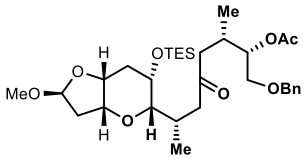
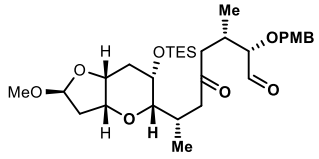
Methyl 13-*O*-acetyl-3,7-anhydro-14-*O*-benzyl-2,5,8,9,11,12-hexadeoxy-8,12-dimethyl-6-*O*-(triethylsilyl)-D-*arabino*-β-L-*galacto*-tetradecofuranosid-10-ulose (39b): To a stirred solution of CuCN (605 mg, 6.75 mmol, 3.0 equiv) in THF (60 mL) was added MeLi (1.6 M in Et_2O, 8.44 mL, 13.5 mmol, 6.0 equiv) at −78 °C. The reaction mixture was stirred at −40 °C for 10 min and then cooled to −78 °C. Then, TMSCl (1.71 mL, 13.5 mmol, 6.0 equiv) and **38a** (1.30 g, 2.25 mmol, 1.0 equiv) in THF (15 mL) were added. The resulting mixture was allowed to warm to −40 °C and stirred for additional 0.5 h before it was quenched by the addition of sat. aq. NH_4Cl solution (40 mL). The mixture was allowed to warm to 23 °C and vigorously stirred for 3 h. The layers were separated and filtered through a pad of celite, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with aq. HCl (0.05 M, 30 mL), $NaHCO_3$ (30 mL, sat. aq.), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexanes/EtOAc 10:1, *v*/*v* → 2:1, *v*/*v*) of the residue afforded ketone **39b** (1.11 g, 1.87 mmol, 83% yield) as a colorless oil.



39b

39b: R_f = 0.60 (SiO_2, hexanes/EtOAc 2:1, *v*/*v*); $[\alpha]_D^{23}$ = +27.5 (*c* = 0.50, EtOAc); FT-IR (film): ν_{max} 2954, 2912, 2877, 1740, 1712, 1455, 1415, 1372, 1311, 1238, 1185, 1139, 1099, 1060, 1027, 972, 943, 880, 789, 737, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.36–7.27 (m, 5 H), 5.16–5.12 (m, 1 H), 4.92 (q, *J* = 5.4 Hz, 1 H), 4.58–4.45 (m, 2 H), 3.91 (ddd, *J* = 10.6, 5.1, 2.5 Hz, 2 H), 3.84 (s, 1 H), 3.57–3.50 (m, 2 H), 3.34 (s, 3 H), 2.81 (d, *J* = 9.5 Hz, 1 H), 2.71 (dd, *J* = 15.9, 4.5 Hz, 1 H), 2.54–2.43 (m, 2 H), 2.41–2.33 (m, 1 H), 2.31–2.17 (m, 4 H), 2.06 (s, 3 H), 1.95 (dt, *J* = 14.3, 4.7 Hz, 1 H), 1.78 (dt, *J* = 15.4, 4.4 Hz, 1 H), 0.98 (t, *J* = 7.9 Hz, 9 H), 0.89 (d, *J* = 6.7 Hz, 3 H), 0.86 (d, *J* = 6.7 Hz, 3 H), 0.67–0.60 (m, 6 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 209.8, 170.8, 138.1, 128.5, 127.8, 127.7, 104.8, 82.2, 77.7, 75.9, 73.2, 72.8, 69.6, 63.1, 55.5, 47.3, 45.6, 41.2, 33.4, 30.5, 30.0, 21.3, 16.7, 16.3, 7.0, 5.3 ppm; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{32}H_{52}O_8SiNa^+$ 615.3324; Found 615.3332.

Methyl (14*S*)-8,12-anhydro-3,4,6,7,10,13-hexadeoxy-2-*O*-(4-methoxybenzyl)-3,7-dimethyl-9-*O*-(triethylsilyl)-D-*lyxo*-D-*manno*-tetradecodialdo-14,11-furanosid-5-ulose (32a): A solution of benzyl ether **12** (30.7 mg, 0.0457 mmol, 1.0 equiv) and excess Raney Ni (~ 200 mg) in EtOH (3 mL) was stirred under a hydrogen atmosphere (1 bar) at 23 °C for 12 h. The resulting mixture was filtrated through a pad of Celite and the filtrate was concentrated under reduced pressure to give the crude alcohol. Flash column chromatography (SiO_2, hexanes/EtOAc 10:1, *v*/*v* → 5:1, *v*/*v*) of the residue afforded the corresponding alcohol intermediate (14.1 mg, 0.0242 mmol, 53% yield), which was used for the next step without further characterization (Note: the yield of the reaction was 39% at 350 mg scale).



32a: fragment A

To a stirred solution of the above alcohol (14.1 mg, 0.0242 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) were added $NaHCO_3$ (14.2 mg, 0.169 mmol, 7.0 equiv) and Dess–Martin periodinane (30.8 mg, 0.0726 mmol, 3.0 equiv) at 0 °C. The reaction mixture was stirred for 1 h at 23 °C before it was quenched by the addition of sat. aq. $Na_2S_2O_3$ solution (5 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexanes/EtOAc 10:1, *v*/*v* → 1:1, *v*/*v*) of the residue afforded aldehyde fragment *A* (**A**) (11.3 mg, 0.0196 mmol, 81% yield) as a colorless oil. **32a:** R_f = 0.50 (SiO_2, hexanes/EtOAc 2:1, *v*/*v*); $[\alpha]_D^{23}$ = +3.3 (*c* = 0.20, $CHCl_3$); FT-IR (film): ν_{max} 2954, 1877, 1731, 1711, 1613, 1514, 1463, 1373, 1303, 1249, 1183, 1249, 1141, 1098, 1029, 973, 742, 726 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): δ 9.43 (d, *J* = 2.0 Hz, 1 H), 7.15 (d, *J* = 8.6 Hz, 2H, one proton merged in solvent peak), 6.78 (d, *J* = 8.6 Hz, 2 H), 5.19 (dd, *J* = 5.8, 3.9 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.18 (d, *J* = 11.4 Hz, 1 H), 3.72 (dt, *J* = 4.7, 2.3 Hz, 1 H), 3.61 (s, 1 H), 3.59 (dd, *J* = 5.4, 2.5 Hz, 1 H), 3.36 (dd, *J* = 4.9, 2.1 Hz, 1 H), 3.30 (s, 3 H), 3.28 (s, 3 H), 2.66–2.49 (m, 5 H), 2.29 (dd, *J* = 14.2, 5.8 Hz, 1 H), 2.18–2.07 (m, 3 H), 2.03 (ddd, *J* = 14.2, 5.5, 3.9 Hz, 1 H), 1.31 (dt, *J* = 15.3, 4.4 Hz, 1 H), 1.08 (t, *J* = 7.9 Hz, 9 H), 0.90 (d, *J* = 6.7 Hz, 6 H), 0.74–0.60 (m, 6 H) ppm; ^{13}C NMR (151 MHz, C_6D_6): δ 208.3, 202.6, 160.0, 130.2, 130.0, 114.2, 105.1, 86.6, 81.8, 77.6, 72.9, 72.5, 63.4, 55.2, 54.8, 47.1, 44.8, 41.8, 33.3, 30.6, 30.2, 16.82, 16.45, 7.2, 5.7 ppm; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{31}H_{50}O_8SiNa^+$ 601.3167; Found 601.3162.