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Influence of Configuration at the 4- and 6-Positions on the Conformation and Anomeric Reactivity and Selectivity of 7-Deoxyheptopyranosyl Donors: Discovery of a Highly Equatorially Selective L-*glycero*-D-*gluco*-Heptopyranosyl Donor

Kapil Upadhyaya, Rahul S. Bagul, and David Crich*

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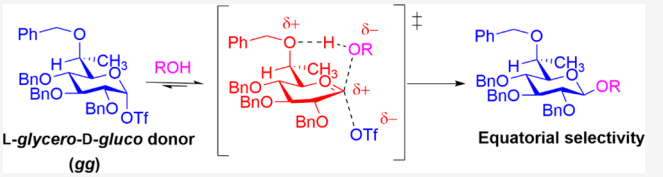
ABSTRACT: The preparation of four per-*O*-benzyl-D- or L-*glycero*-D-*galacto* and D- or L-*glycero*-D-*gluco* heptopyranosyl sulfoxides and the influence of their side-chain conformations on reactivity and stereoselectivity in glycosylation reactions are described. The side-chain conformation in these donors is determined by the relative configuration of its point of attachment to the pyranoside ring and the two flanking centers in agreement with a recent model. In the D- and L-*glycero*-D-*galacto* glycosyl donors, the D-*glycero*-D-*galacto* isomer with the more electron-withdrawing *trans*,*gauche* conformation of its side chain was the more equatorially selective isomer. In the D- and L-*glycero*-D-*gluco* glycosyl donors, the L-*glycero*-D-*gluco* isomer with the least disarming *gauche*,*gauche* side-chain conformation was the most equatorially selective donor. Variable temperature NMR studies, while supporting the formation of intermediate glycosyl triflates at −80 °C in all cases, were inconclusive owing to a change in the decomposition mechanism with the change in configuration. It is suggested that the equatorial selectivity of the L-*glycero*-D-*gluco* isomer arises from H-bonding between the glycosyl acceptor and O6 of the donor, which is poised to deliver the acceptor antiperiplanar to the glycosyl triflate, resulting in a high degree of S_N2 character in the displacement reaction.



INTRODUCTION

Oligosaccharides are important structural motifs in many biological systems and are involved in a vast array of biological processes,[1] and consequently, the construction of glycosidic bonds in an efficient and stereocontrolled manner is of great interest and importance to glycobiology.[2] Most glycosylation reactions, however, occur at the boundary between S_N1 and S_N2 processes, which makes stereoselective glycosylation a complex and sometimes unpredictable task, necessitating further study of the numerous factors affecting selectivity.[3]

In recent years, it has become increasingly apparent that the conformation of the side chain of glycosyl donors contributes significantly to their reactivity and selectivity, with the initial ground rules determined using conformationally locked bicyclic donors.[4−6] More recently, we have demonstrated by the study of a series of sialic acid and Kdo donors isomeric at the 5- and/or 7-positions that side-chain conformation also contributes to reactivity and selectivity in monocyclic donors (Figure 1).[7−10] Finally, recent studies have highlighted the role of side-chain conformation in glycan recognition and as a contributing factor to catalysis by the glycosyl hydrolases, glycosyltransferases, transglycosidases, and glycoside phosphorylases during enzymatic cleavage and the formation of glycosidic bonds.[11]

We define the three staggered conformations of the exocyclic bond to the side chain (hereinafter the side-chain conformation) as being either *gauche*,*gauche* (*gg*), *gauche*,*trans* (*gt*), or *trans*,*gauche* (*tg*) (Figures 1 and 2), where the first and second terms refer to the position of the C6−O6 bond relative to C5−O5 and C5−C4 bonds, respectively.[12−14] As first determined by Marchessault and Perez on the basis of analysis of crystal structure databases[15] and subsequently by many groups using NMR spectroscopy, conformationally mobile glucopyranosides can typically be considered as an ∼50:50 equilibrating mixture of *gg* and *gt* conformers, while the isomeric galactopyranosides can populate an ∼15:55:30 *gg*/*gt*/*tg* mixture (Figure 2).[12−14,16]

Our studies with the 5- and/or 7-*epi*-sialic acid and Kdo series (Figure 1) revealed that the conformational space available to the side chains of higher carbon sugars (here defined as those with a longer side chain than the hydroxymethyl group of typical hexopyranosides) is signifi-

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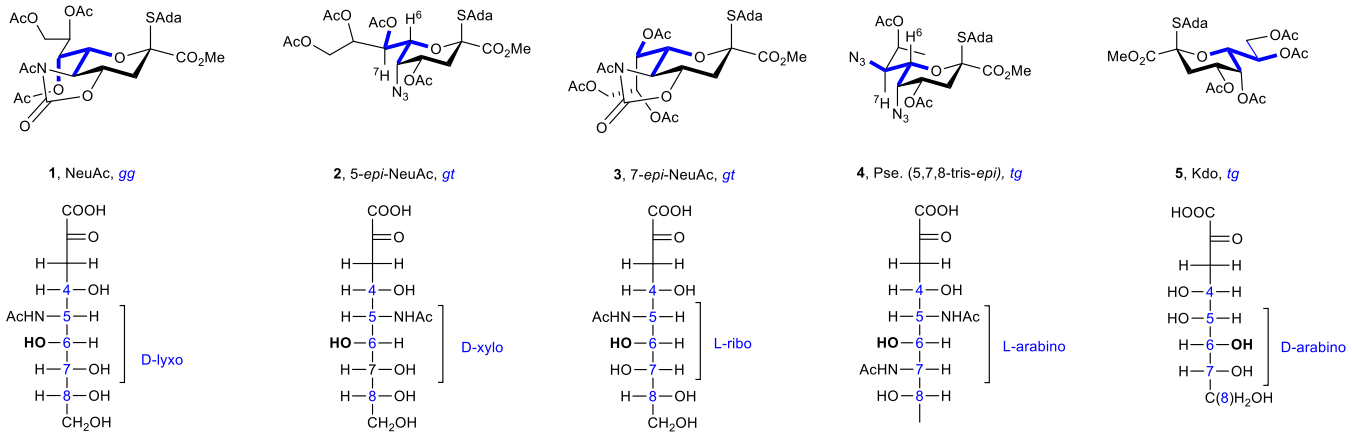

Figure 1. Predominant side-chain conformation of glycosyl donors in the neuraminic acid and ulosonic series and their relative configurations from C5−C7, as depicted on Fischer projection formulas of the parent sugar.

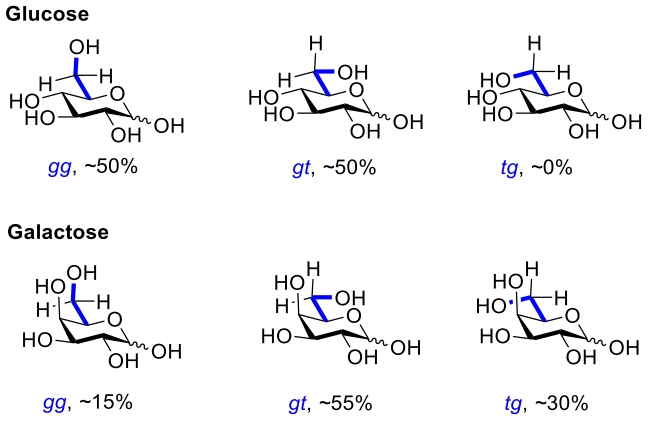

Figure 2. Staggered conformation of the hexopyranose side chain illustrated for D-glucose and D-galactose and their relative populations in free solution.

cantly restricted by the presence of the extra C−C bond that extends the side chain and that the predominant conformation of these higher carbon sugar side chains is controlled by the relative configurations of the stereogenic center at the point of attachment of the side chain to the pyranose ring and by the two flanking centers, that is, by a simple stereotriad comprising C5, C6, and C7 in the sialic acids.[17] On this basis and comparison with the solution- and crystal-phase conformations of the four pentitol sugars, we devised a simple model whereby the arabino configuration of the three centers in question leads to the predominant *tg* conformation of the side chain, while the lyxo configuration results in the predominant population of the *gg* conformation. The ribo and xylo configurations, on the other hand, result in the predominant population of the two *gt* conformations (Figure 1).[17]

In spite of the patterns evident in our studies on the influence of configuration and conformation of sialic acid side chains on reactivity and selectivity at the anomeric center, comparisons were marred to some extent by the different protecting groups employed, which in turn was a function of the complex synthesis required to access the donors in some series. Seeking to generalize the models and standardize them to other higher carbon sugars, we set out to construct and analyze a series of four 7-deoxyheptopyranosyl donors differing in configurations at the 4- and 6-positions, that is,

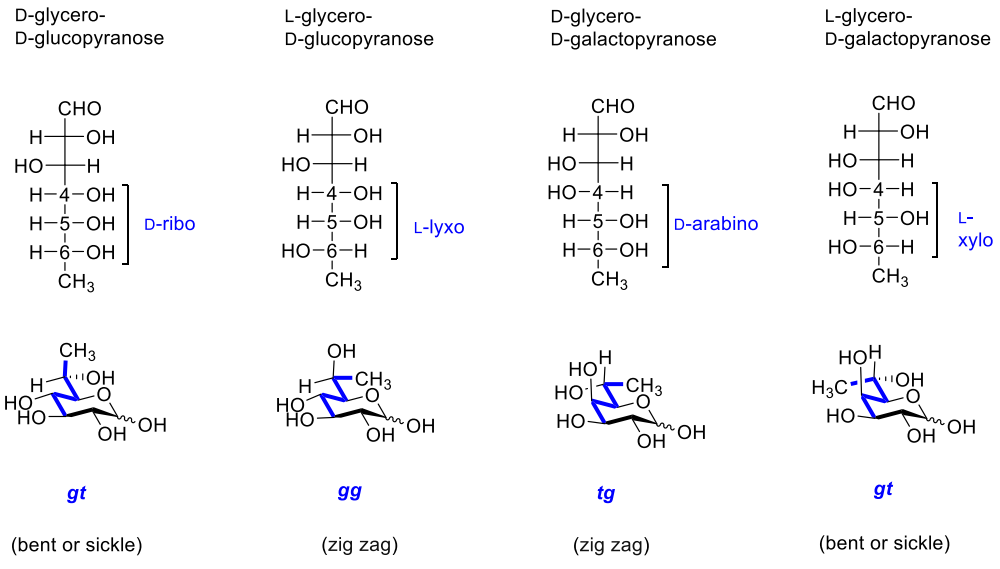

Figure 3. D- and L-*glycero*-D-*gluco* and D- and L-*glycero*-D-*galacto* heptopyranoses and the predicted conformations of their exocyclic bonds.

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comprising the arabino, lyxo, ribo, and xylo configurations of the three contiguous stereogenic centers thought to control side-chain conformation, and all carrying the same suite of protecting groups. We report here on the synthesis and conformational analysis of this series of four such donors (Figure 3) and confirm the predictions of side-chain conformation from our model. Based on a comparative study of the same four donors with a standard series of acceptor alcohols, we determine that the D-*glycero*-D-*galacto* and L-*glycero*-D-*galacto* donors conform to expectation with the former isomer having the *tg* conformation of its side chain being more equatorially selective than the latter with its *gt* side-chain conformation. Unexpectedly, however, the model fails with regard to selectivity in the D- and L-*glycero*-D-*gluco* series where the L-*glycero*-D-*gluco*-configured donors exhibit unanticipatedly high equatorial selectivity despite the *gg* conformation of its side chain. This unexpected and novel selectivity, which reveals the pitfalls in extrapolation from one series (Figure 1) of donors to another (Figure 3), appears to arise from donor−acceptor hydrogen bonding involving the benzyl ether at the 6-position of the L-*glycero*-D-*gluco* configured donor and potentially opens the way for the design of further series of selective glycosyl donors.

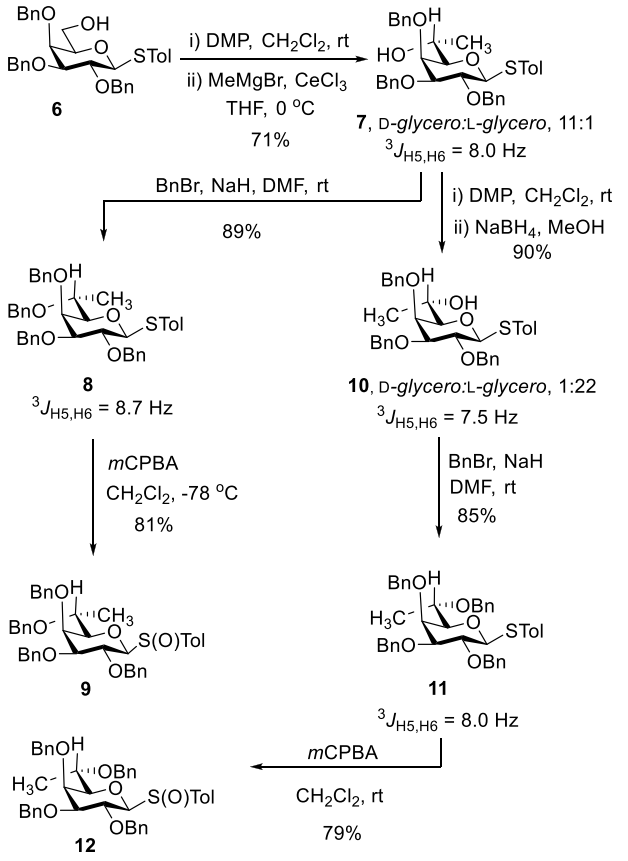
RESULTS AND DISCUSSION

Donor Synthesis. Intermediate **6** was obtained from penta-*O*-acetyl-*β*-D-galactopyranose by the literature protocol.[18] Dess−Martin periodinane oxidation to give the corresponding aldehyde followed by treatment with MeMgBr at −78 °C gave a complex reaction mixture from which only 16% of the desired product could be isolated. In contrast, reaction with the less basic methylcerium reagent, derived by reaction of MeMgBr with cerium chloride,[19] afforded the required *C*-6-methyl-substituted compound **7** in 71% yield and as a 11:1 mixture of diastereomers. After protection of the so-formed alcohol as the benzyl ether **8** in 89% yield, oxidation with *m*CPBA afforded the corresponding sulfoxide (**9**) as a mixture of two stereoisomers in 81% yield. The donor **12**, epimeric with **9** at the 6-postion, was obtained from **7** by Dess−Martin oxidation followed by sodium borohydride reduction, giving **10** in 90% yield as a 1:22 mixture of isomers. Subsequent benzylation and *m*CPBA oxidation then afforded the sulfoxide **12** in 79% yield as a mixture of isomers (Scheme 1).

The D-*glycero*-D-*gluco*- and L-*glycero*-D-*gluco*-configured donors were obtained analogously from **13**, which was obtained by the literature protocol.[20] Thus, oxidation of **13** employing the Dess−Martin periodinane followed by immediate treatment with methyl magnesium chloride in THF furnished the *C*6-methyl-substituted products **14** and **15** in a 3:1 ratio. Protection of the remaining hydroxyl group as the benzyl ether resulted in the thiogycosides **16** and **18**, which were subjected to standard *m*CPBA oxidation conditions to afford sulfoxides **17** and **19** in good yield (Scheme 2).

The configuration at C6 of the donors **9**, **12**, **17**, and **19** was assigned as described in Supporting Information by conversion to a set of rigid bicyclic congeners carrying the 4,6-*O*-benzylidene protecting group (Schemes S1 and S2) and analysis of their NOE and ROE spectra, and $^3J_{H5,H6}$ coupling constants, in the usual manner (Figures S1 and S2). The reversal of stereoselectivity observed in the Grignard

Scheme 1. Synthesis of 7-Deoxy-D-*glycero*-D-galactoheptopyranose and 7-Deoxy-L-*glycero*-D-galactoheptopyranose Donors 9 and 12



additions in going from the galactose to the glucose series (Schemes 1 and 2) is consistent with literature observations and the changes from a chelation model involving O4 in the galactose series to the one invoking the ring oxygen in the glucose series.[21,22]

Side-Chain Conformation. Side-chain conformations were determined at the level of the 6-hydroxy thioglycosides before final benzylation and conversion to the ultimate sulfoxides, because of the less complex nature of the NMR spectra, by a combination of coupling constant analysis and NOE measurements (Figure 4). Thus, the D-*glycero*-D-*galacto* system **7** displayed a $^3J_{H5,H6}$ of 8.0 Hz and an NOE interaction between H_5 and the terminal methyl group consistent with the very predominant population of the *tg* conformation. The L-*glycero*-D-galacto thioglycoside **10**, on the other hand, had a $^3J_{H5,H6}$ of 7.5 Hz and an NOE interaction between H_4 and the methyl group, indicative of a dominant *gt* conformation. In the D-*gluco* series, the D-*glycero* isomer **15** had an NOE interaction between the methyl group and H_4 and a $^3J_{H5,H6}$ of 3.9 Hz consistent with the *gt* conformation, while the L-*glycero* isomer **14** had an NOE interaction between the methyl group and H_5 and a $^3J_{H5,H6}$ of 1.6 Hz indicative of the *gg* conformation. While the magnitudes of $^3J_{H5,H6}$ in **7** and **10** at first sight appear small for a pair of antiperiplanar vicinal hydrogens on the side chain of a hexopyranoside, after correction for the presence of the additional C−C bond, they are consistent with literature values derived from rigid bicyclic systems.[23,24] Similarly, the discrepancy between the two $^3J_{H5,H6}$ coupling constants

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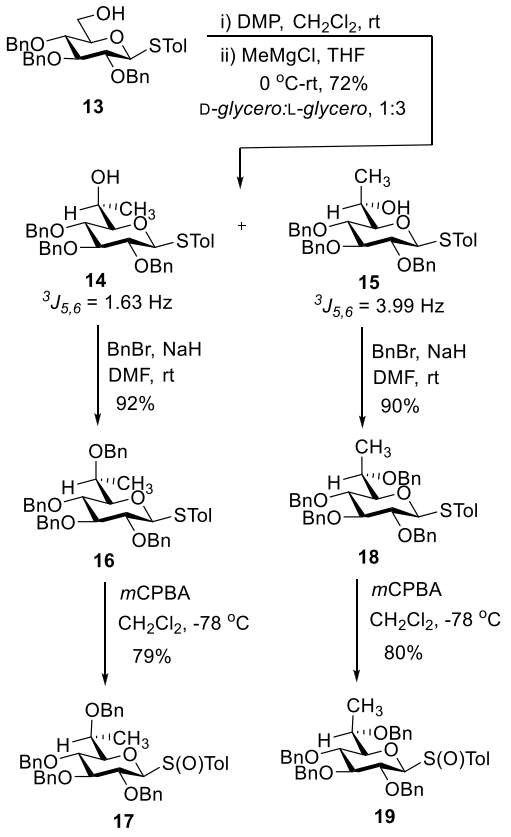
Scheme 2. Synthesis of 7-Deoxy-L-*glycero*-D-*gluco*heptopyranose (17) and 7-Deoxy-D-*glycero*-D-*gluco*heptopyranose (19) Donors



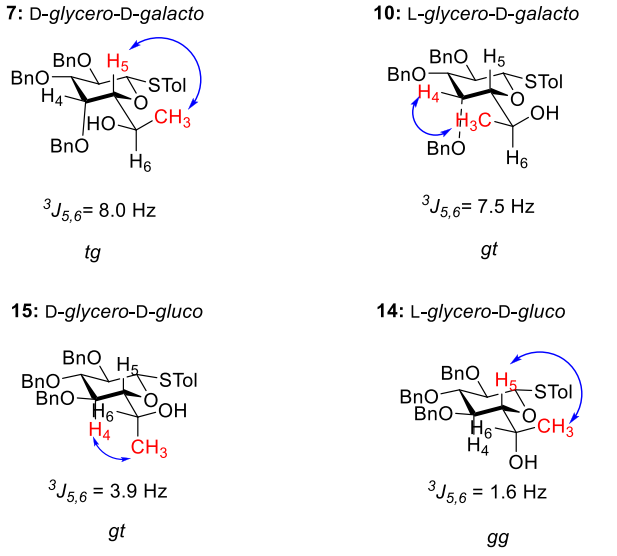


Figure 4. Assigned side-chain conformations with diagnostic data.

between pairs of gauche protons spanning a hexopyranoside side chain is consistent with the presence and location of the addition C−C bond as determined with rigid bicyclic models.[23] No significant differences in the $^3J_{H5,H6}$ coupling constants of the subsequent members of each series were observed, indicating that neither benzylation of O6 nor conversion of the thioglycosides to the corresponding sulfoxides resulted in an appreciable change in side-chain conformation.

The assignment of a predominant *tg* conformation to the side chain of the D-*glycero*-D-*galacto* donor **7** is consistent with the *tg* side-chain conformation of the pseudoenantiomeric sialic acid donors **4** and **5**, while the predominant *gt* conformation assigned to the side chain of its L-*glycero*-D-*galacto* isomer **10** is consistent with that of the pseudoenantiomeric sialic acid donor **2**. Similarly, the assignments of the *gg* conformation to the side chain of the L-*glycero*-D-*gluco* isomer **14** and of the *gt* conformation to the side chain of the D-*glycero*-D-*gluco* donor **15** are consistent with those of the pseudoenantiomeric sialic acids **1** and **3**, respectively, that is, the predictions of side-chain conformations based on the analysis of the relative configurations of the C4−C6 stereotriad presented in Figure 3 are fully borne out. It follows that the differing side-chain conformations in the sialic acids **1**−**5** are predominantly determined by the relative configurations of the C5−C7 stereotriads and not by the differences in alcohol protecting (acetyl vs benzoyl) nor by the differences in electronegative group at the 5 and 7-positions (esters, amides, and azides).

Glycosylation. Glycosylation reactions were carried out by activating sulfoxides **9**, **12**, **17**, and **19** with triflic anhydride in the presence of the hindered non-nucleophilic base TTBP at −78 °C in 0.20 M CH_2Cl_2 followed by the addition of 1.1 equiv of acceptor alcohols in the form of 0.5 M solutions in dichloromethane, giving rise to the coupled products in good yield, as presented in Tables 1 and 2.[25]

The anomeric configuration of the various glycosides obtained was assigned based on the $^3J_{1,2}$ coupling constant in the usual manner, with that for the equatorial isomers found in the range of 7.6−7.8 Hz, as compared to the 3.7−3.9 Hz of the axial anomers.

