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Oligosaccharide Synthesis

Expedient Synthesis of a Linear Nonadecaarabinofuranoside of the *Mycobacterium tuberculosis* Cellular Envelope

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Abstract: The synthesis of oligosaccharides is demanding as it requires multiple steps and long reaction sequences. The choice of glycosylation method and protecting groups is very important for the successful synthesis of any oligosaccharide. In this paper, we show that ethynylcyclohexyl carbonate glycosyl donors are excellent for the synthesis of a nonadecasaccharide fragment of the *Mycobacterium tuberculosis* glycocalyx using a split/react/couple strategy. The synthesis of the target nonadecasaccharide was accomplished using eight different reactions and 23 steps in 6.4 % overall yield.

Introduction

Infection by multidrug-resistant (MDR) and extremely drug-resistant (XDR) strains of *Mycobacterium tuberculosis* has resulted in an increase in worldwide mortality due to tuberculosis, and this has led to a growing socioeconomic burden.[1–4] Patients suffering from tuberculosis have to undergo chemotherapy for a long period of time; this has been attributed to the diminished passage of chemotherapeutic agents due to a thick and waxy cellular envelope.[5] Lipoarabinomannan (LAM) and arabinogalactan (AG) are the two major structural constituents of the cell wall of *M. tuberculosis*, and arabinan is the common motif in both of these.[6–9] These structural motifs are currently attracting unprecedented attention for the development of drugs, vaccines, and diagnostics owing to the xenobiotic status of the saccharide components: arabinose and galactose are in the furanosyl form.[10] Mycobacterial arabinan biosynthesis is arrested in the presence of ethambutol, and so this is prescribed as a drug in combination with others.[11] Mycobacterial arabinan contains α-Araf-(1→5)-α-Araf, α-Araf-(1→3)-α-Araf and β-Araf-(1→2)-α-Araf linkages; α-Araf-(1→5)-α-Araf linkages are predominant, and terminal α-Araf residues are capped with β-Araf-(1→2) linkages.[12–14] In addition, terminal β-Araf-(1→2) residues are further esterified with mycolic acid. The synthesis of arabinan oligosaccharides has received considerable attention due to their immense significance in disease management. Several groups have attempted the synthesis of arabinan motifs;[15–20] a large oligoarabinan with 22 Araf units,[21,22] a henicosasaccharide[23] fragment of AG, and a much larger fragment with 92 saccharide residues[24] have been reported (Figure 1).

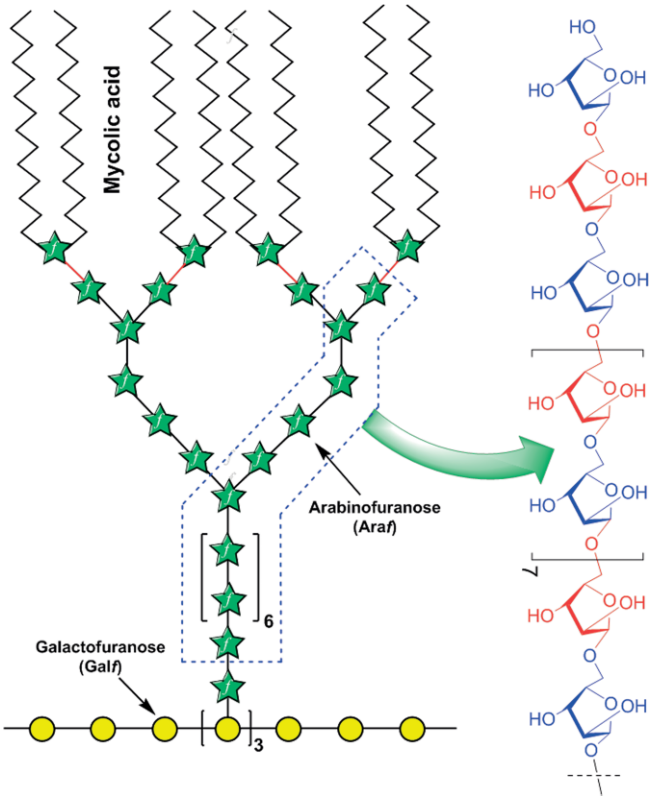

Figure 1. Cartoon representation of arabinogalactan (AG) of the *M. tuberculosis* cell wall, and the target molecule.

Results and Discussion

In this paper, we describe the synthesis of a nonadecaarabinofuranoside with α-Araf(1→5)-Araf linkages, as found in the arabinogalactan of *M. tuberculosis*, using gold-catalysed glycosylations.[25–29] We planned to synthesize the nonadecasaccharide by a split/react/couple strategy in which the glycosyl donor and the acceptor can both be synthesized from the same precursor. The precursor saccharide is *split* into two portions; these then

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react individually with appropriate reagents to synthesize a glycosyl donor and acceptor; and finally these are *coupled* (or glycosylated) to give the saccharide of interest. This is a powerful approach since it significantly decreases the number of steps required for the preparation of the donor and acceptor, and makes the overall synthesis more convergent.

The glycosylation approach that we have used in this synthesis was reported recently by us. In this approach, alkynyl glycosyl carbonates are activated in the presence of Au/Ag catalysts.[29] The salient features of this protocol are the stable glycosyl donors, consistently high yields, mild reaction conditions, and catalytic activation; the approach is also compatible with many of the functional groups found in carbohydrate chemistry.[29]

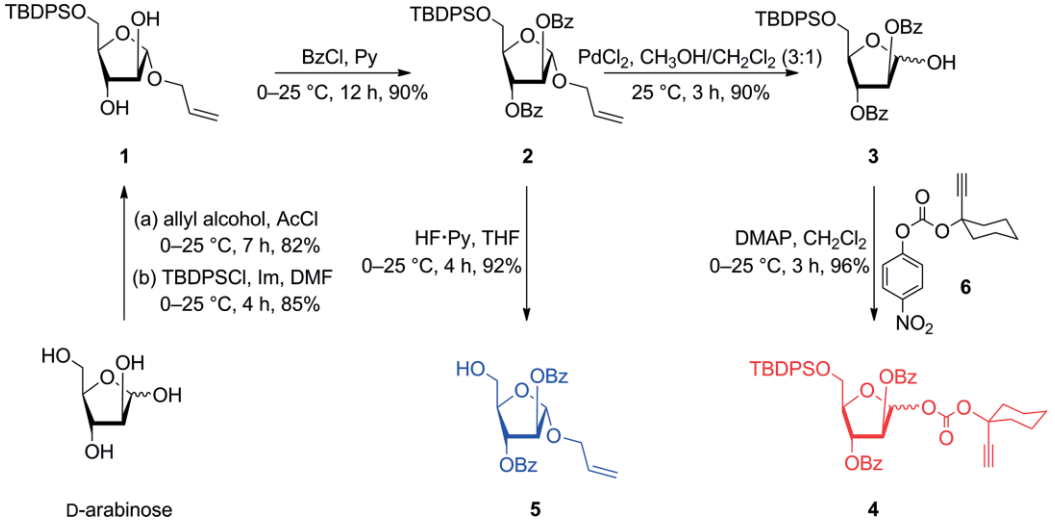
Our exploration started with the synthesis of key arabinofuranoside derivative **1**. D-Arabinose was first locked into the furanosyl form through glycosylation under acidic conditions using allyl alcohol and a catalytic amount of acetyl chloride. This gave an allyl furanoside, which was subsequently protected at the C-5 position using TBDPS-Cl (*tert*-butyldiphenylsilyl chloride) and imidazole at room temperature. The remaining secondary hydroxy groups were converted into benzoates by treatment with BzCl in pyridine. Having obtained the key substrate, compound **2** was *split* into two portions. The first portion was treated with $PdCl_2$ in CH_3OH/CH_2Cl_2 (3:1) to give hemiacetal **3** in 90 % yield. This was then treated with carbonate **6** and DMAP [4-(dimethylamino)pyridine] to give glycosyl donor **4** in 96 % yield. For the second portion of compound **2**, cleavage of the TBDPS ether was carried out with HF·py to give glycosyl acceptor **5** in 92 % yield (Scheme 1).

