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Influence of Silyl Protections on the Anomeric Reactivity of Galactofuranosyl Thioglycosides and Application of the Silylated Thiogalactofuranosides to One-Pot Synthesis of Diverse β-D-Oligogalactofuranosides

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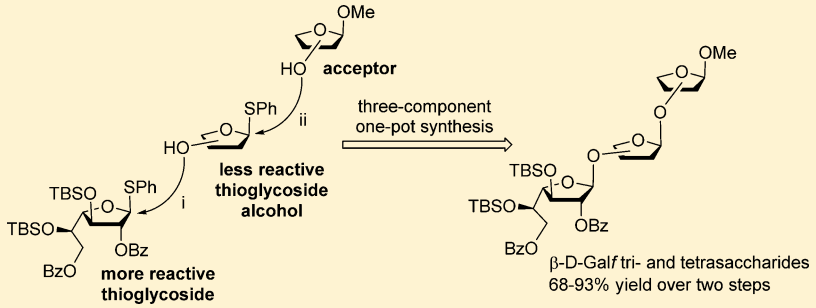
Supporting Information



ABSTRACT: We describe in this paper the tuning effect of silyl protecting groups on the donor reactivity of galactofuranosyl phenyl thioglycosides. Silyl ethers on the galactofuranose ring are found to have an arming effect on the glycosylation reactivity, but the cyclic 3,5-acetal protecting group decreases the reactivity. The reactive phenyl 2,6-di-*O*-Bz-3,5-di-*O*-TBS-1-thio-β-D-galactofuranoside **3** is proved to be a useful glycosyl building block. By taking advantage of this donor, we achieved the highly efficient one-pot solution-phase assembly of a panel of β-D-galactofuranosyl tri- and tetrasaccharides possessing diverse glycosidic linkages.

INTRODUCTION

D-Galactosides are widely distributed in living organisms. The D-galactopyranose (D-Gal*p*) is present only in mammalian carbohydrates while the D-galactofuranose (D-Gal*f*) is restricted to the structural components of polysaccharides found in several pathogenic microorganisms, such as bacteria, parasites, and fungi.[1] Among these polysaccharides, the most impressive examples are arabinogalactan (AG) and lipoarabinomannan (LAM), both of which are major constituents of the cell wall of mycobacterial, including the human pathogens *Mycobacterium tuberculosis* and *Mycobacterium leprae*.[2] AG and LAM are closely connected with the survival and pathogenicity of mycobacteria. Therefore, the enzymes, such as mycobacterial arabino- and galactofuranosyltransferases (Ara*f*Ts and Gal*f*Ts) that participate in the biosynthesis of these mycobacterial cell wall biopolymers are promising drug targets for treatment of mycobacterial diseases.[3] Chemical synthesis of D-Gal*f*-containing oligosaccharides and glycoconjugates from AG has received considerable attention in the past decade, as the synthetic fragments may play significant roles in developing new oligosaccharide-based inhibitors that target the mycobacterial Gal*f*Ts.[4] In this aspect, numerous synthetic methodologies have been developed.[5,6] Among these strategies, one-pot multistep glycosylation, wherein two or more glycosylation steps are sequentially completed in a single reaction flask, is very attractive and shows great promise for rapid construction of oligogalactofuranosides.[7] In 2003, the Ning group[8] first utilized a one-pot glycosylation procedure in furanose synthesis and achieved a concise preparation of a unique 5,6-branched trigalactoside fragment of motif E of the *M. tuberculosis* cell wall. Later, the efficiency of one-pot strategy was further demonstrated by Lowary and co-workers in the production of two linear mycobacterial galactofuranosyl trimers.[9] More recently, upon the preparation of tetrasaccharide portions of mycobacterial AG, a one-pot approach was developed by Gallo-Rodriguez et al. for the rapid assembly of a 5,6-branched trisaccharide lactone intermediate.[10] Furthermore, our group has described the development of a novel regioselective furanosylation methodology based on the use of partially protected furanosyl thioglycosides as central glycosylating agents.[11] This approach has proven to be very useful in one-pot synthesis of a variety of linear and branched arabino- and galactofuranoses of bacterial and plant origins.

In a continuing study on the synthesis of biologically important oligofuranoses, we recently reported the influence of

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silyl protecting groups on the glycosylation reactivity of arabinofuranosyl thioglycosides.[12] We disclosed that thioarabinosides with silyl ether protection exhibit glycosylation reactivity higher than that of armed thioarabinosides with benzyl (Bn) ether protection. On the other hand, thioarabinosides bearing 3,5-*O*-di-*tert*-butylsilylene (DTBS) acetal protection are even less reactive than the fully benzoyl (Bz) group protected disarmed thioarabinosides due to the torsional effect caused by the cyclic DTBS acetal protection. These findings broaden the traditional armed−disarmed concept in carbohydrate chemistry. Then, depending on the use of the obtained superarmed and superdisarmed donors, we realized the first automated one-pot synthesis of two α-arabinofuranosyl trimers. Here we report the tuning effect of silyl protections on the anomeric reactivity of galactofuranosyl thioglycoside donors as well as the application of the silylated thiogalactofuranosides in the one-pot assembly of various linear tri- and tetragalactofuranosides.

RESULTS AND DISCUSSION

Our research started with the design and synthesis of a series of D-galactofuranosyl monosaccharides. As shown in Figure 1, these compounds included fully (**1**) and partially (**2**, **3**) *tert*-butyldimethylsilyl (TBS)-substituted phenylthioglycoside donors as well as a 3,5-*O*-DTBS-blocked donor **4**.[13] In addition, several benzoyl- or benzyl-protected donors **5**−**10** and acceptors **11**−**13** were also designed. Among these sugars, **5**,[14] **6**,[15] and **13**[16] were prepared according to the literature procedures, while the others were synthesized as outlined in Schemes 1 and 2.

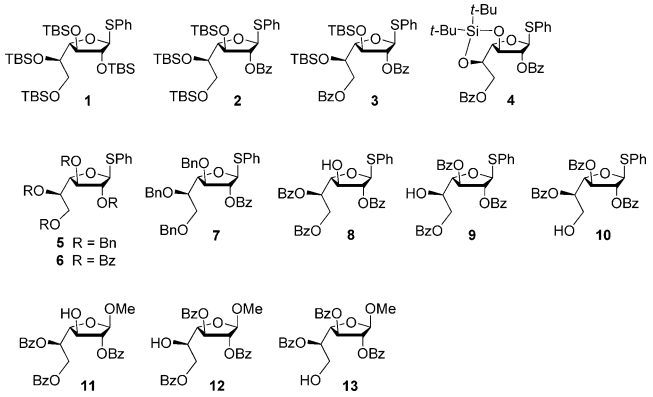
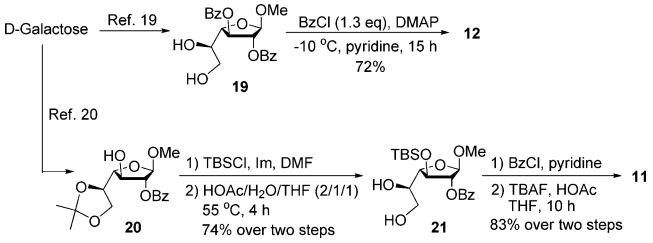


Figure 1. D-Galactofuranosyl donors and acceptors.

Scheme 2. Preparation of Galactofuranosyl Acceptors 11 and 12



The preparation of the required donors was based on the known phenyl 1-thio-β-D-galactofuranoside **14**[17] (Scheme 1). Treatment of **14** with 6 equiv of *tert*-butyldimethylsilyl chloride (TBSCl) in *N*,*N*-dimethylformide (DMF) at 80 °C resulted in persilylated donor **1** in 82% yield. In parallel, sugar **14** underwent 5,6-*O*-acetonide protection and then regioselective monosilylation of the remaining 2,3-OHs with 1.3 equiv of TBSCl to give 2- and 3-*O*-TBS ethers **15** and **16** as a chromatographically separable mixture (**15**/**16**, ca. 2:1).[18] The major product **15** was in turn subjected to a series of steps including removal of the isopropylidene group, benzylation, desilylation, and benzoylation to furnish thioglycoside donor **7** in 47% overall yield. On the other hand, esterification of 2-OH and then liberation of 5,6-OHs of compound **16** were carried out under standard conditions to form the corresponding diol **17**, which is a key precursor to donors **2**−**4** and **8**. Compound **17** was readily silylated upon reaction with 3 equiv of TBSCl to afford the 3,5,6-trisilylated donor **2** in an excellent yield. Meanwhile, **17** underwent regioselective monobenzoylation at

Scheme 1. Preparation of Galactofuranosyl Donors 1−4 and 7−10

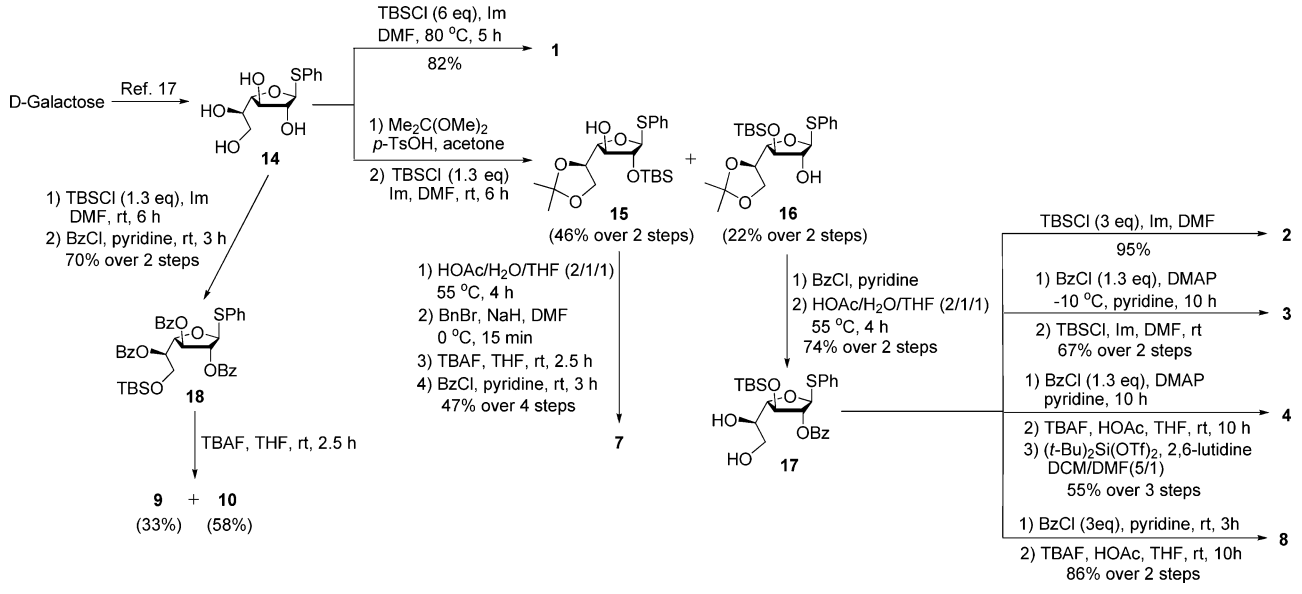


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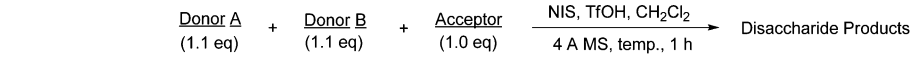
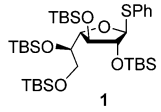
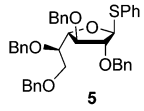
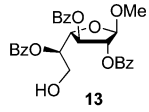
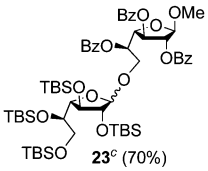
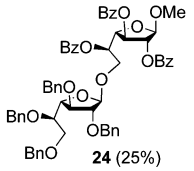
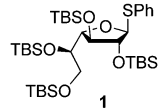
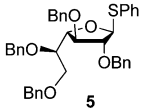
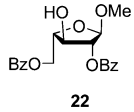
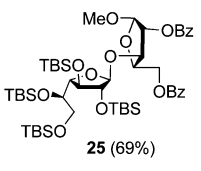
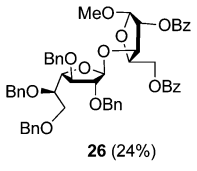
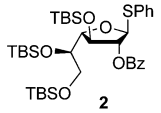
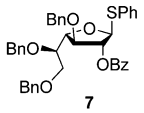
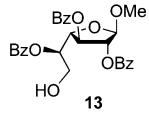
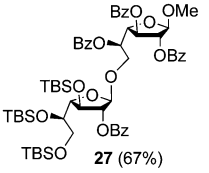
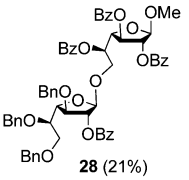
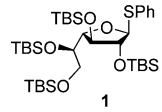
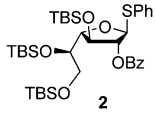
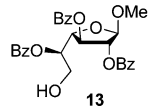
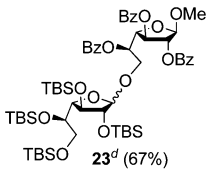
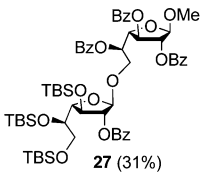
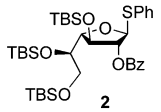
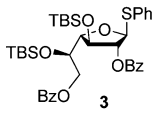
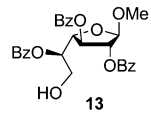
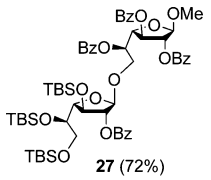
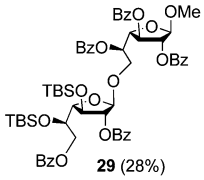
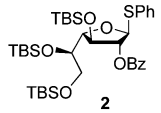
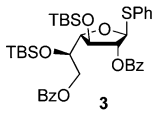
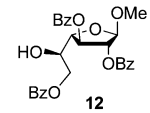
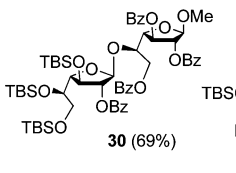
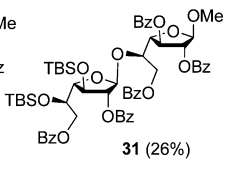
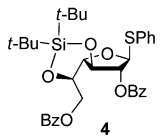
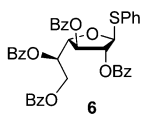
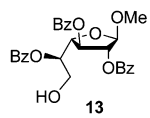
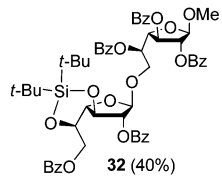
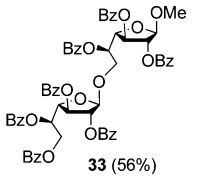
Table 1. Competition Glycosylation Reactions[a]



entry	donor A	donor B	acceptor	temperature	disaccharide product (yield)[b]	
1	 **1**	 **5**	 **13**	-80 to -60 °C	 **23**[c] (70%)	 **24** (25%)
2	 **1**	 **5**	 **22**	-80 to -55 °C	 **25** (69%)	 **26** (24%)
3	 **2**	 **7**	 **13**	-80 to -55 °C	 **27** (67%)	 **28** (21%)
4	 **1**	 **2**	 **13**	-80 to -60 °C	 **23**[d] (67%)	 **27** (31%)
5	 **2**	 **3**	 **13**	-80 to -55 °C	 **27** (72%)	 **29** (28%)
6	 **2**	 **3**	 **12**	-80 to -50 °C	 **30** (69%)	 **31** (26%)
7	 **4**	 **6**	 **13**	-80 to -40 °C	 **32** (40%)	 **33** (56%)

[a]Glycosylations were performed with donors **A**/**B**, acceptor **12**, **13**, or **22**, NIS (1.25 equiv), TfOH (0.1 equiv), and 4 Å molecular sieves (MS) in dry CH_2Cl_2 in 1 h. [b]Isolated yield. [c]α/β = 1/1.8. [d]α/β = 1/1.6. The α/β ratio was measured by ^{1}H NMR analysis of the anomer mixture.

the primary 6-position and then silylation at the 5-position, thereby giving rise to 2,6-di-*O*-Bz-3,5-di-*O*-TBS-protected donor **3** (67% over two steps). Conversion of **17** to the desired **4** was realized via regioselective 6-*O*-benzoylation, 3-*O*-desilylation, and 3,5-*O*-protection with a DTBS acetal moiety in 55% yield over three steps. Additionally, access to 3-OH thioglycoside **8** required acylation of the diol **17** with excess benzoyl chloride (BzCl) and followed by 3-*O*-desilylation with tetrabutylammonium fluoride (TBAF) buffered with acetic acid (HOAc).

