JOC Article

Epimerization of 2′-Carbonylalkyl-*C*-Glycosides via Enolation, *β*-Elimination and Intramolecular Cycloaddition

Zerong Wang, Huawu Shao, Edith Lacroix, Shih-Hsiung Wu,† Harold J. Jennings, and Wei Zou*

Institute for Biological Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada, and Institute of Biological Chemistry, Academia Sinica, Taipei, Taiwan

wei.zou@nrc.ca

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Treatment of 2′-carbonyl-α-*C*-glycopyranosides of *gluco*, *galacto*, *manno*, 2-*deoxy*, and 2-*azido* sugars with 4% NaOMe resulted in anomeric epimerization to give their respective *β*-anomers in good to excellent yields. The epimerization of the 2′-aldehyde of α-*C*-galactopyranoside (**10**) in deuterium methanol, which afforded the *β*-anomer with exclusive deuterium replacements at the 1′-position, excluded the possibility of the *exo*-glycal as being involved as an intermediate. When 2′-aldehyde (**36**) and 2′-ketone (**41**) of 2,3-di-*O*-benzyl-α/*β*-L-*C*-arabinofuranoside were used as substrates we were able to obtain the respective equatorial α-*C*-arabinopyranosides (**37** and **42**). These observations confirmed that the epimerization involves an acyclic α,*β*-unsaturated aldehyde or ketone, which is formed by the enolation of 2′-carbonyl-α-*C*-glycoside with subsequent *β*-elimination. Thereafter an intramolecular hetero-Michael cycloaddition occurs, leading to the formation of thermodynamically controlled stable products, which were exclusively the equatorial *C*-glycopyranosides, except in the case of 2′-carbonyl-*C*-furanosides, where a mixture of two anomers was obtained.

The development of synthetic methodology for *C*-glycosides is largely stimulated by their occurrence as building blocks in a variety of biologically important natural products[1] and by the fact that they may serve as promising biological tools and potential therapeutics.[2] A number of recent reviews have been devoted to this subject.[3] The formation of *C*-glycosides is based on various types of reactions at the anomeric carbon including (1) nucleophilic substitution of glycosyl halides, lactones, glycals, and 1,2-anhydrosugars using carbon-anion reagents, including Lewis acid catalyzed alkylations with stannane and silane reagents to *O*-glycosides or 1-*O*-acetates; (2) electrophilic substitution of anomeric anionic intermediates; (3) radical alkylations activated by samarium, tin, and other reagents; and (4) the de novo synthesis. In general, these methods do provide a certain degree of stereoselectivity, but the observed stereoselectivity depends on both the anomeric configuration and the neighboring group at the 2-*O*-position of the sugar substrates as well as the reaction conditions. The synthesis of *β*-*C*-mannosides are more difficult because they have 1,2-*cis* configurations. For example, reactions using samarium-based approaches result in the formation of 1,2-trans-*C*-glycosides (*gluco* and *galacto* *β*-*C*-glycosides and *manno* α-*C*-glycosides).[4] The Wittig reactions to sugar lactols after intramolecular cyclization selectively afforded *gluco* and *galacto* *β*-*C*-glycosides, but a mixture of anomers (1:1) for the *manno* *C*-glycosides.[5] Reactions of various nucleophiles to sugar lactones may yield *β*-*C*-glycosides but are sometimes problematic to produce

* To whom correspondence should be addressed. Tel.: 613-991-0855. Fax: 613-952-9092.

† Institute of Biological Chemistry, Academia Sinica.

(1) See the following for examples. Polytoxin: (a) Moore, R. E.; Scheuer, P. J. *Science* **1971**, *172*, 495−498. (b) Moore, R. E.; Bartolini, G. J. *J. Am. Chem. Soc.* **1981**, *103*, 2491−2494. (c) Usami, M.; Satake, M.; Ishida, S.; Inoue, A.; Kan, Y.; Yasumoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5389−5390. (d) Suh, E. M.; Kishi, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11205−11206. Polyether macrolides: (e) Hirata, Y.; Uemura, D. *Pure Appl. Chem.* **1986**, *58*, 701−710. (f) Litaudon, M.; Hickford, S. J. H.; Lill, R. E.; Lake, R. J.; Blunt, J. W.; Munro, M. H. G. *J. Org. Chem.* **1997**, *62*, 1868−1871. Polyketides: (g) Trefzer, A.; Hoffmeister, D.; Künzel, E.; Stockert, S.; Weitnauer, G.; Westrich, L.; Rix, U.; Fuchser, J.; Bindseil, K. U.; Rohr, J.; Bechthold, A. *Chem. Biol.* **2000**, *7*, 133−142 and references therein.

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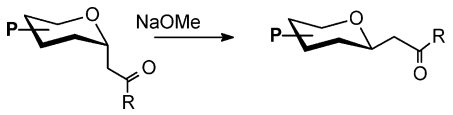
SCHEME 1



manno and *N*-Ac-*manno* β-*C*-glycosides.[6] The methods currently available for the stereoselective syntheses of *manno* β-*C*-glycosides include an intramolecular delivery reported by Beau et al.,[7] in which a silicon-tethered unsaturated group was placed at the 2-*O* position and an intramolecular radical reaction led to the 1,2-*cis* *C*-glycosides; a modified Keck reaction described by Praly et al.,[8] in which a halo *C*-glycoside formed from glycosyl dihalide was reduced from axial direction; a reaction of mannopyranose with a sulfur ylide to form an epoxide followed by intramolecular cyclization; [9] and a Ramberg−Bäcklund rearrangement of *S*-glycosides developed by Taylor and Franck.[10]

In addition to these aforementioned methods we recently reported an effective epimerization that converts 2′-carbonyl-α-*C*-glycopyranosides to their β-anomers including *gluco*, *galacto*, and *manno* β-*C*-glycosides as illustrated in Scheme 1.[11] Since the preliminary report we have extended this epimerization to 2-*deoxy* and 2-*azido* sugars and investigated the mechanism using various sugar substrates. The evidence supports a mechanism in which the epimerization was initiated by the enolation of 2′-carbonyl-α-*C*-glycoside, followed by β-elimination to form an acyclic α,β-unsaturated aldehyde or ketone. Thereafter, an intramolecular hetero-Michael addition led to the formation of β-*C*-glycopyranoside. The evidence also indicates that the stereochemistry observed is entirely controlled by the thermostability of the products.

Synthesis of 2′-Carbonyl-α-*C*-glycosides. Allyl α-*C*-glycosides (**1**−**4** and **6**) were prepared from either methyl *O*-glycosides or glycosyl 1-*O*-acetates and allyltrimethylsilane by Lewis acid (TMS triflate) catalyzed alkylations.[12] 6-*O*-Acetylated allyl α-*C*-mannoside (**5**) was derived from **3** by selective 6-*O*-acetolysis using 0.05% H_2SO_4−Ac_2O. Allyl 2-azido-α-*C*-mannopyranoside (**7**) was prepared from **1** in three steps: (1) Zemplén de-*O*-acetylation, (2) trifluromethylsulfonation (Tf_2O/py), and (3) S_N2 replacement by NaN_3 in DMF. The overall yield (41%) was low because of competing elimination. Under the same conditions we failed to obtain respective allyl 2-azido-3,4,6-tri-*O*-benzyl-α-*C*-glucopyranoside;[13] instead, allyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*erythro*-*C*-hex-2-enopyanoside[14] formed from elimination was isolated as the major product (70−80%). The allyl α-*C*-glycoside of *N*-acetylglucosamine (**8**) was prepared by a previously reported procedure.[15]

With these allyl α-*C*-glycosides in hand we performed ozonolysis (O_3/CH_2Cl_2 at −78 °C) on **1**−**8**, respectively, followed by reduction of ozonides with either Zn/HOAc (overnight) or dimethyl sulfide (2 days). Respective 2′-carbonyl-α-*C*-glycosides (**9**−**15**) were obtained in good yields. However, no expected 2′-aldehyde was obtained from **8** by the same procedure. To prepare 2′-ketone-α-*C*-glycosides, aldehyde **10** obtained above was further subjected to Grignard reactions with MeMgBr and AllylMgBr, respectively, to afford alcohols **16** and **17**. Neither reaction was stereoselective, and two diastereomers were obtained in ca. 1:1 ratio based on NMR assignment. Further oxidation of alcohols (**16** and **17**) using DMSO/Ac_2O led to 2′-ketones (**18** and **19**) in 30−45% yield and significant amount of byproducts; thiomethoxymethyl ethers[16] were also isolated in both cases.

Epimerization. During the preliminary study the epimerization was first performed on *gluco* and *galacto* α-*C*-glycopyranosides (**9** and **10**). When they were treated overnight with 4% NaOMe and $Zn(OAc)_2$, β-*C*-glycosides were obtained as respective acetylated products (**20** and **21**) after reduction with $NaBH_4$, followed by acetylation (Ac_2O/Py). Without reduction and acetylation, 2′-aldehyde-β-*C*-galactoside (**22**) was obtained from **10**. Under the same conditions *manno* α-*C*-glycosides (**11**−**13**) were also converted smoothly to respective β-*C*-glycosides (**23**−**25**) with good to excellent yields (see Table 1). Apparently, the 2-*O*-substitution and configuration do not deter the β-stereoselectivity. Thus, this epimerization provides effective access to *manno* 2′-carbonyl-β-*C*-glycosides.

The utility of this epimerization may also be extended to the synthesis of 2′-carbonyl-β-*C*-glycosides of 2-*deoxy*, 2-*azido*, and 2-*acetamido* sugars, which are important structural elements in some natural products. When 2′-carbonyl-2-*deoxy*-α-*C*-glycoside (**14**) obtained from **6** was subjected to the base treatment with and without $Zn(OAc)_2$, 2′-carbonyl-β-*C*-glycoside (**26**) was obtained in over 90% yield. Similarly, 2′-carbonyl-2-*azido*-β-*C*-mannopyranoside (**27**) was also obtained in good yield from **15** and the stereochemistry at C2-position was not

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(13) The same replacement on allyl *C*-galactoside derivative also failed; see Cipolla, L.; Ferla, B. L.; Lay, L.; Peri, F.; Nicotra, F. *Tetrahedron: Asymmetry* **2000**, *11*, 295−303.

