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Probing the Effect of Acylation on Arabinofuranose Ring Conformation in Di- and Trisaccharide Fragments of Mycobacterial Arabinogalactan

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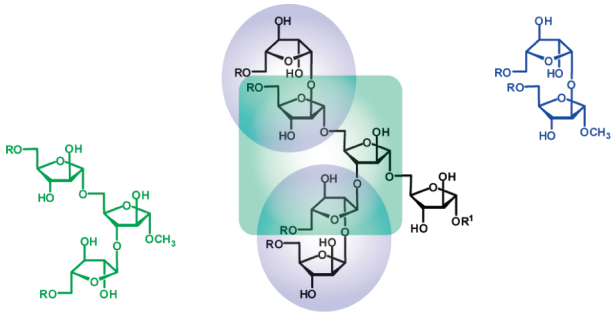

A major component of the cell wall of mycobacteria is the mycolyl−arabinogalactan (mAG) complex. The arabinose and galactose residues in mAG are found solely in the furanose form, and it has been suggested that the flexibility of these five-membered rings allows for the tight packing of mycolic acids. In order to probe the "flexible scaffold hypothesis", we designed and synthesized glycolipids **3**−**6** and **8**−**11** as simple models of the terminal portion of mAG. A set of donors and acceptors were explored for preparing the key β-(1→2) linkage in **2**−**6**, and the best selectivity and yield can be obtained by using the electron-rich thioglycoside donor **14** and the O-5 *p*-methoxybenzyl-protected acceptor **17**. Both α-linkages in the trisaccharides **7**−**11** were formed in a one-pot reaction. The conformations of compounds **2**−**11** were studied using solution-state NMR spectroscopy, but little change was observed in the coupling constants for the ring protons between **2** and **3**−**6** or between **7** and **8**−**11**. However, the rotamer populations about the C-4−C-5 bond for the β-linked ring in disaccharide **2** did change upon acylation at O-5.

Introduction

Tuberculosis remains a major health concern worldwide, with 9.3 million new cases and 1.8 million deaths in 2007.[1] The disease is caused by the bacterium *Mycobacterium tuberculosis*, which produces an unusual cell wall compared to other Gram-positive bacteria.[2] A second lipid bilayer is located outside of the plasma membrane,[3,4] and this bilayer is made up of the unique mycolyl−arabinogalactan (mAG) complex attached to peptidoglycan, as well as various lipids, including trehalose mycolates, phospholipids, and phenolic glycolipids.[2] The mAG complex is essential for the viability of *M. tuberculosis*;[5] in fact, two of the front line drugs used to treat tuberculosis inhibit the biosynthesis of mAG.[6] The mAG is linked to peptidoglycan through a phosphodiester bond to a linker disaccharide of α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*.[7]

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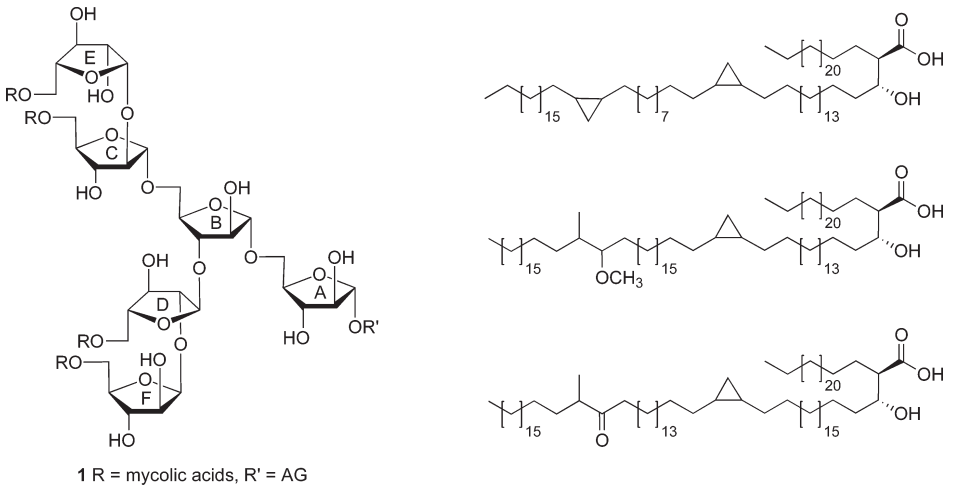

FIGURE 1. (Left) Hexasaccharide motif, **1**, found at the nonreducing end of mycobacterial arabinogalactan (AG). (Right) Three representative examples of mycolic acids found in *M. tuberculosis*.

A linear chain of 30 galactofuranose with alternating β-(1→5) and β-(1→6) linkages is attached to this disaccharide, and at residues 8, 10, and 12 are attached arabinan chains.[8] These arabinose moieties are also in the furanose form, and the 31 monosaccharide residues are linked in a combination of α-(1→5), α-(1→3), and β-(1→2) linkages.[7,9,10] The arabinan chain is capped at the nonreducing end with the branched hexasaccharide shown in Figure 1 and esterified at O-5 of residues C, D, E, and F with mycolic acids, which are α-alkyl, β-hydroxy lipids with 60−90 carbon atoms.[11,12]

An interesting feature of the mAG complex is the presence of only furanose sugars, aside from the pyranose residues of the linker disaccharide. Their unusual configuration has led to the proposal that the significant flexibility of the furanose rings facilitates the tight packing of the mycolic acids, the so-called "flexible scaffold hypothesis".[13,14] The tight packing of these mycolic acids, in turn, provides a dense, low permeability lipid barrier to the passage of antibiotics into the organism, which facilitates its survival. This is an intriguing hypothesis, but there is little experimental support for it. We reasoned that one approach for testing the flexible scaffold hypothesis would be to compare the conformation of the furanose rings in fragments of mycobacterial arabinan with analogues in which O-5 of the terminal residues had been acylated with lipid chains of varying lengths. It could be expected that, if this hypothesis is correct, conformational differences between the acylated and unacylated compounds would be observed. Thus, we describe here the synthesis of a series of di- and trisaccharide glycolipids (Chart 1) and subsequent conformational analysis of these compounds using NMR spectroscopy. These relatively simple analogues were chosen as the first targets as this provided us with the opportunity to develop the methodology that could be used to prepare and study more complicated analogues that bear closer resemblance to the natural polymeric glycolipid. Moreover, such investigations were necessary in the interest of carrying out a systematic study, in which a variety of structural features (e.g., the size of the carbohydrate moiety and the length, branching, and functionalization of the lipid portion) were to be explored.

Results and Discussion

The first challenge to be faced was to select a method for the synthesis of the disaccharide targets **2**−**6**, which contain a 1,2-*cis*-arabinofuranoside (β-arabinofuranoside) linkage. A number of choices exist for the preparation of 1,2-*cis*-arabinofuranosides. For example, previous work[15,16] from our group has led to the development of an indirect method for preparing β-arabinofuranosides by employing 2,3-anhydrofuranosyl donors, which stereroselectively give the β-glycoside. Another indirect method, the intramolecular aglycon delivery approach, has also been reported to be effective for the preparation of β-arabinofuranosides.[17−21] A direct method developed by Kim and co-workers[22] relies on 2-carboxybenzyl donors. Glycosylations with acceptors having benzoyl groups or hindered secondary alcohols afforded excellent yields of the β-glycosides, whereas benzyl-protected alcohols or primary alcohols gave a mixture of α- and β-arabinofuranosides with no significant stereoselectivity. Recently, donors

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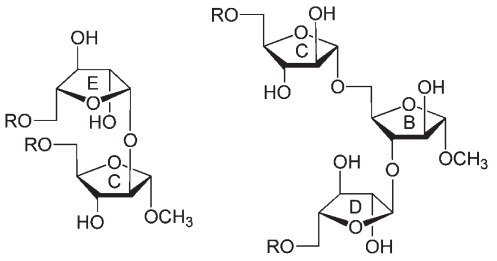
CHART 1. Target Di- and Trisaccharides (The Rings Have Been Labeled To Facilitate Comparison with 1)



2 R = H
3 R = C(O)C_3H_7
4 R = C(O)C_9H_{19}
5 R = C(O)$C_{15}H_{31}$
6 R = C(O)$C_{21}H_{43}$

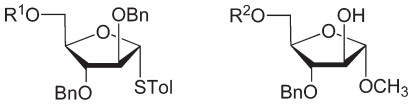
7 R = H
8 R = C(O)C_3H_7
9 R = C(O)C_9H_{19}
10 R = C(O)$C_{15}H_{31}$
11 R = C(O)$C_{21}H_{43}$

containing a cyclic protecting group have been used to increase the β-stereoselectivity in the preparation of arabinofuranosides. Boons and co-workers[23−25] and later Crich[24] and Zhu[26,27] have used a di-*tert*-butyl silane (DTBS) acetal to protect the O-3 and O-5 positions in a thioglycoside donor. By rigidifying the flexible furanose ring, the resulting oxocarbenium ion is locked in a conformation that shields the α-face from attack. The β-face, on the other hand, is less hindered; hence, the glycosylation gives excellent β-selectivities with a range of acceptors having either primary or secondary alcohols. In related work, Ito and co-workers[28] used a 1,3-(1,1,3,3)-tetraisopropyldisiloxanylidene protecting group to protect the O-3 and O-5 positions of a thioglycoside donor to enhance the β-selectivity.

However, the need to install base-sensitive ester linkages on both of the primary hydroxy groups in the disaccharides made many of these approaches impractical (e.g., the 2,3-anhydrosugar method, or the use of 2-carboxybenzyl donors, which provides high selectivity only when acylated acceptors are used) or cumbersome (e.g., the use of DTBS-protected donors, which would require a series of postglycosylation protection−deprotection steps). Therefore, other approaches were explored.

For the design of the donors, it is desirable to install a group that can be readily removed in the presence of other protecting groups because the O-5 position will be acylated in the final products. In addition, O-2 should be protected with nonparticipating benzyl ether, and to maximize the reactivity of the donor, an electron-rich benzyl group should also be used to protect O-3. With regard to the acceptor, the O-3 position should be protected with benzyl ether as its electron-donating nature will increase the nucleophilicity of hydroxyl group at C-2, and O-5 should be protected with groups that could be removed in the presence of benzyl groups. Keeping in mind these criteria, a number of potential donor and acceptor pairs with different electron-donating/withdrawing protecting groups on O-5 can be envisioned. We describe here the development and optimization of this methodology with various donors (**12**−**15**) and acceptors (**16** and **17**, Chart 2) and its application to the synthesis of a panel of disaccharide targets. With this panel of compounds, it was possible to probe the effect of the protecting group on O-5 of the donor and acceptor on reaction stereoselectivity.

CHART 2. Donors (12−15) and Acceptors (16 and 17) Used in β-Arabinofuranosylation Reactions



12 R^1 = PMB
13 R^1 = Bz
14 R^1 = All
15 R^1 = TBDMS

16 R^2 = Bz
17 R^2 = PMB

Preparation of Thioglycoside Donors 12−15. The thioglycoside donors **12** and **13** were synthesized according to the literature.[28−30] Donors **14** and **15** were synthesized from known compound **18**[16,29] (Scheme 1). The free O-5 hydroxyl group in **18** was reacted with sodium hydride and allyl bromide to give donor **14** in excellent (91%) yield. Reaction of the same hydroxyl group with *tert*-butyldimethylsilyl chloride (TBDMSCl) and imidazole gave donor **15** in 75% yield.

Preparation of Acceptors 16 and 17. With the synthesis of the donors finished, we explored the synthesis of acceptors starting from methyl α-D-arabinofuranoside **19** (Scheme 2). By employing Mitsunobu conditions,[31] the epoxide ring was introduced by reaction of **19** with diisopropyl azodicarboxylate (DIAD) and triphenylphosphine, which gave exclusively the desired product **20** in 90% yield.

We optimized the method for the introduction of the benzyl group at O-3, which involved opening of the epoxide ring with sodium benzylate. The best results were obtained when **20** was reacted with 2 equiv of sodium benzylate at high concentration at 100 °C overnight. Under these conditions, the reaction gave diol **21** in 80% yield. The regioselectivity was confirmed by the proton chemical shift of the corresponding acylated derivative of **21**, which has a significant downfield shift of H-2. By controlling the reaction temperature at −10 °C and the amount of benzoyl chloride, selective protection of **21** at the primary position of the diol gave acceptor **16**, which was obtained in 87% yield.

To synthesize acceptor **17**, epoxide **20** was treated with sodium hydride and *p*-methoxybenzyl chloride (PMBCl) to afford the protected epoxide **22** in 80% yield. As before, ring opening of the epoxide in **23** with sodium benzylate gave the desired compound **17** in 77% yield.

Glycosylation of Donors 12−15 and Acceptors 16 and 17. For determining optimal conditions to use in the glycosylations reactions, we studied the reaction of **13** and **16** (Table 1). We first evaluated the effect of temperature (entries 1−5) using

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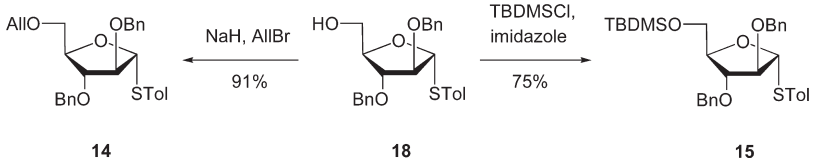
SCHEME 1. Synthesis of Thioglycoside Donors 14 and 15



SCHEME 2. Synthesis of Acceptors 16 and 17

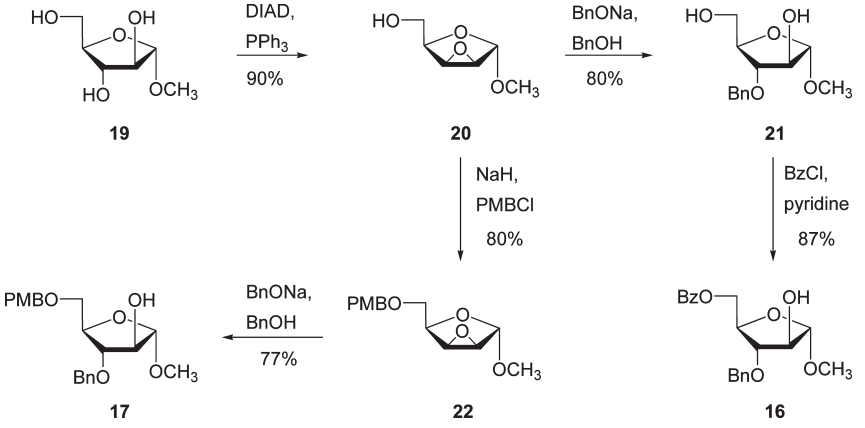
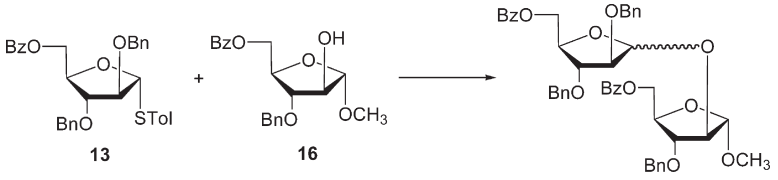


TABLE 1. Optimization of β-Arabinofuranosylation Using Thioglycoside 13 and Acceptor 16



entry	solvent	temperature	time (h)	acceptor concentration (M)	activator	yield (α/β)[d]
1	CH_2Cl_2	−78 °C → rt	4	0.08	NIS−AgOTf[a]	81% (3.1:1)
2	CH_2Cl_2	−78 °C	6	0.08	NIS−AgOTf[a]	85% (3:1)
3	CH_2Cl_2	−60 °C	4	0.08	NIS−AgOTf[a]	91% (3.4:1)
4	CH_2Cl_2	−40 °C	0.5	0.08	NIS−AgOTf[a]	74% (4.6:1)
5	CH_2Cl_2	−60 °C → −40 °C	1	0.08	NIS−AgOTf[a]	89% (4.2:1)
6	CH_2Cl_2	−60 °C → −40 °C	1	1.00	NIS−AgOTf[a]	84% (4.3:1)
7	CH_2Cl_2	−60 °C → −40 °C	1.5	0.05	NIS−AgOTf[a]	85% (4:1)
8	CH_2Cl_2	−60 °C → −40 °C	2	0.01	NIS−AgOTf[a]	93% (3:1)
9	CH_2Cl_2	−60 °C → −40 °C	0.5	0.01	NIS−TMSOTf[b]	78% (5:1)
10	CH_2Cl_2	−60 °C → −40 °C	6	0.01	Ph_2SO−TTBP−Tf_2O[c]	63% (4:1)

[a]Acceptor **16** (1 equiv), donor **13** (1.2 equiv), NIS (1.2 equiv), AgOTf (0.1 equiv). [b]Acceptor **16** (1 equiv), donor **13** (1.2 equiv), NIS (1.2 equiv), TMSOTf (0.1 equiv). [c]Acceptor **16** (1 equiv), donor **13** (1.2 equiv), Ph_2SO (3 equiv), TTBP (6 equiv), Tf_2O (1.1 equiv). [d]Ratio was determined by ^1H NMR spectroscopy.

the standard *N*-iodosuccinimide and silver trifluoromethanesulfonate (NIS−AgOTf) promoter system[32] and dichloromethane as the solvent. When the glycosylations were carried out at −78 °C, the reactions were very slow and usually took 5−6 h to finish. Performing the reaction −60 °C led to reduced reaction times (3−4 h). We then found that at −40 °C the reaction proceeded very quickly but that the yield decreased. Thus, we developed an approach where the reaction was started at −60 °C and then slowly warmed to −40 °C over 2 h. Under these conditions, the reaction gave improved yield and stereoselectivity.

The effect of concentration was also studied (entries 6−8) and was shown not to have a dramatic effect on the yield, although at the lowest concentration investigated (0.01 M), the β-selectivity was sowewhat increased. In addition, other glycoslyaton promoters, such as NIS−trimethylsilyl trifluoromethanesulfonate (TMSOTf)[33,34] and diphenyl sulfoxide, 2,4,6-tri-*tert*-butylpyrimidine, and trifluoromethanesulfonic anhydride (Ph_2SO−TTBP−Tf_2O),[35] were investigated (entires 9 and 10). However, with these promoters, the yield of the product was reduced as was the β-selectivity. Finally, we studied the use of acetonitrile, diethyl ether, toluene, and dioxane as the solvent.

