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Regiospecific Synthesis of 4-Deoxy-D-*threo*-hex-3-enopyranosides by Simultaneous Activation–Elimination of the Talopyranoside Axial 4-OH with the NaH/Im_2SO_2 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-*threo*-hex-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*′-sulfuryldiimidazole 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 at –30 °C. Upon warming these crude products to room temperature, the α-*talo*-4-*O*-imidazylate gives the corresponding hex-3-eno derivative in very high yield, but its α-*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.

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 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

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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**.

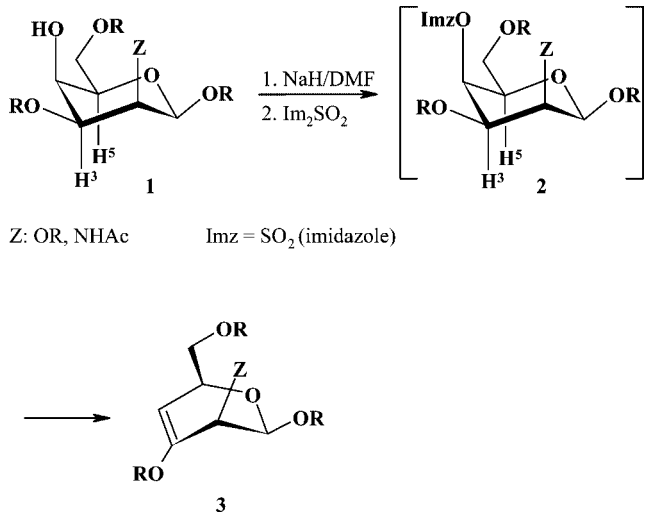


Figure 1. Transformation of 4-OH-containing β-D-talopyranosides into 4-deoxy-β-D-*threo*-hex-3-enopyranosides.

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.

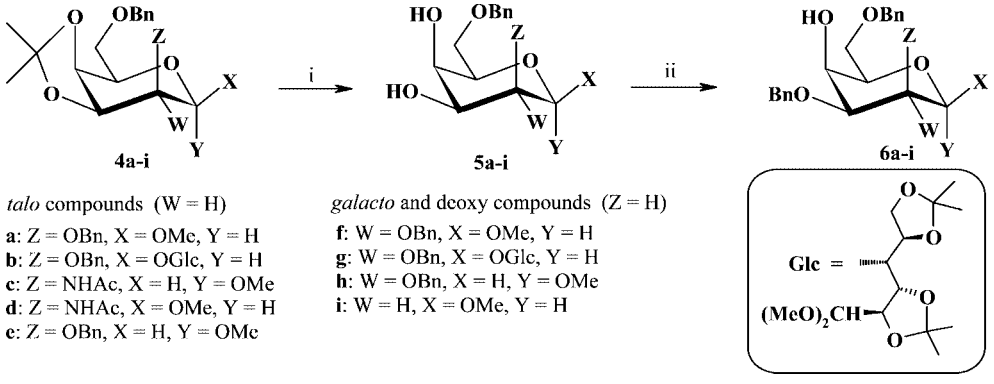
Synthesis of Substrates

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.

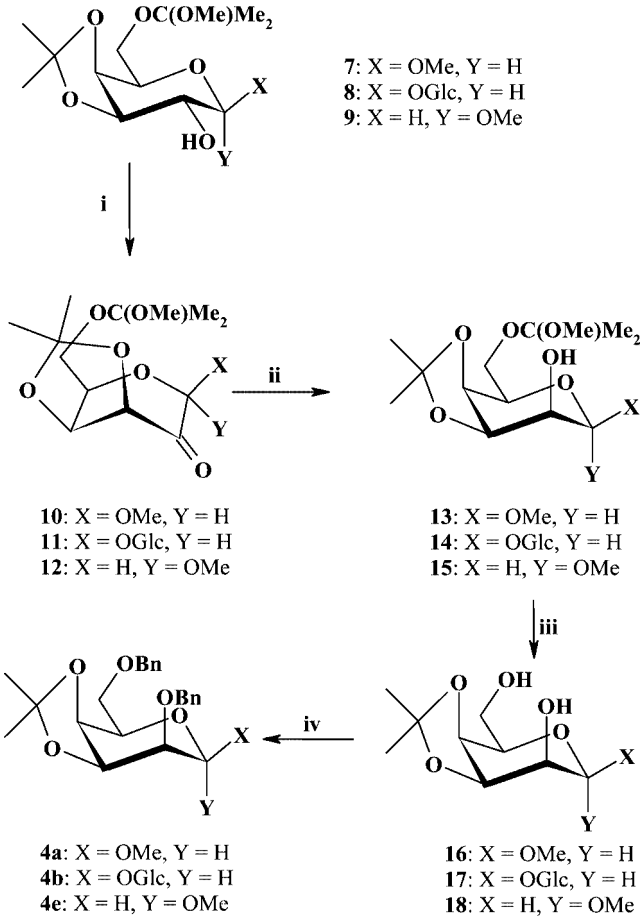
The galactopyranosides **4f**–**h** and the 2-deoxy compound **4i** have been prepared in accordance with methods previously reported in the literature,[18] while the synthesis of the talopyranosides **4a**,**b** and **e** was achieved starting from mixed acetals **7**–**9**[19] (Scheme 2) by a completely 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-*O*-methoxyisopropyl protecting group. The reduction of the two β-2-ulosides **10** and **11** ($NaBH_4$/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.

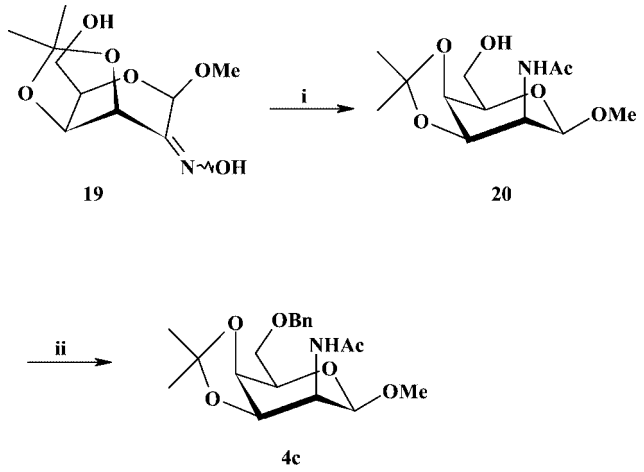


Scheme 1. General Procedure for the Preparation of 4-OH-containing D-galacto- and D-talopyranosides; Reagents and conditions: i: 80% AcOH aq, 50 °C; ii: a) Bu_2SnO, toluene, reflux; b) Bu_4NBr, BnBr, reflux.



