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J. Am. Chem. Soc., **2007**, 129 (32), 9885-9901• DOI: 10.1021/ja072892+ • Publication Date (Web): 26 July 2007

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Published on Web 07/26/2007

Synthesis of the Docosanasaccharide Arabinan Domain of Mycobacterial Arabinogalactan and a Proposed Octadecasaccharide Biosynthetic Precursor

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Abstract: Two major components of the cell wall in mycobacteria, including *Mycobacterium tuberculosis*, the causative agent of tuberculosis (TB), are polysaccharides containing arabinofuranose residues. In one of these polysaccharides, arabinogalactan, this arabinan domain consists of three identical motifs of 22 arabinofuranose residues, which are in turn attached to an underlying galactofuranan backbone. Recent studies have proposed that this docosanasaccharide motif, and a structurally related arabinan present in another cell wall polysaccharide, lipoarabinomannan, are biosynthesized from a common octadecasaccharide precursor. To facilitate the testing of this hypothesis, we report here the first total syntheses of these 18- and 22-residue oligosaccharides both functionalized with an aminooctyl linker arm. The route to the target compounds involved the preparation of four tri- to heptasaccharide building blocks possessing only benzoyl protecting groups that were coupled in a highly convergent manner via glycosyl trichloroacetimidate donors. Each of the targets could be prepared in only six steps from these intermediates, and in both cases more than 10 mg of material was obtained. These compounds are expected to be useful tools in probing the biosynthesis of these arabinan-containing polysaccharides. Such studies are essential prerequisites for the identification of novel anti-TB agents that target arabinan assembly.

Introduction

Mycobacterial infections have received significant attention recently due to their increasing incidence in industrialized countries as well as the emergence of drug-resistant strains of *Mycobacterium tuberculosis*, the organism that causes the most high profile of these diseases, tuberculosis (TB).[1] Notably, in the past year the identification of "extreme" drug-resistant TB (XDR-TB) has raised considerable alarm.[2] Successful treatment of TB requires a regimen of multiple antibiotics that must be administered over a number of months,[3] and failure to complete this process is a major cause of drug resistance.[4] Such protracted treatments are necessitated by the unusual structure of the mycobacterial cell wall, which promotes bacterial survival by acting both as a permeability barrier to the passage of antibiotics and also as a modulator of the host immune system.[5] New drugs to treat TB and other mycobacterial diseases are therefore of great current interest,[6] and the enzymes involved in the biosynthesis of cell wall components are particularly attractive targets for antibiotic action. Indeed, two of the frontline antibiotics used to treat TB, ethambutol and isoniazid, act by preventing the formation of an intact cell wall.[7]

The major structural component of the cell wall complex is the mycolyl−arabinogalactan−peptidoglycan complex, which consists of an arabinogalactan (AG) polysaccharide attached, at its nonreducing end, to mycolic acids and, at its reducing end, to peptidoglycan.[8] The linkage between the AG and peptidoglycan is through a disaccharide phosphate moiety (α-L-Rha*p*-(1→4)-α-D-Glc*p*NAc−O−PO_3) to which is attached a chain of ∼30 D-galactofuranose residues, polymerized via alternating β-(1→5) and β-(1→6) linkages. Along this galactan chain are three pendant arabinan chains,[9] each containing 22 D-arabinofuranose (Ara*f*) residues, in a combination of α-(1→5), α-(1→3), and β-(1→2) linkages, to which the mycolic acids are esterified at the nonreducing end.[10] In addition, recent work[11]

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has confirmed an earlier report[12] that the arabinan domain in some mycobacterial species is further functionalized by the addition of substoichiometric amounts of a single galactosamine residue.

A second important cell wall molecule is lipoarabinomannan (LAM), a major antigen and immunomodulatory molecule.[13] LAM consists of a phosphatidylinositol moiety linked to an α-(1→6)-linked mannopyranan core to which is attached an arabinan similar in structure to that found in AG.[13] LAM can be further elaborated with species-specific capping motifs (e.g., inositol phosphate residues,[14] mannopyranosyl oligosaccharides,[15] or 5-thiomethyl-D-xylofuranose residues[16]), which are attached at the nonreducing end of the arabinan. Succinate moieties are also found as modifications in LAM.[17]

Although both AG and LAM contain an arabinan domain of similar structure, differences between these motifs exist. In particular, increasing evidence has now accumulated to suggest that while the arabinan domain in AG is structurally well defined (i.e., a 22-residue motif), the one present in LAM is more hetereogenous.[13,18] Despite significant advances in recent years, mycobacterial arabinan biosynthesis is still relatively poorly understood.[8,13,19] The majority of the Ara*f* residues appear to be installed by a family of arabinosyltransferases (AraTs), EmbA, EmbB, and EmbC,[20] which utilize decaprenolphosphoarabinose (DPA)[21] as the donor species. It has been proposed that AG biosynthesis is mediated by EmbA and EmbB, while EmbC is involved in LAM biosynthesis.[20b,c] Efforts to purify or recombinantly express these enzymes have not been successful, but it is possible to assay their activity in a mycobacterial membrane preparation.[22] Enzymes other than the Emb proteins may also be involved, and indeed Besra and co-workers have reported that a distinct AraT, designated AftA, installs the first Ara*f* residue attached to the galactan, thus "priming" the molecule for full-length arabinan assembly.[23] In addition, a very recent study[24] has demonstrated that another enzyme, termed AftB, is involved in arabinan biosynthesis, and the available data point to its role as a β-(1→2)-AraT that installs the terminal Ara*f* residues in the arabinan.

As part of the increasing body of work on mycobacterial arabinan biosynthesis, Chatterjee and co-workers have proposed[18] that a key intermediate in the biosynthesis of the arabinan domain of both AG and LAM is a motif (**1**, Figure 1) containing 18 Ara*f* residues attached via α-(1→5) and α-(1→3) linkages. It was further proposed that the complete 22-residue arabinan motif present in AG (**2**) would result from the addition of four β-(1→2)-linked Ara*f* residues by EmbA/EmbB, whereas the action of EmbC on **1** would lead to LAM arabinan. In light of the recent identification of AftB,[24] this enzyme may also be involved in the production of a complete arabinan domain in one or both of these polysaccharides.

Testing these hypotheses would be facilitated by access to milligram quantities of authentic samples of these motifs, which can be most conveniently obtained by chemical synthesis. Thus, we report here synthesis of these motifs, functionalized at the reducing end with an octylamino linker, which can be used for their conjugation to a solid support or in the preparation of neoglycoconjugates. This study represents the first synthesis of these motifs, and the targets **3** and **4** (Figure 1) are some of the largest and most complex oligosaccharides produced by chemical synthesis to date.[25]

Results and Discussion

Impressive syntheses of large fragments of mycobacterial LAM have recently been reported.[25d,26,27] The Seeberger group has synthesized a dodecasaccharide fragment containing six α-Ara*f* and six α-mannopyranose (α-Man*p*) residues via a [6 + 6] strategy in which a key step is the coupling of the mannan and arabinan domains.[26] An even larger (28-residue) fragment, possessing the inositol, 15 α-Man*p*, and 12 α-Ara*f* residues was synthesized via a route in which the key glycosylation was a [12 + 16] coupling between an arabinomannan donor and a mannosylated inositol acceptor.[25d] These are elegant approaches to complicated molecules; however, neither contain the β-Ara*f* residues present in the arabinan domain of mycobacterial AG. Introduction of these β-Ara*f* residues in a stereocontrolled manner is challenging[28] and was a key consideration in planning our approach to the targets **3** and **4**.

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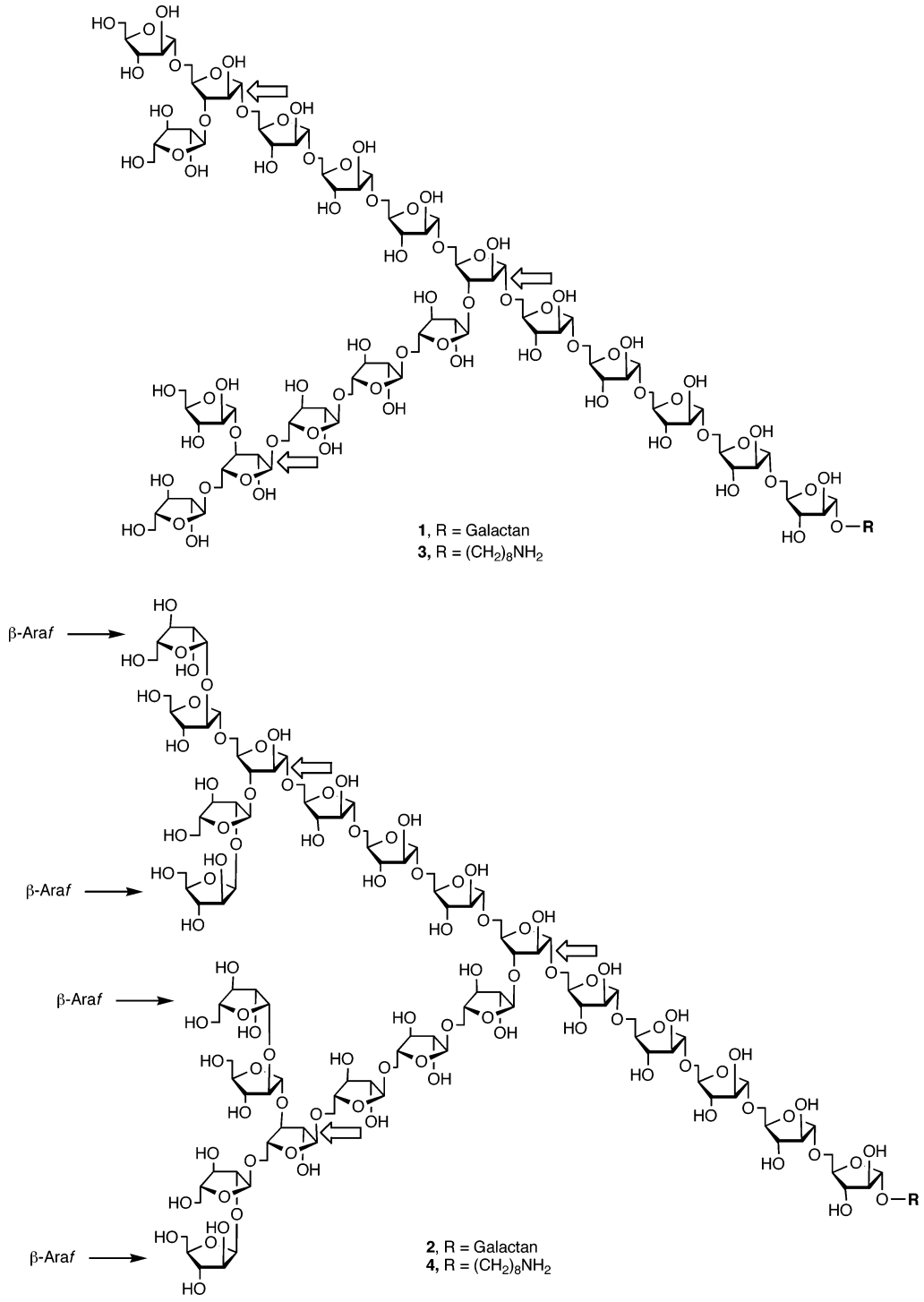

Figure 1. Araf_{22} domain of mycobacterial AG (**2**) and the proposed Araf_{18} biosynthetic precursor **(1)** and aminooctyl glycoside analogues of these motifs (**3** and **4**). The four β-Ara*f* residues in **2** and **4** have been identified for clarity, and key synthetic disconnections are identified by open arrows.

In designing a route to **3** and **4**, we determined that a convergent approach, in which the molecules would be assembled via the sequential coupling of tri- to heptasaccharide building blocks, would be the most efficient. This would allow us to prepare large amounts of these building blocks that, due to their relatively small size, could be readily characterized by NMR spectroscopy. Furthermore, by adding blocks of residues in the glycosylations, we expected that the resulting large changes in molecular weight would facilitate chromatographic separations of reaction mixtures. With regard to the installation of the four β-Ara*f* residues in **4**, we chose to prepare a building block with these linkages already in place, as we envisioned that the separation of any unwanted isomers on relatively small intermediates would be easier than on larger structures. Finally, given the size of the final target molecules, we anticipated that the removal of a large number of benzyl groups at the end of the synthesis could be problematic, and therefore, a key part of the strategy was to use building blocks protected only with acyl (benzoyl) groups.

With these considerations in mind, key disconnections were identified for each molecule (open arrows in Figure 1) and four key building blocks were chosen (**5**−**8**, Figure 2). We envisioned

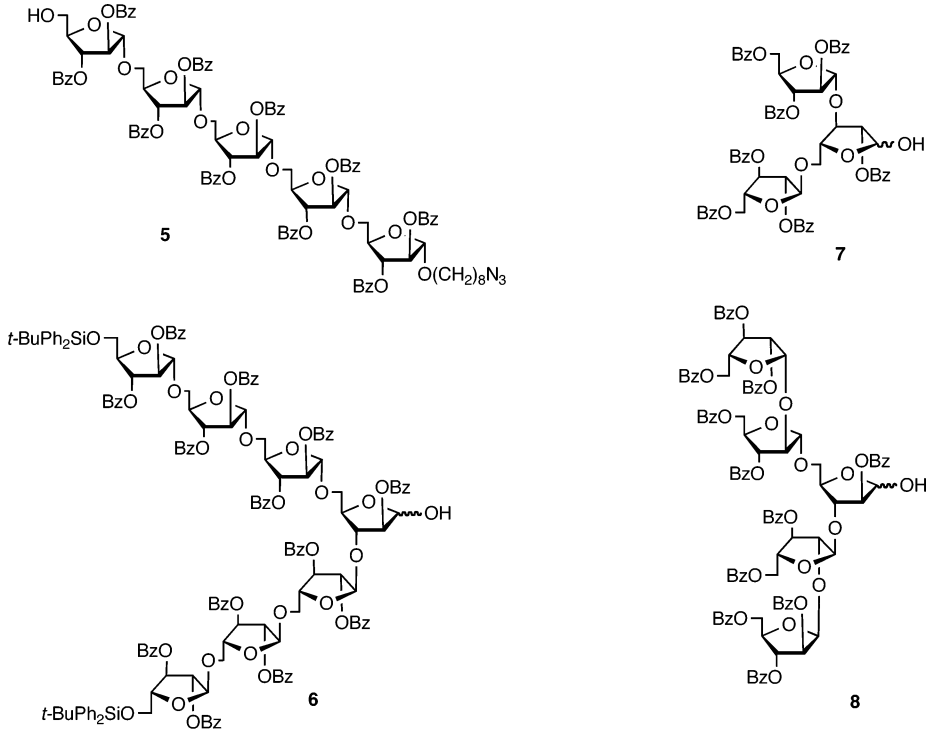

Figure 2. Key building blocks **5**−**8** required for the synthesis of **3** and **4**.

that **3** could be obtained by glycosylation of pentasaccharide **5** with a trichloroacetimidate derived from heptasaccharide **6** to give a dodecasaccharide. Cleavage of the silyl ethers in this Araf_{12} species would provide a diol that could be reacted with an excess of the trichloroacetimidate donor prepared from trisaccharide **7**, in turn yielding a fully benzoylated octadecasaccharide. Treatment with base followed by reduction would afford **3**. A similar approach could be used to access **4** by the use, in the final glycosylation reaction, of a trichloroacetimidate obtained from pentasaccharide **8**, in which the key β-Ara*f* residues are already in place. In the coupling of all these building blocks, the stereochemistry of the newly formed glycosidic linkage would be controlled by neighboring group participation of the benzoyl group at C-2 of the donor.

Synthesis of Pentasaccharide 5. Having developed a general strategy to access the targets, we first addressed the synthesis of the building block that would become the reducing end of both **3** and **4**: pentasaccharide **5** (Scheme 1). The synthesis of **5** started from the protected thioglycoside **9**, which was prepared from D-arabinose in six steps as previously reported.[29] Conversion of **9** into glycoside **10** was carried out by reaction with 8-azido-1-octanol[30] and *N*-iodosuccinimide−silver triflate (NIS−AgOTf).[31] The product was obtained in 92% yield, and the anomeric stereochemistry was determined, as was the case for all glycosylations reported here, using NMR spectroscopy.[32] Consistent with the assigned α-stereochemistry, in the ^{1}H NMR spectrum for **10** the signal for H-1 appeared as a singlet at 5.24 ppm and in the ^{13}C NMR spectrum the C-1 resonance was at 105.6 ppm. Deprotection of **10** to give **11** was achieved upon reaction with HF−pyridine, a transformation that proceeded in 83% yield. Thioglycoside **9** was also hydrolyzed by reaction with NIS−AgOTf in aqueous THF, which afforded lactol **12** in 85% yield as a 1:1 α/β mixture.

