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$InCl_3$-Catalyzed Rapid 1,3-Alkoxy Migration in Glycal Ethers: Stereoselective Synthesis of Unsaturated α-*O*-Glycosides and an α,α-(1→1)-Linked Disaccharide

Paramathevar Nagaraj[a] and Namakkal G. Ramesh*[a]

Dedicated to Dr. Antonius J. H. Klunder

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$InCl_3$ catalyzes a facile stereoselective 1,3-migration of allylic ethers of glycals to afford 2-*C*-methylene- and 2,3-unsaturated-α-*O*-glycosides in high yields. The reaction is rapid (10 min), requires only 20 mol-% of the catalyst, and is compatible with acid-labile functional groups such as epoxides and acetals. This methodology provides a convenient alternative to the Ferrier rearrangement. A direct synthesis of an α,α-(1→1)-linked disaccharide derivative by a domino process is also reported.

Introduction

The rapidly growing interest in understanding the role of oligosaccharides in various biological processes, coupled with the formidable task of isolating them from natural sources, provide organic chemists with tremendous scope for the development of new and efficient strategies for stereoselective construction of glycosidic linkages.[1] Furthermore, glycosides possessing additional synthetically maneuverable functionalities offer added advantages and allow easy access to more complex molecules. In this context, 2,3-unsaturated glycosides have enjoyed widespread applications in organic synthesis for the last four decades, as their unsaturation allowed the introduction of a variety of functionalities.[2] In recent years, 2-*C*-methylene glycosides, a class of unsaturated glycosides with an *exo*-methylene group at *C*2, have gained immense importance as versatile intermediates in the synthesis of natural products and biologically important compounds such as restricticin,[3] cyclophellitol,[4] *C*-disaccharides,[5] carbohydrates from polyenes,[6] and ara-cyclohexenyl-adenine.[7] 2-*C*-Methylene hydroperoxides synthesized from 2-*C*-methylene glycosides have been used as chiral catalysts for enantioselective epoxidation reactions.[8] The 2-*C*-methylene group is also a key structural feature of molecules involved in mechanism-based inactivation of ribonucleotide diphosphate reductase.[9]

Conventionally, 2-*C*-methylene glycosides **2** are accessed through Wittig reactions of the corresponding 2-keto glycosides **1** [Equation (1)].[3,4,7,10] In certain cases it has been reported that the Wittig reaction is very sensitive to the conditions employed.[3,4] An alternative and simple approach to 2-*C*-methylene glycosides **2** using a "New Ferrier system" first developed by Balasubramanian et al.[11] and subsequently exploited by others[12–14] generally involves an acid-catalyzed (Lewis or Brønsted) substitution with allylic rearrangement of 2-*C*-acetoxymethyl glycals **3** [Equation (2)] or 2-*C*-(propargyloxymethyl)-glycals. Some of these methodologies suffer from certain disadvantages such as substrate instability,[15,16] longer reaction times (1–16 h), lack of stereoselectivity in some examples, and requirement for stoichiometric or even larger amounts of catalysts. During the course of our research on 2-*C*-substituted sugars, we encountered a facile route to the synthesis of 2-*C*-methylene glycosides through $InCl_3$-catalyzed 1,3-alkoxy migration in glycal ethers, which we report here. The reaction is general, rapid, stereoselective, yielding only the α-anomers, and also compatible with acid-labile groups such as epoxides and acetals. A novel $InCl_3$-catalyzed one-pot stereoselective synthesis of an α,α-(1→1)-linked disaccharide has also been accomplished.

Results and Discussion

In the last decade, $InCl_3$ has found wide application as a mild Lewis acid in organic chemistry.[17] In carbohydrate

[a] Department of Chemistry, Indian Institute of Technology – Delhi, Hauz Khas,
New Delhi 110016, India
Fax: +91-11-26582037
E-mail: ramesh@chemistry.iitd.ac.in

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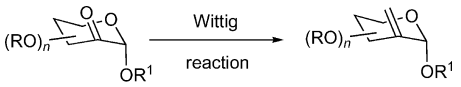

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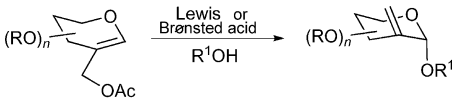
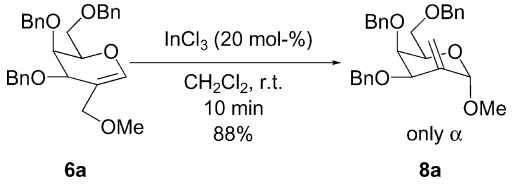


3 2 (2)

chemistry, it is mainly used as a catalyst for glycosylation reactions through the coupling of glycosyl donors with a variety of nucleophiles,[12,18] and its use in a 1,3-migration reaction, to the best of our knowledge, has not been reported so far. With this background, we investigated the reaction between 3,4,6-tri-*O*-benzyl-2-*C*-methoxymethyl galactal **6a** and $InCl_3$ (Scheme 1). When compound **6a** was initially exposed to 50 mol-% of anhydrous $InCl_3$ in dry CH_2Cl_2 at room temperature, we were pleasantly surprised to observe that the starting material was completely consumed within 10 min and that the reaction afforded an 88% yield of a single product that was characterized as methyl 2-*C*-methylene-α-*O*-glycoside **8a**. Subsequently, after few experiments, we observed that just 20 mol-% of $InCl_3$ was sufficient to bring about this reaction without any change in the reaction time, yield, or stereoselectivity. The α-anomeric stereochemistry was confirmed by detailed ^1H NMR NOE studies.[19]



6a **8a**

Scheme 1. $InCl_3$-catalyzed 1,3-migration of ether **6a**.

The facile nature of the reaction prompted us to investigate the efficiency of various Lewis acids in effecting this reaction. From Table 1, it is quite clear that while this reaction has been achieved with a variety of Lewis acids – such as anhydrous $BiCl_3$, $ZnCl_2$, and CAN, etc. – $InCl_3$ was the best among them in terms of yield. Interestingly, with $BF_3{\cdot}Et_2O$, a more popular and more commonly used Lewis acid, only a complex mixture was obtained. Furthermore, use of CH_3CN instead of CH_2Cl_2 as a solvent, while equally effecting the $InCl_3$-mediated transformation in 10 min, resulted, however, in a lower yield of the product (68%).

