Synthesis of Oligoarabinofuranosides from the Mycobacterial Cell Wall

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Oligoarabinofuranosides **1–4**, fragments of the arabinan components found in the mycobacterial cell wall have been synthesized. **1** and **2** are representative of the structural features of the internal core of arabinogalactan, arabinomannan and lipoarabinomannans. **3** is the capping motif of the lipoarabinomannan of *Mycobacterium tuberculosis* and *M. bovis* BCG while **4** is the hexasaccharide found at the non-reducing end of arabinogalactan. Complete stereocontrol was achieved for the elaboration of glycosidic linkages between arabinofuranoside units: α-glycosides were obtained by participation of an ester or carbonate group on the 2-position, while β-arabinofuranosides were secured by an internal aglycon delivery approach.

Introduction

Tuberculosis remains a major worldwide health problem taking millions of lives annually. *Mycobacterium tuberculosis*, the causative agent of human tuberculosis, and *M. leprae*, responsible for leprosy, are the two major pathogens of the mycobacterium genus. The development of new drugs against these infections implies a more precise definition of therapeutic targets. Among them, the mycobacterial arabinan biosynthetic pathway[1] has already been identified as the site of action of ethambutol, a first line antituberculosis drug.[2−5] It is a very promising target as D-arabinose is not used by the human host. In the mycobacterial cell wall, D-arabinose is found in arabinogalactan (AG) and lipoglycans: lipoarabinomannan (LAM) and arabinomannan (AM).[6,7] AG is the major component by weight of the cell wall, it is covalently linked to the peptidoglycan and carries at its ends, the mycolic acids.[8] LAM is a major antigen with various biological properties, depending on the mycobacterial species.[9−11] Although the structural models of the arabinan domain of AG and LAM show small differences, in these compounds, D-arabinose occurs as oligomers of furanosides. The core of the arabinan domain is a chain with α-(1→5)-linked units (squares, see Figure 1) and α-(1→3)-α-(1→5) branching points (diamonds). At the end of the domain are found β-(1→2)-arabinofuranosides (triangles). Two structures have been characterized at the non-reducing end of the arabinan chains. In AG, only branched hexasaccharidic Ara$_6$ motifs were found while in LAM, both linear Ara$_4$ and branched Ara$_6$ were identified (see dotted lines, Figure 1). In LAM, the terminal units (triangles) are substituted on the 5-position by small motifs, called caps, which have been shown to be dependent on the mycobacterial species and crucial for biological activity. The caps of LAM isolated from *M. tuberculosis* and *M. bovis* BCG are mono-, di- and tri-α-(1→2)-mannopyranosides,[12−14] while caps of LAM of *M. smegmatis*, a nonpathogenic species, are inositol phosphates.[15] In AG, about two thirds of both last units (triangles and circles) are esterified on their 5-position by the mycolic acids.[5,16] The development of an arabinosyl transferase assay[4,17,18] has followed the isolation of a mycobacterial arabinose donor.[19] It allows in vitro testing of inhibitors with synthetic oligoarabinofuranosidic acceptors and prompted renewed interest in oligoarabinofuranoside construction.[18,20−27]

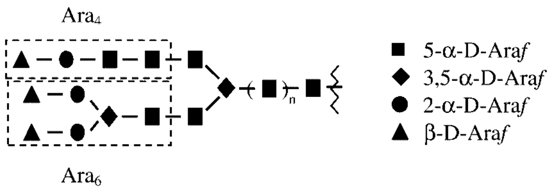

Figure 1. Schematic representation of mycobacterial arabinans

Completing our previous work,[22,23] we describe here the preparation of oligoarabinofuranosides **1−4**, representative of all structural features found in mycobacterial arabinans (Figure 2). Compounds **1−4** were efficiently obtained from previously reported building blocks **5−12** (Figure 3) prepared from 1,2,5-orthoesters of D-arabinose.[27] We have now in hand a comprehensive system for the stereoselective synthesis of any possible glycosidic linkage between oligoarabinofuranosidic units.

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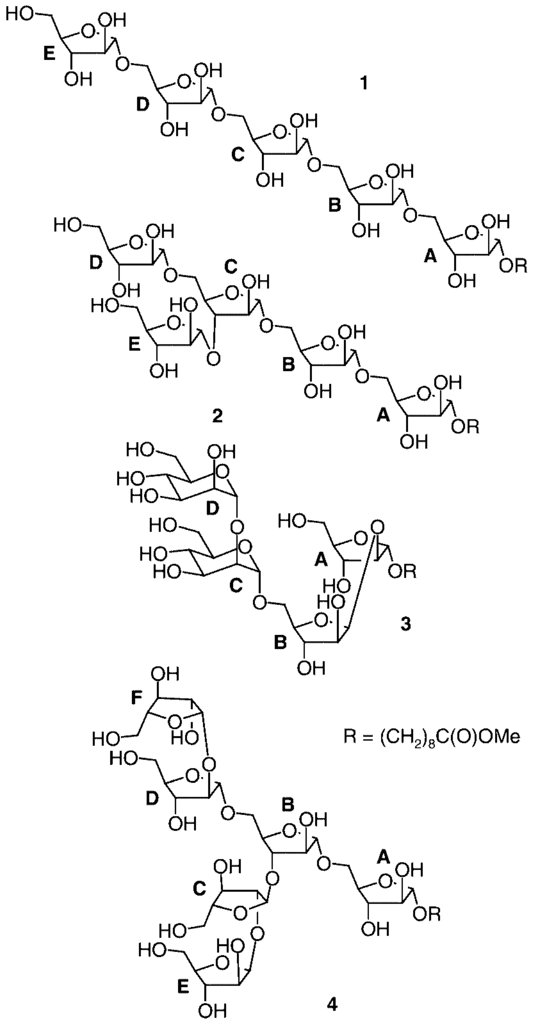


Figure 2. Structural formulas and ring lettering conventions for targeted oligosaccharides **1**−**4**

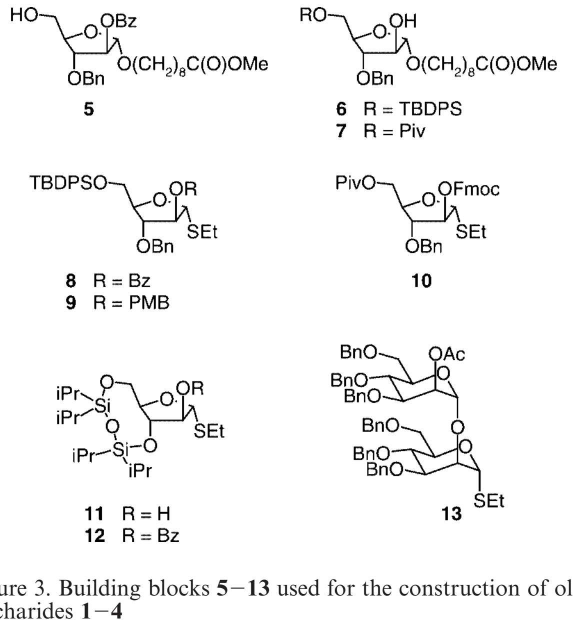
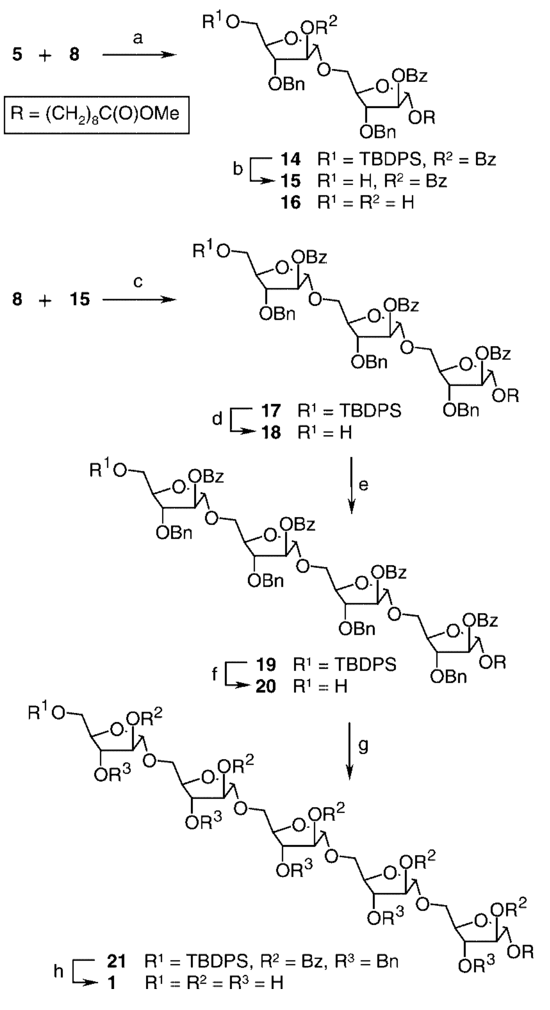


Figure 3. Building blocks **5**−**13** used for the construction of oligosaccharides **1**−**4**

Synthesis of Fragments of the Internal Arabinan Core

Two pentasaccharides, **1** and **2**, found in the internal core of the arabinan domain of AG and LAMs were made. As only α-glycosidic bonds are found in this part, synthetic work was straightforward and required only α-donors **8** and **12** (Figure 3). **8** was used for the introduction of the 5-glycosylated units while **12** was chosen for introduction of the 3,5-branching points. Compound **12** was obtained in quantitative yield by benzoylation of the known alcohol **11**[21] with benzoyl chloride in pyridine.

The synthesis of both **1** and **2** began with glycosylation of acceptor **5** with 1.1 equiv. of thioglycoside donor **8** under *N*-iodosuccinimide (NIS) and catalytic trimethylsilyl tri-

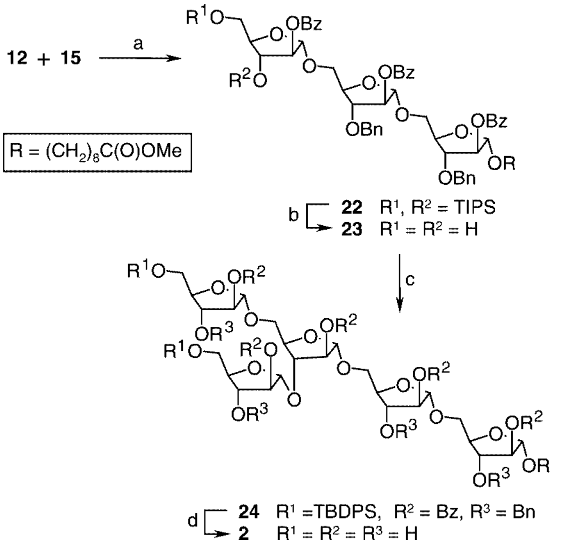


Scheme 1. Synthesis of **1**: a: 1.0 equiv. **5**, 1.1 equiv. **8**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 40 min, 90%; b: HCl, MeOH/Et_2O, room temp., overnight, 86%; c: 1.0 equiv. **15**, 1.1 equiv. **8**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 77%; d: same as b, 36 h, 90%; e: 1.0 equiv. **18**, 1.2 equiv. **8**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 90%; f: same as b, 24 h, 79%; g: 1.0 equiv. **20**, 1.2 equiv. **8**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 90%; h: Bu_4NF, THF, room temp., 3 h, then MeONa, MeOH, room temp., 1.5 h, then H_2, $Pd(OH)_2/C$, MeOH, 0.08 M HCl, 6 h, 65% (three steps)

fluoromethanesulfonate (TMSOTf)[28] activation in CH_2Cl_2 at −15 °C (Scheme 1). α-Disaccharide **14** was obtained in 90% isolated yield and as a single anomer ($\delta_{1B\text{-}H}$ = 5.28 ppm, $^3J_{1B,2B}$ < 0.5 Hz; $\delta_{C\text{-}1B}$ = 105.9 ppm).[29] Removal of the *tert*-butyldiphenylsilyl group with commercial tetrabutylammonium fluoride (Bu_4NF) in THF (1 M solution) gave disaccharide **15** but in a disappointing 60% yield. The main by-product, isolated in 25% yield from the reaction, was diol **16**, where the 2B-benzoyl group has been removed together with the 5B-silyl group (see Figure 2 for the lettering of the rings of oligoarabinofuranosides). This very easy debenzoylation was probably induced by the proximity of the 5B-hydroxy group, liberated during the desilylation reaction, and the slightly basic nature of the reagent. To eliminate this side-reaction, commercial Bu_4NF solution in THF was treated with trifluoroacetic acid until neutrality (pH paper). This reagent was found to give much cleaner reaction in the deprotection of **14** but a considerable loss of reactivity was observed. **15** was obtained in 80% yield but the reaction took 24 h at room temp to go to completion. Finally, desilylation with HCl in a 1:1 diethyl ether/methanol solution[30] was found to be very convenient in terms of selectivity and reaction time, **15** was thus obtained from **14** in 86% yield after overnight reaction at room temperature.

For the synthesis of linear pentasaccharide **1**, **15** was glycosylated with 1.1 equiv. of thioglycoside **8** to give trisaccharide **17** in 77% yield (Scheme 1). Two more cycles of desilylation/glycosylation with compound **8** gave linear tetrasaccharide **19** (81% for the two steps from **17**) and pentasaccharide **21** (71% from **19**). Finally, compound **1** was isolated in 65% yield after three steps of deprotection [commercial Bu_4NF in THF, sodium methoxide in methanol and catalytic hydrogenation in acidic methanol with $Pd(OH)_2/C$ as catalyst].

Branched pentasaccharide **2** was also prepared from **15** by using thioglycoside donor **12** instead of **8** for the introduction of the branching unit C of **2**. Trisaccharide **22** was obtained in 81% yield by reaction of **15** with 1.1 equiv. of **12** under NIS/catalytic TMSOTf activation (Scheme 2). In this case also, the reaction was completely stereoselective and only the α-product was isolated ($\delta_{1C\text{-}H}$ = 5.04 ppm, $^3J_{1C,2C}$ = 1.5 Hz, $\delta_{C\text{-}1C}$ = 105.7 ppm). The TIPS group of **22** was removed (commercial Bu_4NF in THF, 95%) and the resulting diol **23** was bis(α-glycosylated) with 3 equiv. of thioglycoside donor **8** to afford pentaarabinofuranoside **24** in 81% yield. A three-step deprotection sequence (Bu_4NF in THF, NaOMe in MeOH and hydrogenolysis with Pd/C as catalyst) gave pentasaccharide **2** in 63% overall yield.