In the galactose-derived series, the D-*glycero*-D-*galacto*-configured donor **9** with its predominant *tg* side-chain conformation showed excellent selectivity for the formation of the equatorial glycoside with simple primary, secondary, and tertiary alcohols (Table 1, entries 1−3), modest equatorial selectivity with primary carbohydrate acceptors (Table 1, entries 4 and 5), modest to poor equatorial selectivity with two secondary carbohydrate acceptors (Table 1, entries 6 and 7), and finally modest axial selectivity with diacetone-D-glucose as the acceptor (Table 1, entry 8). With epimeric L-*glycero*-D-*galacto*-configured donor **12**, with the predominant *gt* side-chain conformation, the analogous trend in selectivities was seen with the same series of acceptors; however, the overall equatorial selectivity was generally lower than that seen with **9**, and the switch over from equatorial to axial selectivity began with the glucopyranose 4-OH acceptor (Table 1, entry 7) and was much more pronounced with the glucofuranose 3-OH acceptor (Table 1, entry 8). This pattern is consistent with equatorial selectivity being promoted, to a greater extent, in a donor with the *tg* conformation of the side chain than with the more arming *gt* conformation and matches that seen in the sialic acid series. The fall-off in equatorial selectivity with decreased nucleophilicity of the acceptor alcohols is consistent with the patterns observed by Codée and others in the hexopyranoside series of donors.[26]

Turning to the glucose-derived series, we were surprised to discover that the L-*glycero*-D-*gluco*-configured donor **17**, with the predominant *gg* conformation of its side chain, was highly equatorially selective in its couplings with simple alcohols and with a primary carbohydrate acceptor (Table 2, entries 1−3). Significant equatorial selectivity was maintained with two

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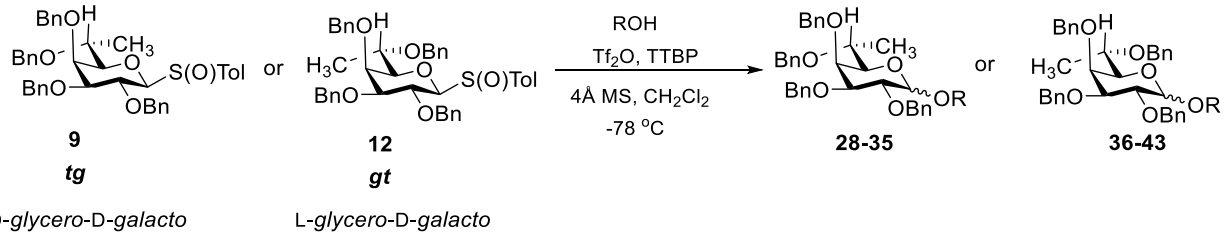
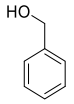
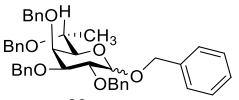
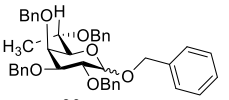
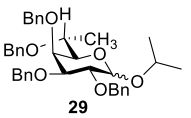
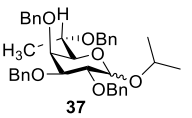
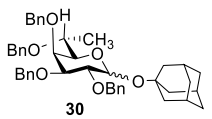
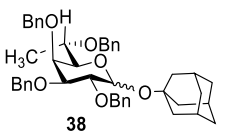
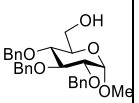
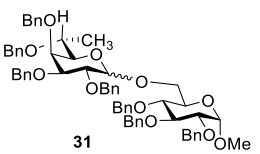
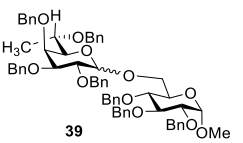
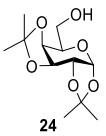
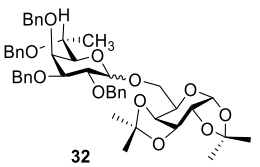
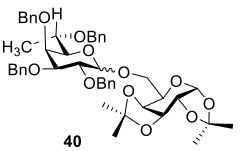
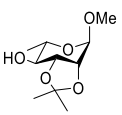
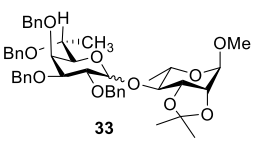
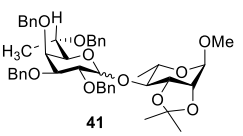
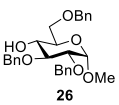
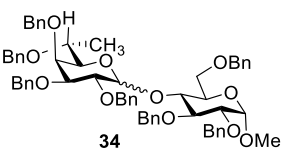
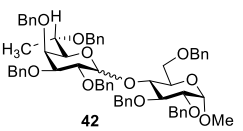
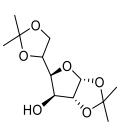
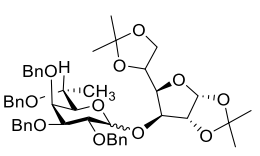
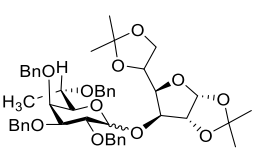
Table 1. Glycosylation Reactions with D-*glycero*-D-*galacto* Donor 9[a] and L-*glycero*-D-*galacto* Donor 12[a]



Entry	Acceptor	Donor	Product	Yield (%)[b]	ax:eq[c]	Donor	Product	Yield (%)[b]	ax:eq[c]
1.	 20	9	 28	64	1:6.0	12	 36	53	1:1.6
2.	 21	9	 29	73	1:16.7	12	 37	58	1:5.9
3.	 22	9	 30	79	1:14.2	12	 38	70	1:4.1
4.	 23	9	 31	70	1:4.0	12	 39	54	1:1.1
5.	 24	9	 32	62	1:3.2	12	 40	60	1:1.7
6.	 25	9	 33	77	1:5.1	12	 41	69	1:1.8
7.	 26	9	 34	55	1:2.1	12	 42	59	3.9:1
8.	 27	9	 35	68	2.9:1	12	 43	61	10.2:1

[a]All reactions were carried out at −78 °C with activation by Tf_2O/TTBP. The donor to acceptor ratio is 1.0:1.1. [b]Isolated yield. [c]Anomeric ratios were determined by integration of the ^1H NMR spectra of the crude reaction mixtures.

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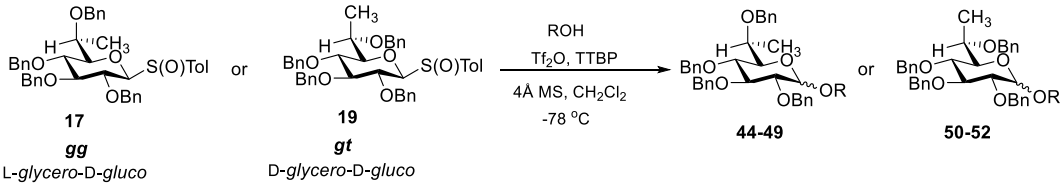
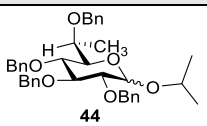
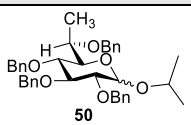
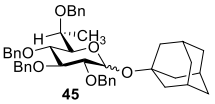
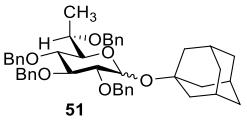
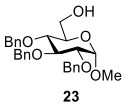
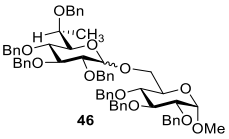
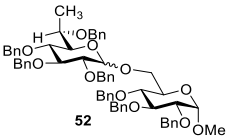
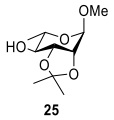
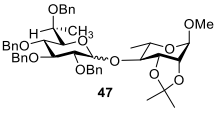
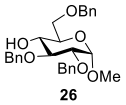
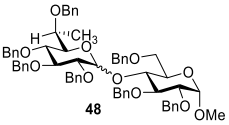
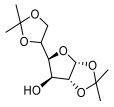
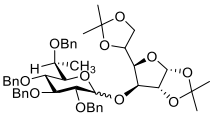
Table 2. Glycosylation Reactions with L-*glycero*-D-*gluco* Donor 17[a] and D-*glycero*-D-*gluco* Donor 19[a]



Entry	Acceptor	Donor	Product	Yield (%)[b]	ax:eq[c]	Donor	Product	Yield (%)[b]	ax:eq[c]
1.	 21	17	 44	57	*eq* only	19	 50	61	1:1.2
2.	 22	17	 45	56	*eq* only	19	 51	52	1:1.1
3.	 23	17	 46	49	1:23.6	19	 52	60	1:1.1
4.	 25	17	 47	63	1:7.9	-	-	-	-
5.	 26	17	 48	59	1:7.7	-	-	-	-
6.	 27	17	 49	63	1:1.7				

[a]All reactions were carried out at −78 °C with activation by Tf_2O/TTBP. The donor to acceptor ratio is 1.0:1.1. [b]Isolated yield. [c]Anomeric ratios were determined by integration of the ^1H NMR spectra of the crude reaction mixtures.

secondary carbohydrate acceptors (Table 2, entries 4 and 5), whereas poor equatorial selectivity was observed with the glucofuranose 3-OH acceptor (Table 2, entry 6). On the other hand, the D-*glycero*-D-*gluco* donor **19**, with the predominant *gt* conformation of its side chain, showed little to no selectivity with the two simple alcohols and a primary carbohydrate-based acceptor (Table 2, entries 1−3) and accordingly was not pursued further.

Overall, the relationships between relative configuration, side-chain conformation, and anomeric selectivity in the series of isomeric donors **9**, **12**, **17**, and **19** studied here are consistent with the patterns established previously in the sialic acid series (Figure 1), with the one major exception of the highly equatorially selective **17**. Thus, the exocyclic bonds of the D-*glycero*-D-*galacto* donor **9** and the pseudaminic acid and Kdo donors **4** and **5** all have the arabino configuration of the branch point and its two flanking centers, the *tg* conformation of the side chain and, with the exception of **17**, the highest equatorial selectivity. The L-*glycero*-D-*galacto* donor **12** has the xylo configuration of the same three stereogenic centers as does the 5-*epi*-neuraminic acid donor **2**, similarly adopts the *gt* conformation of the side chain, and has somewhat reduced anomeric selectivity. The D-*glycero*-D-*gluco*-configured donor **19**, like the 7-*epi*-neuraminic acid donor **3**, has the ribo configuration of the three stereogenic centers that control side-chain conformation and also shares the *gt* conformation of the side chain and modest anomeric selectivity in its glycosylation reactions. The exception to the overall trend of configuration, conformation, and selectivity seen with the sialic acids and the simplified models studied

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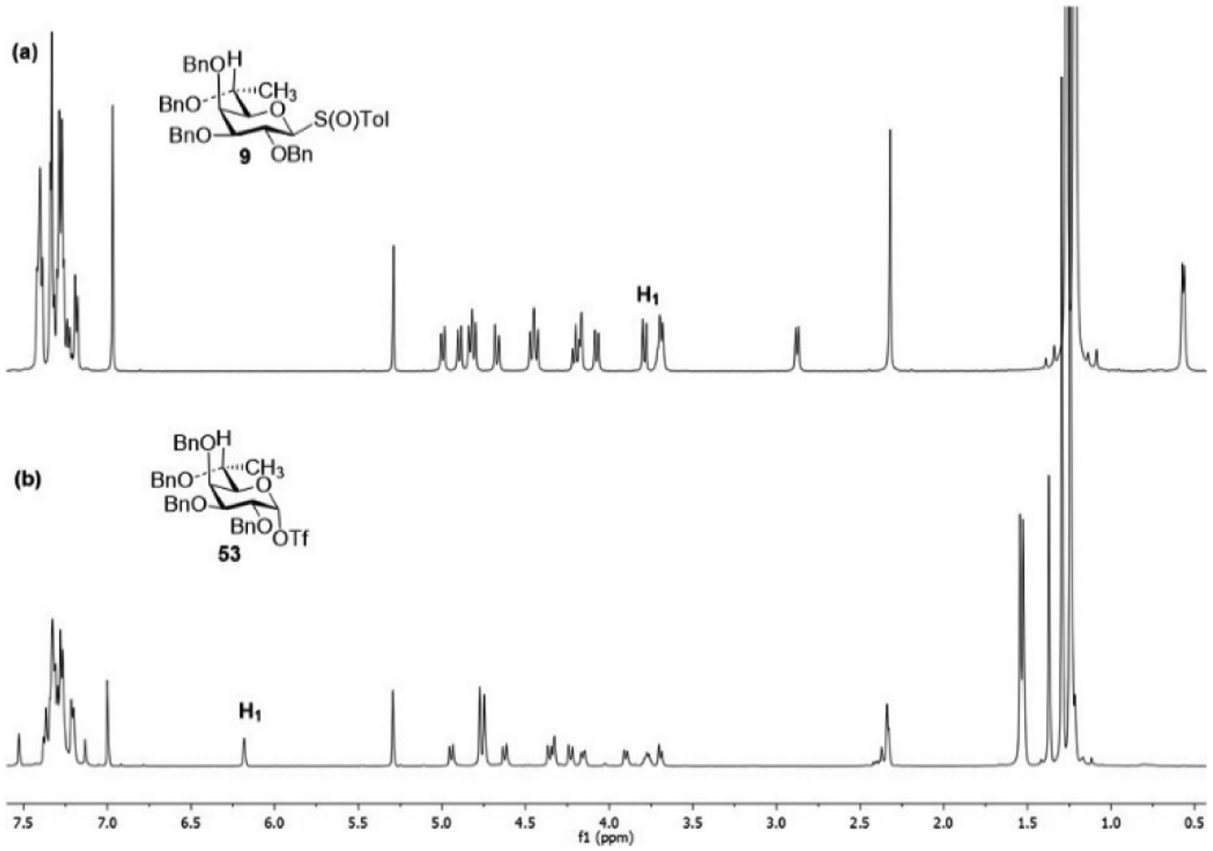

Figure 5. ^{1}H NMR spectra of donor **9** (a) at −80 °C prior to the addition of Tf_2O; the anomeric proton appears at δ 3.80 and (b) after the addition of Tf_2O and warming to −50 °C; the anomeric proton of the glycosyl triflate appears at 6.19 as a doublet ($^{3}J_{1,2}$ = 3.82 Hz).

here is the L-*glycero*-D-*gluco*-configured donor **17**: like the neuraminic acid donor **1**, it has the lyxo configuration of the three key stereogenic centers and the anticipated *gg* conformation of its side chain, but contrary to our initial expectations based on the selectivity observed with **1** and analogous systems, it displays the highest equatorial selectivity among the isomeric donors studied here.

Low-Temperature NMR Studies. In an attempt to understand the unexpected selectivity of donor **17**, we turned to the use of variable temperature NMR spectroscopy to probe the nature of the activated donors and their relative stabilities.[27] Accordingly, the four donors **9**, **12**, **17**, and **19** were activated at −80 °C in deuteriodichloromethane solution in the presence of TTBP by the addition of Tf_2O, and ^{1}H and ^{13}C NMR spectra were recorded at −80 °C. The temperature of the NMR probe was then increased in 10 °C increments, with ^{1}H NMR spectra recorded at each step, until −10 °C (Supporting Information, Pages S153, S161, S171, S179). Finally, decomposition products were isolated and characterized in each case.

Starting with the D-*glycero*-D-*galacto* donor **9**, conversion into the corresponding glycosyl triflate (**53**) began at −80 °C but was not complete until −50 °C when a clean ^{1}H NMR spectrum was observed (Figure 5). The anomeric proton of this glycosyl triflate appears at δ 6.19 as a doublet ($^{3}J_{1,2}$ = 3.82 Hz), whereas the corresponding carbon resonated at δ 107.7. A peak was observed at δ −76.19 in the ^{19}F NMR spectrum (SI). These ^{1}H, ^{13}C, and ^{19}F chemical shifts are fully consistent with the very predominant formation of a covalent axial glycosyl triflate.[27] Warming the NMR probe by 10 °C increments resulted in decomposition of the glycosyl triflate intermediate between −20 and −10 °C, at which point analysis of the reaction mixture by electrospray mass spectrometry revealed the presence of one predominant product with m/z = 559 [M + Na^+], which we attribute to the glycal (**54**). Unfortunately, all attempts to isolate **54** failed but afforded instead the 1,1′-disaccharides **56** and **57** in 43% yield as a mixture of two isomers (α/β, 1:1.5), which nevertheless supports the formation of glycal **54** as the immediate decomposition product from **9**.

In the case of the L-*glycero*-D-*galacto* donor **12**, a different pattern of reactivity was observed (Figure 6). A glycosyl triflate (**58**) was clearly formed at −80 °C, characterized by ^{1}H, ^{13}C, and ^{19}F chemical shifts of δ 6.26 (d, $^{3}J_{1,2}$ = 3.41 Hz), 109.0, and −76.21 for the anomeric proton, carbon, and triflate resonances, respectively, but decomposition was almost complete by −70 °C when only traces of the glycosyl triflate remained and the 1,6-anhydro derivative **59** was observed as the major product. Subsequent isolation afforded **59** in 53% yield.

Analogous study of the NMR study of the L-*glycero*-D-*gluco* donor **17** showed the clean formation of an axial glycosyl triflate (**60**) by −60 °C, with characteristic resonances at δ 6.15 (d, $^{3}J_{1,2}$ = 3.14 Hz), δ 107.5, and δ −76.18 in the ^{1}H, ^{13}C, and ^{19}F NMR spectra (Figure 7b). On gradual warming, this glycosyl triflate decomposed around −40 °C with the formation of the 1,6-anhydro sugar **61**, which was isolated in 43% yield.

Finally, the D-*glycero*-D-*gluco* donor **19** was observed to cleanly form a glycosyl triflate (**62**) by −60 °C as indicated

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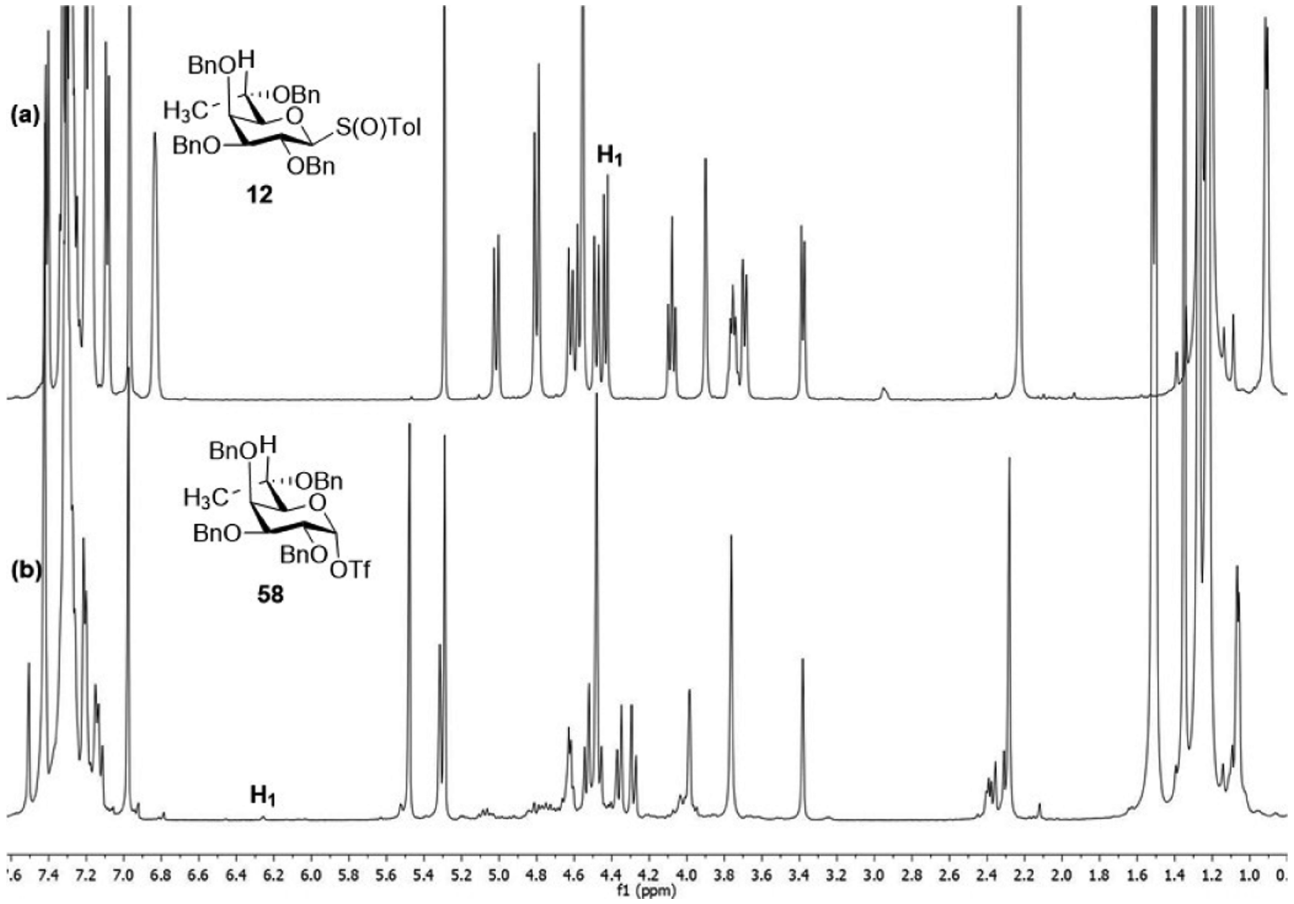

Figure 6. ^{1}H NMR spectra of donor **12** (a) at −80 °C prior to the addition of Tf_2O; the anomeric proton appears at δ 4.43 ppm and (b) after the addition of Tf_2O and warming to −70 °C; the anomeric proton of the residual triflate appears at δ 6.26 ppm as a doublet ($^{3}J_{1,2}$ = 3.41 Hz).

by the anomeric proton that resonated at δ 6.16 (d, $^{3}J_{1,2}$ = 3.08 Hz), the anomeric carbon at δ 107.1, and the glycosyl triflate CF_3 resonance at δ −75.27 in the ^{1}H, ^{13}C, and ^{19}F NMR spectra, respectively (Figure 8b). On warming, decomposition of this triflate began around −40 °C and was complete by −30 °C and afforded primarily the 1,6-anhydro sugar **63** (Figure 9) which could be isolated in 29% yield.

Overall, all four donors afforded an axial glycosyl triflate on activation with triflic anhydride, but the decomposition temperatures of these triflates varied considerably. Three of the four glycosyl triflates decomposed preferentially to give 1,6-anhydro sugars, whereas the fourth underwent apparent elimination to give a glycal, which in turn underwent partial hydration and coupling on attempted isolation. The formation of 1,6-anhydro sugars, side products in many glycosylation reactions,[28] is best explained by intramolecular attack of the side-chain benzyl ether on the glycosyl triflate through an exploded transition state with significant oxocarbenium ion character and a $^{3}H_4$ or $^{2,5}B$ conformation of the pyranose ring (Scheme 3). The formulation of these ring closure reactions as S_N2-like reactions with exploded transition states is consistent with current thinking on *O*-glycosylation reactions[3d,29] and avoids the need to write a disfavored 5-endo-trig ring closure as would be required by a pure S_N1 mechanism. It is apparent that the failure of the D-*glycero*-D-*galacto* configured triflate **53** to undergo ring closure to the endo-substituted 1,6-anhydro derivative **55** is the result of an unfavorable steric interaction by the terminal methyl group and the pseudoequatorial benzyloxy group at the 4-position in either of the proposed transition states for ring closure. The evidently more facile closure of the L-*glycero*-D-*galacto* triflate to the corresponding 1,6-anhydrogalactose derivative **59** also appears to be the result of steric interactions between the terminal methyl group and the benzyloxy group at the 6-position and the pseudoequatorial benzyloxy group at the 4-position, which, in this case, favorably orient the side for ring closure in both the $^{2,5}B$ and $^{4}H_3$ conformers. Any favorable or unfavorable steric interactions between the side chain and the benzyloxy group at the 4-position are alleviated in the D- and L-*glycero*-D-*gluco* triflates, leading to the formation of the 6-endo methyl-1,6-anhydroglucose derivative because of the pseudoaxial nature of the substituent at the 4-position. 1,6-Anhydroglucose derivatives substituted at the 6-endo-position have been described previously,[30] albeit prepared by a different method involving substitution on a pre-existing bicyclic framework.

The fact that the significant difference in stabilities of the D- and L-*glycero*-D-*galacto* triflates can be attributed to steric interactions in the transition states for ring closure to the corresponding 1,6-anhydro derivatives prevents us from drawing any firm conclusions correlating the stability of the two diastereomeric triflates and their influence on selectivity in their respective glycosylation reactions. Similarly, little of any use regarding the influence of the side chain on intermolecular reactivity and glycosylation selectivity can be gleaned from the comparable decomposition temperatures of

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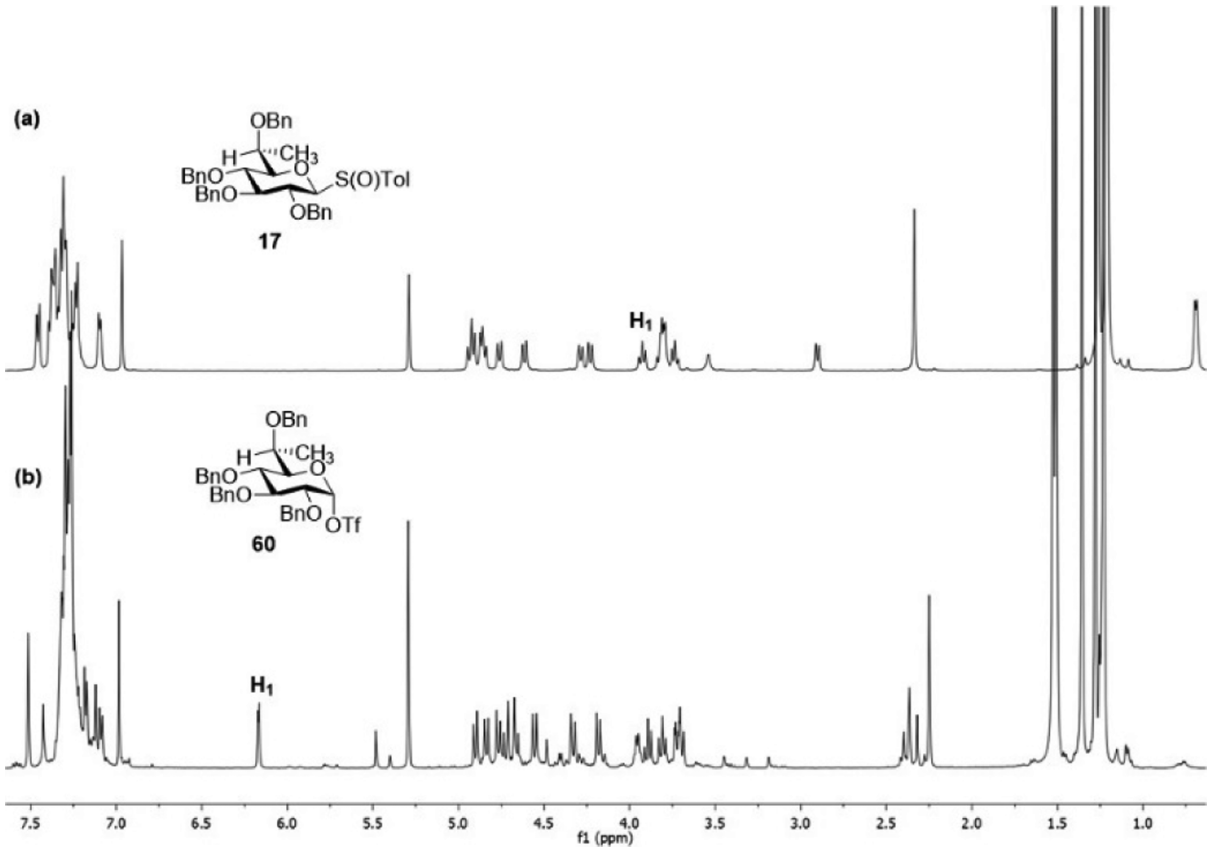

Figure 7. ^{1}H NMR spectra of donor **17** (a) at −80 °C prior to the addition of Tf_2O; the anomeric proton appears at δ 3.91 and (b) after the addition of Tf_2O and warming to −60 °C; the anomeric proton of the glycosyl triflate appears at δ 6.15 (d, $^{3}J_{1,2}$ = 3.14 Hz).

the two D- and L-*glycero*-D-*gluco* triflates as obviously the transition states for ring closure do not resemble those for *O*-glycosylation.

