Supporting Information for:

2,3-Anhydrosugars in Glycoside Bond Synthesis. Highly
Stereoselective Syntheses of Oligosaccharides Containing α - and β -
Arabinofuranosyl Linkages

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Experimental

General. Solvents were distilled from the appropriate drying agents before use. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on silica gel 60 F₂₅₄ (0.25 mm, E. Merck). Spots were detected under UV light or by charring with 10% H₂SO₄ in ethanol. Solvents were evaporated under reduced pressure and below 40 °C (bath). Organic solutions of crude products were dried over anhydrous Na₂SO₄. Chromatography was performed on silica gel 60 (40–60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 21±2 °C. Melting points are uncorrected. ¹H NMR spectra were recorded at 400 or 500 MHz, and chemical shifts are referenced to TMS (0.0, CDCl₃). ¹³C NMR spectra were recorded at 125 MHz, and ¹³C chemical shifts are referenced to CDCl₃ (77.00, CDCl₃). NMR assignments are tentative. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points are uncorrected. Electrospray mass spectra were recorded on samples suspended in mixtures of THF and CH₃OH with added NaCl. Acceptors **18–29**, and **31–33** were either commercially available or prepared as previously reported.¹ Analytical data for compounds **1**, **2**, **35–37**, **39–41**, **43**, **46–48**, **50–54**, **56** has been reported in earlier papers.^{2,3} Product yields from glycosylation reactions are given in Tables 1 and 2.

Crystallographic Details. Diffraction data for **9** and **10** were collected on separate Bruker P4 diffractometers, both equipped with graphite monochromators, using CuKα radiation (1.54178 Å) and MoKα radiation (0.71073 Å), respectively. The cell constants and orientation matrix found prior to data collection were obtained from least squares refinement of 85 reflections, ranging from 7° to 56° in 2θ for **9** and from 94 reflections ranging from 12° to 25° in 2θ for **10**. For both samples, a full sphere of intensity data was collected using $\omega/2\theta$ scans, and three check reflections were collected every 97 reflections to monitor intensity decay. For **9** a total of 2765 were measured, 2278 of which were independent; for **10**, 5674 of 6476 measured reflections were independent. Reflection data in both cases were corrected for Lorentz-polarization and absorption effects using the ω -scan method. Both structures were solved by direct methods, and refined by the full-matrix least-squares on F² technique for all of the data. The structure determinations and refinements were performed using SHELXL97.⁴ Positions for all non-hydrogen atoms were refined anisotropically in both structures, followed by isotropic refinement of all hydrogen positions for **9**, and mixed constrained/independent refinement of hydrogens for **10**. Final refinements converged to R = 0.0987

and $wR_2 = 0.2005$ for all data for **9**, and to $R = 0.1350$ and $wR_2 = 0.2357$ for all data for **10**. The Flack parameters in both cases confirmed the assignment of the absolute configurations. Total parameters refined for **9** were 262, corresponding to 7.3 observations per parameter; and 285 for **10**, corresponding to 19.9 observations per parameter.

General Procedures for Glycosylations

Method A. To a mixture of the alcohol (0.5 mmol, vacuum dried overnight), donor **1** or **5** (0.6 mmol) and 4 Å molecular sieves (0.1 g) was added CH_2Cl_2 (10 mL). The mixture was cooled to $-40\text{ }^\circ\text{C}$ and then *N*-iodosuccinimide (0.6 mmol) and silver triflate (0.15 mmol) were added. After stirring for 15–30 min at this temperature, the reaction mixture turned dark red/brown and then triethylamine was added. The reaction mixture was then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was concentrated to give a crude residue that was purified by chromatography.

Method B. Donor **2** or **6** (0.5 mmol), 2,6-di-*tert*-butyl-4-methyl pyridine (2.0 mmol), 4 Å molecular sieves (0.1 g) were dried for 3 h under vacuum in the presence of P_2O_5 . To this mixture was added CH_2Cl_2 (10 mL) and the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$. Triflic anhydride (0.6 mmol) was added and the mixture was allowed to stir for 10 min. A solution of the vacuum dried acceptor alcohol (0.6 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise via syringe over 5 min. After 15 min, the reaction mixture turned dark brown/green and a saturated solution of NaHCO_3 was added and then the solution was allowed to warm to room temperature. The resulting solution was filtered through Celite, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography.

Method C. Donor **2** or **6** (0.5 mmol), 2,6-di-*tert*-butyl-4-methyl pyridine (2.0 mmol), 4 Å molecular sieves (0.1 g) were dried for 3 h under vacuum in the presence of P_2O_5 . To this mixture was added CH_2Cl_2 (10 mL) and the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$. Triflic anhydride (0.6 mmol) was added and the mixture was allowed to stir for 10 min. The solution was warmed to $-40\text{ }^\circ\text{C}$ and stirred for 20 min followed by the dropwise addition (via syringe) of a solution of the vacuum dried acceptor alcohol (0.6 mmol) in CH_2Cl_2 (1.0 mL) over 5 min. After 15 min, the reaction mixture turned dark brown/green and a saturated solution of NaHCO_3 was added and then the solution was allowed to warm to room temperature. The resulting

solution was filtered through Celite, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography.

Method D. Donor **1** or **5** (0.6 mmol), 1-benzene sulfinyl piperidine⁵ (0.7 mmol), 2,6-di-tert-butyl-4-methyl pyridine (1.2 mmol), 4 Å molecular sieves (0.1 g) were dried for 3 h under vacuum in the presence of P₂O₅. To this mixture was added CH₂Cl₂ (10 mL) and the reaction mixture was cooled to -78 °C. Triflic anhydride (0.6 mmol) was added and the mixture was allowed to stir for 15 min. The solution was warmed to -40 °C and stirred for 10 min followed by the dropwise addition (via syringe) of a solution of the vacuum dried acceptor alcohol (0.8 mmol) in CH₂Cl₂ (1.0 mL) over 2 min. After 20 min, the reaction mixture turned dark brown/green and a saturated solution of NaHCO₃ was added and then the solution was allowed to warm to room temperature. The resulting solution was filtered through Celite, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography.

General Methods for Epoxide Openings

Opening of epoxides with NaN₃. To a solution of the epoxide (1.0 mmol) dissolved in a mixture of EtOH/H₂O (9:1, 10 mL) was added NaN₃ (3.0 mmol) and NH₄Cl (5.0 mmol). The resulting mixture was heated at reflux for 3–6 h, cooled to rt and diluted with EtOAc. The layers were separated and the organic phase was dried, filtered, and concentrated. The crude residue was purified by chromatography (8:1, hexanes/EtOAc) to yield the respective pure products.

Opening of epoxides with LiAlH₄. To a solution of the epoxide (1.0 mmol) dissolved in THF (10 mL) at 0 °C was added LiAlH₄ (1.5 mmol). The solution was heated at reflux for 3 h, cooled to rt, and carefully diluted with EtOAc (5 mL). The resulting mixture was treated with aq. 1M KOH soln. (3 mL) and allowed to stir for 20 min followed by filtration through Celite. After separation of the layers, the organic solution was dried, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography (8:1, hexanes/EtOAc) to yield the respective pure products.

Opening of epoxides with alkoxides. To a solution of the alcohol (ROH[‡], 1.5 mL) was added the alkali metal (M[‡], 3 mmol) and the solution was stirred at 65 °C for 15 min followed by the addition of the Additive[‡] (1.2 mmol). After cooling to rt, the mixture was added via a cannula to a solution of the epoxide (1.0 mmol) dissolved in the alcohol (ROH[‡], 0.5 mL) at rt. The mixture was subsequently warmed to the desired temperature and allowed to stir until the

reaction was complete by TLC. After cooling to rt, the solution was neutralized with acetic acid (3.0 mmol) and diluted with CH₂Cl₂. The organic layer was washed with water, dried, filtered, and concentrated to give a crude residue that was purified by chromatography (10:1, hexanes/Et₂O). Those reactions done in the absence of an additive were carried out in an analogous manner, except that no additive was used. [‡](**R** = benzyl, allyl), (**M** = Li, K, Na), (**A** = 18-Crown-6, 15-Crown-5, (□)-sparteine, TMEDA).

***p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio-□-D-ribofuranoside (**5**) and *p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio-□-D-ribofuranoside (**14**).** To a solution of **13** (2.1 g,

4.36 mmol) in CH₃OH (20 mL) and CH₂Cl₂ (20 mL) was added 1 M NaOCH₃ in CH₃OH (1 mL). After stirring for 8 h at rt, the reaction mixture was neutralized with Amberlite IR-120 H⁺ resin, filtered, and concentrated. The residue was co-evaporated twice with CH₂Cl₂. The resulting oil was subsequently dissolved in dry pyridine (25 mL) and cooled to 0 °C. Benzoyl chloride (0.65 mL, 5.5 mmol) was added dropwise over 10 min. The reaction mixture was allowed to stir for 2 h while warming to rt and then diluted with CH₂Cl₂. The organic layer was washed with a satd. aq. NaHCO₃ solution and then water. The organic layer was dried with Na₂SO₄, filtered and concentrated. The product was purified by chromatography (2:1, hexanes/EtOAc) to yield **5** (1.21 g, 67%) and **14** (0.31 g, 21%) as white solids. (**5**): *R_f* 0.36 (2:1, hexanes:EtOAc); [α]_D +125.4 (*c* 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, □_H) 8.04 (d, 2 H, *J* = 7.2 Hz), 7.61 (dd, 1 H, *J* = 7.5, 7.2 Hz), 7.51–7.42 (m, 4 H), 7.14 (d, 2 H, *J* = 8.0 Hz), 5.49 (s, 1 H, H-1), 4.71 (dd, 1 H, *J* = 3.8, 4.5 Hz, H-4), 4.57 (dd, 1 H, *J* = 3.8, 12.0 Hz, H-5), 4.45 (dd, 1 H, *J* = 4.5, 12.0 Hz, H-5), 4.08 (d, 1 H, *J* = 2.8 Hz, H-2), 3.90 (dd, 1 H, *J* = 2.8 Hz, H-3), 2.37 (s, 3 H); ¹³C NMR (125.7 MHz, CDCl₃, □_C) 166.5, 138.1, 133.8, 132.4, 130.7, 130.3, 130.0, 129.9, 129.0, 87.5 (C-1), 78.2 (C-4), 64.7 (C-5), 59.4 (C-2), 57.7 (C-3), 21.5. Anal. Calcd for C₁₉H₁₈O₄S: C, 66.66, 5.26. Found: C, 66.58; H, 5.30. HRMS (ESI) calcd for (M+Na) C₁₉H₁₈O₄S: 365.0817, found 365.0853.

(**14**): *R_f* 0.39 (2:1, hexanes:EtOAc); [α]_D +82.3 (*c* 0.9, CHCl₃); ¹H NMR (500 MHz, CDCl₃, □_H) 8.15 (d, 2 H, *J* = 7.1 Hz), 7.64 (dd, 1 H, *J* = 7.4, 7.1 Hz), 7.53–7.45 (m, 5 H), 7.16 (d, 2 H, *J* = 8.0 Hz), 5.57 (s, 1 H, H-1), 4.62–4.55 (m, 3 H, H-4, H-5, H-5), 4.05 (d, 1 H, *J* = 2.8 Hz, H-2), 4.03 (d, 1 H, *J* = 2.8 Hz, H-3), 2.37 (s, 3 H); ¹³C NMR (125.7 MHz, CDCl₃, □_C) 166.5, 138.6, 133.7, 133.3, 130.4, 130.3, 130.0, 129.6, 128.9, 128.8, 87.9 (C-1), 77.7 (C-4), 64.1 (C-5),

58.7 (C-2), 57.9 (C-3), 21.6. Anal. Calcd for $C_{19}H_{18}O_4S$: C, 66.66, 5.26. Found: C, 66.60; H, 5.24. HRMS (ESI) calcd for (M+Na) $C_{19}H_{18}O_4S$: 365.0817, found 365.0820.

2,3-anhydro 5-O-benzoyl- β -D-ribofuranosyl *p*-tolyl (R/S) sulfoxide (6). Sulfoxide **6** was synthesized from **5** (1.0 g, 2.92 mmol) as described for the preparation of **2**. The product was purified by chromatography (2:1, hexanes/EtOAc) to provide **6** (0.853 g, 79%) (7:3 mixture of diastereomers) as a white crystalline solid: R_f 0.36 (1:1, hexanes/EtOAc); $[\alpha]_D -158.8$ (c 1.5, $CHCl_3$); mp 78–79 °C; 1H NMR (500 MHz, $CDCl_3$, β_H) 7.99–7.93 (m, 2 H), 7.30–7.75 (m, 7 H) 4.81 (s, 0.3 H), 4.77 (dd, 0.3 H, J = 4.0, 4.0 Hz), 4.66–4.40 (m, 11 H), 4.34 (dd, 0.7 H, J = 4.0, 12.2 Hz), 4.13 (d, 0.7 H, J = 2.8 Hz), 3.97 (d, 0.3 Hz, J = 2.8 Hz), 3.52 (d, 0.3 H, J = 2.8 Hz), 2.47 (s, 0.9 H), 2.45 (s, 2.1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$, β_C) 166.4, 166.3, 143.1, 142.6, 138.9, 137.6, 134.0, 133.9, 130.5, 130.2, 130.0, 129.9, 129.6, 129.5, 129.1, 128.9, 125.5, 125.4, 100.6, 97.4, 79.7, 79.4, 64.5, 64.3, 60.2, 59.2, 57.1, 56.4, 21.9 (2). Anal. Calcd for $C_{19}H_{18}O_5S$: C, 63.68, 5.02. Found: C, 63.64; H, 5.02. HRMS (ESI) calcd for (M+Na) $C_{19}H_{18}O_5S$: 381.0767, found 381.0769.

Methyl 5-O-{3,5-di-O-(2-O- β -D-arabinofuranosyl)- β -D-arabinofuranosyl}- β -D-arabinofuranoside (7). To a solution of **100** (0.150 g, 0.091 mmol) in AcOH/ H_2O (4:1, 10 mL) was added 10% Pd/C (50 mg) and the reaction mixture was stirred under hydrogen atmosphere for 4 h. The mixture was filtered through Celite, concentrated and the residue was purified by chromatography over Iatrobeds (CH_2Cl_2 , CH_3OH , H_2O , 60:35:5) to give **7** (0.068 g, 91%) as a white solid: R_f 0.34 (CH_2Cl_2 , CH_3OH , H_2O , 60:35:5). $[\alpha]_D +46.2$ (c 0.7, D_2O). The NMR data of the product was identical to that previously reported for **7**.⁶

5-O-benzoyl-1,2-di-O-acetyl-3-O-methanesulfonyl- β -D-xylofuranose (12). Compound **11**⁷ (3.0 g, 8.1 mmol) was added to 60% aq. acetic acid (25 mL) containing a catalytic amount of conc. H_2SO_4 and stirred for 36 h at 70 °C. The reaction mixture was neutralized with a satd. aq. $NaHCO_3$ solution and extracted into ethyl acetate. The combined extracts were washed with water, (Na_2SO_4), filtered, and concentrated. The resulting diol (2.7 g, 8.1 mmol) was dissolved

in pyridine (25 mL) and acetic anhydride (3 mL) was added at rt. The solution was stirred for 2 h followed by dilution with water and the stirring continued for 30 min. The mixture was diluted with CH₂Cl₂ and the organic layer washed with sat. aq. NaHCO₃ soln., and water. The organic layer was dried (Na₂SO₄), filtered and concentrated. The resulting crude product was purified by chromatography (6:1, hexanes/EtOAc) to yield **12** (2.95 g, 88%) as a colorless syrup: *R_f* 0.37 (1:1, hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃, δ _H) 8.11–8.08 (m, 2 H), 7.63–7.58 (m, 1 H), 7.51–7.46 (m, 2 H), 6.52 (d, 0.7 H, *J* = 4.5 Hz, H-1'), 6.24 (s, 0.3 H, H-1'), 5.54–5.48 (m, 2 H), 5.40 (s, 0.7 H), 5.25 (dd, 0.3 H, *J* = 0.8, 3.3 Hz), 4.83–4.77 (m, 1 H), 4.68–4.56 (m, 1 H), 3.21 (s, 1 H), 3.14 (s, 2 H), 2.14 (s, 1 H), 2.13 (s, 2 H), 2.13 (s, 1 H), 2.12 (s, 2 H); ¹³C NMR (125.7 MHz, CDCl₃, δ _C) 169.9 (2), 169.7, 169.5, 166.4 (2), 133.8, 133.7, 130.2, 130.1, 129.9 (2), 128.9, 128.8, 99.1 (C-1'), 93.2 (C-1'), 80.3, 80.0, 79.7, 78.8, 75.9, 75.6, 62.6, 62.1, 38.9, 38.8, 21.4, 21.2, 21.0, 20.7. HRMS (ESI) calcd for (M+Na) C₁₇H₂₀O₁₀: 439.0669, found 439.0673.

