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Chemical synthesis of β-arabinofuranosyl containing oligosaccharides derived from plant cell wall extensins†

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Extensins are plant-derived glycoproteins that are densely modified by oligo-arabinofuranosides linked to hydroxyproline residues. These glycoproteins have been implicated in many aspects of plant growth and development. Here, we describe the chemical synthesis of a tetrameric β(1–2)-linked arabinofuranoside that is capped by an α(1–3)-arabinofuranoside and a similar trisaccharide lacking the capping moiety. The challenging β(1–2)-linked arabinofuranosides were installed by using an arabinofuranosyl donor protected with 3,5-*O*-(di-*tert*-butylsilane) and a C-2 2-methylnaphthyl (Nap) ether. It was found that the cyclic silane-protecting group of the glycosyl donor greatly increased β-anomeric selectivity. It was, however, imperative to remove the silane-protecting group of an arabinosyl acceptor to achieve optimal anomeric selectivities. The anomeric linker of the synthetic compounds was modified by a biotin moiety for immobilization of the compounds to microtiter plates coated with streptavidine. The resulting microtiter plates were employed to screen for binding against a panel of antibodies elicited against plant cell wall polysaccharides.

Introduction

Hydroxyproline-rich glycoproteins are ubiquitous components of the growing plant cell wall that have been implicated in all aspects of plant growth and development including stress responses.[1] This family of glycoproteins, which include proline-rich proteins, arabinogalactans and extensins, generally consist of four- to six amino acid repeating motifs that are extensively *O*-glycosylated at hydroxyproline by arabinosides or arabinogalactans.[2,3] Occasionally, serine residues can also be glycosylated, mainly by a single galactoside.

The conservation and widespread occurrence of only a few hydroxyproline-rich glycoprotein modules indicate that they represent functional units whose roles depend on the identity and precise arrangement of the pendent oligosaccharides. Indeed, for most hydroxyproline-rich glycoproteins, the peptide backbone is completely shielded by carbohydrates, very similar to what is observed for eukaryotic mucins,[4,5] and therefore their interactive molecular surface is probably determined by carbohydrate structures.

Plant derived extensins[6] are modified by linear L-arabinofuranosides, which are linked to hydroxyproline residues. The structures of the oligo-arabinosides of *Nicotina tabacum* have been determined, and it was found that they are mainly composed of a tetrameric β(1–2)-linked arabinofuranoside that is capped by an α(1–3)-arabinofuranoside (compound **1**, Fig. 1). In addition, a trisaccharide was detected lacking the capping moiety (compound **2**, Fig. 1).[7]

Recently, a collection of 180 plant cell wall glycan-binding monoclonal antibodies (mAbs) was reported to facilitate an in-depth analysis of plant cell wall structure, function, dynamics, and biosynthesis.[8] An enzyme-linked immunosorbent assay-based screen against a diverse panel of 54 plant polysaccharides was used to characterize the binding patterns of these mAbs. We are generating well-defined synthetic oligosaccharides derived from plant cell wall polysaccharides to determine the fine epitope specificities of the mAbs.[9,10] As part of this

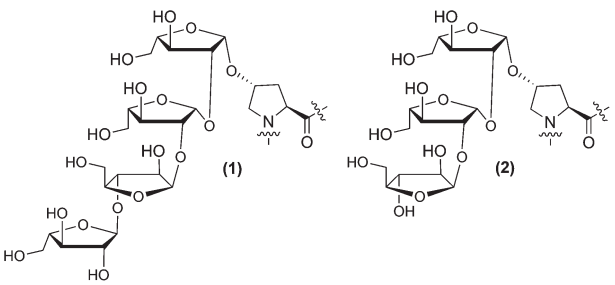

Fig. 1 Arabinofuranosides of plant elastins.

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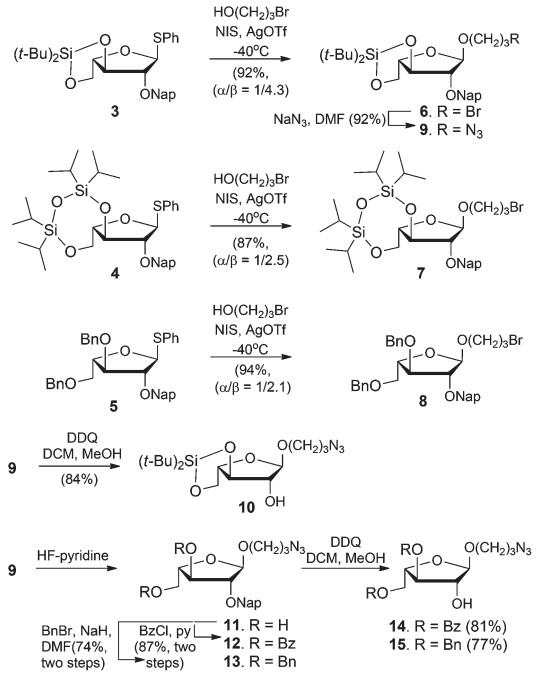
project, we report here the chemical synthesis of two arabinofuranosides derived from plant cell wall extensins.

Results and discussion

In general, α-arabinofuranosides can be obtained in a straightforward manner by neighboring group participation of an acyl ester at C-2 of a furanosyl donor. On the other hand, the stereoselective introduction of β-arabinofuranosides, which requires glycosyl donors having a non-participating protecting group at C-2, often leads to the formation of mixtures of α/β anomers.[11,12] Furanosides exhibit weak anomeric effects, which differ little between the α- and β-anomer, making it difficult to exploit *in situ* anomerization protocols for controlling anomeric selectivities.[13,14] Furthermore, furanosides are inherently flexible due to their ability to assume several twist and envelope conformations, which can interconvert *via* pseudo-rotational itineraries.[12] As a result, furanosides can glycosylate through different transition states, which may compromise anomeric selectivity.[15]

Recently, we reported a practical approach for the stereoselective introduction of β-arabinofuranosides by locking a donor in a conformation in which attack from the β-face is favored.[16] The glycosyl donor was designed by analyzing optimized geometries of low energy conformers of the arabinofuranosyl oxa-carbenium ion. The Newman projection of the E_3 conformer indicated that nucleophilic attack from the α-face is disfavored because an eclipsed H-2 will be encountered. On the other hand, an approach from the β-face was expected to be more favorable because it will experience only staggered substituents. The arabinofuranosyl oxa-carbenium ion could be locked in the E_3 conformation by employing a 3,5-*O*-(di-*tert*-butylsilane)-protecting group, which places C-5 and O-3 in a pseudo-equatorial orientation resulting in a perfect chair conformation of the protecting group. We have shown that the new glycosyl donor gives excellent β-anomeric selectivities in glycosylations with glycosyl acceptors having primary and secondary alcohols. Several other methods have been introduced to conformationally constrain the five-membered ring structure of arabinofuranosyl donors to control β-anomeric selectivity.[17–24]

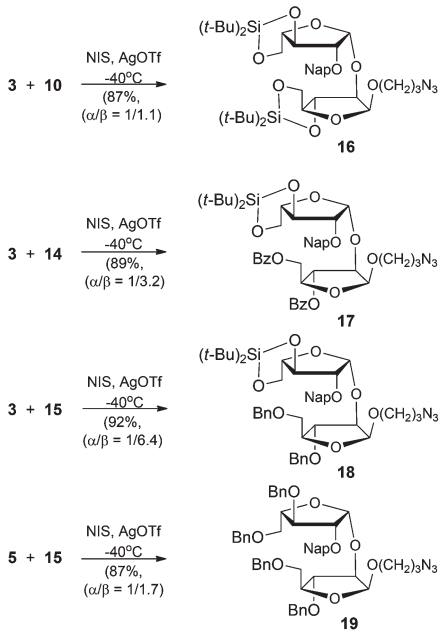
We envisaged that target oligosaccharides **27** and **28** (Scheme 3, spacer modified analogs of **1** and **2**), which contain multiple β-arabinofuranosides, could readily be prepared by using arabinofuranosyl donor **3** (Scheme 1). This compound contains a 3,5-*O*-(di-*tert*-butylsilane) protecting group that was expected to control the β-anomeric selectivity of the glycosylations. Furthermore, the 2-methylnaphthyl (Nap) ether at C-2 can be removed by oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[25,26] to reveal an alcohol that can be glycosylated to install additional β(1–2)-linked arabinofuranosides of the target compounds. Furthermore, donors **4**[20] and **5**[16] were also employed to explore the importance of the 3,5-*O*-(di-*tert*-butylsilane) protecting group for the stereoselective outcome of the glycosylations.



