_{2}O_{8}S$ (594.69): calcd. C 62.61, H 5.76, N 4.71, S 5.39; found C 62.53, H 5.70, N 4.69, S 5.20.

In a repetition of the experiment, the reaction was set up as described in the general procedure. After 1 h at -30 °C, the reacting mixture was warmed to room temperature and stirred until the TLC analysis revealed the complete disappearance of **27h**. The mixture was then quenched and worked up as usual, furnishing a syrupy residue constituted (TLC, 1:1 hexane/EtOAc) by **26h** and other products with $R_{\rm f} = 0$. Chromatography of the residue gave pure hex-4-enopyranoside **26h** (43 mg, 12% yield).

Methyl 3,6-Di-*O*-benzyl-2,4-dideoxy-β-D-*glycero*-hex-3-enopyranoside (25i) and Methyl 3,6-Di-*O*-benzyl-2,4-dideoxy-α-L-*glycero*-hex-4-enopyranoside (26i): Activation–elimination of 6i (207 mg, 0.58 mmol) gave a residue constituted by a mixture of 25i and 26i in a 60:40 ratio, as estimated by NMR spectroscopy. Chromatography on silica gel (8:2 hexane/EtOAc + 0.1% Et₃N) of the residue allowed only partial separation of the two enol ethers 25i (95 mg, containing 10% of 26i, 48% yield) and 26i (63 mg, containing 10% of 25i, 32% yield).

Data for 25i: Clear syrup; $R_f = 0.32$ (2:8 hexane/EtOAc). [α]_D²⁰ = -22.3 (c = 1.3, CHCl₃). ¹H NMR (200 MHz, CD₃CN): $\delta = 7.37$ -7.29 (m, 10 H, Ar-H), 4.74 (m, 3 H, 4-H, PhC H_2), 4.66 (dd, $J_{1,2ax} = 7.1$ Hz, $J_{1,2eq} = 3.9$ Hz, 1 H, 1-H), 4.43 (m, 1 H, 5-H), 4.55 (s, 2 H, PhC H_2), 3.53 (dd, $J_{6a,6b} = 9.8$ Hz, $J_{5,6b} = 6.3$ Hz, 1 H, 6b-H), 3.46 (dd, $J_{5,6a} = 5.3$ Hz, 1 H, 6a-H), 3.42 (s, 3 H, OCH₃), 2.15-2.26 (m, 2 H, 2ax-H, 2eq-H) ppm. ¹³C NMR (50 MHz, CD₃CN): $\delta = 152.6$ (C-3). 139.6 (Ar-C), 138.0 (Ar-C), 129.3–128.4 (Ar-CH), 100.4 (C-1), 95.0 (C-4), 74.5 (PhCH₂), 73.7 (PhCH₂), 72.6 (C-5), 69.7 (C-6), 56.2 (OCH₃), 34.6 (C-2) ppm. C₂₁H₂₄O₅ (340.42): calcd. C 74.09, H 7.11, found C 74.01, H 7.08.

Data for 26i: Clear syrup; $R_f = 0.24$ (2:8 hexane/EtOAc). $[α]_{D}^{20} = -15.2$ (c = 1.1, CHCl₃). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.37-7.25$ (m, 10 H, Ar-H), 5.16 (d, $J_{3,4} = 3.7$ Hz, 1 H, 4-H), 5.02 (dd, $J_{1,2ax} = 4.7$ Hz, $J_{1,2eq} = 3.3$ Hz, 1 H, 1-H), 4.59 (s, 2 H, PhC H_2), 4.60, 4.54 (AB system, $J_{A,B} = 12.1$ Hz, 2 H, PhC H_2), 4.06 (m, 1 H, 3-H), 3.95 (s, 2 H, 6a-H, 6b-H), 3.51 (s, 3 H, OCH₃), 2.10–2.14 (m, 2 H, 2ax-H, 2eq-H) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 149.8$ (C-5), 138.6 (Ar-C), 138.5 (Ar-C), 128.3–127.7 (Ar-CH), 100.4, 98.8 (C-1, C-4), 72.3 (PhCH₂), 69.9, 69.8 (C-6, PhCH₂), 66.2 (C-3), 56.6 (OCH₃), 32.9 (C-2) ppm. C₂₁H₂₄O₅ (340.42): calcd. C 74.09, H 7.11, found C 74.03, H 7.06.

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