***p*-Tolyl 2-*O*-acetyl-5-*O*-benzoyl-3-*O*-methanesulfonyl-1-thio- β -D-xylofuranose (**13**).** To a solution of **12** (2.5 g, 6.0 mmol) and thioscresol (0.97 g, 7.8 mmol) in CH₂Cl₂ at 0 °C was added BF₃·OEt₂ (1.7 mL, 12.0 mmol) dropwise over 15 min. The reaction mixture was allowed to warm to rt over 2

h followed by the addition of triethylamine (2.2 mL, 15.0 mmol). The resulting solution was diluted with CH₂Cl₂ and washed with satd. aq. NaHCO₃ solution and water. The organic layer was dried (Na₂SO₄), filtered, and concentrated. The product was purified by chromatography (8:1, hexanes/EtOAc) to yield **13** (2.60 g, 91%) as a colorless syrup: *R_f* 0.37 (1:1, hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃, δ _H) 8.13–8.09 (m, 2 H), 7.62–7.48 (m, 4 H), 7.44 (d, 1 H, *J* = 8.1 Hz), 7.19 (d, 1 H, *J* = 7.9 Hz), 7.15 (d, 1 H, *J* = 7.9 Hz), 5.87 (d, 0.5 H, *J* = 5.6 Hz), 5.65 (dd, 0.5 H, *J* = 2.8, 5.6 Hz), 5.37 (dd, 0.5 H, *J* = 1.6, 3.4 Hz), 5.33 (dd, 0.5 H, *J* = 2.8, 4.9 Hz), 5.27 (d, 0.5 H, *J* = 3.5 Hz), 5.20 (dd, 0.5 H, *J* = 1.5, 3.3 Hz), 4.85 (dd, 0.5 H, *J* = 5.0, 5.2 Hz), 4.70–4.57 (m, 2.5 H), 3.16 (s, 1.5 H), 3.10 (s, 1.5 H), 2.37 (s, 1.5 H), 2.36 (s, 1.5 H), 2.25 (s, 1.5 H), 2.17 (s, 1.5 H); ¹³C NMR (125.7 MHz, CDCl₃, δ _C) 170.0, 169.9, 166.5, 166.4, 139.2, 138.7, 134.2, 133.7, 133.6, 133.4, 130.3 (2), 130.2, 130.0, 129.6, 128.9, 128.8 (2), 89.8, 89.7, 81.5, 81.2, 80.8, 78.8, 78.0, 75.6, 62.3, 61.7, 39.0, 38.8, 21.6, 21.5, 21.1, 20.9. HRMS (ESI) calcd for (M+Na) C₂₂H₂₄O₈S: 503.0805, found 503.0797.

2,3-anhydro 5-*O*-benzoyl- α -D-ribofuranosyl *p*-tolyl (R/S) sulfoxide (15). Sulfoxide **15** was synthesized from **14** (1.0 g, 2.92 mmol) as described for the preparation of **2**. The product was purified by chromatography (2:1, hexanes/EtOAc) to provide **15** (0.841 g, 77%) (10:1 mixture of diastereomers) as a white crystalline solid (data for major isomer): R_f 0.28 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} +176.0$ (c 3.0, CHCl_3); mp 50–52 °C; ^1H NMR (500 MHz, CDCl_3 , α_H) 8.14 (d, 1 H, J = 8.0 Hz), 7.65–7.36 (m, 8 H), 4.87 (s, 1 H, H-1), 4.75–4.31 (m, 3 H, H-4, H-5, H-5), 4.31 (d, 1 H, J = 2.9 Hz, H-2), 4.06 (d, 1 H, J = 2.9 Hz, H-3), 2.45 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , α_C) 166.5, 142.8, 137.4, 133.9, 130.6, 130.4, 130.3, 130.2, 129.8, 129.0, 128.8, 125.1, 97.6 (C-1), 79.3 (C-4), 64.3 (C-5), 57.8 (C-2), 57.4 (C-3), 21.9. Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5\text{S}$: C, 63.68, 5.02. Found: C, 63.74; H, 5.17. HRMS (ESI) calcd for (M+Na) $\text{C}_{19}\text{H}_{18}\text{O}_5\text{S}$: 381.0767, found 381.0769.

Methyl 5-*O*-(2,3-anhydro- α -D-lyxofuranosyl)-2,3-anhydro- α -D-lyxofuranoside (30). The compound was isolated after Zemplén deacylation⁸ of methyl 5-*O*-(5-*O*-benzoyl-2,3-anhydro- α -D-lyxofuranosyl)-2,3-anhydro- α -D-lyxofuranoside.³ Chromatography (3:1, hexanes/EtOAc) yielded the product as a white solid: R_f 0.15 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +46.9$ (c 0.6, CHCl_3); mp 113–114 °C; ^1H NMR (500 MHz, CDCl_3 , α_H) 5.30 (s, 1 H), 5.14 (s, 1 H), 4.19–4.15 (m, 2 H), 3.93–3.86 (m, 3 H), 3.76 (d, 1 H, J = 2.8 Hz), 3.74 (d, 1 H, J = 2.8 Hz), 3.72–3.66 (m, 3 H), 3.42 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , α_C) 102.6, 102.0, 77.2, 76.8, 75.0, 66.9, 62.1, 56.6, 56.0, 54.6, 54.5. HRMS (ESI) calcd for (M+Na) $\text{C}_{11}\text{H}_{16}\text{O}_7$: 283.0794, found 283.0796.

Methyl 3,5-di-*O*-benzyl- α -D-arabinofuranoside (34).⁹ To a room temperature solution of methyl 5-*O*-benzyl-2,3-anhydro- α -D-lyxofuranoside¹⁰ (1.2 g, 0.5 mmol) dissolved in dry DMF (5 mL) was added 1M sodium benzyolate in benzyl alcohol (1.0 mL, 1.0 mmol). The reaction mixture was stirred at 100 °C for 2.5 h and then cooled and neutralized with acetic acid. The excess benzyl alcohol was removed by vacuum distillation and the crude oil was purified by chromatography (2:1, hexanes/EtOAc) to yield **34** (1.5 g, 84%) as a colorless oil.

1-Adamantyl 2,3-anhydro-5-*O*-benzoyl- α -D-lyxofuranoside (38). The compound was isolated after chromatography (8:1, hexanes/EtOAc) as

an oil: R_f 0.41 (4:1, hexanes/EtOAc); $[\alpha]_D^{25}$ +16.8 (c 1.2, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $[\text{H}]$) 8.09 (d, 2 H, $J = 7.1$ Hz), 7.59 (dd, 1 H, $J = 7.4, 7.3$ Hz), 7.46 (dd, 2 H, $J = 7.9, 7.6$ Hz), 5.43 (s, 1 H, H-1), 4.62–4.54 (m, 2 H, H-5, H-5), 4.17 (dd, 1 H, $J = 6.5, 6.3$ Hz, H-4), 3.78 (d, 1 H, $J = 2.9$ Hz, H-2), 3.70 (d, 1 H, $J = 2.9$ Hz, H-3), 2.19 (br s, 3 H), 1.91–1.85 (m, 6 H), 1.68–1.62 (m, 6 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $[\text{C}]$) 166.6, 133.5, 130.3, 130.1, 128.8, 95.3 (C-1), 75.3 (Ad-O), 74.4 (C-4), 63.6 (C-2), 57.8 (C-2), 54.8 (C-3), 42.7, 36.6, 31.1; $^1J_{\text{C1,H1}} = 161.8$ Hz. HRMS (ESI) calcd for $(\text{M}+\text{Na}) \text{C}_{22}\text{H}_{26}\text{O}_5$: 393.1672, found 393.1687.

Methyl 5-*O*-benzoyl-(2,3-anhydro- β -D-lyxofuranosyl)-2,3-di-*O*-benzyl- β -D-arabinofuranoside (42). The compound was isolated after chromatography (6:1, hexanes/EtOAc) as a clear oil: R_f

0.31 (2:1, hexanes/EtOAc); $[\alpha]_D^{25}$ +31.6 (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $[\text{H}]$) 8.05 (d, 2 H, $J = 7.3$ Hz), 7.64 (dd, 1 H, $J = 7.4, 7.4$ Hz), 7.51 (dd, 2 H, $J = 7.7, 7.7$ Hz), 7.40–7.30 (m, 10 H), 5.47 (s, 1 H, H-1'), 4.96 (s, 1 H, H-1), 4.63–4.50 (m, 6 H), 4.44 (dd, 1 H, $J = 4.3, 11.9$ Hz), 4.24 (ddd, 1 H, $J = 4.2, 4.2, 5.9$ Hz), 4.08 (dd, 1 H, $J = 2.6, 6.2$ Hz), 4.04 (d, 1 H, $J = 2.3$ Hz), 4.00 (dd, 1 H, $J = 4.6, 11.5$ Hz), 3.91 (dd, 1 H, $J = 3.7, 11.5$ Hz), 3.80 (d, 1 H, $J = 2.8$ Hz), 3.79 (d, 1 H, $J = 2.7$ Hz), 3.41 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $[\text{C}]$) 166.5, 138.4, 137.9, 133.8, 130.0, 129.9, 129.0, 128.9, 128.8, 128.4, 128.3 (2), 128.2, 107.8 (C-1), 102.4 (C-1'), 88.5, 83.3, 81.7, 76.5, 72.7, 72.3, 68.5, 65.1, 56.3 (2), 55.4; $^1J_{\text{C1,H1}} = 165.5$ Hz (C-1'), 164.8 Hz (C-1). HRMS (ESI) calcd for $(\text{M}+\text{Na}) \text{C}_{32}\text{H}_{34}\text{O}_9$: 585.2101, found 585.2119.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- β -D-lyxofuranosyl)-2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (44). The compound was isolated after chromatography (4:1,

hexanes/EtOAc) as a colorless oil: R_f 0.43 (2:1, hexanes/EtOAc); $[\alpha]_D^{25}$ +9.1 (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $[\text{H}]$) 8.10 (dd, 2 H, $J = 7.4, 7.3$ Hz, 2 H), 7.60 (dd, 1 H, $J = 7.1, 7.0$ Hz), 7.49–7.28 (m, 17 H), 5.45 (s, 1 H, H-1'), 4.94–4.92 (m, 1 H), 4.78 (d, 1 H, $J = 11.2$ Hz), 4.80 (dd, 2 H, $J = 11.7, 2.2$ Hz), 4.78–4.68 (m, 4 H), 4.60–4.53 (m, 2 H), 4.46 (dd, 1 H, $J = 6.7, 6.7$ Hz), 4.21– (dd, 1 H, $J = 6.6, 6.6$ Hz), 3.87–3.85 (m, 2 H), 3.84–3.80 (m, 2 H), 3.75 (d, 1 H, $J = 3.0$ Hz), 3.60 (dd, 1 H, $J = 4.5, 12.0$ Hz), 3.49–3.47 (m, 4 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $[\text{C}]$) 166.6, 138.9, 138.6, 138.5, 133.7, 130.2, 130.1, 128.9, 128.8, 128.7 (2), 128.4 (2), 128.2, 128.1, 128.0, 127.9, 101.0 (C-1'), 98.7 (C-1), 77.3, 73.7, 73.3, 72.8, 72.2, 72.0, 69.9, 68.6, 65.5, 63.4,

56.3, 55.7, 54.0; $^1J_{\text{C1,H1}} = 166.3$ Hz (C-1'), 172.1 (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2676, found 705.2673.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- β -D-lyxofuranosyl)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (45).

The compound was isolated after chromatography (4:1, hexanes/EtOAc) as a colorless oil: R_f 0.30 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +17.2$ (c 1.1, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.06 (d, 2 H, $J = 8.1$ Hz), 7.59 (dd, 1 H, $J = 8.3, 8.3$ Hz), 7.47–7.34 (m, 17 H), 5.27 (s, 1 H), 5.04 (d, 1 H, $J = 10.6$ Hz), 4.92–4.85 (m, 3 H), 4.77–4.69 (m, 3 H), 4.59 (dd, 1 H, $J = 5.9, 11.2$ Hz), 4.54 (dd, 1 H, $J = 5.9, 11.2$ Hz), 4.22 (dd, 1 H, $J = 5.9, 5.9$ Hz), 4.08–4.05 (m, 3 H), 3.89–3.87 (m, 1 H), 3.79 (d, 1 H, $J = 2.8$ Hz), 3.74 (d, 1 H, $J = 2.8$ Hz), 3.67–3.66 (m, 2 H), 3.45 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.6, 139.3, 138.9, 138.7, 133.6, 130.2, 128.9, 128.8, 128.6, 128.4, 128.3 (2), 128.1, 128.0, 101.6, 98.7, 82.5, 80.3, 77.9, 76.1, 75.4, 74.2, 73.8, 70.4, 66.4, 63.4, 55.7, 55.6, 54.8; $^1J_{\text{C1,H1}} = 166.2$ Hz (C-1'), 169.5 Hz (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2676, found 705.2669.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- β -D-lyxofuranosyl)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (49).

The compound was isolated after chromatography (4:1, hexanes/EtOAc) as a colorless oil: R_f 0.26 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +9.1$ (c 0.9, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 7.99–7.97 (m, 2 H), 7.65–7.25 (m, 18 H), 5.50 (s, 1 H, H-1'), 5.07 (d, 1 H, $J = 12.0$ Hz), 4.85 (d, 1 H, $J = 12.0$ Hz), 4.81 (d, 1 H, $J = 12.0$ Hz), 4.70–4.59 (m, 3 H), 4.51–4.39 (m, 4 H), 4.26 (dd, 1 H, $J = 4.1, 8.3$ Hz), 4.04 (dd, 1 H, $J = 7.6, 7.6$ Hz), 3.85–3.78 (m, 2 H), 3.77 (d, 1 H, $J = 7.6, 7.6$ Hz), 3.77 (d, 1 H, $J = 2.8$ Hz), 3.59 (dd, 1 H, $J = 4.9, 7.7$ Hz), 3.48 (d, 1 H, $J = 2.8$ Hz), 3.44 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 139.4, 138.8, 138.4, 133.8, 129.9, 129.8, 129.0 (2), 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 104.6 (C-1'), 98.3 (C-1), 81.7, 80.4, 78.6, 76.7, 76.1, 73.9, 73.7, 70.1, 69.0, 65.1, 57.1, 57.0, 55.7; $^1J_{\text{C1,H1}} = 166.1$ Hz (C-1'), 171.5 Hz (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2670, found 705.2697.

***n*-Octyl 2,3-anhydro-5-*O*-benzoyl- β -D-ribofuranoside (55).**

The compound was isolated after chromatography (4:1; hexanes/EtOAc) as a colorless oil: R_f 0.28 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} +34.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.05 (d, 2 H, $J = 7.2$ Hz), 7.63 (dd, 2 H, $J = 7.7, 7.8$

Hz), 7.50 (dd, 2 H, $J = 7.7, 7.8$ Hz), 5.32 (s, 1 H, H-1), 4.63 (dd, 1 H, $J = 3.3, 3.3$ Hz, H-4), 4.52 (dd, 1 H, $J = 3.3, 11.9$ Hz, H-5), 4.45 (dd, 1 H, $J = 3.3, 11.9$ Hz, H-5), 3.84–3.81 (m, 3 H, H-2, H-3, octyl OCH₂), 3.58 (ddd, 1 H, $J = 6.6, 6.6, 9.6$ Hz, octyl OCH₂), 1.69–1.64 (m, 2 H), 1.40–1.30 (m, 10 H), 0.91 (t, 3 H, $J = 6.8$ Hz). ¹³C NMR (125.7 MHz, CDCl₃, $\square_c$) 166.5, 133.8, 130.0, 129.9, 129.0, 102.4 (C-1), 76.4 (C-4), 70.5 (octyl OCH₂), 65.1 (C-5), 56.4 (2, C-2, C-3), 32.2, 30.1, 29.7, 29.6, 26.4, 23.0, 14.5; $^1J_{C1,H1} = 164.7$ Hz. HRMS (ESI) calcd for (M+Na) C₂₀H₂₈O₅: 371.1829, found 371.1824.

***t*-Butyl 2,3-anhydro-5-*O*-benzoyl- $\square$ -D-ribofuranoside (57).** The compound was isolated after chromatography (8:1, hexanes/EtOAc) as an oil: R_f 0.21 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} +33.1$ (c 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, $\square_H$) 8.05 (d, 2 H, $J = 7.2$ Hz), 7.62 (dd, 1 H, $J = 7.3, 7.4$ Hz), 7.50 (dd, 2 H, $J = 7.3, 7.4$ Hz), 5.47 (s, 1 H, H-1), 4.62 (dd, 1 H, $J = 3.7, 4.5$ Hz, H-4), 4.50 (dd, 1 H, $J = 3.7, 11.2$ Hz, H-5), 4.43 (dd, 1 H, $J = 4.5, 11.2$ Hz, H-5), 3.76 (d, 1 H, $J = 2.8$ Hz, H-2), 3.72 (dd, 1 H, $J = 0.8, 2.8$ Hz, H-3), 1.30 (s, 9 H); ¹³C NMR (125.7 MHz, CDCl₃, $\square_c$) 166.5, 133.8, 130.0, 129.9, 129.0, 96.9 (C-1), 76.0 (2, C-4, O-C(CH₃)₃), 65.1 (C-5), 57.4 (C-2), 55.7 (C-3), 28.9; $^1J_{C1,H1} = 169.1$ Hz. HRMS (ESI) calcd for (M+Na) C₁₆H₂₀O₅: 315.1208, found 315.1186.