For the synthesis of thioglycoside alcohols **9** and **10**, sugar **14** was first converted into tribenzoate **18** in two steps and 70%

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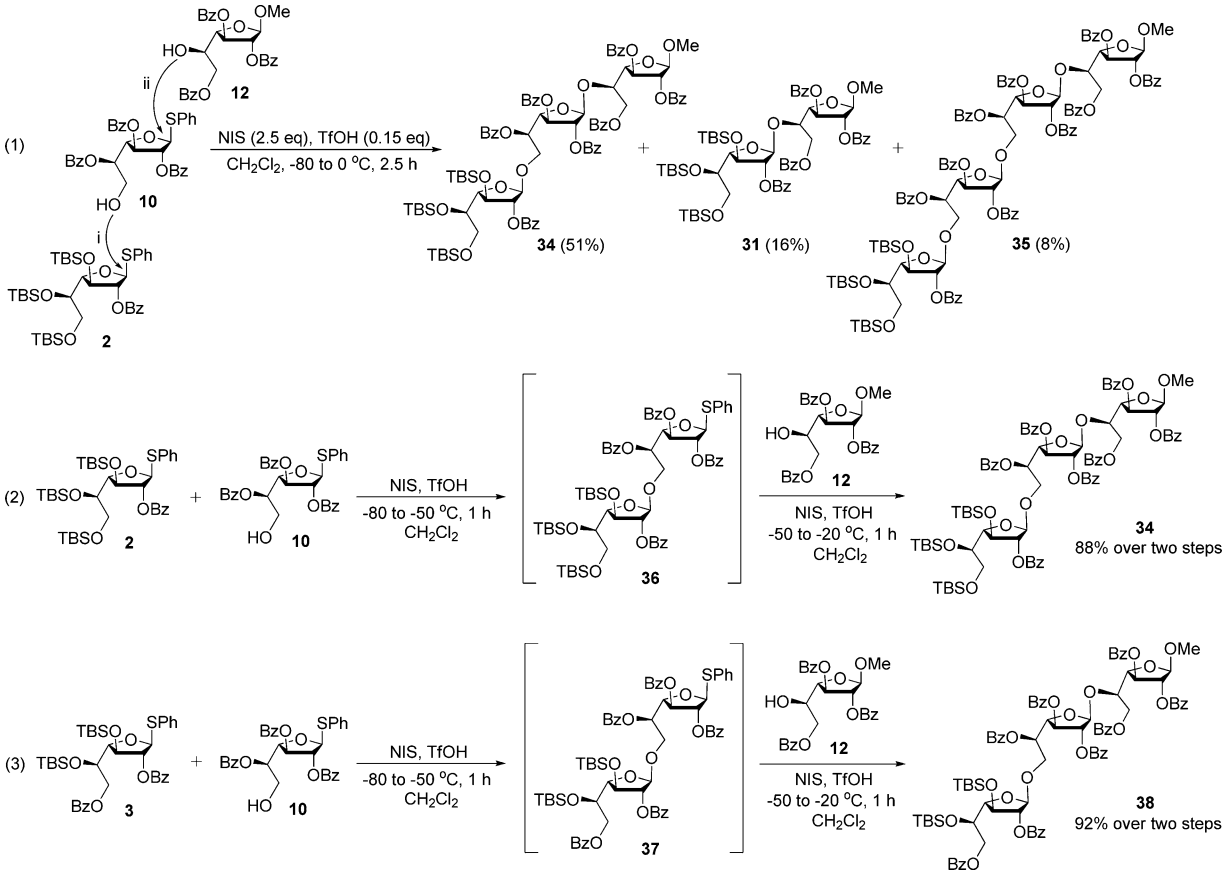
Scheme 3. One-Pot Synthesis of β-D-Galf-(1→6)-β-D-Galf-(1→5)-D-Galf Trisaccharides



yield through regioselective silylation at 6-OH followed by benzoylation of the remaining 2,3,5-tri-OHs. Subsequent desilylation of **18** in the presence of TBAF provided **10** (58% yield) as the major product, together with **9** (33% yield) resulting from migration of the benzoate ester from O-5 to O-6.

The route to glycosyl acceptors **12** and **11** began from the D-Galf monomers **19**[19] and **20**,[20] both of which could be easily synthesized from commercial D-galactose (Scheme 2). 5,6-Diol **19** was treated with 1.3 equiv of BzCl at −10 °C to afford the 5-OH alcohol **12** in 72% yield. In the preparation of **11**, methyl glycoside **20** was first transformed into **21** by protection of the 3-OH with TBS ether and followed by removal of isopropylidene under acidic conditions, which afforded a 74% yield of the product. Then, through the similar two-step procedure as described for the preparation of **8**, the resulting intermediate **21** was readily elaborated into the corresponding 3-OH acceptor **11** in 83% yield over two steps.

With these saccharides in hand, we ran a set of three-component competition glycosylations to estimate the turning effect of silyl protecting groups on glycosylation reactivity. In these experiments, we mixed a silylated thiogalactoside (donor A, 1.1 equiv), a non- or less silylated thiogalactoside (donor B, 1.1 equiv), and an appropriate acceptor (1.0 equiv) into the same reaction flask in dry dichloromethane (CH_2Cl_2). After being stirred for 30 min at room temperature, the reaction mixture was cooled to −80 °C. Then the *N*-iodosuccinimide (NIS, 1.25 equiv)/trifluoromethanesulfonic acid (TfOH, 0.1 equiv) promoter system was added, and the resulting mixture was gradually warmed to activation temperature until the reaction was completed. The two thiogalactoside donors would compete to glycosylate with the acceptor to give disaccharide products. The product ratio will reflect the reactivity difference of the donors. The results of these competition glycosylation reactions are summarized in Table 1.

First, the reactivity of the fully or partially silylated thioglycoside donors and their corresponding benzylated thioglycoside counterparts was compared. Predominant activation of the persilylated donor **1** over the perbenzylated donor **5** with primary glycosyl acceptor **13** took place, affording disaccharide **23** (70%, α/β = 1/1.8) as the major product along with formation of a small amount of disaccharide **24** (25%) (Table 1, entry 1). When the secondary L-arabinosyl alcohol **22**[21] was employed as acceptor, **1** also showed reactivity greater than that of the armed donor **5** (entry 2). Moreover, the 2-*O*-Bz-3,5,6-tri-*O*-TBS-protected galactofuranosyl thioglycoside **2** was also observed to be more reactive toward the glycosylation with **13** than the corresponding 2-*O*-Bz-3,5,6-tri-*O*-Bn-protected **7**, leading to β-disaccharide glycoside products **27** and **28** in 67% and 21% yield, respectively (entry 3). Next, the influence of the amount of silyl group on the reactivity of donors was examined. The persilylated donor **1** is evidently more reactive than the trisilylated donor **2** in the competition reaction with acceptor **13** (Table 1, entry 4), because disaccharide **23** (α/β = 1/1.6) that was derived from the coupling between **1** and **13** was obtained as a major product in 67% yield. Moreover, judging from the product ratios of two sets of competition experiments (Table 1, entries 5 and 6), it is clear that the reactivity of trisilylated donor **2** is higher than that of the disilylated donor **3** in the reaction with acceptor **13** or **12**. Finally, we tested the reactivity of the donor **4** protected as

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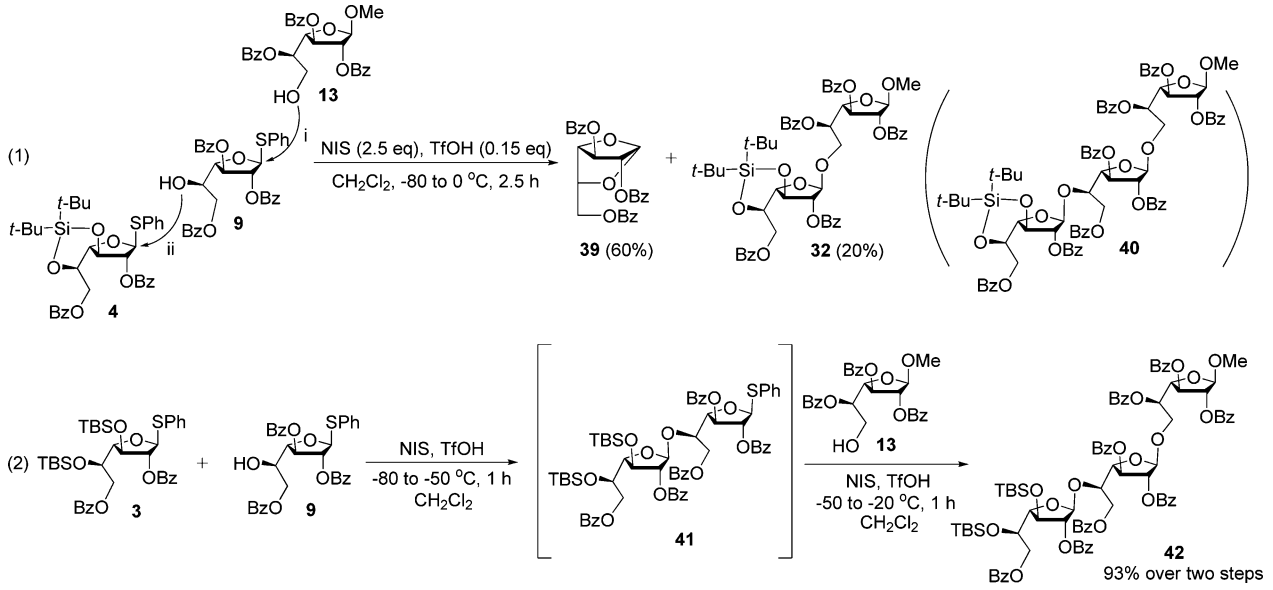
Scheme 4. One-Pot Synthesis of *β*-D-Gal*f*-(1→5)-*β*-D-Gal*f*-(1→6)-D-Gal*f* Trisaccharides



the cyclic DTBS acetal. Here preferential activation of perbenzoylated disarmed donor **6** over 3,5-*O*-DTBS-protected **4** was observed in the three-component reaction of **4**, **6**, and **13**, as disaccharide **33**,[22] the coupling product of **6** with **13**, was formed as the major product (Table 1, entry 7).

Thus, the tuning effect of silyl protecting groups on the glycosylation reactivity of galactofuranosyl thioglycosides was summarized: (i) the reactivity of donors with TBS protection is higher than that of the conventional armed donors with Bn protection. But the origin of the influence of silyl ether protection on the anomeric reactivity is unclear at present; (ii) the amount of silyl groups also affects the reactivity, i.e., a donor with more TBS groups is more reactive than a donor with less TBS groups; (iii) a donor carrying a cyclic 3,5-*O*-silylene acetal group even displays reactivity lower than that of the perbenzoylated disarmed donors. This is due to the disarming effect of the cyclic DTBS acetal protection on the glycosylation reactivity. Overall, the tuning effect of silyl protections on the glycosylation reactivity of galactofuranosyl thioglycosides observed in this study is similar to that observed previously in arabinofuranosyl thioglycosides.[12]

The above silyl group-protected thiogalactofuranosyl donors may prove useful for synthesizing natural galactofuranosides and their structurally related analogues. To examine the synthetic application, we decided to synthesize various oligogalactofuranoses by using a one-pot glycosylation procedure based on the developed silylated thiogalactosyl donors. To this end, two representative linear homotrimers **34** (*β*-D-Gal*f*-(1→6)-*β*-D-Gal*f*-(1→5)-D-Gal*f*, Scheme 3, eq 1) and **40** (*β*-D-Gal*f*-(1→5)-*β*-D-Gal*f*-(1→6)-D-Gal*f*, Scheme 4, eq 1) were first selected as the synthetic targets. These trisaccharide motifs are crucial constituents of the mycolyl−arabinogalactan (mAG) complex from the cell wall polysaccharide of *M. tuberculosis*. Previously, de Lederkremer et al.[23] has synthesized the dec-9-enyl glycoside homologues of **34** and **40** via a glycosylaldonolactone/trichloroacetimidate assembly strategy. Later the one-pot preparation of the octyl glycoside homologues of both trigalactofuranosides with a thioglycoside glycosylation method was reported by the Lowary group.[9] Notably, Lowary et al.[4c] further utilized these synthetic trisaccharide units to probe the specificity of the mycobacterial Gal*f*Ts and uncovered that they are optimal substrates for Gal*f*Ts, which suggests that these small galactofuranosyl oligomers or their analogues are likely to be the inhibitors of the enzymes. Very recently, our group also fulfilled a one-pot assembly of the trisaccharide sequence of **40** based on our developed regioselective glycosylation approach.[11]

Here we attempted to explore a new one-pot approach to these trisaccharides, and the general strategy relies on the utility of the 2-*O*-Bz-3,5,6-tri-*O*-TBS-, 2,6-di-*O*-Bz-3,5-di-*O*-TBS-, and 2,6-di-*O*-Bz-3,5-*O*-DTBS-protected thioglycosides **2**, **3**, and **4**. Take the synthesis of **34** for example (Scheme 3, eq 1). We envisioned that it can be assembled from nonreducing end to reducing end based on the relative reactivity difference of three reactants: the more reactive silylated thioglycoside **2** could be preferentially activated to couple with the 6-OH phenyl thioglycoside **10**, and subsequent glycosylation of the resulting disaccharide thioglycoside with the disarmed 5-OH acceptor **12** would complete the synthesis of the desired trisaccharide product. Two solution-phase one-pot glycosylation techniques were screened to optimize the reaction outcome. One is a one-pot protocol in which the three glycosylating agents and the activating reagents are mixed simultaneously and not added sequentially. In this case, upon activation with NIS (2.5 equiv)/TfOH (0.15 equiv) at −80 °C and warming to 0 °C in CH_2Cl_2, the one-pot glycosylation of the three coupling partners **2**, **10**, and **12** delivered the expected trigalactoside **34** in 51% yield together with 16% of disaccharide **31** and 8% of tetrasaccharide **35** (Scheme 3, eq 1). The other protocol we tried is a sequential one-pot glycosylation method wherein the glycosyl building blocks are added sequentially to control the formation of each glycosidic linkage. As illustrated in Scheme 3, eq 2, the cooled (−50 °C) solution of donor **2** (1.1 equiv), thioglycoside **10** (1.0 equiv), and NIS (1.25 equiv)/TfOH (0.1 equiv) promoter system in dry CH_2Cl_2 was stirred for 1 h, and the TLC monitoring result indicated that materials were converted into a single spot completely. A solution of acceptor **12** (0.95 equiv) in CH_2Cl_2 was added dropwise into the reaction mixture, followed by addition of the NIS and TfOH reagent system. Then the reaction was warmed to −20 °C for 1 h to

