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Regioselective Glycosylation of Unprotected Phenyl 1-Thioglycopyranosides with Phenylboronic Acid as a Transient Masking Group

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A useful protocol is described for the regioselective glycosylation of the secondary alcohols in unprotected glycosyl acceptors. Phenyl 1-thioglycopyranosides derived from D-glucose, D-galactose, D-glucosamine, L-rhamnose, and L-fucose were treated with phenylboronic acid to install a temporary boronic ester, and then submitted to a Koenigs–Knorr glycosylation with perbenzoylated glucopyranosyl or galactopyranosyl bromides. Good yields for coupling to the 3-position in glucosides and galactosides were achieved, but lower yields were obtained with the other acceptors. With phenyl 1-thio-β-D-glucopyranoside, the coupling could also be achieved with a superarmed thiogalactoside donor. The product from a glucose–glucose coupling could be subjected to a second regioselective glycosylation at the 6-position. In the galactose series, a β(1→3)-linked galactotriose could be prepared in good yield by two consecutive glycosylations in one pot, where a free 2-hydroxy group ensures neighboring group participation in the second coupling.

Introduction

The importance and diverse roles of glycans in biological processes continue to be revealed in further detail in the area of glycobiology.[1] This has led to the development of an increasing number of therapeutic agents based on glycans,[2] and has created a high demand for structurally well-defined carbohydrate oligomers. As a result, the chemical synthesis of oligosaccharides has received significant attention over the past three decades.[3] During this period, major progress has been made in the field in terms of glycosyl donors and glycosylation strategies. Significant advances include the development of the trichloroacetimidate[4] and thioglycoside[5] donors, as well as the armed–disarmed,[6] one-pot,[7,8] and solid-phase[8,9] strategies. However, the fundamental principle for forming a glycosidic bond is the same today as in 1982,[10] i.e., a glycosyl donor is activated with a promoter and coupled to a partially protected acceptor with only one free hydroxy group. Irrespective of the donor and the strategy used, this causes the synthesis of a target oligosaccharide to involve a significant number of steps, of which the majority are used for the manipulation of protecting groups. A solution to this problem would come from the development of regioselective glycosylations with unprotected glycosyl acceptors.

Some progress has been made in this area, but in most cases, the more reactive 6-position is selectively glycosylated in a 2,3,4,6-unprotected hexopyranoside. In the absence of any special directing agents, 2-(trimethylsilyl)ethyl β-D-galactopyranoside has been glycosylated in good yield with a number of glycosyl bromides under Koenigs–Knorr conditions.[11] With unprotected gluco- and mannopyranosides, however, the selectivity for the primary alcohol is lower. To improve the regioselectivity, dibutyltin oxide has been introduced to form 4,6-stannylene acetals with 2,3,4,6-unprotected hexopyranosides, and in this way enhance the reactivity of the 6-position. Under these conditions, a number of β-galacto- and β-glucopyranosides have been glycosylated at the primary position in good yield with several donors.[12]

Other positions in 2,3,4,6-unprotected hexopyranosides, however, are more difficult to glycosylate in high yield. Methyl β-D-galactopyranoside has been shown to react at its 3-position with a glycosyl bromide in the presence of dibutyltin oxide and tetrabutylammonium fluoride. The tetrabutylammonium fluoride promotes a shift in regioselectivity from the 6- to the 3-position.[13] Still, the isolated yield of the (1→3)-linked disaccharide was only 40%.[13] *p*-Methoxyphenylboronic acid has been used as an in situ blocking agent for the 4- and 6-positions in hexopyranosides.[14] With this reagent, the Koenigs–Knorr glycosylation of methyl α-D-galactopyranoside and methyl β-D-galactopyranoside with 2,3,4,6-tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide (2 equiv.) gave 50 and 72% yields, respectively, of the (1→3)-linked disaccharides.[14] With methyl α-D-glucopyranoside and methyl β-D-glucopyranoside, however, the yields and selectivities were poor, and mixtures of (1→2)- and (1→3)-linked disaccharides were formed.[14] The reactions were carried out by stirring the donor, the acceptor and the arylboronic acid with molecular sieves (3 Å) in dichloroethane for 16 h, followed by the addition of silver(I) on silica–alumina.[14] Borinic acids have also

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been used to mediate regioselective glycosylations, but high yields of disaccharides were only obtained if the 6-position of the acceptor was protected with a silyl group, or if the acceptor was a 6-deoxy hexose.[15]

Thus, there is still room for further development in this area, and more comprehensive studies are required to explore the scope and limitations of this concept. A particular challenge would be to glycosylate the secondary alcohols in 2,3,4,6-unprotected hexopyranosides, and for this reason we decided to explore the use of the cheaper phenylboronic acid as a transient blocking group. As in our recent study with dibutyltin oxide,[12a] phenyl 1-thioglycopyranosides were chosen as acceptors, since the products of the regioselective couplings would then be thioglycoside building blocks, which are useful glycosyl donors in oligosaccharide synthesis. Thus, in this paper, we report full details of the regioselective glycosylation of unprotected thiohexopyranosides using an in situ blocking strategy with phenylboronic acid.

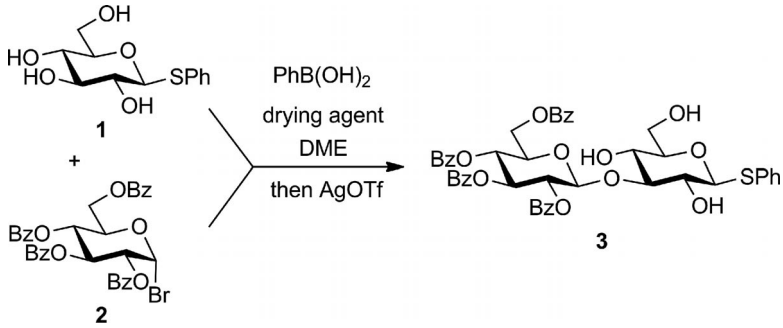
Results and Discussion

Phenyl 1-thio-β-D-glucopyranoside (**1**) was chosen as the acceptor for the initial experiments, since regioselective reactions on glucose are usually more difficult than with other hexoses. When **1** was mixed with phenylboronic acid in acetonitrile, a clear solution was immediately obtained, and then the formation of a white precipitate was observed. The solid was shown by NMR spectroscopy to be the 4,6-phenylboronate of **1** (vide infra). It was not possible to dissolve the boronate effectively in toluene, diethyl ether, dichloromethane, or dichloroethane, but it was completely soluble in dioxane, THF, and DME (1,2-dimethoxyethane). Dioxane and THF were deemed to be too acid labile to use in some glycosylation reactions with silver triflate, and consequently DME was chosen to investigate the couplings.

Thus, a Koenigs–Knorr glycosylation between the preformed 4,6-phenylboronate and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide was studied in the presence of silver oxide, silver carbonate, and silver triflate. In each case, the ratio between the donor and the acceptor was varied, and the best result was obtained with silver triflate and 1.3 equiv. of the donor. This gave the (1→3)-linked disaccharide as the major coupling product, but it was not possible to achieve a yield above 30%. The coupling appeared to be very selective for the 3-position, but the yield was not satisfactory. The low yield seems to be caused by water in the boronate; it was not possible to thoroughly dry the solid under high vacuum due to the partial cleavage and sublimation of phenylboronic acid.

As a result, the formation of the boronate was carried out in the presence of drying agents, and for these studies, the more stable 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide was used as the donor (Table 1). In the first experiment, the boronate was generated in DME solution over molecular sieves (3 Å), and then the glycosyl bromide and silver triflate were added. In the work-up, the boronate was removed with methanol and a weakly basic ion-exchange resin. This, however, gave only a 16% yield of the (1→3)-linked disaccharide (Table 1, entry 1), and it appeared that water was still the main problem. Although the molecular sieves were able to remove the water during the formation of the boronate, the glycosyl bromide is a better drying agent, and seemed to be drying the sieves in the subsequent glycosylation. Therefore, the drying agent should be removed before the glycosylation. Indeed, with this modifica-

Table 1. Optimization of the regioselective glycosylation.[a]



Entry	Drying agent	Yield [%][b]
1[c]	MS (3 Å)	16
2	MS (3 Å)	52
3	MS (4 Å)	19
4	$CaSO_4$	41
5[d]	MS (3 Å)	68
6[e]	MS (3 Å)	61
7[f]	MS (3 Å)	66

[a] Reaction conditions: $PhB(OH)_2$ (0.14 mmol), acceptor **1** (0.14 mmol), drying agent, DME, room temp., 16 h, then drying agent removed, donor **2** (0.18 mmol), AgOTf (0.18 mmol), 0 °C, 3 h, then MeOH, IRA 743. [b] Isolated yields. [c] Drying agent not removed prior to glycosylation. [d] Freshly activated MS (3 Å) added in glycosylation. [e] As for entry 5 with $PhBCl_2$ instead of $PhB(OH)_2$. [f] As for entry 5 with $(PhBO)_3$ (0.33 equiv.) instead of $PhB(OH)_2$.

tion, the yield of the disaccharide increased to 52% (Table 1, entry 2). Under the same conditions, 4 Å molecular sieves and $CaSO_4$ gave lower yields (Table 1, entries 3–4). A further improvement could be achieved by adding a new fresh batch of activated sieves during the glycosylation; this raised the yield to 68% (Table 1, entry 5). This is a quite satisfactory result in light of the previous difficulties with regioselective glycosylations on glucose.

Two other reagents for forming the boronate were also investigated, namely dichlorophenylborane and the anhydride of phenylboronic acid, i.e., triphenylboroxin. The former produces hydrogen chloride upon ester formation, while the latter generates only 1 equiv. of water. Triphenylboroxin is easily prepared by heating phenylboronic acid in an oven at 110 °C.[16] With both reagents, the boronate was formed from acceptor **1** in DME, and the coupling reaction was performed as described in Table 1, entry 5. This resulted in almost the same yield of the (1→3)-linked disaccharide in both cases (Table 1, entries 6–7), and so it was decided to continue the studies with phenylboronic acid as the in situ blocking agent.

The structure of the 4,6-boronate formed from acceptor **1** was confirmed by NMR spectroscopy after the ester was isolated from the DME solution (Figure 1). Distinct changes in the chemical shifts of H-4 and H-6 were observed, and in [D_6]DMSO solution, the couplings to OH-2 and OH-3 were visible, whereas OH-4 and OH-6 were absent. Four additional phenyl thioglycosides were prepared, and the boronates were formed in the same way and characterized by NMR spectroscopy (Figure 1). Galactoside **4** and aminoglucoside **5** both gave 4,6-boronates, while rhamnoside **6** and fucoside **7** gave 2,3- and 3,4-esters, respectively. Phenyl 1-thio-α-D-mannopyranoside was also converted into its phenylboronate, but in this case, the ester was not soluble in DME, and so no further studies were performed with mannose.