1-Adamantyl 2,3-anhydro-5-*O*-benzoyl- $\square$ -D-ribofuranoside (58). The compound was isolated after chromatography (8:1, hexanes/EtOAc) as an oil: R_f 0.19 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} +25.0$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, $\square_H$) 8.06 (d, 2 H, $J = 7.2$ Hz), 7.64 (dd, 1 H, $J = 7.3, 7.4$ Hz), 7.51 (dd, 2 H, $J = 7.3, 7.4$ Hz), 5.60 (s, 1 H, H-1), 4.63 (dd, 1 H, $J = 3.8, 4.7$ Hz, H-4), 4.51 (dd, 1 H, $J = 3.6, 11.8$ Hz, H-5), 4.43 (dd, 1 H, $J = 4.7, 11.8$ Hz, H-5), 3.77 (d, 1 H, $J = 2.8$ Hz, H-2), 3.73 (dd, 1 H, $J = 0.5, 2.8$ Hz, H-3), 2.18 (br s, 3 H), 1.88–1.82 (m, 6 H), 1.68–1.61 (m, 6 H); ¹³C NMR (125.7 MHz, CDCl₃, $\square_c$) 166.5, 133.8, 130.0, 129.9, 129.0, 95.3 (C-1), 76.0 (C-4), 75.2 (Adm-O), 65.1 (C-5), 57.4 (C-2), 55.7 (C-3), 42.6, 36.6, 31.0; $^1J_{C1,H1} = 168.8$ Hz. HRMS (ESI) calcd for (M+Na) C₂₂H₂₆O₅: 393.1672, found 393.1689.

Methyl 5-*O*-(2,3-anhydro-5-*O*-benzoyl- $\square$ -D-ribofuranosyl)-2,3-anhydro- $\square$ -D-lyxofuranoside (59). The compound was isolated after chromatography (3:1, hexanes/EtOAc) as a white solid: R_f 0.26 (3:1, hexanes/EtOAc); $[\alpha]_D^{25} +44.0$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, $\square_H$) 8.02 (d, 2 H, $J = 7.2$ Hz), 7.60 (dd, 1 H, $J = 7.3, 7.4$ Hz), 7.48 (dd, 2 H, $J = 7.3, 7.4$ Hz), 5.47 (s, 1 H, H-1), 4.62 (dd, 1 H, $J = 3.7, 4.5$ Hz, H-4), 4.50 (dd, 1 H, $J = 3.7, 11.2$ Hz, H-5), 4.43 (dd, 1 H, $J = 4.5, 11.2$ Hz, H-5), 3.76 (d, 1 H, $J = 2.8$ Hz, H-2), 3.72 (dd, 1 H, $J = 0.8, 2.8$ Hz, H-3), 1.30 (s, 9 H); ¹³C NMR (125.7 MHz, CDCl₃, $\square_c$) 166.5, 133.8, 130.0, 129.9, 129.0, 96.9 (C-1), 76.0 (2, C-4, O-C(CH₃)₃), 65.1 (C-5), 57.4 (C-2), 55.7 (C-3), 28.9; $^1J_{C1,H1} = 169.1$ Hz. HRMS (ESI) calcd for (M+Na) C₂₂H₂₆O₅: 393.1672, found 393.1689.

Hz), 5.41 (s, 1 H, H-1'), 4.93 (s, 1 H, H-1), 4.61 (dd, 1 H, $J = 3.8, 3.9$ Hz), 4.51 (dd, 1 H, $J = 3.2, 11.2$ Hz), 4.42 (dd, 1 H, $J = 3.9, 11.2$ Hz), 4.24 (dd, 1 H, $J = 5.6, 7.4$ Hz), 3.97 (dd, 1 H, $J = 5.6, 9.9$ Hz), 3.86–3.80 (m, 4 H), 3.66 (d, 1 H, $J = 1.8$ Hz), 3.41 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 133.8, 129.9, 129.8, 129.0, 102.6 (C-1'), 102.3 (C-1), 76.7, 75.1, 67.5, 65.1, 56.8, 56.4, 56.3, 56.2, 54.6; $^1J_{\text{C1,H1}} = 166.0$ Hz (C-1'), 176.0 Hz (C-1). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_8$: C, 59.34, 5.49. Found: C, 59.27; H, 5.55. HRMS (ESI) calcd for (M+Na) $\text{C}_{18}\text{H}_{20}\text{O}_8$ 387.1050, found 387.1033.

Cyclohexyl 5-O-(2,3-anhydro-5-O-benzoyl- β -D-ribofuranosyl)-2,3-anhydro- β -D-ribofuranoside (60).

The compound was isolated after chromatography (3:1, hexanes/EtOAc) as a white solid: R_f 0.33 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +13.7$ (c 1.0, CHCl_3);

^1H NMR (500 MHz, CDCl_3 , δ) 8.12 (d, 2 H, $J = 7.0$ Hz), 7.64 (dd, 1 H, $J = 7.3, 7.2$ Hz), 7.51 (dd, 2 H, 7.3, 7.2 Hz), 5.40 (s, 1 H, H-1'), 5.33 (s, 1 H, H-1), 4.43 (dd, 1 H, $J = 3.8, 4.2$ Hz), 4.36 (dd, 1 H, $J = 3.8, 3.9$ Hz), 3.91 (dd, 1 H, $J = 3.8, 10.8$ Hz), 3.80–3.70 (m, 6 H), 3.65–3.61 (m, 1 H), 2.07–1.96 (m, 3 H), 1.80–1.77 (m, 2 H), 1.59–1.55 (m, 1 H), 1.44–1.19 (m, 5 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 133.8, 130.0, 129.9, 129.0, 102.4 (C-1), 101.1 (C-1'), 79.4, 78.2, 77.2, 69.9, 63.5, 57.3, 56.9, 56.8, 56.7, 33.8, 32.8, 25.9, 24.7 (2); $^1J_{\text{C1,H1}} = 167.8.4$ Hz (C-1), 168.1 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{23}\text{H}_{28}\text{O}_8$: 455.1676, found 455.1669.

***n*-Octyl 5-O-(2,3-anhydro-5-O-benzoyl- β -D-ribofuranosyl)-2,3-di-O-benzoyl- β -D-arabinofuranoside (61).**

The compound was isolated after chromatography (3:1, hexanes/EtOAc) as a colorless oil: R_f 0.29 (2:1, hexanes/EtOAc);

$[\alpha]_D^{25} +29.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.14–8.03 (m, 6 H), 7.64–7.57 (m, 3 H), 7.50–7.45 (m, 6 H), 5.56 (d, 1 H, $J = 4.6$ Hz), 5.52 (s, 1 H, H-1'), 5.50 (d, 1 H, $J = 1.0$ Hz), 5.27 (s, 1 H, H-1), 4.62 (dd, 1 H, $J = 3.8, 3.9$ Hz, H-4), 4.52 (dd, 1 H, $J = 3.8, 11.8$ Hz), 4.49–4.43 (m, 2 H), 4.25 (dd, 1 H, $J = 4.9, 11.1$ Hz), 4.12 (dd, 1 H, $J = 4.9, 11.1$ Hz), 3.84–3.79 (m, 3 H), 3.55 (ddd, 1 H, $J = 6.6, 6.6, 9.6$ Hz), 1.69–1.64 (m, 2 H), 1.45–1.29 (m, 10 H), 0.91 (t, 3 H, $J = 6.8$ Hz); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 166.1, 165.8, 133.8, 133.7, 130.4, 130.3, 130.0, 129.9, 129.8, 129.7, 129.0, 128.8 (2), 106.0 (C-1), 102.2 (C-1'), 82.5, 82.2, 78.2, 76.5, 68.3, 67.9, 65.1, 56.3, 56.1, 32.2, 30.0, 29.8, 29.7, 26.6, 23.0, 14.5; $^1J_{\text{C1,H1}} = 175.0$ Hz, (C-1), 166.7 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{39}\text{H}_{44}\text{O}_{11}$: 711.2775, found 711.2727.

Methyl 5-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-2,3,5-tri-*O*-benzoyl- α -D-galactofuranoside (62). The compound

was isolated after chromatography (3:1, hexanes/EtOAc) as a colorless oil: R_f 0.38 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} + 56.2$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.13 (dd, 2 H, $J = 1.0, 8.1$ Hz), 8.09 (dd, 2 H, $J = 1.0, 8.1$ Hz), 8.04 (dd, 2 H, $J = 1.0, 8.1$ Hz), 7.96 (dd, 2 H, $J = 1.0, 8.1$ Hz), 7.63–7.30 (m, 12 H), 5.90–5.88 (m, 1 H), 5.63 (d, 1 H, $J = 5.5$ Hz), 5.48 (s, 1 H, H-1'), 5.46 (s, 1 H, H-1), 5.22 (s, 1 H), 4.71 (dd, 1 H, $J = 3.5, 5.6$ Hz), 4.48–4.42 (m, 5 H), 3.82 (d, 1 H, $J = 2.8$ Hz), 3.77 (d, 1 H, $J = 2.8$ Hz), 3.51 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 166.2, 166.0, 165.9, 133.8, 133.7, 133.5, 130.4, 130.3, 130.2 (2), 130.0, 129.8, 129.6, 129.5, 129.0, 128.8, 128.7, 107.1 (C-1), 101.9 (C-1'), 82.8, 81.0, 77.9, 76.6, 71.2, 67.2, 65.0, 56.4 (2), 55.2; $^1J_{\text{C1,H1}} = 169.0$ Hz (C-1), 169.5 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{36}\text{O}_{13}$: 747.2054, found 747.2048.

Methyl 5-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-2,3-di-*O*-benzyl- α -D-arabinofuranoside (63). To a mixture of alcohol **26** (0.94 g, 2.73 mmol), thioglycoside **5** (1.21 g, 3.53 mmol), and 4Å molecular sieves (0.5 g) was added CH_2Cl_2 (20 mL). The

mixture was cooled to -40°C and *N*-iodosuccinimide (1.39 g, 1.28 mmol) and silver triflate (0.33 g, 1.28 mmol) were added. After stirring for 10 min at this temperature, the reaction mixture turned dark red and then triethylamine (1.5 mL) was added. The reaction mixture was then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was concentrated to a syrup that was purified by chromatography (5:1, hexanes/EtOAc) to obtain **63** (1.25 g, 82%) as a colorless oil: R_f 0.35 (3:1, hexanes:EtOAc); $[\alpha]_D^{25} + 17.3$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.05 (d, 2 H, $J = 7.3$ Hz), 7.64 (dd, 1 H, $J = 7.3, 7.7$ Hz), 7.51 (dd, 2 H, $J = 7.4, 7.7$ Hz), 7.40–7.30 (m, 10 H), 5.47 (s, 1 H, H-1'), 4.97 (s, 1 H, H-1), 4.63–4.50 (m, 6 H), 4.44 (dd, 1 H, $J = 4.3, 11.9$ Hz), 4.26–4.23 (m, 1 H), 4.08 (dd, 1 H, $J = 2.6, 6.2$ Hz), 4.04 (d, 1 H, $J = 2.3$ Hz), 4.01 (dd, 1 H, $J = 3.6, 11.1$ Hz), 3.91 (dd, 1 H, $J = 3.6, 11.1$ Hz), 3.81–3.79 (m, 2 H), 3.42 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.5, 138.4, 138.0, 133.8, 130.0, 129.9, 129.0, 128.8 (2), 128.3 (2), 128.2, 128.1, 107.8 (C-1), 102.4 (C-1'), 88.5, 83.4, 81.7, 76.5, 72.7, 72.3, 68.5, 65.2, 56.3, 56.2, 55.3; $^1J_{\text{C1,H1}} = 168.1$ Hz (C-1), 163.6 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{34}\text{O}_9$: 585.2095, found 585.2092.

Methyl 5-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-2,3-di-*O*-benzyl- α -D-arabinofuranoside **63** (0.11 g, 6%) as a

colorless oil: R_f 0.45 (3:1, hexanes:EtOAc); $[\alpha]_D^{25} +33.1$ (c 1.0, CHCl_3);

^1H NMR (500 MHz, CDCl_3 , δ) 8.06 (d, 2 H, $J = 7.3$ Hz), 7.44 (dd, 1 H, $J = 7.3$, 7.3 Hz), 7.34 (dd, 2 H, $J = 7.3$, 7.7 Hz), 7.32–7.25 (m, 10 H), 5.08 (s, 1 H, H-1), 4.92 (s, 1 H, H-1'), 4.58–4.31 (m, 7 H), 4.14–4.11 (m, 1 H), 3.96 (dd, 1 H, $J = 3.6$, 1.4 Hz), 3.87 (dd, 1 H, $J = 13.7$, 3.9 Hz), 3.81 (d, 1 H, $J = 3.3$ Hz), 3.76 (dd, 1 H, $J = 12.0$, 3.3 Hz), 3.72 (d, 1 H, $J = 3.3$ Hz), 3.56 (dd, 1 H, $J = 12.0$, 1.8 Hz), 3.35 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.4, 138.1, 137.8, 133.6, 130.2, 130.1, 128.8 (2), 128.3 (2), 128.2, 107.7 (C-1), 102.1 (C-1'), 88.3, 83.5, 80.9, 77.1, 76.4, 72.5, 72.4, 68.6, 64.7, 56.7, 55.5, 55.4; $^1J_{\text{C1,H1}} = 171.3$ (C-1'), 168.1 Hz (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{34}\text{O}_9$: 585.2095, found 585.2090.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-mannopyranoside (**64**). The compound was isolated after chromatography (4:1,

hexanes/EtOAc) as a colorless oil: R_f 0.33 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +19.4$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.12 (d, 2 H, $J = 7.3$ Hz), 7.60 (dd, 1 H, $J = 7.1$, 7.0 Hz), 7.49–7.24 (m, 17 H), 5.40 (s, 1 H, H-1'), 4.92 (d, 1 H, $J = 10.8$ Hz), 4.76 (s, 1 H, H-1), 4.74–4.72 (m, 3 H), 4.60–4.54 (m, 4 H), 4.40 (dd, 1 H, $J = 5.9$, 5.9 Hz), 4.12 (br s, 1 H), 3.96–3.77 (m, 7 H), 3.39 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 166.6, 138.9, 138.8, 138.6, 133.6, 130.3, 130.2, 129.0, 128.9, 128.8, 128.7, 128.3 (2), 128.2, 128.1 (2), 128.0, 103.0 (C-1'), 100.9 (C-1), 80.4, 75.5, 75.2, 74.9, 74.4, 73.8, 73.1, 72.0, 69.6, 63.2, 56.8, 55.1, 54.6; $^1J_{\text{C1,H1}} = 166.3$ Hz (C-1'), 172.1 (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2676, found 705.2671.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (**65**). The compound was isolated after chromatography (4:1;

hexanes/EtOAc) as a colorless oil: R_f 0.18 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +44.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 8.04 (d, 2 H, $J = 8.2$ Hz), 7.64 (dd, 1 H, $J = 8.2$, 8.1 Hz), 7.50 (dd, 2 H, $J = 8.2$, 8.1 Hz), 7.43–7.30 (m, 15 H), 5.44 (s, 1 H, H-1'), 5.03 (d, 1 H, $J = 11.0$ Hz), 4.92 (d, 1 H, $J = 11.0$ Hz), 4.85 (d, 1 H, $J = 11.1$ Hz), 4.82 (d, 1 H, $J = 11.0$ Hz), 4.72 (d, 1 H, $J = 11.1$ Hz), 4.65 (d, 1 H, $J = 3.4$ Hz, H-1), 4.55

(dd, 1 H, $J = 3.6, 9.6$ Hz), 4.51–4.43 (m, 2 H), 4.21 (d, 1 H, $J = 10.3$ Hz), 4.03 (dd, 1 H, $J = 8.2, 8.1$ Hz), 3.85–3.78 (m, 5 H), 3.60 (dd, 1 H, $J = 3.6, 9.6$ Hz), 3.42 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3) 166.4, 139.4, 139.0, 138.6, 133.8, 130.0, 129.9, 129.0, 128.8 (2), 128.5, 128.3, 128.0, 127.9, 101.9 (C-1'), 98.8 (C-1), 82.4, 80.2, 77.8, 76.5, 76.1, 75.5, 73.9, 70.4, 67.2, 65.1, 56.4 (2), 55.6; $^1J_{\text{C1,H1}} = 169.7$ Hz (C-1), 166.3 (C-1') Hz. HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2676, found 705.2647.