With a route to **12** in place, it was reacted with DBU and trichloroacetonitrile, yielding the trichloroacetimidate **13**, which, following a brief purification step, was used to glycosylate the known thioglycoside alcohol **14**[33] using TMSOTf as the promoter.[34] The product disaccharide thioglycoside **15** was obtained in 76% yield over two steps. This glycosyl donor was then reacted with alcohol **11** using NIS−AgOTf promotion, which afforded an 84% yield of the fully protected trisaccharide **16**. Cleavage of the silyl ether protecting group under standard conditions (HF−pyridine) gave trisaccharide alcohol **17** (95% yield), which was subsequently reacted with an excess of disaccharide thioglycoside **15** to afford pentasaccharide **18**. This [2 + 3] glycosylation provided **18** in 86% yield. Conversion of **18** into building block **5** was achieved in 96% yield by treatment with HF−pyridine. In the ^{13}C NMR spectrum of **5**, five anomeric carbons were observed between 105.5 and 105.8 ppm, thus establishing their α-stereochemistry.[32]

Synthesis of Heptasaccharide 6. The precursor to the branched core of both **3** and **4** was heptasaccharide **6**, which was synthesized as shown in Scheme 2. First, thioglycoside **19**, which can be easily obtained in multigram quantities in three steps from D-arabinose,[35] was transformed in 90% yield to the corresponding *p*-methoxyphenyl (PMP) glycoside **20** under standard glycosylation conditions. Removal of the benzoyl groups in **20** was achieved by stirring in sodium methoxide and methanol, affording triol **21** in 87% yield. This triol was then

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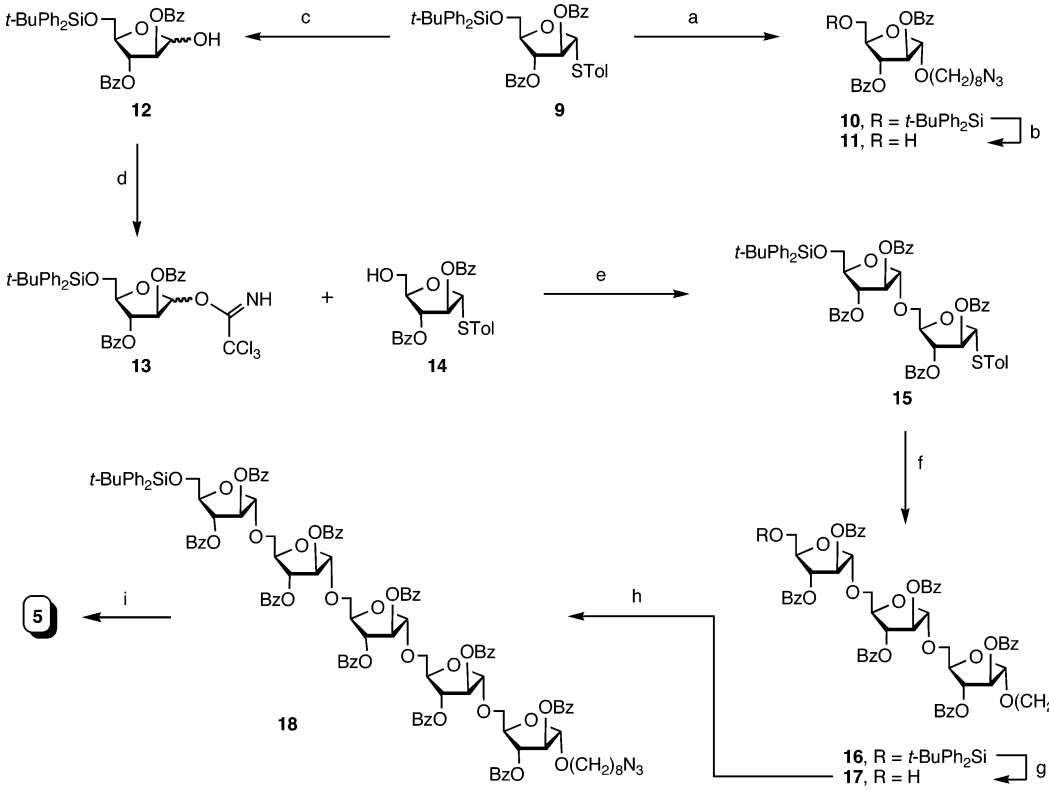
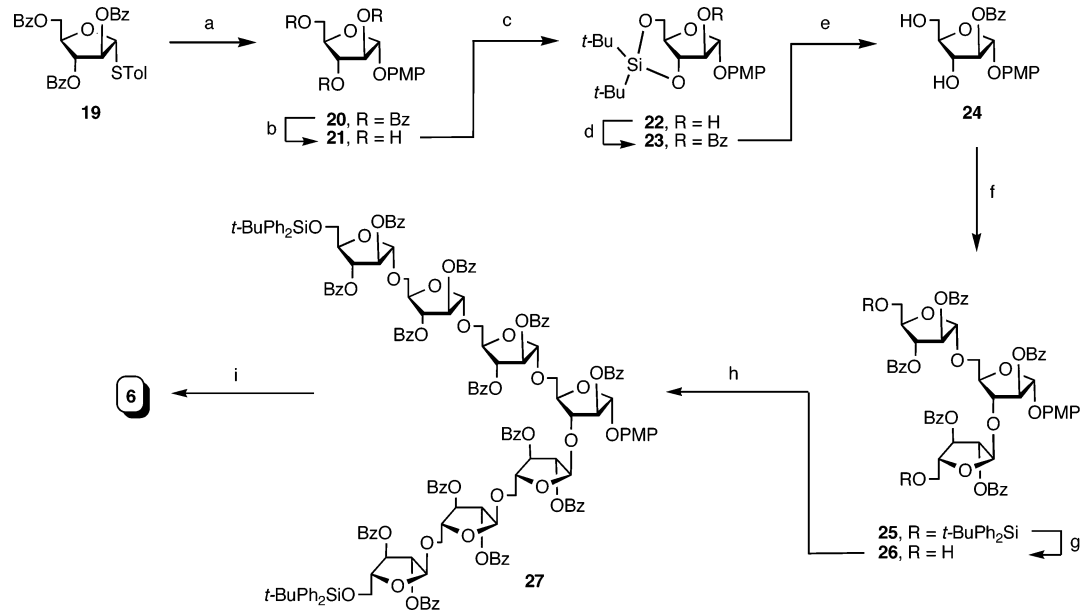
Scheme 1[a]



[a] Reagents and conditions: (a) $HO(CH_2)_8N_3$, NIS, AgOTf, 0 °C, 92%; (b) HF−pyridine, THF, 0 °C → rt, 83%; (c) NIS, AgOTf, THF−H_2O, 0 °C, 85%; (d) CCl_3CN, DBU, CH_2Cl_2, 0 °C → rt; (e) TMSOTf, −30 to −5 °C, 76% over two steps; (f) **11**, NIS, AgOTf, 0 °C, 84%; (g) HF−pyridine, THF, 0 °C → rt, 95%; (h) **15**, NIS, AgOTf, 0 °C, 86%; (i) HF−pyridine, THF, 0 °C → rt, 96%.

Scheme 2[a]



[a] Reagents and conditions: (a) *p*-methoxyphenol, NIS, AgOTf, CH_2Cl_2, 0 → 10 °C, 90%; (b) $NaOCH_3$, $CH_3OH-CH_2Cl_2$, rt, 87%; (c) $(t\text{-Bu})_2Si(OTf)_2$, 2,6-lutidine, CH_2Cl_2−DMF, 0 °C; (d) BzCl, pyridine, 0 °C → rt; (e) HF−pyridine, THF, 0 °C → rt, 76% over three steps; (f) **9**, NIS, AgOTf, CH_2Cl_2, 0 °C, 74%; (g) HF−pyridine, THF, 0 °C → rt, 89%; (h) **15**, NIS, AgOTf, CH_2Cl_2, 0 °C, 89%; (i) CAN, THF−H_2O, 0 °C, 80%.

converted to silyl acetal **22** upon reaction with di-*tert*-butylsilyl bis(trifluoromethanesulfonate) and 2,6-lutidine in a mixture of DMF and dichloromethane. An 87% yield of **22** was obtained. Benzoylation of **22** under conventional conditions provided the fully protected glycoside **23**, which was then partially deprotected upon treatment with HF−pyridine to give the key intermediate diol **24** in 76% yield over three steps from **21**.

Glycosylation of **24** with an excess of thioglycoside **9** (see Scheme 1) afforded a 74% yield of the branched trisaccharide **25**, which was in turn deprotected (HF−pyridine), giving diol

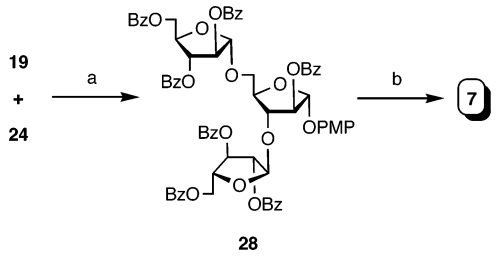
26 in 89% yield. Elongation of this trisaccharide to the heptasaccharide was achieved by reaction of **26** with an excess of disaccharide thioglycoside **15** (Scheme 1) promoted by NIS−AgOTf. This reaction proceeded in 89% yield to give the expected fully protected heptasaccharide **27**, the ^{13}C NMR spectrum of which showed seven α-Ara*f* anomeric carbons between 105.3 and 106.1 ppm. The final step in the preparation of **6** was the removal of the PMP group, which was achieved in 80% yield upon reaction with ceric ammonium nitrate (CAN) in aqueous THF.

Synthesis of Trisaccharide 7. The trisaccharide moiety at the nonreducing end of **3** was to be introduced via hemiacetal **7**, which was straightforwardly obtained as illustrated in Scheme 3. NIS−AgOTf-promoted glycosylation of diol **24** (Scheme 2) with an excess of thioglycoside **19** gave PMP trisaccharide **28** in 92% yield. Subsequent treatment with CAN in aqueous THF led to the formation of **7** as a 1:1 mixture of anomers in 85% yield.

Synthesis of Pentasaccharide 8. For the synthesis of the Araf_{22} target **4**, the protected pentasaccharide **8** was needed for the motif at the nonreducing end of the molecule. A key issue in the preparation of this fragment was the installation of the two β-Ara*f* moieties, which are stereochemically analogous to β-mannopyranosides.[36] A number of methods for the stereoselective formation of β-Ara*f* linkages have been developed over the past several years by our group[37] and others.[38] For the preparation of **8**, we decided to employ the elegant method recently reported first by Boons and co-workers[39] and later by the Ito[40] and Crich[41] groups, which relies on a conformationally rigidified thioglycoside donor.

The synthesis of **8** is shown in Scheme 4 and starts with thioglycoside **29**, which was prepared as previously described.[42] Protection of the alcohol functionality in **29** as the levulinate ester (levulinic acid, DCC, DMAP in dichloromethane) afforded **30** in 90% yield. An excess of this fully protected thioglycoside was then coupled with the PMP glycoside diol **24** (Scheme 2) under our standard thioglycoside coupling conditions (NIS−AgOTf) to yield trisaccharide **31** in 76% yield. As expected, all three glycosidic linkages had the α-stereochemistry, as determined by ^{13}C NMR spectroscopy (three anomeric carbon signals at 106.2, 106.0, and 105.2 ppm). The resonances arising from the anomeric hydrogens of the residues bearing the silyl

Scheme 3[a]



[a] Reagents and conditions: (a) NIS, AgOTf, CH_2Cl_2, 0 °C, 92%; (b) CAN, THF−H_2O, 0 °C, 85%.

acetal were also clearly resolved in the ^1H NMR spectrum appearing at 5.54 and 4.97 ppm as small doublets ($J = 2.2$ and 2.0 Hz, respectively). These *J* values are slightly larger than those normally observed for α-arabinofuranosides. We ascribe this difference to the cyclic protecting group, which rigidifies the conformation of the five-membered ring, relative to those that are not fused to cyclic structures. The two levulinate esters were then cleaved with hydrazine acetate to afford, in 95% yield, diol **32**, the substrate for the key β-arabinofuranosylation reaction.

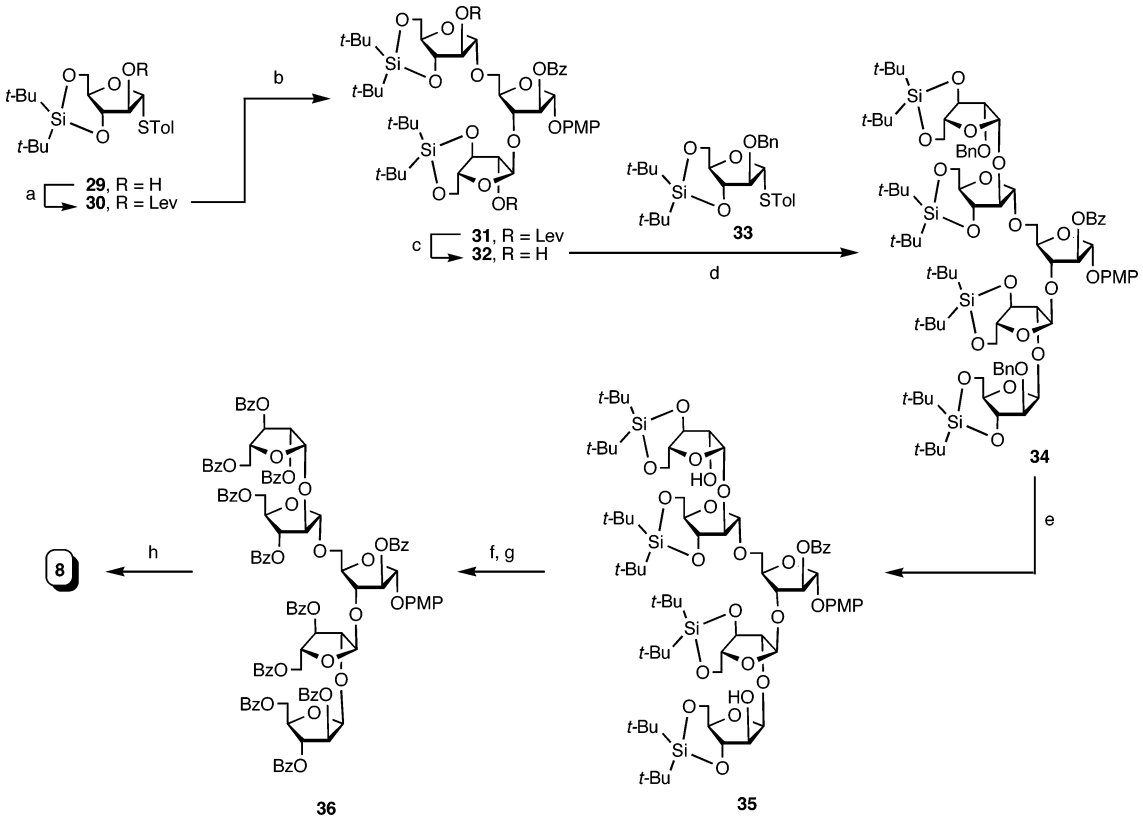
Reaction of **32** with an excess of donor thioglycoside **33**[41,42] and NIS−AgOTf proceeded smoothly to give pentasaccharide **34**, together with a small amount (<8%) of other isomers, which could not be separated. In the ^{13}C NMR spectrum of **34**, three resonances for the anomeric carbons of the α-linked residues appeared at 107.3, 106.5, and 105.1 ppm, which could be correlated (by HMQC) with three signals in the ^1H NMR spectrum at 5.32 ppm (doublet, $J = 3.1$ Hz), 5.03 ppm (doublet, $J = 2.7$ Hz), and 5.71 ppm (singlet), respectively. In addition, the ^1H NMR spectrum of **34** indicated two β-Ara*f* anomeric hydrogens at 5.20 ppm (doublet, $J = 4.8$ Hz) and 4.97 ppm (doublet, $J = 4.8$ Hz) that were correlated to resonances in the ^{13}C NMR spectrum at 99.5 and 99.7 ppm, respectively. As was seen with **31**, the $J_{1,2}$ values are very slightly larger for the rings with the silyl acetal protection than for rings that are not conformationally constrained. These data are all consistent[32,39−41] with the structure of the major isomer of **34** being that shown in Scheme 4.

Having carried out the key β-arabinofuranosylation reaction, pentasaccharide **8** could be obtained by manipulation of protecting groups. Thus, removal of the benzyl groups was done by treatment with hydrogen gas and 10% palladium on carbon, which provided **35** in 84% yield. At this stage it was possible to separate the desired product **35** from the small amount of other isomers produced in the glycosylation reaction between **32** and **33**. The four silyl acetals in **35** were then cleaved by treatment with HF−pyridine to give a product that was not characterized, but instead treated with benzoyl chloride and pyridine. The result of this two-step transformation was the fully benzoylated pentasaccharide **36**, which was obtained in 70% yield. Hydrolysis of the PMP glycoside in **36** was achieved as done previously for the preparation of **6** and **7**. In the present case, **8** was obtained in 79% yield from **36** as a 1:1 mixture of isomers.

