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2,3-Anhydrosugars in glycoside bond synthesis. Application to the preparation of C-2 functionalized α-D-arabinofuranosides

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Abstract—A novel two-step route has been developed for the synthesis of a panel of oligosaccharides (**9**–**17**) containing C-2 functionalized α-D-arabinofuranosyl residues. The first step in this route consists of a highly stereocontrolled glycosylation reaction using a 2,3-anhydrosugar thioglycoside (**6**). In the second step, the epoxide ring in the 2,3-anhydrosugar glycoside is regioselectively opened at C-2 with sodium methoxide and sodium azide thus providing products with the α-D-arabinofuranosyl stereochemistry. This approach to these targets circumvents the potential stereocontrol problems inherent in glycosylations with arabinofuranosyl donors possessing non-participating groups at C-2. The route is also highly convergent, allowing the preparation of a range of C-2′ and C-2″ modified oligosaccharides upon reaction of epoxy glycosides **27**–**29** with nucleophiles.
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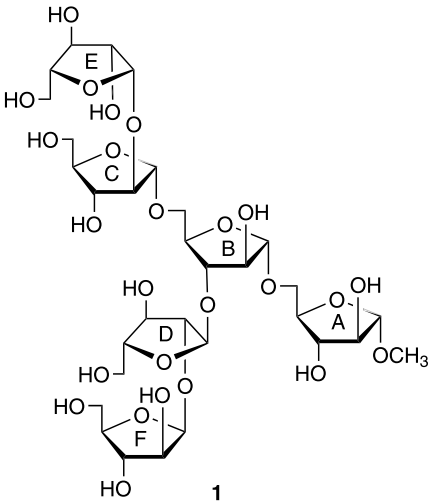
1. Introduction

Over the past few years we have reported[1] syntheses of arabinofuranosyl-containing oligosaccharides that are fragments of two polysaccharides (arabinogalactan and lipoarabinomannan) found in the cell wall of mycobacteria, including the human pathogens *Mycobacterium tuberculosis* and *Mycobacterium leprae*.[2] These synthetic investigations were carried out with the goal of developing routes that would efficiently provide multi-milligram quantities of material for subsequent biochemical studies, including the identification of inhibitors of the enzymes that assemble these cell wall polysaccharides. To date, we have prepared a number of oligosaccharides, the largest of which is hexasaccharide **1** (Chart 1). The glycan portion of **1** is a key structural motif in both mycobacterial arabinogalactan and lipoarabinomannan.[1,2] These synthetic glycans have found application in studies directed towards probing the substrate specificity of mycobacterial arabinosyltransferases (AraT's)[3] as well as in investigations dedicated to mapping the specificities of antibodies that are generated against mycobacterial cell wall polysaccharides.[4]

As part of these investigations, we needed to synthesize di- and trisaccharide analogs in which the C-2 hydroxyl group



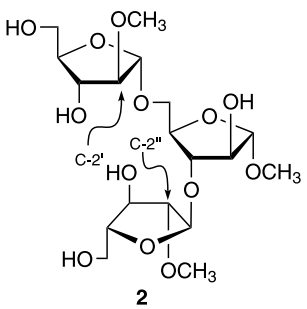


Chart 1.

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in the non-reducing sugar residues (positions C-2′ and C-2″) was replaced with various other functionalities such as amino or methoxy groups (e.g., **2**, Chart 1). We envisioned that such compounds would be potential inhibitors of the AraT's responsible for the installation of the β-(1→2)-linked residues present in hexasaccharide **1**, due to the absence of the reactive hydroxyl group(s) that would serve as the attachment point of the β-arabinofuranosyl residues (rings E and F). We also envisioned, however, that their stereocontrolled preparation by standard methods used in oligosaccharide synthesis would be problematic. For example, using conventional synthetic methodology, the most straightforward approach to **2** would likely involve the preparation of a 2-methoxy glycosyl donor (e.g., **3**, Fig. 1), which could be coupled with the appropriate acceptor species, **4**. A significant problem with this route is that thioglycoside **2** has a non-participating group at C-2 and thus the glycosylation will not benefit from the formation of an acyloxonium ion intermediate that would ensure good 1,2-*trans* selectivity. The product (**5**) will almost certainly be formed as a mixture of four chromatographically similar diastereomers. Although in pyranose systems it is sometimes possible to obtain good 1,2-*trans* stereoselectivity in the absence of a C-2 participating group in the donor (usually in the preparation of α-mannopyranosides),[5] our experience with arabinofuranosides suggests that these reactions will give α/β mixtures of products, which are generally difficult to separate.[1d,6] While it is not difficult to imagine ways to circumvent this problem using conventional synthetic methods, these approaches would be less efficient. For example, a donor that would allow methylation following the glycosylation could be used, or an α-ribofuranoside could be synthesized and then the stereochemistry at C-2′ and C-2″ inverted.

We have discovered recently that 2,3-anhydrosugars thioglycosides and glycosyl sulfoxides are efficient glycosylating agents, providing glycosides with extremely high stereocontrol.[7] The major product formed from these reactions is the one in which the newly formed glycosidic bond is *cis* to the epoxide ring. Thus, glycosylation of alcohols by thioglycoside **6**[7b] (Fig. 2) affords the α-glycoside **7** as the major product. We have further demonstrated that the products of these glycosylations undergo regioselective nucleophilic ring opening of the epoxide at C-2, affording products with the α-D-arabino stereochemistry (**8**, Fig. 2).[8] Based on these previous results, it appeared to us that this methodology was ideally suited for the synthesis of C-2 modified α-D-arabinofuranosides. In this paper, we describe the synthesis of oligosaccharides **9**–**17** (Chart 2) using our 2,3-anhydrosugar methodology. Oligosaccharide analogs in which specific hydroxyl groups have been modified through substitution with various functional groups (e.g., *O*-methyl, amino, fluoro, or azido) have

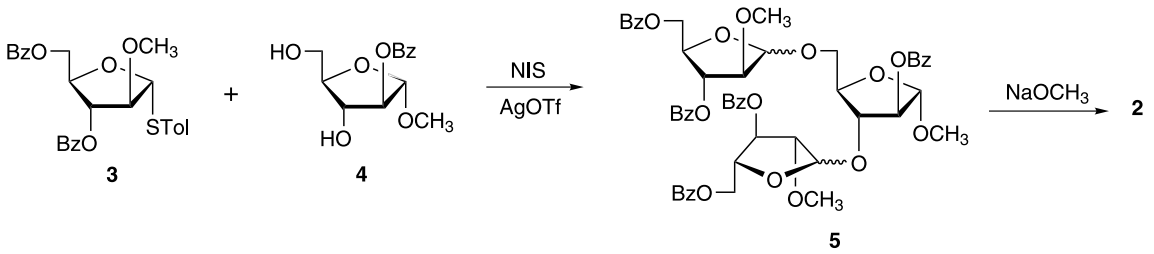


Figure 1. Stereocontrol problem in the synthesis of **5** via the use of a 2-*O*-methylated thioglycoside, **3**.

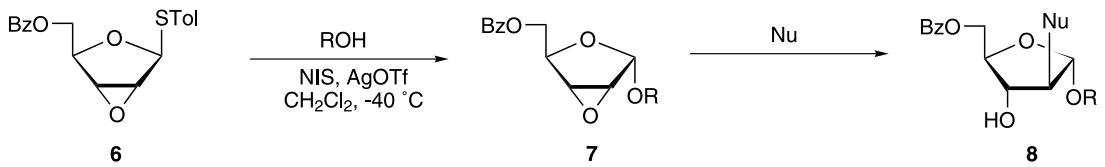


Figure 2. Use of 2,3-anhydrosugar thioglycoside **6** in the synthesis of α-arabinofuranosides (**8**).