(14) ^{1}H NMR ($CDCl_3$) δ 2.28 and 2.51 (m and m, 1H each, CH_2CH=CH_2), 3.55 (dd, 1H, H-6, J = 10.0, 4.4 Hz), 3.65 (dd, 1H, H-6′, J = 10.0, 5.6 Hz), 4.00 (d, 1H, H-4, J = 5.2 Hz), 4.13 (m, 1H, H-5), 4.31 (m, 1H, H-1), 4.48−4.82 (m, 6H, 3 × CH_2Ph), 4.84 (d, 1H, H-2, J = 2.8 Hz), 5.06−5.11 (m, 2H, CH=CH_2), 5.87 (m, 1H, CH=CH_2), 7.24−7.36 (m, 15H, 3 × Ph).

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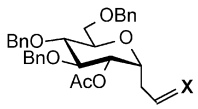
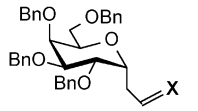
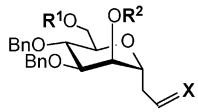
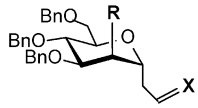
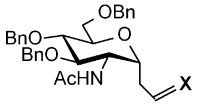
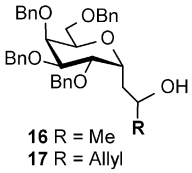
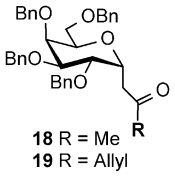
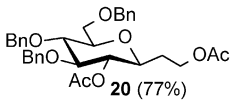
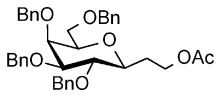
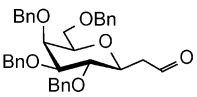
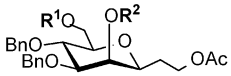
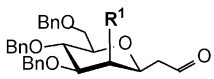
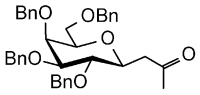
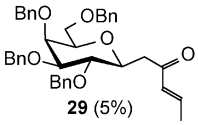
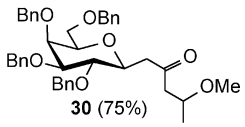
TABLE 1. Epimerization of 2′-Carbonylalkyl-α-*C*-glycopyranosides[a]

	X = CH_2	X = O
	**1**	**9**
	**2**	**10**
	**3** $R^1 = R^2$ = Bn **4** R^1 = Bn, R^2 = Ac **5** R^1 = Ac, R^2 = Bn	**11** $R^1 = R^2$ = Bn **12** R^1 = Bn, R^2 = Ac **13** R^1 = Ac, R^2 = Bn
	**6** R = H **7** R = N_3	**14** R = H **15** R = N_3
	**8**	n.a.
	**16** R = Me **17** R = Allyl	 **18** R = Me **19** R = Allyl

	**20** (77%)
	**21** (62%)
	**22** (66%)
	**23** $R^1 = R^2$ = Bn (61%) **24** R^1 = Bn, R^2 = Ac (60%) **25** R^1 = Ac, R^2 = Bn (67%)
	**26** R = H (94%) **27** R = N_3 (69%)
n.a.	
	**28** (95%)
	**29** (5%)
	**30** (75%)

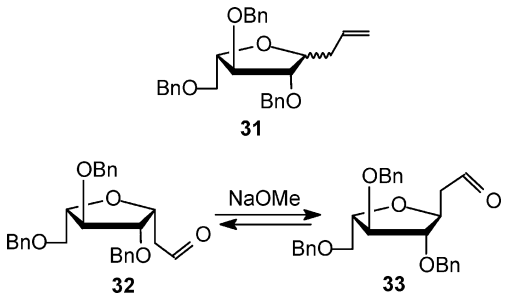
[a] For reaction conditions see General Procedures for Epimerization in Supporting Information.

affected.[17] Disappointingly, however, we were unable to test the epimerization on 2-*acetamido* sugars because of our failure to obtain 2′-aldehyde of 2-*acetamido*-α-*C*-glucopyranoside form **8**.

2′-Ketone-α-*C*-glycosides were also investigated, and both **18** and **19** were epimerized to the *β*-*C*-glycosides (**28** and **29**) under same conditions. The more stable α,*β*-conjugated **29** resulted from double bound migration under basic conditions, and a further 1,4-addition by MeO^- to **29** afforded **30** as a major product.

With the successful conversion of 2′-carbonyl-α-*C*-glycopyranosides to their *β*-anomers we then attempted this epimerization on *C*-glycofuranosides. After ozonolysis of **31** (α/*β* 1:1), we were able to isolate a small amount of pure *β*-*C*-glycofuranoside **32** by chromatography and a mixture of two anomers (**32** and **33** α/*β* 8:10). When **32** was treated with 4% NaOMe overnight a mixture of 2′-carbonyl-α/*β*-L-arabinosides (**32** and **33**) with a ratio of α/*β* ca.1:1 was obtained as determined by NMR analysis. The same α/*β* ratio was also observed when a mixture of **32**/**33** was used as substrates. These experiments suggested that equilibrium was likely reached between two anomers and that epimerization was a thermodynamic process. A similar observation in Wittig reaction to furanose lactol was previously reported by Fraser-Reid et al.[18] The almost equal distribution of the two anomers

SCHEME 2



of the *C*-furanosides indicates that they have similar thermostabilities.

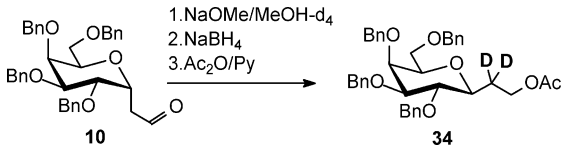
Contrary to our previous hypothesis the new experiments indicate that the presence of additional ions is not essential to the epimerization, because without the addition of Zn^{2+} ion we obtained similar yields and stereoselectivity on **22**, **26**, and **27**. Furthermore, no obvious kinetic difference was observed with additional Zn^{2+} on the epimerization of **11**, which we were able to monitor because two anomers were separable by TLC.

Both anomers of *C*-glycosides were well characterized by various 1D and 2D NMR experiments. In general the chemical shifts of equatorial anomeric protons in α-*C*-glycopyranosides are between 4.5 and 4.8 ppm, whereas

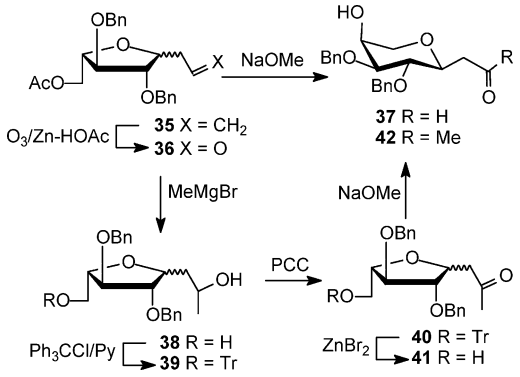
(17) C2 epimerization was encountered in Horner-Emmons nucelophilic addition to *N*-Ac-sugar lactol; see Werner, R. M.; Williams, L. M.; Davis, J. T. *Tetrahedron Lett.* **1998**, *39*, 9135−9138.

(18) Sun, K. M.; Dawe, R. D.; Fraser-Reid, B. *Carbohydr. Res.* **1987**, *171*, 36−47.

SCHEME 3



SCHEME 4



these of the β-anomers in axial configuration are found in the range of 3.3−3.9 ppm. However, direct evidence on the stereochemistry was determined by the NOEs observed in the β-anomers among H-1, H-3, and H-5 in a $^4C_1$ conformation adopted by the β-*C*-glycopyranosides.

Mechanism of Epmerization. Many syntheses of *C*-glycosides involve the formation of *exo*-glycal intermediates, such as in the nucleophilic additions to sugar lactones[6] and Ramberg−Bäcklund rearangement.[10] However, the *exo*-glycal-type intermediate in this epimerization was ruled out because the only product isolated, when the reaction was performed on **10** in CD_3OD, was compound **34**, in which both protons at the 1′-position were replaced by deuteriums (see Scheme 3). This was indicated by the disappearance of resonance of 1′-protons at 1.8 and 2.2 ppm in the ^{1}H NMR spectrum and the absence of D-substitution at the anomeric proton (H-1).

The intermediate we propose is an open chain α,β-unsaturated aldehyde or ketone resulted from β-elimination, similar to that formed in Wittig reaction to sugar lactol. An intramolecular hetero-Michael addition in a ring-closure step leads to a more stable β-*C*-glycoside. The substrates such as 5-hydroxy-L-*C*-arabinofuranosides **36** and **41** should then produce an intermediate after β-elimination with two hydroxy groups, which may compete in the cycloaddition to form either pyranoside or furanoside. Considering the thermodynamic nature of the reaction and knowing that pyranoside is more stable than furanoside, we expected the equatorial α-L-*C*-arabinopyranosides to be the major products. Thus, treatment of **36**, a mixture of two anomers (α/β 1:1), with NaOMe afforded **37** as predicted in 54% yield. In addition, we also synthesized 2′-ketone **41** from **36** (see Scheme 4) by Grignard reaction (MeMgBr), protection, oxidation, and deprotection procedures. Similarly, after treatment of **41** (α/β 1:1) with base, *C*-pyranoside **42** was isolated as major product (61%) and a mixture of *C*-furanosides (α/β ca. 1:1) remained as minor products (22%). It is noteworthy that equilibrium was likely reached because the prolonged reaction did not result in further transformation.

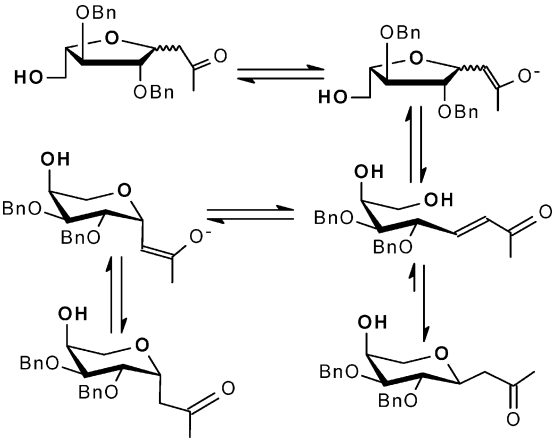


FIGURE 1. The epimerization via enolation, β-elimination, and 1,4-cycloaddition.