Scheme 2. Preparation of protected D-talopyranosides; Reagents and conditions: i: TPAP, NMO, CH_2Cl_2; ii: $NaBH_4$, MeOH; iii: MeOH/H_2O, 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) $LiAlH_4$, Et_2O, b) Ac_2O, 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** ($LiAlH_4/Et_2O$), 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-ManNAc*p*-(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 **6g**. 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% aq 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 CH_3CN, 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-talopyr-

anoside 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).

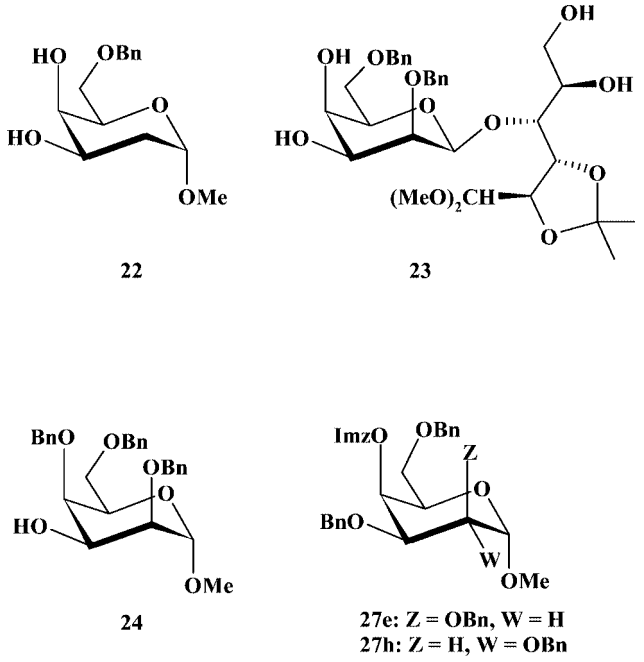
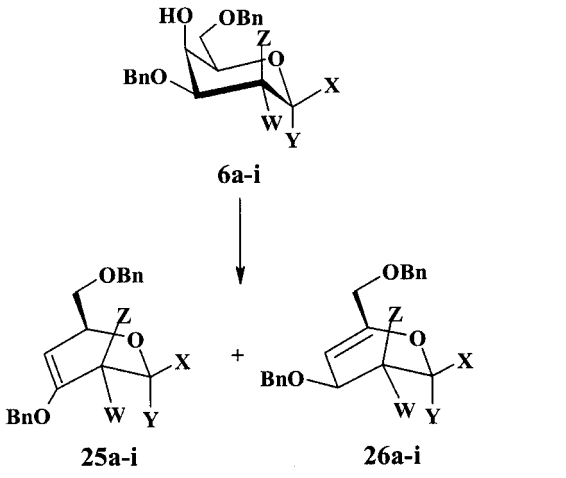


Figure 2. Compounds **22**–**24** and **27e** and **27h**.

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 (Im_2SO_2), 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 activation–elimination 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/Im_2SO_2 system.



Compound	X	Y	Z	W	Time [h][a]	Isolated yield [%]	
						25	**26**
6a	OMe	H	NHAc	H	2	95	–
6b	OMe	H	OBn	H	2	90	–
6c	OGlc	H	OBn	H	2	93	–
6d	OGlc	H	NHAc	H	2	91	–
6e	H	OMe	OBn	H	3	90	–
6f	OMe	H	H	OBn	2	55[b]	25[b]
6g	OGlc	H	H	OBn	2	46	30
6h	H	OMe	H	OBn	6	–	12
6i	OMe	H	H	H	2	48[c]	32[c]

[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 ^{13}C 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/Im_2SO_2 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-

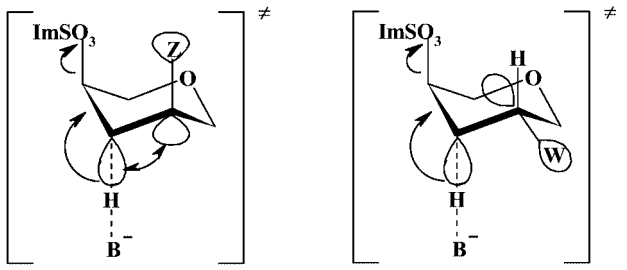
enopyranoside **25e** was the only isolated product (90% yield), while in the case of the *galacto* compound **27h**, the known 4-deoxy-D-*erythro*-hex-4-enopyranoside **26h**,[11a] derived by the elimination with opposite regiochemistry, was obtained in a very poor yield (12%), because of concurrent 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 α-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 $^1J_{C-H}$ values. Recent results from Cuevas and co-workers indicate that any stereoelectronic interaction weakening an axial C–H bond is manifested in a smaller $^1J_{C-Hax}$ value, relative to that of $^1J_{C-Heq}$.[33] Starting from these considerations, we



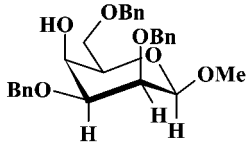
E2 borderline with E1cb in *talo* imidazylates

E2 borderline with E1cb in *galacto* imidazylates

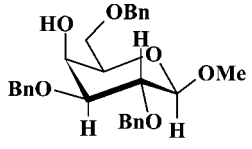
Figure 3. Stereoelectronic interactions affecting the regioselectivity of 4-*O*-imidazylate eliminations.

compared (Table 2) the $^1J_{C-H}$ 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 $^1J_{C1-H1}$ and $^1J_{C3-H3}$ 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 $^1J_{C-H}$ values can be affected by torsional effects of the substituents.[34] However, the $^1J_{C-H}$ 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 $^1J_{C-H}$ values of a talo- and galactopyranoside couple.