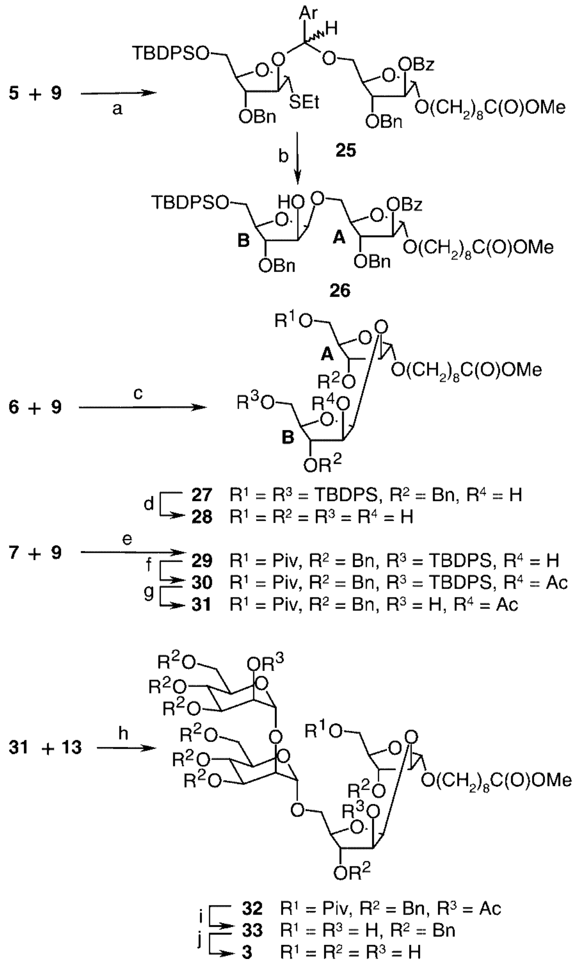
Scheme 2. Synthesis of **2**: a: 1.0 equiv. **15**, 1.1 equiv. **12**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 81%; b: Bu_4NF, THF, room temp., 3 h, 95%; c: 1.0 equiv. **23**, 3 equiv. **8**, 4.0 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 81%; d: Bu_4NF, THF, room temp., 3 h, then NaOMe, MeOH, room temp., 1.5 h, then H_2, Pd/C, MeOH, overnight, 63% (three steps)

Synthesis of β-Arabinofuranosides

After the internal core of mycobacterial arabinans, we embarked on the more challenging synthesis of the terminal β-(1→2)-linkage. Among the numerous methods described for the preparation of 1,2-*cis*-glycosidic linkages,[31,32] we chose to look at Ogawa's internal aglycon delivery approach (IAD)[33,34] for a general synthesis of β-arabinofuranosides.[21−23] Examples of its use for the synthesis of β-D-fructofuranosides have been described.[35,36]

We first tested the method for the formation of β-(1→5)-linkage between arabinofuranosidic units. According to the described protocol,[33,37] acceptor with a free 5-OH group **5** (1 equiv.) and β-donor **9** (1.05 equiv.) were treated with 1.5 equiv. of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in CH_2Cl_2 to give acetal **25**, isolated in 66% yield as a mixture of diastereoisomers on the acetalic carbon atom (Scheme 3). Intramolecular glycosylation of **25** was promoted by 1.2 equiv. of iodonium dicollidine perchlorate (IDCP) in CH_2Cl_2 and gave the β-(1→5)-linked diarabinofuranoside **26** in 79% isolated yield. In order to obtain such a yield, it was found necessary to hydrolyze some 4-methoxybenzaldehyde derivatives, still present after treatment and extraction of the glycosylation reaction. This was done by hydrolysis with catalytic amounts of DDQ in wet acetonitrile.[38] No other disaccharide was isolated and assignment of the β-(D) configuration to the new anomeric center was unambiguously deduced from ^1H and ^{13}C NMR spectroscopic data of **26** in $CDCl_3$. The signal for 1B-H (see Scheme 3) was found at δ = 4.91 ppm in the ^1H NMR spectrum, with a $^3J_{1B,2B}$ coupling constant of 4.5 Hz while C-1B resonated at δ = 102.1 ppm, which are typical values for β-arabinofuranosides.[29]

To obtain the β-(1→2)-linked diarabinofuranoside **27**, the very same sequence of reactions was carried out with β-donor **9** and acceptor with a free 2-OH group **6**. Treatment of **6** with 1.1 equiv. of **9** and 1.5 equiv. of DDQ in CH_2Cl_2 gave a mixture of acetals (75%). IDCP-promoted intramolecular glycosylation afforded the disaccharide **28** in 70% yield. Once again, the reaction was completely stereoselective and only the β-anomer was isolated ($\delta_{1B\text{-}H}$ =



Scheme 3. a: 1.0 equiv. **5**, 1.05 equiv. **9**, 1.5 equiv. DDQ, CH_2Cl_2, molecular sieves (4 Å), room temp., 3 h, 66%; b: 1.2 equiv. IDCP, CH_2Cl_2, molecular sieves (4 Å), room temp., 2 h, 79%; c: 1.0 equiv. **6**, 1.2 equiv. **9**, 1.5 equiv. DDQ, CH_2Cl_2, molecular sieves (4 Å), room temp., 2 h, 75% then 1.2 equiv. IDCP, CH_2Cl_2, molecular sieves (4 Å), room temp., 2 h, 70%; d: Bu_4NF, THF, room temp., 1 h then H_2, Pd/C, EtOAc/MeOH, room temp., 60%, 2 steps; e: 1.0 equiv. **7**, 1.1 equiv. **9**, 1.5 equiv. DDQ, CH_2Cl_2, molecular sieves (4 Å), room temp., 2.5 h, 84%, then 1.2 equiv. IDCP, CH_2Cl_2, molecular sieves (4 Å), room temp., 2 h, 75%; f: Ac_2O, pyridine, room temp., overnight; g: Bu_4NF, THF, room temp., 1 h, 75%, 2 steps; h: 1.0 equiv. **31**, 1.4 equiv. **13**, 1.7 equiv. NIS, 0.15 equiv. TMSOTf, CH_2Cl_2, molecular sieves (4 Å), −15 °C, 1 h, 77%; i: NaOMe, MeOH, room temp., 5 h, 50%; j: H_2, Pd/C, MeOH, room temp., 1 h, 65%

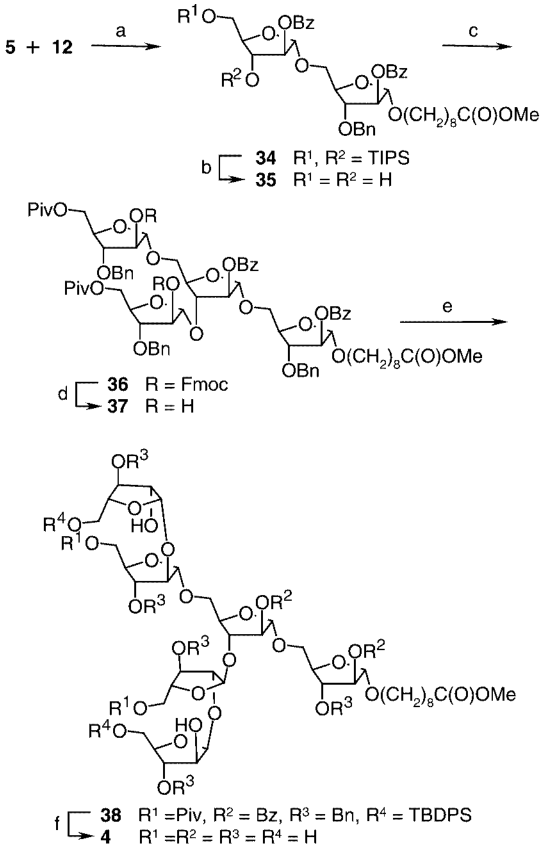
5.14 ppm, $^3J_{1B,2B} = 4.5$ Hz, $\delta_{C\text{-}1B} = 101.4$ ppm). This compound was deprotected in two steps: silyl groups were removed with Bu_4NF in THF and benzyl ethers were hydrogenolyzed with H_2 and 10% Pd/C. This gave a 60% yield of the β-(1→2)-diarabinofuranoside **28**.

Synthesis of the Caps of the LAM of *Mycobacterium tuberculosis*[22]

With the β-(1→2)-diarabinofuranoside in hand, **3**, the major tetrasaccharidic caps of the LAM of *M. tuberculosis* and *M. bovis* BCG were accessible. A convergent strategy was chosen and involved coupling dimannosidic thioglycoside donor **13** (Figure 3) with an appropriate β-(1→2)-diarabinofuranoside acceptor having a hydroxy group in 5B-position. **13** was prepared according to a procedure first described by Ley.[39,40] To obtain the diarabinofuranoside coupling partner, the strategy described above for the preparation of **28** was applied with the pivalate-protected acceptor **7** (Figure 3) instead of **6** to allow selective unmasking of the 5B-position of the intermediate β-(1→2)-diarabinofuranoside. Coupling of building blocks **7** and **9** was done as above with Ogawa's 2-steps procedure and gave **29** in 63% overall yield (Scheme 3). The 2B-hydroxy group of **29** was protected as an acetate with acetic anhydride in pyridine and removal of the TBDPS group of **30** with Bu_4NF in THF gave diarabinofuranoside **31**, isolated in 76% yield for the two steps. Tetrasaccharide **32** was obtained from glycosylation of **31** with 1.5 equiv. of thiodimannoside **13** promoted by NIS and catalytic TMSOTf in CH_2Cl_2. **32** was isolated in 77% yield as a 4:1 α/β mixture on the C-1C anomeric center. Despite the absence of a participating group on the 2C-position of the thiomannosidic donor **13**, an acceptable diastereoselectivity was obtained for the glycosylation at −15 °C, the difficult α-mannosylation of the 5-position of a β-arabinofuranoside has been reported during the synthesis of a related compound.[41] As chromatographic separation of the two anomers could not be obtained at this stage, the mixture of tetrasaccharides was deacylated with sodium methoxide in methanol to a mixture of triols, from which the required α-anomer **33** was isolated. Finally, hydrogenolysis of the benzyl ethers (H_2, Pd/C, 65%) gave **3**, the tetrasaccharidic cap of LAM of *M. tuberculosis* and *M. bovis* BCG.

Synthesis of the Terminal Hexasaccharide of the Arabinan Core of Arabinogalactan

The last characteristic structural feature of mycobacterial arabinans is **4**, the terminal hexaarabinoside found at the non-reducing end of the arabinan domain of AG. In light of the symmetric structure of **4**, the most convergent approach was chosen for its synthesis and involved two successive bis(glycosylations). Firstly, for the introduction of the two α-(1→3)- and α-(1→5)-arabinofuranosides (units C and D, Figure 2) on disaccharide A−B, and later in the synthesis, for the simultaneous formation of the two β-(1→2)-arabinosides E and F. This approach has been successfully applied for the preparation of a related pentaarabinoside motif.[23] Fmoc-protected α-donor **10** was selected for the introduction of units C and D on disaccharide A−B (Figure 1). The Fmoc group will participate during the glycosylation, securing the requested α-configuration for the C→B and D→B linkages, while it can be easily and selectively removed in the presence of benzoate and pivalate esters.[42] This will allow the unmasking of the 2-hydroxy groups of units C and D prior to the β-glycosylations. Disaccharide **34** was obtained in 87% yield from coupling of **5** with 1.2 equiv. of thioglycoside donor **12** under NIS/catalytic TMSOTf activation (Scheme 4). The TIPS group was removed (commercial Bu_4NF, THF) and diarabinofuranoside **35** was isolated in 98% yield. Treatment of acceptor **35** with 2.7 equiv. of thioglycoside α-donor **10** under NIS/TMSOTf activation afforded the tetrasaccharide **36** which was not isolated in pure form. Crude **36** was dissolved in a 4:1 THF/Et_3N mixture to achieve the deprotection of the Fmoc groups and diol **37** was isolated in 75% for the two steps. This bis(α-glycosylation) was completely selective and this was ascertained from the NMR spectroscopic data. Two new anomeric signals were observed in the NMR spectra. In the ^1H NMR spectrum, 1C-H was found as a doublet ($^3J_{1C,2C}$ = 1.1 Hz) at δ = 4.98 ppm while 1D-H resonated as a broad singlet at δ = 5.07 ppm. These two proton signals were correlated with carbon signals found at δ = 108.5 (C-1C) and 108.3 (C-1D) ppm in the ^{13}C NMR spectrum.[29] **37** was then treated with 3 equiv. of β-donor **9** and 3 equiv. of DDQ in CH_2Cl_2 to yield a mixture of diastereoisomeric bis(acetals) in 83% yield isolated yield. This mixture was treated with IDCP (3 equiv.) for 24 h at room temperature. After DDQ treatment, the expected hexasaccharide **38** was obtained in a moderate yield of 33%, no other hexasaccharide was isolated. Two new anomeric signals corresponding to β-arabinofuranosides were found in the NMR spectra. The first one was observed in the ^1H NMR spectrum at δ = 5.11 ppm ($^3J_{1F,2F}$ = 4.7 Hz) and was correlated to a carbon signal at δ_C = 101.6 ppm, while the other β-anomeric proton resonated at δ = 5.21 ppm ($^3J_{1E,2E}$ = 4.7 Hz) and was correlated with a carbon signal at δ = 102.2 ppm. Although moderate, this yield might have been anticipated from calculations made using our previous results for the formation of β-(1→2)-arabinofuranosides. Extrapolation from the observed yields for synthesis of **27** and **29** would have given 27 and 39%, respectively, for the bis(β-glycosylation). This result clearly shows the limitation of Ogawa's internal aglycon delivery approach for the construction of more complex oligoarabinofuranosidic structures by simultaneous polyglycosylations. Final deprotection of **38** in three steps [Bu_4NF/THF, NaOMe in MeOH and H_2 with $Pd(OH)_2/C$] gave the terminal hexaarabinofuranoside of arabinogalactan **4** in 30% overall yield.



Scheme 4. a: 1 equiv. **5**, 1.2 equiv. **12**, 1.3 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (3 Å), 0 °C to room temp., 1 h, 87%; b: Bu_4NF, THF, room temp., 2 h, 98%; c: 1.0 equiv. **35**, 2.7 equiv. **10**, 4.0 equiv. NIS, 0.1 equiv. TMSOTf, CH_2Cl_2, molecular sieves (3 Å), 0 °C to room temp., 1 h; d: 4:1 THF/Et_3N, room temp., 2 h, 75%, 2 steps; e: 1.0 equiv. **37**, 3 equiv. **9**, 3 equiv. DDQ, CH_2Cl_2, molecular sieves (4 Å), 0 °C to room temp., 4 h, then 3.0 equiv. IDCP, CH_2Cl_2, molecular sieves (4 Å), room temp., 24 h, 27%, 2 steps; f: Bu_4NF, THF, room temp., overnight, then MeONa, MeOH, room temp., 22 h, then H_2, $Pd(OH)_2/C$, MeOH, 0.08 M HCl, 30% (three steps)

Conclusion

Oligosaccharides **1−4**, representative of the structural diversity found in the arabinans of the mycobacterial cell wall have been synthesized. Their elaboration relies on the efficient preparation of the various required building blocks and the complete control of the stereochemical outcome of the glycosylation reactions. Monoarabinofuranosidic units, donors and acceptors, were all derived from 1,2,5-orthoesters of D-arabinose.[27] Esters or carbonates efficiently directed the formation of α-glycosides while the more challenging synthesis of β-arabinofuranosides was solved by an internal aglycon delivery approach. Together with our previous results,[22,23] we have now a comprehensive glycosylation system which allows the synthesis of any possible oligoarabinofuranosidic structure and makes these compounds readily accessible for biochemical studies.