The successful synthesis of glycosyl donor **4** and acceptor **5** encouraged us to go ahead with the *coupling* (or glycosylation). Furanosylation between donor **4** and acceptor **5** was successfully carried out in the presence of gold phosphite **7** (8 mol-%) and AgOTf (8 mol-%) in CH_2Cl_2 for 15 min to give the disaccharide **8** in excellent yield.

Continuing our split/react/couple strategy, disaccharide **8** was split into two portions. The first portion was converted into glycosyl donor **10** by Pd-mediated hydrolysis of allyl glycoside followed by conversion into the alkynyl carbonate using reagent **6** as described above. The second portion was treated with HF·py to give the required acceptor **9** in very good yield. Glycosylation between donor **10** and acceptor **9** gave tetraarabinofuranoside **11** in 94 % yield. This was subsequently transformed into acceptor **12** (Scheme 2).

Tetrasaccharide **12** and donor **10** were treated with Au phosphite **7** (8 mol-%) and AgOTf (8 mol-%) in CH_2Cl_2 to give hexasaccharide **13** in 92 % yield (Scheme 3). The formation of the hexasaccharide was confirmed by thorough NMR spectroscopic analysis and mass spectrometry. In the ^1H NMR spectrum, resonances due to the vinylic C*H* moiety can be seen at δ = 5.93 (dddd, J = 16.5, 10.6, 5.9, 5.1 Hz, 1 H) ppm, and the protons of the *tert*-butyl group of the TBDPS group resonate at δ = 1.01 (s, 9 H) ppm. Six anomeric protons of hexasaccharide **13** were identified by six individual singlets at δ = 5.27, 5.35, 5.39, 5.39, 5.40, and 5.41 ppm, and other resonances were also in complete agreement with the structure of hexasaccharide **13**. In the ^{13}C NMR spectrum of compound **13**, resonances due to the six anomeric carbon atoms can be seen at δ = 104.9, 105.8, 105.9, 105.9, 106.0, and 106.0 ppm; the vinylic carbon atoms resonate at δ = 117.5 (CH_2) and 133.8 (*C*H) ppm; twelve signals due to the twelve carbonyl carbon atoms of the benzoate groups can be seen from δ = 165.2 to 165.8 ppm. In addition, the structure of hexasaccharide **13** was further confirmed by HRMS (calcd. for $C_{133}H_{120}O_{37}SiNa$ 2360.7209; found 2360.7206).[30]

In continuation, hexasaccharide **13** was again split into two portions; the first portion was converted into alkynyl glycosyl carbonate donor **14**, and the second portion was transformed into glycosyl acceptor **15** by treatment with HF·py. Hexasaccharide donor **14** and hexasaccharide acceptor **15** were subjected to standard Au/Ag-catalysed furanosylation conditions to give dodecasaccharide **16** in 96 % yield. Cleavage of the silyl ether of dodecasaccharide **16** gave glycosyl acceptor **17**. This was then subjected to glycosylation with hexasaccharide donor **14** to give octadecaarabinofuranoside **18**. For the synthesis of the nonadecaarabinofuranoside, one more arabinofuranoside



Scheme 1. Synthesis of the monosaccharide units.

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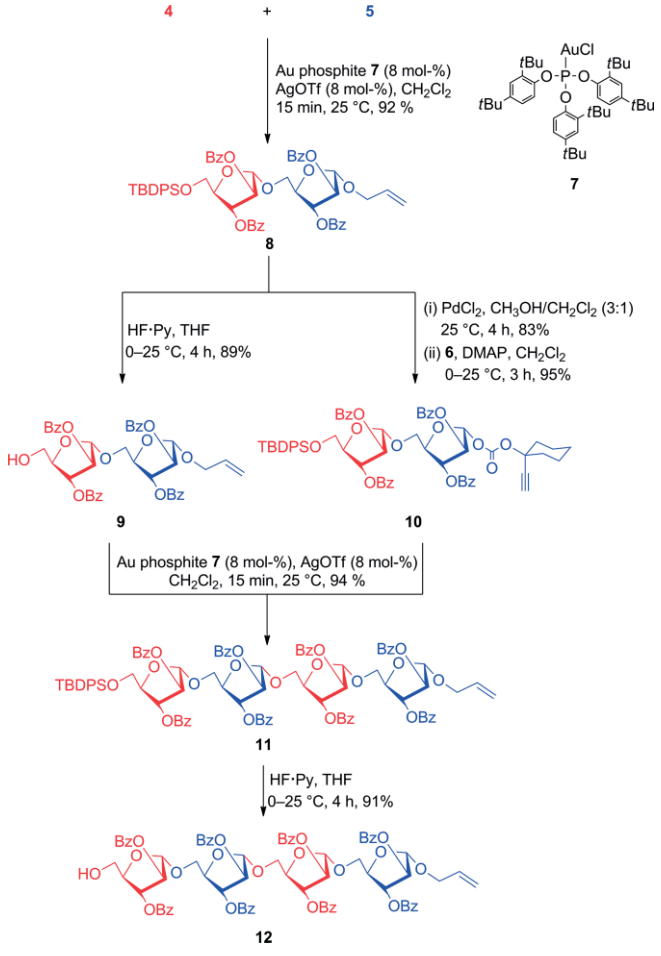
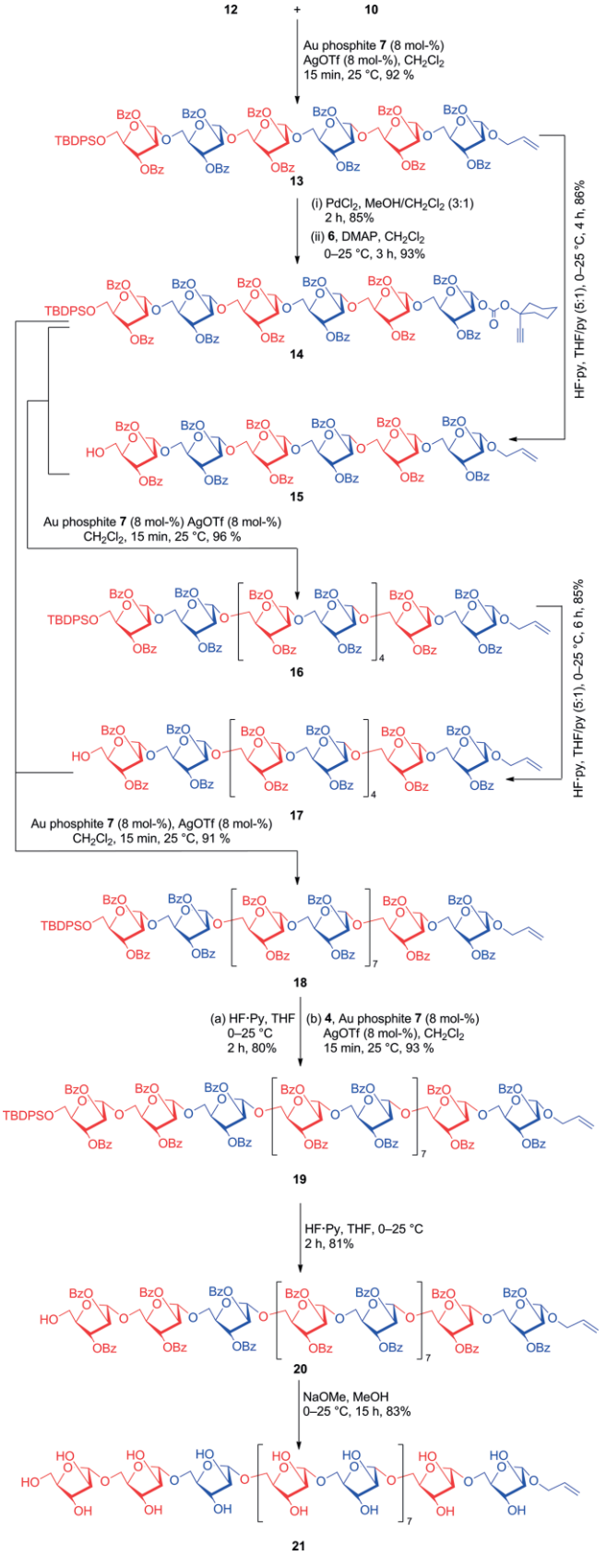


Scheme 2. Synthesis of the tetrasaccharide.