6a



6f

	$^1J_{C-H}$	$^1J_{C-H}$	$\Delta J = J_{gal} - J_{tal}$
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. ^{1}H and ^{13}C NMR measurements were performed with a Bruker AC 200 instrument operating at 200 MHz and 50 MHz, respectively, in an appropriate solvent (Me_4Si as an internal standard). Coupled ^{13}C 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 F_{254} 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. $MgSO_4$ was used as a drying agent for solutions. After isolation, all 6-*O*-(1-methoxy-1-methylethyl) derivatives **10**–**12** and **13**–**15** were stored at –18 °C in the presence of a trace of Et_3N. 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 $NaBH_4$ (3 equiv.). The solution was left to react until TLC analysis showed complete disappearance of the starting material (30 min–1 h). H_2O 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 CH_2Cl_2 (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/H_2O (10:1, 5 mL) was treated with AcOH (28 μL) 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 $NaBH_4$ 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*-(1-methoxy-1-methylethyl)-β-D-talopyranoside (**13**): R_f = 0.33 (EtOAc). ^{1}H NMR (200 MHz, C_6D_6): 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) (OC*H*$_3$-1, OC*H*$_3$–MIP), 1.30 (s, 6 H, 2 × C*H*$_3$–MIP), 1.59 [s, 3 H, C(C*H*$_3$)$_2$], 1.20 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 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 (O*C*H$_3$-1), 48.3 (O*C*H$_3$-MIP), 25.6 [C(*C*H$_3$)$_2$], 25.3 [C(*C*H$_3$)$_2$], 24.7 (*C*H$_3$-MIP), 24.6 (*C*H$_3$-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_f = 0.16 (EtOAc); m.p. 69–72 °C (EtOAc/hexane). $[\alpha]_D^{20}$ = –21.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 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, OC*H*$_3$), 2.51 (br. s, 1 H, OH), 1.58 [s, 3 H, C(C*H*$_3$)$_2$], 1.36 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (O*C*H$_3$), 25.2 [C(*C*H$_3$)$_2$], 25.1 [C(*C*H$_3$)$_2$] 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-*lyxo*-hexopyranosyl-2-ulose]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (**11**): R_f = 0.53 (9:1 CH_2Cl_2/Me_2CO). ^{1}H NMR (200 MHz, C_6D_6): 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 H, 1-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 3′-H, 4′-H, 5′-H, 6′a-H, 6′b-H), 3.24 (s, 3 H, OC*H*$_3$-1), 3.22 (s, 3 H, OC*H*$_3$-1), 3.17 (s, 3 H, OC*H*$_3$-MIP), 1.42 (s, 6 H, 2 × C*H*$_3$-MIP), 1.54 [s, 3 H, C(C*H*$_3$)$_2$], 1.40 [s, 3 H, C(C*H*$_3$)$_2$], 1.35 [s, 3 H, C(C*H*$_3$)$_2$], 1.32 [s, 3 H, C(C*H*$_3$)$_2$], 1.31 [s, 3 H, C(C*H*$_3$)$_2$], 1.20 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 197.3 (C-2′), 111.0 [*C*(CH$_3$)$_2$], 110.7 [*C*(CH$_3$)$_2$], 108.2 [*C*(CH$_3$)$_2$], 105.8 (C-1), 100.9 (C-1′), 100.2 [*C*(CH$_3$)$_2$-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 (O*C*H$_3$-1), 53.5 (O*C*H$_3$-1), 48.4 (O*C*H$_3$-MIP), 27.7 [C(*C*H$_3$)$_2$], 27.4 [C(*C*H$_3$)$_2$],

26.7 [C(*C*H$_3$)$_2$], 26.6 [C(*C*H$_3$)$_2$], 26.2 [C(*C*H$_3$)$_2$], 26.1 [C(*C*H$_3$)$_2$], 24.6 (*C*H$_3$-MIP), 24.5 (*C*H$_3$-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)-β-D-talopyranosyl]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (**14**): R_f = 0.18 (9:1 CH_2Cl_2/Me_2CO). ^{1}H NMR (200 MHz, $CDCl_3$): 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×OC*H*$_3$-1), 3.21 (s, 3 H, OC*H*$_3$-MIP), 2.84 (d, $J_{2,OH}$ = 9.7 Hz, 1 H, OH), 1.58 [s, 3 H, C(C*H*$_3$)$_2$], 1.43 [s, 3 H, C(C*H*$_3$)$_2$], 1.42 [s, 3 H, C(C*H*$_3$)$_2$], 1.38 [s, 3 H, C(C*H*$_3$)$_2$], 1.36 [s, 3 H, C(C*H*$_3$)$_2$], 1.35, [s, 3 H, C(C*H*$_3$)$_2$], 1.34 (s, 6 H, 2×C*H*$_3$-MIP) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 110.0 [*C*(CH$_3$)$_2$], 109.4 [*C*(CH$_3$)$_2$], 107.5 [*C*(CH$_3$)$_2$], 104.7 (C-1), 100.6 [*C*(CH$_3$)$_2$-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 (O*C*H$_3$-1), 52.7 (O*C*H$_3$-1), 48.1 (O*C*H$_3$-MIP), 27.0 [C(*C*H$_3$)$_2$], 26.1 [C(*C*H$_3$)$_2$], 25.9 [C(*C*H$_3$)$_2$], 25.3 [C(*C*H$_3$)$_2$], 25.0 [C(*C*H$_3$)$_2$], 24.8 [C(*C*H$_3$)$_2$], 24.0 (*C*H$_3$-MIP), 23.9 (*C*H$_3$-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, $CHCl_3$). ^{1}H NMR (200 MHz, CD_3CN/D_2O): 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, OC*H*$_3$), 3.39 (s, 3 H, OC*H*$_3$), 1.46 [s, 3 H, C(C*H*$_3$)$_2$], 1.34 [s, 3 H, C(C*H*$_3$)$_2$], 1.33 [s, 3 H, C(C*H*$_3$)$_2$], 1.30 [s, 3 H, C(C*H*$_3$)$_2$], 1.28 [s, 3 H, C(C*H*$_3$)$_2$], 1.27 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, CD_3CN/D_2O): δ = 110.5 [*C*(CH$_3$)$_2$], 110.4 [*C*(CH$_3$)$_2$], 108.8 [*C*(CH$_3$)$_2$], 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 (O*C*H$_3$), 54.6 (O*C*H$_3$), 27.4 [C(*C*H$_3$)$_2$], 26.8 [C(*C*H$_3$)$_2$], 26.7 [C(*C*H$_3$)$_2$], 25.9 [C(*C*H$_3$)$_2$], 25.7 [C(*C*H$_3$)$_2$], 25.5 [C(*C*H$_3$)$_2$] ppm. $C_{23}H_{40}O_{12}$ (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_f = 0.65 (95:5 $CHCl_3$/MeOH). ^{1}H NMR (200 MHz, C_6D_6): δ = 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, OC*H*$_3$-1), 3.11 (s, 3 H, OC*H*$_3$-MIP), 1.37 (s, 6 H, 2×C*H*$_3$-MIP), 1.55 [s, 3 H, C(C*H*$_3$)$_2$], 1.28 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 198.7 (C-2), 110.6 [*C*(CH$_3$)$_2$], 100.9 (C-1), 100.1 [*C*(CH$_3$)$_2$-MIP], 78.0 (C-4), 76.0 (C-3), 67.5 (C-5), 60.4 (C-6), 54.8 (O*C*H$_3$-1), 48.3 (O*C*H$_3$-MIP), 27.4 [C(*C*H$_3$)$_2$], 26.3 [C(*C*H$_3$)$_2$], 24.5 (2×*C*H$_3$-MIP) ppm.

