General experimental protocol.

All reactions were conducted under a dried argon stream. Solvents (PhH 99.8%, CH_2Cl_2 99.8%, PhMe 99.8%, THF, 99.8%) were purchased in capped DriSolv™ bottles from EMD, used without further purification, and stored under argon. TMSI was purchased from Fluka (≥98%) and used without purification unless the color had changed to a dark brown shade, in which case it was either discarded or distilled under an argon atmosphere from quinoline. TMSI was stored at –15 °C under a desiccated atmosphere. HOAc was purchased as a 99% solution from Sigma-Aldrich and used without further purification. Glass-backed EM Science TLC plates (Silica Gel 60 with a 254 nm fluorescent indicator) were purchased from EMD, cut into 2 cm x 5 cm portions, used without further manipulation, and stored over desiccant. Developed TLC plates were visualized under a short-wave UV lamp, stained with an I_2–SiO_2 mixture, and/or treated with a cerium-molybdate solution and charred. Column chromatography was conducted using solvents and Geduran™ flash silica gel (32-63 μm) available from EMD. NMR experiments (1D and 2D) were conducted on Bruker DRX500 MHz and/or DRX600 MHz spectrometers using $CDCl_3$ (Aldrich) at 298 K. Optical data were taken at 24 °C on a JASCO DIP-370 Digital Polarimeter.

Preparation of 1,3,4,6-tetra-O-acetyl-2-deoxy-D-arabino-pyranose (4) [1,2]

Method A – TMSI/HOAc
Tri-*O*-acetyl-D-glucal (113 mg, 0.42 mmol) was dissolved in dry CH_2Cl_2 (5 mL). The mixture was purged with argon and HOAc (0.5 mL) was added. The mixture was cooled to 0 °C for 15 min, after which TMSI (59 μL, 0.4 mmol) was added via syringe. After stirring for 2.5 h at 0 °C, the reaction was diluted with CH_2Cl_2 and neutralized with sat $NaHCO_3$ (aq). The organic layer was further washed with sat $Na_2S_2O_3$ (aq) until the CH_2Cl_2 was colorless. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. TLC revealed the presence of two major spots, R_f = 0.24, 0.12 (40% EtOAc/Hexanes). Silica gel column chromatography using 35 % EtOAc/Hexanes provided 23 mg (16%) of spot 1 and 96 mg (79%) of spot 2. 1H-NMR spectra revealed spot 1 to be the titled compound and spot 2 to be the 3,4,6-tri-*O*-acetyl-2-deoxy-D-arabino-pyranose.

Method B – AcBr/HOAc
Tri-*O*-acetyl-D-glucal (115 mg, 0.43 mmol) was dissolved in dry CH_2Cl_2 (5 mL). The mixture was purged with argon and HOAc (0.5 mL) was added. The mixture was cooled to 0 °C for 15 min, after which AcBr (31 μL, 0.43 mmol) was added via syringe. After stirring for 30 min at 0 °C, the reaction was removed from the ice bath and stirred for at additional 2.5 h. The reaction was then concentrated in vacuo and azeotroped with PhMe. Silica gel column chromatography using 35 % EtOAc/Hexanes provided 50 mg (36%) of the 2-deoxy-tetra-OAc and 65 mg (53%) of the 2-deoxy-tri-OAc. 1H-NMR spectra revealed spot 1 to be the titled compound and spot 2 to be the 3,4,6-tri-*O*-acetyl-2-deoxy-D-arabino-pyranose.

Method C – 30% HBr/HOAc/Ac_2O
Tri-*O*-acetyl-D-glucal (540 mg, 2.0 mmol) was dissolved in dry CH_2Cl_2 (10 mL). The mixture was purged with argon and cooled to 0 °C for 15 min. A solution of 30% HBr/HOAc (98 μL, 0.5 mmol of HBr) and Ac_2O (5 mL) were syringed into the sugar solution. After stirring for 14 h, the reaction was concentrated in vacuo and azeotroped with PhMe. TLC revealed the presence of a major spot, R_f = 0.34 (50% EtOAc/Hexanes). Silica gel column chromatography using 30 % EtOAc/Hexanes provided 623 mg of material. The tetra-acetate was afforded in 92% overall yield and spectroscopic data matched well with products from other preparations.