Scheme 3. Synthesis of the nonadecaarabinofuranoside.

had to be added at the nonreducing end of compound **18**. Hence, fluoride-mediated cleavage of the silyl ether followed by the glycosylation using donor **4** gave the desired nonadecasaccharide **19**. The structure of nonadecasaccharide **19** was thoroughly confirmed by NMR spectroscopy and mass spectrometry. In the ^{1}H NMR spectrum of nonadecasaccharide **19**, resonances due to anomeric protons were identified at $\delta \approx$ 5.41–5.48 ppm, and the presence of the allyl moiety was demonstrated by the olefinic C*H* signal at δ = 6.01 (dddd, J = 16.5, 10.7, 5.8, 5.2 Hz, 1 H) ppm. Furthermore, the ^{13}C NMR spectrum of compound **19** showed signals of all the anomeric carbon atoms at $\delta \approx$ 104.8–106.0 ppm. Additional confirmation was obtained by MS studies (calcd. for $C_{380}H_{328}O_{115}SiNa$ 6784.9619; found 6784.8623).

Cleavage of the silyl ether gave polysaccharide **20**, and saponification under Zemplén conditions gave the fully deprotected allyl nonadecaarabinofuranoside **21** in 67 % over two steps as a fluffy white powder. The global deprotection was confirmed by the complete disappearance of signals in both aliphatic and aromatic regions of the NMR spectra of **21**. The anomeric signals of nonadecasaccharide **21** were identified at δ = 5.07–5.09 ppm in the ^{1}H NMR spectrum and at δ = 107.1–108.0 ppm in the ^{13}C NMR spectrum. Furthermore, the sodium adduct of nonadecasaccharide **21** was observed at m/z = 2590.1692 (calcd. for $C_{98}H_{158}O_{77}Na$ 2590.8379).[30]

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Conclusions

We have described the total synthesis of a linear nonadecaarabinofuranoside fragment of the mycobacterial cell-wall component arabinogalactan. Key features of our strategy were the preparation of the glycosyl donor and acceptor from the same precursor, and repetition of this approach, resulting in a highly convergent synthesis. The strategy implemented in this synthesis is quite general, and can be invoked for the facile synthesis of other linear and branched oligosaccharides. Biophysical experiments are currently underway, and the results will be reported in due course.

Experimental Section

General Methods: Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. 1-Ethynylcyclohexanol, *p*-nitrophenyl chloroformate, and all metal salts were purchased from Sigma–Aldrich. Unless otherwise noted, all reactions were carried out under nitrogen. Removal of solvents in vacuo refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was carried out on precoated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. Optical rotations were measured with a digital polarimeter. IR spectra were recorded with an FTIR spectrometer. Unless otherwise noted, NMR spectra were recorded with a 400, 500, or 600 MHz instrument with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. High-resolution mass spectrometry (HRMS) was carried out with an ESI-MS or MALDI-TOF mass spectrometer. Low-resolution mass spectra (LRMS) were obtained with a UPLC-MS instrument with a TLC interface.

General Procedures

Allyl 5-*O*-*tert*-Butyldiphenylsilyl-α-D-arabinofuranoside (1): Allyl alcohol (100 mL) was cooled to 0 °C, and acetyl chloride (2.5 mL) was added. The mixture was stirred for 1 h; then D-arabinose (10.0 g, 66.6 mmol) was added. The mixture was stirred at 25 °C for a further 1 h, and then it was stirred at 80 °C for a further 5 h. The product was purified by column chromatography (acetone/CH_2Cl_2, 6:4) to give allyl α-D-arabinofuranoside (10.39 g, 82 %) as an off-white solid. Allyl α-D-arabinofuranoside (5.00 g, 26.29 mmol) was dissolved in DMF (30 mL), and imidazole (5.37 g, 78.87 mmol) was added at 25 °C. The mixture was cooled to 0 °C, and TBDPSCl (8.20 mL, 8.67 g, 31.55 mmol) was added dropwise. The reaction mixture was then stirred at 25 °C. After 4 h, the mixture was diluted with water and extracted with ethyl acetate (3 × 50 mL). The combined ethyl acetate layers were washed with brine. The organic layer was filtered, and the filtrate was concentrated in vacuo. The oily residue was purified by silica gel column chromatography using ethyl acetate and petroleum ether as the mobile phase to give compound **1** (9.58 g, 85 %).

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (2): Compound **1** (8.00 g, 18.67 mmol) was dissolved in pyridine (50 mL), and the solution was cooled to 0 °C. Benzoyl chloride (5.42 mL, 6.56 g, 46.66 mmol) was added dropwise, and then the reaction mixture was warmed to 25 °C and stirred for 12 h. The progress of the reaction and formation of compound **2** were checked by TLC. The reaction mixture was diluted with HCl (5 N aq.; 100 mL), CH_2Cl_2 (100 mL) and washed with water, satd. aq. sodium hydrogen carbonate solution, and brine. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude residue was purified by silica gel column chromatography to give compound **2** (8.70 g, 90 %).

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α/β-D-arabinofuranose (3): Compound **2** (5.00 g, 7.85 mmol) was dissolved in a mixture of CH_3OH/CH_2Cl_2 (3:1; 30 mL), and a solution of $PdCl_2$ (278.5 mg, 1.57 mmol) in CH_3OH (5 mL) was added dropwise. The mixture was stirred at 25 °C. After 3 h, the reaction was quenched by the addition of excess triethylamine, and the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether as mobile phase to give compound **3** (4.22 g, 90 %) as a pale yellow solid.

The same procedure was also used in the synthesis of compounds **10** and **14**.

Synthesis of Donors 4, 10, and 14: DMAP (1.23 g, 10.05 mmol) was added to a solution of hemiacetal **3** (5.0 g, 8.38 mmol) in anhydrous CH_2Cl_2 (40 mL), and the mixture was stirred for 20 min. Reagent **6**[29] (2.91 g, 10.05 mmol) was added portionwise (3 ×) after every 30 min, and the mixture was then stirred at 25 °C for 1 h. The mixture was concentrated in vacuo, and the oily residue was partially purified by silica gel column chromatography (*n*-hexane/EtOAc). Fractions containing compound **4** along with trace amounts of 4-nitrophenol were concentrated under reduced pressure. The crude residue was dissolved in CH_2Cl_2 (30 mL), and this solution was washed with satd. aq. $NaHCO_3$ (20 mL) to remove the 4-nitrophenol. This gave alkynyl arabinofuranosyl donor **4** (6.00 g, 96 %) as a fluffy white solid.

The same procedure was also used for the synthesis of alkynyl carbonate donors **10** and **14**.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranoside (5): Silyl ether **2** (7.0 g, 10.99 mmol) was dissolved in a mixture of THF and pyridine (5:1; 50 mL), and HF•Py (2.0 mL) was added at 0 °C. The reaction mixture was then stirred at 25 °C. After 4 h, the mixture was cooled to 0 °C, and silica gel (15 g) was added. Filter column chromatography was carried out. Compound-containing fractions were concentrated under reduced pressure. The resulting residue was then dissolved in CH_2Cl_2 (40 mL), and the solution was washed with HCl (1 N aq.; 20 mL), satd. aq. $NaHCO_3$ (20 mL), and brine (20 mL). The CH_2Cl_2 layer was dried with anhydrous Na_2SO_4, decanted, and concentrated in vacuo to give compound **5** (4.03 g, 92 %) as a viscous syrup.

