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Synthesis of Conformationally-Locked *cis*- and *trans*-Bicyclo[4.4.0] Mono-, Di- and Trioxadecane Modifications of Galacto- and Glucopyranose. Experimental Limiting $^3J_{H,H}$ Coupling Constants for the Estimation of Carbohydrate Side Chain Populations and Beyond

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Abstract

Hexopyranose side chains populate three staggered conformations, whose proportions can be determined from the three sets of ideal limiting $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ coupling constants in combination with the time-averaged experimental coupling constants. Literature values for the limiting coupling constants, obtained by the study of model compounds, the use of the Haasnoot-Altona and related equations, or quantum mechanical computations, can result in computed negative populations of one of the three ideal conformations. Such values arise from errors in the limiting coupling constants and/or from the population of non-ideal conformers. We describe the synthesis and analysis of a series of *cis*- and *trans*-fused mono-, di-, and tri-oxabicyclo[4.4.0]octane-like compounds. Correction factors for the application of data from internal models (-CH(OR)-CH(OR)-) to terminal systems (-CH(OR)-CH₂(OR)) are deduced from comparison of further models, and applied where necessary. Limiting coupling constants so-derived are applied to the side chain conformations of three model hexopyranosides, resulting in calculated conformer populations without negative values. Although, developed primarily for hexopyranose side chains, the limiting coupling constants are suitable, with the correction factors presented, for application to the side chains of higher carbon sugars and to conformation analysis of acyclic diols and their derivatives in a more general sense.

Graphical Abstract

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Supporting Information Available. Tables of 1H Coupling Constants and Chemical Shifts. A complete Table for the assignment of compounds according to Newman projections I-VI, and copies of the 1H and ^{13}C NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.*****

Introduction

The growing need for the synthesis of complex oligosaccharides with which to address and exploit the varied roles in biology of glycosides and their conjugates provides the impetus for the development of improved glycosylation methodology.^{1–3} For this to take place in a rational manner, increased understanding of the mechanism(s) of glycosylation^{4–14} and of the factors that influence the reactivity and selectivity of glycosyl donors and acceptors is required.^{15–23} The conformational dynamics of donors, whether of the furanoside or pyranoside rings themselves or simply of their side chains, is one factor that has a profound influence on reactivity and selectivity.^{24–38} With regard to the side chain, in freely rotating systems the conformation is usually considered as an equilibrium mixture of three staggered conformers (Fig. 1), which are described as *gauche-gauche* (*gg*), *gauche-trans*, and *trans-gauche* (*tg*) where the first and second descriptors refer to the spatial relationship of O⁶ with the pyranoside ring oxygen (O⁵) and C⁴, respectively.^{39–41} The mole fractions (f_{gg} , f_{gt} and f_{tg}) of these conformers at equilibrium can be determined in the usual way from the experimental $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ coupling constants provided that accurate limiting values of these coupling constants ($^3J_{R,gg}$ – $^3J_{S,tg}$) are available for each of the three ideal staggered conformations.^{42–43}

Knowledge of the six limiting coupling constants, whose values vary according to the electronegativity and orientation of the substituents attached to the coupled system,^{44–45} is therefore critical for determining side chain conformational distributions and ultimately for relating them to reactivity. The parameterization of the Karplus,⁴⁶ and Haasnoot-Altona equations,⁴⁷ to take account of substituent effects has resulted in a number of suggested values for $^3J_{R,gg}$ – $^3J_{S,tg}$ whose reliability depends on the underlying models, as summarized by Bock and Duus in 1994,³⁹ and subsequently revisited by various authors.^{48–50} The situation is further complicated by the possible dependence of $^3J_{R,gg}$ – $^3J_{S,tg}$ on the orientation of substituents not directly attached to the coupled system.^{51–53}

An alternative approach to deriving limiting coupling constants makes use of experimental measurements on model compounds. This approach was followed by Bock and Duus, who employed the C1–C2 bonds of the 1,5-anhydroalditol **1** as models of the *gg* conformer, and of **2** and **3** as models of the *tg* conformer, as depicted in Figure 2 where H⁵, H^{6R} and H^{6S} are the side chain hydrogens modeled.³⁹ In **2** and **3** the relationship of the C1–C2 bond to the C5–C6 bond in the D-sugars is formally a pseudoenantiomeric one, but the modelled diastereotopic hydrogens are labelled H^{6R} and H^{6S} for ease of comparison. Subsequently,

Serianni and co-workers, following the earlier work of Ohri et al with related benzylidene acetals,⁵⁴ employed the galacto-configured pyruvate acetal **4**, the *trans*-2,5-(bishydroxymethyl)-1,4-dioxane **5** and the gluco-configured pyruvate acetal **6** as models for the *gt*, *gg* and *tg* conformations, respectively, and determined the relevant coupling constants in D₂O (Fig 2).⁴⁹ Clearly, there are significant differences in the limiting coupling constants for the *gg* and *tg* conformers predicted by the two sets of compounds (Fig 2); only one set of data is available for the *gt* conformer. Earlier models for the *gg* and *gt* conformers, **7** and **8**,⁵⁵ respectively, are of limited value because of ambiguities in the degree to which they model the conformations in question.⁴⁹

Ongoing projects in our laboratory requiring the determination of pyranoside side chain conformational populations,⁵⁶ focused our attention on the discrepancies in the data from the different sets of existing models. We considered that accurate values of the necessary limiting coupling constants would be best accessed by the synthesis and analysis of a series of conformationally rigid oxabicyclo[4.4.0]decane derivatives **9–20** designed to model the full set of staggered conformations in the gluco and galacto series.

Potential problems with the legitimacy of individual members of this set of model compounds including i) the conformational purity in particular of the *cis*-fused systems, and of systems with 1,3-diaxial interactions; ii) the measurement of coupling constants in tetrasubstituted systems as opposed to the trisubstituted ones of the hexose side chains; and iii) the combination of both of these factors led us to prepare a further series of compounds **21–26** (Fig 4) for comparison purposes. Models **21** and **24** additionally enable verification of the literature data obtained with compounds **1** and **2**, and in doing so probe the influence of ether-type protecting groups on the relevant coupling constants. As with models **2** and **3**, the relationship of the C1–C2 bond in compounds **21–23** with the side chain of the D-sugars is pseudoenantiomeric, and the labels H^{6R} and H^{6S} are retained for ease of comparison.

We report here on the synthesis of the twelve compounds **9–20** (Fig 3) and of the further models **21–26** (Fig 4), and on the measurement of the relevant coupling constants in perdeuteriobenzene, chloroform, and methanol. On the basis of careful comparative analysis of the spectral data for **9–26**, and the literature comparators **1–6**, an optimal set of model compounds and the associated limiting coupling constants are defined.

While the primary focus of this Article is on the side chain conformations of the common hexopyranoses, the limiting coupling constants derived from models carrying an additional C–C bond at the 6-position are also directly applicable to the side chains of the octulosonic and nonulosonic acids^{34,57} and to those of other higher carbon sugars such as are frequently found in bacterial oligosaccharides.^{58–61} Finally, the limiting coupling constants presented should also be applicable to the conformational analysis of other organic constructs based on the vicinal dihydroxy or dialkoxyalkane structural motif, whether tri- or tetrasubstituted, as well as to the development of improved computational models.

Results and Discussion

Synthesis

Compounds **10**,⁶² **11**,²⁷ **14**,²⁷ **16**,²⁵ **18**,²⁵ **20**⁶³ and **21–26**^{64–67} were either prepared as previously reported or as described in the experimental section. Compounds **9**, **12**, **17**, and **19** were prepared as outlined in Scheme 1. Thus, reduction of methyl 2,3-*O*-methyl,4,6-*O*-*p*-methoxybenzylidene- α -D-glucopyranoside **27**⁶⁸ with sodium cyanoborohydride in the presence of HCl^{69–70} gave 71% of the 6-*O*-*p*-methoxybenzyl ether **28**, whose unique hydroxyl group was subjected to the Dess-Martin protocol⁷¹ to give ketone **29** in 85% yield. Reaction with allylmagnesium chloride in THF at 0 °C then gave the 4-*C*-allyl galacto- and glucopyranosides **30** and **31** in 54 and 19% yield, respectively. The individual isomers were treated with sodium hydride and methyl iodide to give the corresponding ethers **32** and **33**, from which the PMB groups were cleaved with CAN giving the primary alcohols **34** and **35**. Dess Martin oxidation of the galacto-isomer **34** gave an aldehyde **36** that on treatment with vinylmagnesium bromide in THF at –78 °C gave an 81% overall yield of an inseparable 1.5:1 mixture of the allylic alcohols **38** and **39**, whose relative configurations were assigned retrospectively. Adapting earlier work on the synthesis of bicyclic pyranose derivatives,^{36,72} the mixture of **38** and **39** was subjected to ring-closing metathesis with the second generation Grubbs catalyst⁷³ to give **40** and **41** at which stage separation was achieved. This was followed by saturation of the double bond giving **42** and **43** and finally methylation with sodium hydride and methyl iodide to give **12** and **9**, respectively, at which stage ¹H NMR spectral analysis allowed unambiguous assignment of relative configuration. In an analogous manner oxidation of **35** with the Dess Martin periodinane gave an aldehyde **37**, whose treatment with vinylmagnesium bromide afforded the diastereomeric allylic alcohols **44** and **45** in 12 and 48% yield, respectively. The diastereomers **44** and **45** were then processed individually through the sequence of ring closing metathesis to give **46** and **47**, respectively, hydrogenation to **48**, and **49**, and finally methylation to give **17** and **19** whose ¹H NMR spectra allowed unambiguous assignment of relative configuration.

Compounds **13** and **15** were obtained (Scheme 2) by Dess Martin oxidation of methyl 6-*O*-benzyl-2,3-di-*O*-methyl- α -D-glucopyranoside **50**⁷⁴ to the corresponding ketone **51** followed by treatment with allylmagnesium chloride in THF at 0 °C when the 4-*C*-allyl galacto and 4-*C*-allyl-glucopyranosides **52** and **53** were obtained in 60 and 22% yield, respectively. Etherification with sodium hydride and methyl iodide then gave the ethers **54** and **55**, which were subjected to ozonolysis with reductive work up to give the 4-*C*-(2-hydroxyethyl) derivatives **56** and **57** in good yield. Adapting a protocol previously employed for the synthesis of **11**, **14**, **16**, and **18**,^{25,27} reaction of the galacto-isomer **56** with toluenesulfonyl chloride in pyridine afforded the tosylate **58** in 66% isolated yield, which on hydrogenolysis and subsequent treatment with sodium hydride gave the *trans*-fused bicyclic system **13** in 80% yield. The gluco-isomer **57** was similarly processed through the mesylate to the *cis*-fused bicyclic product **15**. Attempted tosylation of **57**, in direct analogy to the protocol applied to **56**, and under a variety of different conditions afforded an unstable tosylate **60** that decomposed on standing and on attempted silica gel chromatography to give the *cis*-fused dioxabicyclo-[4.3.0]-nonane **61** in varying yields. This compound, which was also a byproduct from the mesylation-hydrogenation-ring closing sequence, was obtained as a

single diastereomer whose structure was assigned on the basis of multiple HMBC correlations and nOe measurements as described in the Supporting Information.

Determination of Coupling Constants and Influence of Solvent and Protecting Groups

^1H NMR spectra of the bicyclic models **9–21** were recorded in C_6D_6 , CDCl_3 , and CD_3OD . All first order couplings were analyzed directly on the spectra. For second order spectra, complicated by the presence of virtual couplings, first order coupling constants were extracted with the help of spectral simulation using the DAISY simulation tool in the Bruker Topspin 3.5 suite of programs. As the spectra of **9–21**, revealed only minimal differences across the three solvents, spectra for the models **22–26** were only obtained in CDCl_3 . The $^3J_{\text{H1,H2}}$ coupling constants obtained in CDCl_3 with the benzylidene protected D-1,5-*O*-glucitol and mannitol derivatives **21** and **24** carrying benzyl ethers at the 2- and 3-positions do not differ in any significant way from those reported by Bock and Duus for the parents, 1,5-anhydroglucitol **2** and mannitol **1**, in water, indicating that neither inclusion in a bicyclic system, nor the ether protecting groups, nor solvents have a substantial influence on these coupling constants.

The complete set of $^3J_{\text{H,H}}$ coupling constants for **9–20** and **21–26** and are tabulated in the Supporting Information (Tables S1 and S2) for ease of comparison. The $^3J_{\text{H5,H6R}}$ and $^3J_{\text{H5,H6S}}$ coupling constants for **9–21** and **24**, and the literature models **1–8** are presented in Tables 1–3. To facilitate comparison and subsequent discussion Tables 1–3 are each broken down into two subsets of data: a first for the $^3J_{\text{H5,H6R}}$ coupling constants followed by a second for the $^3J_{\text{H5,H6S}}$ coupling constants. Further, in each subset, coupling constants modelled for the galacto configuration precede those for the gluco isomer.

Analysis of Bicyclic Systems 9–20—The viability of the bicyclic derivatives **9–20** as accurate models of the staggered conformations of pyranoside side chains depends critically on the adoption of the pure chair-chair conformations depicted in Figure 3. Six of the models are *trans*-decalin analogs and, with one exception, present little reason for concern. Indeed, analysis of the complete set of $^3J_{\text{H,H}}$ coupling constants for compounds **12**, **13**, **16**, **18**, and **20** (Table S1) provides no evidence of significant deviation from the chair-chair conformation. For the benzylidene acetal **20** this is further supported by the examination of literature X-ray crystal structures of cognate structures (eg, CCDC: HEGREQ) that show $<2^\circ$ deviation in torsion angles from the ideal *tg* conformation about the C5–C6 bond.⁷⁵ Comparison of the complete set of ^1H -NMR spectral data of the remaining *trans*-decalinoid structure **9** with that of its diastereomer **12** (Table S1) reveals a significant difference in the axial, equatorial (a,e) coupling constants between H7 and H8, and H8 and H9 suggesting that the unfavorable steric and dipolar interactions between the two axial methoxy groups in **9**, despite the small size of a methoxy group (steric A values range from 0.55–0.75 kcal.mol⁻¹)⁴³ is relieved by distortion of the carbocyclic ring. This distortion is minor as the pattern of nOe interactions around the carbocyclic ring of **9** (Figure 5) are indicative of a chair-like conformation, nevertheless they are sufficient for us to exclude **9** as a model for the ideal *gg* conformation of the galactopyranose side chain. The unfavorable interaction between the two methoxy groups of **9** in a *syn*-pentane conformation is directly comparable to the interaction between O4 and O6 that is responsible for the low population of the *gg*-

conformer of galactopyranose. Indeed, the conformational distortion that this interaction imposes on the bicyclic system **9** strongly suggests that the ideal *gg* conformer of 4,6-di-*O*-methyl ethers of galactopyranose and its derivatives can have no appreciable population.

Compounds **10**, **11**, **14**, **15**, **17**, and **19** on the other hand, because of the inherently more conformationally mobile nature of the *cis*-decalin framework, are of concern even though analysis of the complete set of coupling constants (Table S1) indicates only minor distortions from the ideal chair-chair conformation. Inspection of a previous crystallographic analysis⁷⁶ of two 4,6-*O*-benzylidene-protected galactopyranosides reveals torsion angles of 67° and 68° for O5-C5-C6-O6 and of 52° and 52° for C4-C5-C6-O6 indicating that the benzylidene acetal **10**, and indeed the acetal **4** employed by Serianni, are likely not good models of the ideal *gg* conformation. As compound **15** displays $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ coupling constants that are identical to those in **10** (Table 2), we are forced to conclude that it, too, is not a good model of the ideal staggered *gg* conformation. Comparison of the complete set of $^3J_{H,H}$ coupling constants around the carbocyclic rings of compounds **17** and **19**, which differ only in configuration at C6 also reveals, minor differences in conformation (Table S1). As the $^3J_{H5,H6R}$ coupling constant for **19** is markedly different to those of the *trans*-fused systems **13** and **20**, even after correction for the addition CC bond as discussed below, we conclude that **19** is also not a suitable model for the present purposes even though nOe considerations indicate that any deviation from a chair-chair conformation is minor (Figure 5). Compound **14** displays a $^3J_{H5,H6R}$ coupling constant comparable to that of **19** and substantially smaller than those of **13** and **20**, leading to the conclusion that it also is not a suitable model. The *gt* models **11** and **17** have very similar $^3J_{H5,H6S}$ coupling constants, which also differ only marginally from that determined on the monocyclic model **5** by Serianni, suggesting that of all the *cis*-fused compounds prepared these two may be the most reliable. Overall, of the six *cis*-fused models prepared we exclude **10**, **14**, **15**, and **19** from further consideration.