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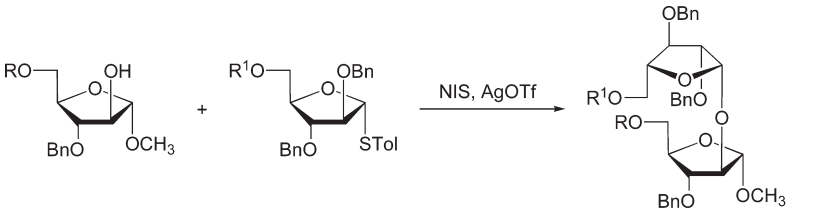
SCHEME 3. Glycosylation of Donors 12−15 with Acceptors 16 and 17



16 R = Bz
17 R = PMB

12 R^1 = PMB
13 R^1 = Bz
14 R^1 = All
15 R^1 = TBDMS

23 R = Bz, R^1 = Bz
24 R = Bz, R^1 = All
25 R = PMB, R^1 = PMB
26 R = PMB, R^1 = Bz
27 R = PMB, R^1 = All
28 R = PMB, R^1 = TBDMS

TABLE 2. Glycosylation with Thioglycosides 12−15

entry	acceptor	donor	product	yield (%)	α/β ratio[a]
1	**16**	**12**	*b*	96	1:3
2	**16**	**13**	**23**	93	3:1
3	**16**	**14**	**24**	96	1:2.5
4	**17**	**12**	**25**	89	1:7.7
5	**17**	**13**	**26**	93	1:4.4
6	**17**	**14**	**27**	93	1:6.3
7	**17**	**15**	**28**	91	1:2

[a]Ratio determined by weight of the isolated pure compounds. [b]The α/β ratio of products could not be separated; ratio was determined by ^{1}H NMR spectroscopy.

However, when performed in any of these solvents, the reactions required extended reaction times and gave poor selectivity compared to those carried out in dichloromethane.

The investigations described above allowed us to identify a set of optimized conditions for coupling donors **12**−**15** with acceptors **16** and **17** (Scheme 3). All reactions were carried out at an acceptor concentration of 0.01 M by cooling the donor (1.2 equiv) and acceptor (1 equiv) in dichloromethane at −60 °C, then NIS and AgOTf were added and the reaction was warmed to −40 °C over 90−120 min. Following workup, the reaction mixture was purified by chromatography, and the isolated anomeric glycosides were characterized. Distinction between α- and β-isomers was achieved by using $\delta_{C\text{-}1}$ and $^3J_{H\text{-}1,H\text{-}2}$ values.[36] For the β-isomer, $\delta_{C\text{-}1}$ = 97−103 ppm, $^3J_{H\text{-}1,H\text{-}2}$ = 3−5 Hz, whereas for the α-isomer, $\delta_{C\text{-}1}$ = 104−111 ppm, $^3J_{H\text{-}1,H\text{-}2}$ = 0−2 Hz. As Table 2 indicates, the yields of these reactions were very good overall, but the α/β ratios changed significantly, depending on the different substituents on the donors and acceptors.

The treatment of the O-5 benzoyl-protected acceptor **16** with any of the donors gave poor to moderate β-selectivity. However, when the *p*-methoxybenzyl-protected acceptor **17** was used, the β/α ratios were enhanced and moderate to good β-selectivity was observed. In other words, the more electron-rich acceptor favored the formation of the β-glycoside. As expected, the structure of the donor also greatly influenced the selectivity. For instance, the ester-protected donor **13** gave poor to moderate selectivity, whereas the two ether-protected species (**12** and **14**) gave better β-selectivity; the *p*-methoxybenzyl ether, **12**, provides slightly more of the β-anomer than the allyl ether, **14**. Finally, the silyl-substituted donor **15** gave poor β-selectivity. One result that remained unclear was why the more electron-rich, "armed" donors **12** and **14** gave better β-selectivity than the less electron-rich, "disarmed" one, **13**. Armed donors[37] are more reactive; thus, the glycosylation should proceed faster and prefer an oxocarbenium ion intermediate resulting in the formation of α/β mixtures. However, in our case, the combination of the most active donor **12** and acceptor **17** gave the best β/α ratio. This finding is consistent with earlier work both from the Ito laboratory[28,29] as well as from our laboratory.[38,39]

Synthesis of Disaccharide Targets 2 and 30. Once the optimization of the β-arabinofuranosyl reaction was complete, we then synthesized the target disaccharides. As indicated in Table 2, treatment of acceptor **17** with donor **12** yielded the best α/β ratio, 1:7.7. However, the separation of the isomers was difficult; therefore, the combination of acceptor **17** and donor **14** was chosen to synthesize the disaccharides. Although the reaction was a bit less stereoselective, 1:6.3 α/β, the α- and β-isomers were easily separated after the removal of the allyl group (Scheme 4). With a route to the pure β-isomer **29** in place, reaction with trifluoroacetic acid cleaved the *p*-methoxybenzyl ether affording **30**, which was ready for acylation. Alternatively, hydrogenolysis of **29** with 20% palladium hydroxide on carbon gave the fully deprotected disaccharide **2** in 85% yield.

Preparation of Trisaccharides 7 and 34. In comparison with the synthesis of the β-linked disaccharide, the target trisaccharides had two α-glycosidic linkages, which can be readily constructed by the use of donors with participating acyl groups on O-2. In designing the synthetic approach to the trisaccharides, we chose an efficient and convergent route, in which the target was assembled by the coupling of a diol acceptor and a single donor to add both α-arabinofuranosyl residues in a single reaction.

With this consideration in mind, trisaccharide **7** was synthesized according to the literature.[40] Similarly, the O-5-deprotected trisaccharide **34** was assembled from known building blocks **31**[40] and **32**[38] in a straightforward way by glycosylation at 0 °C using NIS−AgOTf as the promoter (Scheme 5). Reaction

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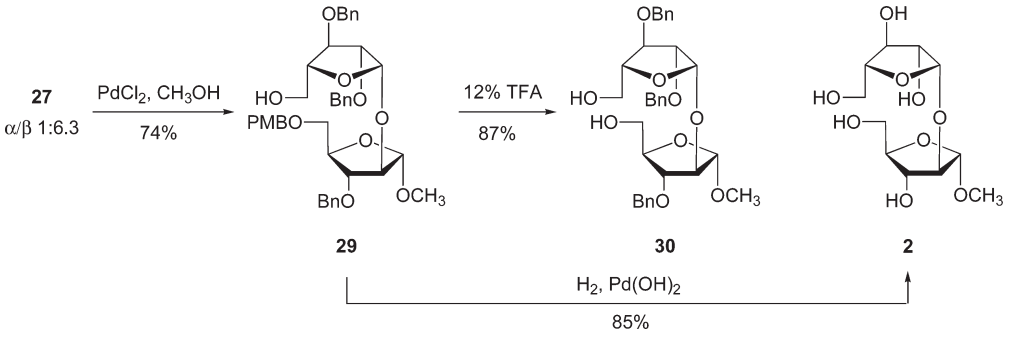
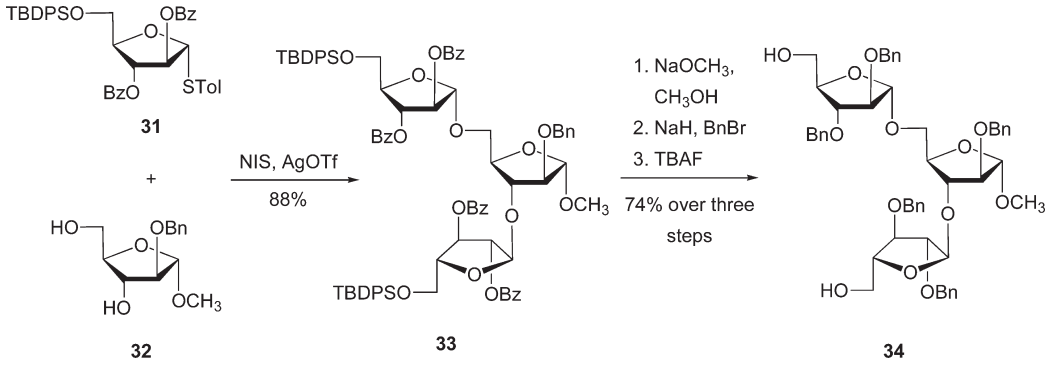
SCHEME 4. Synthesis of Disaccharides 2 and 30



SCHEME 5. Synthesis of Trisaccharide 34



of an excess donor **31** with diol **32** afforded the desired trisaccharide **33** in 88% yield. Conversion of **33** to the target diol **34** was carried out by subsequent removal of the benzoyl groups, benzylation, and cleavage of the silyl ethers, in 74% over three steps. Confirmation of the stereochemistry was again possible by using ^{1}H and ^{13}C NMR spectroscopy. For instance, in **34**, the three anomeric signals in the ^{1}H NMR spectrum, 5.17 ppm (singlet), 5.13 ppm (doublet, J = 1.5 Hz), 4.96 ppm (doublet, $J_{H\text{-}1,H\text{-}2}$ = 1.5 Hz), indicated the presence of three α-arabinofuranosyl linkages. In the ^{13}C NMR spectrum of **34**, these signals are correlated to resonances at 106.9, 106.2, and 105.9 ppm, respectively, by HMQC, which are also indicative of the α-stereochemistry.

Synthesis of Target Glycolipids. Having the sugar moieties of the glycolipid targets in hand, we next explored their coupling with fatty acid counterparts to obtain the target glycolipids. Three carboxylic acid chlorides and one carboxylic acid were chosen to carry out the reactions: butyryl chloride, decanoyl chloride, palmitoyl chloride, and behenic acid. The choice of acyl chloride versus carboxylic acid was made based on commercial availability. The difference between each member of this homologous series of lipids is six carbon atoms.

As expected, the coupling reactions were carried out without problem through the reaction of the disaccharide or trisaccharide diol with the carboxylic acid chloride in pyridine or with the carboxylic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC). The acylated compounds were next debenzylated using palladium hydroxide on carbon under a hydrogen atmosphere to give the target molecules in 68−93% over the two steps, as shown in Scheme 6.

The solvent system used in the debenzylation reactions was a 1:1 mixture of dichloromethane and methanol. Other solvent systems, such as methanol, a mixture of THF and methanol, and a mixture of methanol and ethyl acetate, were also tested. However, only the dichloromethane−methanol system gave a good product yield in a reasonable reaction time, usually overnight, at room temperature. Also, to avoid the possible formation of micelles of the partially deprotected compounds, which we anticipated would slow the heterogeneous debenzylation reaction, the concentration of the substrate was kept low, below 0.01 M.

NMR Analysis for the Measurement of Coupling Constants. While compounds **2** and **7** are fully soluble in D_2O, none of the glycolipids **3**−**6** and **8**−**11** are, which limited the choice of solvents available for conformational analysis. Thus, in all experiments, NMR spectra were acquired using a solution of the target compound in CD_3OD or 1:1 $CDCl_3$−CD_3OD. As outlined below, the choice of solvent had negligible effect on conformation and, in turn, coupling constant values. The assignment process is summarized below.

For the assignment of resonances in the spectra of the oligosaccharides, we followed the "structural reporter group" concept developed by Vliegenthart and co-workers.[41] The α- and β-arabinofuranosides have distinct and well-resolved signals in this region of the spectrum, and the stereochemistry of glycosidic linkages can be determined from their $^3J_{H\text{-}1,H\text{-}2}$ values, as described above. These proton resonances are correlated with carbon signals (110−90 ppm) by using 2D HMQC or HSQC experiments. The remainder of the ring protons were assigned by means of 2D COSY and TOCSY experiments. In addition, all of the 1D ^{1}H NMR spectra were simulated using the program WinDNMR[42] to extract accurate

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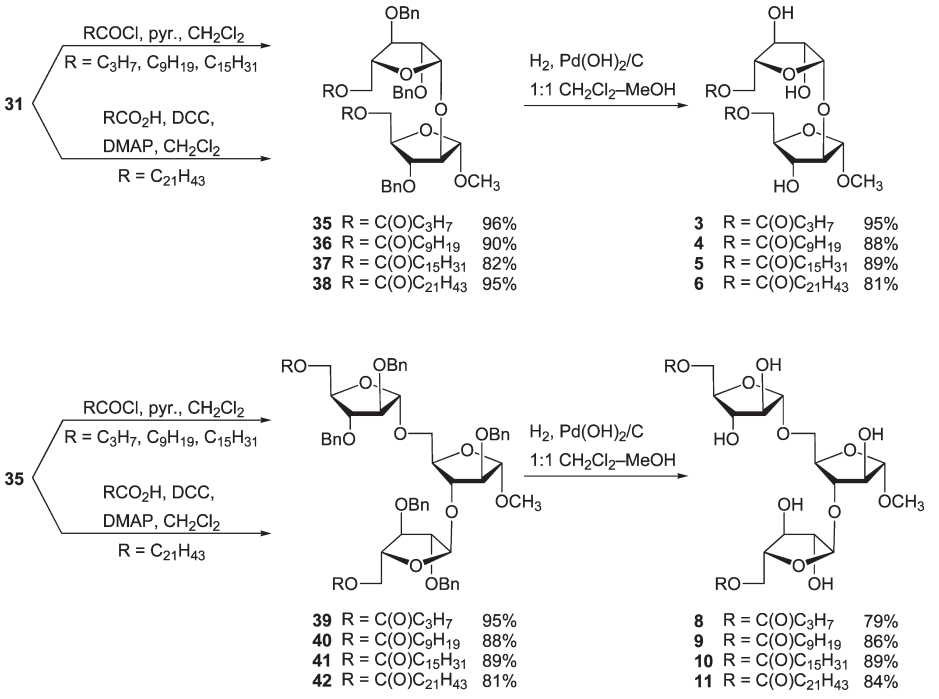
SCHEME 6. Synthesis of Disaccharide Glycolipids 3−6 and Trisaccharide Glycolipids 8−11



$^2J_{H,H}$, $^3J_{H,H}$, or $^4J_{H,H}$ values. The coupling constants for the disaccharides are shown in Table 3, and those for the trisaccharides are given in Table 4. The chemical shifts can be found in the Supporting Information, along with representative examples of the simulated spectra. Assignment of H-5*R* and H-5*S* was based on comparison with previous literature,[43,44] and the $^2J_{H\text{-}5R,H\text{-}5S}$ values are assumed to be negative.[45] At the concentrations used to measure the coupling constants, no broadening of signals was observed, suggesting that the compounds are not aggregating.

The data above demonstrate that acylation has no significant effect on ring conformation as the values for $^3J_{H\text{-}1,H\text{-}2}$, $^3J_{H\text{-}2,H\text{-}3}$, $^3J_{H\text{-}3,H\text{-}4}$, and $^4J_{H\text{-}1,H\text{-}3}$ do not change between compound **2** and **3**−**6** or between **7** and **8**−**11**. Unsurprisingly, when the coupling constants are analyzed in a standard program for determining furanose ring conformation, PSEUROT,[46] the same ring conformations and populations are predicted for **2** as for **3**−**6**, as well as for **7** and **8**−**11** (data not shown). Additionally, changing the NMR solvent from CD_3OD to 1:1 CD_3OD−$CDCl_3$ for **3** and **10** appears to have no significant effect on ring conformation. Because the chemical shifts for the ring protons do not change upon acylation of O-5, we assume that rotation about the glycosidic linkages also remains the same for all of the compounds.

The values for $^3J_{H\text{-}4,H\text{-}5R}$ and $^3J_{H\text{-}4,H\text{-}5S}$ appear to change more significantly upon acylation, and thus we decided to investigate the rotamer populations about the C-4−C-5 bond in more detail. We focused on rings C, D, and E, which have free 5-OH groups in **2** or **7**; the conformation about the C-4−C-5 bond of ring B in the trisaccharides is expected to remain unchanged between **7** and **8**−**11**. Using methods described previously,[43,44,47] we calculated rotamer populations about the C-4−C-5 bond for the terminal rings in compounds **2**−**6** and **7**−**11**. Equations 1 and 2, Karplus relationships[48] derived specifically for the arabinofuranose ring,[49] were used for the parent saccharides **2** and **7**.

$$^3J_{H\text{-}4,H\text{-}5R} = 5.23 + 0.02\cos(\phi + 15.1^\circ) + 4.67\cos(2\phi + 30.2^\circ) \quad (1)$$

$$^3J_{H\text{-}4,H\text{-}5S} = 4.95 - 0.42\cos(\phi) + 4.03\cos(2\phi) \quad (2)$$

TABLE 3. $^2J_{H,H}$, $^3J_{H,H}$, and $^4J_{H,H}$ (Hz) Values for Disaccharide 2 and Disaccharide Glycolipids 3−6

ring	coupling	**2**[a]	**3**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[b]
C	$^3J_{H\text{-}1,H\text{-}2}$	2.2	2.1	2.1	2.1	2.1	2.1
	$^4J_{H\text{-}1,H\text{-}3}$	0.7	0.0	0.0	0.0	0.5	0.0
	$^3J_{H\text{-}2,H\text{-}3}$	5.0	4.6	4.6	4.6	4.7	4.6
	$^3J_{H\text{-}3,H\text{-}4}$	7.6	7.5	7.5	7.5	7.5	7.4
	$^3J_{H\text{-}4,H\text{-}5R}$	5.0	6.3	6.3	6.4	6.3	6.4
	$^3J_{H\text{-}4,H\text{-}5S}$	2.8	3.1	3.1	3.1	3.1	3.1
	$^2J_{H\text{-}5R,H\text{-}5S}$	−12.1	−12.0	−11.9	−12.0	−12.0	−11.9
E	$^3J_{H\text{-}1,H\text{-}2}$	4.4	4.5	4.5	4.5	4.4	4.5
	$^4J_{H\text{-}1,H\text{-}3}$	0.0	0.0	0.0	0.0	0.0	0.0
	$^3J_{H\text{-}2,H\text{-}3}$	8.0	7.8	7.8	7.7	7.4	7.4
	$^3J_{H\text{-}3,H\text{-}4}$	6.8	7.2	7.2	7.2	7.3	7.3
	$^3J_{H\text{-}4,H\text{-}5R}$	6.2	7.2	6.3	6.3	7.5	6.7
	$^3J_{H\text{-}4,H\text{-}5S}$	3.1	3.8	4.5	4.9	3.3	3.8
	$^2J_{H\text{-}5R,H\text{-}5S}$	−12.1	−11.8	−12.0	−12.0	−11.7	−11.8

[a] CD_3OD as solvent. [b] CD_3OD−$CDCl_3$ (1:1) as solvent.

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(49) Taha, H. A.; Castillo, N.; Sears, D. N.; Wasylishen, R. E.; Lowary, T. L. *J. Chem. Theory Comput.* **2010**, *6*, 212–222.

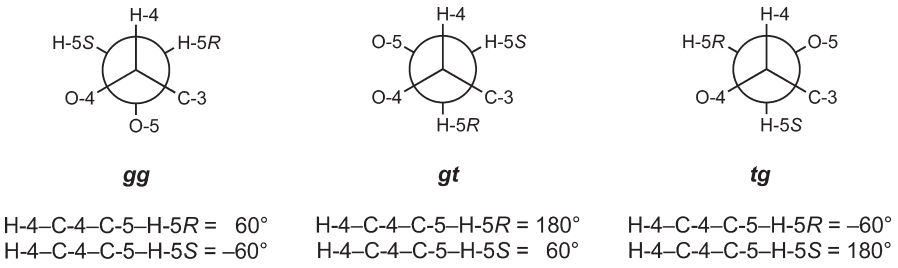

FIGURE 2. Three staggered rotamers about the C-4−C-5 bond of arabinofuranose.

