Synthesis and Biological Evaluation of Imino Sugar−Oligoarabinofuranoside Hybrids, a New Class of Mycobacterial Arabinofuranosyltransferase Inhibitors

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The mycobacterial cell wall is a promising target for the development of new antituberculosis drugs. We report the synthesis and preliminary biological evaluation of imino sugar–oligoarabinofuranoside hybrids, a new class of mycobacterial arabinosyltransferase inhibitors. These hybrids were built from various chiral polyhydroxylated pyrrolidines (imino sugars) linked to small oligoarabinofuranosides. The coupling reaction was a reductive amination of a suitable oligoarabinofuranoside aldehyde with an unprotected amine counterpart. Good in vitro arabinosyl transferase inhibitions were observed for some of these hybrids with radioactive [^{14}C]-DPA as the glycosyl donor and, more importantly, their inhibitory activity was modulated by the length of the oligosaccharide moiety. This result shows that potential inhibitors of these mycobacterial enzymes can be prepared by linking them to an acceptor-like oligoarabinofuranoside.

Introduction

Two major human pathogens are found in the mycobacteria genus, *Mycobacterium leprae*, responsible for leprosy and *M. tuberculosis*, the causative agent of human tuberculosis. Tuberculosis is a major worldwide health problem, taking millions of lives annually and new drugs are urgently needed to fight the disease. For the construction of their cell wall, mycobacteria make an extensive use of D-arabinose, which is found as oligomers of arabinofuranosides in arabinogalactan and lipoglycans.[1,2] As D-arabinose is not used by the human host, the arabinan biosynthetic pathway is a promising antituberculosis therapeutic target. In this respect, ethambutol, a first-line antituberculosis drug, had been shown to interact with the arabinan synthesis[3] by inhibition of mycobacterial arabinosyltransferases.[4]

The chemistry and biochemistry of carbohydrate mimetics is a very dynamic field that emerged with the discovery of glycosidase-inhibition properties of imino sugars and carbasugars.[5−7] Among other interesting biological properties, these mimics were later shown to act also as glycosyltransferase inhibitors.[8] The increasing importance of glycobiology and the involvement of abnormal glycosylations in some diseases made glycosyltransferases potential therapeutic targets for the development of new drugs.[9,10] It had been suggested that the association of an imino sugar with a potential ligand of the aglycon-binding site of the glycosyltransferase should give more potent and selective inhibitors than are the isolated imino sugars. Some examples of such pseudosaccharides have been recently described although few biological data have been published on these compounds.[11−21] We were interested in evaluating the arabinosyltransferase inhibitory properties of various imino sugars and the modulation of these activities by linking them to a small oligoarabinofuranoside moiety. We now report the synthesis of imino sugar−oligoarabinofuranoside hybrids and preliminary results on their in vitro activities as mycobacterial arabinosyltransferase inhibitors.

Synthesis of Imino Sugar−Oligoarabinofuranoside Hybrids

In regard to the imino sugar moiety, we focused our attention on the 1,4-dideoxy-1,4-imino-D-arabinitol pattern, which appeared to be a good mimic of the transferred arabinosyl residue. All the polyhydroxylated pyrrolidines **2**−**6** (see Figure 1) used in this study share this basic structure. Interestingly, the rare examples of potential inhibitors of mycobacterial cell-wall biosynthesis, which embed a similar imino sugar fragment, met only limited success in terms of antimycobacterial activity.[22,23] Compounds **2**−**6** were synthesised by an original methodology starting from a versatile chiral *cis*-α,β-epoxyamine **A**, readily accessible from the corresponding epoxy aldehyde[24] (see Figure 1). Appel cyclisation on the activated primary alcohol, followed by the regiocontrolled opening of the epoxide (either with

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hydroxy or fluoride anion), formed the hydroxylated (or fluorinated) vinylpyrrolidine intermediates **B** possessing the required configurations. Catalytic hydrogenation of this vinylpyrrolidine (X = OH) gave ethyl-substituted pyrrolidine **2**, while oxidative cleavage of the double bond of both pyrrolidines **B** gave rise to the targeted imino sugar **3** or its 2-deoxy-2-fluoro (imino sugar numbering analog **4**. 1,4-Dideoxy-1,4-imino-L-galactitol (**5**), bearing an additional hydroxymethyl substituent, also was found to be a good candidate for mimicking the transferred arabinosyl residue. Thus, it was prepared, as well as its 2-deoxy-2-fluoro analog **6**, from the same vinylpyrrolidines **B**, by diastereoselective dihydroxylation of the olefin. Finally, a simpler member of this family, (*S*)-prolinol (**1**) was also included in this study.

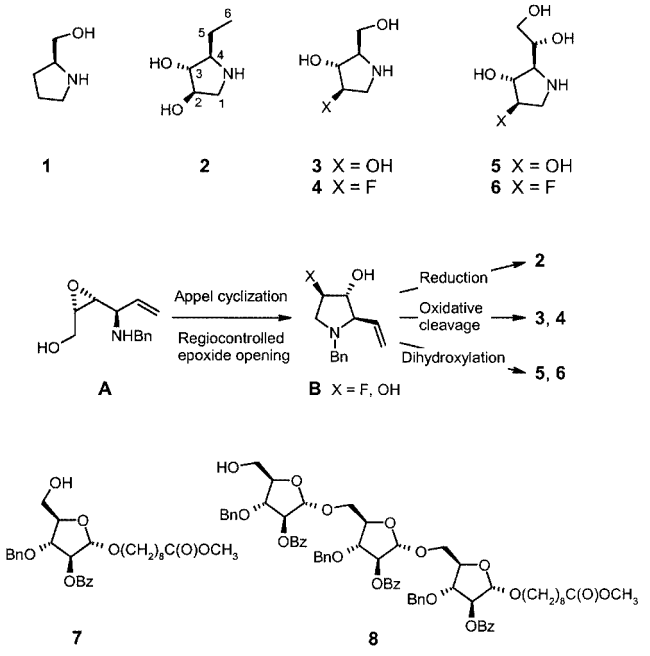


Figure 1. Imino sugars **1**−**6** and oligoarabinofuranosides **7** and **8** used for the construction of hybrid molecules

As addressing compounds, we selected two arabinofuranosides (Figure 1): monoarabinofuranoside **7** possesses the minimum structural recognition element, and triarabinofuranoside **8** was chosen as a model of the elongating arabinan chain. The choice of the anomeric substituent at the reducing end of the arabinoside was based on the analysis that some lipophilic character of the oligoarabinofuranoside acceptor was needed to get good recognition by the enzyme.[25] Compounds **7** and **8** were synthesized from D-arabinose using the 1,2,5-orthoester route.[26−29]

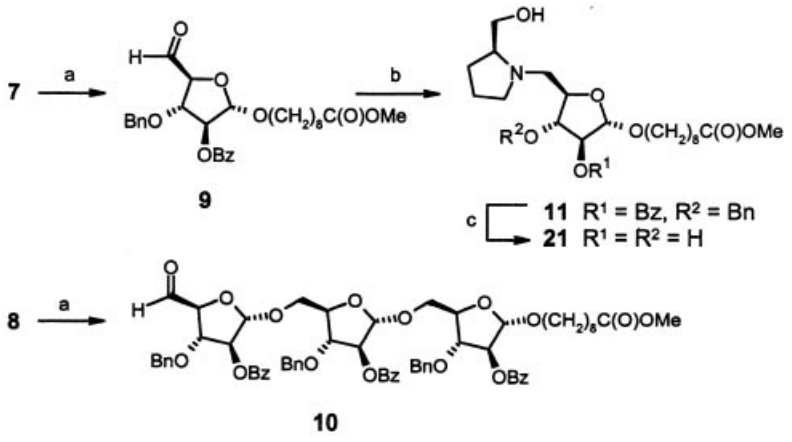
The general route we followed to obtain imino sugar−oligoarabinofuranoside hybrid molecules is depicted in Scheme 1. For coupling with the imino sugar, the free 5-hydroxy groups of **7** and **8** were oxidized to aldehyde units; this process was best done with dicyclohexylcarbodiimide and dichloroacetic acid in anhydrous DMSO.[30,31] Other methods were tried, such as PCC/AcONa and Swern oxidation, but complete decomposition of the product was observed during workup of the reaction. Sensitive aldehydes **9** and **10** were thus obtained from alcohols **7** and **8**. These aldehydes could not be purified on silica, nor isolated in pure form, and the crude product from the workup of the oxidation reaction was directly used for the reductive amination step (see Exp. Sect.).

Aldehyde **9** was treated with 1.5 equiv. of prolinol (**1**) and 5 equiv. of sodium cyanoborohydride[32] in acidic methanol. The reaction was complete after 1.5 h at reflux temperature and coupling product **11** was isolated in 81% yield after chromatography. Final product **21** was obtained after two steps of deprotection: sodium methoxide in methanol removed the benzoate ester, while the benzyl ether unit was hydrogenolyzed at room temperature with $Pd(OH)_2/C$ as catalyst. All other coupling products (see Figure 2) were obtained from aldehydes **9** and **10** and amino derivatives **2**−**6** according to the very same procedure. The results are summarized in Table 1.

Arabinosyltransferase Assays

Arabinosyltransferase assays were carried out as described previously[4,25] with radioactive [1-^{14}C]-β-D-arabinofuranosyl-1-decaprenyl phosphate ([1-^{14}C]-DPA) as the arabinose donor and octyl 5-*O*-α-D-arabinofuranosyl-α-D-arabinofuranoside as the synthetic acceptor. First we checked that none of the compounds **21**−**30** behaved as arabinose acceptors. This test was done by running experiments with [1-^{14}C]-DPA and each synthesized compound at a concentration of 4 mM in the absence of any acceptor. No excess of radioactivity, compared to the blank experiments (no acceptor, no inhibitor), was detected in the products after workup of the reaction and this result showed that no radioactive arabinose had been transferred on our compounds. We then measured the inhibition properties of our hybrids, using concentrations of 0.4 mM for the acceptor and 4 mM for the inhibitor. The results are summarized in Table 2.