Inspection of the complete data set for **9–20** (Table S1) reveals an interesting difference in the magnitude of the $^3J_{H2,H3}$ coupling constant in the pyranoside ring between the six *gluco* and six *galacto* configured compounds. Thus, in the galacto-series (**9–14**) $^3J_{H2,H3}$ is 10.0±0.1 Hz, whereas in the gluco-series (**15–20**) it is 9.4±0.2 Hz, independent of the *cis*- or *trans*-fused nature of the ring junction. We attribute this difference to the β-effect noted by Altona and Haasnoot for a pair of coupled antiperiplanar hydrogens when one of the two is also antiplanar to an electron-withdrawing C-X bond in the β-position, as in the H2, H3 and O4 relationship in the galacto-series, resulting in a mean coupling constant increase of 0.5 Hz.⁵¹

Comparison of the 4,6-*O*-Acetals and the 1,5-Anhydrohexitols as Models for the *tg* Conformation—Comparison of the spectral data for the literature 1,5-anhydrohexitols *tg* models **2** and **3** and the 4,6-*O*-alkylidene derivative **6**, reveals significant differences in the $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ coupling constants. These differences are reflected in the internal comparison of the H1,H2 and H5,H6 coupling constants in the 4,6-*O*-benzylidene protected 1,5-anhydrohexitol **21** (Figure 6), begging the question as to which of the two is the most suitable model for the *tg* conformation. We select the H5,H6R,H6S spin

system in the 4,6-*O*-acetals **6**, **20**, **21** and **24** and in the bicyclic model **13** model over the H1R,H1S,H2 spin system in the 1,5-anhydrohexitols **2**, **3** and **21**, and exclude the latter from further consideration. This choice is grounded in the closer homology of the selected models to the *tg* conformation, and is supported by the similarity between the $^3J_{H5,H6}$ coupling constants in the acetals and in the bicyclic model **13**. This latter indicates that the presence of the acetal function has negligible influence on the coupling constants in the adjacent spin system. The freezing of rotation about the C6–O6 bond in the selected bicyclic models is not expected to exert a significant influence on the measured coupling constants.⁴⁹

Derivation of Correction Factors for the Use of Tetrasubstituted Stereodiads as Models for the Trisubstituted Side Chain of the Hexopyranosides—

The exocyclic C5–C6 bond of the hexopyranoses is trisubstituted whereas the corresponding bond in eight of the bicyclic models (**9**, **11**, **12**, **14**, **16–19**) is tetrasubstituted, leading to concerns about the influence of the extra C–C bond on coupling constants. Altona and Haasnoot addressed this issue in their study of substituent effects on coupling constants in pyranose rings and suggested that no corrections were required to (a,e), and (e,e) couplings for systems carrying the additional C–C bond. However, for (aa) couplings the same authors suggested that one of two alternative interpretations of their data necessitated a + 0.4 Hz correction for (a,a) couplings.⁵¹ The considerable differences in some of the experimental coupling constants between tri- and tetrasubstituted models of the same side chain conformation in **9–20** prompted closer investigation of this issue.

For each configuration, *erythro* or *threo*, of a given stereodiad there are three staggered conformations that can be represented by a total set of six Newman projections, of which two, II and III, are pseudo-enantiomeric (Figure 7).⁷⁷

The three staggered conformations about the tetrasubstituted C5–C6 bond of models **9**, **11**, **12**, **14**, and **16–19** can each be assigned to one of the six Newman projections I–VI as described in detail in Table S5 and summarized in Table 4. When R' is hydrogen, the staggered conformations of the C5–C6 bond in systems **10**, **13**, **15**, and **20**, and of the C2–C1 bonds in **1–3**, **21** and **24** may be similarly assigned. For these trisubstituted systems, containing only a single stereogenic center, projections I and IV are formally identical as are projections II and V, and III and VI. To complete the analysis two further model compounds are required for comparison with the Serianni dioxane **5**. The literature compounds, *cis*-2,3-dimethyl-1,4-dioxane **62** and *trans*-2,3-dimethyl-1,4-dioxane **63** (Figure 8), whose coupling constants were extracted by study of the ^{13}C side bands at low temperature, were selected for this purpose.^{78–79} The Newman projections of the C1–C2 bonds in these compounds were analyzed according to the system of Figure 7 (Table 4).

It follows from Table 4 that comparison of the (a,a)-coupling constants about the C2–C1 bond of entries 2 and 3 yields a correction factor for tri- and tetrasubstituted systems belonging to projection I. Similarly, comparisons of Table 4, entry 6 with 7, entry 8 with 11, entry 1 with 13, entry 6 with 14, and entry 8 with 16 lead to correction factors in the remaining five projections II–VI as summarized in Table 5. We note that for the derivation of each correction factor the tri- and tetrasubstituted compounds employed (Table 5) belong to the same class of compounds, such that minimization of systematic errors can be expected.

The derived correction factors cover a considerable range from -0.5 Hz, through zero, to as much as $+2.0$ Hz, with the two largest corrections involving two coupled antiperiplanar spins. While quantitatively different this pattern parallels the suggestion of Altona and Haasnoot⁵¹ that only (a,a) coupling constant need correction in this manner. The large magnitude of the (a,a) correction factor is corroborated by inspection of the complete set of literature coupling constants for compound **63**. Thus, Gatti and coworkers⁷⁸ reported a coupling constant of 11.5 Hz for the (a,a) coupling in the disubstituted O-CH₂CH₂-O system of **63**,⁸⁰ which is 3.0 Hz more than the 8.5 Hz found for the tetrasubstituted portion O-CHMeCHMe-O system of the same molecule. Assuming a linear relationship, the (a,a) coupling constant in a related trisubstituted system O-CHMeCH₂-O would be $3.0/2 = 1.5$ Hz in reasonable agreement with the 2.0 Hz derived in Table 5. Application of the correction factors leads to a set of revised limiting coupling constants for data derived from tetrasubstituted systems as indicated in Tables 1–3.

Limiting Coupling Constants for the *gg*, *gt*, and *tg*-Conformations

gg-Conformation—On the basis of the above discussion literature compound **4** and the bicyclic systems **9**, **10**, and **15** are considered to be inadequate models and are consequently excluded from further consideration. The bicyclic disiloxane **7** is not considered an appropriate model because of the significant deviation of its $^3J_{H5,H6R}$ coupling from all others in Table 1. After application of the appropriate correction factor for the presence of the extra C-C bond (Table 5) there is good consistency in the $^3J_{H5,H6S}$ coupling constants from the gluco-configured *trans*-fused model **16**, the literature monocyclic model **1**, and its benzyldiene analog **24**, and we consider these three systems to be good models of the *gg*-conformation. Accordingly, limiting coupling constants of 1.0 and 2.2 Hz are recommended for the $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ spin systems, respectively (Table 6, entry 1).

gt-Conformation—After application of the necessary correction factors (Table 5) there is reasonable conformity of the *trans*-fused models **12** and **18** with the literature monocyclic model **5** for the limiting $^3J_{H5,H6R}$ coupling constant in the *gt*-conformation. Taking an average, we arrive at a coupling constant of 11.0 Hz for this spin system (Table 6, entry 1). Again after application of the appropriate correction, there is good agreement between the *cis*-fused bicyclic models **11** and **17**, and the monocyclic model **5** for a value of 2.5 Hz for the limiting coupling constant of the $^3J_{H5,H6S}$ spin system in the *gt*-conformation (Table 6, entry 1). The bicyclic disiloxane **8** does not constitute an appropriate model as its $^3J_{H5,H6S}$ coupling constant is markedly lower than all others in Table 2.

tg-Conformation—Following the above analyses, bicyclic models **14** and **19** are deemed to be inadequate as are the C1–C2 bonds in compounds **2**, **3** and **21**. Models **13**, **20**, the literature model **6**, and the C5–C6 bond of **21**, on the other hand, are considered viable systems leading us to adopt 4.8 and 10.2 Hz as limiting coupling constants for the $^3J_{H5,H6R}$ and $^3J_{H5,H6S}$ spin systems, respectively, in the *tg*-conformation (Table 6, entry 1).

Comparison with Literature Values—In addition to the limiting coupling constant derived here, literature values obtained with the Haasnoot-Altona equation,⁴⁷ experimentally with the models **1**–**3**³⁹ and **4**–**6**⁴⁹ and a related set of peracetylated benzyldiene acetals,⁵⁴

and computationally for **4–6**⁴⁹ are presented in Table 6. With regard to the ${}^3J_{\text{H5,H6R}}$ limiting coupling constants the new set of gg , gt , and tg (Table 6, entry 1) values most closely resemble those obtained on the basis of the Haasnoot-Altona equation (Table 6, entry 2). The largest individual discrepancies in ${}^3J_{\text{H5,H6R}}$ are with the experimental value for the gg conformation derived experimentally from model **4** and computed for the gt on the basis of model **5** (Table 6, entries 4 and 5, respectively). For the ${}^3J_{\text{H5,H6S}}$ limiting coupling constants the data obtained with **1–3** (Table 6, entry 3) are in closest agreement with the values obtained in this study.

Application of the Recommended Values to the Side Chain Conformations of Gluco- and Galactopyranosides

To calculate the side chain populations of representative hexopyranosides we employed a set of literature experimental ${}^3J_{\text{H5,H6R}}$ and $J_{\text{H5,H6S}}$ coupling constants measured by Bock and Duus³⁹ for methyl α -D-glucopyranoside (5.5 and 2.4 Hz), methyl β -D-glucopyranoside (6.1 and 2.5 Hz), and methyl β -D-galactopyranoside (7.5 and 4.8 Hz) and the limiting coupling constants from Table 6 to solve equations 1–3.

$${}^3J_{\text{H5,H6R}} = {}^3J_{\text{R,gg}}f_{\text{gg}} + {}^3J_{\text{R,gt}}f_{\text{gt}} + {}^3J_{\text{R,tg}}f_{\text{tg}} \quad (1)$$

$${}^3J_{\text{H5,H6S}} = {}^3J_{\text{S,gg}}f_{\text{gg}} + {}^3J_{\text{S,gt}}f_{\text{gt}} + {}^3J_{\text{S,tg}}f_{\text{tg}} \quad (2)$$

$$1 = f_{\text{gg}} + f_{\text{gt}} + f_{\text{tg}} \quad (3)$$

The populations of all three test substrates calculated in this manner using the new limiting coupling constants (Table 7, entry 1) compare favorably with those calculated using the various literature coupling constants (Table 7, entries 2–6). The absence of negative population values is noteworthy and marks a clear difference between use of the limiting coupling constants derived from the present series of bicyclic models, and those determined based on the Haasnoot-Altona equation. Such negative populations are usually interpreted as either i) inaccurate limiting coupling constants,³⁹ or ii) the population of non-ideal conformers.^{48–50} The absence of negative populations with the new data set suggests that the equilibration between the three ideal staggered conformation of the side chain is an adequate model.

Application to Higher Carbon Sugars and Non-Carbohydrate Diols

While the limiting coupling constants presented in Table 6, entry 1 were derived with the solution of hexopyranoside side chain populations in mind, they should also be applicable to any terminal vicinal diols (ie, with the HO-CH₂-CHOH-R motif) and related ethers. Limiting coupling constants derived from models **11**, **12**, **16**, **17**, and **18** (Tables 1 and 2)

should be valid, without the application of the correction factors, for direct use in studies of the conformations of internal vicinal diols (ie, with the R-CHOH-CHOH-R' motif) and related ethers. Such systems include the side chains of the higher carbon sugars as found in the bacterial heptopyranosides,^{58–61} octulosonic and nonulosonic acids including the KDO glycosides and the sialic acid glycosides,^{34,57} as well as a host of acyclic polyols.^{81–82} Limiting coupling constants obtained with the trisubstituted systems **13** and **20** (Table 3) should also be suitable for internal vicinal diols following application of the appropriate correction factors from Table 5.

Conclusions

Twelve *cis*- or *trans*-fused bicyclo-[4.4.0]-octane-like systems have been synthesized as models of the ideal *gg*, *gt*, and *tg* staggered conformations of the hexopyranoside side chain. Consideration of the complete set of NMR spectral data leads to the exclusion of some compounds from the data set, mainly in the *cis*-fused series, on the grounds of deviation from the ideal chair-chair conformations. Consideration of a further series of model compounds permits the derivation of correction factors enabling the use of data from tetrasubstituted systems as models for the trisubstituted side chains. Ultimately, a series of limiting coupling constants for the $^3J_{H5,H6R}$ and $J_{H5,H6S}$ coupling constants of the hexopyranose side have been derived and compared to literature values obtained from either other model systems, on the basis of the Haasnoot-Altona equation, or computationally. In conjunction with literature experimental coupling constants, the limiting coupling constants obtained from the rigid bicyclic models lead to calculated populations of the gluco- and galactopyranoside side chains that are essentially devoid of the negative values found with other systems and, in doing so, remove the need for consideration of non-ideal conformations. While the data were derived expressly for use in the hexopyranosides it is expected that, with suitable application of the necessary correction factors, they will also prove useful in the analysis of the side chain conformations of the higher carbon sugars and even acyclic vicinal diols. Finally, the new limiting coupling constants should serve to inform the development of improved computational models for the prediction of saccharide side chain conformations.

Experimental Part

General Experimental

All extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure at ~ 35 °C. Flash column chromatographic purifications were carried out over silica gel unless otherwise stated. Commercially available anhydrous solvents were used for moisture sensitive reactions unless otherwise stated. NMR spectra were recorded in CDCl₃ with 400 or 600 MHz instruments unless otherwise stated. NMR spectra of final compounds were recorded in CD₃OD, CDCl₃, and C₆D₆ at 600 MHz unless otherwise stated. The DAISY 1D-NMR spectra simulation tool in the TopSpin 3.5 pl 7 software package was used to simulate ¹H-NMR spectra. Specific rotations were recorded in dichloromethane unless otherwise stated. ESI-HRMS were recorded using a Waters LCT Premier Xe time of flight mass spectrometer.

Methyl 4,6-O-Benzylidene-2,3-di-O-methyl- α -D-galactopyranoside (10)—

Compound **10** was synthesized following literature protocol.⁶² In CHCl_3 : ^1H NMR (600 MHz, CDCl_3) δ 7.52 – 7.50 (m, 2H), 7.37 – 7.29 (m, 3H), 5.54 (s, 1H), 4.98 (d, J = 3.5 Hz, 1H), 4.34 (dd, J = 3.5, 1.3 Hz, 1H), 4.26 (dd, J = 12.5, 1.8 Hz, 1H), 4.07 (dd, J = 12.5, 1.8 Hz, 1H), 3.78 (dd, J = 10.1, 3.5 Hz, 1H), 3.67 (dd, J = 10.1, 3.5 Hz, 1H), 3.63 (td, J = 1.8, 1.3 Hz, 1H), 3.52 (s, 3H), 3.50 (s, 3H), 3.44 (s, 3H).

In C_6D_6 : ^1H NMR (600 MHz, C_6D_6) δ 7.71 – 7.70 (m, 2H), 7.15 – 7.03 (m, 3H), 5.27 (s, 1H), 4.75 (d, J = 3.5 Hz, 1H), 4.06 (dd, J = 12.2, 1.6 Hz, 1H), 3.80 (dd, J = 10.1, 3.5 Hz, 1H), 3.77 (dd, J = 3.6, 1.1 Hz, 1H), 3.62 (dd, J = 10.1, 3.6 Hz, 1H), 3.44 (dd, J = 12.2, 1.9 Hz, 1H), 3.28 (s, 3H), 3.18 (s, 3H), 3.10 (s, 3H), 3.05 (ddd, J = 1.9, 1.6, 1.1 Hz, 1H).

In CD_3OD : ^1H NMR (600 MHz, CD_3OD) δ 7.49 – 7.47 (m, 2H), 7.36 – 7.30 (m, 3H), 5.59 (s, 1H), 4.95 (d, J = 2.4 Hz, 1H), 4.45 (dd, J = 2.2, 1.1 Hz, 1H), 4.15 (dd, J = 12.5, 1.6 Hz, 1H), 4.12 (dd, J = 12.5, 1.7 Hz, 1H), 3.66 – 3.65 (m, 2H), 3.64 (ddd, J = 1.7, 1.6, 1.1 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H), 3.41 (s, 3H).

Methyl 4,8-Anhydro-7-deoxy-2,3,6-tri-O-methyl- α -D-glycero-D-galactooctopyranoside (11)—

Compound **11** was synthesized following literature protocol.²⁷ In CHCl_3 : ^1H NMR (600 MHz, CDCl_3) δ 4.95 (d, J = 3.7 Hz, 1H), 4.13 (ddd, J = 11.9, 4.8, 1.7 Hz, 1H), 4.00 (dd, J = 3.2, 0.8 Hz, 1H), 3.68 (dd, J = 10.0, 3.7 Hz, 1H), 3.68 (dd, J = 3.2, 0.8, 1H), 3.55 (dd, J = 10.0, 3.2 Hz, 1H), 3.52 (s, 3H), 3.49 (s, 3H), 3.47 (s, 3H), 3.41 (s, 3H), 3.40 (ddd, J = 12.6, 11.7, 2.2, 1H), 3.34 (ddd, J = 11.9, 4.5, 3.2 Hz, 1H), 1.98 (dddd, J = 12.6, 12.4, 11.9, 4.8 Hz, 1H), 1.74 (dddd, J = 12.4, 4.5, 2.2, 1.7 Hz, 1H).