*Preparation of 1,3,4,6-tetra-O-acetyl-2-deoxy-D-lyxo-pyranose (**7**)* [3]

Tri-*O*-acetyl-D-galactal (5.0 g, 18 mmol) was dissolved in dry CH_2Cl_2 (30 mL). The mixture was purged with argon. Glacial HOAc (10 mL) and Ac_2O (15 mL) was syringed into the sugar solution

and stirred for 15 min at 0 °C for 20 min. 30% HBr/HOAc (730 μL) was syringed into the reaction mixture and the mixture was allowed to stir overnight. TLC revealed the presence of a major spot (50% EtOAc/Hexanes). NaOAc (3.0 g, 36 mmol) was added to the reaction mixture and stirred for 20 min and the color lightened. The heterogeneous mixture was diluted with CH_2Cl_2 and filtered over a pad of Celite and washed with CH_2Cl_2. The mother liquor was concentrated to dryness in vacuo and silica gel column chromatography using 30% EtOAc/Hexanes provided 5.3 g (86% yield). Spectroscopic data matched well with products from other preparations.

*Preparation of 1,3,4-tri-O-acetyl-2,6-dideoxy-D-arabino-pyranose (**9**)*[4]

Di-*O*-acetyl-D-rhamnal[5] (1.5 g, 7.0 mmol) was dissolved in dry CH_2Cl_2 (7 mL). The mixture was purged with argon. Glacial HOAc (4.5 mL) and Ac_2O (9 mL) were to the sugar solution and cooled to 0 °C for 15 min. 30% HBr/HOAc (280 μL) was added via syringe and the reaction was stirred overnight (14 h) at rt. TLC revealed a major spot, R_f = 0.37 (50% EtOAc/Hexanes). NaOAc (1.2 g, 14 mmol) was added to the reaction mixture and stirred for 30 min and the color lightened. The heterogeneous mixture was diluted with CH_2Cl_2 (75 mL) and filtered over a pad of Celite and washed with CH_2Cl_2. The mother liquor was concentrated to dryness in vacuo. Silica gel column chromatography using 25% EtOAc/Hexanes provided 1.7 g (89% yield) of the desired 2-deoxy sugar. Spectroscopic data matched well with products from other preparations.

General procedure for the preparation 2-deoxy-glycosyl iodides (**10**, **11**, **12**):

*Preparation of 3,4,6-tri-O-acetyl-2-deoxy-α-D-arabino-pyranosyl iodide (**10**):*

1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-arabino-pyranose (100 mg, 0.30 mmol) was dissolved in dry CH_2Cl_2 (2 mL). The mixture was purged with argon and cooled to 0 °C for 15 min. TMSI (47 μL, 0.33 mmol) was syringed into the cooled solution. After 20 min, a major spot appeared at R_f = 0.22 (50% EtOAc/Hexanes). After which, dry PhMe (5 mL) was added to the reaction and the mixture was concentrated in vacuo. Azeotropic removal of by-products was performed twice more or until a clear distillate persisted from dry PhMe.

400 MHz ^{1}H-NMR δ 6.95 (d, 1H, *J* = 4.4 Hz, H-1), 5.45 (dt, 1H, *J* = 5.2 Hz, 10.4 Hz, H-3), 5.12 (t, 1H, *J* = 10.4 Hz, H-4), 4.36 (dd, 1H, *J* = 4.0 Hz, 12.4 Hz, H-6), 4.06 (dd, 1H, *J* = 2.0 Hz, 12.4 Hz, H-6), 3.96 (m, 1H, H-5), 2.65 (dd, 1H, *J* = 5.2 Hz, 14.0 Hz, H-2), 2.16 (m, 1H, H-2), 2.12 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.00 (s, 3H, 3 OAc)

*Preparation of 1-O-cresyl-2-deoxy-3,4,6-tri-O-acetyl-β-D-arabino-pyranoside (**13**):*

Freshly prepared 2-deoxy-glucosyl iodide (0.29 mmol) was dissolved in dry THF (1 mL) and cooled to 0 °C for 15 min. To a solution of *o*-cresol (16 mg, 0.15 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (291 μL), 18-crown-6 (38 mg, 0.15 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled to 0 ϒC for 5 min. The acceptor mixture was cannulated into the donor solution. After 25 min, TLC (50% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 30% EtOAc/Hexanes provided 48 mg (86% yield) of the β-*O*-aryl-glycoside.