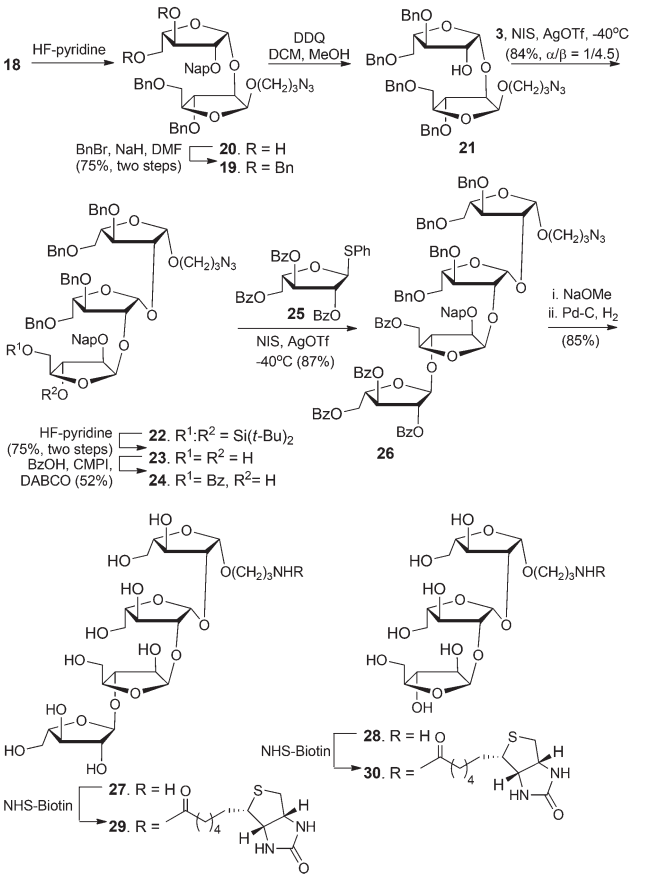
Scheme 1 Installation of an anomeric linker.

First, attention was focused on the installation of an anomeric linker, which is required for the conjugation of the oligosaccharides to carrier proteins or biotin in order to facilitate immunological studies. Thus, a glycosylation of conformationally constrained glycosyl donor **3** with 3-bromopropan-1-ol in the presence of the powerful thiophilic promoter system NIS/AgOTf[27] in DCM at −40 °C gave spacer modified **6** in an excellent yield (92%) as predominantly the β-anomer (α/β 1/4.5). On the other hand, similar glycosylations with the more flexible glycosyl donors **4** and **5** provided spacer-linked derivatives **7** and **8**, respectively, with lower β-anomeric selectivities (α/β 1/2.5 and 1/2.1, respectively). The anomeric configuration of the products was readily assigned by a combination of chemical shift and coupling constant data. In this respect, α-arabinofuranosides are characterized by $^3J_{H\text{-}1,H\text{-}2}$ = 1–3 Hz and δ C-1 = 104–110 ppm whereas similar β-glycosides have $^3J_{H\text{-}1,H\text{-}2}$ = 4–5 Hz and δ C-1 = 97–104 ppm values.[16,21,28] The ^{13}C chemical shift of the anomeric carbon and geminal coupling constant of H-1 of the major product of **6** was in the expected region for a β-anomer (δ C-1 = 100.8 ppm and $^3J_{H\text{-}1,H\text{-}2}$ = 5.1 Hz).

Compound **6** was treated with sodium azide in DMF to convert the bromide into an azide to give compound **9**. The Nap ether of **9** was removed by oxidation with DDQ in a mixture of dichloromethane and methanol to provide glycosyl acceptor **10** in 84% yield. In addition, glycosyl acceptors **14** and **15** were prepared by removal of the di-*tert*-butylsilane protecting group of **9** with HF-pyridine in dichloromethane[29] to give **11**, which was benzylated or benzoylated using standard conditions to provide **12** and **13**, followed by oxidation with DDQ to remove the Nap ethers.



Scheme 2 Protecting groups of the glycosyl donor and acceptor influence the anomeric outcome of arabinofuranosylations.



Scheme 3 Assembly of arabinofuranosides.

Interestingly, glycosylations of silane protected donor **3** with glycosyl acceptors **10**, **14** and **15** gave, in each case, the respective coupling products **16**, **17** and **18** in high yield but with differing anomeric selectivities (Scheme 2). In particular, the use of di-*tert*-butylsilane protected glycosyl acceptor **10** gave disaccharide **16** as a 1/1 mixture of α/β anomers and probably in this specific case, unfavorable steric interactions between the bulky silane protecting groups of the acceptor and donor in the transition state leading to the β-anomer are responsible for the low anomeric selectivity.[30] The use of C-3 and C-5 benzoylated and benzylated acceptors **14** and **15** led to the formation of the corresponding disaccharides **17** and **18**, respectively, with reasonable to good β-anomeric selectivities, and in particular, the benzylated acceptor behaved very well giving spacer modified **18** as a 1/6.5 mixture of α/β anomers that could readily be separated by silica gel column chromatography. As expected, a glycosylation of the conformational flexible donor **5** with glycosyl acceptor **15** in the presence of NIS/AgOTf gave disaccharide **19** as a 1/1.7 mixture of α/β anomers, highlighting that appropriate protection of the glycosyl donor and acceptor is critical for achieving optimal β-anomeric selectivity.

The process of removal of the di-*tert*-butylsilane protecting group using HF-pyridine followed by protection of the resulting diol as benzyl ethers and oxidative removal of the Nap ether was repeated to give glycosyl acceptor **21** (Scheme 3). An NIS/AgOTf promoted glycosylation of the latter compound with glycosyl donor **3** gave trisaccharide **22** as a separable 1/4.5 mixture of α/β anomers. Next, trisaccharide **22** was converted into glycosyl acceptor **24** having a free C-3″ hydroxyl by removal of the di-*tert*-butylsilane protecting group (→**23**) followed by regioselective benzoylation of the primary hydroxyl using benzoic acid in the presence of 2-chloro-1-methylpyridinium iodide (CMPI) and 1,4-diazabicyclo[2.2.2]octane (DABCO). Finally, a glycosylation of **24** with **25** in the presence of NIS/AgOTf[27] gave tetrasaccharide **26** in an excellent yield of 87% as the only α-anomer due to the neighboring group participation of the C-2 benzoyl ester of donor **25**.

Deprotection of **26** and **23** to afford the target compounds **27** and **28**, respectively, was accomplished by a two-step procedure involving saponification of the benzoyl esters using sodium methoxide in methanol, followed by catalytic hydrogenolysis over Pd/C to remove the benzyl and Nap ethers and convert the azido moiety into an amine. NMR and MS analyses confirmed the structural integrity of tetrasaccharide **27** (Araf, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, δ C-1 = 100.0 ppm, Araf′, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, δ C-1 = 99.9 ppm, Araf″, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, δ C-1 = 97.7 ppm, Araf‴, H-1, singlet, δ C-1 = 108.1 ppm). Finally, the amine of the anomeric linker of compounds **28** and **29** was exploited to install a biotin moiety by reaction with biotin *N*-hydroxysuccinimide ester (NHS-Biotin) in phosphate buffer at pH 7.4 to give, after purification by reverse phase C-18 column chromatography, biotin modified derivatives **29** and **30**, respectively.

The compounds were immobilized on microtiter plates coated with streptavidine, which were subsequently used to probe for the binding of a panel of 180 anti-plant polysaccharide mAbs. Surprisingly, none of the antibodies exhibited

binding for compounds **29** and **30**, indicating that the array of antibodies cannot detect oligo-arabinofuranosides. Current efforts are focused on conjugation of the oligosaccharides to a carrier protein, and the use of the resulting conjugates for mouse immunizations and subsequent mAb generation using conventional hybridoma technology.

Conclusions

A concise synthetic strategy has been developed for the preparation of 1,2-linked β-arabinofuranosides commonly found in plant glycoproteins. The difficult to introduce β-arabinofuranosides were installed using an arabinofuranosyl donor protected by a cyclic 3,5-*O*-(di-*tert*-butylsilane). A temporary Nap ether at C-2 of the donor made it possible to further extend the glycosylation products by 1,2-arabinofuranosides. The silane-protecting group of the acceptors, however, needed to be removed to achieve optimal β-anomeric selectivities. The use of conformationally more flexible donors led to glycosylation products having poor anomeric ratios. Thus, it has been found that proper protection of the arabinofuranosyl donor and acceptor is critical for achieving high β-anomeric selectivity. A panel of 180 plant cell wall glycan-binding monoclonal antibodies that is commonly employed for in-depth analysis of the plant cell wall structure, function, dynamics, and biosynthesis did, unfortunately, not recognize the synthetic oligosaccharides.

Experimental

General procedures

Column chromatography was performed on silica gel 60 (EM Science, 70–230 mesh). Reactions were monitored by thin-layer chromatography (TLC) on Kieselgel 60 F254 (EM Science), and compounds were detected by examination under UV light and by charring with 10% sulfuric acid in MeOH. Solvents were removed under reduced pressure at <40 °C. MeOH was dried by refluxing with magnesium methoxide and then was distilled and stored under argon. Pyridine was dried by heating under refluxing over CaH_2 and then distilled and stored over molecular sieves (3 Å). CH_2Cl_2 was freshly distilled from calcium hydride under nitrogen prior to use. AgOTf was co-evaporated with toluene and dried *in vacuo* for 2–3 h prior to application. Molecular sieves (4 Å) were flame activated under vacuum prior to use. All reactions were carried out under an argon atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded with Varian spectrometers (models Inova300 and Inova500) equipped with Sun workstations. ^{1}H NMR spectra were recorded in $CDCl_3$ and referenced to residual $CHCl_3$ at 7.24 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Assignments were made by standard gCOSY and gHSQC. Optical rotations were measured using a 'Jasco P-1020' polarimeter and the specific rotations are provided in degrees $cm^3\ dm^{-1}\ g^{-1}$. High resolution mass spectra were obtained on a Bruker model Ultraflex MALDI-TOF mass spectrometer.

Phenyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-1-thio-α-L-arabinofuranoside (3). To a solution of phenyl 3,5-*O*-(di-*tert*-butylsilanediyl)-1-thio-α-L-arabinofuranoside (4.0 g, 10.4 mmol) in DMF (30 mL) at 0 °C was added 2-(bromomethyl)naphthalene (3.47 g, 15.7 mmol) and NaH (60% dispersion in oil, 0.62 g, 15.7 mmol) in four portions. The reaction mixture was kept stirring at 0 °C for 3 h. Upon completion, the reaction mixture was poured into ice-water (50 mL), stirred until cessation of H_2 evolution, and then extracted with ethyl acetate–diethyl ether (1/1, v/v, 3 × 100 mL). The combined organic phase was washed with cold water (200 mL), separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (4.28 g, 75%). Analytical data for **3**: R_f = 0.57 (ethyl acetate–hexane, 1.2/8.8, v/v); $[\alpha]_D^{22}$ = −119.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.89–7.86 (m, 4H, Ar*H*), 7.57–7.42 (m, 5H, Ar*H*), 7.25–7.23 (m, 3H, Ar*H*), 5.49 (d, $J_{1,2}$ = 5.4 Hz, H-1), 5.05–4.93 (dd, *J* = 12.3 Hz, 2H, CH_2Nap), 4.38 (m, 1H, H-5b), 4.23 (dd, $J_{3,4}$ = 6.9 Hz, 1H, H-3), 4.05 (dd, 1H, $J_{2,3}$ = 5.4 Hz, H-2), 3.99 (m, 2H, H-2, 5a), 1.12 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 135.20, 134.63, 133.56, 133.37, 131.52, 129.14, 128.47, 128.19, 127.97, 127.23, 126.36, 126.21, 126.19, 90.14, 86.82, 81.52, 73.98, 72.50, 67.55, 27.74, 27.35, 22.88, 20.36 ppm; MALDI HR-MS calc. for $C_{30}H_{38}NaO_4SSi$ $[M + Na]^+$: 545.2158, found 545.2163.

Phenyl 3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-2-*O*-(2-naphthyl)methyl-1-thio-α-L-arabinofuranoside (4). To a solution of phenyl 1-thio-α-L-arabinofuranoside (0.43 g, 1.77 mmol) and imidazole (0.53 g, 7.81 mmol) in DMF (7 mL) was added dropwise dichlorotetraisopropyldisiloxane (0.63 mL, 1.95 mmol). After 4 h, excess silylation agent was decomposed by the addition of methanol (2 mL), which was followed by the addition of ethyl acetate (25 mL). The solution was poured into saturated aqueous sodium chloride (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), and the solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford phenyl 3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-1-thio-α-L-arabinofuranoside as a colorless syrup (0.60 g, 70%). MALDI HR-MS calc. for $C_{23}H_{40}NaO_5SSi_2$ $[M + Na]^+$: 545.2158, found 545.2163. Phenyl 3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-1-thio-α-L-arabinofuranoside (0.35 g, 0.72 mmol) was dissolved in DMF (8 mL) and 2-(bromomethyl)naphthalene (0.23 g, 1.08 mmol) and NaH (60% dispersion in oil, 43 mg, 1.08 mmol) were added. The reaction mixture was kept stirring at 0 °C for 3 h. Upon completion, the reaction was poured into ice-water (20 mL), stirred until cessation of H_2 evolution, and then extracted with ethyl acetate–diethyl ether (1/1, v/v, 3 × 30 mL). The combined organic phase was washed with cold water (75 mL), separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to

afford the title compound as a colorless syrup (0.34 g, 77%). Analytical data for **4**: R_f = 0.57 (ethyl acetate–hexane, 1.2/8.8, v/v); $[\alpha]_D^{22}$ = −67.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.81 (m, 4H, Ar*H*), 7.47 (m, 5H, Ar*H*), 7.25 (m, 3H, Ar*H*), 5.51 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.91–4.81 (dd, 2H, *J* = 12.0 Hz, CH_2Nap), 4.38 (m, 1H, H-3), 4.11 (dd, 1H, $J_{2,3}$ = 5.7 Hz, H-2), 4.01 (m, 3H, H-4, 5a, 5b), 1.02–1.09 (m, 28H, CH(CH_3)$_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 135.32, 131.07, 129.06, 128.28, 128.14, 127.90, 127.23, 126.85, 126.29, 126.11, 126.00, 89.67, 89.36, 80.38, 76.13, 73.05, 61.34, 17.68, 17.55, 17.37, 17.35, 17.29, 17.22, 13.77, 13.36, 13.06, 12.78 ppm; MALDI HR-MS calc. for $C_{34}H_{48}NaO_5SSi_2$ $[M + Na]^+$: 647.2659, found 647.2659.

Phenyl 3,5-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-1-thio-α-L-arabinofuranoside (5). Hydrogen fluoride–pyridine (85 μL, 3.28 mmol) was carefully diluted with pyridine (5 mL) at 0 °C. The resulting solution was added slowly to a stirred at 0 °C suspension of **3** (0.45 g, 0.82 mmol) in CH_2Cl_2 (5 mL) and the reaction was allowed to proceed for 2 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with water (10 mL) and $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (EtOAc–hexane, 1/1, v/v) to give a diol intermediate (0.28 g, 81%). MALDI HR-MS calc. for $C_{22}H_{22}NaO_4S$ $[M + Na]^+$: 428.1034, found 428.1041. The diol (0.25 g, 0.62 mmol) and benzyl bromide (0.22 mL, 1.85 mmol) were dissolved in DMF (5 mL), cooled to 0 °C, and treated with NaH (60% dispersion in oil, 74 mg, 1.85 mmol, four portions). The reaction mixture was stirred for 2 h, then poured into ice-water (20 mL), stirred for 10 min, and extracted with ethyl acetate–diethyl ether (1/1 v/v, 3 × 30 mL). The combined organic phase was washed with cold water (50 mL), separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.27 g, 79%). Analytical data for **5**: R_f = 0.47 (ethyl acetate–hexane, 2/8, v/v); $[\alpha]_D^{22}$ = −86.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.80–7.74 (m, 4H, Ar*H*), 7.49–7.39 (m, 5H, Ar*H*), 7.29–7.20 (m, 13H, Ar*H*), 4.76 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Nap), 4.62 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Nap), 4.58–4.42 (m, 4H, 2 × CH_2Ph), 4.39 (m, 1H, H-4), 4.17 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-3), 4.08 (dd, 1H, $J_{3,4}$ = 6.9 Hz, H-3), 3.71–3.62 (dd, *J* = 3.90 Hz and 6.90 Hz, H-5a, 5b) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 138.41, 138.02, 135.20, 135.07, 133.54, 133.42, 131.58, 129.25, 128.73, 128.69, 128.63, 128.30, 128.15, 128.07, 127.96, 127.47, 127.29, 126.58, 126.42, 126.20, 90.66, 88.82, 83.73, 80.84, 73.67, 72.62, 72.60, 68.34 ppm; MALDI HR-MS calc. for $C_{36}H_{34}NaO_4S$ $[M + Na]^+$: 585.2075, found 585.2083.

General glycosylation procedure for the synthesis of mono- and disaccharides

A mixture of a thioglycoside (0.125 mmol), an alcohol (0.10 mmol) and freshly activated molecular sieves (4 Å, 350 mg) in CH_2Cl_2 (2.0 mL) was stirred under argon at room temperature for 30 min. After the mixture was cooled (−40 °C), NIS (0.1875 mmol) followed by AgOTf (0.0375 mmol) were added. The reaction mixture was allowed to warm slowly to room temperature and stirring was continued for 15 min. The reaction was quenched by the addition of Et_3N or pyridine. The suspension was diluted with CH_2Cl_2 (15 mL) and filtered through a pad of Celite, and the filtrate was washed successively with 10% $Na_2S_2SO_3$ (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to give a residue. The residue was purified by silica gel chromatography (ethyl acetate–hexane gradient elution) to afford the corresponding oligosaccharide.

3-Bromopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-β-L-arabinofuranoside (6). Analytical data for **6**: R_f = 0.53 (ethyl acetate–hexane, 2/8, v/v); $[\alpha]_D^{22}$ = +57.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.86–7.81 (m, 4H, Ar*H*), 7.56–7.47 (m, 3H, Ar*H*), 4.97 (dd, 2H, *J* = 12.0 Hz, CH_2Nap), 4.93 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 4.37 (dd, 1H, $J_{4,5a}$ = 9.0 Hz, H-4), 4.30 (dd, 1H, $J_{2,3}$ = 5.1 Hz and $J_{3,4}$ = 9.0 Hz, H-3), 4.00–3.87 (m, 2H, H-2, 5b), 3.83 (m, 1H, 1/2CH_2-linker), 3.68–3.48 (m, 4H, H-5a, 1/2CH_2-linker, CH_2-linker), 2.15 (m, 2H, CH_2-linker), 1.10 (s, 9H, *t*-Bu), 1.01 (s, 9H, *t*-Bu) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 135.51, 133.45, 13.29, 128.37, 138.12, 127.93, 127.16, 126.34, 126.23, 126.16, 100.80, 80.77, 78.95, 73.80, 72.18, 68.71, 66.49, 32.91, 30.74, 27.79, 27.42, 22.83, 20.34 ppm; MALDI HR-MS calc. for $C_{27}H_{39}BrNaO_5Si$ $[M + Na]^+$: 573.1648, found 573.1639.