In C_6D_6 : ^1H NMR (600 MHz, C_6D_6) δ 4.81 (d, J = 3.7 Hz, 1H), 3.88 (dd, J = 10.0, 3.7 Hz, 1H), 3.80 (ddd, J = 11.6, 4.8, 1.8 Hz, 1H), 3.71 (d, J = 3.2 Hz, 1H), 3.57 (dd, J = 10.0, 3.2 Hz, 1H), 3.29 (s, 3H), 3.27 (s, 3H), 3.22 (dd, J = 3.2, 0.8 Hz, 1H), 3.22 (s, 3H), 3.10 (s, 3H), 2.92 (ddd, J = 12.7, 11.6, 2.2 Hz, 1H), 2.80 (ddd, J = 11.8, 4.5, 3.2 Hz, 1H), 2.10 (dddd, J = 12.7, 12.5, 11.8, 4.8 Hz, 1H), 1.31 (dddd, J = 12.5, 4.5, 2.2, 1.8 Hz, 1H).

In CD_3OD : ^1H NMR (600 MHz, CD_3OD) δ 4.90 (d, J = 3.7 Hz, 1H), 4.01 (dd, J = 3.1, 0.7 Hz, 1H), 4.00 (ddd, J = 11.7, 4.9, 1.7 Hz, 1H), 3.77 (dd, J = 3.2, 0.7 Hz, 1H), 3.58 (dd, J = 10.1, 3.7 Hz, 1H), 3.52 (dd, J = 10.1, 3.2 Hz, 1H), 3.45 (ddd, J = 12.0, 4.6, 3.1 Hz, 1H), 3.44 (s, 3H), 3.42 (ddd, J = 12.5, 11.7, 2.0 Hz, 1H), 3.41 (s, 6H), 3.39 (s, 3H), 1.86 (dddd, J = 12.5, 12.4, 12.0, 4.9 Hz, 1H), 1.71 (dddd, J = 12.4, 4.6, 2.0, 1.7 Hz, 1H).

Methyl 4,8-Anhydro-7-deoxy-2,3,6-tri-O-methyl- β -L-glycero-D-galactooctopyranoside (14)—

Compound **14** was prepared using literature protocol.²⁷ In CHCl_3 : ^1H NMR (600 MHz, CDCl_3) δ 4.86 (d, J = 3.6 Hz, 1H), 4.00 (dd, J = 3.4, 1.1 Hz, 1H), 3.84 (ddd, J = 11.4, 5.3, 1.3 Hz, 1H), 3.71 (ddd, J = 13.1, 11.4, 2.6 Hz, 1H), 3.67 (dd, J = 10.1, 3.6 Hz, 1H), 3.61 (dd, J = 3.1, 1.1 Hz, 1H), 3.52 (dd, J = 10.1, 3.4 Hz, 1H), 3.52 (s, 3H), 3.49 – 3.46 (m, 4H), 3.42 (s, 3H), 3.39 (s, 3H), 1.97 (dddd, J = 14.3, 13.1, 5.2, 2.8 Hz, 1H), 1.65 (dddd, J = 14.3, 3.7, 2.6, 1.3 Hz, 1H).

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.84 (d, *J* = 3.6 Hz, 1H), 4.15 (dd, *J* = 3.4, 1.1 Hz, 1H), 4.00 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.76 – 3.69 (m, 3H), 3.40 (ddd, *J* = 3.0, 2.9, 2.8 Hz, 1H), 3.37 (s, 3H), 3.27 (s, 3H), 3.19 (s, 3H), 3.00 (s, 3H), 2.05 (dddd, *J* = 14.1, 13.0, 7.6, 2.8 Hz, 1H), 1.36 (dddd, *J* = 14.1, 2.9, 2.8, 1.1 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.89 (d, *J* = 3.6 Hz, 1H), 4.01 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.73 (ddd, *J* = 11.3, 5.4, 1.2 Hz, 1H), 3.68 (ddd, *J* = 13.2, 11.4, 2.1 Hz, 1H), 3.62 (dd, *J* = 3.1, 1.1 Hz, 1H), 3.60 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.50 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.47 (ddd, *J* = 3.1, 3.0, 2.9 Hz, 1H), 3.46 (s, 3H), 3.41 (s, 3H), 3.40 (s, 3H), 3.40 (s, 3H), 1.95 (dddd, *J* = 14.3, 13.0, 5.4, 2.9 Hz, 1H), 1.67 (dddd, *J* = 14.3, 3.0, 2.8, 1.2 Hz, 1H).

Methyl 4,8-Anhydro-7-deoxy-2,3,6-tri-O-methyl-α-D-glycero-D-glucopyranoside (16)—Compound **16** was synthesized using the literature protocol.²⁵ **In CHCl₃:** ¹H NMR (600 MHz, CDCl₃) δ 4.89 (d, *J* = 3.6 Hz, 1H), 3.75 (ddd, *J* = 11.6, 5.5, 1.5 Hz, 1H), 3.72 (ddd, *J* = 3.6, 2.6, 2.2 Hz, 1H), 3.69 (ddd, *J* = 12.7, 11.6, 2.2 Hz, 1H), 3.60 (s, 3H), 3.56 (dd, 10.1, 8.9 Hz, 1H), 3.54 (dd, 10.1, 2.6 Hz, 1H), 3.50 (s, 3H), 3.46 (dd, *J* = 9.4, 8.9 Hz, 1H), 3.43 (s, 3H), 3.42 (s, 3H), 3.28 (dd, *J* = 9.4, 3.6 Hz, 1H), 1.98 (dddd, *J* = 14.5, 3.6, 2.2, 1.5 Hz, 1H), 1.71 (dddd, *J* = 14.5, 12.7, 5.5, 2.2 Hz, 1H).

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.71 (d, *J* = 3.6 Hz, 1H), 3.96 (dd, *J* = 10.1, 9.2 Hz, 1H), 3.83 (dd, *J* = 9.4, 9.2 Hz, 1H), 3.73 (ddd, *J* = 12.7, 11.4, 2.5 Hz, 1H), 3.68 (s, 3H), 3.63 (dd, *J* = 10.1, 2.6 Hz, 1H), 3.55 (ddd, *J* = 11.4, 5.4, 1.5 Hz, 1H), 3.40 (ddd, *J* = 3.6, 2.6, 2.5 Hz, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 3.24 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.16 (s, 3H), 1.45 (dddd, *J* = 14.1, 3.6, 2.5, 1.5 Hz, 1H), 1.38 (dddd, *J* = 14.1, 12.7, 5.4, 2.5 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.88 (d, *J* = 3.7 Hz, 1H), 3.70 (ddd, *J* = 11.5, 5.6, 1.5 Hz, 1H), 3.70 (ddd, *J* = 3.6, 2.6, 2.4 Hz, 1H), 3.64 (ddd, *J* = 12.8, 11.5, 2.2 Hz, 1H), 3.53 (s, 3H), 3.52 (dd, *J* = 10.1, 2.6 Hz, 1H), 3.48 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.47 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 3.36 (dd, *J* = 9.5, 9.0 Hz, 1H), 3.19 (dd, *J* = 9.5, 3.7 Hz, 1H), 1.95 (dddd, *J* = 14.5, 3.6, 2.2, 1.5 Hz, 1H), 1.74 (dddd, *J* = 14.5, 12.8, 5.6, 2.4 Hz, 1H).

Methyl 4,8-Anhydro-7-deoxy-2,3,6-tri-O-methyl-β-L-glycero-D-glucopyranoside (18)—Compound **18** was synthesized following literature protocol.²⁵ **In CHCl₃:** ¹H NMR (600 MHz, CDCl₃) δ 4.87 (d, *J* = 3.7 Hz, 1H), 4.00 (ddd, *J* = 11.9, 5.3, 1.5 Hz, 1H), 3.61 (s, 3H), 3.52 (s, 3H), 3.50 (t, *J* = 9.3 Hz, 1H), 3.47 (s, 3H), 3.45 (s, 3H), 3.42 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.42 (ddd, *J* = 12.9, 11.9, 2.3 Hz, 1H), 3.30 (ddd, *J* = 11.0, 9.0, 5.1 Hz, 1H), 3.24 (dd, *J* = 9.3, 3.7 Hz, 1H), 2.98 (dd, *J* = 9.3, 9.6 Hz, 1H), 2.04 (dddd, *J* = 13.2, 5.1, 2.3, 1.5 Hz, 1H), 1.55 (dddd, *J* = 13.2, 12.9, 11.0, 5.3 Hz, 1H).

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.65 (d, *J* = 3.7 Hz, 1H), 3.74 (t, *J* = 9.2 Hz, 1H), 3.62 – 3.60 (ddd, *J* = 11.8, 5.2, 1.6 Hz, 1H), 3.59 (s, 3H), 3.57 (dd, *J* = 9.7, 9.4 Hz, 1H), 3.27 (s, 3H), 3.22 (s, 3H), 3.19 (s, 3H), 3.17 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.99 (dd, *J* = 9.7, 9.2 Hz, 1H), 2.99 (ddd, *J* = 11.0, 9.0, 5.1 Hz, 1H), 2.98 (ddd, *J* = 12.7, 11.8, 2.4 Hz, 1H), 1.51 (dddd, *J* = 13.1, 5.1, 2.4, 1.6 Hz, 1H), 1.40 (dddd, *J* = 13.1, 12.7, 11.0, 5.2 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.85 (d, *J* = 3.8 Hz, 1H), 3.94 (ddd, *J* = 11.8, 5.2, 1.6 Hz, 1H), 3.51 (s, 6H), 3.45 (s, 3H), 3.42 (ddd, *J* = 12.8, 11.9, 2.3 Hz, 1H), 3.39 (s, 3H), 3.37 (dd, *J* = 9.4, 9.3 Hz, 1H), 3.33 (ddd, *J* = 10.8, 9.2, 4.8 Hz, 1H), 3.31 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 9.4, 3.8 Hz, 1H), 2.96 (dd, *J* = 9.4, 9.3 Hz, 1H), 2.06 (dddd, *J* = 13.2, 4.8, 2.3, 1.6 Hz, 1H), 1.48 (dddd, *J* = 13.2, 12.8, 10.8, 5.2, 1H).

Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-methyl-α-D-glucopyranoside (20)—

Compound **20** was synthesized by following the literature protocol.⁶³ **In CHCl₃:** ¹H NMR (600 MHz, CDCl₃) δ 7.51 – 7.48 (m, 2H), 7.39 – 7.33 (m, 3H), 5.54 (s, 1H), 4.86 (d, *J* = 3.7 Hz, 1H), 4.28 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.81 (ddd, *J* = 10.1, 9.6, 4.7 Hz, 1H), 3.73 (dd, *J* = 10.2, 10.1 Hz, 1H), 3.69 (dd, *J* = 9.3, 9.2 Hz, 1H), 3.64 (s, 3H), 3.55 (s, 3H), 3.53 (dd, *J* = 9.6, 9.3 Hz, 1H), 3.45 (s, 3H), 3.30 (dd, *J* = 9.2, 3.7 Hz, 1H).

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 7.65 – 7.61 (m, 2H), 7.21 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 5.37 (s, 1H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.16 (dd, *J* = 10.2, 4.9 Hz, 1H), 3.90 (dd, *J* = 10.3, 9.6, 4.9 Hz, 1H), 3.88 (t, *J* = 9.2 Hz, 1H), 3.56 (s, 3H), 3.52 (dd, *J* = 10.3, 10.2 Hz, 1H), 3.50 (dd, *J* = 9.6, 9.2 Hz, 1H), 3.28 (s, 3H), 3.21 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.06 (s, 3H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 7.48 – 7.45 (m, 2H), 7.38 – 7.32 (m, 3H), 5.57 (s, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.21 (dd, *J* = 9.3, 4.0 Hz, 1H), 3.75 (t, *J* = 10.3 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.58 – 3.53 (m, 5H, H-4, OCH₃), 3.49 (s, 3H), 3.43 (s, 3H), 3.32 (dd, *J* = 9.5, 3.6, 1H).

1,5-Anhydro-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucitol (21)—A mixture of *S*-phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thia-β-D-glucopyranoside⁸ (0.025 g, 0.046 mmol), tributylstannane (18.7 μL, 0.069 mmol), and azobisisobutyronitrile (catalytic) in anhydrous benzene (0.5 mL) was sparged with Ar and heated to reflux overnight. Then the reaction mixture was concentrated and partitioned between hexane and acetonitrile, and the acetonitrile layer was concentrated under vacuum. The crude residue was purified by silica gel chromatography, eluting with hexane/ ethylacetate (19:1 to 9:1), to afford **21** (14.5 mg, 72%) with spectral data consistent with the literature.⁶⁴ **In CHCl₃:** ¹H NMR (600 MHz, CDCl₃) 7.51 – 7.48 (m, 2H), 7.41 – 7.27 (m, 13H), 5.56 (s, 1H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.84 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.32 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.01 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.75 (dd, *J* = 9.1, 8.9 Hz, 1H), 3.68 (dd, *J* = 10.2, 10.3 Hz, 1H), 3.66 (ddd, *J* = 10.5, 8.9, 5.7 Hz, 1H), 3.62 (dd, *J* = 9.1, 9.3 Hz, 1H), 3.37 (ddd, *J* = 10.2, 9.3, 5.0 Hz, 1H), 3.33 (dd, *J* = 11.3, 10.5 Hz, 1H).

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 7.63 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.42 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.27 – 7.17 (m, 7H), 7.15 – 7.07 (m, 4H), 5.31 (s, 1H), 5.04 (d, *J* = 11.8 Hz, 1H), 4.85 (d, *J* = 11.8 Hz, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.17 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.87 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.68 (dd, *J* = 9.1, 8.7 Hz, 1H), 3.56 (ddd, *J* = 10.6, 8.7, 5.7 Hz, 1H), 3.47 (dd, *J* = 9.1, 9.3 Hz, 1H), 3.44 (t, *J* = 10.2 Hz, 1H), 3.14 (ddd, *J* = 10.1, 9.3, 5.0 Hz, 1H), 3.09 (dd, *J* = 11.2, 10.6 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 7.48 – 7.45 (m, 2H), 7.37 – 7.22 (m, 13H), 5.58 (s, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.23 (dd, *J* = 10.3, 5.0 Hz, 1H), 4.04 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.70 (dd, *J* = 9.1, 8.7 Hz, 1H), 3.68 (dd, *J* = 10.2, 10.3 Hz, 1H), 3.63 (ddd, *J* = 10.5, 8.7, 5.6 Hz, 1H), 3.60 (dd, *J* = 9.1, 9.3 Hz, 1H), 3.35 (ddd, *J* = 10.2, 9.3, 5.0 Hz, 1H), 3.31 (dd, *J* = 11.2, 10.5 Hz, 1H).

1-Allyl-2,3-di-O-benzyl-4,6-O-benzylidene-1-deoxy-β-D-glucopyranose (22) and 1-Allyl-2,3-di-O-benzyl-4,6-O-benzylidene-1-deoxy-α-D-glucopyranose (23)—A mixture of 2,3,4,6-tetra-*O*-acetyl-1-*C*-allyl-D-glucopyranose⁸³ (α:β = 1:0.2, 0.40 g, 1.1 mmol) and NaOMe (cat.) in anhydrous methanol (5.0 mL) was stirred at room temperature under argon for 5 h before quenching with Amberlyst-15 (pH~5). Then the reaction mixture was filtered and concentrated to dryness. The residue was dissolved in anhydrous acetonitrile (7.8 mL) followed by addition of benzaldehyde dimethyl acetal (0.24 mL, 1.6 mmol) and camphorsulfonic acid (0.012 g, 0.05 mmol). The reaction mixture was stirred at room temperature overnight under argon, before it was quenched by adding triethylamine (0.35 mL) and concentrated to dryness. The crude residue (0.238 g, 0.81 mmol) was dissolved in anhydrous DMF (4.1 mL) and cooled to 0 °C before 60% NaH in mineral oil (0.100 g, 2.44 mmol) was added followed by benzyl bromide (288 μL, 2.44 mmol). The reaction mixture was stirred at room temperature overnight under argon, then cooled to 0 °C before quenching with water. The reaction mixture was partitioned between ethyl acetate and H₂O, the organic layer was separated, washed with brine, dried over anhydrous Na₂SO₄, and concentrated to dryness. The residue was purified using silica gel column chromatography, eluting with hexanes/ethyl acetate (20:1 to 10:1), to afford **22** (0.022 g, 6%) and **23** (0.210 g, 55%), both with spectral data consistent with the literature.

