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Conformational Domino Effect in Saccharides: A Prediction from Alkyl β-(1→6)-Diglucopyranosides

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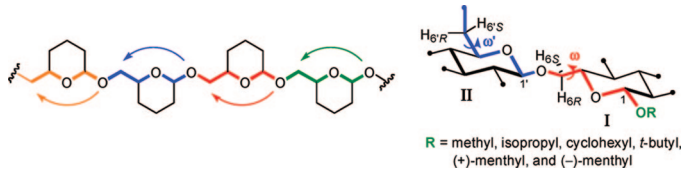

A series of alkyl β-D-glucopyranosyl-(1→6)-β-D-glucopyranosides, containing nonchiral and chiral aglycons, were synthesized and analyzed by NMR and CD. The results, collected from four sets of disaccharides, demonstrated that the rotational properties of the interglycosidic linkage depend on the structural natures of both the aglycon and the solvent. Stereoelectronic and steric factors explain this rotational dependence, the *gauche*−*trans* (*gt*) rotamer being the most stable. Furthermore, correlations between Taft's steric parameters or between the pK_a values of the alkyl substituent (aglycon) versus corresponding rotamer populations were observed. These results point to a natural conformational domino effect in oligosaccharides, where the conformational properties of each (1→6) interglycosidic linkage will depend on the structure of the previous residue or its aglycon. In addition, a very weak rotational population dependence of the hydroxymethyl group at residue II on the aglycon at residue I was observed. The population of the *gauche*−*gauche* (*gg*) rotamer decreased, and that of *gt* increased as the Taft's steric parameters of the remote aglycon increased, independently of the disaccharide series and of the solvent.

Introduction

Many studies on the conformational properties of carbohydrates have been performed, mainly by NMR,[1] X-ray diffraction,[2,3] and molecular modeling.[2] In spite of this, the conformation of an oligosaccharide is very difficult to determine due to the flexibility of the glycosidic linkages and the rotation of hydroxymethyl and other pendant groups. The conformation of a disaccharide in solution depends fundamentally on the rotations around its glycosidic linkage, so the relative orientations of the saccharide units are expressed in terms of the glycosidic linkage torsion angles Φ (O5′−C1′−O−Cx) and Ψ (C1′−O−Cx−C(x−1)), for a 1→x linkage (Figure 1). In addition to these torsion angles, a third torsion angle ω (O5−C5−C6−O6) needs to be considered when the hydroxymethyl group is involved in the linkage. This angle is also used to describe the conformation of unsubstituted hydroxymethyl groups. The conformation of the hydroxymethyl group around the C5−C6 bond is generally described by means of the populations of the *gauche*−*gauche* (*gg*), *gauche*−*trans* (*gt*), and *trans*−*gauche* (*tg*) rotamers (Figure 2).[4]

Many theoretical and experimental studies on the rotational preferences of the hydroxymethyl group have also been carried out,[5–27] mainly with monosaccharides, but the factors governing their conformational preferences in solution are still not fully understood. Our studies in this field, on the basis of NMR and CD data, have shown that the populations of the hydroxymethyl group in alkyl gluco,[24] galacto,[25] and mannopyranosides[26] depend on the structure of the aglycon and its absolute configuration, as well as on the anomeric configuration.

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(4) The first descriptor indicates the torsional relationship between O6 and O5, and the second that between O6 and C4.

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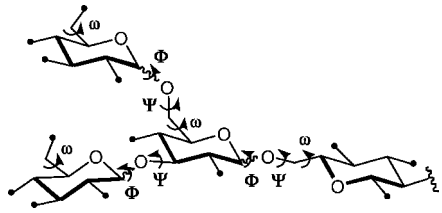


FIGURE 1. Torsion angles Φ and ψ around the glycosidic linkages and ω around the C5−C6 bonds.

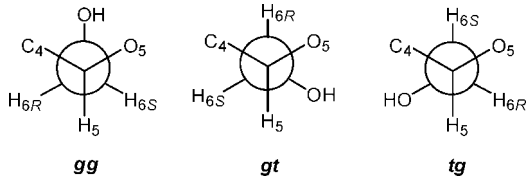
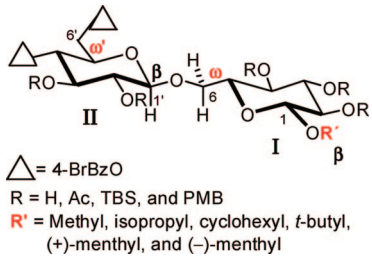


FIGURE 2. Newman projections of the *gg* ($\omega = -60°$), *gt* ($\omega = 60°$), and *tg* ($\omega = 180°$) rotamers around the C5−C6 bond.

Furthermore, studies on disaccharides with different glycosidic linkages but the same aglycon (methyl group) revealed that these populations also depend on the glycosidic linkage type.[27]

The present study performed in solution on β-(1→6)-linked diglucopyranosides with nonchiral and chiral aglycons revealed that the rotational populations of the hydroxymethyl group involved in the glycosidic linkage (residue I) depend clearly on the structural nature of the aglycon, their *gt* and *gg* populations increased and decreased, respectively, as the bulkiness of the aglycon increased. These conclusions predict the existence of a natural conformational domino effect in oligosaccharides.



Results and Discussion

Synthesis. Among the synthetic methods proposed for glycosylation reactions,[28] the direct epoxidation of glycals has become convenient.[29] Therefore, our model disaccharides were synthesized in this way by coupling different alcohols to the disaccharide **9**, which was similarly obtained from the monosaccharides **4** and **7** (Schemes 1 and 2).The glucosyl donor **4** and the glucosyl acceptor **7** were obtained in three steps from D-glucal (**1**) as shown in Scheme 1.

The disaccharide **8** was obtained in a 62% yield by coupling glucosyl donor **4** with glucosyl acceptor **7**, as shown in Scheme 2. Donor **4** was treated with dimethyldioxirane (DMDO) at 0 °C in CH_2Cl_2 to lead to the 1,2-anhydro sugar and then with the glucosyl acceptor **7** and $ZnCl_2$ at −78 °C in THF. The disaccharide **8** was obtained as an α/β mixture, which was acetylated and separated to give the β-disaccharide **9**.

The different alkyl β-D-glucopyranosyl-(1→6)-β-D-glucopyranosides **10**−**16** (Scheme 3) were obtained by coupling different primary, secondary, and tertiary alcohols to disaccharide **9**, protecting the resulting hydroxyl group at C2 as an acetate, and isolating the β-derivatives. Disaccharides **17**−**21** were obtained by deprotection of the *p*-methoxybenzyl group with DDQ.[30] Then, the silyl and acetyl groups were removed in just one step by acetyl chloride/MeOH in diethyl ether, to give disaccharides **22**−**25**. Under these conditions, undesired methanolysis occurs with the *tert*-butyl derivative **21**, so the *tert*-butyl disaccharide **27** was obtained in two steps: deprotection of the silyl groups with HF·Py in CH_3CN, then the acetyl groups with *p*-TsOH (Scheme 4).[31,32] Finally, the penta-*O*-acetyl derivatives **28**−**32** were obtained by treating compounds **22**−**26** with acetic anhydride and pyridine.

Characterization and Spectroscopic Analysis. All these compounds were characterized on the basis of their one- (^{1}H and ^{13}C) and two-dimensional (COSY, HMQC, and T-ROESY) NMR spectra. The anomeric configurations were assigned in each case by analyzing the coupling constant between H1 and H2 for each glucopyranosidic ring ($CDCl_3$, doublet, β-configuration: 7.8−8.0 Hz) (Figure 3). The chemical shifts of C1 and

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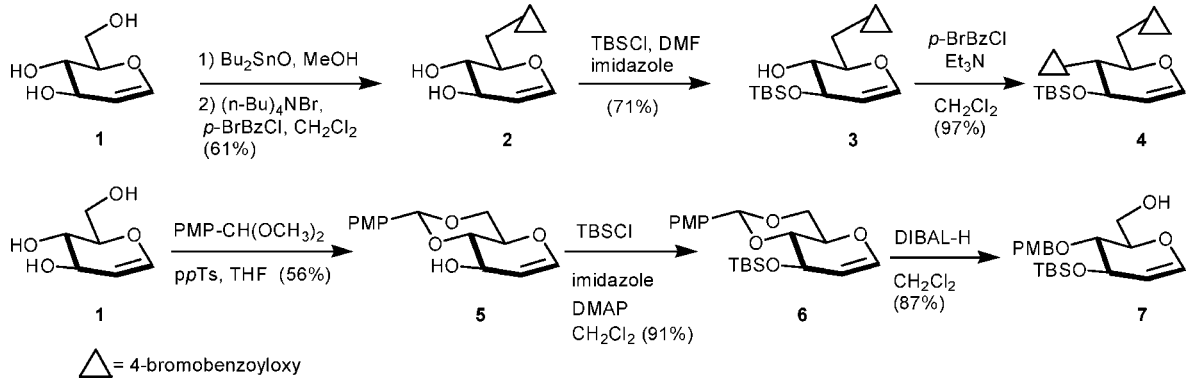
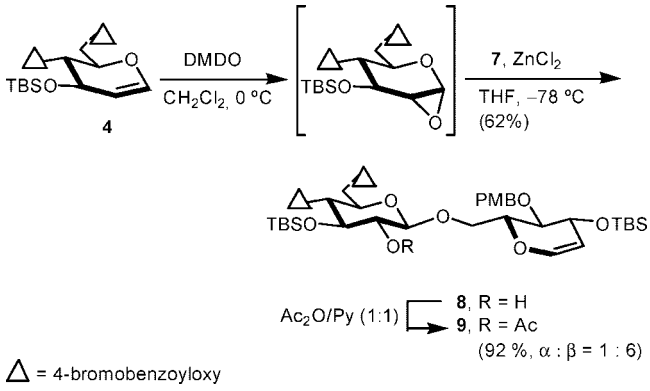
SCHEME 1. Synthesis of Monosaccharide Precursors



SCHEME 2. Synthesis of the Disaccharide Precursor 9



H1 for compounds in the four sets of disaccharides were shielded (95−104 ppm) or deshielded (4.10−4.62 ppm), respectively, from the methyl to *tert*-butyl derivative. Furthermore, as observed for alkyl glucosides,[24–26] comparison of the NMR data of (−)- and (+)-menthyl disaccharides shows chemical shifts for the former compounds at higher fields for C1 (3−4 ppm) and for H1 (0.03−0.11 ppm).

The ^1H NMR signals of the prochiral protons at C6 and C6′ were differentiated according to the data in the literature[5,15] on their chemical shifts and coupling constants; i.e., in general, for the D-*gluco*-series saccharides, the signals of the H6*R* proton are more shielded than those of H6*S* ($\delta_{H6S} > \delta_{H6R}$), and $J_{H5,H6R}$ coupling constants have higher values than $J_{H5,H6S}$. This NMR behavior is also observed in (1→6) glc-glc, gal-gal, or man-man disaccharides. Occasionally, homonuclear spin decoupling was performed for spectral simplification. The rotamer populations of the hydroxymethyl groups were calculated from the $^3J_{H5,H6}$ coupling constants by means of Serianni's equations.[33] Among the different types of Karplus equations,[34] those of Serianni yield the most accurate representation of the rotameric populations in solution and, generally, positive values for the *tg* population.

To analyze by CD the rotational populations of the hydroxymethyl group in C6′ and to obtain less crowded NMR spectra that allow the coupling constants to be determined more accurately under a first-order NMR analysis, the hydroxyl groups at C4′ and C6′ were derivatized with chromophores, namely *p*-bromobenzoates. Therefore, since all model disaccharides contain CD exciton-coupled chromophores,[35] UV and CD spectroscopy was also used to characterize these compounds. The intramolecular charge-transfer band was around 245 nm in the UV, and the exciton Cotton effects were around 251 and 234 nm in the CD spectra.

Conformational Analysis. General. Although there is apparently wide conformational freedom in disaccharides, steric and stereoelectronic effects in these biomolecules lead to a reduced number of conformations. Thus, in gluco-[24] and mannosides,[26] while the *gauche* effect between oxygens O5 and O6 stabilizes the *gg* and *gt* rotamers, the 1,3-diaxial type interaction between the O4 and O6 in the *tg* conformation destabilizes this rotamer, being nil or negligible in all analyzed cases.[5,36] Similarly, in galactosides the *gt* and *tg* rotamers are favored, while the *gg* rotamer is disfavored as a consequence of the axial configuration at C4.[25] In addition, the *exo*-anomeric effect[37,38] restricts the rotation around the glycosidic linkage, the exo-syn conformation being widely accepted as the most stable and predominant (Figure 4). Based on these considerations, we can limit the conformational study to the main staggered rotamers around both C5−C6 and C5′−C6′ bonds.