Ultimately, the most interesting and unexpected observation in this study is the highly selective formation of equatorial glycosides with the L-*glycero*-D-*gluco*-configured donor **17** with the preferred *gg* conformation of the side chain which, according to the earlier bicyclic models,[5,6] should have been the most reactive and least equatorially selective of the compounds studied. We suggest that this observation is best explained by donor−acceptor hydrogen bonding involving the benzyloxy group in the side chain of the donor in its *gg* conformation serving as the H-bond acceptor and directing group. Thus, as the C1 to the OTf bond lengthens and oxocarbenium character develops, the $^{4}C_1$ chair conformer will undergo distortion toward an ^{4}E envelope **64** and/or the closely related $^{4}H_3$ half-chair conformation **65** in either of which O6 is ideally placed to accept a hydrogen bond from the acceptor and stabilize a loose S_N2-like transition state (Scheme 4). This hypothesis is consistent with Whitfield and Guo's DFT computations, including proton transfer from the acceptor to O6 at the transition state, on the reaction of methanol with a tetra-*O*-methyl-α-D-glucopyranosyl donor, and with Liu's recent molecular dynamics study on glycosylation mechanisms.[31] The main difference between the models proposed by Whitfield and Liu and their respective co-workers on with prototypical tetra-*O*-alkyl-α-D-glucopyranosyl donors and that proposed here for the L-*glycero*-β-D-glucopyranosyl triflate **60** is the preorganization of the side chain in the latter into the *gg* conformation ideal for the key donor−acceptor hydrogen bond, which reduces the entropy of activation and so increases selectivity with respect to other transition states giving rise to the opposite anomer of the product. Donor−acceptor hydrogen-bond-mediated aglycone delivery, in general, is a much-discussed concept in recent years, albeit the focus is typically on the use of basic protecting groups in the donor as the hydrogen-bond acceptor.[32]

To test the hypothesis that donor−acceptor hydrogen-bonding factors into the equatorial selectivity observed with donor **17**, we prepared the corresponding 6-*O*-acetyl thioglycoside **66** by acetylation of **14** under standard conditions in 90% yield and converted it to the sulfoxide **67** by *m*CPBA oxidation in 83% yield. The $^{3}J_{5,6}$ coupling constants of 1.78 Hz in the 6-*O*-acetyl glycosyl donor **66** and those of 1.71 and 1.92 Hz for two isomers of sulfoxide **67** are consistent with that of 1.60 Hz seen in the analogous 6-*O*-benzyl donor **16**, indicating that the nature of the protecting group at the 6-position has no significant influence of side-chain conformation in the L-*glycero*-D-*gluco* series and that **66** and **67** retain the *gg* conformation. Coupling of **67** to 1-adamantanol under the standard conditions gave 61% of a 1.94:1 axial to equatorial mixture of glycosides **68** (Scheme 5), which differs significantly from the exclusive formation of the equatorial glycoside observed on coupling of **17** to the same acceptor alcohol (Table 2, entry 2). Clearly, the nature of the protecting group, ether or ester, at the 6-position has a very significant influence on the stereochemical outcome of glycosylations in the L-*glycero*-D-*gluco* series, consistent with the more basic benzyl ether in **17** serving as a better

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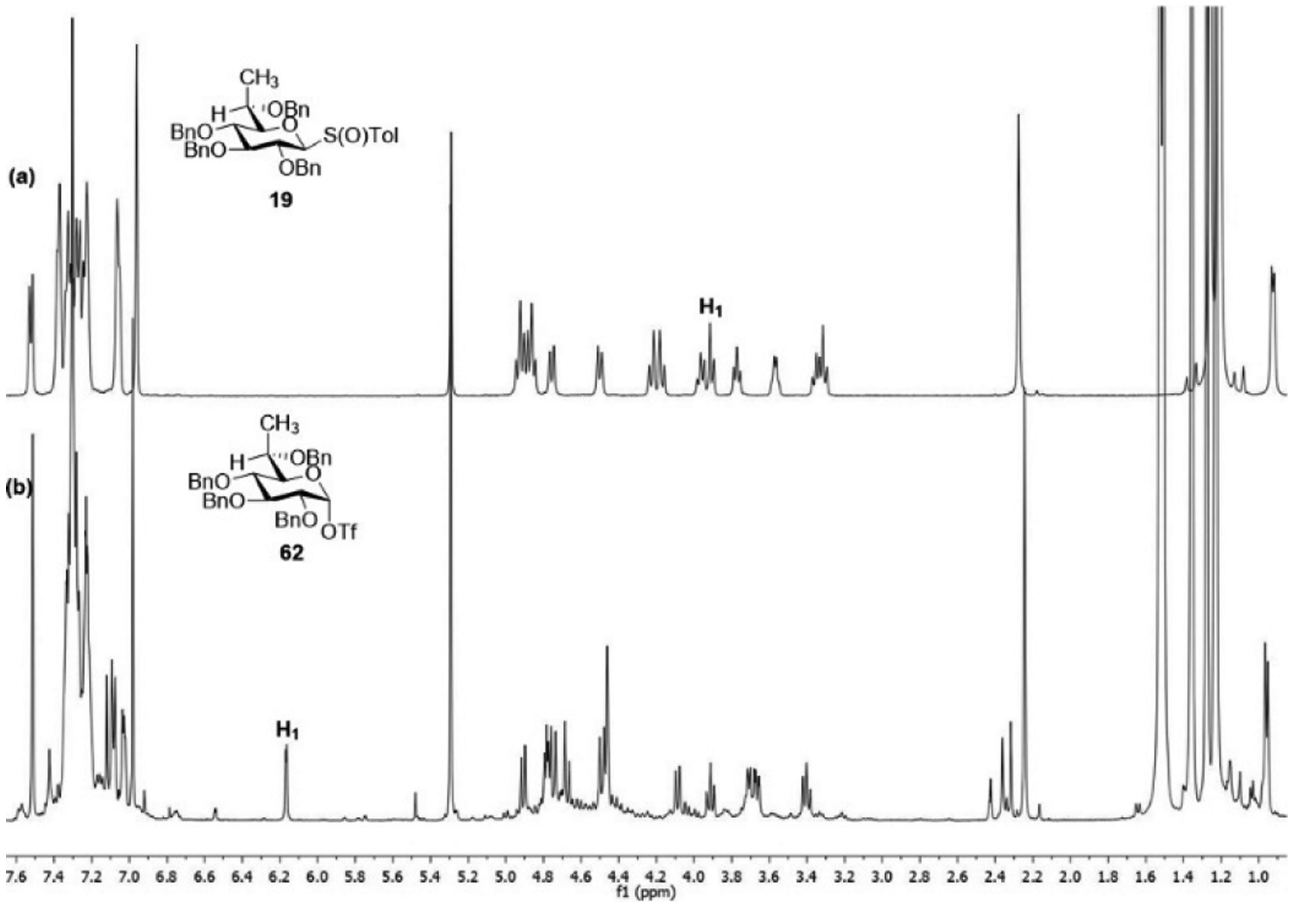

Figure 8. ^{1}H NMR spectra of donor **19** (a) at −80 °C prior to the addition of Tf_2O; the anomeric proton appears at δ 3.91 and (b) after the addition of Tf_2O and warming to −60 °C; the anomeric proton of the glycosyl triflate appears at δ 6.16(d, $^{3}J_{1,2}$ = 3.08 Hz).

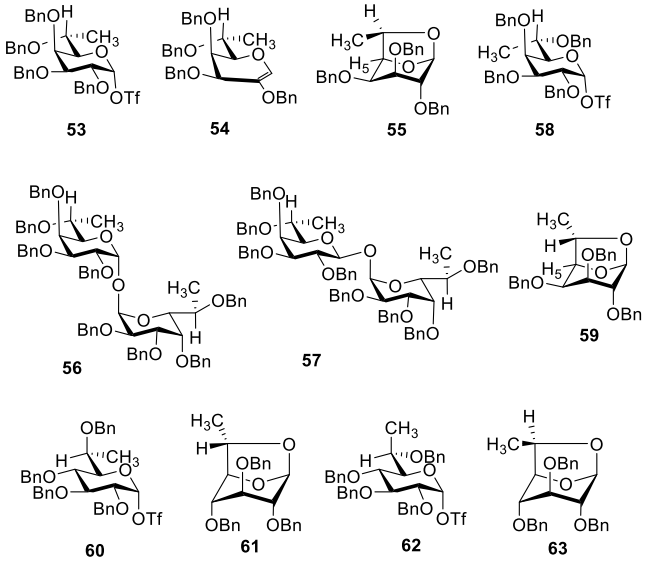

Figure 9. Structures of intermediates and the decomposition products obtained during low-temperature NMR studies.

hydrogen-bond acceptor than the less basic acetate ester of **67**. The alternative possibility of stereodirecting participation by the ester in **67** steering the glycosylation toward preferential axial glycoside formation is considered unlikely.[3d,33]

A final issue concerns the difference between the sialic acid series with which we began and the simple 7-deoxyheptopyranosyl series of donors studied here, namely, that the L-*glycero*-D-*gluco* donor **17** is the most selective in the present series, whereas the neuraminic acid donor **1** is among the least selective in its series despite the fact that both have the same lyxo relative configuration at the point of attachment of the side chain to the pyranose ring and its two flanking centers and both have the *gg* conformation of the side chain. The two series are clearly not the same and differ most prominently not only by the presence of the carboxylate ester at the anomeric position and the absence of a C−O bond at the 2-position of the pyranose ring in the sialic acid series but also by the nature of the protecting groups. If donor−acceptor hydrogen bonding is accepted as the underlying reason for the equatorial selectivity of **17** (Schemes 4 and 5), it is apparent that it cannot play a significant role in the reactions of **1**, which in turn is consistent with the less basic nature of the acetate protecting groups in **1** than the benzyl ethers in **2**. Unfortunately, while research into the use of ethers as protecting groups in sialic acid donors has been initiated,[34] it has not yet been extended under comparable conditions to comparisons of reactivity and selectivity across a spectrum of diastereomeric donors such as those employed here.

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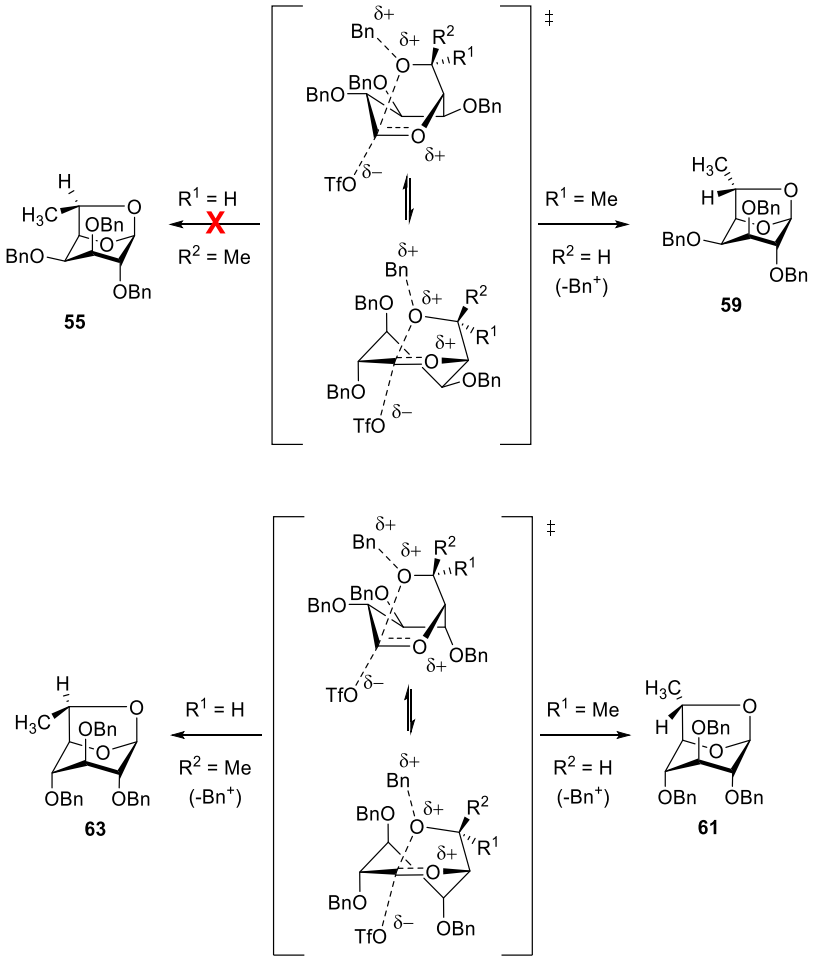
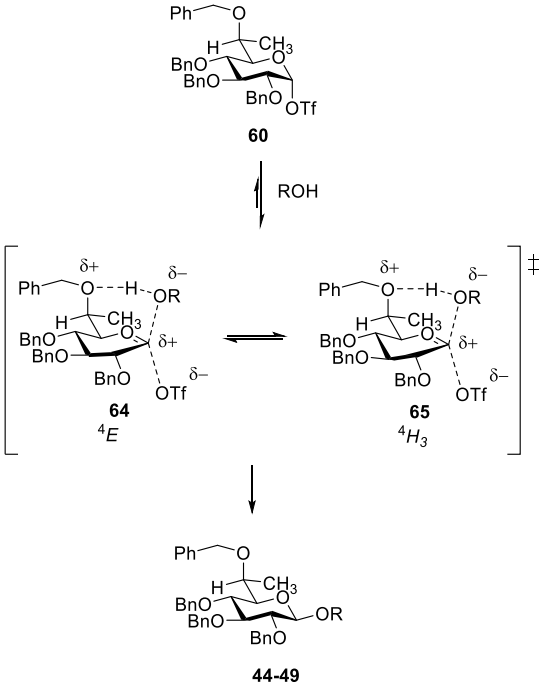
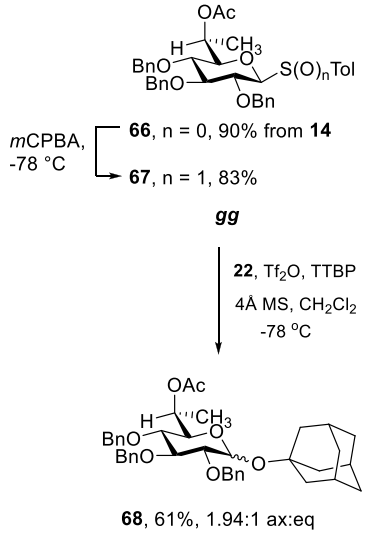
Scheme 3. Mechanism of 1,6-Anhydro Product Formation



Scheme 4. Mechanistic Hypothesis for the Equatorial Selectivity of L-*glycero*-D-*gluco* Donor 17



Scheme 5. Unselective Glycosylation with the 6-*O*-Acetyl-L-*glycero*-D-*gluco* Heptopyranosyl Donor 67



CONCLUSIONS

Continuing our studies on the role of side-chain conformational effects in anomeric reactivity and selectivity, we report the synthesis, conformational analysis, reactivity, and

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selectivity of a series of four diastereomeric 6-C-methyl galacto and glucopyranosyl donors. Consistent with expectations based on earlier studies in the sialic series, the D-*glycero*-D-*galacto* and L-*glycero*-D-*galacto* isomers have the *tg* and *gt* conformations of the side chain, while the D-*glycero*-D-*gluco* and L-*glycero*-D-*gluco* isomers have the *gt* and *gg* conformations: side-chain conformations of higher carbon sugars can be reliably predicted based on a simple model coupled with inspection of Fischer projection formulas. Somewhat to our surprise, however, while the D-*glycero*-D-*galacto* configured donor exhibited significantly greater equatorial selectivity than the L-*glycero*-D-*galacto* isomer consistent with the model, the D-*glycero*-D-*gluco* isomer was more reactive than the L-*glycero*-D-*gluco* isomer which generally exhibited the greatest equatorial selectivity of the whole series. This observation is rationalized in terms of stereodirecting donor−acceptor hydrogen bonding in the L-*glycero*-D-*gluco* isomer with O6 of the donor serving as a H-bond acceptor. Transition states involving ^4E or $^4H_3$ conformations of the activated donor encompassing this type of donor−acceptor hydrogen are consistent with recent DFT and metadynamics studies of the reactions of simple per-*O*-methylated glucopyranosyl donors with simple alcohols and are especially favored in the present case by the *gg* side-chain conformation very predominantly adopted in the ground state by the L-*glycero*-D-*gluco* donor which results in a decrease in entropy of activation and so of the activation energy for the formation of the equatorial glycoside.

General Experimental Details. All reactions were carried out under argon unless otherwise stated. Solvents used for column chromatography were of analytical grade and were purchased from commercial suppliers. Thin-layer chromatography was carried out with 250 μm glass-backed silica (XHL) plates. Detection of compounds was achieved by UV absorption (254 nm) and by staining with 10% sulfuric acid in ethanol. Purification of crude residues was performed by silica gel chromatography using 230−400 mesh grade 60 silica. Specific rotations were measured in chloroform on an automatic polarimeter with a path length of 10 cm. NMR spectra were recorded in C_6D_6 and $CDCl_3$ at either 500, 600, or 900 MHz as indicated. High-resolution (HRMS) mass spectra were recorded in the electrospray mode using an orbitrap mass analyzer (Thermo Fisher ESI-Orbitrap). The chemical shifts (δ) are recorded in ppm, and the multiplicities are abbreviated as follows: s (singlet), m (multiplet), br (broad), d (doublet), t (triplet), and q (quartet).

Preparation of Acceptors. *Methyl 2,3,4-Tri-O-benzyl-α-D-glucopyranoside (**23**).*[20] This acceptor was prepared according to the literature method (1.40 g, 98%) as colorless syrup. The spectral data are consistent with the literature.

*1,2:3,4-O-Di-isopropylidene-α-D-galactopyranoside (**24**).*[35] This acceptor was prepared according to the literature method (0.80 g, 74%) as colorless syrup. The spectral data are consistent with the literature.

*Methyl 2,3-O-Isopropylidene-α-L-rhamnoside (**25**).*[36] This acceptor was prepared according to the literature method (4.62 g, 94%) as colorless syrup. The spectral data are consistent with the literature.

*Methyl 2,3,6-Tri-O-benzyl-α-D-glucopyranoside (**26**).*[37] This acceptor was prepared according to the literature method (4.51 g, 90%) as colorless syrup. The spectral data are consistent with the literature.

*p-Methylphenyl 2,3,4-Tri-O-benzyl-1-thio-β-D-galactopyranoside (**6**).*[18] This compound was prepared according to the literature method (2.60 g, 91%) as white foam. The spectral data are consistent with the literature.

*p-Methylphenyl 2,3,4-Tri-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-galacto-heptopyranoside (**7**).* To a solution of **6** (0.60 g, 1.08 mmol) in dry CH_2Cl_2 (5 mL) was added Dess−Martin periodinane (0.51 g, 1.19 mmol). The mixture was stirred at room temperature for 3 h until complete consumption of the starting material as observed by TLC analysis. The reaction was diluted with 5 mL of sat. $NaHCO_3$ and 5 mL of $Na_2S_2O_3$ solution, the layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude residue which was used immediately without further purification.

THF (5 mL) was added at room temperature to vigorously stirred anhydrous $CeCl_3$ (0.31 g, 1.25 mmol, 2.0 equiv) to form a uniform white suspension, which was stirred for 2 h. The resulting suspension was cooled to 0 °C, and the addition of methylmagnesium bromide (1.88 mL, 1.0 M in THF, 1.88 mmol, 3.0 equiv) was carried out in a dropwise manner over 10 min to form an off-white suspension. The resulting suspension was stirred for 1 h, whereupon glycosyl aldehyde (0.35 g, 0.63 mmol, 1.0 equiv) in THF (3.0 mL) was added dropwise over 5 min, and the reaction mixture warmed gradually to room temperature. After 1 h, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (10 mL), and extracted with EtOAc (2 × 15 mL). The organic extracts were combined, washed with brine (15 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate; 4:1) to yield **7** and **10** stereoisomers in a 11:1 ratio (combined yield: 0.44 g, 71%) as colorless syrup. **7**: $[\alpha]_D^{20}$ −8.3 (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.41 (m, 4H), 7.39−7.27 (m, 13H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 11.7 Hz, 1H), 4.87 (d, *J* = 10.2 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 3H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 9.7 Hz, 1H), 4.10 (d, *J* = 2.7 Hz, 1H), 3.91 (td, *J* = 9.5, 8.9, 4.4 Hz, 2H), 3.58 (dd, *J* = 9.2, 2.7 Hz, 1H), 2.94 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 1.18 (d, *J* = 6.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 138.7, 138.4, 138.3, 137.4, 132.5, 130.4, 129.6, 128.66, 128.60, 128.5, 128.4, 128.0, 127.8, 127.7, 88.6, 84.6, 82.4, 77.9, 75.8, 74.0, 73.1, 71.8, 65.7, 21.2, 20.7. HRMS (ESI): *m*/*z* calcd for $C_{35}H_{38}O_5SNa$ [M + Na], 593.2332; found, 593.2307.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-galacto-heptopyranoside (**8**).* To a solution of **7** (0.50 g, 0.87 mmol) in dry DMF (3 mL) were added sodium hydride (49.10 mg, 1.22 mmol) and BnBr (130 μL, 1.05 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred until completion with monitoring by TLC (hexane/ethyl acetate 4:1, R_f = 0.8) and then quenched with methanol (0.5 mL). It was diluted with ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 9:1) to afford **8** (0.51 g, 89%) as colorless syrup. $[\alpha]_D^{20}$ −9.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.37−7.21 (m, 18H), 7.03 (d, *J* = 7.8

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Hz, 2H), 5.03 (d, J = 11.4 Hz, 1H), 4.82 (d, J = 10.2 Hz, 1H), 4.76−4.71 (m, 3H), 4.59−4.54 (m, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 4.19 (d, J = 2.6 Hz, 1H), 3.95−3.87 (m, 2H), 3.60 (dd, J = 9.3, 2.6 Hz, 1H), 3.15 (d, J = 8.7 Hz, 1H), 2.31 (s, 3H), 1.30 (d, J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.5, 138.4, 137.3, 132.3, 130.4, 129.6, 128.5, 128.48, 128.42, 128.2, 127.89, 127.81, 127.78, 127.70, 127.6, 127.5, 127.3, 88.4, 84.7, 81.7, 77.6, 75.7, 74.4, 73.4, 72.86, 72.81, 70.7, 21.2, 16.7. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_5SNa$ [M + Na], 683.2801; found, 683.2789.