Reduction of crude **12** (2.04 g, 6.7 mmol) with $NaBH_4$ 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 ^{1}H NMR signal integrations. Data for methyl 3,4-*O*-isopropylidene-6-*O*-(1-methoxy-1-methylethyl)-α-D-talopyranoside (**15**): ^{1}H NMR (200 MHz, $CDCl_3$): 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, OC*H*$_3$-1), 3.22 (s, 3 H, OC*H*$_3$-MIP), 2.81 (br. s, 1 H, OH), 1.36 (s, 6 H, 2×C*H*$_3$-MIP), 1.51 [s, 3 H, C(C*H*$_3$)$_2$], 1.35 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 110.1 [*C*(CH$_3$)$_2$], 101.5 (C-1), 100.0 [*C*(CH$_3$)$_2$-MIP], 73.5, 73.3 (C-3, C-4), 68.9, 68.6 (C-2, C-5), 59.7 (C-6), 55.1 (O*C*H$_3$–1), 48.4 (O*C*H$_3$-MIP), 25.9 [C(*C*H$_3$)$_2$], 25.1 [C(*C*H$_3$)$_2$], 24.3 (2×*C*H$_3$-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**: ^{1}H NMR (200 MHz, $CDCl_3$): 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, OC*H*$_3$), 3.35 (br. s, 2 H, OH), 2.10 (br. s, 2 H, OH), 1.52 [s, 3 H, C(C*H*$_3$)$_2$], 1.36 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 110.4 [*C*(CH$_3$)$_2$], 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 (O*C*H$_3$), 25.9 [C(*C*H$_3$)$_2$], 25.0 [C(*C*H$_3$)$_2$] ppm. $C_{10}H_{18}O_6$ (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 Et_2O (50 mL) was added dropwise to a suspension of $LiAlH_4$ (900 mg, 23.7 mmol) in dry Et_2O (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 H_2O (1.0 mL), aq 15% NaOH (3.0 mL) and H_2O (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 Ac_2O (4.0 mL) and left to react at room temperature overnight. The reaction mixture was then repeatedly co-evaporated with toluene (4×10 mL), and purification of the residue by flash chromatography (92:8 CH_2Cl_2/MeOH) allowed the isolation of two pure acetamido derivatives.

Data for 20: White solid (680 mg, 62% yield). R_f = 0.36 (92:8 CH_2Cl_2/MeOH); m.p. 139–142 °C. $[\alpha]_D^{20}$ = +7.5 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 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, OC*H*$_3$), 2.06 (s, 3 H, C*H*$_3$CO), 1.50 [s, 3 H, C(C*H*$_3$)$_2$], 1.31 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.2 (C=O), 110.1 [*C*(CH$_3$)$_2$], 98.3 (C-1), 72.5, 71.7, 71.2 (C-3, C-4, C-5), 62.5 (C-6), 56.0 (O*C*H$_3$), 46.6 (C-2), 25.4 [C(*C*H$_3$)$_2$], 24.7 [C(*C*H$_3$)$_2$], 23.2 (*C*H$_3$CO) ppm. $C_{12}H_{21}NO_6$ (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 CH_2Cl_2/MeOH); m.p. 91–92 °C. $[\alpha]_D^{20}$ = +29.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 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, OC*H*$_3$), 3.18 (m, 1 H, 2-H), 2.01 (s, 3 H, C*H*$_3$CO), 1.52 [s, 3 H, C(C*H*$_3$)$_2$], 1.34 [s, 3 H,