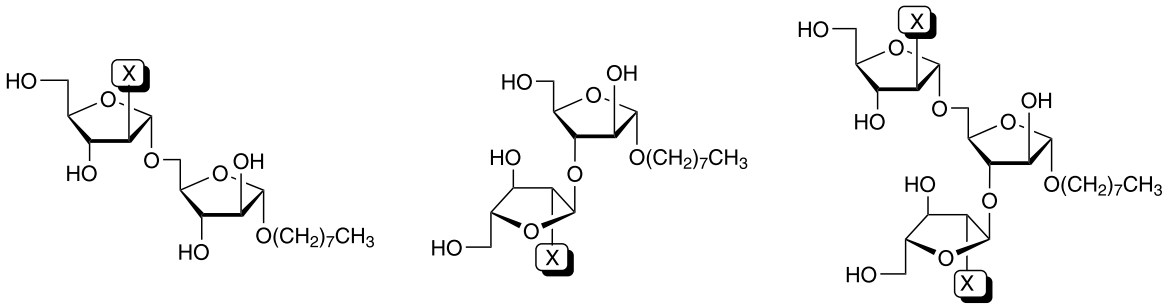


Chart 2.

previously been demonstrated to be inhibitors of glycosyltransferases from mammalian systems[9] as well as those from mycobacteria.[10]

2. Results and discussion

Shown in Figure 3 is the retrosynthetic analysis of the targets. We envisioned that all of the desired compounds could be obtained from one of three anhydrosugar-containing oligosaccharides (**27**–**29**), which in turn could be prepared from four monosaccharide building blocks: **6**, **20**, **22**, and **23**. In addition to circumventing the previously mentioned stereocontrol problems, another advantage of this approach over more conventional ones (e.g., the preparation of a series of C-2 modified monosaccharide donors) is that it is highly convergent. Anhydrosugar glycosides **27**–**29** could be used as precursors to a wide range of C-2′ and C-2″ modified arabinofuranosyl oligosaccharides through reaction with appropriate nucleophiles.

2.1. Synthesis of monosaccharide building blocks

Thioglycoside **6** was synthesized in eight steps from D-xylose as previously described.[7b] The acceptors **20**, **22**, and **23** were prepared without incident from octyl α-D-arabinofuranoside **18**[11] as illustrated in Scheme 1. Treatment of **18** with triphenylmethyl chloride and pyridine in dichloromethane followed by benzoyl chloride gave **19** in 97% yield. Removal of the trityl group with *p*-toluenesulfonic acid in methanol/dichloromethane proceeded in 94% yield to afford **20**. Alternatively, reaction of **18** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine, followed by the addition of benozyl chloride provided the fully protected arabinofuranoside **21** in 89% yield. Subsequent cleavage of the siloxane protecting group with *n*-Bu_4NF was achieved in 92% yield to provide diol **22**. The

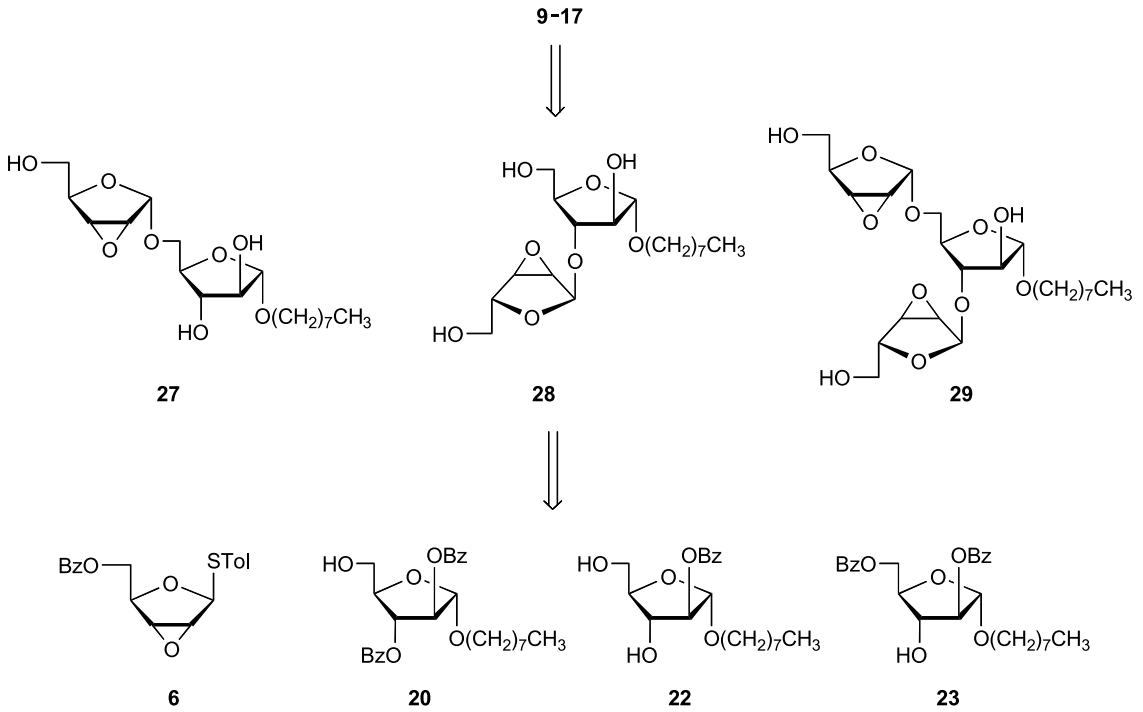
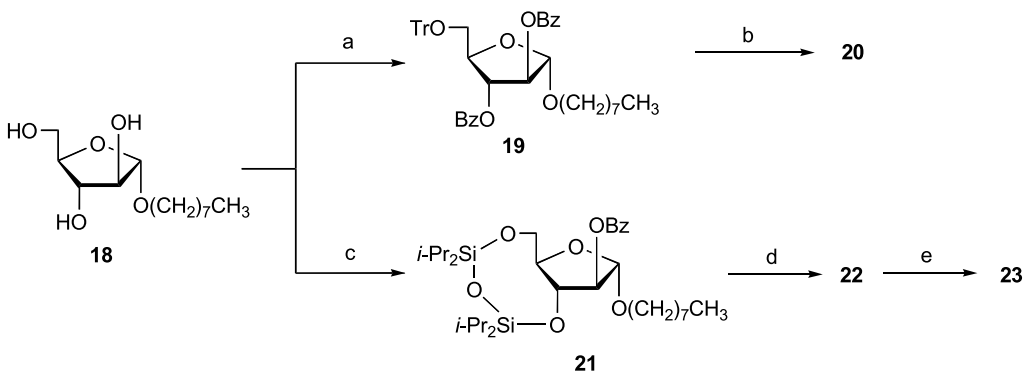
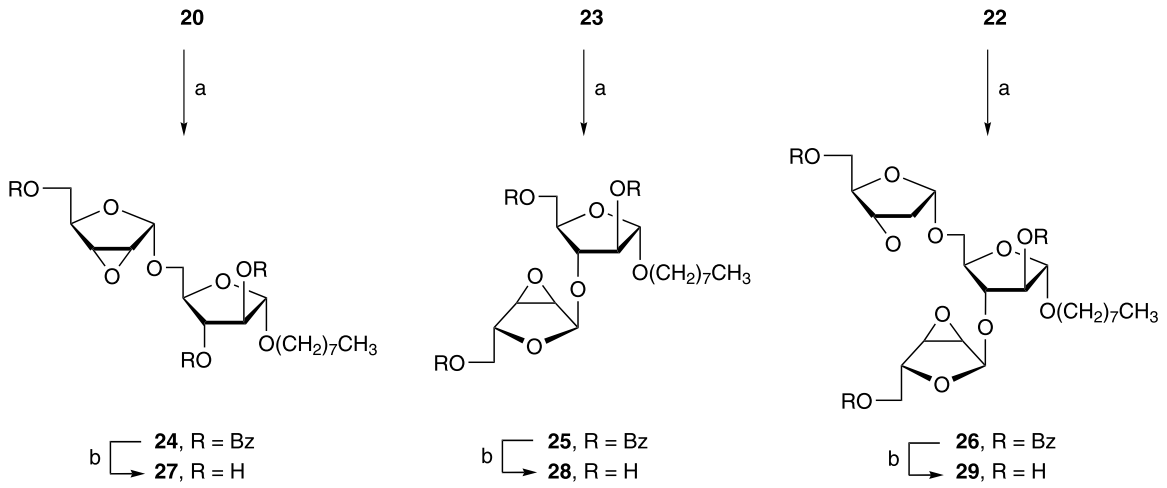