TABLE 4. $^2J_{H,H}$, $^3J_{H,H}$, and $^4J_{H,H}$ (Hz) Values for Trisaccharide **7** and Trisaccharide Glycolipids **8**−**11**

ring	coupling	**7**[a]	**8**[a]	**9**[a]	**10**[a]	**10**[b]	**11**[b]
B	$^3J_{H\text{-}1,H\text{-}2}$	1.4	1.5	1.5	1.5	1.2	1.2
	$^4J_{H\text{-}1,H\text{-}3}$	0.7	0.6	0.5	0.6	0.6	0.6
	$^3J_{H\text{-}2,H\text{-}3}$	2.8	2.9	2.9	2.9	2.4	2.4
	$^3J_{H\text{-}3,H\text{-}4}$	6.0	6.1	6.0	6.2	5.5	5.5
	$^3J_{H\text{-}4,H\text{-}5R}$	3.2	3.0	2.9	2.8	3.0	3.0
	$^3J_{H\text{-}4,H\text{-}5S}$	4.9	5.1	4.9	4.9	4.4	4.5
	$^2J_{H\text{-}5R,H\text{-}5S}$	−11.1	−11.1	−11.2	−11.2	−11.1	−11.2
C	$^3J_{H\text{-}1,H\text{-}2}$	1.6	1.7	1.7	1.6	1.6	1.6
	$^4J_{H\text{-}1,H\text{-}3}$	0.7	0.6	0.7	0.6	0.7	0.5
	$^3J_{H\text{-}2,H\text{-}3}$	3.4	3.6	3.6	3.5	3.4	3.3
	$^3J_{H\text{-}3,H\text{-}4}$	6.0	6.2	6.1	6.2	5.8	5.8
	$^3J_{H\text{-}4,H\text{-}5R}$	5.4	6.0	6.0	6.2	6.1	6.1
	$^3J_{H\text{-}4,H\text{-}5S}$	3.4	3.6	3.6	3.6	3.5	3.5
	$^2J_{H\text{-}5R,H\text{-}5S}$	−11.9	−11.8	−11.8	−11.7	−11.5	−11.5
D	$^3J_{H\text{-}1,H\text{-}2}$	1.7	1.8	1.8	1.8	1.8	1.8
	$^4J_{H\text{-}1,H\text{-}3}$	0.6	0.7	0.7	0.5	0.7	0.6
	$^3J_{H\text{-}2,H\text{-}3}$	3.8	4.1	4.0	4.0	4.0	3.9
	$^3J_{H\text{-}3,H\text{-}4}$	6.6	7.1	7.0	6.9	6.4	6.6
	$^3J_{H\text{-}4,H\text{-}5R}$	5.5	6.1	6.2	6.3	6.2	6.2
	$^3J_{H\text{-}4,H\text{-}5S}$	3.2	3.4	3.4	3.4	3.6	3.6
	$^2J_{H\text{-}5R,H\text{-}5S}$	−12.0	−11.9	−11.9	−11.9	−11.9	−11.9

[a]CD_3OD as solvent. [b]CD_3OD−$CDCl_3$ (1:1) as solvent.

The angle ϕ is the dihedral angle between the coupled protons. These equations were solved to give the maximal coupling constants for the three staggered conformations about the C-4−C-5 bond, where ϕ = 60, 180, and −60° (Figure 2).[40,44,47] The coupling constants measured in solution represent a weighted average of these staggered conformations; the population of each conformation was determined for each ring using eqs 3−5 below:

$$^3J_{H\text{-}4,H\text{-}5R} = 1.18X_{gg} + 9.25X_{gt} + 5.26X_{tg} \quad (3)$$

$$^3J_{H\text{-}4,H\text{-}5S} = 2.73X_{gg} + 2.73X_{gt} + 9.40X_{tg} \quad (4)$$

$$1 = X_{gg} + X_{gt} + X_{tg} \quad (5)$$

Equations 3−5 were solved for compounds **2** and **7**, and the *gg* and *gt* rotamers were found to be favored over the *tg* rotamer, as expected due to the gauche effect.[50] The results for **2** are in Table 5, and the results for **7** are in Table 6. For the α-linked rings (C of **2**, C and D of **7**), the *gg* and *gt* rotamers are about equally populated, giving average values of 46 ± 5% *gg*:48 ± 2% *gt*:6 ± 5% *tg*. For the β-linked ring E in **2**, however, the population of the *gt* rotamer was significantly higher than the *gg* rotamer; the *tg* conformation remained relatively minor: 35% *gg*:59% *gt*:6% *tg*. The C-4−C-5

TABLE 5. Calculated C-4−C-5 Rotamer Distributions (%) for Disaccharides 2−6

ring	rotamer	**2**[a]	**3**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[b]
C	*gg*	52	50	50	48	50	48
	gt	47	46	46	48	46	48
	tg	1	3	3	4	3	4
E	*gg*	35	21	27	20	24	31
	gt	59	57	46	46	61	51
	tg	6	21	27	33	15	18

[a]CD_3OD as solvent. [b]CD_3OD−$CDCl_3$ (1:1) as solvent.

TABLE 6. Calculated C-4−C-5 Rotamer Distributions (%) for Trisaccharides 7−11

ring	rotamer	**7**[a]	**8**[a]	**9**[a]	**10**[a]	**10**[b]	**11**[b]
C	*gg*	43	48	48	44	48	48
	gt	47	43	43	45	44	44
	tg	10	10	10	11	9	9
D	*gg*	43	49	47	45	44	44
	gt	50	44	45	46	45	45
	tg	7	7	8	8	11	11

[a]CD_3OD as solvent. [b]CD_3OD−$CDCl_3$ (1:1) as solvent.

rotamers for the parent disaccharides **2** and **7** are comparable to those for the monosaccharides methyl α-D-arabinofuranoside and methyl β-D-arabinofuranoside. In CD_3OD, we found methyl α-D-arabinofuranoside is 45% *gg*: 47% *gt*: 8% *tg* and methyl β-D-arabinofuranoside is 19% *gg*: 65% *gt*: 16% *tg*. Similar populations have been reported for both monosaccharides in D_2O, as well.[47,51]

For the acylated saccharides **3**−**6** and **8**−**11**, we developed new Karplus-type relationships for $^3J_{H\text{-}4,H\text{-}5R}$ and $^3J_{H\text{-}4,H\text{-}5S}$ in arabinofuranose rings using DFT calculations; the methods are detailed in the Supporting Information. The newly derived eqs 6 and 7 describe the $^3J_{H\text{-}4,H\text{-}5R}$ and $^3J_{H\text{-}4,H\text{-}5S}$ relationships for both anomers of methyl 5-*O*-acetyl-α-D-arabinofuranoside.

$$^3J_{H\text{-}4,H\text{-}5R} = 5.27 - 0.51\cos(\phi) + 4.83\cos(2\phi) + 0.02\sin(\phi) - 0.04\sin(2\phi) \quad (6)$$

$$^3J_{H\text{-}4,H\text{-}5S} = 5.34 - 0.62\cos(\phi) + 4.50\cos(2\phi) + 0.07\sin(\phi) + 2.06\sin(2\phi) \quad (7)$$

Again, the angle ϕ is the dihedral angle between the coupled protons. These equations were solved to give the coupling constants for the staggered conformations about the

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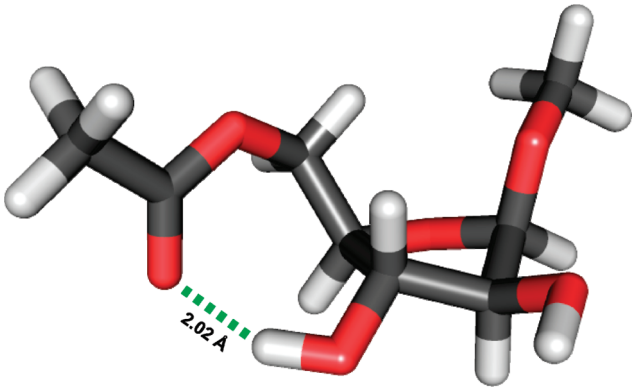

FIGURE 3. Methyl 5-*O*-acetyl-β-D-arabinofuranoside showing the hydrogen bond (green dashed line) from the 3-OH to the carbonyl oxygen of the acetate. This conformation is 2.6 kcal/mol lower in energy than the corresponding conformation without a hydrogen bond, and the distance between the hydrogen and carbonyl oxygen is 2.02 Å. The single point energy was calculated using B3LYP/6-31G(d)[52,53] in Gaussian03.[54] The image was created in PyMol.[55]

C-4−C-5 bond, as described above, to give eqs 8−10 below:

$$^3J_{\text{H-4,H-5}R} = 2.58X_{gg} + 10.62X_{gt} + 2.63X_{tg} \quad (8)$$

$$^3J_{\text{H-4,H-5}S} = 4.50X_{gg} + 1.05X_{gt} + 10.46X_{tg} \quad (9)$$

$$1 = X_{gg} + X_{gt} + X_{tg} \quad (10)$$

Equations 8−10 were solved for compounds **3**−**6** and **8**−**11**, and the rotamer populations for the disaccharides **3**−**6** can be found in Table 5 and those for the trisaccharides **8**−**11** can be found in Table 6. No significant differences in the rotamer populations were seen for the α-linked ring C of **3**−**6** or rings C and D of **8**−**11** when compared to the same rings in **2** and **7**. In the acylated species, the *gg* and *gt* conformations were still favored and were present in about equal in population, with an overall average population of 47 ± 2% *gg*:45 ± 2% *gt*:8 ± 3% *tg* for these rings. However, unlike the α-linked rings, there was a significant change in the β-linked ring E in compounds **3**−**6**. The *tg* population increased from 6% in the unacylated disaccharide **2** to an average 23% in compounds **3**−**6**, with concomitant decreases in both the *gg* and *gt* conformations, to give an average rotamer distribution of 25 ± 4% *gg*:52 ± 7% *gt*:23 ± 7% *tg* for the β-linked rings. One possible explanation for the increase of the *tg* rotamer is that in this conformation the carbonyl oxygen of the acyl group is in the proper orientation to form a weak hydrogen bond to the 3-hydroxyl group, as illustrated in Figure 3. Such interactions would also be anticipated to be important in the relatively hydrophobic outer leaflet of the mycobacterial cell wall, where it is anticipated only limited amounts of water would be present.

Conclusions

In conclusion, we describe here the synthesis of a series of glycolipids (**3**−**6** and **8**−**11**) as simple mimics of the non-reducing end of the mAG complex present in the mycobacterial cell wall. A key step in the synthesis of the disaccharides was the use of an allyl-protected thioglycoside donor with a *p*-methoxybenzyl-protected acceptor to afford the desired β-(1→2) linkage with good selectivity and high yield. Both the α-(1→3) and α-(1→5) linkages of the trisaccharides were formed in excellent yield using a one-pot protocol.

We analyzed the conformation of the final compounds using solution-state NMR spectroscopy to determine all proton−proton coupling constants, and we determined that there was little effect on the ring conformation upon acylation at O-5. In order to see a change in ring conformation, it may be necessary to used branched acyl chains or explore larger compounds, for example, the hexasaccharide shown in Figure 1, which more closely mimic the natural system. We did, however, see a significant increase in the *tg* rotamer about the C-4−C-5 bond in the β-arabinofuranoside rings present in disaccharides **3**−**6** upon acylation, suggesting that the lipid chain has some effect on the conformation of the hydroxymethyl group.

Experimental Section

General Procedure for Hydrogenolysis Leading to 2−6 and 8−11. To a solution of starting material (0.02 mmol) in CH_2Cl_2 (1 mL) and CH_3OH (1 mL) was added 20% $Pd(OH)_2$−C (0.15−0.20 fold by weight) at room temperature. The reaction was stirred under a positive pressure of hydrogen for 12 h. The resulting mixture was filtered through Celite and concentrated. The crude residue was purified on Iatrobeads with CH_2Cl_2−CH_3OH as the eluent.

General Procedures for Glycosylations Leading to 23−28. The acceptor (0.30 mmol) and donor (0.45 mmol) were dried under vacuum in the presence of P_2O_5 for 2 h. To this mixture were added CH_2Cl_2 (30 mL) and 4 Å molecular sieves (0.10 g). The reaction was allowed to stir at room temperature for 30 min and cooled to −60 °C, followed by the addition of *N*-iodosuccinimide (0.36 mmol) and silver triflate (0.03 mmol). After the temperature rose to −40 °C, the reaction mixture turned dark red/brown. Triethylamine was added to quench the reaction after TLC indicated the completion of reactions. The solution was then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was concentrated to give a crude residue that was purified by chromatography to obtain the product.

General Procedure for Acylation Using Carboxylic Acid Chlorides Leading to 35−37 and 39−41. To a solution of the alcohol (0.06 mmol) in CH_2Cl_2 (2 mL) and pyridine (0.05 mL) was added the carboxylic acid chloride (0.15 mmol) at 0 °C. The reaction was kept stirring for 2 h and quenched by the addition of CH_3OH. The resulting solution was concentrated, and the residue was purified by chromatography (4:1 hexane−EtOAc) to obtain the acylated compound.

General Procedure for Acylation Using Behenic Acid Leading to 38 and 42. To a solution of alcohol (0.10 mmol) in CH_2Cl_2 (3 mL) were added behenic acid (131 mg, 0.38 mmol), DCC (79 mg, 0.38 mol), and DMAP (5 mg) at 0 °C. The reaction was kept stirring for 4 h and quenched by the addition of CH_3OH. The resulting solution was concentrated, and the residue was purified by chromatography (10:1 hexane−EtOAc) to obtain the acylated product as a white solid.

Methyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranoside (2): Isolated as a colorless oil, 85%; R_f 0.37 (7:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ −23.2 (*c* 1.0, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 4.95 (d, 1 H, $J_{1E,2E}$ = 4.2 Hz, H-1E), 4.87 (d, 1 H, $J_{1C,2C}$ = 2.1 Hz, H-1C), 4.06−3.95 (m, 4 H, H-2C, H-3C, H-3E, H-2E), 3.88 (ddd, 1 H, $J_{3C,4C}$ = 2.6 Hz, $J_{4C,5Ca}$ = 4.9 Hz, $J_{4C,5Cb}$ = 7.4 Hz, H-4C), 3.81−3.75 (m, 2 H, H-5Ca, H-4E), 3.72 (dd, 1 H, $J_{4E,5Ea}$ = 3.2 Hz, $J_{5Ea,5Eb}$ = 11.8 Hz, H-5Ea), 3.67−3.60 (m, 2 H, H-5Eb,

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H-5Cb), 3.37 (s, 1 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.4 (C-1C), 102.5 (C-1E), 89.5 (C-2E), 84.3 (C-4E), 83.8 (C-4C), 78.8 (C-3C), 76.4 (C-2C), 75.8 (C-3E), 64.4 (C-5E), 62.4 (C-5C), 55.4 (OCH_3); ESIMS m/z calcd for $[C_{11}H_{20}O_9Na]^+$ 319.1000, found 319.0994.

Methyl 5-*O*-butyryl-β-D-arabinofuranosyl-(1→2)-5-*O*-butyryl-α-D-arabinofuranoside (3): Isolated as a colorless oil, 97%; R_f 0.29 (20:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +1.7 (*c* 1.3, CH_3OH); ^{1}H NMR (500 MHz, 1:1 $CDCl_3/CD_3OD$, δ_H) 4.98 (d, 1 H, $J_{1E,2E}$ = 4.4 Hz, H-1E), 4.87 (d, 1 H, $J_{1C,2C}$ = 2.1 Hz, H-1C), 4.31 (dd, 1 H, $J_{4E,5Ea}$ = 3.1 Hz, $J_{5Ea,5Eb}$ = 11.9 Hz, H-5Ea), 4.25−4.19 (m, 2 H, H-5Ca, H-5Cb), 4.14 (dd, 1 H, $J_{4E,5Eb}$ = 6.3 Hz, $J_{5Ea,5Eb}$ = 11.9 Hz, H-5Eb), 4.07−3.92 (m, 6 H, H-4C, H-2C, H-2E, H-3C, H-3E, H-4E), 3.38 (s, 3 H, OCH_3), 2.34−2.30 (m, 4 H, CH_2 × 2), 1.68−1.58 (m, 4 H, CH_2 × 2), 0.96−0.90 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$, δ_C) 175.5 (*C*═O), 175.4 (*C*═O), 108.4 (C-1C), 103.0 (C-1E), 89.8 (C-2C), 81.5 (C-4E), 81.3 (C-4C), 78.5 (C-2E), 77.2 (C-3C), 76.7 (C-3E), 67.1 (C-5E), 64.9 (C-5C), 56.1 (OCH_3), 37.2 (acyl *C*H_2 × 2), 19.5(8) (acyl *C*H_2), 19.5(5) (acyl *C*H_2), 14.4(8) (acyl *C*H_3), 14.4(6) (acyl *C*H_3); ESIMS m/z calcd for $[C_{19}H_{32}O_{11}Na]^+$ 459.1837, found 459.1834.

Methyl 5-*O*-decanoyl-β-D-arabinofuranosyl-(1→2)-5-*O*-decanoyl-α-D-arabinofuranoside (4): Isolated as a colorless oil, 92%; R_f 0.41 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +0.6 (*c* 1.3, CH_3OH); ^{1}H NMR (600 MHz, 1:1 $CDCl_3/CD_3OD$, δ_H) 4.98 (d, 1 H, $J_{1E,2E}$ = 4.5 Hz, H-1E), 4.87 (d, 1 H, $J_{1C,2C}$ = 2.1 Hz, H-1C), 4.32 (dd, 1 H, $J_{4C,5Ca}$ = 3.1 Hz, $J_{5Ca,5Cb}$ = 12.0 Hz, H-5Ca), 4.24−4.20 (m, 2 H, H-5Ea, H-5Eb), 4.14 (dd, 1 H, $J_{4C,5Cb}$ = 6.3 Hz, $J_{5Ca,5Cb}$ = 12.0 Hz, H-5Cb), 4.06 (ddd, 1 H, $J_{3C,4C}$ = 7.5 Hz, $J_{4C,5Ca}$ = 3.1 Hz, $J_{4C,5Cb}$ = 6.3 Hz, H-4C), 4.01 (dd, 1 H, $J_{1C,2C}$ = 2.1 Hz, $J_{2C,3C}$ = 4.5 Hz, H-2C), 4.00−3.91 (m, 4 H, H-2E, H-3C, H-3E, H-4E), 3.36 (s, 3 H, OCH_3), 2.36−2.30 (m, 4 H, CH_2 × 2), 1.64−1.54 (m, 4 H, CH_2 × 2), 1.34−1.08 (m, 24 H, CH_2 × 12), 0.88−0.82 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$, δ_C) 175.7 (*C*═O), 175.6 (*C*═O), 108.4 (C-1C), 103.0 (C-1E), 89.8 (C-2C), 81.5 (C-4E), 81.3 (C-4C), 78.5 (C-2E), 77.2 (C-3C), 76.7 (C-3E), 67.1 (C-5E), 65.0 (C-5C), 56.2 (OCH_3), 35.4 (acyl *C*H_2), 35.3(2) (acyl *C*H_2), 35.3(1) (acyl *C*H_2), 33.1 (acyl *C*H_2), 30.7 (acyl *C*H_2), 30.5(4) (acyl *C*H_2), 30.5(2) (acyl *C*H_2), 30.4(0) (acyl *C*H_2), 30.3(8) (acyl *C*H_2), 30.3(6) (acyl *C*H_2), 26.2(3) (acyl *C*H_2), 26.1(5) (acyl *C*H_2), 26.1(2) (acyl *C*H_2), 23.9 (acyl *C*H_2), 15.0 (acyl CH_3 × 2); ESIMS m/z calcd for $[C_{31}H_{56}O_{11}Na]^+$: 627.3715, found 627.3717.

