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2,3-Anhydrosugars in Glycoside Bond Synthesis. Application to α-D-Galactofuranosides

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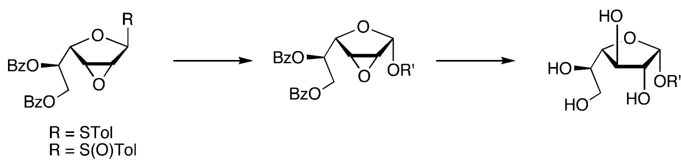

We report here the use of 2,3-anhydro-D-gulofuranosyl thioglycosides and glycosyl sulfoxides in the synthesis of α-D-galactofuranosidic bonds, which are present in a range of bacterial and fungal glycoconjugates. This two-step method involves a stereoselective glycosylation in which a 2,3-anhydro-α-D-gulofuranoside is obtained either as the sole or as the major product, followed by a regioselective opening of the epoxide ring using lithium benzylate in the presence of (−)-sparteine. In exploring the scope of the method, donors protected at O5 and O6 with an isopropylidene acetal, benzyl ethers, or benzoate esters were studied. Overall, the glycosyl sulfoxides provided the products in slightly higher yields and selectivity, with the best results being obtained with benzylated and benzoylated substrates. In the epoxide ring-opening reactions, the acetal- and ether-protected donors afforded poor to modest regioselectivity, whereas the benzoylated products gave good yields of the desired α-D-galactofuranosides. The benzoyl-protected species are, therefore, the donors of choice for these reactions. The utility of the approach was demonstrated through the synthesis of three α-D-galactofuranosyl-containing oligosaccharides.

Introduction

In previous reports, we have described the use of 2,3-anhydrosugar thioglycosides and glycosyl sulfoxides in the stereocontrolled synthesis of oligosaccharides containing arabinofuranosyl residues.[1−3] Glycosylating agents **1** and **2** (Figure 1), upon coupling with a range of different alcohols, provide glycosides with the 2,3-anhydro-*β*-D-*lyxo* stereochemistry (e.g., **3**), which in turn can be converted to *β*-arabinofuranosides (e.g., **4**) by reaction with lithium benzylate (BnOLi) in the presence of (−)-sparteine followed by deprotection.[1,2] Analogously, donors **5** and **6** give α-arabinofuranosides (e.g., **8**) via 2,3-anhydro-α-D-ribofuranosides (e.g., **7**); however, in these cases, the additive is not necessary in the epoxide-opening step.[3] The method has also been applied to the synthesis of nucleosides.[4]

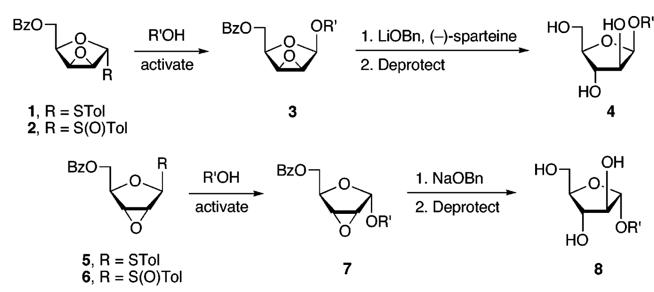

FIGURE 1. 2,3-Anhydro-pentofuranose derivatives in the synthesis of arabinofuranosides.

We subsequently demonstrated[5] that for the sulfoxide donors the high glycosylation selectivity was due to the formation of a single glycosyl triflate intermediate that reacted with the alcohol via an S_N2-like displacement.[6] The origin of the

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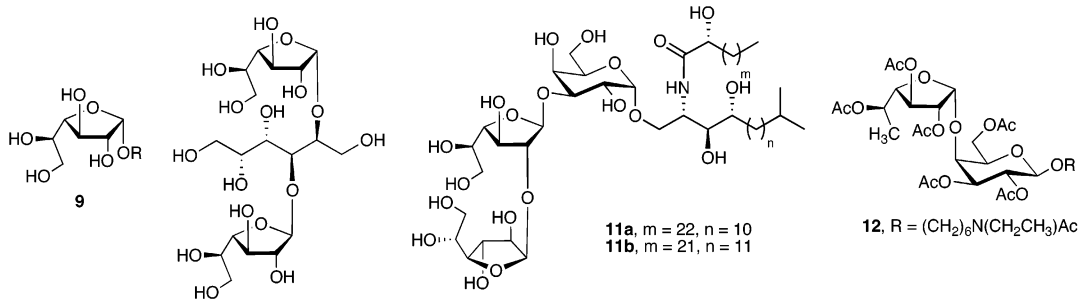
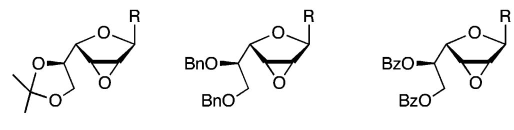
CHART 1



stereoselectivity with the thioglycosides remains unclear. With regard to the epoxide-opening reactions, the high selectivity for C2 attack of the nucleophile in the 2,3-anhydro-α-D-ribofuranosides (**7**) is presumably due to steric effects, the hydroxymethyl substituent disfavoring attack at C3.[7] The preference for nucleophiles to attack C3 in 2,3-anhydro-β-D-lyxofuranosides (**3**) in the presence of (−)-sparteine is unrelated to the chirality of the additive,[2] but the factors that underlie the regioselectivity of this reaction have not been clarified.

Our previous success with this class of glycosylating agent has prompted us to extend our studies to the synthesis of glycoconjugates containing other 1,2-cis-linked furanose residues. We report here the application of the 2,3-anhydrosugar methodology to the synthesis of α-D-galactofuranosides (**9**, Chart 1). Although β-D-galactofuranosides are more widespread in nature,[8] a number of bacterial and fungal glycoconjugates contain α-D-galactofuranosyl[9] or α-D-fucofuranosyl (6-deoxy-D-galactofuranosyl)[10] residues, and the stereoselective synthesis of these glycosidic linkages has been problematic.[11] Indeed, only very recently have studies focused on the stereocontrolled preparation of α-D-galactofuranosyl-containing glycoconjugates been reported.[12−14] These investigations led[13] to the synthesis of the glycan (**10**), liberated upon reductive β-elimination of glycoproteins in the cellulosomes of *Bacteriodies cellulosolvens*.[9e] In this synthesis, a fully benzylated trichloroacetimidiate donor was used to install the α-D-galactofuranosyl residue. In addition, two homologous immunomodulatory glycolipids (**11**), both of which contain a single α-D-galactofuranosyl residue, have been synthesized using carboxybenzyl glycoside donors.[14] Another recent study[15] reported the application of the Ogawa−Ito variant[16] of the intramolecular aglycon delivery method to the synthesis of an α-D-fucofuranosyl-containing disaccharide (**12**) related to an antigenic polysaccharide from *Eubacterium saburreum* strain T19.[17]

CHART 2



Results and Discussion

Synthesis of Glycosyl Donors. The preparation of α-D-galactofuranosides via our 2,3-anhydrosugar methodology requires the synthesis of donors with the 2,3-anhydro-D-gulofuranoside stereochemistry, and thus, we targeted thioglycosides **13−15** (Chart 2) and glycosyl sulfoxides **16−18** for synthesis. In addition to studying the potential of these reagents in glycoside synthesis, we also wanted to evaluate three different classes of protecting groups on O5 and O6 to determine what, if any, effect the protecting group had on the stereoselectivity of the glycosylation. In addition, previous studies[18] suggested that the nature of protecting groups at these positions might also influence the regioselectivity of the epoxide-opening reaction.

The synthesis of **13−18** started from D-galactose. A number of methods have been reported for converting galactose from

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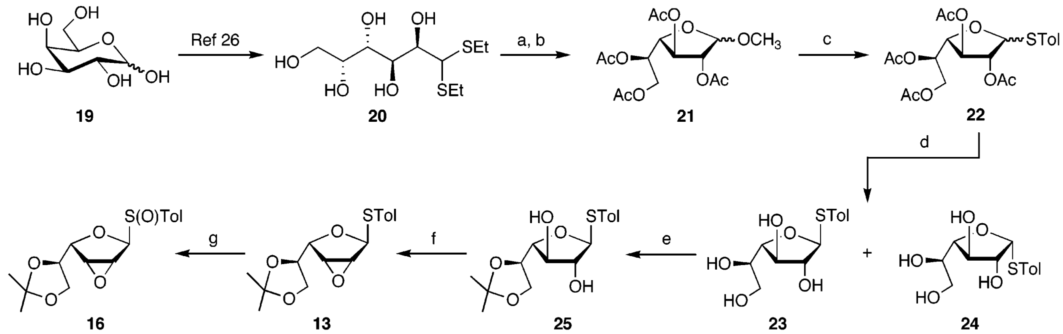
SCHEME 1[a]



[a] Conditions: (a) 1,3-dibromo-5,5-dimethylhydantoin; (b) Ac_2O, pyridine, rt, 61% over two steps; (c) *p*-TolSH, $BF_3 \cdot OEt_2$, CH_2Cl_2, 0 °C, 76%; (d) $NaOCH_3$, CH_3OH, rt, 88%; (e) $(CH_3)_2C(OCH_3)_2$, acetone, *p*-TsOH; (f) DIAD, Ph_3P, THF, 0 °C, 81% from **23**; (g) *m*-CPBA, CH_2Cl_2, −78 °C → rt, 84%.

the thermodynamically more stable pyranose form to the higher energy furanose form, including Fischer glycosylation,[19] high-temperature acylation[20] or anomeric alkylation,[12] reduction of galactonolactones,[21] and the cyclization of dithioacetals[22] or open-chain *S*,*O*-acetals[23] with mercuric salts. Many of these approaches have limitations such as contamination with pyranose forms, modest yields, or the use of expensive or toxic reagents. The cyclization of dithioacetals in the presence of an alcohol and iodine has also been reported.[24] Advantages of this method include a starting material that can be readily prepared in multigram scale (albeit under malodorous conditions), inexpensive reagents, and a lack of contamination by pyranose forms. In the paper describing this chemistry, it was applied to arabinose-, glucose-, and mannose-derived dithioacetals but not to those obtained from galactose. To the best of our knowledge, this method has not since been applied to the preparation of galactofuranose derivatives; however, a recent paper reports an analogous cyclization using 1,3-dibromo-5,5-dimethylhydantoin and we therefore used this method.[25]

Thus, D-galactose (**19**, Scheme 1) was converted into its diethyldithioacetal derivative, **20**, upon treatment with HCl and ethanethiol, as previously reported.[26] Reaction of **20** with 1,3-dibromo-5,5-dimethylhydantoin and methanol followed by acetylation in acetic anhydride and pyridine gave a 35:65 α:β mixture of methyl galactofuranosides, **21**, in 61% yield over two steps. Conversion of **21** into the corresponding *p*-tolyl thioglycoside was achieved in 76% yield under the usual conditions (boron trifluoride etherate and thiocresol),[27] which afforded **22** as a 1:9 α:β mixture (determined by integration of NMR signals, $^3J_{H1,H2}$ of major product = 2.5 Hz). Deacetylation of **22** with sodium methoxide in methanol afforded separable thioglycosides **23** and **24** in a 10:1 ratio (based on isolated yields) in an 88% combined overall yield from **22**. The major compound, **23**, was taken forward, and installation of an isopropylidene ketal at O5 and O6 proceeded without incident. The product of this reaction, **25**, was not characterized but instead was directly treated with diisopropylazodicarboxylate (DIAD) and triphenylphosphine. This sequence afforded **13** in 81% yield from **23**; none of the epoxide with the isomeric stereochemistry was isolated. Oxidation[28] of **13** with *m*-CPBA in dichloromethane afforded an 84% yield of the expected glycosyl sulfoxide donor **16** as a 5.5:1 mixture of diastereomers. The stereochemistry at sulfur in these glycosyl sulfoxides was not established.

The presence of the oxirane ring in **13** and the diastereomers of **16** was clearly demonstrated by the marked upfield shift (∼20 ppm) of the signals for C2 and C3 in the ^{13}C NMR spectrum, which appeared between 54.5 and 56.8 ppm. By analogy with the stereochemically related arabinofuranose series,[2,29] we expected that epoxide formation would proceed to give the expected product. However, it was impossible to determine the orientation of the epoxide ring from the ^1H and ^{13}C NMR data for these compounds. Fortunately, thioglycoside **13** is crystalline, and a single-crystal X-ray diffraction study unambiguously showed that the epoxide moiety is trans to the tolyl moiety and cis to the C5/C6 side chain.[30]

With donors **13** and **16** in hand, we turned our attention to the preparation of the other donors with the different side-chain-protecting groups, a task we assumed could be done straightforwardly via acidic removal of the isopropylidene group in **13** and subsequent installation of benzyl- or benzoyl-protecting groups and oxidation at sulfur. However, all attempts to remove the 5,6-*O*-isopropylidene acetal in **13** failed, despite the evaluation of a number of different conditions (80% aqueous HOAc, 20% aqueous HOAc, and *p*-TsOH/H_2O). TLC monitoring of these reactions showed the formation of one major spot, different from **13**. NMR analysis of the isolated material demonstrated that the epoxide was no longer intact and that the thiotolyl group had migrated to C2 (four methine carbon signals at 54.2−61.0 ppm). In addition, four signals were present in the anomeric region of the ^1H NMR spectrum (4.6−6.0 ppm). On the basis of these data, we propose that this compound is a mixture of the four cyclic forms of 2-deoxy-2-thiotolyl-D-idose (**26**, Figure

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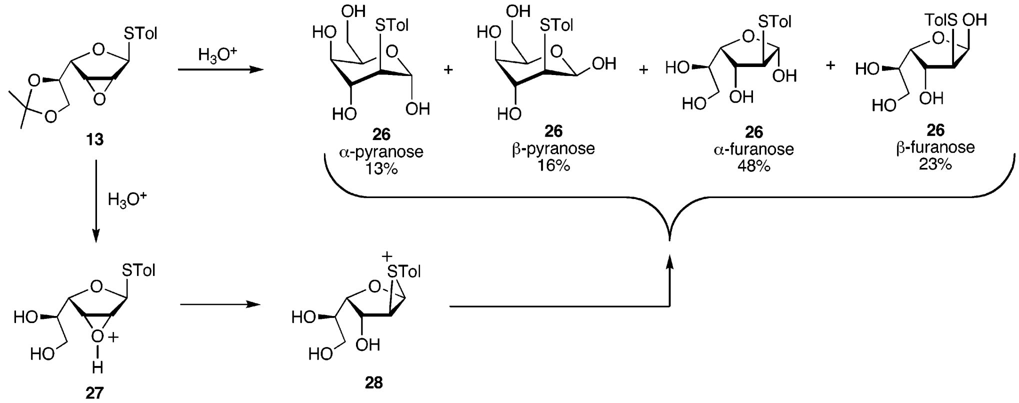
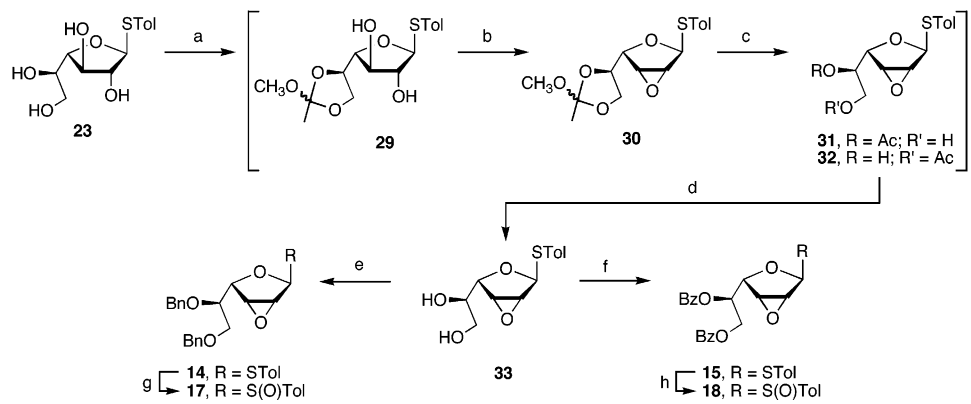


FIGURE 2. Formation of 2-deoxy-2-thiotolyl-D-idose upon attempted hydrolysis of the isopropylidene acetal in **13**. In the proposed reaction pathway, the loss of the isopropylidene acetal has arbitrarily been shown to precede migration.