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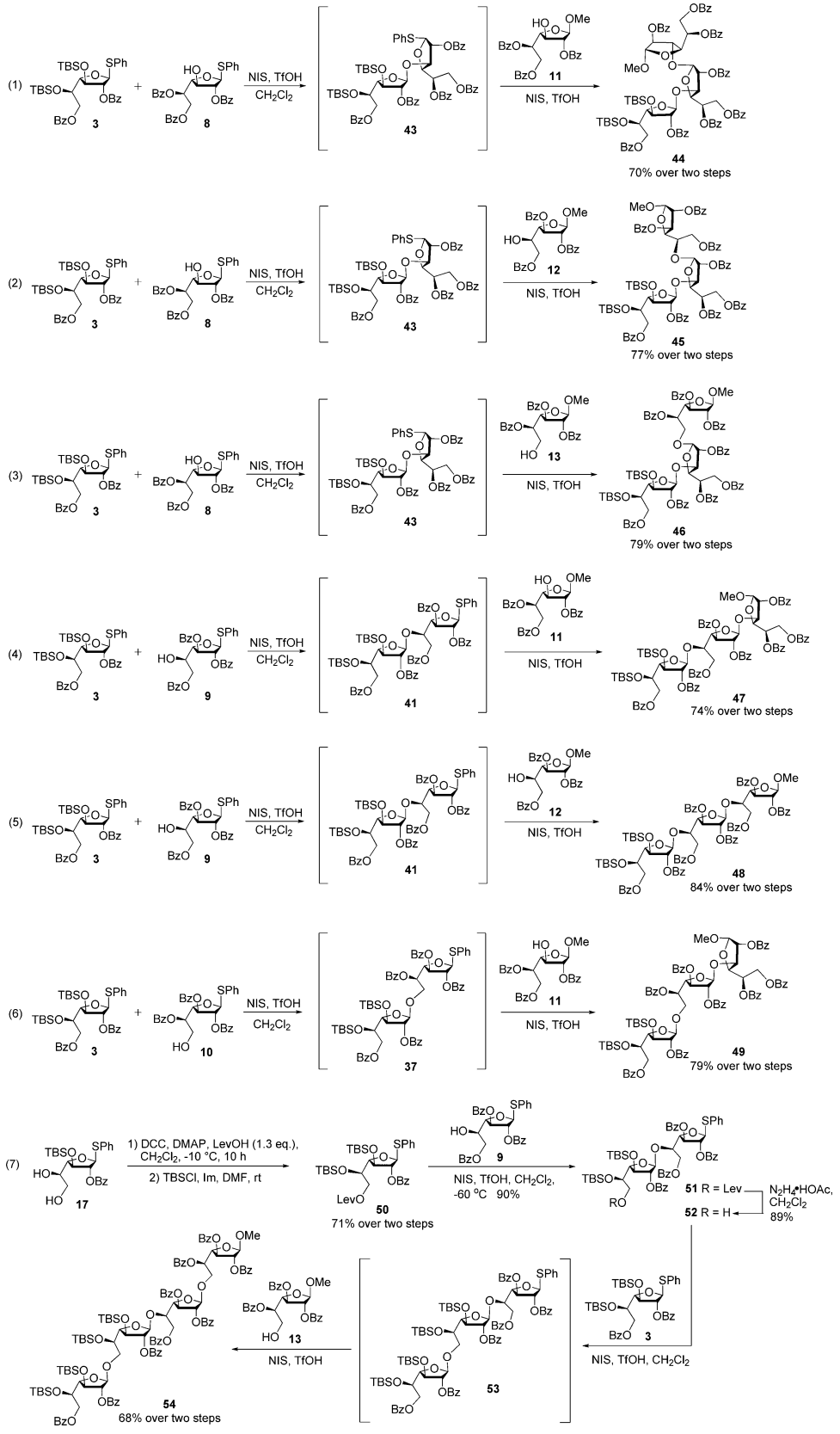
Scheme 5. One-Pot Synthesis of Structurally Diverse Oligogalactofuranoses



yield the β-(1→6)-β-(1→5)-linked trisaccharide **34** in a good yield (88%) over two steps based on the acceptor **12**. Additionally, we chose to employ the 2,6-di-*O*-Bz-3,5-di-*O*-TBS-protected donor **3** rather than **2** in this one-pot synthesis under the same sequential one-pot glycosylation conditions. As a result, the first coupling between **3** and **10** took place smoothly, and then the second glycosylation of the resulting disaccharide **37** with the newly added acceptor **12** provided the

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corresponding trisaccharide **38** in an improved 92% yield (Scheme 3, eq 3).

In contrast to the synthesis of β-(1→6)-β-(1→5)-linked trisaccharide, the preparation of β-(1→5)-β-(1→6)-linked molecule proved to be more problematic. Initially, following a similar one-pot glycosylation procedure via a simultaneous addition of the glycosyl substrates, we anticipated that the target trisacharide **40** would be built from reducing end to nonreducing end via the coupling of 3,5-*O*-DTBS-protected **4** with thioglycoside alcohol **9** and acceptor **13** (Scheme 4, eq 1). But this approach failed to generate any desired trisaccharide product. Instead, a 1,5-anhydro-α-D-galactofuranose derivative **39**[24] (60%) and a disaccharide **32** (20%) derived, respectively, from the intramolecular glycosylation reaction of **9** and the condensation between **4** and **13** were isolated. To solve this problem, we chose the more reactive **3** instead of **4** in the synthesis. In the event, under the similar sequential one-pot glycosylation conditions, **3** was coupled to 5-OH thioglycoside **9** and then the 6-OH acceptor **13** to successfully give, via in situ formed disaccharide intermediate **41**, the expected product **42** in an excellent yield (93%) over two steps (Scheme 4, eq 2).

As mentioned above, in previous studies, Lowary's group[9] has completed the one-pot synthesis of protected β-Gal*f*-(1→6)-β-Gal*f*-(1→5)-Gal*f* and β-Gal*f*-(1→5)-β-Gal*f*-(1→6)-Gal*f* trisaccharide backbones in ca. 41% yields. Our group[11] has also synthesized the protected β-Gal*f*-(1→5)-β-Gal*f*-(1→6)-Gal*f* molecule in a one-pot manner in the yield of 67%. So, in term of the chemical yield, the reactive silylated thioglycoside **3** one-pot glycosylation method offers a new and more efficient one-pot route to these important trisaccharide motifs.

To further demonstrate the viability of the thioglycoside **3** in one-pot syntheses of oligogalactofuranosides, a variety of linear β-galactofuranosyl tri- and tetrasaccharides with diverse glycosidic linkages were synthesized utilizing **3** as key glycosylating agent. As shown in Scheme 5, eqs 1−6, the NIS/TfOH-activated one-pot coupling of the donor **3**, the thioglycoside 3-, 5-, or 6-OH alcohols **8**−**10**, and the methyl glycoside 3-, 5-, or 6-OH acceptors **11**−**13** proceeded without difficulty and efficiently gave protected trisaccharide glycosides **44** (β-D-Gal*f*-(1→3)-β-D-Gal*f*-(1→3)-D-Gal*f*, Scheme 5, eq 1), **45** (β-D-Gal*f*-(1→3)-β-D-Gal*f*-(1→5)-D-Gal*f*, eq 2), **46** (β-D-Gal*f*-(1→3)-β-D-Gal*f*-(1→6)-D-Gal*f*, eq 3), **47** (β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→3)-D-Gal*f*, eq 4), **48** (β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→5)-D-Gal*f*, eq 5), and **49** (β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→3)-D-Gal*f*, eq 6) in good yields (70−84%). We noticed a good correlation between the total yields of the trisaccharide products and the reactivity disparity of the OH groups of the galactofuranosyl acceptors involved in each synthesis. Reactions with more reactive acceptors generally provided better chemical yields than reactions with less reactive acceptors. For example, due to the preferred substitution of OH groups on the D-Gal*f* ring (pseudoaxial secondary 3-OH < secondary 5-OH < primary 6-OH), the yield of **44** with two (1→3) glycosidic bonds is lower than that of **45** with (1→3)-(1→5) glycosidic linkages, while the yield of the latter is lower than that of **46** with (1→3)-(1→6) linkages (70% vs 77% vs 79%, Scheme 5, eqs 1, 2, and 3, respectively). Significantly, to the best of our knowledge, the work described here is the first preparation of such non-natural trigalactofuranose backbones. As the analogues of the natural β-(1→6)-β-(1→5)- and β-(1→5)-β-(1→6)-linked trigalactofuranose scaffolds, these structural types may also hold potential in the study of mycobacterial Gal*f*Ts.

The usefulness of this efficient synthetic technique is also proved by a similar three-component one-pot synthesis of tetrasaccharide substance **54** with a β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-D-Gal*f* motif. Previously, a protected tetragalactosyl saccharide having the same saccharide frame as that of **54** was prepared by Lowary and co-workers.[9] However, their process is a typical example of oligasaccharide synthesis involving tediously selective protection and deprotection steps and time-consuming intermediate purifications. Here we anticipated that the incorporation of our reactive **3** one-pot glycosylation method in the synthesis of the target **54** could simplify the complicated synthetic operation. The successful implementation of this approach is depicted in Scheme 5, eq 7. Thus, subjection of D-galactofuranose 5,6-diol **17** to regioselective substitution of levulinoyl (Lev) group at 6-OH and then TBS ether formation at 5-OH under standard conditions gave **50** (71% over two steps). Subsequently, this 3,5-*O*-disilylated thioglycoside was chemoselectively activated under the promotion of NIS/TfOH to glycosylate with disarmed thioglycoside 5-OH alcohol **9**, affording disaccharide **51** in excellent 90% yield. After removal of the Lev functionality of **51** with hydrazine acetate (N_2H_4·HOAc), the obtained digalactofuranosyl thioglycoside alcohol **52** was used to condense with thioglycoside **3** and acceptor **13** in an analogous one-pot procedure to produce, via trisaccharide intermediate **53**, the tetrasaccharide target **54** in 68% overall yield. Compared with the existing method, this one-pot approach involving the use of silylated thioglycoside **3** greatly speeds up the preparation of the target molecule because the entire one-pot synthetic route can be accomplished without the need of protecting group manipulation and intermediate purification.

The structures of the synthetic tri- and tetrasaccharides were evidently elucidated through the use of NMR and ESI-MS analysis. Take the D-trigalactose **38** for example. In its ^{1}H NMR spectrum, the three anomeric protons appeared as three signals at δ_H 5.74, 5.62, and 5.48 ppm, and in the ^{13}C NMR spectrum, the chemical shifts of the three anomeric carbons were at δ_C 106.64, 106.61, and 105.3 ppm. Both ^{1}H and ^{13}C NMR data support the β-Gal*f* anomeric stereochemistry.[25] Further support for its structure came from high-resolution MS data, which gave an $(M + Na)^+$ signal at *m*/*z* 1601.5575 (calcd 1601.5566).

■ CONCLUSION

The influence of silyl protecting groups on the anomeric reactivity of galactofuranosyl thioglycosides has been experimentally determined. We disclosed that silyl ethers on the furanose ring effectively enhance the glycosylation reactivity, but a 3,5-*O*-cyclic silylene acetal protection has a disarming effect on the reactivity. The 2,6-di-*O*-Bz-3,5-di-*O*-TBS-substituted thiogalactoside **3** is shown to be a very useful glycosylating species. The involvement of this donor in one-pot glycosylations enables the rapid and high-yielding assembly of a wide diversity of β-D-galactofuranosyl tri- and tetrasaccharide structures. Further application of this new one-pot glycosylation technique to the synthesis of oligogalactofuranose libraries is currently underway.

■ EXPERIMENTAL SECTION

Phenyl 2,3,5,6-Tetra-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactofuranoside (1). To a cooled (0 °C) solution of **14** (272 mg, 1.00 mmol) in dry DMF (3.5 mL) was added imidazole (408 mg, 6.00 mmol), followed by TBSCl (904 mg, 6.00 mmol). Then the reaction mixture was warmed gradually to 80 °C and was stirred for 5

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h at the same temperature. The mixture was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography (800:1, petroleum ether−EtOAc) to afford **1** (598 mg, 82%) as a colorless syrup. R_f 0.55 (200:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −73.9 (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, *J* = 7.6 Hz), 7.26 (t, 2H, *J* = 7.6 Hz), 7.20 (t, 1H, *J* = 7.2 Hz), 5.32 (d, 1H, *J* = 3.2 Hz), 4.22 (dd, 1H, *J* = 2.8, 4.0 Hz), 4.17 (dd, 1H, *J* = 3.6, 4.0 Hz), 4.13 (dd, 1H, *J* = 2.8, 3.2 Hz), 3.84 (dd, 1H, *J* = 3.6, 5.6 Hz), 3.70 (dd, 1H, *J* = 6.4, 10.0 Hz), 3.60 (dd, 1H, *J* = 5.6, 10.0 Hz), 0.91 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.85 (s, 9H), 0.11 (s, 12H), 0.10 (s, 3H), 0.09 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.2, 130.8, 128.6, 126.5, 92.7, 85.3, 84.8, 79.8, 73.6, 64.8, 26.0, 25.9, 25.8, 25.7, 18.4, 18.2, 17.9, 17.8, −3.9, −4.12, −4.14, −4.2, −4.6, −4.7, −5.3, −5.4; IR (KBr) 2955, 2932, 2891, 2858, 1469, 1255, 1105, 837, 777 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{72}O_5SSi_4$ [M + Na]$^+$ 751.4070, found 751.4072.

Phenyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactofuranoside (2). To a cooled (0 °C) solution of **17** (490 mg, 1.00 mmol) in dry DMF (3.5 mL) was added imidazole (272 mg, 4.00 mmol), followed by TBSCl (452 mg, 3.00 mmol). Then the reaction mixture was warmed gradually to 30 °C and was stirred for 4 h at the same temperature. The mixture was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford **2** (683 mg, 95%) as a colorless syrup. R_f 0.50 (10:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −79.9 (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 2H, *J* = 7.2 Hz), 7.58 (d, 1H, *J* = 7.2 Hz), 7.54 (dd, 2H, *J* = 1.6, 8.4 Hz),7.43 (t, 2H, *J* = 7.6 Hz), 7.20−7.28 (m, 3H), 5.56 (d, 1H, *J* = 2.8 Hz), 5.38 (t, 1H, *J* = 2.8 Hz), 4.56 (dd, 1H, *J* = 2.8, 5.2 Hz), 4.36 (dd, 1H, *J* = 2.8, 5.2 Hz), 3.85−3.90 (m, 1H), 3.72 (dd, 1H, *J* = 6.8, 10.0 Hz), 3.64 (dd, 1H, *J* = 5.6, 10.0 Hz), 0.91 (s, 9H), 0.90 (s, 9H), 0.88 (s, 9H), 0.12 (s. 6H), 0.10 (s, 3H), 0.09 (s, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.4, 135.0, 133.3, 131.7, 129.8, 129.4, 128.7, 128.4, 127.0, 90.2, 84.8, 84.5, 76.2, 72.9, 64.5, 25.95, 25.90, 25.6, 18.3, 18.2, 17.8, −3.7, −4.4, −4.7, −4.8, −5.3, −5.4; IR (KBr) 2955, 2931, 2890, 2858, 1729, 1469, 1260, 1107, 837, 778 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{62}O_6SSi_3$ [M + Na]$^+$ 741.3467, found 741.3472.

Phenyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactofuranoside (3). To a cooled (−10 °C) solution of **17** (490 mg, 1.00 mmol) in pyridine (3.5 mL) was added DMAP (50 mg). After 15 min, benzoyl chloride (0.15 mL, 1.30 mmol) was added dropwise. The mixture was stirred at −10 °C for 10 h and then was stirred at 0 °C for 1 h. Next, the reaction was quenched by addition of methanol (1 mL), and the resulting mixture was evaporated under reduced pressure. The obtained residue was purified by column chromatography (12:1, petroleum ether−EtOAc) to afford a colorless syrup. Then to a cooled (0 °C) solution of the syrup (416 mg, 0.70 mmol) in dry DMF (2.5 mL) was added imidazole (95 mg, 1.40 mmol), followed by TBSCl (166 mg, 1.10 mmol). The reaction mixture was warmed gradually to 30 °C and was stirred for 3 h at the same temperature. Then the mixture was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (8:1, petroleum ether−EtOAc) to afford **3** (471 mg, 67% over two steps) as a colorless syrup. R_f 0.50 (8:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −77.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, 4H, *J* = 8.0 Hz), 7.58 (t, 2H, *J* = 7.2 Hz), 7.53 (d, 2H, *J* = 7.2 Hz), 7.44 (t, 2H, *J* = 7.6 Hz), 7.43 (t, 2H, *J* = 7.6 Hz), 7.22−7.28 (m, 3H), 5.62 (d, 1H, *J* = 2.0 Hz), 5.40 (t, 1H, *J* = 2.0 Hz), 4.57 (dd, 1H, *J* = 2.0, 5.2 Hz), 4.49 (dd, 1H, *J* = 5.2, 11.2 Hz), 4.38−4.44 (m, 2H), 4.26 (dd, 1H, *J* = 5.2, 10.0 Hz), 0.91 (s, 9H), 0.90 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 165.4, 134.8, 133.4, 133.0, 131.7, 129.84, 129.81, 129.6, 129.1, 128.8, 128.5, 128.4, 127.2, 90.8, 85.7, 84.6, 76.3, 70.1, 66.1, 25.8, 25.6, 18.2, 17.8, −4.2, −4.3, −4.5, −4.9; IR (KBr) 2955, 2931, 2891, 2857, 1725, 1469, 1456, 1271, 1110, 1069, 837, 779 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{52}O_7SSi_2$ [M + Na]$^+$ 731.2864, found 731.2869.