Methyl 5-*O*-palmitoyl-β-D-arabinofuranosyl-(1→2)-5-*O*-palmitoyl-α-D-arabinofuranoside (5). Isolated as a colorless oil, 95%; R_f 0.53 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +2.7 (*c* 2.6, $CHCl_3$); ^{1}H NMR (600 MHz, 1:1 $CDCl_3/CD_3OD$, δ_H) 4.98 (d, 1 H, $J_{1E,2E}$ = 4.5 Hz, H-1E), 4.87 (d, 1 H, $J_{1C,2C}$ = 2.1 Hz, H-1C), 4.31 (dd, 1 H, $J_{4C,5Ca}$ = 3.1 Hz, $J_{5Ca,5Cb}$ = 11.9 Hz, H-5Ca), 4.23−4.21 (m, 2 H, H-5Ea, H-5Eb), 4.14 (dd, 1 H, $J_{4C,5Cb}$ = 6.3 Hz, $J_{5Ca,5Cb}$ = 11.9 Hz, H-5Cb), 4.06 (ddd, 1 H, $J_{3C,4C}$ = 7.5 Hz, $J_{4C,5Ca}$ = 3.1 Hz, $J_{4C,5Ca}$ = 6.3 Hz, H-4C), 4.01 (dd, 1 H, $J_{1C,2C}$ = 2.1 Hz, $J_{2C,3C}$ = 4.7 Hz, H-2C), 4.00−3.91 (m, 4 H, H-2E, H-3C, H-3E, H-4E), 3.36 (s, 3 H, OCH_3), 2.36−2.30 (m, 4 H, CH_2 × 2), 1.64−1.56 (m, 4 H, CH_2 × 2), 1.34−1.18 (m, 48 H, CH_2 × 24), 0.88−0.82 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$, δ_C) 175.7 (*C*═O), 175.6 (*C*═O), 108.4 (C-1C), 103.0 (C-1E), 89.8 (C-2C), 81.5 (C-4E), 81.2 (C-4C), 78.5 (C-2E), 77.2 (C-3C), 76.7 (C-3E), 67.0 (C-5E), 65.0 (C-5C), 56.2 (OCH_3), 35.3(2) (acyl *C*H_2), 35.3(1) (acyl *C*H_2), 33.2 (acyl *C*H_2), 30.9(4) (acyl *C*H_2), 30.9(1) (acyl *C*H_2), 30.8(8) (acyl *C*H_2), 30.7(5) (acyl *C*H_2), 30.6(1) (acyl *C*H_2), 30.5(6) (acyl *C*H_2), 30.4(0) (acyl *C*H_2), 30.3(8) (acyl *C*H_2), 26.1(7) (acyl *C*H_2), 26.1(3) (acyl *C*H_2), 23.9 (acyl *C*H_2), 15.0 (acyl CH_3 × 2); ESIMS m/z calcd for $[C_{43}H_{80}O_{11}Na]^+$: 795.5593, found 795.5589.

Methyl 5-*O*-behenoyl-β-D-arabinofuranosyl-(1→2)-5-*O*-behenoyl-α-D-arabinofuranoside (6): Isolated as a colorless oil, 92%; R_f 0.61 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +4.2 (*c* 1.7, $CHCl_3$); ^{1}H NMR (600 MHz, 1:1 $CDCl_3$−CD_3OD, δ_H) 4.98 (d, 1 H, $J_{1E,2E}$ = 4.4 Hz, H-1E), 4.87 (d, 1 H, $J_{1C,2C}$ = 2.1 Hz, H-1C), 4.31 (dd, 1 H, $J_{4C,5Ca}$ = 3.1 Hz, $J_{5Ca,5Cb}$ = 11.9 Hz, H-5Ca), 4.24−4.20 (m, 2 H, H-5Ea, H-5Eb), 4.14 (dd, 1 H, $J_{4C,5Cb}$ = 6.3 Hz, $J_{5Ca,5Cb}$ = 11.9 Hz, H-5Cb), 4.06 (ddd, 1 H, $J_{3C,4C}$ = 7.5 Hz, $J_{4C,5Ca}$ = 3.1 Hz, $J_{4C,5Cb}$ = 6.3 Hz, H-4C), 4.00 (dd, 1 H, $J_{1C,2C}$ = 2.1 Hz, $J_{2C,3C}$ = 4.7 Hz, H-2C), 3.99−3.91 (m, 4 H, H-2E, H-3C, H-3E, H-4E), 3.36 (s, 3 H, OCH_3), 2.36−2.30 (m, 4 H, CH_2 × 2), 1.64−1.56 (m, 4 H, CH_2 × 2), 1.40−1.06 (m, 72 H, CH_2 × 36), 0.90−0.78 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3$−CD_3OD, δ_C) 175.7 (*C*═O), 175.6 (*C*═O), 108.4 (C-1C), 103.1 (C-1E), 90.0 (C-2C), 81.5 (C-4E), 81.2 (C-4C), 78.5 (C-2E), 77.3 (C-3C), 76.7 (C-3E), 67.0 (C-5E), 65.0 (C-5C), 56.2 (OCH_3), 35.3 (acyl *C*H_2), 33.2 (acyl *C*H_2), 30.9(4) (acyl *C*H_2), 30.9(4) (acyl *C*H_2), 30.9(1) (acyl *C*H_2), 30.8 (acyl *C*H_2), 30.6(1) (acyl *C*H_2), 30.5(7) (acyl *C*H_2), 30.4(1) (acyl *C*H_2), 30.3(9) (acyl *C*H_2), 26.1(7) (acyl *C*H_2), 26.1(4) (acyl *C*H_2), 23.9 (acyl *C*H_2), 15.0 (acyl CH_3 × 2); ESIMS m/z calcd for $[C_{55}H_{104}O_{11}Na]^+$ 963.7471, found 963.7472.

Methyl 5-*O*-butyryl-α-D-arabinofuranosyl-(1→3)-[5-*O*-butyryl-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranoside (8): Isolated as a colorless oil, 79%; R_f 0.29 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +140.7 (*c* 0.4, CH_3OH); ^{1}H NMR (600 MHz, 1:1 $CDCl_3/CD_3OD$, δ_H) 5.00 (d, 1 H, $J_{1D,2D}$ = 1.8 Hz, H-1D), 4.97 (d, 1 H, $J_{1C,2C}$ = 1.4 Hz, H-1C), 4.77 (s, 1 H, H-1B), 4.30−4.25 (m, 2 H, H-5Ca, H-5 Da), 4.19−4.10 (m, 4 H, H-5Cb, H-5Db, H-4C, H-4B), 4.06 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 2.4 Hz, H-2B), 4.05−4.00 (m, 3 H, H-2C, H-2D, H-4D), 3.97 (dd, 1 H, $J_{2B,3B}$ = 2.4 Hz, $J_{3B,4B}$ = 5.5 Hz, H-3B), 3.93 (dd, 1 H, $J_{4B,5Ba}$ = 4.6 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Ba), 3.81−3.78 (m, 2 H, H-3C, H-3D), 3.68 (dd, 1 H, $J_{4B,5Bb}$ = 3.0 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Bb), 3.38 (s, 3 H, OCH_3), 2.34−2.30 (m, 4 H, acyl CH_2 × 2), 1.66−1.60 (m, 4 H, acyl CH_2 × 2), 0.95−0.90 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$, δ_C) 175.4(6) (*C*═O), 175.4(5) (*C*═O), 110.6 (C-1B), 109.6 (C-1C), 109.3 (C-1D), 84.9 (C-3B), 83.4 (C-4D), 83.2(2) (C-4C), 83.1(9) (C-4B), 82.7 (C-2D), 82.5 (C-2C), 81.7 (C-2B), 79.1(0) (C-3D), 79.0(6) (C-3C), 67.9 (C-5B), 65.4 (C-5C), 65.1 (C-5D), 55.9 (OCH_3), 37.1(8) (acyl *C*H_2), 37.1(8) (acyl *C*H_2), 19.6 (acyl *C*H_2 × 2), 14.5(4) (acyl *C*H_3), 14.5(2) (acyl *C*H_3); ESIMS m/z calcd for $[C_{24}H_{40}O_{15}Na]^+$ 591.2259, found 591.2257.

Methyl 5-*O*-decanoyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-decanoyl-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranoside (9): Isolated as a colorless oil, 86%; R_f 0.38 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +115.0 (*c* 1.1, CH_3OH); ^{1}H NMR (600 MHz, 1:1 $CDCl_3$−CD_3OD, δ_H) 5.00 (d, 1 H, $J_{1D,2D}$ = 1.8 Hz, H-1D), 4.97 (d, 1 H, $J_{1C,2C}$ = 1.3 Hz, H-1C), 4.77 (s, 1 H, H-1B), 4.30−4.24 (m, 2 H, H-5Ca, H-5 Da), 4.18−4.10 (m, 4 H, H-5Cb, H-5Db, H-4C, H-4B), 4.06 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 2.4 Hz, H-2B), 4.05−4.00 (m, 3 H, H-2C, H-2D, H-4D), 3.99 (dd, 1 H, $J_{2B,3B}$ = 2.4 Hz, $J_{3B,4B}$ = 5.5 Hz, H-3B), 3.94 (dd, 1 H, $J_{4B,5Ba}$ = 4.6 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Ba), 3.82−3.78 (m, 2 H, H-3C, H-3D), 3.68 (dd, 1 H, $J_{4B,5Bb}$ = 3.0 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Bb), 3.34 (s, 3 H, OCH_3), 2.36−2.31 (m, 4 H, acyl CH_2 × 2), 1.62−1.56 (m, 4 H, acyl CH_2 × 2), 1.34−1.20 (m, 24 H, acyl CH_2 × 12), 0.87−0.82 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$, δ_C) 175.6(4) (C═O), 175.6(3) (C═O), 110.6 (C-1B), 109.6 (C-1C), 109.3 (C-1D), 84.8 (C-3B), 83.4 (C-4D), 83.3 (C-4C), 83.2 (C-4B), 82.7 (C-2D), 82.6 (C-2C), 81.7 (C-2B), 79.1(4) (C-3D), 79.0(8) (C-3C), 67.8 (C-5B), 65.4 (C-5C), 65.2 (C-5D), 55.9 (OCH_3), 35.3(1) (acyl *C*H_2), 35.2(9) (acyl *C*H_2), 33.1 (acyl *C*H_2), 30.7 (acyl *C*H_2), 30.6 (acyl *C*H_2), 30.5(4) (acyl *C*H_2), 30.5(3) (acyl *C*H_2), 30.4(1) (acyl *C*H_2), 30.3(9) (acyl *C*H_2), 26.1 (acyl *C*H_2), 23.9 (acyl *C*H_2), 15.0 (acyl *C*H_3); ESIMS m/z calcd for $[C_{36}H_{64}O_{15}Na]^+$ 759.4137, found 759.4137.

Methyl 5-*O*-palmitoyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-palmitoyl-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranoside (10): Isolated as a colorless oil, 89%; R_f 0.47 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ +64.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, 1:1 $CDCl_3$−CD_3OD, δ_H) 5.00 (d, 1 H, $J_{1D,2D}$ = 1.7 Hz, H-1D), 4.97 (d, 1 H,

$J_{1C,2C}$ = 1.3 Hz, H-1C), 4.77 (s, 1 H, H-1B), 4.30−4.24 (m, 2 H, H-5Ca, H-5 Da), 4.18−4.09 (m, 4 H, H-5Cb, H-5Db, H-4C, H-4B), 4.05 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 2.3 Hz, H-2B), 4.04−4.00 (m, 3 H, H-2C, H-2D, H-4D), 3.99 (dd, 1 H, $J_{2B,3B}$ = 2.3 Hz, $J_{3B,4B}$ = 5.5 Hz, H-3B), 3.94 (dd, 1 H, $J_{4B,5Ba}$ = 4.5 Hz, $J_{5Ba,5Bb}$ = 11.1 Hz, H-5Ba), 3.82−3.78 (m, 2 H, H-3C, H-3D), 3.68 (dd, 1 H, $J_{4B,5Bb}$ = 3.0 Hz, $J_{5Ba,5Bb}$ = 11.1 Hz, H-5Bb), 3.34 (s, 3 H, OCH_3), 2.36−2.30 (m, 4 H, acyl CH_2 × 2), 1.64−1.54 (m, 4 H, acyl CH_2 × 2), 1.34−1.16 (m, 48 H, acyl CH_2 × 24), 0.88−0.80 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3$/CD_3OD, δ_C) 175.6 (C=O × 2), 110.6 (C-1B), 109.6 (C-1C), 109.4 (C-1D), 84.8 (C-3B), 83.4 (C-4D), 83.3 (C-4C), 83.2 (C-4B), 82.7 (C-2D), 82.6 (C-2C), 81.7 (C-2B), 79.1 (C-3D, C-3C), 67.8 (C-5B), 65.4 (C-5C), 65.2 (C-5D), 55.9 (OCH_3), 35.3(2) (acyl CH_2), 35.3(0) (acyl CH_2), 33.2 (acyl CH_2), 30.9(4) (acyl CH_2), 30.9(1) (acyl CH_2), 30.8(8) (acyl CH_2), 30.7(7) (acyl CH_2), 30.7(6) (acyl CH_2), 30.6(1) (acyl CH_2), 30.6(0) (acyl CH_2), 30.5(7) (acyl CH_2), 30.4(3) (acyl CH_2), 30.4(2) (acyl CH_2), 26.1 (acyl CH_2), 23.9 (acyl CH_2), 15.0 (acyl CH_3 × 2); ESIMS *m*/*z* calcd for $[C_{48}H_{88}O_{15}Na]^+$ 927.6015, found 927.6014.

Methyl 5-*O*-behenoyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-behenoyl-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranoside (11): Isolated as a colorless oil, 84%; R_f 0.60 (10:1 CH_2Cl_2−CH_3OH); $[\alpha]_D$ −3.2 (*c* 1.3, CH_3OH); ^{1}H NMR (600 MHz, 1:1 $CDCl_3$−CD_3OD, δ_H) 5.00 (d, 1 H, $J_{1D,2D}$ = 1.7 Hz, H-1D), 4.97 (d, 1 H, $J_{1C,2C}$ = 1.2 Hz, H-1C), 4.77 (s, 1 H, H-1B), 4.30−4.24 (m, 2 H, H-5Ca, H-5 Da), 4.19−4.10 (m, 4 H, H-5Cb, H-5Db, H-4C, H-4B), 4.05 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 2.4 Hz, H-2B), 4.04−4.01 (m, 3 H, H-2C, H-2D, H-4D), 3.99 (ddd, 1 H, $J_{1B,3B}$ = 0.5 Hz, $J_{2B,3B}$ = 2.4 Hz, $J_{3B,4B}$ = 5.5 Hz, H-3B), 3.94 (dd, 1 H, $J_{4B,5Ba}$ = 4.5 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Ba), 3.82−3.77 (m, 2 H, H-3C, H-3D), 3.68 (dd, 1 H, $J_{4B,5Bb}$ = 2.9 Hz, $J_{5Ba,5Bb}$ = 11.2 Hz, H-5Bb), 3.35 (s, 3 H, OCH_3), 2.36−2.30 (m, 4 H, CH_2 × 2), 1.64−1.54 (m, 4 H, CH_2 × 2), 1.40−1.16 (m, 72 H, CH_2 × 36), 0.88−0.80 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, 1:1 $CDCl_3$−CD_3OD, δ_C) 175.6 (C=O × 2), 110.6 (C-1B), 109.6 (C-1C), 109.4 (C-1D), 84.8 (C-3B), 83.4 (C-4D), 83.3 (C-4C), 83.2 (C-4B), 82.7 (C-2D), 82.6 (C-2C), 81.7 (C-2B), 79.1 (C-3D, C-3C), 67.8 (C-5B), 65.4 (C-5C), 65.2 (C-5D), 55.9 (OCH_3), 35.3(2) (acyl CH_2), 35.3(0) (acyl CH_2), 33.2 (acyl CH_2), 30.9(4) (acyl CH_2), 30.9(0) (acyl CH_2), 30.7(8) (acyl CH_2), 30.7(7) (acyl CH_2), 30.6(1) (acyl CH_2), 30.4(3) (acyl CH_2), 30.4(2) (acyl CH_2), 26.2 (acyl CH_2), 23.9 (acyl CH_2), 15.0 (acyl CH_3 × 2); ESIMS *m*/*z* calcd for $[C_{60}H_{112}O_{15}Na]^+$ 1095.7893, found 1095.7892.