Figure 3. Retrosynthetic analysis of **9**–**17**.



Scheme 1. (a) TrCl, pyridine, CH_2Cl_2, rt, then BzCl, rt 97% (two steps, one pot). (b) *p*-TsOH, CH_2Cl_2, CH_3OH, rt, 94%. (c) 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane, pyridine, rt, then BzCl, rt 89% (two steps, one pot). (d) *n*-Bu_4NF, THF, rt, 92%. (e) BzOH, Ph_3P, DEAD, THF, rt, 93%.



Scheme 2. (a) **6**, *N*-iodosuccinimide, $AgOSO_2CF_3$, CH_2Cl_2, −40 °C, 84% (for **20**), 89% (for **23**) 75% (for **22**). (b) $NaOCH_3$, CH_3OH, rt, 92% (for **24**), 98% (for **25**), 89% (for **26**).

remaining acceptor, **23**, was obtained in one step and 93% yield from **22** upon Mitsunobu reaction with benzoic acid.

2.2. Glycosylation reactions and deprotection

With the four monosaccharides in hand, thioglycoside **6** was used to glycosylate alcohols **20**, **22**, and **23** (Scheme 2). These reactions were carried out using our standard protocol,[7b] which involves the coupling of the thioglycoside and acceptor in dichloromethane at −40 °C using activation by *N*-iodosuccinimide and silver triflate.[12] The products **24**, **25** and **26** were obtained in 84, 89, and 75% yield, respectively. The anomeric stereochemistry in the 2,3-anhydrosugar residues was determined by measuring the magnitude of $^1J_{C\text{-}1,H\text{-}1}$.[13] We have previously demonstrated that this parameter is the only reliable method for establishing anomeric stereochemistry in these 2,3-anhydrosugar derivatives.[13] In none of the glycosylations did we isolate any products with the β-stereochemistry and the substrates required for the ring opening reactions, **27**–**29**, were obtained in 89–98% yield by treatment of **24**–**26** with sodium methoxide.

2.3. Epoxide ring opening reactions

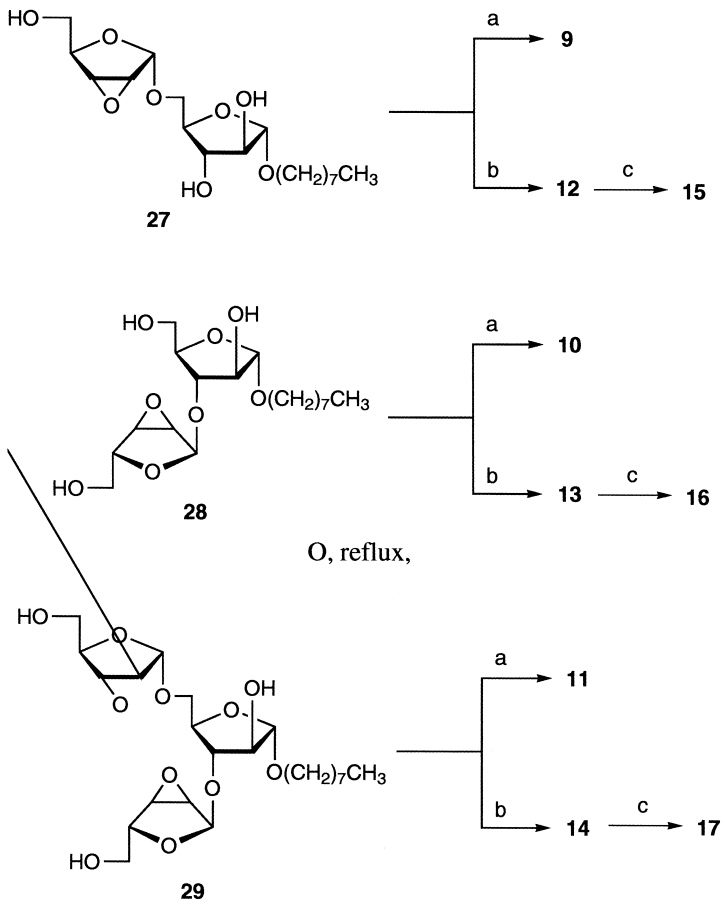
Introduction of the functionality at the C-2′ and C-2″ positions was achieved by heating each of **27**–**29** in the presence of a nucleophile (Scheme 3). Similar to other 2,3-anhydrosugars,[7b,8] the epoxide moiety in these molecules is quite robust and vigorous conditions are required for the reactions to proceed at reasonable rates. Reaction of **27**–**29** with sodium methoxide in methanol at reflux afforded the 2-methoxy derivatives **9**–**11** in yields of 60–82%. Similarly, the azido group was introduced upon heating a solution of the epoxide at reflux in a 3:2 mixture of ethanol and water containing sodium azide and ammonium chloride. Under these conditions, **27**–**29** provided the corresponding C-2′ and C-2″ azidosugar-containing oligosaccharides **12**–**14** in 54–60% yield.

In all cases, the structures of the products could be easily confirmed by ^1H and ^{13}C NMR spectroscopy. For all products the anomeric hydrogen in the ring-opened residues appeared in the ^1H NMR spectrum as a singlet or small doublet ($^3J_{H1,H2}<2.2$ Hz), while the anomeric carbon of these residues appeared in the ^{13}C NMR spectrum between 105 and 109 ppm. These data are consistent with the α-arabino stereochemistry in the products.[14] Attack of the nucleophile at C-3 would have led to products with the α-xylo stereochemistry, in which the anomeric hydrogens would have appeared in the ^1H NMR spectrum as a doublet with $^3J_{H1,H2}>4$ Hz and the anomeric carbon resonance would have appeared in the ^{13}C NMR spectrum between 100 and 104 ppm.[14] We also explored the use of NOE spectroscopy to provide further support for the identity of the ring-opened products. However, as might be expected given the inherent flexibility of five-membered rings, only weak intra-residue NOE's were observed. For example, for **9**, a very weak NOE was observed between H-2′ and H-4′ and somewhat larger NOE was seen between H-3′ and the H-5′s. These NOE's were consistent with the structures determined using other NMR parameters, but their small magnitudes provided little additional insight into the product structures.

