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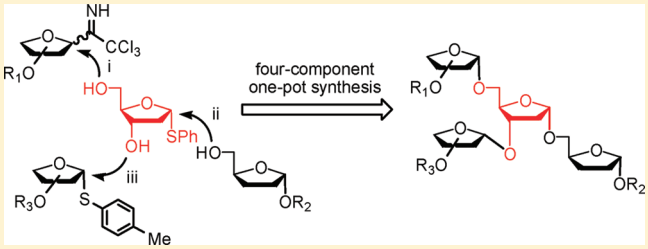
Regioselective Glycosylation Method Using Partially Protected Arabino- and Galactofuranosyl Thioglycosides as Key Glycosylating Substrates and Its Application to One-Pot Synthesis of Oligofuranoses

Li-Min Deng, Xia Liu, Xing-Yong Liang, and Jin-Song Yang*

Key Laboratory of Drug Targeting, Ministry of Education, and Department of Chemistry of Medicinal Natural Products, West China School of Pharmacy, Sichuan University, Chengdu 610041, People's Republic of China

Supporting Information

ABSTRACT: We describe in this paper the development of a novel regioselective furanosylation methodology using partially protected furanosyl thioglycosides as central glycosylating building blocks and its application in the efficient one-pot synthesis of a series of linear and branched-type arabino- and galactofuranoside fragments structurally related to the cell wall polysaccharides of *Mycobacterium tuberculosis*, *Streptococcus pneumoniae* serostype 35A, and sugar beet.



INTRODUCTION

Arabinofuranose (Araf) and galactofuranose (Galf) are very common structural constituents of polysaccharides present in many lower organisms including bacteria,[1,2] parasites,[3] and fungi.[4] The most impressive examples of these polysaccharides are two important glycoconjugates, an arabinogalactan (AG) and a lipoarabinomannan (LAM), which are major components of the cell wall of mycobacterial, including the human pathogens *Mycobacterium tuberculosis* and *Mycobacterium leprae*.[5] The ability of the organism to make these polysaccharides is crucial to its survival and pathogenicity, and therefore, the enzymes, such as mycobacterial arabino- and galactofuranosyltransferases (ArafTs and GalfTs), involved in the biosynthesis of the mycobacterial biopolymers are promising therapeutic targets of new drugs for treatment of mycobacterial diseases.[6] Chemical synthesis of the structural fragments of AG and LAM is holding current appeal, as the synthetic fragments play significant roles not only in probing the biosynthetic pathway by which these glycans are assembled[7] but also in exploring new oligosaccharide-based inhibitors that target the enzymes.[8] In this aspect, a variety of synthetic strategies have been developed,[9,10] among which one-pot multistep glycosylations, wherein several glycosylation steps are sequentially completed in a single reaction vessel, are very attractive and produce target oligosaccharides without the need both for selectively removing protecting groups and for purifying the reaction intermediates. In 2003, Ning et al.[10r] first focused on the application of a one-pot method in furanose synthesis and realized a concise preparation of a 5,6-branched trisaccharide portion present in motif E of the *M. tuberculosis* cell wall by taking advantage of the reactivity difference between the secondary C-5 and primary C-6 hydroxyl (OH) groups of galactofuranose. On the synthesis of Galf-containing substrates for mycobacterial GalfTs, Lowary et al.[10l] reported the particularly great efficiency of a one-pot strategy for producing two linear galactofuranosyl trimers. The rapidity and simplicity of this strategy was also demonstrated by our group[10s] for assembly of a tri- and tetraarabinofuranoses. More recently, during the synthesis of tetrasaccharide fragments of mycobacterial AG, a one-pot procedure was developed by Gallo-Rodriguez et al.[10m] for the synthesis of a 5,6-branched trisaccharide lactone intermediate which involved a glycosylation−deprotection−glycosylation sequence. However, compared with the considerable progress in the one-pot synthesis of pyranosidic oligosaccharides,[11] similar studies of furanosidic oligosaccharides have been little explored so far. Furthermore, the one-pot approach is not applicable to all furanosides. For instance, the synthesis of oligoarabinofuranosides with 3,5-branched framework in a one-pot manner has not been forthcoming. Therefore, there has been a continuous pursuit of a new one-pot glycosylation protocol for the convenient synthesis of furanosides.

In 1997, Boons and co-workers[12a,b] developed a novel "two-directional approach". The basic concept of their approach relies on the use of partially protected central building blocks, such as glycosyl fluorides and thioglycosides, which are capable of displaying both donor and acceptor properties. The method has the advantage that once the central building block has been regioselectively glycosylated with a sugar alcohol, the free OH-containing di- or trisaccharide product can be utilized as an acceptor in the next glycosylation process without a single protecting group manipulation. The effectiveness of the methodology was further demonstrated by Boons et al. in

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efficient syntheses of trisaccharide libraries[12c] and other biologically important oligosaccharides.[12d,e] Later, an acceptor-mediated regioselective glycosylation strategy[13] and an iterative orthogonal strategy[14] for oligosaccharide synthesis were reported, respectively, by the groups of Seeberger and Fraser-Reid. These strategies are also based on the regioselective glycosyl coupling of the key partially protected glycosyl phosphates and mannosyl *n*-pentenyl orthoester donors with glycosyl acceptors. We envisioned that if the two-directional approach employed in pyranoses could be adopted to one-pot glycosylation of furanose systems, it would be an attractive way for the preparation of arabino- and galactofuranosyl oligosaccharides. On the basis of these considerations, a series of furanose thioglycosides **1**−**6** (Figure 1), all with one or two hydroxyl groups unprotected, were

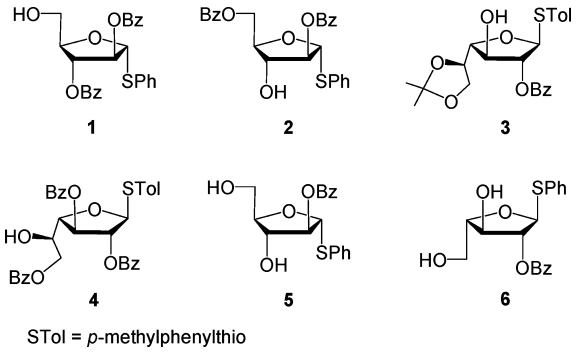

Figure 1. Partially protected furanosyl thioglycosides **1**−**6**.

designed to serve as candidate glycosylating substrates. Incorporation of a benzoyl protecting group serving as a neighboring participating group at the C-2 position of each thioglycoside is to ensure the control of the stereochemistry of each glycosylation. Here, we present the development of a new regioselective glycosylation method that uses these furanosyl thioglycosides as well as the demonstration of the efficiency the method possesses with one-pot solution-phase syntheses of five linear and branched-type arabino- and galactofuranosides.

RESULTS AND DISCUSSION

The D-arabino- and D-galactofuranose derivatives **1**,[10s] **4**,[10l] and **5**[10s] were synthesized according to the literature procedures. The preparation of monosaccharide alcohols **2**, **3**, and **6** was carried out as outlined in Scheme 1. The synthesis of D-arabinofuranose derivative **2** began with the known methyl 2,5-di-*O*-benzoyl-α-D-arabinofuranoside (**7**), which was easily prepared in three steps from the commercial D-arabinose.[15] Protection of the 3-OH group in **7** as *tert*-butyldiphenylsilyl (TBDPS) ether gave saccharide **8** in 90% yield. The latter was in turn coupled with thiophenol (PhSH) under the agency of boron trifluoride etherate ($BF_3{\cdot}Et_2O$) to give an 81% yield of **9**, which was transformed into **2** in 80% yield by treatment with *n*-tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) (Scheme 1, eq 1). Compound **3** was obtained as the major product in a yield of 45% from *p*-tolyl 5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (**10**)[16] via regioselective benzoylation conditions (Scheme 1, eq 2). L-Arabinose diol **6** was synthesized easily from 3,5-*O*-di-*tert*-butylsilylene acetal **11**,[17] which was prepared by the known methods in five steps from L-arabinofuranose, by benzoylation of the C-2 hydroxyl group to benzoate **12** (94% yield), followed by simple unmasking of the 3,5-di-OH groups with fluoride ion (71% yield) (Scheme 1, eq 3).

With the partially protected thioglycosides in hand, we first investigated the glycosyl donor properties of thioglycosides **1**−**4**, each bearing only one hydroxyl group (Table 1). Glycosylation between **1** and 1 equiv of arabinofuranosyl acceptor **13**,[18] both carrying free 5-OH, under the promotion of *N*-iodosuccinimide (NIS, 1.25 equiv) and a catalytic amount of trifluoromethanesulfonic acid (TfOH) in anhydrous dichloromethane (CH_2Cl_2) at −40 to −20 °C gave (1→5)-linked disaccharide alcohol **14a** as a single α-isomer in 65% yield, along with trisaccharide **14b** in 22% yield (Table 1, entry 1). The stereochemical outcome resulted from the neighboring group participation of the benzoyl group at the C-2 position of the donor. The trisaccharide product turned out to be the result of the second glycosylation of **14a** with donor **1**. Likewise, arabinosylation of **1** with another 5-OH acceptor **15**[10h] also gave a mixture of disaccharide **16a**[19] as the major product and a

Scheme 1. Preparation of Monosaccharides 2, 3, and 6

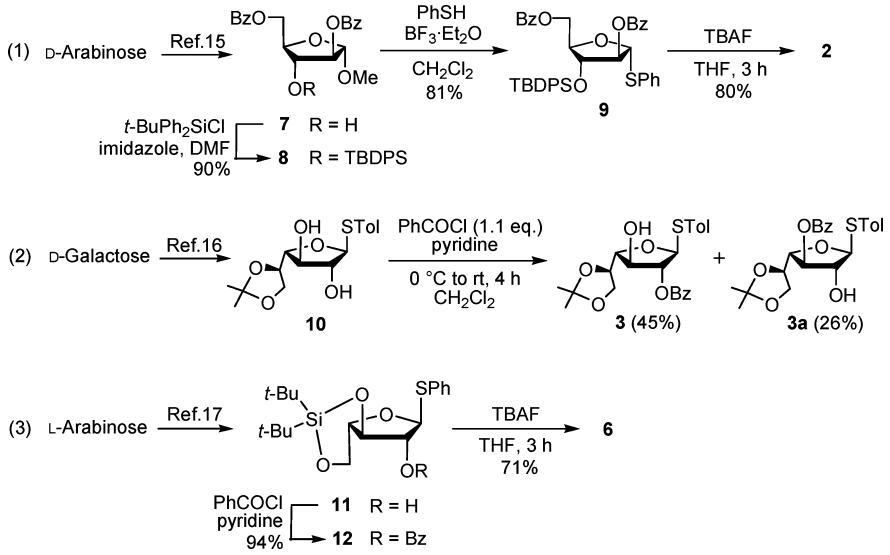

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Table 1. Glycosylations with Partially Protected Arabino- and Galactofuranosyl Thioglycosides[a]

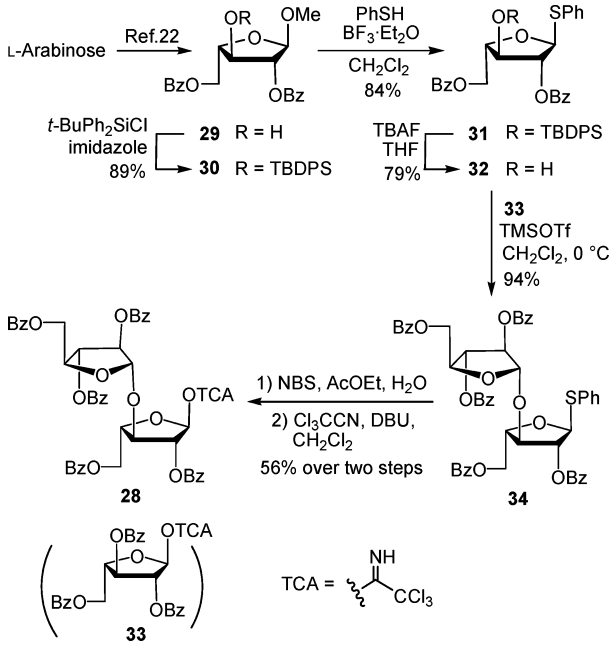
Entry	Donor	Acceptor	Product (yield)[b]	
1	**1**	**13**	**14a** (65%)	**14b** (22%)
2	**1**	**15**	**16a** (74%)	**16b** (22%)
3	**2**	**15**	**17** (93%)	
4	**2**	**18**	**19** (94%)	
5	**2**	**7**	**20** (61%)	
6	**3**	**21**	**22a** (75%)	**22b** (14%)
7	**4**	**21**	**23** (80%)	
8	**3**	**24**	**25** (79%)	
9	**26**	**5**	**27** (86%)	
10	**28**	**6**	**35** (76%)	