The same procedure was also used for the synthesis of compounds **9**, **12**, **15**, **17**, and **20**.

Synthesis of Compounds 8, 11, 13, 16, 18, and 19: AgOTf (138 mg, 0.54 mmol) and gold phosphite **7** (471 mg, 0.54 mmol) were added to a solution of donor **5** (5.00 g, 6.69 mmol) and acceptor **4** (2.67 g, 6.69 mmol) in anhydrous CH_2Cl_2 (40 mL) containing powdered molecular sieves (4 Å; 400 mg). The mixture was stirred at 25 °C for 15 min; then it was concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to give disaccharide **8** (6.02 g, 92 %) as a viscous syrup.

Synthesis of Compound 21: Compound **20** (120 mg, 18.4 μmol) was dissolved in CH_3OH, and NaOMe (0.5 M solution in CH_3OH; 2 mL) was added. The reaction mixture was stirred at 25 °C. After 15 h, the mixture was neutralized with Amberlite IR 120 (H^+) resin, filtered, and concentrated under reduced pressure. The residue was washed with ethyl acetate (2 × 2 mL) and CH_3OH (2 × 2 mL) to give compound **21** (39 mg, 83 %).

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Compound Characterization Data

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (2): M.p. 62.7 °C. $[\alpha]_{25}^{D}$ = –14.6 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3068, 2928, 2858, 1727, 1599, 1456, 1268, 1108, 1066, 971, 932, 707 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 4.02 (d, *J* = 4.6 Hz, 2 H), 4.11 (ddt, *J* = 13.1, 6.0, 1.3 Hz, 1 H), 4.29 (ddt, *J* = 13.2, 5.0, 1.5 Hz, 1 H), 4.40 (q, *J* = 4.6 Hz, 1 H), 5.22 (dq, *J* = 10.5, 1.3 Hz, 1 H), 5.27 (s, 1 H), 5.37 (dq, *J* = 17.2, 1.7 Hz, 1 H), 5.49 (d, *J* = 1.5 Hz, 1 H), 5.62 (d, *J* = 1.4 Hz, 1 H), 5.96 (dddd, *J* = 16.5, 10.6, 5.9, 5.1 Hz, 1 H), 7.31–7.41 (m, 8 H), 7.43–7.47 (m, 2 H), 7.54–7.60 (m, 2 H), 7.70–7.73 (m, 4 H), 7.98–8.00 (m, 2 H), 8.05–8.07 (m, 2 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 26.8, 26.8, 26.9, 63.7, 67.9, 77.5, 82.6, 83.1, 105.0, 117.4, 127.7, 127.7, 127.7, 127.7, 128.4, 128.4, 128.4, 128.4, 129.3, 129.5, 129.7, 129.7, 130.0, 130.0, 130.0, 130.0, 133.3, 133.4, 133.4, 133.4, 134.0, 135.7, 135.7, 135.7, 135.7, 165.5, 165.7 ppm. HRMS (ESI-MS): calcd. for $[C_{38}H_{40}O_7SiNa]^+$ 659.2441; found 659.2439.

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α/β-D-arabinofuranose (3): α/β = 1:1.1. Syrup. $[\alpha]_{25}^{D}$ = –41.1 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3012, 2935, 2860, 1728, 1603, 1455, 1366, 1268, 1107, 952, 704 cm^{-1}. ^1H NMR (399.78 MHz, $CDCl_3$): δ = 1.03 (s, 9 H), 1.10 (s, 9 H), 3.42 (d, *J* = 4.1 Hz, 1 H), 3.91 (dd, *J* = 11.1, 2.5 Hz, 1 H), 3.97 (dd, *J* = 4.6, 1.2 Hz, 2 H), 4.06 (dd, *J* = 11.1, 3.0 Hz, 1 H), 4.22–4.27 (q, *J* = 4.6 Hz, 1 H), 4.38 (d, *J* = 10.5 Hz, 1 H), 4.56 (q, *J* = 4.6 Hz, 1 H), 5.47 (d, *J* = 1.7 Hz, 1 H), 5.55 (dd, *J* = 5.6, 4.9 Hz, 1 H), 5.60 (d, *J* = 3.7 Hz, 1 H), 5.64 (dd, *J* = 4.8, 1.5 Hz, 1 H), 5.71 (dd, *J* = 10.5, 4.8 Hz, 1 H), 6.02 (dd, *J* = 5.7, 4.1 Hz, 1 H), 7.27–7.46 (m, 20 H), 7.48–7.59 (m, 4 H), 7.68–7.71 (m, 6 H), 7.78–7.80 (m 2 H), 7.94–7.97 (m, 2 H), 7.99–8.10 (m, 6 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.5, 19.5, 26.9, 27.0, 27.0, 27.0, 27.1, 27.1, 63.8, 65.2, 76.6, 77.7, 79.5, 82.8, 83.1, 83.6, 95.6, 101.3, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 128.2, 128.2, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 129.3, 129.3, 129.4, 129.5, 129.9, 129.9, 130.0, 130.0, 130.1, 130.1, 130.1, 130.2, 130.3, 130.4, 131.9, 132.2, 133.3, 133.4, 133.6, 133.6, 133.6, 133.6, 133.7, 133.7, 135.7, 135.7, 135.8, 135.8, 135.8, 135.9, 136.1, 136.1, 165.8, 165.8, 166.0, 166.3 ppm. HRMS (ESI-MS): calcd. for$[C_{35}H_{36}O_7SiNa]^+$ 619.2128; found 619.2126.