In those reactions for which the yields are modest, we saw no evidence of formation of products with the α-xylo stereochemistry. Instead, the remainder of the mass balance was unreacted starting material. We found that at prolonged reaction times that some substrate decomposition began to occur and therefore it was advantageous to stop the reaction before all of the starting material was gone. The final targets, the amino oligosaccharides **15**–**17**, were obtained in 63–81% yield upon reduction of **12**–**14** with triphenylphosphine and water.

3. Conclusions

In conclusion, we describe here efficient syntheses of oligosaccharides containing C-2 modified α-arabinofuranosyl residues (**9**–**17**). The method we have used for the synthesis of these glycans involves a two-step process that combines a highly stereocontrolled glycosylation reaction of a 2,3-anhydrosugar thioglycoside (**6**) with a highly regioselective epoxide ring opening reaction. This



Scheme 3. (a) $NaOCH_3$, CH_3OH, reflux, 82% (for **27**), 71% (for **28**), 60% (for **29**). (b) NaN_3, NH_4CL, EtOH, H_2O, reflux, 60% (for **27**), 54% (for **28**), 56% (for **29**). (c) Ph_3P, H_2O, THF, rt, 70% (for **12**), 63% (for **13**), 81% (for **14**).

approach circumvents the potential stereocontrol problems inherent in glycosylations with arabinofuranose donors with non-participating groups at C-2.[1d,6] Furthermore, this route is highly convergent, allowing the preparation of a range of C-2′ and C-2″ modified oligosaccharides upon reaction of **27**–**29** with any given nucleophile. In its present form, the method is somewhat limited by the vigorous conditions required to open the epoxide moieties and we are currently investigating methods by which these reactions can be made to proceed at lower temperatures. The testing of **27**–**29** as inhibitors of mycobacterial AraT's is in progress and will be reported separately.

4. Experimental

4.1. General methods

Solvents were distilled from appropriate drying agents before use. Unless stated otherwise, all reactions were carried out at room temperature and under a positive pressure of argon and were monitored by TLC on silica gel 60 F_{254}. Spots were detected under UV light or by charring with 10% H_2SO_4, in EtOH. Unless otherwise indicated, all column chromatography was performed on silica gel 60 (40–60 μM). Iatrobeads refers to a beaded silica gel 6RS-8060, which is manufactured by Iatron Laboratories (Tokyo). 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 400 or 500 MHz and chemical shifts are referenced to either TMS (0.0, $CDCl_3$) or HOD (4.78, D_2O). ^{13}C NMR spectra were recorded at 100 or 125 MHz and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (77.23, $CDCl_3$) or external dioxane (67.40, D_2O). Electrospray mass spectra were recorded on samples suspended in mixtures of THF and CH_3OH with added NaCl.

4.1.1. Octyl 5-*O*-(2-*O*-methyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (9). To a solution of **27** (60 mg, 0.15 mmol) in dry CH_3OH (10 mL), was added a 1 M solution of $NaOCH_3$ in CH_3OH (3 mL, 3 mmol). The reaction mixture was heated at reflux for 24 h, then cooled and neutralized with acetic acid (0.2 mL). The solution was concentrated and purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **9** (50 mg, 82%) as a colorless oil: R_f 0.67 (CH_2Cl_2/CH_3OH, 6:1); $[\alpha]_D$ +71.9 (*c* 0.9, CH_3OH); ^{1}H NMR (400 MHz, D_2O, δ_H) 5.12 (s, 1H), 4.96 (s, 1H), 4.26 (s, 1H), 4.13–4.09 (m, 2H), 4.07–4.02 (m, 2H), 3.87–3.83 (m, 2H), 3.79–3.70 (m, 3H), 3.55–3.47 (m, 2H), 3.48 (s, 3H), 1.67–1.65 (m, 2H), 1.35–1.33 (m, 10H), 0.89–0.87 (m, 3H); ^{13}C NMR (100 MHz, D_2O, δ_C) 107.4, 105.5, 87.4, 83.7, 82.2, 81.8, 78.8, 77.2, 68.6, 66.7, 61.1, 57.9, 33.2, 29.8 (2), 29.7, 26.3, 22.9, 14.2; HR-ESI-MS calcd for $[C_{19}H_{36}O_9]Na^+$ 431.2251, found 431.2261.

4.1.2. Octyl 3-*O*-(2-*O*-methyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (10). Epoxide **28** (35 mg, 0.09 mmol)

was dissolved in CH_3OH (10 mL) and treated with a 1 M solution of $NaOCH_3$ in CH_3OH (3 mL, 0.3 mmol) as described for the preparation of **9**. The product was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **10** (25 mg, 71%) as a colorless oil: R_f 0.81 (CH_2Cl_2/CH_3OH, 6:1); $[\alpha]_D$ +92.5 (*c* 0.8, CH_3OH); ^1H NMR (500 MHz, D_2O, δ_H) 5.17 (d, 1H, *J*=1.4 Hz), 4.94 (s, 1H), 4.15 (s, 1H), 4.06–4.02 (m, 2H), 3.96–3.92 (m, 2H), 3.81–3.77 (m, 2H), 3.74–3.72 (m, 2H), 3.71–3.62 (m, 3H), 3.41 (s, 3H), 1.56–1.52 (m, 2H), 1.27–1.26 (m, 10H), 0.86–0.83 (m, 3H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.1, 105.0, 91.8, 83.3, 83.2, 83.0, 82.1, 80.1, 74.9, 68.1, 61.2, 57.8, 32.2, 29.7 (2), 29.6, 26.3, 22.9, 14.2; HR-ESI-MS calcd for $[C_{19}H_{36}O_9]Na^+$ 431.2251, found 431.2233.

4.1.3. Octyl 3,5-di-*O*-(2-*O*-methyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (11). Epoxide **29** (32 mg, 0.06 mmol) was dissolved in CH_3OH (10 mL) and treated with a 1 M solution of $NaOCH_3$ in CH_3OH (3 mL, 0.3 mmol) as described for the preparation of **9**. The product was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **11** (20 mg, 60%) as a colorless oil: R_f 0.65 (CH_2Cl_2/CH_3OH, 6:1); $[\alpha]_D$ +91.4 (*c* 0.7, CH_3OH); ^1H NMR (500 MHz, D_2O, δ_H) 5.16 (d, 1H, *J*=1.0 Hz), 5.08 (s, 1H), 4.96 (s, 1H), 4.19–4.16 (m, 1H), 4.05–4.01 (m, 2H), 3.96–3.92 (m, 3H), 3.89–3.86 (m, 1H), 3.79–3.76 (m, 4H), 3.68–3.63 (m, 3H), 3.47–3.45 (m, 1H), 3.40 (s, 3H), 3.40 (s, 3H), 1.56–1.50 (m, 2H), 1.14–1.11 (m, 10H), 0.86–0.81 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.6, 105.5, 105.3, 91.6, 90.5, 86.4, 85.4, 82.9, 81.9, 80.2, 76.2, 75.2, 68.2, 66.3, 65.7, 63.3, 58.2, 58.0, 32.3, 29.9, 29.8, 29.7, 26.1, 23.1, 14.6; HR-ESI-MS calcd for $[C_{25}H_{46}O_{13}]Na^+$ 577.2831, found 577.2814.