Phenyl 2,6-Di-*O*-benzoyl-3,5-*O*-(di-*tert*-butylsilanediyl)-1-thio-β-D-galactofuranoside (4). To a cooled (−10 °C) solution of **17** (490 mg, 1.00 mmol) in pyridine (3.5 mL) was added DMAP (50 mg). After 15 min, benzoyl chloride (0.15 mL, 1.30 mmol) was added dropwise. The mixture was stirred at −10 °C for 10 h and then was stirred at 0 °C for 1 h. The reaction was quenched by addition of methanol (1 mL), and the resulting mixture was evaporated under reduced pressure. The obtained residue was purified by column chromatography (12:1, petroleum ether−EtOAc) to afford a colorless syrup. Next, the syrup (416 mg, 0.70 mmol) was dissolved in tetrahydrofuran (7.0 mL). Acetic acid (20 μL, 0.35 mmol) was added at 0 °C. After 5 min, TBAF (1 M in THF, 1.10 mL, 1.10 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature and then was evaporated under reduced pressure. The residue was purified by column chromatography (2:1, petroleum ether−EtOAc) to afford the corresponding diol compound as a colorless syrup. Finally, to a cooled (0 °C) solution of the diol syrup (309 mg, 0.64 mmol) and 2,6-lutidine (0.30 mL, 2.56 mmol) in dry DMF/CH_2Cl_2 (1.1 mL/5.5 mL) was added $(t\text{-Bu})_2Si(OTf)_2$ (0.31 mL, 0.96 mmol). The reaction mixture was stirred at room temperature for 6 h and then was quenched by addition of MeOH (0.2 mL). The resulting solution was coevaporated with toluene to dryness. The obtained residue was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was further purified by column chromatography (8:1, petroleum ether−EtOAc) to afford **4** (337 mg, 55% over three steps) as a colorless syrup. R_f 0.60 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −53.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, 4H, *J* = 7.6 Hz), 7.61 (t, 1H, *J* = 8.0 Hz), 7.59 (t, 1H, *J* = 8.0 Hz), 7.49 (d, 2H, *J* = 7.6 Hz), 7.45 (t, 4H, *J* = 7.6 Hz), 7.20−7.25 (m, 3H), 5.49−5.55 (m, 2H), 4.87 (dd, 1H, *J* = 6.4, 11.6 Hz), 4.75 (dd, 1H, *J* = 4.4, 12.0 Hz), 4.66 (dd, 1H, *J* = 6.4, 10.0 Hz), 4.55 (dd, 1H, *J* = 6.8, 11.6 Hz), 4.53 (dd, 1H, *J* = 6.8, 9.6 Hz), 1.06 (s, 9H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.5, 165.5, 134.1, 133.5, 133.0, 131.0, 130.1, 129.9, 129.7, 129.2, 128.9, 128.5, 128.4, 127.3, 89.4, 81.6, 75.3, 74.7, 70.9, 64.5, 27.1, 26.9, 21.6, 20.8; IR (KBr) 3554, 2938, 2894, 2860, 1728, 1474, 1271, 1102, 1059, 830, 710 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{40}O_7SSi$ [M + Na]$^+$ 643.2156, found 643.2164.

Phenyl 2-*O*-Benzoyl-3,5,6-tri-*O*-benzyl-1-thio-β-D-galacto-furanoside (7). Compound **15** (426 mg, 1.00 mmol) was dissolved in a mixture of acetic acid, water, and tetrahydrofuran (2/1/1, v/v/v, 50.3 mL), and the solution was stirred at 55 °C for 4 h. The reaction was quenched by addition of Et_3N to adjust the pH value to pH 7, and the resulting mixture was evaporated under reduced pressure. The obtained residue was dissolved with CH_2Cl_2, and the organic solution was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (1:1, petroleum ether−EtOAc) to give the triol intermediate as a colorless syrup. To a cooled (0 °C) solution of the triol (301 mg, 0.78 mmol) in dry DMF (16.0 mL) was added benzyl bromide (0.55 mL, 4.7 mmol). The reaction mixture was stirred at 0 °C for 30 min, followed by the addition of NaH (74 mg, 3.12 mmol). After being stirred at 0 °C for 15 min, the reaction mixture was poured into ice water rapidly, and the resulting mixture was extracted with CH_2Cl_2. Then the obtained organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (20:1, petroleum ether−EtOAc) to afford the tribenzylated product as a colorless syrup. Next, the syrup (358 mg, 0.55 mmol) was dissolved in tetrahydrofuran (5.5 mL). TBAF (1 M in THF, 0.28 mL, 0.28 mmol) was added at 0 °C. After being stirred at room temperature for 2.5 h, the reaction mixture was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2, and the resulting organic mixture was washed with saturated aqueous NH_4Cl and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford the desilylated compound as a colorless syrup. Finally, to a cooled (0

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°C) solution of the above syrup (265 mg, 0.49 mmol) in dry pyridine (2.5 mL) was added benzoyl chloride (85 μL, 0.74 mmol). The reaction was stirred at room temperature for 3 h and then was quenched by addition of methanol (0.5 mL). The resulting mixture was evaporated under reduced pressure, and the residue was purified by column chromatography (20:1, petroleum ether−EtOAc) to afford **7** as a colorless syrup (301 mg, 47% over four steps). R_f 0.50 (12:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −130.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, 2H, *J* = 0.8, 8.0 Hz), 7.57 (t, 1H, *J* = 7.6 Hz), 7.47−7.52 (m, 3H), 7.40 (t, 2H, *J* = 8.0 Hz), 7.15−7.30 (m, 17H), 5.72 (s, 1H), 5.49 (s, 1H), 4.73 (d, 1H, *J* = 12.0 Hz), 4.69 (d, 1H, *J* = 12.0 Hz), 4.55 (dd, 1H, *J* = 2.8, 6.0 Hz), 4.49 (s, 2H), 4.43 (d, 1H, *J* = 12.0 Hz), 4.34 (d, 1H, *J* = 12.0 Hz), 4.13 (d, 1H, *J* = 6.4 Hz), 3.79−3.82 (m, 1H), 3.74 (dd, 1H, *J* = 6.8, 10.0 Hz), 3.66 (dd, 1H, *J* = 5.6, 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 165.4, 138.0, 137.9, 137.3, 134.1, 133.6, 133.3, 131.7, 130.1, 129.7, 129.2, 128.7, 128.4, 128.33, 128.30, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.2, 90.8, 82.6, 82.5, 82.1, 76.1, 73.4, 72.2, 70.5; IR (KBr) 3454, 3424, 1717, 1637, 1401, 1264, 1111, 1068, 696 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{38}O_6S$ $[M + Na]^+$ 669.2281, found 669.2316.

Phenyl 2,5,6-Tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (8). To a solution of **17** (490 mg, 1.00 mmol) in dry pyridine (10.0 mL) was added benzoyl chloride (0.35 mL, 3.00 mmol). After being stirred at room temperature for 3 h, the reaction was quenched by addition of methanol (1.5 mL), and the mixture was evaporated under reduced pressure. The obtained residue was purified by column chromatography (18:1, petroleum ether−EtOAc) to afford a colorless syrup. Next, the syrup (663 mg, 0.95 mmol) was dissolved in tetrahydrofuran (9.5 mL). Acetic acid (27 μL, 0.48 mmol) was added at 0 °C. After 5 min, TBAF (1 M in THF, 1.43 mL, 1.43 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 10 h and then was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2, and the resulting organic mixture was washed with saturated aqueous NH_4Cl and brine, dried over anhydrous Na_2SO_4, and concentrated. Finally, the crude product was purified by column chromatography (6:1, petroleum ether−EtOAc) to afford compound **8** (499 mg, 86% over two steps) as a colorless syrup. R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −97.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 2H, *J* = 7.6 Hz), 7.99 (d, 2H, *J* = 7.6 Hz), 7.96 (d, 2H, *J* = 7.6 Hz), 7.57 (t, 2H, *J* = 7.6 Hz), 7.52 (t, 3H, *J* = 7.2 Hz), 7.40 (dd, 2H, *J* = 2.0, 7.6 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 7.2 Hz), 7.25 (t, 1H, *J* = 7.2 Hz), 7.20 (t, 2H, *J* = 7.6 Hz), 5.82−5.87 (m, 1H), 5.74 (d, 1H, *J* = 3.2 Hz), 5.18 (t, 1H, *J* = 3.2 Hz), 4.73 (dd, 1H, *J* = 4.4, 11.6 Hz), 4.63−4.69 (m, 2H), 4.26−4.30 (m, 1H), 3.59 (d, 1H, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 167.1, 166.1, 166.0, 133.7, 133.3, 133.1, 133.0, 132.6, 129.9, 129.7, 129.5, 129.4, 128.9, 128.6, 128.5, 128.40, 128.38, 128.0, 89.2, 86.7, 80.6, 77.2, 70.5, 63.2; IR (KBr) 3467, 1724, 1451, 1269, 1110, 710 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}O_8S$ $[M + Na]^+$ 607.1397, found 607.1401.

Phenyl 2,3,6-Tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (9) and Phenyl 2,3,5-Tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (10). To a cooled (0 °C) solution of **18** (487 mg, 0.70 mmol) in tetrahydrofuran (7.0 mL) was added TBAF (1 M in THF, 0.35 mL, 0.35 mmol). After being stirred at room temperature for 2.5 h, the reaction mixture was concentrated under reduced pressure, and the residue was dissolved with CH_2Cl_2. The obtained organic mixture was washed with saturated aqueous NH_4Cl and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford compounds **9** (135 mg, 33%) and **10** (237 mg, 58%) as colorless syrups. **9**: R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −81.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, 2H, *J* = 1.2, 8.4 Hz), 8.05−8.01 (m, 4H), 7.38−7.64 (m, 11H), 7.25−7.28 (m, 3H), 5.81 (s, 1H), 5.75 (s, 1H), 5.73 (d, 1H, *J* = 1.6 Hz), 4.66 (dd, 1H, *J* = 1.6, 4.4 Hz), 4.47−4.61 (m, 3H), 2.79 (d, 1H, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 166.5, 165.9, 165.2, 133.7, 133.6, 133.3, 133.1, 132.3, 130.0, 129.9, 129.7, 129.6, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 91.7, 83.2, 81.8, 78.2, 68.9, 66.1; IR (KBr) 3470, 1723, 1603, 1451, 1399, 1273, 1110, 710 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}O_8S$ $[M + Na]^+$ 607.1397, found 607.1405. **10**: R_f 0.55 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −94.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, 2H, *J* = 1.6, 7.6 Hz), 8.06 (d, 2H, *J* = 8.0 Hz), 7.95 (d, 2H, *J* = 7.6 Hz), 7.62−7.50 (m, 5H), 7.46 (t, 2H, *J* = 8.0 Hz), 7.35 (t, 2H, *J* = 8.0 Hz), 7.29−7.31 (m, 5H), 5.83 (s, 1H), 5.65−5.71 (m, 3H), 4.93 (t, 1H, *J* = 4.4 Hz), 4.00−4.10 (m, 2H), 2.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 165.7, 165.3, 133.7, 133.5, 133.3, 133.0, 132.5, 130.0, 129.9, 129.8, 129.5, 129.1, 128.74, 128.72, 128.5, 128.4, 128.3, 128.0, 91.0, 82.3, 82.2, 78.0, 73.3, 62.4; IR (KBr) 3474, 3420, 1724, 1602, 1451, 1272, 1109, 710 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}O_8S$ $[M + Na]^+$ 607.1397, found 607.1402.

Methyl 2,5,6-Tri-*O*-benzoyl-β-D-galactofuranoside (11). To a solution of **21** (412 mg, 1.00 mmol) in dry pyridine (10.0 mL) was added benzoyl chloride (0.35 mL, 3.00 mmol). After 3 h, the reaction mixture was quenched by addition of methanol (1.5 mL) and then was evaporated under reduced pressure. The residue was purified by column chromatography (18:1, petroleum ether−EtOAc) to afford a colorless syrup. Next, the syrup (570 mg, 0.92 mmol) was dissolved in tetrahydrofuran (9.2 mL). Acetic acid (26 μL, 0.46 mmol) was added at 0 °C. After 5 min, TBAF (1 M in THF, 1.38 mL, 1.38 mmol) was added dropwise. The mixture was stirred overnight and was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2, and then the resulting organic mixture was washed with saturated aqueous NH_4Cl and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (8:1, petroleum ether−EtOAc) to afford compound **11** (419 mg, 83% over two steps) as a colorless syrup. R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −35.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, 2H, *J* = 1.2, 8.0 Hz), 7.98 (dd, 2H, *J* = 1.2, 8.0 Hz), 7.95 (dd, 2H, *J* = 1.2, 8.0 Hz), 7.49−7.55 (m, 3H), 7.39 (t, 2H, *J* = 8.0 Hz), 7.38 (t, 2H, *J* = 8.0 Hz), 7.34 (t, 2H, *J* = 8.0 Hz), 5.81−5.85 (m, 1H), 5.20 (s, 1H), 5.11 (dd, 1H, *J* = 0.8, 2.8 Hz), 4.75 (dd, 1H, *J* = 4.4, 12.0 Hz), 4.68 (dd, 1H, *J* = 7.6, 12.0 Hz), 4.45 (dd, 1H, *J* = 4.4, 6.4 Hz), 4.25 (dd, 1H, *J* = 2.8, 6.8 Hz), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.6, 166.1, 166.0, 133.5, 133.2, 133.1, 129.8, 129.7, 129.6, 129.5, 129.4, 128.8, 128.4, 128.3, 106.3, 85.9, 81.8, 77.0, 70.5, 63.4, 55.0; IR (KBr) 3495, 2935, 1723, 1602, 1451, 1267, 1109, 711 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}O_9$ $[M + Na]^+$ 529.1469, found 529.1469.

Methyl 2,3,6-Tri-*O*-benzoyl-β-D-galactofuranoside (12). To a cooled (−10 °C) solution of **19** (402 mg, 1.00 mmol) in pyridine (3.5 mL) was added DMAP (40 mg). After 15 min, benzoyl chloride (0.15 mL, 1.30 mmol) was added dropwise. The mixture was stirred at −10 °C for 15 h and then was warmed to 0 °C for another 1 h. The reaction mixture was quenched by addition of methanol (1 mL) and was evaporated under reduced pressure. The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford compound **12** (364 mg, 72%) as a colorless syrup. R_f 0.45 (5:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +23.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 2H, *J* = 8.0 Hz), 8.04 (d, 4H, *J* = 8.0 Hz), 7.58 (t, 1H, *J* = 8.0 Hz), 7.54 (t, 2H, *J* = 7.6 Hz), 7.44 (t, 3H, *J* = 7.6 Hz), 7.41 (t, 3H, *J* = 8.0 Hz), 5.66 (d, 1H, *J* = 4.8 Hz), 5.52 (s, 1H), 5.17 (s, 1H), 4.62 (dd, 1H, *J* = 8.0, 12.8 Hz), 4.49−4.52 (m, 2H), 4.39 (dd, 1H, *J* = 2.0, 5.2 Hz), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.5, 166.1, 165.4, 133.5, 133.1, 129.9, 129.8, 129.7, 129.6, 129.0, 128.9, 128.5, 128.4, 128.3, 106.9, 82.9, 81.5, 78.1, 68.9, 66.1, 55.0; IR (KBr) 3497, 2932, 1723, 1602, 1451, 1272, 1112, 712 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}O_9$ $[M + Na]^+$ 529.1469, found 529.1474.