Table 1. Effect of Lewis acids on [1,3]-migration in ether **6a** to afford the 2-*C*-methylene glycoside **8a**.

Entry	Lewis acid	mol-%	Time (min)	Yield (%)[a]
1	$InCl_3$	20	10	88
2	$ZnCl_2$	20	10	73
3	CAN[b]	20	10	69
4	$BiCl_3$	20	10	63
5	$BF_3{\cdot}Et_2O$	20	10	complex mixture

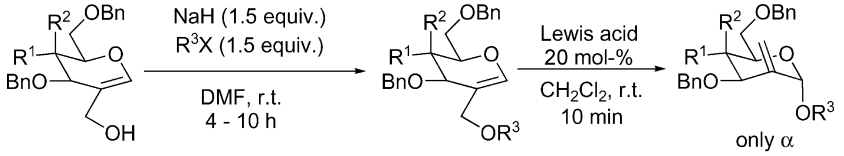
[a] Isolated yield after column chromatography. [b] Ceric ammonium nitrate.

Intrigued by the simplicity and success, we prepared several hitherto unknown glycal ethers[20,21] possessing diverse functional groups (**6a**–**g**, **7a**–**c**) from the corresponding alcohols **4** and **5**,[22] and the $InCl_3$-mediated 1,3-migration reaction was tested on them (Scheme 2, Table 2). In all cases the allylic rearrangement occurred rapidly with just 20 mol-% of anhydrous $InCl_3$, affording the corresponding 2-*C*-methylene glycosides (**8a**–**g**, **9a**–**c**) exclusively as their α-anomers in high yields. The reaction works with equal ease in both the galactal (Entries 1–7; Table 2) and the glucal series (Entries 8–10; Table 2). Comparison of a few ex-

Table 2. Synthesis of glycal ethers **6** and **7** and their allylic rearrangement catalyzed by $InCl_3$.

Entry	R-OH	Time (h)	Ether	R^3	Yield[a] (%)	Glycoside[b]	Cat.[c]	Yield[a] (%)
1	**4**	4	**6a**	CH_3	77	**8a**[d]	$InCl_3$	88
							$ZnCl_2$	73
2	**4**	4	**6b**	CH_2CH_3	70	**8b**[d]	$InCl_3$	89
3	**4**	5	**6c**	$CH_2CH{=}CH_2$	70	**8c**	$InCl_3$	73
							$ZnCl_2$	60
4	**4**	4	**6d**	$CH_2{-}C{\equiv}CH$	73	**8d**	$InCl_3$	83
5	**4**	8	**6e**	$CH_2CH(OCH_3)_2$	57	**8e**	$InCl_3$	64
6	**4**	10	**6f**[e]	CH_2-CH-CH_2 (O)	70	**8f**[e]	$InCl_3$	70
							$ZnCl_2$[f]	–
7	**4**	4	**6g**	CH_2Ph	74	**8g**[d]	$InCl_3$	91
							$ZnCl_2$	78
8	**5**	4	**7a**	CH_3	55	**9a**[d]	$InCl_3$	67
9	**5**	8	**7b**[e]	CH_2-CH-CH_2 (O)	56	**9b**[e]	$InCl_3$	60
							$ZnCl_2$[f]	–
10	**5**	5	**7c**	CH_2Ph	70	**9c**[d]	$InCl_3$	72

[a] Isolated yields after column chromatography. [b] In all cases, only α-anomer was obtained. [c] All the reactions were performed with 20 mol-% of anhydrous catalyst in dry CH_2Cl_2 at room temperature over 10 min. [d] The spectroscopic data were consistent with the literature values[11,12,13,14]. [e] Racemic epichlorohydrin was used for the etherification, and the 1:1 diastereomeric mixtures of **6f** and **7b** were subjected to subsequent allylic rearrangement without separation. [f] A complex mixture was obtained.



4 R^1 = H; R^2 = OBn
5 R^1 = OBn; R^2 = H

6 R^1 = H; R^2 = OBn
7 R^1 = OBn; R^2 = H

8 R^1 = H; R^2 = OBn
9 R^1 = OBn; R^2 = H

Scheme 2. Synthesis of glycal ethers (**6** and **7**) and their $InCl_3$-catalyzed allylic rearrangement.

amples carried out with 20 mol-% of anhydrous $ZnCl_2$ displayed the catalytic superiority of $InCl_3$ (Entries 1, 3, 6, 7, and 9; Table 2).

In order to demonstrate the functional group compatibility, ethers bearing acid-labile groups such as epoxides (**6f** and **7b**) and an acetal (**6e**) were synthesized and subjected to the $InCl_3$-mediated reaction. Gratifyingly, the alkoxy migration reaction occurred very readily to afford the corresponding 2-*C*-methylene glycosides (**8f**, **9b**, and **8e**) in good yields and with the acid labile groups remaining intact. In view of the literature background that $InCl_3$ rapidly catalyzed the rearrangement of epoxides to carbonyl compounds,[23] the preference for the 1,3-migration reaction over the epoxide rearrangement in the case of compounds **6f** and **7b** merits special mention. It is noteworthy that $ZnCl_2$ failed to bring about the expected allylic rearrangements of compound **6f** and **7b**, resulting in complex mixtures.