SCHEME 2[a]



[a] Conditions: (a) trimethylorthoacetate, *p*-TsOH, rt; (b) DIAD, Ph_3P, 0 °C → rt; (c) HCl wash, rt; (d) $NaOCH_3$, CH_3OH, rt, 72% from **23**; (e) BnBr, NaH, DMF, 0 °C → rt, 93%; (f) BzCl, pyridine, 0 °C → rt, 90%; (g) *m*-CPBA, CH_2Cl_2, −78 °C → rt, 87%; (h) *m*-CPBA, CH_2Cl_2, −78 °C → rt, 86%.

2), which presumably is formed by protonation of the epoxide in **13** to give **27** and subsequent migration of the thiotolyl group to form a sulfonium ion species (**28**) that is in turn hydrolyzed. Analogous migration products have previously been identified as byproducts in glycosylation reactions of 2,3-anhydrosugar thioglycosides.[1,2] Interestingly, the equilibrium mixture of **26** exists[31] predominantly in the furanose form (71:29 furanose: pyranose), in contrast to the parent sugar D-idose, which adopts a ∼25:75 furanose:pyranose mixture.[32] These differences are presumably due to unfavorable steric interactions between the thiotolyl moiety at C2 and O4 in the pyranose form[33] and the orientation of this large group on the top face of the ring in the furanose forms, which is trans to the other bulky substituent, the C5/C6 side chain.

Faced with this difficulty, we chose an alternate route to the benzyl- and benzoyl-protected donors **14**, **15**, **17**, and **18**. Key to this new route was the use of an orthoester-protecting group on O5 and O6. We reasoned that as an orthoester is more acid labile than an isopropylidene acetal, that very mild cleavage conditions could be used to liberate the diol following the Mitsunobu reaction thus leaving the epoxide intact. This approach was successful, as outlined in Scheme 2; however, the acid-sensitive nature of the orthoester required the initial stages of the sequence to be carried out without purification of intermediate products. Thus, reaction of **23** with trimethylorthoacetate and *p*-toluenesulfonic acid led to the formation of two new products that ran faster on TLC, which we assumed were the diastereomeric orthoesters **29**. Following neutralization of the solution with triethylamine, DIAD and triphenylphosphine were added, leading to the formation of a new spot on TLC, presumably epoxide **30**. The solution was concentrated, diluted with ethyl acetate, and then washed in a separatory funnel with dilute aqueous HCl (0.3%), providing two new spots on TLC, which we assign as a mixture of acetate esters **31** and **32**. Treatment of the mixture of **31** and **32** with sodium methoxide provided a single product, which was purified and shown to be

(31) The ratio of cyclic forms was calculated by the integration of anomeric proton signals in the ^{1}H NMR spectrum, with the peak assignments being made by ^{1}H−^{1}H COSY and HMQC experiments. Assignment of anomeric carbon signals in the ^{13}C NMR spectrum was done by comparison with published data for D-idose (Bock, K.; Pedersen, C. *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27−66). Anomeric proton resonances: 5.51 ppm ($^3J_{1,2}$ = 4.8 Hz, correlated to ^{13}C signal at 97.7 ppm; *β*-furanose), 5.25 ppm ($^3J_{1,2}$ = 2.6 Hz, correlation to ^{13}C signal at 94.1 ppm; α-pyranose), 5.17 ppm ($^3J_{1,2}$ = 2.1 Hz, correlated to ^{13}C signal at 103.5 ppm; α-furanose), 5.08 ppm ($^3J_{1,2}$ = 4.1 Hz, correlation to ^{13}C signal at 95.3 ppm; *β*-pyranose).

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(33) If the pyranose ring were to flip into the other chair conformation, the C5 hydroxymethyl group would be axial, which is energetically disfavored although not impossible; alternative ring forms are also possible. However, in the α-pyranose form, the $^3J_{H1,H2}$ and $^3J_{H2,H3}$ values are 2.6 and 3.2 Hz, respectively, which suggests that this ring adopts predominantly the $^4C_1$ chair conformer. For the *β*-pyranose form, $^3J_{H1,H2}$ = 4.1 Hz and $^3J_{H2,H3}$ = 6.2 Hz, suggesting that other ring conformers are present. Nevertheless, we feel the ratio of cyclic forms can be rationalized by these simple steric arguments.

CHART 3

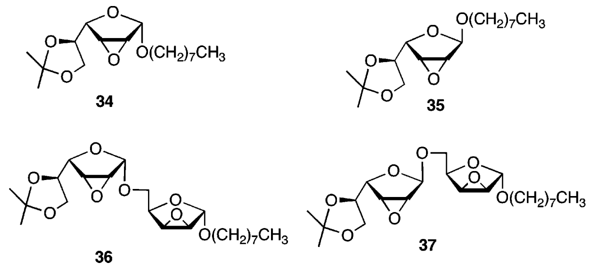


TABLE 1. Selected NMR Parameters in 34−37[a]

	compound			
	34	**35**	**36**	**37**
C1 stereochemistry	α	*β*	α	*β*
H1/O_{ep} relationship	trans	cis	trans	cis
δ_{H1} (ppm)	5.08	5.09	5.18	5.16
δ_{C1} (ppm)	101.6	101.3	101.6	101.8
$^{1}J_{C1,H1}$[b] (Hz)	163	174	167	174

[a] Spectra measured in $CDCl_3$. [b] Measured using ^{1}H-coupled HMQC experiments.

diol **33**. The conversion of **23** into **33** proceeded in excellent overall yield, 72%. With **33** in hand, its conversion to the benzyl-protected thioglycoside under standard conditions was straightforward, affording the product **14** in 93% yield. Similarly, benzoylation of **33** afforded a high (90%) yield of **15**. Oxidation of **14** and **15** to the corresponding glycosyl sulfoxides **17** and **18** proceeded uneventfully in 87% and 86% yields, respectively. As in the synthesis of **16** from **13** (Scheme 1), sulfoxides **17** and **18** were obtained as a mixture of diastereomers on sulfur (2:1 for **17** and 1.7:1 for **18**), but the stereochemistry was not determined.

Distinguishing Anomeric Stereochemistry in 2,3-Anhydrogulofuranosides. Before investigating glycosylation reactions with **13−18**, it was necessary to establish a reliable method for easily distinguishing 2,3-anhydro-α-D-gulofuranosides, the desired products of these reactions, from their *β*-glycoside counterparts. Previous work[34] from our laboratory demonstrated that the one-bond coupling constant between C1 and H1 in 2,3-anhydro-*O*-pentofuranosides (e.g., **3** and **7**, Figure 1) is diagnostic of the stereochemistry at the anomeric center. For glycosides in which H1 is trans to the epoxide moiety, $^{1}J_{C1,H1}$ = 163−168 Hz; when this hydrogen is cis to the oxirane ring, $^{1}J_{C1,H1}$ = 171−174 Hz. However, because the results of our previous study were based on glycosides with the *lyxo* and *ribo* stereochemistry, model studies were necessary to verify the suitability of this parameter for differentiating 2,3-anhydro-D-gulofuranosides. Therefore, two α/*β* pairs of 2,3-anhydro-D-gulofuranosides, **34−37** (Chart 3), were synthesized by unambiguous routes (see Supporting Information), and the $^{1}J_{C1,H1}$ values were measured (Table 1). These data demonstrate that the trends we identified earlier can be applied to products obtained from glycosylations of **13−18**. Also presented in Table 1 are data underscoring that the chemical shifts of the anomeric hydrogen or anomeric carbon resonances are not reliable predictors of stereochemistry in 2,3-anhydrosugar glycosides, as was reported in our earlier study.[34]

Glycosylation Reactions. With the donors in hand and an NMR method in place for distinguishing between the two glycosylation products, we explored the reaction of **13−18** with a range of alcohols (**38−45**).[35] This panel of acceptors included primary, secondary, and tertiary simple alcohols, as well as primary and secondary carbohydrate acceptors (Chart 4).

Activation of thioglycosides **13−15** was achieved by the treatment of a solution of the donor and acceptor in dichloromethane at −40 °C with *N*-iodosuccinimide and silver trifluoromethanesulfonate (NIS/AgOTf).[36] As a comparison with the NIS/AgOTf method, we also explored the activation of thioglycoside **15** using 1-benzenesulfinylpiperidine and trifluoromethanesulfonic anhydride (BSP/Tf_2O) in dichloromethane.[37] With sulfoxide donors **16−18**, we employed Tf_2O activation[38] in dichloromethane using the protocol developed by Crich and Sun[39] and modified by our group for 2,3-anhydrosugar glycosyl sulfoxides.[2] Under these conditions, the sulfoxide was first treated with Tf_2O in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), and then the solution was stirred at −78 °C for 10 min. The solution was then warmed to −40 °C and stirred for another 20 min prior to the addition of the alcohol.

The results of these glycosylations (Tables 2 and 3) clearly indicate that donors **13−18** do efficiently glycosylate a range of alcohols with a high degree of stereocontrol. Primary, secondary, and tertiary alcohols are readily glycosylated in high yields. Primary and secondary carbohydrate acceptors also work well. In all of these examples, the major or exclusive product is the α-glycoside, in which the newly formed glycosidic linkage is cis to the epoxide moiety; the stereochemistry of all products was determined by measurement of the $^{1}J_{C1,H1}$ as described above.

On the basis of the yields and α:*β* ratios shown in Tables 2 and 3, some trends can be identified. First, in general, the yields and α-selectivity of the glycosylation reactions decrease with increasing steric hindrance on the acceptor alcohol. For example, tertiary alcohols (Table 2, entry 8, and Table 3, entry 3) and carbohydrate secondary alcohol acceptors (Table 2, entry 10, and Table 3, entry 5) give somewhat lower yields and poorer selectivities compared to other acceptors. However, the α:*β* ratios are better than 4:1 in most cases. The worst selectivity (3:1 α:*β*) is observed in the reactions of relatively hindered alcohols **40** and **42** with thioglycoside **14** (Table 2, entries 8 and 10). Second, a comparison of the glycosylation reactions with thioglycosides **13−15** (Table 2) versus sulfoxides **16−18** (Table 3) reveals that these sulfoxide donors generally provide better α-selectivities, regardless of the structure of the acceptor. Third, the thioglycoside glycosylations appear to be only slightly affected by switching the promoter from NIS/AgOTf to BSP/Tf_2O (Table 2, entries 14, 15, 18, and 19). Both methods lead to glycoside formation although the yields and selectivities are marginally lower with BSP/Tf_2O activation; the reactions are

(34) Callam, C. S.; Gadikota, R. R.; Lowary, T. L. *J. Org. Chem.* **2001**, *66*, 4549−4558.

(35) Alcohols **38−40** are commercially available. All others were prepared by reported methods. **41**: ref 34. **42**: ref 2. **43**: Pozsgay, V.; Brisson, J. R.; Jennings, H. J. *Can. J. Chem.* **1987**, *65*, 2764−2769. **44**: Beignet, J.; Tiernan, J.; Woo, C. H.; Kariuki, B. M.; Cox, L. R. *J. Org. Chem.* **2004**, *69*, 6341−6356. **45**: Garegg, P. J.; Hultberg, H.; Wallin, S. *Carbohydr. Res.* **1982**, *108*, 97−101.

(36) Konradsson, P.; Udodong, U. E.; Fraser-Reid, B. *Tetrahedron Lett.* **1990**, *31*, 4313−4316.

(37) Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015−9020.

(38) (a) Yan, L.; Kahne, D. *J. Am. Chem. Soc.* **1996**, *118*, 9239−9248. (b) Gildersleeve, J.; Pascal, R. A., Jr.; Kahne, D. *J. Am. Chem. Soc.* **1998**, *120*, 5961−5969. (c) Gildersleeve, J.; Smith, A.; Sakurai, K.; Raghavan, S.; Kahne, D. *J. Am. Chem. Soc.* **1999**, *121*, 6176−6182.

(39) (a) Crich, D.; Sun, S. *J. Org. Chem.* **1997**, *62*, 1198−1199. (b) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 4506−4507.

CHART 4

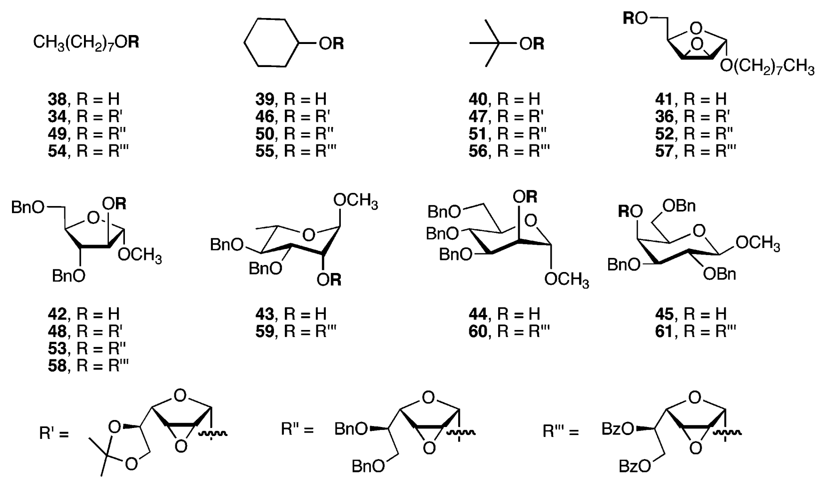
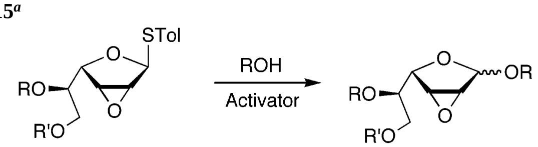


TABLE 2. Glycosylation of Alcohols with Thioglycoside Donors 13−15[a]

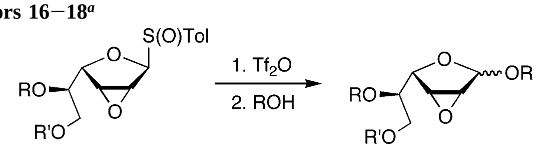


13, R,R' = $C(CH_3)_2$
14, R = R' = Bn
15, R = R' = Bz

entry	donor	activator	acceptor	product	yield (%)	α:*β* ratio[b]
1	**13**	NIS/AgOTf	**38**	**34**	82	α only
2	**13**	NIS/AgOTf	**39**	**46**	83	α only
3	**13**	NIS/AgOTf	**40**	**47**	82	α only
4	**13**	NIS/AgOTf	**41**	**36**	79[c]	5:1
5	**13**	NIS/AgOTf	**42**	**48**	56[d]	10:1
6	**14**	NIS/AgOTf	**38**	**49**	87	9:1
7	**14**	NIS/AgOTf	**39**	**50**	80	5:1
8	**14**	NIS/AgOTf	**40**	**51**	80	3:1
9	**14**	NIS/AgOTf	**41**	**52**	81	7:1
10	**14**	NIS/AgOTf	**42**	**53**	75	3:1
11	**15**	NIS/AgOTf	**38**	**54**	81	α only
12	**15**	NIS/AgOTf	**39**	**55**	79	α only
13	**15**	NIS/AgOTf	**40**	**56**	80	9:1
14	**15**	NIS/AgOTf	**41**	**57**	82	10:1
15	**15**	NIS/AgOTf	**42**	**58**	75	α only
16	**15**	NIS/AgOTf	**43**	**59**	78	8:1
17	**15**	NIS/AgOTf	**45**	**61**	72	8:1
18	**15**	BSP/Tf_2O	**41**	**57**	78	6:1
19	**15**	BSP/Tf_2O	**42**	**58**	74	7:1

[a] See Experimental Section for activation procedure. [b] Ratio determined by weights of isolated pure compounds. [c] 15% migration product was isolated (see text). [d] 19% migration product was isolated (see text).