As expected, inhibitory activities for imino sugars **3**−**6** were low to moderate as these compounds are known to be fairly weak inhibitors of glycosyltransferases.[8] Linking these imino sugars, however, to a single arabinofuranoside unit (compounds **23**−**26**) gave greatly enhanced inhibitors and promising activities were obtained. Compare, for example, the moderate activity (22%) of **3** with the high inhibition (80%) obtained for **23**, at the same concentration of 4 mM. Moreover, this effect is general, with the exception of the D-galactitol residue **5**, with which no differences were observed between the imino sugar and the hybrid compound (Compare **5** with **25**, Table 2). Even the simplest members of the series, prolinol (**1**) and ethyl-substituted imino sugar **2**, showed good inhibitory activities when they were attached to the arabinoside (compounds **21** and **22**). When a longer arabinofuranoside (three arabinosyl units) was used as the addressing moiety (products **27**−**30**, Figure 2), a dramatic decrease in the activities was observed for every imino sugar we tested. The origin of this decrease



Scheme 1. General route to imino sugar−oligoarabinofuranoside hybrids: a) 4.0 equiv. DCC, 0.5 equiv. $CHCl_2COOH$, DMSO, room temp., 18 h; b) 1.0 equiv. **9**, 1.5 equiv. **1**, 5 equiv. $NaBH_3CN$, MeOH, reflux, 81%; c) NaOMe, MeOH, room temp., then H_2, $Pd(OH)_2$/C, 0.05 M HCl, MeOH, room temp., 41% over two steps

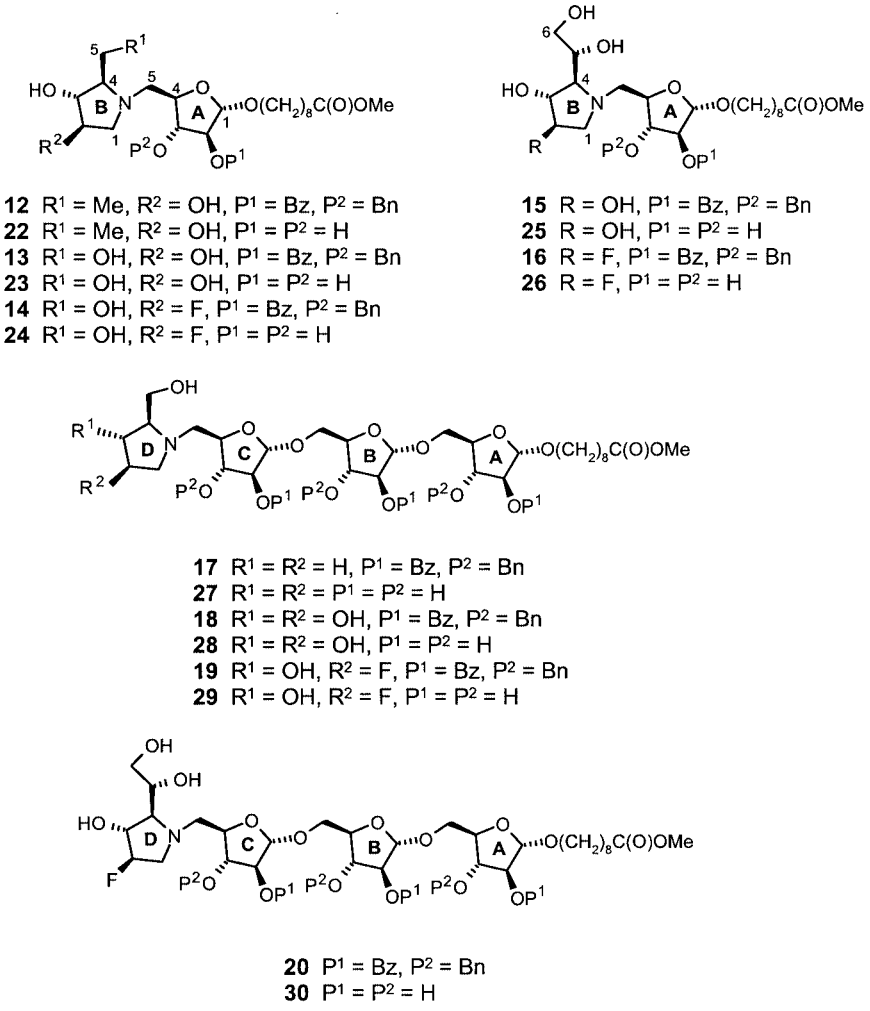


Figure 2. Structural formulas for products **12**−**30**

is not known, but might be related to the change in the lipophilic properties of the products. It shows, however, that a small arabinoside is sufficient to address the imino sugar to the enzyme.

Analysis of these data also revealed a sharp influence of the imino sugar fragment on the level of inhibition and some general trends emerged from these experiments. The D-arabinitol moiety, which corresponds to the closest mimic

Table 1. Synthesis of compounds **11**−**30**

Amine	Alcohol	Product[a]	Yield (%)[b]	Deprotected compound[a]	Yield (%)[c]
1	**7**	**11**	81	**21**	41
2	**7**	**12**	37	**22**	58
3	**7**	**13**	80	**23**	52
4	**7**	**14**	86	**24**	64
5	**7**	**15**	57	**25**	67
6	**7**	**16**	81	**26**	62
1	**8**	**17**	73	**27**	44
3	**8**	**18**	73	**28**	56
4	**8**	**19**	75	**29**	81
6	**8**	**20**	53	**30**	72

[a] For structural formulas, see Scheme 1 and Figure 2. [b] Yields are for two steps: oxidation of the alcohol and reductive amination of the intermediate aldehyde. [c] Overall yields for the two steps of deprotection; see text.

Table 2. Arabinosyltransferase inhibitory activities of compounds **3**−**6** and **21**−**30**

Product	**3**	**4**	**5**	**6**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Inhibition (%)	22	0	46	34	64	80	80	58	47	59	0	34	5	0

of arabinose, tended to give the best results (derivatives **3**, **23**, and **28**). Replacement of a hydroxy group in the pyrrolidine ring with a fluorine atom was generally accompanied with a decrease of activity (derivatives **4** vs. **3**, **6** vs. **5**, **24** vs. **23**, and **29** vs. **28**). Galactitol derivatives **25** and **26** are the only exceptions to this rule, as deoxy-fluoro compound **26** was found to be more active than the hydroxylated parent **25**; the origin of this particularity is not known. The crucial importance of the chiral secondary alcohols, compared to the primary one, in enzymatic recognition had been previously observed with other free deoxy-fluoro-imino sugars.[33] Removal of the two secondary hydroxy groups also gave a lowered inhibition (compound **21** vs. **23**). Prolinol-derived inhibitor **21**, however, appears quite attractive in regard to its simplicity of structure. Finally, the influence of the hydroxymethyl unit of the D-arabinitol moiety was found to be limited, since its replacement by an ethyl radical did not affect the activity (derivatives **22** vs. **23**).

Conclusion

Imino sugar−oligoarabinofuranoside hybrids have been synthesised efficiently using the reductive amination of an oligofuranosidic aldehyde with unprotected hydroxylated pyrrolidines. Some of these compounds showed promising arabinosyltransferase inhibitor activities in vitro and up to 80% inhibition was obtained at 4 mM concentration. More interestingly, the inhibition properties of the imino sugars were modulated by the length of the attached oligoarabinofuranoside moiety. The best results were obtained when a single arabinose unit was linked to the pyrrolidine ring while use of a longer oligosaccharide was deleterious for the inhibition. Although the exact origin of this effect has to be clarified, it shows that linking simple inhibitors to a small oligoarabinofuranoside can enhance their arabinosyltransferase inhibition properties. Further work in this direction is currently being undertaken.

Experimental Section

General Remarks: All reactions were run under argon in oven-dried glassware. Anhydrous methanol was distilled from magnesium, DMSO was stored in the presence of activated 4-Å molecular sieves (MS). 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 and AMX-400 spectrometers, working at 250 MHz (or 400 MHz) for ^{1}H and 62.89 MHz (or 100.62 MHz) for ^{13}C. All chemical shifts are expressed in ppm from internal tetramethylsilane. Conventions for the lettering of the rings of compounds **11**−**30** is shown in Figure 2. Optical rotations were measured at 25 °C with a Perkin−Elmer 41 polarimeter. Elemental analyses were obtained by the Laboratoire de Chimie de Coordination du CNRS at Toulouse (France). High-resolution mass spectra were obtained from the Centre d'Etudes Structurales et d'Analyse des Molécules Organiques (CESAMO) at Talence (France).

General Procedure for Oxidation of Alcohols 7 and 8: A solution of the alcohol in anhydrous DMSO (0.03 M solution) was treated at room temp. with DCC (4 equiv.) and dichloroacetic acid (0.5 equiv.). The reaction was left at room temp. overnight. The mixture was quenched with oxalic acid (3 equiv.), stirred for 20 min, diluted with EtOAc, and then left at 0 °C for 3 h. The precipitated dicyclohexylurea was filtered off and the organic phase treated with satd. $NaHCO_3$. The aqueous phase was extracted twice with EtOAc and the combined organic phases were washed with water and satd NaCl. Evaporation of the solvent gave the crude aldehyde, which was used immediately.

General Procedure for Reductive Amination of Aldehydes 9 and 10: The aldehyde was dissolved in MeOH (0.03 M solution) and then 3-Å MS, the amine reagent (1.5 equiv.), $NaBH_3CN$ (5 equiv.), and a few drops of acetic acid were added. The mixture was heated under reflux until the reaction was complete (TLC, less than 2 h) and then filtered through Celite. Extraction of the filtrate (CH_2Cl_2/dilute NaOH) and column chromatography gave the product.