(22).⁶⁵ ¹H NMR (600 MHz, CDCl₃) δ 7.52 – 7.49 (m, 2H), 7.41 – 7.27 (m, 13H), 5.91 – 5.83 (m, 1H), 5.59 (s, 1H), 5.12 – 5.07 (m, 2H), 5.01 (d, *J* = 11.2 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H), 4.35 (dd, *J* = 10.4, 5.0 Hz, 1H), 3.85 (dd, *J* = 9.3, 8.4 Hz, 1H), 3.72 (t, *J* = 10.3 Hz, 1H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.49 (ddd, *J* = 9.6, 7.2, 3.3 Hz, 1H), 3.42 (ddd, *J* = 10.3, 9.3, 5.0 Hz, 1H), 3.38 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.61 (dddt, *J* = 14.8, 6.4, 3.3, 1.6 Hz, 1H), 2.30 (dtt, *J* = 14.8, 7.4, 1.1 Hz, 1H).

(23).^{65,67} ¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.52 (m, 2H), 7.43 – 7.29 (m, 13H), 5.80 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.60 (s, 1H), 5.18 – 5.11 (m, 2H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.31 – 4.24 (m, 1H), 4.11 (ddd, *J* = 8.3, 7.2, 5.8 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.79 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.73 – 3.65 (m, 3H), 2.57 (br t, *J* = 7.1 Hz, 2H).

1,5-Anhydro-4,6-O-benzylidene-2,3-di-O-benzyl-D-mannitol (24)—Compound **24** was synthesized using literature protocol.⁶⁶ ¹H NMR (600 MHz, CDCl₃) 7.60-7.20 (m, 15H); 5.56 (s, 1H); 4.85-4.65 (d x4, *J* = 12.5, 12.1 Hz, 4H); 4.29 (dd, 4.8, 10.3 Hz, 1H); 4.26 (dd, 9.9 Hz, 9.5 Hz, 1H); 4.07 (dd, 12.5, 2.2 Hz, 1H); 3.86 (t, 9.9, 10.3 Hz, 1H); 3.28 (m, 1.1, 2.2, 3.3 Hz, 1H); 3.68 (dd, 3.3, 9.9 Hz, 1H); 3.44 (dd, 12.5, 1.1 Hz, 1H); 3.34 (dt, 9.9, 4.8 Hz, 1H).

1-Allyl-2,3-di-O-benzyl-4,6-O-benzylidene-1-deoxy-β-D-mannopyranose (25)—

Compound **25** was synthesized as described in literature.⁶⁷ ¹H NMR (600 MHz, CDCl₃) δ 7.20–7.60 (m, 15H); 5.69 (m, 1H); 5.66 (s, 1H); 5.10, 4.71 (d x2, *J* = 12.5 Hz, 2H); 5.08–5.02 (m, 2H); 4.95, 4.78 (d x2, *J* = 12.5 Hz, 2H); 4.30 (dd, *J* = 4.8, 10.3 Hz, 1H); 4.27 (dd, *J* = 9.9, 9.5 Hz, 1H); 3.87 (t, *J* = 9.9, 10.3 Hz, 1H); 3.82 (br.d, *J* = 1.1, 2.9 Hz, 1H); 3.75 (dd, *J* = 2.9, 9.9 Hz, 1H); 3.64 (t, *J* = 1.1, 7.0 Hz, 1H); 3.40 (dt, *J* = 9.5, 9.9, 4.8 Hz, 1H, H5); 2.48 (m, 1H); 2.28 (m, 1H).

1-Allyl-2,3-di-O-benzyl-4,6-O-benzylidene-1-deoxy-α-D-mannopyranose (26)—

Compound **26** was synthesized as described in literature.⁶⁷ ¹H NMR (600 MHz, CDCl₃) δ 7.10–7.60 (m, 15H); 5.65 (s, 1H); 5.60 (m, 1H); 5.02 (dd, *J* = 9.2, 1.1 Hz, 1H); 4.95 (dd, *J* = 16.9, 1.1 Hz, 1H); 4.81 (d, *J* = 12.5 Hz, 1H); 4.74 (s, 2H); 4.65 (d, *J* = 12.5 Hz, 1H); 4.27 (dd, *J* = 9.9, 9.5 Hz, 1H); 4.21 (dd, *J* = 4.8, 10.3 Hz, 1H); 4.04 (dt, *J* = 1.5, 7.7 Hz, 1H); 3.84 (dd, *J* = 3.3, 9.9 Hz, 1H); 3.83 (t, *J* = 9.9, 10.3 Hz, 1H); 3.69 (dd, *J* = 1.5, 3.3 Hz, 1H); 3.60 (dt, *J* = 9.5, 9.9, 4.8 Hz, 1H); 2.42 (m, 1H); 2.17 (m, 1H).

Methyl 6-O-(*p*-Methoxybenzyl)-2,3-di-O-methyl-α-D-glucopyranoside (28)—To a stirred solution of compound **27**⁶⁸ (6.5 g, 18.9 mmol) and NaCNBH₃ (5.97 g, 94.9 mmol) in dry THF (100 mL) was added 2 M HCl in diethyl ether at 0 °C. After 0.5 h at 0 °C, the reaction mixture was poured into an ice-cold solution of saturated aqueous NaHCO₃. The aqueous phase was extracted with EtOAc. The combined extracts were washed with saturated aqueous 1 N HCl, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude compound was purified by silica gel column chromatography, eluting with hexanes/ethyl acetate 1:1, to yield **28** (4.6g, 71%) as a colorless oil. [α]_D²² = +82.3 (*c* 1.05, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.76 (d, *J* = 3.5 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 3.67 (s, 3H), 3.64 – 3.55 (m, 3H), 3.53 (s, 3H), 3.46 – 3.41 (m, 1H), 3.38 (s, 3H), 3.37 (t, *J* = 9.4 Hz, 1H), 3.33 (s, 3H), 3.26 (br s, 1H), 3.14 (dd, *J* = 9.3, 3.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 130.0, 129.2, 113.7, 113.7, 97.3, 83.0, 81.6, 73.1, 70.5, 70.0, 69.1, 61.0, 58.4, 55.1, 55.1. HRMS (ESI) *m/z* calcd for C₁₇H₂₆O₇Na [M+Na]⁺, 365.1576; found, 365.1580.

Methyl 6-O-(*p*-Methoxybenzyl)-2,3-di-O-methyl-α-D-xylo-hexopyranosid-4-ulose (29)

—Dess-Martin periodinane (4.48 g, 10.7 mmol) was added to a mixture of alcohol **28** (2.80 g, 8.2 mmol) in anhydrous CH₂Cl₂ (94 mL) at room temperature. The reaction mixture was stirred overnight before addition of CH₂Cl₂ (80 mL) and a mixture of saturated aqueous NaHCO₃, saturated aqueous Na₂S₂O₃ and water (1:1:1, 120 mL). The reaction mixture was then stirred for another 0.5 h before the organic layer was separated. The organic layer was dried over anhydrous Na₂SO₄ and concentrated to dryness. The residue was purified over silica gel, eluting with hexanes/ethyl acetate (2:1 to 1:2), to obtain the ketone **29** (2.4 g, 85%). [α]_D²² = +71.2 (*c* 2.00, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.26 – 7.22 (m, 2H), 6.87 – 6.83 (m, 2H), 5.02 (d, *J* = 3.5 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.24 (dd, *J* = 6.2, 3.5 Hz, 1H), 4.09 (d, *J* = 10.2 Hz, 1H), 3.85 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.78 (s, 3H), 3.64 (dd, *J* = 11.0, 6.2 Hz, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 3.52 – 3.51 (m, 1H), 3.51 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 201.8, 159.2, 129.9,

129.3, 113.7, 97.6, 84.5, 82.4, 73.3, 72.6, 67.2, 60.2, 59.7, 56.1, 55.2; HRMS (ESI) m/z calcd for $C_{17}H_{24}O_7Na$ $[M+Na]^+$, 363.1420; found, 363.1415.

Methyl 4-C-Allyl-6-O-(*p*-methoxybenzyl)-2,3-di-O-methyl- α -D-galactopyranoside (30) and Methyl 4-C-Allyl-6-O-(*p*-methoxybenzyl)-2,3-di-O-methyl- α -D-glucopyranoside (31)—A freshly prepared solution of allyl magnesium chloride in THF (1 M, 30 mL, 30.0 mmol) was added to a solution of ketone **29** (2.50 g, 7.3 mmol) in anhydrous THF (36 mL) at 0 °C. Then the reaction mixture was stirred at 0 °C until the completion as indicated by TLC (50% ethyl acetate in hexane). The reaction was quenched by addition of saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness. The resultant residue (30:31 = 8:3) was purified by silica gel chromatography, eluting with hexanes/ethyl acetate (7:3 to 1:1), to give **30** (1.52 g, 54 %) and **31** (0.53 g, 19 %) as colorless oils.

(30). $[\alpha]_D^{22} = +89.6$ (c 1.50, CH_2Cl_2); 1H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 2H), 6.86 – 6.83 (m, 2H), 5.70 (ddt, $J = 17.5, 10.2, 7.5$ Hz, 1H), 5.04 (dd, $J = 10.2, 1.5$ Hz, 1H), 4.99 (dd, $J = 17.0, 1.6$ Hz, 1H), 4.87 (d, $J = 3.7$ Hz, 1H), 4.54 – 4.49 (d, $J = 11.7$ Hz, 1H), 4.44 (d, $J = 11.7$ Hz, 1H), 3.77 (s, 3H), 3.76 – 3.69 (m, 3H), 3.66 (dd, $J = 9.5, 3.7$ Hz, 1H), 3.58 (s, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 3.38 (d, $J = 9.5$ Hz, 1H), 3.16 (br s, 1H), 2.61 (dd, $J = 14.2, 7.4$ Hz, 1H), 2.14 (dd, $J = 14.2, 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 132.6, 129.6, 129.5, 118.8, 113.8, 97.6, 80.1, 79.0, 76.1, 73.3, 69.6, 68.8, 61.3, 58.8, 55.3, 55.2, 39.9; HRMS (ESI) m/z calcd for $C_{20}H_{30}O_7Na$ $[M+Na]^+$, 405.1889; found, 405.1888.

(31). $[\alpha]_D^{22} = +67.9$ (c 2.20, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 2H), 6.86 – 6.84 (m, 2H), 6.02 – 5.86 (m, 1H), 5.13 – 5.06 (m, 2H), 4.82 (d, $J = 3.7$ Hz, 1H), 4.46 (d, $J = 11.2$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 3.91 (dd, $J = 7.1, 5.2$ Hz, 1H), 3.78 (s, 3H), 3.72 (dd, $J = 9.7, 5.3$ Hz, 1H), 3.60 – 3.54 (m, 1H'), 3.58 (s, 3H), 3.47 (s, 3H), 3.46 (d, $J = 10.1$ Hz, 1H), 3.42 (s, 3H), 3.25 (dd, $J = 10.0, 3.9$ Hz, 1H), 2.90 (br s, 1H), 2.58 (dd, $J = 14.4, 6.2$ Hz, 1H), 2.31 (dd, $J = 14.5, 8.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.5, 129.8, 129.2, 118.0, 113.7, 97.2, 85.7, 80.0, 74.9, 73.0, 71.8, 68.7, 61.8, 58.8, 55.2, 55.0, 34.1; HRMS (ESI) m/z calcd for $C_{20}H_{30}O_7Na$ $[M+Na]^+$, 405.1889; found, 405.1882.

Methyl 4-C-Allyl-6-O-(*p*-methoxybenzyl)-2,3,4-tri-O-methyl- α -D-galactopyranoside (32)—To a stirred solution of alcohol **30** (1.5 g, 3.92 mmol) in dry DMF (10 mL) was added NaH (60%, 313 mg, 7.84 mmol) followed by MeI (0.49 mL, 7.84 mmol) dropwise at 0 °C (ice-water bath). The reaction mixture was stirred at 0 °C for 0.5 h before TLC (60 % ethyl acetate in hexane) showed completion. The reaction mixture was quenched with water, extracted with EtOAc, and washed with brine solution. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Column chromatography on silica gel (eluent: 40% ethyl acetate in hexane) afforded **32** (1.3 g, 84%) as a colorless oil. $[\alpha]_D^{22} = +86.9$ (c 1.40, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 2H), 6.86 – 6.84 (m, 2H), 5.80 – 5.67 (m, 1H), 5.14 – 5.04 (m, 2H), 4.89 (d, $J = 3.6$ Hz, 1H), 4.54 (d, $J = 11.7$ Hz, 1H), 4.40 (d, $J = 11.7$ Hz, 1H), 3.82 (dd, $J = 7.1, 2.8$ Hz, 1H), 3.80 – 3.75 (m, 1H), 3.77 (s, 3H), 3.68 (dd, $J = 10.0, 3.7$ Hz, 1H), 3.56 (s, 3H), 3.54 – 3.47 (m, 2H), 3.50 (s, 3H), 3.42 (s, 6H), 2.97 (dd, $J = 13.6, 7.8$ Hz, 1H), 2.15 (dd, $J = 13.6,$

7.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 159.1, 132.2, 130.3, 129.1, 119.3, 113.7, 97.4, 80.9, 80.2, 79.3, 73.0, 72.1, 68.5, 61.8, 58.6, 55.2, 52.8, 33.7; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{Na}$ $[\text{M}+\text{Na}]^+$, 419.2046; found, 419.2039.

Methyl 4-C-Allyl-6-O-(*p*-methoxybenzyl)-2,3,4-tri-O-methyl- α -D-glucopyranoside (33)—NaH (60%, 0.08 g, 1.9 mmol) followed by MeI (0.12 ml, 1.9 mmol) were added to a stirred solution of **31** (0.37 g, 1.0 mmol) in anhydrous DMF (3.4 ml) at 0 °C. The reaction mixture was stirred at room temperature for 0.5 h. The reaction was quenched with H_2O after cooling to 0 °C, and extracted with ethyl acetate, and the organic layers were washed with brine and dried over anhydrous Na_2SO_4 before evaporation to dryness. The resultant residue was purified by silica gel chromatography, eluting with hexane/ethyl acetate (9:1 to 7:3) to afford **33** (0.30 g, 80%) as a colorless oil. $[\alpha]_D^{22} = +61.4$ (c 1.0, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.26–7.21 (m, 2H), 6.89–6.83 (m, 2H), 5.94 (dddd, $J = 17.1, 10.1, 8.8, 5.2$ Hz, 1H), 5.07 (dd, $J = 17.2, 1.0$ Hz, 1H), 5.02–4.95 (m, 1H), 4.83 (d, $J = 4.0$ Hz, 1H), 4.53 (d, $J = 11.6$ Hz, 1H), 4.43 (d, $J = 11.6$ Hz, 1H), 4.04 (d, $J = 8.0$ Hz, 1H), 3.79 (s, $J = 3.8$ Hz, 3H), 3.76–3.65 (m, 2H), 3.63–3.56 (m, 4H), 3.51–3.48 (m, 3H), 3.46 (s, 3H), 3.38–3.32 (m, 4H 1H), 2.38 (dd, $J = 15.2, 8.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 135.0, 130.7, 129.1, 116.8, 113.8, 97.0, 81.4, 80.9, 78.6, 73.1, 71.3, 68.9, 60.7, 58.9, 55.4, 55.1, 50.8, 32.9; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{Na}$ $[\text{M}+\text{Na}]^+$, 419.2046; found, 419.2045.

Methyl 4-C-Allyl-2,3,4-tri-O-methyl- α -D-galactopyranoside (34)—To a stirred solution of **32** (1.2 g, 3.03 mmol) in CH_3CN (120 mL) was added a solution of CAN (8.3g, 15.13 mmol) in water (35 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 min, then diluted with CH_2Cl_2 and washed with water. The combined organic phases were dried, concentrated, and purified by silica gel column chromatography (eluent: 60% EtOAc in hexane) to give **34** (0.9 g, 80%) as a colorless oil. $[\alpha]_D^{22} = +84.0$ (c 1.85, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.73 (ddt, $J = 17.3, 10.1, 7.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.18 (dd, $J = 17.0, 1.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.15 (d, $J = 10.2, 1.2$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 4.91 (d, $J = 3.7$ Hz, 1H), 3.90 (dd, $J = 11.9, 6.3$ Hz, 1H), 3.74–3.71 (m, 1H'), 3.69 (dd, $J = 10.0, 3.7$ Hz, 1H), 3.63 (dd, $J = 6.3, 3.0$ Hz, 1H), 3.55 (s, 3H), 3.50 (s, 3H), 3.49 (d, $J = 9.8$ Hz, 1H), 3.46 (s, 3H), 3.39 (s, 3H), 3.03 (dd, $J = 13.9, 7.3$ Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.65 (d, $J = 7.3$ Hz, 1H), 2.19 (dd, $J = 13.9, 7.6$ Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$); ^{13}C NMR (150 MHz, CDCl_3) δ 131.9, 119.6, 97.8, 81.0, 80.2, 80.1, 71.7, 61.9, 61.0, 58.8, 55.3, 52.8, 33.6; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 299.1471; found, 299.1476.