Methyl 3-*O*-(2,3-anhydro-5-*O*-benzoyl- β -D-ribofuranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene- β -D-glucopyranoside (66). The compound was isolated after chromatography (4:1, hexanes/EtOAc) as a colorless oil: R_f 0.27 (1:1, hexanes/EtOAc); $[\alpha]_D^{25} +67.2$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.98 (d, 2 H, $J = 7.1$ Hz), 7.52 (dd, 1 H, $J = 8.3, 8.3$ Hz), 7.50–7.30 (m, 12 H), 5.60 (s, 1 H), 5.58 (s, 1 H, H-1'), 5.00 (d, 1 H, $J = 12.2$ Hz), 4.81 (d, 1 H, $J = 12.2$ Hz), 4.67 (d, 1 H, $J = 3.4$ Hz, H-1), 4.63 (dd, 1 H, $J = 3.4, 4.5$ Hz), 4.50 (dd, 1 H, $J = 3.3, 11.9$ Hz), 4.37 (dd, 1 H, $J = 4.6, 11.9$ Hz), 4.32 (dd, 1 H, $J = 4.8, 10.1$ Hz), 4.27 (dd, 1 H, $J = 9.3, 9.3$ Hz), 3.87–3.85 (m, 2 H), 3.81 (d, 1 H, $J = 2.8$ Hz), 3.77–3.73 (m, 1 H), 3.66–3.59 (m, 2 H), 3.44 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 166.5, 138.9, 137.8, 133.7, 129.9, 129.8, 129.4, 129.0, 128.7 (2), 128.1, 126.4, 104.1, 101.9 (C-1'), 100.1 (C-1), 81.9, 79.2, 77.9, 76.7, 74.4, 69.5, 65.2, 62.6, 57.3, 57.2, 55.8; $^1J_{\text{C1,H1}} = 167.0$ Hz (C-1'), 171.6 Hz (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{33}\text{H}_{34}\text{O}_{10}$: 613.2050, found 613.2029.

Methyl 6-*O*-(2,3-anhydro-5-*O*-benzoyl- β -D-ribofuranosyl)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (67).

The compound was isolated after chromatography (4:1, hexanes/EtOAc) as a colorless oil: R_f 0.22 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +19.0$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.98 (dd, 2 H, $J = 1.0, 8.2$ Hz), 7.61 (dd, 1 H, $J = 8.2, 8.3$ Hz), 7.46–7.24 (m, 17 H), 5.50 (s, 1 H, H-1), 5.07 (d, 1 H, $J = 11.2$ Hz), 4.85 (d, 1 H, $J = 11.3$ Hz), 4.80 (d, 1 H, $J = 11.1$ Hz), 4.70–4.67 (m, 2 H), 4.60 (d, 1 H, $J = 11.3$ Hz), 4.53 (d, 1 H, $J = 11.3$ Hz), 4.50 (dd, 1 H, $J = 6.4, 6.5$ Hz), 4.26 (dd, 1 H, $J = 3.4, 12.0$ Hz), 4.40 (dd, 1 H, $J = 4.6, 12.0$ Hz), 4.04 (dd, 1 H, $J = 9.1, 9.2$ Hz), 3.87–3.77 (m, 4 H), 3.72 (d, 1 H, $J = 2.1$ Hz), 3.59 (dd, 1 H, $J = 3.5, 9.6$ Hz), 3.49 (d, 1 H, $J = 3.0$ Hz), 3.42 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 166.4, 139.3, 138.8, 138.4, 133.8, 129.9, 129.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5 (2), 128.3, 128.1 (2), 128.0, 127.8, 104.6 (C-1'), 98.3 (C-1), 81.7, 80.4, 78.5, 76.7, 76.1, 73.8, 73.6,

70.0, 68.9, 65.1, 57.0 (2), 55.5; $^1J_{\text{C1,H1}} = 168.4$ Hz (C-1), 163.3 Hz C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{42}\text{O}_{10}$: 705.2670, found 705.2697.

Methyl 2-*O*-(2,3-anhydro-5-*O*-benzoyl- α -D-ribofuranosyl)-3,5-di-*O*-benzyl- α -D-arabinofuranoside (68). The compound was isolated after chromatography in (2:1, hexanes/EtOAc) as a colorless oil: R_f 0.31 (2:1, hexanes/EtOAc); $[\alpha]_D^{25} +17.4$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , α_H) 8.04 (dd, 1 H, $J = 1.0, 8.2$ Hz), 7.65 (dd, 1 H, $J = 8.2, 8.3$ Hz), 7.51 (dd, 2 H, $J = 8.2, 8.3$ Hz), 7.39–7.27 (m, 10 H), 5.27 (s, 1 H, H-1'), 5.09 (s, 1 H, H-1), 4.67–4.58 (m, 5 H), 4.52 (dd, 1 H, $J = 2.8, 10.2$ Hz), 4.43 (dd, 1 H, $J = 2.8, 10.2$ Hz), 4.30 (dd, 1 H, $J = 0.8, 1.8$ Hz), 4.25–4.23 (m, 1 H), 3.95 (dd, 1 H, $J = 2.7, 5.2$ Hz), 3.81 (d, 1 H, $J = 2.8$ Hz), 3.69 (d, 1 H, $J = 2.8$ Hz), 3.67–3.63 (m, 2 H), 3.43 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , α_C) 166.4, 138.6, 138.4, 133.9, 130.0, 129.8, 129.0, 128.8, 128.7, 128.2, 128.1, 128.0, 108.1 (C-1), 101.6 (C-1'), 87.7, 84.2, 81.1, 76.7, 73.8, 72.7, 70.2, 64.9, 56.5, 56.4, 55.5; $^1J_{\text{C1,H1}} = 165.3$ Hz (C-1'), 175.5 Hz (C-1). HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{34}\text{O}_9$: 585.2101, found 585.2160.

***p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio- α -D-lyxofuranoside (70).** *p*-Tolyl 1-thio- α -D-arabinofuranoside¹¹ (0.2 g, 0.78 mmol), triphenylphosphine (0.52 g, 2.0 mmol) and benzoic acid (0.142 g, 1.2 mmol) were dissolved in THF (20 mL) and the solution was cooled to 0 °C. Diisopropylazodicarboxylate (0.386 mL, 1.95 mmol) was added dropwise over a period of 10 min. After the addition was complete, the reaction mixture was warmed to rt and stirred for 45 min. The solution was subsequently concentrated to yield a crude oil that, upon trituration with cold diethyl ether, precipitated triphenylphosphine oxide. The solid was filtered and the filtrate concentrated. The product was purified by chromatography (10:1 hexanes, EtOAc) to yield **70** (0.21 g, 81%) as a colorless oil: $R_f = 0.31$ (2:1, hexanes: EtOAc); $[\alpha]_D^{25} +56.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , α_H) 8.03 (d, 2 H, $J = 7.0$ Hz), 7.62 (dd, 1 H, $J = 7.0, 6.9$ Hz), 7.53–7.43 (m, 4 H), 7.16 (d, 2 H, $J = 8.0$ Hz), 5.49 (s, 1 H, H-1), 4.71 (dd, 1 H, $J = 3.7, 4.5$ Hz, H-4), 4.58 (dd, 1 H, $J = 3.7, 12.0$ Hz, H-5), 4.44 (dd, 1 H, $J = 4.5, 12.0$ Hz, H-5), 4.09 (d, 1 H, $J = 2.8$ Hz, H-2), 3.90 (d, 1 H, $J = 2.8$ Hz, H-3), 2.38 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , α_C) 166.5, 138.0, 133.8, 132.4, 130.7, 130.3, 130.0, 129.8, 129.0, 87.6 (C-1), 78.2 (C-4), 64.7 (C-5), 59.4 (C-2), 57.7 (C-3), 21.5. HRMS (ESI) calcd for (M+Na) $\text{C}_{19}\text{H}_{18}\text{O}_4\text{S}$: 365.0817, found 365.0853.

Methyl 6-*O*-(2-azido-5-*O*-benzoyl- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside

(**74a, de Benzoylated**). In order to separate the compound from other organic impurities it was necessary to remove the

benzoate ester with sodium methoxide. R_f = 0.57 (2:1, hexanes: EtOAc); $[\alpha]_D^{25} +71.0$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ) 7.41–7.33 (m, 15 H), 5.38 (s, 1 H, H-1'), 5.02 (d, 1 H, J = 11.0 Hz), 4.93–4.89 (m, 2 H), 4.85 (d, 1 H, J = 12.1 Hz), 4.81 (d, 1 H, J = 10.6 Hz), 4.73 (d, 1 H, J = 12.1 Hz), 4.67 (d, 1 H, J = 3.6 Hz, H-1), 4.27 (dd, 1 H, J = 4.1, 4.1, Hz), 4.19 (dd, 1 H, J = 2.3, 10.8 Hz), 4.03 (dd, 1 H, J = 9.1, 9.1 Hz), 3.85–3.59 (m, 8 H), 3.42 (s, 3 H); ¹³C NMR (125.7 MHz, CDCl₃, δ) 139.3, 139.1, 138.6, 128.9, 128.8 (2), 128.6, 128.5, 128.3 (2), 128.1, 127.9, 101.9 (C-1'), 98.8 (C-1), 82.4, 80.3, 79.4, 77.9, 76.1, 75.5, 73.9, 70.4, 67.1, 63.5, 57.1, 56.9, 55.6. HRMS (ESI) calcd for (M+Na) C₄₀H₄₃O₁₀N₃: 748.2846, found 748.2837.

Methyl 6-*O*-(2-deoxy- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (74b**)**

. R_f 0.21 (3:1, hexanes:EtOAc); $[\alpha]_D^{25} +41.7$ (c 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ) 7.42–7.31 (m, 15 H), 5.32 (d, 1 H, J = 4.2 Hz,

H-1'), 5.03 (d, 1 H, J = 10.8 Hz), 4.95 (d, 1 H, J = 10.9 Hz), 4.86 (d, 1 H, J = 11.3 Hz), 4.84 (d, 1 H, J = 11.3 Hz), 4.73–4.65 (m, 3 H), 4.27–4.18 (m, 2 H), 4.06–3.99 (m, 2 H), 3.85–3.75 (m, 1 H), 3.70–3.53 (m, 4 H), 3.51 (dd, 1 H, J = 9.5, 9.5 Hz), 3.41 (s, 3 H), 2.92 (d, 1 H, J = 6.7 Hz), 2.19–2.09 (m, 2 H); ¹³C NMR (125.7 MHz, CDCl₃, δ) 139.1, 138.7, 138.5, 128.9, 128.8, 128.4, 128.3, 128.2, 128.0, 104.6 (C-1'), 98.5 (C-1), 87.9, 82.4, 80.4, 78.7, 76.2, 75.5, 73.8, 73.2, 70.1, 66.1, 63.4, 55.6, 42.0 (C-2'). HRMS (ESI) calcd for (M+Na) C₃₃H₄₀O₉: 603.2564, found 603.2611.

Methyl 6-*O*-(2-*O*-benzyl- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (74c**)**

. R_f 0.34 (3:1, hexanes:EtOAc); $[\alpha]_D^{25} +31.0$ (c 0.9, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ) 7.41–7.35 (m, 20 H), 5.21 (s, 1 H, H-1'), 5.06

(d, 1 H, J = 10.9 Hz), 4.96 (d, 1 H, J = 11.0 Hz), 4.88 (d, 1 H, J = 10.9 Hz), 4.85 (d, 1 H, J = 10.9 Hz), 4.72 (d, 1 H, J = 10.9 Hz), 4.68–4.60 (m, 4 H), 4.19–4.18 (m, 1 H), 4.14 (dd, 1 H, J = 4.6, 5.2 Hz), 4.07 (dd, 1 H, J = 8.1, 8.2 Hz), 3.99 (d, 1 H, J = 1.0 Hz), 3.97 (dd, 1 H, J = 5.1, 7.2 Hz), 3.84–3.70 (m, 4 H), 3.57 (dd, 1 H, J = 5.2, 3.6 Hz), 3.53 (dd, 1 H, J = 6.3, 6.2 Hz) 3.43 (s, 3 H);

^{13}C NMR (125.7 MHz, CDCl_3 , $[\alpha]_D$) 138.6, 138.5, 137.5, 129.0 (2), 128.9 (3), 128.5, 128.4 (2), 128.3 (2), 128.2, 128.1, 127.4, 106.0 (C-1'), 98.5 (C-1), 87.8, 86.5, 82.4, 80.4, 78.6, 77.8, 76.2, 75.7, 75.5, 73.8, 72.3, 70.1, 66.0, 62.7, 55.7. HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{46}\text{O}_{10}$: 709.2989, found 709.2972.

Methyl 6-*O*-(2-*O*-allyl- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (74d). R_f 0.21 (3:1, hexanes:EtOAc); $[\alpha]_D$ +36.1 (c 1.1, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $[\alpha]_D$) 7.36–7.26 (m, 15 H), 5.90–5.80 (m, 1 H),

5.28 (dd, 1 H, J = 15.7, 1.7 Hz), 5.25 (dd, 1 H, J = 1.8, 8.9 Hz), 5.10 (s, 1 H, H-1'), 4.97 (d, 1 H, J = 13.5 Hz), 4.89 (d, 1 H, J = 12.9 Hz), 4.80 (d, 1 H, J = 12.8 Hz), 4.77 (d, 1 H, J = 13.0 Hz), 4.65 (d, 1 H, J = 13.1 Hz), 4.64–4.57 (m, 2 H), 4.06–4.01 (m, 6 H), 3.90–3.88 (m, 2 H), 3.75–3.64 (m, 4 H), 3.51 (dd, 1 H, J = 8.1, 4.4 Hz), 3.48 (dd, 1 H, J = 8.2, 8.1 Hz), 3.35 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $[\alpha]_D$) 139.0, 138.5, 138.3, 134.0, 128.9, 128.8 (2), 128.4, (2), 128.3, 128.1 (2), 118.3, 105.9 (C-1'), 98.4 (C-1), 87.5, 86.6, 82.3, 80.3, 78.6, 76.2, 75.7, 75.4, 73.7, 71.0, 70.0, 65.9, 62.7, 55.6. HRMS (ESI) calcd for (M+Na) $\text{C}_{36}\text{H}_{44}\text{O}_{10}$: 659.2826, found 659.2850.

Methyl 6-*O*-(3-azido-3-deoxy- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (76a) and Methyl 6-*O*-(2-azido-2-deoxy- α -D-xylofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (77a). Isolated as a mixture: ^1H anomeric 5.08 (s, 1 H), (xylo), 5.01 (d, 1 H, J = 4.9 Hz) (arabino); ^{13}C 106.4 (xylo), 102.7 (arabino) HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{43}\text{O}_{10}\text{N}_3$: 748.2846, found 748.2830.

Methyl 6-*O*-(3-deoxy- α -D-threo-pentofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (76b) and Methyl 6-*O*-(2-deoxy- α -D-erythro-pentofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (77b). Isolated as a mixture: ^1H anomeric 5.10 (dd, 1 H J = 4.8, 0.8 Hz) (xylo), 5.02 (d, 1 H, J = 4.8 Hz) (arabino); ^{13}C 106.8 (xylo), 101.8 (arabino) HRMS (ESI) calcd for (M+Na) $\text{C}_{33}\text{H}_{40}\text{O}_9$: 603.2570, found 603.2555.

Methyl 6-*O*-(3-*O*-benzyl- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (76c).

R_f 0.23 (2:1, hexanes:EtOAc); $[\alpha]_D^{25} +22.9$ (c 1.1, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 7.44–7.32 (m, 20 H), 5.03 (s, 1 H, H-1), 5.01–4.99 (m, 2 H), 4.95–4.61 (m, 9 H), 4.26–4.24 (m, 1 H), 4.10–4.05 (m, 1 H), 4.00–3.97 (m, 1 H), 3.91–3.85 (m, 2 H), 3.83 (d, 1 H, J = 1 Hz), 3.77 (dd, 1 H, J = 8.0, 8.3 Hz), 3.66 (d, 1 H, J = 10.1 Hz), 3.55 (dd, 1 H, J = 6.8, 12.2 Hz), 3.57–3.53 (m, 1 H), 3.41 (s, 3 H), 2.74 (d, 1 H, J = 10.1 Hz), 2.10 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 139.1, 138.8, 138.6, 138.3, 129.0, 128.9, 128.8 (4), 128.5, 128.3, 128.2 (2), 128.1, 128.0 (2), 103.3 (C-1'), 99.4 (C-1), 83.1, 82.9, 79.3, 78.6, 75.5, 74.9, 74.1, 74.0, 72.4, 70.2, 69.8, 63.6, 56.1. HRMS (ESI) calcd for (M+Na) $\text{C}_{40}\text{H}_{46}\text{O}_{10}$: 709.2989, found 709.2969.

Methyl 6-*O*-(3-*O*-allyl- α -D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (76d) and Methyl 6-*O*-(2-*O*-benzyl- α -D-xylofuranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (77d).