General Procedure for Deprotection: Protected imino sugar−oligoarabinofuranoside hybrid was dissolved in 0.1 M NaOMe in methanol (concentration of substrate: 0.05 M) and left at room temp. After completion of the reaction, the mixture was neutralized with solid NH_4Cl (1 equiv. based on NaOMe) and the solvent was evaporated. The residue was taken up in CH_2Cl_2, the NaCl was filtered off, and the solvent of the filtrate was evaporated. The residue was taken up in a 0.05 M methanolic solution of HCl (concentration of substrate: 0.05 M) and hydrogenolyzed at room temp. and atmospheric pressure with $Pd(OH)_2$/C as the catalyst. The reaction was complete within a few hours. Filtration of the catalyst, evaporation of the solvent, and column chromatography of the residue, gave the product.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-[(4*S*)-4-(hydroxymethyl)pyrrolidin-1-yl]-α-D-arabinofuranoside (11): From **7** (55.4 mg, 107 μmol) and **1** (16.5 mg, 163 μmol). Chromatography:

dichloromethane/methanol, 20:1; colorless oil (51.8 mg, 81%). $[\alpha]_D^{25} = +64$ (c = 1.39, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.26−1.42 (m, 8 H, octyl CH_2), 1.59−1.87 (m, 8 H, octyl CH_2, 2 × 2B-H, 2 × 3B-H), 2.32 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 2.35 (m, 1 H, 1B-H), 2.66 (dd, $^2J_{5A,5A}$ = 13.1, $^3J_{5A,4A}$ = 6.2 Hz, 1 H, 5A-H), 2.66 (m, 1 H, 4B-H), 2.88 (dd, $^3J_{5A,4A}$ = 2.6 Hz, 1 H, 5A-H), 3.11 (m, 1 H, 1B-H), 3.33 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 3.2 Hz, 1 H, 5B-H), 3.49 (td, ^2J = 9.7, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.54 (dd, $^3J_{5B,4B}$ = 3.3 Hz, 1 H, 5B-H), 3.68 (s, 3 H, OCH_3), 3.75 (td, 1 H, octyl CH_2O), 3.82 (td, $^3J_{3A,4A}$ = 5.4 Hz, 1 H, 3A-H), 4.27 (m, 1 H, 4 A-H), 4.63, 4.86 (d, ^2J = 12.4 Hz, 1 H, benzyl CH_2), 5.16 (s, 1 H, 1A-H), 5.37 (d, $^3J_{2A,3A}$ = 1.4 Hz, 1 H, 2A-H), 7.20−8.07 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 24.4, 25.4, 26.0, 26.4, 27.7, 29.5, 29.6, 29.6, 29.8 (CH_2), 34.5 (CH_2CO), 51.9 (OCH_3), 56.3 (C-1B), 57.1 (C-5A), 63.0 (C-5B), 65.7 (C-4B), 68.1 (octyl CH_2O), 72.4 (benzyl CH_2), 82.2 (C-2A), 82.3 (C-4A), 85.5 (C-3A), 106.4 (C-1A), 128.3, 128.5, 128.8, 128.9, 130.2, 133.9 (Ar), 165.9 (*C*OOPh), 174.8 (*C*OOCH$_3$) ppm. HRMS (FAB) $C_{34}H_{48}NO_8$: calcd. 598.3380, found 598.3397.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,4,5-trideoxy-1,4-imino-5-*C*-methyl-D-arabinitol-*N*-yl)-α-D-arabinofuranoside (12): From **7** (30.1 mg, 58 μmol) and **2** (11.5 mg, 87 μmol). Chromatography: dichloromethane/methanol, 20:1; colorless oil (13.7 mg, 37%). $[\alpha]_D^{25} = +90$ (c = 1.16, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.94 (t, ^2J = 7.3 Hz, 3 H, 3 × 6B-H), 1.25−1.50 (m, 10 H, octyl CH_2, 2 × 5B-H), 1.57−1.71 (m, 4 H, octyl CH_2), 2.30 (m, 1 H, 1B-H), 2.32 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.54 (m, 1 H, 4B-H), 2.58 (dd, $^2J_{5A,5A}$ = 13.3, $^3J_{5A,4A}$ = 2.7 Hz, 1 H, 5A-H), 2.99 (dd, $^3J_{5A,4A}$ = 7.5 Hz, 1 H, 5A-H), 3.49 (td, ^2J = 9.6, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.69 (s, 3 H, OCH_3), 3.70 (m, 1 H, 1B-H), 3.74 (td, 1 H, octyl CH_2O), 3.81 (br. d, $^3J_{3B,2B}$ = 3.6 Hz, 1 H, 3B-H), 3.86 (td, $^3J_{3A,4A}$ = 5.8 Hz, 1 H, 3A-H), 4.11 (m, 1 H, 2B-H), 4.29 (m, 1 H, 4A-H), 4.62, 4.86 (d, ^2J = 12.2 Hz, 1 H, benzyl CH_2), 5.15 (s, 1 H, 1A-H), 5.36 (d, $^3J_{2A,3A}$ = 1.4 Hz, 1 H, 2 A-H), 7.26−8.06 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 11.1 (C-6B), 25.3, 26.4, 29.5, 29.6, 29.6, 29.8, 30.1 (CH_2), 34.5 (CH_2CO), 52.0 (OCH_3), 54.7 (C-5A), 61.5 (C-1B), 67.7 (C-4B), 68.0 (octyl CH_2O), 72.5 (benzyl CH_2), 76.5 (C-2B), 78.1 (C-3B), 81.2 (C-4A), 82.3 (C-2A), 85.0 (C-3A), 106.3 (C-1A), 128.3, 128.9, 129.0, 130.1, 133.9 (Ar), 165.9 (*C*OOPh), 174.9 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{35}H_{50}NO_9$ calcd. 628.3486, found 628.3485.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,4-dideoxy-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranoside (13): From **7** (50.7 mg, 98 μmol) and **3** (20.0 mg, 148 μmol). Chromatography: dichloromethane/methanol, 10:1; colorless oil (49.8 mg, 80%). $[\alpha]_D^{25} = +57$ (c = 0.96, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.26−1.42 (m, 8 H, octyl CH_2), 1.58−1.67 (m, 4 H, octyl CH_2), 2.31 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.59 (m, 1 H, 4B-H), 2.71 (dd, $^2J_{5A,5A}$ = 13.5, $^3J_{5A,4A}$ = 6.8 Hz, 1 H, 5A-H), 2.87 (dd, $^2J_{1B,1B}$ = 12.5, $^3J_{1B,2B}$ = 5.2 Hz, 1 H, 1B-H), 2.92 (dd, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 3.01 (br. d, 1 H, 1B-H), 3.47 (td, ^2J = 9.6, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.62 (dd, $^2J_{5B,5B}$ = 11.6, $^3J_{5B,4B}$ = 2.0 Hz, 1 H, 5B-H), 3.67 (dd, $^3J_{5B,4B}$ = 3.3 Hz, 1 H, 5B-H), 3.68 (s, 3 H, OCH_3), 3.73 (td, 1 H, octyl CH_2O), 3.81 (br. d, $^3J_{3A,4A}$ = 6.0 Hz, 1 H, 3A-H), 3.92 (td, $^3J_{2B,1B}$ = 5.2 Hz, 1 H, 2B-H), 4.03 (dd, $^3J_{3B,4B}$ = 3.7, $^3J_{3B,2B}$ = 2.2 Hz, 1 H, 3B-H), 4.23 (m, 1 H, 4A-H), 4.62, 4.83 (d, ^2J = 12.2 Hz, 1 H, benzyl CH_2), 5.13 (s, 1 H, 1A-H), 5.35 (d, $^3J_{2A,3A}$ = 1.6 Hz, 1 H, 2A-H), 7.25−8.06 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.3, 26.4, 29.5, 29.6, 29.8 (CH_2), 34.5 (CH_2CO), 52.0 (OCH_3), 56.1 (C-5A), 60.7 (C-5B), 61.1 (C-1B), 68.0 (octyl CH_2O), 72.6 (benzyl CH_2), 72.6 (C-4B), 76.8 (C-2B), 80.4 (C-3B), 81.7 (C-4A), 82.3 (C-2A), 85.4 (C-3A), 106.4 (C-1A), 128.4, 128.6, 128.9, 129.0, 129.7, 130.2, 134.0, 137.9 (Ar), 165.9 (*C*OOPh), 175.0 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{34}H_{47}NO_{10}$ calcd. 630.3278, found 630.3282.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-D-arabinitol-*N*-yl)-D-arabinofuranoside (14): From **7** (52.0 mg, 101 μmol) and **4** (20.5 mg, 151 μmol). Chromatography: dichloromethane/methanol, 20:1; colorless oil (54.7 mg, 86%). $[\alpha]_D^{25} = +61$ (c = 0.96, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.28−1.43 (m, 8 H, octyl CH_2), 1.58−1.70 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 2.53 (m, 1 H, 4B-H), 2.58 (dd, $^2J_{5A,5A}$ = 13.6, $^3J_{5A,4A}$ = 6.0 Hz, 1 H, 5A-H), 2.78 (ddd, $^3J_{1B,F}$ = 33.8, $^2J_{1B,1B}$ = 12.0, $^3J_{1B,2B}$ = 5.3 Hz, 1 H, 1B-H), 2.93 (dd, $^3J_{5A,4A}$ = 4.5 Hz, 1 H, 5A-H), 3.21 (dd, $^2J_{1B,F}$ = 21.32 Hz, 1 H, 1B-H), 3.49 (td, ^2J = 9.7, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.61 (dd, $^2J_{5B,5B}$ = 11.1, $^3J_{5B,4B}$ = 2.7 Hz, 1 H, 5B-H), 3.68 (dd, $^3J_{5B,4B}$ = 3.7 Hz, 1 H, 5B-H), 3.68 (s, 3 H, OCH_3), 3.73 (td, 1 H, octyl CH_2O), 3.81 (td, $^3J_{3A,4A}$ = 5.9, $^3J_{3A,2A}$ = 0.9 Hz, 1 H, 3A-H), 4.22 (m, 1 H, 4A-H), 4.27 (m, 1 H, 3B-H), 4.61, 4.84 (d, ^2J = 12.2 Hz, 1 H, benzyl CH_2), 4.82 (tdd, $^2J_{2B,F}$ = 52.9 Hz, 1 H, 2B-H), 5.13 (s, 1 H, 1A-H), 5.36 (d, $^3J_{2A,3A}$ = 1.5 Hz, 1 H, 2A-H), 7.25−8.06 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.3, 26.0, 26.4, 29.5, 29.6, 29.8 (CH_2), 34.5 (CH_2CO), 52.0 (OCH_3), 55.4 (C-5A), 55.5, 59.7 (C-1B), 59.9 (C-5B), 68.1 (octyl CH_2O), 72.5 (C-4B), 72.7 (benzyl CH_2), 77.6 (C-3B), 81.8 (C-4A), 82.2 (C-2A), 85.0 (C-3A), 96.7, 98.5 (C-2B), 106.4 (C-1A), 128.4, 128.6, 128.7, 128.9, 129.0, 129.7, 130.2, 133.9, 137.8 (Ar), 165.9 (*C*OOPh), 175.0 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{34}H_{47}FNO_9$ calcd. 632.3235, found 632.3239.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,4-dideoxy-1,4-L-galactitol-*N*-yl)-α-D-arabinofuranoside (15): From **7** (21.0 mg, 41 μmol) and **5** (10.0 mg, 61 μmol). Chromatography: dichloromethane/methanol, 20:1; colorless oil (15.4 mg, 57%). $[\alpha]_D^{25} = +52$ (c = 1.16, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.42 (m, 8 H, octyl CH_2), 1.57−1.66 (m, 4 H, octyl CH_2), 2.30 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.52 (dd, $^3J_{4B,3B}$ = 5.3, $^3J_{4B,5B}$ = 1.3 Hz, 1 H, 4B-H), 2.62 (dd, $^2J_{5A,5A}$ = 13.5, $^3J_{5A,4A}$ = 6.8 Hz, 1 H, 5A-H), 2.83 (dd, $^2J_{1B,1B}$ = 10.9, $^3J_{1B,2B}$ = 6.2 Hz, 1 H, 1B-H), 2.91 (dd, $^3J_{5A,4A}$ = 4.1 Hz, 1 H, 5A-H), 3.06 (dd, $^3J_{1B,2B}$ = 2.2 Hz, 1 H, 1B-H), 3.45 (td, ^2J = 9.6, ^3J = 6.6 Hz, 1 H, octyl CH_2O), 3.64 (m, 1 H, 6B-H), 3.67 (s, 3 H, OCH_3), 3.71 (td, 1 H, octyl CH_2O), 3.75−3.85 (m, 3 H, 6B-H, 5B-H, 3A-H), 4.04 (m, 1 H, 2B-H), 4.16 (dd, $^3J_{3B,4B}$ = 5.3, $^3J_{3B,2B}$ = 2.8 Hz, 1 H, 3B-H), 4.25 (td, $^3J_{4A,5A}$ = 6.3, $^3J_{4A,5A}$ = 4.1 Hz, 1 H, 4A-H), 4.59, 4.81 (d, ^2J = 12.1 Hz, 1 H, benzyl CH_2), 5.10 (s, 1 H, 1A-H), 5.33 (d, $^3J_{2A,3A}$ = 1.7 Hz, 1 H, 2A-H), 7.20−8.06 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.3, 26.4, 29.5, 29.6, 29.6, 29.8, 30.1 (CH_2), 34.5 (CH_2CO), 52.0 (OCH_3), 55.9 (C-5A), 60.4 (C-1B), 64.2 (C-6B), 68.1 (octyl CH_2O), 68.8 (C-5B), 72.7 (benzyl CH_2), 74.0 (C-4B), 76.4 (C-2B), 77.1 (C-3B), 81.3 (C-4A), 82.2 (C-2A), 85.7 (C-3A), 106.48 (C-1A), 128.4, 128.5, 128.9, 129.0, 129.7, 130.2, 134.0, 137.9 (Ar), 165.9 (*C*OOPh), 175.0 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{35}H_{50}NO_{11}$ calcd. 660.3384, found 660.3407.