A plausible mechanism for the 1,3-migration reaction with the observed α-stereoselectivity is given in Scheme 3. Initial coordination of $InCl_3$ with the side-chain alkoxy group at *C*-2 of **6** (to afford intermediate **I**) followed by its departure would result in the formation of a highly stabilized anomeric carbocation **II**. It is likely that the anomeric carbocation **II** would be stabilized not only by the ring oxygen atom but also by the remote oxygen atom of the *C*-6 benzyloxy group, thereby sterically blocking the β-face for attack of the departing alkoxy group and thus resulting in exclusive formation of α-anomers. Stereoselective glycosylation reactions through the anchimeric assistance of remote acyl, ester, or carbamate groups are well documented in the literature.[24] It has also been reported that esters are better stereodirecting agents than alkoxy groups. However, most of these reports have dealt with saturated pyranosides, except for the one by Srivastava et al.,[24a] who observed such remote stereocontrol in an endocyclic unsaturated sugar. In the present case, in order to find out whether the exclusive formation of α-anomers in all these examples is influenced by the remote stereocontrolling effect of the *C*-6 benzyloxy group, semiempirical AM1 calculations were performed with HyperChem.[25] First of all, AM1 calculations indicate that the preferred low-energy conformation of compound **6a** is $^5H_4$ (with a minimum calculated energy of –7.0 kcal), in which the (pseudo)axial *C*-6 benzyloxy group positions itself close to the anomeric carbon, with a spatial distance of 2.91 Å between the *C*-6 benzyloxy oxygen atom and the anomeric carbon (Figure 1). In the carbocation **II**, this spatial distance decreases to 2.74 Å, presumably due to the interaction between the lone pair of electrons on the oxygen atom of the *C*-6 benzyloxy group and the positive charge at the anomeric carbon (Figure 1). Such an interaction would not only provide additional stability for **II**, but would also sterically block the β-face for attack of the nucleophile. On the other hand, the spatial distance between the oxygen atom of the *C*-3 benzyloxy group and the anomeric carbon increases from 3.28 Å in **6a** to 3.39 Å in carbocation **II**. Preliminary AM1 calculations are thus suggestive of a possible involvement of the *C*-6 benzyloxy group in stereodirecting the glycosylation step, resulting in exclusive formation of α-anomers. However, detailed mechanistic investigations taking the effect of solvents, temperature, reagents,

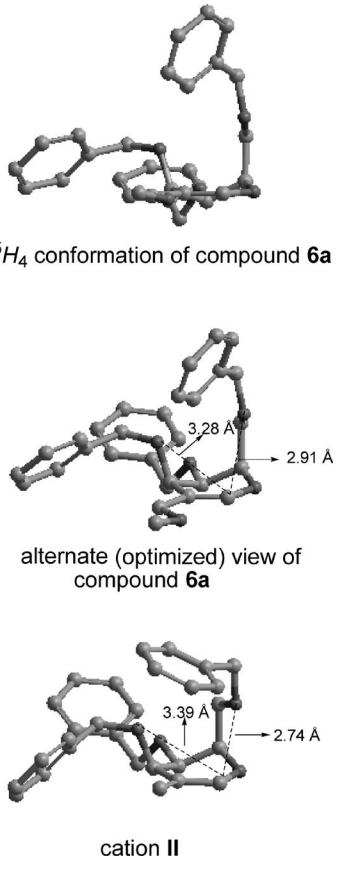
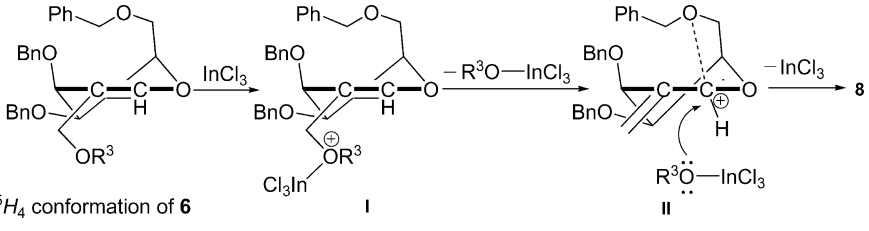


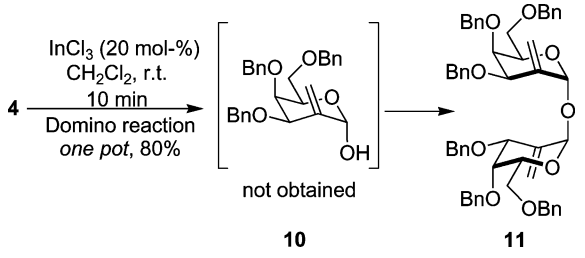
Figure 1. Low-energy conformations of compound **6a** and carbocation **II**. Hydrogens are omitted for clarity.



Scheme 3. Putative mechanism for stereoselective formation of α-glycosides **8** and **9**.

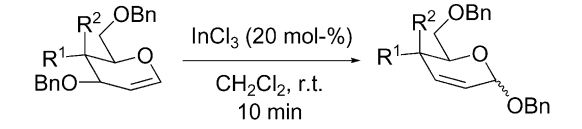
reaction conditions, etc. into account would need to be done to explain the observed stereoselectivity unambiguously.

A novel and interesting observation was the direct synthesis of an α,α-(1→1)-linked disaccharide **11** as a single diastereomer in 80% yield in just 10 min (Scheme 4) when alcohol **4** itself was exposed to a catalytic amount of anhydrous $InCl_3$. The formation of the disaccharide was suggested by the absence of any OH stretching frequency in its IR spectrum, as well as the absence of any exchangeable proton in its ^1H NMR spectrum. This was further supported by the ESI HRMS data, which showed a peak at 879.3998 {$[M + Na]^+$} due to the formation of the disaccharide. The C_2 symmetry of the molecule was evidenced from its ^{13}C NMR spectrum, which displayed signals corresponding to only half the number of carbon atoms. The α,α-anomeric stereochemistry was confirmed by detailed ^1H NMR NOE studies. It is likely that the reaction proceeds through an initial [1,3]-migration of alcohol **4** to give the hemiacetal **10**, which could not be isolated under the reaction conditions, followed by a rapid in situ glycosylation reaction resulting directly in the stereoselective formation of an α,α-(1→1)-linked disaccharide **11**. To the best of our knowledge, formation of an α,α-(1→1)-linked disaccharide through such a domino process has no precedence. Given the biological significance of trehalose {α,α-(1→1)-linked glucoside} and its analogues,[26] the one-pot synthesis of compound **11** reported here assumes synthetic significance.



Scheme 4. Domino one-pot synthesis of disaccharide **11**.

An earlier report by Descotes and Martin[27] on the $BF_3{\cdot}Et_2O$-catalyzed rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal **12** to the 2,3-unsaturated α-benzyl glycoside **14** prompted us to examine this reaction with $InCl_3$ as a catalyst. As in our earlier cases, treatment of **12** with 20 mol-% of $InCl_3$ proceeded with equal feasibility to afford **14** in 64% yield, as an anomeric mixture in a 5:1 ratio.[28,29] $InCl_3$ also mediated a rapid transformation of 3,4,6-tri-*O*-benzyl-D-galactal **13** into the glycoside **15** as a single anomer in 77% yield (Scheme 5).[30] Interestingly, with $ZnCl_2$ as a catalyst, the above reactions again proved to be futile. It is worth mentioning that Ferrier rearrangements of protected galactals are not as easy reactions as those of protected glucals,[31] and the methodology reported here for the synthesis of 2,3-unsaturated galactoside through [1,3]-alkoxy migration should prove to be synthetically attractive.