600 MHz ^{1}H-NMR δ 7.13 (m, 2H, PhH), 7.00 (d, 1H, *J* = 7.8 Hz, PhH), 6.95 (t, 1H, *J* = 7.8 Hz), 5.15 (d, 1H, *J* = 9.6 Hz, H-1), 5.11 (m, 1H, H-3), 5.05 (t, 1H, *J* = 8.4 Hz, H-4), 4.32 (dd, 1H, *J* = 5.4 Hz, 12.0 Hz, H-6), 4.15 (d, 1H, *J* = 12.0 Hz, H-6), 3.77 (m, 1H, H-5), 2.54 (apparent dd, 1H, *J* = 4.8 Hz, 11.5 Hz, H-2eq), 2.21 (s, 3H, PhMe), 2.11 (apparent t, 1H, *J* = 11.5 Hz, H-2ax), 2.06 (s, 9H, 3 OAc).
600 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 159.6 Hz

*Preparation of 1-O-cresyl-2-deoxy-3,4,6-tri-O-acetyl-β-D-lyxo-pyranoside (**14**):*

Freshly prepared 2-deoxy-galactosyl iodide (0.27 mmol) was dissolved in dry THF (1 mL) and cooled to 0 ϒC for 15 min. To a solution of *o*-cresol (14 mg, 0.13 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (267 μL), 18-crown-6 (35 mg, 0.13 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled 0 °C for 5 min. The acceptor mixture was cannulated into the donor solution. After 20 min, TLC (50% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 30% EtOAc/Hexanes provided 46 mg (91% yield) of the β-*O*-aryl-glycoside.

500 MHz ^{1}H-NMR δ 7.12 (apparent q, 2H, PhH), 7.02 (d, 1H, *J* = 7.8 Hz, PhH), 6.94 (t, 1H, *J* = 7.8 Hz), 5.31 (d, 1H, *J* = 2.0 Hz, H-4), 5.12 (dd, 1H, *J* = 2.0 Hz, 9.5 Hz, H-1), 5.08 (dt, 1H, *J* = 3.5 Hz, 11.0 Hz, H-3), 4.22 (dd, 1H, *J* = 7.0 Hz, 11.5 Hz, H-6), 4.15 (dd, 1H, *J* = 7.0 Hz, 11.5 Hz, H-6'), 3.95 (t, 1H, *J* = 7.0 Hz, H-5), 2.54 (apparent q, 1H, *J* = 12.0 Hz, 12.5 Hz, H-2ax), 2.23 (s, 3H, PhMe), 2.19 (dd, 1H, *J* = 3.0 Hz, 11.5 Hz, H-2eq), 2.16 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc).
500 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 160.3 Hz
125 MHz ^{13}C-NMR δ 170.40 (OAc), 170.19 (OAc), 169.97 (OAc), 155.11 (Ph), 130.83 (Ph), 127.65 (Ph), 126.72 (Ph), 122.58 (Ph), 114.82 (Ph), 98.21 (C-1), 71.18 (C-5), 68.25 (C-3), 65.23 (C-4), 61.87 (C-6), 31.86 (C-2), 20.73 (OAc), 20.66 (OAc), 20.62 (OAc), 16.25 (PhMe)

*Preparation 1-O-cresyl-3,4-di-O-acetyl-2,6-dideoxy-β-D-arabino-pyranoside (**15**):*

Freshly prepared 2,6-dideoxy-rhamnosyl iodide (0.44 mmol) was dissolved in dry THF (1 mL) and cooled to 0 ϒC for 15 min. To a solution of *o*-cresol (24 mg, 0.22 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (436 μL), 18-crown-6 (58 mg, 0.22 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled 0 °C for 5 min. The acceptor mixture was cannulated into the donor solution. After 15 min, TLC (30% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 10% EtOAc/Hexanes provided 26 mg (42% yield) of the β-*O*-aryl-glycoside.