Conformational Analysis of the Hydroxymethyl Group around the C5−C6 Bond (Residue I). The model disaccharides **10**−**32** are divided into four sets of compounds on the basis of their substituents. T-ROESY experiments performed with the model disaccharides showed the main cross-peaks indicated in Figure 5, clearly confirming the anomeric configuration of both sugar residues. Moreover, in many cases, the cross-peaks are

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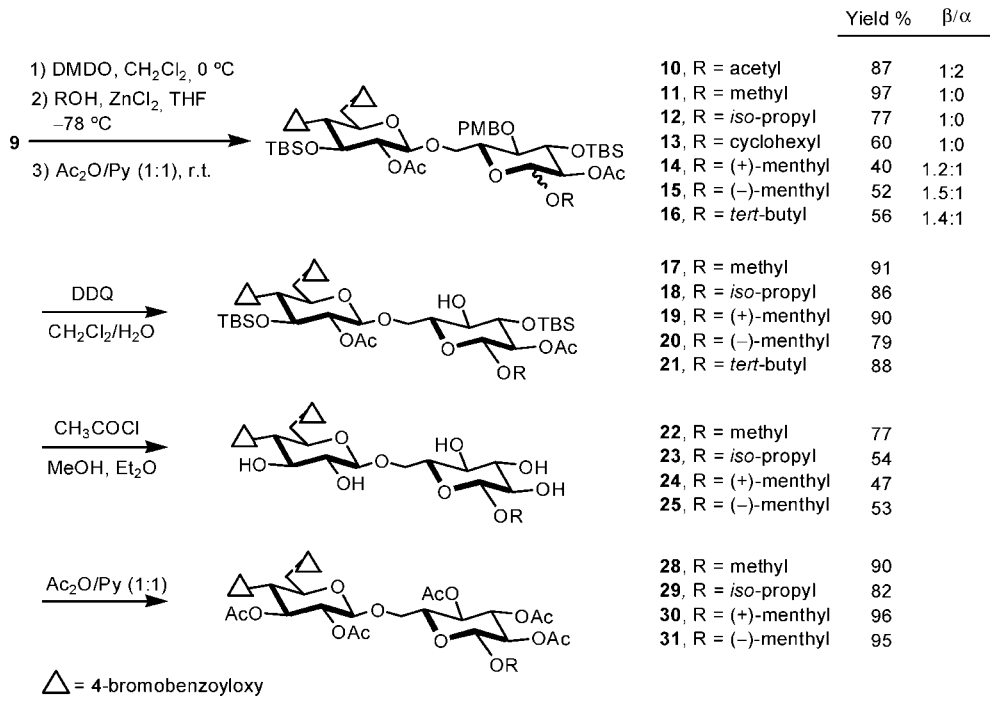
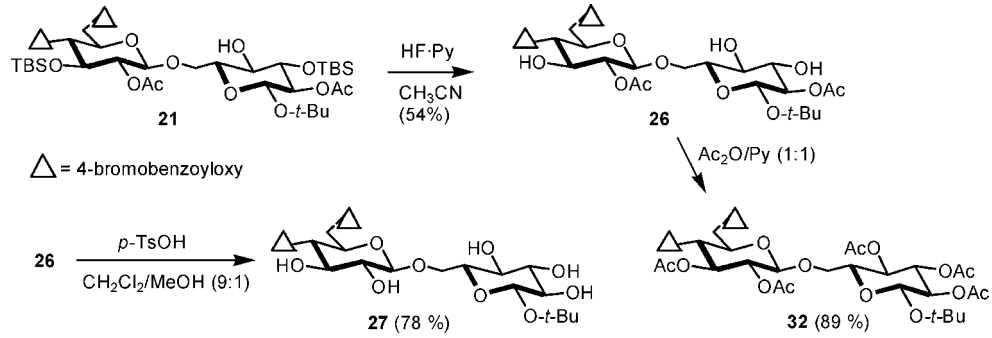
SCHEME 3. Synthesis of the Model Disaccharides



	Yield %	β/α
10, R = acetyl	87	1:2
11, R = methyl	97	1:0
12, R = *iso*-propyl	77	1:0
13, R = cyclohexyl	60	1:0
14, R = (+)-menthyl	40	1.2:1
15, R = (–)-menthyl	52	1.5:1
16, R = *tert*-butyl	56	1.4:1
17, R = methyl	91	
18, R = *iso*-propyl	86	
19, R = (+)-menthyl	90	
20, R = (–)-menthyl	79	
21, R = *tert*-butyl	88	
22, R = methyl	77	
23, R = *iso*-propyl	54	
24, R = (+)-menthyl	47	
25, R = (–)-menthyl	53	
28, R = methyl	90	
29, R = *iso*-propyl	82	
30, R = (+)-menthyl	96	
31, R = (–)-menthyl	95	

SCHEME 4. Synthesis of the *tert*-Butyl Disaccharides 27 and 32



totally in agreement with exo-syn and *gt* conformations for the glycosidic linkage. Thus, strong cross-peaks were observed between H1′ and H6*R*, and between H6*S* and H5, as well as weak cross-peaks between H6*R* and H4.

^{1}H NMR analysis of the alkyl *β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosides **22**−**25** and **27** were measured in DMSO-d_6, showing high values of the $J_{H5,H6R}$ in this solvent (Table 1). Furthermore, the signals corresponding to the H6*S* protons appeared as doublets ($J \approx 11$ Hz), meaning a very low value of the $J_{H5,H6S}$ coupling constants and therefore of the *tg* population. NMR measurements of these compounds in polar solvents such as C_5D_5N or $CDCl_3/CD_3OD$ led to superimposed or complex signals, while in solvents $(CD_3)_2CO$, CD_3OD, C_6D_6, or $CDCl_3$, they were not soluble. To calculate the rotational populations of these disaccharides, the $J_{H5,H6S}$ coupling constant values are introduced into the equations. So, as an approximation, a low value of 0.9 Hz was assigned to this constant for the purpose.[34c] The resulting calculated populations (Table 1) reflect a higher *gt* than *gg* population in all cases and confirm the rotational population around C5−C6 to be dependent on the structure of the aglycon.

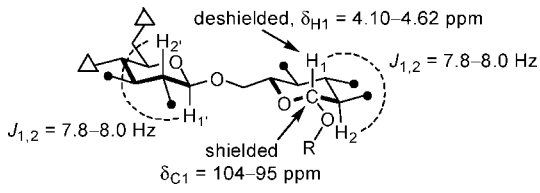


FIGURE 3. General NMR characteristics of model disaccharides.

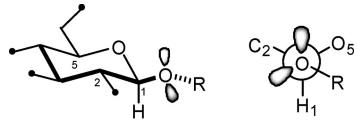


FIGURE 4. Exo-syn rotamer around the O1−C1 bond.

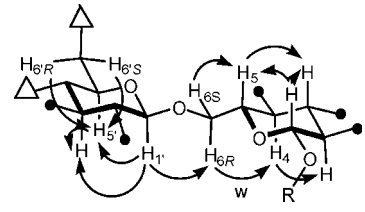


FIGURE 5. Main cross-peaks observed for the model disaccharides in the T-ROESY experiments ($CDCl_3$).

TABLE 1. Coupling Constants and Calculated Rotameric Populations (%) around the C5−C6 Bond (Residue I) for the Model Disaccharides 22−25 and 27 (DMSO-d_6)

compd	R	$J_{H5,H6R}$	$J_{H5,H6S}$[a]	P_{gg}	P_{gt}	P_{tg}
22	Me	6.8	-	44	56	0
23	*iso*-Pr	7.0	-	42	58	0
24	(+)-Mn	7.4	-	38	62	0
25	(−)-Mn	6.6	-	46	54	0
27	*tert*-Bu	7.2	-	40	60	0

[a] Not detected. An estimated value of 0.9 Hz was used for calculations.

TABLE 2. Coupling Constants and Calculated Rotameric Populations (%) around the C5−C6 Bond (Residue I) for the Model Disaccharides 28−32 ($CDCl_3$)

compd	R	$J_{H5,H6R}$	$J_{H5,H6S}$	P_{gg}	P_{gt}	P_{tg}
28	Me	7.4	1.8	36	64	0
29	*iso*-Pr	7.7	1.7	33	67	0
30	(+)-Mn	–[a]	–[a]	–	–	–
31	(−)-Mn	6.5	1.9	44	56	0
32	*tert*-Bu	7.8	1.7	32	68	0

[a] H6*R* and H6*S* signals are isochronous.

The $J_{H5,H6}$ coupling constants for the model penta-*O*-acetyl disaccharides **28−32** in $CDCl_3$ are shown in Table 2, together with the calculated rotameric populations around the C5−C6 bond. An increase in the $J_{H5,H6R}$ coupling constant around the C5−C6 bond (ω) was observed as the bulkiness of the aglycon increased. Thus, this coupling constant gradually increased from the methyl derivative **28** (7.4 Hz), to the isopropyl **29** (7.7 Hz), and to the *tert*-butyl derivative **32** (7.8 Hz). On the other hand, the $J_{H5,H6S}$ value remained more or less constant (around 1.8 Hz). The (−)-menthyl derivative **31** showed the smallest value of the $J_{H5,H6R}$ coupling constant, pointing to the existence of nonbonded interactions between the isopropyl group in the menthyl aglycon and the hydroxymethyl group at C6 or the residue II, as will be discussed below.

The rotamer populations around C5−C6 of the alkyl β-D-glucopyranosyl-(1→6)-β-D-glucopyranosides **28−32** were calculated by applying the Serianni equations system,[33] using the experimental $J_{H5\ H6R}$ and $J_{H5\ H6S}$ coupling constants (Table 2). It was observed that the *gt* rotamer was the most populated in all cases and that its population slightly increases from 56% ((−)-menthyl) to 68% (*tert*-butyl) at the expense of the *gg*, from 44% ((−)-menthyl) to 32% (*tert*-butyl). Since it is accepted that the ω population depends to some extent on solvation effects,[39] ^{1}H NMR analyses of these disaccharides were run in nonpolar as well as polar solvents with different dielectric constants and dynamic viscosity coefficients. Analyzing vertically the data in Table 3, the $J_{H5,H6R}$ coupling constants depend on the structural nature of the aglycon. For compounds possessing a nonchiral aglycon, the $J_{H5,H6R}$ increased from the methyl, to isopropyl, and *tert*-butyl derivative, these differences being less effective and even disappearing as the dielectric constant of the solvent increased (Figure 6). For compounds with a chiral aglycon, the (+)- and (−)-menthyl derivatives **30** and **31**, the $J_{H5,H6R}$ coupling constant showed a higher dependence on the nature of the solvent, the (−)-methyl derivative showing an equal or smaller value than the (+)-derivative (Figure 6). On the other hand, the $J_{H5,H6S}$ coupling constant remained almost constant for each solvent. Horizontal analysis of the data contained in Table 3 reveals, independently of the aglycon, similar $J_{H5,H6R}$ values for nonpolar solvents and smaller values for the polar ones, especially for acetonitrile. This result means that the *gt* rotamer is less favored in polar solvents.

As seen from Figure 7, there is a linear correlation[40] between the *gg* and *gt* rotational populations around the C5−C6 bond for compounds **22−25** and **27** with the corresponding Taft's steric parameters.[41] The E_S values are composite terms, derived from both potential energy steric effects (steric strains) and entropy effects (steric hindrances to motions). According to Taft,[41] introduction of a straight-chain alkyl group in place of the standard hydrogen substituent raises the activation energy due to steric hindrance. Therefore, the bulkier alkyl groups freeze out the rotation around the O1−C1 bond, and therefore the more stable exo-syn rotamer increases its population (Figure 8). Simultaneously to steric hindrances to motions, steric factors between the aglycon and the substituent at position 2 are also probably involved in the conformational behavior around the glucosidic bond,[42] reducing the population of the non-exo rotamer as the aglycon increases in size.

The plot of the rotamer populations of the totally protected disaccharides **10−16**, also containing the acetyl and cyclohexyl disaccharides, was carried out against the pK_a of bonded alcohols instead of the E_S values, to be able to include the acetyl group (Figure 9). Since pK_a values of bonded alcohols are related to steric bulk, this plot is a good approximation for studying these compounds. The *gt* rotamer increased from the acetyl derivative (39%) to the methyl derivative (60%), and to the isopropyl and cyclohexyl disaccharides (65 and 64%, respectively). The bulkier (+)- and (−)-menthyl and the *tert*-butyl disaccharides showed smaller *gt* (56, 57, and 63%, respectively) and higher *gg* populations (43, 44, and 37%, respectively) than expected from the experimental regression line (see below).[24]

These correlations are explained by the exo-anomeric effect,[37,38] which rises as the charge delocalization from the aglycon to the anomeric carbon becomes easier.[43,44] Thus, as the aglycon becomes branched, the exo-syn population increases at the expense of the non-exo conformation, due to steric hindrances to motions and/or steric factors, as explained above. So, the stereoelectronic $n_S \rightarrow \sigma^*_{CO}$ interaction (the exo-anomeric effect) increases. Very recently, studies performed with *C*-glycosides,[45,46] which enabled the exo-syn, exo-anti, and non-exo populations to be calculated, have demonstrated that the population exo-syn rotamer increased and that of the non-exo decreased as the substitution of the *C*-aglycon increased, supporting our explanation.

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(40) Regression line equations: (a) Figure 7: $P_{gg} = 3.2057E_S + 3.725$; $R^2 = 0.8399$; $P_{gt} = -3.2057E_S + 56.275$; $R^2 = 0.8399$. (b) Figure 11: $P_{gg} = 2.2014E_S + 58.909$; $R^2 = 0.6116$; $P_{gt} = -2.1415E_S + 35.948$; $R^2 = 0.8566$. (c) Figure 12: $P_{gt} = -2.1415E_S + 35.948$; $R^2 = 0.8566$ (blue line); $P_{gt} = -1.317E_S + 35.738$; $R^2 = 0.8100$ (green line); and $P_{gt} = -1.8599E_S + 31.618$; $R^2 = 0.7023$ (red line).