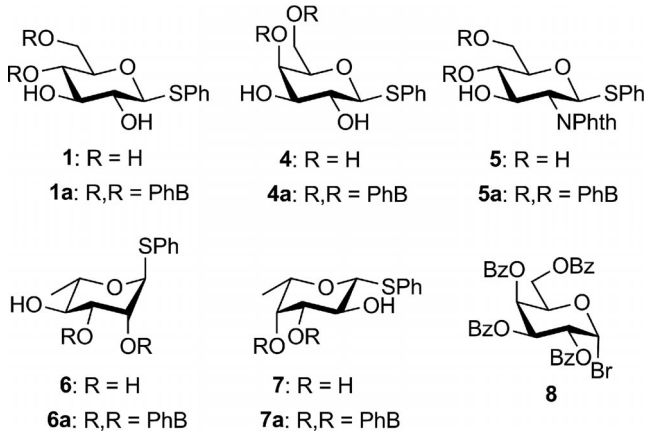
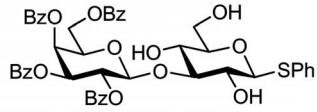
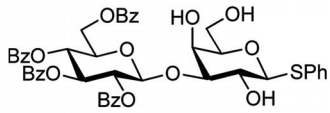
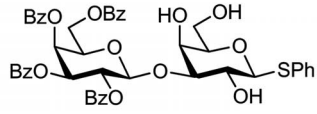
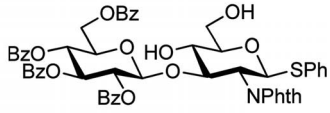
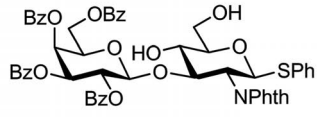
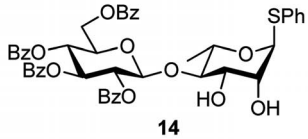
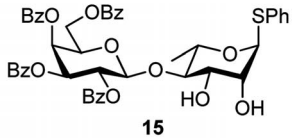
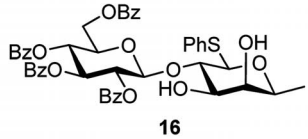
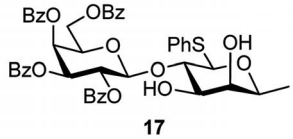


Figure 1. Glycosyl acceptors, the corresponding boronates, and donor **8**.

With this information, the substrate scope could now be investigated further under the optimized conditions from Table 1, entry 5. In addition to donor **2**, the corresponding galactosyl bromide **8** (Figure 1) was also included in the

Table 2. Koenigs–Knorr glycosylation of unprotected phenyl 1-thioglycopyranosides.[a]

Entry	Donor	Acc.	Product	Yield[b]
1	**8**	**1**	 **9**	67%
2	**2**	**4**	 **10**	82%
3	**8**	**4**	 **11**	75%
4	**2**	**5**	 **12**	34%
5	**8**	**5**	 **13**	38%
6	**2**	**6**	 **14**	48%
7	**8**	**6**	 **15**	56%
8	**2**	**7**	 **16**	32%
9	**8**	**7**	 **17**	30%

[a] Reaction conditions: $PhB(OH)_2$ (0.14 mmol), acceptor (0.14 mmol), MS (3 Å), DME, room temp., 16 h, then donor (0.18 mmol), AgOTf (0.18 mmol), MS (3 Å), 0 °C, 3 h, then MeOH, IRA 743. [b] Isolated yields.

study. When donor **8** was coupled with glucoside **1**, the yield of the product was essentially the same as that of the product obtained with donor **2** (Table 2, entry 1).

Better results were observed with both donors in coupling reactions with galactoside **4**, where 82 and 75% yields of the (1→3)-linked disaccharides were obtained (Table 2, entries 2–3). Glucosamine acceptor **5**, on the other hand, gave poor yields in the glycosylations (Table 2, entries 4–5). This is most probably due to the lower reactivity of the acceptor, since the 3-position in phthalimido-protected β-glucosamines is known to be the least reactive.[17] With rhamnoside **6**, moderate yields of the (1→4)-linked disaccharides were obtained, and fucoside **7** gave poor yields of the (1→2)-linked products. These low yields may again be attributed to the lower reactivity of the hydroxy group in the acceptor.[18] No coupling products other than the isolated disaccharides were formed in any of the reactions; only donor-derived decomposition products and unreacted acceptor were seen. Neither was any aglycon transfer of the thiophenyl group from the acceptor to the donor observed. The positions of the glycosidic linkages were established from NMR spectroscopy. The free hydroxy groups were visible in the ^{1}H NMR spectra, and deshielding of the carbon signals was observed in the ^{13}C NMR spectra.

In addition to glycosyl bromides, a thioglycoside and two trichloroacetimidates were also tested as glycosyl donors. Thioglycoside **18** was coupled in the presence of *N*-iodosuccinimide (NIS) and silver triflate, while imidates **19** and **20** were activated with triethylsilyl triflate (Figure 2). Thioglycoside **18** is a so-called superarmed donor,[19] and a selective coupling to another thioglycoside should therefore be possible. Indeed, the glycosylation between **18** and glucoside **1** gave a 66% yield of disaccharide **21** (Table 3, entry 1). Unfortunately, the same coupling with galactoside **4** gave only a 40% yield of the disaccharide product (Table 3, entry 2), and similar results were obtained with the imidate donors (Table 3, entries 3–6). In all, the regioselective glycosylations with phenylboronic acid have shown that good-yielding reactions can be achieved at the 3-position in β-glucosides and β-galactosides under Koenigs–Knorr conditions. This represents an improvement over the previous procedure with *p*-methoxyphenylboronic acid, where a poor yield was observed in the coupling with glucosides.[14]

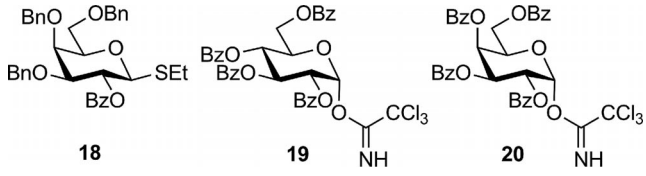
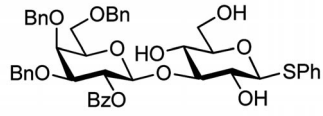
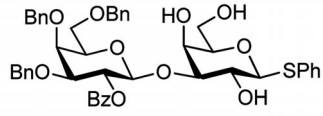


Figure 2. Thioglycoside donor **18** and imidate donors **19** and **20**.

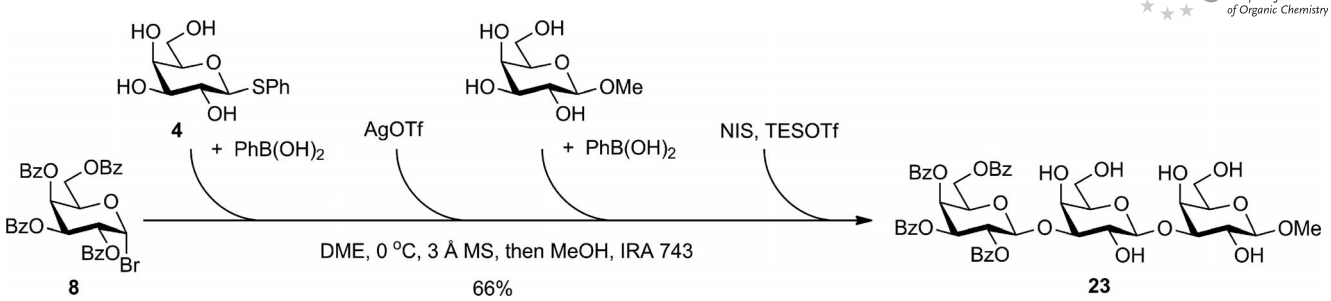
Finally, it was decided to investigate whether several consecutive glycosylations could be carried out using this method to prepare trisaccharides and higher oligosaccharides. First, an iterative approach was studied, since the initially formed disaccharides (shown in Tables 1, 2, and 3) are protected with a phenylboronate group, and may therefore serve as glycosyl donors for a further glycosylation reaction in the same reaction vessel. As glucosides and galactosides had been identified as the most effective acceptors, these experiments were only performed with thioglycosides **1** and **4**. The initially formed disaccharides have a free hydroxy group at the 2-position, and the effectiveness of a second glycosylation will therefore depend on the reactivity of the new acceptor. The first experiment was done in the galactose series, and began with the Koenigs–Knorr coupling of bromide **8** and thioglycoside **4** (Scheme 1). Instead of isolating the disaccharide as in Table 2, entry 3, the 4,6-phenylboronate of methyl β-D-galactopyranoside was formed separately and was then added to the reaction mixture together with *N*-iodosuccinimide and triethylsilyl triflate. This resulted in a second glycosylation, and galactotriose **23** was isolated in a satisfactory 66% yield after work-up with methanol and a weakly basic ion-exchange resin. Notably, the second glycosylation gave only the β-linked product, which is consistent with earlier observations with 2-hydroxy glycosyl donors, and may indicate that neighboring group participation is occurring with the free hydroxy group and that the mechanism goes via an epoxide.[20]

The same sequence was performed in the glucose series, and began with the coupling of bromide **2** and thioglycoside **1** as described in Table 1, entry 5. The 4,6-phenylboronate

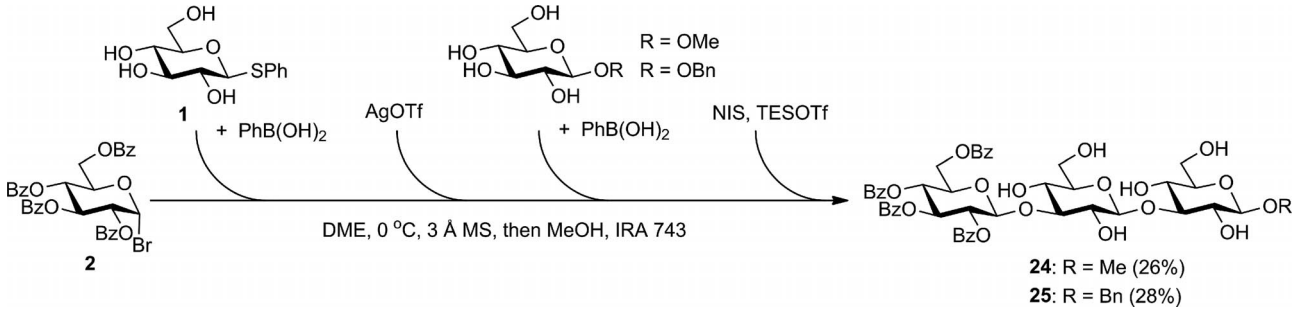
Table 3. Glycosylation of unprotected phenyl 1-thioglycopyranosides with donors **18**–**20**.