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-1-*O*-{[(1-ethynylcyclohexyl)oxy]carbonyl}-D-arabinofuranose (4): α/β = 2:1. M.p. 51.4 °C. $[\alpha]_{25}^{D}$ = –21.0 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2929, 2857, 1762, 1729, 1598, 1454, 1240, 1108, 1071, 1018, 945, 910, 849, 707 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.03 (s, 9 H), 1.04 (s, 9 H), 1.29–1.40 (m, 3 H), 1.45–1.48 (m, 1 H), 1.49–1.60 (m, 3 H), 1.61–1.73 (m, 6 H), 1.89–1.97 (m, 3 H), 1.98–2.24 (m, 4 H), 2.37 (s, 1 H), 2.65 (s, 1 H), 3.93–4.02 (m, 4 H), 4.34 (q, *J* = 5.6 Hz, 1 H), 4.58 (q, *J* = 4.6 Hz, 1 H), 5.67 (d, *J* = 1.5 Hz, 1 H), 5.73–5.76 (m, 2 H), 6.11 (dd, *J* = 7.2, 6.1 Hz, 1 H), 6.32 (s, 1 H), 6.47 (d, *J* = 4.6 Hz, 1 H), 7.31–7.48 (m, 20 H), 7.53–7.71 (m, 12 H), 7.94–8.12 (m, 8 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.3, 19.4, 22.4, 22.4, 22.6, 22.6, 25.0, 25.1, 26.8, 26.8, 26.8, 26.9, 26.9, 26.9, 36.6, 36.8, 36.8, 36.9, 63.2, 64.7, 74.7, 75.4, 76.6, 76.8, 78.0, 78.4, 81.5, 82.2, 82.6, 82.7, 85.5, 85.5, 97.1, 102.6, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.9, 129.1, 129.3, 129.4, 129.8, 129.8, 129.8, 129.8, 130.0, 130.1, 130.1, 130.1, 130.1, 130.1, 130.1, 130.3, 133.1, 133.1, 133.2, 133.2, 133.4, 133.5, 133.5, 133.6, 135.7, 135.7, 135.7, 135.7, 135.8, 135.8, 135.8, 135.8, 151.1, 151.1, 165.2, 165.5, 165.5, 165.6 ppm. HRMS (ESI-MS): calcd. for $[C_{44}H_{46}O_9\ SiNa]^+$ 769.2809; found 769.2805.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranoside (5): Syrup. $[\alpha]_{25}^{D}$ = –29.5 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3489, 3068, 2927, 1723, 1603, 1453, 1268, 1110, 1067, 1033, 982, 712 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 2.70 (s, 1 H), 3.97–4.08 (m, 2 H), 4.13 (ddt, *J* = 13.1, 5.9, 1.4 Hz, 1 H), 4.31 (ddt, *J* = 13.1, 4.9, 1.6 Hz, 1 H), 4.38 (q, *J* = 4.0 Hz, 1 H), 5.24 (dq, *J* = 10.4, 1.5 Hz, 1 H), 5.32 (s, 1 H), 5.39 (dq, *J* = 17.2, 1.7 Hz, 1 H), 5.49 (dd, *J* = 5.0, 1.4 Hz, 1 H), 5.59 (d, *J* = 1.4 Hz, 1 H), 5.97 (dddd, *J* = 16.4, 10.5, 5.9, 5.1 Hz, 1 H), 7.45 (m, 4 H), 7.55–7.62 (m, 2 H), 8.08 (m, 4 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.3, 67.9, 77.8, 82.0, 83.8, 104.8, 117.4, 128.5, 128.5, 128.5, 128.5, 129.1, 129.2, 129.9, 129.9, 129.9, 129.9, 133.5, 133.6, 133.7, 165.4, 166.2 ppm. HRMS (ESI-MS): calcd. for $[C_{22}H_{22}O_7Na]^+$ 421.1263; found 421.1260.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (8): Syrup. $[\alpha]_{25}^{D}$ = –7.23 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3068, 2930, 2860, 1724, 1600, 1454, 1356, 1266, 1106, 1065, 1027, 968, 707 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 3.96 (dd, *J* = 11.2, 2.9 Hz, 2 H), 4.01 (dd, *J* = 4.4, 1.3 Hz, 1 H), 4.09 (ddt, *J* = 13.2, 4.9, 1.4 Hz, 1 H), 4.23 (dd, *J* = 11.2, 4.6 Hz, 1 H), 4.31 (ddt, *J* = 13.2, 4.9, 1.4 Hz, 1 H), 4.54 (m, 2 H), 5.22 (dd, *J* = 10.5, 1.3 Hz, 1 H), 5.30 (s, 1 H), 5.37 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.41 (s, 1 H), 5.58 (d, *J* = 1.1 Hz, 1 H), 5.60 (d, *J* = 1.1 Hz, 1 H), 5.66 (t, *J* = 4.9 Hz, 2 H), 5.96 (dddd, *J* = 16.4, 10.6, 5.9, 5.0 Hz, 1 H), 7.28–7.40 (m, 11 H), 7.40–7.52 (m, 5 H), 7.57 (m, 2 H), 7.69–7.75 (m, 4 H), 7.92–7.97 (m, 2 H), 7.97–8.03 (m, 4 H), 8.05–8.11 (m, 2 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 26.9, 26.9, 26.9, 63.5, 66.2, 67.9, 77.5, 77.5, 82.0, 82.0, 82.3, 83.3, 105.0, 106.1, 117.5, 127.8, 127.8, 127.8, 127.8, 128.3, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 129.1, 129.4, 129.4, 129.4, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.1, 130.1, 133.2, 133.3, 133.4, 133.4, 133.5, 133.5, 133.9, 135.8, 135.8, 135.8, 135.8, 165.4, 165.5, 165.6, 165.8 ppm. HRMS (ESI-MS): calcd. for $[C_{57}H_{56}O_{13}SiNa]^+$ 999.3388; found 999.3389.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (9): M.p. 120.2 °C. $[\alpha]_{25}^{D}$ = –20.4 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3524, 3067, 2929, 1718, 1602, 1490, 1453, 1257, 1176, 1106, 1066, 1027, 969, 712 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 2.37 (s, 1 H), 3.91 (dd, *J* = 11.2, 2.9 Hz, 2 H), 3.96 (dd, *J* = 13.1, 5.9 Hz, 1 H), 4.02 (dd, *J* = 13.1, 5.9 Hz, 1 H), 4.14 (dd, *J* = 11.2, 4.5 Hz, 1 H), 4.21 (dd, *J* = 13.1, 4.8 Hz, 1 H), 4.38–4.47 (m, 2 H), 5.13 (d, *J* = 10.4 Hz, 1 H), 5.22 (s, 1 H), 5.28 (d, *J* = 11.2 Hz, 1 H), 5.35 (s, 1 H), 5.37 (d, *J* = 4.5 Hz, 1 H), 5.50 (s, 1 H), 5.57 (d, *J* = 5.1 Hz, 1 H), 5.59 (s, 1 H), 5.86 (dddd, *J* = 16.6, 10.4, 5.8, 5.1 Hz, 1 H), 7.21 (m, 2 H), 7.37 (m, 8 H), 7.50 (m, 2 H), 7.87 (m, 2 H), 7.97 (m, 6 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.2, 66.0, 67.7, 77.3, 77.7, 81.6, 81.8, 81.8, 83.7, 104.7, 105.7, 117.3, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.4, 128.9, 129.0, 129.1, 129.1, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.2, 133.3, 133.4, 133.4, 133.7, 165.0, 165.3, 165.7, 166.0 ppm. HRMS (ESI-MS): calcd. for $[C_{41}H_{38}O_{13}Na]^+$ 761.2210; found 761.2207.

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-*O*-{[(1-ethynylcyclohexyl)oxy]carbonyl}-α/β-D-arabinofuranose (10): α/β = 6:1. M.p. 69.8 °C. $[\alpha]_{25}^{D}$ = –6.0 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2935, 2860, 1760, 1725, 1599, 1453, 1265, 1175, 1106, 1067, 1022, 965, 824, 708 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.01 (s, 9 H), 1.04 (s, 9 H), 1.30–1.40 (m, 1 H), 1.43–1.47 (m, 1 H), 1.50–1.60 (m, 2 H), 1.59–1.79 (m, 8 H), 2.08 (m, 8 H), 2.35 (s, 1 H), 2.66 (s, 1 H), 3.91–4.06 (m, 6 H), 4.12–4.28 (m, 2 H), 4.49–4.72 (m, 4 H), 5.35–5.39 (m, 2 H), 5.55 (m, 2 H), 5.64–5.72 (m, 2 H), 5.74–5.75 (m, 3 H), 5.78–6.13 (m, 1 H), 6.25–6.90 (m, 2 H), 7.31–7.41 (m, 24 H), 7.42–7.50 (m, 7 H), 7.53–7.61 (m, 5 H), 7.69–7.65 (m, 8 H), 7.94–8.04 (m, 12 H), 8.09–8.19 (m, 4 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 19.4, 22.6, 22.6, 22.7, 22.7, 24.9, 25.1, 26.9, 26.9, 26.9, 26.9, 26.9, 27.0, 36.6, 36.6, 36.8, 36.9, 63.4, 63.5, 65.9, 67.7, 74.9, 75.2, 75.5, 76.3, 76.9, 77.2, 77.3, 77.4, 78.3, 78.5, 80.9, 81.0, 82.2, 82.6, 82.7, 83.4, 83.6, 84.4, 96.9,