Assembly of Octadecasaccharide 3. Octadecasaccharide **3** could be produced from building blocks **5**−**7** without difficulty as illustrated in Scheme 5. First, heptasaccharide lactol **6** was treated with trichloroacetonitrile and DBU to provide the corresponding imidate that was quickly purified following its

(36) (a) Gridley, J. J.; Osborn, H. M. I. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1471−1491. (b) Crich, D. Chemistry of Glycosyl Triflates: Synthesis of β-Mannopyranosides. In *Glycochemistry: Principles, Synthesis and Applications*; Wang, P. G., Bertozzi, C. R., Eds.; Marcel-Dekker: New York, 2001; pp 53−75.
(37) (a) D'Souza, F. W.; Lowary, T. L. *Org. Lett.* **2000**, *2*, 1493−1495. (b) Yin, H.; D'Souza, F. W.; Lowary, T. L. *J. Org. Chem.* **2002**, *67*, 892−903. (b) Gadikota, R. R.; Callam, C. S.; Wagner, T.; Del Fraino, B.; Lowary, T. L. *J. Am. Chem. Soc.* **2003**, *125*, 4155−4165. (c) Callam, C. S.; Gadikota, R. R.; Krein, D. M.; Lowary, T. L. *J. Am. Chem. Soc.* **2003**, *125*, 13112−13119. (d) Darwish, O.; Callam, C. S.; Hadad. C. M.; Lowary, T. L. *J. Carbohydr. Chem.* **2003**, *22*, 963−981.
(38) (a) Mereyala, H. B.; Hotha, S.; Gurjar, M. K. *J. Chem. Soc., Chem. Commun.* **1998**, 685−686. (b) Désiré, J.; Prandi, J. *Carbohydr. Res.* **1999**, *317*, 110−118. (b) Bamhaoud, T.; Sanchez, S.; Prandi, J. *Chem. Commun.* **2000**, 659−660. (c) Sanchez, S.; Bamhaoud, T.; Prandi, J. *Tetrahedron Lett.* **2000**, *41*, 7447−7452. (d) Lee, Y. J.; Lee, K.; Jung, E. H.; Jeon, H. B.; Kim, K. S. *Org. Lett.* **2005**, *7*, 3263−3266. (e) Ishiwata, A.; Akao, H.; Ito, Y.; Sunagawa, M.; Kusunose, N.; Kashiwazaki, Y. *Bioorg. Med. Chem.* **2006**, *14*, 3049−3061.
(39) Zhu, X.; Kawatkar, S.; Rao, Y.; Boons, G.-J. *J. Am. Chem. Soc.* **2006**, *128*, 11948−11957.
(40) Ishiwata, A.; Akao, H.; Ito, Y. *Org. Lett.* **2006**, *8*, 5525−5528.
(41) Crich, D.; Pedersen, C. M.; Bowers, A. A.; Wink, D. J. *J. Org. Chem.* **2007**, *72*, 1553−1565.
(42) Nacario, R. C.; Lowary, T. L.; McDonald, R. *Acta Crystallogr., Sect. E* **2007**, *63*, o498−o500.

Scheme 4[a]



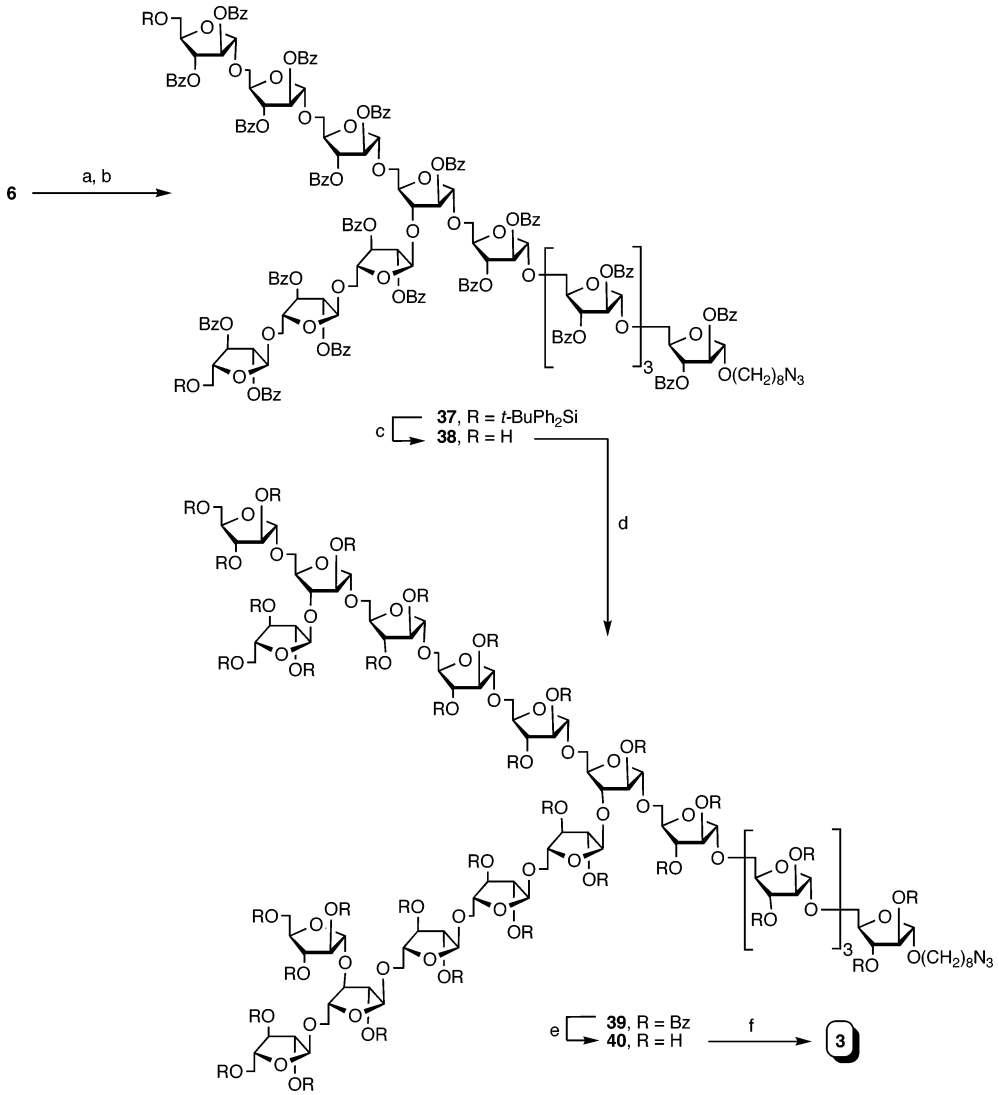
[a] Reagents and conditions: (a) levulinic acid, DCC, DMAP, CH_2Cl_2, rt, 90%; (b) **24**, NIS, AgOTf, CH_2Cl_2, 0 °C, 76%; (c) H_2NNH_2−HOAc, THF, rt, 95%; (d) NIS, AgOTf, CH_2Cl_2, −30 °C, 70%; (e) 10% Pd−C, H_2, EtOAc, rt, 84%; (f) HF−pyridine, THF, 0 °C → rt; (g) BzCl, pyridine, 0 °C, 70% over two steps; (h) CAN, THF−H_2O, 0 °C, 79%.

formation, but not characterized. Instead, this donor was immediately reacted with pentasaccharide alcohol **5** and TMS-OTf, which gave a 77% yield of dodecasaccharide **37**. Given the size of this molecule and the presence of only α-Ara*f* monosaccharide residues, there was, as expected, significant overlap in the ^1H and ^{13}C spectra of **37**. That a dodecasaccharide had been produced could be ascertained from the electrospray mass spectrum, which showed a peak at $m/z = 4651$, which corresponds to the sodium adduct of **37** ($C_{261}H_{241}N_3O_{72}Si_2Na$). Although the donor in the glycosylation reaction leading to **37** had a participating group at C-2, which we expected would provide only the α-glycoside, it was necessary to establish this. This was possible by inspection of the ^{13}C NMR spectrum, which indicated that all of the anomeric carbon resonances were between 105 and 106 ppm. Had the *β*-glycoside been formed, a resonance at higher field (100−105 ppm) would have been expected.[32]

Conversion of the fully protected dodecasaccharide **37** into the diol required for the synthesis of the octadecasaccharide was achieved under the usual HF−pyridine conditions, which provided the product **38** in 83% yield. With **38** in hand, it was converted to the fully protected octadecasaccharide **39** in 77% yield after reaction with an excess of the trichloroacetimidate derived from trisaccharide **7**. As was done for the dodecasaccharide, a combination of mass spectrometry and ^{13}C NMR spectroscopy could be used to establish the product structure ($m/z = 6425.0$ for $C_{357}H_{309}N_3O_{110}Na^+$ and all anomeric carbon resonances between 105 and 106 ppm). Deprotection of **39** could be accomplished without incident by stirring with sodium methoxide for 36 h. Following neutralization and concentration of the reaction mixture, purification was achieved by dissolving the residue in water and extraction with organic solvent to remove methyl benzoate; lyophilization of the aqueous layer gave a quantitative yield of **40**. Conversion of this Araf_{18} azide species into the corresponding amine was carried out by hydrogenation (H_2, Pd/C, methanol, water), which afforded **3** in 87% yield. High-resolution electrospray mass spectrometry of **3** revealed $m/z = 2544.8972$ for the corresponding sodium adduct, as compared to the calculated $m/z = 2544.8965$. In the ^{13}C NMR spectrum of **3**, all of the anomeric carbon resonances could be found clustered between 108 and 109 ppm as would be expected given the presence of only α-Ara*f* residues (Figure 3A).

Assembly of Docosanasaccharide 4. The dodecasaccharide diol intermediate **38** employed in the synthesis of octadecasaccharide **3** was also used in the preparation of docosanasaccharide **4** (Scheme 6). Like the synthesis of **3**, this was straightforwardly done. Thus, reaction of pentasaccharide **8** with DBU and trichloroacetonitrile afforded the expected trichloroacetimidate donor that was, without purification, reacted with **38** and TMS-OTf to provide the desired docosanasaccharide **41** in 77% yield. Characterization of the product by MALDI-TOF mass spectrometry showed that the compound had the expected mass ($m/z = 7785.0$ for $C_{433}H_{373}N_3O_{134}Na$). The presence of both α-Ara*f* and *β*-Ara*f* linkages was apparent from the ^{13}C NMR spectrum, which showed anomeric carbon resonances not only between 105 and 107 ppm (α-Ara*f* residues), but also around 100 ppm (*β*-Ara*f* residues). Removal of the benzoyl groups as described for **39** afforded the deprotected azido docosanasaccharide **42**,

Scheme 5[a]



[a] Reagents and conditions: (a) CCl_3CN, DBU, CH_2Cl_2, 0 °C → rt; (b) **5**, TMSOTf, CH_2Cl_2, −30 → −5 °C, 77% over two steps; (c) HF−pyridine, THF, 0 °C → rt, 83%; (d) **7**, CCl_3CN, DBU, CH_2Cl_2, 0 °C → rt, then TMSOTf, CH_2Cl_2, −30 → −5 °C, 77% over two steps; (e) $NaOCH_3$, $CH_3OH-CH_2Cl_2$, rt, quantitative; (f) 10% Pd−C, H_2, CH_3OH-H_2O, rt, 87%.

which was subsequently reduced by hydrogenation. The target **4** was obtained in 89% yield in two steps from **41**.

The high-resolution electrospray mass spectrum of docosanasaccharide **4** showed a molecular ion of the sodium adduct at $m/z = 3073.0655$, which was identical to the calculated exact mass for this molecule. In the 125 MHz ^{13}C NMR spectrum (Figure 3B), the majority of the anomeric carbon signals were, as in the case of **3**, located between 108 and 109 ppm. These resonances arise from 14 of the α-Ara*f* residues and were not sufficiently resolved for assignment. Although at this field strength the signals arising from the remaining eight anomeric carbons did not fully resolve, appearing instead as four resonances, they provide further important support for the structure of **4**. Two of these signals, corresponding to the four *β*-Ara*f* moieties in **4**, were present at 101.5 and 101.6 ppm. Two peaks were also present at 106.3 and 106.5 ppm, which, on the basis of previous assignments,[43] we assign as the four α-Ara*f* residues that bear the *β*-Ara*f* moieties on O-2. We note that these chemical shifts and doubling of resonances are consistent with those reported for the arabinan domain of AG in a recent solid-state NMR study of live mycobacteria.[44]

Conclusions

In summary, we report here the first total synthesis of the 22-residue arabinan domain of mycobacterial arabinogalactan and a proposed octadecasaccharide biosynthetic precursor, both functionalized with an aminooctyl linker arm. Key features of the route to the targets **3** and **4** were the preparation of tri- to heptasaccharide building blocks possessing only benzoyl protection that were coupled in a highly convergent manner via glycosyl trichloroacetimidate donors. Once the four building blocks were in hand, each of the targets could be obtained in only six steps. This route produced 11 and 17 mg quantities of **3** and **4**, respectively, which will be useful tools in probing mycobacterial arabinan biosynthesis, a critical prerequisite for

(43) Rademacher, C.; Shoemaker, G. K.; Kim, H.-S.; Zheng, R. B.; Taha, H.; Liu, C.; Nacario, R. C.; Schriemer, D. C.; Klassen, J. S.; Peters, T.; Lowary, T. L. *J. Am. Chem. Soc.* **2007**. In press.

(44) Lee, R. E. B.; Li, W.; Chatterjee, D.; Lee, R. E. *Glycobiology* **2005**, *15*, 139−151.

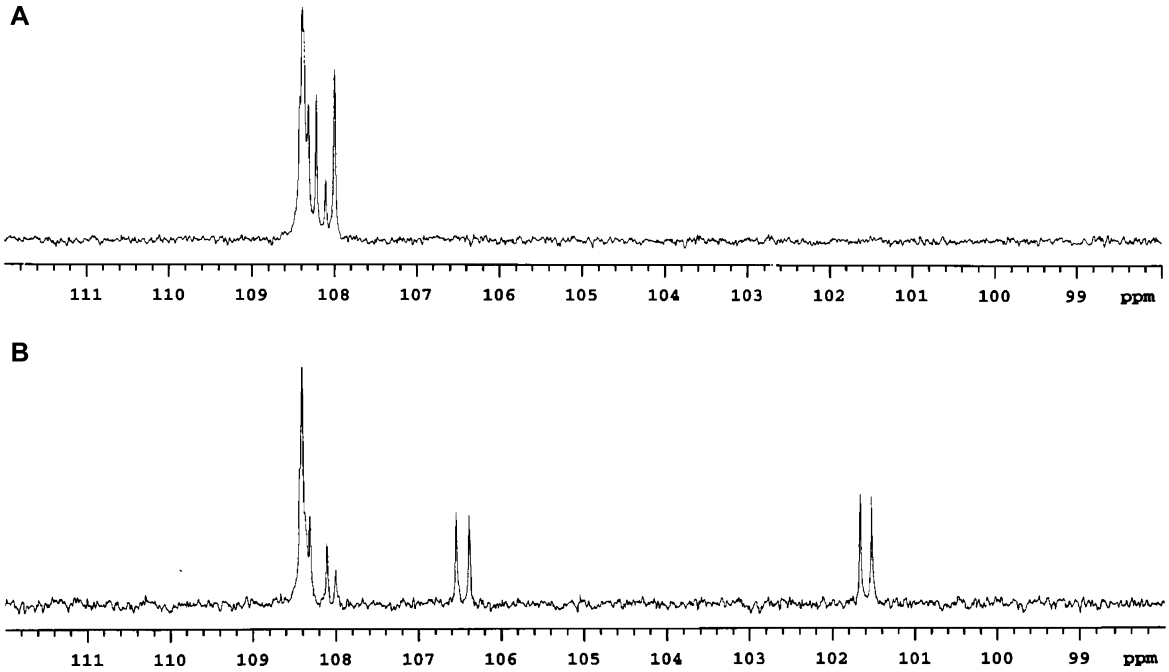
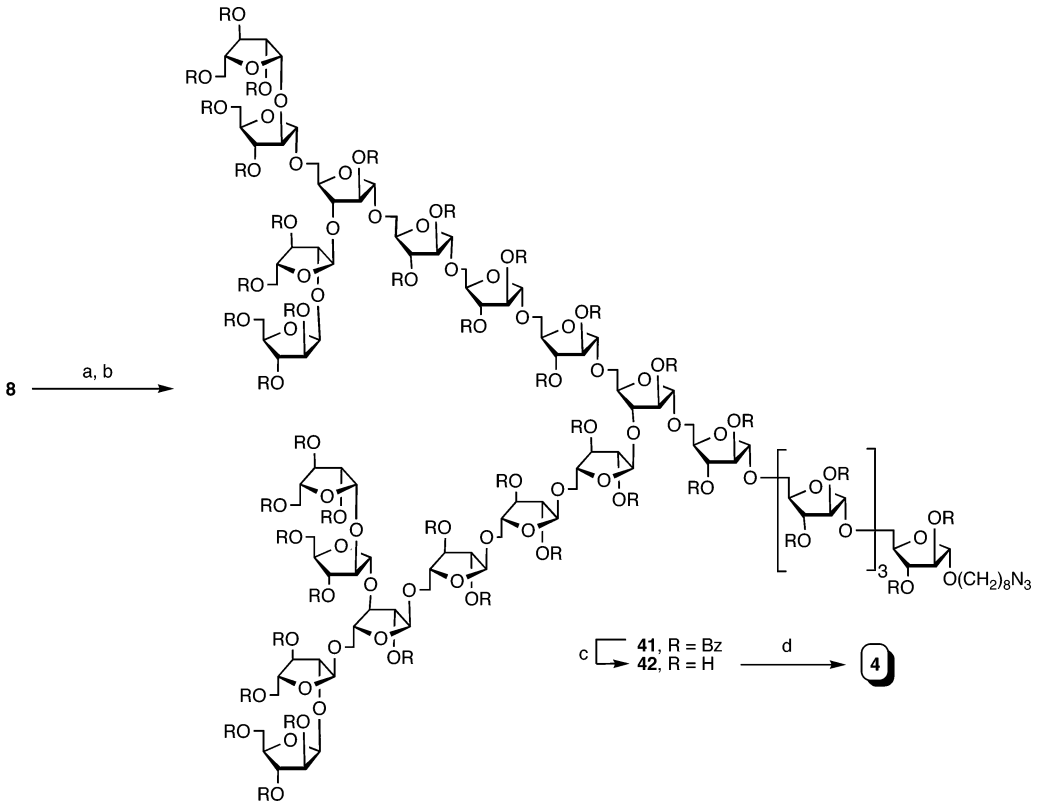


Figure 3. Partial ^{13}C NMR spectra of **3** and **4**. (A) Anomeric carbon region for **3**. As expected for the molecule, which contains only α-Ara*f* residues, all signals are clustered between 108 and 109 ppm. (B) Anomeric carbon region for **4**. The presence of the *β*-Ara*f* residues is clearly apparent from the resonances around 101.5 ppm; the resonances around 106.5 ppm are proposed to arise from the anomeric carbons of the four α-Ara*f* moieties that are glycosylated by *β*-Ara*f* on O-2.