***p*-Tolyl 5-*O*-allyl-2,3-di-*O*-benzyl-1-thio-α-D-arabinofuranoside (14).** To a solution of compound **18** (2.34 g, 5.36 mmol) in DMF (25 mL) were added NaH (343 mg, 8.58 mmol, 60% dispersion in oil) and AllBr (0.70 mL, 8.04 mmol) at 0 °C. The mixture was stirred at this temperature for 2 h, and the reaction was quenched by the addition of CH_3OH. The solution was diluted with EtOAc and washed with water. The organic layer was dried ($MgSO_4$), concentrated, and purified by chromatography (8:1 hexane−EtOAc) to afford **14** (2.33 g, 91%) as a colorless syrup: R_f 0.54 (4:1 hexane−EtOAc); $[\alpha]_D$ +120.4 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.42−7.28 (m, 12 H, Ar), 7.12−7.10 (m, 2 H, Ar), 5.93−5.84 (m, 1 H, CH_2=C*H*−CH_2O), 5.53 (d, 1 H, $J_{1,2}$ = 3.0 Hz, H-1), 5.30−5.24 (m, 1 H, CH_2=CH−CH_2O), 5.20−5.16 (m, 1 H, CH_2=CH−CH_2O), 4.68−4.50 (m, 4 H, PhCH_2O), 4.40−4.35 (m, 1 H, H-4), 4.13 (dd, 1 H, $J_{1,2}$ = $J_{2,3}$ = 3.0 Hz, H-2), 4.06−3.98 (m, 3 H, CH_2=CH−CH_2O × 2, H-3), 3.67 (dd, 1 H, $J_{4,5a}$ = 3.9 Hz, $J_{5a,5b}$ = 10.9 Hz, H-5a), 3.61 (dd, 1 H, $J_{4,5b}$ = 5.1 Hz, $J_{5a,5b}$ = 10.9 Hz, H-5b), 2.34 (s, 3 H, tolyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 137.8 (Ar), 137.4(4) (Ar), 137.3(7) (Ar), 134.6 (Ar), 132.0 (Ar × 2), 131.0 (Ar), 129.7 (CH_2=*C*H−CH_2O), 128.4(4) (Ar × 2), 128.4(0) (Ar × 2), 128.0 (Ar × 2), 127.9 (Ar × 2), 127.8(4) (Ar), 127.7(9) (Ar × 2), 117.0 (*C*H_2=CH−CH_2O), 90.6 (C-1), 88.5 (C-2), 83.5 (C-3), 80.4 (C-4), 72.4 (Ph*C*H_2O), 72.3 (Ph*C*H_2O), 72.1 (CH_2=CH−*C*H_2O), 69.2 (C-5), 21.1 (tolyl *C*H_3); ESIMS *m*/*z* calcd for $[C_{29}H_{32}O_4SNa]^+$ 499.1914, found 499.1911.

***p*-Tolyl 2,3-di-*O*-benzyl-5-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-arabinofuranoside (15).** To a solution of compound **18** (57 mg, 0.13 mmol) in CH_2Cl_2 (1.3 mL) *tert*-butyldimethylsilyl chloride (50 mg, 0.33 mmol) were added imidazole (45 mg, 0.60 mmol) and DMAP (10 mg). The solution was stirred for 2 h, and then the reaction was quenched by the addition of CH_3OH. The solution was concentrated, and the residue was purified by chromatography (4:1 hexane−EtOAc) to obtain **15** (54 mg, 75%) as a colorless syrup: R_f 0.32 (4:1 hexane−EtOAc); $[\alpha]_D$ +76.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.47−7.41 (m, 2 H, Ar), 7.40−7.29 (m, 10 H, Ar), 7.15−7.11 (m, 2 H, Ar), 5.52 (d, 1 H, $J_{1,2}$ = 3.0 Hz, H-1), 4.67 (d, 1 H, *J* = 11.9 Hz, PhCH_2O), 4.60 (s, 2 H, PhCH_2O), 4.54 (d, 1 H, *J* = 11.8 Hz, PhCH_2O), 4.28 (ddd, 1 H, $J_{3,4}$ = 6.3 Hz, $J_{4,5a}$ = 4.4 Hz, $J_{4,5b}$ = 4.6 Hz, H-4), 4.15 (dd, 1 H, $J_{1,2}$ = $J_{2,3}$ = 3.0 Hz, H-2), 4.06 (dd, 1 H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 6.3 Hz, H-3), 3.82 (dd, 1 H, $J_{4,5a}$ = 4.4 Hz, $J_{5a,5b}$ = 11.0 Hz, H-5a), 3.79 (dd, 1 H, $J_{4,5b}$ = 4.6 Hz, $J_{5a,5b}$ = 11.0 Hz, H-5b), 2.35 (s, 3 H, tolyl CH_3), 0.92 (s, 9 H, *t*-butyl CH_3 × 3), 0.08 (s, 6 H, TBDMS CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 137.9 (Ar), 137.5 (Ar), 137.2 (Ar), 131.9 (Ar × 2), 131.1 (Ar), 129.6 (Ar × 2), 128.4(2) (Ar × 2), 128.3(8) (Ar × 2), 127.9(1) (Ar × 2), 127.8(5) (Ar), 127.7(3) (Ar × 2), 127.7(1) (Ar), 90.5 (C-1), 88.4 (C-2), 83.4 (C-3), 82.2 (C-4), 72.2 (Ph*C*H_2O), 72.1 (Ph*C*H_2O), 62.7 (C-5), 25.9 (*t*-butyl *C*H_3 × 3), 21.1 (tolyl *C*H_3), 18.3 (*t*-butyl *C*), −5.2(7) (Si *C*H_3), −5.3(4) (Si *C*H_3); ESIMS *m*/*z* calcd for $[C_{32}H_{42}O_4SiSNa]^+$ 573.2465, found 573.2463.

Methyl 5-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (16). Compound **21** (246 mg, 0.97 mmol) was dissolved in CH_2Cl_2 (19 mL) and pyridine (0.47 mL), and the solution was cooled to −10 °C. Benzoyl chloride (0.16 mL, 1.28 mmol) was added dropwise to the mixture over a period of 30 min with stirring. The reaction was subsequently quenched by the addition of CH_3OH, concentrated and the residue purified by chromatography (2:1 hexane−EtOAc) to obtain **16** (301 mg, 87%) as a colorless syrup: R_f 0.32 (2:1 hexane−EtOAc); $[\alpha]_D$ +90.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.04−8.01 (m, 2 H, Ar), 7.58−7.54 (m, 1 H, Ar), 7.46−7.41 (m, 2 H, Ar), 7.34−7.24 (m, 5 H, Ar), 4.88 (s, 1 H, H-1), 4.71 (d, 1 H, *J* = 12.1 Hz, PhCH_2O), 4.62 (d, 1 H, *J* = 12.1 Hz, PhCH_2O), 4.55 (dd, 1 H, $J_{4,5a}$ = 3.1 Hz, $J_{5a,5b}$ = 11.5 Hz, H-5a), 4.43−4.35 (m, 2 H, H-5b, H-4), 4.26 (dd, 1 H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 2.5 Hz, H-2), 3.88 (dd, 1 H, $J_{2,3}$ = 2.5 Hz, $J_{3,4}$ = 5.8 Hz, H-3), 3.42 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.4 (C=O), 137.5 (Ar), 133.1 (Ar), 129.8 (Ar), 129.7 (Ar × 2), 128.5 (Ar × 2), 128.4 (Ar × 2), 128.0 (Ar), 127.9 (Ar × 2), 109.5 (C-1), 85.4 (C-3), 80.6 (C-2), 80.1 (C-4), 72.5 (Ph*C*H_2O), 64.3 (C-5), 55.1 (OCH_3); ESIMS *m*/*z* calcd for $[C_{20}H_{22}O_6Na]^+$ 381.1309, found 381.1313.

Methyl 3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (17). To a solution of compound **22** (1.88 g, 7.06 mmol) dissolved in benzyl alcohol (8 mL) was added 1 M BnONa in benzyl alcohol (8.50 mL, 8.50 mmol). The reaction mixture was stirred at 100 °C for 24 h. After cooling to rt, the solution was neutralized with acetic acid, diluted with CH_2Cl_2, and washed with water. The organic layer was then concentrated, and the residue was purified by chromatography (4:1 hexane−EtOAc) to yield **17** (2.03 g, 77%) as a colorless oil: R_f 0.21 (2:1 hexane−EtOAc); $[\alpha]_D$ +129.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.34−7.27 (m, 5 H, Ar), 7.20−7.16 (m, 2 H, Ar), 6.88−6.84 (m, 2 H, Ar), 4.90 (s, 1 H, H-1), 4.69 (d, 1 H, *J* = 12.3 Hz, PhCH_2O), 4.54 (d, 1 H, *J* = 11.4 Hz, PhCH_2O), 4.52 (d, 1 H, *J* = 12.3 Hz, PhCH_2O), 4.40 (d, 1 H, *J* = 11.4 Hz, PhCH_2O), 4.27 (ddd, 1 H, $J_{3,4}$ = $J_{4,5a}$ = 2.4 Hz, $J_{4,5b}$ = 2.6 Hz, H-4), 4.11 (d, 1 H, $J_{2,OH}$ = 10.9 Hz, H-2), 3.83−3.80 (m, 4 H, H-3, PMBOCH_3), 3.63 (dd, 1 H, $J_{4,5a}$ = 2.4 Hz, $J_{5a,5b}$ = 10.4 Hz, H-5a), 3.44−3.40 (m, 4 H, H-5b, OCH_3), 3.37 (d, 1 H, $J_{2,OH}$ = 10.9 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.5 (Ar), 137.7 (Ar), 129.5 (Ar × 2), 129.0 (Ar), 128.4 (Ar × 2), 127.9 (Ar × 2),

127.8 (Ar), 114.0 (Ar × 2), 110.6 (C-1), 85.0 (C-2), 83.7 (C-3), 77.8 (C-4), 73.4 (Ph*C*H$_2$O), 72.1 (Ph*C*H$_2$O), 69.4 (C-5), 55.3 (PMBO*C*H$_3$, O*C*H$_3$); ESIMS *m*/*z* calcd for $[C_{21}H_{26}O_6Na]^+$ 397.1622, found 397.1621.

Methyl 2,3-anhydro-α-D-lyxofuranoside (20). Methyl α-D-arabinofuranoside **19** (2.69 g, 16.4 mmol) and triphenylphosphine (5.16 g, 19.7 mmol) were dissolved in tetrahydrofuran (50 mL), and the solution was cooled to 0 °C. Diisopropylazodicarboxylate (3.88 mL, 19.7 mmol) was added dropwise over a period of 10 min. After complete addition of the reagent, the reaction mixture was warmed to room temperature and was stirred for 1 h. The solution was subsequently concentrated and purified by chromatography (4:1 hexane−EtOAc) to obtain **20** (2.16 g, 90%) as a white crystalline solid: R_f 0.14 (2:1 hexane−EtOAc); $[\alpha]_D$ +97.1 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 4.98 (s, 1 H, H-1), 4.17−4.13 (m, 1 H, H-4), 3.91−3.88 (m, 2 H, H-5a, H-5b), 3.75 (dd, 1 H, $J_{1,2}$ = 0.7 Hz, $J_{2,3}$ = 2.9 Hz, H-2), 3.66 (d, 1 H, $J_{2,3}$ = 2.9 Hz, H-3), 3.43 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 102.2 (C-1), 76.2 (C-4), 61.9 (C-5), 55.8 (C-3), 55.6 (O*C*H$_3$), 54.1 (C-2); ESIMS *m*/*z* calcd for $[C_6H_{10}O_4Na]^+$ 169.0471, found 169.0472.

Methyl 3-*O*-benzyl-α-D-arabinofuranoside (21). To a solution of compound **20** (0.72 g, 2.71 mmol) dissolved in benzyl alcohol (4 mL) was added 1 M BnONa in benzyl alcohol (4.10 mL, 4.10 mmol). The reaction mixture was stirred at 100 °C for 24 h. After cooling to rt, the solution was neutralized with acetic acid, diluted with CH_2Cl_2, and washed with water. The organic layer was then concentrated, and the residue was purified by chromatography (4:1 hexane−EtOAc) to yield **21** (0.55 g, 80%) as a colorless syrup: R_f 0.38 (2:1 hexane−EtOAc); $[\alpha]_D$ +149.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 7.35−7.30 (m, 4 H, Ar), 7.26−7.24 (m, 1 H, Ar), 4.79 (s, 1 H, H-1), 4.67 (d, 1 H, *J* = 11.9 Hz, PhC*H*$_2$O), 4.55 (d, 1 H, *J* = 11.9 Hz, PhC*H*$_2$O), 4.12 (dd, 1 H, $J_{1,2}$ = 1.1 Hz, $J_{2,3}$ = 2.6 Hz, H-2), 4.03 (ddd, 1 H, $J_{3,4}$ = 5.9 Hz, $J_{4,5a}$ = 3.6 Hz, $J_{4,5b}$ = 5.6 Hz, H-4), 3.76 (ddd, 1 H, $J_{1,3}$ = 0.6 Hz, $J_{2,3}$ = 2.6 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 3.69 (dd, 1 H, $J_{4,5a}$ = 3.6 Hz, $J_{5a,5b}$ = 11.9 Hz, H-5a), 3.61 (dd, 1 H, $J_{4,5b}$ = 5.6 Hz, $J_{5a,5b}$ = 11.9 Hz, H-5b), 3.38 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 139.5 (Ar), 129.4 (Ar × 2), 128.9 (Ar × 2), 128.8 (Ar), 111.1 (C-1), 86.8 (C-2), 84.5 (C-3), 81.5 (C-4), 73.1 (Ph*C*H$_2$O), 63.3 (C-5), 55.1 (O*C*H$_3$); ESIMS *m*/*z* calcd for $[C_{13}H_{18}O_5Na]^+$ 277.1047, found 277.1046.

Methyl 2,3-anhydro-5-*O*-*p*-methoxybenzyl-α-D-lyxofuranoside (22). To a solution of compound **20** (1.29 g, 8.86 mmol) in DMF (15 mL) were added NaH (425 mg, 10.6 mmol, 60% dispersion in oil) and PMBCl (1.48 mL, 10.6 mmol) at 0 °C. The mixture was stirred at this temperature for 1 h, and the reaction was then quenched by the addition of CH_3OH. The solution was diluted with EtOAc and washed with water. The organic layer was dried ($MgSO_4$) and concentrated, and the residue was purified by chromatography (6:1 hexane−EtOAc) to afford **22** (1.88 g, 80%) as a colorless oil: R_f 0.25 (6:1 hexane−EtOAc); $[\alpha]_D$ +21.8 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.30−7.26 (m, 2 H, Ar), 6.91−6.87 (m, 2 H, Ar), 4.95 (s, 1 H, H-1), 4.55 (d, 1 H, *J* = 11.7 Hz, PhC*H*$_2$O), 4.51 (d, 1 H, *J* = 11.7 Hz, PhC*H*$_2$O), 4.18 (dd, 1 H, $J_{4,5a}$ = $J_{4,5b}$ = 6.3 Hz, H-4), 3.81 (s, 3 H, PMBOC*H*$_3$), 3.75 (d, 1 H, $J_{2,3}$ = 2.3 Hz, H-2), 3.65−3.61 (m, 2 H, H-3, H-5), 3.42 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.3 (Ar), 130.0 (Ar), 129.4 (Ar × 2), 113.8 (Ar × 2), 102.3 (C-1), 76.8 (C-4), 73.3 (Ph*C*H$_2$O), 68.2 (C-5), 56.2 (C-3), 55.6 (O*C*H$_3$), 55.3 (PMBO*C*H$_3$), 54.4 (C-2); ESIMS *m*/*z* calcd for $[C_{14}H_{18}O_5Na]^+$ 289.1047, found 289.1048.

Methyl 5-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-5-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (23): Isolated as a colorless oil, 23%; R_f 0.35 (3:1 hexane−EtOAc); $[\alpha]_D$ +4.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.05−8.02 (m, 2 H, Ar), 7.98−7.95 (m, 2 H, Ar), 7.54−7.50 (m, 2 H, Ar), 7.40−7.18 (m, 19 H, Ar), 5.11 (d, 1 H, $J_{1E,2E}$ = 4.5 Hz, H-1E), 4.90 (s, 1 H, H-1C), 4.75−4.68 (m, 2 H, PhC*H*$_2$O), 4.64−4.58 (m, 3 H, PhC*H*$_2$O), 4.50−4.44 (m, 3 H, PhC*H*$_2$O, H-5Ca, H-5Ea), 4.40−4.32 (m, 4 H, H-2C, H-4C, H-5Cb, H-5Eb), 4.27 (ddd, 1 H, $J_{3E,4E}$ = $J_{4E,5Eb}$ = 6.6 Hz, $J_{4E,5Ea}$ = 4.5 Hz, H-4E), 4.25 (dd, 1 H, $J_{2E,3E}$ = $J_{3E,4E}$ = 6.6 Hz, H-3E), 4.14 (dd, 1 H, $J_{1E,2E}$ = 4.5 Hz, $J_{2E,3E}$ = 6.6 Hz, H-2E), 4.08 (dd, 1 H, $J_{2C,3C}$ = 2.5 Hz, $J_{3C,4C}$ = 5.8 Hz, H-3C), 3.40 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.3 (*C*═O), 166.1 (*C*═O), 137.7 (Ar), 137.6 (Ar), 137.5 (Ar), 133.7 (Ar), 133.1 (Ar), 133.0 (Ar), 130.2 (Ar), 129.9 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 128.5(5) (Ar × 2), 128.4(7) (Ar), 128.4(4) (Ar), 128.3(5) (Ar × 2), 128.3(4) (Ar × 2), 128.3(0) (Ar × 2), 128.1(3) (Ar × 2), 128.0(7) (Ar), 127.8 (Ar), 127.7(1) (Ar × 2), 127.6(9) (Ar), 107.1 (C-1C), 100.9 (C-1E), 86.3 (C-2C), 84.5 (C-3C), 83.9 (C-2E), 82.3 (C-3E), 80.2 (C-4C), 78.8 (C-4E), 72.8 (Ph*C*H$_2$O), 72.6(2) (Ph*C*H$_2$O), 72.5(7) (Ph*C*H$_2$O), 66.3 (C-5E), 64.4 (C-5C), 54.9 (O*C*H$_3$); ESIMS *m*/*z* calcd for $[C_{46}H_{46}O_{11}Na]^+$ 797.2932, found 797.2935.

Methyl 5-*O*-allyl-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-5-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (24): Isolated as a colorless oil, 69%; R_f 0.60 (2:1 hexane−EtOAc); $[\alpha]_D$ −5.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.07−8.04 (m, 2 H, Ar), 7.56−7.51 (m, 1 H, Ar), 7.42−7.38 (m, 2 H, Ar), 7.37−7.24 (m, 15 H, Ar), 5.82−5.74 (m, 1 H, CH_2═C*H*−CH_2O), 5.18−5.13 (m, 1 H, C*H*$_2$═CH−CH_2O), 5.10−5.04 (m, 2 H, C*H*$_2$═CH−CH_2O, H-1E), 4.99 (s, 1 H, H-1C), 4.76−4.55 (m, 6 H, PhC*H*$_2$O), 4.49 (dd, 1 H, $J_{4C,5Ca}$ = 3.9 Hz, $J_{5Ca,5Cb}$ = 11.7 Hz, H-5Ca), 4.42 (dd, 1 H, $J_{4C,5Cb}$ = 5.7 Hz, $J_{5Ca,5Cb}$ = 11.7 Hz, H-5Cb), 4.37 (ddd, 1 H, $J_{3C,4C}$ = $J_{4C,5Cb}$ = 5.7 Hz, $J_{4C,5Ca}$ = 3.9 Hz, H-4C), 4.31 (dd, 1 H, $J_{1C,2C}$ = 1.1 Hz, $J_{2C,3C}$ = 2.6 Hz, H-2C), 4.14−4.06 (m, 4 H, H-2E, H-3E, H-3C, H-4E), 3.91−3.82 (m, 2 H, CH_2═CH−C*H*$_2$O), 3.53−3.44 (m, 2 H, H-5Ea, H-5Eb), 3.38 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.3 (*C*═O), 138.2 (Ar), 137.7 (Ar), 137.6 (Ar), 134.4 (Ar), 133.0 (Ar), 129.9 (Ar), 129.8 (Ar × 2), 129.5 (Ar × 2), 129.3(7) (Ar × 3), 128.3(6) (Ar × 3), 128.1 (Ar), 128.0 (CH$_2$═*C*H−CH_2O), 127.7(6) (Ar × 3), 128.7(5) (Ar × 3), 127.7(0) (Ar), 117.1 (*C*H$_2$═CH−CH_2O), 107.2 (C-1C), 100.5 (C-1E), 86.0 (C-2C), 84.2 (C-3C), 84.0 (C-2E), 82.8 (C-4C), 80.1 (C-3E), 80.0 (C-4E), 72.6 (Ph*C*H$_2$O), 72.4(4) (Ph*C*H$_2$O), 72.4(2) (Ph*C*H$_2$O), 72.1 (CH_2═CH−*C*H$_2$O), 71.9 (C-5E), 64.5 (C-5C), 54.9 (O*C*H$_3$); ESIMS *m*/*z* calcd for $[C_{42}H_{46}O_{10}Na]^+$ 733.2983, found 733.2986.