4.1.4. Octyl 5-*O*-(2-azido-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (12). A solution of **27** (45 mg, 0.12 mmol), NaN_3 (150 mg, 2.16 mmol) and NH_4Cl (140 mg, 2.45 mmol) in ethanol (15 mL) and water (10 mL) was heated at reflux for 24 h. The reaction mixture was cooled, concentrated, and the residue was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **12** (30 mg, 60%) as a colorless oil: R_f 0.38 (CH_2Cl_2/CH_3OH, 10:1); $[\alpha]_D$ +84.3 (*c* 0.8, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 5.08 (d, 1H, *J*=2.1 Hz), 4.98 (s, 1H), 4.18–4.16 (m, 2H), 4.10–4.08 (m, 1H), 4.05 (s, 1H), 3.98–3.95 (m, 2H), 3.91–3.86 (m, 2H), 3.77–3.70 (m, 3H), 3.46–3.41 (m, 1H), 1.61–1.59 (m, 2H), 1.25–1.23 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 108.6, 105.0, 85.4, 83.1, 81.8, 79.6, 75.2, 71.1, 68.4, 65.5, 61.9, 32.0, 29.7, 29.5, 29.4, 26.3, 22.8, 14.3; HR-ESI-MS calcd for $[C_{18}H_{33}O_8N_3]Na^+$ 442.2160, found 442.2168.

4.1.5. Octyl 3-*O*-(2-azido-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (13). Epoxide **28** (30 mg, 0.08 mmol) was treated as described for the preparation of **12** with NaN_3 (140 mg, 2.15 mmol) and NH_4Cl (130 mg, 2.43 mmol) in ethanol (15 mL) and water (10 mL). The product was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **13** (18 mg, 54%) as a colorless oil: R_f 0.42 (CH_2Cl_2/CH_3OH, 10:1); $[\alpha]_D$ +81.3 (*c* 0.8, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 5.17 (d, 1H, *J*=1.9 Hz), 4.94 (s, 1H), 4.16 (s, 1H), 4.11 (m, 1H), 4.05–3.96 (m, 3H), 3.87–3.78 (m, 5H), 3.73–3.64 (m, 1H), 3.44–3.38 (m, 1H), 1.59–1.54 (m, 2H), 1.29–1.27 (m, 10H), 0.90–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 108.0, 104.9, 84.5, 82.7, 82.5, 79.9, 75.2, 71.4, 68.0, 61.6, 61.1, 31.9, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1; HR-ESI-MS calcd for $[C_{18}H_{33}O_8N_3]Na^+$ 442.2160, found 442.2166.

4.1.6. Octyl 3,5-di-*O*-(2-azido-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (14). Epoxide **29** (33 mg, 0.06 mmol) was treated as described for the preparation of **12** with NaN_3 (330 mg, 6.5 mmol) and NH_4Cl (350 mg, 6.5 mmol) in ethanol (15 mL) and water (10 mL). The product was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **14** (20 mg, 56%) as a colorless oil: R_f 0.35 (CH_2Cl_2/CH_3OH, 10:1); $[\alpha]_D$ +75.6 (*c* 0.8, CH_3OH); ^1H NMR (400 MHz, D_2O, δ_H) 5.13 (d, 1H, *J*=1.9 Hz), 5.07 (d, 1H, *J*=2.1 Hz), 4.97 (s, 1H), 4.23–4.20 (m, 2H), 4.17–4.14 (m, 1H), 4.08–4.04 (m, 4H), 3.91–3.89 (m, 1H), 3.83–3.79 (m, 4H), 3.71–3.63 (m, 4H), 3.34–3.33 (m, 1H), 1.53–1.50 (m, 2H), 1.15–1.11 (m, 10H), 0.83–0.80 (m, 3H); ^{13}C NMR (100 MHz, D_2O, δ_C) 108.5, 105.2, 104.9, 84.0, 83.7, 81.9, 81.6, 81.4, 78.7, 69.3, 67.8, 67.5, 65.5, 61.6, 61.1, 33.3, 31.2, 31.0, 30.9, 30.8, 27.5, 24.1, 15.6; HR-ESI-MS calcd for $[C_{23}H_{40}O_{11}N_6]Na^+$ 599.2647, found 599.2689.

4.1.7. Octyl 5-*O*-(2-amino-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (15). A solution of **12** (25 mg, 0.06 mmol) and triphenylphosphine (24 mg, 0.09 mmol) in THF (5 mL) and few drops of water was stirred for 24 h at rt. The solvent was concentrated and the residue purified by chromatography ($CHCl_3/CH_3OH$, 2:1 with 2% Et_3N) to give **15** (15 mg, 70%) as a white solid: R_f 0.14 ($CHCl_3/CH_3OH$, 2:1); $[\alpha]_D$ +91.2 (*c* 0.8, CH_3OH); ^1H NMR (400 MHz, D_2O, δ) 5.09 (d, 1H, *J*=1.8 Hz), 4.98 (s, 1H), 4.20–4.16 (m, 2H), 4.14–4.09 (m, 1H), 4.04 (dd, 1H, *J*=5.4, 11.6 Hz), 3.98–3.94 (m, 2H), 3.89–3.85 (m, 2H), 3.58–3.48 (m, 3H), 3.37–3.29 (m, 1H), 1.57–1.53 (m, 2H), 1.25–1.21 (m, 10H), 0.82–0.79 (m, 3H); ^{13}C NMR (100 MHz, D_2O, δ) ^{13}C NMR (100 MHz, D_2O, δ_C) 108.2, 105.7, 84.8, 81.2, 80.8, 79.7, 75.5, 72.0, 68.7, 62.0, 60.0, 59.7, 31.5, 29.0, 28.7, 25.6, 22.4, 13.8; HR-ESI-MS calcd for $[C_{18}H_{35}O_8N]Na^+$ 416.2255, found 416.2259.

4.1.8. Octyl 3-*O*-(2-amino-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (16). Azide **13** (20 mg, 0.05 mmol) was converted to **16** as described for the preparation of **15** with triphenylphosphine (24 mg, 0.09 mmol) in THF (5 mL) and few drops of water. Purification of the product by chromatography ($CHCl_3/CH_3OH$, 2:1 with 2% Et_3N) gave **16** (10 mg, 63%) as a white solid: R_f 0.14 ($CHCl_3/CH_3OH$, 2:1); $[\alpha]_D$ +83.2 (*c* 0.7, CH_3OH); ^1H NMR (400 MHz, D_2O, δ_H) 5.07 (d, 1H, *J*=2.1 Hz), 4.84 (s, 1H), 4.06 (m, 1H), 4.05–3.96 (m, 4H), 3.87–3.78 (m, 3H), 3.73–3.64 (m, 2H), 3.44–3.38 (m, 1H), 3.01–2.99 (m, 1H),1.59–1.54 (m, 2H), 1.34–1.29 (m, 10H), 0.90–0.86 (m, 3H); ^{13}C NMR (100 MHz, D_2O, δ_C) 108.2, 105.0, 84.5, 83.7, 82.5, 82.6, 69.2, 68.4, 64.0, 60.6, 59.1, 31.9, 29.6, 29.4, 29.3, 26.1, 22.6, 14.1; HR-ESI-MS calcd for $[C_{18}H_{35}O_8N]Na^+$ 416.2255, found 416.2252.