Although this epimerization resembles the mechanism of Wittig-type reactions to sugar lactol, the generality and excellent stereoselectivity of the method could be very useful particularly for the synthesis of *manno* and 2-*azido*-*manno* 2′-carbonyl-β-*C*-glycopyranosides.

On the basis of the above observations we conclude that the stereochemistry of the epimerization is dictated by the difference in thermostability between equatorial and axial *C*-glycosides. The mechanism of the reaction involves enolation and subsequent β-elimination to an acyclic α,β-unsaturated aldehyde (or ketone), followed by an intramolecular 1,4-addition in a ring-closure step. Cycloaddition and β-elimination are reversible reactions and eventually lead to more stable products (see Figure 1). As a result of the absence of an anomeric effect, the *C*-glycopyranosides with an equatorial substitution are more stable than the axial substituted anomers. However, in *C*-furanosides, such differences are less apparent and the distribution of the anomers depends on their relative thermostability.

Experimental Section

3-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-propene (5). To a solution of **3** (10 g, 17.7 mmol) in Ac_2O (57 mL) at 0 °C was added a solution of 1% H_2SO_4−Ac_2O (3 mL). The mixture was stirred for 16 h while the temperature was slowly warmed to room temperature. The mixture was diluted by the addition of EtOAc (200 mL) and aqueous $NaHCO_3$ (50 mL). The organic phase was subsequently washed with aqueous $NaHCO_3$ and water, dried, and concentrated to a residue. Purification by chromatography (hexane/EtOAc 5:1) gave **5** (6.4 g, 70%) as a syrup: ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H, OAc), 2.26−2.35 (m, 2H, CH_2CH=CH_2), 3.63 (dd, 1H, H-2, J = 4.0, 2.4 Hz), 3.75−3.82 (m, 3H, H-3, 4, 5), 4.07 (m, 1H, H-1), 4.25 (dd, 1H, H-6, J = 12.0, 2.8 Hz), 4.40 (dd, 1H, H-6′, J = 12.0, 6.4 Hz), 4.51−4.73 (m, 6H, 3 × CH_2Ph), 4.76−5.04 (m, 2H, CH=CH_2), 5.78 (m, 1H, CH=CH_2), 7.24−7.36 (m, 15H, 3 × Ph); ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3CO), 34.8 (CH_2CH=CH_2), 63.6 (C-6), 71.9 (CH_2Ph), 72.4 (C-5), 72.5 (CH_2Ph), 72.6 (CH_2Ph), 74.3 (C-1), 75.1 (C-2), 75.4 (C-3), 77.3 (C-4), 117.6 (CH=CH_2), 127.6, 128.0, 128.2, 128.3, 128.6, 128.7, 129.2 (3 × Ph), 134.3 (CH=CH_2), 138.2, 138.4 (3 × Ph), 171.1 (C=O); HRFABMS anal. calcd for $C_{32}H_{37}O_6$ [M + H] 517.2590, found 517.2873.

3-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-propene (6). To a solution of methyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyanoside (2.7 g, 6.2 mmol) in dry MeCN (20 mL) were added allyltrimethylsilane (1.4 g, 12.3 mmol) and TMS

triflate (0.53 mL, 3.1 mmol) at −40 °C. The mixture was stirred overnight while the temperature was slowly warmed to room temperature. The mixture was diluted by the addition of ethyl acetate (60 mL), and the organic phase was subsequently washed with aqueous $NaHCO_3$ and water, dried, and concentrated to a residue. Purification by chromatography (hexane/EtOAc 6:1−4:1) afforded **6** (2.43 g, 86%) as a syrup: ^{1}H NMR ($CDCl_3$) δ 1.76 (m, 1H, H-2ax), 1.99 (m, 1H, H-2eq), 2.22 and 2. 45 (m and m, 1H each, CH_2CH=CH_2), 3.54 (dd, 1H, H-4, J = 7.2, 6.8 Hz), 3.66 (dd, 1H, H-6, J = 12.4, 5.2 Hz), 3.74−3.82 (m, 3H, H-6′, 5, 3), 4.04 (m, 1H, H-1), 4.51 (d, 1H, CH_2Ph, J = 12.4 Hz), 4.53 (d, 1H, CH_2Ph, J = 11.2 Hz), 4.56 (d, 1H, CH_2-Ph, J = 10.4 Hz), 4.60 (d, 2H, CH_2Ph, J = 12.0 Hz), 4.78 (d, 1H, CH_2Ph, J = 11.2 Hz), 5.02−5.06 (m, 2H, CH=CH_2), 5.76 (m, 1H, CH=CH$_2$), 7.20−7.34 (m, 15H, 3 × Ph); ^{13}C NMR ($CDCl_3$) δ 32.6 (C-2), 37.0 (CH_2CH=CH_2), 69.2 (C-6), 70.8 (C-1), 71.5 (CH_2Ph), 73.0 (C-5), 73.6 (CH_2Ph), 74.3 (CH_2Ph), 76.6 (C-3), 77.1 (C-4), 117.2 (CH=CH_2), 127.7, 127.8, 128.0, 128.1, 128.5, 128.5 (3 × Ph), 134.8 (CH=CH$_2$), 138.4, 138.5, 138.6 (3 × Ph); HRFABMS anal. calcd for $C_{30}H_{35}O_4$ [M + H] 459.2535, found 459.2587.

3-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranosyl)-propene (7). A solution of **1** (300 mg, 0.58 mmol) in 0.1% NaOMe (3 mL) was kept at room temperature for 2 h and was neutralized by the addition of Dowex-50 (H^+). The filtrate was concentrated to a residue. To this residue in dry CH_2Cl_2 (5 mL) and pyridine (103 μL, 1.27 mmol) was added trifluoromethanesulfonic anhydride (230 mg, 0.82 mmol) at −30 °C. The reaction was allowed to proceed at 0 °C for 1 h. Ice−water was added, and the organic phase was subsequently washed with water, cold 1 N HCl, and brine, dried, and concentrated to an oil. Without further purification, a solution of the above crude in DMF (5 mL) was treated with sodium azide (152 mg 2.34 mmol) for 6 days at 70 °C. Water was added, and the aqueous solution was extracted with ether. The ether extracts were washed with brine, dried, and concentrated to oil. Purification by chromatography (hexane/EtOAc 10:1−4:1) afforded **7** (120 mg, 41%) as oil: ^{1}H NMR ($CDCl_3$) δ 2.27 (dd, 2H, CH_2CH=CH$_2$, J = 6.4, 6.0 Hz), 3.35 (m, 1H, H-1), 3.45 (m, 1H, H-5), 3.63−3.67 (m, 2H, H-3, 4), 3.68−3.75 (m, 2H, H-6, 6′), 4.56 (d, 2H, CH_2Ph, J = 12.0 Hz), 4.62 (d, 1H, CH_2Ph, J = 12.4 Hz), 4.66 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.79 (d, 1H, CH_2Ph, J = 12.8 Hz), 4.82 (d, 1H, CH_2Ph, J = 11.6 Hz), 4.91 (m, 1H, H-2), 5.03−5.09 (m, 2H, CH=CH_2), 5.85 (m, 1H, CH=CH$_2$), 7.17−7.34 (m, 15H, 3 × Ph); ^{13}C NMR ($CDCl_3$) δ 31.2 (CH_2CH=CH$_2$), 69.1 (C-6), 73.5 (CH_2Ph), 73.9 (C-2), 75.2 (CH_2Ph), 75.4 (CH_2Ph), 77.7 (C-1), 78.6 (C-4), 79.4 (C-5), 84.8 (C-3), 117.2 (CH=CH_2), 127.7, 127.9, 128.2, 128.6 (3 × Ph), 134.1 (CH=CH$_2$), 138.1, 138.5, 138.4 (3 × Ph); HRFABMS anal. calcd for $C_{30}H_{34}O_4N_3$ [M + H] 500.2549, found 500.2553.

2-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-ethyl Aldehyde (9). This compound was obtained from **1** by ozonolysis and purified by chromatography (hexane/EtOAc 4:1): ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3H, AcO), 2.63 (dd, 1H, CH_2-CHO, J = 16.5, 5.5 Hz), 2.75 (ddd, 1H, CH_2CHO, J = 16.5, 8.5, 2.5 Hz), 3.63 (d, 1H, H-6, J = 8.0 Hz), 3.67−3.74 (m, 3H, H-4, 5, 6), 3.77 (dd, 1H, H-3, J = 8.0, 7.0 Hz), 4.48 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.50 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.58 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.69 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.71 (d, 1H, CH_2Ph, J = 11 Hz), 4.74 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.78 (m, 1H, H-1), 5.08 (dd, 1H, H-2, J = 8.0, 5.5 Hz), 7.16−7.34 (m, 15H, 3 × Ph), 9.72 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3CO), 42.3 (CH_2CO), 67.2 (C-1), 68.4 (C-6), 71.7 (C-2), 73.1 (C-5), 73.5 (CH_2Ph), 74.4 (CH_2Ph), 74.5 (CH_2-Ph), 76.5 (C-4), 79.1 (C-3), 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 128.4, 128.4, 128.4, 137.8, 137.9, 138.0, 169.9 (COCH$_3$), 199.2 (CHO); HRFABMS anal. calcd for $C_{31}H_{35}O_7$ [M + H] 519.2383, found 519.2609.

2-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-ethyl Aldehyde (10). This compound was obtained from **2** by ozonolysis and purified by chromatography (hexane/EtOAc 5:1): ^{1}H NMR ($CDCl_3$) δ 2.63 (d, 2H, CH_2CHO, J = 6.0 Hz), 3.65 (dd, 1H, H-6, J = 10.5, 5.0 Hz), 3.69 (dd, 1H, H-3, J = 7.0, 2.0 Hz), 3.78 (m, 1H, H-2), 3.84 (dd, 1H, H-6′, J = 10.5, 7.5 Hz), 3.99 (dd, 1H, H-4, J = 3.0, 2.0 Hz), 4.03 (m, 1H, H-5), 4.46 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.47 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.50 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.52 (m, 1H, H-1), 4.56 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.58 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.61 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.69 (d, 2H, CH_2-Ph, J = 11.5 Hz), 7.22−7.34 (m, 20H, 4 × Ph), 9.67 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 42.8 (CH_2CHO), 66.9 (C-1, 6), 72.9 (CH_2Ph), 73.1 (CH_2Ph), 73.2 (C-5), 73.3 (CH_2Ph), 73.7 (C-4), 76.1 (C-2), 76.7 (C-3), 127.5, 127.6, 127.659, 127.7, 127.8 (2), 127.9, 128.1, 128.3, 128.4 (3), 137.7, 138.2, 138.3 (2), 200.6 (CHO); HRFABMS anal. calcd for $C_{36}H_{39}O_6$ [M + H] 567.2747, found 567.2849.