Methyl 2,3-di-*O*-benzyl-5-*O*-*p*-methoxybenzyl-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (25): Isolated as a colorless oil, 79%; R_f 0.28 (3:1 hexane−EtOAc); $[\alpha]_D$ −22.7 (*c* 0.5, $CHCl_3$); NMR (600 MHz, $CDCl_3$, δ_H) 7.36−7.01 (m, 17 H, Ar), 7.16−7.12 (m, 2 H, Ar), 6.87−6.84 (m, 2 H, Ar), 6.82−6.78 (m, 2 H, Ar), 5.07 (d, 1 H, $J_{1E,2E}$ = 4.2 Hz, H-1E), 4.90 (s, 1 H, H-1C), 4.68−4.64 (m, 2 H, PhC*H*$_2$O), 4.62−4.55 (m, 3 H, PhC*H*$_2$O), 4.48−4.44 (m, 3 H, PhC*H*$_2$O), 4.38−4.30 (m, 2 H, PhC*H*$_2$O), 4.26 (dd, 1 H, $J_{1C,2\ C}$ = 1.3 Hz, $J_{2C,3C}$ = 2.9 Hz, H-2C), 4.23 (ddd, 1 H, $J_{3C,4C}$ = $J_{4C,5Cb}$ = 6.0 Hz, $J_{4C,5Ca}$ = 4.3 Hz, H-4C), 4.12−4.06 (m, 3 H, H-2E, H-3E, H-4E), 3.99 (dd, 1 H, $J_{2C,3C}$ = 2.9 Hz, $J_{3C,4C}$ = 6.0 Hz, H-3C), 3.78 (s, 3 H, PMBOC*H*$_3$), 3.76 (s, 3 H, PMBOC*H*$_3$), 3.58−3.48 (m, 4 H, H-5Ca, H-5Cb, H-5Ea, H-5Eb), 3.38 (s, 3 H, O*C*H$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.1(9) (Ar), 159.1(6) (Ar), 138.2 (Ar), 138.1 (Ar), 137.7 (Ar), 130.3 (Ar), 130.1 (Ar), 129.4 (Ar × 2), 129.2 (Ar × 2), 128.5 (Ar × 2), 128.3(2) (Ar × 2), 129.2(6) (Ar × 2), 127.9(7) (Ar × 2), 127.9(0) (Ar), 127.7(4) (Ar × 2), 127.7(0) (Ar × 2), 127.6(2) (Ar), 127.5(6) (Ar), 113.7 (Ar × 4), 107.0 (C-1C), 100.3 (C-1E), 86.0 (C-2C), 84.0 (C-2E, C-3C), 83.1 (C-3E), 81.4 (C-4C), 80.1 (C-4E), 73.0 (Ph*C*H$_2$O), 72.8 (Ph*C*H$_2$O), 72.5 (Ph*C*H$_2$O), 72.4 (Ph*C*H$_2$O), 72.2 (Ph*C*H$_2$O), 71.8 (C-5E), 69.8 (C-5C), 55.2(3) (PMBO*C*H$_3$), 55.2(2) (PMBO*C*H$_3$), 54.9 (O*C*H$_3$); ESIMS *m*/*z* calcd for $[C_{48}H_{54}O_{11}Na]^+$ 829.3558, found 829.3558.

Methyl 5-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (26): Isolated as a colorless oil, 76%; R_f 0.40 (3:1 hexane−EtOAc); $[\alpha]_D$ −11.6 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H)

8.02−7.98 (m, 2 H, Ar), 7.56−7.52 (m, 2 H, Ar), 7.40−7.26 (m, 12 H, Ar), 7.24−7.20 (m, 6 H, Ar), 6.84−6.82 (m, 2 H, Ar), 5.14 (d, 1 H, $J_{1E,2E}$ = 4.4 Hz, H-1E), 4.93 (s, 1 H, H-1C), 4.73 (d, 1 H, J = 11.6 Hz, PhCH_2O), 4.67−4.55 (m, 4 H, PhCH_2O), 4.48−4.42 (m, 4 H, PhCH_2O, H-5Eb), 4.33 (dd, 1 H, $J_{4E,5Ea}$ = 6.9 Hz, $J_{5Ea,5Eb}$ = 11.4 Hz, H-5Ea), 4.28−4.24 (m, 2 H, H-2C, H-4E), 4.23−4.17 (m, 2 H, H-4C, H-3E), 4.12 (dd, 1 H, $J_{1E,2E}$ = 4.4 Hz, $J_{2E,3E}$ = 6.9 Hz, H-2E), 3.98 (dd, 1 H, $J_{2C,3C}$ = 2.6 Hz, $J_{3C,4C}$ = 6.0 Hz, H-3C), 3.77 (s, 3 H, PMBOCH_3), 3.56−3.50 (m, 2 H, H-5Ca, H-5Cb), 3.39 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (*C*=O), 159.2 (Ar), 137.9 (Ar), 137.8 (Ar), 137.6 (Ar), 133.1 (Ar × 2), 130.2 (Ar), 129.8 (Ar), 129.7 (Ar × 2), 129.4 (Ar × 2), 128.5 (Ar × 2), 128.4(1) (Ar × 2), 128.3(7) (Ar × 2), 128.2 (Ar × 2), 128.0 (Ar × 3), 127.8 (Ar), 127.7 (Ar × 3), 127.5 (Ar), 113.7(3) (Ar), 113.7(0) (Ar), 107.0 (C-1C), 100.9 (C-1E), 86.8 (C-2C), 84.3 (C-3C), 83.9 (C-2E), 82.5 (C-3E), 81.6 (C-4C), 78.8 (C-4E), 72.9 (Ph*C*H_2O), 72.6 (Ph*C*H_2O × 2), 72.4 (Ph*C*H_2O), 69.8 (C-5C), 66.3 (C-5E), 55.2 (PMBO*C*H_3), 54.9 (O*C*H_3); ESIMS m/z calcd for $[C_{47}H_{50}O_{11}Na]^+$ 813.3245, found 813.3237.

Methyl 5-*O*-allyl-2,3-di-*O*-benzyl-*β*-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (27): Isolated as a colorless oil, 80%; R_f 0.38 (3:1 hexane−EtOAc); $[\alpha]_D$ −22.7 (*c* 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.36−7.23 (m, 17 H, Ar), 6.87−6.84 (m, 2 H, Ar), 5.84−5.76 (m, 1 H, CH_2=C*H*−CH_2O), 5.20−5.15 (m, 1 H, CH_2=CH−CH_2O), 5.11−5.08 (m, 1 H, CH_2=CH−CH_2O), 5.05 (d, 1 H, $J_{1E,2E}$ = 3.7 Hz, H-1E), 4.89 (s, 1 H, H-1C), 4.70−4.55 (m, 5 H, PhCH_2O), 4.51−4.47 (m, 3 H, PhCH_2O), 4.26 (dd, 1 H, $J_{1C,2C}$ = 1.2 Hz, $J_{2C,3C}$ = 2.9 Hz, H-2C), 4.20 (ddd, 1 H, $J_{3C,4C}$ = 6.0 Hz, $J_{4C,5Ca}$ = $J_{4C,5Cb}$ = 4.2 Hz, H-4C), 4.10−4.05 (m, 3 H, H-2E, H-3E, H-4E), 3.98 (dd, 1 H, $J_{2C,3C}$ = 2.9 Hz, $J_{3C,4C}$ = 6.0 Hz, H-3C), 3.91−3.82 (m, 2 H, CH_2=CH−CH_2O), 3.79 (s, 3 H, PMBOCH_3), 3.59−3.53 (m, 2 H, H-5Ca, H-5Ea), 3.51−3.45 (m, 2 H, H-5Cb, H-5Eb), 3.38 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.2 (Ar), 138.2 (Ar), 138.1 (Ar), 137.7 (Ar), 134.6 (Ar), 130.2 (Ar), 129.4 (Ar × 3), 128.5 (Ar × 2), 128.4 (Ar × 2), 128.3 (Ar × 2), 128.0 (CH_2=*C*H−CH_2O), 127.9 (Ar), 127.7(5) (Ar × 4), 127.6(8) (Ar), 127.5(9) (Ar), 116.9 (*C*H_2=CH−CH_2O), 113.7 (Ar × 2), 107.0 (C-1C), 100.3 (C-1E), 86.0 (C-2C), 84.0(4) (C-2E), 84.0(2) (C-3C), 83.1 (C-3E), 81.3 (C-4C), 80.1 (C-4E), 73.0 (Ph*C*H_2O), 72.5 (Ph*C*H_2O), 72.4 (Ph*C*H_2O), 72.2 (Ph*C*H_2O), 72.1(2) (CH_2=CH−*C*H_2O), 72.0(8) (C-5E), 69.8 (C-5C), 55.3 (PMBO*C*H_3), 54.9 (O*C*H_3); ESIMS m/z calcd for $[C_{43}H_{50}O_{10}Na]^+$ 749.3296, found 749.3292.

Methyl 2,3-di-*O*-benzyl-5-*O*-*tert*-butyldimethylsilyl-*β*-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (28): Isolated as a colorless oil, 61%; R_f 0.33 (4:1 hexane−EtOAc); $[\alpha]_D$ −24.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38−7.24 (m, 17 H, Ar), 6.89−6.86 (m, 2 H, Ar), 5.08 (d, 1 H, $J_{1E,2E}$ = 3.8 Hz, H-1E), 4.93 (s, 1 H, H-1C), 4.73−4.55 (m, 5 H, PhCH_2O), 4.52−4.48 (m, 3 H, PhCH_2O), 4.28−4.25 (m, 1 H, H-2C), 4.24−4.20 (m, 1 H, H-4C), 4.12−4.07 (m, 2 H, H-4E, H-2E), 4.02−3.96 (m, 2 H, H-3E, H-3C), 3.80 (s, 3 H, PMBOCH_3), 3.76−3.66 (m, 2 H, H-5Ea, H-5Eb), 3.60−3.54 (m, 2 H, H-5Ca, H-5Cb), 3.40 (s, 3 H, OCH_3), 0.90−0.87 (m, 9 H, *t*-butyl CH_3 × 3), 0.05−0.02 (m, 6 H, TBDMS CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.2 (Ar), 138.3 (Ar), 138.0 (Ar), 137.8 (Ar), 130.2 (Ar × 2), 129.4 (Ar × 2), 128.4(4) (Ar × 2), 128.3(5) (Ar × 2), 128.2(9) (Ar × 2), 128.0 (Ar × 2), 127.8(7) (Ar), 127.7 (Ar × 2), 127.6(7) (Ar × 2), 127.6(2) (Ar), 113.7 (Ar × 2), 107.0 (C-1C), 100.5 (C-1E), 86.2 (C-2C), 84.1(8) (C-3C), 84.1(6) (C-2E), 84.1(1) (C-4E), 82.2 (C-3E), 81.3 (C-4C), 73.0 (Ph*C*H_2O), 72.5 (Ph*C*H_2O), 72.3(3) (Ph*C*H_2O), 72.3(0) (Ph*C*H_2O), 69.8 (C-5C), 65.4 (C-5E), 55.3 (PMBO*C*H_3), 54.9 (O*C*H_3), 25.9 (*t*-butyl *C*H_3 × 3), 18.3 (*t*-butyl *C*), −5.2(5) (Si *C*H_3), −5.3(0) (Si *C*H_3); ESIMS m/z calcd for $[C_{46}H_{60}O_{10}SiNa]^+$ 823.3848, found 823.3852.

Methyl 2,3-di-*O*-benzyl-*β*-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-*p*-methoxybenzyl-α-D-arabinofuranoside (29). To a solution of the disaccharide mixture of **27** (1.45 g, 2.01 mmol) in CH_3OH (50 mL) and CH_2Cl_2 (6 mL) was added $PdCl_2$ (71 mg, 0.40 mmol). The solution was stirred for 12 h, the reaction was quenched by the addition of triethylamine, and the mixture was concentrated. Chromatography of the residue (8:1 hexane−EtOAc) gave **29** (1.02 g, 74%) as a colorless syrup: R_f 0.32 (2:1 hexane−EtOAc); $[\alpha]_D$ −23.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38−7.24 (m, 17 H, Ar), 6.89−6.86 (m, 2 H, Ar), 5.05 (d, 1 H, $J_{1E,2E}$ = 4.5 Hz, H-1E), 4.90 (d, 1 H, $J_{1C,2C}$ = 1.6 Hz, H-1C), 4.74 (d, 1 H, J = 11.6 Hz, PhCH_2O), 4.66−4.56 (m, 4 H, PhCH_2O), 4.52−4.44 (m, 3 H, PhCH_2O), 4.28 (dd, 1 H, $J_{2E,3E}$ = 7.1 Hz, $J_{3E,4E}$ = 6.5 Hz, H-3E), 4.23 (dd, 1 H, $J_{1C,2C}$ = 1.6 Hz, $J_{2C,3C}$ = 3.5 Hz, H-2C), 4.18 (ddd, 1 H, $J_{3C,4C}$ = 6.3 Hz, $J_{4C,5Ca}$ = 4.0 Hz, $J_{4C,5Cb}$ = 5.0 Hz, H-4C), 4.12−4.07 (m, 2 H, H-2E, H-3C), 3.99 (ddd, 1 H, $J_{3E,4E}$ = 6.4 Hz, $J_{4E,5Ea}$ = 3.0 Hz, $J_{4E,5Eb}$ = 4.8 Hz, H-4E), 3.80 (s, 3 H, PMBOCH_3), 3.66−3.50 (m, 4 H, H-5Ea, H-5Ca, H-5Eb, H-5Cb), 3.38 (s, 3 H, OCH_3), 2.29 (dd, 1 H, $J_{5Ea,OH}$ = 5.0 Hz, $J_{5Eb,OH}$ = 7.9 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 159.3 (Ar), 138.7 (Ar), 137.8 (Ar), 137.6 (Ar), 130.0 (Ar), 129.5 (Ar × 2), 128.5 (Ar × 2), 128.4 (Ar × 2), 128.3 (Ar × 2), 128.0 (Ar × 2), 127.7(9) (Ar × 2), 127.7(8) (Ar × 2), 127.7(3) (Ar), 127.7(0) (Ar × 2), 113.8 (Ar × 2), 107.0 (C-1C), 100.4 (C-1E), 86.6 (C-2C), 84.2 (C-2E), 83.2 (C-3C), 82.0 (C-4E), 81.0 (C-4C), 80.6 (C-3E), 73.0 (Ph*C*H_2O), 72.7 (Ph*C*H_2O), 72.6 (Ph*C*H_2O), 72.2 (Ph*C*H_2O), 69.3 (C-5C), 63.4 (C-5E), 55.3 (PMBO*C*H_3), 55.1 (O*C*H_3); ESIMS m/z calcd for $[C_{40}H_{46}O_{10}Na]^+$ 709.2983, found 709.2982.

Methyl 2,3-di-*O*-benzyl-*β*-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-α-D-arabinofuranoside (30). To a solution of compound **29** (0.85 g, 1.24 mmol) in CH_2Cl_2 (6 mL) was added trifluoroacetic acid (0.82 mL). The reaction mixture was allowed to stir for 10 min, and the reaction was then quenched by the addition of triethylamine and the solution concentrated. The residue was purified by chromotography to give **30** (0.61 g, 87%) as a colorless syrup: R_f 0.57 (1:1 hexane−EtOAc); $[\alpha]_D$ −0.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.39−7.28 (m, 15 H, Ar), 5.00 (d, 1 H, $J_{1E,2E}$ = 4.6 Hz, H-1E), 4.87 (s, 1 H, H-1C), 4.74−4.68 (m, 2 H, PhCH_2O), 4.63−4.54 (m, 4 H, PhCH_2O), 4.27−4.23 (m, 1 H, H-2E), 4.19 (dd, 1 H, $J_{2C,3C}$ = 2.4 Hz, $J_{3E,4E}$ = 5.6 Hz, H-3C), 4.17−4.16 (m, 1 H, H-2C), 4.14−4.11 (m, 1 H, H-4C), 4.09 (dd, 1 H, $J_{2E,3E}$ = 7.2 Hz, $J_{3E,4E}$ = 4.7 Hz, H-3E), 3.98 (ddd, 1 H, $J_{3E,4E}$ = 4.7 Hz, $J_{4E,5Ea}$ = 2.9 Hz, $J_{4E,5Eb}$ = 6.5 Hz, H-4E), 3.81 (dd, 1 H, $J_{4C,5Ca}$ = 2.9 Hz, $J_{5Ca,5Cb}$ = 12.2 Hz, H-5Ca), 3.67 (dd, 1 H, $J_{4E,5Ea}$ = 2.9 Hz, $J_{5Ea,5Eb}$ = 12.3 Hz, H-5Ea), 3.58−3.53 (m, 2 H, H-5Eb, H-5Cb), 3.38 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.0 (Ar), 137.8 (Ar), 137.5 (Ar), 128.6 (Ar × 2), 128.4 (Ar × 4), 128.0(9) (Ar), 128.0(5) (Ar × 2), 127.9(1) (Ar), 127.8(4) (Ar × 2), 127.8(2) (Ar), 127.7 (Ar × 2), 107.4 (C-1C), 100.8 (C-1E), 87.0 (C-2C), 84.2 (C-3E), 83.1 (C-4C), 82.5 (C-3C), 82.0 (C-4E), 80.4 (C-2E), 72.8 (Ph*C*H_2O × 2), 72.4 (Ph*C*H_2O), 63.2 (C-5C), 62.1 (C-5E), 54.9 (O*C*H_3); ESIMS m/z calcd for $[C_{32}H_{38}O_9Na]^+$ 589.2408, found 589.2411.