*p-Methylphenyl 2,3,4-Tri-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-galacto-heptopyranoside (**10**).* To a solution of **7** (0.20 g, 0.36 mmol) in dry CH_2Cl_2 (2 mL) was added Dess−Martin periodinane (0.30 g, 0.72 mmol). The mixture was stirred at room temperature for 3 h until complete consumption of the starting material as observed by TLC analysis. The reaction was diluted with 2 mL of sat. $NaHCO_3$ and 2 mL of $Na_2S_2O_3$ solution, the layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude residue which was used immediately without further purification.

To a solution of galactosyl ketone (0.19 g, 0.33 mmol) in methanol (2 mL) was added sodium borohydride (26.00 mg, 0.67 mmol) in two portions at 0 °C. The mixture was stirred at 0 °C for 15 min until complete consumption of the starting material as observed by TLC analysis. It was diluted with 10 mL of ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 4:1) to afford **10** and **7** stereoisomers in a 22:1 ratio (combined yield: 0.18 g, 90%) as colorless syrup. **10**: $[\alpha]_D^{20}$ +11.6 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.48−7.44 (m, 2H), 7.43−7.40 (m, 2H), 7.39−7.28 (m, 13H), 7.05 (d, J = 7.9 Hz, 2H), 5.04 (d, J = 11.5 Hz, 1H), 4.86 (d, J = 10.3 Hz, 1H), 4.83−4.74 (m, 3H), 4.63 (d, J = 11.6 Hz, 1H), 4.60 (d, J = 9.6 Hz, 1H), 4.08−4.01 (m, 1H), 3.94 (t, J = 9.4 Hz, 1H), 3.85 (d, J = 2.6 Hz, 1H), 3.60 (dd, J = 9.2, 2.7 Hz, 1H), 3.00 (d, J = 7.5 Hz, 1H), 2.69 (s, 1H), 2.30 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.3, 138.2, 137.7, 132.6, 129.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 88.0, 85.0, 83.2, 77.7, 75.8, 74.2, 73.7, 73.4, 66.9, 21.2, 17.7. HRMS (ESI): m/z calcd for $C_{35}H_{38}O_5SNa$ [M + Na], 593.2332; found, 593.2339.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-galacto-heptopyranoside (**11**).* To a solution of **10** (0.50 g, 0.87 mmol) in dry DMF (3 mL) were added sodium hydride (49.10 mg, 1.22 mmol) and BnBr (130 μL, 1.05 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred until completion with monitoring by TLC (hexane/ethyl acetate 4:1, R_f = 0.70) and then quenched with methanol (0.50 mL). It was diluted with ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 4:1) to afford **11** (0.49 g, 85%) as colorless syrup. $[\alpha]_D^{20}$ −8.8 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.51−7.21 (m, 22H), 6.90 (d, J = 7.9 Hz, 2H), 5.09 (d, J = 11.5 Hz, 1H), 4.87 (d, J = 10.3 Hz, 1H), 4.85−4.72 (m, 3H), 4.67 (d, J = 9.7 Hz, 1H), 4.67−4.52 (m, 3H), 3.94 (t, J = 9.5 Hz, 1H), 3.93−3.81 (m, 2H), 3.61 (dd, J = 9.2, 2.6 Hz, 1H), 3.31 (d, J = 8.0 Hz, 1H), 2.24 (s, 3H), 0.98 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.7, 138.4, 138.3, 136.9, 131.6, 130.9, 129.6, 128.5, 128.49, 128.44, 128.3, 128.0, 127.8, 127.66, 127.63, 127.4, 88.3, 85.3, 83.4, 77.8, 75.7, 75.1, 74.2, 74.0, 73.4, 73.1, 21.1, 16.7. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_5SNa$ [M + Na], 683.2801; found, 683.2784.

General Protocol A for the Oxidation of Thioglycosides to Glycosyl Sulfoxides. To a stirred solution of thioglycoside (0.35 g, 0.53 mmol) in anhydrous dichloromethane (2 mL), *m*CPBA (0.12 g, 0.53 mmol, 77%) was added portionwise at −78 °C under argon. After 3 h, the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ solution (2 mL) and then warmed up to room temperature. The mixture was extracted with dichloromethane (2 × 10 mL); all combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give a crude residue. Purification by flash column chromatography on silica gel (hexane/ethyl acetate, 1:1) afforded the corresponding glycosyl sulfoxides.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-galacto-heptopyranosyl Sulfoxide (**9**).* It was obtained following the general protocol A as colorless syrup (0.29 g, 81%) in a 1:1.51 ratio of two unidentified isomers.

*Isomer **a**.* White amorphous solid; $[\alpha]_D^{23}$ −37.3 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.4 Hz, 2H), 7.37−7.21 (m, 18H), 7.16 (d, J = 7.3 Hz, 2H), 5.04−4.93 (m, 3H), 4.80−4.64 (m, 2H), 4.53 (d, J = 11.6 Hz, 1H), 4.46 (t, J = 9.6 Hz, 1H), 4.40 (d, J = 11.1 Hz, 1H), 4.17−4.04 (m, 2H), 3.85 (d, J = 9.8 Hz, 1H), 3.77 (dt, J = 12.2, 6.1 Hz, 1H), 3.66 (dd, J = 9.5, 2.7 Hz, 1H), 2.92 (d, J = 8.6 Hz, 1H), 2.38 (s, 3H), 0.71 (d, J = 5.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.0, 138.9, 138.3, 138.1, 138.0, 136.9, 129.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.07, 128.03, 127.9, 127.8, 127.78, 127.74, 127.6, 127.5, 127.4, 125.1, 94.7, 84.7, 82.8, 76.0, 74.6, 74.0, 73.2, 72.6, 72.3, 70.4, 21.4, 15.8. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6SNa$ [M + Na], 699.2751; found, 699.2745.

*Isomer **b**.* Colorless syrup; $[\alpha]_D^{23}$ −6.0 (c 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 8.2 Hz, 2H), 7.28 (m, 16H), 7.19 (d, J = 8.1 Hz, 4H), 7.14−7.06 (m, 2H), 4.92 (d, J = 11.7 Hz, 1H), 4.87 (d, J = 10.7 Hz, 1H), 4.82 (d, J = 10.7 Hz, 1H), 4.72 (d, J = 11.7 Hz, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 4.44−4.33 (m, 2H), 4.13 (d, J = 11.1 Hz, 1H), 4.10 (d, J = 2.5 Hz, 1H), 3.98 (t, J = 9.3 Hz, 1H), 3.75−3.63 (m, 2H), 3.19 (d, J = 8.6 Hz, 1H), 2.36 (s, 3H), 1.21 (d, J = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.6, 139.1, 138.2, 138.07, 138.01, 137.0, 129.3, 128.56, 128.52, 128.3, 128.2, 128.1, 127.88, 127.84, 127.81, 127.78, 127.70, 127.1, 126.8, 126.3, 95.7, 84.9, 82.0, 74.7, 74.4, 74.1, 72.8, 72.6, 72.5, 70.6, 21.6, 16.5. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6SNa$ [M + Na], 699.2751; found, 699.2747.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-galacto-heptopyranosyl Sulfoxide (**12**).* It was obtained following the general protocol A as colorless syrup (0.28 g, 79%) in a 1:1.63 ratio of two unidentified isomers.

*Isomer **a**.* White amorphous solid; $[\alpha]_D^{23}$ −109.2 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 7.9 Hz, 2H), 7.49−7.18 (m, 18H), 7.14 (d, J = 8.0 Hz, 2H),

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7.11−7.03 (m, 2H), 5.11 (d, J = 11.7 Hz, 1H), 5.02 (d, J = 2.4 Hz, 2H), 4.84 (s, 2H), 4.63−4.50 (m, 2H), 4.12−4.03 (m, 2H), 3.96 (d, J = 12.0 Hz, 1H), 3.81 (d, J = 2.5 Hz, 1H), 3.79−3.68 (m, 2H), 3.20 (d, J = 7.8 Hz, 1H), 2.15 (s, 3H), 0.84 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.1, 139.2, 138.5, 138.04, 138.00, 136.7, 129.7, 128.68, 128.64, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.2, 125.1, 94.5, 85.4, 76.1, 75.1, 74.1, 74.08, 74.02, 73.2, 73.0, 21.3, 17.1. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6SNa$ [M + Na], 699.2751; found, 699.2747.

Isomer ***b***. White amorphous solid; $[\alpha]_D^{23}$ +17.1 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 8.0 Hz, 2H), 7.36−7.21 (m, 18H), 7.18−7.13 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.01 (d, J = 11.7 Hz, 1H), 4.87 (s, 2H), 4.75 (d, J = 11.6 Hz, 1H), 4.69 (d, J = 11.5 Hz, 1H), 4.60 (d, J = 11.7 Hz, 1H), 4.55−4.45 (m, 3H), 4.12 (t, J = 9.2 Hz, 1H), 3.84 (d, J = 2.4 Hz, 1H), 3.79 (p, J = 6.5 Hz, 1H), 3.68 (dd, J = 9.1, 2.5 Hz, 1H), 3.39 (d, J = 7.6 Hz, 1H), 2.29 (s, 3H), 0.97 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.4, 139.0, 138.6, 138.1, 137.8, 137.3, 129.4, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 125.9, 96.1, 85.4, 83.2, 74.9, 74.6, 74.0, 73.7, 73.5, 72.9, 21.5, 16.6. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6SNa$ [M + Na], 699.2751; found, 699.2742.

Preparation of L-*glycero*-α-D-*gluco* and D-*glycero*-α-D-*gluco* Donors. To a solution of p-methylphenyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside **13**[20] (2.07 g, 3.70 mmol) in anhydrous DCM (20 mL) was added Dess−Martin periodinane (3.15 g, 7.40 mmol). The mixture was stirred at room temperature for 2 h until complete consumption of the starting material as observed by TLC analysis. The reaction was diluted with 25 mL of sat. $NaHCO_3$ and 25 mL of $Na_2S_2O_3$ solution, the layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford crude aldehyde (2.00 g) which was used immediately without further purification. Crude aldehyde was dissolved in THF (10 mL), and the solution was cooled to 0 °C. To this mixture, a solution of methyl magnesium chloride (5.41 mL, 1.0 M in THF, 5.41 mmol, 1.5 equiv) was added in a dropwise manner over 10 min, and the reaction mixture was stirred for 2 h at the same temperature. The reaction was quenched with the dropwise addition of saturated aq. NH_4Cl solution (10 mL) until effervescence stopped. The mixture was then diluted with H_2O (50 mL) and extracted with EtOAc (3 × 30 mL). The organic layer was separated and dried over Na_2SO_4, and solvents were evaporated under reduced pressure. The crude mixture was subjected to column purification (eluent: hexane/ethyl acetate) (93:7) to afford **14** (1.14 g, 54%) and **15** (0.38 g, 18%) stereoisomers in a 3:1 ratio as a white amorphous solid.

*p-Methylphenyl 2,3,4-Tri-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-gluco-heptopyranoside (**14**).* $[\alpha]_D^{20}$ −4.7 (c 1.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (m, 4H), 7.91−6.78 (m, 13H), 7.13 (d, J = 7.9 Hz, 2H), 5.27−4.84 (m, 4H), 4.78 (d, J = 10.3 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 9.6 Hz, 1H), 4.03 (qd, J = 6.6, 1.7 Hz, 1H), 3.76−3.67 (m, 2H), 3.47 (dt, J = 4.8, 2.7 Hz, 1H), 3.13−3.10 (m, 1H), 2.34 (s, 3H), 1.27 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.5, 138.2, 138.1, 138.1, 133.0, 129.8, 129.6, 128.6, 128.5, 128.4, 128.1, 128.07, 128.00, 127.9, 127.85, 127.80, 88.1, 86.7, 81.6, 81.3, 77.9, 75.8, 75.6, 75.3, 65.5, 21.2, 20.5; HRMS: m/z calcd for $C_{35}H_{38}O_5SNa$ $[M + Na]^+$, 593.2332; found, 593.2318.

*p-Methylphenyl 2,3,4-Tri-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-gluco-heptopyranoside (**15**).* $[\alpha]_D^{20}$ +9.0 (c 0.6, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.39−7.31 (m, 4H), 7.33−7.22 (m, 13H), 7.13 (d, J = 7.7 Hz, 2H), 4.97−4.90 (m, 3H), 4.84 (d, J = 10.9 Hz, 1H), 4.75 (d, J = 10.3 Hz, 1H), 4.65 (d, J = 11.1 Hz, 1H), 4.61 (d, J = 9.7 Hz, 1H), 3.99 (m, 1H), 3.74 (t, J = 8.8 Hz, 1H), 3.47 (td, J = 9.4, 4.3 Hz, 2H), 3.31 (dd, J = 9.8, 4.1 Hz, 1H), 2.52 (d, J = 7.0 Hz, 1H), 2.34 (s, 3H), 1.15 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.2, 138.1, 137.9, 137.5, 133.0, 129.7, 128.6, 128.56, 128.54, 128.2, 128.07, 128.00, 127.9, 127.8, 127.7, 87.7, 87.0, 81.4, 81.3, 79.4, 75.8, 75.4, 74.8, 68.1, 21.1, 17.7. HRMS: m/z calcd for $C_{35}H_{38}O_5SNa$ $[M + Na]^+$, 593.2332; found, 593.2318.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-gluco-heptopyranoside (**16**).* To a solution of **14** (0.34 g, 0.60 mmol) in dry DMF (2 mL) were added sodium hydride (28 mg, 0.90 mmol) and BnBr (85 μL, 0.72 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred until completion with monitoring by TLC (hexane/ethyl acetate 4:1, R_f = 0.8) and then quenched with methanol (0.50 mL). It was diluted with ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 95:5) to afford **16** (0.36 g, 92%) as colorless syrup. $[\alpha]_D^{20}$ +4.3 (c 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.52−7.47 (m, 2H), 7.44−7.38 (m, 2H), 7.38−7.21 (m, 16H), 7.16 (dd, J = 7.6, 1.8 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 4.90 (dd, J = 10.5, 9.0 Hz, 2H), 4.81 (dd, J = 10.9, 5.6 Hz, 2H), 4.71 (dd, J = 11.0, 6.2 Hz, 2H), 4.54 (d, J = 9.8 Hz, 1H), 4.47 (d, J = 10.9 Hz, 1H), 4.36 (d, J = 11.7 Hz, 1H), 3.99 (qd, J = 6.3, 1.6 Hz, 1H), 3.85 (t, J = 9.3 Hz, 1H), 3.68 (t, J = 9.0 Hz, 1H), 3.49 (t, J = 9.3 Hz, 1H), 3.19 (dd, J = 9.5, 1.9 Hz, 1H), 2.31 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.9, 138.5, 138.3, 137.7, 133.1, 129.9, 129.6, 128.5, 128.5, 128.46, 128.41, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 88.1, 87.2, 82.1, 80.9, 77.7, 75.9, 75.4, 74.9, 71.6, 70.2, 21.2, 15.6; HRMS: m/z calcd for $C_{42}H_{48}O_5SN$ $[M + NH_4]^+$, 678.3231; found, 678.3234.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-gluco-heptopyranoside (**18**).* To a solution of **15** (0.15 g, 0.26 mmol) in dry DMF (2 mL) were added sodium hydride (16 mg, 0.40 mmol) and BnBr (38 μL, 0.32 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred until completion with monitoring by TLC (hexane/ethyl acetate 4:1, R_f = 0.7) and then quenched with methanol (0.5 mL). It was diluted with ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 95:5) to afford **18** (0.16 g, 90%) as colorless syrup. $[\alpha]_D^{20}$ +3.0 (c 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.50−7.45 (m, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.37−7.24 (m, 16H), 7.16 (dd, J = 7.3, 2.4 Hz, 2H), 7.00 (d, J = 7.9 Hz, 2H), 4.90 (dd, J = 10.6, 7.5 Hz, 2H), 4.81 (d, J = 10.8 Hz, 2H), 4.71 (d, J = 10.3 Hz, 1H), 4.65−4.55 (m, 4H), 4.54 (d, J = 4.7 Hz, 1H), 3.85 (qd, J = 6.6, 1.5 Hz, 1H), 3.54 (dd, J = 10.0, 1.5 Hz, 1H), 3.44 (m, 2H), 2.28 (s, 3H), 1.19 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$

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NMR (126 MHz, $CDCl_3$): δ 139.0, 138.4, 138.2, 138.0, 137.7, 132.9, 129.9, 129.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.94, 127.92, 127.8, 127.6, 127.4, 87.5, 87.4, 81.0, 80.8, 78.2, 75.9, 75.3, 74.7, 74.2, 70.9, 29.8, 21.2, 14.8; HRMS: *m/z* calcd for $C_{42}H_{44}O_5SNa$ $[M + Na]^+$, 683.2801; found, 683.2797.

General Protocol B for the Oxidation of Thioglycosides to Glucosyl Sulfoxides. To a stirred solution of thioglycoside (0.20 g, 0.30 mmol) in anhydrous dichloromethane (2 mL), *m*CPBA (68 mg, 0.30 mmol, 77%) was added portionwise at −78 °C under argon followed by warming to −30 °C in 30 min. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ solution (5 mL) and then warmed up to room temperature. The mixture was extracted with dichloromethane (2 × 10 mL); all combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give a crude residue. Purification by flash column chromatography on silica gel (hexane/ethyl acetate, 2:1) afforded the corresponding glucosyl sulfoxides.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-gluco-heptopyranosyl Sulfoxide (**17**).* It was obtained following the general protocol B as colorless syrup (0.16 g, 79%) in a 2.1:1 ratio of two unidentified isomers.

*Isomer **a**.* $[\alpha]_D^{20}$ +4.4 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.50−7.26 (m, 20H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.92−4.80 (m, 5H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.56−4.50 (m, 2H), 4.45 (d, *J* = 8.5 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 3.98 (q, *J* = 6.7 Hz, 1H), 3.82 (q, *J* = 8.6 Hz, 1H), 3.78 (t, *J* = 9.0 Hz, 1H), 3.36 (d, *J* = 9.4 Hz, 1H), 2.35 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.7, 138.11, 138.10, 137.9, 137.6, 129.4, 128.6, 128.57, 128.53, 128.47, 128.44, 128.38, 128.35, 128.2, 128.0, 127.9, 127.88, 127.83, 127.76, 127.72, 127.66, 127.64, 127.4, 126.6, 94.9, 86.3, 81.7, 77.3, 75.3, 74.6, 74.2, 71.5, 69.8, 21.4, 15.2; HRMS: *m/z* calcd for $C_{42}H_{44}O_6SNa$ $[M + Na]^+$, 699.2751; found, 699.2728.

*Isomer **b**.* $[\alpha]_D^{22}$ −15.1 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.39−7.22 (m, 18H), 7.13 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.04 (d, *J* = 10.3 Hz, 1H), 4.99−4.93 (m, 2H), 4.89 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.30 (d, *J* = 11.8 Hz, 1H), 4.10 (t, *J* = 9.4 Hz, 1H), 3.78 (t, *J* = 9.1 Hz, 1H), 2.97 (dd, *J* = 9.5, 2.1 Hz, 1H), 2.40 (s, 3H), 0.78 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.2, 138.8, 138.4, 138.3, 137.8, 136.4, 129.5, 128.6, 128.59, 128.55, 128.47, 128.41, 128.1, 127.8, 127.75, 127.71, 127.6, 127.5, 125.3, 93.9, 87.0, 83.2, 77.4, 77.0, 75.1, 75.7, 74.9, 71.2, 69.7, 21.5, 14.5. HRMS: *m/z* calcd for $C_{42}H_{44}O_6SNa$ $[M + Na]^+$, 699.2751; found, 699.2761.

*p-Methylphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-1-thio-D-glycero-α-D-gluco-heptopyranosyl Sulfoxide (**19**).* It was obtained following the general protocol B as colorless syrup (0.16 g, 80%) in a 2.3:1 ratio of two unidentified isomers.

*Isomer **a**.* $[\alpha]_D^{20}$ −55.0 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.60−7.55 (m, 2H), 7.45−7.40 (m, 2H), 7.40−7.24 (m, 16H), 7.20 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.18−7.14 (m, 2H), 5.05 (d, *J* = 10.3 Hz, 1H), 5.01−4.94 (m, 2H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.59−4.24 (m, 2H), 4.11 (t, *J* = 9.4 Hz, 1H), 3.92 (d, *J* = 9.7 Hz, 1H), 3.82 (t, *J* = 8.9 Hz, 1H), 3.71 (qd, *J* = 6.7, 1.5 Hz, 1H), 3.55 (dd, *J* = 9.8, 8.8 Hz, 1H), 3.35 (dd, *J* = 9.8, 1.5 Hz, 1H), 2.32 (s, 3H), 1.11 (d, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 141.5, 138.9, 138.3, 137.7, 137.6, 136.3, 129.5, 128.54, 128.51, 128.44, 128.40, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 127.2, 125.6, 93.1, 86.9, 81.7, 75.7, 75.6, 74.7, 74.1, 70.2, 21.4, 14.8; HRMS: *m/z* calcd for $C_{42}H_{44}O_6SNa$ $[M + Na]^+$, 699.2751; found, 699.2729.

*Isomer **b**.* $[\alpha]_D^{20}$ +7.2 (*c* 0.8, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.54−7.45 (m, 2H), 7.42−7.23 (m, 16H), 7.21−7.13 (m, 6H), 4.89−4.75 (m, 4H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.62 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 8.9 Hz, 1H), 4.41 (d, *J* = 12.2 Hz, 1H), 3.88−3.80 (m, 2H), 3.76 (t, *J* = 8.5 Hz, 1H), 3.62 (dd, *J* = 9.6, 1.4 Hz, 1H), 3.47 (dd, *J* = 9.7, 8.4 Hz, 1H), 2.31 (s, 3H), 1.16 (d, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 141.5, 138.7, 137.9, 137.7, 136.7, 129.5, 128.5, 128.4, 128.39, 128.32, 128.27, 128.0, 127.9, 127.9, 127.83, 127.80, 127.7, 127.69, 127.63, 127.5, 127.4, 127.3, 125.6, 95.5, 86.6, 81.5, 77.4, 76.2, 75.5, 74.7, 74.4, 74.0, 71.3, 29.7, 21.3, 15.6; HRMS: *m/z* calcd for $C_{42}H_{44}O_6SNa$ $[M + Na]^+$, 699.2751; found, 699.2733.

*p-Methoxyphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranoside (**S1**).* A mixture of donor **8** (90 mg, 0.14 mmol), *p*-methoxyphenol (21 mg, 0.16 mmol), and activated 4 Å acid-washed powdered molecular sieves (90 mg) in anhydrous CH_2Cl_2 (1.5 mL, 0.1 M) was stirred for 30 min at rt under argon and then cooled to −40 °C. The reaction mixture was then treated with *N*-iodosuccinimide (37 mg, 0.16 mmol) and AgOTf (7 mg, 0.03 mmol) and stirred at −40 °C until completion and then quenched with triethylamine (20 μL) at −40 °C, and gradually, temperature was increased to rt. The reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered through Celite, and washed with 20% aqueous $Na_2S_2O_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (5 mL) twice, and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude residue. Purification by silica gel column chromatography eluting with ethyl acetate/hexane (1:19 to 1:9) afforded the desired product as colorless syrup (83 mg, 92%) in a 1:2.4 ratio of α/β anomers.

S1β. $[\alpha]_D^{23}$ +30.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.36−7.20 (m, 18H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.82−6.78 (m, 2H), 5.44 (d, *J* = 3.6 Hz, 1H), 5.05 (s, 1H), 4.90 (d, *J* = 11.6 Hz, 1H), 4.87−4.76 (m, 2H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.51 (dd, *J* = 11.2, 3.7 Hz, 2H), 4.27 (d, *J* = 2.6 Hz, 1H), 4.24−4.13 (m, 2H), 4.13 (dd, *J* = 10.0, 2.7 Hz, 1H), 3.86−3.73 (m, 4H), 3.65 (d, *J* = 9.1 Hz, 1H), 1.08 (d, *J* = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 154.8, 150.8, 139.0, 138.9, 138.5, 138.4, 128.4 (2C), 128.3, 128.1, 127.9, 127.7 (2C), 127.5, 127.5, 118.1, 114.4, 96.7, 79.5, 76.2, 74.8, 74.7, 74.2, 73.5, 73.3, 72.6, 70.5, 55.7, 16.4. HRMS (ESI): *m/z* calcd for $C_{42}H_{44}O_7Na$ $[M + Na]$, 683.2979; found, 683.2966.