2-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-ethyl Aldehyde (11). This compound was obtained from **3** by ozonolysis and purified by chromatography (hexane/EtOAc 5:1): ^{1}H NMR δ 2.72 (ddd, 1H, CH_2CHO, J = 16.0, 8.0, 2.0 Hz), 2.76 (ddd, 1H, CH_2CHO, J = 16.0, 8.0, 2.0 Hz), 3.71(d, 1H, H-2, J = 7.5 Hz), 3.80−3.95 (m, 4H, H-3, 4, 6, 6′), 4.10 (m, 1H, H-5), 4.51−4.64 (m, 9H, H-1 and 4 × CH_2Ph), 7.31−7.42 (m, 20H, 4 × Ph), 9.78 (t, 1H, CHO, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 45.5 (CH_2CHO), 66.2 (C-1), 68.2 (C-6), 71.3 (CH_2Ph), 72.4 (CH_2Ph), 72.5 (CH_2Ph), 73.2 (CH_2Ph), 74.1 (C-4), 74.2 (C-3), 74.4 (C-5), 75.7 (C-2), 127.6, 127.7, 127.7, 127.8, 127.9 (2), 128.0, 128.1, 128.3, 128.4 (2), 137.7, 137.9, 138.0, 138.2, 200.5 (CHO); HRFABMS anal. calcd for $C_{36}H_{39}O_6$ [M + H] 567.2747, found 567.2898.

2-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-ethyl Aldehyde (12). This compound was obtained from **4** by ozonolysis and purified by chromatography (hexane/EtOAc 4:1): ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3H, AcO), 2.63 (dd, 1H, CH_2-CHO, J = 16.0, 5.5 Hz), 2.75 (ddd, 1H, CH_2CHO, J = 16.0, 8.5, 2.5 Hz), 3.64 (d, 1H, H-6, J = 8.0 Hz), 3.67−3.74 (m, 3H, H-4, 5, 6′), 3.77 (dd, 1H, H-3, J = 8.5, 7.5 Hz), 4.48 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.50 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.58 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.69 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.71 (d, 1H, CH_2Ph, J = 10.5 Hz), 4.74 (d, 1H, CH_2Ph, J = 11.0 Hz), 4.78 (m, 1H, H-1), 5.08 (dd, 1H, H-2, J = 7.5, 5.5 Hz), 7.16−7.34 (m, 15H, 3 × Ph), 9.72 (s, 1H, CHO); ^{13}C NMR δ 20.8 (CH_3CO), 42.3 (CH_2CHO), 67.2 (C-1), 68.4 (C-6), 71.7 (C-2), 73.1 (C-5), 73.4 (CH_2Ph), 74.4 (CH_2Ph), 74.5 (CH_2Ph), 76.5 (C-4), 79.1 (C-3), 127.6, 127.7, 127.8 (3), 127.9, 128.3, 128.4 (2), 137.8, 137.9, 138.0, 169.9 (COCH$_3$), 199.2 (CHO); HRFABMS anal. calcd for $C_{31}H_{35}O_7$ [M + H] 519.2383, found 519.2609.

2-(6-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-ethyl Aldehyde (13). This compound was obtained from **5** by ozonolysis and purified by chromatography (hexane/EtOAc 4:1): ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H, AcO), 2.55 (ddd, 1H, CH_2-CHO, J = 16.0, 8.0, 2.5 Hz), 2.70 (dd, 1H, CH_2CHO, J = 16.0, 4.5 Hz), 3.60−3.62 (m, 2H, H-2, 4), 3.80 (dd, 1H, H-3, J = 4.0, 3.5 Hz), 3.97 (dd, 1H, H-5, J = 8.0, 4.0 Hz), 4.08 (dd, 1H, H-6, J = 12.0, 4.0 Hz), 4.45 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.49 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.50 (d, 3H, CH_2Ph, J = 12.0 Hz), 4.54−4.57 (m, 1H, H-1), 4.60 (d, 1H, CH_2Ph, J = 12.5 Hz), 4.67 (dd, 1H, H-6′, J = 12.0, 8.5 Hz), 7.21−7.35 (m, 15H, 3 × Ph), 9.70 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3CO), 45.5 (CH_2CHO), 61.8 (C-6), 65.7 (C-1), 71.5 (CH_2Ph), 72.5 (CH_2Ph), 72.9 (CH_2Ph), 73.6 (C-5), 73.6 (C-3), 74.5 (C-2), 75.7 (C-4), 127.8, 127.9, 128.1, 128.5 (2), 137.6 (2), 137.7, 170.8 (COCH$_3$), 200.6 (CHO). FABMS for $C_{31}H_{34}O_7$ (518.61): 535 (M + NH_3), 518 (M), 459 (M − OAc), 455, 427, 411.

2-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-ethyl Aldehyde (14). This compound was obtained from **6** by ozonolysis and purified by chromatography (hexane/EtOAc 10:1−4:1): ^{1}H NMR ($CDCl_3$) δ 1.82 (ddd, 1H, H-2ax, J = 13.6, 7.6, 4.0 Hz), 1.94 (ddd, 1H, H-2eq, J = 13.6, 5.6, 4.4 Hz), 2.44 (ddd, 1H, CH_2CHO, J = 16.4, 5.6, 2.0 Hz), 2.74 (ddd, 1H, CH_2-CHO, J = 16.4, 11.0, 2.4 Hz), 3.54 (dd, 1H, H-4, J = 6.0, 6.0 Hz), 3.66 (dd, 1H, H-6, J = 10.4, 4.0 Hz), 3.74 (m, 1H, H-3), 3.79 (dd, 1H, H-6′, J = 10.4, 5.2 Hz), 3.86 (m, 1H, H-5), 4.46−

4.57 (m, 6H, H-1 and 2.5 × CH_2Ph), 4.70 (d, 1H, CH_2Ph, J = 11.2 Hz), 7.21−7.33 (m, 15H, 3 × Ph), 9.72 (dd, 1H, *C*HO, J = 2.4, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 32.7 (C-2), 47.1 (*C*H_2CHO), 65.0 (C-1), 68.6 (C-6), 71.5 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.5 (*C*H_2-Ph), 73.7 (C-5), 75.1 (C-4), 75.3 (C-3), 127.7, 127.8, 127.9, 128.0, 128.5 (2), 138.3 (3), 200.6 (*C*HO); HRFABMS anal. calcd for $C_{29}H_{33}O_5$ [M + H] 461.2328, found 461.2241.

2-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranosyl)-ethyl Aldehyde (15). This compound was obtained from **7** by ozonolysis and purified by chromatography (hexane/EtOAc 6:1−4:1) (33%): ^{1}H NMR ($CDCl_3$) δ 2.62 (ddd, 1H, CH_2-CHO, J = 16.4, 5.6, 1.6 Hz), 2.75 (ddd, 1H, CH_2CHO, J = 16.4, 8.4, 2.8 Hz), 3.62−3.74 (m, 4H, H-6, H-4, H-6′, H-5), 3.77 (dd, 1H H-3, J = 8.0, 7.6 Hz), 4.48 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.50 (d, 1H, CH_2Ph, J = 10.8 Hz), 4.58 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.70 (d, 1H, CH_2Ph, J = 10.8 Hz), 4.72 (d, 1H, CH_2-Ph, J = 11.6 Hz), 4.75 (d, 1H, CH_2Ph, J = 11.6 Hz), 4.77 (ddd, 1H, H-1, J = 10.8, 5.6, 5.6 Hz), 5.08 (dd, 1H, H-2, J = 8.0, 5.2 Hz), 7.13−7.38 (m, 15H, 3 × Ph), 9.72 (dd, 1H, *C*HO, J = 2.8, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 42.5 (*C*H_2CHO), 67.5 (C-1), 68.6 (C-6), 71.9 (C-2), 73.3 (C-5), 73.7 (*C*H_2Ph), 74.8 (2 × *C*H_2Ph), 76.7 (C-4), 79.3 (C-3), 128.0, 128.6, 138.0, 199.3 (*C*HO); HRFABMS anal. calcd for $C_{29}H_{31}O_5N_3$ [M] 501.2264, found 501.2251.

1-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-2-propanol (16). To a solution of **10** (1.0 g, 1.76 mmol) in ether (50 mL) was added MeMgBr (3.0 M in ether, 1.5 mL) at −78 °C, and the mixture was stirred overnight. Water (50 mL) was added to the mixture, and the aqueous solution was extracted with EtOAc (50 mL × 2), dried, and concentrated. Purification by chromatography (hexane/EtOAc 2:1) afforded **16** (0.85 g, 83%) as a mixture of two distereomers (ca. 1:1): ^{1}H NMR ($CDCl_3$) δ 1.17 (d, J = 4.5 Hz, 3H), 1.18 (d, J = 6.0 Hz, 3H), 1.41 and 1.90 (m and m, 1H each, CH_2CHOH), 1.55 and 1.83 (m and m, 1H each, CH_2CHOH), 4.19 (m, 1H, H-1), 4.26 (m, 1H, H-1) 4.43−4.80 (m, 16H, 8 × CH_2Ph), 7.20−7.35 (m, 40H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 23.0 (23.5) (*C*H_3), 64.6, 68.3, 71.2, 73.1, 73.2, 73.3, 73.4, 74.0, 74.2, 76.9, 127.5−128.4, 138.0, 138.3, 138.4.