3-Bromopropyl 2-*O*-(2-naphthyl)methyl-3,5-*O*-(tetraisopropyl-siloxane-1,3-diyl)-β-L-arabinofuranoside (7). Analytical data for **7**: R_f = 0.55 (ethyl acetate–hexane, 2/8, v/v); $[\alpha]_D^{22}$ = +62.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.82 (m, 4H, ArH), 7.48 (m, 3H, ArH), 4.87–4.76 (dd, 2H, *J* = 12.0 Hz, CH_2Nap), 4.70 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.51 (dd, 1H, $J_{3,4}$ = 5.1 Hz, H-3), 3.98 (dd, 1H, $J_{2,3}$ = 7.5 Hz, H-2), 3.94 (dd, 1H, *J* = 9.0 Hz, H-5b), 3.83–3.78 (m, 2H, H-4, H5a), 3.74 (m, 1H, 1/2CH_2-linker), 3.58–3.37 (m, 3H, 1/2CH_2-linker, CH_2-linker), 2.10 (m, 2H, CH_2-linker), 1.12–1.02 (m, 28H, CH(CH_3)$_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 135.65, 133.43, 133.26, 128.33, 128.07, 127.91, 126.85, 126.36, 126.16, 126.05, 99.99, 84.92, 82.12, 78.19, 73.02, 66.86, 65.50, 32.79, 30.76, 17.80, 17.70, 17.67, 17.63, 17.37, 17.31, 17.25, 17.23, 13.73, 13.52, 13.10, 12.72 ppm; MALDI HR-MS calc. for $C_{31}H_{49}BrNaO_6Si$ $[M + Na]^+$: 675.2149, found 675.2155.

3-Bromopropyl 3,5-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-β-L-arabinofuranoside (8). Analytical data for **8**: R_f = 0.56 (ethyl acetate–hexane, 3/7, v/v); $[\alpha]_D^{22}$ = +35.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.81 (m, 2H, Ar*H*), 7.47 (m, 2H, Ar*H*), 7.33–7.28 (m, 8H, Ar*H*), 4.89 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1), 4.76–4.50 (m, 6H, CH_2Nap, 2 × CH_2Ph), 4.12 (m, 3H, H-2, 3, 4), 3.76 (m, 1H, 1/2CH_2-linker), 3.53 (m, 2H, *J* = 5.1 Hz, H-5a, H5b), 3.49–3.39 (m, 3H, 1/2CH_2-linker, CH_2-linker), 2.03 (m, 2H, CH_2-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 138.41, 138.25, 135.44, 133.43, 133.31, 128.59, 128.58, 128.47, 128.13, 128.07, 127.92, 127.86, 127.07, 126.41, 126.26, 126.13, 101.05, 84.49, 83.38, 80.45, 73.56, 72.83, 72.66, 72.60, 65.49, 32.69, 30.83 ppm; MALDI HR-MS calc. for $C_{33}H_{35}BrNaO_5$ $[M + Na]^+$: 613.1566, found 613.1572.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-β-L-arabinofuranoside (9). Compound **6** (0.67 g,

1.21 mmol) and sodium azide (0.79 g, 12.1 mmol) were dissolved in DMF (10 mL). The reaction mixture was stirred at 60 °C for 16 h and then concentrated *in vacuo*. The resulting residue was diluted with ethyl acetate (50 mL), washed with H_2O (30 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.57 g, 92%). Analytical data for **9**: R_f = 0.5 (ethyl acetate–hexane, 2/8, v/v); $[\alpha]_D^{22}$ = +63.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.84 (m, 3H, Ar*H*), 7.56–7.47 (m, 4H, Ar*H*), 5.02–4.90 (m, 3H, $J_{1,2}$ = 3.90 Hz, H-1, C*H*$_2$Nap), 4.39 (dd, 1H, $J_{4,5}$ = 9.30 Hz, H-4), 4.30 (dd, 1H, $J_{3,4}$ = 4.2 Hz, H-3), 3.97 (dd, 1H, $J_{2,3}$ = 5.4 Hz, H-2), 3.92 (dd, 1H, *J* = 6.3 Hz, H-5b), 3.78 (m, 1H, 1/2C*H*$_2$-linker), 3.64 (m, dd, *J* = 5.1 Hz, H-5a), 3.54 (m, 1H, 1/2C*H*$_2$-linker), 3.40 (t, 2H, *J* = 5.7 Hz, C*H*$_2$-linker), 1.88 (m, 2H, C*H*$_2$-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 135.50, 133.44, 133.30, 128.36, 128.10, 127.94, 127.22, 126.35, 126.26, 126.17, 100.77, 80.73, 79.00, 73.77, 72.19, 68.68, 65.79, 48.57, 29.41, 27.7, 27.42, 22.83, 20.33 ppm; MALDI HR-MS calc. for $C_{27}H_{39}N_3NaO_5Si$ $[M + Na]^+$: 536.2557, found 536.2553.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-β-L-arabinofuranoside (10). Compound **9** (0.25 g, 0.48 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (4 : 1, 5 mL) and freshly crystallized DDQ (0.22 g, 0.97 mmol) was added. The reaction mixture was stirred at room temperature for 16 h. The mixture was diluted with CH_2Cl_2 (20 mL), and the organic phase was washed with saturated $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.15 g, 84%). Analytical data for **10**: R_f = 0.40 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{22}$ = +25.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 4.54 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1), 4.14 (dd, $J_{2,3}$ = 4.2 Hz and $J_{3,4}$ = 9.6 Hz, H-3), 4.01 (dd, 1H, *J* = 1.8 Hz and 9.0 Hz, H-5b), 3.90–3.66 (m, 5H, H-2, 4, 5a, C*H*$_2$-linker), 3.48–3.43 (m, 5H, OCH_3, C*H*$_2$-linker), 2.62–2.45 (dd, 1H, *J* = 4.8 Hz, –OH), 1.89 (m, 2H, C*H*$_2$-linker), 1.03 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 103.55, 77.06, 70.20, 68.83, 66.08, 62.87, 55.93, 48.68, 29.46, 27.66, 27.31, 22.91, 20.42 ppm; MALDI HR-MS calc. for $C_{16}H_{31}N_3NaO_5Si$ $[M + Na]^+$: 396.1931, found 396.1910.

3-Azidopropyl 3,5-di-*O*-benzoyl-2-*O*-(2-naphthyl)methyl-β-arabinofuranoside (12). Hydrogen fluoride–pyridine (90 μL, 3.50 mmol) was carefully diluted with pyridine (0.5 mL) at 0 °C. The resulting solution was added slowly to a stirred at 0 °C suspension of **9** (0.45 g, 0.87 mmol) in CH_2Cl_2 (5 mL) and the reaction was allowed to proceed for 2 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (10 mL), $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (EtOAc–hexane, 1/1, v/v) to give the diol intermediate **11** (0.27 g, 81%). MALDI HR-MS calc. for $C_{19}H_{23}N_3NaO_5$ $[M + Na]^+$: 396.1535, found 396.1503. The resulting intermediate (0.27 g, 0.72 mmol) was dissolved in dry pyridine (10 mL), cooled to 0 °C, and benzoyl chloride (0.29 mL, 2.54 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and then washed with 1 N HCl (20 mL), aqueous saturated $NaHCO_3$ (20 mL) and then H_2O (20 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.37 g, 87%). Analytical data for **12**: R_f = 0.45 (ethyl acetate–hexane, 3/7, v/v); $[\alpha]_D^{22}$ = +33.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 8.11–8.04 (m, 4H, Ar*H*), 7.95 (d, 1H, *J* = 8.4 Hz, Ar*H*), 7.80–7.72 (m, 4H, Ar*H*), 7.59–7.36 (m, 8H, Ar*H*), 5.64 (dd, 1H, $J_{3,4}$ = 5.7 Hz, H-3), 5.02 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.89–4.78 (dd, 2H, *J* = 12.0 Hz, C*H*$_2$Nap), 4.74 (dd, 1H, $J_{5a,5b}$ = 11.7 Hz, H-5b), 4.57 (dd, 1H, $J_{4,5a}$ = 7.5 Hz, H-5a), 4.36 (dd, 1H, $J_{2,3}$ = 6.9 Hz, H-2), 4.28 (m, 1H, H-4), 3.88 (m, 1H, 1/2C*H*$_2$-linker), 3.51–3.31 (m, 3H, 1/2C*H*$_2$-linker, C*H*$_2$-linker), 1.85 (m, 2H, C*H*$_2$-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.49, 166.21, 135.07, 133.99, 133.68, 133.41, 133.39, 133.27, 130.43, 130.16, 130.04, 129.50, 128.71, 128.64, 128.56, 128.11, 127.98, 127.04, 126.50, 126.35, 125.93, 101.05, 81.92, 79.59, 77.93, 72.90, 66.4, 65.26, 48.50, 29.13 ppm; MALDI HR-MS calc. for $C_{33}H_{31}N_3NaO_7$ $[M + Na]^+$: 604.2060, found 604.2057.