8-(Methoxycarbonyl)octyl 2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-L-galactitol-*N*-yl)-α-D-arabinofuranoside (16): From **7** (55.9 mg, 109 μmol) and **6** (26.6 mg, 163 μmol). Chromatography: dichloromethane/methanol, 10:1; colorless oil (58.2 mg, 81%). $[\alpha]_D^{25} = +61$ (c = 1.02, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.28−1.43 (m, 8 H, octyl

CH_2), 1.58−1.70 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.7 Hz, 2 H, CH_2CO), 2.47 (dd, $^3J_{4B,3B}$ = 6.6, $^3J_{4B,5B}$ = 2.3 Hz, 1 H, 4B-H), 2.53 (dd, $^2J_{5A,5A}$ = 13.7, $^3J_{5A,4A}$ = 5.9 Hz, 1 H, 5A-H), 2.77 (ddd, $^3J_{1B,F}$ = 32.0, $^2J_{1B,1B}$ = 12.0, $^3J_{1B,2B}$ = 6.0 Hz, 1 H, 1B-H), 2.91 (dd, $^3J_{5A,4A}$ = 4.4 Hz, 1 H, 5A-H), 3.20 (dd, $^3J_{1B,F}$ = 22.0 Hz, 1 H, 1B-H), 3.48 (td, ^2J = 9.6, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.66 (dd, $^2J_{6B,6B}$ = 12.1, $^3J_{6B,5B}$ = 9.1 Hz, 1 H, 6B-H), 3.68 (s, 3 H, OCH_3), 3.72 (td, 1 H, octyl CH_2O), 3.80 (m, 2 H, 3A-H, 5B-H), 3.90 (dd, $^3J_{6B,5B}$ = 4.1 Hz, 1 H, 6B-H), 4.21 (td, $^3J_{4A,5A}$ = 5.9, $^3J_{4A,5A}$ = 4.4 Hz, 1 H, 4A-H), 4.37 (ddd, $^4J_{3B,F}$ = 27.4, $^3J_{3B,4B}$ = 6.7, $^3J_{3B,2B}$ = 2.1 Hz, 1 H, 3B-H), 4.60, 4.84 (d, ^2J = 12.2 Hz, 1 H, benzyl CH_2), 4.85 (md, $^2J_{2B,F}$ = 53.5 Hz, 1 H, 2B-H), 5.11 (s, 1 H, 1A-H), 5.35 (d, $^3J_{2A,3A}$ = 1.5 Hz, 1 H, 2A-H), 7.25−8.06 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.3, 26.0, 26.4, 29.5, 29.6, 29.8 (CH_2), 34.5 (*C*H_2CO), 52.0 (OCH_3), 54.7 (C-5A), 59.6, 59.8 (C-1B), 63.8 (C-6B), 67.4 (C-5B), 68.2 (octyl CH_2O), 72.5 (benzyl CH_2), 74.4 (C-4B), 75.1, 75.4 (C-3B), 81.6 (C-4A), 81.1 (C-2A), 84.8 (C-3A), 96.3, 98.1 (C-2B), 106.4 (C-1A), 128.5, 128.7, 128.9, 129.0, 129.7, 130.2, 134.0, 137.7 (Ar), 165.9 (*C*OOPh), 175.0 (*C*OOCH$_3$) ppm. $C_{35}H_{47}FNO_{10}$ (661.8): calcd. C 63.53, H 7.16; found C 63.33, H 6.96.