1-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-4-penten-2-ol (17). To a solution of **10** (0.53 g, 0.94 mmol) in ether (20 mL) was added allyl-MgBr (1.0 M in ether, 3 mL) at −50 °C, and the mixture was stirred overnight. Similar workup and purification by chromatography (hexane/EtOAc 2:1) afforded **17** (0.45 g, 79%) as a mixture of two distereomers (ca. 1:1): ^{1}H NMR ($CDCl_3$) δ 1.43 and 1.90 (m and m, 1H each, CH_2CHOH), 1.59 and 1.82 (m and m, 1H each, CH_2CHOH), 4.16 (m, 1H, H-1), 4.27 (m, 1H, H-1) 4.46−4.72 (m, 16H, 8 × CH_2Ph), 5.06−5.10 (m, 4H, 2 × CH$_2$CH=CH_2), 5.79 (m, 2H, 2 × CH$_2$C*H*=CH$_2$), 7.23−7.32 (m, 40H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 41.7 (41.9), 117.0 (117.1) (CH=*C*H$_2$), 135.1 (135.2) (*C*H=CH$_2$).

1-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-acetone (18). A solution of **16** (0.27 g, 0.46 mol) in DMSO/Ac_2O (2:1, 5 mL) was kept at room temperature overnight. The mixture was diluted by the addition of EtOAc (50 mL), washed subsequently with water, aqueous $NaHCO_3$, and water, dried, and concentrated. Purification by chromatography (hexane/EtOAc 2:1) gave **18** (0.12 g, 33%) and thiomethoxymethyl ether (0.13 g): ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H, AcO), 2.61 (dd, 1H, C*H*HCOCH$_3$, J = 16.0, 5.5 Hz), 2.71 (dd, 1H, CH*H*COCH$_3$, J = 16.0, 8.0 Hz), 3.65 (dd, 1H, H-6, J = 10.5, 4.5 Hz), 3.68 (dd, 1H, H-3, J = 7.5, 3.0 Hz), 3.80−3.84 (m, 2H, H-2, 6), 3.98 (dd, 1H, H-4, J = 3.5, 3.0 Hz), 4.01 (m, 1H, H-5), 4.44 (d, 2H, CH_2-Ph, J = 12.0 Hz), 4.51 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.53 (m, 1H, H-1), 4.56 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.58 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.63 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.69 (d, 2H, CH_2Ph, J = 12.0 Hz), 7.22−7.34 (m, 20H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 30.5 (*C*H$_3$CO), 42.6 (CH$_3$CO*C*H$_2$), 67.3 (C-6), 67.9 (C-1), 72.8, 73.1, 73.2 (C-5), 73.2, 73.3, 73.9 (C-4), 76.2 (C-2), 76.3 (C-3), 127.5, 127.6 (3), 127.8 (2), 127.9, 128.1, 128.3 (2), 128.4 (2), 138.0, 138.3, 138.4 (2), 206.8 (CH$_3$*C*OCH$_2$); HRFABMS anal. calcd for $C_{37}H_{41}O_6$ [M + H] 581.2903, found 581.2941.

1-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-4-penten-2-one (19). A solution of **17** (0.3 g, 0.49 mmol) in DMSO−Ac_2O (2:1, 5 mL) was kept at room temperature overnight. Routine workup and purification by chromatography (hexane/EtOAc 2:1) gave **19** (0.1 g, 33%) and thiomethoxymethyl ether (0.12 g): ^{1}H NMR ($CDCl_3$) δ 2.64 (dd, 1H, C*H*HCO, J = 16.0, 6.0 Hz), 2.71 (dd, 1H, CH*H*CO, J = 16.0, 7.0 Hz), 3.10 (dd, 1H, CH2COC*H*HCH=CH$_2$, J = 16.5, 7.5 Hz), 3.15 (dd, 1H, CH$_2$COCH*H*CH=CH$_2$, J = 16.5, 7.0 Hz), 3.65 (dd, 1H, H-6, J = 11.0, 5.0 Hz), 3.68 (dd, 1H, H-3, J = 7.2, 3.0 Hz), 3.80−3.84 (m, 2H, H-2, 6), 3.98 (dd, 1H, H-4, J = 3.0, 3.0 Hz), 4.01 (m, 1H, H-5), 4.43 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.44 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.51 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.54 (m, 1H, H-1), 4.55 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.56 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.63 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.68 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.69 (d, 1H, CH_2Ph, J = 11.5 Hz), 5.05−5.13 (m, 2H, CH=CH_2), 5.84 (m, 1H, CH$_2$C*H*=CH$_2$), 7.24−7.34 (m, 20H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 41.3 (*C*H$_2$-CO), 48.1 (CO*C*H$_2$CH=CH$_2$), 67.3 (C-6), 67.8 (C-1), 72.8, 73.0, 73.2, 73.3 (*C*H$_2$Ph, C-5), 73.8 (C-4), 76.1 (C-2, C-3), 118.8 (CH=*C*H$_2$), 127.5 (2), 127.6 (2), 127.8 (2), 127.9, 128.1, 128.3 (3), 128.4, 130.4 (*C*H=CH$_2$), 137.9, 138.3, 138.4, 206.5 (*C*OCH$_3$); HRFABMS anal. calcd for $C_{39}H_{43}O_6$ [M + H] 607.3060, found 607.3137.

2-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-ethyl Acetate (20). See epimerization Procedure A (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 1.75−1.84 (m, 2H, CH_2CH$_2$OAc), 1.94 (s, 3H, AcO), 2.03 (s, 3H, AcO), 3.37 (dd, 1H, H-1, J = 9.5, 3.5 Hz), 3.41 (dd, 1H, H-5, J = 10.0, 3.0 Hz), 3.64 (dd, 1H, H-3, J = 9.5, 9.0 Hz), 3.68−3.73 (m, 3H, H-4, 6, 6′), 4.14−4.24 (m, 2H, CH_2OAc), 4.53 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.56 (d, 1H, CH_2Ph, J = 10.5 Hz), 4.61 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.67 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.78 (d, 1H, CH_2Ph, J = 10.5 Hz), 4.82 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.88 (dd, 1H, H-2, J = 9.5, 9.5 Hz), 7.17−7.33 (m, 15H, 3 × *Ph*); ^{13}C NMR ($CDCl_3$) δ 21.2 (2 × *C*H$_3$), 30.9 (*C*H$_2$CHO), 60.8 (*C*H$_2$-OAc), 68.7 (C-6), 73.5, 73.7 (C-2), 74.7 (C-1), 74.9, 75.1, 78.2 (C-4), 79.1 (C-5), 84.4 (C-3), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.6, 138.1 (2), 138.4 (2), 169.8 (*C*OCH$_3$), 171.2 (*C*OCH$_3$); HRFABMS anal. calcd for $C_{33}H_{39}O_8$ [M + H] 563.2645, found 563.2675.

2-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-ethyl Acetate (21). See epimerization Procedure A (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 1.79 (m, 1H, CH*H*CH$_2$OAc), 2.03 (s, 3H, AcO), 2.22 (m, 1H, C*H*HCH$_2$OAc), 3.36 (dd, 1H, H-1, J = 9.0, 8.5 Hz), 3.53−3.58 (m, 3H, H-5, 6, 6′), 3.62 (dd, 1H, H-3, J = 9.5, 2.0 Hz), 3.71 (dd, 1H, H-2, J = 9.5, 9.0 Hz), 4.02 (s, 1H, H-4), 4.17 and 4.26 (m and m, 1H each, CH_2OAc), 4.43 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.48 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.65 (d, 2H, CH_2Ph, J = 11.0 Hz), 4.69 (d, 1H, CH_2-Ph, J = 10.5 Hz), 4.78 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.96 (d, 1H, CH_2Ph, J = 10.0 Hz), 4.98 (d, 1H, CH_2Ph, J = 10.5 Hz), 7.28−7.40 (m, 20 H, 4 × *Ph*); ^{13}C NMR ($CDCl_3$) δ 21.2 (*C*H$_3$), 31.2 (*C*H$_2$CH$_2$O), 61.4 (*C*H$_2$OAc), 69.0 (C-6), 72.4, 73.7, 73.8 (C-4), 74.7, 75.7, 76.5 (C-1), 77.2 (C-5), 79.0 (C-2), 85.0 (C-3), 127.7, 127.8, 127.9, 128.0 (2), 128.1, 128.3, 128.4 (2), 128.6 (3), 138.1, 138.4, 138.5, 138.9, 171.3 (*C*OCH$_3$).

2-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-ethyl Aldehyde (22). See epimerization Procedure B (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 2.58 (ddd, 1H, CH_2CHO, J = 16.2, 7.8, 2.5 Hz), 2.72 (ddd, 1H, CH_2CHO, J = 16.2, 3.5, 2.5 Hz), 3.52 (d, 2H, H-6, 6′, J = 6.0 Hz), 3.59 (dd, 1H, H-5, J = 7.0, 6.0 Hz), 3.63 (dd, 1H, H-3, J = 9.0, 2.5 Hz), 3.73 (dd, 1H, H-2, J = 9.0, 9.0 Hz), 3.77−3.81 (m, 1H, H-1), 4.01 (dd, 1H, H-4, J = 1.5, 1.0 Hz), 4.40 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.45 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.59 (d, 1H, CH_2Ph, J = 10.5 Hz), 4.61 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.67 (d, 1H, CH_2-Ph, J = 11.5 Hz), 4.76 (d, 1H, CH_2Ph, J = 11.5 Hz), 4.93 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.93 (d, 1H, CH_2Ph, J = 10.5 Hz),

7.24−7.37 (m, 20H, 4 × Ph), 9.69 (bs, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 46.3 (CH_2CHO), 68.7 (C-6), 72.1, 73.5, 73.6 (C-4), 74.5, 74.8 (C-1), 75.2, 77.3 (C-5), 77.9 (C-2), 84.6 (C-3), 127.5, 127.6, 127.7, 127.8, 127.9 (2), 128.1, 128.2, 128.3, 128.4, 128.430, 128.5, 137.8, 137.9, 138.0, 138.5, 200.4 (*C*HO). FABMS for $C_{36}H_{38}O_6$ (566.69): 567.2 (M), 475.1.