Entry	Donor	Acc.	Product	Yield[a]
1[b]	**18**	**1**	 **21**	66%
2[b]	**18**	**4**	 **22**	40%
3[c]	**19**	**1**	**3**	31%
4[c]	**19**	**4**	**10**	49%
5[c]	**20**	**1**	**9**	28%
6[c]	**20**	**4**	**11**	36%

[a] Isolated yields. [b] Reaction conditions: $PhB(OH)_2$ (0.14 mmol), acceptor (0.14 mmol), MS (3 Å), DME, room temp., 16 h, then **18** (0.16 mmol), NIS (0.17 mmol), AgOTf (0.02 mmol), MS (3 Å), –30 °C, 15 min, then MeOH, IRA 743. [c] Reaction conditions: $PhB(OH)_2$ (0.14 mmol), acceptor (0.14 mmol), MS (3 Å), DME, room temp., 16 h, then donor (0.17 mmol), TESOTf (0.03 mmol; TES = triethylsilyl), MS (3 Å), 0 °C, 1 h, then MeOH, IRA 743.



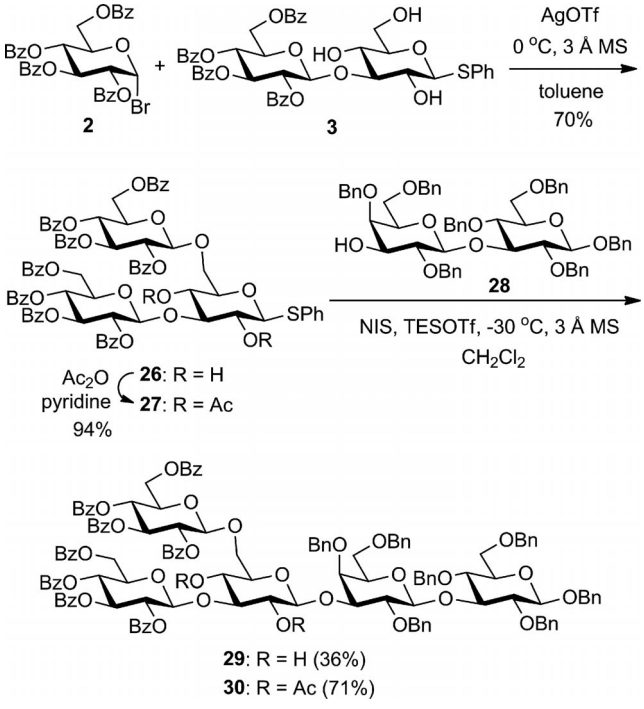
Scheme 1. One-pot glycosylation in the galactose series.



Scheme 2. One-pot glycosylation in the glucose series.

of methyl β-D-glucopyranoside was then added to the reaction mixture, followed by *N*-iodosuccinimide and triethylsilyl triflate (Scheme 2). This gave glucotriose **24** in 26% isolated yield after the usual work-up. The phenylboronate of methyl β-D-glucopyranoside was less soluble in DME and required a slightly more dilute solution, and therefore the sequence was repeated with the corresponding benzyl β-D-glucopyranoside. This, however, enhanced the yield only to 28%, and it appears that the lower coupling yield and reactivity of the acceptor in the glucose series have a detrimental influence on the iterative strategy. Trisaccharides **23**–**25** were subsequently acetylated and deprotected in order to completely characterize the three glycans.

A different approach to consecutive glycosylations would be to use the isolated disaccharide as an acceptor, and to carry out a regioselective glycosylation at the primary position. Since the 3-position is occupied by a bulky monosaccharide, it should be possible to achieve a high selectivity for the 6-position. This was demonstrated with disaccharide **3**, which underwent a Koenigs–Knorr glycosylation with bromide **2** to give branched trisaccharide **26** in 70% yield with no coupling to the other positions being observed (Scheme 3). Inspired by the β-selective glycosylation with 2-hydroxy glycosyl donors, a further glycosylation was carried out with lactoside acceptor **28** to give pentasaccharide **29**. The new glycosidic linkage was formed with complete β-selectivity, although the isolated yield was only 36%. When the same coupling was repeated with acetyl-protected donor **27**, the yield increased to 71%.



Scheme 3. Regioselective glycosylation at the 6-position.

Conclusions

In summary, we have further developed the regioselective glycosylation of unprotected glycosyl acceptors by the use of transient protection with a boronic acid. Phenyl 1-thiohexopyranosides were used as the acceptors, and good coupling yields to the 3-position in glucose and galactose substrates were achieved. This provides an easy route to (1→3)-linked disaccharide thioglycosides, which are valuable building blocks for oligosaccharide synthesis. When the products were used as acceptors, an additional glycosyl-

ation at the 6-position could be performed. Alternatively, they could be used as donors in another glycosylation with a transiently protected acceptor.

Experimental Section

General Remarks: All reactions were performed under an argon atmosphere. Molecular sieves (MS) were flame-dried before use. Dichloromethane and 1,2-dimethoxyethane were dried with MS (3 Å). Phenyl 1-thio-β-D-glucopyranoside (**1**),[21] 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**2**),[22] phenyl 1-thio-β-D-galactopyranoside (**4**),[21] phenyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5**),[21] phenyl 1-thio-α-L-rhamnopyranoside (**6**),[23] phenyl 1-thio-β-L-fucopyranoside (**7**),[23] 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (**8**),[24] ethyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (**18**),[25] 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**19**),[24] 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**20**),[24] and benzyl 2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**28**)[26] were synthesized according to literature procedures. Silver triflate was co-evaporated with dry toluene and dried under high vacuum prior to use. TLC was performed on aluminum plates coated with silica gel 60. The plates were visualized with UV light or developed by dipping into a solution of cerium(IV) sulfate (2.50 g) and ammonium molybdate (6.25 g) in sulfuric acid (10%; 250 mL) followed by heating. Column chromatography was carried out with HPLC grade solvents on silica gel 60 (230–400 mesh). NMR spectra were recorded with Bruker AC 200, Varian Mercury 300, or Varian Unity Inova 500 instruments. Chemical shifts were calibrated to the residual solvent signal in $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) or to TMS. Assignment of ^1H and ^{13}C resonances was based on COSY, HSQC, and HMBC experiments. HRMS analysis was performed using an Agilent 1100 LC system with a diode array detector and a Luna C_{18} column (3 μm, 50 mm × 2 mm). The LC was coupled to a Micromass LCT orthogonal time-of-flight mass spectrometer equipped with Lock Mass probe operating in positive electrospray mode. Optical rotations were measured with a Perkin–Elmer 341 polarimeter. IR spectra were recorded with a Bruker Alpha-P FTIR instrument.

General Procedure for Koenigs–Knorr Glycosylation: Equimolar amounts of phenyl thioglycopyranoside and phenylboronic acid were dissolved in dry DME (5 mL) to give a 50 mg/mL glycoboronate solution. MS (3 Å; 350 mg) were added, and the mixture was stirred overnight or until dry, as monitored by NMR spectroscopy. A decanted aliquot (1 mL) of this solution was added to a mixture of the bromide donor (1.3 equiv.) and MS (3 Å; 175 mg) under argon, and the resulting suspension was stirred overnight. AgOTf (1.3 equiv.) was added at 0 °C, and the reaction mixture was stirred for 3 h (TLC: toluene/acetone, 3:1). CH_2Cl_2, MeOH, and Amberlite IRA 743 (250–300 mg) were then added, and the mixture was stirred overnight. The suspension was filtered through Celite, and the pad was flushed with CH_2Cl_2/MeOH (1:1 mixture). The filtrate was concentrated and the residue was purified by flash chromatography (toluene/acetone, 7:1).

Phenyl 4,6-*O*-Phenylboranylidine-1-thio-β-D-glucopyranoside (1a): ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.79–7.69 (m, 2 H), 7.47–7.40 (m, 3 H), 7.38–7.22 (m, 5 H), 5.64 (d, J = 6.2 Hz, 1 H, 2-OH), 5.56 (d, J = 5.1 Hz, 1 H, 3-OH), 4.88 (d, J = 9.8 Hz, 1 H, 1-H), 4.15 (dd, J = 9.8, 5.0 Hz, 1 H, 6-H), 3.89 (t, J = 9.9 Hz, 1 H, 6-H), 3.75 (td, J = 9.5, 5.0 Hz, 1 H, 5-H), 3.65 (t, J = 9.2 Hz, 1 H, 4-H), 3.46 (td, J = 8.7, 5.1 Hz, 1 H, 3-H), 3.23–3.14 (m, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 134.74, 134.55, 131.61, 130.88, 129.68, 128.26, 128.02, 127.50, 88.08 (C-1), 76.52, 74.97, 73.30, 72.03, 64.15 ppm. HRMS: calcd. for $C_{12}H_{16}O_5S$ [M – C_6H_3B + Na]$^+$ 295.0616; found 295.0614.

Phenyl 4,6-*O*-Phenylboranylidine-1-thio-β-D-galactopyranoside (4a): ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.74 (d, J = 6.7 Hz, 2 H), 7.46 (t, J = 7.3 Hz, 1 H), 7.35 (t, J = 7.4 Hz, 4 H), 7.05 (t, J = 7.3 Hz, 1 H), 6.94 (t, J = 7.5 Hz, 2 H), 5.24 (d, J = 6.0 Hz, 1 H, 2-OH), 5.21 (d, J = 6.6 Hz, 1 H, 3-OH), 4.73 (d, J = 9.5 Hz, 1 H, 1-H), 4.35 (d, J = 2.9 Hz, 1 H, 4-H), 4.22 (d, J = 12.0 Hz, 1 H, 6-H), 4.14–4.00 (m, 2 H, 5-H, 6-H), 3.56 (ddd, J = 9.4, 6.6, 3.0 Hz, 1 H, 3-H), 3.39 (dt, J = 9.2, 6.1 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 134.46, 134.19, 131.42, 130.94, 129.26, 128.14, 127.08, 87.14 (C-1), 74.06, 71.88, 71.87, 68.36, 65.18 ppm. HRMS: calcd. for $C_{18}H_{19}BO_5S$ [M + Na]$^+$ 381.0944; found 381.0975.

Phenyl 2-Deoxy-4,6-*O*-phenylboranylidine-2-phthalimido-1-thio-β-D-glucopyranoside (5a): ^1H NMR (300 MHz, $CDCl_3$): δ = 8.03–7.68 (m, 6 H), 7.53–7.21 (m, 8 H), 5.71 (d, J = 10.5 Hz, 1 H, 1-H), 4.56 (ddd, J = 10.1, 8.6, 3.5 Hz, 1 H, 3-H), 4.35 (t, J = 10.3 Hz, 1 H, 2-H), 4.31–4.22 (m, 1 H, 6-H), 4.01 (t, J = 10.1 Hz, 1 H, 6-H), 3.82 (t, J = 9.0 Hz, 1 H, 4-H), 3.79–3.67 (m, 1 H, 5-H), 2.83 (d, J = 3.6 Hz, 1 H, 3-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.63, 167.75, 134.52, 134.31, 132.94, 131.86, 131.46, 129.23, 128.44, 127.89, 124.14, 123.57, 84.73 (C-1), 76.00, 72.59, 71.69, 64.08, 55.43 ppm. HRMS: calcd. for $C_{20}H_{19}NO_6S$ [M – C_6H_3B + Na]$^+$ 424.0831; found 424.0833.