[a]Glycosylations were performed with donor (1.1−1.25 equiv), acceptor (1.0 equiv), NIS (1.25 equiv), TfOH (0.02 equiv), 4 Å molecular sieves (MS) in anhydrous CH_2Cl_2 at −40 → −20 °C (for entries 1−8), or with donor (1.3 equiv), acceptor (1.0 equiv), TMSOTf (0.13 equiv), 4 Å MS in CH_2Cl_2 at −45 °C (for entries 9 and 10). [b]Isolated yield.

minor quantity of doubly glycosylated trisaccharide **16b**[19] (entry 2). By contrast, condensations of 3-OH donor **2** with primary acceptors **15** (Table 1, entry 3) and its perbenzylated counterpart **18**[10j] (entry 4) at −40 to −20 °C, respectively, afforded solely α-(1→5)-linked disaccharides **17** and **19** with complete regioselectivities and in excellent 93 and 94% yields. Importantly, no other coupled product was detected under these reaction conditions. The result can be attributed to the greater reactivity of the primary hydroxyl groups of **15** and **18** relative to the secondary hydroxyl functionality of **2**. Furthermore, coupling of **2** (1.25 equiv) with acceptor **7** (1.0 equiv), in which the regioselective choice was between two secondary hydroxyl groups, also gave a single disaccharide product **20** but in a relatively low isolated yield (61%, entry 5). In order to broaden the substrate scope, we further tested the couplings between galactofuranose donors **3** or **4** having secondary 3- or 5-OH and galactofuranose acceptor **21**[20] having primary 6-OH (Table 1, entries 6 and 7, respectively). The former coupling (entry 6) led to the formation of disaccharide **22a** accompanied by double glycosylation product **22b** in 75 and 14% yields, respectively. Complete regioselectivity is still retained in the reaction of **4** (1.1 equiv) with **21** (1.0 equiv) (entry 7), as only the disaccharide **23** with β-(1→6) linkage was formed in 80% yield. For another glycosylation of **3** with 3-OH glucopyranose **24**,[21] only disaccharide **25** was obtained in 79% yield (entry 8), displaying that the reactivity of the equatorial C-3 OH group of the glucopyranose ring was higher than that of the pseudoaxial C-3 OH of the galactofuranose ring.

After establishing the regioselective glycosylation of thioglycosides exposing one hydroxyl group, we set out to examine the glycosylation of 3,5-unprotected thioglycosides **5** and **6**. We envisaged that, due to the reactivity difference between the secondary C-3 and primary C-5 OH groups, the C-5 glycosylation events should be preferable over the C-3 glycosylation in chemoselective couplings of **5** or **6** with glycosyl trichloroacetimidates **26**[10r] or **28**, respectively, thereby resulting in (1→5)-linked products. The synthesis of di-L-arabinofuranosyl imidate **28** is shown in Scheme 2. Thioglycoside **32**, a L-isomer of **2**, was readily prepared in three steps from the known methyl 2,5-di-*O*-benzoyl-α-L-arabinofuranoside (**29**)[22] by using the same procedures for the synthesis of **2** from **7** as outlined above (see the Experimental Section). Glycosylation of **32** with 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**33**)[10p] using a chemoselective

Scheme 2. Preparation of Disaccharide Trichloroacetimidate 28



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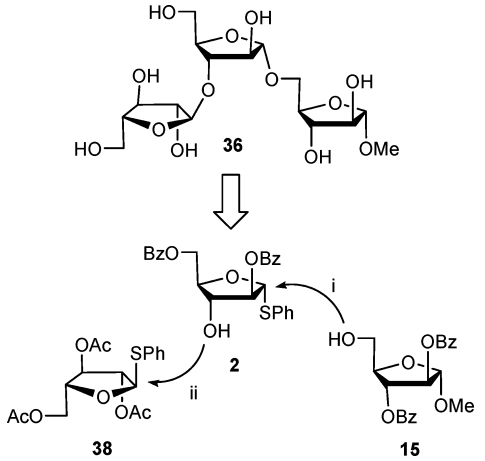
glycosylation approach activated with catalytic amounts of trifluoromethanesulfonate (TMSOTf) furnished disaccharide thioglycoside **34** (94% yield), which was elaborated into imidate **28** by hydrolysis with *N*-bromosuccinimidate (NBS) in wet ethyl acetate, followed by activation of the resulting hemiacetal with trichloroacetonitrile (CCl_3CN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH_2Cl_2.

Activation of imidate donor **26** (1.3 equiv) with catalytic TMSOTf at −45 °C in the presence of diol acceptor **5** (1.0 equiv) in CH_2Cl_2 (Table 1, entry 9) furnished α-(1→5)-linked disaccharide **27**, isolated as the only coupled material in a good 86% yield. The regioselectivity in this process was assured by gHMBC experiment of **27**, namely, the strong correlationship observed between the C-5 signal (δ_C 65.4 ppm) and the anomeric H-1′ resonance (δ_H 5.40 ppm, s) confirmed a (1→5) linkage. Products arising from the C-3 glycosylation and the intermolecular aglycon transformation[23] of **5** were not isolated. Likewise, another regioselective glycosylation of L-arabinofuranosyl 3,5-diol **6** with imidate **28** (Table 1, entry 10), tried under similar conditions, also followed the same trend and led to exclusive formation of the corresponding 5-*O*-α-di-L-arabinofuranosylated trisaccharide **35** in a good 76% isolated yield. These examples indicate that the difference in the reactivity between 3- and 5-hydroxyl groups of arabinofuranose makes it possible to regioselectively glycosylate at the C-5 position.[10q] The newly formed products (i.e., thioglycosides **27** and **35**) can be directly elongated without further protecting group removal and aglycon leaving group adjustment.

This regioselective glycosylation method may prove useful for synthesizing natural arabino- and galactofuranosides and their analogues. To examine the synthetic application, we decided to build various oligofuranose structures by using a one-pot glycosylation procedure based on the developed method. In this way, two linear trisaccharides **36** (α-D-Ara*f*-(1→3)-α-D-Ara*f*-(1→5)-D-Ara*f*, Scheme 3) and **37** (β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-D-Gal*f*, Scheme 5) were first selected as the synthetic targets. These homotrimers are composed of 1,2-*trans*-D-arabino- and galactofuranosyl residues, respectively, and are crucial constituents of the mycolyl-arabinogalactan (mAG) complex from the cell wall of *M. tuberculosis*. Lowary et al. previously synthesized compounds **36**[8a,10h] and the octyl glycoside homologues of **36**[8e] and **37**[10l] with a thioglycoside glycosylation method. Notably, Lowary et al.[7a,8a] further revealed that these small oligosaccharides were substrates for the respective Ara*f*Ts and Gal*f*Ts involved in the biosynthesis of the mycobacterial cell wall, which suggests that the glycans or their analogues are likely to be the inhibitors of the enzymes. Meanwhile, the preparation of the dec-9-enyl glycoside homologue of **37** was reported by de Lederkremer's group[10k] via a glycosylaldonolactone/trichloroacetimidate assembly strategy. In the case of Lowary's preparation[10l] of the octyl glycoside homologue of **37**, they found that migration of benzoyl groups usually occurred from C-5 (secondary) to C-6 (primary) in selective deacetylation steps under acidic reaction conditions. Then, Lowary et al. employed a chemoselective glycosylation-based one-pot protocol in which the target substance was assembled from nonreducing to reducing end, thus not only enabling the rapid production of the molecule but also solving the unwanted acyl migration problem. Here, on the basis of our regioselective glycosylation methodology, we explored a new one-pot synthesis for these trisaccharide skeletons, and the general strategy depends on the utility of thioglycosides **2** and **4**. Take the retrosynthetic analysis of **36** for example (Scheme 3). The sequence of its assembly includes two consecutive glycosylation steps: (i) coupling of thioarabinoside **2**, serving as a key between building block, with arabinofuranosyl acceptor **15**, and (ii) glycosylation of the resulting disaccharide alcohol with thioglycoside donor **38**.[24]

One-pot glycosylation with **2**, **15**, and **38** was examined (cf. Scheme 4). Treatment of the acceptor **15** (1.0 equiv) with the partially protected donor **2** (1.1 equiv) mediated by coupling agent NIS/TfOH in CH_2Cl_2 at −40 to −20 °C within 30 min resulted in the intermediate **17**. Next, the condensation of **17** with donor **38** proceeded at −40 to −20 °C within 30 min with the addition of NIS and TfOH. The fully protected trisaccharide **39** was produced in good yield as only a product in 70% overall yield based on the acceptor **15**. Accomplishment of each glycosylation reaction was checked by TLC analysis. Parallel study was done by the one-pot assembly of trigalactoside **41**, a precursor to **37** (Scheme 5). In the event, the galactofuranose derivative **21** was used for the first glycosylation step with **4** under the activation of NIS/TfOH. Then, the resulting disaccharide **23** was glycosylated in situ with the second donor **40**[10l] to yield the perbenzoylated galactofuranosyl trimer **41** (67% overall yield based on **21**). So, these processes demonstrate the viability of thioglycosides **2** and **4** in sequential one-pot syntheses of linear furanosides. Global deprotection of **39** and **41** with the aid of sodium methoxide ($NaOCH_3$) in methanol furnished the desired **36** and **37**, respectively, in 85 and 90% yields. It is worth pointing out that all glycosyl linkages were built stereoselectively, and the overall yields after two-step one-pot assembly and one deprotection step were ca. 60% for both **36** and **37**. Therefore, our method provides a new expeditious way to these trisaccharides that are suitable for use in assays of mycobacterial Ara*f*Ts and Gal*f*Ts. The structure of triarabinofuranose **36** was confirmed by comparison of its ^1H and ^{13}C NMR data with those published in literature.[8a,10h] The structure of trigalactofuranose **37** was determined through the use of NMR and ESI-MS spectral analysis. Accordingly, in the ^1H NMR spectrum of **37**, the characteristic resonances brought by the three H-1 signals appeared as singlets at δ_H 5.25, 5.04, and 4.94 ppm, and the ^{13}C NMR spectrum revealed that the chemical shifts of the anomeric carbons were at δ_C 110.5, 110.1, and 109.5 ppm. Therefore, both ^1H and ^{13}C NMR data are consistent with the β-galactofuranoside anomeric stereochemistry.[25] The structure of **37** was further confirmed by its high-resolution MS at *m*/*z*