8-(Methoxycarbonyl)octyl 5-*O*-(5-*O*-{2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-[(4-*S*)-4-hydroxymethylpyrrolidin-*N*-yl]-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (17): From **8** (29.6 mg, 26 μmol) and **1** (3.9 mg, 39 μmol). Chromatography: petroleum ether/ethyl acetate, 25:1; colorless oil (23.2 mg, 73%). $[\alpha]_D^{25}$ = +84 (*c* = 0.98, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.09−1.43 (m, 8 H, octyl CH_2), 1.54−1.84 (m, 7 H, octyl CH_2, 3D-H, 2 × 2D-H), 1.96 (m, 1 H, 3D-H), 2.32−2.23 (m, 1 H, 1D-H), 2.31 (t, ^3J = 7. 4 Hz, 2 H, CH_2CO), 2.67−2.55 (m, 2 H, 4D-H, 5C-H), 2.80 (dd, $^2J_{5C,5C}$ = 12.9, $^3J_{5C,4C}$ = 5.5 Hz, 1 H, 5C-H), 3.00 (m, 1 H, 1D-H), 3.28 (dd, $^2J_{5D,5D}$ = 11.1, $^3J_{5D,4D}$ = 2.8 Hz, 1 H, 5D-H), 3.44−3.52 (m, 3 H, 5D-H, octyl CH_2O), 3.68 (s, 3 H, OCH_3), 3.71 (dd, $^2J_{5B,5B}$ = 11.2, $^3J_{5B,4B}$ = 3.7 Hz, 1 H, 5B-H), 3.74 (m, 1 H, 3C-H), 3.75 (m, 1 H, octyl CH_2O), 3.76 (dd, $^2J_{5A,5A}$ = 11.4, $^3J_{5A,4A}$ = 3.5 Hz, 1 H, 5A-H), 3.89 (dd, $^3J_{5B,4B}$ = 4.0 Hz, 1 H, 5B-H), 3.95 (dd, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 4.14 (br. d, $^3J_{3B,4B}$ = 5.5 Hz, 1 H, 3B-H), 4.15 (m, 1 H, 4C-H), 4.18 (md, $^3J_{3A,4A}$ = 5.7 Hz, 1 H, 3A-H), 4.22 (m, 1 H, 4B-H), 4.34 (m, 1 H, 4A-H), 4.45, 4.53, 4.60, 4.63, 4.68, 4.81 (d, ^2J = 12.0 Hz, 1 H, benzyl CH_2), 5.16 (s, 1 H, 1A-H), 5.29 (s, 1 H, 1C-H), 5.32 (s, 1 H, 1B-H), 5.37 (d, $^3J_{2C,3C}$ = 1.1 Hz, 1 H, 2C-H), 5.41 (d, $^3J_{2A,3A}$ = 1.6 Hz, 1 H, 2A-H), 5.45 (d, $^3J_{2B,3B}$ = 1.4 Hz, 1 H, 2B-H), 7.20−8.08 (m, 30 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 24.4 (C-2D), 25.4, 26.0, 26.4, 27.6 (C-3D), 29.5, 29.6, 29.7, 29.8, 30.1 (CH_2), 34.5 (*C*H_2CO), 51.9 (OCH_3), 56.2 (C-1D), 57.1 (C-5C), 62.8 (C-5D), 65.8 (C-5B), 65.9 (C-5A), 68.0 (octyl CH_2O), 72.0, 72.6, 72.8 (benzyl CH_2), 81.6 (C-2C), 81.9 (C-4A), 82.1 (C-2B), 82.4 (C-4B), 82.5 (C-2A), 82.9 (C-4C), 83.6 (C-3A), 83.8 (C-3B), 85.1 (C-3C), 106.3 (C-1A), 106.5 (C-1B), (C-1C), 128.0, 128.1, 128.2, 128.3, 128.4, 128.7, 128.8, 128.9, 129.0, 129.8, 129.9, 130.0, 130.1, 130.2, 133.7, 133.8, 133.9, 137.9, 138.3 (Ar), 165.6, 165.7, 166.0 (*C*OOPh), 174.8 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{72}H_{84}O_{18}N$ calcd. 1250.5688, found 1250.5695.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,4-dideoxy-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranosyl]-2-*O*-benzoyl-3-α-*O*-benzyl--α-D-arabinofuranosyl}-2-*O*-benzyol-3-*O*-benzyl-α-D-arabinofuranoside (18): From **8** (92.6 mg, 80 μmol) and **3** (15.8 mg, 119 μmol). Chromatography: dichloromethane/methanol, 20:1; colorless oil (73.9 mg, 73%). $[\alpha]_D^{25}$ = +87 (*c* = 1.37, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.42 (m, 8 H, octyl CH_2), 1.58−1.67 (m, 4 H, octyl CH_2), 2.31 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.55 (m, 1 H, 4D-H), 2.68 (dd, $^2J_{5C,5C}$ = 13.7, $^3J_{5C,4C}$ = 6.4 Hz, 1 H, 5C-H), 2.78 (dd, $^2J_{1D,1D}$ = 10.3, $^3J_{1D,2D}$ = 5.5 Hz, 1 H, 1D-H), 2.82 (dd, $^3J_{5C,4C}$ = 4.4 Hz, 1 H, 5C-H), 2.87 (br. d, 1 H, 1D-H), 3.45−3.55 (m, 3 H, 2 × 5D-H, octyl CH_2O), 3.68 (s, 3 H, OCH_3), 3.70 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 4.1 Hz, 1 H, 5B-H), 3.75 (m, 1 H, 3C-H), 3.76 (td, 1 H, octyl CH_2O), 3.77 (dd, $^2J_{5A,5A}$ = 11.4, $^3J_{5A,4A}$ = 3.6 Hz, 1 H, 5A-H), 3.82 (m, 1 H, 2D-H), 3.87 (dd, $^3J_{5B,4B}$ = 4.3 Hz, 1 H, 5B-H), 3.93 (m, 1 H, 3D-H), 3.96 (dd, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 4.08−4.13 (m, 2 H, 4C-H, 3B-H), 4.25 (m, 1 H, 4B-H), 4.35 (m, 1 H, 4A-H), 4.45, 4.53, 4.62, 4.64, 4.69, 4.82 (d, ^2J = 12.1 Hz, 1 H, benzyl CH_2), 5.17 (s, 1 H, 1A-H), 5.25 (s, 1 H, 1C-H), 5.32 (s, 1 H, 1B-H), 5.34 (d, $^3J_{2C,3C}$ = 1.4 Hz, 1 H, 2C-H), 5.41 (d, $^3J_{2A,3A}$ = 1.7 Hz, 1 H, 2A-H), 5.45 (d, $^3J_{2B,3B}$ = 1.4 Hz, 1 H, 2B-H), 7.20−8.08 (m, 30 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.4, 26.4, 29.5, 29.6, 29.7, 29.8 (CH_2), 34.5 (*C*H_2CO), 52.0 (OCH_3), 55.9 (C-5C), 60.9 (C-1D), 61.2 (C-5D), 66.1 (C-5A), 66.3 (C-5B), 67.9 (octyl CH_2O), 72.3, 72.6, 72.8 (benzyl CH_2), 72.8 (C-4D), 76.7 (C-2D), 80.6 (C-3D), 81.9 (C-4A), 82.0 (C-2B), 82.0 (C-2C), 82.3 (C-4C), 82.4 (C-4B), 82.5(C-2A), 83.7 (C-3A), 84.0 (C-3B), 85.0 (C-3C), 106.4 (C-1A), 106.6 (C-1B), 106.6 (C-1C), 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 128.8, 128.9, 129.0, 129.7, 129.8, 129.9, 130.1, 133.8, 134.0, 137.8, 138.2, 138.3 (Ar), 165.7, 165.7, 166.0 (*C*OOPh), 174.9 (*C*OOCH$_3$) ppm. $C_{72}H_{83}NO_{20}$ (1282.4): calcd. C 67.43, H 6.52, N 1.09; found C 67.31, H 6.18, N 0.87.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranosyl]-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (19): From **8** (90.0 mg, 77 μmol) and **4** (15.6 mg, 115 μmol). Chromatography: dichloromethane/methanol, 30:1; colorless oil (75.0 mg, 75%). $[\alpha]_D^{25}$ = +90 (*c* = 0.90, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.27−1.42 (m, 8 H, octyl CH_2), 1.58−1.68 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 2.48 (m, 1 H, 4D-H), 2.50 (dd, $^2J_{5C,5C}$ = 13.6, $^3J_{5C,4C}$ = 5.8 Hz, 1 H, 5C-H), 2.69 (ddd, $^3J_{1D,F}$ = 33.6, $^2J_{1D,1D}$ = 11.9, $^3J_{1D,2D}$ = 5.3 Hz, 1 H, 1D-H), 2.81 (dd, $^3J_{5C,4C}$ = 4.8 Hz, 1 H, 5C-H), 3.07 (dd, $^3J_{1D,F}$ = 21.3 Hz, 1 H, 1D-H), 3.48 (td, ^2J = 9.7, ^3J = 6.6 Hz, 1 H, octyl CH_2O), 3.56 (m, 1 H, 5D-H), 3.61 (dd, $^2J_{5D,5D}$ = 11.5, $^3J_{5D,4D}$ = 3.3 Hz, 1 H, 5D-H), 3.68 (s, 3 H, OCH_3), 3.70 (m, 1 H, 5B-H), 3.72 (br. d, $^3J_{3C,4C}$ = 5.7 Hz, 1 H, 3C-H), 3.75 (td, 1 H, octyl CH_2O), 3.77 (dd, $^2J_{5A,5A}$ = 11.3, $^3J_{5A,4A}$ = 5.6 Hz, 1 H, 5A-H), 3.86 (dd, $^2J_{5B,5B}$ = 11.3, $^3J_{5B,4B}$ = 4.1 Hz, 1 H, 5B-H), 3.96 (dd, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 4.09 (m, 1 H, 4C-H), 4.11 (br. d, $^3J_{3B,4B}$ = 5.4 Hz, 1 H, 3B-H), 4.18 (br. d, $^3J_{3A,4A}$ = 5.8 Hz, 1 H, 3A-H), 4.23 (m, 1 H, 4B-H), 4.24 (br. dd, $^4J_{3D,F}$ = 22.2 Hz, 1 H, 3D-H), 4.36 (m, 1 H, 4A-H), 4.43, 4.59 (d, ^2J = 12.3 Hz, 1 H, benzyl CH_2), 4.54, 4.64, 4.69, 4.82 (d, ^2J = 12.0 Hz, 1 H, benzyl CH_2), 4.76 (md, $^2J_{2D,F}$ = 53.0 Hz, 1 H, 2D-H), 5.17 (s, 1 H, 1A-H), 5.25 (s, 1 H, 1C-H), 5.33 (s, 1 H, 1B-H), 5.34 (d, $^3J_{2C,3C}$ = 1.2 Hz, 1 H, 2C-H), 5.41 (d, $^3J_{2A,3A}$ = 1.6 Hz, 1 H, 2A-H), 5.45 (d, $^3J_{2B,3B}$ = 1.4 Hz, 1 H, 2B-H), 7.20−8.08 (m, 30 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.4, 26.0, 26.4, 29.5, 29.6, 29.7, 29.8 (CH_2), 34.5 (*C*H_2CO), 51.9 (OCH_3), 55.2 (C-5C), 59.3, 59.5 (C-1D), 59.8 (C-5D), 66.0 (C-5A), 66.2 (C-5B), 68.0 (octyl CH_2O), 72.1 (benzyl CH_2), 72.6 (C-4D), 72.6, 72.8 (benzyl CH_2), 77.5 (C-3D), 81.7 (C-2A), 81.9 (C-4A), 82.1 (C-4C), 82.3 (C-2B), 82.4 (C-4B), 82.5 (C-2C), 83.7 (C-3A), 83.9 (C-3B), 84.7 (C-3C), 96.5, 98.3 (C-2D), 106.4 (C-1A), 106.5 (C-1B), 106.6 (C-1C), 128.0, 128.1, 128.3, 128.6, 128.7, 128.8, 128.8, 129.0, 129.7, 129.9, 130.2, 130.2, 133.5, 133.8, 133.9, 137.7, 138.2 (Ar), 165.7, 165.7, 166.0 (*C*OOPh), 174.9