Scheme 6[a]



[a] Reagents and conditions: (a) CCl_3CN, DBU, CH_2Cl_2, 0 °C → rt; (b) **38**, TMSOTf, CH_2Cl_2, −30 → −5 °C, 77% over two steps; (c) $NaOCH_3$, $CH_3OH-CH_2Cl_2$, rt, quantitative; (d) 10% Pd−C, H_2, CH_3OH-H_2O, rt, 89%.

the identification of novel anti-TB agents targeting these biochemical pathways. In addition, we envisage that **4** will be a valuable substrate for the mycolyltransferases that add mycolic acids to the AG.[45]

Experimental Section

General Methods. Reactions were carried out in oven-dried glassware. All reagents used were purchased from commercial sources and were used without further purification unless noted. Reaction

solvents were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out at room temperature under a positive pressure of argon and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, E. Merck). TLC spots were detected under UV light or by charring with acidified *p*-anisaldehyde solution in EtOH. Unless otherwise indicated, all column chromatography was performed on silica gel (40−60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C. ^{1}H NMR spectra were recorded at 600, 500, or 400 MHz, and chemical shifts were referenced to the peak for TMS (0.0 ppm, $CDCl_3$), CD_3OD (3.30 ppm, CD_3OD), or HOD (4.78 ppm, D_2O). ^{1}H data were reported as though they were first order. ^{13}C NMR (APT) spectra[46] were recorded at 125 or 100 MHz, and ^{13}C chemical shifts were referenced to the peak for internal $CDCl_3$ (77.23 ppm, $CDCl_3$), CD_3OD (48.9 ppm, CD_3OD), or external acetone (31.07 ppm, D_2O). Assignments of resonances in NMR spectra were done using ^{1}H−^{1}H COSY and HMQC experiments. Organic solutions were concentrated under vacuum at <40 °C. Electrospray mass spectra were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl. MALDI mass spectrometry was performed on a Voyager Elite time-of-flight spectrometer on samples suspended in 2,5-dihydroxybenzoic acid, IAA (*trans*-3-indoleacrylic acid), or DCTB (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile) using the delayed-extraction mode and positive ion detection. HRMS for compounds **3** and **4** was performed on a Bruker APEX-Q FTMS instrument with Apollo II using ESI positive ion detection with heptakis(2,3,6-tri-*O*-benzyl)cyclomaltoheptaose as the internal reference for calibration, and the samples were dissolved in a mixture of CH_2Cl_2−CH_3OH−toluene (2:3:1).

8-Aminooctyl 5-*O*-{α-D-Arabinofuranosyl-(1→3)-[α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→3)-[5-*O*-{α-D-arabinofuranosyl-(1→3)-[α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D -arabinofuranosyl-(1→5)-α-D-arabinofuranoside (3). To a solution of compound **40** (13 mg, 5 μmol) in CH_3OH−H_2O (8:3, 7 mL) was added 10% Pd/C (7 mg), and the reaction mixture was stirred vigorously under hydrogen (1 atm) for 20 h. The reaction mixture was diluted with CH_3OH−H_2O (8:3, 6 mL) and filtered to remove the catalyst. The CH_3OH−H_2O solution was concentrated to give a syrup that was dissolved in distilled water (5 mL), filtered using a 13 mm nylon 0.2 μm syringe filter unit, and lyophilized to give **3** (11.0 mg, 87%) as a fluffy solid: $[\alpha]_D$ +133.9 (*c* 0.3, H_2O); ^{1}H NMR (600 MHz, D_2O, δ_H) 5.16−5.14 (m, 3 H), 5.11 (br s, 3 H), 5.09−5.06 (m, 11 H), 5.00 (d, 1 H, J = 1.8 Hz), 4.33−4.26 (m, 6 H), 4.25−3.67 (m, 85 H), 3.56 (ddd, 1 H, J = 13.2, 10.0, 6.6 Hz, octyl OCH_2), 2.94 (dd, 2 H, J = 7.6, 7.6 Hz, octyl CH_2NH$_2$), 1.65−1.57 (m, 4 H, octyl CH_2), 1.40−1.30 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, D_2O, δ_C) 107.8(5) (C-1), 107.8(1) (C-1), 107.7(8) (C-1), 107.7(6) (C-1), 107.7(2) (C-1), 107.7 (C-1), 107.6 (C-1), 107.5 (C-1), 107.3 (C-1), 84.2(6), 84.2(3), 84.2(0), 82.6(8), 82.6(5), 82.6(1), 82.5, 82.4, 82.0, 81.9(6), 81.9(2), 81.5, 81.3, 81.2, 81.1(8), 81.1(3), 81.0(9), 81.0(7), 79.3(6), 79.3(2), 77.0(8), 77.0(5), 77.0, 76.9(4), 76.9-(2), 76.8(7), 76.8(4), 76.8, 76.7, 68.8 (octyl OCH_2), 67.1(6), 67.1(4) (C-5), 67.0 (C-5), 66.8(9) (C-5), 66.8(6) (C-5), 66.7 (C-5), 66.5 (C-5), 61.4(3) (C-5), 61.4(1) (C-5), 61.3 (C-5), 39.8(5) (octyl CH_2NH_2), 28.8-(2) (octyl CH_2), 28.3(5) (octyl CH_2), 27.2 (octyl CH_2), 25.7 (octyl CH_2), 25.3 (octyl CH_2), 23.5 (octyl CH_2); ESIMS *m*/*z* calcd for $C_{98}H_{163}NO_{73}$ (M + Na) 2544.8965, found 2544.8972.

8-Aminooctyl 5-*O*-{β-D-Arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→3)-[5-*O*-{β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (4). To a solution of compound **42** (20 mg, 6 μmol) in CH_3OH−H_2O (8:3, 7 mL) was added 10% Pd/C (7 mg), and the reaction mixture was stirred vigorously under hydrogen (1 atm) for 20 h. The reaction mixture was diluted with CH_3OH−H_2O (8:3, 8 mL) and filtered to remove the catalyst. The CH_3OH−H_2O solution was concentrated to give a syrup that was dissolved in distilled water (6 mL), filtered using a 13 mm nylon 0.2 μm syringe filter unit, and lyophilized to give **4** (17.5 mg, 89%) as a fluffy solid: $[\alpha]_D$ +96.3 (*c* 0.3, H_2O); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.25 (d, 2 H, J = 1.8 Hz), 5.19−5.16 (m, 3 H), 5.16 (d, 2 H, J = 4.6 Hz, H-1β), 5.15 (d, 2 H, J = 4.6 Hz, H-1β), 5.13−5.11 (br s, 3 H), 5.11−5.07 (m, 9 H), 5.02 (d, 1 H, J = 2.0 Hz), 4.34−4.26 (m, 7 H), 4.25−3.64 (m, 104 H), 3.57 (ddd, 1 H, J = 12.5, 10.1, 6.6 Hz, octyl OCH_2), 2.95 (dd, 2 H, J = 7.6, 7.6 Hz, octyl CH_2NH$_2$), 1.66−1.56 (m, 4 H, octyl CH_2), 1.40−1.30 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.3(9) (C-1), 108.3(6) (C-1), 108.3 (C-1), 108.1 (C-1), 107.9 (C-1), 106.5 (C-1), 106.3 (C-1), 101.6 (C-1), 101.5 (C-1), 87.9, 87.7, 83.7(9), 83.7(3), 83.3, 83.2(7), 83.2(2), 83.0, 82.8, 82.6(2), 82.6, 82.5, 81.9, 81.7(3), 81.7(1), 80.0, 79.9, 77.6(5), 77.6(2), 77.4(6), 77.4(2), 77.3, 77.1, 75.7, 75.6, 75.0(6), 75.0(1), 69.4, 67.7, 67.6 (octyl OCH_2), 67.5 (C-5), 67.3 (C-5), 67.1(9) (C-5), 67.1(1) (C-5), 63.8(6) (C-5), 63.8(2) (C-5), 61.4(9) (C-5), 61.4(7) (C-5), 40.5 (octyl CH_2NH_2), 29.4 (octyl CH_2), 29.0 (octyl CH_2), 28.9 (octyl CH_2), 28.0 (octyl CH_2), 26.3 (octyl CH_2), 25.9 (octyl CH_2); ESIMS *m*/*z* calcd for $C_{118}H_{195}NO_{89}$ (M + Na) 3073.0655, found 3073.0655.

8-Azidooctyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (5). To a solution of compound **18** (2.23 g, 1.06 mmol) in pyridine−THF (1:5, 30 mL) at 0 °C was added HF−pyridine (1.0 mL) dropwise. The reaction mixture was warmed to room temperature and stirred for 16 h before being diluted with EtOAc (50 mL), poured into a saturated aqueous $NaHCO_3$ solution (150 mL), and extracted with EtOAc (70 mL × 2). The combined organic layer was washed with water (75 mL), dried (Na_2SO_4), and concentrated to give a crude syrup that was purified by column chromatography (2:1 hexanes−EtOAc) to afford **5** (1.9 g, 96%) as a syrup: R_f 0.11 (7:3 hexanes−EtOAc); $[\alpha]_D$ +10.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.81(m, 19 H, Ar), 7.61−7.33 (m, 19 H, Ar), 7.30−7.10 (m, 12 H, Ar), 5.69−5.60 (m, 9 H), 5.51 (s, 1 H), 5.43−5.38 (m, 5 H), 5.21 (s, 1 H), 4.64−4.56 (m, 3 H), 4.50−4.40 (m, 2 H), 4.23−4.14 (m, 4 H), 4.02−3.88 (m, 6 H), 3.75 (ddd, 1 H, J = 13.5, 9.4, 6.7 Hz, octyl OCH_2), 3.50 (ddd, 1 H, J = 13.1, 9.4, 6.2 Hz, octyl OCH_2), 3.21 (dd, 2 H, J = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.50−1.22 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C═O), 165.6(4) (C═O), 165.6(2) (C═O), 165.6 (C═O), 165.4 (C═O), 165.1(3) (C═O), 165.1 (C═O), 165.0(9) (C═O), 165.0(7) (C═O), 133.4(8) (Ar), 133.4(4) (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 129.8(7) (Ar), 129.8(5) (Ar), 129.8(1) (Ar), 129.7(7) (Ar), 129.7(5) (Ar), 129.3 (Ar), 129.1(8) (Ar), 129.1(3) (Ar), 129.0(7) (Ar), 129.0(3) (Ar), 128.9 (Ar), 128.4(8) (Ar), 128.4 (Ar), 128.2(9) (Ar), 128.2(3) (Ar), 125.2 (Ar), 105.8(8) (C-1 × 2), 105.8(4) (C-1 × 2), 105.5 (C-1), 83.6, 82.0, 81.9, 81.8, 81.7, 81.6,

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81.5(9), 81.5(6), 77.6, 77.3, 77.2, 67.3 (octyl OCH_2), 66.1 (C-5), 66.0 (C-5), 65.8(6) (C-5), 65.8(3) (C-5), 62.3 (C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.0 (octyl CH_2), 28.8 (octyl CH_2), 26.6 (octyl CH_2), 26.0 (octyl CH_2); ESIMS *m*/*z* calcd for (M + Na) $C_{103}H_{97}N_3O_{31}$ 1894.5999, found 1894.5998.

2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-D-arabinofuranose (6). To a solution of compound **27** (1.85 g, 0.64 mmol) in THF−H_2O (4:1, 90 mL) at 0 °C was added CAN (8.8 g, 16.05 mmol), and the reaction mixture was stirred for 20 min. The reaction mixture was diluted with EtOAc (200 mL) and brine (250 mL) and stirred well. The EtOAc layer was separated, and the aqueous phase was extracted with EtOAc (75 mL × 2). The combined organic layer was washed with water (75 mL), a saturated aqueous $NaHCO_3$ solution (150 mL), and water (75 mL), dried (Na_2SO_4), and concentrated to give a crude that was purified by column chromatography (7:3 hexanes−EtOAc) to afford **6** (1.43 g, 1:1 α/β mixture, 80%) as a syrup. About 5% of the starting material was also recovered. Data for **6**: R_f 0.20 (65:35 hexanes−EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.15−7.85 (m, 26 H, Ar), 7.73−7.65 (m, 8 H, Ar), 7.64−7.20 (m, 51 H, Ar), 5.98−5.90 (m, 0.5 H), 5.83−5.70 (m, 1.5 H), 5.68−5.60 (m, 7 H), 5.58−5.55 (m, 5 H), 5.42−5.27 (m, 6 H), 4.66−4.56 (m, 3 H), 4.52−4.46 (m, 4 H), 4.24−4.14 (m, 5 H), 4.08−3.80 (m, 10 H), 3.67−3.63 (m, 1H), 1.01 (s, 18 H, $C(CH_3)_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (C═O), 165.9(1) (C═O), 165.9 (C═O), 165.6(7) (C═O), 165.6 (C═O), 165.5(7) (C═O), 165.5(3) (C═O), 165.5(2) (C═O), 165.4(9) (C═O), 165.4(5) (C═O), 165.3(6) (C═O), 165.3(4) (C═O), 165.2(C═O), 165.1(7) (C═O), 165.1 (C═O), 165.0(9) (C═O), 165.0(7) (C═O), 165.0(4) (C═O), 135.6(6) (Ar), 135.6(4) (Ar), 133.6 (Ar), 133.5 (Ar), 133.4 (Ar), 133.3(9) (Ar), 133.3(7) (Ar), 133.3(4) (Ar), 133.2(9) (Ar), 133.2(4) (Ar), 133.2(1) (Ar), 133.1 (Ar), 132.9 (Ar), 132.3 (Ar), 129.9 (Ar), 129.8(8) (Ar), 129.8(1) (Ar), 129.7(6) (Ar), 129.7(2) (Ar), 129.6 (Ar), 129.3 (Ar), 129.2 (Ar), 129.1(5) (Ar), 129.1(3) (Ar), 129.0 (Ar), 128.9(9) (Ar), 128.9(6) (Ar), 128.8(8) (Ar), 128.8 (Ar), 128.5 (Ar), 128.4(7) (Ar), 128.4(1) (Ar), 128.3 (Ar), 128.2-(5) (Ar), 128.2(3) (Ar), 128.1 (Ar), 127.6 (Ar), 106.4 (C-1), 106.1 (C-1), 105.9(9) (C-1), 105.9(7) (C-1), 105.9(1) (C-1), 105.8(6) (C-1), 105.8 (C-1), 105.1 (C-1), 103.4 (C-1), 101.1 (C-1), 94.9 (C-1), 84.2, 83.1, 82.8, 82.6(6), 82.6(1), 82.4, 82.3, 82.2, 82.1, 81.9(8), 81.9(4), 81.8, 81.6, 81.5(7), 81.5(2), 81.5, 81.4, 80.1, 79.5, 79.3, 79.1, 78.2, 77.3, 77.2, 76.6, 66.6 (C-5), 65.8 (C-5), 65.7(8) (C-5), 65.7(2) (C-5), 65.6 (C-5), 65.5 (C-5), 63.4 (C-5), 60.3 (C-5), 26.7 (C(CH_3)$_3$), 26.6 (C(CH_3)$_3$) 21.0 (C(CH_3)$_3$), 19.2 (C(CH_3)$_3$); MALDI-TOFMS *m*/*z* calcd for (M + Na) $C_{158}H_{146}O_{42}Si_2$ 2794.7, found: 2794.1

2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-D-arabinofuranose (7). Compound **7** was prepared as a syrup (0.47 g, 1:1 α/β ratio, 85%) from compound **28** (0.60 g, 0.48 mmol) in THF−H_2O (4:1, 30 mL) and CAN (6.58 g, 12.0 mmol) as described for **6**: R_f 0.27 (65:35 hexanes−EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.10−7.90 (m, 14 H, Ar), 7.62−7.20 (m, 21 H, Ar), 5.72 (d, 0.5 H, J = 4.4 Hz), 5.65−5.52 (m, 6 H), 5.45−5.42 (m, 1 H), 5.36 (s, 0.5 H), 5.32 (dd, 0.5 H, J = 6.6, 4.5 Hz), 4.91 (dd, 0.5 H, J = 6.5, 6.5 Hz), 4.83−4.56 (m, 7.5 H), 4.20 (ddd, 0.5 H, J = 9.2, 6.2, 2.9 Hz), 4.14−4.06 (m, 1 H), 3.95 (dd, 0.5 H, J = 11.8, 2.7 Hz), 3.88 (dd, 0.5 H, J = 11.2, 3.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.2 (C═O), 166.1 (C═O), 166.0(4) (C═O), 166.0(2) (C═O), 165.9(4) (C═O), 165.9(1) (C═O), 165.7 (C═O), 165.6(5) (C═O), 165.6(3) (C═O), 165.3 (C═O), 165.2(4) (C═O), 165.2(3) (C═O), 133.6(9) (Ar), 133.6(5) (Ar), 133.5(9) (Ar), 133.5(6) (Ar), 133.5(1) (Ar), 133.4(9) (Ar), 133.4(4) (Ar), 133.4(2) (Ar), 133.2(Ar), 133.0(8) (Ar), 133.0(2) (Ar), 129.9(8) (Ar), 129.9(4) (Ar), 129.9(2) (Ar), 129.9(0) (Ar), 129.8(7) (Ar), 129.8(4) (Ar), 129.7-(6) (Ar), 129.7(3) (Ar), 129.7(0) (Ar), 129.6(Ar), 129.5(Ar), 129.2-(Ar), 129.0(3) (Ar), 129.0(1) (Ar), 128.9(8) (Ar), 128.9(5) (Ar), 128.8(9) (Ar), 128.8(6) (Ar), 128.7 (Ar), 128.5(6) (Ar), 128.5(3) (Ar), 128.5(0) (Ar), 128.4(7) (Ar), 128.4(3) (Ar), 128.3(9) (Ar), 128.3(5) (Ar), 128.3-(3) (Ar), 128.3(2) (Ar), 128.2(Ar), 106.5 (C-1), 106.1 (C-1), 106.0 (C-1), 105.4 (C-1), 101.0 (C-1), 94.9 (C-1), 82.3, 82.2, 82.1(6), 82.1(1), 82,0, 81.7, 81.6, 81.5, 81.4, 81.1, 80.4, 79.1, 78.9, 78.3, 77.7, 77.6, 77.5, 66.6 (C-5), 66.3 (C-5), 63.7 (C-5 × 3), 63.5 (C-5); ESIMS *m*/*z* calcd for (M + Na) $C_{64}H_{54}O_{20}$ 1165.3104, found 1165.3100.