TABLE 3. Glycosylation of Alcohols with Glycosyl Sulfoxide Donors 16−18[a]



16, R,R' = $C(CH_3)_2$
17, R = R' = Bn
18, R = R' = Bz

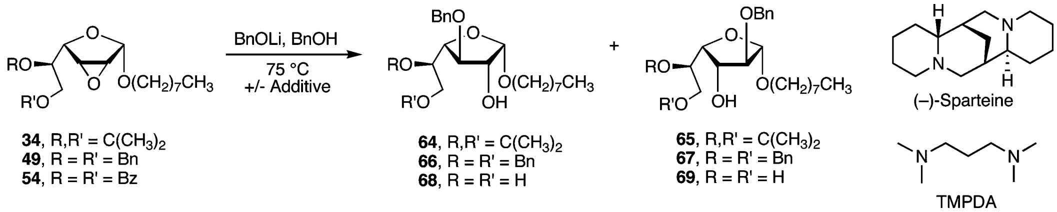
entry	donor	acceptor	product	yield (%)	α:*β* ratio[b]
1	**16**	**38**	**34**	78	α only
2	**16**	**39**	**46**	79	α only
3	**16**	**40**	**47**	71	4:1
4	**16**	**41**	**36**	71	6:1
5	**16**	**42**	**48**	73	5:1
6	**17**	**38**	**49**	82	α only
7	**17**	**39**	**50**	81	α only
8	**17**	**40**	**51**	76	10:1
9	**17**	**41**	**52**	79	α only
10	**17**	**42**	**53**	72	α only
11	**18**	**38**	**54**	87	α only
12	**18**	**39**	**55**	81	α only
13	**18**	**40**	**56**	78	α only
14	**18**	**41**	**57**	82	α only
15	**18**	**42**	**58**	76	α only
16	**18**	**44**	**60**	75	14:1
17	**18**	**45**	**61**	72	α only

[a] See Experimental Section for activation procedure. [b] Ratio determined by weights of isolated pure compounds.

also slower compared to the NIS/AgOTf-promoted glycosylations (45 min vs 12 h). Finally, the protecting groups on O5 and O6 influence the reaction outcome. Glycosylation with both the benzyl- and benzoyl-protected donors (**14**, **15**, **17**, and **18)** gives somewhat higher yields and better α-selectivities than the isopropylidene-protected donors **13** and **16**, especially when carbohydrate acceptors are used (Table 2, entries 5, 10, and 15; Table 3, entries 5, 10, and 15). In some reactions involving thioglycoside **13**, significant amounts of 2-deoxy-2-thiotolyl-α-D-idofuranosides (Chart 5) were produced in addition to the desired 2,3-anhydro-D-gulofuranosyl glycosides (Table 2, entries 4 and 5). These compounds were isolated in a mixture with other reaction components (e.g., unreacted acceptor), and their quantitation was done by integration of signals in the ^{1}H NMR spectrum. The formation of these side products is attributed to the presence of trifluoromethanesulfonic acid generated as the reaction proceeds, which induces the rearrangement process, presumably via a pathway similar to that shown in Figure 2.

Epoxide-Opening Reactions. Having demonstrated that the donors **13**−**18** can be used in the stereocontrolled synthesis of 2,3-anhydro-α-D-gulofuranosides (e.g., **34**, Table 4), we next sought to explore the regioselective opening of the epoxide ring in these molecules. Taking into account only steric considerations, attack of the nucleophile at either C2 or C3 should be equally likely, given that the top face of the furanose ring in 2,3-anhydro-D-gulofuranosides has no substituents that could bias the approach of the nucleophile. However, previous work on the syntheses of the stereochemically analogous *β*-D-arabinofuranosides from the corresponding epoxide precursor (**3** → **4**, Figure 1)[2] indicated that the combined use of BnOLi and (−)-sparteine in benzyl alcohol at 70 °C afforded good to

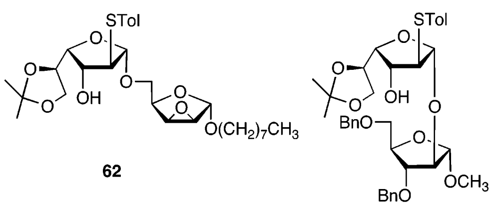
TABLE 4. Opening of Epoxides 34, 49, and 54 with BnOLi[a]



entry	substrate	additive	products (D-Gal*f*, D-Ido*f*)	yield (%)	ratio (Gal*f*:Ido*f*)[b]
1	**34**	–	**64, 65**	75	1:1.8[b]
2	**34**	(–)-sparteine	**64, 65**	75	1:1.5[b]
3	**49**	–	**66, 67**	84	1:3.2[c]
4	**49**	(–)-sparteine	**66, 67**	85	1:2.9[c]
5	**54**	–	**68, 69**	76	3.3:1[b]
6	**54**	(–)-sparteine	**68, 69**	78	4.8:1[b]
7	**54**	TMPDA	**68, 69**	82	1.8:1[b]

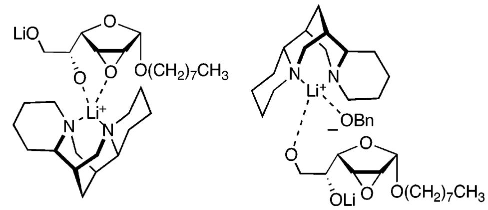
[a] See Experimental Section for reaction conditions. [b] Determined by weights of isolated pure compounds. [c] Determined by integration of anomeric hydrogen resonances in the ^{1}H NMR spectrum obtained on the mixture of **66** and **67**, which were not separable by chromatography.

CHART 5



62 **63**

CHART 6



70 **71**

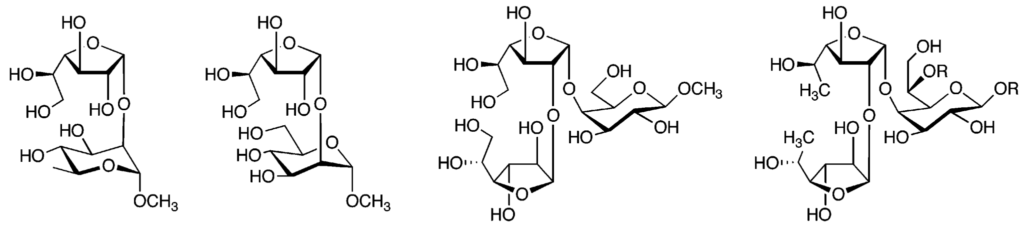
excellent selectivity for attack of the nucleophile at C3. In the case of the 2,3-anhydro-α-D-gulofuranoside ring system, attack of the nucleophile at C3 provides the desired product with the D-galactofuranose (D-Gal*f*) stereochemistry, while reaction at C2 yields products with the D-idofuranose (D-Ido*f*) stereochemistry.

We evaluated three octyl glycosides (**34**, **49**, and **54**) synthesized in the context of the glycosylation studies described previously as model systems. Each of these three epoxides was heated at 75 °C with 6.0 equiv of BnOLi in benzyl alcohol, either in the presence or absence of 1.2 equiv of (–)-sparteine; *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine (TMPDA) was also studied as an additive. The yields and D-Gal*f*:D-Ido*f* ratios for these reactions are presented in Table 4. These compounds could readily be differentiated from their ^{1}H NMR spectra. The anomeric hydrogen of those compounds with the D-Gal*f* stereochemistry appeared as a doublet with a $^3J_{1,2}$ of 3–5 Hz, whereas this signal in the D-Ido*f*-configured products appeared as a singlet.[40] These reactions proceeded efficiently, with combined product yields ranging from 75–85%. However, the regioselectivity of these reactions was variable and depended upon the nature of the protecting group on O5 and O6. With the isopropylidene-protected substrate, **34**, the regioselectivity was poor, and C2 attack was favored, leading to a slight predominance of the D-Ido*f* product (Table 4, entry 1). With the benzyl-protected system, **49** (Table 4, entry 3), the reaction was more regioselective, and again the D-Ido*f* product was favored. With both **34** and **49**, the addition of (–)-sparteine had little effect and, if anything, eroded the regiocontrol slightly. In contrast to these two systems, when the benzoyl-protected substrate **54** was used, the regioselectivity of a nucleophilic attack increased, and moreover, attack at C3 was favored thus leading to a preponderance of the D-Gal*f*-configured product (Table 4, entries 5 and 6). In the absence of (–)-sparteine, a 3.3:1 D-Gal*f*/D-Ido*f* mixture was produced, and this ratio increased to nearly 5:1 in the presence of the additive. The use of TMPDA as the additive provided results inferior to those obtained with (–)-sparteine (Table 4, entry 7).

The role that the O5- and O6-protecting group plays on this process is striking. Clearly, for substrates containing protecting groups that are stable under the reaction conditions (isopropylidene acetal, benzyl ethers), poor to modest regioselectivity is observed, and nucleophilic attack at C2 is favored. In contrast, for the system in which O5 and O6 are protected with base-labile-protecting groups, the reaction is more regioselective, and there is an “inversion” in the favored position of the attack. In our previous studies on the synthesis of β-arabinofuranosides by this approach, the substrates for the ring-opening reactions (e.g., **3**, Figure 1) either were protected at O5 with a benzoyl group or were unprotected.[2] We are unsure as to the origin of these regioselectivity trends, but these results, combined with those obtained in our earlier study, point to the possible importance of a complex formed between the substrate, (–)-sparteine, and the lithium ion. If the assumption is made that the benzoate esters are cleaved rapidly in the initial stages of the reaction, thus liberating the corresponding alkoxide, the formation of a complex of the general type (**70**, Chart 6) can be envisioned, which may, through a currently undetermined mechanism, influence the site of nucleophilic attack. The formation of related complexes has been proposed in the sparteine-mediated enantioselective lithiation of meso epoxides

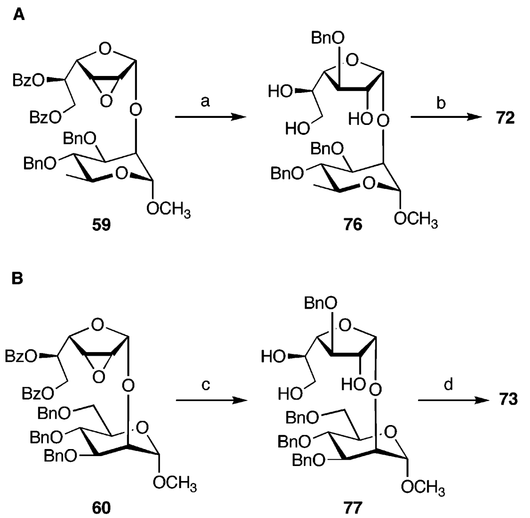
(40) Cyr, N.; Perlin, A. S. *Can. J. Chem.* **1979**, *57*, 2504–2511.

CHART 7



72 73 74 75, R = polysaccharide

SCHEME 3[a]



[a] Conditions: (a) LiOBn, (−)-sparteine, BnOH, 75 °C, 65%; (b) H_2, Pd/C, CH_3OH, rt, 94%; (c) LiOBn, (−)-sparteine, BnOH, 75 °C, 55%; (d) H_2, Pd/C, CH_3OH, rt, quantitative.

by organolithium reagents.[41] An alternate possibility is that a complex of the type **71** is produced, which could lead to the delivery of the nucleophile preferentially to C3. In the absence of the additive, analogous complexes involving lithium ions and additional alkoxide ligands are possible. Despite these postulates, to date we have no evidence for the formation of species such as **70** and **71** in these reactions, and studies exploring their intermediacy, by both experimental and computational approaches, are ongoing. Among the questions to be addressed are the origin of the regioselectivity and the erosion seen when moving from the pentofuranose to the hexofuranose systems, as well as the relatively poor performance of other diamine ligands (e.g., TMPDA).

Application to the Synthesis of α-D-Galactofuranosyl-Containing Oligosaccharides. To illustrate further the utility of this methodology, we selected three small target molecules for synthesis. These were a disaccharide fragment of the lipopolysaccharide from *Salmonella typhimurium* 902[9a] (**72**, Chart 7), the repeating unit of a cell wall polysaccharide from *Talaromyces flavus*[9g] (**73**), and a trisaccharide (**74**) structurally related to an antigenic polysaccharide from *Eubacterium saburreum* strain T19 (**75**).[10b]

The synthesis of **72** is illustrated in Scheme 3A. Disaccharide **59**, which could be obtained from the reaction of alcohol **43** (Chart 4) and **15** as outlined above (Table 2, entry 16), was the starting material. Opening of the epoxide with our standard conditions afforded disaccharide **76** in 65% yield together with 13% of the regioisomeric product, which were separated. Hydrogenation of the benzyl groups in **76** afforded a 94% yield of the target **72**.