Phenyl 2-*O*-*tert*-Butyldimethylsilyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (15) and Phenyl 3-*O*-*tert*-Butyldimethylsilyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (16). To a solution of compound **14** (2.72 g, 10.00 mmol) in dry acetone (50 mL) were added 2,2′-dimethoxypropane (1.85 mL, 15.00 mmol) and *p*-toluenesulfonic acid (0.34 g, 2.00 mmol) at room temperature. After 2 h, the reaction was quenched by addition of Et_3N to adjust the pH value to pH 7. The solvent was evaporated under reduced pressure, and the residue was dissolved with CH_2Cl_2. The resulting organic mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated.

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The crude oil was further purified by column chromatography (3:1, petroleum ether−EtOAc) to afford the 5,6-isopropylidene thioglycoside as a colorless syrup. To a cooled (0 °C) solution of the 5,6-isopropylidene thioglycoside (2.96 g, 9.50 mmol) in DMF (18.5 mL) was added imidazole (0.97 g, 14.3 mmol), followed by the mixture of TBSCl (1.86 g, 12.3 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at 30 °C for 6 h and then was coevaporated with toluene to dryness. The obtained residue was further purified by column chromatography (15:1, petroleum ether−EtOAc) to afford the silyl products **15** (1.94 g, 46% over two steps) and **16** (0.93 g, 22% over two steps) as colorless syrups. **15**: R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −97.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dt, 2H, *J* = 2.0, 8.0 Hz), 7.31 (tt, 2H, *J* = 2.0, 8.0 Hz), 7.25−7.28 (m, 1H), 5.32 (d, 1H, *J* = 3.2 Hz), 4.34 (dd, 1H, *J* = 6.4, 12.0 Hz), 4.15 (t, 1H, *J* = 3.6 Hz), 4.11 (t, 1H, *J* = 6.0 Hz), 4.03 (dd, 1H, *J* = 7.2, 8.4 Hz), 3.94−4.00 (m, 2H), 2.35 (d, 1H, 6.4 Hz), 1.44 (s, 3H), 1.37 (s, 3H), 0.89 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 133.8, 131.9, 129.0, 127.5, 109.7, 92.3, 83.6, 82.9, 78.7, 75.1, 65.3, 26.3, 25.7, 25.1, 17.9, −4.67, −4.73; IR (KBr) 3462, 2954, 2932, 2891, 2858, 1475, 1376, 1256, 1217, 1153, 1064, 840, 781 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{34}O_5SSi$ $[M + Na]^+$ 449.1788, found 449.1789. **16**: R_f 0.55 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −54.5 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, *J* = 7.2 Hz), 7.29 (t, 2H, *J* = 7.2 Hz), 7.21 (t, 1H, *J* = 7.2 Hz), 5.50 (s, 1H), 4.28 (t, 1H, *J* = 7.2 Hz), 4.00−4.18 (m, 6H), 1.42 (s, 3H), 1.40 (s, 3H), 0.94 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 136.6, 130.5, 128.8, 126.6, 109.9, 95.2, 84.7, 82.0, 79.3, 75.7, 65.6, 25.7, 25.6, 25.5, 17.9, −4.7, −4.9; IR (KBr) 3436, 2954, 2932, 2894, 2858, 1473, 1376, 1256, 1218, 1108, 1063, 841 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{34}O_5SSi$ $[M + Na]^+$ 449.1788, found 449.1794.

Phenyl 2-*O*-Benzoyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactofuranoside (17). To a solution of **16** (1.28 g, 3.00 mmol) in dry pyridine (15.0 mL) was added benzoyl chloride (0.52 mL, 4.50 mmol). After being stirred for 3 h at room temperature, the reaction mixture was quenched by addition of methanol (1.5 mL) and was evaporated under reduced pressure. The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford a colorless syrup. Then, the syrup (1.46 g, 2.76 mmol) was dissolved in a mixture of acetic acid, water, and tetrahydrofuran (2/1/1, v/v/v, 138 mL). The reaction was stirred at 55 °C for 4 h and then was quenched by addition of Et_3N to adjust the pH value to pH 7. The solvent was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2, and the resulting mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (2:1, petroleum ether−EtOAc) to give compound **17** (1.08 g, 74% over two steps) as a colorless syrup. R_f 0.50 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −82.1 (*c* 1.10, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, 2H, *J* = 7.2 Hz), 7.59 (t, 1H, *J* = 7.2 Hz), 7.51 (d, 2H, *J* = 7.2 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.26−7.32 (m, 3H), 5.54 (d, 1H, *J* = 1.8 Hz), 5.35 (t, 1H, *J* = 2.4 Hz), 4.56 (dd, 1H, *J* = 3.0, 6.0 Hz), 4.27 (dd, 1H, *J* = 1.8, 6.6 Hz), 3.84−3.87 (m, 1H), 3.74−3.79 (m, 2H), 2.52 (d, 1H, *J* = 8.4 Hz), 2.16−2.19 (m, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 165.4, 134.0, 133.5, 132.3, 129.8, 129.1, 129.0, 128.5, 127.7, 90.9, 84.3, 84.2, 76.2, 69.4, 65.1, 25.6, 17.8, −4.7, −5.0; IR (KBr) 3431, 2954, 2930, 2858, 1727, 1267, 1111, 840 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{34}O_6SSi$ $[M + Na]^+$ 513.1738, found 513.1744.

Phenyl 2,3,5-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactofuranoside (18). To a cooled (0 °C) solution of **14** (272 mg, 1.00 mmol) in dry DMF (3.5 mL) was added imidazole (136 mg, 2.00 mmol), followed by TBSCl (196 mg, 1.30 mmol). The reaction mixture was stirred at 30 °C for 6 h and then was coevaporated with toluene to dryness. The residue was purified by column chromatography (1:1, petroleum ether−EtOAc) to afford the primary hydroxyl-protected product as a colorless syrup. Next, the syrup (289 mg, 0.75 mmol) was dissolved in dry pyridine (2.5 mL) at 0 °C, followed by addition of benzoyl chloride (0.39 mL, 3.37 mmol). After being stirred at 30 °C for 3 h, the reaction mixture was quenched by addition of methanol (1 mL) and was evaporated under reduced pressure. The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to provide the fully protected thioglycoside **18** (487 mg, 70% over two steps) as a colorless syrup: $[\alpha]_D^{20}$ −87.5 (*c* 1.15, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, 2H, *J* = 8.4 Hz), 8.07 (d, 2H, *J* = 7.2 Hz), 7.89 (d, 2H, *J* = 7.2 Hz), 7.57−7.61 (m, 2H), 7.54 (d, 1H, *J* = 7.2 Hz), 7.51 (d, 1H, *J* = 7.8 Hz), 7.47 (t, 2H, *J* = 7.8 Hz), 7.34 (t, 2H, *J* = 7.2 Hz), 7.25−7.31 (m, 6H), 5.80 (s, 1H), 5.65 (dd, 2H, *J* = 4.8, 10.2 Hz), 5.63 (s, 1H), 4.98 (t, 1H, *J* = 4.8 Hz), 3.98 (dd, 1H, *J* = 6.0, 10.2 Hz), 3.95 (dd, 1H, *J* = 6.6, 10.2 Hz), 0.82 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 165.8, 165.5, 165.4, 133.5, 133.4, 133.3, 133.1, 132.5, 130.0, 129.9, 129.8, 129.7, 129.1, 128.9, 128.8, 128.5, 128.4, 128.3, 127.8, 91.0, 82.6, 80.8, 77.8, 73.0, 61.2, 25.7, 18.1, −5.4, −5.5; IR (KBr) 2922, 2853, 1727, 1601, 1452, 1264, 1105, 838, 710 cm^{-1}; HRMS (ESI) calcd for $C_{39}H_{42}O_8SSi$ $[M + Na]^+$ 721.2262, found 721.2273.

Methyl 2-*O*-Benzoyl-3-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranoside (21). To a cooled (0 °C) solution of **20** (338 mg, 1.00 mmol) in DMF (2.8 mL) was added imidazole (136 mg, 2.00 mmol), followed by TBSCl (226 mg, 1.50 mmol). The reaction mixture was stirred at 30 °C for 3 h and then was coevaporated with toluene to dryness. The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford the silylated product as a colorless syrup. The above syrup (430 mg, 0.95 mmol) was dissolved in a mixture of acetic acid, water, and tetrahydrofuran (2/1/1, v/v/v, 63.3 mL) at 55 °C for 4 h. The resulting mixture was quenched by addition of Et_3N to adjust the pH to pH 7 and was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2, and the resulting solution was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude oil was further purified by column chromatography (3:1, petroleum ether−EtOAc) to give **21** (313 mg, 74% over two steps) as a colorless syrup. R_f 0.55 (1:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +11.4 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 2H, *J* = 7.2 Hz), 7.60 (t, 1H, *J* = 7.6 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 5.19 (d, 1H, *J* = 2.4 Hz), 4.94 (s, 1H), 4.53 (dd, 1H, *J* = 3.2, 7.2 Hz), 4.04 (dd, 1H, *J* = 1.2, 7.2 Hz), 3.78−3.85 (m, 3H), 3.42 (s, 3H), 2.46 (d, 1H, *J* = 7.6 Hz), 2.17−2.23 (m, 1H), 0.87 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.7, 133.5, 129.7, 129.2, 128.5, 107.4, 84.9, 83.8, 76.4, 69.5, 65.3, 55.1, 25.6, 17.8, −4.6, −5.0; IR (KBr) 3431, 2955, 2927, 2857, 1727, 1458, 1269, 1109, 840, 780, 713 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{32}O_7Si$ $[M + Na]^+$ 435.1810, found 435.1817.

General Procedure for the Three-Component Competition Glycosylations. To a stirred solution (0.14 M) of donor A (1.1 equiv), donor B (1.1 equiv), and the corresponding acceptor (1.0 equiv) in dry CH_2Cl_2 was added freshly activated 4 Å molecular sieves (250 wt % with respect to the donor). The mixture was stirred under nitrogen for 30 min at room temperature and then was cooled to −80 °C, followed by addition of NIS (1.25 equiv) and TfOH (0.1 equiv). After being gradually warmed to −50 °C and reaction for 1 h, the resulting mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The residue was purified by column chromatography to afford disaccharide products.

Methyl 2,3,5,6-Tetra-*O*-*tert*-butyldimethylsilyl-α,β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (23) and Methyl 2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (24). Prepared from **1** (63.5 mg, 0.087 mmol), **5** (55 mg, 0.087 mmol), and **13** (40 mg, 0.079 mmol). The residue was purified by column chromatography (30:1, petroleum ether−EtOAc) to afford compounds **23** (62 mg, 70%) and **24** (20 mg, 25%) as colorless syrups. **23** was obtained as an inseparable β/α mixture in a 1.8:1 ratio, which gave R_f 0.50 (15:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −14.0 (*c* 1.50, $CHCl_3$). For the major product (β-anomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, 2H, *J* = 7.6 Hz), 8.04 (t, 2H, *J* = 7.2 Hz), 7.83−7.88 (m, 2H), 7.47−7.58 (m, 3H), 7.42 (t, 1H, *J* = 8.0 Hz), 7.41 (t, 1H, *J* = 7.6 Hz), 7.33 (t, 2H, *J* = 8.0 Hz), 7.24 (t, 2H, *J* = 8.0 Hz), 5.78−5.84 (m, 1H), 5.52 (d, 1H, *J* = 5.2 Hz), 5.42 (s, 1H), 5.17 (s, 1H), 4.84 (d, 1H, *J* = 1.2 Hz), 4.62 (dd, 1H, *J* = 2.8, 5.6 Hz), 4.08−4.22 (m, 2H), 3.88−4.01 (m, 2H), 3.73−3.83 (m, 2H), 3.66 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.57 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.48 (s, 3H), 0.89 (s, 9H), 0.87 (s, 9H), 0.84 (s,

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9H), 0.80 (s, 9H), −0.09−0.11 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.7, 165.6, 165.5, 133.3, 133.2, 133.0, 130.0, 129.8, 129.7, 129.1, 129.0, 128.33, 128.31, 128.25, 128.23, 108.4, 106.5, 84.4, 84.2, 82.3, 80.8, 79.5, 77.5, 73.3, 70.8, 65.8, 64.8, 54.8, 26.0, 25.9, 25.7, 18.3, 18.0, 17.8, 17.7, −3.6, −4.0, −4.4, −4.5, −4.6, −5.1, −5.3, −5.4; selected signals for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 1H), 5.15 (s, 1H), 5.08 (d, 1H, J = 3.2 Hz), 4.68 (dd, 1H, J = 2.8, 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 106.8, 102.3, 85.0, 82.4, 80.5, 78.4, 77.4, 76.6, 73.2, 70.5, 66.2, 65.3, 55.0; IR (KBr) 2954, 2932, 2892, 2858, 1729, 1465, 1258, 1108, 1063, 838, 778, 711 cm^{-1}; HRMS (ESI) calcd for $C_{58}H_{92}O_{14}Si_4$ [M + Na]$^+$ 1147.5456, found 1147.5461. **24**: R_f 0.50 (5:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +17.5 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, 2H, J = 0.8, 8.0 Hz), 8.03 (dd, 2H, J = 1.2, 8.0 Hz), 7.89 (dd, 2H, J = 0.8, 8.0 Hz), 7.55 (td, 1H, J = 1.6, 8.0 Hz), 7.50 (td, 2H, J = 1.2, 7.2 Hz), 7.39 (t, 2H, J = 8.0 Hz), 7.13−7.33 (m, 24H), 5.89 (td, 1H, J = 3.2, 6.4 Hz), 5.54 (d, 1H, J = 5.6 Hz), 5.42 (d, 1H, J = 0.8 Hz), 5.22 (d, 1H, J = 4.4 Hz), 5.17 (s, 1H), 4.71 (d, 1H, J = 12.0 Hz), 4.64−4.66 (m, 2H), 4.63 (d, 1H, J = 1.6 Hz), 4.58 (d, 1H, J = 12.0 Hz), 4.47 (d, 1H, J = 12.0 Hz), 4.42 (s, 2H), 4.36 (d, 1H, J = 12.0 Hz), 4.22 (t, 1H, J = 7.2 Hz), 4.06−4.11 (m, 2H), 3.99 (dd, 1H, J = 6.4, 13.6 Hz), 3.96 (dd, 1H, J = 6.4, 11.2 Hz), 3.65 (dd, 1H, J = 5.6, 10.4 Hz), 3.57 (dd, 1H, J = 4.4, 10.4 Hz), 3.50 (dd, 1H, J = 6.0, 10.4 Hz), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.7, 165.6, 165.5, 138.7, 138.2, 138.1, 137.6, 133.4, 133.3, 133.1, 130.0, 129.9, 129.8, 129.6, 129.0, 128.9, 128.34, 128.33, 128.32, 128.31, 128.2, 128.1, 127.78, 127.77, 127.7, 127.54, 127.49, 127.41, 127.3, 106.8, 99.0, 84.1, 82.3, 81.1, 80.8, 80.5, 79.0, 77.4, 73.2, 72.8, 72.1, 72.0, 70.0, 69.9, 64.8, 55.0; IR (KBr) 3423, 2926, 2861, 1725, 1453, 1268, 1109, 1026, 709 cm^{-1}; HRMS (ESI) calcd for $C_{62}H_{60}O_{14}$ [M + Na]$^+$ 1051.3875, found 1051.3875.