3-Azidopropyl 3,5-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-β-arabinofuranoside (13). Hydrogen fluoride–pyridine (250 μL, 9.8 mmol) was carefully diluted with pyridine (2.0 mL) at 0 °C. The resulting solution was added slowly to a stirred at 0 °C suspension of **9** (1.25 g, 2.43 mmol) in CH_2Cl_2 (12 mL) and the reaction was allowed to proceed for 2 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with water (20 mL) and $NaHCO_3$ (20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (EtOAc–hexane, 1/1, v/v) to give the diol intermediate **11** (0.73 g, 81%). MALDI HR-MS calc. for $C_{19}H_{23}N_3NaO_5$ $[M + Na]^+$: 396.1535, found 396.1503. The diol (0.73 g, 1.95 mmol) and benzyl bromide (0.70 mL, 5.86 mmol) were dissolved in DMF (10 mL), cooled to 0 °C, and treated with NaH (60% dispersion in oil, 0.23 g, 5.86 mmol, four portions). The reaction mixture was stirred at 0 °C for 2 h, then poured into ice-water (30 mL), stirred for 10 min, and extracted with ethyl acetate–diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic phase was washed with cold water (100 mL), separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford **13** as a colorless syrup (0.81 g, 74%). Analytical data for **7**: R_f = 0.50 (ethyl acetate–hexane, 3/7, v/v); $[\alpha]_D^{22}$ = +24.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.86 (m, 4H, ArH), 7.53 (m, 3H, ArH), 7.35 (m, 10H, ArH), 4.92 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.80 dd, 2H, *J* = 12.6 Hz, C*H*$_2$Ph), 4.76 (dd, 2H, *J* = 11.7 Hz, C*H*$_2$Nap), 4.59 dd, 2H, *J* = 12.6 Hz, C*H*$_2$Ph), 4.17 (m, 3H, H-2, H5a, H5b), 3.77 (m, 1H, 1/2C*H*$_2$-linker), 3.58 (m, 2H, H-3, H-4), 3.44–3.26 (m, 3H, 1/2C*H*$_2$-linker, C*H*$_2$-linker), 1.84 (m, 2H, C*H*$_2$-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 138.47, 138.20, 133.44, 133.50, 128.66, 128.65, 128.52, 128.18, 128.14, 128.00, 127.93, 127.12, 126.50, 126.34, 126.19, 100.97, 84.54, 83.39, 80.48,

73.59, 72.90, 72.65, 72.62, 64.76, 48.58, 29.20 ppm; MALDI HR-MS calc. $C_{33}H_{35}N_3NaO_5$ for $[M + Na]^+$: 576.2475, found 576.2480.

3-Azidopropyl 3,5-di-*O*-benzoyl-β-L-arabinofuranoside (14). Compound **12** (0.35 g, 0.60 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (4 : 1, v/v, 8 mL) and freshly crystallized DDQ (0.27 g, 1.2 mmol) was added. The reaction mixture was stirred at room temperature for 5 h. The mixture was diluted with CH_2Cl_2 (20 mL), and the organic phase was washed with saturated $NaHCO_3$ (15 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.22 g, 81%). Analytical data for **14**: R_f = 0.44 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{22}$ = +51.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 8.05 (m, 4H, Ar*H*), 7.62–7.52 (m, 3H, Ar*H*), 7.47–7.37 (m, 3H, Ar*H*), 5.45 (dd, $J_{3,4}$ = 6.3 Hz, H-3), 5.09 (d, $J_{1,2}$ = 4.8 Hz, H-1), 4.66 (dd, 1H, *J* = 4.5 Hz and 11.4 Hz, H-5b), 4.57–4.45 (m, 2H, H-2, H-5a), 4.18 (m, 1H, H-4), 3.93 (m, 1H, 1/2CH_2-linker), 3.60 (m, 1H, 1/2CH_2-linker), 3.37 (m, 1H, CH_2-linker), 2.90 (d, 1H, *J* = 8.7 Hz, –OH), 1.85 (dd, 2H, *J* = 6.6 Hz, CH_2-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.65, 166.35, 133.75, 133.35, 130.06, 130.01, 129.93, 129.36, 128.69, 128.58, 101.87, 79.92, 79.45, 76.77, 65.98, 65.79, 48.55, 29.02 ppm; MALDI HR-MS calc. for $C_{22}H_{23}N_3NaO_7$ $[M + Na]^+$: 464.1434, found 464.1437.

3-Azidopropyl 3,5-di-*O*-benzyl-β-L-arabinofuranoside (15). Compound **13** (0.78 g, 1.40 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (4 : 1, v/v, 20 mL) and freshly crystallized DDQ (0.64 g, 2.80 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. The mixture was diluted with CH_2Cl_2 (50 mL), and the organic phase was washed with saturated $NaHCO_3$ (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (0.45 g, 77%). Analytical data for **15**: R_f = 0.44 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{22}$ = +52.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.32 (m, 10H, ArH), 4.94 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 4.76 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Nap), 4.61 (d, 1H, *J* = 12 Hz, 1/2CH_2Nap), 5.54 (dd, 2H, *J* = 12.0 Hz, CH_2Nap), 4.24 (m, 1H, $J_{2,3}$ = 5.7 Hz, H-2), 4.12 (dd, 1H, $J_{4,5a}$ = 11.1 Hz, H-4), 3.83 (m, 2H, H-3, 1/2CH_2-linker), 3.55–3.48 (m, 3H, H-5a, 5b, 1/2CH_2-linker), 3.28 (m, 2H, CH_2-linker), 2.57 (d, *J* = 9.6 Hz, –OH), 1.80 (m, 2H, CH_2-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 138.18, 128.61, 128.01, 127.96, 127.93, 101.95, 84.62, 80.95, 78.09, 73.53, 72.14, 71.97, 65.50, 48.61, 29.11 ppm; MALDI HR-MS calc. for $C_{22}H_{27}NaN_3O_5$ $[M + Na]^+$: 436.1849, found 436.1833.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-α/β-L-arabinofuranosyl-(1→2)-3,5-*O*-(di-*tert*-butylsilanediyl)-β-L-arabinofuranoside (16). Analytical data for **16** (500 MHz, $CDCl_3$): R_f = 0.52 (ethyl acetate–hexane, 2/8, v/v); α/β ^{1}H NMR: δ, 7.81–7.71 (m, 4H, Ar*H*), 7.48–7.38 (m, 3H, Ar*H*), 5.33 (d, 1H, *J* = 3.0 Hz), 5.05 (d, 1H, *J* = 3.0 Hz), 4.94–4.79 (m, 4H, 2 × CH_2Ph), 4.55 (d, 1H, *J* = 4.5 Hz), 4.31–4.15 (m, 3H), 4.07 (m, 1H), 3.92 (m, 2H), 3.82–3.70 (m, 3H), 3.59–3.48 (m, 2H), 3.36–3.30 (m, 2H), 3.17 (m, 2H), 1.68 (m, 2H), 1.01 (s, 18H), 0.91 (s, 18H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ, 136.27, 135.70, 133.45, 133.26, 133.11, 128.37, 128.13, 128.06, 127.97, 127.92, 127.91, 126.94, 126.38, 126.33, 126.25, 126.15, 126.04, 125.96, 104.70, 101.39, 101.37, 81.34, 80.61, 79.05, 78.71, 78.48, 75.24, 76.70, 75.24, 74.02, 73.64, 71.86, 71.49, 68.66, 66.14, 65.16, 55.39, 48.65, 34.89, 31.14, 29.51, 27.28, 27.74, 27.71, 27.64, 27.42, 27.28, 27.25, 27.22, 22.87, 22.76, 22.74, 22.64, 21.32, 20.35, 20.33, 20.20 ppm; MALDI HR-MS calc. for $C_{40}H_{63}N_3NaO_9Si_2$ $[M + Na]^+$: 808.4001, found 808.3993.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-β-L-arabinofuranoside (17). Analytical data for **17**: R_f = 0.50 (ethyl acetate–hexane, 3/7, v/v); $[\alpha]_D^{22}$ = +58.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 8.05–7.99 (m, 3H, Ar*H*), 7.84–7.80 (m, 4H, Ar*H*), 7.56–7.25 (m, 10H, Ar*H*), 5.71 (dd, 1H, $J_{3,4}$ = 7.2 Hz, H-3), 5.08 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 5.04 (d, 1H, $J_{1',2'}$ = 5.1 Hz, H-1′), 4.94 (dd, 2H, *J* = 12.0 Hz, CH_2Ph), 4.71 (dd, 1H, $J_{4,5b}$ = 4.20 Hz and 11.7 Hz, H-5b), 4.57 (dd, 1H, $J_{4,5a}$ = 7.5 Hz and $J_{5a,5b}$ = 11.7 Hz, H-5a), 4.49 (dd, 1H, $J_{2,3}$ = 7.2 Hz, H-2), 4.43 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, H-3′), 4.34 (m, 1H, H-4′), 4.08 (dd, 1H, *J* = 5.1 Hz, 1/2CH_2-linker), 3.98 (dd, 1H, $J_{2',3'}$ = 9.0 Hz), 3.86 (m, 1H, H-4′), 3.76 (dd, 1H, $J_{5a',5b'}$ = 9.0 Hz, H-5b′), 3.60 (m, 1H, 1/2CH_2-linker), 3.49 (m, 1H, H-5a′), 3.35–3.19 (m, 2H, CH_2-linker), 1.74 (m, 2H, CH_2-linker), 1.02 (s, 9H, *t*-Bu), 0.96 (s, 9H, *t*-Bu) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.40, 165.97, 135.51, 133.53, 133.43, 133.28, 133.19, 130.14, 129.98, 129.93, 129.70, 128.65, 128.51, 128.33, 128.08, 127.93, 127.27, 126.35, 126.16, 101.03, 99.97, 80.53, 80.52, 79.39, 78.49, 77.34, 74.27, 71.90, 68.48, 66.34, 65.24, 48.20, 29.10, 27.71, 27.36, 22.76, 20.76 ppm; MALDI HR-MS calc. for $C_{46}H_{5}5N_3NaO_{11}Si$ $[M + Na]^+$: 876.3504, found 876.3489.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (18). Analytical data for **18**: R_f = 0.47 (ethyl acetate–hexane, 2.5/7.5, v/v); $[\alpha]_D^{22}$ = +89.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.84–7.76 (m, 4H, Ar*H*), 7.54–7.45 (m, 4H, Ar*H*), 7.30–7.24 (m, 10H, Ar*H*), 5.07 (d, 1H, $J_{1',2'}$ = 5.1 Hz, H-1), 5.00 (m, 2H, $J_{1,2}$ = 4.5 Hz and *J* = 12.0 Hz, H-1, 1/2CH_2Ph), 4.89 (d, *J* = 12.0 Hz, 1/2CH_2Ph), 4.75 (d, *J* = 12.0 Hz, 1/2CH_2Ph), 4.60 (d, *J* = 12.0 Hz, 1/2CH_2Ph), 4.51–4.45 (m, 3H, H-3′, CH_2Ph), 4.39 (dd, 1H, $J_{2,3}$ = 6.6 Hz, H-2), 4.30 (ds, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 4.18–4.11 (m, 2H, H-5a′, H-5b′), 4.01 (dd, 1H, $J_{2',3'}$ = 9.0 Hz, H-2′), 3.89 (dd, 1H, $J_{5a,5b}$ = 10.5 Hz, H-5b), 3.7–3.65 (m, 2H, H-4′, 1/2CH_2-linker), 3.50 (m, 2H, H-4, H-5a), 3.39 (m, 1H, 1/2CH_2-linker), 3.19 (m, 2H, CH_2-linker), 1.68 (m, 2H, CH_2-linker), 1.06 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 138.25, 135.55, 133.43, 133.28, 128.63, 128.57, 128.32, 128.07, 128.03, 127.94, 127.90, 127.88, 127.23, 126.34, 126.31, 126.15, 100.52, 99.14, 82.20, 81.08, 80.44, 80.36, 78.68, 74.31, 73.50, 72.50, 72.34, 71.66, 68.73, 64.52, 48.32, 29.15, 27.72, 27.39, 22.85, 20.34 ppm; MALDI HR-MS calc. for $C_{46}H_{59}N_3NaO_9Si$ $[M + Na]^+$: 848.3919, found 848.3929.