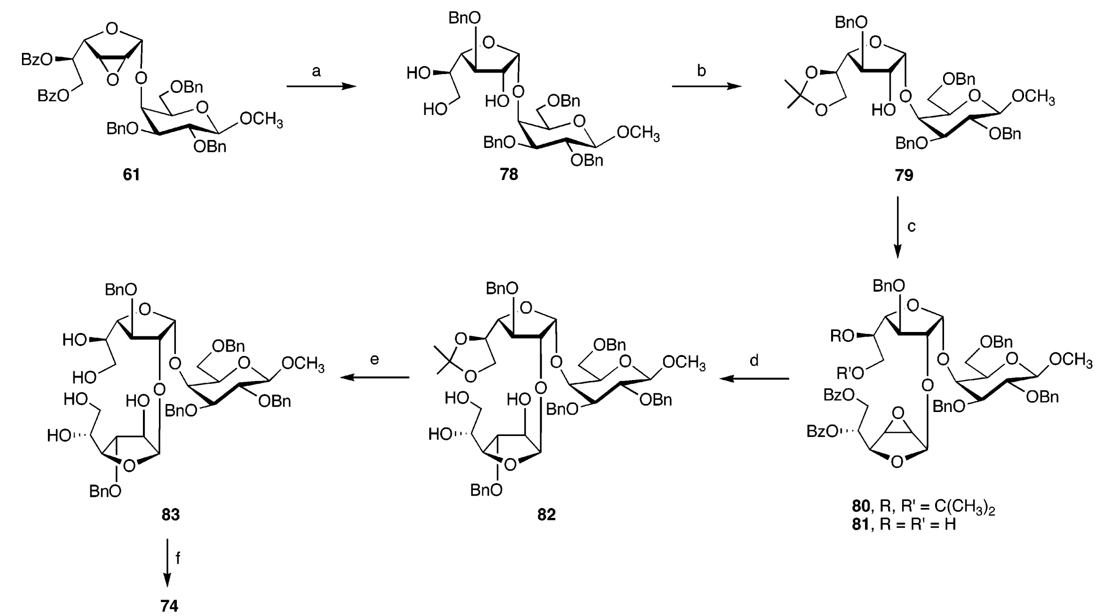
Presented in Scheme 3B is the synthesis of disaccharide **73**, which also began from one of the products obtained in the exploration of the scope of the methodology, **60**. Reaction of this disaccharide with LiOBn and (−)-sparteine afforded the ring-opened product **77** in 55% yield along with the 18% of the regioisomer with the D-Ido*f* stereochemistry. Removal of the benzyl groups by hydrogenation over Pd/C afforded **73** in quantitative yield.

The synthesis of trisaccharide **74** was more involved and is depicted in Scheme 4. The target has two α-D-galactofuranosyl moieties linked (1→2), and, therefore, the glycosylation/ring-opening sequence inherent in the 2,3-anhydrosugar methodology makes this an attractive approach for the synthesis of compounds containing this motif. Thus, disaccharide **61**, obtained by glycosylation of alcohol **45** with glycosyl sulfoxide **18** (Table 3, entry 17), was treated with LiOBn and (−)-sparteine to provide the ring-opened product **78** in 69% yield, together with 5% of the regioisomeric product. The C5/C6 diol motif liberated in the ring opening was protected as an isopropylidene acetal giving an 89% yield of disaccharide **79**.

Glycosylation of the C2′ hydroxyl group in **79** initially proved problematic. We first explored the use of thioglycoside **15** for this purpose, and given the hindered nature of the acceptor, extended reaction times (>2 h) were required for reasonable levels of conversion of the acceptor. Under these conditions, only very small amounts of the desired product, **80**, were produced. The major products were hydrolyzed donor, unreacted **79** and trisaccharide **81**, in which the isopropylidene acetal had been cleaved. It appears that at the extended reaction times necessary for the glycosylation to occur, the trifluoromethanesulfonic acid liberated over the course of the reaction leads to cleavage of the isopropylidene-protecting group. This acetal appears to be particularly susceptible to acid-promoted cleavage. For example, while we could easily record the ^1H NMR spectrum of **80** in $CDCl_3$, when we attempted to obtain the ^{13}C NMR spectrum, we observed cleavage of the acetal over the (longer) course of the experiment. This degradation presumably arises from trace amounts of acid impurities present in commercial preparations of $CDCl_3$. Although we are unsure as to why this acetal is so acid-labile, we believe it is related to the highly hindered nature of the central galactofuranosyl residue in **80**. Faced with this problem, we glycosylated **79** with sulfoxide **18**, a reaction that proceeds under slightly basic conditions. Although again extended reaction times were necessary, we were successful in obtaining disaccharide **80** in 59% yield.

(41) (a) Hodgson, D. M.; Bray, C. D.; Humphreys, P. G. *Synlett* **2006**, 1−22. (b) Hodgson, D. M.; Lee, G. P.; Marriott, R. E.; Thompson, A. J.; Wisedale, R.; Witherington, J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2151−2161.

SCHEME 4[a]



[a] Conditions: (a) LiOBn, (−)-sparteine, BnOH, 75 °C, 69%; (b) $(CH_3)_2C(OCH_3)_2$, acetone, *p*-TsOH, rt, 89%; (c) **18**, Tf_2O, DTBMP, CH_2Cl_2, −78 °C → rt, 59%; (d) LiOBn, (−)-sparteine, BnOH, 75 °C, 61%; (e) HOAc, H_2O, 50 °C, 81%; (f) H_2, $Pd(OH)_2/C$, CH_3OH, rt, quantitative.

Conversion of **80** into the target product proceeded straightforwardly by first epoxide ring opening under the usual conditions, which provided triol **82** in 61% yield together with 13% of the regioisomeric product. Cleavage of the acetal with aqueous acetic afforded **83**, which was then hydrogenated over Pearlman's catalyst thus providing the product **74** in 81% overall yield.

Conclusions

In summary, we have demonstrated that 2,3-anhydro-D-gulofuranosyl thioglycosides and glycosyl sulfoxides **13**−**18** can be used in highly stereoselective synthesis of 2,3-anhydro-α-D-gulofuranosides. The nature of the protecting groups on O5 and O6 influences the stereoselectivity and yield of the glycosylation reactions, with the best results being obtained when benzoate esters are present at these positions. In addition, glycosyl sulfoxides, in general, provide the product in better yields and with higher stereoselectivity. We have also demonstrated that the regioselective opening of the oxirane moiety in the glycosylation products provides compounds with the α-D-galactofuranoside stereochemistry by using a mixture of LiOBn and (−)-sparteine. Here too, the protecting groups on O5 and O6 play a critical role; only the benzoyl-protected substrates yield the desired compounds with good selectivity. We attribute this effect to the formation of a complex between the additive, the nucleophile, and the alkoxide generated in situ upon cleavage of the benzoate esters. The regioselectivities of these opening reactions are not as high as those observed earlier in the synthesis of β-arabinofuranosides,[2] and we are currently investigating the origin of this loss in regioselectivity. Overall, the best results were observed when benzoylated 2,3-anhydrosugar donors were used in glycosylation reactions, and the corresponding benzoylated substrates also gave the best results in the epoxide-opening reactions. It appears, therefore, that acyl-protected species are the donors of choice for these reactions.

Experimental Section

Activation of Thioglycoside Donors by the AgOTf/NIS Method. The donor (0.1 mmol), acceptor (1.2 equiv), and 4 Å molecular sieves were dried overnight under vacuum in the presence of P_2O_5. To this mixture was added CH_2Cl_2 (5 mL); the reaction was cooled to −40 °C, and then NIS (1.2 equiv) and AgOTf (0.3 equiv) were successively added. After stirring for 20 min at −40 °C, the reaction solution was warmed to −25 °C. Once the color of the reaction was changed to pink, it was cooled again to −40 °C. After another 30 min, the reaction mixture turned dark red and was then neutralized by addition of triethylamine, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed with saturated aq $Na_2S_2O_3$ solution, dried (Na_2SO_4), and concentrated to give a crude residue that was purified by chromatography to yield the corresponding separable α (major) and β (minor) glycosides.

Activation of Thioglycoside Donors by the BSP/Tf_2O Method. The donor (0.1 mmol), BSP (1.0 equiv), 2,4,6-tri-*tert*-butylpyrimidine (2.0 equiv), and 4 Å molecular sieves were dried for 4 h under vacuum in the presence of P_2O_5. To this mixture was added CH_2Cl_2 (5 mL), and the reaction mixture was cooled to −60 °C. Tf_2O (1.1 equiv) was added, and the mixture was allowed to stir for 10 min, followed by the addition (via syringe) of a solution of the vacuum-dried acceptor (1.1 equiv) in CH_2Cl_2 (1 mL). After 40 min, the reaction mixture was warmed to rt and was kept stirring for 12 h. A saturated solution of $NaHCO_3$ was then added, and the resulting solution was filtered through Celite, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography.

Activation of Sulfoxide Donors by the Tf_2O/DTBMP Method. The donor (0.1 mmol), DTBMP (4.0 equiv), and 4 Å molecular sieves were dried for 3 h under vacuum in the presence of P_2O_5. To this mixture was added CH_2Cl_2 (5 mL), and the reaction mixture was cooled to −78 °C. Tf_2O (1.2 equiv) was added, and the mixture was allowed to stir for 10 min. The solution was then warmed to −40 °C and stirred for 20 min followed by the addition of the acceptor alcohol (1.2 equiv). After 30−60 min, the reaction mixture turned slight green; a saturated solution of $NaHCO_3$ was then added, and the solution was allowed to warm to rt. The resulting solution was filtered through Celite, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography to give the corresponding separable α (major) and β (minor) glycosides.

General Procedure for Epoxide-Opening Reactions. To a solution of benzyl alcohol (3.0 mL) was added lithium metal (6.0 mmol), and the solution was stirred at 65 °C until all the metal dissolved. After cooling to rt, the mixture was added together with the additive (1.2 mmol) via syringe to a solution of the epoxide (1.0 mmol) dissolved in benzyl alcohol (0.5 mL). The resulting mixture was subsequently warmed to 75 °C and stirred until the reaction was complete. After cooling to rt, the solution was neutralized with HOAc and diluted with EtOAc (10 mL). The organic layer was washed with water, dried (Na_2SO_4), filtered, and concentrated to give a crude residue that was purified by chromatography. Those reactions done in the absence of an additive were carried out in an analogous manner (additive = (−)-sparteine or TMPDA).

***p*-Tolyl 2,3-Anhydro-5,6-*O*-isopropylidene-1-thio-β-D-gulofuranoside (13).** To a solution of **23** (2.15 g, 7.52 mmol) and 2,2-dimethoxypropane (7.4 mL, 60.1 mmol) in acetone (50 mL) was added *p*-toluenesulfonic acid (7 mg) at rt. The solution was allowed to stir for 2 h and neutralized with Et_3N. TLC showed a spot at R_f = 0.40 (15:1 CH_2Cl_2/CH_3OH). The mixture was concentrated, and the resulting oil was dissolved in THF (40 mL) followed by the addition of PPh_3 (2.57 g, 9.78 mmol). DIAD (1.9 mL, 9.78 mmol) was then added dropwise at 0 °C over 10 min. The reaction mixture was allowed to warm to rt over 30 min. The resulting mixture was concentrated, and Et_2O (60 mL) was added to precipitate the $Ph_3P{=}O$, which was subsequently removed by filtration. The organic layer was concentrated, and the residue was purified by chromatography (6:1 hexanes/EtOAc) to yield **13** (1.87 g, 81% over two steps) as a white solid. R_f 0.46 (4:1 hexanes/EtOAc); mp 76−78 °C; $[\alpha]_d$ −187.1 (*c* 1.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 7.45−7.41 (m, 2H, Ar), 7.13−7.11 (m, 2H, Ar), 5.48 (s, 1H, H-1), 4.32 (ddd, 1H, J = 6.3, 6.3, 6.3 Hz, H-5), 4.06 (dd, 1H, J = 8.6, 6.3 Hz, H-6), 4.01−3.97 (m, 2H, H-4, H-6), 3.88 (d, 1H, J = 2.9 Hz, H-2), 3.67 (dd, 1H, J = 2.9, 0.5 Hz, H-3), 2.34 (s, 3H, tolyl CH_3), 1.47 (s, 3H, isopropylidene CH_3), 1.37 (s, 3H, isopropylidene CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 138.4 (Ar), 133.5 (Ar × 2), 129.9 (Ar), 128.6 (Ar × 2), 109.7 (isopropylidene C), 87.3 (C-1), 77.0 (C-4), 74.6 (C-5), 65.6 (C-6), 56.8 (C-2), 54.9 (C-3), 26.6 (isopropylidene CH_3), 21.1 (isopropylidene CH_3), 21.1 (tolyl CH_3). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.54. Found: C, 62.09; H, 6.68. HRMS (ESI): [M + Na] calcd for $C_{16}H_{20}O_4SNa$, 331.0975; found, 331.0976.

***p*-Tolyl 2,3-Anhydro-5,6-di-*O*-benzyl-1-thio-β-D-gulofuranoside (14).** To a solution of **33** (60 mg, 0.22 mmol) in DMF (1.5 mL) at 0 °C was added NaH (3 mg, 0.72 mmol, 60% dispersion in oil), and the mixture was stirred for 5 min. Benzyl bromide (64 μL, 0.54 mmol) was added dropwise at 0 °C, and the mixture was stirred for 6 h at rt. The reaction mixture was then quenched by adding a few drops of CH_3OH, diluted with CH_2Cl_2 (10 mL), and washed with saturated aq $NaHCO_3$ solution (3 × 10 mL) and water (3 × 10 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated, and the resulting residue was purified by chromatography (4:1 hexanes/EtOAc) to provide **14** (93 mg, 93%) as a colorless oil. R_f 0.52 (4:1 hexanes/EtOAc); $[\alpha]_D$ −127.6 (*c* 1.2, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.46−7.43 (m, 2H, Ar), 7.38−7.27 (m, 10H, Ar), 7.13 (d, 2H, J = 7.9 Hz, Ar), 5.50 (s, 1H, H-1), 4.76 (d, 1H, J = 11.8 Hz, PhCH_2), 4.71 (d, 1H, J = 11.8 Hz, PhCH_2), 4.59 (d, 1H, J = 12.0 Hz, PhCH_2), 4.54 (d, 1H, J = 12.0 Hz, PhCH_2), 4.21 (d, 1H, J = 6.3 Hz, H-4), 3.88−3.83 (m, 1H, H-5), 3.84 (d, 1H, J = 2.9 Hz, H-2), 3.77−3.70 (m, 3H, H-3, H-6 × 2), 2.38 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6 (Ar), 138.2 (Ar), 138.15 (Ar), 133.3 (Ar × 2), 129.8 (Ar × 2), 129.1 (Ar), 128.4 (Ar × 2), 128.3 (Ar × 2), 127.8 (Ar × 2), 127.7 (Ar × 2), 127.6 (Ar), 127.5 (Ar), 87.0 (C-1), 77.7 (C-5), 77.5 (C-4), 73.5 (PhCH$_2$), 73.1 (PhCH$_2$), 70.8 (C-6), 56.9 (C-2), 55.4 (C-3), 21.1 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{27}H_{28}O_4SNa$, 471.1601; found, 471.1600.