Scheme 3. Retrosynthetic Analysis of Triarabinofuranose 36



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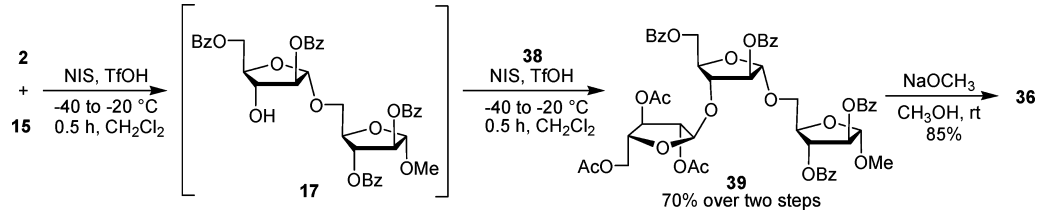
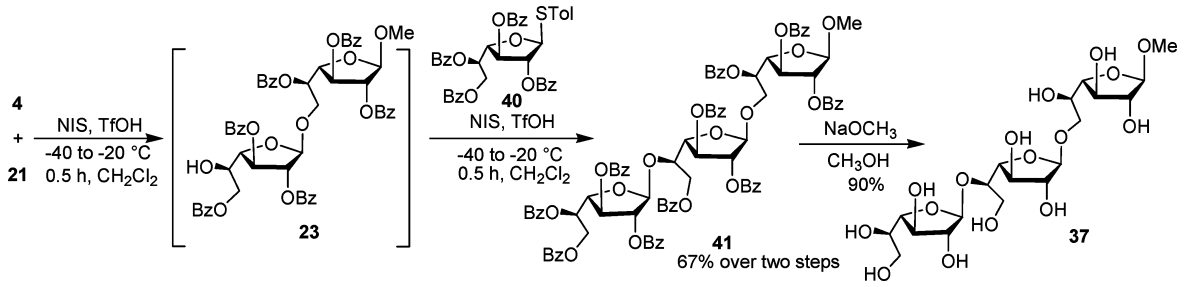
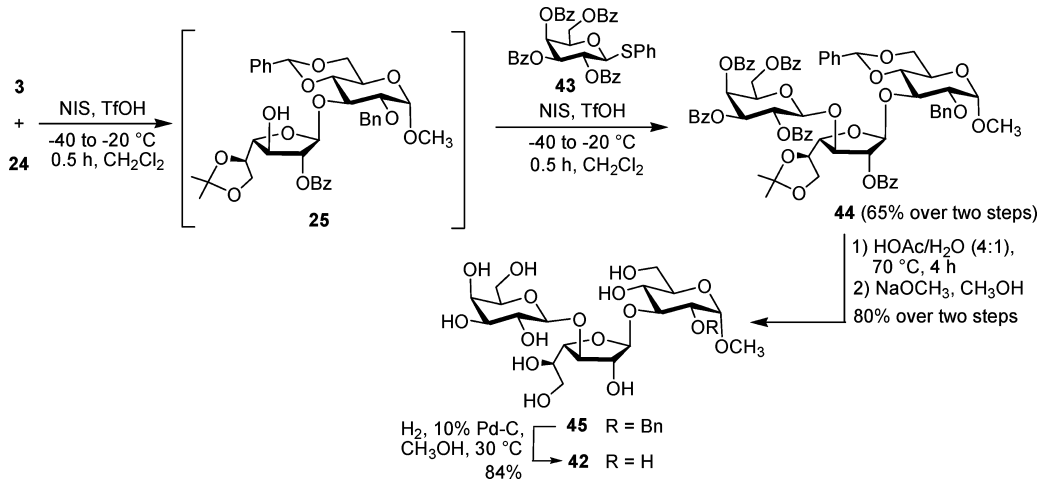
Scheme 4. Synthesis of Triarabinofuranose 36



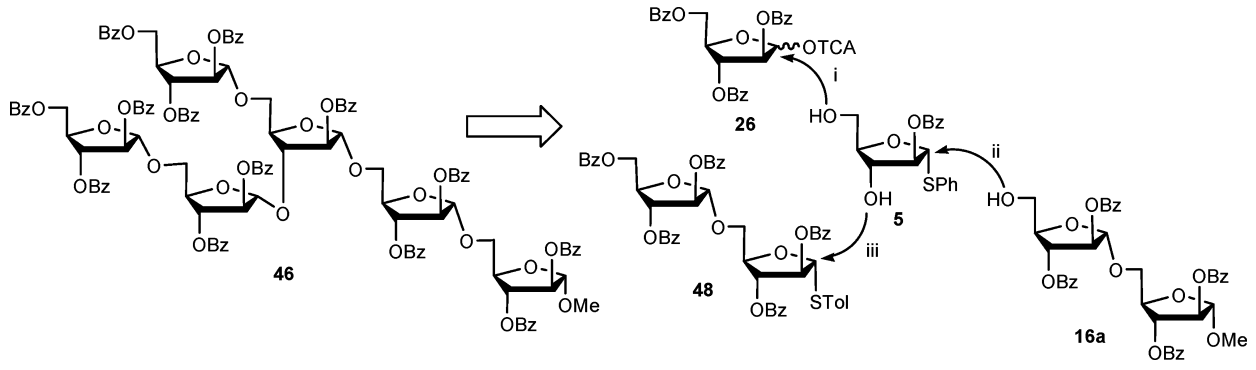
Scheme 5. Synthesis of Trigalactofuranose 37



Scheme 6. Synthesis of Trisaccharide 42



Scheme 7. Retrosynthetic Analysis of Protected Hexa-D-Arabinose 46



541.1740 $(M + Na)^+$, which was identical with the calculated exact mass of the molecule (calcd 541.1745).

The power of this method was also demonstrated by the construction of another linear heterotrisaccharide glycoside **42** (*β*-D-Gal*p*-(1→3)-*β*-D-Gal*f*-(1→3)-D-Glu*p*, Scheme 6), which is contained in the pentasaccharide repeating unit of the capsular polysaccharide (CPS) antigen of *Streptococcus pneumoniae* serotype 35A.[26] Since the CPSs of *S. pneumoniae* are responsible for stimulation of the host's immune system, synthesis of the common antigen determinant is possibly useful for immunological studies. As illustrated in Scheme 6, the synthesis of protected **44**, a protected precursor to **42**, was performed in a one-pot manner in which three monosaccharide units, galactofuranose thioglycoside alcohol **3**, methyl glucopyr-

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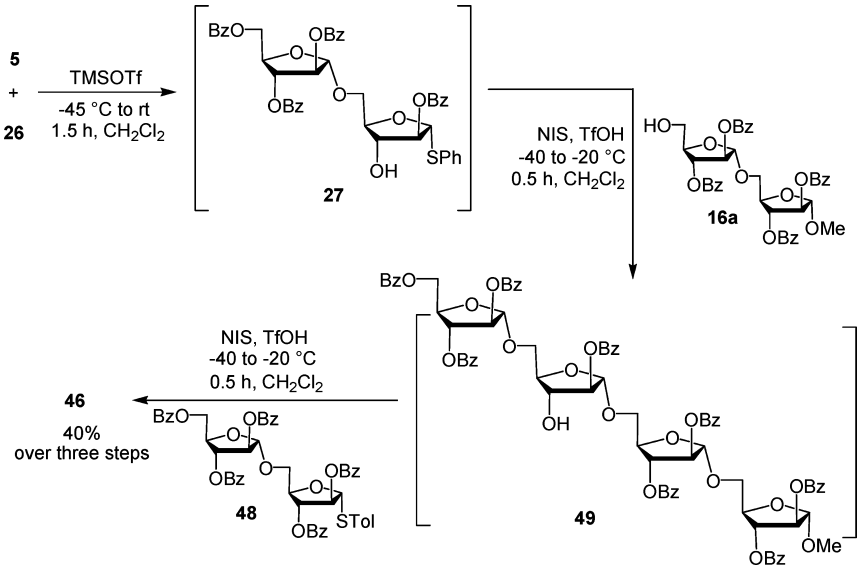
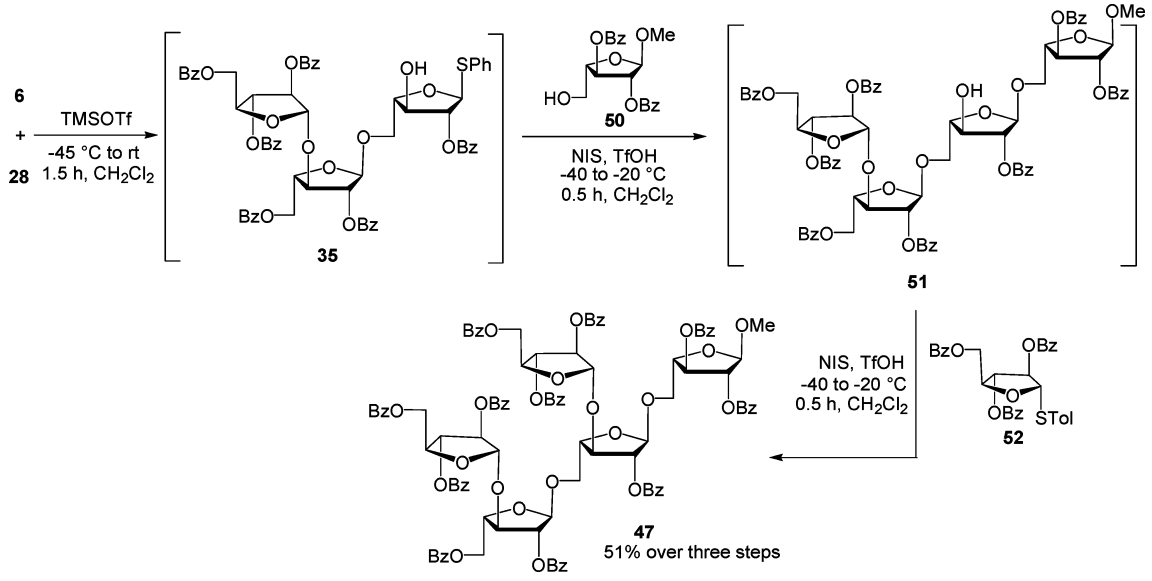
Scheme 8. One-Pot Synthesis of Hexa-D-Arabinose 46



Scheme 9. One-Pot Synthesis of Penta-L-Arabinose 47



anoside **24**, and perbenzoylated galactopyranose thioglycoside **43**,[27] were assembled together through a similar series of reactions via the intermediate **25** to give **44** in a satisfying 65% overall yield (based on **24**). A complete deprotection of **44** was accomplished as follows: acidic hydrolysis of **44** ($HOAc/H_2O$ (4:1), 70 °C, 4 h) followed by methanolysis of the formed trisaccharide alcohol ($NaOCH_3$, CH_3OH, rt, 2 h) secured **45** in 80% yield over two steps. Finally, the remaining benzyl protecting group on **45** was removed with Pd−C-catalyzed hydrogenolysis (H_2, Pd−C, CH_3OH, 30 °C, 24 h) to afford the deprotected **42**. As was done for **36** and **37**, the combination of NMR and MS data could be used to establish the structure of **42**.

Success in the one-pot synthesis of linear furans led us to explore the use of the regioselective glycosylation methodology for synthesis of more complex oligofuranoses with branched architectures, such as **46** and **47** (Schemes 7 and 9, respectively). Compound **46**, a protected hexaarabinan motif which is linked to the core arabinomannan (AM) domain from *M. tuberculosis*, has α-(1→3) and α-(1→5) branch points at the central D-arabinofuranose unit. Creating such branched sugar backbones has long been considered a difficult task in synthetic carbohydrate chemistry. Recently, a protected hexaarabinosyl trichloroacetimidate possessing the same sugar array as that of **46** was prepared by Seeberger and co-workers[10c] to be used as an intermediate in the total synthesis of an AM dodecasaccharide. However, their process is a typical example of oligasaccharide synthesis involving tediously selective protection and deprotection steps and laborious intermediate purifications. We anticipated that the incorporation of our regioselective glycosylation method in the synthesis of the target **46** could simplify this complicated synthetic operation. Here, we present an alternative three-step one-pot synthetic route to **46** by using the 3,5-di-OH thioglycoside **5** as a central building block. As retrosynthetically depicted in Scheme 7, the reaction sequence involves three steps: (i) chemo- and regioselective glycosylation of the primary alcohol of **5** in the presence of the secondary one with trichloroacetimidate **26**,

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followed by (ii) coupling of the resulting disaccharide thioglycoside with acceptor **16a** based on the difference in reactivity between the secondary OH on donor and the primary OH on acceptor, and (iii) glycosylation of the remaining secondary alcohol of **5** with donor **48**[10s] to give **46**.[28]

The successful implementation of this protocol is shown in Scheme 8. Thus, **26** (1.3 equiv) was used to regioselectively glycosylate diol **5** (1.0 equiv) by activation with TMSOTf (cat.) in CH_2Cl_2 at −45 °C to ambient temperature to give disaccharide **27** as the only detected product. Next, the reaction mixture was recooled to −40 °C, and subsequent addition of the 5′-OH disaccharide acceptor **16a** along with NIS/TfOH reagent system to the reaction flask drove the second glycosylation to proceed and afforded the tetrasaccharide intermediate **49** as the sole product after 30 min. Finally, NIS/TfOH-mediated glycosylation of the remaining secondary hydroxyl group of **49** with thioglycoside donor **48** at −40 to −20 °C within half an hour completed the synthesis of the desired **46**. Upon purification by silica gel column chromatography, **46** was acquired as an amorphous solid in an acceptable 40% overall yield based on **5**. This protocol illustrates the usefulness of the diol **5**, able to function as an acceptor, a donor, and an acceptor. Overall, when compared with the existing method, the four-component one-pot approach greatly speeds up the preparation of the target molecule because the entire synthetic route can be accomplished without the need of protecting group manipulation and intermediate workup and thus offers a more practical access to the 3,5-branched arabinofuranosides.