S1α. $[\alpha]_D^{23}$ −7.8 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.21 (m, 20H), 7.02−6.93 (m, 2H), 6.86−6.76 (m, 2H), 5.04 (d, *J* = 11.5 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.88−4.81 (m, 2H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.55 (dd, *J* = 11.3, 6.8 Hz, 2H), 4.23−4.16 (m, 2H), 4.08 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.92 (dq, *J* = 8.7, 6.1 Hz, 1H), 3.76 (s, 3H), 3.59 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.21 (d, *J* = 9.0 Hz, 1H), 1.31 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 155.1, 151.7, 139.0,

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138.6, 138.6, 138.4, 128.5, 128.4, 128.39, 128.34, 128.2, 128.0, 127.9, 127.8, 127.7, 127.69, 127.64, 127.5, 127.4, 118.2, 114.5, 103.2, 82.6, 79.3, 78.0, 75.4, 74.6, 73.3, 73.1, 72.6, 70.6, 55.7, 16.7. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_7Na$ [M + Na], 683.2979; found, 683.2962.

*p-Methoxyphenyl 2,3-Di-O-benzyl-4,6-O-benzylidende-7-deoxy-D-glycero-β-D-galacto-heptopyranoside (**S2**).* To a solution of the compound **S1*β*** (40 mg, 47.56 μmol) in 2 mL of MeOH under a hydrogen atmosphere (balloon pressure) was added 10% Pd/C (53 mg, 47.56 μmol) and stirred for 24 h at room temperature. The reaction mixture was filtered through a pad of Celite, and the filtrate was evaporated under reduced pressure to afford the crude residue which was used subsequently without purification for the next step.

To a stirred solution of unprotected galactoside (22.0 mg, 39.96 μmol) in dry acetonitrile (1.5 mL) were added *p*TSA (2 mg, 11.99 μmol) and benzaldehyde dimethylacetal (7.20 μL, 47.95 μmol). The reaction mixture was stirred at room temperature until completion and then quenched with triethylamine (20 μL). The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated solution of $NaHCO_3$ (5 mL). The aqueous layer was extracted with EtOAc (5 mL) twice, and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude residue. The crude residue obtained was dissolved in dry DMF (1.5 mL). The addition of sodium hydride (8.4 mg, 0.21 mmol) and BnBr (4.8 μL, 0.21 mmol) was carried out at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred until completion with monitoring by TLC (hexane/ethyl acetate 4:1, R_f = 0.6) and then quenched with methanol (0.2 mL). It was diluted with ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane/ethyl acetate 9:1) to afford **S2** (27.0 mg, 71%) as colorless syrup. $[\alpha]_D^{23}$ +41.5 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.56−7.48 (m, 2H), 7.49−7.41 (m, 2H), 7.40−7.19 (m, 11H), 7.06−6.97 (m, 2H), 6.86−6.76 (m, 2H), 5.75 (s, 1H), 5.49 (d, J = 3.5 Hz, 1H), 4.88 (dd, J = 13.9, 12.0 Hz, 2H), 4.81 (d, J = 12.1 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.36 (dd, J = 3.3, 1.0 Hz, 1H), 4.30−4.18 (m, 2H), 4.16 (dd, J = 10.1, 3.3 Hz, 1H), 3.77 (s, 3H), 3.53 (s, 1H), 1.39 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 154.9, 151.2, 138.9, 138.5, 138.2, 128.8, 128.4, 128.2, 128.0, 127.7, 127.6, 126.5, 117.7, 114.6, 97.4, 93.9, 76.3, 75.6, 73.6, 72.3, 72.2, 70.7, 66.3, 55.7, 15.3. HRMS (ESI): m/z calcd for $C_{35}H_{36}O_7Na$ [M + Na], 591.2353; found, 591.2335.

*4-Methoxyphenyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranoside (**S3**).* A mixture of sulfoxide **17** (80.0 mg, 0.11 mmol), TTBP (58.7 mg, 0.23 mmol), and activated 4 Å powdered molecular sieves (160.0 mg) in CH_2Cl_2 (0.25 mL) was stirred for 1 h at room temperature under argon and then cooled to −78 °C and treated with Tf_2O (21.0 μL, 0.13 mmol). After stirring for 10 min, a solution of *p*-methoxy phenol (16.0 mg, 0.13 mmol) in CH_2Cl_2 (50 μL) was added and continued stirring for 10 h before the reaction was quenched with triethylamine (15.0 μL) at −78 °C. The reaction mixture was diluted with dichloromethane (10 mL), molecular sieves were filtered off through a pad of Celite, and the filtrate was washed with saturated $NaHCO_3$. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then subjected to column chromatography over silica (EtOAc/Hexane, 5:95) to afford **S3*β*** (minor compound) and **S3*α*** (major compound) as colorless syrups (combined yield: 57. mg, 73%, α/β = 2:1, separated after column chromatography).

S3β. $[\alpha]_D^{20}$ +4.3 (c 0.9, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.42−7.20 (m, 18H), 7.18−7.13 (m, 2H), 7.03−6.97 (m, 2H), 6.83−6.79 (m, 2H), 5.44 (d, J = 3.5 Hz, 1H), 5.05 (d, J = 10.6 Hz, 1H), 4.87 (d, J = 10.6 Hz, 2H), 4.79 (d, J = 12.0 Hz, 1H), 4.66 (dd, J = 17.1, 11.8 Hz, 2H), 4.32 (dd, J = 11.3, 6.0 Hz, 2H), 4.19 (t, J = 9.3 Hz, 1H), 3.97−3.91 (m, 1H), 3.85 (t, J = 9.4 Hz, 1H), 3.78 (s, 3H), 3.73 (dd, J = 9.7, 3.4 Hz, 1H), 3.62 (d, J = 9.9 Hz, 1H), 1.12 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 154.8, 150.5, 138.6, 138.4, 138.1, 138.0, 128.5, 128.4, 128.1, 127.9, 127.7, 127.69, 127.62, 117.7, 114.4, 95.6, 82.4, 79.7, 77.5, 75.9, 74.9, 74.0, 73.3, 71.0, 70.8, 29.7, 15.6; HRMS: m/z calcd for $C_{42}H_{44}O_7Na$ $[M + Na]^+$, 683.2961; found, 683.2961.

S3α. White solid $[\alpha]_D^{20}$ +10.6 (c 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.41−7.23 (m, 18H), 7.23−7.12 (m, 2H), 7.03 (m, 2H), 6.88−6.82 (m, 2H), 5.10 (d, J = 10.9 Hz, 1H), 4.98 (d, J = 10.8 Hz, 1H), 4.90−4.79 (m, 4H), 4.72 (d, J = 11.8 Hz, 1H), 4.45 (d, J = 10.8 Hz, 1H), 4.41 (d, J = 11.8 Hz, 1H), 4.06 (qd, J = 6.4, 2.0 Hz, 1H), 3.96 (dd, J = 9.7, 8.7 Hz, 1H), 3.81 (s, 3H), 3.80−3.49 (m, 2H), 3.31 (dd, J = 9.6, 2.0 Hz, 1H), 1.40 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 155.2, 151.6, 138.5, 138.44, 138.42, 128.4, 128.38, 128.33, 128.0, 127.9, 127.8, 127.7, 127.67, 127.63, 127.5, 118.3, 114.5, 103.1, 85.1, 82.0, 78.1, 77.4, 75.8, 75.0, 74.8, 71.2, 70.5, 55.7, 15.7; HRMS: m/z calcd for $C_{42}H_{44}O_7Na$ $[M + Na]^+$, 683.2961; found, 683.2953.

*p-Methoxyphenyl 4,6-Di-O-benzylidene-7-deoxy-L-glycero-α-D-gluco-heptopyranoside (**S4**).* To a solution of the compound **S3*α*** (8.7 mg, 0.01 mmol) in MeOH (0.5 mL) under a hydrogen atmosphere (balloon pressure) was added 10% Pd/C (11 mg, 0.01 mmol) and stirred for 24 h at room temperature. The reaction mixture was filtered through a pad of Celite, and the filtrate was evaporated under reduced pressure to afford the crude debenzylated product (3.7 mg), which was dissolved in acetonitrile (0.2 mL) and treated with dimethyl acetal (2.6 mg, 0.02 mmol) and *p*TSA (1.0 mg, 4.3 μmol). The reaction was then stirred for 4 h at room temperature before being quenched with saturated aq. $NaHCO_3$ and extracted with EtOAc (5 mL). The organic layer was separated, collected, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude residue which was purified over silica (eluent: EtOAc/hexane, 1:3) to afford **S4** as a white solid (3 mg, 61%). $[\alpha]_D^{20}$ −33.3 (c 0.2, $CHCl_3$); ^1H NMR (900 MHz, $CDCl_3$): δ 7.51−7.48 (m, 2H), 7.37 (m, 3H), 7.04−7.00 (m, 2H), 6.84 (d, J = 9.1 Hz, 2H), 5.86 (s, 1H), 4.88 (d, J = 7.7 Hz, 1H), 4.58 (p, J = 6.8 Hz, 1H), 3.90−3.86 (m, 2H), 3.79 (s, 3H), 3.78−3.74 (m, 1H), 3.72 (t, J = 7.6 Hz, 1H), 1.49 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (226 MHz, $CDCl_3$): δ 155.7, 150.9, 143.1, 137.3, 129.2, 128.4, 126.4, 118.8, 114.6, 102.5, 94.4, 77.2, 74.1, 73.9, 73.8, 70.4, 68.8, 55.6, 29.7, 11.4; HRMS: m/z calcd for $C_{21}H_{24}O_7Na$ $[M + Na]^+$, 411.1414; found, 411.1400.

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General Procedure C for the Coupling of Glycosyl Donors with Acceptors with TTBP/Tf_2O. A mixture of the donor (1.0 equiv), TTBP (2.0 equiv), and activated 4 Å powdered molecular sieves (2 g/mmol of the donor) in CH_2Cl_2 (0.2 M in the substrate) was stirred for 1 h at room temperature under argon and then cooled to −78 °C and treated with Tf_2O (1.1 equiv). After 15 min of stirring at −78 °C, a solution of the glycosyl acceptor (1.1 equiv) in CH_2Cl_2 (0.5 M in acceptor) was added slowly. The reaction mixture was stirred for further 4−5 h at −78 °C and then quenched with triethylamine (0.2 mL). The reaction mixture was diluted with dichloromethane (10 mL), molecular sieves were filtered off through a pad of Celite, and the filtrate was washed with saturated $NaHCO_3$. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/ethyl acetate) afforded the corresponding α/β-glycopyranosides. The anomeric ratio of the products was determined by integration of the ^1H NMR spectrum of the crude product mixture.

*Benzyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranoside (**28**).* **28α** and **28β** were obtained from the reaction of donor **9** (40.0 mg, 59.10 μmol) and benzyl alcohol (6.76 μL, 65.0 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (24.0 mg, 64%), α/β = 6:1.

28β. Colorless syrup; $[\alpha]_D^{23}$ +15.9 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.19 (m, 25H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.93−4.85 (m, 2H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.71 (dd, *J* = 12.1, 5.6 Hz, 2H), 4.57 (d, *J* = 1.7 Hz, 1H), 4.55 (d, *J* = 2.5 Hz, 1H), 4.51 (d, *J* = 7.3 Hz, 1H), 4.48 (d, *J* = 6.4 Hz, 1H), 4.24 (d, *J* = 2.6 Hz, 1H), 4.20 (d, *J* = 11.1 Hz, 1H), 4.04 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.00 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.83 (dq, *J* = 9.1, 6.0 Hz, 1H), 3.62 (d, *J* = 9.1 Hz, 1H), 1.30 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 139.0, 138.6, 138.4, 137.1, 128.5, 128.4, 128.39, 128.33, 128.2, 127.96, 127.90, 127.8, 127.7, 127.5, 127.48, 127.42, 95.6, 79.7, 76.4, 74.8, 74.7, 73.7, 73.3, 73.2, 72.8, 70.6, 68.6, 16.5. HRMS (ESI): *m*/*z* calcd for $C_{42}H_{44}O_6Na$ [M + Na], 667.3030; found, 667.3016.

28α. Colorless syrup; $[\alpha]_D^{23}$ −21.7 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 6.9 Hz, 2H), 7.37−7.17 (m, 23H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.93 (dd, *J* = 11.4, 5.4 Hz, 2H), 4.80−4.71 (m, 2H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 7.7 Hz, 1H), 4.17 (d, *J* = 11.2 Hz, 1H), 4.13 (d, *J* = 2.8 Hz, 1H), 3.98−3.84 (m, 2H), 3.51 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.10 (d, *J* = 8.8 Hz, 1H), 1.33 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.8, 138.7, 138.4, 137.6, 128.5, 128.44, 128.41, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 103.0, 95.5, 82.8, 79.6, 77.8, 75.2, 74.6, 73.4, 73.2, 72.7, 70.9, 70.6, 16.6. HRMS (ESI): *m*/*z* calcd for $C_{42}H_{44}O_6Na$ [M + Na], 667.3030; found, 667.3021.

*Isopropyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α-D-galacto-heptopyranoside (**29α**).* **29α** and **29β** were obtained from the reaction of donor **9** (40.0 mg, 59.10 μmol) and isopropyl alcohol (5.0 μL, 65.00 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (26.0 mg, 73%), α/β = 16.7:1.

Only **29α** data given here: colorless syrup; $[\alpha]_D^{22}$ −4.0 (*c* 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.19 (m, 20H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.92 (d, *J* = 10.7 Hz, 1H), 4.80−4.66 (m, 3H), 4.53 (dd, *J* = 11.4, 7.2 Hz, 2H), 4.38 (d, *J* = 7.7 Hz, 1H), 4.15 (d, *J* = 11.1 Hz, 1H), 4.11 (d, *J* = 2.8 Hz, 1H), 3.97 (hept, *J* = 6.2 Hz, 1H), 3.88 (dq, *J* = 9.0, 6.0 Hz, 1H), 3.79 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.50 (dd, *J* = 9.8, 2.9 Hz, 1H), 3.08 (d, *J* = 8.8 Hz, 1H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.23 (d, *J* = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.9, 138.8, 138.5, 128.4, 128.39, 128.33, 128.17, 128.14, 128.0, 127.8, 127.7, 127.56, 127.52, 127.3, 103.0, 82.8, 79.7, 77.8, 75.2, 74.5, 73.5, 73.2, 72.8, 72.5, 70.6, 23.6, 22.3, 16.6. HRMS (ESI): *m*/*z* calcd for $C_{38}H_{44}O_6Na$ [M + Na], 619.3030; found, 619.3030.

*Adamantyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranoside (**30**).* **30α** and **30β** were obtained from the reaction of donor **9** (30.0 mg, 44.30 μmol) and 1-adamantanol (7.4 mg, 48.7 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:19); combined yield (24.1 mg, 79%), α/β = 14.2:1.

30β. Colorless syrup; $[\alpha]_D^{22}$ +33.2 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.18 (m, 20H), 5.31 (d, *J* = 3.7 Hz, 1H), 5.01 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 11.6 Hz, 1H), 4.77−4.66 (m, 3H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.47 (d, *J* = 11.2 Hz, 1H), 4.26−4.18 (m, 2H), 4.03 (dd, *J* = 10.2, 3.7 Hz, 1H), 3.97 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.87−3.76 (m, 2H), 2.13 (p, *J* = 3.2 Hz, 3H), 1.90−1.83 (m, 3H), 1.80−1.70 (m, 3H), 1.66−1.57 (m, 6H), 1.27 (d, *J* = 5.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.3, 139.2, 138.9, 138.6, 128.5, 128.3, 128.2, 128.0, 127.84, 127.81, 127.6, 127.5, 127.3, 127.3, 90.5, 79.6, 76.4, 75.0, 74.7, 74.3, 73.3, 73.2, 73.1, 72.8, 70.7, 42.7, 36.4, 30.7, 16.8. HRMS (ESI): *m*/*z* calcd for $C_{45}H_{52}O_6Na$ [M + Na], 711.3656; found, 711.3649.

30α. Colorless syrup; $[\alpha]_D^{22}$ +6.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.20 (m, 20H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.79−4.73 (m, 2H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.61 (d, *J* = 7.8 Hz, 1H), 4.55 (d, *J* = 6.8 Hz, 1H), 4.53 (d, *J* = 6.3 Hz, 1H), 4.17 (d, *J* = 11.2 Hz, 1H), 4.12 (d, *J* = 2.8 Hz, 1H), 3.89 (dq, *J* = 8.9, 6.0 Hz, 1H), 3.80 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.10 (d, *J* = 9.1 Hz, 1H), 2.15 (t, *J* = 3.3 Hz, 3H), 1.98−1.89 (m, 3H), 1.85−1.73 (m, 3H), 1.71−1.57 (m, 6H), 1.29 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 139.0, 138.9, 138.6, 128.4, 128.39, 128.32, 128.16, 128.13, 127.8, 127.7, 127.57, 127.53, 127.50, 127.3, 96.9, 83.1, 79.6, 77.8, 75.3, 74.9, 74.6, 73.6, 73.2, 72.7, 70.6, 42.8, 36.4, 30.8, 16.8. HRMS (ESI): *m*/*z* calcd for $C_{45}H_{52}O_6Na$ [M + Na], 711.3656; found, 711.3638.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-α-D-gluco-pyranoside (**31**).* **31α** and **31β** were obtained from the reaction of donor **9** (30.0 mg, 44.30 μmol) and acceptor **23** (22.7 mg, 48.8 μmol)[20] following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (31.0 mg, 70%), α/β = 4.0:1.

31β. Colorless syrup; $[\alpha]_D^{22}$ +32.0 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35−7.17 (m, 35H), 5.01−4.98 (m, 2H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 4.0 Hz, 1H), 4.78 (d, *J* = 5.0 Hz, 1H), 4.72−4.65 (m, 4H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.55 (d, *J* = 5.4 Hz, 1H), 4.54−4.51 (m, 2H), 4.48 (d, *J* = 11.3 Hz, 1H), 4.20 (d, *J* = 11.3 Hz, 1H), 4.16 (d, *J* = 2.8 Hz, 1H), 4.03 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.96 (t, *J* = 9.2 Hz, 1H), 3.89 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.83−3.71 (m, 3H), 3.68 (d, *J* =

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10.4 Hz, 1H), 3.59 (t, J = 9.4 Hz, 1H), 3.52 (d, J = 9.1 Hz, 1H), 3.40 (dd, J = 9.6, 3.6 Hz, 1H), 3.28 (s, 3H), 1.21 (d, J = 5.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 139.0, 138.9, 138.6, 138.4, 138.3, 128.47, 128.43, 128.3, 128.2, 128.1, 128.0, 128.0, 127.95, 127.90, 127.7, 127.66, 127.62, 127.5, 127.4, 127.3, 97.9, 97.8, 82.1, 80.3, 78.9, 78.0, 76.5, 75.7, 75.1, 74.8, 74.7, 73.6, 73.4, 72.89, 72.84, 72.53, 70.50, 70.3, 66.0, 55.1, 16.4. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4644.

31α. Colorless syrup; $[\alpha]_D^{22}$ +12.1 (c 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.39−7.15 (m, 35H), 5.04−4.89 (m, 3H), 4.83−4.67 (m, 6H), 4.65 (d, J = 12.1 Hz, 1H), 4.60 (d, J = 3.5 Hz, 1H), 4.52 (q, J = 10.8 Hz, 3H), 4.27 (d, J = 7.7 Hz, 1H), 4.20−4.14 (m, 2H), 4.11 (s, 1H), 3.98 (t, J = 9.1 Hz, 1H), 3.87 (dt, J = 16.6, 7.8 Hz, 3H), 3.60 (dd, J = 10.7, 5.5 Hz, 1H), 3.56−3.42 (m, 3H), 3.32 (s, 3H), 3.06 (d, J = 8.7 Hz, 1H), 1.27 (d, J = 6.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 139.0, 138.8, 138.6, 138.5, 138.4, 138.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.97, 127.91, 127.86, 127.81, 127.7, 127.6, 127.5, 127.4, 127.3, 104.7, 98.0, 82.8, 82.2, 80.0, 79.4, 78.2, 77.8, 75.7, 75.2, 74.9, 74.6, 73.5, 73.4, 73.0, 72.7, 70.6, 70.3, 70.0, 68.8, 55.2, 16.6. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4642.

*6-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-1,2:3,4-O-diisopropylidene-α-D-galactopyranose (**32**)*. **32α** and **32β** were obtained from the reaction of donor **9** (30.0 mg, 44.30 μmol) and acceptor **24** (12.7 mg, 48.80 μmol)[35] following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (22.0 mg, 62%), α/β = 3.2:1.

32β. Colorless syrup; $[\alpha]_D^{22}$ +2.8 (c 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.18 (m, 20H), 5.51 (d, J = 5.1 Hz, 1H), 5.02 (d, J = 3.7 Hz, 1H), 4.99 (d, J = 11.3 Hz, 1H), 4.83 (d, J = 11.7 Hz, 1H), 4.78−4.69 (m, 3H), 4.61−4.52 (m, 2H), 4.49 (d, J = 11.2 Hz, 1H), 4.34 (dd, J = 8.0, 1.9 Hz, 1H), 4.26−4.16 (m, 2H), 4.10−3.98 (m, 2H), 3.95 (dd, J = 10.1, 2.7 Hz, 1H), 3.87−3.72 (m, 2H), 3.66 (dd, J = 10.3, 7.7 Hz, 1H), 3.61 (d, J = 8.8 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.32−1.26 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 139.1, 138.8, 138.6, 128.4, 128.36, 128.32, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 109.2, 108.6, 97.6, 96.3, 79.5, 76.3, 74.75, 74.72, 73.5, 73.0, 72.8, 72.7, 70.8, 70.7, 70.5, 65.8, 65.7, 26.2, 26.1, 24.9, 24.7, 16.4. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3716.

32α. Colorless syrup; $[\alpha]_D^{22}$ −32.7 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.45−7.41 (m, 2H), 7.35−7.19 (m, 18H), 5.55 (d, J = 5.0 Hz, 1H), 5.03 (d, J = 11.1 Hz, 1H), 4.99 (d, J = 11.4 Hz, 1H), 4.80 (d, J = 11.9 Hz, 1H), 4.76−4.68 (m, 2H), 4.58 (dd, J = 7.9, 2.4 Hz, 1H), 4.53 (dd, J = 11.3, 6.5 Hz, 2H), 4.39 (d, J = 7.7 Hz, 1H), 4.30 (dd, J = 5.0, 2.4 Hz, 1H), 4.22 (dd, J = 7.9, 1.8 Hz, 1H), 4.17 (d, J = 11.1 Hz, 1H), 4.15−4.04 (m, 3H), 3.93−3.78 (m, 2H), 3.69 (dd, J = 10.1, 7.0 Hz, 1H), 3.51 (dd, J = 9.7, 2.8 Hz, 1H), 3.10 (d, J = 8.6 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.32−1.27 (m, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.16, 139.12, 138.8, 138.4, 128.6, 128.5, 128.3, 128.19, 128.12, 128.0, 127.8, 127.7, 127.54, 127.50, 127.3, 109.4, 108.7, 105.1, 96.5, 82.4, 79.1, 77.7, 74.7, 74.6, 73.5, 73.2, 72.7, 71.5, 70.9, 70.6, 69.4, 67.4, 26.1, 26.0, 25.1, 24.5, 16.6. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3725.

*Methyl 4-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**33**)*. **33α** and **33β** were obtained from the reaction of **9** (40.0 mg, 59.10 μmol) and acceptor **25** (14.2 mg, 65.00 μmol)[36] following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (34.3 mg, 77%), α/β = 5.1:1.

33β. Colorless syrup; $[\alpha]_D^{22}$ +21.5 (c 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.20 (m, 20H), 5.08 (d, J = 3.7 Hz, 1H), 5.02 (d, J = 11.3 Hz, 1H), 4.83−4.72 (m, 4H), 4.67 (d, J = 11.8 Hz, 1H), 4.57 (d, J = 11.2 Hz, 1H), 4.47 (d, J = 11.3 Hz, 1H), 4.25−4.20 (m, 2H), 4.14 (t, J = 6.4 Hz, 1H), 4.11−4.03 (m, 2H), 3.92 (dd, J = 10.2, 2.7 Hz, 1H), 3.86 (dq, J = 9.1, 6.0 Hz, 1H), 3.74 (d, J = 9.0 Hz, 1H), 3.66 (dq, J = 9.9, 6.3 Hz, 1H), 3.34 (s, 3H), 3.29 (dd, J = 9.9, 6.7 Hz, 1H), 1.46 (s, 3H), 1.34−1.31 (m, 6H), 1.28 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.3, 138.9, 138.7, 138.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.65, 127.61, 127.4, 127.3, 127.2, 109.1, 99.2, 98.2, 82.9, 79.4, 76.6, 75.6, 74.9, 74.6, 74.1, 73.9, 73.3, 72.6, 70.5, 64.6, 54.7, 28.0, 26.1, 17.9, 16.4. HRMS (ESI): m/z calcd for $C_{45}H_{54}O_{10}Na$ [M + Na], 777.3609; found, 777.3600.