Phenyl 2,3-*O*-Phenylboranylidine-1-thio-α-L-rhamnopyranoside (6a): ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.76–7.68 (m, 2 H), 7.58–7.49 (m, 3 H), 7.45–7.30 (m, 5 H), 5.91 (s, 1 H, 1-H), 5.65 (d, J = 6.4 Hz, 1 H, 4-OH), 4.72 (dd, J = 7.1, 1.1 Hz, 1 H, 2-H), 4.46 (t, J = 7.3 Hz, 1 H, 3-H), 3.98–3.88 (m, 1 H, 5-H), 3.20–3.10 (m, 1 H, 4-H), 1.06 (d, J = 6.2 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 135.25, 134.74, 133.41, 132.63, 129.84, 128.70, 128.33, 128.01, 84.46 (C-1), 79.73, 78.56, 76.01, 67.89, 18.04 ppm. HRMS: calcd. for $C_{12}H_{16}O_4S$ [M – C_6H_3B + Na]$^+$ 279.0667; found 279.0657.

Phenyl 3,4-*O*-Phenylboranylidine-1-thio-β-L-fucopyranoside (7a): ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.79–7.70 (m, 2 H), 7.55–7.17 (m, 8 H), 5.94 (d, J = 5.8 Hz, 1 H, 2-OH), 4.91 (d, J = 7.6 Hz, 1 H, 1-H), 4.57–4.47 (m, 2 H, 3-H, 4-H), 4.13–4.03 (m, 1 H, 5-H), 3.52–3.44 (m, 1 H, 2-H), 1.29 (d, J = 6.5 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 135.49, 135.22, 134.74, 132.42, 130.13, 129.66, 128.65, 128.01, 127.20, 86.77 (C-1), 79.99, 78.26, 72.35, 71.72, 17.07 ppm. HRMS: calcd. for $C_{18}H_{19}BO_4S$ [M + Na]$^+$ 365.0995; found 365.0942.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1-thio-β-D-glucopyranoside (3): Colorless solid. R_f = 0.38 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +3.2 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3493, 3064, 2962, 2944, 2876, 1729, 1606, 1452, 1316, 1266, 1178, 1094, 1069, 1027, 710 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.3 Hz, 2 H), 7.98 (d, J = 7.3 Hz, 2 H), 7.93 (d, J = 7.3 Hz, 2 H), 7.83 (d, J = 7.3 Hz, 2 H), 7.60–7.50 (m, 3 H), 7.45–7.35 (m, 9 H), 7.32–7.24 (m, 5 H), 5.95 (t, J = 9.7 Hz, 1 H, 3′-H), 5.62 (t, J = 9.7 Hz, 1 H, 4′-H), 5.54 (dd, J = 9.8, 8.1 Hz, 1 H, 2′-H), 5.06 (d, J = 8.0 Hz, 1 H, 1′-H), 4.77 (dd, J = 12.2, 2.4 Hz, 1 H, 6′-H), 4.47 (d, J = 9.8 Hz, 1 H, 1-H), 4.38 (dd, J = 12.2, 6.8 Hz, 1 H, 6′-H), 4.23 (ddd, J = 9.5, 6.7, 2.5 Hz, 1 H, 5′-H), 3.92–3.86 (m, 1 H, 6-H), 3.76 (s, 1 H, 4-OH), 3.74–3.69 (m, 1 H, 6-H), 3.57–3.48 (m, 2 H, 3-H, 4-H), 3.39–3.34 (m, 1 H, 5-H), 3.33–3.27 (m, 1 H, 2-H), 2.12 (d, J = 2.5 Hz, 1 H, 2-OH), 2.02 (t, J = 6.7 Hz, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.37, 165.91, 165.57, 165.45,

133.89, 133.70, 133.64, 133.60, 132.85, 131.62, 130.19, 130.13, 130.04, 129.99, 129.44, 129.31, 129.27, 128.85, 128.73, 128.63, 128.58, 128.52, 128.46, 125.53, 102.72 (C-1′), 89.68, 88.10 (C-1), 79.73, 73.00, 72.66, 72.17, 71.08, 69.60, 69.54, 63.25, 63.07 ppm. HRMS: calcd. for $C_{46}H_{42}O_{14}S$ [M + Na]$^+$ 873.2193; found 873.2222.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-1-thio-β-D-glucopyranoside (9): Colorless solid. R_f = 0.47 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = –23.4 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3489, 3063, 2961, 2914, 2886, 1726, 1602, 1452, 1315, 1265, 1178, 1095, 1069, 1026, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11–8.03 (m, 4 H), 7.98 (d, J = 7.3 Hz, 2 H), 7.79 (d, J = 7.3 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 1 H), 7.59–7.36 (m, 11 H), 7.31–7.21 (m, 5 H), 5.99 (d, J = 3.1 Hz, 1 H, 4′-H), 5.82 (dd, J = 10.4, 8.0 Hz, 1 H, 2′-H), 5.64 (dd, J = 10.4, 3.4 Hz, 1 H, 3′-H), 5.02 (d, J = 8.0 Hz, 1 H, 1′-H), 4.61 (dd, J = 11.6, 4.4 Hz, 1 H, 6′-H), 4.53–4.45 (m, 2 H, 6′-H, 1-H), 4.41 (dd, J = 7.9, 4.4 Hz, 1 H, 5′-H), 3.99 (s, 1 H, 4-OH), 3.93–3.86 (m, 1 H, 6-H), 3.74 (dt, J = 12.0, 6.2 Hz, 1 H, 6-H), 3.61–3.53 (m, 2 H, 3-H, 4-H), 3.42–3.30 (m, 2 H, 2-H, 5-H), 2.18 (d, J = 2.5 Hz, 1 H, 2-OH), 2.10 (t, J = 6.7 Hz, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.31, 165.77, 165.71, 165.65, 134.04, 133.70, 133.65, 132.84, 131.64, 130.25, 130.17, 130.01, 129.99, 129.35, 129.31, 129.27, 128.94, 128.79, 128.73, 128.62, 128.57, 128.52, 128.46, 103.09 (C-1′), 90.01 (C-3), 88.11 (C-1), 79.68, 72.34, 71.62, 71.01, 70.06, 69.71, 68.21, 63.32, 62.78 ppm. HRMS: calcd. for $C_{46}H_{42}O_{14}S$ [M + Na]$^+$ 873.2193; found 873.2228.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1-thio-β-D-galactopyranoside (10): Colorless solid. R_f = 0.41 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +14.8 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3537, 3063, 2950, 2888, 1728, 1601, 1452, 1315, 1266, 1178, 1107, 1093, 1069, 1027, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.3 Hz, 2 H), 7.93 (dd, J = 11.3, 4.1 Hz, 4 H), 7.83 (d, J = 8.3 Hz, 2 H), 7.61–7.14 (m, 17 H), 5.95 (t, J = 9.7 Hz, 1 H, 3′-H), 5.63 (t, J = 9.7 Hz, 1 H, 4′-H), 5.50 (dd, J = 9.8, 7.9 Hz, 1 H, 2′-H), 5.16 (d, J = 7.9 Hz, 1 H, 1′-H), 4.69 (dd, J = 12.2, 2.8 Hz, 1 H, 6′-H), 4.49 (dd, J = 12.2, 6.0 Hz, 1 H, 6′-H), 4.45 (d, J = 9.7 Hz, 1 H, 1-H), 4.22–4.16 (m, 1 H, 5′-H), 4.06 (s, 1 H, 4-H), 3.85 (dd, J = 11.3, 7.1 Hz, 1 H, 6-H), 3.78–3.71 (m, 1 H, 2-H), 3.64 (dd, J = 8.9, 3.2 Hz, 1 H, 3-H), 3.62–3.55 (m, 1 H, 6-H), 3.48–3.43 (m, 1 H, 5-H), 2.69 (s, 1 H, 4-OH), 2.36 (s, 1 H, 2-OH), 2.16–2.10 (m, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.37, 165.95, 165.80, 165.44, 133.85, 133.71, 133.60, 132.51, 132.43, 130.09, 130.00, 129.55, 129.26, 129.18, 128.85, 128.78, 128.72, 128.58, 128.45, 128.08, 101.79 (C-1′), 88.35 (C-1), 83.91 (C-3), 78.33, 72.81, 72.56, 72.42, 69.66, 68.83, 68.53, 62.95, 62.64 ppm. HRMS: calcd. for $C_{46}H_{42}O_{14}S$ [M + Na]$^+$ 873.2187; found 873.2196.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-1-thio-β-D-galactopyranoside (11): Colorless solid. R_f = 0.38 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +92.4 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3524, 3063, 2963, 2925, 2894, 1725, 1601, 1451, 1315, 1266, 1177, 1108, 1094, 1069, 1027, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.2 Hz, 2 H), 8.01 (d, J = 7.2 Hz, 2 H), 7.94 (d, J = 7.3 Hz, 2 H), 7.78 (d, J = 7.3 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 1 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.54–7.33 (m, 10 H), 7.25 (m, 5 H), 5.98 (d, J = 3.1 Hz, 1 H, 4′-H), 5.77 (dd, J = 10.4, 7.9 Hz, 1 H, 2′-H), 5.66 (dd, J = 10.4, 3.4 Hz, 1 H, 3′-H), 5.11 (d, J = 7.9 Hz, 1 H, 1′-H), 4.63 (dd, J = 11.6, 7.5 Hz, 1 H, 6′-H), 4.48 (d, J = 11.6 Hz, 1 H, 6′-H), 4.47 (d, J = 9.9 Hz, 1 H, 1-H), 4.39–4.34 (m, 1 H, 5′-H), 4.08 (s, 1 H, 4-H), 3.88–3.82 (m, 1 H, 6-H), 3.78 (td, J = 9.4, 2.3 Hz, 1 H, 2-H), 3.67 (dd, J = 8.9, 3.2 Hz, 1 H, 3-H), 3.60–3.53 (m, 1 H, 6-H), 3.50–3.44 (m, 1 H, 5-H), 2.81 (s, 1 H, 4-OH), 2.39 (d, J = 2.3 Hz, 1 H, 2-OH), 2.14 (dd, J = 8.9, 3.4 Hz, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.25, 166.04, 165.79, 165.72, 134.02, 133.79, 133.74, 133.66, 132.50, 132.42, 130.27, 130.00, 129.97, 129.44, 129.23, 129.19, 129.00, 128.95, 128.81, 128.75, 128.57, 128.11, 102.17 (C-1′), 88.28 (C-1), 84.25, 78.31, 72.10, 71.41, 70.22, 68.89, 68.46, 68.26, 62.72, 62.48 ppm. HRMS: calcd. for $C_{46}H_{42}O_{14}S$ [M + Na]$^+$ 873.2193; found 873.2213.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (12): Colorless solid. R_f = 0.51 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +40.2 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3480, 3063, 2956, 2943, 2881, 1777, 1714, 1602, 1584, 1451, 1386, 1316, 1262, 1178, 1091, 1069, 1026, 709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15–8.09 (m, 2 H), 7.89–7.85 (m, 2 H), 7.64–7.56 (m, 3 H), 7.52–7.43 (m, 6 H), 7.40–7.31 (m, 5 H), 7.28–7.23 (m, 3 H), 7.21–7.14 (m, 5 H), 7.11 (t, J = 7.8 Hz, 2 H), 6.93 (d, J = 7.3 Hz, 1 H), 5.76 (t, J = 9.7 Hz, 1 H, 3′-H), 5.52 (t, J = 9.7 Hz, 1 H, 4′-H), 5.44 (dd, J = 9.8, 8.0 Hz, 1 H, 2′-H), 5.40 (d, J = 10.5 Hz, 1 H, 1-H), 4.84 (d, J = 8.0 Hz, 1 H, 1′-H), 4.75 (dd, J = 12.3, 2.3 Hz, 1 H, 6′-H), 4.61 (dd, J = 10.2, 8.4 Hz, 1 H, 3-H), 4.39–4.31 (m, 2 H, 2-H, 6′-H), 4.23 (ddd, J = 9.6, 7.1, 2.3 Hz, 1 H, 5′-H), 3.94 (dd, J = 11.8, 3.5 Hz, 1 H, 6-H), 3.79 (dd, J = 11.8, 5.5 Hz, 1 H, 6-H), 3.72 (t, J = 9.0 Hz, 1 H, 4-H), 3.54 (ddd, J = 9.3, 5.4, 3.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.86, 166.94, 166.33, 165.85, 165.28, 164.76, 134.31, 133.90, 133.70, 133.52, 133.04, 132.35, 132.11, 130.95, 130.26, 130.08, 129.89, 129.74, 129.33, 129.20, 128.71, 128.64, 128.59, 128.49, 128.43, 128.12, 123.73, 123.21, 101.58 (C-1′), 84.27 (C-1), 83.91 (C-3), 79.88, 77.45, 73.08, 72.69, 72.03, 70.91, 69.19, 63.39, 63.00 ppm. HRMS: calcd. for $C_{54}H_{45}NO_{15}S$ [M + Na]$^+$ 1002.2402; found 1002.2405.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (13): Colorless solid. R_f = 0.56 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +147.7 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3479, 3062, 2981, 2881, 1777, 1716, 1602, 1452, 1386, 1267, 1178, 1094, 1069, 1026, 711 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.2 Hz, 2 H), 8.04 (d, J = 7.2 Hz, 2 H), 7.65–7.53 (m, 5 H), 7.52–7.41 (m, 7 H), 7.38–7.29 (m, 3 H), 7.28–7.24 (m, 2 H), 7.21–7.16 (m, 3 H), 7.12 (t, J = 7.8 Hz, 2 H), 7.08 (t, J = 7.8 Hz, 2 H), 7.00 (d, J = 7.3 Hz, 1 H), 5.88 (d, J = 3.3 Hz, 1 H, 4′-H), 5.74 (dd, J = 10.4, 8.0 Hz, 1 H, 2′-H), 5.46 (dd, J = 10.4, 3.4 Hz, 1 H, 3′-H), 5.42 (d, J = 10.5 Hz, 1 H, 1-H), 4.85 (d, J = 8.0 Hz, 1 H, 1′-H), 4.68–4.60 (m, 2 H, 3-H, 6′-H), 4.58 (s, 1 H, 4-OH), 4.47–4.35 (m, 3 H, 2-H, 5′-H, 6′-H), 3.99–3.91 (m, 1 H, 6-H), 3.84–3.76 (m, 2 H, 4-H, 6-H), 3.55 (ddd, J = 9.3, 5.2, 3.9 Hz, 1 H, 5-H), 2.07 (t, J = 6.8 Hz, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.30, 165.59, 165.55, 164.95, 134.31, 134.08, 133.92, 133.75, 133.55, 133.07, 132.23, 130.90, 130.24, 129.78, 129.75, 129.23, 129.20, 128.95, 128.74, 128.63, 128.47, 128.42, 128.16, 123.66, 123.14, 101.85 (C-1′), 84.23 (C-1), 84.12 (C-3), 79.82, 72.48, 71.62, 70.99, 70.02, 68.10, 63.41, 62.85, 54.02 ppm. HRMS: calcd. for $C_{54}H_{45}NO_{15}S$ [M + Na]$^+$ 1002.2402; found 1002.2406.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-1-thio-α-L-rhamnopyranoside (14): Colorless solid. R_f = 0.51 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = –97.8 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3500, 3063, 2972, 2938, 2886, 1730, 1602, 1452, 1351, 1265, 1177, 1092, 1069, 1027, 709 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08–7.97 (m, 4 H), 7.92 (d, J = 7.1 Hz, 2 H), 7.82 (d, J = 7.1 Hz, 2 H), 7.60–7.47 (m, 3 H), 7.46–7.22 (m, 14 H), 5.93 (t, J = 9.6 Hz, 1 H, 3′-H), 5.67 (t, J = 9.7 Hz, 1 H, 4′-H), 5.55 (dd, J = 9.8, 8.0 Hz, 1 H, 2′-H), 5.41 (d, J = 1.1 Hz, 1 H, 1-H), 5.24 (d, J = 7.9 Hz, 1 H, 1′-H), 4.70 (dd, J = 12.2, 3.0 Hz, 1 H, 6′-H), 4.48 (dd, J = 12.2, 5.6 Hz, 1 H,