Experimental Section

General: All reactions were run under argon in oven-dried glassware. Anhydrous solvents were distilled before use. Commercial reagents were used as received. Chromatographic separations were run on silica gel (35−70 μm) obtained from SDS (Peypin, France). NMR spectra were recorded with Bruker AM 250, Avance DPX 400 and DMX 500 spectrometers, working at 250 MHz (400 MHz and 500 MHz, respectively) for ^1H NMR and 62.89 MHz (100.62 and 125.72 MHz, respectively) for ^{13}C NMR. All chemical shifts are expressed in ppm from internal tetramethylsilane. Assignment of signals for oligosaccharides were deduced from HOHAHA and HMQC experiments. Optical rotations were measured at 25 °C with a Perkin−Elmer 41 polarimeter. Elemental analyses were obtained from the Laboratoire de Chimie de Coordination du CNRS at Toulouse (France). High resolution mass data were obtained from the Centre d'Etudes Structurale et d'Analyse des Molécules Organiques at Talence (France) and the Centre de Spectrométrie de Masse of Université Claude Bernard at Lyon (France).

General Procedure for α-Glycosylation with NIS/TMSOTf: Acceptor (0.02−0.2 M solution) and thioglycoside donor (1.1−1.3

equiv.) were dissolved in CH_2Cl_2 in the presence of activated powdered molecular sieves (3 or 4 Å). The mixture was stirred for 20 min at room temperature. The temperature was lowered to −15 °C before addition of NIS (1.3 equiv.) and TMSOTf (0.1 equiv. as a 1 M solution in toluene or CH_2Cl_2). After completion of the reaction (TLC), the mixture was neutralized with a few drops of Et_3N and hydrolyzed with dilute aqueous $Na_2S_2O_3$ solution. The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic phases were dried with $MgSO_4$. Evaporation of the solvent and chromatography gave the product.

General Procedure for β-Glycosylation: Acceptor (0.04−0.05 M) and donor (1.05−1.2 equiv.) were dissolved in CH_2Cl_2, powdered molecular sieves (4 Å) was added and the reaction mixture was stirred for 20 min at room temperature. The temperature was lowered to 0 °C before addition of DDQ (1.5 equiv.) and the reaction was left at room temp. After completion (TLC), the reaction mixture was treated according to Ogawa's protocol:[33] neutralization with an ascorbic acid/citric acid/NaOH solution, filtration through Celite (CH_2Cl_2 elution) and washings of the organic phase with water and brine. Chromatography of the residue gave the mixture of acetals. These acetals were taken up in CH_2Cl_2 containing powdered molecular sieves (4 Å) and stirred for 20 min at room temperature before addition of IDCP (1.2 equiv.). After completion of the reaction (TLC, 2−24 h), the mixture was filtered through Celite (CH_2Cl_2 elution) and the organic phase was hydrolyzed with saturated aqueous $Na_2S_2O_3$ solution, washed once with water and dried with $MgSO_4$. After evaporation of the solvent, the residue was filtered through silica, taken up in wet acetonitrile (CH_3CN/H_2O, 9:1) and treated with DDQ (0.1 equiv.) at room temperature for 4 h.[38] Evaporation of the solvents and chromatography gave the product.

Preparation of Neutralized Bu_4NF: Commercial 1 M solution of Bu_4NF in THF was treated dropwise with CF_3COOH until a pH of 7 was obtained according to a pH paper.

General Procedure for Desilylation with Bu_4NF: The silyl ether was dissolved in THF (0.02−0.05 M) and treated at room temperature with a 1 M solution of Bu_4NF in THF (1.2−1.5 equiv. for each silyl group). After completion of the reaction (TLC), the solvent was evaporated. CH_2Cl_2/water extraction and chromatography gave the product.

General Procedure for Desilylation with HCl in Methanol: The silyl ether (final concentration 0.009−0.015 M) was treated at room temperature with a 0.28 M solution of HCl in diethyl ether/methanol (1:1, v/v). After completion of the reaction, the mixture was neutralized with saturated aqueous $NaHCO_3$. CH_2Cl_2/water extraction and chromatography gave the product.

General Procedure for Debenzoylation: The oligosaccharide (0.1 M) was dissolved in a 0.1 M solution of sodium methoxide in methanol at room temperature. In some cases, a small amount of THF was added to effect complete solubilisation of the product. The mixture was left at room temperature until completion of the reaction (2−22 h) and neutralized with H^+ resin. Filtration of the resin, concentration of the filtrate and chromatography gave the product.

General Procedures for Debenzylation

Procedure A: Benzyl ether (0.15 M) was dissolved in methanol and hydrogenolyzed in the presence of 10% Pd/C overnight at room temperature. Filtration of the mixture, concentration of the filtrate and chromatography gave the product.

Procedure B: Benzyl ether (0.04−0.13 M) was dissolved in a 0.08 M methanolic solution of HCl and hydrogenolyzed in the presence of 10% $Pd(OH)_2/C$ at room temperature (1−4 h). The reaction mixture was neutralized with aqueous K_2CO_3 and filtered. Concentration of the filtrate and chromatography gave the product.

Ethyl 2-*O*-Benzoyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-1-thio-α-D-arabinofuranoside (12): Ethyl 3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-1-thio-α-D-arabinofuranoside (**11**)[21] (1.60 g, 3.66 mmol) was dissolved in pyridine (7 mL) and treated at room temperature with benzoyl chloride (640 μL, 5.51 mmol) for 3 h. The pyridine was evaporated and the residue partitioned between CH_2Cl_2 and water. The organic phase was decanted and the water phase extracted once with CH_2Cl_2. Chromatography (petroleum ether/ethyl acetate, 15:1) gave **12** as a colorless oil (1.96 g, quantitative). $[\alpha]_D^{25} = +27$ ($c = 1.20$ in chloroform). ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 0.90-1.17$ [m, 28 H, $(CH_3)_2CH$], 2.28 (t, $^3J = 7.5$ Hz, 3 H, SCH_2CH_3), 2.57−2.82 (m, 2 H, SCH_2CH_3), 4.03 (dd, $^2J_{5,5} = 12.5$, $^3J_{5,4} = 4.0$ Hz, 1 H, 5-H), 4.09 (dd, $^3J_{5,4} = 3$ Hz, 1 H, 5-H), 4.15 (m, 1 H, 4-H), 4.56 (dd, $^3J_{3,4} = 8$, $^3J_{3,2} = 5.5$ Hz, 1 H, 3-H), 5.30 (d, $^3J_{1,2} = 3.5$ Hz, 1 H, 1-H), 5.42 (dd, 1 H, 2-H), 7.42−8.08 (m, 5 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): $\delta = 12.4$, 12.7, 13.1, 13.3, 13.4, 13.5 [$(CH_3)_2CH$], 14.7 (SCH_2CH_3), 16.9, 17.0, 17.2, 17.3, 17.4 [$CH(CH_3)_2$], 25.3 (SCH_2CH_3), 61.0 (C-5), 75.2 (C-4), 80.1 (C-3), 83.7 (C-2), 86.4 (C-1), 129.3, 129.7, 133.3 (Ar), 165.5 (COOPh) ppm. $C_{26}H_{44}O_6SSi$ (540.9): calcd. C 57.74, H 8.20; found C 57.58, H 8.22.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranoside (14): From **5** (99.1 mg, 0.19 mmol) and **8** (133.0 mg, 0.21 mmol). Chromatography with petroleum ether/EtOAc (5:1) gave **14** as a colorless oil (187.6 mg, 90%). $[\alpha]_D^{25} = +65$ ($c = 1.09$ in chloroform). ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 0.97$ [s, 9 H, $C(CH_3)_3$], 1.23−1.40 (m, 8 H, octyl CH_2), 1.53−1.64 (m, 4 H, octyl CH_2), 2.29 (t, $^3J = 7.5$ Hz, 2 H, CH_2CO), 3.46 (td, $^2J = 9.5$, $^3J = 7.0$ Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.67−3.79 (m, 4 H, 5A-H, 2 × 5B-H, octyl OCH_2), 3.92 (dd, $^2J_{5A,5A} = 11.5$, $^3J_{5A,4A} = 4$ Hz, 1 H, 5A-H), 4.05−4.18 (m, 3 H, 3A-H, 3B-H, 4B-H), 4.33 (m, 1 H, 4A-H), 4.45, 4.59, 4.63, 4.77 (4d, $^2J = 12.0$ Hz, 4 × 1 H, benzyl CH_2), 5.13 (s, 1 H, 1A-H), 5.28 (s, 1B-H), 5.38 (d, $^3J_{2A,3A} = 1.5$ Hz, 1 H, 2A-H), 5.43 (d, $^3J_{2B,3B} = 0.7$ Hz, 1 H, 2B-H), 7.12−8.10 (m, 20 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): $\delta = 19.3$ [$C(CH_3)_3$], 24.9, 26.0, 26.7, 29.1, 29.2, 29.4 (octyl CH_2), 34.1 (CH_2CO), 51.4 (CH_3O), 63.0, 65.4, 67.5 (octyl OCH_2), 72.0, 72.3 (benzyl CH_2), 81.4, 81.9, 82.1, 83.0, 83.3, 83.7, 105.9 (C-1B), 106.1 (C-1A), 127.7, 127.8, 128.3, 128.4, 128.5, 129.5, 129.6, 129.8, 133.3, 133.6 (Ar) ppm. $C_{64}H_{74}O_{13}Si$ (1079.4) calcd. C 71.22, H 6.91; found C 71.04, H 6.64.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranoside (15): From **14** (124.1 mg, 0.11 mmoles) by treatment with HCl in $MeOH/Et_2O$ according to the General Procedure. Chromatography with petroleum ether/EtOAc (2:1) gave **15** as a colorless oil (83.6 mg, 86%). $[\alpha]_D^{25} = +82$ ($c = 0.49$ in chloroform). ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 1.25-1.40$ (m, 8 H, octyl CH_2), 1.55−1.66 (m, 4 H, octyl CH_2), 2.29 (t, $^3J = 7.5$ Hz, 2 H, CH_2CO), 3.47 (td, $^2J = 9.5$, $^3J = 7$ Hz, 1 H, octyl OCH_2), 3.49−3.61 (m, 1 H, 5B-H), 3.66 (s, 3 H, CH_3O), 3.67−3.83 (m, 3 H, 5A-H, 5B-H, octyl OCH_2), 3.92 (dd, $^2J_{5A,5A} = 11.5$, $^3J_{5A,4A} = 5.5$ Hz, 1 H, 5A-H), 3.97 (br. d, $^3J_{3B,4B} = 5.5$ Hz, 1 H, 3B-H), 4.07 (m, 1 H, 4B-H), 4.16 (br. d, $^3J_{3A,4A} = 6.0$ Hz, 1 H, 3A-H), 4.34 (m, 1 H, 4A-H), 4.47, 4.62, 4.65, 4.82 (4d, $^2J = 12.0$ Hz, 4 × 1 H, benzyl CH_2), 5.16 (s, 1 H, 1A-H), 5.28 (s, 1 H, 1B-H), 5.39 (m, 2 H, 2A-H, 2B-H), 7.14−8.08 (m, 20 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): $\delta = 24.9$, 26.0, 29.1, 29.2, 29.4 (octyl CH_2), 34.1