4.1.9. Octyl 3,5-di-*O*-(2-amino-2-deoxy-α-D-arabinofuranosyl)-α-D-arabinofuranoside (17). Azide **14** (15 mg, 0.03 mmol) was converted to **17** as described for

the preparation of **16** with triphenylphosphine (17 mg, 0.05 mmol) in THF (5 mL) and few drops of water. Purification of the product by chromatography ($CHCl_3$/CH_3OH, 2:1 with 2% Et_3N) gave **17** (11 mg, 81%) as a white solid: R_f 0.12 ($CHCl_3$/CH_3OH, 2:1); $[\alpha]_D$ +106.7 (*c* 0.7, CH_3OH); ^1H NMR (400 MHz, D_2O, δ_H) 5.10 (d, 1H, *J*=1.8 Hz), 5.07 (d, 1H, *J*=2.1 Hz), 4.89 (s, 1H), 4.19–4.16 (m, 1H), 4.17–4.15 (m, 1H), 4.01–3.98 (m, 1H), 3.94–3.93 (m, 3H), 3.89–3.84 (m, 2H), 3.81–3.77 (m, 3H), 3.72–3.67 (m, 3H), 3.55–3.49 (m, 1H), 3.07–3.03 (m, 2H),1.56–1.52 (m, 2H), 1.26–1.17 (m, 10H), 0.82–0.79 (m, 3H); ^{13}C NMR (100 MHz, D_2O, δ_C) 107.9, 107.8, 107.7, 85.7, 85.2, 84.0, 82.2, 81.8, 81.4, 79.4, 68.4, 66.6, 62.1, 62.0, 59.6 (2), 31.5, 29.0, 28.8, 28.6, 25.6, 22.4, 13.8; HR-ESI-MS calcd for $[C_{23}H_{44}O_{11}N_2]Na^+$ 547.2837, found 547.2836.

4.1.10. Octyl 2,3-di-*O*-benzoyl-5-*O*-triphenylmethyl-α-D-arabinofuranoside (19). To a solution of **18**[11] (500 mg, 1.91 mmol) in dry pyridine (10 mL) and dry CH_2Cl_2 (3 mL) was added dropwise triphenylmethyl chloride (837 mg, 3.0 mmol) and DMAP (90 mg, 0.7 mmol). The reaction mixture was stirred at rt overnight before benzoyl chloride (1.5 mL, 11 mmol) was added dropwise. The solution was again stirred at rt overnight, then diluted with CH_2Cl_2 (20 mL) and washed successively with 0.1 M HCl (30 mL), water (15 mL), and brine (15 mL). After drying (Na_2SO_4), the solution was filtered and concentrated to give **19** (1.2 g, 97%) as a light yellow oil: R_f 0.53 (hexanes/EtOAc, 4:1); $[\alpha]_D$ +81.9 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.21–8.19 (m, 7H), 8.12–8.09 (m, 3H), 8.02–8.00 (m, 2H), 7.72–7.44 (m, 7H), 7.37–7.33 (m, 2H), 7.30–7.12 (m, 3H), 5.61 (d, 1H, *J*=1.9 Hz), 5.48 (s, 1H), 5.28 (s, 1H), 4.49 (dd, 1H, *J*=4.9, 9.9 Hz), 3.97 (s, 1H), 3.86–3.77 (m, 1H), 3.61–3.50 (m, 2H), 3.12 (s, 1H), 1.73–1.68 (m, 2H), 1.48–1.32 (m, 10H), 0.94–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.0, 165.8, 144.2, 135.0, 134.2, 133.7, 131.0, 130.6, 130.3, 130.0, 129.8, 129.3, 129.2, 128.9 (2), 128.8, 128.2 (2), 127.4, 127.3, 106.2, 87.3, 82.4, 78.4, 68.0, 64.1, 32.3, 30.0, 29.9, 29.7, 26.6, 23.1, 14.5; HR-ESI-MS calcd for $[C_{46}H_{48}O_7]Na^+$ 735.3292, found 735.3303.

4.1.11. Octyl 2,3-di-*O*-benzoyl-α-D-arabinofuranoside (20). To a solution of **19** (2.9 g, 4.07 mmol) in CH_2Cl_2/CH_3OH (20 mL, 3:1) was added *p*-TsOH acid (362 mg, 1.9 mmol) at rt and the mixture was stirred for 12 h, before Et_3N (0.1 mL) was added. The solution concentrated and the residue was purified by chromatography (hexanes/EtOAc, 6:1) to give **20** (1.8 g, 94%) as a colorless oil: R_f 0.51 (hexanes/EtOAc, 2:1); $[\alpha]_D$ +91.5 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.09–8.04 (m, 4H), 7.61–7.56 (m, 2H), 7.47–7.43 (m, 4H), 5.52 (d, 1H, *J*=1.3 Hz), 5.42 (dd, 1H, *J*=0.7, 4.7 Hz), 5.23 (s, 1H), 4.33–4.29 (m, 1H), 4.04–3.95 (m, 2H), 3.78–3.73 (m, 1H), 3.55–3.49 (m, 1H), 1.66–1.59 (m, 2H), 1.41–1.23 (m, 10H), 0.87–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.6, 165.8, 133.9, 130.3 (2), 129.7, 129.6, 128.9 (2), 105.9, 84.0, 82.2, 78.3, 68.0, 62.9, 32.2, 30.0, 29.8, 29.7, 26.6, 23.0, 14.5; HR-ESI-MS calcd for $[C_{27}H_{34}O_7]Na^+$ 493.2197, found 493.2189.

4.1.12. Octyl 2-*O*-benzoyl-3,5-*O*-(1,1,3,3-tetraisopropyl-siloxane-1,3-diyl)-α-D-arabinofuranoside (21). To a solution of **18**[11] (500 mg, 1.90 mmol) in dry pyridine (40 mL), at 0 °C, was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (890 mg, 2.8 mmol) dropwise. The reaction mixture was warmed at rt and stirred for 12 h before benzoyl chloride (0.12 mL, 1.14 mmol) was added dropwise. The reaction mixture was stirred at rt overnight, then diluted with CH_2Cl_2 (25 mL) and washed successively with 0.1 M HCl (50 mL), water (25 mL), and brine (25 mL). After drying (Na_2SO_4), the solution was filtered, concentrated, and the residue was purified by chromatography (hexanes/EtOAc, 6:1) to give **21** (1.07 g, 89%) as a colorless oil: R_f 0.7 (hexanes/EtOAc, 6:1); $[\alpha]_D$ −32.6 (*c* 2.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.06–8.03 (m, 2H), 7.59–7.57 (m, 1H), 7.45–7.43 (m, 2H), 5.43 (dd, 1H, *J*=1.5, 4.7 Hz), 5.00 (d, 1H, *J*=1.5 Hz), 4.50 (dd, 1H, *J*=2.3, 5.1 Hz), 4.11–4.06 (m, 2H), 4.01–3.97 (m, 1H), 3.74–3.68 (m, 1H), 3.58–3.43 (m, 1H), 1.63–1.58 (m, 2H), 1.28–1.26 (m, 10H), 1.15–0.98 (m, 28H), 0.88–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 165.8, 133.4, 129.9, 129.8, 128.6 (2), 105.5, 84.7, 81.5, 76.7, 68.2, 62.3, 32.1, 29.8, 29.6, 29.5, 26.3, 22.9, 17.7, 17.6 (3), 17.2 (3), 14.3, 13.7, 13.5, 13.1, 12.8; HR-ESI-MS calcd for $[C_{32}H_{56}O_7Si_2]Na^+$ 631.3457, found 631.3470.