2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-D-arabinofuranose (8). Compound **8** was prepared as a syrup (0.486 g, 1:1 α/β mixture, 79%) from compound **36** (0.65 g, 0.336 mmol) in THF−H_2O (4:1, 35 mL) and CAN (4.61 g, 8.4 mmol) as described for **6**. About 6% of the starting material was also recovered. Data for **8**: R_f 0.22 (65:35 hexanes−EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.80 (m, 23 H, Ar), 7.62−7.18 (m, 36 H, Ar), 6.02−5.88 (m, 2 H), 5.86−5.75 (m, 1 H), 5.74−5.62 (m, 1 H), 5.60−5.49 (m, 1.5 H), 5.48−5.32 (m, 4 H), 5.20 (d, 0.5 H, J = 1.7 Hz), 5.13 (s, 0.5 H), 5.10−5.05 (m, 1 H), 4.82−4.30 (m, 11 H), 4.25−4.10 (m, 1.5 H), 4.01−3.88 (m, 1.5 H), 3.78−3.70 (m, 1.5 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.4 (C═O), 166.1 (C═O), 165.9 (C═O), 165.8 (C═O), 165.7 (C═O), 165.6 (C═O), 165.5 (C═O), 165.4 (C═O), 165.3 (C═O), 133.6 (Ar), 133.5 (Ar), 133.4(8) (Ar), 133.4(3) (Ar), 133.3 (Ar), 133.2(7) (Ar), 133.2(3) (Ar), 133.1 (Ar), 132.8(8) (Ar), 132.8(2) (Ar), 129.9 (Ar), 129.8 (Ar), 129.7(9) (Ar), 129.7(3) (Ar), 129.6(9) (Ar), 129.6(3) (Ar), 129.5 (Ar), 129.2 (Ar), 129.1(8) (Ar), 129.1(2) (Ar), 129.0 (Ar), 128.9(9) (Ar), 128.9(5) (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4(8) (Ar), 128.4(4) (Ar), 128.3(7) (Ar), 128.3(1) (Ar), 128.2 (Ar), 128.1 (Ar), 106.5 (C-1), 105.9 (C-1), 104.9 (C-1), 104.8 (C-1), 100.9 (C-1), 100.5 (C-1), 100.3 (C-1), 100.2 (C-1), 100.1 (C-1), 94.7 (C-1), 85.5, 85.2, 84.9, 84.7, 82.9, 81.7, 80.9, 80.8, 80.5, 80.3, 79.4-(5), 79.4(0), 79.2, 79.0, 78.2, 78.0, 77.9, 77.8, 77.7, 77.6, 77.5, 77.3, 76.5, 76.4, 76.3, 66.5 (C-5), 65.7 (C-5), 65.6 (C-5), 64.3 (C-5), 64.2 (C-5), 64.1 (C-5); ESIMS *m*/*z* calcd for (M + Na) $C_{102}H_{86}O_{32}$ 1845.4996, found 1845.4999.

***p*-Tolyl 2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (15)**. To a solution of alcohol **12** (0.6 g, 1.0 mmol) and trichloroacetonitrile (0.5 mL, 5 mmol) in CH_2Cl_2 (9 mL) at 0 °C was added DBU (15 μL, 0.1 mmol). The reaction mixture was stirred at 0 °C for 30 min and then warmed to room temperature over 30 min. The solvent was then removed under vacuum, and a solution of dry hexane−toluene (2:3, 10 mL) was added. After being stirred for 5 min, this solution was quickly filtered through a short column of silica gel and Na_2SO_4 (∼1:1). The resulting solution was then concentrated to yield the trichloroacetimidate derivative **13**, which was used without any further purification. Alternatively, the syrupy residue obtained after the initial solvent evaporation following the reaction could be quickly filtered through silica gel (4:1 hexanes−EtOAc). The fractions containing the trichloroacetimidate derivative were concentrated and used immediately without any further purification. The trichloroacetimidate derivative **13** in CH_2Cl_2 (6 mL) was added to a solution of alcohol **14**[33] (0.39 g, 0.84 mmol) in CH_2Cl_2 (26 mL) containing 4 Å molecular sieves (0.4 g; stirred already for about 30 min) at −30 °C. A solution of TMSOTf (72 μL, 0.4 mmol) in CH_2Cl_2 (0.72 mL) was added dropwise over a period of 5 min. The reaction mixture was then warmed to −5 °C over a period of ∼20 min and quenched by the addition of Et_3N (0.1 mL). The solution was diluted with CH_2Cl_2 (15 mL) and filtered. The filtrate was concentrated to a syrup that was purified by column chromatography (9:1 hexanes−EtOAc) to afford **15** (0.67 g, 76% over two steps) as a syrup: R_f 0.42 (4:1 hexanes−EtOAc); $[\alpha]_D$ +40.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14−7.92 (m, 8 H, Ar), 7.76−7.70 (m, 4 H, Ar), 7.63−7.53 (m, 2 H, Ar), 7.50−7.22 (m, 18 H, Ar), 7.15−7.05 (m, 2 H, Ar), 5.76−5.71 (m, 3 H, H-1, H-2, H-3), 5.65 (d, 1 H, J = 5.0 Hz, H-3′), 5.57 (d, 1 H, J = 1.3 Hz, H-2′),

5.38 (s, 1 H, H-1′), 4.74 (dd, 1 H, J = 7.5, 4.1 Hz, H-4), 4.52 (dd, 1 H, J = 9.3, 4.6 Hz, H-4′), 4.24 (dd, 1 H, J = 11.3, 4.4 Hz, H-5), 4.22−3.94 (m, 3 H, H-5, H-5′ × 2), 2.30 (s, 3 H, Ar−CH_3), 1.04 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5 (C═O × 2), 165.2-(7) (C═O), 165.2(2) (C═O), 137.8 (Ar), 135.6(7) (Ar), 135.6(5) (Ar), 133.4(8) (Ar), 133.4(2) (Ar), 133.3(Ar), 133.2(7) (Ar), 133.2(2) (Ar), 133.0(Ar), 132.6 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.6 (Ar), 129.2(8) (Ar), 129.2(2) (Ar), 128.9(Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.6 (Ar), 106.0 (C-1′), 91.5 (C-1), 83.2 (C-4′), 82.1, 82.0 (× 2), 77.5 (C-3), 77.3 (C-3′), 65.8 (C-5), 63.4 (C-5′), 26.7 (C(CH_3)$_3$), 21.1 (Ar-CH_3), 19.3 (C(CH_3)$_3$); ESIMS m/z calcd for (M + Na) $C_{61}H_{58}O_{12}SiS$ 1065.3308, found 1065.3310.

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (16). Thioglycoside **15** (2.0 g, 1.92 mmol) and alcohol **11** (0.85 g, 1.67 mmol) were dried over P_2O_5 under vacuum for 6 h and then dissolved in CH_2Cl_2 (60 mL), and the resulting solution was cooled to 0 °C. Powdered 4 Å molecular sieves (0.5 g) were added, and the suspension was stirred for 30 min at 0 °C before *N*-iodosuccinimide (0.52 g, 2.3 mmol) and silver triflate (0.1 g, 0.38 mmol) were added. The reaction mixture was stirred for 20 min, neutralized with Et_3N, diluted with CH_2Cl_2 (30 mL), and filtered through Celite. The filtrate was washed successively with a saturated aqueous $Na_2S_2O_3$ solution (75 mL × 2) and water (75 mL) before being dried (Na_2SO_4) and concentrated. The crude residue was purified by column chromatography (6:1 hexanes−EtOAc) to afford **16** (2.0 g, 84%) as a syrup: R_f 0.34 (4:1 hexanes−EtOAc); [α]$_D$ +5.4 (c 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.85 (m, 13 H, Ar), 7.75−7.65(m, 4 H, Ar), 7.60−7.20 (m, 23 H, Ar), 5.66−5.62 (m, 4 H), 5.57 (s, 1 H), 5.51 (s, 1 H), 5.40 (s, 1 H), 5.39 (s, 1 H), 5.21 (s, 1 H), 4.63 (dd, 1 H, J = 7.7, 4.5 Hz), 4.50 (dd, 1 H, J = 8.4, 4.1 Hz), 4.44 (dd, 1 H, J = 7.6, 4.6 Hz), 4.24−4.17 (m, 2 H), 4.0−3.91 (m, 4 H), 3.75 (ddd, 1 H, J = 13.3, 9.4, 6.7 Hz, octyl OCH_2), 3.50 (ddd, 1 H, J = 10.9, 9.4, 6.2 Hz, octyl OCH_2), 3.22 (dd, 2 H, J = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.42−1.22 (m, 8 H, octyl CH_2), 1.02 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.6(3) (C═O), 165.6 (C═O), 165.4(5) (C═O), 165.4 (C═O), 165.1(8) (C═O), 165.1 (C═O), 135.6(6) (Ar), 135.6 (Ar), 133.3-(6) (Ar), 133.3(4) (Ar), 133.3(1) (Ar), 133.2(3) (Ar), 133.2(1) (Ar), 133.1 (Ar), 133.0 (Ar), 129.9 (Ar), 129.8(7) (Ar), 129.8(3) (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.3(8) (Ar), 129.3(1) (Ar), 129.2(8) (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.4(9) (Ar), 128.4(6) (Ar), 128.4(2) (Ar), 128.3(9) (Ar), 128.3(3) (Ar), 128.2(9) (Ar), 128.2(4) (Ar), 128.1 (Ar), 127.6 (Ar), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 83.1, 82.1(4), 82.1(2), 81.8, 81.7, 81.5, 77.3(6), 77.3(3), 67.3, 66.0 (C-5), 65.8 (C-5), 63.4 (C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.1 (octyl CH_2), 28.8 (octyl CH_2), 26.7 (C(CH_3)$_3$), 26.6 (octyl CH_2), 26.0 (octyl CH_2), 19.2 (C(CH_3)$_3$); ESIMS m/z calcd for (M + Na) $C_{81}H_{83}N_3O_{19}Si$ 1452.5280, found 1452.5282.

8-Azidooctyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (17). Compound **17** was prepared as a syrup (1.55 g, 95%) from compound **16** (1.96 g, 1.37 mmol) and HF−pyridine (1.0 mL) in pyridine−THF (1:5, 30 mL) as described for compound **5**: R_f 0.13 (3:1 hexanes−EtOAc); [α]$_D$ +1.4 (c 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.98 (m, 8 H), 7.98−7.90 (m, 4 H), 7.61−7.32 (m, 14 H), 7.20−7.30 (m, 4 H), 5.67−5.61 (m, 4 H), 5.51 (s, 1 H), 5.44−5.39 (m, 3 H), 5.22 (s, 1 H), 4.63 (dd, 1 H, J = 7.7, 4.5 Hz), 4.47 (dd, 1 H, J = 4.1, 8.4 Hz), 4.43 (dd, 1 H, J = 7.6, 4.6 Hz), 4.23−4.16 (m, 2 H), 4.04−3.90 (m, 4 H), 3.75 (ddd, 1 H, J = 13.3, 9.4, 6.7 Hz, octyl OCH_2), 3.50 (ddd, 1 H, J = 10.9, 9.4, 6.2 Hz, octyl OCH_2), 3.21 (dd, 2 H, J = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.50−1.20 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C═O), 165.6(7) (C═O), 165.6(6) (C═O), 165.4 (C═O), 165.1 (C═O), 165.0 (C═O), 133.4(9) (Ar), 133.4(1) (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 129.8(7) (Ar), 129.8(5) (Ar), 129.8 (Ar), 129.7 (Ar), 129.3 (Ar), 129.1(8) (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.4(9) (Ar), 128.4(1) (Ar), 128.2(9) (Ar), 128.2(5) (Ar), 105.8-(4) (C-1), 105.8(0) (C-1), 105.5 (C-1), 83.6, 82.0, 81.8, 81.7, 81.6(9), 81.6, 77.7, 77.3(7), 77.3(3), 67.3 (octyl OCH_2), 66.1 (C-5), 66.0 (C-5), 62.3 (C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.0 (octyl CH_2), 28.8 (octyl CH_2), 26.6 (octyl CH_2), 26.0 (octyl CH_2); ESIMS m/z calcd for (M + Na) $C_{65}H_{65}N_3O_{19}$ 1214.4103, found 1214.4104.

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (18). Compound **18** was prepared as a syrup (2.32 g, 86%) from thioglycoside **15** (1.53 g, 1.47 mmol), alcohol **17** (1.52 g, 1.28 mmol), 4 Å molecular sieves (0.5 g), *N*-iodosuccinimide (0.4 g, 1.76 mmol), and silver triflate (0.075 g, 0.29 mmol) in CH_2Cl_2 (60 mL) as described for **16**: R_f 0.22 (3:1 hexanes−EtOAc); [α]$_D$ +11.6 (c 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.85 (m, 19 H, Ar), 7.75−7.63 (m, 4 H, Ar), 7.60−7.20 (m, 37 H, Ar), 5.68−5.60 (m, 9 H), 5.56 (s, 1 H), 5.51(s, 1 H), 5.41−5.39 (m, 3 H), 5.37 (s, 1 H), 5.21(s, 1 H), 4.64−4.57 (m, 3 H), 4.49 (dd, 1 H, J = 9.2, 4.5 Hz), 4.43 (dd, 1 H, J = 7.1, 4.2 Hz), 4.23−4.14 (m, 4 H), 4.00−3.88 (m, 5 H), 3.75 (ddd, 1 H, J = 13.5, 9.4, 6.7 Hz, octyl OCH_2), 3.50 (ddd, 1 H, J = 13.1, 9.4, 6.2 Hz, octyl OCH_2), 3.22 (dd, 2 H, J = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.50−1.23 (m, 8 H, octyl CH_2), 1.01(s, 9 H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.6 (C═O), 165.5(9) (C═O), 165.5(7) (C═O), 165.5(5) (C═O), 165.4(5) (C═O), 165.4(2) (C═O), 165.1(5) (C═O), 165.1(3) (C═O), 165.1 (C═O), 165.0 (C═O), 135.6(5) (Ar), 135.6(3) (Ar), 133.3(6) (Ar), 133.3(2) (Ar), 133.2(9) (Ar), 133.2(7) (Ar), 133.2(2) (Ar), 133.2-(1) (Ar), 133.1 (Ar), 133.0(6) (Ar), 133.0(0) (Ar), 129.9 (Ar), 129.8-(8) (Ar), 129.8(2) (Ar), 129.7(Ar), 129.6 (Ar), 129.3(6) (Ar), 129.3(1) (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.4(7) (Ar), 128.4 (Ar), 128.3(8) (Ar), 128.3(3) (Ar), 128.2 (Ar), 128.1 (Ar), 127.6 (Ar), 105.9 (C-1 × 2), 105.8(9) (C-1), 105.8(3) (C-1), 105.5 (C-1), 83.1, 82.1(1), 82.1(0), 81.8, 81.7, 81.5(6), 81.5(1), 77.3, 77.2, 67.3 (octyl OCH_2), 66.0 (C-5), 65.8(6) (C-5), 65.8(3) (C-5 × 2), 63.4 (C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.1 (octyl CH_2), 28.8 (octyl CH_2), 26.7 (C(CH_3)$_3$), 26.6 (octyl CH_2), 26.0 (octyl CH_2), 19.2 (C(CH_3)$_3$); ESIMS m/z calcd for (M + Na) $C_{119}H_{115}N_3O_{31}Si$ 2133.7, found 2133.7.