Methyl 2,3,5,6-Tetra-*O*-*tert*-butyldimethylsily-*β*-D-galactofuranosyl-(1→3)-2,5-di-*O*-benzoyl-*α*-L-arabinofuranoside (25) and Methyl 2,3,5,6-Tetra-*O*-benzyl-*β*-D-galactofuranosyl-(1→3)-2,5-di-*O*-benzoyl-*α*-L-arabinofuranoside (26). Prepared from **1** (63.5 mg, 0.087 mmol), **5** (55 mg, 0.087 mmol), and **22** (29.4 mg, 0.079 mmol). The residue was purified by column chromatography (20:1, petroleum ether−EtOAc) to afford compounds **25** (54 mg, 69%) and **26** (17 mg, 24%) as colorless syrups. **25**: R_f 0.50 (12:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −38.5 (c 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 2H, J = 7.2 Hz), 7.98 (d, 2H, J = 7.2 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.50 (t, 1H, J = 7.2 Hz), 7.38 (t, 2H, J = 8.0 Hz), 7.29 (td, 2H, J = 2.0, 8.0 Hz), 5.32 (s, 1H), 5.08 (d, 1H, J = 2.0 Hz), 5.04 (s, 1H), 4.81 (d, 1H, J = 11.6 Hz), 4.53 (dd, 1H, J = 3.2, 11.6 Hz), 4.40 (s, 2H), 4.13 (dd, 1H, J = 3.2, 4.4 Hz), 4.09 (dd, 1H, J = 2.0, 2.8 Hz), 3.96 (t, 1H, J = 4.4 Hz), 3.72 (dd, 1H, J = 6.0, 10.0 Hz), 3.63 (dd, 1H, J = 6.4, 10.0 Hz), 3.54 (dd, 1H, J = 5.6, 10.0 Hz), 3.44 (s, 3H), 0.88 (s,9H), 0,87 (s, 9H), 0.86 (s, 9H), 0.81 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.02 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.1, 165.4, 133.2, 132.8, 130.0, 129.8, 129.7, 129.4, 128.4, 128.2, 108.1, 106.8, 85.3, 83.8, 83.2, 81.1, 81.0, 79.1, 73.5, 64.6, 63.0, 54.7, 25.9, 25.8, 25.7, 25.6, 18.3, 18.2, 17.9, 17.8, −3.9, −4.2, −4.3, −4.4, −4.5, −4.8, −5.3, −5.4; IR (KBr) 2954, 2932, 2894, 2858, 1728, 1466, 1259, 1110, 839, 778, 711 cm^{-1}; HRMS (ESI) calcd for $C_{50}H_{86}O_{12}Si_4$ [M + Na]$^+$ 1013.5094, found 1013.5086. **26**: R_f 0.55 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +24.2 (c 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, 2H, J = 1.2, 8.4 Hz), 7.96 (dd, 2H, J = 1.2, 8.4 Hz), 7.55 (td, 2H, J = 1.2, 7.6 Hz), 7.17−7.39 (m, 24H), 5.71 (d, 1H, J = 1.6 Hz), 5.07 (d, 1H, J = 4.8 Hz), 5.01 (s, 1H), 4.72 (d, 1H, J = 12.0 Hz), 4.60−4.66 (m, 3H), 4.53−4.59 (m, 2H), 4.50 (d, 1H, J = 12.0 Hz), 4.41−4.44 (m, 1H), 4.24−4.38 (m, 5H), 4.05 (dd, 1H, J = 4.4, 8.0 Hz), 3.93 (dd, 1H, J = 4.0, 7.6 Hz), 3.66−3.70 (m, 1H), 3.53 (s, 1H), 3.51 (s, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 165.6, 138.6, 138.22, 138.20, 137.5, 133.2, 133.1, 129.75, 129.72, 129.70, 129.6, 128.5, 128.41, 128.38, 128.3, 128.2, 128.11, 128.07, 127.97, 127.7, 127.6, 127.5, 127.4, 127.3, 107.3, 100.4, 83.8, 83.0, 82.7, 80.0, 79.7, 79.6, 76.6, 73.1, 72.5, 72.4, 69.9, 63.5, 54.7; IR (KBr) 3063, 3031, 2924, 2869, 1723, 1453, 1273, 1110, 1025, 709 cm^{-1}; HRMS (ESI) calcd for $C_{54}H_{54}O_{12}$ [M + Na]$^+$ 917.3513, found 917.3515.

Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranoside (27) and Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-benzyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranoside (28). Prepared from **2** (54.6 mg, 0.076 mmol), **7** (49 mg, 0.076 mmol), and **13** (35 mg, 0.069 mmol). The residue was purified by column chromatography (15:1, petroleum ether−EtOAc) to afford compounds **27** (51 mg, 67%) and **28** (15 mg, 21%) as colorless syrups. **27**: R_f 0.50 (6:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −94.4 (c 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H, J = 7.6 Hz), 8.04 (d, 2H, J = 7.6 Hz), 7.89 (t, 4H, J = 8.0 Hz), 7.25−7.56 (m, 12H), 5.75−5.81 (m, 1H), 5.56 (d, 1H, J = 5.2 Hz), 5.43 (s, 1H), 5.16 (s, 1H), 5.11 (s, 1H), 5.08 (d, 1H, J = 1.6 Hz), 4.74 (dd, 1H, J = 3.6, 5.6 Hz), 4.39 (dd, 1H, J = 1.2, 5.6 Hz), 4.08−4.12 (m, 2H), 3.92 (dd, 1H, J = 6.0, 10.0 Hz), 3.82 (dd, 1H, J = 6.0, 9.2 Hz), 3.70 (dd, 1H, J = 5.6, 10.0 Hz), 3.60 (dd, 1H, J = 6.4, 10.0 Hz), 3.48 (s, 3H), 0.87 (s, 9H), 0.85 (s, 9H), 0.84 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.7, 165.6, 165.5, 165.3, 133.3, 133.2, 133.1, 132.9, 130.0, 129.82, 129.77, 129.72, 129.4, 129.1, 129.0, 128.34, 128.31, 128.26, 128.25, 106.5, 105.9, 85.1, 84.8, 82.5, 80.3, 77.4, 76.4, 72.8, 71.0, 64.9, 54.8, 26.0, 25.9, 25.6, 18.3, 18.2, 17.8, −3.7, −4.4, −4.8, −4.9, −5.3, −5.4; IR (KBr) 2954, 2931, 2891, 2857, 1727, 1454, 1264, 1109, 1067, 837, 778, 711 cm^{-1}; HRMS (ESI) calcd for $C_{59}H_{82}O_{15}Si_3$ [M + Na]$^+$ 1137.4859, found 1137.4866. **28**: R_f 0.45 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −35.0 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H, J = 7.2 Hz), 8.03 (d, 2H, J = 7.2 Hz), 7.91 (t, 4H, J = 8.8 Hz), 7.09−7.58 (m, 27H), 5.78−5.84 (m, 1H), 5.58 (d, 1H, J = 5.2 Hz), 5.43 (s, 1H), 5.28 (s, 1H), 5.24 (s, 1H), 5.13 (s, 1H), 4.66−4.74 (m, 3H), 4.50 (d, 1H, J = 12.0 Hz), 4.46 (d, 1H, J = 12.0 Hz), 4.33 (d, 2H, J = 12.0 Hz), 4.30 (dd, 1H, J = 2.0, 6.0 Hz), 4.10 (dd, 1H, J = 6.8, 10.0 Hz), 3.99 (d, 1H, J = 5.6 Hz), 3.90 (dd, 1H, J = 6.0, 10.0 Hz), 3.65−3.74 (m, 3H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.7, 165.6, 165.5, 165.2, 138.10, 138.09, 137.7, 133.29, 133.26, 133.2, 133.0, 129.9, 129.8, 129.7, 129.6, 129.3, 129.04, 129.00, 128.35, 128.31, 128.30, 128.29, 128.25, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 106.5, 106.1, 83.0, 82.7, 82.5, 81.7, 80.5, 77.4, 76.2, 73.41, 73.38, 72.1, 70.97, 70.94, 64.7, 54.8; IR (KBr) 2928, 1724, 1452, 1267, 1108, 1066, 710 cm^{-1}; HRMS (ESI) calcd for $C_{62}H_{58}O_{15}$ [M + Na]$^+$ 1065.3673, found 1065.3676.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranoside (29). Prepared from **2** (54.6 mg, 0.076 mmol), **3** (54 mg, 0.076 mmol), and **13** (35 mg, 0.069 mmol). The residue was purified by column chromatography (12:1, petroleum ether−EtOAc) to afford compounds **27** (55 mg, 72%) and **29** (21 mg, 28%) as colorless syrups. **29**: R_f 0.45 (5:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −22.3 (c 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, 2H, J = 7.6 Hz), 8.06 (d, 2H, J = 7.2 Hz), 8.02 (d, 2H, J = 7.2 Hz), 7.93 (d, 2H, J = 7.2 Hz), 7.91 (d, 2H, J = 7.2 Hz), 7.25−7.56 (m, 15H), 5.79−5.84 (m, 1H), 5.57 (d, 1H, J = 5.6 Hz), 5.44 (s, 1H), 5.15 (s, 1H), 5.11−5.13 (m, 2H), 4.74 (dd, 1H, J = 3.6, 5.6 Hz), 4.51 (dd, 1H, J = 4.0, 11.2 Hz), 4.45 (d, 1H, J = 4.8 Hz), 4.35 (dd, 1H, J = 6.4, 11.2 Hz), 4.12−4.24 (m, 3H), 3.91 (dd, 1H, J = 6.0, 10.0 Hz), 3.46 (s, 3H), 0.88 (s, 9H), 0.85 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 165.7, 165.6, 165.5, 165.2, 133.28, 133.25, 133.21, 133.0, 132.9, 129.97, 129.96, 129.9, 129.80, 129.75, 129.73, 129.6, 129.2, 129.1, 129.0, 128.34, 128.33, 128.31, 128.29, 106.5, 105.8, 85.5, 84.8, 82.5, 80.4, 77.4, 76.5, 71.0, 70.2, 66.6, 64.8, 54.8, 25.8, 25.6, 18.2, 17.7, −4.2, −4.4, −4.6, −5.0; IR (KBr) 3425, 2956, 2932, 2857, 1726, 1636, 1453, 1399, 1271, 1112, 838, 711 cm^{-1}; HRMS (ESI) calcd for $C_{60}H_{72}O_{16}Si_2$ [M + Na]$^+$ 1127.4257, found 1127.4252.

Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-*β*-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-*β*-D-galactofuranoside (30) and Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-*β*-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-*β*-D-galactofuranoside (31). Prepared from **2** (54.6 mg, 0.076 mmol), **3** (54 mg, 0.076 mmol), and **12** (35 mg, 0.069 mmol). The residue was purified by column chromatography (12:1, petroleum ether−EtOAc) to afford compounds **30** (53 mg, 69%) and **31** (20 mg, 26%)

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as colorless syrups. **30**: R_f 0.55 (5:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −4.4 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 2H, *J* = 7.2 Hz), 8.05 (d, 2H, *J* = 7.2 Hz), 7.94 (t, 4H, *J* = 8.0 Hz), 7.22−7.60 (m, 12H), 5.74 (d, 1H, *J* = 3.6 Hz), 5.48 (s, 2H), 5.30 (s, 1H), 5.11 (s, 1H), 4.74 (dd, 1H, *J* = 2.0, 10.8 Hz), 4.57−4.63 (m, 3H), 4.48 (dd, 1H, *J* = 2.4, 6.4 Hz), 4.18 (dd, 1H, *J* = 2.8, 6.4 Hz), 3.83−3.86 (m, 1H), 3.71 (dd, 1H, *J* = 4.4, 10.4 Hz), 3.60 (dd, 1H, *J* = 7.2, 10.4 Hz), 3.45 (s, 3H), 0.91 (s, 9H), 0.83 (s, 9H), 0.73 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), −0.01 (s, 3H), −0.02 (s, 3H), −0.03 (s, 3H), −0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 165.5, 165.4, 165.3, 133.4, 133.2, 133.1, 132.8, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 129.2, 128.5, 128.3, 128.2, 128.1, 106.7, 106.0, 85.2, 85.0, 82.1, 81.7, 77.3, 76.3, 74.1, 73.4, 65.6, 64.7, 55.0, 26.0, 25.9, 25.5, 18.4, 18.3, 17.7, −3.6, −4.5, −4.8, −4.9, −5.4; IR (KBr) 2954, 2929, 2857, 1727, 1454, 1268, 1110, 1065, 837, 778, 711 cm^{-1}; HRMS (ESI) calcd for $C_{59}H_{82}O_{15}Si_3$ $[M + Na]^+$ 1137.4859, found 1137.4854. **31**: R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −0.1 (*c* 1.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, 2H, *J* = 1.6, 8.0 Hz), 8.02 (td, 4H, *J* = 1.2, 8.0 Hz), 7.96 (td, 4H, *J* = 0.8, 7.2 Hz), 7.23−7.59 (m, 15H), 5.75 (d, 1H, *J* = 5.2 Hz), 5.47 (s, 1H), 5.46 (d, 1H, *J* = 0.8 Hz), 5.30 (s, 1H), 5.10 (s, 1H), 4.75 (dd, 1H, *J* = 3.6, 11,6 Hz), 4.60−4.65 (m, 2H), 4.53−4.58 (m, 1H), 4.50 (dd, 1H, *J* = 3.6, 11.6 Hz), 4.48 (dd, 1H, *J* = 3.2, 7.2 Hz), 4.29 (dd, 1H, *J* = 4.0, 6.4 Hz), 4.25 (dd, 1H, *J* = 7.2, 11.2 Hz), 4.20 (dd, 1H, *J* = 3.6, 6.8 Hz), 3.45 (s, 3H), 0.90 (s, 9H), 0.84 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H), 0.01 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 166.2, 165.5, 165.4, 165.3, 133.4, 133.3, 133.2, 133.0, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.63, 129.60, 129.21, 129.19, 129.15, 128.5, 128.4, 128.32, 128.29, 128.2, 106.7, 106.0, 85.3, 85.1, 81.8, 81.7, 77.0, 76.4, 74.0, 70.6, 66.8, 64.5, 55.0, 25.9, 25.5, 18.2, 17.7, −4.2, −4.4, −4.5, −5.0; IR (KBr) 2954, 2931, 2857, 1726, 1452, 1270, 1110, 1065, 837, 711 cm^{-1}; HRMS (ESI) calcd for $C_{60}H_{72}O_{16}Si_2$ $[M + Na]^+$ 1127.4257, found 1127.4256.

Methyl 2,6-Di-*O*-benzoyl-3,5-*O*-(di-*tert*-butylsilanediyl)-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (32). Prepared from **4** (50 mg, 0.081 mmol), **6** (55.5 mg, 0.081 mmol), and **13** (37 mg, 0.073 mmol). The residue was purified by column chromatography (8:1, petroleum ether−EtOAc) to afford compounds **32** (30 mg, 40%) and **33** (44 mg, 56%) as colorless syrups. **32**: R_f 0.50 (6:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −4.9 (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24−8.09 (m, 25H), 5.89 (dd, 1H, *J* = 6.0, 9.6 Hz), 5.57 (d, 1H, *J* = 5.2 Hz), 5.43 (d, 1H, *J* = 0.8 Hz), 5.28−5.30 (m, 1H), 5.17 (s, 1H), 5.11 (d, 1H, *J* = 2.0 Hz), 4.78 (td, 1H, *J* = 3.6, 6.8 Hz), 4.69 (dd, 1H, *J* = 3.6, 5.2 Hz), 4.63 (dd, 1H, *J* = 3.2, 12.0 Hz), 4.56 (dd, 1H, *J* = 6.4, 10.4 Hz), 4.52 (dd, 1H, *J* = 7.2, 12.0 Hz), 4.42 (dd, 1H, *J* = 7.2, 10.4 Hz), 4.07 (d, 2H, *J* = 5.6 Hz), 3.49 (s, 3H), 0.99 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.6, 165.8, 165.7, 165.5, 165.4, 133.3, 133.2, 133.1, 133.0, 132.9, 130.2, 130.0, 129.9, 129.8, 129.75, 129.68, 129.66, 129.3, 129.1, 129.0, 128.35, 128.33, 128.31, 107.1, 106.6, 83.3, 82.2, 80.8, 77.5, 76.1, 74.7, 71.2, 70.9, 67.3, 64.8, 54.8, 27.1, 26.9, 21.6, 20.7; IR (KBr) 3433, 2936, 2861, 1727, 1452, 1397, 1271, 1110, 711 cm^{-1}; HRMS (ESI) calcd for $C_{56}H_{60}O_{16}Si$ $[M + Na]^+$ 1039.3548, found 1039.3552.