(*C*OOCH$_3$) ppm. HRMS (FAB): $C_{72}H_{83}FNO_{19}$ calcd. 1284.5543, found 1284.5568.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[2-*O*-Benzoyl-3-*O*-benzyl-5-deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-L-galactitol-*N*-yl)-α-D-arabinofuranosyl]-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (20): From **8** (88.6 mg, 76 μmol) and **6** (18.6 mg, 112 μmol). Chromatography: dichloromethane/methanol, 40:1; colorless oil (52.9 mg, 53%). $[\alpha]_D^{25}$ = +81 (*c* = 1.30, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.42 (m, 8 H, octyl CH_2), 1.58−1.68 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.40 (dd, $^3J_{4D,3D}$ = 6.3, $^3J_{4D,5D}$ = 2.3 Hz, 1 H, 4D-H), 2.43 (dd, $^2J_{5C,5C}$ = 13.7, $^3J_{5C,4C}$ = 5.6 Hz, 1 H, 5C-H), 2.65 (ddd, $^3J_{1D,F}$ = 31.4, $^2J_{1D,1D}$ = 12.2, $^3J_{1D,2D}$ = 6.3 Hz, 1 H, 1D-H), 2.79 (dd, $^3J_{5C,4C}$ = 4.8 Hz, 1 H, 5C-H), 3.07 (dd, $^3J_{1D,F}$ = 21.9 Hz, 1 H, 1D-H), 3.48 (td, ^2J = 9.7, ^3J = 6.6 Hz, 1 H, octyl CH_2O), 3.61 (dd, $^2J_{6D,6D}$ = 12.0, $^3J_{6D,5D}$ = 2.6 Hz, 1 H, 6D-H), 3.68 (s, 3 H, OCH_3), 3.67−3.73 (m, 3 H, 5B-H, 3C-H, 5D-H), 3.75 (td, 1 H, octyl CH_2O), 3.77 (dd, $^2J_{5A,5A}$ = 11.4, $^3J_{5A,4A}$ = 3.6 Hz, 1 H, 5A-H), 3.83−3.88 (m, 2 H, 5B-H, 6D-H), 3.97 (dd, $^3J_{5A,4A}$ = 4.2 Hz, 1 H, 5A-H), 4.07 (m, 1 H, 4C-H), 4.11 (br. d, $^3J_{3B,4B}$ = 5.6 Hz, 1 H, 3B-H), 4.18 (br. d, $^3J_{3A,4A}$ = 5.7 Hz, 1 H, 3A-H), 4.24 (m, 1 H, 4B-H), 4.32 (ddd, $^4J_{3D,F}$ = 28.6, $^3J_{3D,2D}$ = 2.1 Hz, 1 H, 3D-H), 4.36 (m, 1 H, 4A-H), 4.42, 4.54 (d, ^2J = 12.4 Hz, 1 H, benzyl CH_2), 4.58, 4.65, 4.70, 4.82 (d, ^2J = 12.1 Hz, 1 H, benzyl CH_2), 4.86 (md, $^2J_{2D,\ F}$ = 53.8 Hz, 1 H, 2D-H), 5.17 (s, 1 H, 1A-H), 5.24 (s, 1 H, 1C-H), 5.32 (br., 2 H, 1B-H, 2C-H), 5.41 (d, $^3J_{2A,3A}$ = 1.7 Hz, 1 H, 2A-H), 5.45 (d, $^3J_{2B,3B}$ = 1.4 Hz, 1 H, 2B-H), 7.20−8.08 (m, 30 H, Ar-H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 25.4, 26.0, 26.4, 29.5, 29.6, 29.7, 29.8 (CH_2), 34.3 (*C*H_2CO), 51.9 (OCH_3), 54.7 (C-5C), 59.5, 59.8 (C-1D), 63.8 (C-6D), 66.0 (C-5A), 66.2 (C-5B), 67.2 (C-5D), 68.0 (octyl CH_2O), 72.1, 72.7, 72.8 (benzyl CH_2), 74.4 (C-4D), 75.0, 75.3 (C-3D), 81.7 (C-2C), 81.9 (C-4A), 82.0 (C-4C), 82.1 (C-2B), 82.4 (C-4B), 82.5 (C-2A), 83.7 (C-3A), 83.9 (C-3B), 84.4 (C-3C), 96.1, 97.9 (C-2D), 106.4 (C-1A), 106.5 (C-1B), (C-1C), 128.0, 128.1, 128.3, 128.4, 128.6, 128.7, 128.9, 128.9, 129.0, 129.6, 129.9, 130.2, 130.2, 133.8, 133.8, 133.9, 137.7, 138.2 (Ar), 165.6, 165.7, 166.0 (*C*OOPh), 174.9 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{73}H_{85}FNO_{20}$ calcd. 1314.5649, found 1314.5655.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-[(4*S*)-4-(hydroxymethyl)pyrrolidin-1-yl]-α-D-arabinofuranoside (21): From **11** (42.0 mg, 70 μmol). Chromatography: dichloromethane/methanol, 15:1; colorless oil (11.8 mg, 41%). $[\alpha]_D^{25}$ = +41 (*c* = 1.17, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.26−1.41 (m, 8 H, octyl CH_2), 1.53−1.61 (m, 4 H, octyl CH_2), 1.63 (m, 1 H, 3B-H), 1.68−1.80 (m, 2 H, 2 × 2B-H), 1.92 (m, 1 H, 3B-H), 2.29 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.43 (td, $^2J_{1B,1B}$ = 9.5, $^3J_{1B,2B}$ = 7.7 Hz, 1 H, 1B-H), 2.57 (dd, $^2J_{5A,5A}$ = 13.3, $^3J_{5A,4A}$ = 7.7 Hz, 1 H, 5A-H), 2.67 (m, 1 H, 4B-H), 3.18 (dd, $^3J_{5A,4A}$ = 3.3 Hz, 1 H, 5A-H), 3.24 (m, 1 H, 1B-H), 3.38 (td, ^2J = 9.5, ^3J = 6.6 Hz, 1 H, octyl CH_2O), 3.47 (dd, $^2J_{5B,5B}$ = 11.1, $^3J_{5B,4B}$ = 5.9 Hz, 1 H, 5B-H), 3.58 (dd, $^3J_{5B,4B}$ = 4.6 Hz, 1 H, 5B-H), 3.62 (m, 1 H, 3A-H), 3.63 (s, 3 H, OCH_3), 3.67 (td, 1 H, octyl CH_2O), 3.90 (dd, $^3J_{2A,3A}$ = 4.0, $^3J_{2A,1A}$ = 1.7 Hz, 1 H, 2A-H), 3.99 (td, 1 H, 4A-H), 4.79 (d, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 25.2 (C-2B), 27.1, 28.5, 31.3, 31.5, 31.9 (CH_2), 29.7 (C-3B), 35.9 (*C*H_2CO), 53.1 (OCH_3), 58.2 (C-1B), 60.0 (C-5A), 66.0 (C-5B), 68.7 (C-4B), 69.9 (octyl CH_2O), 82.6 (C-3A), 84.4 (C-4A), 84.5 (C-2A), 110.6 (C-1A), 177.1 (*C*OOCH$_3$) ppm. HRMS $C_{20}H_{38}NO_7$: calcd. 404.2648, found 404.2650.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-(1,4,5-trideoxy-1,4-imino-5-*C*-methyl-D-arabinitol-*N*-yl)-α-D-arabinofuranoside (22): From **12** (11.2 mg, 18 μmol). Chromatography: dichloromethane/methanol, 10:1; 4.5 mg (58%). $[\alpha]_D^{25}$ = +82 (*c* = 0.43, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 0.98 (t, ^2J = 7.4 Hz, 3 H, 3 × 6B-H), 1.28−1.43 (m, 8 H, octyl CH_2), 1.53−1.65 (m, 6 H, octyl CH_2, 2 × 5B-H), 2.32 (t, ^3J = 7.5 Hz, 2 H, CH_2CO), 2.34 (m, 1 H, 1B-H), 2.60 (m, 1 H, 4B-H), 2.67 (dd, $^2J_{5A,5A}$ = 13.5, $^3J_{5A,4A}$ = 2.8 Hz, 1 H, 5A-H), 2.96 (dd, $^3J_{5A,4A}$ = 6.0 Hz, 1 H, 5A-H), 3.40 (td, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.59 (dd, $^2J_{1B,1B}$ = 11.3, $^3J_{1B,2B}$ = 5.8 Hz, 1 H, 1B-H), 3.65 (s, 3 H, OCH_3), 3.70 (td, 1 H, octyl CH_2O), 3.73 (dd, $^3J_{3B,4B}$ = 4.6, $^3J_{3B,2B}$ = 2.8 Hz, 1 H, 3A-H), 3.85 (m, 1 H, 3B-H), 3.88 (dd, $^3J_{2A,3A}$ = 2.7, $^3J_{2A,1A}$ = 1.1 Hz, 1 H, 2A-H), 4.00 (m, 1 H, 2B-H), 4.06 (m, 1 H, 4A-H), 4.85 (s, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 11.2 (*C*-6B), 21.0, 26.0, 27.2, 30.1, 30.4, 30.6, 30.8 (CH_2), 34.8 (*C*H_2CO), 52.0 (OCH_3), 58.0 (C-5A), 63.1 (C-1B), 68.7 (octyl CH_2O), 69.9 (C-4B), 77.3 (C-2B), 77.8 (C-3B), 81.2 (C-3A), 82.4 (C-2A), 84.6 (C-4A), 110.1 (C-1A), 176.0 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{21}H_{40}NO_8$ calcd. 434.2754, found 434.2752.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-(1,4-dideoxy-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranoside (23): From **13** (49.8 mg, 79 μmol). Chromatography: dichloromethane/methanol, 5:1; colorless oil (17.8 mg, 52%). $[\alpha]_D^{25}$ = +44 (*c* = 0.91, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.28−1.45 (m, 8 H, octyl CH_2), 1.55−1.67 (m, 4 H, octyl CH_2), 2.34 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.68 (m, 1 H, 4B-H), 2.74 (dd, $^2J_{5A,5A}$ = 13.1, $^3J_{5A,4A}$ = 7.4 Hz, 1 H, 5A-H), 2.74 (dd, $^2J_{1B,1B}$ = 10.9, $^3J_{1B,2B}$ = 5.0 Hz, 1 H, 1B-H), 3.20−3.27 (m, 2 H, 5A-H, 1B-H), 3.42 (td, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.67 (s, 3 H, OCH_3), 3.69 (m, 1 H, 3A-H), 3.71 (td, 1 H, octyl CH_2O), 3.72 (dd, $^2J_{5B,5B}$ = 11.4, $^3J_{5B,4B}$ = 4.7 Hz, 1 H, 5B-H), 3.77 (dd, $^3J_{5B,4B}$ = 4.7 Hz, 1 H, 5B-H), 3.92 (m, 1 H, 3B-H), 3.95 (dd, $^3J_{2A,3A}$ = 4.0, $^3J_{2A,1A}$ = 1.7 Hz, 1 H, 2A-H), 3.99 (m, 1 H, 2B-H), 4.03 (m, 1 H, 4A-H), 4.85 (d, $^3J_{1A,2A}$ = 1.5 Hz, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 25.0, 26.2, 29.2, 29.4, 29.7 (CH_2), 33.8 (*C*H_2CO), 51.0 (OCH_3), 57.9 (C-5A), 61.0 (C-1B), 61.1 (C-5B), 67.8 (octyl CH_2O), 74.4 (C-4B), 76.4 (C-2B), 79.0 (C-3B), 80.6 (C-3A), 81.5 (C-4A), 82.5 (C-2A), 108.5 (C-1A), 175.0 (*C*OOCH$_3$) ppm. HRMS (FAB): $C_{20}H_{38}NO_9$ calcd. 436.2547, found 436.2538.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranoside (24): From **14** (42.7 mg, 67 μmol). Chromatography: dichloromethane/methanol, 10:1; colorless oil (19.0 mg, 64%). $[\alpha]_D^{25}$ = +48 (*c* = 0.75, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.28−1.47 (m, 8 H, octyl CH_2), 1.55−1.64 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.47 (m, 1 H, 4B-H), 2.52 (dd, $^2J_{5A,5A}$ = 13.3, $^3J_{5A,4A}$ = 7.5 Hz, 1 H, 5A-H), 2.78 (ddd, $^3J_{1B,F}$ = 35.8, $^2J_{1B,1B}$ = 12.2, $^3J_{1B,2B}$ = 4.9 Hz, 1 H, 1B-H), 3.19 (dd, $^3J_{5A,4A}$ = 3.5 Hz, 1 H, 5A-H), 3.40 (dd, $^2J_{1B,F}$ = 21.0 Hz, 1 H, 1B-H), 3.41 (td, ^2J = 9.6, ^3J = 6.4 Hz, 1 H, octyl CH_2O), 3.63−3.73 (m, 2 H, 2 × 5B-H), 3.65 (s, 3 H, OCH_3), 3.68 (td, 1 H, octyl CH_2O), 3.68 (m, 1 H, 3A-H), 3.92 (dd, $^3J_{2A,3A}$ = 4.2, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 3.98 (m, 1 H, 4A-H), 4.10 (br. dd, $^4J_{3B,F}$ = 21.9 Hz, 1 H, 3B-H), 4.80 (m, 1 H, 2B-H), 4.81 (d, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 26.0, 27.2, 30.1, 30.3, 30.7 (CH_2), 34.8 (*C*H_2CO), 52.0 (OCH_3), 58.0 (C-5A), 60.2, 60.4 (C-1B), 61.9 (C-5B), 68.8 (octyl CH_2O), 74.3 (C-4B), 78.3 (C-3B), 81.5 (C-3A), 83.0 (C-4A), 83.5 (C-2A), 98.0, 99.8 (C-2B), 109.4 (C-1A), 176.0 (*C*O-OCH$_3$) ppm. HRMS (FAB): $C_{20}H_{37}FNO_8$ calcd. 438.2503, found 438.2498.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-(1,4-dideoxy-1,4-imino-L-galactitol-*N*-yl)-α-D-arabinofuranoside (25): From **15** (38.8 mg, 59 μmol). Chromatography: dichloromethane/methanol, 6:1; colorless