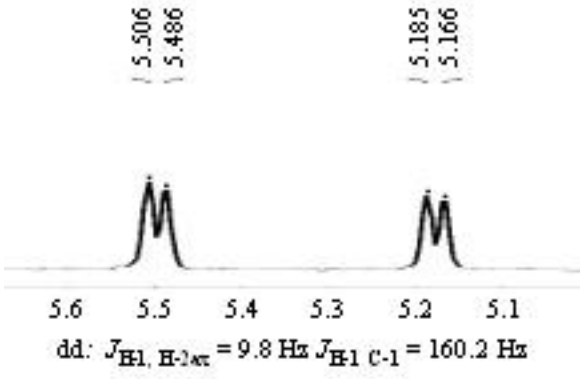
500 MHz ^{1}H-NMR δ 7.14 (m, 2H, PhH), 6.95 (m, 2H, PhH), 5.05 (d, 1H, *J* = 9.5 Hz, H-1), 4.97 (t, 1H, *J* = 10 Hz, H-4), 4.15 (m, 1H, H-3), 3.57 (m, 1H, H-5), 2.81 (d, 1H, *J* = 9.0 Hz, H-2eq), 2.67 (apparent q, 1H, *J* = 9.0 Hz, 13.0 Hz, H-2ax), 2.23 (s, 3H, PhMe), 2.15 (s, 3H, OAc), 2.10 (s, 1H, OAc), 1.28 (d, 3H, J = 6.5 Hz).
500 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 159.5 Hz

*Preparation of 1-O-naphthyl-2-deoxy-3,4,6-tri-O-acetyl-β-D-arabino-pyranoside (**16**):*

Freshly prepared glycosyl iodide (0.30 mmol) was dissolved in dry THF (1 mL) and cooled to 0 °C for 15 min. To a solution of 2-naphthol (22 mg, 0.15 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (300 μL), 18-crown-6 (40 mg, 0.15 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled 0 °C for 5 min. The acceptor mixture was cannulated into the donor solution. After 15 min, TLC (50% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 40% EtOAc/Hexanes provided 57 mg (91% yield) of the desired β-*O*-aryl-glycoside.

500 MHz ^{1}H-NMR δ 7.77 (t, 2H, *J* = 9.0 Hz, PhH), 7.20 (d, 1H, *J* = 8.0 Hz, PhH), 7.45 (t, 1H, *J* = 8.0 Hz, PhH), 7.38 (t, 1H, *J* = 8.0 Hz, PhH), 7.34 (d, 1H, *J* = 1.5 Hz, PhH), 7.20 (dd, 1H, *J* = 1.5

Hz, 9.0 Hz, PhH), 5.32 (dd, 1H, *J* = 1.5 Hz, 9.5 Hz, H-1), 5.15 (m, 1H, H-3), 5.07 (t, 1H, *J* = 9.5 Hz, H-4), 4.32 (dd, 1H, *J* = 6.0 Hz, 12.0 Hz, H-6), 4.18 (dd, 1H, *J* = 2.5 Hz, 12.0 Hz, H-6'), 3.85 (m, 1H, H-5), 2.57 (ddd, 1H, *J* = 2.0 Hz, 5.0 Hz, 12.5 Hz, H-2eq), 2.09 (apparent q, 1H, *J* = 11.5 Hz, 11.0 Hz, 12.5 Hz, H-2ax), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc).
500 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 160.3 Hz



*Preparation of 1-O-naphthyl-2-deoxy-3,4,6-di-O-acetyl-β-D-lyxo-pyranoside (**17**):*

Freshly prepared 2-deoxy-galactosyl iodide (0.31 mmol) was dissolved in dry THF (1 mL) and cooled to 0 ϒC for 15 min. To a solution of 2-naphthol (23 mg, 0.16 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (315 μL), 18-crown-6 (42 mg, 0.16 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled 0 ϒC for 5 min. The acceptor mixture was cannulated into the donor solution. After 20 min, TLC (50% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 30% EtOAc/Hexanes provided 55 mg (93% yield) of the β-*O*-aryl-glycoside.