Methyl 2,3-di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (33). The donor **31** (1.80 g, 2.57 mmol) and acceptor **32** (272 mg, 1.07 mmol) were dried under vacuum in the presence of P_2O_5 for 2 h. To this mixture were added CH_2Cl_2 (15 mL) and 4 Å molecular sieves (2.0 g). The solution was allowed to stir at room temperature for 30 min and cooled to −60 °C, followed by the addition of *N*-iodosuccinimide (627 mg, 2.79 mmol) and silver triflate (110 mg, 0.43 mmol). After the solution turned into red/dark brown, triethylamine was added. The reaction mixture was then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was concentrated, and the resulting syrup was purified by chromatography (4:1 hexane−EtOAc) to give **33** (1.32 g, 88%) as a colorless syrup: R_f 0.44 (3:1 hexane−EtOAc); $[\alpha]_D$ +12.9 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.06−8.01 (m, 4 H,

Ar), 7.95−7.92 (m, 4 H, Ar), 7.70−7.65 (m, 8 H, Ar), 7.58−7.53 (m, 2 H, Ar), 7.51−7.48 (m, 24 H, Ar), 7.22−7.18 (m, 2 H, Ar), 7.16−7.14 (m, 1 H, Ar), 5.65−5.64 (m, 1 H, H-3D), 5.63−5.61 (m, 1 H, H-3C), 5.53 (d, 1 H, $J_{1D,2D}$ = 1.4 Hz, H-2D), 5.43 (d, 1 H, $J_{1C,2C}$ = 1.7 Hz, H-2C), 5.27 (s, 2 H, H-1C, H-1D), 4.94 (d, 1 H, $J_{1B,2B}$ = 1.6 Hz, H-1B), 4.62−4.57 (m, 2 H, PhCH_2O), 4.44 (ddd, 1 H, $J_{3D,4D}$ = $J_{4D,5\ Da}$ = 4.4 Hz, $J_{5\ Da,5Db}$ = 4.6 Hz, H-4D), 4.36 (ddd, 1 H, $J_{3C,4C}$ = 3.8 Hz, $J_{4C,5Ca}$ = $J_{5Ca,5Cb}$ = 4.7 Hz, H-4C), 4.27−4.23 (m, 2 H, H-4B, H-3B), 4.10−4.08 (m, 1 H, H-2B), 4.03−3.90 (m, 5 H, H-5Ba, H-5Ca, H-5Cb, H-5 Da, H-5Db), 3.85−3.82 (m, 1 H, H-5Bb), 3.35 (s, 3 H, OCH_3), 1.04−0.98 (s, 18 H, *t*-butyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.6 (*C*═O), 165.5 (*C*═O), 165.2(2) (*C*═O), 165.2(0) (*C*═O), 137.5 (Ar), 135.7 (Ar), 135.6(3) (Ar × 2), 135.6(2) (Ar × 2), 135.6(0) (Ar × 2), 135.5 (Ar × 2), 133.4 (Ar), 133.3(3) (Ar), 133.3(1) (Ar), 133.2(8) (Ar), 133.2(4) (Ar), 133.1(9) (Ar), 133.1(6) (Ar), 133.1(4) (Ar), 133.1(1) (Ar), 129.9(5) (Ar × 2), 129.9(3) (Ar × 2), 129.9(1) (Ar × 2), 129.8(6) (Ar × 2), 129.7 (Ar × 2), 129.6(1) (Ar × 2), 129.5(7) (Ar), 129.4(5) (Ar), 129.3 (Ar), 129.2 (Ar), 128.4(8) (Ar × 2), 128.4(6) (Ar × 2), 128.3(9) (Ar × 2), 128.3(6) (Ar × 2), 128.3(2) (Ar × 2), 128.2(8) (Ar × 2), 127.9 (Ar × 2), 127.7 (Ar × 2), 127.6 (Ar × 3), 107.2 (C-1B), 105.8 (C-1D), 105.4 (C-1C), 88.3 (C-2B), 83.5 (C-4C), 83.2 (C-4D), 82.3 (C-2D, C-2C), 81.2 (C-3B), 80.0 (C-4B), 77.3 (C-3D, C-3C), 72.0 (Ph*C*H_2O), 66.6 (C-5B), 63.4 (C-5C), 63.3 (C-5D), 54.9 (O*C*H_3), 26.8 (*t*-butyl *C*H_3), 19.3(0) (*t*-butyl *C*), 19.2(6) (*t*-butyl *C*); ESIMS *m*/*z* calcd for $[C_{83}H_{86}O_{17}Si_2Na]^+$ 1433.5296, found 1433.5298.

Methyl 2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (34). To a solution of compound **33** (1.32 g, 0.94 mmol) in 1:1 $CH_3OH-CH_2Cl_2$ (8 mL) was added a 1 M solution of $NaOCH_3$ in CH_3OH until a pH of 11 was obtained. The reaction was stirred at room temperature for 2 h, neutralized by the addition of AcOH, and concentrated. The residue was dissolved in DMF (20 mL) and THF (3 mL), and then the solution was cooled to 0 °C. NaH 60% in mineral oil (203 mg, 5.08 mmol) and BnBr (0.52 mL, 4.40 mmol) were subquently added to the solution. The reaction was allowed to stir for 2 h and then quenched by the addition of CH_3OH. The solution was diluted with EtOAc and washed with water. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was dissolved in THF (10 mL), and then TBAF (2.00 mL, 1 M in THF) was added. The reaction was stirred overnight and concentrated. Chromatography of the residue (1:1 hexane−EtOAc) gave **3** (613 mg, 74% over three steps) as a colorless syrup: R_f 0.29 (1:1 hexane−EtOAc); $[\alpha]_D$ +84.8 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.20 (m, 25 H, Ar), 5.17 (s, 1 H, H-1D), 5.13 (d, 1 H, $J_{1C,2C}$ = 1.5 Hz, H-1C), 4.96 (d, 1 H, $J_{1B,2B}$ = 1.5 Hz, H-1B), 4.62−4.47 (m, 9 H, PhCH_2O), 4.39 (d, 1 H, *J* = 11.8 Hz, PhCH_2O), 4.32 (dd, 1 H, $J_{2B,3B}$ = 3.8 Hz, $J_{3B,4B}$ = 7.4 Hz, H-3B), 4.26 (ddd, 1 H, $J_{3D,4D}$ = 2.9 Hz, $J_{4D,5\ Da}$ = 5.2 Hz, $J_{4D,5Db}$ = 6.5 Hz, H-4D), 4.16−4.08 (m, 3 H, H-2D, H-4B, H-4C), 4.04 (dd, 1 H, $J_{1C,2C}$ = 1.5 Hz, $J_{2C,3C}$ = 3.8 Hz, H-2C), 4.02 (dd, 1 H, $J_{1B,2B}$ = 1.5 Hz, $J_{2B,3B}$ = 3.8 Hz, H-2B), 3.96 (dd, 1 H, $J_{4B,5Ba}$ = 3.9 Hz, $J_{5Ba,5Bb}$ = 11.6 Hz, H-5Ba), 3.92 (dd, 1 H, $J_{2D,3D}$ = 6.6 Hz, $J_{3D,4D}$ = 2.9 Hz, H-3D), 3.86−3.78 (m, 3 H, H-3C, H-5Bb, H-5Db), 3.76 (dd, 1 H, $J_{4C,5Ca}$ = 2.6 Hz, $J_{5Ca,5Cb}$ = 12.2 Hz, H-5Ca), 3.66 (dd, 1 H, $J_{4D,5\ Da}$ = 5.2 Hz, $J_{5\ Da,5Db}$ = 12.1 Hz, H-5 Da), 3.60 (dd, 1 H, $J_{4C,5Cb}$ = 5.9 Hz, $J_{5Ca,5Cb}$ = 12.2 Hz, H-5Cb), 3.40 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 133.8 (Ar), 137.7 (Ar), 137.4(7) (Ar), 137.4(6) (Ar), 137.3 (Ar), 128.4(7) (Ar × 2), 128.4(5) (Ar × 3), 128.4(4) (Ar × 3), 128.4(2) (Ar × 2), 128.4(0) (Ar × 2), 127.9(6) (Ar), 127.9(5) (Ar × 2), 127.9(3) (Ar × 2), 127.8(8) (Ar), 127.8(5) (Ar × 3), 127.7(5) (Ar), 127.7(3) (Ar × 3), 106.9 (C-1B), 106.2 (C-1C), 105.9 (C-1D), 88.8 (C-2B), 88.2 (C-2C), 87.6 (C-2D), 83.0(3) (C-3D), 83.0(0) (C-3C), 82.4 (C-4D), 82.0 (C-4C), 81.0 (C-3B), 79.8 (C-4B), 72.3 (Ph*C*H_2O), 72.2 (Ph*C*H_2O), 72.0 (Ph*C*H_2O), 71.9(7) (Ph*C*H_2O), 71.9(4) (Ph*C*H_2O), 65.0 (C-5B), 62.8 (C-5D), 62.7 (C-5C), 55.0 (O*C*H_3); ESIMS *m*/*z* calcd for $[C_{51}H_{58}O_{13}Na]^+$ 901.3770, found 901.3764.

Methyl 2,3-di-*O*-benzyl-5-*O*-butyryl-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-butyryl-α-D-arabinofuranoside (35): Isolated as a colorless oil, 96%; R_f 0.68 (1:1 hexane−EtOAc); $[\alpha]_D$ −3.7 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38−7.26 (m, 15 H, Ar), 5.07 (d, 1 H, $J_{1E,2E}$ = 3.5 Hz, H-1E), 4.86 (s, 1 H, H-1C), 4.75−4.70 (m, 2 H, PhCH_2O), 4.64−4.50 (m, 4 H, PhCH_2O), 4.30−4.20 (m, 4 H, H-2E, H-5Ea, H-5Ca, H-4E), 4.18−4.13 (m, 3 H, H-5Eb, H-5Cb, H-3C), 4.11−4.08 (m, 2 H, H-2C, H-4C), 3.96 (dd, 1 H, $J_{2E,3E}$ = 2.7 Hz, $J_{3E,4E}$ = 6.1 Hz, H-3E), 3.40 (s, 3 H, OCH_3), 2.32−2.26 (m, 2 H, acyl CH_2), 2.24−2.20 (m, 2 H, acyl CH_2), 1.68−1.56 (m, 4 H, acyl CH_2 × 2), 0.96−0.87 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.3 (*C*═O), 173.2 (*C*═O), 137.8 (Ar), 137.7 (Ar), 137.5 (Ar), 128.5(4) (Ar × 2), 128.4(5) (Ar × 2), 128.3(9) (Ar × 2), 128.1 (Ar), 128.0 (Ar × 2), 127.9 (Ar), 127.8(0) (Ar), 127.7(7) (Ar × 2), 127.7(1) (Ar × 2), 107.0 (C-1C), 100.7 (C-1E), 86.1 (C-2E), 84.1 (C-2C), 83.8 (C-3E), 82.4 (C-4C), 80.0 (C-4E), 78.9 (C-3C), 72.7 (Ph*C*H_2O), 72.5 (Ph*C*H_2O), 72.4 (Ph*C*H_2O), 65.8 (C-5C), 63.7 (C-5E), 54.9 (O*C*H_3), 35.9(3) (acyl *C*H_2), 35.8(9) (acyl *C*H_2), 18.3(4) (acyl *C*H_2), 18.3(0) (acyl *C*H_2), 13.6(4) (acyl *C*H_3), 13.6(0) (acyl *C*H_3); ESIMS *m*/*z* calcd for $[C_{40}H_{50}O_{11}Na]^+$ 729.3245, found 729.3247.

Methyl 2,3-di-*O*-benzyl-5-*O*-decanoyl-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-decanoyl-α-D-arabinofuranoside (36): Isolated as a colorless oil, 90%; R_f 0.48 (2:1 hexane−EtOAc); $[\alpha]_D$ −3.2 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38−7.26 (m, 15 H, Ar), 5.07 (d, 1 H, $J_{1E,2E}$ = 3.7 Hz, H-1E), 4.87 (s, 1 H, H-1C), 4.74−4.70 (m, 2 H, PhCH_2O), 4.64−4.56 (m, 3 H, PhCH_2O), 4.52 (d, 1 H, *J* = 11.8 Hz, PhCH_2O), 4.29 (dd, 1 H, $J_{1C,2C}$ = 1.2 Hz, $J_{2C,3C}$ = 2.9 Hz, H-2C), 4.27 (dd, 1 H, $J_{4E,5Ea}$ = 3.7 Hz, $J_{5Ea,5Eb}$ = 3.7 Hz, H-5Ea), 4.25−4.20 (m, 2 H, H-5Ca, H-4E), 4.17−4.12 (m, 3 H, H-5Eb, H-5Cb, H-3C), 4.11−4.08 (m, 2 H, H-2E, H-4C), 3.95 (dd, 1 H, $J_{2E,3E}$ = 2.9 Hz, $J_{3E,4E}$ = 6.2 Hz, H-3E), 3.38 (s, 3 H, OCH_3), 2.34−2.27 (m, 2 H, acyl CH_2), 2.26−2.18 (m, 2 H, acyl CH_2), 1.64−1.50 (m, 4 H, acyl CH_2 × 2), 1.34−1.20 (m, 24 H, acyl CH_2 × 12), 0.92−0.86 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.5 (*C*═O), 173.3 (*C*═O), 137.8 (Ar), 137.7 (Ar), 137.5 (Ar), 128.5(4) (Ar × 2), 128.4(5) (Ar × 2), 128.3(8) (Ar × 2), 128.1 (Ar), 128.0 (Ar × 2), 127.9 (Ar), 127.7(9) (Ar), 127.7(7) (Ar × 2), 127.6(9) (Ar × 2), 107.0 (C-1C), 100.7 (C-1E), 86.1 (C-2E), 84.1 (C-2C), 83.8 (C-3E), 82.5 (C-4C), 80.0 (C-4E), 78.9 (C-3C), 72.7 (Ph*C*H_2O), 72.5 (Ph*C*H_2O), 72.4 (Ph*C*H_2O), 65.9 (C-5C), 63.8 (C-5E), 54.9 (O*C*H_3), 34.1 (acyl *C*H_2), 31.8(7) (acyl *C*H_2), 31.8(5) (acyl *C*H_2), 29.4(5) (acyl *C*H_2), 29.4(1) (acyl *C*H_2), 29.3(0) (acyl *C*H_2), 29.2(8) (acyl *C*H_2), 29.2(5) (acyl *C*H_2), 29.1(5) (acyl *C*H_2), 29.1(4) (acyl *C*H_2), 24.8(7) (acyl *C*H_2), 24.8(3) (acyl *C*H_2), 22.7 (acyl *C*H_2), 14.1 (acyl *C*H_3 × 2); ESIMS *m*/*z* calcd for $[C_{52}H_{74}O_{11}Na]^+$ 897.5127, found 897.5122.

Methyl 2,3-di-*O*-benzyl-5-*O*-palmitoyl-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-5-*O*-palmitoyl-α-D-arabinofuranoside (37): Isolated as a colorless oil, 82%; R_f 0.56 (4:1 hexane−EtOAc); $[\alpha]_D$ −4.3 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.22 (m, 15 H, Ar), 5.06 (d, 1 H, $J_{1E,2E}$ = 3.6 Hz, H-1E), 4.86 (s, 1 H, H-1C), 4.74−4.69 (m, 2 H, PhCH_2O), 4.64−4.55 (m, 3 H, PhCH_2O), 4.52 (d, 1 H, *J* = 11.7 Hz, PhCH_2O), 4.29−4.27 (m, 2 H, H-2C, H-5Ca), 4.26−4.19 (m, 2 H, H-5Ea, H-4C), 4.16−4.07 (m, 5 H, H-5Eb, H-5Cb, H-3E, H-2E, H-4E), 3.94 (dd, 1 H, $J_{2C,3C}$ = 2.4 Hz, $J_{3C,4C}$ = 6.0 Hz, H-3C), 3.37 (s, 3 H, OCH_3), 2.32−2.27 (m, 2 H, acyl CH_2), 2.24−2.20 (m, 2 H, acyl CH_2), 1.62−1.50 (m, 4 H, acyl CH_2 × 2), 1.34−1.20 (m, 48 H, acyl CH_2 × 24), 0.92−0.86 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.5 (*C*═O), 173.3 (*C*═O), 137.8 (Ar), 137.7 (Ar), 137.5 (Ar), 128.5(3) (Ar × 2), 128.4(5) (Ar × 2), 128.3(8) (Ar × 2), 128.1 (Ar), 128.0 (Ar × 2), 127.8(5) (Ar), 127.7(9) (Ar),

127.7(7) (Ar × 2), 127.6(9) (Ar × 2), 107.0 (C-1C), 100.7 (C-1E), 86.1 (C-2C), 84.1 (C-3C), 83.8 (C-2E), 82.5 (C-4E), 80.0 (C-4C), 78.9 (C-3E), 72.7 (Ph*C*H$_2$O), 72.5 (Ph*C*H$_2$O), 72.4 (Ph*C*H$_2$O), 65.9 (C-5E), 63.8 (C-5C), 54.9 (O*C*H$_3$), 34.0(6) (acyl *C*H$_2$), 34.0(5) (acyl *C*H$_2$), 31.9 (acyl *C*H$_2$), 29.7(0) (acyl *C*H$_2$), 29.6(6) (acyl *C*H$_2$), 29.6(3) (acyl *C*H$_2$), 29.5(1) (acyl *C*H$_2$), 29.4(7) (acyl *C*H$_2$), 29.3(6) (acyl *C*H$_2$), 29.3(2) (acyl *C*H$_2$), 29.2(7) (acyl *C*H$_2$), 29.1(7) (acyl *C*H$_2$), 29.1(5) (acyl *C*H$_2$), 24.8(7) (acyl *C*H$_2$), 24.8(4) (acyl *C*H$_2$), 22.7 (acyl *C*H$_2$), 14.1 (acyl *C*H$_3$ × 2); ESIMS *m*/*z* calcd for $[C_{64}H_{98}O_{11}Na]^+$ 1065.7001, found 1065.7001.