oil (18.8 mg, 67%). $[\alpha]_D^{25}$ = +34 (*c* = 1.30, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.28−1.42 (m, 8 H, octyl CH_2), 1.54−1.65 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.2 Hz, 2 H, CH_2CO), 2.56 (m, 1 H, 4B-H), 2.62 (dd, $^2J_{5A,5A}$ = 13.2, $^3J_{5A,4A}$ = 6.8 Hz, 1 H, 5A-H), 2.79 (dd, $^2J_{1B,1B}$ = 10.4, $^3J_{1B,2B}$ = 4.8 Hz, 1 H, 1B-H), 3.09 (dd, $^3J_{5A,4A}$ = 4.6 Hz, 1 H, 5A-H), 3.16 (br. d, 1 H, 1B-H), 3.40 (td, ^2J = 9.6, ^3J = 6.6 Hz, 1 H, octyl CH_2O), 3.65 (s, 3 H, OCH_3), 3.63−3.68 (m, 2 H, 2 × 6B-H), 3.68 (m, 1 H, 3A-H), 3.69 (td, 1 H, octyl CH_2O), 3.86 (ddd, $^3J_{5B,6B}$ = 6.3, $^3J_{5B,6B}$ = 4.9, $^3J_{5B,4B}$ = 2.8 Hz, 5B-H), 3.91 (m, 1 H, 2B-H), 3.93 (dd, $^3J_{2A,3A}$ = 4.0, $^3J_{2A,1A}$ = 1.7 Hz, 1 H, 2A-H), 3.97 (m, 1 H, 4A-H), 4.05 (br., 1 H, 3B-H), 4.82 (d, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 25.8, 27.0, 29.9, 30.1, 30.2, 30.5 (CH_2), 34.6 (*C*H_2CO), 51.8 (OCH_3), 58.1 (C-5A), 61.5 (C-1B), 64.9 (C-6B), 68.6 (octyl CH_2O), 72.4 (C-5B), 75.4 (C-4B), 77.6 (C-2B), 78.1 (C-3B), 81.5 (C-3A), 82.9 (C-4A), 83.4 (C-2A), 109.2 (C-1A), 175.9 (*C*OOCH_3) ppm. HRMS (FAB): $C_{21}H_{40}NO_{10}$ calcd. 466.2652, found 466.2661.

8-(Methoxycarbonyl)octyl 5-Deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-L-galactitol-*N*-yl)-α-D-arabinofuranoside (26): From **16** (50.0 mg, 76 μmol). Chromatography: dichloromethane/methanol, 10:1; colorless oil (21.9 mg, 62%). $[\alpha]_D^{25}$ = +39 (*c* = 1.09, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.30−1.45 (m, 8 H, octyl CH_2), 1.57−1.67 (m, 4 H, octyl CH_2), 2.33 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.51−2.57 (m, 2 H, 4B-H, 5A-H), 2.81 (ddd, $^3J_{1B,F}$ = 36.6, $^2J_{1B,1B}$ = 12.3, $^3J_{1B,2B}$ = 4.7 Hz, 1 H, 1B-H), 3.17 (dd, $^2J_{5A,5A}$ = 13.5, $^3J_{5A,4A}$ = 3.6 Hz, 1 H, 5A-H), 3.43 (td, ^2J = 9.6, ^3J = 6.8 Hz, 1 H, octyl CH_2O), 3.44 (dd, $^3J_{1B,F}$ = 21.7 Hz, 1 H, 1B-H), 3.67 (s, 3 H, OCH_3), 3.64−3.74 (m, 3 H, 2 × 6B-H, 3A-H) 3.70 (td, 1 H, octyl CH_2O), 3.88 (m, 1 H, 5B-H), 3.94 (dd, $^3J_{2A,3A}$ = 4.3, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 3.99 (m, 1 H, 4A-H), 4.30 (br. dd, $^4J_{3B,F}$ = 21.7, $^3J_{3B,4B}$ = 5 Hz, 1 H, 3B-H), 4.81 (m, 1 H, 2B-H), 4.83 (d, 1 H, 1A-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 26.0, 26.7, 27.2, 30.1, 30.3, 30.7 (CH_2), 34.8 (*C*H_2CO), 52.0 (OCH_3), 57.8 (C-5A), 60.2, 60.5 (C-1B), 65.0 (C-6B), 68.8 (octyl CH_2O), 70.8 (C-5B), 75.1 (C-4B), 76.4, 76.6 (C-3B), 81.5 (C-3A), 82.9 (C-4A), 83.6 (C-2A), 98.2, 100.0 (C-2B), 109.4, 176.0 (*C*OOCH_3) ppm. HRMS (FAB): $C_{21}H_{40}FNO_9$ calcd. 468.2609, found 468.2613.