Isolated as a mixture: ^1H anomeric 5.09 (s, 1 H), (xylo), 5.02 (d, 1 H, J = 4.9 Hz) (arabino); ^{13}C 106.8 (xylo), 103.2 (arabino) HRMS (ESI) calcd for (M+Na) $\text{C}_{36}\text{H}_{44}\text{O}_{10}$: 659.2823, found 659.2839.

Methyl-5-*O*-(3-*O*-benzyl- α -D-arabinofuranosyl)-2,3-di-*O*-benzyl- α -D-arabinofuranoside (76e).

R_f 0.27 (2:1, hexanes:EtOAc); $[\alpha]_D^{25} +33.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ) 7.41–7.32 (m, 15 H), 5.02 (s, 1 H, H-1), 4.94 (d, 1 H, J = 4.9 Hz, H-1'), 4.82 (d, 1 H, J = 11.7 Hz), 4.65–4.58 (m, 3 H), 4.51 (d, 1 H, J = 11.8 Hz), 4.47 (d, 1 H, J = 12.1 Hz), 4.31–4.28 (m, 2 H), 4.12 (dd, 1 H, J = 6.2, 6.2 Hz), 4.09–4.06 (m, 1 H), 4.04 (dd, 1 H, J = 1.0, 2.4 Hz), 3.96 (d, 1 H, J = 11.3 Hz), 3.90 (dd, 1 H, J = 2.3, 5.7 Hz), 3.78 (br d, 1 H, J = 12.5 Hz), 3.65 (dd, 1 H, J = 5.0, 11.3 Hz), 3.58 (m, 1 H), 3.44 (s, 3 H), 3.02 (br d, 1 H, J = 7.3 Hz), 2.85 (d, 1 H, J = 10.6 Hz); ^{13}C NMR (125.7 MHz, CDCl_3 , δ) 138.5, 137.9, 137.6, 128.9 (2), 128.8, 128.6, 128.5, 128.4 (2), 128.2, 128.1, 107.9 (C-1), 102.4 (C-1'), 87.9, 83.6, 83.5, 82.7, 81.6, 79.1, 72.7, 72.6, 72.5, 68.9, 63.2, 55.7. HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{38}\text{O}_9$: 589.2408, found 589.2432.

Octyl 3-*O*-benzyl- α -D-arabinofuranoside (76f). $R_f = 0.27$ (2:1, hexanes: EtOAc); $[\alpha]_D^{+22.0}$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α_H) 7.41–7.31 (m, 5 H), 5.04 (d, 1 H, $J = 4.9$ Hz, H-1), 4.87 (d, 1 H, $J = 11.8$ Hz), 4.66 (d, 1 H, $J = 11.8$ Hz), 4.32–4.28 (m, 1 H), 4.12–4.09 (m, 1 H), 3.92–3.87 (m, 2 H), 3.52 (ddd, 1 H, $J = 6.7, 6.7, 9.5$, octyl CH₂), 3.40–3.33 (m, 2 H), 2.65 (br s, 1 H), 1.69–1.63 (m, 2 H), 1.39–1.31 (m, 10 H), 0.93 (dd, 3 H, $J = 6.8, 7.0$ Hz); ¹³C NMR (125.7 MHz, CDCl₃, α_C) 138.2, 128.9, 128.3, 128.2, 102.2 (C-1), 85.1, 80.9, 78.2, 72.5, 69.4, 54.7, 32.2, 29.9, 29.8, 29.6, 26.5, 23.1, 14.5. HRMS (ESI) calcd for (M+Na) C₂₉H₃₂O₅: 375.2147, found 375.2159.

Methyl-5-*O*-(2,3-anhydro- α -L-lyxofuranosyl)-2,3-di-*O*-benzyl- α -D-arabinofuranoside (84) and Methyl-5-*O*-(2,3-anhydro- α -D-lyxofuranosyl)-2,3-di-*O*-benzyl- α -L-arabinofuranoside (85) and Methyl-5-*O*-(2,3-anhydro- α -L-lyxofuranosyl)-2,3-di-*O*-benzyl- α -L-arabinofuranoside (86). These disaccharides were assembled from the appropriate donors and acceptors using glycosylation method A (See Experimental and Table 1 Legend). Disaccharide **86** was prepared from **S7** and **S3**; **87** was prepared from **S7** and **1**; **84** was prepared from **26** and **1**. All disaccharides were deprotected (without purification) following the glycosylation by treatment with NaOCH₃ (0.5 mL, 1M soln. in MeOH) in CH₃OH (5 mL) and stirring at rt for 1 h. The resulting solution was neutralized with acetic acid (0.1 mL), concentrated and the products were purified by chromatography (10:1 hexanes/EtOAc) to yield the products, all as oils.

(84): R_f 0.27 (2:1, hexanes/EtOAc); $[\alpha]_D^{+36.4}$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α_H) 7.41–7.32 (m, 10 H), 5.23 (s, 1 H, H-1'), 4.98 (s, 1 H, H-1), 4.65–4.52 (m, 4 H), 4.24 (ddd, 1 H, $J = 3.5, 6.5, 6.5$ Hz), 4.08–4.06 (m, 2 H), 4.01–3.97 (m, 2 H), 3.92–3.85 (m, 3 H), 3.70 (d, 1 H, $J = 2.9$ Hz), 3.68 (d, 1 H, $J = 2.9$ Hz), 3.43 (s, 3 H), 2.46 (br s, 1 H); ¹³C NMR (125.7 MHz, CDCl₃, α_C) 138.3, 137.9, 128.8 (2), 128.3 (2), 128.2, 107.8 (C-1), 102.2 (C-1'), 88.5, 83.5, 81.6, 77.1, 72.7, 72.3, 68.5, 62.2, 55.9, 55.4, 55.1; $^1J_{C1,H1} = 169.0$ Hz (C-1), 169.5 Hz (C-1'). HRMS (ESI) calcd for (M+Na) C₂₅H₃₀O₈: 481.1833, found 481.1821.

(85): R_f 0.31 (2:1, hexanes/EtOAc); $[\alpha]_D^{-29.1}$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α_H) 7.41–7.31 (m, 10 H), 5.23 (s, 1 H, H-1'), 4.98 (s, 1 H, H-1), 4.65–4.51 (m, 4 H), 4.24 (ddd, 1 H, $J = 3.5, 6.5, 6.5$

Hz), 4.07–4.04 (m, 2 H), 4.02–3.96 (m, 2 H), 3.92–3.88 (m, 2 H), 3.70–3.67 (m, 2 H), 3.43 (s, 3 H), 2.47 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $\square_{\text{C}}$) 138.3, 137.9, 128.9, 128.8, 128.4, 128.3, 128.2, 107.8 (C-1), 102.1 (C-1'), 88.4, 83.5, 81.6, 77.1, 72.7, 72.3, 68.5, 62.2, 55.9, 55.4, 55.1; $^1J_{\text{C1,H1}} = 169.0$ Hz (C-1), 169.5 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{25}\text{H}_{30}\text{O}_8$: 481.1833, found 481.1810.

(86): R_f 0.22 (2:1, hexanes/EtOAc); $[\square]_{\text{D}} -20.1$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $\square_{\text{H}}$) 7.41–7.31 (m, 10 H), 5.18 (s, 1 H, H-1'), 4.98 (s, 1 H, H-1), 4.63–4.50 (m, 4 H), 4.28 (ddd, 1 H, $J = 3.5, 6.5, 6.5$, Hz), 4.04–3.98 (m, 3 H), 3.92–3.85 (m, 3 H), 3.80 (dd, 1 H, $J = 6.5, 11.5$ Hz), 3.72 (s, 2 H), 3.43 (s, 3 H), 2.49 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $\square_{\text{C}}$) 138.2, 137.9, 128.9, 128.8, 128.4, 128.2, 107.8 (C-1), 101.9 (C-1'), 88.5, 83.9, 81.2, 77.1, 72.6, 72.4, 69.5, 62.2, 55.9, 55.4, 55.2; $^1J_{\text{C1,H1}} = 169.0$ Hz (C-1), 169.5 Hz (C-1'). HRMS (ESI) calcd for (M+Na) $\text{C}_{25}\text{H}_{30}\text{O}_8$: 481.1833, found 481.1813.

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Methyl-5-O-(3-O-benzyl-L-arabinofuranosyl)-2,3-di-O-benzyl-D-arabinofuranoside (87). R_f 0.22 (2:1, hexanes:EtOAc); $[\square]_{\text{D}} -22.4$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $\square_{\text{H}}$) 7.42–7.33 (m, 15 H), 5.00 (s, 2 H, H-1, H-1'), 4.84 (d, 1 H, $J = 12.1$ Hz), 4.65–4.58 (m, 3 H), 4.53 (d, 1 H, $J = 11.8$ Hz), 4.48 (d, 1 H, $J = 12.0$ Hz), 4.31–4.28 (m, 1 H), 4.24 (ddd, 1 H, $J = 2.4, 6.1, 6.1$ Hz), 4.12 (dd, 1 H, $J = 6.3, 6.3$ Hz), 4.09–4.06 (m, 1 H), 4.04 (d, 1 H, $J = 2.1$ Hz), 3.90 (dd, 1 H, $J = 5.6, 10.6$ Hz), 3.88 (dd, 1 H, $J = 5.6, 10.6$ Hz), 3.80–3.75 (m, 2 H), 3.59–3.57 (m, 1 H), 3.41 (s, 3 H), 3.01 (br d, 1 H, $J = 10.1$ Hz), 2.78 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , $\square_{\text{C}}$) 138.5, 137.9, 137.6, 128.9 (2), 128.8, 128.5, 128.4, 128.3 (2), 128.1, 107.9 (C-1), 102.8 (C-1'), 87.9, 83.9, 83.3, 82.7, 81.3, 78.9, 72.7, 72.6, 72.5, 69.5, 63.4, 55.5. HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{38}\text{O}_9$: 589.2408, found 589.2429.

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Methyl-5-O-(3-O-benzyl-L-arabinofuranosyl)-2,3-di-O-benzyl-L-arabinofuranoside (88). R_f 0.22 (2:1, hexanes:EtOAc); $[\square]_{\text{D}} +19.9$ (c 1.1, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , $\square_{\text{H}}$) 7.42–7.33 (m, 15 H), 4.99 (s, 2 H, H-1, H-1'), 4.84 (d, 1 H, $J = 12.1$ Hz), 4.65–4.58 (m, 3 H), 4.53 (d, 1 H, $J = 11.8$ Hz), 4.48 (d, 1 H, $J = 12.0$ Hz), 4.31–4.28 (m, 1 H), 4.24 (ddd, 1 H, $J = 2.4, 6.1, 6.1$ Hz), 4.12 (dd, 1 H, $J = 6.3, 6.3$ Hz), 4.09–4.06 (m, 1 H), 4.04 (d, 1 H, $J = 2.1$ Hz),

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3.88 (dd, 1 H, $J = 5.6, 11.3$ Hz), 4.09–4.07 (m, 1 H), 3.90 (dd, 1 H, $J = 5.6, 10.6$ Hz), 3.88 (dd, 1 H, $J = 5.6, 10.6$ Hz), 3.80–3.75 (m, 2 H), 3.59–3.57 (m, 1 H), 3.43 (s, 3 H), 3.01 (br d, 1 H, $J = 10.1$ Hz), 2.78 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 138.5, 137.9, 137.6, 128.9 (2), 128.8, 128.5, 128.4, 128.3 (2), 128.1, 107.9 (C-1), 102.8 (C-1'), 87.9, 83.9, 83.3, 82.7, 81.3, 78.9, 72.7, 72.6, 72.5, 69.5, 63.4, 55.5. HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{38}\text{O}_9$: 589.2408, found 589.2433.

Methyl-5-*O*-(3-*O*-benzyl- β -L-arabinofuranosyl)-2,3-di-*O*-benzyl- β -L-arabinofuranoside (89). R_f 0.27 (2:1, hexanes:EtOAc);

$[\alpha]_{\text{D}}^{25}$ +31.0 (c 0.9, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.43–7.31 (m, 15 H), 5.02 (s, 1 H, H-1), 4.93 (d, 1 H, $J = 4.9$ Hz, H-1'), 4.82 (d, 1 H, $J = 11.7$ Hz), 4.65–4.58 (m, 3 H), 4.51 (d, 1 H, $J = 11.8$ Hz), 4.47 (d, 1 H, $J = 12.1$ Hz), 4.31–4.28 (m, 2 H), 4.12 (dd, 1 H, $J = 6.2, 6.2$ Hz), 4.09–4.06 (m, 1 H), 4.04 (dd, 1 H, $J = 1.0, 2.4$ Hz), 3.96 (dd, 1 H, $J = 2.7, 11.3$ Hz), 3.90 (dd, 1 H, $J = 2.3, 5.7$ Hz), 3.78 (br d, 1 H, $J = 12.5$ Hz), 3.65 (dd, 1 H, $J = 5.0, 11.3$ Hz), 3.58 (m, 1 H), 3.45 (s, 3 H), 3.04 (br s, 1 H), 2.85 (br d, 1 H, $J = 10.6$ Hz); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 138.5, 137.9, 137.6, 128.9 (2), 128.8, 128.6, 128.5, 128.4 (2), 128.2, 128.1, 107.9 (C-1), 102.4 (C-1'), 87.9, 83.6, 83.5, 82.7, 81.6, 79.1, 72.7, 72.6, 72.5, 68.9, 63.2, 55.7. HRMS (ESI) calcd for (M+Na) $\text{C}_{32}\text{H}_{38}\text{O}_9$: 589.2408, found 589.2420.

***p*-Tolyl 2-*O*-benzoyl-3,5-di-*O*-benzyl-1-thio- β -D-arabinofuranoside (94).** To a solution of **95** (1.90 g, 4.24 mmol) in dry CH_2Cl_2 (30 mL) was added *p*-thiocresol (0.63 g, 5.08 mmol) at 0 °C. $\text{BF}_3\text{-OEt}_2$ (0.9 mL, 8.43 mmol) was added dropwise to the solution over 5 min. The solution was stirred for 1 h at 0 °C followed by the addition of triethylamine (1 mL). After dilution with CH_2Cl_2 , the organic layer was washed with a satd. aq. solution of NaHCO_3 and dried (Na_2SO_4), filtered and concentrated. The resulting oil was purified by column (10:1, hexanes/EtOAc) providing **94** (2.14 g, 93%) as a colorless oil: R_f 0.65 (6:1, hexanes:EtOAc); $[\alpha]_{\text{D}}^{25}$ +28.3 (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 8.05 (dd, 2 H, $J = 6.6, 1.1$ Hz), 7.63 (dd, 1 H, $J = 6.6, 6.4$ Hz), 7.53 (d, 2 H, $J = 8.1$ Hz), 7.48–7.30 (m, 12 H), 7.18 (d, 2 H, $J = 8.1$ Hz), 5.74 (s, 1 H, H-1), 5.64 (dd, 1 H, $J = 3.0, 1.5$ Hz, H-2), 4.89 (d, 1 H, $J = 12.0$ Hz), 4.70–4.56 (m, 4 H), 4.23 (m, 1 H, H-3), 3.78 (dd, 1 H, $J = 4.0, 10.8$ Hz, H-5), 3.74 (dd, 1 H, $J = 4.6, 10.8$ Hz, H-5), 2.39 (s, 3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 165.9, 138.4, 138.1, 137.9, 133.9, 132.9, 131.1, 130.3, 130.1, 129.8, 129.0, 128.9,

128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 92.0 (C-1), 83.7, 82.8, 82.5, 73.8, 72.8, 69.4, 21.6. HRMS (ESI) calcd for (M+Na) C₃₃H₃₂O₅S: 563.1862, found 563.1897.

Methyl 2-*O*-benzoyl-3,5-di-*O*-benzyl- α -D-arabinofuranoside (95).

To a solution of **34** (1.60 g, 4.65 mmol) in pyridine (20 mL) at 0 °C was added benzoyl chloride (0.7 mL, 6.0 mmol) dropwise. The reaction mixture was

stirred for 30 min at room temperature, before being diluted with CH₂Cl₂. The organic layer was washed with aq. 1N HCl, a satd. aq. solution of NaHCO₃, and brine. The organic layer was subsequently dried (Na₂SO₄), filtered, and concentrated. The resulting oil was purified by chromatography (10:1, hexanes/EtOAc) providing **95** (1.95 g, 94%) as a colorless syrup: *R_f* 0.51 (6:1, hexanes:EtOAc); [α]_D +26.9 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α _H) 8.06 (dd, 2 H, *J* = 6.6, 1.1 Hz), 7.63 (dd, 1 H, *J* = 6.6, 6.4 Hz), 7.49–7.46 (m, 2 H), 7.41–7.31 (m, 10 H), 5.46 (d, 1 H, *J* = 1.2 Hz, H-2), 5.17 (s, 1 H, H-1), 4.88 (d, 1 H, *J* = 12.2 Hz), 4.69 (d, 1 H, *J* = 12.2 Hz), 4.64 (d, 1 H, *J* = 12.1 Hz), 4.59 (d, 1 H, *J* = 12.2 Hz), 4.41 (ddd, 1 H, *J* = 5.2, 5.2, 3.6 Hz, H-4), 4.10 (d, 1 H, *J* = 5.3 Hz, H-3), 3.74 (dd, 1 H, *J* = 3.6, 10.7 Hz, H-5), 3.68 (dd, 1 H, *J* = 5.2, 10.7 Hz, H-5), 3.53 (s, 3 H). ¹³C NMR (125.7 MHz, CDCl₃, β) 165.9, 138.4, 138.1, 133.8, 130.2, 129.9, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 107.7 (C-1), 83.7, 82.6, 82.3, 73.9, 72.8, 69.9, 55.4. HRMS (ESI) calcd for (M+Na) C₂₇H₂₈O₆: 471.1778, found 471.1776.