(CH_2CO), 61.9 (C-5B), 67.6 (octyl OCH_2), 72.2, 72.3 (benzyl CH_2), 81.4, 81.7, 82.0, 82.8, 83.2, 83.3, 106.0 (C-1B), 106.2 (C-1A), 127.7, 127.9, 128.4, 128.5, 129.7, 129.8, 133.3, 133.5 (Ar) ppm. $C_{48}H_{56}O_{13}$ (840.9): calcd. C 68.56, H 6.71; found C 68.59, H 6.89.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (17): From **15** (100.0 mg, 0.12 mmol) and **8** (82.0 mg, 0.13 mmol). Chromatography with petroleum ether/EtOAc (4:1) gave **17** a colorless oil (129 mg, 77%). $[\alpha]_D^{25} = +76$ (c = 0.89 in chloroform). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.96 [s, 9 H, $C(CH_3)_3$], 1.22−1.39 (m, 8 H, octyl CH_2), 1.56−1.66 (m, 4 H, octyl CH_2), 2.29 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 3.45 (td, ^2J = 9.7, ^3J = 6.7 Hz, 1 H, octyl OCH_2), 3.66 (dd, $^2J_{5B,5B}$ = 11.3, $^3J_{5B,4B}$ = 3.6 Hz, 5B-H), 3.66 (s, 3 H, CH_3O), 3.68−3.73 (m, 4 H, 5A-H, 2 × 5C-H, octyl OCH_2), 3.84 (dd, $^3J_{5B,4B}$ = 3.8 Hz, 1 H, 5B-H), 3.92 (dd, $^2J_{5A,5A}$ = 11.2, $^3J_{5A,4A}$ = 4.1 Hz, 1 H, 5A-H), 4.00−4.03 (m, 2 H, 3C-H, 4C-H), 4.09 (br. d, $^3J_{3B,4B}$ = 5.4 Hz, 1 H, 3B-H), 4.15 (br. d, $^3J_{3A,4A}$ = 4.6 Hz, 1 H, 3A-H), 4.17 (m, 1 H, 4B-H), 4.32 (m, 1 H, 4A-H), 4.40, 4.47, 4.47, 4.56, 4.61, 4.78 (6d, ^2J = 12.2 Hz, 6 × 1 H, benzyl CH_2), 5.13 (s, 1 H, 1A-H), 5.25 (s, 1 H, 1C-H), 5.28 (s, 1 H, 1B-H), 5.38 (m, 2 H, 2A-H, 2C-H), 5.40 (d, $^3J_{2B,3B}$ = 1.2 Hz, 1 H, 2B-H), 7.10−8.05 (m, 40 H, Ar-H) ppm. ^{13}C NMR (125.78 MHz, $CDCl_3$, 20 °C): δ = 19.7 [$C(CH_3)_3$], 25.1, 26.1, 26.8, 29.2, 29.3, 29.4, 29.5 (octyl CH_2), 34.2 (CH_2CO), 51.6 (CH_3O), 63.0 (C-5C), 65.3 (C-5B), 65.6 (C-5A), 67.7 (octyl OCH_2), 72.0, 72.2, 72.4 (benzyl CH_2), 81.6 (C-4A), 81.9 (C-2A), 82.0 (C-2B), 82.1 (C-4B), 82.3 (C-2C), 83.0 (C-3C), 83.3 (C-3A, C-3B), 83.9 (C-4C), 106.0 (C-1A), 106.2 (C-1B, C-1C), 127.6, 127.7, 127.8, 128.0, 128.4, 128.5, 128.6, 129.5, 129.6, 129.8, 129.9, 133.3, 133.4, 135.7, 137.8, 137.9 (Ar), 164.7, 165.4, 165.7 ($COOPh$), 174.5 ($COOMe$) ppm. $C_{83}H_{92}O_{18}Si$ (1405.7): calcd. C 70.92, H 6.60; found C 70.74, H 6.58.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (18): **17** (252.2 mg, 0.18 mmol) was desilylated with neutralized Bu_4NF in THF according to the general procedure. Chromatography with petroleum ether/EtOAc (2:1) gave **18** as a colorless oil (189 mg, 90%). $[\alpha]_D^{25}$ = +79 (c = 0.90 in chloroform). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.24−1.40 (m, 8 H, octyl CH_2), 1.56−1.65 (m, 4 H, octyl CH_2), 1.75 (dd, $^3J_{OH,5C}$ = 8.6, $^3J_{OH,5C}$ = 4.3 Hz, 1 H, 5C-OH), 2.29 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 3.46 (td, ^2J = 9.6, ^3J = 6.4 Hz, 1 H, octyl OCH_2), 2.52 (ddd, $^2J_{5C,5C}$ = 12.4, $^3J_{5C,4C}$ = 4.0 Hz, 5C-H), 3.66 (s, 3 H, CH_3O), 3.66−3.77 (m, 4 H, 5A-H, 5B-H, 5C-H, octyl OCH_2), 3.83 (dd, $^2J_{5B,5B}$ = 11.5, $^3J_{5B,4B}$ = 4.0 Hz, 1 H, 5B-H), 3.93 (m, 1 H, 3C-H), 3.96 (dd, $^2J_{5A,5A}$ = 13.0, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 3.99 (m, 1 H, 4C-H), 4.09 (br. d, $^3J_{3B,4B}$ = 5.5 Hz, 1 H, 3B-H), 4.16 (br. d, $^3J_{3A,4A}$ = 5.6 Hz, 1 H, 3A-H), 4.19 (m, 1 H, 4B-H), 4.33 (m, 1 H, 4A-H), 4.41, 4.51, 4.57, 4.62, 4.65, 4.81 (6d, ^2J = 12.2 Hz, 6 × 1 H, benzyl CH_2), 5.14 (s, 1 H, 1A-H), 5.24 (s, 1 H, 1C-H), 5.30 (s, 1 H, 1B-H), 5.34 (d, $^3J_{2C,3C}$ = 1.1 Hz, 1 H, 2C-H), 5.39 (d, $^3J_{2A,3A}$ = 1.5 Hz, 1 H, 2A-H), 5.43 (d, $^3J_{2B,3B}$ = 1.2 Hz, 1 H, 2B-H), 7.17−8.06 (m, 30 H, Ar-H) ppm. ^{13}C NMR (125.78 MHz, $CDCl_3$, 20 °C): δ = 25.1, 26.1, 29.2, 29.3, 29.4, 29.5 (octyl CH_2), 34.2 (CH_2CO), 51.6 (CH_3O), 62.0 (C-5C), 65.6 (C-5B), 65.7 (C-5A), 67.7 (octyl OCH_2), 72.2, 72.5 (benzyl CH_2), 81.6 (C-4A), 81.8 (C-2B, C-2C), 82.1 (C-4B), 82.2 (C-2A), 82.8 (C-3C), 83.3 (C-3B), 83.4 (C-3A), 83.5 (C-4C), 106.1 (C-1A), 106.2 (C-1B), 106.3 (C-1C), 127.7, 127.8, 128.0, 128.4, 128.5, 129.4, 129.5, 129.8, 129.9, 133.5, 133.6, 137.7, 138.0 (Ar), 165.3, 165.4, 165.7($COOPh$), 174.5 ($COOMe$) ppm. HRMS (FAB): $C_{67}H_{74}O_{18}Na$: calcd. 1189.4773, found 1189.4773.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-{2-*O*-benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranoside (19): From **18** (143.0 mg, 0.12 mmol) and **8** (92.0 mg, 0.15 mmol). Chromatography with petroleum ether/EtOAc (3:1) gave **19** as a colorless oil (189.7 mg, 90%). $[\alpha]_D^{25}$ = +91 (c = 0.49 in chloroform). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.95 [s, 9 H, $C(CH_3)_3$], 1.22−1.39 (m, 8 H, octyl CH_2), 1.53−1.65 (m, 4 H, octyl CH_2), 2.29 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 3.45 (td, ^2J = 9.9, ^3J = 6.8 Hz, 1 H, octyl OCH_2), 3.63 (dd, $^2J_{5C,5C}$ = 11.4, $^3J_{5C,4C}$ = 3.5 Hz, 1 H, 5C-H), 3.65 (s, 3 H, CH_3O), 3.65−3.75 (m, 5 H, 5A-H, 2 × 5D-H, 5B-H, octyl OCH_2), 3.81 (dd, $^3J_{5C,4C}$ = 3.9 Hz, 1 H, 5C-H), 3.84 (dd, $^2J_{5B,5B}$ = 11.4, $^3J_{5B,4B}$ = 3.9 Hz, 1 H, 5B-H), 3.92 (dd, $^2J_{5A,5A}$ = 11.4, $^3J_{5A,4A}$ = 4.1 Hz, 1 H, 5A-H), 4.01−4.07 (m, 3 H, 3C-H, 3D-H, 4D-H), 4.09 (br. d, $^3J_{3B,4B}$ = 5.8 Hz, 1 H, 3B-H), 4.11 (m, 1 H, 4C-H), 4.15 (m, 1 H, 3A-H), 4.16 (m, 1 H, 4B-H), 4.32 (m, 1 H, 4A-H), 4.39, 4.40, 4.48, 4.53, 4.54, 4.61, 4.61, 4.78 (8d, ^2J = 12.2 Hz, 8 × 1 H, benzyl CH_2), 5.13 (s, 1 H, 1A-H), 5.22 (s, 1 H, 1D-H), 5.24 (s, 1 H, 1C-H), 5.28 (s, 1 H, 1B-H), 5.37 (m, 2 H, 2C-H, 2D-H), 5.38 (d, $^3J_{2A,3A}$ = 1.8 Hz, 1 H, 2A-H), 5.42 (d, $^3J_{2B,3B}$ = 1.4 Hz, 1 H, 2B-H), 7.05−8.05 (m, 50 H, Ar-H) ppm. ^{13}C NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 24.9, 25.9, 26.7 (CH_2), 26.9 [$C(CH_3)_3$], 28.9, 29.3, 29.4, 29.6, 29.8 (CH_2), 34.1 (CH_2CO), 51.4 (CH_3O), 62.8 (C-5D), 65.1 (C-5C), 65.2 (C-5B), 65.4 (C-5A), 67.5 (octyl OCH_2), 71.9, 72.1, 72.2 (benzyl CH_2), 81.3 (C-4A), 81.6 (C-2C, C-2D), 81.8 (C-4B, C-4C), 82.1 (C-2A), 82.6 (C-4D), 82.7 (C-2B), 83.1 (C-3A, C-3B), 83.7 (C-3C, C-3D), 105.8 (C-1A), 106.0 (C-1B, C-1C, C-1D), 127.6, 127.8, 128.1, 128.3, 128.4, 129.6, 129.7, 133.2, 135.5 (Ar) ppm. HRMS (FAB): $C_{102}H_{110}O_{23}SiNa$: calcd. 1753.7105, found 1753.7103.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-{2-*O*-benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranoside (20): **19** (160.0 mg, 92 μmol) was desilylated with HCl in MeOH/Et_2O according to the General Procedure. Chromatography with petroleum ether/EtOAc (2:1) gave **20** as a colorless oil (109.3 mg, 79%). $[\alpha]_D^{25}$ = +110 (c = 1.09 in chloroform). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.24−1.39 (m, 8 H, octyl CH_2), 1.56−1.65 (m, 4 H, octyl CH_2), 1.68 (m, 1 H, 5D-OH), 2.28 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 3.41−3.54 (m, 2 H, 5D-H, octyl OCH_2), 3.63−3.69 (m, 5 H, 5B-H, 5C-H, CH_3O), 3.69−3.76 (m, 3 H, 5A-H, 5D-H, octyl OCH_2), 3.80 (dd, $^2J_{5B,5B}$ = 11.4, $^3J_{5B,4B}$ = 3.8 Hz, 1 H, 5B-H), 3.85 (dd, $^2J_{5C,5C}$ = 11.3, $^3J_{5C,4C}$ = 3.9 Hz, 1 H, 5C-H), 3.89−3.94 (m, 2 H, 3D-H, 5A-H), 3.98 (m, 1 H, 4D-H), 4.06 (br. d, $^3J_{3B,4B}$ = 5.3 Hz, 1 H, 3B-H), 4.09 (br. d, $^3J_{3C,4C}$ = 5.2 Hz, 1 H, 3C-H), 4.11−4.17 (m, 2 H, 3A-H, 4B-H), 4.18 (m, 1 H, 4C-H), 4.31 (m, 1 H, 4A-H), 4.40, 4.44, 4.49, 4.56, 4.57, 4.61, 4.63, 4.77 (8d, ^2J = 12.1 Hz, 8 × 1 H, benzyl CH_2), 5.13 (s, 1 H, 1A-H), 5.21 (s, 1 H, 1D-H), 5.25 (s, 1 H, 1B-H), 5.27 (s, 1 H, 1C-H), 5.33 (d, $^3J_{2D,3D}$ = 1.1 Hz, 1 H, 2D-H), 5.38 (b, 2 H, 2A-H, 2B-H), 5.42 (d, $^3J_{2C,3C}$ = 1.1 Hz, 1 H, 2C-H), 7.15−8.05 (m, 40 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.1, 26.1, 29.2, 29.3, 29.4, 29.5, 29.8 (octyl CH_2), 34.2 (CH_2CO), 51.6 (CH_3O), 62.0 (C-5D), 65.6 (C-5A, C-5B), 65.7 (C-5C), 67.7 (octyl OCH_2), 72.1, 72.2, 72.4 (benzyl CH_2), 81.6 (C-4A), 81.8 (C-2A), 81.9 (C-2B, C-2C, C-2D), 82.1 (C-4C), 82.3 (C-4B), 82.8 (C-3D), 83.2 (C-3B), 83.4 (C-3A, C-3C), 83.4 (C-4D), 106.1 (C-1A), 106.2 (C-1C), 106.3 (C-1B, C-1D), 127.7, 127.8, 128.0, 128.4, 128.6, 129.5, 129.6, 129.7, 129.8, 129.9, 133.4, 133.5, 137.7, 138.0 (Ar), 165.3, 165.4, 165.7 ($COOPh$), 174.5 ($COOMe$) ppm. HRMS (FAB): $C_{86}H_{92}O_{23}Na$: calcd. 1515.5928, found 1515.5922.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-{2-*O*-benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (21): From **20** (72.6 mg, 49 μmol) and **8** (36.6 mg, 58 μmol). Chromatography with petroleum ether/EtOAc (2:1) gave **21** as a colorless oil (89.6 mg, 90%). $[\alpha]_D^{25}$ = +81 (*c* = 1.33 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.93 [s, 9 H, $C(CH_3)_3$], 1.23−1.38 (m, 8 H, octyl CH_2), 1.54−1.63 (m, 4 H, octyl CH_2), 2.29 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 3.43 (td, ^2J = 9.7, ^3J = 6.7 Hz, 1 H, octyl OCH_2), 3.65−3.67 (m, 3 H, 5B-H, 5C-H, 5D-H), 3.64 (s, 3 H, CH_3O), 3.67−3.74 (m, 4 H, octyl OCH_2, 5A-H, 2 × 5E-H), 3.76−3.84 (m, 3 H, 5B-H, 5C-H, 5D-H), 3.90 (dd, $^2J_{5A,5A}$ = 11.3, $^3J_{5A,4A}$ = 4.0 Hz, 1 H, 5A-H), 3.98−4.10 (m, 7 H, 3B-H, 3C-H, 3D-H, 3E-H, 4C-H, 4D-H, 4E-H), 4.11−4.16 (m, 2 H, 3A-H, 4B-H), 4.29 (m, 1 H, 4A-H), 4.36, 4.37, 4.40, 4.46, 4.49, 4.51, 4.52, 4.59, 4.59, 4.76 (10d, ^2J = 12.2 Hz, 10 × 1 H, benzyl CH_2), 5.11 (s, 1 H, 1A-H), 5.20 (s, 1 H, 1E-H), 5.21 (s, 1 H, 1D-H), 5.22 (s, 1 H, 1C-H), 5.26 (s, 1 H, 1B-H), 5.33−5.37 (m, 3 H, 2C-H, 2D-H, 2E-H), 5.38 (d, $^3J_{2A,3A}$ = 1.3 Hz, 1 H, 2A-H), 5.40 (d, $^3J_{2B,3B}$ = 1.3 Hz, 1 H, 2B-H), 7.09−8.03 (m, 60 H, Ar-H) ppm. ^{13}C NMR (125.78 MHz, $CDCl_3$, 20 °C): δ = 25.1, 26.1 (octyl CH_2), 26.8 [$C(CH_3)_3$], 29.2, 29.3, 29.4, 29.5 (octyl CH_2), 34.2 (CH_2CO), 51.6 (CH_3O), 63.0 (C-5E), 65.2 (C-5A), 65.4 (C-5B, C-5C), 65.5 (C-5D), 67.7 (octyl OCH_2), 72.0, 72.1, 72.2, 72.4 (benzyl CH_2), 81.6, 81.8, 81.9, 82.1, 82.3, 82.9, 83.1, 83.2, 83.3, 83.9, 106.0 (C-1A), 106.2 (C-1B, C-1C, C-1D, C-1E), 127.6, 127.7, 127.8, 128.0, 128.3, 128.4, 128.5, 128.9, 129.5, 129.6, 129.8, 129.9, 133.3, 133.4, 135.7, 137.8, 137.9 (Ar), 165.3, 165.4 (*C*OOPh) ppm. HRMS (FAB): $C_{121}H_{128}O_{28}SiNa$: calcd. 2079.8259, found 2079.8262.