33α. Colorless syrup; $[\alpha]_D^{22}$ −8.0 (c 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 7.8 Hz, 2H), 7.36−7.19 (m, 18H), 5.01 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 9.4 Hz, 2H), 4.81−4.65 (m, 3H), 4.55−4.50 (m, 2H), 4.25−4.15 (m, 2H), 4.12−4.04 (m, 2H), 3.89 (dq, J = 8.1, 6.0 Hz, 1H), 3.73 (dd, J = 9.8, 7.6 Hz, 1H), 3.60 (qd, J = 10.0, 5.5 Hz, 2H), 3.54 (dd, J = 9.7, 2.9 Hz, 1H), 3.38 (s, 3H), 3.09 (d, J = 8.7 Hz, 1H), 1.48 (s, 3H), 1.35−1.26 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.3, 139.0, 138.9, 138.4, 128.5, 128.3, 128.2, 128.2, 127.8, 127.75, 127.72, 127.5, 127.4, 127.3, 109.3, 102.5, 98.1, 82.8, 79.8, 78.8, 78.3, 77.7, 75.9, 75.1, 74.6, 73.9, 73.3, 72.8, 70.6, 64.3, 54.9, 28.0, 26.3, 18.1, 16.7. HRMS (ESI): m/z calcd for $C_{45}H_{54}O_{10}Na$ [M + Na], 777.3609; found, 777.3607.

*Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-α-D-glucopyranoside (**34**)*. **34α** and **34β** were obtained from the reaction of **9** (30.0 mg, 44.30 μmol) and acceptor **26** (22.7 mg, 48.80 μmol)[37] following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (25.0 mg, 55%), α/β = 2.1:1.

34β. Colorless syrup; $[\alpha]_D^{22}$ +14.0 (c 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.12 (m, 35H), 5.73 (d, J = 3.8 Hz, 1H), 4.96 (d, J = 4.6 Hz, 1H), 4.94 (d, J = 4.3 Hz, 1H), 4.80 (d, J = 11.4 Hz, 1H), 4.68 (d, J = 12.0 Hz, 2H), 4.64 (d, J = 11.2 Hz, 2H), 4.65−4.50 (m, 6H), 4.46 (t, J = 11.4 Hz, 2H), 4.22 (d, J = 11.2 Hz, 1H), 4.16 (d, J = 3.7 Hz, 1H), 4.07−4.03 (m, 1H), 4.01 (dd, J = 10.3, 3.8 Hz, 1H), 3.92−3.87 (m, 1H), 3.86−3.78 (m, 2H), 3.75 (dd, J = 10.3, 2.6 Hz, 1H), 3.68 (dd, J = 10.3, 2.5 Hz, 1H), 3.61−3.52 (m, 2H), 3.47 (d, J = 8.9 Hz, 1H), 3.38 (s, 3H), 1.28 (d, J = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.0, 138.9, 138.8, 138.7, 138.3, 138.1, 138.0, 128.5, 128.4, 128.3, 128.29, 128.22, 128.1, 128.0, 127.7, 127.67, 127.61, 127.5, 127.4, 127.3, 127.2, 127.0, 97.7, 97.0, 82.2, 80.3, 79.5, 75.6, 74.8, 74.7, 74.4, 74.1, 73.8, 73.5, 73.1, 72.9, 72.6, 70.5, 69.8, 69.4, 55.1, 16.4. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4657.

34α. Colorless syrup; $[\alpha]_D^{22}$ −3.1 (c 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.39−7.19 (m, 32H), 7.19−7.15 (m, 1H), 7.15−7.10 (m, 2H), 5.12−5.00 (m, 2H), 4.86 (d, J =

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12.2 Hz, 1H), 4.79 (s, 2H), 4.75−4.63 (m, 4H), 4.59 (d, J = 3.7 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.47 (dd, J = 11.4, 2.0 Hz, 2H), 4.38 (d, J = 12.0 Hz, 1H), 4.27 (d, J = 7.6 Hz, 1H), 4.17 (d, J = 11.2 Hz, 1H), 4.10 (d, J = 2.8 Hz, 1H), 3.91 (d, J = 9.2 Hz, 1H), 3.88−3.77 (m, 2H), 3.76 (dd, J = 9.7, 7.7 Hz, 1H), 3.71−3.57 (m, 2H), 3.55−3.45 (m, 2H), 3.38 (s, 3H), 3.34 (dd, J = 9.7, 2.9 Hz, 1H), 2.92 (s, 1H), 1.09 (d, J = 5.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.7, 139.5, 139.1, 138.8, 138.7, 138.6, 138.0, 128.49, 128.46, 128.42, 128.37, 128.30, 128.2, 128.1, 128.0, 127.9, 127.89, 127.86, 127.77, 127.72, 127.70, 127.5, 127.45, 127.43, 127.3, 127.2, 126.9, 102.9, 98.6, 83.0, 80.4, 80.2, 79.0, 77.6, 76.5, 75.5, 75.2, 74.5, 73.8, 73.6, 73.3, 72.8, 72.7, 70.5, 70.0, 67.9, 55.4, 16.5. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4653.

*3-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**35**).* **35*α*** and **35*β*** were obtained from the reaction of **9** (30.0 mg, 44.30 μmol) and acceptor **27** (12.7 mg, 48.80 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (25.0 mg, 68%), α/β = 1:2.9.

35β. Colorless syrup; $[\alpha]_D^{22}$ +32.7 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.31 (m, 8H), 7.30−7.21 (m, 12H), 5.88 (d, J = 3.5 Hz, 1H), 5.30 (d, J = 3.8 Hz, 1H), 5.03 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 11.7 Hz, 1H), 4.79−4.70 (m, 3H), 4.59 (dd, J = 7.3, 3.7 Hz, 2H), 4.51−4.44 (m, 2H), 4.27−4.20 (m, 3H), 4.16−4.07 (m, 2H), 4.06−3.98 (m, 2H), 3.95−3.79 (m, 2H), 3.57 (d, J = 9.0 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 3H), 1.35 (d, J = 6.0 Hz, 3H), 1.27 (s, 3H), 1.24 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.0, 138.8, 138.6, 138.2, 128.6, 128.4, 128.36, 128.32, 127.9, 127.89, 127.80, 127.7, 127.6, 127.5, 127.48, 127.42, 111.8, 109.1, 105.2, 98.6, 84.1, 81.4, 80.0, 79.2, 76.3, 74.8, 74.7, 74.4, 73.5, 73.0, 72.9, 72.3, 70.9, 67.2, 27.1, 26.9, 26.3, 25.5, 16.6. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3703.

35α. Colorless syrup; $[\alpha]_D^{22}$ −2.2 (c 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.34−7.22 (m, 20H), 5.75 (d, J = 3.7 Hz, 1H), 5.00 (d, J = 11.6 Hz, 1H), 4.79 (d, J = 11.1 Hz, 1H), 4.74−4.65 (m, 3H), 4.55 (d, J = 11.2 Hz, 1H), 4.53−4.47 (m, 2H), 4.45−4.36 (m, 2H), 4.34 (dd, J = 4.8, 3.1 Hz, 1H), 4.23 (d, J = 3.1 Hz, 1H), 4.20 (d, J = 11.1 Hz, 1H), 4.12 (d, J = 2.7 Hz, 1H), 4.10−4.02 (m, 2H), 3.87 (dq, J = 8.8, 6.1 Hz, 1H), 3.73 (dd, J = 9.7, 7.7 Hz, 1H), 3.51 (dd, J = 9.6, 2.8 Hz, 1H), 3.10 (d, J = 8.6 Hz, 1H), 1.47 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.29 (d, J = 6.0 Hz, 3H), 1.21 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.5, 138.4, 138.3, 129.7, 128.5, 128.4, 128.2, 127.87, 127.81, 127.7, 127.6, 127.58, 127.51, 127.4, 111.8, 108.5, 105.2, 102.5, 82.8, 82.7, 80.9, 80.4, 79.4, 78.0, 75.3, 74.5, 73.5, 73.0, 72.7, 70.6, 65.9, 26.7, 26.6, 26.1, 25.4, 16.5. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3703.

*Benzyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranoside (**36**).* **36*α*** and **36*β*** were obtained from the reaction of donor **12** (25.0 mg, 36.90 μmol) and benzyl alcohol (4.2 μL, 40.60 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (12.6 mg, 53%), α/β = 1.6:1.

36β. Colorless syrup; $[\alpha]_D^{21}$ +64.4 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.43−7.21 (m, 25H), 5.08 (d, J = 11.5 Hz, 1H), 4.97−4.91 (m, 2H), 4.81−4.72 (m, 3H), 4.70 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.61−4.55 (m, 3H), 4.08 (dd, J = 10.0, 3.7 Hz, 1H), 4.02 (dd, J = 10.1, 2.6 Hz, 1H), 3.91 (d, J = 2.6 Hz, 1H), 3.83−3.73 (m, 2H), 0.99 (d, J = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.4, 138.9, 138.7, 138.6, 137.3, 128.6, 128.48, 128.41, 128.3, 128.2, 127.9, 127.8, 127.69, 127.63, 127.59, 127.55, 127.4, 94.6, 80.3, 76.6, 75.7, 75.56, 75.50, 74.3, 73.8, 73.0, 68.0, 16.7. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6Na$ [M + Na], 667.3030; found, 667.3023.

36α. Colorless syrup; $[\alpha]_D^{21}$ −12.4 (c 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.45−7.19 (m, 25H), 5.07 (d, J = 11.6 Hz, 1H), 5.01−4.93 (m, 2H), 4.83 (d, J = 11.7 Hz, 1H), 4.80−4.73 (m, 3H), 4.70−4.60 (m, 3H), 4.47 (d, J = 7.7 Hz, 1H), 3.94 (dd, J = 9.8, 7.7 Hz, 1H), 3.87 (dq, J = 8.2, 6.3 Hz, 1H), 3.78 (d, J = 2.8 Hz, 1H), 3.52 (dd, J = 9.8, 2.8 Hz, 1H), 3.24 (d, J = 8.2 Hz, 1H), 0.92 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.7, 138.5, 137.7, 128.5, 128.4, 128.3, 127.9, 127.75, 127.70, 127.6, 127.5, 102.8, 83.3, 79.8, 79.7, 75.2, 74.1, 74.1, 73.7, 73.3, 70.8, 16.8. HRMS (ESI): m/z calcd for $C_{42}H_{44}O_6Na$ [M + Na], 667.3030; found, 667.3021.

*Isopropyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranoside (**37**).* **37*α*** and **37*β*** were obtained from the reaction of donor **12** (40.0 mg, 59.10 μmol) and isopropyl alcohol (5.0 μL, 65.00 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (20.0 mg, 58%), α/β = 5.9:1.

37β. Colorless syrup; $[\alpha]_D^{23}$ +20.9 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.38 (m, 2H), 7.38−7.32 (m, 4H), 7.32−7.21 (m, 14H), 5.08 (d, J = 11.4 Hz, 1H), 5.01 (d, J = 3.8 Hz, 1H), 4.92 (d, J = 11.5 Hz, 1H), 4.84−4.73 (m, 2H), 4.68 (d, J = 11.4 Hz, 2H), 4.57 (dd, J = 11.6, 3.6 Hz, 2H), 4.07 (dd, J = 10.1, 3.9 Hz, 1H), 4.00−3.93 (m, 2H), 3.90 (dd, J = 2.7, 1.0 Hz, 1H), 3.78−3.70 (m, 2H), 1.21 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.1 Hz, 3H), 0.98 (d, J = 5.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.5, 139.0, 138.83, 138.80, 128.45, 128.41, 128.3, 128.2, 128.1, 127.7, 127.6, 127.55, 127.50, 127.2, 94.9, 80.2, 76.7, 75.9, 75.5, 75.4, 74.3, 73.7, 73.2, 73.0, 68.7, 23.2, 21.1, 16.8. HRMS (ESI): m/z calcd for $C_{38}H_{44}O_6Na$ [M + Na], 619.3030; found, 619.3036.

37α. Colorless syrup; $[\alpha]_D^{23}$ +3.2 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.35 (m, 4H), 7.35−7.23 (m, 16H), 5.05 (d, J = 11.6 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 4.84 (d, J = 11.7 Hz, 1H), 4.79−4.68 (m, 3H), 4.60 (dd, J = 11.6, 10.0 Hz, 2H), 4.42 (d, J = 7.8 Hz, 1H), 4.04 (hept, J = 6.1 Hz, 1H), 3.88−3.79 (m, 2H), 3.75 (dd, J = 2.8, 1.1 Hz, 1H), 3.51 (dd, J = 9.8, 2.8 Hz, 1H), 3.22 (dd, J = 8.3, 1.0 Hz, 1H), 1.30 (d, J = 6.2 Hz, 3H), 1.22 (d, J = 6.1 Hz, 3H), 0.89 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.9, 138.7, 128.5, 128.4, 128.37, 128.34, 128.30, 127.7, 127.69, 127.63, 127.60, 127.4, 102.5, 83.5, 79.7, 79.6, 75.24, 75.21, 74.2, 74.1, 73.8, 73.3, 72.1, 23.8, 22.2, 16.8. HRMS (ESI): m/z calcd for $C_{38}H_{44}O_6Na$ [M + Na], 619.3030; found, 619.3016.

*Adamantyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranoside (**38**).* **38*α*** and **38*β*** were obtained from the reaction of donor **12** (40.0 mg, 59.10 μmol) and 1-adamantanol (9.9 mg, 65.00 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:19); combined yield (20.0 mg, 70%), α/β = 4.1:1.

38β. Colorless syrup; $[\alpha]_D^{23}$ +23.1 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.19 (m, 20H), 5.38 (d, J

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= 3.9 Hz, 1H), 5.10 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.77 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 4.1 Hz, 2H), 4.65 (d, J = 11.3 Hz, 1H), 4.55 (dd, J = 11.5, 2.8 Hz, 2H), 4.06 (dd, J = 10.2, 3.8 Hz, 1H), 3.98 (dd, J = 10.0, 2.7 Hz, 1H), 3.92−3.87 (m, 2H), 3.74 (p, J = 6.4 Hz, 1H), 2.14−2.00 (m, 3H), 1.96−1.85 (m, 3H), 1.79 (dd, J = 9.0, 5.7 Hz, 3H), 1.54 (s, 6H), 1.02 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.3, 139.1, 138.97, 138.90, 128.4, 128.35, 128.30, 128.2, 128.1, 128.0, 127.6, 127.57, 127.55, 127.54, 127.46, 127.44, 127.2, 90.2, 80.1, 76.7, 76.0, 75.7, 74.9, 74.45, 74.40, 73.4, 73.1, 72.9, 42.5, 36.3, 30.7, 16.8. HRMS (ESI): m/z calcd for $C_{45}H_{52}O_6Na$ [M + Na], 711.3656; found, 711.3646.

38α. Colorless syrup; $[\alpha]_D^{23}$ +17.3 (c 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.22 (m, 20H), 5.05 (d, J = 11.6 Hz, 1H), 4.99 (d, J = 10.9 Hz, 1H), 4.84 (d, J = 11.6 Hz, 1H), 4.74 (d, J = 11.3 Hz, 2H), 4.69 (d, J = 11.3 Hz, 1H), 4.64 (d, J = 7.7 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.56 (d, J = 11.2 Hz, 1H), 3.85−3.77 (m, 2H), 3.75 (d, J = 2.8 Hz, 1H), 3.51 (dd, J = 9.9, 2.8 Hz, 1H), 3.20 (d, J = 8.3 Hz, 1H), 2.05 (br s, 3H), 1.95−1.89 (m, 3H), 1.86−1.79 (m, 3H), 1.61−1.52 (m, 6H), 0.88 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.9, 138.7, 128.5, 128.45, 128.41, 128.35, 128.30, 128.2, 127.8, 127.6, 127.5, 127.4, 96.6, 83.8, 79.7, 79.3, 75.3, 75.1, 75.0, 74.2, 74.1, 73.8, 73.2, 42.8, 36.3, 30.7, 16.7. HRMS (ESI): m/z calcd for $C_{45}H_{52}O_6Na$ [M + Na], 711.3656; found, 711.3647.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranosyl)-α-D-glucopyranoside (**39**)*. **39α** and **39β** were obtained from the reaction of donor **12** (30.0 mg, 44.30 μmol) and acceptor **23** (22.7 mg, 48.80 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (24.0 mg, 54%), α/β = 1.1:1.

39β. Colorless syrup; $[\alpha]_D^{23}$ +55.9 (c 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.31 (m, 8H), 7.30−7.17 (m, 27H), 5.10 (d, J = 3.7 Hz, 1H), 5.07 (d, J = 11.5 Hz, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 11.8 Hz, 1H), 4.79 (dd, J = 10.9, 5.9 Hz, 2H), 4.73 (d, J = 11.9 Hz, 1H), 4.73−4.64 (m, 4H), 4.59−4.50 (m, 5H), 4.07 (dd, J = 10.1, 3.6 Hz, 1H), 3.95 (t, J = 9.3 Hz, 1H), 3.94−3.83 (m, 2H), 3.82 (d, J = 3.6 Hz, 1H), 3.78−3.68 (m, 3H), 3.65 (d, J = 8.2 Hz, 1H), 3.61 (t, J = 9.5 Hz, 1H), 3.40 (dd, J = 9.6, 3.6 Hz, 1H), 3.29 (s, 3H), 0.93 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.6, 139.0, 138.9, 138.8, 138.5, 138.3, 128.49, 128.45, 128.42, 128.3, 128.2, 128.1, 128.09, 128.06, 127.97, 127.90, 127.7, 127.64, 127.60, 127.4, 127.3, 127.2, 98.0, 97.5, 82.1, 80.3, 79.4, 78.0, 75.8, 75.7, 75.5, 75.3, 75.1, 74.3, 73.4, 73.4, 72.8, 72.3, 70.6, 66.0, 55.0, 16.7. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4648.

39α. Colorless syrup; $[\alpha]_D^{23}$ +9.3 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.16 (m, 33H), 7.13−7.06 (m, 2H), 5.04 (d, J = 11.5 Hz, 1H), 4.98−4.91 (m, 2H), 4.84−4.73 (m, 5H), 4.71 (d, J = 11.7 Hz, 1H), 4.67−4.62 (m, 2H), 4.59−4.52 (m, 3H), 4.45 (d, J = 11.2 Hz, 1H), 4.35 (d, J = 7.6 Hz, 1H), 4.21 (dd, J = 10.8, 2.0 Hz, 1H), 3.96 (t, J = 9.3 Hz, 1H), 3.89 (dd, J = 9.8, 7.6 Hz, 1H), 3.86−3.78 (m, 2H), 3.76 (d, J = 2.7 Hz, 1H), 3.67 (dd, J = 10.8, 5.1 Hz, 1H), 3.54−3.43 (m, 3H), 3.27 (s, 3H), 3.22 (d, J = 8.0 Hz, 1H), 0.94 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.9, 138.7, 138.6, 138.5, 138.4, 138.2, 128.5, 128.48, 128.40, 128.37, 128.33, 128.30, 128.2, 128.19, 128.15, 128.0, 127.9, 127.67, 127.61, 127.5, 127.4, 104.3, 98.0, 83.3, 82.0, 79.9, 79.8, 79.4, 78.2, 75.7, 75.2, 74.9, 74.8, 74.3, 74.2, 73.5, 73.4, 73.2, 70.0, 68.6, 55.2, 17.0. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4648.

*6-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranosyl)-1,2:3,4-O-diisopropylidene-α-D-galactopyranose (**40**)*. **40α** and **40β** were obtained from the reaction of donor **12** (35.0 mg, 51.70 μmol) and acceptor **24** (14.8 mg, 56.90 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (24.7 mg, 60%), α/β = 1.7:1.

40β. Colorless syrup; $[\alpha]_D^{23}$ +28.3 (c 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 6.9 Hz, 4H), 7.35−7.22 (m, 16H), 5.53 (d, J = 5.0 Hz, 1H), 5.15 (d, J = 3.8 Hz, 1H), 5.05 (d, J = 11.4 Hz, 1H), 4.91 (d, J = 11.7 Hz, 1H), 4.79 (d, J = 11.9 Hz, 1H), 4.76 (d, J = 11.7 Hz, 1H), 4.73−4.68 (m, 2H), 4.58 (d, J = 4.4 Hz, 1H), 4.56 (d, J = 4.0 Hz, 1H), 4.53 (dd, J = 7.9, 2.4 Hz, 1H), 4.28 (dd, J = 5.1, 2.3 Hz, 1H), 4.16 (dd, J = 7.9, 1.9 Hz, 1H), 4.10 (dd, J = 10.0, 3.7 Hz, 1H), 4.04 (td, J = 6.9, 2.0 Hz, 1H), 3.97 (dd, J = 10.0, 2.7 Hz, 1H), 3.90−3.85 (m, 2H), 3.77−3.69 (m, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 0.98 (d, J = 6.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.5, 139.0, 138.8, 138.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.56, 127.52, 127.3, 127.2, 109.2, 108.5, 96.4, 96.1, 80.0, 76.4, 76.3, 75.7, 75.6, 75.35, 75.32, 75.2, 74.3, 73.7, 73.2, 72.9, 72.2, 70.9, 70.8, 70.7, 65.4, 65.1, 26.3, 26.1, 25.0, 24.6, 16.8. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3701.

40α. Colorless syrup; $[\alpha]_D^{23}$ −2.8 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.46−7.42 (m, 2H), 7.38−7.22 (m, 18H), 5.56 (d, J = 4.9 Hz, 1H), 5.06 (d, J = 11.2 Hz, 1H), 5.03 (d, J = 11.6 Hz, 1H), 4.87 (d, J = 11.7 Hz, 1H), 4.74 (dd, J = 11.6, 2.8 Hz, 3H), 4.61 (d, J = 5.1 Hz, 1H), 4.58 (d, J = 5.1 Hz, 2H), 4.55 (dd, J = 7.9, 2.4 Hz, 1H), 4.45 (d, J = 7.6 Hz, 1H), 4.29 (dd, J = 5.0, 2.4 Hz, 1H), 4.24−4.17 (m, 2H), 4.14−4.07 (m, 1H), 3.87 (dd, J = 9.8, 7.6 Hz, 1H), 3.82 (dq, J = 8.5, 6.3 Hz, 1H), 3.78−3.70 (m, 2H), 3.52 (dd, J = 9.8, 2.7 Hz, 1H), 3.25 (d, J = 8.1 Hz, 1H), 1.49 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 0.90 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 139.1, 138.7, 138.6, 128.7, 128.5, 128.4, 128.3, 128.29, 128.20, 127.8, 127.7, 127.69, 127.63, 127.5, 127.45, 127.42, 109.3, 108.6, 104.8, 96.4, 83.0, 79.7, 79.2, 79.1, 75.2, 74.7, 74.2, 74.1, 73.8, 73.4, 71.5, 70.8, 70.6, 69.8, 67.6, 26.1, 26.0, 25.1, 24.5, 16.8. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3698.

*Methyl 4-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**41**)*. **41α** and **41β** were obtained from the reaction of **12** (30.0 mg, 44.30 μmol) and acceptor **25** (10.6 mg, 48.80 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (23.0 mg, 69%), α/β = 1.8:1.

41β. Colorless syrup; $[\alpha]_D^{23}$ +30.5 (c 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.35 (m, 2H), 7.34−7.22 (m, 18H), 5.20 (d, J = 3.7 Hz, 1H), 5.04 (d, J = 11.2 Hz, 1H), 4.82−4.79 (m, 3H), 4.75−4.65 (m, 3H), 4.62−4.56 (m, 2H), 4.27 (dd, J = 7.2, 5.7 Hz, 1H), 4.09 (dd, J = 10.2, 3.7 Hz, 1H), 3.98 (d, J = 2.1 Hz, 1H), 3.97−3.93 (m, 2H), 3.96−3.94 (m, 2H), 3.67 (dq, J = 9.9, 6.3 Hz, 1H), 3.36 (dd, J = 9.9, 7.1 Hz, 1H), 3.33 (s, 3H), 1.43 (s, 3H), 1.32 (d, J =

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6.3 Hz, 3H), 1.17 (s, 3H), 1.11 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.7, 139.0, 138.9, 138.7, 128.4, 128.3, 128.29, 128.22, 127.98, 127.94, 127.6, 127.5, 127.45, 127.40, 127.3, 127.2, 109.0, 98.1 (2C), 81.6, 79.8, 75.7, 75.6, 75.4, 74.2, 73.9, 73.7, 73.0, 72.6, 64.5, 54.7, 28.2, 26.4, 17.9, 16.5. HRMS (ESI): m/z calcd for $C_{45}H_{54}O_{10}Na$ [M + Na], 777.3609; found, 777.3601.