Methyl 4-C-Allyl-2,3,4-tri-O-methyl- α -D-glucopyranoside (35)—A solution of CAN (2.05 g, 3.74 mmol) in H_2O (8.9 mL) was added to a mixture of **33** (0.30 g, 0.75 mmol) in CH_3CN (31.3 mL) at 0 °C, and the resulting mixture was stirred for 15 min at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with water, before it was dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude residue was purified by column chromatography over silica gel, eluting with hexane/ethyl acetate (1:1 to 1:4), to obtain alcohol **35** (0.16 g, 78%) as a colorless oil. $[\alpha]_D^{22} = +112.3$ (c 0.4, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.96 (dddd, $J = 17.2, 10.1, 8.5, 5.3$ Hz, 1H), 5.11 (dd, $J = 17.2, 1.1$ Hz, 1H), 5.03 (dd, $J = 10.1, 0.7$ Hz, 1H), 4.80 (d, $J = 4.0$ Hz, 1H), 3.89 (dd, $J = 7.8,$

4.1 Hz, 1H), 3.82 – 3.72 (m, 2H), 3.69 (d, J = 9.8 Hz, 1H), 3.59 (s, 3H), 3.49 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 3.33 (dd, J = 9.7, 4.0 Hz, 1H), 2.73 – 2.67 (m, 1H), 2.42 (dd, J = 15.3, 8.5 Hz, 1H), 2.06 (br s, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.8, 117.0, 97.2, 81.5, 81.4, 78.8, 72.0, 61.5, 60.6, 59.0, 55.3, 51.3, 32.2; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_6\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 299.1471; found, 299.1475.

Methyl 4-C-Allyl-7,8-dideoxy-2,3,4-tri-O-methyl- α -D-glycero-D-galacto-7-en-octopyranoside and Methyl 4-C-Allyl-7,8-dideoxy-2,3,4-tri-O-methyl- β -L-glycero-D-galacto-7-en-octopyranoside (38 and 39)—To a stirred solution of alcohol **34** (300 mg, 1.08 mmol) in CH_2Cl_2 (11.0 mL) was added Dess–Martin periodinane (690 mg, 1.63 mmol) at room temperature. After 2 h, the excess of oxidant was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) and saturated aqueous NaHCO_3 (15 mL). After 15 min vigorous stirring, the mixture was diluted with CH_2Cl_2 , the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated. A solution of crude aldehyde (300 mg, 1.09 mmol) in dry THF (7 mL) was treated with vinylmagnesium bromide (2.7 mL, 1 M in THF) at -78°C and stirred for 5 h before the temperature was raised to 0°C and the reaction was quenched with saturated aqueous NH_4Cl (10 mL). The reaction mixture was extracted with EtOAc, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified on silica gel column chromatography (eluent: 60% EtOAc in hexane), to give **38** and **39** (265 mg, 81%) as a mixture of diastereomers (1.5:1) as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 6.08 – 5.96 (m, 1H, minor isomer), 5.81 – 5.71 (m, 2.5H, both isomers), 5.64 – 5.57 (m, 1.5H, major isomer), 5.20 – 4.99 (m, 10H, both isomers), 4.79 (d, J = 3.6 Hz, 1.5H, major isomer), 4.73 (d, J = 3.5 Hz, 1H, minor isomer), 4.45 (d, J = 5.3 Hz, 1.5 H, major isomer), 4.29 (br s, 2.5H, both isomers), 3.60 – 3.51 (m, 3.5H, 2H minor isomer, 1H major isomer), 3.44 (s, 4.5H, major isomer), 3.43 (s, 3H, minor isomer), 3.41 (s, 4.5H, major isomer), 3.37 – 3.35 (m, 2.5H, both isomers), 3.37 (s, 4.5H, major isomer), 3.36 (s, 3H, minor isomer), 3.34 (s, 3H, minor isomer), 3.25 (s, 3H, minor isomer), 3.22 (s, 4.5H, major isomer), 3.05 (dd, J = 13.8, 6.9 Hz, 1.5H, major isomer), 2.89 (dd, J = 13.3, 8.2 Hz, 1H, minor isomer), 2.63 (br s, 1H, minor isomer), 2.37 (dd, J = 13.4, 6.2 Hz, 1H, minor isomer), 2.26 (dd, J = 13.8, 7.9 Hz, 1.5H, major isomer); ^{13}C NMR (150 MHz, CDCl_3) δ 138.8, 138.1, 133.0, 131.6, 119.7, 119.1, 115.3, 114.3, 97.6, 97.5, 81.9, 81.0, 80.7, 80.1, 79.9, 79.8, 73.7, 72.0, 71.4, 71.2, 61.8, 61.5, 58.6, 58.5, 55.2, 52.6, 52.4, 33.7, 33.3; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_6\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 325.1627; found, 325.1635.

Methyl 2,3,4-Tri-O-methyl-4,6-(prop-2-en-1,3-diyl)- β -L-glycero- α -D-galactononopyranoside (40) and Methyl 2,3,4-tri-O-methyl-4,6-(prop-2-en-1,3-diyl)- α -D-glycero- α -D-galactononopyranoside (41)—A solution of **38** and **39** (210 mg, 0.69 mmol) in anhydrous CH_2Cl_2 (42 mL) was treated with Grubbs 2nd generation catalyst (11 mg, 5% weight) and heated to reflux for 1 h. The reaction mixture was concentrated to give the crude product, which was purified by silica gel chromatography (eluent: $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 1:1) to give **40** (113 mg, 60%) and **41** (70 mg, 37%) as colorless oils.

(**40**). $[\alpha]_D^{22} = +160.9$ (c 0.55, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.67 – 5.63 (m, 1H), 5.61 – 5.58 (m, 1H), 4.92 (d, J = 3.6 Hz, 1H), 4.39 (d, J = 6.2 Hz, 1H), 3.69 (dd, J = 10.0, 3.6 Hz, 1H), 3.57 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.48 (d, J = 5.4 Hz, 3H), 3.39 (s, 3H), 3.37 (s, 3H), 3.34 (d, J = 10.0 Hz, 1H), 2.94 – 2.90 (m, 1H, H-9), 2.31 (d, J = 3.1 Hz, 1H), 2.01 – 1.96 (m, 1H, H-9'); ^{13}C NMR (150 MHz, CDCl_3) δ 129.2, 123.7, 97.9, 85.2, 79.7, 77.1, 75.7, 68.6, 62.1, 58.8, 55.2, 53.7, 28.9; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 297.1314; found, 297.1309.

(**41**). $[\alpha]_D^{22} = +35.6$ (c 1.30, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.94 (ddd, J = 9.7, 4.8, 3.1 Hz, 1H), 5.71 – 5.61 (m, 1H), 5.03 (d, J = 3.5 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.75 – 3.70 (m, 2H, O-H), 3.59 (d, J = 10.5 Hz, 1H), 3.51 (s, 3H), 3.49 (s, 3H), 3.41 (s, 3H), 3.39 (s, 3H), 3.36 (d, J = 10.2 Hz, 1H), 3.06 – 3.03 (m, 1H, H-9), 1.93 – 1.89 (m, 1H, H-9'); ^{13}C NMR (150 MHz, CDCl_3) δ 130.0, 123.2, 98.3, 85.1, 79.3, 78.1, 70.2, 65.6, 62.2, 58.9, 55.5, 53.3, 29.1; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 297.1314; found, 297.1316.

Methyl 2,3,4-Tri-O-methyl-4,6-(propan-1,3-diyl)- β -L-glycero-D-galactononopyranoside (42**)**—

A stirred solution of **40** (30 mg, 0.11 mmol) in CH_3OH (2.0 mL) was treated with 20% $\text{Pd}(\text{OH})_2/\text{C}$ (3.0 mg) at room temperature and stirred under 1 atm of H_2 (balloon) for 0.5 h. The reaction mixture was filtered through Celite and the combined filtrates were evaporated under vacuum. The crude product was purified using silica gel column chromatography (eluent: 40% EtOAc in hexane) to give **42** (30 mg, quantitative) as a colorless oil. $[\alpha]_D^{22} = +120.0$ (c 1.50, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 4.94 (d, J = 3.7 Hz, 1H), 3.87 (td, J = 10.7, 4.9 Hz, 1H), 3.67 (dd, J = 10.0, 3.7 Hz, 1H), 3.50 (s, 6H), 3.43 (s, 3H), 3.41 (s, 3H), 3.27 (d, J = 10.1 Hz, 1H), 3.25 (d, J = 9.3 Hz, 1H), 2.47 (dd, J = 14.6, 1.7 Hz, 1H, H-9), 2.27 (br s, 1H), 2.01 (d, J = 9.5 Hz, 1H), 1.58 (dd, J = 8.9, 4.8 Hz, 1H), 1.49 – 1.34 (m, 1H'), 1.32 – 1.18 (m, 1H'), 1.08 (td, J = 14.3, 4.1 Hz, 1H, H-9'); ^{13}C NMR (150 MHz, CDCl_3) δ 98.1, 85.5, 79.8, 77.8, 77.5, 68.2, 62.1, 59.0, 55.2, 52.0, 31.5, 26.7, 18.6; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 299.1471; found, 299.1465.

Methyl 2,3,4-Tri-O-methyl-4,6-(propan-1,3-diyl)- α -D-glycero-D-galactononopyranoside (43**)**—

Compound **43** (25 mg, 81%) was prepared by hydrogenation of **41** (30 mg) analogously to **42**. $[\alpha]_D^{22} = +102.5$ (c 0.95, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 4.98 (d, J = 3.7 Hz, 1H), 4.40 (d, J = 9.1 Hz, 1H), 3.97 (d, J = 4.9 Hz, 1H), 3.70 (dd, J = 10.2, 3.7 Hz, 1H), 3.50 (s, 3H), 3.49 (s, 3H), 3.47 (s, 3H), 3.42 (d, J = 3.3 Hz, 1H), 3.41 (s, 3H), 3.22 (d, J = 10.1 Hz, 1H), 2.57 (dd, J = 14.8, 2.5 Hz, 1H, H-9), 1.97 (d, J = 14.4 Hz, 1H), 1.70 – 1.58 (m, 1H), 1.48 – 1.42 (m, 2H', H-8'), 1.08 (td, J = 14.0, 3.3 Hz, 1H, H-9'); ^{13}C NMR (150 MHz, CDCl_3) δ 98.4, 85.1, 79.9, 79.6, 71.2, 68.9, 62.2, 59.0, 55.4, 52.1, 32.5, 26.7, 14.4; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 299.1471; found, 299.1472.

Methyl 2,3,4,6-Tetra-O-methyl-4,6-(propan-1,3-diyl)- β -L-glycero-D-galactononopyranoside (12**)**—

To a stirred solution of alcohol **42** (30 mg, 0.11 mmol) in dry DMF (1.0 mL) was added NaH (60%, 9 mg, 0.22 mmol) followed by MeI (14 μL , 0.22 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h before TLC (40 % ethyl acetate in hexane) showed completion. The reaction mixture was quenched with water, extracted with EtOAc, and washed with brine. The combined extracts were dried over

Na₂SO₄ and concentrated under vacuum. Column chromatography on silica gel (eluent: 30% ethyl acetate in hexane) afforded **12** (28 mg, 90%) as a colorless oil. [α]_D²² = +111.2 (*c* 1.20, CH₂Cl₂); **In CHCl₃**: ¹H NMR (600 MHz, CDCl₃) δ 4.95 (d, *J* = 3.8 Hz, 1H), 3.68 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.50 (s, 3H), 3.49 (s, 3H), 3.46 (s, 3H), 3.42 (s, 6H), 3.40 (ddd, *J* = 10.8, 9.2, 4.9 Hz, 1H), 3.36 (d, *J* = 9.2 Hz, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 2.46 (dddd, *J* = 14.6, 3.3, 2.6, 1.9 Hz, 1H, H-9eq), 2.07 (dddd, *J* = 12.9, 4.9, 3.6, 2.9, 1.9 Hz, 1H), 1.55 (dddd, *J* = 13.7, 4.4, 4.0, 2.9, 2.6 Hz, 1H), 1.38 (tddd, *J* = 13.7, 13.6, 3.6, 3.3 Hz, 1H), 1.15 (dddd, *J* = 13.6, 12.9, 10.8, 4.4 Hz, 1H), 1.02 (ddd, *J* = 14.6, 13.7, 4.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 97.7, 85.6, 79.8, 78.4, 77.5, 77.2, 62.1, 58.9, 58.7, 54.9, 51.8, 30.6, 26.5, 18.5; HRMS (ESI) *m/z* calcd for C₁₄H₂₆O₆Na [M+Na]⁺, 313.1627; found, 313.1614.

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.87 (d, *J* = 3.7 Hz, 1H), 3.78 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.60 (ddd, *J* = 10.9, 9.2, 4.8 Hz, 1H), 3.44 (d, *J* = 9.2 Hz, 1H), 3.43 (s, 3H), 3.38 (s, 3H), 3.36 (s, 3H), 3.32 (d, *J* = 10.0 Hz, 1H), 3.31 (s, 3H), 3.18 (s, 3H), 2.19 (dddd, *J* = 14.6, 3.3, 2.6, 2.1, 1H), 1.95 (dddd, *J* = 12.6, 4.8, 3.7, 2.9, 2.1 Hz, 1H), 1.23 (qdd, *J* = 13.5, 3.7, 3.4 Hz, 1H), 1.20 (dddd, *J* = 13.5, 4.5, 4.4, 2.9, 2.8 Hz, 1H), 1.12 (dddd, *J* = 13.5, 12.6, 10.9, 4.5 Hz, 1H), 0.55 (ddd, *J* = 14.6, 13.5, 4.4 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.89 (d, *J* = 3.8 Hz, 1H), 3.58 (dd, *J* = 10.1, 3.8 Hz, 1H), 3.48 (s, 6H), 3.41 (s, 3H), 3.40 (s, 3H), 3.39 (ddd, *J* = 10.8, 9.2, 4.8 Hz, 1H), 3.38 (s, 3H), 3.35 (d, *J* = 9.2 Hz, 1H), 3.24 (d, *J* = 10.1 Hz, 1H), 2.46 (dddd, *J* = 14.7, 3.3, 2.6, 2.1 Hz, 1H), 2.07 (dddd, *J* = 12.8, 4.8, 3.8, 2.9, 2.1 Hz, 1H), 1.57 (dddd, *J* = 13.7, 4.4, 4.1, 2.9, 2.6 Hz, 1H), 1.38 (qdd, *J* = 13.7, 3.8, 3.3 Hz, 1H), 1.15 (dddd, *J* = 13.7, 12.8, 10.8, 4.4 Hz, 1H), 1.11 (ddd, *J* = 14.7, 13.7, 4.1 Hz, 1H).

Methyl 2,3,4,6-Tetra-O-methyl-4,6-(propan-1,3-diyl)- α -D-glycero-D-galactononopyranoside (9)—Compound **9** (14 mg, 70%) was synthesized from **43** (20 mg) analogously to **12**. [α]_D²² = +10.4 (*c* 0.30, CH₂Cl₂); **In CHCl₃**: ¹H NMR (600 MHz, CDCl₃) δ 4.95 (d, *J* = 3.8 Hz, 1H), 3.85 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.51 (td, *J* = 3.1, 3.0, 1H), 3.50 (s, 3H), 3.48 (s, 3H), 3.44 (s, 3H), 3.41 (s, 3H), 3.40 (d, *J* = 3.1 Hz, 1H), 3.33 (s, 3H), 3.19 (d, *J* = 10.0 Hz, 1H), 2.57 (ddd, *J* = 14.7, 3.4, 3.3 Hz, 1H), 2.09 (ddt, *J* = 14.3, 3.1, 2.8 Hz, 1H), 1.64 (dddd, *J* = 14.1, 13.7, 13.5, 3.4, 2.8 Hz, 1H), 1.35 (dq, *J* = 13.5, 3.3, 2.8 Hz, 1H), 1.26 (dddd, *J* = 14.3, 14.1, 3.3, 3.1 Hz), 1.02 (ddd, *J* = 14.7, 13.7, 3.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 98.5, 86.7, 79.7, 77.3, 72.5, 62.0, 58.9, 57.9, 55.4, 51.8, 27.6, 27.3, 15.1; HRMS (ESI) *m/z* calcd for C₁₄H₂₆O₆Na [M+Na]⁺, 313.1627; found, 313.1617.