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TABLE 3. $J_{H5,H6}$ **Coupling Constants (Residue I) for the Model Disaccharides 28−32 in Different Solvents**[a]

		$J_{H5,H6R}$					$J_{H5,H6S}$				
	R	C_6D_6	$CDCl_3$	$(CD_3)_2CO$	CD_3CN	DMSO	C_6D_6	$CDCl_3$	$(CD_3)_2CO$	CD_3CN	DMSO
ϵ		2.3	4.8	20.7	37.5	46.7					
μ		0.65	0.57	0.32	0.37	2.00					
28	Me	7.3	7.4	6.6	5.8	6.5	2.2	1.8	2.0	2.0	−
29	*iso*-Pr	7.4	7.7	7.1	5.8	6.6	2.2	1.7	1.9	2.0	−
30	(+)-Mn	6.6	−	6.6	6.1	6.3	2.3	−	2.1	2.0	−
31	(−)-Mn	6.6	6.5	5.9	5.4	5.8	2.5	1.9	2.1	2.0	2.1
32	*tert*-Bu	7.7	7.8	6.8	5.8	6.6	2.0	1.7	2.0	2.0	1.6

[a] ϵ = dielectric constant; μ (Poise) = dynamic viscosity coefficient.

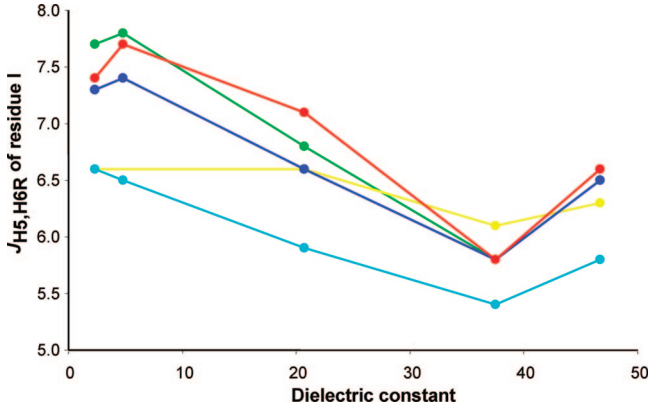

FIGURE 6. Plot of $J_{H5,H6R}$ coupling constants versus dielectric constants for disaccharides **28**−**32**: *tert*-butyl **32** (green line), isopropyl **29** (red line), methyl **28** (dark blue line), (+)-menthyl **30** (yellow line), and (−)-menthyl **31** (blue line).

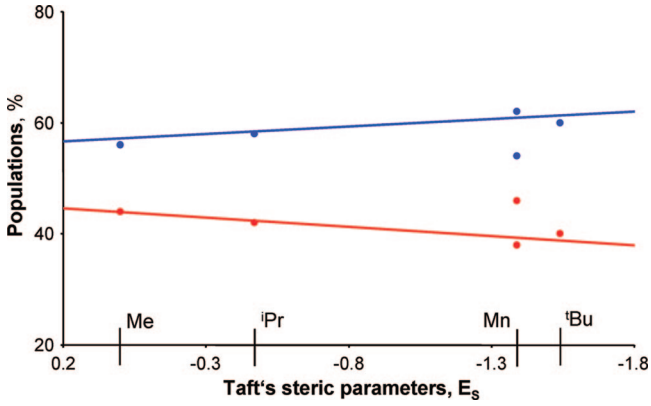

FIGURE 7. Rotational populations of *gg*/*gt* rotamers around the C5−C6 bond versus corresponding E_S values for aliphatic substituents for compounds **22**−**25** and **27** (pentahydroxy disaccharides). P_{gg} (red line) and P_{gt} (blue line).[40a]

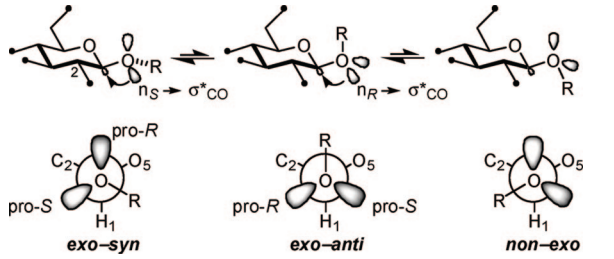

FIGURE 8. Molecular orbitals involved in the exo-anomeric effect for the three idealized staggered rotamers around the C1−O bond.

The progressive shortness of the O1−C1 bond and lengthening of the C1−O5 bond, as the exo-anomeric effect increases, should affect the *gauche* effect between oxygens O5 and O6

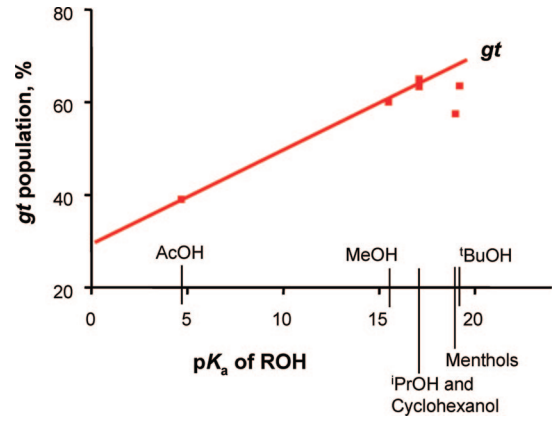

FIGURE 9. Plot of *gt* populations around the C5−C6 bond versus pK_a of bonded alcohols for compounds **10**−**16** (totally protected disaccharides).[40]

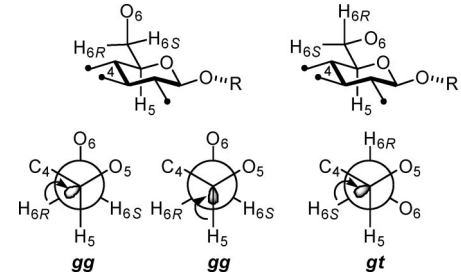

FIGURE 10. Molecular orbitals involved in the *gauche* effect for the two idealized staggered *gg* and *gt* rotamers around the C5−C6 bond.

and modify the conformational preferences around the C5−C6 bond (O5−C5−C6−O6), by varying the effectiveness of the stereoelectronic $\sigma_{CH}-\sigma^*_{CO}$ interactions. Figure 10 shows the hyperconjugative mechanism proposed for the *gauche* effect, two $\sigma_{CH}-\sigma^*_{CO}$ interactions for the *gg*, one for the *gt*, and none for the *tg* rotamer,[5,47] this mechanism having been used to explain the higher stability of the *gg* rotamer in monosaccharides.[5]

In addition to stereoelectronic interactions, nonbonded interactions between the aglycon and the hydroxymethyl group could be important in compounds with bulky aglycons or aglycons with bulky substituents syn to the endocyclic oxygen O5. As seen in Tables 1−3, the (−)-menthyl derivative possesses the smallest $J_{H5,H6R}$ values and therefore the smallest *gt* populations. A reasonable explanation of this could be the existence of nonbonded interactions between the isopropyl group located syn to O5 and the hydroxymethyl group at C6 (residue II in the *gt* conformation). On the other hand, the anti disposition of the

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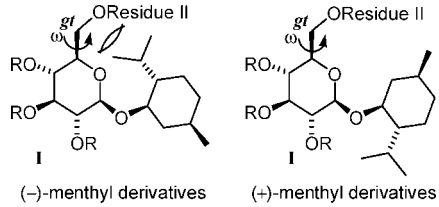
TABLE 4. Coupling Constants, Calculated Rotameric Populations (%) around the C5′−C6′ Bond (Residue II) (in DMSO), and CD Data (in EtOH) for Model Disaccharides 22−25 and 27

compd	R	$J_{H5',H6'R}$	$J_{H5',H6'S}$	P_{gg}	P_{gt}	P_{tg}	1EC	2EC	*A* value
22	Me	4.7	3.1	58	36	6	13.3	−4.2	17.5
23	*iso*-Pr	4.7	2.9	59	37	4	13.1	−4.0	17.1
24	(+)-Mn	4.9	3.1	56	38	6	12.9	−3.9	16.8
25	(−)-Mn	4.9	2.9	57	39	4	13.0	−3.9	16.9
27	*tert*-Bu	5.1	3.0	54	40	6	12.8	−3.9	16.7

isopropyl group in the (+)-menthyl derivative prevents the mentioned nonbonded interactions. Of course, these steric factors depend on the solvent (Table 3) and on the substitution type. For the totally protected disaccharide set, compounds **10**−**16** (Figure 9), both menthyl and the *tert*-butyl derivatives, showed smaller *gt* populations, due probably to severe nonbonded interactions. This does not rule out the participation of the exo-anomeric effect for them since the populations of the menthyl and methyl derivatives are more similar than they are to those of the acetyl derivative **10**. For this compound, the exo-anomeric effect is nil, due to the nonshared electron pair of the exocyclic oxygen being involved by resonance with the carbonyl group. This explains the low value of its *gt* population (*gg*:*gt*:*tg* = 38:39:23%). Therefore, the rotational populations around C5−C6 (residue I) can be explained on the basis of both nonbonded and stereoelectronic effects.



Conformational Analysis of the Hydroxymethyl Group around the C5′-C6′ Bond (Residue II). The rotameric populations around C5′−C6′, calculated from $J_{H5',H6'R}$ and $J_{H5',H6'S}$ coupling constants, for compounds **10**−**32** showed that the *gg* rotamer is the most populated, then the *gt* rotamer, and finally the *tg*, the general relation P_{gg}:P_{gt}:P_{tg} being 60:35:5. T-ROESY experiments also support this conclusion since the cross-peaks between the prochiral H6′ protons and H5′ were of different size (Figure 5), the one between H6′*S* and H5′ being double the magnitude of that between H6′*R* and H5′, indicating a greater *gt* population than *tg*. Besides this, in general, the $J_{H5',H6'R}$ coupling constant was found to increase very slightly as the aglycone changed from methyl to secondary alkyl to tertiary alkyl. Table 4 shows this behavior for the case of the pentahydroxy disaccharides **22**−**25** and **27** in DMSO. The *gt* population slightly increased from the methyl (36%), isopropyl (37%), (+)-menthyl (38%), (−)-menthyl (39%), and *tert*-butyl disaccharides (40%), while the *gg* population decreased from the methyl (58%) to the *tert*-butyl disaccharide (54%). Figure 11 shows the linear correlation between the *gg* and *gt* populations at residue II versus E_S values for aliphatic substituents (aglycon, residue I) for these compounds.[40b] Figure 12 shows how the *gt* population increased linearly as Taft's steric parameters increased, independently of the disaccharide series and the solvent.[40c]

The rotational populations around the C5′−C6′ bond were also analyzed by the CD exciton chirality method.[35] The positive *A* values[48] (Table 4) obtained for all these compounds confirm that the *gg* rotamer is the most populated. As seen in Figure

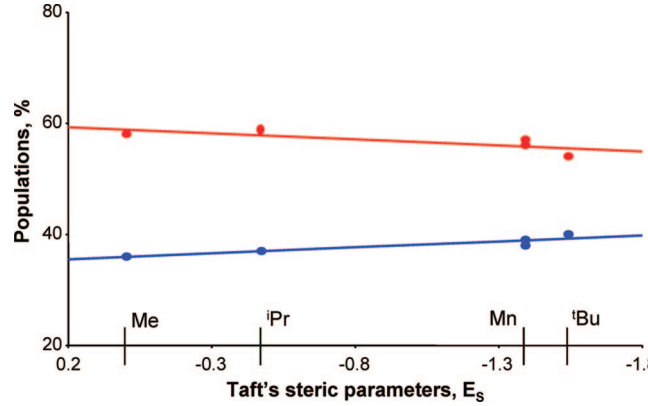


FIGURE 11. Plot of rotamer populations around the C5′−C6′ (in DMSO) versus corresponding E_S values for aliphatic substituents for compounds **22**−**25** and **27** (pentahydroxy disaccharides). P_{gg} (red line) and P_{gt} (blue line).[40b]

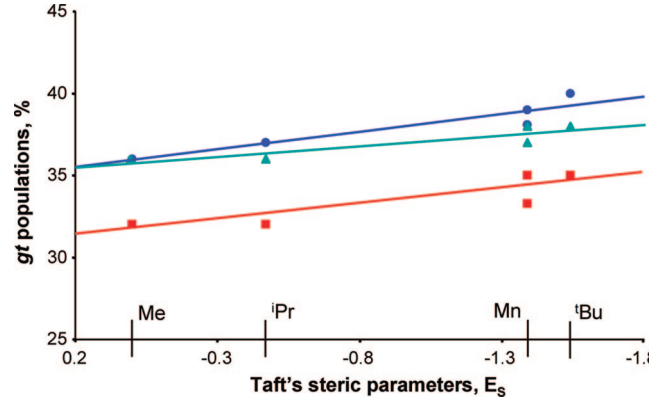


FIGURE 12. Plot of *gt* rotamer populations around the C5′−C6′ versus corresponding E_S values for compounds **22**−**25** and **27** (in DMSO, blue line) and for compounds **28**−**32** (in C_6D_6, green line; in CD_3CN, red line).[40c]

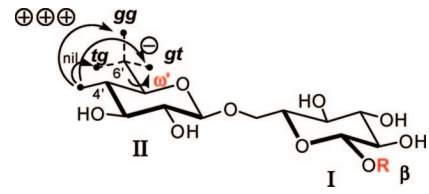


FIGURE 13. Sign and relative intensities for the pairwise interaction between the chromophores at C4 and C6 in the three rotamers.

13, the 4/6 pairwise interaction between the chromophores has a positive exciton coupling for the *gg* rotamer, negative for the *gt*, and nil for the *tg* rotamer. Furthermore, the *A* value slightly decreased from the methyl (17.5), to the isopropyl (17.1), and to the *tert*-butyl disaccharides (16.7) in complete agreement with an increase in the *gt* population from primary, to secondary, to tertiary alkyl disaccharides. Therefore, CD and NMR data are in complete agreement about this remote rotational dependence.