2-(2,3,4,6-Tetra-*O*-benzyl-*β*-D-mannopyranosyl)-ethyl Acetate (23). See epimerization Procedure A (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 1.69 (m, 1H, C*H*HCH$_2$O), 2.04 (s, 3H, AcO), 2.10 (m, 1H, CH*H*CH$_2$O), 3.39−3.43 (m, 2H, H-1, H-5), 3.63 (dd, 1H, H-3, J = 9.5, 3.0 Hz), 3.68−3.76 (m, 3H, H-2, 6, 6′), 3.94 (dd, 1H, H-4, J = 10.0, 10.0 Hz), 4.05 (m, 2H, CH$_2$C*H*$_2$O), 4.54 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.57 (d, 1H, C*H*$_2$-Ph, J = 10.5 Hz), 4.63 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.68 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz, 1H), 4.74 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.79(d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.88 (d, 1H, C*H*$_2$Ph, J = 10.5 Hz), 5.03 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 7.18−7.39 (m, 20H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 20.9 (*C*H$_3$CO), 30.9 (*C*H$_2$-CH$_2$O), 61.6 (*C*H$_2$OAc), 69.8 (C-6), 72.8 (*C*H$_2$Ph), 73.7 (*C*H$_2$-Ph), 74.5 (*C*H$_2$Ph), 75.2 (C-1), 75.4 (*C*H$_2$Ph), 75.6 (C-2), 75.6 (C-4), 80.1 (C-5), 85.5 (C-3), 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4 (2), 128.5, 128.6, 128.7, 138.6 (2), 138.8 (2), 179.5 (*C*OCH$_3$); HRFABMS anal. calcd for $C_{38}H_{43}O_7$ [M + H] 611.3008, found 611.2953.

2-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl)-ethyl Acetate (24). See epimerization Procedure A (Supporting Information). ^{1}H NMR ($CDCl_3$) 1.77 and 1.96 (m and m, 1H each, C*H*$_2$CH$_2$OAc), 2.03 (s, 3H, AcO), 2.17 (s, 3H, AcO), 3.43 (d, 1H, H-5, J = 10.0 Hz), 3.59 (dd, 1H, H-1, J = 8.8, 4.0 Hz), 3.67 (dd, 1H, H-3, J = 9.0, 2.5 Hz), 3.73−3.74 (m, 2H, H-6, 6′), 3.776 (ddd, 1H, H-4, J = 9.8, 9.2, 1.5 Hz), 4.14−4.24 (m, 2H, C*H*$_2$OAc), 4.49 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.50 (d, 1H, C*H*$_2$Ph, J = 10.0 Hz), 4.52 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 4.64 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.75 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 4.86 (d, 1H, C*H*$_2$Ph, J = 10.5 Hz), 5.47 (d, 1H, H-2, J = 3.0 Hz), 7.16−7.35 (m, 15H, 3 × Ph); ^{13}C NMR ($CDCl_3$) δ 20.8 (*C*H$_3$CO), 20.9 (*C*H$_3$CO), 30.4 (CH$_2$CH$_2$OAc), 60.9 (*C*H$_2$-OAc), 69.1 (C-2), 69.2 (C-6), 71.5, 73.4, 73.6 (C-1), 74.3 (C-4), 75.0, 79.3 (C-5), 81.7 (C-3), 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.2 (2), 128.3, 137.7, 138.1, 138.2, 170.6 (*C*═O), 170.8 (*C*═O); HRFABMS anal. calcd for $C_{33}H_{39}O_8$ [M + H] 563.2645, found 563.2635.

2-(6-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl)-ethyl Acetate (25). See epimerization Procedure A (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 1.66 (m, 1H, C*H*HCH$_2$-OAc), 2.02 (s, 3H, AcO), 2.04 (s, 3H, AcO), 2.07 (m, 1H, CH*H*CH$_2$OAc), 3.40 (dd, 1H, H-1, J = 8.8, 4.5 Hz), 3.45 (dd, 1H, H-5, J = 9.5, 6.5 Hz), 3.65 (dd, 1H, H-3, J = 9.5, 2.0 Hz), 3.74 (bs, 1H, H-2), 3.87 (dd, 1H, H-4, J = 9.5, 9.5 Hz), 4.05 (dd, 2H, C*H*$_2$OAc, J = 6.0, 6.0 Hz), 4.22 (dd, 1H, H-6, J = 11.5, 6.5 Hz), 4.34 (d, 1H, H-6′, J = 11.5 Hz), 4.60 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 4.67 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.74 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.80 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.93 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 5.02 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 7.22−7.39 (m, 15 H, 3 × Ph); ^{13}C NMR ($CDCl_3$) δ 20.9 (*C*H$_3$CO), 21.0 (*C*H$_3$CO), 30.6 (CH$_2$CH$_2$OAc), 61.2 (*C*H$_2$OAc), 64.0 (C-6), 72.5, 74.3, 75.0 (C-1), 75.1 (C-4), 75.2, 75.3 (C-2), 77.5 (C-5), 85.1 (C-3), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4 (2), 128.5, 138.0, 138.1, 138.4, 170.6 (2) (*C*OCH$_3$). FABMS for $C_{33}H_{38}O_8$ (562.66): 563 (M), 503 (M − OAc), 455.

2-(3,4,6-Tri-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-ethyl Aldehyde (26). See epimerization Procedure C (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 1.47 (dd, 1H, H-2ax, J = 24.0, 11.2 Hz), 2.20 (ddd, 1H, H-2eq, J = 12.8, 5.2, 1.6 Hz), 2.54 (ddd, 1H, C*H*HCHO, J = 16.8, 5.2, 1.6 Hz), 2.77 (ddd, 1H, CH*H*CHO, J = 16.8, 7.6, 2.4 Hz), 3.42 (ddd, 1H, H-5, J = 9.6, 3.2, 2.8 Hz), 3.52 (dd, 1H, H-4, J = 9.2, 9.2 Hz), 3.69 (m, 3H, H-6′, 3, 6), 3.90 (m, 1H, H-1), 4.52 (d, 1H, C*H*$_2$Ph, J = 12.4 Hz), 4.55 (d, 1H, C*H*$_2$Ph, J = 9.6 Hz), 4.60 (d, 1H, C*H*$_2$Ph, J = 9.6 Hz), 4.62 (d, 1H, C*H*$_2$Ph, J = 8.4 Hz), 4.69 (d, 1H, C*H*$_2$Ph, J = 11.6 Hz), 4.90 (d, 1H, C*H*$_2$Ph, J = 10.8 Hz), 7.18−7.34 (m, 15H, 3 × Ph), 9.79 (dd, 1H, *C*HO, J = 2.4, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 37.0 (C-2), 49.3 (*C*H$_2$CHO), 69.4 (C-6), 70.9 (C-1), 71.7 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 75.3 (*C*H$_2$Ph), 78.2 (C-4), 79.3 (C-5), 80.8 (C-3), 127.8, 128.1, 128.5, 128.6, 138.2, 138.5, 200.6 (*C*HO); HRFABMS anal. calcd for $C_{29}H_{33}O_5$ [M + H] 461.2328, found 461.2232.

2-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-ethyl Aldehyde (27). See epimerization Procedure C (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 2.65 (ddd, 1H, C*H*HCHO, J = 16.4, 8.0, 2.8 Hz), 2.83 (ddd, 1H, CH*H*CHO, J = 16.4, 4.0, 1.6 Hz), 3.36 (m, 1H, H-2), 3.46−3.72 (m, 3H, H-4, 6, 6′), 3.76 (m, 1H, H-1), 4.52 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.59 (d, 1H, C*H*$_2$Ph, J = 10.8 Hz), 4.60 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.71 (d, 1H, CH$_2$Ph, J = 11.6 Hz), 4.80 (d, 1H, C*H*$_2$-Ph, J = 10.8 Hz), 4.98 (d, 1H, C*H*$_2$Ph, J = 11.6 Hz), 7.19−7.37 (m, 15H, 3 × Ph), 9.78 (dd, 1H, *C*HO, J = 2.4, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 46.5 (*C*H$_2$CHO), 68.8 (C-6), 73.6 (*C*H$_2$Ph), 73.7 (C-2), 74.7 (C-1), 75.1 (*C*H$_2$Ph), 75.5 (*C*H$_2$Ph), 78.3 (C-4), 79.5 (C-3), 86.6 (C-5), 128.0, 128.1, 128.2, 128.6, 128.9, 138.0, 138.5, 200.7 (*C*HO); HRFABMS anal. calcd for $C_{29}H_{32}O_5N_3$ [M + H] 502.2342, found 502.2328.

1-(2,3,4,6-Tetra-*O*-benzyl-*β*-D-galactopyranosyl)-acetone (28). See epimerization Procedure B (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H, C*H*$_3$), 2.60 (dd, 1H, C*H*HCO, J = 16.0, 8.5 Hz), 2.71 (dd, 1H, CH*H*CO, J = 16.0, 2.5 Hz), 3.51 (d, 2H, H-6, 6′, J = 5.5 Hz, 2H), 3.58 (dd, 1H, H-5, J = 6.5, 6.0 Hz), 3.62 (dd, 1H, H-3, J = 9.5, 1.5 Hz), 3.68 (dd, 1H, H-2, J = 9.5, 9.0 Hz), 3.75 (ddd, 1H, H-1, J = 9.0, 8.8, 2.5 Hz), 4.00 (d, 1H, H-4, J = 1.0 Hz), 4.39 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.44 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.60 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.61 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.65 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.74 (d, 1H, C*H*$_2$Ph, J = 13.0 Hz), 4.92 (d, 1H, C*H*$_2$Ph, J = 13.0 Hz), 4.95 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 7.23−7.36 (m, 20H, 4 × *Ph*); ^{13}C NMR ($CDCl_3$) δ 30.7 (*C*H$_3$), 46.2 (CH$_2$COCH$_3$), 68.6 (C-6), 72.1, 73.4, 73.7 (C-4), 74.5, 75.1, 75.9 (C-1), 77.0 (C-5), 78.0 (C-2), 84.7 (C-3), 127.5, 127.6 (2), 127.7 (2), 127.8, 128.0, 128.1, 128.2, 128.3, 128.4 (2), 137.8, 138.1, 138.2, 138.6, 206.7 (*C*═O); HRFABMS anal. calcd for $C_{37}H_{41}O_6$ [M + H] 581.2903, found 581.2984.