***p*-Methoxyphenyl 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*-benzoyl-α-D-arabinofuranoside (25)**. Compound **25** was prepared as a syrup (0.7 g, 74%) from thioglycoside **9** (1.34 g, 1.99 mmol), acceptor alcohol **24** (0.23 g, 0.62 mmol), 4 Å molecular sieves (0.5 g), *N*-iodosuccinimide (0.45 g, 1.99 mmol), and silver triflate (0.025 g, 0.09 mmol) in CH_2Cl_2 (30 mL) as described for **16**. In addition about 8% of a monoglycosylated product was also isolated. Data for **25**: R_f 0.24 (4:1 hexanes−EtOAc); [α]$_D$ +26.5 (c 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12−7.90 (m, 10 H, Ar), 7.72−7.61 (m, 8 H, Ar), 7.60−7.20 (m, 27 H, Ar), 7.05 (d, 2 H, J = 8.9 Hz, Ar), 6.78 (d, 2 H, J = 8.9 Hz, Ar), 5.77 (s, 1 H, H-1), 5.66 (s, 1 H), 5.65−5.60 (m, 3 H), 5.60 (s, 1 H, H-1), 5.50 (s, 1 H), 5.33 (s, 1 H, H-1), 4.61−4.53 (m, 2 H), 4.39 (dd, 2 H, J = 9.2, 4.6 Hz), 4.10 (dd, 1 H, J = 11.4, 4.3 Hz), 3.98−3.87 (m, 5 H), 3.73 (s, 3 H, OCH_3), 1.01 (s, 9 H, C(CH_3)$_3$), 0.98 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4(7) (C═O × 2), 165.4(1) (C═O), 165.1(7) (C═O), 165.1(5) (C═O), 155.0 (Ar), 150.3 (Ar), 135.6-(6) (Ar), 135.6(2) (Ar), 135.5 (Ar), 133.3 (Ar), 133.2(9) (Ar), 133.2(7) (Ar), 133.2(4) (Ar), 133.1(8) (Ar), 133.1(4) (Ar), 133.1(1) (Ar), 133.0-(5) (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7(8) (Ar), 129.7(6) (Ar), 129.6 (Ar), 129.4 (Ar), 129.3 (Ar), 129.2(7) (Ar), 129.2 (Ar), 129.1 (Ar), 128.4 (Ar), 128.3(4) (Ar), 128.3 (Ar), 127.6 (Ar), 118.5 (Ar), 114.5 (Ar), 106.2 (C-1), 105.6 (C-1), 105.3 (C-1), 84.0, 83.4, 82.8, 82.7, 82.0, 81.9, 80.7, 77.2, 77.1, 65.9 (C-5), 63.5 (C-5), 63.3

(C-5), 55.6 (OCH_3), 26.7(6) ($C(CH_3)_3$), 26.7(4) ($C(CH_3)_3$), 19.2(8) ($C(CH_3)_3$), 19.2(1) ($C(CH_3)_3$); ESIMS *m*/*z* calcd for (M + Na) $C_{89}H_{88}O_{19}Si_2$ 1539.5349, found 1539.5356.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (26)**. Compound **26** was prepared as a syrup (1.43 g, 89%) from compound **25** (2.35 g, 1.55 mmol) and HF−pyridine (1.0 mL) in THF−pyridine (5:1, 30 mL) as described for **5**: R_f 0.11 (3:2 hexanes−EtOAc); $[\alpha]_D$ +15.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.90 (m, 10 H, Ar), 7.65−7.33 (m, 13 H, Ar), 7.18−7.24 (m, 2 H, Ar), 7.05 (d, 2 H, J = 8.9 Hz, Ar), 6.81 (d, 2 H, J = 8.9 Hz, Ar), 5.77 (s, 1 H, H-1), 5.65 (s, 1 H), 5.62 (d, 2 H, J = 4.3 Hz), 5.35−5.30 (m, 3 H), 5.28 (d, 1 H, J = 4.6 Hz), 4.65 (d, 1 H, J = 5.7 Hz), 4.52−4.48 (m, 1 H), 4.40 (dd, 1 H, J = 8.3, 4.0 Hz), 4.34 (dd, 1 H, J = 8.4, 4.0 Hz), 4.07−4.0 (m, 2 H), 3.98−3.84 (m, 4 H), 3.76 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.2 (C═O), 166.0 (C═O), 165.5 (C═O), 165.1 (C═O), 164.9 (C═O), 155.1 (Ar), 150.2 (Ar), 133.6 (Ar), 133.5(7) (Ar), 133.5 (Ar), 129.9 (Ar), 129.8(5) (Ar), 129.8(3) (Ar), 129.8(1) (Ar), 129.6 (Ar), 129.1 (Ar), 129.0(7) (Ar), 129.0(3) (Ar), 128.8 (Ar), 128.5(8) (Ar), 128.5(5) (Ar), 128.5(4) (Ar), 128.5 (Ar), 128.3 (Ar), 118.3 (Ar), 114.6 (Ar), 105.3(6) (C-1), 105.3-(1) (C-1), 105.1 (C-1), 84.7, 84.1, 82.8, 82.0, 81.4, 81.1, 80.1, 78.2, 77.6, 64.9 (C-5), 62.7 (C-5 × 2), 55.6 (OCH_3); ESIMS *m*/*z* calcd for (M + Na) $C_{57}H_{52}O_{19}$ 1063.2990, found 1063.2995.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (27)**. Compound **27** was prepared as a syrup (1.92 g, 94%) from thioglycoside **15** (1.77 g, 1.7 mmol), alcohol **26** (0.74 g, 0.71 mmol), 4 Å molecular sieves (0.65 g), *N*-iodosuccinimide (0.38 g, 1.7 mmol), and silver triflate (0.04 g, 0.15 mmol) in CH_2Cl_2 (55 mL) as described for **16**. The compound contained 5% of an inseparable impurity and was used directly in the next step. Data for **27**: R_f 0.33 (65:35 hexanes−EtOAc); $[\alpha]_D$ +17.8 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.10−7.84 (m, 24 H, Ar), 7.73−7.66 (m, 8 H, Ar), 7.59−7.20 (m, 53 H, Ar), 7.01 (d, 2 H, J = 8.4 Hz, Ar), 6.75 (d, 2 H, J = 8.4 Hz, Ar), 5.76 (s, 1 H), 5.73 (d, 1 H, J = 4.5 Hz), 5.67 (d, 2 H, J = 5.8 Hz), 5.65 (d, 2 H, J = 4.7 Hz), 5.63−5.60 (m, 4 H), 5.58−5.54 (m, 4 H), 5.38−5.35 (m, 3 H), 5.33 (s, 1 H), 5.30 (s, 1 H), 4.63−4.58 (m, 3 H), 4.56−4.52 (m, 2 H), 4.50−4.44 (m, 3 H), 4.23−4.14 (m, 4 H), 4.06 (dd, 2 H, J = 11.5, 4.5 Hz), 4.02−3.94 (m, 4 H), 3.92−3.84 (m, 4 H), 3.82 (dd, 1 H, J = 11.2, 2.7 Hz), 3.73 (s, 3 H, OCH_3), 1.01 (s, 18 H, $C(CH_3)_3$ × 2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165. 5(7) (C═O), 165.5(6) (C═O × 3), 165.4(8) (C═O), 165.4(5) (C═O × 2), 165.1(6) (C═O), 165.1(5) (C═O), 165.1(4) (C═O), 165.1(1) (C═O), 165.0(5) (C═O), 165.0(3) (C═O), 155.0 (Ar), 150.3 (Ar), 135.6(6) (Ar), 135.6(4) (Ar), 133.4 (Ar), 133.3(4) (Ar), 133.3(0) (Ar), 133.2(8) (Ar), 133.2(6) (Ar), 133.2(2) (Ar), 133.1(4) (Ar), 133.1(1) (Ar), 133.0 (Ar), 132.9 (Ar), 130.0 (Ar), 129.9(8) (Ar), 129.9(4) (Ar), 129.9 (Ar), 129.8(3) (Ar), 129.8(2) (Ar), 129.7(6) (Ar), 129.7(3) (Ar), 129.6 (Ar), 129.3 (Ar), 129.2 (Ar), 129.1(6) (Ar), 129.1(3) (Ar), 129.0(8) (Ar), 129.0(3) (Ar), 128.4(8) (Ar), 128.4(5) (Ar), 128.4(2) (Ar), 128.3(6) (Ar), 128.3(4) (Ar), 128.2(4) (Ar), 128.2(2) (Ar), 128.1 (Ar), 127.6 (Ar), 118.4 (Ar), 114.5 (Ar), 106.1 (C-1), 106.0 (C-1), 105.9 (C-1), 105.8 (C-1 × 2), 105.4 (C-1), 105.3 (C-1), 83.2, 83.1(9), 83.1(7), 83.0, 82.8, 82.6, 82.5, 82.1(7), 82.1(5), 82.1(2), 82.0, 81.4(8), 81.4(5), 80.5, 77.3, 77.2(4), 77.2(2), 76.8, 65.8 (C-5), 65.7(9) (C-5), 65.7(4) (C-5), 65.6(7) (C-5), 65.6(2) (C-5), 63.4 (C-5), 55.6 (OCH_3), 26.7 ($C(CH_3)_3$ × 2), 19.2 ($C(CH_3)_3$ × 2); ESIMS *m*/*z* calcd for (M + Na) $C_{165}H_{152}O_{43}Si_2$ 2901.9, found 2902.0.

***p*-Methoxyphenyl 2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (28)**. Compound **28** was prepared as a syrup (1.12 g, 92%) from thioglycoside **19** (1.77 g, 3.11 mmol), acceptor alcohol **24** (0.35 g, 0.97 mmol), 4 Å molecular sieves (0.5 g), *N*-iodosuccinimide (0.7 g, 3.11 mmol), and silver triflate (0.05 g, 0.19 mmol) in CH_2Cl_2 (40 mL) as described for **16**: R_f 0.28 (7:3 hexanes−EtOAc); $[\alpha]_D$ +29.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.90 (m, 14 H, Ar), 7.63−7.32 (m, 14 H, Ar), 7.29−7.20 (m, 7 H, Ar), 7.06−7.0 (m, 2 H, Ar), 6.80−6.74 (m, 2 H, Ar), 5.78 (s, 1 H, H-1), 5.68 (s, 2 H), 5.62−5.58 (m, 2 H), 5.56 (s, 1 H), 5.53 (d, 1 H, J = 4.4 Hz), 5.39 (s, 1 H, H-1), 4.77 (dd, 1 H, J = 11.4, 3.2 Hz), 4.72 (dd, 1 H, J = 11.4, 3.7 Hz), 4.70−4.52 (m, 6 H), 4.12 (dd, 1 H, J = 11.5, 4.2 Hz, H-5), 3.93 (dd, 1 H, J = 11.5, 2.6 Hz, H-5), 3.74 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (C═O), 166.0 (C═O), 165.6 (C═O), 165.5(8) (C═O), 165.5(3) (C═O), 165.1 (C═O), 155.1 (Ar), 150.2 (Ar), 133.5(2) (Ar), 133.5(0) (Ar), 133.4 (Ar), 133.3 (Ar), 132.9 (Ar), 129.9(7) (Ar), 129.9 (Ar), 129.8 (Ar), 129.7(8) (Ar), 129.7-(6) (Ar), 129.7(2) (Ar), 129.6 (Ar), 129.5 (Ar), 129.0(6) (Ar), 129.0-(5) (Ar), 129.0(2) (Ar), 128.9 (Ar), 128.5(2) (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 118.4 (Ar), 114.5 (Ar), 106.1 (C-1), 105.7 (C-1), 105.2 (C-1), 82.9, 82.5, 81.9, 81.7, 81.6, 80.8, 77.7(3), 77.7(2), 65.7 (C-5), 63.7 (C-5), 63.6 (C-5), 55.6 (OCH_3); ESIMS *m*/*z* calcd for (M + Na) $C_{71}H_{60}O_{21}$ 1271.3522, found 1271.3524.

***p*-Methoxyphenyl 3,5-*O*-(Di-*tert*-butylsilanediyl)-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→3)-[3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (31)**. Compound **31** was prepared as a syrup (2.44 g, 76%) from thioglycoside **30** (4.61 g, 9.31 mmol), acceptor alcohol **24** (1.05 g, 2.91 mmol), 4 Å molecular sieves (1.5 g), *N*-iodosuccinimide (2.09 g, 9.3 mmol), and silver triflate (168 mg, 0.65 mmol) in CH_2Cl_2 (135 mL) as described for **16**: R_f 0.31 (7:3 hexanes−EtOAc); $[\alpha]_D$ +68.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08−8.04 (m, 2 H, Ar), 7.60−7.55 (m, 1 H, Ar), 7.48−7.43 (m, 2 H, Ar), 7.07−7.04 (m, 2 H, Ar), 6.84−6.80 (m, 2 H, Ar), 5.67 (s, 1 H), 5.54 (d, 1 H, J = 2.2 Hz), 5.22−5.18 (m, 2 H), 5.09 (dd, 1 H, J = 6.7, 2.1 Hz), 4.97 (d, 1 H, J = 2.0 Hz), 4.46−4.42 (m, 1 H), 4.35−4.28 (m, 3 H), 4.11 (dd, 1 H, J = 9.6, 7.0 Hz), 4.07 (dd, 1 H, J = 9.6, 6.7 Hz), 3.98 (ddd, 2 H, J = 10.3, 10.1, 5.5 Hz), 3.94−3.87 (m, 3 H), 3.80 (dd, 1 H, J = 11.4, 3.5 Hz), 3.76 (s, 3 H, OCH_3), 2.79−2.74 (m, 2 H, levulinoyl CH_2), 2.73−2.54 (m, 6 H, levulinoyl CH_2 × 3), 2.14 (s, 3 H, levulinoyl $COCH_3$), 2.11 (s, 3 H, levulinoyl $COCH_3$), 1.05 (s, 9 H, $C(CH_3)_3$), 1.03 (s, 9 H, $C(CH_3)_3$), 0.99 (s, 9 H, $C(CH_3)_3$), 0.90 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C═O), 206.0 (C═O), 171.8 (C═O), 171.6 (C═O), 165.4 (C═O), 154.9 (Ar), 150.4 (Ar), 133.3 (Ar), 129.8 (Ar), 129.4 (Ar), 128.5 (Ar), 118.4 (Ar), 114.4 (Ar), 106.2 (C-1), 106.0 (C-1), 105.2 (C-1), 83.0, 82.8, 82.6, 81.7, 81.4, 80.4, 79.9, 73.7, 73.4, 67.4 (C-5), 67.3 (C-5), 66.0 (C-5), 55.6 (OCH_3), 38.0 (levulinoyl CH_2), 37.8 (levulinoyl CH_2), 29.7 (levulinoyl CH_3), 29.6 (levulinoyl CH_3), 27.9 (levulinoyl CH_2), 27.8 (levulinoyl CH_2), 27.3-(9) ($C(CH_3)_3$), 27.3(7) ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$), 22.6-(3) ($C(CH_3)_3$), 22.6(0) ($C(CH_3)_3$), 20.0(8) ($C(CH_3)_3$), 20.0(0) ($C(CH_3)_3$); ESIMS *m*/*z* calcd for (M + Na) $C_{55}H_{80}O_{19}Si_2$ 1123.4725, found 1123.4724.

***p*-Methoxyphenyl 3,5-*O*-(Di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-[3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (32)**. A solution of compound **31** (3.46 g, 3.14 mmol) and hydrazine monohydrate−acetic acid (1:2, v/v; 42 mL) in THF (150 mL) and CH_3OH (15 mL) was stirred for 1.5 h. The solvent was removed, and the resulting oil was diluted with EtOAc (200 mL). The solution was washed with a saturated aqueous $NaHCO_3$ solution (150 mL × 2) and brine (100 mL), dried (Na_2SO_4), and concentrated. The crude residue was purified by column chromatography (4:1 hexanes−EtOAc) to afford **32** (2.71 g, 95%) as a white solid: R_f 0.57 (3:1 hexanes−EtOAc); $[\alpha]_D$ +72.8 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.06−8.04 (m, 2 H, Ar), 7.62−7.58 (m, 1 H, Ar), 7.48−7.44 (m, 2 H, Ar), 7.06−7.03 (m, 2 H, Ar), 6.85−6.82 (m, 2 H, Ar), 5.76 (s, 1 H, H-1), 5.53 (d, 1 H, J = 2.0 Hz, H-2), 5.18 (d, 1 H, J = 3.3 Hz, H-1′), 4.98 (d, 1 H, J = 3.3 Hz, H-1″),

4.46−4.43 (m, 1 H, H-4), 4.31−4.26 (m, 4 H, H-3, H-2′, H-5′ × 2), 4.12−4.10 (m, 1 H, H-2″), 4.02−3.89 (m, 7 H, H-5, H-3′, H-3″, H-5″ × 2, H-4′, H-4″), 3.78 (dd, 1 H, J = 11.4, 3.2 Hz, H-5), 3.77 (s, 3 H, OCH_3), 2.78 (d, 1 H, J = 4.1 Hz, OH), 2.49 (d, 1 H, J = 4.2 Hz, OH), 1.07 (s, 9 H, $C(CH_3)_3$), 1.05 (s, 9 H, $C(CH_3)_3$), 1.01 (s, 9 H, $C(CH_3)_3$), 0.93 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 165.6 (C═O), 155.1 (Ar), 150.1 (Ar), 133.5 (Ar), 129.8 (Ar × 2), 129.3 (Ar), 128.5 (Ar × 2), 118.4 (Ar × 2), 114.5 (Ar × 2), 108.3 (C-1′), 108.2 (C-1″), 105.1 (C-1), 83.6 (C-2), 82.5 (C-3), 82.2 (C-4), 81.4 (C-2′, C-2″), 81.3(9) (C-4′), 81.3(5) (C-4″), 73.9 (C-3′), 73.7 (C-3″), 67.4(6) (C-5″), 67.4 (C-5′), 66.5 (C-5), 55.6 (OCH_3), 27.4(3) ($C(CH_3)_3$), 27.4-(1) ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 22.6(4) ($C(CH_3)_3$), 22.6 ($C(CH_3)_3$), 20.1 ($C(CH_3)_3$), 20.0 ($C(CH_3)_3$); ESIMS m/z calcd for (M + Na) $C_{45}H_{68}O_{15}Si_2$ 927.3989, found 927.3992.