The usefulness of this remarkably efficient synthetic technique is also proved by a similar four-component one-pot synthesis of α-L-arabinofuranosyl pentamer **47** (Scheme 9), and it represents a fully protected form of structural component which belongs to the arabinan found in sugar beet cell wall.[29] This molecule contains a linear α-(1→5)-linked tri-L-arabinose backbone to which two α-(1→3)-linked L-arabinosyl residues are attached. For the one-pot preparation of **47**, the thioglycoside diol **6** was selected to function as the central building block. Glycosylation of the di-L-furanosyl imidate donor **28** with **6** affected by TMSOTf activation at −45 °C to ambient temperature, followed by sequential coupling of the resulting **35** with acceptor **50**[22] promoted again by NIS in combination with catalytic TfOH at low temperature (−40 to −20 °C), provided **51** with the 3′-OH exposed. Its subsequent glycosylation with thioglycosyl building block **52**[10l] delivered the required pentasaccharide glycan **47** in 51% overall yield (based on **6**).

Analysis of the products **46** and **47** by 1D (^{1}H, ^{13}C, 400 MHz) and 2D NMR spectroscopy (gCOSY, HMQC, and gHMBC) confirmed the correct anomeric configuration of each glycosidic linkage. Take D-hexaarabinose **46** for example. In its ^{1}H NMR spectrum, the six anomeric protons appeared as six signals at δ_H 5.55, 5.42, 5.41, 5.39, 5.33, and 5.12 ppm, and in the ^{13}C NMR spectrum, the six anomeric carbon resonances appeared clearly in the range of δ_C 105.3 to 106.8 ppm. Both are characteristic of α-Ara*f* linkages.[10s,24] Further support for its structure came from high-resolution MS data, which gave an $(M + Na)^+$ signal at *m*/*z* 2199.6082 (calcd 2199.6103).

CONCLUSION

In conclusion, the development of a novel regioselective furanosylation methodology and its application in one-pot synthesis of oligofuranosides have been described. We first investigated the glycosylating properties of partially protected arabino- and galactofuranosyl thioglycosides. Compounds **2**−**4** each containing one secondary OH group could function as glycosyl donors to couple regioselectively with glycosyl acceptors under the promotion of NIS/TfOH, giving the corresponding disaccharide alcohols as a sole product. The regioselectivity is based on the relative reactivity difference between OH groups carried on the donors and the acceptors. As for the chemoselective glycosylations of 3,5-dihydroxy-D- and L-arabinothioglycosides **5** and **6** with 1.3 equiv of glycosyl trichloroacetimidates **26** and **28** promoted by catalytic TMSOTf, the C-5 glycosylations took place preferentially over the C-3 glycosylations and afforded solely the (1→5)-linked products in high isolated yields. Next, the use of the method in one-pot glycosylations allowed for the facile and rapid generation of a series of important linear as well as more synthetically challenging branched oligofuranoses that are fragments of the cell wall polysaccharides of *M. tuberculosis*, *S. pneumoniae* serostype 35A, and sugar beet. Application of this new pathway to the synthesis of structurally diverse oligofuranose libraries is currently underway.

EXPERIMENTAL SECTION

Methyl 2,5-Di-*O*-benzoyl-3-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (8). To a solution of **7** (1.02 g, 2.74 mmol) in dry DMF (7 mL) was added imidazole (560.1 mg, 8.22 mmol), followed by TBDPSCl (1.1 mL, 4.11 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred overnight at the same temperature at the end of which time TLC indicated the reaction was complete. Then the mixture was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by column chromatography (30:1, petroleum ether−EtOAc) to afford **8** as a colorless syrup (1.5 g, 90%): R_f 0.52 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +41.3 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, 2H, *J* = 1.2, 8.4 Hz), 7.78 (dd, 2H, *J* = 1.2, 8.4 Hz), 7.60−7.65 (m, 4H), 7.51−7.57 (m, 2H), 7.17−7.38 (m, 10H), 5.28, 4.90 (2 × s, each 1H), 4.43−4.47 (m, 3H), 4.07 (dd, 1H, *J* = 4.0, 12.4 Hz), 3.47 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.2, 135.5, 135.48, 133.0, 132.7, 132.6, 132.2, 129.8, 129.7, 129.5, 128.0, 127.6, 127.5, 106.7, 84.8, 81.3, 77.2, 62.7, 54.7, 26.6, 18.9; IR (KBr) 2932, 2858, 1725, 1602, 1452, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{38}O_7Si$ $[M + Na]^+$ 633.2248, found 633.2278.

Phenyl 2,5-Di-*O*-benzoyl-3-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-arabinofuranoside (9). To a solution of **8** (2.05 g, 3.36 mmol) in CH_2Cl_2 (23.6 mL) was added slowly PhSH (0.41 mL, 4.03 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, then $BF_3{\cdot}Et_2O$ (2.56 mL, 20.16 mmol) was slowly added and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 8 h at the same temperature at the end of which time TLC indicated that it was finished. The reaction was quenched with Et_3N, and the mixture was concentrated. The crude product was purified by column chromatography (30:1, petroleum ether−EtOAc) to give **9** as a colorless syrup (1.87 g, 81%): R_f 0.48 (8:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +98.3 (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 2H, *J* = 7.6 Hz), 7.82 (d, 2H, *J* = 7.6 Hz), 7.64−7.68 (m, 4H), 7.50−7.58 (m, 4H), 7.17−7.37 (m, 13H), 5.60, 5.47 (2 × s, each 1H), 4.72 (td, 1H, *J* = 3.2, 5.2 Hz), 4.45 (dd, 1H, *J* = 1.2, 5.2 Hz), 4.35 (dd, 1H, *J* = 2.8, 12.0 Hz), 4.07 (dd, 1H, *J* = 2.8, 12.0 Hz), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 135.8, 135.7, 134.5, 133.3, 132.9, 132.6, 132.2, 131.8, 130.1, 130.0, 129.7, 129.66, 129.1, 128.9, 128.3, 128.2, 127.9, 127.8, 127.4, 91.3, 85.0, 82.4, 77.5, 63.0, 26.8, 19.2; IR (KBr) 2931, 2858, 1725, 1602, 1585, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{41}H_{40}O_6SSi$ $[M + Na]^+$ 711.2213, found 711.2225.

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Phenyl 2,5-Di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (2). To a solution of **9** (500 mg, 0.73 mmol) in THF (1.5 mL) was added slowly TBAF (0.45 mL, 1.0 M in THF, 0.45 mmol) at 0 °C, and the resulting mixture was warmed gradually to 15 °C. The mixture was stirred for 3 h at the same temperature at the end of which time TLC indicated the reaction was complete. After the solvent was removed under reduced pressure, the residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous NH_4Cl and brine and then dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude material was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **2** as a white solid (262 mg, 80%): R_f 0.25 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +160.0 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−8.04 (m, 4H), 7.52−7.63 (m, 4H), 7.45 (t, 2H, *J* = 8.0 Hz), 7.36 (t, 2H, *J* = 8.0 Hz), 7.30−7.32 (m, 3H), 5.78 (d, 1H, *J* = 3.2 Hz), 5.19 (t, 1H, *J* = 3.2 Hz), 4.61−4.69 (m, 2H), 4.57 (dd, 1H, *J* = 4.8, 11.2 Hz), 4.28−4.32 (m, 1H), 3.55 (d, 1H, *J* = 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.3, 133.8, 133.3, 133.1, 132.2, 129.9, 129.7, 129.6, 129.0, 128.6, 128.57, 128.3, 127.9, 89.2, 87.0, 80.5, 77.4, 63.4; IR (KBr) 3521, 2932, 1711, 1601, 1583, 1453 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}O_6S$ [M + Na]$^+$ 473.1035, found 473.1039.

***p*-Tolyl 2-*O*-Benzoyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (3) and *p*-Tolyl 3-*O*-Benzoyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (3a).** To a solution of **10** (147.1 mg, 0.45 mmol) in pyridine/CH_2Cl_2 (0.6 mL/6.0 mL) was added PhCOCl (58 μL, 0.50 mmol) dropwise at 0 °C, and the resulting mixture was warmed gradually to room temperature. The reaction was stirred for 4 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with methanol, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (4:1, petroleum ether−EtOAc) to afford compound **3** (87.1 mg, 45%) and **3a** (50.3 mg, 26%) as colorless syrups: R_f 0.37 (**3**) and 0.50 (**3a**) (2.5:1, petroleum ether−EtOAc). **3**: $[\alpha]_D^{20}$ −166.9 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−8.04 (m, 9H), 5.64 (d, 1H, *J* = 3.6 Hz), 5.09 (t, 1H, *J* = 3.6 Hz), 4.31−4.36 (m, 1H), 4.19−4.26 (m, 2H), 4.07 (dd, 1H, *J* = 6.8, 8.4 Hz), 4.00 (dd, 1H, *J* = 7.6, 8.4 Hz), 3.55 (br s, 1H), 2.34, 1.43, 1.37 (3 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 138.2, 133.8, 133.0, 129.9, 129.8, 129.3, 128.8, 128.5, 109.7, 89.3, 86.9, 82.0, 77.4, 75.4, 65.3, 26.3, 25.4, 21.1; IR (KBr) 3433, 2919, 1723, 1596, 1492, 1374 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}O_6S$ [M + Na]$^+$ 453.1348, found 453.1351. **3a**: $[\alpha]_D^{20}$ −175.9 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12−8.13 (m, 9H), 5.58 (s, 1H), 5.26 (d, 1H, *J* = 2.0 Hz), 4.61 (td, 1H, *J* = 1.6, 7.6 Hz), 4.47−4.49 (m, 1H), 4.43 (t, 1H, *J* = 1.6 Hz), 4.12 (t, 1H, *J* = 8.0 Hz), 4.05 (t, 1H, *J* = 8.0 Hz), 2.33, 1.43, 1.42 (3 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 137.5, 133.6, 132.0, 131.1, 130.0, 129.8, 129.1, 128.6, 110.2, 95.6, 82.4, 81.1, 79.5, 75.5, 65.5, 25.7, 25.6, 21.1; IR (KBr) 3421, 2987, 1716, 1601, 1452, 1373 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}O_6S$ [M + Na]$^+$ 453.1348, found 453.1353.

Phenyl 2-*O*-Benzoyl-3,5-*O*-(di-*tert*-butylsilylene)-1-thio-α-D-arabinofuranoside (12). To a solution of **11** (382 mg, 1.0 mmol) in pyridine (4.5 mL) was added PhCOCl (0.24 mL, 2.0 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The reaction was stirred overnight at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with methanol, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (100:1, petroleum ether−EtOAc) to afford **12** (457 mg, 94%) as a pale yellow oil: R_f 0.5 (30:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −79.5 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, 2H, *J* = 7.2 Hz), 7.46−7.62 (m, 5H), 7.26−7.33 (m, 3H), 5.53 (dd, 1H, *J* = 4.8, 6.8 Hz), 5.47 (d, 1H, *J* = 4.8 Hz), 4.43 (dd, 1H, *J* = 4.8, 9.6 Hz), 4.36 (dd, 1H, *J* = 6.8, 9.6 Hz), 4.11−4.17 (m, 1H), 4.06 (t, 1H, *J* = 9.6 Hz), 1.06, 1.01 (2 × s, each 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 133.9, 133.4, 131.7, 129.9, 128.9, 128.5, 127.6, 89.5, 81.4, 79.7, 73.5, 67.2, 27.4, 27.0, 22.6, 20.1; IR (KBr) 3526, 2930, 1714, 1601, 1583, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{34}O_5SSi$ [M + Na]$^+$ 509.1788, found 509.1785.

Phenyl 2-*O*-Benzoyl-1-thio-α-D-arabinofuranoside (6). Prepared from glycoside **12** (223 mg, 0.46 mmol) and TBAF (1.8 mL, 1.0 M in THF, 1.8 mmol) in THF (1.2 mL) following the procedure similar to that for **9** → **2**. The crude product was purified by column chromatography (2:1, petroleum ether−EtOAc) to give **6** (113 mg, 71%) as a colorless syrup: R_f 0.34 (1:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −180.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 2H, *J* = 8.0 Hz), 7.61 (t, 1H, *J* = 6.8 Hz), 7.54−7.56 (m, 2H), 7.47 (t, 2H, *J* = 8.0 Hz), 7.29−7.37 (m, 3H), 5.77 (d, 1H, *J* = 2.8 Hz), 5.15 (t, 1H, *J* = 3.2 Hz), 4.35−4.39 (m, 1H), 4.29−4.32 (m, 1H), 3.96−4.01 (m, 1H), 3.80−3.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 133.8, 133.5, 132.0, 129.9, 129.0, 128.7, 128.5, 127.8, 89.3, 87.3, 82.7, 76.1, 61.2; IR (KBr) 3431, 2926, 1719, 1601, 1583, 1450 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}O_5S$ [M + Na]$^+$ 369.0767, found 369.0774.