6′-H), 4.23–4.14 (m, 2 H, 5-H, 5′-H), 4.06 (s, 1 H, 2-H), 3.85–3.76 (m, 1 H, 3-H), 3.70 (t, J = 9.4 Hz, 1 H, 4-H), 2.75 (d, J = 5.2 Hz, 1 H, 3-OH), 2.60 (s, 1 H, 2-OH), 1.25 (d, J = 6.2 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.36, 166.00, 165.46, 165.43, 134.00, 133.76, 133.52, 133.48, 131.69, 130.08, 129.99, 129.66, 129.29, 129.21, 128.94, 128.90, 128.82, 128.68, 128.55, 127.71, 101.18 (C-1′), 87.42 (C-1), 81.87 (C-4), 73.16, 72.78, 72.58, 72.53, 71.41, 69.82, 67.58, 63.11, 17.69 ppm. HRMS: calcd. for $C_{46}H_{42}O_{13}S$ [M + Na]$^+$ 857.2238; found 857.2245.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-1-thio-α-L-rhamnopyranoside (15): Colorless solid. R_f = 0.57 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = –23.4 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3514, 3062, 2976, 2936, 2887, 1727, 1602, 1584, 1451, 1315, 1265, 1177, 1094, 1069, 1027, 709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.3 Hz, 2 H), 8.04–7.98 (m, 4 H), 7.78 (d, J = 7.3 Hz, 2 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.58–7.47 (m, 4 H), 7.45–7.35 (m, 7 H), 7.32–7.22 (m, 5 H), 6.00 (d, J = 3.2 Hz, 1 H, 4′-H), 5.84 (dd, J = 10.3, 8.0 Hz, 1 H, 2′-H), 5.63 (dd, J = 10.4, 3.4 Hz, 1 H, 3′-H), 5.43 (s, 1 H, 1-H), 5.19 (d, J = 8.0 Hz, 1 H, 1′-H), 4.62 (dd, J = 11.5, 7.1 Hz, 1 H, 6′-H), 4.48 (dd, J = 11.5, 5.6 Hz, 1 H, 6′-H), 4.36 (t, J = 6.3 Hz, 1 H, 5′-H), 4.28–4.21 (m, 1 H, 5-H), 4.06 (s, 1 H, 2-H), 3.85–3.80 (m, 1 H, 3-H), 3.73 (t, J = 9.4 Hz, 1 H, 4-H), 2.76 (d, J = 5.0 Hz, 1 H, 3-OH), 2.58 (s, 1 H, 2-OH), 1.33 (d, J = 6.2 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.31, 165.78, 165.58, 134.04, 133.91, 133.80, 133.60, 131.67, 130.24, 130.00, 129.93, 129.51, 129.30, 129.25, 129.18, 128.91, 128.86, 128.73, 128.55, 127.71, 101.74 (C-1′), 87.39 (C-1), 82.41, 72.70, 72.07, 71.82, 71.38, 70.43, 68.44, 67.68, 62.55, 17.82 ppm. HRMS: calcd. for $C_{46}H_{42}O_{13}S$ [M + Na]$^+$ 857.2251; found 857.2244.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-1-thio-β-L-fucopyranoside (16): Colorless solid. R_f = 0.59 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = –2.6 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3496, 3064, 2937, 2873, 1729, 1601, 1584, 1451, 1262, 1262, 1177, 1092, 1069, 1026, 708 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, J = 7.9 Hz, 2 H), 7.97 (d, J = 7.9 Hz, 2 H), 7.94 (d, J = 7.9 Hz, 2 H), 7.81 (d, J = 7.9 Hz, 2 H), 7.59 (t, J = 7.3 Hz, 1 H), 7.53 (t, J = 7.3 Hz, 1 H), 7.43 (m, 6 H), 7.28 (m, 4 H), 7.13–7.01 (m, 5 H), 5.97 (t, J = 9.7 Hz, 1 H, 3′-H), 5.64 (t, J = 9.8 Hz, 1 H, 4′-H), 5.59 (dd, J = 12.3, 9.5 Hz, 1 H, 2′-H), 4.94 (d, J = 7.9 Hz, 1 H, 1′-H), 4.78–4.70 (m, 1 H, 6′-H), 4.51 (d, J = 8.8 Hz, 1 H, 1-H), 4.44 (dd, J = 12.3, 6.6 Hz, 1 H, 6′-H), 4.23–4.17 (m, 1 H, 5′-H), 4.14 (s, 1 H, 3-OH), 3.78 (s, 1 H, 4-H), 3.71–3.66 (m, 2 H, 2-H, 3-H), 3.57–3.51 (m, 1 H, 5-H), 2.35 (s, 1 H, 4-OH), 1.32 (d, J = 6.4 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.25, 165.90, 165.40, 165.38, 133.90, 133.73, 133.56, 133.41, 133.30, 131.63, 130.27, 130.12, 130.09, 129.96, 129.46, 129.34, 128.79, 128.74, 128.56, 127.35, 102.07 (C-1′), 85.78 (C-1), 80.67 (C-2), 74.21, 73.55, 73.05, 72.77, 71.69, 70.84, 69.45, 62.75, 16.84 ppm. HRMS: calcd. for $C_{46}H_{42}O_{13}S$ [M + Na]$^+$ 857.2238; found 857.2258.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→2)-1-thio-β-L-fucopyranoside (17): Colorless solid. R_f = 0.58 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +75.2 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3480, 3062, 2980, 2877, 1728, 1602, 1451, 1315, 1264, 1163, 1095, 1069, 1026, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11–8.04 (m, 4 H), 8.00 (d, J = 7.2 Hz, 2 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 1 H), 7.58 (t, J = 7.4 Hz, 1 H), 7.54–7.39 (m, 5 H), 7.32–7.22 (m, 4 H), 7.19–7.15 (m, 1 H), 7.13–7.09 (m, 1 H), 7.05 (d, J = 4.3 Hz, 4 H), 5.99 (d, J = 3.3 Hz, 1 H, 4′-H), 5.87 (dd, J = 10.4, 8.0 Hz, 1 H, 2′-H), 5.66 (dd, J = 10.4, 3.4 Hz, 1 H, 3′-H), 4.92 (d, J = 8.0 Hz, 1 H, 1′-H), 4.59–4.53 (m, 3 H, 1-H, 6′-H, 6′-H), 4.42–4.38 (m, 1 H, 5′-H), 4.37 (s, 1 H, 3-OH) 3.79 (s, 1 H, 4-H), 3.78–3.70 (m, 2 H, 2-H, 3-H), 3.57 (m, 1 H, 5-H), 2.36 (s, 1 H, 4-OH), 1.34 (d, J = 6.5 Hz, 3 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.17, 165.70, 165.62, 134.03, 133.79, 133.63, 133.43, 133.36, 131.58, 130.26, 130.05, 129.99, 129.45, 129.36, 129.27, 128.95, 128.81, 128.78, 128.73, 128.56, 128.54, 128.46, 127.36, 125.53, 102.39 (C-1′), 85.75 (C-1), 80.85 (C-2), 74.24, 73.56, 72.43, 71.70, 70.85, 69.59, 68.26, 62.65, 16.84 ppm. HRMS: calcd. for $C_{46}H_{42}O_{13}S$ [M + Na]$^+$ 857.2244; found 857.2283.

Phenyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranosyl-(1→3)-1-thio-β-D-glucopyranoside (21): Glycoboronate **1a** was formed in DME as described above and an aliquot (1 mL) of this solution (i.e., 50 mg, 0.14 mmol of glycoboronate **1a**) was added to a mixture of donor **18** (1.1 equiv.), *N*-iodosuccinimide (1.2 equiv.), and MS (3 Å; 175 mg) under argon. The suspension was stirred overnight and then cooled to –30 °C. AgOTf (3–4 mg) was added, and the reaction mixture was stirred for 15 min at –30 °C (TLC: toluene/acetone, 3:1). CH_2Cl_2, MeOH, and IRA 743 were then added, and the mixture was stirred overnight. The suspension was filtered through Celite, and the pad was flushed with CH_2Cl_2/MeOH (1:1 mixture). The filtrate was concentrated, and the residue was purified by flash chromatography (toluene/acetone, 7:1) to give **21** as a colorless solid. R_f = 0.54 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +3.0 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3461, 3063, 3031, 2915, 2876, 1709, 1453, 1349, 1271, 1180, 1102, 1069, 741, 699 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06–7.99 (m, 2 H), 7.61 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 7.7 Hz, 2 H), 7.42–7.15 (m, 20 H), 5.65 (dd, J = 10.0, 8.0 Hz, 1 H), 4.98 (d, J = 11.7 Hz, 1 H), 4.69–4.58 (m, 3 H), 4.56–4.40 (m, 4 H), 4.30 (s, 1 H), 3.91 (d, J = 2.2 Hz, 1 H), 3.87 (d, J = 11.0 Hz, 1 H), 3.74–3.65 (m, 4 H), 3.49 (t, J = 9.0 Hz, 1 H), 3.45–3.39 (m, 2 H), 3.38–3.29 (m, 2 H), 2.35 (d, J = 2.3 Hz, 1 H), 2.19 (s, 1 H, 6-OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.97, 138.11, 137.53, 137.51, 133.47, 132.68, 132.01, 130.04, 130.01, 129.20, 128.70, 128.68, 128.64, 128.59, 128.35, 128.24, 128.13, 128.00, 102.87, 89.97, 87.46, 79.91, 79.57, 74.72, 74.31, 73.96, 72.47, 72.42, 72.38, 70.90, 69.87, 69.22, 63.40 ppm. HRMS: calcd. for $C_{46}H_{48}O_{11}S$ [M + Na]$^+$ 831.2809; found 831.2810.

Phenyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranosyl-(1→3)-1-thio-β-D-galactopyranoside (22): Prepared from donor **18** and acceptor **4** as described above for **21**. Colorless solid. R_f = 0.51 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +17.9 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3486, 3062, 3032, 2874, 1711, 1453, 1366, 1271, 1112, 1070, 1027, 739, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–7.91 (m, 2 H), 7.63–7.53 (m, 1 H), 7.48–7.40 (m, 4 H), 7.39–7.16 (m, 18 H), 5.60 (dd, J = 10.1, 7.9 Hz, 1 H), 4.96 (d, J = 11.6 Hz, 1 H), 4.73 (d, J = 7.9 Hz, 1 H, 1′-H), 4.63 (t, J = 12.3 Hz, 1 H), 4.52 (d, J = 12.3 Hz, 1 H), 4.48–4.41 (m, 3 H), 4.02 (s, 1 H), 3.97 (d, J = 2.7 Hz, 1 H), 3.94–3.86 (m, 1 H), 3.74–3.45 (m, 8 H), 2.81 (s, 1 H), 2.41 (d, J = 2.4 Hz, 1 H), 2.20 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.08, 138.23, 137.80, 137.64, 133.47, 132.61, 132.45, 130.01, 129.97, 129.09, 128.76, 128.68, 128.63, 128.58, 128.23, 128.15, 128.10, 128.07, 127.96, 102.15 (C-1′), 87.93, 83.91, 79.67, 78.27, 74.87, 74.27, 73.87, 72.57, 72.33, 72.26, 69.06, 68.81, 68.38, 62.91 ppm. HRMS: calcd. for $C_{46}H_{48}O_{11}S$ [M + Na]$^+$ 831.2810; found 831.2852.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (23): Glycoboronate **4a** was formed in DME as described above, and an aliquot (1 mL) of this solution (i.e., 50 mg, 0.14 mmol of glycoboronate **4a**) was added to a mixture of bromide **8** (120 mg, 0.18 mmol) and MS (3 Å; 175 mg) under argon. The suspension was stirred overnight and then cooled to 0 °C. AgOTf (47 mg, 0.18 mmol) was added, and the mixture was stirred for 1 h at 0 °C until TLC showed complete product formation (toluene/acetone, 3:1). Then, a decanted

aliquot (1 mL) of a methyl β-D-galactopyranoside phenylboronate solution in DME (i.e., 40 mg, 0.14 mmol of glycoboronate), *N*-iodosuccinimide (38 mg, 0.17 mmol), and TESOTf (6.3 μL, 0.03 mmol) were added, and the mixture was stirred for 1.5 h (TLC, H_2O/*i*PrOH/EtOAc, 1:3:15). The reaction mixture was allowed to warm to room temperature, CH_2Cl_2, MeOH, and IRA 743 were added, and the mixture was stirred overnight. The suspension was filtered through Celite, and the pad was flushed with CH_2Cl_2/MeOH (1:1 mixture). The filtrate was concentrated, and the residue was purified by flash chromatography (H_2O/*i*PrOH/EtOAc, 1:3:15) to give **23** (86 mg, 66%) as a colorless solid. R_f = 0.52 (H_2O/*i*PrOH/EtOAc, 1:3:15). $[\alpha]_D^{20}$ = +86.3 (*c* = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3411, 3063, 2937, 2900, 1727, 1602, 1452, 1268, 1109, 1093, 1070, 1028, 711 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 8.10 (d, *J* = 7.2 Hz, 2 H), 8.04–7.93 (m, 4 H), 7.76 (d, *J* = 7.2 Hz, 2 H), 7.70–7.35 (m, 10 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 5.99 (d, *J* = 2.8 Hz, 1 H), 5.85–5.73 (m, 2 H), 5.36 (d, *J* = 7.4 Hz, 1 H), 4.72–4.52 (m, 2 H), 4.51–4.40 (m, 2 H), 4.17 (d, *J* = 7.0 Hz, 1 H), 4.09–4.01 (m, 2 H), 3.76–3.39 (m, 10 H), 3.50 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 166.29, 166.25, 166.02, 165.47, 133.75, 133.40, 129.72, 129.66, 129.59, 129.53, 129.36, 129.01, 128.66, 128.53, 128.35, 128.28, 105.20, 104.16, 102.56, 83.70, 75.25, 75.00, 72.15, 71.31, 70.85, 70.45, 70.22, 69.94, 68.99, 68.93, 68.49, 62.33, 61.37, 61.28, 56.00 ppm. HRMS: Calcd. for $C_{47}H_{50}O_{20}$ [M + Na]$^+$ *m*/*z*, 957.2787; found 957.2790.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-galactopyranoside (23a): For complete characterization, trisaccharide **23** was acetylated with acetic anhydride in pyridine to give **23a** as a colorless solid. R_f = 0.45 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +59.6 (*c* = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3064, 2983, 2968, 2873, 1733, 1452, 1371, 1248, 1225, 1070, 712 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.1 Hz, 2 H), 8.04 (d, *J* = 7.1 Hz, 2 H), 7.91 (d, *J* = 7.2 Hz, 2 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 3 H), 7.47–7.40 (m, 3 H), 7.37 (t, *J* = 7.8 Hz, 2 H), 7.24 (t, *J* = 7.8 Hz, 2 H), 5.94 (d, *J* = 3.0 Hz, 1 H), 5.68 (dd, *J* = 10.4, 7.7 Hz, 1 H), 5.61 (d, *J* = 3.3 Hz, 1 H), 5.55 (dd, *J* = 10.5, 3.3 Hz, 1 H), 5.34 (d, *J* = 3.0 Hz, 1 H), 5.09 (dd, *J* = 9.9, 8.0 Hz, 1 H), 5.04 (dd, *J* = 10.1, 8.1 Hz, 1 H), 4.90 (d, *J* = 7.7 Hz, 1 H), 4.74 (dd, *J* = 11.2, 6.1 Hz, 1 H), 4.42 (d, *J* = 8.0 Hz, 1 H), 4.36 (dd, *J* = 11.2, 7.1 Hz, 1 H), 4.32–4.25 (m, 2 H), 4.21–4.03 (m, 4 H), 3.84–3.75 (m, 3 H), 3.73 (t, *J* = 6.1 Hz, 1 H), 3.47 (s, 3 H), 2.25 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.01 (s, 3 H), 1.48 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.86, 170.82, 170.16, 169.13, 168.66, 166.25, 165.82, 165.64, 164.88, 133.89, 133.60, 133.48, 130.32, 130.00, 129.58, 129.43, 129.19, 128.88, 128.80, 128.75, 128.52, 101.96, 101.86, 101.26, 75.75, 71.59, 71.47, 71.31, 70.99, 70.03, 69.94, 69.13, 69.11, 69.09, 67.80, 62.38, 62.19, 61.80, 56.84, 21.14, 21.12, 21.04, 21.01, 20.86, 20.06 ppm. HRMS: calcd. for $C_{59}H_{62}O_{26}$ [M + Na]$^+$ 1209.3422; found 1209.3452.