***p*-Methoxyphenyl 2-*O*-Benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-[2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (34)**. To a mixture of **32** (0.24 g, 0.265 mmol), **33**[41] (0.39 g, 0.8 mmol), and 4 Å molecular sieves (0.4 g) in CH_2Cl_2 (40 mL) was added NIS (0.18 g, 0.8 mmol) followed by AgOTf (20 mg, 0.08 mmol) at −30 °C. After being stirred for 30 min, the solution turned dark red, and Et_3N was added. The mixture was then diluted with CH_2Cl_2 (20 mL) and filtered through Celite. The filtrate was washed with a saturated aqueous $Na_2S_2O_3$ solution (40 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by column chromatography (10:1 hexanes−EtOAc) to afford **34** (0.3 g, 70%) as a white semisolid: R_f 0.29 (8:1 hexanes−EtOAc); $[\alpha]_D$ −12.1 (c 0.7, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.01−7.99 (m, 2 H, Ar), 7.58−7.55 (m, 1 H, Ar), 7.45−7.21 (m, 12 H, Ar), 7.02−6.98 (m, 2 H, Ar), 6.81−6.77 (m, 2 H, Ar), 5.71 (s, 1 H, H-1), 5.49 (d, 1 H, J = 1.5 Hz, H-2), 5.32 (d, 1 H, J = 3.1 Hz, H-1′), 5.20 (d, 1 H, J = 4.8 Hz, H-1‴), 5.03 (d, 1 H, J = 2.7 Hz, H-1″), 4.97 (d, 1 H, J = 4.8 Hz, H-1⁗), 4.85 (d, 1 H, J = 12.5 Hz, PhCH_2), 4.81 (d, 1 H, J = 12.5 Hz, PhCH_2), 4.73 (d, 1 H, J = 12.3 Hz, PhCH_2), 4.70 (d, 1 H, J = 12.3 Hz, PhCH_2), 4.50 (dd, 1 H, J = 9.2, 9.2 Hz), 4.45−4.41 (m, 2 H), 4.32−4.24 (m, 5 H), 4.19 (dd, 1 H, J = 7.6, 3.1 Hz, H-2′), 4.12−4.03 (m, 3 H), 4.00−3.86 (m, 8 H), 3.79−3.70 (m, 3 H), 3.75 (s, 3 H, OCH_3), 3.63−3.58 (m, 1 H), 1.09 (s, 9 H, $C(CH_3)_3$), 1.07 (s, 9 H, $C(CH_3)_3$), 1.05 (s, 9 H, $C(CH_3)_3$), 1.03 (s, 9 H, $C(CH_3)_3$), 1.01 (s, 9 H, $C(CH_3)_3$), 1.00 (s, 9 H, $C(CH_3)_3$), 0.99 (s, 9 H, $C(CH_3)_3$), 0.92 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3 (C═O), 155.0 (Ar), 150.2 (Ar), 138.0 (Ar), 137.7 (Ar), 133.4 (Ar), 129.8 (Ar × 2), 129.1 (Ar), 128.4 (Ar × 2), 128.3 (Ar × 2), 128.2 (Ar × 2), 128.1 (Ar × 2), 127.9 (Ar), 127.7(4) (Ar), 127.7(1) (Ar), 127.5 (Ar), 118.1 (Ar × 2), 114.5 (Ar × 2), 107.2 (C-1′), 106.5 (C-1″), 105.0 (C-1), 99.6 (C-1⁗), 99.4 (C-1‴), 86.4, 85.8, 83.3, 82.4, 81.5, 80.5, 80.4, 80.1, 79.8, 78.1, 78.0, 74.3, 74.1(9), 74.1-(7), 73.9, 71.8 (PhCH_2), 71.6 (PhCH_2), 68.8, 68.7, 67.5, 67.4, 66.4, 55.6 (OCH_3), 27.8 ($C(CH_3)_3$), 27.5(7) ($C(CH_3)_3$), 27.5(6) ($C(CH_3)_3$), 27.4(3) ($C(CH_3)_3$), 27.4(1) ($C(CH_3)_3$), 27.2 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 22.6 ($C(CH_3)_3$ × 2), 22.5(9) ($C(CH_3)_3$), 22.5(8) ($C(CH_3)_3$), 20.1(3) ($C(CH_3)_3$), 20.1(1) ($C(CH_3)_3$), 20.0(7) ($C(CH_3)_3$), 20.0(1) ($C(CH_3)_3$); ESIMS m/z calcd for (M + Na) $C_{85}H_{128}O_{23}Si_4$ 1651.7827, found 1651.7827.

***p*-Methoxyphenyl 3,5-*O*-(Di-*tert*-butylsilanediyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-[3,5-*O*-(di-*tert*-butylsilanediyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (35)**. To a solution of compound **34** (0.24 g, 0.15 mmol) in EtOAc (10 mL) was added 10% Pd/C (70 mg), and the reaction mixture was stirred vigorously under hydrogen (1 atm) for 7 h. The reaction mixture was diluted with EtOAc (5 mL) and filtered to remove the catalyst. The filtrate was concentrated to give a syrup that was purified by column chromatography (9:1 hexanes−EtOAc) to afford **35** (0.18 g, 84%) as a syrup: R_f 0.43 (4:1 hexanes−EtOAc); $[\alpha]_D$ −9.7 (c 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−8.06 (m, 2 H, Ar), 7.62−7.56 (m, 1 H, Ar), 7.48−7.42 (m, 2 H, Ar), 7.05−7.00 (m, 2 H, Ar), 6.86−6.82 (m, 2 H, Ar), 5.78 (s, 1 H, H-1), 5.52 (d, 1 H, J = 2.4 Hz), 5.25 (d, 1 H, J = 4.7 Hz, H-1‴), 5.22 (d, 1 H, J = 3.2 Hz, H-1′), 5.05 (d, 1 H, J = 5.0 Hz, H-1⁗), 5.01 (d, 1 H, J = 2.8 Hz, H-1″), 4.39 (ddd, 1 H, J = 6.5, 3.9, 2.8 Hz), 4.32 (dd, 1 H, J = 9.1, 5.1 Hz), 4.30−4.14 (m, 7 H), 4.09−3.84 (m, 12 H), 3.77 (s, 3 H, OCH_3), 3.78−3.72 (m, 2 H), 3.64 (ddd, 1 H, J = 10.5, 8.9, 5.0 Hz), 3.24 (d, 1 H, J = 9.6 Hz, OH), 2.49 (d, 1 H, J = 9.7 Hz, OH), 1.09 (s, 9 H, $C(CH_3)_3$), 1.06 (s, 9 H, $C(CH_3)_3$), 1.04 (s, 9 H, $C(CH_3)_3$), 1.02 (s, 9 H, $C(CH_3)_3$), 1.01 (s, 9 H, $C(CH_3)_3$), 0.99 (s, 18 H, $C(CH_3)_3$), 0.89 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9 (C═O), 155.1 (Ar), 150.1 (Ar), 133.7(Ar), 129.9 (Ar), 129.0 (Ar), 128.5 (Ar), 118.1 (Ar), 114.6 (Ar), 107.3 (C-1′), 106.9 (C-1″), 104.8 (C-1), 100.5 (C-1‴), 99.8 (C-1⁗), 87.5, 87.2, 84.3, 83.3, 81.6, 80.3, 80.0, 79.7, 79.7, 75.7, 75.5, 74.4, 74.0, 73.9(8), 73.9(2), 68.6 (C-5), 68.4 (C-5), 67.4 (C-5 × 2), 65.8 (C-5), 55.6 (OCH_3), 27.6 ($C(CH_3)_3$), 27.5 ($C(CH_3)_3$), 27.3(4) ($C(CH_3)_3$), 27.3(1) ($C(CH_3)_3$), 27.1-(9) ($C(CH_3)_3$), 27.1(6) ($C(CH_3)_3$), 27.1(1) ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$), 22.6(9) ($C(CH_3)_3$), 22.6(8) ($C(CH_3)_3$), 22.6(5) ($C(CH_3)_3$), 22.6(4) ($C(CH_3)_3$), 20.1(5) ($C(CH_3)_3$), 20.1(1) ($C(CH_3)_3$), 20.0 ($C(CH_3)_3$), 19.9 ($C(CH_3)_3$); ESIMS m/z calcd for (M + Na) $C_{71}H_{116}O_{23}Si_4$ 1471.6880, found 1471.6882.

***p*-Methoxyphenyl 2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (36)**. To a solution of compound **35** (0.19 g, 0.13 mmol) in THF−pyridine (2:1; 12 mL) at 0 °C was added HF−pyridine (0.4 mL), and the resulting mixture was stirred for 20 h. The reaction mixture was diluted with a solution of DMF−pyridine−EtOAc (15:5:5, 25 mL), and solid $NaHCO_3$ was added in portions under vigorous stirring until the solution became neutral (stirred for 1 h). The reaction mixture was filtered, and the solids were washed with DMF−pyridine−EtOAc (15:5:5, 15 mL). The combined organic phase was concentrated to give a syrup that was quickly filtered through a short silica gel column. The fractions containing the pentasaccharide (R_f 0.23, 3:1 CH_2Cl_2−CH_3OH) were concentrated to give a syrup that was dissolved in pyridine (15 mL), followed by the addition of benzoyl chloride (0.2 mL, 1.7 mmol) at 0 °C. The resulting reaction mixture was stirred for 12 h and diluted with CH_2Cl_2 (30 mL). Chilled water (20 mL) was then added, and after the reaction mixture was stirred for 15 min, the separated organic layer was washed successively with a saturated aqueous $NaHCO_3$ solution (20 mL × 2) and water (20 mL), dried (Na_2SO_4), and concentrated to give a syrup that was purified by column chromatography (7:3 hexanes−EtOAc) to afford **36** (0.18 g, 70% over two steps) as a syrup: R_f 0.24 (65:35 hexanes−EtOAc); $[\alpha]_D$ −30.5 (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12−7.80 (m, 22 H, Ar), 7.61−7.56 (m, 2 H, Ar), 7.50−7.13 (m, 31 H, Ar), 7.04−6.98 (m, 2 H, Ar), 6.80−6.75 (m, 2 H, Ar), 5.95 (dd, 2 H, J = 11.7, 5.3 Hz), 5.84 (d, 1 H, J = 4.8 Hz, H-1‴), 5.74 (s, 1 H, H-1), 5.71 (d, 1 H, J = 4.8 Hz, H-1⁗), 5.57 (dd, 1 H, J = 6.4, 4.8 Hz), 5.47−5.42 (m, 3 H, H-1″), 5.37−5.33 (m, 2 H), 5.11 (s, 1 H, H-1′), 4.82 (dd, 1 H, J = 11.7, 4.6 Hz), 4.79−4.70 (m, 2 H), 4.69−4.62 (m, 2 H), 4.55 (ddd, 1 H, J = 7.5, 6.4, 4.8 Hz), 4.52 (d, 1 H, J = 1.6 Hz), 4.50−4.32 (m, 7 H), 4.18 (ddd, 2 H, J = 11.3, 6.7, 4.7 Hz), 3.97 (dd, 1 H, J = 11.9, 4.0 Hz), 3.77 (dd, 1 H, J = 11.8, 2.3 Hz), 3.74 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C═O), 165.9(7) (C═O), 165.9(2) (C═O), 165.8(8) (C═O), 165.8(4) (C═O), 165.7(4) (C═O), 165.7(3) (C═O), 165.6 (C═O), 165.3 (C═O × 3), 155.0 (Ar), 150.3 (Ar), 133.5 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2(9) (Ar), 133.2(2) (Ar), 133.1 (Ar), 132.8(6) (Ar), 132.8(3) (Ar), 132.8(1) (Ar), 129.8(9) (Ar), 129.8(7) (Ar), 129.8(5) (Ar), 129.8(1) (Ar), 129.7(8) (Ar), 129.7(3) (Ar), 129.7(1) (Ar), 129.6-(9) (Ar), 129.6(6) (Ar), 129.6(2) (Ar), 129.2 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.7 (Ar), 128.4(9) (Ar), 128.4(7) (Ar), 128.4(5) (Ar), 128.4(1) (Ar), 128.3 (Ar), 128.1(9) (Ar), 128.1(7) (Ar), 118.3

(Ar), 114.5 (Ar), 106.3 (C-1′), 105.1 (C-1), 104.9 (C-1″), 100.2(9) (C-1‴), 100.2(2) (C-1⁗), 85.0, 84.8, 83.4, 82.5, 80.9, 80.5, 80.4, 79.5, 79.1, 78.0, 77.5, 77.4, 76.6, 76.4, 65.8 (C-5), 65.7 (C-5), 65.5 (C-5), 64.3 (C-5), 64.2 (C-5), 55.6 (OCH_3); ESIMS *m*/*z* calcd for (M + Na) $C_{109}H_{92}O_{33}$ 1951.5423, found 1951.5418.

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (37). The trichloroacetimidate derivative of heptasaccharide lactol **6** (1.355 g, 0.49 mmol) was prepared using DBU (15 μL, 0.08 mmol) and trichloroacetonitrile (0.4 mL, 3.9 mmol) in CH_2Cl_2 (20 mL) as described for **15**. Following purification, the trichloroacetimidate was dissolved in CH_2Cl_2 (20 mL) and was added to a solution of linear pentasaccharide **5** (0.91 g, 0.49 mmol) in CH_2Cl_2 (30 mL) containing 4 Å molecular sieves (0.75 g; stirred already for about 30 min) at −30 °C. A solution of TMSOTf (35 μL, 0.19 mmol) in CH_2Cl_2 (0.35 mL) was added dropwise over a period of 5 min. The reaction mixture was then warmed to −5 °C over a period of ∼20 min and quenched by the addition of Et_3N (30 μL). The solution was diluted with CH_2Cl_2 (15 mL) and filtered. The filtrate was concentrated to a syrup that was purified by column chromatography (2:1 hexanes−EtOAc) to afford **37** (1.73 g, 77% over two steps) as a syrup: R_f 0.23 (65:35 hexanes−EtOAc); $[\alpha]_D$ +19.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.80 (m, 45 H, Ar), 7.72−7.66 (m, 8 H, Ar), 7.60−7.17 (m, 82 H, Ar), 5.68−5.49 (m, 25 H), 5.42−5.28 (m, 9 H), 5.22 (d, 2 H, J = 8.3 Hz), 4.63−4.36 (m, 13 H), 4.23−4.09 (m, 9 H), 4.04−3.73 (m, 15 H), 3.50 (ddd, 1 H, J = 12.4, 9.6, 6.3 Hz, octyl OCH_2), 3.22 (dd, 2 H, J = 6.8, 6.8 Hz, octyl CH_2N_3), 1.64−1.45 (m, 4 H, octyl CH_2), 1.45−1.22 (m, 8 H, octyl CH_2), 1.0 (s, 18 H, $C(CH_3)_3 \times 2$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.6 (C═O), 165.5-(9) (C═O), 165.5(3) (C═O), 165.5(1) (C═O), 165.5 (C═O), 165.4(5) (C═O), 165.4(3) (C═O), 165.2(7) (C═O), 165.2(3) (C═O), 165.1(3) (C═O), 165.1 (C═O), 165.0 (C═O), 164.9 (C═O), 164.8 (C═O), 135.6(4) (Ar), 135.6(2) (Ar), 133.3(7) (Ar), 133.3(6) (Ar), 133.3(4) (Ar), 133.3(1) (Ar), 133.2(8) (Ar), 133.2(4) (Ar), 133.2(2) (Ar), 133.1-(9) (Ar), 133.1(3) (Ar), 133.0(4) (Ar), 133.0(2) (Ar), 132.9(7) (Ar), 132.9(5) (Ar), 129.9 (Ar), 129.8(7) (Ar), 129.8(5) (Ar), 129.8 (Ar), 129.7(8) (Ar), 129.7(6) (Ar), 129.7(3) (Ar), 129.6 (Ar), 129.3(6) (Ar), 129.3(2) (Ar), 129.2(9) (Ar), 129.2(4) (Ar), 129.2(3) (Ar), 129.1(3) (Ar), 129.1 (Ar), 129.0 (Ar), 128.4(7) (Ar), 128.4(4) (Ar), 128.4(1) (Ar), 128.3(7) (Ar), 128.3(2) (Ar), 128.3(1) (Ar), 128.2(4) (Ar), 128.2-(2) (Ar), 128.2 (Ar), 128.1 (Ar), 127.6 (Ar), 106.0 (C-1), 105.9(8) (C-1), 105.9(3) (C-1), 105.8(8) (C-1), 105.8(3) (C-1), 105.5 (C-1), 105.1 (C-1), 83.1(6), 83.1(3), 82.6, 82.5, 82.1(9), 82.1(1), 81.9, 81.8, 81.7, 81.6, 81.5, 81.4(5), 81.4, 81.3, 80.4, 77.3(4), 77.3(2), 77.1(9), 77.1(2), 77.0, 76.9, 67.3 (octyl OCH_2), 66.0 (C-5), 65.9 (C-5), 65.8(4) (C-5), 65.8(1) (C-5), 65.8 (C-5), 65.7(2) (C-5), 65.7 (C-5), 65.6(7) (C-5), 65.6-(3) (C-5), 65.6 (C-5), 65.5 (C-5), 65.4(5) (C-5), 63.4 (C-5), 63.3 (C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.0 (octyl CH_2), 28.8 (octyl CH_2), 26.7 ($C(CH_3)_3$), 26.6 (octyl CH_2), 26.0 (octyl CH_2), 19.2 ($C(CH_3)_3$); MALDI-TOFMS *m*/*z* calcd for (M + Na) $C_{261}H_{241}N_3O_{72}Si_2$ 4650.85, found 4651.00.