General Procedure for the One-Pot Glycosylations via Simultaneous Addition of Glycosyl Building Blocks. To a stirred solution (0.14 M) of donor A (1.1 equiv), thioglycoside acceptor B (1.1 equiv), and the methyl glycoside acceptor (1.0 equiv) in dry CH_2Cl_2 was added freshly activated 4 Å molecular sieves (250 wt % with respect to the donor). The mixture was stirred under nitrogen for 30 min at room temperature and then was cooled to −80 °C, followed by addition of NIS (2.5 equiv) and TfOH (0.15 equiv). Then the mixture was gradually warmed to −50 °C for 1 h and next was warmed to 0 °C for another 1 h. Finally, the resulting mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated in vacuo. The residue was purified by column chromatography to afford products.

Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (34) and Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (35). Prepared from **2** (50 mg, 0.070 mmol), **10** (40.5 mg, 0.070 mmol), and **12** (32 mg, 0.063 mmol). The residue was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford compound **34** (51 mg, 51%), **31** (12 mg, 16%) and **35** (11 mg, 8%) as colorless syrups. **34**: R_f 0.50 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −19.7 (*c* 1.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16−8.06 (m, 35H), 5.87−5.90 (m, 1H), 5.80 (d, 1H, *J* = 4.4 Hz), 5.72 (s, 1H), 5.61 (s, 1H), 5.60 (d, 1H, *J* = 5.2 Hz), 5.47 (d, 1H, *J* = 0.8 Hz), 5.10 (s, 1H), 5.04 (d, 1H, *J* = 2.0 Hz), 5.02 (s, 1H), 4.92 (t, 1H, *J* = 4.4 Hz), 4.73−4.78 (m, 1H), 4.64−4.67 (m, 2H), 4.53 (t, 1H, *J* = 4.4 Hz), 4.36 (dd, 1H, *J* = 2.4, 6.4 Hz), 4.03−4.09 (m, 2H), 3.93 (dd, 1H, *J* = 8.0, 11.2 Hz), 3.80 (td, 1H, *J* = 2.4, 5.6 Hz), 3.70 (dd, 1H, *J* = 5.6, 10.0 Hz), 3.60 (dd, 1H, *J* = 6.4, 10.0 Hz), 3.41 (s, 3H), 0.86 (s, 9H), 0.80 (s, 9H), 0.77 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H), 0.01 (s, 3H), −0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.1, 165.8, 165.5, 165.4, 165.3, 165.2, 165.1, 133.4, 133.3, 133.1, 133.03, 132.99, 132.91, 132.7, 129.94, 129.92, 129.8, 129.69, 129.67, 129.4, 129.0, 128.95, 128.90, 128.8, 128.5, 128.4, 128.3, 128.21, 128.19, 128.13, 128.08, 106.7, 106.6, 105.3, 85.2, 84.4, 82.2, 82.1, 82.0, 81.7, 77.9, 77.0, 76.3, 73.0, 72.7, 71.8, 66.8, 65.0, 64.5, 54.8, 26.0, 25.9, 25.6, 18.3, 18.2, 17.7, −3.6, −4.4, −4.9, −5.0, −5.4; IR (KBr) 3449, 3425, 1727, 1637, 1400, 1270, 1113, 838, 711 cm^{-1}; HRMS (ESI) calcd for $C_{86}H_{104}O_{23}Si_3$ $[M + Na]^+$ 1611.6168, found 1611.6180. **35**: R_f 0.50 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −25.6 (*c* 1.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.06−8.05 (m, 50H), 5.83−5.87 (m, 2H), 5.76 (d, 1H, *J* = 5.4 Hz), 5.75 (s, 1H), 5.68 (s, 2H), 5.65 (s, 1H), 5.59 (d, 1H, *J* = 4.8 Hz), 5.44 (s, 1H), 5.07 (s, 1H), 5.01 (d, 1H, *J* = 3.6 Hz), 4.96 (s, 1H), 4.86 (dd, 2H, *J* = 4.8, 8.4 Hz), 4.62−4.75 (m, 6H), 4.50 (t, 1H, *J* = 4.8 Hz), 4.34 (dd, 1H, *J* = 2.4, 6.6 Hz), 4.04 (dd, 1H, *J* = 3.0, 10.8 Hz), 4.02 (dd, 1H, *J* = 3.0, 9.0 Hz), 3.87 (dd, 1H, *J* = 9.0, 10.8 Hz), 3.79 (td, 1H, *J* = 3.0, 6.0 Hz), 3.69 (dd, 1H, *J* = 6.0, 10.2 Hz), 3.58 (dd, 1H, *J* = 6.0, 10.2 Hz), 3.37 (s, 3H), 0.85 (s, 9H), 0.79 (s, 9H), 0.75 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H), −0.01 (s, 3H), −0.03 (s, 3H), −0.06 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) 166.1, 165.9, 165.8, 165.6, 165.5, 165.4, 165.3, 165.2, 165.1, 165.0, 133.4, 133.3, 133.2, 133.05, 132.99, 132.97, 132.94, 132.8, 132.6, 129.97, 129.95, 129.87, 129.84, 129.78, 129.77, 129.73, 129.67, 129.64, 129.62, 129.5, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.18, 128.12, 128.08, 128.0, 106.9, 106.6, 105.2, 105.1, 85.3, 84.5, 83.1, 82.3, 82.2, 81.8, 81.7, 78.1, 77.1, 76.3, 73.0, 72.7, 72.2, 72.0, 67.3, 65.1, 65.0, 64.3, 54.8, 26.0, 25.9, 25.6, 18.3, 18.2, 17.7, −3.7, −4.5, −4.9, −5.0, −5.40, −5.43; IR (KBr) 2954, 2931, 2857, 1726, 1452, 1269, 1110, 838, 711 cm^{-1}; HRMS (ESI) calcd for $C_{113}H_{126}O_{31}Si_3$ $[M + Na]^+$ 2085.7483, found 2085.7483.

General Procedure for the One-Pot Glycosylations via a Sequential Addition of Glycosyl Building Blocks. To a stirred solution (0.14 M) of donor A (1.1 equiv) and thioglycoside acceptor B (1.0 equiv) in dry CH_2Cl_2 was added freshly activated 4 Å molecular sieves (250 wt % with respect to the donor). The mixture was stirred under nitrogen for 30 min at room temperature and then was cooled to −80 °C, followed by addition of NIS (1.25 equiv) and TfOH (0.1 equiv). The reaction mixture was gradually warmed to −50 °C for 1 h, and then the mixture of the methyl glycoside acceptor (0.95 equiv) dissolved in CH_2Cl_2 was added dropwise, followed by addition of NIS (1.25 equiv) and TfOH (0.1 equiv). After being warmed to −20 °C for another 1 h, the resulting mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, concentrated, and purified by column chromatography to afford products.

Methyl 2-*O*-Benzoyl-3,5,6-tri-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (34). Prepared from **2** (50 mg, 0.070 mmol), **10** (37 mg, 0.063 mmol), and **12** (30 mg, 0.060 mmol). The residue was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford compound **34** (88 mg, 88% over two steps) as a colorless syrup.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (38).

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Prepared from **3** (49 mg, 0.069 mmol), **10** (37 mg, 0.063 mmol), and **12** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **38** (92 mg, 92% over two steps) as a colorless syrup. R_f 0.50 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −8.7 (*c* 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−8.04 (m, 40H), 5.87−5.91 (m, 1H), 5.80 (d, 1H, *J* = 5.2 Hz), 5.74 (s, 1H), 5.62 (s, 1H), 5.60 (d, 1H, *J* = 5.2 Hz), 5.48 (d, 1H, *J* = 0.8 Hz), 5.11 (s, 1H), 5.06 (d, 1H, *J* = 1.6 Hz), 5.03 (s, 1H), 4.93 (t, 1H, *J* = 4.4 Hz), 4.73−4.77 (m, 1H), 4.65−4.70 (m, 2H), 4.53 (t, 1H, *J* = 4.4 Hz), 4.43 (dd, 1H, *J* = 3.6, 11.2 Hz), 4.39 (dd, 1H, *J* = 2.0, 5.6 Hz),4.31 (dd, 1H, *J* = 6.4, 11.2 Hz), 4.14−4.18 (m, 1H), 4.10 (dd, 1H, *J* = 4.0, 10.0 Hz), 4.09 (dd, 1H, *J* = 4.0, 11.6 Hz), 3.94 (dd, 1H, *J* = 8.0, 11.2 Hz), 3.41 (s, 3H), 0.84 (s, 9H), 0.76 (s, 9H), 0.06 (s, 6H), 0.01 (s, 3H), −0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 166.1, 165.8, 165.6, 165.5, 165.4, 165.2, 165.1, 133.4, 133.3, 133.2, 133.1, 133.0, 132.92, 132.91, 132.7, 129.97, 129.94, 129.89, 129.88, 129.79, 129.74, 129.71, 129.67, 129.66, 129.59, 129.2, 129.0, 128.96, 128.91, 128.86, 128.5, 128.4, 128.31, 128.28, 128.27, 128.22, 128.16, 128.09, 106.64, 106.61, 105.3, 85.2, 84.8, 82.2, 82.1, 82.0, 81.8, 77.8, 77.1, 76.3, 73.1, 71.7, 70.2, 66.9, 66.7, 64.5, 54.9, 25.8, 25.5, 18.2, 17.7, −4.2, −4.5, −4.6, −5.0; IR (KBr) 3437, 2956, 2931, 1726, 1271, 1111, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ $[M + Na]^+$ 1601.5566, found 1601.5575.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (42). Prepared from **3** (49 mg, 0.069 mmol), **9** (37 mg, 0.063 mmol), and **13** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **42** (93 mg, 93% over two steps) as a colorless syrup. R_f 0.55 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −14.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−8.07 (m, 40H), 5.85 (td, 1H, *J* = 2.8, 6.4 Hz), 5.76 (d, 1H, *J* = 4.8 Hz), 5.54 (d, 1H, *J* = 5.6 Hz), 5.50 (s, 1H), 5.46 (d, 1H, *J* = 0.8 Hz), 5.41 (d, 1H, *J* = 0.8 Hz), 5.33 (dd, 1H, *J* = 1.2, 2.8 Hz), 5.30 (s, 1H), 5.11 (s, 1H), 4.71 (dd, 1H, *J* = 2.8, 5.6 Hz), 4.55−4.70 (m, 4H), 4.47−4.51 (m, 2H), 4.24−4.29 (m, 2H), 4.15−4.20 (m, 2H), 3.94 (dd, 1H, *J* = 6.4, 10.0 Hz), 3.38 (s, 3H), 0.86 (s, 9H), 0.72 (s, 9H), 0.08 (s, 6H), 0.00 (s, 3H), −0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 166.0, 165.71, 165.69, 165.5, 165.4, 165.3, 165.2, 133.30, 133.27, 133.2, 133.0, 132.9, 132.8, 130.01, 129.97, 129.95, 129.89, 129.8, 129.7, 129.65, 129.61, 129.57, 129.24, 129.19, 129.12, 129.1, 129.0, 128.5, 128.4, 128.35, 128.33, 128.30, 128.24, 128.18, 106.8, 105.8, 105.6, 85.2, 85.0, 82.6, 82.3, 81.6, 80.7, 77.5, 77.0, 76.2, 73.4, 70.8, 70.2, 66.9, 65.3, 64.7, 55.0, 25.8, 25.5, 18.2, 17.7, −4.1, −4.4, −4.5, −4.9; IR (KBr) 3430, 2955, 2930, 1726, 1270, 1111, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ $[M + Na]^+$ 1601.5566, found 1601.5571.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranoside (44). Prepared from **3** (49 mg, 0.069 mmol), **8** (37 mg, 0.063 mmol), and **11** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **44** (70 mg, 70% over two steps) as a colorless syrup. R_f 0.40 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −16.1 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−8.20 (m, 40H), 5.96−6.01 (m, 2H), 5.58 (s, 1H), 5.53 (s, 1H), 5.41 (s, 1H), 5.36 (s, 1H), 5.34 (s, 1H), 5.14 (s, 1H), 4.94 (dd, 1H, *J* = 2.8, 12.0 Hz), 4.81 (dd, 1H, *J* = 9.2, 11.6 Hz), 4.74 (dd, 1H, *J* = 2.8, 12.0 Hz), 4.69 (dd, 1H, *J* = 3.6, 11.6 Hz), 4.64 (dd, 1H, *J* = 2.0, 5.6 Hz), 4.42−4.57 (m, 5H), 4.33−4.37 (m, 2H), 4.22 (dd, 1H, *J* = 5.6, 9.2 Hz), 3.46 (s, 3H), 0.84 (s, 9H), 0.75 (s, 9H), 0.15 (s, 3H), 0.11 (s, 6H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.4, 166.1, 165.9, 165.8, 165.6, 165.4, 165.21, 165.19, 133.3, 133.18, 133.17, 133.05, 133.02, 132.83, 132.76, 132.7, 130.1, 130.0, 129.91, 129.88, 129.8, 129.75, 129.71, 129.69, 129.61, 129.58, 129.55, 129.4, 129.2, 129.1, 129.0, 128.5, 128.43, 128.41, 128.33, 128.31, 128.19, 128.15, 128.13, 107.0, 105.1, 103.9, 87.9, 83.5, 82.6, 81.4, 81.32, 81.26, 79.4, 78.9, 76.1, 70.7, 69.8, 69.5, 66.6, 64.7, 64.1, 54.8, 25.8, 25.5, 18.1, 17.7, −4.4, −4.5, −4.7, −5.1; IR (KBr) 3449, 2956, 2932, 1726, 1270, 1111, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ $[M + Na]^+$ 1601.5566, found 1601.5575.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (45). Prepared from **3** (49 mg, 0.069 mmol), **8** (37 mg, 0.063 mmol), and **12** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **45** (77 mg, 77% over two steps) as a colorless syrup. R_f 0.45 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +3.1 (*c* 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−8.13 (m, 40H), 5.91−5.96 (m, 1H), 5.80 (s, 1H), 5.71 (d, 1H, *J* = 4.8 Hz), 5.61 (d, 1H, *J* = 1.6 Hz), 5.59 (s, 1H), 5.39 (s, 1H), 5.12 (s, 1H), 4.93 (s, 1H), 4.84−4.90 (m, 3H), 4.70−4.76 (m, 3H), 4.42−4.53 (m, 3H), 4.20−4.28 (m, 3H), 4.05−4.09 (m, 1H), 3.45 (s, 3H), 0.69 (s, 9H), 0.68 (s, 9H), 0.01 (s, 6H), 0.004 (s, 3H), −0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 166.1, 165.91, 160.90, 165.5, 165.4, 165.1, 164.7, 133.4, 133.1, 132.9, 132.7, 130.1, 129.95, 129.90, 129.86, 129.80, 129.73, 129.69, 129.5, 129.23, 129.18, 129.1, 129.0, 128.5, 128.4, 128.3, 128.26, 128.22, 128.15, 128.14, 106.5, 104.9, 104.0, 87.9, 83.39, 83.36, 82.1, 81.8, 81.5, 78.9, 77.6, 76.3, 72.0, 70.7, 69.8, 66.5, 64.7, 64.2, 54.8, 25.7, 25.4, 18.0, 17.5, −4.4, −4.6, −4.7, −5.5; IR (KBr) 3458, 3421, 2956, 2931, 1725, 1270, 1113, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ $[M + Na]^+$ 1601.5566, found 1601.5575.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (46). Prepared from **3** (49 mg, 0.069 mmol), **8** (37 mg, 0.063 mmol), and **13** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **46** (79 mg, 79% over two steps) as a colorless syrup. R_f 0.50 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −20.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−8.13 (m, 40H), 5.84−5.89 (m, 2H), 5.57 (d, 1H, *J* = 5.6 Hz), 5.45 (d, 1H, *J* = 1.2 Hz), 5.42 (s, 1H), 5.35 (s, 1H), 5.29 (d, 1H, *J* = 1.2 Hz), 5.23 (d, 1H, *J* = 1.6 Hz), 5.15 (s, 1H), 4.84 (dd, 1H, *J* = 3.2, 5.6 Hz), 4.67 (dd, 1H, *J* = 7.6, 11.6 Hz), 4.63 (dd, 1H, *J* = 4.8, 11.6 Hz), 4.54 (dd, 1H, *J* = 2.8, 6.4 Hz), 4.49 (dd, 1H, *J* = 4.0, 11.6 Hz), 4.41−4.45 (m, 2H), 4.31 (dd, 1H, *J* = 6.4, 11.6 Hz), 4.22 (t, 1H, *J* = 5.2 Hz), 4.12−4.18 (m, 2H), 3.97 (dd, 1H, *J* = 6.4, 10.0 Hz), 3.51 (s, 3H), 0.85 (s, 9H), 0.75 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H), −0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 166.0, 165.8, 165.7, 165.54, 165.53, 165.13, 165.11, 133.3, 133.2, 133.1, 133.06, 133.04, 132.9, 132.8, 130.03, 130.00, 129.98, 129.94, 129.85, 129.83, 129.75, 129.74, 129.70, 129.64, 129.59, 129.53, 129.2, 129.11, 129.10, 128.4, 128.34, 128.31, 128.25, 128.22, 128.20, 106.5, 106.2, 104.3, 86.6, 84.4, 82.6, 81.5, 81.2, 80.5, 79.1, 77.5, 76.2, 70.8, 70.7, 69.4, 66.6, 64.8, 63.9, 54.9, 25.8, 25.6, 18.1, 17.7, −4.3, −4.5, −4.6, −5.2; IR (KBr) 3445, 2955, 2930, 1726, 1269, 1111, 839, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ $[M + Na]^+$ 1601.5566, found 1601.5570.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranoside (47). Prepared from **3** (49 mg, 0.069 mmol), **9** (37 mg, 0.063 mmol), and **11** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **47** (74 mg, 74% over two steps) as a colorless syrup. R_f 0.40 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −13.3 (*c* 1.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−8.12 (m, 40H), 5.92−5.97 (m, 1H), 5.85 (d, 1H, *J* = 3.6 Hz), 5.61 (s, 1H), 5.58 (s, 1H), 5.51 (s, 1H), 5.36 (s, 1H), 5.34 (dd, 1H, *J* = 1.6, 3.2 Hz), 5.13 (s, 1H), 4.49−4.74 (m, 10H), 4.30 (dd, 1H, *J* = 6.8, 11.2 Hz), 4.25 (dd, 1H, *J* = 3.2, 6.0 Hz), 4.15−4.18 (m, 1H), 3.43 (s, 3H), 0.86 (s, 9H), 0.66 (s, 9H), 0.09 (s, 6H), −0.05 (s, 3H), −0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 166.0, 165.9, 165.8, 165.40, 165.36, 165.34, 165.1, 133.3, 133.17, 133.16, 133.1, 133.0, 132.9, 132.8, 132.6, 130.1, 129.95, 129.93, 129.91, 129.89, 129.8, 129.7, 129.64, 129.56, 129.54, 129.52, 129.4, 129.33, 129.27, 129.1, 129.0, 128.5, 128.4, 128.32, 128.30, 128.27, 128.2, 128.1, 107.0, 106.2, 105.1, 85.2, 84.5, 83.5, 82.0, 81.4, 81.1, 80.1, 76.8, 75.9, 74.1, 70.1, 69.5, 67.0, 65.4, 63.6, 54.8, 25.9, 25.4, 18.2, 17.6,