8-(Methoxycarbonyl)octyl 5-*O*-[5-*O*-{5-*O*-[5-*O*-(α-d-Arabinofuranosyl)-α-D-arabinofuranosyl]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl]-α-D-arabinofuranoside (1): **21** (79.6 mg, 39 μmol) was submitted to three steps of deprotection without purification of the intermediate compounds. Desilylation (Bu_4NF in THF), debenzoylation and debenzylation (Procedure B) were run according to the General Procedures. Chromatography with dichloromethane/methanol (15:1) gave **1** as a colorless oil (21.5 mg, 65%, 3 steps). $[\alpha]_D^{25}$ = +111 (*c* = 1.02 in methanol). ^{1}H NMR (400 MHz, CD_3OD, 27 °C): δ = 1.26−1.42 (m, 8 H, octyl CH_2), 1.54−1.65 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 3.41 (td, ^2J = 9.6, ^3J = 6.5 Hz, 1 H, octyl OCH_2), 3.65 (s, 3 H, CH_3O), 3.61−3.69 (m, 5 H, 5A-H, 5B-H, 5C-H, 5D-H, 5E-H), 3.69 (td, 1 H, octyl OCH_2), 3.75 (dd, $^2J_{5E,5E}$ = 11.9, $^3J_{5E,4E}$ = 3.3 Hz, 1 H, 5E-H), 3.80−3.92 (m, 9 H, 3A-H, 3B-H, 3C-H, 3D-H, 3E-H, 5A-H, 5B-H, 5C-H, 5D-H), 3.95 (dd, $^3J_{2A,3A}$ = 3.8, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 3.97−4.02 (m, 6 H, 2B-H, 2C-H, 2D-H, 2E-H, 4A-H, 4E-H), 4.06−4.11 (m, 3 H, 4B-H, 4C-H, 4D-H), 4.85 (s, 1 H, 1A-H), 4.95 (b, 4 H, 1B-H, 1C-H, 1D-H, 1E-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 27 °C): δ = 26.0, 27.1, 30.1, 30.3, 30.6 (octyl CH_2), 34.8 (CH_2CO), 52.0 (CH_3O), 63.1 (C-5E), 68.1, 68.2, 68.3 (C-5A, C-5B, C-5C, C-5D), 68.9 (octyl OCH_2), 78.8, 79.1 (C-3A, C-3B, C-3C, C-3D, C-3E), 83.1, 83.2, 83.5, 83.6 (C-2A, C-2B, C-2C, C-2D, C-2E, C-4E), 84.2 (C-4B, C-4C, C-4D), 86.0 (C-4A), 109.5 (C-1A), 109.6, 109.7 (C-1B, C-1C, C-1D), 176.1 (*C*OOMe) ppm. HRMS (FAB): $C_{35}H_{60}O_{23}Na$: calcd. 871.3423, found 871.3463.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-{2-*O*-benzoyl-5-*O*-[2-*O*-benzoyl-3,5-*O*-(1,1,3,3-tetra-*isopropyl*disiloxan-1,3-diyl)-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranoside (22): From **15** (150.0 mg, 0.18 mmol) and **12** (106.0 mg, 0.20 mmol) Chromatography with petroleum ether/EtOAc (4:1) gave **22** as a colorless oil (190.8 mg, 81%). $[\alpha]_D^{25}$ = +58 (*c* = 1.62 in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.81−1.43 [m, 28 H, $(CH_3)_2CH$], 1.21−1.39 (m, 8 H, octyl CH_2), 1.57−1.64 (m, 4 H, octyl CH_2), 2.29 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 3.45 (td, ^2J = 9.7, ^3J = 6.6 Hz, 1 H, octyl OCH_2), 3.60 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 4.5 Hz, 1 H, 5B-H), 3.66 (s, 3 H, CH_3O), 3.73 (td, 1 H, octyl OCH_2), 3.73 (m, 1 H, 5A-H), 3.83 (dd, $^3J_{5B,4B}$ = 4.6 Hz, 1 H, 5B-H), 3.86−3.96 (m, 4 H, 3C-H, 5A-H, 2 × 5C-H), 4.01 (br. d, $^3J_{3B,4B}$ = 5.2 Hz, 1 H, 3B-H), 4.16 (br. d, $^3J_{3A,4A}$ = 5.0 Hz, 1 H, 3A-H), 4.20 (m, 1 H, 4B-H), 4.32 (m, 1 H, 4A-H), 4.43 (m, 1 H, 4C-H), 4.51, 4.62, 4.66, 4.79 (4d, ^2J = 12.0 Hz, 4 × 1 H, benzyl CH_2), 5.04 (d, $^3J_{1C,2C}$ = 1.5 Hz, 1 H, 1C-H), 5.14 (s, 1 H, 1A-H), 5.27 (s, 1 H, 1B-H), 5.38 (d, $^3J_{2A,1A}$ = 1.4 Hz, 1 H, 2A-H), 5.43 (d, $^3J_{2C,1C}$ = 1.7 Hz, 1 H, 2C-H), 5.44 (d, $^3J_{2B,1B}$ = 1.4 Hz, 1 H, 2B-H), 7.17−8.07 (m, 25 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 20 °C): δ = 12.5, 12.9, 13.3, 13.5 [$(CH_3)_2CH$], 17.0, 17.1, 17.4, 17.6 [$(CH_3)_2CH$], 25.1, 26.1, 29.2, 29.3, 29.4, 29.5 (octyl CH_2), 34.2 (CH_2CO), 51.6 (CH_3O), 61.4 (C-5C), 65.6 (C-5A), 67.1 (C-5B), 67.7 (octyl OCH_2), 72.1, 72.5 (benzyl CH_2), 75.9 (C-3C), 81.0 (C-4C), 81.6 (C-4A), 81.6 (C-2B), 82.1 (C-4B), 82.3 (C-2A), 83.0 (C-3A), 83.7 (C-3B), 84.1 (C-2C), 105.7 (C-1C), 106.0 (C-1A), 106.2 (C-1B), 127.7, 127.8, 128.0, 128.4, 128.5, 128.6, 129.6, 129.8, 129.9, 130.0, 133.4, 137.9, 133.4 (Ar), 165.4 (*C*OOPh), 174.5 (*C*OOCH$_3$) ppm. $C_{72}H_{94}O_{19}Si_2$ (1319.7): calcd. C 65.53, H 7.18; found C 65.54, H 6.79.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (23): **22** (87.0 mg, 66 μmol) was desilylated with neutralized Bu_4NF in THF according to the General Procedure. Chromatography with petroleum ether/EtOAc (1:1) gave **23** as a colorless oil (67.5 mg, 95%). $[\alpha]_D^{25}$ = +108 (*c* = 1.01 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.38 (m, 8 H, octyl CH_2), 1.52−1.60 (m, 4 H, octyl CH_2), 2.30 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 3.47 (td, ^2J = 9.7, ^3J = 6.8 Hz, 1 H, octyl OCH_2), 3.65 (s, 3 H, CH_3O), 3.65 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 3.5 Hz, 1 H, 5B-H), 3.68 (m, 1 H, 5C-H), 3.74 (td, 1 H, octyl OCH_2), 3.74−3.84 (m, 3 H, 5A-H, 5B-H, 5C-H), 3.89−3.95 (m, 3 H, 5A-H, 3B-H, 4C-H), 4.09 (m, 1 H, 3C-H), 4.16 (br. d, $^3J_{3A,4A}$ = 6.5 Hz, 1 H, 3A-H), 4.17 (m, 1 H, 4B-H), 4.34 (m, 1 H, 4A-H), 4.49, 4.64, 4.64, 4.82 (4d, ^2J = 12.2 Hz, 4 × 1 H, benzyl CH_2), 4.98 (dd, $^3J_{2C,3C}$ = 2.8, $^3J_{2C,1C}$ = 0.8 Hz, 1 H, 2C-H), 5.16 (s, 1 H, 1A-H), 5.27 (s, 1 H, 1C-H), 5.30 (s, 1 H, 1B-H), 5.39 (d, $^3J_{2A,1A}$ = 1.6 Hz, 1 H, 2A-H), 5.40 (d, $^3J_{2B,1B}$ = 1.3 Hz, 1 H, 2B-H), 7.16−8.10 (m, 25 H, Ar-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 29.4, 29.6, (octyl CH_2), 34.0 (CH_2CO), 51.6 (CH_3O), 61.8 (C-5C), 66.0 (C-5B, C-5A), 67.6 (octyl OCH_2), 72.0, 72.3 (benzyl CH_2), 76.7 (C-3C), 81.4 (C-4A), 81.6 (C-2B), 81.7 (C-4B), 81.8 (C-2A), 83.0 (C-4C), 83.2 (C-3A), 84.1 (C-3B), 86.3 (C-2C), 105.1 (C-1C), 105.8 (C-1A) ppm. $C_{60}H_{66}O_{18}$ (1077.2): calcd. C 66.90, H 6.18; found C 66.29, H 6.04.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-{2-*O*-benzoyl-5-*O*-[2-*O*-benzoyl-3,5-di-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranoside (24): From **23** (106.4 mg, 0.10 mmol) and **8** (185.6 mg, 0.30 mmol). Chromatography with petroleum ether/EtOAc, 3:1 gave **24** as a colorless oil (177.3 mg, 81%). $[\alpha]_D^{25}$ = +85 (*c* = 1.36 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.87, 0.92 [s, 9 H, $C(CH_3)_3$], 1.22−1.38 (m, 8 H, octyl CH_2), 1.55−1.64 (m, 4 H, octyl CH_2), 2.29 (t, ^3J = 7.6 Hz, 2 H, CH_2CO), 3.44 (td, ^2J = 9.7, ^3J = 6.6 Hz, 1 H, octyl OCH_2), 3.65 (s, 3 H, CH_3O), 3.64−3.76 (m, 7

H, 5A-H, 5B-H, 2 × 5D-H, 2 × 5E-H, octyl OCH$_2$), 3.77 (dd, $^2J_{5C,5C}$ = 11.5, $^3J_{5C,4C}$ = 2.7 Hz, 1 H, 5C-H), 3.85 (dd, $^2J_{5B,5B}$ = 11.5, $^3J_{5B,4B}$ = 3.9 Hz, 1 H, 5B-H), 3.91 (dd, $^2J_{5A,5A}$ = 11.5, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 3.94 (dd, $^3J_{5C,4C}$ = 4.6 Hz, 1 H, 5C-H), 4.07 (br. d, $^3J_{3E,4E}$ = 5.4 Hz, 1 H, 3E-H), 4.12 (br. d, $^3J_{3D,4D}$ = 5.6 Hz, 1 H, 3D-H), 4.13−4.24 (m, 7 H, 3A-H, 3B-H, 3C-H, 4B-H, 4C-H, 4D-H, 4E-H), 4.31 (m, 1 H, 4A-H), 4.42 (m, 1 H, 3C-H), 4.41, 4.47, 4.49, 4.57, 4.60, 4.61, 4.69, 4.77 (8d, ^2J = 12.1 Hz, 8 × 1 H, benzyl CH$_2$), 5.12 (s, 1 H, 1A-H), 5.24 (s, 1 H, 1B-H), 5.27 (s, 2 H, 1C-H, 1D-H), 5.34 (d, $^3J_{2E,1E}$ = 1.1 Hz, 1 H, 2E-H), 5.37 (d, $^3J_{2A,3A}$ = 1.6 Hz, 1 H, 2A-H), 5.39 (d, $^3J_{2C,3C}$ = $^3J_{2D,3D}$ = 1.5 Hz, 2 H, 2C-H, 2D-H), 5.44 (d, $^3J_{2B,3B}$ = 1.6 Hz, 1 H, 2B-H), 5.48 (s, 1 H, 1E-H), 7.08−8.05 (m, 65 H, Ar-H) ppm. ^{13}C NMR (125.78 MHz, CDCl$_3$, 25 °C): δ = 25.5 (octyl CH$_2$), 26.4 [(CH$_3$)$_3$CSi), 27.2, 29.7 (octyl CH$_2$), 34.6 (*C*H$_2$CO), 52.0 (CH$_3$O), 63.3 (C-5D, C-5E), 65.9 (C-5B), 66.0 (C-5C), 66.2 (C-5A), 68.1 (octyl O*C*H$_2$), 72.3, 72.6, 72.8, 72.9 (benzyl CH$_2$), 80.6 (C-3C), 82.0 (C-4A), 82.4 (C-2B), 82.5 (C-3B, C-4D, C-4E), 82.6 (C-2E), 82.8 (C-2C, C-2D), 83.2 (C-2A), 83.4 (C-3D, C-3E), 83.7 (C-3A), 84.2 (C-4C), 84.6 (C-4B), 106.0 (C-1E), 106.5 (C-1A), 106.6 (C-1B), 106.7 (C-1C), 106.9 (C-1D), 128−130.1, 130.3, 130.3, 130.4, 133.8, 136.1 (Ar) ppm. HRMS (FAB): $C_{130}H_{140}O_{28}Si_2Na$: calcd. 2227.8967, found 2227.8920.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[3,5-di-*O*-(α-D-Arabinofuranosyl)-α-D-arabinofuranosyl]-α-D-arabinofuranosyl}-α-D-arabinofuranoside (2): 24 (33.6 mg, 15 µmol) was submitted to three steps of deprotection without purification of the intermediate compounds. Desilylation (Bu$_4$NF in THF), debenzoylation and debenzylation (Procedure A) were run according to the General Procedures. Chromatography with dichloromethane/methanol (3:1) gave **2** as a white solid (8.1 mg, 63%, 3 steps). $[\alpha]_D^{25}$ = +123 (*c* = 0.77 in methanol). ^{1}H NMR (500 MHz, D$_2$O, 25 °C): δ = 1.21−1.32 (m, 8 H, octyl CH$_2$), 1.49−1.58 (m, 4 H, octyl CH$_2$), 2.32 (t, ^3J = 7.6 Hz, 2 H, CH$_2$CO), 3.50 (td, ^2J = 9.9, ^3J = 6.7 Hz, 1 H, octyl OCH$_2$), 3.61 (s, 3 H, CH$_3$O), 3.64 (dd, $^2J_{5E,5E}$ = 12.2, $^3J_{5E,4E}$ = 2.4 Hz, 1 H, 5E-H), 3.65 (dd, $^2J_{5D,5D}$ = 12.7, $^3J_{5D,4D}$ = 2.6 Hz, 1 H, 5D-H), 3.67 (td, 1 H, octyl OCH$_2$), 3.69 (dd, $^2J_{5C,5C}$ = 12.2, $^3J_{5C,4C}$ = 2.9 Hz, 1 H, 5C-H), 3.71−3.81 (m, 5 H, 5A-H, 5B-H, 5C-H, 5D-H, 5E-H), 3.82 (dd, $^2J_{5B,5B}$ = 11.6, $^3J_{5B,4B}$ = 5.9 Hz, 1 H, 5B-H), 3.86−3.90 (m, 3 H, 3D-H, 3E-H, 5A-H), 3.92 (dd, $^3J_{3C,4C}$ = 6.4, $^3J_{3C,2C}$ = 3.7 Hz, 1 H, 3C-H), 3.95 (dd, $^3J_{3B,4B}$ = 6.0, $^3J_{3B,2B}$ = 3.0 Hz, 1 H, 3B-H), 3.97 (m, 1 H, 4E-H), 3.98 (dd, 1 H, 2C-H), 4.02 (m, 1 H, 3A-H), 4.04 (m, 1 H, 4D-H), 4.05 (dd, 1 H, 2B-H), 4.06 (dd, $^3J_{2D,3D}$ = 3.3 Hz, 1 H, 2D-H), 4.06 (dd, $^3J_{2E,3E}$ = 3.5 Hz, 1 H, 2E-H), 4.08 (td, 1 H, 4C-H), 4.14 (td, 1 H, 4C-H), 4.22 (dd, $^3J_{2A,3A}$ = 2.1 Hz, 1 H, 2A-H), 4.24 (td, $^3J_{4A,3A}$ = 3.0 Hz, 1 H, 4A-H), 4.95 (d, $^3J_{1C,2C}$ = 1.8 Hz, 1 H, 1C-H), 5.01 (d, $^3J_{1B,2B}$ = 1.4 Hz, 1 H, 1B-H), 5.02 (d, $^3J_{1D,2D}$ = 1.4 Hz, 1 H, 1D-H), 5.05 (b, 1 H, 1A-H), 5.08 (d, $^3J_{1E,2E}$ = 1.4 Hz, 1 H, 1E-H) ppm. ^{13}C NMR (125.78 MHz, D$_2$O, 25 °C): δ = 24.4, 24.6, 24.8, 25.2, 28.2, 28.3, 28.7, 28.8 (octyl CH$_2$), 33.9 (*C*H$_2$CO), 52.3 (CH$_3$O), 61.9 (C-5D, C-5E), 66.6 (C-5B, C-5A), 67.0 (C-5C), 68.9 (octyl O*C*H$_2$), 76.6 (C-3C), 76.7 (C-3D, C-3E), 76.8 (C-3B), 79.3 (C-2A), 80.9 (C-2C), 81.2 (C-2B, C-2D, C-2E), 81.8 (C-4C), 81.9 (C-4A), 82.4 (C-4B), 82.5 (C-3A), 84.1 (C-4E), 84.2 (C-4D), 107.3 (C-1E), 107.4 (C-1C), 107.5 (C-1D), 107.6 (C-1A), 107.7 (C-1B) ppm. HRMS (FAB): $C_{35}H_{60}O_{23}Na$: calcd. 871.3423, found 871.3462.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-*O*-(3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-β-D-arabinofuranosyl)-α-D-arabinofuranoside (26). Formation of the Acetals: From **5** (210 mg, 0.33 mmol) and **9** (176 mg, 0.34 mmol) according to the General Procedure, chromatography with petroleum ether/ethyl acetate (6:1) gave 250 mg of **25** (66%). **Glycosylation:** From **25** (173 mg, 0.15 mmol) according to the General Procedure, chromatography with toluene/ethyl acetate (12:1) gave **26** as a colorless oil (116 mg, 79%). $[\alpha]_D^{25}$= +21 (*c* = 0.81 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.03 [s, 9 H, (CH$_3$)$_3$C], 1.24−1.39 and 1.54−1.69 (2m, 12 H, octyl CH$_2$), 2.30 (t, ^3J = 7.5 Hz, 2 H, CH$_2$CO), 2.62 (d, $^3J_{OH,2B}$ = 9.5 Hz, 1 H, 2B-OH), 3.41 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.52 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 6.5 Hz, 1 H, 5A-H), 3.66 (s, 3 H, CH$_3$O), 3.67 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.74 (m, 2 H, 5B-H), 3.78 (br. d, $^3J_{3A,4A}$ = 6.0 Hz, 1 H, 3A-H), 3.87 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 3.5 Hz, 1 H, 5A-H), 3.92 (m, 1 H, 3B-H), 4.05 (m, 1 H, 4B-H), 4.22 (m, 2 H, 2B-H, 4A-H), 4.56, 4.52, 4.72, 4.77 (4d, ^2J = 12.0 Hz, 4 × 1 H, benzyl CH$_2$), 4.91 (d, $^3J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H), 5.06 (s, 1 H, 1A-H), 5.34 (d, $^3J_{2A,1A}$ = 1.5 Hz, 1 H, 2A-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.2, 24.9, 26.8, 29.1, 29.2, 29.2, 29.3, 34.1, 51.5, 65.4, 67.5, 68.0, 71.8, 72.1, 81.2, 81.8, 82.5, 83.3, 84.6, 102.1 (C-1B), 106.0 (C-1A), 127.6, 127.7, 127.9, 128.0, 128.3, 128.4, 128.5, 129.7, 133.5, 135.6, 164.5, 171.6 ppm. $C_{57}H_{70}O_{12}Si$ (975.3) calcd. C 70.19, H 7.23; found C 69.91, H 6.97.