General Procedure for the NIS/TfOH-Promoted Glycosylations with Partially Protected Arabino- and Galactofuranosyl Thioglycosides 1−4. To a stirred ca. 0.025 M solution of donor (1.1−1.25 equiv) and acceptor (1.0 equiv) in dry CH_2Cl_2 was added freshly activated 4 Å molecular sieves (150 wt % with respect to the donor). The reaction mixture was stirred for 15 min at room temperature and then was cooled to −40 °C. The suspension was stirred for 15 min at −40 °C, then NIS (1.25 equiv) and TfOH (0.02 equiv) were added and the resulting mixture was warmed gradually to −20 °C. The reaction mixture was stirred for 0.5 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The resulting residue was purified by column chromatography. Products **16a** and **16b** are known compounds and their spectroscopic data matched the reported data.[19] Spectral data of new compounds are listed below.

2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-arabinofuranose (14a) and 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-arabinofuranose (14b). Prepared from **13** (45.0 mg, 0.161 mmol) and **1** (90.4 mg, 0.201 mmol). The residue was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford compound **14a** (65.0 mg, 65%) and **14b** (33.8 mg, 22%) as colorless syrups: R_f 0.24 (**14a**) and 0.16 (**14b**) (3:1, petroleum ether−EtOAc). **14a**: $[\alpha]_D^{20}$ −15.0 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−8.09 (m, 4H), 7.22−7.61 (m, 11H), 5.91 (d, 1H, *J* = 4.0 Hz), 5.52 (d, 1H, *J* = 1.2 Hz), 5.41 (d, 1H, *J* = 4.0 Hz), 5.27 (s, 1H), 4.66 (d, 1H, *J* = 4.0 Hz), 4.59 (d, 1H, *J* = 11.6 Hz), 4.47 (d, 1H, *J* = 11.6 Hz), 4.27 (td, 1H, *J* = 3.2, 5.6 Hz), 4.21 (q, 1H, *J* = 4.0 Hz), 4.10 (d, 1H, *J* = 3.2 Hz), 3.93−3.97 (m, 3H), 3.69 (dd, 1H, *J* = 6.0, 10.4 Hz), 2.24−2.27 (m, 1H), 1.56, 1.35 (2 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.2, 133.62, 133.6, 130.0, 129.9, 129.1, 129.0, 128.6, 128.53, 128.5, 128.0, 127.7, 113.1, 105.7, 105.6, 85.3, 83.8, 83.1, 82.5, 81.6, 77.6, 71.7, 66.7, 62.3, 27.2, 26.5; IR (KBr) 3497, 2924, 2854, 1724, 1600, 1453 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{36}O_{11}$ [M + Na]$^+$ 643.2155, found 643.2164. **14b**: $[\alpha]_D^{20}$ −2.7 (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−8.06 (m, 6H), 7.90 (d, 2H, *J* = 7.2 Hz), 7.21−7.61 (m, 17H), 5.90 (d, 1H, *J* = 4.0 Hz), 5.62 (d, 1H, *J* = 1.2 Hz), 5.60 (d, 1H, *J* = 4.8 Hz), 5.51 (s, 1H), 5.42 (d, 1H, *J* = 4.0 Hz), 5.40, 5.26 (2 × s, each 1H), 4.66 (d, 1H, *J* = 4.0 Hz), 4.59 (d, 1H, *J* = 12.0 Hz), 4.49 (d, 1H, *J* = 12.0 Hz), 4.47−4.49 (m, 1H), 4.31 (q, 1H, *J* = 4.0 Hz), 4.26 (q, 1H, *J* = 6.0 Hz), 4.15 (dd, 1H, *J* = 4.0, 11.2 Hz), 4.10 (d, 1H, *J* = 3.2 Hz), 3.90−4.02 (m, 4H), 3.66 (dd, 1H, *J* = 6.8, 10.0 Hz), 2.28−2.31 (m, 1H), 1.55, 1.34 (2 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7, 165.3, 165.1, 137.1, 133.5, 133.49, 133.4, 133.3, 130.0, 129.84, 129.8, 129.2, 129.1, 128.92, 128.9, 128.5, 128.46, 128.3, 127.9, 127.7, 113.0, 105.8, 105.6, 105.5, 85.2, 83.6, 83.0, 82.5, 82.2, 81.6, 81.5, 77.7, 77.1, 71.6, 66.5, 66.0, 62.3, 27.2, 26.4; IR (KBr) 3443, 2925, 2855, 1724, 1602, 1455 cm^{-1}; HRMS (ESI) calcd for $C_{53}H_{52}O_{17}$ [M + Na]$^+$ 983.3102, found 983.3094.

Methyl 2,5-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (17). Prepared from **15** (52.1 mg, 0.140 mmol) and **2** (69.3 mg, 0.154 mmol). The residue

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was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford compound **17** as a colorless syrup (92.5 mg, 93%): R_f 0.24 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +16.5 (*c* 0.65, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−8.08 (m, 8H), 7.29−7.61 (m, 12H), 5.57 (dd, 1H, *J* = 1.6, 5.2 Hz), 5.51 (d, 1H, *J* = 1.6 Hz), 5.44 (s, 1H), 5.22 (d, 1H, *J* = 2.0 Hz), 5.16 (s, 1H), 4.63 (dd, 1H, *J* = 3.2, 11.2 Hz), 4.49−4.57 (m, 2H), 4.43 (q, 1H, *J* = 4.8 Hz), 4.19−4.23 (m, 2H), 3.96 (dd, 1H, *J* = 3.2, 11.2 Hz), 3.48 (s, 3H), 3.45 (d, 1H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 165.8, 165.5, 133.6, 133.56, 133.5, 133.0, 129.95, 129.9, 129.8, 129.7, 129.67, 129.1, 129.0, 128.9, 128.5, 128.46, 128.3, 106.8, 105.3, 85.4, 82.3, 82.1, 81.5, 77.3 (2C), 65.8, 63.8, 55.0; IR (KBr) 3053, 2930, 2857, 1723, 1602, 1453, 1274 cm^{-1}; HRMS (ESI) calcd for $C_{39}H_{36}O_{13}$ $[M + Na]^+$ 735.2054, found 735.2041.

Methyl 2,5-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (19). Prepared from **18** (49.1 mg, 0.143 mmol) and **2** (70.7 mg, 0.157 mmol). The residue was purified by column chromatography (3.5:1, petroleum ether−EtOAc) to afford compound **19** as a colorless syrup (91.7 mg, 94%): R_f 0.31 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +58.7 (*c* 1.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−8.03 (m, 4H), 7.25−7.60 (m, 16H), 5.32 (s, 1H), 5.19 (d, 1H, *J* = 1.6 Hz), 4.96 (s, 1H), 4.42−4.60 (m, 6H), 4.27 (q, 1H, *J* = 5.2 Hz), 4.18−4.26 (m, 2H), 3.99 (d, 1H, *J* = 1.6 Hz), 3.88−3.92 (m, 2H), 3.74 (dd, 1H, *J* = 3.2, 10.8 Hz), 3.48 (d, 1H, *J* = 7.2 Hz), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.26, 137.5, 137.2, 133.6, 133.1, 129.8, 129.7, 129.67, 129.0, 128.6, 128.5, 128.48, 128.4, 128.1, 128.0, 127.9, 107.2, 105.1, 87.3, 84.4, 83.3, 82.8, 80.8, 77.1, 72.1, 72.0, 66.3, 63.9, 55.0; IR (KBr) 3369, 2921, 2852, 1723, 1583, 1439 cm^{-1}; HRMS (ESI) calcd for $C_{39}H_{40}O_{11}$ $[M + Na]^+$ 707.2468, found 707.2474.

Methyl 2,5-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoy-α-D-arabinofuranoside (20). Prepared from **7** (42.0 mg, 0.113 mmol) and **2** (63.2 mg, 0.141 mmol). The residue was purified by column chromatography (4:1, petroleum ether−EtOAc) to afford compound **20** as a colorless syrup (49.2 mg, 61%): R_f 0.12 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +43.8 (*c* 0.54, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−8.06 (m, 20H), 5.70, 5.33 (2 × s, each 1H), 5.22 (d, 1H, *J* = 2.0 Hz), 5.16 (s, 1H), 4.78 (dd, 1H, *J* = 2.8, 12.0 Hz), 4.55−4.60 (m, 2H), 4.45−4.50 (m, 4H), 4.19−4.22 (m, 1H), 3.49 (d, 1H, *J* = 4.4 Hz), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.25, 166.2, 165.6, 133.8, 133.5, 133.1, 130.0, 129.8, 129.7, 129.6, 128.8, 128.6, 128.5, 128.33, 128.3, 106.9, 105.0, 86.5, 82.5, 81.6, 81.3, 81.1, 77.7, 63.7, 63.1, 54.9; IR (KBr) 3498, 2926, 2854, 1723, 1602, 1453 cm^{-1}; HRMS (ESI) calcd for $C_{39}H_{36}O_{13}$ $[M + Na]^+$ 735.2054, found 735.2057.

Methyl 2-*O*-Benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (22a) and Methyl 2-*O*-Benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (22b). Prepared from **21** (32 mg, 0.063 mmol) and **3** (30.1 mg, 0.070 mmol). The residue was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford compound **22a** (38.4 mg, 75%) and **22b** (9.8 mg, 14%) as colorless syrups: R_f 0.30 (**22a**) and 0.22 (**22b**) (1:1, petroleum ether−EtOAc). **22a**: $[\alpha]_D^{20}$ −40.8 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−8.10 (m, 20H), 5.82−5.86 (m, 1H), 5.60 (d, 1H, *J* = 5.2 Hz), 5.45, 5.28, 5.20 (3 × s, each 1H), 5.00 (d, 1H, *J* = 1.6 Hz), 4.62 (dd, 1H, *J* = 3.6, 5.6 Hz), 4.12−4.25 (m, 3H), 3.95−4.04 (m, 3H), 3.87 (dd, 1H, *J* = 7.2, 8.8 Hz), 3.55 (d, 1H, *J* = 7.2 Hz) 3.50 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.0, 165.7, 165.5, 133.6, 133.5, 133.4, 133.2, 129.9, 129.8, 129.77, 129.5, 128.9, 128.5, 128.4, 109.8, 106.7, 105.2, 85.2, 84.9, 82.3, 81.1, 77.6, 77.4, 75.9, 71.3, 66.1, 65.4, 55.0, 26.3, 25.4; IR (KBr) 3453, 2934, 1725, 1602, 1453, 1372 cm^{-1}; HRMS (ESI) calcd for $C_{44}H_{44}O_{15}$ $[M + Na]^+$ 835.2578, found 835.2567. **22b**: $[\alpha]_D^{20}$ −43.4 (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−8.07 (m, 25H), 5.80−5.84 (m, 1H), 5.64 (s, 1H), 5.60 (d, 1H, *J* = 5.6 Hz), 5.43, 5.28, 5.21, 5.17 (4 × s, each 1H), 5.06 (d, 1H, *J* = 2.4 Hz), 4.68 (dd, 1H, *J* = 4.0, 5.2 Hz), 3.93−4.27 (m, 11H), 3.85 (dd, 1H, *J* = 6.8, 8.0 Hz), 3.67 (d, 1H, *J* = 4.0 Hz), 3.50, 1.42, 1.39, 1.35, 1.34 (5 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.8, 165.7, 165.5, 165.2, 133.6, 133.5, 133.3, 133.1, 130.0, 129.93, 129.9, 129.6, 129.1, 129.0, 128.9, 128.45, 128.4, 128.36, 128.3, 109.9, 109.8, 106.8, 105.8, 104.6, 86.9, 84.1, 83.9, 82.3, 81.7, 81.2, 80.8, 77.9, 77.3, 76.2, 75.8, 71.3, 65.7, 65.24, 65.2, 55.1, 26.4, 26.37, 25.4, 25.3; IR (KBr) 3443, 2935, 1725, 1603, 1453, 1376 cm^{-1}; HRMS (ESI) calcd for $C_{60}H_{62}O_{21}$ $[M + Na]^+$ 1141.3681, found 1141.3690.