Methyl 5-*O*-(2-*O*-benzyl- α -D-arabinofuranosyl)-2,3-di-*O*-benzyl- α -D-arabinofuranoside (96). To a solution of **63** (1.10 g, 1.95 mmol) in benzyl alcohol (5 mL) was added sodium benzyolate solution (prepared by dissolving sodium (0.18 g, 7.8 mmol) in benzyl alcohol (5

mL). The reaction mixture was heated at 120 °C for 3 h and then cooled and neutralized with acetic acid. After dilution with CH₂Cl₂ (100 mL) the reaction mixture was washed with water (2 x 50 mL), dried (Na₂SO₄), filtered, and concentrated to obtain the crude product which was purified by chromatography (1:1, hexanes/EtOAc,) to yield **96** (0.92 g, 84%) as a colorless oil: *R_f* 0.15 (3:1, hexanes:EtOAc); [α]_D + 51.3 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α _H) 7.40–7.30 (m, 15 H), 5.16 (s, 1 H, H-1'), 4.96 (s, 1 H, H-1), 4.65–4.49 (m, 5 H), 4.42 (d, 1 H, *J* = 12.3 Hz), 4.22–4.19 (m, 1 H), 4.12 (br d, 1 H, *J* = 8.7 Hz), 4.00 (d, 1 H, *J* = 1.5 Hz), 3.96 (s, 1 H), 3.90 (dd, 1 H, *J* = 3.3, 3.1 Hz), 3.86–3.68 (m, 5 H), 3.40 (s, 3 H), 3.07 (d, 1 H, *J* = 11.4 Hz), 2.19 (dd, 1 H, *J* = 4.6, 7.0 Hz); ¹³C NMR (125.7 MHz, CDCl₃, β _C) 137.8, 137.6, 137.4, 129.0, 128.9 (2), 128.6, 128.5 (2), 128.4, 128.3 (2), 107.6 (C-1), 105.5 (C-1'), 87.7, 87.3, 87.1, 83.9,

81.4, 75.6, 72.5, 72.4, 72.1, 66.1, 63.1, 55.3. HRMS (ESI) calcd for (M+Na) C₃₂H₃₈O₉: 589.2408, found 589.2432.

Methyl 5-*O*-[3,5-di-*O*-(3,5-di-*O*-benzyl-2-*O*-benzoyl- β -D-arabinofuranosyl)-2-*O*-benzyl- β -D-arabinofuranosyl]-2,3-di-*O*-benzyl- β -D-arabinofuranoside (97).

To a mixture of alcohol **96** (0.65 g, 1.14 mmol) donor **94** (2.04 g, 3.70 mmol) and 4Å molecular sieves (1.0 g) was added CH₂Cl₂ (40 mL). The mixture was cooled to 0 °C and then *N*-iodosuccinimide (1.02 g, 4.50 mmol) and silver triflate (0.190 g, 0.73 mmol) were added. After stirring for 20 min at this temperature, the reaction mixture turned dark red/brown and then triethylamine (1.5 mL) was added. The reaction mixture was diluted with CH₂Cl₂ and filtered through a pad of Celite. The filtrate was concentrated and the resulting residue was purified by chromatography (6:1, hexanes/EtOAc) to obtain **97** (1.31 g, 81%) as a colorless oil: *R_f* 0.45 (3:1, hexanes:EtOAc); [α]_D + 36.2 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, [H]) 8.02–8.00 (m, 4 H), 7.37–7.24 (m, 41 H), 5.52 (d, 1 H, *J* = 1.2 Hz), 5.41 (d, 1 H, *J* = 1.2 Hz), 5.37 (s, 1 H, H-1'''), 5.36 (s, 1 H, H-1''), 5.29 (d, 1 H, *J* = 1.6 Hz, H-1'), 4.97 (s, 1 H, H-1), 4.84 (d, 1 H, *J* = 12.3 Hz), 4.78 (d, 1 H, *J* = 12.3 Hz), 4.65–4.48 (m, 12 H), 4.46 (dd, 1 H, *J* = 1.8, 7.6 Hz), 4.36 (dd, 1 H, *J* = 3.3, 8.1 Hz), 4.20–4.15 (m, 3 H), 4.12–4.05 (m, 5 H), 3.92 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.86 (dd, 1 H, *J* = 3.7, 9.7 Hz), 3.74–3.61 (m, 6 H), 3.42 (s, 3 H); ¹³C NMR (125.7 MHz, CDCl₃, [C]) 165.7, 165.6, 138.6, 138.5, 138.4, 138.2, 130.3, 130.2, 128.8, 128.7 (2), 128.4, 128.3 (3), 128.2, 128.0 (2), 127.9 (3), 107.7 (C-1), 106.8, 106.7 (C-1'', C-1'''), 105.5 (C-1') 88.8, 83.9, 83.6 (2), 83.4, 82.8, 82.7, 82.6 (2), 82.1, 82.0, 81.0, 80.9, 80.7, 73.8, 72.8, 72.5, 72.4, 72.3, 69.7, 69.5, 66.8, 55.4. HRMS (ESI) calcd for (M+Na) C₈₄H₈₆O₁₉: 1421.5655, found 1421.5558.

Methyl 5-*O*-[3,5-di-*O*-(3,5-di-*O*-benzyl- β -D-arabinofuranosyl)-2-*O*-benzyl- β -D-arabinofuranosyl]-2,3-di-*O*-benzyl- β -D-arabinofuranoside (98).

To a solution of **97** (1.10 g, 0.78 mmol) in CH₃OH:CH₂Cl₂ (60 mL, 3:1) was added 0.1 M NaOCH₃ in CH₃OH (2 mL). After stirring for 8 h at rt, the reaction mixture was neutralized with Amberlite IR-120 H+ resin, filtered, and concentrated to an oil which was purified by chromatography (2:1, hexanes/EtOAc) to yield **98** (0.91 g, 98%) as a colorless oil: *R_f* 0.61 (2:1, hexanes:EtOAc); [α]_D

+29.1 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_{H}) 7.37–7.28 (m, 35 H), 5.18 (s, 1 H, H-1'), 5.13 (s, 1 H, H-1''), 5.11 (s, 1 H, H-1'''), 4.95 (s, 1 H, H-1), 4.67–4.45 (m, 15 H), 4.37 (dd, 1 H, *J* = 3.4, 6.2 Hz), 4.34–4.33 (m, 1 H), 4.28–4.27 (m, 1 H), 4.25–4.11 (m, 7 H), 4.10–4.02 (m, 2 H), 4.00 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.85–3.90 (m, 3 H), 3.75 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.71 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.64–3.60 (m, 2 H), 3.52–3.49 (m, 2 H), 3.41 (s, 3 H), 3.35 (d, 1 H, *J* = 8.7 Hz), 3.32 (d, 1 H, *J* = 9.1 Hz); ¹³C NMR (125.7 MHz, CDCl₃, δ_{C}) 138.3, 129.0, 128.9 (2), 128.8 (2), 128.4 (2), 128.3 (2), 128.2 (3), 128.1 (2), 128.0, 109.6 (C-1), 108.2 (C-2''), 107.6 (C-2'''), 106.6 (C-1'), 88.8, 88.2, 85.4, 85.1, 83.7, 83.6, 82.8, 81.2, 80.8, 79.6, 78.9, 78.7, 74.1, 74.0, 72.7, 72.5 (2), 72.3, 72.2, 70.2, 70.1, 66.4, 66.3, 55.4. HRMS (ESI) calcd for (M+Na) C₇₀H₇₈O₁₇: 1213.5131, found 1213.5028.

Methyl 5-*O* - {3,5-di-*O*-(2-*O*-[2,3-anhydro-5-*O*-benzoyl- β -D-arabinofuranosyl]-3,5-di-*O*-benzyl- β -D-arabinofuranosyl)-2-*O*-benzyl- β -D-arabinofuranoside (99).

Sulfoxide **2** (0.586 g, 1.63 mmol), 2,6-di-*tert*-butyl-4-methyl pyridine (0.67 g 3.26 mmol), and 4Å molecular sieves (0.6 g) were dried under vacuum in the presence of P₂O₅. To this mixture was added CH₂Cl₂ (20 mL) and the reaction mixture was cooled to –78 °C and Tf₂O (0.36 mL, 1.77 mmol) was added. The reaction mixture was allowed to warm slowly to –40 °C and stirred for 10 min. The reaction mixture was subsequently cooled to –78 °C and a solution of **98** (0.65 g, 0.54 mmol) in CH₂Cl₂ (10 mL) was added (via syringe) over a 5 min period. A satd. aq. NaHCO₃ solution was added and the mixture was allowed to warm to rt over 30 min. The resulting mixture was diluted with CH₂Cl₂ and filtered through Celite. The filtrate was dried (Na₂SO₄), filtered, and concentrated to yield the crude product that was purified by chromatography (2:1, hexanes/EtOAc) to yield **99** (0.66 g, 74%) as a colorless oil: *R_f* 0.52 (1:1, hexanes:EtOAc); $[\alpha]_{\text{D}}^{25}$ +69.1 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_{H}) 8.05 (d, 4 H, *J* = 7.0 Hz), 7.55 (dd, 2 H, *J* = 7.3, 7.2 Hz), 7.43 (dd, 4 H, 7.3, 7.2 Hz), 7.36–7.25 (m, 35 H), 5.22 (d, 1 H, *J* = 1.4 Hz), 5.21 (d, 1 H, *J* = 0.9 Hz), 5.19 (s, 1 H), 5.15 (s, 1 H), 5.06 (s, 1 H), 4.93 (s, 1 H), 4.74 (d, 1 H, *J* = 12.3 Hz), 4.69 (d, 1 H, *J* = 12.3 Hz), 4.61–4.48 (m, 14 H), 4.40 (dd, 1 H, *J* = 1.6, 7.1 Hz), 4.39–4.35 (m, 2 H), 4.25–4.23 (m, 1 H), 4.19–4.01 (m, 10 H), 3.88 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.81 (dd, 1 H, *J* = 3.3, 8.1 Hz), 3.69–3.59 (m, 10 H), 3.39 (s,

3 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 166.6, 166.5, 138.6 (2), 137.9, 133.6, 133.5, 130.2, 128.9, 128.8 (2), 128.7 (2), 128.6 (2), 128.4, 128.3 (3), 128.2, 128.1, 127.9 (2), 107.7, 107.3, 106.6, 106.3, 102.1, 101.8, 88.8, 88.6, 88.3, 83.8, 83.5, 83.4, 81.5, 80.9, 80.8, 75.1, 74.9, 73.7, 72.8, 72.5, 72.4, 72.2, 70.0, 69.9, 66.6, 63.6, 56.5, 56.4, 55.5, 55.4 (2); $^1J_{\text{C1,H1}} = 164.1, 163.2$ Hz (anhydrosugar residues only). HRMS (ESI) calcd for $(\text{M}+\text{Na}) \text{C}_{94}\text{H}_{98}\text{O}_{25}$: 1650.6322, found 1650.5871.

Methyl 5-*O*-{3,5-di-*O*-(2-*O*-[3-*O*-benzyl- β -D-arabinofuranosyl]-3,5-di-*O*-benzyl- β -D-arabinofuranosyl)-2-*O*-benzyl- β -D-arabinofuranosyl}-2,3-di-*O*-benzyl- β -D-arabinofuranoside (100). To a solution of benzyl alcohol (1.5 mL) was added lithium (25 mg, 3.69 mmol) and the solution was stirred at 65 °C for 15 min followed by the addition of (β)-sparteine (0.18 mL, 3.69 mmol). After cooling to rt, the mixture was added via cannula to a solution of **99** (0.31 g, 0.18 mmol) in benzyl alcohol (2 mL) and the reaction

was stirred for 20 min at 70 °C. The reaction mixture was neutralized with acetic acid and the compound was extracted into CH_2Cl_2 . The organic layer was washed with water, dried, filtered, and concentrated to yield a crude oil that was purified by chromatography (4:1, hexanes/EtOAc) to give **100** (0.212 g, 71%) as a colorless oil: R_f 0.51 (1:1, hexanes:EtOAc); $[\alpha]_{\text{D}}^{25} +31.7$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.39–7.30 (m, 45 H), 5.21 (s, 1 H), 5.19 (s, 1 H), 5.15–5.14 (m, 2 H), 5.0 (d, 1 H, $J = 4.8$ Hz), 4.97 (s, 1 H), 4.84 (d, 1 H, $J = 12.2$ Hz), 4.69–4.44 (m, 18 H), 4.36–4.35 (m, 2 H), 4.22–4.11 (m, 8 H), 4.06–3.90 (m, 8 H), 3.89 (dd, 1 H, $J = 3.3, 8.3$ Hz), 3.81 (dd, 1 H, $J = 3.3, 8.3$ Hz), 3.72–3.77 (m, 1 H), 3.70–3.60 (m, 4 H), 3.60–3.50 (m, 4 H), 3.42 (s, 3 H), 2.78 (d, 1 H, $J = 8.1$ Hz), 2.74 (d, 1 H, $J = 8.1$ Hz), 2.41 (br s, 1 H), 2.33 (br s, 1 H); ^{13}C NMR (125.7 MHz, CDCl_3 , δ_{C}) 137.9 (2), 137.8, 137.7, 128.3 (2), 127.9 (2), 127.8 (2), 127.7, 127.6 (2), 127.5, 107.2, 106.2, 106.0, 105.1, 101.5, 101.4, 88.2, 83.2, 82.4 (2), 82.3 (2), 77.7, 77.6, 73.4, 73.3, 72.3, 72.0 (3), 71.9, 71.8, 69.0, 63.1, 63.0, 54.9. HRMS (ESI) calcd for $(\text{M}+\text{Na}) \text{C}_{94}\text{H}_{106}\text{O}_{25}$: 1658.6948, found 1658.6988

***p*-Tolyl 1-thio- α -L-arabinofuranoside (S2).** To a solution of **S1**¹² (2.5 g, 5.3 mmol) and *p*-thiocresol (0.85 g, 6.8 mmol) in CH₂Cl₂ at 0 °C was added BF₃-OEt₂ (1.5 mL, 10.6 mmol) dropwise over the course of 15 min. The reaction mixture was allowed to warm to rt over 2 h followed by the addition of

triethylamine (0.8 mL, 11 mmol). The resulting solution was diluted with CH₂Cl₂ and washed with satd. aq. NaHCO₃ solution and water. The organic layer was dried, filtered, and concentrated. The product was redissolved in MeOH (50 mL) and CH₂Cl₂ (50 mL) and then NaOCH₃ (1 mL, 1 M solution in MeOH) was added. The resulting mixture was stirred for 4 h followed by the addition of acetic acid (0.5 mL). The solution was concentrated and the product was purified by chromatography (10:1 CHCl₃/MeOH) to yield **S2** (1.07 g, 88% two steps) as a clear oil. *R*_f 0.15 (10:1 CHCl₃/MeOH); [α]_D +17.3 (*c* 0.8, D₂O); ¹H NMR (500 MHz, D₂O, [t_H]) 7.31 (d, 2 H, *J* = 7.9 Hz), 6.99 (d, 2 H, *J* = 7.8 Hz), 5.21 (d, 1 H, 5.0 Hz, H-1), 4.03–3.91 (m, 3 H, H-2, H-3, H-4), 3.70 (dd, 1 H, *J* = 2.8, 12.6 Hz, H-5), 3.62 (dd, 1 H, *J* = 4.6, 12.4 Hz, H-5), 2.10 (s, 3 H); ¹³C NMR (125.7 MHz, D₂O, [t_C]) 138.9, 133.2, 130.3, 129.2, 91.1 (C-1), 82.8, 80.9, 75.8, 60.9, 20.8. HRMS (ESI) calcd for (M+Na) C₁₂H₁₆O₄S: 279.0667, found 279.0651.