12 R^1 = OBn; R^2 = H
13 R^1 = H; R^2 = OBn

14 R^1 = OBn; R^2 = H; 64%, α/β = 5/1
15 R^1 = H; R^2 = OBn; 77%, only α

Scheme 5. $InCl_3$-catalyzed synthesis of 2,3-unsaturated glycosides **14** and **15**.

Conclusions

In conclusion, we report a new strategy for the synthesis of relatively less well explored unsaturated glycosides – namely, 2-*C*-methylene glycosides – for which only a few methods are available in the literature. The reaction is highly stereoselective, affording only the α-anomers in all cases. This methodology, while providing a convenient alternative to the Ferrier rearrangement, is also explicitly simple to perform. We have also demonstrated the synthesis of some unique 2-*C*-methyleneglycosides such as **8e**, **8f**, and **9b** that are not accessible by the existing methods. The stereoselective formation of the α,α-(1→1)-linked disaccharide derivative **11** in one-pot fashion is synthetically quite interesting and is likely to spur further interest in this area.

Experimental Section

General Considerations: All solvents were purified by standard procedures. Thin-layer chromatography (TLC) was performed on Merck silica gel pre-coated on aluminium plates. Flash column chromatography was performed on 230–400 mesh silica gel. Optical rotations were recorded on an Autopol II or an Autopol V (Rudolph Research Flanders, New Jersey) instrument. All the rotations were measured at 589 nm (sodium D line). Melting points of the compounds are uncorrected. IR spectra were taken over the 4000–400 cm^{-1} range as KBr pellets on a Nicolet (Madison, USA) FT-IR spectrophotometer (Model protégé 460). All the ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Spectrospin DPX FT-NMR spectrometer. Chemical shifts are reported as δ values (ppm) relative to Me_4Si as internal standard. Mass spectra were recorded with a Waters Micro Mass Q-TOF or an Applied Biosystems Q-Star instrument.