The relationship between the *gg* and *gt* populations at residue II and the Taft's steric parameters of the aglycons at residue I shows a remote conformational relay from the aglycon to the

(48) The amplitude (*A* value) of split CD Cotton effects is defined as $A = \Delta\epsilon_1 - \Delta\epsilon_2$ where $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are intensities of the first and second Cotton effects, respectively. Occasionally, the presence of a background ellipticity alters the intensity of the Cotton effects at short wavelengths. For this reason, the intensities of the second Cotton effects and the amplitudes (*A* values) of the CD spectra of our model compounds may not be precise. The intensities of the first Cotton effects are thus more accurate for comparative analysis.

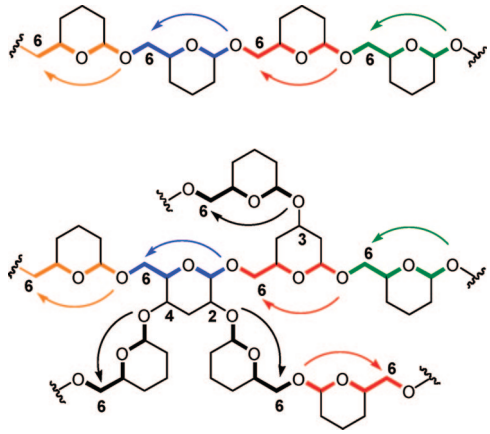


FIGURE 14. Schematic representation of a conformational cascade in linear (top) or branched (bottom) oligosaccharides. (1→2)-, (1→3)-, and (1→4)-bonded saccharides start a new domino effect; however, (1→6)-interglycosidic linkages continue the domino effect.

hydroxymethyl group at residue II, although to a much lesser degree, as a consequence of the greater distance between them. This correlation could be due to minute differences in the values of the exo-anomeric effect on residue II, as a result of the different rotameric populations around C5−C6, since for these disaccharides nonbonded interactions between the aglycon and this distantly located hydroxymethyl group cannot be expected.

Conclusions

The rotational populations of the hydroxymethyl groups of a series of alkyl β-D-glucopyranosyl-(1→6)-β-D-glucopyranosides were analyzed by means of NMR and CD. The experimental data, collected from four sets of disaccharides, proved a rotational dependence of the hydroxymethyl group involved in the glycosidic linkage (torsion angle ω, O5−C5−C6−O6) on the structure of the aglycon and on the solvent nature, *gt* usually being the most stable rotamer. Furthermore, the *gt* and *gg* populations of this hydroxymethyl group increased and decreased, respectively, as Taft's steric parameter for the aglycon increased. This rotational behavior can be explained by the stereoelectronic exo-anomeric effect, steric hindrances to motions, and nonbonded interactions between the aglycon and the substituent at position 2 and/or the hydroxymethyl group at C6 (residue II in the *gt* conformation) altering this stereoelectronic effect. Extending these results, and those previously described on the dependence on the glycosidic linkage type,[27] to oligosaccharides, the existence of a conformational cascade can be predicted, where the conformational preferences around the torsion angle ω in an interglycosidic linkage depend on the stereostructure of the preceding residue and so on repeatedly (Figure 14). This knowledge can be of great help when studying oligosaccharides three-dimensionally.

The results also seem to demonstrate another rotational dependence, namely, a very weak rotational population dependence of the hydroxymethyl group at residue II (torsion angle ω', O5′−C5′−C6′−O6′) on the aglycon at residue I. Furthermore, the populations of *gg*, the most stable rotamer around the C5′−C6′ bond, decreased, and those of *gt* increased as the Taft steric parameters of the remote aglycon increased, independently of the disaccharide series and of the solvent.

Experimental Section

General Procedure for Preparation of Disaccharides 10−16. A solution of dimethyldioxirane in acetone (2 equiv) was added to a stirred solution of disaccharide **9** in dry CH_2Cl_2 (5 mL/mmol) at 0 °C under argon atmosphere, and the reaction was stirred for 30 min. The 1,2-anhydrosugar thus obtained was concentrated under reduced pressure and left under a vacuum for 2 h. Then it was dissolved in dry THF (10 mL/mmol) under argon, and molecular sieves and the corresponding alcohol were added. The reaction mixture was cooled to −78 °C, and then 0.5 equiv of a 1.0 M solution of $ZnCl_2$ in diethyl ether was added. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was diluted with EtOAc, filtered, and washed with water; then the combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. After this, 2 mL of a 1:1 solution of dry pyridine/acetic anhydride was added at room temperature and stirred overnight. Excess solvent was removed under reduced pressure, and the residue was purified with column chromatography.

General Procedure for Debenzylation. An amount of 2.5 equiv of DDQ at room temperature was added to a stirred solution of the starting material in CH_2Cl_2/H_2O (9:1, 50 mL/mmol). Then, this was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 twice, and the combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The residue was purified with column chromatography.

General Procedure for Deprotection of Silyl and Acetyl Groups. A solution of starting material in dry diethylether (40 mL/mmol) was added to a stirred solution of acetyl chloride (40 equiv) in dry methanol (40 mL/mmol). When the reaction was completed, it was concentrated under vacuum, and the residue was purified by Sephadex column chromatography (*n*-hexane/$CHCl_3$/MeOH, 2:1:1).

2,6-Anhydro-1-*O*-(4-bromobenzoyl)-5-deoxy-D-*arabino*-hex-5-enitol (2). To a solution of D-glucal (658 mg, 4.5 mmol) in dry methanol (20 mL) was added 1.35 g of dibutyltin oxide (5.4 mmol, 1.2 equiv) under an argon atmosphere and heated under reflux for 4 h. When the reaction was completed, it was evaporated to dryness. Then the crude reaction mixture was dissolved in 20 mL of CH_2Cl_2, cooled at −10 °C, and treated with 1.74 g (5.4 mmol, 1.2 equiv) of *n*-Bu_4NBr and 1.28 g (5.8 mmol, 1.3 equiv) of *p*-bromobenzoyl chloride. The reaction was quenched with a few drops of water. The solvent was removed under reduced pressure, and the residue was cromatographed. Flash column chromatography (*n*-hexane/EtOAc, 1:1) of the residue afforded **2** (895 mg, 2.7 mmol) in 61% yield: TLC R_f = 0.4 (*n*-hexane/EtOAc, 3:7); colorless syrup; $[\alpha]_D$ = +44.5 (*c* 2.0, $CHCl_3$); MS (FAB) Calcd for $C_{13}H_{14}BrO_5$ $(M+1)^+$ 327, Found 327; ^{1}H NMR ($CDCl_3$) δ 7.93 (dd, J = 8.6 Hz, 2H), 7.61 (dd, J = 8.6 Hz, 2H), 6.34 (dd, J = 1.6 and 6.0 Hz, 1H), 4.90 (dd, J = 3.4 and 12.5 Hz, 1H), 4.76 (dd, J = 2.1 and 6.0 Hz, 1H), 4.52 (dd, J = 2.3 and 12.5 Hz, 1H), 4.34 (dd, J = 2.1 and 7.3 Hz, 1H), 4.02 (m, 1H), 3.60 (dd, J = 7.3 and 10.1 Hz, 1H), 3.36 (br s, 1H), 2.15 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 166.8, 144.2, 131.9–128.2, 102.9, 76.4, 69.7, 69.5, 63.3. Anal. Calcd for $C_{13}H_{13}BrO_5$: C, 47.44; H, 3.98. Found: C, 47.70; H, 4.00.

2,6-Anhydro-1-*O*-(4-bromobenzoyl)-4-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol (3). Compound **2** (435 mg, 1.32 mmol) was dissolved in dry DMF (6.5 mL) under an argon atmosphere and treated with imidazole (198 mg, 2.91 mmol, 2.2 equiv) and *tert*-butyldimethylsilyl chloride (210 mg, 1.39 mmol, 1.05 equiv). When the reaction was completed, it was quenched with a few drops of water, concentrated under vacuum, and the residue purified by column chromatography (*n*-hexane/EtOAc, 8.5:1.5) to lead to compound **3** (416 mg, 0.95 mmol, 71%): TLC R_f = 0.2 (*n*-hexane/EtOAc, 9:1); colorless syrup; $[\alpha]_D$ = +29.6 (*c* 0.7, $CHCl_3$); MS (FAB) Calcd for $C_{19}H_{28}BrO_5Si$ $(M+1)^+$ 441, Found 441; ^{1}H NMR ($CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 6.31 (dd, J = 1.2 and 6.1 Hz, 1H), 4.77 (dd, J = 4.9 and 12.3 Hz, 1H), 4.69 (dd, J = 2.5 and 6.1 Hz, 1H), 4.55 (dd, J = 2.4 and 12.3 Hz, 1H), 4.27 (m, 1H), 4.12 (m, 1H), 3.72 (dd, J = 6.5 and 8.8 Hz, 1H), 2.60 (br s, 1H), 0.91 (s, 9H), 0.12 (s, 6H);

^{13}C NMR ($CDCl_3$) δ 166.2, 143.3, 131.8–128.4, 103.7, 76.3, 69.6, 69.5, 63.4, 25.8 (x3), 18.1, −4.5, −4.6. Anal. Calcd for $C_{19}H_{27}BrO_5Si$: C, 51.47; H, 6.14. Found: C, 51.47; H, 5.83.

2,6-Anhydro-1,3-bis-*O*-(4-bromobenzoyl)-4-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol (4). A solution of **3** (2.36 g, 5.32 mmol) in dry CH_2Cl_2 (30 mL) was treated with Et_3N (2.2 mL, 16.0 mmol, 3 equiv), 2 equiv of *p*-bromobenzoyl chloride (2.33 g, 10.63 mmol), and DMAP as catalyst. The reaction was quenched with the addition of a few drops of water and the solvent removed under reduced pressure. The product was purified by silica gel column chromatography (*n*-hexane/EtOAc, 9:1), obtaining 3.22 g of compound **4** (5.14 mmol, 97%): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 9:1); colorless syrup; $[\alpha]_D = +39.8$ (*c* 1.2, $CHCl_3$); MS (FAB) Calcd for $C_{26}H_{31}Br_2O_6Si$ $(M + 1)^+$ 625, Found 625; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H), 7.59–7.55 (m, 4H), 6.42 (dd, $J = 0.8$ and 6.1 Hz, 1H), 5.38 (t, $J = 5.2$ Hz, 1H), 4.85 (dd, $J = 3.5$ and 6.1 Hz, 1H), 4.64 (dd, $J = 6.6$ and 11.9 Hz, 1H), 4.54 (dd, $J = 3.3$ and 11.9 Hz, 1H), 4.51 (m, 1H), 4.33 (br t, $J = 4.1$ Hz, 1H), 0.86 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.5, 164.5, 143.2, 131.8–128.3, 102.8, 73.8, 71.2, 64.6, 62.8, 25.6 (x3), 17.9, −4.6, −4.9. Anal. Calcd for $C_{26}H_{30}Br_2O_6Si$: C, 49.85; H, 4.83. Found: C, 49.81; H, 4.86.

6-*O*-{2-*O*-Acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-β-D-glucopyranosyl}-1,5-anhydro-3-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-4-*O*-(4-methoxybenzyl)-D-*arabino*-hex-1-enitol (9). A solution of dimethyldioxirane in acetone (2 equiv) was added to a stirred solution of compound **4** (520 mg, 0.83 mmol) in dry CH_2Cl_2 (5 mL/mmol) at 0 °C under argon, and the reaction was stirred for 30 min. The 1,2-anhydrosugar thus obtained was concentrated under reduced pressure and left under vacuum for 2 h. Then it was dissolved in dry THF (10 mL/mmol) under argon, and molecular sieves and compound **7** (474 mg, 1.25 mmol, 1.5 equiv) were added. The reaction mixture was cooled to −78 °C, and then 0.5 equiv of a 1.0 M solution of $ZnCl_2$ in diethyl ether was added. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was diluted with EtOAc, filtered, and washed with water. The combined organic layers were then dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure, giving 527 mg of compound **8** as a mixture (β:α = 6:1) (62% yield). Then, 2 mL of a 1:1 solution of dry pyridine/acetic anhydride was added at room temperature and stirred overnight. Excess solvent was removed under reduced pressure, and the residue was purified with column chromatography (*n*-hexane/EtOAc, 19:1) to lead to **9** (92% yield), its β anomer (505 mg, 0.47 mmol) being isolated in a 57% overall yield: TLC $R_f =$ 0.5 (*n*-hexane/EtOAc, 7:3); colorless syrup; $[\alpha]_D = +5.7$ (*c* 0.8, $CHCl_3$); MS (FAB) Calcd for $C_{48}H_{64}Br_2O_{13}Si_2$ $(M)^+$ 1062, Found 1062; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J =$ 8.4 Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.30 (d, $J =$ 6.2 Hz, 1H), 5.34 (t, $J = 9.3$ Hz, 1H), 5.03 (t, $J = 8.5$ Hz, 1H), 4.71 (d, $J = 11.3$ Hz, 1H), 4.67 (dd, $J = 3.3$ and 6.2 Hz, 1H), 4.57 (d, $J = 11.3$ Hz, 1H), 4.49 (d, $J = 7.9$ Hz, 1H), 4.44 (dd, $J = 3.5$ and 12.1 Hz, 1H), 4.34 (dd, $J = 4.7$ and 12.1 Hz, 1H), 4.21 (t, J = 3.3 Hz, 1H), 4.10 (m, 1H), 4.03–3.96 (m, 2H), 3.85–3.80 (m, 2H), 3.80 (s, 3H), 3.49 (br t, $J = 9.0$ Hz, 1H), 2.09 (s, 3H), 0.87 (s, 9H), 0.72 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), 0.00 (s, 3H), −0.18 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.3, 165.5, 164.3, 159.4, 143.0, 131.8–128.4, 113.9 (x2), 103.0, 101.7, 76.1, 76.0, 73.6, 72.9, 72.8, 72.4, 71.7, 68.3, 67.3, 63.7, 55.3, 25.8 (x3), 25.5 (x3), 21.2, 17.9, 17.8, −4.3 (x2), −4.5, −4.6. Anal. Calcd for $C_{48}H_{64}Br_2O_{13}Si_2$: C, 54.13; H, 6.06. Found: C, 54.11; H, 6.20.