8-(Methoxycarbonyl)octyl 2-*O*-(3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-β-D-arabinofuranosyl)-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (27): From **6** (122 mg, 0.19 mmol) and **9** (150 mg, 0.23 mmol). Chromatography with petroleum ether/ethyl acetate (6:1) gave **27** (110 mg, 52%, 2 steps). $[\alpha]_D^{25}$ = +0.1 (*c* = 1.02 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.01 and 1.02 (2 s, 2 × 9 H, (CH$_3$)$_3$C], 1.21−1.34 and 1.52−1.64 (2 m, 12 H, octyl CH$_2$), 2.28 (t, ^3J = 7.5 Hz, 2 H, CH$_2$CO), 2.39 (d, $^3J_{OH,2B}$ = 8.5 Hz, 1 H, 2B-OH), 3.38 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.64 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.66 (s, 3 H, CH$_3$O), 3.72 (dd, $^2J_{5B,5B}$ = 12.0, $^3J_{5B,4B}$ = 5.5 Hz, 1 H, 5B-H), 3.72 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 5.5 Hz, 1 H, 5A-H), 3.73 (dd, $^2J_{5B,5B}$ = 12.0, $^3J_{5B,4B}$ = 6.5 Hz, 1 H, 5B-H), 3.78 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 3.5 Hz, 1 H, 5A-H), 3.88 (dd, $^3J_{3B,4B}$ = 4.5, $^3J_{3B,2B}$ = 4.5 Hz, 1 H, 3B-H), 3.89 (dd, $^3J_{3A,4A}$ = 6.5, $^3J_{3A,2A}$ = 3.0 Hz, 1 H, 3A-H), 4.03−4.14 (m, 2 H, 4A-H, 4B-H), 4.23 (m, $^3J_{2B,OH}$ = 8.5, $^3J_{2B,3B}$ = 4.5, $^3J_{2B,1B}$ = 4.5 Hz, 1 H, 2B-H), 4.32 (dd, $^3J_{2A,3A}$ = 3.0, $^3J_{2A,1A}$ = 1.0 Hz, 1 H, 2A-H), 4.19, 4.46, 4.60, 4.71 (4d, ^2J = 12.0 Hz, 4 × 1 H, benzyl CH$_2$), 4.96 (br. s, 1 H, 1A-H), 5.14 (d, $^3J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.1, 19.2 [(CH$_3$)$_3$C], 24.9, 26.0, 26.7, 29.0, 29.1, 29.4, 34.0 (*C*H$_2$CO), 51.4 (OCH$_3$), 63.6, 65.7 (C-5A, C-5B), 67.4 (octyl OCH$_2$), 71.8, 72.1 (benzyl CH$_2$), 77.4, 82.2, 82.5, 83.4, 84.9, 86.4, 101.4 (C-1B), 105.6 (C-1A), 127.46, 127.52, 127.6, 127.7, 128.1, 128.3, 129.6, 129.7, 132.9, 133.0, 133.2, 133.3, 135.5, 135.6, 137.7, 137.8, 174.3 (CO) ppm. $C_{66}H_{84}O_{11}Si_2$ (1109.6): calcd. C 71.44, H 7.63; found C 71.15, H 7.52.

8-(Methoxycarbonyl)octyl 2-*O*-β-D-Arabinofuranosyl-α-D-arabinofuranoside (28): 27 (106 mg, 95 µmol) was desilylated with Bu$_4$NF in THF according to the General Procedure. The intermediate triol was filtered through silica (petroleum ether/ethyl acetate, 1:2) and hydrogenolyzed at room temperature (H$_2$, 10% Pd/C, ethyl acetate/methanol). Filtration of the mixture and chromatography (dichloromethane/methanol, 6:1) gave **28** (26 mg, 60%, 2 steps). $[\alpha]_D^{25}$ = −8 (*c* = 1.13 in methanol). ^{1}H NMR (250 MHz, D$_2$O, 25 °C): δ = 1.28−1.38 and 1.56−1.63 (2m, 8 H and 4 H, octyl CH$_2$), 2.38 (t, ^3J = 7.5 Hz, 2 H, CH$_2$CO), 3.55 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.67 (dd, $^3J_{5B,5B}$ = 12.5, $^3J_{5B,4B}$ = 7.0 Hz, 1 H, 5B-H), 3.68 (s, 3 H, CH$_3$O), 3.71 (dd, $^3J_{5A,5A}$ = 12.5, $^3J_{5A,4A}$ = 5.0 Hz, 1 H, 5A-H), 3.75 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl OCH$_2$), 3.75 (m, 2 H, 3A-H, 4A-H), 3.79 (dd, $^2J_{5B,5B}$ = 12.5,

$^{3}J_{5B,4B}$ = 3.5 Hz, 1 H, 5B-H), 3.83 (dd, $^{2}J_{5A,5A}$ = 12.5, $^{3}J_{5A,4A}$ = 3.0 Hz, 1 H, 5A-H), 4.07 (dd, $^{3}J_{3B,2B}$ = 8.0, $^{3}J_{3B,4B}$ = 7.0 Hz, 1 H, 3B-H), 4.11 (dd, $^{2}J_{3A,2A}$ = 5.0, $^{3}J_{3A,4A}$ = 5.0 Hz, 1 H, 3A-H), 4.13 (dd, $^{3}J_{2A,3A}$ = 5.0, $^{3}J_{2A,1A}$ = 2.0, 1 H, 2A-H), 4.14 (dd, $^{3}J_{2B,3B}$ = 8.0, $^{3}J_{2B,1B}$ = 4.5 Hz, 1 H, 2B-H), 5.08 (d, $^{3}J_{1A,2A}$ = 2.0 Hz, 1 H, 1A-H), 5.09 (d, $^{3}J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H) ppm. ^{13}C NMR (62.89 MHz, D_2O, 25 °C): δ = 25.0, 25.9, 28.9, 29.0, 29.1, 29.3, 34.4 (*C*H$_2$CO), 52.7 (CH_3O), 61.0 (C-5A), 63.5 (C-5B), 69.1 (octyl OCH_2), 74.6 (C-3B), 74.9 (C-3), 77.0 (C-2B), 82.7 (C-4B), 82.8 (C-4), 87.3 (C-2B), 101.1 (C-1B), 106.2 (C-1A), 178.1 (CO) ppm. $C_{20}H_{36}O_{11}+0.5H_2O$ (452.5) calcd. C 52.05, H 8.08; found C 52.04, H 8.03.

8-(Methoxycarbonyl)octyl 2-*O*-(3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-β-D-arabinofuranosyl)-3-*O*-benzyl-5-*O*-pivaloyl-α-D-arabinofuranoside (29): From **7** (54 mg, 0.11 mmol) and **9** (77 mg, 0.12 mmol), chromatography with petroleum ether/ethyl acetate (4:1) gave **29** as a colorless oil (65 mg, 63%, 2 steps). $[\alpha]_D^{25}$ = +9 (*c* = 1.13 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.03 [s, 9 H, $(CH_3)_3CSi$], 1.15 [s, 9 H, $(CH_3)_3CO$], 1.28−1.31 and 1.52−1.64 (2m, 12 H, octyl CH_2), 2.29 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 2.50 (d, $^{3}J_{OH,2B}$ = 9.0 Hz, 1 H, 2B-OH), 3.38 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.64 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.75 (m, 2 H, 3A-H, 4A-H), 3.91 (dd, $^{3}J_{3B,4B}$ = 4.5, $^{3}J_{3B,2B}$ = 4.5 Hz, 1 H, 3B-H), 4.05 (dd, $^{2}J_{5B,5B}$ = 11.0, $^{3}J_{5B,4B}$ = 5.5 Hz, 1 H, 5B-H), 4.10 (m, 1 H, 4B-H), 4.10 (dd, $^{2}J_{5A,5A}$ = 10.5, $^{3}J_{5A,4A}$ = 6.0 Hz, 1 H, 5A-H), 4.13 (dd, $^{2}J_{5A,5A}$ = 10.5, $^{3}J_{5A,4A}$ = 5.5 Hz, 1 H, 5A-H), 4.22 (dd, $^{2}J_{5B,5B}$ = 11.0, $^{3}J_{5B,4B}$ = 2.5 Hz, 1 H, 5B-H), 4.25 (m, $^{3}J_{2B,OH}$ = 9.0, $^{3}J_{2B,3B}$ = 4.5, $^{3}J_{2B,1B}$ = 4.5 Hz, 1 H, 2B-H), 4.32 (dd, $^{3}J_{2A,3A}$ = 2.5, $^{3}J_{2A,1A}$ = 1.0 Hz, 1 H, 2A-H), 4.24 and 4.52 (2d, ^{2}J = 11.5 Hz, 2 × 1 H, benzyl CH_2), 4.62 and 4.72 (2d, ^{2}J = 12.0 Hz, 2 × 1 H, benzyl CH_2), 4.94 (s, 1 H, 1A-H), 5.15 (d, $^{3}J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 18.9, 24.6, 25.7, 26.5, 26.8, 28.7, 28.8, 29.1, 33.7, 51.1, 63.0, 65.3, 67.2, 71.5 and 71.9 (benzyl CH_2), 76.2, 79.1, 82.2, 83.5, 84.4, 86.1, 101.5 (C-1B), 105.5 (C-1A), 127.3, 127.4, 127.5, 127.96, 128.05, 129.5, 132.6, 132.7, 135.20, 135.25, 137.1, 174.0 (CH_3OCO), 177.7 [$(CH_3)_3CO$] ppm. $C_{55}H_{74}O_{12}Si$ (955.3): calcd. C 69.15, H 7.81; found C 68.89, H 8.02.