Methyl 2,3,6-Tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (23). Prepared from **21** (40.0 mg, 0.079 mmol) and **4** (52.6 mg, 0.088 mmol). The residue was purified by column chromatography (4.5:1, petroleum ether−EtOAc) to afford compound **23** as a colorless syrup (62.1 mg, 80%): R_f 0.48 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −4.4 (*c* 1.95, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−8.06 (m, 30H), 5.87−5.90 (m, 1H), 5.62 (d, 1H, *J* = 4.8 Hz), 5.56 (d, 1H, *J* = 5.2 Hz), 5.47, 5.42, 5.36, 5.13 (4 × s, each 1H), 4.68 (dd, 1H, *J* = 3.6, 5.2 Hz), 4.59 (dd, 1H, *J* = 8.4, 12.8 Hz), 4.45−4.52 (m, 3H), 4.16 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.99 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.37 (s, 3H), 2.72 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.0, 165.7, 165.68, 165.5, 165.1, 133.5, 133.4, 133.3, 133.1, 133.0, 129.9, 129.88, 129.86, 129.8, 129.77, 129.7, 129.5, 128.9, 128.89, 128.8, 128.5, 128.4, 128.33, 128.3, 106.8, 106.1, 83.6, 82.2, 81.2, 81.0, 78.0, 77.5, 71.0, 69.1, 66.2, 65.8, 54.9; IR (KBr) 3492, 2932, 1724, 1602, 1492, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{55}H_{48}O_{17}$ $[M + Na]^+$ 1003.2789, found 1003.2782.

Methyl 2-*O*-Benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (25). Prepared from **24** (82 mg, 0.22 mmol) and **3** (105 mg, 0.24 mmol). The residue was purified by column chromatography (4.5:1, petroleum ether−EtOAc) to afford compound **25** as an amorphous solid (118 mg, 79%): R_f 0.44 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −19.8 (*c* 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, 2H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.2 Hz), 7.22−7.49 (m, 12H), 5.63, 5.49 (2 × s, each 1H), 5.09 (d, 1H, *J* = 1.6 Hz), 4.71 (d, 1H, *J* = 12.0 Hz), 4.66 (d, 1H, *J* = 12.0 Hz), 4.65 (d, 1H, *J* = 3.6 Hz), 4.35 (t, 1H, *J* = 9.2 Hz), 4.27 (dd, 1H, *J* = 4.8, 10.4 Hz), 4.02−4.09 (m, 3H), 3.85 (td, 1H, *J* = 4.8, 10.0 Hz), 3.68 (t, 1H, *J* = 10.4 Hz), 3.57−3.61 (m, 2H), 3.46−3.52 (m, 2H), 3.40 (s, 3H), 3.13 (d, 1H, *J* = 6.8 Hz), 1.30, 1.29 (2 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 137.6, 137.1, 133.4, 129.7, 129.2, 128.4, 128.37, 128.2, 128.0, 127.9, 126.2, 109.5, 105.1, 101.8, 98.5, 85.0, 83.2, 79.9, 79.8, 77.1, 74.7, 73.1, 72.3, 65.2, 62.5, 55.3, 26.0, 25.5; IR (KBr) 3528, 2928, 1727, 1603, 1456, 1376 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{42}O_{12}$ $[M + Na]^+$ 701.2574, found 701.2578.

Methyl 2,5-Di-*O*-benzoyl-3-*O*-*tert*-butyldiphenylsilyl-α-L-arabinofuranoside (30). Prepared from methyl glycoside **29** (2.06 g, 5.54 mmol), imidazole (1.13 g, 16.62 mmol), and TBDPSCl (2.23 mL, 8.31 mmol) in dry DMF (14 mL) following a procedure similar to that for **7** → **8**. The crude product was purified by column chromatography (30:1, petroleum ether−EtOAc) to give **30** as a colorless syrup (3.01 g, 89%): R_f 0.51 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −43.7 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, 2H, *J* = 1.2, 8.4 Hz), 7.78 (dd, 2H, *J* = 1.2, 8.4 Hz), 7.60−7.65 (m, 4H), 7.51−7.57 (m, 2H), 7.17−7.38 (m, 10H), 5.28, 4.90 (2 × s, each 1H), 4.43−4.47 (m, 3H), 4.06 (dd, 1H, *J* = 4.4, 12.4 Hz), 3.46 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.3, 135.7, 135.66, 133.2, 132.9, 132.8, 132.4, 130.0, 129.9, 129.7, 128.2, 127.8, 127.7, 106.9, 85.0, 81.5, 77.4, 62.9, 54.9, 26.8, 19.1; IR (KBr) 2931, 2858, 1725, 1602, 1452, 1366 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{38}O_7Si$ $[M + Na]^+$ 633.2248, found 633.2280.

Phenyl 2,5-Di-*O*-benzoyl-3-*O*-*tert*-butyldiphenylsilyl-1-thio-α-L-arabinofuranoside (31). Prepared from glycoside **30** (3.37 g, 5.52 mmol), PhSH (0.67 mL, 6.63 mmol), and $BF_3{\cdot}Et_2O$ (4.2 mL, 33.1 mmol) in CH_2Cl_2 (38.7 mL) following a procedure similar to that for **8** → **9**. The crude product was purified by column chromatography (30:1, petroleum ether−EtOAc) to give **31** as a colorless syrup (3.2 g, 84%): R_f 0.45 (8:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −95.6 (*c* 1.35, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, 2H, *J* = 1.2, 7.2 Hz), 7.81 (dd, 2H, *J* = 1.2, 7.2 Hz), 7.64−7.68 (m, 4H), 7.50−7.57 (m, 4H), 7.22−7.37 (m, 13H), 5.60, 5.47 (2 × s, each 1H), 4.71−4.74 (m, 1H), 4.45 (dd, 1H, *J* = 0.8, 4.8 Hz), 4.35 (dd, 1H, *J* = 2.8, 12.0 Hz),

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4.07 (dd, 1H, J = 2.8, 12.0 Hz), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.2, 135.9, 135.8, 134.6, 133.4, 133.0, 132.7, 132.3, 131.9, 130.2, 130.1, 129.8, 129.7, 129.2, 129.0, 128.4, 128.3, 128.0, 127.9, 127.5, 91.4, 85.1, 82.5, 77.6, 63.0, 26.9, 19.3; IR (KBr) 2930, 2858, 1724, 1602, 1585, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{41}H_{40}O_6SSi$ [M + Na]$^+$ 711.2213, found 711.2226.

Phenyl 2,5-Di-*O*-benzoyl-1-thio-α-L-arabinofuranoside (32). Prepared from **31** (600 mg, 0.87 mmol) and TBAF (0.53 mL, 1.0 M in THF, 0.53 mmol) in THF (1.8 mL) following a procedure similar to that for **9** → **2**. The crude product was purified by column chromatography (5:1, petroleum ether−EtOAc) to give **32** as a white solid (310 mg, 79%): R_f 0.21 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −160.4 (c 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−8.07 (m, 4H), 7.52−7.63 (m, 4H), 7.45 (t, 2H, J = 8.0 Hz), 7.36 (t, 2H, J = 8.0 Hz), 7.28−7.32 (m, 3H), 5.78 (d, 1H, J = 2.8 Hz), 5.18 (t, 1H, J = 3.2 Hz), 4.57−4.69 (m, 3H), 4.27−4.31 (m, 1H), 3.53 (d, 1H, J = 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.5, 134.0, 133.5, 133.3, 132.4, 120.1, 129.9, 129.8, 129.2, 128.8, 128.77, 128.5, 128.1, 89.4, 87.2, 80.7, 77.6, 63.5; IR (KBr) 3520, 2932, 1710, 1601, 1583, 1453 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}O_6S$ [M + Na]$^+$ 473.1035, found 473.1038.

Phenyl 2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-L-arabinofuranoside (34). The donor **33** (876 mg, 1.44 mmol) and the acceptor **32** (500 mg, 1.11 mmol) were dried together under high vacuum for 0.5 h. The mixture was dissolved in CH_2Cl_2 (47 mL) and followed by addition of freshly activated 4 Å molecular sieves (1.4 g). The resulting slurry was cooled to 0 °C, then a solution of TMSOTf (26.1 μL, 0.14 mmol) in CH_2Cl_2 (1.0 mL) was added. After being stirred for 30 min at the same temperature, the reaction mixture was quenched with triethylamine and filtered. The filtrates were concentrated to give a residue, which was purified by column chromatography (6:1, petroleum ether−EtOAc) to afford **34** as a colorless syrup (932.5 mg, 94%): R_f 0.20 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −77.0 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−8.17 (m, 30H), 5.82, 5.71, 5.67 (3 × s, each 1H), 5.59−5.60 (m, 2H), 4.82 (q, 1H, J = 4.4 Hz), 4.66−4.74 (m, 3H), 4.56−4.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.08, 165.7, 165.5, 165.3, 133.6, 133.55, 133.1, 133.0, 132.0, 130.1, 130.0, 129.8, 129.7, 129.6, 129.5, 129.49, 129.0, 128.9, 128.8, 128.5, 128.3, 127.6, 105.6, 91.2, 83.3, 82.2, 81.7, 81.4, 81.1, 77.4, 63.7, 62.9; IR (KBr) 2924, 2854, 1723, 1602, 1584, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{51}H_{42}O_{13}S$ [M + Na]$^+$ 917.2244, found 917.2245.

2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (28). To a solution of **34** (680 mg, 0.76 mmol) in EtOAc (105 mL) were added NBS (1.35 g, 7.6 mmol) and water (21 mL) at room temperature. The reaction mixture was allowed to stir for 4 h at the same temperature, and then saturated aqueous $Na_2S_2O_3$ was added. The organic layer was washed with water and brine, dried, and the solvent was evaporated. The crude product was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford a colorless syrup which was directly used for the next step without further purification. To a stirred solution of the obtained syrup (439.5 mg, 0.55 mmol) in CH_2Cl_2 (2.9 mL) were added CCl_3CN (0.27 mL, 2.75 mmol) and DBU (0.16 mL, 1.1 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated the reaction was complete. The resulting mixture was concentrated and the residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **28** as a colorless syrup (404 mg, 56% over two steps): R_f 0.46 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +4.4 (c 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.18−8.08 (m, 25H), 6.63, 5.82, 5.61 (3 × s, each 1H), 5.57−5.61 (m, 2H), 4.54−4.76 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 165.6, 165.3, 165.2, 160.5, 133.7, 133.6, 133.5, 133.2, 133.0, 129.9, 129.86, 129.83, 129.8, 129.74, 129.7, 129.6, 129.5, 129.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.37, 128.3, 128.2, 105.0, 103.2, 97.3, 83.9, 81.9, 81.7, 81.1, 80.2, 77.6, 63.5, 62.9. Attempts to further purify this compound for HRMS analysis were unsuccessful.

General Procedure for the Chemo- and Regioselective Glycosylations of Diol Thioglycosides 5 and 6 with Trichloroacetimidates 26 and 28. A mixture of trichloroacetimidate donor (0.26 mmol, 1.3 equiv), diol thioglycoside acceptor (1.0 equiv), and freshly activated 4 Å molecular sieves (300 mg) in dry CH_2Cl_2 (8.5 mL) was cooled to −45 °C. The suspension was stirred for 15 min, then a solution of TMSOTf (0.026 mmol) in CH_2Cl_2 (1 mL) was added dropwise at −45 °C. The reaction was stirred for 0.5 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The resulting residue was purified by column chromatography eluted with petroleum ether−EtOAc to afford the corresponding di- or trisaccharide thioglycoside products.

Phenyl 2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2-*O*-benzoyl-α-D-arabinofuranoside (27). Prepared from thioglycoside **5** (69.2 mg, 0.20 mmol) and imidate **26** (157.7 mg, 0.26 mmol). The residue was purified by column chromatography (5:1, petroleum ether−EtOAc) to afford compound **27** as a colorless syrup (135.8 mg, 86%): R_f 0.25 (4:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +71.4 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−8.04 (m, 25H), 5.77 (d, 1H, J = 3.6 Hz), 5.57 (br s, 2H), 5.40 (s, 1H), 5.17 (t, 1H, J = 3.6 Hz), 4.79 (dd, 1H, J = 3.2, 11.6 Hz), 4.59−4.67 (m, 2H), 4.44−4.48 (m, 1H), 4.33−4.37 (m, 1H), 4.07 (dd, 1H, J = 4.0, 11.6 Hz), 3.94 (dd, 1H, J = 4.0, 11.6 Hz), 3.60 (d, 1H, J = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.9, 165.4, 165.0, 133.4, 133.3, 133.2, 133.1, 132.7, 131.3, 129.6, 129.5, 129.4, 129.3, 128.7, 128.6, 128.56, 128.4, 128.2, 128.16, 128.1, 128.0, 127.3, 105.6, 88.6, 86.7, 81.6, 81.0, 80.8, 77.3, 76.2, 65.4, 63.3; IR (KBr) 3467, 2925, 1724, 1602, 1584, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{44}H_{38}O_{12}S$ [M + Na]$^+$ 813.1982, found 813.1979.