1,2-Di-*O*-acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-β-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-β-D-glucopyranose (10). Following the general procedure for preparation of disaccharides, 130 mg (0.12 mmol) of compound **9** was treated with 500 μL of water, giving compound **10** (127 mg, 0.11 mmol) as a mixture α:β = 2:1 in an 87% yield, isolated after column chromatography (*n*-hexane/EtOAc, 8:2). Thus, 85.6 mg of α- and 41.7 mg of β-anomer were obtained. Compound **10** (β anomer): colorless syrup; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.21 (d, $J =$ 8.6 Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 5.55 (d, $J = 8.0$ Hz, 1H), 5.32 (t, $J = 9.2$ Hz, 1H), 5.02 (t, $J = 8.4$ Hz, 1H), 4.93 (t, $J = 8.6$ Hz, 1H), 4.71 (d, $J = 10.9$ Hz, 1H), 4.52 (d, $J = 7.8$ Hz, 1H), 4.47 (d, $J = 10.9$ Hz, 1H), 4.46 (dd, $J = 3.7$ and 12.1 Hz, 1H), 4.35 (dd, $J = 5.1$ and 12.1 Hz, 1H), 4.03 (dd, $J = 4.5$ and 13.4 Hz, 1H), 3.99 (t, $J = 8.9$ Hz, 1H), 3.80 (m, 2H), 3.79 (s, 3H), 3.60 (m, 1H), 3.59 (dd, $J = 5.6$ and 13.4 Hz, 1H), 3.37 (t, $J = 8.9$ Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 0.88 (s, 9H), 0.71 (s, 9H), 0.04 (s, 6H), −0.01 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.0, 168.9, 165.2, 164.1, 159.1, 131.6–128.0, 113.6 (x2), 100.5, 91.9, 77.8, 75.4, 74.5, 74.3, 73.0, 72.7, 72.6, 72.1, 71.5, 67.1, 63.4, 55.0, 29.4, 25.5 (x3), 25.1 (x3), 20.9, 20.6, 18.0, 17.6, 17.5, −4.3, −4.7 (x 3). Anal. Calcd for $C_{52}H_{70}Br_2O_{17}Si_2$: C, 52.79; H, 5.96. Found: C, 52.92; H, 6.09.

Methyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-β-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (11). Following the general procedure for preparation of disaccharides, 78.0 mg (0.07 mmol) of compound **9** was treated with 500 μL of methanol to provide 82.2 mg of compound **11** (0.07 mmol, 97% yield) after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7:3); mp = 171.0−171.9 °C; $[\alpha]_D = +8.9$ (*c* 1.1, $CHCl_3$); MS (FAB) Calcd for $C_{51}H_{70}Br_2O_{16}Si_2Na$ $(M + Na)^+$ 1177, Found 1177; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.34 (t, $J = 9.3$ Hz, 1H), 5.03 (t, $J = 8.5$ Hz, 1H), 4.82 (t, $J = 8.6$ Hz, 1H), 4.69 (d, $J = 10.9$ Hz, 1H), 4.56 (d, $J = 8.0$ Hz, 1H), 4.45 (dd, $J = 3.6$ and 12.1 Hz, 1H), 4.42 (d, $J = 10.9$ Hz, 1H), 4.33 (dd, $J = 4.7$ and 12.1 Hz, 1H), 4.18 (d, $J = 8.0$ Hz, 1H), 4.03 (dd, $J = 1.3$ and 10.6 Hz, 1H), 3.96 (t, $J = 8.9$ Hz, 1H), 3.83 (m, 1H), 3.77 (s, 3H), 3.74 (t, $J = 9.0$, 1H), 3.54 (dd, $J = 7.1$ and 10.6 Hz, 1H), 3.50 (m, 1H), 3.47 (s, 3H), 3.26 (t, $J = 9.0$ Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 0.88 (s, 9H), 0.71 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H), −0.02 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.6 (s), 169.1 (s), 165.4, 164.3, 159.3, 131.8–128.3, 113.8 (x2), 101.8, 100.9, 78.9, 75.0, 74.9, 74.7, 73.7, 73.2, 73.0, 72.2, 71.8, 67.6, 63.6, 56.7, 55.3, 25.7 (x3), 25.4 (x3), 21.3, 21.2, 17.9, 17.7, −4.0, −4.4 (x2), −4.5. Anal. Calcd for $C_{51}H_{70}Br_2O_{16}Si_2$: C, 53.00; H, 6.10. Found: C, 53.16; H, 5.80.

***iso*-Propyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-β-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (12).** Following the general procedure, 123 mg (0.12 mmol) of compound **9** was treated with 1 mL of *iso*-propanol to lead, after column chromatography (*n*-hexane/EtOAc, 9:1), to 109 mg of compound **12** (0.09 mmol) in 77% yield: TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 7:3); mp = 176.8−178.1 °C; $[\alpha]_D = +6.3$ (*c* 0.8, $CHCl_3$); MS (FAB) Calcd for $C_{53}H_{74}Br_2O_{16}Si_2Na$ $(M + Na)^+$ 1205, Found 1205; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J =$ 8.5 Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.34 (t, $J = 9.3$ Hz, 1H), 5.02 (t, $J = 8.5$ Hz, 1H), 4.79 (t, $J = 9.0$ Hz, 1H), 4.69 (d, $J = 10.9$ Hz, 1H), 4.58 (d, $J = 8.0$ Hz, 1H), 4.43 (dd, $J = 3.6$ and 12.1 Hz, 1H), 4.40 (d, $J = 11.0$ Hz, 1H), 4.32 (dd, $J = 4.8$ and 12.1 Hz, 1H), 4.30 (d, $J = 7.9$ Hz, 1H), 4.01 (dd, $J = 1.3$ and 10.5 Hz, 1H), 3.94 (t, $J = 9.0$ Hz, 1H), 3.91 (m, 1H), 3.81 (m, 1H), 3.77 (s, 3H), 3.73 (t, $J = 9.0$ Hz, 1H), 3.53 (dd, $J = 7.6$ and 10.5 Hz, 1H), 3.47 (m, 1H), 3.20 (t, $J = 9.1$ Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.22 (d, $J = 6.2$ Hz, 3H), 1.11 (d, $J = 6.2$ Hz, 3H), 0.88 (s, 9H), 0.71 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), −0.02 (s, 3H), −0.21 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.3, 169.0, 165.4, 164.3, 159.3, 131.8–128.4, 113.8 (x2), 100.8, 99.8, 78.9, 75.2 (x2), 74.7, 74.0, 73.4, 73.0, 72.3, 72.2, 71.7, 67.7, 63.6, 55.3, 25.8 (x3), 25.4

(x3), 23.5, 22.0, 21.2 (x2), 17.9, 17.7, −4.1, −4.4, −4.5 (x2). Anal. Calcd for $C_{53}H_{74}Br_2O_{16}Si_2$: C, 53.81; H, 6.30. Found: C, 53.82; H, 6.41.

Cyclohexyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (13). Following the general procedure for disaccharides, 140 mg (0.13 mmol) of compound **9** was treated with 1 mL of cyclohexanol to lead, after column chromatography (*n*-hexane/EtOAc, 9:1), to 96 mg of compound **13** (0.08 mmol) in a 60% yield: TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 7:3); mp = 172.4−174.3 °C; $[\alpha]_D = +3.5$ (*c* 1.1, $CHCl_3$); MS (FAB) Calcd for $C_{56}H_{78}Br_2O_{16}Si_2Na$ $(M + Na)^+$: 1245. Found 1245; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 5.33 (t, $J = 9.3$ Hz, 1H), 5.01 (t, $J = 8.6$ Hz, 1H), 4.81 (dd, $J = 8.1$ and 9.3 Hz, 1H), 4.69 (d, $J = 10.9$ Hz, 1H), 4.58 (d, $J = 8.0$ Hz, 1H), 4.43 (dd, $J = 3.6$ and 12.1 Hz, 1H), 4.40 (d, $J = 11.1$ Hz, 1H), 4.35 (d, $J = 8.1$ Hz, 1H), 4.33 (dd, $J = 4.7$ and 12.1 Hz, 1H), 3.99 (dd, $J = 1.6$ and 11.0 Hz, 1H), 3.94 (t, $J = 8.9$ Hz, 1H), 3.80 (m, 1H), 3.77 (s, 3H), 3.73 (t, $J = 9.0$ Hz, 1H), 3.62 (m, 1H), 3.55 (dd, $J = 7.5$ and 11.0 Hz, 1H), 3.46 (m, 1H), 3.21 (t, $J = 9.2$ Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 1.90–1.20 (m, 10H), 0.88 (s, 9H), 0.71 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), −0.02 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2 (s), 169.0 (s), 165.4, 164.3, 159.3, 131.8–128.4, 113.8 (x2), 100.8, 99.4, 78.9, 77.0, 75.3, 75.1, 74.7, 74.0, 73.4, 73.0, 72.3, 71.7, 67.5, 63.6, 55.2, 33.4, 31.5, 29.7, 25.8 (x3), 25.5, 25.4 (x3), 23.7, 23.4, 21.3, 21.2, 17.9, 17.7, −4.0, −4.4 (x2), −4.5. Anal. Calcd for $C_{56}H_{78}Br_2O_{16}Si_2$: C, 53.99; H, 6.43. Found: C, 53.83; H, 6.58.

(+)-Menthyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (14). Following the general procedure, 136 mg (0.13 mmol) of compound **9** was treated with 100 mg of (+)-menthol (0.64 mmol, 5 equiv) to provide, after column chromatography (*n*-hexane/EtOAc, 9.5:0.5), 65 mg of compound **14** (0.05 mmol) in 40% yield as an anomer mixture ($\beta/\alpha = 1.2{:}1$): TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 7:3); mp = 173.1−174.9 °C; $[\alpha]_D = +11.0$ (*c* 0.5, $CHCl_3$); MS (FAB) Calcd for $C_{60}H_{86}Br_2O_{16}Si_2Na$ $(M + Na)^+$ 1278, Found 1278; ^{1}H NMR ($CDCl_3$) δ 7.80 (d, $J = 8.7$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.34 (t, $J = 9.3$ Hz, 1H), 5.02 (d, $J = 8.5$ Hz, 1H), 4.84 (d, $J = 8.6$ Hz, 1H), 4.67 (d, $J = 10.9$ Hz, 1H), 4.66 (d, $J = 7.8$ Hz, 1H), 4.44 (d, $J = 10.9$ Hz, 1H), 4.43 (dd, $J = 3.6$ and 12.2 Hz, 1H), 4.31 (d, $J = 7.8$ Hz, 1H), 4.29 (dd, $J = 4.9$ and 12.2 Hz, 1H), 3.94 (t, $J = 8.9$ Hz, 1H), 3.91 (dd, $J = 1.0$ and 11.6 Hz, 1H), 3.79 (m, 1H), 3.77 (s, 3H), 3.69 (t, $J = 9.0$ Hz, 1H), 3.67 (dd, $J = 6.8$ and 11.6 Hz, 1H), 3.45 (m, 1H), 3.25 (m, 1H), 3.22 (t, $J = 9.2$ Hz, 1H), 2.11 (m, 1H), 2.09 (s, 3H), 2.07 (m, 1H), 2.05 (s, 3H), 1.61 (m, 2H), 1.25 (m, 1H), 1.11 (m, 1H), 0.97 (d, $J = 6.5$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H), 0.88 (s, 9H), 0.75 (d, $J = 6.9$ Hz, 3H), 0.71 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H), −0.02 (s, 3H), −0.22 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2, 168.9, 165.3, 164.3, 159.2, 131.8–128.3, 113.8 (x2), 102.0, 100.8, 80.8, 78.8, 75.7, 75.1, 74.7, 74.3, 73.6, 73.1, 72.3, 71.7, 67.2, 63.5, 55.2, 48.5, 43.3, 34.1, 31.9, 25.7 (x3), 25.3 (x3), 24.6, 22.7, 22.5, 21.4, 21.3 (x2), 17.8, 17.7, 14.0, −4.1, −4.4, −4.5, −4.6. Anal. Calcd for $C_{60}H_{86}Br_2O_{16}Si_2$: C, 56.30; H, 6.80. Found: C, 56.27; H, 7.01.