4.1.13. Octyl 2-*O*-benzoyl-α-D-arabinofuranoside (22). To a solution of **21** (375 mg, 0.62 mmol) in dry THF (15 mL) was added a solution of 1 M *n*-Bu_4NF in THF (1.55 mL, 1.55 mmol). The reaction mixture was stirred at rt for 2 h and then CH_2Cl_2 (50 mL) and a saturated aqueous solution of $NaHCO_3$ (40 mL) were added. The organic layer was dried (Na_2SO_4) then filtered and concentrated. The residue was purified by chromatography (hexanes/EtOAc, 3:1) to give **22** (209 mg, 92%) as colorless oil: R_f 0.42 (hexanes/EtOAc, 1:1); $[\alpha]_D$ 89.7 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.03–8.01 (m, 2H), 7.61–7.58 (m, 1H), 7.47–7.44 (m, 2H), 5.25 (s, 1H), 5.08 (d, 1H, *J*=2.1 Hz), 4.22–4.15 (m, 2H), 3.95–3.92 (m, 1H), 3.80–3.74 (m, 1H), 3.51–3.45 (m, 1H), 3.26 (d, 1H, *J*=5.3 Hz), 1.63–1.61 (m, 2H), 1.34–1.27 (m, 10H), 0.89–0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 167.1, 134.0, 130.2, 129.5, 128.9, 105.7, 86.4, 84.5, 76.8, 68.4, 62.4, 32.2, 29.9, 29.8, 29.6, 26.5, 23.0, 14.5; HR-ESI-MS calcd for $[C_{20}H_{30}O_6]Na^+$ 389.1935, found 389.1935.

4.1.14. Octyl 2,5-di-*O*-benzoyl-α-D-arabinofuranoside (23). To a solution of **22** (143 mg, 0.39 mmol) in dry THF (5 mL), was added Ph_3P (152 mg, 0.58 mmol) and the mixture was stirred at rt for 15 min. Then, DEAD (0.1 mL, 0.58 mmol) and benzoic acid (71 mg, 0.58 mmol) were added. After 1 h, the reaction mixture was concentrated a syrup before ether (25 mL) was added to precipitate the triphenylphosphine oxide. The two-phase mixture was kept at 4 °C overnight then filtered and the precipitate washed with cold ether. The filtrate was concentrated and, after repeating the precipitation, purified by chromatography (hexanes/EtOAc, 8:1) to give **23** (171 mg, 93%) as a white solid: R_f 0.28 (hexanes/EtOAc, 8:1); $[\alpha]_D$ +78.9 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.05–8.01 (m, 4H), 7.61–7.57 (m, 1H), 7.54–7.50 (m, 1H), 7.46–7.42 (m, 2H), 7.37–7.33 (m, 2H), 5.29 (s, 1H), 5.16 (d, 1H, *J*=1.8 Hz), 4.64 (dd, 1H, *J*=4.0, 11.8 Hz), 4.55–4.51 (m, 1H), 4.47–4.44 (m, 1H), 4.25–4.23 (m, 1H), 3.84–3.78 (m, 1H), 3.55–3.49 (m 1H), 3.44 (d, 1H, *J*=5.9 Hz), 1.66–1.61 (m, 2H), 1.39–1.28 (m, 10H), 0.90–0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.7, 166.5, 133.8, 133.2, 130.0 (2),

129.9, 129.2, 128.7, 128.5, 105.5, 85.6, 82.1, 77.5, 68.2, 64.1, 32.0, 29.7, 29.5, 29.4, 26.2, 22.8, 14.2; HR-ESI-MS calcd for $[C_{27}H_{34}O_7]Na^+$ 493.2197, found 493.2208.

4.1.15. Octyl 5-*O*-(2,3-anhydro-5-*O*-benzoyl-α-D-ribofuranosyl)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (24). A solution of acceptor **20** (92 mg, 0.19 mmol), donor **6**[7b] (80 mg, 0.23 mmol) and powdered molecular sieves (4 Å, 150 mg) in dry CH_2Cl_2 (10 mL) was stirred at −40 °C for 10 min. Then, *N*-iodosuccinimide (52 mg, 0.23 mmol) and silver triflate (10 mg, 0.04 mmol) were added. After stirring for 10 min at −40 °C, Et_3N (0.1 mL) was added. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and filtered through Celite. The filtrate was washed successively with a saturated aqueous solution of $Na_2S_2O_3$ (15 mL), water (15 mL), and brine (15 mL). After drying (Na_2SO_4), the organic phase was filtered and concentrated. The residue was purified by chromatography (hexanes/EtOAc, 3:1) to give **24** (110 mg, 84%) as a colorless oil: R_f 0.51 (hexanes/EtOAc, 2:1); $[\alpha]_D$ +89.1 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.11–8.05 (m, 4H), 8.00–7.98 (m, 2H) 7.60–7.53 (m, 3H), 7.46–7.40 (m, 6H), 5.52 (d, 1H, *J*=4.7 Hz), 5.47 (s, 1H), 5.45 (d, 1H, *J*=1.0 Hz), 5.23 (s, 1H), 4.58 (dd, 1H, *J*=3.9, 3.9 Hz), 4.48 (dd, 1H, *J*=3.2, 12.0 Hz), 4.46–4.38 (m, 2H), 4.20 (dd, 1H, *J*=4.9, 11.1 Hz), 4.07 (dd, 1H, *J*=3.7, 11.1 Hz), 3.80–3.73 (m, 3H), 3.54–3.48 (m, 1H), 1.65–1.58 (m, 2H), 1.47–1.24 (m, 10H), 0.88–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.5, 166.1, 165.9, 133.8, 133.7, 130.4, 130.3, 130.0, 129.9, 129.7, 129.0, 128.8, 128.8, 106.1, 102.3, 82.5, 82.2, 78.3, 76.5, 68.4, 67.9, 65.1, 56.3, 56.2, 32.2, 30.0, 29.8, 29.7, 26.6, 23.1, 14.5; $^1J_{C1,H1}$=167.2 Hz; HR-ESI-MS calcd for $[C_{39}H_{44}O_{11}]Na^+$ 711.2776, found 711.2718.

4.1.16. Octyl 3-*O*-(2,3-anhydro-5-*O*-benzoyl-α-D-ribofuranosyl)-2,5-di-*O*-benzoyl-α-D-arabinofuranoside (25). Disaccharide **25** was prepared from **23** (47 mg, 0.1 mmol) and **6**[7b] (40 mg, 0.12 mmol) and powdered molecular sieves (4 Å, 100 mg) in dry CH_2Cl_2 (10 mL) as described for the synthesis of **24** using *N*-iodosuccinimide (27 mg, 0.12 mmol) and silver triflate (10 mg, 0.04 mmol). Purification of the product by chromatography (hexanes/EtOAc, 4:1) gave **25** (130 mg, 89%) as a colorless oil: R_f 0.19 (hexanes/EtOAc, 2:1); $[\alpha]_D$ +97.6 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.05–7.96 (m, 6H), 7.59–7.55 (m, 2H), 7.49–7.37 (m, 5H), 7.27–7.23 (m, 2H), 5.66 (s, 1H), 5.35 (d, 1H, *J*=1.3 Hz), 5.23 (s, 1H), 4.72 (dd, 1H, *J*=2.8, 11.4 Hz), 4.60–4.51 (m, 3H), 4.44 (dd, 1H, *J*=3.2, 11.6 Hz), 4.37 (d, 1H, *J*=5.7 Hz), 4.29 (dd, 1H, *J*=4.2, 12.0 Hz), 3.93 (dd, 1H, *J*=0.4, 2.7 Hz), 3.79–3.73 (m, 2H), 3.53–3.47 (m, 1H), 1.66–1.60 (m, 2H), 1.38–1.27 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.7, 166.5, 166.0, 133.9, 133.7, 133.4, 130.3, 130.2, 130.1 (2), 129.9, 129.8, 129.0, 128.9, 128.7, 106.1, 102.0, 83.9, 83.8, 80.8, 76.8, 68.1, 65.0, 63.8, 56.6 (2), 32.3, 29.8 (2), 29.6, 26.5, 23.1, 14.5; $^1J_{C1,H1}$=166.9 Hz; HR-ESI-MS calcd for $[C_{39}H_{44}O_{11}]Na^+$ 711.2776, found 711.2723.