Phenyl 2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-L-arabinofuranosyl-(1→5)-2-*O*-benzoyl-α-L-arabinofuranoside (35). Prepared from thioglycoside **6** (65.8 mg, 0.19 mmol) and imidate **28** (233.7 mg, 0.25 mmol). The residue was purified by column chromatography (3.5:1, petroleum ether−EtOAc) to afford compound **35** as a colorless syrup (163.5 mg, 76%): R_f 0.45 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −59.3 (c 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−8.06 (m, 35H), 5.77 (d, 1H, J = 3.6 Hz), 5.70 (s, 1H), 5.48 (d, 1H, J = 4.4 Hz), 5.46 (br s, 2H), 5.42 (s, 1H), 5.19 (t, 1H, J = 3.6 Hz), 4.62−4.67 (m, 2H), 4.46−4.58 (m, 7H), 4.11 (dd, 1H, J = 4.0, 11.6 Hz), 3.90 (dd, 1H, J = 4.0, 11.6 Hz), 3.66 (d, 1H, J = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.4, 166.38, 165.8, 165.7, 165.6, 134.1, 133.9, 133.8, 133.78, 133.4, 133.3, 132.0, 130.2, 130.17, 130.12, 130.1, 130.0, 129.9, 129.7, 129.3, 129.26, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.69, 128.6, 128.56, 127.8, 106.2, 105.0, 89.4, 86.8, 82.3, 81.9, 81.8, 81.7, 81.6, 80.6, 77.6, 76.8, 65.7, 63.9, 63.6; IR (KBr) 3447, 2925, 1724, 1602, 1452, 1272 cm^{-1}; HRMS (ESI) calcd for $C_{63}H_{54}O_{18}S$ [M + Na]$^+$ 1153.2929, found 1153.2917.

One-Pot Synthesis of the Protected Oligosaccharides 39, 41, and 44. Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (39). A mixture of donor **2** (139 mg, 0.31 mmol), methyl glycoside **15** (103 mg, 0.28 mmol), and freshly activated 4 Å molecular sieves (250 mg) in dry CH_2Cl_2 (10 mL) was cooled to −40 °C. The suspension was stirred for 15 min at −40 °C, then NIS (79 mg, 0.35 mmol) and TfOH (0.6 μL, 0.006 mmol) were added and the resulting mixture was gradually warmed to −20 °C. The reaction mixture was stirred for 30 min at the same temperature, at the end of which time TLC indicated the complete consumption of the starting materials. A solution of donor **38** (129 mg, 0.35 mmol) in CH_2Cl_2 (1 mL) was added to the reaction mixture when the temperature was recooled to −40 °C. Then NIS (79 mg, 0.35 mmol) and TfOH (0.6 μL, 0.006 mmol) were added, and the resulting mixture was gradually warmed to −20 °C. After being stirred for 30 min at the same temperature, the reaction mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The resulting residue was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford protected trisaccharide **39** (190 mg, 70%) as a colorless syrup: R_f 0.18 (3:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +36.3 (c 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−8.12 (m, 8H),

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7.18−7.61 (m, 12H), 5.65 (d, 1H, J = 5.2 Hz), 5.51 (s, 1H), 5.41−5.44 (m, 3H), 5.14 (s, 1H), 5.04 (d, 1H, J = 1.2 Hz), 4.89 (dd, 1H, J = 1.6, 5.2 Hz), 4.74 (dd, 1H, J = 2.4, 12.0 Hz), 4.60−4.64 (m, 1H), 4.53 (dd, 1H, J = 4.4, 12.0 Hz), 4.42−4.46 (m, 1H), 4.36 (d, 1H, J = 5.6 Hz), 4.31 (dd, 1H, J = 3.2, 11.6 Hz), 4.21−4.25 (m, 2H), 4.11 (dd, 1H, J = 6.0, 12.0 Hz), 3.95 (dd, 1H, J = 2.4, 11.2 Hz), 3.48, 2.01, 1.97, 1.91 (4 × s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.2, 166.2, 165.7, 165.5, 165.4, 133.51, 133.5, 133.1, 129.9, 129.8, 129.6, 129.2, 129.1, 128.6, 128.53, 128.5, 128.3, 106.7, 105.4, 105.37, 82.8, 82.0, 81.9, 81.3, 81.2 (2C), 80.5, 77.2, 76.9, 65.4, 63.2, 63.0, 54.9, 20.8, 20.6, 20.5; IR (KBr) 2939, 1724, 1603, 1453, 1372, 1274 cm^{-1}; HRMS (ESI) calcd for $C_{50}H_{50}O_{20}$ $[M + Na]^+$ 993.2793, found 993.2801.

Methyl 2,3,5,6-Tetra-*O*-benzoyl-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 (41). Using the same procedures as described for the one-pot preparation of **39**, thioglycoside donor **4** (158 mg, 0.26 mmol) and acceptor **21** (118 mg, 0.23 mmol) were coupled first by activation with NIS (66 mg, 0.29 mmol) and TfOH (0.5 μL, 0.005 mmol), then the resulting disaccharide methyl glycoside **23** was glycosylated with the donor **40** (204 mg, 0.29 mmol) promoted by NIS (66 mg, 0.29 mmol) and TfOH (0.5 μL, 0.005 mmol) to give a crude product, which was purified by column chromatography (4:1, petroleum ether−EtOAc) to afford protected trisaccharide **41** (241 mg, 67%) as a colorless syrup: R_f 0.47 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ −14.9 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−8.07 (m, 50H), 6.03−6.07 (m, 1H), 5.86−5.90 (m, 1H), 5.83 (d, 1H, J = 4.4 Hz), 5.80, 5.67 (2 × s, each 1H), 5.61 (d, 1H, J = 4.2 Hz), 5.56 (d, 1H, J = 4.2 Hz), 5.49, 5.41, 5.31, 5.10 (4 × s, each 1H), 5.06 (t, 1H, J = 4.2 Hz), 4.61−4.79 (m, 7H), 4.16 (dd, 1H, J = 6.8, 10.0 Hz), 3.97 (dd, 1H, J = 6.8, 10.0 Hz), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.95, 165.7, 165.68, 165.67, 165.65, 165.5 165.48, 165.2, 165.1, 133.35, 133.3, 133.2, 133.16, 133.1, 132.9, 132.88, 129.94, 129.92, 129.9, 129.8, 129.78, 129.7, 129.64, 129.6, 129.56, 129.5, 129.46, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.37, 128.35, 128.3, 128.27, 128.2, 128.1, 106.8, 105.8, 105.0, 83.0, 82.2, 82.0, 81.9, 81.5, 80.9, 77.8, 77.5, 77.0, 73.4, 70.8, 70.5, 65.4, 64.7, 63.8, 55.00; IR (KBr) 2926, 2854, 1726, 1602, 1492, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{89}H_{74}O_{26}$ $[M + Na]^+$ 1581.4366, found 1581.4368.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (44). Using the same procedures as described for the one-pot preparation of **39**, thioglycoside donor **3** (129 mg, 0.30 mmol) and acceptor **24** (100 mg, 0.27 mmol) were coupled first by activation with NIS (76 mg, 0.34 mmol) and TfOH (0.5 μL, 0.006 mmol), then the resulting disaccharide methyl glycoside **25** was glycosylated with the donor **43** (234 mg, 0.34 mmol) promoted by NIS (76 mg, 0.34 mmol) and TfOH (0.5 μL, 0.006 mmol) to give a crude product, which was purified by column chromatography (4:1, petroleum−EtOAc) to afford protected trisaccharide **44** (220.5 mg, 65%) as a colorless syrup: R_f 0.43 (2:1, petroleum ether−EtOAc); $[\alpha]_D^{20}$ +53.6 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−8.13 (m, 35H), 6.05 (d, 1H, J = 3.2 Hz), 5.92 (dd, 1H, J = 8.0, 10.4 Hz), 5.74 (dd, 1H, J = 3.6, 10.4 Hz), 5.56 (d, 1H, J = 8.4 Hz), 5.56, 5.40, 5.09 (3 × s, each 1H), 4.65 (dd, 1H, J = 5.2, 9.2 Hz), 4.41−4.49 (m, 3H), 4.27−4.39 (m, 4H), 4.22 (dd, 1H, J = 4.4 10.0 Hz), 4.11 (t, 1H, J = 9.2 Hz), 3.95−3.98 (m, 1H), 3.64 (td, 1H, J = 4.4, 9.6 Hz), 3.52−3.60 (m, 2H), 3.47 (t, 1H, J = 8.0 Hz), 3.31 (s, 3H), 2.76 (t, 1H, J = 9.6 Hz), 2.58 (dd, 1H, J = 3.2, 9.2 Hz), 1.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.50, 165.47, 165.0, 138.0, 137.7, 133.5, 133.47, 133.2, 133.17, 133.0, 130.2, 129.9, 129.8, 129.76, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 128.26, 128.0, 127.9, 127.7, 126.4, 109.4, 104.7, 101.2, 99.1, 98.3, 82.2, 81.9, 81.1, 80.6, 79.2, 75.0, 73.0, 71.8, 71.3, 71.2, 69.5, 68.9, 68.2, 65.2, 62.3, 61.9, 55.0, 25.8, 25.5; IR (KBr) 2982, 2934, 1730, 1603, 1453, 1376 cm^{-1}; HRMS (ESI) calcd for $C_{71}H_{68}O_{21}$ $[M + Na]^+$ 1279.4151, found 1279.4136.

General Procedure for the Deacylation of Trisaccharides Intermediates 39 and 41. To a solution of trisaccharide **39**/**41** (0.03 mmol) in CH_2Cl_2−CH_3OH (1:7, v/v, 2 mL) was added $NaOCH_3$ (4 mg) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with acetic acid, and the resulting mixture was concentrated to dryness. The resulting residue was purified by column chromatography.

Methyl α-D-Arabinofuranosyl-(1→3)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (36). Prepared from **39** (29 mg, 0.03 mmol). The residue was purified by column chromatography (3:1, CH_2Cl_2−MeOH) to afford **36** as a colorless syrup in a yield of 85%. The spectroscopic data for **36** were identical with that previously reported.[8a,10h]

Methyl β-D-Galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranoside (37). Prepared from **41** (41 mg, 0.026 mmol). The residue was purified by column chromatography (3:1, CH_2Cl_2−MeOH) to afford **37** (12.2 mg, 90%) as a colorless syrup: R_f 0.24 (2.5:1, CH_2Cl_2−MeOH); $[\alpha]_D^{20}$ −110.6 (c 0.70, CH_3OH); ^{1}H NMR (400 MHz, D_2O) δ 5.25, 5.04, 4.94 (3 × s, each 1H), 4.08−4.18 (m, 8H), 3.95−4.05 (m, 3H), 3.81−3.92 (m, 4H), 3.62−3.74 (m, 3H), 3.44 (m, 3H); ^{13}C NMR (100 MHz, D_2O) δ 110.5, 110.1, 109.5, 85.4, 84.9, 84.2, 83.7, 83.3, 83.1, 79.1 (2C), 78.9, 78.3, 72.9, 72.0, 71.4, 65.2, 63.4, 57.3; IR (KBr) 3352, 2931, 2856, 1354, 1070, 1027 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{34}O_{16}$ $[M + Na]^+$ 541.1745, found 541.1740.