Methyl 5-*O*-behenoyl-2,3-di-*O*-benzyl-*β*-D-arabinofuranosyl-(1→2)-5-*O*-behenoyl-3-*O*-benzyl-α-D-arabinofuranoside (38): Isolated as a colorless oil, 95%; R_f 0.68 (4:1 hexane−EtOAc); $[\alpha]_D$ +0.4 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.22 (m, 15 H, Ar), 5.06 (d, 1 H, $J_{1E,2E}$ = 3.6 Hz, H-1E), 4.86 (s, 1 H, H-1C), 4.75−4.68 (m, 2 H, PhC*H*$_2$O), 4.65−4.50 (m, 4 H, PhC*H*$_2$O), 4.28 (dd, 1 H, $J_{1C,2C}$ = 1.1 Hz, $J_{2C,3C}$ = 2.7 Hz, H-2C), 4.27−4.20 (m, 3 H, H-5Ca, H-5Ea, H-4C), 4.17−4.07 (m, 5 H, H-5Cb, H-5Eb, H-3E, H-2E, H-4E), 3.94 (dd, 1 H, $J_{2C,3C}$ = 2.7 Hz, $J_{3C,4C}$ = 6.0 Hz, H-3C), 3.37 (s, 3 H, OC*H*$_3$), 2.23−2.26 (m, 2 H, C*H*$_2$), 2.25−2.21 (m, 2 H, C*H*$_2$), 1.66−1.50 (m, 4 H, C*H*$_2$ × 2), 1.38−1.10 (m, 72 H, C*H*$_2$ × 36), 0.94−0.82 (m, 6 H, C*H*$_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.4 (*C*═O), 173.2 (*C*═O), 137.7 (Ar), 137.6 (Ar), 137.3 (Ar), 128.4(3) (Ar × 2), 128.3(4) (Ar × 2), 128.2(8) (Ar × 2), 127.9(5) (Ar), 127.9(2) (Ar × 2), 127.7(5) (Ar), 127.6(9) (Ar), 127.6(6) (Ar × 2), 127.5(8) (Ar × 2), 106.9 (C-1C), 100.5 (C-1E), 86.0 (C-2C), 84.0 (C-4E), 83.7 (C-3C), 82.4 (C-2E), 79.8 (C-4C), 78.8 (C-3E), 72.6 (Ph*C*H$_2$O), 72.4 (Ph*C*H$_2$O), 72.3 (Ph*C*H$_2$O), 65.8 (C-5E), 63.7 (C-5C), 54.8 (O*C*H$_3$), 34.0 (acyl *C*H$_2$), 31.8 (acyl *C*H$_2$), 29.6(1) (acyl *C*H$_2$), 29.5(6) (acyl *C*H$_2$), 29.5(3) (acyl *C*H$_2$), 29.4(2) (acyl *C*H$_2$), 29.3(8) (acyl *C*H$_2$), 29.2(6) (acyl *C*H$_2$), 29.2(3) (acyl *C*H$_2$), 29.1(8) (acyl *C*H$_2$), 29.0(7) (acyl *C*H$_2$), 29.0(5) (acyl *C*H$_2$), 24.7(7) (acyl *C*H$_2$), 24.7(3) (acyl *C*H$_2$), 22.6 (acyl *C*H$_2$), 14.0 (acyl *C*H$_3$ × 2); ESIMS *m*/*z* calcd for $[C_{76}H_{122}O_{11}Na]^+$ 1233.8879, found 1233.8878.

Methyl 2,3-di-*O*-benzyl-5-*O*-butyryl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-5-*O*-butyryl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (39): Isolated as a colorless oil, 95%; R_f 0.25 (4:1 hexane−EtOAc); $[\alpha]_D$ +76.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37−7.22 (m, 25 H, Ar), 5.19 (s, 1 H, H-1C), 5.15 (s, 1 H, H-1D), 4.93 (s, 1 H, H-1B), 4.60−4.43 (m, 9 H, PhC*H*$_2$O), 4.38 (d, 1 H, *J* = 11.7 Hz, PhC*H*$_2$O), 4.30−4.24 (m, 4 H, H-3B, H-5Ca, H-5 Da, H-4C), 4.22−4.16 (m, 3 H, H-5Cb, H-5Db, H-4D), 4.13 (ddd, 1 H, $J_{3B,4B}$ = 7.0 Hz, $J_{4B,5Ba}$ = 4.7 Hz, $J_{4B,5Bb}$ = 2.5 Hz, H-4B), 4.10 (dd, 1 H, $J_{1C,2C}$ = 1.3 Hz, $J_{2C,3C}$ = 3.4 Hz, H-2C), 4.06 (dd, 1 H, $J_{1D,2D}$ = 1.3 Hz, $J_{2D,3D}$ = 3.4 Hz, H-2D), 3.97 (dd, 1 H, $J_{1B,2B}$ = 1.3 Hz, $J_{2B,3B}$ = 3.2 Hz, H-2B), 3.95 (dd, 1 H, $J_{4B,5Ba}$ = 4.7 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Ba), 3.88−3.83 (m, 2 H, H-3C, H-3D), 3.78 (dd, 1 H, $J_{4B,5Bb}$ = 2.5 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Bb), 3.38 (s, 3 H, OC*H*$_3$), 2.28−2.22 (m, 4 H, acyl C*H*$_2$ × 2), 1.70−1.56 (m, 4 H, acyl C*H*$_2$ × 2), 0.92−0.87 (m, 6 H, acyl C*H*$_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.4 (*C*═O), 173.3 (*C*═O), 137.7 (Ar), 137.6 (Ar), 137.5 (Ar), 137.4 (Ar), 137.3 (Ar), 128.5 (Ar × 2), 128.4(3) (Ar × 2), 128.4(0) (Ar × 2), 128.3(9) (Ar × 2), 128.3(6) (Ar × 2), 127.9(6) (Ar), 127.9(3) (Ar × 2), 127.9(1) (Ar × 2), 127.8(5) (Ar × 4), 127.8(0) (Ar), 127.7(8) (Ar × 2), 127.7(5) (Ar × 2), 127.7(2) (Ar), 107.1 (C-1B), 106.5 (C-1C), 105.5 (C-1D), 88.3 (C-2B), 88.1(4) (C-2C), 88.0(5) (C-2D), 83.4(4) (C-3C), 83.3(6) (C-3D), 80.8 (C-4B), 80.5 (C-4C), 79.2 (C-4D), 78.9 (C-3B), 72.2 (Ph*C*H$_2$O), 72.1 (Ph*C*H$_2$O), 72.0(2) (Ph*C*H$_2$O), 72.0(0) (Ph*C*H$_2$O), 71.8 (Ph*C*H$_2$O), 65.8 (C-5B), 63.3(4) (C-5C), 63.3(0) (C-5D), 54.8 (O*C*H$_3$), 35.9(3) (acyl *C*H$_2$), 35.9(1) (acyl *C*H$_2$), 18.3(2) (acyl *C*H$_2$), 18.3(1) (acyl *C*H$_2$), 13.6 (acyl *C*H$_3$ × 2); ESIMS *m*/*z* calcd for $[C_{59}H_{70}O_{15}Na]^+$ 1041.4607, found 1041.4604.

Methyl 2,3-di-*O*-benzyl-5-*O*-decanoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-5-*O*-decanoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (40): Isolated as a colorless oil, 89%; R_f 0.50 (4:1 hexane−EtOAc); $[\alpha]_D$ +35.4 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.37−7.23 (m, 25 H, Ar), 5.19 (d, 1 H, $J_{1C,2C}$ = 1.2 Hz, H-1C), 5.15 (d, 1 H, $J_{1D,2D}$ = 1.2 Hz, H-1D), 4.93 (d, 1 H, $J_{1B,2B}$ = 1.2 Hz, H-1B), 4.60−4.44 (m, 9 H, PhC*H*$_2$O), 4.38 (d, 1 H, *J* = 11.8 Hz, PhC*H*$_2$O), 4.30−4.24 (m, 4 H, H-3B, H-5Ca, H-5 Da, H-4C), 4.22−4.17 (m, 3 H, H-5Cb, H-5Db, H-4D), 4.13 (ddd, 1 H, $J_{3B,4B}$ = 7.0 Hz, $J_{4B,5Ba}$ = 4.6 Hz, $J_{4B,5Bb}$ = 2.5 Hz, H-4B), 4.10 (dd, 1 H, $J_{1C,2C}$ = 1.2 Hz, $J_{2C,3C}$ = 3.4 Hz, H-2C), 4.06 (dd, 1 H, $J_{1D,2D}$ = 1.2 Hz, $J_{2D,3D}$ = 3.4 Hz, H-2D), 3.99 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 3.95 (dd, 1 H, $J_{4B,5Ba}$ = 4.6 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Ba), 3.88−3.85 (m, 2 H, H-3C, H-3D), 3.78 (dd, 1 H, $J_{4B,5Bb}$ = 2.5 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Bb), 3.38 (s, 3 H, OC*H*$_3$), 2.30−2.25 (m, 4 H, acyl C*H*$_2$ × 2), 1.60−1.54 (m, 4 H, acyl C*H*$_2$ × 2), 1.34−1.22 (m, 24 H, acyl C*H*$_2$ × 12), 0.92−0.87 (m, 6 H, acyl C*H*$_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.6 (*C*═O), 173.5 (*C*═O), 137.7 (Ar), 137.6(3) (Ar), 137.5(7) (Ar), 137.4 (Ar), 137.3 (Ar), 128.5 (Ar × 2), 128.4(2) (Ar × 3), 128.4(0) (Ar × 3), 128.3(5) (Ar × 2), 127.9(6) (Ar), 127.9(2) (Ar × 2), 127.8(9) (Ar × 2), 127.8(5) (Ar × 3), 127.7(9) (Ar × 2), 127.7(6) (Ar × 2), 127.7(3) (Ar × 2), 127.7(1) (Ar), 107.1 (C-1B), 106.5 (C-1C), 105.5 (C-1D), 88.3 (C-2B), 88.1 (C-2C), 88.0 (C-2D), 83.4(3) (C-3C), 83.3(5) (C-3D), 80.8 (C-4B), 80.5 (C-3B), 79.2 (C-4D), 79.0 (C-4C), 72.2 (Ph*C*H$_2$O), 72.1 (Ph*C*H$_2$O), 72.0 (Ph*C*H$_2$O × 2), 71.8 (Ph*C*H$_2$O), 65.8 (C-5B), 63.3 (C-5D), 63.2 (C-5C), 54.8 (O*C*H$_3$), 34.1 (acyl *C*H$_2$), 34.0 (acyl *C*H$_2$), 31.9 (acyl *C*H$_2$), 29.4 (acyl *C*H$_2$), 29.3(0) (acyl *C*H$_2$), 29.2(8) (acyl *C*H$_2$), 29.1(6) (acyl *C*H$_2$), 24.8 (acyl *C*H$_2$), 22.7 (acyl *C*H$_2$), 14.1 (acyl *C*H$_3$ × 2); ESIMS *m*/*z* calcd for $[C_{71}H_{94}O_{15}Na]^+$ 1209.6485, found 1209.6489.

Methyl 2,3-di-*O*-benzyl-5-*O*-palmitoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-5-*O*-palmitoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (41): Isolated as a colorless oil, 89%; R_f 0.45 (4:1 hexane−EtOAc); $[\alpha]_D$ +40.8 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37−7.22 (m, 25 H, Ar), 5.19 (d, 1 H, $J_{1C,2C}$ = 1.1 Hz, H-1C), 5.15 (d, 1 H, $J_{1D,2D}$ = 1.1 Hz, H-1D), 4.93 (d, 1 H, $J_{1B,2B}$ = 1.2 Hz, H-1B), 4.60−4.43 (m, 9 H, PhC*H*$_2$O), 4.38 (d, 1 H, *J* = 11.8 Hz, PhC*H*$_2$O), 4.30−4.23 (m, 4 H, H-3B, H-5Ca, H-5 Da, H-4C), 4.22−4.16 (m, 3 H, H-5Cb, H-5Db, H-4D), 4.13 (ddd, 1 H, $J_{3B,4B}$ = 7.0 Hz, $J_{4B,5Ba}$ = 4.6 Hz, $J_{4B,5Bb}$ = 2.5 Hz, H-4B), 4.10 (dd, 1 H, $J_{1C,2C}$ = 1.2 Hz, $J_{2C,3C}$ = 3.4 Hz, H-2C), 4.03 (dd, 1 H, $J_{1D,2D}$ = 1.1 Hz, $J_{2D,3D}$ = 3.4 Hz, H-2D), 3.98 (dd, 1 H, $J_{1B,2B}$ = 1.2 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 3.95 (dd, 1 H, $J_{4B,5Ba}$ = 4.6 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Ba), 3.88−3.84 (m, 2 H, H-3C, H-3D), 3.78 (dd, 1 H, $J_{4B,5Bb}$ = 2.5 Hz, $J_{5Ba,5Bb}$ = 11.9 Hz, H-5Bb), 3.38 (s, 3 H, OC*H*$_3$), 2.29−2.24 (m, 4 H, acyl C*H*$_2$ × 2), 1.60−1.53 (m, 4 H, acyl C*H*$_2$ × 2), 1.34−1.20 (m, 48 H, acyl C*H*$_2$ × 24), 0.92−0.87 (m, 6 H, acyl C*H*$_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.6 (*C*═O), 173.5 (*C*═O), 137.8 (Ar), 137.6(4) (Ar), 137.5(8) (Ar), 137.4 (Ar), 137.3 (Ar), 128.5 (Ar × 2), 128.4(1) (Ar × 2), 128.3(8) (Ar × 4), 128.3(4) (Ar × 2), 127.9(4) (Ar), 127.9(0) (Ar × 2), 127.8(8) (Ar × 2), 127.8(4) (Ar × 4), 127.7(7) (Ar), 127.7(4) (Ar × 2), 127.7(2) (Ar × 2), 127.6(9) (Ar), 107.1 (C-1B), 106.5 (C-1C), 105.5 (C-1D), 88.3 (C-2B), 88.1(4) (C-2C), 88.0(7) (C-2D), 83.5 (C-3C), 83.4 (C-3D), 80.8 (C-4B), 80.5 (C-3B), 79.2 (C-4D), 79.0 (C-4C), 72.2 (Ph*C*H$_2$O), 72.1 (Ph*C*H$_2$O), 72.0 (Ph*C*H$_2$O), 71.9 (Ph*C*H$_2$O), 71.8 (Ph*C*H$_2$O), 65.8 (C-5B), 63.3 (C-5D), 63.2 (C-5C), 54.8 (O*C*H$_3$), 34.1 (acyl *C*H$_2$), 34.0 (acyl *C*H$_2$), 31.9 (acyl *C*H$_2$), 29.7(1) (acyl *C*H$_2$), 29.6(9) (acyl *C*H$_2$), 29.6(6) (acyl *C*H$_2$), 29.5 (acyl *C*H$_2$), 29.4 (acyl *C*H$_2$), 29.3(2) (acyl *C*H$_2$), 29.3(0) (acyl acyl *C*H$_2$), 29.2 (acyl *C*H$_2$), 24.8 (acyl *C*H$_2$), 22.7 (acyl *C*H$_2$), 14.1 (acyl *C*H$_3$ × 2); ESIMS *m*/*z* calcd for $[C_{83}H_{118}O_{15}Na]^+$ 1377.8363, found 1377.8369.

Methyl 5-*O*-behenoyl-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-behenoyl-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranoside (42): Isolated as a colorless oil, 81%; R_f 0.64 (4:1 hexane−EtOAc); $[\alpha]_D$ +51.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.36−7.23 (m, 25 H, Ar), 5.18

(d, 1 H, $J_{1C,2C}$ = 0.8 Hz, H-1C), 5.14 (d, 1 H, $J_{1D,2D}$ = 0.9 Hz, H-1D), 4.92 (d, 1 H, $J_{1B,2B}$ = 0.9 Hz, H-1B), 4.59−4.42 (m, 9 H, PhCH_2O), 4.37 (d, 1 H, J = 11.8 Hz, PhCH_2O), 4.29−4.22 (m, 4 H, H-3B, H-5Ca, H-5 Da, H-4C), 4.21−4.16 (m, 3 H, H-5Cb, H-5Db, H-4D), 4.12 (ddd, 1 H, $J_{3B,4B}$ = 7.0 Hz, $J_{4B,5Ba}$ = 4.7 Hz, $J_{4B,5Bb}$ = 2.6 Hz, H-4B), 4.09 (dd, 1 H, $J_{1C,2C}$ = 1.1 Hz, $J_{2C,3C}$ = 3.4 Hz, H-2C), 4.02 (dd, 1 H, $J_{1D,2D}$ = 1.1 Hz, $J_{2D,3D}$ = 3.4 Hz, H-2D), 3.97 (dd, 1 H, $J_{1B,2B}$ = 1.1 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 3.94 (dd, 1 H, $J_{4B,5Ba}$ = 4.7 Hz, $J_{5Ba,5Bb}$ = 11.8 Hz, H-5Ba), 3.87−3.83 (m, 2 H, H-3C, H-3D), 3.77 (dd, 1 H, $J_{4B,5Bb}$ = 2.6 Hz, $J_{5Ba,5Bb}$ = 11.8 Hz, H-5Bb), 3.37 (s, 3 H, OCH_3), 2.30−2.22 (m, 4 H, acyl CH_2 × 2), 1.60−1.50 (m, 4 H, acyl CH_2 × 2), 1.36−1.20 (m, 72 H, acyl CH_2 × 36), 0.92−0.84 (m, 6 H, acyl CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.6 (*C*═O), 173.5 (*C*═O), 137.8 (Ar), 137.6(4) (Ar), 137.5(7) (Ar), 137.4 (Ar), 137.3 (Ar), 128.5 (Ar × 2), 128.4(3) (Ar × 2), 128.3(9) (Ar × 3), 128.3(5) (Ar × 2), 127.9(6) (Ar), 127.9(2) (Ar × 3), 127.8(9) (Ar × 3), 127.8(6) (Ar × 3), 127.7(9) (Ar), 127.7(6) (Ar × 2), 127.7(3) (Ar × 2), 127.7(1) (Ar), 107.1 (C-1B), 106.5 (C-1C), 105.5 (C-1D), 88.3 (C-2B), 88.1(3) (C-2C), 88.0(5) (C-2D), 83.4(3) (C-3C), 83.3(6) (C-3D), 80.8 (C-4B), 80.5 (C-3B), 79.2 (C-4D), 79.0 (C-4C), 72.2 (Ph*C*H_2O), 72.1 (Ph*C*H_2O), 72.0 (Ph*C*H_2O × 2), 71.8 (Ph*C*H_2O), 65.8 (C-5B), 63.3 (C-5D), 63.2 (C-5C), 54.8 (O*C*H_3), 34.1 (acyl *C*H_2), 34.0 (acyl *C*H_2), 31.9 (acyl *C*H_2), 29.7(2) (acyl *C*H_2), 29.6(7) (acyl *C*H_2), 29.5 (acyl *C*H_2), 29.4 (acyl *C*H_2), 29.3(4) (acyl *C*H_2), 29.3(2) (acyl *C*H_2), 29.2 (acyl *C*H_2), 24.8 (acyl *C*H_2), 22.7 (acyl *C*H_2), 14.1 (acyl *C*H_3 × 2); ESIMS m/z calcd for $[C_{95}H_{142}O_{15}Na]^+$ 1546.0241, found 1546.0244.

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Supporting Information Available: Examples of simulated ^{1}H NMR spectra used to determine the coupling constants in Tables 3 and 4; computational methods and Cartesian coordinates for methyl 5-*O*-acetyl-α-D-arabinofuranoside used to determine eqs 6 and 7; ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.