(−)-Menthyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (15). Following the general procedure for preparation of disaccharides, 140 mg (0.13 mmol) of compound **9** was treated with 100 mg of (−)-menthol (0.64 mmol, 5 equiv) to give, after column chromatography (*n*-hexane/EtOAc, 9.5:0.5), 87 mg (0.07 mmol) of compound **15** in 52% yield as an anomer mixture ($\beta/\alpha = 1.5{:}1$): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); mp = 171.3−173.6 °C; $[\alpha]_D = -12.3$ (*c* 0.3, $CHCl_3$); MS (FAB) Calcd for $C_{60}H_{86}Br_2O_{16}Si_2Na$ $(M + Na)^+$ 1278, Found 1278; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 5.33 (t, $J = 9.3$ Hz, 1H), 5.00 (d, $J = 8.5$ Hz, 1H), 4.78 (d, $J = 8.7$ Hz, 1H), 4.70 (d, $J = 10.9$ Hz, 1H), 4.61 (d, $J = 7.9$ Hz, 1H), 4.43 (dd, $J = 3.6$ and 12.1 Hz, 1H), 4.40 (d, $J = 10.9$ Hz, 1H), 4.34 (d, $J = 8.0$ Hz, 1H), 4.29 (dd, $J = 4.9$ and 12.1 Hz, 1H), 3.96 (dd, $J = 1.3$ and 11.8 Hz, 1H), 3.93 (t, $J = 8.9$ Hz, 1H), 3.76 (s, 3H), 3.75 (m, 1H), 3.71 (t, $J = 8.9$ Hz, 1H), 3.62 (dd, $J = 6.7$ and 11.8 Hz, 1H), 3.40 (m, 2H), 3.26 (t, $J = 9.2$ Hz, 1H), 2.25 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.97 (m, 1H), 1.63 (m, 3H), 1.26 (m, 2H), 0.92 (m, 6H), 0.87 (s, 9H), 0.81 (d, $J = 6.8$ Hz, 3H), 0.72 (s, 9H), 0.04 (s, 6H), −0.02 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2, 168.9, 165.3, 164.3, 159.2, 131.8–128.2, 113.8 (x2), 101.1, 97.9, 78.9, 77.0, 75.6, 75.2, 74.7, 74.1, 73.8, 73.0, 72.3, 71.6, 68.4, 63.5, 55.2, 47.7, 40.5, 34.3, 31.4, 25.7 (x3), 25.4 (x3), 25.2, 23.3, 22.3, 21.3 (x2), 21.0 (x2), 17.8, 17.7, 16.4, −4.1, −4.3, −4.5 (x2). Anal. Calcd for $C_{60}H_{86}Br_2O_{16}Si_2$: C, 56.30; H, 6.80. Found: C, 56.38; H, 6.81.

***tert*-Butyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (16).** Following the general procedure, 151 mg (0.14 mmol) of compound **9** was treated with 1 mL of *tert*-butanol to give, after column chromatography (*n*-hexane/EtOAc, 9:1), 84 mg (0.07 mmol) of compound **16** in a 56% yield as an anomer mixture ($\beta/\alpha = 1.4{:}1$): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); colorless syrup; $[\alpha]_D = +7.2$ (*c* 0.4, $CHCl_3$); MS (FAB) Calcd for $C_{54}H_{76}Br_2O_{16}Si_2Na$ $(M + Na)^+$ 1219, Found 1219; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 5.33 (t, $J = 9.3$ Hz, 1H), 5.01 (t, $J = 8.5$ Hz, 1H), 4.78 (dd, $J = 8.2$ and 9.1 Hz, 1H), 4.68 (d, $J = 10.9$ Hz, 1H), 4.55 (d, $J = 8.0$ Hz, 1H), 4.43 (d, $J = 7.9$ Hz, 1H), 4.40 (d, $J = 10.9$ Hz, 1H), 4.41 (dd, $J = 3.2$ and 12.1 Hz, 1H), 4.32 (dd, $J = 4.8$ and 12.1 Hz, 1H), 3.98 (dd, $J = 1.0$ and 9.6 Hz, 1H), 3.93 (t, $J = 8.9$ Hz, 1H), 3.81 (m, 1H), 3.76 (s, 3H), 3.74 (t, $J = 9.0$ Hz, 1H), 3.52 (dd, $J = 7.5$ and 10.7 Hz, 1H), 3.47 (m, 1H), 3.18 (t, $J = 9.1$ Hz, 1H), 2.06 (s, 6H), 1.21 (s, 9H), 0.90 (s, 9H), 0.71 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), −0.02 (s, 3H), −0.21 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.9 (x2), 165.4, 164.4, 159.3, 131.8–128.4, 113.8 (x2), 100.8, 95.5, 78.7, 75.7, 75.3, 75.0, 74.7, 74.1, 73.3, 73.1, 71.7, 67.6, 63.6, 55.3, 28.7 (x3), 25.8 (x3), 25.4 (x3), 21.4 (x2), 17.7 (x2), −4.0, −4.2, −4.4 (x2). Anal. Calcd for $C_{54}H_{76}Br_2O_{16}Si_2$: C, 54.20; H, 6.40. Found: C, 54.34; H, 6.17.

Methyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranoside (17). Following the general procedure for debenzylation, 82.3 mg (0.07 mmol) of compound **11** yielded 67.8 mg (0.06 mmol) of compound **17** (91%): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 7:3); mp = 82.0−82.7 °C; $[\alpha]_D = +1.0$ (*c* 1.0, $CHCl_3$); MS (FAB) Calcd for $C_{43}H_{63}Br_2O_{15}Si_2$ $(M + 1)^+$ 1057, Found 1057; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, $J = 8.5$ Hz, 4H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.3$ Hz, 2H), 5.36 (t, $J = 9.4$ Hz, 1H), 5.03 (dd, $J = 8.2$ and 8.8 Hz, 1H), 4.80 (dd, $J = 8.3$ and 9.1 Hz, 1H), 4.61 (d, $J = 8.0$ Hz, 1H), 4.50 (dd, $J = 3.4$ and 12.2 Hz, 1H), 4.35 (dd, $J = 4.6$ and 12.2 Hz, 1H), 4.21 (d, $J = 8.0$ Hz, 1H), 4.09 (dd, $J = 2.2$ and 10.8 Hz, 1H), 4.00 (t, $J = 9.0$ Hz, 1H), 3.88 (m, 1H), 3.77 (m, 1H), 3.61 (t, $J = 9.1$ Hz, 1H), 3.46 (s, 3H), 3.46–3.42 (m, 2H), 2.43 (s, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 0.85 (s, 9H), 0.71 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.5, 169.3, 165.5, 164.3, 131.9–128.4, 101.9, 101.1, 75.8, 74.4, 73.5, 73.4, 73.0, 72.4, 72.0, 71.9, 68.8, 63.2, 56.7, 25.7 (x3), 25.4 (x3), 21.3 (x2), 18.0, 17.7, −4.2, −4.5 (x2), −4.7. Anal. Calcd for $C_{43}H_{62}Br_2O_{15}Si_2$: C, 49.90; H, 6.04. Found: C, 49.99; H, 6.00.

***iso*-Propyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-**

[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranoside (18). Following the general procedure for debenzylation, 70.0 mg (0.06 mmol) of compound **12** yielded 54.0 mg (0.05 mmol) of compound **18** (86%): TLC R_f = 0.4 (*n*-hexane/EtOAc, 7:3); mp = 82.1−83.8 °C; $[\alpha]_D$ = −2.4 (*c* 1.1, $CHCl_3$); MS (FAB) Calcd for $C_{45}H_{66}Br_2O_{15}Si_2Na$ $(M + Na)^+$ 1085, Found 1085; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 4H), 7.55 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 5.34 (t, J = 9.3 Hz, 1H), 5.02 (dd, J = 8.2 and 8.8 Hz, 1H), 4.76 (dd, J = 8.2 and 9.1 Hz, 1H), 4.62 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 3.1 and 12.2 Hz, 1H), 4.34 (m, 2H), 4.08 (dd, J = 2.9 and 11.1 Hz, 1H), 3.99 (t, J = 9.0 Hz, 1H), 3.89 (m, 1H), 3.88 (m, 1H), 3.76 (dd, J = 6.0 and 11.1 Hz, 1H), 3.60 (t, J = 9.1 Hz, 1H), 3.46–3.36 (m, 2H), 2.40 (d, J = 3.2 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.1 Hz, 3H), 0.85 (s, 9H), 0.71 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2 (x2), 165.5, 164.3, 131.9–128.3, 101.0, 99.9, 75.9, 74.5, 73.7, 73.5, 73.0, 72.5, 72.3, 72.1, 71.9, 69.0, 63.3, 25.7 (x2), 25.4 (x2), 23.4, 22.0, 21.3, 21.1, 18.0, 17.7, −4.3, −4.5 (x2), −4.7. Anal. Calcd for $C_{45}H_{66}Br_2O_{15}Si_2$: C, 50.85; H, 6.26. Found: C, 50.99; H, 6.36.

(+)-Menthyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranoside (19). Following the general procedure for debenzylation, 162 mg (0.13 mmol) of compound **14** yielded 133 mg (0.11 mmol) of compound **19** (90%): TLC R_f = 0.4 (*n*-hexane/EtOAc, 8:2); mp = 75.8−77.4 °C; $[\alpha]_D$ = +10.6 (*c* 1.1, $CHCl_3$); MS (FAB) Calcd for $C_{52}H_{78}Br_2O_{15}Si_2Na$ $(M + Na)^+$ 1181, Found 1181; ^{1}H NMR ($CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 5.35 (t, J = 9.4 Hz, 1H), 5.02 (t, J = 8.5 Hz, 1H), 4.81 (t, J = 9.2 Hz, 1H), 4.66 (d, J = 8.0 Hz, 1H), 4.54 (dd, J = 3.3 and 12.1 Hz, 1H), 4.34 (d, J = 7.9 Hz, 1H), 4.33 (dd, J = 4.8 and 12.1 Hz, 1H), 4.02–3.97 (m, 2H), 3.88−3.84 (m, 2H), 3.60 (t, J = 9.0 Hz, 1H), 3.45–3.37 (m, 2H), 3.24 (dt, J = 4.3 and 10.5 Hz, 1H), 2.55 (s, 1H), 2.11 (s, 3H), 2.08 (m, 2H), 2.04 (s, 3H), 1.56 (m, 2H), 1.25 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H), 0.85 (s, 9H), 0.74 (d, J = 6.9 Hz, 3H), 0.72 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.19 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2 (x2), 165.5, 164.3, 131.9–128.4, 102.2, 101.1, 81.5, 75.9, 74.4, 73.9, 73.7, 73.0, 72.7, 72.1, 72.0, 69.1, 63.2, 48.3, 43.2, 34.1, 31.8, 25.7 (x3), 25.4 (x3), 24.7, 22.7, 22.4, 21.3, 21.2, 21.1, 18.1, 17.7, 15.9, −4.1, −4.4, −4.5, −4.7. Anal. Calcd for $C_{52}H_{78}Br_2O_{15}Si_2$: C, 53.88; H, 6.78. Found: C, 53.88; H, 6.92.

(−)-Menthyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranoside (20). Following the general procedure for debenzylation, 150 mg (0.12 mmol) of compound **15** yielded 107 mg (0.09 mmol) of compound **20** (79%): TLC R_f = 0.4 (*n*-hexane/EtOAc, 8:2); mp = 76.0−77.6 °C; $[\alpha]_D$ = −11.7 (*c* 0.8, $CHCl_3$); MS (FAB) Calcd for $C_{52}H_{78}Br_2O_{15}Si_2Na$ $(M + Na)^+$ 1181, Found 1181; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 4H), 7.56 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 5.35 (t, J = 9.3 Hz, 1H), 5.02 (t, J = 8.4 Hz, 1H), 4.76 (t, J = 9.1 Hz, 1H), 4.62 (d, J = 7.9 Hz, 1H), 4.53 (dd, J = 3.3 and 12.1 Hz, 1H), 4.35 (d, J = 8.9 Hz, 1H), 4.33 (dd, J = 4.8 and 12.1 Hz, 1H), 3.99 (m, 2H), 3.84 (m, 1H), 3.80 (dd, J = 5.3 and 11.2 Hz, 1H), 3.61 (t, J = 9.3 Hz, 1H), 3.46 (m, 1H), 3.34 (m, 2H), 2.52 (br s, 1H), 2.24 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.94 (br d, J = 10.6 Hz, 1H), 1.59 (m, 2H), 1.26 (m, 2H), 0.91 (d, J = 6.2 Hz, 3H), 0.86 (d, J = 6.2 Hz, 3H), 0.85 (s, 9H), 0.74 (d, J = 7.0 Hz, 3H), 0.72 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.19 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2 (x2), 165.5, 164.3, 131.9–128.4, 101.1, 98.6, 77.9, 75.9, 74.4, 73.8, 73.6, 72.9, 72.7, 72.1, 72.0, 69.4, 63.3, 47.6, 40.7, 34.3, 31.5, 25.7 (x3), 25.4 (x3), 25.0, 23.2, 22.3, 21.2 (x2), 20.9, 17.8, 17.7, 16.4, −4.1, −4.3, −4.5 (x2). Anal. Calcd for $C_{52}H_{78}Br_2O_{15}Si_2$: C, 53.88; H, 6.78. Found: C, 53.88; H, 6.70.