***p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio- α -L-lyxofuranoside (S3).** This compound was synthesized from **S2** as described for the preparation of **1** from **8**. The compound was purified chromatography (5:1 hexanes/EtOAc) to provide **S3** (81%) as a white solid. *R*_f 0.45 (3:1 hexanes/EtOAc); [α]_D +121.0 (*c*

1.0, CHCl₃), m.p. = 62–63 °C; ¹H NMR (500 MHz, CDCl₃, [t_H]) 8.07 (dd, 2 H, *J* = 0.9, 7.1 Hz), 7.60 (dd, 1 H, *J* = 7.3, 7.3 Hz), 7.47–7.42 (m, 4 H), 7.13 (d, 2 H, *J* = 7.9 Hz), 5.52 (s, 1 H, H-1), 4.56 (dd, 1 H, *J* = 5.3, 11.3 Hz, H-5), 4.51 (dd, 1 H, *J* = 5.6, 11.0 Hz, H-5), 4.29 (dd, 1 H, *J* = 5.6, 5.3 Hz, H-4), 3.93 (d, 1 H, *J* = 2.9 Hz, H-2), 3.84 (d, 1 H, *J* = 2.9 Hz, H-3), 2.34 (s, 3 H); ¹³C NMR (125.7 MHz, CDCl₃, [t_C]) 166.0, 138.2, 133.2, 133.0, 129.8, 129.6 (2), 128.4, 128.3, 87.0 (C-1), 74.0 (C-4), 62.2 (C-5), 57.5 (C-2), 55.5 (C-3), 21.0. HRMS (ESI) calcd for (M+Na) C₁₉H₁₈O₄S: 365.0823, found 365.0829.

Methyl α -L-arabinofuranoside (S4). To a solution of **S1** (10 g, 21 mmol) in CH₂Cl₂ (100 mL) and MeOH (100 mL) was added NaOCH₃ (1 mL, 1 M soln in MeOH). The solution was allowed to stir at rt for 6 h followed by

neutralization with acetic acid (0.5 mL). The resulting mixture was concentrated and the residue was purified by chromatography (10:1 CHCl₃/MeOH) to yield **S4** (3.4 g, quant) as a clear oil. The NMR data for this compound matched those previously reported.¹³

Methyl 5-*O*-triphenylmethyl α -L-arabinofuranoside (S5). To a solution of **S4** (3.0 g, 18.3 mmol) in pyridine (100 mL) was added triphenylmethyl chloride (6.1 g, 22.0 mmol) at rt. The resulting solution was stirred overnight followed by the addition of H₂O (100 mL) and CH₂Cl₂ (100 mL). The organic layer was washed with sat. aq. soln of NaHCO₃ and water, dried, filtered, and concentrated. The product was purified by chromatography (3:1 hexanes/EtOAc) to yield **S5** (6.0 g, 81%) as a white foam. *R_f* 0.58 (5:1, hexanes/EtOAc); [α]_D –67.1 (*c* 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H) 7.48–7.25 (m, 15 H), 5.05 (s, 1 H, H-1), 4.16 (dd, 1 H, *J* = 2.3, 4.7 Hz), 4.03 (d, 1 H, *J* = 10.8 Hz), 3.93 (d, 1 H, *J* = 10.9 Hz), 3.80 (d, 1 H, *J* = 10.9 Hz), 3.70 (dd, 1 H, *J* = 2.9, 10.5 Hz), 3.46 (s, 3 H), 3.31 (dd, 1 H, *J* = 2.2, 10.5 Hz), 2.83 (d, 1 H, *J* = 11.1 Hz); ¹³C NMR (125.7 MHz, CDCl₃, δ _C) 143.3, 129.2, 128.5, 127.9, 109.8 (C-1), 88.8, 86.8, 79.3, 78.7, 63.9, 55.3. HRMS (ESI) calcd for (M+Na) C₂₅H₂₆O₅; 425.1678, found 425.1670.

Methyl 2,3-di-*O*-benzyl-5-*O*-triphenylmethyl α -L-arabinofuranoside (S6). To a solution of **S5** (5.0 g, 12.3 mmol) in DMF at 0 °C was added NaH (740 mg, 30.8 mmol) and the mixture was allowed to stir for 15 min. To the mixture was added benzyl bromide (5.2 mL, 31 mmol) dropwise over the course of 20 min. The solution was allowed to slowly warm to rt while stirring for 3 h followed by the careful addition of H₂O (10 mL). The mixture was diluted and copiously extracted with Et₂O (4 x 100 mL). The organic fractions were combined and washed with H₂O (5 x 100 mL), dried, filtered, and concentrated. The product was purified by chromatography (10:1, hexanes/ EtOAc) to yield **S6** (6.3 g, 87%) as an oil. *R_f* 0.31 (5:1, hexanes/ EtOAc); [α]_D –81.0 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ _H) 7.54–7.53 (m, 6 H), 7.36–7.25 (m, 19 H), 5.05 (s, 1 H, H-1), 4.60–4.52 (m, 4 H), 4.30 (ddd, 1 H, *J* = 4.9, 7.5, 7.5 Hz), 4.07–4.04 (m, 2 H), 3.48 (s, 3 H), 3.35–3.32 (m, 2 H); ¹³C NMR (125.7 MHz, CDCl₃, δ _C) 144.4, 138.3, 138.1, 129.2, 128.9, 128.8, 128.2, 128.1, 128.0, 127.4, 107.7 (C-1), 88.6, 87.1, 84.1, 81.8, 72.5, 72.2, 64.3, 55.3. HRMS (ESI) calcd for (M+Na) C₃₉H₃₈O₅; 609.2671, found 609.2666.

Methyl 2,3-di-*O*-benzyl- α -L-arabinofuranoside (S7). To a solution of **S6** (6.0 g, 10.2 mmol) in CH₃OH (25 mL) and CH₂Cl₂ (50 mL) at rt was added *p*-TsOH (10 mg). The resulting solution was allowed to stir at rt for 6 h followed by the addition of triethylamine (0.3 mL). The resulting solution was concentrated and the residue was purified by chromatography (8:1 hexanes/EtOAc) to yield **S7** (3.3 g, 93%) as a clear oil. *R*_f 0.37 (4:1, hexanes/EtOAc); [α]_D –44.1 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃, α _H) 7.41–7.34 (m, 10 H), 4.99 (s, 1 H, H-1), 4.65 (d, 1 H, *J* = 12.0 Hz), 4.60–4.54 (m, 3 H), 4.19 (ddd, 1 H, *J* = 3.0, 4.1, 6.5 Hz), 4.06 (dd, 1 H, *J* = 0.9, 2.6 Hz), 4.04 (dd, 1 H, *J* = 2.6, 6.2 Hz), 3.88 (dd, 1 H, *J* = 2.8, 12.0 Hz), 3.70 (dd, 1 H, *J* = 3.8, 12.0 Hz), 3.44 (s, 3 H), 2.10 (br s, 1 H). ¹³C NMR (125.7 MHz, CDCl₃, α _C) 138.2, 137.8, 128.9, 128.4, 128.3 (2), 128.2, 107.9 (C-1), 88.3, 83.1, 82.8, 72.8, 72.4, 62.7, 55.4. HRMS (ESI) calcd for (M+Na) C₂₀H₂₄O₅; 367.1521, found 367.1530.

Table S1.Effect of sulfoxide stereochemistry on product yields and reaction stereoselectivity.^a

Entry	Donor ^b	Alcohol	Product	Yield (%)	□:□ ratio
1	2-fast	18	35	81	□-only
2	2-slow	18	35	79	□-only
3	2-fast	26	42	83	□-only
4	2-slow	26	42	81	□-only
5	2-mix	26	42	83	□-only

^aActivation protocol: Stir sulfoxide (0.5 mmol), Tf₂O (0.6 mmol), DTBMP (2.0 mmol) and crushed 4Å molecular sieves in 10 mL CH₂Cl₂ at -78 °C for 10 min. Raise the temperature to -40 °C and stir for 20 min and then add the alcohol (0.6 mmol). ^b**2-fast**: (sulfoxide diastereomer with higher R_f). ^c**2-slow**: (sulfoxide diastereomer with lower R_f). **2-mix**: (mixture of sulfoxide diastereomers).

Scheme S1

Structure plot (50% ellipsoids) for
p-Toluyyl 2,3-Anhydro-5-*O*-*p*-nitrobenzoyl- α -D-lyxofuranoside (**9**).

9

Table S1. Crystal data and structure refinement for *p*-Toluyyl 2,3-Anhydro-5-*O*-*p*-nitrobenzoyl- β -D-lyxofuranoside (**9**).

Identification code	<i>p</i> -Toluyyl 2,3-Anhydro-5- <i>O</i> - <i>p</i> -nitrobenzoyl- β -D-lyxofuranoside.	
Empirical formula	C ₁₉ H ₁₇ NO ₆ S	
Formula weight	387.40	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	
Unit cell dimensions	a = 6.342(4) Å b = 7.192(3) Å c = 39.592(12) Å	alpha = 90° beta = 90° gamma = 90°
Volume, Z	1805.8(13) Å ³ , 4	
Density (calculated)	1.425 Mg/m ³	
Absorption coefficient	1.924 mm ⁻¹	
F(000)	808	
Crystal size	0.24 x 0.08 x 0.06 mm	
θ range for data collection	1.12 to 56.97°.	
Limiting indices	$-6 \leq h \leq 6$, $-7 \leq k \leq 7$, $-43 \leq l \leq 43$	
Reflections collected	2823	
Independent reflections	2278 [R _{int} = 0.0234]	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2278 / 0 / 314	
Goodness-of-fit on F ²	1.097	
Final R indices [I > 2 σ (I)]	R ₁ (F) = 0.0706, wR ₂ (F ²) = 0.1642	
R indices (all data)	R ₁ (F) = 0.0987, wR ₂ (F ²) = 0.2005	
Absolute structure parameter	$\pm$ 0.04(6)	
Extinction coefficient	0.0028(8)	
Largest diff. peak and hole	0.389 and $\pm$ 0.425 e. Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	7487(4)	520(3)	618(1)	79(1)
O(1)	5751(8)	1586(7)	1220(1)	68(1)
O(2)	9359(9)	2464(8)	1514(1)	82(2)
O(3)	5922(8)	4171(7)	1822(1)	74(1)
O(4)	2992(9)	4756(8)	2113(1)	79(2)
O(5)	11622(10)	2938(9)	3258(1)	87(2)
O(6)	8798(10)	3192(8)	3553(1)	86(2)
N(1)	9740(12)	3252(8)	3283(2)	67(2)
C(1)	7566(14)	726(11)	1075(2)	68(2)
C(2)	9360(13)	1952(12)	1165(2)	71(2)
C(3)	8461(14)	3732(12)	1265(2)	73(2)
C(4)	6156(13)	3590(11)	1238(2)	68(2)
C(5)	4827(17)	4393(14)	1511(2)	73(2)
C(6)	4848(12)	4443(9)	2106(2)	57(2)
C(7)	6216(11)	4236(9)	2406(2)	53(2)
C(8)	8272(12)	3687(10)	2383(2)	59(2)
C(9)	9482(13)	3412(10)	2670(2)	65(2)
C(10)	8555(12)	3733(9)	2978(2)	58(2)
C(11)	6507(13)	4369(10)	3014(2)	64(2)
C(12)	5308(14)	4623(10)	2722(2)	65(2)
C(13)	5895(11)	1465(9)	559(2)	60(2)
C(14)	3960(13)	1672(12)	702(2)	75(2)
C(15)	2707(16)	3235(13)	636(2)	82(2)
C(16)	3437(13)	4609(10)	419(2)	67(2)
C(17)	5394(16)	4410(11)	279(2)	77(2)
C(18)	6626(16)	2856(12)	342(2)	72(2)
C(19)	2070(20)	6282(15)	346(3)	103(3)

Table S3. Bond lengths and angles for **9**.

Bond	Length (Å)
S(1)–C(13)	1.765(7)
S(1)–C(1)	1.817(7)
O(1)–C(1)	1.426(10)
O(1)–C(4)	1.466(10)
O(2)–C(2)	1.428(8)
O(2)–C(3)	1.459(9)
O(3)–C(6)	1.329(8)
O(3)–C(5)	1.420(9)
O(4)–C(6)	1.199(8)
O(5)–N(1)	1.219(7)
O(6)–N(1)	1.224(7)
N(1)–C(10)	1.466(9)
C(1)–C(2)	1.483(11)
C(2)–C(3)	1.455(12)
C(3)–C(4)	1.470(12)
C(4)–C(5)	1.489(11)
C(6)–C(7)	1.481(10)
C(7)–C(8)	1.365(10)
C(7)–C(12)	1.406(10)
C(8)–C(9)	1.384(10)
C(9)–C(10)	1.372(9)
C(10)–C(11)	1.384(10)
C(11)–C(12)	1.396(10)
C(13)–C(14)	1.359(10)
C(13)–C(18)	1.398(10)
C(14)–C(15)	1.401(12)
C(15)–C(16)	1.389(12)
C(16)–C(17)	1.367(11)
C(16)–C(19)	1.511(12)
C(17)–C(18)	1.386(11)
Angle	Degree
C(13)–S(1)–C(1)	102.4(3)
C(1)–O(1)–C(4)	107.7(6)
C(2)–O(2)–C(3)	60.5(5)
C(6)–O(3)–C(5)	117.7(6)
O(5)–N(1)–O(6)	122.9(7)
O(5)–N(1)–C(10)	118.5(6)

O(6)–N(1)–C(10)	118.6(7)
O(1)–C(1)–C(2)	105.4(6)
O(1)–C(1)–S(1)	114.4(5)
C(2)–C(1)–S(1)	108.0(5)
O(2)–C(2)–C(3)	60.8(5)
O(2)–C(2)–C(1)	112.6(7)
C(3)–C(2)–C(1)	106.7(7)
C(2)–C(3)–O(2)	58.7(5)
C(2)–C(3)–C(4)	108.0(8)
O(2)–C(3)–C(4)	113.2(8)
O(1)–C(4)–C(3)	104.2(7)
O(1)–C(4)–C(5)	108.5(7)
C(3)–C(4)–C(5)	118.9(7)
O(3)–C(5)–C(4)	108.0(7)
O(4)–C(6)–O(3)	123.5(7)
O(4)–C(6)–C(7)	125.1(7)
O(3)–C(6)–C(7)	111.4(6)
C(8)–C(7)–C(12)	120.5(7)
C(8)–C(7)–C(6)	122.4(6)
C(12)–C(7)–C(6)	117.1(7)
C(7)–C(8)–C(9)	121.1(7)
C(10)–C(9)–C(8)	117.8(7)
C(9)–C(10)–C(11)	123.4(7)
C(9)–C(10)–N(1)	118.3(7)
C(11)–C(10)–N(1)	118.2(6)
C(10)–C(11)–C(12)	117.9(7)
C(11)–C(12)–C(7)	119.2(7)
C(14)–C(13)–C(18)	118.5(7)
C(14)–C(13)–S(1)	123.3(6)
C(18)–C(13)–S(1)	118.1(6)
C(13)–C(14)–C(15)	121.6(8)
C(16)–C(15)–C(14)	119.7(8)
C(17)–C(16)–C(15)	118.7(8)
C(17)–C(16)–C(19)	121.7(9)
C(15)–C(16)–C(19)	119.6(9)
C(16)–C(17)–C(18)	121.5(8)
C(17)–C(18)–C(13)	120.0(8)

Symmetry transformations were used to generate equivalent atoms.