***p*-Tolyl 2,3-Anhydro-5,6-di-*O*-benzoyl-1-thio-β-D-gulofuranoside (15).** Benzoyl chloride (850 μL, 7.5 mmol) was added dropwise to a solution of **33** (800 mg, 3.0 mmol) in pyridine (10 mL) at 0 °C. The reaction mixture was warmed to rt and stirred for 12 h. The solution was diluted with CH_2Cl_2 (50 mL) and washed with saturated aq $NaHCO_3$ solution (3 × 40 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and purified by chromatography (6:1 hexanes/EtOAc) to yield **15** (1.28 g, 90%) as a white semisolid foam. R_f 0.48 (3:1 hexanes/EtOAc); $[\alpha]_D$ −90.8 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−8.07 (m, 2H, Ar), 8.03−8.00 (m, 2H, Ar), 7.56−7.40 (m, 8H, Ar), 7.12−7.09 (m, 2H, Ar), 5.78 (dd, 1H, J = 5.4, 5.0 Hz, H-5), 5.52 (s, 1H, H-1), 4.73 (d, 2H, J = 5.4 Hz, H-6 × 2), 4.33 (dd, 1H, J = 5.0, 0.6 Hz, H-4), 3.90 (dd, 1H, J = 2.8, 0.6 Hz, H-3), 3.89 (d, 1H, J = 2.8 Hz, H-2), 2.32 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (C=O), 165.9 (C=O), 138.4 (Ar × 2), 133.4 (Ar × 2), 133.3 (Ar), 133.2 (Ar), 129.9 (Ar × 4), 129.8 (Ar), 129.7 (Ar × 2), 128.6 (Ar), 128.5 (Ar × 2), 128.4 (Ar × 2), 87.1 (C-1), 74.8 (C-4), 70.8 (C-5), 63.4 (C-6), 57.0 (C-2), 55.0 (C-3), 21.1 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{27}H_{24}O_6SNa$, 499.1186; found, 499.1188.

2,3-Anhydro-5,6-*O*-isopropylidene-β-D-gulofuranosyl-*p*-tolyl-(*R*/*S*)-sulfoxide (16a/16b). To a solution of **13** (620 mg, 2.0 mmol) in CH_2Cl_2 (40 mL) at −78 °C was added *m*-CPBA (430 mg, 1.8 mmol). After stirring for 2 h, the reaction mixture was warmed to rt and stirred for 30 min. The solution was washed with a saturated aq solution of $NaHCO_3$ (3 × 30 mL) and then water (3 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to yield a crude oil that was purified by chromatography (8:1 hexanes/EtOAc) to provide **16a** (380 mg, 71%) and **16b** (160 mg, 13%) as white semisolids. **16a**: R_f 0.32 (1:1 hexanes/EtOAc); $[\alpha]_D$ +216.0 (*c* 1.3, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 7.50 (d, 2H, J = 8.5 Hz, Ar), 7.38 (d, 2H, J = 8.5 Hz, Ar), 4.74 (s, 1H, H-1), 4.43 (dd, 1H, J = 6.5, 0.7 Hz, H-4), 4.27 (q, 1H, J = 6.5 Hz, H-5), 4.09 (dd, 1H, J = 8.5, 6.5 Hz, H-6), 3.94 (d, 1H, J = 2.9 Hz, H-2), 3.93 (dd, 1H, J = 8.5, 6.5 Hz, H-6), 3.84 (dd, 1H, J = 2.9, 0.7 Hz, H-3), 2.44 (s, 3H, tolyl CH_3), 1.48 (s, 3H, isopropylidene CH_3), 1.37 (s, 3H, isopropylidene CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 142.1 (Ar), 136.4 (Ar), 130.3 (Ar × 2), 124.1 (Ar × 2), 110.1 (isopropylidene C), 96.3 (C-1), 81.0 (C-4), 74.9 (C-5), 65.5 (C-6), 55.5 (C-3), 54.5 (C-2), 26.7 (isopropylidene CH_3), 25.2 (isopropylidene CH_3), 21.4 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{16}H_{20}O_5SNa$, 347.0924; found, 347.0926. **16b**: R_f 0.20 (1:1 hexanes/EtOAc); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 7.58−7.54 (m, 2H, Ar), 7.37−7.33 (m, 2H, Ar), 4.88 (s, 1H, H-1), 4.23−4.16 (m, 3H, H-4, H-5, H-2), 4.02 (dd, 1H, J = 8.5, 6.5 Hz, H-6), 3.86 (dd, 1H, J = 8.5, 5.5 Hz, H-6), 3.72 (dd, 1H, J = 2.9, 0.7 Hz, H-3), 2.44 (s, 3H, tolyl CH_3), 1.45 (s, 3H, isopropylidene CH_3), 1.34 (s, 3H, isopropylidene CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 142.4 (Ar), 136.0 (Ar), 130.04 (Ar), 130.0 (Ar), 125.3 (Ar × 2), 109.9 (isopropylidene C), 94.4 (C-1), 81.7 (C-4), 74.9 (C-5), 65.4 (C-6), 55.8 (C-2), 55.7 (C-3), 26.7 (isopropylidene CH_3), 25.2 (isopropylidene CH_3), 21.5 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{16}H_{20}O_5SNa$, 347.0924; found, 347.0922.

2,3-Anhydro-5,6-di-*O*-benzyl-β-D-gulofuranosyl-*p*-tolyl-(*R*/*S*)-sulfoxide (17a/17b). To a solution of **14** (410 mg, 0.91 mmol) in CH_2Cl_2 (25 mL) at −78 °C was added *m*-CPBA (0.20 g, 0.82 mmol). After stirring for 2 h, the reaction mixture was warmed to rt and stirred for 30 min. The solution was then washed with a saturated aq solution of $NaHCO_3$ (3 × 15 mL) and then water (15 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to yield a crude oil that was purified by chromatography (3:1 hexanes/EtOAc) to provide **17a** (220 mg, 58%) and **17b** (110 mg, 29%) as white semisolids. **17a**: R_f 0.27 (2:1 hexanes/EtOAc); $[\alpha]_D$ +104.4 (*c* 0.6, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.53−7.50 (m, 2H, Ar), 7.40−7.26 (m, 12H, Ar), 4.70 (d, 1H, J = 11.8 Hz, PhCH_2), 4.68 (s, 1H, H-1), 4.64 (d, 1H, J = 11.8 Hz, PhCH_2), 4.58 (d, 1H, J = 12.0 Hz, PhCH_2), 4.54 (d, 1H, J = 12.0 Hz, PhCH_2), 4.53 (dd, 1H, J = 6.8, 0.7 Hz, H-4), 4.05 (d, 1H, J =

2.8 Hz, H-2), 3.92 (dd, 1H, J = 2.8, 0.7 Hz, H-3), 3.77 (ddd, 1H, J = 6.8, 5.0, 4.0 Hz, H-5), 3.71 (dd, 1H, J = 10.8, 4.0 Hz, H-6), 3.69 (dd, 1H, J = 10.8, 5.0 Hz, H-6), 2.42 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 142.0 (Ar), 138.4 (Ar), 137.9 (Ar), 137.2 (Ar), 130.1 (Ar × 2), 128.4 (Ar × 2), 128.3 (Ar × 2), 127.8 (Ar × 3), 127.7 (Ar × 2), 127.6 (Ar), 124.6 (Ar × 2), 96.3 (C-1), 81.5 (C-4), 78.0 (C-5), 73.6 (Ph*C*H_2), 73.1 (Ph*C*H_2), 70.2 (C-6), 56.0 (C-3), 55.1 (C-2), 21.4 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{27}H_{28}O_5SNa$, 487.1550; found, 487.1550. **17b**: R_f 0.18 (2:1 hexanes/EtOAc); $[\alpha]_D$ −176.8 (c 0.16, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.56 (d, 2H, J = 8.2 Hz, Ar), 7.36−7.26 (m, 12H, Ar), 4.82 (s, 1H, H-1), 4.66 (d, 1H, J = 11.8 Hz, PhC*H*$_2$), 4.60 (d, 1H, J = 11.8 Hz, PhC*H*$_2$), 4.55 (d, 1H, J = 12.0 Hz, PhC*H*$_2$), 4.50 (d, 1H, J = 12.0 Hz, PhC*H*$_2$), 4.41 (dd, 1H, J = 6.8, 0.8 Hz, H-4), 4.12 (d, 1H, J = 2.8 Hz, H-2), 3.81 (dd, 1H, J = 2.8, 0.8 Hz, H-3), 3.72−3.69 (m, 1H, H-5), 3.66−3.61 (m, 2H, H-6 × 2), 2.41 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 142.3 (Ar), 138.5 (Ar), 136.5 (Ar), 129.9 (Ar), 128.4 (Ar × 2), 128.2 (Ar × 2), 127.8 (Ar × 2), 127.7 (Ar × 3), 127.6 (Ar × 2), 127.5 (Ar), 125.4 (Ar × 2), 94.6 (C-1), 82.6 (C-4), 78.0 (C-5), 73.5 (Ph*C*H_2), 73.0 (Ph*C*H_2), 70.4 (C-6), 56.4 (C-3), 56.0 (C-2), 21.5 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{27}H_{28}O_5S$, 487.1550; found, 487.1551.

2,3-Anhydro-5,6-di-*O*-benzoyl-β-D-gulofuranosyl-*p*-tolyl-(*R*/*S*)-sulfoxide (18a/18b). To a solution of **15** (360 mg, 0.75 mmol) in CH_2Cl_2 (20 mL) at −78 °C was added *m*-CPBA (160 mg, 0.68 mmol). After stirring for 2 h, the reaction mixture was warmed to rt and stirred for 30 min. The solution was washed with a saturated aq solution of $NaHCO_3$ (3 × 15 mL) and then water (3 × 15 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to yield a crude oil that was purified by chromatography (2:1 hexanes/EtOAc) to provide the diastereomers **18a** (200 mg, 54%) and **18b** (120 mg, 32%) as white semisolids. **18a**: R_f 0.18 (2:1 hexanes/EtOAc); $[\alpha]_D$ +185.2 (c 0.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08−8.05 (m, 2H, Ar), 8.03−8.00 (m, 2H, Ar), 7.60−7.54 (m, 2H, Ar), 7.50 (d, 2H, J = 8.2 Hz, Ar), 7.47−7.40 (m, 4H, Ar), 7.34 (d, 2H, J = 8.2 Hz, Ar), 5.72 (ddd, 1H, J = 5.9, 5.9, 4.3 Hz, H-5), 4.78−4.67 (m, 4H, H-1, H-4, H-6 × 2), 4.08 (d, 1H, J = 2.9 Hz, H-3), 3.98 (d, 1H, J = 2.9 Hz, H-2), 2.40 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.7 (C=O), 142.2 (Ar), 136.4 (Ar), 133.3 (Ar), 133.2 (Ar), 130.2 (Ar × 2), 129.9 (Ar × 2), 129.7 (Ar × 2), 129.6 (Ar), 129.5 (Ar), 128.5 (Ar × 2), 128.4 (Ar × 2), 124.1 (Ar × 2), 95.9 (C-1), 78.6 (C-4), 71.0 (C-5), 63.1 (C-6), 55.6 (C-3), 54.9 (C-2), 21.4 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{27}H_{24}O_7SNa$, 515.1135; found, 515.1136. **18b**: R_f 0.09 (2:1 hexanes/EtOAc); $[\alpha]_D$ −194.9 (c 0.47, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05−7.98 (m, 4H, Ar), 7.60−7.50 (m, 4H, Ar), 7.46−7.40 (m, 4H, Ar), 7.27−7.23 (m, 2H, Ar), 5.63 (ddd, 1H, J = 5.8, 5.8, 4.8 Hz, H-5), 4.80 (s, 1H, H-1), 4.69 (dd, 1H, J = 5.8, 0.8 Hz, H-4), 4.67−4.60 (m, 2H, H-6 × 2), 4.22 (d, 1H, J = 2.8 Hz, H-2), 4.03 (dd, 1H, J = 2.8, 0.8 Hz, H-3), 2.35 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.7 (C=O), 142.5 (Ar × 2), 136.2 (Ar), 133.2 (Ar × 2), 129.9 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 129.5 (Ar), 128.5 (Ar × 2), 128.4 (Ar × 2), 125.2 (Ar × 2), 94.3 (C-1), 79.7 (C-4), 70.9 (C-5), 63.0 (C-6), 56.1 (C-2), 55.8 (C-3), 21.5 (tolyl CH_3). HRMS (ESI): [M + H] calcd for $C_{27}H_{25}O_7S$, 493.1316; found, 493.1315.

Methyl 2,3,5,6-Tetra-*O*-acetyl-α/β-D-galactofuranoside (21). D-Galactose diethyl dithioacetal **20** (1.2 g, 4.2 mmol) was dissolved in DMF (8.4 mL), and CH_3OH (250 μL) was added followed by 1,3-dibromo-5,5-dimethylhydantoin (1.2 g, 4.2 mmol). After being stirred for 30 min, the solution was diluted with pyridine (30 mL). Acetic anhydride (6 mL, 63 mmol) was added, and then the solution was allowed to stir for 5 h at rt. The reaction mixture was then poured into ice−H_2O (150 mL) containing $NaHCO_3$ (2.0 g) and extracted with CH_2Cl_2 (2 × 150 mL). The organic layers were combined and washed with a saturated aq $NaHCO_3$ (200 mL) solution and H_2O (200 mL), then dried (Na_2SO_4), filtered, and concentrated to yield the crude product. Chromatography (2:1 hexane/EtOAc) yielded **21** (0.92 g, 61% over two steps) as a colorless oil. R_f 0.43 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.57 (t, 0.35H, J = 6.8 Hz, H-3α), 5.38 (ddd, 0.65H, J = 8.1, 4.4, 4.4 Hz, H-5β), 5.30 (s, 0.35H, H-1α), 5.24−5.19 (m, 0.35H, H-5α), 5.07−4.99 (m, 1.65H, H-2, H-3, H-2α), 4.92 (s, 0.65H, H-1β), 4.36 (dd, 0.35H, J = 11.8, 4.5 Hz, H-6α), 4.33 (dd, 0.65H, J = 12.0, 4.5 Hz, H-6β), 4.25−4.09 (m, 2H, H-4α, H-4β, H-6α, H-6β), 3.39 (s, 1.95H, OCH_3β), 3.37 (s, 1.05H, OCH_3α), 2.14 (s, 1.95H, acyl CH_3β), 2.13 (s, 1.05H, acyl CH_3α), 2.11 (s, 3H, acyl CH_3α, acyl CH_3β), 2.09 (s, 1.95H, acyl CH_3β), 2.07 (s, 1.05H, acyl CH_3α), 2.06 (s, 1.95H, acyl CH_3β), 2.05 (s, 1.05H, acyl CH_3α); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.5 (C=O), 170.4 (C=O), 170.0 (C=O × 2), 169.9 (C=O × 2), 169.8 (C=O), 169.6 (C=O), 106.6 (C-1β), 100.5 (C-1α), 81.3 (C-2β), 79.9 (C-4β), 77.7 (C-4α), 76.5 (C-3β), 76.4 (C-3α), 73.6 (C-2α), 70.6 (C-5α), 69.3 (C-5β), 62.6 (C-6β), 62.2 (C-6α), 55.3 (OCH_3α), 55.0 (OCH_3β), 20.82 (acyl CH_3), 20.8 (acyl CH_3), 20.74 (acyl CH_3), 20.7 (acyl CH_3), 20.66 (acyl CH_3 × 2), 20.6 (acyl CH_3 × 2). HRMS (ESI): [M + Na] calcd for $C_{15}H_{22}O_{10}Na$, 385.1104; found, 385.1105.