4.1.17. Octyl 3,5-di-*O*-(2,3-anhydro-5-*O*-benzoyl-α-D-ribofuranosyl)-2-*O*-benzoyl-α-D-arabinofuranoside (26). Trisaccharide **26** was prepared from **22** (100 mg, 0.27 mmol) and **6**[7b] (233 mg, 0.68 mmol) and powdered molecular sieves (4 Å, 100 mg) in dry CH_2Cl_2 (15 mL) as described for the synthesis of **24** using *N*-iodosuccinimide (153 mg, 0.68 mmol) and silver triflate (44 mg, 0.17 mmol). Purification of the product by chromatography (hexanes/EtOAc, 4:1) gave **26** (165 mg, 75%) as a colorless oil: R_f 0.14 (hexanes/EtOAc, 2:1); $[\alpha]_D$ +91.2 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 8.00–7.90 (m, 6H), 7.60–7.52 (m, 3H), 7.46–7.38 (m, 6H), 5.58 (s, 1H), 5.45 (s, 1H), 5.33 (s, 1H), 5.15 (s, 1H), 4.53–4.52 (m, 2H), 4.46 (dd, 2H, *J*=2.9, 12.1 Hz), 4.39–4.28 (m, 4H), 4.12 (dd, 1H, *J*=4.1, 11.7 Hz), 4.02–3.99 (m, 1H), 3.91 (d, 1H, *J*=2.3 Hz), 3.75–3.69 (m, 4H), 3.47–3.42 (m, 1H), 1.62–1.58 (m, 2H), 1.33–1.27 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.5, 166.4, 166.0, 133.8, 133.7, 130.2, 130.1, 130.0, 129.9, 129.8, 129.0, 128.4, 106.1, 102.4, 102.2, 83.7, 83.5, 82.1, 76.6, 76.4, 68.0, 67.7, 65.1, 65.0, 56.5 (2), 56.2 (2), 32.2, 29.8, 29.8, 29.6, 26.4, 23.1, 14.5; $^1J_{C1,H1}$=168.4, 167.9; HR-ESI-MS calcd for $[C_{44}H_{50}O_{14}]Na^+$ 825.3093, found 825.3161.

4.1.18. Octyl 5-*O*-(2,3-anhydro-α-D-ribofuranosyl)-α-D-arabinofuranoside (27). To a solution of **24** (90 mg, 0.13 mmol) in dry CH_3OH (10 mL), was added a 0.1 M solution of $NaOCH_3$ in CH_3OH until the pH of the solution was 11. The reaction mixture was stirred at rt overnight and then neutralized with few drops of acetic acid. The solution was concentrated and the residue was purified by chromatography (CH_2Cl_2/CH_3OH, 8:1) to give **27** (45 mg, 92%) as a colorless oil: R_f 0.65 (CH_2Cl_2/CH_3OH, 6:1); $[\alpha]_D$ +97.6 (*c* 0.7, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 5.34 (s, 1H), 5.01 (s, 1H), 4.35 (dd, 1H, *J*=3.8, 3.8 Hz), 4.19 (d, 1H, *J*=2.1 Hz), 4.05 (d, 1H, *J*=10.5 Hz), 4.00–3.96 (m, 1H), 3.89 (dd, 1H, *J*=2.5, 10.7 Hz), 3.85–3.83 (m, 2H), 3.75–3.64 (m, 3H), 3.46–3.40 (m, 1H), 3.11 (d, 1H, *J*=10.8 Hz), 1.58–1.55 (m, 2H), 1.28–1.27 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 108.7, 101.7, 86.3, 79.9, 79.7, 78.7, 68.4, 68.1, 63.3, 58.0, 57.1, 32.2, 29.9, 29.7, 29.6, 26.5, 23.0, 14.5; HR-ESI-MS calcd for $[C_{18}H_{32}O_8]Na^+$ 399.1989, found 399.2004.

4.1.19. Octyl 3-*O*-(2,3-anhydro-α-D-ribofuranosyl)-α-D-arabinofuranoside (28). Disaccharide **25** (130 mg, 0.19 mmol) dissolved in dry CH_3OH (20 mL) was debenzoylated with a 0.1 M solution of $NaOCH_3$ in CH_3OH as described for the synthesis of **27**. The product was purified by chromatography (CH_2Cl_2/CH_3OH, 10:1) to give **28** (70 mg, 98%) as a colorless oil: R_f 0.67 (CH_2Cl_2/CH_3OH, 6:1); $[\alpha]_D$ +100.2 (*c* 0.6, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 5.51 (s, 1H), 4.92 (s, 1H), 4.32 (m, 1H), 4.20–4.10 (m, 3H), 3.86–3.85 (m, 3H), 3.75 (m, 1H), 3.68 (d, 1H, *J*=2.7 Hz), 3.67–3.63 (m, 2H), 3.41–3.38 (m, 1H), 1.59–1.55 (m, 2H), 1.28–1.27 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 108.1, 101.9, 84.0, 82.3, 81.1, 79.8, 68.2, 63.1, 61.0, 56.8 (2), 32.2, 29.9, 29.8, 29.7, 26.5, 23.0, 14.5; HR-ESI-MS calcd for $C_{18}H_{32}O_8]Na^+$ 399.1989, found 399.1980.

4.1.20. Octyl 3,5-di-*O*-(2,3-anhydro-α-D-ribofuranosyl)-α-D-arabinofuranoside (29). Trisaccharide **26** (70 mg, 0.08 mmol) dissolved in dry CH_3OH (10 mL) was debenzoylated with a 0.1 M solution of $NaOCH_3$ in CH_3OH as described for the synthesis of **27**. The product was purified by chromatography (CH_2Cl_2/CH_3OH, 6:1) to give **29** (35 mg, 89%) as a colorless oil: R_f 0.60 (CH_2Cl_2/

CH_3OH, 6:1); $[\alpha]_D$ +68.9 (*c* 1.0, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 5.46 (s, 1H), 5.37 (s, 1H), 4.95 (s, 1H), 4.34–4.31 (m, 2H), 4.22–4.17 (m, 3H), 4.11–4.08 (m, 1H), 3.91–3.85 (m, 3H), 3.75–3.62 (m, 6H), 3.43–3.37 (m, 1H), 1.58–1.55 (m, 2H), 1.28–1.26 (m, 10H), 0.89–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 108.4, 102.4, 102.0, 84.7, 81.8, 80.8, 79.8, 79.6, 68.3 (2), 63.2 (2), 57.5, 57.1, 56.7 (2), 32.2, 29.9, 29.8, 29.7, 26.4, 23.1, 14.5; HR-ESI-MS calcd for $[C_{23}H_{38}O_{11}]Na^+$ 513.2306, found 513.2289.

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