8-Azidooctyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-α-D-arabinofuranosyl(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2, 3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (38). Compound **38** was prepared as a syrup (0.93 g, 83%) from compound **37** (1.25 g, 0.27 mmol) and HF−pyridine (1.0 mL) in THF−pyridine (4:1, 25 mL) as described for **5**: R_f 0.20 (1:1 hexanes−EtOAc); $[\alpha]_D$ +19.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.10−7.79 (m, 45 H, Ar), 7.60−7.15 (m, 70 H, Ar), 5.70−5.20 (m, 35 H), 4.65−4.32 (m, 13 H), 4.23−4.04 (m, 9 H), 4.02−3.70 (m, 16 H), 3.50 (ddd, 1 H, J = 12.5, 9.5, 6.3 Hz, octyl OCH_2), 3.21 (dd, 2 H, J = 7.0, 7.0 Hz, octyl CH_2N_3), 2.50−2.40 (m, 2 H, OH × 2), 1.64−1.45 (m, 4 H, octyl CH_2), 1.45−1.20 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9(9) (C═O), 165.9(7) (C═O), 165.6(4) (C═O), 165.6 (C═O), 165.5(8) (C═O), 165.5(7) (C═O), 165.5(6) (C═O), 165.5(5) (C═O), 165.5(2) (C═O), 165.4(8) (C═O), 165.4(3) (C═O), 165.2(8) (C═O), 165.2(3) (C═O), 165.1(4) (C═O), 165.1(3) (C═O), 165.1(1) (C═O), 165.0(8) (C═O), 165.0(7) (C═O), 165.0(3) (C═O), 165.0(1) (C═O), 164.8 (C═O), 133.4(8) (Ar), 133.4(6) (Ar), 133.3(7) (Ar), 133.3(5) (Ar), 133.3(2) (Ar), 133.2(3) (Ar), 133.2 (Ar), 133.1(8) (Ar), 133.1(4) (Ar), 133.1(1) (Ar), 133.0(7) (Ar), 133.0(4) (Ar), 133.0(1) (Ar), 129.8(7) (Ar), 129.8-(4) (Ar), 129.8(2) (Ar), 129.7(8) (Ar), 129.7(1) (Ar), 129.3(6) (Ar), 129.3(1) (Ar), 129.1(9) (Ar), 129.1(3) (Ar), 129.1 (Ar), 129.0(5) (Ar), 129.0(2) (Ar), 128.9(Ar), 128.4(8) (Ar), 128.4(1) (Ar), 128.3(6) (Ar), 128.3(3) (Ar), 128.3 (Ar), 128.2(8) (Ar), 128.2(5) (Ar), 128.2(3) (Ar), 128.2(1) (Ar), 105.9 (C-1), 105.8(4) (C-1), 105.8 (C-1), 105.7 (C-1), 105.5 (C-1), 105.3 (C-1), 83.7(1), 83.7, 82.7(2), 82.6, 82.5, 82.2, 82.1, 82.0, 81.9, 81.8, 81.7(9), 81.7(1), 81.6, 81.5, 81.3, 80.5, 77.6, 77.3, 77.2(6), 77.2(4), 77.2(1), 76.9, 67.3 (octyl OCH_2), 66.0 (C-5), 65.9(5) (C-5), 65.9(1) (C-5), 65.8(4) (C-5), 65.8(2) (C-5), 65.5(5) (C-5), 65.5 (C-5), 65.4(6) (C-5), 65.4(1) (C-5), 62.2(6) (C-5), 62.2(4) (C-5), 51.4 (octyl CH_2N_3), 29.4(9) (octyl CH_2), 29.2 (octyl CH_2), 29.0 (octyl CH_2), 28.8 (octyl CH_2), 26.6 (octyl CH_2), 26.0 (octyl CH_2); ESIMS *m*/*z* calcd for (M + Na) $C_{229}H_{205}N_3O_{72}$ 4173.2, found 4173.0; FTIR 2096.5 cm^{-1} (N_3).

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-{2,3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2, 3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-{2,3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (39). The trichloroacetimidate derivative of the trisaccharide lactol **7** (0.23 g, 0.2 mmol) was prepared using DBU (5 μL, 0.03 mmol) and trichloroacetonitrile (0.16 mL, 1.58 mmol) in CH_2Cl_2 (5 mL) as described for **15**. Following purification, the trichloroacetimidate was dissolved in CH_2Cl_2 (8 mL), and this solution was added to a solution of **38** (0.36 g, 0.086 mmol) in CH_2Cl_2 (13 mL) containing 4 Å molecular sieves (0.3 g; stirred already for about 30 min) at −30 °C. A solution of TMSOTf (15 μL, 0.08 mmol) in CH_2Cl_2 (0.15 mL) was added dropwise over a period of 5 min. The reaction mixture was then warmed to −5 °C over a period of ∼20 min and quenched by the addition of Et_3N (15 μL). The solution was diluted with CH_2Cl_2 (15 mL) and filtered. The filtrate was concentrated to a syrup that was purified by column chromatography (1:1 hexanes−EtOAc) to afford **39** (0.43 g, 77% over two steps) as a syrup: R_f 0.38 (1:1 hexanes−EtOAc); $[\alpha]_D$ +25.7 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.10−7.74 (m, 73 H, Ar), 7.60−7.10 (m, 112 H, Ar), 5.65−5.20 (m, 50 H), 4.80−4.34 (m, 29 H), 4.22−4.0 (m, 14 H), 4.0−3.70 (m, 16 H), 3.50 (ddd, 1 H, J = 12.6, 9.4, 6.4 Hz, octyl OCH_2), 3.22 (dd, 2 H, J = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.42−1.20 (m, 8 H, octyl CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.0 (C═O), 165.8 (C═O), 165.5 (C═O), 165.4-(9) (C═O), 165.4(3) (C═O), 165.3(9) (C═O), 165.3(5) (C═O), 165.3-

(3) (C═O), 165.2 (C═O), 165.1(7) (C═O), 165.1(3) (C═O), 165.0(8) (C═O), 165.0(4) (C═O), 165.0(3) (C═O), 164.9(9) (C═O), 164.9(4) (C═O), 164.9 (C═O), 164.7(6) (C═O), 164.7(2) (C═O), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9(7) (Ar), 132.9(3) (Ar), 132.9(0) (Ar), 132.8 (Ar), 132.7 (Ar), 129.8 (Ar), 129.7(5) (Ar), 129.7(1) (Ar), 129.6-(5) (Ar), 129.6(1) (Ar), 129.5(4) (Ar), 129.5 (Ar), 129.2 (Ar), 129.1-(8) (Ar), 129.1(3) (Ar), 129.0 (Ar), 128.9(7) (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.3(7) (Ar), 128.3(1) (Ar), 128.2(5) (Ar), 128.2(1) (Ar), 128.1 (Ar), 128.0 (Ar), 105.9 (C-1), 105.8(9) (C-1), 105.8(1) (C-1), 105.7(3) (C-1), 105.7 (C-1), 105.6 (C-1), 105.5 (C-1), 105.4 (C-1), 82.7, 82.5, 82.4, 82.0(8), 82.0, 81.8, 81.7, 81.6(9), 81.6(2), 81.5(6), 81.5(4), 81.4(7), 81.4(0), 81.3, 81.2, 80.9, 77.7, 77.5, 77.1(5), 77.1(2), 77.0, 76.8, 67.2 (octyl OCH_2), 65.9 (C-5), 65.7(3) (C-5), 65.7(0) (C-5), 65.4 (C-5), 65.3 (C-5), 65.2 (C-5), 63.6 (C-5), 63.4 (C-5), 51.3 (octyl CH_2N_3), 29.3(8) (octyl CH_2), 29.1 (octyl CH_2), 29.0 (octyl CH_2), 28.7 (octyl CH_2), 26.5 (octyl CH_2), 25.9 (octyl CH_2); ESIMS *m*/*z* calcd for $C_{357}H_{309}N_3O_{110}$ (M + 2Na) 3223.4, found 3223.0; MALDI-TOFMS *m*/*z* calcd for $C_{357}H_{309}N_3O_{110}$ (M + Na) 6424.2, found 6425; FTIR 2096.5 cm^{-1} (N_3).

8-Azidooctyl 5-*O*-{α-D-Arabinofuranosyl-(1→3)-[α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→3)-[5-*O*-{α-D-arabinofuranosyl-(1→3)-[α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (40). To a solution of **39** (0.1 g, 0.015 mmol) in CH_2Cl_2−CH_3OH (2:1, 6 mL) was added $NaOCH_3$ (4 mg, 0.074 mmol). The reaction mixture was stirred for 36 h with occasional addition of CH_3OH (3 mL × 4) and was neutralized with the careful addition of Amberlyst-15 (H^+) cation exchange resin. The solution was filtered and concentrated to give a syrup that was dissolved in distilled water (10 mL). The aqueous phase was washed with EtOAc (10 mL × 2) and CH_2Cl_2 (10 mL) and then lyophilized to give **40** (0.04 g, quantitative) as a fluffy solid: $[\alpha]_D$ +138.5 (*c* 0.3, H_2O); ^1H NMR (500 MHz, D_2O, δ_H) 5.18−5.07 (m, 17 H), 5.02 (d, 1 H, *J* = 2.2 Hz), 4.34−4.27 (m, 6 H), 4.25−3.68 (m, 85 H), 3.58 (ddd, 1 H, *J* = 12.4, 9.5, 6.4 Hz, octyl OCH_2), 3.32 (dd, 2 H, *J* = 6.9, 6.9 Hz, octyl CH_2N_3), 1.65−1.58 (m, 4 H, octyl CH_2), 1.40−1.32 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.4 (C-1), 108.3(9) (C-1), 108.3(7) (C-1), 108.3(1) (C-1), 108.2 (C-1), 108.0 (C-1), 107.9 (C-1), 84.8(6), 84.8, 83.2(7), 83.2(6), 83.2, 83.0, 82.5(6), 82.5(3), 82.1, 81.8, 81.7, 79.9, 77.6(8), 77.6(4), 77.6(2), 77.4, 77.3, 69.4, 67.7(9) (octyl OCH_2), 67.7-(8) (C-5), 67.7(5) (C-5), 67.3 (C-5), 67.1 (C-5), 62.0(4) (C-5), 62.0 (C-5), 52.1 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.0(6) (octyl CH_2), 29.0-(2) (octyl CH_2), 28.8 (octyl CH_2), 26.7 (octyl CH_2), 25.9 (octyl CH_2); ESIMS *m*/*z* calcd for $C_{98}H_{161}N_3O_{73}$ (M + 2Na) 1297.4, found 1297.4.

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-{2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-5-*O*-{2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (41). The trichloroacetimidate derivative of pentasaccharide lactol **8** (0.42 g, 0.23 mmol) was prepared using DBU (7 μL, 0.05 mmol) and trichloroacetonitrile (0.18 mL, 1.8 mmol) in CH_2Cl_2 (9 mL) as described for **15**. Following purification, the trichloroacetimidate was dissolved in CH_2Cl_2 (8 mL), and this solution was added to a solution of **42** (0.4 g, 0.097 mmol) in CH_2Cl_2 (16 mL) containing 4 Å molecular sieves (0.4 g; stirred already for about 30 min) at −30 °C. A solution of TMSOTf (16 μL, 0.09 mmol) in CH_2Cl_2 (0.16 mL) was added dropwise over a period of 5 min. The reaction mixture was then warmed to −5 °C over a period of ∼20 min and quenched by the addition of Et_3N (15 μL). The solution was diluted with CH_2Cl_2 (15 mL) and filtered. The filtrate was concentrated to a syrup that was purified by column chromatography (1:1 hexanes−EtOAc) to afford **41** (0.58 g, 77% over two steps) as a foam: R_f 0.40 (1:1 hexanes−EtOAc); $[\alpha]_D$ −9.4 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.75 (m, 90 H, Ar), 7.60−7.08 (m, 135 H, Ar), 5.98−5.88 (m, 4 H), 5.73−5.50 (m, 30 H), 5.44−5.28 (m, 20 H), 5.27−5.22 (m, 2H), 5.15−5.08 (m, 2 H), 4.80−4.72 (m, 4 H), 4.70−4.24 (m, 37 H), 4.24−3.69 (m, 34 H), 3.50 (ddd, 1 H, *J* = 12.5, 9.6, 6.3 Hz, octyl OCH_2), 3.22 (dd, 2 H, *J* = 6.9, 6.9 Hz, octyl CH_2N_3), 1.70−1.50 (m, 4 H, octyl CH_2), 1.45−1.22 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9 (C═O), 165.8 (C═O), 165.6(8) (C═O), 165.6(4) (C═O), 165.6(1) (C═O), 165.5(5) (C═O), 165.5(2) (C═O), 165.4(9) (C═O), 165.4(3) (C═O), 165.3(8) (C═O), 165.3(2) (C═O), 165.2(7) (C═O), 165.2(3) (C═O), 165.1(3) (C═O), 165.1(1) (C═O), 165.0(7) (C═O), 165.0(1) (C═O), 164.9 (C═O), 133.5(2) (Ar), 133.5(1) (Ar), 133.4 (Ar), 133.3(9) (Ar), 133.3(5) (Ar), 133.3(2) (Ar), 133.2 (Ar), 133.1 (Ar), 133.0(9) (Ar), 133.0(7) (Ar), 133.0 (Ar), 132.8(Ar), 132.7 (Ar), 129.8(7) (Ar), 129.8(2) (Ar), 129.7(8) (Ar), 129.7(6) (Ar), 129.7(1) (Ar), 129.6 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2(9) (Ar), 129.2(7) (Ar), 129.1(9) (Ar), 129.1(4) (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.4(7) (Ar), 128.4(4) (Ar), 128.4(2) (Ar), 128.3(5) (Ar), 128.3(2) (Ar), 128.2(7) (Ar), 128.2(3) (Ar), 128.1(7) (Ar), 128.1-(2) (Ar), 106.4 (C-1), 105.9(7) (C-1), 105.9(2) (C-1), 105.8(8) (C-1), 105.8(4) (C-1), 105.5 (C-1), 105.2(5) (C-1), 100.2(7) (C-1), 100.2(1) (C-1), 84.9, 84.8, 83.4, 82.6, 82.1(9), 82.1(1), 82.0(2), 82.0(0), 81.8-(7), 81.8(0), 81.7, 81.5, 81.4(7), 81.4(3), 80.7, 80.6, 79.3, 79.1, 78.0-(8), 78.0(7), 77.4, 77.2, 76.7, 76.4, 67.3 (octyl OCH_2), 66.0 (C-5), 65.8 (C-5), 65.7 (C-5), 65.5 (C-5), 64.4 (C-5), 64.1(C-5), 51.4 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.1 (octyl CH_2), 28.8 (octyl CH_2), 26.6 (octyl CH_2), 26.0 (octyl CH_2); MALDI-TOFMS *m*/*z* calcd for $C_{433}H_{373}N_3O_{134}$ (M + Na) 7785.53, found 7785.00; FTIR 2096.2 cm^{-1} (N_3).

8-Azidooctyl 5-*O*-{β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→3)-[5-*O*-{β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (42). Compound **42** was prepared as a fluffy solid (34 mg, quantitative) from compound **41** (87 mg, 11 μmol) and $NaOCH_3$ (3 mg, 0.056 mmol) in CH_2Cl_2−CH_3OH (2:1, 6 mL) as described for **40**: $[\alpha]_D$ +87.0 (*c* 0.4, H_2O); ^1H NMR (500 MHz, D_2O, δ_H) 5.25 (d, 2 H, *J* = 1.8 Hz), 5.20−5.05 (m, 19 H), 5.02 (d, 1 H, *J* = 2.0 Hz), 4.34−4.26 (m, 7 H), 4.25−3.64 (m, 104 H), 3.57 (ddd, 1 H, *J* = 13.2, 10.1, 6.6 Hz, octyl OCH_2), 3.32 (dd, 2 H, *J* = 6.8, 6.8 Hz, octyl CH_2N_3), 1.64−1.56 (m, 4 H, octyl CH_2), 1.40−1.31 (m, 8 H, octyl CH_2); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.4 (C-1), 108.3(6) (C-1), 108.3 (C-1), 108.1 (C-1), 108.0 (C-1), 106.5 (C-1), 106.3 (C-1), 101.6 (C-1), 101.5 (C-1), 87.9, 87.7, 83.7(9), 83.7(2), 83.3, 83.2(7), 83.2(1), 83.0(8), 83.0(6), 82.8, 82.6, 82.5(7), 82.5(4), 81.9, 81.7(4), 81.7(1), 80.0, 79.9, 77.6(9), 77.6(5), 77.6(3), 77.4(7), 77.4(2), 77.3,

77.1, 75.7, 75.6, 75.0(6), 75.0(1), 69.4, 67.7 (octyl OCH_2), 67.6 (C-5), 67.5 (C-5), 67.3 (C-5), 67.2 (C-5), 67.1 (C-5), 63.8(6) (C-5), 63.8(2) (C-5), 61,4(9), 61.4(7), 52.1 (octyl CH_2N_3), 29.4 (octyl CH_2), 29.0(8) (octyl CH_2), 29.0(3) (octyl CH_2), 28.8 (octyl CH_2), 26.7 (octyl CH_2), 25.9 (octyl CH_2); ESIMS *m*/*z* calcd for (M + Na) $C_{118}H_{193}N_3O_{89}$ 3100.1, found 3100.0.

Acknowledgment. This work was supported by the University of Alberta, The Natural Sciences and Engineering Research Council of Canada, and the Alberta Ingenuity Centre for Carbohydrate Science.

Supporting Information Available: Experimental details and characterization data for the preparation of monosaccharide building blocks **10**−**12**, **20**−**24**, and **30** and ^1H and ^{13}C NMR spectra of all previously unreported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JA072892+