1-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-3-penten-2-one (29) and 1-(2,3,4,6-Tetra-*O*-benzyl-*β*-D-galactopyranosyl)-4-methoxy-pentan-2-one (30). See epimerization Procedure B (Supporting Information). For **29**: ^{1}H NMR ($CDCl_3$) δ 1.81 (d, 3H, CH$_3$, J = 7.0 Hz), 2.72 (dd, 1H, C*H*HCO, J = 15.8, 8.0 Hz), 2.78 (dd, 1H, CH*H*CO, J = 15.8, 2.5 Hz), 3.48−3.54 (m, 2H, H-6, 6′), 3.58 (dd, 1H, H-5, J = 6.5, 6.0 Hz), 3.64 (dd, 1H, H-3, J = 9.5, 2.0 Hz), 3.70 (dd, 1H, H-2, J = 9.5, 9.0 Hz), 3.83 (ddd, 1H, H-1, J = 9.0, 8.5, 2.5 Hz), 4.01 (s, 1H, H-4), 4.38 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.44 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.62 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.63 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 4.66 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.75 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.93 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.96 (d, 1H, C*H*$_2$Ph, J = 11.0 Hz), 6.08 (d, 1H, COCH═C, J = 15.5 Hz), 6.69−6.76 (m, 1H, C═C*H*CH$_3$), 7.26−7.36 (m, 20H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 18.2 (*C*H$_3$), 42.6 (*C*H$_2$CO), 68.6 (C-6), 72.1, 73.4, 73.8 (C-4), 74.6, 75.0, 75.8 (C-1), 76.7 (C-5), 78.1 (C-2), 84.8 (C-3), 127.5, 127.6 (2), 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4 (2), 132.2 (═*C*HCH$_3$), 138.0, 138.2, 138.3, 138.7, 142.8 (CO*C*H═), 197.6 (*C*═O); HRFABMS anal. calcd for $C_{39}H_{42}O_6$ [M] 606.2981, found 606.2770. For **30**: a mixture of *R* and *S* (ca. 1:1); ^{1}H NMR ($CDCl_3$) δ 1.08 (dd, 3H, *C*H$_3$, J = 9.5 Hz), 2.38 (ddd, 1H, CH$_3$CHOMeC*H*H, J = 16.5, 7.5, 7.5 Hz), 2.60 (dd, 1H, CH$_3$CHOMeCH*H*, J = 16.0, 8.5 Hz), 2.68 (dd, 1H, COC*H*H, J = 16.0, 7.0 Hz), 2.73 (ddd, 1H, COCH*H*, J = 16.0, 3.5, 3.0 Hz), 3.22 (s, 3H, OMe), 3.48−3.54 (m, 2H, H-6, 6′), 3.57 (dd, 1H, H-5, J = 6.5, 6.5 Hz), 3.62 (dd, 1H, H-3, J = 7.0, 2.0 Hz), 3.67 (dd, 1H, H-2, J = 9.5, 3.5 Hz), 3.70−3.74 (m, 1H, CH$_3$C*H*OMe), 3.77 (m, 1H, H-1), 3.98 (s, 1H, H-4), 4.38 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.43 (d, 1H, C*H*$_2$-Ph, J = 12.0 Hz), 4.61 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.62 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.65 (d, 1H, C*H*$_2$Ph, J = 12.0 Hz), 4.74 (d, 1H, C*H*$_2$Ph, J = 11.5 Hz), 4.92 (d, 1H, C*H*$_2$Ph, J =

12.0 Hz), 4.95 (d, 1H, CH_2Ph, J = 11.5 Hz), 7.22−7.35 (m, 20H, 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 19.2 (19.3) (CH_3), 45.9 (46.1) (CH_2C=O), 50.1 (50.4) (COCH_2), 56.0 (56.1) (OMe), 68.5 (68.6) (C-6), 72.1, 72.7 (72.76) (*C*HOMe), 73.4, 73.7 (C-4), 74.5, 75.0 (75.1), 75.7 (C-1), 76.9 (C-5), 77.8 (77.9) (C-2), 84.6 (84.7) (C-3), 127.5, 127.6, 127.7, 127.8, 127.9, 128.00, 128.1, 128.2, 128.3, 128.4, 137.8, 138.1, 138.2, 138.6, 206.9 (207.0) (*C*=O). FABMS for $C_{40}H_{46}O_7$ (638.8): 639 (M), 607, 547.

2-(2, 3, 5-Tri-*O*-benzyl-*β*-L-arabinofuranosyl)-ethyl Aldehyde (32) and 2-(2, 3, 5-tri-*O*-benzyl-α-L-arabinofuranosyl)-ethyl Aldehyde (33). Compound **31** (α/*β* 1:1, 0.8 g, 1.8 mmol) in dichloromethane (30 mL) was ozonalized, and the ozonide was reduced by Zn/HOAc (see general procedure). The products were purified by chromatography (hexane/EtOAc 8:1−4:1), and pure *β*-anomer (**32**) (0.06 g) was obtained together with an anomeric mixture (**32/33** 8:10, 0.6 g). For **32**: ^{1}H NMR ($CDCl_3$) δ 2.82 (d, 2H, CH_2CHO, J = 6.0 Hz), 3.51 (dd, 1H, H-5, J = 10.0, 6.0 Hz), 3.60 (dd, 1H, H-5′, J =10.0, 6.0 Hz), 3.93 (d, 1H, H-3, J = 2.8 Hz), 3.98 (d, 1H, H-2, J = 3.6 Hz), 4.09 (m, 1H, H-4), 4.32 (d, 1H, CH_2Ph, J = 11.6 Hz), 4.46 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.47 (m, 1H, H-1), 4.51 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.52 (s, 2H, CH_2Ph), 4.58 (d, 1H, CH_2Ph, J = 12.0 Hz), 7.19−7.38 (m, 15H, 3 × Ph), 9.78 (dd, 1H, CHO, J = 1.6, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 43.5 (*C*H_2CHO), 70.5 (C-5), 71.6 (*C*H_2Ph), 71.7 (*C*H_2Ph), 73.5 (*C*H_2Ph), 76.6 (C-1), 82.9 (C-4), 83.2 (C-2), 83.8 (C-3), 128.0, 128.5, 128.6, 137.6, 137.7, 138.2, 200.6 (*C*HO); HRFABMS anal. calcd for $C_{28}H_{31}O_5$ [M + H] 447.2171, found 447.2157. For **33**: (data extracted from the spectra of mixture) ^{1}H NMR ($CDCl_3$) δ 2.69 (ddd, 1H, C*H*HCHO, J = 16.4, 5.6, 1.2 Hz), 2.79 (ddd, 1H, CH*H*CHO, J = 16.4, 7.2, 2.0 Hz), 3.56 (m, 2H, H-5, 5′), 3.87 (dd, 1H, H-2, J = 4.0, 2.8 Hz), 4.04 (dd, 1H, H-3, J = 2.8, 2.4 Hz), 4.25 (m, 1H, H-4), 4.43−4.59 (m, 7H, H-1, 3 × CH_2Ph), 7.19−7.37 (m, 15H, 3 × Ph), 9.76 (dd, 1H, CHO, J = 2.0, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 47.2 (*C*H_2CHO), 70.4 (C-5), 72.0 (*C*H_2Ph), 72.1 (*C*H_2-Ph), 73.5 (*C*H_2Ph), 77.9 (C-1), 84.4 (C-4), 85.0 (C-3), 87.1 (C-2), 127.8, 127.9, 128.0, 128.5, 128.6, 137.6, 137.7, 138.2, 200.6 (*C*HO).

Epimerization of 32. A solution of **32** (48 mg, 0.108 mmol) in 4% NaOMe (3 mL) was kept at room temperature overnight, then neutralized with acetic acid, and concentrated to dryness. The residue was purified by flash chromatography (hexane/EtOAc 8:1−4:1) to afford a mixture of **32/33** (ca. 1:1) (40 mg, 83%) as an oil.

3-(5-*O*-Acetyl-2,3-di-*O*-benzyl-α/*β*-L-arabinofuranosyl)-propene (35). To a solution of **31** (9.5 g, 21.4 mmol) in Ac_2O (25 mL) at 0 °C was added a solution of 0.1% H_2SO_4/Ac_2O (25 mL). Routine work up and purification by chromatography (hexane/EtOAc 7:1) gave compound **35** (α/*β* 1:1, 5.93 g, 70%): ^{1}H NMR ($CDCl_3$) δ 2.04 and 2.06 (s and s, 3H each, α and *β* CO*CH*$_3$), 2.41−2.45 (m, 2H, α CH_2CH=CH$_2$), 2.52−2.55 (m, 2H, *β* CH_2CH=CH$_2$), 3.85−3.87 (m, 2H, H-2*β* and H-4*β*), 3.92−3.90 (m, 1H, H-2α), 3.95−3.97 (m, 1H, H-3α), 3.99−4.28 (m, 8H, H-1α, H-4α, 5α and *β*, 5′ α and *β*, H-1*β*, H-3*β*), 4.44−4.55 (m, 8H, CH_2Ph α and *β*), 4.58−5.13 (m, 4H, α and *β* CH=CH_2), 5.78−5.87 (m, 2H, α and *β* C*H*=CH$_2$), 7.24−7.39 (m, 20H, α and *β* 4 × Ph); ^{13}C NMR ($CDCl_3$) δ 21.3 (CO*C*H$_3$), 33.5 (*C*H$_2$-CH=CH$_2$ α), 38.0 (*C*H$_2$CH=CH$_2$ *β*), 64.6 and 65.2 (C-5α, 5*β*), 71.9−72.3 (2 × *C*H$_2$Ph α and *β*), 76.8 and 78.1 (2 × *C*H=CH$_2$ α and *β*), 80.7−82.5 (C-1α, 4α, 3*β*, 1*β*), 82.6 and 83.9 (C-2*β*, 4*β*), 85.3 (C-3α), 86.62 (C-2α), 117.4 and 117.9 (CH=*C*H$_2$ α and *β*), 171.03 (*C*OCH$_3$); HRFABMS anal. calcd for $C_{24}H_{28}O_5$ [M + H] 397.2015, found 397.2063.