***p*-Tolyl 2,3,5,6-Tetra-*O*-acetyl-1-thio-α/β-D-galactofuranoside (22).** To a solution of *p*-thiocresol (2.24 g, 17.7 mmol) and **21** (5.82 g, 16.1 mmol) in dry CH_2Cl_2 (80 mL) was added $BF_3 \cdot Et_2O$ (6.1 mL, 48.2 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then diluted with CH_2Cl_2 (100 mL), washed with a saturated aq $NaHCO_3$ solution (3 × 150 mL), dried (Na_2SO_4), and concentrated. Chromatography (4:1 hexane/EtOAc) yielded **22** (5.51 g, 76%) in a 1:9 α:β ratio as a slightly yellow syrup. R_f 0.37 (4:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41−7.36 (m, 2H, Ar), 7.12 (d, 2H, J = 7.9 Hz, Ar), 5.52 (d, 0.1H, J = 5.2 Hz, H-1α), 5.46 (dd, 0.1H, J = 5.2, 3.8 Hz, H-2α), 5.43 (d, 0.9H, J = 2.5 Hz, H-1β), 5.40−5.35 (m, 1H, H-5α, H-5β), 5.31 (dd, 0.1H, J = 5.0, 3.8 Hz, H-3α), 5.21 (dd, 0.9H, J = 2.7, 2.5 Hz, H-2β), 5.04 (dd, 0.9H, J = 6.1, 2.7 Hz, H-3β), 4.46 (dd, 0.9H, J = 6.1, 3.8 Hz, H-4β), 4.40 (dd, 0.1H, J = 12.0, 4.1 Hz, H-6α), 4.32 (dd, 0.9H, J = 11.8, 4.6 Hz, H-6β), 4.22−4.18 (m, 0.1H, H-6α), 4.18 (dd, 0.9H, J = 11.8, 6.1 Hz, H-6β), 4.08 (dd, 0.1H, J = 5.1, 5.0 Hz, H-4α), 2.33 (s, 3H, tolyl CH_3), 2.17 (s, 0.3H, acyl CH_3α), 2.14 (s, 0.3H, acyl CH_3α), 2.11 (s, 2.7H, acyl CH_3β), 2.10 (s, 5.7H, acyl CH_3), 2.07 (s, 0.3H, acyl CH_3α), 2.40 (s, 2.7H, acyl CH_3β); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.4 (C=O), 170.0 (C=O), 169.9 (C=O), 169.6 (C=O), 138.3 (Ar), 138.0 (Ar), 133.0 (Ar × 2), 132.7 (Ar × 2), 129.9 (Ar × 2), 129.8 (Ar × 2), 129.2 (Ar × 2), 90.7 (C-1β), 89.6 (C-1α), 81.2 (C-2β), 80.6 (C-2α), 79.6 (C-4β), 77.0 (C-4α), 76.5 (C-3β), 75.9 (C-3α), 69.7 (C-5α), 69.1 (C-5β), 62.6 (C-6α), 62.5 (C-6β), 21.1 (tolyl CH_3), 20.8 (acyl CH_3), 20.7 (acyl CH_3 × 3). HRMS (ESI): [M + Na] calcd for $C_{21}H_{26}O_9SNa$, 477.1190; found, 477.1194.

***p*-Tolyl 1-Thio-β-D-galactofuranoside (23).** To a solution of **22** (4.76 g, 10.5 mmol) in CH_3OH (100 mL) and CH_2Cl_2 (100 mL) was added solid $NaOCH_3$ until the pH was ∼10. The solution was allowed to stir at rt for 4 h and then neutralized with acetic acid. The mixture was concentrated, and the resulting crude was purified by chromatography (10:1 CH_2Cl_2/CH_3OH) to yield the anomers **23** (2.41 g, 80%) and **24** (0.25 g, 8%) as white solids. Data for **23**: R_f 0.21 (10:1 CH_2Cl_2/CH_3OH); $[\alpha]_D$ −231.1 (c 0.8, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD, δ_H) 7.42−7.38 (m, 2H, Ar), 7.14−7.10 (m, 2H, Ar), 5.15 (d, 1H, J = 5.0 Hz, H-1), 4.07 (dd, 1H, J = 7.6, 5.4 Hz, H-3), 3.96−3.10 (m, 2H, H-2, H-4), 3.71 (ddd, 1H, J = 6.9, 5.9, 2.9 Hz, H-5), 3.62−3.58 (m, 2H, H-6 × 2), 2.30 (s, 3H, tolyl CH_3); ^{13}C NMR (100 MHz, CD_3OD, δ_C) 138.8 (Ar), 133.7 (Ar × 2), 132.2 (Ar), 130.6 (Ar × 2), 93.3 (C-1), 83.1 (C-2), 83.0 (C-4), 77.8 (C-3), 72.0 (C-5), 64.6 (C-6), 21.1 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{13}H_{18}O_5SNa$, 309.0767; found, 309.0764.

***p*-Tolyl 2,3-Anhydro-1-thio-β-D-gulofuranoside (33).** To a solution of **23** (1.95 g, 6.82 mmol) and trimethylorthoacetate (1.0 mL, 8.1 mmol) in THF (50 mL) was added *p*-toluenesulfonic acid (0.025 g) at rt. The solution was stirred for 3 h and then neutralized with Et_3N. TLC showed two new spots at R_f 0.50 (major) and R_f 0.42 (minor) (10:1 CH_2Cl_2/CH_3OH). The mixture was then cooled to 0 °C, followed by the addition of PPh_3 (7.15 g, 27.3 mmol); DIAD (5.6 mL, 27.3 mmol) was subsequently added dropwise at 0 °C over 10 min. The reaction mixture was warmed to rt over 60 min. TLC showed one major new spot at R_f 0.45 (4:1 hexanes/EtOAc). The reaction mixture was then concentrated and redissolved in EtOAc (200 mL), followed by washing with a 0.3% aq HCl solution (100 mL) until the previous spot disappeared and two new spots formed at R_f 0.28 (major) and R_f 0.20 (minor) (15:1 CH_2Cl_2/CH_3OH), which corresponded to the putative 5-*O*-acetyl and 6-*O*-acetyl derivatives. The solution was dried (Na_2SO_4), filtered, and concentrated to give a yellow oil, which was dissolved in CH_3OH (50 mL) and CH_2Cl_2 (50 mL) before solid $NaOCH_3$ was added until the pH was ~10. The solution was stirred at rt for 14 h, followed by neutralization with HOAc. The resulting mixture was concentrated and purified by chromatography (2:1 hexanes/EtOAc) to yield **33** (1.32 g, 72% over four steps) as a colorless oil. R_f 0.21 (2:1 hexanes/EtOAc); $[\alpha]_D$ −19.1 (*c* 0.3, CH_2Cl_2); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.45−7.42 (m, 2H, Ar), 7.15−7.12 (m, 2H, Ar), 5.45 (s, 1H, H-1), 3.93 (dd, 1H, *J* = 6.2, 0.7 Hz, H-4), 3.92 (d, 1H, *J* = 2.9 Hz, H-2), 3.82 (dd, 1H, *J* = 2.9, 0.7 Hz, H-3), 3.79 (ddd, 1H, *J* = 6.2, 6.2, 4.4 Hz, H-5), 3.66 (dd, 1H, *J* = 11.6, 4.4 Hz, H-6), 3.61 (dd, 1H, *J* = 11.6, 6.2 Hz, H-6), 2.31 (s, 3H, tolyl CH_3); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 139.4 (Ar), 134.5 (Ar × 2), 130.8 (Ar × 2), 130.6 (Ar), 88.3 (C-1), 79.2 (C-4), 72.8 (C-5), 64.6 (C-6), 58.3 (C-2), 56.2 (C-3), 21.1 (tolyl CH_3). HRMS (ESI): [M + Na] calcd for $C_{13}H_{16}O_4SNa$, 291.0662; found, 291.0660.

Methyl 2,3-Anhydro-5,6-di-*O*-benzoyl-α-D-gulofuranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (59). The glycosylation of thioglycoside **15** (472 mg, 0.99 mmol) and sugar acceptor **43** (351 mg, 0.98 mmole) was carried out following the general protocol, and the crude reaction mixture was purified by chromatography (2:1 hexanes/EtOAc) to give disaccharide **59** (217 mg, 69%) as a colorless syrup. R_f 0.26 (2:1 hexanes/EtOAc); $[\alpha]_D$ +14.7 (*c* 2.5, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.08 (d, 2H, *J* = 8.4 Hz, Ar), 8.00 (d, 2H, *J* = 8.4 Hz, Ar), 7.60−7.54 (m, 2H, Ar), 7.48−7.40 (m, 4H, Ar), 7.36−7.20 (m, 10H, Ar), 5.88−5.84 (m, 1H, H-5′), 5.38 (s, 1H, H-1′), 4.97 (d, 1H, *J* = 10.9 Hz, PhC*H*₂), 4.81 (br s, 1H, H-2), 4.77 (dd, 1H, *J* = 12.1, 6.6 Hz, H-6′), 4.75 (s, 1H, H-1), 4.72 (dd, 1H, *J* = 12.1, 4.0 Hz, H-6′), 4.68 (d, 1H, *J* = 11.2 Hz, PhC*H*₂), 4.63 (d, 1H, *J* = 10.9 Hz, PhC*H*₂), 4.50 (d, 1H, *J* = 11.2 Hz, PhC*H*₂), 4.20 (d, 1H, *J* = 5.0 Hz, H-4′), 3.84 (dd, 1H, *J* = 9.3, 3.2 Hz, H-3), 3.78 (d, 1H, *J* = 2.9 Hz, H-2′), 3.69 (qd, 1H, *J* = 9.2, 6.2 Hz, H-5), 3.63 (d, 1H, *J* = 2.9 Hz, H-3′), 3.50 (dd, 1H, *J* = 9.3, 9.2 Hz, H-4), 3.39 (s, 3H, OCH_3), 1.31 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.8 (C=O), 138.8 (Ar), 138.5 (Ar), 133.2 (Ar × 2), 129.9 (Ar × 2), 129.8 (Ar), 129.7 (Ar × 2), 129.6 (Ar), 128.4 (Ar × 4), 128.3 (Ar × 2), 128.2 (Ar × 2), 127.9 (Ar × 2), 127.8 (Ar × 2), 127.5 (Ar), 127.4 (Ar), 100.8 (C-1), 99.9 (C-1′), 80.5 (C-4), 78.8 (C-3), 75.3 (PhCH_2), 74.0 (C-4′), 72.1 (PhCH_2), 70.9 (C-5′), 70.7 (C-2), 67.5 (C-5), 63.4 (C-6′), 55.4 (C-3′), 54.8 (OCH_3), 53.5 (C-2′), 18.0 (C-6). HRMS (ESI): [M + Na] calcd for $C_{41}H_{42}O_{11}Na$, 733.2619; found, 733.2621.

Methyl 2,3-Anhydro-5,6-di-*O*-benzoyl-α-D-gulofuranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (60). The coupling of sulfoxide **18** (140 mg, 0.28 mmol) and acceptor **44** (110 mg, 0.24 mmol) was carried out following the general protocol, and after workup, the product was purified by chromatography (2:1 hexanes/EtOAc) to give **60** (163 mg, 70%) as a white foam. R_f 0.23 (2:1 hexanes/EtOAc); $[\alpha]_D$ +36.9 (*c* 1.4, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.06−8.00 (m, 4H, Ar), 7.58−7.52 (m, 2H, Ar), 7.45−7.14 (m, 19H, Ar), 5.81 (ddd, 1H, *J* = 5.2, 5.2, 5.2 Hz, H-5′), 5.40 (s, 1H, H-1′), 4.88 (s, 1H, H-1), 4.87 (d, 1H, *J* = 10.5 Hz, PhC*H*₂), 4.78 (d, 2H, *J* = 5.2 Hz, H-6′ × 2), 4.74 (d, 1H, *J* = 11.5 Hz, PhCH₂), 4.68 (d, 1H, *J* = 12.0 Hz, PhC*H*₂), 4.62 (d, 1H, *J* = 11.5 Hz, PhC*H*₂), 4.56 (d, 1H, *J* = 12.0 Hz, PhC*H*₂), 4.50 (d, 1H, *J* = 10.5 Hz, PhC*H*₂), 4.36 (s, 1H, H-2), 4.27 (d, 1H, *J* = 5.2 Hz, H-4′), 3.92−3.86 (m, 2H, H-3, H-4), 3.83 (d, 1H, *J* = 2.9 Hz, H-2′), 3.81−3.79 (m, 3H, H-5, H-6 × 2), 3.76 (d, 1H, *J* = 2.9 Hz, H-3′), 3.28 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.9 (C=O), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 133.2 (Ar), 129.9 (Ar), 129.7 (Ar), 129.67 (Ar), 128.4 (Ar), 128.39 (Ar), 128.35 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.4 (Ar), 100.7 (C-1′), 100.1 (C-1), 79.2 (C-3), 75.1 (PhCH_2), 74.7 (C-4′), 74.69 (C-4), 73.4 (PhCH_2), 72.0 (C-2), 71.6 (C-5), 71.6 (PhCH_2), 71.5 (C-5′), 69.4 (C-6), 63.4 (C-6′), 55.3 (C-3′), 54.8 (OCH_3), 54.5 (C-2′). HRMS (ESI): [M + Na] calcd for $C_{48}H_{48}O_{12}Na$, 839.3038; found, 839.3041.

Methyl 2,3-Anhydro-5,6-di-*O*-benzoyl-α-D-gulofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (61). The glycosylation of sulfoxide **18** (241 mg, 0.49 mmol) and alcohol **45** (216 mg, 0.46 mmol) was carried out following the general protocol, and after workup, the product was purified by chromatography (3:1 hexanes/EtOAc) to yield **61** (275 mg, 72%) as a white foam. R_f 0.34 (2:1 hexanes/EtOAc); $[\alpha]_D$ +23.7 (*c* 1.3, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.09−7.99 (m, 4H, Ar), 7.59−7.54 (m, 2H, Ar), 7.46−7.18 (m, 19H, Ar), 5.74 (ddd, 1H, *J* = 6.6, 5.0, 3.8 Hz, H-5′), 5.24 (s, 1H, H-1′), 4.92 (d, 1H, *J* = 10.9 Hz, PhC*H*₂), 4.75 (dd, 1H, *J* = 12.3, 6.6 Hz, H-6′), 4.74 (d, 1H, *J* = 10.9 Hz, PhC*H*₂), 4.69 (dd, 1H, *J* = 12.3, 3.8 Hz, H-6′), 4.67 (d, 1H, *J* = 11.2 Hz, PhC*H*₂), 4.58 (d, 1H, *J* = 11.2 Hz, PhC*H*₂), 4.57 (d, 1H, *J* = 3.2 Hz, H-4), 4.49 (d, 1H, *J* = 12.0 Hz, PhC*H*₂), 4.44 (d, 1H, *J* = 12.0 Hz, PhC*H*₂), 4.30 (d, 1H, *J* = 7.7 Hz, H-1), 4.11 (d, 1H, *J* = 5.0 Hz, H-4′), 3.80 (dd, 1H, *J* = 10.7, 4.2 Hz, H-6), 3.74−3.66 (m, 2H, H-2, H-6), 3.69 (d, 1H, *J* = 3.0 Hz, H-3′), 3.58 (s, 3H, OCH_3), 3.59−3.56 (m, 1H, H-5), 3.51 (d, 1H, *J* = 3.0 Hz, H-2′), 3.40 (dd, 1H, *J* = 9.7, 3.2 Hz, H-3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.8 (C=O), 138.9 (Ar), 138.4 (Ar), 138.35 (Ar), 133.3 (Ar), 133.2 (Ar), 129.8 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.26 (Ar), 128.2 (Ar), 128.15 (Ar), 129.0 (Ar), 127.6 (Ar), 127.5 (Ar), 127.46 (Ar), 127.45 (Ar), 104.8 (C-1), 100.0 (C-1′), 80.7 (C-3), 79.8 (C-2), 75.2 (PhCH_2), 73.8 (C-5), 73.6 (PhCH_2), 73.5 (C-4′), 73.4 (PhCH_2), 71.2 (C-5′), 70.5 (C-6), 70.1 (C-4), 63.2 (C-6′), 57.0 (OCH_3), 55.4 (C-2′), 53.3 (C-3′). HRMS (ESI): [M + Na] calcd for $C_{48}H_{48}O_{12}Na$, 839.3038; found, 839.3038.