3-Azidopropyl 3,5-*O*-di-benzyl-2-*O*-(2-naphthyl)methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (19). Analytical data for **19**: R_f = 0.42 (ethyl acetate–hexane,

3/7, v/v); $[\alpha]_D^{22}$ = +83.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): *δ*, 7.82–7.75 (m, 4H, Ar*H*), 7.51–7.46 (m, 3H, Ar*H*), 7.29–7.19 (m, 20H, Ar*H*), 5.17 (d, 1H, $J_{1',2'}$ = 3.0 Hz, H-1′), 5.07 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.91 (d, 1H, *J* = 11.4 Hz, 1/2CH_2Ph), 4.71–4.57 (m, 5H, 2 × CH_2Ph, 1/2CH_2Ph), 4.51 (dd, 2H, *J* = 12.0 Hz, CH_2Ph), 4.46 (dd, 1H, $J_{2,3}$ = 5.7 Hz, H-2), 4.42 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Ph), 4.31 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Ph), 4.18–4.13 (m, 6H, H-2′, H-5a′, H-5b′, H-3, H-5a, H-5b), 3.75 (m, 1H, 1/2CH_2-linker), 3.61–3.39 (m, 5H, H-3′, H-4′, H-3, CH_2-linker), 3.15 (m, 2H, CH_2-linker), 1.68 (m, 2H, CH_2-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): *δ*, 138.34, 138.30, 138.24, 135.57, 133.47, 133.28, 128.58, 128.55, 128.53, 128.39, 128.10, 128.07, 128.00, 127.98, 127.94, 127.90, 127.86, 127.83, 127.76, 126.88, 126.83, 126.19, 126.13, 100.36, 98.77, 84.25, 83.18, 82.50, 81.02, 80.57, 79.37, 73.52, 73.32, 72.64, 72.52, 72.46, 72.01, 64.56, 48.36, 29.28 ppm; MALDI HR-MS calc. for $C_{52}H_{55}N_3NaO_9$ $[M + Na]^+$: 888.3836, found 888.3821.

3-Azidopropyl 3,5-di-*O*-benzyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (21). Compound **19** (530 mg, 0.61 mmol) was dissolved in a mixture of DCM and MeOH (4 : 1, v/v, 15 mL) and freshly crystallized DDQ (278 mg, 1.22 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The mixture was diluted with CH_2Cl_2 (30 mL), and the organic phase was washed with saturated $NaHCO_3$ (20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to give the alcohol as a colorless syrup (315 mg, 71%). Analytical data for **21**: R_f = 0.47 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{22}$ = +86.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): *δ*, 7.32–7.22 (m, 20H, Ar*H*), 5.00 (d, 1H, $J_{1',2'}$ = 4.8 Hz, H-1′), 4.97 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.78 (d, 1H, *J* = 12.0 Hz, 1/2CH_2Ph), 4.64 (dd, 2H, *J* = 11.7 Hz, CH_2Ph), 4.53 (dd, 2H, *J* = 12.3 Hz, CH_2Ph), 4.98 (d, 3H, *J* = 12.0 Hz, 1/2CH_2Ph, CH_2Ph), 4.43–4.35 (m, 3H, H-2, CH_2Ph), 4.24 (m, 1H, H-2′), 4.15–4.09 (dd, 2H, *J* = 5.7 Hz, H5a′, H-5b′), 3.87 (dd, 1H, $J_{3',4'}$ = 6.3 Hz, H-3′), 3.77 (m, 1H, H-4′), 3.56 (dd, 2H, *J* = 5.7 Hz, H-4, H-5b), 3.48 (dd, 2H, *J* = 6.0 Hz, H-5a, 1/2CH_2-linker), 3.41 (m, 1H, 1/2CH_2-linker), 3.29 (m, 2H, CH_2-linker), 3.09 (d, 1H, *J* = 8.7 Hz, OH), 1.77 (m, 2H, CH_2-linker) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): *δ*, 138.21, 138.20, 138.15, 126.61, 128.58, 128.54, 128.03, 127.96, 127.89, 127.82, 102.46, 100.38, 84.31, 82.47, 82.42, 81.22, 80.49, 78.07, 73.55, 73.40, 72.45, 72.30, 72.05, 72.02, 64.79, 48.42, 28.99 ppm; MALDI HR-MS calc. for $C_{41}H_{47}N_3NaO_9$ $[M + Na]^+$: 748.3210, found 748.3520.