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.85 (d, *J* = 3.7 Hz, 1H), 3.88 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.53 (s, 3H), 3.49 (s, 3H), 3.48 (dt, *J* = 3.2, 3.1, 1H), 3.39 (s, 3H), 3.35 (d, *J* = 3.2 Hz, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 3.19 (s, 3H), 3.16 (s, 3H), 2.41 (ddd, *J* = 14.6, 3.4, 3.2 Hz, 1H, H-9), 1.89 (ddt, *J* = 14.3, 3.1, 2.9 Hz, 1H), 1.85 (dddt, *J* = 13.5, 13.4, 3.4, 2.9 Hz, 1H), 1.10 (dq, *J* = 13.4, 3.2, 2.9 Hz, 1H), 1.03 (dddd, *J* = 14.3, 13.5, 3.2, 3.1 Hz, 1H), 0.63 (ddd, *J* = 14.6, 13.5, 3.2 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.91 (d, *J* = 3.8 Hz, 1H), 3.64 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2), 3.51 (dt, *J* = 3.3, 3.2 Hz, 1H), 3.48 (d, *J* = 3.2 Hz, 1H), 3.48 (s, 3H), 3.47 (s, 3H), 3.40 (s, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 3.20 (d, *J* = 10.1 Hz, 1H), 2.55 (ddd, *J* = 14.7,

3.1, 2.8 Hz, 1H), 2.06 (dq, $J = 14.4, 3.3$ Hz, 1H), 1.58 (dtdd, $J = 14.0, 13.3, 3.3, 3.1$ Hz, 1H), 1.35 (dddt, $J = 13.3, 3.3, 3.0, 2.8$ Hz, 1H), 1.36 (dddd, $J = 14.4, 14.0, 3.3, 3.0$ Hz, 1H), 1.13 (ddd, 14.7, 13.3, 2.8 Hz, 1H).

Methyl 4-C-Allyl-7,8-dideoxy-2,3,4-tri-O-methyl- α -D-glycero-D-glucopyranoside (44) and Methyl 4-C-Allyl-7,8-dideoxy-2,3,4-tri-O-methyl- β -L-glycero-D-glucopyranoside (45)—A mixture of alcohol **35** (0.15 g, 0.56 mmol) and Dess-Martin Periodinane (0.36 g, 0.84 mmol) in anhydrous CH_2Cl_2 (5.7 mL) was stirred for 2.5 h before addition of CH_2Cl_2 (5.0 mL) and a mixture of saturated aqueous NaHCO_3 , saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$, and H_2O (1:1:1, 7.5 mL). The reaction mixture was stirred for another 0.5 h before the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 , and the combined organic layers were washed with brine before it was dried over anhydrous Na_2SO_4 and concentrated to dryness. The residue was dissolved in anhydrous THF (3.9 mL), cooled to 0 °C, and treated with vinyl magnesium bromide in THF (1 M, 1.4 mL, 1.4 mmol). The reaction mixture was stirred for 25 min before it was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude residue (**44**:**45** = 0.4:1.0) was then purified by column chromatography over silica gel, eluting with hexane/ethyl acetate (7:3 to 1:1), to give **44** (0.02 g, 12%) and **45** (0.08 g, 48%) as colorless oils.

(44), $[\alpha]_D^{22} = +103.6$ (c 0.4, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 6.16 – 6.08 (m, 1H), 5.98 – 5.90 (m, 1H), 5.39 (d, $J = 17.2$ Hz, 1H), 5.26 – 5.17 (m, 2H), 5.12 (d, $J = 10.2$ Hz, 1H), 4.74 (d, $J = 4.0$ Hz, 1H), 4.43 (dd, $J = 9.3, 5.6$ Hz, 1H), 3.63 (d, $J = 9.8$ Hz, 1H), 3.59 (s, 3H), 3.51 – 3.44 (m, 7H), 3.37 (s, 3H), 3.31 (dd, $J = 9.8, 4.0$ Hz, 1H), 2.87 (dd, $J = 15.3, 5.9$ Hz, 1H), 2.64 (dd, $J = 15.3, 8.1$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.5, 133.9, 118.1, 116.0, 97.0, 82.8, 81.4, 81.0, 71.6, 71.5, 60.5, 58.8, 55.5, 52.4, 31.6; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 325.1627; found, 325.1630.

(45), $[\alpha]_D^{22} = +80.5$ (c 0.6, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 6.20 – 6.10 (m, 1H), 5.99 (ddd, $J = 17.1, 10.5, 5.3$ Hz, 1H), 5.36 (dt, $J = 17.2, 1.5$ Hz, 1H), 5.20 – 5.13 (m, 2H), 5.06 (dd, $J = 10.2, 0.9$ Hz, 1H), 4.83 (d, $J = 4.0$ Hz, 1H), 4.52 – 4.46 (m, 1H), 3.66 (d, $J = 9.9$ Hz, 1H), 3.61 (d, $J = 3.4$ Hz, 1H), 3.59 (s, 3H), 3.48 (s, $J = 10.7$ Hz, 3H), 3.40 (s, $J = 4.7$ Hz, 3H), 3.38 (dd, $J = 9.9, 4.0$ Hz, 1H), 3.35 (s, 3H), 2.79 – 2.72 (m, 1H), 2.59 (dd, $J = 15.2, 8.1$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.8, 117.0, 97.2, 81.5, 81.4, 78.8, 72.0, 61.5, 60.6, 59.0, 55.3, 51.3, 32.2; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 325.1627; found, 325.1630.

Methyl 2,3,4-Tri-O-methyl-4,6-(prop-2-en-1,3-diyl)- α -D-glycero- α -D-glucopyranoside (46)—A mixture of **44** (9 mg, 0.03 mmol) and Grubbs 2nd generation catalyst (1 mg, 10% weight) in anhydrous CH_2Cl_2 (1.2 mL) was heated to reflux for 1 h before concentration. The crude residue was purified by silica gel chromatography, eluting with hexane/ethyl acetate (7:3 to 1:1), to give **46** (0.006 g, 76%) as a colorless oil. $[\alpha]_D^{22} = +80.0$ (c 0.4, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.73 – 5.64 (m, 2H), 4.86 (d, $J = 4.1$ Hz, 1H), 4.41 – 4.35 (m, 1H), 4.00 (d, $J = 4.7$ Hz, 1H), 3.70 (d, $J = 9.1$ Hz, 1H), 3.60 (s, 3H), 3.50 (s, 3H), 3.44 (s, 3H), 3.37 (s, 3H), 3.36 (dd, $J = 9.2, 4.2$ Hz, 1H), 2.35 – 2.25 (m, 2H),

2.20 – 2.14 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 128.3, 125.1, 97.4, 82.3, 77.4, 66.1, 65.0, 60.8, 59.0, 55.3, 51.1, 26.1; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 297.1314; found, 297.1318.

Methyl 2,3,4-Tri-O-methyl-4,6-(prop-2-en-1,3-diyl)- β -L-glycero- α -D-glucopyranoside (47)—Compound **47** was synthesized, by the same procedure as described for the compound **46** from diene **45** (9 mg, 0.03 mmol) and Grubbs 2nd generation catalyst (1 mg, 10% weight) in anhydrous CH_2Cl_2 (1.2 mL). After purification by silica gel column chromatography, eluting with hexane/ethyl acetate (1:1 to 2:8), **47** (0.006 g, 75%) was obtained as a colorless oil. $[\alpha]_{\text{D}}^{22} = +213.3$ (c 0.4, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 5.93 – 5.88 (m, 1H), 5.80 – 5.75 (m, 1H), 4.79 (d, $J = 4.1$ Hz, 1H), 3.91 – 3.84 (m, 2H), 3.64 (d, $J = 9.3$ Hz, 1H), 3.59 (s, 3H), 3.48 (s, 3H), 3.45 (s, 3H), 3.39 (s, 3H), 3.27 (dd, $J = 9.3, 4.1$ Hz, 1H), 2.68 (d, $J = 11.3$ Hz, 1H), 2.58 (dd, $J = 19.2, 5.5$ Hz, 1H), 2.15 – 2.08 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 127.3, 124.5, 97.2, 84.8, 82.5, 76.0, 68.8, 67.1, 60.7, 58.7, 55.4, 52.1, 23.3. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 297.1314; found, 297.1321.

Methyl 2,3,4,6-Tetra-O-methyl-4,6-(propan-1,3-diyl)- α -D-glycero-D-glucopyranoside (17)—A mixture of **46** (6 mg, 0.02 mmol) and 20% $\text{Pd}(\text{OH})_2$ (3 mg) in CH_3OH (0.4 mL) was stirred under H_2 atmosphere (1 atm) over night at room temperature, then filtered through Celite before concentration to dryness. The resultant crude compound **48** was dissolved in anhydrous DMF (0.2 mL) and cooled to 0 °C before addition of 60% NaH (0.002 g, 0.04 mmol) followed by MeI (2.6 μL , 0.04 mmol). The reaction mixture was stirred under an argon atmosphere for 2 h and cooled to 0 °C before quenching with H_2O . The reaction mixture was partitioned between ethyl acetate and H_2O , the organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 before concentration to dryness. The residue was purified by column chromatography over silica gel, eluting with hexane/ethyl acetate (7:3 to 1:1), to afford **17** (4.7 mg, 76%) as a colorless oil. $[\alpha]_{\text{D}}^{22} = +150.0$ (c 0.3, CH_2Cl_2); **In CHCl_3** : ^1H NMR (600 MHz, CDCl_3) δ 4.87 (d, $J = 3.9$ Hz, 1H), 3.96 (d, $J = 3.1$ Hz, 1H, H-5), 3.63 (d, $J = 9.5$ Hz, 1H), 3.58 (s, 3H), 3.49 (s, 3H), 3.46 (ddd, $J = 11.7, 4.4, 3.1$ Hz, 1H), 3.46 (s, 3H), 3.39 (s, 3H), 3.38 (s, 3H), 3.30 (dd, $J = 9.5, 3.9$ Hz, 1H), 1.94 (ddd, $J = 13.7, 3.4, 3.4$ Hz, 1H), 1.82 (dddd, $J = 11.9, 4.4, 3.4, 3.0$, 1H), 1.62 (dddt, $J = 12.3, 3.9, 3.6, 3.4$, 1H), 1.52 (dddd, $J = 12.8, 11.9, 11.7, 3.6$ Hz, 1H), 1.46 (dddd, $J = 13.1, 12.8, 12.3, 3.3, 3.0$ Hz, 1H), 1.39 (dddd, $J = 13.7, 13.1, 3.9$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 97.5, 82.5, 82.0, 78.3, 76.6, 66.1, 60.7, 58.9, 56.6, 55.2, 50.5, 25.1, 23.2, 19.0; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{26}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$, 313.1627; found, 313.1630.

In C_6D_6 : ^1H NMR (600 MHz, C_6D_6) δ 4.72 (d, $J = 4.0$ Hz, 1H), 4.17 (d, $J = 3.0$ Hz, 1H), 3.81 (d, $J = 9.4$ Hz, 1H), 3.59 (ddd, $J = 11.0, 5.0, 3.0$, 1H), 3.50 (s, 3H), 3.30 (s, 3H), 3.26 (dd, $J = 9.4, 4.0$ Hz, 1H), 3.23 (s, 6H), 3.17 (s, 3H), 2.20 – 2.14 (m, 1H), 1.88 – 1.80 (m, 2H), 1.54 – 1.44 (m, 3H).

In CD_3OD : ^1H NMR (600 MHz, CD_3OD) δ 4.86 (d, $J = 4.0$ Hz, 1H), 3.94 (d, $J = 3.1$ Hz, 1H), 3.54 (d, $J = 9.5$ Hz, 1H), 3.53 (s, 3H), 3.48 (ddd, $J = 11.6, 4.5, 3.1$ Hz, 1H), 3.44 (s, 3H), 3.41 (s, 3H), 3.374 (s, 3H), 3.369 (s, 3H), 3.33 (dd, $J = 9.5, 4.0$ Hz, 1H), 1.93 (br d, $J =$

14.1 Hz, 1H), 1.76 (br d, $J = 11.9$ Hz, 1H), 1.60 (br d, $J = 12.3$ Hz, 1H), 1.52 (dddd, $J = 12.7$, 11.9, 4.5, 3.4 Hz, 1H), 1.46 (dddt, $J = 12.7$, 12.6, 12.3, 3.1 Hz, 1H), 1.39 (ddd, $J = 14.1$, 12.6, 3.4 Hz, 1H).

Methyl 2,3,4,6-Tetra-O-methyl-4,6-(propan-1,3-diyl)- β -L-glycero-D-glucopyranoside (19)—A solution of **47** (0.006 g, 0.02 mmol) and 20% Pd(OH)₂ (0.003 g) in CH₃OH (0.4 mL) was stirred under H₂ atmosphere (1 atm) overnight followed by filtration through Celite and concentration to dryness. The resultant crude alcohol **49** was dissolved in anhydrous DMF (0.2 mL) and cooled to 0 °C before addition of 60% NaH (0.002 g, 0.04 mmol) followed by MeI (2.6 μ L, 0.04 mmol). The reaction mixture was then stirred under an argon atmosphere for 3 h and cooled to 0 °C before quenching with H₂O. The crude compound **19** was obtained by following the same workup as described for compound **17**. The residue was purified by column chromatography over silica gel, eluting with hexane/ethyl acetate (7:3 to 1:1), to afford **19** (5.2 mg, 78 %) as a colorless oil. $[\alpha]_D^{22} = +99.4$ (c 0.3, CH₂Cl₂); **In CHCl₃**: ¹H NMR (600 MHz, CDCl₃) δ 4.75 (d, $J = 3.8$ Hz, 1H), 3.87 (br s, 1H, H-5), 3.71 (d, $J = 9.6$ Hz, 1H), 3.58 (s, 3H), 3.49 (s, 3H), 3.41 (s, 3H), 3.39 – 3.33 (m, 6H), 3.35 (q, $J = 2.8$ Hz, 1H, H-6_{eq}), 3.25 (dd, $J = 9.6$, 3.8 Hz, 1H), 1.95 (br d, $J = 14.1$ Hz, 1H), 1.82 (dtd, $J = 14.0$, 3.3, 2.8 Hz, 1H), 1.76 (dddt, $J = 13.5$, 13.3, 13.0, 3.3 Hz, 1H), 1.50 (dddd, $J = 14.0$, 13.5, 3.6, 2.8 Hz, 1H), 1.39 (ddd, $J = 14.1$, 13.3, 3.7 Hz, 1H, H-9_{ax}), 1.33 (dddd, $J = 13.0$, 3.7, 3.6, 3.3, 3.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 97.4, 81.4, 80.9, 78.8, 76.4, 64.7, 60.9, 59.0, 57.4, 55.3, 50.6, 25.1, 25.0, 15.4; HRMS (ESI) m/z calcd for C₁₄H₂₆O₆Na [M+Na]⁺, 313.1627; found, 313.1635.

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.63 (d, $J = 3.8$ Hz, 1H), 4.15 (br s, 1H), 3.99 (d, $J = 9.6$ Hz, 1H), 3.58 (s, 3H), 3.48 (q, $J = 2.8$ Hz, 1H), 3.39 (s, 3H), 3.27 (s, 3H), 3.26 (dd, $J = 9.6$, 2.8 Hz, 1H), 3.20 (s, 3H), 3.17 (s, 3H), 2.33 (ddd, $J = 14.1$, 3.4, 3.3 Hz, 1H), 2.24 (dddd, $J = 13.9$, 13.3, 13.2, 3.3, 3.1 Hz, 1H), 1.89 (dddd, $J = 13.9$, 3.2, 3.1, 2.8 Hz, 1H), 1.70 (tdd, $J = 13.9$, 3.7, 2.8 Hz, H-7_{ax}), 1.58 (ddd, $J = 14.1$, 13.3, 3.6 Hz, 1H), 1.38 (dddd, $J = 13.2$, 3.7, 3.6, 3.4, 3.2 Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.80 (d, $J = 3.8$ Hz, 1H), 3.86 (br s, 1H), 3.64 (d, $J = 9.6$ Hz, 1H), 3.53 (s, 3H), 3.45 (s, 3H), 3.39 (s, 3H), 3.36 (q, $J = 2.7$ Hz, 1H), 3.34 (s, 3H), 3.34 (s, 3H), 3.27 (dd, $J = 9.6$, 3.8 Hz, 1H, H-2), 1.90 (dt, $J = 14.1$, 3.3 Hz, 1H), 1.78 (dtd, $J = 14.0$, 3.0, 2.7 Hz, 1H), 1.74 (dddd, $J = 13.6$, 13.3, 13.1, 3.3, 3.0 Hz, 1H), 1.55 (dddd, $J = 14.0$, 13.6, 3.8, 2.7 Hz, 1H), 1.44 (ddd, $J = 14.1$, 13.1, 3.8 Hz, 1H), 1.31 (dtdd, $J = 13.3$, 3.8, 3.3, 3.0 Hz, 1H).