C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0 (C=O), 110.1 [*C*(CH$_3$)$_2$], 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 (O*C*H$_3$), 28.1 [C(*C*H$_3$)$_2$], 26.2 [C(*C*H$_3$)$_2$], 23.6 (*C*H$_3$CO) ppm. $C_{12}H_{21}NO_6$ (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/H_2O (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 CH_2Cl_2 (10 mL) and washed with H_2O (4 mL). The two phases were separated, and the aqueous phase was further extracted with CH_2Cl_2 (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. $[\alpha]_D^{20}$ = –19.5 (*c* = 1.4, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 10 H, Ar-H), 4.78 (s, 2 H, PhCH_2), 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, PhCH_2), 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, OCH_3), 1.56 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.1 (Ar-C), 137.8 (Ar-C), 128.2–127.5 (Ar-CH), 110.2 [*C*(CH$_3$)$_2$], 99.6 (C-1), 73.4 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 72.1, 72.0, 71.6, 71.0 (C-2, C-3, C-4, C-5), 69.8 (C-6), 56.1 (O*C*H$_3$), 25.4 [C(*C*H$_3$)$_2$], 25.1 [C(*C*H$_3$)$_2$] ppm. $C_{24}H_{30}O_6$ (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-β-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_f = 0.34 (6:4 hexane/EtOAc). $[\alpha]_D^{20}$ = –6.3 (*c* = 1.4, $CHCl_3$). ^{1}H NMR (200 MHz, CD_3CN): δ = 7.44–7.27 (m, 10 H, Ar-H), 4.73 (s, 2 H, PhCH_2), 4.67 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 4.54 (s, 2 H, PhCH_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, OCH_3), 3.31 (s, 3 H, OCH_3), 1.39 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$], 1.31 [s, 3 H, C(CH_3)$_2$], 1.30 [s, 3 H, C(CH_3)$_2$], 1.28 [s, 3 H, C(CH_3)$_2$], 1.27 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 139.7 (Ar-C), 139.6 (Ar-C), 129.2 –128.2 (Ar-CH), 110.5 [*C*(CH$_3$)$_2$], 110.4 [*C*(CH$_3$)$_2$], 108.8, [*C*(CH$_3$)$_2$], 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 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 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 (O*C*H$_3$), 54.34 (O*C*H$_3$), 27.4 [C(*C*H$_3$)$_2$], 27.2 [C(*C*H$_3$)$_2$], 26.9 [C(*C*H$_3$)$_2$], 26.1 [C(*C*H$_3$)$_2$], 26.0 [C(*C*H$_3$)$_2$], 25.3 [C(*C*H$_3$)$_2$] ppm. $C_{37}H_{52}O_{12}$ (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-D-talopyranoside (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). $[\alpha]_D^{20}$ = +9.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, CD_3CN): 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, PhCH_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, OCH_3), 1.90 (s, 3 H, CH_3CO), 1.41 [s, 3 H, C(CH_3)$_2$], 1.26 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 170.4 (C=O), 139.6 (Ar-C), 129.2–128.4 (Ar-CH), 110.0 [*C*(CH$_3$)$_2$], 100.2 (C-1), 73.6 (Ph*C*H$_2$), 73.0 (C-3), 72.7 (C-4), 71.9 (C-5), 70.4 (C-6), 56.5 (O*C*H$_3$), 48.3 (C-2), 26.1 [C(*C*H$_3$)$_2$], 25.4 [C(*C*H$_3$)$_2$], 23.3 (*C*H$_3$CO) ppm. $C_{19}H_{27}NO_6$ (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_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: ^{1}H NMR (200 MHz, $CDCl_3$): 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, PhCH_2), 4.59, 4.52 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhCH_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, OCH_3), 3.43 (dd, $J_{2,3}$ = 2.8 Hz, 1 H, 2-H), 1.50 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.2 (Ar-C), 137.8 (Ar-C), 128.2–127.4 (Ar-CH), 110.4 [*C*(CH$_3$)$_2$], 101.4 (C-1), 75.0, 74.5, 74.4, 73.4 (C-2, C-3, C-4, C-5), 73.2 (Ph*C*H$_2$), 72.3 (Ph*C*H$_2$), 68.9 (C-6), 54.9 (O*C*H$_3$), 26.1 [C(*C*H$_3$)$_2$], 25.2 [C(*C*H$_3$)$_2$] ppm. $C_{24}H_{30}O_6$ (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_f = 0.17 (6:4 hexane/EtOAc). $[\alpha]_D^{20}$ = –82.3 (*c* = 1.4, $CHCl_3$). ^{1}H NMR (200 MHz, CD_3CN): δ = 7.39–7.28 (m, 10 H, Ar-H), 4.86, 4.66 (AB system, $J_{A,B}$ = 11.4 Hz, 2 H, PhCH_2), 4.55 (s, 2 H, PhCH_2), 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, OCH_3), 3.08 (br. s, 2 H, 2 × OH) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 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 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 70.4 (C-6), 70.7, 69.8 (C-3, C-4), 57.2 (O*C*H$_3$) ppm. $C_{21}H_{26}O_6$ (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_f = 0.51 and R_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, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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 Hz, 2 H, PhCH_2), 4.54 (m, 1 H, 2-H), 4.57, 4.50 (AB system, $J_{A,B}$ = 12.0 Hz, 2 H, PhCH_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×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(CH_3)$_2$], 1.35 [s, 3 H, C(CH_3)$_2$], 1.34 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.0 (Ar-C), 137.7 (Ar-C), 128.5–127.6 (Ar-CH), 109.9 [C(CH$_3$)$_2$], 107.8 [C(CH$_3$)$_2$], 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 (PhCH_2), 73.4 (PhCH_2), 69.3, 69.2 (C-3′, C-4′), 68.4 (C-6′), 64.8 (C-6), 55.4 (OCH_3), 52.9 (OCH_3), 26.9 [C(CH_3)$_2$], 26.8 [C(CH_3)$_2$], 26.5 [C(CH_3)$_2$], 24.9 [C(CH_3)$_2$] ppm. $C_{34}H_{48}O_{12}$ (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, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): 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, PhCH_2), 4.54 (s, 2 H, PhCH_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×OCH_3), 3.20 (br. s, 3 H, 3× OH), 1.40 [s, 3 H, C(CH_3)$_2$], 1.39 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.9 (Ar-C), 137.6 (Ar-C), 128.5–127.7 (Ar-CH), 110.0 [C(CH$_3$)$_2$], 104.7 (C-1), 101.2 (C-1′), 79.0, 77.1 (C-2′, C-3), 75.7 (PhCH_2), 73.5 (PhCH_2), 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 (OCH_3), 53.6 (OCH_3), 26.9 [C(CH_3)$_2$], 26.8 [C(CH_3)$_2$] ppm. $C_{31}H_{44}O_{12}$ (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_f = 0.26 (92:8 CH_2Cl_2/MeOH). $[\alpha]_D^{20}$ = –50.6 (c = 1.6, $CHCl_3$). ^1H NMR (200 MHz, CD_3CN): δ = 7.37–7.32 (m, 5 H, Ar-H), 6.69 (d, $J_{2,NH}$ = 9.6 Hz, 1 H, NH), 4.55 (s, 2 H, PhCH_2), 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, OCH_3), 1.88 (s, 3 H, CH_3CO) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 173.7 (C=O), 139.1 (Ar-C), 129.3–128.6 (Ar-CH), 102.0 (C-1), 75.1 (C-5), 73.7 (PhCH_2), 70.5 (C-6), 69.1 (C-4), 68.5 (C-3), 57.1 (OCH_3), 52.8 (C-2), 23.5 (CH$_3$CO) ppm. $C_{16}H_{23}NO_6$ (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-α-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_f = 0.37 (1:1 hexane/EtOAc); m.p. 73–75 °C. $[\alpha]_D^{20}$ = +11.2 (c = 1.1, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, $J_{A,B}$ = 11.4 Hz, 2 H, PhCH_2), 4.63, 4.53 (AB system, $J_{A,B}$ = 11.9 Hz, 2 H, PhCH_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, OCH_3), 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.1 (Ar-C), 136.9 (Ar-C), 128.5–127.5 (Ar-CH), 98.4 (C-1), 78.5 (C-2), 73.7 (PhCH_2), 73.4 (PhCH_2), 70.4, 70.1 (C-3, C-5), 69.8 (C-6), 66.0 (C-4), 55.0 (OCH_3) ppm. $C_{21}H_{26}O_6$ (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.[18d] 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, $CDCl_3$): 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 ^{13}C NMR signals (50 MHz, $CDCl_3$): δ = 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**, OCH_3), 54.7 (**22**, OCH_3), 34.7 (**5i**, C-2), 32.7 (**22**, C-2) ppm. Method B [with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)]: Compound **4i**[18d] (820 mg, 2.66 mmol) was dissolved in a CH_3CN/H_2O (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_f = 0.23 (1:9 hexane/EtOAc); m.p. 81–82 °C, $[\alpha]_D^{20}$ = –42.4 (c = 1.1, $CHCl_3$); ref.[18d] $[\alpha]_D^{20}$ = –33 (c = 3.6, $CHCl_3$), m.p. 81–82 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 5 H, Ar-H), 4.58 (s, 2 H, PhCH_2), 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, OCH_3), 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.8 (Ar-C), 128.1–127.4 (Ar-CH), 101.0 (C-1), 73.5 (C-5), 73.2 (PhCH_2), 69.6 (C-6), 68.3, 67.5 (C-3, C-4), 56.2 (OCH_3), 34.3 (C-2) ppm. $C_{14}H_{20}O_5$ (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_f = 0.23 (7:3 hexane/EtOAc). $[\alpha]_D^{20}$ = –47.1 (c = 1.5, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 15 H, Ar-H), 4.95, 4.80 (AB system, $J_{A,B}$ = 11.9 Hz, 2 H, PhCH_2), 4.59 (s, 2 H, PhCH_2), 4.67, 4.48 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhCH_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, $J_{4,OH}$ = 10.3 Hz, 1 H, OH), 3.56 (s, 3 H, OCH_3), 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (PhCH_2), 73.6 (PhCH_2), 69.4, 69.3 (C-6, PhCH_2), 66.8 (C-4), 57.0 (OCH_3) ppm. $C_{28}H_{32}O_6$ (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_f = 0.19 (7:3 hexane/EtOAc); m.p. 90–94 °C. $[\alpha]_D^{20}$ = –31.2 (c = 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.25 (m, 15 H, Ar-H), 4.93, 4.81 (AB system, $J_{A,B}$ = 11.6 Hz, 2 H, PhCH_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, PhCH_2), 4.64, 4.48 (AB system, $J_{A,B}$ = 12.3 Hz, 2 H, PhCH_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×OCH_3), 3.27 (t, $J_{2',3'}$ = $J_{3',4'}$ = 2.9 Hz, 1 H, 3′-H), 1.36 [s, 3 H, C(CH_3)$_2$], 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.2 (Ar-C), 138.0 (Ar-C), 137.8 (Ar-C), 128.4–127.6 (Ar-CH), 110.0 [C(CH$_3$)$_2$], 107.8 [C(CH$_3$)$_2$], 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 (PhCH_2), 73.5 (PhCH_2), 69.4, 68.6 (C-6′, PhCH_2), 66.6 (C-4′), 64.9 (C-6), 55.4 (OCH_3), 52.8 (OCH_3), 27.0 [C(CH$_3$)$_2$], 26.7 [C(CH$_3$)$_2$], 26.5 [C(CH$_3$)$_2$], 24.9 [C(CH$_3$)$_2$] ppm. $C_{41}H_{54}O_{12}$ (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_f = 0.13 (2:8 hexane/EtOAc). $[\alpha]_D^{20}$ = –81.5 (c = 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 10 H, Ar-H), 6.73 (d, $J_{2,NH}$ = 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, PhCH_2), 4.57 (s, 2 H, PhCH_2), 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, OCH_3), 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, CH_3CO) ppm. ^{13}C NMR (50 MHz, CD_3CN): 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 (PhCH_2), 69.2 (PhCH_2), 67.6 (C-4), 56.8 (OCH_3), 47.7 (C-2), 23.5 (CH$_3$CO) ppm. $C_{23}H_{29}NO_6$ (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). $[\alpha]_D^{20}$ = +36.2 (c = 1.1, $CHCl_3$). ^1H NMR (200 MHz, CD_3CN): 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, PhCH_2), 4.67, 4.54 (AB system, $J_{A,B}$ = 11.8 Hz, 2 H, PhCH_2), 4.54 (s, 2 H, PhCH_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, OCH_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. ^{13}C NMR (50 MHz, CD_3CN): 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 (PhCH_2), 73.7 (PhCH_2), 71.4 (C-5), 70.9, 70.2 (C-6, PhCH_2), 68.5 (C-4), 55.2 (OCH_3) ppm. $C_{28}H_{32}O_6$ (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). $[\alpha]_D^{20}$ = +15.3 (c = 0.9, $CHCl_3$). ^1H NMR (200 MHz, CD_3CN): δ = 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, PhCH_2), 4.69, 4.52 (AB system, $J_{A,B}$ = 11.3 Hz, 2 H, PhCH_2), 4.57, 4.50 (AB system, $J_{A,B}$ = 11.8 Hz, 2 H, PhCH_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, OCH_3), 2.42 (br. s, 1 H, OH) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 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 (PhCH_2), 73.8 (PhCH_2), 73.7 (PhCH_2), 70.3 (C-6), 70.1 (C-5), 67.4 (C-3), 55.2 (OCH_3) ppm. $C_{28}H_{32}O_6$ (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_f = 0.37 (7:3 hexane/EtOAc). $[\alpha]_D^{20}$ = +3.3 (c = 1.0, $CHCl_3$); ref.[26] $[\alpha]_D^{20}$ = +3.4 (c = 3.6, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.22 (m, 15 H, Ar-H), 4.89, 4.71 (AB system, $J_{A,B}$ = 11.0 Hz, 2 H, PhCH_2), 4.70 (s, 2 H, PhCH_2), 4.58 (s, 2 H, PhCH_2), 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, OCH_3), 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (PhCH_2), 73.6 (PhCH_2), 72.3 (PhCH_2), 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_f = 0.47 (4:6 hexane/EtOAc). $[\alpha]_D^{20}$ = +1.3 (c = 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): 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, PhCH_2), 4.91, 4.63 (AB system, $J_{A,B}$ = 11.2 Hz, 2 H, PhCH_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 Hz, 2 H, PhCH_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, OCH_3), 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(CH_3)$_2$], 1.41 [s, 3 H, C(CH_3)$_2$], 1.40 [s, 3 H, C(CH_3)$_2$], 1.32 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.6 (Ar-C), 138.5 (Ar-C), 137.8 (Ar-C), 128.2–127.5 (Ar-CH), 110.2 [C(CH$_3$)$_2$], 108.4 [C(CH$_3$)$_2$], 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 (PhCH$_2$), 73.6 (PhCH$_2$), 72.3 (PhCH$_2$), 68.4 (C-6′), 66.4 (C-4′), 65.5 (C-6), 55.4 (OCH$_3$), 52.6 (OCH$_3$), 27.5 [C(CH$_3$)$_2$], 26.7 [C(CH$_3$)$_2$], 26.6 [C(CH$_3$)$_2$], 25.3 [C(CH$_3$)$_2$] ppm. $C_{41}H_{54}O_{12}$ (738.87): calcd. C 66.65, H 7.37; found C 66.62, H 7.35.