41α. Colorless syrup; $[\alpha]_D^{23}$ −4.4 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.37 (m, 2H), 7.36−7.23 (m, 18H), 5.07 (d, J = 11.6 Hz, 1H), 4.93 (d, J = 11.2 Hz, 1H), 4.87 (d, J = 7.8 Hz, 1H), 4.85−4.81 (m, 2H), 4.76−4.68 (m, 3H), 4.63−4.55 (m, 2H), 4.23 (t, J = 6.4 Hz, 1H), 4.07 (d, J = 5.8 Hz, 1H), 3.85−3.70 (m, 5H), 3.65 (dq, J = 9.7, 6.1 Hz, 1H), 3.55 (dd, J = 9.8, 2.9 Hz, 1H), 3.38 (s, 3H), 3.23 (d, J = 7.9 Hz, 1H), 1.39 (s, 3H), 1.36 (d, J = 6.2 Hz, 3H), 1.29 (s, 3H), 0.95 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 138.9, 138.7, 128.44, 128.41, 128.3, 128.28, 128.20, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 109.3, 102.3, 98.2, 83.3, 79.8, 79.3, 78.7, 78.4, 75.9, 75.1, 74.9, 74.8, 74.2, 73.7, 73.1, 64.5, 54.9, 27.9, 26.3, 18.1, 16.8. HRMS (ESI): m/z calcd for $C_{45}H_{54}O_{10}Na$ [M + Na], 777.3609; found, 777.3592.

*Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranosyl)-α-D-gluco-pyranoside (**42**).* **42*α*** and **42*β*** were obtained from the reaction of **12** (30.0 mg, 44.30 μmol) and acceptor **26** (22.7 mg, 48.80 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (26.0 mg, 59%), α/β = 1:3.9.

42β. Colorless syrup; $[\alpha]_D^{23}$ +28.2 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.15 (m, 35H), 5.70 (d, J = 3.9 Hz, 1H), 5.02 (d, J = 11.4 Hz, 1H), 4.93 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 11.6 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.69−4.61 (m, 4H), 4.59−4.49 (m, 6H), 4.37 (d, J = 12.3 Hz, 1H), 4.05−3.99 (m, 2H), 3.91−3.86 (m, 1H), 3.82−3.76 (m, 3H), 3.75−3.65 (m, 2H), 3.60 (dd, J = 10.6, 6.5 Hz, 1H), 3.56 (d, J = 8.2 Hz, 1H), 3.43 (dd, J = 9.6, 3.5 Hz, 1H), 3.36 (s, 1H), 0.93 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.5, 139.2, 138.7, 138.6, 138.4, 138.2, 128.4, 128.3, 128.29, 128.25, 127.9, 127.8, 127.74, 127.71, 127.6, 127.56, 127.50, 127.4, 127.2, 127.0, 126.9, 97.6, 97.1, 81.9, 80.2, 80.0, 76.0, 75.8, 75.6, 75.4, 74.3, 74.0, 73.5, 73.4, 73.4, 73.1, 72.8, 70.4, 69.6, 55.1, 16.5. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4630.

42α. Colorless syrup; $[\alpha]_D^{23}$ +26.2 (c 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.37 (m, 2H), 7.37−7.10 (m, 31H), 7.07−7.02 (m, 2H), 5.16 (d, J = 11.2 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 4.87−4.70 (m, 7H), 4.68 (d, J = 10.6 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.54−4.49 (m, 3H), 4.38 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 7.7 Hz, 1H), 4.08 (d, J = 12.2 Hz, 1H), 3.94 (t, J = 9.6 Hz, 1H), 3.86−3.75 (m, 4H), 3.70 (p, J = 6.6 Hz, 1H), 3.60 (dt, J = 10.2, 2.7 Hz, 1H), 3.55 (dd, J = 10.6, 2.0 Hz, 1H), 3.39−3.32 (m, 4H), 3.19 (dd, J = 9.7, 3.7 Hz, 1H), 3.07 (d, J = 7.8 Hz, 1H), 1.01 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 140.2, 139.4, 139.0, 138.68, 138.62, 138.1, 129.0, 128.48, 128.40, 128.29, 128.25, 128.1, 128.0, 127.99, 127.93, 127.7, 127.67, 127.62, 127.5, 127.48, 127.42, 127.1, 126.7, 102.5, 98.7, 83.4, 80.5, 80.26, 80.21, 78.9, 75.9, 75.7, 75.2, 74.7, 74.6, 73.9, 73.5, 73.3, 73.2, 70.3, 68.1, 55.3, 17.7. HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ [M + Na], 1023.4653; found, 1023.4633.

*3-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-galacto-heptopyranosyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**43**).* **43*α*** and **43*β*** were obtained from the reaction of **12** (60.0 mg, 88.60 μmol) and acceptor **27** (25.4 mg, 97.60 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:4); combined yield (44.0 mg, 61%), α/β = 1:10.2.

43β. Colorless syrup; $[\alpha]_D^{23}$ +14.0 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.39−7.19 (m, 20H), 5.83 (d, J = 3.6 Hz, 1H), 5.19 (d, J = 3.7 Hz, 1H), 5.08 (d, J = 11.4 Hz, 1H), 4.91 (d, J = 3.6 Hz, 1H), 4.88 (d, J = 11.7 Hz, 1H), 4.78−4.72 (m, 3H), 4.71−4.66 (m, 1H), 4.55 (dd, J = 11.8, 5.7 Hz, 2H), 4.47 (q, J = 6.3 Hz, 1H), 4.19 (dd, J = 6.8, 2.8 Hz, 1H), 4.15 (d, J = 2.8 Hz, 1H), 4.11−4.04 (m, 2H), 4.01 (dd, J = 8.5, 5.3 Hz, 1H), 3.88−3.83 (m, 2H), 3.76 (dq, J = 8.2, 6.3 Hz, 1H), 3.61 (d, J = 8.3 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.21 (s, 3H), 1.02−0.91 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.76, 138.71, 138.6, 128.49, 128.40, 128.29, 128.25, 128.1, 127.7, 127.68, 127.61, 127.5, 127.3, 111.6, 108.8, 105.3, 99.5, 82.9, 82.8, 81.0, 79.5, 76.1, 75.6, 75.5, 74.4, 73.6, 73.2, 73.0, 72.8, 66.7, 26.9, 26.8, 26.0, 25.3, 16.7. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3712.

43α. Colorless syrup; $[\alpha]_D^{23}$ −14.8 (c 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.26 (m, 20H), 5.73 (d, J = 3.7 Hz, 1H), 5.06 (d, J = 11.6 Hz, 1H), 4.83−4.68 (m, 5H), 4.61 (d, J = 11.6 Hz, 1H), 4.57 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 3.8 Hz, 1H), 4.43 (dd, J = 6.8, 4.1 Hz, 2H), 4.35 (d, J = 3.2 Hz, 1H), 4.30 (dd, J = 5.1, 3.1 Hz, 1H), 4.11−4.02 (m, 2H), 3.85−3.74 (m, 3H), 3.52 (dd, J = 9.7, 2.8 Hz, 1H), 3.24 (d, J = 8.1 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.20 (s, 3H), 0.93 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.0, 138.6, 138.5, 138.3, 128.55, 128.50, 128.3, 128.04, 128.01, 127.8, 127.74, 127.70, 127.6, 127.5, 111.7, 108.6, 105.2, 101.7, 83.3, 82.7, 80.3, 80.1, 80.0, 79.3, 75.3, 74.5, 74.3, 74.2, 73.6, 73.3, 66.0, 26.7, 26.6, 26.1, 25.4, 16.9. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3704.

*Isopropyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α-D-gluco-heptopyranoside (**44**).* **44*α*** was obtained from the reaction of **17** (35.0 mg, 51.70 μmol) and acceptor isopropyl alcohol (4.4 μL, 56.10 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 3:97); yield (17.2 mg, 57%), only α.

44α. Colorless syrup; $[\alpha]_D^{20}$ +15.7 (c 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.42−7.19 (m, 18H), 7.13 (d, J = 7.2 Hz, 2H), 4.96 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 10.8 Hz, 1H), 4.82 (d, J = 10.9 Hz, 1H), 4.76−4.63 (m, 3H), 4.39 (m, 3H), 4.06−3.93 (m, 2H), 3.83 (t, J = 9.2 Hz, 1H), 3.62 (t, J = 9.1 Hz, 1H), 3.46 (t, J = 8.5 Hz, 1H), 3.19−3.10 (m, 1H), 1.32 (d, J = 6.4 Hz, 3H), 1.30 (d, J = 6.1 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.8, 138.73, 138.72, 128.44, 128.41, 128.3, 128.0, 127.9, 127.7, 127.65, 127.61, 127.5, 102.9, 85.4, 82.4, 78.0, 77.7, 75.7, 74.8, 74.7, 72.5, 71.4, 70.5, 23.8, 22.3, 15.6; HRMS (ESI): m/z calcd for $C_{38}H_{44}O_6Na$ $[M + Na]^+$, 619.3030; found, 619.3007.

*Adamantyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α-D-gluco-heptopyranoside (**45**).* **45*α*** was obtained from the reaction of **17** (35.0 mg, 51.70 μmol) and 1-adamantanol (8.6 mg, 56.10 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 5:95); yield (19.8 mg, 56%), only α.

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45α. Colorless syrup; $[\alpha]_D^{20}$ +13.6 (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.18 (m, 18H), 7.14 (dd, *J* = 8.8, 7.3 Hz, 2H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.75−4.64 (m, 3H), 4.60 (d, *J* = 7.8 Hz, 1H), 4.42−4.33 (m, 2H), 3.96 (tt, *J* = 6.4, 3.2 Hz, 1H), 3.82 (t, *J* = 9.3 Hz, 1H), 3.62 (dd, *J* = 12.2, 6.0 Hz, 1H), 3.49−3.41 (m, 1H), 3.13 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.14 (s, 3H), 1.92 (d, *J* = 11.3 Hz, 3H), 1.80 (d, *J* = 11.4 Hz, 3H), 1.68−1.58 (m, 6H), 1.30 (t, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.73, 138.71, 138.69, 138.66, 134.5, 133.7, 130.2, 129.8, 129.0, 128.5, 128.35, 128.31, 128.27, 128.25, 128.24, 128.0, 127.95, 127.56, 127.54, 127.4, 96.8, 85.6, 82.2, 77.9, 77.7, 75.7, 74.9, 74.9, 74.6, 71.2, 70.4, 45.3, 45.3, 42.9, 42.8, 36.3, 36.1, 30.7, 30.7, 30.7, 15.9; HRMS (ESI): *m*/*z* calcd for $C_{45}H_{52}O_6Na$ $[M + Na]^+$, 711.3656; found, 711.3642.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranosyl)-α-D-glucopyranoside (**46**)*. **46α** and **46β** were obtained from the reaction of donor **17** (35.0 mg, 51.70 μmol) and acceptor **23** (26.0 mg, 56.93 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (25.0 mg, 49%), α/β = 23.6:1.

46β. Colorless syrup; $[\alpha]_D^{20}$ +6.0 (*c* 0.1, $CHCl_3$); ^1H NMR (900 MHz, $CDCl_3$): δ 7.71−6.93 (m, 35H), 5.04 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.95 (dd, *J* = 10.9, 7.0 Hz, 2H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.6 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.70−4.63 (m, 4H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 3.6 Hz, 1H), 4.33 (dd, *J* = 11.5, 5.7 Hz, 2H), 4.01 (t, *J* = 9.3 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 1H), 3.83−3.77 (m, 2H), 3.77−3.73 (m, 1H), 3.71−3.65 (m, 2H), 3.58 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.54 (dd, *J* = 9.8, 1.7 Hz, 1H), 3.47 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.37 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (226 MHz, $CDCl_3$): δ 138.8, 138.79, 138.6, 138.5, 138.4, 138.3, 128.5, 128.45, 128.43, 128.41, 128.37, 128.33, 128.27, 128.21, 128.1, 128.02, 128.01, 128.0, 127.9, 127.8, 127.7, 127.66, 127.63, 127.61, 127.59, 127.57, 127.4, 127.3, 97.9, 97.0, 82.2, 80.2, 79.9, 77.8, 77.6, 77.2, 75.7, 75.6, 75.0, 74.6, 73.4, 73.4, 72.3, 71.2, 70.8, 70.3, 65.8, 55.1, 14.1; HRMS (ESI): *m*/*z* calcd for $C_{63}H_{72}O_{11}N$ $[M + NH_4]^+$, 1018.5073; found, 1018.5068.

46α. Colorless syrup; $[\alpha]_D^{20}$ +25.3 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.71−6.93 (m, 35H), 4.97 (ddd, *J* = 10.1, 7.3, 2.0 Hz, 2H), 4.90 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.83−4.60 (m, 8H), 4.58 (t, *J* = 2.8 Hz, 1H), 4.51 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.41 (dd, *J* = 10.9, 2.0 Hz, 1H), 4.35 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.28 (dd, *J* = 7.8, 2.0 Hz, 1H), 4.18 (dd, *J* = 10.8, 2.3 Hz, 1H), 3.98 (td, *J* = 9.1, 2.2 Hz, 2H), 3.90−3.79 (m, 2H), 3.66−3.57 (m, 2H), 3.50 (ddd, *J* = 9.3, 6.2, 2.9 Hz, 2H), 3.47−3.40 (m, 1H), 3.30 (d, *J* = 1.9 Hz, 3H), 3.11 (d, *J* = 9.5 Hz, 1H), 1.31 (dd, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.8, 138.6, 138.5, 138.4, 138.1, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 127.5, 127.49, 127.41, 104.6, 97.9, 85.2, 82.1, 82.0, 79.9, 78.2, 77.8, 77.6, 75.7, 75.6, 74.8, 74.8, 74.7, 73.3, 71.5, 70.3, 70.0, 68.9, 55.2, 15.4; HRMS (ESI): *m*/*z* calcd for $C_{63}H_{68}O_{11}Na$ $[M + Na]^+$, 1023.4653; found, 1023.4614.

*Methyl 4-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**47**)*. **47α** and **47β** were obtained from the reaction of **17** (80.0 mg, 0.12 mmol) and acceptor **25** (28.3 mg, 0.13 mmol) following the general procedure for glycosylation (ethyl acetate/hexane, 7:93); combined yield (57.4 mg, 63%), α/β = 7.9:1.

47β. Colorless syrup; $[\alpha]_D^{20}$ +7.4 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.71−7.06 (m, 20H), 5.11 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 10.6 Hz, 1H), 4.90−4.73 (m, 4H), 4.68 (dd, *J* = 11.7, 4.4 Hz, 2H), 4.39−4.33 (m, 2H), 4.17−4.06 (t, *J* = 6.5 Hz, 1H), 4.11−4.10 (d, *J* = 6.02 Hz, 1H), 4.05−3.98 (m, 2H), 3.85−3.79 (m, 2H), 3.74−3.69 (m, 1H), 3.61−3.59 (dd, *J* = 9.88, 3.42 Hz, 1H), 3.36 (s, 3H), 3.30 (dd, *J* = 10.0, 6.6 Hz, 1H), 1.48 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.29 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.7, 138.7, 138.5, 138.2, 129.7, 128.5, 128.4, 128.2, 128.17, 128.15, 127.8, 127.65, 127.61, 127.5, 109.1, 98.5, 98.2, 83.1, 82.2, 80.5, 78.1, 77.4, 75.7, 74.9, 74.1, 73.9, 71.8, 70.7, 64.6, 54.8, 28.1, 26.2, 17.9, 15.7; HRMS (ESI): *m*/*z* calcd for $C_{45}H_{54}O_{10}Na$ $[M + Na]^+$, 777.3609; found, 777.3598.

47α. Colorless syrup; $[\alpha]_D^{20}$ +13.5 (*c* l.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.09−6.21 (m, 20H), 4.92 (dd, *J* = 11.0, 6.0 Hz, 2H), 4.88−4.80 (m, 3H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.69−4.63 (m, 2H), 4.47 (d, *J* = 10.9 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.21 (t, *J* = 6.0 Hz, 1H), 4.09 (d, *J* = 5.7 Hz, 1H), 4.00 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.84 (t, *J* = 9.3 Hz, 1H), 3.71−3.60 (m, 3H), 3.42 (t, *J* = 8.5 Hz, 1H), 3.38 (s, 3H), 3.17 (dd, *J* = 9.7, 2.1 Hz, 1H), 1.49 (s, 3H), 1.36 (d, *J* = 4.9 Hz, 3H), 1.33−1.32 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.9, 138.8, 138.7, 128.4, 128.4, 128.37, 128.32, 127.9, 127.7, 127.68, 127.64, 127.62, 127.57, 127.50, 109.4, 102.4, 98.1, 85.3, 82.4, 79.0, 78.4, 77.9, 77.7, 76.0, 75.6, 74.8, 74.7, 71.4, 70.1, 64.3, 54.9, 28.1, 26.3, 18.1, 15.7; HRMS (ESI): *m*/*z* calcd for $C_{45}H_{54}O_{10}Na$ $[M + Na]^+$, 777.3609; found, 777.3585.

*Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranosyl)-α-D-glucopyranoside (**48**)*. **48α** and **48β** were obtained from the reaction of **17** (80.0 mg, 0.12 mmol) and acceptor **26** (60.0 mg, 0.13 mmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (71.0 mg, 59%), α/β = 7.7:1.

48β. Colorless syrup; $[\alpha]_D^{20}$ +30.0 (*c* 0.1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.98−6.79 (m, 35H), 5.70 (d, *J* = 3.5 Hz, 1H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.92−4.83 (m, 2H), 4.80 (dd, *J* = 11.9, 8.9 Hz, 1H), 4.73 (d, *J* = 10.6 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.63−4.59 (m, 2H), 4.59−4.53 (m, 3H), 4.51−4.45 (m, 2H), 4.37−4.32 (m, 2H), 4.06 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.90 (dd, *J* = 9.9, 8.4 Hz, 1H), 3.88−3.82 (m, 2H), 3.81−3.71 (m, 2H), 3.69 (dd, *J* = 10.7, 2.3 Hz, 1H), 3.58 (ddd, *J* = 8.1, 6.0, 3.5 Hz, 2H), 3.54 (dd, *J* = 9.8, 1.9 Hz, 1H), 3.51 (dd, *J* = 9.9, 3.5 Hz, 1H), 3.38 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 139.0, 138.9, 138.6, 138.3, 138.1, 138.0, 137.9, 128.4, 128.38, 128.34, 128.30, 128.26, 128.21, 128.19, 128.12, 128.0, 127.9, 127.7, 127.65, 127.64, 127.57, 127.50, 126.8, 97.8, 96.2, 82.3, 82.1, 80.2, 79.7, 77.8, 75.6, 74.7, 74.3, 74.1, 73.4, 73.4, 73.2, 72.4, 71.4, 70.6, 69.6, 69.1, 55.1, 15.2; HRMS (ESI): *m*/*z* calcd for $C_{63}H_{68}O_{11}Na$ $[M + Na]^+$, 1023.4653; found, 1023.4615.

48α. Colorless syrup; $[\alpha]_D^{20}$ +23.0 (*c* 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.44−7.38 (m, 2H), 7.34−7.21 (m, 28H), 7.20−7.15 (m, 2H), 7.14−7.06 (m, 3H), 5.19 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.85−4.71 (m, 6H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.61 (m, 2H), 4.58−4.56 (m, 2H), 4.49 (d, *J* = 11.1 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H),

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4.34 (d, J = 7.8 Hz, 1H), 4.03−3.90 (m, 2H), 3.86 (q, J = 9.5 Hz, 3H), 3.58 (d, J = 10.0 Hz, 1H), 3.52−3.45 (m, 3H), 3.40 (t, J = 8.5 Hz, 1H), 3.35 (s, 3H), 3.02 (dd, J = 9.7, 2.1 Hz, 1H), 1.30 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.8, 138.9, 138.8, 138.7, 138.6, 138.0, 128.6, 128.5, 128.49, 128.41, 128.38, 128.32, 128.2, 128.1, 128.0, 127.91, 127.88, 127.75, 127.6, 127.5, 127.35, 127.31, 127.0, 102.9, 98.6, 85.4, 83.0, 80.9, 79.0, 77.9, 77.8, 75.7, 75.7, 74.9, 74.7, 73.8, 73.5, 72.1, 70.3, 69.9, 67.9, 55.4, 15.3; HRMS (ESI): m/z calcd for $C_{63}H_{72}O_{11}N$ $[M + NH_4]^+$, 1018.5100; found, 1018.5063.

*3-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranosyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**49**).* **49α** and **49β** were obtained from the reaction of **17** (40.0 mg, 59.10 μmol) and acceptor **27** (16.9 mg, 65.00 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (30.0 mg, 63%), α/β = 1.7:1.

49β. Colorless syrup; $[\alpha]_D^{22}$ +40.9 (c 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35−7.22 (m, 18H), 7.16−7.12 (m, 2H), 5.87 (d, J = 3.7 Hz, 1H), 5.39 (d, J = 3.5 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 4.84 (d, J = 10.6 Hz, 1H), 4.79−4.74 (m, 2H), 4.71−4.64 (m, 2H), 4.58 (d, J = 3.7 Hz, 1H), 4.46 (ddd, J = 8.6, 6.1, 4.5 Hz, 1H), 4.36 (d, J = 11.6 Hz, 1H), 4.30 (d, J = 10.7 Hz, 1H), 4.25 (d, J = 2.8 Hz, 1H), 4.09 (dd, J = 8.5, 2.8 Hz, 1H), 4.06−3.99 (m, 3H), 3.95 (t, J = 9.4 Hz, 1H), 3.78 (t, J = 9.4 Hz, 1H), 3.60 (dd, J = 9.8, 3.6 Hz, 1H), 3.54 (dd, J = 9.8, 1.4 Hz, 1H), 1.48 (s, 3H), 1.42−1.34 (m, 6H), 1.27 (s, 3H), 1.24 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.6, 138.3, 138.1, 128.56, 128.50, 128.1, 128.0, 127.9, 127.89, 127.84, 127.80, 127.7, 127.6, 111.8, 109.2, 105.2, 97.5, 84.2, 81.9, 81.4, 79.9, 79.6, 77.7, 75.7, 75.2, 74.5, 73.0, 72.3, 71.1, 70.9, 67.3, 27.1, 26.8, 26.2, 25.6, 15.7. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3724.

49α. Colorless syrup; $[\alpha]_D^{22}$ +6.7 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.34−7.21 (m, 18H), 7.17 (dd, J = 7.8, 1.8 Hz, 2H), 5.76 (d, J = 3.7 Hz, 1H), 4.90 (d, J = 10.9 Hz, 1H), 4.85−4.76 (m, 2H), 4.73 (s, 2H), 4.65 (d, J = 11.7 Hz, 1H), 4.52−4.44 (m, 3H), 4.43−4.34 (m, 3H), 4.27 (d, J = 3.0 Hz, 1H), 4.12−4.03 (m, 2H), 4.01 (qd, J = 6.4, 2.0 Hz, 1H), 3.85 (t, J = 9.3 Hz, 1H), 3.64 (t, J = 9.1 Hz, 1H), 3.40 (dd, J = 9.2, 7.8 Hz, 1H), 3.17 (dd, J = 9.6, 2.1 Hz, 1H), 1.48 (s, 3H), 1.42 (s, 3H), 1.34 (d, J = 6.5 Hz, 3H), 1.29 (s, 3H), 1.23 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.7, 138.5, 138.4, 138.3, 128.5, 128.49, 128.40, 127.89, 127.86, 127.80, 127.77, 127.73, 127.70, 127.6, 127.5, 111.9, 108.5, 105.2, 102.2, 85.1, 82.9, 82.2, 80.8, 80.4, 78.1, 77.5, 75.7, 75.0, 74.9, 73.5, 71.4, 70.1, 65.9, 26.7, 26.7, 26.1, 25.2, 15.3. HRMS (ESI): m/z calcd for $C_{47}H_{56}O_{11}Na$ [M + Na], 819.3714; found, 819.3729.

*Isopropyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-gluco-heptopyranoside (**50**).* **50α** and **50β** were obtained from the reaction of donor **19** (35.0 mg, 51.70 μmol) and acceptor isopropyl alcohol (4.4 μL, 56.10 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 3:97); combined yield (18.5 mg, 61%), α/β = 1.2:1.

50β. Colorless syrup; $[\alpha]_D^{20}$ +38.4 (c 0.1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.82−6.79 (m, 20H), 5.02 (d, J = 10.8 Hz, 1H), 4.89 (d, J = 3.6 Hz, 1H), 4.80 (d, J = 10.7 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 11.3 Hz, 2H), 4.59−4.51 (m, 3H), 4.07−4.00 (m, 2H), 3.96 (dd, J = 8.8, 3.9 Hz, 1H), 3.78 (d, J = 6.7 Hz, 1H), 3.53−3.46 (m, 1H), 3.35−3.29 (m, 1H), 1.27 (dd, J = 6.3, 1.7 Hz, 3H), 1.17 (dd, J = 6.2, 1.7 Hz, 3H), 1.07 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.9, 138.7, 138.3, 138.0, 128.45, 128.42, 128.38, 128.3, 128.2, 128.14, 128.12, 128.0, 127.9, 127.8, 127.64, 127.60, 127.5, 127.4, 94.2, 82.5, 80.3, 78.6, 76.8, 75.8, 74.8, 73.1, 73.0, 72.1, 70.9, 70.6, 69.5, 68.5, 23.3, 21.0, 13.9; HRMS (ESI): m/z calcd for $C_{38}H_{44}O_6Na$ $[M + Na]^+$, 619.3030; found, 619.3011.

50α. Colorless syrup; $[\alpha]_D^{20}$ +6.9 (c 0.1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.66−7.17 (m, 18H), 7.17 (dd, J = 6.7, 2.9 Hz, 2H), 5.00 (d, J = 10.8 Hz, 1H), 4.96 (d, J = 10.9 Hz, 1H), 4.84 (d, J = 10.9 Hz, 1H), 4.79 (d, J = 10.9 Hz, 1H), 4.72 (d, J = 10.9 Hz, 1H), 4.62−4.56 (m, 2H), 4.48 (d, J = 7.8 Hz, 1H), 4.06−4.02 (m, 2H), 3.84 (qd, J = 6.6, 1.5 Hz, 1H), 3.67 (t, J = 9.0 Hz, 1H), 3.54 (dd, J = 9.9, 1.5 Hz, 1H), 3.42 (ddd, J = 9.9, 8.2, 3.4 Hz, 2H), 1.34 (d, J = 6.2 Hz, 3H), 1.27 (d, J = 6.1 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.9, 138.6, 138.5, 138.0, 128.5, 128.4, 128.39, 128.31, 128.27, 128.21, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 102.4, 85.3, 82.5, 78.1, 76.8, 76.0, 75.7, 74.8, 74.6, 73.6, 72.6, 70.6, 29.7, 23.9, 22.4, 14.4; ESI-HRMS: m/z calcd for $C_{38}H_{44}O_6Na$ $[M + Na]^+$, 619.3030; found, 619.3009.

*Adamantyl 2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-gluco-heptopyranoside (**51**).* **51α** and **51β** were obtained from the reaction of donor **19** (35.0 mg, 51.70 μmol) and 1-adamantanol (8.6 mg, 56.10 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 5:95) as colorless syrup; combined yield (18.2 mg, 52%), α/β = 1.1:1.

51α/β. ^1H NMR (600 MHz, $CDCl_3$): δ 7.99−6.88 (m, 40H), 5.31 (d, J = 3.7 Hz, 1H), 5.04 (dd, J = 10.9, 4.5 Hz, 2H), 4.95 (d, J = 10.8 Hz, 1H), 4.88−4.79 (m, 4H), 4.72 (dd, J = 9.6, 6.7 Hz, 5H), 4.64−4.54 (m, 6H), 4.23 (dd, J = 10.4, 1.5 Hz, 1H), 4.09 (t, J = 9.2 Hz, 1H), 3.82 (qt, J = 7.3, 3.5 Hz, 2H), 3.68 (t, J = 8.9 Hz, 1H), 3.55 (dd, J = 10.1, 1.7 Hz, 1H), 3.49 (dd, J = 9.7, 3.7 Hz, 1H), 3.46−3.33 (m, 3H), 2.17−2.13 (m, 8H), 1.97−1.92 (m, 7H), 1.89−1.81 (m, 8H), 1.68−1.59 (m, 12H), 1.16 (d, J = 6.6 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 139.0, 138.9, 138.7, 138.6, 138.3, 138.1, 128.4, 128.39, 128.36, 128.24, 128.22, 128.14, 128.06, 128.0, 127.94, 127.90, 127.75, 127.72, 127.58, 127.54, 127.51, 127.4, 127.3, 127.28, 127.25, 96.5, 89.5, 85.7, 82.5, 82.4, 80.5, 78.9, 78.3, 77.2, 75.7, 75.6, 75.6, 74.8, 74.8, 74.6, 74.5, 73.7, 72.7, 70.7, 70.5, 70.5, 42.8, 42.5, 36.3, 36.3, 30.7, 30.7, 29.7, 22.7, 14.4, 14.3; HRMS (ESI): m/z calcd for $C_{45}H_{52}O_6Na$ $[M + Na]^+$, 711.3656; found, 711.3621.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-gluco-heptopyranosyl)-α-D-glucopyranoside (**52**).* **52α** and **52β** were obtained from the reaction of donor **19** (35.0 mg, 51.70 μmol) and acceptor **23** (26.0 mg, 56.10 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (45.0 mg, 60%), α/β = 1.1:1.

52β. Colorless syrup; $[\alpha]_D^{20}$ +6.0 (c 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.48−6.58 (m, 35H), 4.99 (d, J = 3.5 Hz, 1H), 4.94 (dd, J = 10.9, 2.0 Hz, 2H), 4.89 (d, J = 11.0 Hz, 1H), 4.84 (d, J = 11.1, 1H), 4.80 (d, J = 10.9 Hz, 1H), 4.75 (d, J = 10.8 Hz, 1H), 4.70−4.58 (m, 4H), 4.57−4.46 (m, 4H), 4.42 (d, J = 12.2 Hz, 1H), 4.03−3.92 (m, 3H), 3.85 (dd, J = 11.6, 4.7 Hz, 1H), 3.78−3.73 (m, 3H), 3.62 (t, J = 9.4 Hz, 1H), 3.51−3.44 (m, 1H), 3.41−3.38 (m, 1H), 3.34

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(s, 3H), 3.32−3.25 (m, 1H), 1.05 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.0, 138.8, 138.7, 138.6, 138.55, 138.53, 138.3, 128.5, 128.46, 128.43, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 98.0, 96.8, 82.2, 80.4, 80.3, 78.3, 78.0, 75.8, 75.2, 74.6, 73.5, 73.3, 72.2, 71.0, 70.6, 70.5, 65.8, 55.2, 14.1; HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ $[M + Na]^+$, 1023.4653; found, 1023.4622.

52α. Colorless syrup; $[\alpha]_D^{20}$ −1.6 (c 0.7, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.67−6.28 (m, 35H), 4.99 (dd, J = 11.0, 5.7 Hz, 2H), 4.94 (d, J = 10.8 Hz, 1H), 4.89−4.76 (m, 5H), 4.73−4.63 (m, 3H), 4.58 (d, J = 9.1 Hz, 2H), 4.51 (d, J = 11.1 Hz, 1H), 4.34 (d, J = 7.7 Hz, 1H), 4.25 (dd, J = 10.6, 1.6 Hz, 1H), 4.01 (t, J = 9.3 Hz, 1H), 3.86−3.81 (m, 2H), 3.75−3.65 (m, 2H), 3.63−3.45 (m, 4H), 3.43 (d, J = 9.2 Hz, 1H), 3.36 (s, 3H), 1.15 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.9, 138.8, 138.5, 138.4, 138.3, 138.1, 137.9, 128.5, 128.4, 128.38, 128.36, 128.33, 128.24, 128.20, 128.1, 128.08, 128.03, 128.01, 127.96, 127.92, 127.89, 127.85, 127.78, 127.75, 127.6, 127.5, 127.4, 103.8, 98.1, 85.3, 82.2, 82.0, 79.7, 78.1, 77.9, 76.3, 75.8, 75.7, 74.9, 74.9, 74.6, 73.7, 73.4, 70.7, 69.8, 68.3, 55.2, 53.4, 53.2, 53.0, 52.9, 52.7, 14.5; HRMS (ESI): m/z calcd for $C_{63}H_{68}O_{11}Na$ $[M + Na]^+$, 1023.4653; found, 1023.4620.

General Procedure for VT ^1H NMR Experiment. A solution of **9**, **12**, **17**, or **19** (20.0 mg, 0.03 mmol) in CD_2Cl_2 (0.7 mL) containing TTBP (7.3 mg, 0.03 mmol) was placed into an NMR tube and cooled to −80 °C in the NMR probe. The first ^1H spectrum was obtained; then, the sample was quickly removed from the probe, and the addition of Tf_2O (9.9 μL, 0.06 mmol) precooled at −78 °C was carried out quickly. The sample was returned to the NMR probe, and the ^1H spectrum was recorded after 10 min. The temperature was increased by 10 °C increments every 10 min, and ^1H NMR spectra were acquired at each temperature.

*1-O-(2,3,4,6-Tetra-O-benzyl-7-deoxy-D-glycero-α/β-D-galacto-heptopyranosyl)-2,3,4,6-tetra-O-benzyl-7-deoxy-D-glycero-β-D-galacto-heptopyranoside (**56** & **57**)*. These compounds were obtained from the decomposition of donor **9** when variable temperature NMR studies were carried out following the general procedure for VT study. The reaction mixture was quenched with triethylamine (20 μL) at rt, diluted with dichloromethane (5 mL), and washed with saturated $NaHCO_3$ (2 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (4:1, hexane/ethyl acetate) afforded the desired product as colorless syrup (7.0 mg, 43%) in a 1:1.5 ratio of α/β anomers.

56β. Colorless syrup; $[\alpha]_D^{23}$ +29.5 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35−7.15 (m, 40H), 5.26 (d, J = 3.5 Hz, 2H), 4.97 (d, J = 11.2 Hz, 2H), 4.75 (s, 8H), 4.53 (d, J = 11.4 Hz, 2H), 4.46 (d, J = 11.2 Hz, 2H), 4.23 (d, J = 2.6 Hz, 2H), 4.19 (d, J = 11.4 Hz, 2H), 4.14 (dd, J = 10.1, 3.5 Hz, 2H), 4.06 (dd, J = 10.1, 2.6 Hz, 2H), 3.89−3.78 (m, 4H), 1.21 (d, J = 5.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.2, 138.96, 138.90, 138.6, 128.3, 128.2, 128.0, 127.7, 127.5, 127.49, 127.43, 127.3, 92.3, 79.5, 75.7, 74.7, 73.8, 73.6, 72.8, 72.6, 70.2, 16.2. HRMS (ESI): m/z calcd for $C_{70}H_{74}O_{11}Na$ $[M + Na]$, 1113.5123; found, 1113.5115.

57α. Colorless syrup; $[\alpha]_D^{23}$ +4.9 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.13 (m, 40H), 5.24 (d, J = 3.0 Hz, 1H), 5.05−4.94 (m, 3H), 4.77 (d, J = 11.8 Hz, 1H), 4.76−4.66 (m, 5H), 4.67−4.57 (m, 2H), 4.56−4.47 (m, 4H), 4.25−4.13 (m, 3H), 4.12 (d, J = 2.9 Hz, 1H), 4.07 (dd, J = 6.3, 2.7 Hz, 2H), 3.93−3.77 (m, 4H), 3.52 (dd, J = 9.8, 2.8 Hz, 1H), 3.13 (d, J = 8.8 Hz, 1H), 1.31 (d, J = 6.0 Hz, 3H), 1.25 (d, J = 5.7 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.3, 139.2, 139.1, 138.9, 138.8, 138.7, 138.4, 128.5, 128.4, 128.3, 128.25, 128.20, 128.0, 127.86, 127.81, 127.7, 127.6, 127.56, 127.52, 127.4, 127.28, 127.25, 102.5, 98.6, 82.6, 80.0, 79.4, 78.2, 76.3, 74.88, 74.82, 74.5, 74.3, 73.5, 73.3, 72.9, 70.6, 70.3, 16.9, 16.3. HRMS (ESI): m/z calcd for $C_{70}H_{74}O_{11}Na$ $[M + Na]$, 1113.5123; found, 1113.5083.

*1,6-Anhydro-2,3,4-tri-O-benzyl-7-deoxy-L-glycero-α-D-galacto-heptopyranose (**59**)*. This compound was obtained from the decomposition of donor **12** when variable temperature NMR studies were carried out following the general procedure for VT study. The reaction mixture was quenched with triethylamine (20.0 μL) at rt, diluted with dichloromethane (5 mL), and washed with saturated $NaHCO_3$ (2 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (9:1, hexane/ethyl acetate) afforded the decomposed product **59** (7.1 mg, 53%) as colorless syrup.

$[\alpha]_D^{23}$ −32.1 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.26 (m, 13H), 7.25−7.22 (m, 2H), 5.36 (t, J = 1.6 Hz, 1H), 4.82 (q, J = 6.5 Hz, 1H), 4.61 (d, J = 12.1 Hz, 1H), 4.57 (s, 2H), 4.51 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.3 Hz, 1H), 4.37 (d, J = 12.3 Hz, 1H), 3.98 (dd, J = 3.8, 1.4 Hz, 1H), 3.84 (dd, J = 5.2, 3.8 Hz, 1H), 3.79 (dt, J = 5.2, 1.5 Hz, 1H), 3.47 (t, J = 1.9 Hz, 1H), 1.15 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.4, 138.2, 137.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 100.8, 77.9, 76.6, 74.3, 73.5, 73.1, 72.1, 71.3, 71.2, 21.3. HRMS (ESI): m/z calcd for $C_{28}H_{30}O_5Na$ $[M + Na]$, 469.1985; found, 469.1985.

*1,6-Anhydro-2,3,4-tri-O-benzyl-7-deoxy-L-glycero-α-D-gluco-heptopyranose (**61**)*. This compound was obtained from the decomposition of donor **17** when variable temperature NMR studies were carried out following the general procedure for VT study. The reaction mixture was quenched with triethylamine (20 μL) at rt, diluted with dichloromethane (5 mL), and washed with saturated $NaHCO_3$ (2 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (9:1, hexane/ethyl acetate) afforded the decomposed product **61** (4.3 mg, 43%) as colorless syrup. $[\alpha]_D^{20}$ −20.4 (c 0.21, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.36−7.24 (m, 15H), 5.47 (s, 1H), 4.61 (d, J = 12.5 Hz, 1H), 4.53−4.38 (m, 3H), 4.18 (qd, J = 6.2, 1.0 Hz, 1H), 4.14−4.10 (m, 1H), 3.60 (dq, J = 2.7, 1.3 Hz, 1H), 3.39−3.34 (m, 1H), 3.32−3.28 (m, 1H), 1.16 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 138.0, 137.9, 137.9, 128.5, 128.43, 128.41, 128.0, 127.9, 127.9, 127.7, 101.2, 79.7, 76.5, 72.7, 72.2, 71.7, 71.2, 29.7, 21.0; HRMS (ESI): m/z calcd for $C_{28}H_{30}O_5Na$ $[M + Na]^+$, 469.1985; found, 469.1964.

*1,6-Anhydro-2,3,4-tri-O-benzyl-7-deoxy-D-glycero-α-D-gluco-heptopyranose (**63**)*. This compound was obtained from the decomposition of donor **19** when variable temperature NMR studies were carried out following the general procedure for VT study. The reaction mixture was quenched with triethylamine (20.0 μL) at rt, diluted with dichloromethane (5 mL), and washed with saturated

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$NaHCO_3$ (2 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (9:1, hexane/ethyl acetate) afforded the decomposed product **63** (8.0 mg, 29%) as colorless syrup. $[\alpha]_D^{22}$ −11.4 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.27 (m, 15H), 5.37 (s, 1H), 4.69−4.56 (m, 6H), 4.34 (d, *J* = 4.3 Hz, 1H), 3.98 (qd, *J* = 6.5, 4.1 Hz, 1H), 3.70 (t, *J* = 4.7 Hz, 1H), 3.60 (d, *J* = 4.9 Hz, 1H), 3.35 (d, *J* = 4.5 Hz, 1H), 1.21 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.3, 138.0, 137.9, 128.5, 128.4, 128.0, 127.97, 127.92, 127.7, 101.3, 81.1, 79.9, 78.8, 75.0, 73.5, 73.2, 71.9, 71.7, 14.7. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{30}O_5Na$ $[M + Na]^+$, 469.1985; found, 469.1988.

*p-Methylphenyl 6-O-Acetyl-2,3,4,-tri-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-gluco-heptopyranoside (**66**).* Acetic anhydride (0.11 mL, 1.16 mmol) was added to a stirred solution of **14** (0.33 g, 0.58 mmol) and 4-dimethylaminopyridine (7.0 mg, 0.06 mmol) in anhydrous pyridine (2.5 mL) at 0 °C. After complete addition, it was shifted to room temperature and stirred for 2 h. It was quenched with ice cold 1 N HCl solution (5 mL) and diluted with ethyl acetate (10 mL). The organic layer was washed with saturated $NaHCO_3$ solution (5 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by silica gel chromatography (1:4, EtOAc/hexane) to give **66** (0.32 g, 90%) as a white solid. mp: 130−134 °C, $[\alpha]_D^{22}$ −13.5 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.53−7.46 (m, 2H), 7.44−7.40 (m, 2H), 7.37−7.25 (m, 13H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.30 (qd, *J* = 6.5, 1.8 Hz, 1H), 4.98−4.91 (m, 2H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 10.2 Hz, 1H), 4.57 (d, *J* = 9.7 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 3.70 (t, *J* = 8.9 Hz, 1H), 3.55 (t, *J* = 9.4 Hz, 1H), 3.50 (t, *J* = 9.3 Hz, 1H), 3.23 (dd, *J* = 9.7, 1.8 Hz, 1H), 2.34 (s, 3H), 2.10 (s, 3H), 1.34 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.5, 138.3, 138.08, 138.04, 137.6, 133.0, 129.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 88.2, 87.0, 81.0, 80.3, 75.9, 75.5, 75.3, 67.7, 21.4, 21.2, 16.5; HRMS (ESI): *m*/*z* calcd for $C_{37}H_{40}O_6SNa$ $[M + Na]$, 635.2437; found, 635.2443.

*p-Methylphenyl 6-O-Acetyl-2,3,4-tri-O-benzyl-7-deoxy-1-thio-L-glycero-α-D-gluco-heptopyranosyl Sulfoxide (**67**).* It was obtained following the general protocol B for sulfoxide as a white solid (0.17 g, 83%) in a 1:1.6 ratio of two unidentified isomers.

Mixture of (*R*) and (*S*) sulfoxides: ^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.9 Hz, 5.8H), 7.41 (d, *J* = 6.9 Hz, 2H), 7.38−7.18 (m, 48H), 5.23 (qd, *J* = 6.7, 1.7 Hz, 1.6H), 5.11 (qd, *J* = 6.5, 1.9 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 5.02−4.94 (m, 2H), 4.92 (d, *J* = 11.2 Hz, 1H), 4.89−4.76 (m, 8H), 4.72 (d, *J* = 10.2 Hz, 1.6H), 4.44−4.41 (m, 1.7H), 4.41−4.35 (m, 2.3H), 4.13 (t, *J* = 9.4 Hz, 1H), 3.86 (d, *J* = 9.8 Hz, 1H), 3.84−3.76 (m, 4.5H), 3.60 (t, *J* = 9.3 Hz, 1H), 3.48−3.41 (m, 1.6H), 3.37 (dd, *J* = 9.8, 1.7 Hz, 1.6H), 2.99 (dd, *J* = 9.7, 2.0 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 5.1H), 2.06 (s, 3H), 2.00 (s, 5.1H), 1.24 (d, *J* = 6.5 Hz, 5.4H), 0.75 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 170.5, 170.2, 141.8, 141.5, 138.2, 137.9, 137.6, 137.4, 137.1, 136.0, 129.6, 129.4, 128.66, 128.63, 128.5, 128.47, 128.45, 128.3, 128.2, 128.1, 128.0, 127.96, 127.93, 127.90, 127.6, 126.1, 125.3, 95.0, 93.8, 86.9, 86.0, 81.4, 79.8, 77.3, 77.1, 76.9, 76.7, 75.9, 75.7, 75.4, 75.2, 74.9, 74.1, 67.6, 67.3, 21.5, 21.4, 21.2, 16.4, 15.4; HRMS (ESI): *m*/*z* calcd for $C_{37}H_{40}O_7SNa$ $[M + Na]$, 651.2387; found, 651.2386.

*Adamantyl 6-O-Acetyl-2,3,4-tri-O-benzyl-7-deoxy-L-glycero-α/β-D-gluco-heptopyranoside (**68**).* **68*α*** and **68*β*** were obtained from the reaction of **67** (33.0 mg, 52.50 μmol) and 1-adamantanol (8.8 mg, 57.70 μmol) following the general procedure for glycosylation (ethyl acetate/hexane, 1:9); combined yield (21.0 mg, 61%), α/β = 1:1.94.

68β. Colorless syrup; $[\alpha]_D^{22}$ +22.5 (*c* 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.26 (m, 15H), 5.39 (qd, *J* = 6.6, 1.5 Hz, 1H), 5.36 (d, *J* = 3.6 Hz, 1H), 5.00 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 9.8 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.69 (d, *J* = 2.0 Hz, 2H), 4.40 (d, *J* = 9.9 Hz, 1H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.84 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.52 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.42 (dd, *J* = 10.0, 8.8 Hz, 1H), 2.23−2.10 (m, 3H), 2.07 (s, 3H), 1.88−1.74 (m, 6H), 1.68−1.51 (m, 8H), 1.29 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.5, 138.8, 138.2, 137.9, 128.6, 128.56, 128.53, 128.2, 128.1, 128.0, 127.98, 127.93, 127.7, 89.8, 82.0, 80.0, 78.1, 76.9, 75.7, 75.5, 74.8, 73.0, 71.8, 68.1, 42.9, 42.7, 36.3, 30.7, 21.3, 17.1. HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}O_7Na$ $[M + Na]$, 663.3292; found, 663.3278.

68α. Colorless syrup; $[\alpha]_D^{22}$ +2.9 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.33 (m, 2H), 7.32−7.22 (m, 13H), 5.27 (qd, *J* = 6.5, 2.0 Hz, 1H), 5.01 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 10.1 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.63 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 10.2 Hz, 1H), 3.64 (t, *J* = 9.0 Hz, 1H), 3.54 (t, *J* = 9.3 Hz, 1H), 3.44 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.19 (dd, *J* = 9.7, 2.0 Hz, 1H), 2.16 (p, *J* = 3.0 Hz, 3H), 2.04 (s, 3H), 1.95−1.88 (m, 3H), 1.80 (dq, *J* = 11.4, 2.6 Hz, 3H), 1.68−1.57 (m, 6H), 1.53 (s, 2H), 1.32 (d, *J* = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.7, 138.6, 138.5, 137.8, 128.5, 128.49, 128.46, 128.3, 128.0, 127.9, 127.7, 96.7, 85.3, 82.2, 77.4, 76.3, 75.8, 75.3, 75.2, 75.0, 67.5, 42.9, 36.3, 30.7, 21.4, 16.7. HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}O_7Na$ $[M + Na]$, 663.3292; found, 663.3290.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01535.

Copies of ^1H and ^{13}C NMR spectra for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

David Crich − *Department of Pharmaceutical and Biomedical Sciences, University of Georgia, Athens, Georgia 30602, United States; Complex Carbohydrate Research Center, University of Georgia, Athens, Georgia 30602, United States; Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States;* orcid.org/0000-0003-2400-0083; Email: David.crich@uga.edu

Authors

Kapil Upadhyaya − *Department of Pharmaceutical and Biomedical Sciences, University of Georgia, Athens, Georgia 30602, United States*

Rahul S. Bagul − *Department of Pharmaceutical and Biomedical Sciences, University of Georgia, Athens, Georgia*

https://doi.org/10.1021/acs.joc.1c01535
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30602, United States; Complex Carbohydrate Research Center, University of Georgia, Athens, Georgia 30602, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c01535

Notes

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