Typical Procedure for the Synthesis of Ethers 6 and 7: Alcohol **4** or **5**[22] (1.0 g, 2.2 mmol) was dissolved in dry DMF (5.0 mL), and the mixture was cooled to 0 °C. Sodium hydride (0.131 g, 3.3 mmol, 60% in paraffin oil) was added. After 5 min, alkyl halide (3.3 mmol) was added, and the reaction mixture was stirred at room temperature for the specified time. After completion, the reaction mixture was quenched with water and extracted with ethyl acetate (4 × 50 mL). The organic layer was washed with saturated sodium hydrogen carbonate solution, followed by water, and was then dried with sodium sulfate, filtered, and concentrated. Column chromatography of the crude reaction mixture with hexane/ethyl acetate (5:1) as an eluent afforded ethers **6** or **7**, respectively.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-methoxymethyl-D-*lyxo*-hex-1-enitol (6a): Compound **6a** (0.80 g, 77% yield) was obtained as a colorless liquid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and methyl iodide (0.213 mL, 3.3 mmol) over 4 h. $[\alpha]_D^{28}$ = +11.5 (*c* = 0.33, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.23 (m, aromatic, 15 H), 6.39 (s, 1 H, 1-H), 4.81 (d, *J* = 11.7 Hz, 1 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.64 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 11.7 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.40 (d, *J* = 12.0 Hz, 1 H), 4.26 (m, 2 H), 4.14 (d, *J* = 11.1 Hz, 1 H), 3.96 (t, *J* = 3.3 Hz, 1 H), 3.80–3.78 (m, 1 H), 3.68 (dd, *J* = 10.5, 4.2 Hz, 1 H), 3.59 (d, *J* = 10.5 Hz, 1 H), 3.23 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (C-1), 138.4, 138.0, 137.9,137.7, 128.7,128.4, 127.8, 127.7, 127.6, 127.4, 127.3 (C_{aryl}), 109.7 (C), 75.4 (OCH), 73.2 (OCH_2), 73.0 (OCH_2), 72.8 (OCH_2), 72.2 (OCH), 71.6 (OCH), 69.8 (OCH_2), 67.8 (OCH_2), 56.8 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2870, 1663, 1455, 1350, 1088, 952, 907, 741, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{32}NaO_5$ $[M + Na]^+$ 483.2147; found 483.2145.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-ethoxymethyl-D-*lyxo*-hex-1-enitol (6b): Compound **6b** (0.74 g, 70% yield) was obtained as a colorless liquid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and ethyl iodide (0.268 mL, 3.3 mmol) over 4 h. $[\alpha]_D^{28}$ = +13.6 (*c* = 0.22, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 15 H, aromatic), 6.44 (s, 1 H, 1-H), 4.87 (d, *J* = 11.7 Hz, 1 H), 4.84 (d, *J* = 11.7 Hz, 1 H), 4.72 (d, *J* = 15.0 Hz, 1 H), 4.70 (d, *J* = 11.7 Hz, 1 H), 4.56 (d, *J* = 11.7 Hz, 1 H), 4.45 (d, *J* = 12.0 Hz, 1 H), 4.33 (m, 1 H), 4.20 (d, *J* = 10.8 Hz, 1 H), 4.02 (t, *J* = 3.6 Hz, 1 H), 3.86 (dd, *J* = 10.5, 3.5 Hz, 1 H), 3.80–3.71 (m, 2 H), 3.54–3.35 (m, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4 (C-1), 138.3, 137.8, 137.6, 127.9, 127.5, 127.4, 127.3, 127.2, 127.1 (C_{aryl}), 109.9 (C), 75.2 (OCH), 73.0 (OCH_2), 72.8 (2 × OCH_2), 72.7 (OCH_2), 72.1 (OCH), 70.6 (OCH), 67.7 (OCH_2), 64.5 (OCH_2), 14.8 (OCH_2CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2969, 2863, 1663, 1489, 1454, 1353, 1091, 741, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{34}NaO_5$ $[M + Na]^+$ 497.2304; found 497.2304.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(prop-2′-enyloxy)-methyl-D-*lyxo*-hex-1-enitol (6c): Compound **6c** (0.76 g, 70% yield) was obtained as a colorless liquid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and allyl bromide (0.287mL, 3.3 mmol) over 5 h. $[\alpha]_D^{28}$ = +20.0 (*c* = 0.28, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.28 (m, aromatic, 15 H), 6.45 (s, 1 H, 1-H), 6.00–5.87 (m, 1 H), 5.30 (d, *J* = 17.1 Hz, 1 H), 5.21 (d, *J* = 10.5 Hz, 1 H), 4.87 (d, *J* = 12.0 Hz, 1 H), 4.86 (d, *J* = 11.4 Hz, 1 H), 4.71 (d, *J* = 11.4 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 4.35 (m, 2 H), 4.25 (d, *J* = 11.1 Hz, 1 H), 4.04–3.97 (m, 4 H), 3.64–3.56 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0 (C-1), 138.6, 138.19, 137.9, 134.8, 128.1, 127.87, 127.81, 127.67, 127.60, 127.4 (C_{aryl}), 116.9 (=CH_2), 110.0 (C), 75.7 (OCH), 73.4 (OCH_2), 73.2 (OCH_2), 73.0 (OCH_2), 72.3 (OCH), 71.0 (OCH), 70.3 (OCH_2), 68.0 (OCH_2), 67.7 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2861, 1662, 1456, 1348, 1183, 1071, 922, 741, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{34}NaO_5$ $[M + Na]^+$ 509.2304; found 509.2298.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(2′,2′-dimethoxyethoxy)methyl-D-*lyxo*-hex-1-enitol (6e): Compound **6e** (0.672 g, 57% yield) was obtained as a colorless liquid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and α-chloroacetaldehyde dimethyl acetal (0.398 mL, 3.3 mmol) over 8 h. $[\alpha]_D^{28}$ = +97.1 (*c* = 0.35, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.24 (m, aromatic, 15 H), 6.39 (s, 1 H, 1-H), 4.808 (d, *J* = 12.0 Hz, 1 H), 4.801 (d, *J* = 11.7 Hz, 1 H), 4.66 (d, *J* = 11.7 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.53–4.38 (m, 3 H), 4.29–4.25 (m, 3 H), 3.96 (t, *J* = 3.6 Hz, 1 H), 3.83–3.63 (m, 3 H), 3.45–3.40 (m, 2 H), 3.35 [s, 6 H, $C(OMe)_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2 (C-1), 138.7, 138.1, 138.0, 128.3, 128.2, 127.89, 127.85, 127.69, 127.64, 127.5 (C_{aryl}), 109.7 (C), 102.6 [$CH(OCH_3)_2$], 75.7 (OCH), 73.5 (OCH_2), 73.3 (OCH_2), 73.1 (OCH_2),72.4 (OCH), 71.0 (OCH), 69.0 (OCH_2), 68.7 (OCH_2), 68.1 (OCH_2), 53.7 (OCH_3), 53.6 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2867, 1671, 1497, 1449, 1390, 1256, 1191, 1091, 743, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{38}O_7Na$ $[M + Na]^+$ 557.2515; found 557.2528.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(2′,3′-epoxypropyloxy)methyl-D-*lyxo*-hex-1-enitol (6f): Compound **6f** (0.78 g, 70% yield) was obtained as a colorless liquid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and epichlorohydrin (0.263 mL, 3.3 mmol) over 10 h. The spectroscopic data and specific rotation reported are for a 1:1 mixture of diastereomers. $[\alpha]_D^{28}$ = +20.0 (*c* = 0.22, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.19 (m, aromatic, 30 H), 6.38 (s, 2 H, 1-H), 4.80 (d, *J* = 12.0 Hz, 2 H), 4.78 (d, *J* = 11.4 Hz, 2 H), 4.64 (d, *J* = 11.4 Hz, 2 H), 4.61 (d, *J* = 12.0 Hz, 2 H), 4.50 (d, *J* = 11.7 Hz, 2 H), 4.40 (d, *J* = 11.7 Hz, 2 H), 4.26–4.20 (m, 6 H), 3.96 (m, 2 H), 3.83–3.51 (m, 8 H), 3.28–3.21 (m, 2 H), 3.06 (m, 2 H), 2.71 (t, *J* = 4.2 Hz, 2 H), 2.51 (m, 2 H) ppm. ^{13}C NMR(75 MHz, $CDCl_3$): δ = 143.2 (C-1), 143.1, 138.5, 138.0, 137.8, 128.2, 127.77, 127.71, 127.59, 127.52, 127.3 (C_{aryl}), 109.6 (C), 75.6 (OCH), 73.3 (OCH_2), 73.1 (OCH_2),73.0 (OCH_2), 72.2 (OCH), 70.9 (OCH), 69.9 (OCH_2), 69.6 (OCH_2), 68.8 (OCH_2), 68.6 (OCH_2), 68.0 (OCH_2), 50.6 (OCH), 44.18 (OCH_2), 44.12 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2863, 2361, 1663, 1456, 1347, 1185, 1088, 742, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{34}NaO_6$ $[M + Na]^+$ 525.2253; found 525.2242.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-benzyloxymethyl-D-*lyxo*-hex-1-enitol (6g): Compound **6g** (0.89g, 74% yield) was obtained as a colorless low-melting solid by treatment of glycal **4** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and benzyl chloride (0.381 mL, 3.3 mmol) over 4 h. $[\alpha]_D^{28}$ = +27.5 (*c* = 0.16, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.24 (m, aromatic, 20 H), 6.39 (s, 1 H, 1-H), 4.80 (d, *J* = 11.7 Hz, 1 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 11.4 Hz, 1 H), 4.57 (d, *J* = 11.7 Hz, 1 H), 4.53–4.35 (m, 4 H), 4.27–4.24 (m, 2 H), 3.95 (t, *J* = 3.3 Hz, 1 H), 3.83–3.53 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2 (C-1), 138.6, 138.4, 138.1, 138.0, 128.36, 128.30, 127.8, 127.7, 127.6, 127.5, 126.9 (C_{aryl}), 110.0 (C), 75.7 (OCH), 73.6 (OCH_2), 73.3 (OCH_2), 73.1 (OCH_2), 72.5 (OCH), 71.5 (OCH_2), 71.1 (OCH), 68.1 (OCH_2), 67.9 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2903, 2861, 1658, 1453, 1346, 1211, 1172, 1094, 890, 735, 690, 602, 468 cm^{-1}. HRMS (ESI): calcd. for $C_{35}H_{36}NaO_5$ $[M + Na]^+$ 559.2460; found 559.2430.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-methoxymethyl-D-*arabino*-hex-1-enitol (7a): Compound **7a** (0.56 g, 55% yield) was obtained as a colorless liquid by treatment of glycal **5** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and methyl iodide (0.213 mL, 3.3 mmol) over 4 h. $[\alpha]_D^{28}$ = +34.5 (*c* = 0.39, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.24 (m, aromatic, 15 H), 6.47 (s, 1 H, 1-H), 4.73 (d, *J* = 11.7 Hz, 1 H), 4.63–4.53 (m, 5 H), 4.20–4.17 (m, 3 H), 3.89 (t, *J* = 6.3 Hz, 1 H), 3.80 (dd, *J* = 10.5, 5.7 Hz, 1 H), 3.70 (dd, *J* = 10.5, 3.3 Hz, 1 H), 3.59 (d, *J* = 11.4 Hz, 1 H), 3.25 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7 (C-1), 138.4, 138.0, 137.9, 128.48, 128.42, 127.89, 127.85, 127.77, 127.70 (C_{aryl}), 109.7 (C), 76.6 (OCH), 74.3 (OCH), 73.8 (OCH), 73.4 (OCH_2), 73.1 (OCH_2), 72.8 (OCH_2), 70.0 (OCH_2), 68.2 (OCH_2), 56.9 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2862, 1666, 1455, 1362, 1168, 1089, 740, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{32}NaO_5$ $[M + Na]^+$ 483.2147; found 483.2152.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(2′,3′-epoxypropyloxy)methyl-D-*arabino*-hex-1-enitol (7b): Compound **7b** (0.624 g, 56% yield) was obtained as a colorless liquid by treatment of glycal **5** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and epichlorohydrin (0.263 mL, 3.3 mmol) over 8 h. The spectroscopic data and specific rotation reported are for a 1:1 mixture of diastereomers. $[\alpha]_D^{28}$ = +32.5 (*c* = 0.22, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.24 (m, aromatic, 30 H), 6.46 (s, 2 H, 1-H), 4.72 (d, *J* = 11.4 Hz, 2 H), 4.64–4.52 (m, 10 H), 4.30–4.15 (m, 6 H), 3.88 (t, *J* = 5.4 Hz, 2 H), 3.79–3.64 (m, 6 H), 3.53 (m, 2 H), 3.36–3.24 (m, 2 H), 3.10 (m, 2 H), 2.75 (m, 2 H), 2.55 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9 (C-1), 143.8 (C-1), 138.3, 137.9, 128.5, 128.47, 128.41, 127.8, 127.7, 127.6 (C_{aryl}), 109.4 (C), 109.3 (C), 76.6 (OCH), 76.5 (OCH), 73.9 (OCH), 73.7 (OCH), 73.4 (OCH_2), 73.0 (OCH_2), 72.79 (OCH_2), 72.76 (OCH_2),71.2 (OCH_2),69.58 (OCH_2), 69.53 (OCH_2), 69.4 (OCH_2), 68.8 (OCH_2), 68.6 (OCH_2), 68.2 (OCH_2), 50.9 (OCH), 50.7 (OCH), 44.36 (OCH_2), 44.32 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2863, 1958, 1879, 1813, 1723, 1666, 1487, 1456, 1361, 1253, 1169, 914, 847, 743, 699, 607, 473 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{34}NaO_6$ $[M + Na]^+$ 525.2253; found 525.2249.