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U11 + \dots + 2hk a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
S(1)	111(2)	64(1)	63(1)	8(1)	5(1)	20(1)
O(1)	73(3)	63(3)	69(3)	7(2)	4(3)	8(3)
O(2)	82(3)	90(4)	73(3)	18(3)	13(3)	7(3)
O(3)	70(3)	92(4)	59(3)	11(2)	1(3)	9(3)
O(4)	73(4)	83(4)	82(3)	7(3)	4(3)	2(3)
O(5)	80(4)	103(5)	79(3)	4(3)	6(3)	7(3)
O(6)	12(4)	88(4)	56(3)	8(2)	3(3)	10(4)
N(1)	80(5)	55(4)	66(4)	2(3)	3(4)	14(4)
C(1)	75(5)	64(4)	66(4)	0(3)	4(4)	13(5)
C(2)	61(5)	89(6)	64(4)	14(4)	5(4)	1(5)
C(3)	84(6)	66(5)	67(4)	10(4)	10(4)	4(5)
C(4)	83(6)	58(4)	62(4)	4(4)	5(4)	1(4)
C(5)	78(7)	81(6)	59(4)	9(4)	10(4)	16(5)
C(6)	56(5)	38(3)	77(5)	5(3)	8(4)	5(3)
C(7)	56(5)	42(3)	61(4)	2(3)	3(4)	8(3)
C(8)	68(5)	52(4)	58(4)	0(3)	6(4)	8(4)
C(9)	72(5)	55(4)	68(4)	2(3)	6(4)	7(4)
C(10)	73(5)	43(3)	58(4)	2(3)	12(4)	14(4)
C(11)	85(6)	48(4)	59(4)	6(3)	16(4)	5(4)
C(12)	75(5)	46(4)	73(5)	3(4)	5(4)	2(4)
C(13)	69(5)	48(3)	63(4)	10(3)	0(4)	6(4)
C(14)	69(5)	74(5)	82(5)	9(4)	15(4)	0(5)
C(15)	85(6)	80(5)	80(5)	7(4)	14(5)	13(6)
C(16)	88(6)	61(4)	53(4)	8(3)	5(4)	8(4)
C(17)	06(7)	57(4)	68(5)	11(4)	6(5)	0(5)
C(18)	80(6)	71(5)	64(4)	2(4)	9(4)	7(4)
C(19)	45(11)	69(6)	94(6)	5(5)	3(7)	38(7)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
H(1)	7730(110)	700(100)	1181(14)	64(17)
H(2)	10690(90)	1750(80)	1055(13)	40(15)
H(3)	9410(160)	4990(140)	1250(20)	110(30)
H(4)	6180(110)	4180(100)	1001(17)	71(19)
H(5A)	3460(120)	4040(100)	1510(16)	60(20)
H(5B)	4630(110)	5740(110)	1447(17)	70(20)
H(8)	9050(90)	3490(80)	2166(13)	43(15)
H(9)	11230(120)	2910(100)	2658(15)	68(19)
H(11)	5930(90)	4560(90)	3249(15)	51(16)
H(12)	3750(150)	5110(120)	2730(20)	100(30)
H(14)	3260(140)	700(140)	850(20)	110(30)
H(15)	1530(120)	3330(120)	740(18)	80(30)
H(17)	5700(140)	4970(120)	110(20)	90(30)
H(18)	8130(100)	2700(80)	267(14)	45(17)
H(19A)	400(300)	6200(200)	320(40)	200(60)
H(19B)	2340(140)	6810(130)	120(20)	110(30)
H(19C)	2830(180)	7470(170)	420(20)	140(40)

Structure plot (50% ellipsoids) for
p-Toluy1 2,3-Anhydro-5-*O*-*p*-nitrobenzoyl- β -D-ribofuranoside (**10**).

Table S6. Crystal data and structure refinement for *p*-Toluyyl 2,3-Anhydro-5-*O*-*p*-nitrobenzoyl- β -D-ribofuranoside (**10**).

Name	<i>p</i> -Toluyyl 2,3-Anhydro-5- <i>O</i> - <i>p</i> -nitrobenzoyl- β -D-ribofuranoside	
Empirical formula	C ₁₉ H ₁₇ NO ₆ S	
Formula weight	387.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 5.5357(10)$ Å $\alpha = 90^\circ$. $b = 10.2275(14)$ Å $\beta = 98.311(14)^\circ$. $c = 17.318(2)$ Å $\gamma = 90^\circ$.	
Volume, Z	970.2(3) Å ³ , 2	
Density (calculated)	1.326 Mg/m ³	
Absorption coefficient	0.201 mm ⁻¹	
F(000)	404	
Crystal size	0.06 x 0.24 x 0.22 mm	
2θ range for data collection	2.32 to 29.99°.	
Limiting indices	$-7 \leq h \leq 7$, $-14 \leq k \leq 14$, $-243 \leq l \leq 24$	
Reflections collected	6476	
Independent reflections	5674 [$R_{\text{int}} = 0.0869$]	
Absorption correction	Empirical	
Max. and min. transmission	0.9024 and 0.6582	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5674 / 1 / 285	
Goodness-of-fit on F ²	0.960	
Final R indices [$I > 2\sigma(I)$]	$R_1(F) = 0.0790$, $wR_2(F^2) = 0.1932$	
R indices (all data)	$R_1(F) = 0.1350$, $wR_2(F^2) = 0.2357$	
Absolute structure parameter	0.12(14)	
Largest diff. peak and hole	0.288 and -0.176 e. Å ⁻³	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	Ueq
S(1)	5537(3)	4925(1)	3260(1)	91(1)
O(1)	4754(4)	7139(3)	4008(2)	67(1)
O(2)	8288(6)	5863(3)	4944(2)	88(1)
O(3)	7657(5)	9424(2)	3892(2)	66(1)
O(4)	6905(6)	11577(3)	3817(2)	86(1)
O(5)	15228(10)	11850(6)	1165(3)	143(2)
O(6)	15758(12)	9794(8)	1279(4)	60(2)
N(1)	14795(10)	10803(8)	1441(3)	114(2)
C(1)	6579(6)	6522(4)	3632(2)	65(1)
C(2)	8810(7)	6450(4)	4233(3)	75(1)
C(3)	8365(7)	7295(5)	4884(2)	77(1)
C(4)	5912(7)	7872(4)	4672(2)	67(1)
C(5)	6041(8)	9314(4)	4474(2)	70(1)
C(6)	7969(7)	10632(4)	3623(2)	65(1)
C(7)	9732(7)	10652(4)	3057(2)	64(1)
C(8)	10172(9)	11834(4)	2690(3)	82(1)
C(9)	11800(10)	11893(5)	2165(3)	90(1)
C(10)	13021(8)	10765(6)	2001(2)	84(1)
C(11)	12646(10)	9583(5)	2354(3)	89(1)
C(12)	11000(9)	9535(5)	2884(3)	79(1)
C(13)	3929(9)	5391(4)	2332(3)	84(1)
C(14)	1802(12)	6078(7)	2263(3)	108(2)
C(15)	593(12)	6479(9)	1545(4)	128(2)
C(16)	1476(14)	6163(12)	879(3)	151(4)
C(17)	3594(15)	5375(14)	955(4)	174(5)
C(18)	4788(12)	5051(10)	1657(4)	129(2)
C(19)	90(20)	6560(20)	81(5)	260(10)

Table S8. Bond lengths and angles for **10**.

Bond	Length (Å)
S(1)–C(13)	1.785(5)
S(1)–C(1)	1.819(4)
O(1)–C(1)	1.426(4)
O(1)–C(4)	1.443(5)
O(2)–C(2)	1.437(5)
O(2)–C(3)	1.469(6)
O(3)–C(6)	1.341(5)
O(3)–C(5)	1.445(5)
O(4)–C(6)	1.205(5)
O(5)–N(1)	1.211(8)
O(6)–N(1)	1.213(9)
N(1)–C(10)	1.476(7)
C(1)–C(2)	1.498(6)
C(2)–C(3)	1.469(7)
C(3)–C(4)	1.477(6)
C(4)–C(5)	1.518(6)
C(6)–C(7)	1.479(6)
C(7)–C(12)	1.396(6)
C(7)–C(8)	1.403(6)
C(8)–C(9)	1.371(7)
C(9)–C(10)	1.387(8)
C(10)–C(11)	1.384(7)
C(11)–C(12)	1.384(7)
C(13)–C(14)	1.362(8)
C(13)–C(18)	1.369(7)
C(14)–C(15)	1.387(10)
C(15)–C(16)	1.355(10)
C(16)–C(17)	1.413(14)
C(16)–C(19)	1.534(13)
C(17)–C(18)	1.339(11)
Angle	Degree
C(13)–S(1)–C(1)	99.79(18)
C(1)–O(1)–C(4)	109.4(3)
C(2)–O(2)–C(3)	60.7(3)
C(6)–O(3)–C(5)	116.0(3)
O(5)–N(1)–O(6)	122.9(6)
O(5)–N(1)–C(10)	118.1(7)

O(6)–N(1)–C(10)	119.1(6)
O(1)–C(1)–C(2)	105.8(3)
O(1)–C(1)–S(1)	110.5(2)
C(2)–C(1)–S(1)	12.9(3)
O(2)–C(2)–C(3)	60.7(3)
O(2)–C(2)–C(1)	111.6(3)
C(3)–C(2)–C(1)	106.9(3)
C(2)–C(3)–O(2)	58.5(3)
C(2)–C(3)–C(4)	107.2(3)
O(2)–C(3)–C(4)	112.4(4)
O(1)–C(4)–C(3)	106.1(3)
O(1)–C(4)–C(5)	110.7(3)
C(3)–C(4)–C(5)	111.8(3)
O(3)–C(5)–C(4)	106.7(3)
O(4)–C(6)–O(3)	123.3(4)
O(4)–C(6)–C(7)	124.7(4)
O(3)–C(6)–C(7)	111.9(3)
C(12)–C(7)–C(8)	118.8(4)
C(12)–C(7)–C(6)	122.1(3)
C(8)–C(7)–C(6)	119.1(4)
C(9)–C(8)–C(7)	120.8(4)
C(8)–C(9)–C(10)	119.1(4)
C(11)–C(10)–C(9)	121.8(4)
C(11)–C(10)–N(1)	118.0(5)
C(9)–C(10)–N(1)	120.2(5)
C(12)–C(11)–C(10)	118.6(5)
C(11)–C(12)–C(7)	120.9(4)
C(14)–C(13)–C(18)	117.3(6)
C(14)–C(13)–S(1)	122.0(4)
C(18)–C(13)–S(1)	120.7(5)
C(13)–C(14)–C(15)	122.1(5)
C(16)–C(15)–C(14)	120.4(7)
C(15)–C(16)–C(17)	116.9(7)
C(15)–C(16)–C(19)	120.5(10)
C(17)–C(16)–C(19)	122.4(9)
C(18)–C(17)–C(16)	121.3(6)
C(17)–C(18)–C(13)	121.7(7)

Symmetry transformations were used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U11 + \dots + 2hk a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
S(1)	119(1)	53(1)	107(1)	2(1)	33(1)	$\bar{2}$ (1)
O(1)	50(1)	73(2)	77(1)	$\bar{8}$ (1)	9(1)	1(1)
O(2)	77(2)	95(2)	93(2)	43(2)	14(1)	4(2)
O(3)	71(1)	59(1)	70(1)	$\bar{3}$ (1)	16(1)	$\bar{1}$ (1)
O(4)	103(2)	64(20)	90(2)	$\bar{7}$ (1)	12(2)	16(2)
O(5)	146(4)	164(50)	129(3)	38(3)	49(3)	$\bar{23}$ (3)
O(6)	165(5)	176(5)	158(5)	$\bar{1}$ (4)	93(4)	6(4)
N(1)	103(3)	157(5)	80(2)	3(3)	13(2)	$\bar{28}$ (4)
C(1)	60(2)	64(2)	73(2)	11(2)	22(2)	4(2)
C(2)	55(2)	87(3)	87(2)	30(2)	23(2)	8(2)
C(3)	64(2)	99(3)	65(2)	21(2)	6(2)	$\bar{13}$ (2)
C(4)	56(2)	87(3)	62(2)	$\bar{1}$ (2)	16(2)	$\bar{8}$ (2)
C(5)	69(2)	73(2)	70(2)	$\bar{18}$ (2)	16(2)	$\bar{3}$ (2)
C(6)	69(2)	58(2)	66(2)	$\bar{5}$ (2)	0(2)	4(2)
C(7)	70(2)	59(2)	60(2)	1(2)	$\bar{3}$ (1)	$\bar{4}$ (2)
C(8)	97(3)	62(2)	83(2)	3(2)	6(2)	0(2)
C(9)	108(3)	84(3)	78(3)	18(2)	8(2)	$\bar{25}$ (3)
C(10)	77(3)	110(3)	63(2)	7(2)	3(2)	$\bar{15}$ (2)
C(11)	87(3)	93(3)	88(3)	6(2)	21(2)	6(3)
C(12)	83(3)	68(2)	87(3)	10(2)	23(2)	1(2)
C(13)	93(3)	75(2)	91(3)	$\bar{23}$ (2)	35(2)	$\bar{26}$ (2)
C(14)	114(4)	133(5)	82(3)	$\bar{14}$ (3)	30(3)	11(3)
C(15)	106(4)	171(7)	104(4)	$\bar{23}$ (4)	9(3)	0(4)
C(16)	109(4)	265(11)	76(3)	$\bar{25}$ (4)	8(3)	$\bar{48}$ (6)
C(17)	116(5)	324(15)	86(4)	$\bar{57}$ (6)	34(4)	$\bar{21}$ (7)
C(18)	106(4)	179(7)	107(4)	$\bar{45}$ (4)	33(3)	3(4)
C(19)	161(7)	520(30)	90(4)	9(9)	$\bar{10}$ (5)	$\bar{9}$ (12)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**.

	x	y	z	U(eq)
H(14)	1139	6285	2712	130
H(15)	□832	6969	1520	153
H(17)	4170	5076	508	208
H(18)	6239	4583	1687	155
H(19A)	962	6254	□324	390
H(19B)	□30	7499	54	390
H(19C)	□1512	6189	15	390
H(1)	6930(60)	6980(40)	3180(20)	52(8)
H(2)	0290(90)	6300(50)	4100(20)	74(12)
H(3)	9800(90)	7700(40)	5200(20)	75(12)
H(4)	4140(110)	9560(50)	4230(30)	105(17)
H(5A)	4880(100)	7740(50)	5030(30)	83(12)
H(5B)	6690(70)	9700(40)	4870(20)	63(10)
H(8)	10600(100)	8820(70)	3090(30)	99(17)
H(9)	12170(80)	12610(50)	1880(30)	79(12)
H(11)	13660(110)	8950(70)	2200(30)	104(17)
H(12)	9300(110)	12600(70)	2850(40)	119(19)

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CONVENT	55536

SOLVENT	LOC	34
NS		

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DW	48,400	usec

DE	6.00 μ sec
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D1 1.00000000 sec

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64.759

77.201

77.456

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Current Data Parameters
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7715715 MHz

===== CHANNEL f2 =====
CDEPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 18.80 dB
PL13 18.80 dB
SFO2 500.132005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

10 NMR plot parameters
CX 34.00 cm
F1 173.044 ppm
F2 22013.10 Hz
F3 -3.446 ppm
F4 -684.30 Hz
PPOW 5.30852 dBW/cm
HZCM 687.58801 Hz/cm

Current Data Parameters
 NAME 02-10-01
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20010210
 Time 7.47
 INSTRUM spect
 PROBHD 5 mm BBO BB-1
 PULPROG zg30
 TO 65536
 SOLVENT CDCl₃
 NS 31
 DS 2
 SMH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.171923 sec
 RG 114
 DM 48.400 usec
 DE 5.00 usec
 TE 300.0 K
 D1 1.0000000 sec

===== CHANNEL f1 =====
 NUC1 ¹H
 P1 13.70 usec
 PL1 -1.00 dB
 SF01 500.1300865 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 34.00 cm
 F1P 8.585 ppm
 F1 4293.55 Hz
 F2P -0.955 ppm
 F2 -277.70 Hz
 PPM0H 0.26883 ppm/cm
 HZCM 134.44859 Hz/cm

Current Data Parameters
 NAME 02-10-01
 EXPNO 31
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20010210
 Time 7.52
 INSTRUM spect
 PROBHD 5 mm BB0 BB-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 103
 DS 4
 SWH 31446.541 Hz
 FIDRES 0.479836 Hz
 AQ 1.0420724 sec
 RG 8192
 DM 15.900 usec
 DE 6.00 usec
 TE 300.0 K
 O1 2.00000000 sec
 O11 0.03000000 sec
 O12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 8.00 usec
 PL1 3.00 dB
 SFO1 125.7715719 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 PL2 -1.00 dB
 PL12 16.80 dB
 PL13 16.80 dB
 SFO2 500.1320005 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7577590 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 34.00 cm
 F1P 182.439 ppm
 F1 22943.05 Hz
 F2P -10.375 ppm
 F2 -1304.87 Hz
 PPMCM 5.67102 ppm/cm
 HZCM 713.17456 Hz/cm

Current Data Parameters
NAME rajnixa
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010620
Time 7.27
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
GB 48.400 usec
DA 5.00 usec
DE 300.0 K
TE 1.00000000 sec
D1

===== CHANNEL f1 =====
NUC1 H1
P1 13.70 usec
PL1 -1.00 dB
F1 500.1330895 MHz
SFO1 500.1330895 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SS 0
LB 0.30 Hz
GB 0
PC 1.00

10 MHz plot parameters
CX 34.00 cm
CY 5.336 mm
F1 2659.62 Hz
F2 3.140 mm
F3 1570.63 Hz
G 0.06493 mm/cm
H 32.32309 Hz/cm
HZCM

Current Data Parameters
NAME rajhwa
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20010520
Time 7:31
INSTRUM spect
PROBHD 5 mm BBO BB1
PULPROG zgpg30
TD 65535
FID 65535
SOLVENT D2O
NS 1456
DS 4
SWH 31445.541 Hz
FIDRES 0.479355 Hz
AQ 1.0447024 sec
RG 1600
DM 15.500 usec
DE 6.0 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00000000 sec

===== CHANNEL f1 =====
NUC1 ¹³C
P1 8.00 usec
PL1 3.00 dB
SF01 125.7715719 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.80 dB
PL13 18.80 dB
SF02 500.1300005 MHz

F2 - Processing parameters
SI 32768
SF 125.7578042 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CA 34.00 cm
F1P 112.886 ppm
F1 14197.51 Hz
F2P 47.951 ppm
F2 6931.44 Hz
PACM 1.93995 ppm/cm
ALCM 240.17859 Hz/cm