Methyl 4-C-Allyl-6-O-benzyl-2,3-di-O-methyl- α -D-galactopyranoside (52) and Methyl 4-C-Allyl-6-O-benzyl-2,3-di-O-methyl- α -D-glucopyranoside (53)—A mixture of alcohol **50**^{74,84} (0.53 g, 1.70 mmol) and Dess-Martin periodinane (0.94 g, 2.21 mmol) in anhydrous CH₂Cl₂ (23.0 mL) was stirred overnight under an argon atmosphere before dilution with CH₂Cl₂ and addition of a mixture of saturated aqueous NaHCO₃, saturated aqueous Na₂S₂O₃, and H₂O (1:1:1, 60 mL). The reaction mixture was then stirred for another 0.5 h before the organic layer was separated. The organic layer was dried over anhydrous Na₂SO₄ and concentrated to dryness. The resultant crude ketone **51** was dissolved in anhydrous THF (8.0 mL) and cooled to 0 °C before a freshly prepared solution

of allyl magnesium chloride in THF (1 M, 12.0 mL, 12.00 mmol) was added. The reaction mixture was stirred for 15 min at 0 °C before it was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The combined organic layers were washed with brine, and the organic layer was dried over anhydrous Na₂SO₄ before concentration. The residue (**52**:**53** = 2.8:1) was purified by column chromatography over silica gel, eluting with hexane/ethyl acetate (7:3 to 1:1), to obtain **52** (0.36 g, 60 %) and **53** (0.13 g, 22 %) as colorless oils.

(**52**), $[\alpha]_D^{22} = +101.3$ (*c* 1.30, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.24 (m, 5H), 5.72 (ddt, *J* = 17.5, 10.1, 7.5 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.1 Hz, 1H, H-9), 5.00 (dd, *J* = 17.0, 1.3 Hz, 1H, H-9'), 4.89 (d, *J* = 3.7 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.81 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.77 (dd, *J* = 10.6, 4.9 Hz, 1H'), 3.76 – 3.73 (m, 1H), 3.66 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.59 (s, 3H), 3.49 (s, 3H), 3.41 (s, 3H), 3.40 (d, *J* = 9.2 Hz, 1H), 3.09 (s, 1H), 2.62 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.17 (dd, *J* = 14.3, 7.6 Hz, 1H'); ¹³C NMR (150 MHz, CDCl₃) δ 137.6, 132.5, 128.4, 127.8, 118.8, 97.6, 80.1, 78.9, 76.0, 73.7, 69.7, 69.1, 61.3, 58.7, 55.3, 39.9; HRMS (ESI) *m/z* calcd for C₁₉H₂₈O₆Na [M+Na]⁺, 375.1784; found, 375.1786.

(**53**), $[\alpha]_D^{22} = +85.1$ (*c* 0.85, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 5H), 6.01 – 5.90 (m, 1H), 5.16 – 5.06 (m, 2H), 4.84 (d, *J* = 3.9 Hz, 1H), 4.53 (br m, 2H), 3.99 – 3.92 (m, 1H), 3.77 (dd, *J* = 9.9, 4.8 Hz, 1H), 3.62 (dd, *J* = 9.9, 2.5 Hz, 1H), 3.60 (s, 3H), 3.49 (s, 3H), 3.48 – 3.47 (m, 1H), 3.44 (s, 3H), 3.27 (dd, *J* = 10.1, 3.9 Hz, 1H), 2.84 (br s, 1H), 2.60 (dd, *J* = 14.4, 6.2 Hz, 1H), 2.33 (dd, *J* = 14.5, 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 134.4, 128.7, 128.4, 128.0, 127.7, 127.5, 118.2, 97.2, 85.7, 80.1, 74.8, 73.3, 71.9, 69.1, 61.9, 58.8, 55.0, 34.1; HRMS (ESI) *m/z* calcd for C₁₉H₂₈O₆Na [M+Na]⁺, 375.1784; found, 375.1777.

Methyl 4-C-Allyl-6-O-benzyl-2,3,4-tri-O-methyl-α-D-galactopyranoside (54)—To a stirred solution of alcohol **52** (0.2 g, 0.56 mmol) in dry DMF (5 mL) was added NaH (60%, 0.045 g, 1.13 mmol) followed by MeI (0.24 mL, 3.84 mmol) dropwise at 0 °C (ice-water bath). The reaction mixture was stirred at 0 °C for 0.5 h before it was quenched with water (5 mL), extracted with EtOAc, and washed with brine. The combined extracts were dried over anhydrous Na₂SO₄ and concentrated under vacuum. Column chromatography on silica gel (eluent: 20% ethyl acetate in hexane) afforded **54** (0.19 g, 93%) as a colorless oil. $[\alpha]_D^{22} = +84.4$ (*c* 2.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.23 (m, 5H), 5.76 (ddt, *J* = 17.4, 10.2, 7.5 Hz, 1H), 5.15 – 5.05 (m, 2H), 4.90 (d, *J* = 3.7 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.81 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.69 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.58 – 3.56 (m, 1H), 3.57 (s, 3H), 3.53 (d, *J* = 10.1 Hz, 1H), 3.51 (s, 3H), 3.44 (s, 3H), 3.43 (s, 3H), 2.98 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.16 (dd, *J* = 13.6, 7.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 132.3, 128.3, 127.5, 119.3, 97.4, 80.9, 80.2, 79.3, 73.4, 72.2, 68.8, 61.8, 58.7, 55.2, 52.8, 33.7; HRMS (ESI) *m/z* calcd for C₂₀H₃₀O₆Na [M+Na]⁺, 389.1940; found, 389.1933.

Methyl 4-C-Allyl-6-O-benzyl-2,3,4-tri-O-methyl-α-D-glucopyranoside (55)—A solution of alcohol **53** (0.076 g, 0.22 mmol) in anhydrous DMF (0.8 mL) was cooled to 0 °C before addition of 60% NaH (0.017 g, 0.43 mmol) followed by MeI (27.0 μL, 0.43 mmol). The reaction mixture was stirred under an argon atmosphere for 0.5 h at room temperature.

The reaction mixture was cooled to 0 °C before it was quenched with H₂O and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated to dryness. The crude residue was purified by column chromatography over silica gel (eluting with hexane/ethyl acetate 9:1 to 1:1) to obtain **55** (0.068 g, 86 %) as a sticky gum. $[\alpha]_D^{22} = +71.9$ (*c* 1.1, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.24 (m, 5H), 5.94 (dddd, *J* = 17.2, 10.1, 8.8, 5.2 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 4.84 (d, *J* = 4.0 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.07 (d, *J* = 7.9 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.67 – 3.61 (m, 1H), 3.60 (s, 3H), 3.50 (s, 3H), 3.47 (s, 3H), 3.38 – 3.33 (m, 4H), 2.70 – 2.60 (m, 1H), 2.39 (dd, *J* = 15.2, 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 135.0, 128.4, 127.6, 127.4, 116.8, 97.0, 81.5, 81.0, 78.6, 73.4, 71.4, 69.2, 60.7, 58.9, 55.1, 50.8, 32.8; HRMS (ESI) *m/z* calcd for C₂₀H₃₀O₆Na [M + Na]⁺, 389.1940; found, 389.1935.

Methyl 6-O-Benzyl-4-C-(2-hydroxyethyl)-2,3,4-tri-O-methyl-α-D-galactopyranoside (56)—

Ozone was bubbled through a solution of olefin **54** (0.18 g, 0.49 mmol) in CH₂Cl₂/MeOH (30 mL/20 mL) at –78 °C until the solution turned to a persistent blue color. Ar gas was bubbled through the solution for 5 min to remove excess ozone before NaBH₄ (0.18 g, 4.90 mmol) was added at –78 °C. The reaction mixture was slowly brought to room temperature, stirred for 10 h, and concentrated under reduced pressure. The crude reaction mixture was dissolved in ethyl acetate and washed with aqueous hydrochloric acid (1 M), brine, dried over Na₂SO₄, and concentrated to dryness. Silica gel column chromatography (eluent: hexane/ethyl acetate = 3:2) afforded **56** (129 mg, 71%) as a colorless oil. $[\alpha]_D^{22} = +55.8$ (*c* 2.75, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.25 (m, 5H), 4.88 (d, *J* = 3.7 Hz, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 3.93 (t, *J* = 5.0 Hz, 1H), 3.85 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.76 – 3.66 (m, 3H), 3.57 (d, *J* = 10.6 Hz, 1H), 3.55 (s, 3H), 3.54 – 3.51 (m, 1H), 3.50 (s, 3H), 3.43 (s, 6H), 2.47 (dt, *J* = 13.8, 6.1 Hz, 1H), 2.17 (br s, 1H), 1.71 (dt, *J* = 14.3, 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 128.4, 127.8, 127.7, 97.5, 81.4, 80.0, 78.7, 73.5, 72.1, 69.3, 61.9, 58.7, 58.4, 55.3, 52.8, 31.4; HRMS (ESI) *m/z* calcd for C₁₉H₃₀O₇Na [M + Na]⁺, 393.1889; found, 393.1888.

Methyl 6-O-benzyl-4-C-(2-hydroxyethyl)-2,3,4-tri-O-methyl-α-D-glucopyranoside (57)—

A solution of alkene **55** (0.051 g, 0.14 mmol) in a 2:1 mixture of CH₂Cl₂/CH₃OH (14.2 mL) was cooled to –78 °C before being sparged with ozone until a persistent blue was color observed. The solution was then purged with argon and treated with NaBH₄ (0.053 g, 1.39 mmol) at –78 °C. The reaction mixture was then stirred at room temperature for 4 h before concentration. The crude residue was dissolved in ethyl acetate and washed with 1 N HCl. The organic layer was dried over anhydrous Na₂SO₄ and concentrated. The crude was purified using silica gel column chromatography, eluting with hexane/ethyl acetate (1:1 to 1:4), to afford **57** (0.043g, 85 %) as a colorless oil; $[\alpha]_D^{22} = +86.2$ (*c* 1.2, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.27 (m, 5H), 4.83 (d, *J* = 3.9 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.13 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.89 (d, *J* = 9.8 Hz, 1H), 3.84 – 3.76 (m, 1H), 3.73 (dd, *J* = 10.6, 1.4 Hz, 1H), 3.67 – 3.59 (m, 4H), 3.53 – 3.46 (m, 8H), 3.31 (s, 3H), 2.09 – 1.99 (m, 1H), 1.62 – 1.53 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 128.5, 127.8, 127.5, 97.2, 81.3, 78.9, 78.8, 73.6, 70.3,

68.3, 61.2, 59.2, 58.2, 55.2, 49.8, 33.9; HRMS (ESI) m/z calcd for $C_{19}H_{30}O_7Na$ $[M+Na]^+$, 393.1889; found, 393.1895.

Methyl 6-O-Benzyl-2,3,4-tri-O-methyl-4-C-(*p*-toluenesulfonyloxyethyl)- α -D-galactopyranoside (58)—To a stirred solution of alcohol **56** (0.07 g, 0.18 mmol) in pyridine (1 mL) was added tosyl chloride (0.043 g, 0.22 mmol) and DMAP (2.5 mg, 0.018 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h before TLC (40% ethyl acetate in hexane) showed completion. The reaction mixture was concentrated to dryness, and the residue was dissolved in ethyl acetate, washed with 1 N HCl, washed with brine, and dried over anhydrous Na_2SO_4 . The organic layer was concentrated under vacuum and the residue was purified by silica gel column chromatography, eluting with 40 % EtOAc in hexane, to afford **58** (65 mg, 66%) as a colorless oil. $[\alpha]_D^{22} = +55.5$ (c 1.70, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H), 7.37 – 7.24 (m, 7H), 4.84 (d, $J = 3.6$ Hz, 1H), 4.50 (d, $J = 11.9$ Hz, 1H), 4.44 (d, $J = 11.9$ Hz, 1H), 4.16 (td, $J = 9.4, 6.5$ Hz, 1H), 4.06 (td, $J = 9.5, 5.7$ Hz, 1H), 3.72 (dd, $J = 10.2, 4.4$ Hz, 1H), 3.66 – 3.60 (m, 2H), 3.52 – 3.47 (m, 1H), 3.48 (s, 3H), 3.45 (s, 3H), 3.39 (s, 3H), 3.38 (s, 3H), 3.35 (d, $J = 9.8$ Hz, 1H), 2.59 – 2.50 (m, 1H), 2.41 (s, 3H), 1.95 – 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.9, 132.8, 129.9, 128.4, 127.9, 127.6, 127.5, 97.4, 81.6, 79.8, 77.9, 73.4, 71.9, 69.0, 66.4, 61.8, 58.8, 55.4, 52.9, 28.6, 21.6; HRMS (ESI) m/z calcd for $C_{26}H_{36}O_9SNa$ $[M+Na]^+$, 547.1978; found, 547.1953.

Methyl 4-C,6-O-(Ethan-1,2-diyl)-2,3,4-tri-O-methyl- α -D-galacto-octopyranoside (13)—A solution of tosylate **58** (0.060 g, 0.011 mmol) in $CH_3OH:EtOAc$ (2 mL, 1:1) was treated with $Pd(OH)_2/C$ (20 mg, 20 wt%) and stirred under 1 atm of H_2 (balloon) for 1 h, then filtered through Celite. The combined filtrates were evaporated under vacuum to give a crude alcohol (0.05g, 0.011 mmol), which was taken up in dry DMF (1.0 mL), treated with NaH (14 mg, 0.034 mmol, 60% in oil) at 0 °C and stirred for 1 h at room temperature. The reaction mixture was poured into iced water and extracted with EtOAc. The extracts were washed with brine, dried over Na_2SO_4 , and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/hexane 5% to 20%) to afford **13** (24 mg, 80%) as a colorless oil. $[\alpha]_D^{22} = +138.9$ (c 1.10, CH_2Cl_2); In $CHCl_3$: 1H NMR (600 MHz, $CDCl_3$) δ 4.88 (d, $J = 3.8$ Hz, 1H), 3.73 (ddd, $J = 11.5, 5.0, 1.5$ Hz, 1H), 3.70 (dd, $J = 9.9, 3.8$ Hz, 1H), 3.66 (dd, $J = 9.7, 5.8$ Hz, 1H), 3.62 – 3.61 (m, 1H), 3.61 – 3.60 (m, 1H), 3.52 (s, 3H), 3.50 (s, 6H), 3.49 (ddd, $J = 12.7, 11.5, 2.1$ Hz, 1H), 3.39 (s, 3H), 3.31 (d, $J = 9.9$ Hz, 1H), 2.41 (ddd, $J = 14.8, 2.1, 1.5$ Hz, 1H), 1.45 (ddd, $J = 14.8, 12.7, 5.0$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 98.4, 85.2, 79.9, 74.2, 68.9, 64.2, 62.9, 62.1, 58.9, 55.3, 52.2, 27.9; HRMS (ESI) m/z calcd for $C_{12}H_{22}O_6Na$ $[M+Na]^+$, 285.1314; found, 285.1323.

In C_6D_6 : 1H NMR (600 MHz, C_6D_6) δ 4.75 (d, $J = 3.7$ Hz, 1H), 3.93 (dd, $J = 10.5, 10.0$ Hz, 1H), 3.80 (dd, $J = 10.0, 4.8$ Hz, 1H), 3.77 (dd, $J = 10.0, 3.7$ Hz, 1H), 3.73 (dd, $J = 10.5, 4.8$ Hz, 1H), 3.52 (ddd, $J = 11.4, 5.0, 1.4$ Hz, 1H), 3.38 (ddd, $J = 12.6, 11.4, 2.1$ Hz, 1H), 3.37 (s, 3H), 3.33 (d, $J = 10.0$ Hz, 1H), 3.32 (s, 3H), 3.14 (s, 3H), 3.08 (s, 3H), 2.01 (ddd, $J = 14.7, 2.1, 1.4$ Hz, 1H), 1.07 (ddd, $J = 14.7, 12.6, 5.0$ Hz, 1H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.86 (d, *J* = 3.8 Hz, 1H), 3.71 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H, 7eq), 3.66–3.62 (m, 1H), 3.62 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.55 – 3.53 (m, 2H), 3.51 (s, 3H), 3.47 (ddd, *J* = 12.7, 11.5, 2.1 Hz, 1H), 3.49 (s, 3H), 3.47 (s, 3H), 3.37 (s, 3H), 3.31 (d, *J* = 10.0 Hz, 1H), 2.44 (ddd, *J* = 14.9, 2.1, 1.5 Hz, 1H), 1.49 (ddd, *J* = 14.9, 12.7, 5.0 Hz, 1H).