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102.5, 106.0, 106.3, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.7, 128.7, 128.9, 129.0, 129.3, 129.3, 129.3, 129.3, 129.4, 129.6, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 130.1, 130.1, 130.1, 130.1, 130.1, 130.1, 130.1, 130.3, 130.3, 133.2, 133.3, 133.3, 133.3, 133.4, 133.4, 133.4, 133.4, 133.6, 133.6, 133.7, 133.7, 135.8, 135.8, 135.8, 135.8, 135.8, 135.8, 135.8, 135.8, 135.8, 151.1, 151.1, 165.2, 165.4, 165.4, 165.6, 165.6, 165.7, 165.7, 165.7 ppm. HRMS (ESI-MS): calcd. for $[C_{63}H_{62}O_{15}SiNa]^+$ 1109.3756; found 1109.3752.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (11): M.p. 65.2 °C. $[\alpha]_{25}^{D}$ = +6.3 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2927, 2858, 1723, 1601, 1454, 1426, 1265, 1176, 1107, 966, 707 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.09 (s, 9 H), 4.03 (m, 5 H), 4.12–4.19 (m, 1 H), 4.22–4.39 (m, 4 H), 4.57 (m, 2 H), 4.71 (m, 2 H), 5.26 (dd, *J* = 10.4, 1.4 Hz, 1 H), 5.35 (s, 1 H), 5.42 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.47 (s, 1 H), 5.49 (s, 1 H), 5.50 (s, 1 H), 5.65 (d, *J* = 1.1 Hz, 1 H), 5.66 (d, *J* = 1.1 Hz, 1 H), 5.69–5.77 (m, 6 H), 6.00 (dddd, *J* = 16.5, 10.6, 5.9, 5.1 Hz, 1 H), 7.28–7.51 (m, 25 H), 7.58 (m, 5 H), 7.77 (m, 4 H), 7.94–8.01 (m, 6 H), 8.02–8.07 (m, 4 H), 8.07–8.14 (m, 6 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.3, 26.8, 26.8, 26.8, 63.5, 65.9, 66.0, 66.0, 67.8, 77.3, 77.4, 77.4, 77.4, 81.6, 81.6, 82.0, 82.0, 82.2, 82.2, 82.2, 83.3, 104.9, 105.9, 106.0, 106.0, 117.4, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 129.1, 129.1, 129.2, 129.2, 129.2, 129.3, 129.3, 129.3, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 133.1, 133.2, 133.2, 133.2, 133.2, 133.3, 133.3, 133.4, 133.4, 133.4, 133.5, 133.8, 135.7, 135.7, 135.7, 135.7, 165.2, 165.2, 165.2, 165.4, 165.5, 165.6, 165.7, 165.7 ppm. HRMS (ESI-MS): calcd. for $[C_{95}H_{88}O_{25}SiNa]^+$ 1680.5315; found 1680.5317.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (12): M.p. 85.1 °C. $[\alpha]_{25}^{D}$ = +2.2 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3532, 3067, 2928, 2860, 1722, 1602, 1453, 1266, 1176, 1109, 1068, 1027, 966, 710 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 2.41 (s, 1 H), 3.98 (m, 5 H), 4.12 (ddt, *J* = 13.1, 5.9, 1.5 Hz, 1 H), 4.17–4.27 (m, 3 H), 4.31 (ddt, *J* = 13.1, 4.9, 1.6 Hz, 1 H), 4.50 (m, 2 H), 4.65 (m, 2 H), 5.23 (dd, *J* = 10.5, 1.4 Hz, 1 H), 5.31 (s, 1 H), 5.38 (dd, *J* = 17.2, 1.7 Hz, 1 H), 5.42–5.48 (m, 4 H), 5.59 (d, *J* = 1.4 Hz, 1 H), 5.61–5.72 (m, 6 H), 5.97 (dddd, *J* = 16.4, 10.5, 5.9, 5.1 Hz, 1 H), 7.22–7.33 (m, 6 H), 7.38–7.49 (m, 13 H), 7.50–7.63 (m, 5 H), 7.86–7.99 (m, 6 H), 8.00–8.13 (m, 10 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.3, 65.9, 65.9, 66.1, 67.8, 77.3, 77.3, 77.3, 77.7, 81.6, 81.6, 81.7, 81.9, 81.9, 82.0, 82.1, 83.7, 104.8, 105.8, 105.9, 105.9, 117.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 129.0, 129.0, 129.1, 129.1, 129.1, 129.1, 129.2, 129.3, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 133.2, 133.2, 133.3, 133.4, 133.4, 133.4, 133.4, 133.5, 133.8, 165.1, 165.2, 165.2, 165.4, 165.7, 165.7, 165.7, 166.1 ppm. HRMS (ESI-MS): calcd. for $[C_{79}H_{70}O_{25}Na]^+$ 1441.4104; found 1441.4098.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (13): M.p. 109.5 °C. $[\alpha]_{25}^{D}$ = +12.2 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2933, 2859, 1723, 1602, 1453, 1356, 1266, 1176, 1108, 1069, 1027, 966, 709 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.01 (s, 9 H), 3.88–3.95 (m, 5 H), 3.95–3.99 (m, 2 H), 4.08 (ddt, *J* = 13.3, 6.0, 1.3 Hz, 1 H), 4.19 (m, 5 H), 4.28 (ddt, *J* = 13.2, 4.9, 1.5 Hz, 1 H), 4.48 (m, 2 H), 4.61 (m, 4 H), 5.20 (dt, *J* = 10.4, 1.4 Hz, 1 H), 5.27 (s, 1 H), 5.34 (dt, *J* = 10.4, 1.4 Hz, 1 H), 5.35 (s, 1 H), 5.39 (s, 1 H), 5.39 (s, 1 H), 5.40 (s, 1 H), 5.41 (s, 1 H), 5.55–5.58 (m, 2 H), 5.65 (m, 10 H), 5.93 (dddd, *J* = 16.5, 10.6, 5.9, 5.1 Hz, 1 H), 7.18–7.46 (m, 36 H), 7.46–7.61 (m, 6 H), 7.64–7.75 (m, 4 H), 7.82–7.93 (m, 10 H), 7.95–7.98 (m, 4 H), 8.00–8.06 (m, 10 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 26.8, 26.8, 26.8, 63.4, 65.8, 65.9, 65.9, 65.9, 66.0, 67.8, 77.3, 77.3, 77.3, 77.3, 77.4, 77.4, 81.5, 81.6, 81.6, 81.6, 82.0, 82.0, 82.1, 82.2, 82.2, 82.2, 82.2, 83.2, 104.9, 105.8, 105.9, 105.9, 106.0, 106.0, 117.5, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 129.1, 129.1, 129.1, 129.1, 129.1, 129.1, 129.2, 129.2, 129.2, 129.3, 129.3, 129.3, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 133.1, 133.2, 133.2, 133.2, 133.2, 133.3, 133.3, 133.4, 133.4, 133.4, 133.5, 133.5, 133.5, 133.5, 133.8, 135.7, 135.7, 135.7, 135.7, 165.2, 165.2, 165.2, 165.2, 165.3, 165.5, 165.6, 165.6, 165.7, 165.7, 165.7, 165.8 ppm. HRMS (ESI-MS): calcd. for $[C_{133}H_{120}O_{37}SiNa]^+$ 2360.7209; found 2360.7206.