Methyl 2,3,6-Tri-*O*-benzyl-α-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_f = 0.23 (7:3 hexane/EtOAc). $[\alpha]_D^{20}$ = +32.7 (*c* = 1.1, $CHCl_3$); ref.[26] $[\alpha]_D^{20}$ = +34 (*c* = 3.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 15 H, Ar-H), 4.80, 4.69 (AB system, $J_{A,B}$ = 11.6 Hz, 2 H, PhC*H*$_2$), 4.68 (dd, $J_{1,2}$ = 4.1 Hz, 1 H, 1-H), 4.82, 4.66 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhC*H*$_2$), 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, OC*H*$_3$), 2.62 (br. s, 1 H, OH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (PhCH$_2$), 73.4 (PhCH$_2$), 72.6 (PhCH$_2$), 69.5 (C-6), 68.2, 67.9 (C-4, C-5), 55.2 (OCH$_3$) 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_f = 0.36 (6:4 hexane/EtOAc). $[\alpha]_D^{20}$ = –11.9 (*c* = 1.1, $CHCl_3$), ref.[18d] $[\alpha]_D^{20}$ = –13. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 10 H, Ar-H), 4.60 (s, 2 H, PhC*H*$_2$), 4.64, 4.57 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhC*H*$_2$), 4.33 (dd, $J_{1,2eq}$ = 2.3 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, OC*H*$_3$), 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. ^{13}C NMR (50 MHz, $CDCl_3$): 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 (PhCH$_2$), 69.9, 69.5 (C-6, PhCH$_2$), 64.9 (C-4), 56.4 (OCH$_3$), 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 Im_2SO_2 (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 × 20 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% Et_3N). R_f = 0.47 (6:4 hexane/EtOAc). $[\alpha]_D^{20}$ = –1.6 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 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. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (PhCH$_2$), 73.1 (PhCH$_2$), 72.6 (PhCH$_2$), 72.5, 72.1 (C-2, C-5), 69.1 (C-6), 56.7 (OCH$_3$) ppm. $C_{28}H_{30}O_5$ (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% Et_3N). R_f = 0.42 (6:4 hexane/EtOAc). $[\alpha]_D^{20}$ = +4.3 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): 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, PhC*H*$_2$), 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, OC*H*$_3$), 3.32 (s, 3 H, OC*H*$_3$), 1.42 [s, 3 H, C(C*H*$_3$)$_2$], 1.38 [s, 3 H, C(C*H*$_3$)$_2$], 1.35 [s, 3 H, C(C*H*$_3$)$_2$], 1.34 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 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*(CH$_3$)$_2$], 107.8 [*C*(CH$_3$)$_2$], 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 (PhCH$_2$), 73.1 (PhCH$_2$), 72.7 (PhCH$_2$), 72.9, 72.7 (C-2′, C-5′), 69.2 (C-6′), 65.0 (C-6), 55.3 (OCH$_3$), 52.9 (OCH$_3$), 27.2 [C(CH$_3$)$_2$], 26.6 [C(CH$_3$)$_2$], 26.5 [C(CH$_3$)$_2$], 25.1 [C(CH$_3$)$_2$] ppm. $C_{41}H_{52}O_{11}$ (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-β-D-*threo*-hex-3-enopyranoside (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% Et_3N). R_f = 0.21 (2:8 hexane/EtOAc). $[\alpha]_D^{20}$ = +2.2 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (200 MHz, CD_3CN): δ = 7.38–7.29 (m, 10 H, Ar-H), 6.32 (d, $J_{2,NH}$ = 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, PhC*H*$_2$), 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, OC*H*$_3$), 1.82 (s, 3 H, C*H*$_3$CO) ppm. ^{13}C NMR (50 MHz, CD_3CN): 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 (PhCH$_2$), 73.3 (PhCH$_2$), 72.2 (C-5), 69.2 (C-6), 55.9 (OCH$_3$), 48.6 (C-2), 22.8 (*C*H$_3$CO) ppm. $C_{23}H_{27}NO_5$ (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-3-enopyranosyl)-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% Et_3N). R_f = 0.24