***tert*-Butyl 2-*O*-Acetyl-6-*O*-{2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranosyl}-3-*O*-[*tert*-butyl(dimethyl)silyl]-*β*-D-glucopyranoside (21).** Following the general procedure for debenzylation, 143 mg (0.12 mmol) of compound **16** yielded 113 mg (0.11 mmol) of compound **21** (88%): TLC R_f = 0.4 (*n*-hexane/EtOAc, 7:3); colorless syrup; $[\alpha]_D$ = +7.7 (*c* 0.7, $CHCl_3$); MS (FAB) Calcd for $C_{46}H_{68}Br_2O_{15}Si_2Na$ $(M + Na)^+$ 1099, Found 1099; ^{1}H NMR ($CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 5.34 (t, J = 9.4 Hz, 1H), 5.01 (dd, J = 8.0 and 9.0 Hz, 1H), 4.75 (dd, J = 8.0 and 9.3 Hz, 1H), 4.59 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 3.3 and 12.1 Hz, 1H), 4.44 (d, J = 8.0 Hz, 1H), 4.32 (dd, J = 5.0 and 12.1 Hz, 1H), 4.05 (dd, J = 3.1 and 11.0 Hz, 1H), 3.98 (t, J = 9.0 Hz, 1H), 3.86 (m, 1H), 3.76 (dd, J = 6.1 and 11.0 Hz, 1H), 3.61 (dd, J = 8.2 and 9.3 Hz, 1H), 3.42 (m, 2H), 2.40 (d, J = 3.4 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 1.20 (s, 9H), 0.85 (s, 9H), 0.71 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2, 169.1, 165.5, 164.4, 131.9–128.3, 100.9, 95.6, 77.2, 76.0, 75.8, 74.3, 73.7, 73.5, 73.0, 72.6, 72.1, 71.9, 69.1, 63.3, 28.6 (x3), 25.7 (x3), 25.4 (x3), 21.3 (x2), 18.1, 17.7, −4.3, −4.5 (x2), −4.7. Anal. Calcd for $C_{46}H_{68}Br_2O_{15}Si_2$: C, 51.30; H, 6.36. Found: C, 51.51; H, 6.00.

Methyl 6-*O*-[4,6-Bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (22). Following the general procedure for desilylation and deacetylation, 50.0 mg (0.05 mmol) of compound **17** yielded 27.1 mg (0.04 mmol) of compound **22** (77%): TLC R_f = 0.2 (CH_2Cl_2/MeOH, 9:1); mp = 151.3−153.6 °C; $[\alpha]_D$ = +7.0 (*c* 0.5, $CHCl_3$); MS (FAB) Calcd for $C_{27}H_{30}Br_2O_{13}Na$ $(M + Na)^+$ 745, Found 745; ^{1}H NMR (DMSO) δ 7.89 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 5.50 (d, J = 5.7 Hz, 1H), 5.37 (d, J = 5.0 Hz, 1H), 5.11 (d, J = 4.9 Hz, 1H), 5.08 (d, J = 5.4 Hz, 1H), 5.06 (d, J = 5.6 Hz, 1H), 5.03 (t, J = 9.6 Hz, H-4′), 4.53 (d, J = 7.8 Hz, 1H), 4.40 (dd, J = 3.1 and 12.1 Hz, H-6′$_{proS}$), 4.33 (dd, J = 4.7 and 12.1 Hz, H-6′$_{proR}$), 4.07 (d, J = 7.8 Hz, H-1), 4.05 (br d, J = 10.5 Hz, H-6$_{proS}$), 3.96 (m, H-5′), 3.65 (dd, J = 6.8 and 11.5 Hz, H-6$_{proR}$), 3.63 (dd, J = 5.8 and 9.2 Hz, H-3′), 3.42 (s, 3H), 3.35 (m, H-5), 3.22 (m, H-2′), 3.18 (m, H-3), 3.10 (m, H-4), 3.00 (m, H-2); ^{13}C NMR (DMSO) δ 165.1, 164.8, 132.2–127.8, 104.2, 103.9, 76.9, 75.9, 74.1, 73.9, 73.7, 72.6, 71.0, 70.4, 69.4, 63.9, 56.4; UV (EtOH)λ_{max} 245 nm; CD (EtOH) $\lambda(\Delta\varepsilon)$ 251 (13.3), 234 nm (−4.2). Anal. Calcd for $C_{27}H_{30}Br_2O_{13}$: C, 44.90; H, 4.19. Found: C, 44.90; H, 4.62.

***iso*-Propyl 6-*O*-[4,6-Bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (23).** Following the general procedure for desilylation and deacetylation, 63.7 mg (0.06 mmol) of compound **18** yielded 24.6 mg (0.03 mmol) of compound **23** (54%): TLC R_f = 0.2 (CH_2Cl_2/MeOH, 9:1); mp = 153.1−154.9 °C; $[\alpha]_D$ = +15.6 (*c* 0.7, $CHCl_3$); MS (FAB) Calcd for $C_{29}H_{34}Br_2O_{13}Na$ $(M + Na)^+$ 773, Found 773; ^{1}H NMR (DMSO) δ 7.89 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 5.52 (d, J = 5.6 Hz, 1H), 5.36 (d, J = 5.0 Hz, 1H), 5.04 (m, 2H), 5.02 (t, J = 9.5 Hz, H-4′), 4.95 (d, J = 5.0 Hz, 1H), 4.53 (d, J = 7.9 Hz, H-1′), 4.40 (dd, J = 2.9 and 12.0 Hz, H-6′$_{proS}$), 4.32 (dd, J = 4.7 and 12.0 Hz, H-6′$_{proR}$), 4.20 (d, J = 7.8 Hz, H-1), 4.02 (br d, J = 11.1 Hz, H-6$_{proS}$), 3.96–3.91 (m, 2H), 3.66 (dd, J = 7.0 and 11.6 Hz, H-6$_{proR}$), 3.61 (m, H-3′), 3.38 (m, H-5), 3.24–3.15 (m, H-2′, H-3), 3.08 (m, H-4), 2.95 (m, H-2), 1.16 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (DMSO) δ 165.7, 165.4, 132.8–128.4, 104.5, 102.1, 77.7, 76.4, 74.6, 74.3 (x2), 73.2, 71.6, 71.0 (x2), 70.1, 64.5, 24.5, 22.8; UV (EtOH)λ_{max} 245 nm; CD (EtOH) $\lambda(\Delta\varepsilon)$ 251 (13.1), 234 nm (−4.0). Anal. Calcd for $C_{29}H_{34}Br_2O_{13}$: C, 46.42; H, 4.57. Found: C, 46.44; H, 4.65.

(+)-Menthyl 6-*O*-[4,6-Bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (24). Following the general procedure for desilylation and deacetylation, 111 mg (0.10 mmol) of compound **19** yielded 38 mg (0.05 mmol) of compound **24** (47%): TLC R_f = 0.4 (CH_2Cl_2/MeOH, 9:1); mp = 154.2−155.6 °C; $[\alpha]_D$ = +33.0 (*c* 0.3, $CHCl_3$); MS (FAB) Calcd for $C_{36}H_{46}Br_2O_{13}Na$

(M + Na)$^+$ 869, Found 869; ^{1}H NMR (DMSO) δ 7.86 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 5.52 (d, J = 5.3 Hz, 1H), 5.38 (d, J = 4.3 Hz, 1H), 5.08 (d, J = 4.8 Hz, 1H), 5.02 (t, J = 9.8 Hz, H-4′), 4.98 (m, 2H), 4.59 (d, J = 7.8 Hz, H-1′), 4.41 (dd, J = 3.1 and 12.1 Hz, H-6′$_{proS}$), 4.31 (d, J = 4.9 and 12.1 Hz, H-6′$_{proR}$), 4.18 (d, J = 7.7 Hz, H-1), 4.00 (br d, J = 11.4 Hz, H-6$_{proS}$), 3.90 (m, H-5′), 3.69 (dd, J = 7.4 and 12.1 Hz, H-6$_{proR}$), 3.60 (m, H-3′), 3.42 (m, H-5), 3.36 (m, 1H), 3.21 (m, H-2′), 3.15 (br t, J = 8.8 Hz, H-3), 3.03–2.97 (m, H-2, H-4), 2.44 (m, 1H), 2.22 (m, 1H), 1.59 (m, 2H), 1.39 (m, 1H), 1.17 (m, 2H), 0.90 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 7.1 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H); ^{13}C NMR (DMSO) δ 165.6, 165.4, 132.7–128.5, 105.1, 104.5, 80.4, 76.9, 74.7 (x2), 74.5, 73.2, 71.6, 71.2, 70.0, 64.6, 49.4, 44.4, 34.9, 32.0, 24.8, 23.4, 23.2, 22.1, 16.9; UV (EtOH)λ_{max} 245 nm; CD (EtOH) $\lambda(\Delta\varepsilon)$ 251 (12.9), 234 nm (−3.9). Anal. Calcd for $C_{36}H_{46}Br_2O_{13}$: C, 51.08; H, 5.48. Found: C, 51.06; H, 5.58.

(−)-Menthyl 6-*O*-[4,6-Bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (25). Following the general procedure for desilylation and deacetylation, 50.0 mg (0.04 mmol) of compound **20** yielded 19.3 mg (0.02 mmol) of compound **25** (53%): TLC R_f = 0.3 (CH_2Cl_2/MeOH, 9:1); mp = 151.3−153.6 °C; $[\alpha]_D$ = −9.4 (*c* 0.7, $CHCl_3$); MS (FAB) Calcd for $C_{36}H_{46}Br_2O_{13}Na$ (M + Na)$^+$ 869, Found 869; ^{1}H NMR (DMSO) δ 7.88 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 5.51 (d, J = 5.4 Hz, 1H), 5.31 (d, J = 4.3 Hz, 1H), 5.02 (m, 2H), 5.01 (t, J = 9.5 Hz, H-4′), 4.91 (d, J = 4.7 Hz, 1H), 4.48 (d, J = 7.8 Hz, H-1′), 4.38 (dd, J = 2.9 and 12.0 Hz, H-6′$_{proS}$), 4.27 (dd, J = 4.9 and 12.0 Hz, H-6′$_{proR}$), 4.23 (d, J = 7.9 Hz, H-1), 4.01 (br d, J = 10.9 Hz, H-6$_{proS}$), 3.91 (m, H-5′), 3.68 (dd, J = 6.6 and 11.6 Hz, H-6$_{proR}$), 3.60 (m, H-3′), 3.46 (dt, J = 3.9 and 10.5 Hz, 1H), 3.35 (m, H-5), 3.22 (m, H-2′), 3.14 (m, H-3, H-4), 2.95 (m, H-2), 2.23 (m, 1H), 2.05 (m, 1H), 1.59 (m, 2H), 1.30 (m, 2H), 1.14 (m, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.83 (d, J = 7.2 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H); ^{13}C NMR (DMSO) δ 165.6, 165.3, 132.7–128.4, 104.5, 100.6, 77.8, 76.6, 76.2, 74.6, 74.4, 74.2, 73.2, 71.6, 71.1, 70.4, 64.6, 48.4, 44.4, 35.0, 31.7, 25.5, 23.6, 23.2, 21.8, 16.7; UV (EtOH)λ_{max} 245 nm; CD (EtOH) $\lambda(\Delta\varepsilon)$ 251 (13.0), 234 nm (−3.9). Anal. Calcd for $C_{36}H_{46}Br_2O_{13}$: C, 51.08; H, 5.48. Found: C, 51.08; H, 5.49.

***tert*-Butyl 2-*O*-Acetyl-6-*O*-[2-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (26).** Compound **21** (40.0 mg, 0.04 mmol) was dissolved in dry acetonitrile under an argon atmosphere at 0 °C, treated with 2.5 equiv of HF-Py, and left at room temperature. When the reaction was completed, it was diluted with CH_2Cl_2 and washed with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2 times). The combined extracts were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography of the residue (*n*-hexane/$CHCl_3$/MeOH, 2:1:1) furnished **26** (17.1 mg, 0.02 mmol) in 54% yield: TLC R_f = 0.5 (CH_2Cl_2/MeOH, 9:1); colorless syrup; $[\alpha]_D$ = +3.0 (*c* 1.1, $CHCl_3$); MS (FAB) Calcd for $C_{34}H_{40}Br_2O_{15}Na$ (M + Na)$^+$ 871, Found 871; ^{1}H NMR (DMSO) δ 7.89 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 5.29 (t, J = 9.5 Hz, H-4′), 4.94 (dd, J = 7.9 and 9.3 Hz, H-2′), 4.69 (dd, J = 7.9 and 9.3 Hz, H-2), 4.66 (d, J = 7.6 H-1′), 4.61 (dd, J = 3.0 and 12.1 Hz, H-6′$_{proS}$), 4.53 (d, J = 7.9 Hz, H-1), 4.39 (dd, J = 5.1 and 12.1 Hz, H-6′$_{proR}$), 4.08 (dd, J = 2.3 and 11.2 Hz, H-6$_{proS}$), 3.93 (m, H-5′), 3.88 (t, J = 9.3 Hz, H-3′), 3.78 (dd, J = 5.8 and 10.9 Hz, H-6$_{proR}$), 3.56 (t, J = 9.2 Hz, H-3), 3.46 (m, H-5, H-4′), 2.12 (s, 3H), 2.10 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (DMSO) δ 170.9, 170.8, 165.5, 165.3, 131.9–127.9, 100.7, 95.2, 76.1, 75.8, 74.4, 74.2, 74.1, 73.8, 72.2, 72.0, 71.8, 69.3, 63.2, 28.6 (x3), 20.9 (x2). Anal. Calcd for $C_{34}H_{40}Br_2O_{15}$: C, 48.13; H, 4.75. Found: C, 48.21; H, 5.01.