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-*O*-{[(1-ethynylcyclohexyl)oxy]carbonyl}-α-D-arabinofuranose (14): α/β = 4:1. M.p. 114.5 °C. $[\alpha]_{25}^{D}$ = +10.8 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 2936, 2858, 1760, 1725, 1601, 1453, 1269, 1176, 1110, 1069, 1028, 910, 709 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.10 (s, 9 H), 1.10 (s, 9 H), 1.26–1.43 (m, 2 H), 1.52–1.78 (m, 10 H), 1.99 (m, 4 H), 2.27 (m, 4 H), 2.51 (s, 1 H), 2.74 (s, 1 H), 4.05 (m, 14 H), 4.30 (m, 10 H), 4.46–4.82 (m, 12 H), 5.50 (m, 10 H), 5.64–5.80 (m, 21 H), 5.80–6.70 (m, 5 H), 7.26–7.41 (m, 34 H), 7.47 (m, 37 H), 7.52–7.65 (m, 13 H), 7.78 (m, 8 H), 7.97 (m, 19 H), 8.10 (m, 29 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 19.4, 22.6, 22.6, 22.6, 22.6, 24.8, 25.0, 26.8, 26.8, 26.9, 26.9, 26.9, 26.9, 36.6, 36.6, 36.8, 36.9, 63.5, 63.5, 65.8, 65.8, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 66.0, 66.0, 74.5, 75.3, 75.6, 76.2, 76.8, 77.2, 77.2, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.4, 77.4, 77.4, 78.3, 78.4, 80.7, 81.0, 81.6, 81.6, 81.6, 81.6, 81.9, 82.2, 82.2, 82.2, 82.2, 82.2, 82.3, 82.3, 82.6, 82.6, 83.3, 83.3, 83.3, 83.3, 84.4, 84.4, 96.6, 102.4, 105.7, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 106.1, 106.1, 106.1, 127.7–127.8 (12 C), 128.3 (16 C), 128.4 (6 C), 128.5 (4 C), 128.6 (16 C), 128.7 (6 C), 129.1 (10 C), 129.2 (6 C), 129.3 (8 C), 129.7 (4 C), 129.8 (20 C), 129.9 (16 C), 130.0 (6 C), 130.1, 130.2, 133.1 (2 C), 133.2 (8 C), 133.3 (3 C), 133.4 (7 C), 133.5 (3 C), 133.6 (2 C), 133.7 (3 C), 135.7, 135.7, 135.7, 135.7, 135.7, 135.7, 135.7, 135.7, 151.0, 151.1, 165.1 (3 C), 165.2 (9 C), 165.5 (3 C), 165.6 (4 C), 165.7 (4 C), 165.8 ppm. HRMS (ESI-MS): calcd. for $[C_{139}H_{126}O_{39}SiNa]^+$ 2470.7577; found 2470.7568.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (15): M.p. 123.2 °C. $[\alpha]_{25}^{D}$ = +13.3 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2931, 2857, 1721, 1602, 1490, 1453, 1259, 1176, 1106, 1069, 1026, 965, 709 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 2.60 (s, 1 H), 3.93–4.08 (m, 7 H), 4.14 (dd, *J* = 13.2, 5.9 Hz, 1 H), 4.18–4.40 (m, 6 H), 4.52 (q, *J* = 4.5 Hz, 2 H), 4.65–4.70 (m, 4 H), 5.24 (dd, *J* = 17.2, 1.6 Hz, 1 H),

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5.34 (s, 1 H), 5.40 (dd, J = 17.2, 1.6 Hz, 1 H), 5.46–5.48 (m, 6 H), 5.63 (d, J = 1.1 Hz, 1 H), 5.65–5.77 (m, 10 H), 5.98 (dddd, J = 16.6, 10.5, 5.9, 5.1 Hz, 1 H), 7.28 (m, 10 H), 7.44 (m, 20 H), 7.50–7.57 (m, 4 H), 7.59 (m, 2 H), 7.84–8.02 (m, 10 H), 8.08 (m, 14 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.3, 65.9, 65.9, 65.9, 65.9, 66.1, 67.8, 77.2, 77.3, 77.3, 77.3, 77.3, 77.7, 81.6, 81.6, 81.6, 81.6, 81.7, 82.0, 82.0, 82.1, 82.2, 82.2, 82.2, 83.8, 104.8, 105.8, 105.9, 105.9, 105.9, 105.9, 117.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 129.0, 129.0, 129.1, 129.1, 129.1, 129.1, 129.1, 129.1, 129.1, 129.1, 129.2, 129.3, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 133.2, 133.2, 133.2, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 133.5, 133.5, 133.5, 133.8, 165.1, 165.1, 165.2, 165.2, 165.2, 165.4, 165.6, 165.7, 165.7, 165.7, 165.7, 166.0 ppm. HRMS (ESI-MS): calcd. for $[C_{117}H_{102}O_{37}Na]^+$ 2122.6031; found 2122.6033.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (16): M.p. 125.6 °C. $[\alpha]^D_{25}$ = +15.9 (c = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3066, 2926, 2860, 1723, 1602, 1453, 1267, 1176, 1109, 1070, 1027, 966, 709 cm^{-1}. ^{1}H NMR (400.31 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 3.92–4.01 (m, 13 H), 4.05–4.34 (m, 14 H), 4.47–4.66 (m, 12 H), 5.22 (d, J = 10.5 Hz, 1 H), 5.30 (s, 1 H), 5.33–5.48 (m, 12 H), 5.56–5.62 (m, 2 H), 5.65–5.70 (m, 21 H), 5.95 (dddd, J = 16.5, 10.4, 5.9, 4.9 Hz, 1 H), 7.21–7.29 (m, 21 H), 7.32–7.46 (m, 45 H), 7.45–7.61 (m, 12 H), 7.70–7.73 (m, 4 H), 7.87–7.94 (m, 22 H), 7.99–8.07 (m, 26 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.4, 26.9, 26.9, 26.9, 63.5, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 66.0, 66.0, 66.0, 67.9, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.4, 77.4, 77.4, 77.5, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.7, 81.7, 81.7, 82.0, 82.1, 82.2, 82.2, 82.2, 82.2, 82.2, 82.2, 82.2, 82.2, 82.2, 82.2, 82.3, 83.3, 104.9, 105.9, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 106.1, 106.1, 117.5, 127.8, 127.8, 127.8, 127.8, 128.4 (20 C), 128.5 (4 C), 128.6 (24 C), 129.1 (10 C), 129.2 (12 C), 129.4 (2 C), 129.8 (2 C), 129.9 (32 C), 130.0 (14 C), 130.1 (2 C), 133.2–133.3 (12 C), 133.4–133.5 (14 C), 133.9, 135.8, 135.8, 135.8, 135.8, 165.2 (9 C), 165.3 (2 C), 165.5, 165.6, 165.7 (10 C), 165.8 ppm. HRMS (MALDI-TOF): calcd. for $[C_{247}H_{216}O_{73}SiNa]^+$ 4402.2924; found 4402.4847.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (17): M.p. 137.0 °C. $[\alpha]^D_{25}$ = +18.1 (c = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3066, 2927, 2856, 1722, 1602, 1453, 1176, 1108, 1070, 1027, 965, 710 cm^{-1}. ^{1}H NMR (400.31 MHz, $CDCl_3$): δ = 2.44 (s, 1 H), 3.89–4.07 (m, 13 H), 4.10–4.27 (m, 12 H), 4.32 (dd, J = 13.2, 4.9 Hz, 1 H), 4.51 (m, 2 H), 4.56–4.70 (m, 10 H), 5.24 (dd, J = 10.4, 1.4 Hz, 1 H), 5.32 (s, 1 H), 5.39 (dd, J = 17.1, 1.7 Hz, 1 H), 5.43–5.47 (m, 12 H), 5.61 (d, J = 1.2 Hz, 1 H), 5.66–5.73 (m, 22 H), 5.97 (dddd, J = 16.5, 10.6, 5.8, 5.3 Hz, 1 H), 7.24–7.31 (m, 22 H), 7.40–7.48 (m, 37 H), 7.49–7.63 (m, 13 H), 7.89–7.96 (m, 22 H), 8.02–8.11 (m, 26 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.3, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.9, 66.1, 67.8, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.3, 77.3, 77.3, 77.7, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.6, 81.6, 81.6, 81.7, 81.9, 82.0, 82.0, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 83.7, 104.8, 105.8, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 117.4, 128.3 (24 C), 128.5 (24 C), 129.0 (2 C), 129.1 (20 C), 129.2, 129.3, 129.8 (40 C), 129.9 (8 C), 133.1 (8 C), 133.2 (2 C), 133.3, 133.4 (12 C), 133.5, 133.8, 165.1 (10 C), 165.2, 165.4, 165.6 (10 C), 165.7, 166.1 ppm. HRMS (MALDI-TOF): calcd. for $[C_{231}H_{198}O_{73}Na]^+$ 4164.1746; found 4164.4248.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (18): M.p. 130.8 °C. $[\alpha]^D_{25}$ = +23.6 (c = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2932, 2858, 1722, 1602, 1490, 1453, 1176, 1069, 1026, 965, 709 cm^{-1}. ^{1}H NMR (400.31 MHz, $CDCl_3$): δ = 1.08 (s, 9 H), 4.00 (m, 19 H), 4.11–4.42 (m, 20 H), 4.49–4.78 (m, 18 H), 5.26 (d, J = 10.5 Hz, 1 H), 5.35 (s, 1 H), 5.47 (m, 18 H), 5.65 (m, 2 H), 5.72 (m, 33 H), 6.00 (dddd, J = 16.5, 10.6, 5.9, 5.1 Hz, 1 H), 7.20–7.34 (m, 34 H), 7.35–7.50 (m, 62 H), 7.55 (m, 18 H), 7.76 (m, 4 H), 7.95 (m, 33 H), 8.06 (m, 39 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.3, 26.8, 26.8, 26.8, 63.5, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 66.0, 67.8, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.3, 77.3, 77.4, 77.4, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 82.0, 82.0, 82.1, 83.3, 104.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 106.0, 117.4, 127.7 (6 C), 128.3 (30 C), 128.4 (6 C), 128.5 (36 C), 129.1 (14 C), 129.2 (18 C), 129.3 (4 C), 129.7, 129.7, 129.8 (30 C), 129.9 (38 C), 130.0, 130.0, 133.1 (2 C), 133.2 (16 C), 133.3 (2 C), 133.4 (14 C), 133.5 (4 C), 133.8, 135.7, 135.7, 135.7, 135.7, 165.2 (16 C), 165.4, 165.4, 165.5, 165.5, 165.6 (12 C), 165.7, 165.7, 165.7, 165.7 ppm. HRMS (MALDI-TOF): calcd. for $[C_{361}H_{312}O_{109}SiNa]^+$ 6444.8672; found 6446.9458.

Allyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabino-

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furanosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (19): M.p. 155.8 °C. $[\alpha]_{25}^{D}$ = +25.2 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3066, 2926, 1723, 1602, 1453, 1265, 1176, 1108, 1070, 1028, 966, 710 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 1.09 (s, 9 H), 3.96–4.01 (m, 18 H), 4.02–4.06 (m, 2 H), 4.16 (dd, *J* = 13.2, 6.0 Hz, 1 H), 4.20–4.29 (m, 18 H), 4.35 (dd, *J* = 13.2, 4.7 Hz, 1 H), 4.51–4.60 (m, 2 H), 4.65–4.75 (m, 17 H), 5.28 (d, *J* = 10.4 Hz, 1 H), 5.35 (s, 1 H), 5.41–5.48 (m, 19 H), 5.64 (m, 2 H), 5.70–5.72 (m, 36 H), 6.01 (dddd, *J* = 16.5, 10.7, 5.8, 5.2 Hz, 1 H), 7.24–7.35 (m, 36 H), 7.36–7.51 (m, 66 H), 7.54–7.61 (m, 18 H), 7.77 (m, 4 H), 7.92–7.99 (m, 36 H), 8.04–8.13 (m, 40 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 19.3, 26.8, 26.8, 26.8, 63.4, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.9, 65.9, 65.9, 65.9, 65.9, 65.9, 66.0, 67.8, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.3, 77.3, 77.4, 77.4, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.5, 81.6, 81.6, 81.6, 81.6, 81.9, 81.9, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 83.2, 104.8, 105.8, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 106.0, 106.0, 117.4, 127.7 (6 C), 128.3 (34 C), 128.4 (4 C), 128.5 (38 C), 129.1 (35 C), 129.3 (3 C), 129.7 (2 C), 129.8 (70 C), 129.9 (2 C), 130.0 (2 C), 133.0, 133.1 (16 C), 133.2 (2 C), 133.3 (4 C), 133.4 (17 C), 133.8, 135.7, 135.7, 135.7, 135.7, 165.1 (16 C), 165.2, 165.2, 165.4, 165.5, 165.6 (17 C), 165.7 ppm. HRMS (MALDI-TOF): calcd. for $[C_{380}H_{328}O_{115}SiNa]^+$ 6784.9619; found 6784.8623.

Allyl 2,3-Di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (20): M.p. 135.3 °C. $[\alpha]_{25}^{D}$ = +22.4 (*c* = 1.0 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 2931, 2861, 1722, 1602, 1490, 1453, 1176, 1102, 1069, 1027, 965, 709 cm^{-1}. ^1H NMR (400.31 MHz, $CDCl_3$): δ = 2.47 (s, 1 H), 3.90–4.95 (m, 20 H), 4.12 (dd, *J* = 6.5, 1.7 Hz, 1), 4.15 (dd, *J* = 6.5, 1.7 Hz, 1 H), 4.20–4.28 (m, 16 H), 4.33 (dd, *J* = 13.2, 4.9 Hz, 1 H), 4.52 (q, *J* = 4.7 Hz, 2 H), 4.61–4.69 (m, 16 H), 5.25 (dd, *J* = 10.5, 1.5 Hz, 1 H), 5.33 (s, 1 H), 5.36–5.49 (m, 19 H), 5.62 (d, *J* = 1.2 Hz, 1 H), 5.67–5.72 (m, 33 H), 5.98 (dddd, *J* = 16.6, 10.5, 5.9, 5.0 Hz, 1 H), 7.24–7.30 (m, 35 H), 7.40–7.48 (m, 55 H), 7.49–7.63 (m, 18 H), 7.90–7.97 (m, 34 H), 8.05–8.10 (m, 38 H) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$): δ = 62.3, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.8, 65.9, 66.1, 67.8, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.2, 77.3, 77.3, 77.3, 77.7, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.6, 81.7, 82.0, 82.0, 82.0, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 82.1, 83.7, 104.8, 105.8, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 105.9, 117.4, 128.3 (36 C), 128.5 (36 C), 129.0, 129.0, 129.0, 129.0, 129.1 (28 C), 129.2, 129.2, 129.3, 129.3, 129.8 (32 C), 129.9 (40 C), 133.2 (16 C), 133.3, 133.4 (12 C), 133.5 (6 C), 133.6, 133.8, 165.1 (12 C), 165.2 (5 C), 165.4, 165.6 (12 C), 165.7 (5 C), 166.1 ppm. HRMS (MALDI-TOF): calcd. for $[C_{345}H_{294}O_{109}Na]^+$ 6206.7494; found 6206.1763.

Allyl α-D-Arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (21): M.p. 254.3 °C. $[\alpha]_{25}^{D}$ = +113.2 (*c* = 1.0 in H_2O). IR ($CHCl_3$): $\tilde{\nu}$ = 3355, 1696, 1642, 1425, 1368, 1237, 1095 cm^{-1}. ^1H NMR (600.40 MHz, D_2O, internal standard CH_3COCH_3): δ = 2.22 (CH_3COCH_3), 3.71 (dd, *J* = 12.3, 5.8 Hz, 1 H), 3.78–3.82 (m, 18 H), 3.84–3.90 (m, 19 H), 3.95 (dd, *J* = 6.0, 3.3 Hz, 1 H), 4.00–4.01 (m, 18 H), 4.08–4.10 (m, 3 H), 4.11–4.13 (m, 18 H), 4.18–4.23 (m, 18 H), 4.23–4.27 (m, 1 H), 5.07–5.09 (m, 19 H), 5.28 (dt, *J* = 10.5, 1.4 Hz, 1 H), 5.36 (dt, *J* = 17.3, 1.5 Hz, 1 H), 5.97 (dddd, *J* = 16.5, 10.8, 5.7, 5.3 Hz, 1 H) ppm. ^{13}C NMR (100.67 MHz, D_2O, internal standard CH_3COCH_3): δ = 30.8 (CH_3), 61.7, 67.3, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 67.4, 69.4, 77.0, 77.0, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 77.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.3, 81.4, 81.4, 82.6, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 82.9, 84.5, 107.1, 107.9, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 108.0, 119.1, 133.9, 215.9 (CO) ppm. HRMS (MALDI-TOF): calcd. for $[C_{98}H_{158}O_{77}Na]^+$ 2590.8379; found 2590.1692.

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