3-Azidopropyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-naphthyl)-methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-2-*O*-naphthyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (22). A mixture of the glycosyl donor **3** (360 mg, 0.68 mmol), glycosyl acceptor **21** (400 mg, 0.55 mmol), and freshly activated 4 Å molecular sieves (1 g) in CH_2Cl_2 (15 mL) was stirred at room temperature for 30 min and then cooled to −40 °C. NIS (235 mg, 1.03 mmol) followed by AgOTf (53 mg, 0.20 mmol) was added. The reaction mixture was stirred at −40 °C for 2 h and then warmed slowly to room temperature and stirring was continued for 30 min. The reaction was quenched by the addition of Et_3N or pyridine. The suspension was diluted with CH_2Cl_2 (20 mL) and filtered through a pad of Celite, and the filtrate was washed successively with 10% $Na_2S_2SO_3$ (20 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to give the trisaccharide **22** (432 mg, 69%). Analytical data for **22**: R_f = 0.42 (ethyl acetate–hexane, 3/7, v/v); $[\alpha]_D^{23}$ = +84.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *δ*, 7.83 (s, 1H, Ar*H*), 7.73 (d, 1H, *J* = 8.5 Hz, Ar*H*), 7.65 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.51 (dd, 1H, *J* = 8.5 Hz, Ar*H*), 7.42–7.38 (m, 2H, Ar*H*), 7.33–7.22 (m, 14H, Ar*H*), 7.15–7.11 (m, 4H, Ar*H*), 6.88 (dd, 2H, *J* = 6.5 Hz, Ar*H*), 5.38 (d, 1H, *J* = 4.5 Hz), 5.12 (d, 1H, *J* = 4.5 Hz), 5.10 (d, 1H, *J* = 11.5 Hz), 5.04 (d, 1H, *J* = 4.5 Hz), 4.78 (d, 1H, *J* = 12.0 Hz), 4.70 (dd, 2H, *J* = 11.5 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.52–4.49 (m, 2H), 4.46 (d, 1H, *J* = 10 Hz), 4.41 (m, 1H), 4.35 (dd, 1H, *J* = 5.0 Hz and 9.0 Hz), 4.31 (d, 1H, *J* = 12.5 Hz), 4.18 (m, 3H), 4.09 (d, 1H, *J* = 11.5 Hz), 4.05–4.00 (m, 3H), 3.90 (dd, 1H, *J* = 10.5 Hz), 3.82–3.74 (m, 3H), 3.40 (m, 2H), 3.44–3.35 (m, 3H), 3.20 (m, 2H), 1.75 (m, 2H, CH_2-linker), 1.05 (s, 9H), 1.00 (s, 9H) ppm; ^{13}C NMR(75 MHz, $CDCl_3$): *δ*, 138.35, 138.17, 138.15, 138.03, 136.04, 133.47, 133.22, 128.63, 128.49, 128.35, 128.21, 128.08, 127.98, 127.93, 127.77, 127.70, 127.64, 127.51, 126.65, 126.30, 126.24, 126.04, 100.09, 98.19, 97.69, 83.12, 81.85, 81.19, 80.95, 80.41, 79.88, 79.12, 78.21, 74.61, 73.50, 73.22, 72.71, 72.56, 72.40, 71.91, 71.43, 69.03, 64.81, 48.42, 29.36, 27.73, 27.40, 22.92, 20.35 ppm; MALDI HR-MS calc. for $C_{65}H_{79}N_3NaO_{13}Si$ $[M + Na]^+$: 1160.5280, found 1160.5261.

3-Azidopropyl 5-*O*-benzoyl-2-*O*-(2-naphthyl)methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-2-*O*-naphthyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (24). Hydrogen fluoride–pyridine (32 μL, 1.24 mmol) was carefully diluted with pyridine (200 μL) at 0 °C. The resulting solution was added slowly to a stirred at 0 °C suspension of **22** (360 mg, 0.31 mmol) in CH_2Cl_2 (5 mL) and the reaction was allowed to proceed for 2 h at 0 °C and another 3 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with water (5 mL) and saturated $NaHCO_3$ (5 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (EtOAc–hexane, 1/1, v/v) to give diol **23** (280 mg, 88%). MALDI HR-MS calc. for $C_{57}H_{63}NaN_3O_{13}$ $[M + Na]^+$: 1020.4259, found 1020.4230. The resulting diol (280 mg, 0.28 mmol) was dissolved in dry CH_2Cl_2 (2 mL), cooled to 0 °C, and treated with benzoic acid (0.44 g, 7.4 mmol) and 2-chloromethyl pyridinium iodide (CMPI) (2.36 g, 9.25 mmol). The mixture was stirred for 15 minutes at room temperature followed by the addition of 1,4 diazabicyclo[2,2,2]octane (DABCO) (0.980 g, 8.75 mmol). Stirring was continued until TLC indicated consumption of starting material (~1.5 h). The reaction mixture was filtered through Celite, diluted with EtOAc (40 mL), and washed with brine (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to give the trisaccharide acceptor **24** (161 mg,

52%). Analytical data for **22**: R_f = 0.54 (ethyl acetate–hexane, 1/1, v/v); $[\alpha]_D^{23}$ = +78.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ, 8.06 (d, 2H, *J* = 7.5 Hz), 8.86 (s, 1H, Ar*H*), 7.73 (d, 1H, *J* = 8.0 Hz, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.45–7.39 (m, 4H, Ar*H*), 7.29–7.09 (m, 18H, Ar*H*), 6.85 (d, 2H, *J* = 7.0 Hz, Ar*H*), 5.51 (d, 1H, *J* = 4.5 Hz), 5.16 (d, 1H, *J* = 4.0 Hz), 5.07 (d, 1H, *J* = 11.0 Hz), 5.05 (d, 1H, *J* = 4.0 Hz), 4.65 (dd, 1H, *J* = 12.0 Hz), 4.61–4.56 (m, 3H, *J* = 4.5 Hz), 4.49 (m, 2H, *J* = 7.0 Hz), 4.44–4.36 (m, 3H), 4.30 (d, 1H, *J* = 12.0 Hz), 4.25 (dd, 1H, *J* = 5.0 Hz), 4.18 (m, 3H), 4.07–3.98 (m, 4H), 3.80 (m, 2H), 3.49–3.37 (m, 4H), 3.31 (dd, 1H, *J* = 5.0 Hz and 10.0 Hz), 3.26 (m, 2H), 1.79 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.61, 138.31, 138.11, 138.04, 137.99, 135.55, 133.47, 133.34, 133.31, 130.02, 128.67, 128.60, 128.58, 128.52, 128.48, 128.33, 128.17, 128.06, 127.94, 127.87, 127.75, 127.70, 127.61, 127.38, 126.92, 126.44, 126.24, 99.59, 98.31, 98.17, 84.33, 83.17, 82.20, 81.04, 80.35, 80.10, 79.48, 79.19, 76.27, 73.45, 73.20, 72.62, 72.58, 72.29, 72.26, 72.01, 67.01, 64.95, 48.51, 29.36 ppm; MALDI HR-MS calc. for $C_{64}H_{67}N_3NaO_{14}$ $[M + Na]^+$: 1124.4521, found 1124.4507.

Phenyl 2,3,5-tri-*O*-benzoyl-1-thio-α-L-arabinofuranoside (25). To a solution of phenyl 1-thio-α-L-arabinofuranoside (0.65 g, 2.68 mmol) in pyridine (15 mL) at 0 °C was added dropwise benzoyl chloride (1.25 mL, 10.75 mmol). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (50 mL) and then washed with 1 N HCl (30 mL), saturated $NaHCO_3$ (30 mL) and then H_2O (30 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound as a colorless syrup (1.26 g, 85%). Analytical data for **25**: R_f = 0.62 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{22}$ = −52.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ, 8.15 (d, *J* = 7.2 Hz, 2H, Ar*H*), 8.02 (dd, *J* = 7.2 Hz, 3H, Ar*H*), 7.64–7.25 (m, 15H, Ar*H*), 5.84 (s, 1H, H-1), 5.72 (dd, 1H, *J* = 1.5 Hz, H-2), 5.66 (dd, 1H, $J_{3,4}$ = 4.5 Hz, H-3), 4.86 (m, 1H, $J_{4,5}$ = 8.7 Hz, H-4), 4.76–4.83 (m, 2H, *J* = 8.5 Hz, H-5a, 5b) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.38, 165.80, 165.57, 133.90, 133.83, 133.67, 133.31, 132.53, 130.27, 130.13, 129.99, 129.90, 129.30, 129.18, 129.09, 128.80, 128.77, 128.55, 128.08, 91.66, 82.78, 81.38, 78.27, 63.74 ppm; MALDI HR-MS calc. for $C_{32}H_{26}NaO_7S$ $[M + Na]^+$: 577.1297, found 577.1301.