8-(Methoxycarbonyl)octyl 2-*O*-(2-*O*-Acetyl-3-*O*-benzyl-β-D-arabinofuranosyl)-3-*O*-benzyl-5-*O*-pivaloyl-α-D-arabinofuranoside (31): Disaccharide **29** (61 mg, 64 µmoles) was dissolved in pyridine (1.2 mL) and treated with acetic anhydride (0.8 mL). The mixture was left overnight at room temperature before hydrolysis with aqueous saturated $NaHCO_3$ solution and extraction with CH_2Cl_2. The organic phase was dried with $MgSO_4$ and the solvent evaporated. The residue was coevaporated three times with toluene to give crude **30** (63 mg, 99%). This crude product was desilylated with Bu_4NF in THF in 1 h according to the General Procedure. Chromatography with toluene/ethyl acetate (4:1) gave **31** as a colorless oil (37 mg, 76%). $[\alpha]_D^{25}$ = −21 (*c* = 1.13 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.18 (s, 9 H, *t*Bu), 1.25−1.36 and 1.50−1.66 (2 m, 12 H octyl CH_2), 2.06 (s, 3 H, CH_3CO), 2.18 (dd, $^{3}J_{OH,5B}$ = 8.0, $^{3}J_{OH,5B}$ = 5.0 Hz, 1 H, 5B-OH), 2.30 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 3.39 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.58 (ddd, $^{2}J_{5B,5B}$ = 12.0, $^{3}J_{5B,OH}$ = 8.0, $^{3}J_{5B,4B}$ = 4.5 Hz, 1 H, 5B-H), 3.60 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.72 (ddd, $^{2}J_{5B,5B}$ = 12.0, $^{3}J_{5B,OH}$ = 5.0, $^{3}J_{5B,4B}$ = 3.5 Hz, 1 H, 5B-H), 3.86 (dd, $^{3}J_{3A,4A}$ = 6.0, $^{3}J_{3A,2A}$ = 3.0 Hz, 1 H, 3A-H), 4.07 (ddd, $^{3}J_{4B,3B}$ = 6.0, $^{3}J_{4B,5B}$ = 4.5, $^{3}J_{4B,5B}$ = 3.0 Hz, 1 H, 4B-H), 4.10−4.21 (m, 3 H, 4A-H, 5A-H), 4.26 (dd, $^{3}J_{2A,3A}$ = 3.0, $^{3}J_{2A,1A}$ = 1.0 Hz, 1 H, 2A-H), 4.35 (dd, $^{3}J_{3B,2B}$ = 7.0, $^{3}J_{3B,4B}$ = 6.0 Hz, 1 H, 3B-H), 4.52, 4.66 (2d, ^{2}J = 11.5 Hz, 2 × 1 H, benzyl CH_2), 4.60, 4.68 (2d, ^{2}J = 12.0 Hz, 2 × 1 H, benzyl CH_2), 4.80 (d, $^{3}J_{1A,2A}$ = 1.0 Hz, 1 H, 1A-H), 4.91 (dd, $^{3}J_{2B,3B}$ = 7.0, $^{3}J_{2B,1B}$ = 5.0 Hz, 1 H, 2B-H), 5.38 (d, $^{3}J_{1B,2B}$ = 5.0 Hz, 1 H, 1B-H), 7.25−7.40 (m, 10 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 20.5 (*C*H$_3$CO), 24.8, 25.6, 25.9, 26.5, 27.0, 29.0, 29.1, 29.4, 34.0 (*C*H$_2$CO), 38.7 [CO*C*(CH$_3$)$_3$], 51.4 (OCH_3), 63.0 and 63.4 (C-5A, C-5B), 67.7 (octyl OCH_2), 72.1 and 72.6 (benzyl CH_2), 79.0, 79.2, 81.4, 83.3, 85.5, 99.3 (C-1B), 105.4 (C-1A), 127.6, 127.8, 127.9, 128.4, 128.4, 137.4, 137.5, 170.3 (CH$_3$*C*O), 174.3 (*C*O-OCH$_3$), 178.1 [*C*OC(CH$_3$)] ppm. $C_{41}H_{58}O_{13}$ (758.9): calcd. C 64.89, H 7.70; found C 64.94, H 7.62.

8-(Methoxycarbonyl)octyl 3-*O*-Benzyl-2-*O*-{3-*O*-benzyl-5-*O*-[2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl]-β-D-arabinofuranosyl}-α-D-arabinofuranoside (33): Glycosylation of diarabinoside **31** (46 mg, 61 µmoles) with dimannoside **13** (82 mg, 85 µmoles) was carried out with NIS (23 mg, 104 µmoles) and TMSOTf (9 µL of a 1 M solution in toluene, 9 µmol) according to the General Procedure. Chromatography with toluene/ethyl acetate (8:1) gave tetrasaccharide **32** (77 mg, 77%) as a 4:1 α/β-anomeric mixture on the C-1C anomeric center. This mixture (100 mg, 60 µmol) was treated with a 0.5 M NaOMe solution in MeOH for 5 h at room temp before neutralization with solid NH_4Cl (3.5 mg, 66 µmol). CH_2Cl_2/water extraction and chromatography (toluene/acetone, 5:1) gave the 1C-H β-anomer of **33** (14 mg, 16%), an equimolar mixture of anomers (8 mg, 9%) and **33** (46 mg, 50%). $[\alpha]_D^{25}$ = +25 (*c* = 1.10 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.24−1.34 and 1.48−1.67 (2m, 12 H, octyl CH_2), 2.30 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 2.34−2.40 (m, 2 H, 5A-OH, 2D-OH), 2.53 (d, $^{3}J_{OH,2B}$ = 9.0 Hz, 1 H, 2B-OH), 3.34 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, 1 H, octyl OCH_2), 3.51 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.66−4.27 (m, 22 H), 4.41−4.84 (m, 16 H, benzyl CH_2), 4.94 (s, 1 H, 1A-H), 4.98 (d, $^{3}J_{1C,2C}$ = 2.0 Hz, 1 H, 1C-H), 5.12 (d, $^{3}J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H), 5.13 (d, $^{3}J_{1D,2D}$ = 2.0 Hz, 1 H, 1D-H), 7.10−7.40 (m, 40 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 24.9, 26.0, 29.0, 29.1, 29.4, 29.7, 34.0 (*C*H$_2$CO), 51.5 (CH_3O), 61.4 (C-5A), 67.4 (octyl OCH_2), 68.4, 68.8, 68.9, 69.2, 71.4, 71.9, 72.0, 72.5, 73.3, 74.2, 74.5, 74.7, 75.1, 75.2, 79.8, 79.9, 80.1, 82.4, 82.9, 84.0, 87.9, 98.9 (C-1C), 101.0 (C-1B), 102.2 (C-1D), 106.1 (C-1A), 127.4, 127.5, 127.5, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 128.3, 128.4, 137.6, 137.9, 137.9, 138.0, 138.1, 138.2, 138.2, 138.3, 174.3 (*C*OOCH$_3$) ppm. $C_{88}H_{104}O_{21}$ (1497.8): calcd. C 70.57, H 7.00; found C 70.44, H 6.84.