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−4.1, −4.52, −4.53, −5.0; IR (KBr) 3444, 2955, 2930, 1726, 1271, 1111, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ [M + Na]$^+$ 1601.5566, found 1601.5574.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (48). Prepared from **3** (49 mg, 0.069 mmol), **9** (37 mg, 0.063 mmol), and **12** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **48** (84 mg, 84% over two steps) as a colorless syrup. R_f 0.50 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −1.2 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−8.09 (m, 40H), 5.82 (dd, 1H, *J* = 1.6, 5.2 Hz), 5.80 (d, 1H, *J* = 5.2 Hz), 5.74 (s, 1H), 5.71 (d, 1H, *J* = 1.6 Hz), 5.50 (s, 1H), 5.43 (d, 1H, *J* = 0.8 Hz), 5.36−5.38 (m, 1H), 5.07 (s, 1H), 4.83 (dd, 1H, *J* = 3.2, 5.2 Hz), 4.46−4.75 (m, 9H), 4.24−4.31 (m, 2H), 4.12−4.17 (m, 1H), 3.39 (s, 3H), 0.84 (s, 9H), 0.70 (s, 9H), 0.06 (s, 6H), −0.03 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.18, 166.16, 165.9, 165.6, 165.5, 165.4, 165.3, 165.2, 133.4, 133.3, 133.2, 132.91, 132.90, 132.8, 132.7, 130.1, 130.0, 129.9, 129.86, 129.83, 129.74, 129.72, 129.67, 129.54, 129.52, 129.25, 129.23, 129.1, 128.9, 128.6, 128.5, 128.34, 128.30, 128.28, 128.2, 128.1, 128.0, 106.6, 105.7, 105.3, 85.4, 84.7, 82.8, 82.3, 81.9, 81.8, 77.2, 77.0, 76.0, 73.3, 73.2, 70.1, 67.1, 65.0, 64.5, 54.8, 25.9, 25.5, 18.2, 17.7, −4.1, −4.5, −4.6, −4.9; IR (KBr) 3450, 2955, 2929, 1726, 1272, 1112, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ [M + Na]$^+$ 1601.5566, found 1601.5573.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,5,6-tri-*O*-benzoyl-β-D-galactofuranoside (49). Prepared from **3** (49 mg, 0.069 mmol), **10** (37 mg, 0.063 mmol), and **11** (30 mg, 0.060 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **49** (79 mg, 79% over two steps) as a colorless syrup. R_f 0.50 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −18.0 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−8.08 (m, 40H), 5.96−5.99 (m, 1H), 5.87−5.91 (m, 1H), 5.62 (d, 1H, *J* = 4.4 Hz), 5.60 (s, 1H), 5.55 (s, 1H), 5.37 (d, 1H, *J* = 0.8 Hz), 5.14 (s, 1H), 5.12 (s, 1H), 5.07 (d, 1H, *J* = 2.0 Hz), 4.77 (t, 1H, *J* = 4.0 Hz), 4.72 (d, 1H, *J* = 2.0 Hz), 4.71 (s, 1H), 4.57 (dd, 1H, *J* = 2.8, 6.0 Hz), 4.47−4.51 (m, 2H) 4.43 (dd, 1H, *J* = 2.0, 6.0 Hz), 4.36 (dd, 1H, *J* = 6.4, 11.2 Hz), 4.16−4.21 (m, 3H), 3.98 (dd, 1H, *J* = 7.6, 11.2 Hz), 3.44 (s, 3H), 0.85 (s, 9H), 0.77 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.03 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 166.0, 165.9, 165.8, 165.43, 165.41, 165.2, 165.1, 133.2, 133.1, 133.0, 132.9, 132.7, 130.0, 129.98, 129.9, 129.8, 129.72, 129.7, 129.61, 129.59, 129.5, 129.4, 129.28, 129.27, 129.0, 128.8, 128.4, 128.3, 128.28, 128.26, 128.2, 128.1, 106.9, 106.4, 105.3, 85.2, 85.1, 82.8, 82.0, 81.6, 81.3, 80.5, 77.5, 76.3, 71.6, 70.1, 69.7, 66.7, 66.6, 63.7, 54.8, 25.8, 25.6, 18.2, 17.7, −4.2, −4.5, −4.6, −5.0; IR (KBr) 3445, 2955, 2931, 1726, 1270, 1111, 711 cm^{-1}; HRMS (ESI) calcd for $C_{87}H_{94}O_{24}Si_2$ [M + Na]$^+$ 1601.5566, found 1601.5575.

Phenyl 2-*O*-Benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-6-*O*-levulinoyl-1-thio-β-D-galactofuranoside (50). To a cooled (−10 °C) solution of **17** (490 mg, 1.00 mmol) in CH_2Cl_2 (20 mL) were added DMAP (18.3 mg, 0.15 mmol), DCC (516 mg, 2.50 mmol), and levulinic acid (151 mg, 1.30 mmol). The mixture was stirred at −10 °C for 10 h and then was stirred at 0 °C for 1 h. The reaction mixture was diluted with CH_2Cl_2, filtered, and concentrated. The residue was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford a colorless syrup. Next, to a cooled (0 °C) solution of the syrup (441 mg, 0.75 mmol) in dry DMF (2.5 mL) was added imidazole (102 mg, 1.50 mmol), followed by TBSCl (170 mg, 1.13 mmol). The mixture was stirred at 30 °C for 3 h and then was coevaporated with toluene to dryness. The residue was purified by column chromatography (11:1, petroleum ether−EtOAc) to afford **50** (500 mg, 71% over two steps) as a colorless syrup. R_f 0.50 (8:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −67.4 (*c* 1.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, 2H, *J* = 1.2, 8.0 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 7.52 (d, 2H, *J* = 7.2 Hz), 7.45 (t, 2H, *J* = 8.0 Hz), 7.21−7.31 (m, 3H), 5.58 (d, 1H, *J* = 2.0 Hz), 5.36 (t, 1H, *J* = 2.0 Hz), 4.48 (dd, 1H, *J* = 2.0, 5.2 Hz), 4.25−4.32 (m, 2H), 4.08−4.13 (m, 2H), 2.70−2.75 (m, 2H), 2.55−2.60 (m, 2H), 2.18 (s, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.12 (s, 3H), 0.11 (s, 6H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.3, 172.4, 165.4, 134.8, 133.4, 131.6, 129.8, 129.1, 128.8, 128.5, 127.2, 90.7, 85.4, 84.5, 76.2, 70.0, 66.0, 37.8, 29.8, 27.8, 25.8, 25.6, 18.2, 17.8, −4.2, −4.4, −4.6, −4.9; IR (KBr) 2955, 2931, 2891, 2857, 1725, 1469, 1361, 1263, 1111, 838, 779, 711 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{54}O_8SSi_2$ [M + Na]$^+$ 725.2970, found 725.2974.

Phenyl 2-*O*-Benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside (52). To a stirred solution of **50** (40 mg, 0.057 mmol) and **9** (32 mg, 0.054 mmol) in dry CH_2Cl_2 (1.50 mL) was added freshly activated 4 Å molecular sieves (250 wt % with respect to the donor). The mixture was stirred under nitrogen for 30 min at room temperature and then was cooled to −80 °C, followed by addition of NIS (14 mg, 0.063 mmol) and TfOH (1 μL, 0.011 mmol). After being gradually warmed to −60 °C, the solution was stirred at the same temperature for 1 h, and then the resulting mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The obtained crude material was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford the disaccharide product as a colorless syrup. Next, the disaccharide syrup (57 mg, 0.048 mmol) was dissolved in CH_3OH−CH_2Cl_2 (2:1, v/v, 1.4 mL) with addition of hydrazine acetate (8.8 mg, 0.096 mmol). The mixture was stirred overnight at room temperature and then was concentrated. The residue was purified by column chromatography (6:1, petroleum ether−EtOAc) to afford **52** (46 mg, 81% over two steps) as a colorless syrup. R_f 0.45 (5:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −53.9 (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H, *J* = 7.6 Hz), 8.10 (d, 2H, *J* = 7.2 Hz), 7.93 (t, 4H, *J* = 7.2 Hz), 7.61 (t, 1H, *J* = 7.6 Hz), 7.56 (d, 4H, *J* = 7.6 Hz), 7.48 (d, 2H, *J* = 7.6 Hz), 7.45 (d, 2H, *J* = 7.6 Hz), 7.40 (t, 3H, *J* = 7.6 Hz), 7.20−7.33 (m, 5H), 5.91 (dd, 1H, *J* = 2.4, 4.8 Hz), 5.80 (d, 1H, *J* = 2.4 Hz), 5.69 (t, 1H, *J* = 2.4 Hz), 5.45 (s, 1H), 5.33 (dd, 1H, *J* = 0.8, 2.4 Hz), 4.77 (dd, 1H, *J* = 3.2, 4.8 Hz), 4.67 (d, 1H, *J* = 1.6 Hz), 4.65 (s, 1H), 4.54−4.59 (m, 1H), 4.49 (dd, 1H, *J* = 2.8, 6.4 Hz), 4.35 (dd, 1H, *J* = 2.4, 6.8 Hz), 3.84−3.88 (m, 1H), 3.64−3.71 (m, 1H), 3.51−3.57 (m, 1H), 2.89 (t, 1H, *J* = 6.0 Hz), 0.88 (s, 9H), 0.74 (s, 9H), 0.12 (s, 6H), 0.01 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 166.1, 165.6, 165.3, 133.7, 133.5, 133.4, 133.2, 132.9, 132.0, 130.09, 130.07, 129.7, 129.6, 129.5, 129.3, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 127.6, 106.0, 90.5, 85.5, 83.9, 82.0, 81.4, 77.5, 76.1, 73.9, 71.5, 64.8, 63.4, 25.9, 25.5, 18.2, 17.7, −3.8, −4.4, −4.5, −4.9; IR (KBr) 3473, 3422, 2955, 2929, 2856, 1727, 1454, 1398, 1271, 1112, 837, 778, 711 cm^{-1}; HRMS (ESI) calcd for $C_{58}H_{70}O_{14}SSi_2$ [M + Na]$^+$ 1101.3917, found 1101.3917.

Methyl 2,6-Di-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→6)-2-*O*-benzoyl-3,5-di-*O*-*tert*-butyldimethylsilyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (54). Prepared from **3** (33 mg, 0.047 mmol), **52** (46 mg, 0.043 mmol), and **13** (31 mg, 0.041 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **54** (61 mg, 68% over two steps) as a colorless syrup. R_f 0.40 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −19.3 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−8.09 (m, 45H), 5.83 (td, 1H, *J* = 2.8, 6.4 Hz), 5.75 (d, 1H, *J* = 4.8 Hz), 5.53 (d, 1H, *J* = 5.6 Hz), 5.47 (s, 1H), 5.45 (s, 1H), 5.41 (d, 1H, *J* = 1.2 Hz), 5.28−5.33 (m, 2H), 5.22 (d, 1H, *J* = 1.2 Hz), 5.11 (s, 1H), 4.82 (s, 1H), 4.71 (dd, 1H, *J* = 2.8, 5.2 Hz), 4.67 (dd, 1H, *J* = 4.4, 12.4 Hz), 4.51−4.64 (m, 4H), 4.40−4.45 (m, 3H), 4.32 (dd, 1H, *J* = 6.4, 11.2 Hz), 4.14−4.19 (m, 2H), 4.06−4.12 (m, 2H), 3.98−4.04 (m, 1H), 3.94 (dd, 1H, *J* = 6.8, 10.0 Hz), 3.84 (dd, 1H, *J* = 1.2, 10.0 Hz), 3.38 (s, 3H), 0.88 (s, 9H), 0.85 (s, 18H), 0.71 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H), 0.06 (s, 6H), −0.01 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 166.0, 165.68, 165.67, 165.5, 165.35, 165.26, 165.23, 165.16, 133.27, 133.26, 133.25, 133.24, 133.10, 133.08, 133.0, 132.9, 132.7, 130.01, 129.96, 129.92, 129.90, 129.81, 129.80, 129.7, 129.63, 129.60, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.43, 128.42, 128.34, 128.30, 128.1, 106.7, 106.0, 105.8, 105.7, 85.7, 85.6, 84.9, 84.6, 82.5, 82.4, 81.5, 80.6, 77.5, 77.0, 76.6, 76.3, 73.5, 71.7, 70.6, 70.2, 70.1, 66.5, 65.2, 64.7, 55.0, 26.1, 25.8, 25.7, 25.5, 18.4, 18.2, 17.8,

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17.6, −3.7, −4.3, −4.4, −4.5, −4.6, −4.7, −5.0, −5.1; IR (KBr) 3440, 2954, 2930, 2857, 1727, 1270, 1112, 838, 712 cm^{-1}; HRMS (ESI) calcd for $C_{112}H_{136}O_{30}Si_4$ $[M + Na]^+$ 2095.8086, found 2095.8083.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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