3-Azidopropyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-5-*O*-benzoyl-2-*O*-naphthyl-β-L-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-2-*O*-(2-naphthyl)methyl-β-L-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-β-L-arabinofuranoside (26). A mixture of glycosyl donor **25** (114 mg, 0.20 mmol), glycosyl acceptor **24** (150 mg, 0.14 mmol), and freshly activated 4 Å molecular sieves (500 mg) in CH_2Cl_2 (7.5 mL) was stirred at room temperature for 30 min. The mixture was cooled to −20 °C, and NIS (70 mg, 0.31 mmol) and AgOTf (16 mg, 0.06 mmol) were added. The reaction mixture was stirred at −20 °C for 2 h and then warmed slowly to room temperature and stirring was continued for 1 h. The reaction was quenched by the addition of pyridine. The suspension was diluted with CH_2Cl_2 (15 mL) and filtered through a pad of Celite, the filtrate was washed successively with 10% $Na_2S_2SO_3$ (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to give the tetrasaccharide **26** (183 mg, 87%). Analytical data for **26**: R_f = 0.45 (ethyl acetate–hexane, 4/6, v/v); $[\alpha]_D^{24}$ = +55.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ, 8.03 (d, 2H, *J* = 7.5 Hz, Ar*H*), 7.96 (dd, 4H, *J* = 7.5 Hz, Ar*H*), 7.76 (s, 1H, Ar*H*), 7.66 (d, 1H, *J* = 8.0 Hz, Ar*H*), 7.55 (m, 4H, Ar*H*), 7.48–7.10 (m, 31H, Ar*H*), 6.90 (d, 2H, *J* = 7.0 Hz, Ar*H*), 5.68 (s, 1H), 5.57 (s, 1H), 5.56 (d, 1H, *J* = 4.0 Hz), 5.52 (d, 1H, *J* = 4.0 Hz), 5.17 (d, 1H, *J* = 4.0 Hz), 5.07 (d, 1H, *J* = 4.0 Hz), 5.01 (dd, 1H, *J* = 11.5 Hz), 4.79 (dd, 1H, *J* = 4.5 Hz and 11 Hz), 4.72–4.39 (m, 14H), 4.30 (d, 1H, *J* = 12.5 Hz), 4.25 (dd, 1H, *J* = 4.0 Hz and 7.0 Hz), 4.20–412 (m, 4H), 4.05 (m, 2H), 3.85 (dd, 1H, *J* = 7.0 Hz), 3.81 (m, 1H), 3.50 (dd, 1H, *J* = 4.0 Hz and 9.5 Hz), 3.44 (m, 3H), 3.37 (dd, 1H, *J* = 5.0 Hz and 10.0 Hz), 3.26 (m, 2H), 1.78 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 166.36, 166.26, 165.84, 165.57, 138.30, 138.12, 138.05, 135.65, 133.72, 133.69, 133.41, 133.25, 133.19, 130.19, 130.15, 130.11, 130.08, 130.00, 129.94, 129.89, 129.33, 129.23, 129.17, 128.72, 128.59, 128.53, 128.50, 128.48, 129.36, 128.12, 128.30, 127.93, 127.88, 127.77, 127.73, 127.64, 127.42, 126.60, 126.30, 126.07, 105.75, 100.02, 98.42, 98.24, 84.15, 83.21, 82.52, 82.37, 81.60, 81.14, 81.04, 80.37, 79.47, 79.40, 79.23, 77.78, 77.56, 73.48, 73.23, 72.59, 72.53, 72.48, 72.34, 72.29, 71.88, 48.47, 29.34, 27.68 ppm; MALDI HR-MS calc. for $C_{90}H_{87}N_3NaO_{21}$ $[M + Na]^+$: 1568.5730, found 1568.5741.

3-Aminopropyl α-L-arabinofuranosyl-(1→3)-β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranoside (27). To a solution of **26** (100 mg, 0.103 mmol) in methanol (1.0 mL) was added 1 M NaOMe until pH ~ 10 (~0.1 mL) was achieved. The reaction mixture was stirred for 4 h at room temperature and then neutralized with Dowex (H^+), filtered, and concentrated *in vacuo*. The crude residue was dissolved in MeOH–H_2O–HOAc (5 mL, 3/1/1, v/v/v), and 10% Pd–C (20 mg) was added. The reaction mixture was stirred under an atmosphere of H_2 for 15 h. The catalyst was then filtered-off, washed with methanol and H_2O, and the combined filtrates were concentrated under reduced pressure. The residue was passed through a small amount of latrobeads and slowly eluted with H_2O. Fractions containing the product were collected and concentrated *in vacuo* to afford the fully deprotected tetrasaccharide **25** (33.2 mg, 85% for 2 steps). Analytical data for **27**: $[\alpha]_D^{26}$ = +58.2° (*c* 1.0, H_2O); ^{1}H NMR (500 MHz, D_2O): δ, 5.15 (d, 1H, *J* = 4.5 Hz), 5.87 (s, 1H), 5.04 (d, 1H, *J* = 4.5 Hz), 4.99 (d, 1H, *J* = 4.5 Hz), 4.22 (m, 2H, *J* = 4.5 Hz), 4.15 (dd, 1H, *J* = 4.5 Hz and 8.0 Hz), 4.10 (dd, 1H, *J* = 7.5 Hz), 4.08–4.05 (m, 2H, *J* = 7.0 Hz), 4.02 (m, 1H), 3.95–3.90 (m, 2H), 3.85 (m, 1H), 3.83–3.77 (m, 5H), 3.73–3.67 (m, 3H), 3.65–3.55 (m, 5H), 3.54–3.40 (m, 2H), 3.00 (m, 2H), 1.84 (m, 1H) ppm; ^{13}C NMR (75 MHz, D_2O): δ, 108.09, 99.90, 97.72, 99.98, 84.44, 81.88, 81.68, 81.57, 81.38, 80.64, 80.44, 76.78, 76.22, 72.96, 72.59, 66.27, 62.75, 62.72, 62.66, 61.42, 38.29, 26.59 ppm; MALDI HR-MS calc. for $C_{23}H_{41}NNaO_{17}$ $[M + Na]^+$: 626.2272, found 626.2265.

***N*-Biotinyl-3-aminopropyl α-L-arabinofuranosyl-(1→3)-β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranoside (29).** Compound **27** (5 mg, 8.2 μmol) was dissolved

in PBS buffer pH 7.4 (0.5 mL) and NHS-Biotin (2.8 mg, 8.2 μmol) in PBS buffer pH 7.4 (0.2 mL) was added. The resulting mixture was stirred for 2 h at room temperature. The mixture was directly transferred to a reverse phase C-18 column and purified by eluting with 0–10% MeOH–H_2O. The appropriate fractions were collected and concentrated *in vacuo* to afford **29** (5.6 mg, 81%) as a white solid. Analytical data for **29**: ^{1}H NMR (500 MHz, D_2O): δ, 5.14 (d, 1H, J = 4.0 Hz), 5.09 (s, 1H), 5.07 (d, 1H, J = 5.0 Hz), 5.05 (d, 1H, J = 4.5 Hz), 4.50 (m, 1H), 4.32 (dd, 1H, J = 4.5 Hz), 4.24–4.16 (m, 4H), 4.08–4.03 (m, 3H), 3.95–3.92 (m, 2H), 3.87 (m, 1H), 3.84–3.79 (m, 3H), 3.73–3.57 (m, 8H), 3.51 (dd, 1H, J = 7.0 Hz and 12.0 Hz), 3.43 (m, 1H), 3.26–3.18 (m, 3H), 3.10 (dd, 1H, J = 6.5 Hz), 2.89 (dd, 1H, J = 5.0 Hz), 2.68 (dd, 1H, J = 7.0 Hz), 2.16 (dd, 1H, J = 7.0 Hz), 2.10 (dd, 1H, J = 7.5 Hz), 1.71 (dd, 1H, J = 7.0 Hz), 1.68–1.44 (m, 5H), 1.30 (m, 2H) ppm; ^{13}C NMR (HSQC, 125 MHz, D_2O): δ, 108.96, 99.83, 98.15, 99.50 (four anomeric carbons) ppm; MALDI HR-MS calc. for $C_{33}H_{55}N_3NaO_{20}S$ $[M + Na]^+$: 868.2998, found 868.4810.

***N*-Biotinyl-3-aminopropyl β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranosyl-(1→2)-β-L-arabinofuranoside (30).** To a solution of **23** (70 mg, 70.2 μmol) in MeOH–H_2O–HOAc (3 mL/1 mL/1 mL) was added 10% Pd–C (14 mg). The reaction mixture was stirred under an atmosphere of H_2 for 15 h. The catalyst was then filtered-off, washed with methanol and H_2O, and the filtrate was concentrated under reduced pressure. The residue was passed through a small amount of latrobeads and slowly eluted with H_2O. Fractions containing the product were collected and concentrated *in vacuo* to afford the fully deprotected trisaccharide **28** (23.5 mg, 79%). MALDI HR-MS calc. for $C_{18}H_{33}NNaO_{13}$ $[M + Na]^+$: 494.1850, found 494.1854. The fully deprotected trisaccharide (5 mg, 10.6 μmol) was dissolved in PBS buffer pH 7.4 (0.5 mL), and NHS-Biotin (3.6 mg, 10.6 μmol) in PBS buffer pH 7.4 (0.2 mL) was added. The resulting mixture was stirred for 2 h at room temperature. The mixture was directly transferred to a reverse phase C-18 column and purified by eluting with 0–10% MeOH–H_2O. The appropriate fractions were collected and concentrated *in vacuo* to afford **30** (6.7 mg, 89%) as a white solid. Analytical data for **30**: ^{1}H NMR (500 MHz, D_2O): δ, 5.12 (d, 1H, J = 4.5 Hz), 5.04 (d, 1H, J = 4.5 Hz), 5.02 (d, 1H, J = 3.0 Hz), 4.48 (dd, 1H, J = 5.0 Hz and 8.0 Hz), 4.30 (dd, 1H, J = 4.5 Hz and 8.0 Hz), 4.20–4.13 (m, 3H), 4.05–3.99 (m, 3H), 3.86 (m, 1H), 3.80 (m, 2H), 3.72–3.66 (m, 4H), 3.66–3.57 (m, 3H), 3.50 (dd, 1H, J = 7.5 Hz and 12.5 Hz), 3.42 (m, 1H), 3.22 (m, 1H), 3.18 (m, 1H), 3.10 (dd, 1H, J = 6.5 Hz), 2.89–2.86 (m, 3H), 2.68–2.62 (m, 2H), 2.14 (m, 2H), 1.69 (m, 2H), 1.62–1.45 (m, 6H), 1.31 (m, 2H) ppm; ^{13}C NMR (HSQC, 125 MHz, D_2O): δ, 100.51, 99.51, 98.48 (three anomeric carbons) ppm; MALDI HR-MS calc. for $C_{28}H_{47}N_3O_{16}S$ $[M + Na]^+$: 736.2575, found 736.2582.

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