2-(5-*O*-Acetyl-2, 3-di-*O*-benzyl-α/*β*-L-arabinofuranosyl)-ethyl Aldehyde (36). Ozonolysis of **35** afforded **36** in 76% yield (α/*β* 1:1): ^{1}H NMR ($CDCl_3$) δ 2.03 and 2.06 (s and s, 3H each, α and *β* AcO), 2.71 and 2.80 (ddd and ddd, 1H each, *β* CH_2CHO, J = 16.4, 6.0, 1.6 Hz), 2.85 (dd, 2H, α CH_2CHO, J = 7.2, 1.6 Hz), 3.85 (bd, 1H, H-3α, J = 2.0 Hz), 3.89 (dd, 1H, H-2*β*, J = 3.5, 2.0 Hz), 3.94 (dd, 1H, H-3*β*, J = 3.0, 3.0 Hz), 4.01 (d, 1H, H-2α, J = 4.0 Hz), 4.10 (m, 1H, H-4α), 4.11−4.21 (m, 4H, H-5α, 5′α and 5*β*, 5′*β*), 4.26 (m, 1H, H-4*β*), 4.38 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.47 (m, 1 H, H-1α), 4.50−4.59 (m, 7H, 3.5 × CH_2Ph), 4.57 (m, 1H, H-1*β*), 7.24−7.38 (m, 20H, 4 × Ph), 9.75 (t, 1H, C*H*O, J = 1.6 Hz), 9.78 (t, 1H, CHO, J = 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1 (CO*C*H$_3$), 43.5, 47.2, 64.5, 64.8, 71.9, 72.0, 72.1, 72.2, 76.7, 78.1, 81.3, 81.7, 82.7, 83.8, 84.8, 86.5, 127.8, 127.9, 128.1, 128.2, 128.6, 128.7, 137.3, 137.4, 137.5, 170.9 (*C*OCH$_3$), 200.9 (*C*HO); HRFABMS anal. calcd for $C_{23}H_{26}O_6$ [M + H] 399.1808, found 399.2169.

2-(2, 3-Di-*O*-benzyl-α-L-arabinopyranosyl)-ethyl Aldehyde (37). See epimerization Procedure C (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 2.51 (bs, 1H, 4-OH), 2.56 (ddd, 1H, CH_2CHO, J = 16.4, 8.0, 2.4 Hz), 2.74 (ddd, 1H, CH_2CHO, J = 16.4, 4.0, 2.0 Hz), 3.48 (bd, 1H, H-5ax, J = 12.8 Hz), 3.57 (dd, 1H, H-2, J = 9.2, 9.1 Hz), 3.64 (dd, 1H, H-3, J = 9.2, 3.2 Hz), 3.69 (ddd, 1H, H-1, J = 9.2, 8.0, 4.0 Hz), 4.01−4.05 (m, 2H, H-4, 5eq) 4.60 and 4.91 (d and d, 1H each, CH_2Ph, J = 11.2 Hz), 4.69 and 4.74 (d and d, 1 H each, CH_2Ph, J = 11.6 Hz), 7.27−7.36 (m, 10H, 2 × Ph), 9.71 (dd, 1H, C*H*O, J = 2.4 Hz, 2.0 Hz);^{13}C NMR ($CDCl_3$) δ 46.4 (*C*H_2CHO), 67.0 (C-4), 69.5 (C-5), 72.0 (*C*H_2Ph), 75.1 (*C*H_2Ph), 75.5 (C-1), 77.7 (C-2), 82.7 (C-3), 128.1, 128.2, 128.4, 128.7, 128.9, 137.6, 137.9, 200.3 (*C*HO); HRFABMS anal. calcd for $C_{21}H_{25}O_5$ [M + H] 357.1702, found 357.2155.

1-(2, 3-Di-*O*-benzyl-α/*β*-L-arabinofuranosyl)-2-propanol (38). To a solution of **36** (4.7 g, 11.8 mmol) in ether (100 mL) was added MeMgBr (3.0 M in ether, 10 mL) at −78 °C, and the mixture was stirred overnight. Water (50 mL) was added to the mixture and the aqueous solution was extracted with EtOAc (100 mL × 2), dried and concentrated. Purification by chromatagraphy (hexane/EtOAc 1:3) afforded **38** (3.8 g, 87%); HRFABMS anal. calcd for $C_{22}H_{29}O_5$ [M + H] 373.2015, found 373.1869.

1-(2, 3-Di-*O*-benzyl-5-*O*-trityl-α/*β*-L-arabinofuranosyl)-2-propanol (39). To a solution of **38** (3.7 g, 9.9 mmol) in pyridine (50 mL) was added trityl chloride (4.2 g) at room temperature. The mixture was stirred overnight and diluted by the addition of ethyl acetate (200 mL), washed with water, 0.1 N HCl, and water, dried, and concentrated. Purification by chromatography gave **39** (2.4 g) as a mixture of four diasteromers (45%).

1-(2, 3-Di-*O*-benzyl-6-*O*-trityl-α/*β*-L-arabinofuranosyl)-acetone (40). To a solution of **39** (2.3 g, 3.7 mmol) in CH_2Cl_2 (25 mL) were added 4 Å molecular sieves (2.0 g), NaOAc (0.48 g), and PCC (1.04 g), and the mixture was stirred at room temperature overnight and filtered through Celite. The filtrate was washed with water, aqueous $NaHCO_3$, and water, dried, and concentrated. After purification by chromatography **40** was obtained (0.7 g, 31%) as an α/*β* mixture: ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, *β* CH_3), 2.16 (s, 3H, α CH_3), 2.71(dd, 1H, α CH_3COC*H*H, J = 16.5, 6.0 Hz), 2.79 (dd, 1H, *β* CH_3-COCH*H*, J = 15.0, 7.5 Hz), 2.80 (dd, 1H, α CH3COCH*H*, J = 16.5, 9.0 Hz), 2.86 (dd, 1H, *β* CH3COC*H*H, J = 17.5, 7.0 Hz), 3.12 (dd, 1H, H-5*β*, J = 9.5, 7.0 Hz), 3.20 (dd, 1H, H-5α, J = 10.0, 6.5 Hz), 3.30 (dd, 1H, H-5′α, J = 9.5, 5.5 Hz), 3.34 (dd, 1H, H-5′*β*, J = 9.0, 4.5 Hz), 3.83 (dd, 1H, H-2α, J = 3.5, 2.5 Hz), 3.96−3.99 (m, 2H, H-2*β*, H-3*β*), 4.06−4.09 (m, 2H, H-3α, H-4*β*), 4.21 (m, 1H, H-4α), 4.23 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.38 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.43 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.44 (m, 1H, H-1*β*), 4.47 (m, 1H, H-1α), 4.50 (s, 2H, CH_2Ph), 4.52 (d, 1H, CH_2Ph, J = 12.0 Hz), 4.53 (d, 2H, CH_2-Ph, J = 11.5 Hz), 7.19−7.43 (m, 50H, 10 × Ph); ^{13}C NMR-($CDCl_3$) δ 30.6 (CH_3), 43.1 (*β* CH_3CO*C*H$_2$), 47.1 (α CH_3CO*C*H$_2$), 64.1 (C-5*β*), 64.2 (C-5α), 71.3, 71.4, 71.6, 71.8, 76.9 (C-1*β*), 78.6 (C-1α), 82.4 (C-4α), 82.6 (C-4*β*), 83.1 (C-3*β*), 83.5 (C-2*β*), 85.0 (C-3α), 86.7 (C-2α), 87.1 (Ph$_3$*C*-O), 126.9, 126.9, 127.5, 127.5, 127.6, 127.6, 127.7, 127.8, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 137.7 (2), 143.8, 143.9, 206.7 (*C*=O).

1-(2, 3-Di-*O*-benzyl-α/*β*-L-arabinofuranosyl)-acetone (41). A mixture of **40** (0.35 g, 0.057 mmol) and $ZnBr_2$ (1.26 g) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. Routine workup and purification by chromatography gave **41** (0.15 g, 71%) as an anomeric mixture (1:1): ^{1}H NMR ($CDCl_3$)

δ 2.15 (s, CH_3), 2.71 (dd, 1H, CH_3COCHH, J = 16.5, 6.5 Hz), 2.83 (dd, 1H, CH_3COCHH, J = 16.5, 6.5 Hz), 3.63−3.74 (m, 2H, H-5, 5′), 3.88 (bs, 1H, H-2), 4.02 (bs, 1H, H-3), 4.13 (ddd, 1H, H-4, J = 8.5, 3.5, 3.5 Hz), 4.55 (m, 1H, H-1), 4.34−4.62 (m, 4H, 2 × CH_2Ph), 7.26−7.37 (m, 10H, 2 × *Ph*); ^{13}C NMR ($CDCl_3$) δ 30.7, 46.3, 63.0, 71.6, 72.1, 78.8, 83.6, 84.4, 86.1, 137.4, 137.5, 206.7; for β-anomer 30.5, 42.7, 68.9, 71.7, 71.9, 77.1, 82.7, 82.9, 84.3; HRFABMS anal. calcd for $C_{22}H_{27}O_5$ [M + H] 371.1858, found 371.1871.

1-(2, 3-Di-*O*-benzyl-α-L-arabinopyranosyl)-acetone (42). See epimerization Procedure C (Supporting Information). ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H, CH_3), 2.60 (dd, 1H, CH_3COCHH, J = 11.0, 11.0 Hz), 2.72 (dd, 1H, CH_3COCHH, J = 20., 4.0 Hz), 3.46 (d, 1H, H-5ax, J = 15.0 Hz), 3.54 (dd, 1H, H-2, J = 11.5, 11.5 Hz), 3.63 (dd, 1H, H-3, J = 11.0, 4.0 Hz), 3.68 (dd, 1H, H-1, J = 20.0, 4.0 Hz), 3.99 (dd, 1H, H-5eq, J = 15.8, 3.0 Hz), 4.01 (dd, 1H, H-4, J = 4.0, 3.0 Hz), 4.61 (d, 1H, CH_2Ph, J = 13.5 Hz), 4.68 (d, 1H, CH_2Ph, J = 14.5 Hz), 7.28−7.37 (m, 10H, 2 × Ph); ^{13}C NMR ($CDCl_3$) δ 31.0 (CH_3), 45.8 (CH_3CO*C*H_2), 66.8 (C-4), 69.2 (C-5), 71.7, 75.1, 75.9 (C-1), 77.5 (C-2), 82.6 (C-3), 127.9, 128.1, 128.4, 128.6, 137.5, 138.1, 206.7 (*C*OCH_3); HRFABMS anal. calcd for $C_{22}H_{27}O_5$ [M + H] 371.1858, found 371.1905.

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Supporting Information Available: Experimental procedures and ^{1}H, ^{13}C NMR, COSY, and NOESY spectra of products (**6**, **7**, **14**, **15**, **23**, **26**, **27**, **32/33**, **36**, **37**, **41**, **42**). For those of compounds **20**−**22**, **24**, **25**, and **28**−**30**, see Supporting Information of ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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