8-(Methoxycarbonyl)octyl 5-*O*-(5-*O*-{5-Deoxy-5-[(4*S*)-4-(hydroxymethyl)pyrrolidin-1-yl]-α-D-arabinofuranosyl}-α-D-arabinofuranosyl)-α-D-arabinofuranoside (27): From **17** (14.9 mg, 12 μmol). Chromatography: dichloromethane/methanol, 10:1; colorless oil (3.5 mg, 44%). $[\alpha]_D^{25}$ = +92 (*c* = 0.33, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.30−1.44 (m, 8 H, octyl CH_2), 1.57−1.65 (m, 4 H, octyl CH_2), 1.67−1.75 (m, 1 H, 3D-H), 1.80−1.89 (m, 2 H, 2 × 2D-H), 1.96−2.06 (m, 1 H, 3D-H), 2.34 (t, ^3J = 7. 4 Hz, 2 H, CH_2CO), 2.62 (m, 1 H, 1D-H), 2.76 (m, 1 H, 5C-H), 2.88 (m, 1 H, 4D-H), 3.36 (m, 1 H, 5C-H), 3.37 (m, 1 H, 1D-H), 3.43 (td, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.67 (s, 3 H, OCH_3), 3.65 (dd, $^2J_{5D,5D}$ = 11.4, $^3J_{5D,4D}$ = 4.7 Hz, 1 H, 5D-H), 3.71−3.65 (m, 3 H, 5D-H, 5B-H, 5A-H), 3.69 (br. dd, $^3J_{3C,4C}$ = 6.4, $^3J_{3C,2C}$ = 3.6 Hz, 1 H, 3C-H), (3.72 (td, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.84 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 3.9 Hz, 1 H, 5A-H), 3.86 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 3.8 Hz, 1 H, 5B-H), 3.90 (br. dd, $^3J_{3A,4A}$ = 6.7, $^3J_{3A,2A}$ = 3.9 Hz, 1 H, 3A-H), 3.92 (br. dd, $^3J_{3B,4B}$ = 6.2, $^3J_{3B,2B}$ = 3.5 Hz, 1 H, 3B-H), 3.96 (dd, 1 H, 2A-H), 4.00 (dd, 1 H, 2C-H), 4.02 (m, 1 H, 4A-H), 4.03 (dd, 1 H, 2B-H), 4.09 (ddd, 1 H, 4B-H), 4.12 (ddd, 1 H, 4C-H), 4.86 (d, 1 H, 1A-H), 4.96 (m, 2 H, 1B-H, 1C-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 23.9 (C-2D), 25.9, 27.1, 28.2 (C-3D), 30.0, 30.2, 30.3, 29.6, (CH_2), 32.9 (*C*H_2CO), 51.9 (OCH_3), 57.1 (C-1D), 58.6 (C-5C), 67.9 (C-5B), 68.0 (C-5D, C-5A), 68.8 (octyl CH_2O), 78.9 (C-3B), 79.0 (C-3A), 81.3 (C-3C), 82.7 (C-2C), 83.2 (C-2B), 83.3 (C-2A), 83.6 (C-4A, C-4C), 83.8 (C-4B), 109.4 (C-1A), 109.6 (C-1B, C-1C) ppm. HRMS (FAB): $C_{30}H_{54}NO_{15}$ calcd. 668.3493, found 668.3497.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[5-Deoxy-5-(1,4-dideoxy-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabinofuranosyl]-α-D-arabinofuranosyl}-α-D-arabinofuranoside (28): From **18** (79.1 mg, 62 μmol). Chromatography: dichloromethane/methanol, 4:1; colorless oil (24.2 mg, 56%). $[\alpha]_D^{25}$ = +81 (*c* = 1.12, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.30−1.40 (m, 8 H, octyl CH_2), 1.57−1.67 (m, 4 H, octyl CH_2), 2.34 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.75 (m, 1 H, 4D-H), 2.81 (dd, $^2J_{1D,1D}$ = 13.2, $^3J_{1D,2D}$ = 7.6 Hz, 1 H, 1D-H), 2.99 (dd, $^2J_{5C,5C}$ = 11.8, $^3J_{5C,4C}$ = 4.8 Hz, 1 H, 5C-H), 3.27−3.33 (m, 2 H, 5C-H, 1D-H), 3.43 (td, ^2J = 9.6, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.65−3.70 (m, 5 H, 5A-H, 5B-H, OCH_3), 3.72 (m, 1 H, 3C-H), 3.72 (td, 1 H, octyl CH_2O), 3.74 (m, 1 H, 5D-H), 3.80 (dd, $^2J_{5D,5D}$ = 11.5, $^3J_{5D,4D}$ = 4.7 Hz, 1 H, 5D-H), 3.85 (dd, $^2J_{5A,5A}$ = 11.0, $^3J_{5A,4A}$ = 3.4 Hz, 1 H, 5A-H), 3.86 (dd, $^2J_{5B,5B}$ = 11.0, $^3J_{5B,4B}$ = 3.4 Hz, 1 H, 5B-H), 3.91 (m, 1 H, 3B-H, 3D-H), 3.97 (dd, $^3J_{2A,3A}$ = 3.8, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 4.01 (m, 2 H, 4A-H, 4C-H), 4.01 (dd, $^3J_{2C,3C}$ = 3.6, $^3J_{2C,1C}$ = 1.4 Hz, 1 H, 2C-H), 4.03 (dd, $^3J_{2B,3B}$ = 3.4, $^3J_{2B,1B}$ = 1.5 Hz, 1 H, 2B-H), 4.08−4.14 (m, 2 H, 2D-H, 4B-H), 3.86 (d, 1 H, 1A-H), 4.97 (d, 1 H, 1C-H), 4.98 (d, 1 H, 1B-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 25.0, 26.2, 29.1, 29.3, 29.4, 29.6 (CH_2), 33.8 (*C*H_2CO), 51.0 (OCH_3), 58.0 (C-1D), 61.0 (C-5C, C-5D), 67.1 (C-5A, C-5B), 67.9 (octyl CH_2O), 74.7 (C-4D), 76.3 (C-4A, C-4C), 78.0 (C-3A, C-4B), 78.8 (C-3D), 80.5 (C-3C), 81.9 (C-2D), 82.0 (C-2C), 82.2 (C-2B), 82.6 (C-2A), 83.0 (C-3B), 108.5 (C-1A), 108.7 (C-1B, C-1C) ppm. HRMS (FAB): $C_{30}H_{54}NO_{17}$ calcd. 700.3392, found 700.3379.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[5-Deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-D-arabinitol-*N*-yl)-α-D-arabino-furanosyl]-α-D-arabinofuranosyl}-α-D-arabinofuranoside (29): From **19** (68.2 mg, 53 μmol). Chromatography: dichloromethane/methanol, 4:1; colorless oil (30.0 mg, 81%). $[\alpha]_D^{25}$ = +88 (*c* = 0.80, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.29−1.42 (m, 8 H, octyl CH_2), 1.54−1.64 (m, 4 H, octyl CH_2), 2.32 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.49 (m, 1 H, 4D-H), 2.55 (dd, $^2J_{5C,5C}$ = 13.6, $^3J_{5C,4C}$ = 7.6 Hz, 1 H, 5C-H), 2.80 (ddd, $^3J_{1D,F}$ = 36.0, $^2J_{1D,1D}$ = 12.3, $^3J_{1D,2D}$ = 4.9 Hz, 1 H, 1D-H), 3.19 (dd, $^3J_{5C,4C}$ = 3.5 Hz, 1 H, 5C-H), 3.41 (td, ^2J = 9.5, ^3J = 6.4 Hz, 1 H, octyl CH_2O), 3.44 (dd, $^3J_{1D,F}$ = 25.6 Hz, 1 H, 1D-H), 3.65 (dd, $^2J_{5B,5B} \approx {}^2J_{5A,5A}$ = 11.0, $^3J_{5B,4B}$ = $^3J_{5A,4A}$ = 3.5 Hz, 2 H, 5B-H, 5A-H), 3.66 (s, 3 H, OCH_3), 3.73−3.67 (m, 4 H, 5D-H, 3C-H, octyl CH_2O), 3.83 (dd, $^2J_{5A,5A}$ = 11.1, $^3J_{5A,4A}$ = $^3J_{5B,4B}$ = 5.1 Hz, 2 H, 5A-H, 5B-H), 3.87−3.92 (m, 2 H, 3B-H, 3A-H), 3.94 (dd, $^3J_{2A,3A}$ = 3.8, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 3.98 (dd, $^3J_{2C,3C}$ = 3.7, $^3J_{2C,1C}$ = 1.5 Hz, 1 H, 2C-H), 4.00 (m, 1 H, 4A-H), 4.01 (dd, $^3J_{2B,3B}$ = 3.5, $^3J_{2B,1B}$ = 1.5 Hz, 1 H, 2B-H), 4.02−4.09 (m, 2 H, 4B-H, 4C-H), 4.10 (m, 1 H, 3D-H), 4.81 (br. dd, $^2J_{2D,\ F}$ = 52.8 Hz, 1 H, 2D-H), 4.84 (d, 1 H, 1A-H), 4.91 (d, 1 H, 1C-H), 4.94 (d, 1 H, 1B-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 26.7, 26.8, 27.2, 30.1, 30.3, 30.4, 30.6 (CH_2), 34.8 (*C*H_2CO), 52.0 (OCH_3), 58.2 (C-5C), 60.1, 60.3 (C-1D), 61.7 (C-5D), 67.9 (C-5A), 68.1 (C-5B), 68.9 (octyl CH_2O), 74.4 (C-4D), 78.0, 78.2 (C-3D), 78.9 (C-3B), 79.8 (C-3A), 81.4 (C-3C), 83.1 (C-2C), 83.3 (C-2B), 83.4 (C-4A), 83.7 (C-4C), 83.9 (C-2A), 84.0 (C-4B), 98.0, 99.8 (C-2D), 109.4 (C-1A), 109.5 (C-1C), 109.7 (C-1B), 176.1 (*C*OOCH_3) ppm. HRMS (FAB): $C_{30}H_{53}FNO_{16}$ calcd. 702.3348, found 702.3349.

8-(Methoxycarbonyl)octyl 5-*O*-{5-*O*-[5-Deoxy-5-(1,2,4-trideoxy-2-fluoro-1,4-imino-L-galactitol-*N*-yl)-α-D-arabinofuranosyl]-α-D-arabinofuranosyl}-α-D-arabinofuranoside (30): From **20** (49.5 mg, 38 μmol). Chromatography: dichloromethane/methanol, 4:1; colorless oil (19.7 mg, 72%). $[\alpha]_D^{25} = +86$ (c = 1.13, methanol). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.30−1.43 (m, 8 H, octyl CH_2), 1.57−1.65 (m, 4 H, octyl CH_2), 2.34 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.54 (dd, $^3J_{4D,3D}$ = 5.0, $^3J_{4D,5D}$ = 3.6 Hz, 1 H, 4D-H), 2.58 (dd, $^2J_{5C,5C}$ = 13.7, $^3J_{5C,4C}$ = 7.7 Hz, 1 H, 5C-H), 2.82 (ddd, $^3J_{1D,F}$ = 36.7, $^2J_{1D,1D}$ = 12.2, $^3J_{1D,2D}$ = 4.6 Hz, 1 H, 1D-H), 3.17 (dd, $^3J_{5C,4C}$ = 3.8 Hz, 1 H, 5C-H), 3.43 (td, ^2J = 9.6, ^3J = 6.5 Hz, 1 H, octyl CH_2O), 3.46 (dd, $^3J_{1D,F}$ = 20.3 Hz, 1 H, 1D-H), 3.67 (s, 3 H, OCH_3), 3.64−3.72 (m, 5 H, 5A-H, 5B-H, 3C-H, 2 × 6D-H), 3.72 (td, 1 H, octyl CH_2O), 3.84 (dd, $^2J_{5B,5B}$ = 10.9, $^3J_{5B,4B}$ = 5.3 Hz, 1 H, 5A-H), 3.86 (dd, $^2J_{5A,5A}$ = 11.1, $^3J_{5A,4A}$ = 5.1 Hz, 1 H, 5A-H), 3.85−3.93 (m, 3 H, 3A-H, 3B-H, 5D-H), 3.96 (dd, $^3J_{2A,3A}$ = 3.8, $^3J_{2A,1A}$ = 1.8 Hz, 1 H, 2A-H), 4.00 (dd, $^3J_{2C,3C}$ = 3.8, $^3J_{2C,1C}$ = 1.5 Hz, 1 H, 2C-H), 4.01 (m, 1 H, 4A-H), 4.02 (dd, $^3J_{2B,3B}$ = 3.5, $^3J_{2B,1B}$ = 1.6 Hz, 1 H, 2B-H), 4.06 (m, 1 H, 4C-H), 4.10 (m, 1 H, 4B-H), 4.31 (ddd, $^4J_{3D,F}$ = 21.7, $^3J_{3D,2D}$ = 5.0 Hz, 1 H, 3D-H), 4.81 (br. dd, $^2J_{2D,F}$ = 52.6, $^3J_{2D,3D}$ = 4.8 Hz, 1 H, 2D-H), 4.86 (d, 1 H, 1A-H), 4.93 (d, 1 H, 1C-H), 4.96 (d, 1 H, 1B-H) ppm. ^{13}C NMR (100.62 MHz, CD_3OD, 25 °C): δ = 25.0, 25.7, 26.2, 29.1, 29.3, 29.4, 29.6 (CH_2), 33.8 (CH_2CO), 51.0 (OCH_3), 56.8 (C-5C), 59.2, 59.4 (C-1D), 64.0 (C-6D), 67.0 (C-5A), 67.1 (C-5B), 67.9 (octyl CH_2O), 69.7 (C-5D), 74.0 (C-4D), 75.3, 75.6 (C-3D), 78.0 (C-3A, C-3B), 80.4 (C-3C), 82.2 (C-4A), 82.3 (C-2B), 82.4 (C-2C, C-4C), 82.7 (C-2A), 82.9 (C-4B), 97.2, 99.0 (C-2D), 108.5 (C-1A, C-1C), 108.6 (C-1B), 175.1 ($COOCH_3$) ppm. HRMS (FAB): $C_{31}H_{55}FNO_{17}$ calcd. 732.3454, found 732.3476.

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