Methyl β-D-Galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (23b): Deprotection of **23a** with sodium methoxide in methanol gave **23b** as a white solid. R_f = 0.24 (H_2O/*i*PrOH/EtOAc, 1:2:2). ^1H NMR (300 MHz, D_2O): δ = 4.50 (d, *J* = 7.5 Hz, 1 H, 1-H), 4.45 (d, *J* = 7.4 Hz, 1 H, 1-H), 4.21 (d, *J* = 7.9 Hz, 1 H, 1-H), 4.04 (d, *J* = 3.0 Hz, 2 H, 4-H, 4-H), 3.76 (d, *J* = 3.1 Hz, 1 H, 4-H), 3.71–3.44 (m, 15 H), 3.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, D_2O): δ = 104.40, 104.13, 103.57, 82.50, 82.13, 75.18, 74.80, 74.78, 72.63, 71.15, 70.34, 69.94, 68.64, 68.44, 61.04, 57.23 ppm. ^{13}C NMR spectroscopic data are consistent with literature values.[27]

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (24): Prepared from bromide **2**, thioglycoside **1**, and methyl β-D-glucopyranoside [with phenylboronate in DME (1.3 mL)], as described above for **23**, to give **24** as a colorless solid. R_f = 0.69 (H_2O/*i*PrOH/EtOAc, 1:3:15). $[\alpha]_D^{20}$ = +21.7 (*c* = 1, MeOH). IR (neat): $\tilde{\nu}$ = 3437, 3069, 2915, 2888, 1729, 1602, 1584, 1452, 1266, 1092, 1070, 1044, 1027, 710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.2 Hz, 2 H), 7.95 (d, *J* = 7.3 Hz, 2 H), 7.93 (d, *J* = 7.3 Hz, 2 H), 7.82 (d, *J* = 7.4 Hz, 2 H), 7.66–7.09 (m, 12 H), 5.92 (t, *J* = 9.4 Hz, 1 H), 5.63 (t, *J* = 9.4 Hz, 1 H), 5.54 (dd, *J* = 9.7, 8.2 Hz, 1 H), 5.04 (d, *J* = 8.1 Hz, 1 H), 4.77 (dd, *J* = 12.4, 2.2 Hz, 1 H), 4.44–4.30 (m, 2 H), 4.26–4.17 (m, 2 H), 3.97–3.84 (m, 2 H), 3.83–3.62 (m, 3 H), 3.54 (s, 3 H), 3.57–3.27 (m, 7 H) ppm. ^{13}C NMR (50 MHz, CD_3OD): δ = 167.61, 167.05, 166.96, 166.77, 134.76, 134.44, 130.80, 130.59, 130.19, 129.52, 105.27, 104.91, 102.55, 87.99, 86.50, 77.61, 77.56, 75.12, 74.76, 74.28, 73.63, 73.26, 71.13, 70.06, 69.81, 64.22, 62.58, 57.29 ppm. HRMS: calcd. for $C_{47}H_{50}O_{20}$ [M + Na]$^+$ 957.2787; found 957.2791.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (24a): Trisaccharide **24** was acetylated with acetic anhydride in pyridine to give **24a** as a colorless solid. R_f = 0.34 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = –34.4 (*c* = 0.5, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3069, 2965, 2874, 1738, 1452, 1372, 1264, 1223, 1093, 1069, 1044, 712 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.2 Hz, 2 H), 7.89–7.83 (m, 4 H), 7.78 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.52–7.46 (m, 2 H), 7.44–7.38 (m, 3 H), 7.38–7.30 (m, 4 H), 7.28–7.21 (m, 2 H), 5.89 (t, *J* = 9.7 Hz, 1 H, 3′′-H), 5.67 (t, *J* = 9.7 Hz, 1 H, 4′′-H), 5.40 (dd, *J* = 9.7, 7.9 Hz, 1 H, 2′′-H), 5.00 (t, *J* = 9.5 Hz, 1 H, 4-H), 4.86 (d, *J* = 7.9 Hz, 1 H, 1′′-H), 4.84–4.77 (m, 3 H, 2′-H, 2-H, 4′-H), 4.59 (dd, *J* = 12.1, 3.4 Hz, 1 H, 6′′-H), 4.53 (dd, *J* = 12.2, 4.7 Hz, 1 H, 6′′-H), 4.42 (d, *J* = 8.1 Hz, 1 H, 1′-H), 4.33–4.23 (m, 2 H, 1-H, 6-H), 4.17–4.09 (m, 3 H, 5′′-H, 6′-H, 6′-H), 4.01 (dd, *J* = 12.3, 2.3 Hz, 1 H, 6-H), 3.89 (t, *J* = 9.3 Hz, 1 H, 3-H), 3.83 (t, *J* = 9.3 Hz, 1 H, 3′-H), 3.67–3.61 (m, 1 H, 5′-H), 3.56–3.50 (m, 1 H, 5-H), 3.44 (s, 3 H, OCH_3), 2.12 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.53, 171.35, 169.82, 169.78, 169.53, 169.16, 166.82, 166.59, 165.87, 165.76, 134.21, 134.08, 133.88, 130.49, 130.39, 130.03, 129.36, 129.26, 129.18, 129.13, 129.02, 128.85, 102.13, 102.09, 101.40, 79.57, 78.75, 77.93, 73.50, 73.13, 72.70, 72.56, 72.44, 70.27, 69.05, 68.85, 63.79, 62.77, 62.66, 57.33, 21.77, 21.50, 21.44, 21.31, 21.23, 21.17 ppm. HRMS: calcd. for $C_{59}H_{62}O_{26}$ [M + Na]$^+$ 1209.3422; found 1209.3439.

Methyl β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (24b): Deprotection of **24a** with sodium methoxide in methanol gave **24b** as a white solid. R_f = 0.50 (H_2O/*i*PrOH/EtOAc, 1:2:2). ^1H NMR (500 MHz, D_2O): δ = 4.59–4.55 (m, 2 H), 4.23 (d, *J* = 8.1 Hz, 1 H), 3.78–3.70 (m, 3 H), 3.64–3.50 (m, 5 H), 3.40 (s, 3 H), 3.38–3.28 (m, 7 H), 3.27–3.22 (m, 1 H), 3.21–3.15 (m, 2 H) ppm. ^{13}C NMR (50 MHz, D_2O): δ = 103.80, 103.64, 103.36, 85.29, 85.06, 76.83, 76.39, 74.28, 74.06, 73.66, 70.41, 68.98, 61.52, 58.06 ppm. ^{13}C NMR spectroscopic data are consistent with literature values.[28]

Benzyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (25): Prepared from bromide **2**, thioglycoside **1**, and benzyl β-D-glucopyranoside, as described above for **23**, to give **25** as a colorless solid. R_f = 0.81 (H_2O/*i*PrOH/EtOAc, 1:3:15). $[\alpha]_D^{20}$ = +3.6 (*c* = 0.3, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3467, 3064, 3033, 2907, 2884, 1730, 1601, 1451, 1264, 1093, 1070, 1049, 1027, 709, 687 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07

(d, J = 7.7 Hz, 2 H), 7.94 (d, J = 7.6 Hz, 2 H), 7.92 (d, J = 7.6 Hz, 2 H), 7.82 (d, J = 7.7 Hz, 2 H), 7.61–7.22 (m, 17 H), 5.93 (t, J = 9.7 Hz, 1 H), 5.63 (t, J = 9.7 Hz, 1 H), 5.54 (dd, J = 9.8, 8.0 Hz, 1 H), 5.03 (d, J = 7.9 Hz, 1 H, 1-H), 4.87 (d, J = 11.9 Hz, 1 H, C*H*H), 4.74 (dd, J = 12.4, 2.5 Hz, 1 H), 4.64 (d, J = 11.9 Hz, 1 H, C*H*H), 4.42–4.32 (m, 2 H), 4.25–4.15 (m, 1 H), 3.92–3.82 (m, 2 H), 3.78–3.63 (m, 3 H), 3.55–3.25 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.09, 165.63, 165.36, 165.14, 136.85, 133.57, 133.31, 129.82, 129.19, 129.01, 128.35, 128.02, 104.27, 102.40, 101.50, 87.86, 75.87, 75.28, 72.65, 72.48, 71.88, 71.38, 69.25, 69.10, 62.73, 62.43 ppm. HRMS: calcd. for $C_{53}H_{54}O_{20}$ [M + Na]$^+$ 1033.3101; found 1033.3103.

Benzyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (25a): Trisaccharide **25** was acetylated with acetic anhydride in pyridine to give **25a** as a colorless solid. R_f = 0.21 (heptane/EtOAc, 1:1). $[\alpha]_D^{20}$ = –38.8 (c = 0.3, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3066, 3032, 2966, 2879, 1739, 1602, 1584, 1452, 1371, 1264, 1224, 1093, 1069, 1045, 712 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.5 Hz, 2 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.78 (d, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.4 Hz, 1 H), 7.51–7.45 (m, 2 H), 7.43–7.30 (m, 9 H), 7.29–7.23 (m, 5 H), 5.88 (t, J = 9.7 Hz, 1 H, 3′′-H), 5.66 (t, J = 9.7 Hz, 1 H, 4′′-H), 5.39 (dd, J = 9.5, 8.1 Hz, 1 H, 2′′-H), 4.99 (t, J = 9.4 Hz, 1 H, 4′-H), 4.96–4.91 (m, 1 H, 2-H), 4.87–4.77 (m, 4 H, 1′′-H, 2′-H, 4-H, C*H*H), 4.61–4.49 (m, 3 H, 6′′-H, 6′′-H, C*H*H), 4.39 (d, J = 8.1 Hz, 1 H, 1′-H), 4.36 (d, J = 8.0 Hz, 1 H, 1-H), 4.26 (dd, J = 12.4, 4.4 Hz, 1 H, 6′-H), 4.17–4.11 (m, 3 H, 5′′-H, 6-H, 6-H), 3.99 (dd, J = 12.3, 2.1 Hz, 1 H, 6′-H), 3.88 (t, J = 9.3 Hz, 1 H, 3′-H), 3.81 (t, J = 9.3 Hz, 1 H, 3-H), 3.61 (dt, J = 9.4, 3.0 Hz, 1 H, 5-H), 3.52–3.47 (m, 1 H, 5′-H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.03, 170.85, 169.32, 169.29, 169.01, 168.68, 166.34, 166.10, 165.38, 165.28, 137.03, 133.73, 133.59, 133.56, 133.40, 130.07, 130.01, 129.98, 129.92, 129.90, 129.55, 128.88, 128.78, 128.69, 128.67, 128.64, 128.54, 128.38, 128.17, 127.98, 101.60, 100.86, 99.20, 79.07, 78.20, 77.45, 73.14, 73.03, 72.70, 72.21, 72.07, 71.98, 71.96, 70.42, 69.79, 68.60, 68.35, 63.29, 62.30, 62.19, 21.21, 21.04, 20.95, 20.82, 20.74, 20.67 ppm. HRMS: calcd. for $C_{65}H_{66}O_{26}$ [M + Na]$^+$ 1285.3735; found 1285.3743.