1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-benzyloxymethyl-D-*arabino*-hex-1-enitol (7c): Compound **7c** (0.82 g, 70% yield) was obtained as a colorless liquid by treatment of glycal **5** (1.0 g, 2.2 mmol) with NaH (0.131 g, 3.3 mmol) and benzyl chloride (0.381 mL, 3.3 mmol) over 4 h. $[\alpha]_D^{28}$ = +36.1 (*c* = 0.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.25 (m, aromatic, 20 H), 6.50 (s, 1 H, 1-H), 4.75 (d, *J* = 11.4 Hz, 1 H), 4.66–4.63 (m, 3 H), 4.60–4.52 (m, 3 H), 4.39 (d, *J* = 11.7 Hz, 1 H), 4.34–4.24 (m, 3 H), 3.94 (t, *J* = 5.4 Hz, 1 H), 3.76 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6 (C-1), 138.3, 138.2, 137.88, 137.85, 128.6, 128.3, 128.2, 128.1, 128.0, 127.75, 127.73, 127.6, 127.5, 127.4 (C_{aryl}), 109.5 (C), 76.4 (OCH), 74.0 (OCH), 73.7 (OCH),73.3 (OCH_2), 72.9 (OCH_2),72.6 (OCH_2), 70.8 (OCH_2) 68.1 (OCH_2), 67.5 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2860, 1664, 1456, 1361, 1169, 1067, 740, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{35}H_{36}NaO_5$ $[M + Na]^+$ 559.2460; found 559.2467.

General Procedure for $InCl_3$-Mediated [1,3]-Migrations in Glycal Ethers 6 and 7 to form 8 and 9: Glycal ether **6** or **7** (1 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and dried with activated molecular sieves (4 Å) in order to remove any moisture if present. The solution was then transferred by syringe to a dry three-necked round-bottomed flask (flame-dried and cooled under argon). Anhydrous $InCl_3$ (0.2 mmol) was added to the reaction mixture in one lot, and the reaction was allowed to proceed under argon. After 10 min, the reaction mixture was quenched with water and extracted with chloroform (3 × 50 mL). The combined organic layer was washed with water, dried with sodium sulfate, filtered, and concentrated. The crude product was purified by column chromatography with hexane/ethyl acetate (5:1) mixture as an eluent to provide 2-*C*-methylene glycosides **8** or **9**, respectively.

Methyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (8a): Compound **8a** (0.22 g, 88% yield) was obtained by treatment of ether **6a** (0.250 g, 0.54 mmol) with anhyd. $InCl_3$ (0.022 g, 0.108 mmol) over 10 min. Colorless liquid. $[\alpha]_D^{28}$ = +5.6 (*c* = 0.53, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.23 (m, aromatic, 15 H), 5.43 (s, 1 H), 5.28 (s, 1 H), 5.10 (s, 1 H, 1-H), 4.91 (d, *J* = 11.7 Hz, 1 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 4.65 (d, *J* = 13.5 Hz, 1 H), 4.61 (d, *J* = 13.5 Hz, 1 H), 4.45 (d, *J* = 11.7 Hz, 1 H), 4.43–4.39 (m, 2 H), 4.09 (t, *J* = 6.3 Hz, 1 H), 3.97 (m, 1 H), 3.62–3.54 (m, 2 H), 3.38 (s, 3 H, OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7 (C-2), 138.5, 138.3, 138.0, 128.4, 128.3, 128.2, 128.0, 127.7, 127.5, 127.4, 127.0 (C_{aryl}), 111.5 (=CH_2), 102.5 (C-1), 78.0 (OCH), 75.4 (OCH), 73.9 (OCH_2), 73.3 (OCH_2), 71.5 (OCH_2), 70.6 (OCH), 69.3 (OCH_2), 54.7 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2910, 2359, 1597, 1454, 1358, 1194, 1092, 1055, 966, 916, 740, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{32}NaO_5$ $[M + Na]^+$ 483.2147; found 483.2186.

Prop-2-enyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (8c): Compound **8c** (0.175g, 76% yield) was obtained by treatment of ether **6c** (0.230 g, 0.47 mmol) with anhyd. $InCl_3$ (0.020 g, 0.094 mmol) over 10 min. Colorless liquid. $[\alpha]_D^{28}$ = +16 (*c* = 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ = 7.36–7.21 (m, aromatic, 15 H), 5.97–5.84 (m, 1 H), 5.40 (s, 1 H), 5.28–5.14 (m, 4 H), 4.89 (d, *J* = 12.0 Hz, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.63 (d, *J* = 11.7 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.49–4.37 (m, 3 H), 4.19–4.09 (m, 2 H) 4.04–3.97 (m, 2 H), 3.54–3.50 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.7 (C-2), 138.6, 138.3, 138.0, 134.0,128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.6, 127.59, 127.49, 127.44, 127.0 (C_{aryl}), 117.2 (=CH_2), 111.4 (=CH_2), 100.6 (C-1), 78.1 (OCH), 75.4 (OCH), 73.9 (OCH_2), 73.3 (OCH_2), 71.5 (OCH_2), 70.7 (OCH), 69.3 (OCH_2), 67.7 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2917, 2862, 2359, 1597, 1492, 1455, 1358, 1149, 1093, 1022, 740, 698 cm^{-1}. HRMS (ESI) calcd. for $C_{31}H_{34}NaO_5$ $[M + Na]^+$ 509.2304; found 509.2291.

Prop-2-ynyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (8d): Compound **8d** (0.165 g, 83% yield) was obtained by treatment of ether **6d** (0.200 g, 0.413 mmol) with anhyd. $InCl_3$ (0.018 g, 0.082 mmol) over 10 min. Colorless liquid. $[\alpha]_D^{28}$ = +20.8 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.20 (m, aromatic,15 H), 5.45 (s, 1 H, 1-H), 5.38 (s, 1 H), 5.31 (s, 1 H), 4.90 (d, *J* = 12.0 Hz, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 12.0 Hz, 1 H), 4.44–4.37 (m, 2 H), 4.23 (m, 2 H), 4.09 (t, *J* = 6.6 Hz, 1 H), 3.98 (m, 1 H), 3.54 (m, 2 H), 2.39 (t, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.0 (C-2), 138.5, 138.3, 137.9, 128.4, 128.38, 128.34, 128.1, 127.9, 127.7, 127.6, 127.55, 127.51, 127.0 (C_{aryl}), 112.4 (=CH_2), 100.1 (C-1), 79.0 (C), 78.0 (=CH), 75.2 (OCH),74.5 (OCH_2), 74.0 (OCH_2), 73.4 (OCH_2), 71.6 (OCH_2), 71.1 (OCH), 69.1 (OCH_2), 54.0 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 2861, 1636, 1455, 1358, 1092, 1028, 740, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{32}NaO_5$ $[M + Na]^+$ 507.2140; found 507.2139.

(2′,2′-Dimethoxy)ethyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (8e): Compound **8e** (0.18 g, 64% yield) was obtained by treatment of ether **6e** (0.280 g, 0.524 mmol) with anhyd. $InCl_3$ (0.022 g, 0.104 mmol) over 10 min. Colorless liquid. $[\alpha]_D^{28}$ = +9.3 (*c* = 0.6, $CHCl_3$). ^1H NMR (300MHz, $CDCl_3$): δ = 7.36–7.21 (m, aromatic, 15 H), 5.41 (s, 1 H, 1-H), 5.26 (s, 1 H), 5.22 (s, 1 H), 4.89 (d, *J* = 11.7 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.63–4.57 (m, 2 H), 4.53 (t, *J* = 5.4 Hz, 1 H), 4.48–4.37 (m, 3 H), 4.15 (t, *J* = 6.3 Hz, 1 H), 3.98 (m, 1 H), 3.66 (dd, *J* = 11.1, 6.3 Hz, 1 H), 3.59–3.49 (m, 3 H), 3.35 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6 (C-2), 138.6, 138.4, 138.0, 128.48, 128.44, 128.3, 128.1, 127.8, 127.7, 127.5, 127.1 (C_{aryl}), 111.9 (=CH_2), 102.6 (C-1), 101.9 (OCH), 78.0 (OCH), 75.3 (OCH), 74.0 (OCH_2), 73.4 (OCH_2), 71.6 (OCH_2), 70.8 (OCH), 69.4 (OCH), 66.8 (OCH_2), 53.9 (OCH_3), 53.7 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1633, 1496, 1454, 1403, 1358, 1325, 1192, 1107, 1072, 1031, 973, 919, 738, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{38}NaO_7$ $[M + Na]^+$ 557.2515; found 557.2540.