8-(Methoxycarbonyl)octyl 2-*O*-[5-*O*-(2-*O*-α-D-Mannopyranosyl-α-D-mannopyranosyl)-β-D-arabinofuranosyl]-α-D-arabinofuranoside (3): Compound **33** (12 mg, 8 µmol) in MeOH (2 mL) was hydrogenolyzed according to Procedure A. Chromatography with ethyl acetate/methanol/water (8:3:1) gave **3** as a white solid (4 mg, 65%). $[\alpha]_D^{25}$ = +19 (*c* = 0.40 in water). ^{1}H NMR (500 MHz, D_2O, 25 °C): δ = 1.28−1.37 and 1.56−1.63 (2m, 12 H, octyl CH_2), 2.38 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 3.56 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.60 (t, $^{3}J_{4D,3D} \approx {}^{3}J_{4D,5D} \approx$ 9.5 Hz, 1 H, 4D-H), 3.64 (ddd, $^{3}J_{5C,4C}$ = 10.0, $^{3}J_{5C,6C}$ = 6.0, $^{3}J_{5C,6C}$ = 2.0 Hz, 1 H, 5C-H), 3.68 (s, 3 H, CH_3O), 3.70 (dd, $^{2}J_{5B,5B}$ = 9.5, $^{3}J_{5B,4B}$ = 6.0 Hz, 1 H, 5B-H), 3.70 (dd, $^{2}J_{6C,6C}$ = 12.0, $^{3}J_{6C,5C}$ = 6.0 Hz, 1 H, 6C-H), 3.73 (dd, $^{2}J_{5A,5A}$ = 12.0, $^{3}J_{5A,4A}$ = 3.0 Hz, 1 H, 5A-H), 3.75 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.76 (dd, $^{2}J_{6D,6D}$ = 12.0, $^{3}J_{6D,5D}$ = 6.0 Hz, 1 H, 6D-H), 3.77 (dd, $^{3}J_{4C,5C}$ = 10.0, $^{3}J_{4C,3C}$ = 9.5 Hz, 1 H, 4C-H), 3.78 (ddd, $^{3}J_{5D,4D}$ = 9.5, $^{3}J_{5D,6D}$ = 6.0, $^{3}J_{5D,6D}$ = 2.0 Hz, 1 H, 5D-H), 3.79 (dd, $^{2}J_{6D,6D}$ = 12.0, $^{3}J_{6D,5D}$ = 2.0 Hz, 1 H, 6D-H), 3.83 (dd, $^{2}J_{5B,5B}$ = 9.5, $^{3}J_{5B,4B}$ = 6.0 Hz, 1 H, 4B-H), 3.84 (dd, $^{3}J_{3D,4D}$ = 9.5, $^{3}J_{3D,2D}$ = 3.5 Hz, 1 H, 3D-H), 3.84 (dd, $^{2}J_{5A,5A}$ = 12.0, $^{3}J_{5A,4A}$ = 3.0 Hz, 1 H, 5A-H), 3.89 (dd, $^{2}J_{6C,6C}$ = 12.0, $^{3}J_{6C,5C}$ = 2.0 Hz, 1 H, 6C-H), 3.95 (dd, $^{3}J_{4C,3C}$ = 9.5, $^{3}J_{3C,2C}$ = 3.5 Hz, 1 H, 3C-H), 4.02 (m, 1 H, 4B-H), 4.02 (dd, $^{3}J_{2C,3C}$ = 3.5, $^{3}J_{2C,1C}$ = 1.7 Hz, 1 H, 2C-H), 4.04 (dd, $^{3}J_{4A,3A}$ = 5.0, $^{3}J_{4A,5A}$ = 3.0 Hz, 1 H, 4A-H), 4.07 (dd, $^{3}J_{2D,3D}$ = 3.5, $^{3}J_{2D,1D}$ = 2.0 Hz, 1 H, 2D-H), 4.09 (dd, $^{3}J_{3A,4A}$ = 5.0, $^{3}J_{3A,2A}$ = 4.0 Hz, 1 H, 3A-H), 4.11 (dd, $^{3}J_{2A,3A}$ = 4.0, $^{3}J_{2A,1A}$ = 2.0 Hz, 1 H, 2A-H), 4.11 (dd, $^{3}J_{3B,2B}$ = 8.0, $^{3}J_{3B,4B}$ = 7.0 Hz, 1 H, 3B-H), 4.14 (dd, $^{3}J_{2B,3B}$ = 8.0, $^{3}J_{2B,1B}$ = 4.5 Hz, 1 H, 1B-H), 5.02 (d, $^{3}J_{1D,2D}$ = 2.0 Hz, 1 H, 1D-H), 5.10 (d, $^{3}J_{1A,2A}$ = 2.0 Hz, 1 H, 1A-H), 5.11 (d, $^{3}J_{1B,2B}$ = 4.5 Hz, 1 H, 1B-H), 5.16 (d, $^{3}J_{1C,2C}$ = 1.7 Hz, 1 H, 1B-H) ppm. ^{13}C NMR (125.72 MHz, D_2O, 25 °C): δ = 24.9, 25.8, 28.8, 28.9, 29.2, 34.4 (CH_2CO), 52.7 (OCH_3), 61.1 (C-5A), 61.5 and 61.8 (C-6C, C-6D), 67.5 (C-4D), 67.6 (C-4C), 69.0 (C-5B), 69.2 (OCH_2 octyl), 70.6 (C-2D), 70.8 (C-3C), 70.9 (C-3D), 73.5 (C-5C), 73.9 (C-5D), 74.7 (C-3B), 75.2 (C-3A), 76.7 (C-2B), 79.4 (C-4B), 80.4 (C-2C), 83.1 (C-4A), 87.5 (C-2A), 98.8 (C-1C), 101.0 (C-1B), 103.0 (C-1D), 106.1 (C-1A), 174.3 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{32}H_{56}O_{21}Na$: calcd. 799.3212, found 799.3218.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (34): From **5** (230.0 mg, 0.45 mmol) and **12** (290.0 mg, 0.54 mmol). Chromatography with petroleum ether/EtOAc (9:1) gave **34** as a colorless oil (385.0 mg, 87%). $[\alpha]_D^{25}$ = +37 (c = 1.20 in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90−1.16 [m, 28 H, $(CH_3)_2$CH], 1.25−1.40 (m, 8 H, octyl CH_2), 1.56−1.65 (m, 4 H, octyl CH_2), 2.30 (t, ^{3}J = 7.7 Hz, 2 H, CH_2CO), 3.45 (td, ^{2}J = 9.6, ^{3}J = 6.6 Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.68 (m, 1 H, 5A-H), 3.72 (td, 1 H, octyl OCH_2), 3.90 (dd, $^{2}J_{5A,5A}$ = 11.2, $^{3}J_{5A,4A}$ = 4.7 Hz, 1 H, 5A-H), 3.93−3.99 (m, 3 H, 3B-H, 2 × 5B-H), 4.08 (br. d, $^{3}J_{3A,4A}$ = 4.9 Hz, 1 H, 3A-H), 4.33 (m, 1 H, 4A-H), 4.45 (m, 1 H, 4B-H), 4.64, 4.83 (2d, ^{2}J = 12.0 Hz, 2 × 1 H, benzyl CH_2), 5.08 (d, $^{3}J_{1B,2B}$ = 1.6 Hz, 1 H, 1B-H), 5.12 (s, 1 H, 1A-H), 5.40 (d, $^{3}J_{2A,3A}$ = 1.4 Hz, 1 H, 2A-H), 5.48 (dd, $^{3}J_{2B,3B}$ = 5.6, $^{3}J_{2B,1B}$ = 1.6 Hz, 1 H, 2B-H), 7.28−8.09 (m, 15 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 20 °C): δ = 12.8, 13.2, 13.6, 13.9, $(CH_3)_2$*C*H], 17.3, 17.4, 17.8, 17.9 [(*C*H$_3$)$_2$CH], 25.4, 26.4, 29.5, 29.6, 29.7, 29.8 (octyl CH_2), 34.5 (*C*H$_2$CO), 51.9 (CH_3O), 61.7 (C-5B), 67.6 (C-5A), 68.0 (octyl OCH_2), 72.6 (benzyl CH_2), 76.2 (C4-B), 81.4 (C-3B), 81.9 (C-4A), 82.3 (C-2A), 84.1 (C-3A), 84.4 (C-2B), 106.0 (C-1B), 106.3 (C-1A), 128.1, 128.3, 128.8, 128.9, 129.9, 130.1, 130.3, 133.6, 133.8, 138.2 (Ar), 165.8, 166.0 (*C*OOPh), 174.8 (*C*OOCH$_3$) ppm.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-(2-*O*-benzoyl-α-D-arabinofuranosyl)-3-*O*-benzyl-α-D-arabinofuranoside (35): **34** (112.0 mg, 0.11 mmol) was desilylated with neutralized Bu_4NF in THF according to the General Procedure. Chromatography with petroleum ether/EtOAc (1:1) gave **35** as a colorless oil (83.3 mg, 98%). $[\alpha]_D^{25}$ = +93 (c = 1.09 in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.27−1.40 (m, 8 H, octyl CH_2), 1.58−1.65 (m, 4 H, octyl CH_2), 2.29 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 3.47 (td, ^{2}J = 9.6, ^{3}J = 6.5 Hz, 1 H, octyl OCH_2), 3.65 (s, 3 H, CH_3O), 3.73 (m, 1 H, 5B-H), 3.74 (m, 1 H, 5A-H), 3.75 (td, 1 H, octyl OCH_2), 3.84 (dd, $^{2}J_{5B,5B}$ = 12.1, $^{3}J_{5B,4B}$ = 3.3 Hz, 1 H, 5B-H), 3.92 (dd, $^{2}J_{5A,5A}$ = 11.1, $^{3}J_{5A,4A}$ = 5.0 Hz, 1 H, 5A-H), 4.05 (br. d, $^{3}J_{3A,4A}$ = 6.3 Hz, 1 H, 3A-H), 4.07 (m, 1 H, 4B-H), 4.15 (dd, $^{3}J_{3B,4B}$ = 6.1, $^{3}J_{3B,2B}$ = 2.5 Hz, 1 H, 3B-H), 4.34 (m, 1 H, 4A-H), 4.64, 4.84 (2d, ^{2}J = 12.1 Hz, 2 × 1 H, benzyl CH_2), 5.10 (d, $^{3}J_{2B,1B}$ = 2.1 Hz, 1 H, 2B-H), 5.17 (s, 1 H, 1A-H), 5.31 (s, 1 H, 1B-H), 5.39 (d, $^{3}J_{2A,1A}$ = 1.4 Hz, 1 H, 2A-H), 7.21−8.05 (m, 15 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 20 °C): δ = 24.8, 25.1, 29.0, 29.1, 29.3 (octyl CH_2), 34.0 (*C*H$_2$CO), 51.4 (CH_3O), 61.6 (C-5B), 66.0 (C-5A), 67.5 (octyl O*C*H$_2$), 72.2 (benzyl CH_2), 76.2 (C-3B), 81.3 (C-4A), 81.8 (C-2A), 83.2 (C-3A), 84.2 (C4-B), 85.8 (C-2B), 105.2 (C-1B), 105.9 (C-1A), 127.7, 128.5, 128.4, 129.7, 133.4, 133.5, 137.6 (Ar), 174.3 (*C*OOCH$_3$) ppm. $C_{41}H_{50}O_{13}$ (750.8): calcd. C 65.59, H 6.71; found C 65.51, H 6.45.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-[2-*O*-benzoyl-3,5-di-*O*-(3-*O*-benzyl-5-*O*-pivaloyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl]-3-*O*-benzyl-α-D-arabinofuranoside (37): Glycosylation of **35** (40.0 mg, 53 μmol) with **10** (85.0 mg, 0.14 mmol) was carried out according to the General Procedure. After workup of the reaction, the residue containing **36** was taken up in a 4:1 THF/Et_3N mixture and left at room temp for 2 h. Concentration and chromatography with petroleum ether/EtOAc (3:1) gave **37** as a colorless oil (54.3 mg, 75%, 2 steps). $[\alpha]_D^{25}$ = +100 (c = 0.90 in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.10−1.18 [m, 18 H, 2 × $C(CH_3)_3$], 1.23−1.40 (m, 8 H, octyl CH_2), 1.56−1.66 (m, 4 H, octyl CH_2), 2.29 (t, ^{3}J = 7.4 Hz, 2 H, CH_2CO), 2.35 (d, $^{3}J_{OH,2D}$ = 4.8 Hz, 1 H, OH-2D), 2.52 (d, $^{3}J_{OH,2C}$ = 5.9 Hz, 1 H, OH-2C), 3.47 (td, ^{2}J = 9.6, ^{3}J = 6.6 Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.66 (dd, $^{2}J_{5B,5B}$ = 11.4, $^{3}J_{5B,4B}$ = 3.3 Hz, 1 H, 5B-H), 3.69−3.77 (m, 4 H, 2C-H, 2D-H, 5A-H, octyl OCH_2), 3.90 (dd, $^{2}J_{5A,5A}$ = $^{2}J_{5B,5B}$ = 11.4, $^{3}J_{5A,4A}$ = $^{3}J_{5B,4B}$ = 4.3 Hz, 1 H, 5A-H, 5B-H), 4.06−4.31 (m, 11 H, 3A-H, 3B-H, 3C-H, 3D-H, 4B-H, 4C-H, 4D-H, 2 × 5C-H, 2 × 5D-H), 4.33 (m, 1 H, 4A-H), 4.41, 4.48, 4.50, 4.60, 4.61, 4.81 (6d, ^{2}J = 12.1 Hz, 6 × 1 H, benzyl CH_2), 4.98 (d, $^{3}J_{1C,2C}$ = 1.1 Hz, 1 H, 1C-H), 5.07 (b, 1 H, 1D-H), 5.15 (s, 1 H, 1A-H), 5.28 (d, $^{3}J_{2B,3B}$ = 1.5 Hz, 1 H, 2B-H), 5.29 (s, 1 H, 1B-H), 5.39 (d, $^{3}J_{2A,3A}$ = 1.2 Hz, 1 H, 2A-H), 7.19−8.09 (m, 25 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 20 °C): δ = 25.0 (octyl CH_2), 26.1, 27.1, 27.2, 27.3 [C(*C*H$_3$)$_3$], 29.2, 29.3, 29.5 (octyl CH_2), 34.2 (*C*H$_2$CO), 51.6 (CH_3O), 63.4 (C-5C, C-5D), 65.9 (C-5A, C-5B), 67.8 (octyl OCH_2), 71.8, 72.1, 72.4, 72.5 (benzyl CH_2), 79.7, 79.9 (C-3B), 80.7, 81.6, 81.4, 81.6 (C-4A), 81.9 (C-2A), 82.1 (C-4B), 83.1 (C-2B), 83.4 (C-3A), 84.3 (C-2C), 84.8 (C-2D), 105.8 (C-1B), 106.0 (C-1A), 108.3 (C-1D), 108.5 (C-1C), 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 128.4, 128.7, 128.8, 129.3, 129.6, 129.9, 130.0, 133.6, 133.7, 137.6, 137.7, 137.8 (Ar), 165.8 (*C*OOPh), 174.7 (*C*OOCH$_3$), 178.3, 178.4 [$(CH_3)_3$C*C*O) ppm. HRMS (FAB): $C_{75}H_{94}O_{23}Na$: calcd. 1385.6083, found 1385.6085.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-5-*O*-{2-*O*-benzoyl-3,5-di-*O*-[2-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-β-D-arabinofuranosyl)-3-*O*-benzyl-5-*O*-pivaloyl-α-D-arabinofuranosyl]-α-D-arabinofuranosyl}-3-*O*-benzyl-α-D-arabinofuranoside (38): From **37** (100.0 mg, 73 μmol) and **9** (141.0 mg, 0.22 mmol) according to the General Procedure. Chromatography with petroleum ether/EtOAc (3:1) gave **38** as a colorless oil (45.5 mg, 27%). $[\alpha]_D^{25}$ = +40 (c = 0.80 in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.01, 1.02 [2 s, 18 H, 2 × SiC(C*H*$_3$)$_3$], 1.08, 1.09 [2 s, 18 H, 2 × COC(C*H*$_3$)$_3$], 1.24−1.36 (m, 8 H, octyl CH_2), 1.55−1.77 (m, 4 H, octyl CH_2), 2.29 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 2.53 (d, $^{3}J_{OH,2F}$ = 8.3 Hz, 1 H, 2F-OH), 2.81 (d, $^{3}J_{OH,2E}$ = 7.8 Hz, 1 H, 2E-OH), 3.42 (td, ^{2}J = 9.7, ^{3}J = 6.7 Hz, 1 H, octyl OCH_2), 3.65 (s, 3 H, CH_3O), 3.67−3.77 (m, 9 H, 3C-H, 3D-H, 5A-H, 5B-H, 2 × 5E-H, 2 × 5F-H, octyl OCH_2), 3.85 (m, 2 H, A-H, B-H), 3.91 (m, 1 H, 3F-H), 3.93−4.17 (m, 14 H, 3A-H, 3B-H, 3E-H, 4B-H, 4C-H, 4D-H, 4E-H, 4F-H, 2 × 5C-H, 2 × 5D-H, 2 × benzyl CH_2), 4.17−4.32 (m, 6 H, 2C-H, 2D-H, 2E-H, 2F-H, 4A-H, benzyl CH_2), 4.45, 4.54, 4.62, 4.65, 4.70, 4.73, 4.74 (7 d, ^{2}J = 12.0 Hz, 7 × 1 H, benzyl CH_2), 5.01 (b, 1 H, 1D-H), 5.10 (s, 1 H, 1A-H), 5.11 (d, $^{3}J_{1F,2F}$ = 4.7 Hz, 1 H, 1F-H), 5.17 (s, 1 H, 1C-H), 5.21 (d, $^{3}J_{1E,2E}$ = 4.7 Hz, 1 H, 1E-H), 5.24 (d, $^{3}J_{2B,3B}$ = 2.0 Hz, 1 H, 2B-H), 5.28 (s, 1 H, 1B-H), 5.35 (d, $^{3}J_{2A,3A}$ = 1.3 Hz, 1 H, 2A-H), 6.95−8.02 (m, 55 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 20 °C): δ = 24.6, 25.6 (octyl CH_2), 26.4, 26.6, 26.7, 26.8 [$C(\mathit{C}H_3)_3$], 28.7, 28.8, 28.9, 29.0 (octyl CH_2), 33.7 ($\mathit{C}H_2CO$), 51.1 (CH_3O), 62.6, 63.1 (C-5C, C-5D), 65.3 (C-5A, C-5F), 65.4 (C-5E), 65.5 (C-5B), 67.2 (octyl OCH_2), 71.4, 71.5, 71.9, 72.0 (benzyl CH_2), 77.1 (C-2E, C-2F), 79.4 (C-4C, C-4D), 81.0 (C-4A), 81.2 (C-4B), 81.5 (C-2A), 82.0 (C-4E), 82.1 (C-4F), 82.9 (C-3D), 83.1 (C-3A), 83.5 (C-3C), 83.9 (C-2B), 84.5 (C-3E), 84.6 (C-3F), 86.0 (C-2D), 86.5 (C-2C), 101.6 (C-1F), 102.2 (C-1E), 105.3 (C-1B), 105.5 (C-1A), 106.4 (C-1D), 106.6 (C-1C), 127.1, 127.2, 127.3, 127.4, 127.5, 127.8, 127.9, 128.0, 128.1, 128.2, 128.7, 129.0, 129.4, 129.5, 132.5, 135.6, 132.7, 133.1, 135.2, 135.3, 136.9, 137.3, 137.5, 137.6 (Ar), 165.1, 165.4 ($Ph\mathit{C}O$), 174.0 ($\mathit{C}OOCH_3$), 177.6 [$(CH_3)_3C\mathit{C}O$) ppm.

8-(Methoxycarbonyl)octyl 5-*O*-[3,5-Di-*O*-(2-*O*-β-D-arabinofuranosyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl]-α-D-arabinofuranoside (4): 38 (45.0 mg, 20 µmol) was submitted to three steps of deprotection without purification of the intermediate compounds. Desilylation (Bu_4NF in THF), debenzoylation and debenzylation (Procedure B) were run according to the General Procedures. Chromatography with dichloromethane/methanol (2:1) gave **4** as a colorless oil (5.8 mg, 30%, 3 steps). $[\alpha]_D^{25}$ = +45.5 (c = 0.58 in methanol). ^{1}H NMR (400 MHz, CD_3OD, 20 °C): δ = 1.28−1.42 (m, 8 H, octyl CH_2), 1.55−1.65 (m, 4 H, octyl CH_2), 2.32 (t, ^{3}J = 7.5 Hz, 2 H, CH_2CO), 3.42 (td, ^{2}J = 9.5, ^{3}J = 6.4 Hz, 1 H, octyl OCH_2), 3.66 (s, 3 H, CH_3O), 3.60−3.68 (m, 5 H, 5A-H, 5C-H, 5D-H, 5E-H, 5F-H), 3.71 (m, 1 H, octyl OCH_2), 3.70−3.84 (m, 6 H, 5A-H, 5B-H, 5C-H, 5D-H, 5E-H, 5F-H), 3.89−4.08 (m, 15 H, 2A-H, 2B-H, 2E-H, 2F-H, 3A-H, 1C-H, 3D-H, 3E-H, 3F-H, 4A-H, 4C-H, 4D-H, 4E-H, 4F-H, 5B-H), 4.13 (dd, $^{3}J_{2D,3D}$ = 5.2, $^{3}J_{2D,1D}$ = 2.4 Hz, 1 H, 2D-H), 4.14 (dd, $^{3}J_{2C,3C}$ = 4.9, $^{3}J_{2C,1C}$ = 2.3 Hz, 1 H, 2C-H), 4.16 (dd, $^{3}J_{3B,4B}$ = 2.8, $^{3}J_{3B,2B}$ = 1.3 Hz, 1 H, 3B-H), 4.19 (m, 1 H, 4B-H), 4.88 (m, 1 H, 1A-H), 4.98 (b, 1 H, 1B-H), 5.03 (d, $^{3}J_{1F,2F}$ = 3.9 Hz, 1 H, 1F-H), 5.03 (d, $^{3}J_{1E,2E}$ = 4.0 Hz, 1 H, 1E-H), 5.08 (d, $^{3}J_{1C,2C}$ = 2.1 Hz, 1 H, 1C-H), 5.16 (d, $^{3}J_{1D,2D}$ = 2.3 Hz, 1 H, 1D-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 20 °C): δ = 26.0, 27.2, 30.1, 30.4, 30.7 (octyl CH_2), 34.8 ($\mathit{C}H_2CO$), 52.0 (CH_3O), 62.3 (C-5F), 62.4 (C-5E), 64.3 (C-5D), 64.4 (C-5C), 67.4 (C-5A), 67.8 (C-5B), 68.9 (octyl OCH_2), 75.6, 75.7, 76.2, 76.4, 78.6 (C-3A), 78.7 (C-3C, C-3D, C-3E, C-3F), 81.6 (C-3B), 82.9, 83.3, 83.7 (C-2A), 83.8, 83.9, 84.3, 84.6, 89.2 (C-2C), 89.4 (C-2D), 102.4 (C-1F), 102.5 (C-1E), 107.0 (C-1D), 107.4 (C-1C), 109.4 (C-1A), 109.5 (C-1B), 176.1 ($\mathit{C}OOCH_3$) ppm.

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