500 MHz ^{1}H-NMR δ 7.78 (t, 2H, *J* = 9.0 Hz, PhH), 7.73 (d, 1H, J = 8.0 Hz, PhH), 7.46 (t, 1H, 7.5 Hz, PhH), 7.38 (m, 2H, PhH), 7.22 (dd, 1H, *J* = 2.5 Hz, 9.0 Hz, PhH), 5.35 (d, 1H, *J* = 1.5 Hz, H-4), 5.31 (dd, 1H, *J* = 1.5 Hz, 9.5 Hz, H-1), 5.13 (dt, 1H, *J* = 9.0 Hz, 11.5 Hz, H-3), 4.25 (dd, 1H, *J* = 7.5 Hz, 11.5 Hz, H-6), 4.19 (dd, 1H, J = 7.5 Hz, 11.5 Hz, H-6'), 4.03 (t, 1H, J = 11.5 Hz, H-5), 2.32 (apparent q, 1 H, J = 12.0 Hz, 10.0 Hz, H-2ax), 2.24 (dd, 1H, J = 3.0 Hz, 12.0 Hz, H-2eq), 2.17 (s, 3H, PhMe), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.65 (br, 1H, OH)
500 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 158.1 Hz

*Preparation of 1-O-naphthyl-3,4-di-O-acetyl-2,6-dideoxy-β-D-arabino-pyranoside (**18**)*

Freshly prepared 2,6-dideoxy-rhamnosyl iodide (0.47 mmol) was dissolved in dry THF (1 mL) and cooled to 0 ϒC for 15 min. To a solution of 2-naphthol (34 mg, 0.23 mmol) in THF (1 mL) was added 0.5M KHMDS/PhMe (467 μL), 18-crown-6 (62 mg, 0.23 mmol), and 4 Å MS (50 mg). The acceptor solution was allowed to stirred for 20 min and then cooled 0 ϒC for 5 min. The acceptor mixture was cannulated into the donor solution. After 15 min, TLC (30% EtOAc/Hexanes) revealed the absence of glycosyl iodide. The reaction was diluted with EtOAc and filtered over a pad of Celite. The mother liquor was washed with 2 x 15 mL sat. $Na_2S_2O_3$ (aq), brine, and concentrated in vacuo and silica gel column chromatography using 10% EtOAc/Hexanes provided 41 mg (49% yield) of the desired β-*O*-aryl-glycoside. 3-O-deacetylated sugar was also recovered 35 mg.

500 MHz ^{1}H-NMR δ 7.78 (t, 2H, *J* = 9.0 Hz, PhH), 7.74 (d, 2H, *J* = 8.4 Hz, PhH), 7.45 (t, 1H, *J* = 6.6 Hz, PhH), 7.38 (t, 1H, J = 6.6 Hz, PhH), 7.33 (s, 1H, PhH), 7.20 (dd, 1H, J = 1.8 Hz, 8.4 Hz, PhH), 5.33 (d, 1H, *J* = 9.6 Hz, H-1), 5.11 (m, 1H, H-3), 4.87 (t, 1H, *J* = 9.6 Hz, H-4), 3.71 (m, 1H, H-5), 2.56 (dd, 1H, *J* = 4.8 Hz, 10.8 Hz, H-2eq), 2.11 (s, 3H, OAc), 2.07 (overlapped q, 1H, H-2ax), 2.04 (s, 3H, OAc), 1.32 (d, 3H, J = 6.0 Hz).
500 MHz HSQC without ^{1}H-decoupling: $J_{H1,\ C1}$ = 158.8 Hz

---

[1] Hall, L.D.; Manville, J.F. *Can. J. Chem.* **1967**, *45(11)*, 1299-1303.

[2] Brimble, M.A.; Brenstrum, T.J. *J. Chem. Soc., Perkin Trans. 1* **2001**, *(14)*, 1612-1623.

[3] Plettenburg, O.; Bodmer-Narkevitch, V.; Wong, C.-H. *J. Org. Chem.* **2002**, *67(13)*, 4559-4564.

[4] Giese, B.; Gilges, S.; Groninger, K.S.; Lamberth, G.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615-617.

[5] Di-*O*-acetyl-D-rhamnal was prepared via the method of Pihko, A.J.; Nicolau, K.C.; Koskinen, A.M.P. *Tetrahedron Asym.* **2001**, *12*, 937-942.