Methyl 4-C,6-O-(Ethan-1,2-diyl)-2,3,4-tri-O-methyl-α-D-glucopyranoside (15) and Methyl 6-O-Benzyl-3-O,4-C-(ethan-1,2-diyl)-2,4-di-O-methyl-α-D-glucopyranoside (61)—Compound **57** (7.2 mg, 0.019 mmol) was dissolved in anhydrous pyridine (0.2 mL) and cooled to 0 °C before addition of MsCl (1.9 μL, 0.024 mmol). The reaction mixture was stirred for 1.5 h at 0 °C before it was diluted with ethyl acetate and washed with H₂O. The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated to dryness. The resultant residue and 20% Pd(OH)₂ (3 mg) were stirred in a 1:1 mixture of CH₂Cl₂/CH₃OH (0.3 mL) under 1 atm of H₂ atmosphere for 6 h. The reaction mixture was filtered through Celite and concentrated to dryness. The residue was purified by column chromatography, eluting with hexane/ethyl acetate (7:3 to 1:1), to obtain **15** (0.0011 g, 21%) and **61** (0.0012 g, 23%) as colorless oils.

(15). [α]_D²² = +72.0 (*c* 0.2, CH₂Cl₂); **In CHCl₃:** ¹H NMR (600 MHz, CDCl₃) δ 4.87 (d, *J* = 3.8 Hz, 1H), 3.83 (dd, *J* = 12.4, 1.7 Hz, 1H), 3.80 (dt, *J* = 11.2, 3.2 Hz, 1H), 3.76 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.68 (d, *J* = 9.5 Hz, 1H), 3.66 – 3.62 (m, 1H), 3.59 (s, 3H), 3.52 (br s, 1H), 3.50 (s, 3H), 3.42 (s, 3H), 3.40 (s, 3H), 3.34 (dd, *J* = 9.5, 3.8 Hz, 1H), 1.89 – 1.86 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 97.7, 81.9, 81.3, 73.8, 66.2, 65.2, 63.3, 60.6, 58.9, 55.4, 50.6, 25.3; HRMS (ESI) *m/z* calcd for C₁₂H₂₂O₆Na [M+Na]⁺, 285.1314; found, 285.1325.

In C₆D₆: ¹H NMR (600 MHz, C₆D₆) δ 4.68 (d, *J* = 3.7 Hz, 1H), 3.90 – 3.89 (m, 2H), 3.81 (d, *J* = 9.5 Hz, 1H), 3.80 (dt, *J* = 11.0, 3.5 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.50 (br s, 1H), 3.47 (s, 3H), 3.25 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.15 (s, 6H), 3.08 (s, 3H), 1.98 – 1.95 (m, 2H).

In CD₃OD: ¹H NMR (600 MHz, CD₃OD) δ 4.86 (d, *J* = 3.8, 1H), 3.80 (dd, *J* = 12.4, 1.7 Hz, 1H), 3.71 (dt, *J* = 11.3, 3.6 Hz, 1H), 3.67 (dd, *J* = 12.4, 1.6, 1H), 3.65 – 3.63 (m, 1H), 3.61 (d, *J* = 9.5 Hz, 1H), 3.54 (s, 3H), 3.52 (br s, 1H), 3.46 (s, 3H), 3.39 (s, 3H), 3.38 (s, 3H), 3.33 (dd, *J* = 9.5, 3.8 Hz, 1H), 1.85 – 1.82 (m, 2H).

(61). [α]_D²² = +74.0 (*c* 0.3, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 5H), 4.84 (d, *J* = 3.7 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.36 (d, *J* = 8.1 Hz, 1H), 4.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.04 – 3.98 (m, 2H), 3.81 (dd, *J* = 10.7, 2.0 Hz, 1H), 3.60 – 3.57 (m, 1H), 3.54 (s, 3H), 3.49 (s, 3H), 3.30 (s, 3H), 3.12 (dd, *J* = 8.2, 3.7 Hz, 1H), 2.16 (dt, *J* = 13.1, 9.9 Hz, 1H), 1.78 (ddd, *J* = 13.3, 5.8, 3.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 138.4, 129.7, 128.6, 128.5, 127.7, 127.6, 97.4, 83.1, 79.8, 79.2, 73.6, 69.3, 66.6, 66.0, 58.9, 55.6, 51.2, 31.9; HRMS (ESI) *m/z* calcd for C₁₈H₂₆O₆Na [M+Na]⁺, 361.1627; found, 361.1627.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Staggered Conformations of the Hexopyranose Side Chain Illustrated for Methyl α -D-Glucopyranoside, and the Associated Limiting Coupling Constants.

Figure 2. 1,5-Anhydroalditols and Other Models for the *gg*, *gt*, and *tg* Conformers (Numbers in bold colors refer to the hydrogens modeled in the hexopyranose side chain).^{39,49,55}

Galactose **9**, galacto gg **10**, galacto gg **11**, galacto gt **12**, galacto gt **13**, galacto tg **14**, galacto tg**Glucose** **15**, gluco gg **16**, gluco gg **17**, gluco gt **18**, gluco gt **19**, gluco tg **20**, gluco tg**Figure 3.**

Oxa-, Dioxo-, and Trioxadecalins for the Determination of Limiting $^3J_{H,H}$ Coupling Constants About the C5–C6 bond in Galacto- and Glucopyranosides (Numbers in bold colors refer to the hydrogens modeled in the hexopyranose side chain).

Figure 4. Further Bicyclic Model Systems for Comparison of Coupling Constants Between Tri- and Tetrasubstituted Systems (Numbers in bold colors refer to the hydrogens modeled in the hexopyranose side chain).

$$^3J(\text{H}^{7\text{ax}}, \text{H}^{8\text{ax}}) = 13.5\text{--}14.1 \text{ Hz}$$

$$^3J(\text{H}^{8\text{ax}}, \text{H}^{9\text{ax}}) = 13.3\text{--}13.5 \text{ Hz}$$

$$^3J(\text{H}^{7\text{ax}}, \text{H}^{8\text{ax}}) = 13.5\text{--}13.9 \text{ Hz}$$

$$^3J(\text{H}^{8\text{ax}}, \text{H}^{9\text{ax}}) = 13.1\text{--}13.3 \text{ Hz}$$

Figure 5.
Selected nOe Interactions and Coupling Constants (Mean values across the three solvents employed) Diagnostic of Chair-Chair-like Conformations for **9** and **19**.

$$\begin{aligned} {}^3J_{\text{H}1\text{e},\text{H}2} &= 5.7 \text{ Hz}, & {}^3J_{\text{H}1\text{a},\text{H}2} &= 10.5 \text{ Hz} \\ {}^3J_{\text{H}5,\text{H}6\text{R}} &= 5.0 \text{ Hz}, & {}^3J_{\text{H}5,\text{H}6\text{S}} &= 10.2 \text{ Hz} \end{aligned}$$

Figure 6. Comparison of ${}^3J_{\text{H,H}}$ Coupling Constants in the 4,6-*O*-Benzylidene Protected 1,5-Anhydrohexitol **21**.

Figure 7.

The Staggered Conformations of the C5–C6 Bonds in the Bicyclic Models **9–20** and other 4,6-*O*-Acetals, the C2–C1 Bonds in the 1,5-Anhydrohexitols, and the C1–C2 Bonds in the 1,4-Dioxanes **5**, **62** and **63**. In the Tetrasubstituted Stereodiads R' is an Alkyl Group, whereas in the Trisubstituted Systems it is a Hydrogen Atom.

62: $J_{a,e'} = 3.2$ Hz

63: $J_{a,a'} = 8.5$ Hz

Figure 8.
cis- and *trans*-2,3-Dimethyl-1,4-dioxanes **62** and **63**.

Scheme 1.
 Synthesis of the Bicyclic Pyranosides **9**, **12**, **17**, and **19**.

Scheme 2.

Synthesis of the Bicyclic Pyranosides **13** and **15** and the Dioxahydrindane Derivative **61**.

Table 1

$^5\text{H}^{\text{C}}\text{H}^{\text{O}^{\text{R}}}$ Coupling constants for *gg* conformers

Entry	Cmpd (bond) ^a	Config	Ring fusion	C6 Subst	Correction (Hz) ^b	Experimental and (corrected) ³ J _{H5,H6} values (Hz)			Comment ^c
						C ₆ D ₆	CDCl ₃	CD ₃ OD	
H ⁵ ,H ^{6R}									
1	10	galacto	cis	CH ₂	na	1.9	1.8	1.7	exclude
2	15	gluco	cis	CH ₂	na	1.7	1.7	1.7	exclude
3	24 (C1,C2)	-	-	CH ₂	na	nd	1.1	nd	include
4	1 (C1,C2)	-	-	CH ₂	na	0.9 ^d			include
5	4	galacto	cis	CH ₂	na	1.8 ^d			exclude
6	7	gluco	-	CH ₂	na	5.4			exclude
H ⁵ ,H ^{6S}									
7	9	galacto	trans	CH	-0.5	3.2 (2.7)	3.0 (2.5)	3.2 (2.7)	exclude
8	10	galacto	cis	CH ₂	na	1.6	1.8	1.6	exclude
9	16	gluco	trans	CH	-0.5	2.6 (2.1)	2.6 (2.1)	2.6 (2.1)	include
10	15	gluco	cis	CH ₂	na	1.6	1.6	1.6	exclude
11	24	-	-	CH ₂	na	nd	2.2	nd	include
12	1 (C1,C2)	-	-	CH ₂	na	2.2 ^d			include
13	4	-	cis	CH ₂	na	1.8 ^d			exclude
14	7	gluco	-	CH ₂	na	1.2			exclude

^aUnless otherwise stated the C5–C6 bond is considered.

^bCorrection factor for the presence of the additional CC bond per Table 5 and text.

^cCompounds are either excluded or included from further consideration as valid models as discussed in the text.

^dMeasured in D₂O

Table 2

Coupling constants for *g* and *g* conformers

Entry	Cmpd (bond) ^a	Config	Ring fusion	C6 Subst	Correction (Hz) ^b	Experimental and (corrected) ³ J _{H5,H6} values (Hz)			Comment ^c
						C ₆ D ₆	CDCl ₃	CD ₃ OD	
H ⁵ ,H ^{6R}									
1	12	galacto	trans	CH	+2.0	9.2 (11.2)	9.2 (11.2)	9.2 (11.2)	include
2	18	gluco	trans	CH	+2.0	9.2 (11.2)	9.0 (11.0)	9.2 (11.2)	include
3	5 (C1,C2)	-	-	CH ₂	na	10.7 ^d			include
4	8	gluco	-	CH ₂		9.5			exclude
H ⁵ ,H ^{6S}									
5	11	galacto	cis	CH	-0.5	3.2 (2.7)	3.2 (2.7)	3.1 (2.6)	include
6	17	gluco	cis	CH	-0.5	3.0 (2.5)	3.1 (2.6)	3.1 (2.6)	include
7	5 (C1,C2)	-	-	CH ₂	na	2.5 ^d			include
8	8	gluco		CH ₂	na	1.5			exclude

^a Unless otherwise stated the C5–C6 bond is considered.^b Correction factor for the presence of the additional CC bond per Table 5 and text.^c Compounds are either excluded or included from further consideration as valid models as discussed in the text.^d Measured in D₂O

Table 3

$^5\text{H}_\text{C}$, $^5\text{H}_\text{C}^{\text{OR}}$ Coupling constants for *tg* conformers

Entry	Cmpd (bond) ^a	Config	Ring fusion	C6 Subst	Correction (Hz) ^b	Experimental and (corrected) ³ J _{H5,H6} values (Hz)			Comment ^c
						C ₆ D ₆	CDCl ₃	CD ₃ OD	
H ⁵ ,H ^{6R}									
1	13	galacto	trans	CH ₂	na	4.8	4.4	4.7	include
2	14	galacto	cis	CH	0	3.0	3.1	3.1	exclude
3	19	gluco	cis	CH	0	2.8	2.8	2.7	exclude
4	20	gluco	trans	CH ₂	na	4.9	4.7	4.7	include
5	21 (C1,C2)	-	trans	CH ₂	na	5.7	5.7	5.6	exclude
6	2	-	-	CH ₂	na	5.5 ^d			exclude
7	3	-	-	CH ₂	na	5.6 ^d			exclude
8	6	gluco	trans	CH ₂	na	5.0 ^d			include
9	21 (C5,C6)	gluco	trans	CH ₂	na	5.0	5.0	5.0	include
H ⁵ ,H ^{6S}									
10	13	galacto	trans	CH ₂	na	10.5	10.1	10.3	include
11	20	gluco	trans	CH ₂	na	10.3	10.1	10.2	include
12	21 (C1,C2)	-	trans	CH ₂	na	10.6	10.5	10.5	exclude
13	2	-	-	CH ₂	na	10.8 ^d			exclude
14	3	-	-	CH ₂	na	~10 ^d			exclude
15	6	gluco	trans	CH ₂	na	~10.3 ^d			include
16	21 (C5,C6)	gluco	trans	CH ₂	na	10.2	10.2	10.2	include

^a Unless otherwise stated the C5–C6 bond is considered.

^b Correction factor for the presence of the additional CC bond per Table 5 and text.

^c Compounds are either excluded or included from further consideration as valid models as discussed in the text.

^d Measured in D₂O

Table 4

Assignment of Compounds According to Newman Projections I–VI.

Entry	cmpd	bond	config	projection
1	6, 13, 20, 21, 24	5-6	-	I (and IV)
2	<i>ent-2, ent-3, ent-21</i>	2-1	-	I (and IV)
3	<i>ent-22</i>	2-1	<i>erythro</i>	I
4	4, 10, 15	5-6	-	II (and V)
5	9, 16	5-6	<i>erythro</i>	II
6	1, 24	2-1	-	II (and V)
7	26	2-1	<i>erythro</i>	II
8	5	1-2	-	III (and VI)
9	<i>ent-9, ent-16</i>	6-5	<i>erythro</i>	III
10	11, 17	5-6	<i>erythro</i>	III
11	62	1-2	<i>erythro</i>	III
12	14, 19	5-6	<i>threo</i>	IV
13	<i>ent-23</i>	2-1	<i>threo</i>	IV
14	25	2-1	<i>threo</i>	V
15	12, 18	5-6	<i>threo</i>	VI
16	63	1-2	<i>threo</i>	VI

Table 5

Derivation of Correction Factors for Use with Tetrasubstituted Models

Config	Project	Type	Correction Derivation		Correction (Hz) ^a	Relevant Models
			Trisubs cmpd, <i>J</i> (Hz)	Tetrasubs cmpd, <i>J</i> (Hz)		
<i>erythro</i>	I	(a,a)	21, 10.5	22, 9.6	+1.0	-
<i>erythro</i>	II	(e,e)	24, 2.2	26, 1.5	+0.5	-
<i>erythro</i>	III	(a,e)	5, 2.5	62, 3.2	-0.5	9, 11, 16, 17
<i>threo</i>	IV	(a,e)	21, 5.7	23, 5.8	0	14, 19
<i>threo</i>	V	(a,e)	24, 1.1	25, 1.1	0	-
<i>threo</i>	VI	(a,a)	5, 10.7	63, 8.5	+2.0	12, 18

^aCorrections are rounded to the nearest 0.5 Hz.

Table 6

Recommended and Literature Limiting Coupling Constants.

Entry	Source	$^3J_{\text{H5,H6R}}$			$^3J_{\text{H5,H6S}}$		
		<i>gg</i>	<i>gt</i>	<i>tg</i>	<i>gg</i>	<i>gt</i>	<i>tg</i>
1	This work	1.0	11.0	4.8	2.2	2.5	10.2
2	Haasnoot–Altona ⁴⁷	0.9	10.7	5.0	2.8	3.1	10.7
3	Bock-Duus ³⁹	0.9	10.7	5.5	2.2	2.5	10.7
4	Serianni (expt) ⁴⁹	1.8	10.7	5.0	1.8	2.5	10.3
5	Serianni (calc) ⁴⁹	0.8	9.9	4.5	1.3	1.5	10.8
6	Nishida ⁵⁴	1.7	10.8	4.1	2.2	2.4	11.1

Table 7

Calculated Side Chain Populations.

Entry	Source	Me α -D-Glc ^d		Me β -D-Glc ^d		Me β -D-Gal ^d	
		gg	gt	gg	gt	gg	gt
1	This work	54	45	1	48	50	2
2	Haasnoot–Altona ⁴⁷	57	50	-7	50	56	-6
3	Bock-Duus ³⁹	53	47	1	46	52	2
4	Seriani (expt) ⁴⁹	56	40	4	49	47	4
5	Seriani (calc) ⁴⁹	42	47	11	35	54	12
6	Nishida ⁵⁴	57	41	1	50	48	2

^dPopulations calculated using the experimental coupling constants of Bock and Duus;³⁹ Me α -D-Glc, $^3J_{H5,H6R} = 5.5$ Hz, $^3J_{H5,H6S} = 2.4$ Hz; Me β -D-Glc, $^3J_{H5,H6R} = 6.1$ Hz, $^3J_{H5,H6S} = 2.5$ Hz; Me β -D-Gal, $^3J_{H5,H6R} = 7.5$ Hz, $^3J_{H5,H6S} = 4.8$ Hz.