***tert*-Butyl 6-*O*-[4,6-Bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (27).** Compound **26** (13.0 mg, 0.02 mmol) was dissolved in 2 mL of CH_2Cl_2/MeOH (9:1), and 1.5 equiv of *p*-TsOH-H_2O (6.0 mg, 0.03 mmol) was added. When the reaction was completed, it was diluted with CH_2Cl_2 and washed with a saturated $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 (2 times). The combined extracts were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography of the residue (*n*-hexane/$CHCl_3$/MeOH, 2:1:1), led to **27** (10.8 mg, 0.02 mmol) in 78% yield: TLC R_f = 0.2 (CH_2Cl_2/MeOH, 9:1); colorless syrup; $[\alpha]_D$ = +15.8 (*c* 0.8, $CHCl_3$); MS (FAB) Calcd for $C_{30}H_{36}Br_2O_{13}Na$ (M + Na)$^+$ 787, Found 787; ^{1}H NMR (DMSO) δ 7.89 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 5.50 (br d, J = 5.6 Hz, 1H), 5.29 (br d, J = 5.0 Hz, 1H), 5.03 (br d, J = 4.6 Hz, H-4′), 4.97 (br d, J = 4.5 Hz, 1H), 4.79 (br d, J = 4.6 Hz, 1H), 4.51 (d, J = 7.8 Hz, H-1′), 4.41 (dd, J = 3.0 and 12.0 Hz, H-6′$_{proS}$), 4.31 (dd, J = 5.1 and 12.0 Hz, H-6′$_{proR}$), 4.29 (d, J = 7.8 Hz, H-1), 3.97 (br d, J = 10.5 Hz, H-6$_{proS}$), 3.94 (m, H-5′), 3.65 (dd, J = 7.2 and 11.6 Hz, H-6$_{proR}$), 3.64 (m, H-3′), 3.38 (m, H-5), 3.22–3.15 (m, H-3, H-2′), 3.07 (m, H-4), 2.92 (m, H-2), 1.20 (s, 9H); ^{13}C NMR (DMSO) δ 165.2, 164.9, 132.3–127.9, 105.9, 97.7, 77.3, 75.6, 74.9, 74.1, 74.0, 73.9, 72.7, 71.1, 70.6, 69.8, 64.0, 29.0 (x3); UV (EtOH)λ_{max} 245 nm; CD (EtOH) $\lambda(\Delta\varepsilon)$ 251 (12.8), 234 nm (−3.9). Anal. Calcd for $C_{30}H_{36}Br_2O_{13}$: C, 47.14; H, 4.75. Found: C, 47.17; H, 4.53.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (28). Compound **22** (45.0 mg, 0.06 mmol) was dissolved in 1 mL of a 1:1 dry pyridine/acetic anhydride solution. Excess solvent was removed under reduced pressure to give, after column chromatography (*n*-hexane/EtOAc, 8:2), compound **28** (50.1 mg, 0.05 mmol) in 90% yield: TLC R_f = 0.3 (*n*-hexane/EtOAc, 1:1); mp = 199.2−204.6 °C (decomp.); $[\alpha]_D$ = +8.2 (*c* 1.7, $CHCl_3$); MS (FAB) Calcd for $C_{37}H_{40}Br_2O_{18}Na$ (M + Na)$^+$ 955, Found 955; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 4H), 5.43–5.38 (m, H-3′, H-4′), 5.19 (t, J = 9.5 Hz, H-3), 5.08 (t, J = 7.9 Hz, H-2′), 4.93 (dd, J = 8.0 and 9.5 Hz, H-2), 4.88 (t, J = 9.5 Hz, H-4), 4.70 (d, J = 7.9 Hz, H-1′), 4.53 (dd, J = 3.2 and 12.2 Hz, H-6′$_{proS}$), 4.39 (d, J = 8.0 Hz, H-1), 4.38 (dd, J = 4.9 and 12.2 Hz, H-6′$_{proR}$), 3.96 (m, H-5′), 3.89 (dd, J = 1.8 and 10.8 Hz, H-6$_{proS}$), 3.69 (m, H-5), 3.63 (dd, J = 7.4 and 10.8 Hz, H-6$_{proR}$), 3.51 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.2, 170.1, 169.6, 169.4, 169.3, 165.3, 164.4, 132.0–127.5, 101.5, 101.0, 73.3, 72.8, 72.4, 71.8, 71.3, 71.2, 69.7, 69.2, 68.3, 63.0, 57.0, 20.7, 20.6 (x3), 20.5. Anal. Calcd for $C_{37}H_{40}Br_2O_{18}$: C, 47.66; H, 4.32. Found: C, 47.65; H, 4.33.

***iso*-Propyl 2,3,4-Tri-*O*-acetyl-6-*O*-[2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (29).** Compound **23** (20.0 mg, 0.03 mmol) was dissolved in 1 mL of a 1:1 solution of dry pyridine/acetic anhydride. Excess solvent was removed under reduced pressure to give, after column chromatography (*n*-hexane/EtOAc, 8:2), compound **29** (21.0 mg, 0.05 mmol) in 82% yield: TLC R_f = 0.4 (*n*-hexane/EtOAc, 1:1); mp = 198.9−204.0 °C (decomp.); $[\alpha]_D$ = −3.6 (*c* 1.2, $CHCl_3$); MS (FAB) Calcd for $C_{39}H_{44}Br_2O_{18}Na$ (M+Na)$^+$ 983, Found 983; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.8 Hz, 4H), 5.40–5.35 (m, H-3′, H-4′), 5.19 (t, J = 9.5 Hz, H-3), 5.08 (dd, J = 7.9 and 9.5 Hz, H-2′), 4.89 (dd, J = 7.9 and 9.7 Hz, H-2), 4.85 (t, J = 9.5 Hz, H-4), 4.71 (d, J = 7.9 Hz, H-1′), 4.54 (dd, J = 3.2 and 12.2 Hz, H-6′$_{proS}$), 4.52 (d, J = 7.9 Hz, H-1), 4.37 (dd, J = 5.0 and 12.2 Hz, H-6′$_{proR}$), 3.94–3.89 (m, 2H), 3.85 (d, J = 9.2 Hz, H-6$_{proS}$), 3.69 (m, H-5), 3.65 (dd, J = 7.7 and 10.6 Hz, H-6$_{proR}$), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H), 1.24 (d, J = 6 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.2, 170.1, 169.6, 169.3, 169.2, 165.3, 164.4, 132.0–127.5, 100.8, 99.4, 73.4, 72.8, 72.7, 72.4, 71.9, 71.6, 71.2, 69.7, 69.2, 68.3, 63.0, 23.4, 21.9, 20.6 (x3), 20.5, 20.4. Anal. Calcd for $C_{39}H_{44}Br_2O_{18}$: C, 48.76; H, 4.62. Found: C, 48.74; H, 4.34.

(+)-Menthyl 2,3,4-Tri-*O*-acetyl-6-*O*-[2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (30). Compound **24** (10.0 mg, 0.01 mmol) was dissolved in 1

mL of a 1:1 solution of dry pyridine/acetic anhydride. Excess solvent was removed under reduced pressure to give, after column chromatography (*n*-hexane/EtOAc, 8:2), compound **30** (12.2 mg, 0.01 mmol, 96% yield): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 6:4); mp = 198.2−201.9 °C (decomp.); $[\alpha]_D = +9.3$ (*c* 0.4, $CHCl_3$); MS (FAB) Calcd for $C_{46}H_{56}Br_2O_{18}Na$ $(M + Na)^+$ 1077, Found 1077; ^{1}H NMR ($CDCl_3$) δ 7.84 (d, $J = 8.6$ Hz, 2H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 5.42–5.35 (m, H-3′, H-4′), 5.17 (t, $J = 9.5$ Hz, H-3), 5.05 (dd, $J = 7.9$ and 9.6 Hz, H-2′), 4.94 (dd, $J = 8.0$ and 9.7 Hz, H-2), 4.87 (t, $J = 9.7$ Hz, H-4), 4.79 (d, $J = 7.9$ Hz, H-1′), 4.55 (dd, $J = 3.3$ and 12.2 Hz, H-6′$_{proS}$), 4.53 (d, $J = 8.1$ Hz, H-1), 4.38 (dd, $J = 4.9$ and 12.2 Hz, H-6′$_{proR}$), 3.94 (m, H-5′), 3.82–3.77 (m, 2H-6), 3.70 (m, H-5), 3.32 (dt, $J = 4.4$ and 10.4 Hz, 1H), 2.12 (m, 1H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.67 (m, 1H), 1.56 (m, 2H), 1.21 (m, 2H), 1.13 (m, 1H), 0.96 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 7.0$ Hz, 3H), 0.74 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.3, 170.0, 169.5, 169.2 (x2), 165.3, 164.4, 132.0–127.5, 101.7, 100.8, 82.2, 73.7, 73.0, 72.5, 71.9 (x2), 71.4, 69.8, 69.1, 68.0, 63.1, 48.4, 43.2, 34.1, 31.6, 24.8, 22.8, 22.3, 21.1, 20.7, 20.6 (x3), 20.5, 16.0. Anal. Calcd for $C_{46}H_{56}Br_2O_{18}$: C, 52.28; H, 5.34. Found: C, 52.26; H, 5.26.

(−)-Menthyl 2,3,4-Tri-*O*-acetyl-6-*O*-[2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (31). Compound **25** (13.0 mg, 0.02 mmol) was dissolved in 1 mL of a 1:1 solution of dry pyridine/acetic anhydride. Excess solvent was removed under reduced pressure to give, after column chromatography (*n*-hexane/EtOAc, 8:2), compound **31** (15.1 mg, 0.02 mmol, 95% yield): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); mp = 192.1−195.4 °C (decomp.); $[\alpha]_D = -22.0$ (*c* 1.4, $CHCl_3$); MS (FAB) Calcd for $C_{46}H_{56}Br_2O_{18}Na$ $(M + Na)^+$ 1077, Found 1077; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.77 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 5.38 (m, H-3′, H-4′), 5.17 (t, $J = 9.5$ Hz, H-3), 5.05 (dd, $J = 7.9$ and 9.7 Hz, H-2′), 4.92 (t, $J = 9.6$ Hz, H-4), 4.88 (dd, $J = 8.0$ and 9.6 Hz, H-2), 4.71 (d, $J = 7.9$ Hz, H-1′), 4.56 (d, $J = 8.0$ Hz, H-1), 4.52 (dd, $J = 3.3$ and 12.2 Hz, H-6′$_{proS}$), 4.36 (dd, $J = 4.9$ and 12.2 Hz, H-6′$_{proR}$), 3.92 (m, H-5′), 3.84 (dd, $J = 1.9$ and 11.0 Hz, H-6$_{proS}$), 3.67 (dd, $J = 6.5$ and 11.0 Hz, H-6$_{proR}$), 3.64 (m, H-5), 3.40 (dt, $J = 4.1$ and 10.5 Hz, 1H), 2.21 (m, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.95 (m, 1H), 1.90 (s, 3H), 1.63 (m, 2H), 1.31 (m, 1H), 1.19 (m, 1H), 0.93 (m, 1H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.86 (d, $J = 7.1$ Hz, 3H), 0.77 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.3, 170.0, 169.5, 169.3, 169.2, 165.3, 164.4, 132.0–127.5, 100.7, 98.0, 78.1, 73.3, 73.0, 72.5, 71.8, 71.6, 71.2, 69.7, 69.2, 68.3, 63.1, 47.6, 40.5, 34.2, 31.4, 25.1, 23.1, 22.2, 20.9, 20.7 (x2), 20.6 (x2), 20.5, 16.0. Anal. Calcd for $C_{46}H_{56}Br_2O_{18}$: C, 52.28; H, 5.34. Found: C, 52.26; H, 5.35.

***tert*-Butyl 2,3,4-Tri-*O*-acetyl-6-*O*-[2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-*β*-D-glucopyranosyl]-*β*-D-glucopyranoside (32).** Compound **26** (16.2 mg, 0.02 mmol) was dissolved in 1 mL of a 1:1 solution of dry pyridine/acetic anhydride. Excess solvent was removed under reduced pressure to give, after column chromatography (*n*-hexane/EtOAc, 8:2), compound **32** (17.4 mg, 0.02 mmol, 89% yield): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 1:1); mp = 195.3−200.2 °C (decomp.); $[\alpha]_D = +3.0$ (*c* 0.6, $CHCl_3$); MS (FAB) Calcd for $C_{40}H_{46}Br_2O_{18}$ $(M)^+$ 901, Found 901; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.78 (d, $J = 8.6$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 5.38 (m, H-3′, H-4′), 5.19 (t, $J = 9.5$ Hz, H-3), 5.05 (dd, $J = 7.9$ and 9.6 Hz, H-2′), 4.88 (dd, $J = 8.0$ and 9.7 Hz, H-2), 4.83 (t, $J = 9.6$ Hz, H-4), 4.69 (d, $J = 7.9$ Hz, H-1′), 4.62 (d, $J = 8.0$ Hz, H-1), 4.54 (dd, $J = 3.2$ and 12.2 Hz, H-6′$_{proS}$), 4.35 (dd, $J = 5.1$ and 12.2 Hz, H-6′$_{proR}$), 3.93 (m, H-5′), 3.81 (dd, $J = 1.7$ and 10.3 Hz, H-6$_{proS}$), 3.68 (m, H-5), 3.65 (dd, $J = 7.8$ and 10.3 Hz, H-6$_{proR}$), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.89 (s, 3H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.3, 170.1, 169.7, 169.2 (x2), 165.3, 164.4, 132.0–127.5, 100.5, 95.3, 76.5, 73.2, 73.0, 72.5, 71.8, 71.6, 71.2, 69.7, 69.2, 68.2, 63.0, 28.5 (x3), 20.7 (x2), 20.6 (x2), 20.5. Anal. Calcd for $C_{40}H_{46}Br_2O_{18}$: C, 49.30; H, 4.76. Found: C, 49.32; H, 4.82.

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Supporting Information Available: Synthesis and characterization of known compounds **5**–**7**, Tables containing $J_{H5,H6}$ and $J_{H5',H6'}$ coupling constants and calculated rotameric populations (%) for disaccharides **10**–**21** and **28**–**32**, as well as ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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