(8:2 hexane/EtOAc). $[\alpha]_D^{20}$ = +73.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, PhCH_2), 4.74, 4.64 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhCH_2), 4.64, 4.57 (AB system, $J_{A,B}$ = 12.0 Hz, 2 H, PhCH_2), 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, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (Ph*C*H_2), 73.0 (Ph*C*H_2), 71.0 (Ph*C*H_2), 68.4 (C-6), 67.2 (C-5), 55.3 (O*C*H_3) ppm. $C_{28}H_{30}O_5$ (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, CD_3CN): 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, PhCH_2), 4.57 (s, 2 H, PhCH_2), 4.56, 4.52 (AB system, $J_{A,B}$ = 11.4 Hz, 2 H, PhCH_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, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 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 (Ph*C*H_2), 73.4 (Ph*C*H_2), 71.3 (Ph*C*H_2), 68.7 (C-6), 55.4 (O*C*H_3) 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-4-enopyranoside (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% Et_3N) 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, $CDCl_3$) signals of **25f**: 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, OCH_3), 3.44 (dd, $J_{5,6a}$ = 6.0 Hz, 1 H, 6a-H) ppm. Selected ^{13}C NMR (50 MHz, $CDCl_3$) signals of **25f**: δ = 151.4 (C-3). 102.1 (C-1), 96.9 (C-4), 74.1 (C-2), 73.6 (Ph*C*H_2), 73.2 (Ph*C*H_2), 72.7 (Ph*C*H_2), 71.0 (C-5), 69.0 (C-6), 55.9 (O*C*H_3) ppm. Spectroscopic data for the minor product **26f** completely agreed with those reported in the literature.[37] $C_{28}H_{30}O_5$ (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% Et_3N) 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_f = 0.18 (2:8 hexane/EtOAc). $[\alpha]_D^{20}$ = –30.4 (*c* = 0.9, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, PhCH_2), 4.73, 4.70 (AB system, $J_{A,B}$ = 11.3 Hz, 2 H, PhCH_2), 4.54 (s, 2 H, PhCH_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×OCH_3), 1.41 [s, 3 H, C(CH_3)$_2$], 1.40 [s, 3 H, C(CH_3)$_2$], 1.39 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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*(CH$_3$)$_2$], 108.3 [*C*(CH$_3$)$_2$], 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 (Ph*C*H_2), 73.3 (Ph*C*H_2), 72.9 (Ph*C*H_2), 71.1 (C-5′), 69.4 (C-6′), 65.5 (C-6), 55.3 (O*C*H_3), 52.8 (O*C*H_3), 27.4 [C(*C*H_3)$_2$], 26.7 [C(*C*H_3)$_2$], 26.6 [C(*C*H_3)$_2$], 25.2 [C(*C*H_3)$_2$] ppm. $C_{41}H_{52}O_{11}$ (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, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, PhCH_2), 4.56 (s, 2 H, PhCH_2), 4.54 (s, 2 H, PhCH_2), 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×OCH_3), 1.41 [s, 3 H, C(CH_3)$_2$], 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. ^{13}C NMR (50 MHz, $CDCl_3$): 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*(CH$_3$)$_2$], 108.3 [*C*(CH$_3$)$_2$], 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 (Ph*C*H_2), 72.6 (Ph*C*H_2), 70.9 (Ph*C*H_2), 68.5 (C-6′), 65.3 (C-6), 55.7 (O*C*H_3), 52.9, (O*C*H_3), 27.3 [C(*C*H_3)$_2$], 26.6 [C(*C*H_3)$_2$], 26.5 [C(*C*H_3)$_2$], 25.2 [C(*C*H_3)$_2$] ppm. $C_{41}H_{52}O_{11}$ (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). $[\alpha]_D^{20}$ = +76.8 (*c* = 1.2, $CHCl_3$); ref.[11a] $[\alpha]_D^{20}$ = +78 (*c* = 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, PhCH_2), 4.62 (s, 2 H, PhCH_2), 4.56, 4.50 (AB system, $J_{A,B}$ = 11.9 Hz, 2 H, PhCH_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, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 (Ph*C*H_2), 72.1 (Ph*C*H_2), 71.3 (Ph*C*H_2), 69.0 (C-6), 56.6 (O*C*H_3) ppm.