2′,3′-Epoxypropyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (8f): Compound **8f** (0.19 g, 70% yield) was obtained by treatment of ether **6f** (0.270 g, 0.53 mmol) with anhyd.

$InCl_3$ (0.022 g, 0.106 mmol) over 10 min. Colorless liquid; the spectroscopic data and specific rotation reported are for a 1:1 mixture of diastereomers. $[\alpha]_D^{28}$ = +7.5 (*c* = 0.4, $CHCl_3$). ^1H NMR (300MHz, $CDCl_3$): δ = 7.37–7.21 (m, aromatic, 30 H) 5.42 (s, 2 H),5.27 (s, 2 H), 5.24 (s, 1 H), 5.23 (s, 1 H), 4.90 (d, *J* = 11.7 Hz, 2 H), 4.73–4.58 (m, 6 H), 4.50–4.37 (m, 6 H), 4.14 (d, *J* = 4.2 Hz, 2 H), 3.97–3.69 (m, 4 H), 3.63–3.47 (m, 6 H), 3.18–3.16 (m, 2 H), 2.77–2.73 (m, 2 H), 2.58–2.55 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.4 (C-2), 138.5, 138.3, 138.0, 128.3, 128.0, 127.6, 127.5, 127.0 (C_{aryl}), 111.9 (2×=CH_2), 101.8 (C-1), 101.5 (C-1), 77.9 (OCH), 75.3 (OCH), 74.0 (OCH_2), 73.3 (OCH_2), 71.6 (OCH_2), 70.8 (OCH), 70.7 (OCH), 69.4 (OCH_2), 69.2 (OCH_2), 68.3 (OCH_2), 67.5 (OCH_2), 50.5 (OCH), 50.2 (OCH), 44.5 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 2861, 1635, 1491, 1456, 1358, 1249, 1206, 1092, 740, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{34}NaO_6$ $[M + Na]^+$ 525.2253; found 525.2255.

2′,3′-Epoxypropyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-C-methylene-α-D-*arabino*-hexopyranoside (9b): Compound **9b** (0.130 g, 56% yield) was obtained by treatment of allyl ether **7b** (0.230 g, 0.45 mmol) with anhyd. $InCl_3$ (0.020 g, 0.090 mmol) over 10 min. Colorless liquid; the spectroscopic data and specific rotation reported are for a 1:1 mixture of diastereomers. $[\alpha]_D^{28}$ = +10.5 (*c* = 0.40, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.16 (m, aromatic, 30 H) 5.33 (s, 2 H), 5.23–5.19 (m, 4 H), 4.89 (d, *J* = 10.8 Hz, 2 H),4.76 (m, 4 H), 4.62–4.44 (m, 8 H), 3.98 (m, 2 H), 3.88–3.49 (m, 10 H), 3.20–3.19 (m, 2 H), 2.81 (t, *J* = 5.4 Hz, 2 H), 2.79–2.61 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.9 (C-2), 138.2, 138.0, 128.7, 128.5, 128.3, 128.3, 127.9, 127.8, 127.6 (C_{aryl}), 111.1 (2×=CH_2), 101.6 (C-1), 101.5 (C-1), 81.0 (OCH), 77.9 (OCH), 75.0 (OCH_2), 73.5 (OCH_2), 73.46 (OCH_2), 73.43 (OCH_2), 71.78 (OCH_2), 71.70 (OCH), 68.8 (OCH_2), 68.7 (OCH), 68.3 (OCH_2), 67.4 (OCH_2), 50.5 (OCH), 50.2 (OCH), 44.67 (OCH_2), 44.62 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2921, 2862, 1633, 1455, 1359, 1258, 1208, 1105, 1029, 740, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{34}NaO_6$ $[M + Na]^+$ 525.2253; found 525.2259.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranosyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-*lyxo*-hexopyranoside (11): Alcohol **4** (0.280 g, 0.673 mmol) was dissolved in dry CH_2Cl_2 (4 mL), and the mixture was dried with activated molecular sieves (4 Å) in order to remove any moisture if present. The solution was then transferred by syringe to a dry three-necked round-bottomed flask (flame-dried and cooled under argon). Anhydrous $InCl_3$ (0.028 g, 0.134 mmol) was added to the mixture, and the reaction was allowed to proceed under argon. After 10 min, the reaction mixture was quenched with water and extracted with chloroform (3×50 mL). The combined organic layer was washed with water, dried with sodium sulfate, filtered, and concentrated. The crude product was purified by column chromatography with a hexane/ethyl acetate (5:1) mixture as an eluent to provide compound **11** (0.140 g, 80% yield) as a colorless liquid. $[\alpha]_D^{28}$ = +33.7 (*c* = 0.64, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, aromatic, 15 H), 5.56 (s, 1 H), 5.39 (s, 1 H), 5.32 (s, 1 H), 4.93 (d, *J* = 12.0 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.66 (d, *J* = 12.0 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.450 (d, *J* = 11.7 Hz, 1 H), 4.43 (d, *J* = 11.7 Hz, 1 H), 4.34 (d, *J* = 2.1 Hz, 1 H), 4.12 (t, *J* = 6.6 Hz, 1 H), 4.01 (d, *J* = 1.8 Hz, 1 H), 3.59–3.56 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3 (C-2), 138.5, 138.3, 138.0, 128.7, 128.5, 128.3, 128.1, 127.6, 127.57, 127.51, 127.0 (C_{aryl}), 111.4 (=CH_2), 97.04 (C-1), 77.8 (OCH), 75.2 (OCH), 74.0 (OCH_2), 73.3 (OCH_2), 71.4 (OCH_2), 71.2 (OCH), 69.2 (OCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2918, 2864, 1642, 1491, 1455, 1358, 1246, 1208, 1095, 956, 740, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{56}H_{58}NaO_9$ $[M + Na]^+$ 897.3979; found 897.3998.

Supporting Information (see also the footnote on the first page of this article): Spectral data for compounds **6d**, **8b**, **8g**, **9a**, **9c**, **14**, **15** (p. S4–S6), copies of ^1H and ^{13}C NMR spectra (p. S7–S52).

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[21] While our work was in progress, 2-*C*-(propargyloxymethyl)-galactal (**6d**) was reported by Hotha et al.; see ref. 14.

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