Methyl α-D-Galactofuranosyl-(1→2)-α-L-rhamnopyranoside (72). To a solution of compound **76** (37 mg, 0.06 mmol) in CH_3OH (2 mL) was added 10% Pd/C (5 mg), and the reaction mixture was stirred under a hydrogen atmosphere for 5 h. The mixture was then filtered through Celite and concentrated, and the residue was purified on Iatrobeads (5:1 CH_2Cl_2/CH_3OH) to yield compound **72** (19 mg, 94%) as a white foam. R_f 0.27 (5:1 CH_2Cl_2/CH_3OH); $[\alpha]_D$ +38.7 (*c* 1.7, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 4.90 (d, 1H, *J* = 4.8 Hz, H-1′), 4.60 (d, 1H, *J* = 1.6 Hz, H-1), 4.25 (dd, 1H, *J* = 8.6, 7.5 Hz, H-3′), 3.92 (dd, 1H, *J* = 8.6, 4.8 Hz, H-2′), 3.81−3.79 (m, 1H, H-2), 3.79 (dd, 1H, *J* = 7.5, 1.8 Hz, H-4′), 3.64−3.57 (m, 4H, H-3, H-4, H-6′ × 2), 3.55 (dq, 1H, *J* = 9.5, 6.3 Hz, H-5), 3.36−3.32 (m, 4H, H-5′, OCH_3), 1.27 (d, 3H, *J* = 6.3 Hz, H-6); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 103.7 (C-1′), 101.2 (C-1), 82.6 (C-4′), 80.8 (C-2), 78.7 (C-2′), 74.7 (C-3′), 74.2 (C-5′), 71.6 (C-3, C-4), 69.8 (C-5), 64.4 (C-6′), 55.3 (OCH_3), 17.9 (C-6). HRMS (ESI): [M + Na] calcd for $C_{13}H_{24}O_{10}Na$, 363.1262; found, 363.1263.

Methyl α-D-Galactofuranosyl-(1→2)-α-D-mannopyranoside (73). To a solution of **77** (10 mg, 0.014 mmol) in CH_3OH (2 mL) was added 10% Pd/C (3 mg), and the reaction mixture was stirred under a hydrogen atmosphere for 12 h. The mixture was filtered through Celite and concentrated to yield compound **73** (5 mg, 100%) as a white foam. R_f 0.25 (4:1 CH_2Cl_2/CH_3OH); $[\alpha]_D$ +53.7 (*c* 0.5, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 5.07 (d, 1H, *J* = 1.7 Hz, H-1), 4.99 (d, 1H, *J* = 4.7 Hz, H-1′), 4.19 (dd, 1H, *J* = 8.6, 7.5 Hz, H-3′), 3.95 (dd, 1H, *J* = 8.6, 4.7 Hz, H-2′), 3.86 (dd, 1H, *J* = 12.0, 1.8 Hz, H-6), 3.77 (dd, 1H, *J* = 3.4, 1.7 Hz, H-2), 3.74 (dd, 1H, *J* = 7.5, 3.1 Hz, H-4′), 3.74−3.67 (m, 2H, H-3, H-6), 3.64−3.58 (m, 1H, H-6′), 3.58−3.52 (m, 4H, H-5′, H-4, H-6′, H-5), 3.39 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 104.7 (C-1′), 101.0 (C-1), 83.4 (C-4′), 81.9 (C-2), 78.9 (C-2′), 75.2 (C-3′), 75.0 (C-5), 72.8 (C-3), 72.0 (C-5′), 69.2 (C-4), 64.8 (C-6′), 62.8 (C-6), 55.6 (OCH_3). HRMS (ESI): [M + Na] calcd for $C_{13}H_{24}O_{11}Na$, 379.1211; found, 379.1210.

Methyl α-D-Galactofuranosyl-(1→2)-α-D-galactofuranosyl-(1→4)-*β*-D-galactopyranoside (74). To a solution of **83** (12 mg, 0.012 mmol) in CH_3OH (2 mL) was added 10% $Pd(OH)_2/C$ (8 mg), and the reaction mixture was stirred under a hydrogen atmosphere for 12 h. The mixture was then filtered through Celite and concentrated to yield **74** (6.5 mg, 100%) as a white foam. R_f 0.53 (1:4 CH_2Cl_2/CH_3OH); $[\alpha]_D$ +56.5 (*c* 0.5, CH_3OH); ^1H NMR (600 MHz, CD_3OD, δ_H) 5.03 (d, 1H, *J* = 4.7 Hz, H-1′), 5.01 (d, 1H, *J* = 4.8 Hz, H-1″), 4.43 (dd, 1H, *J* = 8.9, 8.3 Hz, H-3″), 4.24 (dd, 1H, *J* = 8.5, 7.8 Hz, H-3′), 4.14 (d, 1H, *J* = 7.6 Hz, H-1), 4.06 (dd, 1H, *J* = 8.9, 4.8 Hz, H-2″), 3.95 (dd, 1H, *J* = 8.5, 4.7 Hz, H-2′), 3.90 (d, 1H, *J* = 2.1 Hz, H-4), 3.82 (dd, 1H, *J* = 10.8, 8.1 Hz, H-6), 3.79 (d, 1H, *J* = 8.3 Hz, H-4″), 3.78 (dd, 1H, *J* = 7.8, 3.5 Hz, H-4′), 3.73−3.69 (m, 1H, H-5′), 3.69 (dd, 1H, *J* = 10.8, 5.8 Hz, H-6), 3.65−3.56 (m, 5H, H-6′ × 2, H-6″ × 2, H-5″), 3.53 (dd, 1H, *J* = 8.1, 5.8 Hz, H-5), 3.51 (s, 3H, OCH_3), 3.45−3.44 (m, 2H, H-2, H-3); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 106.2 (C-1), 103.1 (C-1″), 102.3 (C-1′), 84.2 (C-2″), 82.6 (C-4′), 81.6 (C-4″), 79.4 (C-4), 79.1 (C-2′), 76.2 (C-5), 75.4 (C-3′), 74.3 (C-2), 72.9 (C-3″), 72.7 (C-5′), 72.5 (C-3), 71.5 (C-5″), 64.3 (C-6″), 64.2 (C-6′), 60.6 (C-6), 57.5 (OCH_3). HRMS (ESI): [M + Na] calcd for $C_{19}H_{34}O_{16}Na$, 541.1739; found, 541.1739.

Methyl 3-*O*-Benzyl-α-D-galactofuranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (76). Compound **59** (160 mg, 0.225 mmol) was subjected to the general epoxide-opening protocol, and the resulting residue was purified by chromatography (2:1 hexanes/EtOAc) to give **76** (80 mg, 65%) as a colorless oil. R_f 0.29 (1:1 hexanes/EtOAc); $[\alpha]_D$ +22.3 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.25 (m, 15H, Ar), 4.98 (d, 1H, *J* = 3.8 Hz, H-1′), 4.95 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.93 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.80 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.74 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.69 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.68 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.55 (d, 1H, *J* = 1.8 Hz, H-1), 4.28−4.24 (m, 2H, H-2′, H-4′), 4.00−3.96 (m, 1H, H-3′), 4.96−4.94 (m, 1H, H-2), 3.89 (dd, 1H, *J* = 9.4, 3.0 Hz, H-3), 3.78 (br s, 1H, OH), 3.67 (qd, 1H, *J* = 9.5, 6.3 Hz, H-5), 3.62−3.59 (m, 1H, H-5′), 3.46 (dd, 1H, *J* = 9.5, 9.4 Hz, H-4), 3.40 (dd, 1H, *J* = 12.3, 4.3 Hz, H-6′), 3.55−3.51 (m, 4H, H-6′, OCH_3), 1.60 (br s, 2H, OH × 2), 1.30 (d, 3H, *J* = 6.3 Hz, H-6 × 3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2 (Ar), 138.1 (Ar), 137.3 (Ar), 128.5 (Ar × 2), 128.4 (Ar × 4), 128.1 (Ar), 128.0 (Ar × 2), 127.9 (Ar × 2), 127.8 (Ar), 127.7 (Ar × 3), 103.4 (C-1′), 99.1 (C-1), 82.6 (C-4′), 82.3 (C-3′), 80.6 (C-4), 78.5 (C-3), 77.7 (C-2′), 77.5 (C-2), 75.5 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 71.2 (C-5′), 67.9 (C-5), 65.0 (C-6′), 54.8 (OCH_3), 18.0 (C-6). HRMS (ESI): [M + Na] calcd for $C_{34}H_{42}O_{10}Na$, 633.2670; found, 633.2671.

Methyl 3-*O*-Benzyl-α-D-galactofuranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (77). Epoxide **60** (80 mg, 0.098 mmol) was opened following the general protocol, and the product was purified by chromatography (1:2 hexanes/EtOAc) to yield **77** (41 mg, 55%) as a colorless oil. R_f 0.33 (1:2 hexanes/EtOAc); $[\alpha]_D$ +18.1 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.18 (m, 20H, Ar), 4.98 (d, 1H, *J* = 4.8 Hz, H-1′), 4.96 (d, 1H, *J* = 1.6 Hz, H-1), 4.89 (d, 1H, *J* = 11.3 Hz, PhC*H*$_2$), 4.83 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.69−4.55 (m, 5H, PhC*H*$_2$), 4.52 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.31 (dd, 1H, *J* = 6.4, 4.8 Hz, H-2′), 4.19 (dd, 1H, *J* = 6.4, 6.1, Hz, H-3′), 4.01 (dd, 1H, *J* = 6.1, 3.7 Hz, H-4′), 3.96−3.92 (m, 1H, H-3), 3.82−3.80 (m, 1H, H-2), 3.80−3.76 (m, 2H, H-4, H-5), 3.76−3.67 (m, 3H, H-6 × 2, H-5′), 3.62−3.54 (m, 2H, H-6′ × 2), 3.36 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2 (Ar), 138.1 (Ar), 138.0 (Ar), 137.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.37 (Ar), 128.0 (Ar), 127.99 (Ar), 127.9 (Ar), 127.8 (Ar), 127.77 (Ar), 127.7 (Ar), 127.6 (Ar), 104.4 (C-1′), 99.1 (C-1), 83.5 (C-3′), 83.2 (C-4′), 79.0 (C-3), 78.6 (C-2′), 78.1 (C-2), 75.2 (Ph*C*H$_2$), 75.0 (C-5), 73.4 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.7 (C-5′), 71.4 (C-4), 69.0 (C-6), 64.5 (C-6′), 55.2 (OCH_3). HRMS (ESI): [M + Na] calcd for $C_{41}H_{48}O_{11}Na$, 739.3089; found, 739.3081.

Methyl 3-*O*-Benzyl-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (78). Disaccharide **61** (404 mg, 0.49 mmol) was subjected to the general protocol to open the epoxide ring, and the crude residue was purified by chromatography (3:1 hexanes/EtOAc) to give **78** (207 mg, 69%) as a colorless oil. R_f 0.55 (1:1 hexanes/EtOAc); $[\alpha]_D$ +29.4 (*c* 1.5, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$, δ_H) 7.42−7.25 (m, 20H, Ar), 4.97 (d, 1H, *J* = 5.0 Hz, H-1′), 4.93 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.90 (dd, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.86 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.78 (d, 1H, *J* = 12.5, PhC*H*$_2$), 4.76 (d, 1H, *J* = 12.5 Hz, PhC*H*$_2$), 4.65 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.54 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.51 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.25 (d, 1H, *J* = 7.6 Hz, H-1), 4.24 (dd, 1H, *J* = 7.6, 7.5 Hz, H-3′), 4.18−4.15 (m, 1H, H-2′), 4.13 (d, 1H, *J* = 11.5 Hz, OH), 4.08 (d, 1H, *J* = 3.0 Hz, H-4), 3.88 (dd, 1H, *J* = 7.5, 1.5 Hz, H-4′), 3.70 (dd, 1H, *J* = 9.2, 9.1 Hz, H-6), 3.68 (dd, 1H, *J* = 9.9, 7.6 Hz, H-2), 3.59 (dd, 1H, *J* = 9.2, 5.4 Hz, H-6), 3.59−3.55 (m, 1H, H-5′), 3.53 (s, 3H, OCH_3), 3.50 (dd, 1H, *J* = 9.1, 5.4 Hz, H-5), 3.47 (dd, 1H, *J* = 9.9, 3.0 Hz, H-3), 3.43−3.32 (m, 2H, H-6′ × 2), 2.75 (d, 1H, *J* = 10.5 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.5 (Ar), 138.1 (Ar), 137.3 (Ar), 137.2 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.35 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.95 (Ar), 127.8 (Ar), 127.7 (Ar), 105.1 (C-1), 103.6 (C-1′), 82.6 (C-3′), 81.4 (C-4′), 79.6 (C-2), 79.59 (C-3), 78.0 (C-2′), 75.6 (C-4), 75.4 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.3 (C-5), 70.8 (C-5′), 66.7 (C-6), 65.0 (C-6′), 57.3 (OCH_3). HRMS (ESI): [M + Na] calcd for $C_{41}H_{48}O_{11}Na$, 739.3089; found, 739.3091.