Benzyl β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (25b): Deprotection of **25a** with sodium methoxide in methanol gave **25b** as a white solid. R_f = 0.77 (H_2O/*i*PrOH/EtOAc, 1:2:2). $[\alpha]_D^{20}$ = –27.5 (c = 1, MeOH). IR (neat): $\tilde{\nu}$ = 3379, 2918, 2887, 1452, 1367, 1155, 1075, 1037 cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ = 7.53–7.39 (m, 5 H), 4.96 (d, J = 11.6 Hz, 1 H), 4.77–4.73 (m, 3 H), 4.57 (d, J = 8.0 Hz, 1 H), 3.98–3.87 (m, 3 H), 3.81–3.68 (m, 5 H), 3.60–3.47 (m, 8 H), 3.43–3.33 (m, 2 H) ppm. ^{13}C NMR (50 MHz, D_2O): δ = 139.18, 131.40, 131.16, 105.46, 105.18, 103.63, 87.00, 86.86, 78.66, 78.24, 76.11, 75.89, 75.58, 74.20, 72.24, 70.81, 63.36 ppm. HRMS: calcd. for $C_{25}H_{38}O_{16}$ [M + Na]$^+$ 617.2052; found 617.2053.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-1-thio-β-D-glucopyranoside (26): Bromide **2** (97 mg, 0.15 mmol) was added to a mixture of disaccharide **3** (104 mg, 0.12 mmol) and MS (3 Å; 175 mg) in toluene (1 mL), and the solution was stirred for 1 h under argon. The mixture was then cooled to 0 °C, AgOTf (44 mg, 0.17 mmol) was added, and the resulting mixture was stirred for 1 h. Then CH_2Cl_2 (1 mL), MeOH (1 mL), and Et_3N (1 mL) were added, and the mixture was stirred for a further 30 min. The mixture was filtered through Celite and concentrated, and the residue was purified by flash chromatography (toluene/acetone, 7:1) to give **26** (122 mg, 70%) as a colorless solid. R_f = 0.63 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +13.9 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3498, 3064, 2961, 2887, 1727, 1602, 1451, 1315, 1263, 1177, 1092, 1069, 1027, 708 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.3 Hz, 2 H), 8.02 (d, J = 7.3 Hz, 2 H), 7.98 (d, J = 7.3 Hz, 2 H), 7.95–7.82 (m, 10 H), 7.60–7.49 (m, 5 H), 7.48–7.25 (m, 24 H), 5.92 (t, J = 9.7 Hz, 1 H, 3′-H), 5.86 (t, J = 9.6 Hz, 1 H, 3′′-H), 5.66 (t, J = 9.7 Hz, 1 H, 4′′-H), 5.60 (t, J = 9.7 Hz, 1 H, 4′-H), 5.54 (dd, J = 9.6, 8.0 Hz, 1 H, 2′′-H), 5.50 (dd, J = 9.7, 8.1 Hz, 1 H, 2′-H), 4.96 (d, J = 8.0 Hz, 1 H, 1′-H), 4.92 (d, J = 7.9 Hz, 1 H, 1′′-H), 4.75 (dd, J = 12.2, 2.4 Hz, 1 H, 6′-H), 4.63 (dd, J = 12.1, 3.0 Hz, 1 H, 6′′-H), 4.44 (dd, J = 12.1, 5.2 Hz, 1 H, 6′′-H), 4.39–4.30 (m, 2 H, 1-H, 6′-H), 4.23–4.13 (m, 2 H, 5′-H, 6-H), 4.09–3.99 (m, 1 H, 5′′-H), 3.81 (dd, J = 12.0, 6.3 Hz, 1 H, 6-H), 3.46–3.35 (m, 2 H, 3-H, 5-H), 3.34–3.25 (m, 1 H, 4-H), 3.05 (t, J = 9.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.33, 166.30, 166.01, 165.90, 165.46, 165.28, 133.89, 133.66, 133.60, 133.42, 133.34, 132.82, 131.84, 130.22, 130.12, 130.03, 130.01, 129.80, 129.48, 129.43, 129.32, 129.10, 129.05, 128.86, 128.72, 128.65, 128.60, 128.53, 128.47, 102.63 (C-1′), 101.80 (C-1′′), 89.63, 88.15 (C-1), 79.88, 73.15, 72.91, 72.75, 72.35, 72.13, 72.05, 70.80, 70.03, 69.59, 69.16, 68.33, 63.29, 63.06 ppm. HRMS: calcd. for $C_{80}H_{68}O_{23}S$ [M + Na]$^+$ 1451.3764; found 1451.3836.

Phenyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-1-thio-β-D-glucopyranoside (27): Diol **26** (20 mg, 0.014 mmol) was dissolved in pyridine (1 mL), and acetic anhydride (1 mL) was added. The mixture was stirred until complete conversion was observed by TLC (toluene/acetone, 3:1), then it was concentrated, and the residue was purified by flash chromatography (toluene/acetone, 8:1) to give **27** (20 mg, 94%) as a colorless solid. R_f = 0.73 (toluene/acetone, 3:1). $[\alpha]_D^{20}$ = +8.29 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3063, 2959, 2880, 1729, 1602, 1452, 1263, 1216, 1092, 1068, 1027, 709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08–8.00 (m, 4 H), 7.95–7.78 (m, 12 H), 7.58–7.47 (m, 5 H), 7.46–7.25 (m, 24 H), 5.90 (t, J = 9.6 Hz, 1 H), 5.80 (t, J = 9.5 Hz, 1 H), 5.69–5.63 (m, 2 H), 5.64–5.57 (m, 1 H), 5.53–5.46 (m, 1 H), 5.43–5.34 (m, 1 H), 4.93 (d, J = 7.9 Hz, 1 H), 4.87 (d, J = 8.0 Hz, 1 H), 4.82 (t, J = 9.6 Hz, 1 H), 4.70 (t, J = 9.6 Hz, 1 H), 4.66–4.56 (m, 2 H), 4.53–4.42 (m, 3 H), 4.16–4.09 (m, 1 H), 4.05–3.98 (m, 1 H), 3.90 (t, J = 9.2 Hz, 1 H), 3.85–3.71 (m, 2 H), 3.54 (dd, J = 12.3, 4.7 Hz, 1 H), 1.98 (s, 3 H), 1.92 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.76, 168.73, 166.30, 166.25, 166.12, 165.97, 165.45, 165.39, 165.34, 165.3, 133.72, 133.58, 133.48, 133.42, 133.39, 133.34, 131.75, 130.01, 129.96, 129.88, 129.73, 129.63, 129.55, 129.39, 129.06, 128.98, 128.85, 128.80, 128.73, 128.67, 128.55, 128.52, 128.49, 128.40, 128.21, 101.39, 100.67, 86.32 (C-1), 79.99, 78.46, 73.22, 73.13, 72.48, 72.36, 72.28, 72.09, 71.64, 69.95, 69.74, 68.69, 68.17, 63.19, 21.21, 20.79 ppm. HRMS: calcd. for $C_{84}H_{72}O_{25}S$ [M + Na]$^+$ 1535.3976; found 1535.8269.

Benzyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (29): Trisaccharide **26** (62 mg, 0.044 mmol) was added to a mixture of lactoside **28** (55 mg, 0.057 mmol) and MS (3 Å; 175 mg) in CH_2Cl_2 (1 mL), and the solution was stirred for 1 h under argon. The mixture was cooled to –30 °C, and *N*-iodosuccinimide (13 mg, 0.057 mmol) and TESOTf (2.0 μL, 0.009 mmol) were added. After 1 h, the reaction mixture was diluted with CH_2Cl_2 (1 mL) and Et_3N (1 mL). The mixture was filtered through Celite and concentrated, and the residue was purified by flash chromatography (heptane/EtOAc, 2:1) to give **29**

(36 mg, 36%) as a colorless solid. R_f = 0.55 (EtOAc/heptane, 1:1). $[\alpha]_D^{20}$ = +15.6 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3508, 3063, 3031, 2938, 2914, 2870, 1732, 1602, 1452, 1265, 1093, 1069, 1027, 710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.15–8.05 (m, 1 H), 8.02–7.77 (m, 14 H), 7.60–7.05 (m, 59 H), 5.97–5.80 (m, 2 H), 5.68–5.57 (m, 2 H), 5.56–5.40 (m, 2 H), 5.01 (dd, J = 10.7, 5.4 Hz, 1 H), 4.97–4.86 (m, 3 H), 4.83–4.61 (m, 7 H), 4.60–4.10 (m, 13 H), 4.05–3.82 (m, 4 H), 3.79–3.18 (m, 15 H), 3.08–2.97 (m, 1 H), 2.93–2.83 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.99, 165.66, 165.10, 165.07, 164.91, 164.74, 139.20, 139.03, 138.90, 138.57, 138.27, 138.13, 137.92, 137.49, 133.55, 133.26, 133.13, 104.24, 102.39, 102.08, 94.87, 88.01, 87.49, 82.88, 82.23, 81.66, 79.06, 78.14, 75.25, 74.96, 74.37, 73.29, 73.04, 72.65, 72.40, 71.97, 71.82, 70.82, 70.15, 70.13, 69.72, 69.46, 69.36, 68.84, 68.18, 67.73, 67.20, 63.08 ppm. HRMS: calcd. for $C_{135}H_{126}O_{34}$ $[M + Na]^+$ 2313.8023; found 2313.8582.

Benzyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (30): Trisaccharide **27** (51 mg, 0.034 mmol) was treated with lactoside **28** (45 mg, 0.046 mmol) as described above for **29** to give **30** (57 mg, 71%) as a colorless solid. R_f = 0.67 (EtOAc/heptane, 1:1). $[\alpha]_D^{20}$ = –14.1 (c = 1, $CDCl_3$). IR (neat): $\tilde{\nu}$ = 3063, 3032, 2941, 2871, 1733, 1602, 1495, 1452, 1367, 1268, 1214, 1092, 1068, 1027, 710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07–7.98 (m, 4 H), 7.93–7.73 (m, 12 H), 7.57–7.04 (m, 59 H), 5.95–5.79 (m, 2 H), 5.71–5.56 (m, 2 H), 5.52–5.37 (m, 2 H), 5.01–4.80 (m, 7 H), 4.78–4.59 (m, 6 H), 4.54–4.44 (m, 4 H), 4.43–4.20 (m, 7 H), 4.18–3.99 (m, 2 H), 3.96–3.29 (m, 17 H), 1.93 (s, 3 H), 1.68 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.25, 167.31, 165.77, 165.71, 165.57, 165.39, 164.83, 164.74, 164.64, 138.89, 138.69, 138.29, 137.98, 137.90, 137.20, 133.17, 133.09, 132.98, 132.94, 132.83, 132.69, 129.46, 129.36, 129.19, 129.15, 129.01, 128.68, 128.44, 128.34, 128.25, 128.18, 128.10, 128.03, 127.96, 127.94, 127.88, 127.74, 127.61, 127.54, 127.48, 127.35, 127.26, 127.15, 127.08, 126.77, 102.18, 102.05, 100.82, 100.60, 100.56, 82.64, 81.43, 79.97, 79.94, 78.50, 76.90, 76.51, 76.06, 75.20, 75.00, 74.74, 74.66, 74.60, 73.31, 73.11, 72.83, 72.71, 72.58, 72.53, 72.36, 71.98, 71.71, 71.64, 71.35, 70.57, 69.15, 68.69, 67.90, 62.67, 62.60, 20.29 ppm. HRMS: calcd. for $C_{139}H_{130}O_{36}$ $[M + Na]^+$ 2397.8234; found 2397.6738.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra for all products.

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