Data for 27h: Clear syrup; R_f = 0.39 (1:1 hexane/EtOAc). $[\alpha]_D^{20}$ = +39.3 (*c* = 1.4, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 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, PhCH_2), 4.79, 4.57 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhCH_2), 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, PhCH_2), 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, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 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 (Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 67.2 (C-6), 66.7 (C-5), 55.6 (O*C*H$_3$) ppm. $C_{31}H_{34}N_2O_8S$ (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_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% Et$_3$N) 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). $[\alpha]_D^{20}$ = –22.3 (c = 1.3, CHCl$_3$). ^{1}H NMR (200 MHz, CD$_3$CN): δ = 7.37–7.29 (m, 10 H, Ar-H), 4.74 (m, 3 H, 4-H, PhCH_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, PhCH_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, OCH_3), 2.15–2.26 (m, 2 H, 2ax-H, 2eq-H) ppm. ^{13}C NMR (50 MHz, CD$_3$CN): δ = 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 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 72.6 (C-5), 69.7 (C-6), 56.2 (O*C*H$_3$), 34.6 (C-2) ppm. $C_{21}H_{24}O_5$ (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). $[\alpha]_D^{20}$ = –15.2 (c = 1.1, CHCl$_3$). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 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, PhCH_2), 4.60, 4.54 (AB system, $J_{A,B}$ = 12.1 Hz, 2 H, PhCH_2), 4.06 (m, 1 H, 3-H), 3.95 (s, 2 H, 6a-H, 6b-H), 3.51 (s, 3 H, OCH_3), 2.10–2.14 (m, 2 H, 2ax-H, 2eq-H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 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 (Ph*C*H$_2$), 69.9, 69.8 (C-6, Ph*C*H$_2$), 66.2 (C-3), 56.6 (O*C*H$_3$), 32.9 (C-2) ppm. $C_{21}H_{24}O_5$ (340.42): calcd. C 74.09, H 7.11, found C 74.03, H 7.06.

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