Methyl β-D-Galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-α-D-glucopyranoside (45). Trisaccharide **44** (181 mg, 0.144 mmol) was dissolved in HOAc−H_2O (4:1, v/v, 10 mL), and the resulting mixture was warmed gradually to 70 °C. The mixture was stirred for 4 h at the same temperature, at the end of which time TLC indicated it was finished. The mixture was cooled and concentrated to give a residue. To a stirred solution of the obtained residue in CH_3OH (3 mL) was added $NaOCH_3$ (22 mg) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with acetic acid, and the resulting mixture was concentrated to dryness. The resulting residue was purified by column chromatography (3.5:1, CH_2Cl_2−MeOH) to afford compound **45** as a colorless syrup (70 mg, 80% over two steps): R_f 0.17 (3.5:1, CH_2Cl_2−MeOH); $[\alpha]_D^{20}$ −13.2 (c 1.50, CH_3OH); ^{1}H NMR (400 MHz, D_2O) δ 7.47 (br s, 5H), 5.28 (s, 1H), 4.72 (br s, 2H), 4.54 (d, 1H, J = 7.6 Hz), 4.24−4.28 (m, 2H), 4.20 (br s, 1H), 3.94−3.97 (m, 2H), 3.83−3.88 (m, 2H), 3.76−3.80 (m, 2H), 3.60−3.73 (m, 7H), 3.54 (dd, 1H, J = 8.0, 10.0 Hz), 3.36−3.44 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ 139.6, 131.2, 131.15, 130.9, 110.7, 105.0, 99.5, 87.1, 84.5, 82.2, 81.2, 80.5, 77.6, 75.2, 74.9, 73.8, 73.0, 72.8, 70.9, 70.2, 65.3, 63.4, 62.8, 57.2; IR (KBr) 3342, 2982, 2934, 1604, 1453, 1374 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{40}O_{16}$ $[M + Na]^+$ 631.2214, found 631.2208.

Methyl β-D-Galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-glucopyranoside (42). To a solution of **45** (32 mg, 0.053 mmol) in CH_3OH (2 mL) was added 10% Pd/C (30 mg), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 24 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction mixture was filtered, and the filtrate was concentrated to give a residue, which was purified by column chromatography (1:1, CH_2Cl_2−MeOH) to afford compound **42** as a colorless syrup (23 mg, 84%): R_f 0.27 (1:1, CH_2Cl_2−MeOH); $[\alpha]_D^{20}$ +4.1 (c 1.15, CH_3OH); ^{1}H NMR (400 MHz, D_2O) δ 5.28 (s, 1H), 4.81 (d, 1H, J = 3.6 Hz), 4.56 (d, 1H, J = 7.6 Hz), 4.35 (br s, 1H), 4.27−4.32 (m, 2H), 3.96−4.00 (m, 1H), 3.93 (d, 1H, J = 3.2 Hz), 3.88 (dd, 1H, J = 2.0, 12.4 Hz), 3.66−3.84 (m, 10H), 3.54 (dd, 1H, J = 8.0, 10.0 Hz), 3.43−3.47 (m, 1H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ 110.8, 105.0, 101.6, 86.7, 84.4, 82.2, 82.1, 77.6, 74.9, 73.9, 73.6, 73.0, 72.6, 70.9, 70.2, 65.3, 63.4, 62.8, 57.4; IR (KBr) 3342, 2934, 2858, 1360, 1070, 1028 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{34}O_{16}$ $[M + Na]^+$ 541.1745, found 541.1742.

One-Pot Synthesis of the Protected Oligosaccharides 46 and 47. Methyl 2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-(1→5)-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-

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(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (46). A solution of trichloroacetimidate **26** (137.2 mg, 0.226 mmol), 3,5-diol thioglycoside **5** (60.2 mg, 0.174 mmol), and freshly activated 4 Å molecular sieves (520 mg) in dry CH_2Cl_2 (6.5 mL) was stirred at room temperature for 15 min. Then the suspension was cooled to −45 °C, and a solution of TMSOTf (4.2 μL, 0.023 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After being stirred for 30 min at the same temperature, the reaction was gradually warmed to ambient temperature. The reaction mixture was stirred for a further 1 h at the same temperature, at the end of which time TLC indicated the complete consumption of the starting materials. The resulting slurry was recooled to −40 °C, and a solution of 5′-OH disaccharide acceptor **16a** (123.9 mg, 0.174 mmol) in CH_2Cl_2 (0.3 mL) was added. Then NIS (49.1 mg, 0.218 mmol) and TfOH (0.35 μL, 0.004 mmol) were added at −40 °C, and the resulting mixture was warmed to −20 °C. The reaction mixture was stirred for 30 min at the same temperature, at the end of which time TLC indicated it was finished. A solution of thioglycoside donor **48** (198.0 mg, 0.218 mmol) in CH_2Cl_2 (0.3 mL) was added when the temperature was recooled to −40 °C. Then NIS (49.1 mg, 0.218 mmol) and TfOH (0.35 μL, 0.004 mmol) were added, and the resulting mixture was warmed to −20 °C. After being stirred for 30 min at the same temperature, the reaction mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. The resulting residue was purified by column chromatography (3:1, petroleum ether−acetone) to afford **46** (151.5 mg, 40% based on **5**) as an amorphous solid: R_f 0.26 (2:1, petroleum ether−acetone). Tetrasaccharide intermediate **49**: $[\alpha]_D^{20}$ +13.4 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−8.06 (m, 40H), 5.61−5.63 (m, 2H), 5.50−5.54 (m, 4H), 5.44 (s, 1H), 5.40 (br s, 2H), 5.18 (d, 1H, *J* = 2.0 Hz), 5.13 (s, 1H), 4.80 (dd, 1H, *J* = 3.2, 12.0 Hz), 4.57−4.67 (m, 3H), 4.39−4.46 (m, 2H), 4.20−4.27 (m, 2H), 4.15 (dd, 1H, *J* = 4.8, 11.2 Hz), 4.02 (dd, 1H, *J* = 4.8, 11.6 Hz), 3.84−3.97 (m, 3H), 3.47 (d, 1H, *J* = 7.2 Hz), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.2, 165.7, 165.67 (2C), 165.4, 165.22, 165.2, 133.5, 133.49, 133.4, 133.38, 133.2, 132.0, 129.9, 129.8, 129.77, 129.7, 129.6, 129.1, 129.0, 128.96, 128.93, 128.9, 128.5, 128.4, 128.3, 128.25, 106.8, 105.8, 105.78, 105.1, 85.7, 82.8, 81.9, 81.8, 81.79, 81.7, 81.6, 81.2, 77.7, 77.3, 77.28, 76.6, 66.1, 65.9, 65.7, 63.6, 54.8; IR (KBr) 3436, 2926, 1724, 1602, 1491, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{77}H_{68}O_{25}$ [M + Na]$^+$ 1415.3947, found 1415.3937. Hexasaccharide **46**: $[\alpha]_D^{20}$ +13.0 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−8.08 (m, 65H), 5.59−5.65 (m, 4H), 5.55 (s, 1H), 5.50−5.54 (m, 7H), 5.42, 5.41, 5.39, 5.33, 5.12 (5 × s, each 1H), 4.74−4.79 (m, 2H), 4.58−4.68 (m, 5H), 4.54 (br s, 2H), 4.41−4.46 (m, 2H), 4.16−4.23 (m, 3H), 4.07−4.12 (m, 1H), 3.92−3.97 (m, 3H), 3.85 (dd, 1H, *J* = 2.4, 11.2 Hz), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 165.7, 165.67, 165.64, 165.6, 165.57, 165.5, 165.32, 165.3, 165.12, 165.1, 164.9, 133.4, 133.3, 133.1, 133.0, 129.9, 129.8, 129.76, 129.6, 129.2, 129.1, 129.05, 129.0, 128.9, 128.8, 128.5, 128.47, 128.4, 128.37, 128.3, 128.26, 106.8, 105.9, 105.85, 105.8, 105.7, 105.3, 82.7, 82.5, 82.2, 82.0, 81.9, 81.7 (2C), 81.6 (2C), 81.5 (2C), 81.0, 80.6, 77.7 (2C), 77.3, 77.1, 77.0, 66.0, 65.7 (2C), 65.5, 63.6, 63.58, 54.9; IR (KBr) 2928, 1725, 1602, 1492, 1452, 1271 cm^{-1}; HRMS (ESI) calcd for $C_{122}H_{104}O_{38}$ [M + Na]$^+$ 2199.6103, found 2199.6082.

Methyl 2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-L-arabinofuranosyl-(1→5)-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-(1→3)-2-*O*-benzoyl-α-L-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-L-arabinofuranoside (47). Using the same procedures as described for the one-pot preparation of **46**, trichloroacetimidate donor **28** (178.1 mg, 0.189 mmol) and 3,5-diol thioglycoside **6** (50.1 mg, 0.145 mmol) were coupled first by activation with TMSOTf (3.44 μL, 0.019 mmol), then the resulting trisaccharide thioglycoside **35** was glycosylated with the acceptor **50** (53.9 mg, 0.145 mol) promoted by NIS (40.8 mg, 0.181 mmol) and TfOH (0.3 μL, 0.003 mmol) to give tetrasaccharide **51**. Finally, thioglycoside donor **52** (100.1 mg, 0.181 mmol) and promoters NIS (40.8 mg, 0.181 mmol) and TfOH (0.3 μL, 0.003 mmol) were added to glycosylate with it. The resulting residue was purified by column chromatograph (3:1, petroleum ether−EtOAc) to afford **47** (135.7 mg, 51% based on **6**) as a colorless syrup: R_f 0.27 (2:1, petroleum ether−EtOAc). Tetrasaccharide intermediate **51**: $[\alpha]_D^{20}$ −20.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−8.06 (m, 40H), 5.68 (s, 1H), 5.55 (d, 1H, *J* = 4.0 Hz), 5.48 (s, 1H), 5.44−5.46 (m, 2H), 5.43 (s, 1H), 5.40 (br s, 2H), 5.16 (d, 1H, *J* = 2.4 Hz), 5.13 (s, 1H), 4.62−4.68 (m, 2H), 4.49−4.55 (m, 3H), 4.36−4.49 (m, 5H), 4.17 (dd, 1H, *J* = 4.8, 11.2 Hz), 4.04 (dd, 1H, *J* = 4.0, 11.2 Hz), 3.93 (dd, 1H, *J* = 4.0, 11.2 Hz), 3.87 (dd, 1H, *J* = 4.8, 11.2 Hz), 3.52 (d, 1H, *J* = 5.2 Hz), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.1, 166.0, 165.7, 165.5, 165.48, 165.3, 165.1, 133.5, 133.45, 133.4, 133.1, 132.9, 129.9, 129.8, 129.76, 129.7, 129.6, 129.5, 129.4, 129.1, 129.06, 129.0, 128.96, 128.9, 128.8, 128.5, 128.47, 128.4, 128.38, 128.24, 128.2, 106.7, 105.9, 105.3, 104.8, 85.9, 82.5, 82.0, 81.8 (2C), 81.76, 81.4, 81.2, 80.3, 77.3 (2C), 76.5, 66.0, 65.5, 63.7, 63.2, 54.9; IR (KBr) 3444, 2927, 1724, 1603, 1492, 1452 cm^{-1}; HRMS (ESI) calcd for $C_{77}H_{68}O_{25}$ [M + Na]$^+$ 1415.3947, found 1415.3936. Pentasaccharide **47**: $[\alpha]_D^{20}$ −17.1 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−8.07 (m, 55H), 5.70 (s, 1H), 5.68 (s, 1H), 5.66 (d, 1H, *J* = 4.8 Hz), 5.57 (s, 1H), 5.49−5.51 (m, 4H), 5.41−5.43 (m, 4H), 5.11 (s, 1H), 4.76−4.81 (m, 1H), 4.65−4.68 (m, 5H), 4.48−4.57 (m, 6H), 4.40−4.43 (m, 1H), 4.23 (dd, 1H, *J* = 4.0, 10.8 Hz), 4.11 (dd, 1H, *J* = 4.8, 11.6 Hz), 4.00 (dd, 1H, *J* = 4.8, 11.6 Hz), 3.91 (dd, 1H, *J* = 4.0, 10.8 Hz), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.95, 165.9, 165.6, 165.5, 165.49, 165.4, 165.36, 165.2, 165.0, 164.9, 133.4, 133.3, 133.2, 133.15, 133.0, 132.9, 132.8, 129.8, 129.77, 129.7, 129.66, 129.6, 129.55, 129.5, 129.4, 129.1, 129.06, 129.0, 128.94, 128.9, 128.86, 128.8, 128.4, 128.38, 128.32, 128.3, 128.2, 128.15, 128.1, 106.5, 105.6, 105.5, 105.47, 104.8, 82.7, 82.2, 82.0, 81.96, 81.7, 81.63 (2C), 81.6, 81.4, 81.2, 80.9, 80.4, 77.7, 77.5, 77.0, 65.5, 65.4, 63.6, 63.5, 63.0, 54.9; IR (KBr) 2928, 1724, 1602, 1492, 1452, 1271 cm^{-1}; HRMS (ESI) calcd for $C_{103}H_{88}O_{32}$ [M + Na]$^+$ 1859.5156, found 1859.5137.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yjs@scu.edu.cn, yjscd@163.com.

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