Methyl 3-*O*-Benzyl-5,6-*O*-isopropylidene-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (79). To a mixture of compound **78** (198 mg, 0.28 mmol) and 2,2-dimethoxypropane (0.27 mL, 2.2 mmol) in dry acetone (5 mL) was added *p*-TsOH (2 mg), and the reaction mixture was stirred at rt for 4 h. Two drops of Et_3N were added, and the reaction mixture was concentrated. Column chromatography (3:1 hexanes/EtOAc) of the residue gave the disaccharide **79** (0.185 g, 89%) as a colorless oil. R_f 0.38 (2:1 hexanes/EtOAc); $[\alpha]_D$ +45.9 (*c* 0.6, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.41−7.24 (m, 20H, Ar), 5.19 (d, 1H, *J* = 4.8 Hz, H-1′), 4.98 (d, 1H, *J* = 13.3 Hz, PhC*H*$_2$), 4.91 (d, 1H, *J* = 11.5 Hz, PhC*H*$_2$), 4.88 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.80 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.62 (d, 1H, *J* = 13.3 Hz, PhC*H*$_2$), 4.59 (d, 1H, *J* = 11.5 Hz, PhC*H*$_2$), 4.53 (s, 2H, PhC*H*$_2$), 4.36 (ddd, 1H, *J* = 8.0, 7.0, 7.0 Hz, H-5′), 4.27 (d, 1H, *J* = 3.0 Hz, H-4), 4.24 (d, 1H, *J* = 7.5 Hz, H-1), 4.17 (dd, 1H, *J* = 6.8, 4.8 Hz, H-2′), 3.90 (dd, 1H, *J* = 8.0, 7.0 Hz, H-4′), 3.84−3.74 (m, 2H, H-6′ × 2), 3.74 (dd, 1H, *J* = 7.0, 6.8 Hz, H-3′), 3.68−3.59 (m, 2H, H-6 × 2), 3.57 (dd, 1H, *J* = 9.8, 7.5 Hz, H-2), 3.54 (s, 3H, OCH_3), 3.49 (dd, 1H, *J* = 8.7, 5.5 Hz, H-5), 3.43 (dd, 1H, *J* = 9.8, 3.0 Hz, H-3), 1.39 (s, 3H, isopropylidene CH_3), 1.21 (s, 3H, isopropylidene CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6 (Ar), 138.5 (Ar), 137.7 (Ar), 137.2 (Ar), 128.6 (Ar), 128.5 (Ar), 128.2 (Ar), 128.16 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.6 (Ar), 127.56 (Ar), 127.3 (Ar), 109.5 (isopropylidene C), 105.0 (C-1), 103.0 (C-1′), 83.3 (C-3′), 82.3 (C-4′), 78.8 (C-3), 78.7 (C-2), 78.33 (C-2′), 78.30 (C-5′), 75.0 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 72.4 (C-5), 72.1 (C-4), 71.9 (Ph*C*H$_2$), 70.5 (Ph*C*H$_2$), 67.0 (C-6), 65.0 (C-6′), 57.2 (OCH_3), 26.7 (isopropylidene CH_3), 25.3 (isopropylidene CH_3). HRMS (ESI): [M + Na] calcd for $C_{44}H_{52}O_{11}Na$, 779.3402; found, 779.3404.

Methyl 2,3-Anhydro-5,6-di-*O*-benzoyl-α-D-gulofuranosyl-(1→2)-3-*O*-benzyl-5,6-*O*-isopropylidene-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (80). The glycosylation of disaccharide **79** (283 mg, 0.37 mmol) and donor **18** (553 mg, 1.12 mmol) was carried out following the general protocol, and after workup, the product was purified by column chromatography (2:1 hexanes/EtOAc) to yield **80** (243 mg, 59%) as a white foam. R_f 0.30 (3:2 hexanes/EtOAc); $[\alpha]_D$ +48.6 (*c* 0.5, CH_2Cl_2);

^{1}H NMR (600 MHz, CD_2Cl_2, δ_H) 8.04−7.97 (m, 4H, Ar), 7.58−7.54 (m, 2H, Ar), 7.45−7.38 (m, 6H, Ar), 7.35−7.20 (m, 18H, Ar), 5.75 (ddd, 1H, *J* = 6.4, 5.2, 4.0 Hz, H-5″), 5.14 (d, 1H, *J* = 4.3 Hz, H-1′), 5.06 (s, 1H, H-1″), 4.92 (d, 1H, *J* = 12.8 Hz, PhC*H*$_2$), 4.82 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.81 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.76 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.76−4.70 (m, 2H, H-6″ × 2), 4.61 (d, 1H, *J* = 12.8 Hz, PhC*H*$_2$), 4.57 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.56 (d, 1H, *J* = 12.1 Hz, PhC*H*$_2$), 4.49 (d, 1H, *J* = 12.1 Hz, PhC*H*$_2$), 4.44 (dd, 1H, *J* = 6.6, 4.3 Hz, H-2′), 4.35 (ddd, 1H, *J* = 6.8, 6.8, 6.8 Hz, H-5′), 4.24 (d, 1H, *J* = 7.6 Hz, H-1), 4.19 (dd, 1H, *J* = 5.2, 0.9 Hz, H-4″), 4.12 (d, 1H, *J* = 3.0 Hz, H-4), 4.00 (dd, 1H, *J* = 6.7, 6.6 Hz, H-3′), 3.82−3.79 (m, 2H, H-6′, H-3″), 3.76−3.73 (m, 2H, H-6′, H-4′), 3.69 (d, 1H, *J* = 3.1 Hz, H-2″), 3.66−3.63 (m, 3H, H-2, H-6 × 2), 3.52 (s, 3H, OCH_3), 3.52−3.50 (m, 1H, H-5), 3.40 (dd, 1H, *J* = 9.8, 3.0 Hz, H-3), 1.34 (s, 3H, isopropylidene CH_3), 1.20 (s, 3H, isopropylidene CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 166.3 (C═O), 166.1 (C═O), 139.6 (Ar), 139.3 (Ar), 138.6 (Ar), 138.4 (Ar), 133.7 (Ar), 133.6 (Ar), 130.2 (Ar), 130.1 (Ar), 130.0 (Ar), 128.9 (Ar), 128.83 (Ar), 128.8 (Ar), 128.6 (Ar), 128.55 (Ar), 128.5 (Ar), 128.3 (Ar), 128.24 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.7 (Ar), 127.6 (Ar), 109.6 (isopropylidene C), 105.4 (C-1), 102.5 (C-1′), 101.0 (C-1″), 82.2 (C-2′), 81.54 (C-3′), 81.5 (C-4′), 80.5 (C-3), 79.4 (C-2), 78.6 (C-5′), 75.5 (C-4″), 75.3 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 73.6 (C-4), 73.55 (C-5), 72.4 (Ph*C*H$_2$), 71.8 (C-5″), 71.7 (Ph*C*H$_2$), 69.2 (C-6), 65.4 (C-6′), 63.7 (C-6″), 57.3 (OCH_3), 55.7 (C-2″), 54.4 (C-3″), 27.0 (isopropylidene CH_3), 25.6 (isopropylidene CH_3). HRMS (ESI): [M + Na] calcd for $C_{64}H_{68}O_{17}Na$, 1131.4354; found, 1131.4351.

Methyl 2,3-Anhydro-5,6-di-*O*-benzoyl-α-D-gulofuranosyl-(1→2)-3-*O*-benzyl-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (81). R_f 0.12 (3:2 hexanes/EtOAc); $[\alpha]_D$ +36.7 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.02−8.00 (m, 4H, Ar), 7.60−7.52 (m, 2H, Ar), 7.45−7.25 (m, 22H, Ar), 7.28−7.20 (m, 2H, Ar), 5.77 (br s, 1H, H-5″), 5.02 (d, 1H, *J* = 4.3 Hz, H-1′), 4.93 (s, 1H, H-1"), 4.90−4.80 (m, 3H, PhC*H*$_2$), 4.77 (d, 1H, *J* = 10.6 Hz, PhC*H*$_2$), 4.77−4.73 (m, 1H, H-6″), 4.70 (d, 1H, *J* = 12.3 Hz, PhC*H*$_2$), 4.70−4.64 (m, 2H, H-6″, H-2′), 4.64 (d, 1H, *J* = 11.5 Hz, PhC*H*$_2$), 4.55 (d, 1H, *J* = 12.3 Hz, PhC*H*$_2$), 4.48 (d, 1H, *J* = 12.3 Hz, PhC*H*$_2$), 4.42 (dd, 1H, *J* = 7.3, 7.2 Hz, H-3′), 4.21 (d, 1H, *J* = 7.6 Hz, H-1), 4.05 (d, 1H, *J* = 5.0 Hz, H-4″), 3.82−3.77 (m, 2H, H-4, H-4′), 3.74 (br s, 1H, H-3″), 3.72−3.62 (m, 4H, H-2, H-5′, H-6′ × 2), 3.54 (s, 1H, H-2″), 3.54 (s, 3H, OCH_3), 3.46 (dd, 1H, *J* = 11.4, 4.0 Hz, H-6), 3.42−3.35 (m, 3H, H-5, H-3, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C═O), 165.7 (C═O), 138.7 (Ar), 138.4 (Ar), 138.3 (Ar), 137.5 (Ar), 133.4 (Ar), 133.3 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 128.5 (Ar), 128.47 (Ar), 128.44 (Ar), 128.4 (Ar), 128.3 (Ar), 128.28 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.63 (Ar), 127.6 (Ar), 127.55 (Ar), 104.9 (C-1), 103.9 (C-1′), 99.9 (C-1″), 80.5 (C-4′), 80.4 (C-3′), 80.2 (C-2′, C-3), 80.1 (C-2), 79.3 (C-4), 75.4 (Ph*C*H$_2$), 74.5 (C-4″), 73.7 (C-5), 73.3 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 71.3 (C-5′, C-5″), 69.1 (C-6′), 64.6 (C-6), 63.2 (C-6″), 57.1 (OCH_3), 55.2 (C-2″), 53.4 (C-3″). HRMS (ESI): [M + Na] calcd for $C_{61}H_{64}O_{17}Na$, 1091.4034; found, 1091.4036.

Methyl 3-*O*-Benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-benzyl-5,6-*O*-isopropylidene-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (82). Compound **80** (110 mg, 0.1 mmol) was subjected to the general protocol to open the epoxide, and after workup, the product was purified by chromatography (1:1 hexanes/EtOAc) to give **82** (61 mg, 61%) as a colorless syrup. R_f 0.29 (1:1 hexanes/EtOAc); $[\alpha]_D$ +57.0 (*c* 0.6 CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.42−7.26 (m, 25H, Ar), 5.16 (d, 1H, *J* = 4.2 Hz, H-1′), 4.96 (d, 1H, *J* = 4.9 Hz, H-1″), 4.90−4.86 (m, 3H, PhC*H*$_2$), 4.82 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.65 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.63−4.58 (m, 4H, PhC*H*$_2$), 4.46 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.32 (d, 1H, *J* = 3.0 Hz, H-4), 4.27 (d, 1H, *J* = 7.6 Hz, H-1), 4.24−4.19 (m, 2H, H-2″, H-5′), 4.14−4.06 (m, 3H, H-3′, H-3″, H-2′), 3.97 (dd, 1H, *J* = 6.0, 4.8 Hz, H-4′), 3.94−3.89 (m, 2H, H-6′, H-4″), 3.77 (dd, 1H, *J* = 9.2, 7.0 Hz, H-6′), 3.71 (dd, 1H, *J* = 9.8, 7.6 Hz, H-2), 3.69−3.65 (m, 1H, H-5″), 3.59−3.49 (m, 5H, H-6″ × 2, H-6 × 2, H-5), 3.33 (s, 3H, OCH_3), 3.44 (dd, 1H, *J* = 9.8, 3.0 Hz, H-3), 2.84 (br s, 1H, OH), 1.39 (s, 3H, isopropylidene CH_3), 1.16 (s, 3H, isopropylidene CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.8 (Ar), 138.4 (Ar), 137.9 (Ar), 137.6 (Ar), 137.1 (Ar), 128.6 (Ar), 128.56 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.54 (Ar), 127.5 (Ar), 109.2 (isopropylidene C), 105.0 (C-1), 103.0 (C-1″), 101.2 (C-1′), 82.9 (C-3″), 82.7 (C-2′), 82.1 (C-4″), 82.0 (C-4′), 81.9 (C-3′), 79.8 (C-3), 79.0 (C-2), 77.7 (C-2″), 76.5 (C-5′), 75.3 (Ph*C*H$_2$), 73.8 (Ph*C*H$_2$), 72.4 (C-5), 72.3 (C-5″), 72.1 (Ph*C*H$_2$), 71.8 (Ph*C*H$_2$), 71.3 (C-4), 71.2 (Ph*C*H$_2$), 67.2 (C-6), 65.1 (C-6′), 64.2 (C-6″), 57.2 (OCH_3), 26.4 (isopropylidene CH_3), 24.5 (isopropylidene CH_3). HRMS (ESI): [M + Na] calcd for $C_{57}H_{68}O_{16}Na$, 1031.4405; found, 1031.4407.

Methyl 3-*O*-Benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-benzyl-α-D-galactofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranoside (83). A solution of compound **82** (49 mg, 0.049 mmol) in HOAc/H_2O/THF (5:3:2) was stirred at 50 °C for 12 h. The reaction mixture was concentrated, and the resulting residue was purified by chromatography (1:1 hexanes/EtOAc) to give **83** (38 mg, 81%) as a colorless syrup. R_f 0.4 (1:3 hexanes/EtOAc); $[\alpha]_D$ +50.7 (*c* 0.4, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 7.40−7.25 (m, 25H, Ar), 5.12 (d, 2H, *J* = 4.4 Hz, H-1′, H-1″), 4.86−4.82 (m, 4H, PhC*H*$_2$), 4.73 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.71 (d, 1H, *J* = 12.5 Hz, PhC*H*$_2$), 4.65 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.64 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.59 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.54 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.53 (dd, 1H, *J* = 6.8, 6.4 Hz, H-3″), 4.27 (dd, 1H, *J* = 6.8, 4.4 Hz, H-2″), 4.26 (d, 1H, *J* = 7.7 Hz, H-1), 4.20 (dd, 1H, *J* = 6.6, 4.4 Hz, H-2′), 4.12 (dd, 1H, *J* = 6.6, 6.4 Hz, H-3′), 4.07 (d, 1H, *J* = 3.0 Hz, H-4), 4.02 (dd, 1H, *J* = 6.4, 2.5 Hz, H-4″), 3.90 (dd, 1H, *J* = 6.4, 6.0 Hz, H-4′), 3.84 (dd, 1H, *J* = 9.3, 7.7 Hz, H-6), 3.77 (ddd, 1H, *J* = 6.3, 6.1, 6.0 Hz, H-5′), 3.65−3.58 (m, 3H, H-2, H-6, H-5), 3.57−3.52 (m, 3H, H-3, H-6′, H-5″), 3.48 (s, 3H, OCH_3), 3.43 (dd, 1H, *J* = 11.5, 6.3 Hz, H-6′), 3.40−3.34 (m, 2H, H-6" × 2); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 140.3 (Ar), 139.8 (Ar), 139.6 (Ar), 139.5 (Ar), 139.0 (Ar), 129.5 (Ar), 129.44 (Ar), 129.4 (Ar), 129.3 (Ar), 129.23 (Ar), 129.2 (Ar), 129.15 (Ar), 129.1 (Ar), 129.05 (Ar), 129.02 (Ar), 129.0 (Ar), 128.96 (Ar), 128.9 (Ar), 128.7 (Ar), 128.5 (Ar), 106.2 (C-1), 104.1 (C-1″), 103.0 (C-1′), 83.9 (C-3′), 82.7 (C-4′), 82.3 (C-2″), 82.0 (C-3″), 81.9 (C-4″), 81.3 (C-3), 80.8 (C-2), 78.8 (C-2′), 77.3 (C-4), 76.3 (Ph*C*H$_2$), 74.4 (Ph*C*H$_2$), 74.3 (C-5′), 73.93 (C-5), 73.9 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 73.0 (Ph*C*H$_2$), 72.9 (C-5″), 68.7 (C-6), 64.2 (C-6′, C-6″), 57.6 (OCH_3). HRMS (ESI): [M + Na] calcd for $C_{54}H_{64}O_{16}Na$, 991.4087; found, 991.4088.

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Note Added after ASAP Publication. Due to an oversight by the corresponding author, the preparation of **21** in Scheme 1 and in the Experimental Section was incorrectly described in the version published ASAP November 23, 2006; the corrected version was published ASAP November 29, 2006.

Supporting Information Available: Details on the synthesis of **34**−**37**, data for additional new compounds not included above, and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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